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Development of Nickel-Catalyzed Cross-Coupling, Cross-Electrophile Coupling and Domino Reaction

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Development of Nickel-Catalyzed Cross-Coupling, Cross-Electrophile Coupling, and Domino Reactions

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Kirsten Anne Hewitt

Dissertation Committee:
Professor Elizabeth R. Jarvo, Chair
Professor Scott D. Rychnovsky
Associate Professor Sergey V. Pronin

2022

DEDICATION

To Mom, Dad, Kasey, Stephen and Brennan

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I acknowledge MDPI for permission to include Chapter 1, which was originally published in *Molecules*. I acknowledge Elsevier for permission to include portions of Chapter 2, which was originally published in *Comprehensive Organometallic Chemistry IV*. I acknowledge the American Chemical Society for permission to include portions of Chapter 3 and Chapter 4, which were originally published in *Journal of Organic Chemistry* and *ACS Catalysis*, respectively. Finally, I am I am thankful to the Allergan graduate research fellowship and UCI department of chemistry dissertation fellowship for providing financial support for my research.

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I am also grateful to my friends from Philadelphia, Brianna, Victoria, Nick, Chris, and Joe. Thank you for your constant support and love from 2,000 miles away. I am very excited to be back on the same coast as you all.

To Kasey, Stephen and Brennan, thank you for being my first students when I wanted to play school and for being supportive throughout my life. I am the luckiest girl in the world to have siblings like you.

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To my Mom, as you say “you only get one” and I am very thankful you are my “one”. I would not be here today without your endless support and love along the way. I appreciate you more than I can put into words.

Finally, to Justin. I cannot even begin to describe the impact you have had on my life. Thank you for your love, your encouragement, your advice and for being you. I am endlessly grateful for you.

VITA

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EDUCATION

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2017–2022	Doctoral Research (University of California, Irvine) *Development of Nickel-Catalyzed Cross-Coupling, Cross-Electrophile Coupling and Domino Reactions* Advisor: Professor Elizabeth R. Jarvo
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PUBLICATIONS

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Hewitt, K. A.; Xie, P.-P.; Thane, T. A.; Hirbawi, N.; Zhang, S.-Q.; Matus, A. C.; Lucas, E. L.; Hong, X.; Jarvo, E. R. “Nickel-Catalyzed Domino Cross-Electrophile Coupling–Carbodifunctionalization of Propargylic Sulfonamides for Vinylcyclopropane Synthesis.” *ACS Catal.* **2021**, *11*, 14369–14380.

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Kang, H.; Lee, Y. E.; Reddy, P. V. G.; Dey, S.; Allen, S. E.; Niederer, S. E.; Sung, P.; Hewitt, K.; Torruellas, C.; Herling, M. R.; Kozlowski, M. C. "Asymmetric Oxidative Coupling of Phenols and Hydroxycarbazoles." *Org. Lett.* **2017**, *19*, 5505–5508.

CONFERENCE PRESENTATIONS

Hewitt, K. A.; Jarvo E. R. Nickel-Catalyzed Domino Cross-Electrophile Coupling Dicarbofunctionalization Reactions to Afford Vinylcyclopropanes. 263rd ACS National Meeting and Exposition. San Diego, CA. March 2022.

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Hewitt, K. A.; Jarvo, E. R. Nickel-Catalyzed Cross-Electrophile Coupling and Domino Reactions of Sulfonamides. Empowering Women in Organic Chemistry, Joint Virtual Symposium. October 2021.

Hewitt, K. A.; Lucas, E. L.; Thane, T. A.; Hirbawi, N.; Matus, A. C.; Jarvo, E. R. Nickel-Catalyzed Cross-Electrophile Coupling Reactions of Sulfonamides. Merck SoCal Symposium. Virtual Poster Presentation. July 2021.

Hewitt, K. A.; Jarvo E. R. Nickel-Catalyzed Cross-Electrophile Coupling Reactions of Sulfonamides: Expansion to Domino Reactions. Virtual 262nd ACS National Meeting and Exposition. August 2021.

Hewitt, K. A.; Lucas, E. L.; Thane, T. A.; Hirbawi, N.; Matus, A. C.; Jarvo, E. R. Nickel-Catalyzed Cross-Electrophile Coupling Reactions of Sulfonamides: Expansion to Domino Reactions. Empowering Women in Organic Chemistry National Conferences. Virtual Poster Presentation. June 2021.

Hewitt, K. A.; Jarvo E. R. Nickel-Catalyzed Domino Reactions for the Synthesis of Substituted Vinylcyclopropanes. 25th Annual Green Chemistry & Engineering Conference. June 2021.

Hewitt, K. A.; Jarvo, E. R. Nickel Catalyzed Domino Reactions of Alkynyl Piperidines. Virtual 261st ACS National Meeting and Exposition. April 2021.

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Hewitt, K. A.; Lucas, E. L.; Castro, A. J.; Jarvo, E. R. Nickel Catalyzed Domino Reactions. 259th ACS National Meeting & Exposition, Philadelphia, PA. March 2020.

Hewitt, K. A.; Lucas, E. L.; Jarvo, E. R Stereospecific Nickel-Catalyzed Cross-Coupling and Cross-Electrophile Couplings of Sulfonamides. 258th ACS National Meeting & Exposition, San Diego, CA. August 2019.

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2016–2017	Penn Undergraduate Chemistry Society Historian
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2017–Present	Iota Sigma Pi (ISP) Calcium Chapter

ABSTRACT OF THE DISSERTATION

Development of Nickel-Catalyzed Cross-Coupling, Cross-Electrophile Coupling, and Domino Reactions

by

Kirsten Anne Hewitt

Doctor of Philosophy in Chemistry

University of California, Irvine, 2022

Professor Elizabeth R. Jarvo, Chair

The world around us, from the medicines we take, to the food we eat, to the plants and animals surrounding us, is composed of carbon-carbon (C–C) bonds. In order to construct these C–C bonds, we rely on previously developed methodologies. In an ever growing world, the need for new technologies to tackle more challenging problems has grown significantly. Catalysis has emerged in the last century as a reliable, efficient and sustainable method to synthesize C-C bonds. In particular, first row transition-metal catalysis has stood out for its unique reactivity and interesting mechanistic pathways. Herein, four nickel-catalyzed transformations that provide highly complex carbon scaffolds will be discussed. In addition, key mechanistic features will be examined.

First, a nickel-catalyzed Kumada cross-coupling reaction of benzylic sulfonamides will be discussed (Chapter 1). A significant by-product that was initially was observed was substituted styrenes resulting from β-hydride elimination. In order to address this problem, we synthesized highly branched substrates and this diminished the formation of the undesired by-product. In addition, the scope of the includes heterocycles and alternative Grignard reagents.

Next, cross-electrophile coupling reactions of benzylic, allylic and propargylic sulfonamides will be presented (Chapter 2–4). These strategies allow for the synthesis of highly strained cyclopropanes in a diastereoselective manner. During the mechanistic investigation, we discovered that catalytic turnover was rate determining and we hypothesized that known elementary steps could be inserted to develop a domino reaction. To this end, we established a domino reaction of propargylic sulfonamides that involved discrete cross-electrophile coupling and dicarbofunctionalization to afford tetrasubstituted vinylcyclopropanes. Based on experimental and mechanistic experiments, we proposed a bifurcated mechanism that produces both diastereomers of product.

Finally, a conjunctive cross-electrophile coupling reaction involving mesylate electrophiles and an internal olefin will be discussed (Chapter 5). This methodology builds on our laboratory's previously developed cross-electrophile coupling reaction 1,3-dimesylates. The scope of the reaction contains electron-withdrawing and electron-donating functional groups. Additionally, we performed preliminary mechanistic experiments to demonstrate that the mechanism likely generates diiodides in-situ, initiates at the secondary center and proceeds through radical intermediates.

Chapter One

Nickel-Catalyzed Kumada Cross-Coupling Reaction of Benzylic Sulfonamides

1.1 Introduction

Transition-metal catalyzed cross-coupling (XC) reactions have transformed modern synthetic organic chemistry by creating an arsenal of carbon-carbon bond forming reactions.[1,2] The significance of these transformations was highlighted when Richard Heck, Akira Suzuki, and Ei-ichi Negishi were awarded the 2010 Nobel Prize in chemistry for their work on palladium-catalyzed XC reactions.[3] In the past several decades, nickel complexes have emerged as a powerful and efficient transition metal catalyst with comparable reactivity to palladium.[4] One major advantage is that nickel is more cost effective than palladium and platinum. In its elemental form nickel costs approximately 2,000 times less than palladium and 10,000 less than platinum.[5] Additionally, nickel is more electropositive than its d^{10} counterparts which allows for more facile oxidative addition.[6] Consequently, electrophiles that are considered unreactive under palladium catalysis can now be activated via oxidative addition with nickel. Moreover, nickel and palladium complexes display differing reactivity towards β-hydride elimination. This elementary step typically leads to unwanted side products in catalytic reactions and tends to be slower for nickel

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[1] Portions of this chapter have been published in Molecules: Hewitt, K. A.; Herbert, C. A.; Matus, A. C.; Jarvo, E. R. *Molecules* **2021**, *26*, 5947–5971.

[2] For reviews on XC reactions see: (a) *Metal-Catalyzed Cross-Coupling Reactions.* 2nd ed. De Meijere, A. Diederich, F., Eds.; Wiley-VCH: Winheim, Germany **2004**. (b) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books. Sausalito, CA, **2010**. (c) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417–1492. (d) Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *Chem. Rev.* **2015**, *115*, 9587–9652. (e) Choi, J.; Fu, G. C. *Science*, **2017**, *356*, eaaf7230. (f) Campeau, L.-C.; Hazari, N. *Organometallics*, **2019**, *38*, 3–35.

[3] Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085.

[4] (a) Tamaru, Y. *Modern Organonickel Chemistry*; Wiley-VCH: Weinheim, Germany, 2005. (b) Ogoshi, S. (Ed.) *Nickel Catalysis in Organic Synthesis: Methods and Reactions*; Wiley: Hoboken, NJ, USA, 2020. (c) Singer, R. A.; Monfette, S.; Bernhardson, D.; Tcyrulnikov, S.; Hubbell, A. K.; Hansen, E. C. *Org. Process. Res. Dev.* **2021**, *25*, 1802–1815.

[5] Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299–309.

[6] Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319–6332.

than for palladium.[7] Finally, nickel exhibits additional modes of reactivity compared to palladium because it can easily access oxidation states ranging from 0–IV whereas palladium typically accesses the 0 and II oxidation states. Common catalytic cycles for nickel include both polar and radical mechanisms.[5]

Intense research efforts have been employed in the development of nickel-catalyzed XC reactions of sluggish electrophiles, such as aryl and alkyl halides, sulfonates, esters, and ethers.[2,8] However, the XC reaction of alkyl amine derivatives has remained a significant challenge.[9] Historically, in order to facilitate nickel-catalyzed reactions, activation of these carbon-nitrogen bonds has been achieved via incorporation into strained aziridine rings, transformation to ammonium salts or activation of amides.[10]

Ring-strain promoted XC of aziridines has been accomplished (Scheme 1.1).[11] Early stoichiometric work by Hillhouse established that aziridines undergo facile oxidative addition with nickel complexes.[12] Catalytic Negishi reactions of sulfonylaziridines have subsequently been established. The Doyle laboratory reported a regioselective Negishi XC reaction of styrenyl aziridines with alkylzinc reagents with substitution at the benzylic position (Scheme 1.1a).[13] Key to their success was the use of an electron deficient fumarate ligand.[14] Shortly thereafter, the Doyle

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[7] (a) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109–7116. (b) Lin, B.-L.; Liu, L.; Fu, Y.; Luo, S.-W.; Chen. Q.; Gui, Q.-X. *Organometallics* **2004**, *23*, 2114–2123.

[8] For selected reviews, see: (a) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. *Chem. Rev*. **2011**, *111*, 1346–1416. (b) Tollefson, E. J.; Hanna, L. E.; Jarvo, E. R. *Acc. Chem. Res.* **2015**, *48*, 2344–2353. (c) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486–1495.

[9] For recent reviews, see (a) Ouyang, K.; Hao, W.; Zhang, W.-X.; Xi, Z. *Chem. Rev.* **2015**, *115*, 12045–12090. (b) Wang, W.; Su, Y.; Li, L.; Huang, H. *Chem. Soc. Rev.* **2016**. *45*, 1257–1272. (c) Pound, S. M.; Watson, M. P. *Chem. Commun.* **2018**, *54*, 12286–12301. (d) Dander, J. E.; Garg, N. K. *ACS Catal.* **2017**, *7*, 1413–1423. (e) Li, G.; Ma, S.; Szostak, M. *Trends Chem.* **2020**, *2*, 914–928.

[10] For an example of a stereoablative copper-catalyzed Kumada XC reaction of sulfonimides, see: Li, M.-B.; Tang, X.-L.; Tian, S.-K. *Adv. Synth. Catal.* **2011**, *353*, 1980–1984.

[11] Huang, C.-Y.; Doyle, A. G. *Chem. Rev.* **2014**, *114*, 8153–8198.

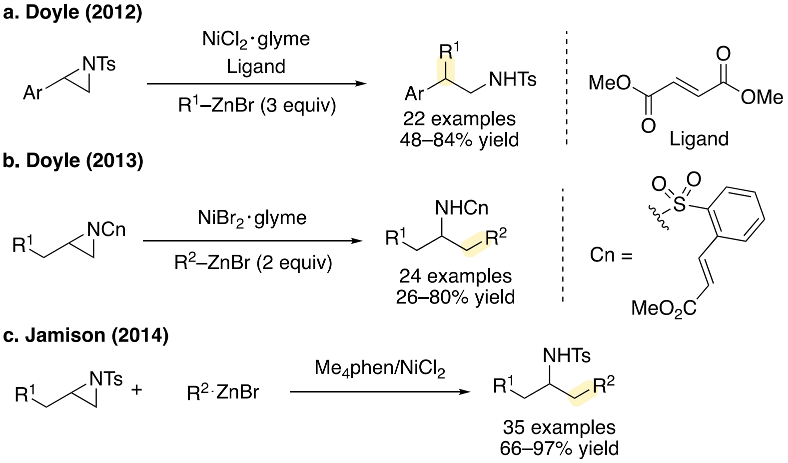
[12] Lin, B. L.; Clough, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 2890–2891.

[13] (a) Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2012**, *134*, 9541–9544. (b) Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2015**, *137*, 5638–5641

[14] Estrada, J. G.; Williams, W. L.; Ting, S. I.; Doyle, A. G. *J. Am. Chem. Soc.* **2020**, *142*, 8928–8937.

and Jamison groups independently described a regioselective Negishi XC reaction of alkyl aziridines with alkylzinc reagents to forge the desired carbon-carbon bond (Scheme 1.1b and c).[15] The differing regioselectivity of these reactions can be explained by comparing the oxidative addition events of the C–N bonds. Styrenyl aziridines preferentially undergo oxidative addition at the benzylic center to afford η^3-benzylnickel complexes. In contrast, alkyl aziridines, which do not contain an aromatic ring to direct the nickel complex, preferentially undergo oxidative addition at the less hindered position.[12] These reports demonstrate the ability to activate the C–N bond in strained rings.

Scheme 1.1 Cross-Coupling (XC) Reactions of Aziridines



Development of XC reactions of acyclic benzylamine derivatives has relied upon formation of highly reactive electrophiles (i.e. charged ammonium salts).[16] The earliest reports of carbon-nitrogen XC coupling reactions utilized aniline derivatives (Scheme 1.2). In a seminal report, the Wenkert laboratory disclosed the Kumada XC reaction of aryl trimethylammonium salts with Grignard reagents (Scheme 1.2a).[17] In 2003, the MacMillan group reported the Suzuki-Miyaura

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[15] (a) Nielsen, D. K.; Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2013**, *135*, 13605–13609. (b) Jensen, K. L.; Standley, E. A.; Jamison, T. F. *J. Am. Chem. Soc.* **2014**, *136*, 11145–11152.

[16] For a recent review see: Wang, Z.-X.; Yang, B. *Org. Biomol. Chem.* **2020**, *18*, 1057.

[17] Wenkert, E.; Han, A.-L.; Jenny, C.-J. *J. Chem. Soc., Chem. Commun.* **1998***,* 975–976.

XC reaction of a similar trimethylammonium derivative.[18] The modifications implemented included the utilization of a weakly coordinating counterion (i.e. triflate) and the use of boronic acids as the organometallic reagent, which significantly improved the yield and functional group tolerance of the reaction (Scheme 1.2b). In 2011, the Wang laboratory developed Negishi XC reactions of aryl trimethylammonium iodides with aryl zinc reagents (Scheme 1.2c).[19] This reaction displayed similar functional group tolerance to the Suzuki-Miyaura XC reaction and proceeded in moderate to excellent yields. The Wang group has extensively studied this reaction and have developed an effective pincer ligand for the nickel-catalyzed XC reactions.[20] Additionally, it has been demonstrated that trimethylammonium triflates were tolerated under these reaction conditions.[21] More recently, Uchiyama and coworkers described the Stille XC reaction of aryl ammonium salts with aryl trimethyl tin reagents (Scheme 1.2d).[22] Finally, the Uchiyama and Wang groups independently demonstrated the XC reaction of trimethylammonium salts with organoaluminium reagents (Scheme 1.2e).[23]

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[18] Blakey, S. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2003**, *125*, 6046–6047.

[19] Xie, L.-G.; Wang, Z.-X. *Angew. Chem. Int. Ed.* **2011**, *50*, 4901–4904.

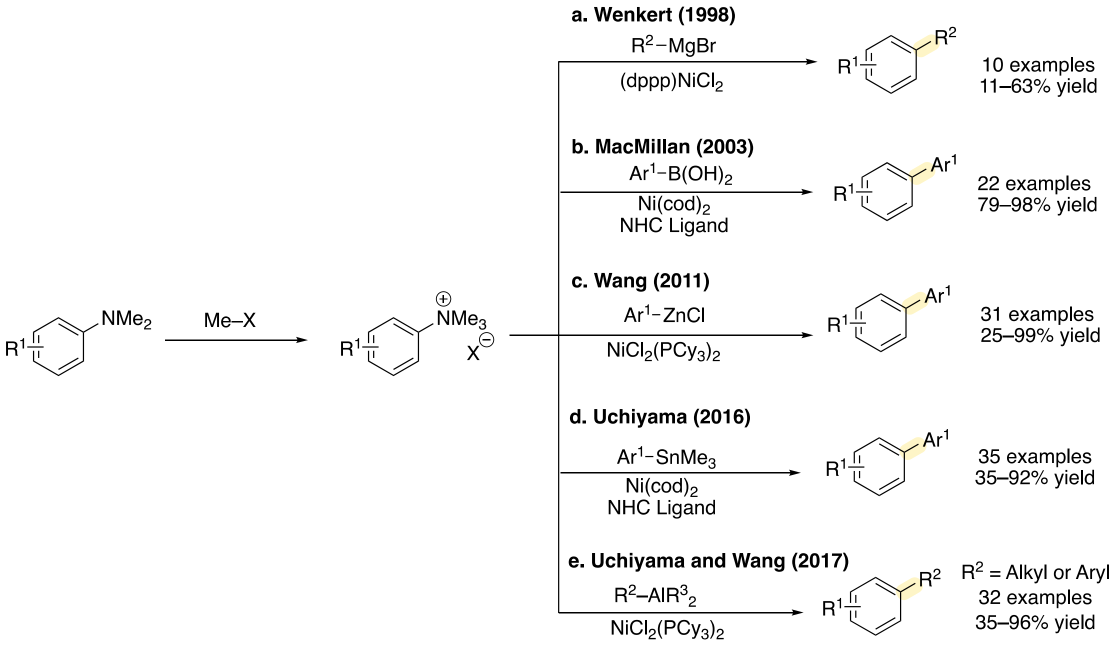
[20] (a) Zhang, X.-Q.; Wang, Z.-X. *J. Org. Chem.* **2012**, *77*, 3658–3663. (b) Yang, X.; Wang, Z.-X. *Organometallics* **2014**, *33*, 5863–5873.

[21] Wu, D.; Tao, J.-L.; Wang, Z.-X. *Org. Chem. Front.* **2015**, *2*, 265–273.

[22] Wang, D.-Y.; Kawahata, M.; Yang, Z.-K.; Miyamoto, K.; Komagawa, S.; Yamaguchi, K.; Wang, C; Uchiyama, M. *Nat. Commun.* **2016**, *7*, 12937.

[23] (a) Ogawa, H.; Yang, Z.-K.; Minami, H.; Kojima, K.; Saito, T.; Wang, C.; Uchiyama, M. *ACS Catal.* **2017,** *7*, 3988–3994. (b) He, F.; Wang, Z.-X. *Tetrahedron* **2017**, *73*, 4450–4457.

Scheme 1.2 Cross-Coupling Reactions of Aryl Trimethylammonium Salts



The extension of XC reactions to include alkyl electrophiles has proven difficult due to unwanted β-hydride elimination of the alkylmetal species. One particularly successful strategy has been the implementation of substituted benzylamines. For example, the Watson laboratory demonstrated that benzylic trimethylammonium salts are competent electrophiles in Suzuki-Miyaura XC reactions with aryl and vinylboronic acids (Scheme 1.3a).[24] Similarly, the Wang laboratory disclosed the XC reaction of benzylic trimethylammonium salts with organoaluminum reagents to forge the desired carbon-carbon bond (Scheme 1.3b).[23b]

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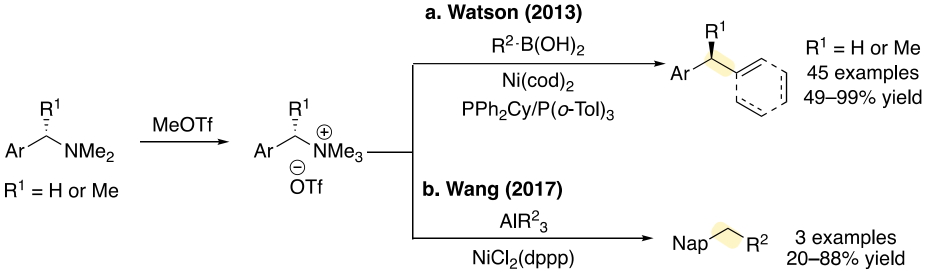
[24] (a) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 280–285. (b) Shacklady-McAtee, D. M.; Roberts, K. M.; Basch, C. H.; Song, Y.-G.; Watson, M. P. *Tetrahedron* **2014**, *70*, 4257–4263.

Scheme 1.3 Cross-Coupling Reactions of Trimethylammonium salts.



The use of Katritzky salts to activate amines has proven to be sufficient for activation of benzylic and alkyl amines for Suzuki-Miyaura and Negishi XC reactions. Previously, it has been observed that Katritzky salts participate in SN2, radical, and Minisci-type reactions, and in recent years, many transition-metal catalyzed reactions have been developed.[25,26] The Watson laboratory hypothesized that these air and moisture stable salts would be suitable electrophiles in a XC reaction.[27] To test their hypothesis, primary amines were converted to Katritzky salts via a condensation reaction with 2,4,6-triphenylpyrylium tetrafluoroborate and the corresponding salts were subjected to Suzuki-Miyaura XC reactions with aryl boronic acids. The desired cross-coupled products were obtained in good yields (Scheme 1.4a).[28] This strategy was amenable to the coupling of primary benzylic Katritzky salts as well (Scheme 1.4b).[29] Additionally, vinyl boranes and alkylborane reagents, generated in situ by hydroboration of alkenes, participated in XC with

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[25] (a) Bapat, J. B.; Blade, R. J.; Boulton, A. J.; Epsztajn, J.; Katritzky, A. R.; Lewis, J.; Molina-Buendia, P.; Nie, P.-L.; Ramsden, C. A. *Tet. Lett.* **1976**, *17*, 2691–2694. (b) Katritzky, A. R.; De Ville, G.; Patel, R. C. *Tetrahedron* **1981**, *37*, 25–30. (c) Katritzky, A. R.; Marson, C. M. *Angew. Chem. Int. Ed.* **1984**, *23*, 420–429. (d) Said, S. A.; Fiksdahl, A. *Tetrahedron: Asymmetry* **2001**, *12*, 1947–1951. (e) Klauck, F. J.; James, M. J.; Glorius, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 12336–12339.

[26] For reviews on transition metal-catalyzed reactions with Katritzky salts see (a) He, F.-S.; Ye, S.; Wu, J. *ACS Catal.* **2019**, *9*, 8943–8960. (b) Pang, Y.; Moser, D.; Cornella, J. *Synthesis* **2020**, *52*, 489–503. (c) Rössler, S. L.; Jelier, B. J.; Magnier, E.; Dagousset, G.; Carreira, E. M.; Togni, A. *Angew. Chem. Int. Ed.* **2020**, *59*, 9264–9280. (d) Li, Y.-N.; Xiao, F.; Guo, Y.; Zeng, Y.-F. *Eur. J. Org. Chem.* **2021**, *2021*, 1215– 1228. (e) Kong, D.; Moon, P. J.; Lundgren, R. J. *Nat. Catal.* **2019**, *2*, 473– 476

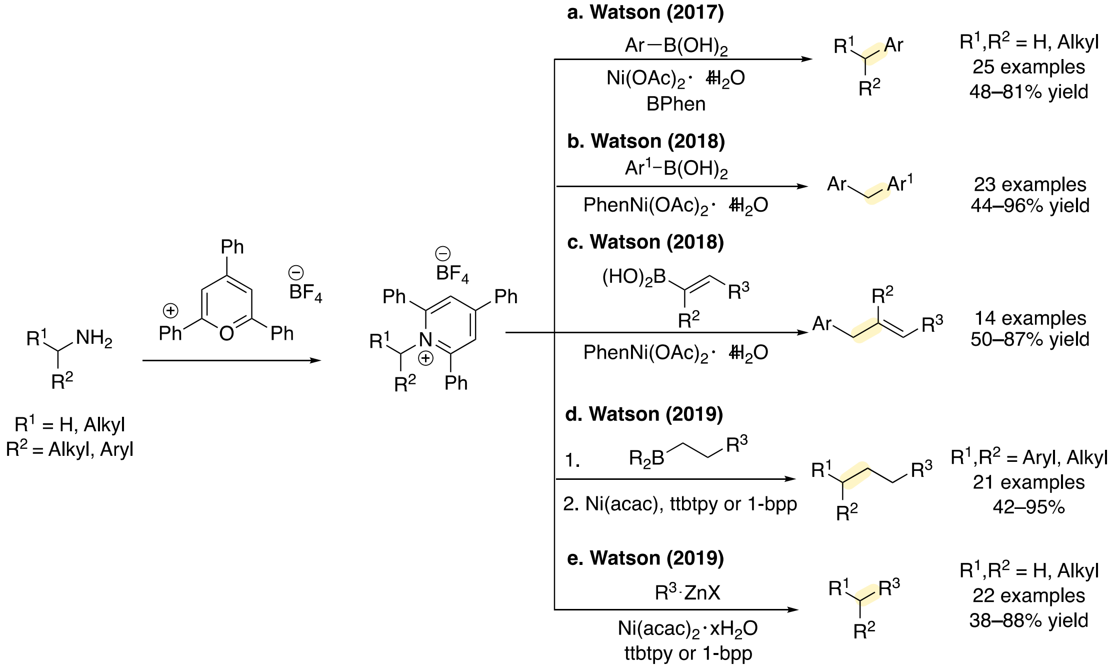
[27] Basch, C. H.; Liao, J.; Xu, J.; Piane, J. J.; Watson, M. P. *J. Am. Chem. Soc.* **2017**, *139*, 5313–5316.

[28] Hoerner, M, E.; Baker, K. M.; Basch, C. H.; Bampo, E. M.; Watson, M. P. *Org. Lett.* **2019**, *21*, 7356–7360.

[29] Liao, J.; Guan, W.; Boscoe, B. P.; Tucker, J. W.; Tomlin, J. W.; Garnsey, M. R.; Watson, M. P. *Org. Lett.* **2018**, *20*, 3030–3033.

Katritzky salts (Scheme 1.4c and d).[30] This strategy has been extended beyond Suzuki-Miyaura reactions to include Negishi XC reactions with alkylzinc reagents (Scheme 1.4e). [31]

Scheme 1.4. Cross-Coupling Reactions of Katritzky Salts



These methods establish strain- and charge-based strategies to activate amines for use as the electrophilic partner in XC reactions. However the requirement for aziridines or functionalization as highly reactive ammonium salts remains a major limitation in broad application of these methods. In this Chapter, we report the first nickel-catalyzed Kumada XC reaction of simple benzylic sulfonamides with methylmagnesium iodide (Scheme 1.5). Previously, the Jarvo laboratory disclosed the Kumada XC reaction of benzylic ethers which proceeded in excellent yields, and enantio- and diastereoselectivity.[8b,32] Building on this work, we aimed to develop an analogous reaction that employed benzylic sulfonamides. Ethers and sulfonamides

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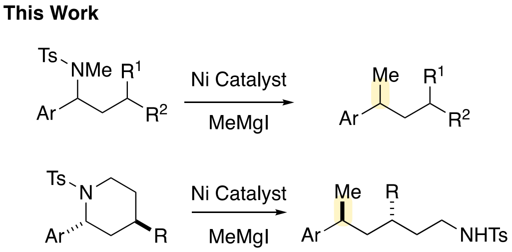
[30] (a) Baker, K. M.; Baca, D. L.; Plunkett, S.; Daneker, M. E.; Watson, M. P. *Org. Lett.* **2019**, *21*, 9738–9741. (b) Guan, W.; Liao, J.; Watson, M. P. *Synthesis* **2018**, *50*, 3231–3237.

[31] Plunkett, S.; Basch, C. H.; Santana, S. O.; Watson, M. P. *J. Am. Chem. Soc.* **2019**, *141*, 2257–2262.

[32] (a) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389–391. (b) Tollefson, E. J.; Dawson, D. D.; Osborne, C. A.; Jarvo, E. R. *J. Am. Chem. Soc.* **2014**, *136*, 14951–14958.

have similar leaving group abilities, as the conjugate bases have similar pK_a's, and we hypothesized sulfonamides would behave similarly to ethers in a XC reaction.[33,34] In addition, these moieties are appealing because they are common functional groups in synthesis. Furthermore, we demonstrate that sulfonamides undergo stereospecific XC reactions, in contrast to the stereoablative reactivity typically observed with styrenyl aziridines and Katritzky salts. [35,36,37,38] This stereospecific manifold allows for rapid diastereoselective construction of acyclic fragments bearing 1,3-substitution.[39]

Scheme 1.5 Kumada Cross-Coupling Reactions of Benzylic Sulfonamides



1.2. Results and Discussion

1.2.1 Optimization of Kumada XC Reaction of Benzylic Sulfonamides

We began our investigation into the Kumada XC reaction with benzylic sulfonamide **1.1**, which was synthesized in three steps from the commercially available aldehyde.[40] Previously,

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[33] Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 940–941.

[34] We have demonstrated that sulfonamides and ethers behave similarly in XEC reactions, see: Lucas, E. L.; Hewitt, K. A.; Chen, P.-P.; Castro, A. J.; Hong, X.; Jarvo, E. R. *J. Org. Chem.* **2020**, *85*, 1775–1793.

[35] Stereochemical outcome with styrenyl aziridines, see: ref. 13.

[36] For representative mechanistic experiments for XEC reactions of styrenyl aziridines which are proposed to proceed through alkyl iodides, see: Steinman, T. J.; Liu, J.; Mengiste, A.; Doyle, A. G. *J. Am. Chem. Soc.* **2020**, *142*, 7598–7605.

[37] Stereochemical outcome with Katritzky ammonium salts, see: Tcyrulnikov, S.; Cai, Q.; Twitty, J. C.; Xu, J.; Atifi, A.; Bercher, O. P.; Yap, G. P. A.; Rosenthal, J.; Watson, M. P.; Kozlowski, M. C. *ACS Catal.* **2021**, *11*, 8456–8466. (b) ref 26

[38] Reactions of ammonium salts can be stereospecific or stereoablative: (a) Xu, J.; Bercher, O. P.; Talley, M. R.; Watson, M. P. *ACS Catal.* **2021**, *11*, 1604–1612. (b) Moragas, T.; Gaydou, M.; Martin, R. *Angew. Chem. Int. Ed.* **2016**, *55*, 5053– 5057

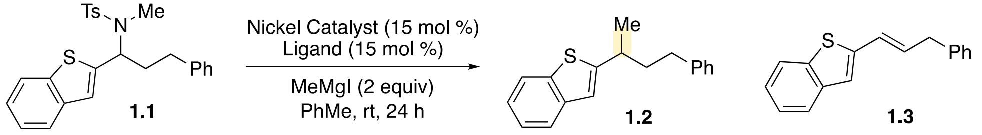
[39] (a) Hanessian, S.; Giroux, S.; Mascitti, V. *Synthesis* **2006**, *7*, 1057–1076. (b) Chen, R.; Shen, Y.; Yang, S.; Zhang, Y. *Angew. Chem. Int. Ed.* **2020**, *59*, 14198–14210.

[40] See Experimental Section for substrate synthesis.

Kumada XC reactions of benzylic ethers employed Ni(cod)$_2$ and racemic BINAP as the optimal reaction conditions.[8b,32] Under these conditions, we were excited to observe 25% yield of the desired cross-coupled product **1.2** (Table 1.1, entry 1). Increasing the catalyst loading to 15 mol % improved the yield of the reaction (entry 2). However, it also increased the yield of the undesired styrene product **1.3** arising from β-hydride elimination. In an effort to improve the ratio between desired product **1.2** and styrene product **1.3**, we investigated a series of bidentate phosphine, NHC, and pyridine ligands. DPEPhos improved the yield of **1.2** and decreased the amount of styrene **1.3** (entry 3). However, all other ligands evaluated did not improve the yield of **1.2** (entries 4–7).

We next investigated an alternative precatalyst. Previously, the Jarvo laboratory reported the cross-electrophile coupling (XEC) reaction of benzylic and allylic sulfonamides which employed a BINAP-ligated nickel (II) precatalyst.[34,41] Utilizing these conditions, with 15 mol % of catalyst, we were delighted to observe the desired product in 54% yield and 40% yield of styrene **1.3**. We elected to proceed with the nickel (II) precatalyst as it provided the desired product in the highest yield.

Table 1.1 Optimization of Kumada XC Reaction of Benzylic Sulfonamides



Entry	Nickel Catalyst	Ligand	Yield 1.2 (%)[a]	Yield 1.3 (%)[a]	RSM 1.1 (%)[a]
1[b]	Ni(cod)$_2$	*rac*-BINAP	25	10	19
2	Ni(cod)$_2$	*rac*-BINAP	34	30	7
3	Ni(cod)$_2$	DPEPhos	42	20	0
4	Ni(cod)$_2$	XantPhos	0	<5	37
5	Ni(cod)$_2$	dppe	0	<5	65
6	Ni(cod)$_2$	SiMes·BF$_4$	12	0	86
7	Ni(cod)$_2$	BPhen	0	0	61
8	(*R*-BINAP)NiCl$_2$	–	54	40	0

[a]Yield of 1.2 and 1.3 and Recovered Starting Material (RSM) determined by ^{1}H NMR based on comparison to PhTMS as internal standard. [b]5 mol % Ni(cod)$_2$

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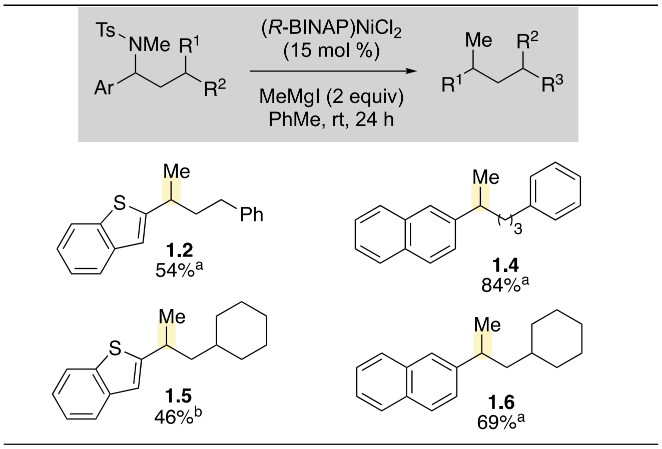
[41] For the original synthesis and characterization of (*R*-BINAP)NiCl$_2$ see: (a) Standley, E. A.; Smith, S. J.; Müller, P.; Jamison, T. F. A *Organometallics* **2014**, *33*, 2012–2018. (b) Dawson, D. D.; Oswald, V. F.; Borovik, A. S.; Jarvo, E. R. *Chem. Eur. J.* **2020**, *26*, 3044–3048.

1.2.2 Evaluation of the Substrate Scope of the Kumada XC Reaction

With optimized conditions in hand, we evaluated the scope of the Kumada XC reaction (Scheme 1.6).[42] Naphthyl substrates were well tolerated under the standard reaction conditions and product **1.4** was observed in 84% yield. Notably, products such as **1.5** and **1.6** with branching at the β-position provided good yields of cross-coupled products with lesser amounts of styrenes formed from β-hydride elimination (20–30%) when compared to product **1.2**. We hypothesized that this increase in steric bulk destabilized the conformation necessary for β-hydride elimination to proceed.

Scheme 1.6 Scope of the Kumada XC Reaction of Acyclic Sulfonamides.



aYield determined by ^{1}H NMR based on comparison to PhTMS as internal standard. bIsolated yield.

We also sought to evaluate a series of arylpiperidines, with the expectation that a stereospecific XC reaction at the benzylic position would provide synthetic access to highly substituted acyclic fragments. Furthermore, products would bear a pendant sulfonamide moiety, available for subsequent functionalization.[34] Rapid synthesis of the requisite cyclic sulfonamides

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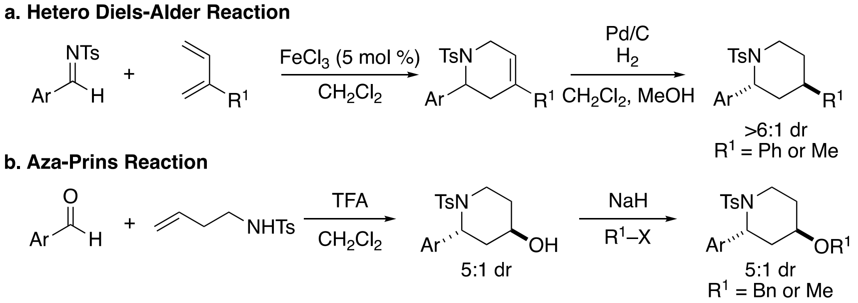
[42] Substrates **1.4–1.6** synthesized by Alissa C. Matus.

was achieved by hetero Diels-Alder (HDA) cycloadditions or aza-Prins reactions.[43,44] For substrates with alkyl substituents in the 4-position, [4+2] HDA reactions provided the requisite starting materials (Scheme 1.7a). For substrates bearing ether groups in the 4-position, an aza-Prins reaction provided the requisite 2-aryl-4-hydroxylpiperidine that could be subsequently methylated or benzylated. (Scheme 1.7b).

Scheme 1.7 Arylpiperidine Synthesis via (a) Hetero Diels-Alder (HDA) Reaction and (b) Aza-Prins Reaction.



With rapid and diastereoselective access to the desired piperidines, we examined these cyclic substrates in ring-opening Kumada XC reactions (Scheme 1.8).[45] Phenyl and methyl substituents (products **1.7** and **1.8**) were well tolerated and minimal amounts (<5%) of β-hydride elimination were observed. Methylated and benzylated ethers were well tolerated and provided the desired products in good yields (**1.9**, **1.10**, and **1.11**).[46] It is important to note that the diastereomeric ratio observed in the products is consistent with the diastereomeric ratio of the starting material.[47] Therefore, preliminary data supports a stereospecific Kumada XC reaction.

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[43] Tomifuji, R.; Maeda, K.; Takahashi, T.; Kurahashi, T.; Mastubara, S. *Org. Lett.* **2018**, *20*, 7474–7477.

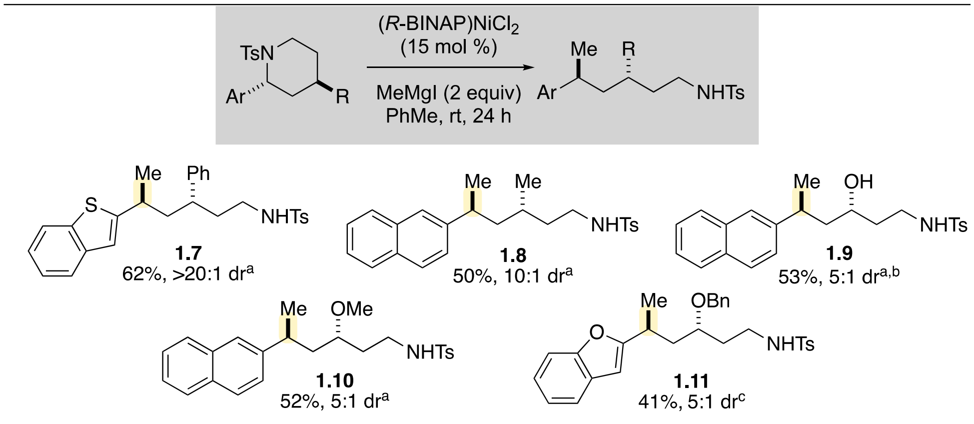
[44] (a) Sabitha, G.; Reddy, N. M.; Prasad, M. N.; Yadav, J. S. *Helv. Chim. Acta* **2009**, *92*, 967–976. (b) Tollefson, E. J.; Erickson, L. W.; Jarvo, E. R. *J. Am. Chem. Soc.* **2015**, *137*, 9760–9763.

[45] Substrates **1.8**–**1.11** synthesized by Claire A. Herbert.

[46] Deprotection of benzyl group of substrate **9** was accomplished under the standard reaction conditions. For a previous report of benzyl deprotection with a Grignard reagent see: Kawana, M. *Chem. Lett.* **1981**, 1541–1542.

[47] See Experimental Details section for more information.

Scheme 1.8 Scope of the Kumada XC Reaction of Cyclic Sulfonamides.



[a] Isolated yield.
[b] R = OBn in starting material and provided the free alcohol in product.
[c] Yield determined by ^{1}H NMR based on comparison to PhTMS as internal standard.

To further develop the potential scope of this reaction, we sought to establish ring-opening of a sulfonyl piperidine with an aryl Grignard reagent (Scheme 1.9). Such transformations would provide synthetic access to diarylalkanes bearing pendant sulfonamides, including rapid assembly of stereochemically-rich analogs of ATPase inhibitor **1.14**.[48,49] We have previously observed that in Kumada XC reactions of benzylic ethers employing aryl Grignard reagents, the optimal nickel catalyst is ligated by dppe.[50] We were pleased to see that this trend applied to benzylic

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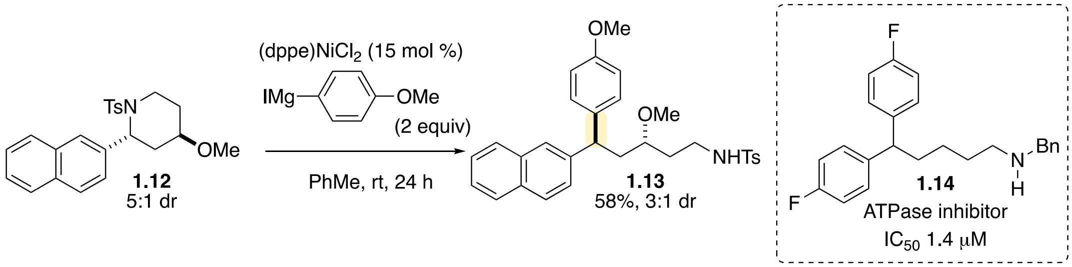
[48] Pöhler, R.; Krahn, J. H.; van den Boom, J.; Dobrynin, G.; Kaschani, F.; Eggenweiler, H.-M.; Zenke, F. T.; Kaiser, M.; Meyer, H. *Angew. Chem. Int. Ed.* **2018**, *57*, 1576–1580.

[49] Diarylalkanes are known to exhibit potent biological activity. For selected references see: (a) Wetterau, J. R.; Gregg, R. E.; Harrity, T. W.; Arbeeny, C.; Cap, M.; Connolly, F.; Chu, C.-H.; George, R. J.; Gordon, D. A.; Jamil, H.; Jolibois, K. G.; Kunselman, L. K.; Lan, S.-J.; Maccagnan, T. J.; Ricci, B.; Yan, M.; Young, D.; Chen, Y.; Fryszman, O. M.; Logan, J. V. H.; Musial, C. L.; Poss, M. A.; Robl, J. A.; Simpkins, L. M.; Slusarchyk, W. A.; Sulsky, R.; Taunk, P.; Magnin, D. R.; Tino, J. A.; Lawrence, R. M.; Dickson, J. K.; Biller, S. A. *Science* **1998**, *282*, 751. (b) Kimura, M.; Masuda, T.; Yamada, K.; Mitani, M.; Kubota, N.; Kawakatsu, N.; Kishii, K.; Inazu, M.; Kiuchi, Y.; Oguchi, K.; Namiki, T. *Bioorg. Med. Chem.* **2003**, *11*, 1621–1630. (c) Dei, S.; Coronnello, M.; Bartolucci, G.; Manetti, D.; Romanelli, M. N.; Udomtanakunchai, C.; Salerno, M.; Teodori, E. *Eur. J. Med. Chem.* **2018**, *147*, 7–20. (d) Ameen, D.; Snape, T. J. *MedChemComm* 2**013**, *4*, 893–907.

[50] Yonova, I. M.; Johnson, A. G.; Osborne, C. A.; Moore, C. E.; Morrissette, N. S.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 2422–2427.

sulfonamides: employing the commercially available precatalyst, (dppe)$NiCl_2$, the XC reaction proceeded smoothly to provide the desired product **1.13** in 58% isolated yield.[51.52]

Scheme 1.9 Kumada XC Reaction with Aryl Grignard Reagent



1.3 Proposed Mechanism of the Kumada XC Reaction

We propose the following catalytic cycle for the Kumada XC reaction based on related mechanisms for the Kumada XC reaction of benzylic ethers and the XEC reaction of benzylic sulfonamides (Scheme 1.10).[34,53] First, reduction of the nickel(II) precatalyst with the Grignard reagent provides the substrate ligated active Ni(0) catalyst **1.15**. Next, oxidative addition of the benzylic sulfonamide affords the Ni(II) intermediate **1.16**. Based on the calculated reaction coordinate diagram and transition state energies for related transformations, we hypothesize that rate-determining oxidative addition occurs with inversion of the benzylic carbon.[8b,32,53] This step is facilitated by Lewis acidic magnesium salts that activate the sulfonamide moiety. Transmetallation with the Grignard reagent provides alkylnickel complex **1.17**. Subsequent reductive elimination, which occurs with retention at the benzylic center, affords the desired product and turns over the catalyst. Alternatively, intermediate **1.16** can undergo β-hydride elimination to afford the observed styrene by-product.

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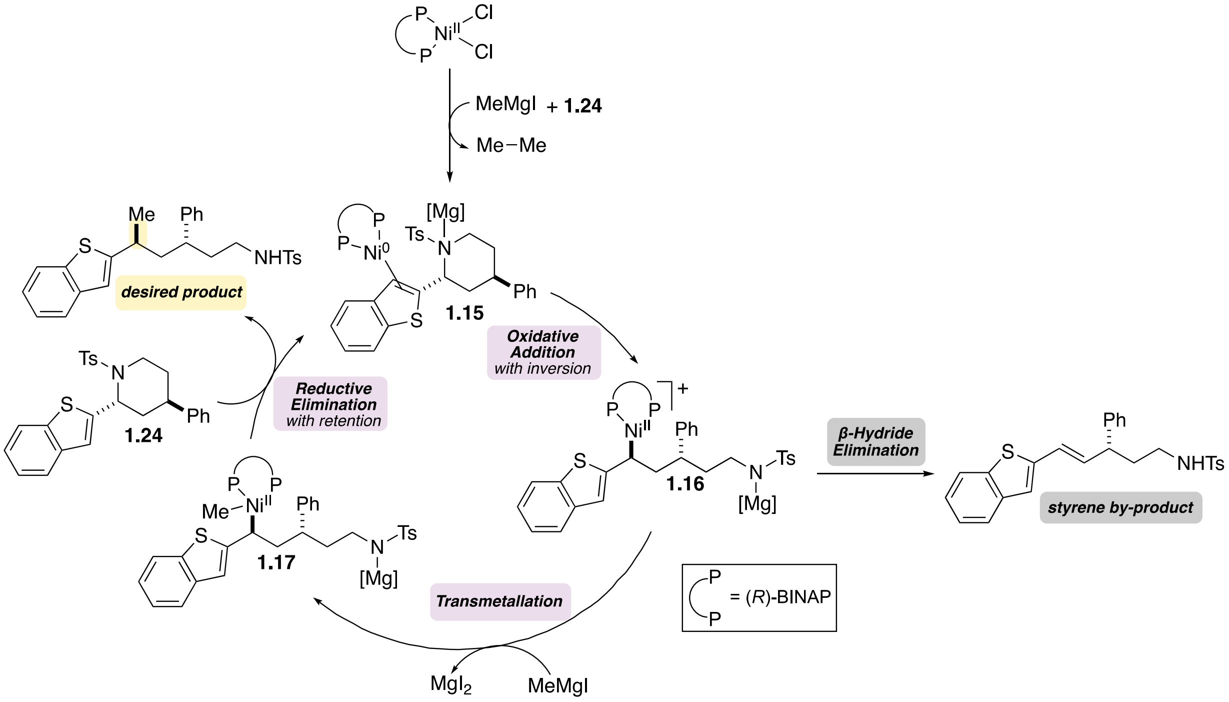
[51] Experiment performed by Claire A. Herbert.

[52] When (*R*-BINAP)$NiCl_2$ was employed as the precatalyst, the desired product was not observed and 44% of starting material was recovered. For more information, see ref. 1.

[53] Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, S.; Tollefson, E. J.; Erickson, L. W.; Taylor, B. L.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835–5855.

Scheme 1.10 Proposed Mechanism of Kumada XC Reaction.



1.4 Conclusions

In conclusion, we have developed a Kumada XC reaction of benzylic sulfonamides with Grignard reagents including methylmagnesium iodide and arylmagnesium iodide. This reaction utilizes readily available starting materials that are not activated prior to the XC reaction. We have demonstrated that increasing the steric bulk adjacent to the reactive center destabilizes the conformation necessary for β-hydride elimination to occur. A stereospecific ring opening Kumada XC reaction has been established to synthesize highly substituted acyclic fragments. This work provides a basis for the XC reaction of simple benzylic sulfonamides.

1.5 Experimental Details

1.5.1 General Procedures

All reactions were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 h) to remove H_2O.[54] All other solvents utilized were purchased anhydrous commercially, or purified as described. ^{1}H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^{1}H, 100 MHz ^{13}C, 376.5 MHz ^{19}F), GN-500 (500 MHz ^{1}H, 125.4 MHz ^{13}C), or CRYO-500 (500 MHz ^{1}H, 125.8 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublet (dd), doublet of doublet of doublets (ddd), doublet of doublet of doublet of doublets (dddd), doublet of triplet (dt), doublet of doublet of triplet (ddt), doublet of triplet of doublet (dtd), triplet (t), broad triplet (br t), triplet of doublet (td), triplet of doublet of doublet (tdd), triplet of triplet (tt), quartet (q), quartet of doublet (qd), quartet of doublet of doublets (qdd), quintet (quint), apparent quintet (appar quint), sextet, apparent sextet (appar sextet), multiplet (m)]. coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 °C. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$ or CAM. Flash chromatography was performed using SiliaFlash F60 (40-63 μm, 60 Å) from SiliCycle. Automated chromatography was carried out on a Teledyne Isco CombiFlash Rf Plus. Melting points (m.p.) were obtained using a Mel-Temp melting point

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[54] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

apparatus and are uncorrected. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center.

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (–20 °C) under an atmosphere of N_2 and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored in a glovebox and used as received. The methylmagnesium iodide was titrated with iodine prior to use.[55] All other chemicals were purchased commercially and used as received, unless otherwise noted.

1.5.2 General Kumada Cross-Coupling Reaction Procedures

1.5.2.1 Method A: Kumada Cross-Coupling Reaction

In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with sulfonamide substrate (1.0 equiv), nickel precatalyst (15 mol %) and PhMe (0.10–0.20 M in substrate). The Grignard reagent (2.0 equiv) was then added dropwise via a syringe. After 24 h, the reaction was removed from the glovebox, quenched with methanol, filtered through a plug of silica gel eluting with 100% Et_2O and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 μL, 0.050 mmol) was added and the yield was determined by ^1H NMR based on comparison to PhTMS as internal standard before purification by column chromatography.

For reactions in which 1.0 equiv of MgI_2 is added, the vial is wrapped in aluminum foil for the duration of the reaction due to the light sensitivity of MgI_2.

1.5.2.1.1 Preparation of Grignard Reagent

Under a N_2 atmosphere, a three-necked flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was charged with magnesium turnings (1.1 g, 45 mmol). The flask and magnesium turnings were then flame-dried under vacuum and the flask was back-filled with

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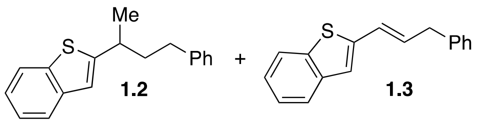
[55] Krasoviskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890.

N_2. Anhydrous Et_2O (7.0 mL) and a crystal of iodine (ca. 2.0 mg) were added to the flask. Freshly distilled iodomethane (1.9 mL, 31 mmol) or 4-iodoanisole as a solution in Et_2O (4.7 g, 20. mmol, 6.7 M in Et_2O) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature then filtered through the fritted Schlenk filter into a Schlenk flask under N_2 atmosphere. The magnesium turnings were washed with Et_2O (2 x 1.0 mL) then the Schlenk flask was sealed, removed, and placed under an N_2 atmosphere. The resulting methylmagnesium iodide was typically between 2.4 and 3.0 M as titrated by Knochel's method[55] and could be stored, sealed under N_2 atmosphere or in a glovebox, for up to 4 weeks.

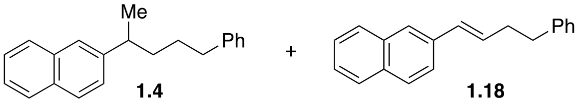
1.5.2.1.2 Preparation of (*R*-BINAP)$NiCl_2$

This method was adapted from a procedure reported by Jamison.[41a] To a flame-dried 50 mL round bottom flask equipped with a stir bar was added $NiCl_2{\cdot}6H_2O$ (0.24 g, 1.0 mmol, 1.0 equiv). The flask was placed under vacuum and flame-dried until nearly all of the nickel compound had turned from emerald green to yellow-orange. Some of the green hexahydrate is necessary for the reaction to proceed. The flask was allowed to cool to room temperature then (*R*-BINAP) (0.62 g, 1.0 mmol, 1.0 equiv) was added. The flask was then equipped with a reflux condenser and was evacuated and backfilled with N_2. The solids were then dissolved in MeCN (20 mL, 0.05 M) and the reaction mixture was allowed to reflux for 24 h. Upon completion, the reaction was cooled to room temperature and the black crystalline precipitate was filtered under vacuum to yield a fine black powder (0.53 g, 0.71 mmol, 71% yield).

1.5.3 Characterization Data for Kumada Cross-Coupled Products



2-(4-Phenylbutan-2-yl)benzo[*b*]thiophene (1.2) was prepared according to Method A. The following amounts of reagents were used: sulfonamide **1.1** (87 mg, 0.20 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (23 mg, 30. µmol, 15 mol %), PhMe (1.0 mL, 0.20 M), and methylmagnesium iodide (0.16 mL, 0.40 mmol, 2.0 equiv, 2.5 M in Et_2O). Before purification, a ^{1}H NMR yield of 54% was obtained containing 40% styrene **1.3** based on comparison to PhTMS as an internal standard. The residue was purified by flash chromatography (0–5% EtOAc/hexanes) to yield a mixture of the title compound and styrene **1.3**. To separate the major product and the styrene, an Upjohn dihydroxylation was performed.[44] The following amounts of reagents were used: substrate (30 mg, 0.12 mmol, 1.0 equiv), OsO_4 (7.6 µL, 1.2 µmol, 1.0 mol%, 4% solution in H_2O), *N*-methylmorpholine *N*-oxide (NMO) (16 mg, 0.13 mmol, 1.1 equiv), acetone (0.25 mL) and H_2O (0.05 mL). The residue was purified by flash column chromatography to afford the title compound as a colorless oil. (13 mg, 48 µmol, 24% yield over two steps) with a small amount of styrene **1.3** (1.1 mg, 4.5 µmol, 2.2% yield). **TLC R$_f$** = 0.8 (5% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.45–7.22 (m, 4H), 7.22–7.12 (m, 3H), 7.04 (s, 1H), 3.12 (sextet, *J* = 7.0 Hz, 1H), 2.73–2.50 (m, 2H), 2.12–1.92 (m, 2H), 1.41 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 152.5, 142.1, 140.0, 139.0, 128.5 (2C), 128.4 (2C), 125.8, 124.1, 123.5, 122.9, 122.3, 119.5, 40.5, 35.8, 33.6, 23.1; **IR** (neat) 2927, 1456, 904, 726 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{18}SNa$ 289.1027, found 289.1024.



2-(5-Phenylpentan-2-yl)naphthalene (1.4)[56] was prepared according to Method A. The following amounts of reagents were used: sulfonamide **1.19** (22 mg, 50. µmol, 1.0 equiv), (*R*-

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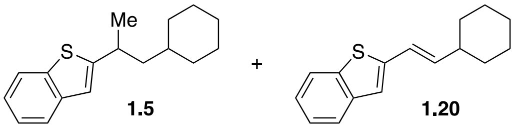
[56] Compound **1.4** synthesized by Alissa C. Matus.

BINAP)NiCl$_2$ (5.6 mg, 7.5. μmol, 15 mol %), PhMe (0.25 mL, 0.20 M), and methylmagnesium iodide (40. μL, 0.10 mmol, 2.0 equiv, 2.8 M in Et$_2$O). Before purification, a ^{1}H NMR yield of 84% was obtained containing 13% styrene **1.18** based on comparison to PhTMS as an internal standard. The residue was purified by flash chromatography (100% hexanes) to yield the title compound as yellow oil (10. mg, 36 μmol, 74% yield) containing styrene **1.18** (1.3 mg, 5.0 μmol, 10%) and CH$_2$Cl$_2$ (0.8 mg, 9.4 μmol, 19%). **TLC R$_f$** = 0.8 (5% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.81–7.74 (m, 3H), 7.60–7.55 (s, 1H), 7.42 (dddd, *J* = 16.3, 8.2, 6.8, 1.4 Hz, 2H), 7.33 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.17–7.09 (m, 3H), 2.88 (sextet, *J* = 7.0 Hz, 1H), 2.64–2.53 (m, 2H), 1.79–1.55 (m, 4H), 1.31 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$) δ 145.2, 142.7, 133.8, 132.3, 128.5 (2C), 128.4 (2C), 128.0, 127.7, 127.7, 125.9, 125.9, 125.8, 125.3, 125.2, 40.2, 38.0, 36.1, 29.7, 22.5; **HRMS** (TOF MS Cl+) *m/z*: [M]$^+$ calcd for C$_{21}$H$_{22}$ 274.1721, found 274.1710.



2-(1-Cyclohexylpropan-2-yl)benzo[*b*]thiophene (1.5)[57] was prepared according to Method A. The following amounts of reagents were used: sulfonamide **1.21** (43 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (11 mg, 15 μmol, 15 mol %), PhMe (0.50 mL, 0.20 M), and methylmagnesium iodide (70. μL, 0.20 mmol, 2.0 equiv, 2.8 M in Et$_2$O). The residue was purified by flash column chromatography (0–15% Et$_2$O/pentanes) to afford the title compound as a clear, colorless oil (12 mg, 46 μmol, 46% yield) containing styrene **1.20** (7.3 mg, 30. μmol, 30%) and minimal amounts of solvent. **TLC Rf** = 0.7 (100% pentanes); **^{1}H NMR:** (600 MHz, CDCl$_3$) δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.26–7.22 (m, 1H), 7.00 (s, 1H), 3.27

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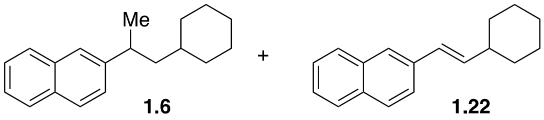
[57] Compound **1.5** synthesized by Alissa C. Matus.

(sextet, *J* = 12.6 Hz, 1H), 1.84–1.76 (m, 1H), 1.70–1.57 (m, 5H), 1.53–1.44 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H), 1.32–1.23 (m, 2H), 1.19–1.11 (m, 2H), 0.96–0.85 (m, 2H).**^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 153.6, 140.2, 138.9, 124.1, 123.4, 122.9, 122.4, 119.0, 66.0, 46.7, 35.2, 33.7, 33.3, 26.8, 26.4, 23.8, 15.4; **HRMS** (TOF MS CI+) *m/z* [M]+ calcd for $C_{17}H_{22}S$ 258.1442, found 258.1453.



1.6 **1.22**

2-(1-Cyclohexylpropan-2-yl)naphthalene (1.6)[58] was prepared according to Method A. The following amounts of reagents were used: sulfonamide **1.23** (44 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (11 mg, 15 μmol, 15 mol %), PhMe (0.50 mL, 0.20 M), and methylmagnesium iodide (70. μL, 0.20 mmol, 2.0 equiv, 2.9 M in Et_2O). Before purification, a ^{1}H NMR yield of 69% was obtained with 22% styrene **1.22** based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a colorless oil (14 mg, 54 μmol, 54% yield) with a small amount of styrene **1.22** (3.7 mg, 15 μmol, 15% yield). **TLC R$_f$** = 0.7 (100% hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85–7.73 (m, 3H), 7.60 (s, 1H), 7.47–7.38 (m, 2H), 7.35 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.99 (sextet, *J* = 6.8 Hz, 1H), 1.81 (d, *J* = 13.0 Hz, 1H), 1.63 (tdd, *J* = 14.2, 8.1, 5.0 Hz, 5H), 1.50–1.41 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.19–1.06 (m, 4H), 0.95–0.83 (m, 2H); **^{13}C NMR** (125.8 MHz, CDCl3) δ 145.8, 133.8, 132.3, 128.0, 127.72, 127.68, 126.0, 125.9, 125.2, 125.1, 46.3, 37.0, 35.3, 33.9, 33.5, 26.9, 26.4, 26.4, 23.1; **HRMS** (TOF MS CI+) *m/z*: [M]+ calcd for $C_{19}H_{24}$ 252.1878, found 252.1868.

1.5.4 Characterization Data for Ring Opening Kumada XC Products

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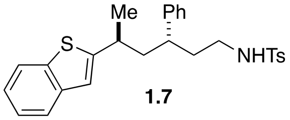
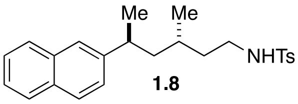
[58] Compound **1.6** synthesized by Alissa C. Matus.



1.7

***N*-(5-(benzo[*b*]thiophen-2-yl)-3-phenylhexyl)-4-methylbenzenesulfonamide (1.7)** was prepared according to Method A. The following amounts of reagents were used: piperidine **1.24** (38 mg, 80 μmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (9.0 mg, 12 μmol, 15 mol %), methylmagnesium iodide (60. μL, 0.16 mmol, 2.0 equiv, 2.6 M in Et$_2$O), and PhMe (0.5 mL). Before purification, a ^{1}H NMR yield of 64% was obtained. The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as pale yellow oil (23 mg, 49 μmol, 62% yield). The ratio of diastereomers was determined by integration of the resonances attributed to amine hydrogen in the ^{1}H NMR spectrum. The relative configuration of **1.7** was assigned based on analogy to a compound that has been previously reported.[32] **TLC R$_f$** = 0.8 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.67–7.56 (m, 3H), 7.37–7.13 (m, 9H), 7.07–7.00 (m, 2H), 6.93 (s, 1H), 2.85 (q, *J* = 6.7 Hz, 1H), 2.83–2.69 (m, 2H), 2.70–2.59 (m, 1H), 2.40 (s, 3H), 2.07–1.95 (m, 1H), 1.93–1.77 (m, 2H), 1.76–1.64 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 152.7, 143.5, 143.4, 140.0, 138.9, 136.9, 129.9, 129.8 (2C), 128.9 (2C), 127.7, 127.6 (2C), 127.2 (2C), 126.8, 124.2, 123.6, 123.0, 122.3, 119.1, 45.8, 41.5, 40.9, 36.6, 33.4, 22.0, 21.7; **HRMS** (TOF MS ES+) *m/z* [M+Na] calcd for $C_{27}H_{29}NO_2S_2Na$ 486.1537, found 486.1524.



1.8

4-Methyl-*N*-(3-methyl-5-(naphthalen-2-yl)hexyl)benzenesulfonamide (1.8)[59] was prepared according to Method A. The following amounts of reagents were used: piperidine **1.25** (10. mg,

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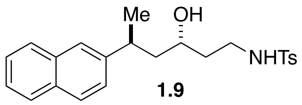
[59] Compound **1.8** synthesized by Claire A. Herbert.

30. μmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (3.0 mg, 40. μmol, 15 mol %), methylmagnesium iodide (10. μL, 60. μmol, 2.0 equiv, 2.9 M in Et_2O), and PhMe (0.30 mL). Before purification, a ^{1}H NMR yield of 48% and 10:1 dr was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–15% EtOAc/hexanes) to afford the title compound as a colorless oil (5.4 mg, 14 μmol, 50% yield, 6:1 dr) with a small amount of styrene (0.6 mg, 0.2 μmol, 6%). The ratio of diastereomers was determined by integration of the resonances attributed to amine hydrogen in the ^{1}H NMR spectrum. The relative configuration of the major **1.8** was assigned based on analogy to ring opened compound **1.7**. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.7 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS E+) *m/z* [M+Na] calcd for $C_{24}H_{29}NO_2SNa$, 418.1817; found, 418.1830.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.6 (s, 1H), 7.47–7.40 (m, 2H), 7.31–7.26 (m, 3H), 4.29 (t, *J* = 5.9 Hz, 1H), 3.03–2.82 (m, 3H), 2.41 (s, 3H), 1.49 (t, *J* = 6.2 Hz, 1H), 1.43–1.46 (m, 1H), 1.30–1.25 (m, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (125.8, $CDCl_3$) δ 145.1, 148.4, 133.7, 132.2, 129.7 (2C), 128.1, 127.6, 127.6, 127.1 (2C), 126.0, 125.6, 125.2, 125.0, 45.6, 41.1, 37.2, 36.5, 28.1, 29.1, 22.1, 21.5, 19.6.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3H), 7.69 (d, *J* = 8.3, 2H), 7.63 (s, 1H), 7.47–7.40 (m, 2H), 7.31–7.26 (m, 3H), 4.39 (t, *J* = 5.5 Hz, 1H), 3.03–2.82 (m, 3H), 2.41 (s, 3H), 1.49 (t, *J* = 6.2 Hz, 1H), 1.43–1.46 (m, 1H), 1.30–1.25 (m, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.7, 3H); **^{13}C NMR** (125.8, $CDCl_3$) δ 145.1, 148.4, 133.7, 132.2, 129.7 (2C), 128.1, 127.6, 127.6, 127.1 (2C), 126.0, 125.7, 125.2, 125.0, 45.6, 41.5, 37.2, 36.5, 29.7, 29.1, 22.1, 21.5, 19.6.



1.9

***N*-(3-hydroxy-5-(naphthalen-2-yl)hexyl)-4-methylbenzenesulfonamide (1.9)**[60] was prepared according to Method A. The following amounts of reagents were used: piperidine **1.26** (93 mg, 0.20 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (23 mg, 30. μmol, 15 mol %), methylmagnesium iodide (0.14 mL, 0.40 mmol, 2.0 equiv, 2.9 M in Et$_2$O), and PhMe (2.0 mL). The residue was purified by flash column chromatography (0–15% EtOAc/hexanes) to afford the title compound as a colorless oil (42 mg, 0.11 mmol, 53% yield, 5:1 dr). The ratio of diastereomers was determined by integration of the resonances attributed to amine hydrogen in the ^{1}H NMR spectrum. The relative configuration of the major **1.9** was assigned based on analogy to ring opened compound **1.7**. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.5 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS E+) *m/z* [M+Na] calcd for $C_{23}H_{27}NO_3SNa$, 420.1609; found, 420.1604.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.79–7.75 (m, 3H), 7.69 (d, *J* = 8.15 Hz, 2H), 7.59 (s, 1H), 7.43 (appar quint, *J* = 7.44 Hz, 2H), 7.31 (d, *J* = 8.82 Hz, 1H), 7.23 (d, *J* = 8.17 Hz, 2H), 5.27 (t, *J* = 5.55 Hz, 1H), 3.74–3.70 (m, 1H), 3.12–3.06 (m, 1H), 3.01–2.93 (m, 2H), 2.37 (s, 3H), 1.89 (br s, 1H), 1.86–1.80 (m, 1H), 1.72–1.62 (m, 2H), 1.53–1.46 (m, 1H), 1.28 (d, *J* = 7.23 Hz, 3H); **^{13}C NMR** (125.8, CDCl$_3$) δ 144.4, 143.3, 136.9, 133.7, 132.3, 129.7 (2C), 128.4, 127.7, 127.6, 127.1 (2C), 126.1, 125.5, 124.4, 125.0, 69.2, 45.9, 40.8, 37.0, 36.0, 22.2, 21.5.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.79–7.75 (m, 3H), 7.65 (d, *J* = 8.14 Hz, 2H), 7.59 (s, 1H), 7.43 (appar quint, *J* = 7.44 Hz, 2H), 7.29 (d, *J* = 8.91 Hz, 1H), 7.19 (d, *J* = 8.05

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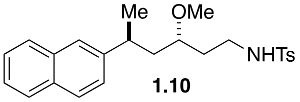
[60] Compound **1.9** synthesized by Claire A. Herbert.

Hz, 2H), 5.19 (t, *J* = 5.57 Hz, 1H), 3.43–3.39 (m, 1H), 3.12–3.06 (m, 1H), 2.91–2.82 (m, 2H), 2.35 (s, 3H), 1.86–1.80 (m, 1H), 1.76 (br s, 1H), 1.72–1.62 (m, 2H), 1.53–1.46 (m, 1H), 1.29 (d, *J* = 6.40 Hz, 3H); **^{13}C NMR** (125.8, $CDCl_3$) δ 143.7, 143.3, 136.8, 133.7, 132.3, 129.7 (2C), 128.4, 127.7, 127.6, 127.1 (2C), 126.1, 125.5, 124.4, 125.0, 68.7, 45.6, 40.8, 36.45, 36.42 23.2, 21.5.



1.10

***N*-(3-methoxy-5-(naphthalen-2-yl)hexyl)-4-methylbenzenesulfonamide (1.10)**[61] was prepared according to Method A. The following amounts of reagents were used: piperidine **1.12** (58 mg, 0.15 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (15 mg, 20. µmol, 15 mol %), methylmagnesium iodide (0.11 mL, 0.30 mmol, 2.0 equiv, 2.8 M in Et_2O), and PhMe (1.5 mL). The residue was purified by flash column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a colorless oil (32 mg, 80. µmol, 52% yield, 5:1 dr). The ratio of diastereomers was determined by integration of the resonances attributed to amine hydrogen in the ^{1}H NMR spectrum. The relative configuration of the major **1.10** was assigned based on analogy to ring opened compound **1.7**. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.4 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS E+) *m/z* [M+Na] calcd for $C_{24}H_{29}NO_3SNa$, 424.1766; found, 434.1775.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3H), 7.68 (d, *J* = 8.37 Hz, 2H), 7.55 (s, 1H), 7.47–7.40 (m, 2H), 7.29 (dd, *J* = 8.48, 1.70 Hz, 1H), 7.26–7.24 (m, 1H), 7.21 (d, *J* = 7.97 Hz, 1H), 5.11 (t, *J* = 5.53 Hz, 1H), 3.15 (s, 3H), 3.08–2.91 (m, 3H), 2.86 (appar sextet, *J* = 7.37 Hz, 1H), 2.34 (s, 3H), 1.96 (ddd, *J* = 14.3, 8.50, 5.78 Hz, 1H), 1.82–1.76 (m, 1H), 1.58–

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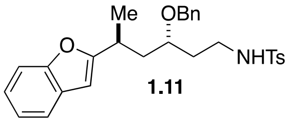
[61] Compound **1.10** synthesized by Claire A. Herbert.

1.50 (m, 2H), 1.28 (d, *J* = 6.98 Hz, 3H); **^{13}C NMR** (125.8, $CDCl_3$) δ 144.1, 143.2, 136.8, 133.6, 132.3, 129.7 (2C), 128.3, 127.7, 127.6, 127.1 (2C), 126.1, 125.4, 125.24, 125.17 78.4, 56.3, 40.9, 40.5, 36.3, 32.0, 22.9, 21.5.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 3H), 7.70 (d, *J* = 8.60 Hz, 2H), 7.55 (s, 1H), 7.47–7.40 (m, 2H), 7.29 (dd, *J* = 8.48, 1.70 Hz, 1H), 7.26–7.24 (m, 1H), 7.21 (d, *J* = 7.97 Hz, 1H), 5.03 (t, *J* = 5.52 Hz, 1H), 3.20 (s, 3H), 3.08–2.91 (m, 3H), 2.86 (appar sextet, *J* = 7.37 Hz, 1H), 2.38 (s, 3H), 1.96 (ddd, *J* = 14.3, 8.50, 5.78 Hz, 1H), 1.71–1.66 (m, 1H), 1.47–1.40 (m, 2H), 1.27 (d, *J* = 7.32 Hz, 3H) **^{13}C NMR** (125.8, $CDCl_3$) δ 144.2, 143.2, 136.9, 133.6, 132.3, 129.7 (2C), 128.3, 127.7, 127.6, 127.1 (2C), 126.1, 125.52, 125.46 125.4, 78.4, 56.3, 40.9, 40.5, 36.3, 32.0, 22.9, 21.5.



1.11

***N*-(5-(benzofuran-2-yl)-3-(benzyloxy)hexyl)-4-methylbenzenesulfonamide (1.11)**[62] was prepared according to Method A. The following amounts of reagents were used: piperidine **1.27** (78 mg, 0.17 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (22 mg, 30. µmol, 15 mol %), methylmagnesium iodide (0.23 mL, 0.68 mmol, 4.0 equiv, 2.9 M in Et_2O), and PhMe (1.5 mL). The residue was purified by flash column chromatography (0–15% EtOAc/hexanes) to afford a mixture of the title compound and styrene. To separate the major product and the styrene, a dihydroxylation was performed. The following amounts of reagents were used: AD-mix-β (52 mg, 1.4 g/mmol), *t*-BuOH (1.0 mL), and H_2O (1.0 mL). The residue was purified by flash column chromatography to afford the title compound as a colorless oil. (7.0 mg, 15 µmol, 8.6 % yield over two steps, 5:1 dr). The ratio of diastereomers was determined by integration of the resonances attributed to amine

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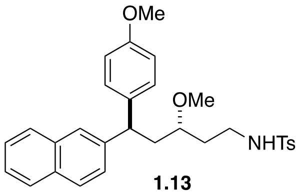
[62] Compound **1.11** synthesized by Claire A. Herbert.

hydrogen in the ^{1}H NMR spectrum. The relative configuration of the major **1.11** was assigned based on analogy to ring opened compound **1.7**. When the reaction was performed with 2.0 equivalents of methylmagnesium iodide, a ^{1}H NMR yield of 41% was obtained based on comparison to PhTMS as an internal standard before purification. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.5 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS E+) *m/z* [M+Na] calcd for $C_{28}H_{31}NO_4SNa$, 500.1872; found, 500.1861.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.27–7.16 (m, 8H), 6.33 (s, 1H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.31 (d, *J* = 11.4 Hz, 1H), 3.49–3.42 (m, 1H), 3.09–2.95 (m, 3H), 2.38 (s, 3H), 2.12 (appar quint, *J* = 6.9 Hz, 1H), 1.87–1.81 (m, 1H), 1.65–1.54 (m, 3H), 1.29 (d, *J* = 6.9 Hz, 3H) **^{13}C NMR** (125.8, CDCl$_3$) δ 162.6, 154.5, 143.3, 137.9, 136.9, 129.7 (2C), 128.5 (2C), 128.1 (2C), 127.9, 127.1 (2C), 123.4, 122.6, 120.5, 110.9, 101.1, 75.0, 70.7, 40.2, 39.1, 32.9, 30.3, 29.7, 21.5, 19.7.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 (d, *J* = 7.9 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.27–7.16 (m, 8H), 6.25 (s, 1H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.40 (s, 2H), 3.53–3.48 (m, 1H), 3.09–2.95 (m, 3H), 2.73 (appar quint, *J* = 6.5 Hz, 1H), 2.40 (s, 3H), 1.80–1.77 (m, 1H), 1.65–1.60 (m, 3H), 0.88 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125.8, CDCl$_3$) δ 162.6, 154.5, 143.3, 137.9, 136.9, 129.4 (2C), 128.7 (2C), 128.3 (2C), 127.9, 127.1 (2C), 123.4, 122.6, 120.5, 110.9, 101.4, 75.6, 71.4, 39.9, 39.1, 32.8, 30.5, 29.7, 21.5, 20.2.



1.13

N-3-methoxy-5-(4-methoxyphenyl)-5-(naphthalen-2-yl)pentyl)-4-methylbenzenesulfonamide (1.13)[63] was prepared according to Method A. The following amounts of reagents were used: piperidine **1.12** (37 mg, 90 µmol, 1.0 equiv), Ni(dppe)Cl_2 (7.0 mg, 10. µmol, 15 mol %), (4-methoxyphenyl)magnesium iodide (0.11 mL, 0.18 mmol, 2.0 equiv, 1.7 M in Et_2O), and PhMe (0.90 mL). Before purification, a ^{1}H NMR yield of 56% was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (26 mg, 50. µmol, 58% yield, 3:1 dr). The ratio of diastereomers was determined by integration of the resonances attributed to methyl hydrogens of the tosyl group in the ^{1}H NMR spectrum. The relative configuration of the major **1.13** was assigned based on analogy to ring opened compound **1.7**. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.3 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS E+) *m/z* [M+H] calcd for $C_{30}H_{34}NO_4S$, 504.2209; found, 504.2206.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.70–7.69 (m, 3H), 7.61 (s, 1H), 7.43 (dt, *J* = 20.4, 7.3 Hz, 2H), 7.29–7.19 (m, 3H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.09–5.-5 (m, 1H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 3.20 (s, 3H), 3.13–3.09 (m, 1H), 3.05–2.97 (m, 2H), 2.30 (s, 3H), 2.25 (appar sext, *J* = 7.3 Hz, 1H), 2.02–1.97 (m, 1H), 1.85–1.80 (m, 1H), 1.58–1.52 (m, 1H); **^{13}C NMR** (125.8, $CDCl_3$) δ 158.2, 143.4, 142.4, 136.8, 135.2, 133.6, 129.7 (2C), 129.0 (2C), 128.8, 128.3, 127.8, 127.7, 127.2 (2C), 126.5, 126.2, 125.6, 125.5, 114.1 (2C), 78.0, 56.7, 55.3, 46.5, 40.3, 39.1, 31.8, 21.5.

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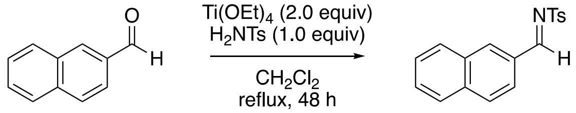
[63] Compound **1.12** synthesized by Claire A. Herbert.

Minor Diastereomer: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.73–7.70 (m, 3H), 7.63 (s, 1H), 7.43 (dt, *J* = 20.4, 7.3 Hz, 2H), 7.29–7.19 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.09–5.-5 (m, 1H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 3.19 (s, 3H), 3.13–3.09 (m, 1H), 3.05–2.97 (m, 2H), 2.35 (s, 3H), 2.25 (appar sext, *J* = 7.3 Hz, 1H), 2.06–2.03 (m, 1H), 1.76–1.78 (m, 1H), 1.58–1.52 (m, 1H); ^{13}**C NMR** (125.8, $CDCl_3$) δ 158.2, 143.4, 142.0, 136.9, 136.5, 133.6, 129.7 (2C), 129.0 (2C), 128.8, 128.4, 127.8, 127.7, 127.2 (2C), 126.5, 126.2, 125.9, 125.6, 114.1 (2C), 78.0, 56.7, 55.3, 46.5, 40.3, 39.1, 31.9, 21.6.

1.5.5 General Procedures for the Synthesis of Starting Materials

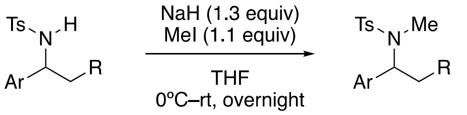
1.5.5.1 Method B: Condensation Reaction



(1.1)

This method was adapted from a procedure reported by Ruano et al.[64] A flame-dried two-neck flask equipped with a stir bar, condenser, septum and N_2 inlet was charged with aldehyde (1.0 equiv), and *p*-toluenesulfonamide (1.0 equiv) and CH_2Cl_2 (330 mL). Then $Ti(OEt)_4$ (2.0 equiv) was added dropwise. The deep orange solution was brought to reflux (~45 °C) and allowed to stir for 48 h. The solution was cooled to room temperature and was quenched with H_2O. The mixture was vacuum filtered and the filtrate was concentrated in vacuo.

1.5.5.2 Method C: Methylation of Sulfonamide with Methyl Iodide



(1.2)

This method was adapted from a procedure reported by Jarvo.[32a] To a suspension of NaH (1.3 equiv) in THF (0.10 M) was added a solution of sulfonamide (1.0 equiv) in THF (0.15 M) at 0 °C.

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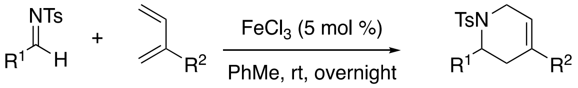
[64] García Ruano, J. L.; Alemán, J.; Belén Cid, M.; Parra, A. *Org. Lett.* **2005**, *7*, 179–182.

The mixture was warmed to rt and allow to stir for 1 h before the addition of iodomethane (1.1 equiv). The reaction was allowed to stir overnight at rt. The excess NaH was quenched with sat. NH_4Cl and the solution was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated in vacuo, and purified by flash column chromatography.

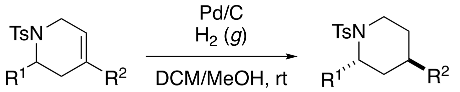
1.5.5.3 Method D: Fe-Catalyzed Formal [4+2] Cycloaddition



(1.3)

This method was adapted from a procedure reported by Matsubara.[43] To a flame-dried round-bottom flask equipped with a stir bar was added imine (1.0 equiv), $FeCl_3$ (5.0 mol %), and PhMe (0.1 M). Once the solution was homogenous, diene (2.0 equiv) was added. The reaction mixture was allowed to stir at rt overnight. After completion, the reaction mixture was filtered through a short pad of silica, washed with excess ethyl acetate, and concentrated in vacuo.

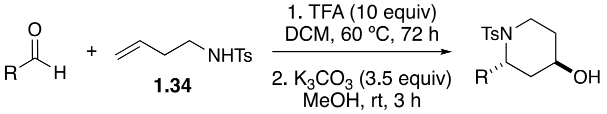
1.5.5.4 Method E: Pd/C Reduction of Alkenes



(1.4)

A flame-dried round-bottom flask with stir bar was charged with palladium on carbon (1.0 mg/3.5 mmol of substrate), flushed with N_2, and capped with septum. Slowly, DCM was added, until Pd/C was fully submerged. Then MeOH (0.2 M in substrate), and alkene (1.0 equiv) were added. Vacuum was pulled on the flask until the solvent began to bubble, at which point the flask was backfilled with N_2 (x 3). An H_2 balloon was added and the reaction mixture was allowed to stir vigorously until complete by ^{1}H NMR. The balloon was then removed, and the flask was purged with N_2 for 30 min. The septum was removed, and the reaction mixture was filtered through Celite using MeOH (100 mL). The collected solvent was then concentrated in vacuo.

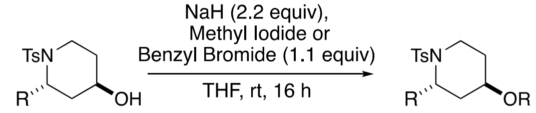
1.5.5.5 Method F: TFA Mediated aza-Prins Cyclization



(1.5)

This method was adapted from a procedure reported by Sabitha.[44] To a flame-dried pressure tube equipped with a stir bar was added aldehyde (1.0 equiv), homoallylic sulfonamide **1.34** (1.1 equiv), and CH_2Cl_2 (0.10 M). Then trifluoroacetic acid (10.0 equiv) was added slowly via syringe. The solution was warmed to 60 °C and allowed to stir for 72 h. The solution was then cooled to rt and quenched with saturated aq. $NaHCO_3$. Then the pH was adjusted to >7 by the addition of Et_3N. The solution was transferred to a separatory funnel, and the aqueous layer was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then redissolved in MeOH, and K_2CO_3 (3.5 equiv) was added to the flask and the slurry was allowed to stir at rt for 3 h. The solvent was removed under reduced pressure, then H_2O was added and the residue was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo.

1.5.5.6 Method G: Alkylation of Secondary Alcohol



(1.6)

This method was adapted from a procedure reported by Yang.[65] In a glovebox to a flame-dried round bottom flask equipped with a stir bar was added NaH (2.2 equiv). The flask was removed from the glovebox and NaH was dissolved in THF (0.2 M). Alcohol (1.0 equiv) was added dropwise as a solution in THF (0.3 M) and the reaction mixture was allowed to stir at rt for 1 h.

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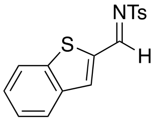
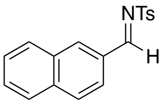
[65] Fu, M.; Chen, L.; Jiang, Y.; Jiang, Z.-X.; Yang, Z. *Org. Lett.* **2016**, *18*, 348–351.

Methyl iodide or benzyl bromide was then added dropwise to the stirring slurry and the reaction mixture was allowed to stir at rt overnight. The reaction was then quenched with saturated aq. NH_4Cl and extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo.

1.5.6 Synthesis and Characterization Data of Sulfonamide Starting Materials

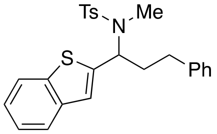


***N*-(benzo[*b*]thiophen-2-ylmethylene)-4-methylbenzenesulfonamide (1.28)** was prepared according to Method B. The following amounts of reagents were used: benzo[*b*]thiophene-2-carbaldehyde (3.2 g, 20. mmol, 1.0 equiv), *p*-toluenesulfonamide (3.1 g, 20. mmol, 1.0 equiv), $Ti(OEt)_4$ (8.4 mL, 40. mmol, 2.0 equiv), and CH_2Cl_2 (330 mL). The residue was purified by flash column chromatography (5–25% EtOAc/hexanes) to yield the title compound as a pale yellow solid (5.0 g, 16 mmol, 80 %). **m.p.** 148–150°C; **TLC R_f**= 0.5 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.02 (s, 1H), 7.90 (d, *J* = 8.3, 3H), 7.86 (d, *J* = 8.2, 1H), 7.50 (td, *J* = 8.3, 1.2, 1H), 7.42 (td, *J* = 8.4, 1.2, 1H), 7.35 (d, *J* = 8.4, 2H), 2.44 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.3, 144.8, 143.6, 138.9, 138.3, 137.3, 135.3, 130.0 (2C), 128.7, 128.2 (2C), 126.1, 125.5, 123.2, 21.8; **IR** (neat) 3259, 2921, 1566, 1305, 1292, 1152, 1087, 752 cm^{-1}; **HRMS** (TOF MS ES+) m/z calcd for $C_{16}H_{13}NO_2S_2$ $[M + Na]^+$ 338.0285, found 338.0283.

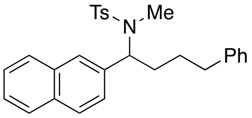


4-Methyl-*N*-(naphthalen-2-ylmethylene)benzenesulfonamide (1.29) was prepared according to Method B. The following amounts of reagents were used: 2-naphthaldehyde (0.31 g, 2.0 mmol, 1.0 equiv), *p*-toluenesulfonamide (0.34 g, 2.0 mmol, 1.0 equiv), $Ti(OEt)_4$ (0.59 mL, 4.0 mmol, 2.0

equiv), and CH_2Cl_2 (33 mL). The residue was purified by flash column chromatography (0–25% EtOAc/hexanes) to yield the title compound as a pale yellow solid (0.31 g, 1.0 mmol, 50% yield). Analytical data is consistent with literature values.[66] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.34 (s, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98–7.86 (m, 5H), 7.67–7.55 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H).



***N*-(1-(benzo[*b*]thiophen-2-yl)-3-phenylpropyl)-*N*,4-dimethylbenzenesulfonamide (1.1)** was prepared according to Method C. The following amounts of reagents were used: *N*-(1-(benzo[*b*]thiophen-2-yl)-3-phenylpropyl)-4-methylbenzenesulfonamide (0.68 g, 1.6 mmol, 1.0 equiv), NaH (50. mg, 2.1 mmol, 1.3 equiv), methyl iodide (0.11 mL, 1.8 mmol, 1.1 equiv) and THF (30 mL). The residue was purified by flash column chromatography (5–25 % EtOAc/hexanes) to yield the title compound as a yellow oil (0.52 g, 1.2 mmol, 68% yield) **TLC R$_f$** = 0.8 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.70–7.62 (m, 3H), 7.40–7.27 (m, 4H), 7.27–7.19 (m, 3H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.06 (s, 1H), 5.42 (t, *J* = 7.5 Hz, 1H), 2.77 (s, 3H), 2.69 (qdd, *J* = 14.1, 10.4, 5.9 Hz, 2H), 2.40 (s, 3H), 2.30 (dddd, *J* = 13.7, 10.3, 7.2, 5.4 Hz, 1H), 2.08 (dddd, *J* = 13.9, 10.5, 7.8, 6.3 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 143.31, 143.30, 141.0, 139.6, 139.2, 137.0, 129.6 (2C), 128.6 (2C), 128.5 (2C), 127.3 (2C), 126.3, 124.5, 124.4, 123.6, 122.9, 122.3, 56.5, 34.6, 33.0, 29.0, 21.6; **HRMS** (TOF MS ES+) *m/z:* $[M + Na]^+$ calcd for $C_{25}H_{25}NO_2S_2Na$ 458.1224, found 458.1235.



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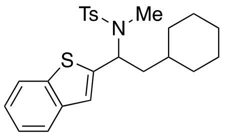
[66] Syu, S.; Lee, Y.-T.; Jang, Y.-J.; Lin, W. *J. Org. Chem.* **2011**, *76*, 2888–2891.

***N*,4-dimethyl-*N*-(1-(naphthalen-2-yl)-4-phenylbutyl)benzenesulfonamide (1.19)**[67] was prepared according to Method C. The following amounts of reagents were used: 4-methyl-*N*-(1-(naphthalen-2-yl)-4-phenylbutyl)benzenesulfonamide (0.50 g, 1.2 mmol, 1.0 equiv), NaH (36 mg, 1.5 mmol, 1.3 equiv), methyl iodide (80. µL, 1.3 mmol, 1.1 equiv) and THF (23 mL). The residue was purified by flash column chromatography (0–25% EtOAc/hexanes) to yield the title compound as a pale yellow solid (0.42 g, 0.95 mmol, 82% yield). **TLC R$_f$** = 0.3 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (td, *J* = 8.1, 7.1, 4.1 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.75 (dt, *J* = 6.1, 3.7 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.58–7.50 (m, 3H), 7.46–7.39 (m, 1H), 7.36–7.31 (m, 2H), 7.26 (t, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 2H), 5.34 (t, *J* = 7.7 Hz, 1H), 2.72 (td, *J* = 7.5, 2.3 Hz, 2H), 2.68 (s, 3H), 2.44 (s, 3H), 2.16–2.06 (m, 1H), 1.88 (ddd, *J* = 15.6, 14.0, 7.6 Hz, 1H), 1.70 (quint, *J* = 9.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.1, 141.9, 135.9, 133.1, 132.9, 129.9, 129.6 (2C), 128.53 (2C), 128.46 (2C), 128.3, 128.1, 127.7, 127.6, 127.3 (2C), 126.7, 126.4, 126.3, 126.0, 60.0, 35.5, 30.0, 28.9, 28.3, 21.6; **HRMS** (TOF MS ES+) *m/z*: [M + Na] calcd for $C_{28}H_{29}NO_2S$ 466.1817, found 466.1816.



***N*-(1-benzo[*b*]thiophen-2-yl)-2-cyclohexylethyl)-*N*,4-dimethylbenzenesulfonamide (1.21)**[68] was prepared according to Method C. The following amounts of reagents were used: *N*-(1-(benzo[*b*]thiophen-2-yl)-2-cyclohexylethyl)-4-methylbenzenesulfonamide (170 mg, 0.41 mmol, 1.0 equiv), NaH (31 mg, 0.53 mmol, 1.3 equiv), methyl iodide (30. µL, 0.45 mmol, 1.1 equiv), and THF (8.2 mL). The residue was purified by flash column chromatography (20% EtOAc/hexanes)

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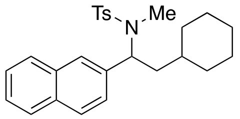
[67] Compound **1.19** was synthesized by Alissa C. Matus.

[68] Compound **1.21** was synthesized by Alissa C. Matus.

to afford the title compound as a clear, colorless oil (170 mg, 0.40 mmol, 98% yield). **TLC** $\mathbf{R_f}$ **=** 0.40 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl3) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.30 (dtd, *J* = 16.4, 7.2, 1.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 5.50 (t, *J* = 7.6, 1H), 2.71 (s, 3H), 2.39 (s, 3H), 1.92–1.78 (m, 2H), 1.76–1.59 (m, 5H), 1.33–1.23 (m, 1H), 1.20–1.10 (m, 3H), 1.04–0.83 (m, 2H); **^{13}C NMR** (125.8 MHz, CDCl3) δ 144.1, 143.0, 139.4, 139.1, 137.0, 129.4 (2C), 127.2 (2C), 124.2, 123.3, 122.3, 122.5, 122.1, 53.9, 40.3, 34.0, 33.4, 33.0, 28.7, 26.3, 26.0, 25.9, 21.4; **HRMS** (TOF MS ES+) *m/z* [M + Na]$^+$ calcd for $C_{24}H_{29}NO_2S_2Na$ 450.1537, found 450.1530.



***N*-(2-cyclohexyl-1(napthalen-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (1.23)**[69] was prepared according to Method C. The following amounts of reagents were used: *N*-(2-cyclohexyl-1-(naphthalen-2-yl)ethyl)-4-methylbenzenesulfonamide (190 mg, 0.46 mmol, 1.0 equiv), NaH (17 mg, 0.70 mmol, 1.5 equiv), methyl iodide (40. µL, 0.60 mmol, 1.1 equiv), and THF (11 mL). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (180 mg, 0.43 mmol, 86% yield). **TLC Rf** = 0.4 (10% EtOAc/hexanes); **1H NMR** (500 MHz, CDCl3) δ 7.87 (d, *J* = 9.2 Hz, 1H), 7.82 (dd, *J* = 11.3, 7.5 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.65 (br s, 1H), 7.56–7.51 (m, 2H), 7.49 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.45 (br t, *J* = 7.7 Hz, 1H), 2.72 (s, 3H), 2.46 (s, 3H), 2.02–1.88 (m, 2H), 1.81 (d, *J* = 12.5 Hz, 1H), 1.78–1.72 (m, 2H), 1.72–1.60 (m, 2H), 1.26– 1.12 (m, 4H), 1.09–0.87 (m, 2H); **13C NMR** (125.8 MHz, CDCl3) δ 143.1, 137.6, 136.3, 133.1, 132.9, 129.6 (2C), 128.2, 128.1, 127.6,

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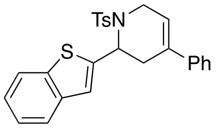
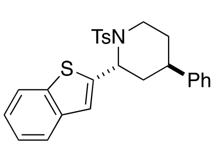
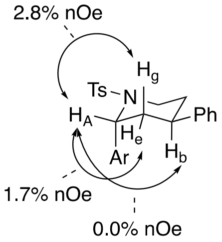
[69] Compound **1.23** was synthesized by Alissa C. Matus.

127.3 (2C), 126.8, 126.6, 126.2, 57.5 (2C), 38.2, 34.2, 33.5, 33.4, 28.9, 26.6, 26.22, 26.21, 21.6; **HRMS** (TOF MS ES+) *m/z* [M + Na]+ calcd for C26H31NO2SNa 444.1973, found 444.1968.



2-(Benzo[*b*]thiophen-2-yl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (1.30) was prepared according to Method D. The following amounts of reagents were used: imine **1.28** (240 mg, 0.75 mmol, 1.0 equiv), buta-1,3-dien-2-ylbenzene (190 mg, 1.5 mmol, 2.0 equiv)[70], $FeCl_3$ (6.0 mg, 40. µmol, 5.0 mol %), and PhMe (10. mL). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (154 mg, 0.34 mmol, 46% yield). **TLC R$_f$** = 0.5 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.36–7.22 (m, 8H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 5.95 (s, 1H), 5.80 (d, *J* = 6.1 Hz, 1H), 4.35 (dt, *J* = 18.6, 3.5 Hz, 1H), 3.84 (dq, *J* = 18.7, 2.8 Hz, 1H), 2.96 (ddt, *J* = 16.3, 6.4, 3.2 Hz, 1H), 2.87 (d, *J* = 17.2 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 144.6, 143.6, 140.0, 139.9, 129.9 (2C), 129.2, 128.8 (2C), 128.4, 127.4 (2C), 126.8 (2C), 124.5, 124.3, 123.5, 122.3, 122.3, 53.9, 42.2, 37.1, 36.7, 31.7, 21.7.





2-(Benzo[*b*]thiophen-2-yl)-4-phenyl-1-tosylpiperidine (1.24) was prepared according to Method E. The following amounts of reagents were used: substrate **1.30** (100 mg, 0.22 mmol, 1.0 equiv), Pd/C (20 mg), DCM (2.0 mL) and MeOH (5.0 mL). The residue was purified by column

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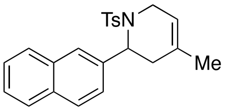
[70] Buta-1,3-dien-2-ylbenzene was prepared according to the following method: Fiorito, D.; Folliet, S.; Liu, Y.; Mazet, C. *ACS Catal.* **2018**, *8*, 1392–1398.

chromatography (0–10% EtOAc/hexanes) to afford the title compound as a pale yellow oil (24 mg, 53 μmol, 25% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on nOe analysis. **TLC R$_f$** = 0.5 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.40–7.26 (m, 6H), 7.23–7.18 (m, 1H), 7.13 (d, *J* = 1.5 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 5.70 (d, *J* = 5.2 Hz, 1H), 4.03 (d, *J* = 14.0 Hz, 1H), 3.34 (ddd, *J* = 14.1, 12.7, 3.0 Hz, 1H), 2.93 (tt, *J* = 12.6, 3.6 Hz, 1H), 2.43 (s, 3H), 2.33 (d, *J* = 13.0 Hz, 1H), 2.01 (td, *J* = 13.5, 5.5 Hz, 1H), 1.68 (d, *J* = 12.5 Hz, 1H), 1.61 (td, *J* = 12.7, 4.4 Hz, 1H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 144.8, 144.5, 139.9, 139.8, 129.8 (2C), 129.1, 128.7 (2C), 128.3, 127.3 (2C), 126.7 (2C), 124.4, 124.2, 123.4, 122.2, 122.2, 76.8, 53.8, 42.1, 36.9, 36.6, 31.6, 21.6; **HRMS** (TOF MS ES+) *m/z* [M+Na] calcd for $C_{26}H_{25}NO_2S_2Na$ 470.1224, found 470.1228.



4-Methyl-2-(naphthalen-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (1.31)[71] was prepared according to Method D. The following amounts of reagents were used: imine **1.29** (0.31 g, 1.0 mmol, 1.0 equiv), isoprene (1.5 mL, 15 mmol, 15 equiv), FeCl$_3$ (16 mg, 0.10 mmol, 10. mol %), and PhMe (10. mL, 0.10 M). The residue was purified by flash column chromatography (0–5% EtOAc/hexanes) to afford the title compound as a yellow oil (150 mg, 0.40 mmol, 40% yield). **TLC R$_f$** = 0.5 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.78–7.71 (m, 3H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.56 (s, 1H), 7.48–7.40 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.43 (d, *J* = 3.5 Hz,

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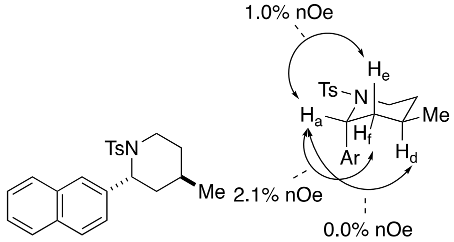
[71] Compound **1.31** was synthesized by Claire A. Herbert.

1H), 5.29 (s, 1H), 4.11 (d, *J* = 18.0 Hz, 1H), 3.35 (d, *J* = 18.1 Hz, 1H), 2.40–2.30 (m, 2H), 2.35 (s, 3H), 1.68 (s, 3H).



4-Methyl-2-(naphthalen-2-yl)-1-tosylpiperidine (1.25)[72] was prepared according to Method E. The following amounts of reagents were used: substrate **1.31** (53 mg, 0.14 mmol, 1.0 equiv), Pd/C (27 mg), DCM (1.0 mL) and MeOH (1.0 mL). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a pale yellow oil (9.6 mg, 25 μmol, 18% yield, 6:1 dr cis:trans). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on nOe analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.5 (10% EtOAc/hexanes); **HRMS** (TOF MS ES+) *m/z* [M+H] calcd for $C_{23}H_{26}NO_2S_2$ 380.1684, found 380.1689.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.76 (m, 4H), 7.73–7.71 (m, 1H), 7.63 (s, 1H), 7.46–7.44 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.48 (d, *J* = 4.5 Hz, 1H), 3.96 (d, *J* = 14.4 Hz, 1H), 3.06 (ddd, *J* = 14.0, 13.2, 3.1 Hz, 1H), 2.69 (d, *J* = 25.9 Hz, 1H), 2.42 (s, 3H), 2.30 (d, *J* = 13.3 Hz, 1H), 1.43–1.36 (m, 2H), 0.98 (ddd, *J* = 24.5, 12.4, 4.5 Hz, 1H), 0.82 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.1, 138.8, 136.7, 133.3, 132.3, 129.7 (2C), 128.4, 128.0, 127.5, 127.1 (2C), 126.1, 125.9, 125.8, 125.1, 55.6, 42.0, 36.0, 33.0, 25.3, 22.2, 21.5.

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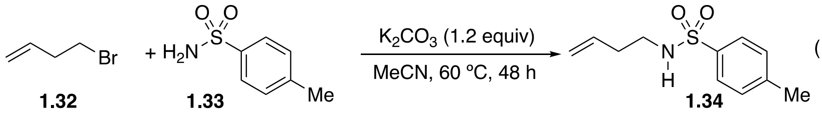
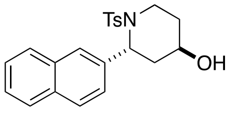
[72] Compound **1.25** was synthesized by Claire A. Herbert.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.76 (m, 4H), 7.73–7.71 (m, 1H), 7.63 (s, 1H), 7.46–7.44 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.25 (d, *J* = 4.9 Hz, 1H), 3.88 (d, *J* = 10.6 Hz, 1H), 3.04–2.98 (m, 1H), 2.42 (s, 3H), 2.38 (d, *J* = 3.86 Hz, 1H), 2.14 (d, *J* = 13.7 Hz, 1H), 1.43–1.36 (m, 2H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.1, 138.8, 136.7, 133.3, 132.3, 129.6 (2C), 129.3, 128.0, 127.6, 127.1 (2C), 126.1, 125.9, 125.8, 124.0, 55.2, 41.8, 36.0, 33.1, 25.2, 23.3, 21.5.



(1.7)

***N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide (1.34)** was prepared according to a procedure reported by Jiang.[73] To a flame-dried flask equipped with a stir bar was added 4-bromo-1-butene **1.32** (4.1 mL, 40. mmol, 1.0 equiv), *p*-toluenesulfonamide **1.33** (6.8 g, 40. mmol, 1.0 equiv), K_2CO_3 (6.6 g, 48 mmol, 1.2 equiv), and MeCN (160 mL). The mixture was heated to 60 °C and allowed to stir for 3 d. The reaction mixture was quenched with saturated NH_4Cl (100 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (5–25% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (5.4 g, 24 mmol, 60 %). Analytical data is consistent with literature values.[73] **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2, 2H), 7.30 (d, *J* = 8.1, 2H), 5.63 (ddt, *J* = 17.1, 10.4, 6.8, 1H), 5.11 (br s, 1H), 5.02–4.93 (m, 2H), 2.99 (q, *J* = 6.7, 2H), 2.41 (s, 3H), 2.20 (q, *J* = 6.9, 2 H).



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[73] Huang, J.; Zheng, J.; Wu, W.; Li, J.; Ma, J.; Ren, Y.; Jiang, H. *J. Org. Chem.* **2017**, *82*, 8191–8198.

2-(Naphthalen-2-yl)-1-tosylpiperidin-4-ol (1.35)[74] was prepared according to Method F. The following amounts of reagents were used: 2-napthaldehyde (0.94 g, 6.0 mmol, 1.0 equiv), homoallylic sulfonamide **1.34** (1.1 mL, 6.0 mmol, 1.0 equiv), TFA (4.6 mL, 60. mmol, 10 equiv), and CH_2Cl_2 (60 mL, 0.10 M). The residue was purified by flash column chromatography (0–30% EtOAc/hexanes) to afford the title compound as an orange solid (0.72 g, 1.8 mmol, 31 % yield, 5:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^1H NMR spectrum. The relative configuration of the major **34** was assigned based on analogy to compound **1.24**. For clarity, the ^1H NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.1 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS ES+) *m/z* [M+H] calcd for $C_{22}H_{24}NO_3S$ 382.1477, found 382.1483.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.77 (m, 4H), 7.68 (s, 1H), 7.49–7.41 (m, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.54 (d, *J* = 4.5 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 3.74 (tt, *J* = 10.9, 7.9 Hz, 1H), 3.03 (td, *J* = 15.3, 2.7 Hz, 1H), 2.63 (dt, *J* = 13.3, 2.0 Hz 1H), 2.43 (s, 3H), 1.70 (br s, 1H), 1.58 (ddd *J* = 13.6, 11.3, 5.5 Hz, 1H), 1.26–1.18 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 138.3, 135.9, 133.3, 132.5, 130.0 (2C), 128.7, 128.0, 127.5, 127.0 (2C), 126.3, 126.2, 125.5, 124.7, 64.7, 55.8, 40.7, 36,2, 33.8, 21.6.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.70 (m, 4H), 7.63 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.49–7.41 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.10 (t, *J* = 5.1 Hz, 1H), 3.99 (d, *J* = 15.0 Hz, 1H), 3.67 (tt, *J* = 13.4, 4.6 Hz, 1H), 3.03 (td, *J* = 15.3, 2.7 Hz, 1H), 2.63 (dt, *J* = 13.3, 2.0 Hz 1H), 2.36 (s, 3H), 1.81–1.73 (m, 1H), 1.67 (br s, 1H), 1.26–1.18 (m, 2H). **^{13}C NMR** (151 MHz,

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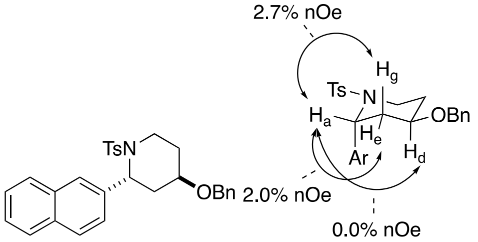
[74] Compound **1.35** was synthesized by Claire A. Herbert.

$CDCl_3$) δ 143.3, 137.7, 135.9, 133.2, 132.5, 129.6 (2C), 128.7, 128.2, 127.5, 127.2 (2C), 126.3, 126.0, 125.3, 124.8, 65.1, 55.5, 39.0, 37.0, 31.9, 21.5.



4-(Benzyloxy)-2-(naphthalen-2-yl)-1-tosylpiperidine (1.26)[75] was prepared according to Method G. The following amounts of reagents were used: alcohol **1.35** (0.25 g, 0.66 mmol, 1.0 equiv), NaH (63 mg, 2.6 mmol. 4.0 equiv), benzyl bromide (90. µL, 0.73 mmol, 1.1 equiv), and THF (2.3 mL, 0.2 M). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a white solid (140 mg, 0.30 mmol, 56 % yield, 5:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on nOe analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.8 (20% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS ES+) *m/z* [M+Na] calcd for $C_{29}H_{29}NO_3SNa$ 494.1766, found 494.1758.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz , 4H), 7.70 (d, 1H), 7.61 (s, 1H), 7.48–7.45 (m, 3H), 7.32–7.26 (m, 7H), 5.55 (d, *J* = 3.8 Hz, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.02 (d, *J* = 14.7 Hz, 1H), 3.52 (tt, *J* = 10.8 Hz, 1H), 3.04 (td, *J* = 14.5, 2.5 Hz, 1H), 2.68 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 1.80 (d, *J* = 11.5 Hz, 1H), 1.62 (ddd, *J* = 17.7, 11.9, 6.1 Hz, 1H), 1.31–1.34 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 138.3, 136.0, 133.2,

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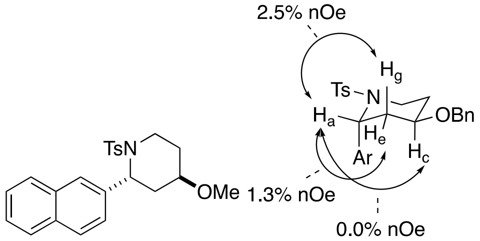
[75] Compound **1.26** was synthesized by Claire A. Herbert.

132.5, 130.0 (2C), 129.5, 128.6, 128.5 (2C), 128.0, 127.8, 127.7 (2C), 127.5, 127.0 (2C), 126.2, 126.1, 125.5, 124.8, 71.3, 70.2, 55.8, 40.8, 33.4, 30.8, 21.6.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz , 4H), 7.70 (d, 1H), 7.59 (s, 1H), 7.48–7.45 (m, 3H), 7.32–7.26 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.3 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.17 (t, *J* = 5.1 Hz, 1H), 4.24, 4.20 (ABq, J_{AB} = 12.3 Hz, 2H), 3.80–3.68 (m, 3H), 2.53 (dt, *J* = 14.4, 9.4 Hz, 1H), 2.35 (s, 3H), 2.06 (ddd, *J* = 14.3, 5.3, 2.9 Hz, 1H), 1.81–1.80 (m, 2H), 1.31–1.34 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 138.4, 136.0, 133.2, 132.5, 130.0 (2C), 129.5, 128.6, 128.5 (2C), 128.0, 127.8, 127.7 (2C), 127.5, 127.19 (2C), 127.16, 125.9, 125.6, 125.2, 71.2, 69.8, 55.8, 39.3, 34.2, 30.8, 21.6.



4-Methoxy-2-(naphthalen-2-yl)-1-tosylpiperidine (1.12)[76] was prepared according to Method G. The following amounts of reagents were used: alcohol **1.35** (110 mg, 0.30 mmol, 1.0 equiv), NaH (16 mg, 0.67 mmol. 2.2 equiv), methyl iodide (20. µL, 0.33 mmol, 1.1 equiv), and THF (1.5 mL, 0.20 M). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a pale yellow solid (61 mg, 0.15 mmol, 52 % yield, 5:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on nOe analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

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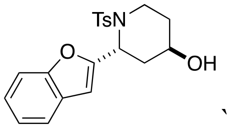
[76] Compound **1.12** was synthesized by Claire A. Herbert.

TLC R_f = 0.6 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS ES+) *m/z* [M+Na] calcd for $C_{23}H_{25}NO_3SNa$ 396.1633, found 396.1636.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.76 (m, 5H), 7.72 (s, 1H), 7.54–7.51 (m, 1H), 7.48–7.46 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.56 (s, 1H), 4.04 (d, *J* = 14.1 Hz, 1H), 3.29 (tt, *J* = 7.4, 3.0 Hz, 1H), 3.25 (s, 3H), 3.09 (t, *J* = 13.1 Hz, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 2.42 (s, 3H), 1.80 (d, *J* = 11.5 Hz, 1H), 1.53 (td, *J* = 12.2 Hz, 1H), 1.16 (qd, *J* = 11.6, 5.8 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 138.4, 136.1, 133.4, 132.5, 130.0 (2C), 126.7, 128.1, 127.6, 127.0 (2C), 126.3, 126.1, 125.5, 124.7, 73.2, 55.8, 55.5, 40.8, 33.2, 30.2, 21.6.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.76 (m, 5H), 7.72 (s, 1H), 7.54–7.51 (m, 1H), 7.48–7.46 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.99 (t, *J* = 5.38 Hz, 1H), 3.77–3.71 (m, 1H), 3.60 (dt, *J* = 13.6, 4.6 Hz, 1H), 3.42 (br s, 1H), 3.03 (s, 3H), 2.37–2.29 (m, 1H), 2.33 (s, 3H), 2.02 (d, *J* = 15.2 Hz, 1H), 1.86–1.82 (m, 1H), 1.72–1.68 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.0, 138.3, 137.4, 133.1, 132.5, 129.4 (2C), 126.7, 128.0, 127.5, 127.2 (2C), 125.8, 125.7, 125.5, 125.2, 73.5, 56.4, 55.5, 40.0, 34.1, 29.6, 21.5.



2-(Naphthalen-2-yl)-1-tosylpiperidin-4-ol (1.36)[77] was prepared according to Method F. The following amounts of reagents were used: 2-benzofurancarboxaldehyde (0.60 mL, 5.0 mmol, 1.0 equiv), homoallylic sulfonamide **1.34** (0.91 mL, 5.0mmol, 1.0 equiv), TFA (3.8 mL, 50. mmol, 10 equiv), CH_2Cl_2 (50 mL, 0.10 M). The residue was purified by flash column chromatography (0–50% EtOAc/hexanes) to afford the title compound as an orange solid (0.42 g, 1.1 mmol, 22% yield, 5:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to

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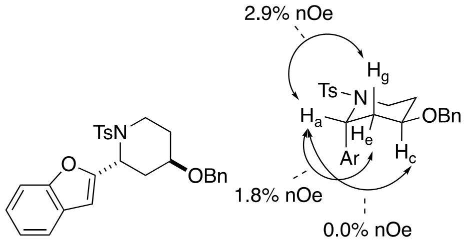
[77] Compound **1.36** was synthesized by Claire A. Herbert.

the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on analogy to compound **1.26**. For clarity, the ^{1}H NMR data of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.1 (30% EtOAc/hexanes, stained with CAM).

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.29 Hz, 2H), 7.46 (dd, *J* = 6.75, 2.12 Hz, 1H), 7.21–7.18 (m, 3H), 7.15 (d, *J* = 8.61 Hz, 2H), 6.49 (t, *J* = 2.0 Hz, 1H), 5.51 (d, *J* = 5.48 Hz, 1H), 3.97–3.90 (m, 2H), 3.23 (td, *J* = 13.5, 2.7 Hz, 1H), 2.51–2.45 (m, 1H), 2.33 (s, 3H), 1.94–1.88 (m, 1H), 1.75 (ddd, *J* = 13.0, 11.6, 5.9 Hz, 1H), 1.53 (d, *J* = 5.0 Hz, 1H), 1.44 (ddd, *J* = 24.1, 12.8, 4.5 Hz, 1H).

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.29 Hz, 2H), 7.46 (dd, *J* = 6.75, 2.12 Hz, 1H), 7.21–7.18 (m, 3H), 7.15 (d, *J* = 8.61 Hz, 2H), 6.51 (t, *J* = 1.1 Hz, 1H), 5.33 (d, *J* = 5.6 Hz, 1H), 4.14–4.10 (m, 2H), 3.64 (td, *J* = 10.9, 4.0 Hz, 1H), 2.51–2.45 (m, 1H), 2.32 (s, 3H),), 2.12 (ddd, *J* = 14.4, 6.7, 3.3 Hz, 1H), 1.94–1.88 (m, 1H), 1.53 (d, *J* = 5.0 Hz, 1H), 1.44 (ddd, *J* = 24.1, 12.8, 4.5 Hz, 1H).



2-(benzofuran-2-yl)-4-(benzyloxy)-1-tosylpiperidine (1.27)[78] was prepared according to method G. The following amounts of reagents were used: alcohol **1.36** (0.15 g, 0.40 mmol, 1.0 equiv), NaH (46 mg, 1.9 mmol. 4.7 equiv), benzyl bromide (52 µL, 0.44 mmol, 1.1 equiv), and THF (3.0 mL, 0.2 M). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to

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[78] Compound **1.27** was synthesized by Claire A. Herbert.

afford the title compound as a yellow solid (87 mg, 0.19 mmol, 47% yield, 5:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on nOe analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.8 (30% EtOAc/hexanes, stained with CAM); **HRMS** (TOF MS ES+) *m/z* [M+Na] calcd for $C_{27}H_{27}NO_4SNa$ 484.1559, found 484.1542.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.45, (d, *J* = 8.3 Hz, 1H), 7.30–7.17 (m, 8H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.44 (s, 1H), 5.52 (d, *J* = 5.3 Hz, 1H), 4.49 (s, 2H), 3.94 (d, *J* = 13.7 Hz, 1H), 3.66 (tt, *J* = 11.2, 4.0 Hz, 1H), 3.20 (td, *J* = 13.4, 2.6 Hz, 1H), 2.57 (dt, *J* = 13.2, 1.8 Hz, 1H), 2.32 (s, 3H), 1.97 (d, *J* = 12.3 Hz, 1H), 1.78 (ddd, *J* = 13.0, 11.7, 5.8 Hz, 1H), 1.45 (qd, *J* = 12.8, 4.8 Hz, 1H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 155.3, 154.7, 143.3, 138.2, 137.2, 129.5 (2C), 128.5 (2C), 128.1, 128.0, 127.8, 127.1, 126.9, 124.1, 122.9, 120.9, 111.1, 104.8, 71.8, 70.2, 51.7, 41.4, 34.2, 31.3, 21.5.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.35, (d, *J* = 4.4 Hz, 1H), 7.30–7.17 (m, 5H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.6, 2H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.42 (s, 1H), 5.36 (d, *J* = 6.4 Hz, 1H), 4.28 (s, 2H), 3.76–3.73 (m, 2H), 3.66 (tt, *J* = 11.2, 4.0 Hz, 1H), 2.70 (d, *J* = 14.1 Hz, 1H), 2.32 (s, 3H), 1.97 (d, *J* = 12.3 Hz, 1H), 1.83 (d, *J* = 13.8 Hz, 1H), 1.72–1.68 (m, 1H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 155.3, 154.7, 143.3, 138.2, 137.2, 129.5 (2C), 128.5 (2C), 128.1, 128.0, 127.8, 127.1, 126.9, 123.6, 122.6, 120.7, 110.9, 103.2, 71.8, 70.0, 49.6, 37.6, 31.0, 29.3, 15.3.

Chapter Two

C–C Bond Formation Through Cross-Electrophile Coupling Reactions

2.1 Introduction

Cross-electrophile coupling (XEC) reactions are excellent methods to construct carbon-carbon bonds from widely commercially available electrophiles.[1,2] An advantage of XEC reactions is that they do not require preformed organometallic reagents. Typically, the organometallic reagents used in traditional cross-coupling (XC) reactions are prepared from the corresponding alkyl or aryl halides, whereas XEC reactions allow for the direct conversion of these electrophiles. Unlike traditional XC reactions where the electrophile favors oxidative addition and the organometallic reagent favors transmetallation, XEC reactions contain two electrophiles that favor oxidative addition. Therefore, the transition metal catalyst must be able to differentiate the two electrophiles in order to obtain cross-selectivity. This inherent challenge resulted in delayed efforts to explore and optimize these reactions, when compared to traditional XC reactions. Some of the strategies for optimal cross-selectivity that have been developed include electronic differentiation of starting materials, steric matching between catalyst and substrate, and tethering of the electrophiles.[2a,2h]

In this Chapter, inter- and intramolecular XEC reactions will be discussed. It will focus on the dimerization and cross-selective XEC reactions of C(sp^2) electrophiles, including aryl and vinyl halides (Scheme 2.1, Type A). The next two classes of XEC reactions between C(sp^2)

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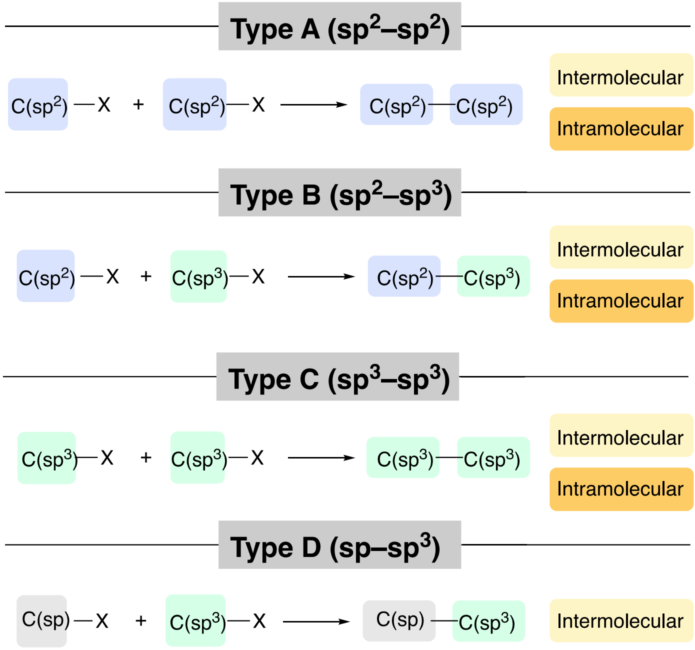
[1] Portions of this Chapter have been published in Comprehensive Organometallic Chemistry, see: Hewitt, K. A.; Lin, P. C.; Raffman, E. T. A.; Jarvo, E. R. C–C Bond Formation Through Cross-Electrophile Coupling Reactions. In *Comprehensive Organometallic Chemistry IV*; Elsevier, **2021**.

[2] (a) Everson, D. A.; Weix, D. J. *J. Org. Chem.* **2014**, *79*, 4793–4798. (b) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi Von Wangelin, A. *Chem. Eur. J.* **2014**, *20*, 6828–6842. (c) Poremba, K. E.; Dibrell, S. E.; Reisman, S. E. *ACS Catal.* **2020**, *10*, 8237–8246. (d) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1411–1421. (e) Weix, D. J. *Acc. Chem. Res.* **2015**, *48*, 1767–1775. (f) Iwasaki, T.; Kambe, N. *Top. Curr. Chem.* **2016**, *374*, 1–36. (g) Wang, X.; Dai, Y.; Gong, H. *Top. Curr. Chem.* **2016**, *374*, 1–29. (h) Lucas, E. L.; Jarvo, E. R. *Nat. Rev. Chem.* **2017**, *1*, 0065. (i) Campeau, L. C.; Hazari, N. *Organometallics* **2019**, *38*, 3–35. (j) Jin, Y.; Wang, C. *Synlett* **2020**, *31*, 1843–1850. (k) Liu, J.; Ye, Y.; Sessler, J. L.; Gong, H. *Acc. Chem. Res.* **2020**, *53*, 1833–1845. (l) Sanford, A. B.; Jarvo, E. R. *Synlett* **2021**, *32*, 1151–1156. (m) Xue, W.; Jia, X.; Wang, X.; Tao, X.; Yin, Z.; Gong, H. *Chem. Soc. Rev.* **2021**, *50*, 4162–4184. (n) Li, Y.; Fan, Y.; Jia, Q. *Chinese J. Org. Chem.* **2019**, *39*, 350.

and C(sp^3) electrophiles (Type B) and C(sp^3) electrophiles (Type C) are covered elsewhere.[1,3] Finally, the least common XEC reaction, coupling of C(sp) and C(sp^3) electrophiles, will be outlined (Type D). This Chapter will be broken into two sections to highlight the use of stoichiometric reducing metals (Section 2.3) and electrochemical reductions (Section 2.4).

Scheme 2.1 Patterns in Cross-Electrophile Coupling Reactions



The focus of this Chapter will be transition metal-catalyzed XEC reactions with stoichiometric reducing agents and electrochemical reductions to forge C–C bonds. Commonly in the literature, these transformations are referred to as "reductive coupling", "reductive cross-coupling" or "cross-electrophile coupling" reactions. Furthermore, XEC Reactions of type A are often referred to as "Ullman-type coupling" reactions.[4] I will employ the term XEC reaction for all of these carbon-carbon bond forming reactions conducted under reducing conditions. I will not include examples of dual photoredox-transition metal catalysis for the formation of C–

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[3] For a full discussion on Type B and Type C written by Patricia C. Lin and Ethan T. A. Raffman, see ref. 1

[4] (a) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139–196. (b) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327–3359. (c) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem. Int. Ed.* **1990**, *29*, 977–991. (d) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470. (e) Fanta, P. E. *Synthesis* **1974**, *1974*, 9–21.

C bonds.[5] In addition, reductive coupling reactions utilizing CO_2[6] or carbonyls[7] have been extensively covered elsewhere. Conjunctive or interrupted XEC reactions, where two organohalides are combined with an olefin or alkyne, will also not be included in this Chapter.[8]

2.2 Proposed Mechanisms of Cross-Electrophile Coupling (XEC) Reactions

Several mechanisms have been proposed for XEC reactions to account for formation of the observed products.[2c,2e,2h] The mechanisms are outlined below, using as an example a nickel catalyst and reducing metal, designated as M, to illustrate general features of each catalytic cycle. The common mechanisms include: (I) in-situ formation of the organometallic reagent (II) sequential reduction (III) radical chain and (IV) oxidative addition, intramolecular S_N2 (Figure 2.1). All mechanisms share certain key features with traditional cross-coupling (XC) reactions such as oxidative addition (OA) and reductive elimination (RE) steps.[9] As in XC reactions, oxidative events can occur via polar or radical pathways. However in XEC reactions, excluding mechanism (I), there are no stoichiometric organometallic reagents, and reduction events are crucial for product formation and catalytic turnover. In addition, the reduction steps can be achieved with stoichiometric reducing metals, such as Zn or Mn, or electrochemically.

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[5] (a) Prier, C. K.; MacMillan, D. W. C. Dual Photoredox Catalysis: The Merger of Photoredox Catalysis with Other Catalytic Activation Modes. In *Visible Light Photocatalysis in Organic Chemistry*; Wiley-VCH: Weinheim, Germany, 2018; pp 299–333. (b) Milligan, J. A.; Phelan, J. P.; Badir, S. O.; Molander, G. A. *Angew. Chem. Int. Ed.* **2019**, *58*, 6152–6163. (c) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. *Acc. Chem. Res.* **2016**, *49*, 1429–1439. (d) Tóth, B. L.; Tischler, O.; Novák, Z. *Tetrahedron Lett.* **2016**, *57*, 4505–4513. (e) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035–10074. (f) Gui, Y.-Y.; Sun, L.; Lu, Z.-P.; Yu, D.-G. *Org. Chem. Front.* **2016**, *3*, 522–526.

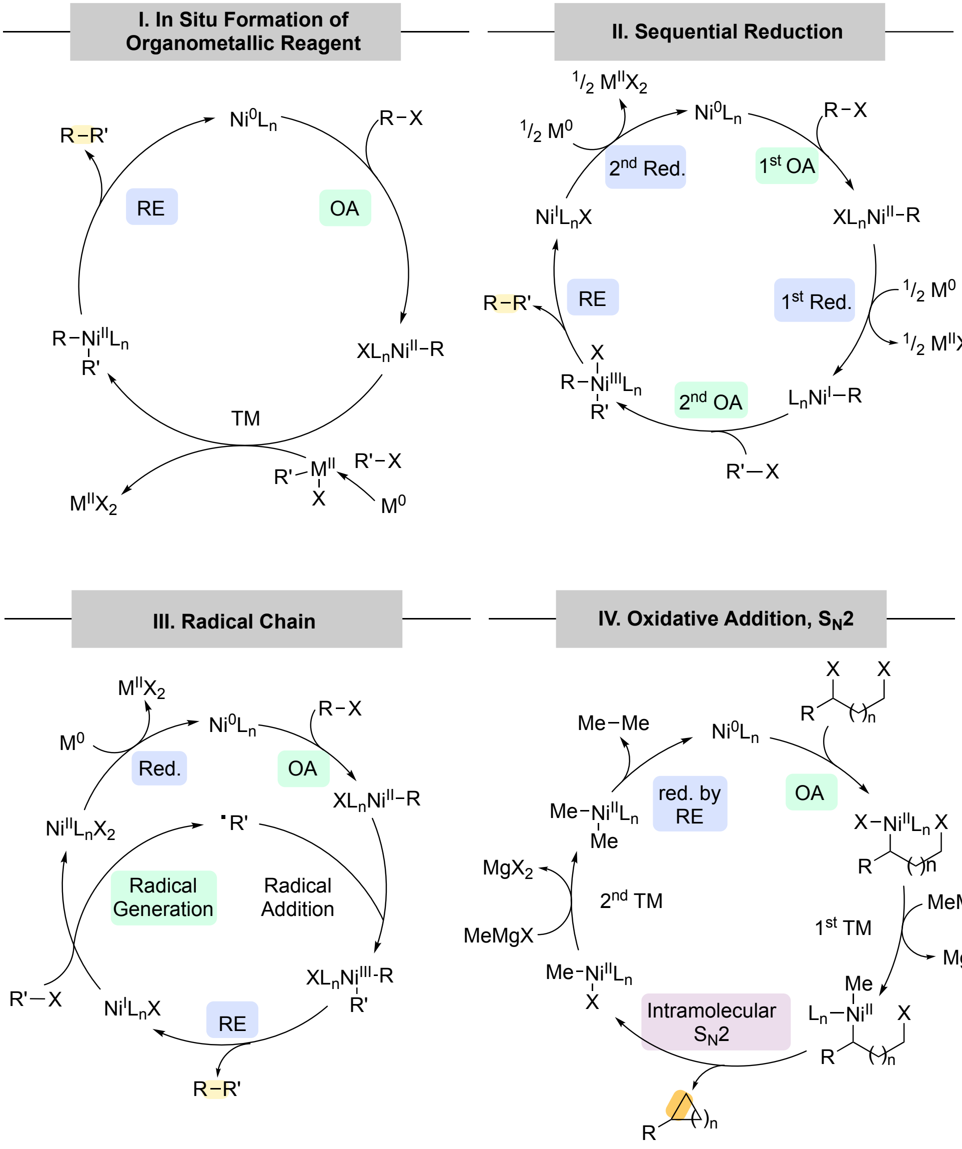
[6] (a) Börjesson, M.; Moragas, T.; Gallego, D.; Martin, R. *ACS Catal.* **2016**, *6*, 6739–6749. (b) Moragas, T.; Correa, A.; Martin, R. *Chem. Eur. J.* **2014**, *20*, 8242–8258. (c) Correa, A.; León, T.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 1062–1069. (d) Tortajada, A.; Börjesson, M.; Martin, R. *Acc. Chem. Res.* **2021**, *54*, 3941–3952. (e) Davies, J.; Lyonnet, J. R.; Zimin, D. P.; Martin, R. *Chem.* **2021**, *7*, 2927–2942.

[7] (a) Fürstner, A. *Chem. Rev.* **1999**, *99*, 991–1046. (b) Hargaden, G. C.; Guiry, P. J. *Adv. Synth. Catal.* **2007**, *349*, 2407–2424. (c) Santana, C. G.; Krische, M. J. *ACS Catal.* **2021**, *11*, 5572–5585.

[8] (a) Durandetti, M.; Hardou, L.; Lhermet, R.; Rouen, M.; Maddaluno, J. *Chem. Eur. J.* **2011**, *17*, 12773–12783. (b) Derosa, J.; Tran, V. T.; van der Puyl, V. A.; Engle, K. M. *Aldrichimica Acta* **2018**, *51*, 21–32. (c) Dhungana, R. K.; KC, S.; Basnet, P.; Giri, R. *Chem. Rec.* **2018**, *18*, 1314–1340. (d) Qi, X.; Diao, T. *ACS Catal.* **2020**, *10*, 8542–8556. (e) Derosa, J.; Apolinar, O.; Kang, T.; Tran, V. T.; Engle, K. M. *Chem. Sci.* **2020**, *11*, 4287–4296. (f) Diccianni, J.; Lin, Q.; Diao, T. *Acc. Chem. Res.* **2020**, *53*, 906–919.

[9] Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books, **2010.**

Figure 2.1: Proposed Mechanisms for Cross-Electrophile Coupling (XEC) Reactions.



When stoichiometric reducing metals, such as Zn, are employed it is feasible to propose in-situ formation of organometallic reagents (Figure 2.1, I). The catalytic cycle is then that of a traditional cross-coupling reaction, wherein oxidative addition occurs with one electrophile. Transmetallation (TM) occurs with the organometallic reagent that was formed in situ. Finally, reductive elimination (RE) produces the desired C–C bond. Identifying this mechanistic manifold is often reasonably straightforward by substitution of one electrophile and the reducing metal with the corresponding organometallic reagent. An alternative test to exclude this mechanism is to demonstrate that the XEC reaction can be conducted with organic reductants, such as tetrakis(dimethylamino)ethylene (TDAE), which is inconsistent with the formation of an organometallic reagent in situ.[2b,10]

The majority of XEC reactions typically undergo either sequential reduction or radical chain mechanisms (Figure 2.1, II and III). The Weix and Durandetti groups have performed extensive studies to elucidate the key steps of these mechanisms.[2a,2e,11,12] The two catalytic cycles are similar, in that both involve two oxidative events and two reductive events, and one oxidative event often involves formation of an alkyl radical. In a sequential reduction mechanism (Figure 2.1, II), one electrophile selectively engages the catalyst for oxidative addition, frequently by a concerted oxidative addition. This step is followed by reduction of the catalyst to form the Ni(I) intermediate. A second OA then occurs, and when C(sp^3) electrophiles are employed, this step frequently involves halogen atom abstraction and a short-lived organic radical.[13,14] Subsequent reductive elimination produces the C–C bond. A second reduction step turns over the catalyst.

In contrast, the radical chain mechanism involves a radical propagation step (Figure 2.1, III). The Ni(II) intermediate generated from oxidative addition captures the radical intermediate and leads to a Ni(III) complex. This species promptly undergoes reductive elimination, generating the desired product and a Ni(I) intermediate.[15,16] Next the Ni(I) species generates the alkyl radical via halogen atom abstraction. The resulting Ni(II) halide complex can be reduced to Ni(0) to re-enter the catalytic cycle.

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[10] Kuroboshi, M.; Waki, Y.; Tanaka, H. *J. Org. Chem.* **2003**, *68*, 3938–3942.
[11] Biswas, S.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 16192–16197.
[12] Durandetti, M.; Nédélec, J. Y.; Périchon, J. *J. Org. Chem.* **1996**, *61*, 1748–1755.
[13] Kehoe, R.; Mahadevan, M.; Manzoor, A.; McMurray, G.; Wienefeld, P.; Baird, M. C.; Budzelaar, P. H. M. *Organometallics* **2018**, *37*, 2450–2467.
[14] Diccianni, J. B.; Katigbak, J.; Hu, C.; Diao, T. *J. Am. Chem. Soc.* **2019**, *141*, 1788–1796.
[15] Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319–6332.
[16] Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547–7560.

Recently, the Jarvo and Hong groups reported a distinct mechanism for the intramolecular XEC reaction (Figure 2.1, IV).[17,18] In contrast to the sequential reduction and radical chain mechanisms, this mechanism involves a single oxidative addition and reductive elimination event. These reactions have employed methylmagnesium iodide, not as a coupling partner, but as the terminal reducing agent. In this mechanism, oxidative addition selectively occurs at the benzylic or secondary electrophile. Transmetallation with the Grignard reagent produces the key alkylnickel intermediate which undergoes the proposed intramolecular S_N2-type reaction to afford the cyclized product. Subsequent transmetalation and reductive elimination of ethane regenerates the active nickel catalyst.

The mechanism for a given XEC reaction can be difficult to predict by simple inspection of the starting materials, catalyst, and reagents. In particular, deciphering whether the sequential reduction or radical chain mechanism is operative is quite difficult and requires extensive mechanistic studies. However, it is crucial to identify and elucidate the key mechanistic steps as it allows for development of new methods that build upon these elementary steps.

2.3 XEC Reactions Employing Stoichiometric Reductants

2.3.1 Reactions of C(sp^2) Electrophiles (Type A)

2.3.1.1 Dimerization Reactions of C(sp^2) electrophiles

The reductive dimerization reaction of aryl halides has been known since the early twentieth century when Ullman and co-workers reported the first reductive dimerization reaction of an aryl bromide in the presence of copper powder in 1901.[4,19] This original report employed stoichiometric copper powder and high temperatures (>200 °C). Since this

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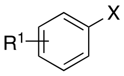
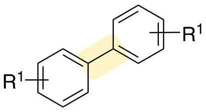
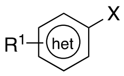
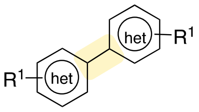
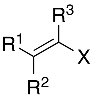
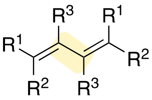
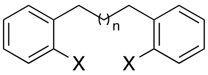
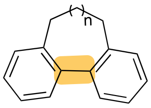
[17] Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, S.-Q.; Tollefson, E. J.; Erickson, L. W.; Taylor, B. L. H.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835–5855.

[18] Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen, P. P.; Hong, X.; Jarvo, E. R. *J. Am. Chem. Soc.* **2020**, *142*, 5017–5023.

[19] Ullmann, F.; Bielecki, J. *Berichte der Dtsch. Chem. Gesellschaft* **1901**, *34*, 2174–2185.

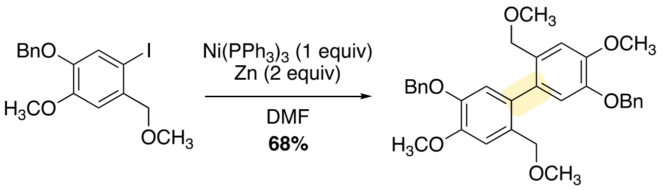
publication, stoichiometric and catalytic variations have been developed to accomplish C–C bond formation. A wide range of aryl, heteroaryl, and vinyl halides and pseudohalides have been employed (Table 2.1).

Table 2.1: Dimerization Reactions of $C(sp^2)$ Electrophiles

Entry	Starting Material[a]	Product	Metal Catalyst	Reducing Agent
1			Ni, Pd, Co	Cu, Zn, Mn, TDAE, Mg, LiH
2			Ni, Pd	Cu, Zn, Polyethylene Glycol
3			Cu, Ni	Zn
4			Cu, Ni	Zn

[a]X = I, Br, Cl, OTs, OTf, or OMs

Early examples of reductive dimerization reactions were mediated by reducing metals such as Cu, Ni and Pd to accomplish the C–C bond formation.[10,19,20,21,22,23,24,25,26] In 1975, Kende and co-workers reported the synthesis of highly substituted biaryls with one equivalent of a nickel triphenylphosphine complex (eq 2.1).[21]



(2.1)

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[20] Semmelhack, M. F.; Helquist, P. M.; Jones, L. D. *J. Am. Chem. Soc.* **1971**, *93*, 5908–5910.

[21] Kende, A. S.; Liebeskind, L. S.; Braitsch, D. M. *Tetrahedron Lett.* **1975**, *16*, 3375–3378.

[22] Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. S.; Gorzynski Smith, J.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460–6471.

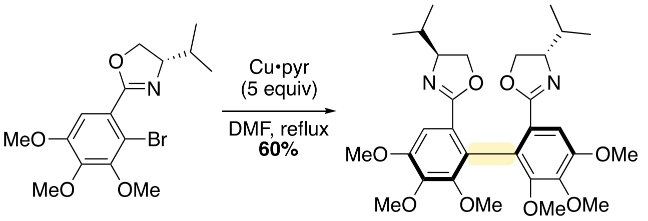
[23] Inaba, S.; Matsumoto, H.; Rieke, R. D. *Tetrahedron Lett.* **1982**, *23*, 4215–4216.

[24] Matsumoto, H.; Inaba, S.; Rieke, R. D. *J. Org. Chem.* **1983**, *48*, 840–843.

[25] Reisch, H. A.; Enkelmann, V.; Scherf, U. *J. Org. Chem.* **1999**, *64*, 655–658.

[26] Zhang, S.; Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1997**, *62*, 2312–2313.

In addition, stoichiometric metals have been utilized to synthesize dimeric heterocycles.[27] Asymmetric variations have been developed for the synthesis of biphenyl compounds by incorporating a chiral auxiliary on the aryl halide moiety (eq 2.2).[28,29,30,31] This strategy has been applied to the total synthesis of axially chiral natural products, such as *o*-permethyl tellimagrandin I.[32]



(2.2)

It was realized in the early 1990s that catalytic quantities of metal complexes could also accomplish biaryl bond formation, if a stoichiometric amount of a sacrificial reducing agent was included.[21,22,33,34,35,36,37,38,39,40,41,42,43,44,45,46] Such bimetallic methods are advantageous because an abundant and inexpensive reducing agent can be employed to affect turnover of a transition-metal catalyst that is more precious and/or more toxic.[47] Typically, the sacrificial metal reductants utilized in XEC reactions are zinc and manganese. As an example, in 1995 Percec and co-workers reported the dimerization reaction of aryl sulfonates in the presence of

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[27] Tiecco, M.; Testaferri, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1984**, *1984*, 736–738.

[28] Meyers, A. I.; McKennon, M. J. *Tetrahedron Lett.* **1995**, *36*, 5869–5872.

[29] Nelson, T. D.; Meyers, A. I. *Tetrahedron Lett.* **1993**, *34*, 3061–3062.

[30] Nelson, T. D.; Meyers, A. I. *Tetrahedron Lett.* **1994**, *35*, 3259–3262.

[31] Nelson, T. D.; Meyers, A. I. *J. Org. Chem.* **1994**, *59*, 2655–2658.

[32] Nelson, T. D.; Meyers, A. I. *J. Org. Chem.* **1994**, *59*, 2577–2580.

[33] Zembayashi, M.; Tamao, K.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1977**, *18*, 4089–4091.

[34] Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627–2637.

[35] Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80–87.

[36] Percec, V.; Bae, J. Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176–185.

[37] Massicot, F.; Schneider, R.; Fort, Y. *J. Chem. Res.* **1999**, *2*, 664–665.

[38] Leadbeater, N. E.; Resouly, S. M. *Tetrahedron Lett.* **1999**, *40*, 4243–4246.

[39] Howarth, J.; James, P.; Dai, J. *Tetrahedron Lett.* **2000**, *41*, 10319–10321.

[40] Zuo, Z.; Kim, R. S.; Watson, D. A. *J. Am. Chem. Soc.* **2021**, *143*, 1328–1333.

[41] Takagi, K.; Hayama, N.; Sasaki, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1887–1890.

[42] Jutand, A.; Mosleh, A. *Synlett* **1993**, 568–570.

[43] Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, *62*, 261–274.

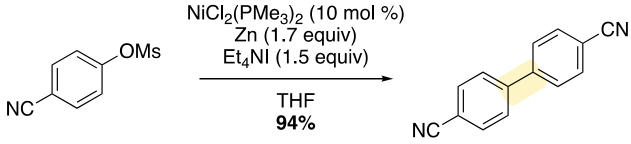
[44] Wang, L.; Zhang, Y.; Liu, L.; Wang, Y. *J. Org. Chem.* **2006**, *71*, 1284–1287.

[45] Bhattacharjya, A.; Klumphu, P.; Lipshutz, B. H. *Nat. Commun.* **2015**, *6*, 1–6.

[46] Moncomble, A.; Le Floch, P.; Gosmini, C. *Chem. Eur. J.* **2009**, *15*, 4770–4774.

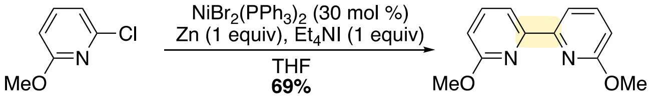
[47] Kasprzak, K. S.; Diwan, B. A.; Rice, J. M.; Misra, M.; Riggs, C. W.; Olinski, R.; Dizdaroglu, M. *Chem. Res. Toxicol.* **1992**, *5*, 809–815.

a nickel catalyst and zinc powder (eq 2.3).[36] In addition to aryl electrophiles, the reductive dimerization reactions of vinyl halides have been employed to afford symmetrical dienes.[21,22,26,40]



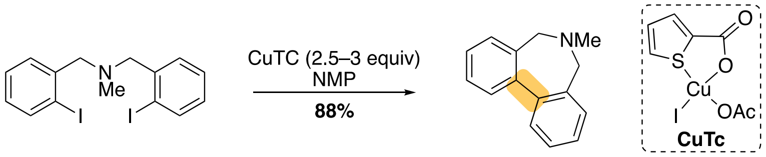
(2.3)

The dimerization reaction of halopyridines has also been established (eq. 2.4).[35,38,44,48] This method has been employed for the synthesis of bipyridine ligands, which are a common ligand scaffold used in XEC reactions themselves.[49,50,51,52] Additionally, heterocycles such as thiophene, thiazole, pyrrole, and furan undergo efficient dimerization reactions.[22,26,33,34,41,44,45,53,54]



(2.4)

Finally, intramolecular variations have been reported, including formation of medium-sized rings.[22,26] For example, Liebeskind and co-workers demonstrated that seven membered rings could be constructed via an intramolecular XEC reaction (eq 2.5).[26]



(2.5)

2.3.1.2 Cross-Selective XEC Reactions of C(sp^2) Electrophiles

The XEC reaction between two different C(sp^2) hybridized electrophiles was not realized until the early 2000's.[55] Since then, a wide range of cross-selective reactions that

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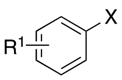
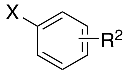
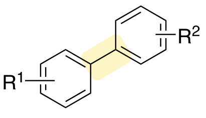
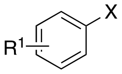
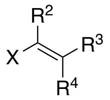
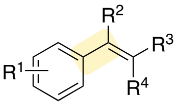
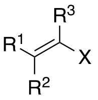
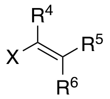
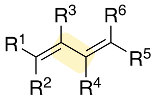
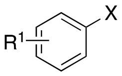
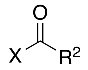
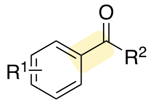
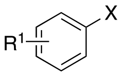
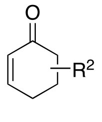
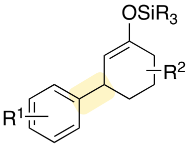
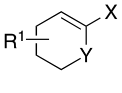
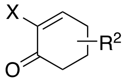
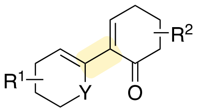
[48] Chan, K. S.; Tse, A. K. S. *Synth. Commun.* **1993**, *23*, 1929–1934.
[49] Constable, E. C.; Morris, D.; Carr, S. *New J. Chem.* **1998**, *22*, 287–294.
[50] Zhang, B.; Breslow, R. *J. Am. Chem. Soc.* **1997**, *119*, 1676–1681.
[51] Janiak, C. *Synthesis* **1999**, 959–964.
[52] Wong, H. L.; Tian, Y.; Chan, K. S. *Tetrahedron Lett.* **2000**, *41*, 7723–7726.
[53] Venkatraman, S.; Li, C.-J. *Org. Lett.* **1999**, *1*, 1687–1687.
[54] Sessler, J. L.; Hoehner, M. C. *Synlett* **1994**, 211–212.
[55] Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron* **2001**, *57*, 7845–7855.

combine aryl halides and pseudohalides, as well as vinyl halides and pseudohalides, acid chlorides, and enones have been reported (Table 2.2).

Table 2.2: Cross-Selective XEC Reactions of C(sp^2) Electrophiles

Entry	Starting Material 1^a	Starting Material 2^a	Product	Metal Catalyst	Reducing Agent
1				Ni, Pd, Co, Fe	Zn, Mn, Mg, $B_2(pin)_2$ Polyethylene glycol
2				Ni, Co, Fe	Zn, Mn, Mg
3				Ni, Pd	Zn
4				Ni, Pd	Zn
5				Ni	Mn
6				Co	Mn

^{a}X = I, Br, Cl, CN, OTs, OTf, OMs, OAc, SO_2CF_2H, NR_2, OCOR, or O*t*-Bu

A major goal in the development of these reactions is achieving cross-selectivity between two electrophiles under practical conditions with synthetically useful yields. There have been several successful strategies employed including using excess of one C(sp^2) electrophile,[41,55,56] electronic differentiation of the two electrophiles[57,58,59] or the use of co-catalysts.[60,61,62,63,64]

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[56] Amatore, M.; Gosmini, C. *Angew. Chem. Int. Ed.* **2008**, *47*, 2089–2092.

[57] Qian, Q.; Zang, Z.; Wang, S.; Chen, Y.; Lin, K.; Gong, H. *Synlett* **2013**, *24*, 619–624.

[58] Chen, Z.; Wang, X. A *Org. Biomol. Chem.* **2017**, *15*, 5790–5796.

[59] Dorval, C.; Tricoire, M.; Begouin, J. M.; Gandon, V.; Gosmini, C. *ACS Catal.* **2020**, *10*, 12819–12827.

[60] Ackerman, L. K. G.; Lovell, M. M.; Weix, D. J. *Nature* **2015**, *524*, 454.

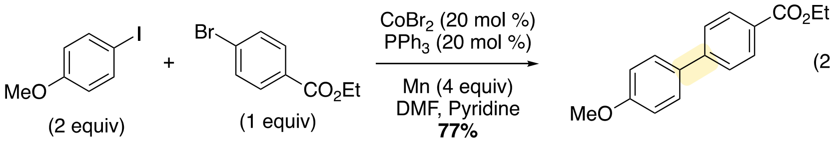
[61] Hanna, L. E.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 15618–15620.

[62] Huang, L.; Ackerman, L. K. G.; Kang, K.; Parsons, A. M.; Weix, D. J. *J. Am. Chem. Soc.* **2019**, *141*, 10978–10983.

[63] Xiong, B.; Li, Y.; Wei, Y.; Kramer, S.; Lian, Z. *Org. Lett.* **2020**, *22*, 6334–6338.

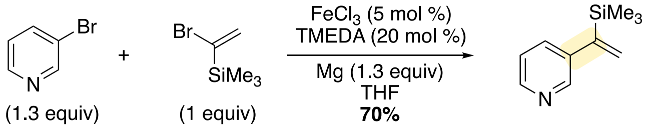
[64] Kang, K.; Huang, L.; Weix, D. J. *J. Am. Chem. Soc.* **2020**, *142*, 10634–10640.

For example, in a reaction of aryl halides, Gosmini and co-workers utilized an excess of the more reactive aryl iodide to ensure conversion of the less reactive aryl bromide to the cross product (eq 2.6). In addition, the authors noted that the aryl halides must be electronically differentiated in order to achieve the desired unsymmetrical biaryl.[56] This requirement can lead to limitations in substrate scope. Similar methods, including nickel- and palladium-catalyzed reactions, involve the XEC reaction of heterocyclic electrophiles.[10,20,21,44,55,56,57,60,62,65,66,67,68,69]



(2.6)

Another successful strategy to promote cross-reactivity is to employ two C(sp^2) electrophiles with different electronic or steric features. For example, Wangelin and co-workers exhibited cross-selectivity between aryl bromides and vinyl bromides (eq 2.7).[69] Interestingly, they utilized an earth abundant iron catalyst. The XEC reaction of vinyl halides have also been realized with nickel- and cobalt-catalysts.[69,70,71,72,73,74,75] In addition, functionalized ketones have been synthesized via XEC reactions of acyl electrophiles.[76,77,78]



(2.7)

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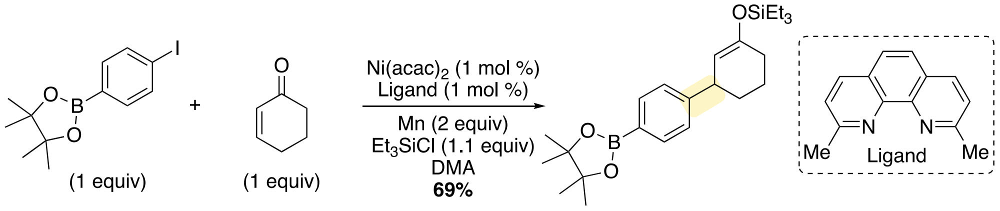
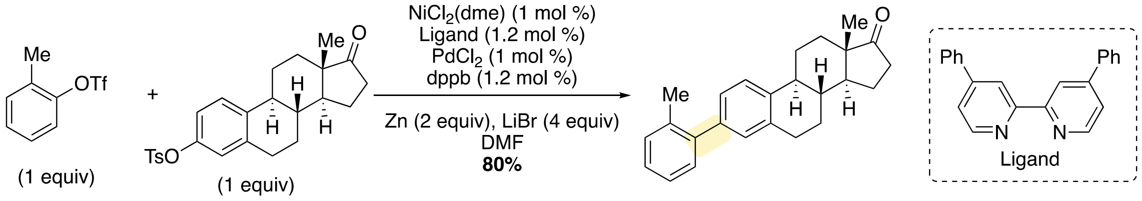
[65] Gosmini, C.; Bassene-Ernst, C.; Durandetti, M. *Tetrahedron* **2009**, *65*, 6141–6146.
[66] Liao, L. Y.; Kong, X. R.; Duan, X. F. *J. Org. Chem.* **2014**, *79*, 777–782.
[67] Gong, C.; Huo, C.; Wang, X.; Quan, Z. *Chinese J. Chem.* **2017**, *35*, 1137–1366.
[68] Miao, W.; Ni, C.; Xiao, P.; Jia, R.; Zhang, W.; Hu, J. *Org. Lett.* **2021**, *23*, 711–715.
[69] Czaplik, W. M.; Mayer, M.; Jacobi von Wangelin, A. *ChemCatChem* **2011**, *3*, 135–138.
[70] Liu, J.; Ren, Q.; Zhang, X.; Gong, H. *Angew. Chem. Int. Ed.* **2016**, *55*, 15544–15548.
[71] Xiong, B.; Wang, T.; Sun, H.; Li, Y.; Kramer, S.; Cheng, G. J.; Lian, Z. *ACS Catal.* **2020**, *10*, 13616–13623.
[72] Amatore, M.; Gosmini, C.; Périchon, J. *Eur. J. Org. Chem.* **2005**, *2005*, 989–992.
[73] Moncomble, A.; Floch, P. Le; Lledos, A.; Gosmini, C. *J. Org. Chem.* **2012**, *77*, 5056–5062.
[74] Olivares, A. M.; Weix, D. J. *J. Am. Chem. Soc.* **2018**, *140*, 2446–2449.
[75] Sha, Y.; Liu, J.; Wang, L.; Liang, D.; Wu, D.; Gong, H. *Org. Biomol. Chem.* **2021**, *19*, 4887–4890.
[76] Ni, S.; Zhang, W.; Mei, H.; Han, J.; Pan, Y. *Org. Lett.* **2017**, *19*, 2536–2539.
[77] Lin, T.; Mi, J.; Song, L.; Gan, J.; Luo, P.; Mao, J.; Walsh, P. J. *Org. Lett.* **2018**, *20*, 1191–1194.
[78] Zhu, Z.; Gong, Y.; Tong, W.; Xue, W.; Gong, H. *Org. Lett.* **2021**, *23*, 2158–2163.

Reductive coupling reactions have been expanded to include α,β-unsaturated ketones[79] and α-bromo enones.[80] An interesting example of a reductive conjugate addition involves an aryl iodide with α,β-unsaturated enone (eq 2.8).[79] The authors demonstrated that aryl boronic acids and esters are well tolerated which can potentially lead to subsequent Suzuki-Miyaura coupling reactions.[81]



(2.8)

Finally, the Weix and Lian research groups independently demonstrated that a co-catalysis strategy could selectivity engage two different sulfonates to achieve cross-selectivity (eq 2.9).[63,64] In order for this strategy to be successful, each catalyst must preferentially engage one electrophile. It was previously demonstrated that electron-rich palladium complexes could selectively engage aryl triflates over aryl halides.[82] The authors propose that the nickel complex catalyzes conversion of the aryl tosylate to the arylzinc reagent, which then undergoes palladium-catalyzed XC with the aryl triflate.[60,83]



(2.9)

2.3.2 XEC Reactions of C(sp) Electrophiles (Type D)

While the XEC reactions of C(sp^2) and C(sp^3) have been well established, the incorporation of C(sp) electrophiles has lagged. Traditionally, the Sonogashira coupling

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[79] Shrestha, R.; Dorn, S. C. M.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 751–762.

[80] Beng, T. K.; Sincavage, K.; Silaire, A. W. V; Alwali, A.; Bassler, D. P.; Spence, L. E.; Beale, O. *Org. Biomol. Chem.* **2015**, *13*, 5349–5353.

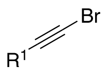
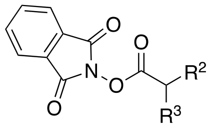
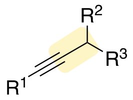
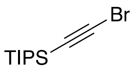
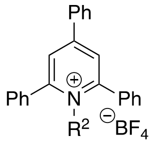
[81] Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

[82] Kamikawa, T.; Hayashi, T. *Tetrahedron Lett.* **1997**, *38*, 7087–7090.

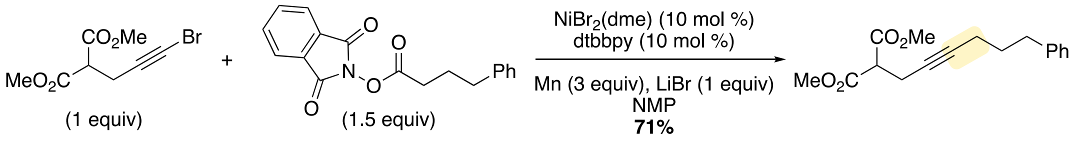
[83] Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 194–202.

reaction is used for the formation of C(sp)–C(sp^2) bonds and is typically a straightforward approach to synthesis of these compounds.[84,85] XEC reactions provide a mechanistically interesting alternative that allows for facile coupling of bromoalkynes with alkyl electrophiles. (Table 2.3)

Table 2.3: XEC Reactions of C(sp) and C(sp^3) Electrophiles

Entry	Starting Material 1	Starting Material 2	Product	Metal Catalyst	Reducing Agent
1				Ni	Mn
2				Ni	Zn

Both reported examples employed alkynyl bromides and radical precursors to achieve the C(sp)–C(sp^3) coupling reaction.[86,87] For example, in 2016, the Weix group reported the XEC reaction of bromoalkynes and NHP esters (eq 2.10).[87]



(2.10)

2.4 XEC Reactions Employing Electrochemical Reductions

Electrochemical reductions have been utilized in XEC reactions.[88,89,90] These methods avoid the need for stoichiometric reducing metals. The difficulties associated with employing metal powders such as Zn and Mn are the formation of heterogenous reaction mixtures and the necessity to use high boiling point amide solvents, such as DMA or DMF. Electrochemistry,

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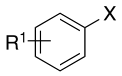
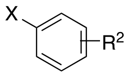
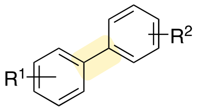
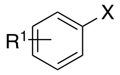
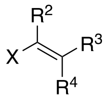
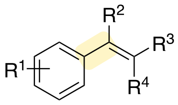
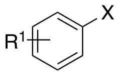
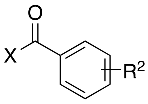
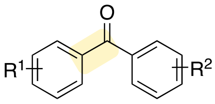
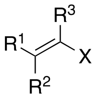
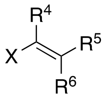
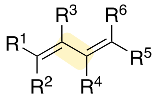
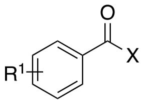
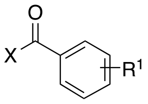
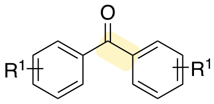
[84] Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874–922.
[85] Chinchilla, R.; Nájera, C. *Chem. Soc. Rev.* **2011**, *40*, 5084.
[86] Ni, S.; Li, C. X.; Mao, Y.; Han, J.; Wang, Y.; Yan, H.; Pan, Y. *Sci. Adv.* **2019**, *5*, 9516–9544.
[87] Huang, L.; Olivares, A. M.; Weix, D. J. *Angew. Chem. Int. Ed.* **2017**, *56*, 11901–11905.
[88] Jutand, A. *Chem. Rev.* **2008**, *108*, 2300–2347.
[89] Nédélec, J.-Y.; Périchon, J.; Troupel, M. *Top. Curr. Chem.* **1997**, 141–173.
[90] Gale-Day, Z. J. *Synthesis* **2021**, *53*, 879–888.

on the other hand, is a simple, homogenous and inexpensive method that provides the electrons necessary for catalyst turnover. Additionally, electroreductive methods are ideal for industrial scale processes because large amounts of metallic waste are not produced. Furthermore, there is less of a need for metal scavengers to remove trace metals in reaction products. This can facilitate rapid and efficient syntheses of potential drug candidates. Despite these advantages, electroreductive coupling reactions are less common that the methods employing stoichiometric reductants. Nonetheless, it has been demonstrated that electrochemical conditions can be used for the majority of substrate classes typically employed in XEC reactions.

2.4.1 XEC Reactions of C(sp^2) Electrophiles (Type A)

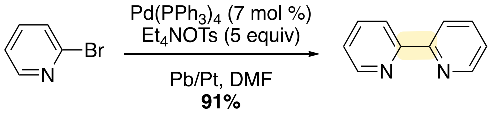
Some of the earliest examples of XEC reactions of aryl electrophiles employed electroreductive methods to forge the desired C–C bond. The methods have allowed for the synthesis of unsymmetrical biaryls including heterocyclic compounds. In addition, styrenes, dienes and unsymmetrical ketones have also been efficiently constructed with electroreductive methods. With judicious choice of cathode, anode, electrolyte, and solvent, successful XEC reactions are possible (Table 2.4).

Table 2.4: Electrochemical XEC Reactions of C(sp^2) Electrophiles

Entry	Starting Material 1	Starting Material 2	Product	Metal Catalyst	Electrode[a]
1				Ni, Pd, Co	Ni/Cu; Pb/Pt; Pt/Pt; Au/Mg; Ni/Fe; Ni/Zn; Pt/Ni; Fe/Fe; Glassy Carbon/Pt; Carbon Cloth/Mg
2				Ni, Co, Fe	Fe/Fe; Ni/Zn; Ni/Al
3				Ni	Au/Zn
4				Ni, Pd	Au/Mg; Ni/Al
5				Ni	Ni/Ni

X = I, Br, Cl, OTf, OAc
[a]cathode/anode

Dimerization reactions have been a useful method to forge biaryls.[43,91,92,93,94,95,96,97,98,99,100,101,102] This concept has been applied to the synthesis of bipyridines (eq 2.11).[95,103,104]



(2.11)

Cross-selective examples of electroreductive XEC reactions lagged behind the dimerization of aryl electrophiles because of the difficulties associated with cross-selectivity

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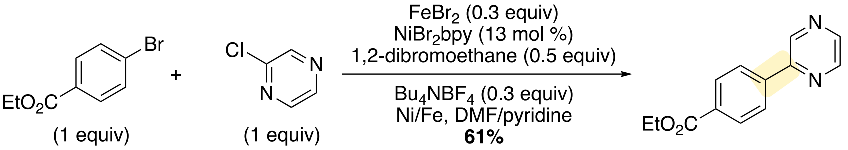
[91] Jennings, P. W.; Pillsbury, D. G.; Hall, J. L.; Brice, V. T. *J. Org. Chem.* **1976**, *41*, 719–722.
[92] Schiavon, G.; Bontempelli, G.; Corain, B. *J. Chem. Soc., Dalt. Trans.* **1981**, *202*, 1074–1081.
[93] Mori, M.; Hashimoto, Y.; Ban, Y. *Tetrahedron Lett.* **1980**, *21*, 631–634.
[94] Troupel, M.; Rollin, Y.; Sibille, S.; Perichon, J.; Fauvarque, J.-F. *J. Organomet. Chem.* **1980**, *202*, 435–446.
[95] Torii, S.; Tanaka, H.; Morisaki, K. *Tetrahedron Lett.* **1985**, *26*, 1655–1658.
[96] Rollin, Y.; Troupel, M.; Tuck, D. G.; Perichon, J. *J. Organomet. Chem.* **1986**, *303*, 131–137.
[97] Meyer, G.; Rollin, Y.; Perichon, J. *J. Organomet. Chem.* **1987**, *333*, 263–267.
[98] Fox, M. A.; Chandler, D. A.; Lee, C. *J. Org. Chem.* **1991**, *56*, 3246–3255.
[99] Jutand, A.; Négri, S.; Mosleh, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1729–1730.
[100] Courtois, V.; Barhdadi, R.; Troupel, M.; Périchon, J. *Tetrahedron* **1997**, *53*, 11569–11576.
[101] Yasuhara, A.; Kasano, A.; Sakamoto, T. *J. Synth. Org. Chem. Japan* **2000**, *58*, 192–198.
[102] Courtois, V.; Barhdadi, R.; Condon, S.; Troupel, M. *Tetrahedron Lett.* **1999**, *40*, 5993–5996.
[103] Cassol, T. M.; Demnitz, F. W. J.; Navarro, M.; Neves, E. A. *Tetrahedron Lett.* **2000**, *41*, 8203–8206.
[104] de França, K. W. R.; Navarro, M.; Léonel, É.; Durandetti, M.; Nédélec, J.-Y. *J. Org. Chem.* **2002**, *67*, 1838–1842.

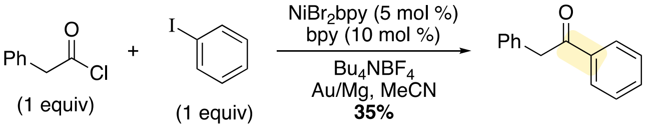
(vide supra).[97,98,105,106,107] The Gosmini group reported a cross-selective reaction between aryl bromides and 2-chloropyrimidine (eq 2.12).[108] Key to their success was the use of sub-stoichiometric $FeBr_2$ which prevented strong ligation of pyrimidine to the nickel catalyst.



(2.12)

Similar strategies have been employed to achieve the cross-selective XEC reaction of other aryl electrophiles and heterocyclic substrates.[108,109,110,111,112,113,114] Additionally, vinyl electrophiles are well suited to undergo reductive dimerization reactions[96,115] and cross selective reactions.[12,115,116]

Finally, XEC reactions have been achieved with acid chlorides.[117,118] For example, Marzouk et. al reported the cross-selective XEC reaction between aryl iodides and acid chlorides (eq 2.13).[117]



(2.13)

2.4.2 XEC Reactions of $C(sp^2)$ and $C(sp^3)$ Electrophiles (Type B)

Similar to XEC reactions with reducing agents, the most common combination reported for XEC is $C(sp^2)$–$C(sp^3)$ coupling reactions (Table 2.5). This is because the partners often

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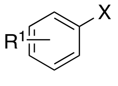
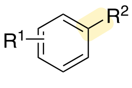
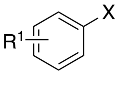
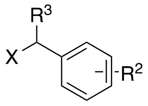
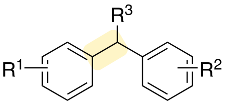
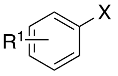
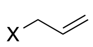
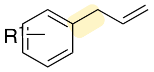
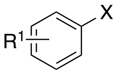
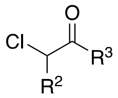
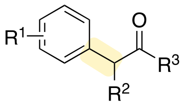
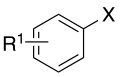
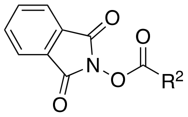
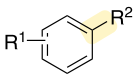
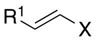
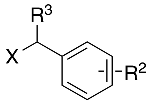
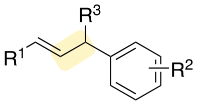
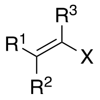
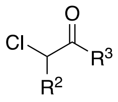
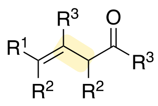
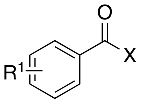
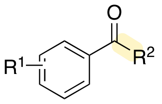
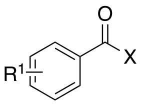
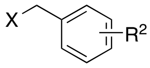
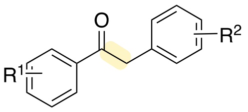
[105] Amatore, C.; Carré, E.; Jutand, A.; Tanaka, H.; Ren, Q.; Torii, S. *Chem. Eur. J.* **1996**, *2*, 957–966.
[106] Meyer, G.; Troupel, M.; Périchon, J. *J. Organomet. Chem.* **1990**, *393*, 137–142.
[107] Gomes, P.; Fillon, H.; Gosmini, C.; Labbé, E.; Périchon, J. *Tetrahedron* **2002**, *58*, 8417–8424.
[108] Gosmini, C.; Nédélec, J. Y.; Périchon, J. *Tetrahedron Lett.* **2000**, *41*, 201–203.
[109] Gosmini, C.; Lasry, S.; Nedelec, J. Y.; Perichon, J. *Tetrahedron* **1998**, *54*, 1289–1298.
[110] Gosmini, C.; Nédélec, J. Y.; Périchon, J. *Tetrahedron Lett.* **2000**, *41*, 5039–5042.
[111] Sengmany, S.; Léonel, E.; Polissaint, F.; Nédélec, J.-Y.; Pipelier, M.; Thobie-Gautier, C.; Dubreuil, D. *J. Org. Chem.* **2007**, *72*, 5631–5636.
[112] Sengmany, S.; Le Gall, E.; Léonel, E. *Molecules* **2011**, *16*, 5550–5560.
[113] Sengmany, S.; Vitu-Thiebaud, A.; Le Gall, E.; Condon, S.; Léonel, E.; Thobie-Gautier, C.; Pipelier, M.; Lebreton, J.; Dubreuil, D. *J. Org. Chem.* **2013**, *78*, 370–379.
[114] Sengmany, S.; Vasseur, S.; Lajnef, A.; Le Gall, E.; Léonel, E. *Eur. J. Org. Chem.* **2016**, *2016*, 4865–4871.
[115] Cannes, C.; Condon, S.; Durandetti, M.; Périchon, J.; Nédélec, J.-Y. *J. Org. Chem.* **2000**, *65*, 4575–4583.
[116] Gomes, P.; Gosmini, C.; Périchon, J. *Tetrahedron* **2003**, *59*, 2999–3002.
[117] Marzouk, H.; Rollin, Y.; Folest, J. C.; Nédélec, J. Y.; Périchon, J. *J. Organomet. Chem.* **1989**, *369*, C47–C50.
[118] Folest, J. C.; Pereira-Martins, E.; Troupel, M.; Périchon, J. *Tetrahedron Lett.* **1993**, *34*, 7571–7574.

engage the catalyst in mechanistically distinct pathways (vide supra). The partners are differentiated therefore promoting cross-selectivity.

Table 2.5: Electrochemical XEC Reactions of C(sp^2) and C(sp^3) Electrophiles

Entry	Starting Material 1	Starting Material 2	Product	Metal Catalyst	Electrode[a]
1		X–R^2		Ni	RVC/Zn; Ni/Zn; RVC/HN(*i*-Pr)$_2$ Graphite/Ni
2				Ni	Ni/Zn; Ni/Al Graphite/Ni
3				Ni	Ni/Zn; Ni/Al
4				Ni	Au/Hg; Ni/Zn; Ni/Al Carbon Fiber/Al Carbon Fiber/Zn
5				Ni	RVC/RVC; RVC/Zn
6				Ni	RVC/Zn; Ni/Zn
7				Ni	Ni/Al
8		X–R^2		Ni	Au/Zn; Au/Mg
9				Ni	Au/Zn; Au/Mg

X = I, Br, Cl, OH, OAc
[a] cathode/anode

A common functional group utilized in the 1990s and early 2000s was the α-chlorocarbonyl.[12,115,119,120,121,122] This electrophile cleanly undergoes an XEC reaction with a variety of electrophiles including aryl, heterocyclic and vinylic halides. For example,

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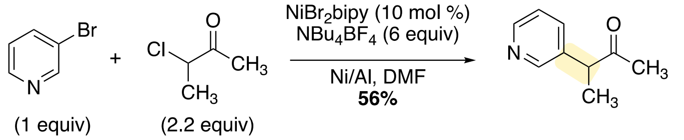
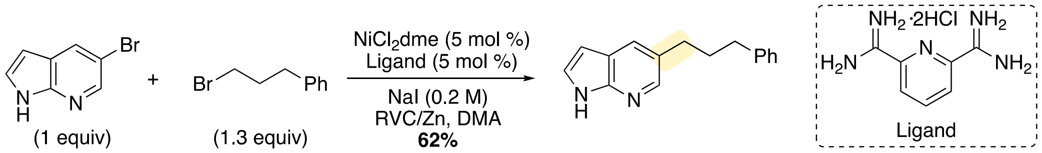
[119] Folest, J. C.; Périchon, J.; Fauvarque, J. F.; Jutand, A. *J. Organomet. Chem.* **1988**, *342*, 259–261.
[120] Conan, A.; Sibille, S.; D'Incan, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1990**, 48–49.
[121] Durandetti, M.; Sibille, S.; Nédélec, J.-Y.; Périchon, J. *Synth. Commun.* **1994**, *24*, 145–151.
[122] Durandetti, M.; Périchon, J.; Nédélec, J.-Y. *J. Org. Chem.* **1997**, *62*, 7914–7915.

Durandetti and co-workers reported the coupling of aryl bromides with α-chloroketones (eq 2.14).[121]



(2.14)

Additionally, electroreductive methods have been applied to coupling of aryl and alkyl electrophiles.[12,123,124,125,126,127,128,129] Recently, a group at Pfizer developed an electrochemical XEC reaction with a range of heterocyclic bromides, including an aza-indole (eq 2.15).[123] The authors noted that XEC reactions are ideal targets for drug design and electrochemistry can improve their scale up processes significantly compared to stoichiometric metals.



(2.15)

Building on previous enantioselective XEC reactions of vinyl bromides from their laboratory,[130] the Reisman group demonstrated that an enantioselective reaction under electroreductive conditions was feasible (eq 2.16).[131] The high enantioselectivity achieved with a bisoxazoline ligand is consistent with the proposed mechanisms involving halogen atom abstraction, since the enantiodetermining step should remain the same whether catalyst turnover is electrochemical or medicated by a reducing metal.

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[123] Perkins, R. J.; Pedro, D. J.; Hansen, E. C. *Org. Lett.* **2017**, *19*, 3755–3758.

[124] Perkins, R. J.; Hughes, A. J.; Weix, D. J.; Hansen, E. C. *Org. Process Res. Dev.* **2019**, *23*, 1746–1751.

[125] Truesdell, B. L.; Hamby, T. B.; Sevov, C. S. *J. Am. Chem. Soc.* **2020**, *142*, 5884–5893.

[126] Li, Z.; Sun, W.; Wang, X.; Li, L.; Zhang, Y.; Li, C. *J. Am. Chem. Soc.* **2021**, *143*, 3536–3543.

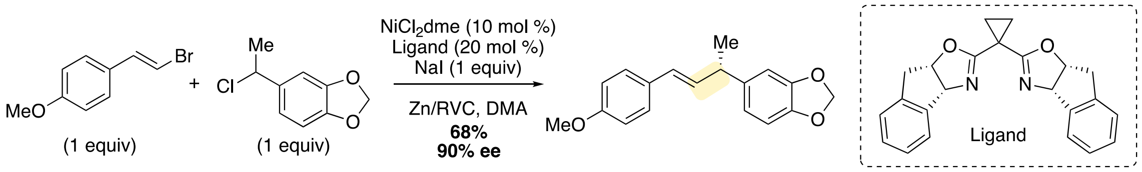
[127] Li, H.; Breen, C. P.; Seo, H.; Jamison, T. F.; Fang, Y. Q.; Bio, M. M. *Org. Lett.* **2018**, *20*, 1338–1341.

[128] Koyanagi, T.; Herath, A.; Chong, A.; Ratnikov, M.; Valiere, A.; Chang, J.; Molteni, V.; Loren, J. *Org. Lett.* **2019**, *21*, 816–820.

[129] Gomes, P.; Gosmini, C.; Périchon, J. *J. Org. Chem.* **2003**, *68*, 1142–1145.

[130] Cherney, A. H.; Reisman, S. E. *J. Am. Chem. Soc.* **2014**, *136*, 14365–14368.

[131] Delano, T. J.; Reisman, S. E. *ACS Catal.* **2019**, *9*, 6751–6754.

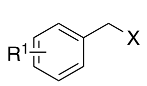
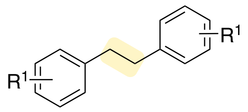
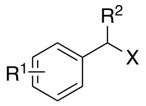
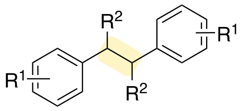
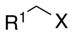
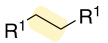
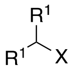
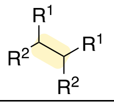


(2.16)

2.4.3 XEC Reactions of C(sp^3) Electrophiles (Type C)

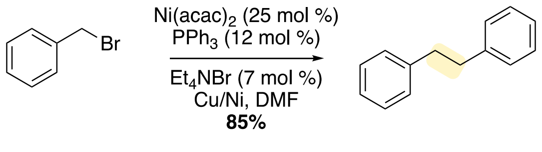
Although less common than the cross-selective XEC reactions of C(sp^2) and C(sp^3) electrophiles, reductive dimerization reactions of benzylic and aliphatic electrophiles have been established (Table 2.6).[91,92,96,132]

Table 2.6: Electrochemical Dimerization Reactions of C(sp^3) Electrophiles

Entry	Starting Material	Product	Metal Catalyst	Electrode^a
1			Ni	Cu/Ni; Pt/Pt; Au/Mg
2			Ni	Au/Mg
3			Ni, Fe	Ni/Ni; Al/Al; Pt/Pt Au/Mg; Hg/Pt
4			Fe	Ni/Ni

X = I, Br, Cl, OTf
^{a}cathode/anode

To illustrate, the Jennings group reported the dimerization reaction of benzyl bromide in good yield (eq 2.17).[91] In this report they were also able to achieve a good yield for a simple aliphatic electrophile, 1-octylbromide. Another report has demonstrated that secondary alkyl halides can efficiently undergo an iron-catalyzed dimerization reaction utilizing a Ni/Ni undivided cell.[132]



(2.17)

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[132] Mabrouk, S.; Pellegrini, S.; Folest, J.-C.; Rollin, Y.; Perichon, J. *J. Organomet. Chem.* **1986**, *301*, 391–400.

2.5 Conclusions

Transition metal-catalyzed XEC reactions have gained popularity over the past two decades as an efficient method to construct carbon-carbon bonds. Many of the methods discussed employ sustainable first-row transition metal catalysts, earth abundant metal reductants or electrochemistry and mild reaction conditions. We anticipate that as mechanistic insights grow and more general methods emerge, XEC reactions will become an essential tool in the organic chemist synthetic toolbox.

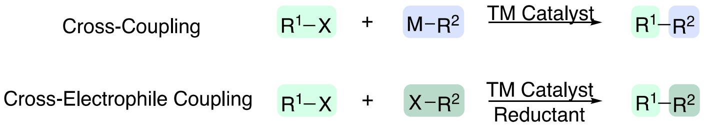
Chapter Three

Intramolecular Nickel-Catalyzed Cross-Electrophile Coupling Reactions of Sulfonamides

3.1 Introduction

Cross-electrophile coupling (XEC) reactions have emerged as a powerful tool in synthetic organic chemistry.[1,2] In contrast to traditional cross-coupling (XC) reactions where an electrophile (R–X) and an organometallic reagent (R–M) are coupled together in the presence of a transition metal (TM) catalyst, XEC reactions utilizes two electrophilic reagents, a TM catalyst, and a terminal reductant to forge the desired carbon-carbon bond. (Scheme 3.1).

Scheme 3.1 Cross-Coupling v. Cross-Electrophile Coupling Reactions



There are several advantages of XEC reactions. The first is that alkyl and aryl halides typically have greater commercial availability than the commonly used organometallic reagents. Additionally, the organometallic reagents are often prepared from the corresponding alkyl or aryl halides, whereas, XEC reactions would allow for the direct coupling of these electrophiles. Finally, due to the reactivity of organometallic reagents, they frequently require the extrusion of oxygen and moisture and are typically less functional group tolerant than the corresponding electrophiles which can limit the scope of the reaction.

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[1] Portions of this chapter have been published in the Journal of Organic Chemistry, see: Lucas, E. L.; Hewitt, K. A.; Chen, P.-P.; Castro, A. J.; Hong, X.; Jarvo, E. R. *J. Org. Chem.* **2020**, *85*, 1775–1793.

[2] For selected reviews on XEC reactions, see: (a) Hewitt, K. A.; Lin, P. C.; Raffman, E. T. A.; Jarvo, E. R. C–C Bond Formation via Cross-Electrophile Coupling Reactions. *Comprehensive Organometallic Chemistry IV*. **2021**. 10.1016/B978-0-12-820206-7.00092-5. (b) Everson, D. A.; Weix, D. *J. Org. Chem.* **2014**, *79*, 4793–4798. (c) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. *Chem. Eur. J.* **2014**, *20*, 6828–6842. (d) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1411–1421. (e) Wang, X.; Dai, Y.; Gong, H. *Top. Curr. Chem.* **2016**, *374*, 43. (f) Lucas, E. L.; Jarvo, E. R. *Nat. Rev. Chem*. **2017**, *1*, 0065. (g) Campeau, L.-C.; Hazari, N. *Organometallics* **2019**, *38*, 3–35. (h) Goldfogel, M. J.; Huang, L.; Weix, D. J. Cross-Electrophile Coupling: Principles and New Reactions. In *Nickel Catalysis in Organic Synthesis*; Ogoshi, S. Ed.; Wiley, 2020; pp 183–222.

The major challenge associated with this strategy is the homocoupling of electrophiles. The first reported example of the transition-metal mediated reductive homocoupling of electrophiles was the Ullman dimerization of aryl halides in 1901.[3,4] The selective XEC between two different electrophiles was not realized until later in the 20th century.[5] Unlike traditional XC reactions where the electrophile favors oxidative addition and the nucleophilic reagent favors transmetalation, in XEC reactions both reagents favor oxidative addition and the catalyst must be able to distinguish them in order to obtain cross-selectivity. This inherent challenge resulted in delayed efforts to explore and optimize these reactions.

Several strategies have been developed for optimal cross-selectivity (Scheme 3.2).[2a,2b,2f] One strategy includes employing an excess of one of the electrophiles. This allows for the isolation of statistical mixtures of homocoupled products and the desired cross-coupled product. As an example, the Gong group demonstrated that secondary and primary bromides could be coupled together by utilizing three equivalents of the more reactive primary bromide (Scheme 3.2a).[6] Another strategy is to electronically differentiate the starting materials. As an example, the Reisman group reported the XEC reaction between benzylic chlorides with acid chlorides and observed exclusive formation of the desired cross-coupled product (Scheme 3.2b).[7] Co-catalytic strategies have also been successful for the cross-selective XEC reactions. The Weix group reported a nickel and titanium co-catalytic strategy to forge the desired benzylic alcohols in high yield, diastereoselectivity and enantioselectivity (Scheme 3.2c).[8] Finally, the electrophiles can be

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[3] Ullmann, F.; Bielecki, J. *Chem. Ber.* **1901**, *34*, 2174–2185.

[4] For reviews on the Ullman coupling, see: (a) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139–196. (b) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327–3359. (c) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem. Int. Ed.* **1990**, *29*, 977–991. (d) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470. (e) Fanta, P. E. *Synthesis* **1974**, *1974*, 9–21.

[5] For progress on cross-selective XEC reactions between two electrophiles, see ref 2.

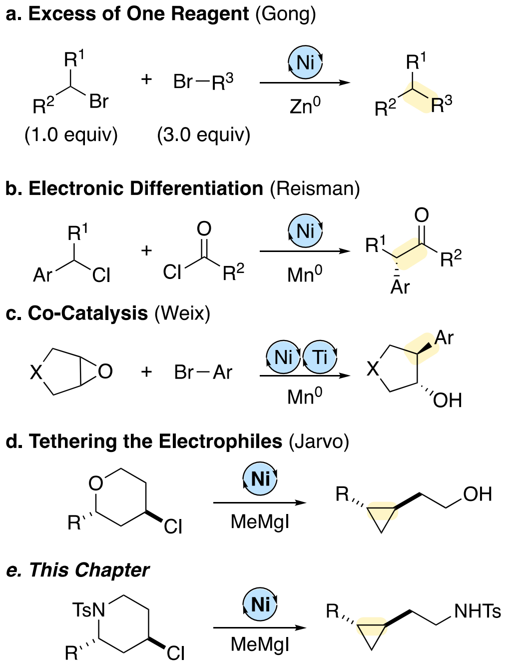
[6] Yu, X.; Yang, T.; Wang, S.; Xu, H.; Gong, H. *Org. Lett.* **2011**, *13*, 2138–2141.

[7] Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442–7445.

[8] Zhao, Y.; Weix, D. J. *J. Am. Chem. Soc.* **2015**, *137*, 3237–3240.

tethered together and the cyclized product can be isolated in high yield. For example, the Jarvo group reported the ring contraction of tetrahydrofurans to afford disubstituted cyclopropanes in high yield and diastereoselectivity (Scheme 3.2d).[9] We aimed to exploit this strategy of tethering the electrophiles together to develop an analogous XEC reaction of benzylic and allylic sulfonamides (Scheme 3.2e).[1]

Scheme 3.2 Representative Examples of Strategies for Cross-Selective XEC Reactions



In addition, the goal of this method was to activate the carbon-nitrogen bond in the sulfonamide. Amine derivatives are elusive electrophiles in XEC reactions and have been occasionally activated via transition-metal catalysis.[10] This functional group is also prevalent in natural products, biomolecules, and pharmaceutical agents which makes it an ideal candidate for

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[9] (a) Tollefson, E. J.; Erickson, L. W.; Jarvo, E. R. *J. Am. Chem. Soc.* **2015**, *137*, 9760–9763. (b) Erickson, L. W.; Lucas, E. L.; Tollefson, E. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2016**, *138*, 14006–14011.

[10] For recent reviews on cross-coupling reaction of C–N bonds, see: (a) Ouyang, K.; Hao, W.; Zhang, W.-X.; Xi, Z. *Chem. Rev.* **2015,** *115*, 12045−12090. (b) Wang, Q.; Su, Y.; Li, L.; Huang, H. *Chem. Soc. Rev.* **2016**, *45*, 1257−1272. (c) Pound, S. M.; Watson, M. P. *Chem. Commun.* **2018**, *54*, 12286–12301. (d) Huang, C.-Y.; Doyle, A. G. *Chem. Rev.* **2014**, *114*, 8153–8198.

further manipulation.[11] Finally, the carbon-nitrogen bond exhibits orthogonal reactivity compared with traditional electrophiles, such as halides and pseudohalides, which allows for selective functionalization.

Similar to the traditional XC reaction of amine derivatives, the current examples of XEC reactions require the activation of the carbon-nitrogen bond by the formation of ammonium salts or incorporation into strained rings.[10c,10d,12] For example, the Shu laboratory reported the XEC reaction of aryl ammonium triflates with vinylic acetates to afford the desired carbon-carbon bond (Scheme 3.3a).[13] Similarly, the Martin group reported the XEC reaction between benzylic trimethylammonium salts and CO_2 to afford carboxylic acids (Scheme 3.3b).[14] More recently, the Watson group developed the XEC reaction of benzylic Katritzky salts with aryl bromides to forge the desired carbon-carbon bond (Scheme 3.3c).[15] Finally, the Doyle and Sigman laboratories disclosed the XEC reaction of styrenyl aziridines with aryl iodides to yield enantioenriched 2-arylphenethylsulfonamides (Scheme 3.3d).[16] These examples demonstrate the feasibility of the development of XEC reactions of alkyl amine derivatives but also exemplify the current limitations.

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[11] (a) Nicolaou, K. C.; Montagnon, T. *Molecules that Changed the World*; Wiley-VCH: Germany, 2008. (b) Transition-Metal Catalyzed C–N Bond Activation; Fattorusso, E.; Taglialatela-Scafati, O., Eds. Modern Alkaloids: Structure, Isolation, Synthesis and Biology; Wiley-VCH, 2008. (c) Lawrence, S. A. *Amines: Synthesis, Properties, and Applications.* Cambridge University Press: New York, 2004.

[12] For examples of traditional XC reactions of amine derivatives, see (a) ref 10. (b) Chapter 1 of this thesis.

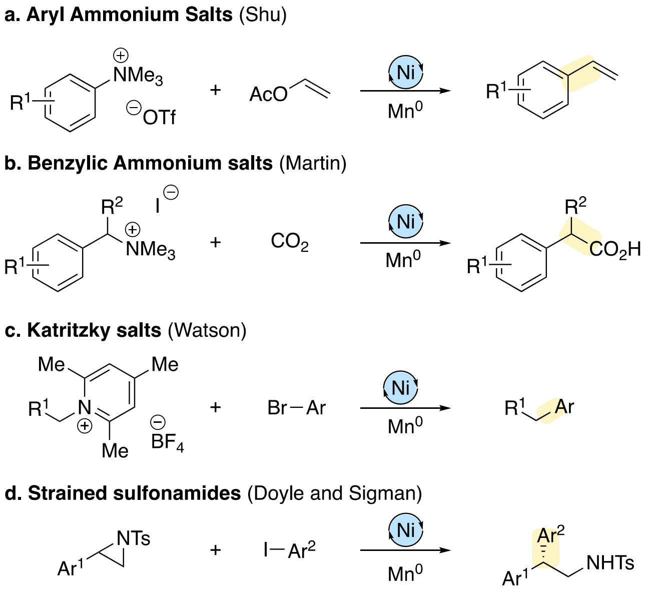
[13] He, R.-D.; Li, C.-L.; Pan, Q.-Q.; Guo, O.; Liu, X.-Y.; Shu, X.-Z. *J. Am. Chem. Soc.* **2019**, *141*, 12481–12486.

[14] Moragas, T.; Gaydou, M.; Martin, R. *Angew. Chem. Int. Ed.* **2016,** *55*, 5053–5057.

[15] Liao, J.; Basch, C. H.; Hoerner, M. E.; Talley, M. R.; Boscoe, B. P.; Tucker, J. W.; Garnsey, M. R.; Watson, M. P.. *Org. Lett.* **2019**, *21*, 2941–2946.

[16] Woods, B. P.; Orlandi, M.; Huang, C.-Y.; Sigman, M. S.; Doyle, A. G. *J. Am. Chem. Soc.* **2017**, *139*, 5688–5691.

Scheme 3.3 Representative Example of XEC Reactions of Amine Derivatives



In this Chapter, we report a nickel-catalyzed XEC reaction of benzylic and allylic sulfonamides (Scheme 3.2e). Optimization and implementation of the aza-Prins reaction is presented for the synthesis of the requisite starting materials. In addition, we demonstrate that *N*-tosyl-4-chloropiperidines undergo a ring contraction reaction to afford *trans*-substituted cyclopropanes in high yield and excellent diastereoselectivity. This work is a significant development because activation of the carbon-nitrogen bond is achieved without the utilization of a charged ammonium salt or a strained ring. Moreover, it demonstrates the ability to manipulate the structure of sulfonamides. New methods for the manipulation of these functional groups would be valuable because sulfonamides comprise nearly 30% of the newly FDA approved drugs bearing sulfur-containing functional groups.[17] This work sets the foundation for further development of nickel-catalyzed XEC reactions of amine derivatives and provides a structural rearrangement of sulfonamides by transforming *N*-tosylpiperidines to *N*-tosyl(aminoethyl)cyclopropanes.

3.2 Results and Discussion

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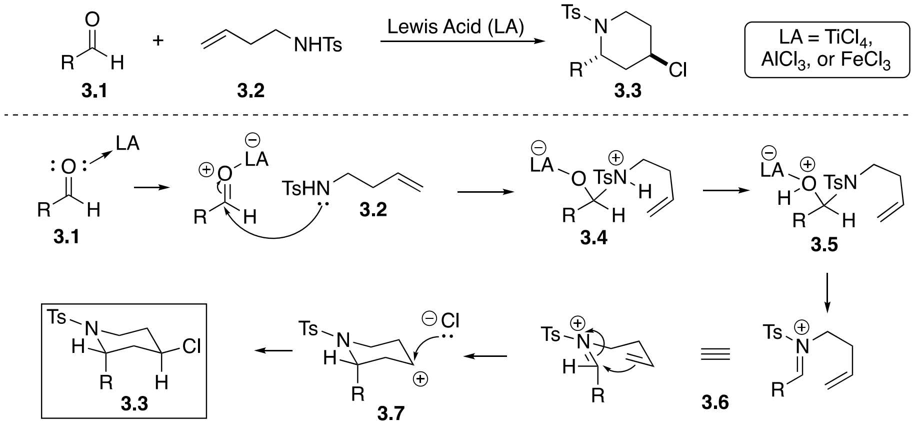
[17] Ilardi, E. A.; Vitaku, E.; Njardarson, J. T. *J. Med. Chem.* **2014**, *57*, 2832–2842.

3.2.1 Optimization of the Aza-Prins Cyclization

N-Tosyl-4-chloropiperidines were selected as the starting materials for the XEC reaction because they can be synthesized in one step via highly diastereoselective aza-Prins cyclizations from commercially available aldehydes.[18] The mechanism of the aza-Prins reaction is outlined in Figure 3.1. Coordination of the Lewis acid to the aldehyde (**3.1**) increases the electrophilicity of the carbonyl moiety and allows for the nucleophilic addition of the sulfonamide (**3.2**). A condensation reaction cleanly affords the imine with the tethered olefin (**3.6**). Olefin attack of the imine leads to the formation of the cyclized intermediate **3.7**. The resulting carbocation can be quenched with a nucleophile (Cl^-) in solution in a diastereoselective fashion to afford the desired piperidine **3.3**.

Figure 3.1 Mechanism of the Prins Cyclization



The aza-Prins cyclization selectively forms the *trans* diastereomer of the piperidine. The allylic strain imparted by the sulfonyl group drives the aryl or vinyl group to the axial position.[19] Addition of the chloride is highly stereoselective to avoid 1,3-diaxial interactions (see Figure 3.1,

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[18] For reviews on the Prins cyclization see: (a) Arundale, E.; Mikeska, L. A. *Chem. Rev.* **1952**, *51*, 505–555. (b) Adams, D. R.; Bhatnagar, S. P. *Synthesis*, **1977**, 661–672. (c) Olier, C.; Kaafarani, M.; Gastaldi, S.; Bertrand, M. P. *Tetrahedron*, **2010**, *66*, 413–445. (d) Pastor, I. M.; Yus, M. *Curr. Org. Chem.* **2012**, *16*, 1277–1312. (e) Reddy, B. V. S.; Nair, P. N.; Antony, A.; Lalli, C.; Grée, R. *Eur. J. Org. Chem.* **2017**, 1805–1819.

[19] (a) Zhang, H.; Muñiz, K. *ACS Catal.* **2017**, *7*, 4122−4125. (b) Seel, S.; Thaler, T.; Takatsu, K.; Zhang, C.; Zipse, H.; Straub, B. F.; Mayer, P.; Knochel, P. *J. Am. Chem. Soc.* **2011**, *133*, 4774−4777.

intermediate **3.7**). Given the high diastereoselectivity and range of commercially available aldehydes, it is clear that the aza-Prins reaction would be an ideal synthesis for *N*-tosyl-4-chloropiperidines. In this section, we describe the modification and optimization of the aza-Prins cyclization for the synthesis of a range of *N*-tosyl-4-chloropiperidines.

The initial condensation reaction to form imine intermediate **3.6** often requires the coordination of a Lewis acid (LA) to the aldehyde. This increases the electrophilicity of the aldehyde and allows for facile formation of the imine. Some of the common Lewis acids utilized in these reactions include $FeCl_3$, $BiCl_3$, $BF_3{\cdot}Et_2O$, $InCl_3$, $AlCl_3$, and $TiCl_4$.[18] We found that the choice of Lewis acid for the reaction conditions needs to match the reactivity of aldehyde starting material. For example, when simple aromatic substrates or an extended aromatic heterocycles were employed, titanium-promoted aza-Prins reactions were utilized.[20] However, for aromatic rings that are sensitive to strong Lewis acids, a milder $AlCl_3$-catalyzed aza-Prins cyclization can be employed.[21] Finally, for substituted cinnamaldehydes, $FeCl_3$-mediated aza-Prins reactions were found to afford the desired products in synthetically useful yields.[22]

Our investigation into the aza-Prins cyclization began with 2-naphthaldehyde. Utilizing previously reported conditions by the van de Weghe laboratory, piperidine **3.8** was synthesized in 41% yield via $TiCl_4$ and *p*-$TsOH{\cdot}H_2O$ promoted aza-Prins cyclization (Table 3.1, entry 1).[20,23] With this result in hand, we aimed to synthesize substrates bearing heterocycles. However, when the same reaction conditions were applied to benzofuran-2-carbaldehyde for 48 h there was no product formation observed (entry 2). Increasing the reaction time to seven days provided a modest

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[20] Durel, V.; Lalli, C.; Roisnel, T.; van de Weghe, P. *J. Org. Chem.* **2016**, *81*, 849−859.

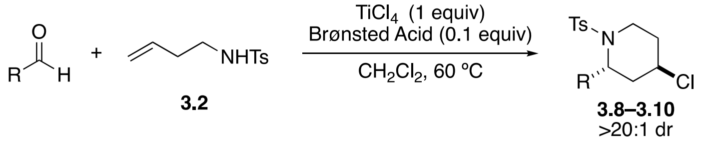
[21] Liu, G. Q.; Cui, B.; Xu, R.; Li, Y. M. *J. Org. Chem.* **2016**, *81*, 5144−5161.

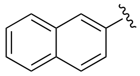
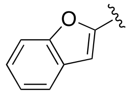
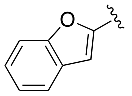
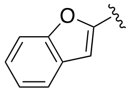
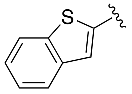
[22] Osawa, C.; Tateyama, M.; Miura, K.; Tayama, E.; Iwamoto, H.; Hasegawa, E. *Heterocycles* **2012**, *86*, 1211–1226.

[23] This substrate was synthesized by Dr. Erika Lucas. For more information, see: Lucas, E. L. Development of Stereospecific Nickel-Catalyzed Cross-Electrophile Coupling Reactions for Cyclopropane Synthesis. Ph.D. Dissertation, University of California, Irvine, Irvine, CA, **2019**.

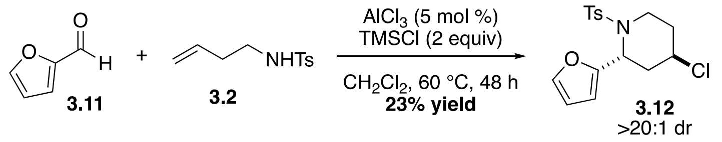
yield of the desired product, which was encouraging for further optimization (Table 3.1, entry 3). The conditions developed by van de Weghe contained one source of chlorine anion ($TiCl_4$) in solution and this anion is necessary for product formation (See Figure 3.1, intermediate **3.7** to product **3.3**). We hypothesized that if the Brønsted acid was modified to a chlorine containing acid the amount of chlorine ions in solution would increase and allow for more facile preparation of the desired product. To test this hypothesis, we employed HCl as the Brønsted acid rather than *p*-TsOH·H_2O and piperidine **3.9** was isolated in a 48% yield (entry 4). Applying the modified conditions to another heterocyclic aldehyde benzo[*b*]thiophene-2-carbaldehyde, piperidine **3.10** was isolated in a 26% yield (entry 5). Although the aza-Prins cyclization proceeds in moderate yields, it allows for the diastereoselective formation of the desired product in one step from commercially available aldehydes.

Table 3.1 Optimization of Titanium-Promoted Aza-Prins Reaction



Entry	R	Compound	Brønsted Acid	Time	Yield (%)
1		**3.8**	*p*-TsOH•H_2O	48 h	41
2		**3.9**	*p*-TsOH•H_2O	48 h	0
3		**3.9**	*p*-TsOH•H_2O	7 d	16
4		**3.9**	HCl	48 h	48
5		**3.10**	HCl	48 h	26

Encouraged by the success of benzofuran and benzothiophene, we aimed to expand the scope of the aza-Prins cyclization to include non-extended aromatic heterocycles, such as furan. 2-furaldehyde (**3.11**) was subjected to a $TiCl_4$-promoted aza-Prins reaction; unfortunately, with either *p*-TSA·H_2O or HCl, the reaction failed to provide the desired product and no starting material was recovered. Substituted furan rings are known to be sensitive to hydrolysis under strongly acidic conditions,[24] so we investigated milder Lewis acids. Inspired by work published by the Li laboratory,[21] we employed catalytic $AlCl_3$ and one equivalent of trimethylsilyl chloride (TMSCl) and only starting material was recovered after 24 h. We were encouraged, however, that the furaldehyde was not decomposing or hydrolyzing under these reactions conditions. Further optimization, such as increasing catalyst loading, the equivalents of TMSCl, or heating the reaction to reflux, failed to afford any desired product. Finally, I found that 5 mol% of $AlCl_3$, two equiv of TMSCl, and heating the reaction to 60 °C in a sealed pressure tube for 48 hours afforded piperidine **3.12** in a 23% yield and as single diastereomer (eq 3.1).



3.11 **3.2** **3.12** >20:1 dr

(3.1)

The next targeted substrates were allylic sulfonamides. The aza-Prins cyclizations presented thus far were not compatible with the cinnamaldehyde starting material and only lead to decomposition by-products. Recently, Iwamoto and co-workers disclosed a $FeCl_3$- and $BmimPF_6$-mediated aza-Prins cyclization which included substituted cinnamaldehydes in their scope.[22] Therefore, aldehyde **3.13** was subjected to these reported conditions and piperidine **3.15** was isolated in an 11% yield, with 80% of the recovered aldehyde. While this result indicated that this

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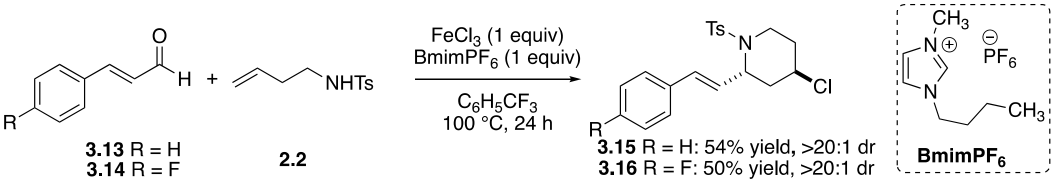
[24] For selected examples, see (a) Joule, J. A.; Keith, M. *Heterocyclic Chemistry*; Blackwell Publishing Ltd.: Chichester, U. K., 2010. (b) Liang, X.; Haynes, B. S.; Montoya, A. *Energy Fuels*, **2018**, *32*, 4139–4148. (c) Nikbin, N.; Caratzoulas, S.; Vlachos, D. G. *ChemSusChem* **2013**, *6*, 2066–2068.

reaction was suitable for vinyl aldehydes, further optimization was needed. Gratifyingly, heating the reaction mixture to reflux afforded the piperidine **3.15** in 54% yield and as a single diastereomer (Scheme 3.4). The scope was expanded to include a cinnamaldehyde derivative bearing a fluorine atom (**3.16)** in 50% yield (Scheme 3.4).

Scheme 3.4 $FeCl_3$- and $BmimPF_6$-Mediated Aza-Prins Reaction



In summary, the aza-Prins cyclization provided an efficient and successful synthetic route to *N*-tosyl-4-chloropiperidines. In one step, the desired *trans*-substituted piperidines were produced in synthetically useful yields and excellent diastereoselectivity. The reported conditions were modified and optimized to improve reaction efficiency.

3.2.2 Development of XEC Reaction of *N*-Tosyl-4-chloropiperidines

Naphthyl-substituted piperidine **3.8** was selected to evaluate the XEC reaction. The optimal conditions for the previously developed ring contraction of aryl substituted tetrahydropyrans utilized $Ni(cod)_2$ as the precatalyst and *rac*-BINAP as the ligand (see Scheme 3.2d).[9a] Applying these conditions in a reaction with piperidine **3.8**, a 30% ^1H NMR yield of the cyclopropane **3.17** was observed (Table 3.2, entry 1). Five additional ligands were evaluated and surprisingly all failed to provide the cyclopropane product (entries 2–6). We next turned our attention to Ni(II) precatalysts. When the reaction was performed with (*R*-BINAP)$NiCl_2$, the desired cyclopropane was observed in a 77% yield (entry 7).[25] Lewis acidic magnesium iodide (MgI_2) is hypothesized

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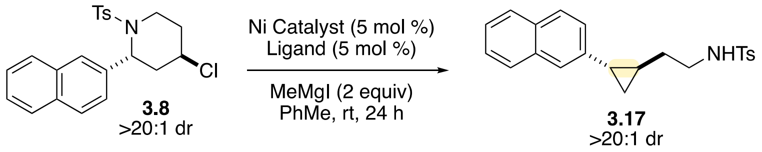
[25] For synthesis and characterization of (*R*-BINAP)$NiCl_2$, see: (a) Standley, E. A.; Smith, S. J.; Müller, P.; Jamison, T. F. *Organometallics* **2014**, *33*, 2012–2018. (b) Dawson, D. D.; Oswald, V. F.; Borovik, A. S.; Jarvo. E. R. *Chem. Eur. J.* **2020**, *26*, 3044–3048. (c) Vogler, A. *Inorg. Chem. Commun.* **2016**, *65*, 39−40.

to accelerate the rate of oxidative addition of sluggish electrophiles.[26,27] The addition of one equivalent of MgI_2 increased the yield to 96% (entry 8).

Table 3.2 Optimization of XEC reaction[28]



Entry	Nickel Catalyst	Ligand	Yield (%)[a]
1	$Ni(cod)_2$	*rac*-BINAP	30
2	$Ni(cod)_2$	XantPhos	0
3	$Ni(cod)_2$	dppe	0
4	$Ni(cod)_2$	BPhen	0
5	$Ni(cod)_2$	bipy	0
6	$Ni(cod)_2$	$SiMes\cdot BF_4$	0
7	(*R*-BINAP)$NiCl_2$	–	77
8[b]	(*R*-BINAP)$NiCl_2$	–	96

[a] Yield determined by ^1H NMR based on the comparison to PhTMS as internal standard.
[b] Reaction performed with 1 equiv of MgI_2 added

In order to confirm that either enantiomer of the catalyst would deliver identical results and that stereochemical information is not conferred from the chiral catalyst, a control experiment was designed. When piperidine **3.9** was subjected to the XEC reaction conditions with each enantiomer of the catalyst, the reactions afforded similar yields of cyclopropane **3.18** and the same diastereoselectivity (Table 3.3, entries 1 and 2). When a mixture of both diastereomers of the catalyst was employed in the reaction conditions, it provided cyclopropane **3.18** in a similar yield

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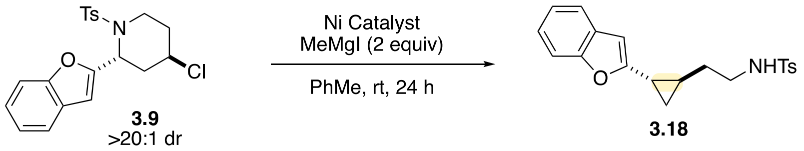
[26] (a) Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. *Org. Lett.* **2012**, *14*, 4293–4296. (b) Felkin, H.; Swierczewski, G. *Tetrahedron Lett.* **1972**, *13*, 1433–1436

[27] Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, S.-Q.; Tollefson, E. J.; Erickson, L. W.; Taylor, B. L. H.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835–5855.

[28] Optimization of the XEC reaction with piperidine **3.8** was performed by Dr. Erika Lucas.

and diastereoselectivity (entry 3).[29] This experiment demonstrates that either enantiomer of catalyst can be employed in this XEC reaction.

Table 3.3 Comparison of (*R*-BINAP)$NiCl_2$ and (*S*-BINAP)$NiCl_2$ as catalysts in the XEC Reaction



Entry	Ni Catalyst	Catalyst Loading	Yield (%)[a]	dr (trans:cis)
1	(*R*-BINAP)$NiCl_2$	5 mol %	86	>20:1
2	(*S*-BINAP)$NiCl_2$	5 mol %	85	>20:1
3	(*R*-BINAP)$NiCl_2$ + (*S*-BINAP)$NiCl_2$	2.5 mol % + 2.5 mol %	88	>20:1

[a]Yield determined by ^{1}H NMR based on comparison to PhTMS as internal standard

Next, we hypothesized that the chiral catalyst could selectively react with one enantiomer over the other enantiomer and we wanted to investigate if a kinetic resolution was occurring with the chiral catalyst.[30] We designed a control reaction to test this hypothesis where the reaction would be quenched at low conversion of starting material and the enantiomeric excess (ee) of the starting material and product would be assessed (eq. 3.2). Racemic starting material **3.9** was subjected to the standard reaction conditions and the reaction was quenched after 5 h with 33% conversion of starting material. The starting material was recovered, the product was isolated and the enantiomeric excess (ee) was determined using chiral SFC. The starting material and product were both racemic (0% ee). This experiment confirms the absence of a kinetic resolution.

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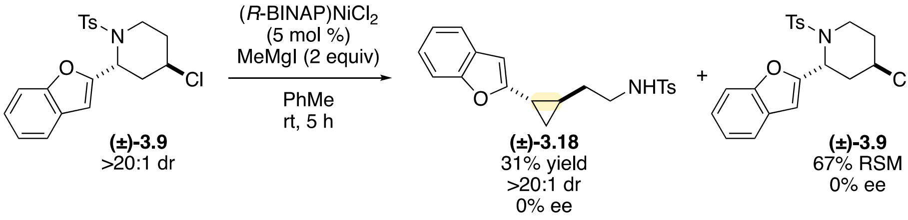
[29] The racemic catalyst, (*rac*-BINAP)$NiCl_2$, was synthesized and resulted in a viscous oil which led to difficulties in reaction set-up. We elected to utilize the chiral catalyst because it afforded fine black powder which could easily be added to the reaction flask

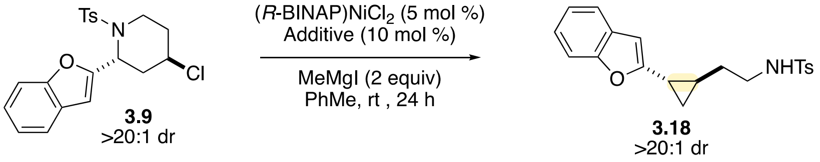
[30] For reviews on kinetic resolutions, see: (a) Huerta, F. F.; Minidis, A. B. E.; Bäckvall, J.-E. *Chem. Soc. Rev.* **2001**, *30*, 321–331. (b) Cook, G. R. *Curr. Org. Chem.* **2000**, *4*, 869.



(3.2)

In order to understand the importance of the nickel (II) precatalyst and why diminished yields were observed when Ni(cod)$_2$ was employed as the precatalyst, a control experiment was designed. We hypothesized was that 1,5-cyclooctadiene (cod) was inhibiting the XEC reaction by strong ligation to the catalyst and producing a stable, off-cycle nickel complex. This would prevent the catalyst from engaging the substrate and entering the catalytic cycle. In order to confirm this hypothesis, the XEC reaction of piperidine **3.9** was performed with (*R*-BINAP)NiCl$_2$ as the catalyst and exogenous cod as an additive. It was confirmed that cod significantly inhibits the XEC reaction of piperidine **3.9** and the desired product **3.18** was observed in only 6% yield (Table 3.4, entry 2).

Table 3.4 Cod Inhibition Experiment with Piperidine **3.9**

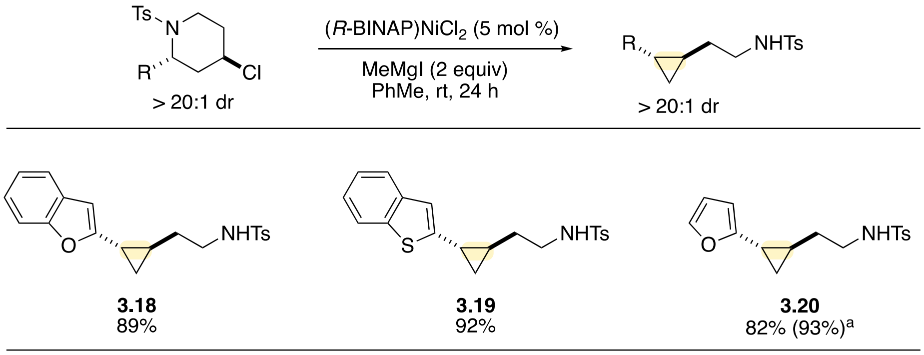


Entry	Additive	Yield (%)[a]	RSM (%)[a]
1	–	93	0
2	cod	6	90

[a]Yield determined by ^{1}H NMR based on the comparison to PhTMS as internal standard

Once the optimal conditions for the XEC reaction were identified, the scope was expanded to include substrates with pendant heterocyclic functionalities (Scheme 3.5). When benzofuran and benzothiophene substituted piperidines **3.9** and **3.10** were subjected to the standard XEC reaction, disubstituted cyclopropanes **3.18** and **3.19** were isolated in 89% and 92% yields, respectively. Additionally, non-extended aromatic systems were well-tolerated under these reaction conditions and furanyl-substituted cyclopropane (**3.20**) was isolated in an 82% yield. Importantly, all cyclopropane products were synthesized with excellent diastereoselectivity.

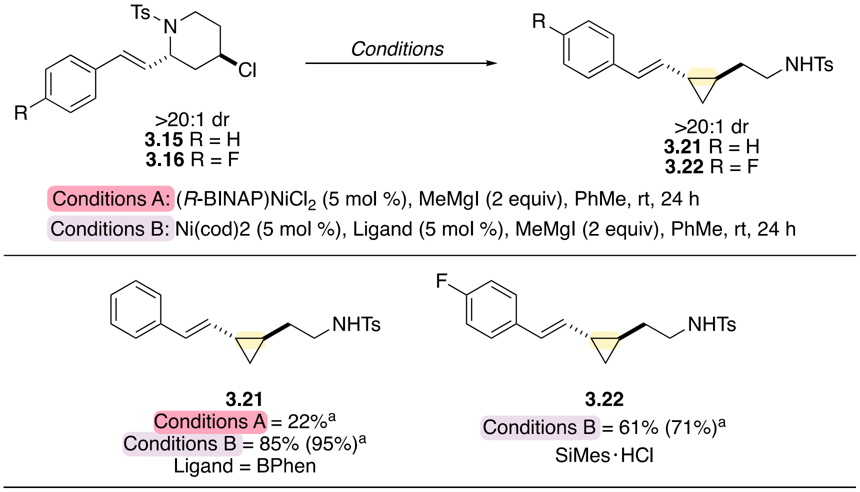
Scheme 3.5 Substrate Scope for Ring Contraction of Heteroaryl-Piperidines



[a]Yields in parenthesis determined by ^{1}H NMR compared to PhTMS as an internal standard.

Motivated by the previously developed method by the Jarvo laboratory to prepare vinylcyclopropanes from vinyltetrahydropyrans, we aimed to develop a complementary approach to synthesize vinylcyclopropanes from vinylpiperidines.[9b] It was hypothesized that these substrates would perform similarly to the aryl substrates in this ring contraction because the allylic carbon-nitrogen bond is a comparable electrophile to the benzylic sulfonamides. Surprisingly, when piperidine **3.15** was subjected the optimal reaction conditions, cyclopropane **3.21** was observed in a 22% yield (Scheme 3.6, Conditions A). We hypothesized that the vinylpiperidine is capable of competing with cod for the ligation to the nickel catalyst. To test this hypothesis, the XEC reaction of piperidine **3.15** was performed with Ni(cod)$_2$ and bathophenanthroline (BPhen) and cyclopropane **3.21** was observed in 95% ^{1}H NMR yield (Scheme 3.6, Conditions B). We applied these conditions to the remaining vinylpiperidine that was synthesized and the scope was expanded to include an electron withdrawing group (**3.22**) utilizing Conditions B. This substrate cleanly underwent the XEC reaction and furnished the disubstituted cyclopropane **3.22** in 61% yield.[31]

Scheme 3.6 Substrate Scope for Ring Contraction of Vinyl Piperidines



>20:1 dr
3.15 R = H
3.16 R = F

>20:1 dr
3.21 R = H
3.22 R = F

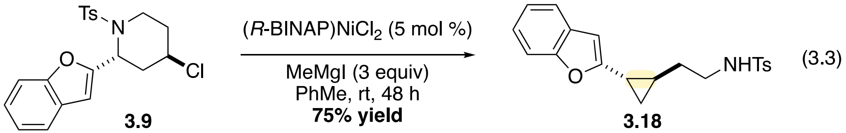
Conditions A: (*R*-BINAP)$NiCl_2$ (5 mol %), MeMgI (2 equiv), PhMe, rt, 24 h
Conditions B: Ni(cod)2 (5 mol %), Ligand (5 mol %), MeMgI (2 equiv), PhMe, rt, 24 h

3.21
Conditions A = 22%[a]
Conditions B = 85% (95%)[a]
Ligand = BPhen

3.22
Conditions B = 61% (71%)[a]
SiMes·HCl

[a]Yields determined by ^{1}H NMR compared to PhTMS as an internal standard.

Interestingly, the XEC reaction employed the air stable (*R*-BINAP)$NiCl_2$, however, all of the reactions were performed in the glovebox. To demonstrate that a glovebox was not necessary, the XEC reaction of piperidine **3.9** was performed on the benchtop with three equivalents of methylmagnesium iodide for 48 h, and the desired cyclopropane **3.18** was isolated in a 75% yield (eq. 3.3).[32]



3.9
>20:1 dr

3.18
>20:1 dr

(3.3)

Finally, we demonstrated that the pendant sulfonamide was a synthetically useful intermediate. The tosyl group was efficiently deprotected in the presence of samarium (II) diiodide

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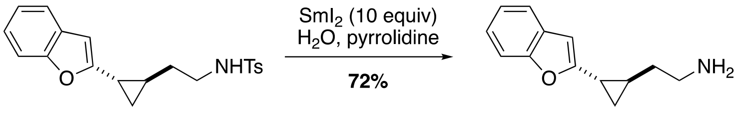
[31] It is important to note that various ligands were evaluated for the synthesis of the vinylcyclopropanes and all of these ligands provided the product in similar yields. The yields and ligands reported in Scheme 3.6 are the conditions that produced the highest yields of the vinylcyclopropane. See Experimental Section for more information.

[32] The standard reaction conditions were modified to increase the yield of the XEC reaction on the benchtop. See Experimental Section for more information.

to afford the primary amine **3.23** in a 72% yield (eq. 3.4). Primary amines themselves are important synthetic intermediates that can be further functionalized and are prevalent in biologically active compounds, pharmaceuticals, and natural products.[33]



3.18 **3.23** (3.4)

3.3 Proposed Mechanism

In 2019, the Jarvo and Hong laboratories published an experimentally and computationally supported mechanism for the nickel-catalyzed XC and XEC reactions of benzylic ethers.[9,27] These reactions share similar features with the ring contraction of piperidines including a BINAP-ligated nickel complex and methylmagnesium iodide as the reductant. Because of these similar features, we hypothesized that these reactions may also share some fundamental mechanistic details. A competition experiment between piperidine **3.9** and ether **3.24** was designed to gain further insight into the mechanistic information (Scheme 3.7). Piperidine **3.9** and ether **3.24** were subjected to the reaction conditions and after 5 h the corresponding cyclopropanes were produced in a 1.2:1 ratio slightly favoring the alcohol **3.25**. The Hong group also calculated the transition state energies for the oxidative addition events and confirmed that the barrier heights are similar for the ether and the sulfonamide and in agreement with the results of the competition experiment.[34] This allowed us to conclude that the two reactions shared the same rate-determining step for cyclopropane formation which we hypothesized is the oxidative addition of the carbon-heteroatom bond.

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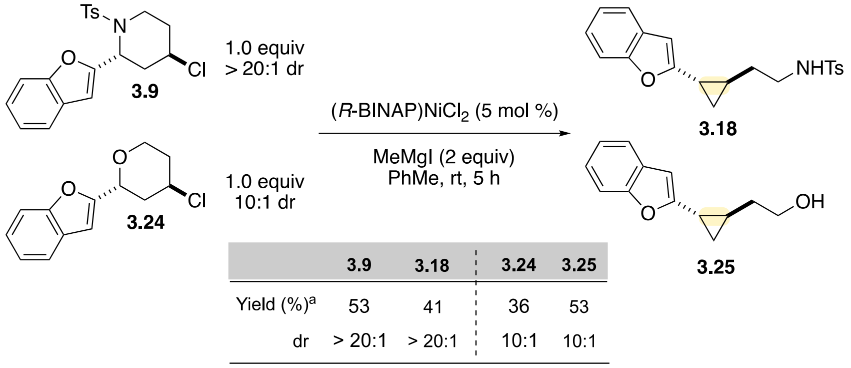
[33] (a) Ruiz-Castillo, P.; Buchwald, S. L. *Chem. Rev.* **2016,** *116*, 12564–12649.; (b) McGrath, N. A.; Brichacek, M.; Njardarson, J. T. *J. Chem. Educ.* **2010**, *87,* 1348; (c) Liu, Y.; Ge, H. *Nat. Chem.* **2017**, *9*, 26.

[34] For more information of the computational results, see ref 1.

Scheme 3.7 Competition Experiment of Piperidine **3.9** and Ether **3.24**[35]



	3.9	3.18	3.24	3.25
Yield (%)[a]	53	41	36	53
dr	> 20:1	> 20:1	10:1	10:1

[a]Yield determined by ^{1}H NMR based on comparison to PhTMS as internal standard

Based on this insight, we propose the following plausible catalytic cycle (Figure 3.2). The nickel catalyst engages the arene or alkene (**3.32**), followed by oxidative addition of the carbon-nitrogen bond. This step can be accelerated with the addition of Lewis acidic magnesium diiodide (see Table 3.1). Next, transmetalation with methylmagnesium iodide affords nickel(II) species **3.28**. This key intermediate undergoes the proposed intramolecular SN2-type reaction to afford the magnesium ligated cyclopropane product **3.29**. A second transmetalation and subsequent reductive elimination of ethane turns over the catalytic cycle.

The XEC reaction is proposed to be a stereospecific reaction. To understand the overall stereochemical outcome of the reaction, we need to understand the individual elementary steps. We hypothesized that the oxidative addition of the C–N bond proceeds via an SN2 mechanism with inversion of stereochemistry at the benzylic carbon. Next, the SN2-type reaction for the formation of the cyclopropane (**3.28** to **3.29**), can be envisaged as an SE2-type reaction at the benzylic nickel center and an SN2-type reaction at the alkyl chloride.[36] This leads to double inversion (i.e., net retention) at the benzylic center and inversion at the alkyl chloride.

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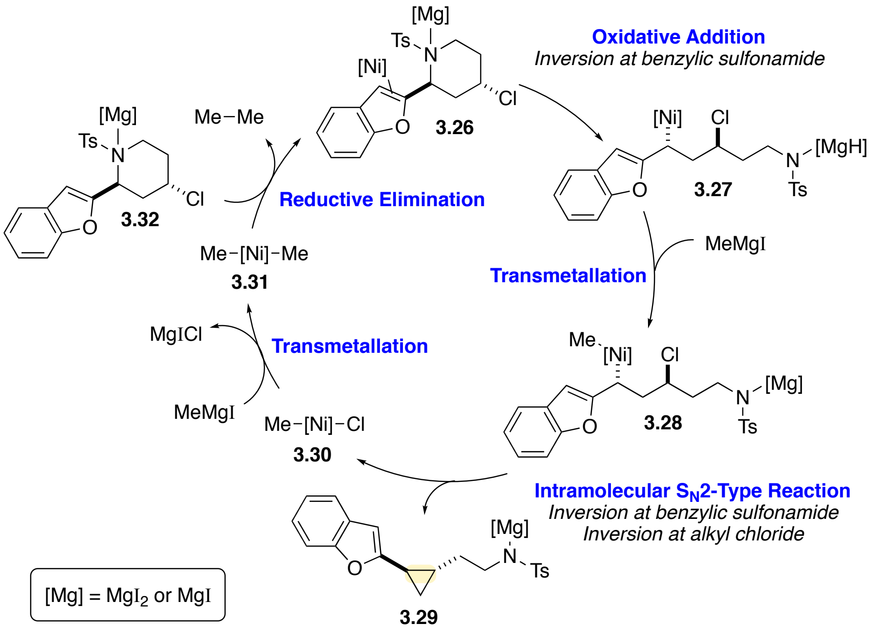
[35] Competition experiment performed by Dr. Erika Lucas.

[36] Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177−184.

Figure 3.2 Proposed Catalytic Cycle for the XEC Reaction of *N*-Tosyl-Piperidines



3.4 Conclusion

In conclusion, we have optimized the aza-Prins cyclization for the synthesis of heterocyclic and vinylic piperidines. This reaction proceeds in moderate to good yield and excellent diastereoselectivity and furnishes the desired piperidine in a single step from commercially available aldehydes. Additionally, we have developed the first intramolecular nickel-catalyzed XEC reaction of *N*-tosyl-4-chloropiperidines. The XEC reaction utilizes an air-stable nickel (II) precatalyst and can be performed without the use of a glovebox. The reaction proceeds in great yield and with excellent diastereoselectivity. It is tolerant of heterocyclic functionalities and has been expanded to include vinylcyclopropanes. In this Chapter, we have established precedent for the activation of unstrained, neutral carbon-nitrogen bonds and have provided a framework for the development of new catalysts for the activation of other carbon-nitrogen bonds.[37]

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[37] For the nickel-catalyzed XC reaction of unstrained, neutral carbon-nitrogen bond, see: (a) Chapter 1 of this thesis. (b) Hewitt, K. A.; Herbert, C. A.; Matus, A. C.; Jarvo, E. R. *Molecules* **2021**, *26*, 5947–5971.

3.5 Experimental Details

3.5.1 General Procedures

All reactions were carried out under an atmosphere of N_2 when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), methanol (MeOH), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h) to remove H_2O.[38] All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C), GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C), CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or AVANCE-600 (600 MHz ^1H, 150 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt), doublet of triplets (dt), triplet (t), triplet of doublets (td), triplet of triplets (tt), quartet (q), quartet of doublets (qd), quintet (quin), apparent singlet (as), apparent doublet (ad), apparent doublets of doublets (add), apparent doublet of triplets (adt), apparent doublet of quintets (adquin), apparent doublet of septets (adsept), apparent triplet (at), apparent triplet of doublets (atd), apparent triplet of triplets (att), apparent quartet (aq), apparent quartet of doublets (aqd), apparent quartet of triplets (aqt), apparent quintet of doublets (aquin d), apparent sextet (asext), apparent septet (asept), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ºC.

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[38] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp. Flash chromatography was performed using SiliaFlash F60 (40-63 μm, 60 Å) from SiliCycle. Automated chromatography was carried out on a Teledyne Isco CombiFlash Rf Plus. Melting points (M.p.) were obtained using a MelTemp melting point apparatus and are uncorrected. SFC Determinations of enantiopurity were determined by chiral SFC analysis and performed on an Agilent Technologies HPLC (1260 series) system. Analytical Instruments using OD-H Chiralpak column (100 bar, 50ºC, 254 nm). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center.

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (–20 °C) under an atmosphere of N_2 and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored under N_2 atmosphere and used as received. The methylmagnesium iodide was titrated with iodine prior to use.[39] All other chemicals were purchased commercially and used as received, unless otherwise noted.

3.5.2 General Cross-Electrophile Coupling Reaction Procedures

3.5.2.1 Method A: Cross-Electrophile Coupling Reaction with (*R*-BINAP)$NiCl_2$

In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with substrate (1 equiv), (*R*-BINAP)$NiCl_2$ (5 mol %), and PhMe (0.2 M in substrate). A solution of MeMgI in Et_2O (2 equiv) was then added dropwise via syringe. After 24 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O,

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[39] Krasoviskiy, A.; Knochel, P. *Synthesis*, **2006**, *5,* 890–891.

and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 µL, 50. µmol) was added and the yield was determined by ^{1}H NMR based on comparison to PhTMS as internal standard before purification by column chromatography.

For challenging substrates, 1.0–1.5 equiv MgI_2 was added to the reaction mixture and the vial was wrapped in foil for the duration of the reaction due to the light sensitivity of MgI_2.

3.5.2.2 Preparation of Methylmagnesium Iodide

Under a N_2 atmosphere, a three-necked flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was charged with magnesium turnings (2.80 g, 115 mmol). The flask and magnesium turnings were then flame-dried under vacuum and the flask was backfilled with N_2. Anhydrous Et_2O (25 mL) and a crystal of iodine (ca. 2 mg) were added to the flask. Freshly distilled iodomethane (5.0 mL, 80 mmol) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature then filtered through the fritted Schlenk filter into a pear-shaped flask under a N_2 atmosphere. The pear-shaped flask was capped with a septum, sealed with parafilm, and stored in the glovebox under a N_2 atmosphere for up to eight weeks. The resulting methyl Grignard reagent was typically between 2.4 and 3.0 M as titrated by Knochel's method.[39]

3.5.2.3 Preparation of (*R*-BINAP)$NiCl_2$

(*R*-BINAP)$NiCl_2$ was synthesized according to a procedure reported by Jamison.[25a] To a 50 mL round-bottom flask equipped with a stir bar was added $NiCl_2{\cdot}6H_2O$ (240 mg, 1.0 mmol, 1.0 equiv). The flask was placed under vacuum and flame-dried until nearly all of the nickel compound had turned from green to yellow-orange (a small amount of remaining green of the hexahydrate is necessary for the reaction to proceed). After cooling to room temperature, (*R*)-BINAP (620 mg, 1.0 mmol, 1.0 equiv) was added to the flask and a reflux condenser was attached.

The flask was evacuated, backfilled with N_2, and then anhydrous MeCN (20 mL) was added. The reaction mixture was allowed to reflux for 24 h, at which point the solution was cooled to room temperature and filtered under vacuum to yield a fine, black powder (530 mg, 0.71 mmol, 71% yield)

3.5.2.4 Method B: Cross-Electrophile Coupling Reaction with $Ni(cod)_2$

In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with substrate (1 equiv), $Ni(cod)_2$ (5 mol %), ligand (5 mol %) and PhMe (0.2 M in substrate). A solution of MeMgI in Et_2O (2 equiv) was then added dropwise via syringe. After 24 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 μL, 50. μmol) was added and the yield was determined by ^1H NMR based on comparison to PhTMS as internal standard before purification by column chromatography.

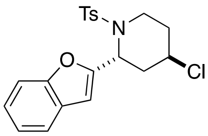
3.5.3 Control Experiment: Comparison of (*R*-BINAP)$NiCl_2$ to (*S*-BINAP)$NiCl_2$ in the XEC Reaction

In order to confirm that either enantiomer of the nickel catalyst would deliver identical results when employed in the XEC reaction, a control experiment was designed. The control experiment was performed according to Method A. Vial 1 was charged with substrate **3.9** (39 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (3.7 mg, 5.0 μmol, 5.0 mol %), methylmagnesium iodide (80. μL, 0.20 mmol, 2.0 equiv, 2.5 M in Et_2O) and PhMe (0.50 mL). Vial 2 was charged with substrate **3.9** (39 mg, 0.10 mmol, 1.0 equiv), (*S*-BINAP)$NiCl_2$ (3.7 mg, 5.0 μmol, 5.0 mol %), methylmagnesium iodide (80. μL, 0.20 mmol, 2.0 equiv, 2.5 M in Et_2O) and PhMe (0.50 mL). Vial 3 was charged with substrate **3.9** (39 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (1.9 mg, 2.5 μmol, 2.5 mol %), (*S*-BINAP)$NiCl_2$ (1.9 mg, 2.5 μmol, 2.5 mol %), methylmagnesium iodide

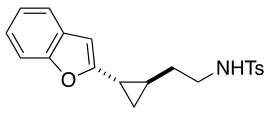
(80. µL, 0.20 mmol, 2.0 equiv, 2.5 M in Et_2O) and PhMe (0.50 mL). After 24 h, the reaction vials were removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 µL, 50. µmol) was added and the yields were determined by ^1H NMR compared to PhTMS as an internal standard. The results of this control experiment are tabulated in **Table 3.3**.

3.5.4 Control Experiment: Kinetic Resolution with Chiral Catalyst

In order to identify the presence or absence of a kinetic resolution, a control experiment was designed. The control experiment was performed according to Method A. The following amounts of reagents were used: substrate **3.9** (39 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (3.8 mg, 5.0 µmol, 5.0 mol %), methylmagnesium iodide (70. µL, 0.20 mmol, 2.0 equiv, 2.9 M in Et_2O), and PhMe (0.5 mL). After 5 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. The results of this control experiment are outlined in eq. 3.2. The analytical data for both starting material and product are tabulated below.



Before purification, it was determined that 67% of the starting material was recovered by ^1H NMR based on comparison to PhTMS. The residue was purified by column chromatography to recover piperidine **3.9** (24 mg, 63 µmol, 63% recovery of starting material). Refer to **3.9** below for analytical data. **SFC Analysis** (Chiralcel OD-H, 20% IPA, 2.0 mL/min, 250 nm) indicated 0% ee. t_R (only diastereomer, enantiomer 1) = 27.7 minutes, t_R (only diastereomer, enantiomer 2) = 29.9 minutes.

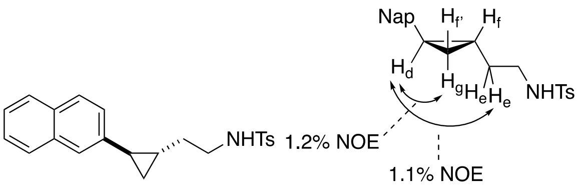


Before purification, a ^{1}H NMR yield of 31% yield was determined based on comparison to PhTMS. The residue was purified by column chromatography to yield the desired product **3.18** (11 mg, 31 μmol, 31% yield). Refer to **3.18** below for analytical data. **SFC Analysis** (Chiralcel OD-H, 5% IPA, 2.0 mL/min, 250 nm) indicated 0% ee. t_R (only diastereomer, enantiomer 1) = 10.4 minutes, t_R (only diastereomer, enantiomer 2) = 12.9 minutes.

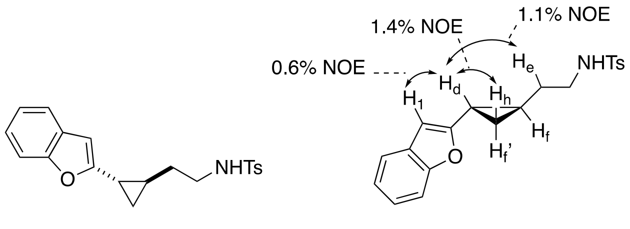
3.5.5 Cod Inhibition Experiment

In order to determine whether 1,5-cyclooctadiene (cod) was inhibiting the XEC reaction when $Ni(cod)_2$ was employed as a precatalyst, a control experiment was designed. In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with substrate (39 mg, 0.10 mmol, 1.0 equiv) and (*R*-BINAP)$NiCl_2$ (3.8 mg, 5.0 μmol, 5 mol %). Then 1,5-cycloctadiene (PhMe (0.5 mL). Then methylmagnesium iodide (70. μL, 0.20 mmol, 2.0 equiv, 2.9 M in Et_2O) was added dropwise via syringe. After 24 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Cyclopropane **3.18** was observed in 6% ^{1}H NMR yield and piperidine **3.9** was recovered in 90% ^{1}H NMR yield compared to PhTMS. The results from this control experiment are tabulated in **Table 3.4**.

3.5.6 Characterization Data for Cyclopropane Products



4-Methyl-*N*-(2-(*trans*-2-(naphthalen-2-yl)cyclopropyl)ethyl)benzenesulfonamide (3.17)[40] was prepared according to Method A. The following amounts of reagents were used: piperidine **3.8** (40. mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), MgI$_2$ (28 mg, 0.10 mmol, 1.0 equiv), PhMe (0.5 mL, 0.2 M in substrate) and methylmagnesium iodide (0.10 mL, 0.20 mmol, 2.0 equiv, 2.1 M in Et$_2$O). Before purification, a ^{1}H NMR yield of 96% was obtained. The residue was purified by column chromatography (0–30% EtOAc/hexanes) to afford the product as a white solid (30. mg, 82. μmol, 82% yield, > 20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 93–95 °C; **TLC R$_f$** = 0.2 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (ad, *J* = 8.2 Hz, 4H), 7.45–7.36 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 1H), 4.68 (t, *J* = 6.2 Hz, 1H), 3.08 (q, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 1.79–1.73 (m, 1H), 1.63–1.55 (m, 2H), 1.06–0.96 (m, 2H), 0.83–0.78 (m, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 143.5, 140.4, 137.0, 133.7, 132.1, 129.8 (2C), 128.1, 127.7, 127.4, 127.2 (2C), 126.3, 125.2, 124.6, 123.8, 43.4, 34.4, 23.3, 21.6, 20.9, 15.8; **HRMS** (TOF MS ES+) *m/z* [M + Na]$^+$ calcd for $C_{22}H_{23}NO_2SNa$, 388.1347, found 388.1348.



***N*-(2-(*trans*-2-(Benzofuran-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide (3.18)** was prepared according to Method A. The following amounts of reagents were used: (*R*-BINAP)NiCl$_2$ (7.5 mg, 10. μmol, 5.0 mol %), piperidine **3.9** (77 mg, 0.20 mmol, 1.0 equiv), PhMe (1.0 mL, 0.20

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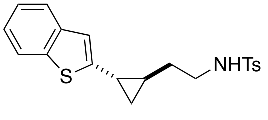
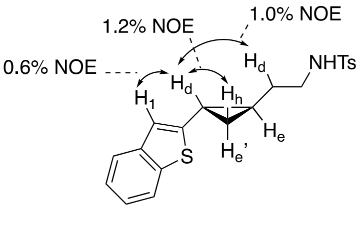
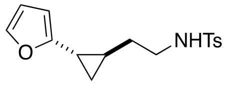
[40] Substrate synthesized by Dr. Erika Lucas.

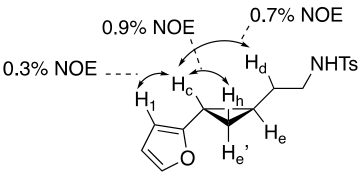
M in substrate), and methylmagnesium iodide (0.16 mL, 0.40 mmol, 2.0 equiv, 2.5 M solution in Et$_2$O). The residue was purified by column chromatography (5–25% EtOAc/hexanes) to afford the product as a white solid (44 mg, 0.12 mmol, 89% yield, > 20:1 dr trans:cis). The dr was based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 85–87°C; **TLC R$_f$** = 0.5 (5–25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.43 (dd, *J* = 6.6 Hz, 1.9 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 2.8 Hz, 2H), 7.17 (att, *J* = 7.3 Hz, 5.8 Hz, 2H), 6.31 (s, 1H), 4.65 (t, *J* = 7.5 Hz, 1H), 3.12–3.05 (m, 2H), 2.39 (s, 3H), 1.76 (dt, *J* = 9.2 Hz, 4.9 Hz, 1H), 1.66–1.49 (m, 2H), 1.23–1.17 (m, 1H), 1.17–1.10 (m, 1H), 0.79 (dt, *J* = 8.6 Hz, 5.3 Hz, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 159.3, 154.3, 143.6, 137.0, 129.9 (2C), 129.1, 127.2 (2C), 123.2, 122.7, 120.1, 110.7, 100.6, 43.2, 33.8, 21.6, 19.0, 16.6, 13.7; **IR** (neat) 3295, 2923, 1602, 1455, 1417, 1362, 1256, 1154, 1090, 1074, 891, 820, 754, 661 cm^{-1}; **HRMS** (TOF MS ES+) *m/z* [M + H]$^+$ calcd for C$_{20}$H$_{22}$NO$_3$S, 356.1320, found 356.1317.





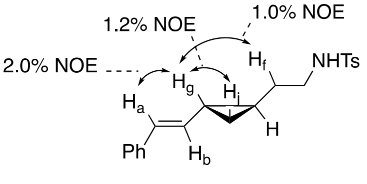
***N*-(2-(*trans*-2-(Benzo[b]thiophene-2-yl)cyclopropyl)ethyl)-4-xmethylbenzenesulfonamide (3.19)** was prepared according to Method A. The following amounts of reagents were used: (*R*-BINAP)NiCl$_2$ (7.5 mg, 10. µmol, 5.0 mol %), piperidine **3.10** (81 mg, 0.20 mmol, 1.0 equiv), PhMe (1.0 mL, 0.20 M in substrate), and methylmagnesium iodide (0.14 mL, 0.40 mmol, 2.0 equiv, 2.9 M solution in Et$_2$O). The residue was purified by chromatography (5−25% EtOAc/hexanes) to afford the product as a white solid (68 mg, 0.18 mmol, 92% yield, > 20:1 dr trans:cis). The dr was based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 93−94 °C; **TLC R$_f$** = 0.5 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) 7.74 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.37−7.16 (m, 4H), 6.89 (s, 1H), 4.66 (t, *J* = 6.2 Hz, 1H), 3.09 (q, *J* = 6.7 Hz, 2H), 2.39 (s, 3H), 1.88 (dt, *J* = 9.1 Hz, 4.8 Hz, 1H), 1.58 (q, *J* = 6.8 Hz, 2H), 1.11−1.03 (m, 1H), 1.01 (dt, *J* = 8.9 Hz, 4.9 Hz, 1H), 0.85 (dt, *J* = 8.6 Hz, 4.7 Hz, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 148.0, 143.5, 140.2, 138.4, 136.9, 129.8 (2C), 127.1 (2C), 124.3, 123.5, 122.6, 122.1, 118.8, 43.1, 34.0, 21.8, 21.6, 19.1, 16.6; **IR** (neat) 3249, 2919, 1596, 141.01 37, 1293, 1144, 1092, 1782 1067, 1043, 899, 745, 645 cm^{-1}; **HRMS** (TOF MS ES+) *m/z* [M + Na]$^+$ calcd for $C_{20}H_{21}NO_2S_2Na$ 394.0912, found 394.0911.



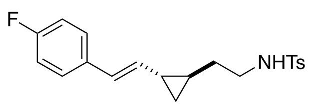


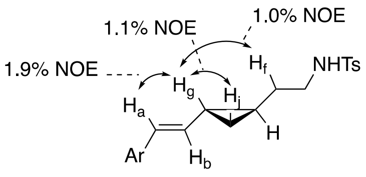
***N*-(2-(*trans*-2-(Furan-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**3.20**) was prepared according to Method A. The following amounts of reagents were used: (*R*-BINAP)NiCl$_2$ (7.5 mg, 10. μmol, 5.0 mol %), piperidine **3.12** (69 mg, 0.20 mmol, 1.0 equiv), PhMe (1.0 mL, 0.20 M in substrate), and methylmagnesium iodide (0.14 mL, 0.40 mmol, 2.0 equiv, 2.8 M solution in Et$_2$O). Before purification, a ^{1}H NMR yield of 93% was obtained. The residue was purified by column chromatography (5–20% EtOAc/hexanes) to afford the product as a yellow oil (50 mg, 0.16 mmol, 82% yield, > 20:1 dr trans:cis). The dr was based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R$_f$** = 0.5 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 1.8 Hz, 0.9 Hz, 1H), 6.24 (dd, *J* = 3.3 Hz, 1.9 Hz, 1H), 5.89 (d, *J* = 3.2 Hz, 1H), 4.55 (t, *J* = 6.3 Hz, 1H), 3.07 (septet, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.61 (dt, *J* = 9.3 Hz, 4.8 Hz, 1H), 1.52 (q, *J* = 6.9 Hz, 2H), 1.04– 0.96

(m, 1H), 0.94 (dt, *J* = 8.5 Hz, 4.8 Hz, 1H), 0.65 (dt, *J* = 8.8 Hz, 4.8 Hz, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 156.3, 143.5, 140.6, 137.1, 129.8 (2C), 127.2 (2C), 110.4, 103.7, 43.2, 33.7, 21.7, 18.2, 16.0, 13.1; **HRMS** (TOF MS ES+) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{19}NO_3SNa$ 328.0983, found 328.0981.



(*E*)-4-Methyl-*N*-(2-(*trans*-2-styrylcyclopropyl)ethyl)-benzenesulfonamide (3.21) was prepared according to Method B. The following amounts of reagents were used: piperidine **3.15** (38 mg, 0.10 mmol, 1.0 equiv), $Ni(cod)_2$ (1.4 mg, 5.0 μmol, 5.0 mol %), BPhen (1.7 mg, 5.0 μmol, 5.0 mol %), PhMe (0.50 mL, 0.20 M in substrate), and methylmagnesium iodide (0.080 mL, 0.40 mmol, 2.0 equiv, 2.5 M solution in Et_2O). Before purification, a ^{1}H NMR yield of 95% was obtained. The residue was purified by column chromatography (5−20% EtOAc/ hexanes) to afford the product as a clear, colorless oil (29 mg, 85 μmol, 85% yield, > 20:1 dr trans/cis). The dr was determined based on the integration of the resonances attributed to the allylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R_f** = 0.3 (25% EtOAc/ hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32−7.23 (m, 6H), 7.17 (quin, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.69 (dd, *J* = 15.8 Hz, 8.8 Hz, 1H), 4.42 (t, *J* = 6.4 Hz, 1H), 3.23−2.93 (m, 2H), 2.41 (s, 3H), 1.51 (q, *J* = 6.9 Hz, 2H), 1.39−1.18 (m, 1H), 0.82−0.73 (m, 1H), 0.69 (dt, *J* = 8.7 Hz, 4.9 Hz, 1H), 0.61 (dt, *J* = 8.2 Hz, 4.1 Hz, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.4, 137.5, 137.0, 133.2, 129.8 (2C), 128.6 (2C), 127.8, 127.2 (2C), 126.8, 125.6 (2C), 43.3, 33.8, 21.9, 21.6, 18.7, 14.0; **IR** (neat) 3284, 3026, 2926, 2254, 1651, 1598, 1448, 1324, 1160, 1094, 1042, 959, 908, 731, 694 cm^{-1}; **HRMS** (TOF MS ES+) *m/z* $[M + H]^+$ calcd for $C_{20}H_{24}NO_2S$ 342.1528, found 342.1545.





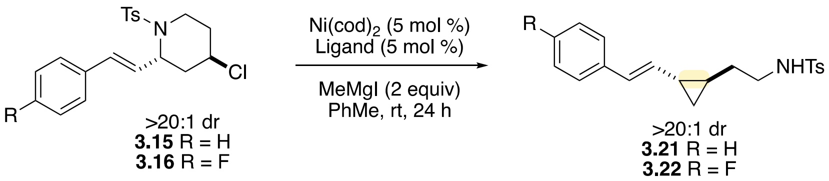
***N*-(2-(*trans*-2-((*E*)-4-Fluorostyryl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide (3.22)** was prepared according to Method B. The following amounts of reagents were used: piperidine **3.16** (61 mg, 0.15 mmol, 1.0 equiv), Ni(cod)$_2$ (2.1 mg, 7.5 µmol, 5.0 mol %), SiMes·HCl (2.6 mg, 7.5 µmol, 5.0 mol %), PhMe (0.75 mL, 0.2 M in substrate), and methylmagnesium iodide (0.10 mL, 0.30 mmol, 2.0 equiv, 2.9 M solution in Et$_2$O). Before purification a ^{1}H NMR yield of 71% was obtained. The residue was purified by column chromatography (5−25% EtOAc/ hexanes) to afford the product a clear, colorless oil (32 mg, 89 µmol, 61% yield, > 20:1 dr trans/cis). The dr was determined based on the integration attributed to the allylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R$_f$** = 0.2 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25− 7.20 (m, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 5.61 (dd, *J* = 15.8 Hz, 8.8 Hz, 1H), 4.50 (t, *J* = 6.3 Hz, 1H), 3.05 (qd, *J* = 6.7 Hz, 2.0 Hz, 2H), 2.41 (s, 3H), 1.49 (qd, *J* = 6.9 Hz, 2.6 Hz, 2H), 1.28 (ddd, *J* = 12.9 Hz, 8.6 Hz, 4.2 Hz, 1H), 0.81−0.73 (m, 1H), 0.68 (dt, *J* = 8.3 Hz, 4.8 Hz, 1H), 0.61 (dt, *J* = 8.2 Hz, 5.1 Hz, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 161.9, 143.6, 137.1, 133.8 (d, *J* = 245.5 Hz), 133.1 (d, *J* = 3.3 Hz), 129.9 (2C), 127.3 (2C), 127.1 (d, *J* = 7.9 Hz, 2C), 126.8, 115.5 (d, *J* = 21.7, 2C), 43.3, 33.9, 22.0, 21.7, 18.7, 14.1; **HRMS** (TOF MS ES+) *m/z* $[M + H]^+$ calcd for $C_{20}H_{23}FNO_2S$ 360.1433, found 360.1440.

3.5.7 Evaluation of Various Ligands in the XEC Reaction of Vinylpiperidines

Ligand evaluation was performed according to Method C. The following amounts of reagents were used: substrate **3.15** or **3.16** (39 mg, 0.10 mmol, 1.0 equiv), Ni(cod)$_2$ (1.4 mg, 5.0 µmol, 5.0 % mol%), methylmagnesium iodide (70. µL, 0.20 mmol, 2.0 equiv, 2.9 M in Et$_2$O), and PhMe (0.5

mL). Ligands evaluated: *rac*-BINAP (3.1 mg, 5.0 μmol, 5.0 mol %), BPhen (1.7 mg, 5.0 μmol, 5.0 mol %), XantPhos (2.9 mg, 5.0 μmol, 5.0 mol %), SiMes·BF_4 (2.0 mg, 5.0 μmol, 5.0 mol %), PCy_3 (1.4 mg, 5.0 μmol, 5.0 mol %), and SiMes·HCl (1.7 mg, 5.0 μmol, 5.0 mol %). After 24 h, the reaction vials were removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 μL, 50. μmol) was added and the yield was determined by ^{1}H NMR based on comparison to PhTMS as internal standard. The results from this screen are tabulated in Table 3.5.

Table 3.5 Ligand Screen for XEC Reaction of Vinylpiperidines



>20:1 dr
3.15 R = H
3.16 R = F

>20:1 dr
3.21 R = H
3.22 R = F

Entry	R	Ligand	Yield (%)[a]
1	H	*rac*-BINAP	19
2	H	BPhen	95
3	H	XantPhos	90
4	H	SiMes·BF_4	88
5	H	PCy_3	73
6	F	*rac*-BINAP	25
7	F	BPhen	53
8	F	SiMes·HCl	62
9	F	PCy_3	68

[a]Yield determined by ^{1}H NMR based on the comparison to PhTMS as internal standard

3.5.8 Benchtop Reaction to Demonstrate Stability of (*R*-BINAP)$NiCl_2$

This experiment was performed according to a modified version of Method A. On the benchtop, a flame dried 7-mL vial was charged with substrate **3.9** (78 mg, 0.20 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (7.5 mg, 1.0 μmol, 5.0 mol %). The vial was evacuated and backfilled with N_2 (x 3). Then anhydrous PhMe (1.0 mL) was added followed by methylmagnesium iodide (0.22 mL, 0.60 mmol, 3.0 equiv, 2.8 M in Et_2O) dropwise via a syringe. The reaction was allowed to stir for

48 h at rt. After 48 h, the reaction vials were removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Before purification, a ^1H NMR yield of 79% was determined based on comparison to PhTMS as internal standard. The residue was purified by column chromatography to yield the cyclopropane **3.19** as a white solid (53 mg, 0.15 mmol, 75% yield, >20:1 dr). Refer above for analytical data of the product.

3.5.9 General Procedures for the Synthesis of Piperidine Substrates

3.5.9.1 Method C: Aza-Prins Reaction with *p*-TsOH·H_2O and $TiCl_4$ for Piperidine Synthesis

This method is based on a procedure reported by van de Weghe.[20] To a flame-dried pressure tube equipped with a stir bar was added aryl aldehyde (1 equiv), homoallylic sulfonamide **3.2** (1 equiv), and CH_2Cl_2 (0.1 M). To the stirring reaction mixture was added *p*TsOH·H_2O (0.10 equiv) or HCl (0.10 equiv, 1.0 M) The reaction mixture was stirred open to air for an additional 15 min, and then $TiCl_4$ (1 equiv) was added. The pressure tube was capped, and the reaction mixture was allowed to stir at 60 ºC for 7 days. The solution was cooled to room temperature, quenched with sat aq $NaHCO_3$, and extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by column chromatography. The allylic strain imparted by the sulfonyl group drives the aryl group to the axial position; therefore, only the trans diastereomer was isolated for most of the aza-Prins reactions.

Frequently, the desired Prins product was isolated as a mixture with unreacted aldehyde. To remove unreacted aldehyde from the desired product, the crude mixture was subjected to $NaBH_4$ reduction according to a modified procedure reported by Wang and Franzén.[41] The unpurified aza-Prins reaction mixture was concentrated and dissolved in MeOH. $NaBH_4$ (1.6 equiv

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[41] Wang, Y.; Franzen, R. *Synlett* **2012**, *23*, 925–929.

relative to the remaining aldehyde as determined by ^{1}H NMR integration) was added in one portion and the reaction stirred for 20 min at rt. The reaction mixture was then concentrated in vacuo to remove the MeOH. The resulting solid was dissolved in EtOAc and transferred to a separatory funnel. The organic layer was washed with water (x3) and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Note: A CAPFE O-ring was used for the pressure tube cap. CH_2Cl_2 will disintegrate Viton O-rings.

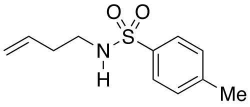
3.5.9.2 Method D: AlCl$_3$-Catalyzed Aza-Prins Reaction for Piperidine Synthesis

This method is a modified version of a procedure reported by Li.[21] In a glovebox, $AlCl_3$ (33 mg, 0.25 mmol, 0.050 equiv) was added to a flame-dried pressure tube equipped with a stir bar. The tube was sealed with a septum, brought out of the glovebox and placed under an N_2 atmosphere. Using a syringe, the sealed tube was then charged with the 2-furaldehyde **3.11** (0.42 mL, 5.0 mmol, 1.0 equiv), homoallylic sulfonamide **3.2** (0.91 mL, 5.0 mmol, 1.0 equiv), and CH_2Cl_2 (25 mL, 0.20 M in aldehyde). Then freshly distilled TMSCl (1.3 mL, 10. mmol, 2.0 equiv) was added dropwise. The septum was then removed and the pressure tube was sealed with a Teflon screw cap, heated to 60 °C, and was allowed to stir for 48 h. The reaction mixture was cooled to room temperature and allowed to stir for an additional 1 h. Then excess CH_2Cl_2 was added, and the reaction mixture was quenched with H_2O. The two phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (x3). The combined organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by column chromatography.

3.5.9.3 Method E: : FeCl$_3$/BmimPF$_6$-Mediated Aza-Prins Reaction

This method was adapted from a procedure reported by Iwamoto.[22] In a glovebox, $FeCl_3$ (1.5 equiv) was added to a flame-dried round-bottom flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. Benzotrifluoride (0.10 M in homoallylic sulfonamide) was added to the flask, followed by dropwise addition of $BmimPF_6$ (1.5 equiv). In a separate flask, a solution of aldehyde (1.5 equiv) and homoallylic sulfonamide **3.2** (1.0 equiv) in benzotrifluoride (0.10 M in aldehyde) was prepared. Using a syringe, the solution of aldehyde and sulfonamide was added to the flask containing $FeCl_3$. The flask was fitted with a reflux condenser and N_2 inlet. The solution was heated to reflux in an oil bath and allowed to stir for 24 h. The reaction mixture was cooled to room temperature and was then quenched with H_2O. The layers were separated, and the aqueous layer was extracted with Et_2O (x 2). The combined organic layers were washed sequentially with sat aq $Na_2S_2O_3$, sat aq $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by column chromatography.

3.5.10 Characterization Data for Piperidine Substrates



***N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide (3.2)** was synthesized according to a procedure reported by Jiang.[42] To a flame-dried flask equipped with a stir bar was added 4-bromo-1-butene (4.1 mL, 40. mmol, 1.0 equiv), *p*-toluenesulfonamide (6.8 g, 40. mmol, 1.0 equiv), K_2CO_3 (6.6 g, 48 mmol, 1.2 equiv), and MeCN (160 mL). The mixture was heated to 60 °C in an oil bath and allowed to stir for 3 d. The reaction mixture was quenched with saturated NH_4Cl (100 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, and was concentrated in vacuo. The residue was purified by column chromatography (5–25% EtOAc/hexanes) to afford the product as a clear, colorless oil (5.4 g, 24 mmol, 60 % yield). Analytical data is consistent with literature values.[42] **^{1}H NMR** (400

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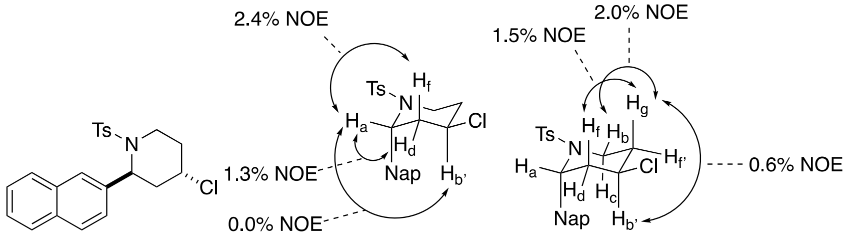
[42] Huang, J.; Zheng, J.; Wu, W.; Li, J.; Ma, J.; Ren, Y.; Jiang, H. *J. Org. Chem.* **2017**, *82*, 8191–8198.

MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2, 2H), 7.30 (d, *J* = 8.1, 2H), 5.63 (ddt, *J* = 17.1, 10.4, 6.8, 1H), 5.11 (br s, 1H), 5.02–4.93 (m, 2H), 2.99 (q, *J* = 6.7, 2H), 2.41 (s, 3H), 2.20 (q, *J* = 6.9, 2H).



***trans*-4-Chloro-2-(naphthalen-2-yl)-1-tosylpiperidine (3.8)**[43] was synthesized according to Method C. The following amounts of reagents were used: 2-naphthaldeyde **3.33** (1.61 g, 10.3 mmol, 1.00 equiv), homoallylic sulfonamide **3.2** (2.63 g, 10.3 mmol, 1.00 equiv), *p*-TsOH·H_2O (196 mg, 1.03 mmol, 10.0 mol %), $TiCl_4$ (1.13 mL, 10.3 mmol, 1.00 equiv), and CH_2Cl_2 (103 mL, 0.100 M). The reaction mixture was allowed to stir at 60 ºC for 48 h. The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the product as a white solid (1.68 g, 4.20 mmol, 41% yield, > 20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 136–138 °C; **TLC R$_f$** = 0.3 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84–7.71 (m, 5H), 7.65 (s, 1H), 7.50–7.43 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.54 (as, 1H), 4.05–3.94 (m, 2H), 3.10 (at, *J* = 13.8 Hz, 1H), 2.86 (ad, *J* = 14.1 Hz, 1H), 2.45 (s, 3H), 2.01–1.90 (m, 2H), 1.62 (qd, *J* = 12.7 Hz, 4.8 Hz, 1H); **^{13}C NMR** (125.5 MHz, $CDCl_3$) δ 143.8, 138.2, 134.9, 133.4, 132.7, 130.1 (2C), 129.0, 128.1, 127.7, 127.2 (2C), 126.6, 126.4, 125.7, 124.6, 56.4, 53.0, 41.7, 37.9, 35.4, 21.7; **HRMS** (TOF MS ES+) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{22}ClNO_2SNa$ 422.0957, found 422.0938.

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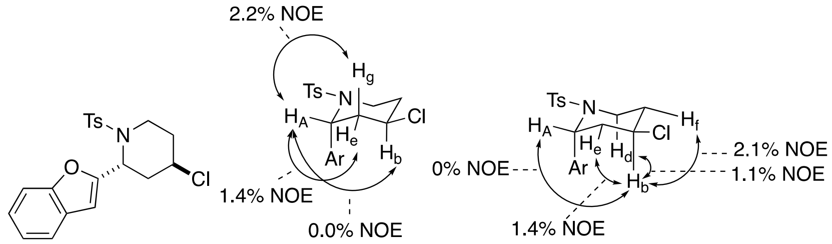
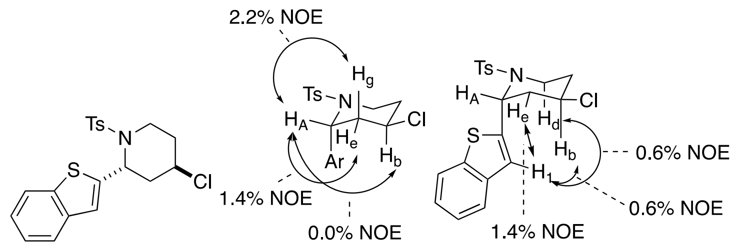
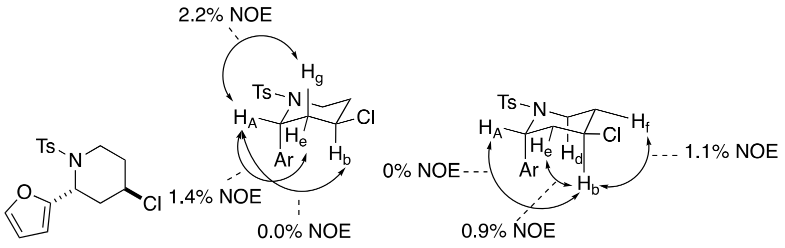
[43] This substrate was synthesized by Dr. Erika Lucas.



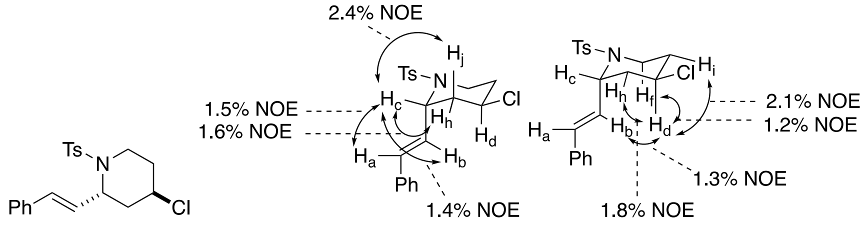
***trans*-2-(Benzofuran-2-yl)-4-chloro-1-tosylpiperidine (3.9)** was prepared according to a modified version of Method C where HCl was used instead of *p*-TsOH·H_2O. The following amounts of reagents were used: benzo[b]furan-2-carboxaldehyde **3.34** (0.12 mL, 1.0 mmol, 1.0 equiv), homoallylic sulfonamide **3.2** (0.18 mL, 1.0 mmol, 1.0 equiv), HCl (0.10 mL, 0.10 mmol, 10. mol %, 1.0 M aqueous solution), $TiCl_4$ (0.11 mL, 1.0 mmol, 1.0 equiv), CH_2Cl_2 (10. mL, 0.10 M in aldehyde). The residue was purified by column chromatography (5−25% EtOAc/hexanes) to afford the product as a tan solid (190 mg, 0.48 mmol, 48% yield, > 20:1 dr trans/cis). The dr was based on the integration of the resonances attributed to the benzylic protons in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 89−91 °C; **TLC R$_f$** = 0.8 (25% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.36−7.17 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.50 (s, 1H), 5.49 (ad, *J* = 5.6 Hz, 1H), 4.16 (att, *J* = 12.0 Hz, 4.2 Hz, 1H), 3.93 (ad, *J* = 13.5 Hz, 1H), 3.26 (atd, *J* = 13.4 Hz, 2.7 Hz, 1H), 2.66 (ad, *J* = 13.5 Hz, 1H), 2.32 (s, 3H), 2.13 (atd, *J* = 12.6 Hz, 5.6 Hz, 2H), 1.81 (aqd, *J* = 12.6 Hz, 4.8 Hz, 1H); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$) δ 154.8, 154.5, 143.6, 136.8, 129.6 (2C), 127.9, 127.2 (2C), 124.5, 123.2, 121.1, 111.2, 105.4, 53.0, 52.0, 42.4, 38.9, 35.7, 21.6.; **IR** (neat) 2952, 2868, 1596, 1454, 1375, 1256, 1155, 1090, 741 cm^{-1}; **HRMS** (TOF MS ES+) *m/z* [M + Na]$^+$ calcd for $C_{20}H_{20}ClNO_3SNa$ 412.0750, found 412.0756.



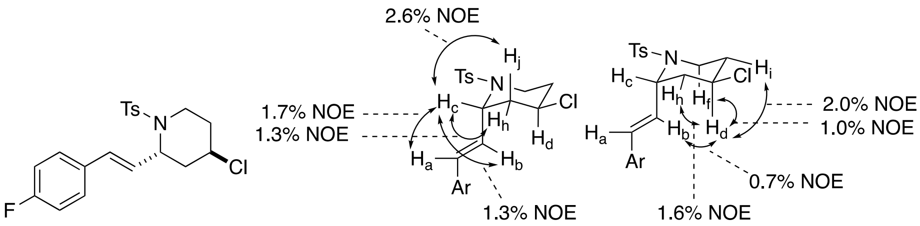
***trans*-2-(Benzo[b]thiophene-2-yl)-4-chloro-1-tosylpiperidine (3.10)** was prepared according to a modified version of method C where HCl was used instead of p-TsOH·H_2O. The following amounts of reagents were used: benzo[b]thiophene-2-carbaldehyde **3.35** (810 mg, 5.0 mmol, 1.0 equiv), homoallylic sulfonamide **3.2** (0.91 mL, 5.0 mmol, 1.0 equiv), HCl (0.10 mL, 0.10 mmol, 10. mol %, 5.0 M aqueous solution), $TiCl_4$ (0.50 mL, 5.0 mmol, 1.0 equiv), CH_2Cl_2 (50. mL, 0.10 M). The residue was purified by column chromatography (5−25% EtOAc/hexanes) to afford the product as a pale yellow solid (0.52 g, 1.3 mmol, 26% yield, > 20:1 dr trans/cis). The dr was based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned base on NOE analysis. **mp** 120−123 °C; **TLC R$_f$** = 0.7 (25% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.37−7.27 (m, 4H), 7.11 (s, 1H), 5.64 (d, J = 5.4 Hz, 1H), 4.13 (tt, J = 12.1 Hz, 4.2 Hz, 1H), 3.96 (dt, J = 14.4 Hz, 2.4 Hz, 1H), 3.22 (td, J = 14.0 Hz, 2.6 Hz, 1H), 2.67 (dt, J = 13.6 Hz, 1.9 Hz, 1H), 2.43 (s, 3H), 2.09 (td, J = 12.9 Hz, 5.8 Hz, 1H), 2.00 (add, J = 12.9 Hz, 2.9 Hz, 1H), 1.68 (qd, J = 12.8 Hz, 4.7 Hz, 1H); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$) δ 144.0, 143.4, 139.8, 139.8, 137.5, 130.0 (2C), 127.3 (2C), 124.7, 124.6, 123.6, 122.4, 122.3, 54.3, 52.8, 41.7, 39.3, 35.3, 21.7; **IR** (neat) 3104, 2928, 1238, 1154, 1056, 751 cm^{-1}; **HRMS** (TOF MS ES +) m/z [M + Na]$^+$ calcd for $C_{20}H_{20}ClNO_2S_2Na$ 428.0522, found 428.0541.



trans-4-Chloro-2-(furan-2-yl)-1-tosylpiperidine (3.12) was prepared according to Method D. The following amount of reagents were used: the 2-furaldehyde **3.11** (0.42 mL, 5.0 mmol, 1.0 equiv), homoallylic sulfonamide **3.2** (0.91 mL, 5.0 mmol, 1.0 equiv), $AlCl_3$ (33 mg, 0.25 mmol, 0.050 equiv), TMSCl (1.3 mL, 10. mmol, 2.0 equiv), and CH_2Cl_2 (25 mL, 0.20 M). The residue was purified by column chromatography (5−25% EtOAc/hexanes) to yield product as a white solid (388 mg, 1.14 mmol, 23% yield, > 20:1 dr trans/cis). The dr was based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 65−67 °C; **TLC R_f** = 0.6 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 3H), 6.26 (dd, *J* = 3.3 Hz, 1.9 Hz, 1H), 6.12 (dd, *J* = 3.5 Hz, 1.0 Hz, 1H), 5.36 (d, *J* = 5.8 Hz, 1H), 4.15 (tt, *J* = 12.1 Hz, 4.2 Hz, 1H), 3.84 (dt, *J* = 13.8 Hz, 2.4 Hz, 1H), 3.12 (td, *J* = 13.3 Hz, 2.7 Hz, 1H), 2.54 (ddt, *J* = 13.2 Hz, 4.2 Hz, 2.2 Hz, 1H), 2.41 (s, 3H), 2.15−2.08 (m, 1H), 2.04 (dt, *J* = 12.7 Hz, 6.3 Hz, 1H), 1.76 (qd, *J* = 12.7 Hz, 4.8 Hz, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 152.1, 143.5, 142.3, 137.1, 129.7 (2C), 127.3 (2C), 110.5, 108.4, 53.2, 51.6, 42.1, 39.0, 35.7, 21.7. **IR** (neat) 2959, 2928, 1597, 1495, 1339, 1304, 1157, 1092, 854, 728, 655 cm^{-1}; **HRMS** (TOF MS ES+) *m/z* [M + Na]$^+$ calcd for $C_{16}H_{18}ClNO_3SNa$ 362.0594, found 362.0581.



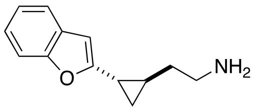
***trans*-4-Chloro-2-((*E*)-styryl)-1-tosylpiperidine** (**3.15)** was prepared according to Method E. The following amounts of reagents were used: *trans*-cinnamaldehyde **3.13** (0.18 mL, 1.5 mmol, 1.5 equiv), homoallylic sulfonamide **3.2** (0.18 mL, 1.0 mmol, 1.0 equiv), $FeCl_3$ (0.24 g, 1.5 mmol, 1.5 equiv), $BmimPF_6$ (0.30 mL, 1.5 mmol, 1.5 equiv), and benzotrifluoride (10. mL, 0.10 M). The residue was purified by column chromatography (5−25% EtOAc/hexanes) to afford the product as a white solid (150 mg, 0.41 mmol, 54% yield, > 20:1 dr trans/cis). The dr was based on the integration of the resonances attributed to allylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 127−129 °C; **TLC** $\mathbf{R_f}$ = 0.7 (25% EtOAc/hexanes); $\mathbf{^1H}$ **NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.26−7.21 (m, 3H), 7.18 (d, *J* = 7.3 Hz, 2H), 6.41 (d, *J* = 16.1 Hz, 1H), 5.89 (dd, *J* = 16.1 Hz, 5.7 Hz, 1H), 4.86 (s, 1H), 4.06 (tt, *J* = 11.7 Hz, 4.1 Hz, 1H), 3.87 (dt, *J* = 14.2 Hz, 3.9 Hz, 1H), 3.11 (td, *J* = 13.1 Hz, 2.8 Hz, 1H), 2.37 (s, 3H), 2.28 (dt, *J* = 13.2 Hz, 4.3 Hz, 1H), 2.10 (d, *J* = 12.5 Hz, 1H), 1.99 (td, *J* = 12.5 Hz, 5.3 Hz, 1H), 1.76 (qd, *J* = 12.3 Hz, 4.7 Hz, 1H); $\mathbf{^{13}C\{^1H\}}$ **NMR** (125.7 MHz, $CDCl_3$) δ 143.6, 137.3, 136.1, 133.0, 129.9 (2C), 128.7 (2C), 128.2, 127.5 (2C), 126.5 (2C) 125.3, 55.7, 53.2, 41.5, 40.7, 35.8, 21.6; **IR** (neat) 2923, 2862, 1595, 1494, 1446, 1330, 1153, 1089, 935, 723 cm^{-1}; **HRMS** (TOF MS ES+) *m/z* [M + Na]$^+$ calcd for $C_{20}H_{22}ClNO_2SNa$ 398.0957, found 398.0951.



***trans*-4-Chloro-2-((*E*)-4-fluorostyryl)-1-tosylpiperidine (3.16)** was prepared accord to Method E. The following amounts of reagents were used: (*E*)-4-fluorocinnamaldehyde **3.14** (0.40 mL, 3.0

mmol, 1.5 equiv), homoallylic sulfonamide **3.2** (0.37 mL, 2.0 mmol, 1.0 equiv), $FeCl_3$ (0.48 g, 3.0 mmol, 1.5 equiv), $BmimPF_6$ (0.62 mL, 3.0 mmol, 1.5 equiv) and benzotrifluoride (20. mL, 0.10 M). The residue was purified by column chromatography (5−25% EtOAc/ hexanes) to afford the product as a yellow oil (390 mg, 1.0 mmol, 50% yield, > 20:1 dr trans:cis). The dr was based on the integration of the resonances attributed to allylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R$_f$** = 0.6 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.20−7.10 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 6.38 (dd, *J* = 16.0 Hz, 1.7 Hz, 1H), 5.83 (dd, *J* = 16.0 Hz, 5.8 Hz, 1H), 4.82 (s, 1H), 4.05 (tt, *J* = 11.6 Hz, 4.1 Hz, 1H), 3.85 (dt, *J* = 13.6 Hz, 3.2 Hz, 1H), 3.11 (td, *J* = 12.9 Hz, 2.8 Hz, 1H), 2.36 (s, 3H), 2.25 (d, *J* = 13.1 Hz, 1H), 2.09 (dd, *J* = 12.8 Hz, 2.2 Hz, 1H), 1.96 (td, *J* = 12.4 Hz, 5.5 Hz, 1H), 1.73 (qd, *J* = 12.2 Hz, 4.6 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.8 Hz), 143.6, 137.1, 132.2 (d, *J* = 3.7 Hz), 131.7, 129.8 (2C), 128.1 (d, *J* = 7.9 Hz, 2C), 127.3 (2C), 125.0 (d, *J* = 2.3 Hz), 115.5 (d, *J* = 21.7 Hz, 2C), 55.6, 53.1, 41.4, 40.6, 35.6, 21.5; **HRMS** (TOF MS ES+) *m/z* $[M + Na]^+$ calcd for $C_{20}H_{21}ClFNO_2SNa$ 416.0863, found 416.0872.

3.5.11 Characterization Data for Derivatized Products



2-(*trans*-2-(Benzofuran-2-yl)cyclopropyl)ethan-1-amine (3.33). was prepared according to a procedure reported by Hilmersson.[44] To a flame-dried Schlenk flask equipped with a stir bar was added cyclopropane **3.18** (67 mg, 0.20 mmol, 1.0 equiv). The flask was sealed with a septum and placed under an atmosphere of N_2. Using a syringe, the flask was then charged with SmI_2 (54 mL,

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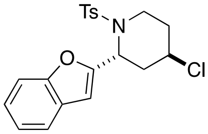
[44] Ankner, T.; Hilmersson, G. *Org. Lett.* **2009**, *11*, 503−506

2.0 mmol, 10. equiv, 40. mM in THF),[45] followed by H_2O (0.88 mL, 49 mmol, 240 equiv) and pyrrolidine (2.64 mL, 32 mmol, 160 equiv). The solution became white upon addition of the amine. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and treated with a solution of potassium sodium tartrate (50 mL, 10% w/v) and K_2CO_3 (50 mL, 10% w/v). The aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (0−30% MeOH/CH_2Cl_2) to afford the product as a light yellow solid (29 mg, 0.14 mmol, 72% yield, >20:1 dr trans/cis). The dr was based on the integration of the resonances attributed to allylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **mp** 141−143 °C; **TLC R$_f$** = 0.3 (10% MeOH/CH_2Cl_2, CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.4 Hz, 2.3 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.13 (tt, *J* = 7.3 Hz, 5.6 Hz, 2H), 6.31 (s, 1H), 3.13 (t, *J* = 7.6 Hz, 2H), 1.78 (dq, *J* = 14.8 Hz, 7.6 Hz, 1H), 1.85 (dt, *J* = 9.2 Hz, 4.9 Hz, 1H), 1.78 (dq, *J* = 14.8 Hz, 7.6 Hz, 1H), 1.39−1.29 (m, 1H), 1.19 (dt, *J* = 9.1 Hz, 5.0 Hz, 1H), 0.88 (dt, *J* = 8.8 Hz, 5.2 Hz, 1H); **^{13}C NMR** (125.4 MHz, $CDCl_3$) δ 158.9, 154.4, 129.1, 123.3, 122.7, 120.2, 110.8, 100.9, 40.0, 31.8, 18.3, 16.6, 14.0; **HRMS** (TOF MS ES+) *m/z* [M + H]$^+$ calcd for $C_{13}H_{16}NO$ 202.1232, found 202.1231.

3.5.12 Synthesis and Characterization for the Competition Experiment



***trans*-2-(benzofuran-2-yl)-4-chloro-1-tosylpiperidine (3.9)** refer above for analytical data.

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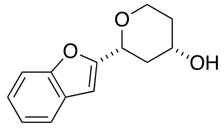
[45] SmI_2 was freshly prepared from Sm metal and diiodoethane. For the preparation, see: Szostak, M.; Spain, M.; Procter, D. J. *J. Org. Chem.* **2012**, *77*, 3049−3059.



***trans*-2-(Benzofuran-2-yl)tetrahydro-2H-pyran-4-ol (3.36)**[46] was prepared according to a procedure reported by Yadav.[47] To a flame-dried round-bottom flask under N_2 equipped with a stir bar and septum were added benzo[b]furan-2-carboxaldehyde **3.34** (1.8 mL, 15 mmol, 1.0 equiv) and CH_2Cl_2 (63 mL, 0.24 M in aldehyde). Trifluoroacetic acid (11.6 mL, 150. mmol, 10.0 equiv) was slowly added to the flask. The reaction mixture was allowed to stir at room temperature for 3 h, then saturated aq. $NaHCO_3$ (60 mL) was slowly added. Et_3N was then added to the flask until the pH reached >7. The aqueous layer was extracted with CH_2Cl_2 (3 x 60 mL), and then the combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was then redissolved in MeOH (50. mL, 0.30 M in aldehyde), K_2CO_3 (7.1 g, 51 mmol, 3.4 equiv) was added, and the reaction mixture was allowed to stir for 30 m at room temperature. The solution was concentrated in vacuo, and then H_2O (60 mL) was added to the residue. The solution was extracted with CH_2Cl_2 (3 x 60 mL), then the combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography to afford the title compound as an off-white solid (1.1 g, 5.0 mmol, 33% yield, >20:1 dr cis/trans). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^1H NMR spectrum. Analytical data is consistent with literature values.[9a] **TLC Rf** = 0.7 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.29−7.25 (m, 1H), 7.21 (at, *J* = 7.3 Hz, 1H), 6.65 (s, 1H), 4.53 (dd, *J* = 11.7 Hz, 1.3 Hz, 1H), 4.19 (add, *J* = 12.0 Hz,

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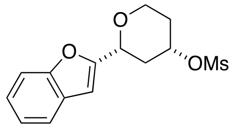
[46] This substrate was synthesized by Dr. Erika Lucas.

[47] Sabitha, G.; Reddy, N. M.; Prasad, M. N.; Yadav, J. S. *Helv. Chim. Acta* **2009**, *92*, 967.

4.9 Hz, 1H), 3.99−3.91 (m, 1H), 3.63 (atd, *J* = 12.5 Hz, 2.0 Hz, 1H), 2.33 (adquin, *J* = 12.4 Hz, 2.2 Hz, 1H), 1.99 (adquin, *J* = 12.8 Hz, 2.5 Hz, 1H), 1.85 (aq, *J* = 11.9 Hz, 1H), 1.76 (d, *J* = 3.8 Hz, 1H), 1.69 (aqd, *J* = 12.6 Hz, 5.1 Hz, 1H).



***trans*-2-(Benzofuran-2-yl)tetrahydro-2H-pyran-4-yl methanesulfonate (3.37)**[48] was prepared according to a procedure reported by Wallace.[49] To a flame-dried flask equipped with a stir bar was added **3.36** (1.1 g, 5.0 mmol, 1.0 equiv). The flask was evacuated, backfilled with N_2, and capped with a septum. CH_2Cl_2 (83 mL, 0.060 M in substrate) was added to the flask, and the reaction mixture was cooled to 0 °C. Et_3N (1.04 mL, 7.44 mmol, 1.50 equiv) was added, and the reaction mixture was allowed to stir at 0 °C for 10 min. Methanesulfonyl chloride (0.46 mL, 6.0 mmol, 1.2 equiv) was slowly added to the flask, and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was quenched with saturated aq. $NaHCO_3$ (80 mL) and then extracted with CH_2Cl_2 (3 x 80 mL). The combined organic layers were washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (0−40% EtOAc/hexanes) to afford the title compound as a yellow oil (1.08 g, 3.66 mmol, 74% yield, >20:1 dr cis/trans). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. Analytical data is consistent with literature values.[9a] **TLC Rf** = 0.3 (30% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.27 (at, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 5.00−4.91 (m, 1H), 4.58 (add, *J* = 11.7 Hz, 1.6 Hz, 1H), 4.20 (add, *J* =

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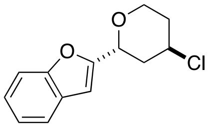
[48] This substrate was synthesized by Dr. Erika Lucas.

[49] Crombie, B. S.; Smith, C.; Varnavas, C. Z.; Wallace, T. W. *J. Chem. Soc., Perkin Trans.* **2001**, *1*, 206− 215.

12.1 Hz, 1.2 Hz, 1H), 3.66 (atd, *J* = 12.5 Hz, 1.8 Hz, 1H), 3.05 (s, 3H), 2.55−2.48 (m, 1H), 2.19−2.11 (m, 2H), 1.97 (aqd, *J* = 12.5 Hz, 5.0 Hz, 1H).



2-(*trans*-4-Chlorotetrahydro-2H-pyran-2-yl)benzofuran (3.24)[50] was prepared according to a modified procedure reported by Moyeux.[51] To a round-bottom flask equipped with a stir bar was added mesylate **3.37** (1.1 g, 3.7 mmol, 1.0 equiv) and tetrabutylammonium chloride (2.0 g, 7.3 mmol, 2.0 equiv). The flask was equipped with a reflux condenser and then evacuated and backfilled with N_2. The condenser was capped with a septum, THF (50. mM in tosylate) was added, and the reaction mixture was refluxed in an oil bath for 18 h. The reaction mixture was quenched with H_2O and extracted with EtOAc (x 2). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography to afford the title compound as a white solid (0.78 g, 3.3 mmol, 90% yield, 10:1 dr trans/cis). The dr was determined based on the integration of the resonances attributed to the benzylic hydrogens in the ^{1}H NMR spectrum. Analytical data is consistent with literature values.[9a] **TLC Rf** = 0.5 (5% EtOAc/ hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.27 (at, *J* = 7.6 Hz, 1H), 7.21 (at, *J* = 7.6 Hz, 1H), 6.65 (s, 1H), 5.10 (dd, *J* = 10.8 Hz, 2.3 Hz, 1H), 4.69 (aquin, *J* = 3.6 Hz, 1H), 4.16 (atd, *J* = 11.7 Hz, 2.2 Hz, 1H), 4.02− 3.96 (m, 1H), 2.48−2.39 (m, 1H), 2.28−2.18 (m, 2H), 1.94−1.88 (m, 1H).

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[50] Substrate **3.24** was synthesized by Dr. Erika Lucas.

[51] Cahiez, G.; Lefevre, N.; Poizat, M.; Moyeux, A. *Synthesis* **2013**, *45*, 231−236.

Chapter Four

Nickel-Catalyzed Domino Cross-Electrophile Coupling Dicarbofunctionalization Reaction to Afford Tetrasubstituted Vinylcyclopropanes

4.1 Introduction

Domino reactions provide powerful strategies to build molecular complexity by forging multiple C–C bonds and stereogenic centers in a single reaction flask.[1,2] Development of these reactions typically builds on mechanistic understanding of discrete elementary steps, established in simpler transformations. Incorporation of cross-electrophile coupling (XEC) reactions into domino sequences is in its early stages.[3] Recent efforts have established nickel-catalyzed conjunctive XEC reactions where two organohalides are utilized to functionalize an alkene in the presence of a reducing agent (Scheme 4.1a).[4,5,6] These reactions intersect traditional XEC reaction mechanisms because they involve two oxidative addition events and, frequently, alkyl radical

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[1] Portions of this chapter have been published in *ACS Catalysis*, see: Hewitt, K. A.; Xie, P.-P.; Thane, T. A.; Hirbawi, N.; Zhang, S.-Q.; Matus, A. C.; Lucas, E. L.; Hong, X.; Jarvo, E. R. *ACS Catal.* **2021**, *11*, 14369–14380.

[2] For reviews of transition-metal catalyzed domino reactions see: (a) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115–136. (b) Ikeda, S.-I. *Acc. Chem. Res.* **2000**, *33*, 511–519. (c) Montgomery, J. *Angew. Chem. Int. Ed.* **2004**, *43*, 3890–3908. (d) Nicolaou, K. C.; Edmonds, D. J.; Bulger, P. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 7134–7186. (e) Pellissier, H. *Chem. Rev.* **2013**, *113*, 442–524. (f) Tietze, L. F. *Domino Reactions: Concepts for Efficient Organic Synthesis.* Wiley-VCH: Weinheim, **2014.**

[3] For reviews of XEC reactions, see: (a) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. *Chem. Eur. J.* **2014**, *20,* 6828–6842. (b) Goldfogel, M. J.; Huang, L.; Weix, D. J. Cross-Electrophile Coupling: Principles and New Reactions. In *Nickel Catalysis in Organic Synthesis*; Ogoshi, S., Ed.; Wiley, **2020**; pp 183–222. (c) Wang, X.; Dai, Y.; Gong, H. *Top. Curr. Chem. (Z)* **2016**, *374*, 61–89. (d) Lucas, E. L.; Jarvo, E. R. *Nat. Rev. Chem*. **2017**, *1*, 0065. (e) Poremba, K. E.; Dibrell, S. E.; Reisman, S. E. *ACS Catal.* **2020**, *10*, 8237–8246. (f) Campeau, L.-C.; Hazari, N. *Organometallics* **2019**, *38*, 3–35. (g) Hewitt, K. A.; Lin, P. C.; Raffman, E. T. A.; Jarvo, E. R. C–C Bond Formation via Cross-Electrophile Coupling Reactions. *Comprehensive Organometallic Chemistry IV*. **2021**. 10.1016/B978-0-12-820206-7.00092-5

[4] For recent reviews on conjunctive XEC reactions see: (a) Qi, X.; Diao, T. *ACS Catal.* **2020**, *10*, 8542–8556. (b) Derosa, J.; Apolinar, O.; Kang, T.; Tran, V. T.; Engle, K. M. *Chem. Sci.* **2020**, *11*, 4287–4296.

[5] For recent reviews on nickel-catalyzed conjunctive XC reactions see: (a) Derosa, J.; Tran, V. T.; van der Puyl, V. A.; Engle, K. M. *Aldrichimica Acta.* **2018**, *51*, 21–32. (b) Dhungana, R. K.; KC, S.; Basnet, P.; Giri, R. *Chem. Rec.* **2018**, *18*, 1314–1340. (c) Luo, Y.-C. Xu, C.; Zhang, X. *Chin. J. Chem.* **2020**, *38*, 1371–1394. For lead examples with alkynes: (d) Terao, H.; Bando, F.; Kambe, N. *Chem. Commun.* **2009**, 7336–7338. (e) Xue, F.; Zho, J.; Hor, T. S. A.; Hayashi, T. *J. Am. Chem. Soc.* **2015**, *137*, 3189–3192. (f) Wickham, L. M.; Giri, R. *Acc. Chem. Res.* **2021**, *54*, 3415–3437.

[6] For a recent review of the mechanisms of inter- and intramolecular conjunctive XEC reactions see: (a) Diccianni, J.; Lin, Q.; Diao, T. *Acc. Chem. Res.* **2020**, *53*, 906–919. (b) Lin, Q.; Diao, T. *J. Am. Chem. Soc.* **2019**, *141*, 17937–17948.

intermediates.[7,8] *Domino methods that combine XEC reactions with additional C–C bond-forming reactions have not been reported.*

We sought to develop a domino reaction building on our nickel-catalyzed XEC reactions of ethers and sulfonamides (Scheme 4.1b).[9,10] In contrast with other XEC mechanisms, these reactions avoid radical intermediates, initiate with a polar oxidative addition of an activated C–O or C–N bond,[11] and cascade forward via an intramolecular SN2-type reaction. Based on the calculated reaction coordinate, catalyst turnover by reduction of Ni(II) to Ni(0) with formation of ethane is rate-determining. Therefore, this catalytic cycle presents an opportunity to develop new domino transformations by inserting elementary steps known for Ni(II) intermediates.[12,13,14] In this Chapter, I desrcibe a nickel-catalyzed domino reaction that combines intramolecular XEC and

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[7] For lead examples of three-component conjunctive XEC reactions of alkenes, see: (a) García-Domínguez, A.; Li, Z.; Nevado, C. *J. Am. Chem. Soc.* **2017**, *139*, 6835–6838. (b) Shu, W.; García-Domínguez, A.; Quirós, M. T.; Mondal, R.; Cárdenas, D. J.; Nevado, C. *J. Am. Chem. Soc.* **2019,** *141*, 13812–13821. (c) Anthony, D.; Lin, Q.; Baudet, J.; Diao, T. *Angew. Chem. Int. Ed.* **2019**, *58*, 3198–3202. (d) Wei, X.; Shu, W.; García-Domínguez, A.; Merino, E.; Nevado C. *J. Am. Chem. Soc.* **2020**, *142*, 13515–13522. (e) Anthony, D.; Diao, T. *Synlett* **2020**, *31*, 1443–1447. (f) García-Domínguez, A.; Li, Z.; Nevado, C. *Chimia.* **2018**, *72*, 212–215. (g) Zhao, X.; Tu, H.-Y.; Guo, L.; Zhu, S.; Qing, F.-L.; Chu, L. *Nat. Commun.* **2018**, *9*, 3488. (h) Yang, T.; Chen, X.; Rao, W.; Koh, M. J. *Chem.* **2020**, *6*, 738–751. (i) Tu, H.-T.; Wang, F.; Huo, L.; Li, Y.; Zhu, S.; Zhao, X.; Li, H.; Qing, F.-L.; Chu, L. *J. Am. Chem. Soc.* **2020**, *142*, 9604–9611.

[8] For lead examples of two component conjunctive XEC reactions of alkenes, see: (a) Yan, C.-S.; Peng, Y.; Xu, X.-B.; Wang, Y.-W. *Chem. Eur. J.* **2012,** *18*, 6039–6048. (b) Xiao, J.; Wang, Y-W.; Peng, Y. *Synthesis* **2017**, *49*, 3576–3581. (c) Kuang, Y.; Wang, X.; Anthony, D.; Diao, T. *Chem. Commun.* **2018,** *54*, 2558. (d) Wang, K.; Ding, Z.; Zhou, Z.; Kong, W. *J. Am. Chem. Soc.* **2018**, *140*, 12364–12368. (e) Jin, Y.; Wang, C. *Angew. Chem. Int. Ed.* **2019**, *58*, 6722–6726. (f) Xu, S.; Wang, K.; Kong, W. *Org. Lett.* **2019**, *21*, 7498–7503. (g) Tian, Z.-X.; Qiao, J.-B.; Xu, G.-L.; Pang, X.; Qi, L.; Ma, W.-Y.; Zhao, Z.-Z.; Duan, J.; Du, Y.-F.; Su, P.; Liu, X.-Y.; Shu, X.-Z. *J. Am. Chem. Soc.* **2019**, *141*, 7637–764

[9] (a) Tollefson, E. J.; Erickson, L. W.; Jarvo, E. R. *J. Am. Chem. Soc.* **2015**, *137*, 9760–9763. (b) Erickson, L. W.; Lucas, E. L.; Tollefson, E. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2016**, *138*, 14006–14011. (c) Lucas, E. L.; Hewitt, K. A.; Chen, P.-P.; Castro, A. J.; Hong, X.; Jarvo, E. R. *J. Org. Chem.* **2020**, *85*, 1775–1793.

[10] Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, S.-Q.; Tollefson, E. J.; Erickson, L. W.; Taylor, B. L. H.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835– 5855.

[11] (a) Tollefson, E. J.; Hanna, L. E.; Jarvo, E. R. *Acc. Chem. Res.* **2015**, *48*, 2344–2353. (b) Zhang, S.-Q.; Hong, X. *Acc. Chem. Res.* **2021**, *54*, 2158–2171.

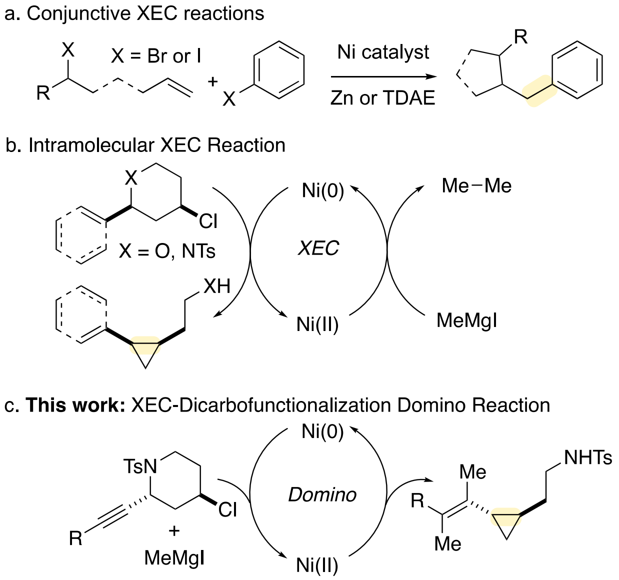
[12] For reviews of nickel catalysis, see: (a) *Modern Organonickel Chemistry*; Tamaru, Y., Ed.; Wiley-VCH: Weinheim; 2005. (b) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299–309. (c) *Nickel Catalysis in Organic Synthesis*: *Methods and Reactions*; Ogoshi, S., Ed.; Wiley, **2020**.

[13] Dicarbofunctionalization of alkynes with two equivalents of Grignard reagents have been reported, see: Dong, C.-G.; Yeung, P.; Hu, Q.-S. *Org. Lett.* **2007**, *9*, 363–366.

[14] For an example of a nickel-catalyzed domino reaction that builds on XEC reactivity, see: Ping, Y.; Wang, K.; Pan, Q.; Ding, Z.; Zhou, Z.; Guo, Y.; Jong, W. *ACS Catal.* **2019**, *9*, 7335–7342.

dicarbofunctionalization reactions to produce substituted vinylcyclopropanes (Scheme 4.1c). This multicomponent transformation produces three new carbon–carbon bonds and a strained ring. The cyclopropane moiety is produced with high stereochemical fidelity. In addition, we provide experimental and computational evidence that the mechanism involves a single oxidative addition, an intramolecular S_N2-type reaction and a single reductive elimination. All elementary steps are stereospecific and product isomers result from divergent pathways from a key allenylnickel intermediate.

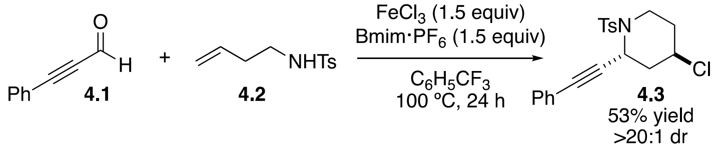
Scheme 4.1 Nickel-Catalyzed Domino XEC Reactions



4.2 Results and Discussion

4.2.1 Starting Material Synthesis via the Aza-Prins Reaction

At the outset, we recognized that a critical component of our approach would be the rapid and efficient synthesis of the requisite starting materials. We envisioned that an aza-Prins reaction could generate 4-halo-2-alkynyl piperidines directly from ynals. Unfortunately, there were no Prins or aza-Prins reactions of simple ynals in the literature.[15] The closest precedence was a cobalt-mediated reaction, where the cobalt complex serves to mask the alkyne to produce protected 2-alkynyl tetrahydropyrans.[16] We were encouraged, however, by iron-promoted aza-Prins reactions of enals for synthesis of 2-vinyl piperidines.[17] We applied similar conditions for the aza-Prins reaction of ynals (eq 4.1). Gratifyingly, this reaction afforded the desired 2-alkynyl-4-chloropiperidine **4.3** in 53% yield and as a single diastereomer. As expected, the *trans*-diastereomer was preferred due to minimization of A(1,3)-strain.[18] This transformation proved to be robust across a range of aryl- and alkyl-substituted ynals (*vide infra*).[19]



(4.1)

4.2.2 Development of Nickel-Catalyzed Domino Reactions

We investigated the feasibility of the proposed domino reaction employing *N*-tosyl piperidine **4.3**.[20] We began with the previously developed conditions for the XEC reaction of aryl and vinyl sulfonamides with (*R*-BINAP)NiCl$_2$ as the precatalyst (Table 4.1, entry 1).[9c,21] We

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[15] For reviews of the Prins/aza-Prins reaction see (a) Arundale, E.; Mikeska, L. A. *Chem. Rev.* **1952**, *51*, 505–555. (b) Adams, D. R.; Bhatnagar, S. P. *Synthesis*, **1977**, 661–672. (c) Olier, C.; Kaafarani, M.; Gastaldi, S.; Bertrand, M. P. *Tetrahedron*, **2010**, *66*, 413–445. (d) Pastor, I. M.; Yus, M. *Curr. Org. Chem.* **2012**, *16*, 1277–1312. (e) Reddy, B. V. S.; Nair, P. N.; Antony, A.; Lalli, C.; Grée, R. *Eur. J. Org. Chem.* **2017**, 1805–1819.

[16] Olier, C.; Gastaldi, S.; Gil, G.; Bertrand, M. P. *Tetrahedron Lett.* **2007**, *48*, 7801–7804.

[17] (a) Osawa, C.; Tateyama, M; Miura, K.; Tayama, E.; Iwamoto, H.; Hasegawa, E. *Heterocycles* **2012**, *86*, 1211–1226. (b) ref 9c

[18] (a) Zhang, H.; Muñiz, K. *ACS Catal.* **2017**, *7*, 4122−4125. (b) Seel, S.; Thaler, T.; Takatsu, K.; Zhang, C.; Zipse, H.; Straub, B. F.; Mayer, P.; Knochel, P. *J. Am. Chem. Soc.* **2011**, *133*, 4774−4777.

[19] See Experimental Section for more information.

[20] For lead references of XEC of ammonium salts, aziridines, and pyridinium salts, see: (a) Moragas, T.; Gaydou, M.; Martin, R. *Angew. Chem., Int. Ed.* **2016**, *55*, 5053−5057. (b) Woods, B. P.; Orlandi, M.; Huang, C.-Y.; Sigman, M. H.; Doyle, A. G. *J. Am. Chem. Soc.* **2017**, *139*, 5688−5691. (c) Liao, J.; Basch, C. H.; Hoerrner, M. E.; Talley, M. R.; Boscoe, B. P.; Tucker, J. W.; Garnsey, M. R.; Watson, M. P. *Org. Lett.* **2019**, *21*, 2941−2946. (d) Wang, J.; Hoerner, M. E.; Watson, M. P.; Weix, D. J. *Angew. Chem. Int. Ed.* **2020**, *59*, 13484–13489. For reviews on the activation of C–N bonds see: (e) Ouyang, K.; Hao, W.; Zhang, W.-X.; Xi, Z. *Chem. Rev.* **2015**, *115*, 12045−12090. (f) Wang, Q.; Su, Y.; Li, L.; Huang, H. *Chem. Soc. Rev.* **2016**, *45*, 1257−1272.

[21] For synthesis of (*R*-BINAP)NiCl$_2$, see: (a) Standley, E. A.; Smith, S. J.; Muller, P.; Jamison, T. F. *Organometallics* **2014**, *33*, 2012– 2018. (b) Dawson, D. D.; Oswald, V. F.; Borovik, A. S.; Jarvo, E. R. *Chem. Eur. J.* **2020**, *26*, 3044–3048.

evaluated two halide leaving groups, and the chloride produced the functionalized cyclopropane **4.4** in greater yield as compared to the fluoride (entries 1 and 2).[22] We determined by NMR analysis that the cyclopropane moiety is exclusively produced as the *trans* configuration while the olefin is generated as a mixture of (*E*)- and (*Z*)-alkene isomers.[23] In an attempt to improve diastereoselectivity, we cooled the reaction to 0 °C, however, no product was formed and 98% starting material was recovered (entry 3). Previously, our laboratory has found that Lewis acidic MgI_2 can accelerate the rate of oxidative addition of sluggish electrophiles,[10,24] however, the yield of the domino reaction did not improve with the addition of one equivalent of MgI_2 (entry 4). When the number of equivalents of the Grignard reagent was lowered, the yield improved (entries 5 and 6). Next, we evaluated alternative precatalysts. The commercially available Jamison catalyst, *cis*-(*R*-BINAP)Ni(o-tolyl)Cl, afforded similar yield and *E*:*Z* ratios of cyclopropane **4.4** (entry 7).[21a] $Ni(cod)_2$ and racemic BINAP provided decreased yield, consistent with our prior observation that cod inhibits XEC reactions of sulfonamides.[9c] Other precursors also afforded modest yields (entries 9 and 10).[25] Finally, we observed that the nickel catalyst was essential for the domino reaction to take place. In the absence of catalyst, simple propargylic displacement by the Grignard reagent occurred in 15% yield (entry 11).[26,27] We hypothesized that allenylcopper intermediates

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[22] Fluoride leaving groups were evaluated due to the success of the XEC Reactions of vinyl tetrahydropyrans. See ref 9b for further information.

[23] See Experimental Section for more information.

[24] (a) Greene, M. A., Yonova, I. M., Williams, F. J., Jarvo, E. R. *Org. Lett.* **2012**, *14*, 4293–4296. (b) Felkin, H.; Swierczewski, G. *Tetrahedron Lett.* **1972**, *13*, 1433–1436.

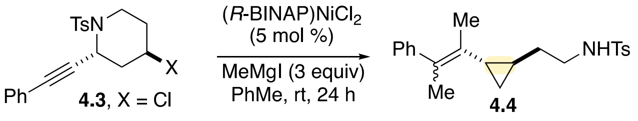
[25] Tran, V. T.; Li, Z.-Q.; Apolinar, O.; Derosa, J.; Joannou, M. V.; Wisniewski, S. R.; Eastgate, M. D.; Engle, K. M. *Angew. Chem. Int. Ed.* **2020**, *59*, 7409–7413.

[26] Allene **4.61** was the observed product. See Experimental Details Section **4.4.6** for full characterization of product.

[27] For examples of propargylic displacement by Grignard reagents, see (a) Gore, J.; Dulcere, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 866–867. (b) Krause, N.; Hoffmann-Röder, A. *Tetrahedron* **2004**, *60*, 11671–11694.

could potentially engage in an XEC reaction.[28,29,30] However, in preliminary investigations, when the nickel precatalyst was replaced with a copper salt no reaction was observed (entry 12). Therefore, we concluded that the optimal domino conditions employ a nickel(II) precatalyst, BINAP as the ligand, and two equivalents of methylmagnesium iodide.

Table 4.1. Optimization of Nickel-Catalyzed Domino Reaction



Entry	Deviation from Standard Conditions	Yield (%)[a]	*E*:*Z*
1	none	61	1.5 : 1
2	X = F	51	1.1 : 1
3	0 °C instead of rt	<5	–
4	1.0 equiv of MgI$_2$ added	61	1.7 : 1
5	2.5 equiv MeMgI	68	1.5 : 1
6	**2 equiv MeMgI**	**72 (71)[b]**	**1.7 : 1**
	(R-BINAP)NiCl$_2$ replaced with 5 mol% of:		
7	*cis*-(*R*-BINAP)Ni(*o*-tolyl)Cl	74	1.2 : 1
8	Ni(cod)$_2$, *rac*-BINAP	30	1 : 2
9[c]	Ni(cod)(DQ), *rac*-BINAP	42	1 : 1.2
10[c]	Ni(acac)$_2$, *rac*-BINAP	52	1 : 1.6
11	No Nickel Catalyst	<5	–
12[d]	Cu(CH$_3$CN)$_4$OTf	<5	–

[a]Determined by ^{1}H NMR based on comparison to PhTMS as an internal standard. [b]Isolated yield. [c]2 equiv of methylmagnesium iodide. [d] PhMe replaced with DCM.

To determine the functional group compatibility of this reaction, a series of experiments to probe the reaction robustness were performed (Figure 4.1).[31] Since this transformation employs a nucleophilic Grignard reagent, we first targeted functional groups that are sensitive to methylmagnesium iodide. We began by evaluating acidic moieties. Phenol, thiophenol, and aniline

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[28] Copper catalysts are also known to promote propargyl substitution reactions. For lead references, see (a) Zhang, D.-E.; Hu, X.-P. *Tetrahedron Lett.* **2015**, *56*, 283–295. (b) Roy, R.; Saha, S. *RSC. Adv.* **2018**, *8*, 31129–31193. (c) Miyake, Y.; Uemura, S.; Nishibayashi, Y. *ChemCatChem* **2009**, *1*, 342–356.

[29] For copper-catalyzed reactions with propargylic ammonium salts see: (a) Guisán-Ceinos, M.; Martín-Heras, V; Soler-Yanes, R.; Cárdenas, D. J.; Tortosa, M. *Chem. Commun.* **2018**, *54*, 8343–8346. (b) Guisán-Ceinos, M.; Martín-Heras, V; Tortosa, M. *J. Am. Chem. Soc.* **2017**, *139*, 8448–8451.

[30] Copper catalysts are known to promote dicarbofunctionalization reactions. For representative examples, see: (a) You, W.; Brown, M. K. *J. Am. Chem. Soc.* **2014**, *136*, 14730–14733. (b) You, W.; Brown, M. K. *J. Am. Chem. Soc.* **2015**, *137*, 14578–14581. (c) Thapa, S.; Basnet, P.; Giri, R. *J. Am. Chem. Soc.* **2017**, *139*, 5700–5703.

[31] Collins, K., Glorius, F. A. *Nature Chem.* **2013**, *5*, 597–601.

were all tolerated under the reaction conditions, given excess Grignard reagent to account for proton transfer, allowing for moderate to good yields of cyclopropane **4.4**. We were also pleased to note that a silyl ether was well tolerated. Nitrobenzene inhibited the nickel catalyst and poor yields of cyclopropane **4.4** were observed. With excess Grignard reagent, a nitrile and an aldehyde were cleanly converted to the amine and alcohol, respectively, and these moieties did not interfere with nickel catalyst: cyclopropane **4.4** was generated in good yields.

Next, we targeted additives with functional groups that can react with or serve as ligands for nickel catalysts (Figure 4.1). Aryl and alkyl chlorides did not outcompete the propargyl sulfonamide; the substituted vinylcyclopropane was observed in good yield. Alkenes strongly ligate nickel catalysts, so we evaluated two alkenes: cyclohexene and styrene. Cyclohexene was well-tolerated and did not inhibit the reaction, however, styrene inhibited the domino reaction likely due to strong ligation to the active catalyst. Finally, we evaluated nitrogen-containing heterocycles, common ligands for transition metals. In the presence of pyridine and a substituted pyridine the yield of cyclopropane **4.4** was lowered. Interestingly, when pyridine was the additive, (*Z*)-alkene **4.4** was the major product.[32] Indole and *N*-methyl indole did not affect the yields of the domino transformation. Finally, *N*-methylmorpholine inhibited the domino reaction resulting in diminished yield of cyclopropane **4.4**. Taken together, numerous functional groups are tolerated under our reaction conditions providing a robust domino reaction.

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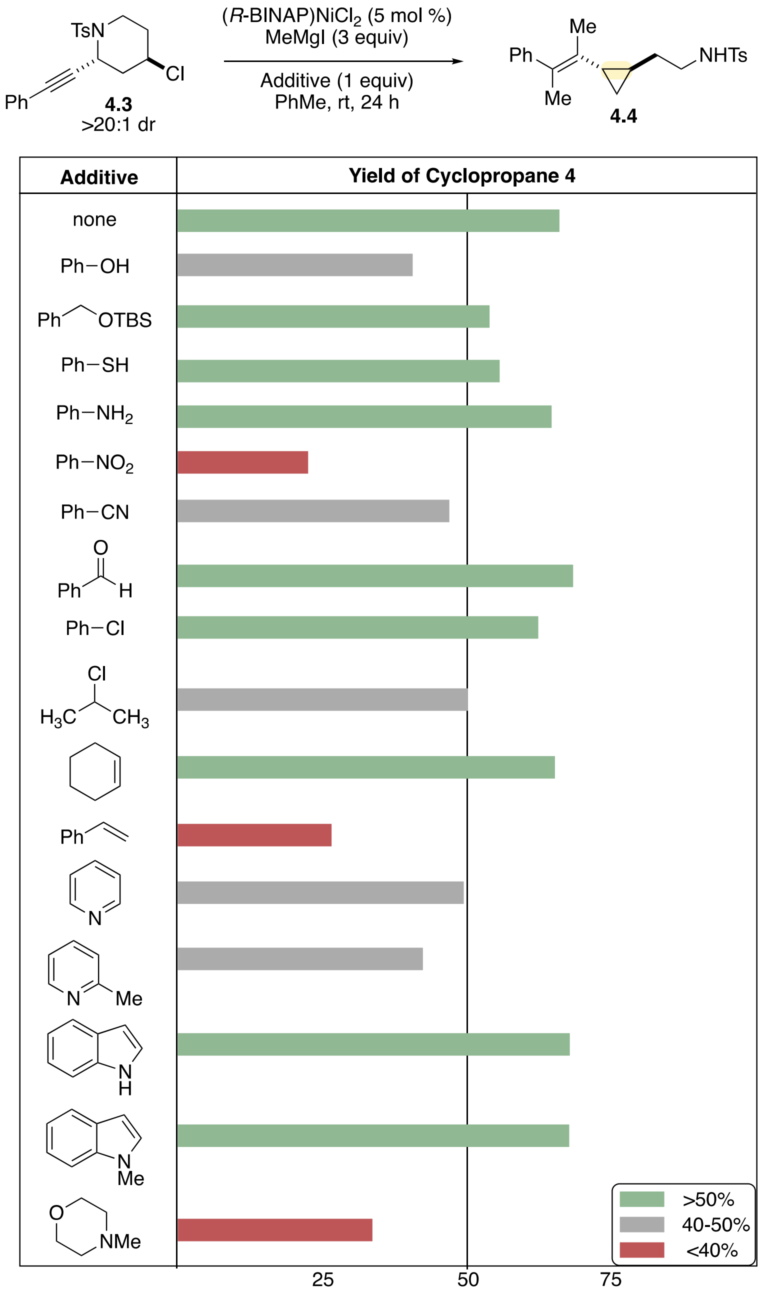
[32] See Experimental Section **4.4.3** for more information.

Figure 4.1 Robustness Screen to Establish Functional Group Compatability[a,b]



(a) Yield of cyclopropane 4 determined by ^{1}H NMR based on comparison to PhTMS as an internal standard. (b) Unless otherwise noted, products were observed as ~1.5:1 mixture of (*E*)- and (*Z*)-alkene isomers.

Next, we evaluated the scope of the domino reaction (Scheme 4.2). Historically, cyclopropanes have been synthesized via Simmons–Smith reactions, transition metal-catalyzed carbene insertions, cycloisomerizations, and nucleophilic displacement reactions.[33] This method establishes an alternative to these strategies, while also providing a rapid synthesis of highly substituted vinylcyclopropanes.[34,35,36] First, we evaluated substituted aromatic rings (**4.4–4.12**).[37] We found that electron donating groups were well tolerated in the domino reaction, producing the desired product in excellent yields and moderate *E*:*Z* ratios. Interestingly, this reaction could be scaled up tenfold (to 1.0 mmol) and still retain good yield. The electron withdrawing CF_3 group provided the desired product albeit in moderate yield and diastereoselectivity. Interestingly, the sterically bulky *t*-Bu substrate provided (*Z*)-alkene **4.11** as the major product. We hypothesize that the *t*-Bu groups hinder the carbometallation step and favor the intramolecular transmetalation leading to (*Z)*-vinylcyclopropane as the major product (*vide infra*). We were delighted to observe that aromatic groups were not necessary and alkyl substrates were able to undergo the transformation in excellent yields (**4.13–4.18**).[38] It is important to note that cyclopropane **4.13** derived from propyne is obtained in excellent diastereoselectivity (>20:1) further confirming that cyclopropane formation is highly stereoselective.

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[33] For reviews on the synthesis of vinylcyclopropanes see: (a) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charett, A. B. *Chem. Rev.* **2003**, *103*, 977–1050. (b) Bartoli, G.; Bencivenni, G.; Dalpozzo, R. *Synthesis*, **2014**, *46*, 979–1029. (c) Ebner, C.; Carreira, E. M. *Chem. Rev.* **2017**, *117*, 11651–11679; (d) Wu, W.; Lin, Z.; Jiang, H. *Org. Biomol. Chem.* **2018**, *16*, 7315–7329. (e) Mato, M.; Franchino, A.; García-Morales, C.; Echavarren, A. M. *Chem. Rev.* **2021**, *121*, 8613–8684.

[34] For selected cross-coupling approaches for the synthesis of vinylcyclopropanes, see (a) Charette, A. B.; Giroux, A. *J. Org. Chem.* **1996**, *61,* 8718–8719. (b) Yao, M.-L.; Deng, M.-Z. *Tetrahedron Lett.* **2000**, *41*, 9083–9087. (c) Hu, L.; Shen, P.-X.; Shao, Q.; Hong, K.; Qiao, J.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2018**, *58*, 2134–2138.

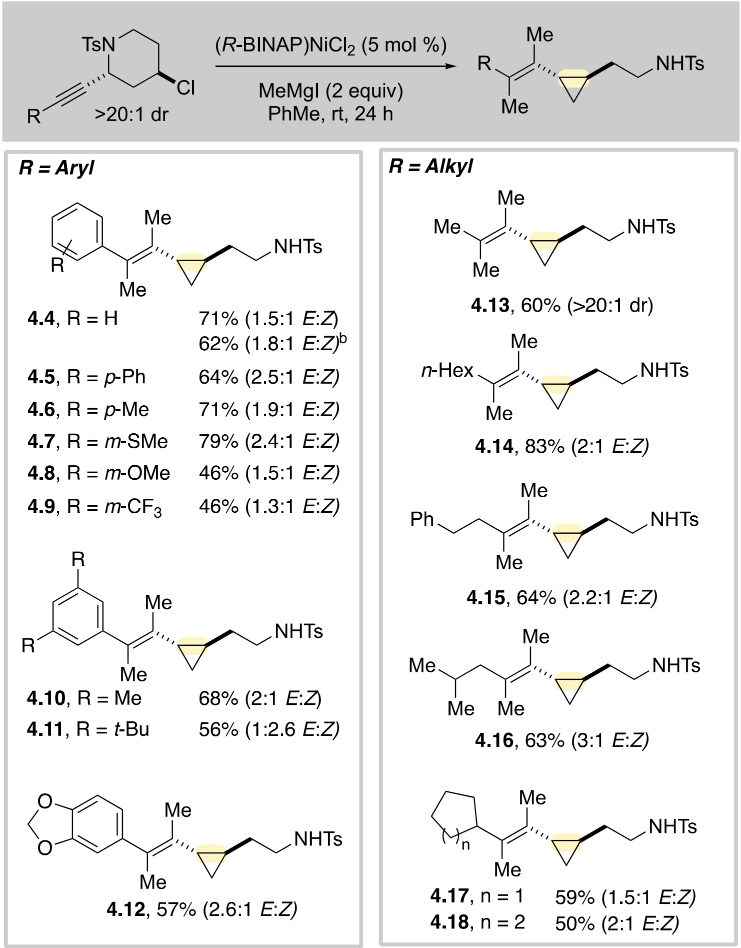
[35] For transformations of vinylcyclopropanes, see: (a) Jiao, L.; Yu, Z.-X. *J. Org. Chem.* **2013**, *78*, 6842–6848. (b) Rubin, M.; Rubina, M.; Gevorgyan, V. *Chem. Rev.* **2007**, *107*, 3117–3179 (d) Souillart, L.; Cramer, N. *Chem. Rev.* **2015**, *115*, 9410–9464. (e) Wang, J.; Blaszczyk, S. A.; Li, X.; Tang, W. *Chem. Rev.* **2020**, *121*, 110–139.

[36] For Fe-catalyzed conjunctive XC reactions of vinylcyclopropanes that proceeds with ring-opening, see: (f) Liu, L.; Lee, W.; Yuan, M.; Acha, C.; Geherty, M. B.; Williams, B.; Guiterrez, O. *Chem. Sci.* **2020**, *11*, 3146–3151

[37] Substrates **4.8** and **4.9** synthesized by Nadia Hirbawi.

[38] Substrates **4.15**, **4.16**, and **4.17** synthesized by Taylor A. Thane

Scheme 4.2 Substrate Scope[a]



[a]Reactions performed on 0.1–0.2 mmol scale. Isolated yields.
[b]Reaction performed on 1.0 mmol scale.

Vinylcyclopropane and amine-substituted cyclopropane moieties are present in numerous biologically active compounds, natural products and pharmaceutical agents.[39,40] For example, amino-substituted vinylcyclopropanes have been established as lysine specific demethylase (LSD1) inhibitors with potent anti-leukemia activity.[41] To demonstrate the synthetic potential of

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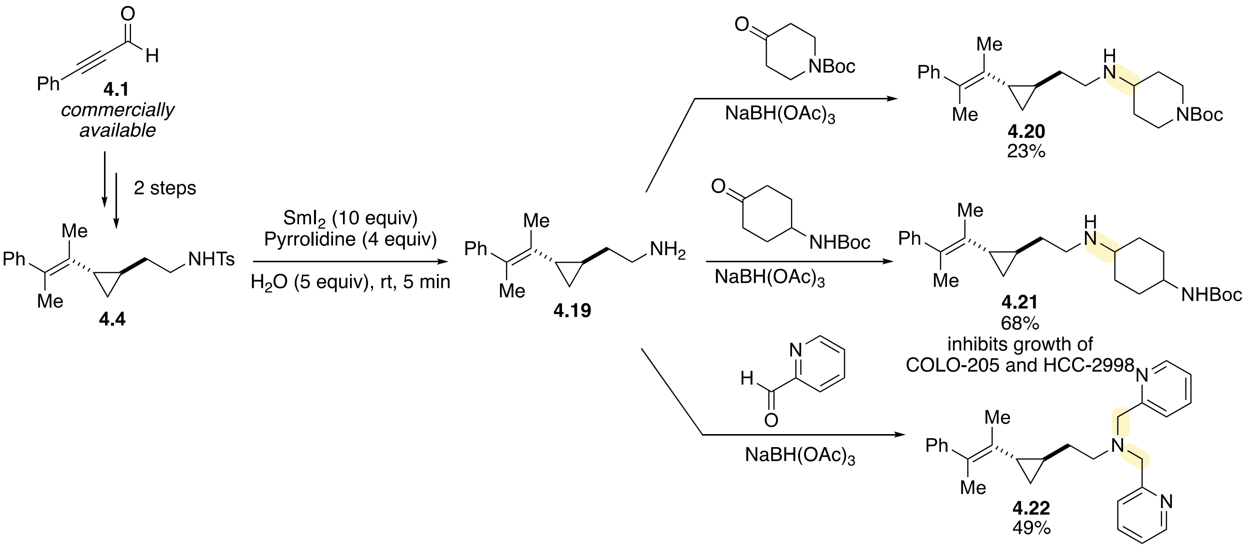
[39] For reviews on biological activity of substituted vinyl cyclopropanes, see: (a) Talele, T. T. *J. Med. Chem.* **2016**, *59*, 8712–8756. (b) Salaün, J. Cyclopropane Derivatives and their Diverse Biological Profile. In *Small Ring Compounds in Organic Synthesis VI*. de Meijere, A. Ed. **2000**. pp. 1–67.

[40] For discussions on the biological activity of substituted alkenes, see: (a) Avendano, C.; Menendez, J. C. *Medicinal Chemistry of Anticancer Drugs*, Elsevier, Oxford, **2015**, pp. 87–95. (b) Flynn, A. B.; Ogilvie, W. W. *Chem. Rev.* **2007**, *107*, 4698–4745.

[41] Albrecht, B. K.; Audia, J. E.; Cote, A.; Duplessis, M.; Gehling, V. S.; Harmange, J.-C.; Vaswani, R. G. LSD1 Inhibitors and Uses Thereof. WO 2016/172496 A1. 20

our domino reaction, we synthesized a series of analogs of LSD1 inhibitors (Scheme 4.3). First, we performed a SmI_2 deprotection of the pendant sulfonamide.[42] The resulting primary amine **4.19** was subjected to three different reductive amination reactions to produce **4.20**, **4.21**, and **4.22**. Interestingly, amine **4.21** demonstrated significant cell death against colon cancer cell lines (COLO-205 and HCC-2998).[43,44] Therefore, this domino reaction provides rapid access to bioactive structural motifs in four steps from commercially available materials.

Scheme 4.3 Derivatization of Cyclopropane Products



4.3 Proposed Mechanism of the Domino XEC Reaction

4.3.1 Mechanistic Experiments to Probe the Domino Reaction.

Next, we aimed to elucidate the mechanism of this multicomponent reaction. A series of control experiments were consistent with initiation of the catalytic cycle by oxidative addition of the nickel catalyst with the propargylic sulfonamide moiety. First, employing an alternative Grignard reagent, EtMgI, led to formation of alkynylcyclopropane **4.23** in 15% yield (Scheme

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[42] (a) Szostak, M.; Spain, M.; Procter, D. J. *J. Org. Chem.* **2012**, *77*, 3049– 3059. (b) Ankner, T.; Hilmersson, G. *Org. Lett.* **2009**, *11*, 503– 506.

[43] (a) Shoemaker, R. H. *Nat. Rev. Cancer* **2006**, *6*, 813–823. (b) National Institute of Health, "National Cancer Institute Developmental Therapeutics Program," can be found under https://dtp. cancer.gov/, 2021.

[44] Product **4.21** synthesized by Nadia Hirbawi and product **4.22** synthesized by Taylor A. Thane.

4a).[45] This observation is consistent with oxidative addition of the propargylic sulfonamide to produce an allenylnickel complex that proceeds through an XEC pathway. A simple propargylic sulfonamide, **4.24**, lacking a pendant alkyl halide, underwent substitution to form allene **4.25** (Scheme 4.4b). This further supports that the mechanism initiates by oxidative addition of the propargylic sulfonamide. Additionally, simple alkynes did not undergo dicarbofunctionalization under standard reaction conditions (Scheme 4.4c and 4.4d). Alkynyl cyclopropane **4.26** did not undergo a 1,2-dicarbofunctionalization under standard reaction conditions, employing catalytic or stoichiometric quantities of nickel complex.[46] Similarly, in a competition experiment, propargylic sulfonamide **4.3** reacted while alkyne **4.27** was not functionalized.[47] Therefore, even in the presence of relevant catalytically active organonickel intermediates, a simple alkyne was not engaged. Taken together, these experiments support initiation of the domino reaction by oxidative addition of the propargylic sulfonamide moiety.

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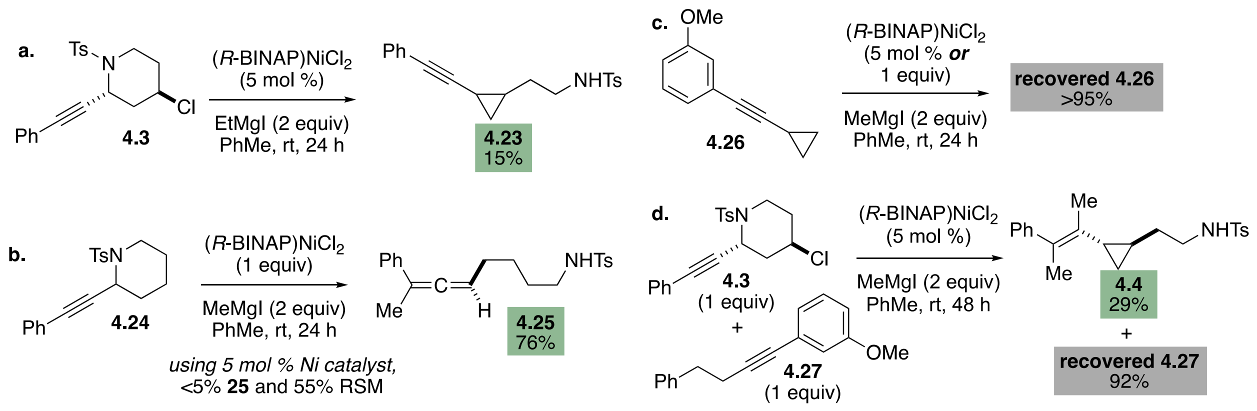
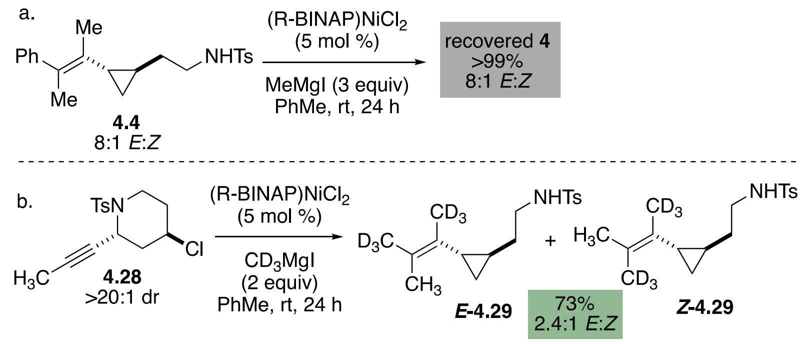
[45] Control experiment in Scheme 4.4a performed by Taylor A. Thane
[46] Control experiment in Scheme 4.4c performed by Taylor A. Thane
[47] Control experiment in Scheme 4.4d performed by Nadia Hirbawi

Scheme 4.4 Mechanistic Control Experiments



Next, we examined subsequent steps in the catalytic cycle, with a particular focus on the steps that would bifurcate to afford (*E*)- and (*Z*)-isomers of the alkene. To ensure that the product distribution was a kinetic distribution, we performed a control experiment (Scheme 4.5a). Resubjecting vinylcyclopropane **4.4** (8:1 *E*:*Z*) to the reaction conditions resulted in no isomerization. To determine whether the relative stability of product diastereomers is reflected in key transition states, we examined a substrate devoid of a steric preference for product formation (Scheme 4.5b).[48] Employing a deuterated Grignard reagent provided vinylcyclopropane **4.29** as a 1:2.4 mixture (*E*:*Z*). Therefore, we concluded that the relative stability of product isomers does not impact the selectivity of the reaction.

Scheme 4.5 Kinetic and Thermodynamic Stability of Products



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[48] Control reaction in Scheme 4.5b performed by Taylor A. Thane.

Next, we aimed to understand the stereoselective formation of the cyclopropane moeity. A stereochemical proof was performed to experimentally confirm that the cyclopropane ring formation is enantiospecific and occurs with retention (double inversion) at the sulfonamide-bearing carbon, and inversion at the alkyl chloride. To synthesize the desired enantioenriched *trans*-piperidine (+)-**4.34**, the following synthesis was performed (Scheme 4.6). First, a diastereoselctive TFA-promoted aza-Prins reaction afforded racemic alkynylpiperidine **4.31**. Enantioenriched alkynylpiperidine **(+)-4.32** was prepared by lipase-catalyzed kinetic resolution.[49] Deprotection of the acetate group followed by a oxidation with DMP and reduction with L-selectride afforded the *cis*-alkynylpiperidine **(+)-4.33**. Absolute configuration of alcohol (+)-**4.33** was unambigously assigned by X-ray crystallography. Finally, a mesylation reaction followed by a chlorination reaction produced alkynylpiperidine **(+)-4.34**. The enantioenriched piperidine was subjected to the standard conditions and the major diastereomer was isolated in an 31% yield. I attempted to crystalize this material and confirm the absolute configuration by X-ray cyrstallography, however, all attempts to grow X-ray quality crystals were unsuccessful. The product was derivatized to sulfonimide **(+)-4.35** and the absolute configuration of was determined by comparing the experimental circular dichroism (CD) spectrum to the simulated spectrum.[50,51]

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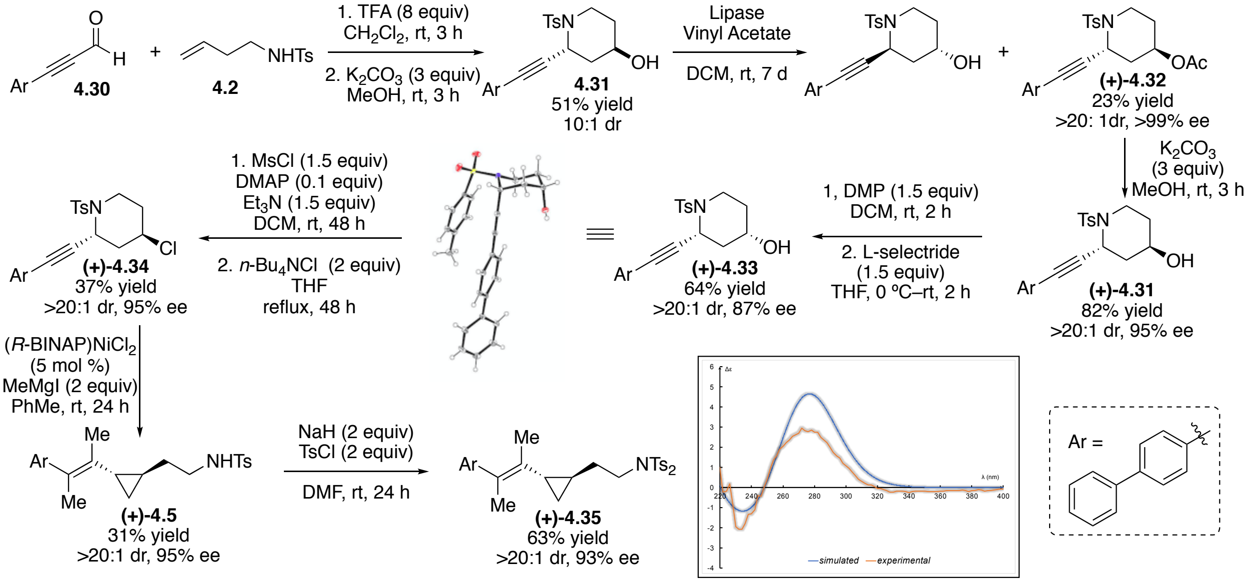
[49] Yadav, J. S.; Reddy, B. V. S.; Padmavani, B.; Venugopal, C.; Rao, A. B. *Tetrahedron Lett.* **2007**, *48*, 4631–4633.

[50] Bannwarth, C.; Grimme, S. *Comput. Theor. Chem.* **2014**, *1040–1041*, 45–53.

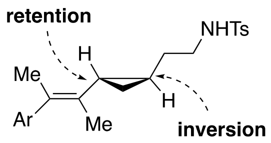
[51] Experimental CD spectra collected by Dr. Dima Fishman and the UCI laser spectroscopy lab

Scheme 4.6 Stereochemical Outcome of the Domino Reaction



In our previous investigation of the XEC reaction of benyzlic and allylic sulfonamides, we hypothesized that the ring contraction was stereospecific.[9c,52] The proposed oxidative addition proceeded with inversion and the intramolecular SN2-type reaction proceeded with inversion at both the benzylic position and the alkyl chloride. We aimed to prove this experimentally but we were unable to obtain X-ray crystallographic data for the cyclopropane product. With the stereochemical proof presented in Scheme 4.6, we are able to definitely prove that the ring contraction of sulfonamides proceeds with double inversion (net retention) at the propargylic carbon and inversion at the alkyl chloride (Figure 4.2).

Figure 4.2 Stereochemical Outcome of the Domino XEC Reaction



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[52] For more information, see Chapter 3, section 3.3.

4.3.2 Proposed Mechanism of the Domino Reaction

Based on the experimental and computational mechanistic experiments, we propose the following domino mechanism (Scheme 4.7).[1,10,53] Initiation of the catalytic cycle occurs with oxidative addition of the propargylic sulfonamide. The key allenylnickel intermediate **4.37** can react via two pathways. Carbometallation by nucleophilic attack of the pendant organomagnesium complex affords metallacyclobutane **4.42**, and eventually leads to formation of the major diastereomer, (*E*)-**4.4**. Alternatively, allenylnickel complex **4.37** can undergo transmetallation and subsequently attack the pendant electrophilic alkyl chloride, leading to formation of the minor diastereomer, (*Z*)-**4.4**. The pathways that diverge from allenylnickel intermediate **4.37** have transition states that are similar in energy, consistent with the observed modest levels of diastereoselectivity.[1] Each elementary step is stereospecific, with *anti*-carbometallation and *syn*-reductive elimination providing (*E*)-**4.4** and *syn*-migratory insertion and *syn*-reductive elimination generating (*Z*)-**4.4**

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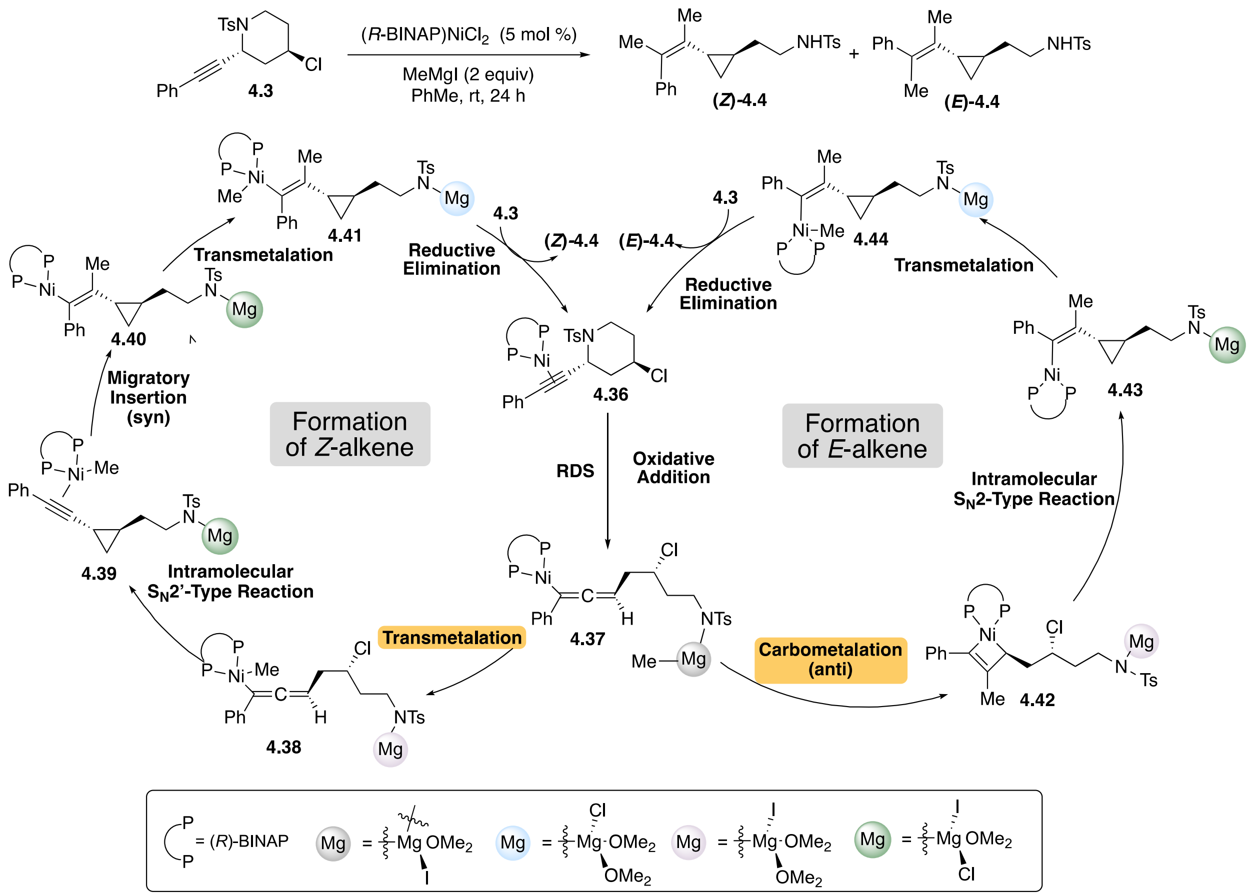
[53] For details on the computational data and calculated reaction coordinate diagrams, see ref 1

Scheme 4.7 Proposed Mechanism of the Domino Reaction



Interestingly, this proposed bifurcated mechanism is consistent with the known ambiphilic reactivity of allenylmetal intermediates (Scheme 4.8).[54] Nucleophiles tend to add to the central carbon, leading to formation of metallocyclobutene intermediates **4.46**. These metallocyclobutenes can equilibrate with vinylcarbene complexes **4.47**. In contrast, electrophiles tend to add to the terminal carbon. In our system, allenylmetal complex **4.37** reacts with coordinated nucleophilic Grignard reagent to form metallocyclobutene **4.42**. However, if transmetallation proceeds, the

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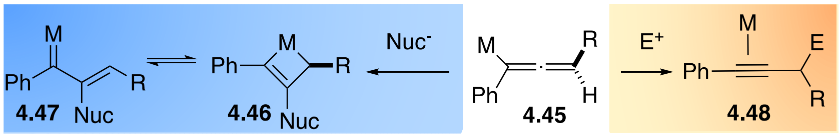
[54] (a) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225–242. (b) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722–733. (c) Chen, J.-T. *Coord. Chem. Rev.* **1999**, *190–192*, 1143–1168. (d) Tsuji, J.; Mandai, T. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2589–2612. (e) Ma, S. *Eur. J. Org. Chem.* **2004**, *6*, 1175–1183. (f) Cheng, Y.-C.; Chen, Y.-K.; Huang, T.-M.; Yu, C.-I.; Lee, G.-H.; Wang, Y.; Chen, J.-T. *Organometallics* **1998**, *17*, 2953–2957. (g) Holland, R. L.; Bunker, K. D.; Chen, C. H.; DiPasquale, A. G.; Rheingold, A. L.; Baldridge, K. K.; O'Connor, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 10093–10095.

resultant electron-rich allenylnickel moiety of **4.36** quickly attacks the pendant electrophilic alkyl chloride.

Scheme 4.8 Ambiphilic Pathways for Allenylmetal Species



4.4 Conclusions

In conclusion, we report a nickel-catalyzed domino reaction, to the best of our knowledge, the first example that includes separate XEC and dicarbofunctionalization reactions. The net transformation consists of ring-contraction of the piperidine and dicarbomethylation of the alkyne, generating highly substituted cyclopropanes bearing tetrasubstituted olefins and aminoethyl substituents. The reaction products are structurally related to histone demethylase inhibitors and we report the synthesis of derivatives that demonstrate selective inhibition of colon and non-small cell lung cancer cell lines. In addition, to accomplish rapid synthesis of the requisite starting materials, we report the first aza-Prins reaction of simple ynals to afford alkynyl piperidines, the starting materials for this domino reaction. Experimental and computational analysis of the reaction mechanism support a bifurcated reaction mechanism that accounts for product distributions. After oxidative addition, a key allenylnickel intermediate partitions into two different pathways, each with similar barrier heights, that lead to the observed reaction products. Future studies will include the development of related domino reactions and transformations that employ ambiphilic allenylnickel complexes.

4.5 Experimental Details

4.5.1 General Procedures

All reactions were carried out under an atmosphere of N_2, or Ar when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), dichloroethane (DCE), dimethylformamide (DMF), triethylamine (Et_3N), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 h) to remove H_2O.[55] All other solvents utilized were purchased anhydrous commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C, 376.5 MHz ^{19}F), GN-500 (500 MHz ^1H, 125.4 MHz ^{13}C), CRYO-500 (500 MHz ^1H, 125.8 MHz ^{13}C) or AVANCE-600 (600 MHz ^1H, 150 MHz ^{13}C, 564.6 MHz ^{19}F) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), sextet (sext), septet (sept), multiplet (m), broad singlet (bs), broad triplet (bt), doublet of doublet (dd), doublet of triplet (dt), doublet of quartet (dq), doublet of doublet of doublet (ddd), doublet of doublet of triplet (ddt), doublet of triplet of doublet (dtd), triplet of doublet (td), triplet of triplet (tt), triplet of doublet of doublet (tdd), quartet of doublet (qd), quartet of triplet (qt), quartet of doublet of doublet (qdd), apparent singlet (as), apparent triplet (at), apparent quintet (aquin), apparent doublet of quintet (aquin), apparent triplet of doublet (aqd), apparent quartet of doublet (aqd)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Fluorine chemical shifts are reported in ppm (δ) relative to the absolute frequency of 0.00 ppm in the proton spectrum. Unless otherwise indicated, NMR data were collected at 25 °C. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5

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[55] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with $KMnO_4$ or CAM. Flash chromatography was performed using SiliaFlash F60 (40-63 μm, 60 Å) from SiliCycle. Automated chromatography was carried out on a Teledyne Isco CombiFlash Rf Plus. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research Analytical Autopol III Automatic Polarimeter. SFC Determinations of enantiopurity were determined by chiral SFC analysis and performed on an Agilent Technologies HPLC (1260 series) system or Agilent Technologies HPLC (1200 series) Analytical Instruments using OJ-H, OD-H, and AD-H Chiralpak columns (100 bar, 50ºC, 254 nm). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Circular dichroism spectra were performed by the University of California, Irvine Laser Spectroscopy Labs and were collected on a Jasco J-810 spectropolarimeter (163–900 nm).

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (–20 °C) under an atmosphere of N_2 and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored in a glovebox and used as received. The methylmagnesium iodide was titrated with iodine prior to use.[56] All other chemicals were purchased commercially and used as received, unless otherwise noted.

4.5.2 General Domino XEC 1,2-Dicarbofunctionalizaton Reaction Procedures

4.5.2.1 Method A: Domino XEC 1,2-Dicarbofunctionalization with (*R*-BINAP)$NiCl_2$

In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with substrate

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[56] Krasoviskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890.

(1 equiv), (*R*-BINAP)$NiCl_2$ (5 mol %), and PhMe (0.2 M in substrate). A solution of MeMgI in Et_2O (2 equiv) was then added dropwise via syringe. After 24 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 µL, 50. µmol) was added and the yield was determined by ^1H NMR based on comparison to PhTMS as internal standard before purification by column chromatography.

4.4.2.2. Preparation of Methylmagnesium Iodide

Under a N_2 atmosphere, a three-necked flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was charged with magnesium turnings (2.80 g, 115 mmol). The flask and magnesium turnings were then flame-dried under vacuum and the flask was backfilled with N_2. Anhydrous Et_2O (25 mL) and a crystal of iodine (ca. 2 mg) were added to the flask. Freshly distilled iodomethane (5.0 mL, 80 mmol) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature then filtered through the fritted Schlenk filter into a pear-shaped flask under a N_2 atmosphere. The pear-shaped flask was capped with a septum, sealed with parafilm, and stored in the glovebox under a N_2 atmosphere for up to eight weeks. The resulting methyl Grignard reagent was typically between 2.4 and 3.0 M as titrated by Knochel's method.[56]

4.5.2.3 Preparation of (*R*-BINAP)$NiCl_2$

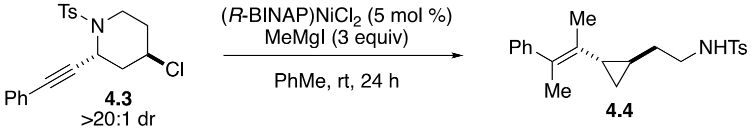
(*R*-BINAP)$NiCl_2$ was synthesized according to a procedure reported by Jamison.[21a] To a 50 mL round-bottom flask equipped with a stir bar was added $NiCl_2 \cdot 6H_2O$ (152 mg, 0.64 mmol, 1.0 equiv). The flask was placed under vacuum and flame-dried until nearly all of the nickel compound had turned from green to yellow-orange (a small amount of remaining green of the hexahydrate is necessary for the reaction to proceed). After cooling to room temperature, (*R*)-

BINAP (0.40 g, 0.64 mmol, 1.0 equiv) was added to the flask and a reflux condenser was attached. The flask was evacuated, backfilled with N_2, and then anhydrous MeCN (20 mL) was added. The reaction mixture was heated to reflux in an oil bath for 24 h, at which point the solution was cooled to room temperature and filtered under vacuum to yield a fine, black powder (0.33 mg, 0.44 mmol, 68% yield).

4.5.3 Robustness Screen to Establish Functional Group Compatibility

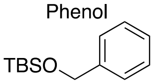
In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with piperidine 3 (1 equiv), (*R*-BINAP)$NiCl_2$ (5 mol %), and PhMe (0.4 M in substrate). The reaction was sealed with a septum cap, brought out of the glovebox, and placed under an N_2 atmosphere. Then the additive (0.1 mmol, 1.0 equiv) was added via microsyringe followed by dropwise addition of a solution of MeMgI in Et_2O (3 equiv). After 24 h, the reaction mixture was quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 µL, 50. µmol) was added and the yield was determined by ^1H NMR based on comparison to PhTMS as internal standard before purification by column chromatography. The results from this experiment are pictorially presented via a bar graph in Figure 4.1 and tabulated below in Table 4.2.

Table 4.2 Robustness Screen Results.



4.3
>20:1 dr

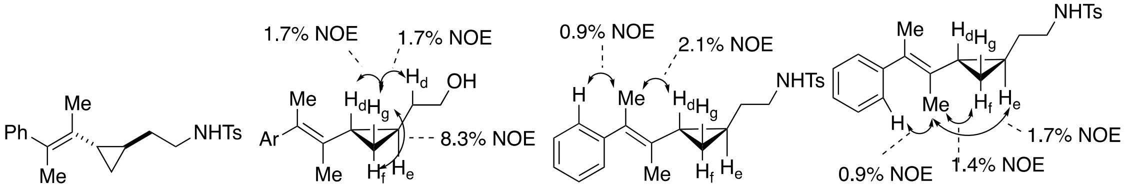
4.4

Entry	Additive	Conversion (Additive)[a]	Yield (*E*:*Z*)[a]
1	none	n/a	61% (1.6 : 1)
2	Phenol	55%	43% (1.2 : 1)
3	 TBSO	<5%	53% (1.8 : 1)
4	Thiophenol	37%	56% (1.8 : 1)
5	Aniline	30%	59% (1 : 1)
6	Nitrobenzene	>95%	23% (2.2 : 1)
7	Benzonitrile	>95%	48% (2.4 : 1)
8	Benzaldehyde	>95%	65% (2.2 : 1)
9	Chlorobenzene	64%	57% (2.1 : 1)
10	2-Chloropropane	53%	50% (2.3 : 1)
11	Cyclohexene	82%	60% (1.3 : 1)
12	Styrene	89%	28% (2.1 : 1)
13	Pyridine	>95%	49% (1 : 1. 6)
14	2-Methylpyridine	50%	41% (1 : 1.2)
15	Indole	<5%	65% (1.6 : 1)
16	1-Methyl-1*H*-indole	30%	66% (1.5 : 1)
17	4-Methylmorpholine	>95%	38% (1.2 : 1)

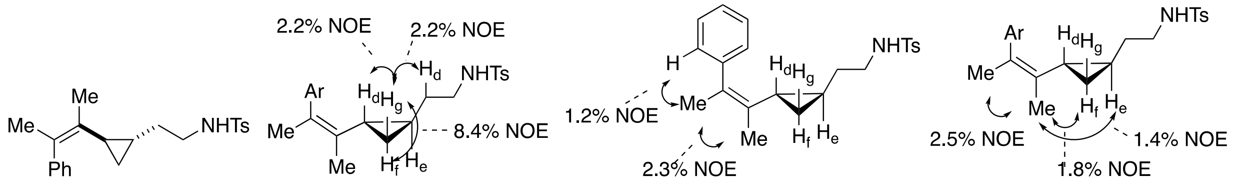
[a]Yield determined by ^{1}H NMR based on comparison to PhTMS as an internal standard.

4.5.4 Characterization Data for Cyclopropane Products

***N*-(2-*trans*-2-(3-phenylbut-2-en-2-yl)cyclopropyl)ethyl)4-methylbenzenesulfonamide (4.4):** was prepared according to Method A. The following amounts of reagents were used: piperidine **4.3** (37 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 5.0 µmol, 5.0 mol %), MeMgI (90. µL, 0.20 mmol, 2.3 M in Et$_2$O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification a ^{1}H NMR yield of 72% was obtained based on comparison to PhTMS as an internal standard. The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound a pale yellow oil (26 mg, 71. µmol, 71% yield, 1.5:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H$_g$ in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)- and minor (*Z*)-**4.4** were assigned based on NOE analysis. A second column was performed and the diastereomers were separated. The alkene isomers were characterized separately to demonstrate the stereochemical outcome of the reaction.

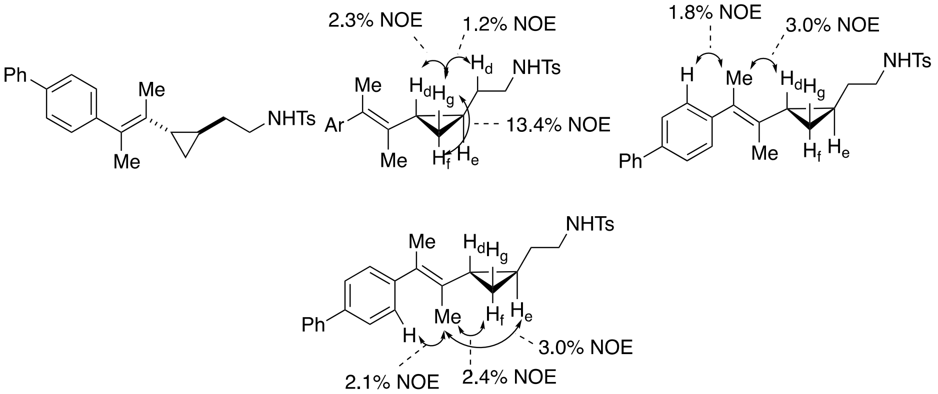


Major Diastereomer: TLC R$_f$ = 0.6 (25% EtOAc/hexanes); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.34–7.27 (m, 4H), 7.23–7.14 (m, 1H), 7.11–7.05 (m, 2H), 4.41 (s, 1H), 3.08 (qd, *J* = 6.7, 2.3 Hz, 2H), 2.42 (s, 3H), 2.04 (d, *J* = 1.5 Hz, 3H), 1.71–1.55 (m, 1H), 1.52–1.39 (m, 2H), 1.25 (d, *J* = 1.6 Hz, 3H), 0.87–0.77 (m, 1H), 0.77–0.70 (m, 1H), 0.49 (dt, *J* = 9.3, 4.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 125.7 MHz) δ 145.5, 143.5, 137.0, 132.0, 129.8 (2C), 129.5, 128.4 (2C), 128.0 (2C), 127.2 (2C), 125.9, 76.8, 43.4, 34.3, 22.2, 21.6, 20.8, 16.0, 15.6, 11.7; **IR** (neat) 3284, 2925, 2860, 1599, 1324, 1160, 905, 728, 650 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na]$^{+}$ calculated for $C_{22}H_{27}NO_2SNa$, 392.1660; found, 392.1667.

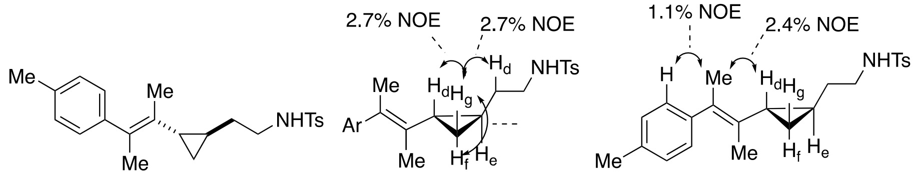


Minor Diastereomer: TLC R$_f$ = 0.6 (25% EtOAc/hexanes); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.30 (t, *J* = 6.2 Hz, 1H), 2.98–2.83 (m, 2H), 2.42 (s, 3H), 1.96 (s, 3H), 1.43 (d, *J* = 1.5 Hz, 3H), 1.30–1.15 (m, 3H), 0.69–0.63 (m, 1H), 0.59 (dt, *J* = 8.8, 5.0 Hz, 1H), 0.16 (dt, *J* = 9.4, 4.9 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 125.7 MHz) δ 143.3, 131.3, 129.7 (2C), 129.5, 128.7 (2C), 128.5, 128.1 (2C), 127.8, 127.1 (2C), 125.9, 43.2, 33.7, 22.9, 21.6, 21.6, 15.6, 13.9, 11.6; **IR** (neat) 3284, 2925, 2860, 1599, 1324, 1160, 905, 728, 650 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na]$^{+}$ calculated for $C_{22}H_{27}NO_2SNa$, 392.1660; found, 392.1667.

Scale Up Reaction: In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with piperidine **4.3** (0.37 g, 1.0 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (38 mg, 50. µmol, 5.0 mol %), and PhMe (5.0 mL, 0.2 M in substrate). Then MeMgI (0.80 mL, 2.0 mmol, 2.0 equiv, 2.5 M in Et$_2$O) was then added dropwise via syringe. After 24 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et$_2$O, and concentrated in vacuo. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear and colorless oil (230 mg, 0.62 mmol, 62% yield, 1.8:1 *E*:*Z*). Refer above to cyclopropane **4.4** for analytical data.



***N*-(2-(*trans*-2-(3-([1,1'-Biphenyl]-4-yl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**4.5**) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.34** (45 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 50. µmol, 5.0 mol %), MeMgI (90. µL, 0.20 mmol, 2.3 M in Et$_2$O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 70% and 2.8:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a pale yellow solid (29 mg, 65 µmol, 64% yield, 2.5:1 *E*:*Z*). A second column was performed and the diastereomers were separated. The major diastereomer is fully characterized below. The ratio of alkene isomers was determined by integration of the resonances attributed to H_g in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)-**4.5** was assigned based on NOE analysis. **m.p.** 134–137 °C; **TLC R_f** = 0.2 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.34–7.28 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.75 (t, *J* = 6.2 Hz, 1H), 3.07 (qd, *J* = 6.9 Hz, 1.3 Hz, 2H), 2.41 (s, 3H), 2.06 (q, *J* = 1.4 Hz, 3H), 1.69–1.57 (m, 1H), 1.51–1.39 (m, 2H), 1.31 (q, *J* = 1.4 Hz, 3H), 0.88–0.79 (m, 1H), 0.77–0.71 (m, 1H), 0.52–0.46 (m, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 144.6, 143.5, 141.1, 138.7, 137.1, 131.5, 130.1, 129.8 (2C), 128.9 (2C), 128.8 (2C), 127.3 (2C), 127.2, 127.1 (2C), 126.8 (2C), 43.4, 34.4, 22.4, 21.6, 20.8, 16.2, 15.8, 11.9. **IR** (neat) 3304, 2922, 2861, 1597, 1318, 1151, 812, 727, 657 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na]$^+$ calculated for $C_{28}H_{31}NO_2SNa$, 468.1973; found, 468.1978.

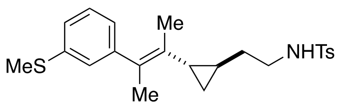


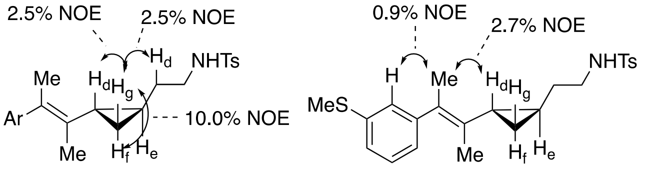
4-methyl-*N*-(2-(*trans*-2-(3-(*p*-tolyl)but-2-en-2-yl)cyclopropyl)ethyl)benzenesulfonamide (**4.6**) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.49** (39 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (3.8 mg, 5.0 µmol, 5.0 mol %), MeMgI (90 µL, 0.20 mmol, 2.3 M in Et_2O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 65% and 1.4:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear yellow oil (27 mg, 0.070 mmol, 71% yield, 1.9:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H_g in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)-**4.6** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.5 (20% EtOAc/hexanes); **IR** (neat) 3280, 2923, 1599, 1485, 1325, 1238, 1160, 1039, 905, 729 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{23}H_{29}NO_2SNa$, 406.1817; found, 406.1805.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 3H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 4.55 (t, *J* = 6.2 Hz, 1H), 3.07 (qd, *J* = 6.3, 2.2 Hz, 2H), 2.42 (s, 7H), 2.33 (s, 7H), 2.02 (s, 3H), 1.68–1.62 (m, 1H), 1.50–1.42 (m, 2H), 1.26 (s, 5H), 0.86–0.75 (m, 1H), 0.72 (dt, *J* = 9.2, 5.1 Hz, 1H), 0.47 (dt, *J* = 9.6, 5.0 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 143.4, 142.5, 137.0, 135.4, 129.8 (2C), 128.8, 128.7 (2C), 128.6, 128.2 (2C), 127.2 (2C), 43.4, 34.3, 22.2, 21.6, 21.1, 20.8, 16.1, 15.6, 11.7.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.28 (s, 2H), 7.08 (s, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 4.36 (t, *J* = 6.2 Hz, 1H), 2.91 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.94 (s, 3H), 1.41 (s, 3H), 1.24–1.18 (m, 2H), 0.92–0.83 (m, 1H), 0.71–0.63 (m, 1H), 0.59 (dt, *J* = 9.0, 5.1 Hz, 1H), 0.16 (dt, *J* = 9.4, 4.9 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 142.2, 135.5, 129.9 (2C), 129.8 (2C), 129.3, 129.1, 128.9 (2C), 128.7 (2C), 127.3, 43.3, 33.8, 23.0, 21.8, 21.3, 20.1, 15.6, 13.8, 11.6.





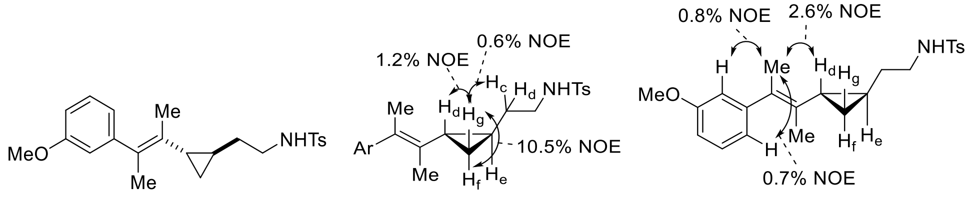
4-methyl-*N*-(2-(*trans*-2-(3-(3-(methylthio)phenyl)but-2-en-2-yl)cyclopropyl)ethyl)benzenesulfonamide (4.7) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.50** (42 mg, 0.10 mmol, 1.0 equiv), (*R*-

BINAP)NiCl$_2$ (3.8 mg, 5.0 µmol, 5.0 mol %), MeMgI (90. µL, 0.20 mmol, 2.3 M in Et$_2$O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 65% and 2.8:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear yellow oil (33 mg, 79 µmol, 79% yield, 2.4:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H$_g$ in the ^{1}H NMR spectrum. The relative configuration of the major product (*E*)-**4.7** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.5 (20% EtOAc/hexanes); **IR** (neat) 3279, 2921, 1585, 1323, 1158, 1094, 905, 728 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{23}H_{29}NO_2S_2Na$, 438.1537; found, 438.1533.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.22 (t, *J* = 6.6 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.99 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.57 (t, *J* = 6.2 Hz, 1H), 3.14–3.01 (m, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 2.02 (s, 3H), 1.71–1.61 (m, 1H), 1.51–1.46 (m, 2H), 1.25 (s, 3H), 0.87–0.77 (m, 1H), 0.73 (dt, *J* = 8.4, 5.1 Hz, 1H), 0.49 (dt, *J* = 9.5, 5.0 Hz, 1H);**^{13}C NMR** (125.7 MHz, CDCl$_3$) δ 146.2, 143.5, 137.9, 137.0, 131.5, 130.1, 129.8 (2C), 128.5, 127.2 (2C), 126.5, 125.2, 124.1, 43.4, 34.3, 22.1, 21.6, 20.7, 16.0, 15.9, 15.7, 11.7.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 5.2 Hz, 1H), 7.06 (s, 1H), 6.99 (s, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.40 (t, *J* = 6.1 Hz, 1H), 2.91 (q, *J* = 6.7 Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 1.94 (s, 3H), 1.42 (s, 3H), 1.31 (dt, *J* = 13.8, 6.8 Hz, 1H), 1.20–1.13 (m, 2H), 0.70–0.64 (m, 1H), 0.59 (dt, *J* = 8.4, 5.1 Hz, 1H), 0.18 (dt, *J* = 9.5, 5.0 Hz, 1H); **^{13}C NMR** (125.7 MHz, CDCl$_3$) δ 145.7, 143.3, 137.1, 130.8, 130.0, 129.7 (2C), 128.6, 127.1 (2C), 127.1, 126.9, 125.6, 124.0, 43.1, 33.6, 23.0, 21.5, 20.6, 15.8, 15.7, 13.9, 11.7.



***N*-(2-(*trans*-2-(3-(3-Methoxyphenyl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide (4.8)**[57] was prepared according to Method A. The following amounts of reagents were used: piperidine **4.51** (40.4 mg, 0.100 mmol, 1.00 equiv), (*R*-BINAP)NiCl_2 (3.8 mg, 5.0 µmol, 5.0 mol %), MeMgI (71 µL, 0.20 mmol, 2.8 M in Et_2O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 47% and 2.2:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear colorless oil (18 mg, 46 µmol, 46% yield, 1.5:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H_g in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)-**4.8** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.4 (20% EtOAc/hexanes); **IR** (neat) 3279, 2921, 1597, 1575, 1320, 1157, 1093, 1043 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_3\text{SNa}$, 422.1766; found, 422.1760.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl_3) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25–7.17 (m, 1H), 6.78–6.70 (m, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.64 (as, 1H), 4.63 (t, *J*

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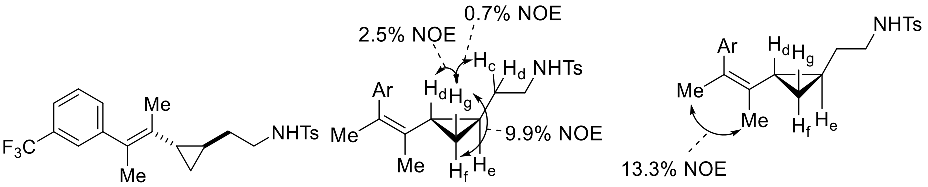
[57] Cyclopropane **4.8** synthesized by Nadia Hirbawi.

= 5.9 Hz, 1H), 3.79 (s, 3H), 3.07 (qd, *J* = 6.6, 3.0 Hz, 2H), 2.42 (s, 3H), 2.02 (as, 3H), 1.69–1.55 (m, 1H), 1.50–1.48 (m, 2H), 1.26 (as, 3H), 0.87–0.77 (m, 1H), 0.72 (dt, *J* = 8.5, 5.0 Hz, 1H), 0.48 (dt, *J* = 8.7, 5.0 Hz, 1H); **^{13}C NMR** (125.9 MHz, CDCl$_3$) δ 159.38, 147.1, 143.5, 137.0, 131.9, 129.8 (2C), 129.66, 129.03, 127.19 (2C), 120.9, 114.1, 111.3, 55.2, 43.4, 34.3, 22.1, 21.6 (2C), 16.0, 15.64, 11.7.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.25–7.17 (m, 1H), 6.78–6.70, (m, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.64 (as, 1H), 4.45 (t, *J* = 5.8 Hz, 1H), 3.79 (s, 3H), 2.91 (q, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 1.95 (as, 3H), 1.41 (as, 3H), 1.33–1.23 (m, 1H), 1.23–1.12 (m, 2H), 0.69–0.61 (m, 1H), 0.59 (dt, *J* = 8.5, 5.0 Hz, 1H), 0.18 (dt, *J* = 8.8, 5.0 Hz, 1H); **^{13}C NMR** (125.9 MHz, CDCl$_3$) δ 159.42, 146.6, 143.3, 137.1, 131.1, 129.71 (2C), 129.6, 129.07, 127.15 (2C), 121.3, 114.4, 111.4, 55.2, 43.2, 33.7, 22.9, 20.7 (2C), 15.56, 13.8, 11.5.



***N*-(2-(*trans*-2-(3-(3-Trifluoromethylphenyl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**4.9**)[58] was prepared according to Method A. The following amounts of reagents were used: piperidine **4.52** (44 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), MeMgI (80. μL, 0.20 mmol, 2.5 M in Et$_2$O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 47% and 1.4:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a mixture of alkene

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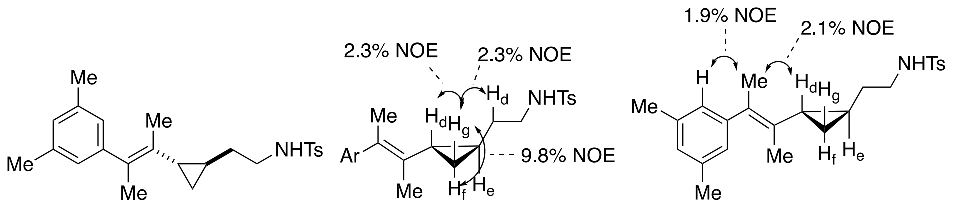
[58] Cyclopropane **4.9** synthesized by Nadia Hirbawi.

diastereomers as a clear yellow oil (20. mg, 46 μmol, 46% yield, 1.3:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H_g in the ^{1}H NMR spectrum. Due to overlapping peaks of the major (*E*)-**4.9**, the relative configuration of the minor (*Z*)-**4.9** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.5 (25% EtOAc/hexanes); **IR** (neat) 3278, 2923, 1331, 1159, 1122, 1094, 1072 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{23}H_{26}F_3NO_2SNa$, 460.1534; found, 460.1545.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.46–7.38 (m, 3H), 7.36–7.33 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.61 (t, *J* = 5.8 Hz, 1H), 3.07 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 2.09–2.02 (m, 3H), 1.63 (quin, *J* = 6.9 Hz, 1H), 1.50–1.40 (m, 2H), 1.23 (s, 3H), 0.89–0.80 (m, 1H), 0.77–0.71 (m, 1H), 0.51 (dt, *J* = 8.7, 4.7 Hz, 1H); **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 146.2, 143.5, 136.94, 131.8, 131.1, 130.6, 130.4 (q, *J* = 31.7 Hz), 129.73 (2C), 128.50, 127.14 (2C), 125.1 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.4 Hz), 122.67 (q, *J* = 3.6 Hz), 43.3, 34.3, 22.1, 21.50, 20.6, 16.0, 15.7, 11.78; **^{19}F NMR** (564.7 MHz, $CDCl_3$) δ –62.53 (3F).

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.46–7.38 (m, 3H), 7.36–7.33 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.43 (t, *J* = 6.0 Hz, 1H), 2.91 (q, *J* = 6.7, 2H), 2.42 (s, 3H), 1.97 (s, 3H), 1.45 (s, 3H), 1.35 (quin, *J* = 6.8 Hz, 1H), 1.16–1.05 (m, 2H), 0.73–0.67 (m,1H), 0.59 (dt, *J* = 8.4, 5.2 Hz, 1H), 0.20 (dt, *J* = 8.8, 4.9 Hz, 1H); **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 145.7, 143.4, 136.96, 132.1 (s), 131.2, 130.3 (q, *J* = 32.1 Hz), 129.8, 129.69 (2C), 128.53, 127.08 (2C), 125.6 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.4 Hz), 122.65 (q, *J* = 3.6 Hz), 43.1, 33.5, 22.9, 21.51, 21.3, 15.8, 14.0, 11.82; **^{19}F NMR** (564.7 MHz, $CDCl_3$) δ –62.49 (3F).

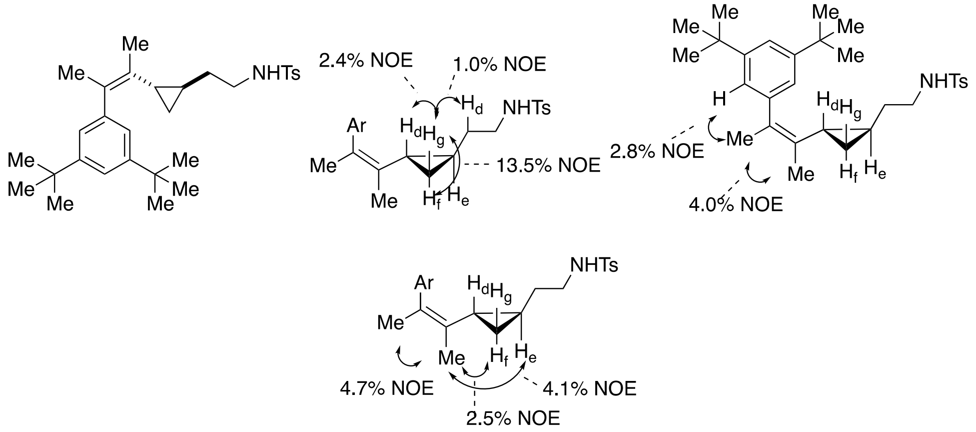


***N*-(2-(*trans*-2-(3-(3,5-dimethylphenyl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**4.10**) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.53** (50 mg, 0.12 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (4.6 mg, 6.0 µmol, 5.0 mol %), MeMgI (0.10 mL, 0.24 mmol, 2.5 M in Et_2O, 2.0 equiv), PhMe (0.60 mL, 0.20 M in substrate). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear yellow oil (32 mg, 80. µmol, 68% yield, 2.0:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H_g in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)-**4.10** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.4 (20% EtOAc/hexanes); **IR** (neat) 3280, 2922, 2860, 1598, 1323, 1184, 907, 724 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{31}NO_2SNa$, 398.2154; found, 398.2155.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.83 (s, 1H), 6.70 (s, 2H), 4.50 (t, *J* = 6.3 Hz, 1H), 3.07 (qd, *J* = 6.5, 2.9 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 6H), 2.00 (s, 3H), 1.67–1.59 (m, 1H), 1.49–1.41 (m, 2H), 1.25 (d, *J* = 1.9 Hz, 3H), 0.84–0.75 (m, 1H), 0.71 (dt, *J* = 8.9, 5.0 Hz, 1H), 0.47 (dt, *J* = 9.5, 4.9 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 145.6, 143.5, 137.5, 132.3, 129.8 (2C), 129.2, 127.6 (2C), 127.3 (2C), 126.6, 126.2 (2C), 43.5, 34.4, 22.2, 21.7, 21.5 (2C), 20.9, 16.2, 15.7, 11.8.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.83 (s, 1H), 6.76 (s, 2H), 4.32 (t, *J* = 6.1 Hz, 1H), 2.92 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 6H), 1.94 (s, 3H), 1.40 (s, 3H), 1.33–1.26 (m, 1H), 1.23–1.15 (m, 2H), 0.69–0.63 (m, 1H), 0.59 (dt, *J* = 8.9, 5.1 Hz, 1H), 0.16 (dt, *J* = 9.5, 4.9 Hz, 1H); **^{13}C NMR** (125.7 MHz, CDCl$_3$) δ 145.1, 143.4, 137.6, 137.1, 131.5, 129.8 (2C), 129.1, 127.6 (2C), 127.2 (2C), 126.2 (2C), 43.3, 33.7, 23.1, 21.7, 21.6, 20.9, 15.6, 13.8, 11.6.

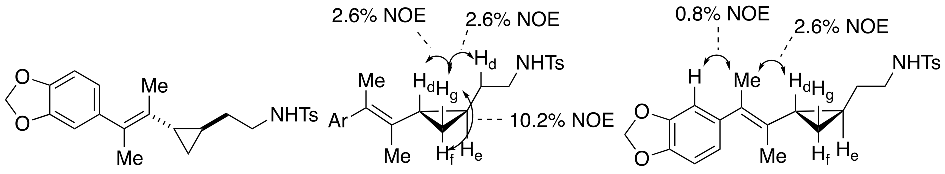


***N*-(2-(*trans*-2-(3-(3,5-di-*tert*-butylphenyl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**4.11**) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.54** (44 mg, 90. µmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.4 mg, 4.5 µmol, 5.0 mol %), MeMgI (80. µL, 0.18 mmol, 2.3 M in Et$_2$O, 2.0 equiv), PhMe (0.45 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 56% and 2.3:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear yellow oil (24 mg, 50. µmol, 56% yield, 1:2.6 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H$_g$ in the ^{1}H NMR spectrum. The relative configuration of the major (*Z*)-**4.11** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.6 (20% EtOAc/hexanes); **IR** (neat) 3277, 2962, 2865, 1591, 1324, 1159, 1094, 907, 730 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{30}H_{43}NO_2SNa$, 504.2919; found, 504.2912.

Major (*Z*) Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ7.77 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.07 (d, *J* = 1.8 Hz, 2H), 7.00 (d, *J* = 1.8 Hz, 1H), 4.43 (s, 1H), 2.99 (q, *J* = 6.6 Hz, 2H), 2.48 (d, *J* = 2.9 Hz, 3H), 2.05 (s, 3H), 1.59–1.51 (m, 1H), 1.49 (s, 3H), 1.37 (s, 18H), 1.33–1.32 (m, 1H), 1.08 (dq, *J* = 14.5, 7.2 Hz, 1H), 0.76 (tt, *J* = 8.3, 5.2 Hz, 1H), 0.64 (dt, *J* = 8.2, 5.1 Hz, 1H), 0.22 (dt, *J* = 9.5, 5.0 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 150.2, 144.1, 143.4, 137.2, 132.5, 129.8 (2C), 129.0, 127.2 (2C), 123.1 (2C), 119.8 (2C), 43.4, 34.9, 33.8, 31.7 (6C), 23.0, 21.9, 21.7, 15.7 (2C), 13.9, 11.7.

Minor (*E*) Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ7.84 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 1.8 Hz, 2H), 7.00 (d, *J* = 1.8 Hz, 1H), 4.60 (d, *J* = 7.0 Hz, 1H), 3.15 (hept, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 2.12 (d, *J* = 1.9 Hz, 3H), 1.76–1.67 (m, 1H), 1.59–1.50 (m, 1H), 1.39 (s, 18H), 1.33 (s, 3H), 1.05–0.85 (m, 2H), 0.85–0.78 (m, 1H), 0.55 (dt, *J* = 9.4, 5.0 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 150.1, 144.4, 143.4, 137.1, 132.4, 129.7 (2C), 129.0, 127.2 (2C), 127.1, 122.6 (2C), 119.6 (2C), 43.4, 34.9, 34.3, 31.6, 31.5 (6C), 22.2, 20.9, 16.1, 15.6, 11.7.

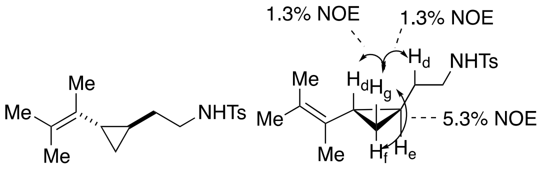


***N*-(2-(*trans*-2-(3-(benzo[*d*][1,3]dioxol-5-yl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**4.12**) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.55** (32 mg, 80. μmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (2.9 mg, 3.8 μmol, 5.0 mol %), MeMgI (70. μL, 0.16 mmol, 2.3 M in Et_2O, 2.0 equiv), PhMe (0.40 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 55% and 2.6:1 *E*:*Z* was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear pale yellow oil (19 mg, 45 µmol, 57% yield, 2.8:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances attributed to H_g in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)-**4.12** was assigned based on NOE analysis. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

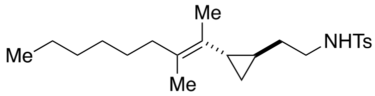
TLC R$_f$ = 0.7 (20% EtOAc/hexanes); **IR** (neat) 3276, 2922, 1598, 1323, 1094, 903, 726 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{23}H_{27}NO_4SNa$, 436. 1559; found, 436.1570.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 8.0, 1H), 6.58 (s, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 5.93 (s, 2H), 4.58 (t, *J* = 6.1 Hz, 1H), 3.14–3.00 (m, 2H), 2.42 (s, 3H), 1.99 (d, *J* = 1.7 Hz, 3H), 1.72–1.54 (m, 1H), 1.48–1.40 (m, 2H), 1.27–1.25 (m, 3H), 0.85–0.75 (m, 1H), 0.74–0.66 (m, 1H), 0.47 (dt, *J* = 9.5, 4.9 Hz, 1H);**^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 147.2, 145.5, 143.4, 139.5, 137.0, 131.5, 129.8 (2C), 127.2 (2C), 121.4, 109.0, 108.0, 100.8, 43.4, 34.3, 22.9, 22.2, 21.6, 20.9, 16.1, 15.7, 11.7.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.34–7.30 (m, 2H), 6.71 (s, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.60 (d, *J* = 1.6 Hz, 1H), 5.94 (s, 2H), 4.37 (t, *J* = 6.3 Hz, 1H), 2.92 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.92–1.90 (m, 3H), 1.39 (s, 3H), 1.35–1.27 (m, 2H), 1.25–1.17 (m, 1H), 0.85–0.75 (m, 1H), 0.62–0.56 (m, 1H), 0.19 (dt, *J* = 9.4, 4.9 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 147.3, 145.6, 143.4, 139.6, 139.0, 130.7, 129.7 (2C), 127.1 (2C), 121.7, 109.3, 108.9, 108.0, 100.8, 43.2, 33.7, 22.9, 21.7, 20.6, 15.5, 13.8, 11.6.



4-methyl-*N*-(2-(*trans*-2-(3-methylbut-2-en-2-yl)cyclopropyl)ethyl)benzenesulfonamide (4.13) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.28** (24 mg, 80. μmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (2.9 mg, 4.0 μmol, 5.0 mol %), MeMgI (70. μL, 0.16 mmol, 2.3 M in Et$_2$O, 2.0 equiv), PhMe (0.40 mL, 0.20 M in substrate). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a clear yellow oil (15 mg, 49 μmol, 60% yield, >20:1 dr). The dr was based on the integration of the resonances attributed to H$_g$ in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R$_f$** = 0.3 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.51 (s, 1H), 3.03 (ddt, *J* = 12.8, 10.3, 6.1 Hz, 2H), 2.43 (s, 3H), 1.73 (d, *J* = 1.5 Hz, 3H), 1.65 (s, 3H), 1.60 (d, *J* = 4.0 Hz, 1H), 1.53 (td, *J* = 14.0, 7.1 Hz, 1H), 1.39 (dq, *J* = 13.9, 6.9 Hz, 1H), 1.32 (s, 3H), 0.69–0.62 (m, 1H), 0.59 (dt, *J* = 8.3, 5.0 Hz, 1H), 0.36 (dt, *J* = 9.3, 4.7 Hz, 1H); **^{13}C NMR** (125.7 MHz, CDCl$_3$) δ 143.5, 137.1, 129.81 (2C), 129.78, 127.3 (2C), 126.0, 43.5, 34.3, 22.0, 21.7, 21.3, 20.5, 15.4, 14.6, 11.6; **IR** (neat) 3279, 2921, 2859, 1598, 1324, 1159, 1094, 905, 729 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{17}H_{25}NO_2SNa$, 330.1504; found, 330.1500.



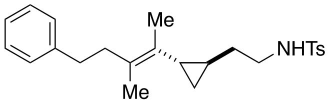
4-methyl-*N*-(2-(*trans*-2-(3-methylnon-2-en-2-yl)cyclopropyl)ethyl)benzenesulfonamide (4.14) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.56** (42 mg, 0.11 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (4.1 mg, 5.5 μmol, 5.0 mol %), MeMgI (0.10 mL, 0.22 mmol, 2.3 M in Et$_2$O, 2.0 equiv), PhMe (0.55 mL, 0.20 M in substrate).

Before purification, a ^{1}H NMR yield of 60% was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear yellow oil (35 mg, 0.093 mmol, 83% yield, 2:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances in the ^{13}C NMR spectrum. The relative configuration of the major (*E*)-**4.14** was assigned based on analogy to cyclopropane **4.4**.

TLC R_f = 0.2 (20% EtOAc/hexanes); **IR** (neat) 3278, 2924, 2856, 1598, 1455, 1324, 1158, 1094, 841, 660 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{35}NO_2SNa$, 400. 2286; found, 400.2289.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.54 (t, *J* = 6.5 Hz, 1H), 3.09–2.96 (m, 2H), 2.43 (s, 3H), 2.10 (td, *J* = 7.1, 3.3 Hz, 1H), 1.98 (td, *J* = 7.0, 2.2 Hz, 1H), 1.62 (d, *J* = 1.0 Hz, 3H), 1.6–1.47 (m, 1H), 1.42–1.19 (m, 13H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.73–0.62 (m, 1H), 0.62–0.55 (m, 1H), 0.40–0.30 (m, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 143.3, 137.1, 130.4, 129.7 (2C), 127.2 (2C), 126.1, 43.3, 35.3, 34.3, 34.3, 31.9, 29.5, 28.4, 22.7, 21.6, 19.3, 15.1, 14.3, 14.2, 11.4.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.54 (t, *J* = 6.5 Hz, 1H), 3.09–2.96 (m, 2H), 2.43 (s, 3H), 2.10 (td, *J* = 7.1, 3.3 Hz, 1H), 1.98 (td, *J* = 7.0, 2.2 Hz, 1H),), 1.70 (d, *J* = 1.3 Hz, 3H), 1.61–1.47 (m, 1H), 1.42 – 1.19 (m, 13H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.73–0.62 (m, 1H), 0.62–0.55 (m, 1H), 0.40–0.30 (m, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 143.3, 137.0, 130.7, 129.7 (2C), 127.2 (2C), 126.1, 43.4, 35.3, 34.2, 31.9, 29.4, 28.2, 22.7, 22.1, 21.4, 18.5, 15.5, 14.2, 14.2, 11.6.



4-Methyl-*N*-(2-(*trans*-2-(3-methyl-5-phenylpent-2-en-2-yl)cyclopropyl)ethyl)benzenesulfonamide (4.15)[59] was prepared according to Method A. The following amounts of reagents were used: piperidine **4.57** (40. mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), MeMgI (90. μL, 0.20 mmol, 2.0 equiv), and PhMe (0.5 mL, 0.2 M in substrate). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear oil (26 mg, 0.64 mmol, 64% yield, 2.2:1 *E:Z).* The ratio of alkene isomers was determined by integration of the resonances in the ^{13}C NMR spectrum. The relative configuration of the major (*E*)-**4.15** was assigned based on analogy to cyclopropane **4.4**. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.5 (25% EtOAc/hexanes); **IR** (neat) 3276, 3062, 3026, 2998, 2924, 2860, 1599 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{24}H_{31}NO_2SNa$, 420.1973; found, 420.1975.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76–7.72 (m, 2H), 7.31–7.24 (m, 4H), 7.17–7.14 (m, 3H), 4.58–4.52 (m, 1H), 3.04–2.96 (m, 2H), 2.68–2.60 (m, 2H), 2.43–2.41 (m, 2H), 2.39 (s, 3H), 1.68 (s, 3H), 1.55–1.48 (m, 1H), 1.30 (s, 3H), 1.28–1.20 (m, 2H), 0.67–0.62 (m, 1H), 0.58–0.53 (m, 1H), 0.32–0.28 (m, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 143.4, 142.6, 137.0, 129.7 (2C), 129.3, 128.4 (2C), 128.3 (2C), 127.3, 127.2 (2C), 125.8, 43.3, 36.6, 34.8, 34.3, 21.6, 21.4, 19.3, 15.2, 14.5, 11.5.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76–7.72 (m, 2H), 7.31–7.24 (m, 4H), 7.17–7.14 (m, 3H), 4.58–4.52 (m, 1H), 3.04–2.96 (m, 2H), 2.68–2.60 (m, 2H), 2.39 (s, 3H), 2.31–2.27 (m, 2H), 1.75 (s, 3H), 1.40–1.36 (m, 1H), 1.28–1.20 (m, 2H), 1.23 (s, 3H), 0.67–0.62 (m, 1H), 0.58–0.53 (m, 1H), 0.38–0.34 (m, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 143.4, 142.5, 137.0,

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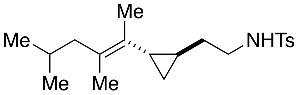
[59] Cyclopropane **4.15** was synthesized by Taylor A. Thane

129.8 (2C), 129.3, 128.5 (2C), 128.3 (2C), 127.4, 127.2 (2C), 125.7, 43.4, 37.5, 34.5, 34.3, 22.1, 21.6, 18.6, 15.5, 14.1, 11.7.



***N*-(2-(*trans*-2-(3,5-dimethylhex-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide (4.16)**[60] was prepared according to Method A. The following amounts of reagents were used: piperidine **4.58** (35 mg, 0.10 mmol, 1.0 equiv), (*R*–BINAP)NiCl$_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), MeMgI (90. μL, 0.20 mmol, 2.0 equiv), and PhMe (0.5 mL, 0.2 M in substrate). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear oil (23 mg, 0.66 mmol, 66% yield, 3:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances in the ^{13}C NMR spectrum. The relative configuration of the major (*E*)-**4.16** was assigned based on analogy to cyclopropane **4.4**.

TLC R$_f$ = 0.5 (25% EtOAc/hexanes); **IR** (neat) 3279, 3056, 2951, 2924, 2866 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{20}H_{31}NO_2SNa$, 372.1973; found, 372.1969.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.74 (d, *J* = 7.9 Hz, 2H), 8.30 (d, *J* = 7.9 Hz, 2H), 5.50 (t, *J* = 6.2 Hz, 1H), 4.01 (q, *J* = 6.7 Hz, 2H), 3.01 (d, *J* = 7.6 Hz, 2H), 2.77–2.71 (m, 1H), 2,.61 (s, 3H), 2.58–2.53 (m, 1H), 2.38–2.30 (m, 2H), 2.27 (s, 3H), 1.89–1.79 (m, 6H), 1.69–1.67 (m, 1H), 1.61–1.58 (m, 1H), 1.34–1.31 (m, 1H), 0.73–0.64 (m, 1H), 0.61–0.58 (m, 1H), 0.34–0.31 (m, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 143.4, 137.2, 129.8 (2C), 129.4, 127.3 (2C), 127.2, 43.43, 43.41, 34.3 (2C), 27.5 (2C), 22.81, 22.76, 21.75, 21.65, 15.3, 11.5.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.74 (d, *J* = 7.9 Hz, 2H), 8.30 (d, *J* = 7.9 Hz, 2H), 5.50 (t, *J* = 6.2 Hz, 1H), 4.01 (q, *J* = 6.7 Hz, 2H), 2,90 (d, *J* = 7.5 Hz, 2H), 2.77–2.71 (m,

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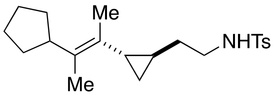
[60] Cyclopropane **4.16** was synthesized by Taylor A. Thane

1H), 2.69 (s, 3H), 2.58–2.53 (m, 1H), 2.38–2.30 (m, 2H), 2.33 (s, 3H), 1.89–1.79 (m, 6H), 1.69–1.67 (m, 1H), 1.61–1.58 (m, 1H), 1.37–1.34 (m, 1H), 0.73–0.64 (m, 1H), 0.61–0.58 (m, 1H), 0.39–0.35 (m, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 143.4, 137.2, 129.8 (2C), 129.4, 127.3 (2C), 127.2, 44.4, 43.5, 34.4 (2C), 22.7, 22.6, 22.3, 21.8, 19.1, 15.7, 14.9, 11.8.



***N*-(2-(*trans*-2-(3-cyclopentylbut-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide (4.17)**[61] was prepared according to Method A. The following amounts of reagents were used: piperidine **4.59** (36 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), MeMgI (80. μL, 0.20 mmol, 2.0 equiv), and PhMe (0.5 mL, 0.2 M in substrate). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear oil (22 mg, 0.59 mmol, 59% yield, 1.5:1 *E*:*Z*). The ratio of alkene isomers was determined by the integration of the resonances attributed to cyclopentyl methine in the ^{1}H NMR spectrum. The relative configuration of the major (*E*)-**4.17** was assigned based on analogy to cyclopropane **4.4**. For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.5 (25% EtOAc/hexanes); **IR** (neat) 3278, 2949, 2865, 1599 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for C$_{21}$H$_{31}$NO$_2$SNa, 384.1973; found, 384.1976.

Major Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.56 (bs, 1H), 3.17–3.11 (m, 1H), 3.02 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.65–1.47 (m, 11H), 1.43–1.25 (m, 6H), 0.69–0.63 (m, 1H), 0.61–0.56 (m, 1H), 0.38–0.33 (m, 1H); **^{13}C NMR**

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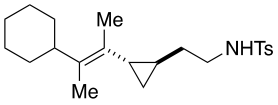
[61] Cyclopropane **4.17** was synthesized by Taylor A. Thane

(125.8 MHz, $CDCl_3$) δ 143.5, 137.1, 132.9, 129.8 (2C), 127.3 (2C), 126.6, 43.4, 42.2, 34.5, 30.6, 30.4, 26.2 (2C), 21.64, 21.59, 15.58, 15.55, 14.2, 11.9;

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.56 (bs, 1H), 3.02 (q, *J* = 6.7 Hz, 2H), 2.90–2.83 (m, 1H), 2.42 (s, 3H), 1.65–1.47 (m, 11H), 1.43–1.25 (m, 6H), 0.69–0.63 (m, 1H), 0.61–0.56 (m, 1H), 0.38–0.33 (m, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.5, 137.1, 132.6, 129.8 (2C), 127.3 (2C), 126.2, 43.5, 43.1, 34.3, 30.4, 30.3, 26.1, 26.0, 22.6, 21.6, 15.7, 14.3, 13.6, 11.8.



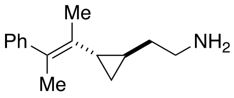
***N*-(2-(*trans*-2-(3-cyclohexylbut-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide** (**4.18**) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.60** (38 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (3.8 mg, 5.0 µmol, 5.0 mol %), MeMgI (90. µL, 0.20 mmol, 2.3 M in Et_2O, 2.0 equiv), PhMe (0.50 mL, 0.20 M in substrate). Before purification, a ^{1}H NMR yield of 52% was obtained based on comparison to PhTMS as an internal standard. The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a mixture of alkene diastereomers as a clear yellow oil (19 mg, 51 µmol, 50% yield, 2:1 *E*:*Z*). The ratio of alkene isomers was determined by integration of the resonances in the ^{13}C NMR spectrum. The relative configuration of the major (*E*)-**4.18** was assigned based on analogy to cyclopropane **4.4**.

TLC R_f = 0.2 (20% EtOAc/hexanes); **IR** (neat) 3278, 2924, 2851, 1599, 1446, 1325, 1158, 1094, 838, 660 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{33}NO_2SNa$, 398.2130; found, 398.2119.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.3, 2.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.46 (t, *J* = 6.2 Hz, 1H), 3.03 (qt, *J* = 8.1, 4.1 Hz, 2H), 2.71–2.63 (m, 1H), 2.43 (s, 3H), 1.77–1.71 (m, 2H), 1.68–1.64 (m, 1H), 1.61 (d, *J* = 1.7 Hz, 1H), 1.53–1.51 (m, 3H), 1.46–1.34 (m, 3H), 1.34 (s, 3H), 1.32–1.20 (m, 5H), 1.19–1.09 (m, 1H), 0.69–0.60 (m, 1H), 0.58 (dt, *J* = 8.5, 5.1 Hz, 1H), 0.36 (dt, *J* = 9.4, 4.9 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 143.4, 137.0, 135.5, 129.7 (2C), 127.1 (2C), 125.2, 43.4, 41.2, 34.4, 31.0, 30.9, 26.9, 26.8, 26.4, 21.6, 21.3, 15.6, 15.5, 14.3, 11.9.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.3, 2.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.46 (t, *J* = 6.2 Hz, 1H), 3.03 (qt, *J* = 8.1, 4.1 Hz, 2H), 2.71–2.63 (m, 1H), 2.43 (s, 3H), 1.77–1.71 (m, 2H), 1.68–1.64 (m, 1H), 1.53–1.51 (m, 2H), 1.61 (d, *J* = 1.7 Hz, 3H), 1.47–1.36 (m, 2H), 1.35 (d, *J* = 1.6 Hz, 3H), 1.32–1.20 (m, 5H), 1.19–1.09 (m, 1H), 0.69–0.60 (m, 1H), 0.58 (dt, *J* = 8.5, 5.1 Hz, 1H), 0.36 (dt, *J* = 9.4, 4.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.4, 137.0, 135.3, 129.7 (2C), 127.2 (2C), 125.1, 43.4, 41.9, 34.2, 30.8, 30.7, 26.8, 26.8, 26.4, 22.4, 21.3, 15.7, 15.5, 14.1, 13.7.

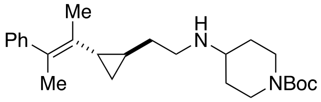
4.5.5 Synthesis and Characterization of Derivatization of Cyclopropane Products



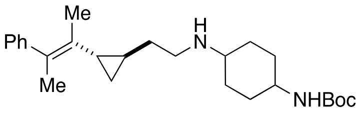
***trans*-2-(3-phenylbut-2-en-2-yl)cyclopropyl)ethan-1-amine** (**4.19**) was prepared according to modified procedure reported by Hilmerson.[42b] To a flame-dried round bottom flask equipped with a stir bar was added freshly prepared SmI_2 (40. mL, 3.2 mmol, 10. equiv, 80. mM in THF).[42a] Then cyclopropane **4.4** (120 mg, 0.32 mmol, 1.0 equiv) was added a solution in minimal amount of THF. This was immediately followed by H_2O (0.17 mL, 9.6 mmol, 30. equiv), and pyrrolidine (0.53 mL, 6.4 mmol, 20. equiv). The solution became white upon the addition of the amine. The reaction mixture was diluted with CH_2Cl_2 and treated with a solution of potassium sodium tartrate (50 mL, 10% w/w) and K_2CO_3 (50 mL, 10% w/w). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The unpurified reaction mixture was carried onto the next step without further purification.

4.5.5.1 Method B: Reductive Amination of Primary Amines

This method was adapted from a procedure reported by Albrecht.[41] To a suspension of amine **4.19** (1.0–1.3 equiv) in dichloroethane (0.10–0.20 M in amine) was added the corresponding ketone or aldehyde (1.0 equiv). Then $NaBH(OAc)_3$ (2.0–3.2 equiv) was added at rt and was allowed to stir for 30 mins. Then additional ketone or aldehyde (0.3 equiv) was added and the reaction mixture was allowed to stir for 30 mins. The mixture was quenched with saturated $NaHCO_3$ and extracted with methyl *t*-Butyl ether (x 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography.



***tert*-butyl-4-*trans*-2-(3-phenylbut-2-en-2-yl)cyclopropyl)ethyl)amino)piperidine-1-carboxylate** (**4.20**) was prepared according Method B. The following amounts of reagents were used: amine **4.19** (26 mg, 0.12 mmol, 1.3 equiv), 1-boc-piperidone (19 mg, 90. µmol, 1.0 equiv), $NaBH(OAc)_3$ (61 mg, 0.29 mmol, 3.2 equiv), and DCE (1.2 mL, 0.10 M in amine). The residue was purified by column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a yellow oil (27 mg, 70. µmol, 23% yield over two steps). **TLC Rf** = 0.3 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.33 (m, 4H, both diastereomers), 7.26 (d, *J* = 7.5 Hz, 4H, both diastereomers), 7.20–7.13 (m, 2H, both diastereomers), 4.10 (bs, 4H, both diastereomers), 2.96–2.77 (m, 6H, both diastereomers), 2.77–2.56 (m, 3H, one diastereomer), 2.18–2.10 (m, 3H, one diastereomer), 2.03 (s, 3H, one diastereomer), 1.99–1.79 (m, 3H, one diastereomer), 1.76–1.57 (m, 2H, one diastereomer), 1.54 (s, 3H, one diastereomer), 1.52 (s, 16H, both diastereomers), 1.46–1.26 (m, 9H, both diastereomers), 1.09–0.88 (m, 1H, one diastereomer), 0.88–0.79 (m, 1H, one diastereomer), 0.69 (dt, $J = 9.0, 5.1$ Hz, 1H, one diastereomer), 0.60 (dt, $J = 9.5, 5.0$ Hz, 1H, one diastereomer), 0.30 (dt, $J = 9.4, 5.0$ Hz, 1H, one diastereomer); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.0 (one diastereomer), 154.9 (one diastereomer), 145.8 (one diastereomer), 145.3 (one diastereomer), 140.1 (one diastereomer), 131.7 (one diastereomer), 130.9 (one diastereomer), 130.3 (one diastereomer), 130.2 (one diastereomer), 128.9 (2C, one diastereomer), 128.53 (one diastereomer), 128.51 (2C, one diastereomer), 128.45 (one diastereomer), 128.4 (one diastereomer), 128.11 (4C, both diastereomers), 128.09 (one diastereomer), 125.92 (one diastereomer), 125.90 (one diastereomer), 125.8 (one diastereomer), 79.6 (one diastereomer), 55.4 (one diastereomer), 55.1 (one diastereomer), 51.6 (one diastereomer), 46.7 (one diastereomer), 46.3 (one diastereomer), 34.9 (one diastereomer), 34.2 (one diastereomer), 28.6 (6C, both diastereomers), 23.1 (2C, one diastereomer), 22.4 (2C, one diastereomer), 21.7 (2C, one diastereomer), 20.9 (2C, one diastereomer), 16.5 (one diastereomer), 16.4 (one diastereomer), 16.2 (one diastereomer), 14.1(one diastereomer), 12.0 (one diastereomer), 11.9 (one diastereomer). **IR** (neat) 2926, 2854, 1682, 1427, 1169, 906, 716 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{39}N_2O_2$, 399.3011; found, 399. 3011.



***tert*-butyl-(4-*trans*-2-(3-phenylbut-2-en-2-yl)cyclopropyl)ethyl)amino)cyclohexyl) carbamate** (**4.21**)[62] was prepared according to Method B. The following amounts of reagents were used: amine **4.19** (50 mg, 0.23 mmol, 1.0 equiv), *N*-4-Boc-aminocyclohexanone (49 mg, 0.23 mmol, 1.0 equiv), $NaBH(OAc)_3$ (98 mg, 0.46 mmol, 2.0 equiv), and DCE (1.0 mL, 0.20 M in amine). The

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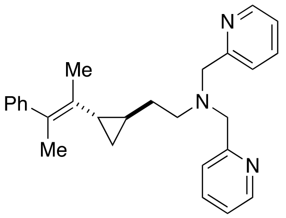
[62] Substrate **4.21** synthesized by Nadia Hirbawi.

residue was purified by column chromatography (0–10% MeOH/CH_2Cl_2) to afford the title compound as a yellow oil (64 mg, 0.16 mmol, 68% yield over two steps). The product was characterized as a 1.7:1.7:1.0:1 mixture of diastereomers. **TLC Rf** = 0.6 (10% MeOH/CH_2Cl_2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.24 (m, 8H, four diastereomers), 7.22–7.14 (m, 8H, four diastereomers), 7.09 (d, *J* = 7.9 Hz, 4H, four diastereomers), 4.72 (bs, 2H, two diastereomers), 4.39 (bs, 2H, two diastereomers), 3.68 (bs, 2H, two diastereomers), 3.42 (bs, 2H, two diastereomers), 2.83 (t, *J* = 7.3 Hz, 8H, four diastereomers), 2.69–2.43 (m, 8H, four diastereomers), 2.11–1.94 (m, 12H, two diastereomers), 2.07 (s, 6H, two diastereomers), 1.97 (s, 6H, two diastereomers), 1.84–1.50 (m, 16H, two diastereomers), 1.50–1.22 (m, 12H, four diastereomers), 1.48 (s, 6H, two diastereomers), 1.44 (s, 36H, four diastereomers), 1.30 (s, 6H, two diastereomers), 1.30–1.26 (m, 2H, two diastereomers), 1.21–1.03 (m, 4H, two diastereomers), 0.98–0.84 (m, 2H, two diastereomers), 0.82–0.71 (m, 2H, two diastereomers), 0.68–0.59 (m, 2H, two diastereomers), 0.59–0.50 (m, 2H, two diastereomers), 0.24 (dt, *J* = 13.2, 4.4 Hz, 2H, two diastereomers); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 155.4 (2C, two diastereomers), 155.3 (2C, two diastereomers), 145.7 (2C, two diastereomers), 145.2 (2C, two diastereomers), 131.8 (2C, two diastereomers), 131.03 (one diastereomer), 130.99 (one diastereomer), 130.0 (2C, two diastereomers), 129.97 (one diastereomer), 129.95 (one diastereomer), 128.8 (4C, two diastereomers), 128.4 (4C, two diastereomers), 128.1 (2C, two diastereomers), 128.07 (2C, two diastereomers), 128.06 (2C, two diastereomers), 125.9 (2C, two diastereomers), 125.86 (2C, two diastereomers), 125.85 (2C, two diastereomers), 79.2 (4C, four diastereomers), 56.4 (2C, two diastereomers), 56.1 (2C, two diastereomers), 54.6 (2C, two diastereomers), 54.3 (2C, two diastereomers), 49.3 (4C, four diastereomers), 46.5 (2C, two diastereomers), 46.07 (one diastereomer), 46.02 (one diastereomer), 31.94 (4C, two diastereomers), 31.91 (4C, two diastereomers), 30.4 (2C, two diastereomers), 29.8

(2C, two diastereomers), 28.5 (12C, four diastereomers), 23.02 (one diastereomer), 22.99 (one diastereomer), 22.39 (one diastereomer), 22.35 (one diastereomer), 21.7 (4C, two diastereomers), 20.9 (4C, two diastereomers), 16.28 (2C, two diastereomers), 16.25 (2C, two diastereomers), 16.20 (2C, two diastereomers), 14.1 (2C, two diastereomers), 11.9 (2C, two diastereomers), 11.8 (2C, two diastereomers). **IR** (neat) 3367, 2928, 2855, 1686, 1519, 1455, 1364, 1247, 1169, 764, 702 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{41}N_2O_2$, 413.3168; found, 413.3159.



***trans*-2-(3-Phenylbut-2-en-2-yl)cyclopropyl)-*N*,*N*-bis(pyridin-2-ylmethyl)ethan-1-amine (4.22)**[63] was prepared according to Method B. The following amounts of reagents were used: amine **4.19** (43 mg, 0.20 mmol, 1.1 equiv), 2-pyridinecarbozaldehyde (17 μL, 0.18 mmol, 1.0 equiv), $NaBH(OAc)_3$ (0.11 g, 0.50 mmol, 2.8 equiv), and DCE (2 mL). The residue was purified by flash column chromatography (0–10% MeOH/DCM) to afford the title compound as a clear oil (34 mg, 86 μmol, 49% yield over two steps). For clarity, the ^{1}H NMR and ^{13}C NMR data of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.3 (10% MeOH/DCM); **HRMS** (TOF MS Cl+) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{32}N_3$, 398.2596; found, 398.2598.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53–8.49 (m, 2H), 7.66–7.55 (m, 4H), 7.30–7.23 (m, 2H), 7.22–7.07 (m, 5H), 3.85 (s, 4H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.98 (s, 3H), 1.70–1.64 (m, 1H), 1.38–1.28 (m, 2H), 1.26 (s, 3H), 0.92–0.84 (m, 1H), 0.71–0.67 (m, 1H), 0.46–0.41 (m, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 160.2 (2C), 149.11 (2C), 145.9, 136.5 (2C), 130.51,

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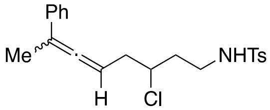
[63] Substrate **4.22** synthesized by Taylor A. Thane.

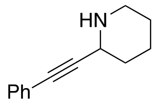
128.5 (2C), 128.1 (2C), 125.8 (2C), 122.9 (2C), 122.0 (2C), 60.7 (2C), 54.4, 32.3, 23.3, 20.8, 16.6, 16.0, 12.0.

Minor Diastereomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53–8.49 (m, 2H), 7.66–7.55 (m, 4H), 7.30–7.23 (m, 2H), 7.22–7.07 (m, 5H), 3.85 (s, 4H), 2.54 (t, *J* = 6.6 Hz, 2H), 1.95 (s, 3H), 1.59–1.52 (m, 1H), 1.44 (s, 3H), 1.37–1.17 (m, 2H), 0.83–0.76 (m, 1H), 0.59–0.54 (m, 1H), 0.17–0.12 (m, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 160.3 (2C), 149.1 (2C), 145.3, 136.4 (2C), 130.48, 128.9 (2C), 128.0 (2C), 125.8 (2C), 122.9 (2C), 121.9 (2C), 60.6 (2C), 54.3, 31.8, 22.6, 21.7, 16.59, 13.9, 11.9.

4.5.6 Experimental Data for Mechanistic Experiments



***N*-(3-chloro-7-phenylocta-5,6-dien-1-yl)-4-methylbenzenesulfonamide (4.61)** was prepared according to a modified version of Method A. The following amounts of reagents were used: piperidine **4.3** (37 mg, 0.10 mmol, 1.0 equiv), MeMgI (0.10 mL, 0.30 mmol, 3.0 equiv, 3.0 M in Et_2O), PhMe (0.5 mL, 0.2 M). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear and colorless oil (6.0 mg, 15 μmol, 15% yield, 4:1 dr). **TLC R_f** = 0.3 (20% EtOAc/hexanes); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82–7.74 (m, 2H), 7.48–7.43 (m, 2H), 7.42–7.33 (m, 4H), 7.28 (t, *J* = 7.3 Hz, 1H), 5.48 (tt, *J* = 6.6, 3.1 Hz, 1H), 4.55 (t, *J* = 6.4 Hz, 1H), 4.08 (td, *J* = 8.5, 7.1, 4.8 Hz, 1H), 3.30–3.13 (m, 2H), 2.56 (qd, *J* = 6.9, 6.3, 3.5 Hz, 2H), 2.48 (s, 3H), 2.15 (dd, *J* = 5.3, 2.9 Hz, 3H), 1.96–1.82 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 205.6, 143.7, 136.9, 131.8, 129.9 (2C), 128.5 (2C), 127.2 (2C), 126.9, 125.9 (2C), 101.4, 88.5, 59.6, 40.8, 38.3, 37.6, 32.1, 29.9, 21.7, 17.2, 14.3; **HRMS** (TOF MS Cl+) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{25}ClNO_2S$, 390.1295; found, 390.1306.



2-(phenylethynyl)piperidine (**4.62**) was prepared according to a procedure reported by Seidel.[64] To a solution of piperidine (0.49 mL, 5.0 mmol, 1.0 equiv) in Et_2O (10 mL, 0.5 M), was added *n*-BuLi (2.0 mL, 5.0 mmol, 1.0 equiv, 2.5 M in hexanes) at –78 °C. The reaction mixture was allowed to stir for 10 mins. Then 2,2,2-trifluoroacetophenone (0.84 mL, 6.0 mmol, 1.2 equiv) was added as a solution in Et_2O (6.0 mL, 1.0 M) and allowed to stir for an additional 10 mins. This was followed by the addition of freshly prepared lithium acetylide (7.5 mmol, 1.5 equiv). The reaction mixture was warmed to rt and allowed to stir for 2 h.

The lithium acetylide was prepared according the following method. In a flame dried round bottom flask equipped with a stir bar was added phenylacetylene (0.82 mL, 7.5 mmol, 1.5 equiv), PhMe (7.5 mL, 1.0 M), and THF (2.0 mL, 3.8 M). The flask was cooled to –78 °C and *n*-BuLi (3.0 mL, 7.5 mmol, 1.5 equiv) was added dropwise via syringe. The reaction mixture was allowed to stir for 30 mins at –78 °C.

To quench, the flask was cooled to 0 °C and MeOH was added. The mixture was transferred to a separatory funnel, was diluted with Et_2O and washed with 1.0 M NaOH. The aqueous layer was extracted with Et_2O (x 3). The combined organic layers were washed sequentially with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (0–5% MeOH/DCM) to afford the title compound as a pale yellow oil (0.31 g, 1.7 mmol, 33% yield). **TLC R_f** = 0.1 (5% MeOH/DCM). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.34–7.23 (m, 3H), 3.88 (dd, *J* = 7.4, 3.6 Hz, 1H), 3.21–3.10 (m, 1H), 2.91 (bs, 1H),

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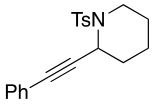
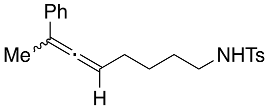
[64] Paul, A.; Seidel, D. *J. Am. Chem. Soc.* **2019**, *141*, 8778–8782.

2.77 (ddd, *J* = 11.7, 6.8, 4.3 Hz, 1H), 1.94 (ddt, *J* = 12.4, 6.9, 3.4 Hz, 1H), 1.88–1.78 (m, 1H), 1.72 (dtd, *J* = 11.6, 7.6, 3.6 Hz, 1H), 1.6–1.47 (m, 3H).



2-(phenylethynyl)-1-tosylpiperidine (**4.24**) was prepared according to a procedure reported by Smith.[65] To a stirring solution of piperidine **4.62** (0.31 g, 1.7 mmol, 1.0 equiv) in DCM (3.4 mL, 0.5 M) was added Et_3N (0.48 mL, 3.4 mmol, 2.0 equiv) and TsCl (0.30 g, 1.9 mmol, 1.1 equiv) at rt. The reaction mixture was allowed to stir overnight. To quench, 1.0 M HCl was added slowly. The biphasic mixture was transferred to a separatory funnel and the aqueous layer was extracted with DCM (x 3). The combined organic layers were washed with $NaHCO_3$, then brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a white solid (350 mg, 1.0 mmol, 67% yield). Analytical data is consistent with literature values.[66] **^{1}H NMR** (500 MHz, $CDCl_3$) 7.71 (d, *J* = 8.3 Hz, 2H), 7.31–7.14 (m, 5H), 6.98 (dt, *J* = 7.0, 1.5 Hz, 2H), 5.05 (s, 1H), 3.76 (dd, *J* = 12.1, 3.6 Hz, 1H), 2.88 (td, *J* = 11.8, 2.8 Hz, 1H), 2.27 (s, 3H), 1.97–1.82 (m, 2H), 1.77–1.61 (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.3, 135.1, 131.5 (2C), 129.3 (2C), 128.2, 128.1 (2C), 128.0 (2C), 122.4, 86.9, 84.4, 46.9, 42.4, 31.7, 25.4, 21.4, 19.5; **HRMS** (TOF MS Cl+) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{21}NO_2SNa$, 362.1191; found, 362.1187.



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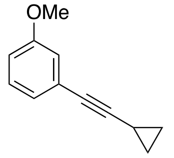
[65] Spoehrle, S. S. M.; West, T. H.; Taylor J. E.; Slawin, A. M.; Smith, A. D. *J. Am. Chem. Soc.* **2017**, *139*, 11895–11902.

[66] Daniels, D. S. B.; Jones, A. S.; Thompson, A. L.; Paton, R. S.; Anderson, E. A. *Angew. Chem. Int. Ed.* **2014**, *53*, 1915–1920.

4-Methyl-*N*-(7-phenylocta-5,6-dien-1-yl)benzenesulfonamide (4.25) was prepared according to Method A. The following amounts of reagents were used: piperidine **4.24** (28 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (75 mg, 0.10 mmol, 1.0 equiv), MeMgI (80. μL, 0.20 mmol, 2.0 equiv), and PhMe (0.5 mL, 0.2 M in substrate). The residue was purified by flash column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a clear oil (21 mg, 76 µmol, 76% yield). **TLC R$_f$** = 0.4 (25% hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.32–7.25 (m, 4H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.37 (bs, 1H), 4.40 (bt, 1H), 2.91 (q, *J* = 6.5 Hz, 2H), 2.41 (s, 3H), 2.06 (s, 3H), 1.54–1.48 (m, 2H), 1.46–1.40 (m, 2H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 204.3, 143.5, 137.6, 137.1, 129.8 (2C), 128.4 (2C), 127.2 (2C), 126.6, 125.7 (2C), 100.9, 92.5, 43.2, 29.2, 28.4, 26.0, 21.6, 17.3; **IR** (neat) 3282, 3082, 3060, 3027, 2931, 2858, 1948 cm^{-1}.



1-(Cyclopropylethynyl)-3-methoxybenzene (4.26)[67] was prepared according to Method D. The following amounts of reagents were used: cyclopropylacetylene (0.13 mL, 1.5 mmol, 1.1 equiv), 3-iodoanisole (0.17 mL, 1.4 mmol, 1.0 equiv), Pd(PPh$_3$)$_2$Cl$_2$ (13 mg, 0.18 mmol, 1.0 mol %), CuI (6.9 mg, 40 µmol, 2.0 mol %), and Et$_3$N (6 mL). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a clear oil (94 mg, 0.55 mmol, 39% yield). Analytical data are consistent with literature values.[68] **TLC R$_f$** = 0.8 (10% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.16 (t, *J* = 7.9, 1H), 6.97–6.95 (m, 1H), 6.91–

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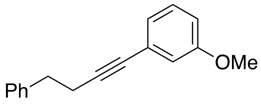
[67] Cyclopropane **4.26** synthesized by Taylor A. Thane.

[68] Siebeneicher, H.; Doye, S. *Eur. J. Org. Chem.* **2002**, *7*, 1213–1220.

6.90 (m, 1H), 6.82–6.79 (m, 1H), 3.77 (s, 3H), 1.47–1.40 (m, 1H), 0.88–0.82 (m, 2H), 0.81–0.72 (m, 2H).



1-methoxy-3-(4-phenylbut-1-yn-1-yl)benzene (**4.27**)[69] was prepared according to a procedure reported by Guant.[70] In a glovebox, CuI (15 mg, 80. µmol, 4.0 mol %) was added to a flame-dried round bottom flask equipped with a stir bar. The flask was sealed with a septum, removed from the glovebox, and placed under a N_2 atmosphere. Then $Pd(PPh_3)Cl_2$ (28 mg, 40. µmol, 2.0 mol %) was added, followed by THF (10. mL, 0.20 M in 3-iodoanisole). The suspension was allowed to stir at room temperature for 5 min. Then, 3-iodoanisole (0.24 mL, 2.0 mmol, 1.0 equiv), Et_3N (2.4 mL, 14 mmol, 7.0 equiv), and but-3-yn-1-ylbenzene (0.31 mL, 2.2 mmol, 1.1 equiv) were added via syringe. The reaction was allowed to stir at rt and monitored by TLC until the aryl iodide was completely consumed. To quench, the reaction mixture was filtered through a pad of Celite and washed with excess Et_2O. The filtrate concentrated in vacuo and purified by flash column chromatography (0–2% EtOAc/hexanes) to afford the title compound as a colorless oil (180 mg, 0.74 mmol, 37% yield). **TLC R_f** = 0.6 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.14 (m, 6H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.90 (as, 1H), 6.83 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.79 (s, 3H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H). Analytical data are consistent with literature values.[71]

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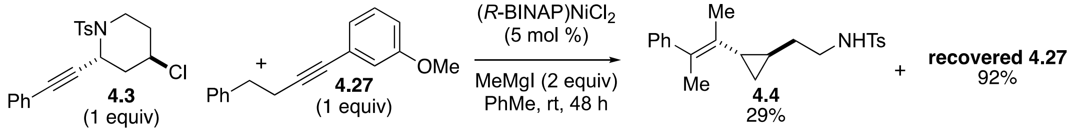
[69] alkyne **4.27** synthesized by Nadia Hirbawi

[70] Walkinshaw, A. J.; Xu, W.; Suero, M. G.; Guant, M. J. *J. Am. Chem. Soc.* **2013**, *135*, 12532–12535.

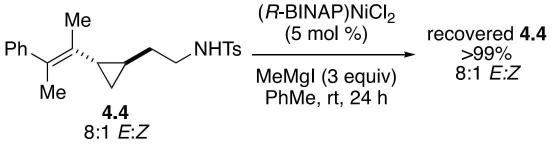
[71] Basu, B.; Das, S.; Das, P.; Mandal, B.; Banerjee, D.; Almqvist, F. *Synthesis* **2009**, *7*, 1137–1146.

4.5.6.1 Crossover Experiment[72]



(4.2)

In a glovebox, an oven-dried 7 mL vial equipped with a stir bar was charged with piperidine **4.3** (37 mg, 0.10 mmol, 1.0 equiv), alkyne **4.27** (24 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), and PhMe (0.50 mL, 0.20 M in substrate). Then MeMgI (81 μL, 0.20 mmol, 2.5 M in Et$_2$O, 2.0 equiv) was added dropwise via syringe. After 48 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et$_2$O, and concentrated in vacuo. The reaction was judged to be 35% recovered piperidine >20:1 dr, 29% yield of cyclopropane **4.4** 1.4:1 *E*:*Z*, 92% recovered alkyne **4.27** based on comparison to PhTMS as an internal standard by ^{1}H NMR spectroscopy. For piperidine **4.3**, the dr was determined based on the integration of the resonances attributed to the propargylic protons in the ^{1}H NMR spectrum. For cyclopropane **4.4**, the dr was determined based on the integration of the resonances attributed to H$_g$ in the ^{1}H NMR spectrum. See above (cyclopropane **4.4**) for full characterization of the product. See below (piperidine **4.3**) for full characterization of the starting material.



(4.3)

The control reaction was carried out according to a modified version of Method A. The following amounts of reagents were used: cyclopropane **4.4** (16 mg, 40. μmol, 1.0 equiv, 8:1 *E*:*Z*), (*R*-BINAP)NiCl$_2$ (1.5 mg, 2.0 μmol, 5 mol %), MeMgI (40. μL, 0.12 mmol, 2.8 M in Et$_2$O, 3.0 equiv),

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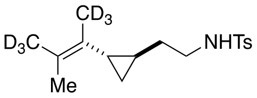
[72] Crossover experiment performed by Nadia Hirbawi.

PhMe (0.2 mL, 0.2 M in substrate). A ^{1}H NMR yield of >99% and 8:1 *E*:*Z* was obtained based on comparison to PhTMS as internal standard.

4.5.6.2 Preparation of CD_3MgI:

Under a N_2 atmosphere, a three-necked flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was charged with magnesium turnings (2.80 g, 115 mmol). The flask and magnesium turnings were then flame-dried under vacuum and the flask was backfilled with N_2. Anhydrous Et_2O (25 mL) and a crystal of iodine (ca. 2 mg) were added to the flask. Freshly distilled D_3-iodomethane (5.0 mL, 80 mmol) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature then filtered through the fritted Schlenk filter into a pear-shaped flask under a N_2 atmosphere. The pear-shaped flask was capped with a septum, sealed with parafilm, and stored in the glovebox under a N_2 atmosphere for up to eight weeks. The resulting methyl Grignard reagent titrated to 2.9 M as titrated by Knochel's method.[56]



4-Methyl-*N*-(2-(*trans*-2-(3-methylbut-2-en-2-yl-1,1,1,4,4,4-d_6)cyclopropyl)ethyl)benzene sulfonamide (**4.29**)[73] was prepared according to Method A. The following amounts of reagents were used: piperidine **4.28** (31 mg, 0.10 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (3.8 mg, 5.0 μmol, 5.0 mol %), MeMgI (80. μL, 0.20 mmol, 2.0 equiv), and PhMe (0.50 mL, 0.20 M in substrate). A ^{1}H NMR yield of 70% was obtained based on comparison to PhTMS as internal standard. The residue was purified by flash column chromatography (0–25% EtOAc/hexanes) to afford the title

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[73] cyclopropane **4.29** synthesized by Taylor A. Thane.

compound as a clear oil (23 mg, 73 μmol, 73% yield, 1:2.4 *E*:*Z*). The *E*:*Z* ratio was determined based on the integration of the resonances attributed to CD_3 in the ^{2}H NMR spectrum.

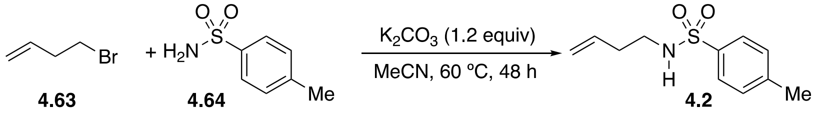
TLC R$_f$ = 0.5 (25% hexanes); **IR** (neat) 3279, 3065, 2996, 2923, 2859, 2236, 2189, 2058, 1598 cm^{-1}; **HRMS** (TOF MS Cl+) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{20}D_6NO_2S$, 314.2061; found, 314.2164. >99% ^{2}H Incorporation.

Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.60 (bt, *J* = 6.0 Hz, 1H), 3.05–2.98 (m, 2H), 2.43 (s, 3H), 1.71 (s, 3H), 1.57–1.48 (m, 1H), 1.43 (m, 1H), 1.32–1.25 (m, 1H), 0.68–0.62 (m, 1H), 0.60–0.55 (m, 1H), 0.37–0.33 (m, 1H); **^{2}H NMR** (400 MHz, $CDCl_3$) δ 1.62 (bs, 3H), 1.29 (bs, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.5, 137.1, 129.8 (2C), 127.3 (2C), 126.0, 125.9, 43.6, 43.5, 34.3, 29.8, 21.9, 21.6, 20.41, 15.4, 11.5;

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.60 (bt, *J* = 6.0 Hz, 1H), 3.05–2.98 (m, 2H), 2.43 (s, 3H), 1.64 (s, 3H), 1.57–1.48 (m, 1H), 1.43 (m, 1H), 1.32–1.25 (m, 1H), 0.68–0.62 (m, 1H), 0.60–0.55 (m, 1H), 0.37–0.33 (m, 1H); **^{2}H NMR** (400 MHz, $CDCl_3$) δ 1.70 (bs, 3H), 1.29 (bs, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.5, 137.1, 129.8 (2C), 127.3 (2C), 126.0, 125.9, 43.6, 43.5, 34.3, 29.8, 21.9, 21.6, 20.41, 15.4, 11.5.

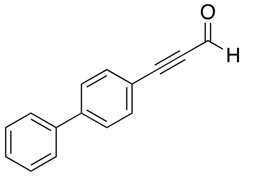
4.5.7 Proof of Stereochemical Outcome

4.5.7.1 Characterization Data for Stereochemical Proof



(4.4)

***N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide (4.2)** was prepared according to a procedure reported by Jiang.[74] To a flame-dried flask equipped with a stir bar was added 4-bromo-1-butene **4.63** (4.1 mL, 40. mmol, 1.0 equiv), *p*-toluenesulfonamide **4.64** (6.8 g, 40. mmol, 1.0 equiv), K_2CO_3 (6.6 g, 48 mmol, 1.2 equiv), and MeCN (160 mL). The mixture was heated to 60 °C and allowed to stir for 3 d. The reaction mixture was quenched with saturated NH_4Cl (100 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with H_2O (50 mL) and brine (50 mL), dried over Na_2SO_4, and was concentrated in vacuo. The residue was purified by column chromatography (5–25% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (5.4 g, 24 mmol, 60 %). Analytical data is consistent with literature values.[74] **^{1}H NMR:** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2, 2H), 7.30 (d, *J* = 8.1, 2H), 5.63 (ddt, *J* = 17.1, 10.4, 6.8, 1H), 5.11 (br s, 1H), 5.02–4.93 (m, 2H), 2.99 (q, *J* = 6.7, 2H), 2.41 (s, 3H), 2.20 (q, *J* = 6.9, 2 H).



3-([1,1'-Biphenyl]-4-yl)propiolaldehyde (4.30) was prepared according to Method C. The following amounts of reagents were used: 4-ethynylbiphenyl (0.71 g, 4.0 mmol, 1.0 equiv), *n*-BuLi (1.7 mL, 4.0 mmol, 1.0 equiv, 2.4 M solution in hexanes), DMF (0.62 mL, 8.0 mmol, 2.0 equiv), THF (10. mL, 0.40 M). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow solid (0.21 g, 1.0 mmol, 25% yield). **TLC R_f** = 0.6 (10% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.70–7.58 (m, 6H), 7.47 (at, *J* = 7.1 Hz, 2H), 7.40 (tt, *J* = 7.3 Hz, 1.3 Hz, 1H).

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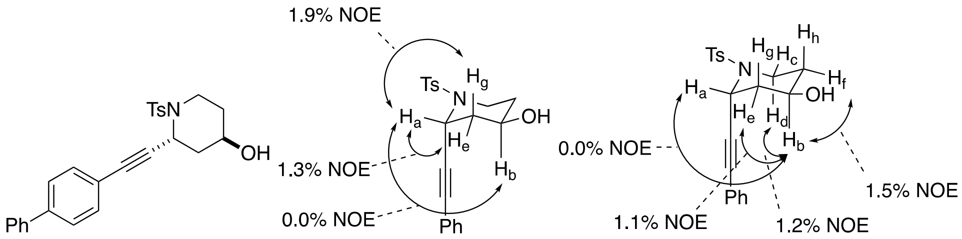
[74] Huang, J.; Zheng, J.; Wu, W.; Li, J.; Ma, J.; Ren, Y.; Jiang, H. *J. Org. Chem.* **2017**, *82*, 8191–8198.



***trans*-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-ol** (**4.31**) was prepared according to a procedure reported by Sabitha.[75] To a flame dried round bottom flask equipped with a stir bar was added aldehyde **4.30** (1.5 g, 5.0 mmol, 1.0 equiv), homoallylic sulfonamide **4.2** (1.3 g, 5.5 mmol, 1.1 equiv), and CH_2Cl_2 (50. mL, 0.10 M). Then trifluoroacetic acid (3.1 mL, 40. mmol, 8.0 equiv) was added slowly via syringe. The mixture was allowed to stir for 3 h at rt and was quenched with saturated aq. $NaHCO_3$. Then the pH was adjusted to >7 by the addition of Et_3N. The solution was transferred to a separatory funnel, and the aqueous layer was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was then redissolved in MeOH and K_2CO_3 (2.4 g, 18 mmol, 3.5 equiv) was added to the flask and was allowed to stir at rt for 1 h. The solvent was removed under reduced pressure, then H_2O was added the residue was transferred to separatory funnel. The aqueous layer was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (0–50% EtOAc/hexanes) to afford the title compound as an orange solid (1.1 g, 2.5 mmol, 51% yield, 10:1 dr, trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration of the major (trans) diastereomer was determined by NOE analysis. **m.p.** = 68–72 °C; **TLC R$_f$** = 0.4 (50% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.58–7.53 (m,

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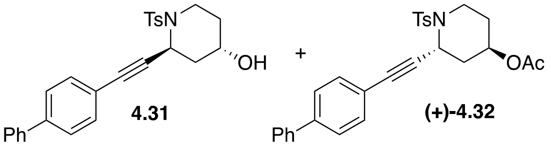
[75] (a) Sabitha, G.; Reddy, N. M.; Prasad, M. N.; Yadav, J. S. *Helv. Chim. Acta* **2009**, *92*, 967–976. (b) see ref 9b.

2H), 7.48–7.42 (m, 4H), 7.40–7.34 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.17 (s, 1H), 4.14–3.99 (m, 1H), 3.87 (dt, *J* = 12.0, 2.1 Hz, 1H), 2.99 (td, *J* = 12.5, 2.7 Hz, 1H), 2.30 (s, 3H), 2.22 (ddt, *J* = 12.2, 4.6, 2.4 Hz, 1H), 2.09–2.02 (m, 1H), 1.84 (td, *J* = 11.9, 4.9 Hz, 1H), 1.66 (qd, *J* = 12.0, 4.8 Hz, 1H), 1.55 (bs, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.6, 141.4, 140.3, 135.1, 132.0 (2C), 129.6 (2C), 129.1 (2C), 128.2 (2C), 127.9, 127.1 (2C), 126.9 (2C), 120.9, 87.1, 84.5, 65.7, 46.8, 41.2, 40.2, 34.7, 21.6; **IR** (neat) 3536, 2941, 2219, 1515, 1161, 986, 766 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{26}H_{25}NO_3SNa$, 454.1453; found, 454.1445.



(2*S*,4*S*)-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-ol (4.31) and **(2*R*,4*R*)-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-yl acetate ((+)-4.32)** were prepared according to a lipase resolution procedure reported by Yadav.[76] To a round bottom flask equipped with a stir bar was added piperidine **4.31** (0.91 g, 2.1 equiv, 1.0 equiv), lipase from *Candida artica* (0.82 g, 20% w/w), vinyl acetate (6.3 mL, 68 mmol, 16 equiv), and CH_2Cl_2 (42 mL, 0.050 M in piperidine). The reaction was allowed to stir open to air for 120 h. The reaction mixture was filtered through a pad of Celite and the solvent was removed under reduced pressure. The residue was purified by column chromatography (0–50% EtOAc/hexanes) to separate the alcohol and the acetate products.

Analytical Data for 4.31 (Alcohol): The title compound was isolated as an orange solid (0.62 g, 1.4 mmol, 67% recovered). **TLC R$_f$** = 0.4 (50% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.59–7.54 (m, 2H), 7.50–7.42 (m, 4H), 7.41–7.34 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 5.18 (s, 1H), 4.09 (ddt, *J* = 15.8, 11.1, 5.9 Hz, 1H), 3.88 (dt,

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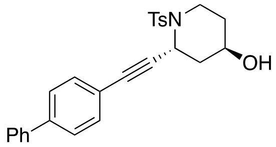
[76] Yadav, J. S.; Reddy, B. V. S.; Padmavani, B.; Venugopal, C.; Rao, A. B. *Tetrahedron Lett.* **2007**, *48*, 4631–4633.

J = 13.2, 2.8 Hz, 1H), 3.01 (td, *J* = 12.5, 2.7 Hz, 1H), 2.31 (s, 3H), 2.23 (ddt, *J* = 12.3, 4.6, 2.4 Hz, 1H), 2.11–2.02 (m, 1H), 1.85 (td, *J* = 11.9, 4.9 Hz, 1H), 1.67 (qd, *J* = 12.5, 4.8 Hz, 1H), 1.55 (bs, 1H).

Analytical Data for (+)-4.32 (Acetate): The title compound was isolated as an off white solid (230 mg, 0.49 mmol, 23% yield, >20:1 dr, >99% ee) **m.p. =** 147–149 °C; **TLC R$_f$** = 0.6 (50% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.59–7.53 (m, 2H), 7.50–7.42 (m, 4H), 7.41–7.35 (m, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 5.21 (s, 1H), 5.13 (tt, *J* = 11.5, 4.5 Hz, 1H), 3.89 (dt, *J* = 12.2, 2.1 Hz, 1H), 3.06 (td, *J* = 12.5, 2.7 Hz, 1H), 2.31 (s, 3H), 2.28–2.21 (m, 1H), 2.19–2.11 (m, 1H), 2.06 (s, 3H), 1.98 (td, *J* = 12.0, 4.9 Hz, 1H), 1.73 (qd, *J* = 12.3, 4.9 Hz, 1H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 170.4, 143.7, 141.4, 140.3, 135.0, 132.1 (2C), 129.6 (2C), 129.0 (2C), 128.2 (2C), 127.9, 127.1 (2C), 126.8 (2C), 120.8, 87.5, 83.8, 68.1, 46.7, 41.0, 36.8, 31.1, 21.6, 21.3; **IR** (neat) 2927, 2867, 2224, 1730, 1595, 1349, 1159, 1031, 767, 588 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{28}H_{27}NO_4SNa$, 496.1559; found, 496.1564; **[α]$^{23}_D$** + 10.52 (*c* 8.6 mg/1.5 mL CHCl$_3$); **SFC Analysis** (Chiralcel OJ-H, 5% IPA, 2.0 mL/min, 254 nm) indicated >99% ee t$_R$ (only diastereomer, major enantiomer) = 12.8 minutes, t$_R$ (only diastereomer, minor enantiomer) = 15.7 minutes.



(2*R*,4*R*)-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-ol (**(+)-4.31**) was prepared according to a procedure reported by Sabitha.[77] To a round bottom flask equipped with a stir bar was added acetate (+)-**4.32** (0.34 g, 0.71 mmol, 1.0 equiv) and dissolved in excess MeOH and a minimal amount of THF. Then K_2CO_3 (0.34 g, 2.5 mmol, 3.5 equiv) was added and the mixture

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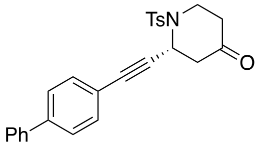
[77] Sabitha, G.; Reddy, N. M.; Prasad, M. N.; Yadav, J. S. *Helv. Chim. Acta* **2009**, *92*, 967–976.

was allowed to stir at rt for 3 h. Then solvent was removed under reduced pressure, then H_2O was added the residue was transferred to separatory funnel. The aqueous layer was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (0–50% EtOAc/hexanes) to afford the title compound as a white solid (0.25 g, 0.58 mmol, 82% yield, >20:1 dr, 95% ee). Refer to **4.31** above for analytical data. **$[\alpha]^{23}_{D}$** + 52.19 (*c* 10 mg/mL $CHCl_3$); **SFC Analysis** (Chiralcel AD-H, 15% IPA, 2.0 mL/min, 254 nm) indicated 95% ee t_R (only diastereomer, minor enantiomer) = 17.1 minutes, t_R (only diastereomer, major enantiomer) = 19.3 minutes.



(*R*)-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-one (4.65) was prepared according to a modified procedure reported by Huang.[78] To a stirring solution of piperidine **(+)-4.31** (240 mg, 0.55 mmol, 1.0 equiv) in CH_2Cl_2 (2.8 mL, 0.20 M), was added DMP (0.36 g, 0.84 mmol, 1.5 equiv). The mixture was allowed to stir at rt for 2 h. To quench, saturated $NaHCO_3$ was added and the reaction was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a white solid (220 mg, 0.55 mmol, 98% yield). **m.p. =** 163–166 °C; **TLC R_f** = 0.6 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.57–7.50 (m, 2H), 7.44 (dtd, *J* = 8.1, 3.8, 1.6 Hz, 4H), 7.39–7.33 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 5.43 (dt, *J* = 6.3, 2.1 Hz, 1H), 4.12 (ddt, *J* = 11.6, 7.5, 1.9 Hz, 1H), 3.31 (td, *J* = 12.2, 3.6 Hz, 1H), 2.98 (dd, *J* = 14.4, 6.3

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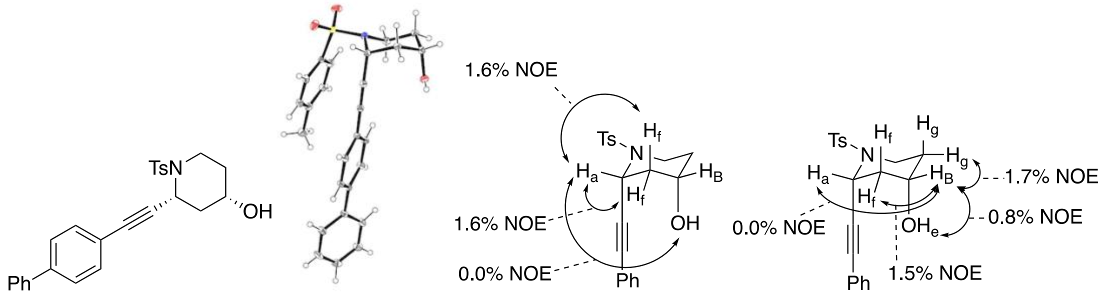
[78] Huang, R.; Chen, X.; Mou, C.; Luo, G.; Li, Y.; Li, X.; Xue, W.; Jin, Z.; Chi, Y. R. *Org. Lett.*. **2019**, *21*, 4340–4344.

Hz, 1H), 2.73 (ddd, *J* = 15.1, 12.2, 7.5 Hz, 1H), 2.62 (dt, *J* = 14.4, 2.1 Hz, 1H), 2.47 (dt, *J* = 15.2, 1.6 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.0, 144.2, 141.8, 140.2, 134.6, 132.2 (2C), 129.8 (2C), 129.0 (2C), 128.2 (2C), 128.0, 127.1 (2C), 126.9 (2C), 120.3, 88.7, 82.9, 48.0, 47.5, 41.7, 40.7, 21.6; **IR** (neat) 2873, 2224, 1722, 1598, 1486, 1092, 765 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{23}NO_3SNa$, 452.1296; found, 452.1300.



(2*R*,4*S*)-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-ol ((+)-4.33) was prepared according to a procedure reported by Andersen.[79] To a solution of ketone **4.65** (240 mg, 0.55 mmol, 1.0 equiv) in THF (2.8 mL, 0.20 M) at 0 ºC, was added L-selectride (0.61 mL, 0.61 mmol, 1.1 equiv, 1.0 M in THF) slowly via syringe. The mixture was allowed to stir at 0 ºC for 30 mins and then was allowed to warm to rt and stir for an additional 2 h. To quench, 1 M HCl was added and extracted with EtOAc (x 3). The combined organic layer was washed with $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (0–50% EtOAc/hexanes) to afford the title compound as a white solid (160 mg, 0.34 mmol, 65% yield, >20:1 dr, 87% ee). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was determined by NOE analysis. Absolute configuration was determined by X-ray crystallography (CCDC 2104034). **m.p. =** 145–147 °C; **TLC R$_f$** = 0.4 (50% EtOAc/hexanes); **^{1}H NMR** (500 MHz,

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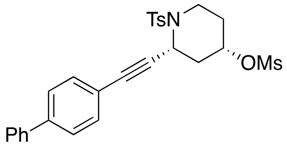
[79] Andersen, C.; Ferey, V.; Daumas, M.; Bernardelli, P.; Guérinot, A.; Cossy, J. *Org. Lett.* **2019**, *21*, 2285–2289.

$CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.57–7.53 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 4H), 7.40–7.34 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.08 (t, *J* = 3.4 Hz, 1H), 4.16 (as, 1H), 3.75 (dt, *J* = 12.0, 3.0 Hz, 1H), 3.38–3.21 (m, 1H), 2.65 (d, *J* = 7.4 Hz, 1H), 2.27 (s, 3H), 2.21–2.17 (m, 2H), 1.98–1.91 (m, 2H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.6, 141.6, 140.2, 135.1, 132.0 (2C), 129.6 (2C), 129.1 (2C), 128.2 (2C), 128.0, 127.1 (2C), 126.9 (2C), 120.4, 87.5, 86.1, 64.4, 43.4, 37.6, 37.1, 32.7, 21.6; **IR** (neat) 3503, 2921, 2870, 2224, 1651, 1594, 1487, 1181, 901, 757 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{25}NO_3SNa$, 454.1453; found, 454.1445; **$[\alpha]^{23}_D$** + 27.58 (*c* 9.3 mg/1.5 mL $CHCl_3$); **SFC Analysis** (Chiralcel AD-H, 15% IPA, 2.0 mL/min, 254 nm) indicated 87% ee t_R (only diastereomer, minor enantiomer) = 15.2 minutes, t_R (only diastereomer, major enantiomer) = 18.2 minutes.



(2*R*,4*S*)-2-([1,1'-biphenyl]-4-ylethynyl)-1-tosylpiperidin-4-yl methanesulfonate (4.66) was prepared according to a procedure reported by Sanford.[80] To a flame dried round bottom flask equipped with a stir bar was added alcohol **(+)-4.33** (150 mg, 0.34 mmol, 1.0 equiv) and CH_2Cl_2 (1.7 mL, 0.20 M). Then Et_3N (70. µL, 0.51 mmol, 1.5 equiv), DMAP (4.1 mg, 3.4 µmol, 0.10 equiv), and MsCl (40. µL, 0.51 mmol, 1.5 equiv) were added in that order. The reaction mixture was allowed to stir at rt for 48 h. Once complete by TLC, sat. $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was carried onto the next step without further purification. **TLC R_f** = 0.5 (50% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d,

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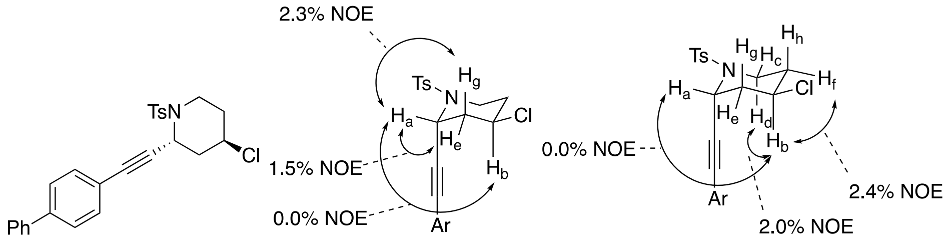
[80] Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen, P.-P.; Hong, X.; Jarvo, E. R. *J. Am. Chem. Soc.* **2020**, *142*, 5017–5023.

J = 8.3 Hz, 2H), 7.59–7.54 (m, 2H), 7.49–7.43 (m, 4H), 7.41–7.35 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.18–5.12 (m, 2H), 3.81 (d, *J* = 12.6 Hz, 1H), 3.34 (td, *J* = 12.5, 2.7 Hz, 1H), 2.89 (s, 3H), 2.44 (dd, *J* = 14.8, 2.6 Hz, 1H), 2.29–2.26 (m, 4H), 2.26–2.17 (m, 1H), 2.16–2.04 (m, 1H).



(2*R*,4*R*)-2-([1,1'-biphenyl]-4-ylethynyl)-4-chloro-1-tosylpiperidine ((+)-4.34) was prepared according to a procedure reported by Cahiez.[81] In a glovebox, n-Bu$_4$NCl (100 mg, 0.44 mmol, 2.0 equiv) was added to a flame dried round bottom flask. The flask was sealed with a septum and removed from the glovebox. In a separate flask, a solution mesylate **4.66** (110 mg, 0.22 mmol, 1.0 equiv) in THF (1.1 mL, 0.10 M) was prepared. The solution of mesylate was then transferred to the reaction flask containing n-Bu$_4$NCl via syringe. The mixture was heated to reflux and allowed to stir for 48 h. The reaction mixture was then cooled to rt and quenched with H_2O. The mixture was transferred to a separatory funnel and extracted with EtOAc (x 2), then hexanes (x 1). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a white solid (51 mg, 0.11 mmol, 52% yield, >20:1 dr trans:cis, 91% ee). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration of the major diastereomer was determined by NOE analysis. Absolute configuration was determined by analogy to piperidine **(+)-4.33**. **m.p.** =

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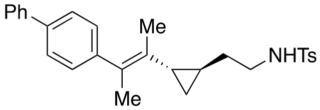
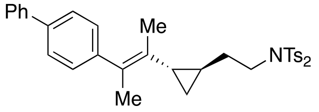
[81] (a) Cahiez, G.; Lefèvre, N.; Poizat, M.; Moyeux, A. *Synthesis,* **2013**, *45*, 213–216. (b) see ref 9b.

111–114 °C; **TLC R$_f$** = 0.4 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.57–7.53 (m, 2H), 7.48–7.42 (m, 4H), 7.37 (tt, *J* = 7.3 Hz, 1.3 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.17–5.13 (m, 1H), 4.22 (att, *J* = 11.9 Hz, 4.3 Hz, 1H), 3.86 (adquin, *J* = 12.2 Hz, 2.3 Hz, 1H), 2.99 (atd, *J* = 12.4 Hz, 2.5 Hz, 1H), 2.40 (adquin, *J* = 12.8 Hz, 2.0 Hz, 1H), 2.31–2.13 (m, 5H), 1.98 (aqd, *J* = 12.6 Hz, 4.9 Hz, 1H); **^{13}C NMR** (125.8 MHz, CDCl$_3$) δ 143.8, 141.6, 140.2, 134.9, 132.0 (2C), 129.6 (2C), 129.1 (2C), 128.2 (2C), 128.0, 127.1 (2C), 126.9 (2C), 120.6, 87.7, 83.5, 53.0, 47.5, 42.1, 41.6, 36.0, 21.6; **IR** (neat) 2063, 3032, 2921, 2864, 2223, 1596, 1344, 1161, 766, 725 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{26}H_{24}ClNO_2SNa$, 472.1114; found, 472.1122; **[α]$^{23}_{D}$** + 7.17 (*c* 6.9 mg/1.5 mL CHCl$_3$); **SFC Analysis** (Chiralcel AD-H, 15% IPA, 2.0 mL/min, 254 nm) indicated 91% ee t$_R$ (only diastereomer, major enantiomer) = 13.3 minutes, t$_R$ (only diastereomer, minor enantiomer) = 20.6 minutes.



***N*-(2-((1*R*,2*S*)-2-((*E*)-3-([1,1'-biphenyl]-4-yl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methylbenzenesulfonamide ((+)-4.5)** was prepared according to Method A. The following amounts of reagents were used: piperidine (+)-**4.34** (70. mg, 0.16 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (6.0 mg, 8.0 μmol, 5.0 mol %), MeMgI (0.12 mL, 0.32 mmol, 2.8 M in Et$_2$O, 2.0 equiv), and PhMe (0.8 mL). The residue was purified by column chromatography (0–10% EtOAc/hexanes) and the diastereomers were separated to afford the major (*E*)-diastereomer as a pale yellow solid (22 mg, 50. μmol, 31% yield, >20:1 *E*:*Z*, 95% ee). Refer to cyclopropane **4.5** above for analytical data. **[α]$^{23}_{D}$** + 9.34 (*c* 22 mg/1.5 mL CHCl$_3$); **SFC Analysis** (Chiralcel OD-H, 20% IPA, 2.0 mL/min, 250 nm) indicated 95% ee t_R (only diastereomer, minor enantiomer) = 27.9 minutes, t_R (only diastereomer, major enantiomer) = 29.7 minutes.



***N*-(2-((1*R*,2*S*)-2-((*E*)-3-([1,1'-biphenyl]-4-yl)but-2-en-2-yl)cyclopropyl)ethyl)-4-methyl-*N*-tosylbenzenesulfonamide ((+)-4.36)** was prepared according to a literature procedure.[9c] In a glovebox, NaH (1.4 mg, 60. µmol, 2.0 equiv) was added to a flame dried round bottom flask equipped with a stir bar. The flask was sealed with a septum, brought out of the glovebox, and placed under N_2 atmosphere. Then DMF (1.0 mL) was added followed by a solution of cyclopropane (+)-**4.5** (14 mg, 30. µmol, 1.0 equiv) in DMF (0.5 mL). The solution was allowed to stir at rt for 1 h and then TsCl (11 mg, 60. µmol, 2.0 equiv) was added as a solution in DMF (0.5 mL). The resulting solution was allowed to stir at rt for 24 h. The reaction mixture was quenched with saturated NH_4Cl and the aqueous layer was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a white solid (11 mg, 18 µmol, 63% yield, >20:1 *E*:*Z*, 93% ee). The *E*:*Z* ratio was determined based on the integration of the resonances attributed to protons on the cyclopropane in the ^{1}H NMR spectrum. The relative configuration was determined by NOE analysis. Absolute configuration was determined by comparing the experimental CD spectrum with the calculated CD spectrum (see below). **TLC R_f** = 0.6 (30% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 4H), 7.63–7.58 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38–7.30 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.78 (t, *J* = 8.1 Hz, 2H), 2.46 (s, 6H), 2.10 (d, *J* = 1.0 Hz, 3H), 1.84 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.67 (dq, *J* = 14.7, 7.7 Hz, 1H), 1.33 (d, *J* = 1.7 Hz, 3H), 0.92–0.79 (m, 2H), 0.76 (dt, *J* = 8.2, 4.8 Hz, 1H), 0.54 (dt, *J* = 9.4, 4.8 Hz, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 145.0, 144.7, 141.2, 138.8, 137.3, 130.3, 129.8 (4C), 129.0 (2C), 128.9 (2C), 128.4 (4C), 127.20, 127.18, 127.1 (2C), 126.8 (2C), 49.1, 35.0, 29.9, 22.4, 21.8 (2C), 20.9, 16.3, 15.7, 11.9, 1.2; **IR** 2969, 2926, 1597, 1376, 1162, 950, 767 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{37}NO_4S_2Na$, 622.2062; found, 622.2072; **$[\alpha]^{23}_{D}$** + 66 (*c* 5.7 mg/1.5 mL $CHCl_3$); **SFC Analysis** (Chiralcel OD-H, 15% IPA, 2.0 mL/min, 250 nm) indicated 93% ee t_R (only diastereomer, minor enantiomer) = 27.7 minutes, t_R (only diastereomer, major enantiomer) = 29.5 minutes.

4.5.7.2 Experimental (blue) and Simulated (red) CD Spectra.

Experimental data collected was collected in CH_2Cl_2 (concentration = 7.48 x 10^{-4} M). Calculated conformational averaged ECD spectrum and experimental ECD spectrum of (+)-**4.36** at TD-ωB97XD/def2-TZVPP-SMD(CH2Cl2)//B3LYPD3(BJ)/def2-SV(P)-SMD(CH2Cl2). Conformers population were obtained with electronic energies(EE) at ωB97XD/def2-TZVPP-SMD(CH2Cl2)//B3LYP-D3(BJ)/def2-SV(P)- SMD(CH2Cl2). Number of states solved during TD-DFT calculation were set to 50. Full width at half maximum (FWHM) was set to 0.5 eV with Gaussian broadening function.[1,82]

Figure 4.3: Experiment and Computation Circular Dichroism Spectra to Confirm Absolute Configurations

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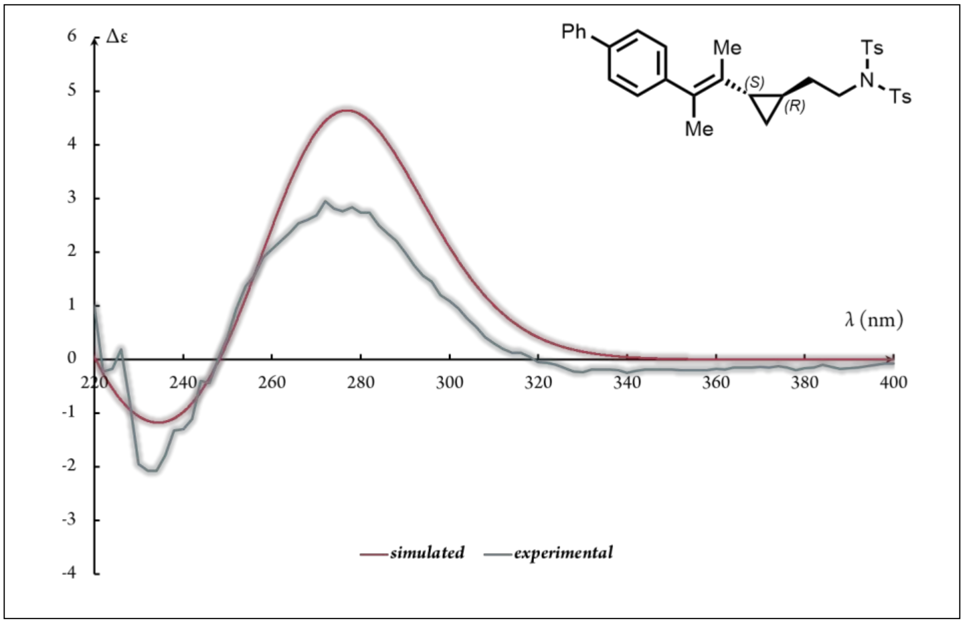
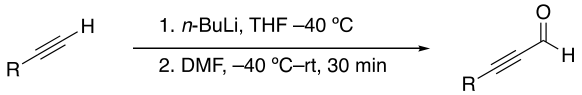
[82] Bannwarth, C.; Grimme, S. *Comput. Theor. Chem.* **2014**, *1040–1041*, 45–53.



4.5.8 General Procedures for the Synthesis of Starting Materials

4.5.8.1 Method C: Synthesis of Propargyl Aldehydes with *n*-BuLi and DMF



(4.5)

This method was adapted from a procedure reported by Larsen.[83] To a flame-dried round-bottom flask equipped with a stir bar was added alkyne (1 equiv). The flask was evacuated, backfilled with N_2, and capped with a septum. THF (0.4 M in alkyne) was added and the solution was cooled to –40 ºC. Then *n*-BuLi (1 equiv) was added dropwise, followed by DMF (2 equiv). The mixture was allowed to warm to room temperature and stir for an additional 30 mins. The solution was poured into a vigorously stirred biphasic solution of 10% aqueous KH_2PO_4 and Et_2O cooled over ice. The layers were separated, and the organic layer was washed with H_2O (x 2). The combined aqueous layers were extracted with Et_2O. Then the combined organic layers were dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography.

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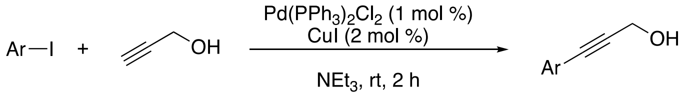
[83] Journet, M.; Cai, D.; DiMichele, L. M.; Larsen, R. D. *Tetrahedron Lett.* **1998**, *39*, 6427–6428.

4.5.8.2 Method D: Sonogashira Cross-Coupling Reaction of Aryl Halides and Propargyl Alcohol

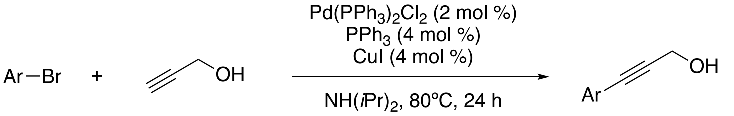
4.5.8.2.1 Sonogashira Cross-Coupling Reactions with Aryl Iodides



(4.6)

This method was adapted from a procedure reported by Tambar.[84] To a flame-dried round bottom flask equipped with a stir bar was added Pd(PPh$_3$)$_2$Cl$_2$ (1 mol %) and CuI (2 mol %). Et$_3$N (0.01 M in CuI) was added to the flask, and the suspension was allowed to stir for five minutes. A solution of aryl iodide (1.0 equiv) and propargyl alcohol (1.1 equiv) in Et$_3$N (1.0 M in aryl iodide) was prepared, and the solution was added dropwise to the reaction mixture. The reaction was allowed to stir at rt until the aryl iodide was consumed. The reaction mixture was filtered through a pad of Celite and washed with excess EtOAc. The combined solution was concentrated in vacuo and purified by column chromatography.

4.5.8.2.1 Sonogashira Cross-Coupling Reactions with Aryl Bromides



(4.7)

The method was adapted from a procedure reported by Nagumo.[85] In a glovebox, CuI (4.0 mol %) was added to a flame-dried round bottom flask. The flask was seal with a septum, removed from the glovebox and placed under a N$_2$ atmosphere. Then Pd(PPh$_3$)Cl$_2$ (2.0 mol %) and Ph$_3$P (4.0 mol %) was added followed by freshly distilled diisopropylamine (0.5 M in aryl bromide). The suspension was allowed to stir at room temperature for 5 min. In a separate flask, a solution of aryl bromide (1.0 equiv) and propargyl alcohol (1.3 equiv) in diisopropylamine (1.0 M in aryl bromide)

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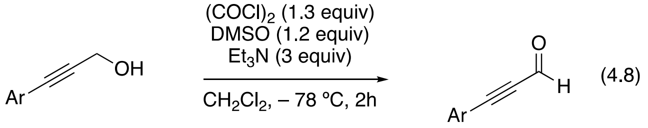
[84] Xu, B.; Gartman, J. A.; Tambar, U. K. *Tetrahedron* **2017**, *73*, 4150–4159.

[85] Sakata, Y.; Yasui, E.; Mizukami, M.; Nagumo, S. *Tetrahedron Lett.* **2019**, *60*, 755–759.

was prepared and added dropwise to the reaction flask. The flask was then fitted with a reflux condenser, heated to reflux, and was allowed to stir for 24 h. The reaction mixture was cooled to rt and filtered through a pad of Celite and washed with EtOAc (x 3). Then the solution was concentrated in vacuo and purified by column chromatography.

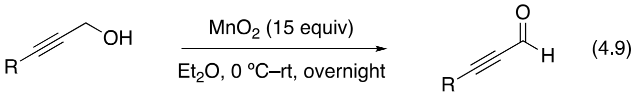
4.5.8.3 Method E: Swern Oxidation of Propargyl Alcohols



(4.8)

This method was adapted from a procedure reported by Kobayashi.[86] A flame-dried round bottom flask equipped with stir bar was charged with oxalyl chloride (1.3 equiv) and CH_2Cl_2 (0.4 M). The flask was cooled to –78 °C and DMSO (1.2 equiv) was added dropwise under N_2 with a vent. This was allowed to stir at –78 °C for 15 min. Then propargyl alcohol (1.0 equiv) was added as a solution in CH_2Cl_2 (0.2 M). The reaction mixture was allowed to stir at –78 ºC for 2 h. Then, triethylamine (3.0 equiv) was added and the reaction was allowed to warm to rt. The reaction mixture was quenched with saturated NH_4Cl, extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography.

4.5.8.4 Method F: MnO_2 Oxidation of Propargyl Alcohols



(4.9)

This method was adapted from a procedure reported by Fürstner.[87] Propargyl alcohol (1.0 equiv) was added to a vigorously stirring suspension of MnO_2 (10. equiv) in Et_2O at 0 ºC. This suspension

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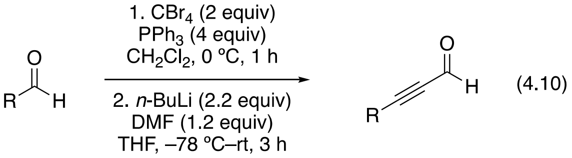
[86] Shinohara, R.; Morita, M.; Ogawa, N.; Kobayashi, Y. *Org. Lett.* **2019**, *21*, 3247–3251.

[87] Persich, P.; Llaveria, J.; Lhermet, R.; de Haro, T.; Stade, R.; Kondoh, A.; Fürstner, A. *Chem. Eur. J.* **2013**, *19*, 13047–13058.

was warmed to rt and allowed to stir overnight. Additional MnO_2 (5.0 equiv) was added and was allowed to stir for an additional 4 h. The reaction mixture was filtered through a pad of Celite and the filtrated was concentrated in vacuo. For lower boiling point substrates, a stream of air could be used to evaporate the Et_2O.

4.5.8.5 Method G: Corey-Fuchs Reaction



This method was adapted from a procedure reported by Ghosh.[88] To flame-dried round bottom flask equipped with a stir bar was added PPh_3 (4 equiv) and DCM (0.3 M in substrate). The reaction mixture was cooled to 0 °C and CBr_4 (2 equiv) was added. Then the desired aldehyde (1 equiv) was added dropwise to the reaction flask and was allowed to stir at 0 °C for 1 hour. The reaction mixture was concentrated. The residue was diluted with 1:1 Et_2O:hexanes and filtered through a pad of silica gel. The filter cake was washed with excess 1:1 mixture of Et_2O:hexanes.

To a flame-dried round bottom flask, was added the residue (1.0 equiv) and THF (0.4 M in substrate). The reaction mixture was cooled to –78 °C and *n*-BuLi (2.2 equiv) was added dropwise. After stirring at –78 °C for 1 h, the reaction flask was allowed to stir at rt for 1 h. The reaction mixture was cooled to –78 °C and the DMF (1.2 equiv) was added in one portion. After stirring at –78°C for 1 h, the reaction mixture was quenched with NH_4Cl, extracted with Et_2O (x3), dried over Na_2SO_4, and concentrated. The residue was carried forward without purification.

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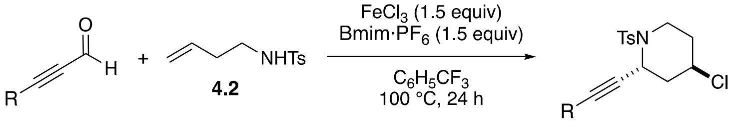
[88] Ghosh, A. K.; Wang, Y. *J. Am. Chem. Soc.* **2000**, *122,* 11027–11028.

4.5.8.6 Method H: $FeCl_3$/Bmim·PF_6-Promoted aza-Prins Reaction



(4.11)

This method was adapted from a procedure reported by Iwamoto.[17a] In a glovebox, $FeCl_3$ (1.5 equiv) was added to a flame-dried round-bottom flask equipped with a stir bar. The flask was sealed with a septum and removed from the glovebox. Benzotrifluoride (0.3 M in $FeCl_3$) was added to the flask, followed by dropwise addition of Bmim·PF_6 (1.5 equiv). In a separate flask, a solution of aldehyde (1.5 equiv) and homoallylic sulfonamide **2** (1.0 equiv) in benzotrifluoride (0.3 M in homoallylic sulfonamide) was prepared. Using a syringe, the solution of aldehyde and sulfonamide was added to the flask containing $FeCl_3$. The reaction flask was fitted with a reflux condenser and N_2 inlet. The solution was heated to reflux and allowed to stir for 24 h. The reaction mixture was cooled to room temperature and was then quenched with H_2O. The layers were separated, and the aqueous layer was extracted with Et_2O (x 2). The combined organic layers were washed sequentially with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in vacuo, and purified by column chromatography. After purification by column chromatography, the bright orange product was passed through an activated charcoal plug to remove the colored impurities.

Frequently, the desired product was isolated as a mixture with unreacted aldehyde. To remove unreacted aldehyde from the desired product, the mixture was subjected to $NaBH_4$ reduction by a modified procedure reported by Wang and Franzén.[89] The unpurified reaction mixture was concentrated and dissolved in MeOH. $NaBH_4$ (1.6 equiv relative to 1.0 equiv of remaining aldehyde as determined by ^1H NMR integration) was added in one portion and the reaction stirred

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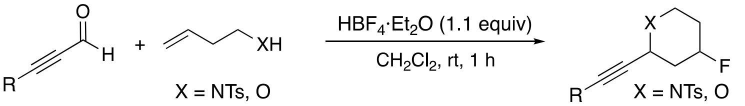
[89] Wang, Y.; Franzén, R. *Synlett* **2012**, *23*, 925–929.

20 min at rt. The reaction mixture was then concentrated in vacuo to remove the MeOH. The resulting solid was dissolved in CH_2Cl_2 and transferred to a separatory funnel. The organic layer was washed with water (x 3), brine, dried over Na_2SO_4, filtered, and concentrated in vacuo.

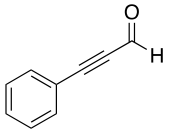
4.4.8.7 Method I: $HBF_4{\cdot}Et_2O$ Mediated Prins/aza-Prins Reaction



(4.12)

This method was adapted from a procedure reported by Reddy.[90] A flame dried round bottom flask was charged with aldehyde (1 equiv) and homoallylic sulfonamide **4.2** or 3-buten-1-ol (1.1 equiv) in CH_2Cl_2 (0.2 M in aldehyde). Then $HBF_4{\cdot}Et_2O$ (1 equiv) was added dropwise via syringe over 10 mins. The resulting deep red solution was allowed to stir for 1 h. Then the reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography.

4.5.9 Characterization Data for Starting Materials



3-phenylpropiolaldehyde (**4.1**) was prepared according to Method C. The following amounts of reagents were used: phenylacetylene (0.55 mL, 5.0 mmol, 1.0 equiv), *n*-BuLi (4.2 mL, 5.0 mmol, 1.2 equiv, 1.2 M in THF), DMF (0.78 mL, 10. mmol, 2.0 equiv), THF (13 mL, 0.40 M).The residue was purified by column chromatography (0–5% EtOAc/hexanes) to afford the title compound as an orange oil (0.56 g, 4.3 mmol, 86% yield). **TLC R_f** = 0.6 (10% EtOAc/hexanes); **^{1}H NMR** (400

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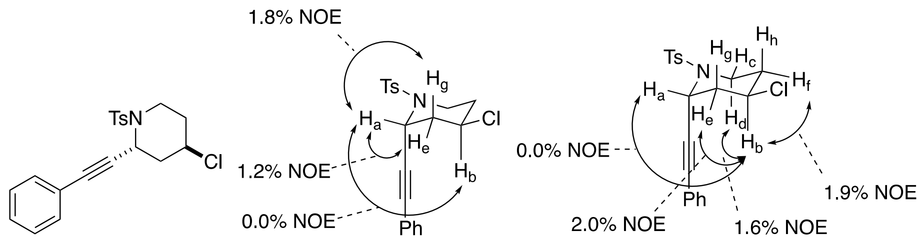
[90] Yadav, J. S.; Reddy, B. V. S.; Anusha, B.; Reddy, U. V. S.; Reddy, V. V. B. *Tetrahedron Lett.* **2010**, *51*, 2872–2874.

MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.63–7.57 (m, 2H), 7.48 (tt, J = 7.4, 1.4 Hz, 1H), 7.40 (ddd, J = 8.7, 6.7, 1.6 Hz, 2H). Analytical data are consistent with literature values.[91]



trans**-4-Chloro-2-(phenylethynyl)-1-tosylpiperidine (4.3)** was prepared according to Method H. The following amounts of reagents were used: 3-phenylpropiolaldehyde **4.1** (0.45 g, 3.5 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.43 mL, 2.3 mmol, 1.0 equiv), $FeCl_3$ (0.56 g, 3.5 mmol, 1.5 equiv), Bmim·PF_6 (0.72 mL, 3.5 mmol, 1.5 equiv), benzotrifluoride (23 mL, 0.10 M in homoallylic sulfonamide). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a pale yellow solid (0.46 g, 1.2 mmol, 53% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 107–109 ºC; **TLC R$_f$** = 0.5 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.78 (d, J = 8.3 Hz, 2H), 7.38–7.33 (m, 1H), 7.32–7.25 (m, 4H), 7.04 (d, J = 8.5 Hz, 2H), 5.19 (as, 1H), 4.26 (tt, J = 12.0, 4.3 Hz, 1H), 3.91 (dt, J = 12.4, 2.1 Hz, 1H), 3.04 (td, J = 12.4, 2.6 Hz, 1H), 2.44 (ddt, J = 12.5, 4.1, 2.3 Hz, 1H), 2.34 (s, 3H), 2.33–2.27 (m, 1H), 2.23 (td, J = 12.7, 4.7 Hz, 1H), 2.04 (qd, J = 12.6, 4.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 143.7, 134.7, 131.5 (2C), 129.5 (2C), 128.7, 128.1 (2C), 128.1 (2C), 121.7, 87.7, 82.8, 52.9, 47.3, 42.0, 41.5, 35.9, 21.4; **IR** (neat) 2971, 2934, 2235, 1596, 1488, 1397, 1340, 1160, 1084, 856, 762, 723, 691 cm^{-1};

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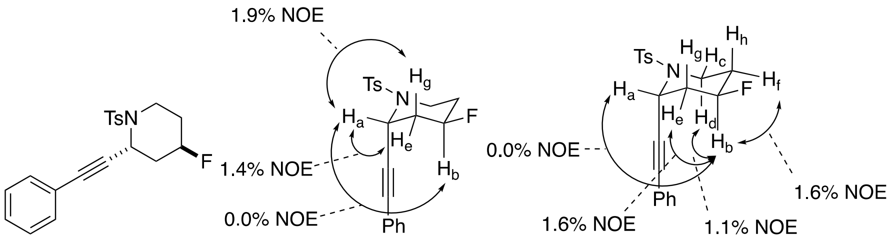
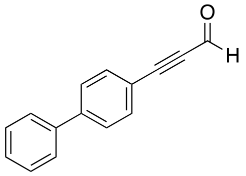
[91] Noro, M.; Masuda, T.; Ichimura, A. S.;Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1994**, *116*, 6179–6190.

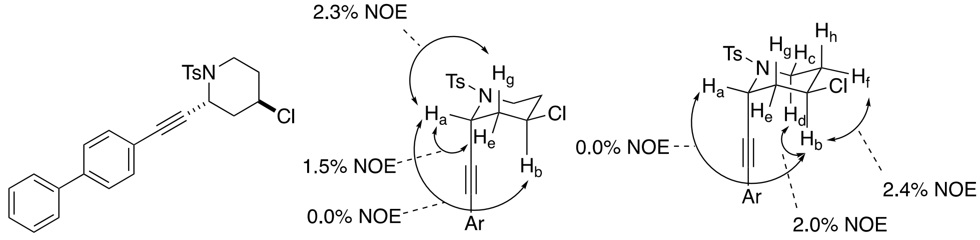
HRMS (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{20}H_{20}ClNO_2SNa$, 396.0801; found, 396.0807.



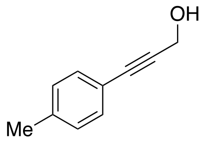
***trans*-4-Fluoro-2-(phenylethynyl)-1-tosylpiperidine** (**4.67**) was prepared according to Method I. The following amounts of reagents were used: 3-phenylpropiolaldehyde **4.1** (93 mg, 0.71 mmol, 1.0 equiv), homoallylic sulfonamide **4.2** (0.14 mL, 0.78 mmol, 1.1 equiv), $HBF_4 \cdot Et_2O$ (0.10 mL, 0.71 mmol, 1.0 equiv), CH_2Cl_2 (3.6 mL, 0.20 M). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a pale yellow solid (118 mg, 0.33 mmol, 47% yield, 10:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^1H NMR spectrum. The relative configuration was assigned based on NOE analysis. The major (*trans*) diastereomer is characterized below. **m.p.** 122–125 ºC; **TLC R_f** = 0.7 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.38–7.21 (m, 5H), 7.04 (d, *J* = 7.1 Hz, 2H), 5.25 (s, 1H), 4.95 (dtt, *J* = 48.2, 10.9, 4.8 Hz, 1H), 3.96 (d, *J* = 10.4 Hz, 1H), 3.04 (t, *J* = 12.5 Hz, 1H), 2.49–2.37 (m, 1H), 2.35 (s, 3H), 2.28–2.21 (m, 1H), 2.08 (tdd, *J* = 12.1, 8.2, 4.9 Hz, 1H), 1.99–1.84 (m, 1H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 140.8, 134.7, 131.5 (2C), 129.5 (2C), 128.7, 128.2 (2C), 128.03 (2C), 121.6, 88.2, 86.8, 46.4 (d, *J* = 15.3 Hz), 40.5 (d, *J* = 14.0 Hz), 37.5 (d, *J* = 20.8 Hz), 32.5, 31.9 (d, *J* = 20.0 Hz), 21.5; **^{19}F NMR** (565 MHz,$CDCl_3$) δ –180.41 (d, *J* = 48.0 Hz); **IR** (neat) 2958, 2864, 2228, 1598, 1489, 1147, 1065, 814, 754 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{20}H_{20}FNO_2SNa$, 380.1096; found, 380.1096.



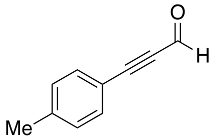
3-([1,1'-Biphenyl]-4-yl)propiolaldehyde (4.30) see above for full characterization.



***trans*-2-([1,1'-Biphenyl]-4-ylethynyl)-4-chloro-1-tosylpiperidine (4.34)** was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.30** (160 mg, 0.75 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (110 mg, 0.50 mmol, 1.0 equiv), $FeCl_3$ (120 mg, 0.75 mmol, 1.5 equiv), Bmim·PF_6 (0.15 mL, 0.75 mmol, 1.5 equiv), and benzotrifluoride (5.0 mL, 0.10 M in sulfonamide). The residue was purified by column chromatography (0–15% EtOAc/hexanes) to yield the title compound as a yellow solid (118 mg, 0.261 mmol, 52% yield, > 20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R$_f$** = 0.4 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.57–7.53 (m, 2H), 7.48–7.42 (m, 4H), 7.37 (tt, *J* = 7.3 Hz, 1.3 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 5.17–5.13 (m, 1H), 4.22 (att, *J* = 11.9 Hz, 4.3 Hz, 1H), 3.86 (adquin, *J* = 12.2 Hz, 2.3 Hz, 1H), 2.99 (atd, *J* = 12.4 Hz, 2.5 Hz, 1H), 2.40 (adquin, *J* = 12.8 Hz, 2.0 Hz, 1H), 2.31–2.13 (m, 5H), 1.98 (aqd, *J* = 12.6 Hz, 4.9 Hz, 1H). See above (**(+)-35**) for full characterization.



3-(*p*-tolyl)prop-2-yn-1-ol (**4.68**)[92] was prepared according to Method D. The following amounts of reagents were used: 1-bromo-4-methylbenzene (1.7 g, 10. mmol, 1.0 equiv), propargyl alcohol (0.76 mL, 13 mmol, 1.3 equiv), Pd(PPh$_3$)$_2$Cl$_2$ (140 mg, 0.20 mmol, 2.0 mol %), CuI (76 mg, 0.40 mmol, 4.0 mol %), triphenylphosphine (0.11 g, 0.40 mmol, 4.0 mol %), diisopropylamine (15 mL). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (0.65 g, 4.4 mmol, 44 % yield). **TLC R$_f$** = 0.4 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 3.2 Hz, 2H), 4.56–4.45 (m, 2H), 2.36 (s, 3H), 1.70 (s, 1H).



3-(*p*-tolyl)propiolaldehyde (**4.69**) was prepared according to Method E. This reaction was performed in triplicate. The following amounts of reagents were used in each reaction flask: propargyl alcohol **4.68** (0.31 g, 2.2 mmol, 1.0 equiv), oxalyl chloride (0.24 mL, 2.8 mmol, 1.3 equiv), dimethyl sulfoxide (0.18 mL, 2.6 mmol, 1.2 equiv), triethylamine (0.91 mL, 6.5 mmol, 3.0 equiv), CH$_2$Cl$_2$ (11 mL). The three reaction mixtures were combined, and the residue was purified by column chromatography (0–40% CH$_2$Cl$_2$/hexanes) to afford the title compound as a yellow oil (0.52 g, 3.6 mmol, 56% yield). **^{1}H NMR** (500 MHz, CDCl$_3$) δ 9.43 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H).

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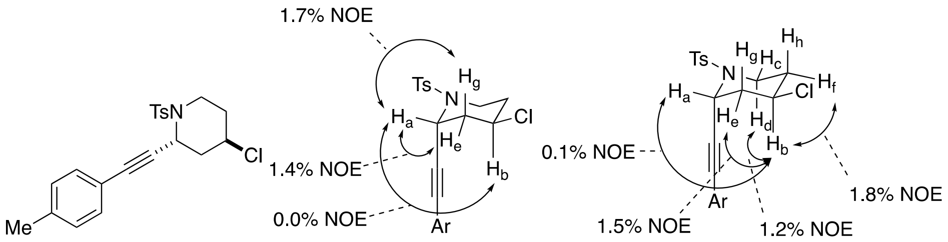
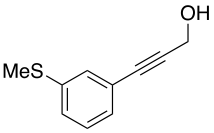
[92] Substrates **4.68** and **4.69** synthesized by Alissa C. Matus



***trans*-4-chloro-2-(*p*-tolylethynyl)-1-tosylpiperidine (4.49)**[93] was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.69** (0.52 g, 3.6 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.54 g, 2.4 mmol, 1.0 equiv), $FeCl_3$ (0.58 g, 3.6 mmol, 1.5 equiv), Bmim·PF_6 (0.74 mL, 3.6 mmol, 1.5 equiv), benzotrifluoride (60 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a pale yellow solid (0.60 g, 1.6 mmol, 66% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 107–109 ºC; **TLC R_f** = 0.6 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.23–7.20 (m, 2H), 7.06–7.01 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 5.12 (s, 1H), 4.20 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.83 (ddt, *J* = 12.1, 4.5, 2.1 Hz, 1H), 2.97 (td, *J* = 12.5, 2.6 Hz, 1H), 2.37 (ddt, *J* = 12.6, 4.6, 2.4 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 2.27–2.19 (m, 1H), 2.19–2.11 (m, 1H), 1.97 (qd, *J* = 12.6, 4.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 143.8, 138.9, 134.9, 131.5 (2C), 129.6 (2C), 129.0 (2C), 128.1 (2C), 118.7, 87.9, 82.1, 53.1, 47.5, 42.1, 41.6, 36.0, 21.6, 21.5; **IR** (neat) 2926, 2860, 2227, 1509, 1346, 1159, 915, 725 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{21}H_{22}ClNO_2SNa$, 410.0957; found, 410.0962.



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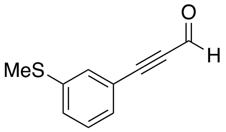
[93] Piperidine **4.49** synthesized by Alissa C. Matus. Characterization data collected by Kirsten A. Hewitt

3-(3-(methylthio)phenyl)prop-2-yn-1-ol (**4.70**)[94] was prepared according to Method D. The following amounts of reagents were used: (3-bromophenyl)(methyl)sulfane (1.4 mL, 10. mmol, 1.0 equiv), propargyl alcohol (0.76 mL, 13 mmol, 1.3 equiv), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.20 mmol, 2.0 mol %), CuI (76 mg, 0.40 mmol, 4.0 mol %), triphenylphosphine (0.11 mg, 0.40 mmol, 4.0 mol %), diisopropylamine (30 mL). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (1.21g, 6.76 mmol, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 1H), 7.24–7.17 (m, 3H), 4.49 (d, *J* = 6.1 Hz, 2H), 2.48 (s, 3H), 1.67 (t, *J* = 6.2 Hz, 1H).



3-(3-(methylthio)phenyl)propiolaldehyde (**4.71**) was prepared according to Method E. This reaction was run in quadruplicate. The following amounts of reagents were used in each reaction flask: propargyl alcohol **4.70** (0.30 g, 1.7 mmol, 1.0 equiv), oxalyl chloride (0.19 mL, 2.2 mmol, 1.3 equiv), dimethyl sulfoxide (0.14 mL, 2.1 mmol, 1.2 equiv), triethylamine (0.71 mL, 5.1 mmol, 3.0 equiv), CH_2Cl_2 (9.7 mL). The four reaction mixtures were combined, and the residue was purified by column chromatography (0–40% CH_2Cl_2/hexanes) to afford the title compound as a yellow oil (0.65 g, 3.7 mmol, 55% yield). **TLC R_f** = 0.4 (65% CH_2Cl_2/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.45 (t, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 2.8, 1.7 Hz, 1H), 7.36 (dd, *J* = 1.7, 1.1 Hz, 1H), 7.34–7.29 (m, 1H), 2.51 (s, 3H).

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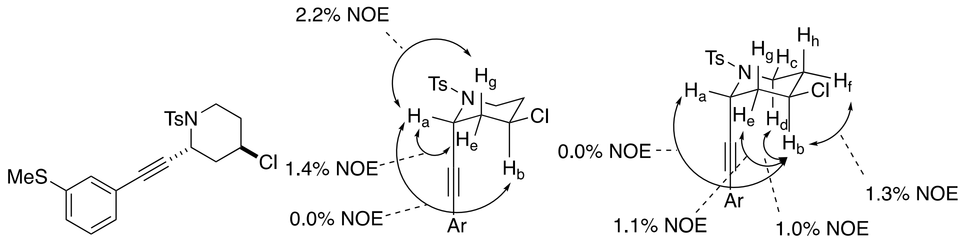
[94] Substrates **4.70** and **4.71** synthesized by Alissa C. Matus.



***trans*-4-chloro-2-((3-(methylthio)phenyl)ethynyl)-1-tosylpiperidine (4.50)**[95] was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.71** (0.65 g, 3.6 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.53 g, 2.4 mmol, 1.0 equiv), $FeCl_3$ (0.59 g, 3.6 mmol, 1.5 equiv), Bmim·PF_6 (0.73 mL, 3.6 mmol, 1.5 equiv), benzotrifluoride (59 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow solid (0.31 mg, 0.75 mmol, 31% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 99–101 ºC; **TLC R$_f$** = 0.4 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18–7.12 (m, 2H), 6.84 (s, 1H), 6.78–6.73 (m, 1H), 5.13 (t, *J* = 2.1 Hz, 1H), 4.18 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.85 (ddt, *J* = 12.2, 4.6, 2.2 Hz, 1H), 2.96 (td, *J* = 12.5, 2.7 Hz, 1H), 2.46 (s, 3H), 2.37 (ddt, *J* = 12.7, 4.5, 2.3 Hz, 1H), 2.32 (s, 3H), 2.27–2.20 (m, 1H), 2.16 (td, *J* = 12.4, 4.8 Hz, 1H), 1.97 (qd, *J* = 12.6, 4.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 143.9, 138.9, 134.7, 129.5 (2C), 129.4, 128.5, 128.06 (2C), 128.05 126.6, 122.2, 87.2, 83.1, 52.9, 47.3, 42.0, 41.4, 35.9, 21.5, 15.7; **IR** (neat) 2923, 2859, 2250, 1584, 1345, 1158m 936, 725 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{21}H_{22}ClNO_2S_2Na$, 442.0678; found, 442.0670.

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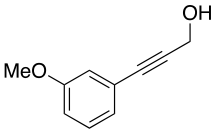
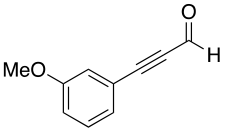
[95] Piperidine **4.50** synthesized by Alissa C. Matus. Characterization data collected by Kirsten A. Hewitt



3-(3-methoxyphenyl)prop-2-yn-1-ol (**4.72**)[96] was prepared according to Method D. The following amounts of reagents were used: 1-iodo-3-methoxybenzene (0.60 mL, 5.0 mmol, 1.0 equiv), propargyl alcohol (0.32 mL, 0.32 mmol, 5.5 equiv), $Pd(PPh_3)_2Cl_2$ (35 mg, 50. µmol, 1.0 mol %), CuI (19 mg, 0.10 mmol, 2.0 mol %), triethylamine (15 mL). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (0.75 g, 4.7 mmol, 93% yield). **TLC R_f** = 0.1 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.88 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.50 (s, 2H), 3.80 (s, 3H), 1.72 (s, 1H).



3-(3-methoxyphenyl)propiolaldehyde (4.73) was prepared according to Method E. The reaction was run in triplicate. The following amounts of reagents were used in each reaction flask: propargyl alcohol **4.72** (0.25 g, 1.5 mmol, 1.0 equiv), oxalyl chloride (0.17 mL, 2.0 mmol, 1.3 equiv), dimethyl sulfoxide (0.13 mL, 1.8 mmol, 1.2 equiv), triethylamine (0.64 mL, 4.6 mmol, 3.0 equiv), CH_2Cl_2 (9.2 mL). The three reaction mixtures were combined, and the residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (0.29 mg, 1.8 mmol, 59% yield). **TLC R_f** = 0.5 (20% EtOAc/hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.20 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.13–7.10 (m, 1H), 7.04 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 3.82 (s, 3H).

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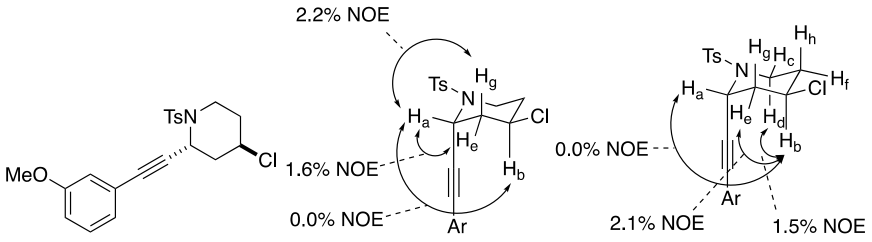
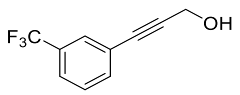
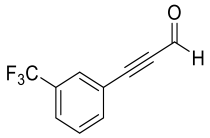
[96] Substrates **4.72**, **4.73** and **4.51** synthesized by Nadia Hirbawi.



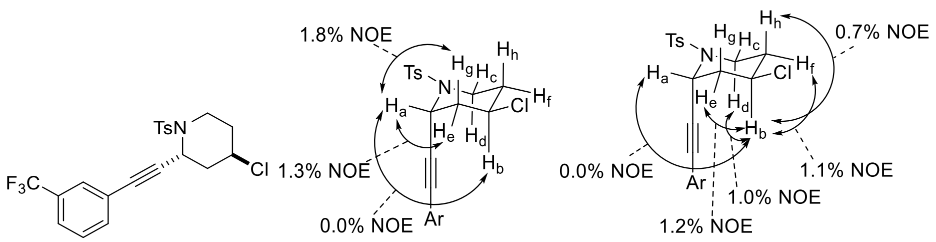
4-chloro-2-((3-methoxyphenyl)ethynyl)-1-tosylpiperidine (4.51) was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.73** (0.29 g, 1.8 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.60 mL, 1.2 mmol, 1.0 equiv), $FeCl_3$ (0.29 mg, 1.8 mmol, 1.5 equiv), Bmim·PF_6 (0.37 mL, 1.8 mmol, 1.5 equiv), $C_6H_5CF_3$ (18 mL, 0.10 M in sulfonamide). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow solid (0.16 mg, 0.39 mmol, 32%, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 115–117 °C; **TLC R_f** = 0.5 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 6.84 (dd, J = 8.4, 2.6 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.49 (s, 1H), 5.12 (s, 1H), 4.20 (tt, J = 12.0, 4.3 Hz, 1H), 3.85 (dt, J = 12.3, 2.2 Hz, 1H), 3.78 (s, 3H), 2.96 (td, J = 12.5, 2.6 Hz, 1H), 2.38 (ddt, J = 12.7, 4.5, 2.4 Hz, 1H), 2.30 (s, 3H), 2.23 (ddt, J = 12.1, 4.6, 2.3 Hz, 1H), 2.16 (td, J = 12.4, 4.8 Hz, 1H), 1.97 (qd, J = 12.6, 4.9 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.3, 143.9, 134.8, 129.6 (2C), 129.3, 128.1 (2C), 124.1, 122.7, 117.1, 114.6, 87.7, 82.6, 55.4, 53.0, 47.4, 42.1, 41.5, 36.0, 21.5; **IR** (neat) 2925, 2856, 2232, 1597, 1345, 1158, 926, 725 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{21}H_{22}ClNO_3SNa$, 426.0907; found, 426.0903.



3-(3-Trifluoromethylphenyl)prop-2-yn-1-ol (**4.74**)[97] was prepared according to Method D. The following amounts of reagents were used: 3-iodobenzotrifluoride (0.55 mL, 3.8 mmol, 1.0 equiv), propargyl alcohol (0.24 mL, 4.2 mmol, 1.1 equiv), CuI (14 mg, 76 μmol, 2.0 mol %), $Pd(PPh_3)_2Cl_2$ (26 mg, 38 μmol, 1.0 mol %), Et_3N (11 mL). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as an orange oil (0.72 g, 3.6 mmol, 95% yield). **TLC R_f** = 0.4 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.63–7.54 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 4.51 (as, 2H), 1.75 (br s, 1H). Analytical data are consistent with literature values.[98]



3-(3-Trifluoromethylphenyl)propiolaldehyde (4.75) was prepared according to Method F. The following amounts of reagents were used: propargylic alcohol **4.74** (0.72 mg, 3.6 mmol, 1.0 equiv), MnO_2 (4.7 g, 54 mmol, 15 equiv), CH_2Cl_2 (36 mL, 0.10 M). The compound was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (0.45 g, 2.4 mmol, 66% yield). **TLC R_f** = 0.6 (10% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.88 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.8 H, 1H), 7.57 (t, *J* = 7.8 Hz, 1H).



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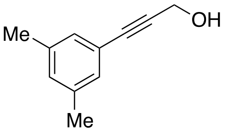
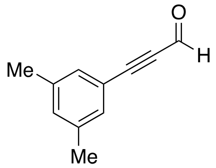
[97] Substrates **4.74**, **4.75**, and **4.52** synthesized by Nadia Hirbawi.

[98] Donnelly, K.; Zhang, H.; Baumann, M. *Molecules* **2019**, *24*, 3658–3671.

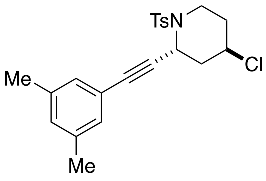
***trans*-4-Chloro-2-((3-trifluoromethylphenyl)ethynyl)-1-tosylpiperidine** (**4.52**) was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.75** (0.47 g, 2.4 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.39 mg, 1.6 mmol, 1.0 equiv), $FeCl_3$ (0.39 mg, 2.4 mmol, 1.5 equiv), Bmim·PF_6 (0.49 mL, 2.4 mmol, 1.5 equiv), and benzotrifluoride (16 mL, 0.10 M). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to yield the title compound as a white solid (160 mg, 0.35 mmol, 22% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^1H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 124–127°C; **TLC R_f** = 0.7 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.26–7.18 (m, 4H), 5.15 (as, 1H), 4.17 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.88 (ddt, *J* = 12.4, 4.5, 2.2 Hz, 1H), 2.96 (td, *J* = 12.6, 2.7 Hz, 1H), 2.39 (ddt, *J* = 12.7, 4.2, 2.4 Hz, 1H), 2.30–2.14 (m, 2H), 2.27 (s, 3H), 1.99 (qd, *J* = 12.6, 4.8 Hz, 1H); **^{13}C NMR** (150.9 MHz, $CDCl_3$) δ 144.0, 134.7, 134.6, 130.9 (q, *J* = 32.6 Hz), 129.5 (2C), 128.9, 128.2 (q, *J* = 3.9 Hz), 128.1 (2C), 125.3 (q, *J* = 3.9 Hz), 123.6 (q, *J* = 272.5 Hz), 122.6, 86.1, 84.5, 52.7, 47.2, 42.1, 41.2, 35.8, 21.3; **^{19}F NMR** (564.7 MHz, $CDCl_3$) δ –63.0; **IR** (neat) 2926, 1596, 1434, 1329, 1248, 1158, 1122, 1072 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{19}ClF_3NO_2SNa$, 464.0675; found, 464.0669.

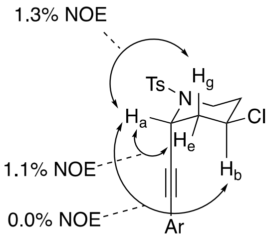


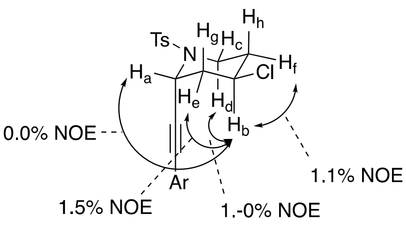
3-(3,5-dimethylphenyl)prop-2-yn-1-ol (**4.76**) was prepared according to Method D. The following amounts of reagents were used: 1-iodo-3,5-dimethylbenzene (0.85 mL, 3.0 mmol, 1.0 equiv), propargyl alcohol (0.19 mL, 3.3 mmol, 1.1 equiv), $Pd(PPh_3)_2Cl_2$ (21 mg, 30. μmol, 1.0 mol %), CuI (11 mg, 60 μmol, 2.0 mol %), triethylamine (9 mL). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (294 mg, 1.83 mmol, 61% yield). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.07 (s, 2H), 6.96 (s, 1H), 4.48 (d, *J* = 5.8 Hz, 2H), 2.28 (d, *J* = 0.7 Hz, 6H), 2.02–1.90 (m, 1H).



3-(3,5-dimethylphenyl)propiolaldehyde (**4.77**) was prepared according to Method F. The following amounts of reagents were used: propargyl alcohol **4.76** (0.29 mg, 1.8 equiv, 1.0 mmol), MnO_2 (2.4 g, 27 mmol, 15 equiv), Et_2O (4.0 mL). The residue was purified by column chromatography (0–25% EtOAc/hexanes) to yield the title compound a yellow oil (130 mg, 0.82 mmol, 45% yield). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.20 (s, 2H), 7.09 (s, 1H), 2.30 (s, 6H).

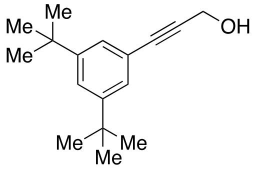




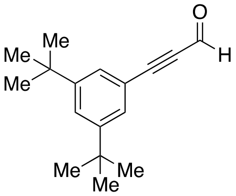


***trans*-4-chloro-2-((3,5-dimethylphenyl)ethynyl)-1-tosylpiperidine** (**4.53**) was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.77** (130 mg, 0.82 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.10 mL, 0.55 mmol, 1.0 equiv), $FeCl_3$ (0.11 mg, 0.82 mmol, 1.5 equiv), Bmim·PF_6 (0.17 mL, 0.82 mmol, 1.5 equiv), benzotrifluoride (5.5 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as tan solid (72 mg, 0.18 mmol, 22% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 123–

125 ºC **TLC R$_f$** = 0.6 (20% EtOAc/hexanes); **^{1}H NMR** (CDCl$_3$, 500 MHz) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 6.61 (s, 2H), 5.12 (t, *J* = 2.0 Hz, 1H), 4.20 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.83 (ddt, *J* = 12.1, 4.4, 2.1 Hz, 1H), 2.97 (td, *J* = 12.5, 2.7 Hz, 1H), 2.37 (ddt, *J* = 12.4, 4.5, 2.4 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 6H), 2.21 (dt, *J* = 4.5, 2.5 Hz, 1H), 2.16 (td, *J* = 12.4, 4.8 Hz, 1H), 1.97 (qd, *J* = 12.6, 5.0 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 126 MHz) δ 143.7, 137.8, 134.9, 130.6 (2C), 129.6 (2C), 129.3 (2C), 128.2 (2C), 121.4, 88.2, 82.0, 53.1, 47.4, 42.0, 41.7, 36.0, 21.6, 21.2 (2C); **IR** (neat) 2923, 2860, 2224, 1598, 1346, 1184, 932, 853, 726 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{22}H_{24}ClNO_2SNa$, 424.1114; found, 424.1113.



3-(3,5-di-*tert*-butylphenyl)prop-2-yn-1-ol (**4.78**)[99] was prepared according to Method D. The following amounts of reagents were used: 1-bromo-3,5-di-*tert*-butylbenzene (2.7 g, 10. mmol, 1.0 equiv), propargyl alcohol (0.76 mL, 13 mmol, 1.3 equiv), Pd(PPh$_3$)$_2$Cl$_2$ (140 mg, 0.20 mmol, 2.0 mol %), CuI (76 mg, 0.40 mmol, 4.0 mol %), triphenylphosphine (110 mg, 0.40 mmol, 4.0 mol %), diisoproylamine (15 mL). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow solid (2.27 g, 9.20 mmol, 92 % yield). **^{1}H NMR** (400 MHz, CDCl$_3$) 7.41–7.36 (m, 1H), 7.31–7.28 (m, 2H), 7.27–7.23 (m, 1H), 4.50 (d, *J* = 6.0 Hz, 2H), 1.31 (s, 18H).



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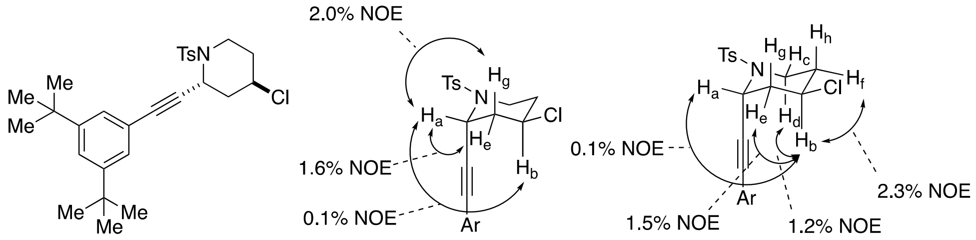
[99] Substrate **4.78** and **4.79** synthesized by Alissa Matus.

3-(3,5-di-*tert*-butylphenyl)propiolaldehyde (**4.79**) was prepared according to Method E. Due to issue with scale, the reaction was run in four reaction flasks. The following amounts of reagents were used in each reaction flask: propargyl alcohol **4.78** (0.49 mg, 2.0 mmol, 1.0 equiv), oxalyl chloride (0.22 mL, 2.6 mmol, 1.3 equiv), dimethyl sulfoxide (0.17 mL, 2.4 mmol, 1.2 equiv), triethylamine (0.84 mL, 6.0 mmol, 3.0 equiv), CH_2Cl_2 (12 mL). The four reaction mixtures were combined, and residue was purified by column chromatography (0–30% CH_2Cl_2/hexanes) to afford the title compound as a pale yellow oil (0.69 mg, 3.0 mmol, 33% yield). **TLC R$_f$** = 0.3 (40% CH_2Cl_2/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.57 (t, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 1.9 Hz, 2H), 1.34 (s, 18H).



***trans*-4-Chloro-2-((3,5-di-*tert*-butylphenyl)ethynyl)-1-tosylpiperidine (4.54)**[100] was prepared according to Method H. The following amounts of reagents were used: Aldehyde **4.79** (0.69 g, 3.0 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.46 g, 2.0 mmol, 1.0 equiv), $FeCl_3$ (0.49 g, 3.0 mmol, 1.5 equiv), Bmim·PF_6 (0.62 mL, 3.0 mmol, 1.5 equiv), benzotrifluoride (50 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a pale yellow solid (0.35 g, 0.73 mmol, 36% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 60–62 ºC; **TLC R$_f$** = 0.7 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.74 (d, *J* = 8.4 Hz,

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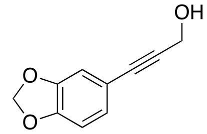
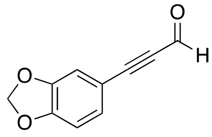
[100] Piperidine **4.54** synthesized by Alissa C. Matus. Characterization data collected by Kirsten A. Hewitt

2H), 7.39 (t, *J* = 1.9 Hz, 1 H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 1.9 Hz, 2H), 5.19 (t, *J* = 2.1 Hz, 1H), 4.25 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.83 (dt, *J* = 12.3, 2.2 Hz, 1H), 3.01 (td, *J* = 12.5, 2.6, 1 H), 2.41 (ddt, *J* = 12.7, 4.4, 2.3 Hz, 1H), 2.27–2.24 (m, 1H), 2.23 (s, 3H), 2.16 (td, *J* = 12.4, 4.8 Hz, 1H), 1.97 (qd, *J* = 12.6, 4.9 Hz, 1H), 1.30 (s, 18H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 150.9 (2C), 143.7, 135.1, 129.5 (2C), 128.2 (2C), 125.7 (2C), 123.2, 121.0, 88.8, 81.6, 53.2, 47.5, 42.0, 41.8, 36.1, 34.9 (2C), 31.4 (6C), 21.6; **IR** (neat) 2964, 2905, 2867, 2254, 1590, 1346, 1186, 904, 724 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{28}H_{36}ClNO_2SNa$, 508.2053; found, 508.2067.



3-(benzo[*d*][1,3]dioxol-5-yl)prop-2-yn-1-ol (**4.80**)[101] was prepared according to Method D. The following amounts of reagents were used: 5-iodobenzo[*d*][1,3]dioxole (1.0 mL, 8.0 mmol, 1.0 equiv), propargyl alcohol (0.51 mL, 8.8 mmol, 1.1 equiv), $Pd(PPh_3)_2Cl_2$ (56 mg, 80. µmol, 1.0 mol %), CuI (30 mg, 0.16 mmol, 2.0 mol %), triethylamine (24 mL). The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a white solid (1.29 g, 7.31 mmol, 91 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 4.47 (d, *J* = 6.2 Hz, 2H), 1.57 (t, *J* = 6.2 Hz, 1H).



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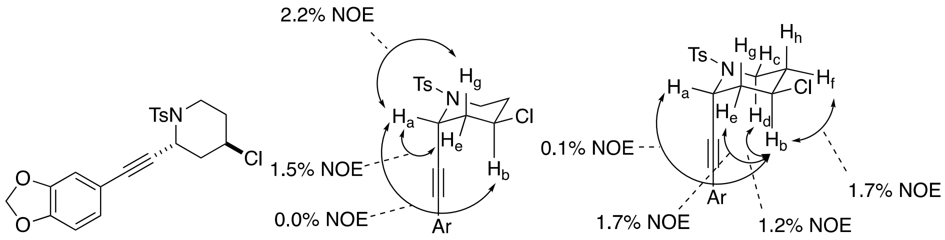
[101] Substrates **4.80** and **4.81** synthesized by Alissa C. Matus.

3-(benzo[*d*][1,3]dioxol-5-yl)propiolaldehyde (**4.81**) was prepared according to Method E. Due to issue with scale, the reaction was run in four reaction flasks. The following amounts of reagents were used in each reaction flask: propargyl alcohol **4.80** (0.31 g, 1.6 mmol, 1.0 equiv), oxalyl chloride (0.20 mL, 2.3 mmol, 1.3 equiv), dimethyl sulfoxide (0.15 mL, 2.1 mmol, 1.2 equiv), triethylamine (0.74 mL, 5.3 mmol, 3.0 equiv), CH_2Cl_2 (11 mL). The four reaction mixtures were combined, and the residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow solid (108 mg, 1.20 mmol, 37 % yield). **TLC R$_f$** = 0.6 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.19 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.04 (s, 2H).



***trans*-2-(Benzo[*d*][1,3]dioxol-5-ylethynyl)-4-chloro-1-tosylpiperidine (4.55)**[102] was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.81** (0.45 g, 2.6 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.39 mg, 1.7 mmol, 1.0 equiv), $FeCl_3$ (0.42 g, 2.6 mmol, 1.5 equiv), Bmim·PF_6 (0.54 mL, 2.6 mmol, 1.5 equiv), benzotrifluoride (43 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a white solid (58 mg, 0.14 mmol, 17% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 132–134 ºC; **TLC R$_f$** = 0.4 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.71 (d, *J* = 8.3 Hz,

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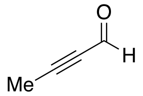
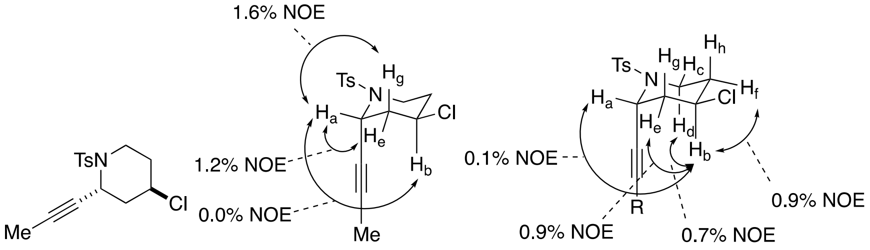
[102] Piperidine **4.55** synthesized by Alissa C. Matus. Characterization data collected by Kirsten A. Hewitt

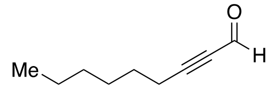
2H), 7.24 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.0 Hz, 1H), 6.53 (dd, J = 8.0, 1.6 Hz, 1H), 6.33 (d, J = 1.6 Hz, 1H), 5.95 (d, J = 1.8 Hz, 2H), 5.10 (t, J = 2.0 Hz, 1H), 4.18 (tt, J = 12.0, 4.3 Hz, 1H), 3.84 (dt, J = 12.1, 2.4 Hz, 1H), 2.95 (td, J = 12.5, 2.6 Hz, 1H), 2.38–2.35 (m, 1H), 2.34 (s, 3H), 2.26–2.19 (m, 1H), 2.15 (td, J = 12.4, 4.7 Hz, 1H), 1.96 (qd, J = 12.6, 4.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 126 MHz) δ 148.2, 147.3, 143.8, 134.9, 129.6 (2C), 128.1 (2C), 126.2, 114.9, 111.6, 108.3, 101.51, 87.6, 81.2, 53.0, 47.4, 42.1, 41.6, 36.0, 21.5; **IR** (neat) 2927, 2254, 11598, 1346, 1160, 904, 723 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{21}H_{20}ClNO_4SNa$, 440.0699; found, 440.0692.



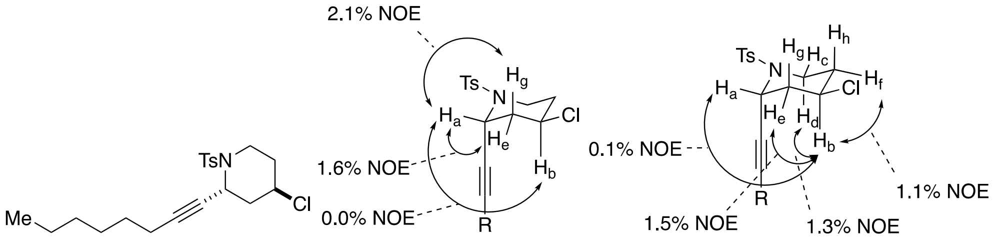
but-2-ynal (4.82) was prepared according to Method C. The following amounts of reagents were used: propyne (0.23 mL, 3.0 mmol, 1.0 equiv, 3% solution in heptane), *n*-BuLi (1.2 mL, 3.0 mmol, 1.0 equiv, 2.5 M in hexanes), DMF (0.46 mL, 6.0 mmol, 2 equiv), THF (7.5 mL, 0.40 M). Due to the volatility of the compound, it was carried onto the next step without further purification.



***Trans*-4-chloro-2-(prop-1-yn-1-yl)-1-tosylpiperidine (4.28)** was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.82** (3.0 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.37 mL, 2.0 mmol, 1.0 equiv), FeCl$_3$ (0.48 g, 3.0 mmol, 1.5 equiv), Bmim·PF$_6$ (0.62 mL, 3.0 mmol, 1.5 equiv), benzotrifluoride (30 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound white solid (24 mg, 76 µmol, 3% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 109–111 °C; **TLC R_f** = 0.3 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.88 (dq, *J* = 4.5, 2.3 Hz, 1H), 4.18–4.07 (m, 1H), 3.73 (ddt, *J* = 12.3, 4.6, 2.2 Hz, 1H), 2.87 (td, *J* = 12.5, 2.6 Hz, 1H), 2.42 (s, 3H), 2.27–2.13 (m, 2H), 2.03 (td, *J* = 12.3, 4.7 Hz, 1H), 1.89 (qd, *J* = 12.6, 4.8 Hz, 1H), 1.46 (d, *J* = 2.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 143.6, 135.0, 129.2 (2C), 128.3 (2C), 83.7, 73.1, 53.1, 47.1, 41.8, 41.7, 36.0, 21.7, 3.3; **IR** (neat) 2918, 2860, 2229, 1596, 1340, 1159, 927, 727 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{15}H_{18}ClNO_2SNa$, 334.0645; found, 334.0642

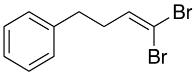


non-2-ynal (4.83) was prepared according to Method C. The following amounts of reagents were used: octyne (0.44 mL, 3.0 mmol, 1.0 equiv), *n*-BuLi (1.2 mL, 3.0 mmol, 1.0 equiv, 2.5 M in hexanes), dimethylformamide (0.46 mL, 6.0 mmol, 2.0 equiv), THF (7.5 mL). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as an orange oil (0.38 g, 2.7 mmol, 91% yield). The residue was carried into the next step without further purification.



***trans*-4-Chloro-2-(oct-1-yn-1-yl)-1-tosylpiperidine (4.56)** was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.83** (0.38 g, 2.7 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.33 mL, 1.8 mmol, 1.0 equiv), $FeCl_3$ (0.44 mg, 2.7 mmol, 1.5

equiv), Bmim·PF_6 (0.56 mL, 2.7 mmol, 1.5 equiv), benzotrifluoride (18 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as bright red oil (0.33 g, 0.86 mmol, 47% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **TLC R_f** = 0.8 (10% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.90 (t, *J* = 2.0 Hz, 1H), 4.13 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.75 (ddt, *J* = 12.2, 4.6, 2.2 Hz, 1H), 2.87 (td, *J* = 12.5, 2.7 Hz, 1H), 2.41 (s, 3H), 2.28–2.13 (m, 2H), 2.04 (td, *J* = 12.3, 4.7 Hz, 1H), 1.98–1.73 (m, 3H), 1.33–1.22 (m, 2H), 1.21–1.13 (m, 6H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 143.6, 135.1, 129.3 (2C), 128.2 (2C), 88.5, 73.7, 53.1, 47.0, 41.8, 41.7, 36.0, 31.3, 28.6, 28.3, 22.6, 21.6, 18.5, 14.1; **IR** (neat) 2931, 2859, 2255, 1598, 1346, 1161, 904, 724 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* [M + Na] calculated for $C_{20}H_{28}ClNO_2SNa$, 404.1427; found, 404.1426.



(4,4-Dibromobut-3-en-1-yl)benzene (4.84)[103] was prepared according to Method G. The following amounts of reagents were used: phenyl propionaldehyde (0.66 mL, 5.0 mmol, 1.0 equiv), CBr_4 (3.3 g, 10. mmol, 2.0 equiv), PPh_3 (5.2 g, 20. mmol, 4.0 equiv), and CH_2Cl_2 (16 mL, 0.30 M in substrate). The residue was carried forward without further purification. **TLC R_f** = 0.9 (100% hexanes) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.24–7.16 (m, 3H), 6.41 (t, *J* = 7.1 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.53 Hz, 2H).

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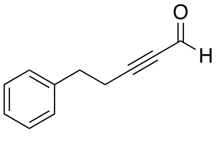
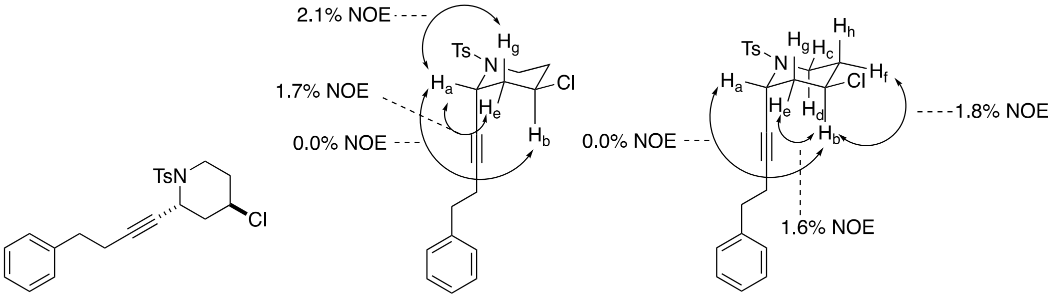
[103] substrates **4.84**, **4.85**, and **4.57** synthesized by Taylor A. Thane.

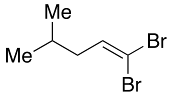


5-Phenylpent-2-ynal (4.85) was prepared according to Method G. The following amounts of reagents were used: **4.84** (0.92 g, 3.1 mmol, 1.0 equiv), *n*-BuLi (3.1 mL, 6.8 mmol, 2.2 equiv), DMF (0.29 mL, 3.7 mmol, 1.2 equiv), and THF (8 mL, 0.4 M in substrate). The residue was carried forward without further purification. **TLC R_f** = 0.5 (10% EtOAc/hexanes) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.34–7.27 (m, 2H), 7.25–7.16 (m, 3H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H).

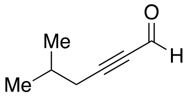


***trans*-4-Chloro-2-(4-phenylbut-1-yn-1-yl)-1-tosylpiperidine (4.57)** was prepared according to Method H. The following amounts of reagents were used: **4.84** (0.28 g, 1.8 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.27 g, 1.2 mmol, 1.0 equiv), $FeCl_3$ (0.29 g, 1.8 mmol, 1.5 equiv), Bmim·PF_6 (0.37 mL, 1.8 mmol, 1.5 equiv), and benzotrifluoride (18 mL). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow solid (113 mg, 0.28 mmol, 23% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 111–113°C; **TLC R_f** = 0.7 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.29–7.19 (m, 5H), 7.02 (d, *J* = 7.4 Hz, 2H), 4.84–4.82 (m, 1H), 3.85 (tt, *J* = 11.9, 4.3 Hz, 1H), 3.65–3.60 (m, 1H), 2.60 (td, *J* = 12.4, 2.5 Hz, 1H), 2.56–2.43 (m, 2H), 2.41 (s, 3H), 2.24–2.07 (m, 3H), 2.04–

1.94 (m, 2H), 1.81 (qd, *J* = 12.6, 4.9 Hz, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.5, 140.2, 135.1, 129.3 (2C), 128.5 (2C), 128.4 (2C), 128.2 (2C), 126.6, 87.5, 74.9, 52.9, 46.9, 41.7 (2C), 35.9, 34.4, 21.7, 20.3; **IR** (neat) 3062, 3027, 2928, 2860 2232 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{24}ClNO_2SNa$, 424.1114; found, 424.1102.



1,1-Dibromo-4-methylpent-1-ene (4.86)[104] was prepared according to Method G. The following amounts of reagents were used: isovaleraldehyde (0.54 mL, 5.0 mmol, 1.0 equiv), CBr_4 (3.3 g, 10. mmol, 2.0 equiv), PPh_3 (5.2 g, 20. mmol, 4.0 equiv), and DCM (15 mL). The residue was passed through a silica plug eluting with 100% hexanes. The resulting oil was carried forward without further purification. **TLC R$_f$** = 0.9 (100% hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.40 (t, *J* = 7.5 Hz, 1H), 1.99 (t, *J* = 7.1 Hz, 2H), 1.75 (sept, *J* = 6.7 Hz, 1H), 0.93 (d, *J* = 6.6 Hz, 6H).



5-Methylhex-2-ynal (4.87) was prepared according to Method G. The following amounts of reagents were used: **4.86** (0.88 g, 3.7 mmol, 1.0 equiv), *n*-BuLi (3.2 mL, 8.0 mmol, 2.2 equiv), DMF (0.34 mL, 4.4 mmol, 1.2 equiv), and THF (9 mL). The residue was carried forward without further purification. **TLC R$_f$** = 0.5 (10% hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 2.31 (d, *J* = 6.6 Hz, 2H), 1.94 (sept, *J* = 6.6 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 6H).

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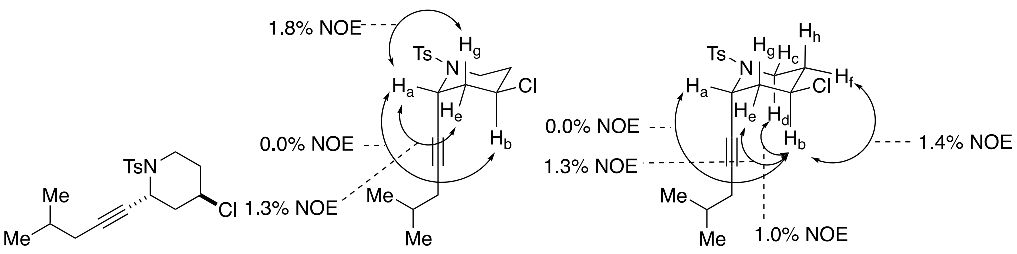
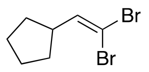
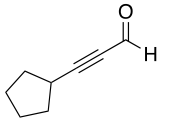
[104] Substrates **4.86**, **4.87**, and **4.58** synthesized by Taylor A. Thane



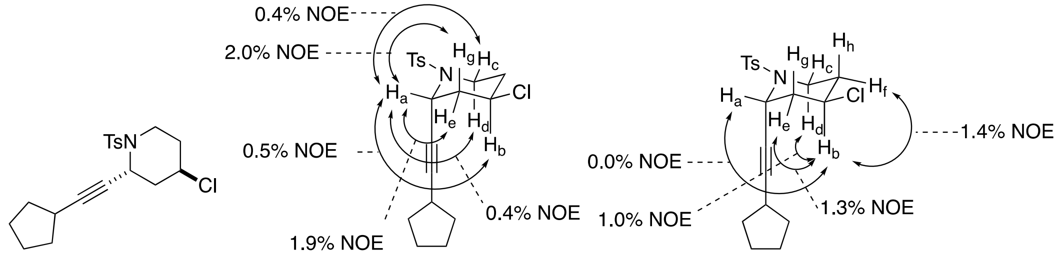
***trans*-4-Chloro-2-(4-methylpent-1-yn-1-yl)-1-tosylpiperidine (4.58)** was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.87** (0.17 g, 1.6 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.23 g, 1.0 mmol, 1.0 equiv), $FeCl_3$ (0.25 g, 1.6 mmol, 1.5 equiv), Bmim·PF_6 (0.32 mL, 1.6 mmol, 1.5 equiv), and benzotrifluoride (15 mL). The residue was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as pale yellow solid (59 mg, 0.16 mmol, 10% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 63–65 °C; **TLC** **R_f** = 0.7 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 4.94 4.91 (m, 1H), 4.14 (tt, *J* = 12.1, 4.2 Hz, 1H), 3.78 3.74 (m, 1H), 2.90 (td, *J* = 12.4, 2.7 Hz, 1H), 2.41 (s, 3H), 2.27–2.23 (m, 1H), 2.21–2.16 (m, 1H), 2.0 (td, *J* = 12.5, 4.8, 1H), 1.90 (qd, *J* = 12.5, 4.4, 1H), 1.73 (qdd, *J* = 13.8, 6.9, 1.9, 2H), 1.48 (sept, *J* = 6.7, 1H), 0.79 (d, *J* = 6.7, 3H), 0.77 (d, *J* = 6.7, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.5, 135.3, 129.4 (2C), 128.2 (2C), 87.3, 74.8, 53.2, 47.0, 42.0, 41.8, 36.1, 27.82, 27.76, 22.07, 22.05, 21.6; **IR** (neat) 2957, 2927, 2868, 2230 cm^{-1}; **HRMS** (TOF MS ES+) *m/z*: [M + Na]$^+$ calcd for $C_{18}H_{24}ClNO_2SNa$, 376.1114; found, 376.1108.



(2,2-dibromovinyl)cyclopentane (4.88)[105] was prepared according to Method G. The following amounts of reagents were used: cyclopentanecarboxaldehyde (0.53 mL, 5.0 mmol, 1.0 equiv), CBr_4 (3.3 g, 10. mmol, 2.0 equiv), PPh_3 (5.2 g, 20. mmol, 4.0 equiv), and CH_2Cl_2 (16 mL, 0.30 M in substrate). The residue was carried forward without further purification. **TLC R_f** = 0.9 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.31 (d, *J* = 9.0 Hz, 1H), 2.67 (sext, *J* = 8.7 Hz, 1H), 1.91–1.87 (m, 2H), 1.69–1.56 (m, 4H), 1.32–1.26 (m, 2H).



3-cyclopentylpropiolaldehyde (4.89) was prepared according to Method G. The following amounts of reagents were used: **4.88** (0.75 g, 2.9 mmol, 1.0 equiv), *n*-BuLi (2.6 mL, 6.5 mmol, 2.2 equiv), DMF (0.28 mL, 3.6 mmol, 1.2 equiv), and THF (8.0 mL, 0.40 M in substrate). The residue was carried forward without further purification. **TLC R_f** = 0.6 (10% EtOAc/hexanes) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 2.86–2.78 (m, 1H), 2.03–1.96 (m, 2H), 1.79–1.67 (m, 4H), 1.66–1.58 (m, 2H).



***trans*-4-chloro-2-(cyclopentylethynyl)-1-tosylpiperidine (4.59)** was prepared according to Method H. The following amounts of reagents were used: **4.89** (180 mg, 1.5 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (230 mg, 1.0 mmol, 1.0 equiv), $FeCl_3$ (240 mg, 1.5 mmol, 1.5 equiv), Bmim·PF_6 (0.31 mL, 1.5 mmol, 1.5 equiv), and benzotrifluoride (15 mL). The residue was purified

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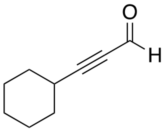
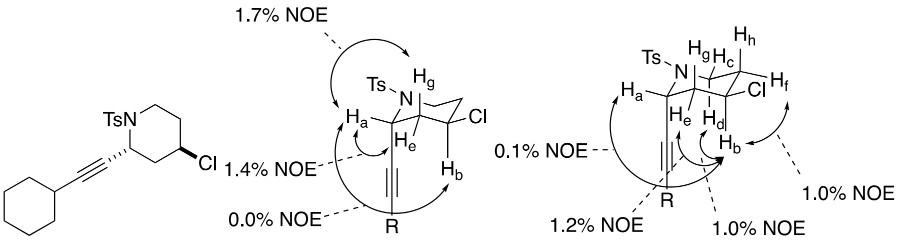
[105] Substrates **4.88**, **4.89**, and **4.59** synthesized by Taylor A. Thane.

by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a pale-yellow solid (220 mg, 0.59 mmol, 5.9% yield over 3 steps, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 84–86 °C; **TLC R$_f$** = 0.7 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.91–4.88 (m, 1H), 4.13 (tt, *J* = 11.8, 4.4 Hz, 1H), 3.78–3.73 (m, 1H), 2.89 (td, *J* = 12.5, 2.5 Hz, 1H), 2.41 (s, 3H), 2.31–2.15 (m, 3H), 2.05 (td, *J* = 12.3, 4.9 Hz, 1H), 1.90 (qd, *J* = 12.3, 4.9 Hz, 1H), 1.72–1.59 (m, 2H), 1.69–1.62 (m, 2H), 1.51–1.42 (m, 2H), 1.23–1.13 (m, 2H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 143.5, 135.4, 129.5 (2C), 128.1 (2C), 92.8, 73.3, 53.2, 47.0, 42.0, 41.7, 36.1, 33.6, 33.5, 29.8, 25.04, 25.01, 21.6; **IR** (neat) 2958, 2868, 2232, 1598; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{24}ClNO_2SNa$, 388.1114; found, 388.1107.

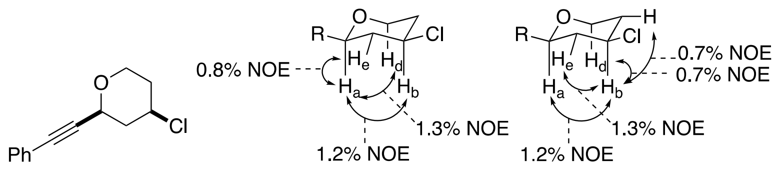


3-cyclohexylpropiolaldehyde (**4.90**) was prepared according to Method C. The following amounts of reagents were used: ethynylcyclohexane (0.65 mL, 5.0 mmol, 1.0 equiv), *n*-BuLi (4.5 mL, 5.0 mmol, 1.0 equiv, 2.5 M in hexanes), DMF (0.77 mL, 10. mmol, 2.0 equiv), THF (13 mL). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow solid (0.39 g, 2.9 mmol, 58% yield). **TLC R$_f$** = 0.8 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 2.58 (tt, *J* = 8.8, 3.9 Hz, 1H), 1.84 (ddt, *J* = 12.8, 6.7, 3.5 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.51 (ddd, *J* = 13.3, 9.6, 6.9 Hz, 4H), 1.34 (tdd, *J* = 10.1, 5.9, 2.6 Hz, 3H).



***trans*-4-chloro-2-(cyclohexylethynyl)-1-tosylpiperidine (4.60)** was prepared according to Method H. The following amounts of reagents were used: aldehyde **4.90** (0.63 g, 4.6 mmol, 1.5 equiv), homoallylic sulfonamide **4.2** (0.56 mL, 3.1 mmol, 1.0 equiv), $FeCl_3$ (0.74 g, 4.63 mmol, 1.5 equiv), Bmim·PF_6 (0.94 mL, 4.6 mmol, 1.5 equiv), benzotrifluoride (31 mL). The residue was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound white solid (0.67 mg, 1.8 mmol, 57% yield, >20:1 dr trans:cis). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 110–113 °C; **TLC R_f** = 0.7 (20% EtOAc/hexanes); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.96 (s, 1H), 4.20 (tt, *J* = 12.0, 4.3 Hz, 1H), 3.82 (ddt, *J* = 12.2, 4.6, 2.2 Hz, 1H), 2.96 (td, *J* = 12.5, 2.7 Hz, 1H), 2.47 (s, 3H), 2.35 – 2.20 (m, 2H), 2.16 – 2.04 (m, 2H), 1.97 (qd, *J* = 12.6, 4.9 Hz, 1H), 1.62 – 1.46 (m, 6H), 1.32 – 1.17 (m, 3H), 1.16 – 1.01 (m, 2H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 143.4, 135.3, 129.4, 128.0, 92.6, 73.6, 53.1, 46.9, 41.9, 41.6, 36.0, 32.3, 32.2, 28.8, 25.7, 24.8, 21.5; **IR** (neat) 2927, 2853, 2230, 1598, 1346, 1185, 933, 726 cm^{-1}; **HRMS** (TOF MS ES+) *m/z:* $[M + Na]^+$ calculated for $C_{20}H_{28}ClNO_2SNa$ 402.1270, found 402.1272.

4.5.10. Synthesis and Characterization of Tetrahydropyran Substrates



***trans*-4-Chloro-2-(phenylethynyl)tetrahydro-2*H*-pyran (4.91)** was prepared according to a modified procedure reported by Grée.[106] In a glovebox, $ZnCl_2$ (0.39 g, 2.9 mmol, 1.1 equiv) was added to a flame dried flask equipped with a stir bar. The flask was sealed with a septum, removed from the glovebox, and placed under an inert atmosphere of N_2. Then *p*-TsOH (0.54 g, 2.9 mmol, 1.1 equiv) and CH_2Cl_2 (13 mL) were added via syringe. In a separate flame dried round bottom flask, aldehyde **4.1** (0.33 g, 2.6 mmol, 1.0 equiv), 3-butenol (0.25 mL, 2.9 mmol, 1.1 equiv) were dissolved in CH_2Cl_2 (13 mL). This mixture was allowed to stir for 5 mins at rt. Then the solution containing aldehyde and 3-butenol was added to the solution of $ZnCl_2$ and *p*-TsOH. The reaction mixture was allowed to stir at rt overnight. Sat. $NaHCO_3$ was added to quench the reaction mixture. The biphasic solution was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a white solid (0.21 g, 0.97 mmol, 37% yield, >20:1 dr cis:trans). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^1H NMR spectrum. The relative configuration was assigned based on NOE analysis. **m.p.** 51–53 °C; **TLC R$_f$** = 0.8 (20% EtOAc/hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.35–7.27 (m, 3H), 4.30 (dd, *J* = 11.2, 2.3 Hz, 1H), 4.11 (ddd, *J* = 12.2, 4.7, 2.1 Hz, 1H), 4.02 (tt, *J* = 11.5, 4.5 Hz, 1H), 3.49 (td, *J* = 12.1, 2.1 Hz, 1H), 2.47 (ddt, *J* = 13.1, 4.4, 2.2 Hz, 1H), 2.16–2.06 (m, 2H), 1.95 (qd, *J* = 12.5, 12.0, 4.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.0 (2C), 128.8, 128.4 (2C), 122.3, 86.6, 85.4, 67.9, 67.0, 54.3, 43.0, 36.5; **IR** (neat) 2861, 2835, 2234, 1595, 1488, 1364, 1212, 1022, 757, 724 cm^{-1}; **HRMS** (MS TOF Cl+) *m/z*: $[M–Cl]^+$ calculated for $C_{13}H_{13}O$, 185.0966; found, 185.0961.

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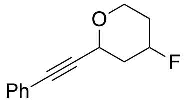
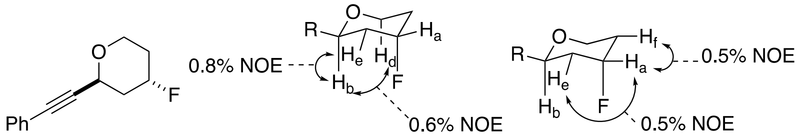
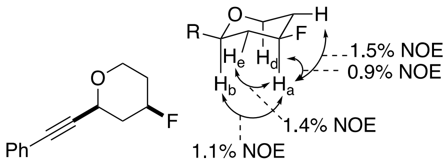
[106] Borkar, P.; van de Weghe, O.; Reddy, B. V. S.; Yadav, J. S.; Grée, R. *Chem. Commun.* **2012**, *48*, 9316–9318.



4-fluoro-2-(phenylethynyl)tetrahydro-2H-pyran (4.92) was prepared according to Method I. The following amounts of reagents were used: aldehyde **4.1** (0.50 g, 3.8 mmol, 1.0 equiv), 3-butenol (0.36 mL, 4.2 mmol, 1.1 equiv), HBF_4•Et_2O (0.52 mL, 3.8 mmol, 1.0 equiv). CH_2Cl_2 (19 mL, 0.20 M). The residue was purified by column chromatography and the diastereomers were separated (0–10% EtOAc/hexanes) to afford the *trans*-diastereomer as a pale yellow solid (0.22 g, 1.1 mmol, 29% yield, >20:1 dr *trans*:*cis*) and the *cis*-diastereomer as a white solid (0.20 g, 0.99 mmol, 26% yield, >20:1 dr *cis*:*trans*). The dr was determined based on the integration of the resonances attributed to the propargylic hydrogens in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. For clarity, the data of the major and minor diastereomers have been tabulated individually.

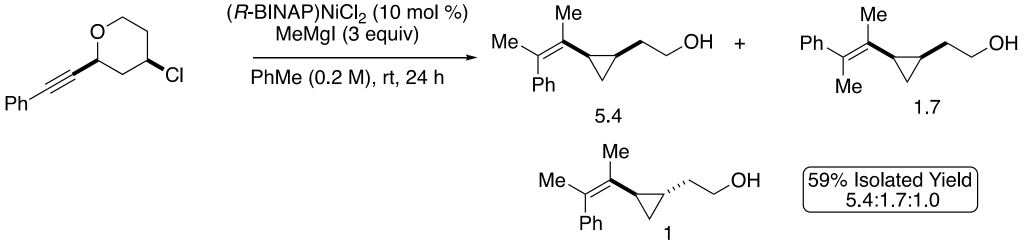


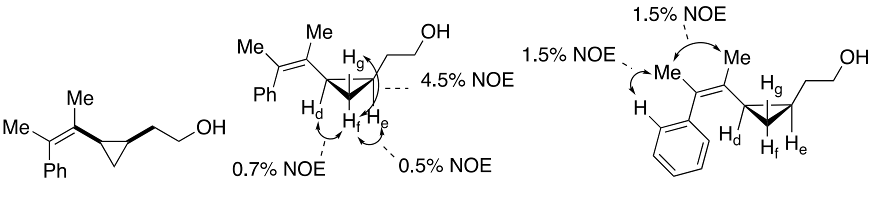
***trans*-diastereomer: TLC R$_f$** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54–7.47 (m, 2H), 7.41–7.34 (m, 3H), 5.11 (dtt, *J* = 48.1, 5.9, 3.2 Hz, 1H), 4.88 (dd, *J* = 8.7, 3.6 Hz, 1H), 4.07–4.00 (m, 1H), 3.96 (tdd, *J* = 11.8, 3.4, 1.9 Hz, 1H), 2.26–2.11 (m, 2H), 2.10–1.85 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.9 (2C), 128.7, 128.4 (2C), 122.4, 87.12, 87.09, 85.79 (d, *J* = 23.4 Hz), 63.92 (d, *J* = 4.7 Hz), 62.34 (d, *J* = 4.1 Hz), 37.58 (d, *J* = 19.6 Hz), 31.35 (d, *J* = 19.7 Hz); **^{19}F NMR (**565 MHz, $CDCl_3$) δ –183.2 (s); **IR** (neat) 2958, 2864, 2228, 1598, 1498, 1147, 1086, 754, 690 cm^{-1}; **HRMS** (TOF MS Cl+) *m/z*: $[M + NH_4]^+$ calculated for $C_{13}H_{21}FN_2O$, 222.1294; found, 222.1285.



***cis*-diastereomer: TLC R_f** = 0.4 (5% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.34–7.27 (m, 3H), 4.72 (dtt, *J* = 48.6, 9.8, 4.7 Hz, 1H), 4.35 (ddd, *J* = 10.3, 2.8, 1.9 Hz, 1H), 4.16 (dtd, *J* = 12.0, 5.0, 3.4 Hz, 1H), 3.52–3.44 (m, 1H), 2.42–2.34 (m, 1H), 2.08–1.92 (m, 2H), 1.89–1.77 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.9 (2C), 128.6, 128.3 (2C), 122.3, 88.4, 87.0, 86.8 (d, *J* = 2.3 Hz), 66.0 (d, *J* = 12.4 Hz), 64.2 (d, *J* = 11.0 Hz), 38.7 (d, *J* = 18.5 Hz), 32.4 (d, *J* = 18.2 Hz); **^{19}F NMR** (565 MHz, $CDCl_3$) δ –172.41 (d, *J* = 48.3 Hz); **IR** (neat) 2958, 2864, 2228, 1598, 1498, 1147, 1086, 754, 690 cm^{-1}; **HRMS** (TOF MS Cl+) *m/z*: $[M + NH_4]^+$ calculated for $C_{13}H_{21}FN_2O$, 222.1294; found, 222.1283.

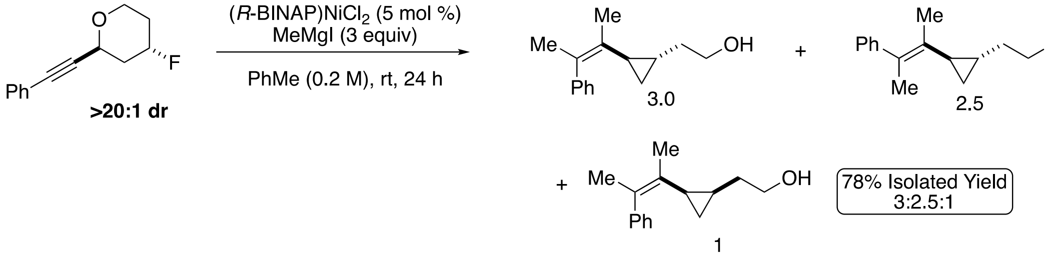
4.5.10.1 Results from Tetrahydropyran Ring Contraction



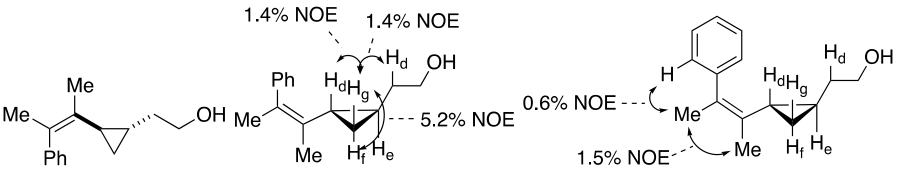


(3-phenylbut-2-en-2-yl)cyclopropyl)ethan-1-ol (4.93) was prepared according to a modified version of Method A. The reaction was performed in triplicate. The following amounts of reagents were used in each flask: **4.92** (44 mg, 0.20 mmol, 1.0 equiv), (*R*-BINAP)NiCl$_2$ (15 mg, 20. μmol, 10. mol %), MeMgI (0.24 mL, 0.60 mmol, 2.5 M in Et$_2$O, 3.0 equiv), and PhMe (1.0 mL, 0.20 M).

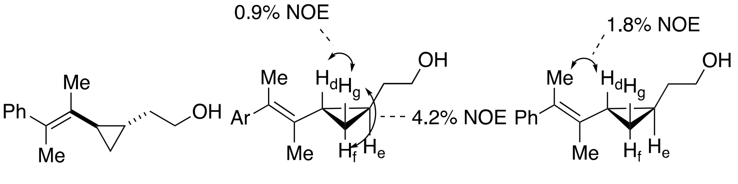
The reaction mixtures were combined, and residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (76 mg, 0.35 mmol, 59% yield, 5.4:1.7:1.0 mixture of diastereomers). The dr was based on the integration of resonances associated with Hg in the ^{1}H NMR spectrum. The relative configuration of the major diastereomer was assigned based on NOE analysis. The ^{1}H NMR of the major diastereomer is given below. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23–7.15 (m, 4H), 7.13–7.08 (m, 1H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.09–2.06 (m, 2H), 2.01 (s 3H), 1.77 (s, 3H), 1.15–1.03 (m, 2H), 0.82–0.70 (m, 1H), 0.56 (tdd, *J* = 8.4, 5.0, 0.9 Hz, 1H), –0.03 (q, *J* = 5.6 Hz, 1H).



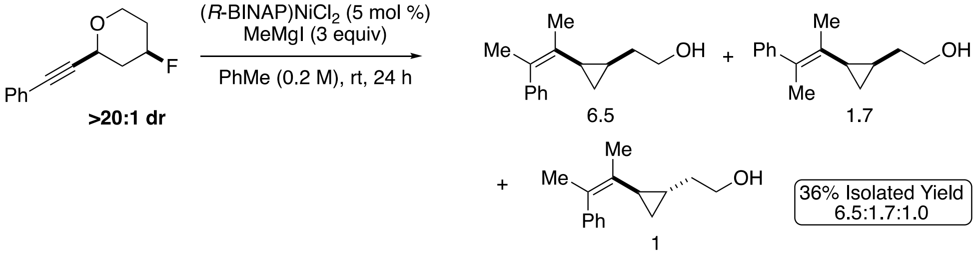
4.5.10.2 NOE correlations for major diastereomer:



4.5.10.3 NOE correlations for minor diastereomer:



(3-phenylbut-2-en-2-yl)cyclopropyl)ethan-1-ol (4.93) was prepared according to a modified version of Method A. The following amounts of reagents were used **4.92** (45 mg, 0.22 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (8.3 mg, 11 μmol, 5.0 mol %), MeMgI (0.26 mL, 0.66 mmol, 2.5 M in Et_2O, 3.0 equiv), and PhMe (1.1 mL, 0.20 M). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (37 mg, 0.17 mmol, 78% yield, 3:2.5:1 mixture of diastereomers). The dr was based on the integration of resonances associated with Hg in the ^{1}H NMR spectrum. The relative configuration of the major and minor diastereomer was assigned based on NOE analysis. The ^{1}H NMR of the major diastereomer is given below. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 3H), 3.59 (t, *J* = 6.5 Hz, 2H), 1.98 (s, 3H), 1.49 (s, 3H), 1.42 (dq, *J* = 13.2, 6.5 Hz, 1H), 1.31–1.23 (m, 2H), 0.85 (dq, *J* = 13.2, 6.5, 5.9 Hz, 1H), 0.66 (dt, *J* = 9.3, 5.1 Hz, 1H), 0.26 (dt, *J* = 9.5, 5.0 Hz, 1H).



(3-phenylbut-2-en-2-yl)cyclopropyl)ethan-1-ol (4.93) was prepared according to a modified version of Method A. The following amounts of reagents were used **4.92** (46 mg, 0.23 mmol, 1.0 equiv), (*R*-BINAP)$NiCl_2$ (8.6 mg, 12 μmol, 5.0 mol %), MeMgI (0.28 mL, 0.69 mmol, 2.5 M in Et_2O, 3.0 equiv), and PhMe (1.2 mL, 0.20 M). The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (17 mg, 79 μmol, 36% yield, 6.5:1.7:1 mixture of diastereomers). The dr was based on the integration of resonances associated with Hg in the ^{1}H NMR spectrum. The relative configuration was assigned based on NOE analysis. See above for NOE correlations of the major diastereomer. The ^{1}H NMR of the major diastereomer is given below. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 3H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.01 (s, 3H), 1.77 (s, 3H), 1.72 (ddt, *J* = 16.3, 11.0, 5.2 Hz, 1H), 1.55–1.45 (m, 2H), 0.74 (dtd, *J* = 14.3, 9.2, 5.2 Hz, 1H), 0.56 (td, *J* = 8.4, 5.0 Hz, 1H), –0.03 (q, *J* = 5.7 Hz, 1H).

4.6 Circular Dichroism Experimental Data

Experimental data collected was collected in CH_2Cl_2 (concentration = 7.48 x 10^{-4} M).

Figure 4.4 Experimental Circular Dichroism Spectrum of (+)-**4.35**

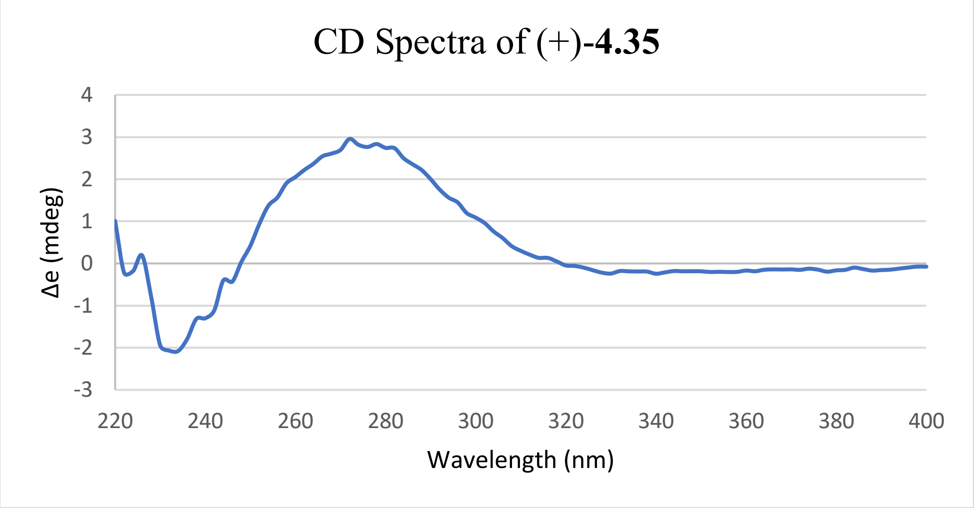


Table 4.3 Experimental Values for CD Spectra of (+)-**4.35**

Wavelength (nm)	**Δe (mdeg)**
400	-0.0759497
398	-0.0751904
396	-0.0969728
394	-0.121212
392	-0.147048
390	-0.156384
388	-0.168732
386	-0.133429
384	-0.0984882
382	-0.151537
380	-0.164564
378	-0.194577
376	-0.148106
374	-0.124022
372	-0.151128
370	-0.140436
368	-0.14309
366	-0.141069
364	-0.149368

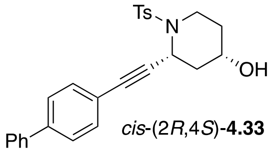
362	-0.184781
360	-0.168379
358	-0.200113
356	-0.202217
354	-0.198336
352	-0.202217
350	-0.186079
348	-0.184813
346	-0.185545
344	-0.179994
342	-0.211313
340	-0.243334
338	-0.192655
336	-0.190551
334	-0.187009
332	-0.179927
330	-0.239985
328	-0.217697
326	-0.160824
324	-0.0992894
322	-0.0588276
320	-0.0472567
318	0.047425
316	0.132352
314	0.133412
312	0.208498
310	0.30016
308	0.410641
306	0.602357
304	0.7589
302	0.958575
300	1.08812
298	1.19775
296	1.44968
294	1.56305
292	1.75573
290	2.00229
288	2.21936
286	2.35494

284	2.49864
282	2.73679
280	2.74398
278	2.83456
276	2.76474
274	2.81699
272	2.95532
270	2.69466
268	2.60762
266	2.54433
264	2.36611
262	2.22114
260	2.05217
258	1.90347
256	1.56613
254	1.36982
252	0.938061
250	0.41649
248	0.0341021
246	-0.430506
244	-0.401459
242	-1.11161
240	-1.30017
238	-1.31937
236	-1.78829
234	-2.076
232	-2.06933
230	-1.94643
228	-0.795606
226	0.186215
224	-0.178137
222	-0.224473
220	1.00859

4.7 Crystallographic Data

1) X-ray Data Collection, Structure Solution and Refinement for *cis*-(2*R*,4*S*)-4.33

CCDC: 2104034



cis-(2*R*,4*S*)-**4.33**

A colorless crystal of approximate dimensions 0.122 x 0.367 x 0.392 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[107] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT[108] and SADABS[109] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[110] program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[111] for neutral atoms were used throughout the analysis.

Hydrogen atoms associated with C(26) were included using a riding model. The remaining hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

Least squares analysis yielded wR2 = 0.0933 and Goof = 1.093 for 369 variables refined against 5859 data (0.73 Å), R1 = 0.0381 for those 5519 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter[112].

Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

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[107] APEX2 Version 2014.11-0, Bruker AXS, Inc.; Madison, WI 2014.

[108] SAINT Version 8.34a, Bruker AXS, Inc.; Madison, WI 2013.

[109] Sheldrick, G. M. SADABS, Version 2014/5, Bruker AXS, Inc.; Madison, WI 2014.

[110] Sheldrick, G. M. SHELXTL, Version 2014/7, Bruker AXS, Inc.; Madison, WI 2014.

[111] *International Tables for Crystallography* **1992**, Vol. C., Dordrecht: Kluwer Academic Publishers.

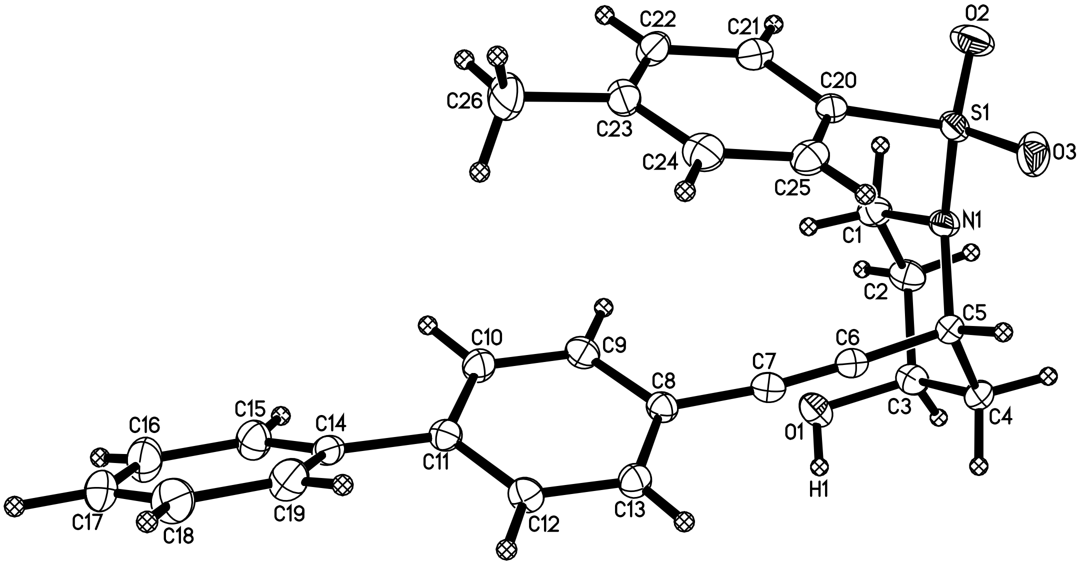
[112] Parsons, S., Flack, H. D., Wagner, T. *Acta Cryst.* **2013**, *B69*, 249–259.

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

Figure 4.5 X-Ray Crystallographic Structure of (+)-4.33



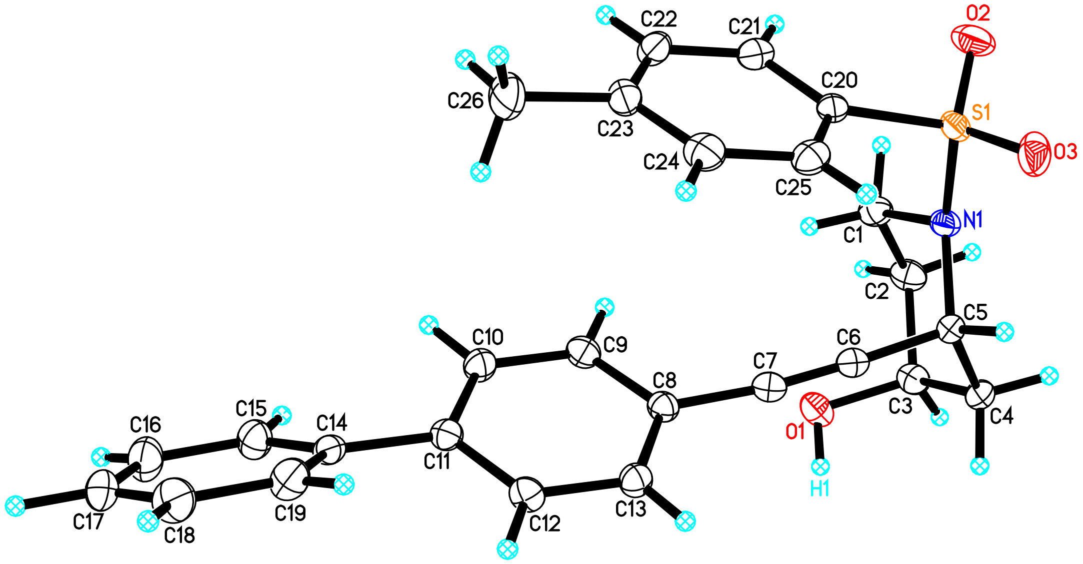


Table 4.4 Crystal data and structure refinement for erj39.

Identification code	erj39 (Kirsten Hewitt)	
Empirical formula	$C_{26} H_{25} N O_3 S$	
Formula weight	431.53	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.9745(4) Å	α = 90°.
	b = 10.8981(5) Å	β = 90°.
	c = 25.0685(13) Å	γ = 90°.
Volume	2178.63(19) Å^3	
Z	4	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	0.177 mm^{-1}	
F(000)	912	
Crystal color	colorless	
Crystal size	0.392 x 0.367 x 0.122 mm^3	
Theta range for data collection	1.625 to 29.129°	
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-34 \leq l \leq 34$	
Reflections collected	51864	

Independent reflections	5859 [R(int) = 0.0425]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8622 and 0.7838
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5859 / 0 / 369
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I) = 5519 data]	R1 = 0.0381, wR2 = 0.0915
R indices (all data, 0.73 Å)	R1 = 0.0416, wR2 = 0.0933
Absolute structure parameter	0.020(16)
Largest diff. peak and hole	0.349 and -0.213 e.Å^{-3}

Table 4.5 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for erj39.[113]

	x	y	z	U(eq)
S(1)	3362(1)	1493(1)	8849(1)	20(1)
O(1)	8990(2)	3531(2)	9010(1)	23(1)
O(2)	2026(2)	2237(2)	9057(1)	33(1)
O(3)	3392(2)	202(2)	8960(1)	29(1)
N(1)	5082(2)	2069(2)	9106(1)	17(1)
C(1)	5338(3)	3403(2)	9048(1)	21(1)
C(2)	6488(3)	3854(2)	9493(1)	23(1)
C(3)	8143(3)	3173(2)	9485(1)	20(1)
C(4)	7848(3)	1788(2)	9506(1)	19(1)
C(5)	6646(3)	1325(2)	9071(1)	16(1)
C(6)	7410(2)	1368(2)	8535(1)	17(1)
C(7)	7987(2)	1456(2)	8098(1)	17(1)
C(8)	8555(2)	1652(2)	7562(1)	16(1)
C(9)	8168(3)	2765(2)	7308(1)	20(1)
C(10)	8630(3)	2962(2)	6784(1)	19(1)
C(11)	9494(2)	2070(2)	6493(1)	17(1)

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[113] U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

C(12)	9902(3)	969(2)	6752(1)	18(1)
C(13)	9451(3)	766(2)	7278(1)	18(1)
C(14)	9980(2)	2277(2)	5929(1)	18(1)
C(15)	10377(3)	3442(2)	5737(1)	23(1)
C(16)	10909(3)	3603(2)	5214(1)	28(1)
C(17)	11044(3)	2605(2)	4873(1)	28(1)
C(18)	10622(3)	1454(2)	5056(1)	29(1)
C(19)	10090(3)	1284(2)	5574(1)	24(1)
C(20)	3422(3)	1696(2)	8154(1)	18(1)
C(21)	2930(3)	2810(2)	7929(1)	22(1)
C(22)	3140(3)	2977(2)	7382(1)	25(1)
C(23)	3839(3)	2071(2)	7065(1)	25(1)
C(24)	4280(3)	960(2)	7298(1)	24(1)
C(25)	4080(3)	762(2)	7838(1)	21(1)
C(26)	4137(3)	2286(3)	6478(1)	38(1)

Table 4.6 Bond lengths [Å] and angles [°] for erj39.

S(1)-O(3)	1.4339(18)
S(1)-O(2)	1.4371(18)
S(1)-N(1)	1.6396(18)
S(1)-C(20)	1.758(2)
O(1)-C(3)	1.425(3)
O(1)-H(1)	0.84(3)
N(1)-C(1)	1.476(3)
N(1)-C(5)	1.491(3)
C(1)-C(2)	1.526(3)
C(1)-H(1A)	0.96(3)
C(1)-H(1B)	0.96(3)
C(2)-C(3)	1.515(3)
C(2)-H(2A)	0.97(3)
C(2)-H(2B)	1.01(3)
C(3)-C(4)	1.528(3)
C(3)-H(3A)	0.97(3)
C(4)-C(5)	1.537(3)

C(4)-H(4A)	0.99(3)
C(4)-H(4B)	0.98(3)
C(5)-C(6)	1.477(3)
C(5)-H(5A)	0.93(2)
C(6)-C(7)	1.192(3)
C(7)-C(8)	1.434(3)
C(8)-C(13)	1.397(3)
C(8)-C(9)	1.404(3)
C(9)-C(10)	1.382(3)
C(9)-H(9A)	0.96(3)
C(10)-C(11)	1.397(3)
C(10)-H(10A)	0.98(3)
C(11)-C(12)	1.404(3)
C(11)-C(14)	1.483(3)
C(12)-C(13)	1.383(3)
C(12)-H(12A)	0.92(3)
C(13)-H(13A)	0.88(3)
C(14)-C(15)	1.394(3)
C(14)-C(19)	1.403(3)
C(15)-C(16)	1.390(3)
C(15)-H(15A)	0.93(3)
C(16)-C(17)	1.387(4)
C(16)-H(16A)	0.92(3)
C(17)-C(18)	1.377(4)
C(17)-H(17A)	1.03(3)
C(18)-C(19)	1.380(3)
C(18)-H(18A)	0.83(3)
C(19)-H(19A)	0.92(3)
C(20)-C(25)	1.391(3)
C(20)-C(21)	1.395(3)
C(21)-C(22)	1.394(3)
C(21)-H(21A)	0.96(3)
C(22)-C(23)	1.385(4)
C(22)-H(22A)	0.93(3)
C(23)-C(24)	1.390(3)
C(23)-C(26)	1.508(3)

C(24)-C(25)	1.381(3)
C(24)-H(24A)	0.95(3)
C(25)-H(25A)	0.93(3)
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
O(3)-S(1)-O(2)	119.70(12)
O(3)-S(1)-N(1)	106.61(10)
O(2)-S(1)-N(1)	105.18(10)
O(3)-S(1)-C(20)	108.34(10)
O(2)-S(1)-C(20)	107.99(10)
N(1)-S(1)-C(20)	108.58(9)
C(3)-O(1)-H(1)	105.9(18)
C(1)-N(1)-C(5)	114.47(16)
C(1)-N(1)-S(1)	117.02(14)
C(5)-N(1)-S(1)	117.95(14)
N(1)-C(1)-C(2)	109.15(17)
N(1)-C(1)-H(1A)	106.6(15)
C(2)-C(1)-H(1A)	108.1(16)
N(1)-C(1)-H(1B)	108.8(18)
C(2)-C(1)-H(1B)	112.4(18)
H(1A)-C(1)-H(1B)	112(2)
C(3)-C(2)-C(1)	110.84(17)
C(3)-C(2)-H(2A)	108.9(19)
C(1)-C(2)-H(2A)	108.4(17)
C(3)-C(2)-H(2B)	111.0(14)
C(1)-C(2)-H(2B)	108.5(14)
H(2A)-C(2)-H(2B)	109(2)
O(1)-C(3)-C(2)	106.84(17)
O(1)-C(3)-C(4)	111.90(17)
C(2)-C(3)-C(4)	110.47(18)
O(1)-C(3)-H(3A)	108.4(15)
C(2)-C(3)-H(3A)	112.5(15)
C(4)-C(3)-H(3A)	106.8(15)
C(3)-C(4)-C(5)	113.30(17)

C(3)-C(4)-H(4A)	110.8(17)
C(5)-C(4)-H(4A)	104.9(17)
C(3)-C(4)-H(4B)	109.6(16)
C(5)-C(4)-H(4B)	109.6(16)
H(4A)-C(4)-H(4B)	108(2)
C(6)-C(5)-N(1)	112.39(16)
C(6)-C(5)-C(4)	112.22(17)
N(1)-C(5)-C(4)	107.57(16)
C(6)-C(5)-H(5A)	107.9(14)
N(1)-C(5)-H(5A)	107.6(15)
C(4)-C(5)-H(5A)	109.1(15)
C(7)-C(6)-C(5)	176.8(2)
C(6)-C(7)-C(8)	174.3(2)
C(13)-C(8)-C(9)	118.54(18)
C(13)-C(8)-C(7)	122.48(18)
C(9)-C(8)-C(7)	118.97(18)
C(10)-C(9)-C(8)	120.50(18)
C(10)-C(9)-H(9A)	122.9(17)
C(8)-C(9)-H(9A)	116.6(17)
C(9)-C(10)-C(11)	121.30(19)
C(9)-C(10)-H(10A)	118.5(16)
C(11)-C(10)-H(10A)	120.2(16)
C(10)-C(11)-C(12)	117.89(19)
C(10)-C(11)-C(14)	121.39(19)
C(12)-C(11)-C(14)	120.72(18)
C(13)-C(12)-C(11)	121.16(19)
C(13)-C(12)-H(12A)	118.8(17)
C(11)-C(12)-H(12A)	120.0(17)
C(12)-C(13)-C(8)	120.59(19)
C(12)-C(13)-H(13A)	116.9(17)
C(8)-C(13)-H(13A)	122.5(18)
C(15)-C(14)-C(19)	117.95(19)
C(15)-C(14)-C(11)	121.79(18)
C(19)-C(14)-C(11)	120.24(19)
C(16)-C(15)-C(14)	120.7(2)
C(16)-C(15)-H(15A)	123.4(18)

C(14)-C(15)-H(15A)	115.7(17)
C(17)-C(16)-C(15)	120.3(2)
C(17)-C(16)-H(16A)	119.2(17)
C(15)-C(16)-H(16A)	120.4(17)
C(18)-C(17)-C(16)	119.4(2)
C(18)-C(17)-H(17A)	124.4(17)
C(16)-C(17)-H(17A)	116.1(17)
C(17)-C(18)-C(19)	120.7(2)
C(17)-C(18)-H(18A)	120(2)
C(19)-C(18)-H(18A)	119(2)
C(18)-C(19)-C(14)	120.9(2)
C(18)-C(19)-H(19A)	122.5(18)
C(14)-C(19)-H(19A)	116.6(18)
C(25)-C(20)-C(21)	120.87(19)
C(25)-C(20)-S(1)	118.79(16)
C(21)-C(20)-S(1)	120.18(17)
C(22)-C(21)-C(20)	118.6(2)
C(22)-C(21)-H(21A)	123.4(16)
C(20)-C(21)-H(21A)	118.1(16)
C(23)-C(22)-C(21)	121.3(2)
C(23)-C(22)-H(22A)	120.9(18)
C(21)-C(22)-H(22A)	117.7(18)
C(22)-C(23)-C(24)	118.8(2)
C(22)-C(23)-C(26)	120.8(2)
C(24)-C(23)-C(26)	120.4(2)
C(25)-C(24)-C(23)	121.3(2)
C(25)-C(24)-H(24A)	118.7(18)
C(23)-C(24)-H(24A)	120.0(18)
C(24)-C(25)-C(20)	119.1(2)
C(24)-C(25)-H(25A)	119.8(16)
C(20)-C(25)-H(25A)	121.0(17)
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C) 109.5

Table 4.7 Anisotropic displacement parameters (Å^2 x 10^3) for erj39.[114]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	14(1)	31(1)	16(1)	4(1)	0(1)	-4(1)
O(1)	22(1)	21(1)	27(1)	-1(1)	7(1)	-2(1)
O(2)	15(1)	59(1)	24(1)	-2(1)	3(1)	2(1)
O(3)	28(1)	36(1)	24(1)	10(1)	-7(1)	-14(1)
N(1)	13(1)	24(1)	16(1)	0(1)	0(1)	0(1)
C(1)	19(1)	21(1)	22(1)	-1(1)	0(1)	4(1)
C(2)	21(1)	23(1)	24(1)	-6(1)	2(1)	1(1)
C(3)	18(1)	25(1)	18(1)	-4(1)	0(1)	-1(1)
C(4)	17(1)	24(1)	17(1)	3(1)	-3(1)	0(1)
C(5)	15(1)	17(1)	16(1)	2(1)	0(1)	1(1)
C(6)	15(1)	17(1)	19(1)	0(1)	-1(1)	1(1)
C(7)	15(1)	17(1)	19(1)	-2(1)	-1(1)	0(1)
C(8)	15(1)	19(1)	16(1)	-1(1)	0(1)	-1(1)
C(9)	19(1)	20(1)	19(1)	-3(1)	3(1)	4(1)
C(10)	21(1)	17(1)	20(1)	1(1)	1(1)	4(1)
C(11)	16(1)	19(1)	15(1)	-2(1)	-1(1)	0(1)
C(12)	20(1)	16(1)	18(1)	-4(1)	2(1)	2(1)
C(13)	20(1)	16(1)	19(1)	1(1)	1(1)	1(1)
C(14)	16(1)	21(1)	15(1)	-1(1)	-1(1)	5(1)
C(15)	28(1)	22(1)	19(1)	-2(1)	1(1)	2(1)
C(16)	35(1)	28(1)	23(1)	5(1)	3(1)	2(1)
C(17)	29(1)	42(1)	15(1)	2(1)	0(1)	7(1)
C(18)	34(1)	33(1)	19(1)	-10(1)	-2(1)	9(1)
C(19)	30(1)	21(1)	20(1)	-3(1)	-2(1)	5(1)
C(20)	13(1)	26(1)	17(1)	3(1)	-3(1)	-4(1)

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[114] The anisotropic displacement factor exponent takes the form: -2□^{2} [h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}]

C(21)	18(1)	26(1)	23(1)	1(1)	-2(1)	2(1)
C(22)	21(1)	29(1)	26(1)	10(1)	-5(1)	-2(1)
C(23)	18(1)	41(1)	16(1)	3(1)	-5(1)	-11(1)
C(24)	21(1)	32(1)	21(1)	-5(1)	-3(1)	-2(1)
C(25)	20(1)	21(1)	22(1)	-1(1)	-5(1)	-2(1)
C(26)	32(1)	63(2)	18(1)	6(1)	-4(1)	-11(1)

Table 4.8 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for erj39.

	x	y	z	U(eq)
H(26A)	3820	3129	6387	57
H(26B)	3459	1710	6270	57
H(26C)	5327	2159	6397	57
H(1)	9840(40)	3080(20)	8989(11)	22(7)
H(1A)	4260(30)	3780(20)	9094(10)	20(6)
H(1B)	5790(40)	3560(30)	8698(12)	31(7)
H(2A)	6700(40)	4720(30)	9439(11)	29(7)
H(2B)	5890(30)	3740(20)	9845(10)	16(6)
H(3A)	8850(30)	3380(20)	9787(10)	17(6)
H(4A)	7310(40)	1550(30)	9847(12)	31(7)
H(4B)	8930(40)	1360(30)	9477(11)	27(7)
H(5A)	6360(30)	510(20)	9144(9)	11(5)
H(9A)	7560(40)	3350(20)	7513(11)	27(7)
H(10A)	8310(40)	3740(20)	6613(11)	25(7)
H(12A)	10530(40)	380(20)	6577(11)	24(7)
H(13A)	9750(30)	60(20)	7419(10)	20(6)
H(15A)	10180(40)	4090(30)	5970(11)	28(7)
H(16A)	11240(40)	4360(30)	5096(11)	27(7)
H(17A)	11470(40)	2790(30)	4493(12)	39(8)
H(18A)	10700(40)	850(30)	4855(14)	45(9)
H(19A)	9790(40)	530(30)	5705(11)	28(7)
H(21A)	2470(30)	3430(20)	8161(11)	20(6)

H(22A)	2840(40)	3740(30)	7238(12)	32(8)
H(24A)	4770(40)	330(30)	7089(12)	39(8)
H(25A)	4360(30)	10(20)	7985(10)	22(6)

Table 4.9 Torsion angles [°] for erj39.

O(3)-S(1)-N(1)-C(1)	-179.52(15)
O(2)-S(1)-N(1)-C(1)	-51.45(17)
C(20)-S(1)-N(1)-C(1)	63.95(17)
O(3)-S(1)-N(1)-C(5)	37.64(17)
O(2)-S(1)-N(1)-C(5)	165.71(15)
C(20)-S(1)-N(1)-C(5)	-78.89(16)
C(5)-N(1)-C(1)-C(2)	-60.7(2)
S(1)-N(1)-C(1)-C(2)	155.18(14)
N(1)-C(1)-C(2)-C(3)	57.2(2)
C(1)-C(2)-C(3)-O(1)	67.5(2)
C(1)-C(2)-C(3)-C(4)	-54.4(2)
O(1)-C(3)-C(4)-C(5)	-65.4(2)
C(2)-C(3)-C(4)-C(5)	53.5(2)
C(1)-N(1)-C(5)-C(6)	-66.4(2)
S(1)-N(1)-C(5)-C(6)	77.35(19)
C(1)-N(1)-C(5)-C(4)	57.6(2)
S(1)-N(1)-C(5)-C(4)	-158.64(14)
C(3)-C(4)-C(5)-C(6)	71.0(2)
C(3)-C(4)-C(5)-N(1)	-53.1(2)
C(13)-C(8)-C(9)-C(10)	1.6(3)
C(7)-C(8)-C(9)-C(10)	-177.08(19)
C(8)-C(9)-C(10)-C(11)	-0.2(3)
C(9)-C(10)-C(11)-C(12)	-0.9(3)
C(9)-C(10)-C(11)-C(14)	179.6(2)
C(10)-C(11)-C(12)-C(13)	0.6(3)
C(14)-C(11)-C(12)-C(13)	-179.85(19)
C(11)-C(12)-C(13)-C(8)	0.8(3)
C(9)-C(8)-C(13)-C(12)	-1.9(3)
C(7)-C(8)-C(13)-C(12)	176.74(19)
C(10)-C(11)-C(14)-C(15)	31.9(3)
C(12)-C(11)-C(14)-C(15)	-147.6(2)
C(10)-C(11)-C(14)-C(19)	-149.6(2)
C(12)-C(11)-C(14)-C(19)	30.9(3)
C(19)-C(14)-C(15)-C(16)	-1.8(3)

C(11)-C(14)-C(15)-C(16)	176.8(2)
C(14)-C(15)-C(16)-C(17)	0.4(4)
C(15)-C(16)-C(17)-C(18)	0.9(4)
C(16)-C(17)-C(18)-C(19)	-0.8(4)
C(17)-C(18)-C(19)-C(14)	-0.6(4)
C(15)-C(14)-C(19)-C(18)	1.8(3)
C(11)-C(14)-C(19)-C(18)	-176.7(2)
O(3)-S(1)-C(20)-C(25)	-23.0(2)
O(2)-S(1)-C(20)-C(25)	-154.06(17)
N(1)-S(1)-C(20)-C(25)	92.38(18)
O(3)-S(1)-C(20)-C(21)	161.57(17)
O(2)-S(1)-C(20)-C(21)	30.5(2)
N(1)-S(1)-C(20)-C(21)	-83.02(19)
C(25)-C(20)-C(21)-C(22)	-1.1(3)
S(1)-C(20)-C(21)-C(22)	174.15(17)
C(20)-C(21)-C(22)-C(23)	-0.8(3)
C(21)-C(22)-C(23)-C(24)	2.3(3)
C(21)-C(22)-C(23)-C(26)	-177.0(2)
C(22)-C(23)-C(24)-C(25)	-1.9(3)
C(26)-C(23)-C(24)-C(25)	177.4(2)
C(23)-C(24)-C(25)-C(20)	0.0(3)
C(21)-C(20)-C(25)-C(24)	1.5(3)
S(1)-C(20)-C(25)-C(24)	-173.84(16)

Table 4.10 Hydrogen bonds for erj39 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84(3)	1.98(3)	2.804(2)	169(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

Chapter Five

Synthesis of Vicinal Carbocycles by Intramolecular Nickel-Catalyzed Conjunctive Cross-Electrophile Coupling Reaction

5.1 Introduction

Nickel-catalyzed conjunctive cross-electrophile coupling (XEC) reactions allow for the rapid and efficient synthesis of highly complex scaffolds, beginning with two electrophilic partners and an olefin (Scheme 5.1)[1,2,3] These reactions pose major challenges in achieving high levels of stereo-, regio-, and chemoselectivity, particularly when performing three-component reactions (Scheme 5.1a). Building upon the mechanistic insights from XEC reactions,[4,5] several strategies have been established to achieve selectivity, including mechanistic differentiation of the

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[1] Portions of this chapter have been submitted for publication.

[2] For reviews of nickel catalysis, see: (a) Modern Organonickel Chemistry; Tamaru, Y., Ed.; Wiley-VCH: Weinheim; **2005**. (b) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299–309. (c) Nickel Catalysis in Organic Synthesis: Methods and Reactions; Ogoshi, S., Ed.; Wiley, **2020**.

[3] For reviews of conjunctive XC and XEC reactions, see: (a) Derosa, J.; Tran, V. T.; van der Puyl, V. A.; Engle, K. M. *Aldrichim. Acta* **2018**, *51*, 21– 32. (b) Zhang, J.-S.; Liu, L.; Chen. T.; Han, L.-B. *Chem. Asian J.* **2018**, *13*, 2277–2291. (c) Qi, X.; Diao, T. *ACS Catal.* **2020**, *10*, 8542– 8556. (d) Derosa, J.; Apolinar, O.; Kang, T.; Tran, V. T.; Engle, K. M. *Chem. Sci.* **2020**, *11*, 4287– 4296. (e) Badir, S. O.; Molander, G. A. *Chem.* **2020**, *6*, 1327–1339. (f) Tu, H.-Y.; Zhu, S.; Qing, F.-L.; Chu, L. *Synthesis* **2020**, *52*, 1346–1356. (g) Ping, Y.; Kong, W. *Synthesis* **2020**, *52*, 979–992. (h) Wickham, L. M.; Giri, R. *Acc. Chem. Res.* **2021**, *54*, 3415–3437. (i) Gao, P.; Niu, Y.-J.; Yang, F.; Guo, L.-N.; Duan, X.-H. *Chem. Commun.* **2022**, *58*, 730–746.

[4] For reviews of XEC reactions, see: (a) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. *Chem. Eur. J.* **2014**, *20*, 6828–6842. (b) Everson, D. A.; Weix D. J. *J. Org. Chem.* **2014**, *79*, 4793–4798. (c) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front.* **2015**, *2*, 1411–1421. (c) Goldfogel, M; Huang, L. Weix, D. J. Cross-Electrophile Coupling. In *Nickel Catalysis in Organic Synthesis*; Ogoshi, S., Ed.; Wiley, **2020**; 183– 222. (f) Richmond, E.; Moran, J. *Synthesis* **2019**, *50*, 499–513. (h) Campeau, L.-C.; Hazari, N. *Organometallics* **2019**, *38*, 3–35. (i) Hewitt, K. A.; Lin, P. C.; Raffman, E. T. A.; Jarvo, E. R. *Comprehensive Organometallic Chemistry IV.* 2021. DOI: 10.1016/B978-0-12-820206-7.00092-5.

[5] For a discussion of the mechanism of the conjunctive XEC reaction, see: (a) Lin, Q.; Diao, T. *J. Am. Chem. Soc.* **2019**, *141*, 17937–17948. (b) Diccianni, J.; Lin, Q.; Diao, T. *Acc. Chem. Res.* **2020**, *53*, 906–919.

electrophiles or employing an excess of one reagent.[6,7,8,9] In addition, the use of directing groups can also favor regio- and chemoselective reactions and allow for the use of unactivated conjunctive reagents.[10] An additional strategy, tethering one electrophile and alkene together to afford a two-component reaction, also significantly addresses the selectivity challenges and at the same time constructs cyclic fragments (Scheme 5.1b).[11,12,13] We envisioned a fully intramolecular nickel-catalyzed conjunctive XEC reaction to provide vicinal ring systems (Scheme 5.1c).[14] This

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[6] For representative examples of conjunctive XEC reactions in which an activated alkene is used, see: (a) García-Domínguez, A.; Li, Z.; Nevado, C. *J. Am. Chem. Soc.* **2017**, *139*, 6835– 6838. (b) Wang, L.; Wang, C. *Org. Lett.* **2020**, *22*, 8829–8835. (c) Zhao, Q.-W.; Yang, Z.-F.; Fu, X.-P.; Zhang, X. *Synlett* **2021**, *32*, 1565–1569. (d) Wang, X.-X.; Lu, X.; He, S.-J.; Fu, Y. *Chem. Sci.* **2020**, *11*, 7950–7956. (e) Feng, X.; Guo, L.; Zhu, S.; Chu, L. *Synlett* **2021**, *32*, 1519–1524.

[7] For a representative example of conjunctive XEC reactions with terminal alkenes see: Shu, W.; García-Domínguez, A.; Quirós, M. T.; Mondal, R.; Cárdenas, D. J.; Nevado, C. *J. Am. Chem. Soc*. **2019**, *141*, 13812–13821.

[8] For lead examples of enantioselective conjunctive XEC reactions, see: (a) Anthony, D.; Lin, Q.; Baudet, J.; Diao, T. *Angew. Chem., Int. Ed.* **2019**, *58*, 3198–3202. (b) Wei, X.; Shu, W.; García-Domínguez, A.; Merino, E.; Nevado, C. *J. Am. Chem. Soc.* **2020**, *142*, 13515–13522. (c) Tu, H.-Y.; Wang, F.; Huo, L.; Li, Y.; Zhu, S.; Zhao, X.; Li, H.; Qing, F.-L.; Chu, L. *J. Am. Chem. Soc.* **2020**, *142*, 9604–9611.

[9] For lead examples of conjunctive XEC reactions that employ dual photoredox and nickel-catalysis, see: (a) Guo, L.; Tu, H.-Y.; Zhu, S.; Chu, L.; *Org. Lett.* **2019**, *21*, 4771–4776. (b) García-Domínguez, A.; Mondal, R.; Nevado, C.; *Angew. Chem. Int. Ed.* **2019**, *58*, 12286–12290. (c) Qian, P.; Guan, H.; Wang, Y.-E.; Lu, Q.; Zhang, F.; Xiong, D.; Walsh, P. J.; Mao, J. *Nat. Comm.* **2021**, *12*, 6613.

[10] For lead examples of conjunctive XEC reactions with directing groups, see: (a) Yang, T.; Chen, X.; Rao, W.; Koh, M. J. *Chem* **2020**, *6*, 738–751. (b) Yang, T.; Jiang, Y.; Luo, Y.; Lim, J. J. H.; Lan, Y.; Koh, M. J. *J. Am. Chem. Soc.* **2020**, *142*, 21410–21419. (c) Pan, R.; Shi, C.; Zhang, D.; Tian, Y.; Guo, S.; Yao, H.; Lin, A. *Org. Lett.* **2019**, *21*, 8915–8920. (d) Zhao, X.; Tu, H.-Y.; Guo, L.; Zhu, S.; Qing, F.-L.; Chu, L. *Nat. Commun.* **2018**, *9*, 3488.

[11] For lead examples of two component conjunctive XEC reactions where the C(sp^2) electrophile is tethered to the alkene, see: (a) Yan, C.-S.; Peng, Y.; Xu, X.-B.; Wang, Y.-W. *Chem. Eur. J.* **2012**, *18*, 6039–6048. (b) Wang, K.; Ding, Z.; Zhou, Z.; Kong, W. *J. Am. Chem. Soc.* **2018**, *140*, 12364–12368. (c) Jin, Y.; Wang, C. *Angew. Chem., Int. Ed.* **2019**, *58*, 6722–6726. (d) Tian, Z.-X.; Qiao, J.-B.; Xu, G.-L.; Pang, X.; Qi, L.; Ma, W.-Y.; Zhao, Z.-Z.; Duan, J.; Du, Y.-F.; Su, P.; Liu, X.-Y.; Shu, X.-Z. *J. Am. Chem. Soc.* **2019**, *141*, 7637–7643. (e) Ma, T.; Chen, Y.; Li, Y.; Ping, Y.; Kong, W. *ACS Catal.* **2019**, *9*, 9127–9133 (f) Fan, P.; Lan, Y.; Zhang, C.; Wang, C. *J. Am. Chem. Soc.* **2020**, *142*, 2180–2186. (g) Yang, J.; Yang, L.; Gu, J.; Shuai, L.; Wang, H.; Ouyang, Q.; Li, Y.-L.; Liu, H.; Gong, L. *Org. Lett.* **2022**, *24*, 2376–2380.

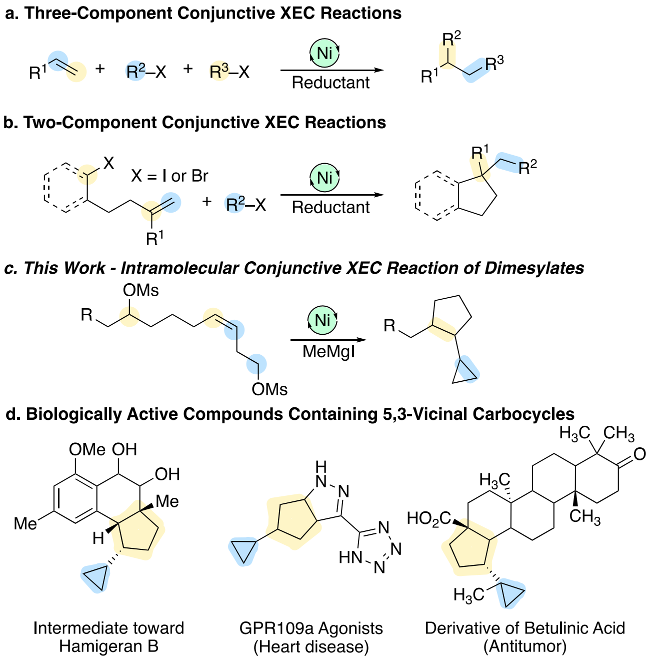
[12] For lead examples of two component conjunctive XEC reactions where the C(sp^3) electrophile is tethered to the alkene, see: (a) ref. 11 a. (b) Yin, H.; Zhoa, C.; You, H.; Lin, K.; Gong, H. *Chem. Commun.* **2012**, *48*, 7034–7036. (c) Peng, Y.; Xu, X.-B.; Xiao, J.; Wang, Y.-W. *Chem. Commun.* **2014**, *50*, 472–474. (d) Kuang, Y.; Wang, X.; Anthony, D.; Diao, T. *Chem. Commun.* **2018**, *54*, 2558–2561. (f) Weires, N. A.; Slutskyy, Y.; Overman, L. E. *Angew. Chem. Int. Ed.* **2019**, *58*, 8561–8565.

[13] For lead examples of two component conjunctive XEC reactions where the two electrophiles are tethered together, see: Wang, H.; Huang, H.; Gong, C.; Diao, Y.; Chen, J.; Wu, S.-H.; Wang, L. *Org. Lett.* **2022**, *24*, 328–333.

[14] For examples of fully intramolecular conjunctive XEC reactions, see: (a) ref. 11a. (b) Xiao, J.; Wang, Y.-W.; Peng, Y. *Synthesis* **2017**, *49*, 3576–3581. (c) Peng, Y.; Xiao, J.; Xu, X.-B.; Duan, S.-M.; Ren, L.; Shao, Y.-L.; Wang, Y.-W. *Org. Lett.* **2016**, *18*, 5170–5173. (d) Xiao, J.; Cong, X.-W.; Yang, G.-Z.; Wang, Y.-W.; Peng, Y. *Org. Lett.* **2018**, *20*, 1651–1654. (e) Xiao, J.; Wang, Y.-W.; Qiu, Z.-P.; Peng, Y. *Synlett* **2021**, *32*, 1662–1664.

manifold engages two unactivated electrophiles and an internal olefin, and generates two carbocycles in a single step.

Scheme 5.1 Previous Work in Conjunctive XEC Reactions and Medicinally Relevant Vicinal Carbocycles



Vicinal 3,5-carbocyclic motifs are present in a number of biologically active compounds and natural products.[15,16,17,18] In addition, cyclopropanes themselves a common moieties in

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[15] For lead reviews on cascade reactions in total synthesis, see: (a) Nicolaou, K. C.; Edmonds, D. J.; Bulger, P. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 7134–7186. (b) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993–3009. (c) Sebren, L. J.; Devery, J. J.; Stephenson, C. R. J. *ACS Catal.* **2014**, *4*, 703–716. (d) Yu, C.; Huang, H.; Sheng, C.; Wang, W. Designing Efficient Cascade Reactions in Drug Discovery. In *Green Chemistry in Drug Discovery*; Richardson, P. F., Ed.; **2022**; 213–235.

[16] (a) For the synthesis of the intermediate to Hamigeran B, see: Taber, D. F.; Tan, W. *J. Org. Chem.* **2008**, *73*, 7560–7564. (b) For activity of Hamigeran B, see: Wellington, K. D.; Cambie, R. C.; Rutledge, P. S.; Bergquist, P. C. *J. Nat. Prod.* **2000**, *63*, 79–85.

[17] For the synthesis and biological activity of the GPR109a agonist, see: Imbriglio, J. E.; Chang, S.; Liang, R.; Raghavan, S.; Schmidt, D.; Smenton, A.; Tria, S.; Schrader, T. O.; Jung, J.-K.; Esser, C.; Taggart, A. K. P.; Cheng, K.; Carballo-Jane, E.; Waters, M. G.; Tata, J. R.; Colletti, S. L. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2121–2124.

[18] For the synthesis and biological activity of the derivative of betulinic Acid, see: Symon, A. V.; Veselova, N. N.; Kaplun, A. P.; Vlasenkova, N. K.; Fedorova, G. A.; Lyutik, A. I.; Gerasimova, G. K.; Shvets, V. I. *Rus. J. Bioorg, Chem.* **2005**, *31*, 286–291.

medicinal chemistry (Scheme 5.1d).[19] We sought to prepare vicinal 3,5-carbocycles by a nickel-catalyzed conjunctive XEC reaction, where a single cascade reaction would construct both carbocyclic moieties. In this manuscript, we report an intramolecular nickel-catalyzed conjunctive XEC reaction (Scheme 5.1c). The mechanistic framework of this reaction builds on our laboratory's development of intramolecular XEC reactions of 1,3-dimesylates.[20] In addition, it compliments traditional radical reactions that initiate at alkyl halides and cascade forward to forge multiple ring systems.[21,22] We provide preliminary mechanistic experiments to demonstrate that this reaction likely involves radical intermediates.

5.2 Results and Discussion

5.2.1 Optimization and Scope of the Conjunctive XEC Reaction

To begin, we designed a model substrate, dimesylate **5.1**, that contained two alkyl mesylates and an internal olefin. Based on previously developed cross-coupling and XEC reactions in our laboratory, we hypothesized that the secondary mesylate would be activated by the nickel catalyst and cascade forward through a 5-exo-trig cyclization.[20,23,24] The proposed reaction would terminate by 3-exo-tet cyclization to afford the desired vicinal carbocycle **5.2**. First, we examined

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[19] For the biological activity of cyclopropanes, see: (a) Talele, T. *J. Med. Chem.* **2016**, *59*, 8712–8756. (b) Salaün, J. Cyclopropane Derivatives and their Diverse Biological Profile. *In Small Ring Compounds in Organic Synthesis VI*. A. de Meijere, Ed. **2000**. 1– 67.

[20] Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen, P.-P.; Hong, X.; Jarvo, E. R. *J. Am. Chem. Soc.* **2020**, *142*, 5017–5023.

[21] For lead reviews on domino or cascade reactions, see: (a) Ikeda, S.-I. *Acc. Chem. Res.* **2000**, *33*, 511–519. (c) Tietze, L. F. Domino Reactions: Concepts for Efficient Organic Synthesis. Wiley-VCH: Weinheim, **2014**. (d) Malacria, M. *Chem. Rev.* **1996**, *96*, 289–306. (e) Liu, Z.-Q. Radical Cascade Reactions. In *Free Radicals: Fundamentals and Applications in Organic Synthesis 2*; Georg Thieme Verlag KG: Stuttgart, **2021**. (f) Jahn, U. *Top. Curr. Chem.* **2011**, 323–451. (g) Zhang, G.; Liu, Y.; Zhao, J.; Li, Y.; Zhang, Q. *Sci. China Chem.* **2019**, *62*, 1476–1491. (h) Romero, K. J.; Galliher, M. S.; Pratt, D. A.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2018**, *47*, 7851–7866. (i) For a review on polyene cyclizations in the synthesis of natural products, see: Yoder, R. A.; Johnston, J. N. *Chem. Rev.* **2005**, *105*, 4730–4756. (j) For a review on "zipper"-type cascade reactions, see: Negishi, E.-I. *Pure & Appl. Chem.* **1992**, *64*, 323–334.

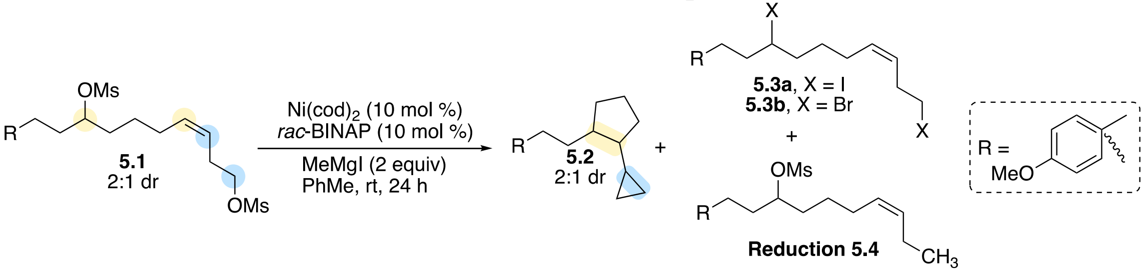
[22] For reviews, see: (a) Plesniak, M. P.; Huang, H.-M.; Procter, D. J. *Nat. Rev.* **2017**, *1*, 0077. (b) Huang, H.-M.; Garduño-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, *48*, 4626–4638.

[23] Harris, M. R.; Konev, M. O.; Jarvo, E. R. *J. Am. Chem. Soc.* **2014**, *136*, 7825–7828.

[24] Dimesylate **5.1** was prepared in five steps from commercially available aryl iodides. See Experimental Section **5.4** for more information.

the previously developed conditions for the synthesis of cyclopropanes from 1,3-dimesylates, employing Ni(cod)$_2$, racemic BINAP and methylmagnesium iodide. We were delighted to observe the desired product in 85% yield (Table 5.1, entry 1). Next, to confirm that a *rac*-BINAP ligated nickel-catalyst was responsible for the conjunctive XEC reaction, we performed the reaction without ligand and a decreased yield of 29% was observed (entry 2).

Table 5.1 Cascade Reaction Optimization



Entry	Deviation From Standard Conditions	Recovered 5.1 (%)[a]	Yield 5.2 (%)[a]	Dihalide 5.3 (%)[a]	Reduction 5.4 (%)[a]
1	**None**	**0**	**85**	**0**	**0**
2	No Ligand	0	29	18	12
3	dppm instead of *rac*-BINAP	0	45	0	0
4	BPhen instead of *rac*-BINAP	0	82	22	0
5	bipy instead of *rac*-BINAP	0	72	0	0
6	No Nickel or ligand	0	0	86	0
7[b]	Zn and NaI instead of MeMgI	15	<5	17	23
8[c]	Zn and MgBr$_2$ instead of MeMgI	0	<5	54	19
9[d]	Mn and NaI/TMSCl instead of MeMgI	38	0	0	11
10[e]	TDAE and NaI instead of MeMgI	22	<5	0	12

[a]Yields determined by ^{1}H NMR compared to PhTMS as an internal standard. [b]2 equiv of Zn and 8 equiv of NaI
[c]2 equiv of Zn and MgBr$_2$. [d]2 equiv of Mn and NaI and 1 equiv of TMSCl. [e]2 equiv of TDAE and NaI

With these results, we then evaluated a series of ligands. While all ligands provided the desired product, *rac*-BINAP proved to be the optimal ligand (compare entry 1 v. entries 3–5). In the absence of the nickel catalyst and ligand, only diiodide (**5.3a**) was observed in an 86% yield (entry 6). This result is consistent with formation of diiodides in situ as reactive intermediates.[20,25] It also confirms that the nickel catalyst is necessary for the conjunctive XEC reaction to occur.

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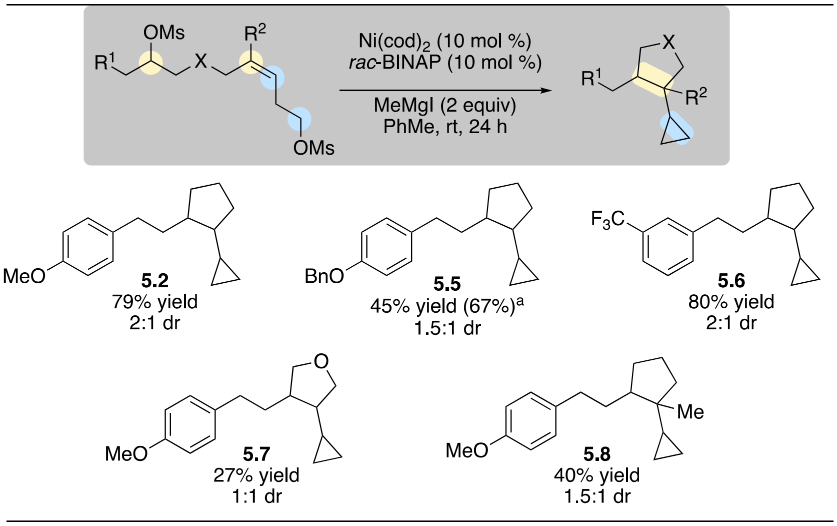
[25] For examples of nickel-catalyzed reactions that produce alkyl halides, see: (a) Prisnsell, M. R.; Everson, D. A.; Weix, D. J. *Chem. Commun.* **2010**, *46*, 5743–5745. (b) Do, H. Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc*. **2013**, *135*, 16288−16291. (c) Liang, Z.; Xue, W.; Lin, K.; Gong, H. *Org. Lett.* **2014**, *16*, 5620−5623. (e) Duan, J.; Du, Y.-F.; Pang, X.; Shu, X.-Z. *Chem. Sci*. **2019**, *10*, 8706−8712.

Finally, we evaluated alternative reductants and halide sources, including zinc, manganese, and TDAE, and found that the Grignard reagent provided the highest yield (entries 7–10).

With the optimal reaction conditions in hand, we investigated the scope of the cascade reaction (Scheme 5.2). We were delighted to observe that both electron-donating and electron-withdrawing substituents were well tolerated under our standard reaction conditions (**5.2**, **5.5**, **5.6**). The cascade reaction also allowed for synthesis of a substituted tetrahydrofuran (**5.7**). Finally, a trisubstituted alkene was subjected to the reaction conditions and afforded adjacent quaternary and tertiary centers (**5.8**), albeit in moderate yield.

Scheme 5.2 Conjunctive XEC Reaction Scope

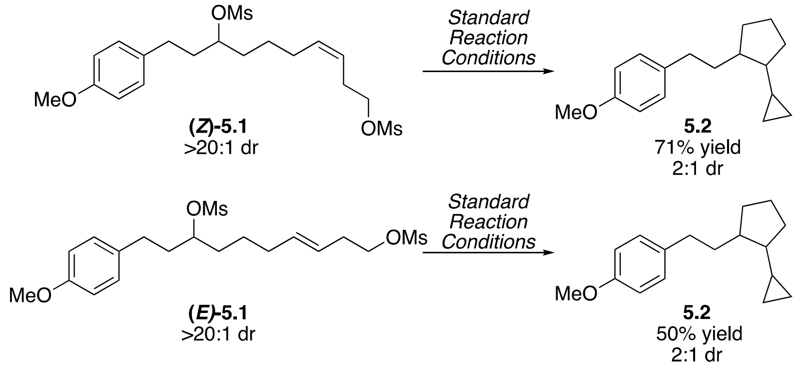


[a] Yield in Parentathesis is ^{1}H NMR yield compared to PhTMS as an internal standard

5.2.2 Investigation of the Mechanism of the Conjunctive XEC Reaction

Next, we turned our attention towards determining key features of the mechanism of this conjunctive XEC reaction. We hypothesized that the mechanism could proceed via two different pathways, involving either migratory insertion of an organonickel intermediate or a radical cyclization. Performing the cascade reaction with single olefin isomer of dimesylate **5.1** provides a probe for radical versus organometallic cyclization (Scheme 5.3).[26] Migratory insertion is a stereospecific process,[27] and would be expected to provide a single diastereomer of cyclopentane **5.2**. In contrast, radical cyclization would be stereoablative and lead to formation of both diastereomers. We separated the alkene diastereomers, employing silver impregnated silica gel,[28] and subjected them separately to the cascade reaction. We observed that both (*E*)- and (*Z*)-**5.1** produced the same major diastereomer in 2:1 dr. This result is consistent with a radical exo-trig cyclization and not migratory insertion of an organonickel species.

Scheme 5.3 Control Reaction with Single Alkene Diastereomer



We aimed to further corroborate the proposed radical exo-trig cyclization by examining reactions of diiodide 3a. First, to confirm that diiodide was a competent intermediate in the catalytic cycle, we subjected **5.3a** to the standard reaction conditions and observed product **5.2** in 73% yield (Table 5.2, entry 1). Therefore, we propose that dimesylate **5.1** is converted to diiodide **5.3a** in situ, and this intermediate engages the nickel catalyst by halogen atom transfer (XAT).[29] If radical intermediates are operative, we should observe a decrease in yield with known radical

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[26] For a discussion of hybrid organometallic-radical mechanisms, see: Kwiatkowski, M. R.; Alexanian, E. J. *Acc. Chem. Res.* **2019**, *52*, 1134–1144. (b) Wang, K.; Kong, W. *Chin. J. Chem.* **2018,** *36*, 247–256.

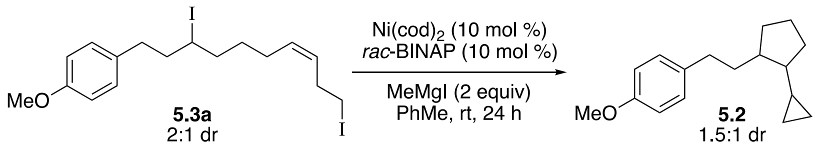
[27] (a) Heck, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6707–6714. (b) Hartwig, J. F. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books, 2010.

[28] B. M. Lawrence *J. Chromatog.* **1968**, *38*, 535–537.

[29] For discussion of the mechanism of halogen atom transfer, see: (a) Kehoe, R.; Mahadevan, M.; Manzoor, A.; McMurray, G.; Wienfield, P.; Baird, M. C.; Budzelaar, P. H. M. *Organometallics* **2018**, *37*, 2450–2467. (b) Diccianni, J. B.; Katigbak, J.; Hu, C.; Diao, T. T. *J. Am. Chem. Soc.* **2019**, *141*, 1788–1796. (c) See reference 20.

inhibitors. Indeed, when one equivalent of TEMPO was added to the standard reaction conditions, we observed a decrease in yield (entry 2). In addition, we hypothesized that radical initiators, such as SmI_2, should produce the desired carbocyclic system.[22] Upon subjecting diiodide to a reaction with freshly prepared SmI_2,[30] we were excited to observe the desired cascade product in 56% yield and as a 1.5:1 mixture of diastereomers (entry 3). These results are consistent with radical formation at one of the electrophilic centers and indicate that one or both cyclizations are radical mediated.

Table 5.2 Control Reactions with Diiodide **5.3a**



Entry	Deviation From Standard Conditions	Yield 5.2 (%)[a]
1	None	73
2	1 equiv of TEMPO added	48
3	SmI_2 and THF instead of Ni, ligand and MeMgI	56[b]

[a]Yield determined by ^1H NMR compared to PhTMS as an internal standard
[b]Isolated Yield

Finally, we aimed to understand which electrophile was activated first. Based on the selectivity of XAT reactions, we hypothesized that the reaction initiated at the secondary center.[20,22] However, we had observed the formation of reduction product **5.4** in the optimization studies (vide supra) and considered that the primary iodide may engage the nickel complex first. We designed the following competition experiment to investigate the order of events. We synthesized two mesylates: one with a 2° mesylate (**5.9**) and one with a 1° mesylate (**5.12**). In a competition experiment between dimesylate **5.1** and 2° mesylate (**5.9**), we observed a 1.5:1 ratio of products (Scheme 5.4a). However, in a similar competition experiment, now employing 1° mesylate (**5.12**), the product ratio observed was 2.6:1 (Scheme 5.4b). The 2° mesylate reacted at a

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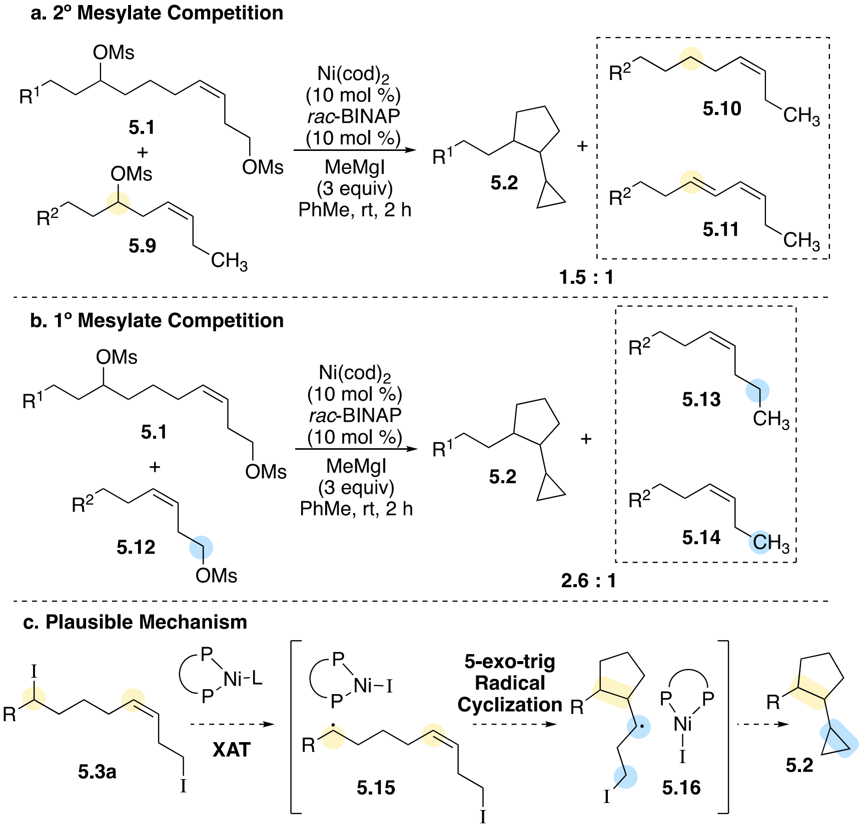
[30] For the preparation of SmI_2, see: Szostak, M.; Spain, M.; Procter, D. J. *J. Org. Chem.* **2012**, *77*, 3049–3059.

competitive rate compared to dimesylate **5.1** and demonstrated that the 2° mesylate reacted faster than the 1° mesylate. These results indicate that the productive pathway for the conjunctive XEC reaction initiates at the secondary center. This selectivity is consistent with previous observations that secondary alkyl halides react at a faster rate than primary halides with nickel catalysts.[20,29]

Scheme 5.4 Competition Experiment between Dimesylate **5.1** and 2° and 1° Mesylates **5.9** and **5.12**, and Proposed Reaction Mechanism.[31]



Based on the mechanistic experiments, we proposed the following plausible reaction mechanism (Scheme 5.4c). Beginning from diiodide **5.3a**, generated in situ, halogen atom transfer occurs at the secondary alkyl iodide to generate alkyl radical **5.15**. This secondary alkyl radical

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[31] R^1 = 4-MeO-C_6H_4, R^2 = 4-BnO-C_6H_4.

cyclizes to afford the cyclopentane ring **5.16**.[32] This radical cyclization is consistent with formation of a mixture of diastereomers from either cis- or trans-alkenes (vide supra). Following this step, radical or nickel-mediated 3-exo-tet cyclization would afford cyclopropane **5.2**. Both pathways lead to a nickel(II) complex, which is reduced by the Grignard reagent to regenerate the nickel(0) catalyst.[33]

5.3 Conclusions

In conclusion, we have developed a nickel-catalyzed cascade reaction for synthesis of 3,5-vicinal carbocyclic motifs. We have demonstrated the scope of the reaction to include electron donating and withdrawing groups. In addition, we have provided preliminary mechanistic experiments to demonstrate that alkyl iodides are likely generated in situ and that the cascade reaction likely proceeds through radical intermediates. Future work includes delineating the remaining steps of the reaction mechanism and development of related cascade reactions.

5.4 Experimental Details

5.4.1 General Procedures

All reactions were carried out under an atmosphere of N_2 when noted. All glassware was oven- or flame-dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM), methanol (MeOH), triethylamine (Et_3N), dimethylformamide (DMF), and toluene (PhMe) were degassed with Ar and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h)

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[32] For a nickel-catalyzed Heck reactions that proceed through radical cyclization and/or organonickel intermediates, see: (a) Kwiatkowski, M. R.; Alexanian, E. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 16857–16860. (b) Tang, S.; Liu, C.; Lei, A. *Chem. Commun.* **2013**, *49*, 2442–2444. (c) Liu, C.; Tang, S.; Liu, D.; Yuan, J.; Zheng, L.; Meng, L.; Lei, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 3638–3641. (d) Matsubara, R.; Gutierrez, A. C.; Jamison, T. F. *J. Am. Chem. Soc.* **2011**, *133*, 19020–19023. (e) Standley, E. A.; Jamison, T. F. *J. Am. Chem. Soc.* **2013**, *135*, 1585–1592.

[33] Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, Z.-Q.; Tollefson, E. J.; Erickson, L. W.; Taylor, B. L. H.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835–5855.

to remove H_2O.[34] All other solvents utilized were purchased "anhydrous" commercially, or purified as described. ^1H NMR spectra were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C), GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C), CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or AVANCE-600 (600 MHz ^1H, 150 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt), doublet of triplets (dt), triplet (t), triplet of doublets (td), triplet of triplets (tt), quartet (q), quartet of doublets (qd), quintet (quin), apparent singlet (as), apparent doublet (ad), apparent doublets of doublets (add), apparent doublet of triplets (adt), apparent doublet of quintets (adquin), apparent doublet of septets (adsept), apparent triplet (at), apparent triplet of doublets (atd), apparent triplet of triplets (att), apparent quartet (aq), apparent quartet of doublets (aqd), apparent quartet of triplets (aqt), apparent quintet of doublets (aquin d), apparent sextet (asext), apparent septet (asept), multiplet (m)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 ºC. Infrared (IR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR tip (neat) and are reported in terms of frequency of absorption (cm^{-1}). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp. Flash chromatography was performed using SiliaFlash F60 (40-63 µm, 60 Å) from SiliCycle. Automated chromatography was carried out on a Teledyne Isco CombiFlash Rf Plus. Melting points (M.p.) were obtained using a MelTemp melting point

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[34] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

apparatus and are uncorrected. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center.

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (–20 °C) under an atmosphere of N_2 and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored under N_2 atmosphere and used as received. The methylmagnesium iodide was titrated with iodine prior to use.[35] All other chemicals were purchased commercially and used as received, unless otherwise noted.

5.4.2 Conjunctive XEC Reaction Procedures

5.4.2.1 Method A: Nickel-Catalyzed Conjunctive XEC Reaction

In a glovebox, an oven-dried 7 mL dram vial equipped with a stir bar was charged with dimesylate (1.0 equiv), $Ni(cod)_2$ (10. mol %), *rac*-BINAP (10. mol %) and PhMe (0.20 M in substrate). A solution of MeMgI in Et_2O (2.0 equiv) was then added dropwise via syringe. After 24 h, the reaction vial was removed from the glovebox, quenched with MeOH, filtered through a plug of silica gel eluting with Et_2O, and concentrated in vacuo. Phenyltrimethylsilane (PhTMS; 8.6 µL, 50. µmol) was added and the yield was determined by ^{1}H NMR based on comparison to PhTMS as internal standard before purification by column chromatography.

To remove olefin by-products resulting from β-hydride elimination, a Sharpless asymmetric dihydroxylation was performed.[36] To a flame-dried 7-mL dram vial was added AD-mix-β (1.4 g/mmol of substrate). The flask was sealed with a septum cap and placed under an atmosphere of N_2. Then *t*-BuOH (0.50 mL) and H_2O (0.50 mL) were added via syringe. The vial was cooled to 0 ºC and then unpurified reaction mixture was added dropwise as a solution in *t*-

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[35] Krasoviskiy, A.; Knochel, P. *Synthesis*, **2006**, *5,* 890–891.

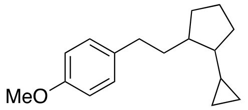
[36] (a) For the orginal report of the asymmetric dihydroxylation, see: Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroeder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110,* 1968–1970. (b) For the procedure that was employed, see: Holl, K.; Schepmann, D.; Daniliuc, C. G.; Wünsch, B. *Tetrahedron Asymmetry*, **2014**, *25*, 268–277.

BuOH (0.50 mL) and H_2O (0.5 mL) via syringe. The mixture was allowed to stir at 0 ºC for 24 h. To quench, saturated aq. $Na_2S_2O_3$ (1.0 mL) was added and the mixture was allowed to warm to rt and stir for 1 h. Then the mixture was transferred to a separatory funnel, and the organic layer was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo.

5.4.2.2 Preparation of Grignard Reagent

Under a N_2 atmosphere, a three-necked flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was charged with magnesium turnings (1.1 g, 45 mmol, 1.5 equiv). The flask and magnesium turnings were then flame-dried under vacuum and the flask was back-filled with N_2. Anhydrous Et_2O (7.0 mL) and a crystal of iodine (ca. 2.0 mg) were added to the flask. Freshly distilled iodomethane (1.9 mL, 31 mmol, 1.0 equiv) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature then filtered through the fritted Schlenk filter into a Schlenk flask under N_2 atmosphere. The magnesium turnings were washed with Et_2O (2 x 1.0 mL) then the Schlenk flask was sealed, removed, and placed under an N_2 atmosphere. The resulting methylmagnesium iodide was typically between 2.4 and 3.0 M as titrated by Knochel's method[35] and could be stored, sealed under N_2 atmosphere or in a glovebox, for up to 4 weeks.

5.4.3 Characterization Data for Conjunctive XEC Reaction Products



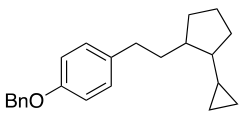
1-(2-(2-cyclopropylcyclopentyl)ethyl)-4-methoxybenzene (5.2) The following amounts of reagents were used: dimesylate **5.1** (61 mg, 0.14 mmol, 1.0 equiv), $Ni(cod)_2$ (3.9 mg, 14 µmol, 10. mol %), *rac*-BINAP (8.7 mg, 14 µmol, 10 mol %), MeMgI (0.11 mL, 0.28 mmol, 2.0 equiv, 2.5

M in Et_2O), PhMe (0.70 mL), AD-mix-β (0.20 g, 1.4 g/mmol of dimesylate), *t*-BuOH (0.50 mL), and H_2O (0.50 mL). Purification by column chromatography (100% hexanes) afforded the title compound as a clear and colorless oil (24 mg, 0.10 mmol, 71% yield, 2:1 dr). The dr was determined by the integration of resonances attributed to the aromatic carbons in ^{13}C NMR. For clarity, the ^1H and ^{13}C data are tabulated individually.

TLC R_f = 0.7 (5% EtOAc/hexanes, CAM Stain); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{17}H_{24}O$, 244.1827; found 244.1831.

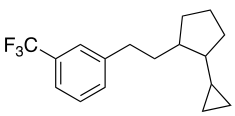
Major Diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.08–6.98 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 3.70 (d, *J* = 1.6 Hz, 3H), 2.60–2.38 (m, 2H), 1.92–1.80 (m, 1H), 1.79–1.56 (m, 2H), 1.55–1.37 (m, 3H), 1.38–1.00 (m, 3H), 0.94–0.68 (m, 1H), 0.53–0.43 (m, 1H), 0.37 (ddq, *J* = 21.2, 8.5, 4.3 Hz, 1H), 0.26 (dtt, *J* = 22.5, 8.9, 4.7 Hz, 1H), 0.05 (tq, *J* = 9.4, 4.6 Hz, 1H), -0.10 (tq, *J* = 9.5, 4.6 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.7, 135.6, 129.3 (2C), 113.8 (2C), 55.4, 48.5, 43.1, 34.6, 33.5, 31.8, 30.7, 23.0, 11.8, 5.5, 3.0.

Minor Diastereomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.08–6.98 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 3.70 (d, *J* = 1.6 Hz, 3H), 2.60–2.38 (m, 2H), 1.92–1.80 (m, 1H), 1.79–1.56 (m, 2H), 1.55–1.37 (m, 3H), 1.38–1.00 (m, 3H), 0.94–0.68 (m, 1H), 0.53–0.43 (m, 1H), 0.37 (ddq, *J* = 21.2, 8.5, 4.3 Hz, 1H), 0.26 (dtt, *J* = 22.5, 8.9, 4.7 Hz, 1H), 0.05 (tq, *J* = 9.4, 4.6 Hz, 1H), -0.10 (tq, *J* = 9.5, 4.6 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.7, 135.4, 129.3 (2C), 113.8 (2C), 55.4, 51.0, 46.2, 37.6, 34.2, 32.6, 32.1, 23.6, 15.4, 4.4, 2.3.

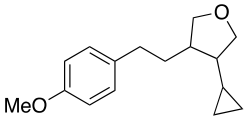


1-(benzyloxy)-4-(2-(2-cyclopropylcyclopentyl)ethyl)benzene (5.5) was prepared according to Method A. The following amounts of reagents were used: dimesylate **5.17** (32 mg, 60. μmol, 1.0

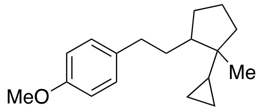
equiv), Ni(cod)$_2$ (1.7 mg, 6.0 μmol, 10 mol %), *rac*-BINAP (3.7 mg, 6.0 μmol, 10 mol %), MeMgI (40. μL, 0.12 mmol, 2.0 equiv, 3.0 M in Et$_2$O), PhMe (0.30 mL), AD-mix-β (84 mg, 1.4 g/mmol), *t*-BuOH (1.0 mL) and H$_2$O (1.0 mL). Purification by column chromatography (0–10% EtOAc/hexanes) afforded the title compound as a pale yellow oil (8.6 mg, 28 μmol, 45% yield, 1.5:1 dr). The dr was determined by the integration of resonances attributed to the aromatic carbons in ^{13}C NMR. **TLC R$_f$** = 0.8 (10% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 7.3 Hz, 4H, both diastereomers), 7.38 (t, *J* = 7.4 Hz, 4H, both diastereomers), 7.34–7.29 (m, 2H, both diastereomers), 7.14–7.09 (m, 4H, both diastereomers), 6.92–6.87 (m, 4H, both diastereomers), 5.04 (s, 4H, both diastereomers), 2.62 (dddd, *J* = 13.6, 10.4, 5.3, 2.8 Hz, 2H, both diastereomers), 2.52 (dtd, *J* = 13.9, 10.0, 6.1, 2H, both diastereomers), 1.99–1.86 (m, 2H, both diastereomers), 1.86–1.61 (m, 6H, both diastereomers), 1.62–1.55 (m, 2H, both diastereomers), 1.54–1.46 (m, 2H, both diastereomers), 1.45–1.27 (m, 2H, both diastereomers), 1.21 (dq, *J* = 12.5, 8.5 Hz, 1H, minor diastereomer), 1.13 (dq, *J* = 11.3, 6.0, 1H, major diastereomer), 0.99–0.76 (m, 4H, both diastereomers), 0.55 (dddt, *J* = 13.1, 7.9, 5.3, 2.9 Hz, 2H, both diastereomers), 0.47 (dddd, *J* = 9.4, 8.1, 5.5, 4.2 Hz, 1H, major diastereomer), 0.44–0.39 (m, 1H, minor diastereomer), 0.40–0.34 (m, 1H, major diastereomer), 0.34–0.29 (m, 1H, minor diastereomer), 0.12 (tdd, *J* = 9.3, 5.2, 4.1 Hz, 2H, both diastereomers), -0.01–-0.06 (m, 2H, both diastereomers); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 156.96 (major diastereomer) 156.95 (minor diastereomer), 137.4 (2C, both diastereomers), 135.9 (minor diastereomer), 135.8 (major diastereomer), 129.4 (2C, major diastereomer), 129.3 (2C, minor diastereomer), 128.7 (4C, both diastereomers), 128.0 (2C, both diastereomers), 127.6 (4C, both diastereomers), 114.78 (2C, minor diastereomer), 114.76 (2C, major diastereomer), 70.20 (2C, both diastereomers), 51.0 (minor diastereomer), 48.5 (major diastereomer), 46.2 (minor diastereomer), 43.1 (major diastereomer), 37.6 (minor diastereomer), 34.6 (major diastereomer), 34.2 (minor diastereomer), 33.5 (major diastereomer), 32.6 (minor diastereomer) 32.1 (minor diastereomer), 31.8 (major diastereomer), 30.7 (major diastereomer), 23.6 (minor diastereomer), 23.0 (major diastereomer), 15.4 (minor diastereomer), 11.8 (major diastereomer), 5.5 (major diastereomer), 4.4 (minor diastereomer), 3.0 (major diastereomer), 2.3 (minor diastereomer); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{23}H_{28}O$, 320.2140, found 320.2154.



1-(2-(2-cyclopropylcyclopentyl)ethyl)-3-(trifluoromethyl)benzene (5.6) was prepared according to Method A. The following amounts of reagents were used: dimesylate **5.18** (43 mg, 92 µmol, 1.0 equiv), $Ni(cod)_2$ (2.5 mg, 9.2 µmol, 10 mol %), *rac*-BINAP (5.7 mg, 9.2 µmol, 10 mol %), MeMgI (70. µL, 0.18 mmol, 2.0 equiv, 2.5 M in Et_2O), and PhMe (0.50 mL). Purification by column chromatography (100% hexanes) afforded the title compound as a clear and colorless oil (21 mg, 74 µmol, 80% yield, 2:1 dr). The dr was determined by the integration of resonances attributed to the aromatic carbons in ^{13}C NMR. **TLC R_f** = 0.8 (10% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47–7.41 (m, 4H, both diastereomers), 7.40–7.36 (m, 4H, both diastereomers), 2.74 (ddt, *J* = 13.7, 10.3, 5.1 Hz, 2H, both diastereomers), 2.65 (ddt, *J* = 13.8, 10.5, 6.8 Hz, 2H, both diastereomers), 2.07–1.88 (m, 4H, both diastereomers), 1.87–1.67 (m, 4H, diastereomers), 1.66–1.55 (m, 2H, both diastereomers), 1.54–1.48 (m, 2H, both diastereomers), 1.47–1.30 (m, 4H, both diastereomers), 1.28–1.19 (m, 1H, major diastereomer), 1.15 (dq, *J* = 11.5, 6.2 Hz, 1H, minor diastereomer), 1.00–0.79 (m, 2H, both diastereomers), 0.56 (dddd, *J* = 14.9, 8.1, 5.7, 4.0 Hz, 2H, both diastereomers), 0.52–0.46 (m, 1H, major diastereomers), 0.44 (ddd, *J* = 8.2, 5.4, 4.2 Hz, 1H, minor diastereomer), 0.39 (dddd, *J* = 9.3, 8.2, 5.4, 4.1 Hz, 1H, major diastereomer), 0.34 (dddd, *J* = 9.4, 8.3, 5.4, 4.2 Hz, 1H, minor diastereomer), 0.13 (dt, *J* = 9.8, 4.9 Hz, 2H, both diastereomers), 0.04 to -0.04 (m, 2H, both diastereomers); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.3 (major diastereomer), 144.2 (minor diastereomer), 131.91 (q, *J* = 1.7 Hz, major diastereomer), 131.89 (q, *J* = 1.7 Hz, minor diastereomer), 130.7 (q, *J* = 31.5 Hz, 2C, both diastereomers), 128.8 (2C, both diastereomers), 125.2 (q, *J* = 3.3 Hz, major diastereomer), 125.1 (q, *J* = 3.9 Hz, minor diastereomer), 124.5 (q, *J* = 272.6 Hz, 2C, both diastereomers), 122.6 (q, *J* = 3.9 Hz, 2C, both diastereomers), 50.9 (minor diastereomer), 48.4 (major diastereomer), 46.2 (minor diastereomer), 43.1 (major diastereomer), 37.1 (minor diastereomer), 35.3 (major diastereomer), 35.0 (minor diastereomer), 33.1 (major diastereomer), 32.6 (minor diastereomer), 32.1 (minor diastereomer), 31.7 (major diastereomer), 30.7 (major diastereomer), 23.6 (minor diastereomer), 23.0 (major diastereomer), 15.4 (minor diastereomer), 11.8 (major diastereomer), 5.5 (major diastereomer), 4.4 (minor diastereomer), 3.1 (major diastereomer), 2.3 (minor diastereomer);**^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.5 (3F, major diastereomer), -62.6 (3F, minor diastereomer); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{17}H_{21}F_3$, 282.1595, found 282.1595.

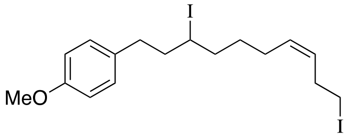


3-cyclopropyl-4-(4-methoxyphenethyl)tetrahydrofuran (5.7) was prepared according to Method A. The following amounts of reagents were used: dimesylate **5.19** (58 mg, 0.13 mmol, 1.0 equiv), $Ni(cod)_2$ (3.6 mg, 13 μmol, 10. mol %), *rac*-BINAP (8.1 mg, 13 μmol, 10 mol %), MeMgI (90. μL, 0.26 mmol, 2.0 equiv, 2.9 M in Et_2O), and PhMe (0.70 mL). Before purification a ^{1}H NMR yield of 28% yield was obtained based on comparison to PhTMS as an internal standard. The residue was purified by column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a clear and colorless oil (8.2 mg, 33 μmol, 27% yield, 1:1 dr). The dr was determined by the integration of resonances attributed to the aromatic carbons in ^{13}C NMR. **TLC R$_f$** = 0.2 (10% EtOAc/Hexanes, CAM Stain); **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.10 (at, *J* = 8.9 Hz, 4H, both diastereomers), 6.84 (dd, *J* = 8.9, 3.4 Hz, 4H, both diastereomers), 4.03 (dd, *J* = 8.4, 7.4 Hz, 1H, one diastereomer), 3.93 (dt, *J* = 20.4, 7.6 Hz, 2H, both diastereomers), 3.88 (dd, *J* = 8.3, 6.4 Hz, 1H, one diastereomer), 3.79 (s, 6H, both diastereomers), 3.69 (dd, *J* = 8.3, 4.6 Hz, 1H, one diastereomer), 3.59–3.53 (m, 2H, both diastereomers), 3.44 (dd, *J* = 8.4, 7.7 Hz, 1H, one diastereomer), 2.62–2.52 (m, 4H, both diastereomers), 2.23 (dq, *J* = 12.9, 7.6 Hz, 1H, one diastereomer), 2.07–1.87 (m, 3H, both diastereomer), 1.70 (dtd, *J* = 13.4, 9.1, 6.5 Hz, 1H, one diastereomer), 1.56–1.50 (m, 1H, one diastereomer), 1.49–1.42 (m, 1H, one diastereomer), 1.20 (dq, *J* = 9.0, 7.4 Hz, 1H, one diastereomer), 0.74–0.67 (m, 1H, one diastereomer), 0.67–0.61 (m, 1H, one diastereomer), 0.57 (dddd, *J* = 9.7, 8.2, 5.5, 4.4 Hz, 1H, one diastereomer), 0.52–0.44 (m, 2H, both diastereomers), 0.41 (dddd, *J* = 9.3, 8.0, 5.4, 4.4 Hz, 1H, one diastereomer), 0.18 (dquint *J* = 10.1, 5.2 Hz, 2H, both diastereomers), 0.05 (td, *J* = 9.6, 4.8 Hz, 2H, both diastereomers); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 157.93 (one diastereomer), 157.92 (one diastereomer), 134.5 (one diastereomer), 134.4 (one diastereomer), 129.33 (2C, one diastereomer), 129.29 (2C, one diastereomer), 113.9 (4C, both diastereomers), 74.2 (one diastereomer), 73.7 (one diastereomer), 73.4 (one diastereomer), 72.7 (one diastereomer), 55.4 (2C, both diastereomers), 50.8 (one diastereomer), 47.9 (one diastereomer), 45.7 (one diastereomer), 42.4 (one diastereomer), 35.4 (one diastereomer), 34.4 (one diastereomer), 34.1 (one diastereomer), 30.6 (one diastereomer), 13.3 (one diastereomer), 10.0 (one diastereomer), 5.0 (one diastereomer), 3.7 (one diastereomer), 3.1 (one diastereomer), 2.7 (one diastereomer); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{16}H_{22}O_2$, 246.1620, found 246.1614.



1-(2-(2-cyclopropyl-2-methylcyclopentyl)ethyl)-4-methoxybenzene (5.8) was prepared according to Method A. The following amount of reagents were used: dimesylate **5.20** (27 mg, 60. µmol, 1.0 equiv), Ni(cod)$_2$ (1.7 mg, 6.0 µmol, 10 mol %), *rac*-BINAP (3.7 mg, 6.0 µmol, 10 mol %), MeMgI (40. µL, 0.12 mmol, 2.0 equiv, 3.0 M in Et$_2$O), PhMe (0.30 mL), AD-mix-β (84 mg, 1.4 g/mmol), *t*-BuOH (1.0 mL) and H$_2$O (1.0 mL). Purification by column chromatography (0–10% EtOAc/hexanes) afforded the title compound as a pale yellow oil (6.0 mg, 23 µmol, 40% yield, 1.5:1 dr). The dr was determined by the integration of resonances attributed to the aromatic carbons in ^{13}C NMR. **TLC R$_f$** = 0.7 (10% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (600 MHz, CDCl$_3$) δ 7.12 (d, *J* = 8.4 Hz, 4H, both diastereomers), 6.83 (dd, *J* = 9.1, 3.0 Hz, 4H, both diastereomers), 3.79 (s, 6H, both diastereomers), 2.66 (ddd, *J* = 15.0, 10.6, 4.9 Hz, 1H, minor diastereomer), 2.45 (ddd, *J* = 13.8, 10.2, 6.4 Hz, 1H, major diastereomers), 1.94 (qd, *J* = 10.1, 9.0, 1H, major diastereomer), 1.83 (dddd, *J* = 13.3, 9.9, 6.4, 3.0 1H, minor diastereomer), 1.70–1.55 (m, 2H, both diastereomers), 1.52–1.43 (m, 2H, both diastereomers), 1.44–1.36 (m, 2H, both diastereomers), 1.35–1.24 (m, 6H, both diastereomers), 1.21 (ddd, *J* = 12.8, 6.4, 3.3 Hz, 2H, both diastereomers), 0.91–0.79 (m, 4H, both diastereomers), 0.73 (s, 3H, major diastereomer), 0.69 (s, 3H, minor diastereomer), 0.67–0.62 (m, 2H, both diastereomers), 0.24 (dqd, *J* = 13.0, 8.9, 4.2 Hz, 4H, both diastereomers), 0.18–0.08 (m, 4H, both diastereomers); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 157.72 (minor diastereomer), 157.70 (major diastereomer), 135.59 (major diastereomer), 135.58 (minor diastereomer), 129.4 (2C, minor diastereomer), 129.3 (2C, major diastereomer), 113.80 (2C, major diastereomer), 113.78 (2C, minor diastereomer), 55.4 (2C, both diastereomers) 51.1 (2C, both diastereomers), 43.1 (2C, both diastereomers), 38.1 (2C, both diastereomers), 34.8 (2C, both diastereomers), 32.7 (2C, both diastereomers), 31.1 (2C, both diastereomers), 23.4 (2C, both diastereomers), 22.0 (2C, both diastereomers), 15.6 (2C, both diastereomers) 1.2 (minor diastereomer), 1.1 (major diastereomer), 0.3 (major diastereomer), 0.2 (minor diastereomer); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{18}H_{26}O$, 258.1984, found 258.1980.

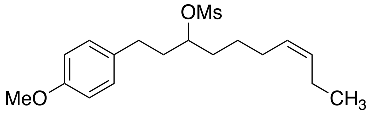
5.4.4 Characterization Data for By-Products Formed from Optimization Studies



(3,10-diiododec-7-en-1-yl)-4-methoxybenzene (5.3a) was observed as a by-product from the optimization studies as a 2:1 mixture of alkene diastereomers (see Table 5.1). Below is the characterization of the title compound. For clarity the ^1H and ^{13}C data are tabulated separately. **TLC R$_f$** = 0.7 (10% EtOAc/hexanes, CAM Stain); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{17}H_{24}I_2O$, 497.9917; found 497.9906.

Major Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.59–5.42 (m, 1H), 5.40–5.28 (m, 1H), 4.04 (tt, *J* = 8.8, 4.3 Hz, 1H), 3.80 (s, 3H), 3.15 (td, *J* = 7.2, 4.0 Hz, 2H), 2.84 (ddd, *J* = 13.9, 8.9, 5.0 Hz, 1H), 2.74–2.65 (m, 1H), 2.62 (aq, *J* = 7.2, 6.1 Hz, 2H), 2.15 (dtd, *J* = 14.3, 9.1, 5.0 Hz, 1H), 2.09–1.84 (m, 4H), 1.81–1.69 (m, 1H), 1.68–1.57 (m, 1H), 1.54–1.42 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 133.0, 131.8, 129.6 (2C), 128.7, 114.1 (2C), 55.4, 42.6, 40.3, 39.0, 34.8, 31.6, 29.4, 26.7, 5.5.

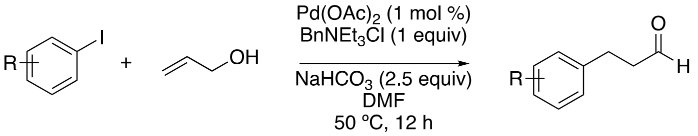
Minor Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.59–5.42 (m, 1H), 5.40–5.28 (m, 1H), 4.04 (tt, *J* = 8.8, 4.3 Hz, 1H), 3.80 (s, 3H), 3.15 (td, *J* = 7.2, 4.0 Hz, 2H), 2.84 (ddd, *J* = 13.9, 8.9, 5.0 Hz, 1H), 2.74–2.65 (m, 1H), 2.55 (aq, *J* = 7.2, 6.7 Hz, 2H), 2.15 (dtd, *J* = 14.3, 9.1, 5.0 Hz, 1H), 2.09–1.84 (m, 4H), 1.81–1.69 (m, 1H), 1.68–1.57 (m, 1H), 1.54–1.42 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.1, 132.8, 131.8, 129.6 (2C), 129.2, 114.0 (2C), 55.4, 42.6, 40.1, 39.2, 36.7, 31.7, 29.1, 26.7, 6.3.



(4-Methoxyphenyl)dec-7-en-3-yl methanesulfonate (5.4) was observed as a by-product from the optimization studies (see Table 1). Below is the characterization for the major diastereomer. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.57–5.22 (m, 2H), 4.75 (sextet, *J* = 6.1 Hz, 1H), 3.79 (s, 3H), 2.99 (s, 3H), 2.67 (qdd, *J* = 14.1, 9.5, 6.1 Hz, 2H), 2.15–1.87 (m, 4H), 1.74 (tt, *J* = 9.1, 6.0 Hz, 2H), 1.68–1.52 (m, 1H), 1.52–1.14 (m, 3H), 0.96 (tdd, *J* = 7.5, 3.5, 1.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 133.1, 132.7, 129.4 (2C), 128.2, 114.1 (2C), 83.4, 55.4, 38.9, 36.5, 32.2, 30.5, 26.8, 24.9, 20.7, 14.1; **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{28}O_4SNa$, 363.1606; found 363.1615.

5.4.5 General Procedures for the Synthesis of Dimesylate Starting Materials

5.4.5.1 Method B: Pd-Catalyzed Heck Reaction



(5.1)

This method was adapted from a procedure reported by Su.[37] A flame dried pressure tube equipped with a stir bar was charged with aryl iodide[38] (1.0 equiv), $NaHCO_3$ (2.5 equiv), and $BnNEt_3Cl$ (1.0 equiv). The flask was sealed with a septum and pumped into a glovebox. Then the pressure tube was charged with $Pd(OAc)_2$ (1.0 mol %), sealed with septum, removed from the glovebox and placed under an atmosphere of N_2. Then DMF (0.20 M) was added via syringe followed by allyl

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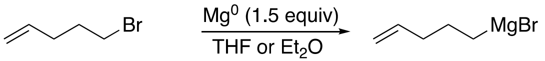
[37] Shang, Y., Jie, X., Jonnada, K. Zafar, S. N.; Su, W. *Nat Commun*. **2017**, *8*, 2273.

[38] Note: if the aryl iodide starting material is a liquid, it was added via syringe after the flask was removed from the glovebox.

alcohol (1.5 equiv). The pressure tube was sealed with a teflon cap, heated to 50 ºC and allowed to stir at that temperature for at least 5 h. After the reaction was complete, the flask was cooled to rt and allowed to stir at that temperature for 1 h. The mixture was then filtered through a pad of silica gel eluting with EtOAc. The filtrate was concentrated to remove the excess EtOAc and then transferred to a separatory funnel. The organic layer was washed with excess H_2O (x 5) and then brine. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by column chromatography.

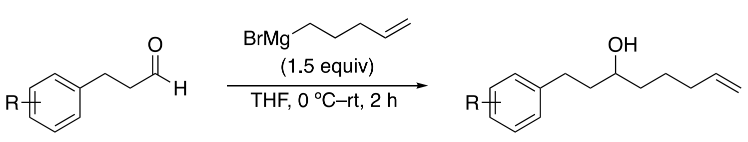
5.4.5.2 Method C: Preparation of Grignard Reagent



5.21 **5.22** (5.2)

To a flame dried two-neck round bottom flask equipped with a stir bar, was added magnesium turnings (1.5 equiv). The flask and magnesium turnings were then flame-dried under vacuum and the flask was back-filled with N_2. Anhydrous Et_2O or THF (2.0 M) and a crystal of iodine (ca. 2.0 mg) were added to the flask. Then alkyl bromide **5.21** (1.0 equiv) was slowly added neat over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature The resulting Grignard reagent was titrated according to Knochel's method and used immediately.[35]

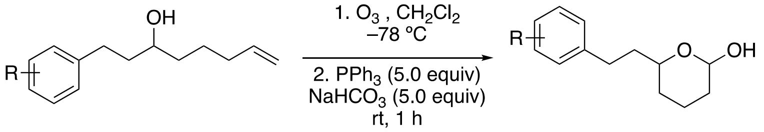
5.4.5.3 Method D: Nucleophilic Grignard Addition into Aldehyde



(5.3)

To a flame dried round bottom flask equipped with a stir bar, was added aldehyde (1.0 equiv) as a solution in THF or Et_2O (0.20 M). The flask was cooled to 0 ºC and the freshly prepared Grignard reagent (1.5 equiv) was added dropwise via syringe. The flask is warmed to rt and allowed to stir for 2 h. To quench, saturated aq. NH_4Cl was added to the reaction mixture. The biphasic solution was transferred to a separatory funnel and the organic layer was extracted with EtOAc. The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo.

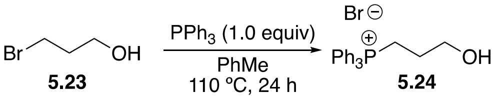
5.4.5.4 Method E: Ozonolysis of Terminal Alkenes



(5.4)

This method was adapted from a procedure reported by was prepared by Taber.[39] A round-bottom flask equipped with stir bar was charged with alkene (1.0 equiv), and CH_2Cl_2 (0.10 M). The reaction was then cooled to –78 ºC, and ozone was bubbled through mixture until the solution turned blue. Ozone flow was then discontinued, and O_2 was passed through the solution for 5 min. PPh_3 (5.0 equiv) and $NaHCO_3$ (5.0 equiv) were then added to flask and the mixture was allowed stirred for at least 1 h. Then H_2O was added and the biphasic mixture was transferred to a separatory funnel. The organic layer was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo.

5.4.5.5 Method F: Preparation of Wittig Salt 5.24



5.23 **5.24**

(5.5)

To a flame dried round bottom flask equipped with a stir bar and reflux condenser was added 3-bromopropanol **5.23** (1.0 equiv) and PhMe (1.1 M). Then PPh_3 (1.0 equiv) was added, the reaction mixture was heated to reflux and allowed to stir until white precipitate formed (~15–24 h). The flask was cooled to rt, the precipitate was filtered and washed with hexanes. The white solids were collected and dried under vacuum overnight.

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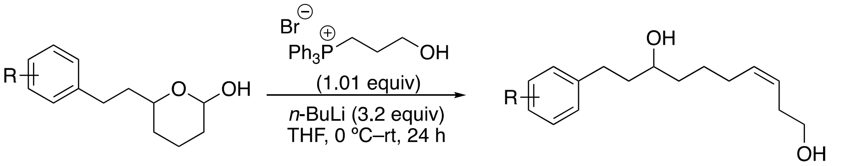
[39] Taber, D. F.; Guo, P. *J. Org. Chem.* **2008**, *73*, 9479–9481.

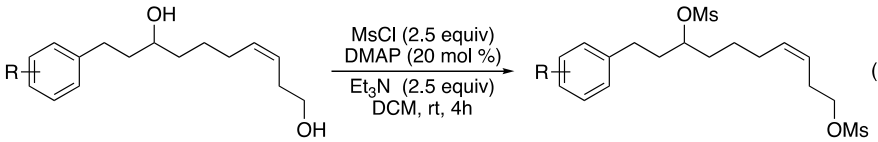
5.4.5.6 Method G: Wittig Reaction



(5.6)

This method was adapted from a procedure reported by Taber.[39] To a flame dried round bottom flask equipped with stir bar was added the Wittig salt **5.24** (1.01 equiv) and THF (0.2 M). The flask is cooled to 0 ºC and *n*-BuLi (3.2 equiv, 2.5 M in hexanes) was added dropwise. The dark red solution was allowed to stir at 0 ºC for 1 h. Then, a solution of lactol (1.0 equiv) in THF (1.0 M) was added and the reaction mixture was warmed to rt. The resulting orange solution was allowed to stir at rt for 24 h. To quench, saturated aq. NH_4Cl was added dropwise. The biphasic mixture was transferred to a separatory funnel. The organic layer was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo.

5.4.5.7 Method H: Mesylation Reaction

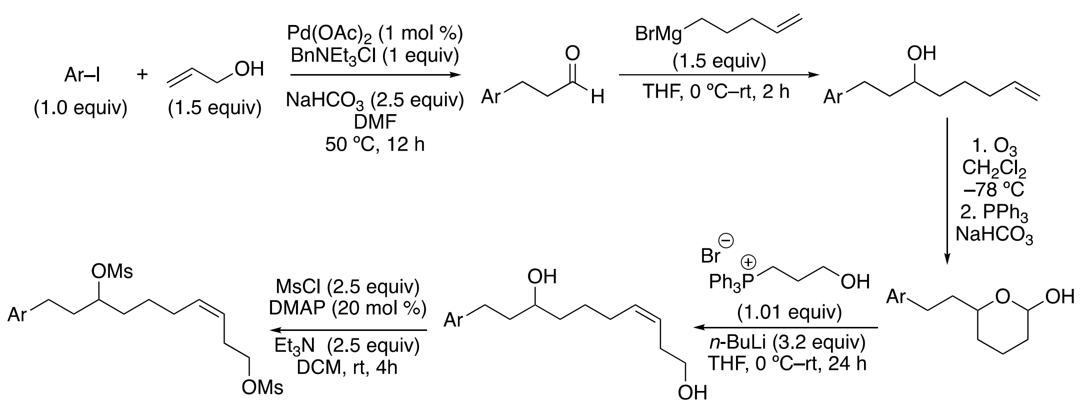


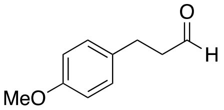
(5.7)

A flame dried round bottom flask equipped with a stir bar was charged with diol (1.0 equiv) and CH_2Cl_2 (0.20 M) under N_2. Then, Et_3N (1.5 equiv), DMAP (20 mol %), and MsCl (2.5 equiv) were added in that order. The reaction mixture was then stirred at rt for at least 4 h. Once complete, sat. $NaHCO_3$ was added and the reaction mixture was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

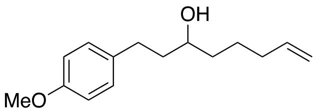
5.4.6 Synthesis and Characterization Data for Dimesylate Starting Materials

Scheme 5.5 General Synthesis of Dimesylate Starting Material





3-(4-Methoxyphenyl)propanal (5.25) was prepared according to Method B. The following amounts of reagents were used: 4-iodoanisole (4.9 g, 20. mmol, 1.0 equiv), allyl alcohol (2.0 mL, 30. mmol, 1.5 equiv), Pd(OAc)2 (45 mg, 0.20 mmol, 1.0 mol %), BnEt3NCl (4.6 g, 20. mmol, 1.0 equiv), NaHCO3 (4.3 g, 50. mmol, 2.5 equiv), and DMF (80 mL). Purification by column chromatography (0–10% EtOAc/hexanes) afforded the title compound as a clear and colorless oil (2.6 g, 16 mmol, 81% yield). Analytical data is consistent with literature values.[40] ^{1}H NMR (400 MHz, CDCl3) δ 9.75 (t, *J* = 1.5 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.73 – 2.65 (m, 2H).



1-(4-Methoxyphenyl)oct-7-en-3-ol (5.26) was prepared according to Method D. The following amount of reagents were used: aldehyde **5.25** (1.4 g, 8.6 mmol, 1.0 equiv), Grignard reagent **5.22** (10. mL, 13 mmol, 1.5 equiv, 1.3 M in Et2O) and Et2O (43 mL, 0.20 M). Purification by column chromatography (0–30% EtOAc/hexanes) afforded the title compound as a pale yellow oil (1.9 g,

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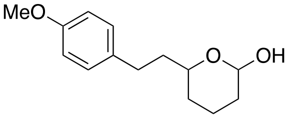
[40] C. C. Frost, B. C. Hartley, *Org. Lett.* **2007**, *9*, 4259–4261.

8.1 mmol, 94% yield). Analytical data consistent with literature values.[39] **TLC R$_f$** = 0.3 (20% EtOAc/hexanes, KMnO$_4$ stain); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.15–7.10 (m, 2H), 6.87–6.81 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.97 (dq, *J* = 10.2, 1.7 Hz, 1H), 3.79 (s, 3H), 3.68–3.57 (m, 1H), 2.68 (dddd, *J* = 46.8, 13.8, 9.5, 6.3 Hz, 2H), 2.12–2.04 (m, 2H), 1.82–1.66 (m, 2H), 1.60–1.39 (m, 4H).



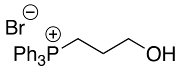
6-(4-Methoxyphenethyl)tetrahydro-2*H*-pyran-2-ol (5.27) was prepared according to Method E. The following amounts of reagents were used: alcohol **5.26** (0.42 g, 1.8 mmol, 1.0 equiv), ozone (excess), CH$_2$Cl$_2$ (18 mL), PPh$_3$ (0.85 g, 2.0 g/1g of alcohol), and NaHCO$_3$ (0.85 g, 2.0 g/1g of alcohol). Purification by column chromatography (0–50% EtOAc/hexanes) afforded the title compound as a white solid (0.19 g, 0.83 mmol, 46% yield, 1.5:1 mixtures of diastereomers). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually. The analytical data is consistent with literature values.[39]

TLC R$_f$ = 0.3 (20% EtOAc/hexanes, CAM stain); **HRMS** (TOF MS ES+) *m/z*: [M+Na]$^+$ calcd for C$_{14}$H$_{20}$O$_3$Na, 259.1310; found 259.1309.

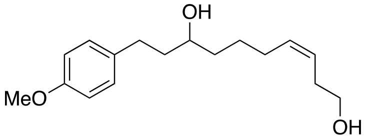
Major diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.69 (t, *J* = 7.7 Hz, 1H), 3.78 (s, 3H), 3.46–3.34 (m, 1H), 3.19 (s, 1H), 2.65–2.51 (m, 2H), 1.92–1.79 (m, 2H), 1.79–1.55 (m, 3H), 1.54–1.43 (m, 1H), 1.38–1.15 (m, 2H); **^{13}C NMR** (126 MHz, CDCl$_3$) δ 157.8, 134.3, 129.4 (2C), 113.9 (2C), 96.6, 75.6, 55.4, 38.0, 33.1, 30.9, 30.6, 22.2.

Minor Diastereomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H), 3.98–3.90 (m, 1H), 3.78 (s, 3H), 3.19 (s, 1H), 3.14 (d, *J* = 6.2 Hz, 1H), 2.79–2.66 (m, 1H), 1.92–1.79 (m, 2H), 1.79–1.55 (m, 3H), 1.56–1.42 (m, 1H), 1.38–1.15 (m, 2H); **^{13}C**

NMR (126 MHz, $CDCl_3$) δ 157.8, 134.5, 129.4 (2C), 113.9 (2C), 92.1, 68.1, 55.4, 38.2, 31.3, 30.9, 30.0, 17.6.



(3-Hydroxypropyl)triphenylphosphonium bromide (5.24) was prepared according to Method F. The following amounts of reagents were used: 4-bromoproanol **5.23** (0.89 mL, 10. mmol, 1.0 equiv), PPh_3 (2.6 g, 10. mmol, 1.0 equiv), and PhMe (9.1 mL). Analytical data is consistent with literature data.[41] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.75 (m, 9H), 7.74–7.67 (m, 6H), 4.93 (s, 1H) 3.94–3.62 (m, 4H), 1.95–1.74 (m, 2H).



(4-Methoxyphenyl)dec-3-ene-1,8-diol (5.28) was prepared according to Method G. The following amounts of reagents were used: lactol **5.27** (0.19, 0.83 mmol, 1.0 equiv), Wittig salt **5.24** (0.34 g, 0.84 mmol, 1.0 equiv), *n*-BuLi (1.1 mL, 2.7 mmol, 3.2 equiv, 2.5 M in hexane) and THF (4.2 mL). Purification by column chromatography (0–70% EtOAc/hexanes) afforded the title compound as a yellow oil (0.16 g, 0.57 mmol, 69% yield, 2:1 mixture of diastereomers). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.2 (20% EtOAc/hexanes, $KMnO_4$ stain); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{17}H_{26}O_3Na$, 301.1780; found 301.1788.

Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.62 (dt, *J* = 10.7, 7.5 Hz, 1H), 5.45 (dtt, *J* = 10.5, 7.3, 1.5 Hz, 1H), 3.85 (s, 3H), 3.70 (t, *J* = 6.5 Hz, 2H), 2.79 (ddd, *J* = 14.8, 9.5, 5.8 Hz, 1H), 2.68 (ddd, *J* = 13.9, 9.4, 6.9 Hz, 1H), 2.37

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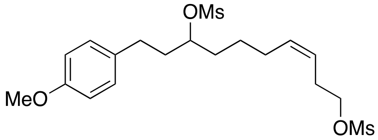
[41] Kandula, S. R. V.; Kumar, P. *Tetrahedron Asymmetry* **2005**, *16*, 3268–3274.

(q, J = 7.0 Hz, 2H), 2.14 (tquint, J = 13.9, 7.5 Hz, 2H), 1.89–1.71 (m, 2H), 1.66 (br s, 5H), 1.61–1.41 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 134.3, 133.0, 129.4 (2C), 125.6, 114.0 (2C), 71.3, 62.4, 55.4, 39.5, 37.1, 31.3, 30.9, 27.4, 25.8.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 5.60 (dt, J = 15.3, 6.7 Hz, 1H), 5.45 (dt, J = 15.3, 6.9 Hz, 1H), 3.85 (s, 3H), 3.69 (t, J = 6.3 Hz, 2H), 2.79 (ddd, J = 14.9, 9.5, 5.8 Hz, 1H), 2.68 (ddd, J = 13.9, 9.4, 6.8 Hz, 1H), 2.33 (q, J = 6.4 Hz, 2H), 2.10 (d, J = 7.1 Hz, 2H), 1.91–1.70 (m, 2H), 1.67–1.39 (m, 5H), 1.03–0.80 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 134.3, 133.9, 129.4 (2C), 126.4, 114.0 (2C), 71.3, 62.2, 55.4, 39.5, 37.2, 36.1, 32.7, 31.3, 25.5.

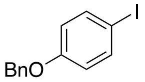


(4-Methoxyphenyl)dec-3-ene-1,8-diyl dimethanesulfonate (5.1) was prepared according to Method H. The following amounts of reagents were used: diol **5.28** (0.59 g, 2.1 mmol, 1.0 equiv), MsCl (0.41 mL, 5.3 mmol, 2.5 equiv), Et_3N (0.73 mL, 5.3 mmol, 2.5 equiv), DMAP (51 mg, 0.42 mmol, 20 mol %), and CH_2Cl_2 (11 mL). Purification by column chromatography (0–50% EtOAc/hexanes) afforded the title compound as a yellow oil (0.76 g, 1.7 mmol, 83% yield, 2:1 dr). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually. **TLC R$_f$** = 0.4 (50% EtOAc/hexanes, CAM stain); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{30}O_7S_2Na$, 457.1331; found 457.1314.

Major Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.54 (dt, J = 10.7, 7.4 Hz, 1H), 5.38 (dt, J = 10.8, 7.2 Hz, 1H), 4.75 (quint, J = 6.0 Hz, 1H), 4.20 (t, J = 6.8 Hz, 2H), 3.78 (s, 3H), 2.99 (d, J = 1.8 Hz, 6H), 2.76–2.58 (m, 2H), 2.49 (q, J = 6.8 Hz, 2H), 2.18–1.88 (m, 4H), 1.75 (dtd, J = 9.4, 6.2, 3.9 Hz, 2H), 1.57–1.39 (m, 2H); **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 158.2, 133.2, 133.0, 129.5 (2C), 124.0, 114.2 (2C), 83.1, 69.4, 55.5, 39.0, 37.7, 36.6, 34.2, 30.6, 27.6, 27.1, 24.9.

Minor Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.55 (dt, *J* = 15.4, 6.7 Hz, 1H), 5.40 (dt, *J* = 15.3, 6.6 Hz, 1H), 4.75 (quint, *J* = 6.1 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.79 (s, 3H), 3.00 (d, *J* = 1.1 Hz, 6H), 2.76–2.59 (m, 2H), 2.45 (q, *J* = 6.7 Hz, 2H), 2.10–1.94 (m, 3H), 1.81–1.66 (m, 2H), 1.49 (dt, *J* = 15.7, 7.4 Hz, 1H), 0.96 – 0.79 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 133.8, 132.9, 129.4 (2C), 124.7, 114.1 (2C), 83.2, 69.6, 55.4, 38.9, 37.6, 36.5, 34.0, 32.5, 32.2, 30.5, 24.5.



1-(Benzyloxy)-4-iodobenzene (5.29) was prepared according to a procedure reported by Fukuyama.[42] To a round bottom flask equipped with a stir bar was added 4-iodophenol (1.1 g, 5.0 mmol, 1.0 equiv), K_2CO_3 (0.89 g, 6.5 mmol, 1.3 equiv), benzyl bromide (0.65 mL, 5.5 mmol, 1.1 equiv), and DMF (2.5 mL). The reaction flask was fitted with a reflux condenser, and the mixture was heated to 60 ºC and allowed to stir overnight. To quench, H_2O was added at rt and the solution was transferred to a separatory funnel. The aqueous layer was extracted with Et_2O (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (0–10% EtOAc/hexanes) afforded the title compound as a white solid (1.2 g, 3.7 mmol, 74% yield). Analytical data is consistent with literature data.[42] **TLC R_f** = 0.7 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 9.0 Hz, 2H), 7.56–7.47 (m, 4H), 7.47–7.40 (m, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.12 (s, 2H).

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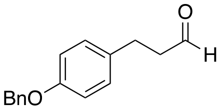
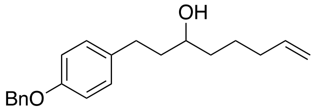
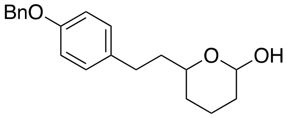
[42] W. Kurosawa, T. Kan, T. Fukuyama, *J. Am. Chem. Soc.* **2003**, *125*, 8112–8113.



3-(4-(Benzyloxy)phenyl)propanal (5.30) was prepared according to Method B. The following amounts of reagents were used: iodide **5.29** (1.0 g, 3.2 mmol, 1.0 equiv), allyl alcohol (0.33 mL, 4.8 mmol, 1.5 equiv), $Pd(OAc)_2$ (7.0 mg, 32 µmol, 1.0 mol %), $BnEt_3NCl$ (0.73 g, 3.2 mmol, 1 equiv), $NaHCO_3$ (0.67 g, 8.0 mmol, 2.5 equiv), and DMF (13 mL). Purification by column chromatography (0–10% EtOAc/hexanes) afforded the title compound as a white solid (0.74 g, 3.1 mmol, 97% yield). **TLC R_f** = 0.3 (10% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.5 Hz, 1H), 7.54–7.34 (m, 5H), 7.24–7.11 (m, 2H), 7.02–6.95 (m, 2H), 5.09 (s, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 157.3, 132.7, 129.2 (2C), 128.5 (2C), 127.9, 127.4 (2C), 114.9 (2C), 70.0,



1-(4-(Benzyloxy)phenyl)oct-7-en-3-ol (5.31) was prepared according to Method D. The following amounts of reagents were used: aldehyde **5.30** (0.87 g, 3.6 mmol, 1.0 equiv), Grignard reagent **5.22** (5.0 mL, 1.5 mmol, 1.5 equiv, 1.1 M in THF), and THF (19 mL). The crude reaction mixture was filtered through a pad of silica gel eluting with 100% EtOAc to remove excess magnesium salts. The title compound was afforded as a white solid (1.1 g, 3.5 mmol, 97 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.86 (ddtd, *J* = 16.9, 10.2, 6.7, 1.5 Hz, 1H), 5.11–4.97 (m, 4H), 3.73–3.59 (m, 1H), 2.83–2.72 (m, 1H), 2.66 (ddd, *J* = 14.0, 9.4, 6.8 Hz, 1H), 2.18–2.03 (m, 2H), 1.85–1.66 (m, 3H), 1.64–1.40 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 138.7, 137.3, 134.6, 129.4 (2C), 128.6 (2C), 127.9, 127.5 (2C), 122.7, 114.9 (2C), 71.2, 70.1, 39.3, 37.0, 33.8, 31.2, 24.9; **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{26}O_2Na$, 333.1830; found 333.1828.

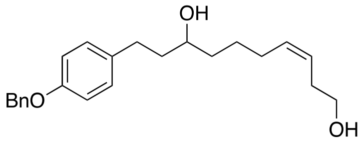


6-(4-(Benzyloxy)phenethyl)tetrahydro-2*H*-pyran-2-ol (5.32) was prepared according to a modified version of Method E. The following amounts of reagents were used: alcohol **5.31** (1.1 g, 3.5 mmol, 1.0 equiv), ozone (excess), CH_2Cl_2 (3.5 mL), MeOH (7.0 mL), PPh_3 (2.2 g, 2.0 g/1.0 mmol of alcohol) and $NaHCO_3$ (2.2 g, 2.0 g/1.0 g of alcohol). Purification by column chromatography (0–30% EtOAc/hexanes) afforded the title compound as a white solid (0.36 g, 1.2 mmol, 33% yield, 2:1 dr). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually.

TLC R_f = 0.3 (50% EtOAc/hexanes); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}O_3Na$, 335.1623; found 335.1610.

Major Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.32 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.40–5.32 (m, 1H) 5.06 (s, 2H), 4.73 (d, *J* = 9.5 Hz, 1H), 3.44 (dtd, *J* = 10.4, 5.3, 2.6 Hz, 1H), 2.83–2.54 (m, 2H), 1.98–1.82 (m, 2H), 1.82–1.58 (m, 2H), 1.58–1.44 (m, 2H), 1.42–1.18 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 137.3, 134.6, 129.4 (2C), 128.6 (2C), 127.9, 127.5 (2C), 114.8 (2C), 96.6, 75.6, 70.1, 37.8, 33.0, 30.9, 30.5, 22.2.

Minor Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.32 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.32–5.13 (m, 1H), 5.06 (s, 2H), 4.73 (d, *J* = 9.5 Hz, 1H), 4.08–3.92 (m, 1H), 2.83–2.54 (m, 2H), 1.98–1.82 (m, 2H), 1.82–1.58 (m, 2H), 1.58–1.44 (m, 2H), 1.42–1.18 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 137.3, 134.7, 129.4 (2C), 128.6 (2C), 127.9, 127.5 (2C), 114.8 (2C), 91.9, 75.6, 68.2, 38.1, 33.0, 31.2, 30.0, 17.5.



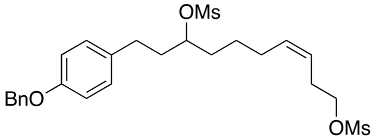
(4-Benzyloxy)phenyl-dec-3-ene-1,8-diol (5.33) was prepared according to Method G. The following amounts of reagents were used: lactol **5.32** (56 mg, 0.18 mmol, 1.0 equiv), Wittig salt **5.24** (73 mg, 0.18 mmol, 1.0 equiv), *n*-BuLi (0.30 mL, 0.58 mmol, 3.2 equiv, 2.5 M in hexanes), and THF (0.90 mL). Purification by column chromatography (0–50% yield) afforded the title compound as a white solid (27 mg, 80. μmol, 42% yield). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.2 (50% EtOAc/hexanes, KMnO$_4$ stain); **HRMS** (TOF MS ES+) *m/z*: calcd for $C_{23}H_{30}O_3Na$, 377.2093; found 377.3075

Major Diastereomer: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.49 (d, *J* = 7.0 Hz, 2H), 7.44 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.38 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.64–5.57 (m, 1H), 5.49–5.41 (m, 1H), 5.10 (s, 2H), 3.73–3.64 (m, 3H), 2.79 (ddd, *J* = 14.8, 9.5, 5.7 Hz, 1H), 2.67 (ddd, *J* = 13.9, 9.5, 6.8 Hz, 1H), 2.37 (qt, *J* = 6.8, 1.9 Hz, 1H), 2.21–2.05 (m, 2H), 1.87–1.70 (m, 2H), 1.62–1.40 (m, 7H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 157.2, 137.3, 134.6, 133.1, 129.4 (2C), 128.7 (2C), 128.0, 127.6 (2C), 125.7, 115.0 (2C), 71.3, 70.2, 62.4, 39.4, 37.2, 31.3, 30.9, 27.4, 25.8.

Minor Diastereomer: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.49 (d, *J* = 7.0 Hz, 2H), 7.44 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.38 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.64–5.57 (m, 1H), 5.49–5.41 (m, 1H), 5.10 (s, 2H), 3.73–3.64 (m, 3H), 2.79 (ddd, *J* = 14.8, 9.5, 5.7 Hz, 1H), 2.67 (ddd, *J* = 13.9, 9.5, 6.8 Hz, 1H), 2.32 (qd, *J* = 6.3, 1.2 Hz, 1H), 2.21–2.05 (m, 2H), 1.87–1.70 (m, 2H), 1.62–1.40 (m, 7H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 157.2, 137.3, 134.6, 133.9, 129.4

(2C), 128.7 (2C), 128.0, 127.6 (2C), 126.4, 115.0 (2C), 71.3, 70.2, 62.2, 39.4, 37.2, 36.1, 32.7, 27.4, 25.5.



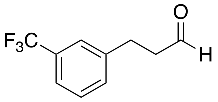
(4-(Benzyloxy)phenyl)dec-3-ene-1,8-diyl dimethanesulfonate (5.17) was prepared according to Method H. The following amounts of reagents were used: diol **5.33** (27 mg, 80. μmol, 1.0 equiv), MsCl (20. μL, 0.20 mmol, 2.5 equiv), Et_3N (30. μL, 0.20 mmol, 2.5 equiv), and CH_2Cl_2 (0.50 mL). The crude reaction mixture was filtered through a pad a silica gel eluting with 100% CH_2Cl_2 and the title compound was isolated as a pale yellow oil (35 mg, 68 μmol, 85% yield). For clarity, the ^1H and ^{13}C of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.3 (30% EtOAc/hexanes); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{34}O_7S_2Na$, 533.1644; found 533.1658.

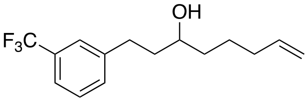
Major Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 (dd, *J* = 8.5, 5.9 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.60 (q, *J* = 8.5, 7.4 Hz, 1H), 5.51 – 5.40 (m, 1H), 5.10 (d, *J* = 3.3 Hz, 2H), 4.81 (quint, *J* = 6.0 Hz, 1H), 4.30–4.24 (m, 2H), 3.72 (d, *J* = 1.0 Hz, 2H), 3.05 (s, 6H), 2.73 (qdd, *J* = 14.3, 9.6, 6.3 Hz, 2H), 2.55 (q, *J* = 7.0 Hz, 2H), 2.22–1.94 (m, 2H), 1.90–1.71 (m, 2H), 1.61–1.45 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.3, 137.2, 133.2, 133.1, 129.4 (2C), 128.7 (2C), 128.0, 127.6 (2C), 123.9, 115.0 (2C), 83.0, 70.1, 69.3, 38.8, 37.6, 36.4, 34.1, 31.7, 27.5, 27.0, 24.8.

Minor Diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 (dd, *J* = 8.5, 5.9 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.60 (q, *J* = 8.5, 7.4 Hz, 1H), 5.51–5.40 (m, 1H), 5.10 (d, *J* = 3.3 Hz, 2H), 4.81 (p, *J* = 6.0 Hz, 1H), 4.30–4.24 (m, 2H), 3.19 (d, *J* = 1.0 Hz, 1H), 3.05 (s, 6H), 2.73 (qdd, *J* = 14.3, 9.6, 6.3 Hz, 2H), 2.50 (q, *J* =

7.0 Hz, 2H), 2.22–1.94 (m, 2H), 1.90–1.71 (m, 2H), 1.61–1.45 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.3, 133.8, 133.2, 133.1, 129.4 (2C), 128.7 (2C), 128.0, 127.6 (2C), 124.7, 115.0 (2C), 83.1, 70.1, 69.6, 38.8, 34.0, 32.5, 32.2, 31.7, 27.5, 27.0, 24.5.

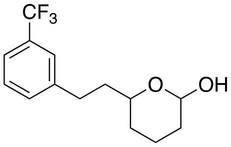


3-(3-(Trifluoromethyl)phenyl)propanal (5.34) was prepared according to Method B. The following amounts of reagents were used: 1-iodo-3-(trifluoromethyl)benzene (0.72 mL, 5.0 mmol, 1.0 equiv), allyl alcohol (0.51 mL, 7.5 mmol, 1.5 equiv), $Pd(OAc)_2$ (11 mg, 5.0 µmol, 1.0 mol %), $BnEt_3NCl$ (1.1 g, 5.0 mmol, 1.0 equiv), $NaHCO_3$ (1.1 g, 13 mmol, 2.5 equiv), and DMF (20. mL). **TLC R$_f$** = 0.2 (10% EtOAc/hexanes, CAM stain); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.49–7.44 (m, 2H), 7.43–7.37 (m, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.8, 141.5, 131.9 (q, *J* = 1.4 Hz), 131.0 (q, *J* = 32.4 Hz), 129.2, 125.2 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.4 Hz), 123.3 (q, *J* = 3.7 Hz), 45.1, 27.9; **^{19}F NMR** (565 MHz, $CDCl_3$) δ –62.7 (3F); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{10}H_9F_3Na$, 202.0605; found 202.0615.



1-(3-(Trifluoromethyl)phenyl)oct-7-en-3-ol (5.35) was prepared according to Method D. The following amounts of reagents were used: aldehyde **5.34** (0.43 g, 2.1 mmol, 1.0 equiv), Grignard reagent **5.22** (6.0 mL, 3.2 mmol, 1.5 equiv, 0.50 M in Et_2O), and Et_2O (11 mL). Purification by column chromatography (0–20% EtOAc/hexanes) afforded the title compound as a yellow oil (0.44 g, 1.6 mmol, 75% yield). **TLC R$_f$** = 0.6 (20% EtOAc/hexanes, $KMnO_4$ stain); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.38 (d, *J* = 4.8 Hz, 2H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04–4.92 (m, 2H), 3.62 (tt, *J* = 7.9, 4.2 Hz, 1H), 2.86 (ddd, *J* = 15.0, 10.1, 5.5 Hz, 1H), 2.72 (ddd,

J = 13.8, 10.0, 6.6 Hz, 1H), 2.19–2.00 (m, 2H), 1.85–1.66 (m, 3H), 1.62–1.37 (m, 3H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 143.2, 138.6, 132.0 (q, J = 1.2, 0.7 Hz), 130.8 (q, J = 31.8 Hz), 128.9, 124.4 (q, J = 272.1 Hz), 125.17 (q, J = 3.8 Hz), 122.79 (q, J = 3.8 Hz), 114.8, 71.1, 40.0, 37.1, 33.8, 32.0, 25.0; **^{19}F NMR** (565 MHz, CDCl$_3$) δ -62.6 (3F); **HRMS** (TOF MS CI+) *m/z*: [M+NH$_4$]$^+$ calcd for C$_{15}$H$_{19}$F$_3$ONH$_4$ 290.1732, found 290.1728.

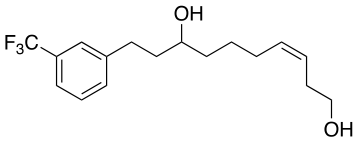


6-(3-(Trifluoromethyl)phenethyl)tetrahydro-2*H*-pyran-2-ol (5.36) was prepared according to Method E. The following amount of reagents were used: alkene **5.35** (0.72 g, 2.6 mmol, 1.0 equiv), ozone (excess), CH$_2$Cl$_2$ (20 mL), PPh$_3$ (1.7 g, 2.0 g/1.0 g of alcohol), NaHCO$_3$ (1.7 g. 2.0 g/1.0 g of alcohol). Purification by column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a white solid (0.47 g, 1.7 mmol, 65% yield, 2:1 dr). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually.

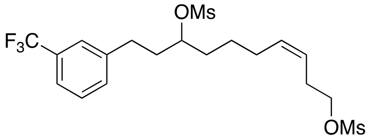
TLC R$_f$ = 0.2 (20% EtOAc/hexanes, CAM Stain); **HRMS** (TOF MS ES+) *m/z*: [M+Na]$^+$ calcd for C$_{14}$H$_{17}$F$_3$O$_2$Na, 297.1078; found 297.1077.

Major Diastereomer: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.46–7.41 (m, 2H), 7.40–7.33 (m, 2H, 4.70 (ddd, J = 9.0, 6.4, 2.1 Hz, 1H), 3.56 (br s, 1H), 3.41 (dddd, J = 10.5, 8.1, 4.4, 2.0 Hz, 1H), 2.91–2.63 (m, 2H), 1.98–1.42 (m, 6H), 1.41–1.15 (m, 2H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 143.1, 132.0 (q, J = 1.1 Hz), 130.72 (q, J = 32.1 Hz), 128.9, 125.3 (q, J = 3.8 Hz), 124.4 (q, J = 272.6 Hz), 122.78 (q, J = 3.9 Hz), 96.7, 75.5, 37.5, 33.0, 31.6, 30.5, 22.1; **^{19}F NMR** (565 MHz, CDCl$_3$) δ -62.6 (3F).

Minor Diastereomer: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.46–7.41 (m, 2H), 7.40–7.33 (m, 2H), 5.34 (s, 1H), 4.02–3.90 (m, 1H), 3.56 (br s, 1H), 2.91–2.63 (m, 2H), 1.98–1.42 (m, 6H), 1.41–1.15 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.3, 131.9 (q, $J = 1.1$ Hz), 130.69 (q, $J = 31.5$ Hz), 128.8, 125.3 (q, $J = 3.3$ Hz), 124.4 (q, $J = 272.6$ Hz), 122.75 (q, $J = 3.9$ Hz), 92.0, 68.0, 37.8, 31.2 30.0, 22.1, 17.5; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.6 (3F).



(3-(Trifluoromethyl)phenyl)dec-3-ene-1,8-diol (5.37) was prepared according to Method G. The following amounts of reagents were used: lactol **5.36** (0.47 g, 1.7 mmol, 1.0 equiv), Wittig salt **5.24** (0.69 g, 1.7 mmol, 1.0 equiv), *n*-BuLi (2.2 mL, 5.4 mmol, 3.2 equiv, 2.5 M in hexanes), and THF (8.5 mL). Purification by column chromatography (0–5% MeOH/CH_2Cl_2) afforded a mixture of the title compound and triphenylphosphine oxide. This mixture was carried onto the next step without further purification.



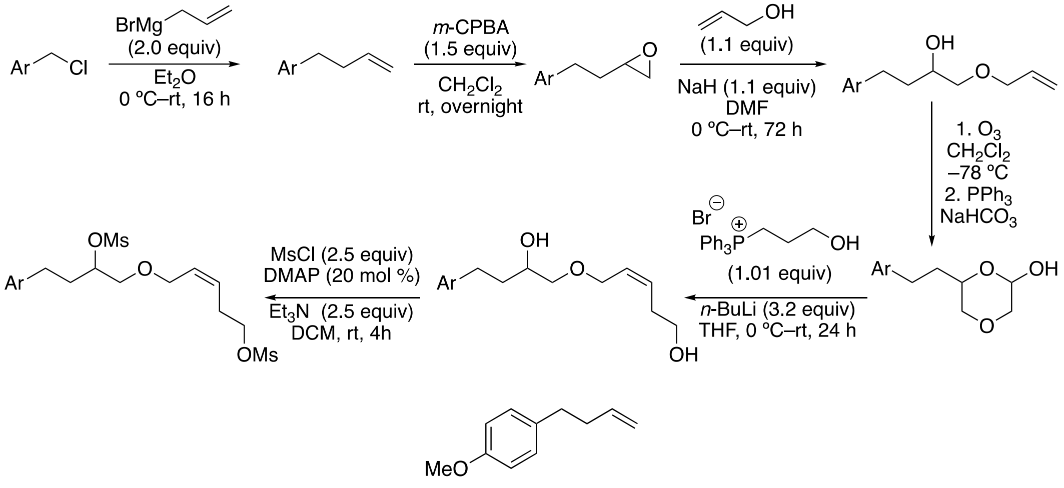
(3-(Trifluoromethyl)phenyl)dec-3-ene-1,8-diyl dimethanesulfonate (5.18) was prepared according to Method H. The following amounts of reagents were used: diol **5.37** (0.34 g, 1.1 mmol, 1.0 equiv), methanesulfonyl chloride (0.21 mL, 2.7 mmol, 2.5 equiv), DMAP (26 mg, 0.22 mmol, 20. mol %), Et_3N (0.38 mL, 2.7 mmol, 2.5 equiv), and CH_2Cl_2 (5.4 mL). Purification by column chromatography (0–30% EtOAc/hexanes) afforded the title compound as a pale yellow oil (0.40 g, 0.94 mmol, 78% yield, 2:1 cis:trans). For clarity, the ^{1}H and ^{13}C of the major and minor diastereomers have been tabulated individually.

TLC R$_f$ = 0.6 (50% EtOAc/hexanes, CAM Stain); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{27}F_3O_6S_2Na$, 495.1099; found 495.1080.

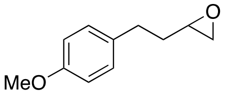
Major Diastereomer: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 (dd, *J* = 6.6, 1.7 Hz, 2H), 7.42–7.39 (m, 2H), 5.59–5.51 (m, 1H), 5.44–5.36 (m, 1H), 5.30 (s, 1H), 4.82–4.74 (m, 1H), 4.28–4.16 (m, 2H), 3.03 (s, 3H), 3.00 (s, 3H), 2.84 (ddd, *J* = 14.0, 10.2, 6.0 Hz, 1H), 2.77 (ddd, *J* = 14.2, 10.1, 6.4 Hz, 1H), 2.50 (q, *J* = 7.0 Hz, 1H), 2.16–1.97 (m, 4H), 1.85–1.69 (m, 2H), 1.49 (dddd, *J* = 20.3, 17.1, 13.5, 6.7 Hz, 2H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 141.9, 133.6, 132.9, 130.7 (q, *J* = 31.5 Hz), 129.0, 125.0 (q, *J* = 3.9 Hz), 124.8, 124.2 (q, *J* = 272.4), 123.1 (q, *J* = 3.9 Hz), 82.5, 69.3, 60.4, 38.7, 35.9 (2C), 34.0, 31.1, 26.9, 24.7; **^{19}F NMR** (565 MHz, CDCl$_3$) δ –62.5 (3F).

Minor Diastereomer: ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 (dd, *J* = 6.6, 1.7 Hz, 2H), 7.42–7.39 (m, 2H), 5.59–5.51 (m, 1H), 5.44–5.36 (m, 1H), 5.30 (s, 1H), 4.82–4.74 (m, 1H), 4.28–4.16 (m, 2H), 3.03 (s, 3H), 3.00 (s, 3H), 2.84 (ddd, *J* = 14.0, 10.2, 6.0 Hz, 1H), 2.77 (ddd, *J* = 14.2, 10.1, 6.4 Hz, 1H), 2.44 (q, *J* = 6.7 Hz, 1H), 2.16–1.97 (m, 4H), 1.85–1.69 (m, 2H), 1.49 (dddd, *J* = 20.3, 17.1, 13.5, 6.7 Hz, 2H); **^{13}C NMR** (151 MHz, CDCl$_3$) δ 141.9, 133.6, 131.9, 130.7 (q, *J* = 31.5 Hz), 129.0, 125.0 (q, *J* = 3.9 Hz), 124.8, 124.2 (q, *J* = 272.4), 123.1 (q, *J* = 3.9 Hz), 82.6, 69.6, 60.4, 37.4 (2C), 33.8, 32.4, 32.0, 27.4, 24.5; **^{19}F NMR** (565 MHz, CDCl$_3$) δ –62.5 (3F).

Scheme 5.6 Synthesis of Ether Containing Dimesylate Starting Material



1-(but-3-en-1-yl)-4-methoxybenzene (5.38) was prepared according to a procedure reported by Taber.[39] To a flame dried round bottom flask equipped with a stir bar was added 4-methoxybenzyl chloride (1.4 mL, 10. mmol, 1.0 equiv), and THF (50 mL, 0.20 M). The flask was cooled to 0 ºC and allylmagnesium bromide (20. mL, 20. mmol, 2.0 equiv, 1.0 M in Et_2O) was added dropwise. The flask was warmed to rt and allowed to stir overnight. To quench, saturated aq. NH_4Cl was added dropwise. The biphasic mixture was transferred to a separatory funnel and extracted with EtOAc (x 3). The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (0–10% EtOAc/hexanes) afforded the desired product as a clear and colorless oil (1.5 g, 9.3 mmol, 93% yield). Analytical data is consistent with literature values.[43] **TLC R_f** = 0.8 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.90 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.16 – 4.95 (m, 2H), 3.83 (s, 3H), 2.71 (t, *J* = 8.4 Hz, 2H), 2.40 (tdt, *J* = 7.8, 6.6, 1.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 138.4, 134.2, 129.5 (2C), 115.1, 114.0 (2C), 55.4, 36.0, 34.7.



2-(4-methoxyphenethyl)oxirane (5.39) was prepared according to a procedure reported by Taber.[39] A flame dried round bottom flask equipped with a stir bar is charged with alkene **5.38** (1.5 g, 9.3 mmol, 1.0 equiv), CH_2Cl_2 (93 mL, 0.1 M), and *m*-CPBA (3.4 g, 14 mmol, 1.5 equiv, 70% w/w in H_2O). The reaction mixture was allowed to stir at rt for 16 h. Upon completion the reaction mixture was diluted with CH_2Cl_2 and quenched with saturated aq. $NaHSO_3$. The biphasic mixture was transferred to a separatory funnel and the layers were separated. The product was

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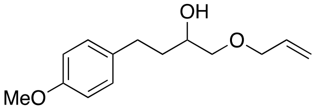
[43] S. Datta, C.-L. Chang, K.-L. Yeh, R.-S. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 9294–9295.

extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with 1 M NaOH, then brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (0–20% EtOAc/hexanes) afforded the title compound as a yellow oil (1.3 g, 7.0 mmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.95 (dddd, *J* = 6.4, 5.1, 4.0, 2.8 Hz, 1H), 2.84–2.66 (m, 3H), 2.47 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.92–1.76 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 133.3, 129.3 (2C), 113.9 (2C), 55.2, 51.7, 47.2, 34.5, 31.3.



1-(allyloxy)-4-(4-methoxyphenyl)butan-2-ol (5.40) was prepared according to a procedure reported by Isaacs.[44] In a glovebox, a flame dried round bottom flask equipped with a stir bar was charged with NaH (66 mg, 2.8 mol, 1.1 equiv). The flask was sealed with a septum, removed from the glovebox and placed under an atmosphere of N_2. Next, DMF (13 mL, 0.2 M) was added via syringe and the reaction mixture was cooled to 0 ºC. To the resulting suspension was added a solution of epoxide **5.39** (0.45 g, 2.5 mmol, 1.0 equiv) in DMF (2.5 mL, 1.0 M) dropwise via syringe. The reaction mixture was warmed to rt and allowed to stir for 72 h. The reaction was quenched with addition of H_2O and extracted with EtOAc (x 3). The combined organic layers were washed with excess H_2O (x 5) and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (0–20% EtOAc/hexanes) afforded the title compound as a pale yellow oil (0.29 g, 1.2 mmol, 50% yield). **TLC R_f** = 0.5 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.3

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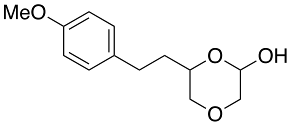
[44] Isaacs, R. C. A.; Thompson, W. J.; Williams, P. D.; Su, D.-S.; Wenkatraman, S.; Embrey, M. W.; Fisher, T. E.; Wai, J. S.; Dubost, D. C.; Ball, R. C.; Choi, E. J.; Pei, T.; Trice, S. L.; Campbell, N.; Maddess, M.; Maligres, P. E.; Shevlin. M.; Song, Z. J.; Steinhuebel, D. P.; Strotman, N. A.; Yin, J. HIV Integrase Inhibitors. US 2010.0087419 A1, **2010**.

Hz, 2H), 5.89 (ddt, *J* = 16.4, 10.8, 5.6 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.03–3.97 (m, 2H), 3.76 (s, 3H), 3.44 (dd, *J* = 9.6, 3.1 Hz, 1H), 3.30 (t, *J* = 9.0 Hz, 1H), 2.83–2.70 (m, 1H), 2.68–2.49 (m, 2H), 1.81–1.62 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 134.6, 134.1, 129.4 (2C), 117.3, 113.9 (2C), 74.6, 72.3, 69.7, 55.3, 35.1, 30.9; **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{20}O_3$, 259.1310; found 259.1322.

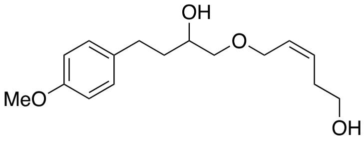


6-(4-methoxyphenethyl)-1,4-dioxan-2-ol (5.41) was prepared according to Method E. The following amounts of reagents were used: alkene **5.40** (0.16 g, 0.67 mmol, 1.0 equiv), ozone (excess), CH_2Cl_2 (25 mL), PPh_3 (0.32 g, 2.0 g/1.0 g of alcohol), $NaHCO_3$ (0.32 g, 2.0 g/1.0 g of alcohol). Purification by column chromatography (0–70% EtOAc/hexanes) afforded the desired product as a white solid (79 mg, 0.33 mmol, 50% yield, 1.5:1 dr). For clarity, the ^{1}H and ^{13}C are tabulated individually.

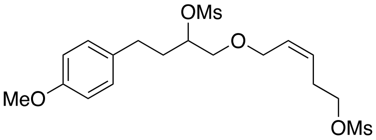
m.p. = 106–108 ºC; **TLC R_f** = 0.5 (60% EtOAc/hexanes); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{13}H_{18}O_4$, 238.1200; found 238.1205.

Major Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.04 (d, *J* = 6.2 Hz, 1H), 4.14 (dddd, *J* = 10.7, 7.9, 4.7, 2.8 Hz, 1H), 3.78 (s, 3H), 3.73 (ddd, *J* = 11.9, 6.4, 1.8 Hz, 2H), 3.62 (dd, *J* = 11.8, 2.0 Hz, 1H), 3.33 (dd, *J* = 11.5, 10.4 Hz, 1H), 3.27 (s, 1H), 2.78–2.51 (m, 2H), 1.84–1.52 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 133.7, 129.4 (2C), 114.0 (2C), 89.8, 71.4, 69.3, 66.6, 55.4, 33.4, 30.3.

Minor Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.87 (ddd, *J* = 9.0, 6.7, 2.6 Hz, 1H), 3.83 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.78 (s, 3H), 3.73 (ddd, *J* = 11.9, 6.4, 1.8 Hz, 2H), 3.62 (dd, *J* = 11.8, 2.0 Hz, 1H), 3.27 (s, 1H), 3.20–3.06 (m, 1H), 2.78–2.51 (m, 2H), 1.84–1.52 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 133.6, 129.4 (2C), 114.0 (2C), 92.3, 73.9, 70.2, 69.8, 55.4, 33.0, 30.4.



(2-Hydroxy-4-(4-methoxyphenyl)butoxy)pent-3-en-1-ol (5.42) was prepared according to Method G. The following amounts of reagents were used: lactol **5.41** (0.21 g, 0.88 mmol, 1.0 equiv), Wittig salt **5.24** (0.36 g, 0.89 mmol, 1.0 equiv), *n*-BuLi (1.2 mL, 2.8 mmol, 3.2 equiv, 2.5 M in hexanes), and THF (4.4 mL). Purification by column chromatography afforded a mixture of the title compound with triphenylphosphine oxide. This mixture was carried onto the next step without further purification.

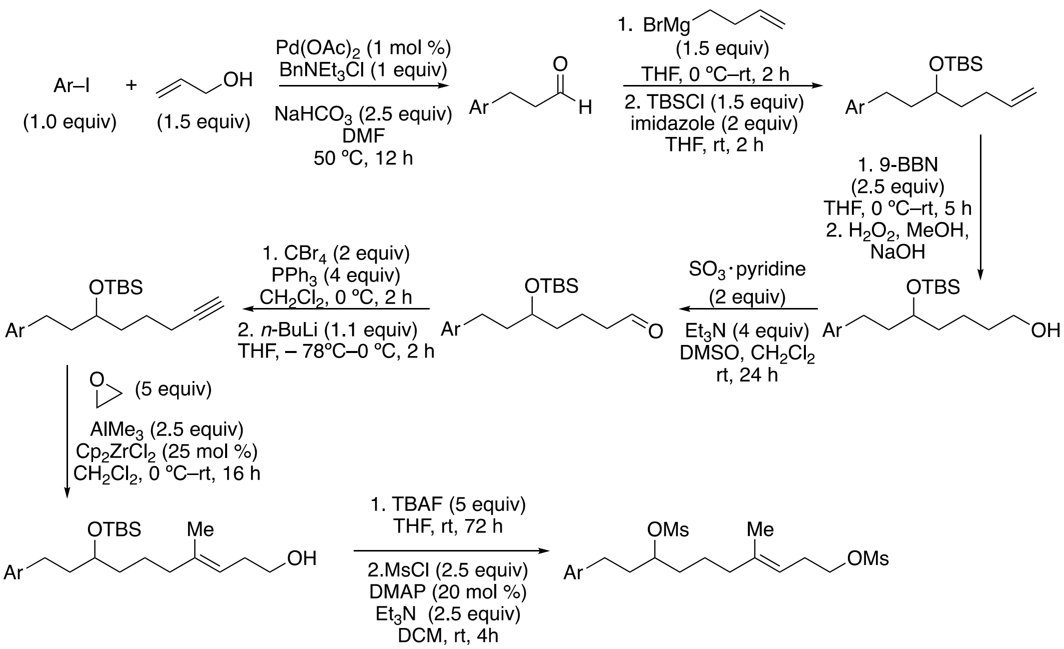


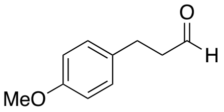
(4-Methoxyphenyl)-1-((5-((methylsulfonyl)oxy)pent-2-en-1-yl)oxy)butan-2-yl methanesulfonate (5.19) was prepared according to Method H. The following amounts of reagents were used: diol **5.42** (0.29 g, 1.0 mmol, 1.0 equiv), MsCl (0.20 mL, 2.6 mmol, 2.5 equiv), DMAP (25 mg, 0.21 mmol, 20 mol %), Et_3N (0.36 mL, 2.6 mmol, 2.5 equiv), and DCM (5.2 mL). Purification by column chromatography (0–60% EtOAc/hexanes) afforded the desired product as a pale yellow oil (197 mg, 0.45 mmol, 44% yield, 2:1 dr). For clarity, the ^{1}H and ^{13}C are tabulated individually. **TLC R_f** = 0.6 (60% EtOAc/hexanes); **HRMS** (TOF MS ES+) *m/z*: $[M+NH_4]^+$ calcd for $C_{18}H_{32}NO_8S_2$ 454.1569, found 454.1582.

Major Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.75–5.54 (m, 2H), 4.80 (dddd, *J* = 9.1, 7.8, 4.5, 1.2 Hz, 1H), 4.23 (dt, *J* = 9.7, 6.6 Hz, 2H), 4.15–3.92 (m, 2H), 3.77 (s, 3H), 3.64–3.52 (m, 2H), 3.06 (s, 3H), 2.99 (s, 3H), 2.81–2.60 (m, 2H), 2.57–2.44 (m, 2H), 1.95 (tddt, *J* = 14.4, 9.8, 6.7, 4.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 132.7, 129.3 (2C), 128.2, 127.4, 114.0 (2C), 81.7, 71.7, 68.9, 66.6, 55.3, 38.7, 37.4, 33.6, 30.3, 27.8.

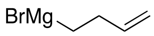
Minor Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.75–5.54 (m, 2H), 4.80 (dddd, *J* = 9.1, 7.8, 4.5, 1.2 Hz, 1H), 4.23 (dt, *J* = 9.7, 6.6 Hz, 2H), 4.15–3.92 (m, 2H), 3.77 (s, 3H), 3.64–3.52 (m, 2H), 3.06 (s, 3H), 2.99 (s, 3H), 2.81–2.60 (m, 2H), 2.57–2.44 (m, 2H), 1.95 (tddt, *J* = 14.4, 9.8, 6.7, 4.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 132.7, 129.7, 129.4 (2C), 127.4, 114.1 (2C), 81.7, 71.7, 68.8, 66.6, 55.3, 38.7, 37.5, 33.6, 30.3, 27.8.

Scheme 5.7 Synthesis of Trisubstituted Alkene Dimesylate Starting Material

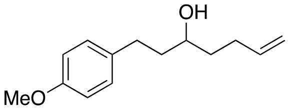




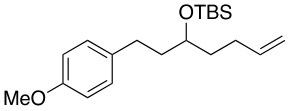
3-(4-Methoxyphenyl)propanal (5.25) was prepared according to Method B. Refer above for analytical data.



But-3-en-1-ylmagnesium bromide (5.43) was prepared according to Method C. The following amounts of reagents were used: 4-bromo-butene (4.1 mL, 40. mmol, 1.0 equiv), Mg^0 (1.4 g, 60. mmol, 1.5 equiv), and THF (20 mL). The resulting Grignard reagent was titrated to be 1.3 M.[35]



1-(4-methoxyphenyl)hept-6-en-3-ol (5.44) was prepared according to a modified version of Method D. The following amounts of reagents were used: aldehyde **5.25** (2.6 g, 16 mmol, 1.0 equiv), Grignard reagent **5.43** (19 mL, 24 mmol, 1.5 equiv, 1.3 M in THF), and THF (80 mL). The crude reaction mixture was passed through a plug of silica gel eluting with 100% EtOAc to remove any remaining magnesium salts and was carried into the next step without further purification.



***tert*-Butyl((1-(4-methoxyphenyl)hept-6-en-3-yl)oxy)dimethylsilane (5.45)** was prepared according a procedure reported by Jia.[45] To a flame dried round bottom flask equipped with a stir bar was added alcohol **5.44** (3.5 g, 16 mmol, 1.0 equiv), imidazole (2.2 g, 32 mmol, 2.0 equiv), *tert*-butyldimethylsilyl chloride (3.6 g, 24 mmol, 1.5 equiv), and CH_2Cl_2 (81 mL, 0.20 M). The reaction mixture was allowed to stir at rt for 24 h. After the reaction was complete, H_2O was added and the mixture was transferred to a separatory funnel. The mixture was extracted with CH_2Cl_2 (x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (0-30% EtOAc/hexanes) afforded the title compound as a pale yellow oil (4.6 g, 13 mmol, 86% yield). **TLC R_f** = 0.8 (20% EtOAc/hexanes);

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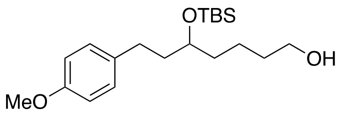
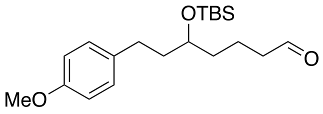
[45] Zhou, S.; Jia, Y. *Org. Lett.* **2014**, *16*, 3416–3418.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 5.99–5.83 (m, 1H), 5.17–4.98 (m, 2H), 3.84 (s, 4H), 2.80–2.58 (m, 2H), 2.29–2.13 (m, 2H), 1.83 (aq, *J* = 7.8, 7.3, 6.6 Hz, 2H), 1.69 (aq, *J* = 7.9, 7.4, 6.7 Hz, 2H), 1.05–1.02 (m, 9H), 0.16 (dd, *J* = 3.3, 1.5 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 139.1, 134.9, 129.4 (2C), 114.6, 114.1 (2C), 71.6, 55.4, 39.5, 36.5, 31.0, 29.9, 26.2 (3C), 18.4, -4.1 (2C); **HRMS** (TOF MS CI+) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{34}O_2SiH$ 335.2406, found 335.2402.



5-((*tert*-butyldimethylsilyl)oxy)-7-(4-methoxyphenyl)heptan-1-ol (5.46) was prepared according a procedure reported by Hartwig.[46] To a flame dried round bottom flask equipped with a stir bar was added silyl protected alcohol **5.45** (4.6 g, 14 mmol, 1.0 equiv) and THF (36 mL, 0.20 M). The reaction mixture was cooled to 0 ºC and 9-BBN (69 mL, 35 mmol, 1.5 equiv, 0.50 M in THF) was added dropwise via syringe. The mixture was warmed to rt and allowed to stir for at least 5 h. Then MeOH (42 mL, 3.0 mL/mmol), H_2O_2 (14 mL, 30%, 1.0 mL/mmol), and NaOH (42 mL, 1.0 M, 3.0 mL/mmol) were added, and the reaction stirred for at least 3 h. Once complete, H_2O (10 mL) was added. The reaction mixture was then extracted with EtOAc (x 3) and combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by column chromatography (0–30% EtOAc/hexanes) afforded a mixture of the title compound and unreacted 9-BBN as a pale yellow oil. This mixture was carried into the next step without further purification.



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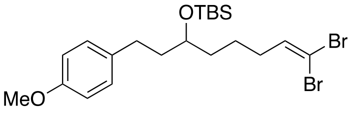
[46] Stanley, L. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 8971–8983.

5-((*tert*-butyldimethylsilyl)oxy)-7-(4-methoxyphenyl)heptanal (5.47) was prepared according to a procedure reported by Nicolaou.[47] To a flame dried round bottom flask equipped with a stir bar was added alcohol **5.46** (1.1 g, 3.0 mmol, 1.0 equiv), SO_3·pyridine (0.96 g, 6.0 mmol, 2.0 equiv), Et_3N (1.7 mL, 12 mmol, 4.0 equiv), DMSO (3 mL), and CH_2Cl_2 (3 mL). The reaction mixture was allowed to stir at rt for 24 h. Once complete, saturated aq. NH_4Cl (10 mL) was added. The reaction mixture was then extracted with CH_2Cl_2 (x 3) and combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.[48] Purification by column chromatography (0–10% EtOAc/hexanes) afforded the title compound as a yellow oil (0.80 g, 2.3 mmol, 76% yield). **TLC R_f** = 0.6 (20% EtOAc/hexanes, CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.7 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.72 (p, *J* = 5.7 Hz, 1H), 2.57 (qt, *J* = 13.8, 8.1 Hz, 2H), 2.46–2.37 (m, 2H), 1.95–1.82 (m, 2H), 1.79–1.59 (m, 2H), 1.59–1.46 (m, 2H), 0.91 (s, 9H), 0.05 (d, *J* = 5.6 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.6, 157.9, 134.7, 129.3 (2C), 113.9 (2C), 71.6, 55.4, 44.1, 42.1, 39.2, 36.4, 30.8, 26.1 (3C), 18.0, -4.3 (2C); **HRMS** (TOF MS ES+) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{34}O_3SiH$, 351.2355; found 351.2349.



***tert*-butyl((8,8-dibromo-1-(4-methoxyphenyl)oct-7-en-3-yl)oxy)dimethylsilane (5.48)** was prepared according to a procedure reported by Fürstner.[49] To a flame dried round bottom flask equipped with a stir bar was added aldehyde **5.47** (0.31 g, 0.88 mmol, 1.0 equiv), CBr_4 (0.58 g,

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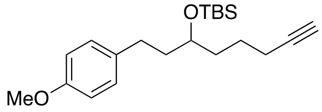
[47] Nicolaou, K. C.; Peng, X.-S.; Sun, Y.-P.; Polet, D.; Zou, B.; Lim, C. S.; Chen. D. Y. K. *J. Am. Chem. Soc.* **2009**, *131*, 10587–10597.

[48] Note: We observed that the yield of the Parikh-Doering oxidation decreases with increasing scale. We typically performed this reaction on less than 5.0 mmol of primary alcohol.

[49] Wölfl, B.; Mata, G.; Fürstner, A. *Chem. Eur. J.* **2019**, *25*, 255–259.

1.8 mmol, 2.0 equiv), and CH_2Cl_2 (4.4 mL, 0.20 M). The reaction mixture was cooled to 0 ºC and then PPh_3 (0.92 g, 3.5 mmol, 4.0 equiv) was added dropwise as a solution in CH_2Cl_2 (5.8 mL, 0.60 M). The reaction was allowed to stir at 0 ºC for 2 h. To quench, hexanes was added and the reaction mixture was filtered through a pad of silica gel eluting with 50% Et_2O in hexanes. The filtrate was concentrated and carried into the next step without further purification. The resulting crude reaction mixture was carried into the next step without further purification (0.38 g, 0.70 mmol, 84% yield). **TLC R_f** = 0.6 (20% EtOAc/hexanes, CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.40 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.78–3.71 (m, 1H), 2.70–2.45 (m, 3H), 2.45–2.37 (m, 1H), 2.16–2.08 (m, 2H), 1.90 (dtt, *J* = 9.0, 6.2, 2.6 Hz, 2H), 1.75 (tdd, *J* = 8.5, 5.7, 1.2 Hz, 2H), 0.95 (s, 9H), 0.11–0.06 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 138.8, 134.7, 129.3 (2C), 113.9 (2C), 89.0, 71.6, 55.4, 39.3, 36.4, 33.3, 30.9, 26.1 (3C), 23.6, 18.3, -4.2 (2C).



***tert*-butyl((1-(4-methoxyphenyl)oct-7-yn-3-yl)oxy)dimethylsilane (5.49)** was prepared according to a procedure reported by Ghosh.[50] The unpurified dibromide **5.48** (1.1 g, 2.1 mmol, 1.0 equiv) was dissolved in THF (10 mL, 0.20 M) and the mixture was cooled to – 78 ºC. Then *n*-BuLi (2.3 mL, 3.2 mmol, 1.5 equiv, 1.4 M in hexanes) was added dropwise and the mixture was allowed to slowly warm to 0 ºC over 2 h. To quench, saturated aq. NH_4Cl was added dropwise and the biphasic mixture was transferred to separatory funnel. The organic layer was extracted with EtOAc (x 3). The combined organic layers were washed sequentially with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (0–10%

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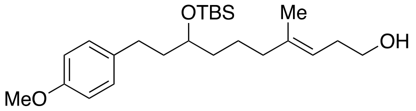
[50] Chandrasekhar, B.; Athe, S.; Reddy, P. P.; Ghosh, S. *Org. Biomol. Chem.* **2015**, *13*, 115–124.

EtOAc/hexanes) afforded the title compound as a pale yellow oil (0.43 g, 1.2 mmol, 53% yield). **TLC R$_f$** = 0.6 (20% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.10 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.74 (p, *J* = 5.4 Hz, 1H), 2.69–2.49 (m, 2H), 2.25–2.15 (m, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.74 (ddd, *J* = 9.1, 7.9, 5.7 Hz, 2H), 1.67–1.55 (m, 3H), 0.92 (s, 10H), 0.07 (d, *J* = 2.8 Hz, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 157.8, 134.8, 129.3 (2C), 113.9 (2C), 84.6, 71.6, 68.5, 55.4, 39.4, 36.1, 30.9, 26.1 (3C), 24.4, 18.8, 18.3, -4.2 (2C).



(*E*)-8-((*tert*-butyldimethylsilyl)oxy)-10-(4-methoxyphenyl)-4-methyldec-3-en-1-ol (5.50) was prepared according to a procedure reported by Sigman.[51] A flame dried round bottom flask equipped with a stir bar is charged with Cp$_2$ZrCl$_2$ (31 mg, 0.11 mmol, 25 mol %) and CH$_2$Cl$_2$ (0.21 mL, 2.0 M). The flask was cooled to 0 ºC and AlMe$_3$ (0.54 mL, 1.1 mmol, 2.5 equiv, 2.0 M in PhMe) was added dropwise via syringe and the mixture was allowed to stir for 30 mins. Then, a solution of alkyne **5.49** (150 mg, 0.43 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (0.45 mL, 0.25 M) was added via syringe. The reaction mixture was warmed to rt and allowed to stir overnight. Then the mixture was cooled to 0 ºC and ethylene oxide (1.1 mL, 2.2 mmol, 5.0 equiv, 2.5–3.3 M in THF) was added in one portion via syringe. The mixture was allowed to stir for an additional 3 h. To quench, the reaction mixture was cooled to 0 ºC and 1 M HCl was added dropwise. The mixture was then passed through a pad of Celite eluting with 100% CH$_2$Cl$_2$. The biphasic mixture was transferred to a separatory funnel and extracted with CH$_2$Cl$_2$ (x 3). The combined organic layers were washed with 1 M HCl and then brine. Then the organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (0–30% EtOAc/hexanes) afforded

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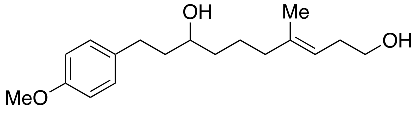
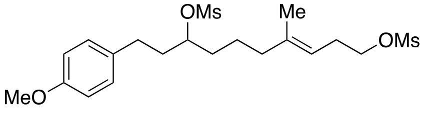
[51] Patel, H. H.; Sigman, M. S. *J. Am. Chem. Soc.* **2016**, *138*, 14226–14229.

the desired product as a pale yellow oil (69 mg, 0.17 mmol, 40% yield, >20:1 dr). **TLC R$_f$** = 0.3 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.14 (t, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.71 (t, *J* = 5.0 Hz, 1H), 3.66–3.60 (m, 3H), 3.58 (t, *J* = 5.3 Hz, 1H), 2.75–2.46 (m, 2H), 2.30 (q, *J* = 6.8 Hz, 2H), 2.00 (d, *J* = 9.0 Hz, 2H), 1.80–1.70 (m, 4H), 1.46 (qd, *J* = 11.9, 7.2 Hz, 4H), 0.92 (s, 9H), 0.07 (d, *J* = 4.4 Hz, 6H); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 157.8, 138.8, 134.9, 129.3 (2C), 120.0, 113.9 (2C), 71.9, 69.3, 62.6, 55.4, 40.0, 36.7, 31.7, 31.0, 26.1 (3C), 23.6, 18.3, 16.2, -4.2 (2C).



(*E*)-10-(4-methoxyphenyl)-4-methyldec-3-ene-1,8-diol (5.51) was prepared according to a procedure reported by Knochel.[52] To a flame dried round bottom flask equipped with a stir bar was added silylprotected alcohol **5.50** (69 mg, 0.17 mmol, 1.0 equiv) and THF (0.85 mL, 0.20 M). Then, tetrabutyl ammonium fluoride (TBAF, 0.85 mL, 0.85 mmol, 5.0 equiv, 1.0 M in THF) was added dropwise at rt. The reaction mixture was allowed to stir at rt for 72 h. The reaction was quenched with H$_2$O. The biphasic mixture was transferred to a separatory funnel and the product was extracted with EtOAc (x 3). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. Purification by column chromatography (0–30% EtOAc/hexanes) afforded the title compound as a pale yellow oil (40 mg, 0.14 mmol, 80% yield).



(*E*)-10-(4-methoxyphenyl)-4-methyldec-3-ene-1,8-diyl dimethanesulfonate (5.20) was prepared according to Method H. The following amounts of reagents were used: diol **5.51** (40 mg,

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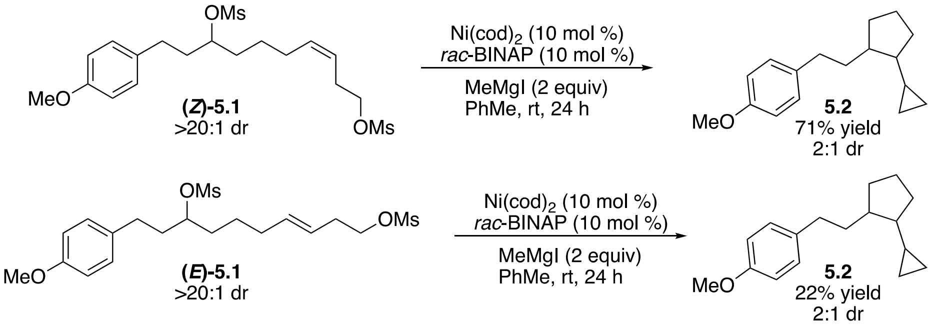
[52] Seel, S.; Thaler, T.; Takatsu, K.; Zhang, C.; Zipse, H.; Straub, B. F; Mayer, P.; Knochel, P. *J. Am. Chem. Soc.* **2011**, *133*, 4774–4777.

0.14 mmol, 1.0 equiv), MsCl (30. µL, 0.35 mmol, 2.5 equiv), DMAP (3.4 mg, 28 µmol, 20 mol %), Et_3N (50. µL, 0.35 mmol, 2.5 equiv), and CH_2Cl_2 (0.70 mL). Purification by column chromatography (0–50% EtOAc/hexanes) afforded the desired product as a pale yellow oil (27 mg, 61 µmol, 44% yield). **TLC R$_f$** = 0.4 (50% EtOAc/hexanes, CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.12 (t, *J* = 6.8 Hz, 1H), 4.76 (h, *J* = 6.5, 6.0 Hz, 1H), 4.18 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 3.06–2.92 (m, 6H), 2.78–2.58 (m, 2H), 2.46 (q, *J* = 7.0 Hz, 1H), 2.09–1.89 (m, 4H), 1.80–1.65 (m, 2H), 1.60–1.43 (m, 3H), 1.09 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 138.9, 133.0, 129.4 (2C), 118.5, 114.1 (2C), 83.2, 69.6, 55.4, 39.2, 38.9, 37.6, 36.5, 34.1, 30.5, 28.2, 23.0, 16.2.

5.4.7 Synthesis and Characterization Data for Mechanistic Experiments

5.4.7.1 Mechanistic Experiment with Single Alkene Diastereomer

Scheme 5.8 Results from Single Alkene Diastereomer Experiment



The control reaction was performed according to Method A. Two separate reactions were set up in 7-mL dram vials. The following amounts of reagents were used:

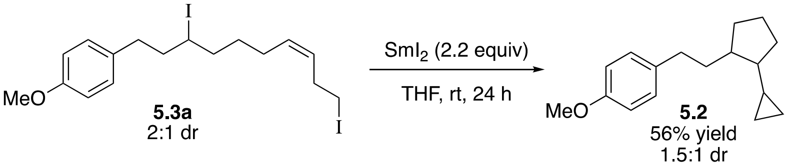
Vial 1: (*Z*)-**5.1** (61 mg, 0.14 mmol, 1.0 equiv), $Ni(cod)_2$ (3.9 mg, 14 µmol, 10 mol %), *rac*-BINAP (8.7 mg, 14 µmol, 10 mol %), MeMgI (0.11 mL, 0.28 mmol, 2.0 equiv, 2.9 M in Et_2O), PhMe (0.70 mL), AD-mix-β (196 mg, 1.4 g/mol substrate), *t*-BuOH (0.50 mL), and H_2O (0.50 mL). Purification by column chromatography (0–10% EtOAc/hexanes) afforded the desired product **5.2** (24 mg, 98 µmol, 71% yield, 2:1 dr).

Vial 2: (*E*)-**5.1** (17 mg, 40 μmol, 1.0 equiv), Ni(cod)$_2$ (1.1 mg, 4.0 μmol, 10 mol %), *rac*-BINAP (2.5 mg, 4.0 μmol, 10 mol %), MeMgI (30. μL, 80. μmol, 2.0 equiv, 2.9 M in Et$_2$O), PhMe (0.20 mL), AD-mix-β (56 mg, 1.4 g/mol substrate), *t*-BuOH (0.30 mL), and H$_2$O (0.30 mL). Purification by column chromatography (0–10% EtOAc/hexanes) afforded the desired product **5.2** (2.1 mg, 8.5 μmol, 22% yield, 2:1 dr).

5.4.7.2 Separation of Alkene Diastereomers on Silver Impregnated Silica

AgNO$_3$ (10 g) was dissolved in H$_2$O (2.5 mL) and MeCN (100 mL) in a 500 mL erlenmeyer flask. The stock solution was poured into a 500 mL round bottom flask that contained 100 g of silica gel and a stir bar. The slurry was allowed to stir at rt for 2 h and then was concentrated in vacuo in the dark. The silica gel was dried on a high vacuum manifold overnight and resulted in a cream colored powder. The silica gel was then used to separate the alkene diastereomers.[53]

5.4.7.3 SmI$_2$ Control Reaction



(5.8)

Preparation of SmI$_2$ in THF: SmI$_2$ was prepared as a solution in THF according to a procedure reported by Procter.[30] In a glovebox, Sm metal (0.60 g, 4.0 mmol, 2.0 equiv) was added to a flame dried Schlenk flask equipped with a stir bar. The flask was sealed with a septum, removed from the glovebox, and placed under an N$_2$ atmosphere. Then freshly washed 1,2-diiodoethane (0.56 g, 2.0 mmol, 1.0 equiv) was added. The flask was evacuated and backfilled with N$_2$ (x 3). Then THF (20 mL) was added via syringe and the resulting yellow solution was evacuated until the solvent began to bubble and backfilled with N$_2$ (x 3). Then the mixture was allowed to stir overnight at rt

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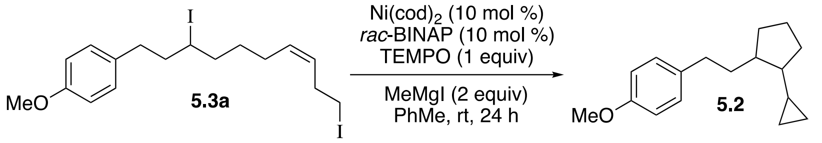
[53] (a) see ref: 28. (b) The silver impregnated silica gel is sensitive to light. All preparations of the silica gel were performed in the dark. The column was performed by wrapping the glassware in aluminum foil and in the dark.

in the dark and resulted in a dark blue solution. The SmI_2 was titrated according to a procedure reported by Hilmersson and used immediately.[54]

Control Reaction with SmI_2: To a flame dried round bottom flask equipped with a stir bar was added diiodide **5.3a** (27 mg, 54 µmol, 1.0 equiv) and THF (0.27 mL). Then SmI_2 (3.0 mL, 0.12 mmol, 2.2 equiv, 0.042 M in THF) was added dropwise via syringe. The reaction mixture was stirred at rt overnight. MeOH was added to quench and the reaction mixture was filtered through a pad of silica gel eluting with 100% Et_2O. Purification by column chromatography (100% hexanes) afforded the cascade product **5.2** (7.4 mg, 30 µmol, 56% yield, 1.5:1 dr). Refer above for characterization data.

5.4.7.4 TEMPO Control Reaction



(5.9)

The mechanistic experiment with TEMPO as an additive was performed according to a modified version of Method A. The following amounts of reagents were used: diiodide **5.3a** (25 mg, 50. µmol, 1.0 equiv), $Ni(cod)_2$ (1.4 mg, 5.0 µmol, 10. mol %), *rac*-BINAP (3.1 mg, 5.0 µmol, 10. mol %), MeMgI (30. µL, 0.10 mmol, 2.0 equiv, 2.9 M in Et_2O), TEMPO (7.8 mg, 50. µmol, 1.0 equiv), and PhMe (0.25 mL). The reaction was quenched with MeOH and filtered through a pad of silica gel eluting with 100% Et_2O. A 48% ^1H NMR yield of **5.2** was observed compared to PhTMS as an internal standard.

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[54] Dahlén, A.; Hilmersson, G. *Eur. J. Inorg. Chem.* **2004**, *15*, 3020–3024.

5.4.8 Competition Experiment

The competition experiment was performed according to a modified version of Method A. Two separate reactions were set up for each additive in different 7-mL dram vials. The following amounts of reagents were used:

Vial 1: dimesylate **5.1** (47 mg, 0.11 mmol, 1.0 equiv), secondary mesylate **5.9** (45 mg, 0.11 mmol, 1.0 equiv), Ni(cod)$_2$ (3.1 mg, 11 µmol, 10. mol %), *rac*-BINAP (6.8 mg, 11 µmol, 10. mol %), MeMgI (0.11 mL, 0.33 mmol, 3.0 equiv, 3.0 M in Et_2O), and PhMe (0.55 mL). The crude reaction mixture was concentrated to remove PhMe and was diluted to 300 µM in DCM and analyzed by GCMS. All area percent values were obtained from GCMS spectrum.

Vial 2: dimesylate **5.1** (43 mg, 0.10 mmol, 1.0 equiv), primary mesylate **5.12** (36 mg, 0.10 mmol, 1.0 equiv), Ni(cod)$_2$ (2.8 mg, 10. µmol, 10. mol %), *rac*-BINAP (6.2 mg, 10. µmol, 10. mol %), MeMgI (0.10 mL, 0.30 mmol, 3.0 equiv, 3.0 M in Et_2O), and PhMe (0.50 mL). The crude reaction mixture was concentrated to remove PhMe and was diluted to 300 µM in DCM and analyzed by GCMS. All area percent values were obtained from GCMS spectrum.

Table 5.3. Area Percent Values and Ratio Calculations for the Competition Experiment

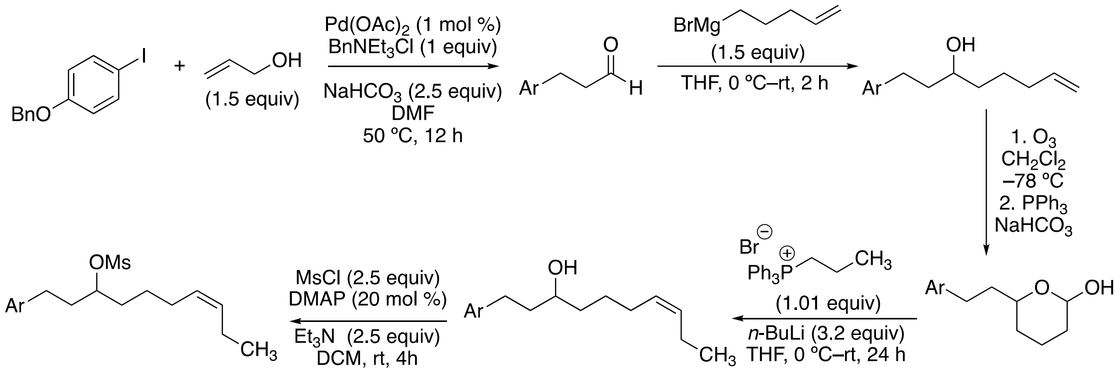
Compound	Area	Area Percent	
PhTMS	16627132	16.69231113	
Trimethoxybenzene	33349020	33.47974972	**Ratio**
Product (**5.2**)	30001111	30.11871676	1.52815348
Products from 2° mesylate (**5.10, 5.11**)	19632263	19.70922239	
Total	99609526		

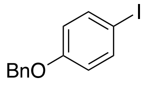
Compound	Area	Area Percent	
PhTMS	28142418.73	16.81324325	
Trimethoxybenzene	48364556.51	28.89463983	
Product **2**	37642540.71	22.48894096	
Products from 1° mesylate (**5.14**)	5668865.774	3.386774253	**Ratio**
Kumada (**5.13**)	8612848	5.145609901	2.63571594
Iodide (**5.52**)	38951221.83	23.27079181	

Total	167382451.6

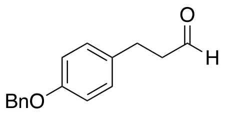
5.4.8.1 Synthesis and Characterization Data for Competition Experiment

Scheme 5.9 Synthesis of Secondary Mesylate **5.9** for Competition Experiment

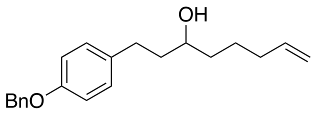




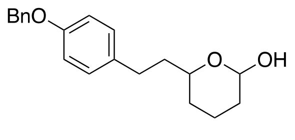
1-(Benzyloxy)-4-iodobenzene (5.29) refer above for synthesis and characterization data.



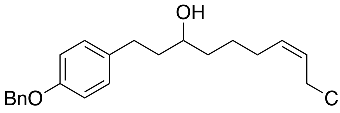
3-(4-(Benzyloxy)phenyl)propanal (5.30) refer above for synthesis and characterization data.



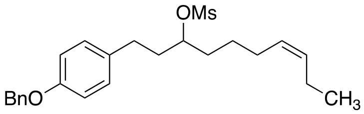
1-(4-(Benzyloxy)phenyl)oct-7-en-3-ol (5.31) refer above for synthesis and characterization data.



6-(4-(Benzyloxy)phenethyl)tetrahydro-2*H*-pyran-2-ol (5.32) refer above for synthesis and characterization data.

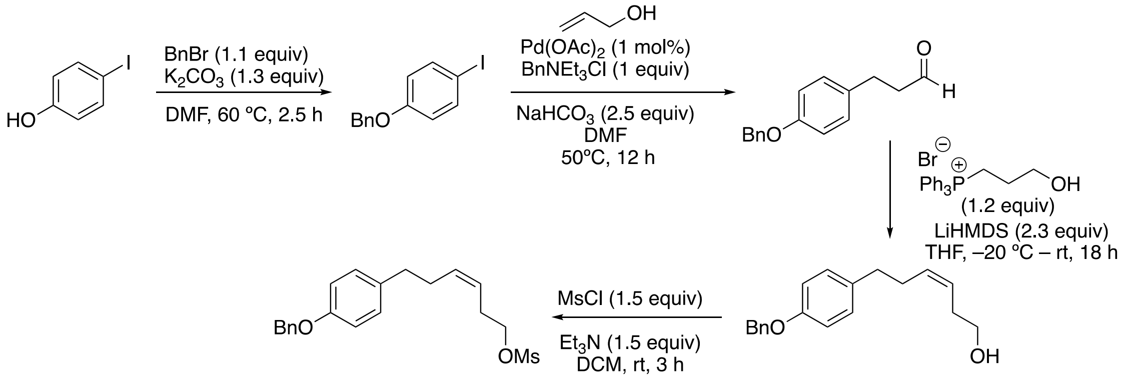


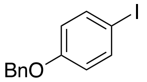
(4-(benzyloxy)phenyl)dec-7-en-3-ol (5.53) was prepared according to Method G. The following amounts of reagents were used: lactol **5.32** (0.10 g, 0.32 mmol, 1.0 equiv), propyltriphenylphosphonium bromide (0.13 g, 0.32 mmol, 1.0 equiv), *n*-BuLi (0.40 mL, 0.96 mmol, 3.0 equiv, 2.5 M in hexanes), and THF (1.6 mL). Purification by column chromatography (0–50% EtOAc/hexanes) afforded the title compound as a white solid (59 mg, 0.17 mmol, 55% yield, 2:1 dr). **TLC R_f** = 0.3 (30% EtOAc/hexanes, $KMnO_4$ stain); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45–7.40 (m, 4H, both diastereomers), 7.37 (ddd, *J* = 9.9, 5.6, 1.6 Hz, 4H, both diastereomers), 7.33–7.28 (m, 2H, both diastereomers), 7.11 (d, *J* = 8.5 Hz, 4H, both diastereomers), 6.90 (d, *J* = 8.5 Hz, 4H, both diastereomers), 4.68 (br s, 2H, both diastereomers), 5.47–5.25 (m, 4H, both diastereomers), 5.03 (s, 4H, both diastereomers), 3.60 (tt, *J* = 8.1, 4.0 Hz, 2H, both diastereomers), 2.72 (ddd, *J* = 14.9, 9.6, 5.7 Hz, 2H, both diastereomers), 2.60 (ddd, *J* = 13.9, 9.5, 6.8 Hz, 2H, both diastereomers), 2.09–1.93 (m, 8H, both diastereomers), 1.81–1.63 (m, 4H, both diastereomers), 1.54–1.32 (m, 8H, both diastereomers), 0.95 (td, *J* = 7.4, 4.4 Hz, 6H, both diastereomers); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.1 (2C, both diastereomers), 137.3 (2C, both diastereomer), 134.6 (2C, both diastereomers), 132.5 (minor diastereomer), 132.1 (major diastereomer), 129.4 (4C, both diastereomers), 128.9 (2C, both diastereomers), 128.7 (4C, both diastereomers), 128.0 (2C, both diastereomer), 127.6 (4C, both diastereomers), 114.9 (4C, both diastereomers), 71.3 (2C, both diastereomers), 70.1 (2C, both diastereomers), 39.4 (2C, both diastereomers), 37.2 (major diastereomers), 37.1 (minor diastereomer), 31.2 (2C, both diastereomers), 27.1 (2C, both diastereomers), 25.8 (major diastereomer), 25.7 (minor diastereomers), 20.6 (2C, both diastereomers), 14.5 (major diastereomer), 14.1 (minor diastereomer); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{30}O_2Na$, 361.2144; found 361.2129.



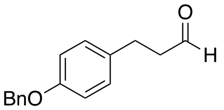
(*Z*)-1-(4-(benzyloxy)phenyl)dec-7-en-3-yl methanesulfonate (5.9) was prepared according to Method H. The following amounts of reagents were used: alcohol **5.53** (0.12 g, 0.34 mmol, 1.0 equiv), MsCl (40. µL, 0.51 mmol, 1.5 equiv), Et_3N (70. µL, 0.51 mmol, 1.5 equiv), and CH_2Cl_2 (1.7 mL). Purification by column chromatography (0–30% EtOAc/hexanes) afforded the title compound as a yellow oil (124 mg, 0.30 mmol, 87% yield). **TLC R$_f$** = 0.8 (50% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.9 Hz, 4H, both diastereomers), 7.38 (t, *J* = 7.7 Hz, 4H, both diastereomers), 7.34–7.29 (m, 2H, both diastereomers), 7.11 (d, *J* = 8.5 Hz, 4H, both diastereomers), 6.90 (d, *J* = 8.5 Hz, 4H, both diastereomers), 5.54–5.21 (m, 4H, both diastereomers), 5.04 (s, 4H, both diastereomers), 4.75 (quint, *J* = 6.0 Hz, 2H, both diastereomers), 2.98 (s, 6H, both diastereomers), 2.75–2.58 (m, 4H, both diastereomers), 2.11–1.91 (m, 12H, both diastereomers), 1.80–1.68 (m, 4H, both diastereomers), 1.53–1.39 (m, 4H, both diastereomers), 0.96 (td, *J* = 7.4, 4.1 Hz, 6H, both diastereomers); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.35 (major diastereomer), 157.34 (minor diastereomer), 137.2 (2C, both diastereomers), 133.4 (minor diastereomer), 133.1 (major diastereomer), 132.7 (2C, both diastereomers), 129.4 (4C, both diastereomers), 128.7 (4C, both diastereomers), 128.3 (minor diastereomer), 128.2 (major diastereomer), 128.1 (2C, both diastereomers), 127.6 (4C, both diastereomers), 115.1 (4C, both diastereomers), 83.43 (minor diastereomer), 84.36 (major diastereomer), 70.2 (2C, both diastereomers), 38.9 (2C both diastereomers), 36.49 (major diastereomer), 36.47 (minor diastereomer), 34.13 (major diastereomer), 34.00 (minor diastereomer), 32.24 (minor diastereomer), 30.51 (minor diastereomer), 30.50 (major diastereomer), 26.8 (major diastereomer), 25.7 (minor diastereomer), 25.1 (major diastereomer), 24.9 (minor diastereomer), 20.69 (major diastereomers), 14.47 (major diastereomer), 14.06 (minor diastereomer); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{32}O_4SNa$, 439.1919; found 439.1915.

Scheme 5.10 Synthesis of Primary Mesylate **5.12** for Competition Experiment

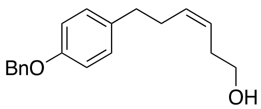




1-(Benzyloxy)-4-iodobenzene (5.29) refer above for synthesis and characterization data.



3-(4-(Benzyloxy)phenyl)propanal (5.30) refer above for synthesis and characterization data.



(4-(benzyloxy)phenyl)hex-3-en-1-ol (5.54) was prepared according to a procedure reported by Liu.[55] To a flame dried round bottom flask was added Wittig salt **5.24** (0.45 g, 1.1 mmol, 1.2 equiv) and THF (2.4 mL). The flask was cooled to – 20 ºC[56] and LiHMDS (0.36 mg, 2.2 mmol, 2.3 equiv)

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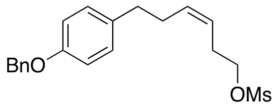
[55] Wang, Y.; Jiang, M.; Liu, J.-T. *Adv. Synth. Catal.* **2016**, *358*, 1322–1327.

[56] A – 20 ºC bath was prepared using ice water and NaCl.

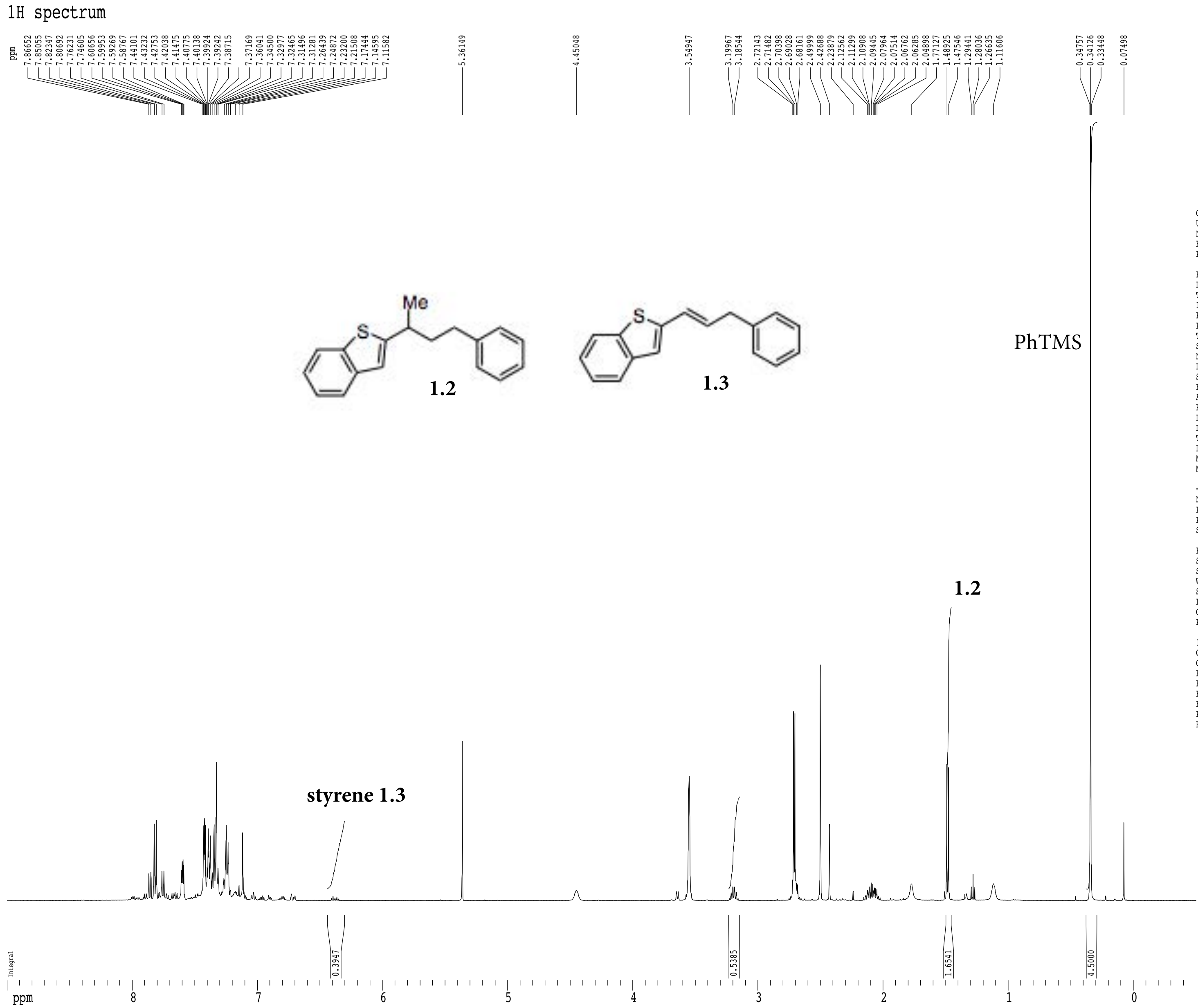
was added as a solution in PhMe (1.0 M) dropwise via syringe. The dark orange suspension was allowed to stir at – 20 ºC for 1 h, then aldehyde **5.30** (0.27 g, 1.1 mmol, 1.0 equiv) was added as a solution in THF (1.0 mL) dropwise. The reaction mixture was allowed to stir at – 20 ºC for 2 h and then slowly allowed to warm to rt overnight. To quench, saturated aq NH_4Cl was added dropwise. The biphasic mixture was transferred to a separatory funnel and extracted with EtOAc (x 3). The combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by column chromatography (0–20% EtOAc/hexanes) afforded the title compound as a white solid (140 mg, 0.50 mmol, 45% yield, 1.5:1 dr). **TLC R_f** = 0.3 (30% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.29 (m, 10H, both diastereomers), 7.11 (dd, *J* = 8.7, 7.1 Hz, 4H, both diastereomers), 6.93 (d, *J* = 8.4 Hz, 4H, both diastereomers), 5.66–5.53 (m, 2H, both diastereomers), 5.49–5.32 (m, 2H, both diastereomers), 5.06 (s, 4H, both diastereomers), 3.59 (dt, *J* = 10.5, 6.4 Hz, 4H, both diastereomers), 2.65 (td, *J* = 7.6, 4.9 Hz, 4H, both diastereomers), 2.32 (ddt, *J* = 37.5, 12.4, 6.8 Hz, 8H, both diastereomers); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.2 (2C, both diastereomers), 137.4 (2C, both diastereomers), 137.4 (minor diastereomer), 133.3 (major diastereomer), 132.2 (2C, both diastereomers), 129.5 (4C, both diastereomers), 128.7 (4C, both diastereomers), 128.0 (2C, both diastereomer), 127.6 (4C, both diastereomers), 126.8 (major diastereomer), 126.0 (minor diastereomer), 114.9 (4C, both diastereomers), 70.2 (2C, both diastereomers), 62.3 (minor diastereomer), 62.1 (major diastereomer), 36.1 (2C, both diastereomers), 35.1 (major diastereomer), 34.8 (minor diastereomer), 30.9 (minor diastereomer), 29.6 (major diastereomer); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{22}O_2Na$, 305.1518; found 305.1521.



(4-(benzyloxy)phenyl)hex-3-en-1-yl methanesulfonate (5.12) was prepared according to Method H. The following amounts of reagents were used: alcohol **5.54** (140 mg, 0.50 mmol, 1.0 equiv), MsCl (60. μL, 0.74 mmol, 1.5 equiv), Et_3N (0.10 mL, 0.74 mmol, 1.5 equiv) and CH_2Cl_2 (2.5 mL). Purification by column chromatography (0–30% EtOAc/hexanes) afforded the title compound as a yellow oil (120 mg, 0.33 mmol, 68% yield, 1.5:1 dr). **TLC R_f** = 0.5 (50% EtOAc/hexanes, CAM Stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 4H, both diastereomers), 7.38 (t, *J* = 7.2 Hz, 4H, both diastereomers), 7.34–7.28 (m, 2H, both diastereomers), 7.08 (dd, *J* = 7.2, 4.8 Hz, 4H, both diastereomers), 6.90 (d, *J* = 8.5 Hz, 4H, both diastereomers), 5.66–5.53 (m, 2H, both diastereomers), 5.43–5.31 (m, 2H, both diastereomers), 5.04 (s, 4H, both diastereomers), 4.18 (t, *J* = 6.8 Hz, 2H, both diastereomers), 4.05 (t, *J* = 6.9 Hz, 2H, both diastereomers), 2.95 (s, 3H, major diastereomer), 2.94 (s, 3H, minor diastereomer), 2.62 (t, *J* = 7.6 Hz, 4H, both diastereomers), 2.46–2.25 (m, 8H, both diastereomers); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.23 (minor diastereomer), 157.17 (major diastereomer), 137.34 (major diastereomer), 137.31 (minor diastereomer), 134.2 (major diastereomer), 134.1 (minor diastereomer), 134.0 (major diastereomer), 133.0 (minor diastereomer), 129.6 (2C, minor diastereomer), 129.5 (2C, major diastereomers), 128.7 (4C, both diastereomers), 128.01 (minor diastereomer), 128.00 (major diastereomer), 127.59 (2C, minor diastereomer), 127.58 (2C, minor diastereomer), 124.4 (major diastereomer), 123.7 (minor diastereomer), 114.9 (2C, minor diastereomer), 114.8 (2C, major diastereomer), 70.2 (2C, both diastereomers), 69.6 (major diastereomer), 69.3 (minor diastereomer), 37.56 (minor diastereomer), 37.53 (minor diastereomer), 34.89 (major diastereomer), 34.81 (major diastereomer), 34.6 (major diastereomer), 32.5 (minor diastereomer), 29.6 (major diastereomer), 27.43 (minor diastereomer); **HRMS** (TOF MS ES+) *m/z*: $[M+Na]^+$ calcd for $C_{20}H_{24}O_4SNa$, 378.1739; found 378.1747.

APPENDIX A.1

^{1}H, ^{13}C, COSY, NOE NMR SPECTRA FOR CHAPTER 1



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EXPNO                  2
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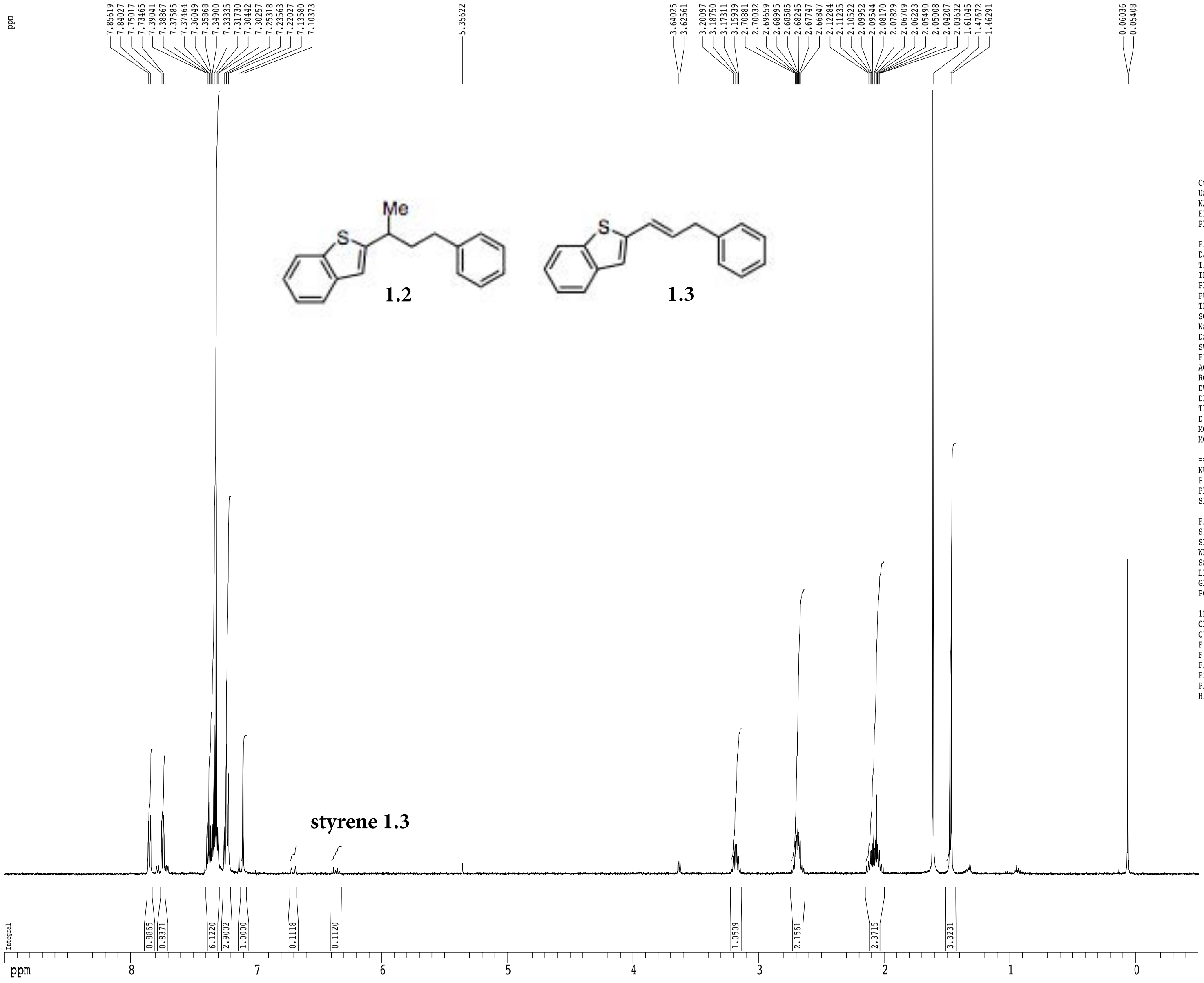
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1      500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

1H spectrum



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PROCNO                1

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SOLVENT          CDCl3T
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DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG               1824.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -6.00 dB
SFO1        498.6534906 MHz

F2 - Processing parameters
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SF          498.6500000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4487.85 Hz
F2P              -0.500 ppm
F2              -249.32 Hz
PPMCM           0.41667 ppm/cm
HZCM          207.77084 Hz/cm
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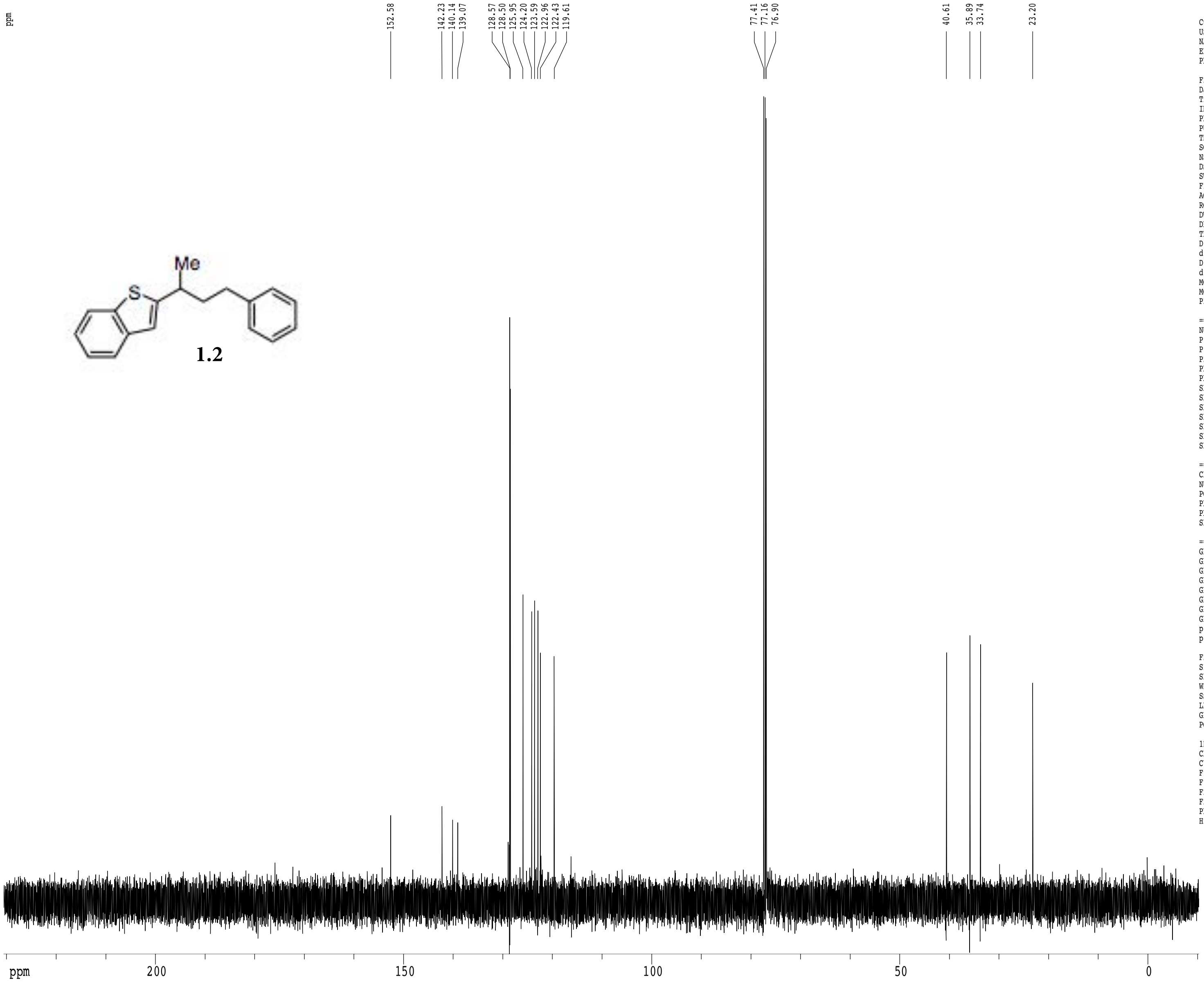
Z-restored spin-echo 13C spectrum with 1H decoupling



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PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT             CDCl3
NS                    120
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P12               2000.00 usec
P20                500.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP2                  2.70 dB
SP4                  2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2               0.00 Hz
SPOFF4               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                23.54 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804071 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               230.637 ppm
F1                29009.68 Hz
F2P               -10.287 ppm
F2               -1293.96 Hz
PPMCM            10.56688 ppm/cm
HZCM           1329.10693 Hz/cm
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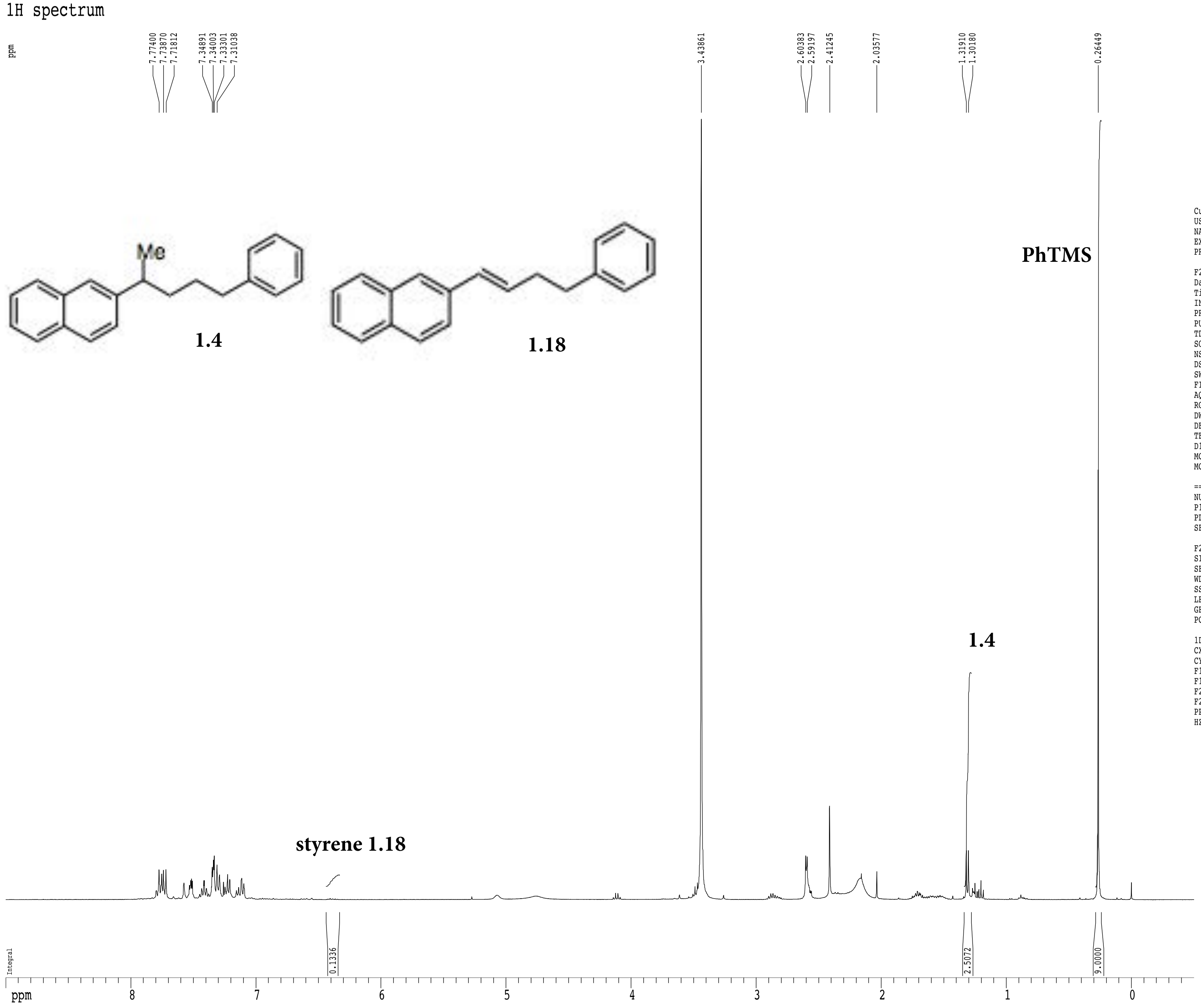

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PROCNO                 1

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TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300215 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
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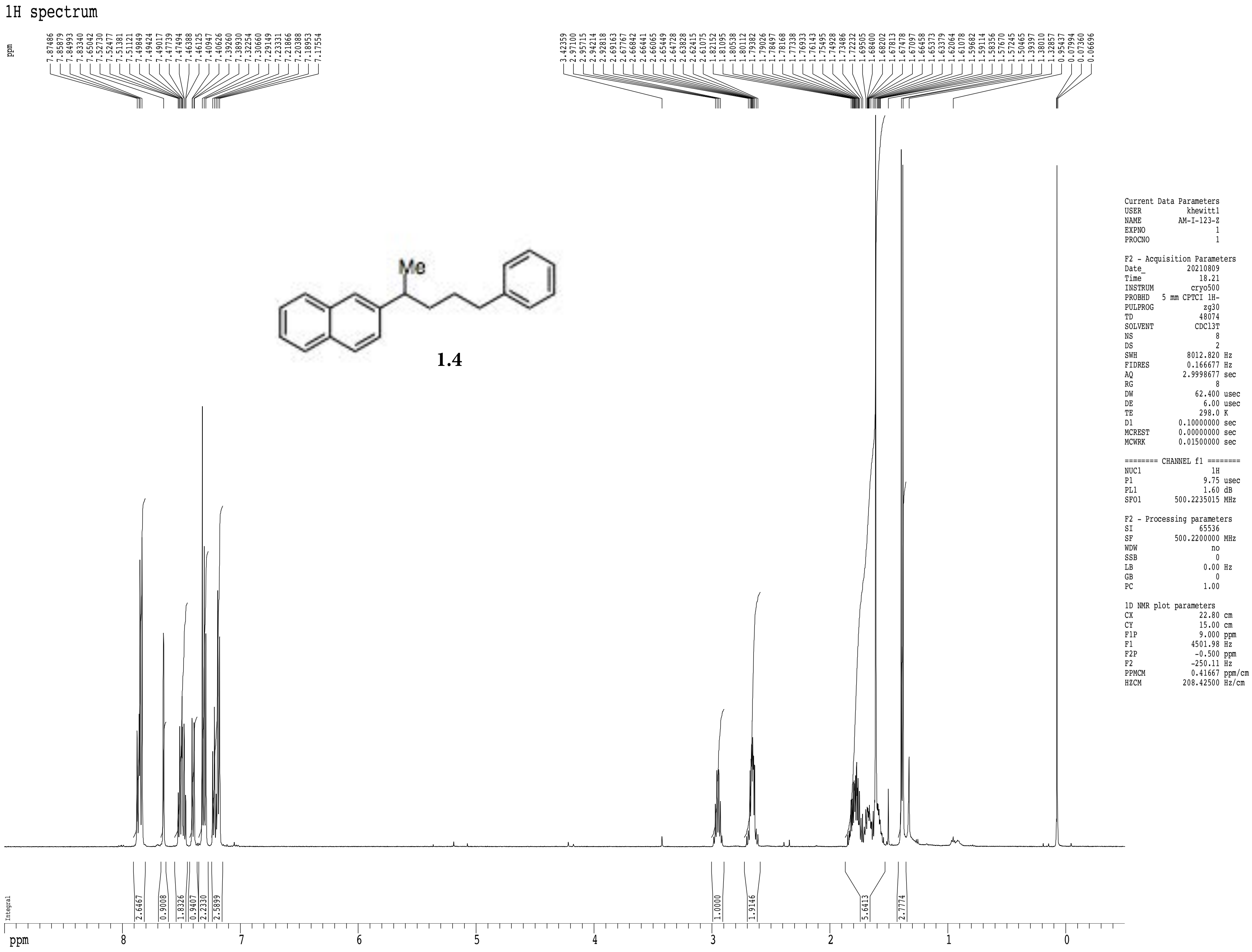
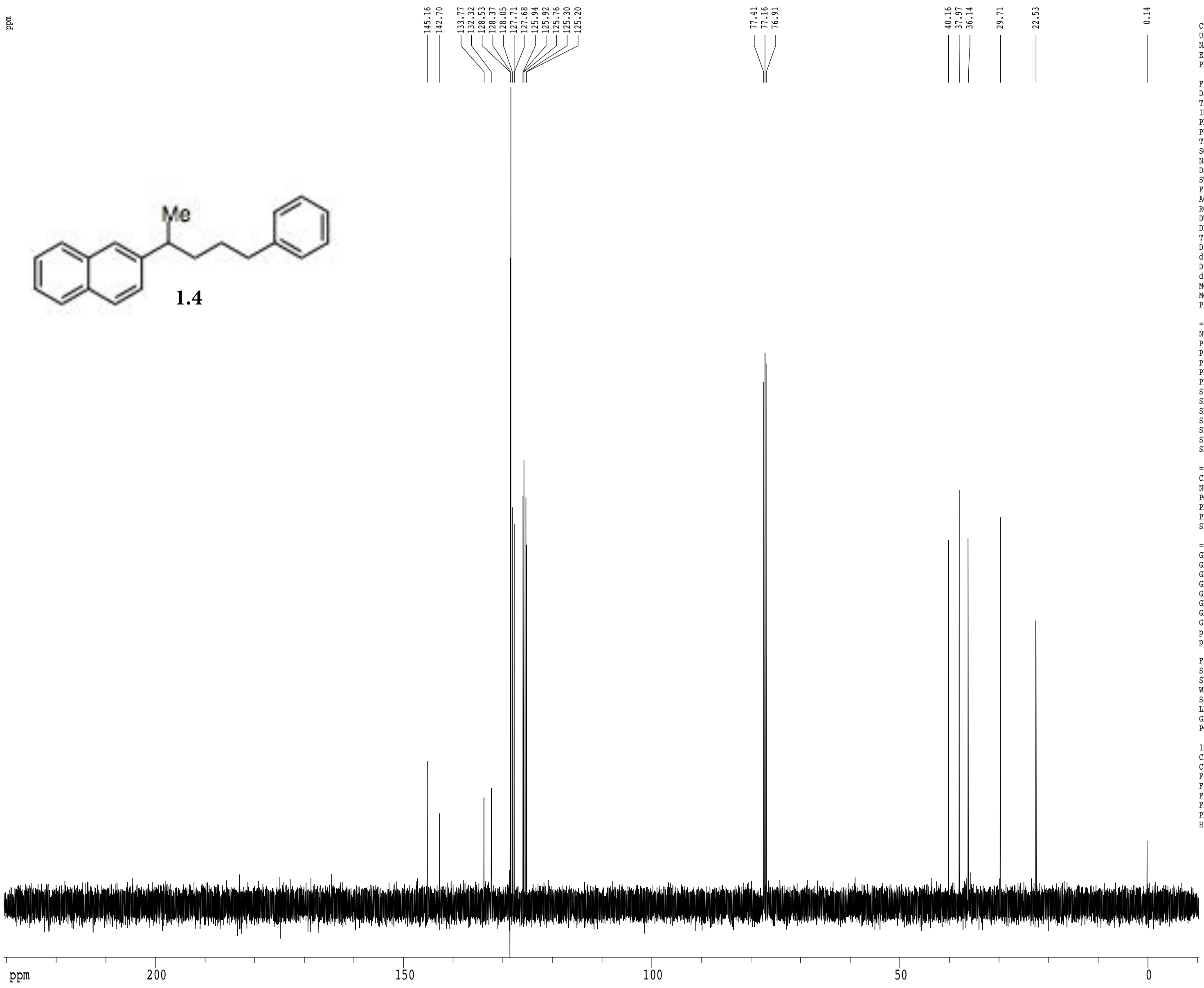


1H spectrum

1.4

Z-restored spin-echo 13C spectrum with 1H decoupling



1.4

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SOLVENT          CDCl3
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DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG             14596.5
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               37.70 usec

======== CHANNEL f1 ========
NUC1               13C
P1               18.85 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               1.55 dB
SP4               1.55 dB
SPNAM2     Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             22.00 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
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GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7804071 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            230.637 ppm
F1            29009.68 Hz
F2P            -10.287 ppm
F2            -1293.96 Hz
PPMCM         10.56688 ppm/cm
HZCM        1329.10693 Hz/cm
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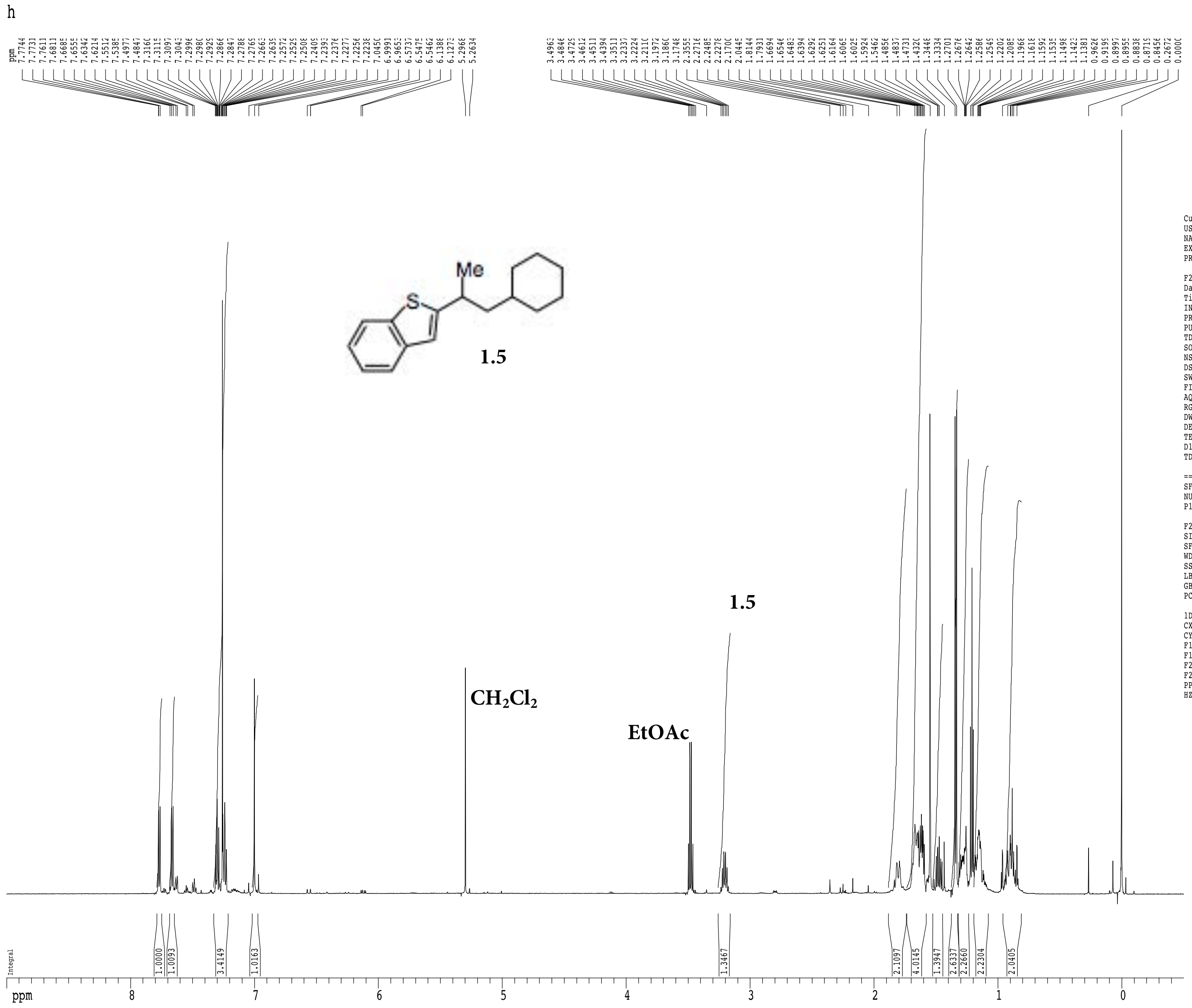

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PULPROG               zg30
TD                   98074
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               9615.385 Hz
FIDRES            0.098042 Hz
AQ               5.0998979 sec
RG                      10
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           600.1342009 MHz
NUC1                    1H
P1                   12.00 usec

F2 - Processing parameters
SI                   65536
SF             600.1300376 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 5401.17 Hz
F2P                 -0.500 ppm
F2                 -300.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             250.05420 Hz/cm
```
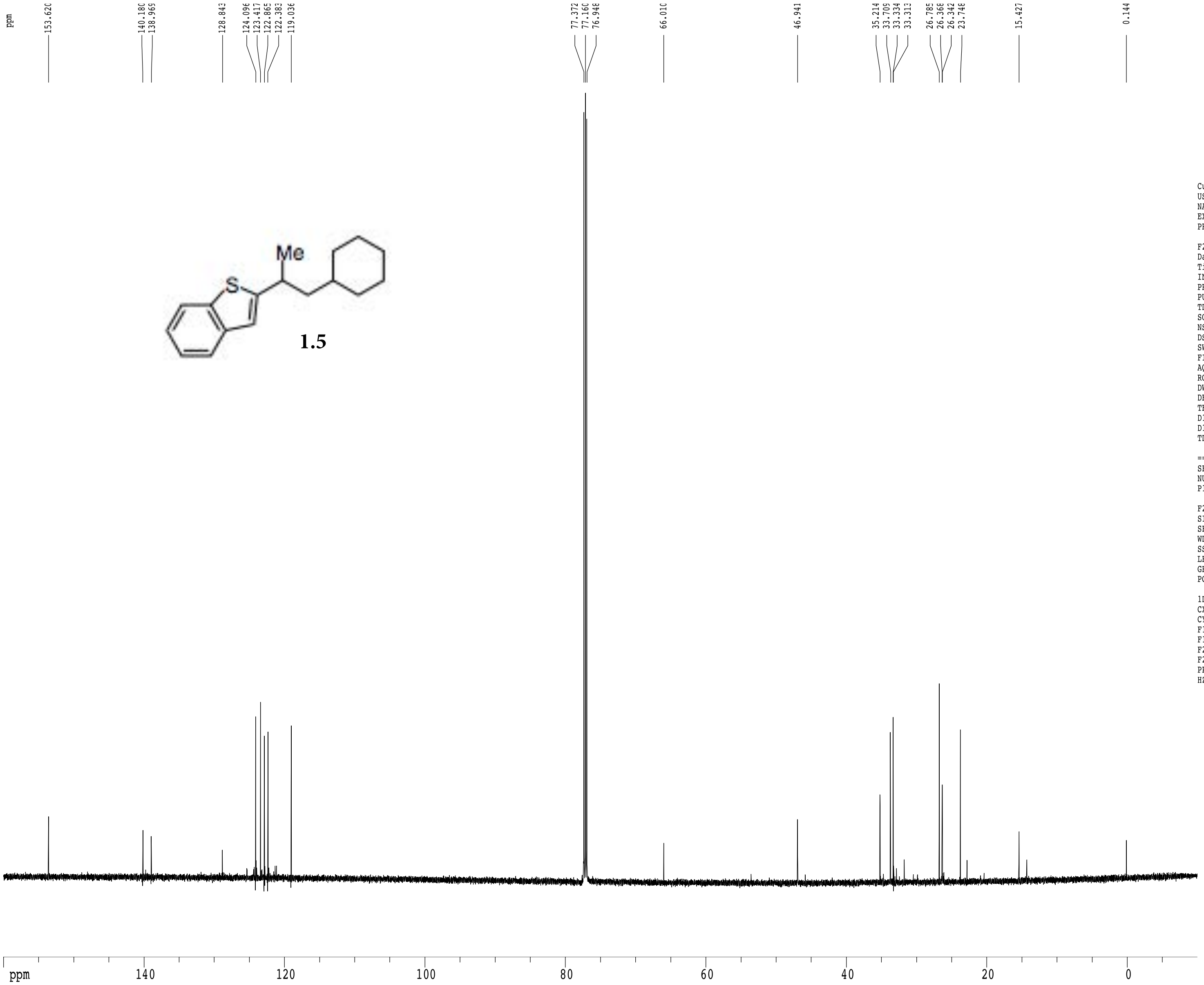
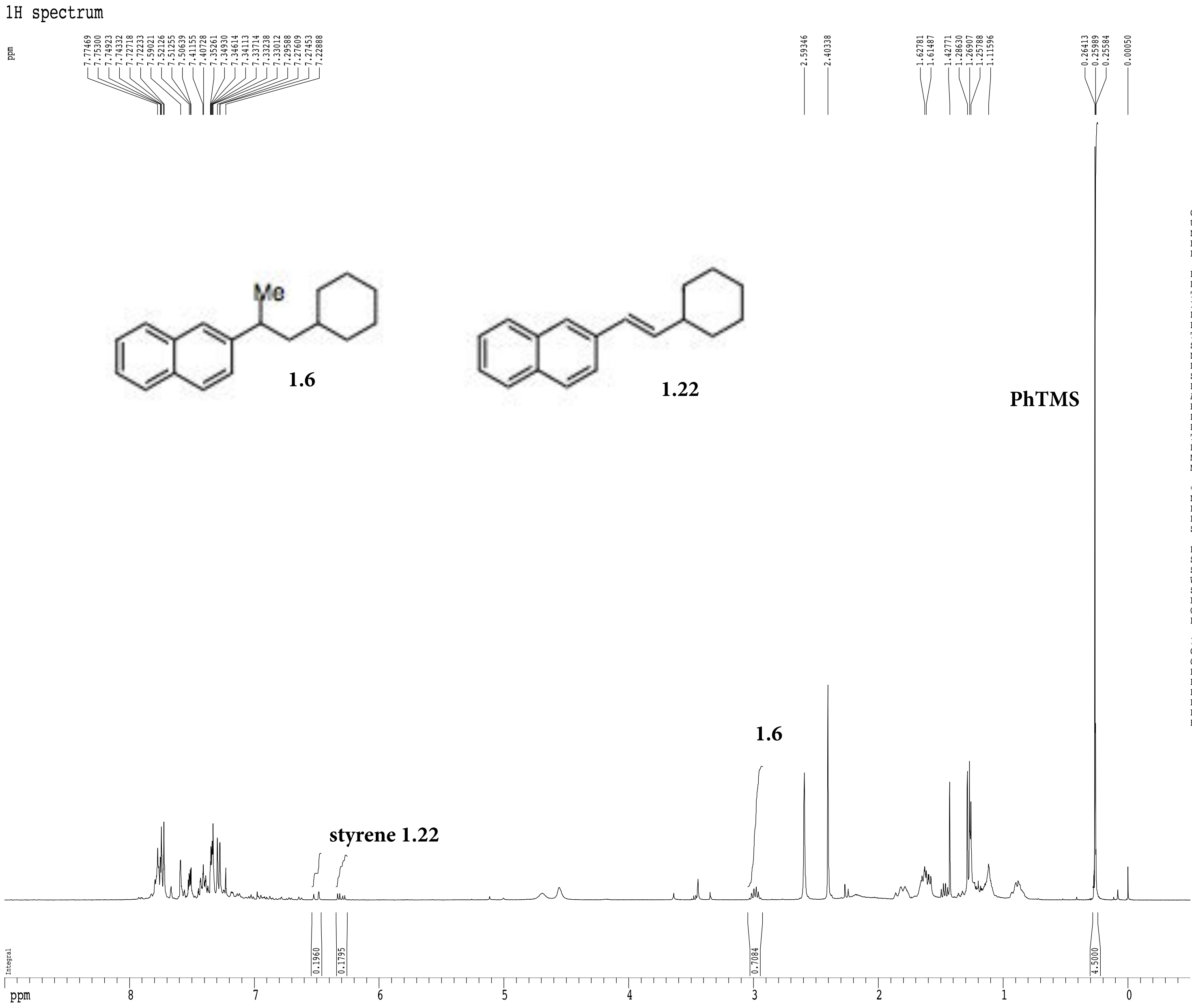

13C spectrum with 1H decoupling

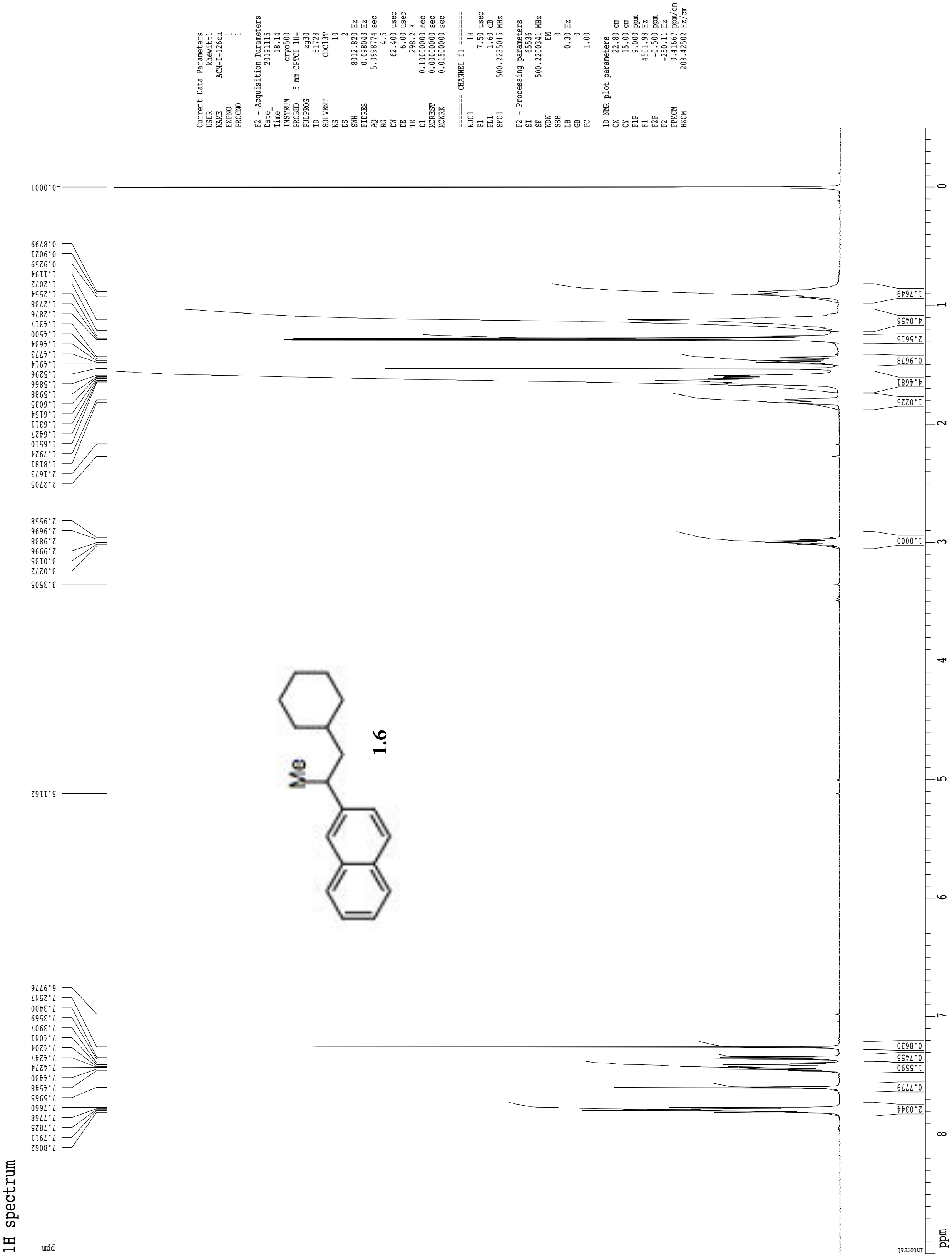


1.5

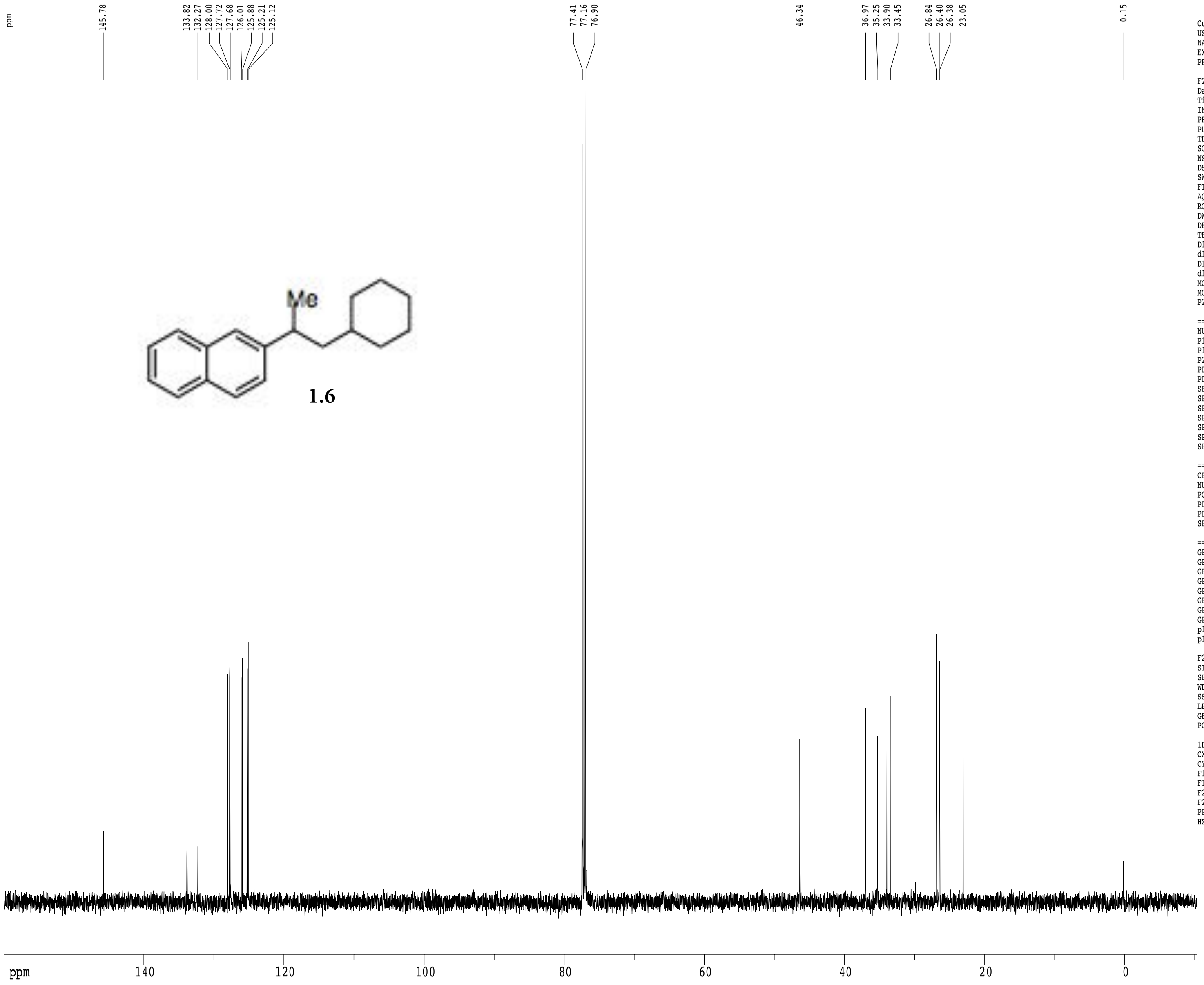
```
Current Data Parameters
USER          khewitt1
NAME     ACM-I-123-benzoCH
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20191115
Time              18.30
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  447
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF         150.9027936 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             160.000 ppm
F1             24144.45 Hz
F2P             -10.000 ppm
F2             -1509.03 Hz
PPMCM           7.45614 ppm/cm
HZCM         1125.15234 Hz/cm
```



```
Current Data Parameters
USER          khewitt1
NAME          ACM-I-41
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20190625
Time             14.48
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               65536
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG                71.8
DW              78.000 usec
DE                4.50 usec
TE               298.1 K
D1         0.10000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300337 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -0.500 ppm
F2             -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```


1H spectrum
1.6
Me
Current Data Parameters
USER khewitt1
NAME ACM-I-126ch
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191115
Time 18.14
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 10
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 298.2 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200341 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
ppm
-0.0001
0.8799
0.9021
0.9259
1.1194
1.2072
1.2554
1.2738
1.2876
1.4317
1.4500
1.4634
1.4773
1.4914
1.5296
1.5866
1.5988
1.6035
1.6154
1.6311
1.6427
1.6510
1.7924
1.8181
2.1673
2.2705
2.9558
2.9696
2.9838
2.9996
3.0135
3.0272
3.3505
5.1162
6.9776
7.2547
7.3400
7.3569
7.3907
7.4041
7.4204
7.4247
7.4274
7.4430
7.4548
7.5965
7.7660
7.7768
7.7825
7.7911
7.8062
1.7649
4.0456
2.5615
0.9678
4.4681
1.0225
1.0000
0.8630
0.7455
1.5590
0.7779
2.0344
Integral
ppm
0
1
2
3
4
5
6
7
8

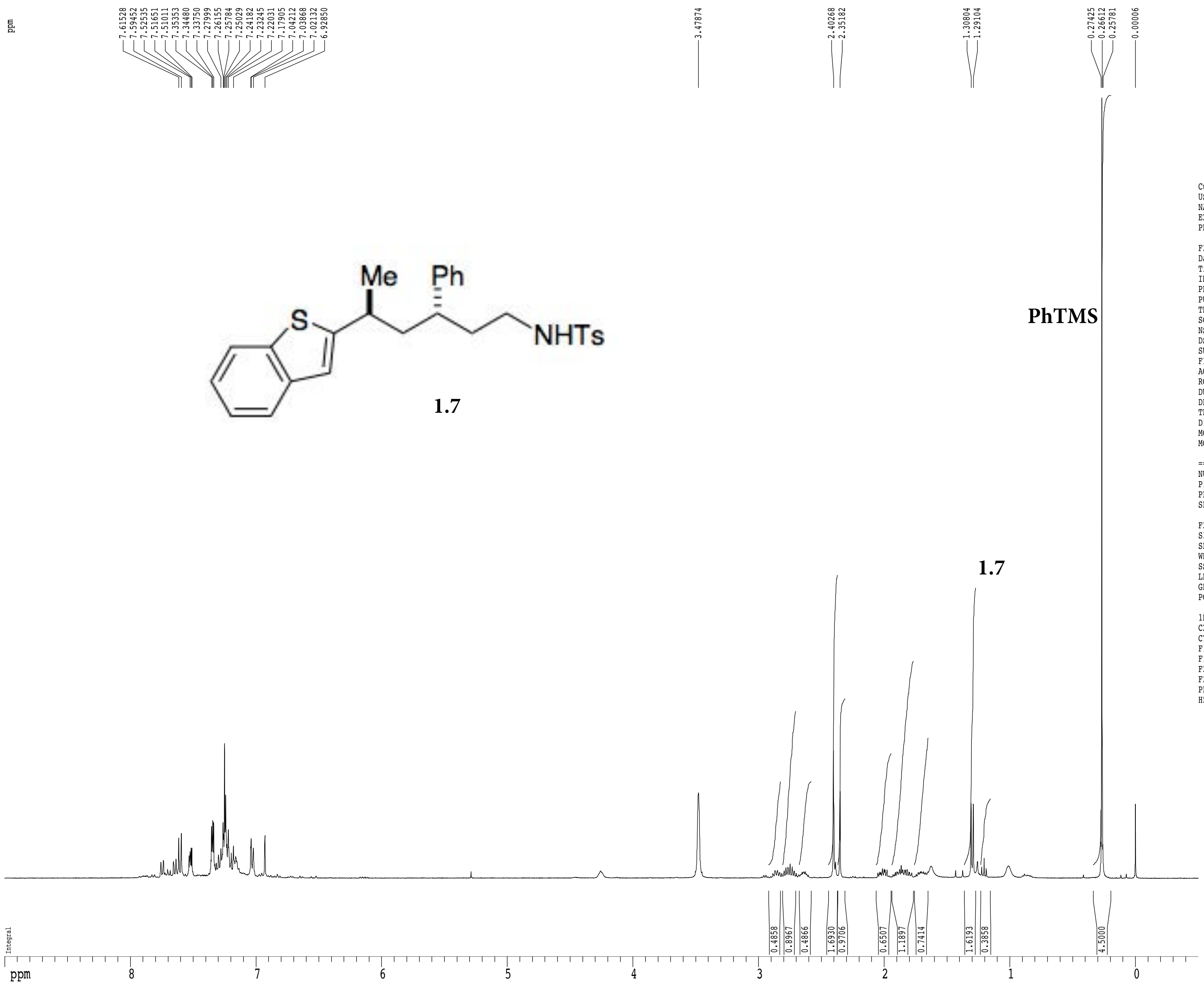
Z-restored spin-echo 13C spectrum with 1H decoupling



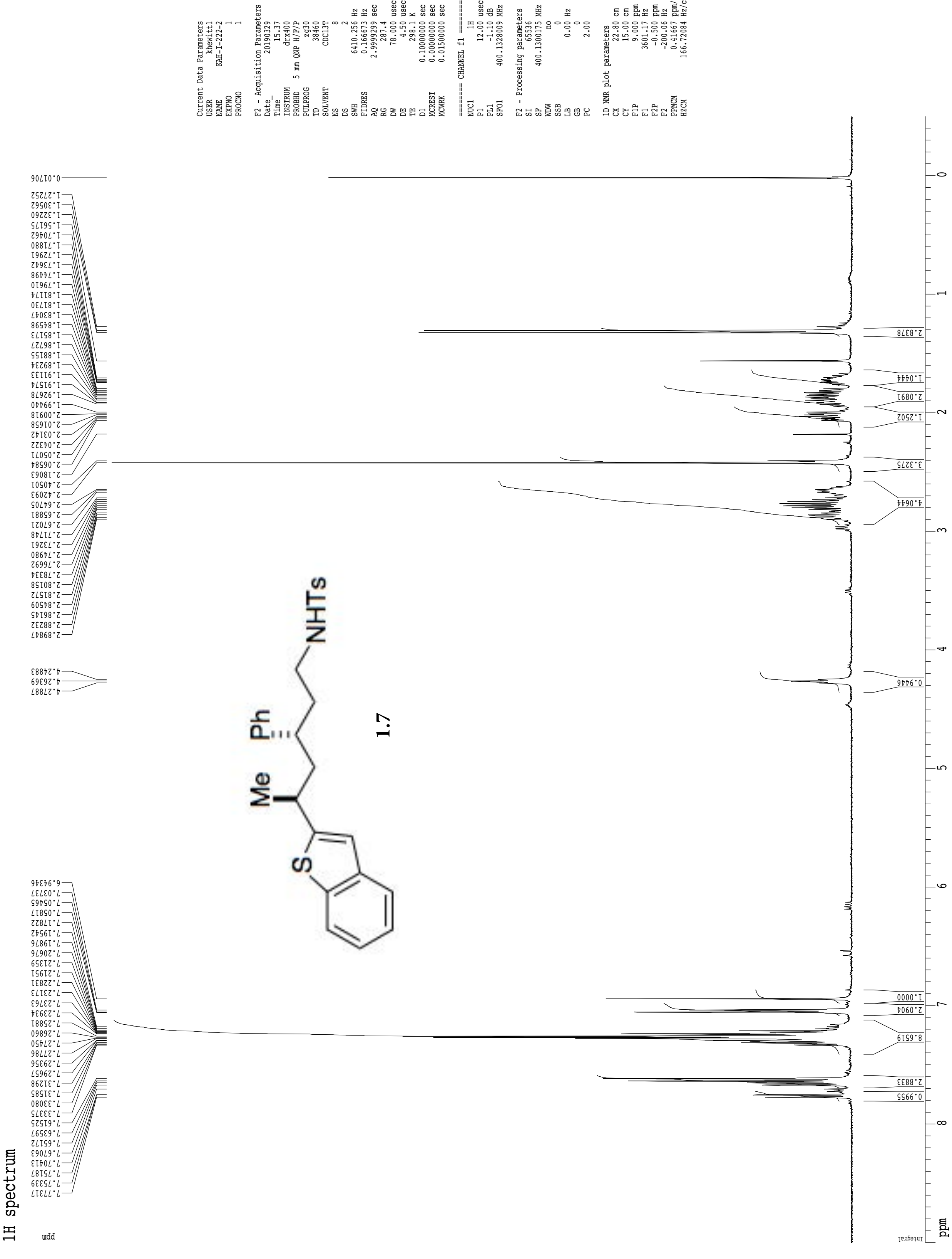
1.6

```
Current Data Parameters
USER            khewitt1
NAME          ACM-I-126ch
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191115
Time               18.29
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   616
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804062 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              160.000 ppm
F1              20124.87 Hz
F2P              -10.358 ppm
F2              -1302.84 Hz
PPMCM            7.47185 ppm/cm
HZCM           939.81177 Hz/cm
```

1H spectrum

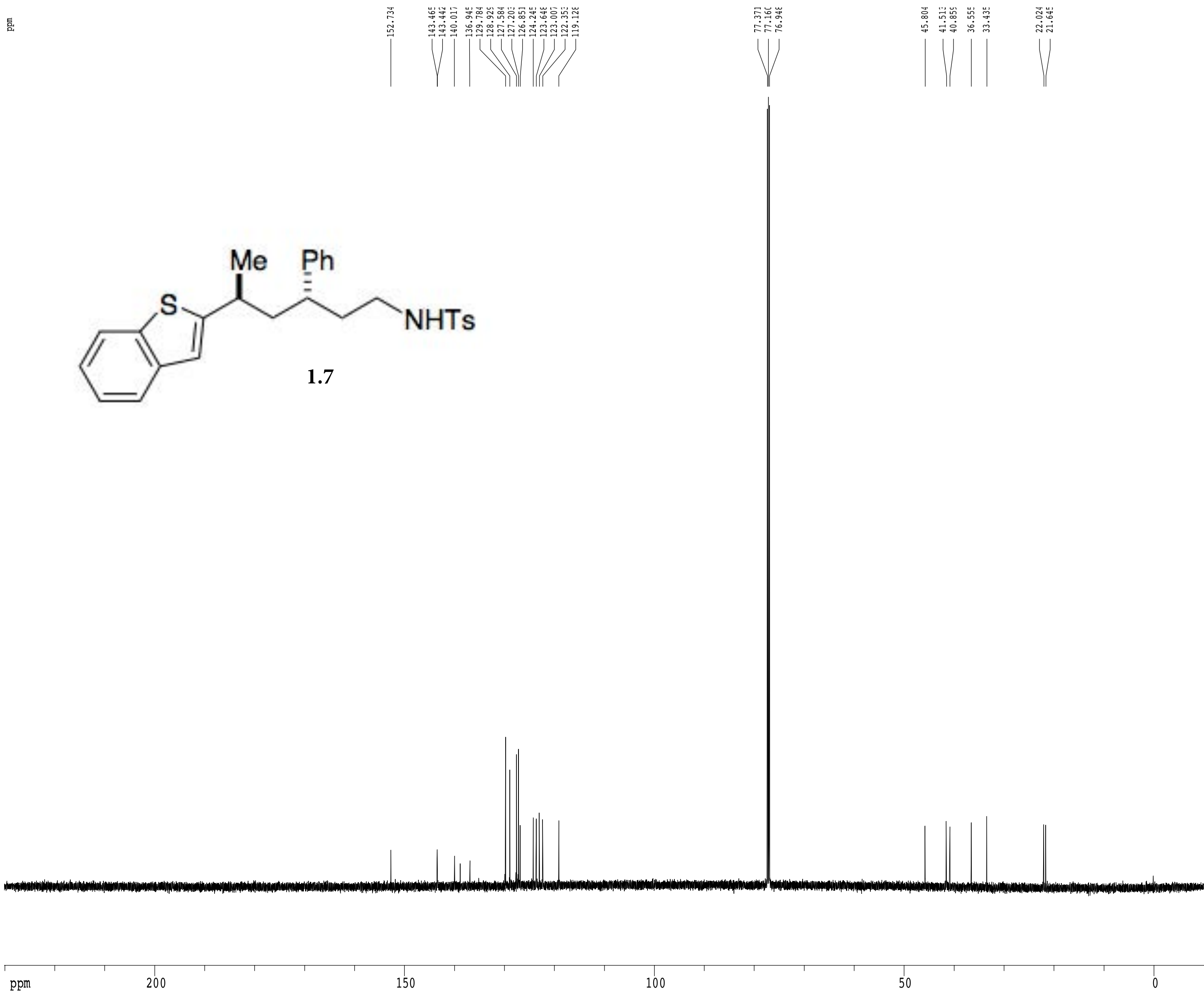


```
Current Data Parameters
USER            khewitt1
NAME           KAH-I-222
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181208
Time               14.51
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                   181
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300249 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```


1H spectrum
ppm
0.01706
1.27252
1.30562
1.32260
1.56175
1.70462
1.71880
1.72961
1.73642
1.74498
1.79610
1.81174
1.81730
1.83047
1.84598
1.85173
1.86727
1.88155
1.89234
1.91133
1.91574
1.92678
1.99440
2.00918
2.01658
2.03142
2.04322
2.05071
2.06584
2.18063
2.40501
2.42093
2.64705
2.65881
2.67021
2.71748
2.73261
2.74980
2.76692
2.78334
2.80158
2.81572
2.84509
2.86145
2.88232
2.89847
4.24883
4.26369
4.27887
6.94346
7.03737
7.05465
7.05817
7.17822
7.19542
7.19876
7.20676
7.21359
7.21951
7.22831
7.23173
7.23763
7.23934
7.25881
7.26860
7.27450
7.27786
7.29356
7.29657
7.31298
7.31585
7.33080
7.33375
7.61525
7.63597
7.65172
7.67063
7.70413
7.75187
7.75339
7.77317
Current Data Parameters
USER khewitt1
NAME KAH-I-222-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190329
Time 15.37
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3T
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 287.4
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
Me
Ph
S
NHTs
2.8378
1.0444
2.0891
1.2502
3.3275
4.0644
0.9446
1.0000
2.0904
8.6519
2.8833
0.9955
Integral
0
1
2
3
4
5
6
7
8
ppm

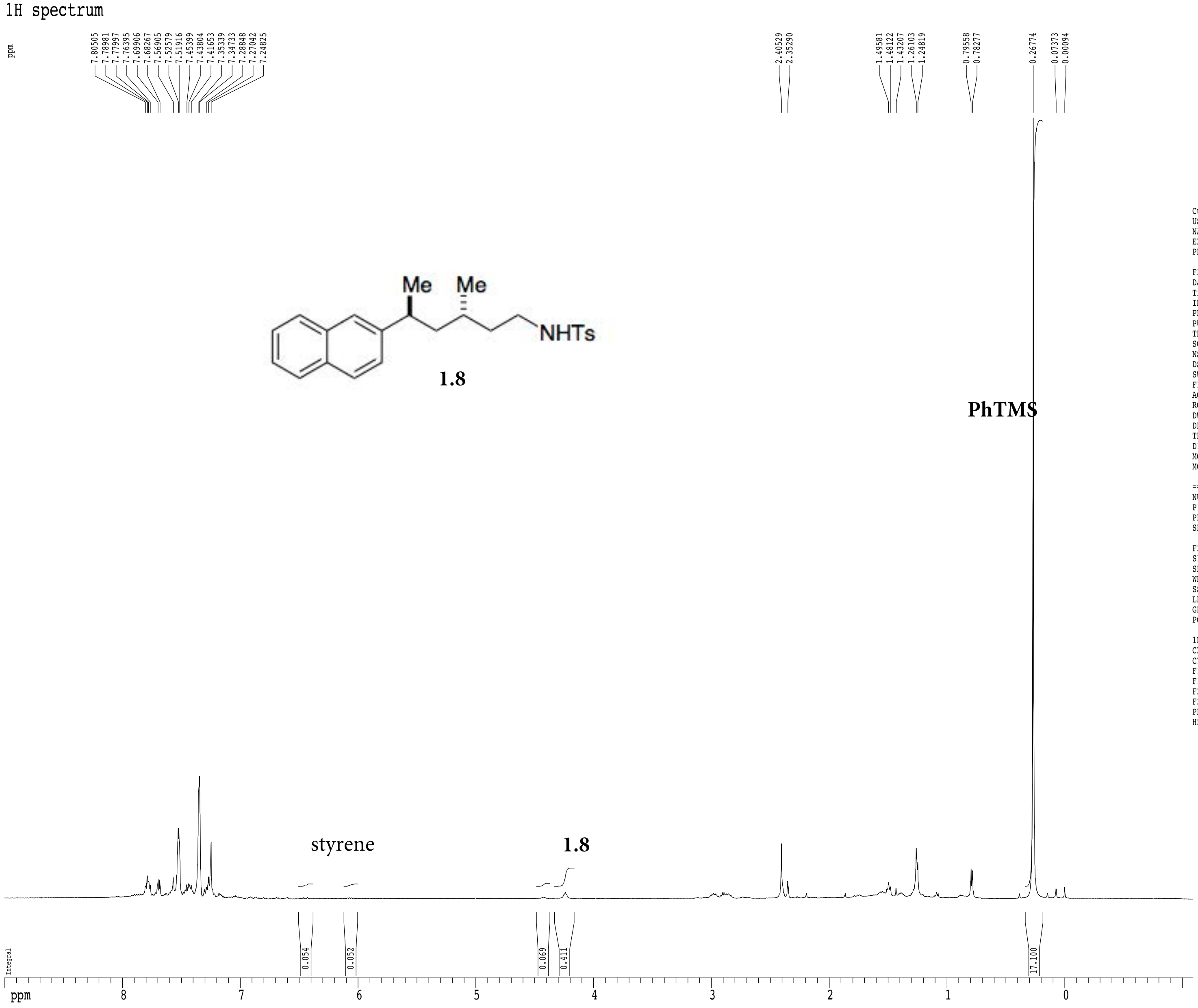
1.7

c13.c



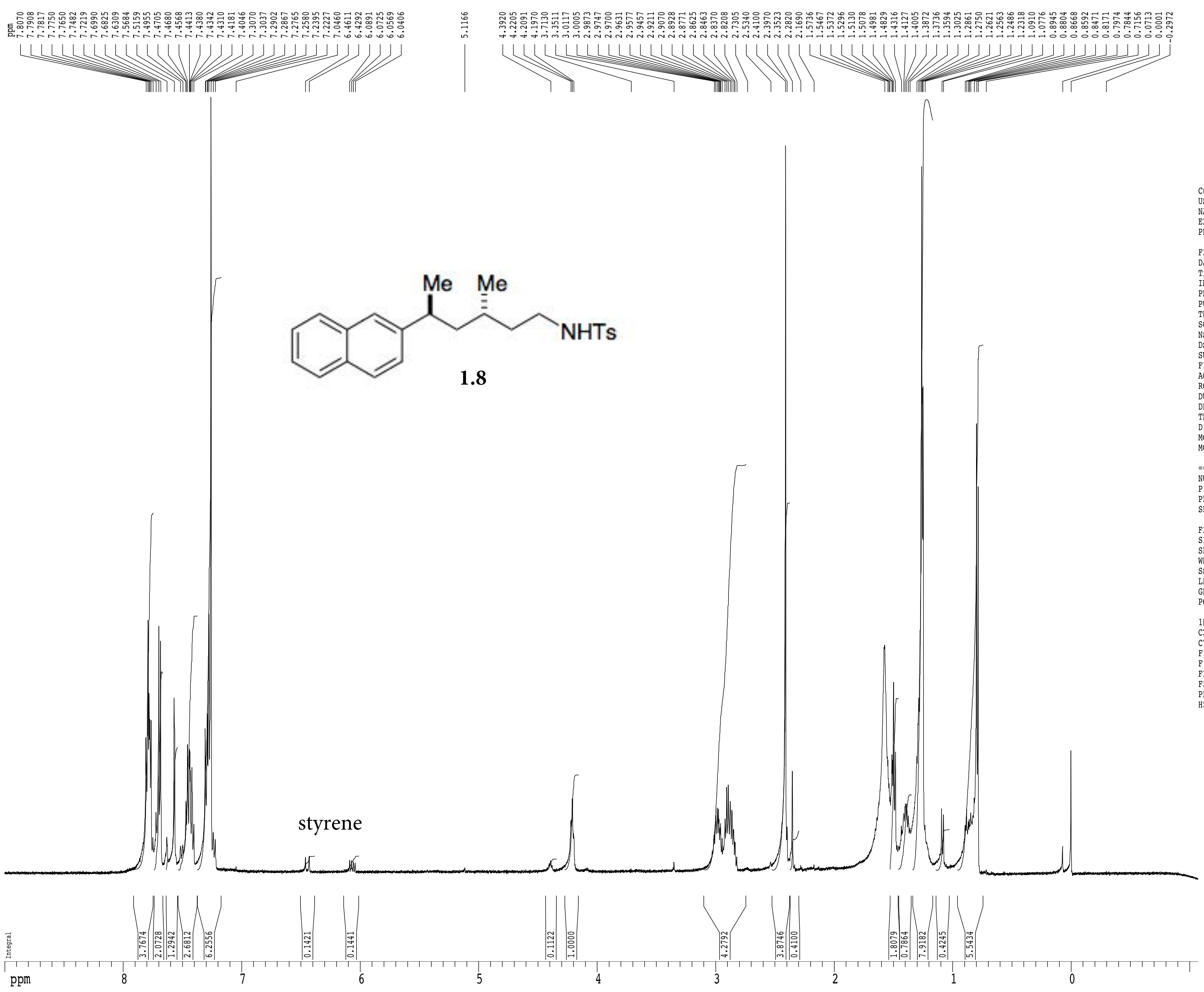
1.7

```
Current Data Parameters
USER            khewitt1
NAME      KAH-I-222-Z-C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210713
Time              14.14
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  146
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9027958 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             230.136 ppm
F1             34728.11 Hz
F2P              -9.965 ppm
F2             -1503.78 Hz
PPMCM          10.53074 ppm/cm
HZCM         1589.11780 Hz/cm
```



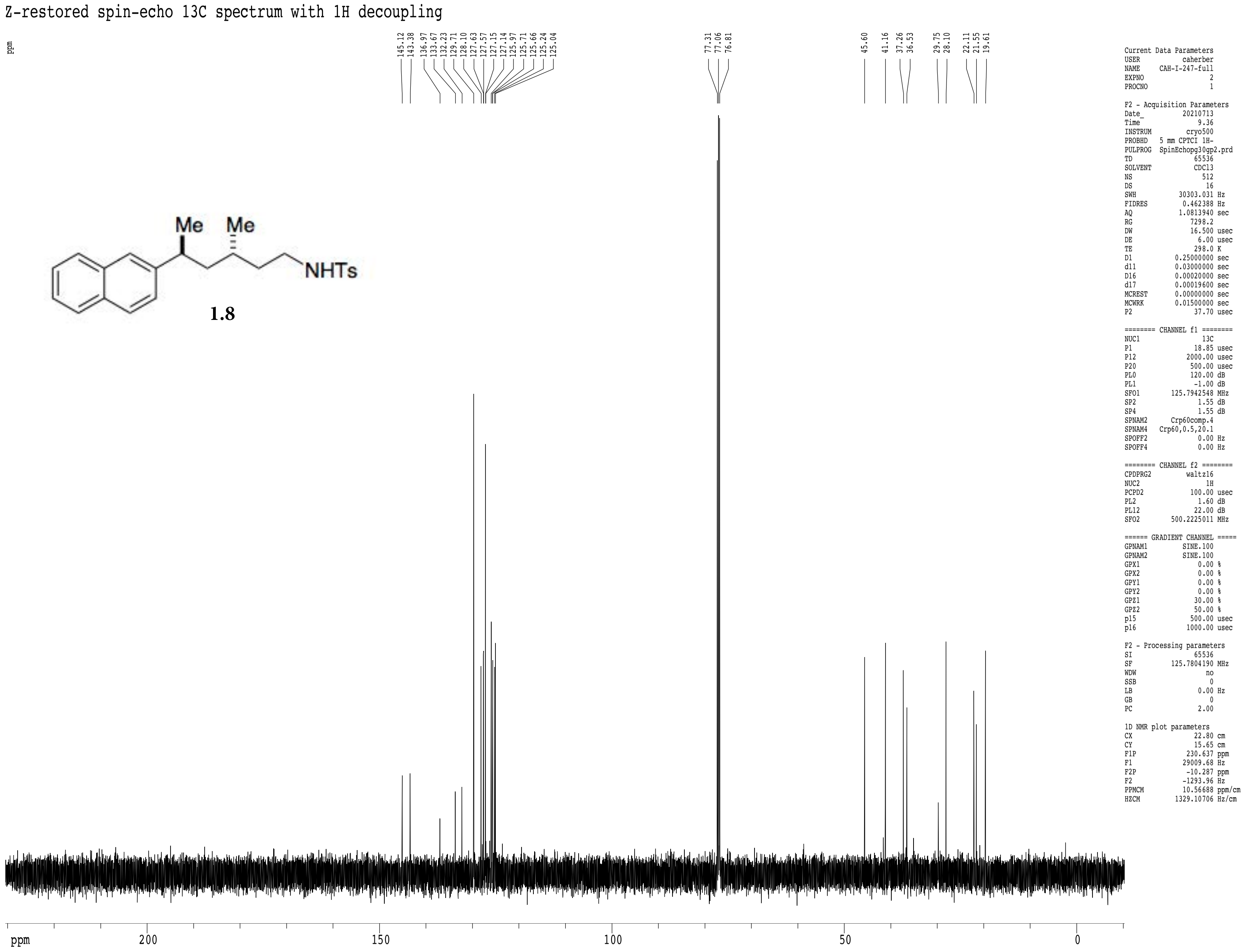
```
Current Data Parameters
USER           caherber
NAME     CAH-I-247-Crude
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210710
Time              11.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200370 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -1.083 ppm
F2              -541.88 Hz
PPMCM           0.44225 ppm/cm
HZCM          221.22217 Hz/cm
```

1H spectrum

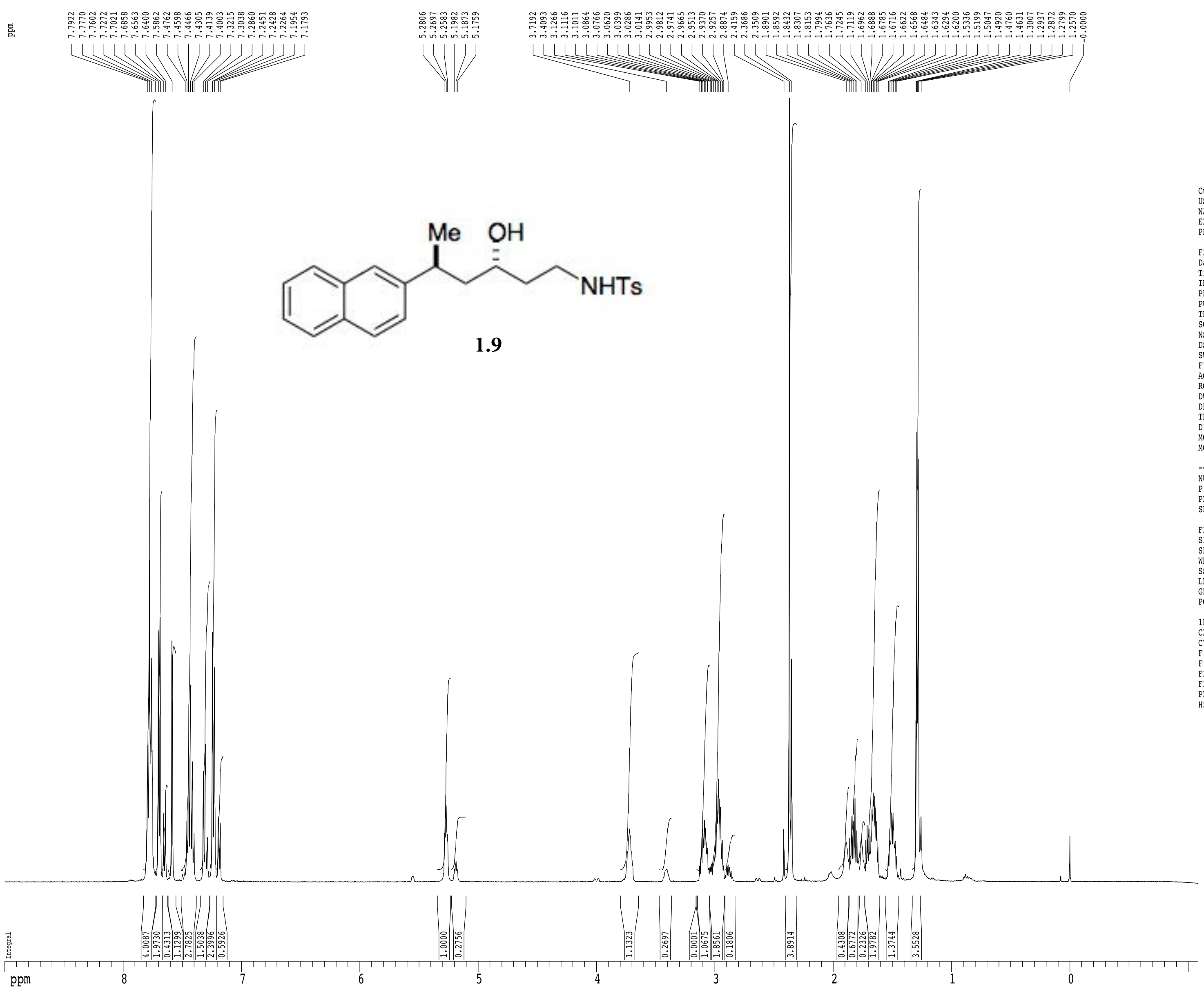


1.8

```
Current Data Parameters
USER          caherber
NAME     CAH-I-247-full
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210713
Time               9.25
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200315 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -1.072 ppm
F2              -536.38 Hz
PPMCM           0.44177 ppm/cm
HZCM          220.98083 Hz/cm
```


Z-restored spin-echo 13C spectrum with 1H decoupling
ppm
145.12
143.38
136.97
133.67
132.23
129.71
128.10
127.63
127.57
127.15
127.14
125.97
125.71
125.66
125.24
125.04
77.31
77.06
76.81
45.60
41.16
37.26
36.53
29.75
28.10
22.11
21.55
19.61
Me
Me
NHTs
1.8
Current Data Parameters
USER caherber
NAME CAH-I-247-full
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210713
Time 9.36
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 512
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 37.70 usec
======== CHANNEL f1 ========
NUC1 13C
P1 18.85 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 1.55 dB
SP4 1.55 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 22.00 dB
SFO2 500.2225011 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 230.637 ppm
F1 29009.68 Hz
F2P -10.287 ppm
F2 -1293.96 Hz
PPMCM 10.56688 ppm/cm
HZCM 1329.10706 Hz/cm
ppm
200
150
100
50
0

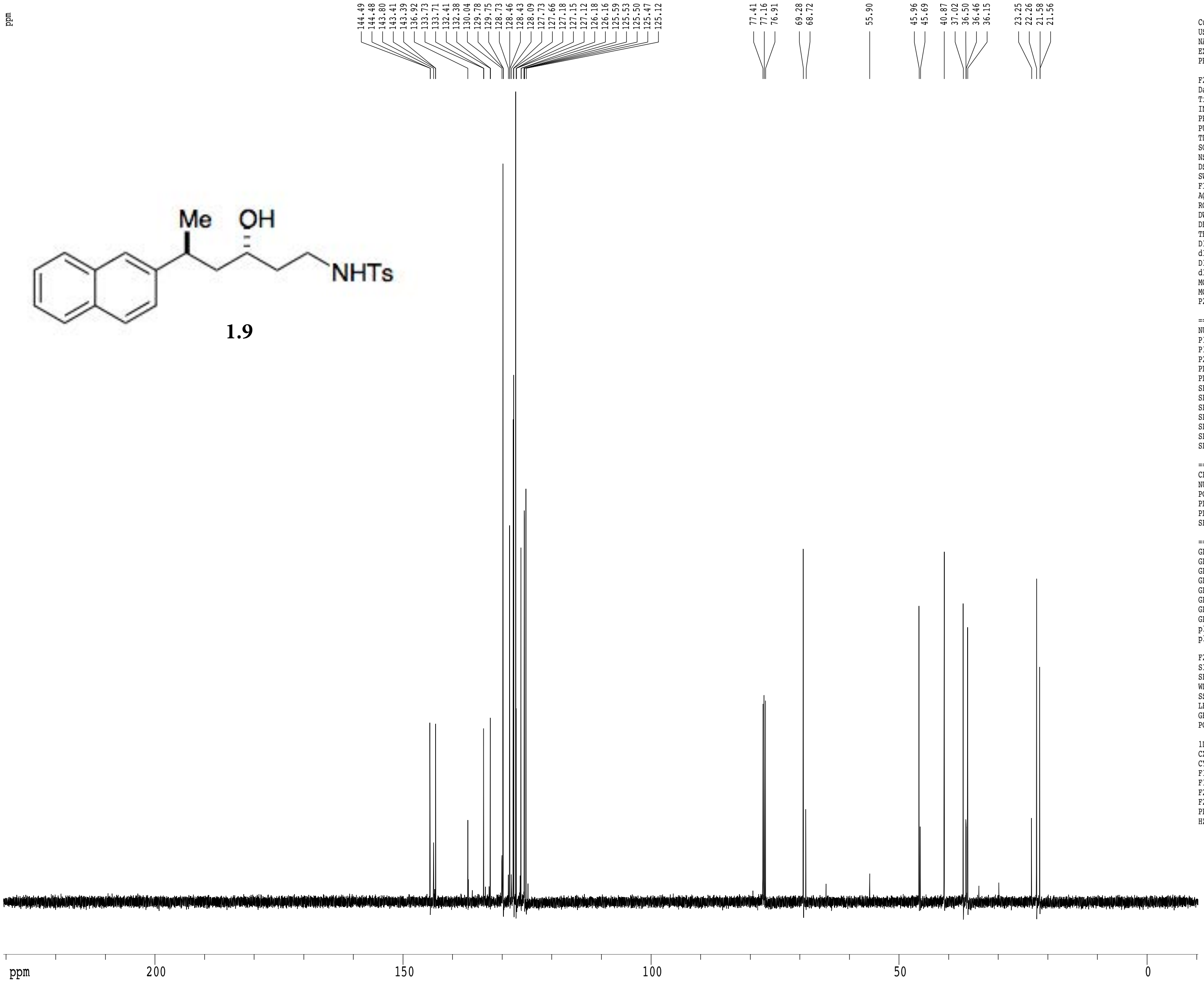
1H spectrum



1.9

```
Current Data Parameters
USER          caherber
NAME     CAH-I-239-full
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20210623
Time             11.35
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998774 sec
RG                   5
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                9.75 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200379 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4501.98 Hz
F2P             -1.085 ppm
F2             -542.74 Hz
PPMCM          0.44232 ppm/cm
HZCM         221.25967 Hz/cm
```

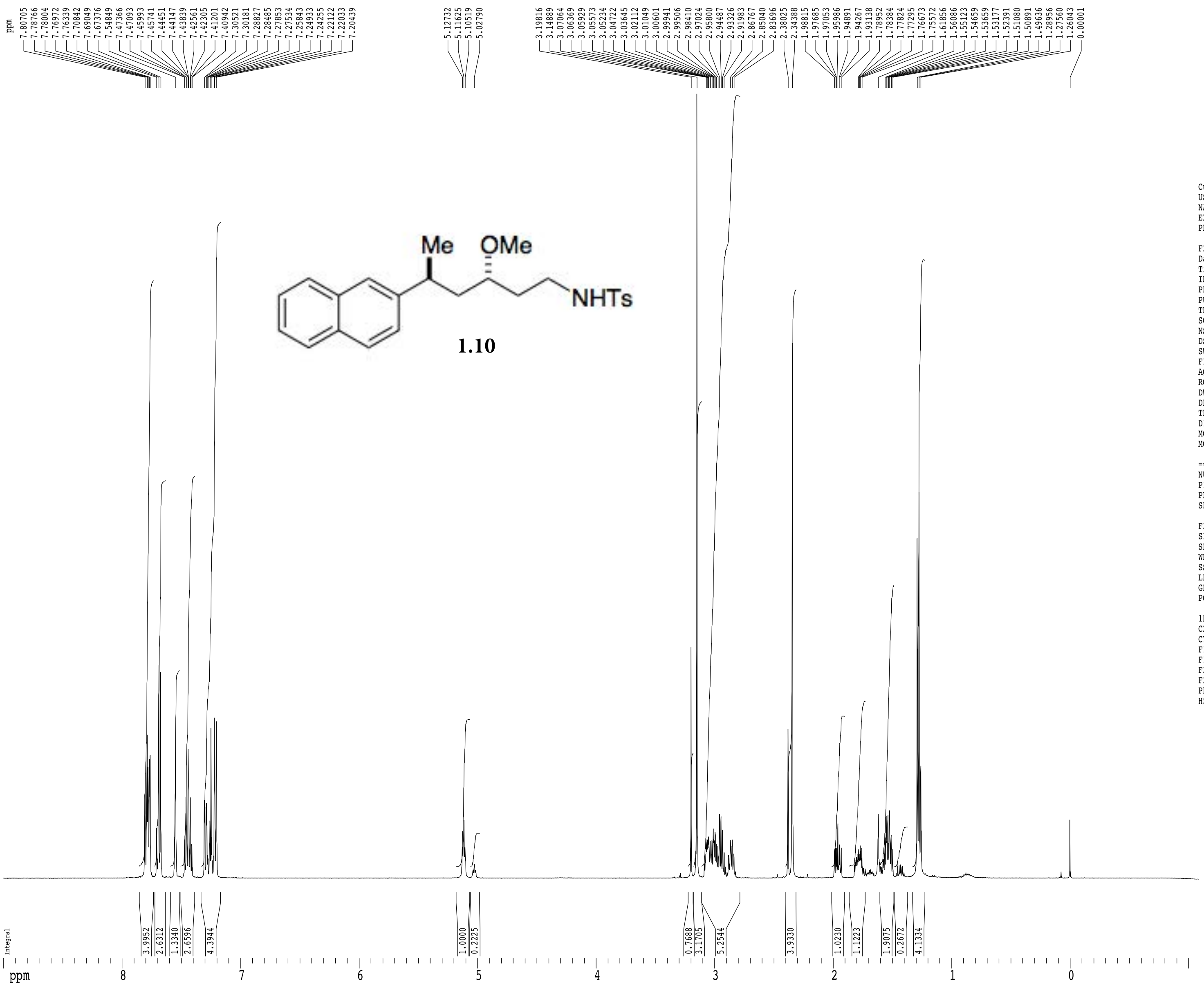
Z-restored spin-echo 13C spectrum with 1H decoupling



1.9

```
Current Data Parameters
USER           caherber
NAME     CAH-I-239-full
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210623
Time              11.43
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  296
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG              14596.5
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804131 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```

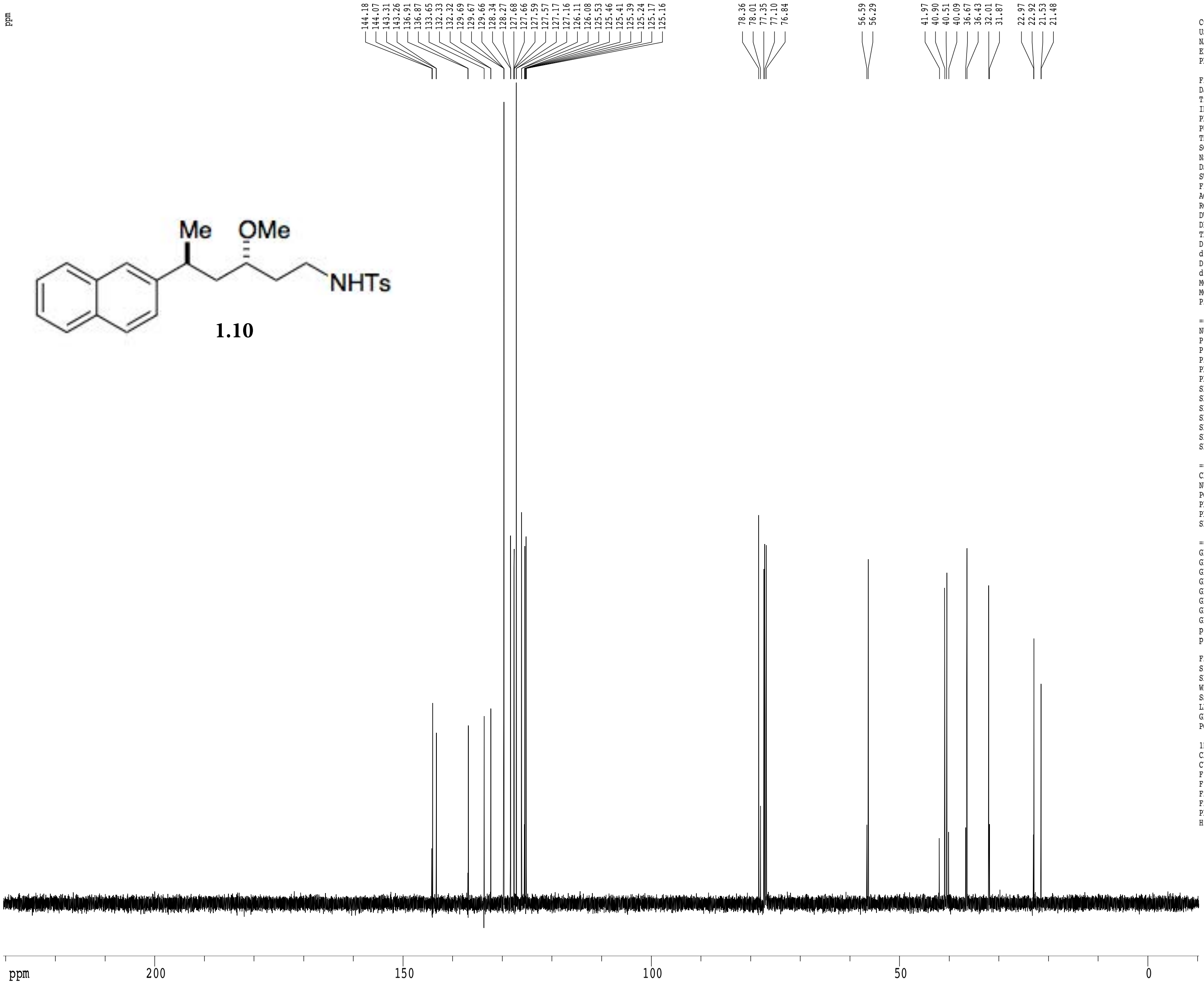
1H spectrum



1.10

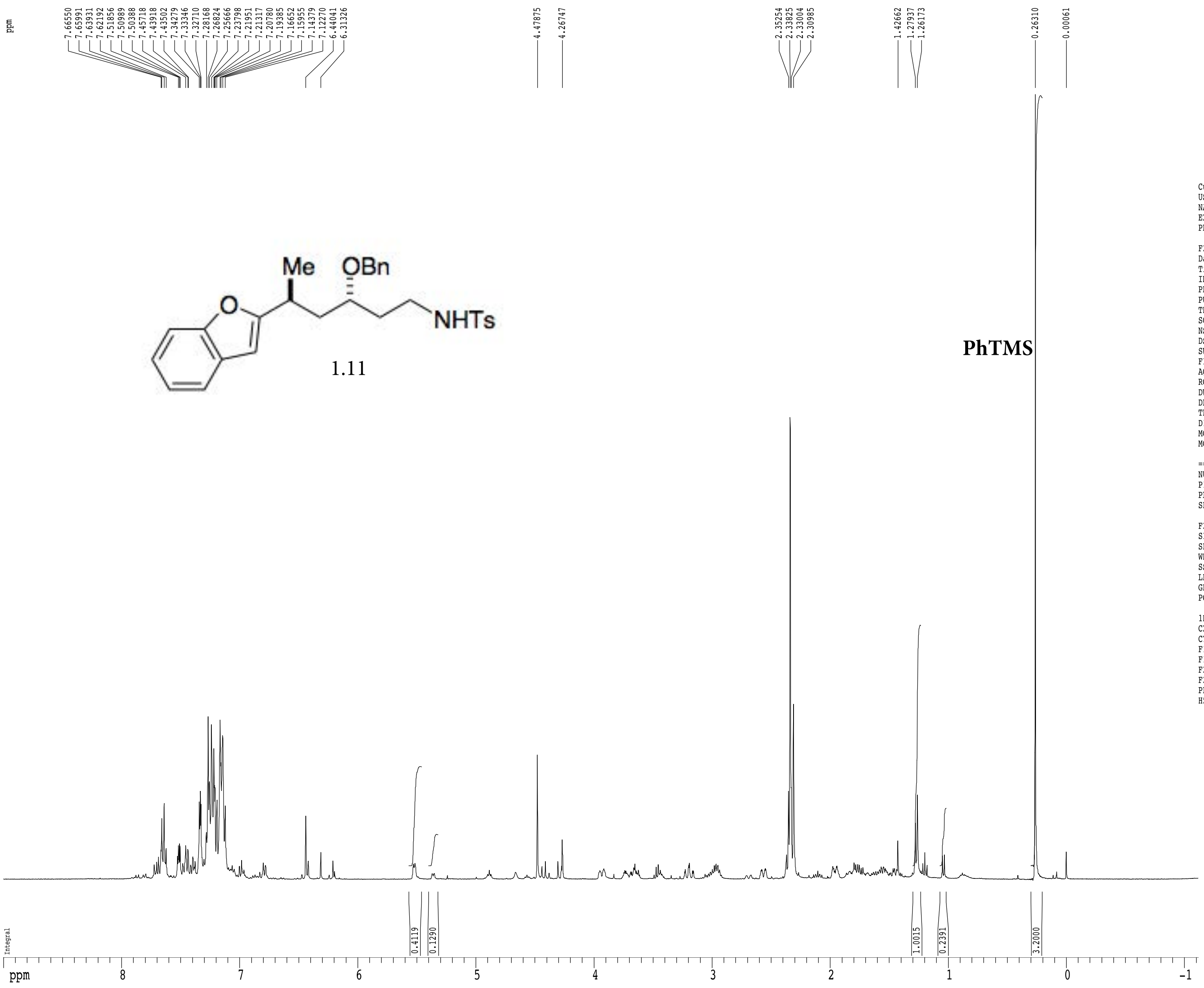
```
Current Data Parameters
USER            caherber
NAME           CAH-I-212
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210508
Time               10.24
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     4
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200364 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -1.082 ppm
F2               -541.27 Hz
PPMCM            0.44220 ppm/cm
HZCM           221.19518 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



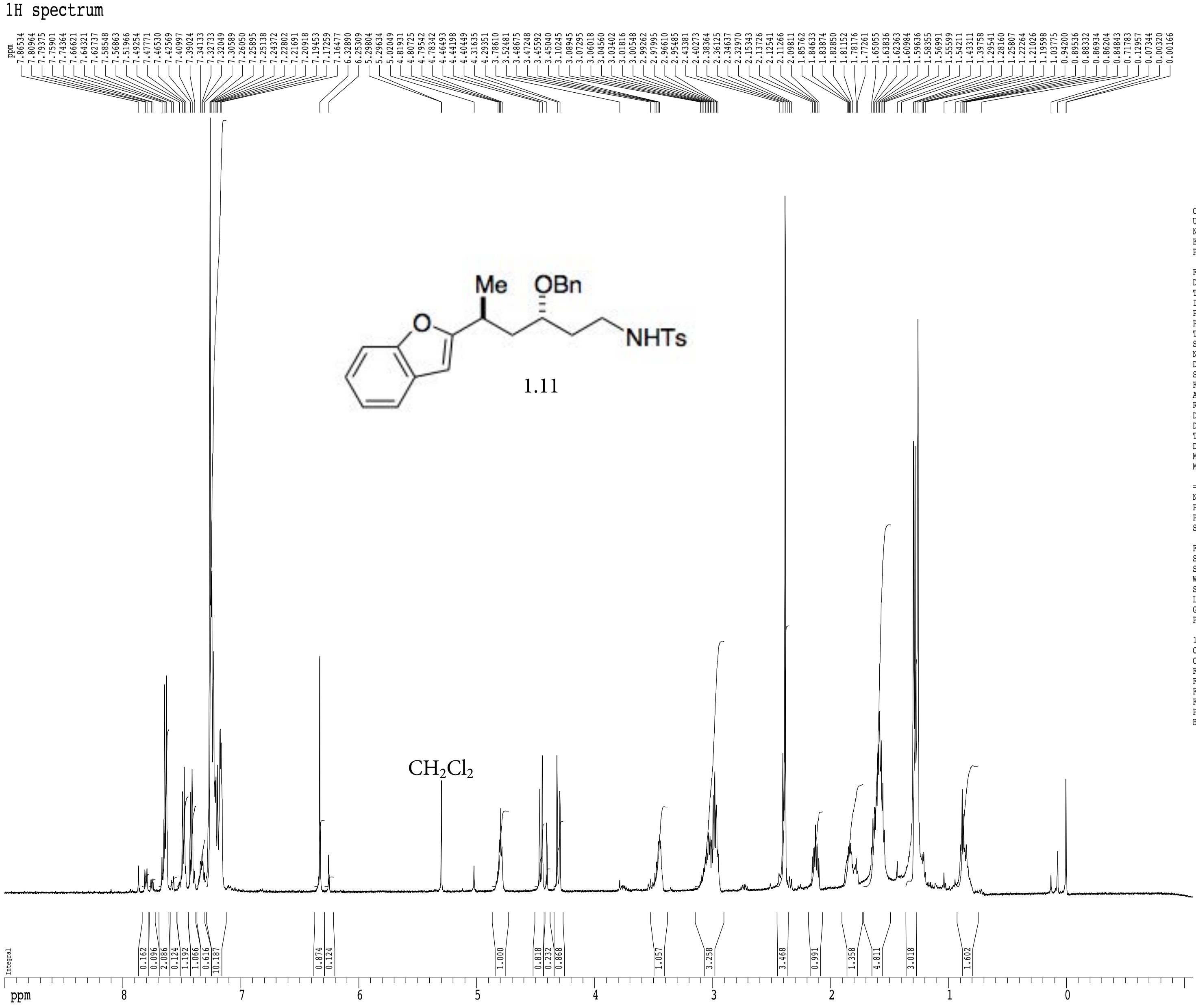
```
Current Data Parameters
USER            caherber
NAME          CAH-I-212
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20210508
Time              10.28
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  144
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               2896.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

1H spectrum



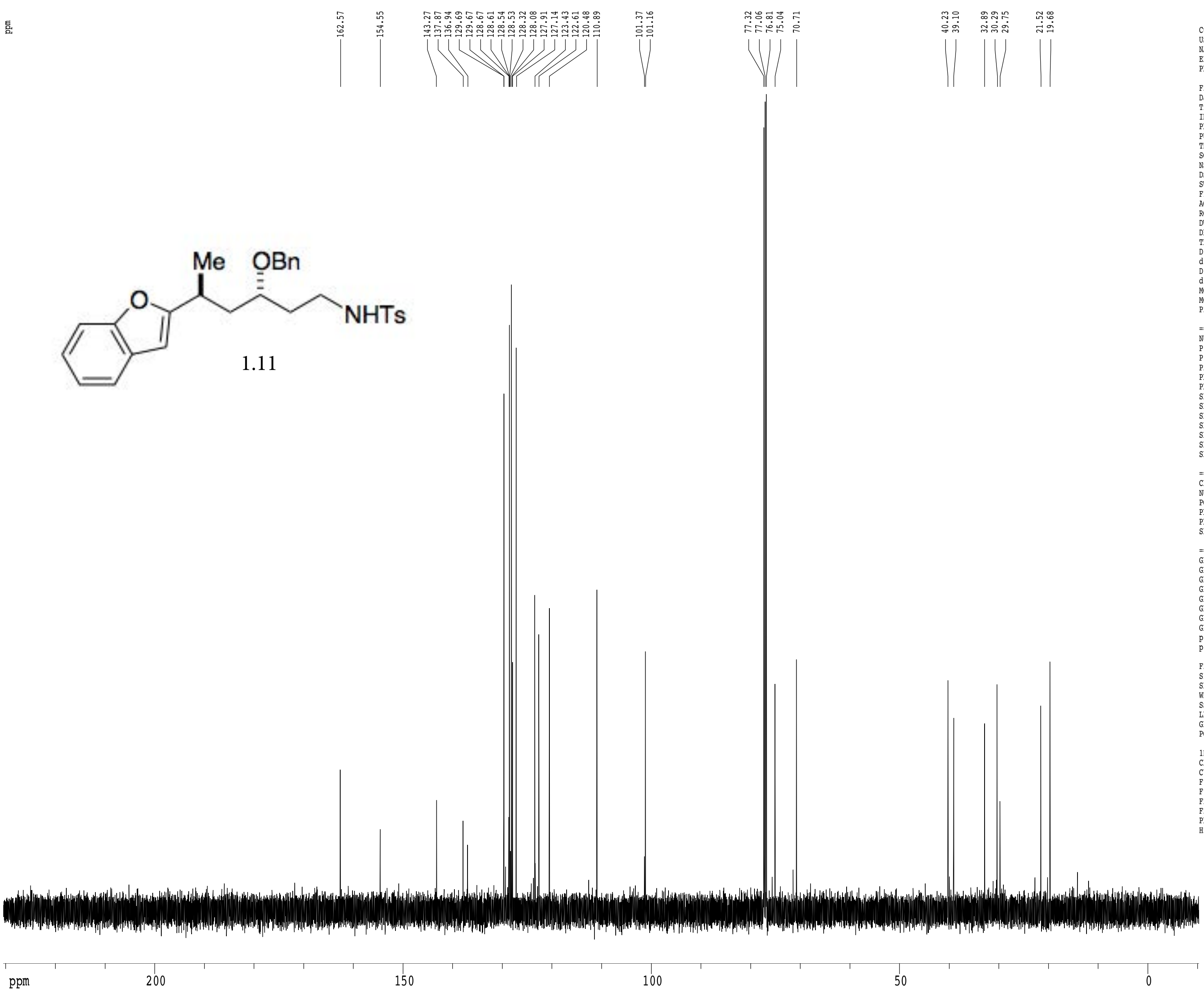
1.11

```
Current Data Parameters
USER            caherber
NAME      CAH-I-233-Crude
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210604
Time               16.44
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300427 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.117 ppm
F2               -446.91 Hz
PPMCM            0.44372 ppm/cm
HZCM           177.54726 Hz/cm
```



```
Current Data Parameters
USER          caherber
NAME     CAH-I-246-full
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210708
Time              11.14
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200313 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -1.072 ppm
F2              -536.14 Hz
PPMCM           0.44175 ppm/cm
HZCM          220.97008 Hz/cm
```

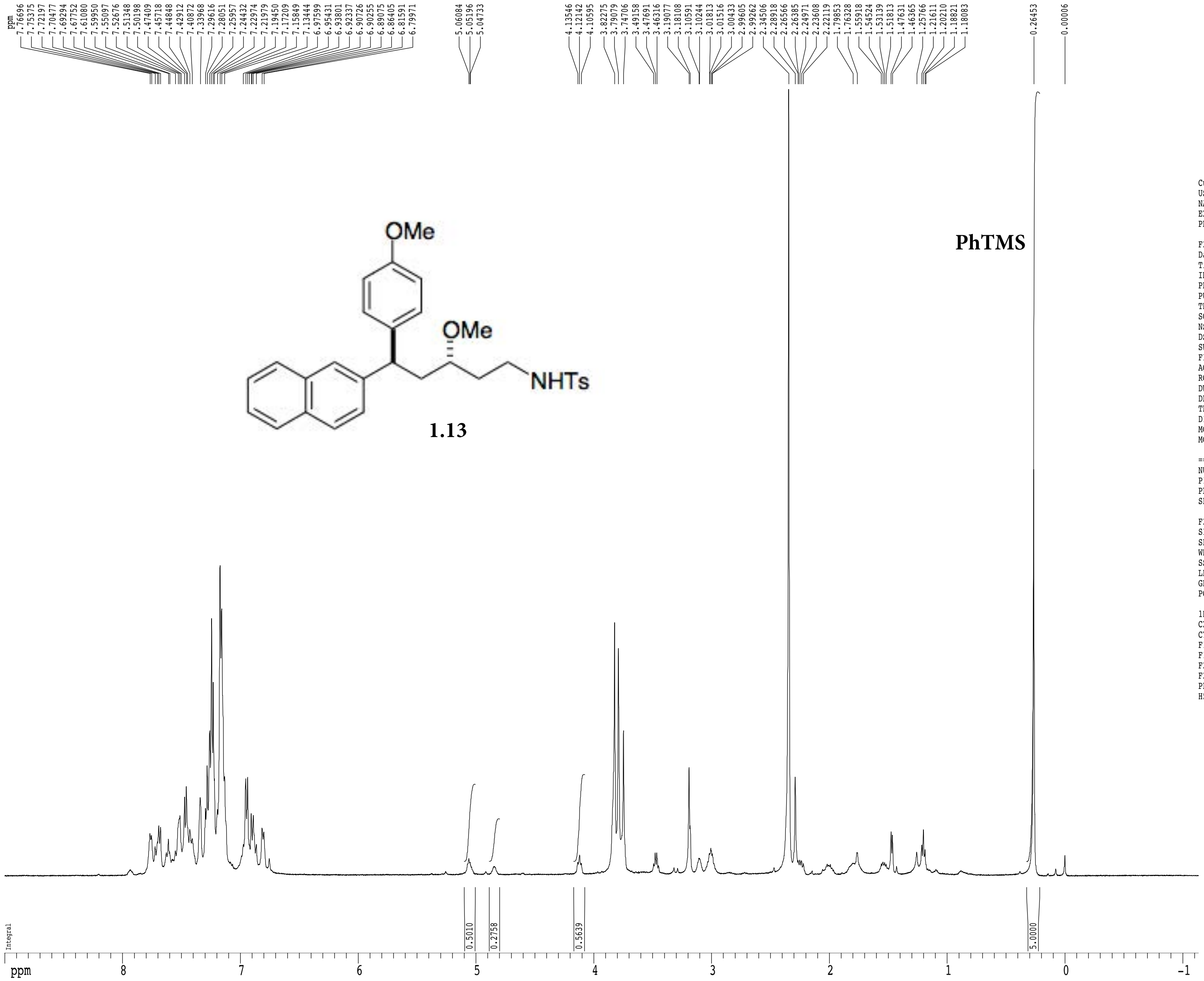
Z-restored spin-echo 13C spectrum with 1H decoupling



1.11

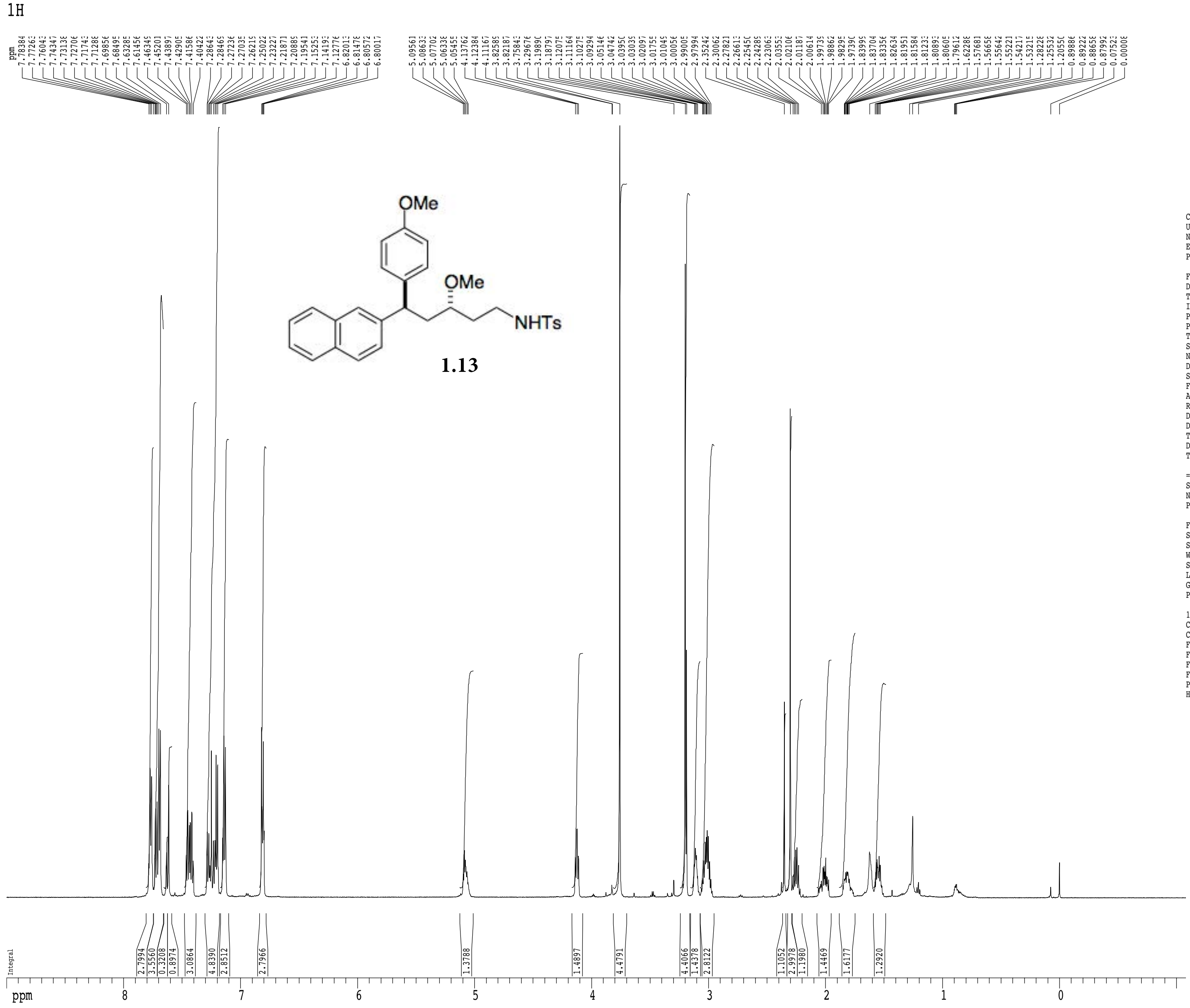
```
Current Data Parameters
USER            caherber
NAME     CAH-I-246-full
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210708
Time              11.23
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  448
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG              14596.5
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1               18.85 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1        125.7942548 MHz
SP2               1.55 dB
SP4               1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

1H spectrum



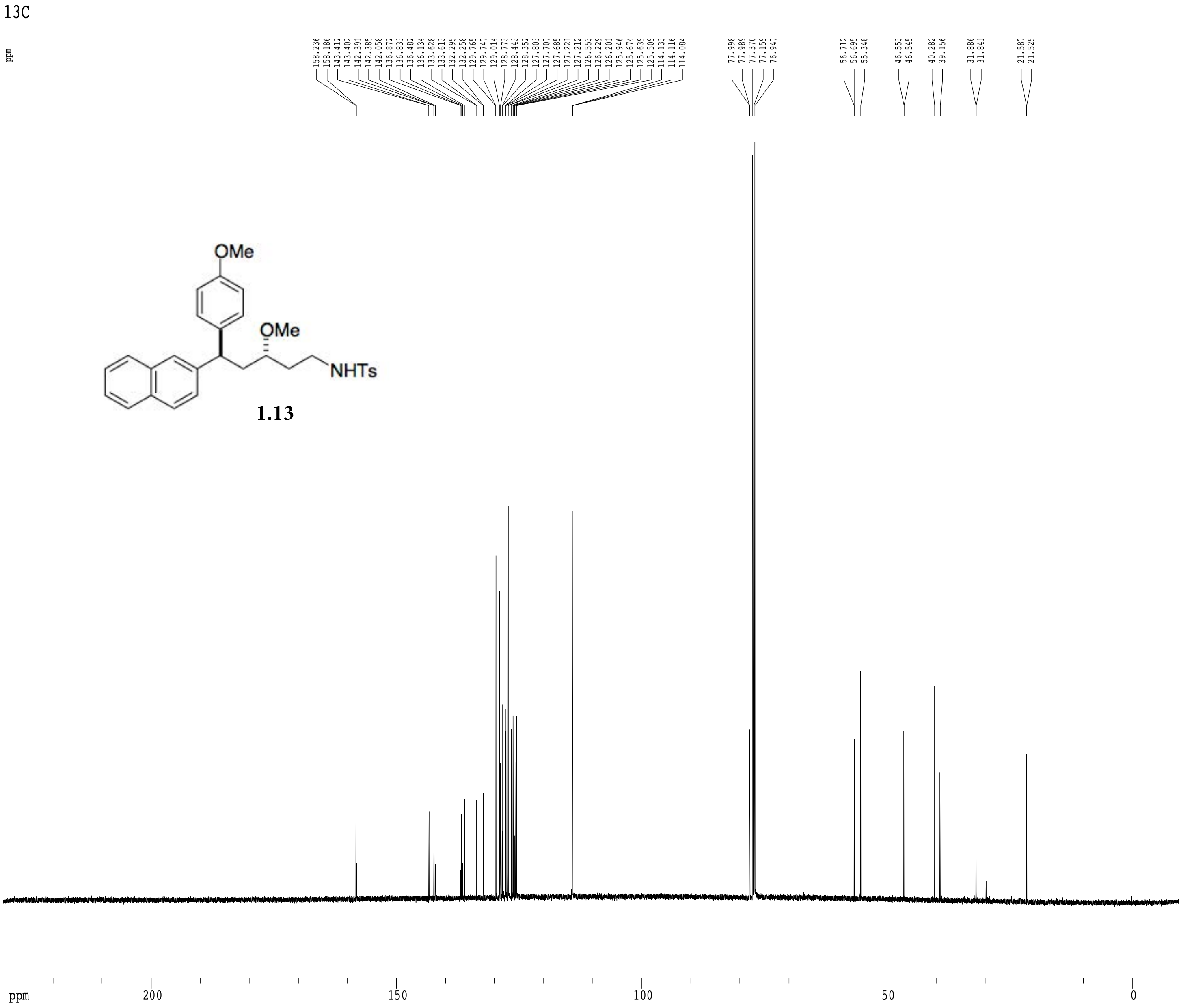
1.13

```
Current Data Parameters
USER          caherber
NAME     CAH-I-284-Crude
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20210917
Time              10.29
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                 90.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -6.00 dB
SFO1        498.6534906 MHz

F2 - Processing parameters
SI                65536
SF          498.6500485 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4487.85 Hz
F2P              -1.132 ppm
F2              -564.38 Hz
PPMCM           0.44438 ppm/cm
HZCM          221.58908 Hz/cm
```



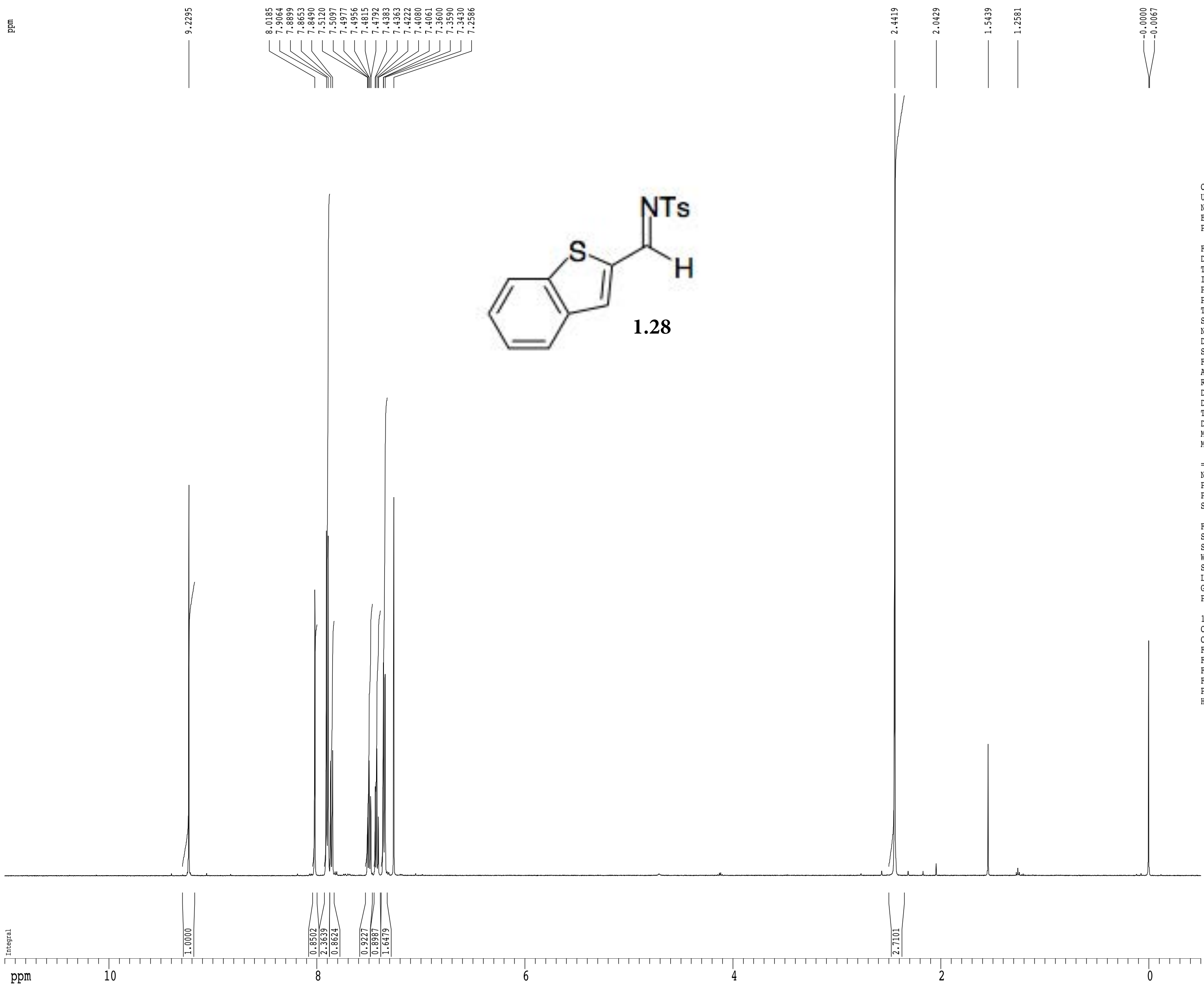
1.13

```
Current Data Parameters
USER          caherber
NAME     CAH-I-285-f11-600
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_          20210920
Time              10.59
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998979 sec
RG                   10
DW               52.000 usec
DE                14.23 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.50 usec

F2 - Processing parameters
SI                65536
SF          600.1300407 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              5401.17 Hz
F2P              -1.079 ppm
F2              -647.47 Hz
PPMCM           0.44206 ppm/cm
HZCM          265.29141 Hz/cm
```



```
Current Data Parameters
USER            caherber
NAME     CAH-I-285-f11-600
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210920
Time               11.09
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   307
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 298.1 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9027986 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.117 ppm
F1              34725.34 Hz
F2P               -9.984 ppm
F2              -1506.54 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11780 Hz/cm
```

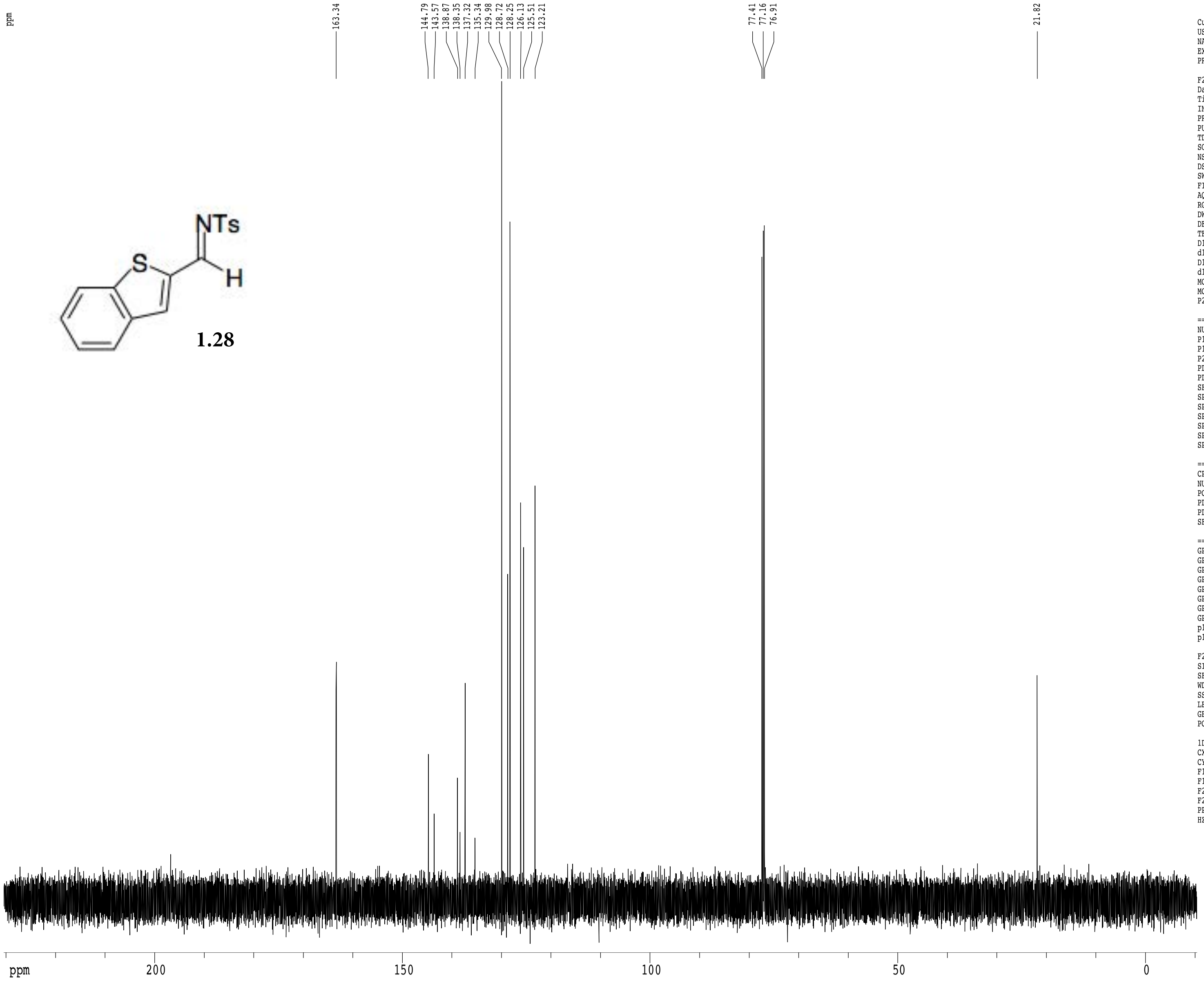
1H spectrum



1.28

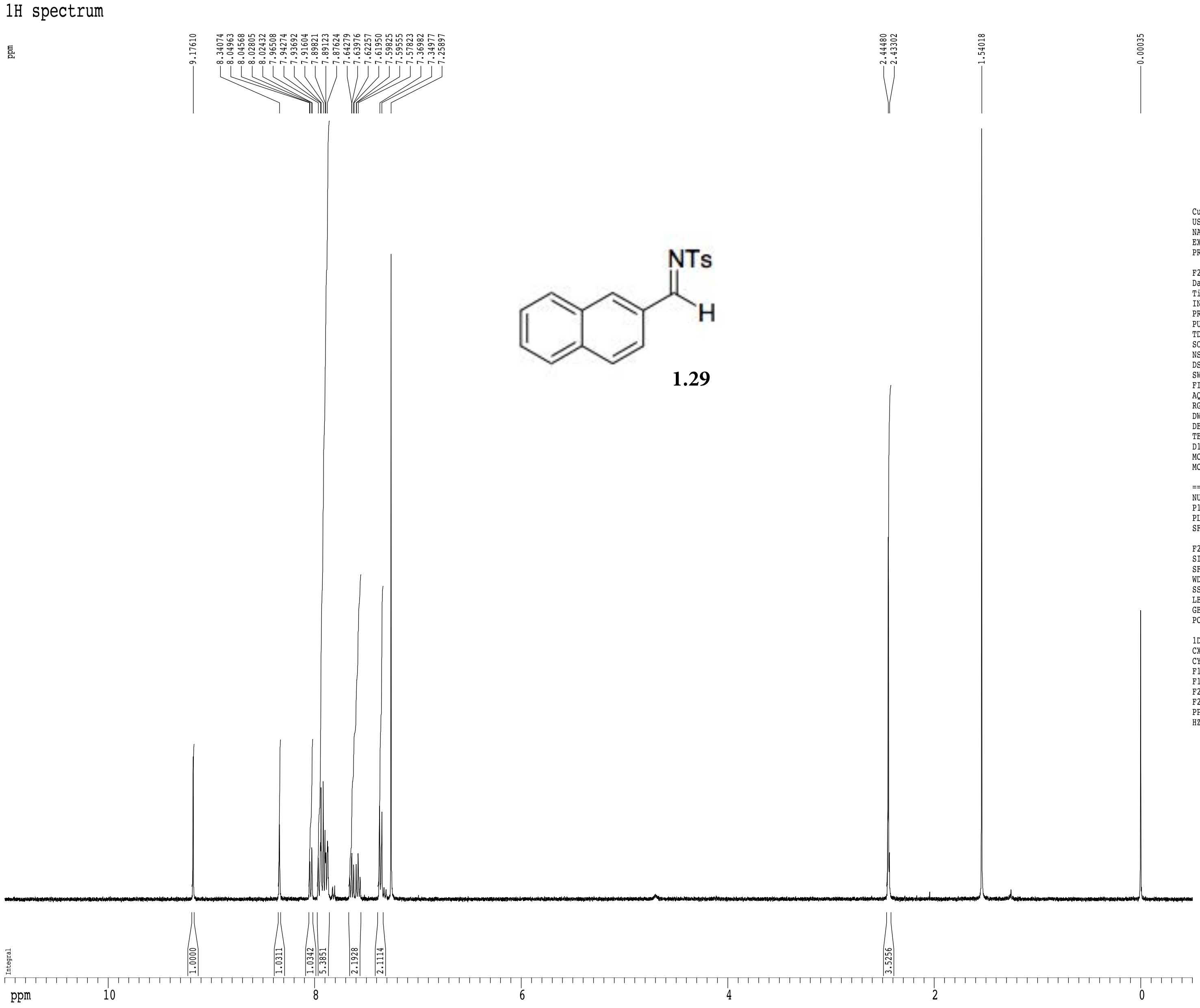
```
Current Data Parameters
USER            khewitt1
NAME       KAH-I-153-Z-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181110
Time               17.24
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                  10.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200329 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               11.000 ppm
F1               5502.42 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.50439 ppm/cm
HZCM           252.30397 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



1.28

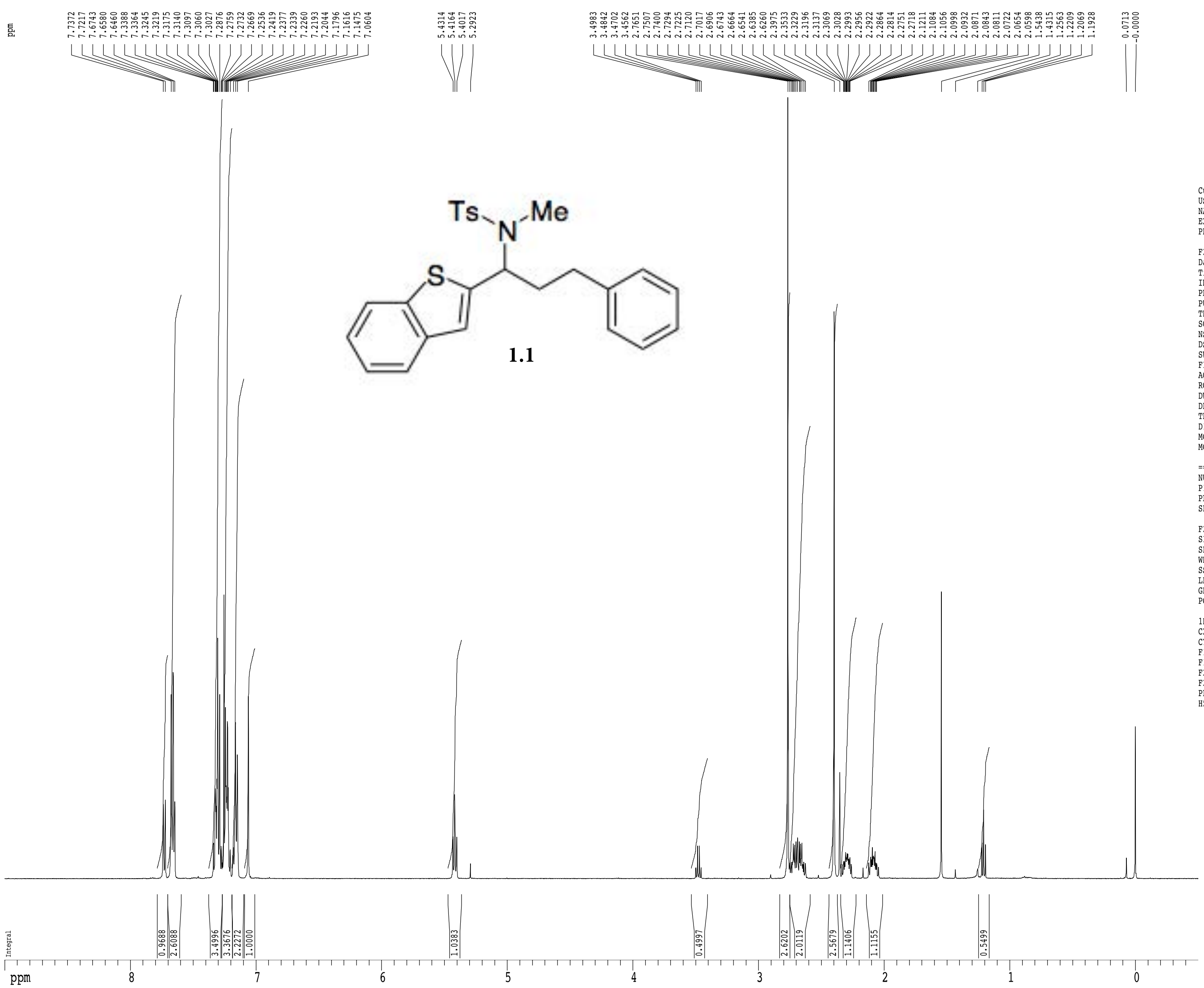
```
Current Data Parameters
USER           khewitt1
NAME      KAH-I-153-Z-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20181110
Time              17.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  154
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                13004
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804071 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.50

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.460 ppm
F1             28987.37 Hz
F2P             -10.460 ppm
F2             -1315.66 Hz
PPMCM          10.56667 ppm/cm
HZCM         1329.08020 Hz/cm
```



1.29

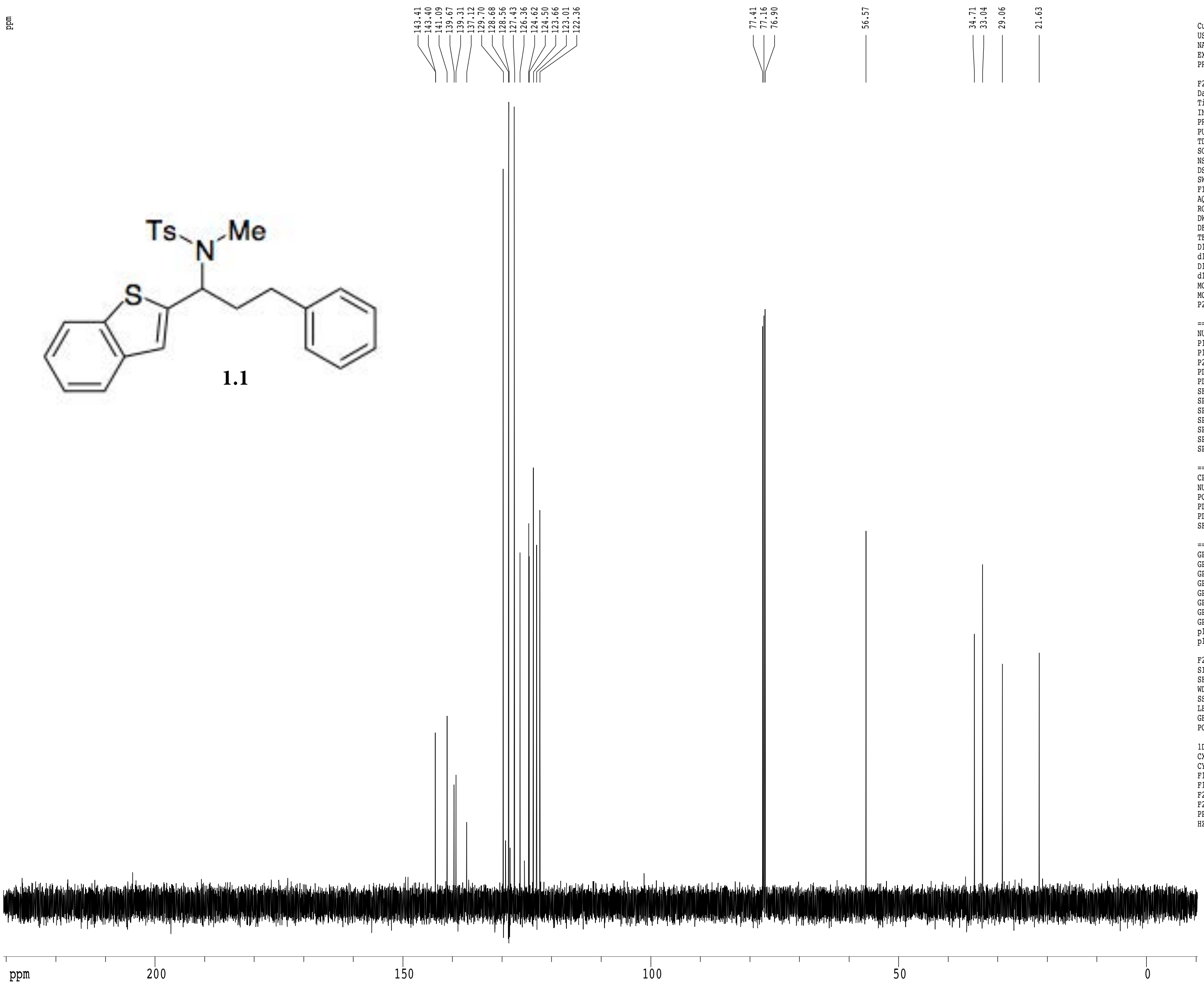
```
Current Data Parameters
USER           khewitt1
NAME          CAH-I-219
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210506
Time               9.54
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG               1149.4
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300220 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER            khewitt1
NAME         KAH-I-172-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20181107
Time              21.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    9
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200355 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

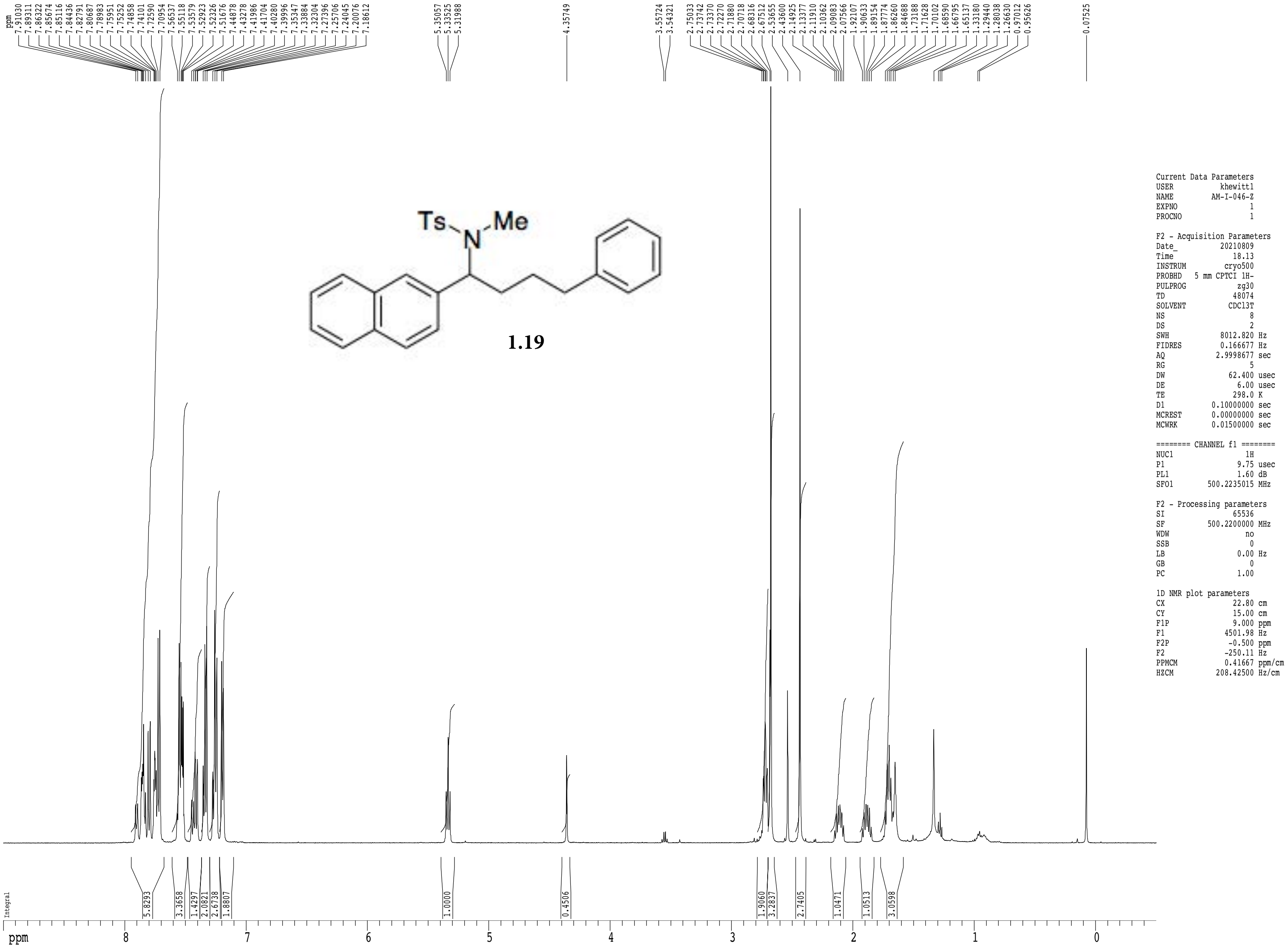
Z-restored spin-echo 13C spectrum with 1H decoupling



1.1

```
Current Data Parameters
USER             khewitt1
NAME          KAH-I-172-Z
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20181107
Time                21.12
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT             CDCl3
NS                    196
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 2896.3
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P12               2000.00 usec
P20                500.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP2                  2.70 dB
SP4                  2.70 dB
SPNAM2        Crp60comp.4
SPNAM4     Crp60,0.5,20.1
SPOFF2               0.00 Hz
SPOFF4               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                23.54 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804080 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.50

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               230.637 ppm
F1               29009.68 Hz
F2P               -10.287 ppm
F2               -1293.96 Hz
PPMCM            10.56688 ppm/cm
HZCM           1329.10693 Hz/cm
```

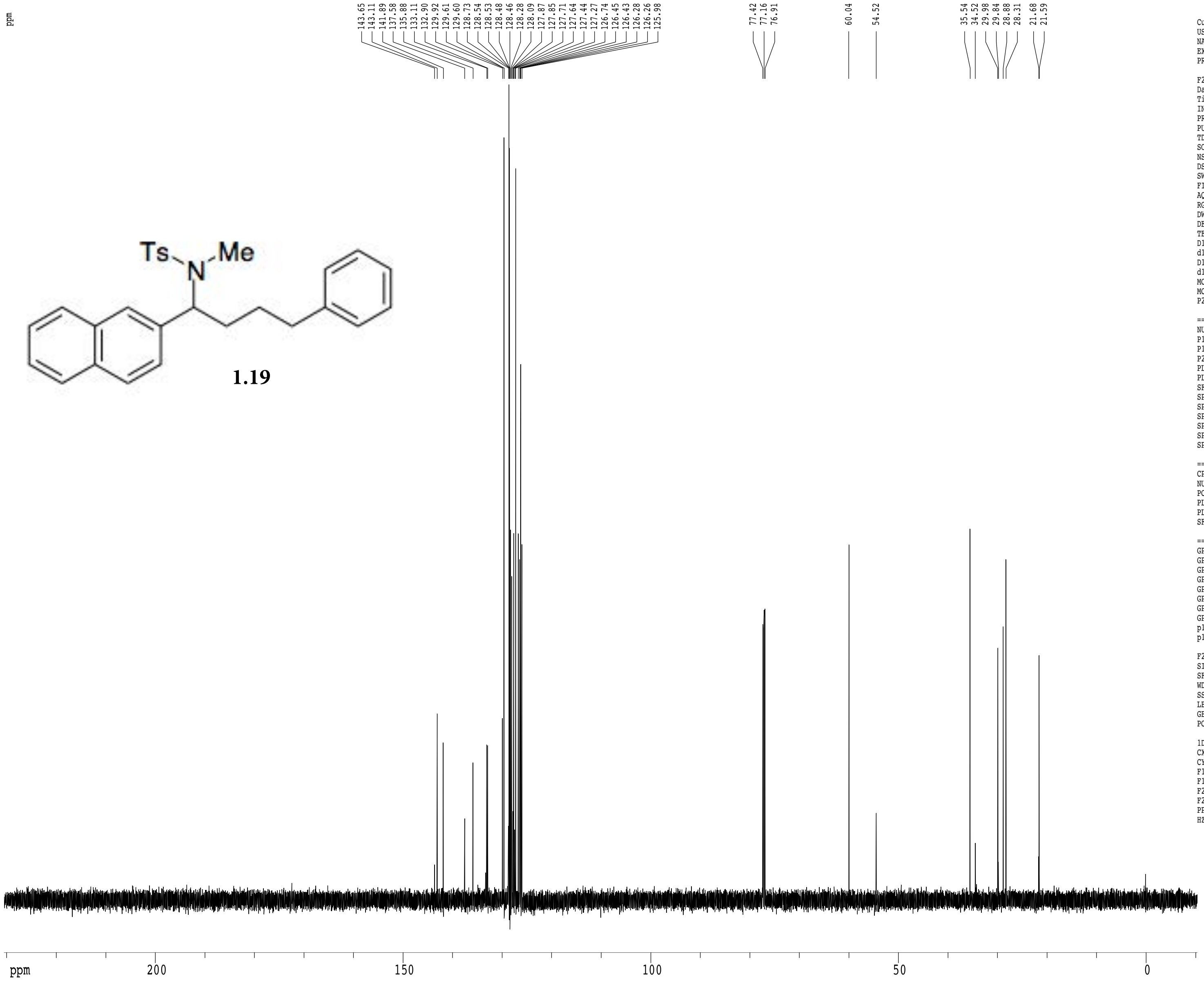
1H spectrum



1.19

```
Current Data Parameters
USER            khewitt1
NAME          AM-I-046-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210809
Time               18.13
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

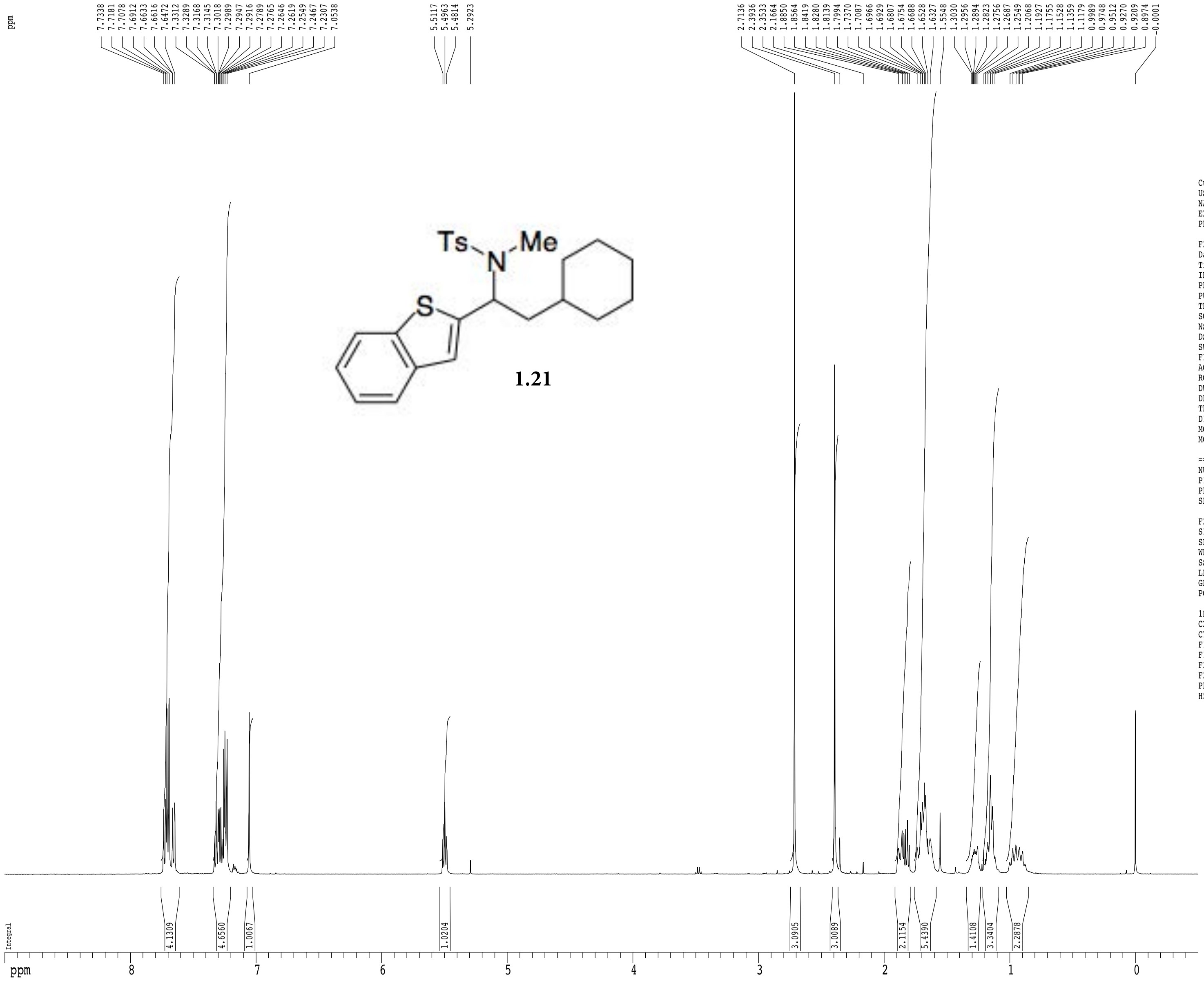
Z-restored spin-echo 13C spectrum with 1H decoupling



1.19

```
Current Data Parameters
USER             khewitt1
NAME            AM-I-046-Z
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210809
Time                 18.16
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     152
DS                      16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                   37.70 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   18.85 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   1.55 dB
SP4                   1.55 dB
SPNAM2         Crp60comp.4
SPNAM4      Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 22.00 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804099 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                230.637 ppm
F1                29009.68 Hz
F2P                -10.287 ppm
F2                -1293.96 Hz
PPMCM             10.56688 ppm/cm
HZCM            1329.10693 Hz/cm
```

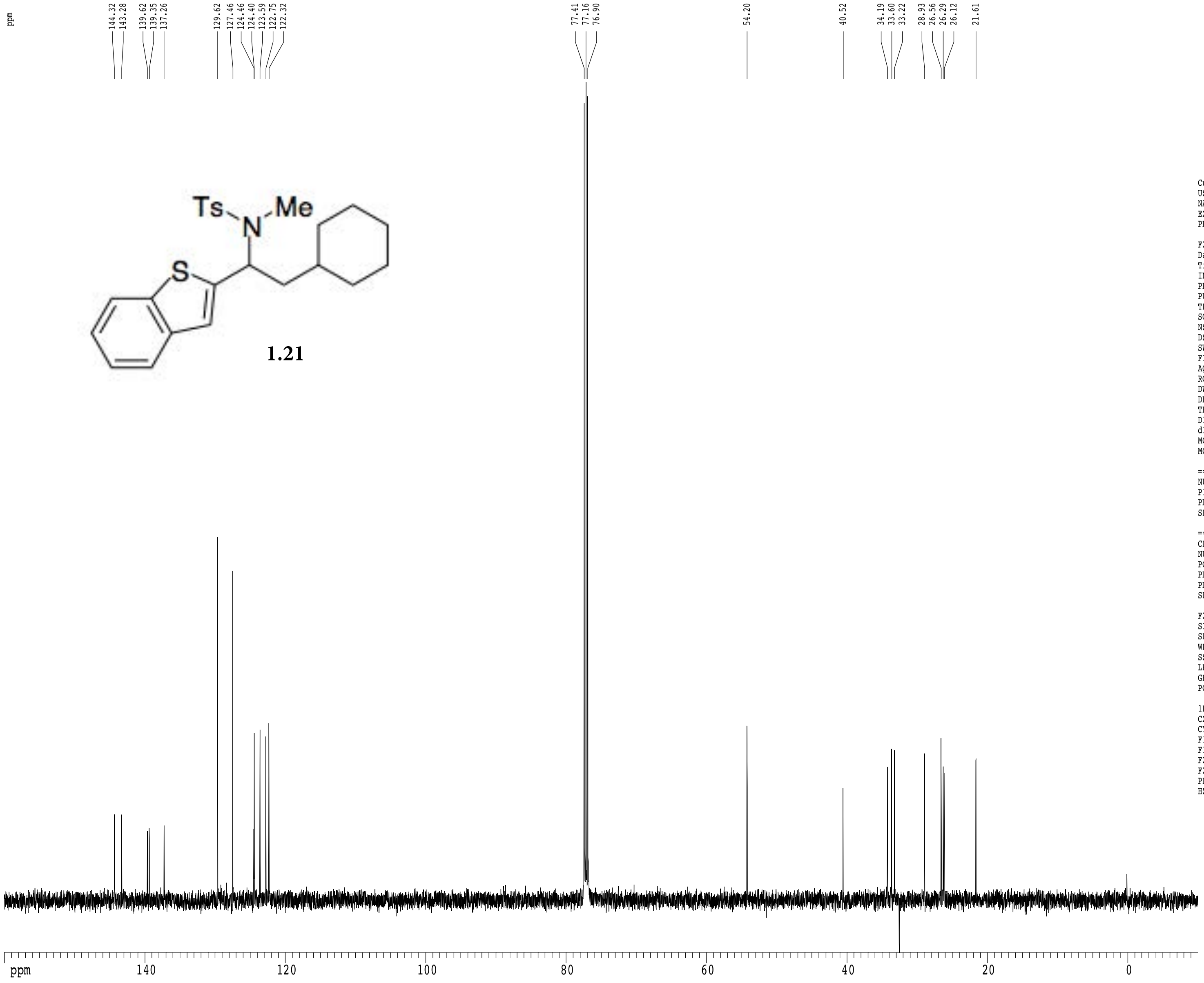
1H spectrum



1.21

```
Current Data Parameters
USER            khewitt1
NAME      ACM-I-120-benzCH
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191112
Time                9.06
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                    10
DS                     2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998774 sec
RG                   181
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1               12.00 usec
PL1              -5.00 dB
SFO1       498.8534919 MHz

F2 - Processing parameters
SI                 65536
SF         498.8500296 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4489.65 Hz
F2P               -0.500 ppm
F2               -249.42 Hz
PPMCM            0.41667 ppm/cm
HZCM           207.85419 Hz/cm
```

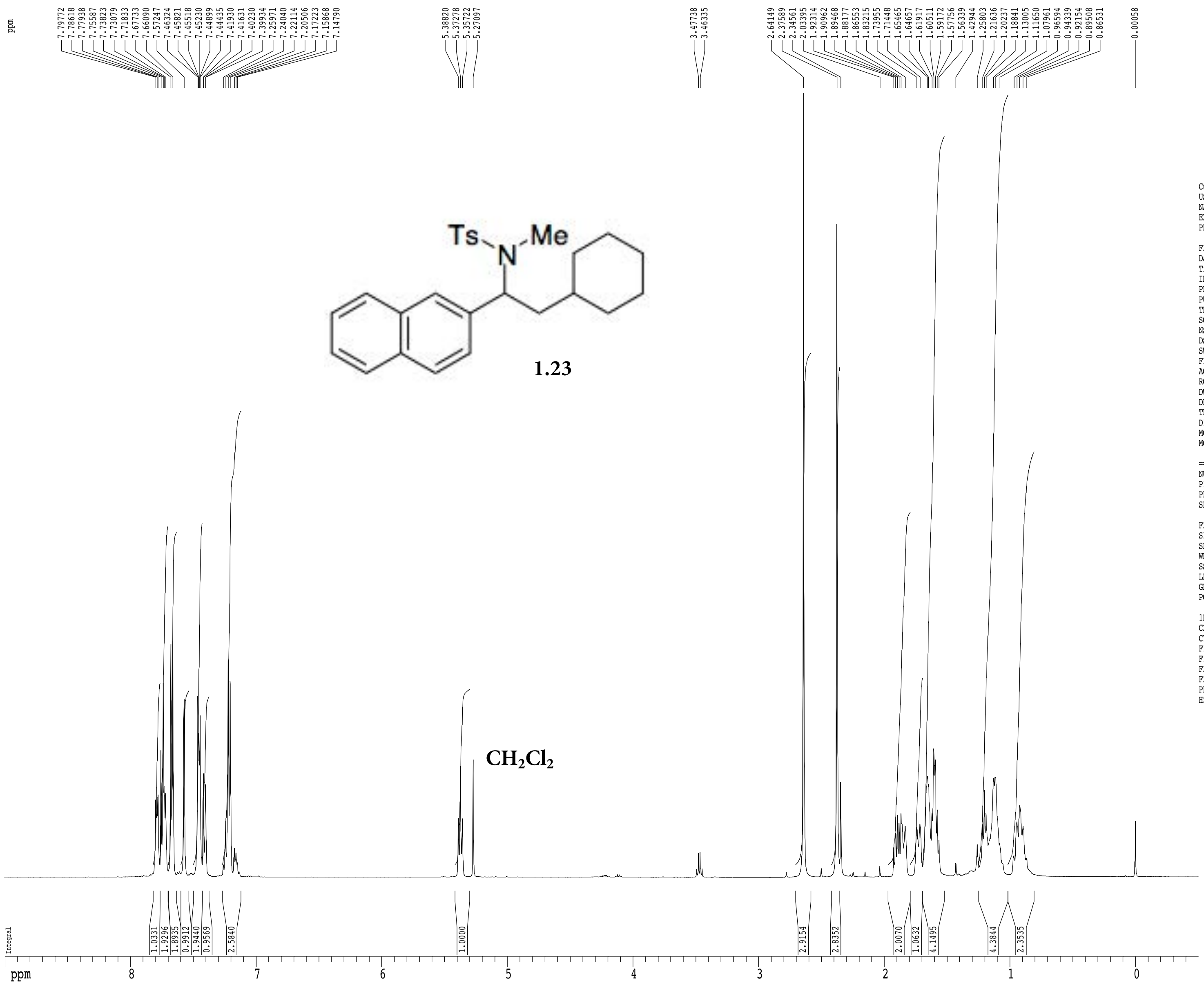
13C spectrum with 1H decoupling



1.21

```
Current Data Parameters
USER            khewitt1
NAME      ACM-I-120-benzCH
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191112
Time                9.07
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   544
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                 46341
DW                16.500 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                -6.00 dB
SFO1         125.4497300 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -5.00 dB
PL12               13.20 dB
SFO2         498.8524943 MHz

F2 - Processing parameters
SI                 65536
SF           125.4359203 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              160.000 ppm
F1               20069.75 Hz
F2P              -10.000 ppm
F2              -1254.36 Hz
PPMCM            7.45614 ppm/cm
HZCM           935.26788 Hz/cm
```

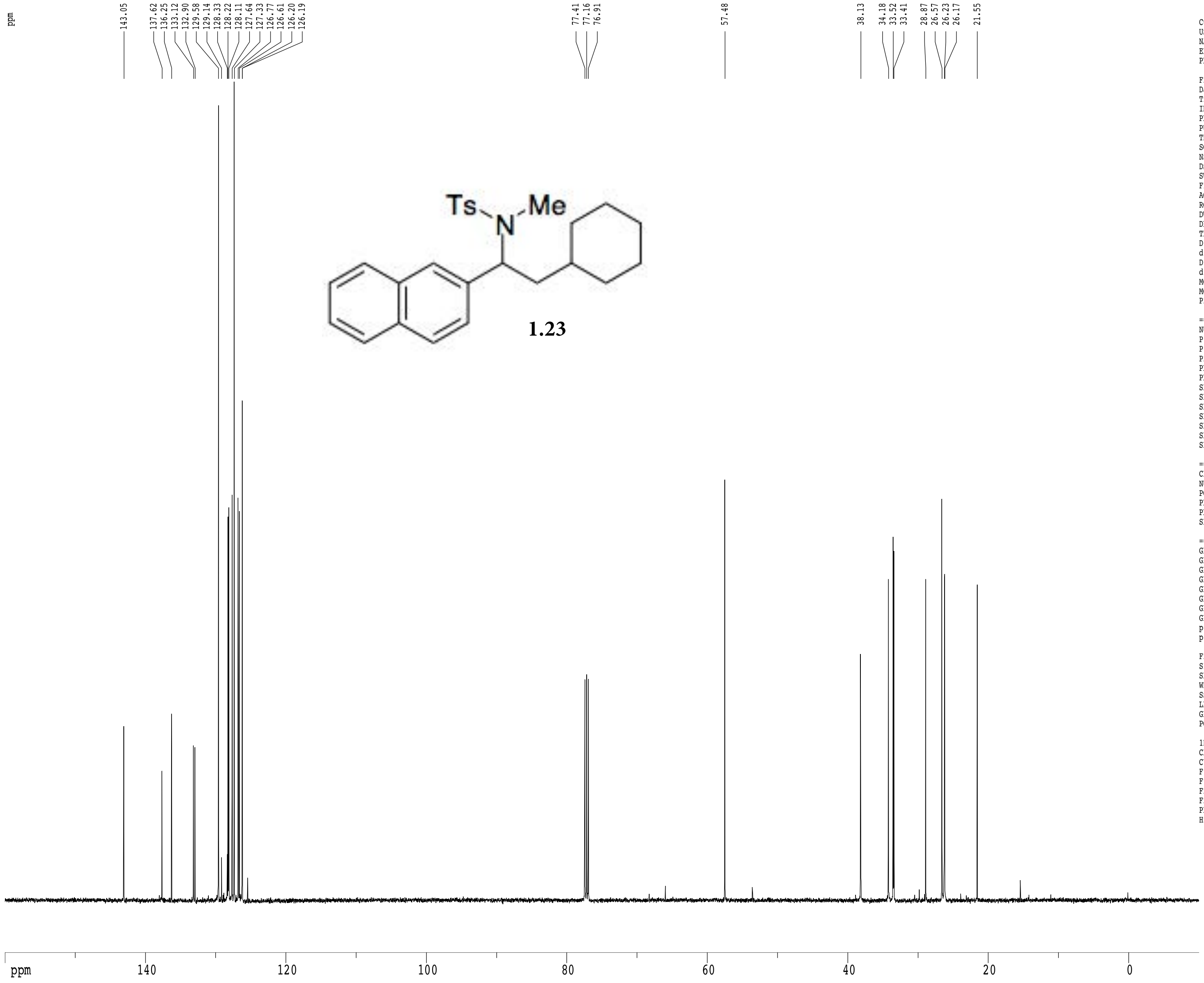
1H spectrum



1.23

```
Current Data Parameters
USER            khewitt1
NAME      ACM-I-120nap-CH
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191112
Time                9.24
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3T
NS                    10
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200411 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

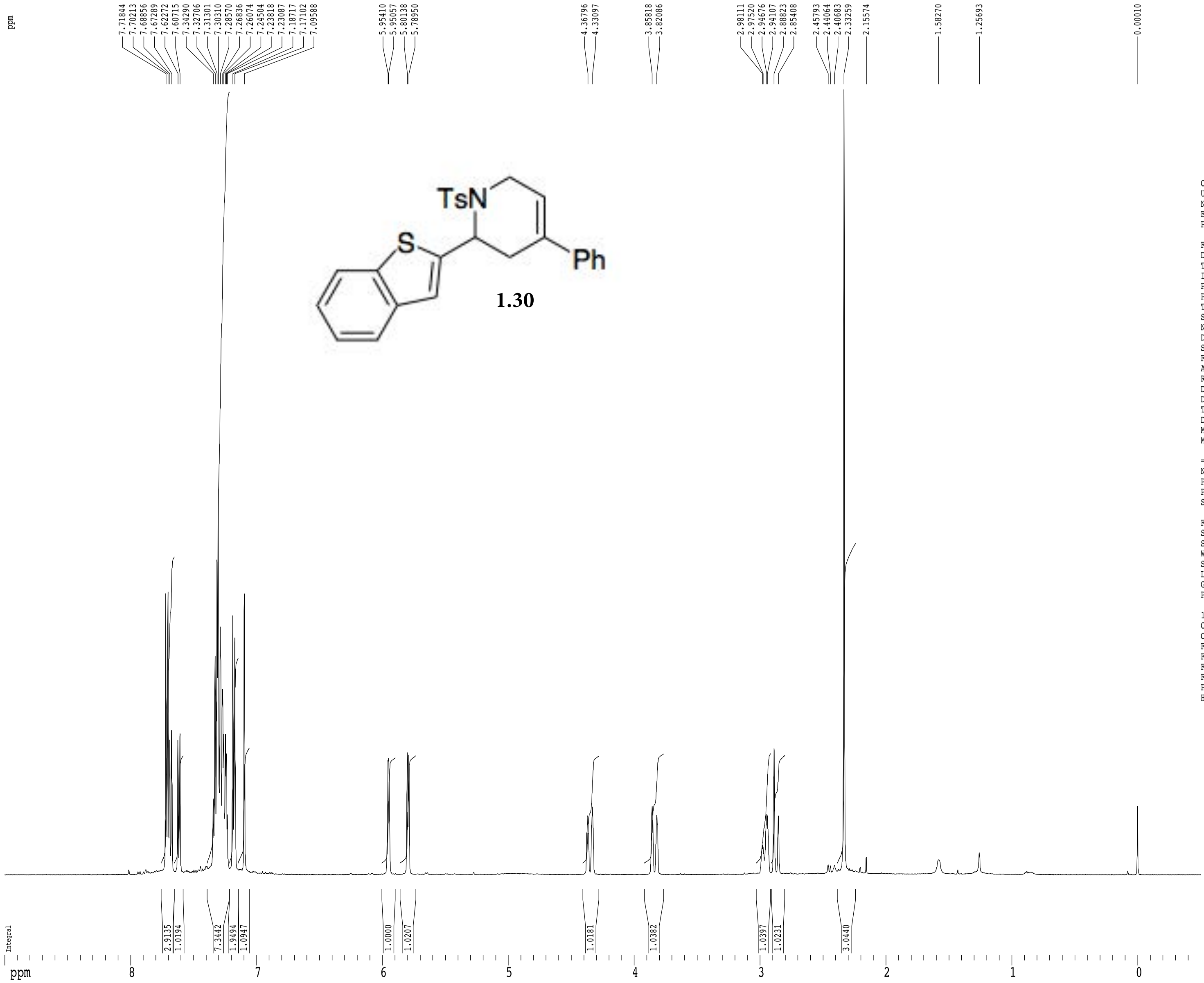
Z-restored spin-echo 13C spectrum with 1H decoupling



1.23

```
Current Data Parameters
USER           khewitt1
NAME     ACM-I-120nap-CH
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20191112
Time               9.37
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  504
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.2 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804136 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             160.000 ppm
F1             20124.87 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           7.45614 ppm/cm
HZCM          937.83643 Hz/cm
```

1H spectrum

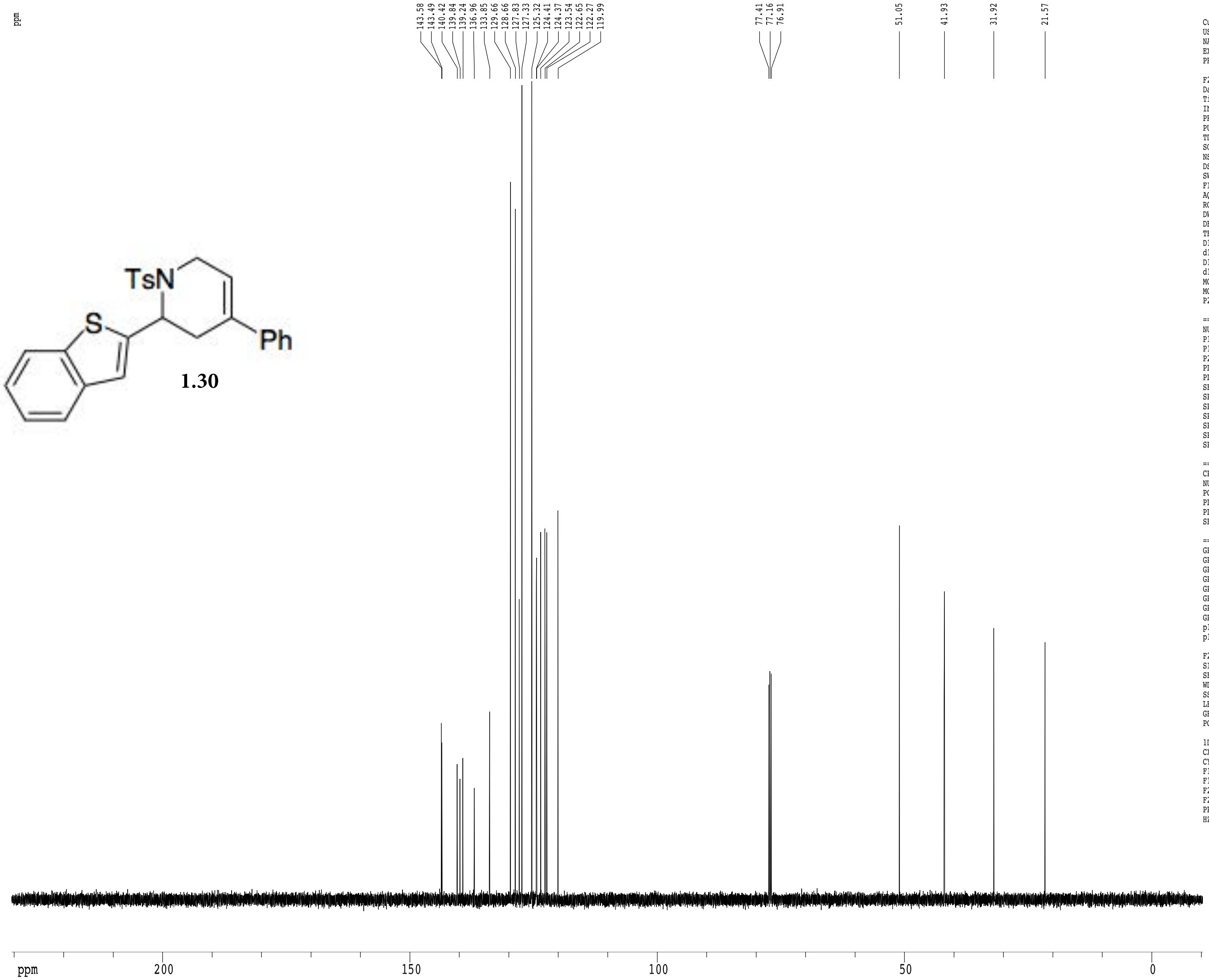


1.30

```
Current Data Parameters
USER           khewitt1
NAME         KAH-I-291-Z
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20190302
Time              14.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200426 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

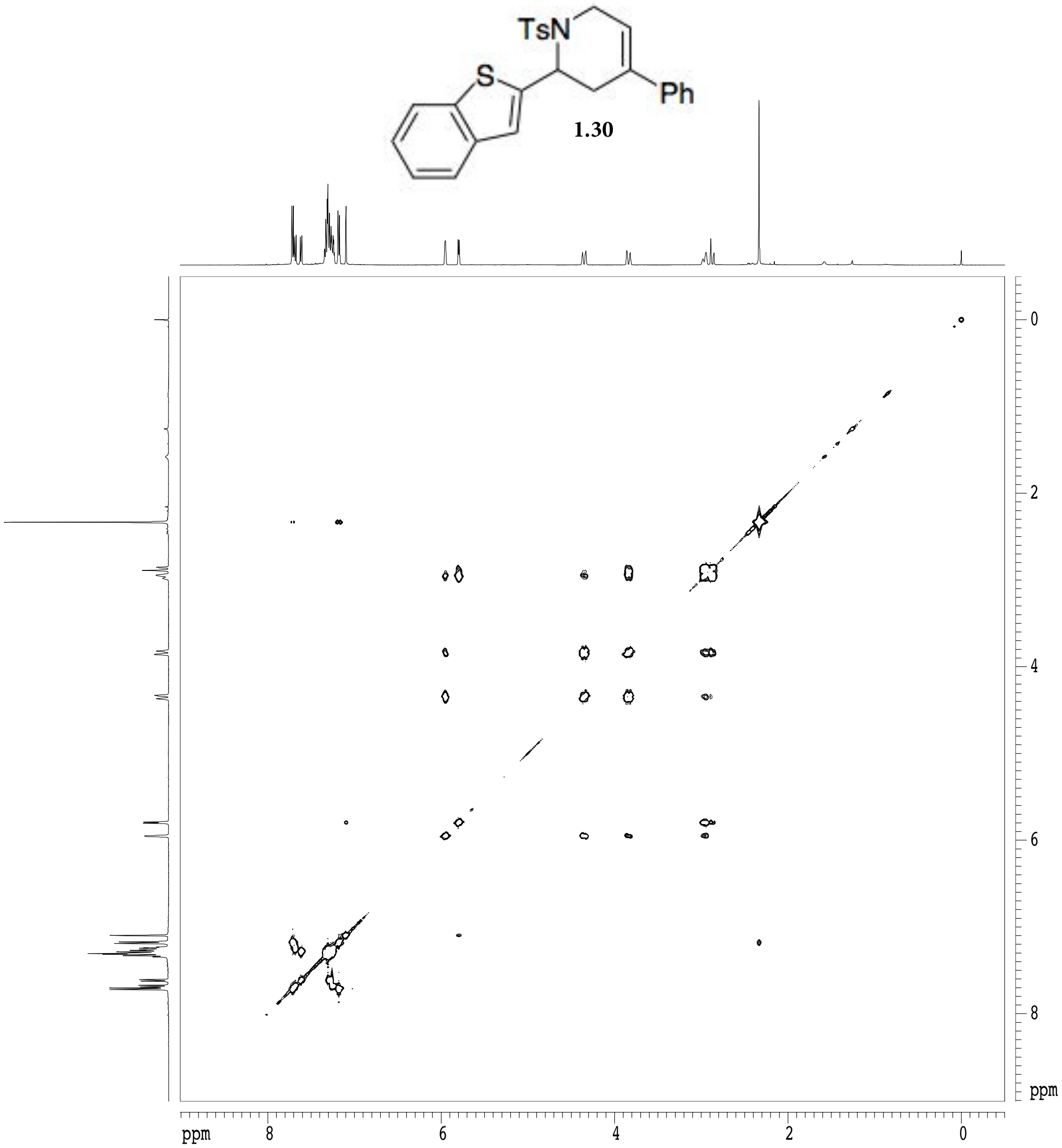
Z-restored spin-echo 13C spectrum with 1H decoupling

1.30



```
Current Data Parameters
USER            khewitt1
NAME          KAH-I-291-Z
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190302
Time               14.39
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   216
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                 13004
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804136 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

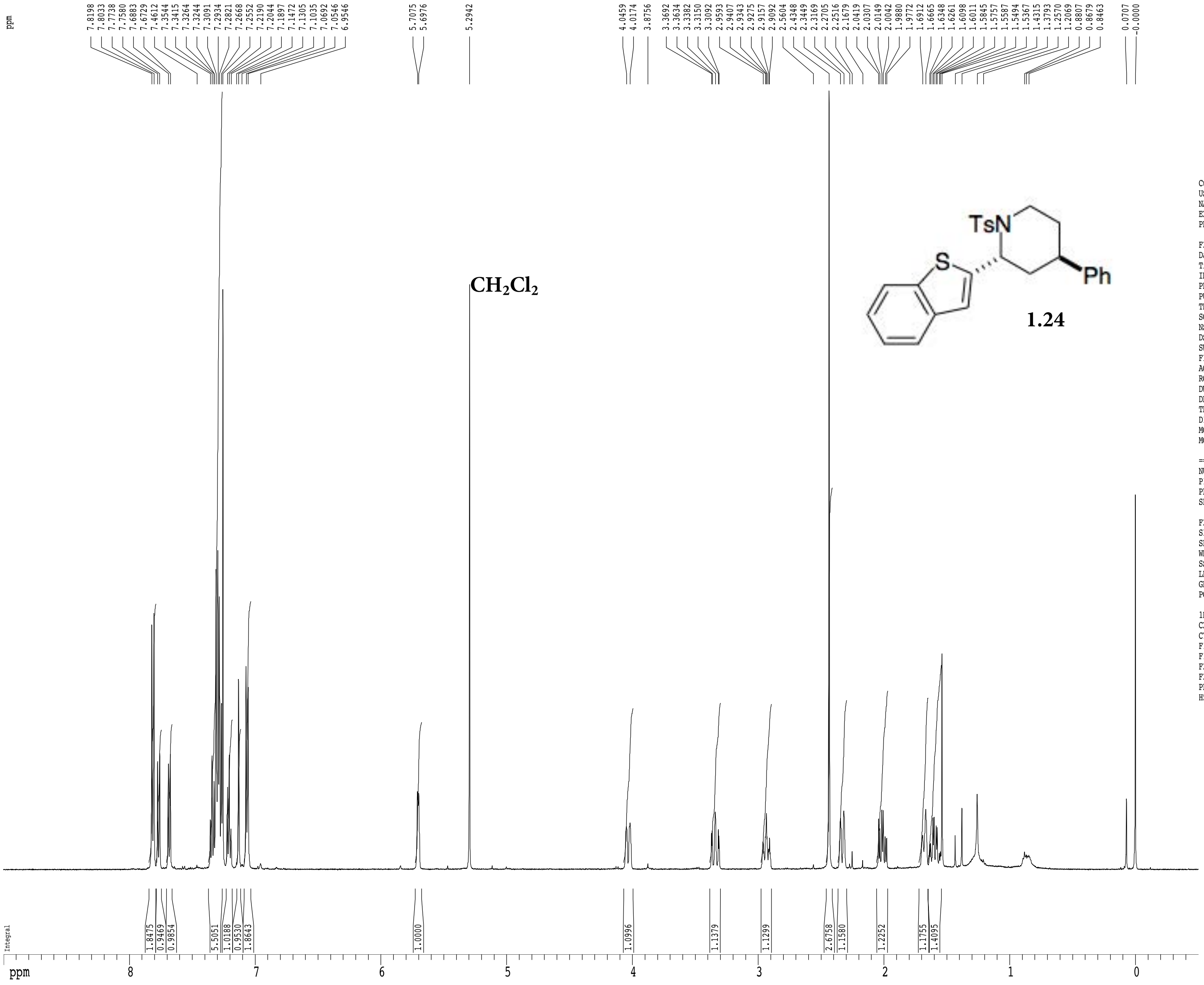
gcosy60



1.30

```
      Current Data Parameters
USER           khewitt1
NAME        KAH-I-291-Z
EXPNO                 4
PROCNO                1

      F2 - Acquisition Parameters
Date_          20190302
Time              14.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                  114
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200426 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200426 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.011 ppm
F2LO            4507.45 Hz
F2PHI            -0.500 ppm
F2HI            -250.16 Hz
F1PLO             9.011 ppm
F1LO            4507.45 Hz
F1PHI            -0.500 ppm
F1HI            -250.16 Hz
F2PPMCM         0.63407 ppm/cm
F2HZCM        317.17413 Hz/cm
F1PPMCM         0.63407 ppm/cm
F1HZCM        317.17413 Hz/cm
```

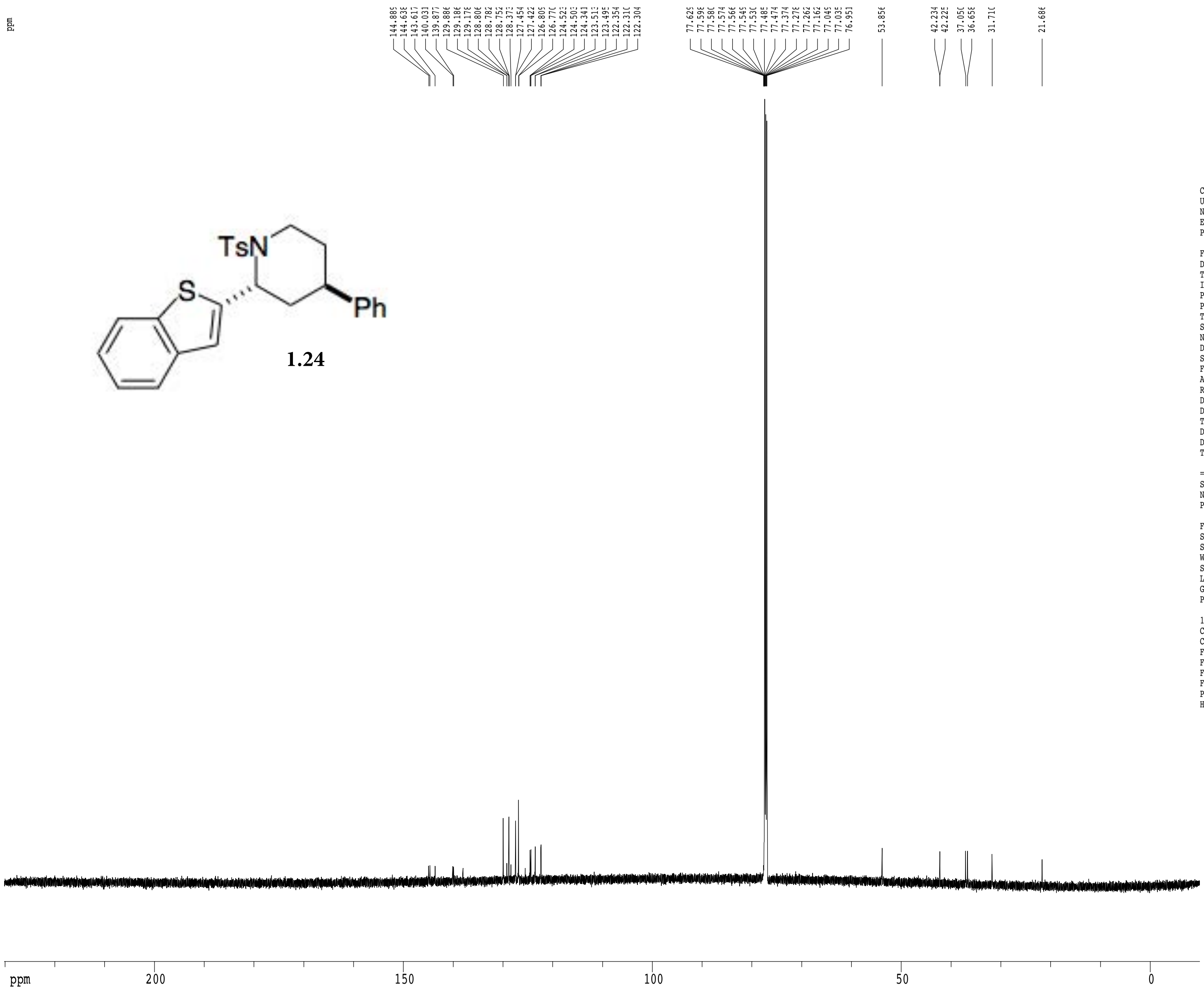
1H spectrum



1.24

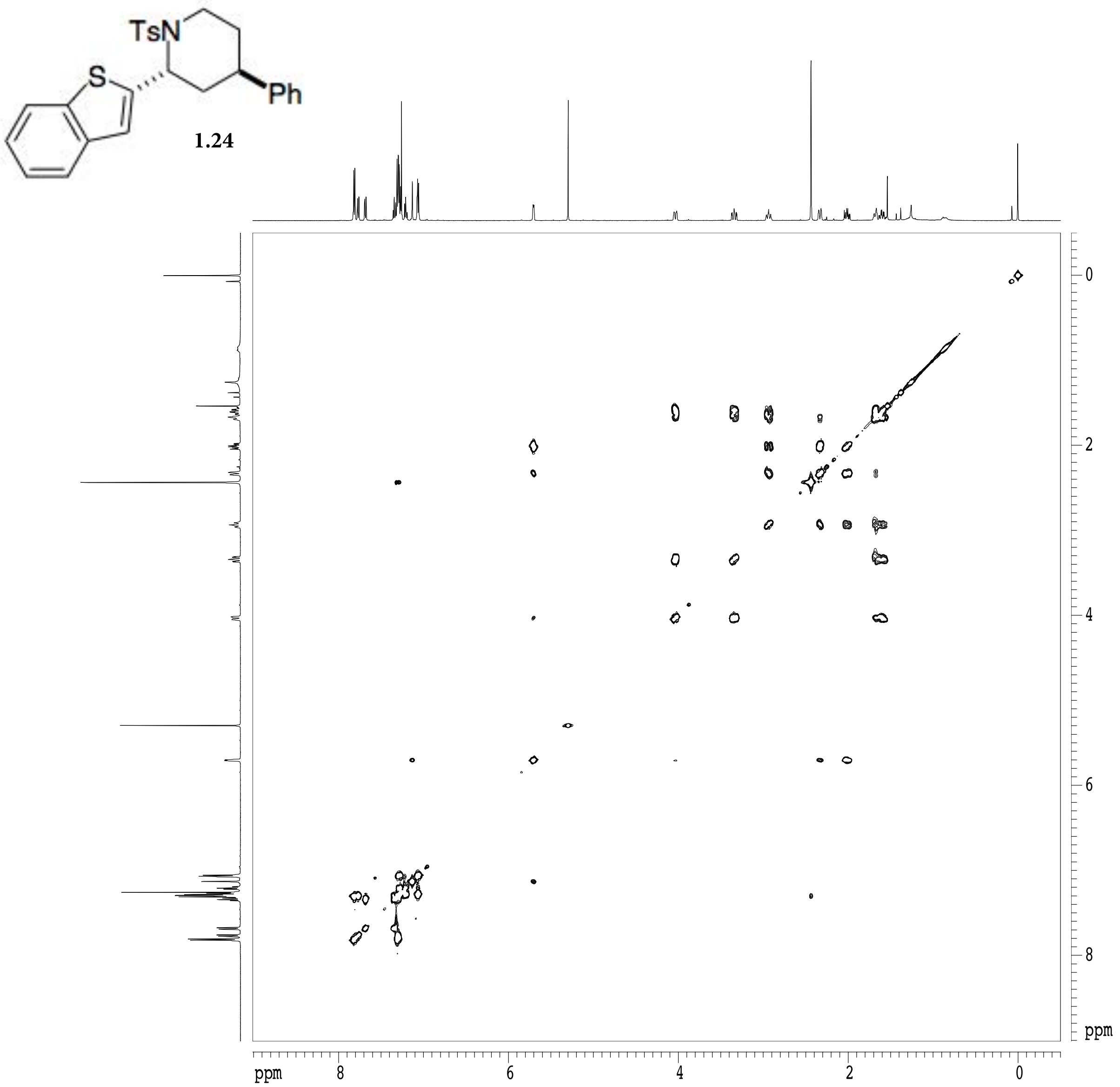
```
Current Data Parameters
USER          khewitt1
NAME        KAH-I-214-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20181204
Time              11.04
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200349 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

c13.c



```
Current Data Parameters
USER          khewitt1
NAME      KAH-I-214-Z-C
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20210714
Time             11.13
INSTRUM          av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgdc30
TD               65536
SOLVENT         CDCl3T
NS                1024
DS                   4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                2050
DW              13.800 usec
DE               19.63 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1               13C
P1               10.10 usec

F2 - Processing parameters
SI               65536
SF         150.9027936 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                0.10

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P            230.150 ppm
F1            34730.32 Hz
F2P             -9.951 ppm
F2            -1501.56 Hz
PPMCM         10.53074 ppm/cm
HZCM        1589.11768 Hz/cm
```

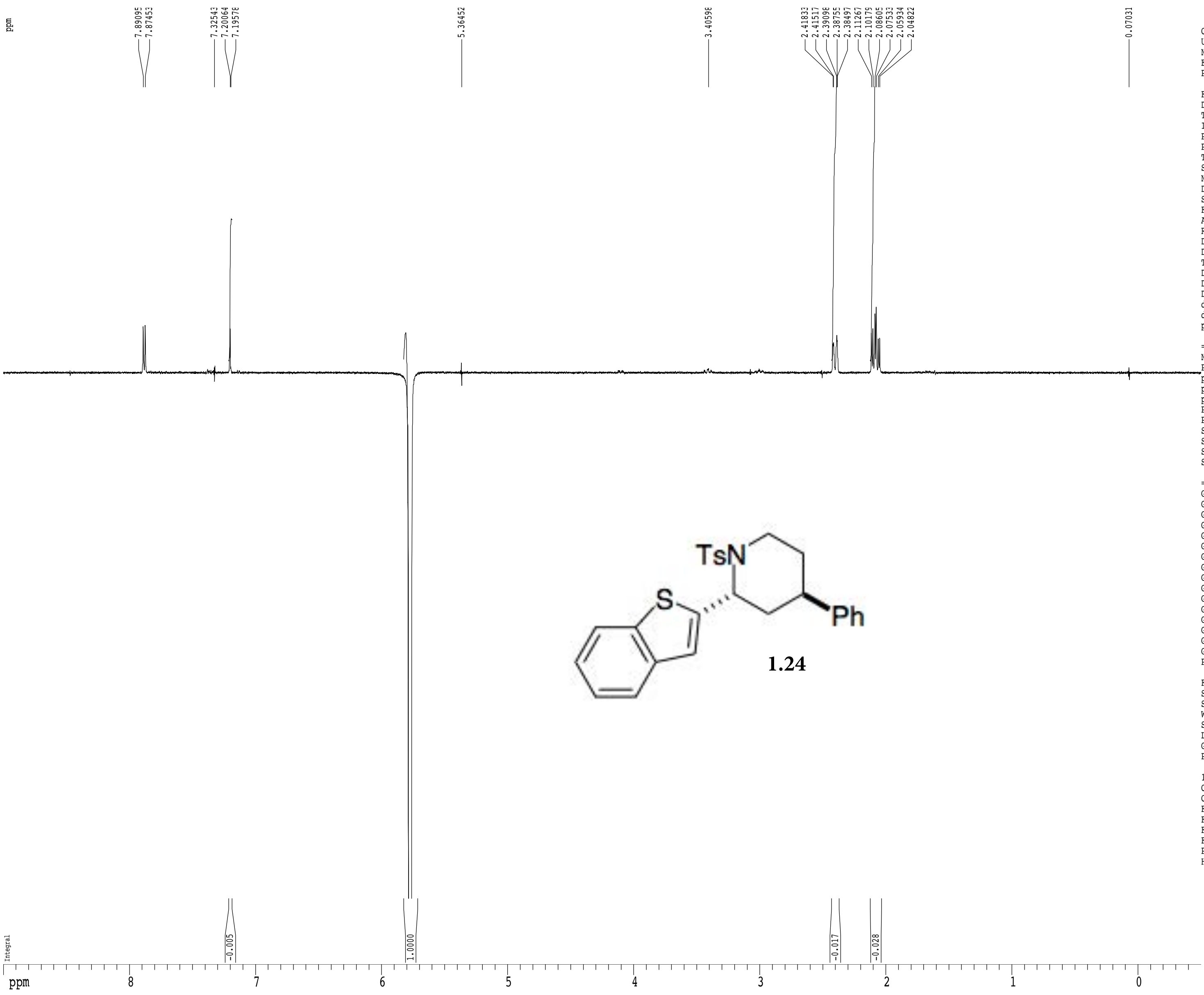
gcosy60



1.24

```
        Current Data Parameters
USER            khewitt1
NAME          KAH-I-214-Z
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20181204
Time               11.06
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   362
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200349 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200349 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

         2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.011 ppm
F2LO             4507.33 Hz
F2PHI             -0.500 ppm
F2HI             -250.28 Hz
F1PLO              9.011 ppm
F1LO             4507.33 Hz
F1PHI             -0.500 ppm
F1HI             -250.28 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```

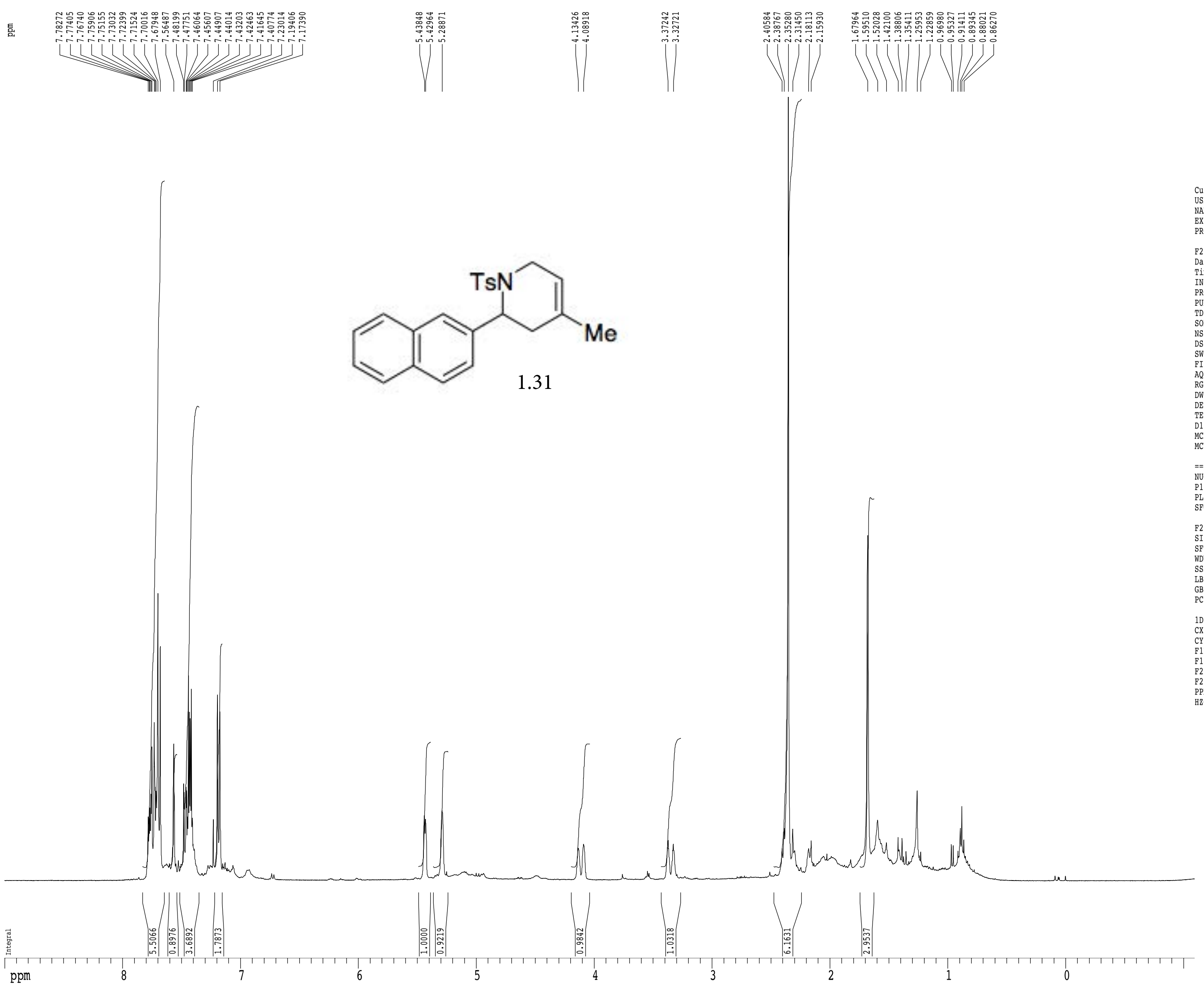
gnoe



1.24

```
Current Data Parameters
USER              khewitt1
NAME            KAH-I-214-Z
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20181204
Time                 11.30
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                     114
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2228874 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

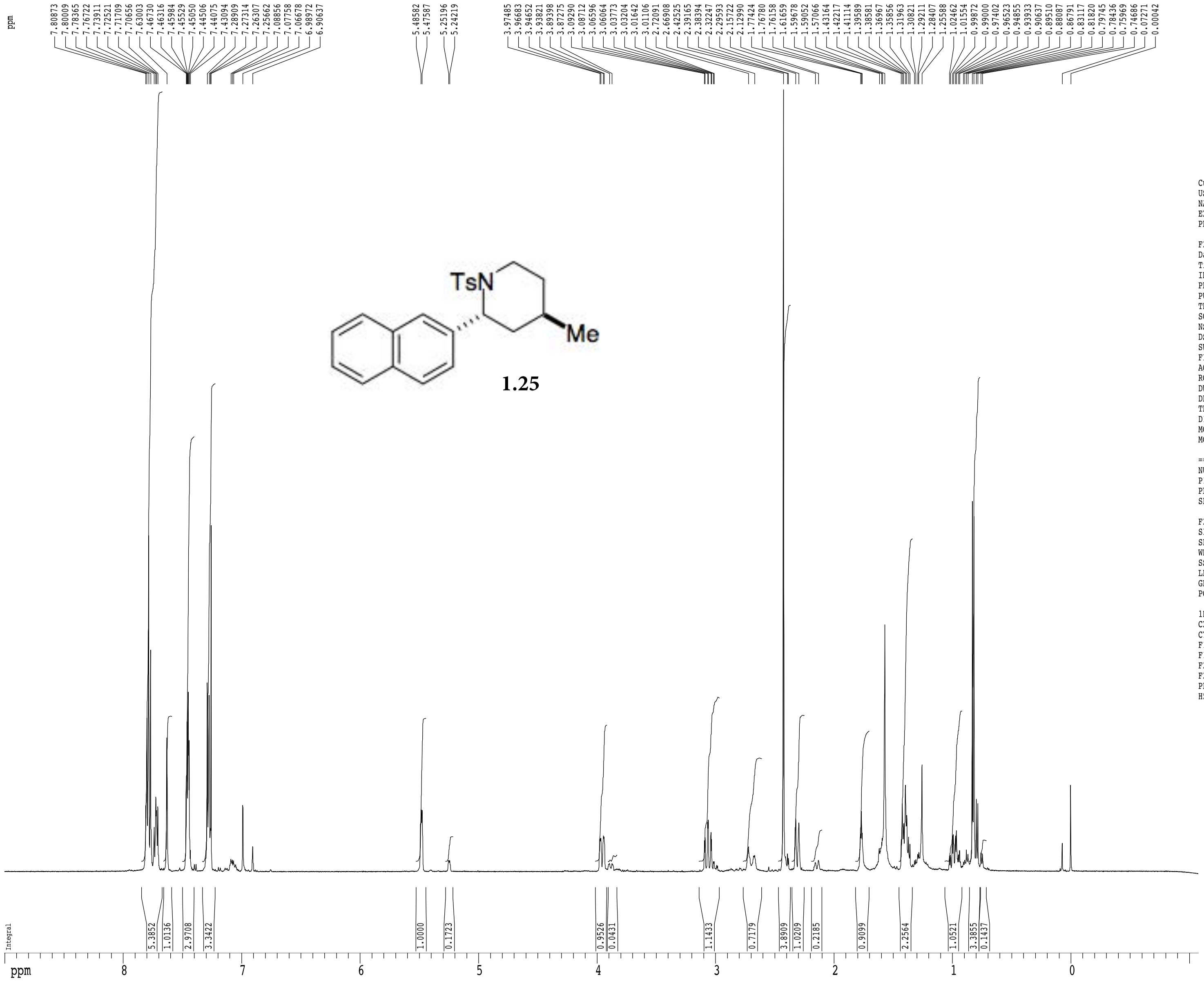
1H spectrum



1.31

```
Current Data Parameters
USER          caherber
NAME          CAH-I-221
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20210525
Time             11.17
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG                50.8
DW              78.000 usec
DE                4.50 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.60 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300333 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -1.093 ppm
F2             -437.51 Hz
PPMCM          0.44269 ppm/cm
HZCM         177.13533 Hz/cm
```

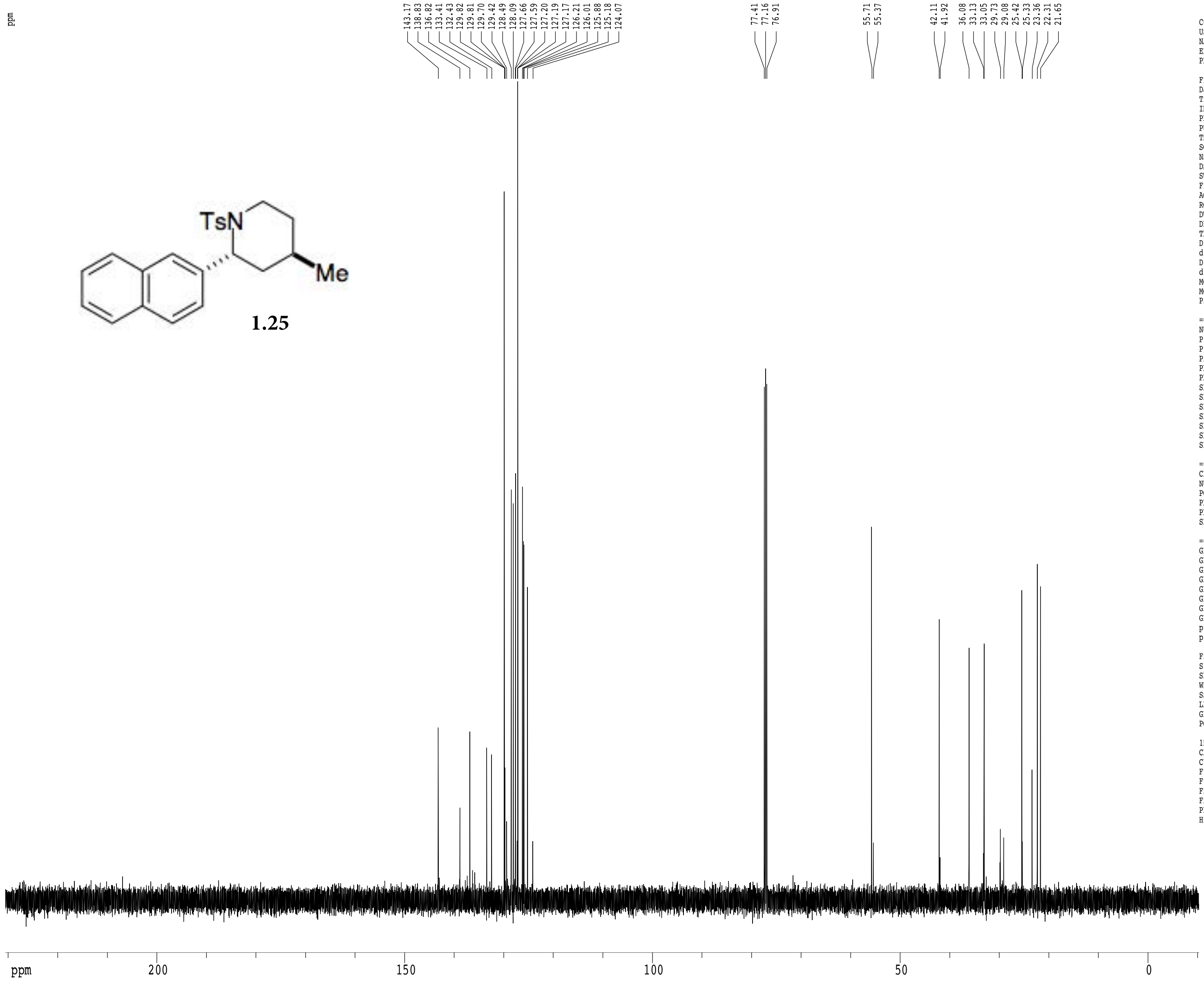
1H spectrum



1.25

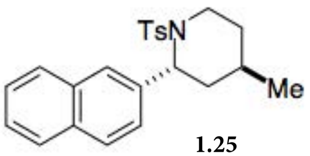
```
Current Data Parameters
USER              caherber
NAME        CAH-I-241-full
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210707
Time                 11.46
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998774 sec
RG                     6.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
PL1                   1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF          500.2200327 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -1.075 ppm
F2                 -537.60 Hz
PPMCM              0.44187 ppm/cm
HZCM             221.03436 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



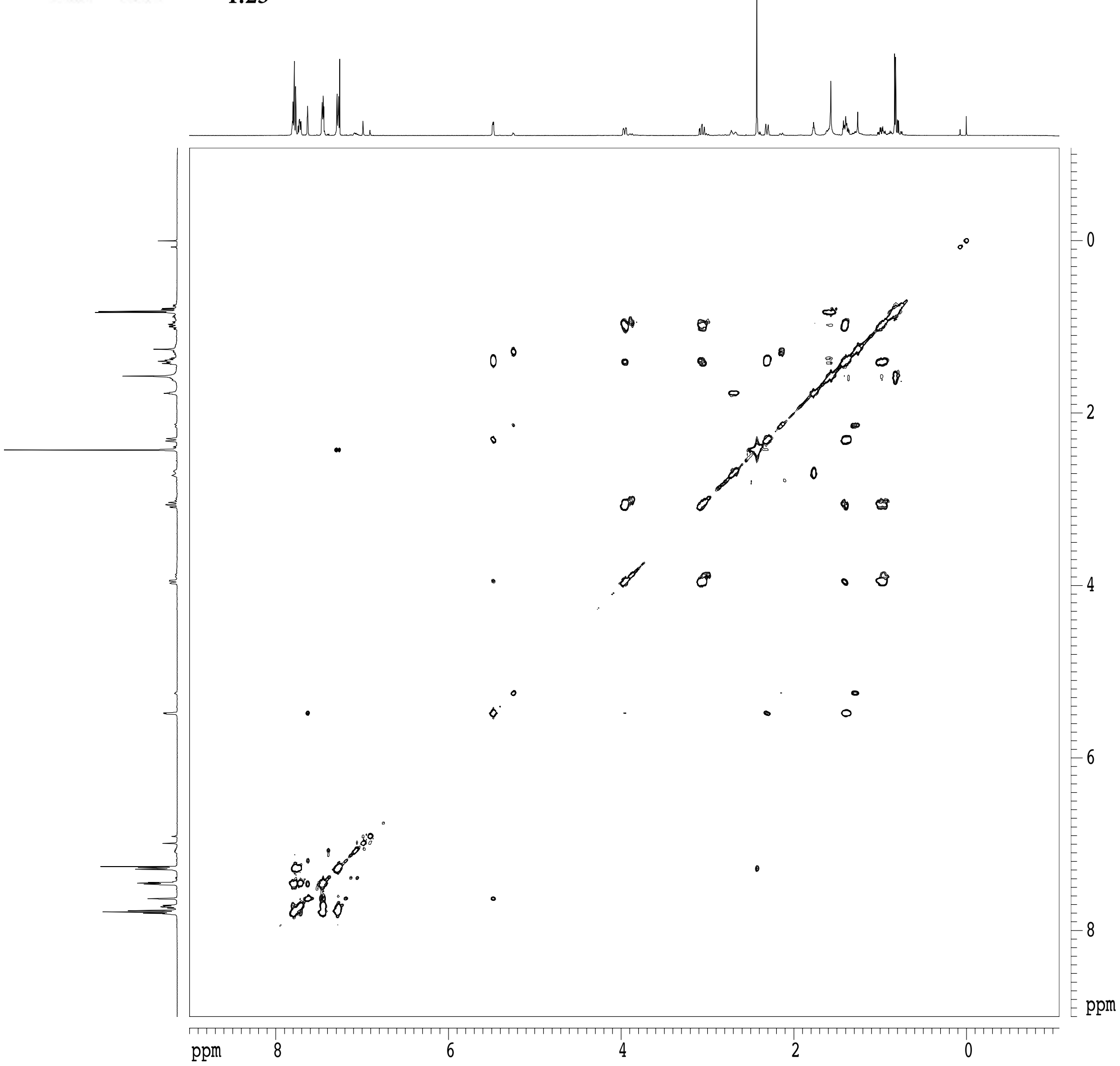
1.25

```
Current Data Parameters
USER            caherber
NAME       CAH-I-241-full
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210707
Time               13.59
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   264
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804076 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

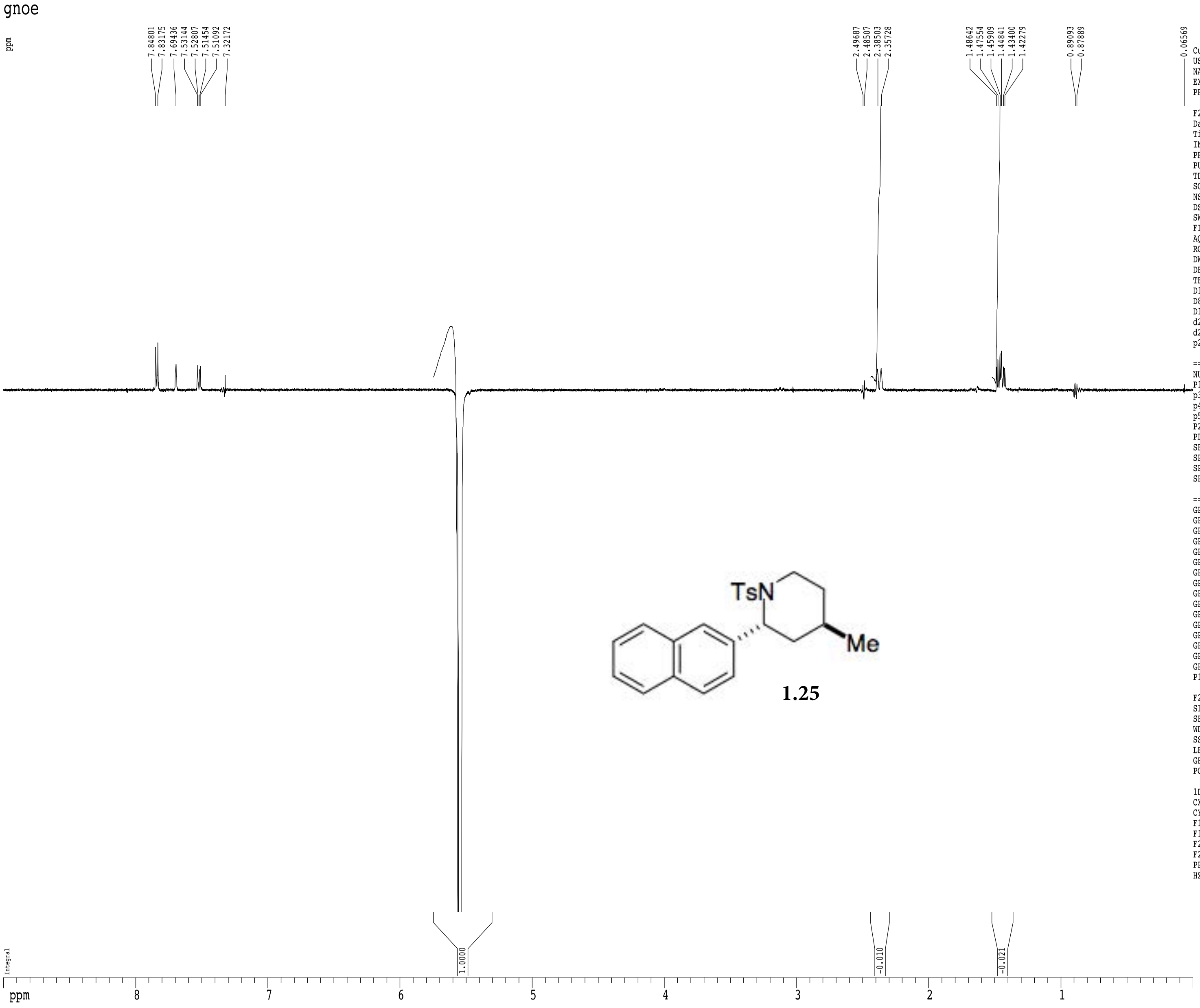


1.25

gcosy60



```
       Current Data Parameters
USER           caherber
NAME      CAH-I-241-full
EXPNO                 2
PROCNO                1

     F2 - Acquisition Parameters
Date_          20210707
Time              11.49
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                143.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

    ======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

     F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

     F2 - Processing parameters
SI                 1024
SF          500.2200327 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

     F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200327 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

       2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.000 ppm
F2LO            4501.98 Hz
F2PHI            -1.075 ppm
F2HI            -537.60 Hz
F1PLO             9.000 ppm
F1LO            4501.98 Hz
F1PHI            -1.075 ppm
F1HI            -537.60 Hz
F2PPMCM         0.67165 ppm/cm
F2HZCM        335.97217 Hz/cm
F1PPMCM         0.67165 ppm/cm
F1HZCM        335.97217 Hz/cm
```

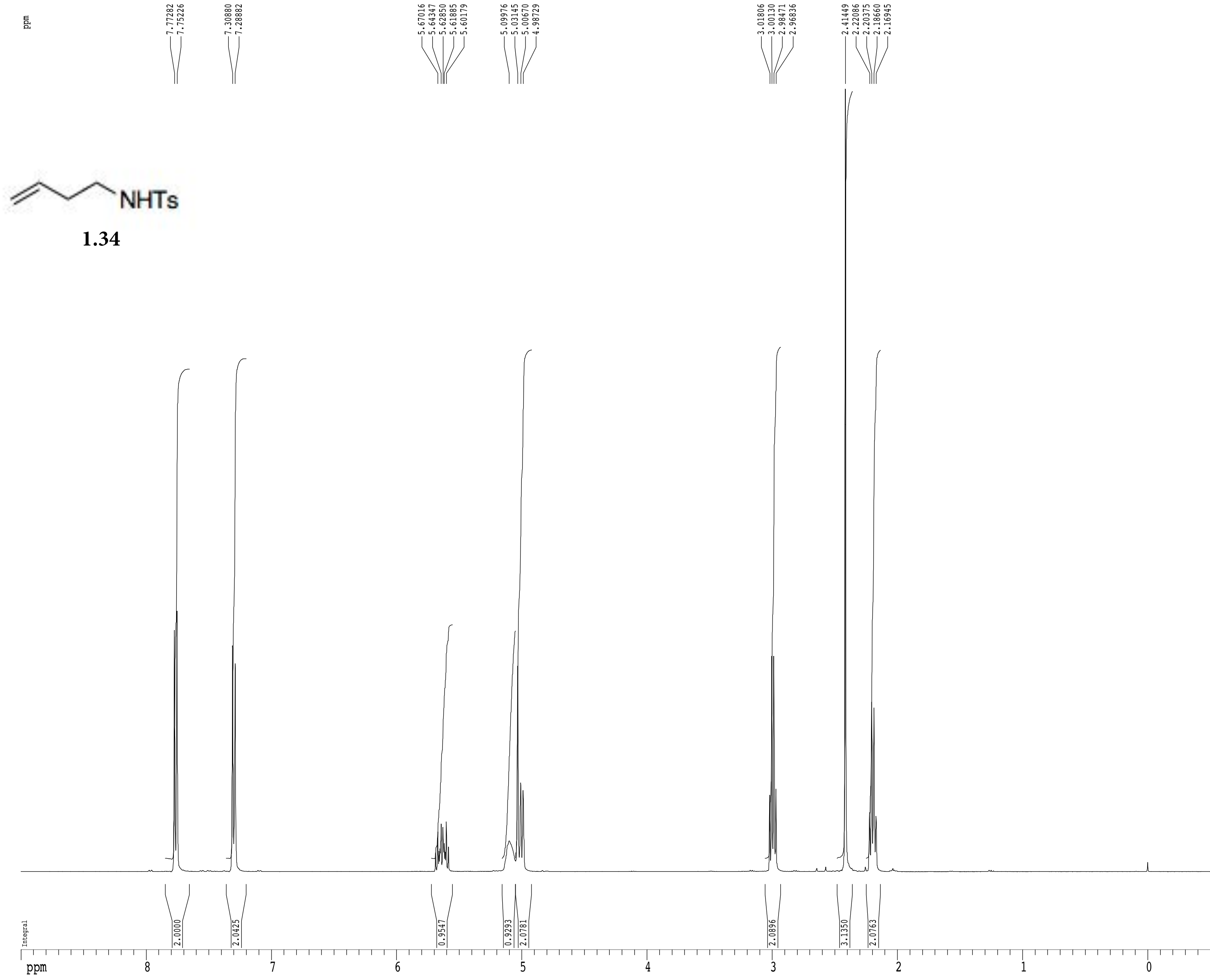


1.25

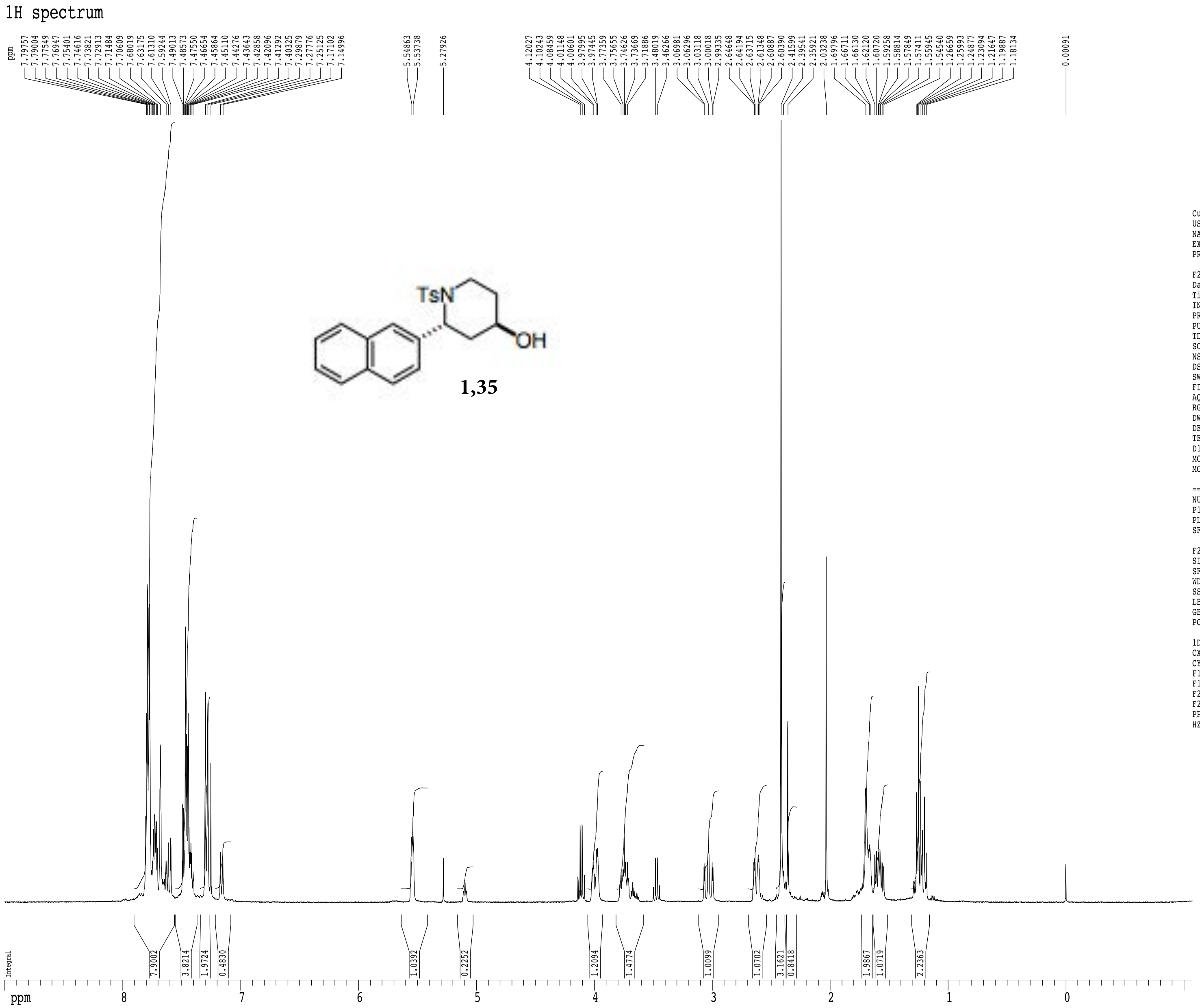
```
Current Data Parameters
USER             caherber
NAME      CAH-I-241-full
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210707
Time                13.52
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  101.6
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33375451 sec
d22            0.16399699 sec
p2                  19.50 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.75 usec
p3                  29.25 usec
p4                  39.00 usec
p5                  26.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2227742 MHz
SP9                 60.00 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         SMSQ10.100
GPNAM2         SMSQ10.100
GPNAM3         SMSQ10.100
GPNAM4         SMSQ10.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                 0.000 ppm
F2                   0.00 Hz
PPMCM             0.39474 ppm/cm
HZCM            197.45528 Hz/cm
```

1H spectrum

1.34



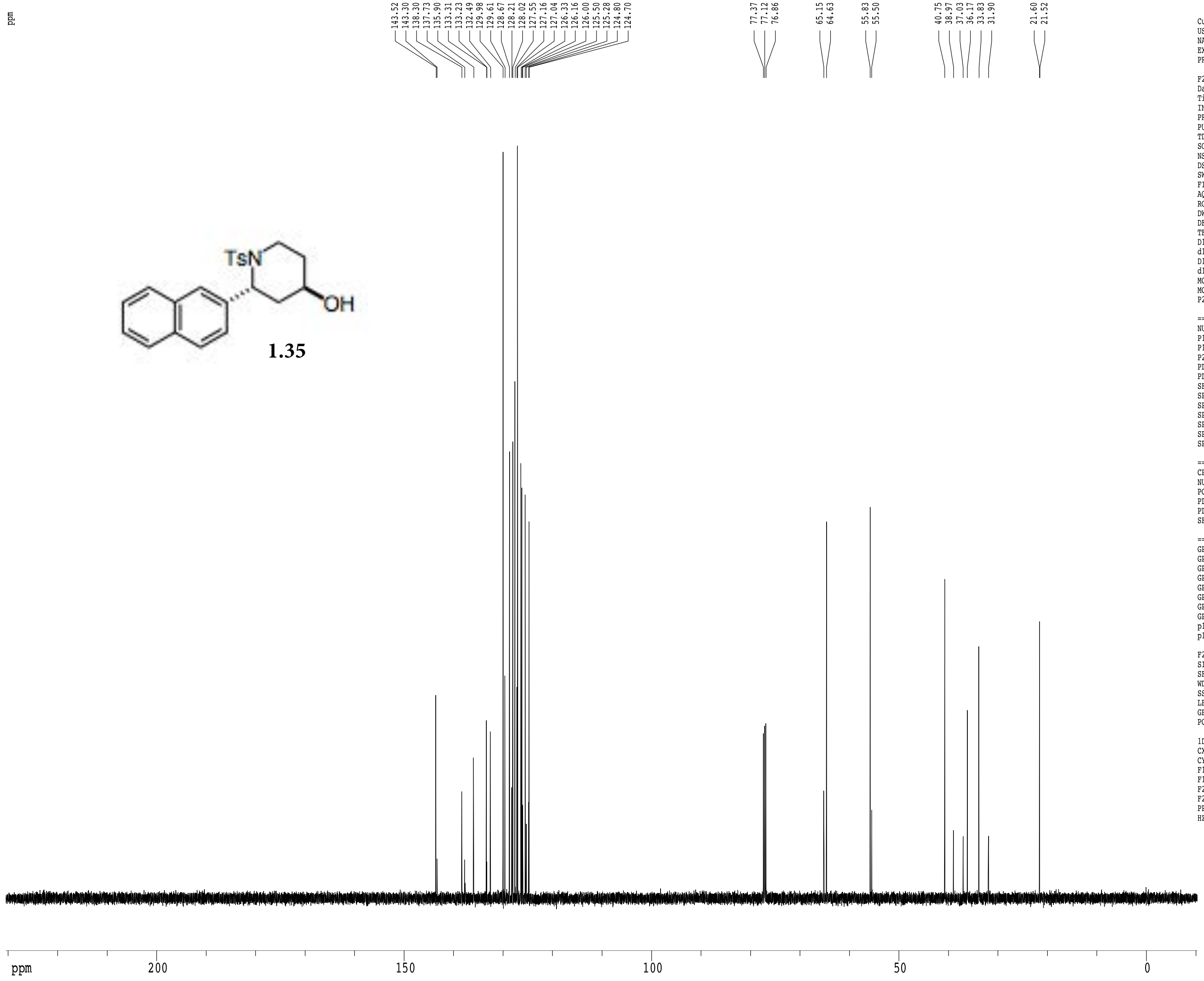
```
Current Data Parameters
USER            khewitt1
NAME          KAH-I-102Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180922
Time               12.03
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    32
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300086 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```



1,35

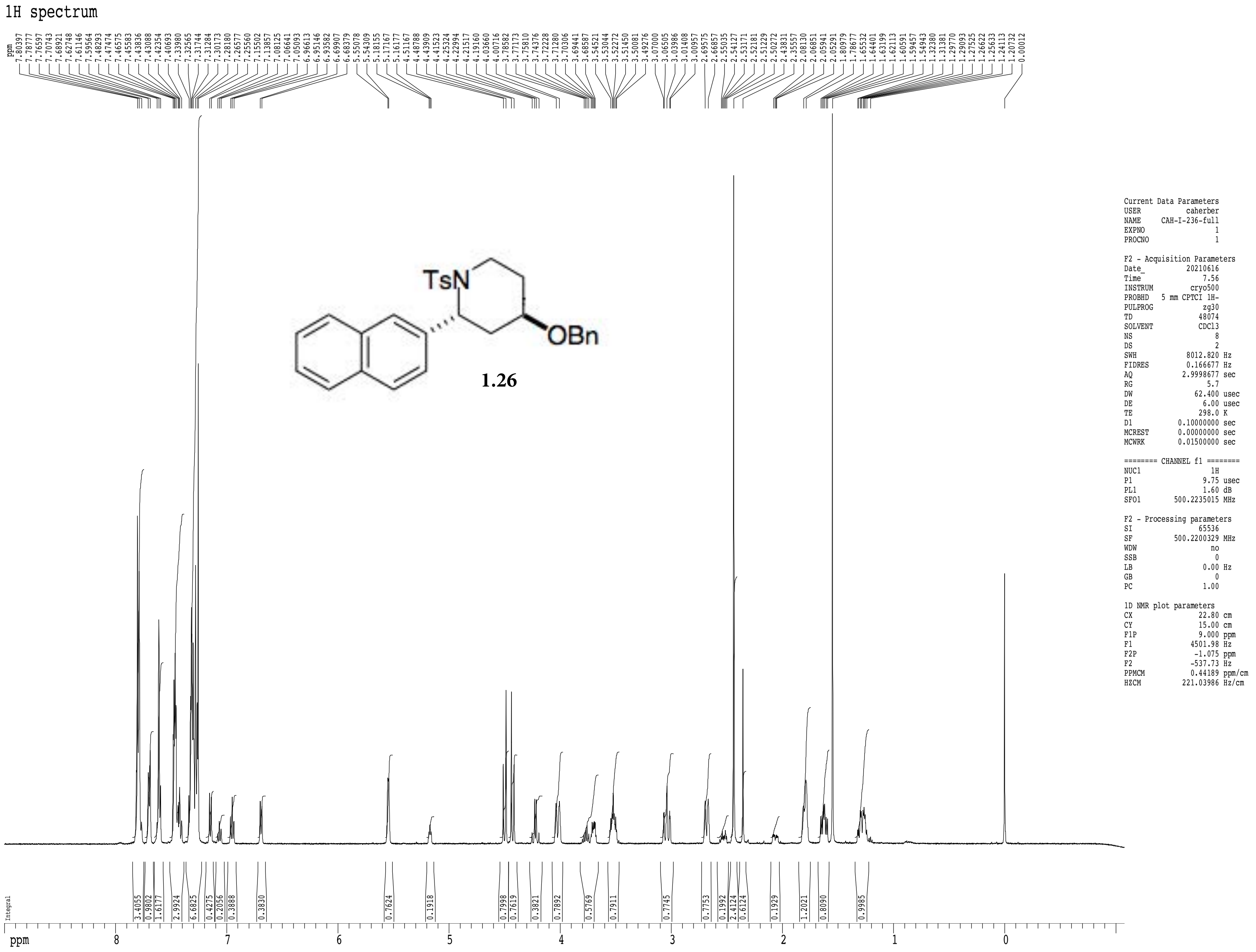
```
Current Data Parameters
USER          caherber
NAME          CAH-I-201
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20210330
Time              18.04
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                  128
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300245 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.071 ppm
F2              -428.71 Hz
PPMCM           0.44173 ppm/cm
HZCM          176.74925 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



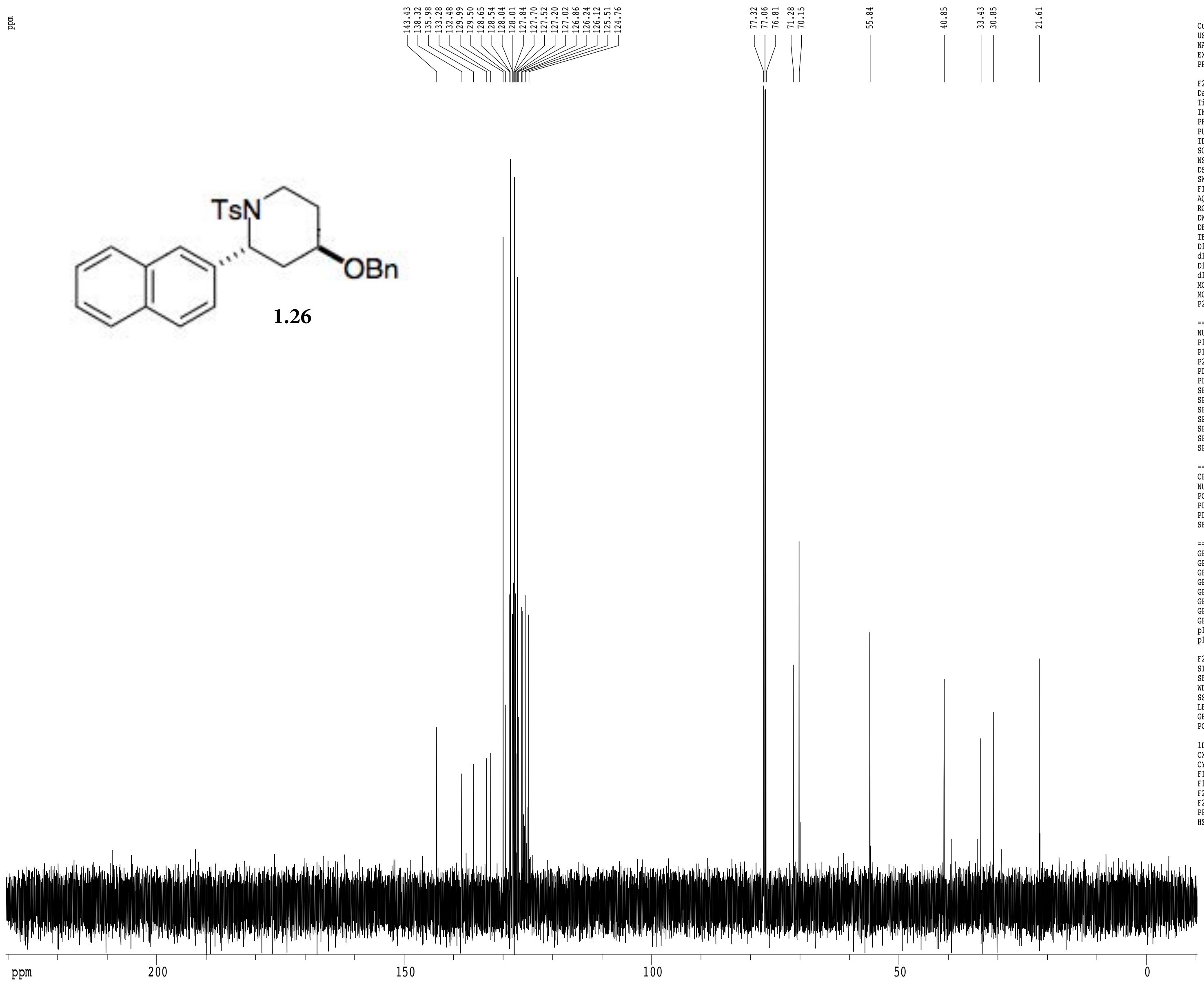
1.35

```
Current Data Parameters
USER            caherber
NAME        CAH-I-202-13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210828
Time               14.09
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                 13004
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804190 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10706 Hz/cm
```

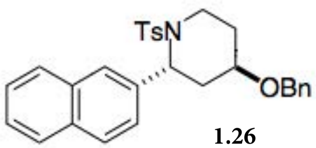

1H spectrum
ppm
7.80397
7.78777
7.76597
7.70743
7.68921
7.62748
7.61146
7.59564
7.48293
7.47474
7.46575
7.45583
7.43836
7.43088
7.42354
7.40693
7.33980
7.32565
7.31744
7.31284
7.30173
7.28180
7.26577
7.25560
7.15502
7.13857
7.08125
7.06641
7.05093
6.96613
6.95146
6.93582
6.69907
6.68379
5.55078
5.54309
5.18155
5.17167
5.16177
4.51167
4.48788
4.43909
4.41523
4.25324
4.22994
4.21517
4.19160
4.03660
4.00716
3.78582
3.77173
3.75810
3.74376
3.72228
3.71280
3.70306
3.69441
3.68587
3.54521
3.53044
3.52272
3.51450
3.50081
3.49276
3.07000
3.06505
3.03986
3.01408
3.00957
2.69575
2.66857
2.55035
2.54127
2.53171
2.52181
2.51229
2.50272
2.43831
2.35557
2.08130
2.06851
2.05941
2.05291
1.80979
1.78677
1.65532
1.64401
1.63199
1.62113
1.60591
1.59457
1.54943
1.32380
1.31381
1.29770
1.29093
1.27525
1.26622
1.25633
1.24113
1.20732
0.00012
TsN
OBn
Current Data Parameters
USER caherber
NAME CAH-I-236-full
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210616
Time 7.56
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 48074
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.9998677 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200329 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -1.075 ppm
F2 -537.73 Hz
PPMCM 0.44189 ppm/cm
HZCM 221.03986 Hz/cm
Integral
3.4055
0.9802
1.6177
2.9924
6.6825
0.4275
0.2056
0.3888
0.3830
0.7624
0.1918
0.7998
0.7619
0.3821
0.7892
0.5769
0.7911
0.7745
0.7753
0.1992
2.4124
0.6124
0.1929
1.2021
0.8090
0.9985
ppm
8
7
6
5
4
3
2
1
0

1.26

Z-restored spin-echo 13C spectrum with 1H decoupling

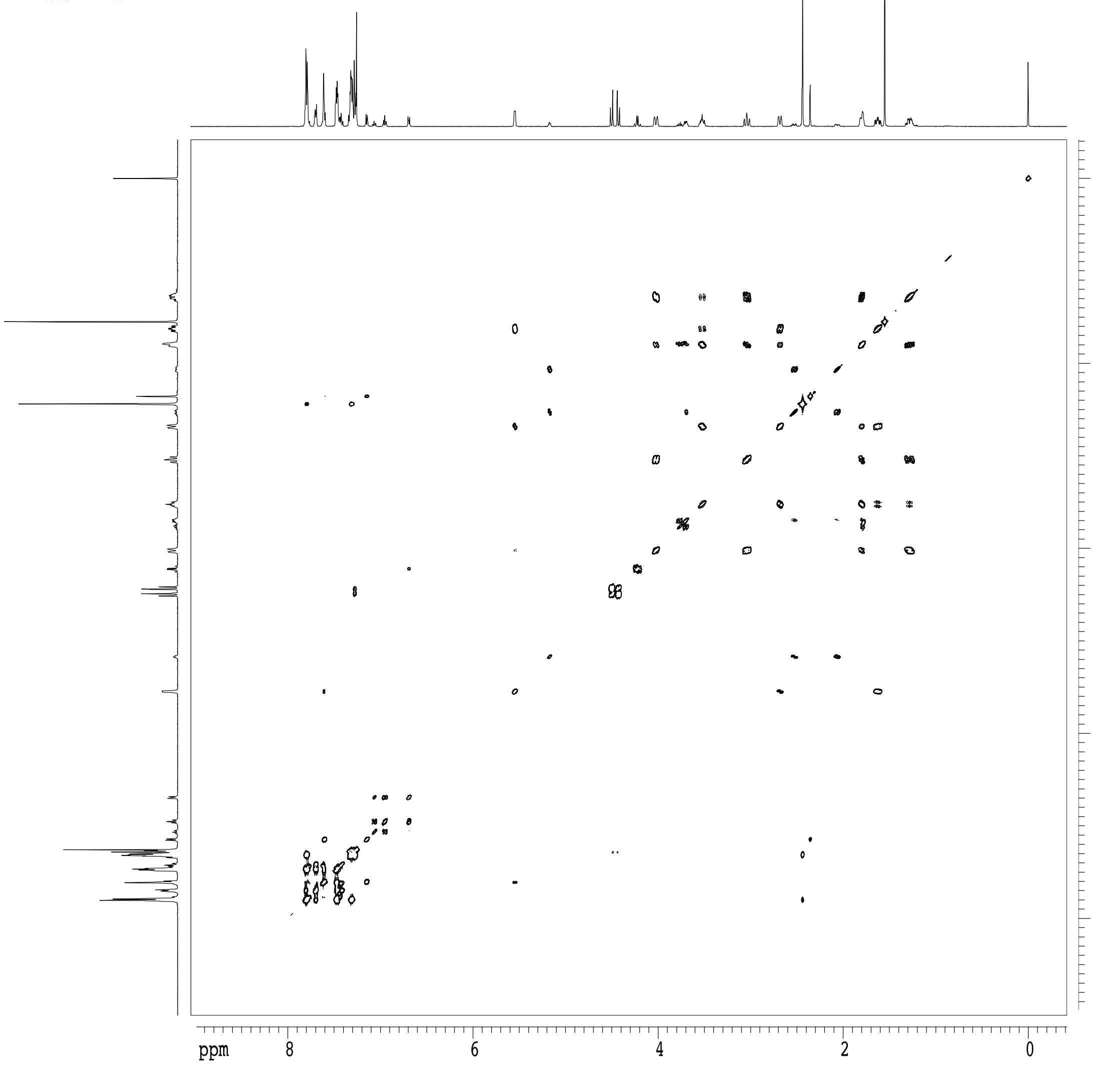

1.26

```
Current Data Parameters
USER           caherber
NAME     CAH-I-236-full
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20210616
Time               8.47
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```



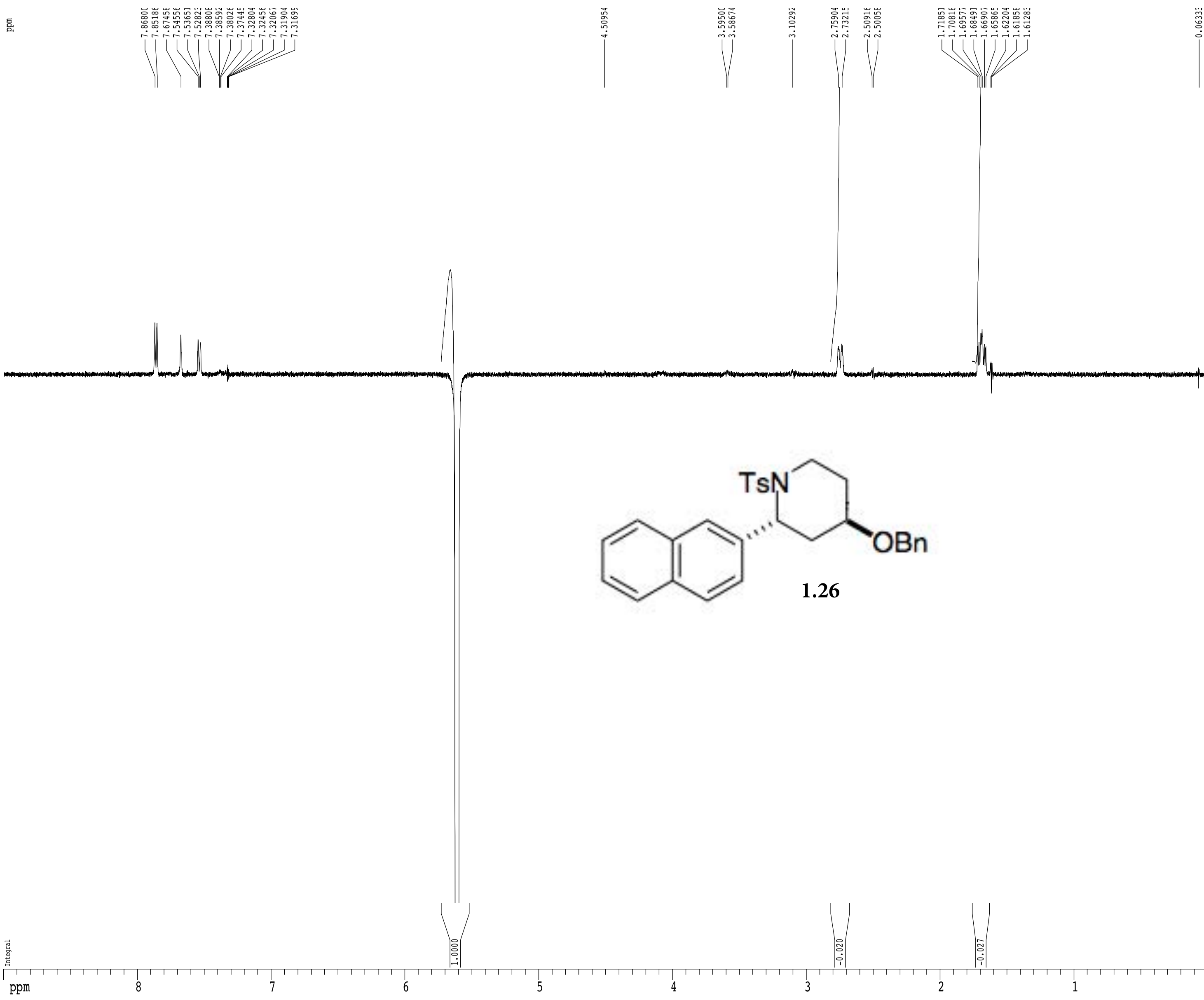
1.26

gcosy60



```
        Current Data Parameters
USER            caherber
NAME      CAH-I-236-full
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20210616
Time                8.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG     cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             4734.849 Hz
FIDRES          2.311938 Hz
AQ             0.2163188 sec
RG                 322.5
DW               105.600 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00021120 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2221588 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2222 MHz
FIDRES          9.247751 Hz
SW                 9.465 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200329 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200329 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

         2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.048 ppm
F2LO             4526.21 Hz
F2PHI             -0.417 ppm
F2HI             -208.63 Hz
F1PLO              9.048 ppm
F1LO             4526.21 Hz
F1PHI             -0.417 ppm
F1HI             -208.63 Hz
F2PPMCM          0.63104 ppm/cm
F2HZCM         315.65659 Hz/cm
F1PPMCM          0.63104 ppm/cm
F1HZCM         315.65659 Hz/cm
```

gnoe



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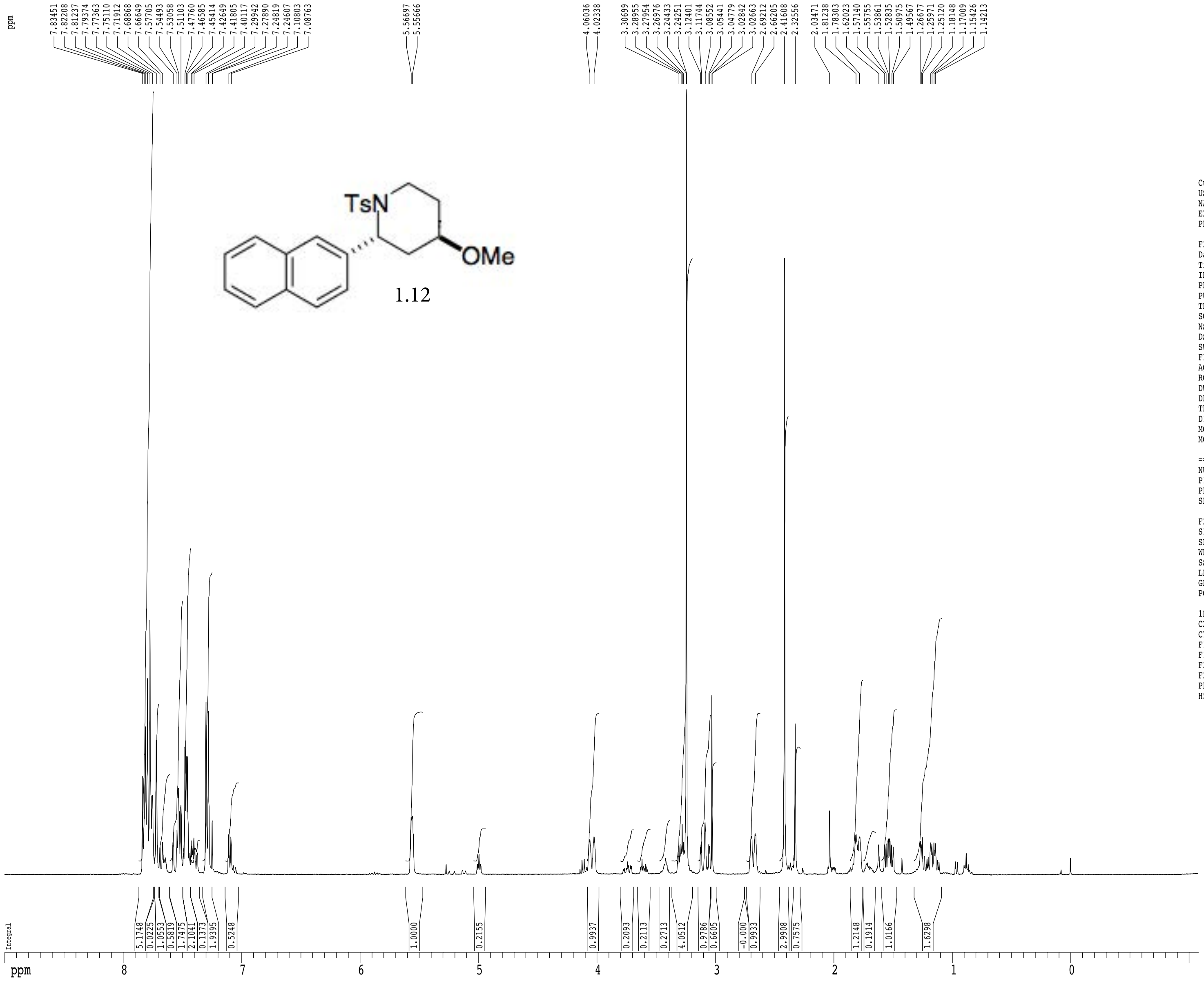
```
Current Data Parameters
USER             caherber
NAME        CAH-I-236-full
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210616
Time                  8.29
INSTRUM            cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                   161.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33375451 sec
d22             0.16399699 sec
p2                   19.50 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
p3                   29.25 usec
p4                   39.00 usec
p5                   26.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2228073 MHz
SP9                  60.00 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         SMSQ10.100
GPNAM2         SMSQ10.100
GPNAM3         SMSQ10.100
GPNAM4         SMSQ10.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                  0.000 ppm
F2                    0.00 Hz
PPMCM              0.39474 ppm/cm
HZCM             197.45528 Hz/cm
```

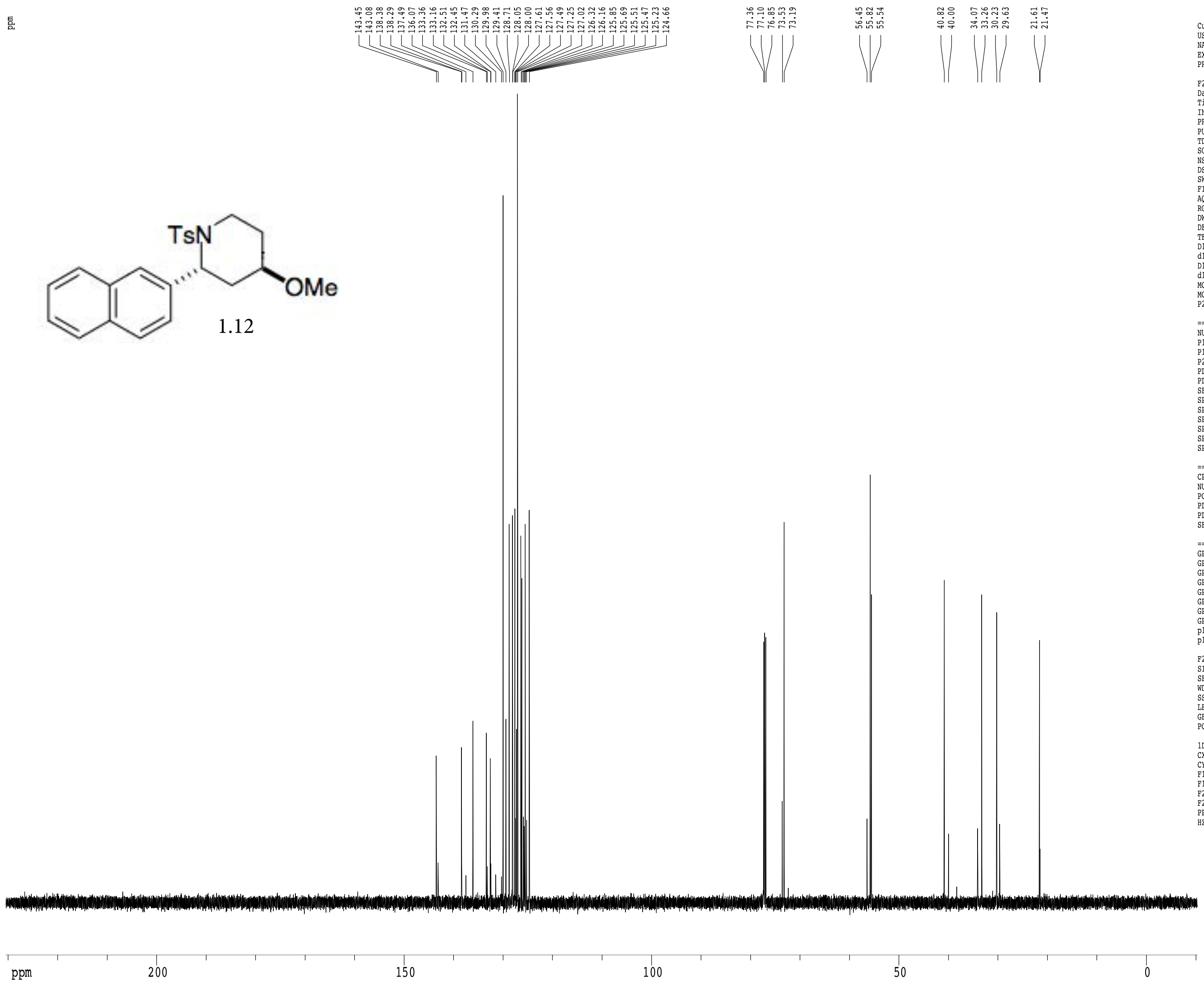
1H spectrum



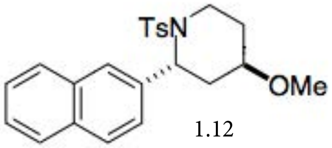
1.12

```
Current Data Parameters
USER           caherber
NAME          CAH-I-209
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210415
Time              17.05
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                  114
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300267 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -1.077 ppm
F2              -430.96 Hz
PPMCM           0.44198 ppm/cm
HZCM          176.84787 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

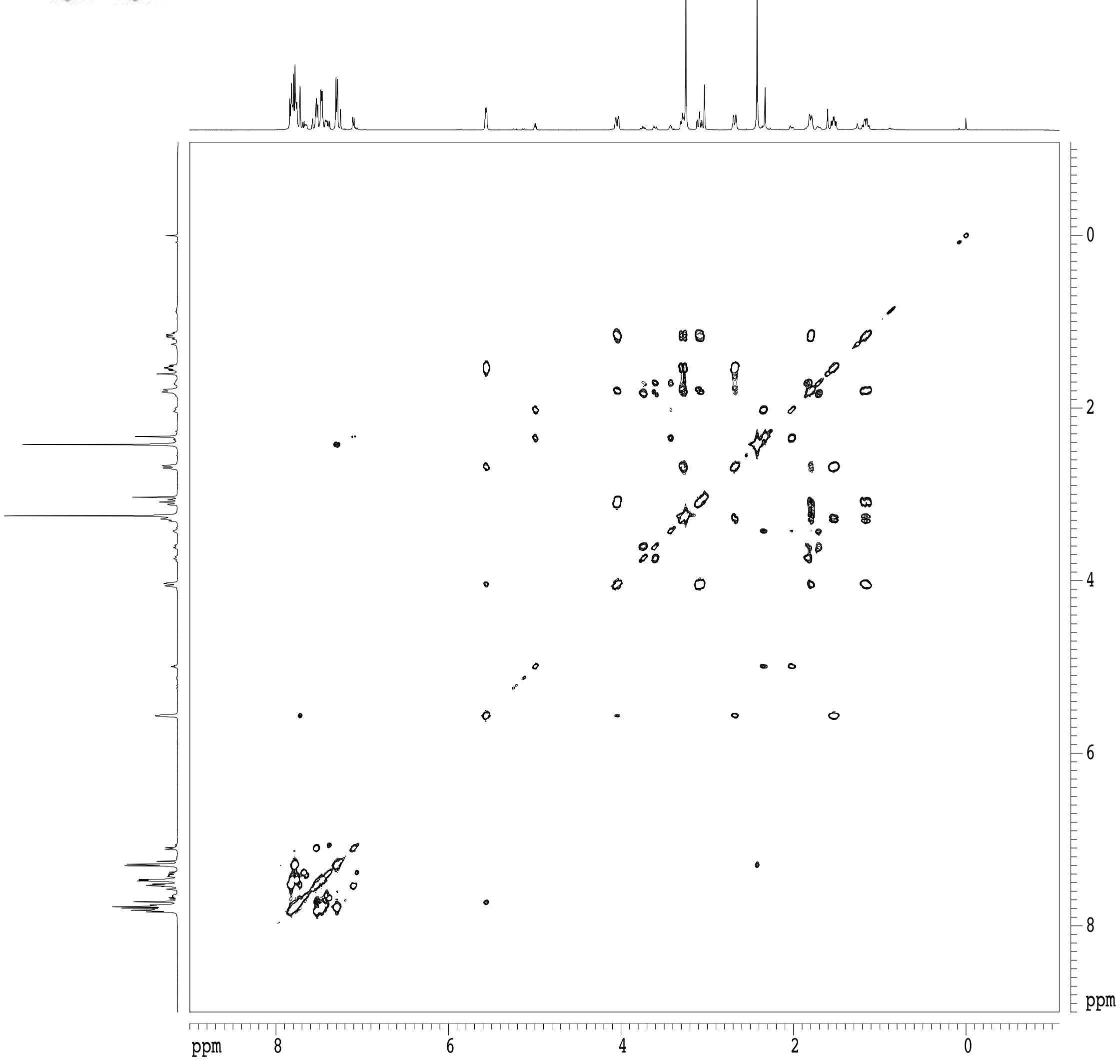


```
Current Data Parameters
USER           caherber
NAME     CAH-I-209-COSY
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20210417
Time              11.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  296
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               2580.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

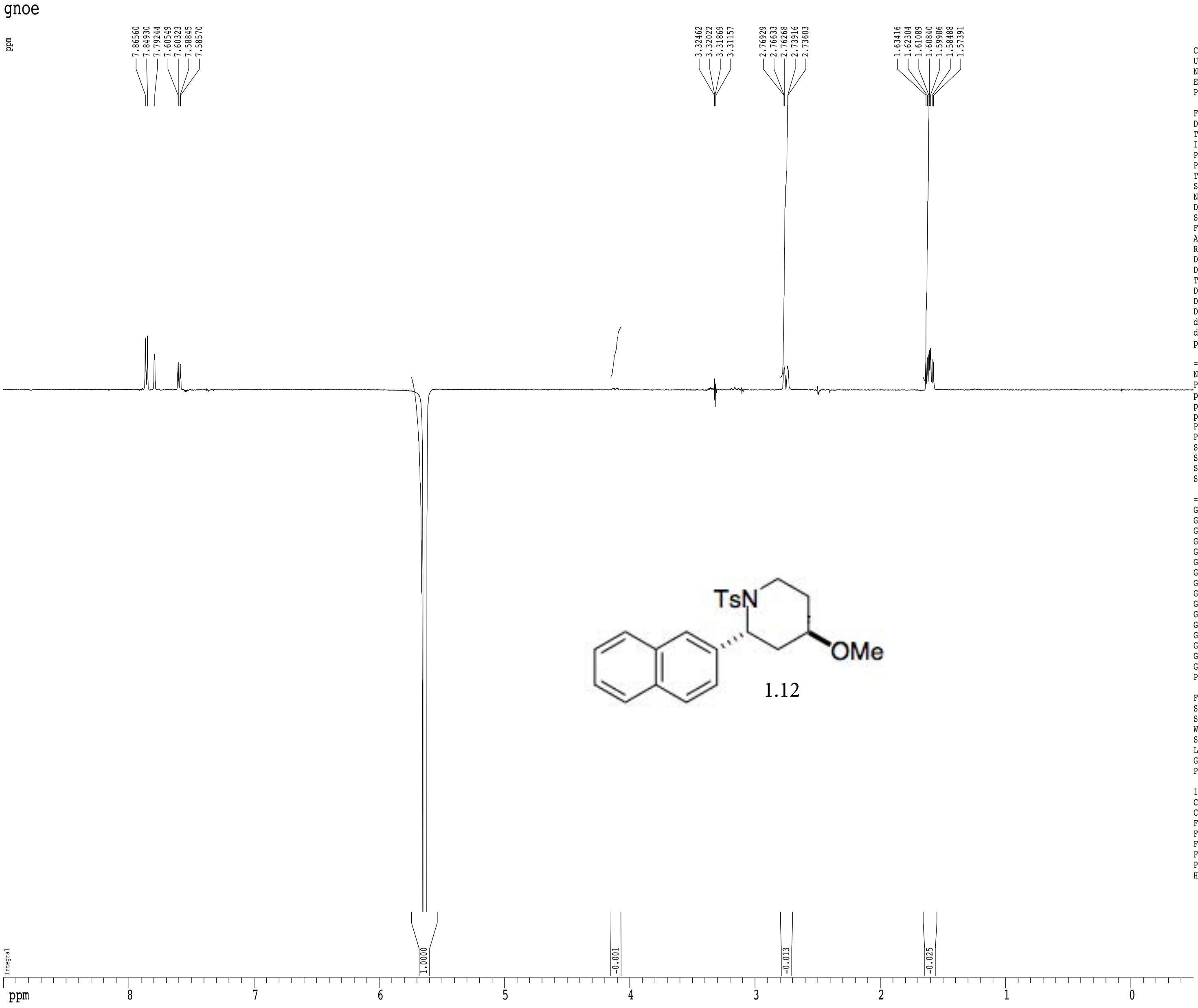


1.12

gcosy60



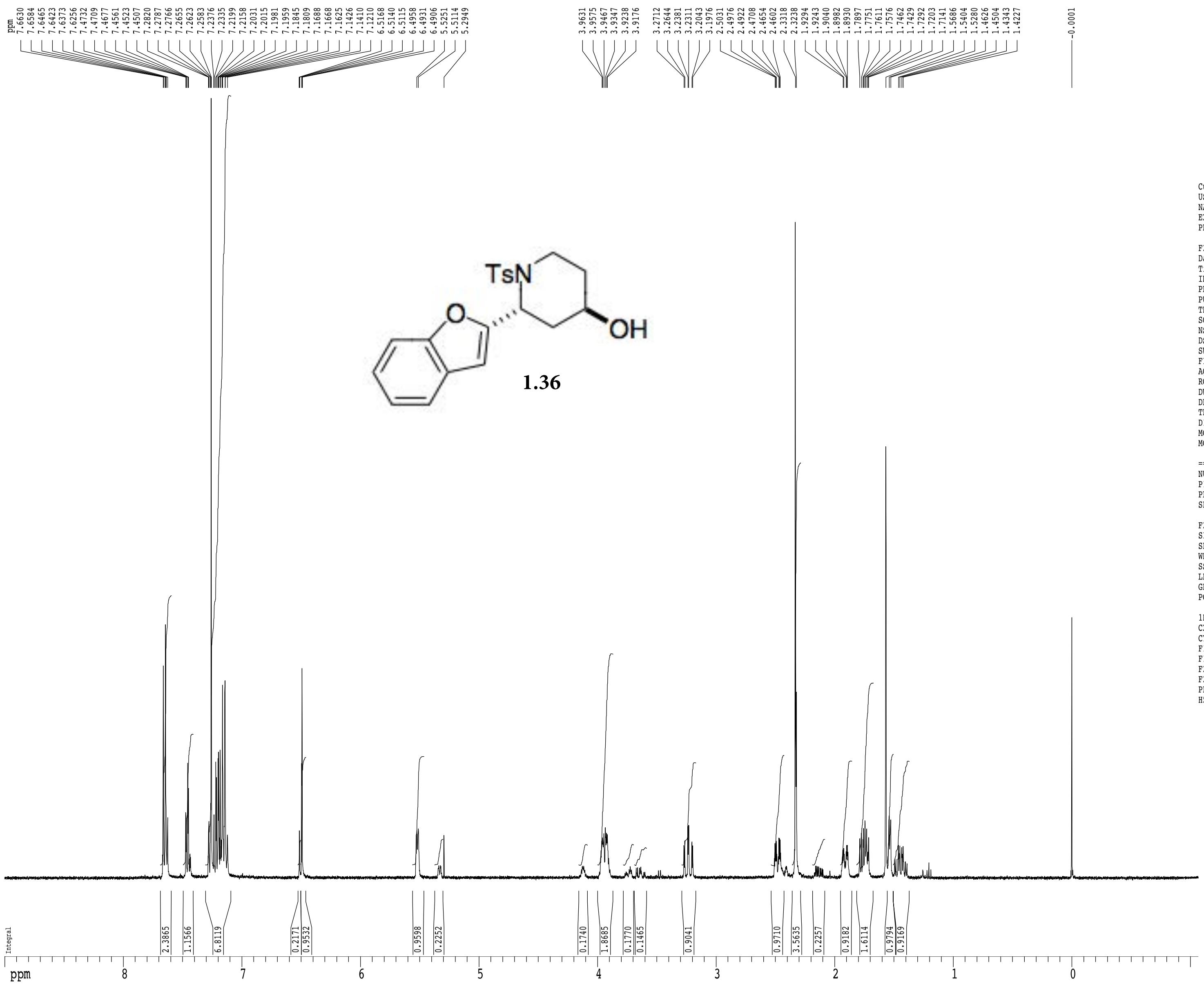
```
        Current Data Parameters
USER            caherber
NAME       CAH-I-209-COSY
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20210417
Time               10.51
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG     cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                  35.9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200362 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200362 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

         2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.000 ppm
F2LO             4501.98 Hz
F2PHI             -1.082 ppm
F2HI             -541.03 Hz
F1PLO              9.000 ppm
F1LO             4501.98 Hz
F1PHI             -1.082 ppm
F1HI             -541.03 Hz
F2PPMCM          0.67211 ppm/cm
F2HZCM         336.20062 Hz/cm
F1PPMCM          0.67211 ppm/cm
F1HZCM         336.20062 Hz/cm
```



1.12

```
Current Data Parameters
USER          caherber
NAME      CAH-I-209-noe
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210417
Time              14.16
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 80.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33375451 sec
d22          0.16399699 sec
p2                19.50 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
p3                29.25 usec
p4                39.00 usec
p5                26.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2228198 MHz
SP9               60.00 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPNAM3       SMSQ10.100
GPNAM4       SMSQ10.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

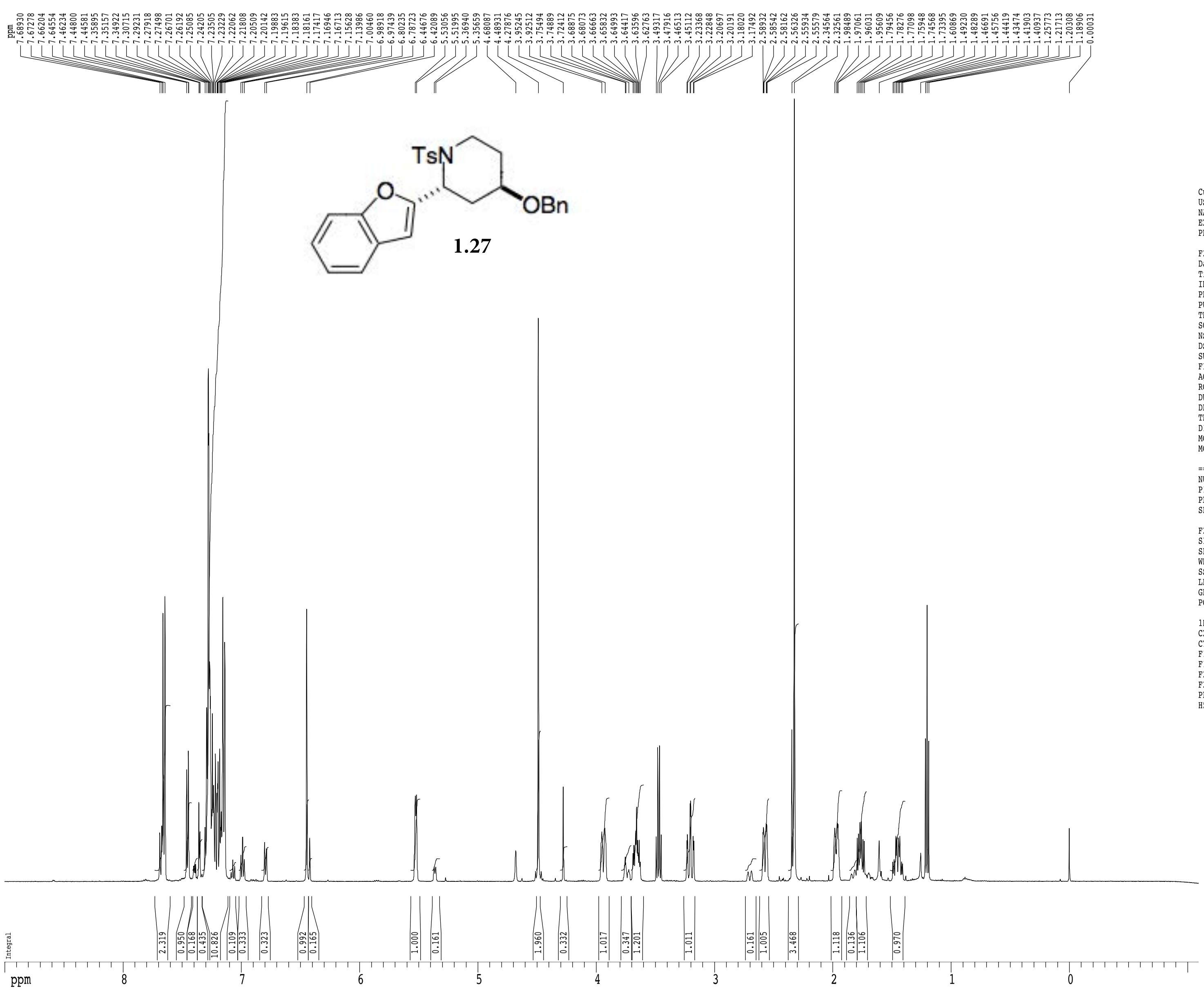
1H spectrum



1.36

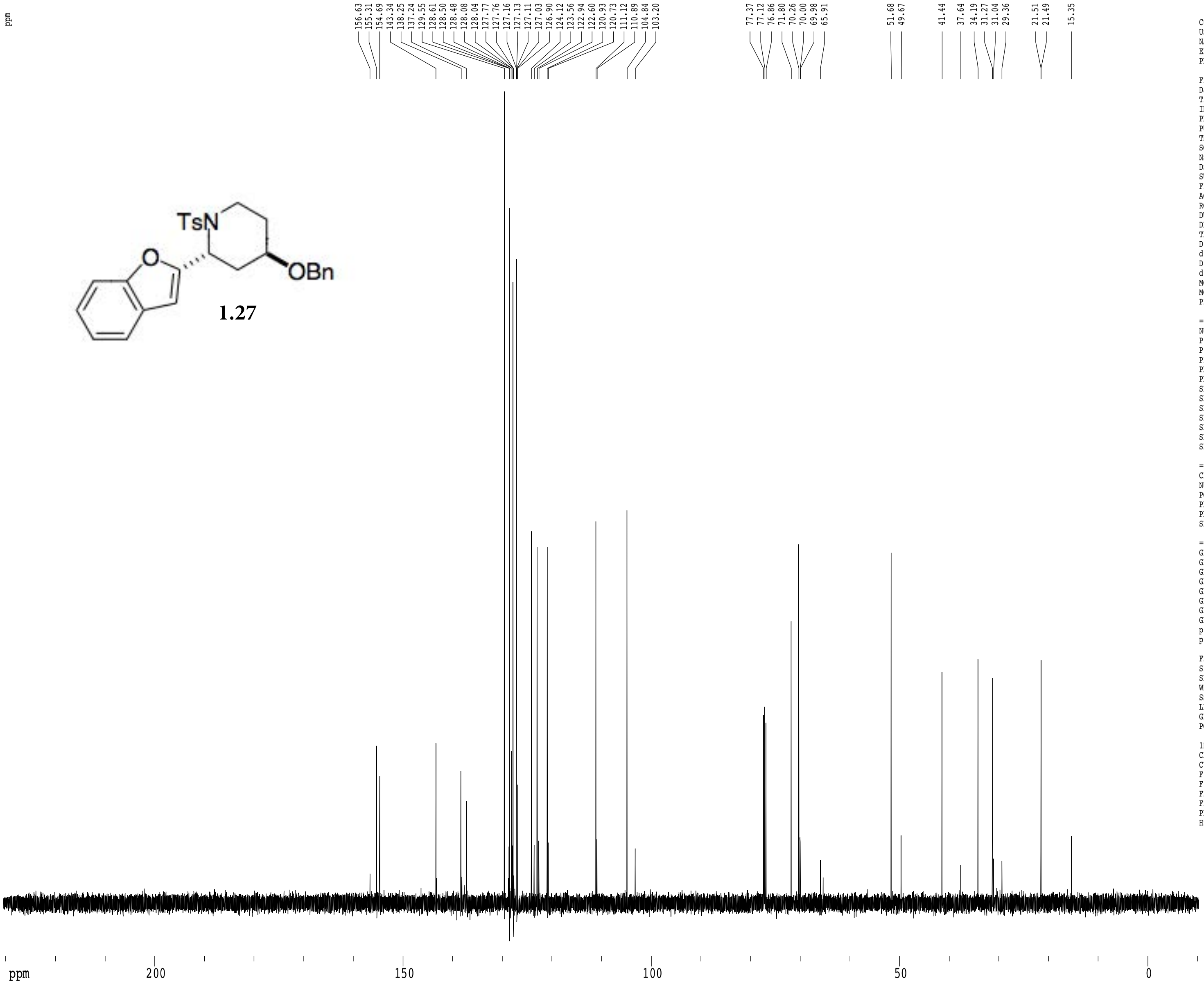
```
Current Data Parameters
USER            caherber
NAME           CAH-I-215
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210503
Time               13.54
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                   512
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300223 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -1.066 ppm
F2               -426.56 Hz
PPMCM            0.44149 ppm/cm
HZCM           176.65485 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER          caherber
NAME     CAH-I-220-full
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210506
Time              17.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    4
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1     500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200401 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -1.089 ppm
F2              -544.94 Hz
PPMCM           0.44252 ppm/cm
HZCM          221.35622 Hz/cm
```

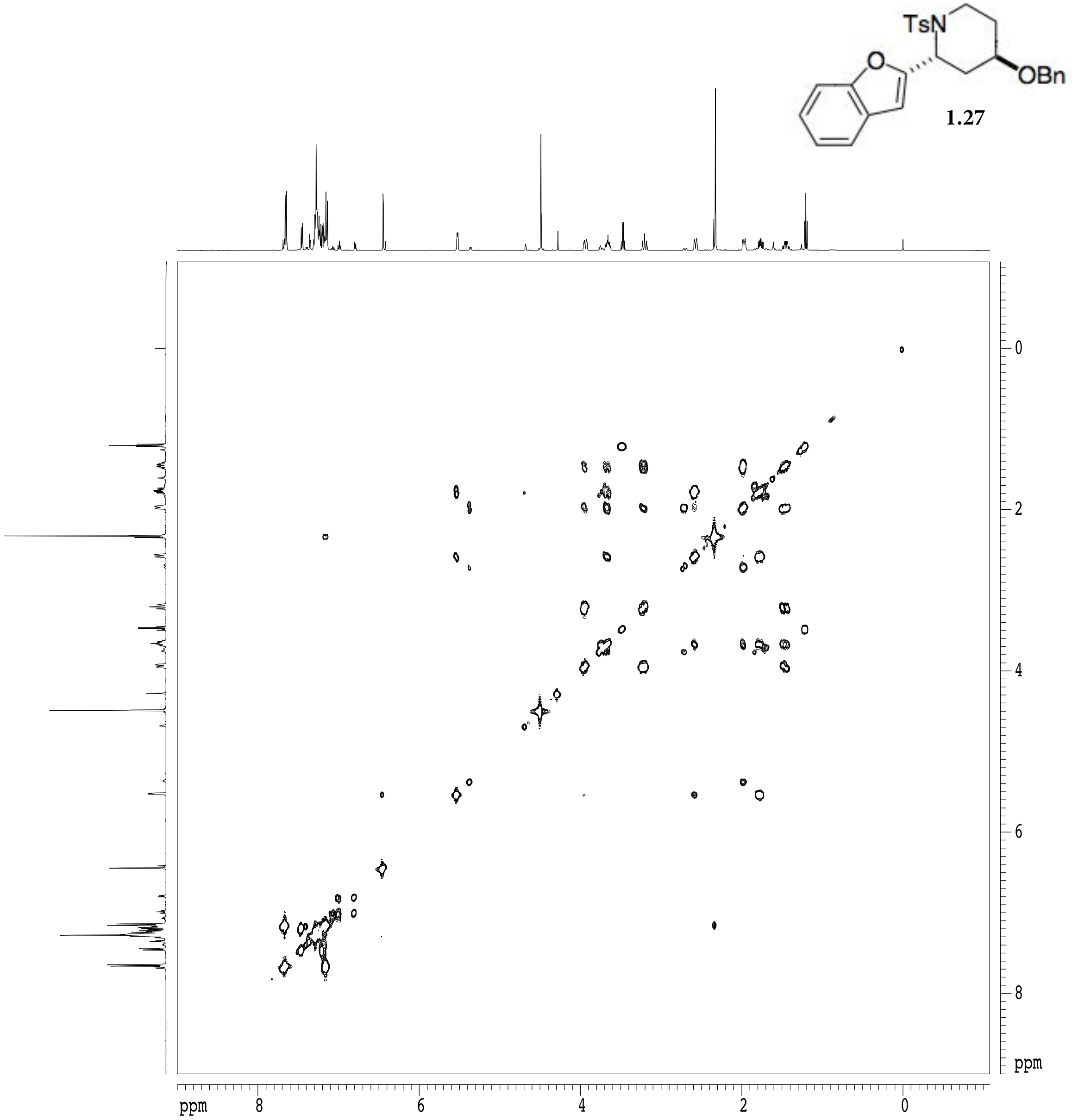
Z-restored spin-echo 13C spectrum with 1H decoupling



1.27

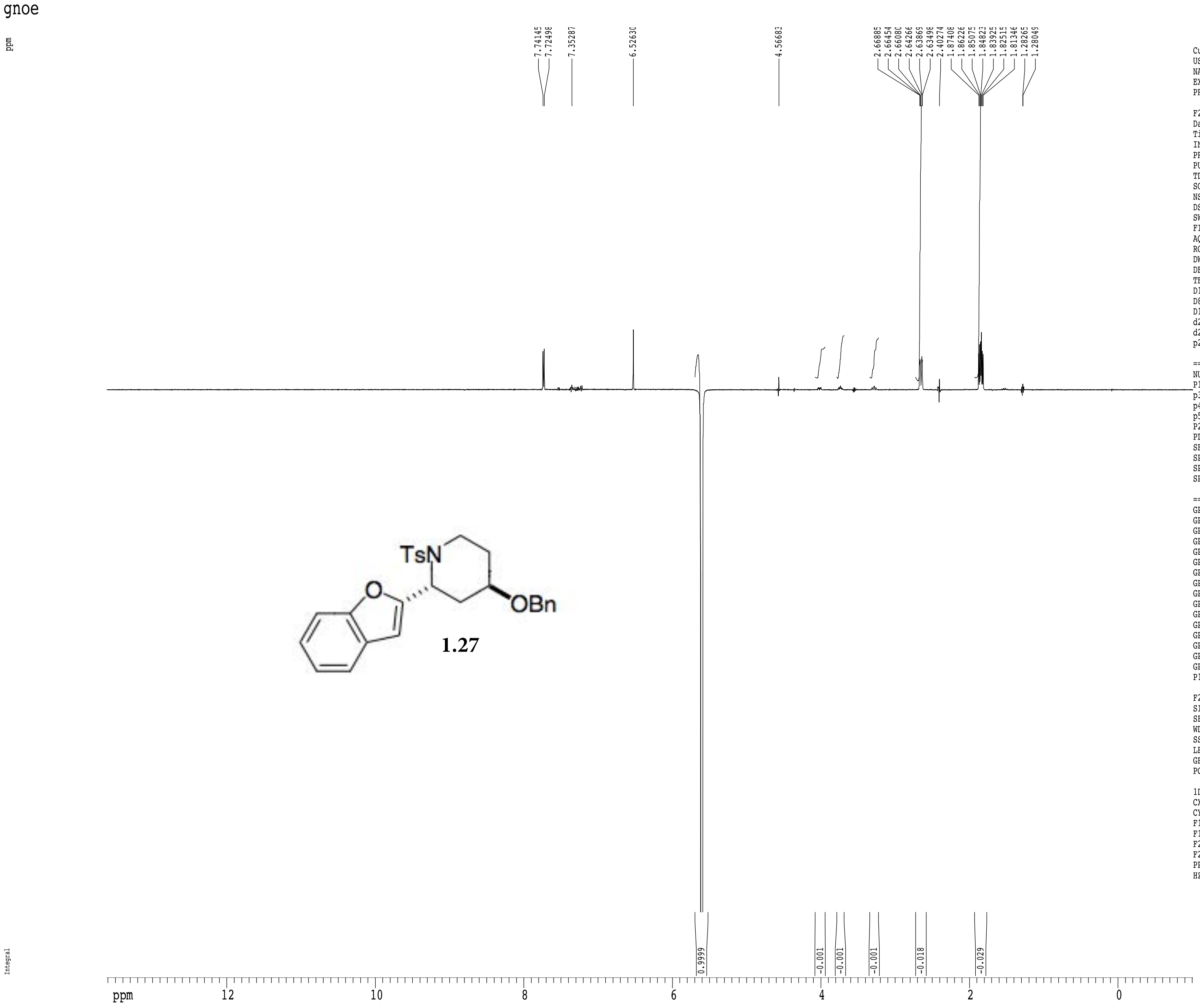
```
Current Data Parameters
USER            caherber
NAME      CAH-I-220-full
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210506
Time               18.09
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                    96
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  4096
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804190 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10706 Hz/cm
```

gcosy60



1.27

```
        Current Data Parameters
USER           caherber
NAME     CAH-I-220-full
EXPNO                 2
PROCNO                1

      F2 - Acquisition Parameters
Date_          20210506
Time              17.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    2
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                 35.9
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  269
SFO1           500.2235 MHz
FIDRES        29.787437 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200329 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200329 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

          2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.000 ppm
F2LO            4501.98 Hz
F2PHI            -1.075 ppm
F2HI            -537.73 Hz
F1PLO             9.000 ppm
F1LO            4501.98 Hz
F1PHI            -1.075 ppm
F1HI            -537.73 Hz
F2PPMCM         0.67167 ppm/cm
F2HZCM        335.98087 Hz/cm
F1PPMCM         0.67167 ppm/cm
F1HZCM        335.98087 Hz/cm
```



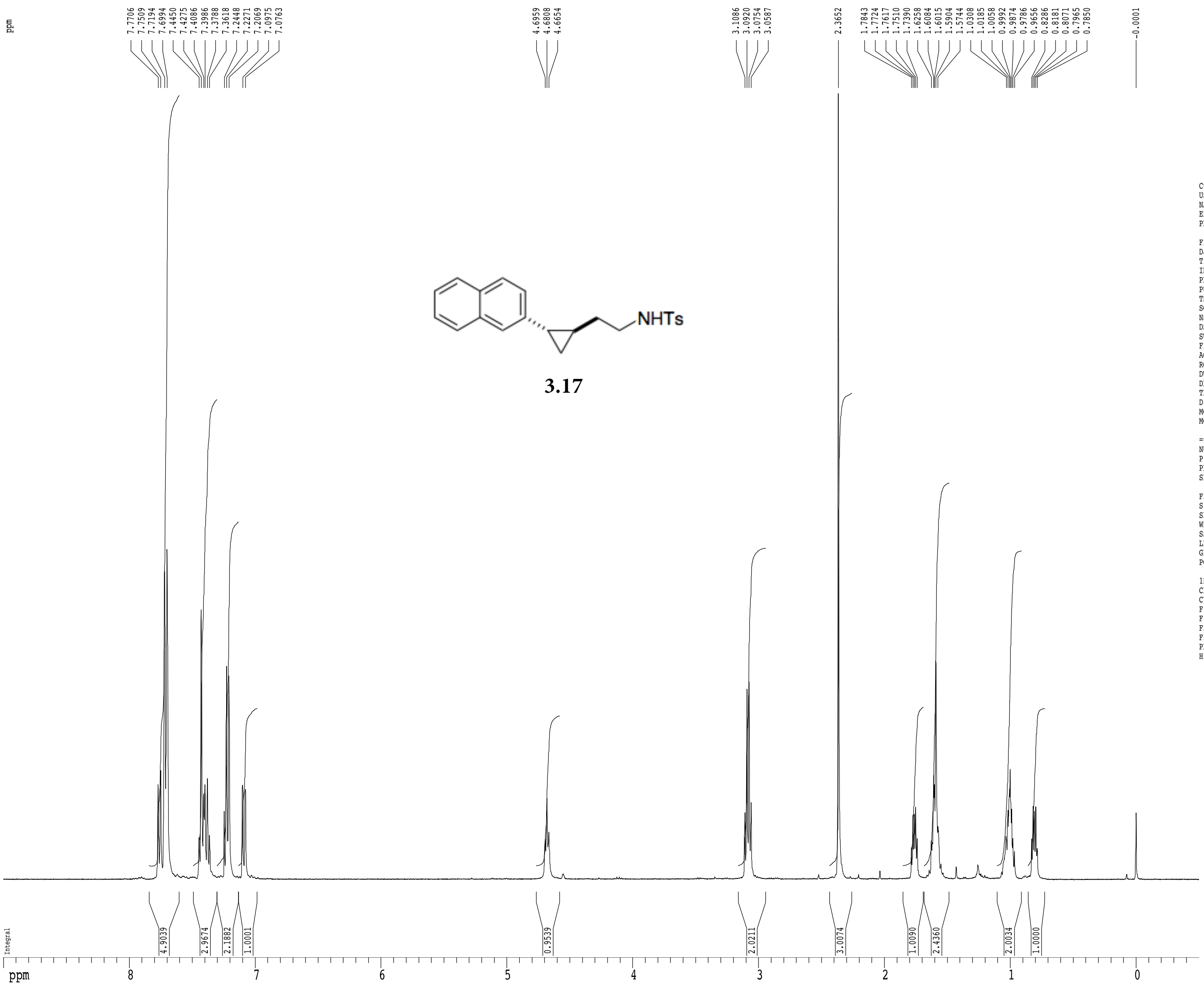
1.27

```
Current Data Parameters
USER              caherber
NAME          CAH-I-220-full
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_            20210506
Time                17.52
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   90.5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33375451 sec
d22            0.16399699 sec
p2                  19.50 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.75 usec
p3                  29.25 usec
p4                  39.00 usec
p5                  26.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2228033 MHz
SP9                 60.00 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         SMSQ10.100
GPNAM2         SMSQ10.100
GPNAM3         SMSQ10.100
GPNAM4         SMSQ10.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                15.009 ppm
F1                7507.95 Hz
F2P                -1.009 ppm
F2                -504.87 Hz
PPMCM             0.70257 ppm/cm
HZCM            351.43951 Hz/cm
```

APPENDIX A.2

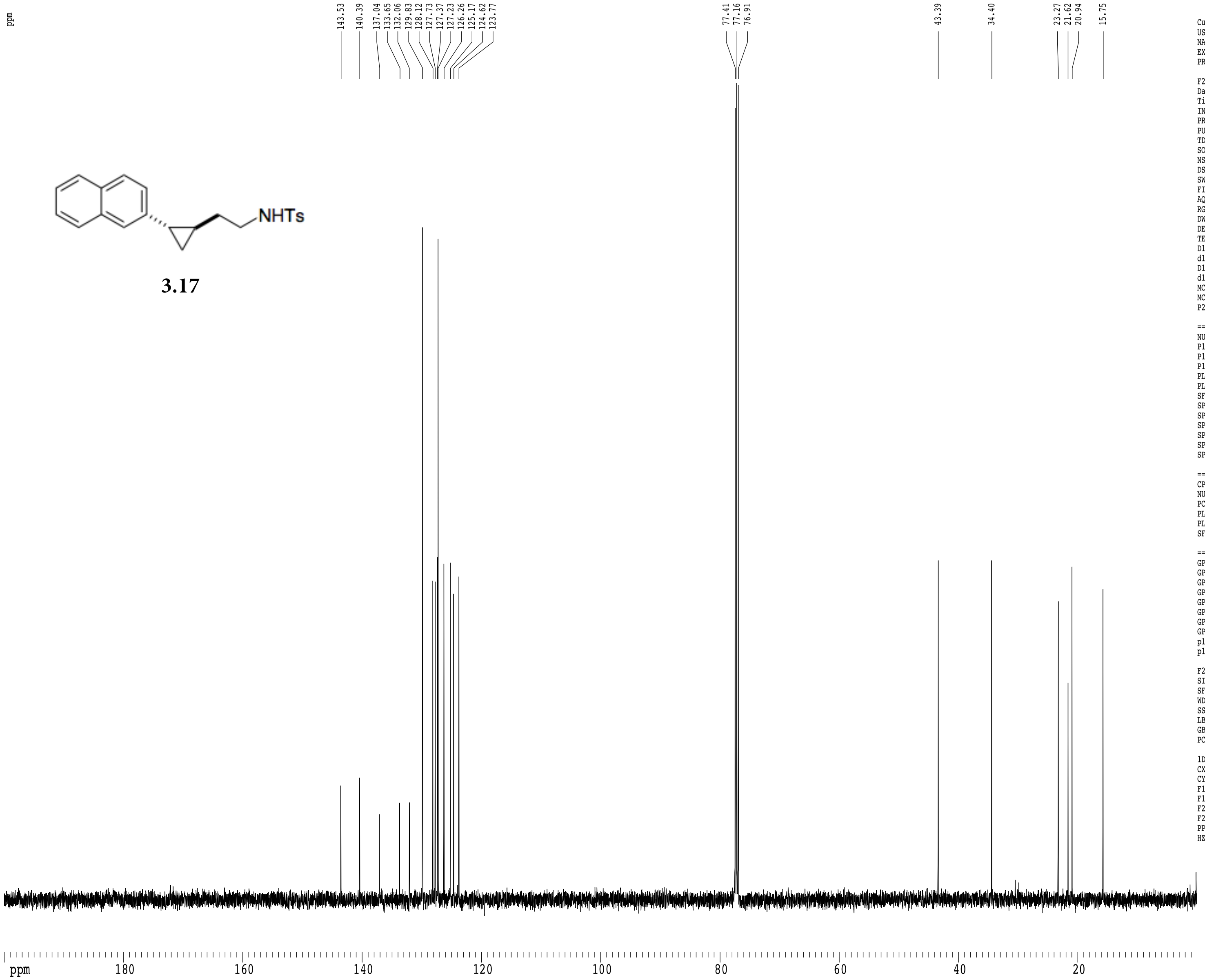
^{1}H, ^{13}C, COSY, NOE NMR SPECTRA, SFC TRACES FOR CHAPTER 3

1H spectrum



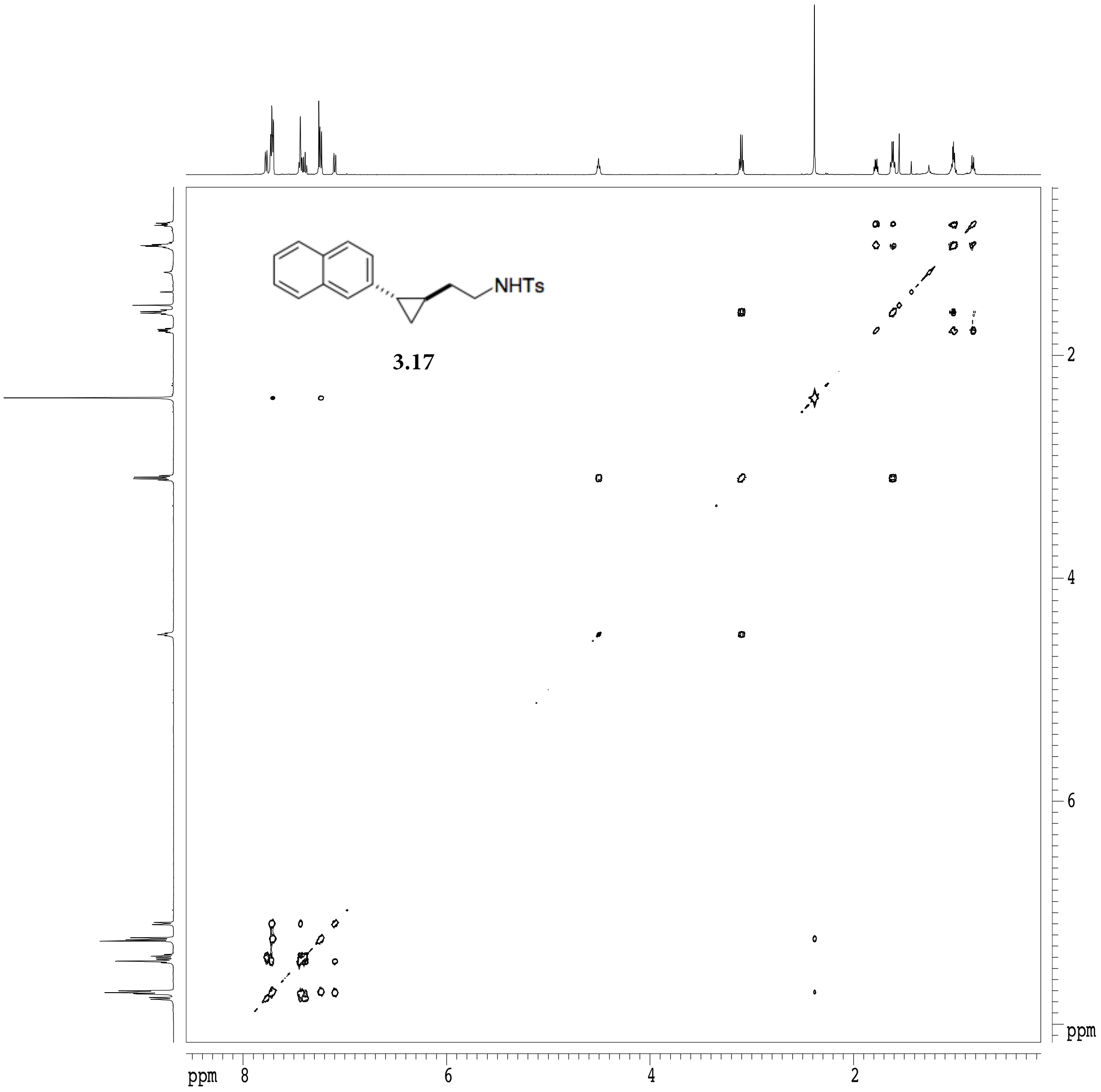
```
Current Data Parameters
USER              erikal
NAME     ELL-III-206-isolated
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180818
Time               19.42
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                 161.3
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300273 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



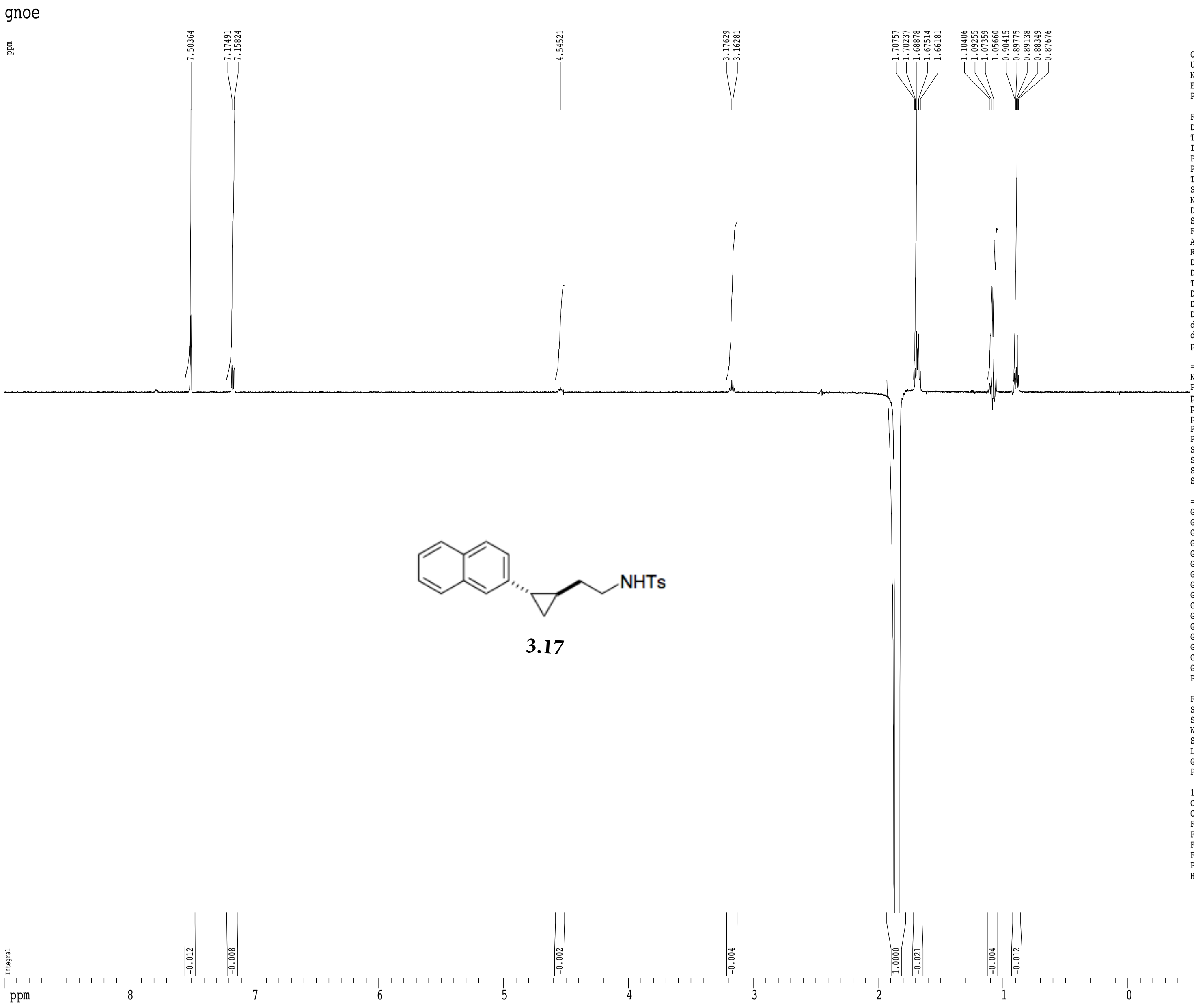
```
Current Data Parameters
USER              erikal
NAME      ELL-II-278-pdt
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171118
Time               14.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   410
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                5160.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804071 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33691 Hz/cm
```

gcosy60



3.17

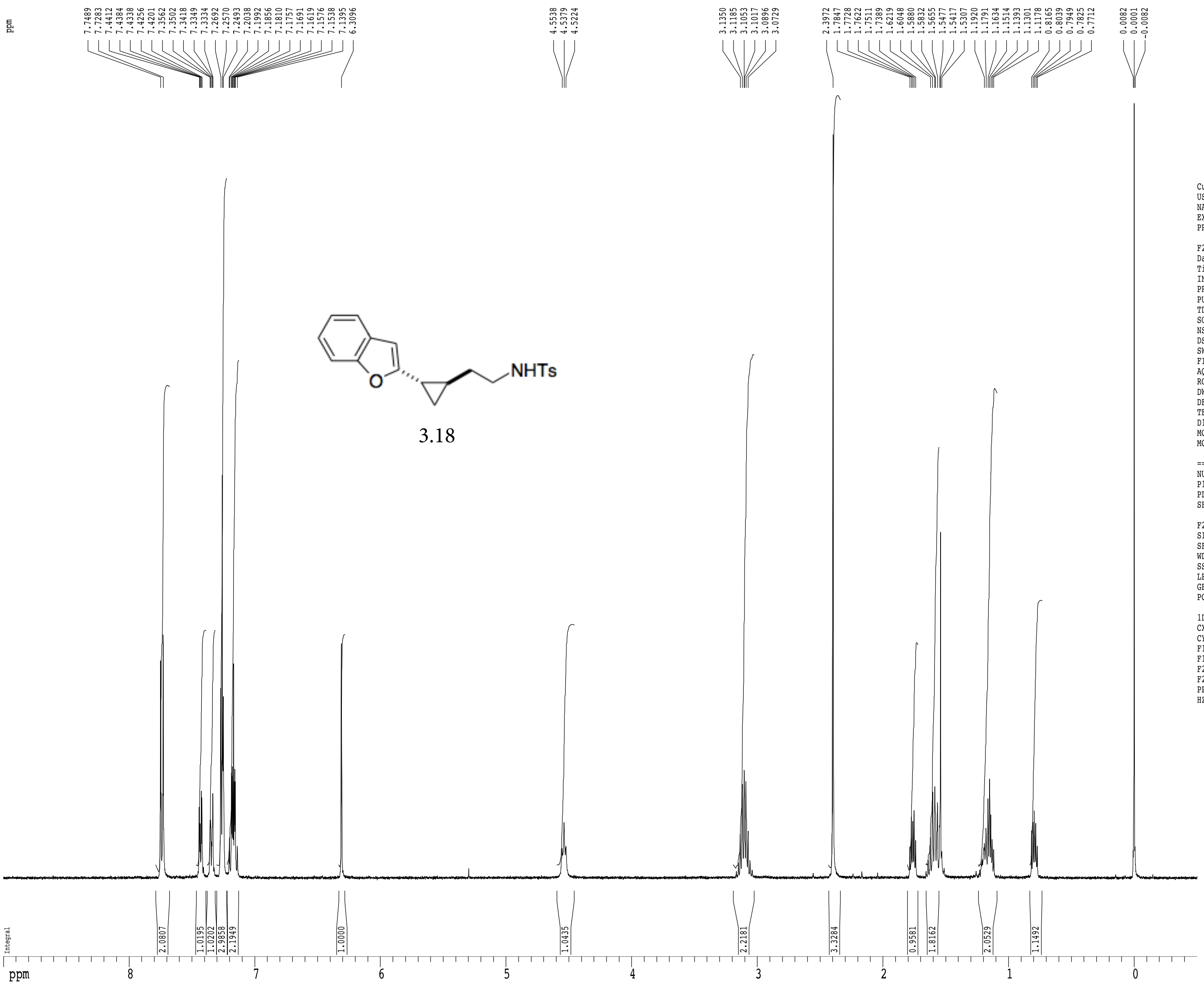
```
        Current Data Parameters
USER              erikal
NAME      ELL-II-278-pdt
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20171118
Time               13.36
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     2
DS                    16
SWH             4734.849 Hz
FIDRES          2.311938 Hz
AQ             0.2163188 sec
RG                 203.2
DW               105.600 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00021120 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2221599 MHz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2222 MHz
FIDRES          9.247751 Hz
SW                 9.465 ppm
FnMODE         undefined

      F2 - Processing parameters
SI                  1024
SF           500.2200340 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200340 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              8.561 ppm
F2LO             4282.25 Hz
F2PHI              0.158 ppm
F2HI               79.15 Hz
F1PLO              8.163 ppm
F1LO             4083.43 Hz
F1PHI              0.491 ppm
F1HI              245.61 Hz
F2PPMCM          0.56017 ppm/cm
F2HZCM         280.20688 Hz/cm
F1PPMCM          0.51148 ppm/cm
F1HZCM         255.85446 Hz/cm
```



3.17

```
Current Data Parameters
USER              erikal
NAME      ELL-II-278-pdt
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171120
Time               14.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG       gnoe1cc.wu
TD                 65536
SOLVENT           CDCl3T
NS                   256
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  40.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P12             40000.00 usec
PL1                 1.60 dB
SFO1         500.2209230 MHz
SP1                61.60 dB
SPNAM1        gauss1.512
SPOFF1              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

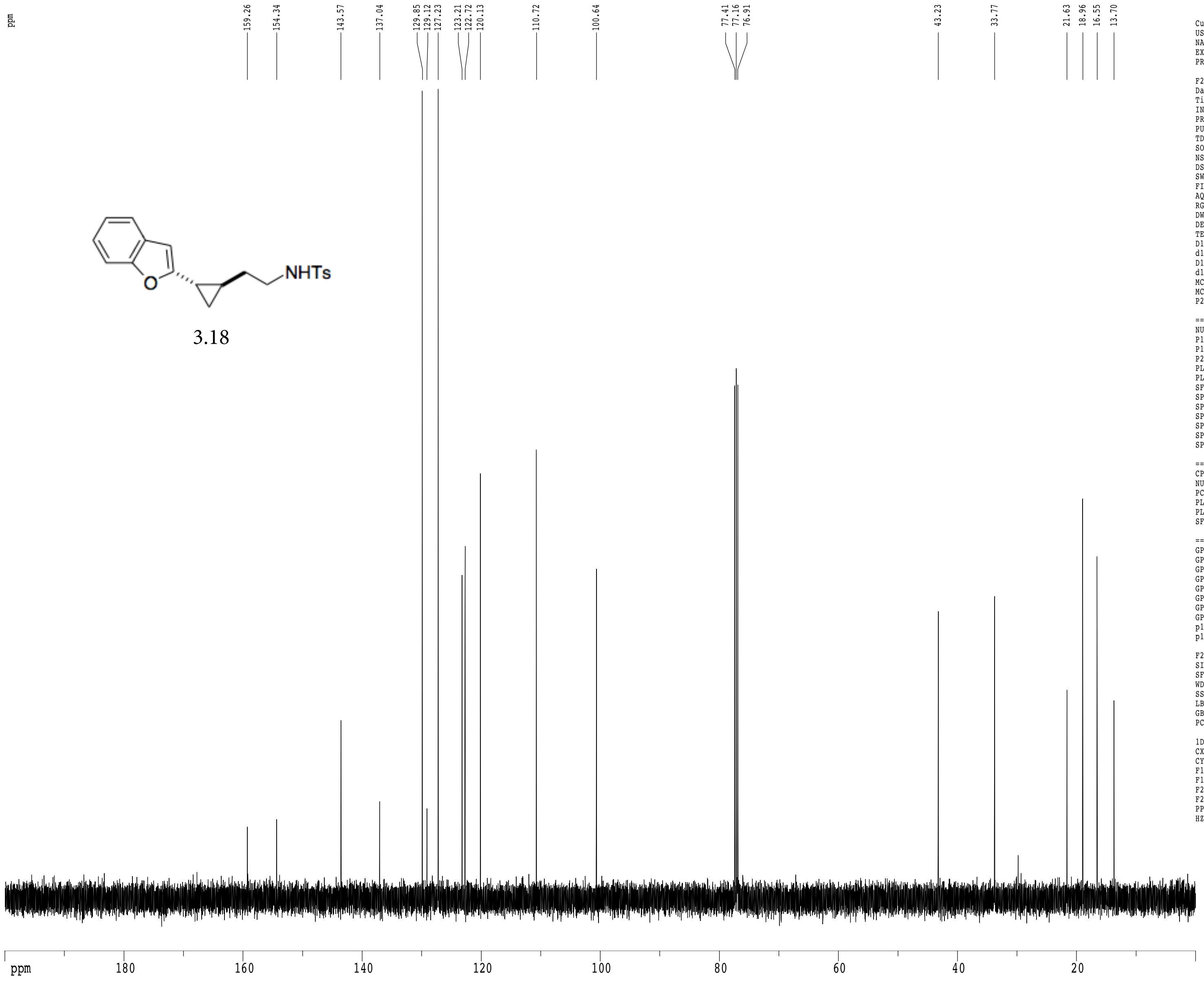
1H spectrum



3.18

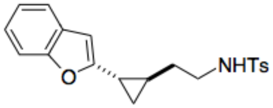
```
Current Data Parameters
USER           khewitt1
NAME     KAH-II-111 check
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20190725
Time              12.04
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                724.1
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300222 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

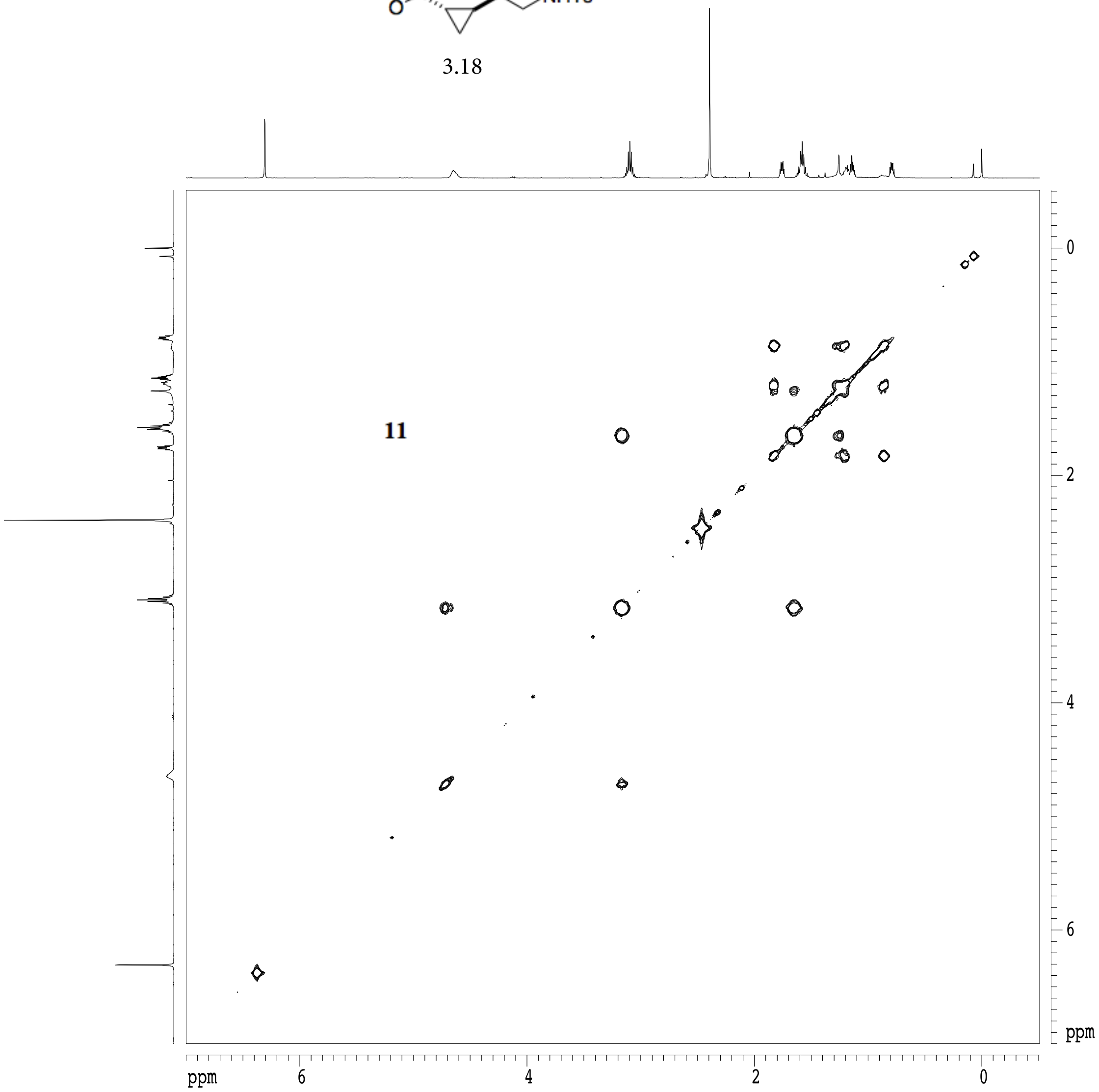

3.18

```
Current Data Parameters
USER              khewitt1
NAME            KAH-I-069-Z
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20180917
Time                  15.48
INSTRUM             cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                    65536
SOLVENT               CDCl3
NS                      105
DS                       16
SWH               30303.031 Hz
FIDRES             0.462388 Hz
AQ                1.0813940 sec
RG                   7298.2
DW                   16.500 usec
DE                     6.00 usec
TE                    298.0 K
D1               0.25000000 sec
d11              0.03000000 sec
D16              0.00020000 sec
d17              0.00019600 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec
P2                    33.10 usec

======== CHANNEL f1 ========
NUC1                    13C
P1                    16.55 usec
P12                 2000.00 usec
P20                  500.00 usec
PL0                  120.00 dB
PL1                   -1.00 dB
SFO1            125.7942548 MHz
SP2                    2.70 dB
SP4                    2.70 dB
SPNAM2          Crp60comp.4
SPNAM4       Crp60,0.5,20.1
SPOFF2                 0.00 Hz
SPOFF4                 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    1.60 dB
PL12                  23.54 dB
SFO2            500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1             SINE.100
GPNAM2             SINE.100
GPX1                   0.00 %
GPX2                   0.00 %
GPY1                   0.00 %
GPY2                   0.00 %
GPZ1                  30.00 %
GPZ2                  50.00 %
p15                  500.00 usec
p16                 1000.00 usec

F2 - Processing parameters
SI                    65536
SF              125.7804085 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.65 cm
F1P                 200.000 ppm
F1                 25156.08 Hz
F2P                   0.000 ppm
F2                     0.00 Hz
PPMCM               8.77193 ppm/cm
HZCM             1103.33691 Hz/cm
```

gcosy60

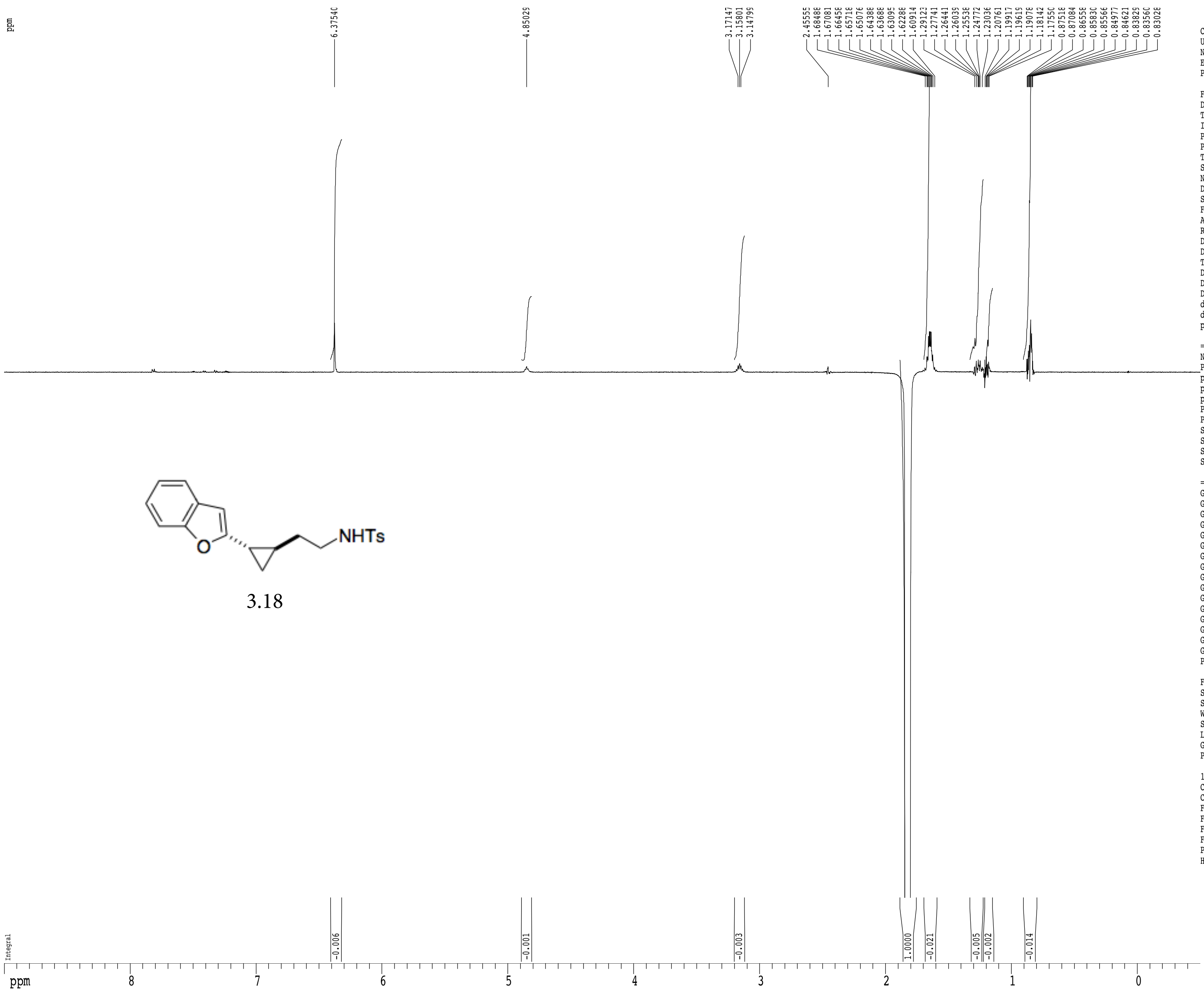


3.18



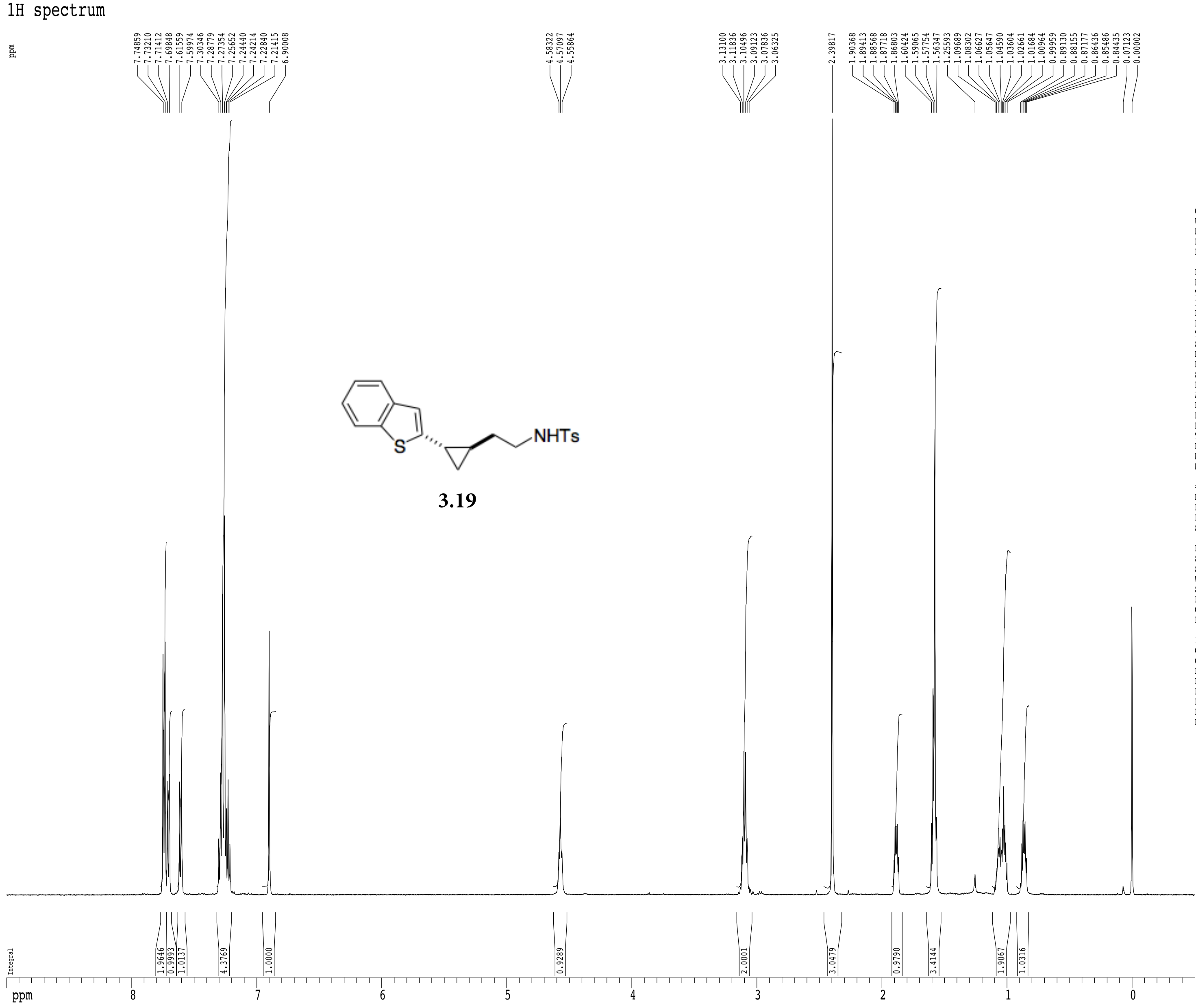
```
         Current Data Parameters
USER           khewitt1
NAME         KAH-I-069-Z
EXPNO                 2
PROCNO                1

      F2 - Acquisition Parameters
Date_          20180917
Time              15.35
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                  256
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

       F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

       F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

          2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             7.000 ppm
F2LO            3501.54 Hz
F2PHI            -0.509 ppm
F2HI            -254.47 Hz
F1PLO             7.000 ppm
F1LO            3501.54 Hz
F1PHI            -0.509 ppm
F1HI            -254.47 Hz
F2PPMCM         0.50058 ppm/cm
F2HZCM        250.40063 Hz/cm
F1PPMCM         0.50058 ppm/cm
F1HZCM        250.40063 Hz/cm
```

gnoe



3.18

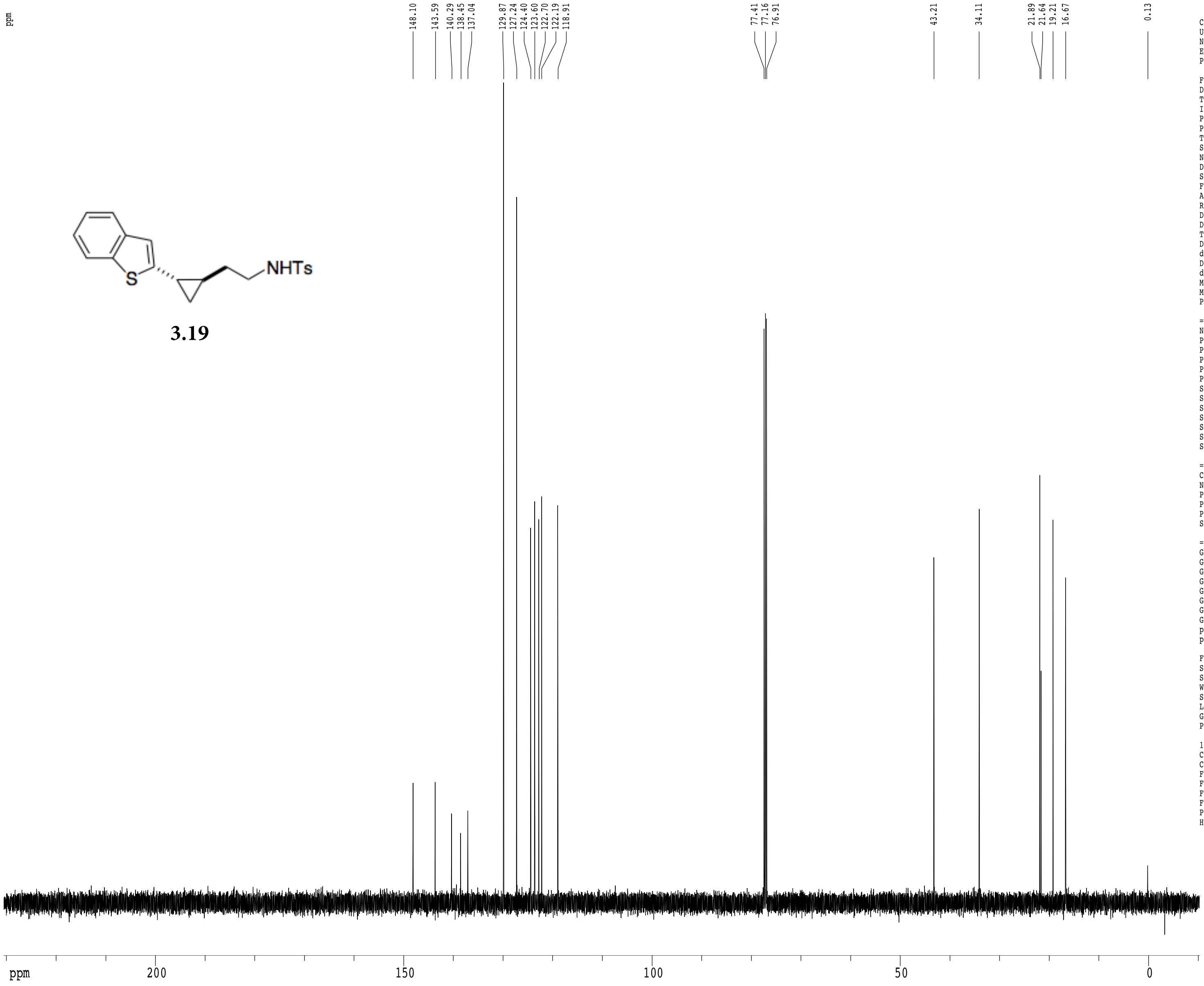
```
Current Data Parameters
USER              khewitt1
NAME            KAH-I-069-Z
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180917
Time                 20.12
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    90.5
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2209124 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```



3.19

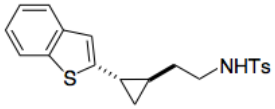
```
Current Data Parameters
USER            khewitt1
NAME          KAH-II-071Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190721
Time               15.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200333 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

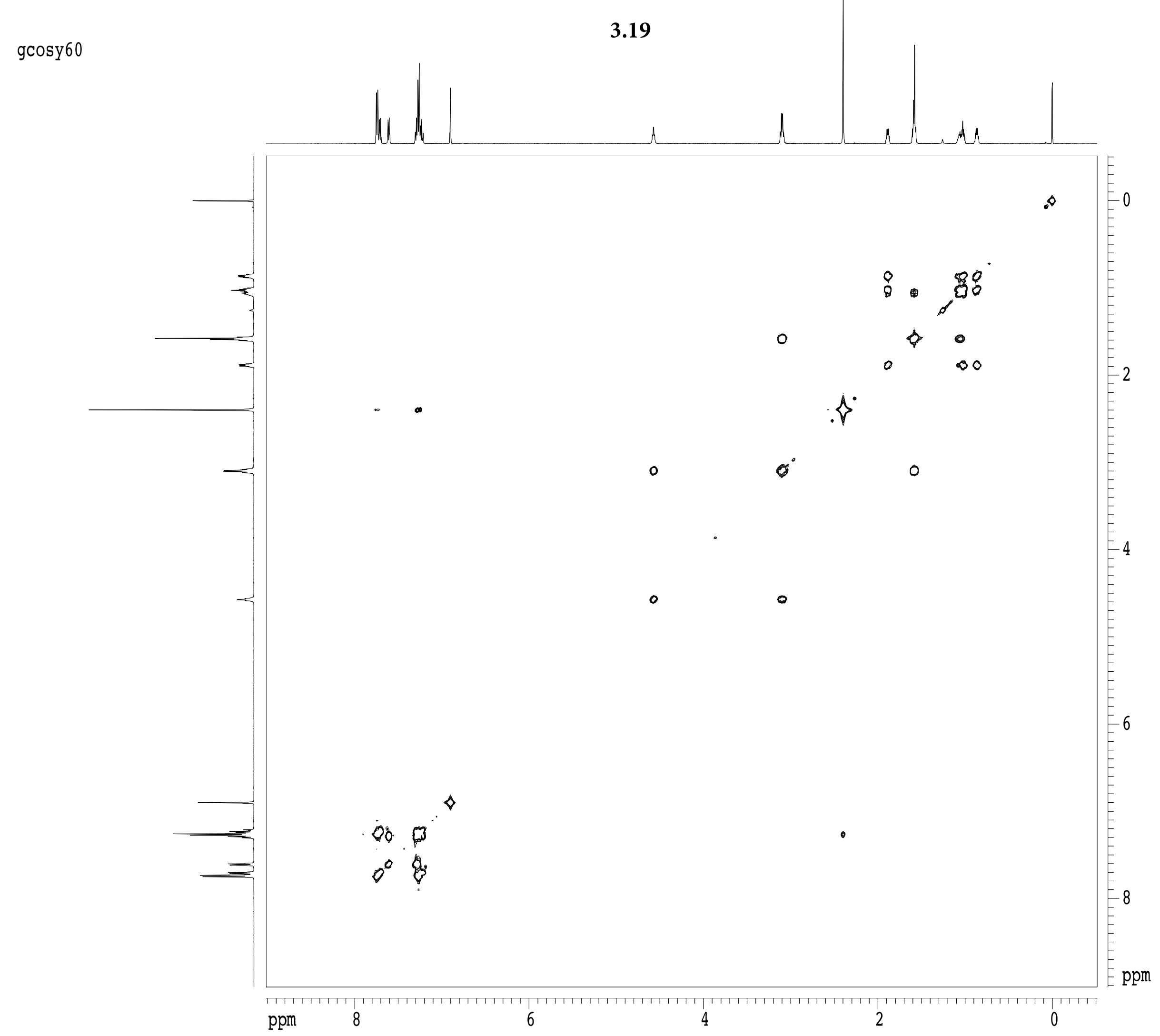


3.19

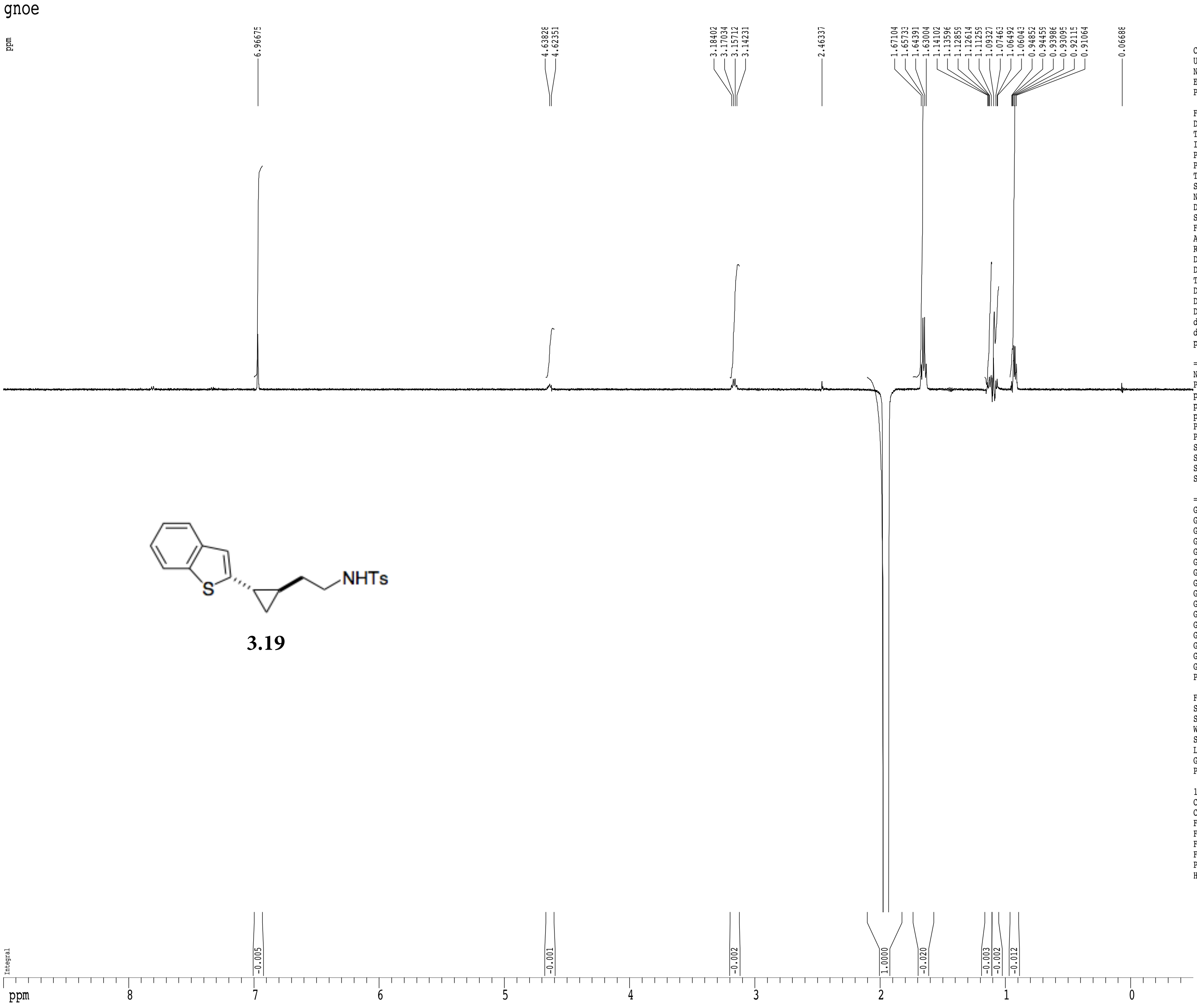
```
Current Data Parameters
USER            khewitt1
NAME         KAH-II-071Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190721
Time               15.26
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   608
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804080 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



3.19

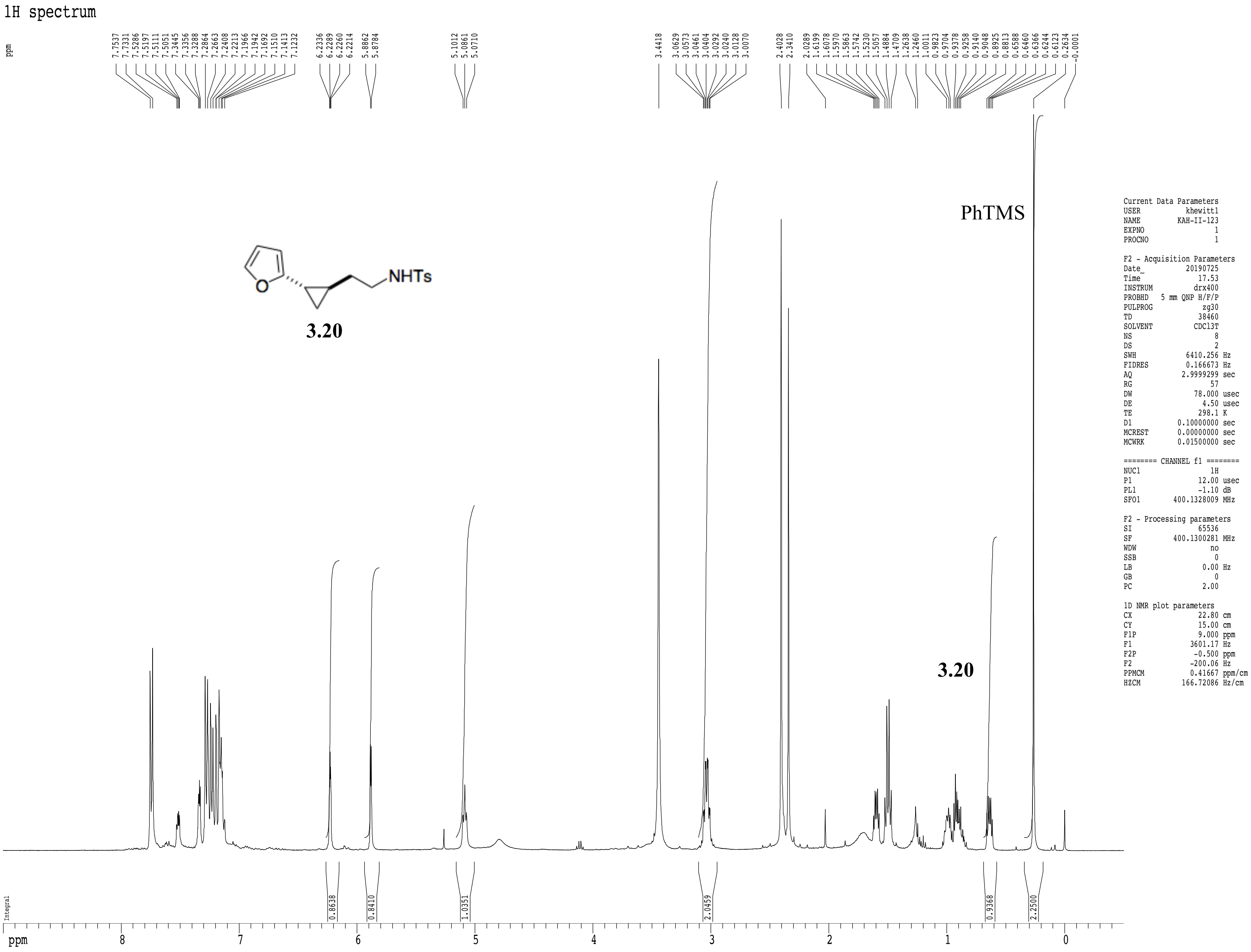


```
        Current Data Parameters
USER             khewitt1
NAME          KAH-II-071Z
EXPNO                   2
PROCNO                  1

      F2 - Acquisition Parameters
Date_            20190721
Time                15.03
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                     16
SWH              8012.820 Hz
FIDRES           3.912510 Hz
AQ              0.1278452 sec
RG                  456.1
DW                 62.400 usec
DE                   6.00 usec
TE                  298.1 K
d0             0.00000300 sec
D1             1.00000000 sec
d13            0.00000300 sec
D16            0.00020000 sec
IN0            0.00012480 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                17.00 %
GPZ2                17.00 %
P16               1000.00 usec

      F1 - Acquisition parameters
ND0                     1
TD                    512
SFO1             500.2235 MHz
FIDRES          15.650040 Hz
SW                 16.018 ppm
FnMODE                 QF

      F2 - Processing parameters
SI                   1024
SF            500.2200333 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

      F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.2200333 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0

        2D NMR plot parameters
CX2                 15.00 cm
CX1                 15.00 cm
F2PLO               9.014 ppm
F2LO              4508.92 Hz
F2PHI              -0.513 ppm
F2HI              -256.52 Hz
F1PLO               9.014 ppm
F1LO              4508.92 Hz
F1PHI              -0.513 ppm
F1HI              -256.52 Hz
F2PPMCM           0.63511 ppm/cm
F2HZCM          317.69580 Hz/cm
F1PPMCM           0.63511 ppm/cm
F1HZCM          317.69580 Hz/cm
```



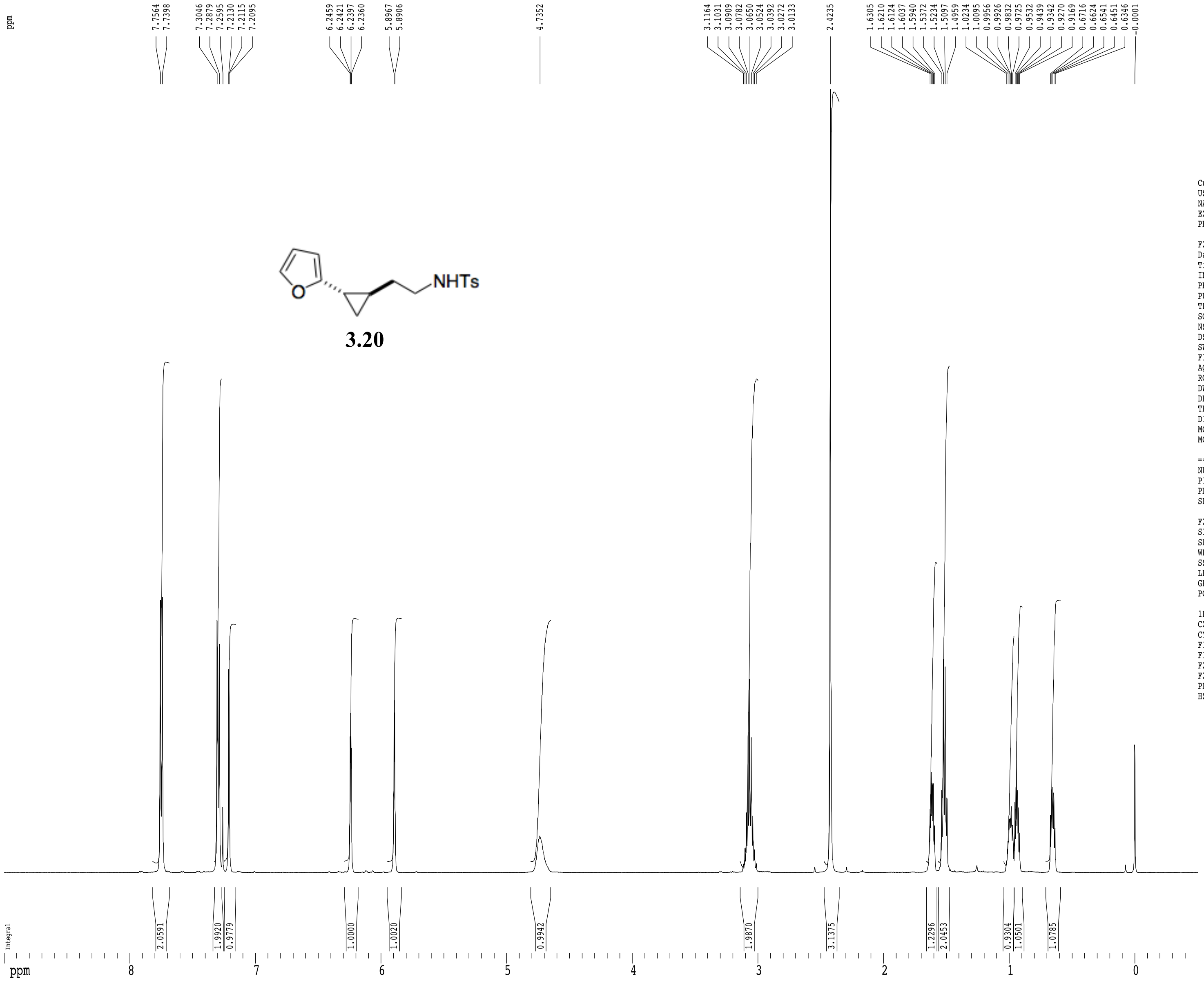
3.19

```
Current Data Parameters
USER              khewitt1
NAME           KAH-II-071Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190721
Time                 15.43
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                   161.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.2 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2209766 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```



```
Current Data Parameters
USER          khewitt1
NAME         KAH-II-123
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20190725
Time             17.53
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               38460
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                  57
DW              78.000 usec
DE                4.50 usec
TE               298.1 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300281 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -0.500 ppm
F2             -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```

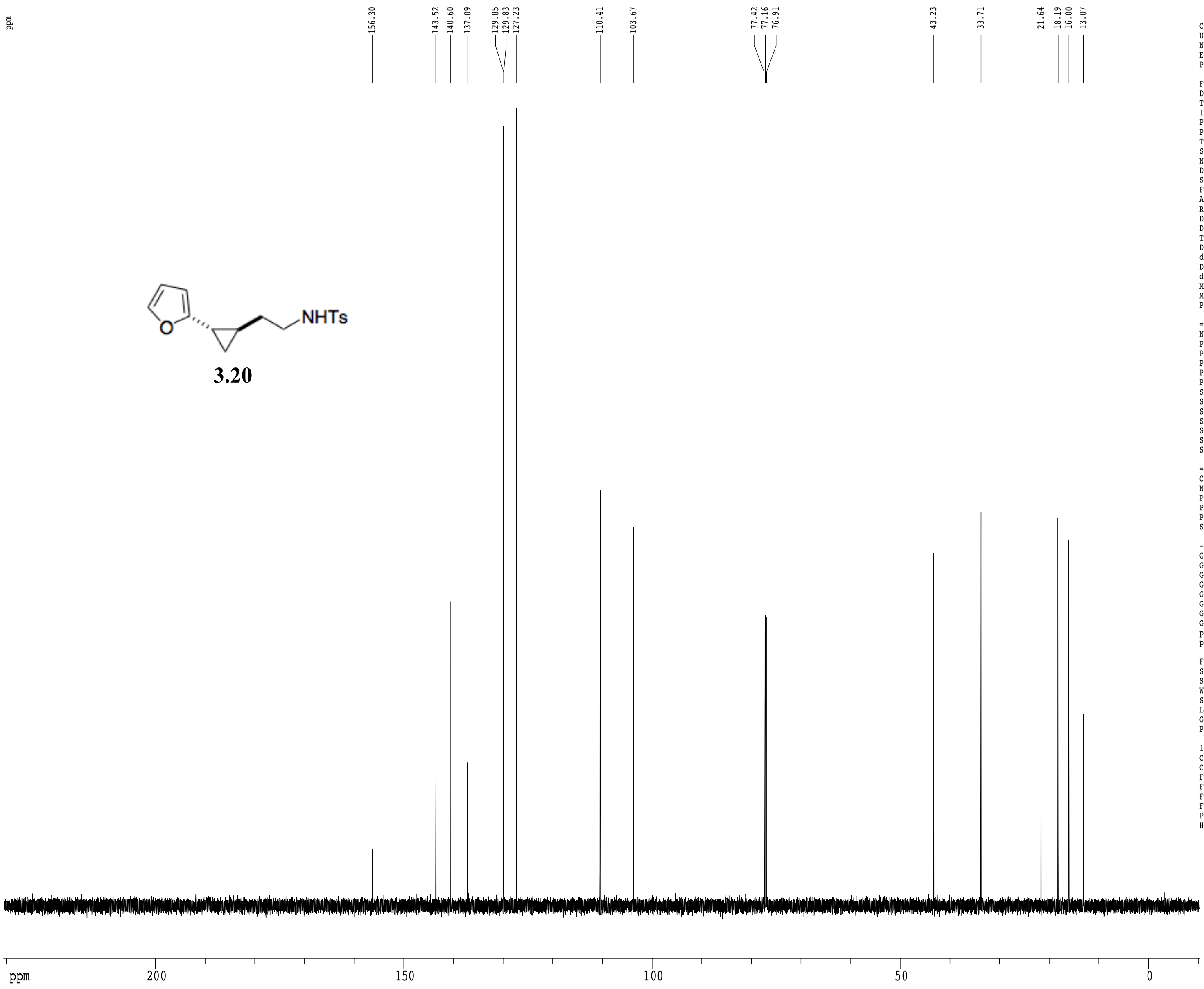
1H spectrum



3.20

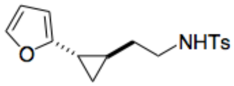
```
Current Data Parameters
USER           khewitt1
NAME       KAH-II-120-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20190727
Time              12.44
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200316 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



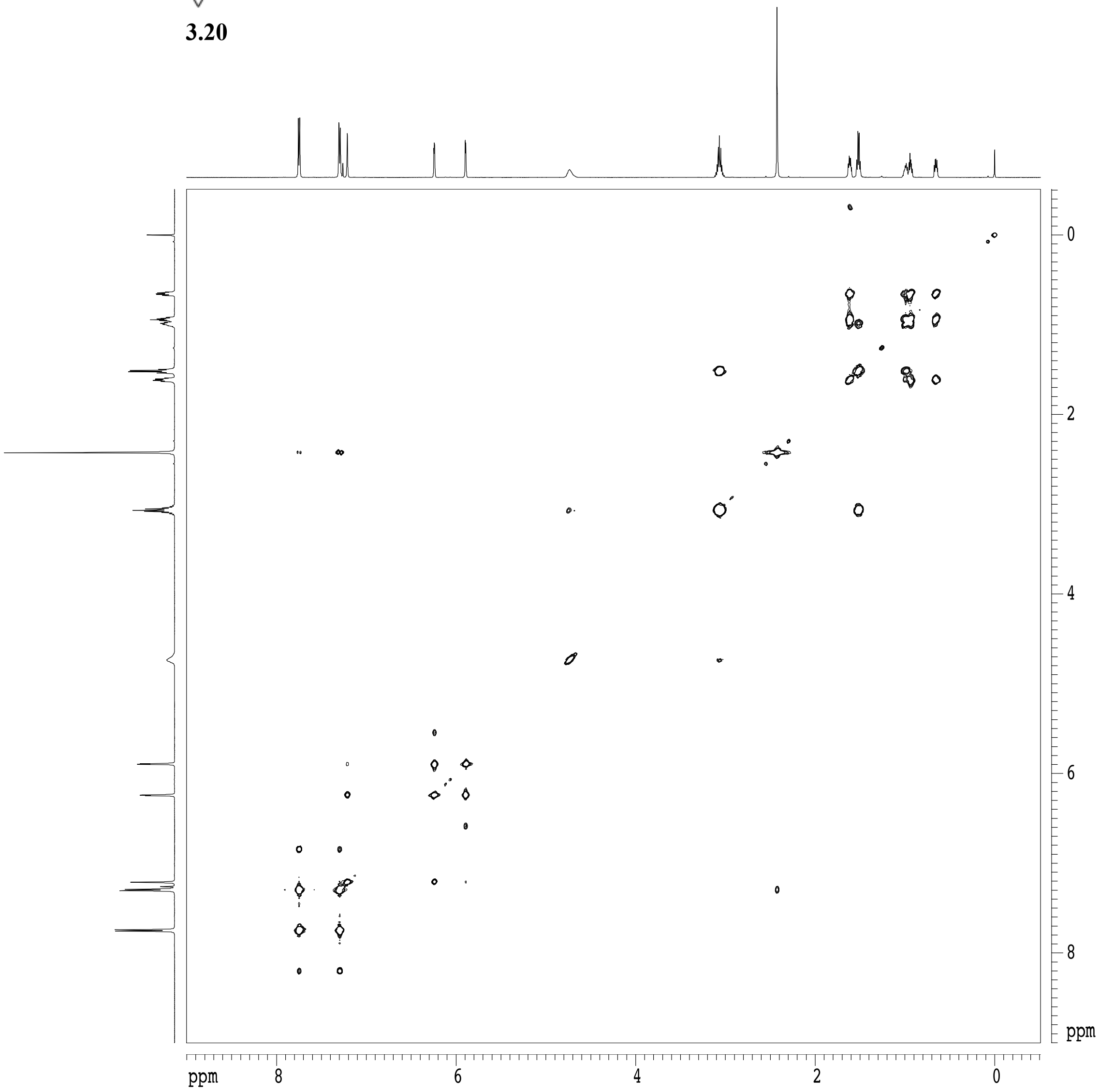
3.20

```
Current Data Parameters
USER            khewitt1
NAME         KAH-II-120-Z
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190727
Time               13.00
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   152
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.1 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804094 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

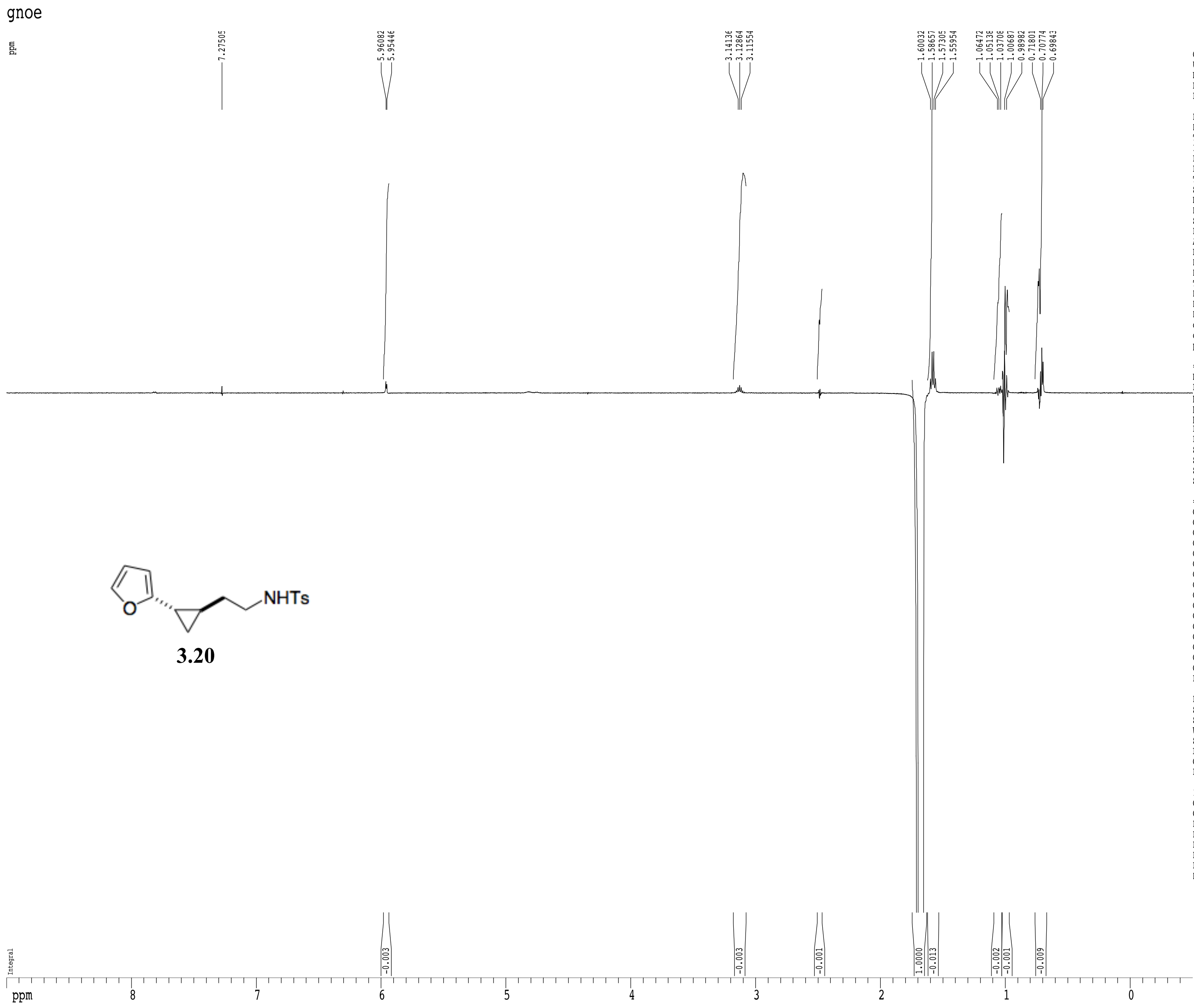


3.20

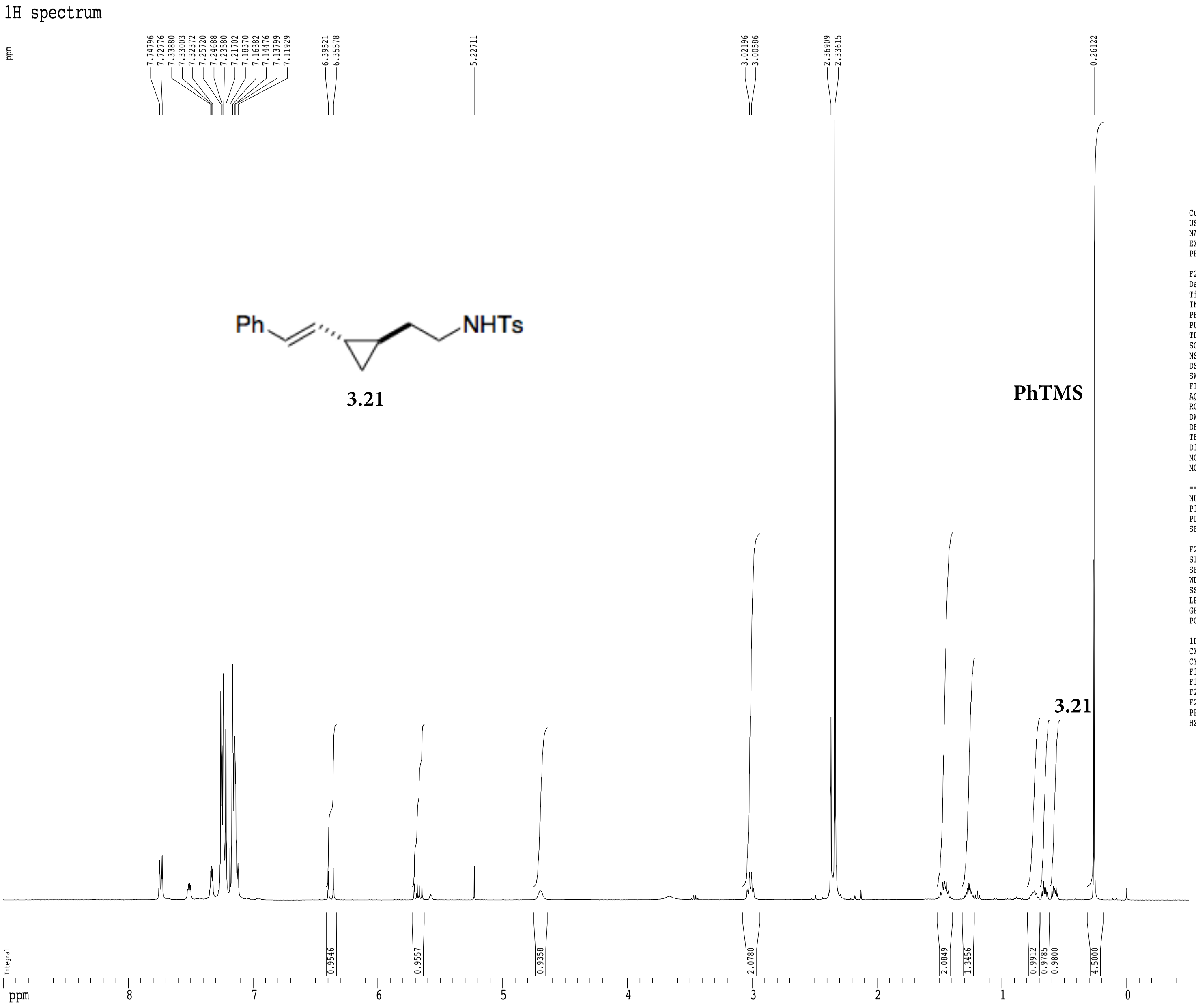
gcosy60



```
        Current Data Parameters
USER              khewitt1
NAME           KAH-II-120-Z
EXPNO                    3
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20190727
Time                 12.47
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG       cosygp60.prd
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                      16
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                     114
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
d0              0.00000300 sec
D1              1.00000000 sec
d13             0.00000300 sec
D16             0.00020000 sec
IN0             0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 17.00 %
GPZ2                 17.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      1
TD                     512
SFO1              500.2235 MHz
FIDRES           15.650040 Hz
SW                  16.018 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             500.2200315 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.2200315 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

        2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                9.002 ppm
F2LO               4502.93 Hz
F2PHI               -0.509 ppm
F2HI               -254.68 Hz
F1PLO                9.002 ppm
F1LO               4502.93 Hz
F1PHI               -0.509 ppm
F1HI               -254.68 Hz
F2PPMCM            0.63407 ppm/cm
F2HZCM           317.17413 Hz/cm
F1PPMCM            0.63407 ppm/cm
F1HZCM           317.17413 Hz/cm
```

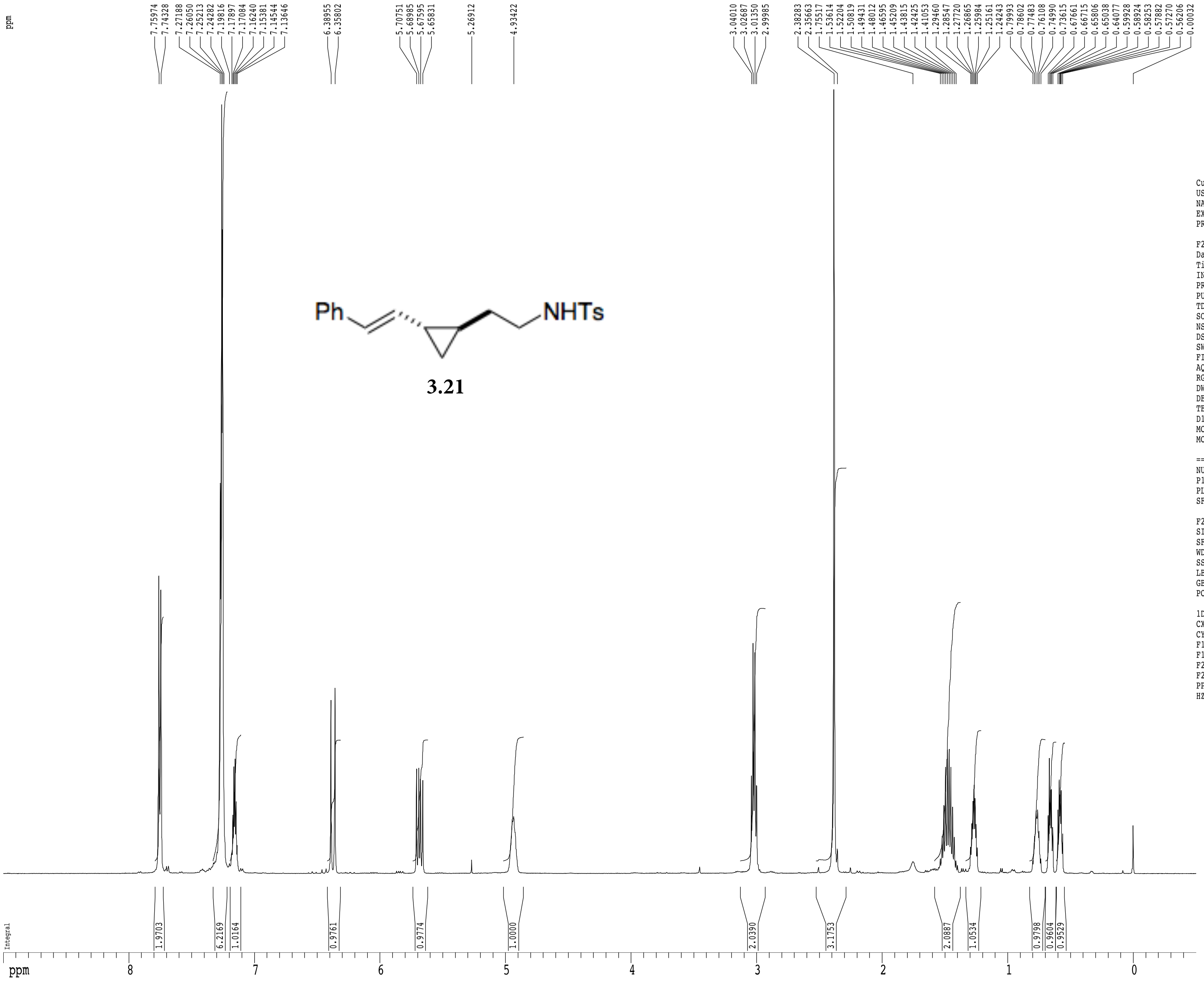


```
Current Data Parameters
USER              khewitt1
NAME           KAH-II-120-Z
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_          20190727
Time              17.23
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                     1H
P1                     7.50 usec
p3                    22.50 usec
p4                    30.00 usec
p5                    20.00 usec
P29                40000.00 usec
PL1                    1.60 dB
SFO1            500.2208380 MHz
SP9                   61.60 dB
SPNAM9          gauss1.512
SPOFF9                 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



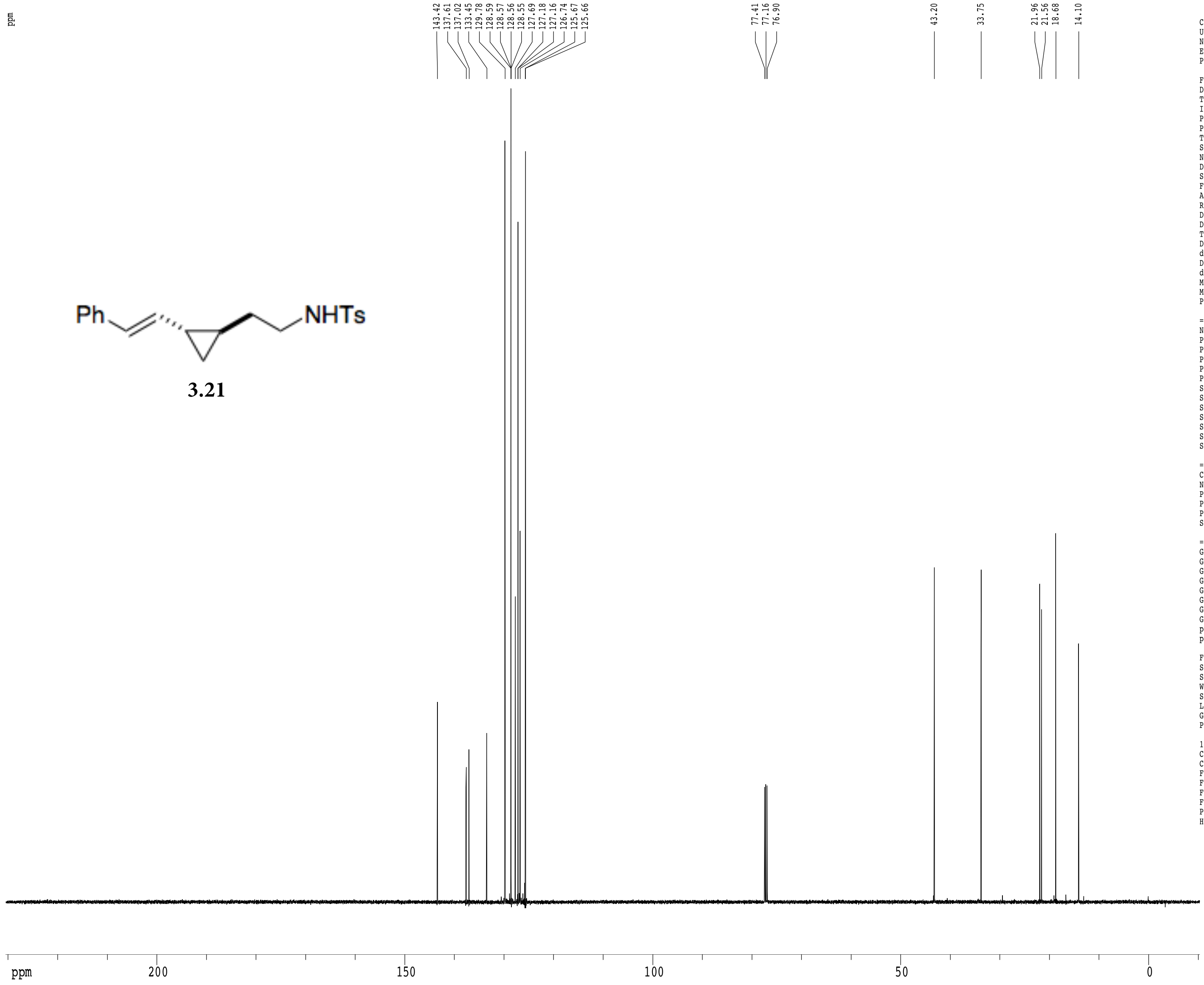
```
Current Data Parameters
USER            khewitt1
NAME          KAH-I-264
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190131
Time               16.37
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    64
DW                78.000 usec
DE                  4.50 usec
TE                 298.1 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300514 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72087 Hz/cm
```

1H spectrum


3.21

```
Current Data Parameters
USER           khewitt1
NAME         KAH-I-264Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190721
Time              15.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.2 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200398 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

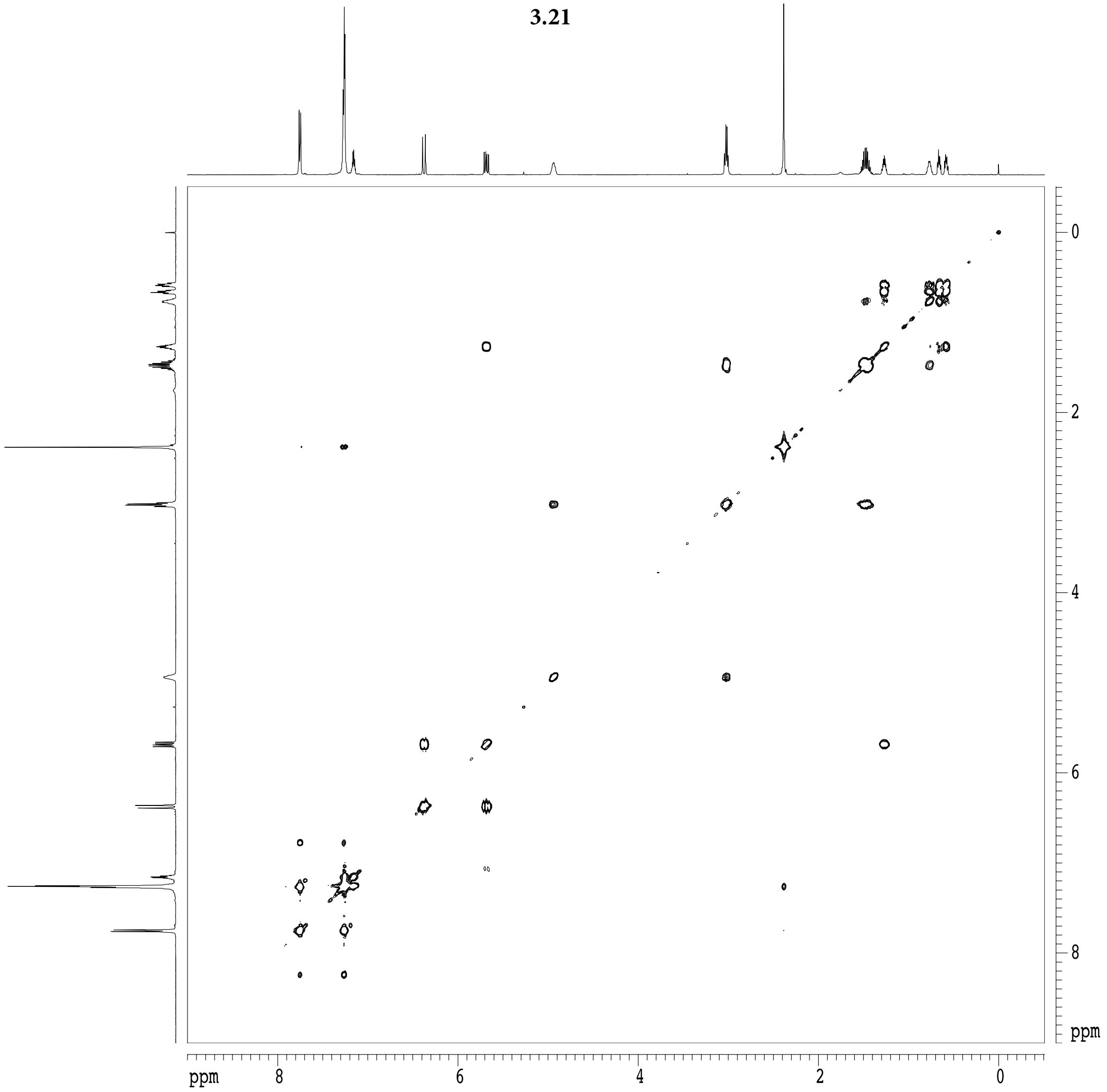
Z-restored spin-echo 13C spectrum with 1H decoupling


3.21

```
Current Data Parameters
USER            khewitt1
NAME          KAH-I-264Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190721
Time               16.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   496
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804191 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10706 Hz/cm
```

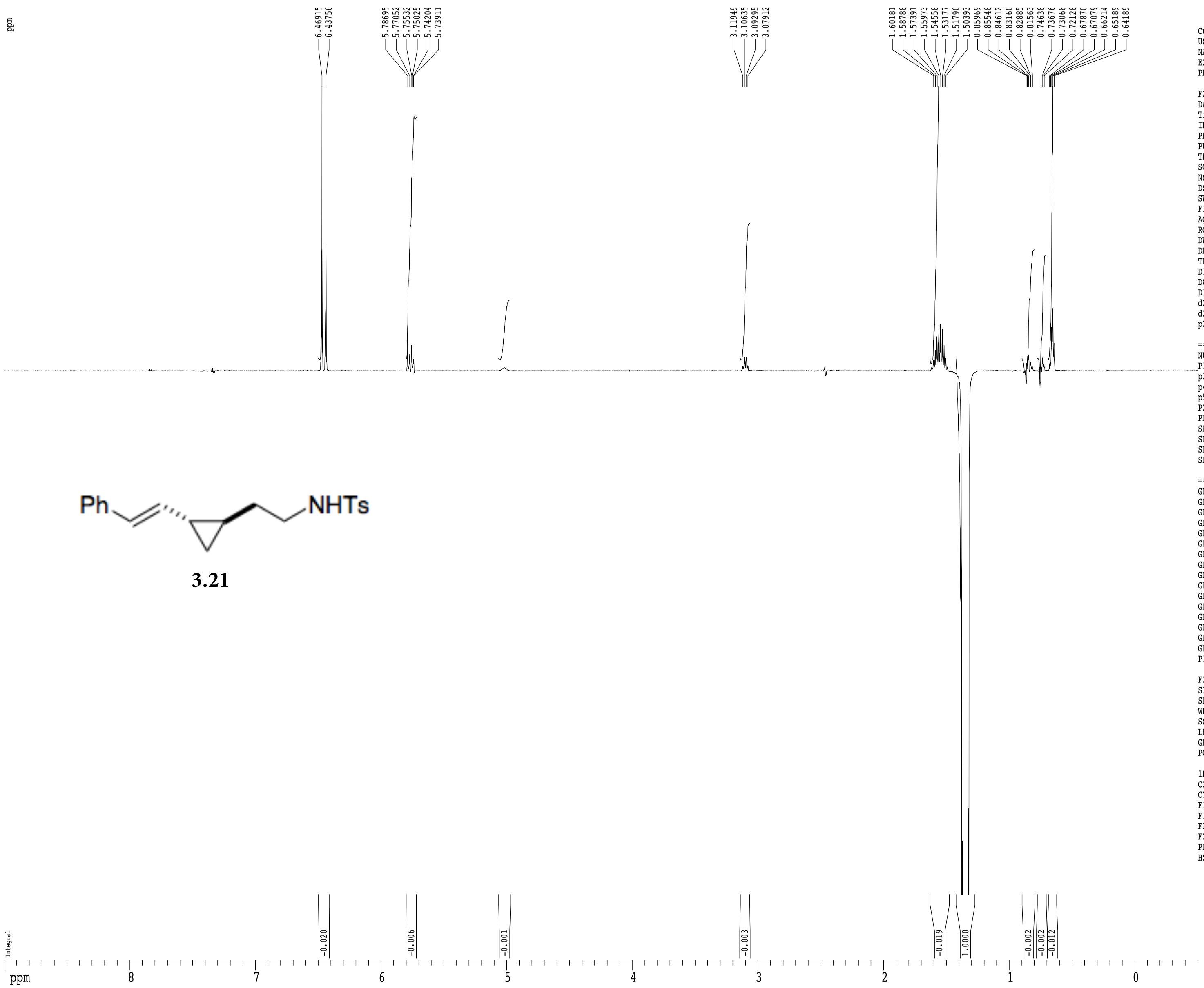
3.21

gcosy60



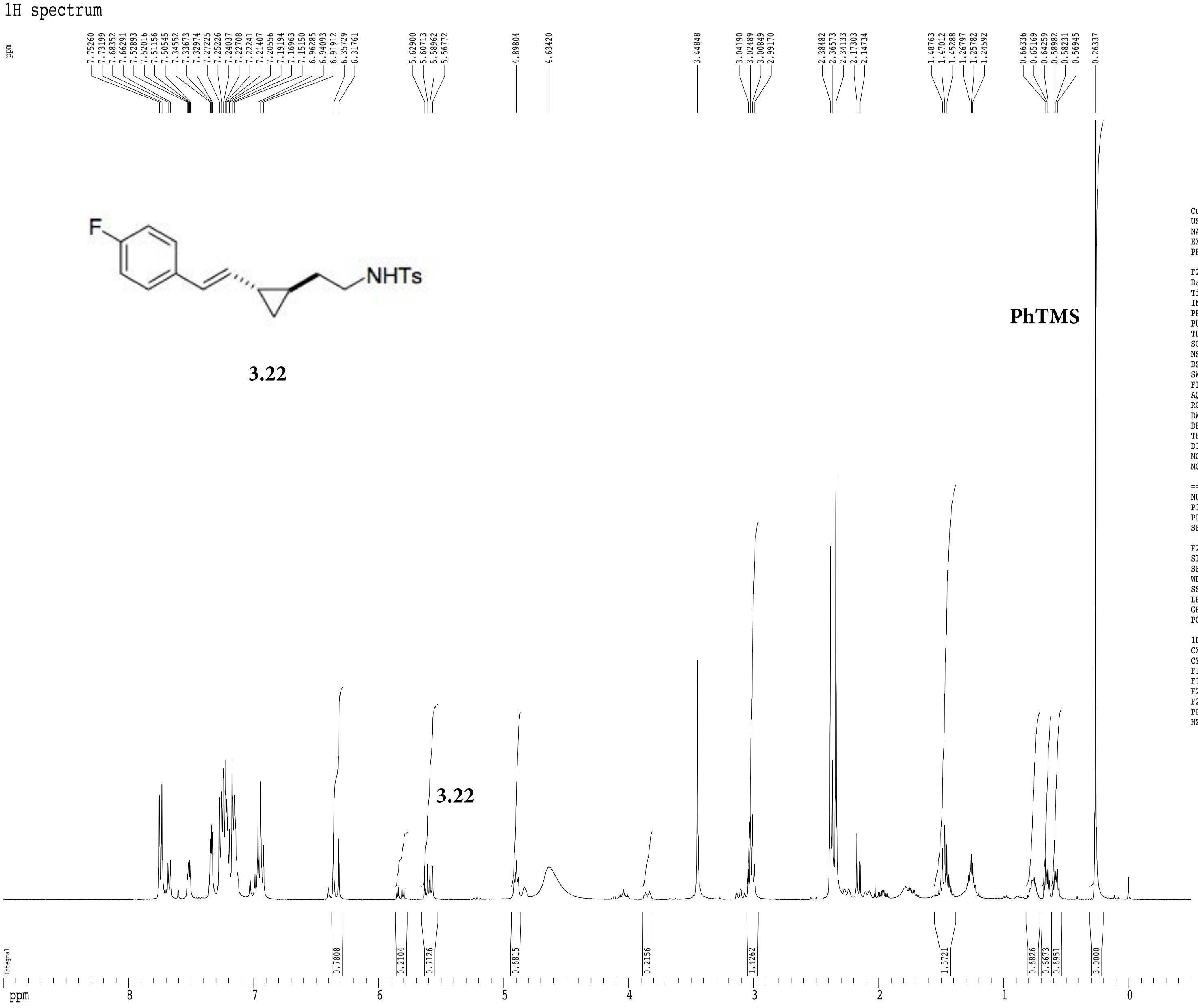
```
        Current Data Parameters
USER            khewitt1
NAME           KAH-I-264Z
EXPNO                   2
PROCNO                  1

      F2 - Acquisition Parameters
Date_            20190721
Time                15.51
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      cosygp60.prd
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                     16
SWH              8012.820 Hz
FIDRES           3.912510 Hz
AQ              0.1278452 sec
RG                   35.9
DW                 62.400 usec
DE                   6.00 usec
TE                  298.2 K
d0             0.00000300 sec
D1             1.00000000 sec
d13            0.00000300 sec
D16            0.00020000 sec
IN0            0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                17.00 %
GPZ2                17.00 %
P16               1000.00 usec

      F1 - Acquisition parameters
ND0                     1
TD                    512
SFO1             500.2235 MHz
FIDRES          15.650040 Hz
SW                 16.018 ppm
FnMODE                 QF

      F2 - Processing parameters
SI                   1024
SF            500.2200398 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

      F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.2200398 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0

         2D NMR plot parameters
CX2                 15.00 cm
CX1                 15.00 cm
F2PLO               9.001 ppm
F2LO              4502.44 Hz
F2PHI              -0.510 ppm
F2HI              -255.17 Hz
F1PLO               9.001 ppm
F1LO              4502.44 Hz
F1PHI              -0.510 ppm
F1HI              -255.17 Hz
F2PPMCM           0.63407 ppm/cm
F2HZCM          317.17413 Hz/cm
F1PPMCM           0.63407 ppm/cm
F1HZCM          317.17413 Hz/cm
```

gnoe



3.21

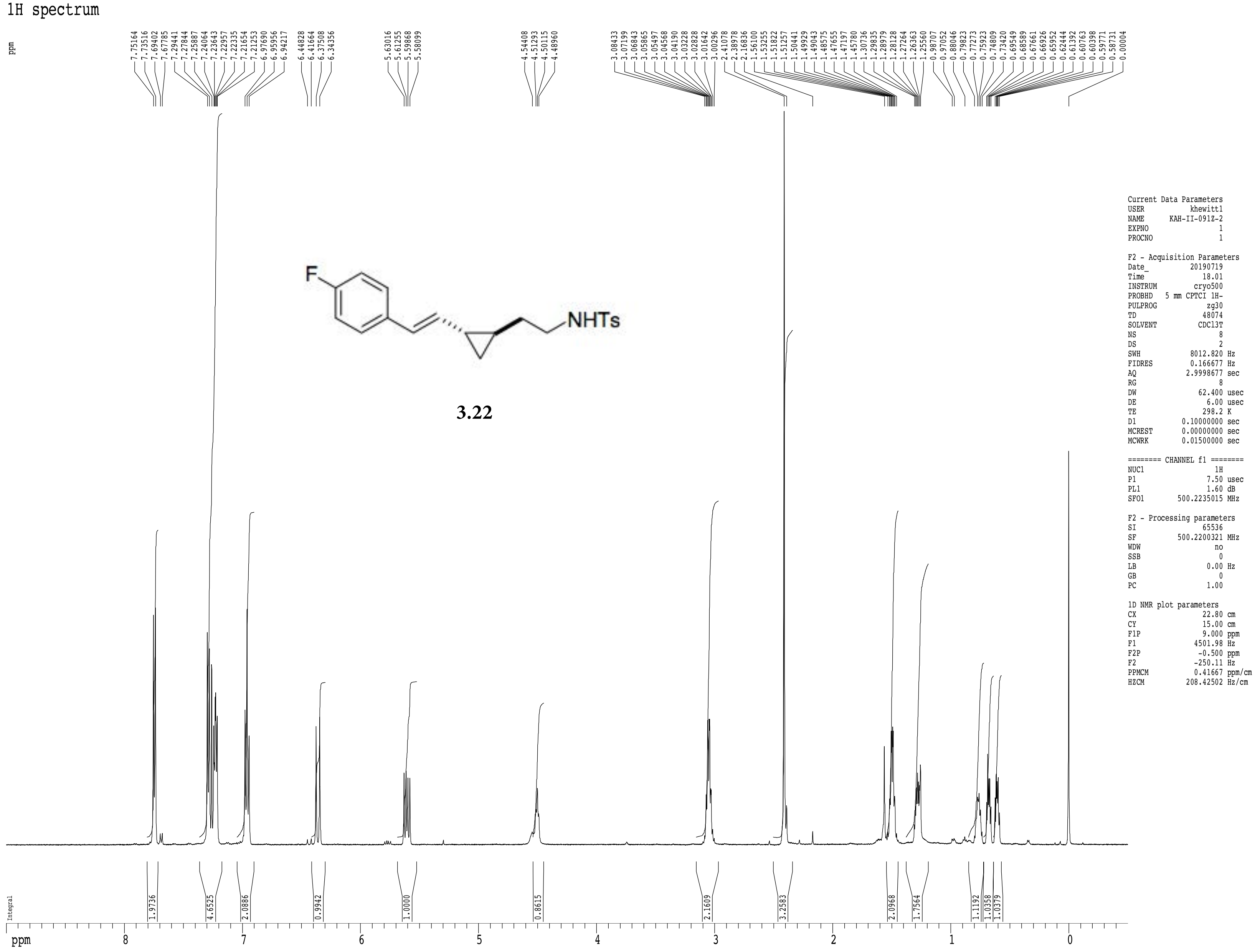
```
Current Data Parameters
USER              khewitt1
NAME            KAH-I-264Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190721
Time                 16.29
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                   161.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.2 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2206743 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```



3.22

```
Current Data Parameters
USER          khewitt1
NAME        KAH-II-047
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20190405
Time             16.47
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               38460
SOLVENT          CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                  57
DW              78.000 usec
DE                4.50 usec
TE               297.9 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300304 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -0.500 ppm
F2             -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```

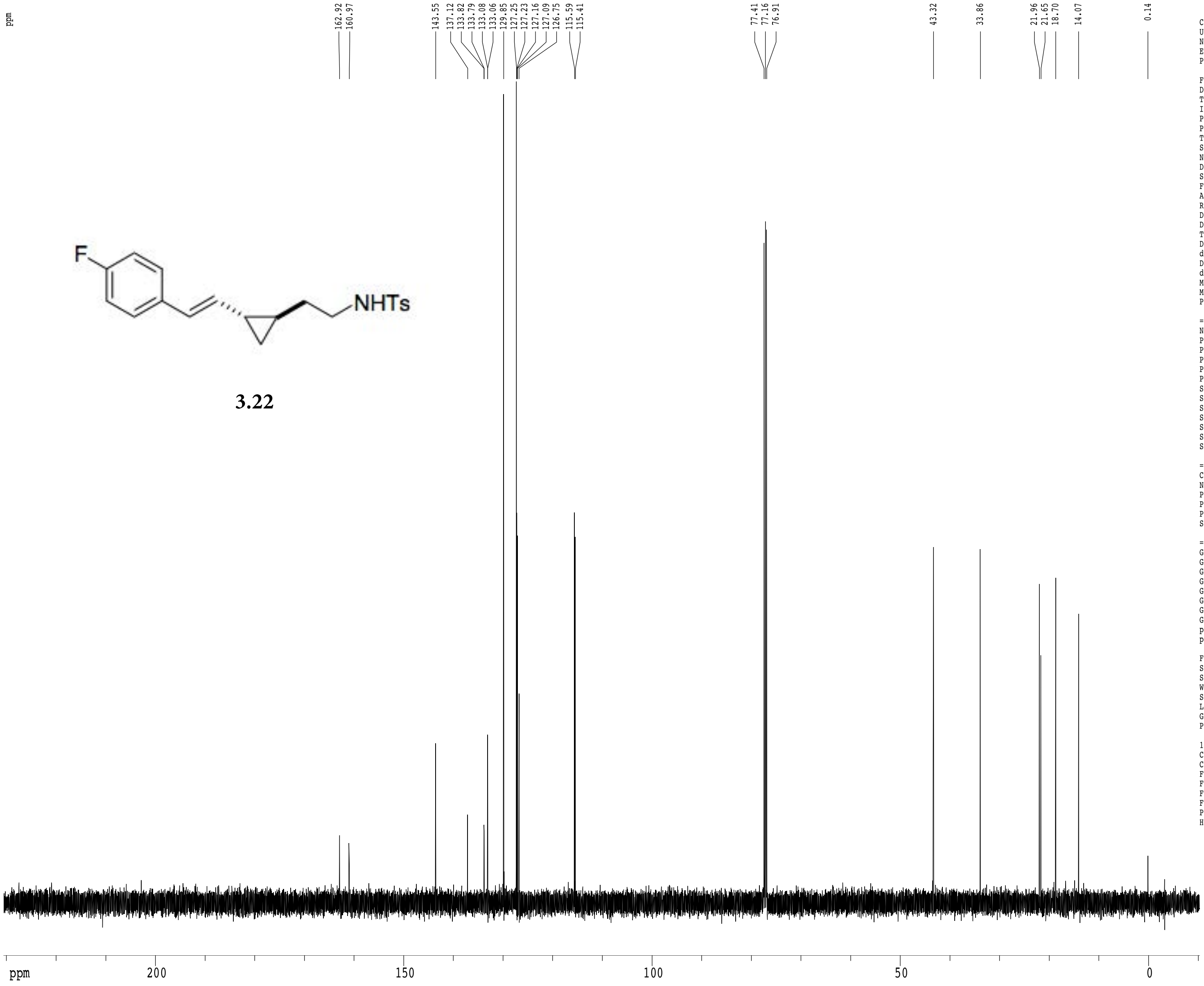
1H spectrum



3.22

```
Current Data Parameters
USER            khewitt1
NAME       KAH-II-091Z-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190719
Time               18.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200321 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

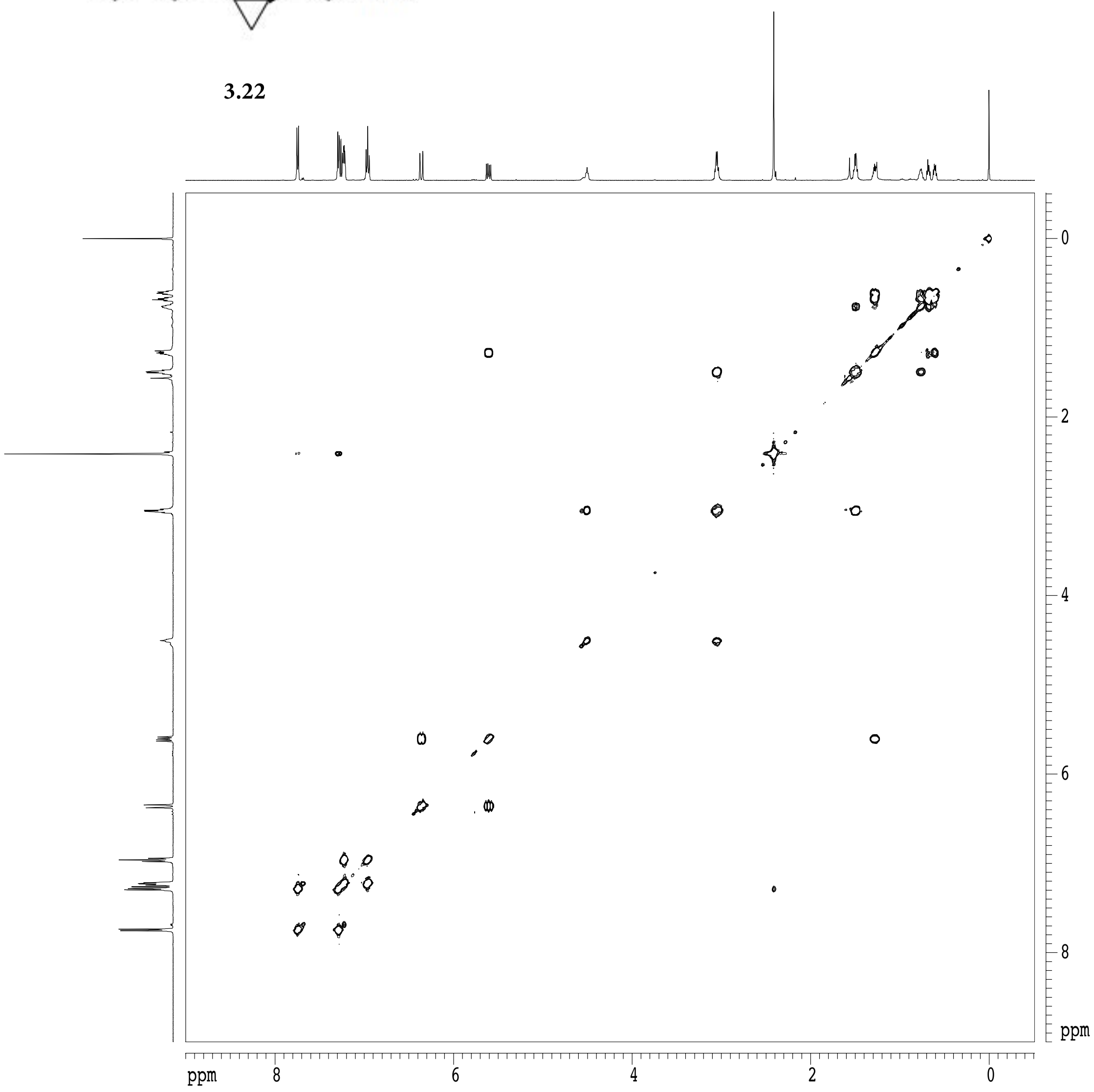
Z-restored spin-echo 13C spectrum with 1H decoupling



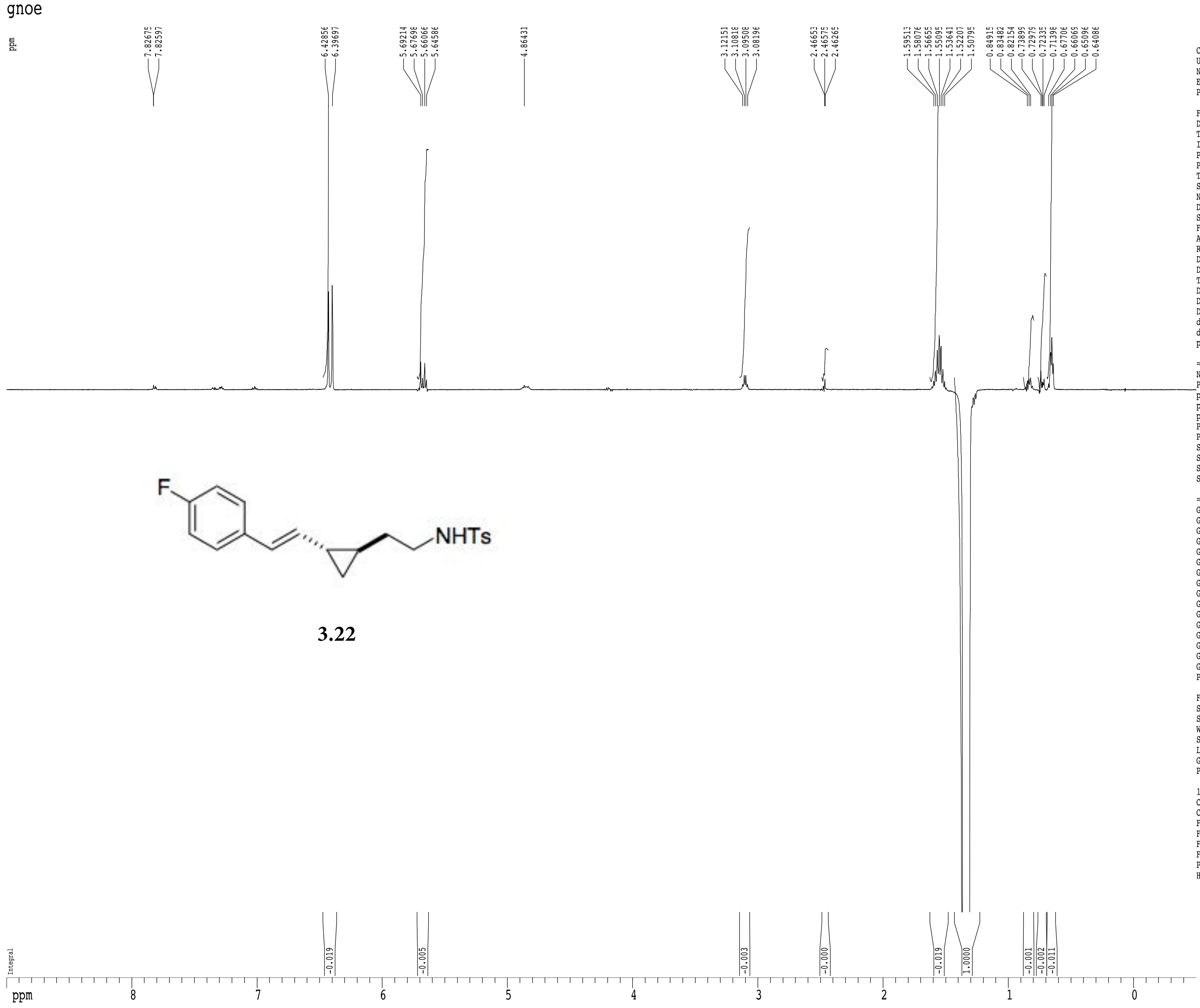
3.22

```
Current Data Parameters
USER            khewitt1
NAME        KAH-II-091Z-2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190719
Time               18.16
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   392
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.2 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804071 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

3.22



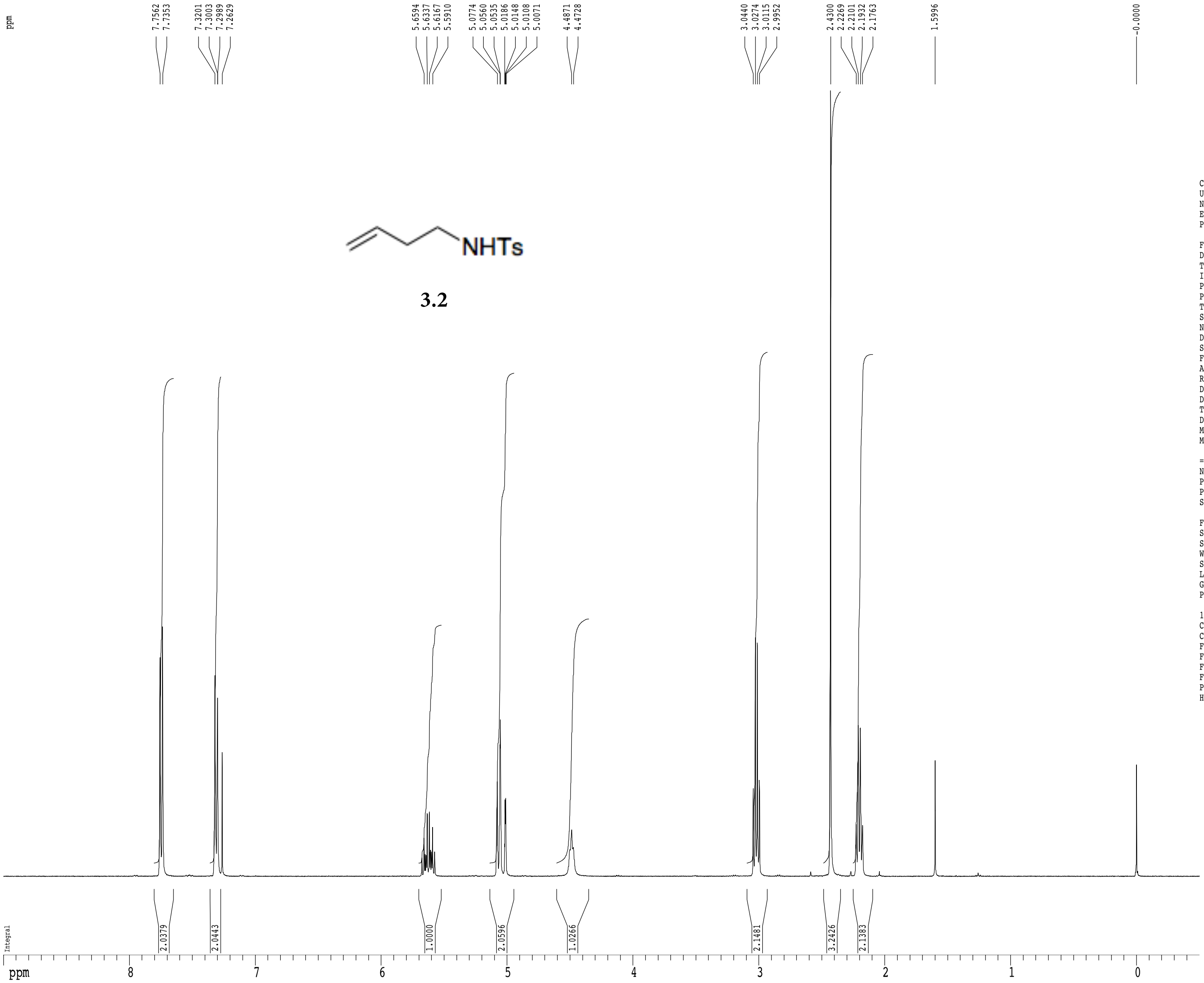
```
        Current Data Parameters
USER           khewitt1
NAME        KAH-II-091Z-2
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_          20190719
Time              18.03
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                456.1
DW               62.400 usec
DE                 6.00 usec
TE                298.2 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200321 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200321 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.001 ppm
F2LO            4502.32 Hz
F2PHI            -0.510 ppm
F2HI            -255.29 Hz
F1PLO             9.001 ppm
F1LO            4502.32 Hz
F1PHI            -0.510 ppm
F1HI            -255.29 Hz
F2PPMCM         0.63407 ppm/cm
F2HZCM        317.17413 Hz/cm
F1PPMCM         0.63407 ppm/cm
F1HZCM        317.17413 Hz/cm
```



3.22

```
Current Data Parameters
USER            khewitt1
NAME       KAH-II-039-Z
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190402
Time               13.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2206699 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

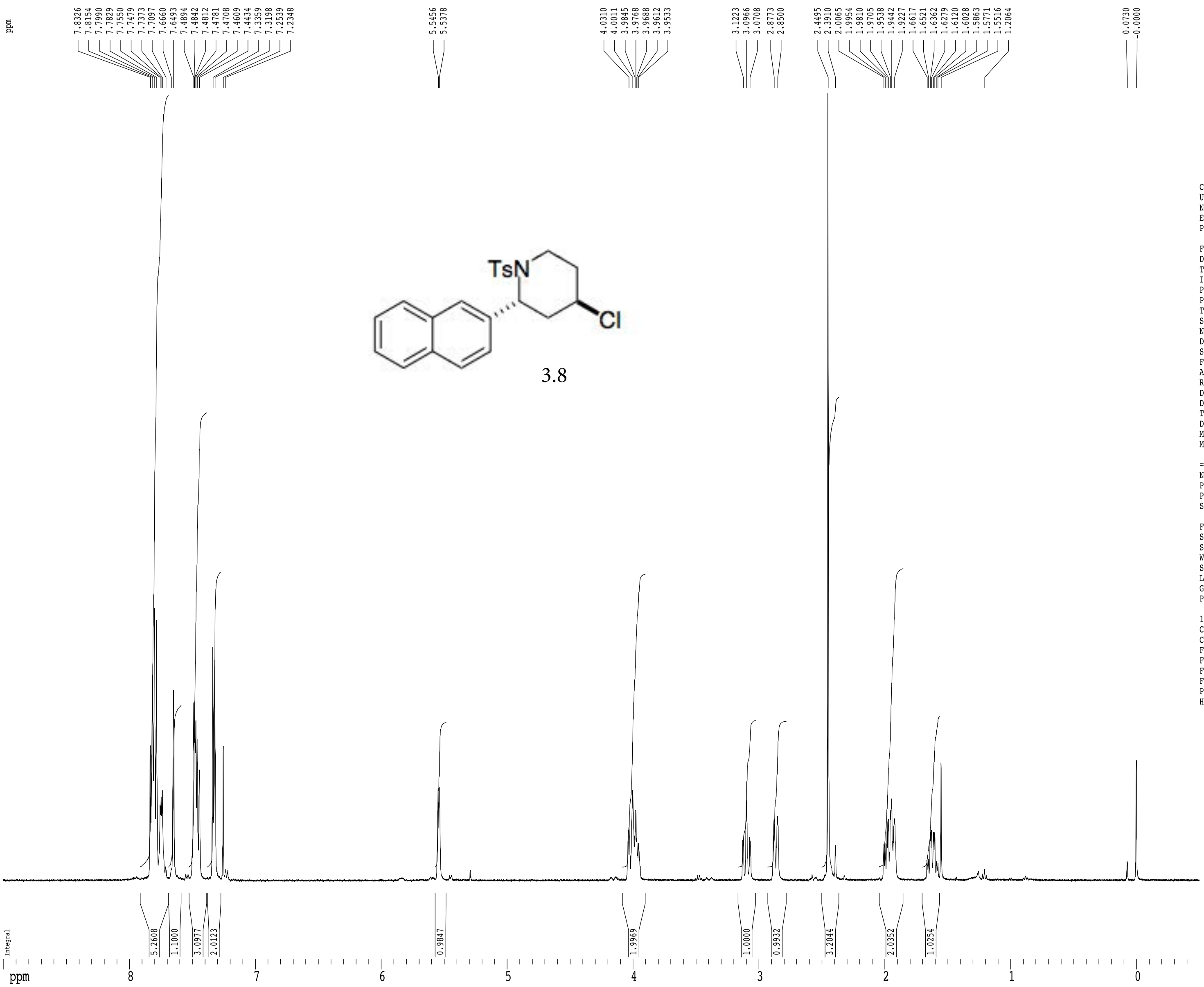
1H spectrum



3.2

```
Current Data Parameters
USER              erikal
NAME          ELL-IV-122
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190226
Time               10.14
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                 287.4
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300201 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

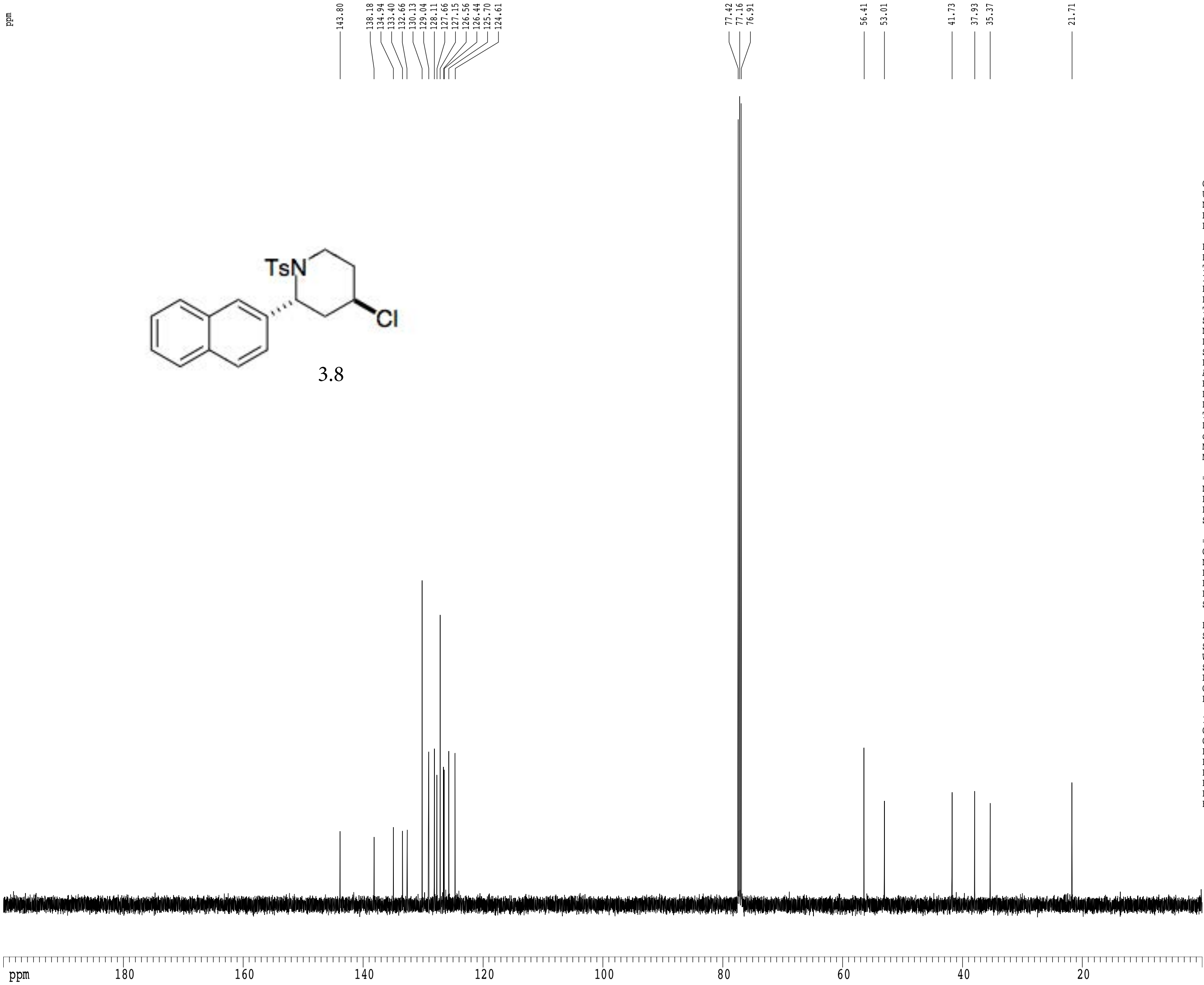
1H spectrum



3.8

```
Current Data Parameters
USER              erikal
NAME         ELL-II-281
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20171108
Time              19.50
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                645.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -5.80 dB
SFO1        498.9534926 MHz

F2 - Processing parameters
SI                65536
SF          498.9500328 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4490.55 Hz
F2P              -0.500 ppm
F2              -249.47 Hz
PPMCM           0.41667 ppm/cm
HZCM          207.89586 Hz/cm
```

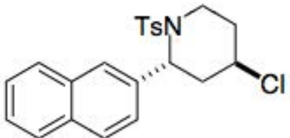
13C spectrum with 1H decoupling



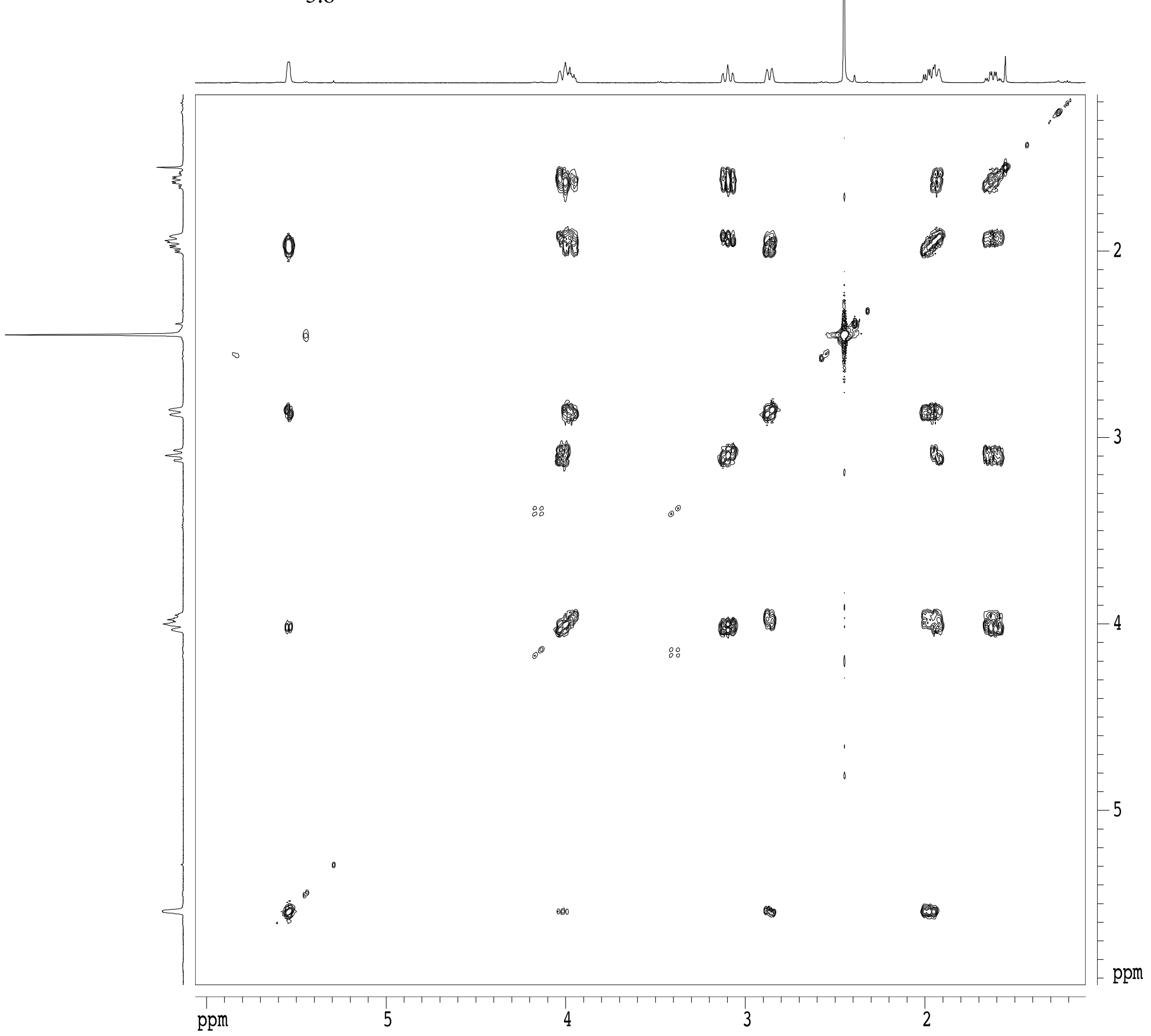
3.8

```
Current Data Parameters
USER              erikal
NAME          ELL-II-281
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171108
Time               20.22
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   788
DS                     4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                  3251
DW                16.500 usec
DE                  4.50 usec
TE                 298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                -0.60 dB
SFO1         125.4748777 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               12.80 dB
SFO2         498.9524948 MHz

F2 - Processing parameters
SI                 65536
SF           125.4610662 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25092.21 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1100.53577 Hz/cm
```

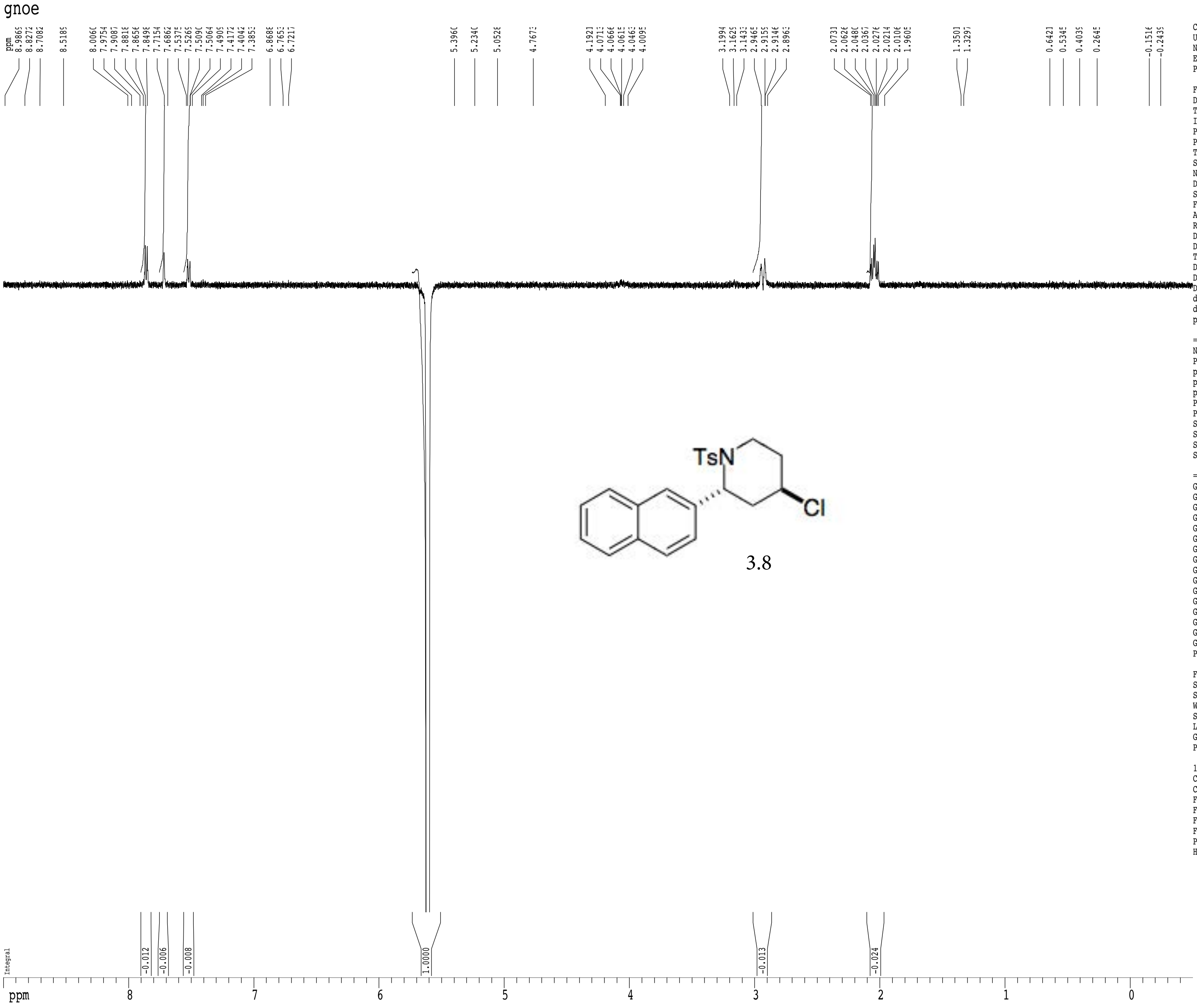
gcosy60



3.8

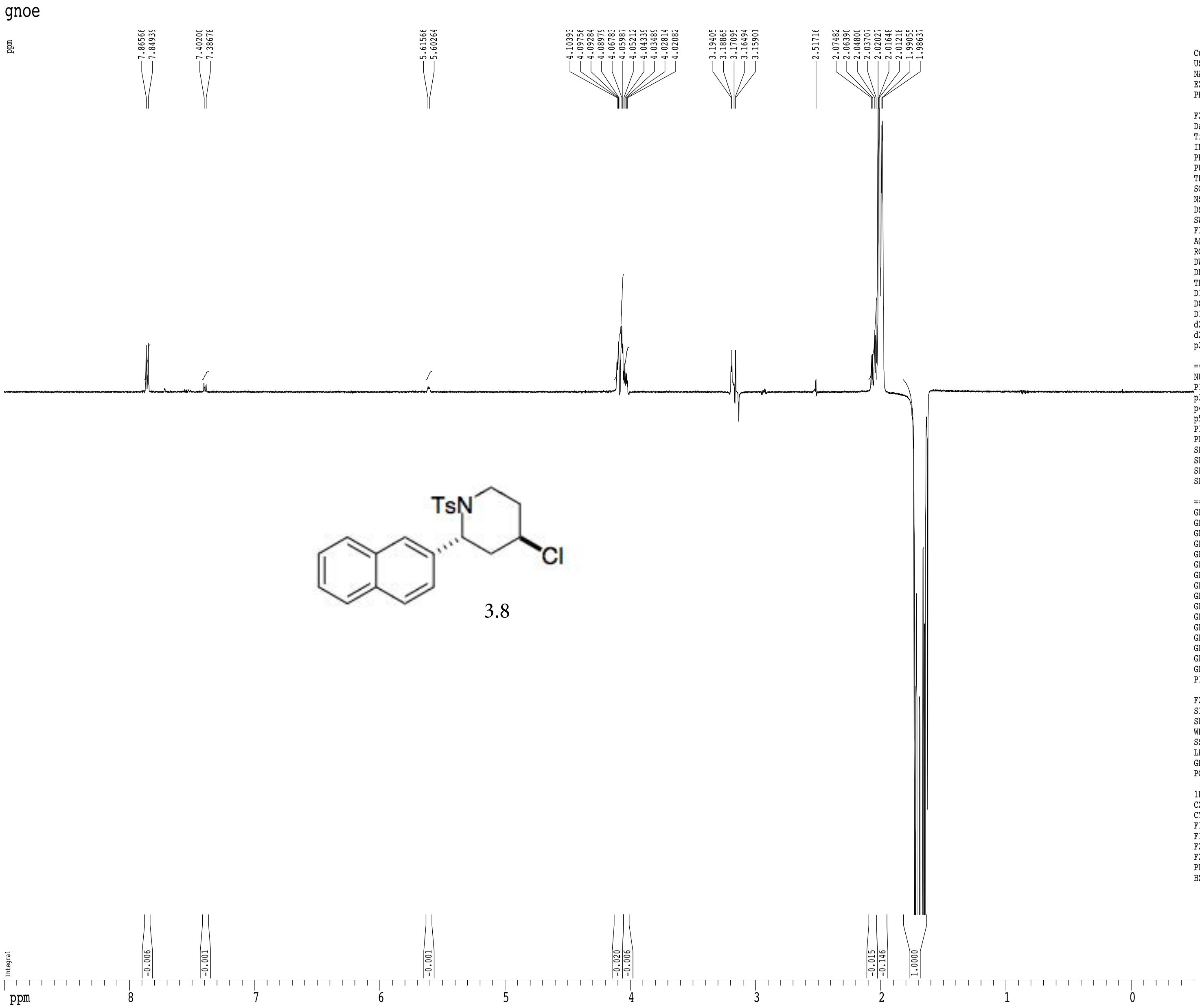


```
        Current Data Parameters
USER              erikal
NAME          ELL-II-281
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20171108
Time               19.53
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     2
DS                    16
SWH             3591.954 Hz
FIDRES          1.753884 Hz
AQ             0.2851316 sec
RG                2896.3
DW               139.200 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00025000 sec
IN0           0.00027840 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -5.80 dB
SFO1         498.9523665 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   256
SFO1            498.9524 MHz
FIDRES         14.031071 Hz
SW                 7.199 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           498.9500328 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           498.9500328 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              6.062 ppm
F2LO             3024.77 Hz
F2PHI              1.106 ppm
F2HI              551.79 Hz
F1PLO              5.936 ppm
F1LO             2961.63 Hz
F1PHI              1.162 ppm
F1HI              579.85 Hz
F2PPMCM          0.33042 ppm/cm
F2HZCM         164.86508 Hz/cm
F1PPMCM          0.31824 ppm/cm
F1HZCM         158.78494 Hz/cm
```



3.8

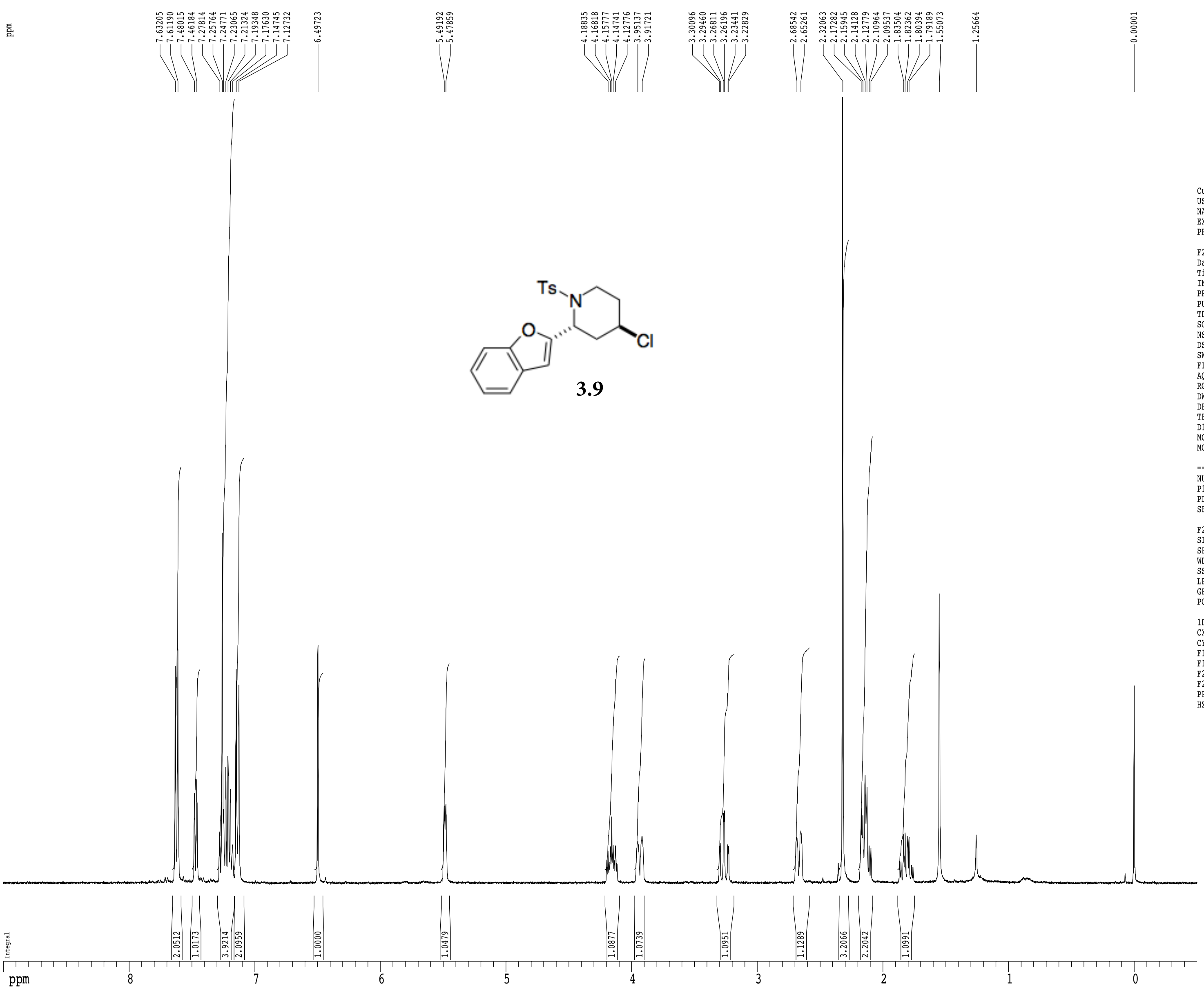
```
Current Data Parameters
USER               erikal
NAME          ELL-II-281
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171108
Time               20.50
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG      gnoe1cc.wu
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                5160.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33374399 sec
d22          0.16399699 sec
p2                24.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                12.00 usec
p3                36.00 usec
p4                48.00 usec
p5                32.00 usec
P12            40000.00 usec
PL1               -5.80 dB
SFO1        498.9527981 MHz
SP1               53.60 dB
SPNAM1       gauss1.512
SPOFF1             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                 65536
SF          498.9500000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4490.55 Hz
F2P               -0.500 ppm
F2               -249.47 Hz
PPMCM            0.41667 ppm/cm
HZCM           207.89584 Hz/cm
```



3.8

```
Current Data Parameters
USER               erikal
NAME          ELL-II-281
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_          20171109
Time              12.20
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      gnoe1cc.wu
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 80.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P12            40000.00 usec
PL1                1.60 dB
SFO1        500.2208445 MHz
SP1               61.60 dB
SPNAM1       gauss1.512
SPOFF1             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

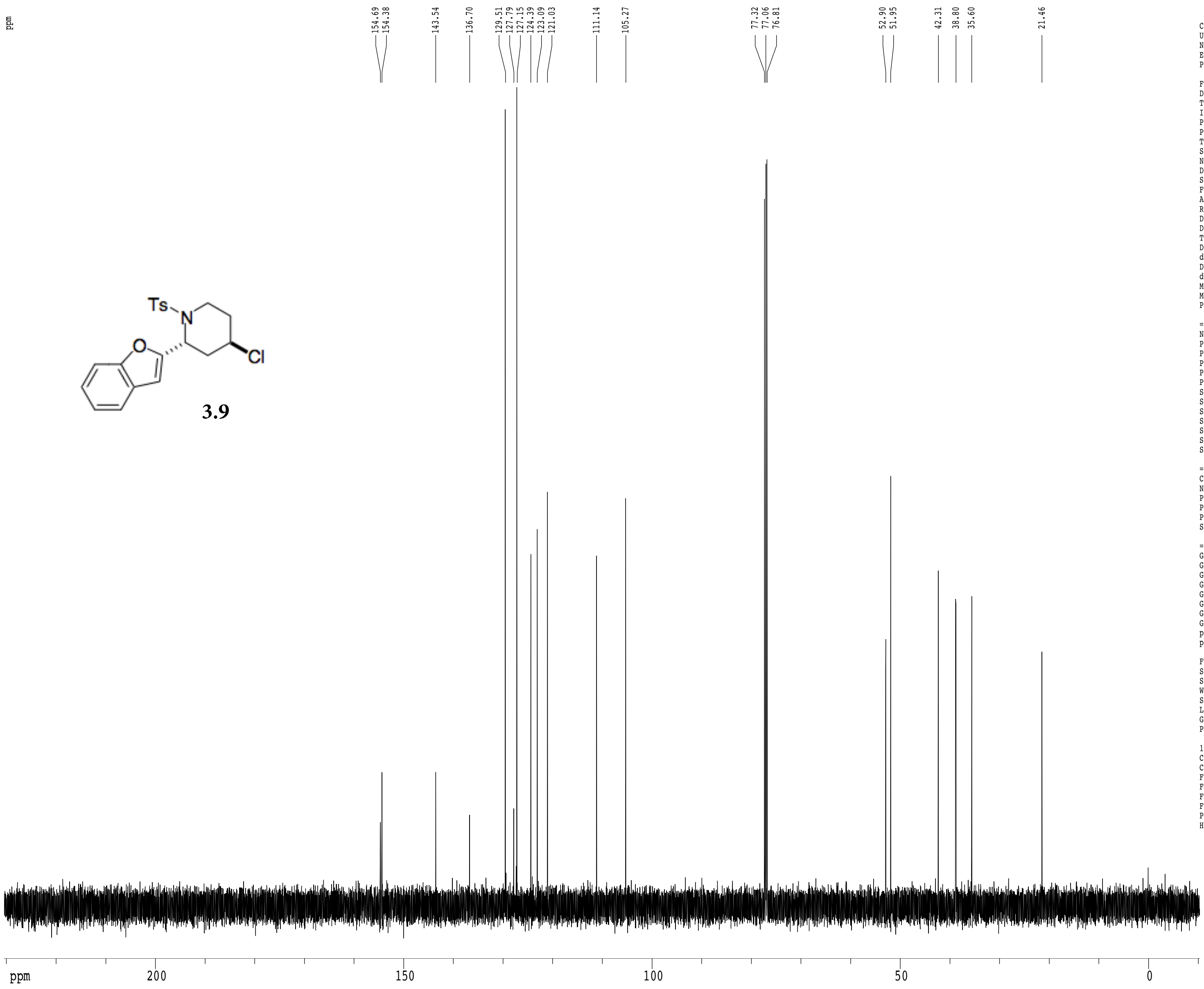
1H spectrum



3.9

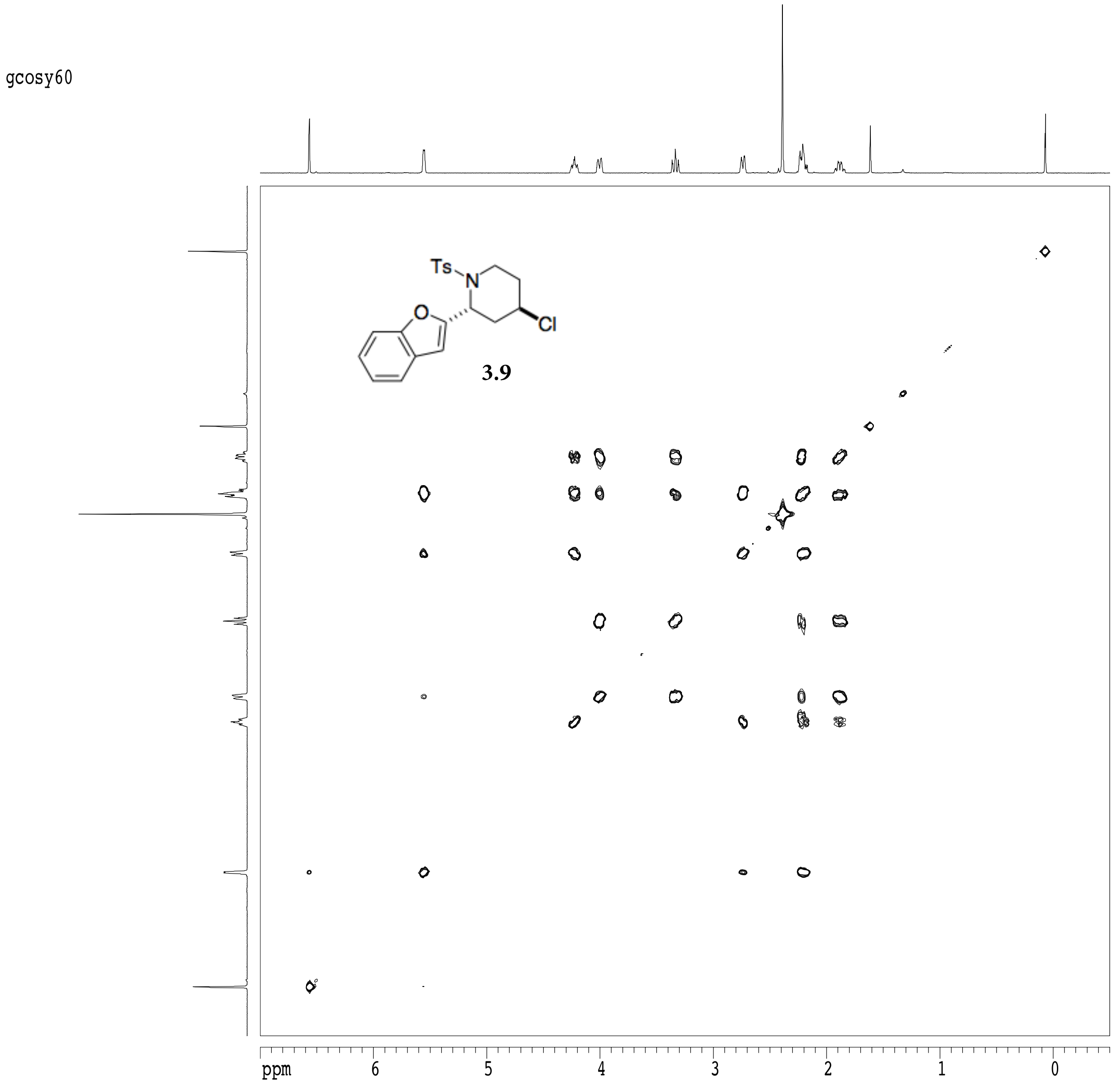
```
Current Data Parameters
USER           khewitt1
NAME        KAH-I-018-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180629
Time              14.43
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                  362
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300221 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



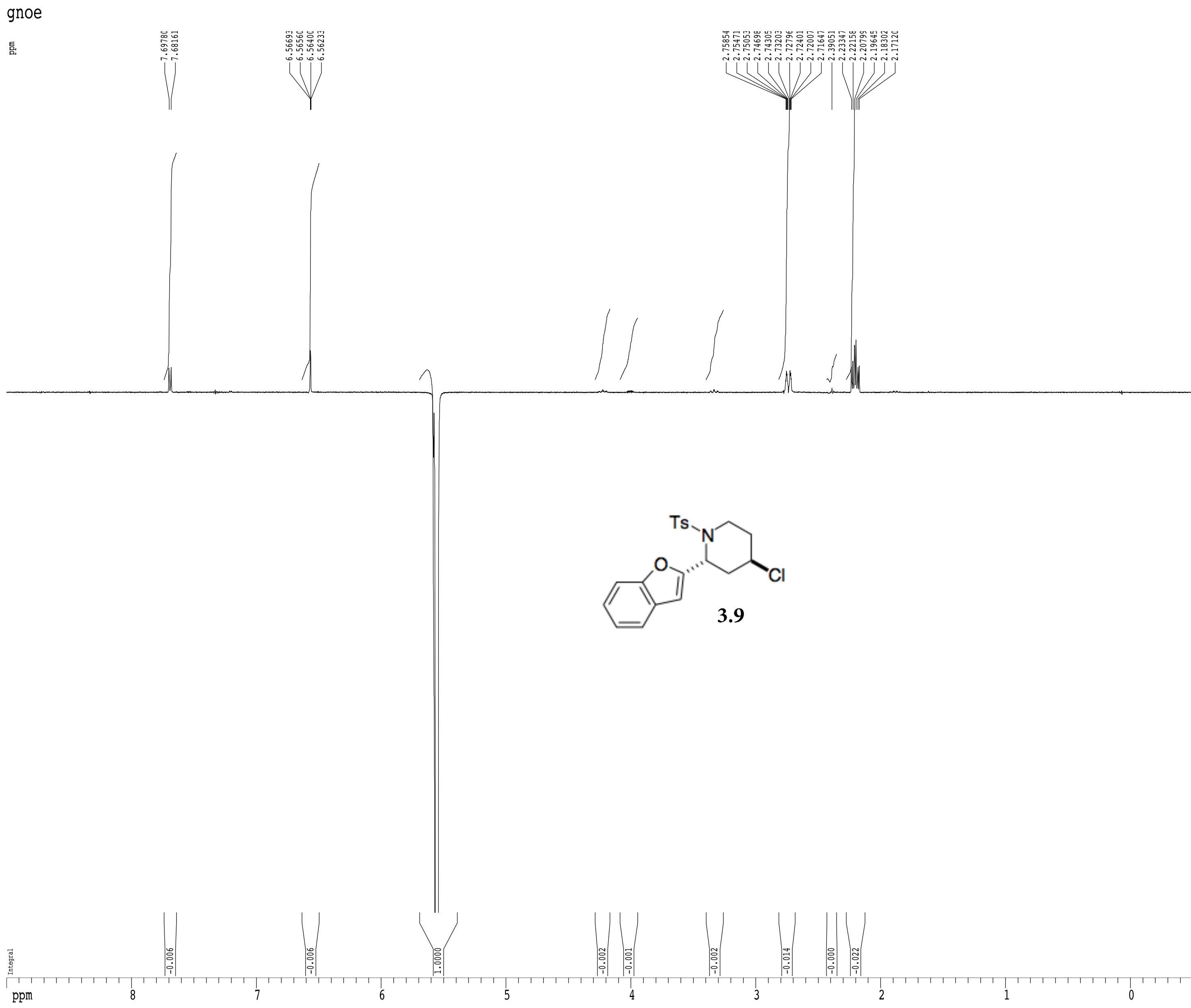
3.9

```
Current Data Parameters
USER          khewitt1
NAME        KAH-II-103C
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20190727
Time              17.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  376
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```



3.9

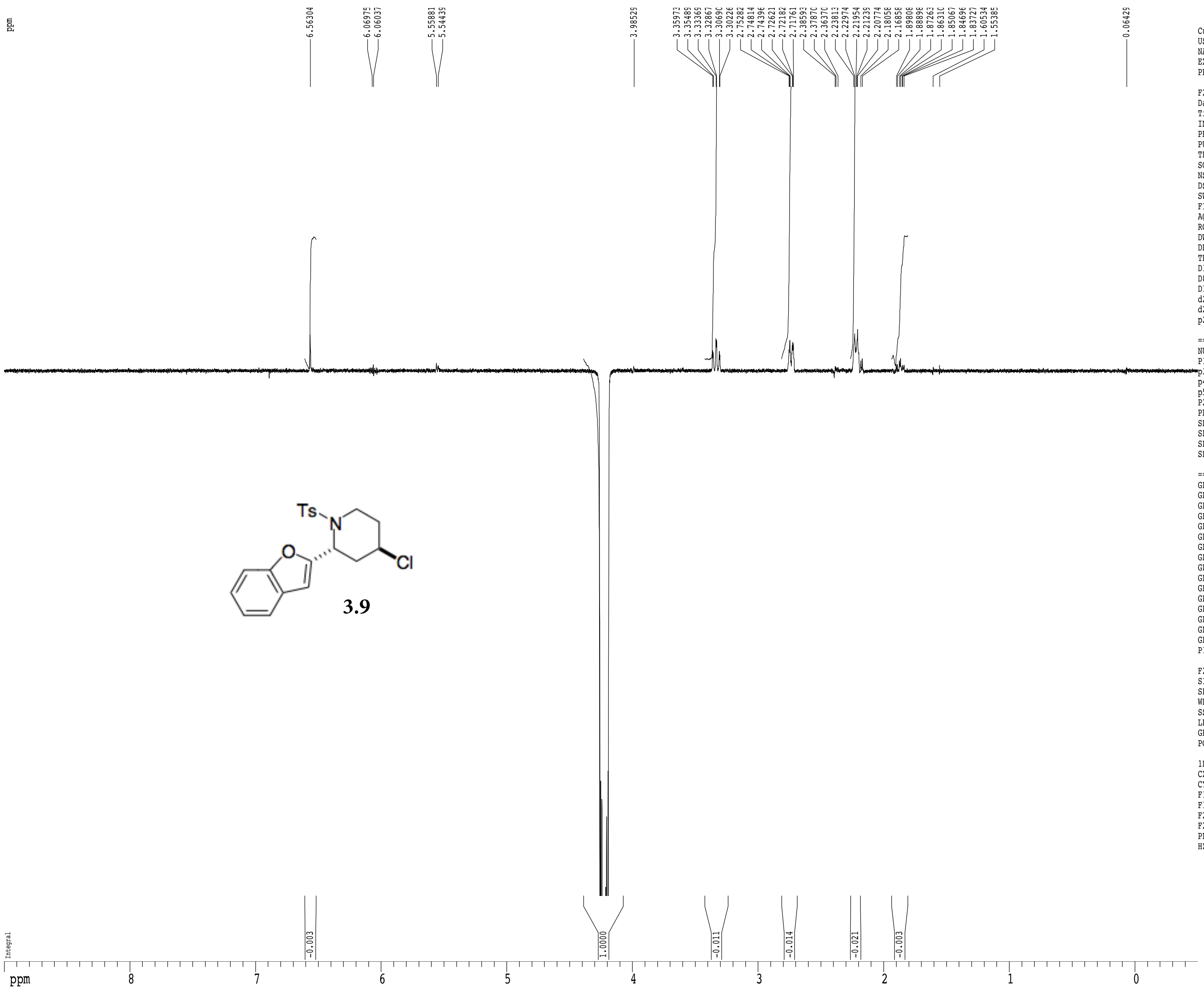
```
        Current Data Parameters
USER            khewitt1
NAME           KAH-I-018
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20180209
Time               16.07
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     2
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   362
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE         undefined

      F2 - Processing parameters
SI                  1024
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

          2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              7.000 ppm
F2LO             3501.54 Hz
F2PHI             -0.500 ppm
F2HI             -250.11 Hz
F1PLO              7.000 ppm
F1LO             3501.54 Hz
F1PHI             -0.509 ppm
F1HI             -254.47 Hz
F2PPMCM          0.50000 ppm/cm
F2HZCM         250.11000 Hz/cm
F1PPMCM          0.50058 ppm/cm
F1HZCM         250.40063 Hz/cm
```



3.9

```
Current Data Parameters
USER             khewitt1
NAME             KAH-I-018
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180209
Time                18.10
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      gnoe1cc.wu
TD                  65536
SOLVENT            CDCl3T
NS                    256
DS                      8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   71.8
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P12              40000.00 usec
PL1                  1.60 dB
SFO1          500.2227781 MHz
SP1                 61.60 dB
SPNAM1         gauss1.512
SPOFF1               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

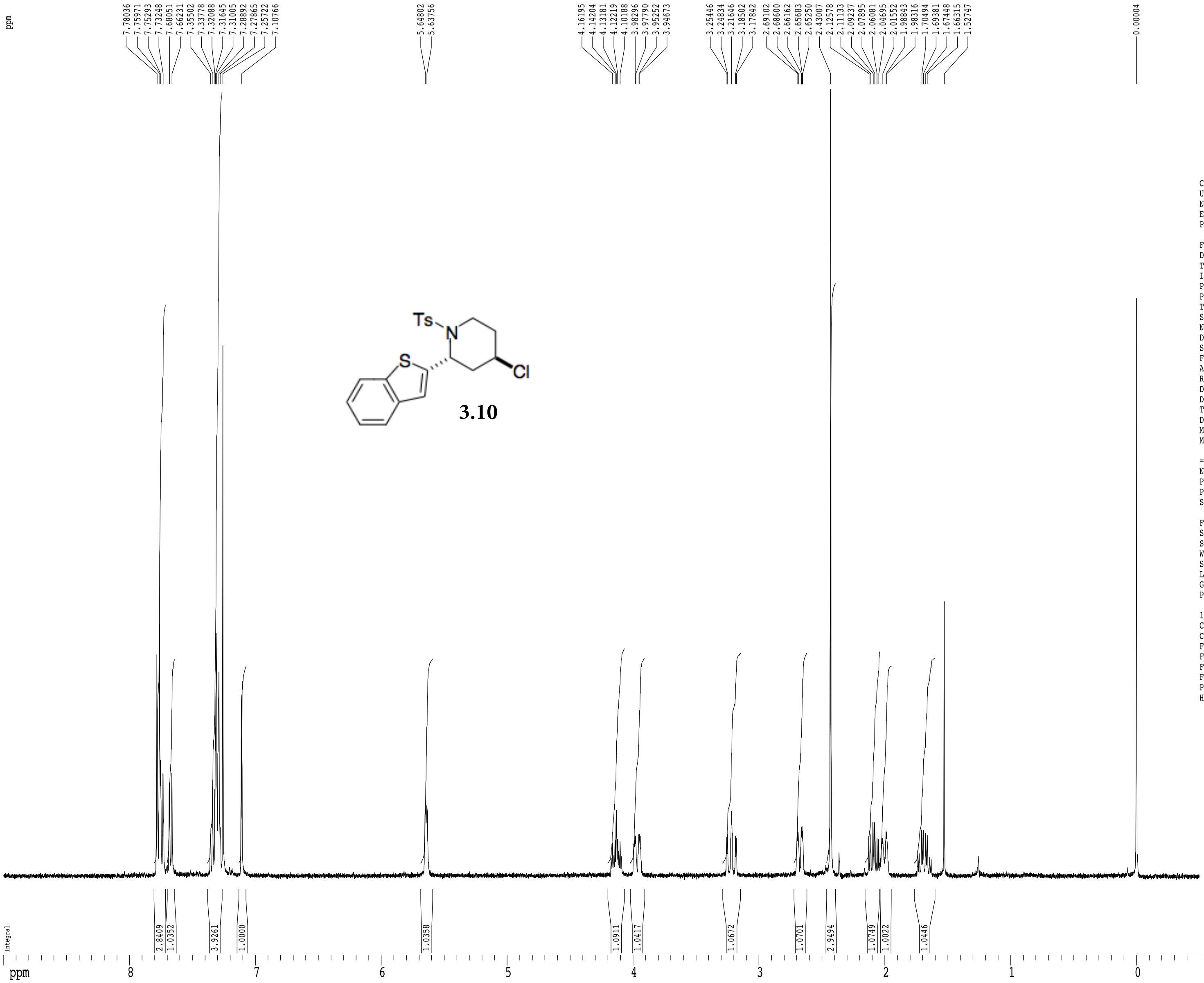
gnoe



3.9

```
Current Data Parameters
USER            khewitt1
NAME     KAH-II-103 NOE-2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20190729
Time              17.32
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                101.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2221122 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

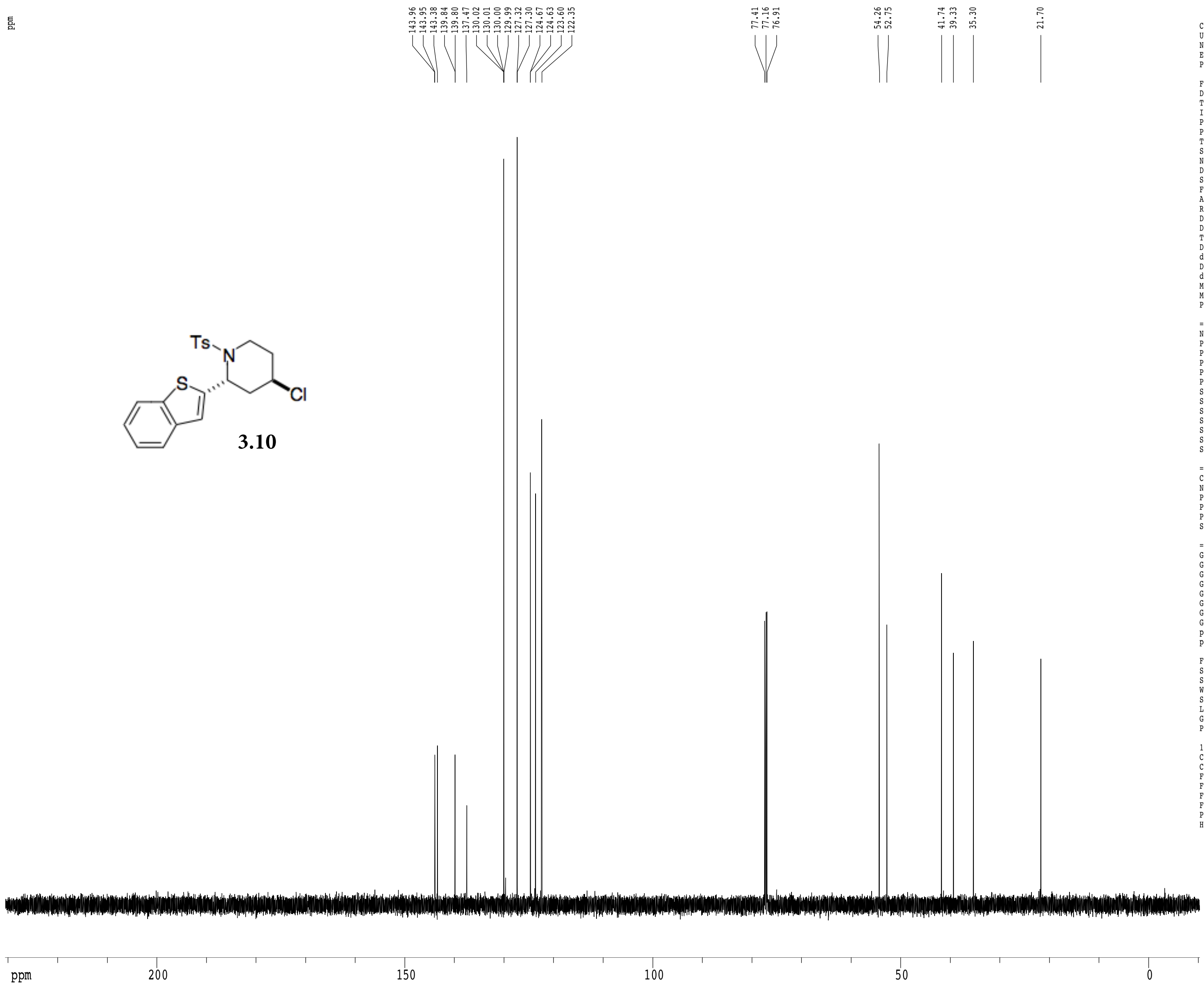
1H spectrum



3.10

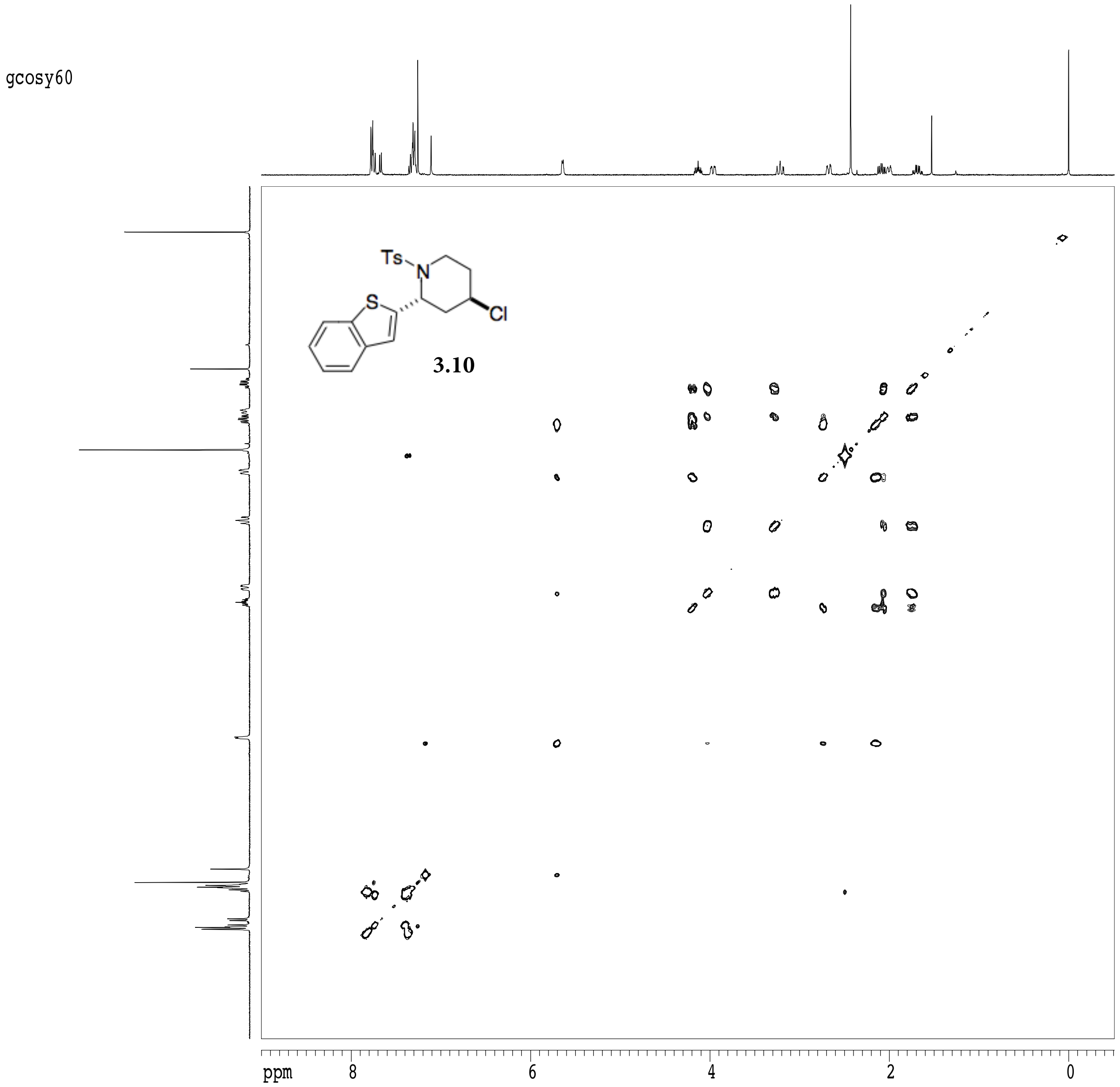
```
Current Data Parameters
USER           khewitt1
NAME         KAH-I-057-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20180728
Time              16.38
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                574.7
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300225 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



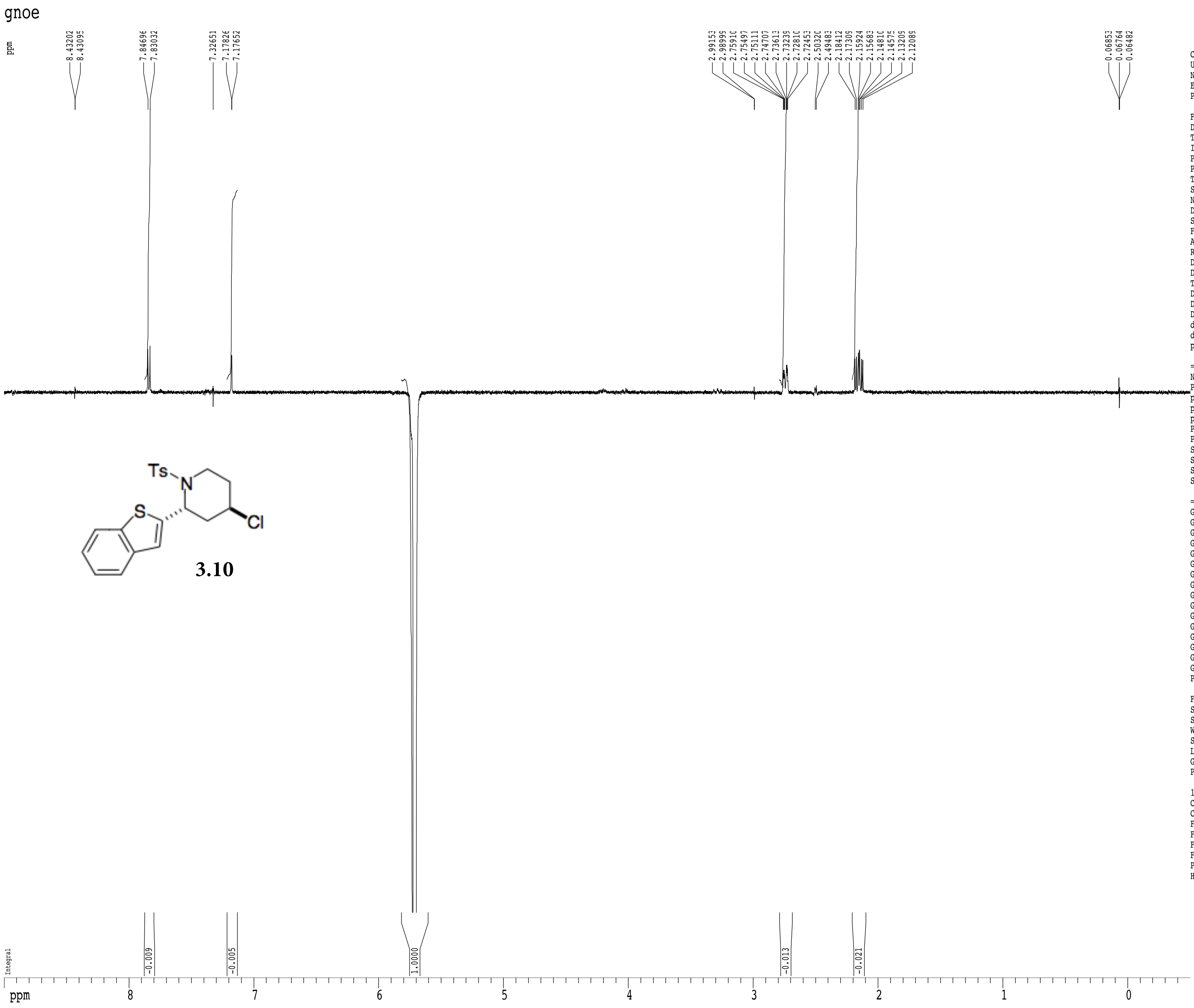
3.10

```
Current Data Parameters
USER            khewitt1
NAME          KAH-I-057-C
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20181110
Time                17.12
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT            CDCl3T
NS                    232
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                  13004
DW                 16.500 usec
DE                   6.00 usec
TE                  298.1 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P12               2000.00 usec
P20                500.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP2                  2.70 dB
SP4                  2.70 dB
SPNAM2        Crp60comp.4
SPNAM4     Crp60,0.5,20.1
SPOFF2               0.00 Hz
SPOFF4               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                23.54 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804094 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               230.637 ppm
F1               29009.68 Hz
F2P               -10.287 ppm
F2               -1293.96 Hz
PPMCM            10.56688 ppm/cm
HZCM           1329.10693 Hz/cm
```



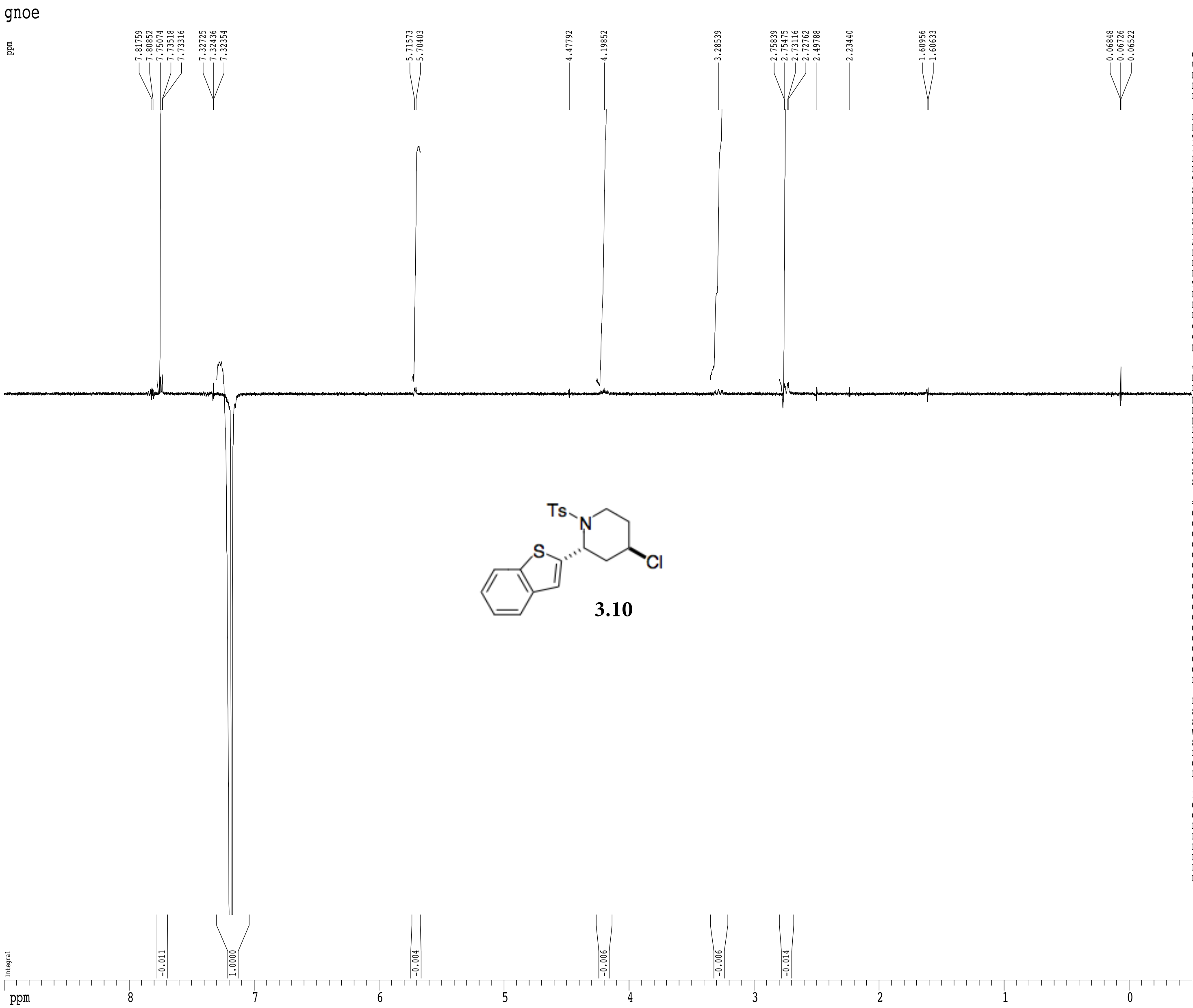
3.10

```
        Current Data Parameters
USER            khewitt1
NAME        KAH-I-057-Z
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20180728
Time               17.06
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                 724.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.002 ppm
F2LO             4503.14 Hz
F2PHI             -0.509 ppm
F2HI             -254.47 Hz
F1PLO              9.002 ppm
F1LO             4503.14 Hz
F1PHI             -0.509 ppm
F1HI             -254.47 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17416 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17416 Hz/cm
```



3.10

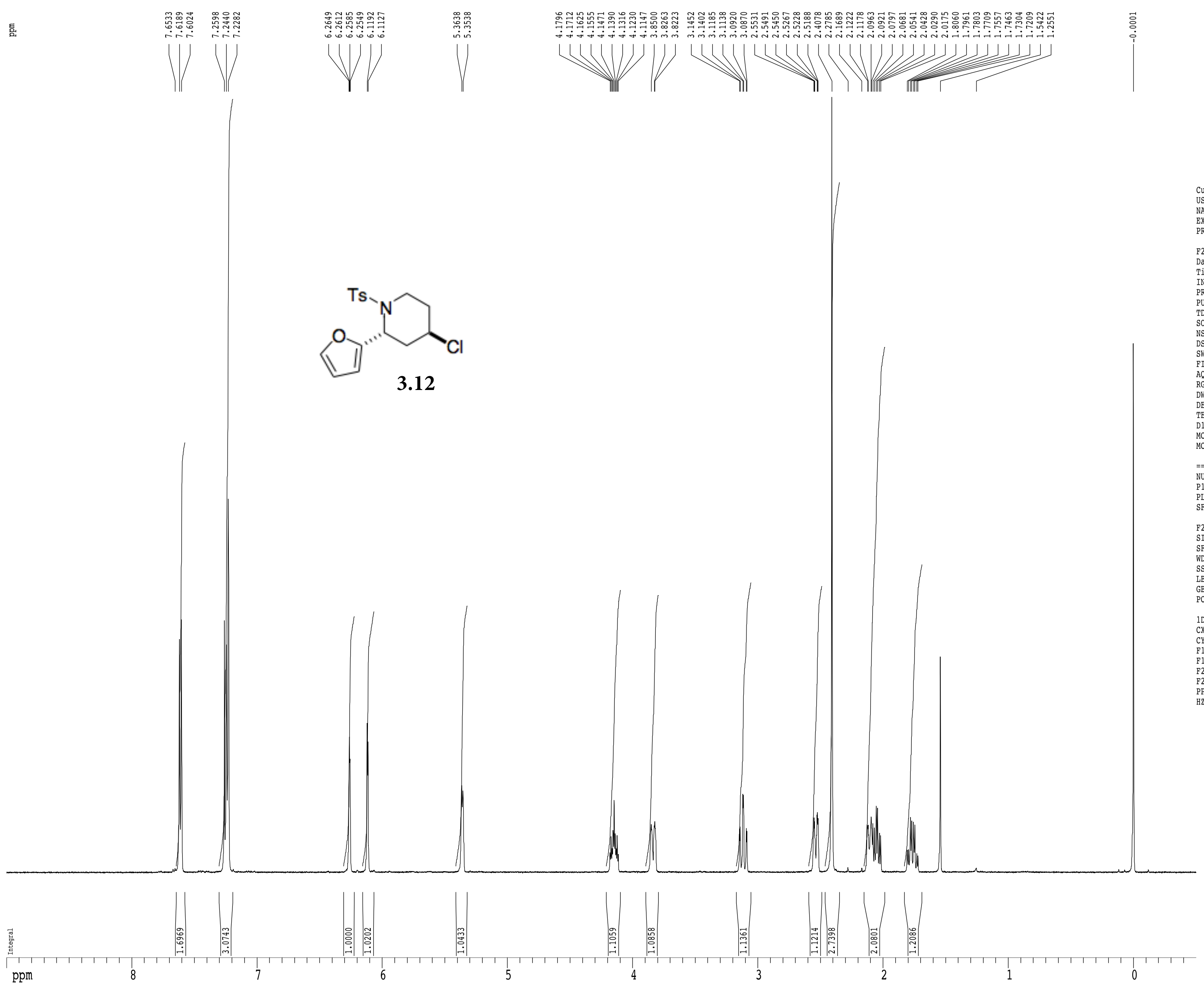
```
Current Data Parameters
USER              khewitt1
NAME            KAH-I-057-Z
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_             20181019
Time                 12.46
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                      64
DW                  62.400 usec
DE                    6.00 usec
TE               389108.7 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2228565 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```



3.10

```
Current Data Parameters
USER             khewitt1
NAME           KAH-I-057R
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20181220
Time                11.40
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    112
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   71.8
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2235904 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

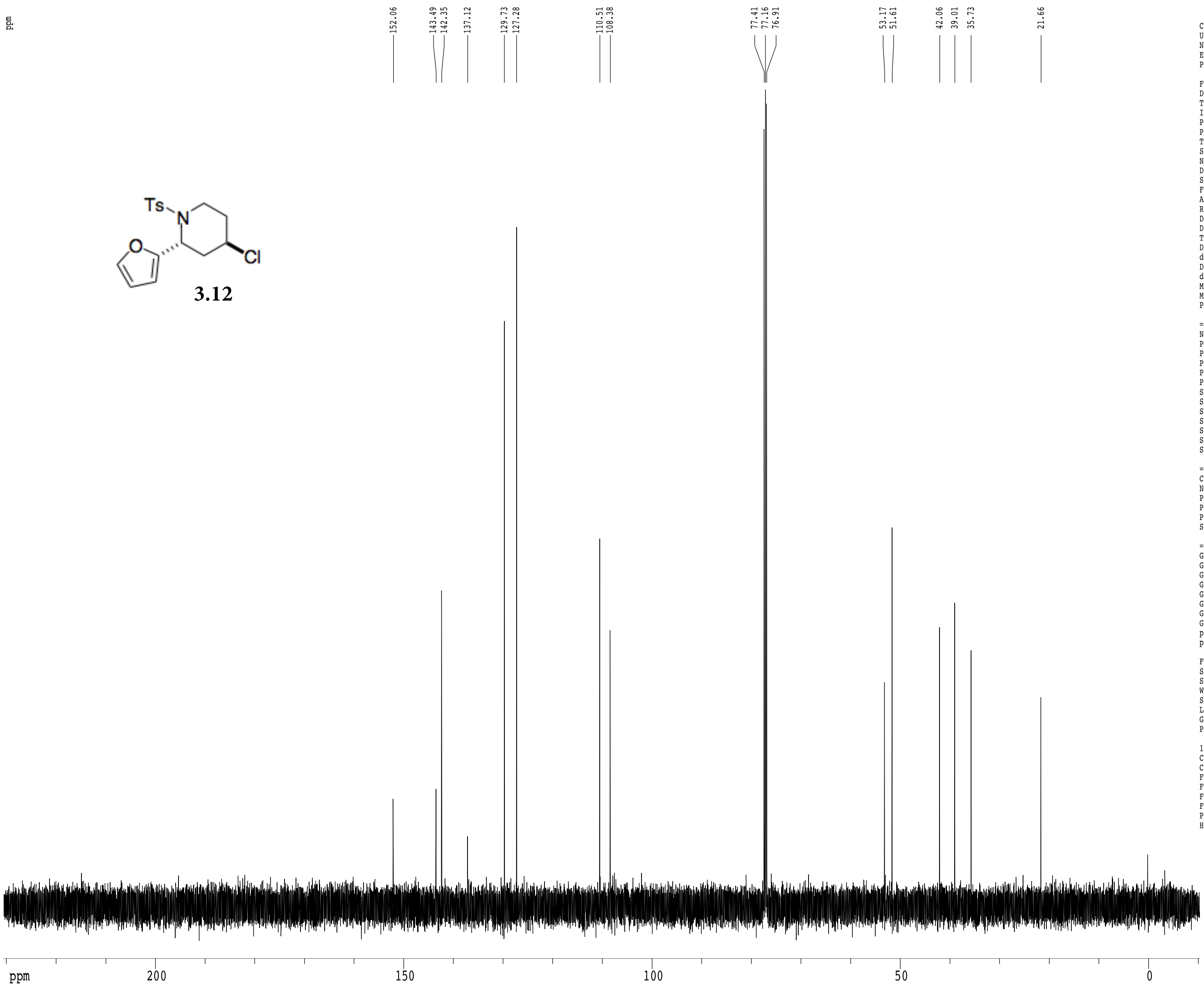
1H spectrum



3.12

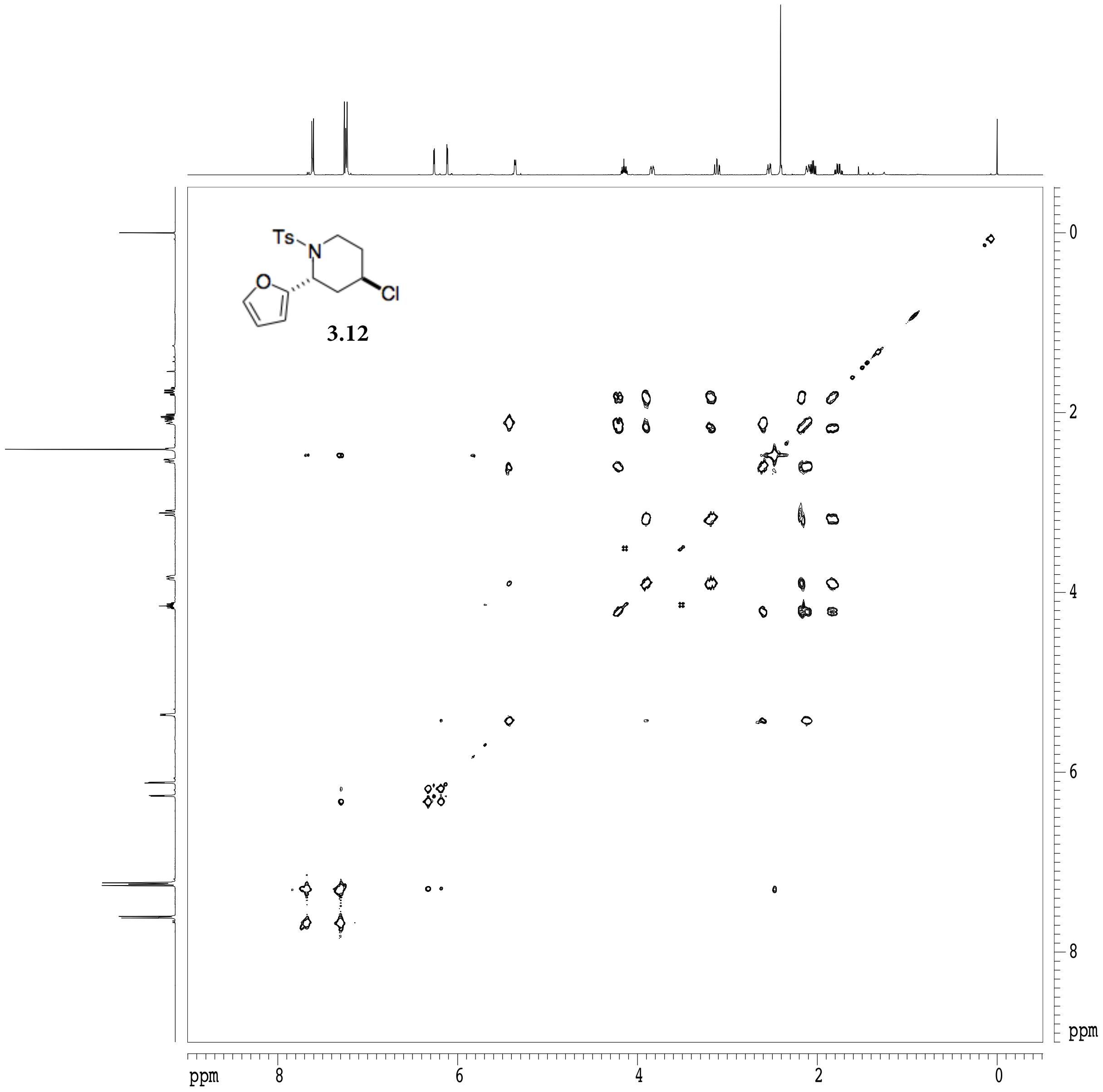
```
Current Data Parameters
USER           khewitt1
NAME       KAH-II-115-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190723
Time              14.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.2 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200319 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



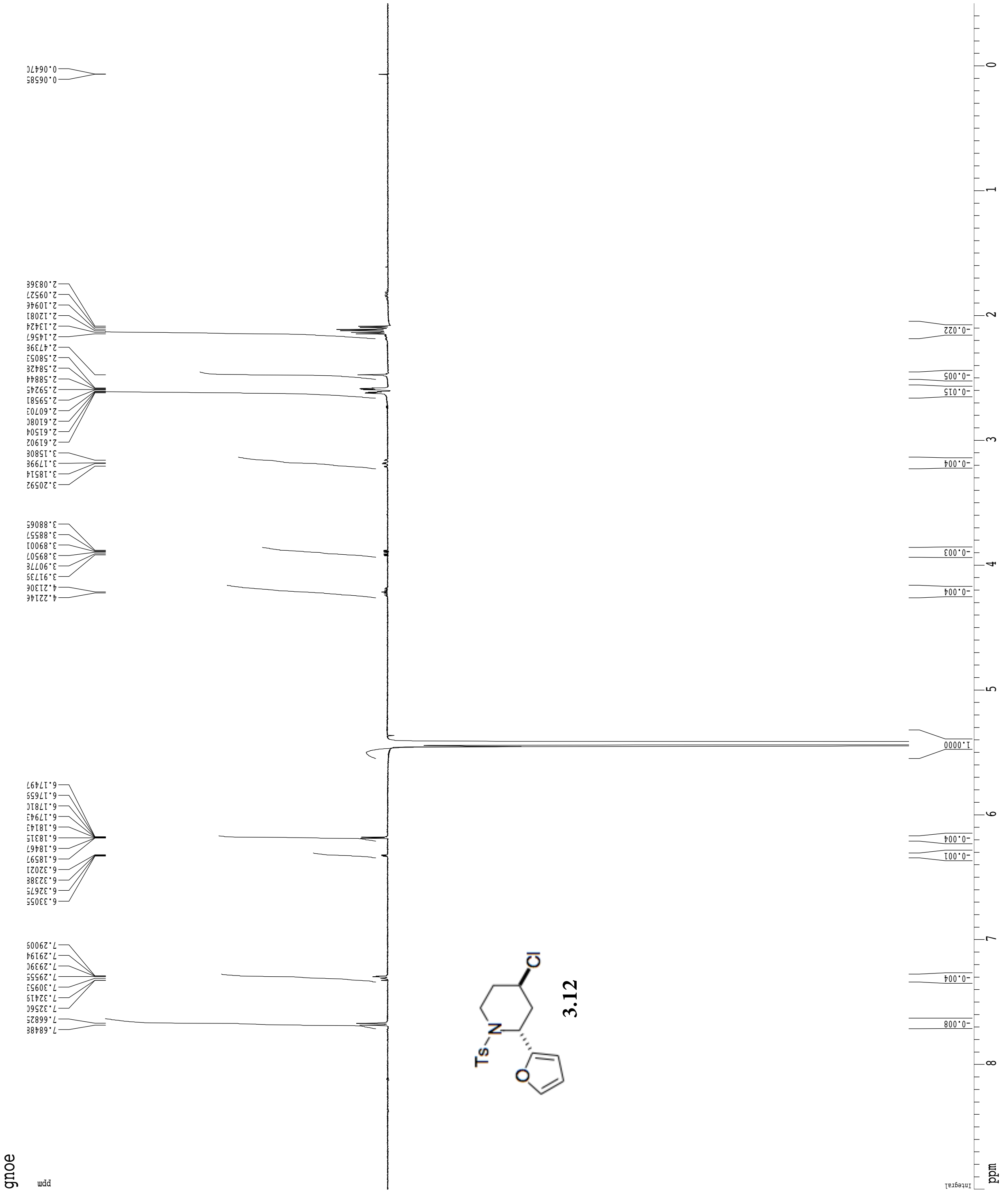
```
Current Data Parameters
USER            khewitt1
NAME       KAH-II-115-Z
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20190723
Time              14.51
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.1 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804062 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```

gcosy60



3.12

```
        Current Data Parameters
USER             khewitt1
NAME          KAH-I-134-Z
EXPNO                   2
PROCNO                  1

      F2 - Acquisition Parameters
Date_            20181015
Time                18.25
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      cosygp60.prd
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                     16
SWH              8012.820 Hz
FIDRES           3.912510 Hz
AQ              0.1278452 sec
RG                  406.4
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
d0             0.00000300 sec
D1             1.00000000 sec
d13            0.00000300 sec
D16            0.00020000 sec
IN0            0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                17.00 %
GPZ2                17.00 %
P16               1000.00 usec

      F1 - Acquisition parameters
ND0                     1
TD                    512
SFO1             500.2235 MHz
FIDRES          15.650040 Hz
SW                 16.018 ppm
FnMODE                 QF

      F2 - Processing parameters
SI                   1024
SF            500.2200000 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

      F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.2200000 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0

         2D NMR plot parameters
CX2                 15.00 cm
CX1                 15.00 cm
F2PLO               9.002 ppm
F2LO              4503.14 Hz
F2PHI              -0.509 ppm
F2HI              -254.47 Hz
F1PLO               9.002 ppm
F1LO              4503.14 Hz
F1PHI              -0.509 ppm
F1HI              -254.47 Hz
F2PPMCM           0.63407 ppm/cm
F2HZCM          317.17416 Hz/cm
F1PPMCM           0.63407 ppm/cm
F1HZCM          317.17416 Hz/cm
```


gnoe
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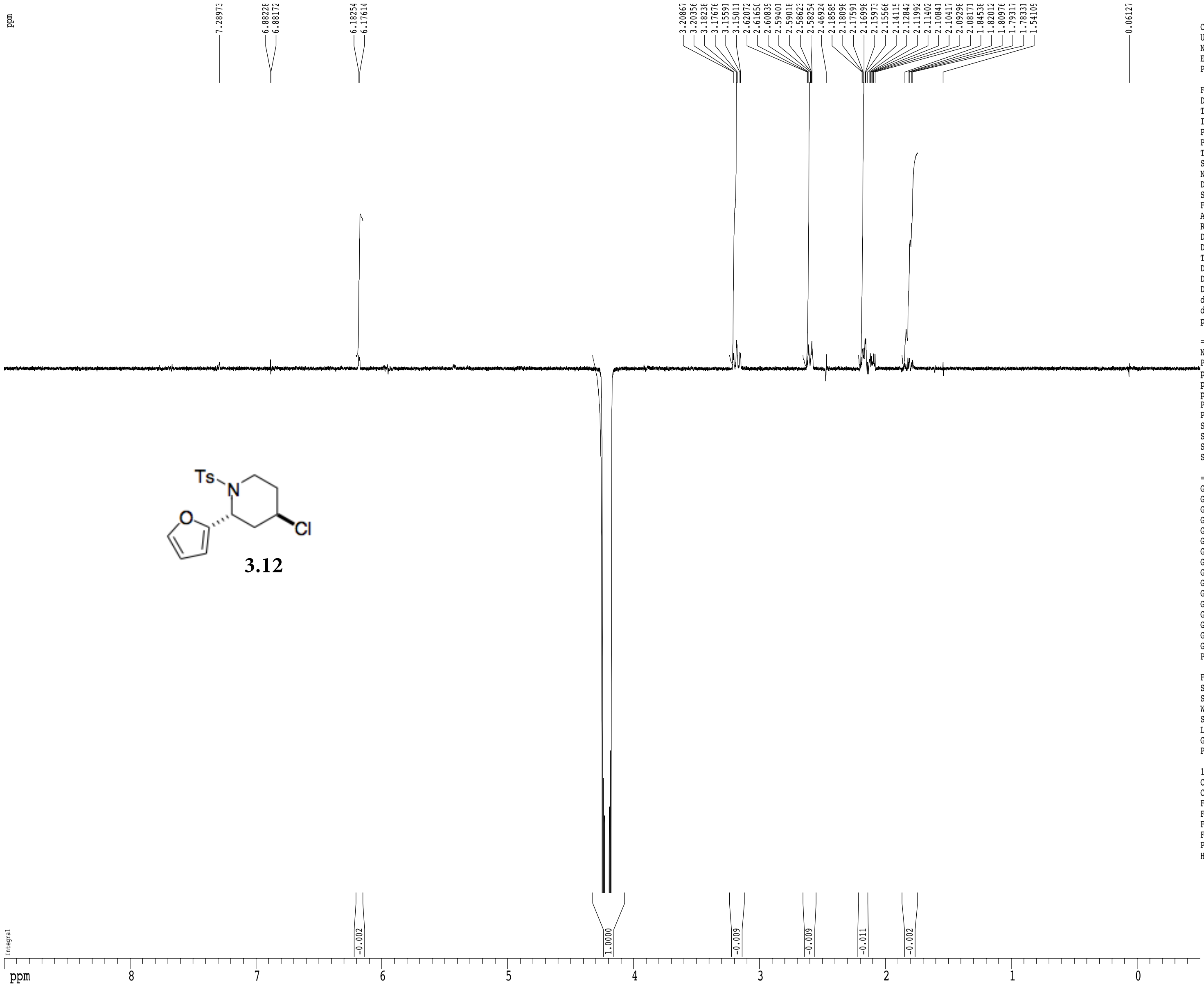
0.06585
2.08368
2.09527
2.10946
2.12081
2.13424
2.14567
2.47398
2.58053
2.58428
2.58844
2.59245
2.59581
2.60703
2.61080
2.61504
2.61902
3.15808
3.17998
3.18514
3.20592
3.88065
3.88557
3.89001
3.89507
3.90778
3.91739
4.21306
4.22146
6.17497
6.17659
6.17810
6.17943
6.18143
6.18315
6.18467
6.18597
6.32021
6.32388
6.32675
6.33055
7.29009
7.29194
7.29390
7.29555
7.30953
7.32419
7.32560
7.66825
7.68488
Ts
N
Cl
O
-0.022
-0.005
-0.015
-0.004
-0.003
-0.004
1.0000
-0.004
-0.001
-0.004
-0.008
Integral
0
1
2
3
4
5
6
7
8
ppm

3.12

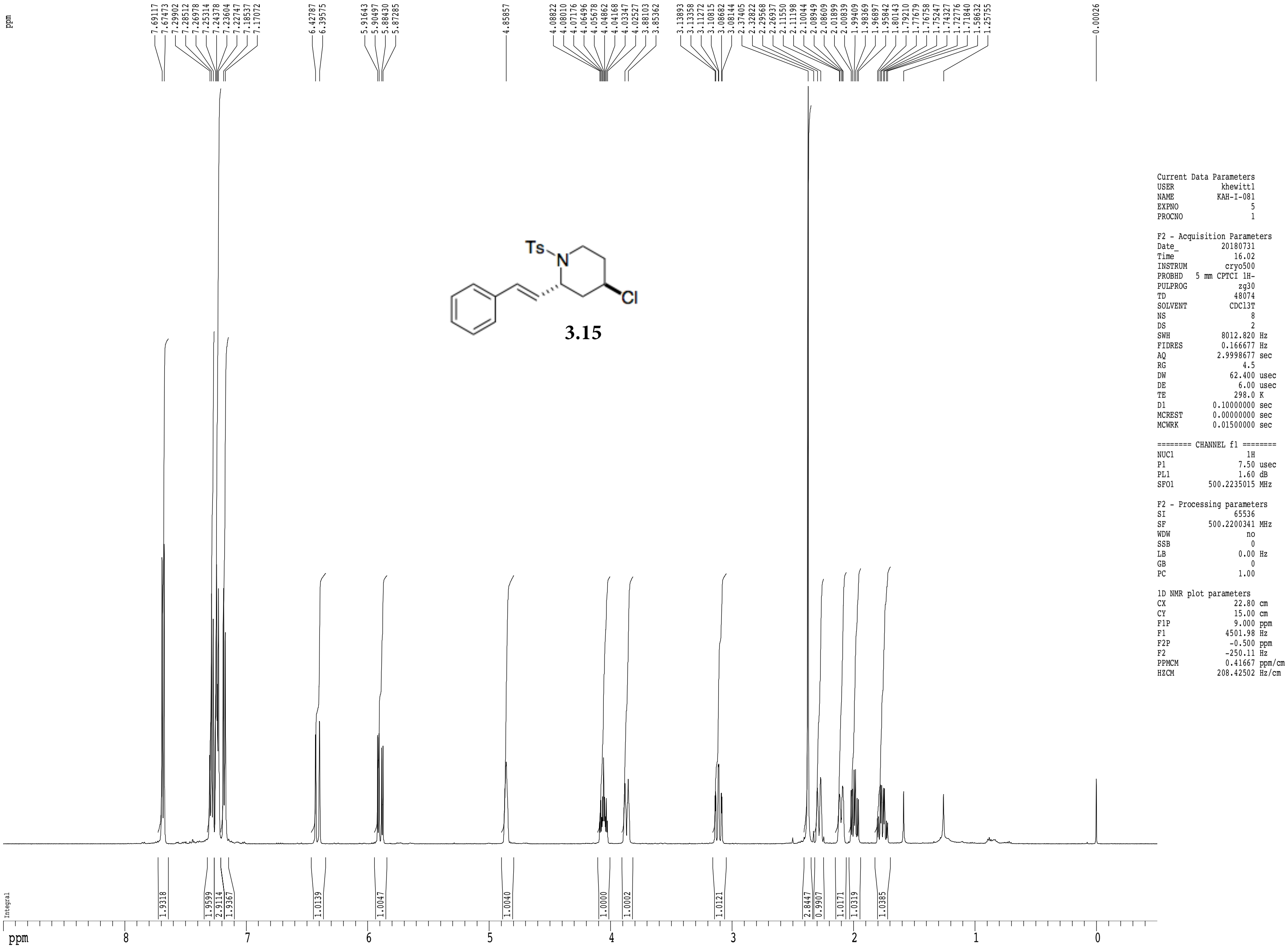
gnoe



3.12

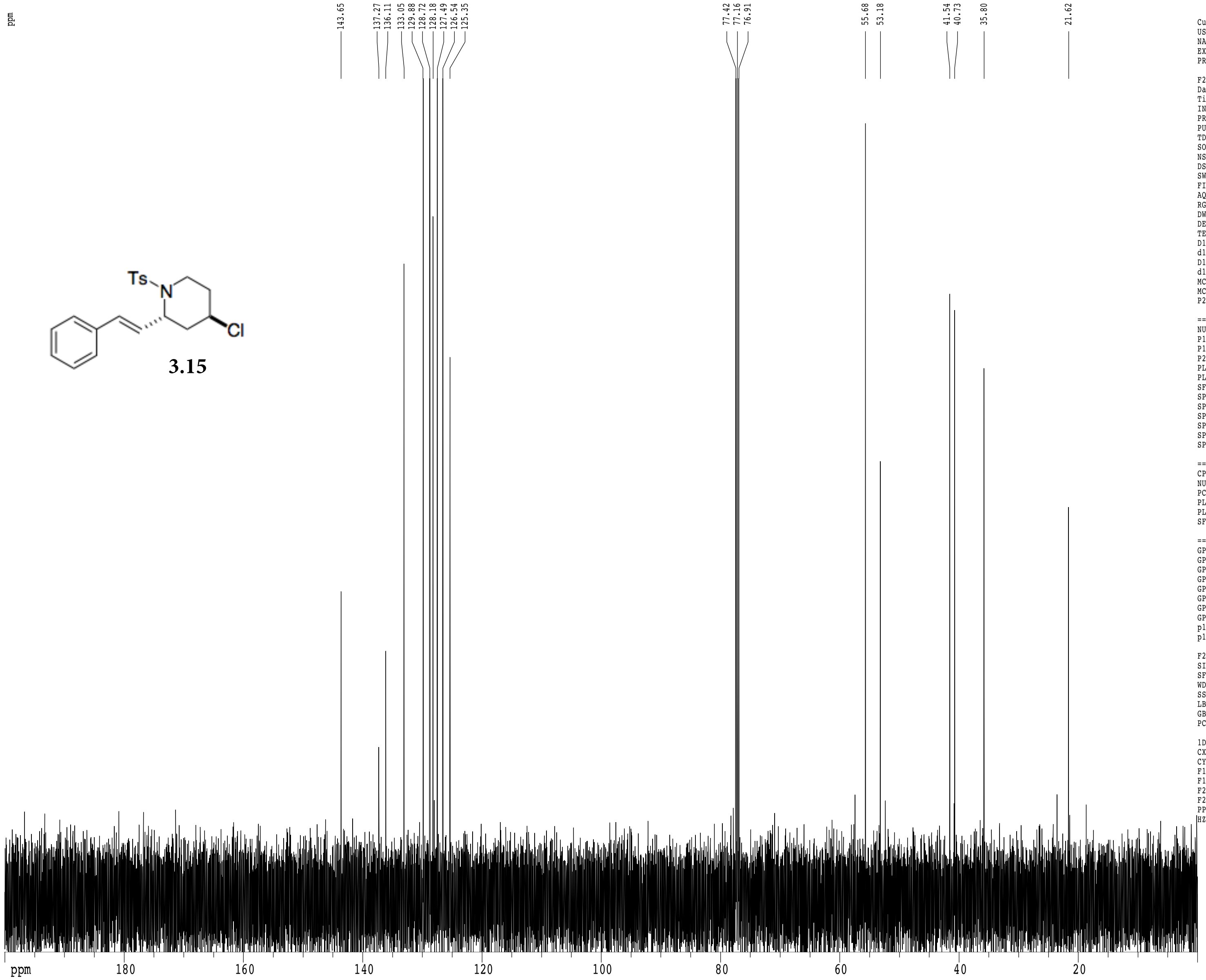
```
Current Data Parameters
USER             khewitt1
NAME          KAH-II-115-Z
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190723
Time                14.49
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   80.6
DW                 62.400 usec
DE                   6.00 usec
TE                  298.2 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2221064 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

1H spectrum



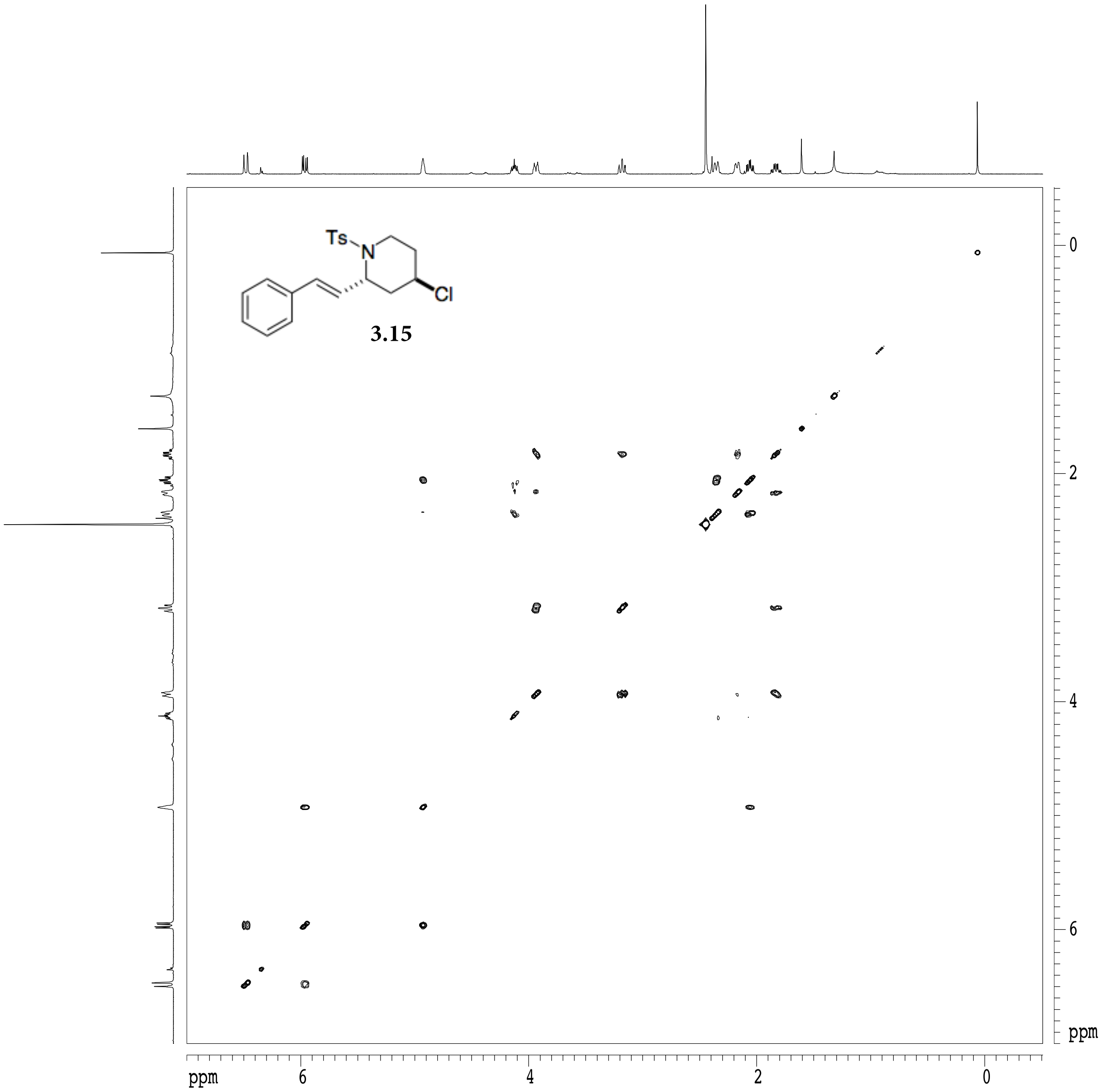
3.15

Z-restored spin-echo 13C spectrum with 1H decoupling

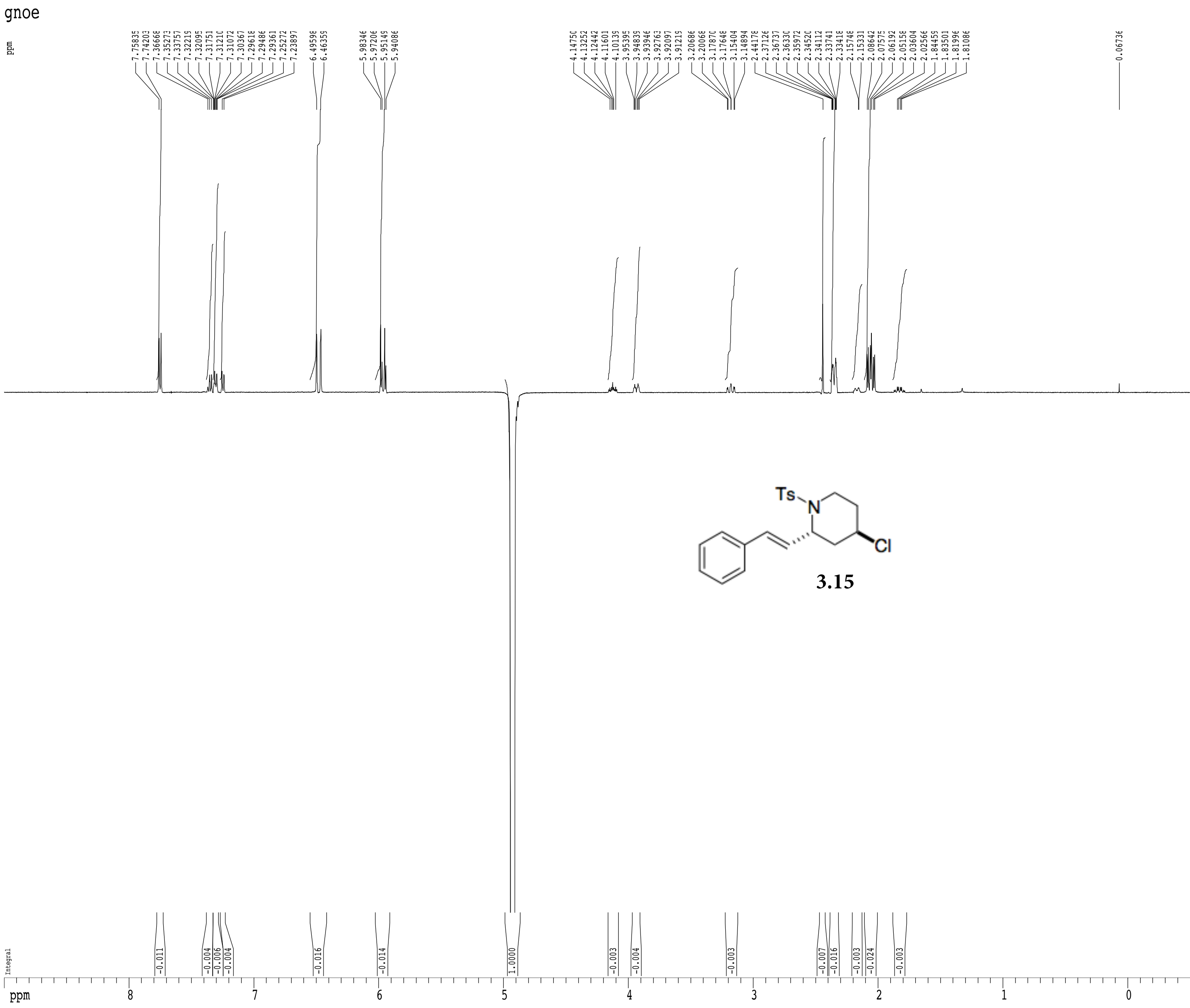


```
Current Data Parameters
USER            khewitt1
NAME           KAH-I-081
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180801
Time               15.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT          CDCl3T
NS                   151
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804062 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.50

1D NMR plot parameters
CX                 22.80 cm
CY                 30.00 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            8.77193 ppm/cm
HZCM          1103.33691 Hz/cm
```

gcosy60

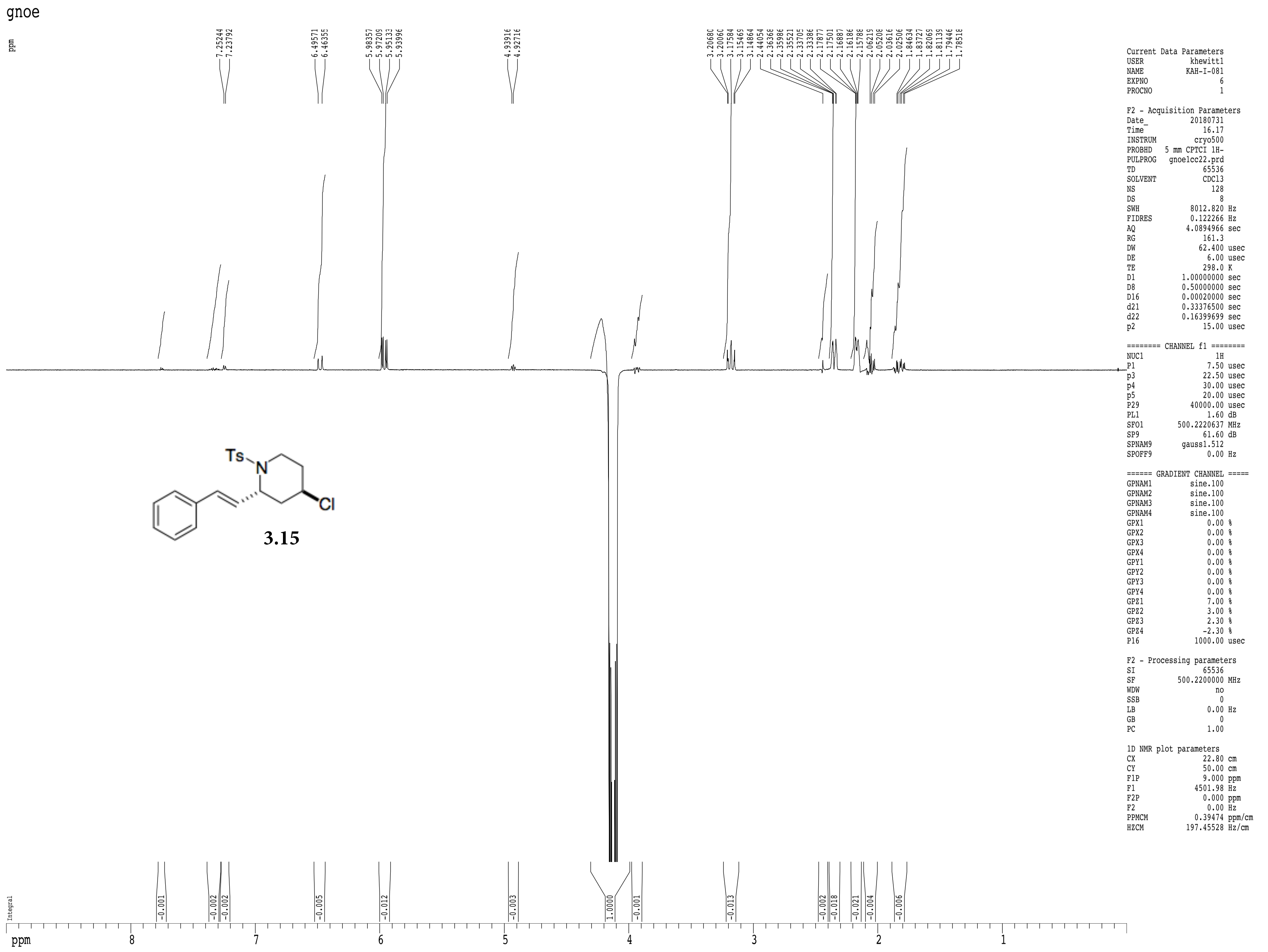


```
     Current Data Parameters
USER            khewitt1
NAME          KAH-I-071-2
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20180728
Time               15.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   362
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

 ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

 ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

       2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              7.000 ppm
F2LO             3501.54 Hz
F2PHI             -0.509 ppm
F2HI             -254.47 Hz
F1PLO              7.000 ppm
F1LO             3501.54 Hz
F1PHI             -0.509 ppm
F1HI             -254.47 Hz
F2PPMCM          0.50058 ppm/cm
F2HZCM         250.40063 Hz/cm
F1PPMCM          0.50058 ppm/cm
F1HZCM         250.40063 Hz/cm
```



3.15

```
Current Data Parameters
USER            khewitt1
NAME           KAH-I-081
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180731
Time               16.28
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                    91
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 101.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2224645 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

gnoe
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5.93996
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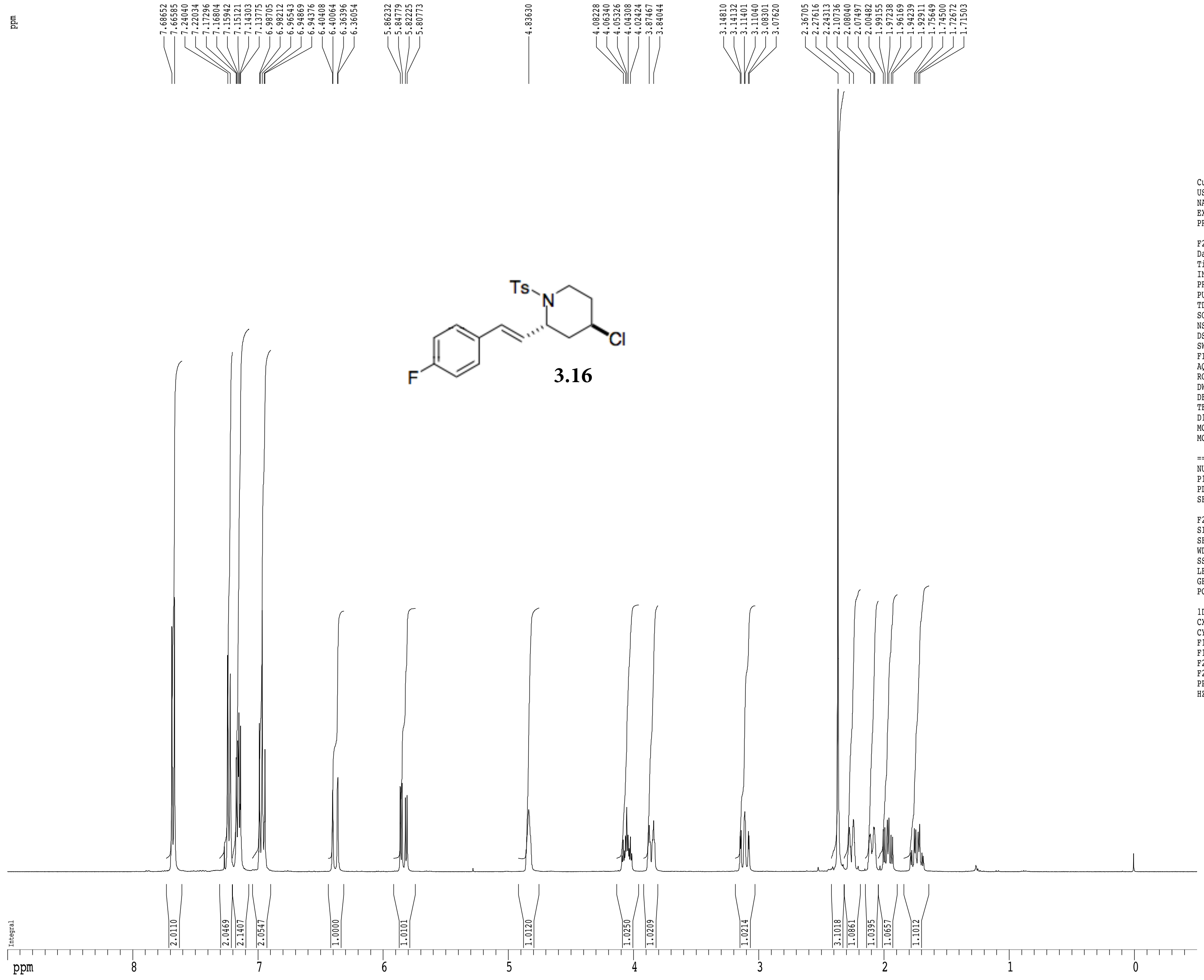
4.92716
3.20680
3.20060
3.17584
3.15469
3.14864
2.44054
2.36368
2.35986
2.35521
2.33705
2.33386
2.17877
2.17501
2.16887
2.16186
2.15788
2.06219
2.05208
2.03618
2.02506
1.84634
1.83727
1.82069
1.81139
1.79446
1.78518
Ts
N
Cl
Integral
-0.001
-0.002
-0.002
-0.005
-0.012
-0.003
1.0000
-0.001
-0.013
-0.002
-0.018
-0.021
-0.004
-0.006
ppm
8
7
6
5
4
3
2
1
Current Data Parameters
USER khewitt1
NAME KAH-I-081
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180731
Time 16.17
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoe1cc22.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2220637 MHz
SP9 61.60 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz
====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm

3.15

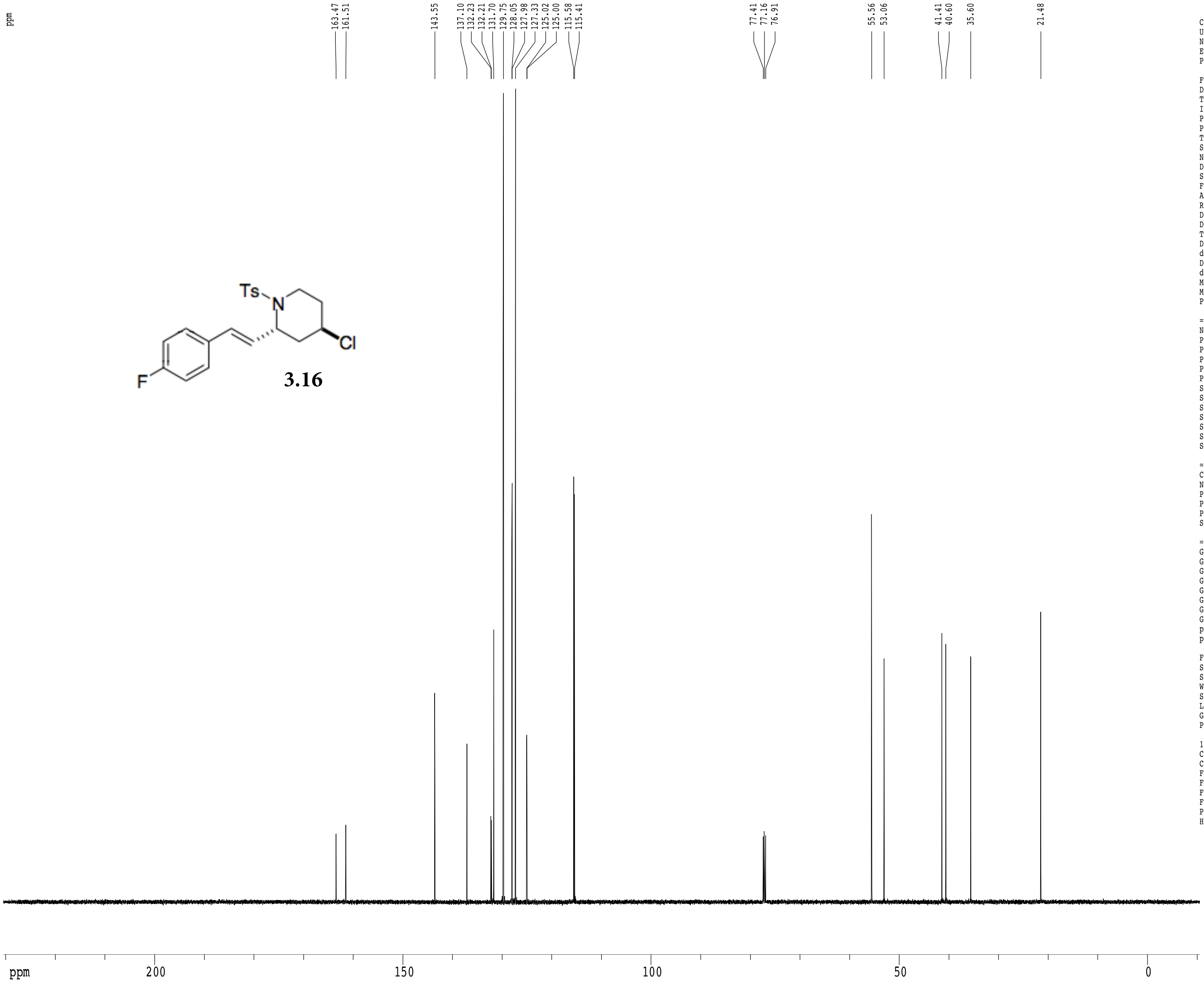
1H spectrum



3.16

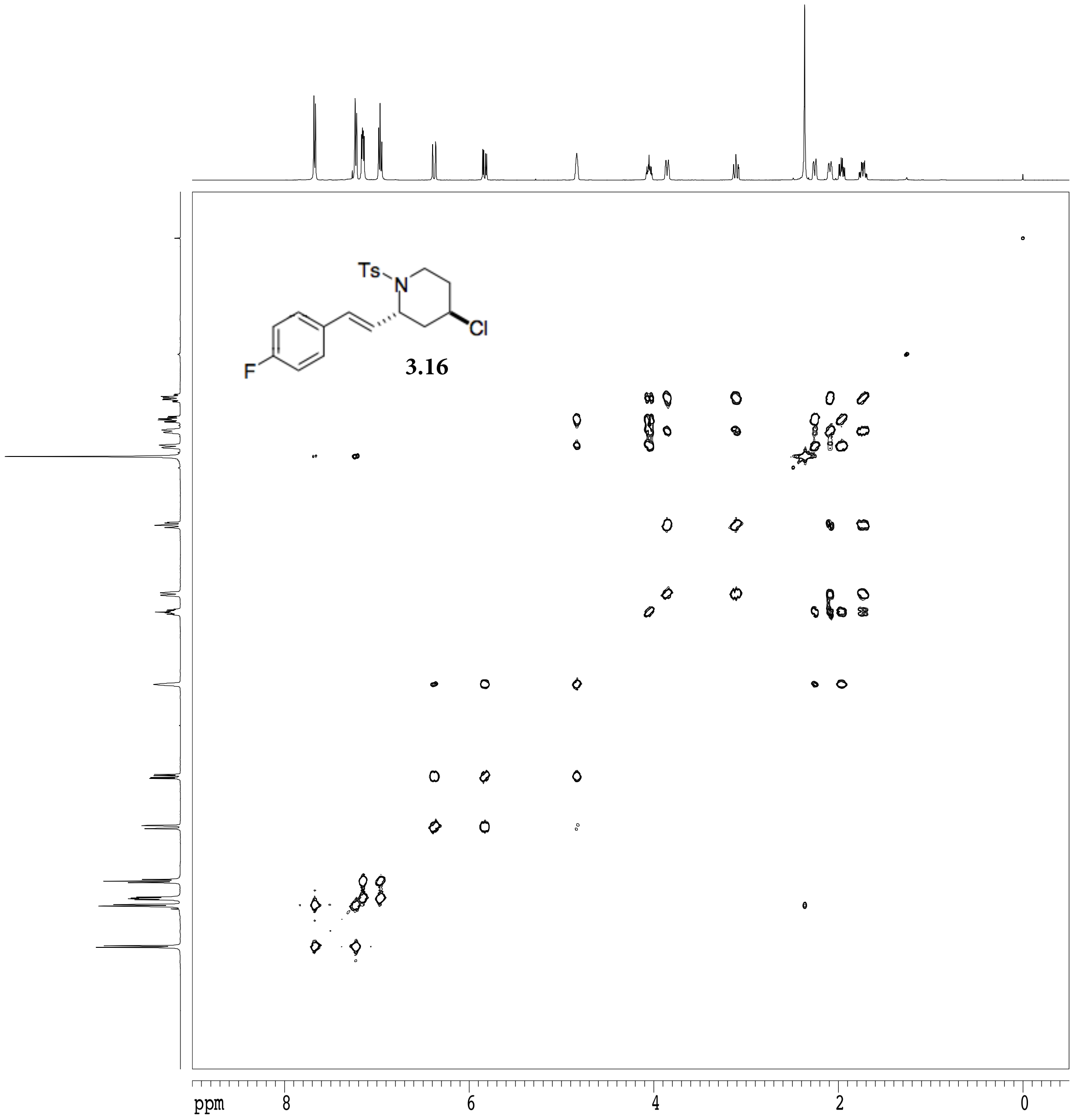
```
Current Data Parameters
USER           khewitt1
NAME       KAH-II-042-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190403
Time              10.13
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                   32
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



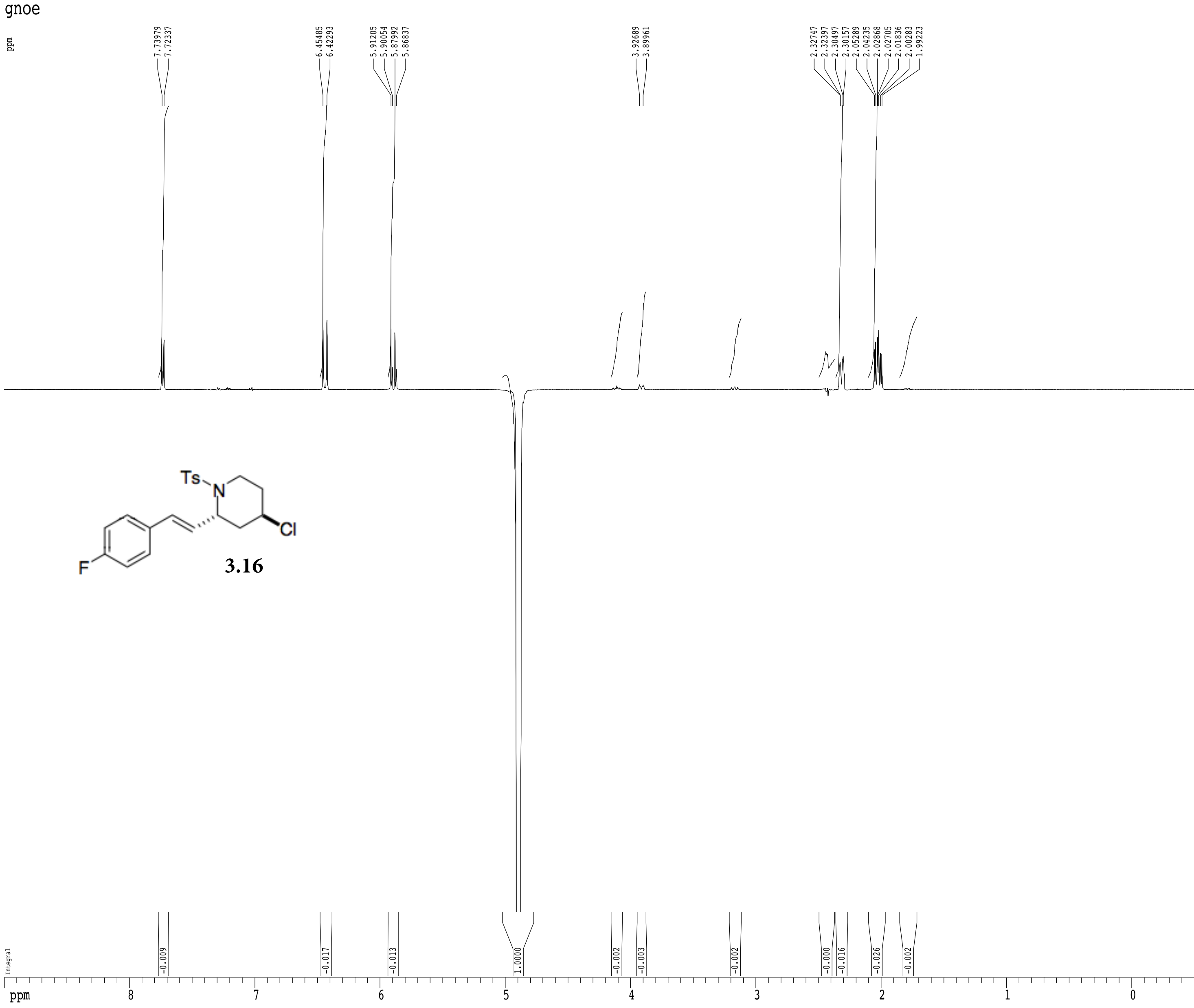
3.16

```
Current Data Parameters
USER             khewitt1
NAME          KAH-II-042-Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190403
Time                 10.45
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                      96
DS                      16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                    6502
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   2.70 dB
SP4                   2.70 dB
SPNAM2        Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 23.54 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804237 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                230.422 ppm
F1                28982.62 Hz
F2P                -10.498 ppm
F2                -1320.42 Hz
PPMCM             10.56667 ppm/cm
HZCM            1329.08032 Hz/cm
```



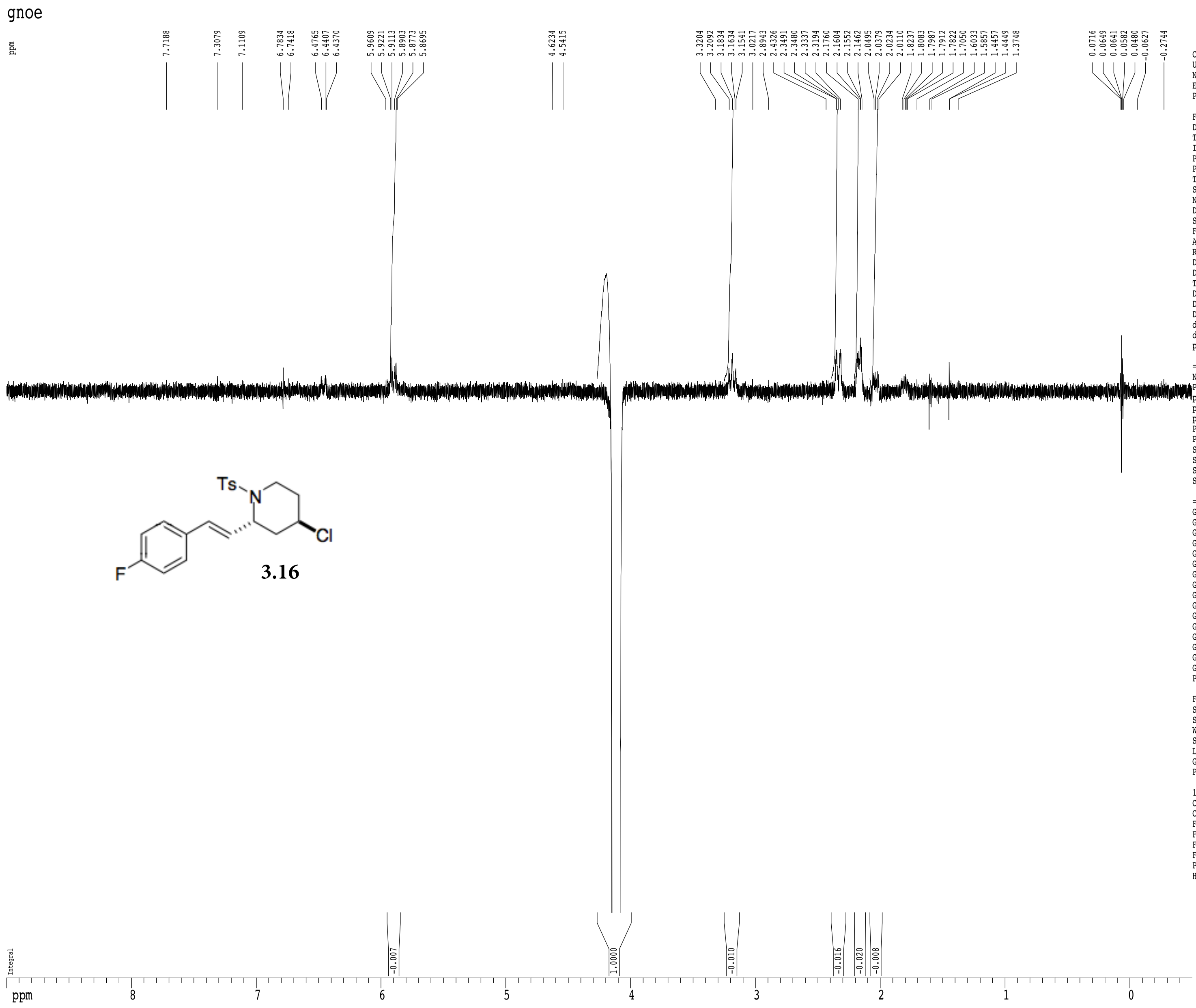
3.16

```
      Current Data Parameters
USER           khewitt1
NAME       KAH-II-042-Z
EXPNO                 3
PROCNO                1

      F2 - Acquisition Parameters
Date_          20190403
Time              10.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                 28.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

    ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200300 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200300 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.000 ppm
F2LO            4501.98 Hz
F2PHI            -0.500 ppm
F2HI            -250.11 Hz
F1PLO             9.000 ppm
F1LO            4501.98 Hz
F1PHI            -0.500 ppm
F1HI            -250.11 Hz
F2PPMCM         0.63333 ppm/cm
F2HZCM        316.80603 Hz/cm
F1PPMCM         0.63333 ppm/cm
F1HZCM        316.80603 Hz/cm
```



3.16

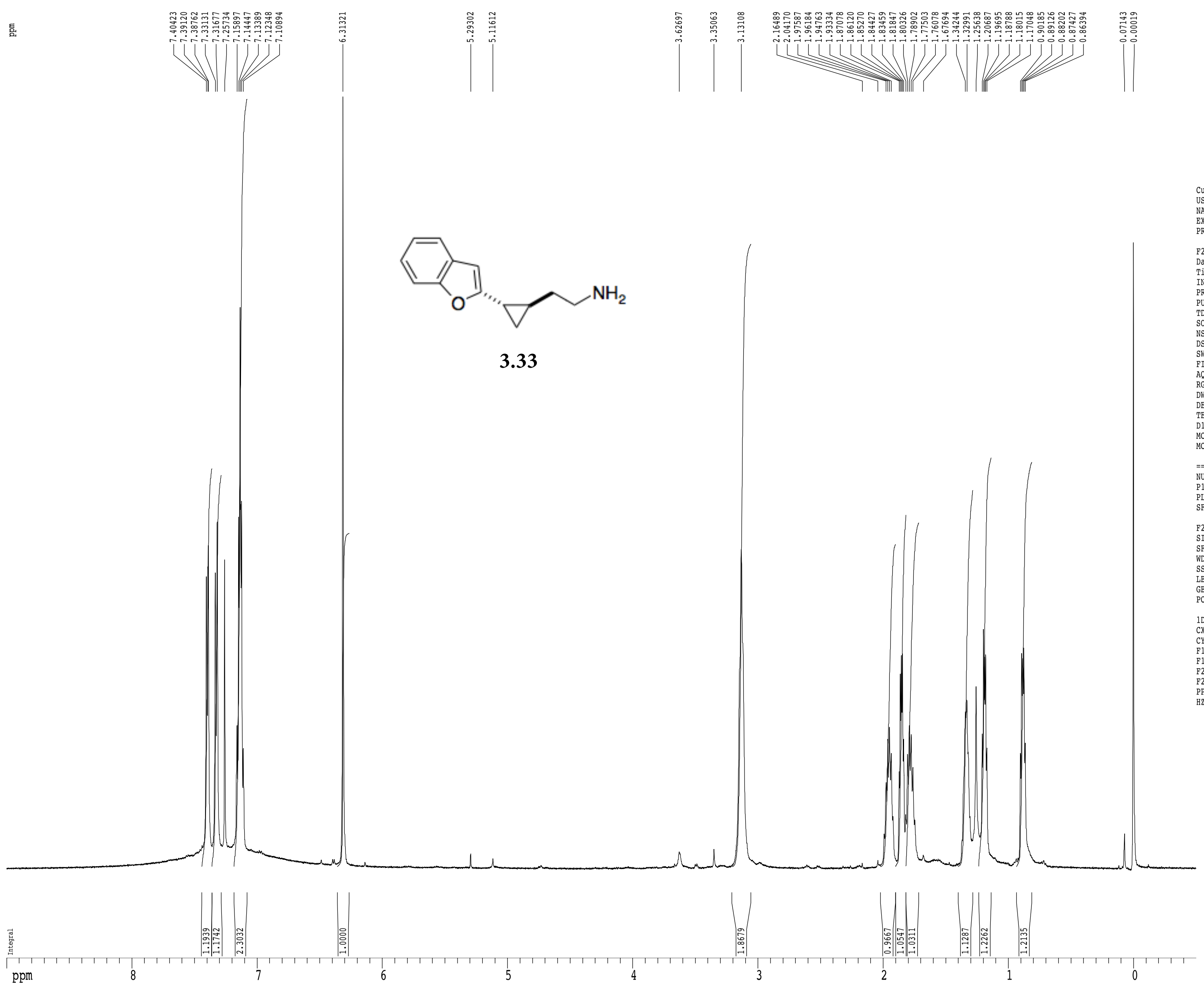
```
Current Data Parameters
USER            khewitt1
NAME         KAH-II-042-Z
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190403
Time               17.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                    57
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2224475 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



3.16

```
Current Data Parameters
USER           khewitt1
NAME      KAH-II-042-NOE
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20190727
Time              16.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                101.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2220584 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

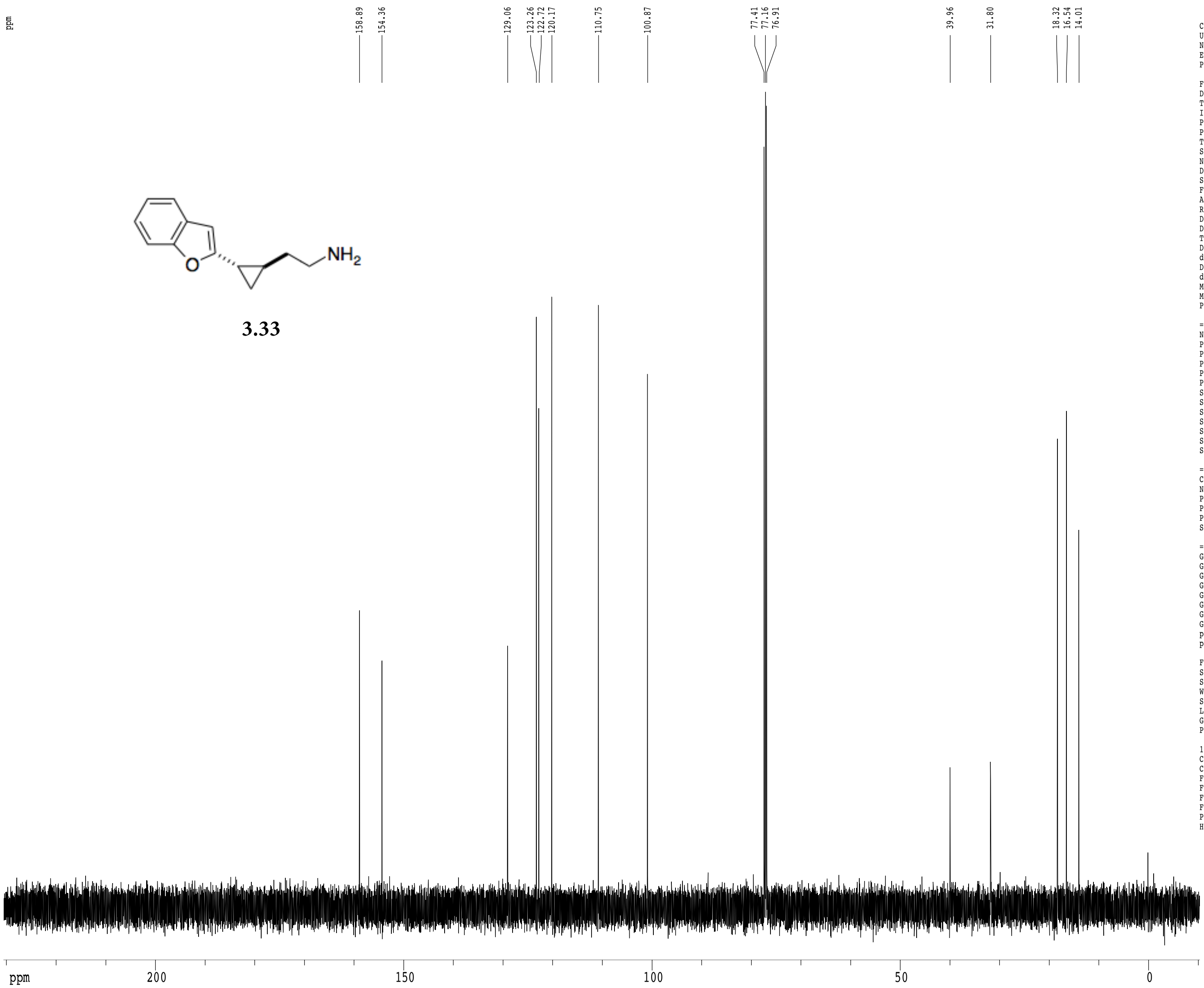
1H spectrum



3.33

```
Current Data Parameters
USER           khewitt1
NAME        KAH-II-119Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190726
Time              16.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200332 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

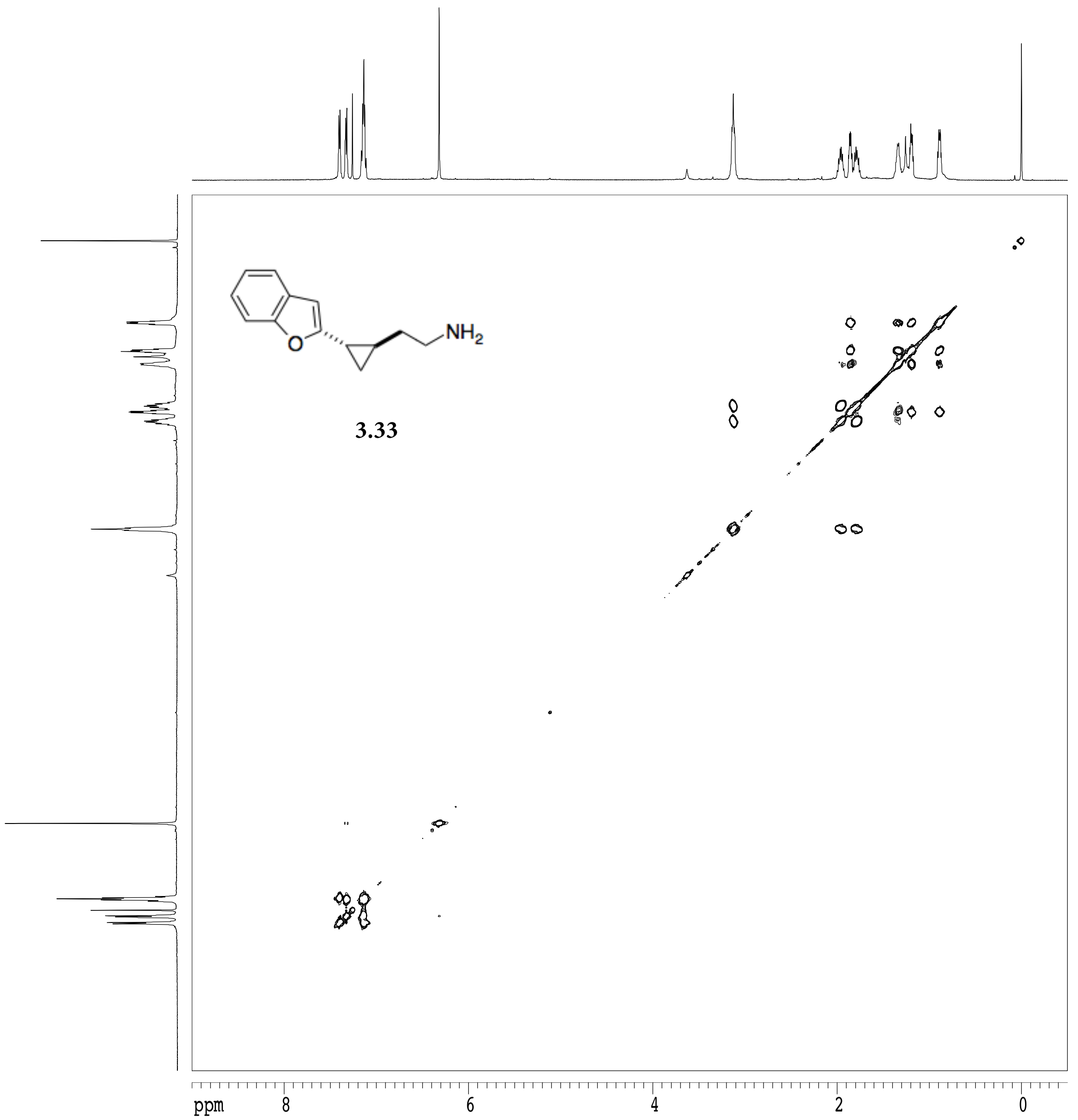
Z-restored spin-echo 13C spectrum with 1H decoupling



3.33

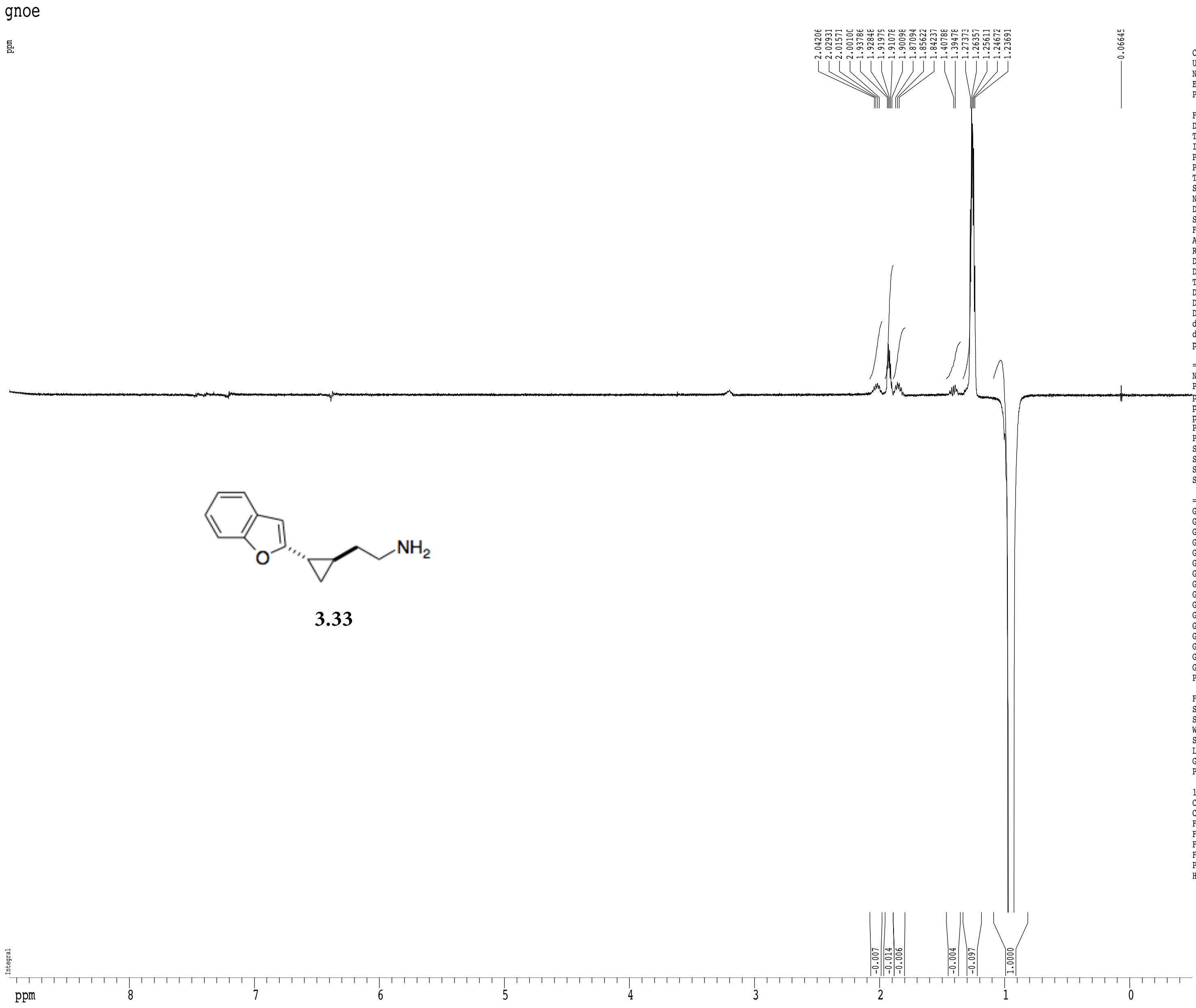
```
Current Data Parameters
USER          khewitt1
NAME        KAH-II-119Z
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20190726
Time             16.42
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD               65536
SOLVENT          CDCl3
NS                 224
DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG              5792.6
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1      125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2      500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF        125.7804076 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            230.637 ppm
F1            29009.68 Hz
F2P            -10.287 ppm
F2            -1293.96 Hz
PPMCM         10.56688 ppm/cm
HZCM        1329.10693 Hz/cm
```

gcosy60



3.33

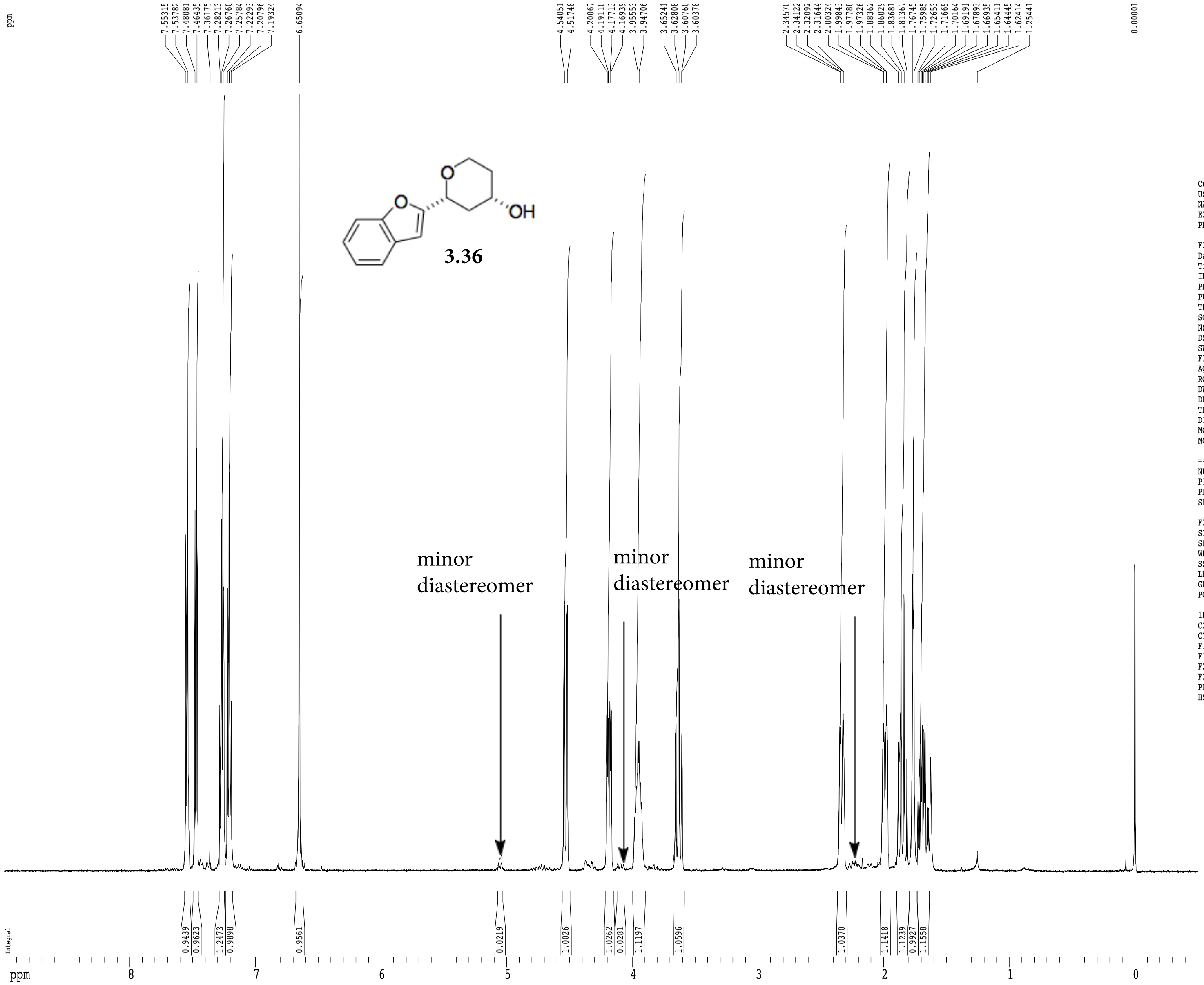
```
        Current Data Parameters
  USER           khewitt1
NAME     KAH-II-119 COSY-2
  EXPNO                 2
  PROCNO                1

      F2 - Acquisition Parameters
  Date_          20190725
  Time              14.10
  INSTRUM         cryo500
  PROBHD   5 mm CPTCI 1H-
  PULPROG    cosygp60.prd
  TD                 2048
  SOLVENT           CDCl3
  NS                    1
  DS                   16
  SWH            8012.820 Hz
  FIDRES         3.912510 Hz
  AQ            0.1278452 sec
  RG                287.4
  DW               62.400 usec
  DE                 6.00 usec
  TE                298.0 K
  d0           0.00000300 sec
  D1           1.00000000 sec
  d13          0.00000300 sec
  D16          0.00020000 sec
  IN0          0.00012480 sec

     ======== CHANNEL f1 ========
  NUC1                 1H
  P1                 7.50 usec
  PL1                1.60 dB
  SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
  GPNAM1         sine.100
  GPNAM2         sine.100
  GPX1               0.00 %
  GPX2               0.00 %
  GPY1               0.00 %
  GPY2               0.00 %
  GPZ1              17.00 %
  GPZ2              17.00 %
  P16             1000.00 usec

      F1 - Acquisition parameters
  ND0                   1
  TD                  512
  SFO1           500.2235 MHz
  FIDRES        15.650040 Hz
  SW               16.018 ppm
  FnMODE               QF

      F2 - Processing parameters
  SI                 1024
  SF          500.2200320 MHz
  WDW                SINE
  SSB                   0
  LB                 0.00 Hz
  GB                    0
  PC                 1.00

      F1 - Processing parameters
  SI                 1024
  MC2                  QF
  SF          500.2200320 MHz
  WDW                SINE
  SSB                   0
  LB                 0.00 Hz
  GB                    0

         2D NMR plot parameters
  CX2               15.00 cm
  CX1               15.00 cm
  F2PLO             9.000 ppm
  F2LO            4501.98 Hz
  F2PHI            -0.500 ppm
  F2HI            -250.11 Hz
  F1PLO             9.000 ppm
  F1LO            4501.98 Hz
  F1PHI            -0.500 ppm
  F1HI            -250.11 Hz
  F2PPMCM         0.63333 ppm/cm
  F2HZCM        316.80603 Hz/cm
  F1PPMCM         0.63333 ppm/cm
  F1HZCM        316.80603 Hz/cm
```



3.33

```
Current Data Parameters
USER              khewitt1
NAME           KAH-II-119Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190726
Time                 17.00
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                     114
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2204747 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

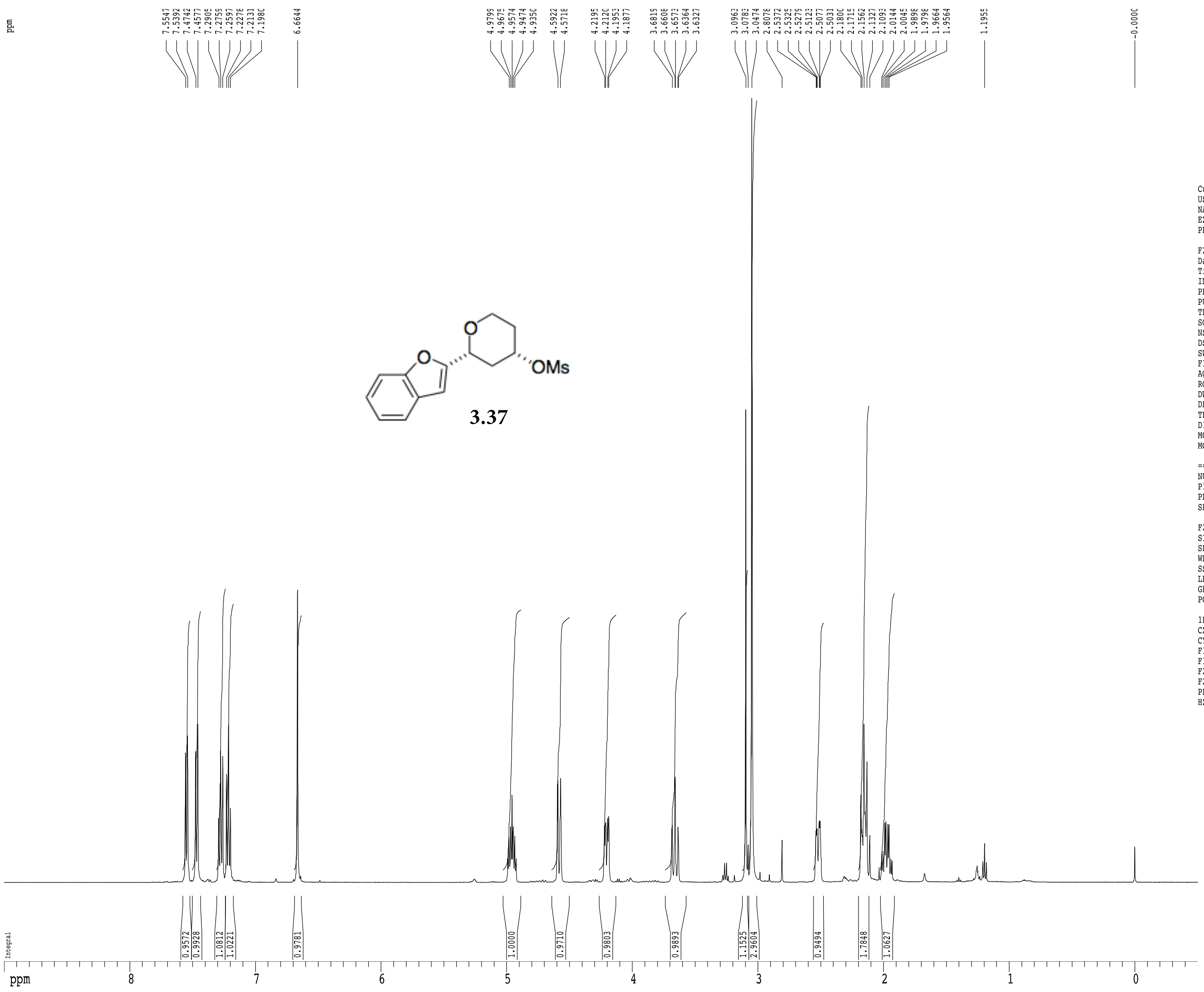
1H spectrum



3.36

```
Current Data Parameters
USER                emilyt
NAME       LWE-III-019 OH
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150718
Time                 17.04
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0999398 sec
RG                     7.1
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF          500.2200326 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42502 Hz/cm
```

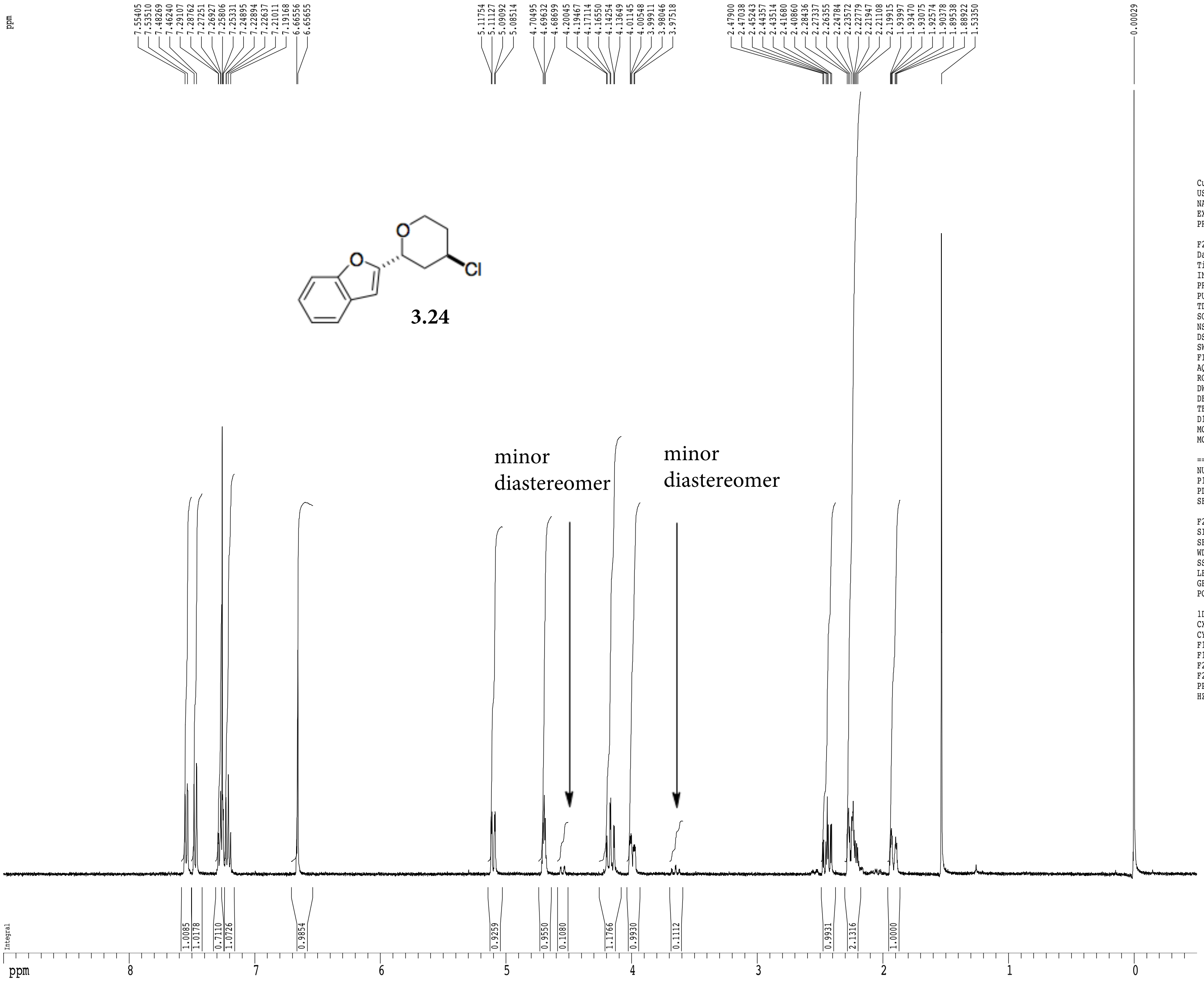
1H spectrum



3.37

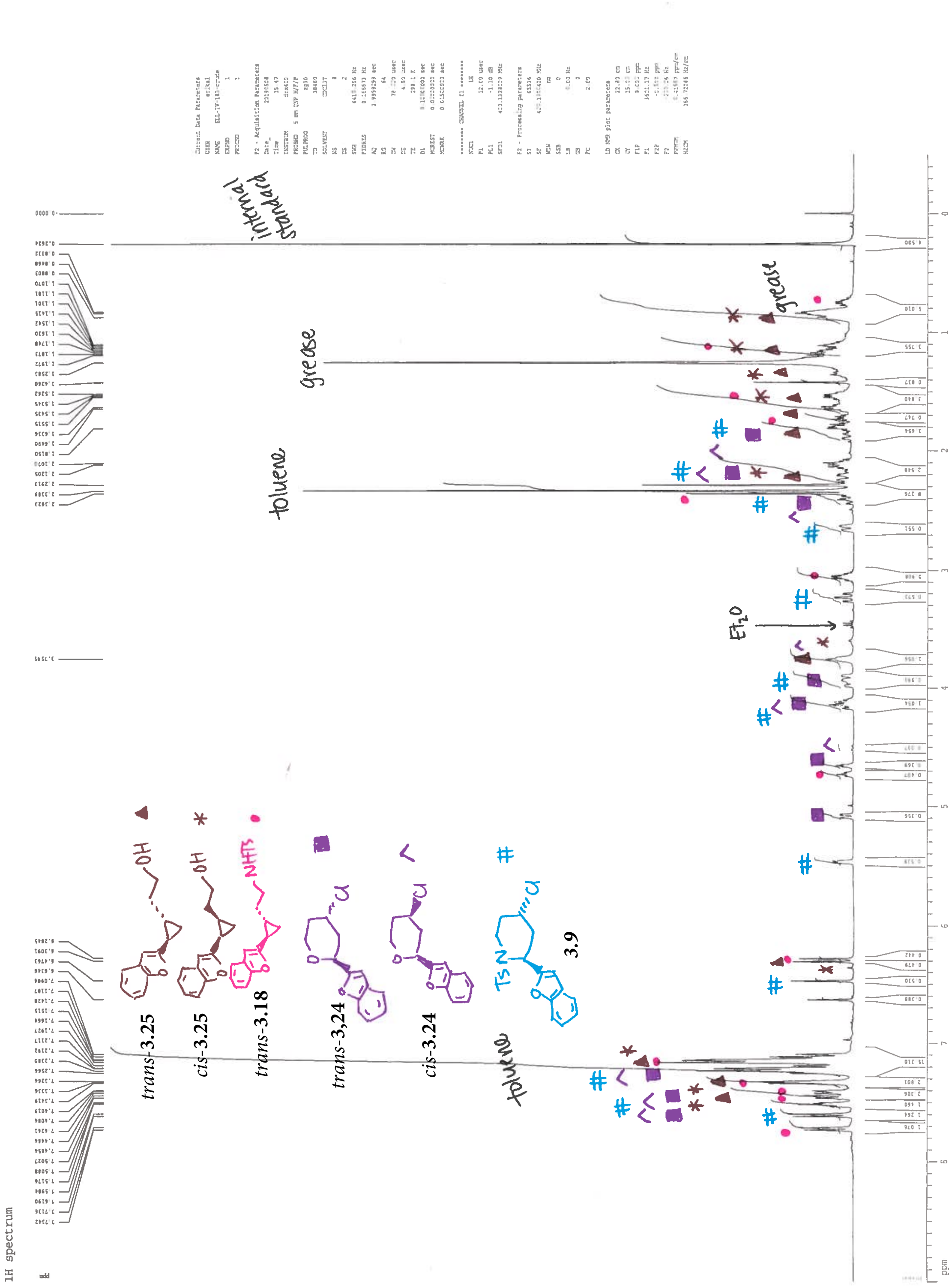
```
Current Data Parameters
USER              emilyt
NAME      LWE-III-022 OMs
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150719
Time               11.18
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                     4
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200310 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

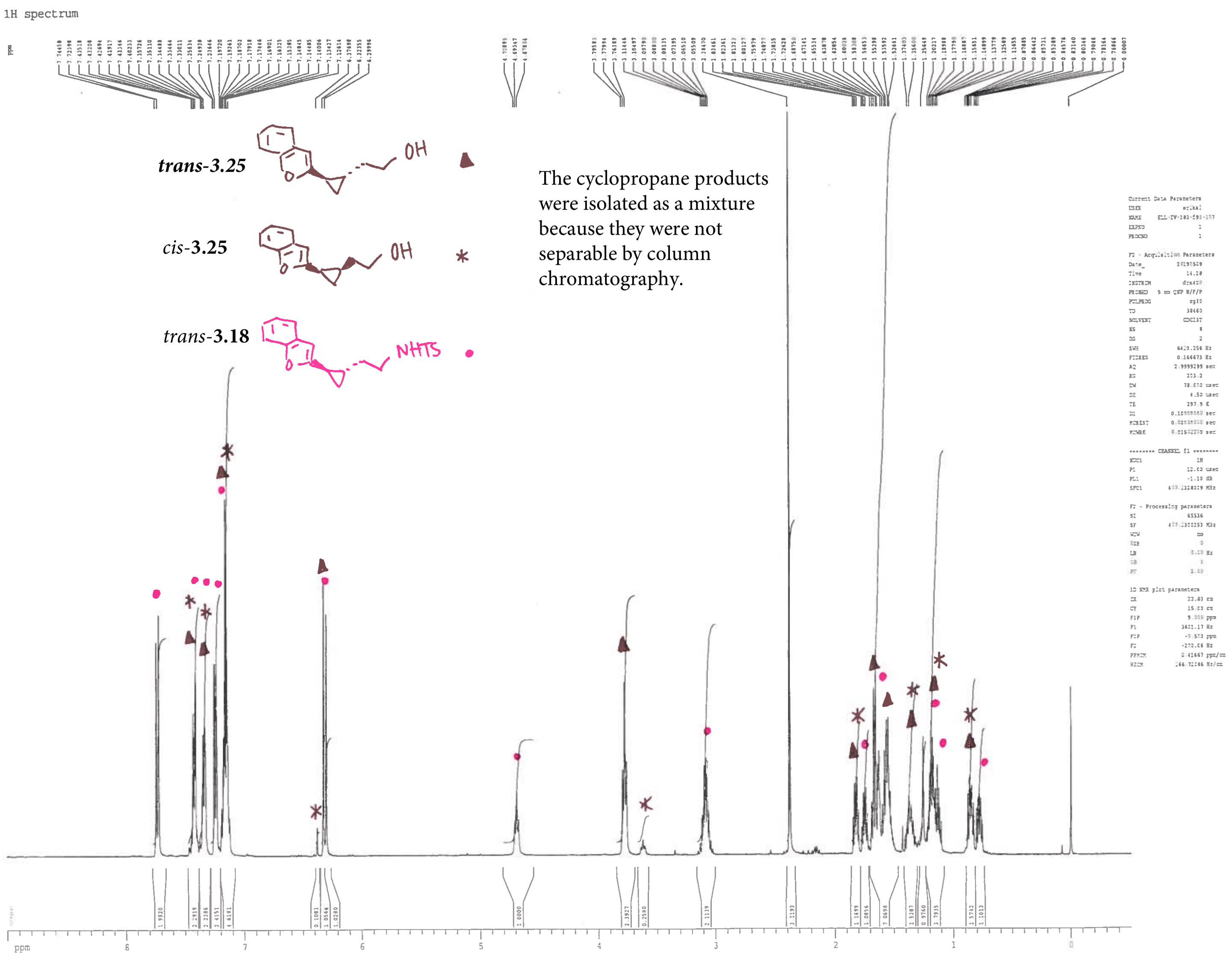
1H spectrum



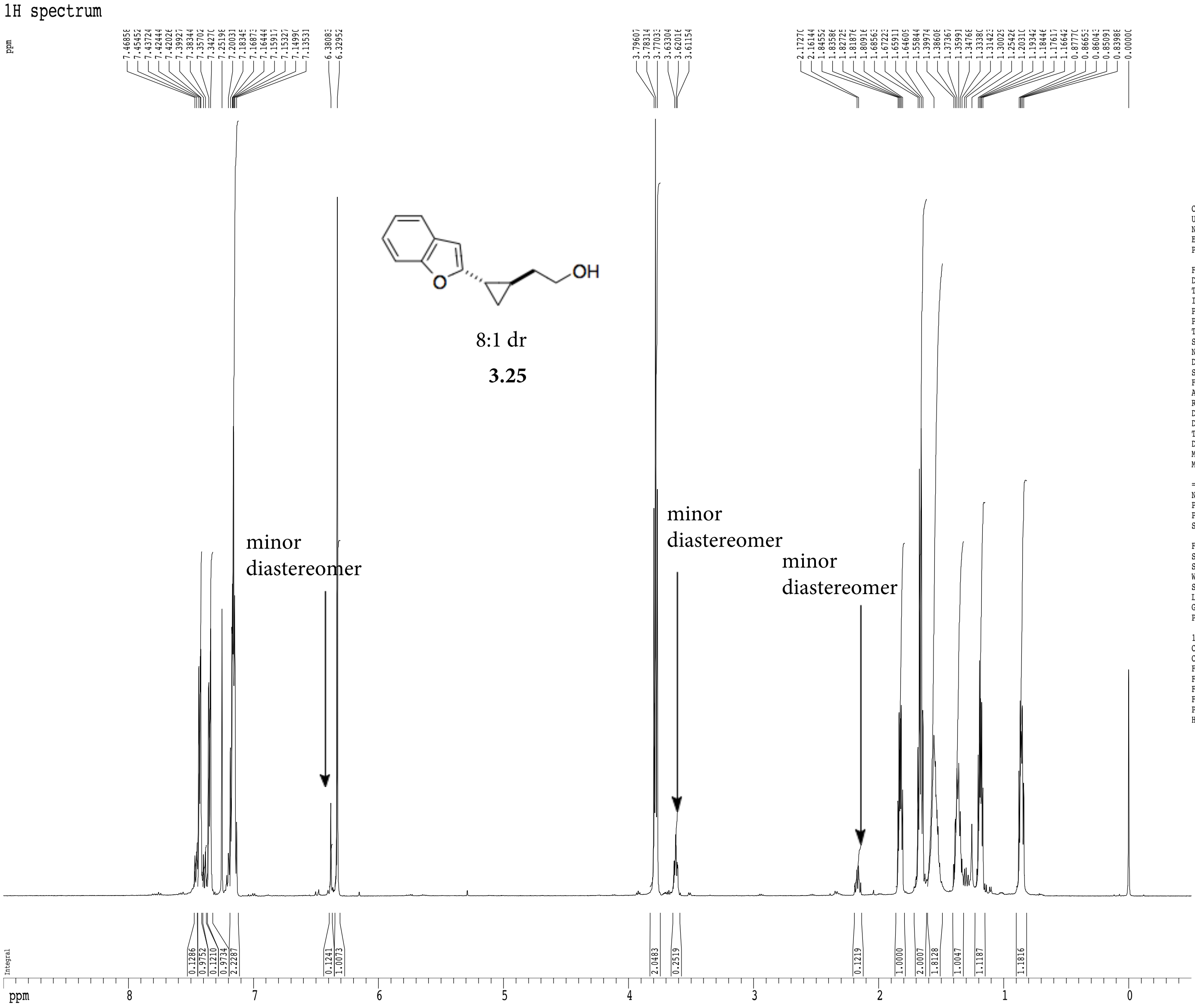
3.24

```
Current Data Parameters
USER              erikal
NAME        ELL-IV-179-dr
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190507
Time                9.58
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                  1024
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300217 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```


1H spectrum
internal standard
grease
grease
toluene
toluene
Et2O
trans-3.25
cis-3.25
trans-3.18
trans-3.24
cis-3.24
3.9
OH
OH
NHTs
Cl
Cl
TsN
ppm



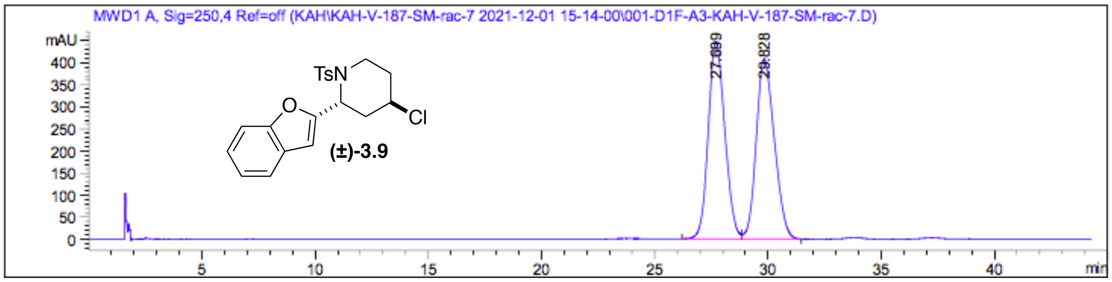
The cyclopropane products were isolated as a mixture because they were not separable by column chromatography.



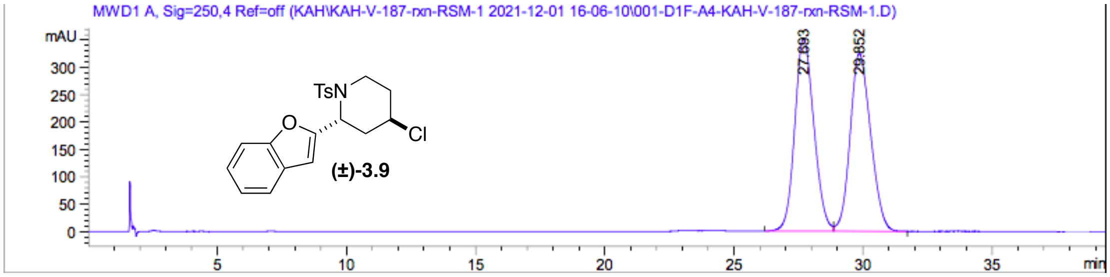
8:1 dr

3.25

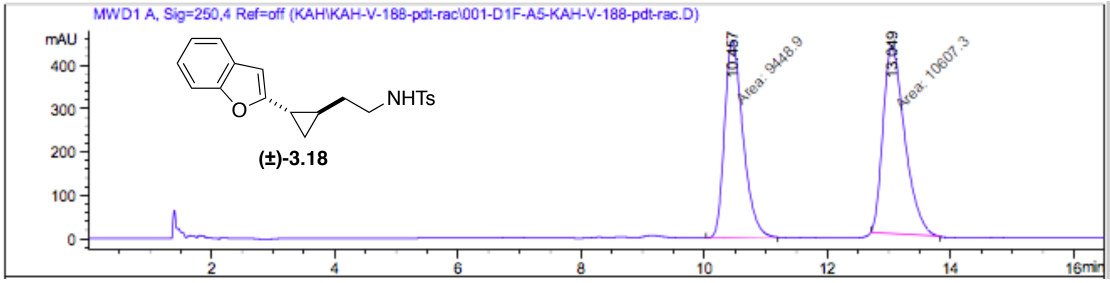
```
Current Data Parameters
USER              emilyt
NAME      LWE-III-024 prod
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150717
Time               14.21
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0999398 sec
RG                  10.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200353 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```



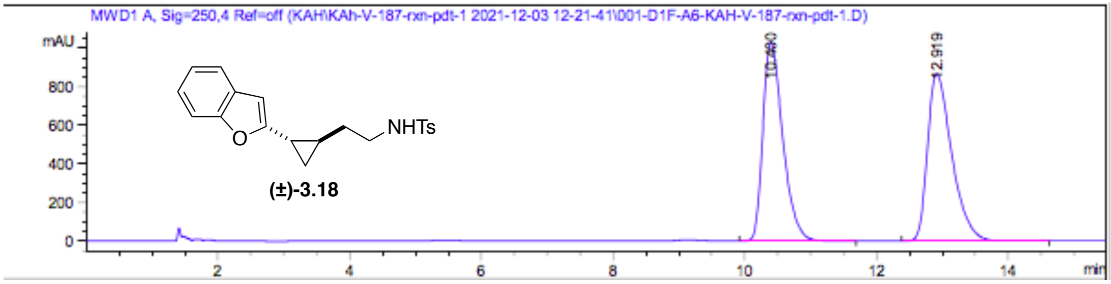
```
Signal 1: MWD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  27.699 VV R  0.7747 2.27162e4  447.14914  50.0210
   2  29.828 VB    0.8196 2.26971e4  407.65872  49.9790

Totals :                  4.54133e4  854.80786
```



```
Signal 1: MWD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  27.693 BV    0.7571 1.81977e4  353.17920  50.3969
   2  29.852 VV R  0.8092 1.79111e4  324.90347  49.6031

Totals :                  3.61088e4  678.08267
```



```
Signal 1: MWD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.457 MM    0.3468 9448.90332  454.14722  47.1121
   2  13.049 MM    0.4096 1.06073e4  431.57236  52.8879

Totals :                  2.00562e4  885.71957
```

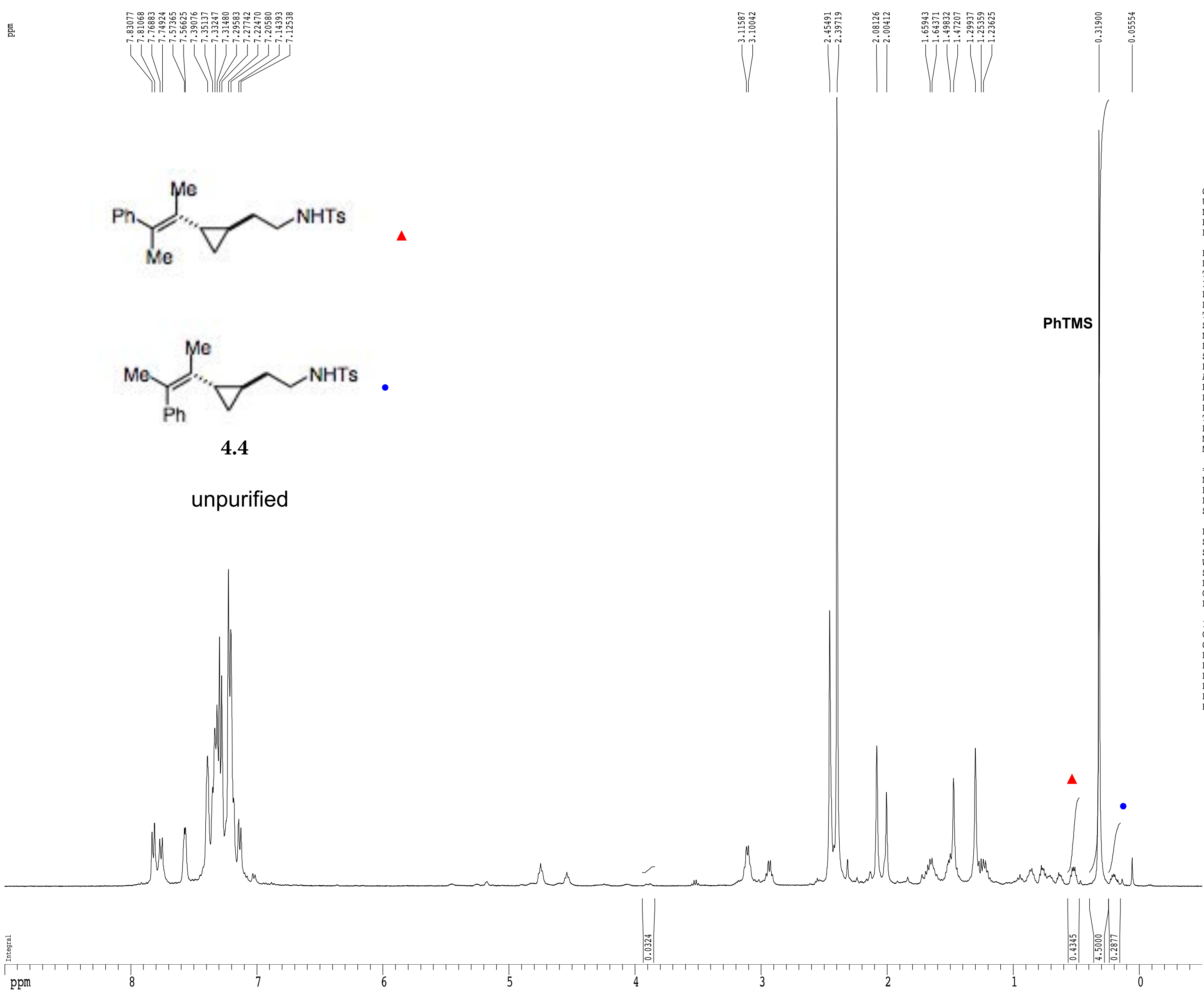


```
Signal 1: MWD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.400 BB    0.3222 2.15896e4 1031.54016 49.3558
   2  12.919 BV R  0.3899 2.21532e4  867.65588 50.6442

Totals :                  4.37428e4 1899.19604
```

APPENDIX A.3

^{1}H, ^{13}C, COSY, NOE NMR SPECTRA, SFC TRACES FOR CHAPTER 4

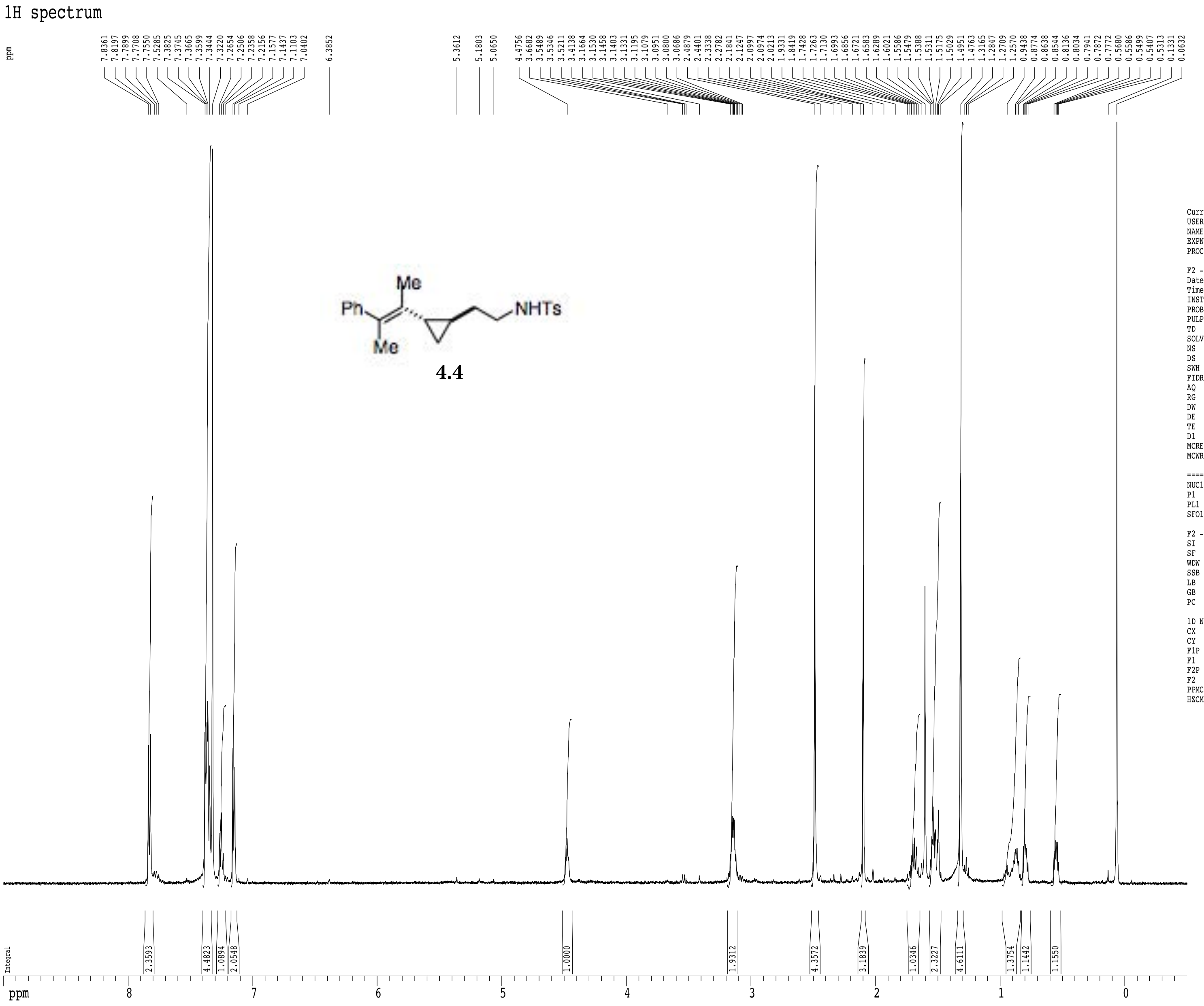
1H spectrum



4.4

unpurified

```
Current Data Parameters
USER            khewitt1
NAME             TATiv50
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200630
Time               10.11
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

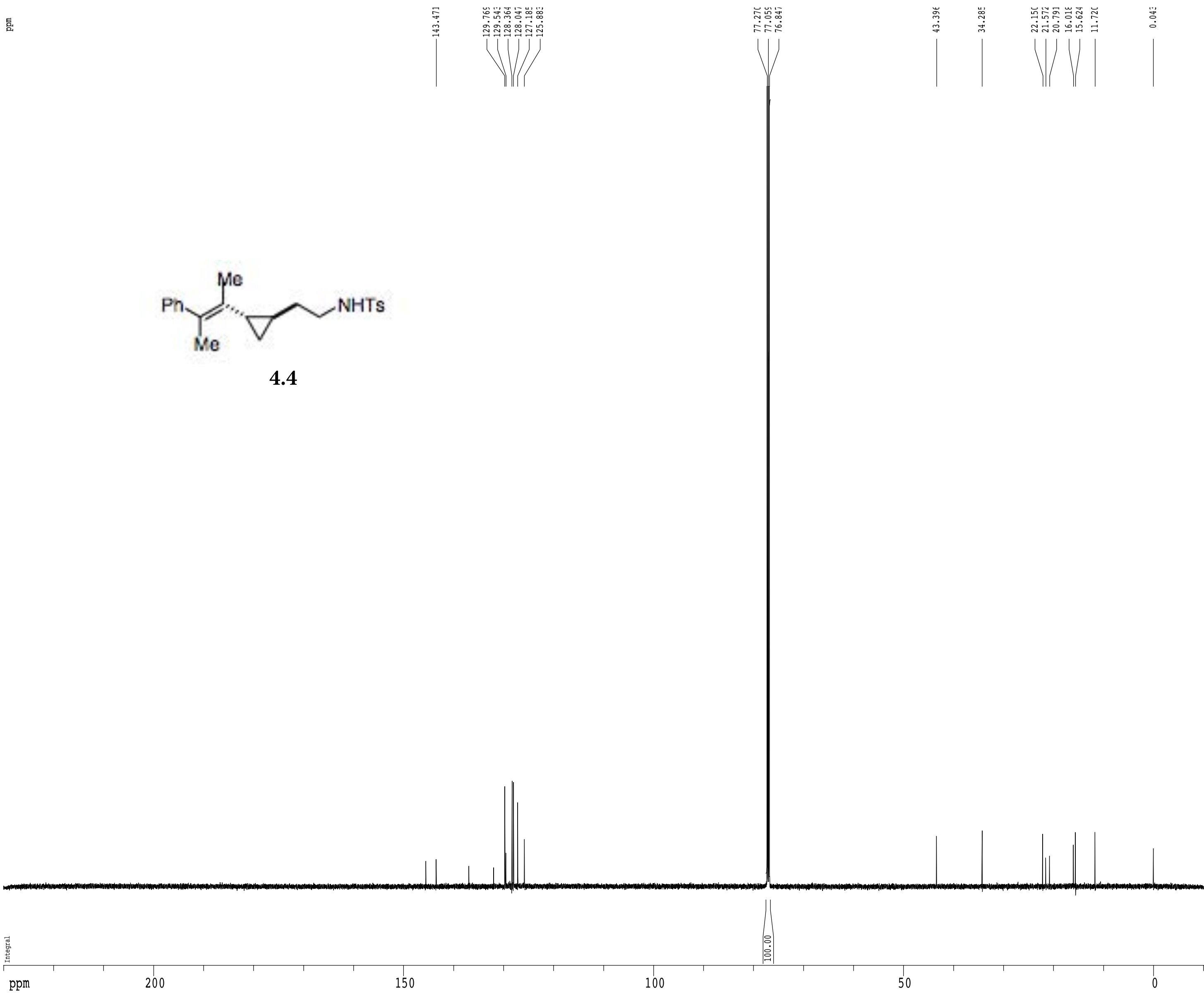


1H spectrum

4.4

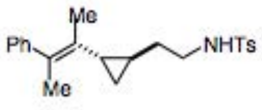
```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-031-z-cryo
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200117
Time              17.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

1H spectrum



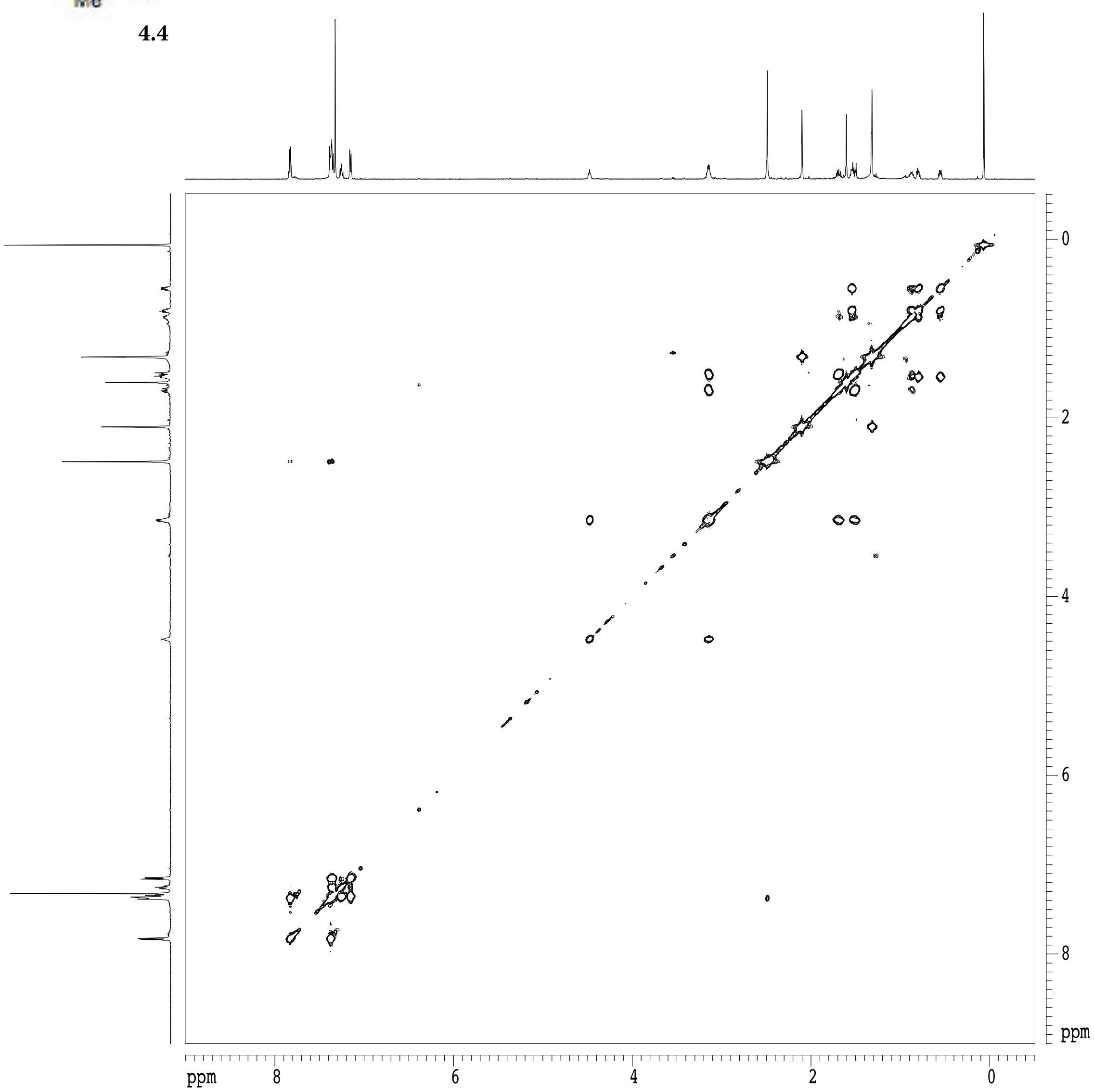
4.4

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-031-C-600
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200120
Time               11.25
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   736
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9028085 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 24.30 cm
F1P              230.052 ppm
F1              34715.42 Hz
F2P              -10.049 ppm
F2              -1516.47 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11780 Hz/cm
```

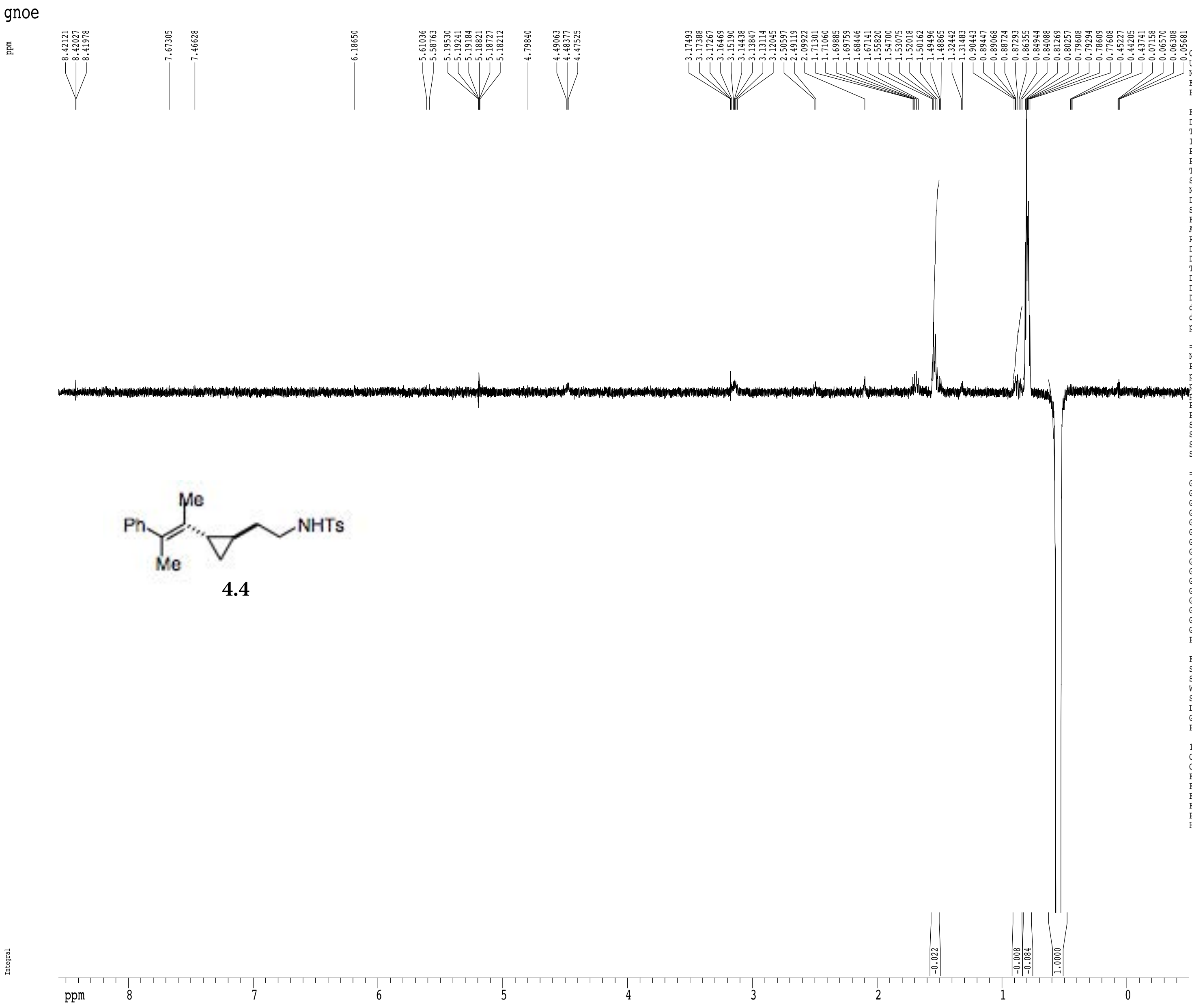


4.4

gcosy60



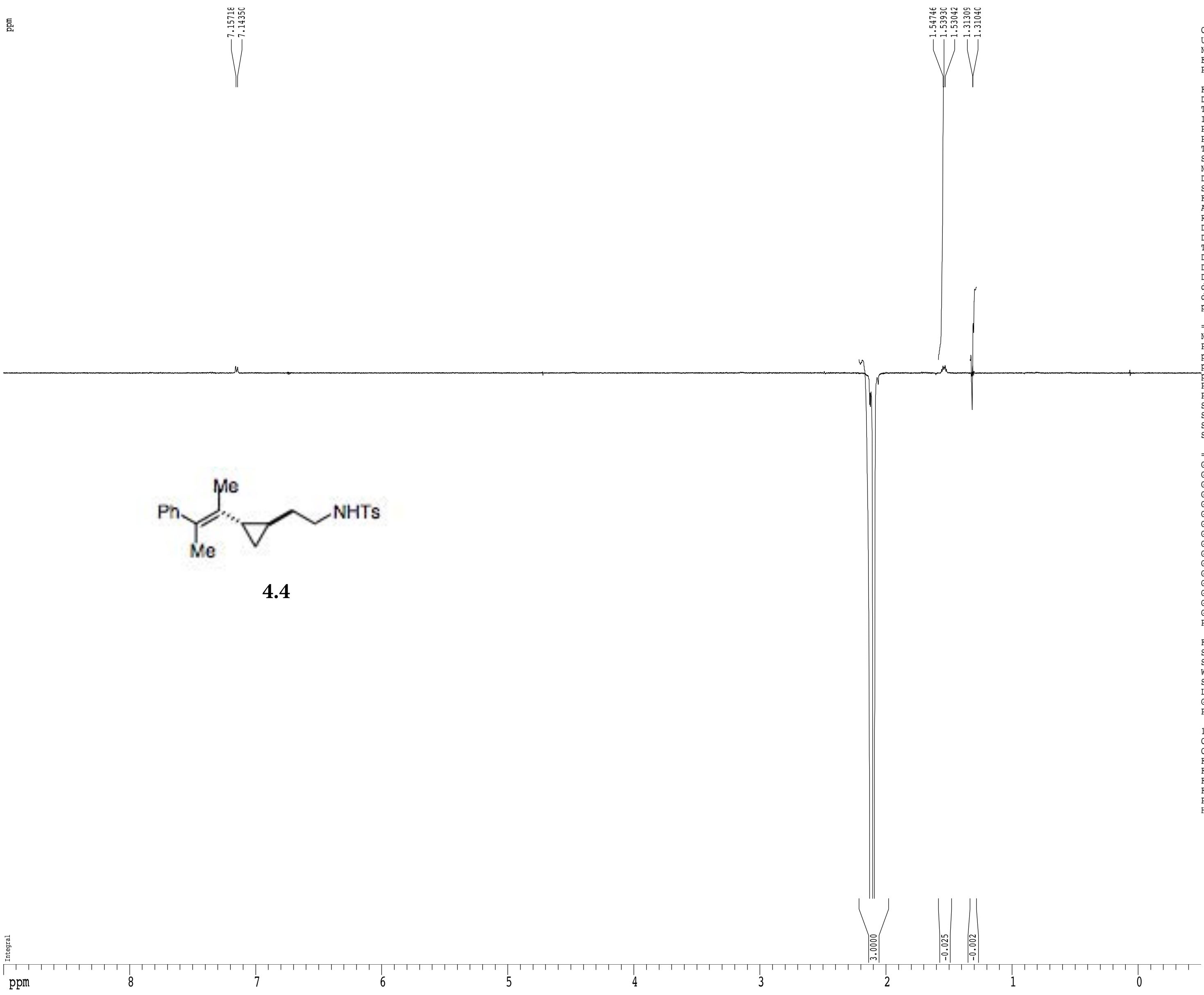
```
        Current Data Parameters
  USER            khewitt1
NAME     KAH-III-031-z-cryo
  EXPNO                  2
  PROCNO                 1

      F2 - Acquisition Parameters
  Date_           20200117
  Time               17.57
  INSTRUM          cryo500
  PROBHD   5 mm CPTCI 1H-
  PULPROG    cosygp60.prd
  TD                  2048
  SOLVENT            CDCl3
  NS                     1
  DS                    16
  SWH             8012.820 Hz
  FIDRES          3.912510 Hz
  AQ             0.1278452 sec
  RG                 812.7
  DW                62.400 usec
  DE                  6.00 usec
  TE                 298.0 K
  d0            0.00000300 sec
  D1            1.00000000 sec
  d13           0.00000300 sec
  D16           0.00020000 sec
  IN0           0.00012480 sec

     ======== CHANNEL f1 ========
  NUC1                  1H
  P1                  7.50 usec
  PL1                 1.60 dB
  SFO1         500.2235015 MHz

     ====== GRADIENT CHANNEL =====
  GPNAM1          sine.100
  GPNAM2          sine.100
  GPX1                0.00 %
  GPX2                0.00 %
  GPY1                0.00 %
  GPY2                0.00 %
  GPZ1               17.00 %
  GPZ2               17.00 %
  P16              1000.00 usec

      F1 - Acquisition parameters
  ND0                    1
  TD                   512
  SFO1            500.2235 MHz
  FIDRES         15.650040 Hz
  SW                16.018 ppm
  FnMODE                QF

      F2 - Processing parameters
  SI                  1024
  SF           500.2200000 MHz
  WDW                 SINE
  SSB                    0
  LB                  0.00 Hz
  GB                     0
  PC                  1.00

      F1 - Processing parameters
  SI                  1024
  MC2                   QF
  SF           500.2200000 MHz
  WDW                 SINE
  SSB                    0
  LB                  0.00 Hz
  GB                     0

        2D NMR plot parameters
  CX2                15.00 cm
  CX1                15.00 cm
  F2PLO              9.002 ppm
  F2LO             4503.14 Hz
  F2PHI             -0.509 ppm
  F2HI             -254.47 Hz
  F1PLO              9.002 ppm
  F1LO             4503.14 Hz
  F1PHI             -0.509 ppm
  F1HI             -254.47 Hz
  F2PPMCM          0.63407 ppm/cm
  F2HZCM         317.17416 Hz/cm
  F1PPMCM          0.63407 ppm/cm
  F1HZCM         317.17416 Hz/cm
```



4.4

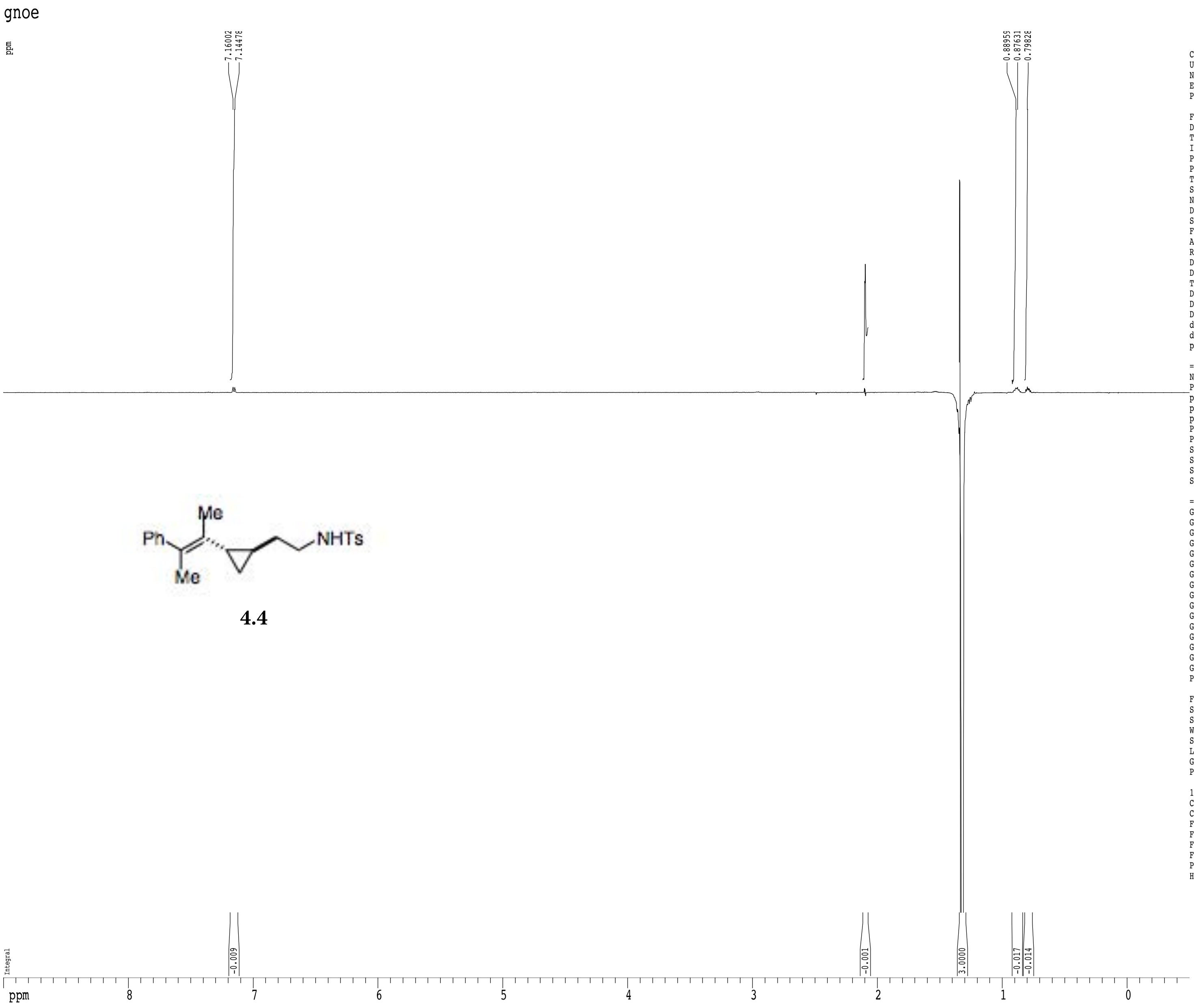
```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-031-z-cryo
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200118
Time               15.48
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    57
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2202749 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

gnoe



4.4

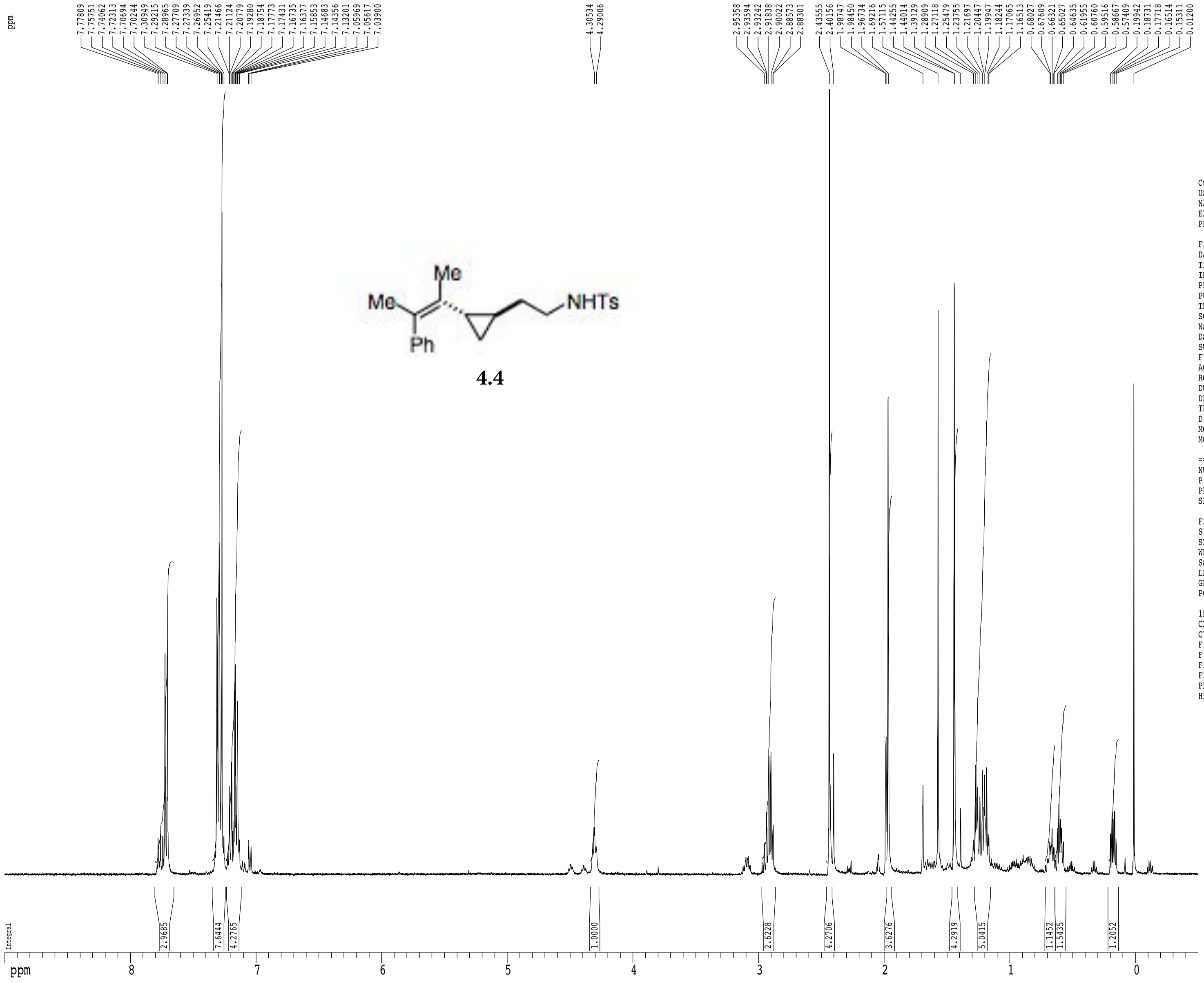
```
Current Data Parameters
USER              khewitt1
NAME      KAH-III-031-z-cryo
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200118
Time                 16.02
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    gnoelcc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    80.6
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2210495 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```



4.4

```
Current Data Parameters
USER             khewitt1
NAME       Table 1 - major
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200914
Time                18.16
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   90.5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2206582 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

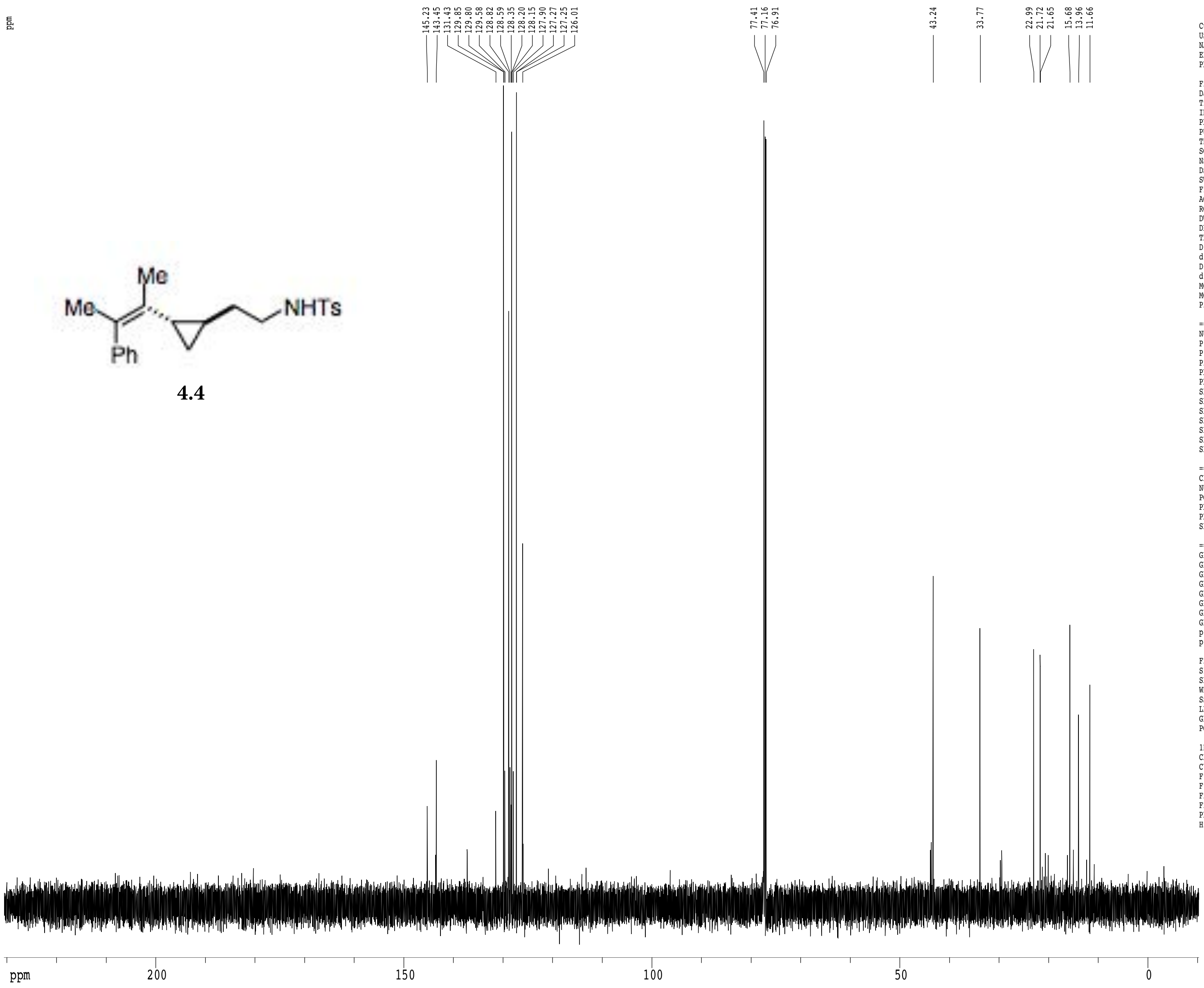
1H spectrum



4.4

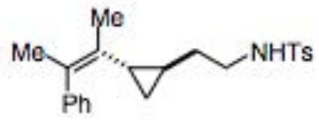
```
Current Data Parameters
USER           khewitt1
NAME     Table 1 - minor
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200904
Time              17.23
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                406.4
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



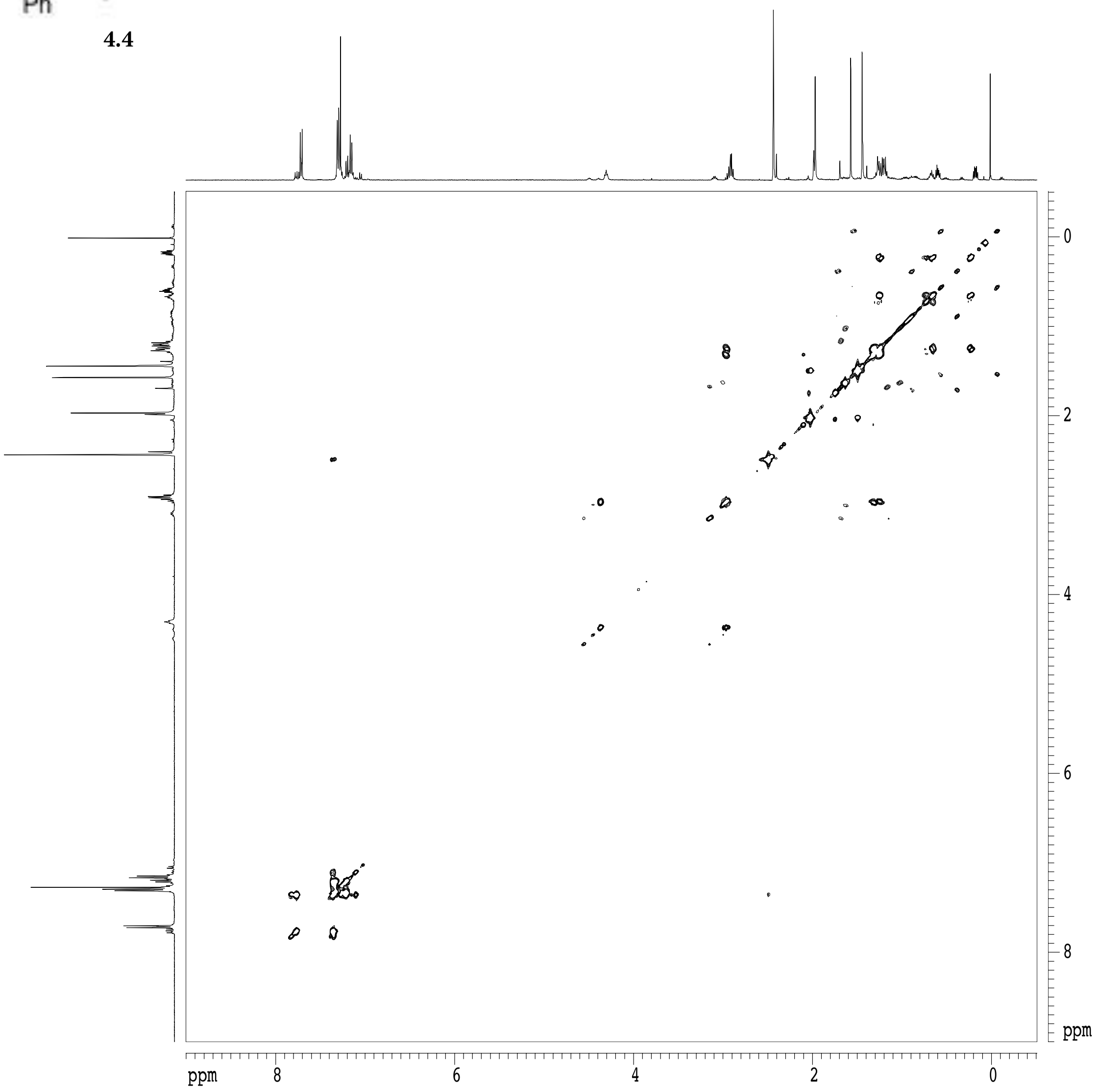
4.4

```
Current Data Parameters
USER           khewitt1
NAME     Table 1 - minor
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20200904
Time              18.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  216
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804076 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```



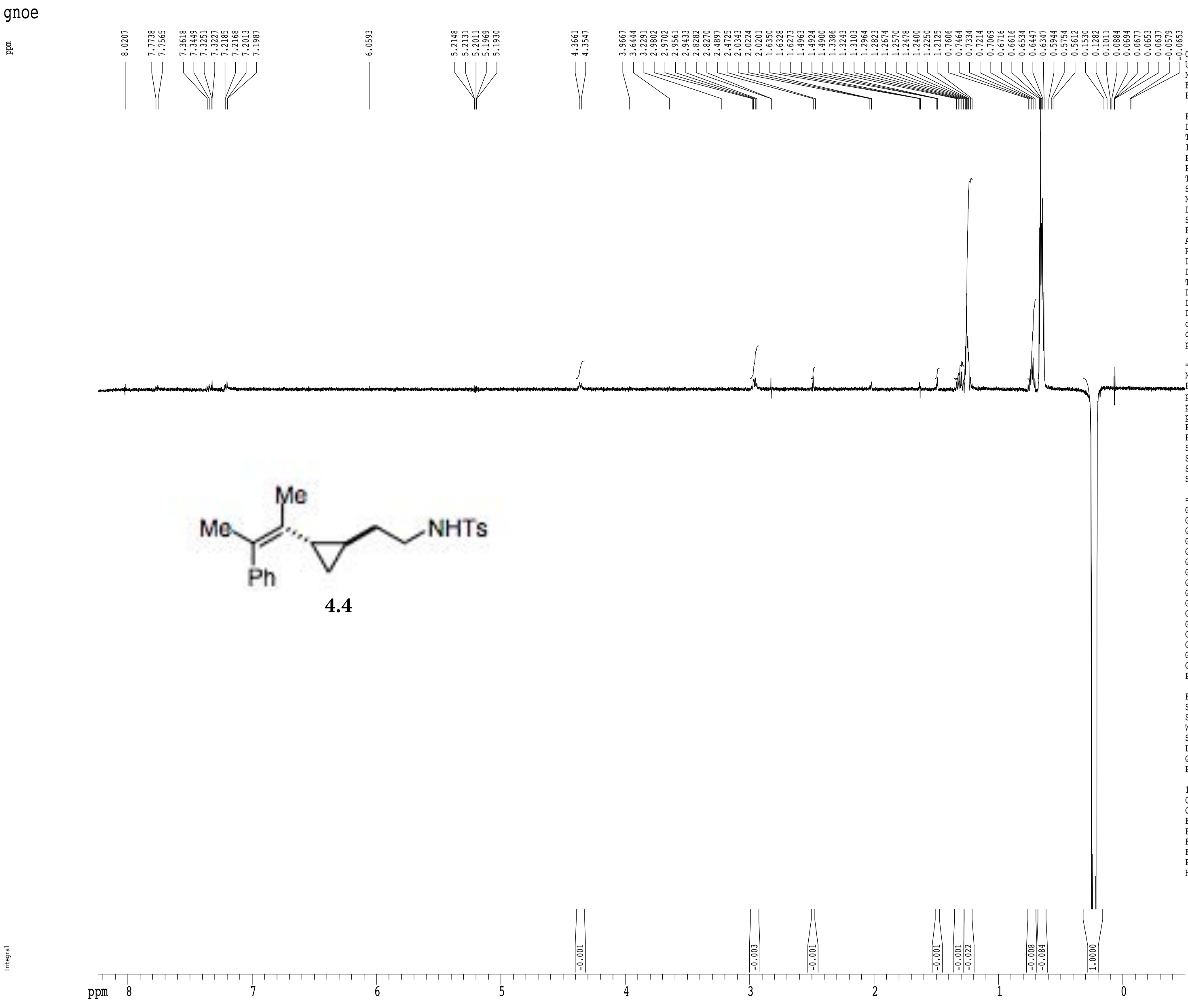
4.4

gcosy60



```
        Current Data Parameters
 USER           khewitt1
NAME     Table 1 - minor
 EXPNO                5
 PROCNO               1

      F2 - Acquisition Parameters
 Date_          20200904
 Time              18.43
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG    cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            8012.820 Hz
 FIDRES         3.912510 Hz
 AQ            0.1278452 sec
 RG                287.4
 DW               62.400 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00012480 sec

     ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  512
 SFO1           500.2235 MHz
 FIDRES        15.650040 Hz
 SW               16.018 ppm
 FnMODE               QF

       F2 - Processing parameters
 SI                 1024
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

       F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

          2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             9.002 ppm
 F2LO            4503.14 Hz
 F2PHI            -0.509 ppm
 F2HI            -254.47 Hz
 F1PLO             9.002 ppm
 F1LO            4503.14 Hz
 F1PHI            -0.509 ppm
 F1HI            -254.47 Hz
 F2PPMCM         0.63407 ppm/cm
 F2HZCM        317.17416 Hz/cm
 F1PPMCM         0.63407 ppm/cm
 F1HZCM        317.17416 Hz/cm
```

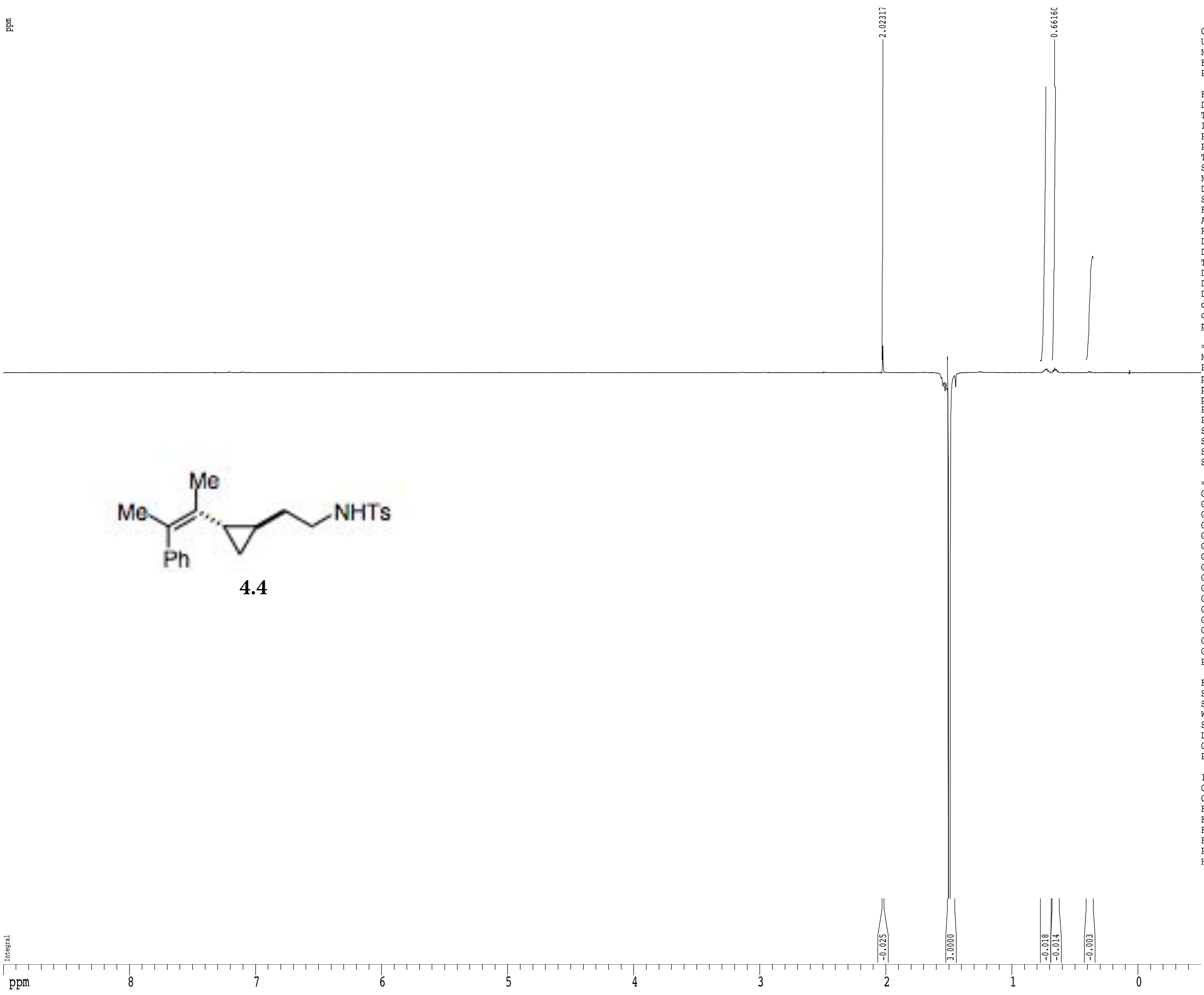
gnoe



4.4

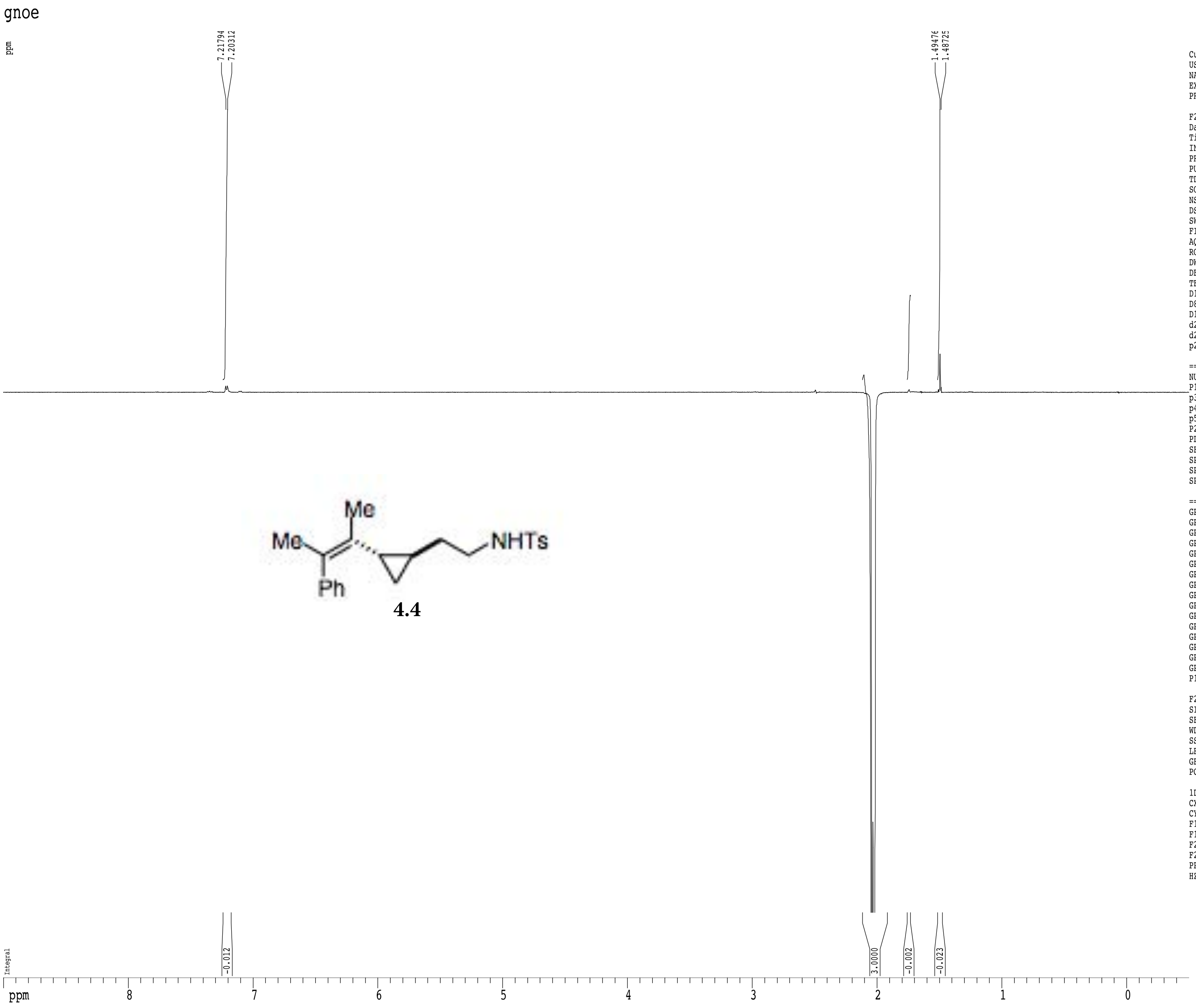
```
Current Data Parameters
USER              khewitt1
NAME      Table 1 - minor
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20200904
Time               18.27
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2201154 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

gnoe



4.4

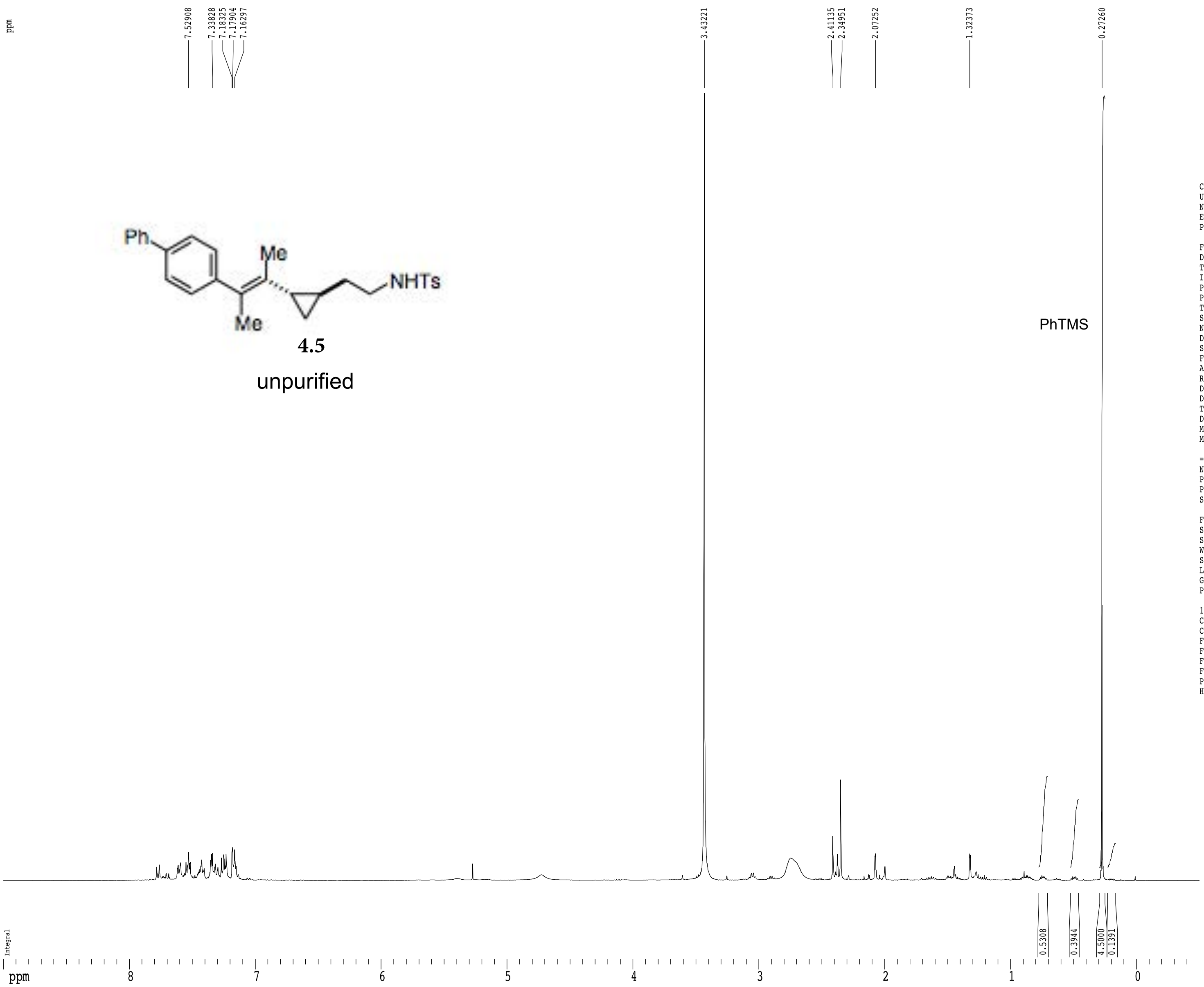
```
Current Data Parameters
USER           khewitt1
NAME     Table 1 - minor
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20200904
Time              18.41
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2207477 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



4.4

```
Current Data Parameters
USER            khewitt1
NAME     Table 1 - minor
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200907
Time               18.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2210112 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

1H spectrum

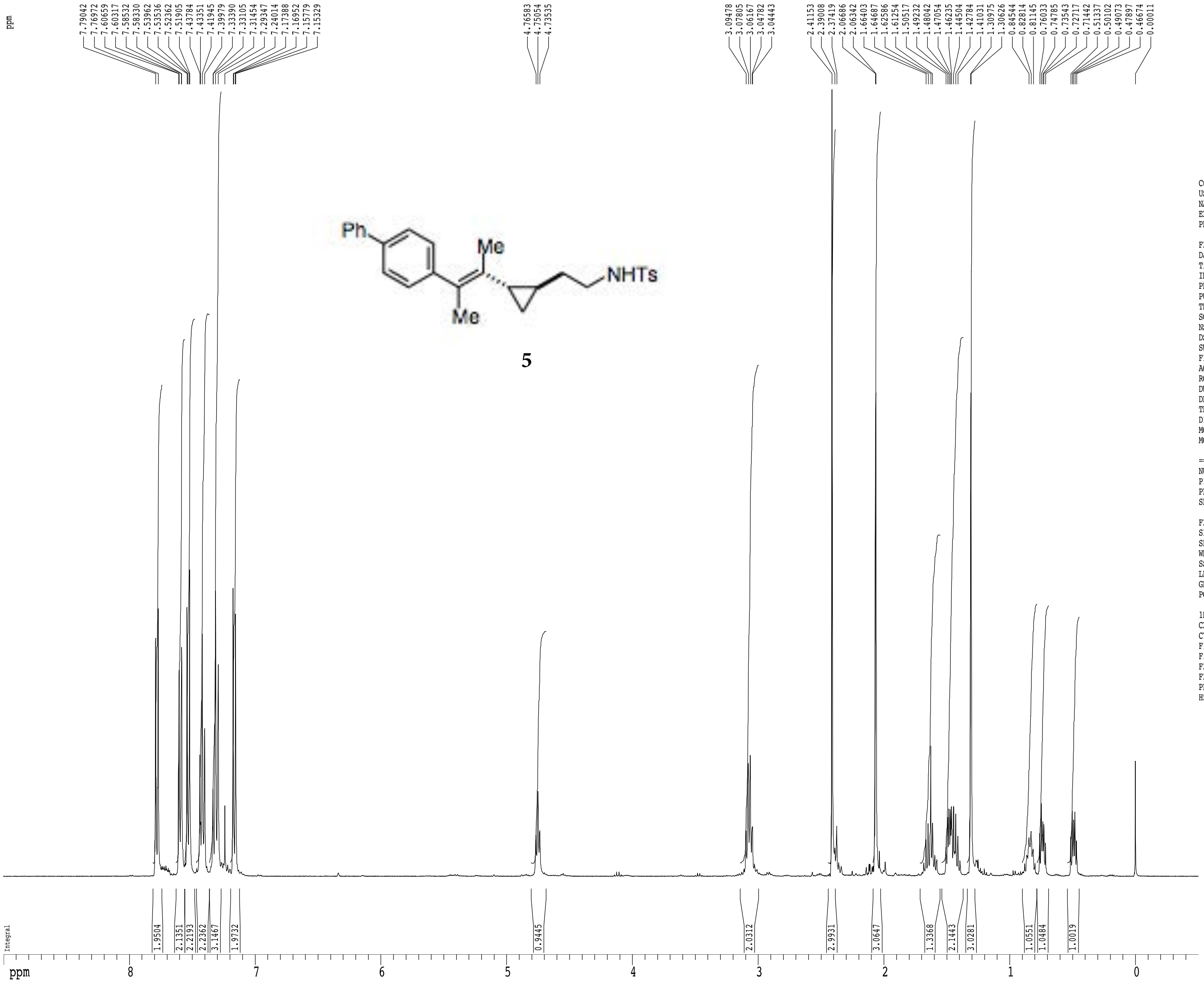


4.5

unpurified

```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-212-crude
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200728
Time              16.39
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                   32
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

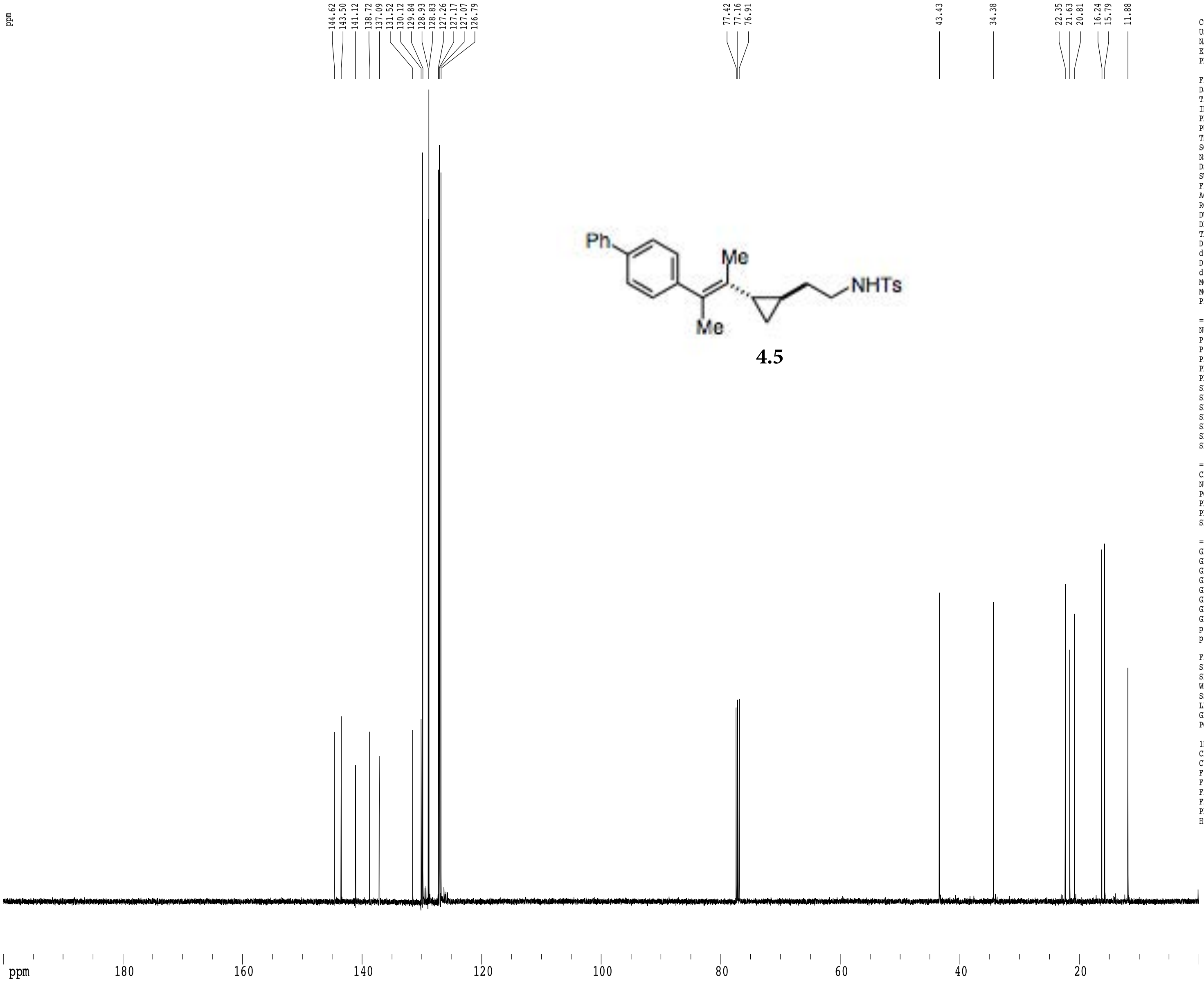
1H spectrum



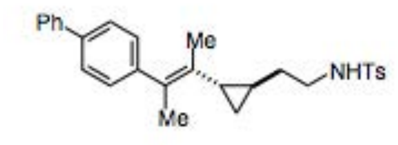
5

```
Current Data Parameters
USER            khewitt1
NAME      ELL-IV-212-char
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190628
Time              14.31
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                  114
DW               78.000 usec
DE                 4.50 usec
TE                297.9 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300290 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

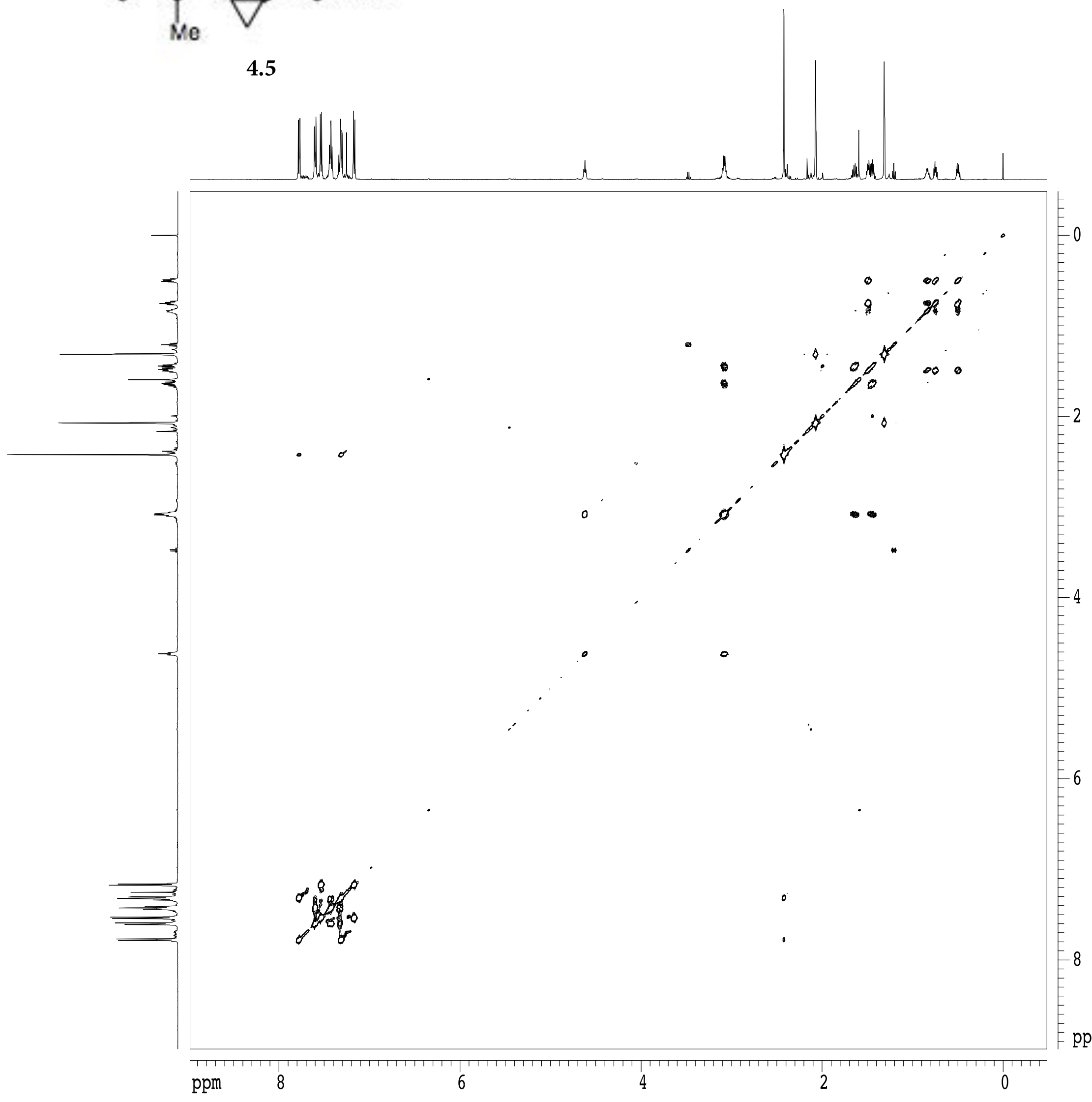


```
Current Data Parameters
USER           khewitt1
NAME     ELL-IV-212-char
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20190628
Time              16.41
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT          CDCl3T
NS                  704
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG                 6502
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1               16.55 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                65536
SF         125.7804136 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            200.000 ppm
F1            25156.08 Hz
F2P              0.000 ppm
F2                0.00 Hz
PPMCM          8.77193 ppm/cm
HZCM        1103.33691 Hz/cm
```

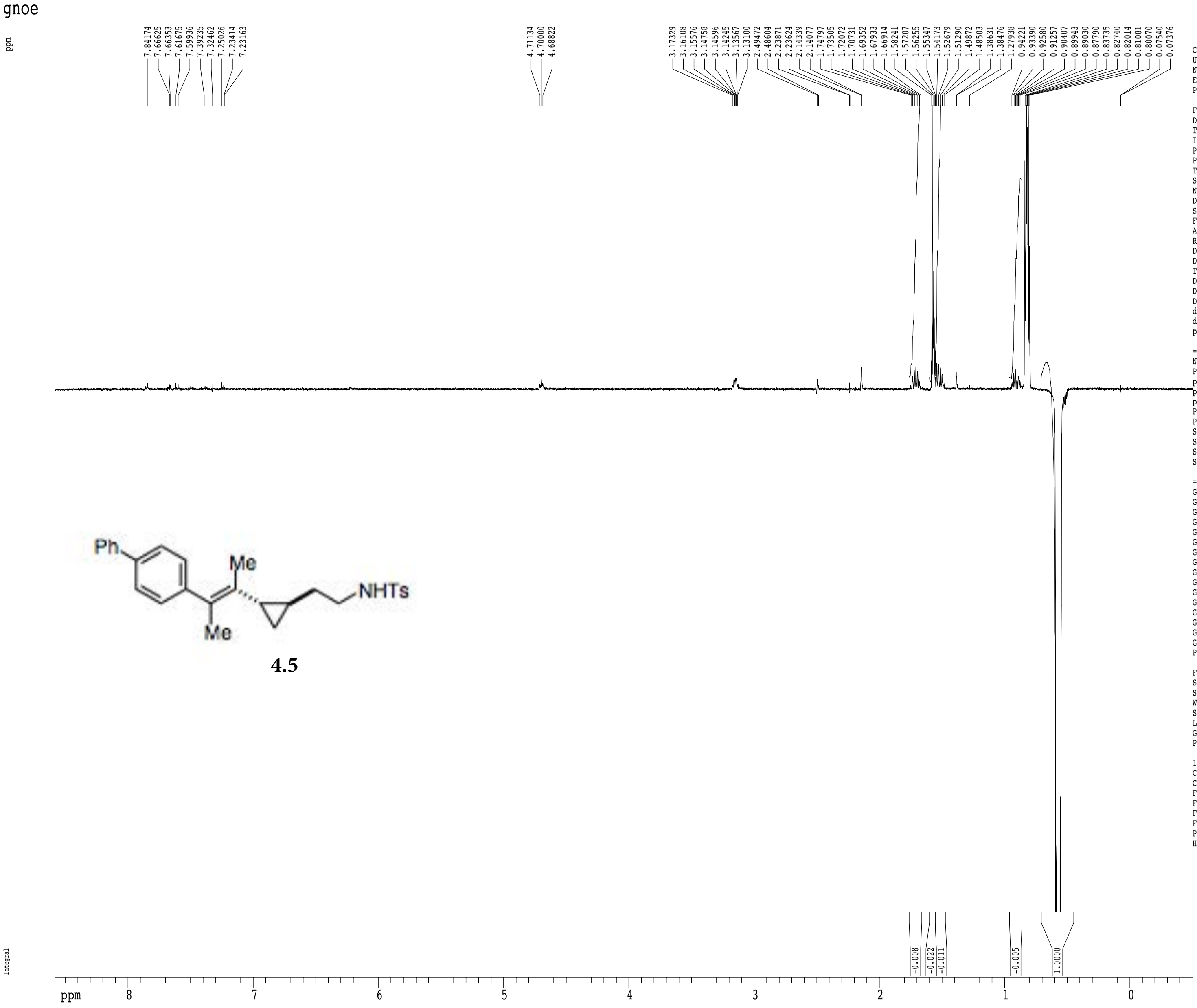


4.5

gcosy60

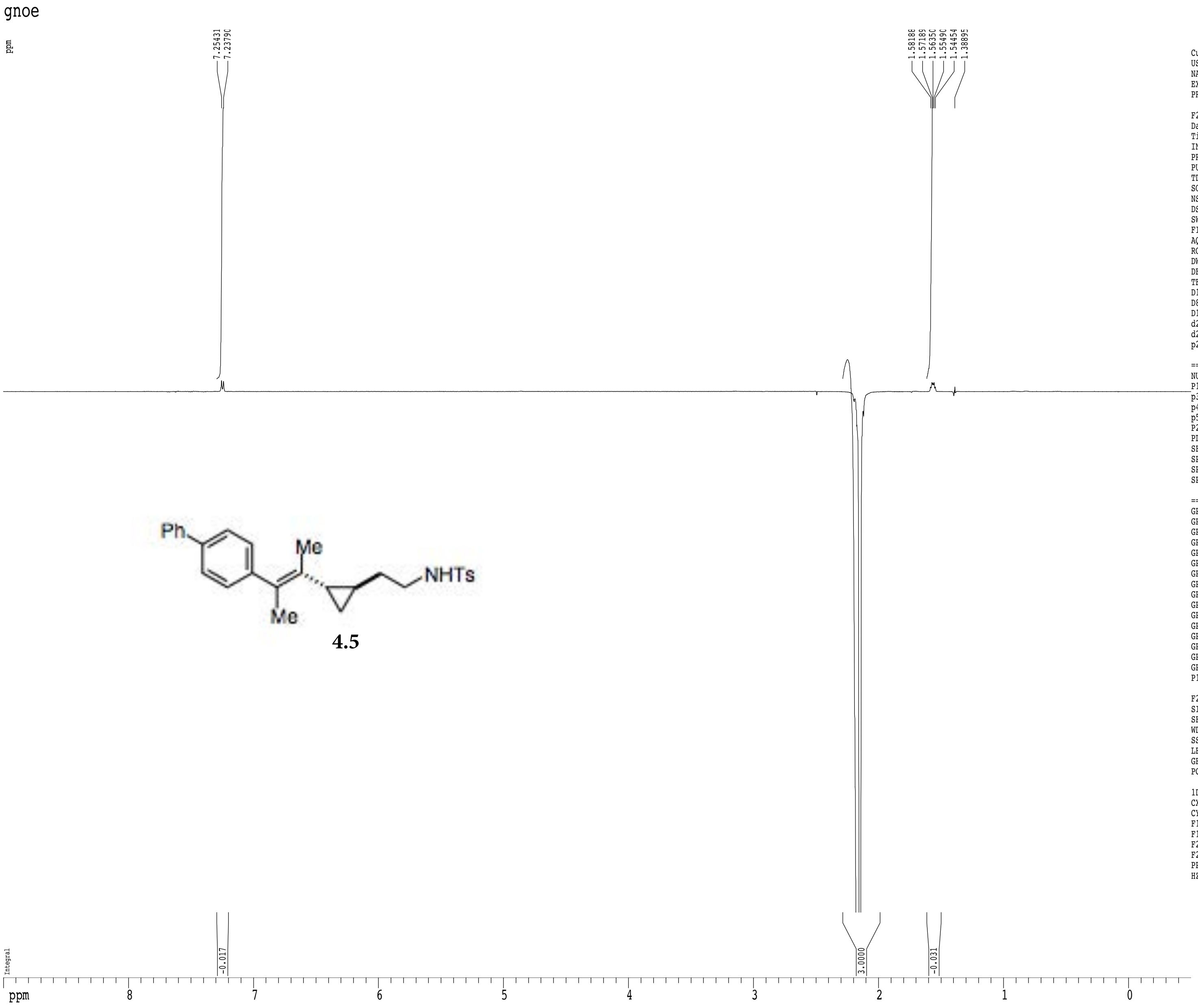


```
      Current Data Parameters
USER              khewitt1
NAME      ELL-IV-132-f46-48
EXPNO                    3
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20190309
Time                 11.35
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                      16
SWH               4734.849 Hz
FIDRES            2.311938 Hz
AQ               0.2163188 sec
RG                     114
DW                 105.600 usec
DE                    6.00 usec
TE                   298.0 K
d0              0.00000300 sec
D1              1.00000000 sec
d13             0.00000300 sec
D16             0.00020000 sec
IN0             0.00021120 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2221627 MHz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 17.00 %
GPZ2                 17.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      1
TD                     512
SFO1              500.2222 MHz
FIDRES            9.247751 Hz
SW                   9.465 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             500.2200368 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.2200368 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

      2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                8.983 ppm
F2LO               4493.36 Hz
F2PHI               -0.483 ppm
F2HI               -241.49 Hz
F1PLO                8.983 ppm
F1LO               4493.36 Hz
F1PHI               -0.483 ppm
F1HI               -241.49 Hz
F2PPMCM            0.63104 ppm/cm
F2HZCM           315.65656 Hz/cm
F1PPMCM            0.63104 ppm/cm
F1HZCM           315.65656 Hz/cm
```



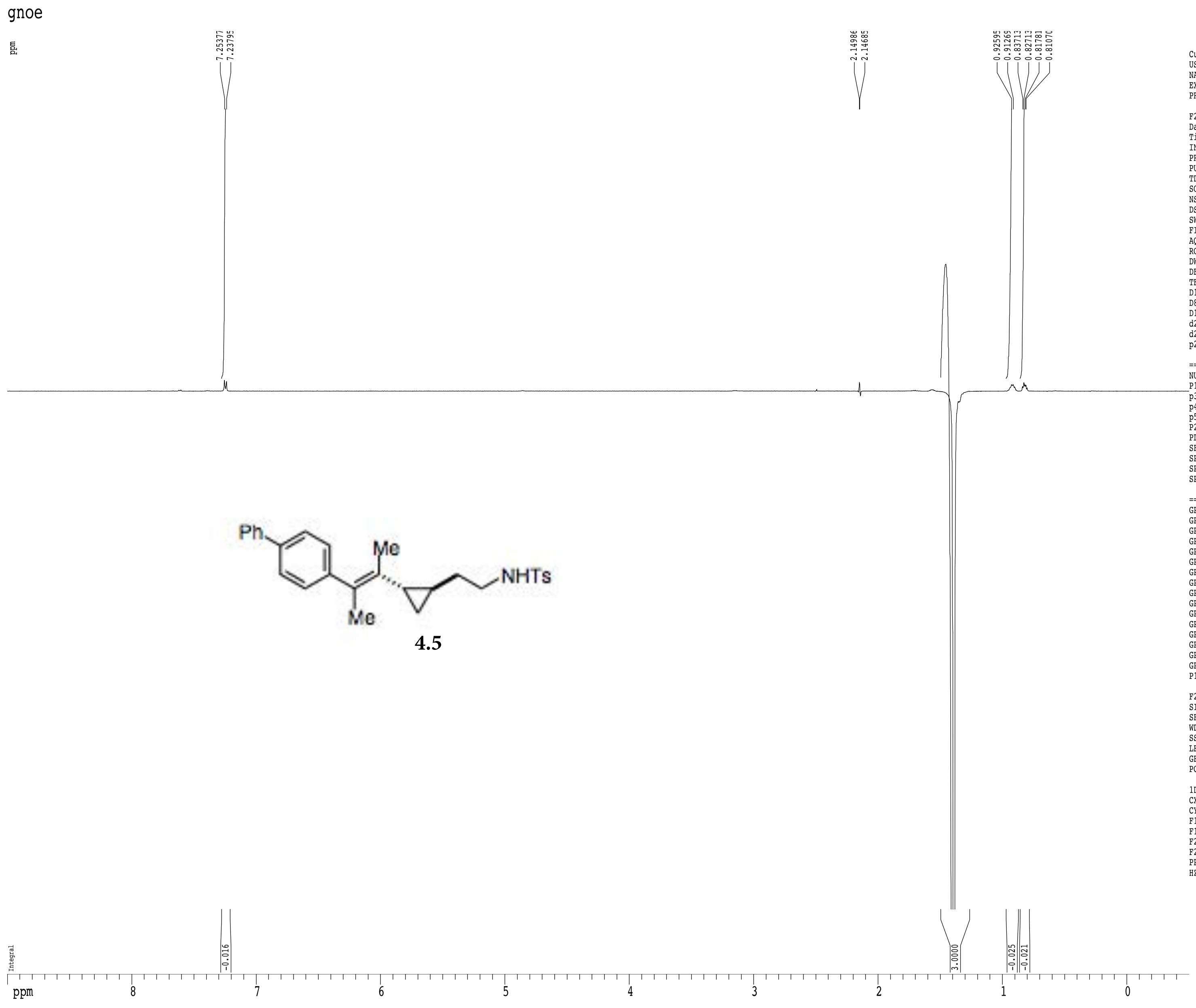
4.5

```
Current Data Parameters
USER            khewitt1
NAME     ELL-IV-132-f46-48
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190309
Time               12.54
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                    50
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2202857 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



4.5

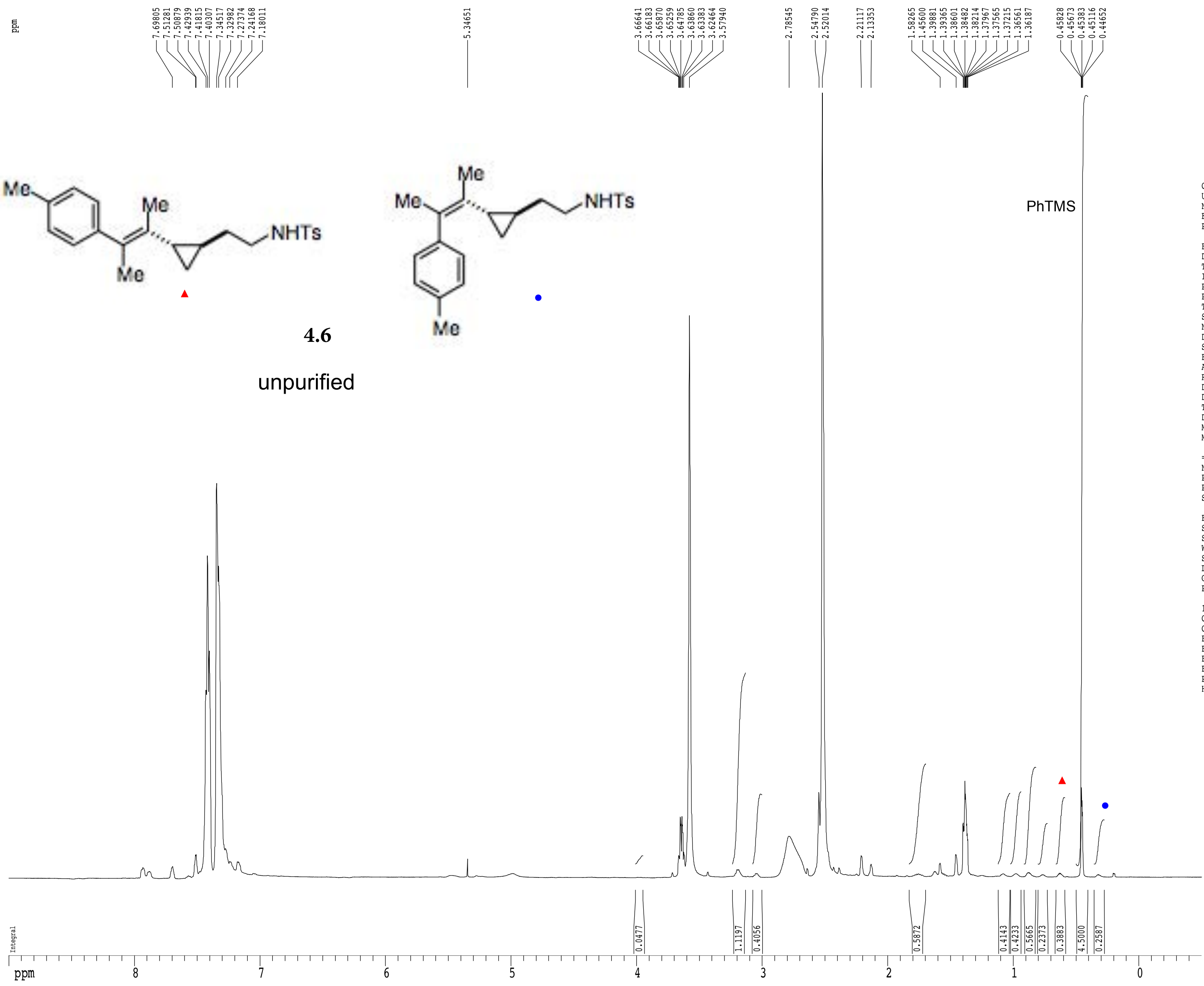
```
Current Data Parameters
USER             khewitt1
NAME     ELL-IV-212-noes
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190718
Time               16.23
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 143.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.2 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2210747 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



4.5

```
Current Data Parameters
USER            khewitt1
NAME      ELL-IV-212-noes
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190718
Time               16.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.2 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2206957 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

1H spectrum

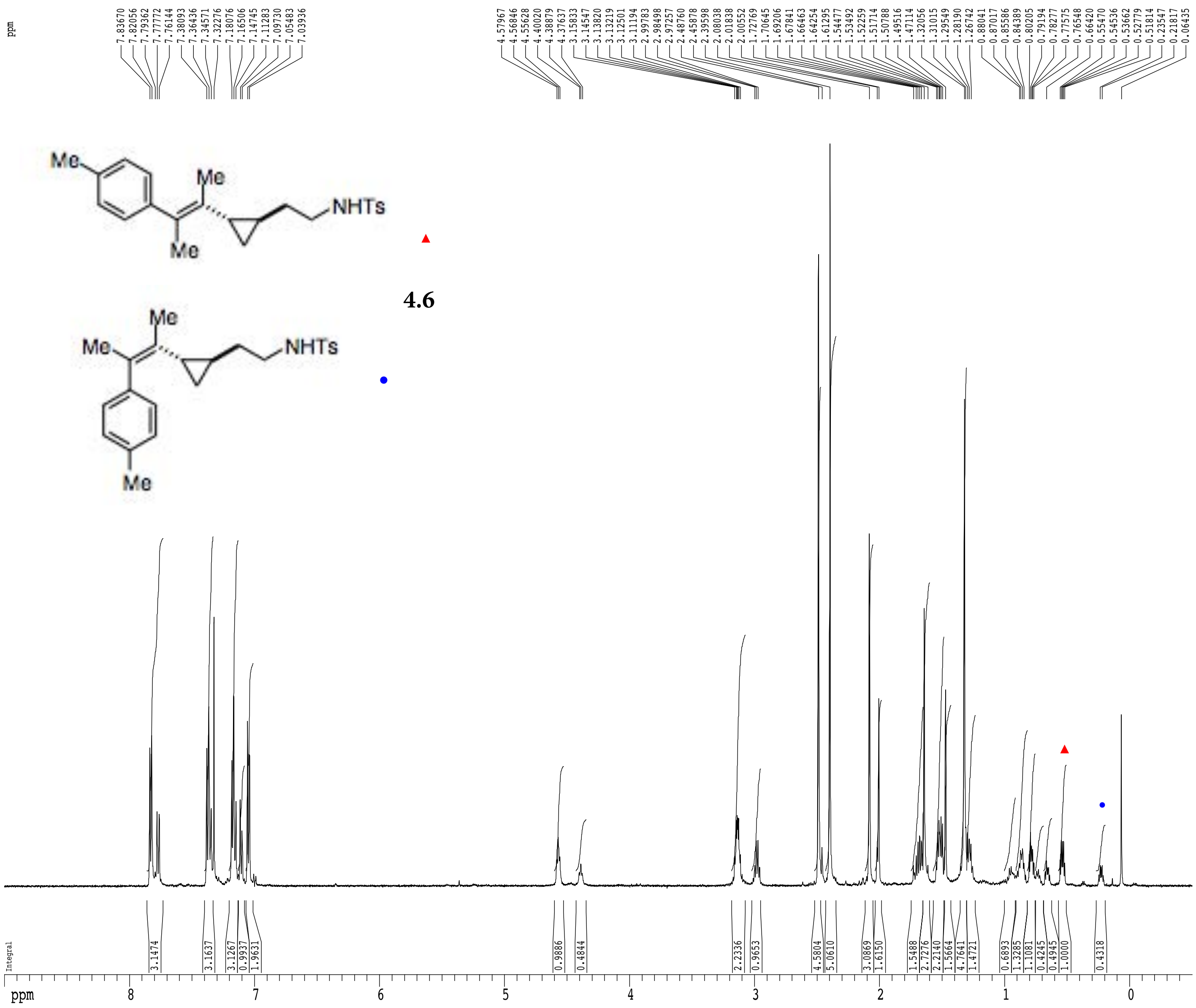


4.6

unpurified

```
Current Data Parameters
USER             khewitt1
NAME      KAH-III-192-crude
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200716
Time                17.58
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  48074
SOLVENT             CDCl3T
NS                      8
DS                      2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    3.2
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

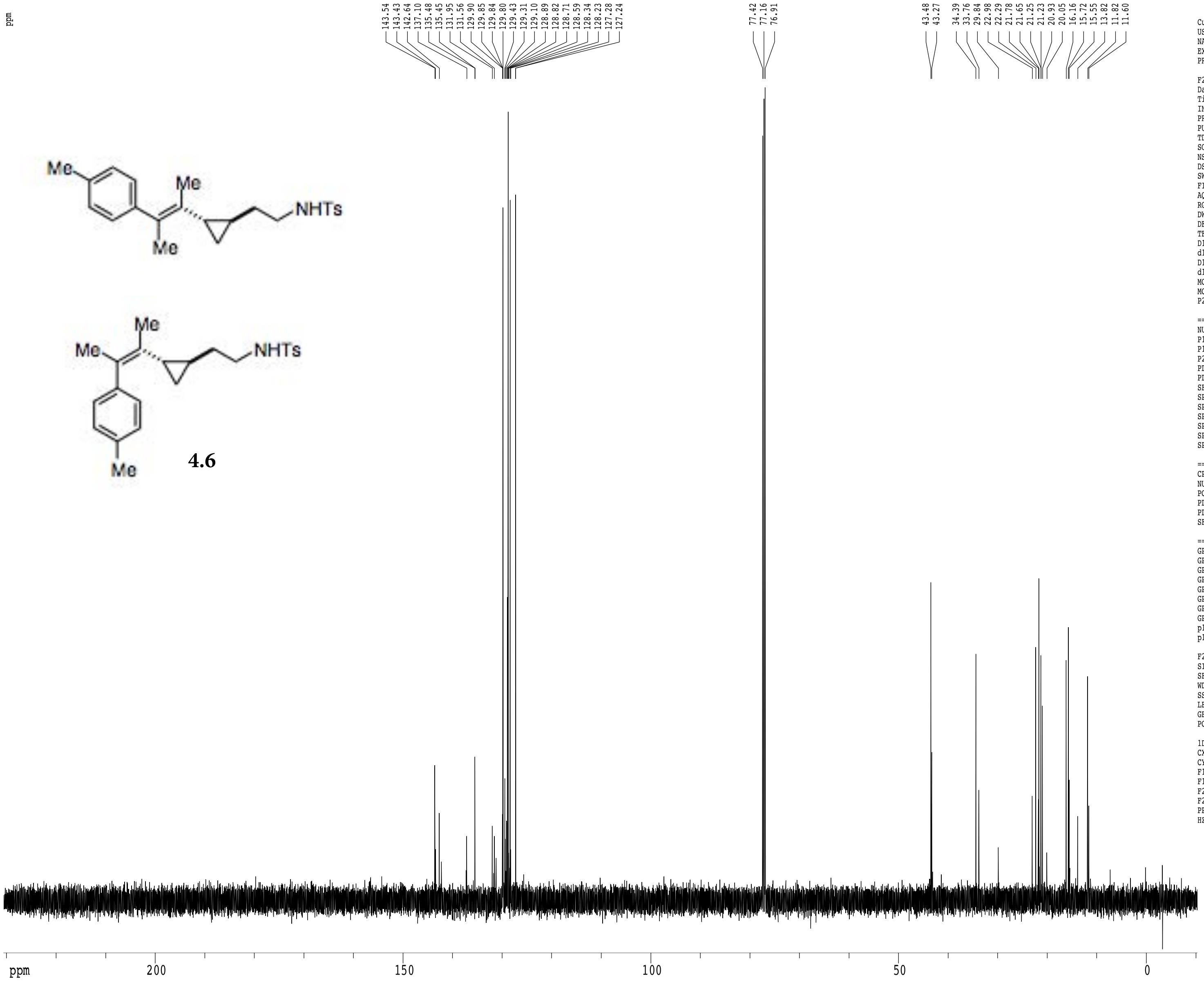
1H spectrum



4.6

```
Current Data Parameters
USER               khewitt1
NAME            KAH-III-192-Z
EXPNO                     9
PROCNO                    1

F2 - Acquisition Parameters
Date_              20200911
Time                  13.33
INSTRUM               gn500
PROBHD    5 mm broadband
PULPROG                zg30
TD                    48074
SOLVENT              CDCl3T
NS                        8
DS                        2
SWH               8012.820 Hz
FIDRES            0.166677 Hz
AQ               2.9998677 sec
RG                    912.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.4 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    12.00 usec
PL1                   -6.00 dB
SFO1            498.7534913 MHz

F2 - Processing parameters
SI                    65536
SF              498.7500000 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    20.00 cm
CY                    12.50 cm
F1P                   9.000 ppm
F1                  4488.75 Hz
F2P                  -0.500 ppm
F2                  -249.38 Hz
PPMCM               0.47500 ppm/cm
HZCM              236.90625 Hz/cm
```

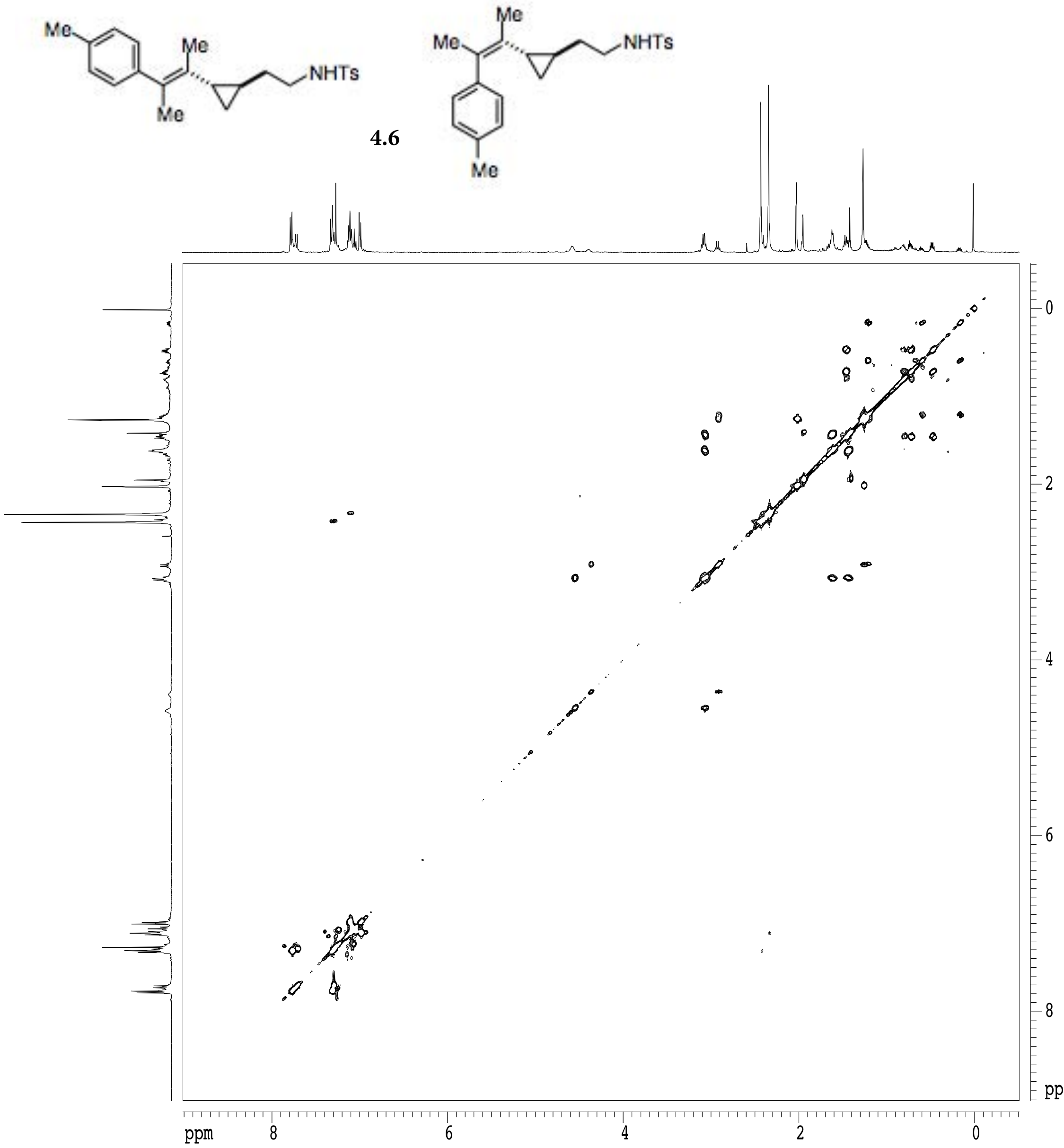
Z-restored spin-echo 13C spectrum with 1H decoupling



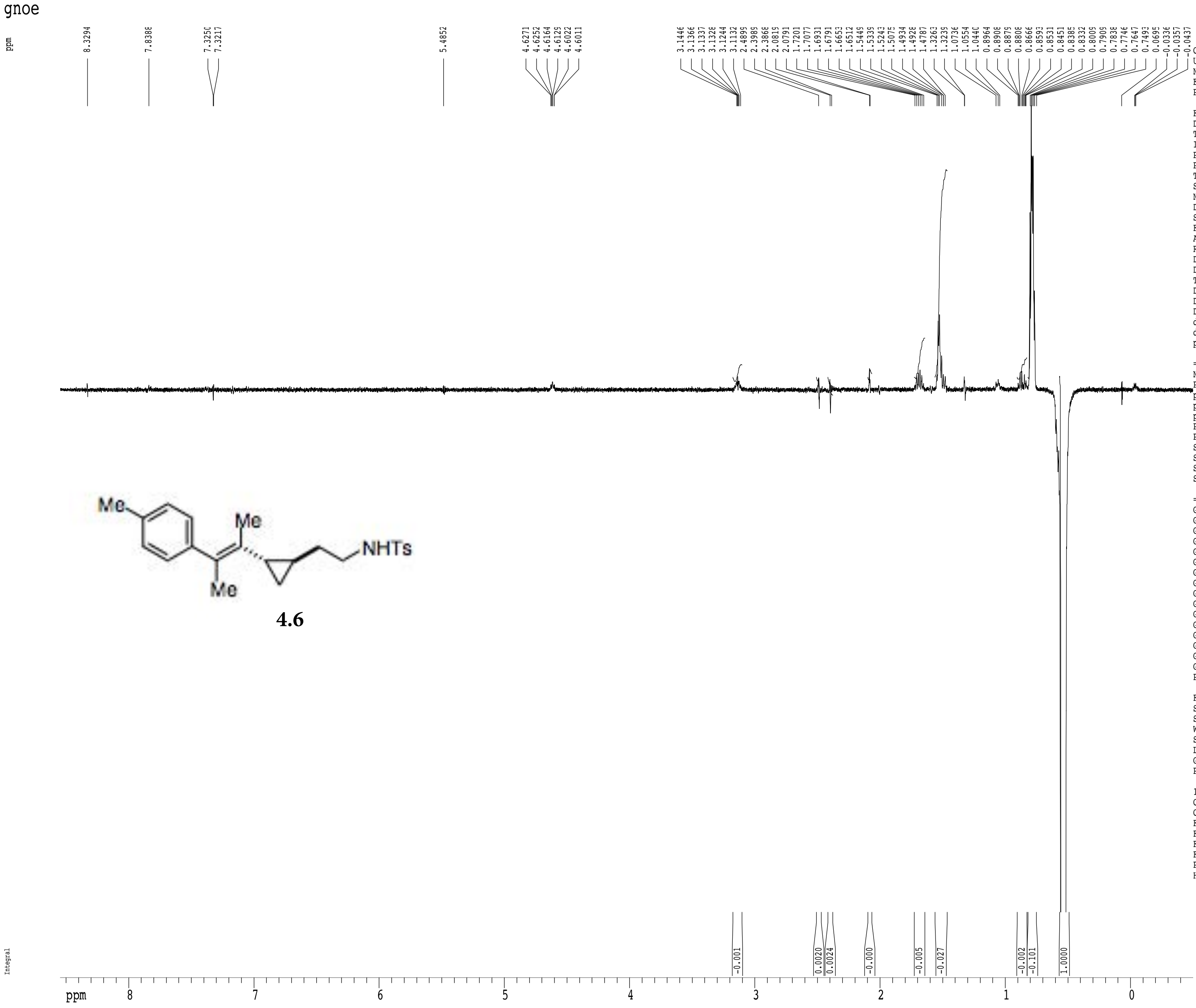
4.6

```
Current Data Parameters
USER              khewitt1
NAME          KAH-III-192-Z
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200909
Time                 18.29
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     528
DS                      16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                    4096
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1               16.55 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                   65536
SF         125.7804080 MHz
WDW                     no
SSB                      0
LB                0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            230.637 ppm
F1             29009.68 Hz
F2P            -10.287 ppm
F2             -1293.96 Hz
PPMCM         10.56688 ppm/cm
HZCM        1329.10693 Hz/cm
```

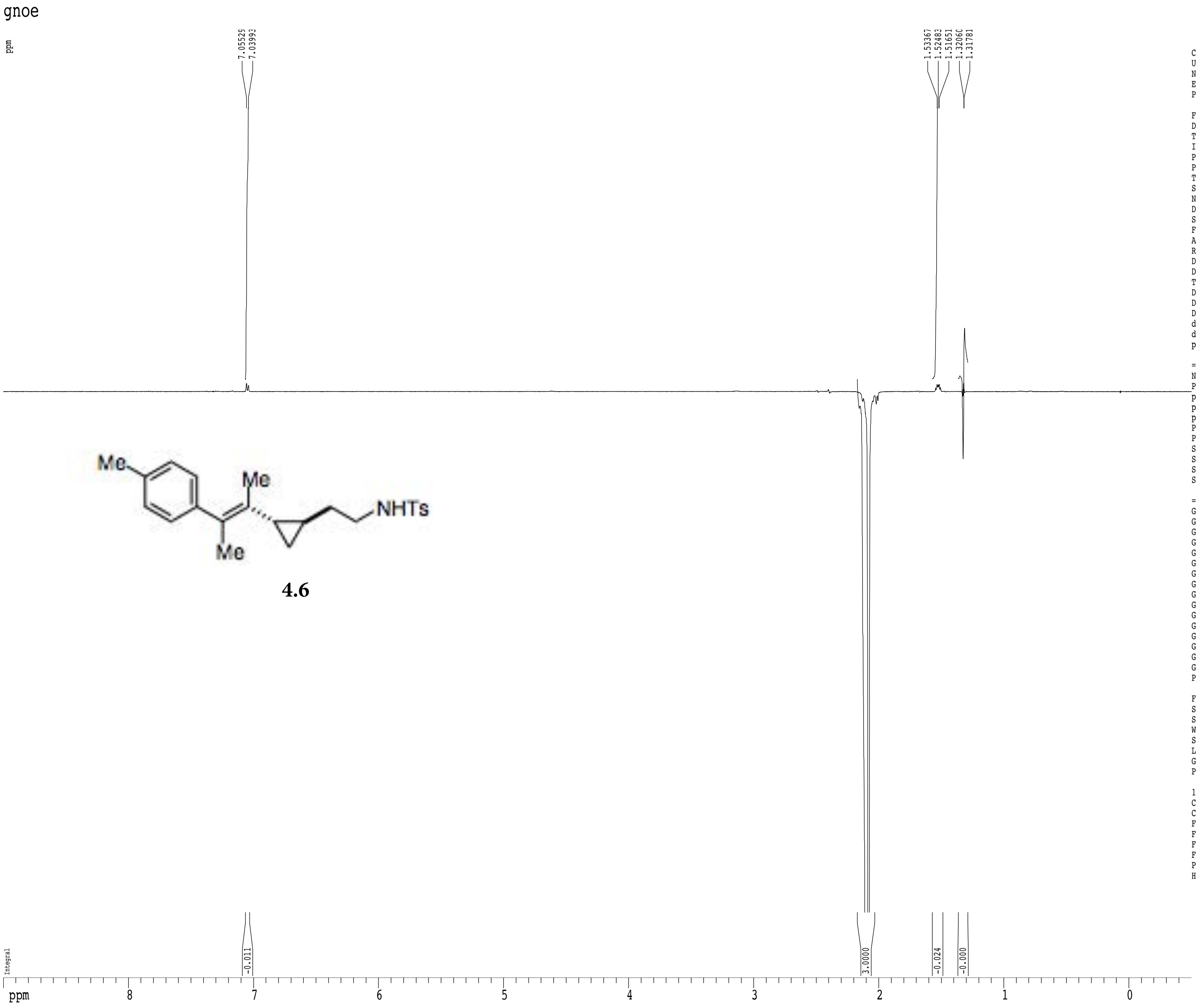
gcosy60


4.6

```
        Current Data Parameters
USER           khewitt1
NAME      KAH-III-192-Z
EXPNO                 3
PROCNO                1

       F2 - Acquisition Parameters
Date_          20200909
Time              18.03
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                  128
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

       F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

       F2 - Processing parameters
SI                 1024
SF          500.2200326 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

       F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200326 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.015 ppm
F2LO            4509.66 Hz
F2PHI            -0.511 ppm
F2HI            -255.78 Hz
F1PLO             9.015 ppm
F1LO            4509.66 Hz
F1PHI            -0.511 ppm
F1HI            -255.78 Hz
F2PPMCM         0.63511 ppm/cm
F2HZCM        317.69580 Hz/cm
F1PPMCM         0.63511 ppm/cm
F1HZCM        317.69580 Hz/cm
```



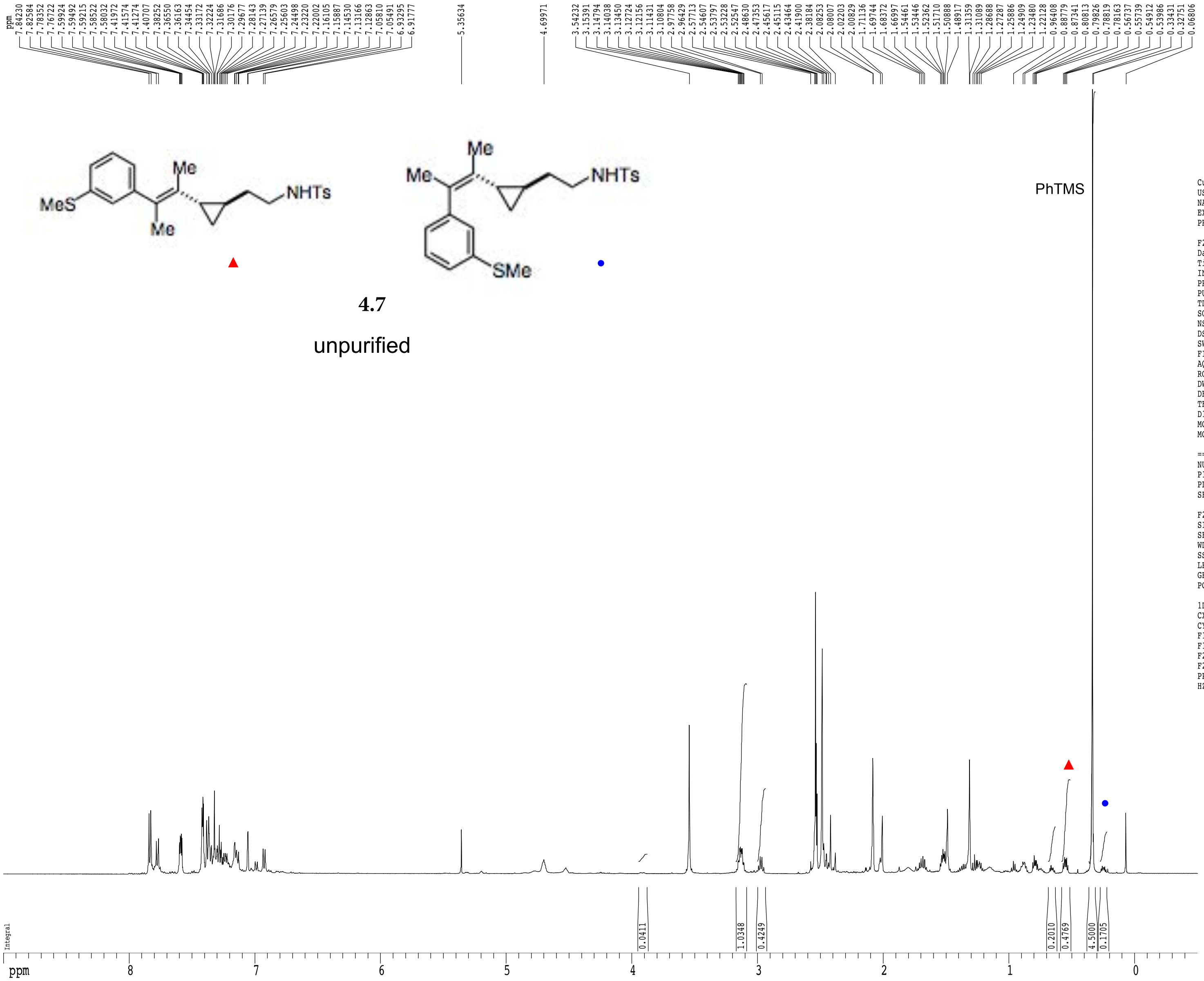
```
Current Data Parameters
USER          khewitt1
NAME      KAH-III-192-Z
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_          20200909
Time              18.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                101.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2202682 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



4.6

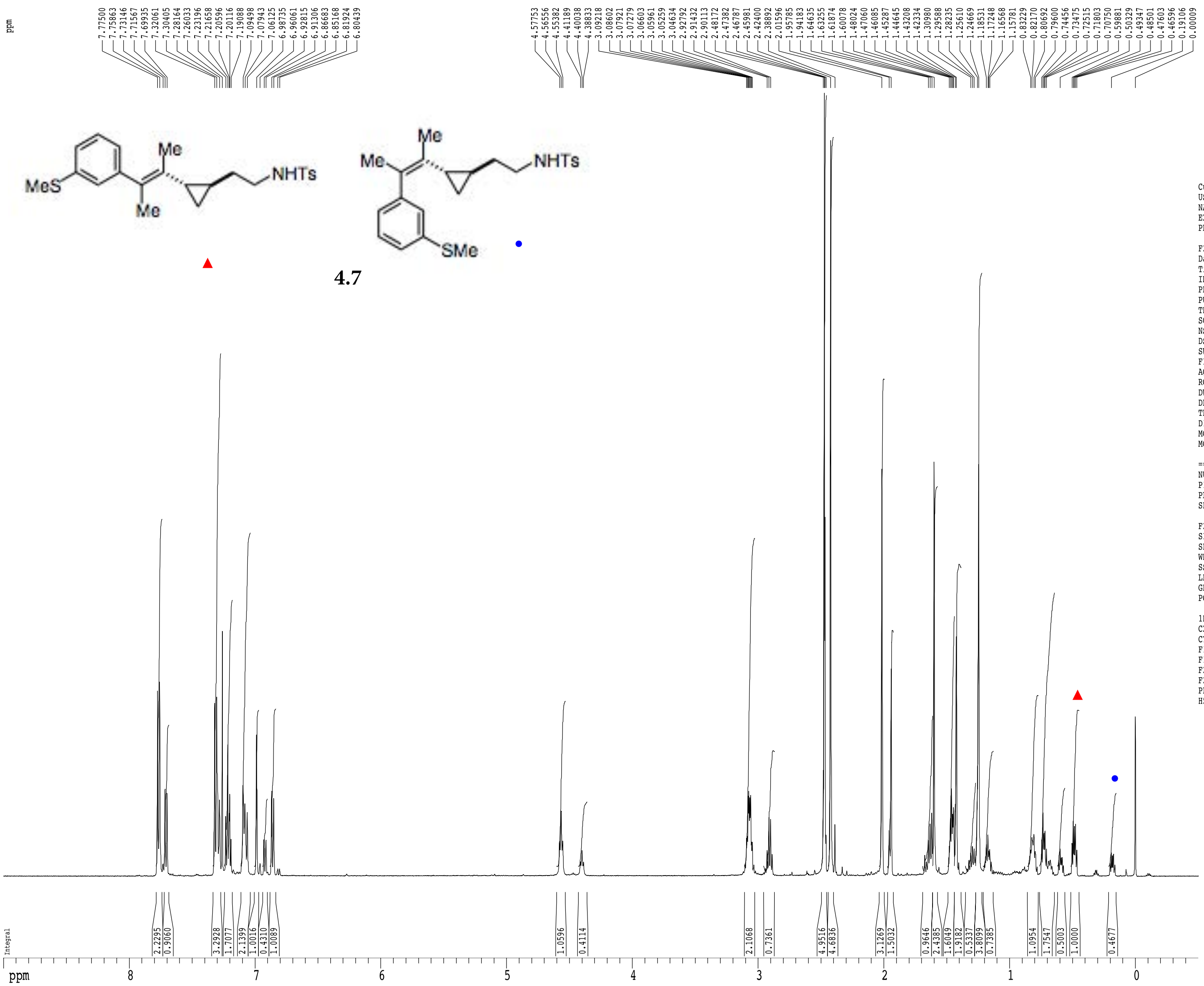
```
Current Data Parameters
USER             khewitt1
NAME          KAH-III-192-Z
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200909
Time                18.54
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  161.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2210408 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-193-crude
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_           20200716
Time               18.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

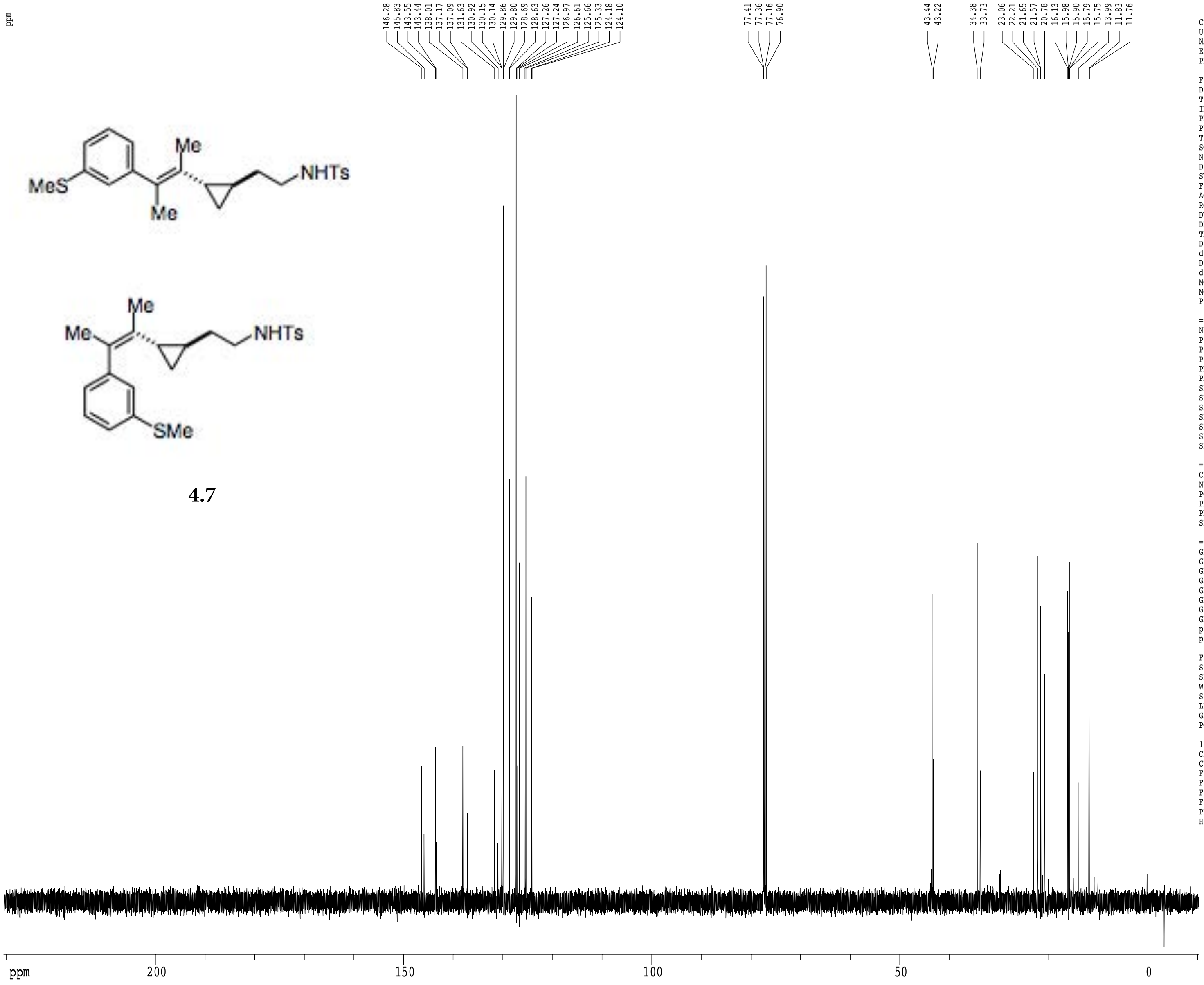
1H spectrum



4.7

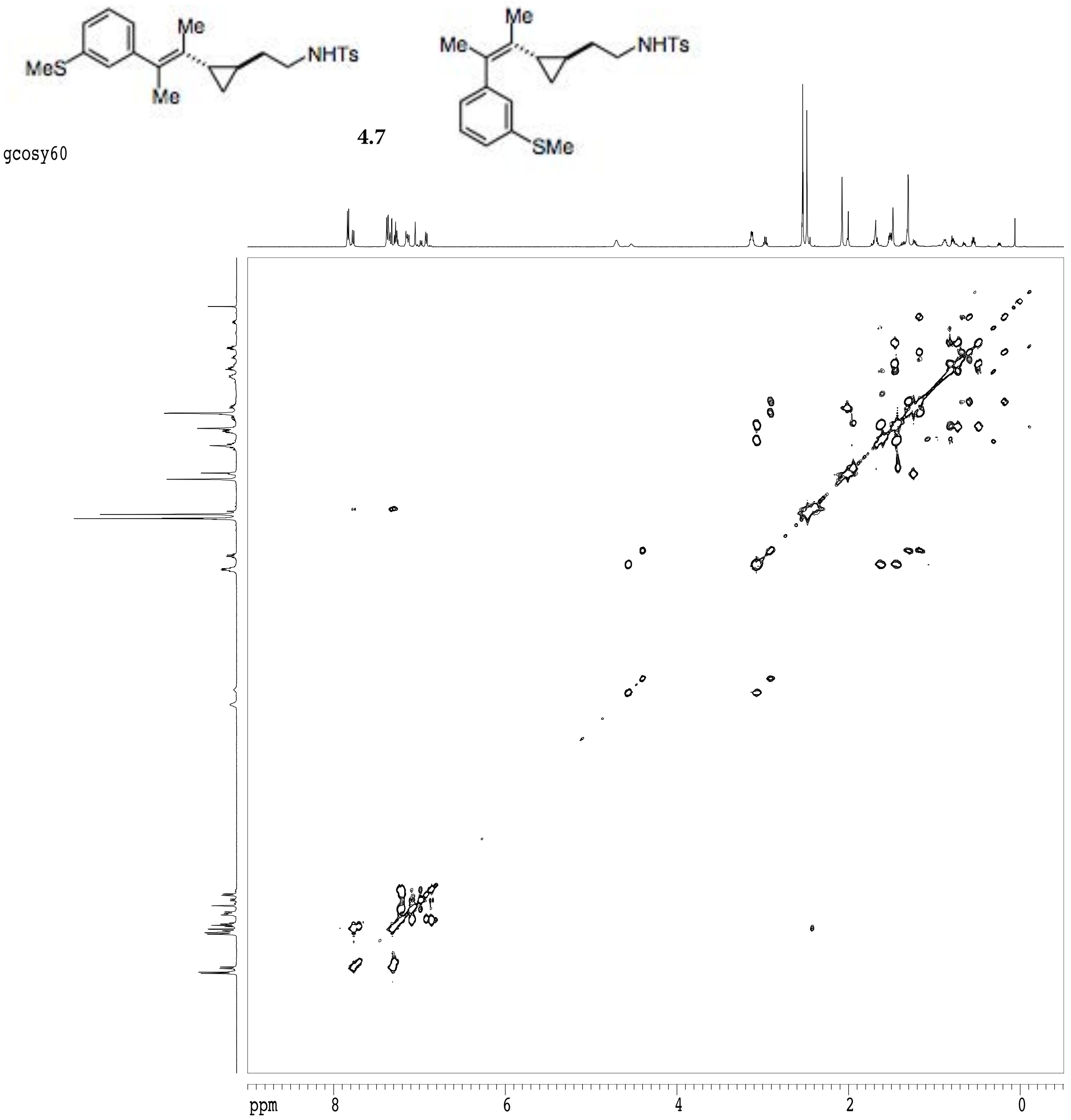
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-193-Z
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200909
Time                18.59
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  48074
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.166677 Hz
AQ              2.9998677 sec
RG                    7.1
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200316 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



4.7

```
Current Data Parameters
USER            khewitt1
NAME       KAH-III-193-Z
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200909
Time               19.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2      Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804090 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

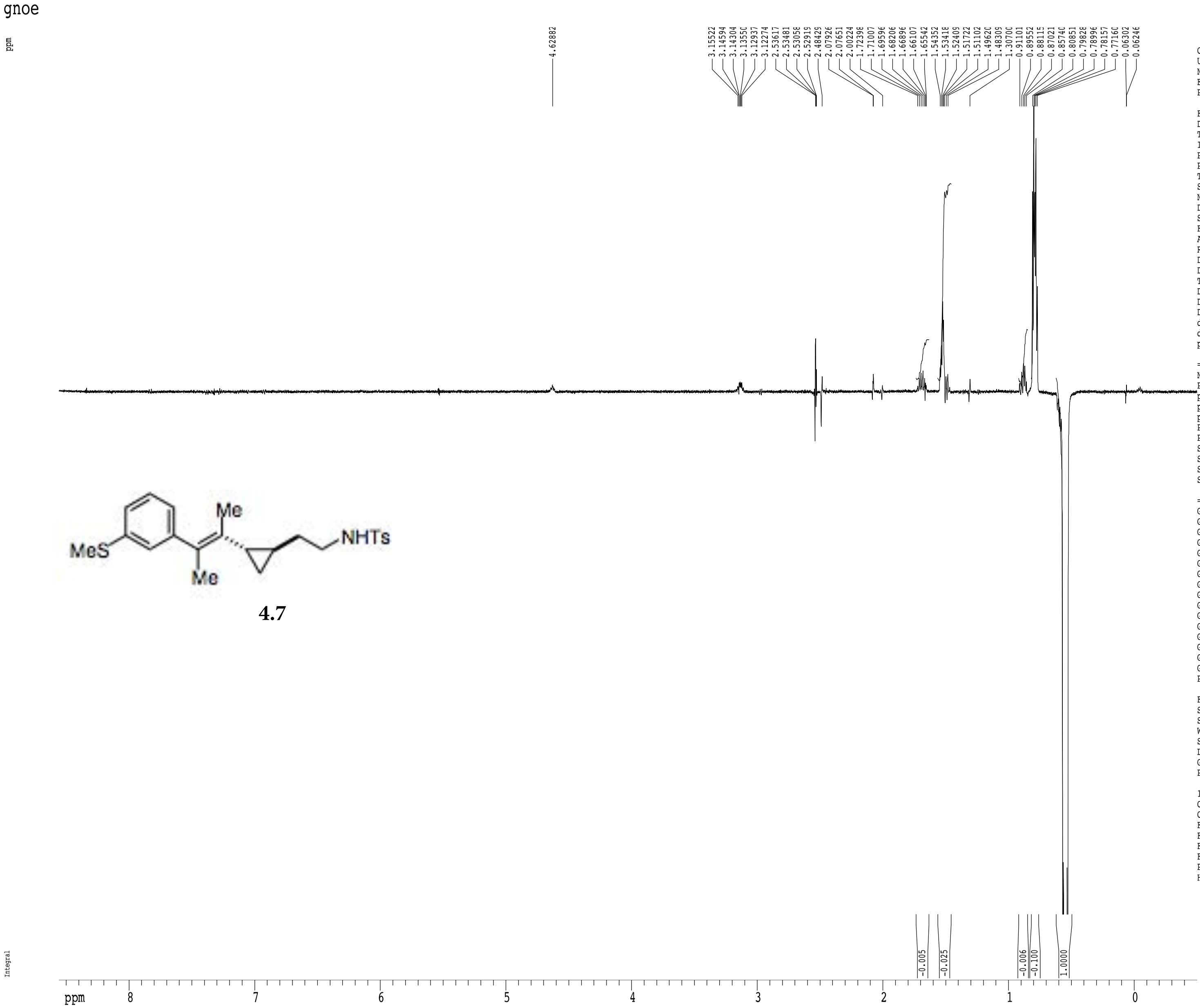


4.7

gcosy60

```
        Current Data Parameters
USER            khewitt1
NAME      KAH-III-193-Z
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20200909
Time               19.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   181
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200315 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200315 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

      2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.002 ppm
F2LO             4502.93 Hz
F2PHI             -0.509 ppm
F2HI             -254.68 Hz
F1PLO              9.002 ppm
F1LO             4502.93 Hz
F1PHI             -0.509 ppm
F1HI             -254.68 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```

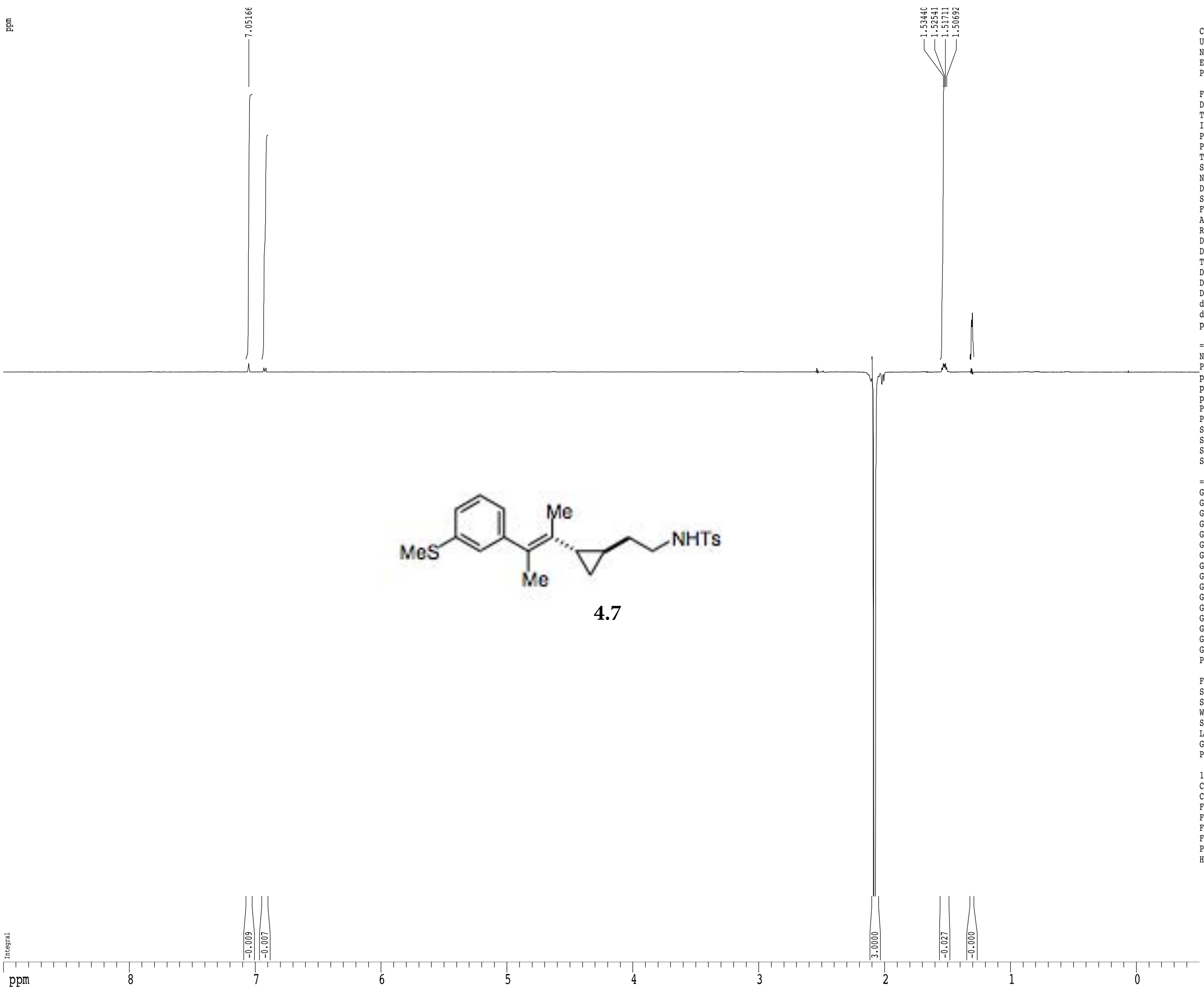
gnoe



4.7

```
Current Data Parameters
USER             khewitt1
NAME         KAH-III-193-Z
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_          20200909
Time              19.25
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 80.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2202741 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

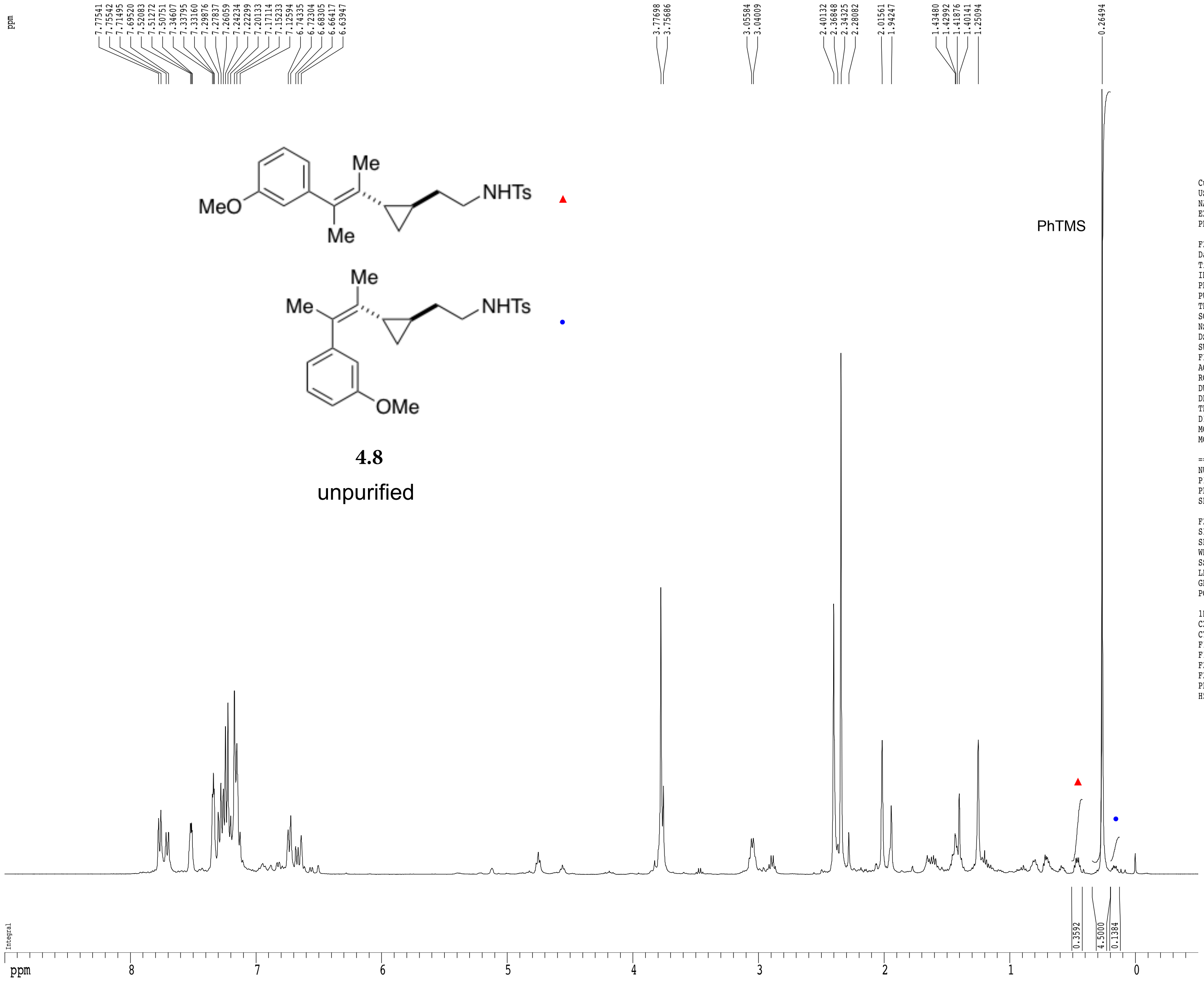
gnoe



4.7

```
Current Data Parameters
USER           khewitt1
NAME      KAH-III-193-Z
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20200909
Time              19.39
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                161.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2210401 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

1H spectrum

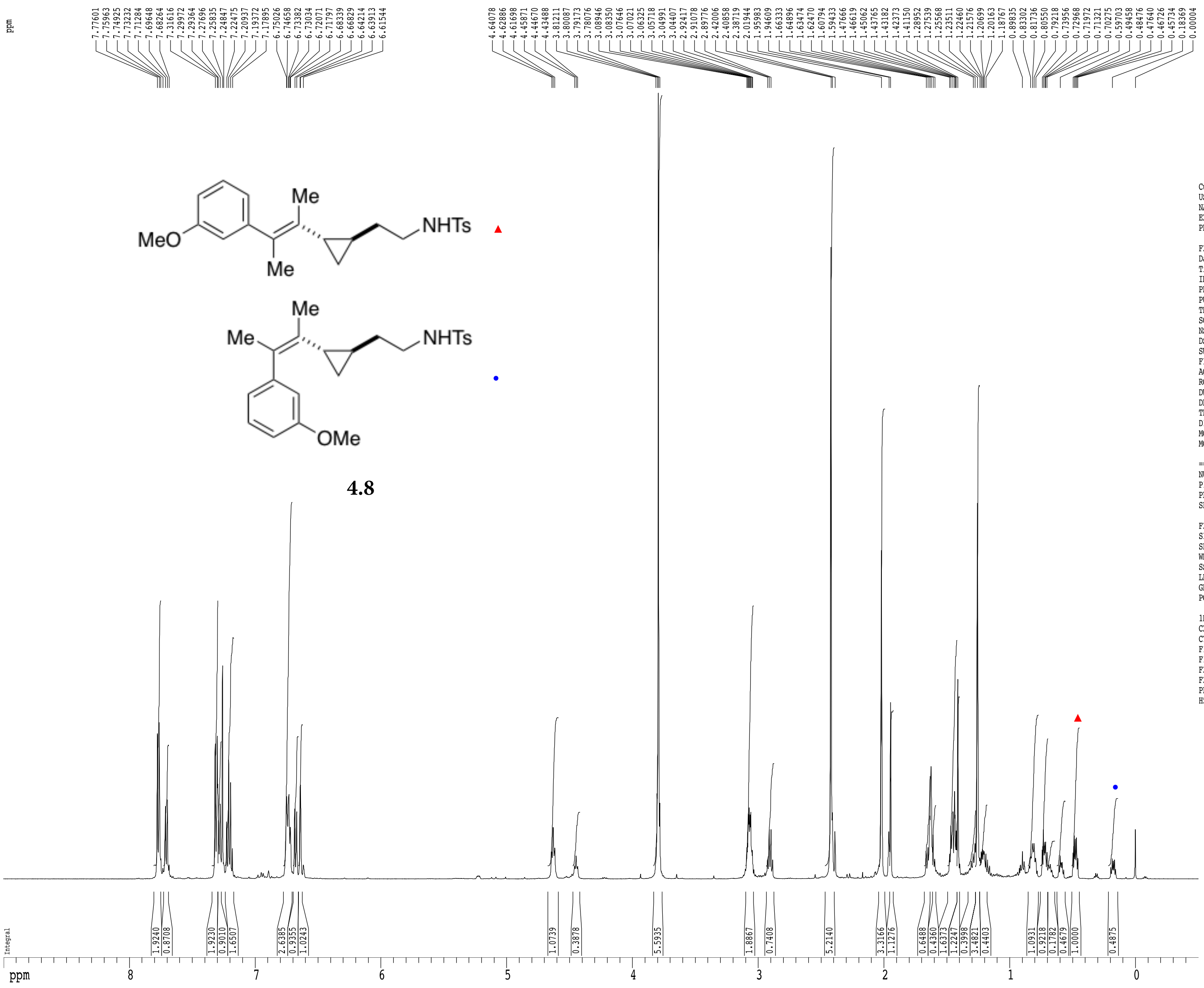


4.8

unpurified

```
Current Data Parameters
USER            nhirbawi
NAME        NH-1-57-crude
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200922
Time               17.05
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 295.1 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300365 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

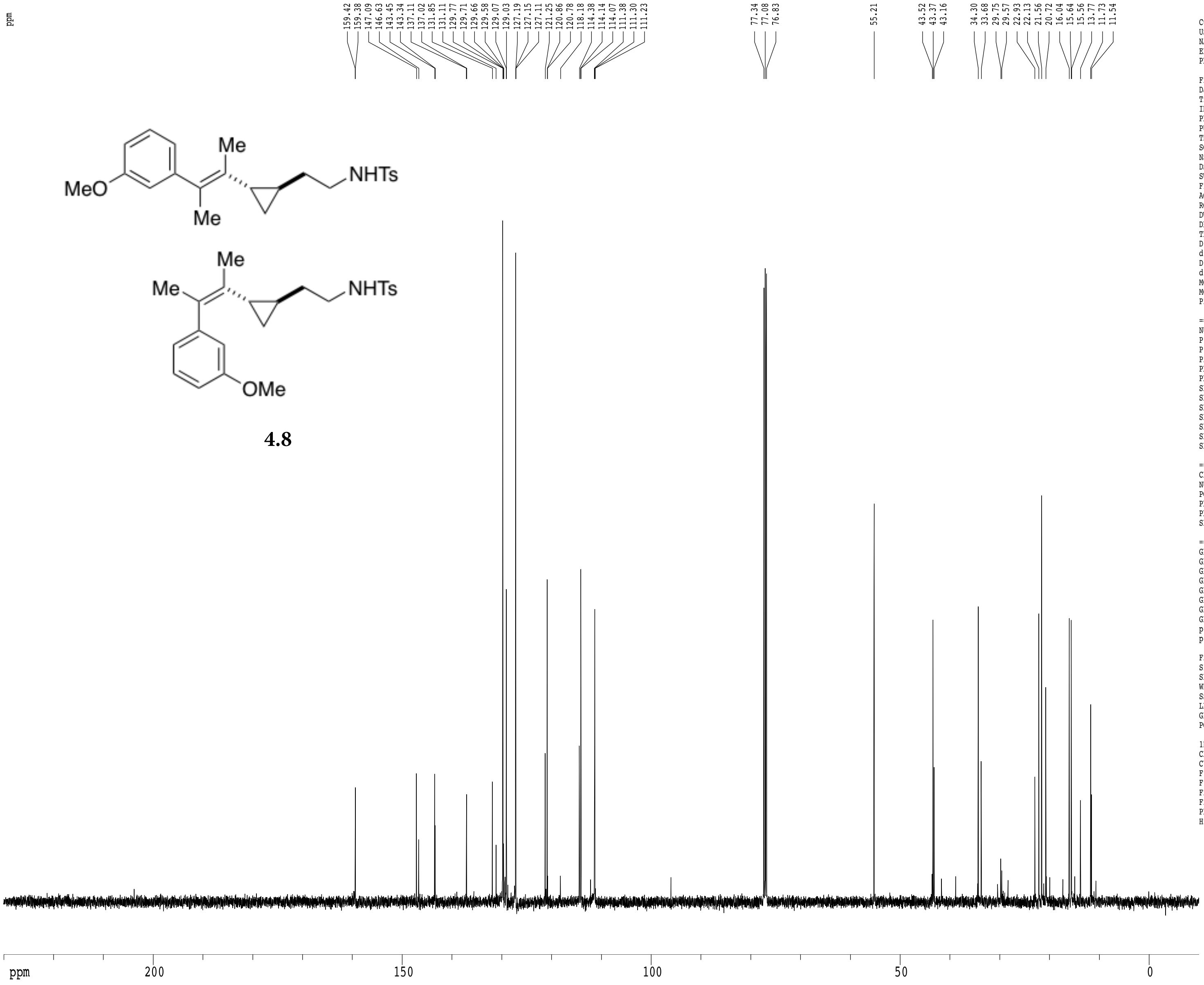
1H spectrum



4.8

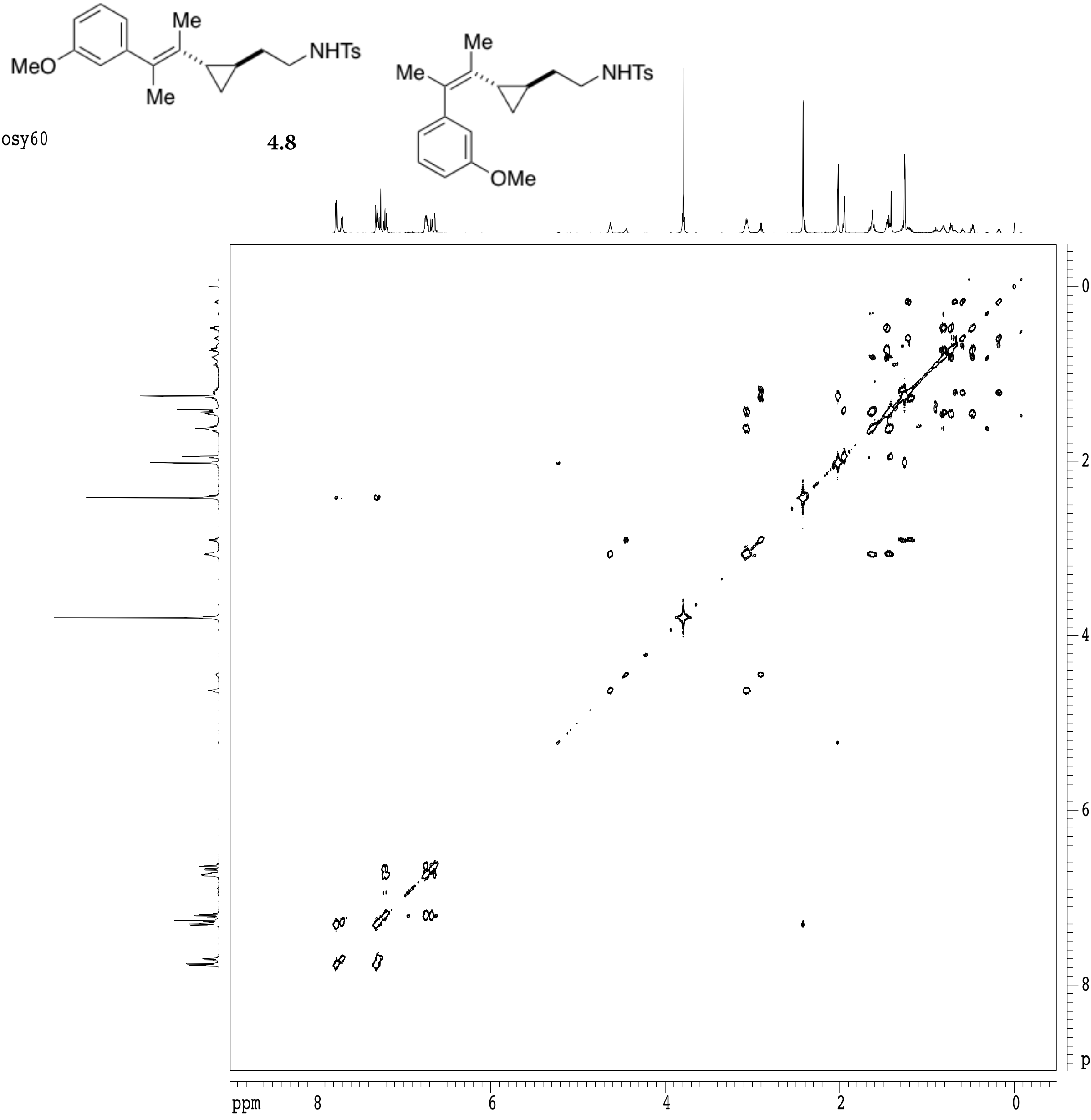
```
Current Data Parameters
USER           nhirbawi
NAME      NH-1-57-HandCOSY
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200928
Time              17.33
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200322 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



4.8

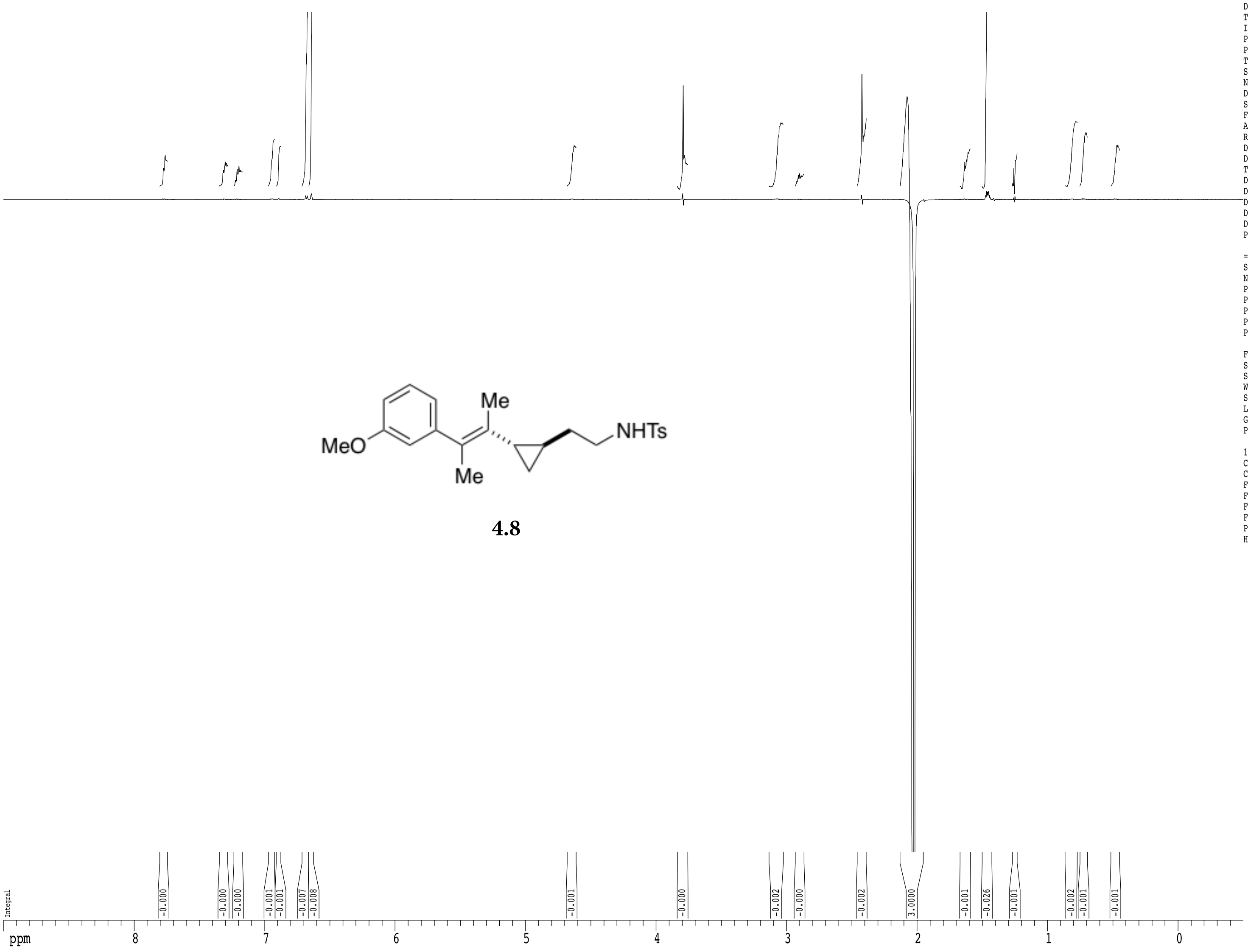
```
Current Data Parameters
USER            nhirbawi
NAME     NH-1-57-HandCOSY
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200928
Time               17.58
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                    16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG                  4096
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1               16.55 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                 65536
SF         125.7804190 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX               22.80 cm
CY               13.00 cm
F1P            230.000 ppm
F1            28929.50 Hz
F2P            -10.000 ppm
F2            -1257.80 Hz
PPMCM         10.52632 ppm/cm
HZCM        1324.00439 Hz/cm
```



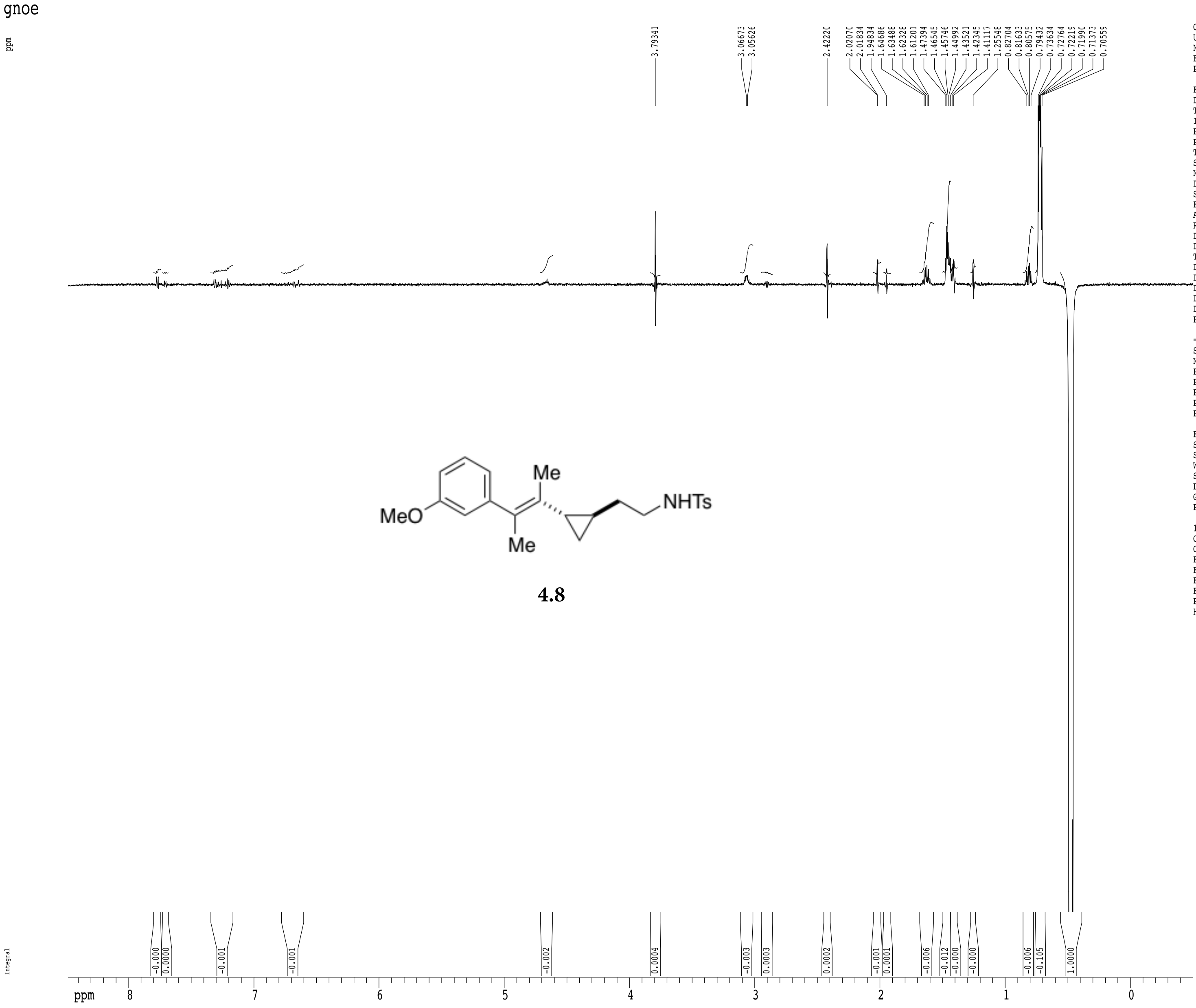
4.8

```
       Current Data Parameters
 USER           nhirbawi
NAME     NH-1-57-HandCOSY
 EXPNO                 2
 PROCNO                1

      F2 - Acquisition Parameters
 Date_          20200928
 Time              17.36
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG    cosygp60.prd
 TD                 2048
 SOLVENT          CDCl3T
 NS                    2
 DS                   16
 SWH            4734.849 Hz
 FIDRES         2.311938 Hz
 AQ            0.2163188 sec
 RG                  128
 DW              105.600 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00021120 sec

     ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2221582 MHz

     ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  256
 SFO1           500.2222 MHz
 FIDRES        18.495502 Hz
 SW                9.465 ppm
 FnMODE               QF

      F2 - Processing parameters
 SI                 1024
 SF          500.2200323 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

      F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200324 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

        2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             8.983 ppm
 F2LO            4493.29 Hz
 F2PHI            -0.483 ppm
 F2HI            -241.56 Hz
 F1PLO             8.982 ppm
 F1LO            4493.23 Hz
 F1PHI            -0.483 ppm
 F1HI            -241.62 Hz
 F2PPMCM         0.63104 ppm/cm
 F2HZCM        315.65659 Hz/cm
 F1PPMCM         0.63104 ppm/cm
 F1HZCM        315.65659 Hz/cm
```

gnoe



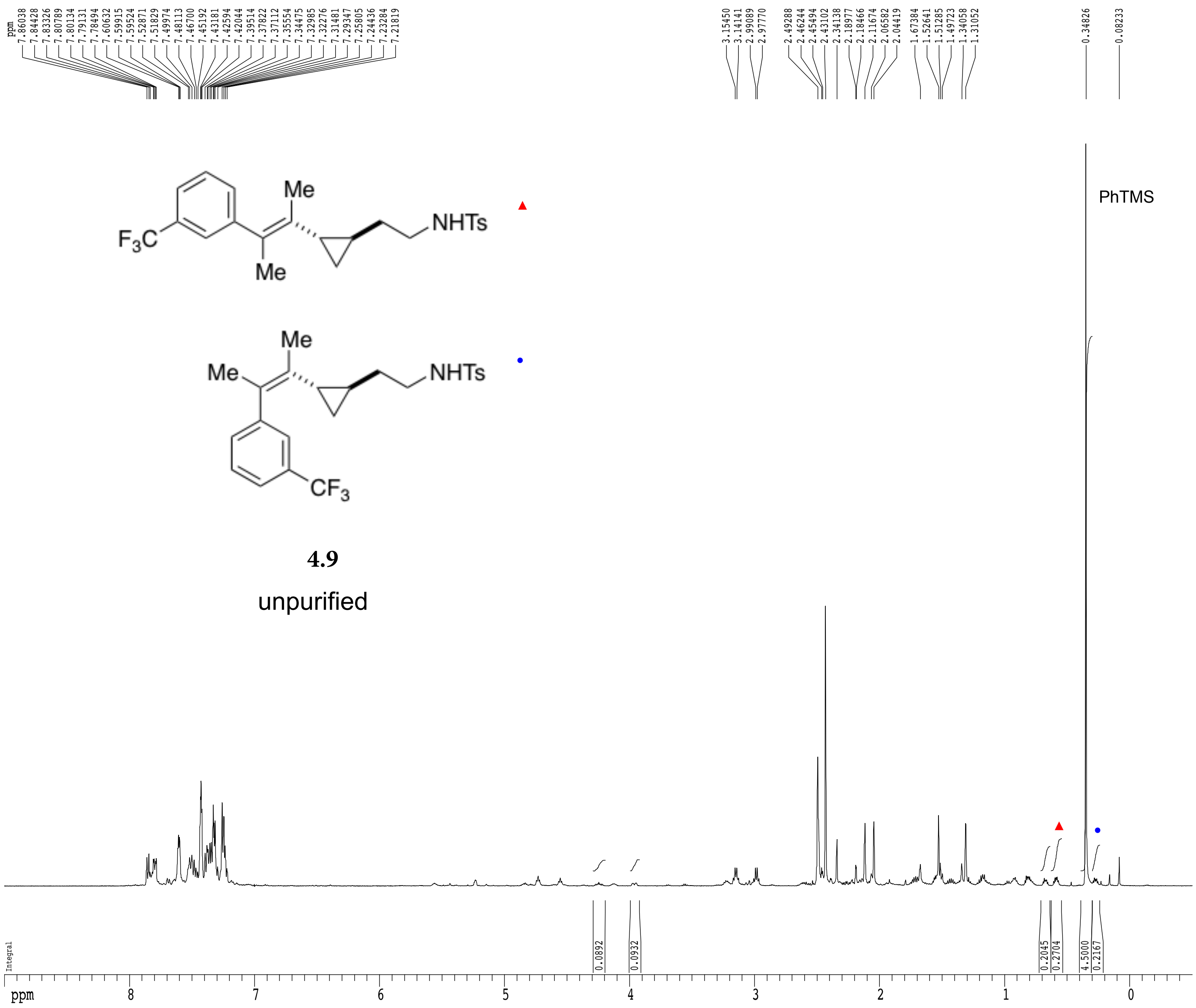
```
Current Data Parameters
USER            nhirbawi
NAME      NH-1-57-600NOE1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200928
Time               18.29
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG      gnoe1cc.wu
TD                 98074
SOLVENT           CDCl3T
NS                   158
DS                     8
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                    32
DW                52.000 usec
DE                 10.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
D21           0.33375570 sec
D22           0.16399699 sec
P2                 19.00 usec

======== CHANNEL f1 ========
SFO1         600.1312476 MHz
NUC1                  1H
P1                  9.50 usec
P3                 28.50 usec
P4                 38.00 usec
P5                 25.33 usec
P12             80000.00 usec

F2 - Processing parameters
SI                 65536
SF           600.1300365 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05420 Hz/cm
```



4.8

```
Current Data Parameters
USER          nhirbawi
NAME     NH-1-57-600NOE2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20201001
Time              17.12
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG      gnoe1cc.wu
TD                98074
SOLVENT          CDCl3T
NS                  158
DS                    8
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998979 sec
RG                 20.2
DW               52.000 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
D21          0.33375570 sec
D22          0.16399699 sec
P2                19.00 usec

======== CHANNEL f1 ========
SFO1        600.1303190 MHz
NUC1                 1H
P1                 9.50 usec
P3                28.50 usec
P4                38.00 usec
P5                25.33 usec
P12            80000.00 usec

F2 - Processing parameters
SI                65536
SF          600.1300361 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              5401.17 Hz
F2P              -0.500 ppm
F2              -300.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          250.05420 Hz/cm
```

1H spectrum

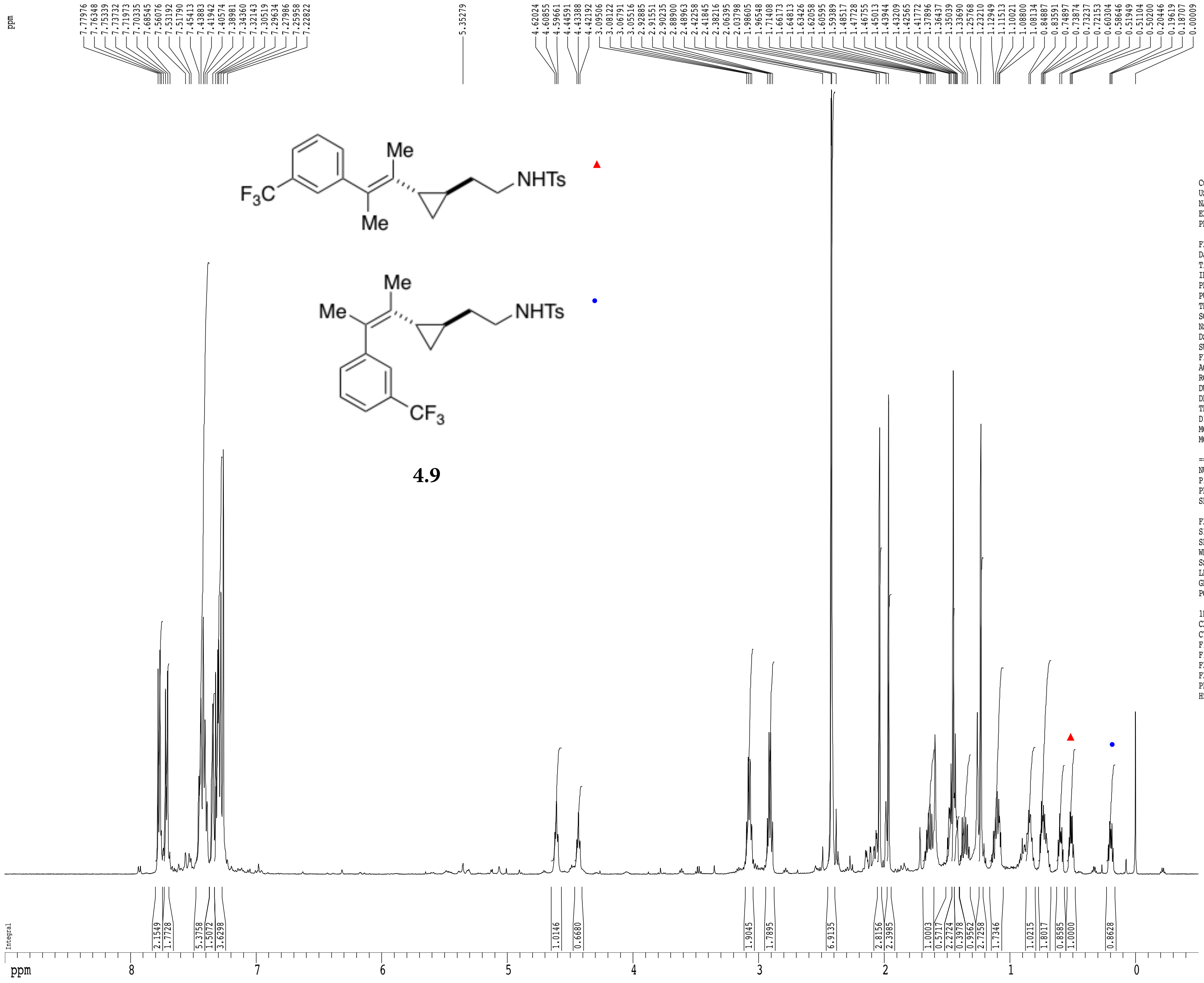


4.9

unpurified

```
Current Data Parameters
USER                tthane
NAME            TATiv134nmr
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200909
Time                 11.34
INSTRUM              gn500
PROBHD    5 mm broadband
PULPROG               zg30
TD                   81728
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998774 sec
RG                     114
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -6.00 dB
SFO1           498.7534913 MHz

F2 - Processing parameters
SI                   65536
SF             498.7500000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
CY                   12.50 cm
F1P                  9.000 ppm
F1                 4488.75 Hz
F2P                 -0.500 ppm
F2                 -249.38 Hz
PPMCM              0.47500 ppm/cm
HZCM             236.90625 Hz/cm
```

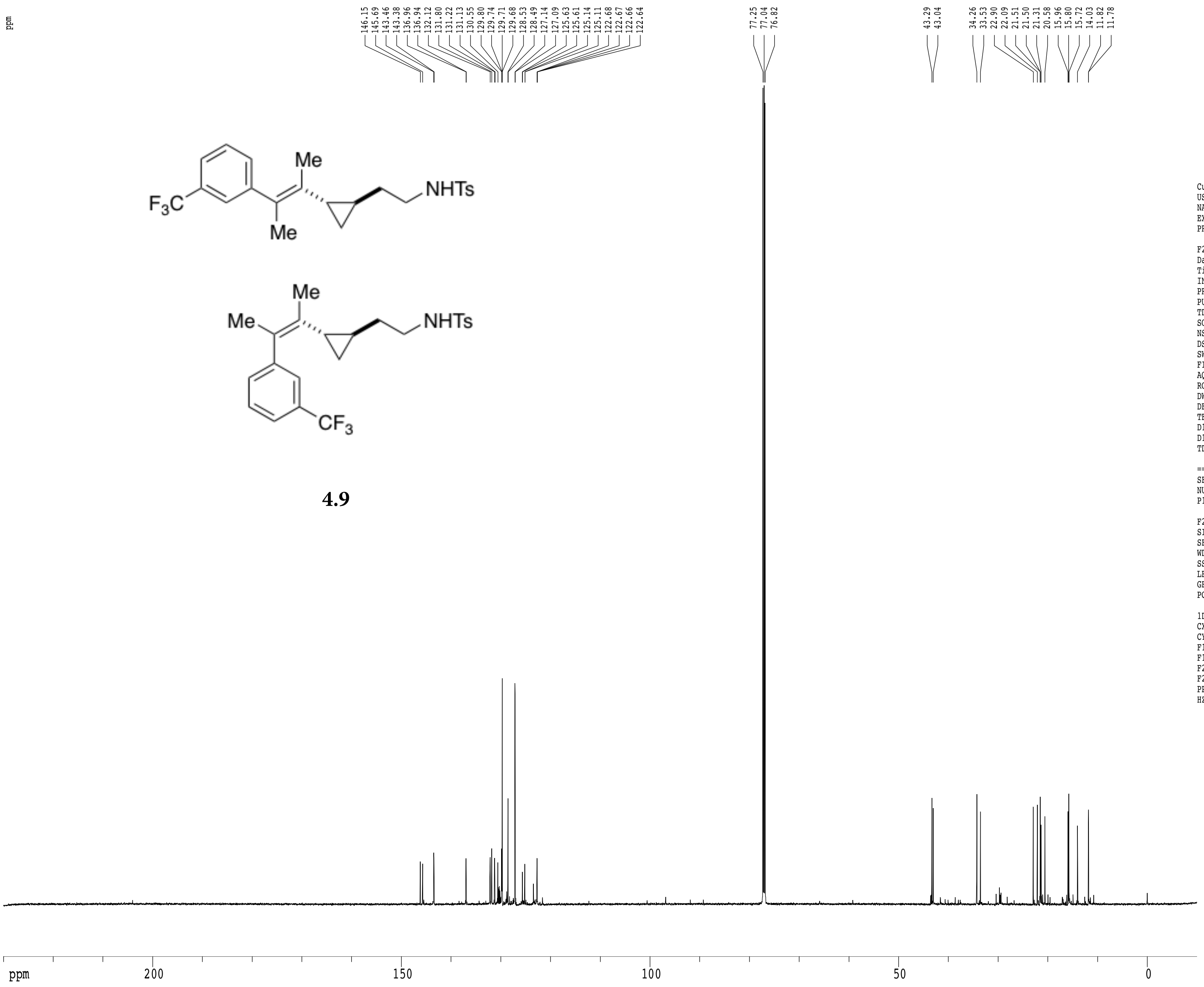
1H spectrum



4.9

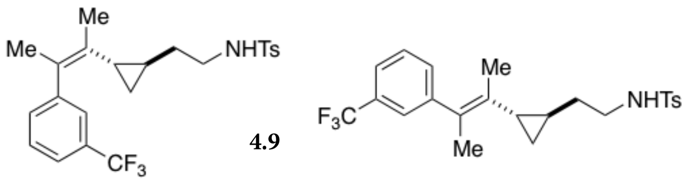
```
Current Data Parameters
USER          nhirbawi
NAME     TAT-mCF3-HCOSYC
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20201010
Time              13.14
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200321 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

13C spectrum with 1H decoupling



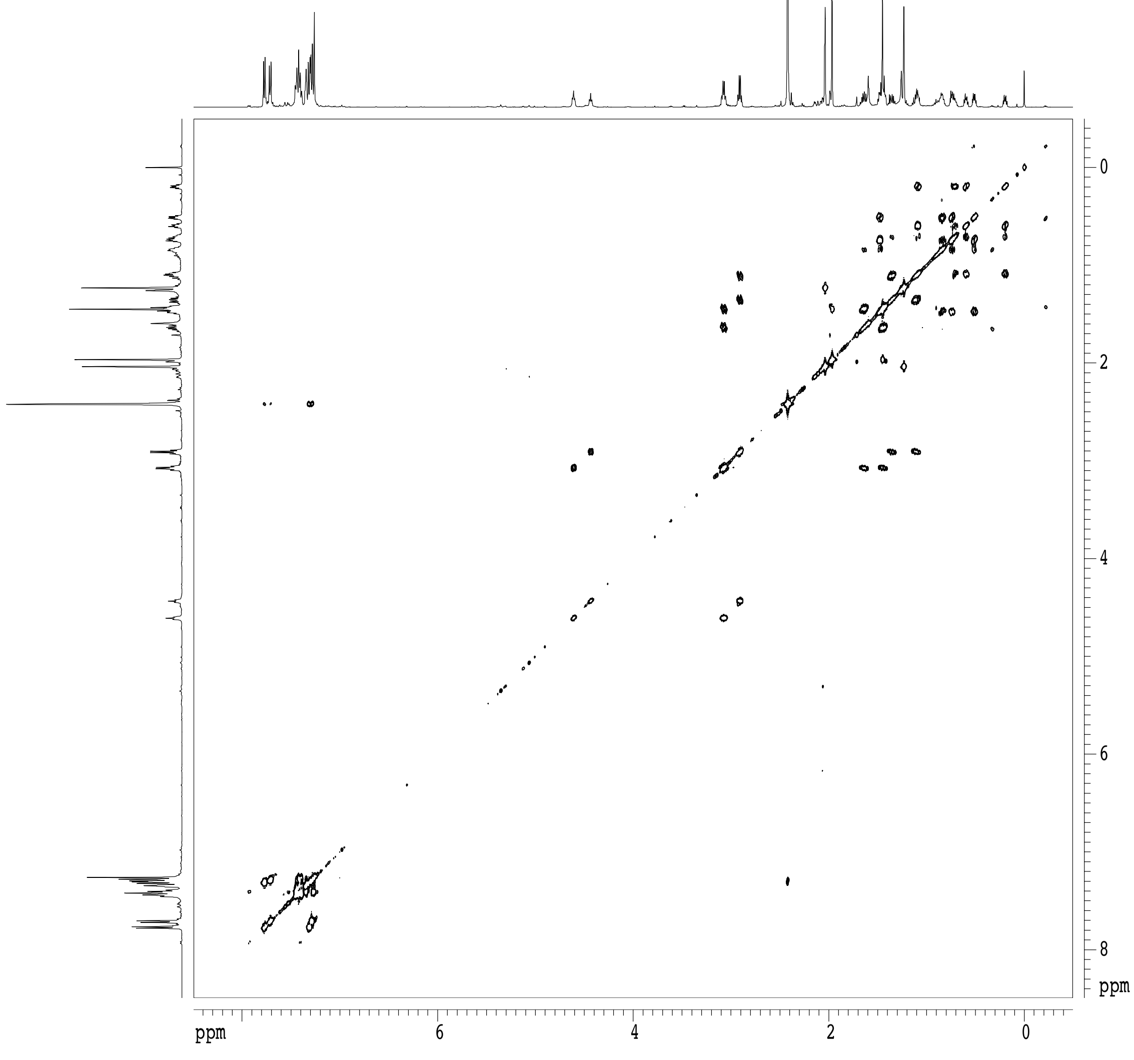
4.9

```
Current Data Parameters
USER           nhirbawi
NAME     TAT-mCF3-FandC
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20201012
Time              17.47
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  840
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                298.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9028141 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.000 ppm
F1             34707.65 Hz
F2P             -10.000 ppm
F2             -1509.03 Hz
PPMCM          10.52632 ppm/cm
HZCM         1588.45081 Hz/cm
```

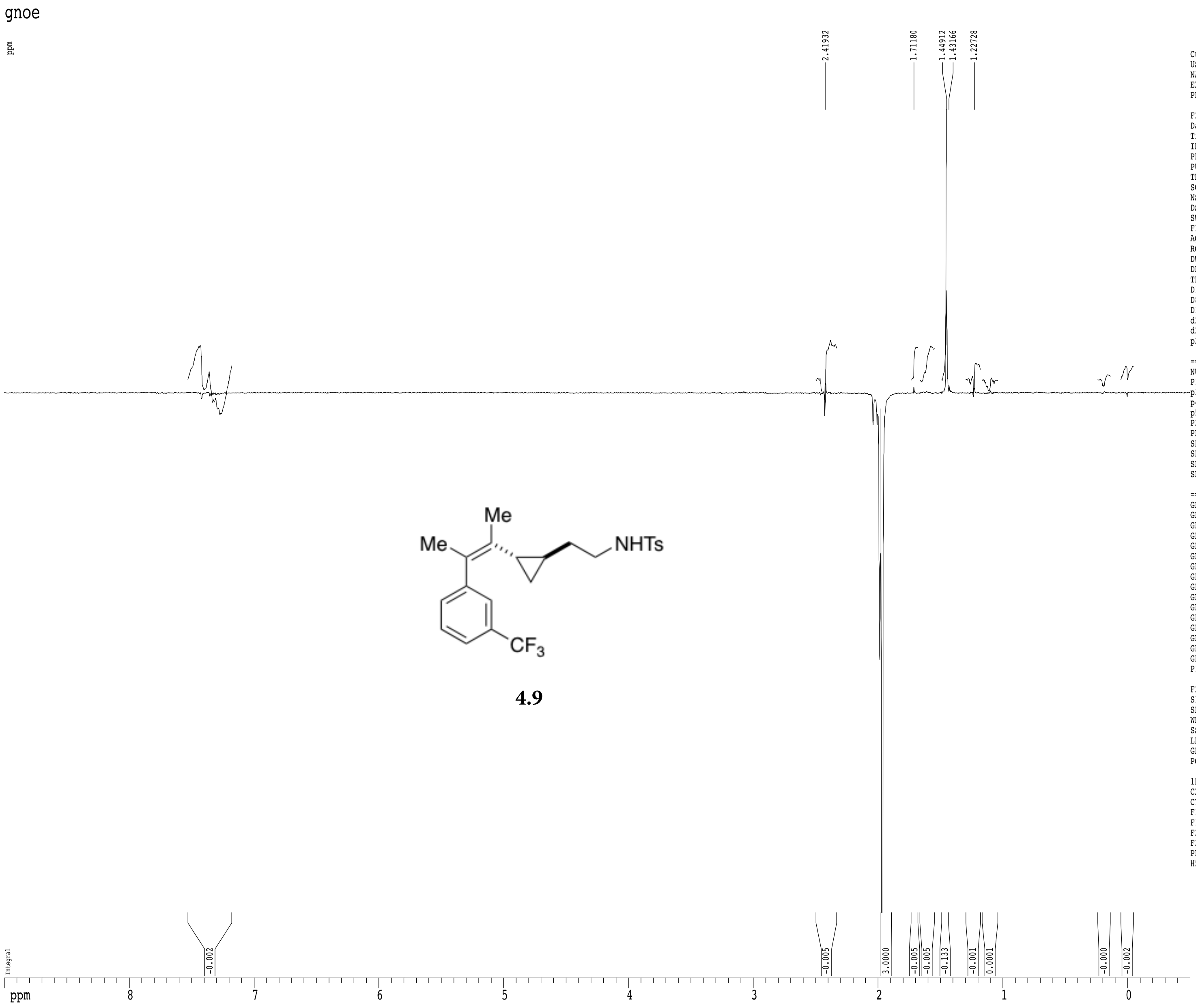


4.9

gcosy60

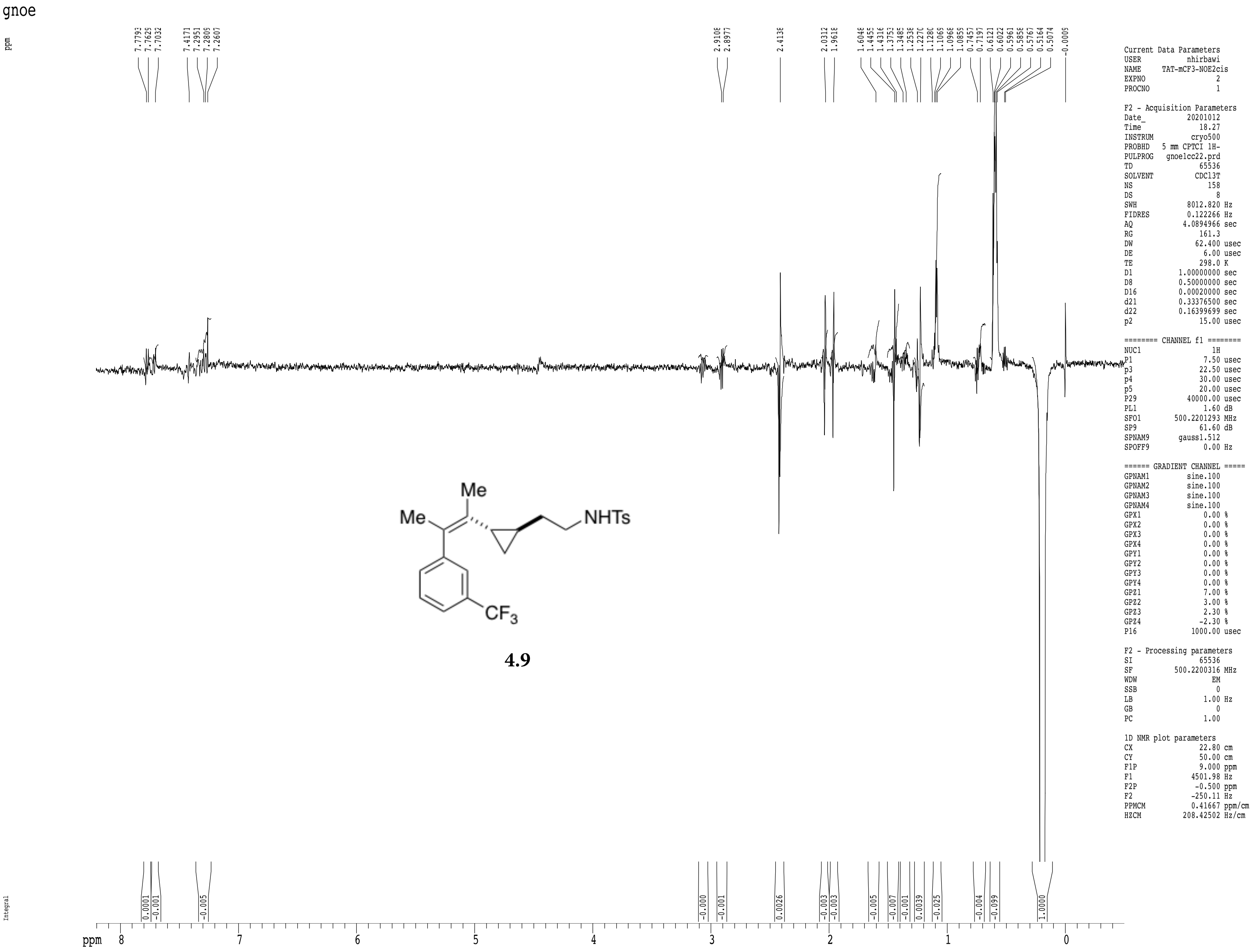


```
        Current Data Parameters
USER              nhirbawi
NAME        TAT-mCF3-HCOSYC
EXPNO                    2
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20201010
Time                 13.17
INSTRUM            cryo500
PROBHD     5 mm CPTCI 1H-
PULPROG        cosygp60.prd
TD                    2048
SOLVENT             CDCl3T
NS                       2
DS                      16
SWH               4496.403 Hz
FIDRES            2.195509 Hz
AQ               0.2277876 sec
RG                   203.2
DW                 111.200 usec
DE                    6.00 usec
TE                   298.0 K
d0              0.00000300 sec
D1              1.00000000 sec
d13             0.00000300 sec
D16             0.00020000 sec
IN0             0.00022240 sec

     ======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2220330 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 17.00 %
GPZ2                 17.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      1
TD                     256
SFO1               500.222 MHz
FIDRES           17.564074 Hz
SW                   8.989 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             500.2200322 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.2200322 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

        2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                8.494 ppm
F2LO               4249.00 Hz
F2PHI               -0.495 ppm
F2HI               -247.40 Hz
F1PLO                8.494 ppm
F1LO               4248.96 Hz
F1PHI               -0.495 ppm
F1HI               -247.44 Hz
F2PPMCM            0.59926 ppm/cm
F2HZCM           299.76016 Hz/cm
F1PPMCM            0.59926 ppm/cm
F1HZCM           299.76016 Hz/cm
```



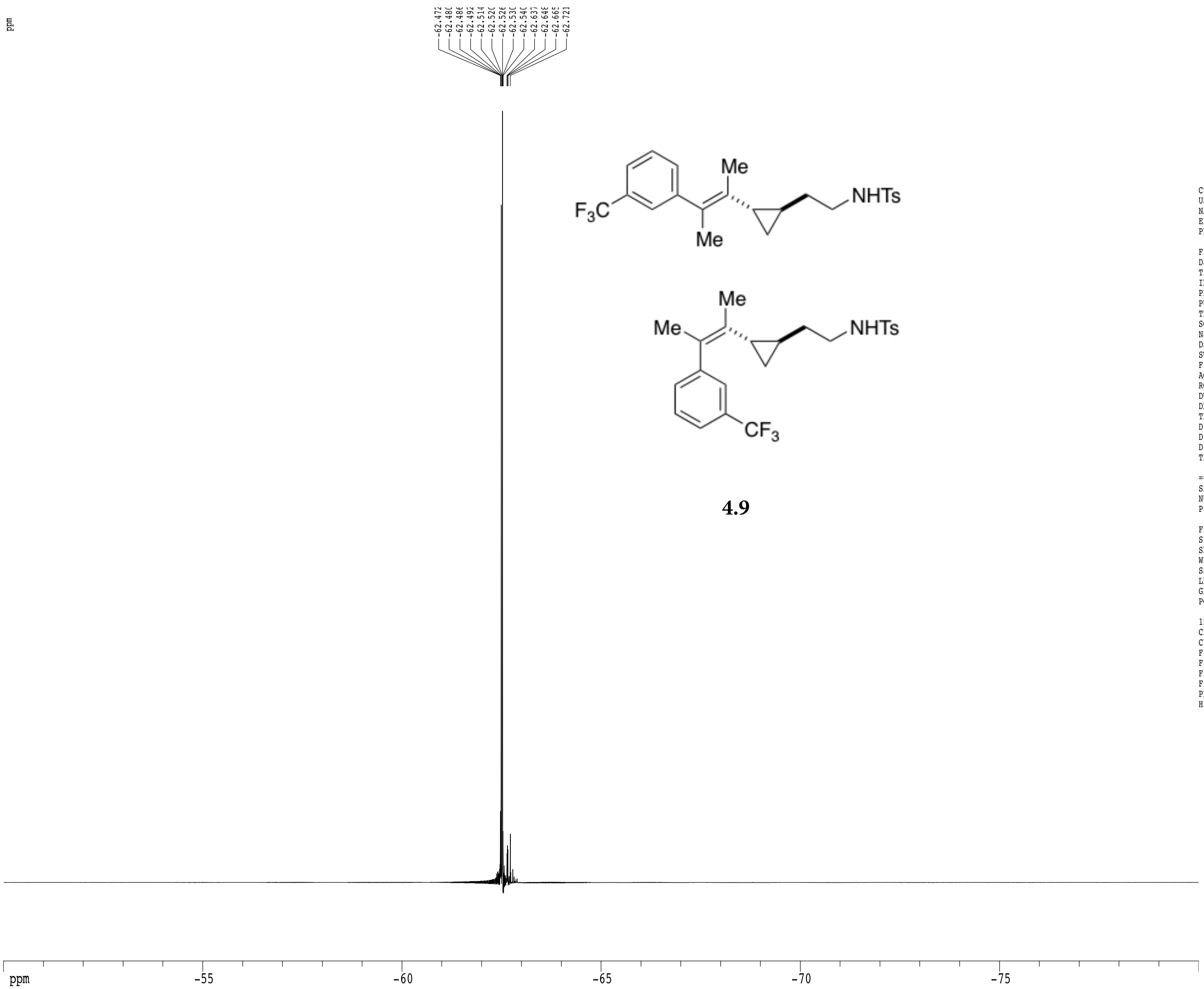
4.9

```
Current Data Parameters
USER            nhirbawi
NAME     TAT-mCF3-NOE1cis
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201013
Time               18.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT           CDCl3T
NS                   158
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2210144 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200315 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```


gnoe
ppm
7.7793
7.7629
7.7032
7.4171
7.2951
7.2809
7.2607
2.9108
2.8977
2.4138
2.0312
1.9618
1.6048
1.4455
1.4316
1.3753
1.3485
1.2538
1.2270
1.1280
1.1069
1.0968
1.0859
0.7457
0.7197
0.6121
0.6022
0.5961
0.5858
0.5767
0.5164
0.5074
-0.0009
Current Data Parameters
USER nhirbawi
NAME TAT-mCF3-NOE2cis
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201012
Time 18.27
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoe1cc22.prd
TD 65536
SOLVENT CDCl3T
NS 158
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2201293 MHz
SP9 61.60 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz
====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 500.2200316 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Me
Me
NHTs
CF3
Integral
0.0001
-0.001
-0.005
-0.000
-0.001
0.0026
-0.003
-0.003
-0.005
-0.007
-0.001
0.0039
-0.025
-0.004
-0.099
1.0000
ppm
8
7
6
5
4
3
2
1
0

4.9

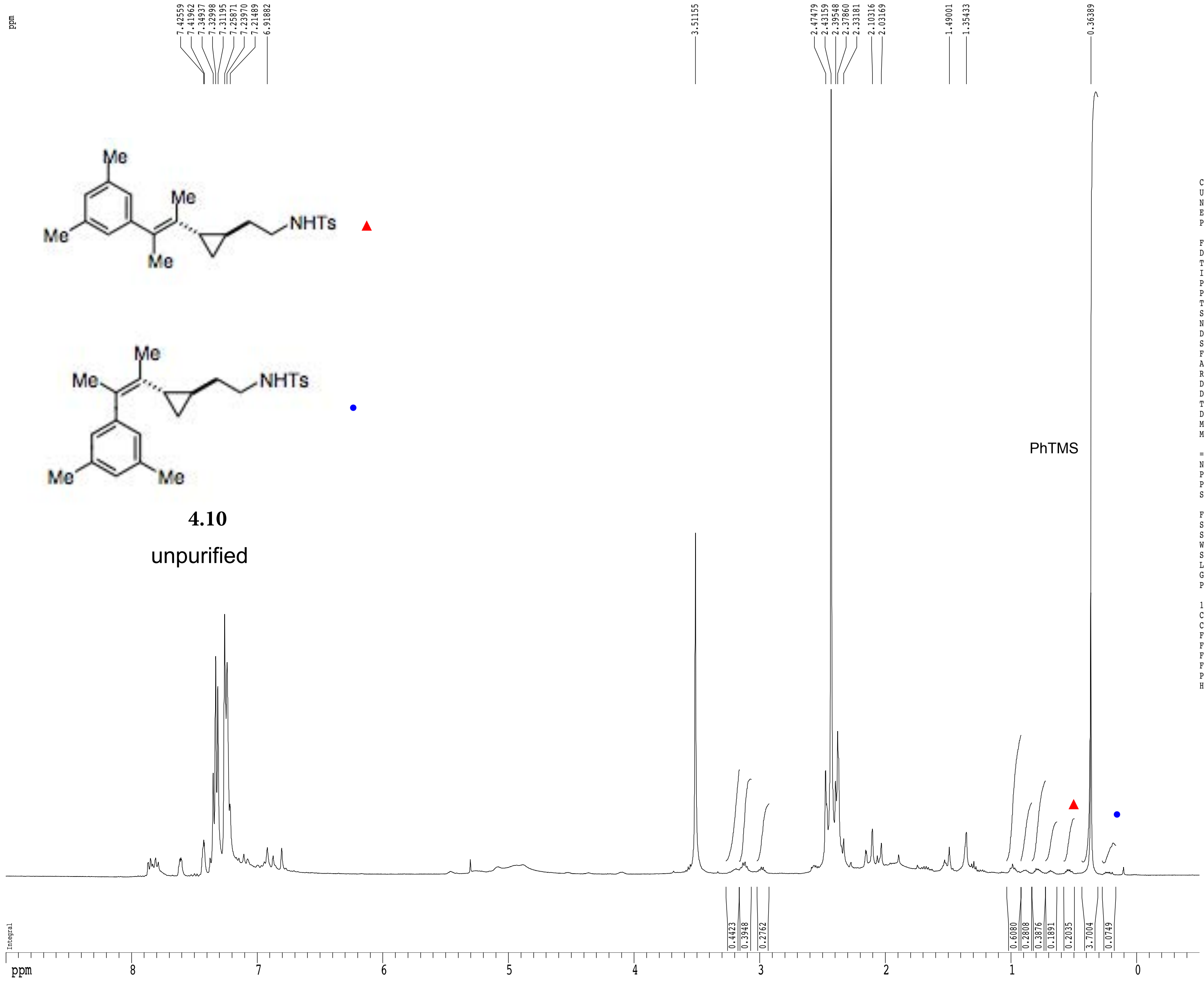
19F spectrum with inverse gated 1H decoupling



4.9

```
Current Data Parameters
USER            nhirbawi
NAME      TAT-mCF3-FandC
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20201012
Time              17.36
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG    zgfhigqn30.2
TD               131072
SOLVENT          CDCl3T
NS                   16
DS                    4
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                  575
DW                2.800 usec
DE                18.00 usec
TE                298.0 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        564.6045085 MHz
NUC1                19F
P1                18.25 usec

F2 - Processing parameters
SI               131072
SF          564.6864208 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             -50.000 ppm
F1            -28234.32 Hz
F2P             -80.000 ppm
F2            -45174.91 Hz
PPMCM           1.31579 ppm/cm
HZCM          743.00842 Hz/cm
```

1H spectrum

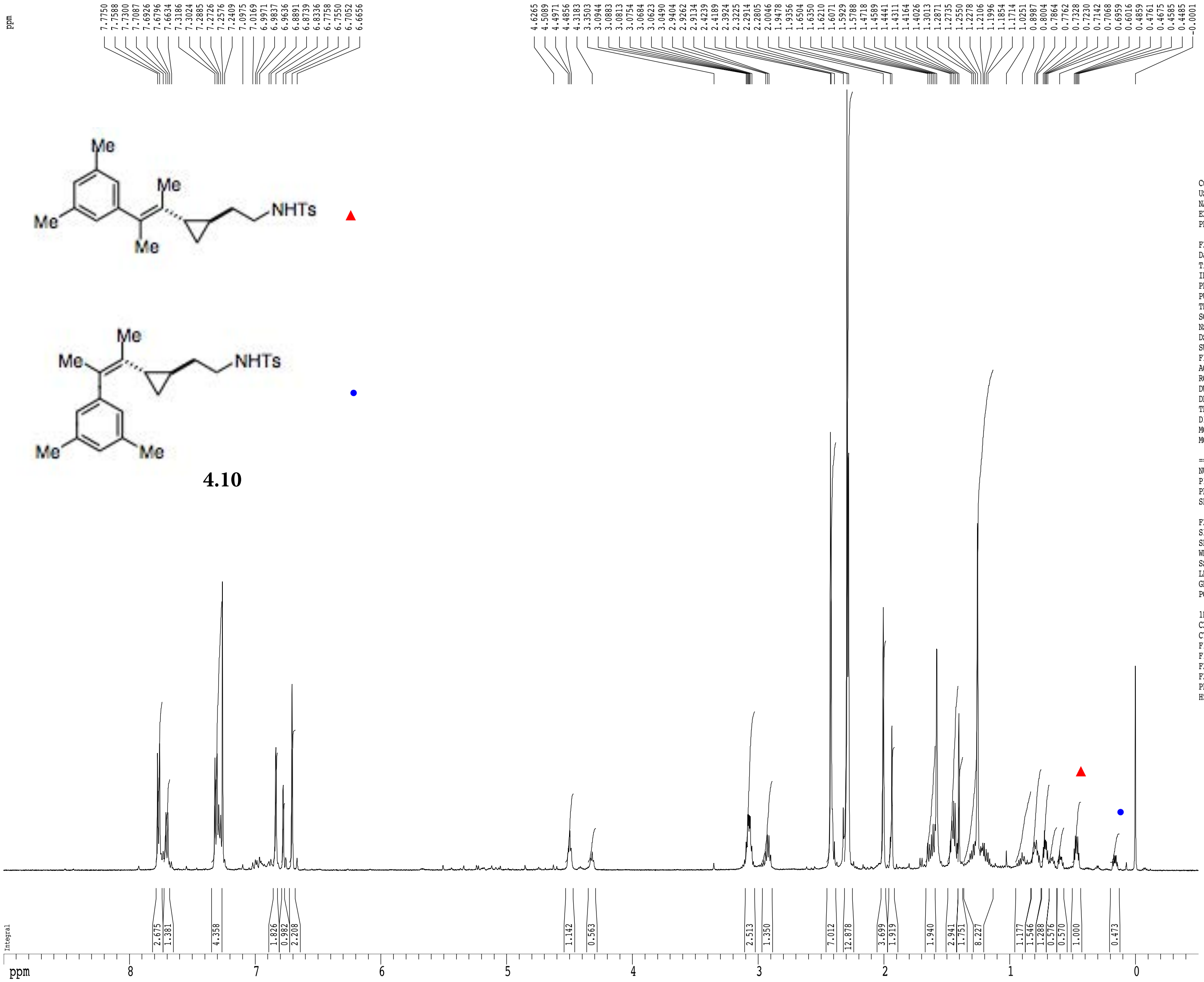


4.10

unpurified

```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-281-crude
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200923
Time               18.06
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    32
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

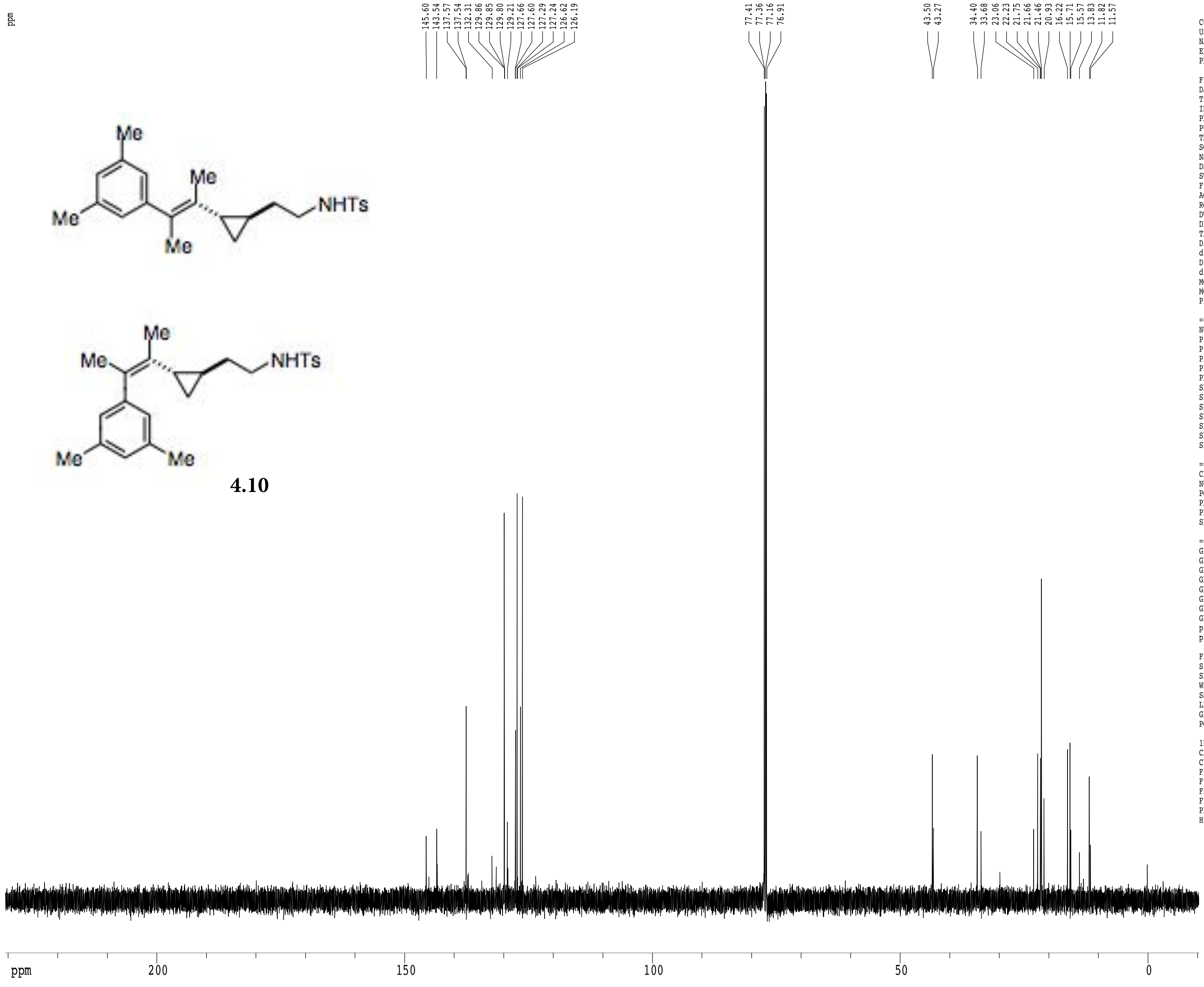
1H spectrum



4.10

```
Current Data Parameters
USER            khewitt1
NAME       KAH-III-281-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201010
Time               12.48
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200332 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

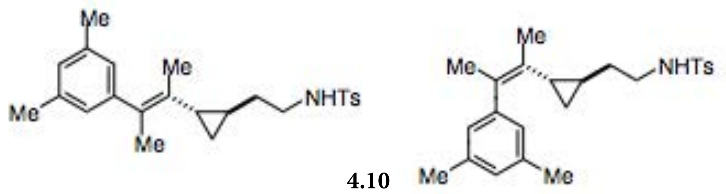
Z-restored spin-echo 13C spectrum with 1H decoupling



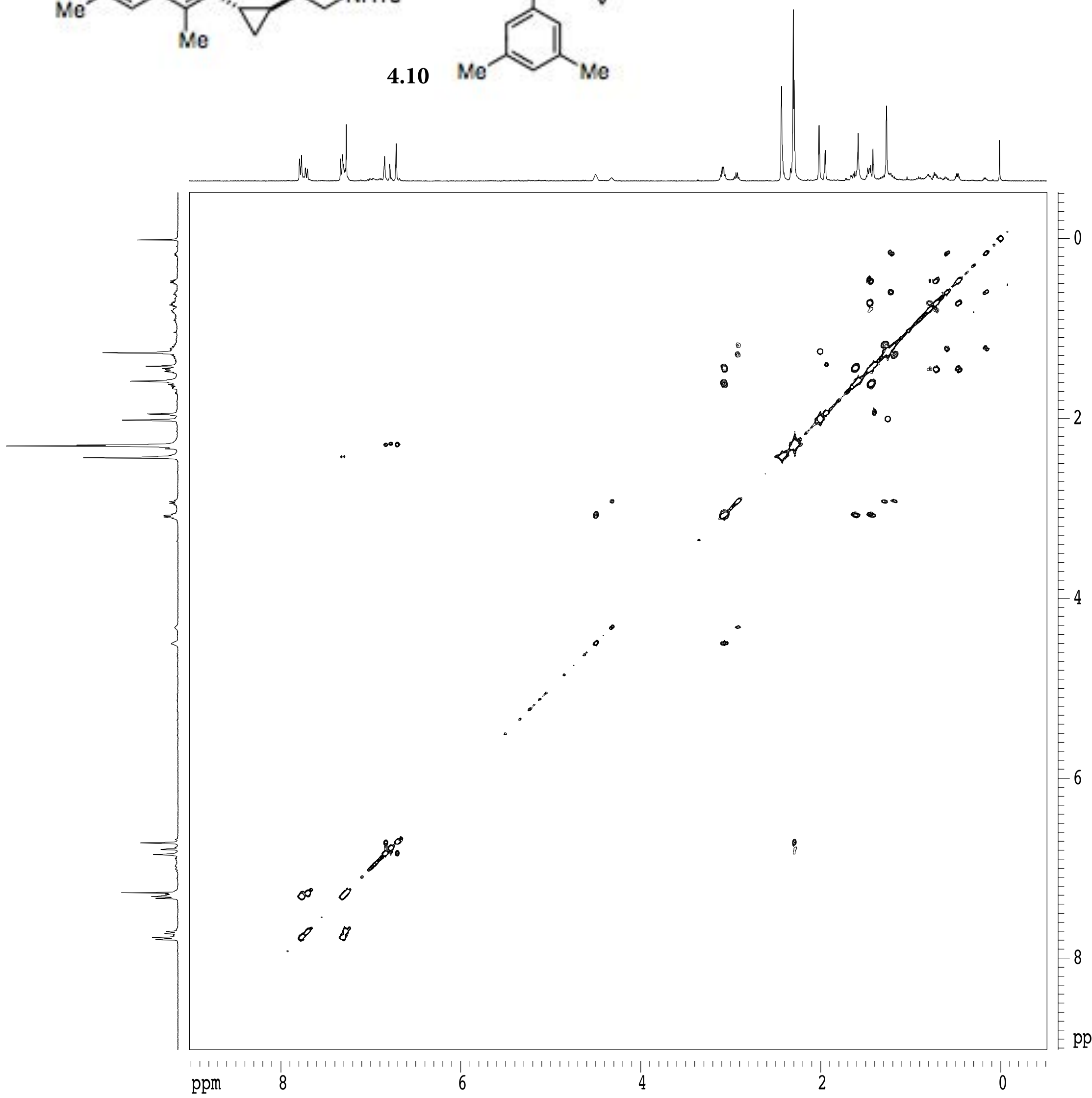
4.10

```
Current Data Parameters
USER              khewitt1
NAME          KAH-III-281-Z
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_             20201014
Time                 19.13
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT             CDCl3T
NS                     800
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813940 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   2.70 dB
SP4                   2.70 dB
SPNAM2         Crp60comp.4
SPNAM4      Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 23.54 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804076 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                230.637 ppm
F1                29009.68 Hz
F2P                -10.287 ppm
F2                -1293.96 Hz
PPMCM             10.56688 ppm/cm
HZCM            1329.10693 Hz/cm
```

gcosy60

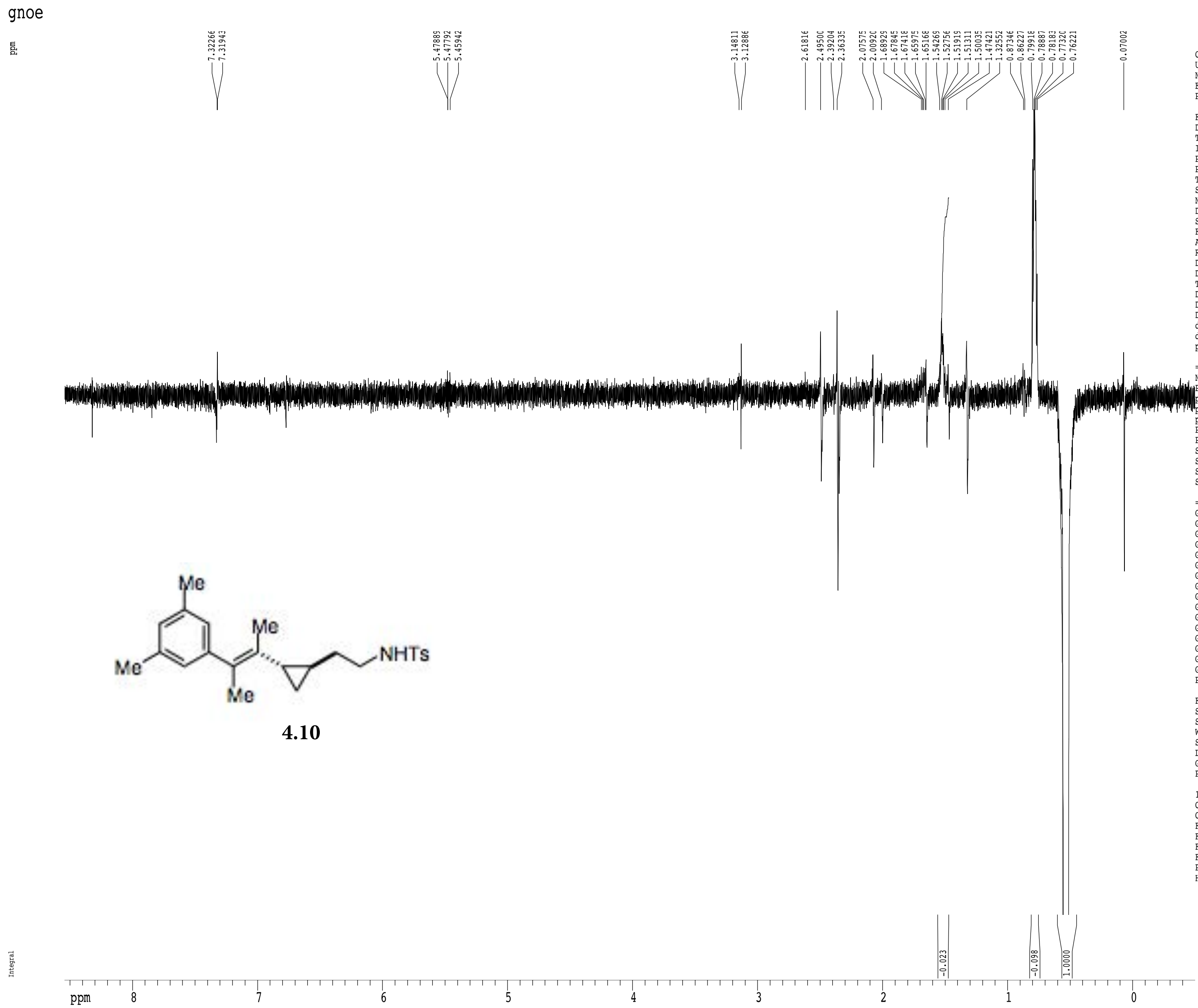


4.10



```
Current Data Parameters
USER          khewitt1
NAME      KAH-III-281-Z
EXPNO                 3
PROCNO                1

     F2 - Acquisition Parameters
Date_          20201010
Time              12.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                322.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

     F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

     F2 - Processing parameters
SI                 1024
SF          500.2200332 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

     F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200332 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

       2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.014 ppm
F2LO            4509.04 Hz
F2PHI            -0.513 ppm
F2HI            -256.39 Hz
F1PLO             9.014 ppm
F1LO            4509.04 Hz
F1PHI            -0.513 ppm
F1HI            -256.39 Hz
F2PPMCM         0.63511 ppm/cm
F2HZCM        317.69580 Hz/cm
F1PPMCM         0.63511 ppm/cm
F1HZCM        317.69580 Hz/cm
```

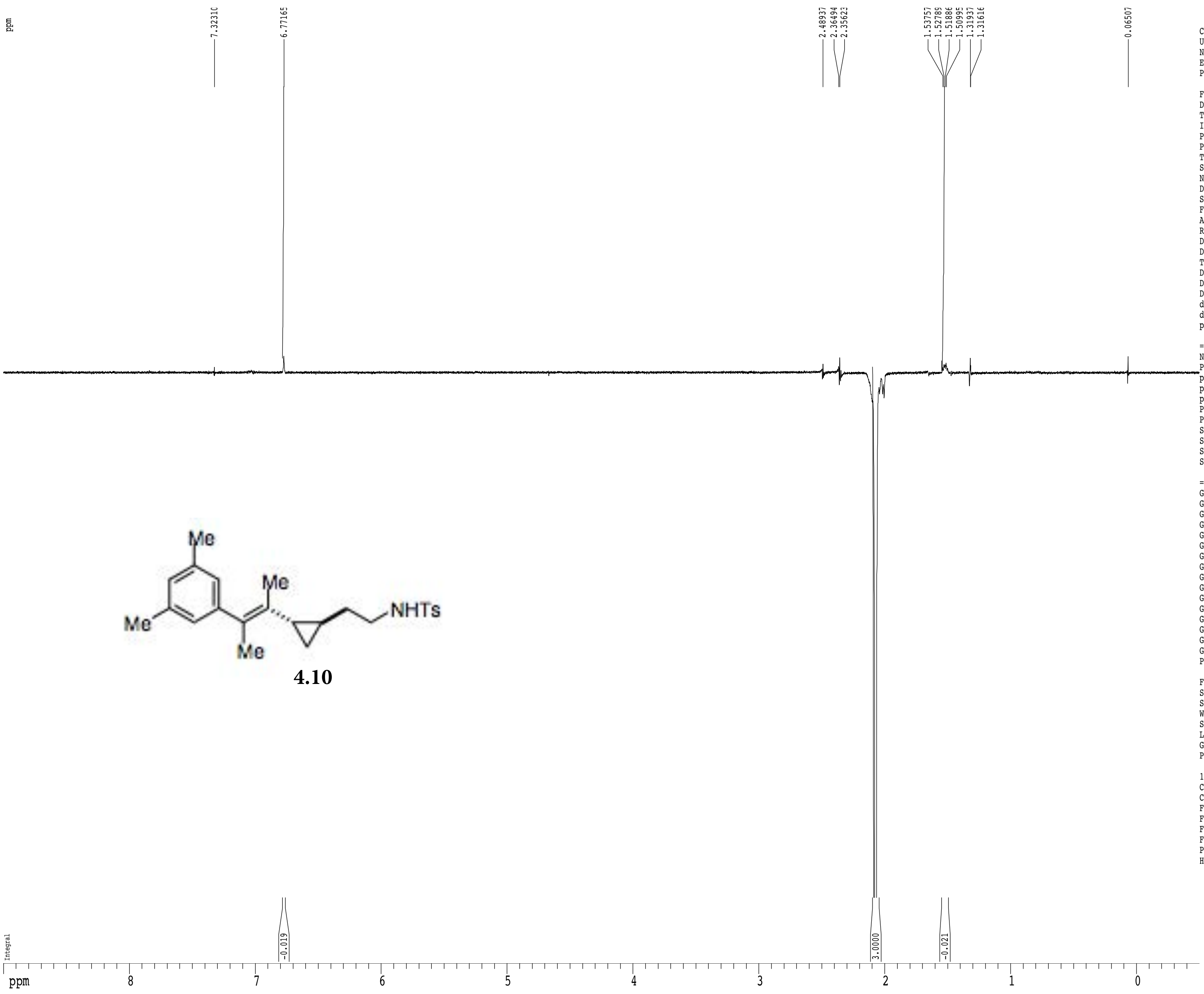
gnoe



4.10

```
Current Data Parameters
USER             khewitt1
NAME         KAH-III-281-Z
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201010
Time                17.36
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   90.5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2202666 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

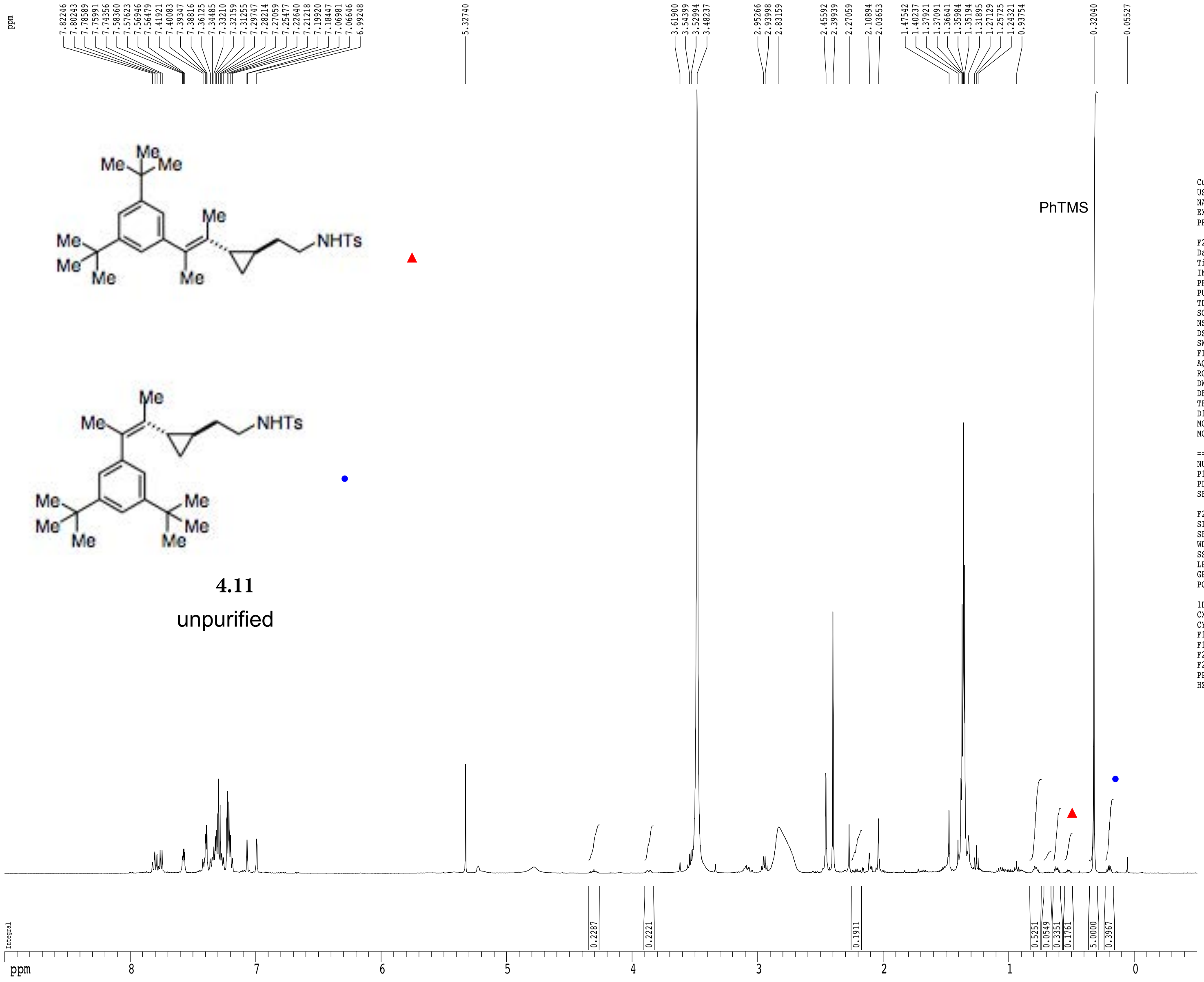
gnoe



4.10

```
Current Data Parameters
USER           khewitt1
NAME       KAH-III-281-Z
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20201010
Time              17.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                143.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2210358 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

1H spectrum

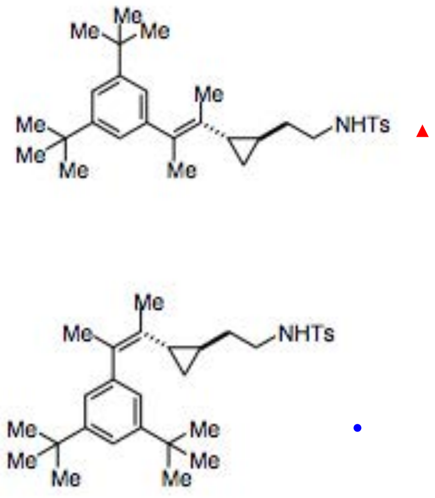


4.11

unpurified

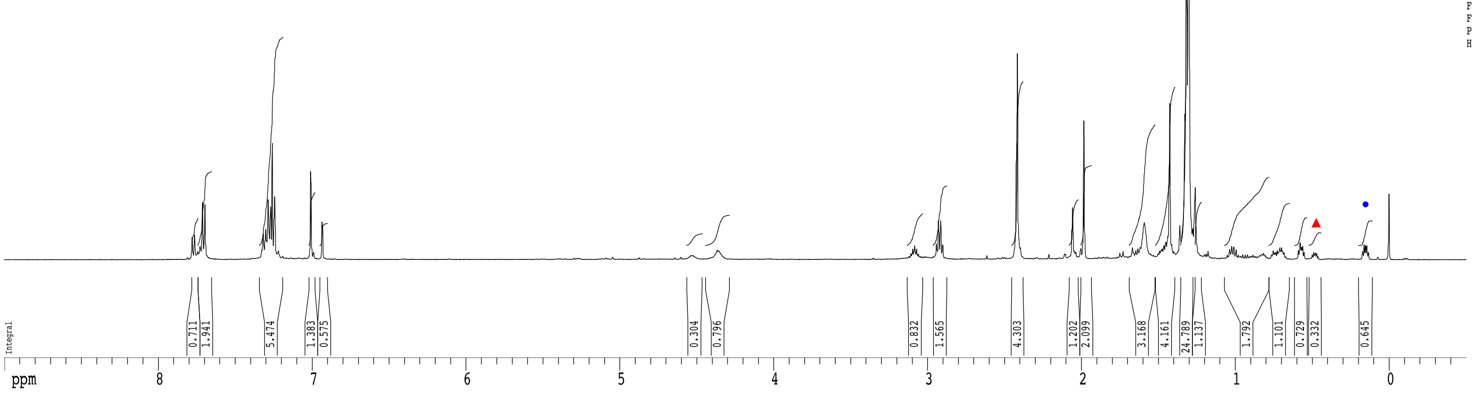
```
Current Data Parameters
USER             khewitt1
NAME       KAH-III-190-crude
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200716
Time                17.53
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  48074
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.166677 Hz
AQ              2.9998677 sec
RG                      4
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

1H spectrum

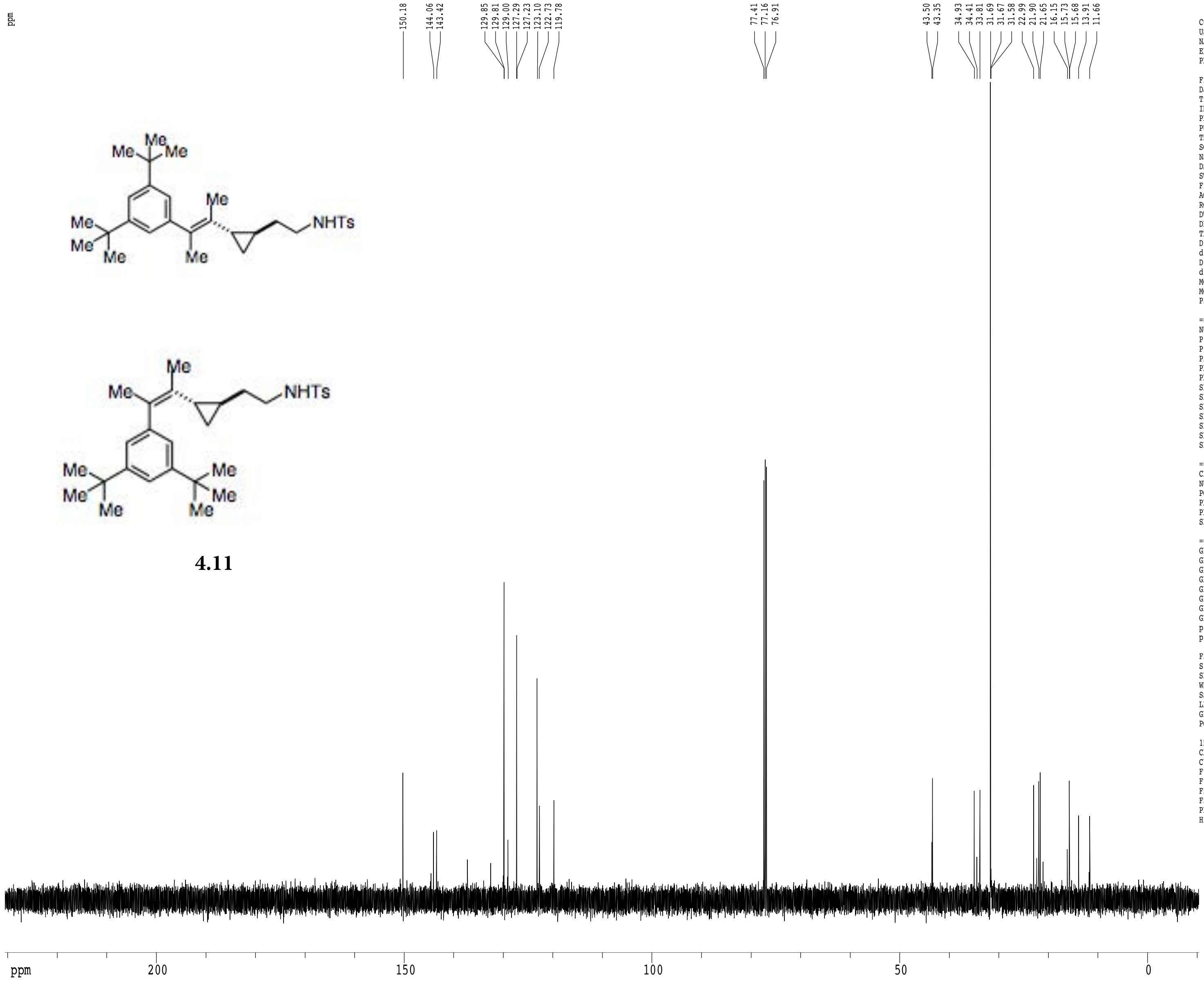


4.11

```
Current Data Parameters
USER          khewitt1
NAME      KAH-III-190-Z
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20200911
Time             10.40
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               48074
SOLVENT          CDCl3T
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.166677 Hz
AQ           2.9998677 sec
RG                 6.3
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200331 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4501.98 Hz
F2P             -0.500 ppm
F2             -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42502 Hz/cm
```

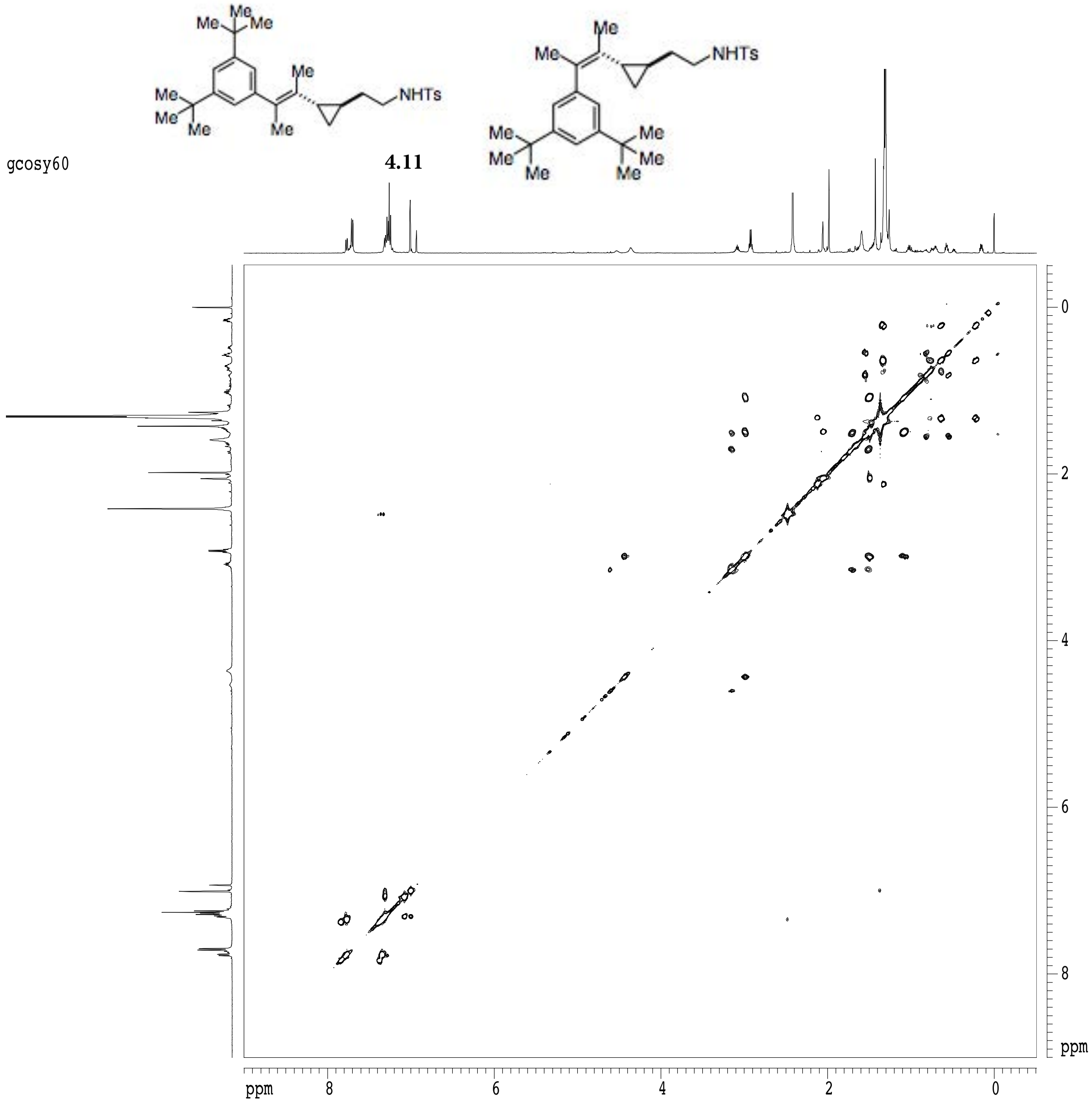


Z-restored spin-echo 13C spectrum with 1H decoupling

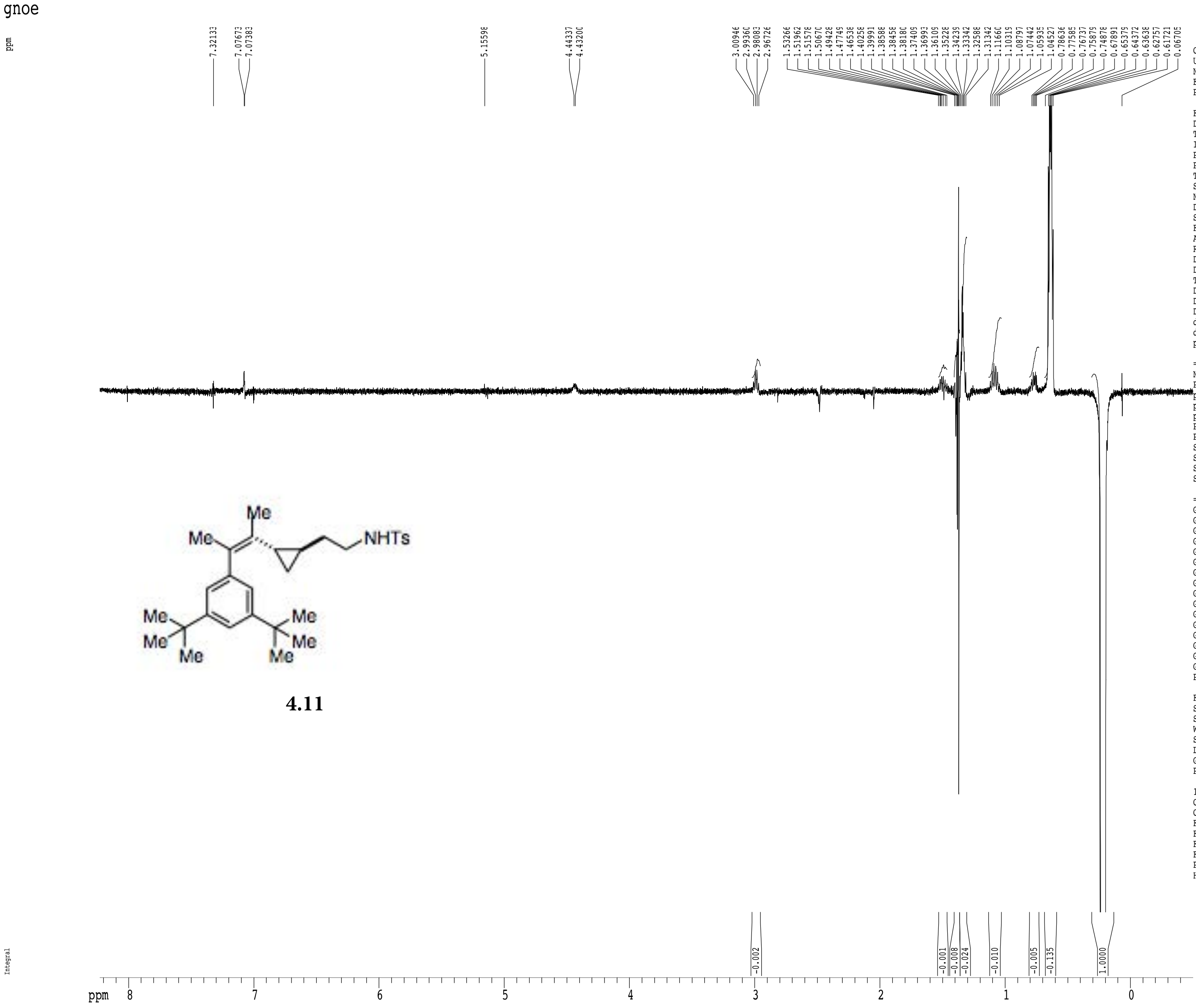


4.11

```
Current Data Parameters
USER          khewitt1
NAME      KAH-III-190-Z
EXPNO                5
PROCNO               1

F2 - Acquisition Parameters
Date_         20200911
Time             11.07
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD               65536
SOLVENT          CDCl3
NS                 128
DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG              2896.3
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7804076 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            230.551 ppm
F1            28998.79 Hz
F2P            -10.369 ppm
F2            -1304.23 Hz
PPMCM         10.56667 ppm/cm
HZCM        1329.08032 Hz/cm
```

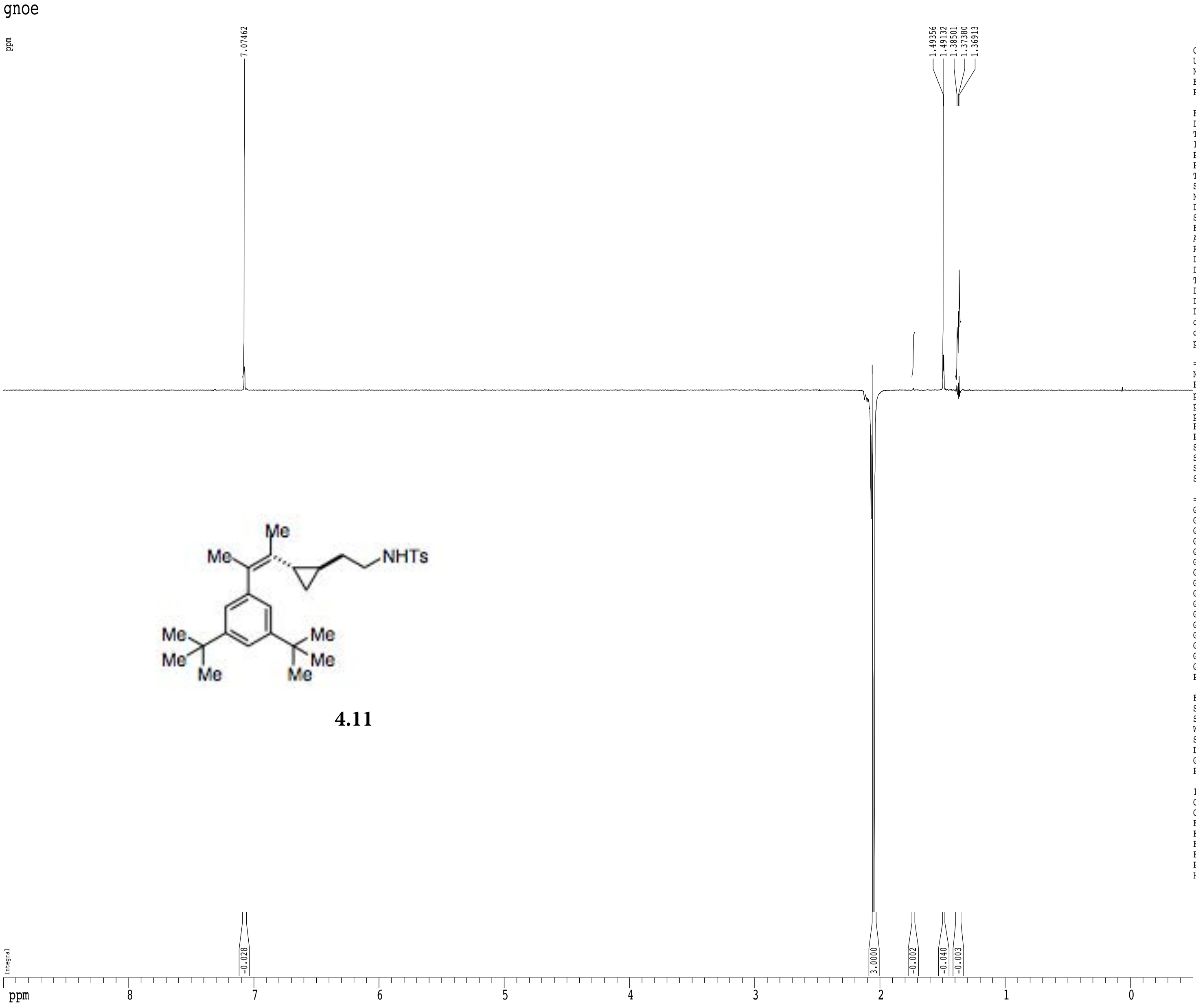

4.11

```
        Current Data Parameters
USER            khewitt1
NAME        KAH-III-190-Z
EXPNO                  4
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20200911
Time               10.55
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   181
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

         2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.002 ppm
F2LO             4503.14 Hz
F2PHI             -0.509 ppm
F2HI             -254.47 Hz
F1PLO              9.002 ppm
F1LO             4503.14 Hz
F1PHI             -0.509 ppm
F1HI             -254.47 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17416 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17416 Hz/cm
```



4.11

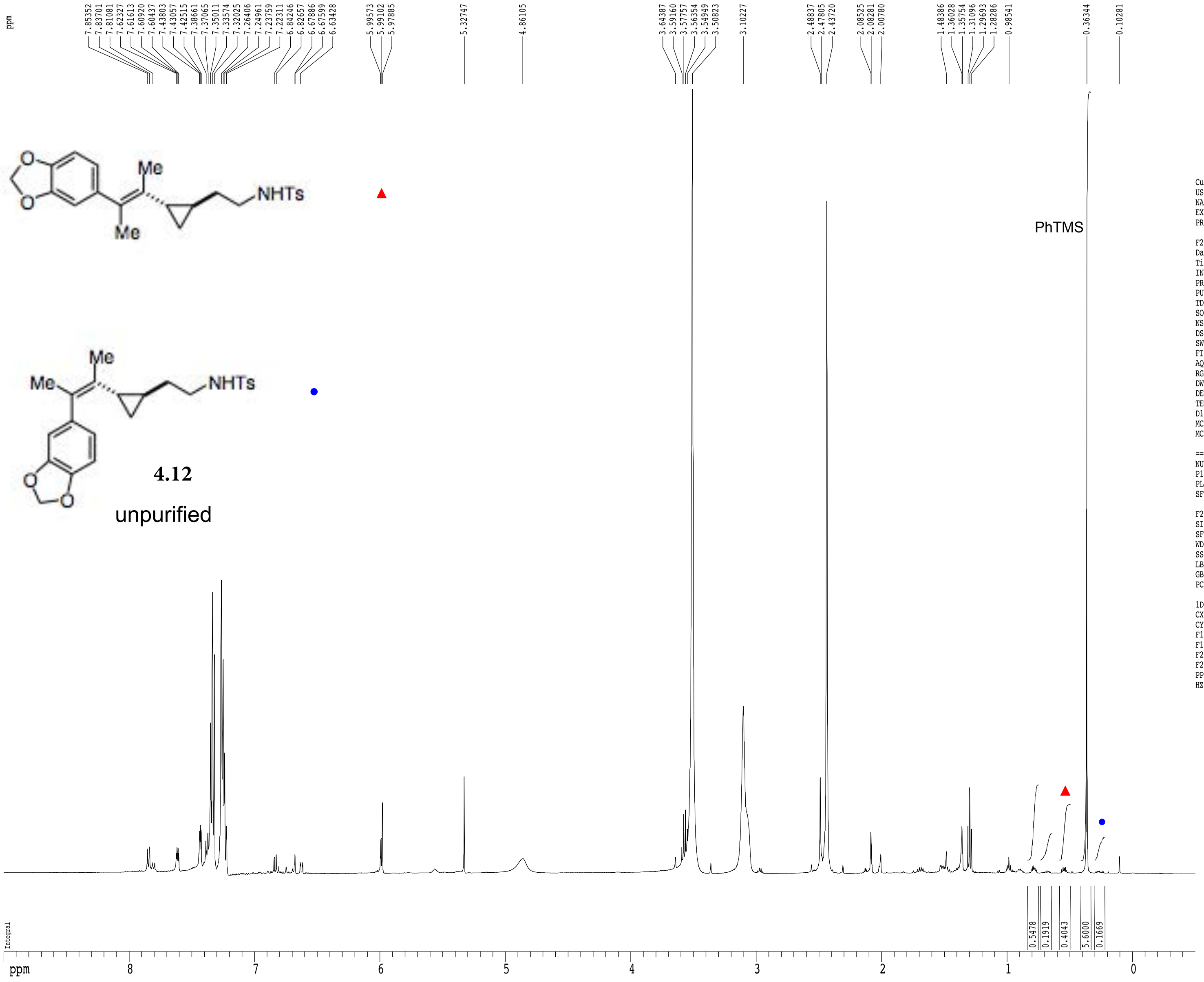
```
Current Data Parameters
USER             khewitt1
NAME       KAH-III-190-Z
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200911
Time                10.54
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   71.8
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1        500.2201096 MHz
SP9                 61.60 dB
SPNAM9        gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```



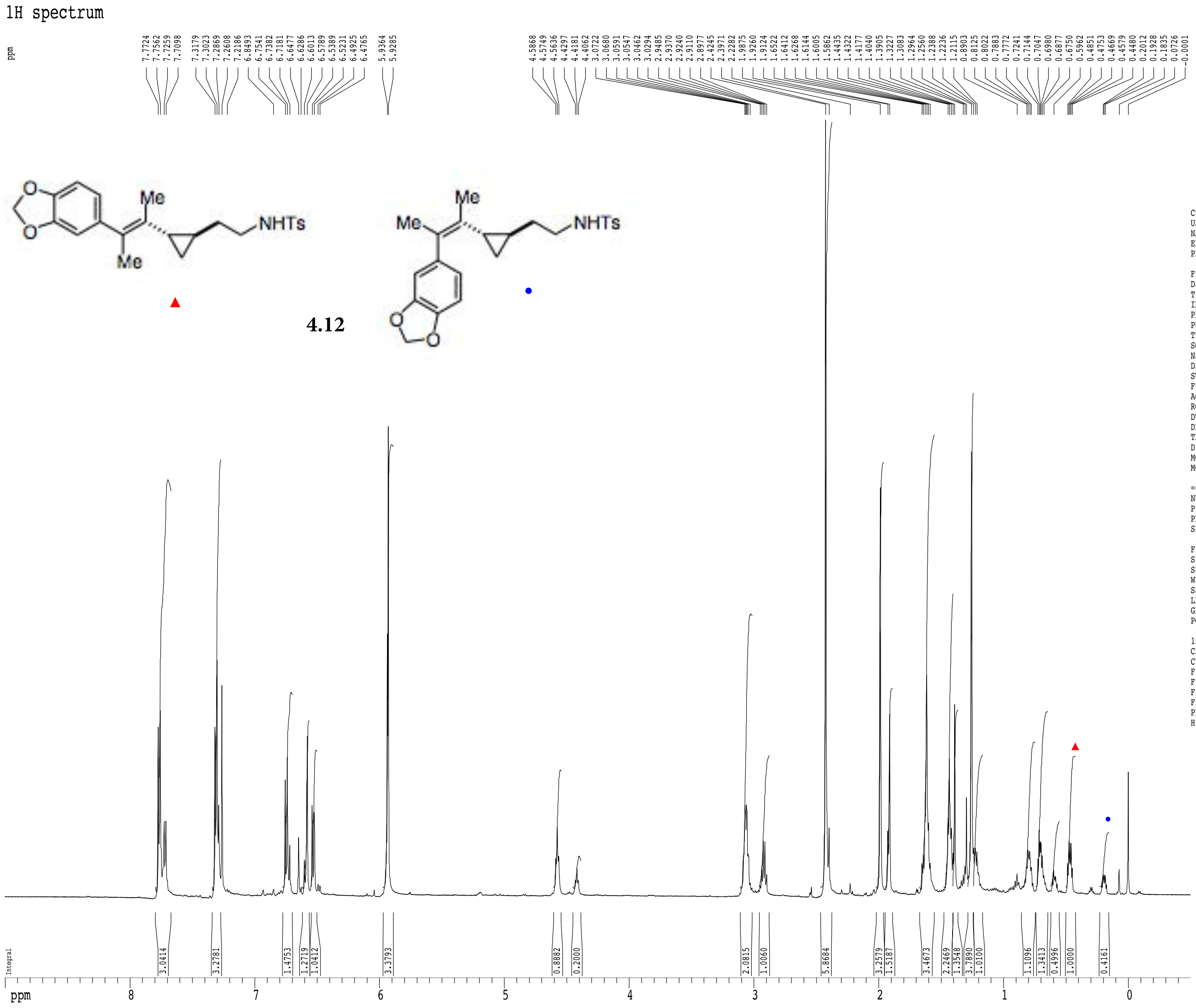
4.11

```
Current Data Parameters
USER            khewitt1
NAME       KAH-III-190-Z
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200911
Time               18.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2210249 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

1H spectrum



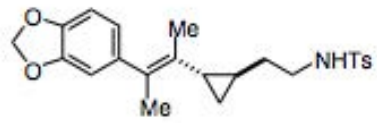
```
Current Data Parameters
USER              khewitt1
NAME       KAH-III-191-crude
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200716
Time                 17.56
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   48074
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.166677 Hz
AQ               2.9998677 sec
RG                     3.2
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

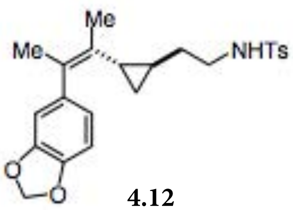


4.12

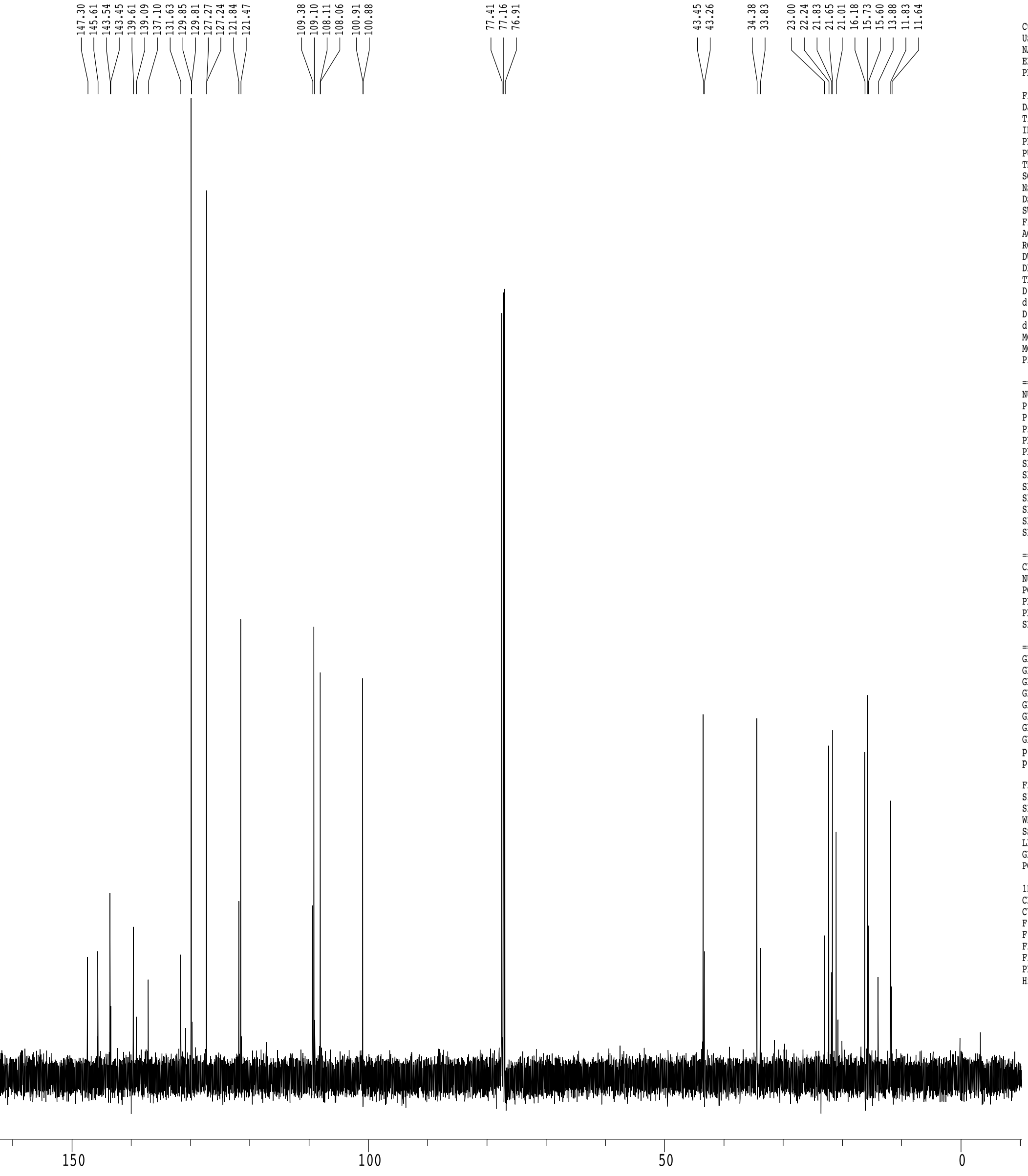
```
Current Data Parameters
USER           khewittl
NAME      KAH-III-191-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20200908
Time              18.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200313 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

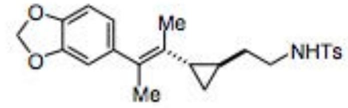




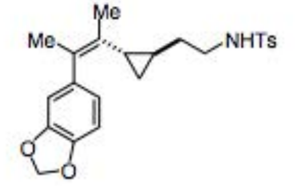
4.12



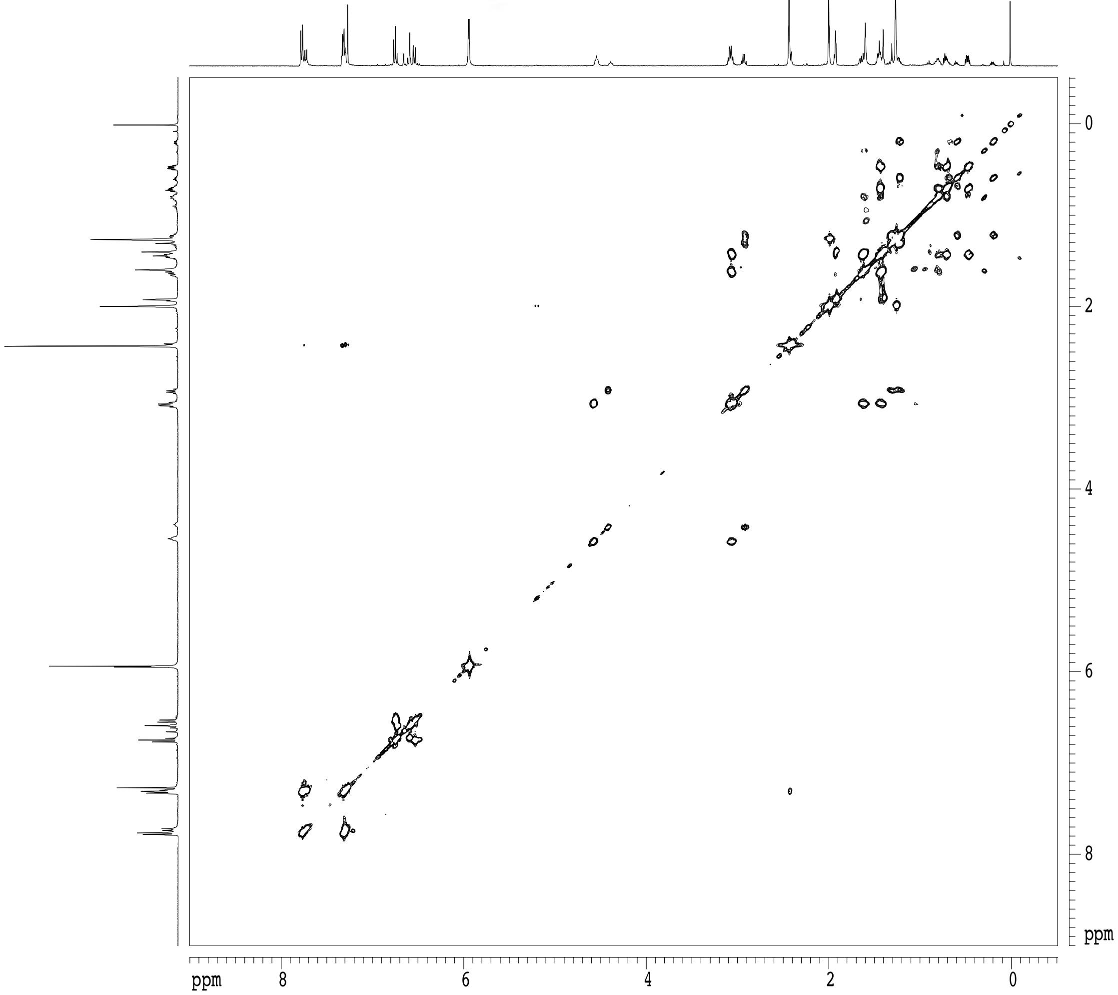
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-191-Z
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200908
Time               19.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   280
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



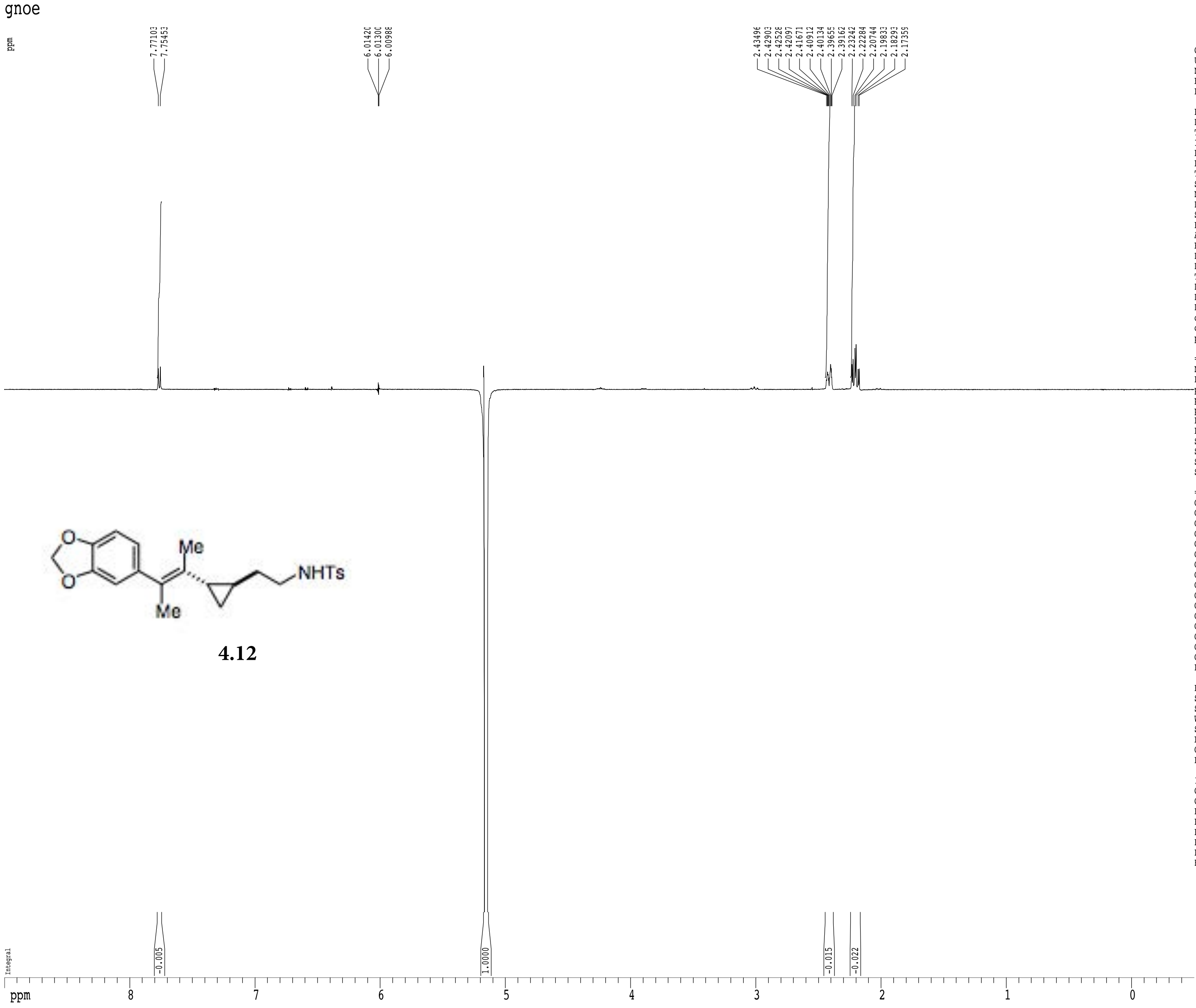
4.12



gcosy60

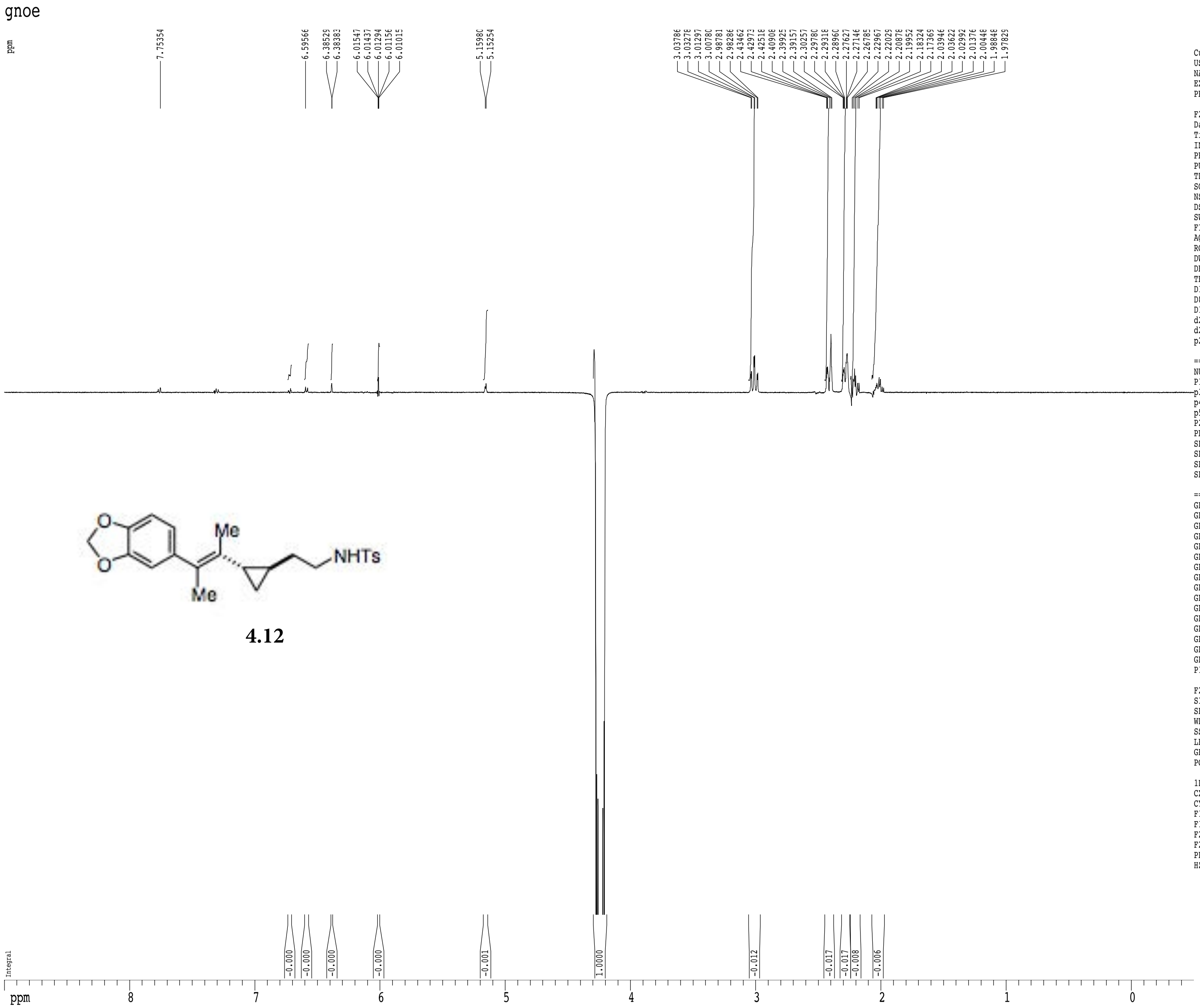


```
        Current Data Parameters
USER            khewitt1
NAME       KAH-III-191-Z
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20200908
Time               18.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   181
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

       F2 - Processing parameters
SI                  1024
SF           500.2200313 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

       F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200313 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

          2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.002 ppm
F2LO             4503.17 Hz
F2PHI             -0.509 ppm
F2HI             -254.44 Hz
F1PLO              9.002 ppm
F1LO             4503.17 Hz
F1PHI             -0.509 ppm
F1HI             -254.44 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```



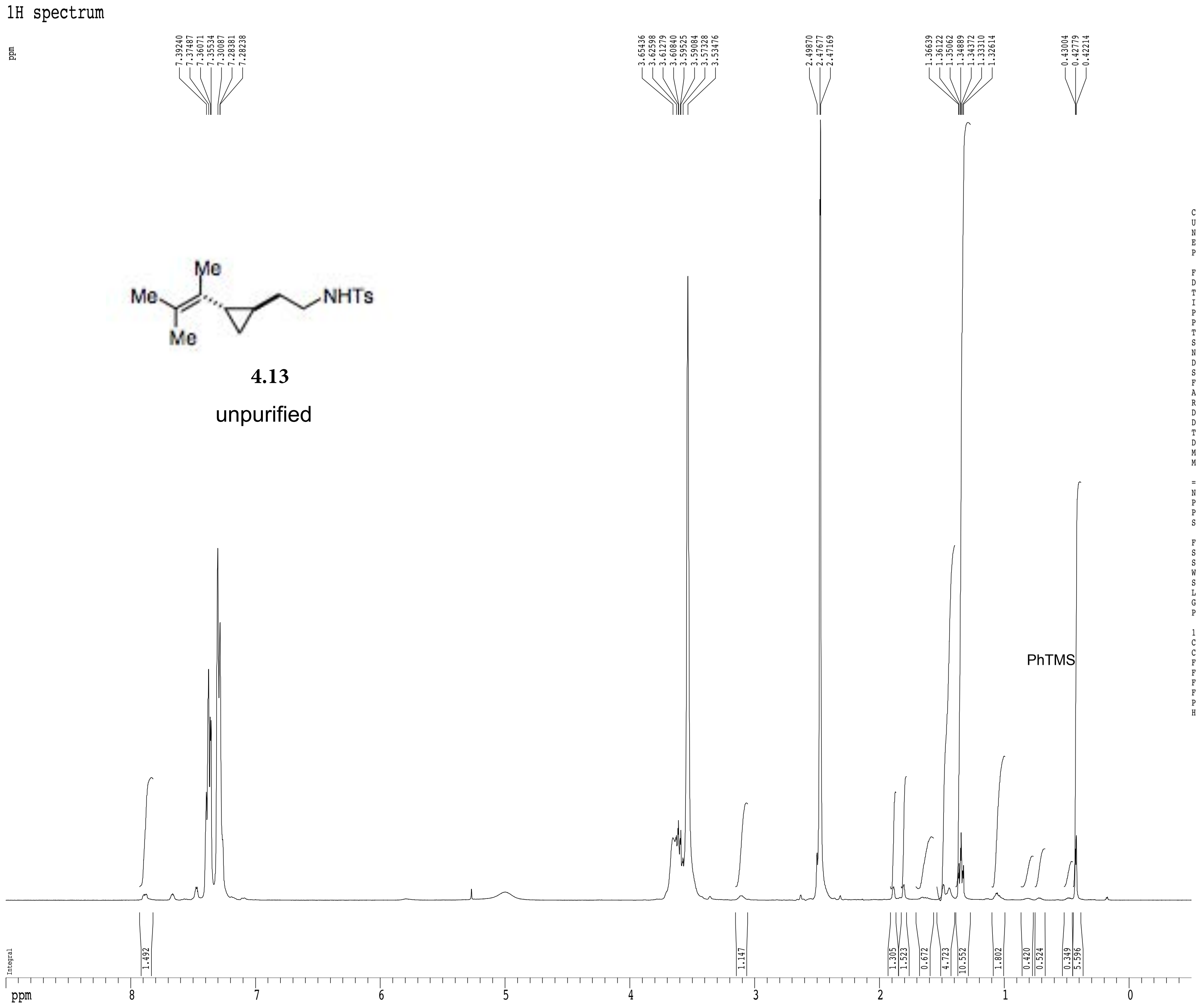
4.12

```
Current Data Parameters
USER             khewitt1
NAME     KAH-III-191-SM-Z
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200711
Time                17.19
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   90.5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2225782 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```



4.12

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-191-SM-Z
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200711
Time               17.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 161.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1         500.2221214 MHz
SP9               61.60 dB
SPNAM9        gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

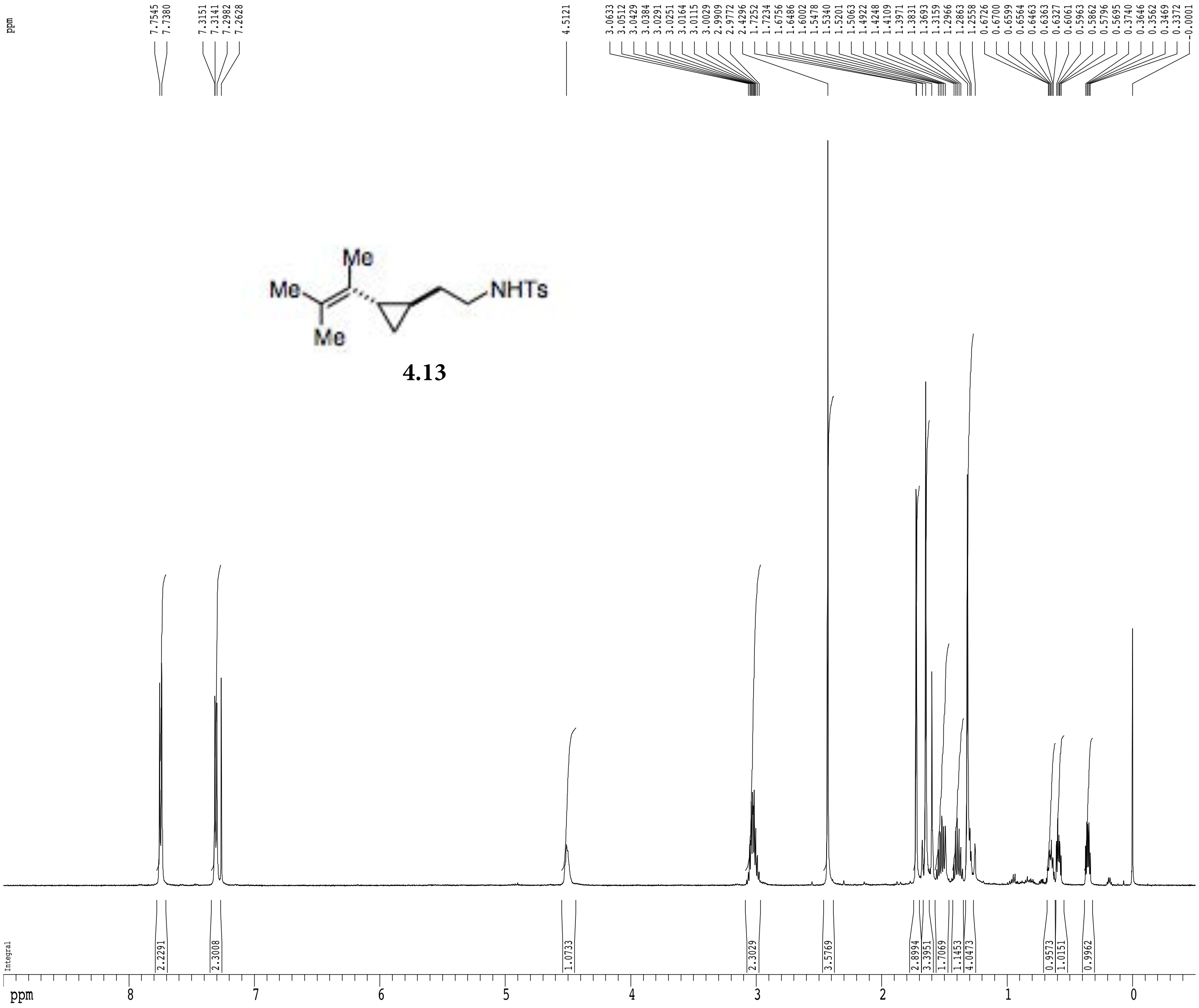


4.13

unpurified

```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-239-crude
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200815
Time              10.45
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                 20.2
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

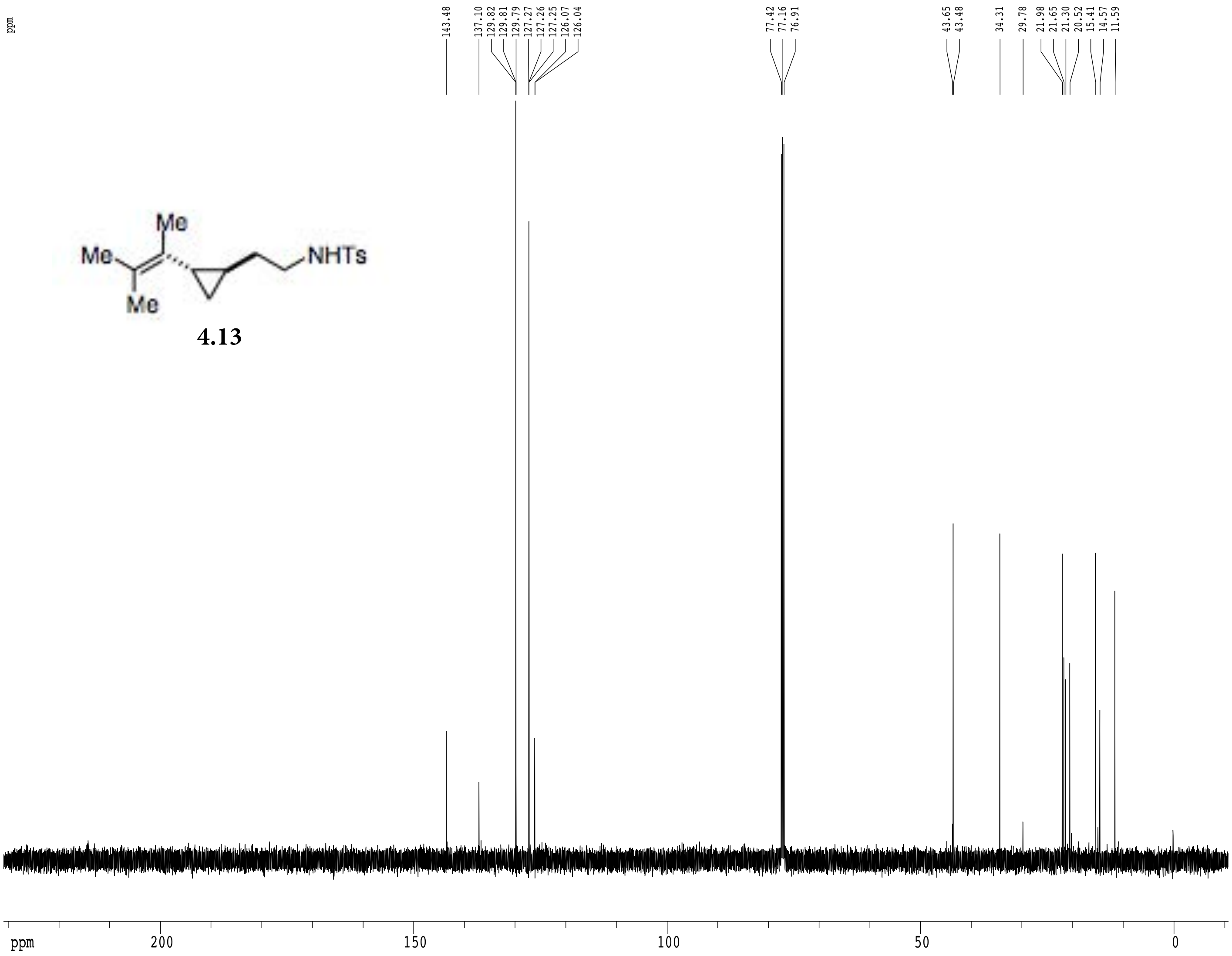
1H spectrum



4.13

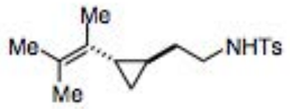
```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-239-COSY
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200821
Time               11.57
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                 812.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500299 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```

13C spectrum with 1H decoupling



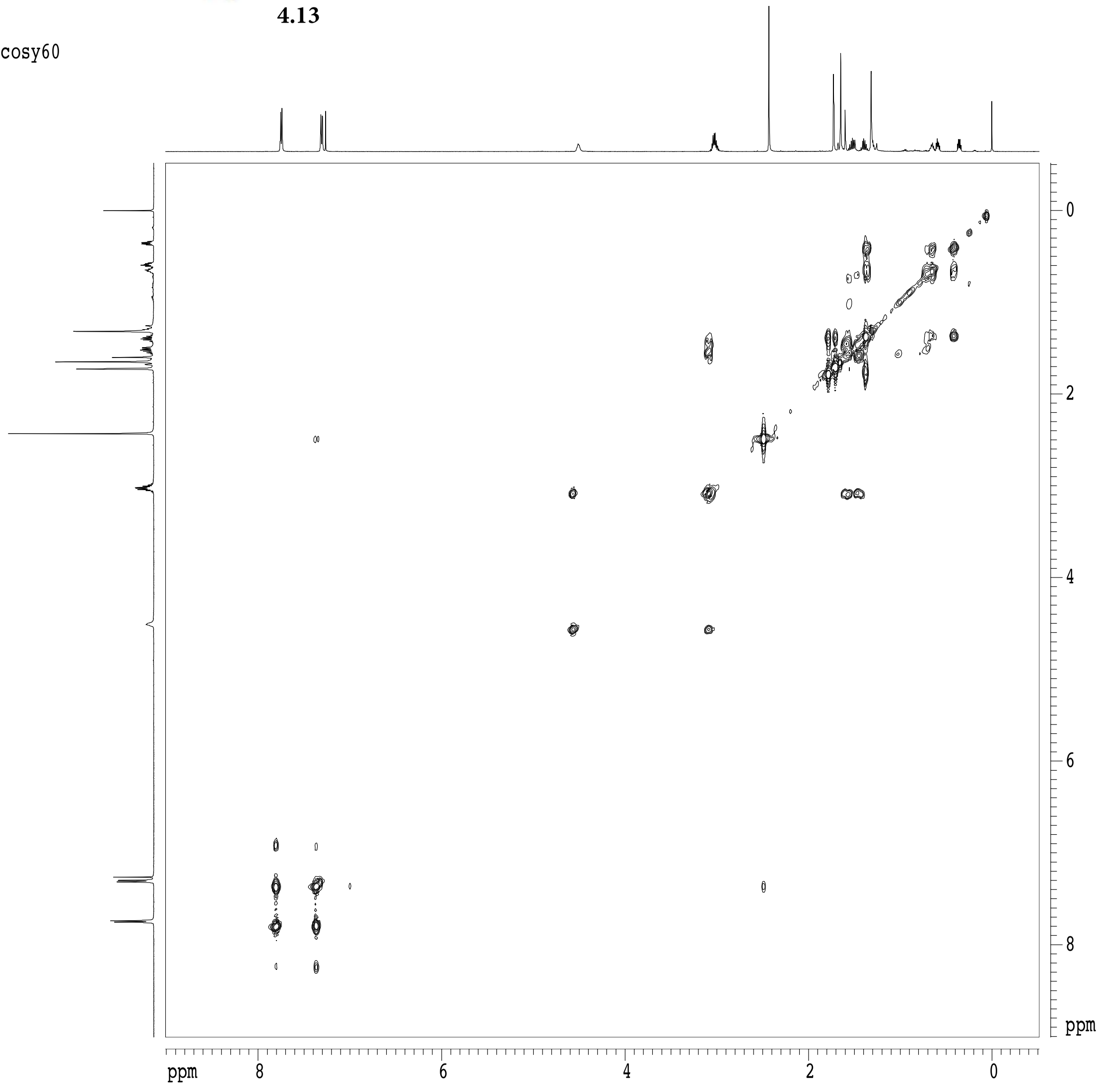
4.13

```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-239-13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200819
Time              11.41
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG         zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  632
DS                    4
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG               5792.6
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.20 usec
PL1               -6.00 dB
SFO1        125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.30 dB
SFO2        498.7524937 MHz

F2 - Processing parameters
SI                65536
SF          125.4107757 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P             230.907 ppm
F1             28958.26 Hz
F2P             -10.723 ppm
F2             -1344.77 Hz
PPMCM          12.08151 ppm/cm
HZCM         1515.15149 Hz/cm
```

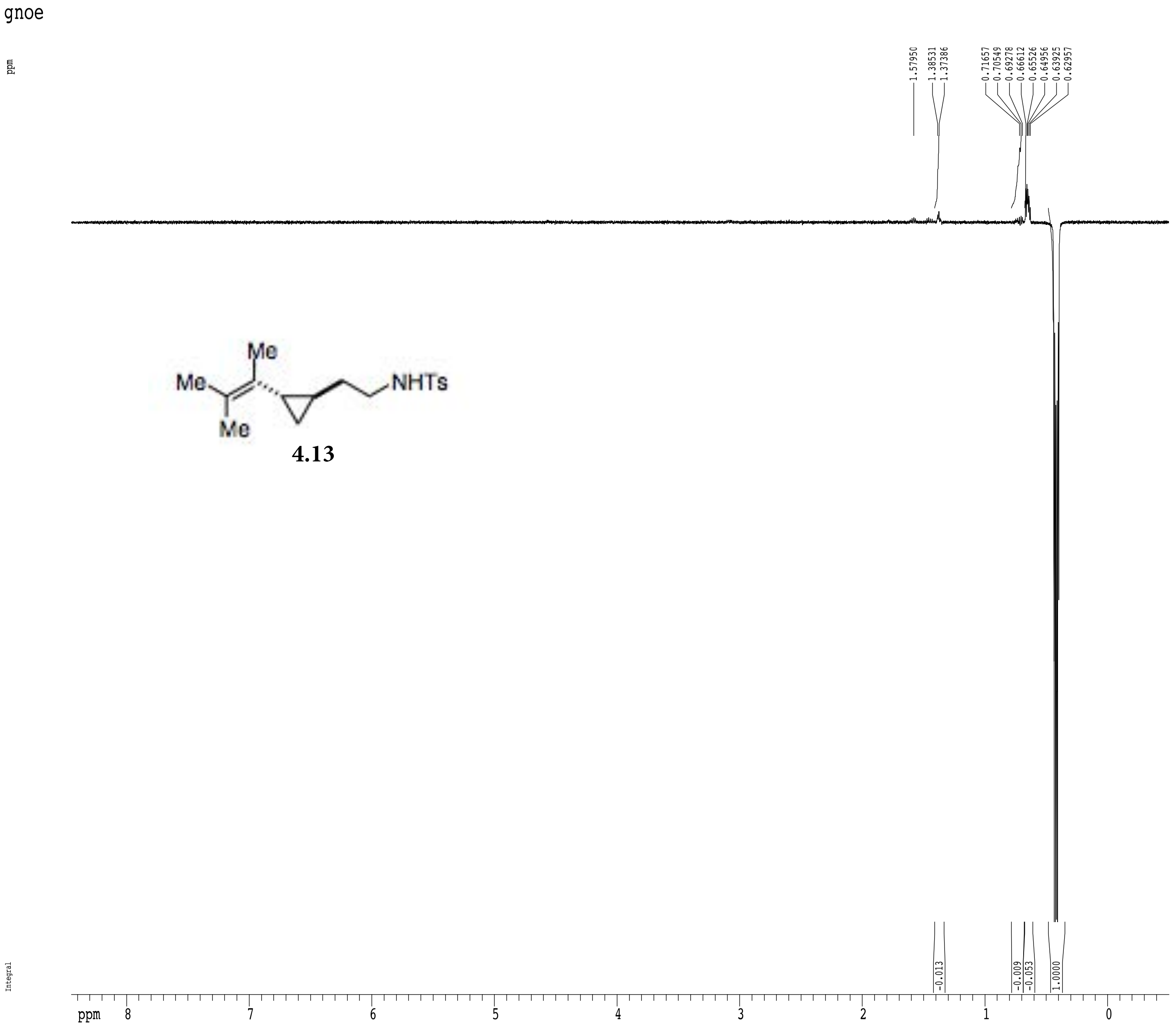


4.13

gcosy60

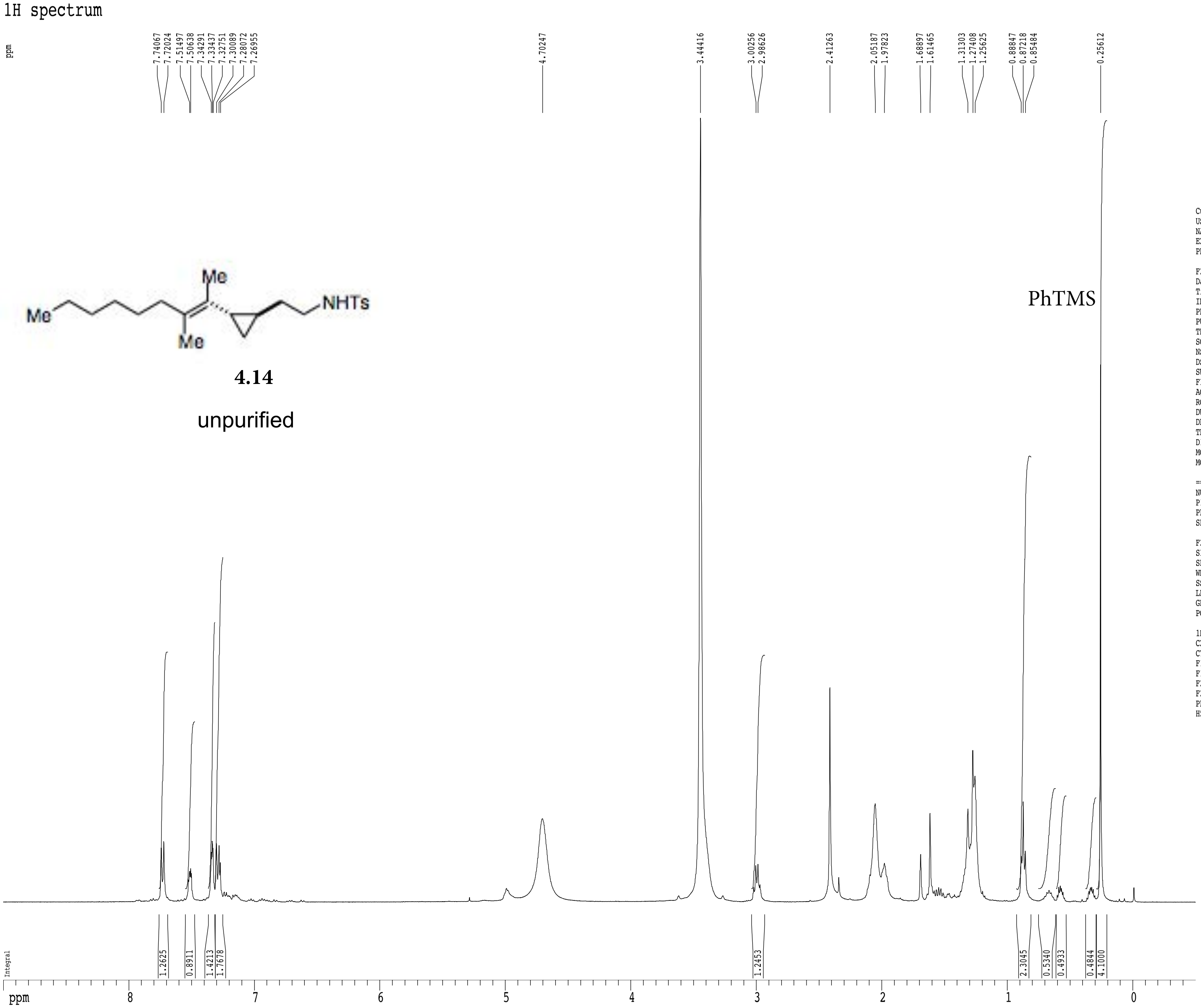


```
        Current Data Parameters
 USER           khewitt1
NAME      KAH-III-239-COSY
 EXPNO                 2
 PROCNO                1

      F2 - Acquisition Parameters
 Date_          20200821
 Time              11.58
 INSTRUM           gn500
 PROBHD   5 mm broadband
 PULPROG    cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            8012.820 Hz
 FIDRES         3.912510 Hz
 AQ            0.1278452 sec
 RG                 4096
 DW               62.400 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00012480 sec

     ======== CHANNEL f1 ========
 NUC1                 1H
 P1                12.00 usec
 PL1               -6.00 dB
 SFO1        498.7534913 MHz

     ====== GRADIENT CHANNEL =====
 GPNAM1         SINE.100
 GPNAM2         SINE.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  256
 SFO1           498.7535 MHz
 FIDRES        31.300079 Hz
 SW               16.066 ppm
 FnMODE               QF

      F2 - Processing parameters
 SI                 1024
 SF          498.7500000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

      F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          498.7500000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

        2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             9.008 ppm
 F2LO            4492.85 Hz
 F2PHI            -0.515 ppm
 F2HI            -256.94 Hz
 F1PLO             9.008 ppm
 F1LO            4492.85 Hz
 F1PHI            -0.515 ppm
 F1HI            -256.94 Hz
 F2PPMCM         0.63489 ppm/cm
 F2HZCM        316.65247 Hz/cm
 F1PPMCM         0.63489 ppm/cm
 F1HZCM        316.65247 Hz/cm
```



4.13

```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-239-NOE
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200821
Time               17.44
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG    gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                5792.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33374399 sec
d22           0.16399699 sec
p2                 24.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
p3                 36.00 usec
p4                 48.00 usec
p5                 32.00 usec
P29             40000.00 usec
PL1                -6.00 dB
SFO1         498.7502076 MHz
SP9                53.20 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           498.7500000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90625 Hz/cm
```

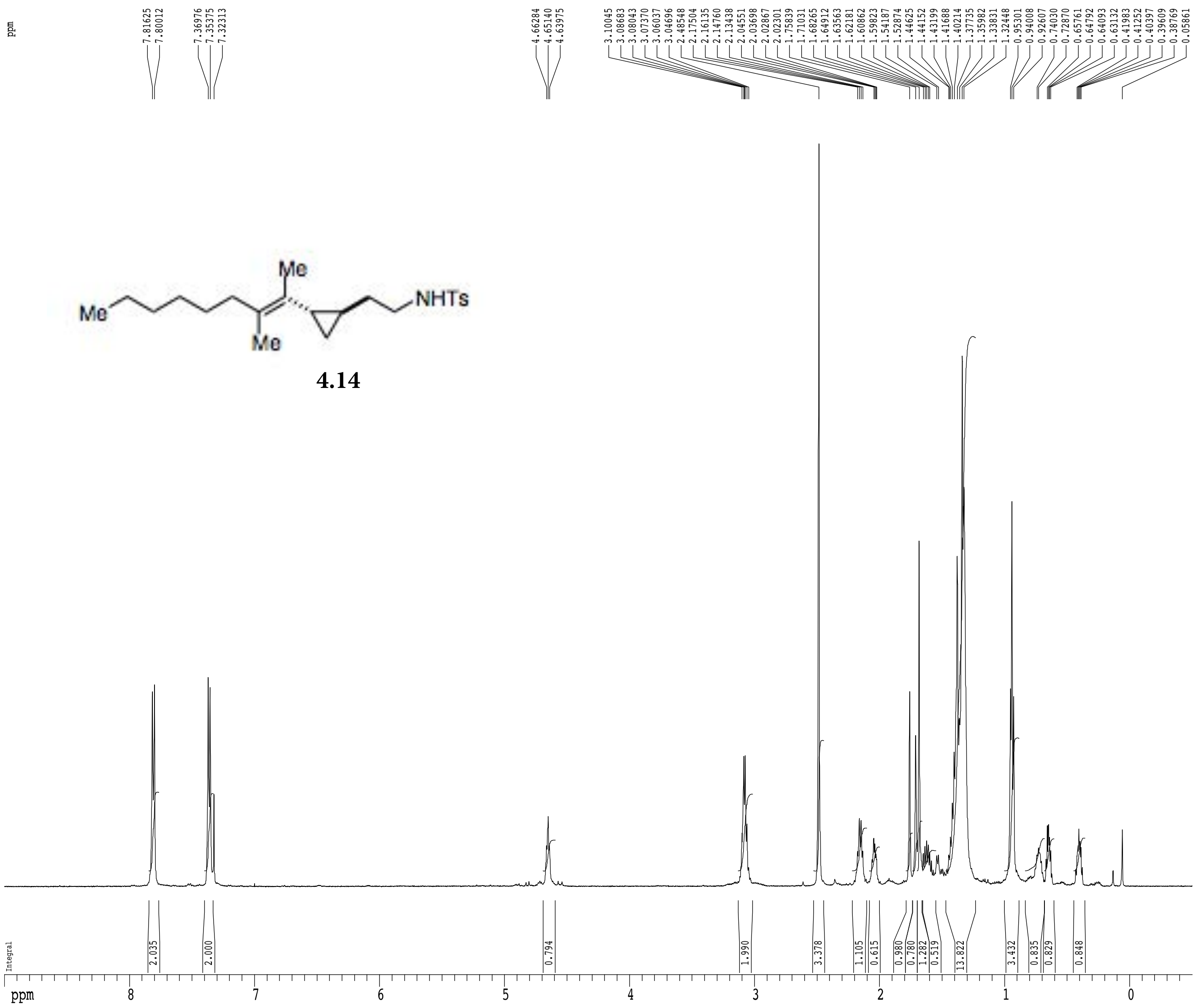


4.14

unpurified

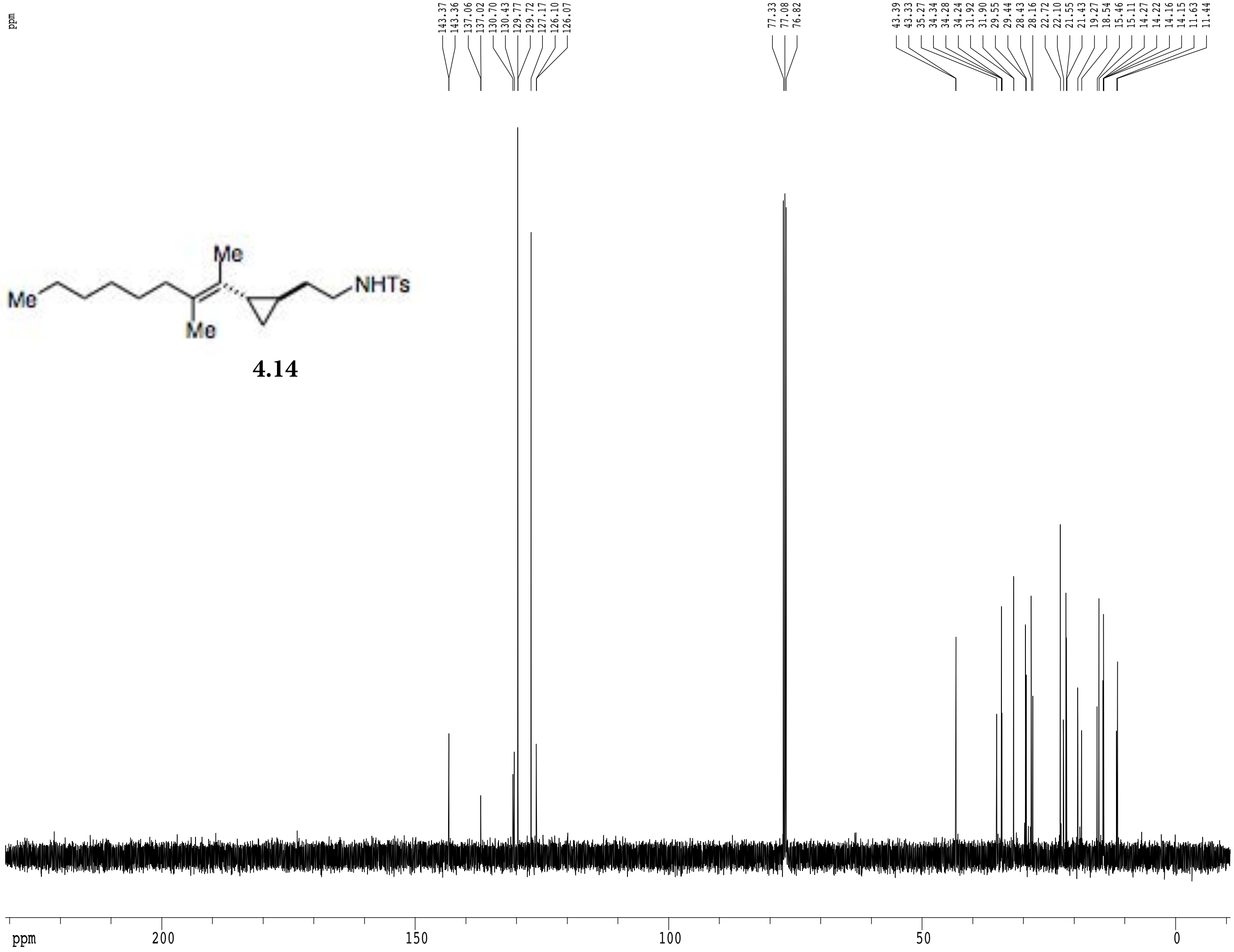
```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-206-crude
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200724
Time              14.46
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                   64
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

1H spectrum


4.14

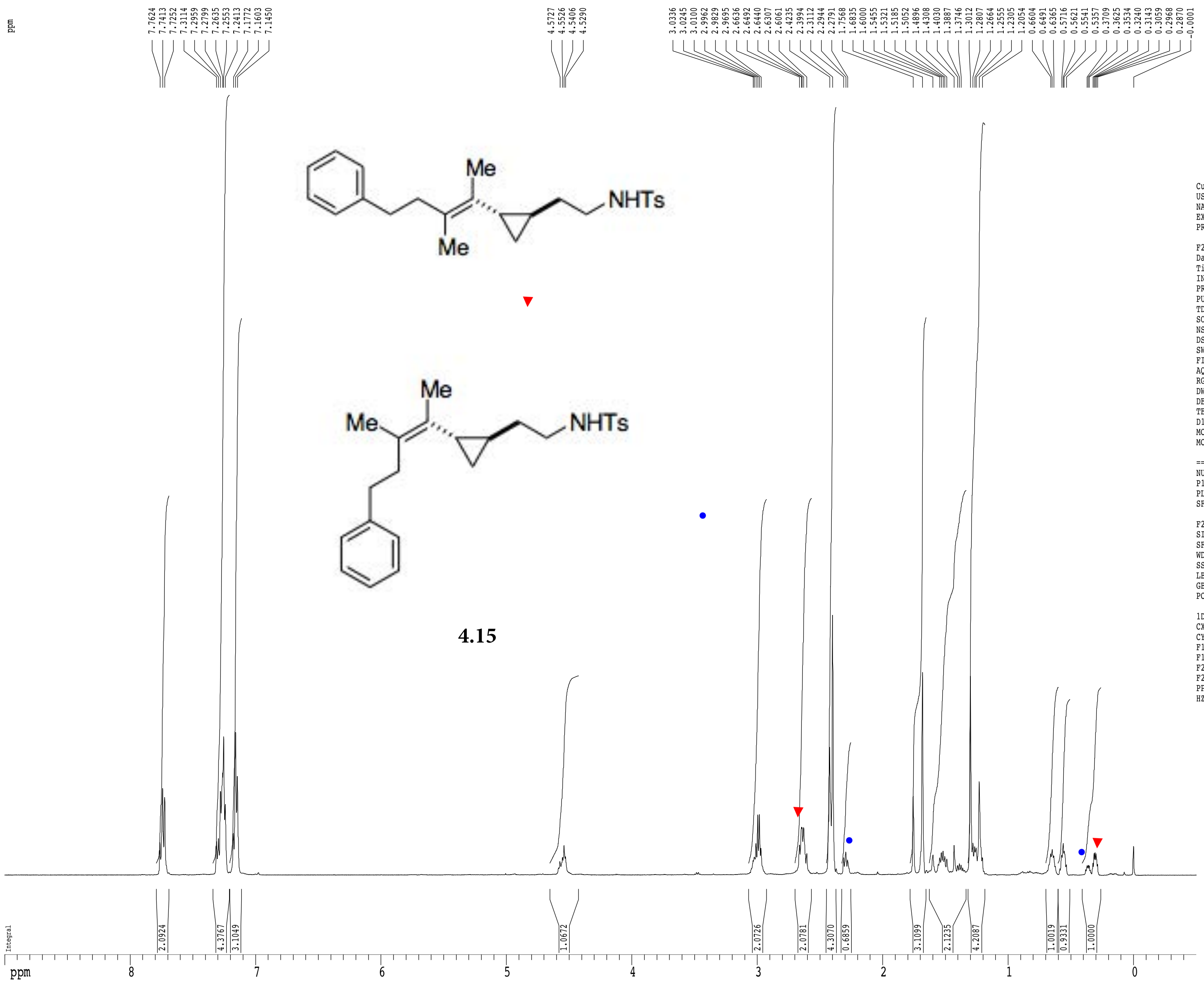
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-206-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20200911
Time              13.40
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  114
DW               62.400 usec
DE                 6.00 usec
TE                298.4 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -6.00 dB
SFO1        498.7534913 MHz

F2 - Processing parameters
SI                65536
SF          498.7500000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P               9.000 ppm
F1              4488.75 Hz
F2P              -0.500 ppm
F2              -249.38 Hz
PPMCM           0.47500 ppm/cm
HZCM          236.90625 Hz/cm
```

13C spectrum with 1H decoupling



4.14

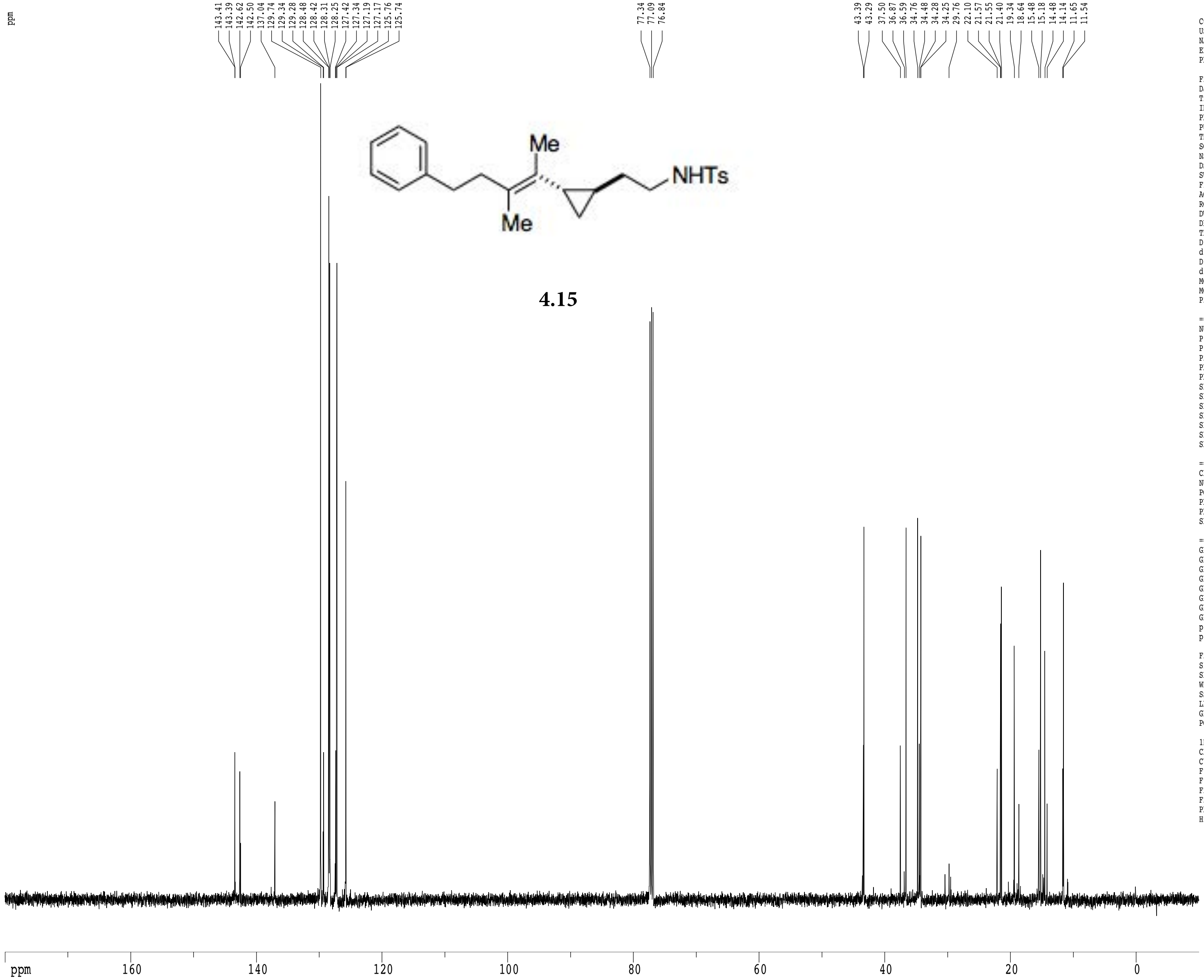
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-206-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200911
Time               13.49
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   544
DS                     4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                 46341
DW                16.500 usec
DE                  6.00 usec
TE                 298.4 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 14.20 usec
PL1                -6.00 dB
SFO1         125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.30 dB
SFO2         498.7524937 MHz

F2 - Processing parameters
SI                 65536
SF           125.4107870 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              230.817 ppm
F1              28946.95 Hz
F2P              -10.813 ppm
F2              -1356.08 Hz
PPMCM           12.08151 ppm/cm
HZCM          1515.15149 Hz/cm
```



4.15

```
Current Data Parameters
USER              tthane
NAME      TATiv120carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201008
Time               16.23
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200359 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  5.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

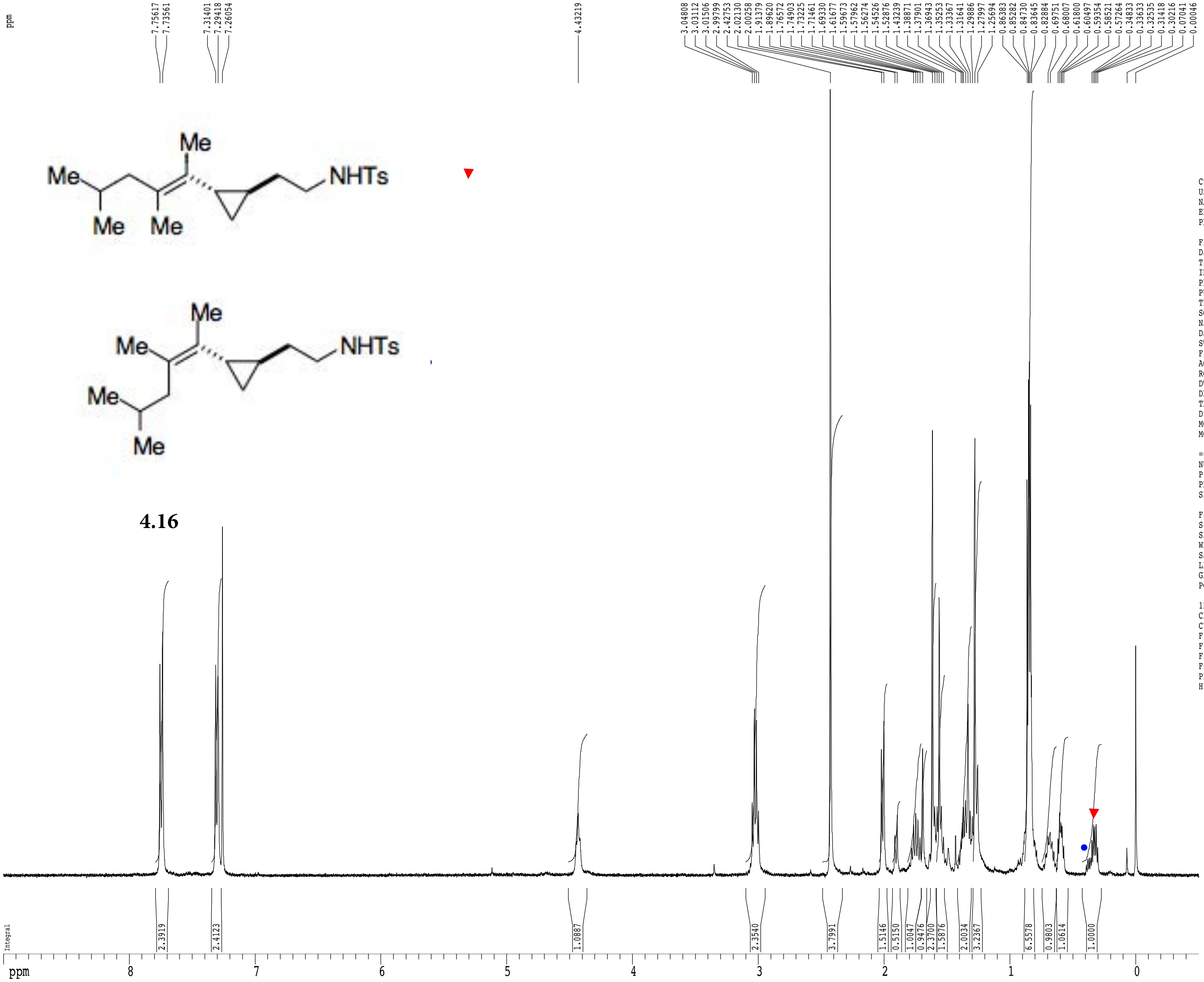
Z-restored spin-echo 13C spectrum with 1H decoupling



4.15

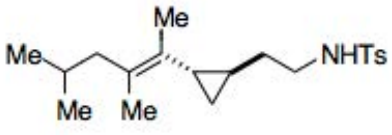
```
Current Data Parameters
USER                tthane
NAME        TATiv120carbon
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20201008
Time                 16.25
INSTRUM            cryo500
PROBHD       5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     520
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813940 sec
RG                    6502
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   2.70 dB
SP4                   2.70 dB
SPNAM2         Crp60comp.4
SPNAM4      Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 23.54 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804190 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                180.000 ppm
F1                22640.47 Hz
F2P                -10.000 ppm
F2                -1257.80 Hz
PPMCM              8.33333 ppm/cm
HZCM            1048.17017 Hz/cm
```

1H spectrum



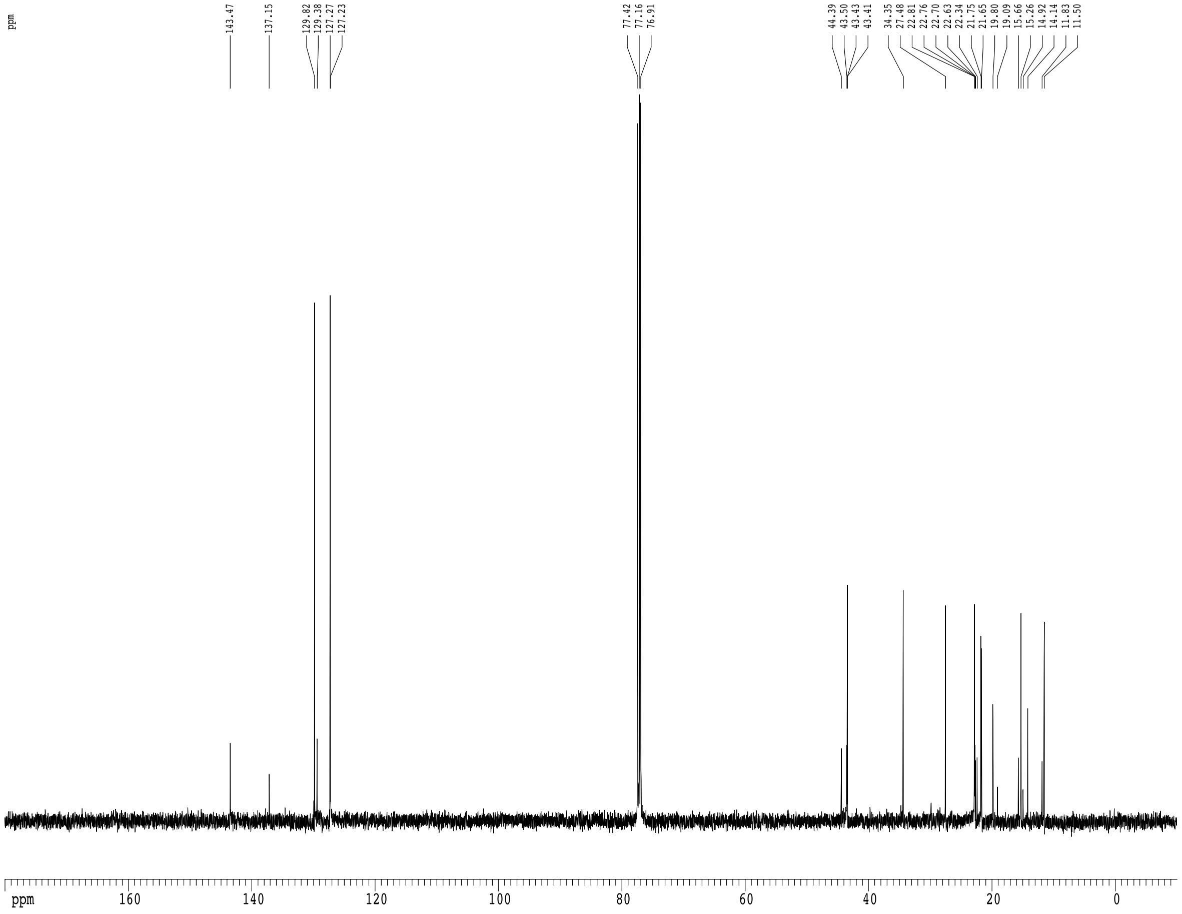
4.16

```
Current Data Parameters
USER              tthane
NAME     TATiv72-9-11-2020
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200911
Time               11.13
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                 322.5
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300214 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```



4.16

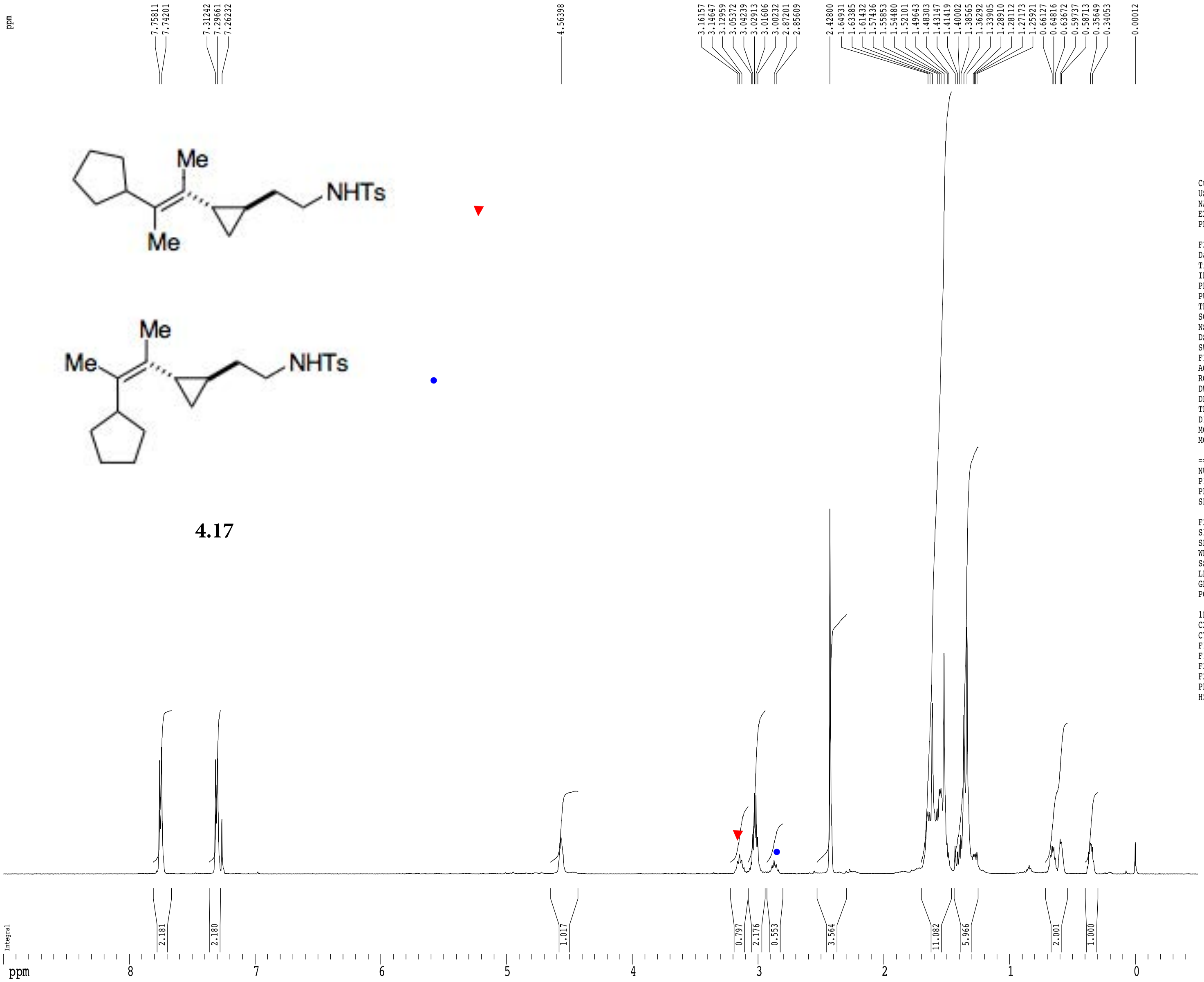
13C spectrum with 1H decoupling



```
Current Data Parameters
USER              tthane
NAME        TATiv72carbon
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200718
Time               11.45
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   704
DS                     4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                5792.6
DW               16.500 usec
DE                 6.00 usec
TE                297.9 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 14.20 usec
PL1                -6.00 dB
SFO1         125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.30 dB
SFO2         498.7524937 MHz

F2 - Processing parameters
SI                 65536
SF           125.4107752 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              180.000 ppm
F1              22573.94 Hz
F2P              -10.000 ppm
F2              -1254.11 Hz
PPMCM            9.50000 ppm/cm
HZCM          1191.40234 Hz/cm
```

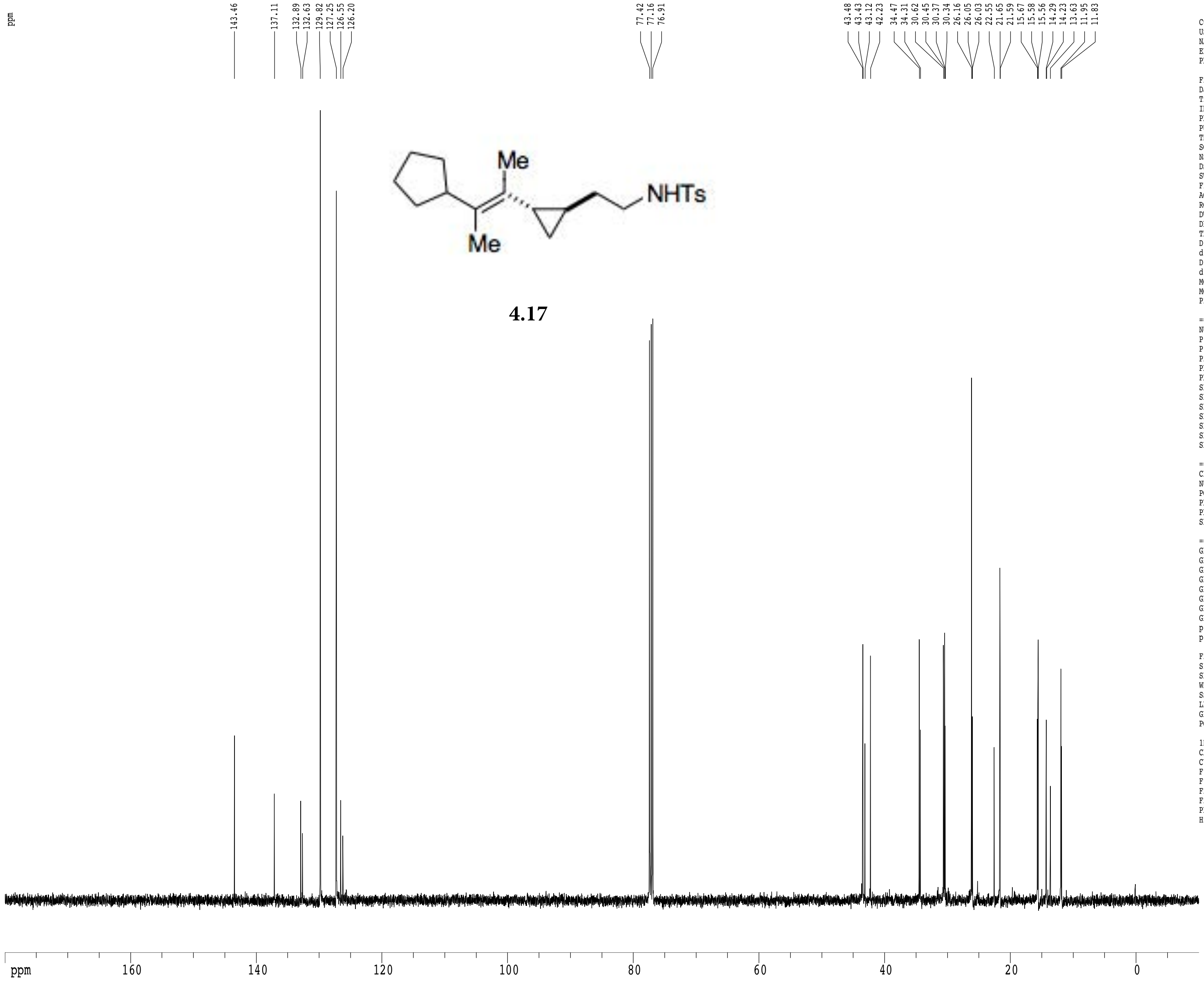
1H spectrum

4.17



```
Current Data Parameters
USER             tthane
NAME     TATiv132carbon
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20201008
Time              17.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200311 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                 7.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

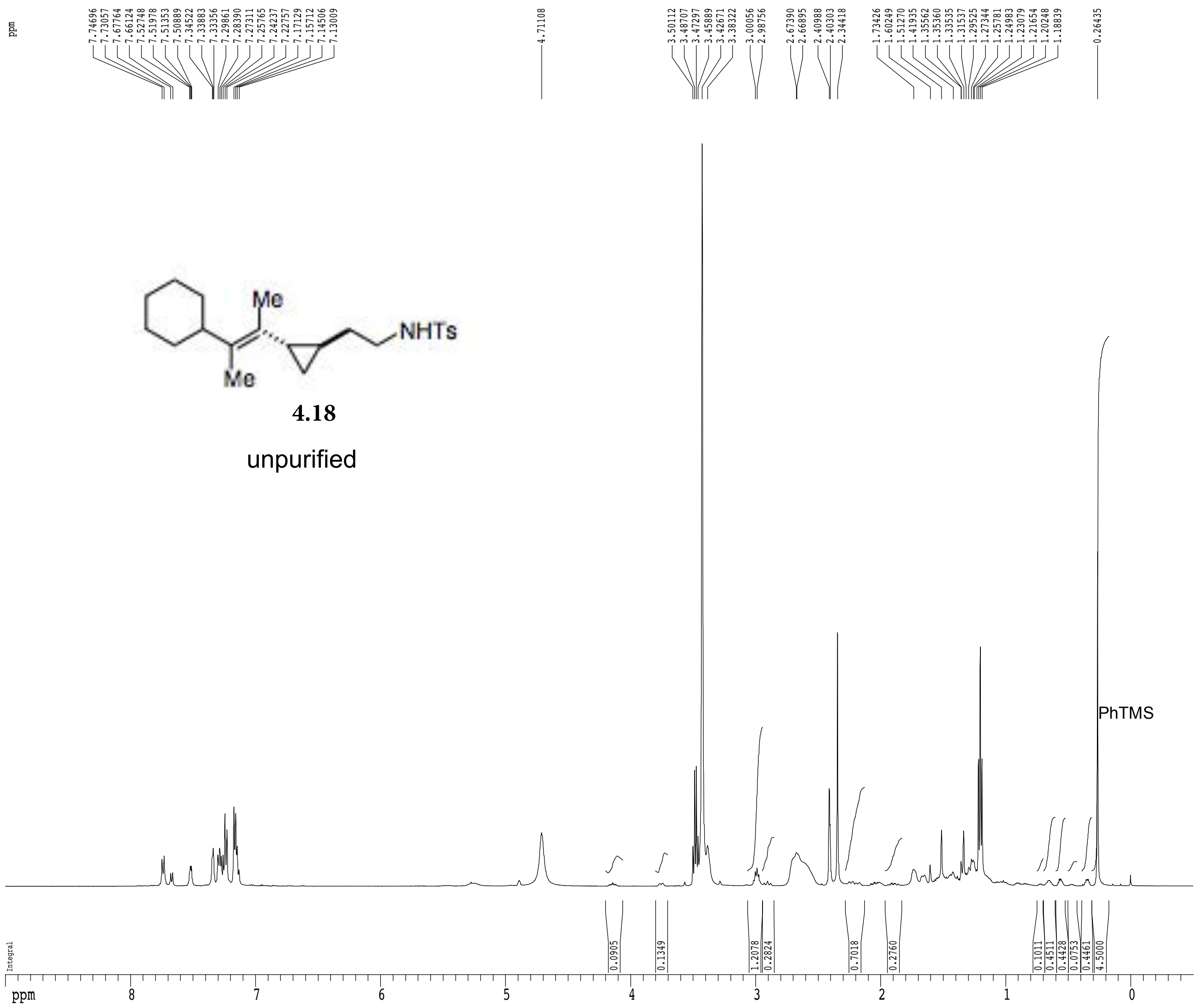
Z-restored spin-echo 13C spectrum with 1H decoupling



4.17

```
Current Data Parameters
USER              tthane
NAME       TATiv132carbon
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201008
Time               17.26
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   448
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.17017 Hz/cm
```

1H spectrum

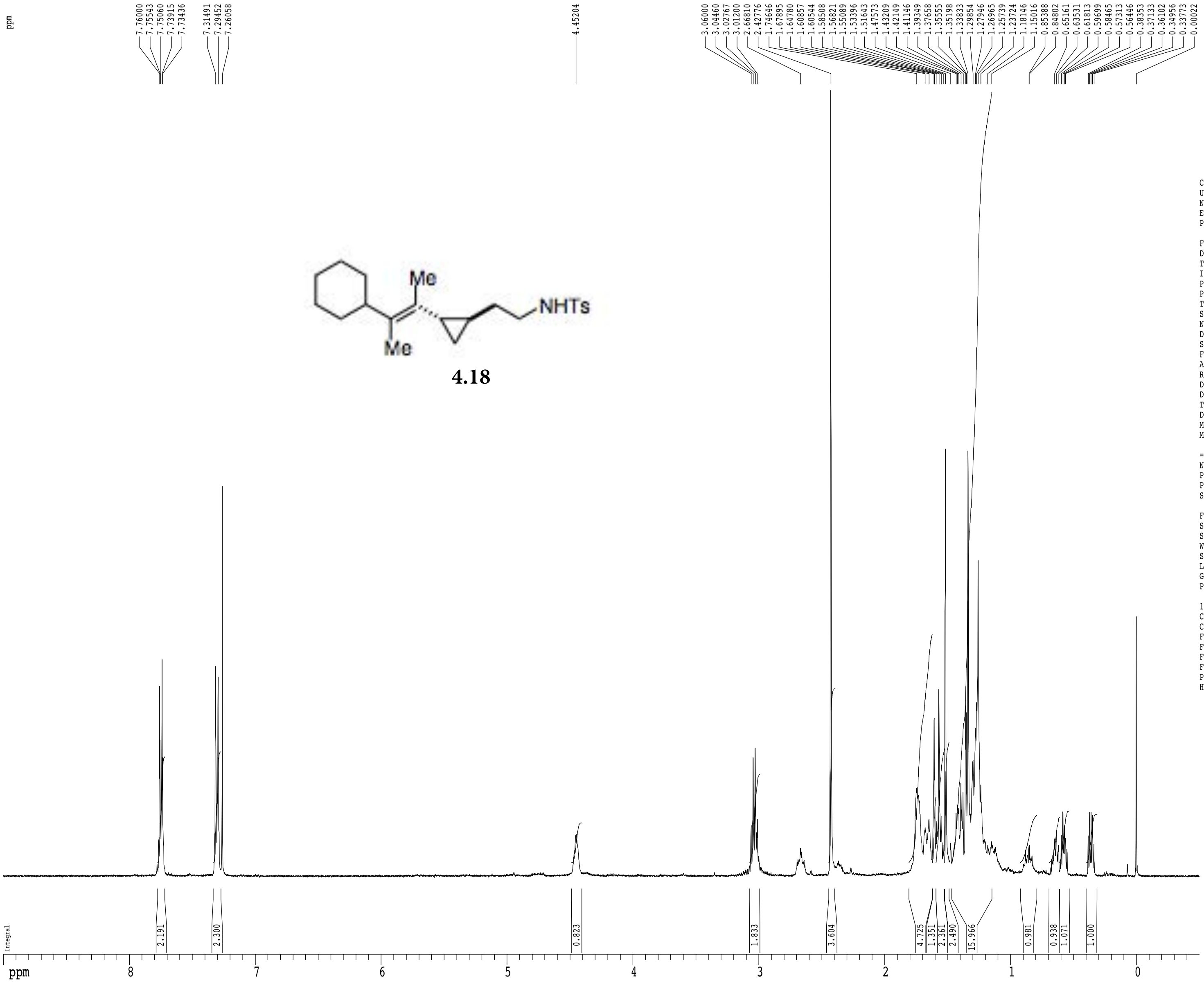


4.18

unpurified

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-145-crude
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200617
Time               18.55
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                  40.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500244 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```

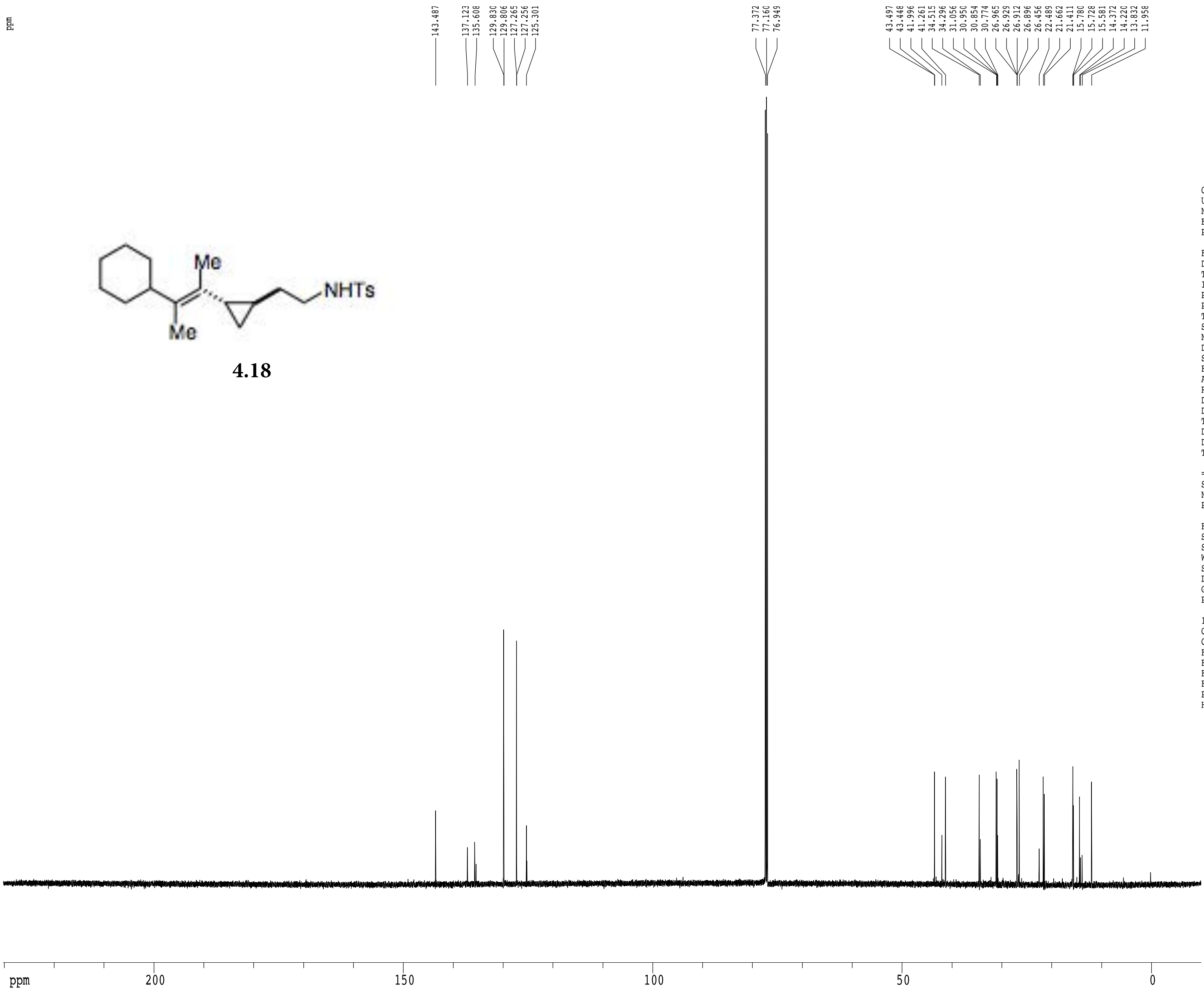
1H spectrum



4.18

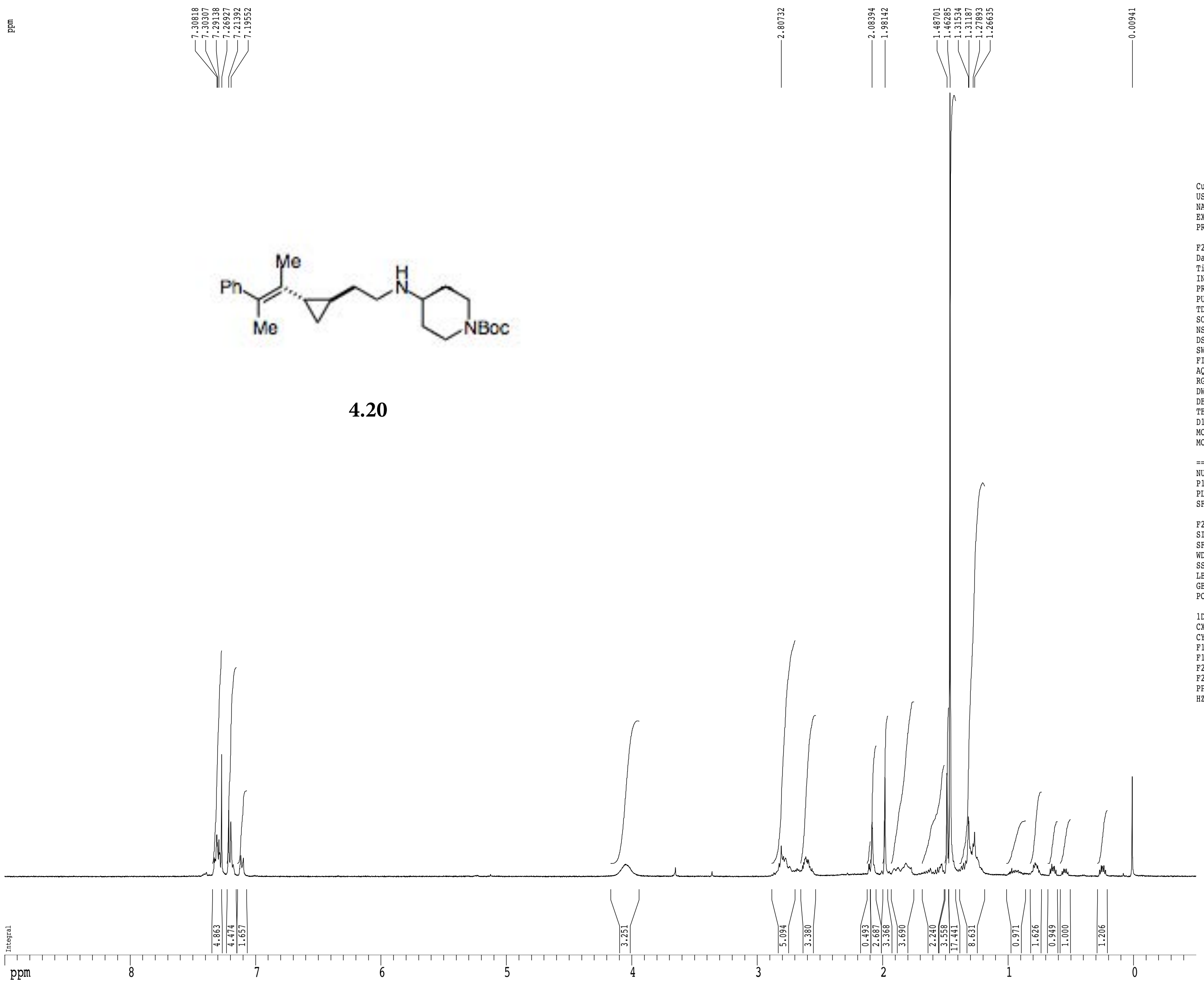
```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-145-dried
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200624
Time               12.47
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                   256
DW                78.000 usec
DE                  4.50 usec
TE                 298.1 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300210 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

4.18



```
Current Data Parameters
USER              khewitt1
NAME        KAH-III-145-600
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200627
Time                 12.15
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT             CDCl3T
NS                     192
DS                       4
SWH             36231.883 Hz
FIDRES           0.552855 Hz
AQ              0.9044468 sec
RG                    2050
DW                  13.800 usec
DE                   19.63 usec
TE                   298.1 K
D1              0.40000001 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                   13C
P1                   10.10 usec

F2 - Processing parameters
SI                   65536
SF           150.9027942 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                230.147 ppm
F1                34729.77 Hz
F2P                 -9.954 ppm
F2                -1502.12 Hz
PPMCM             10.53074 ppm/cm
HZCM            1589.11780 Hz/cm
```

1H spectrum

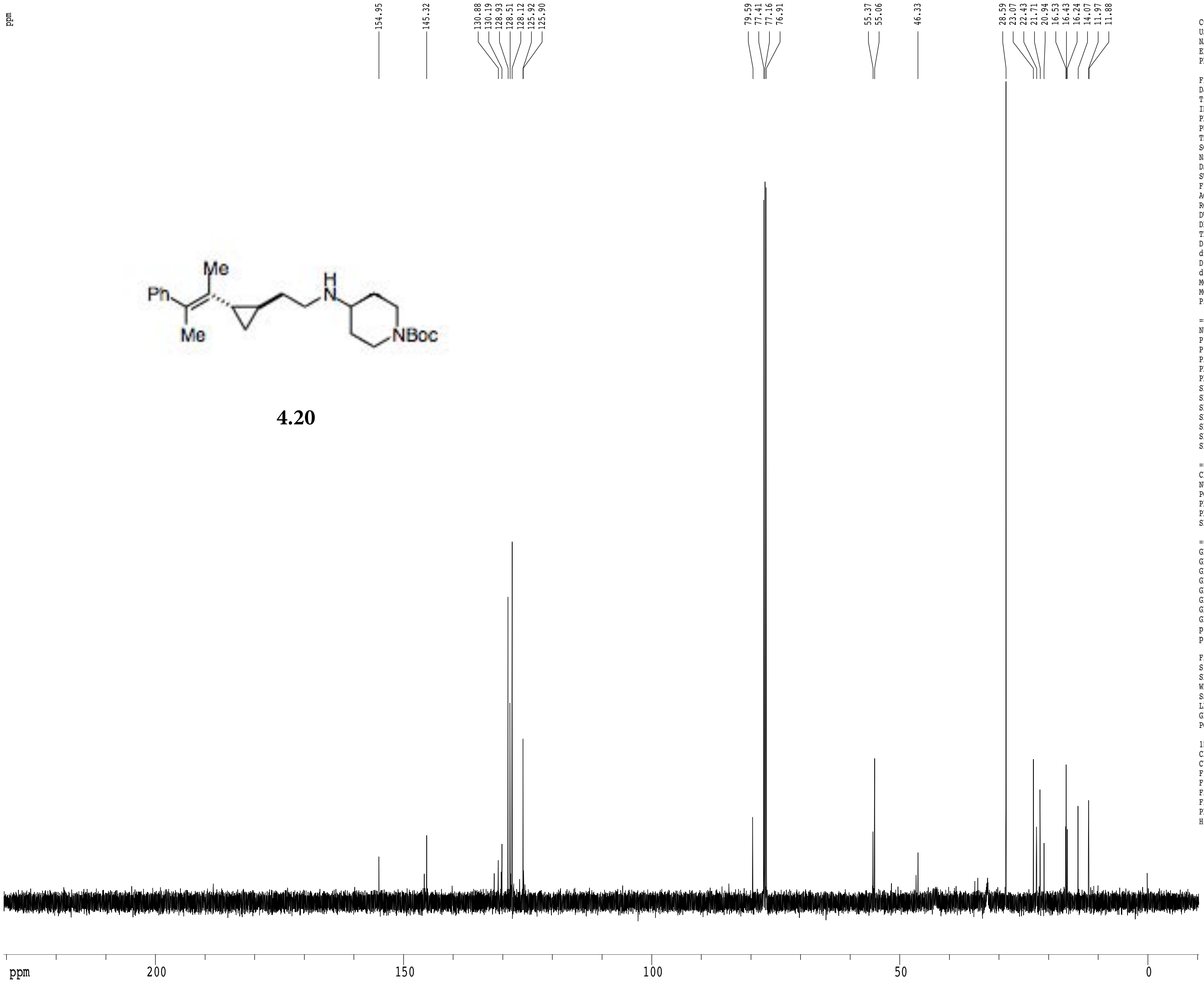


4.20

```
Current Data Parameters
USER            khewitt1
NAME      KAH-IV-141-chk
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210301
Time                9.55
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                   362
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF          400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

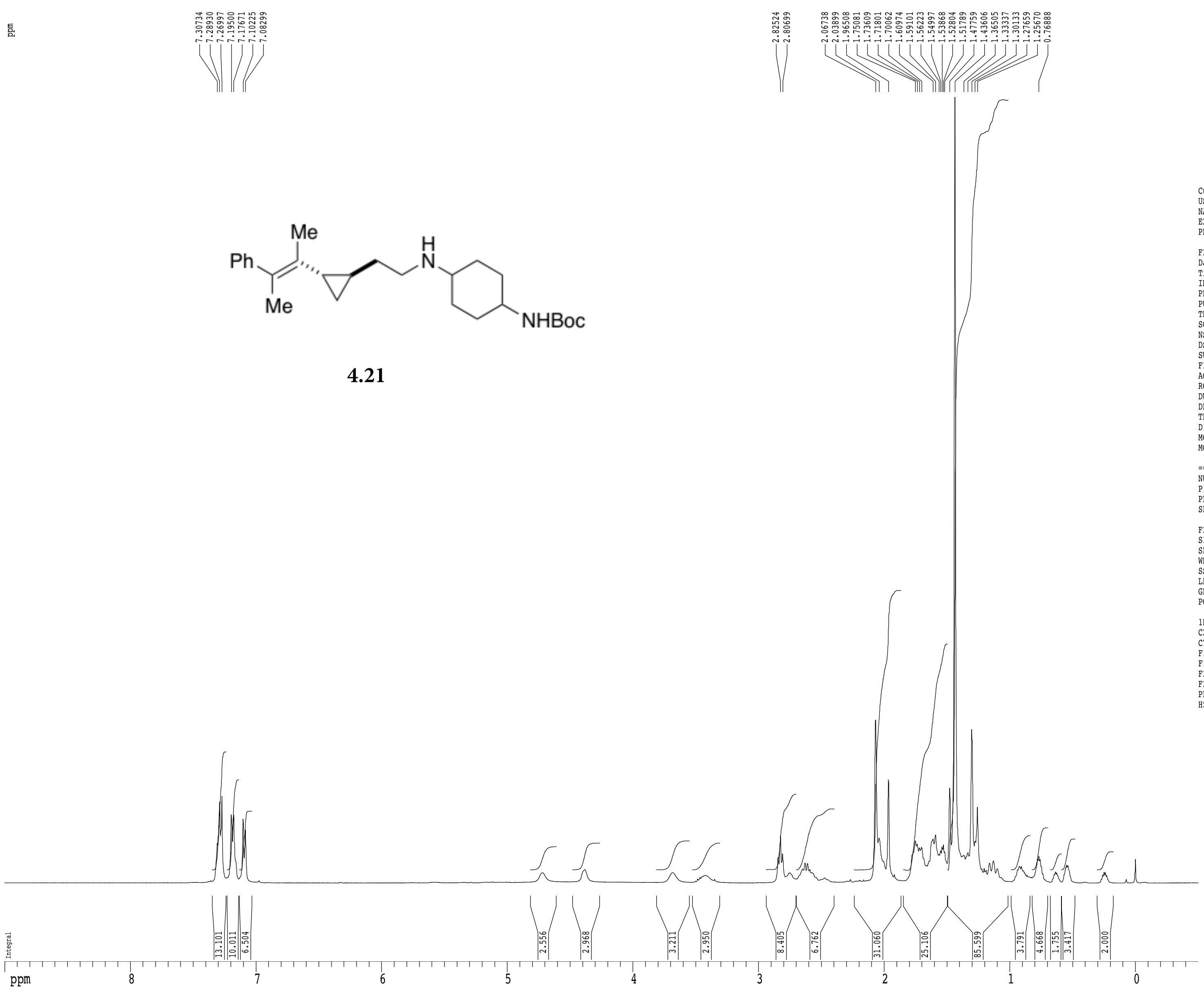
Z-restored spin-echo 13C spectrum with 1H decoupling

4.20



```
Current Data Parameters
USER              khewitt1
NAME      KAH-IV-141-chk
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_          20210301
Time              10.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG                 6502
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  18.85 usec
P12               2000.00 usec
P20                500.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP2                  1.55 dB
SP4                  1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2               0.00 Hz
SPOFF4               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                22.00 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804066 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```

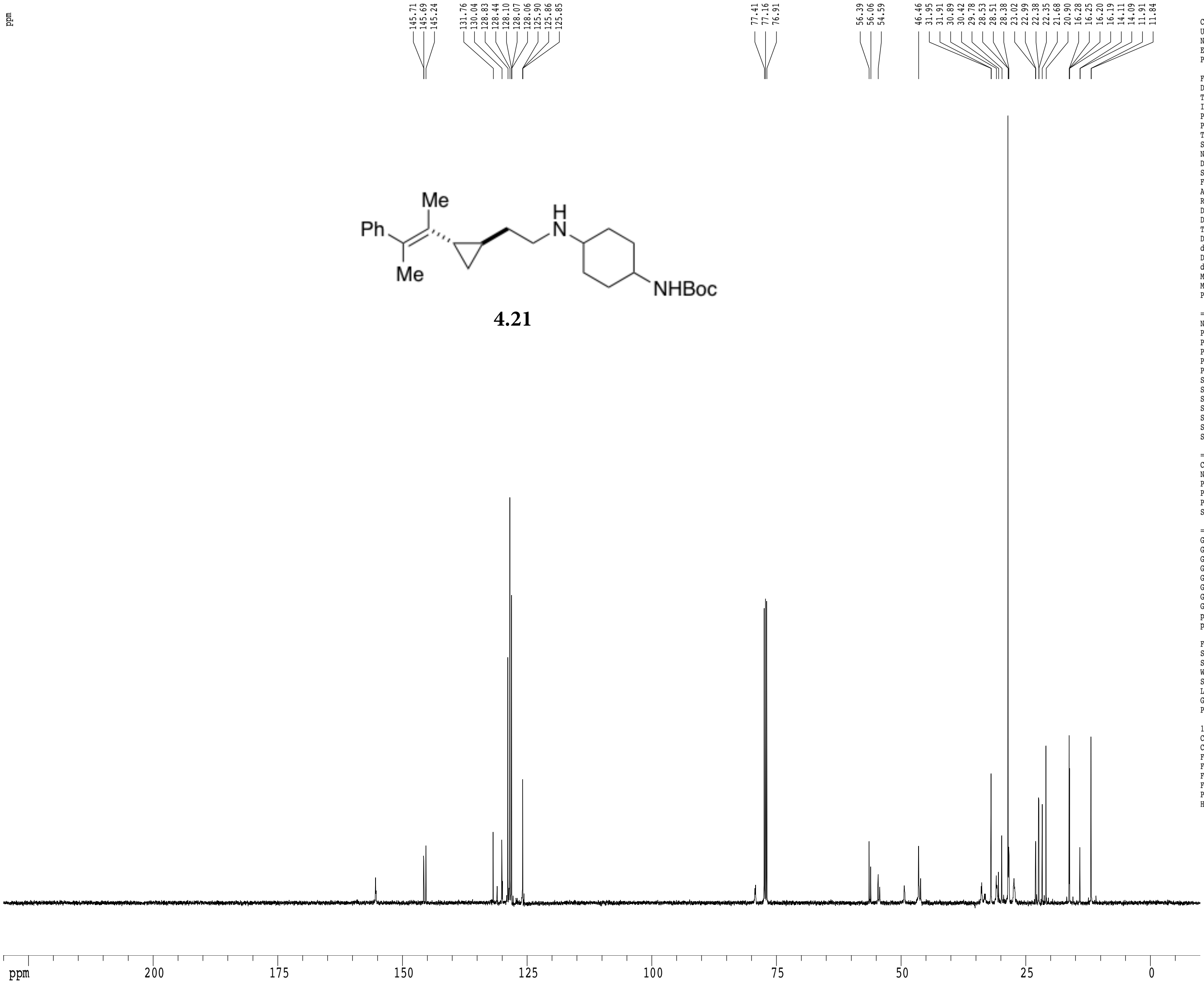
1H spectrum



4.21

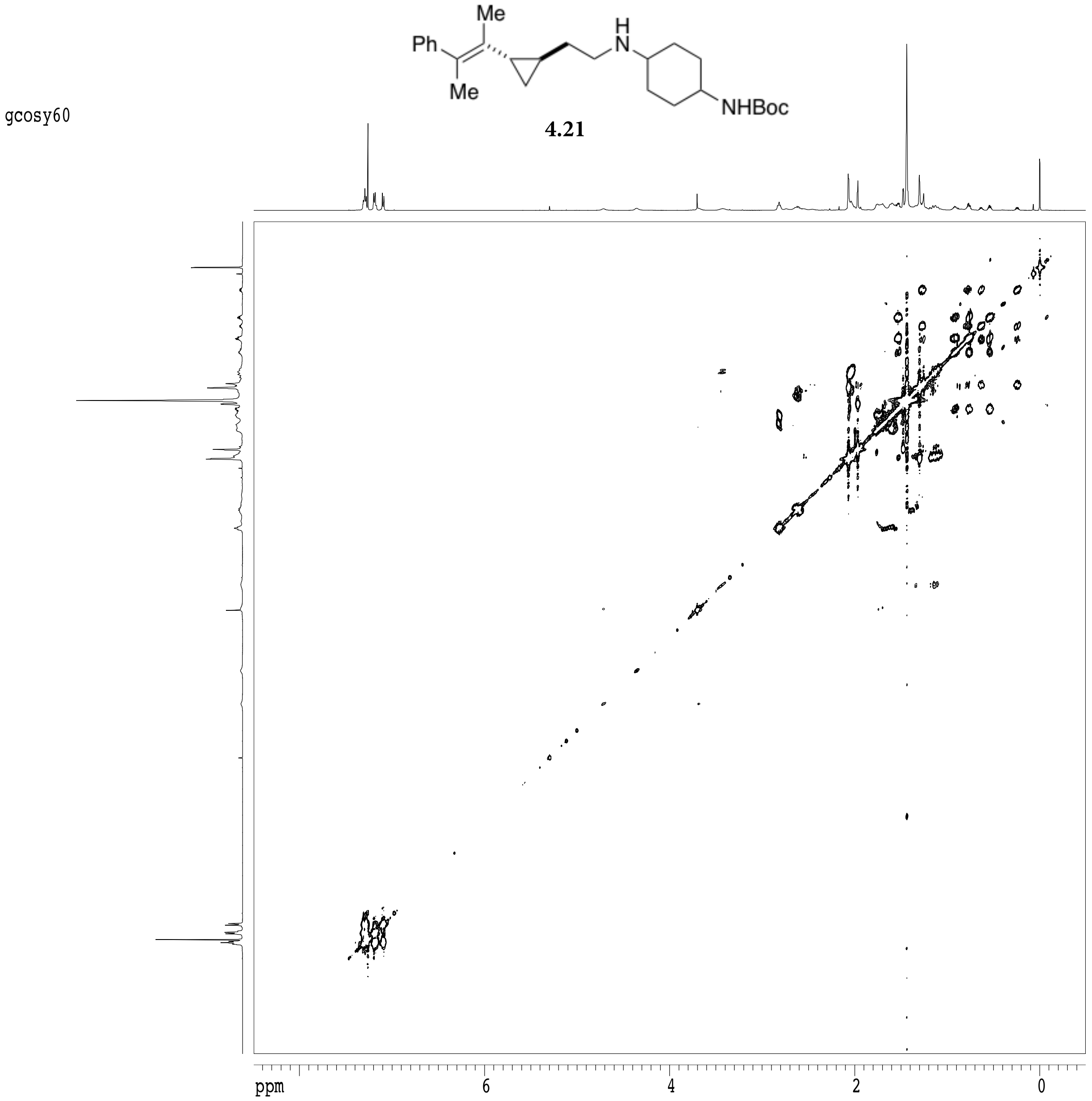
```
Current Data Parameters
USER            nhirbawi
NAME       NH-1-176-column
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210225
Time               18.44
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



4.21

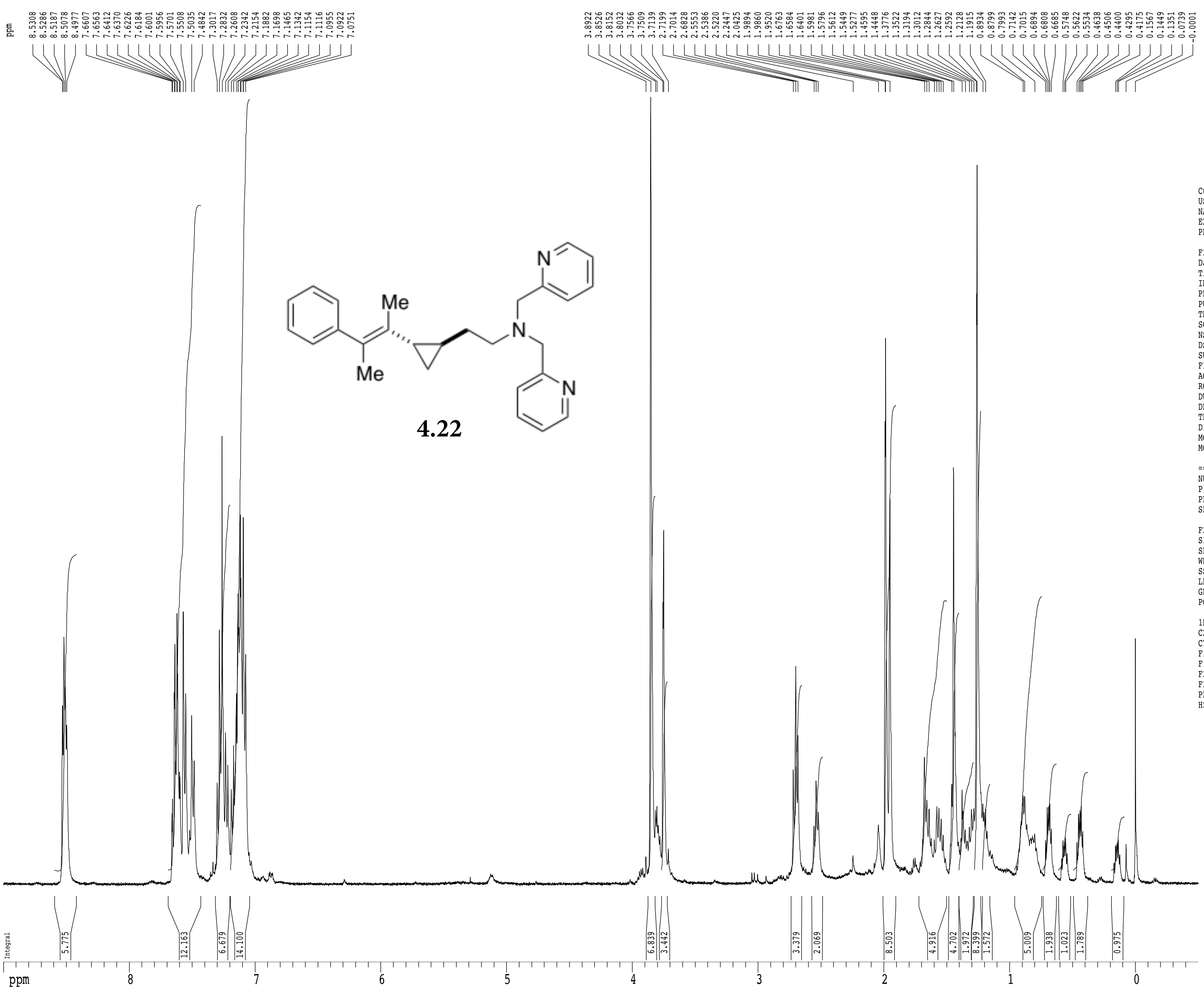
```
Current Data Parameters
USER            nhirbawi
NAME      NH-1-176-5-14-carbon
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210514
Time               15.14
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804127 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.000 ppm
F1              28929.49 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM           10.52632 ppm/cm
HZCM          1324.00439 Hz/cm
```



4.21

```
        Current Data Parameters
USER          nhirbawi
NAME     NH-1-155-HCandCOSY
EXPNO                 2
PROCNO                1

      F2 - Acquisition Parameters
Date_            20210223
Time                17.33
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                   2048
SOLVENT            CDCl3T
NS                      2
DS                     16
SWH              4496.403 Hz
FIDRES           2.195509 Hz
AQ              0.2277876 sec
RG                  143.7
DW                111.200 usec
DE                   6.00 usec
TE                  298.0 K
d0             0.00000300 sec
D1             1.00000000 sec
d13            0.00000300 sec
D16            0.00020000 sec
IN0            0.00022240 sec

     ======== CHANNEL f1 ========
NUC1                   1H
P1                   9.75 usec
PL1                  1.60 dB
SFO1          500.2220314 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1          SMSQ10.100
GPNAM2          SMSQ10.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                17.00 %
GPZ2                17.00 %
P16               1000.00 usec

      F1 - Acquisition parameters
ND0                     1
TD                    256
SFO1              500.222 MHz
FIDRES          17.564074 Hz
SW                  8.989 ppm
FnMODE                 QF

      F2 - Processing parameters
SI                   1024
SF            500.2200305 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

      F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.2200305 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0

        2D NMR plot parameters
CX2                 15.00 cm
CX1                 15.00 cm
F2PLO               8.494 ppm
F2LO              4249.08 Hz
F2PHI              -0.494 ppm
F2HI              -247.32 Hz
F1PLO               8.494 ppm
F1LO              4249.08 Hz
F1PHI              -0.494 ppm
F1HI              -247.32 Hz
F2PPMCM           0.59926 ppm/cm
F2HZCM          299.76016 Hz/cm
F1PPMCM           0.59926 ppm/cm
F1HZCM          299.76016 Hz/cm
```

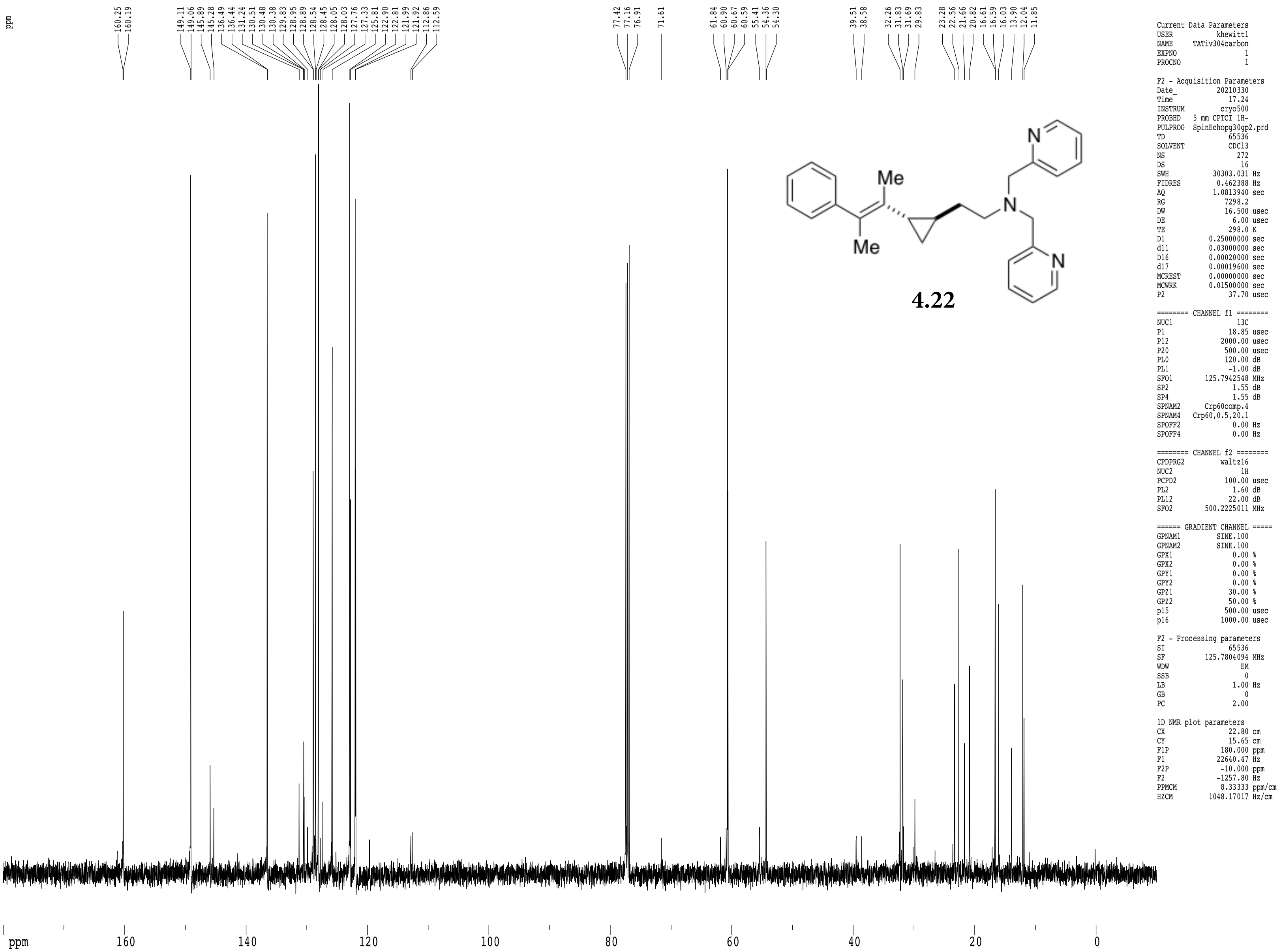
1H spectrum



4.22

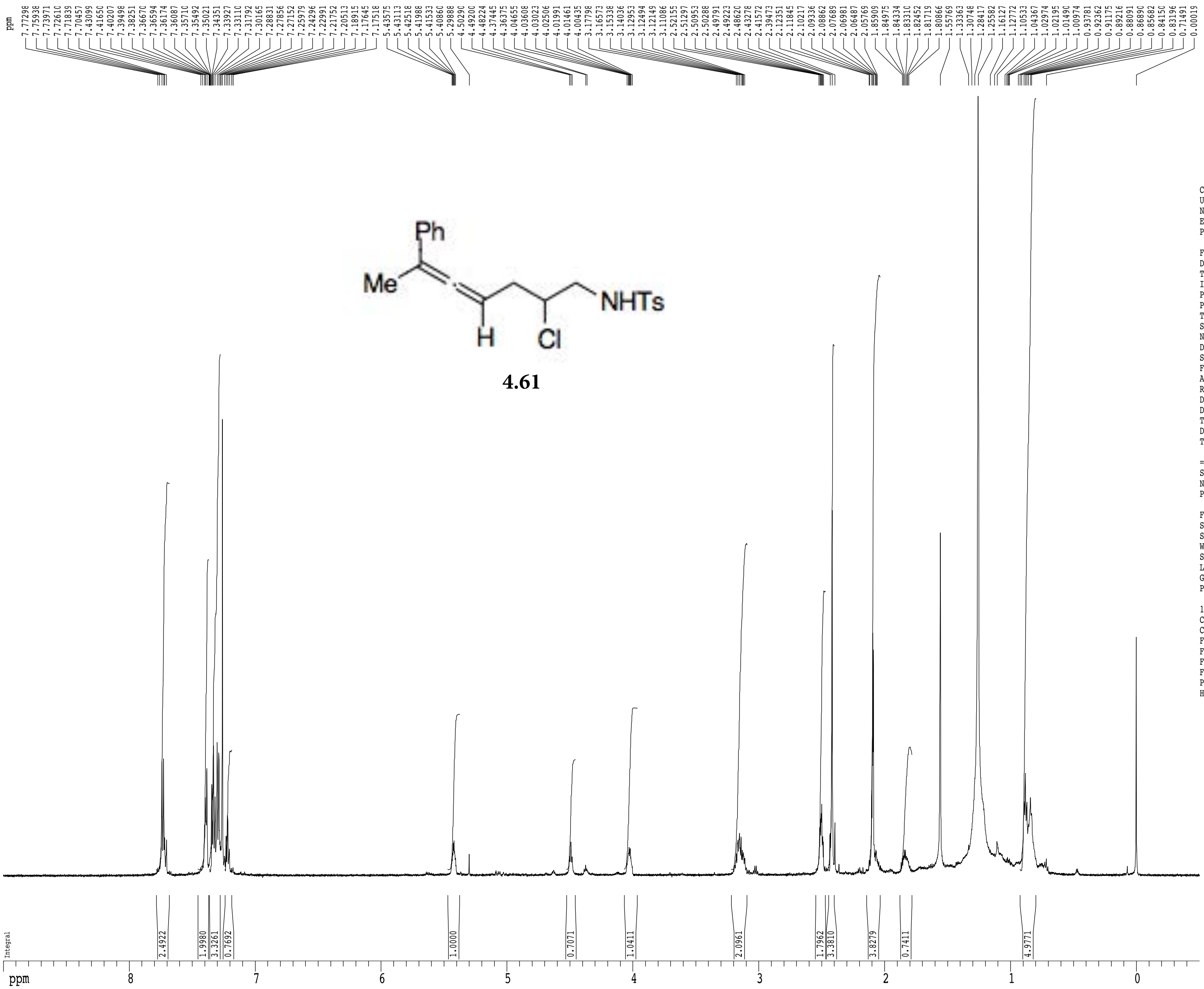
```
Current Data Parameters
USER              tthane
NAME           TATiv304c
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210330
Time               16.18
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                 161.3
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300216 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



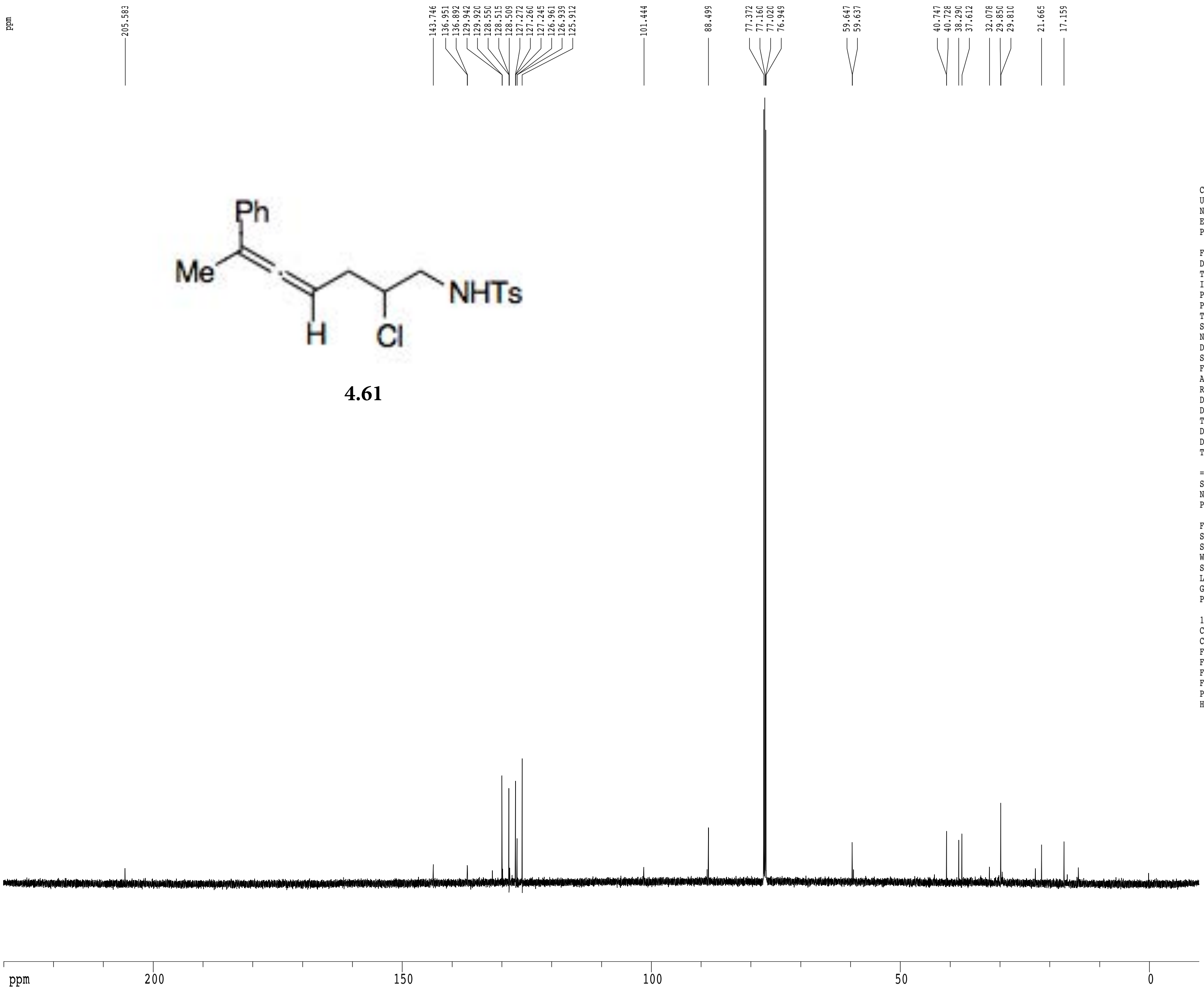
4.22

```
Current Data Parameters
USER            khewitt1
NAME      TATiv304carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210330
Time               17.24
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   272
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          125.7804094 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.17017 Hz/cm
```



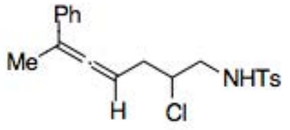
4.61

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-141-600
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200627
Time               11.58
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                    10
DW                52.000 usec
DE                 14.23 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.50 usec

F2 - Processing parameters
SI                 65536
SF           600.1300351 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```



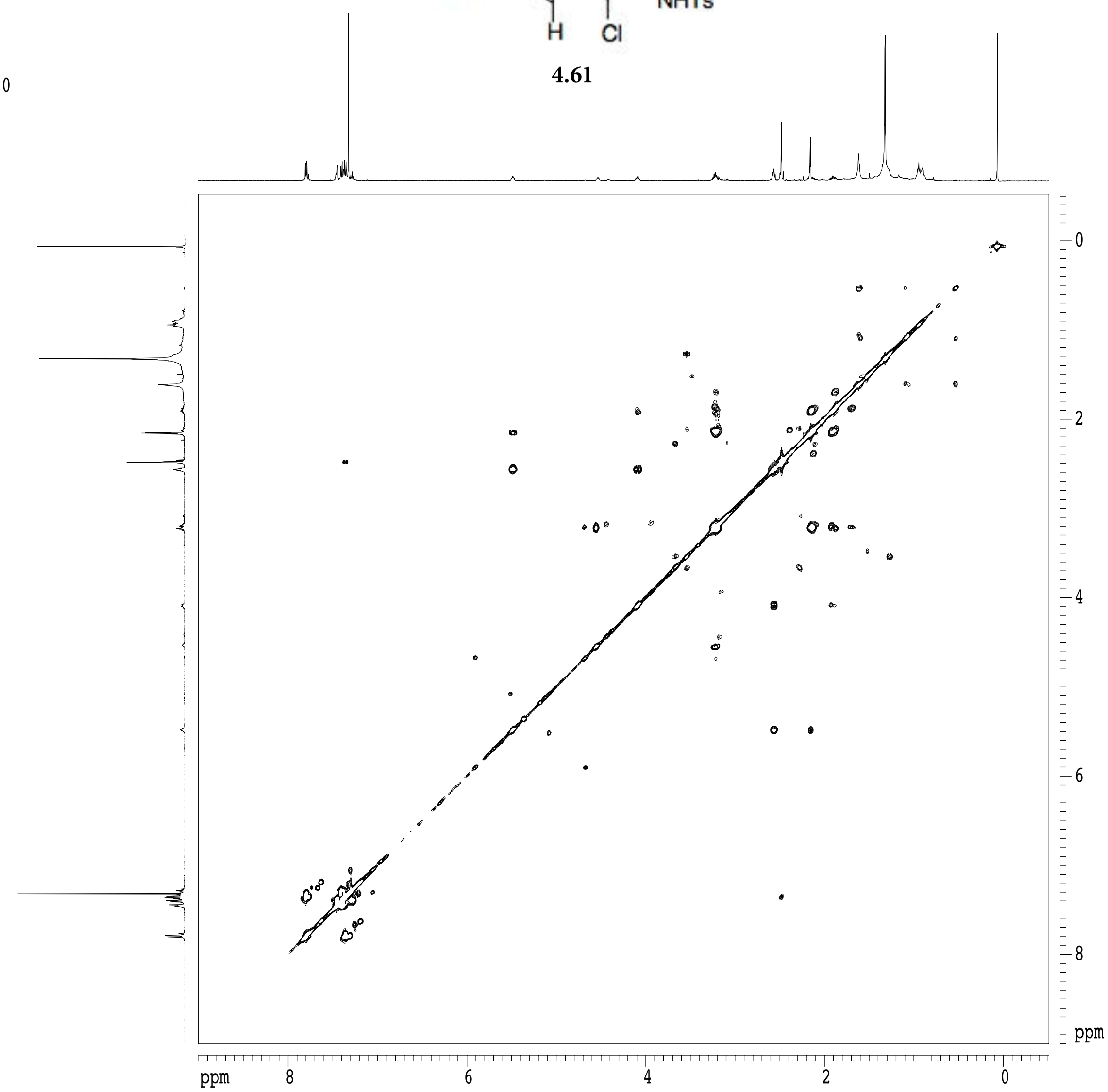
4.61

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-141-600
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200627
Time               12.03
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   224
DS                     4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9027936 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  0.05

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.051 ppm
F1              34715.41 Hz
F2P              -10.049 ppm
F2              -1516.47 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11743 Hz/cm
```



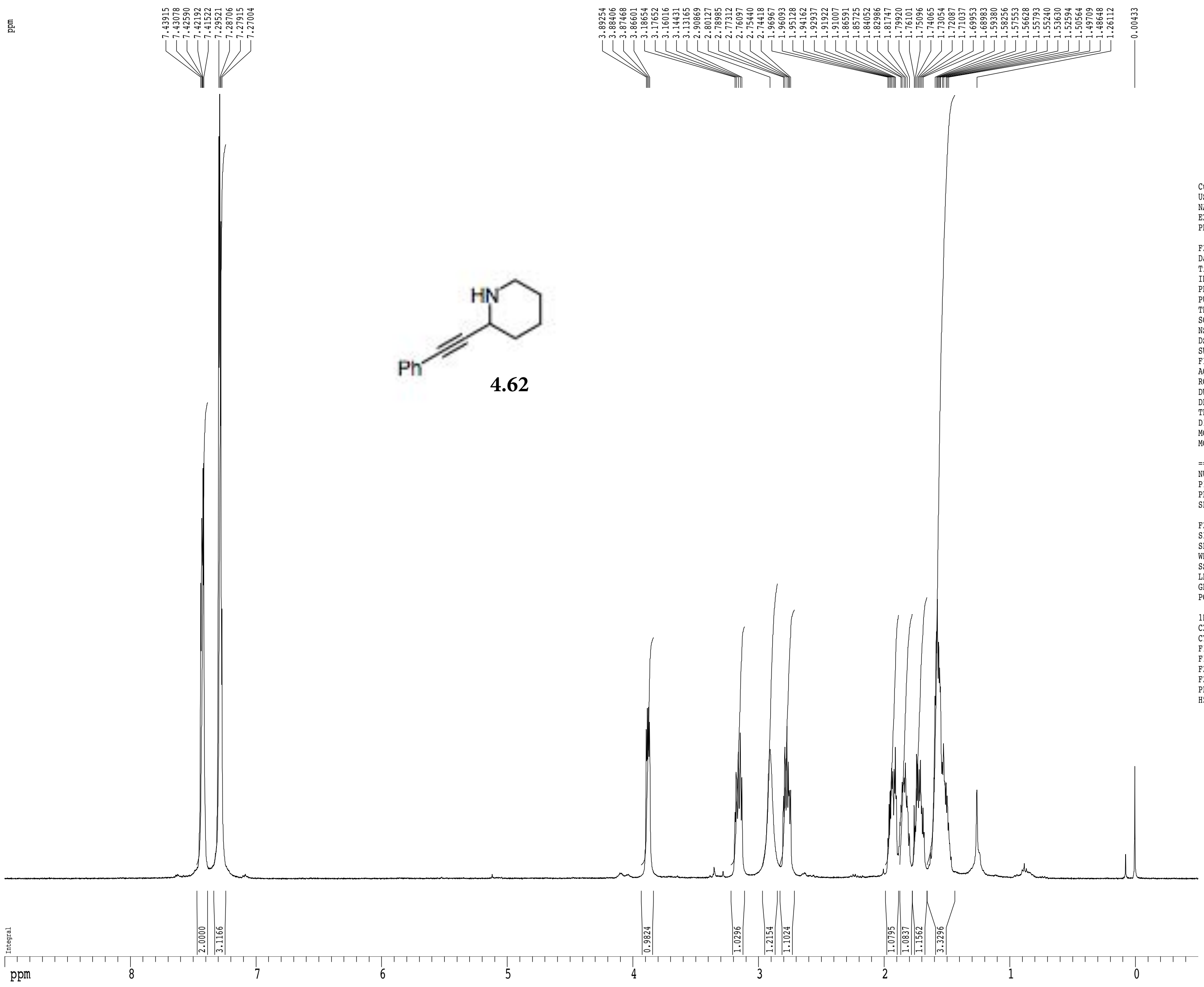
4.61

gcosy60



```
        Current Data Parameters
USER           khewitt1
NAME     KAH-III-141-2D
EXPNO                 3
PROCNO                1

      F2 - Acquisition Parameters
Date_          20200702
Time              17.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                912.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.002 ppm
F2LO            4503.14 Hz
F2PHI            -0.509 ppm
F2HI            -254.47 Hz
F1PLO             9.002 ppm
F1LO            4503.14 Hz
F1PHI            -0.524 ppm
F1HI            -262.29 Hz
F2PPMCM         0.63407 ppm/cm
F2HZCM        317.17416 Hz/cm
F1PPMCM         0.63511 ppm/cm
F1HZCM        317.69583 Hz/cm
```

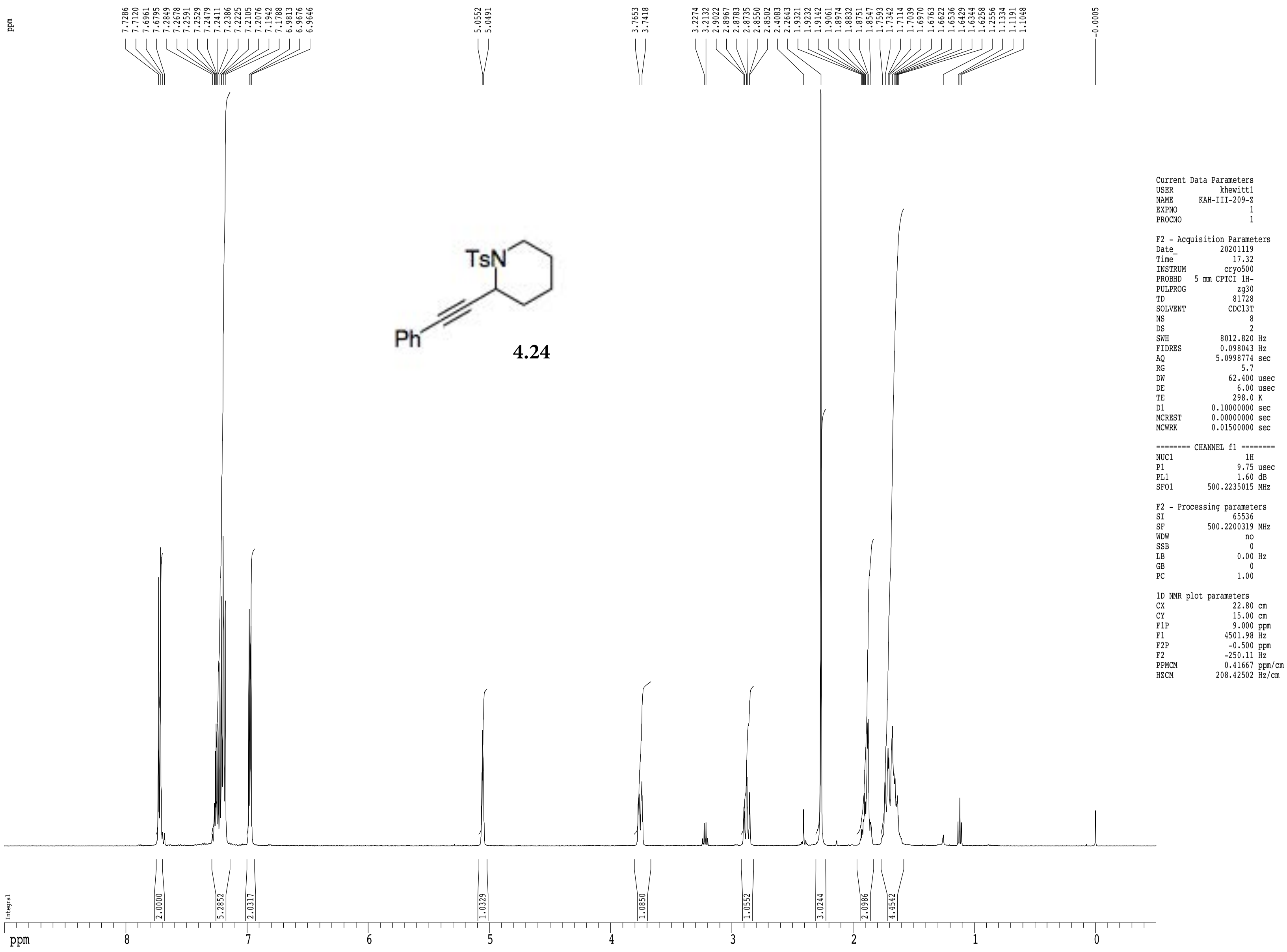
1H spectrum



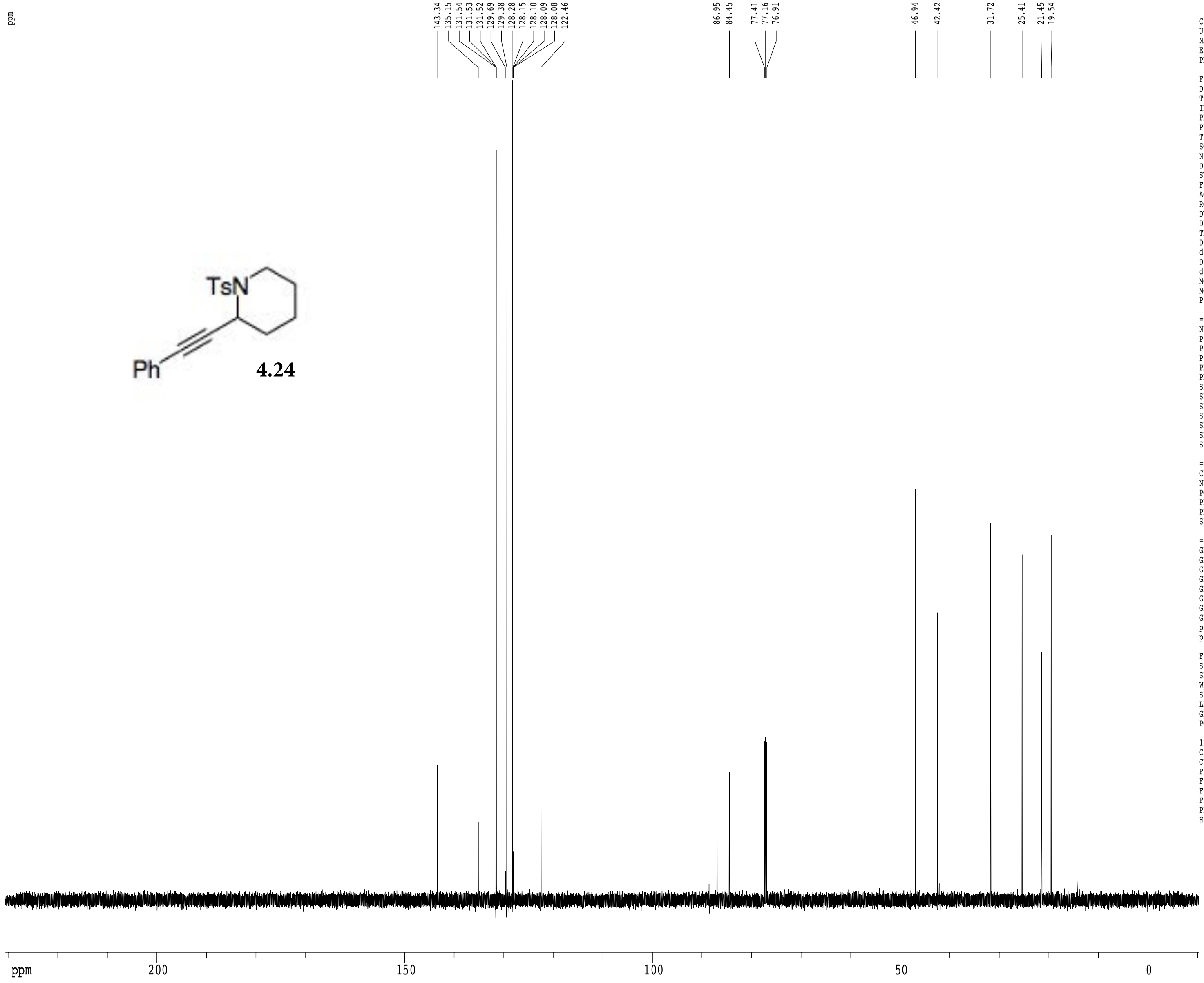
4.62

```
Current Data Parameters
USER           khewitt1
NAME       KAH-III-187-2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200718
Time              12.11
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                143.7
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

1H spectrum


ppm
7.7286
7.7120
7.6961
7.6795
7.2849
7.2678
7.2591
7.2529
7.2479
7.2411
7.2386
7.2225
7.2105
7.2076
7.1942
7.1788
6.9813
6.9676
6.9646
5.0552
5.0491
3.7653
3.7418
3.2274
3.2132
2.9022
2.8967
2.8783
2.8735
2.8550
2.8502
2.4083
2.2643
1.9321
1.9232
1.9142
1.9061
1.8974
1.8832
1.8751
1.8547
1.7593
1.7342
1.7114
1.7039
1.6970
1.6763
1.6622
1.6536
1.6429
1.6344
1.6258
1.2556
1.1334
1.1191
1.1048
-0.0005
TsN
Ph
4.24
Current Data Parameters
USER khewitt1
NAME KAH-III-209-Z
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201119
Time 17.32
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200319 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Integral
2.0000
5.2852
2.0317
1.0329
1.0850
1.0552
3.0244
2.0986
4.4542
ppm
8
7
6
5
4
3
2
1
0

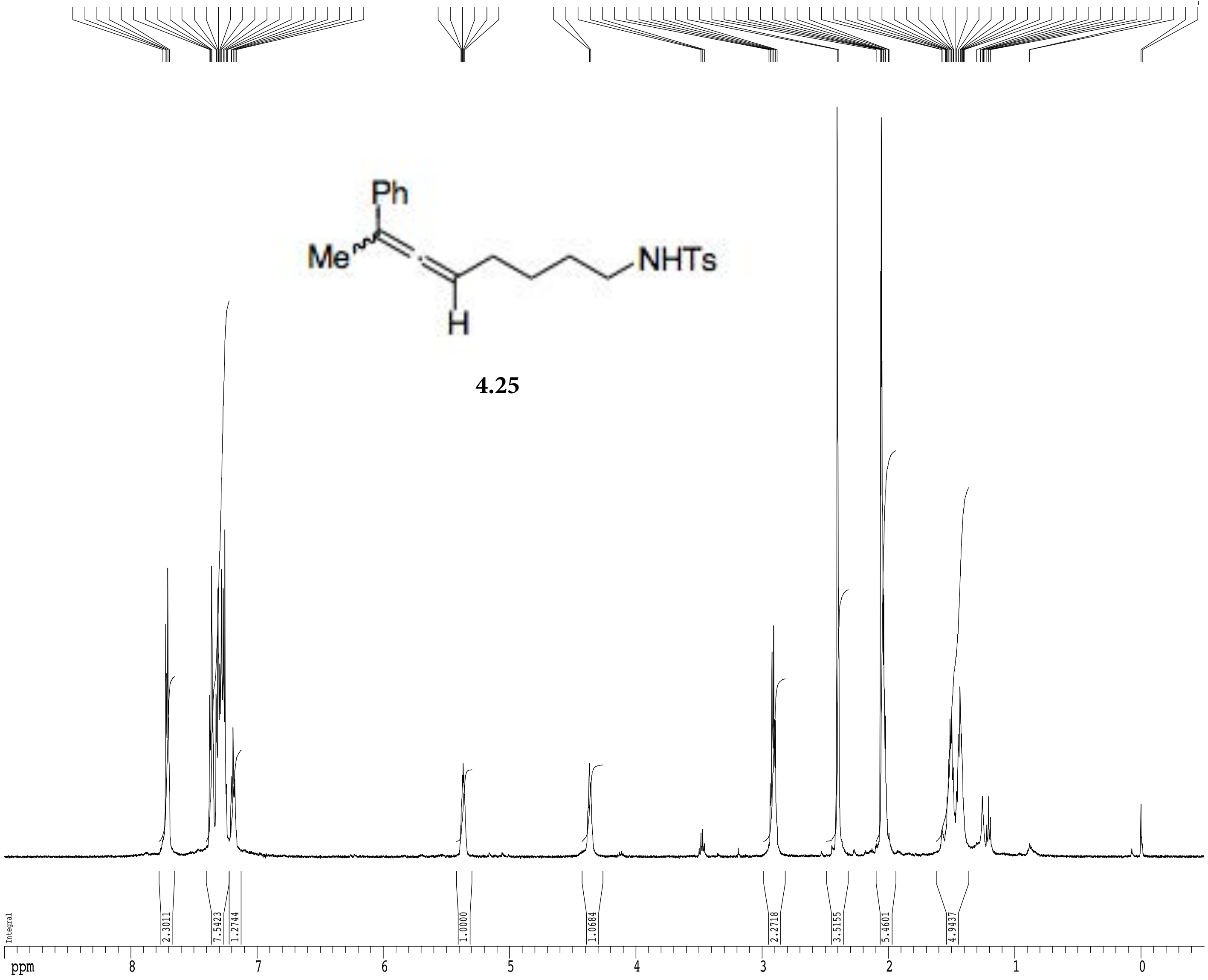
Z-restored spin-echo 13C spectrum with 1H decoupling



4.24

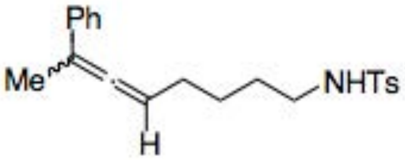
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-209-Z
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20201119
Time               17.33
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                    48
DS                    16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG             18390.4
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1               18.85 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               1.55 dB
SP4               1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             22.00 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI                 65536
SF         125.7804122 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            230.637 ppm
F1            29009.68 Hz
F2P            -10.287 ppm
F2            -1293.96 Hz
PPMCM         10.56688 ppm/cm
HZCM        1329.10693 Hz/cm
```

1H spectrum



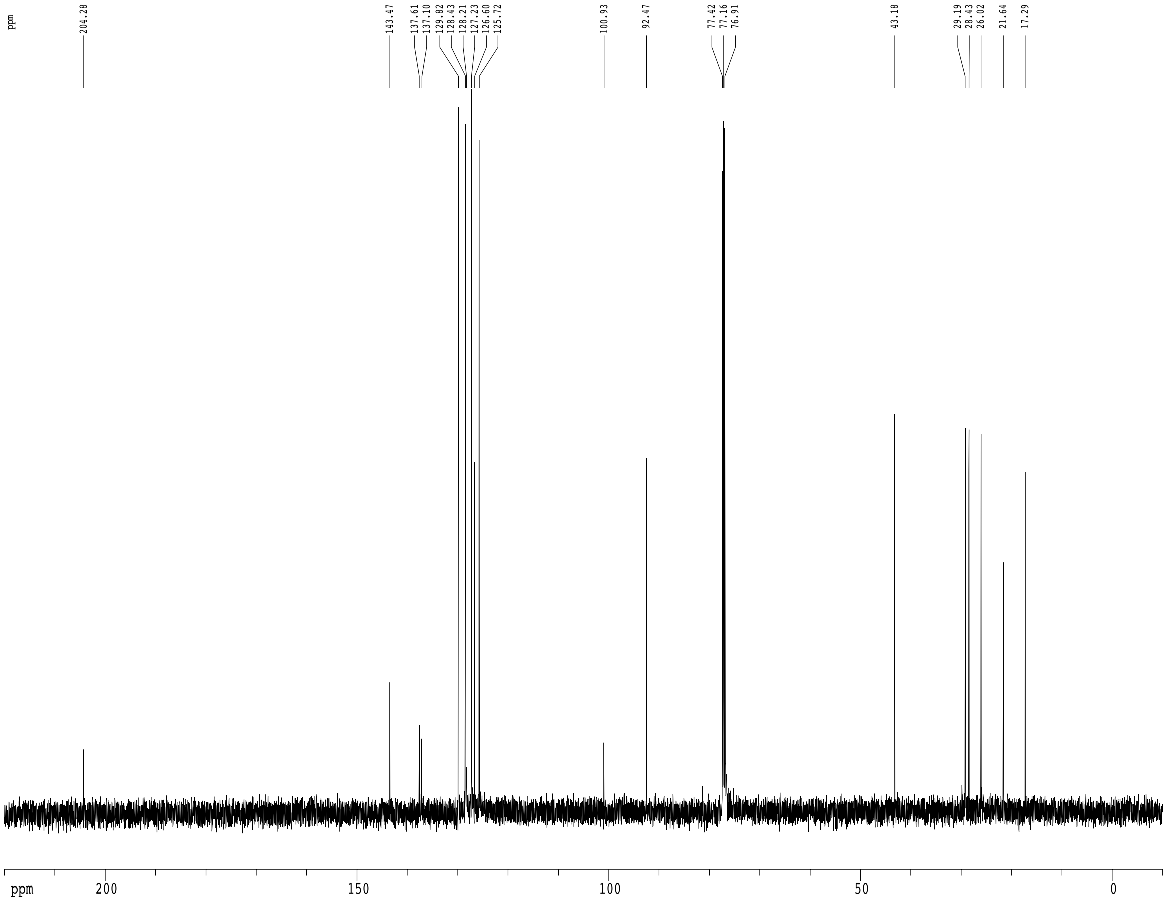
4.25

```
Current Data Parameters
USER            khewitt1
NAME          TATiv187f2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201116
Time               10.32
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                 812.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500352 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```



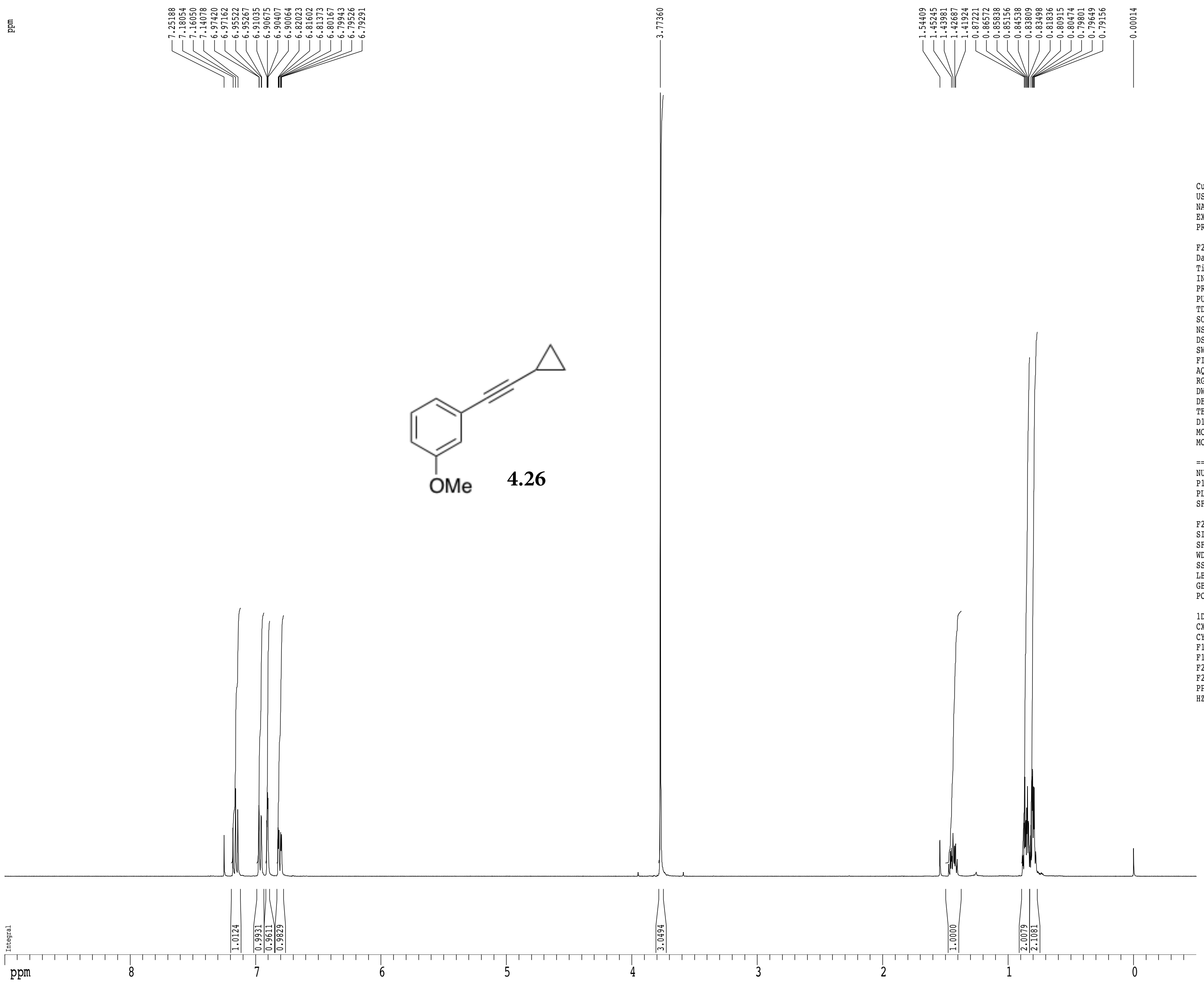
4.25

13C spectrum with 1H decoupling



```
Current Data Parameters
USER           khewitt1
NAME         TATiv187f2
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20201116
Time              10.34
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG         zgdc30
TD                65536
SOLVENT           CDCl3
NS                  616
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                 4096
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.20 usec
PL1               -6.00 dB
SFO1        125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.30 dB
SFO2        498.7524937 MHz

F2 - Processing parameters
SI                65536
SF          125.4107762 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P             220.000 ppm
F1             27590.37 Hz
F2P             -10.000 ppm
F2             -1254.11 Hz
PPMCM          11.50000 ppm/cm
HZCM         1442.22388 Hz/cm
```

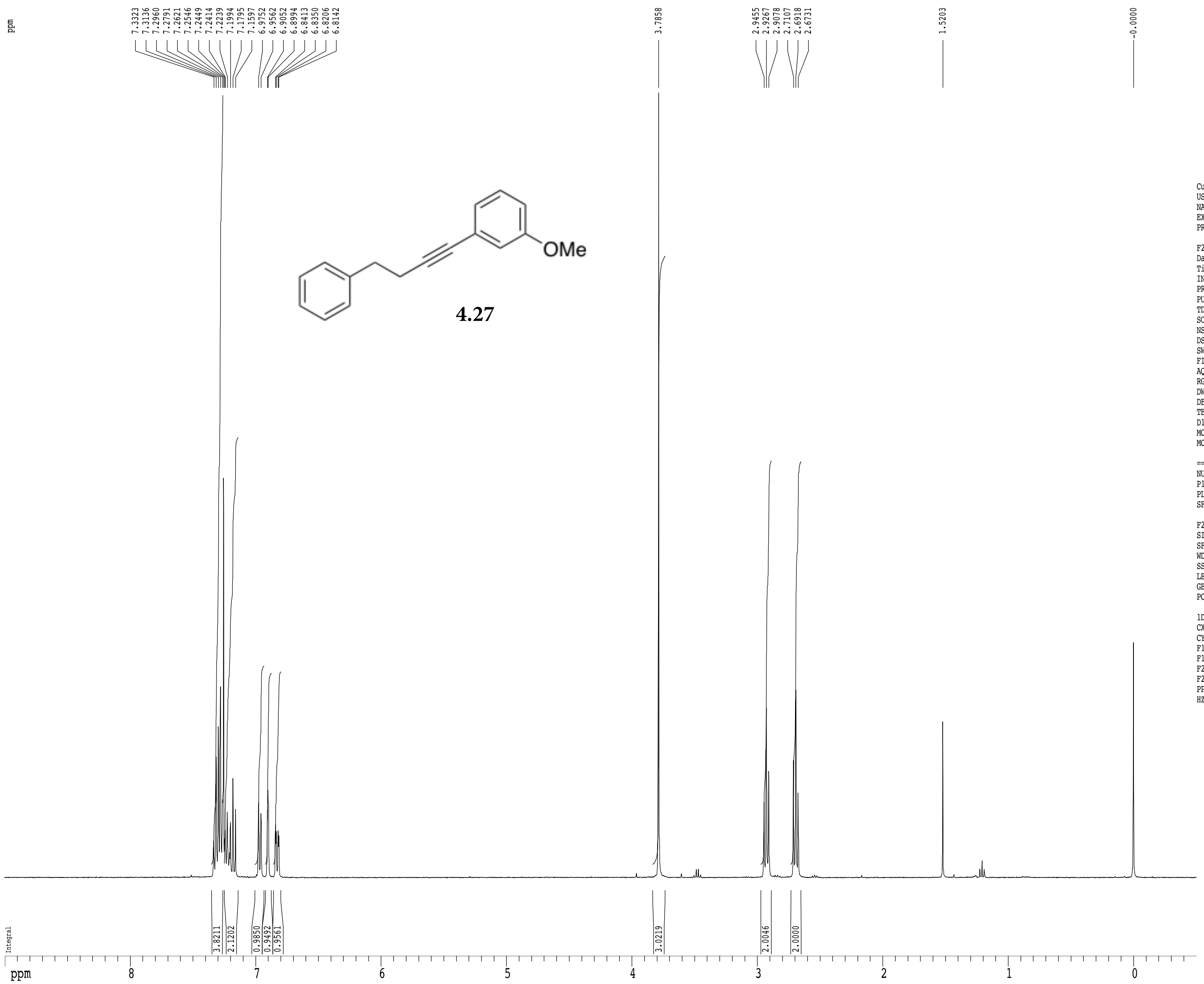
1H spectrum



4.26

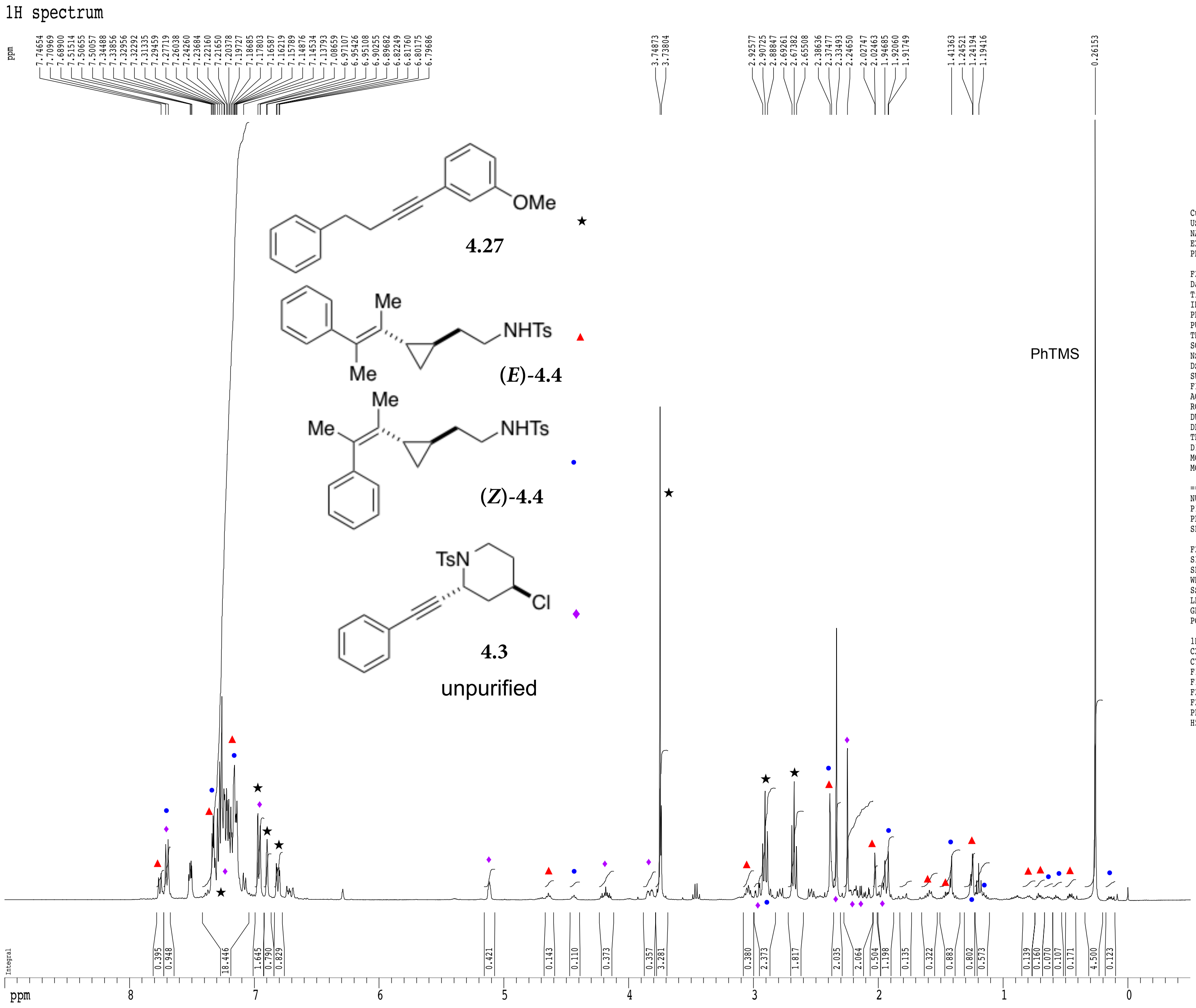
```
Current Data Parameters
USER              tthane
NAME       TATiv105check
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200824
Time                8.58
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                 161.3
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300249 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

1H spectrum



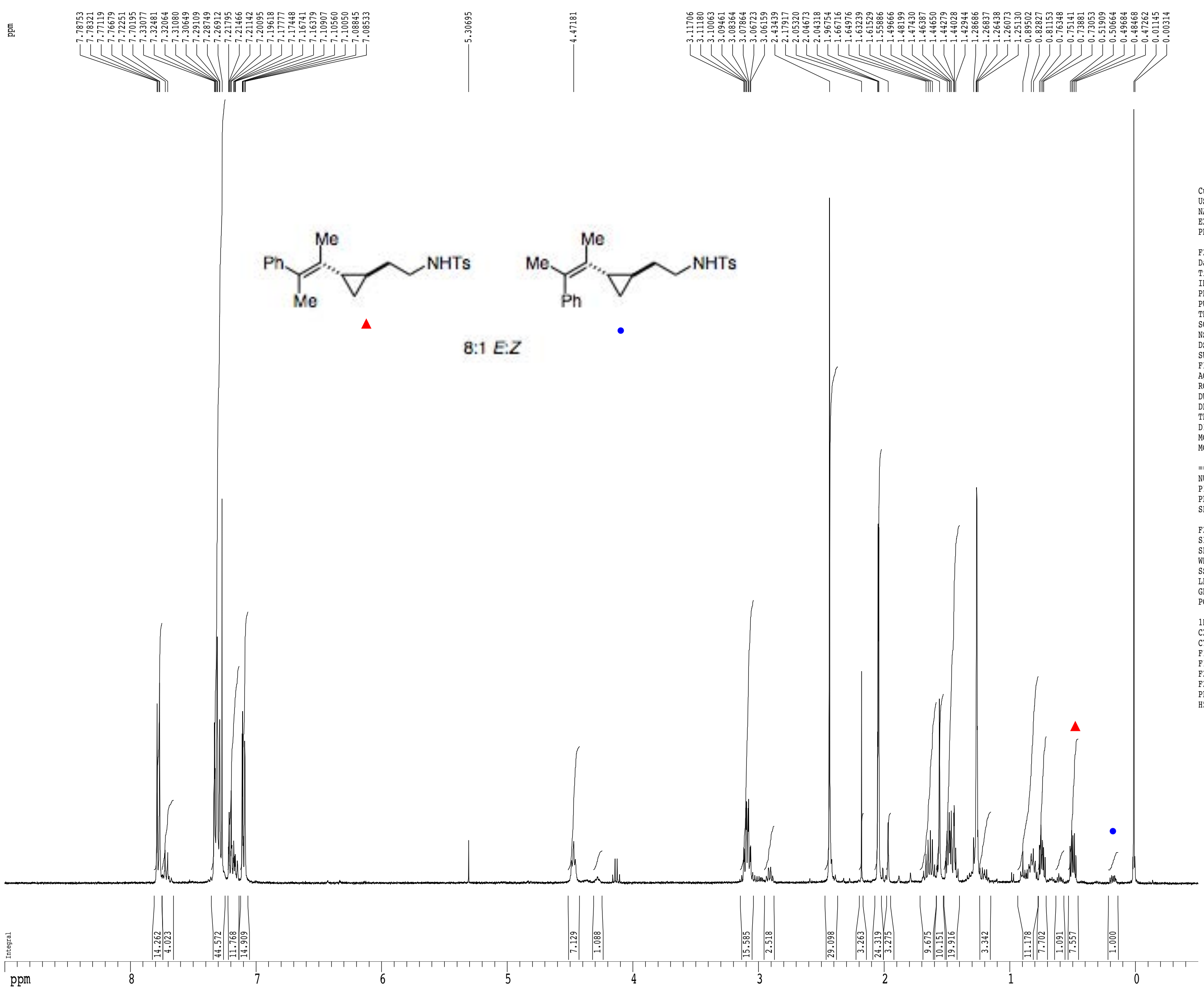
4.27

```
Current Data Parameters
USER          nhirbawi
NAME     NH-1-62-column
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20201003
Time              14.26
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                812.7
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300234 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

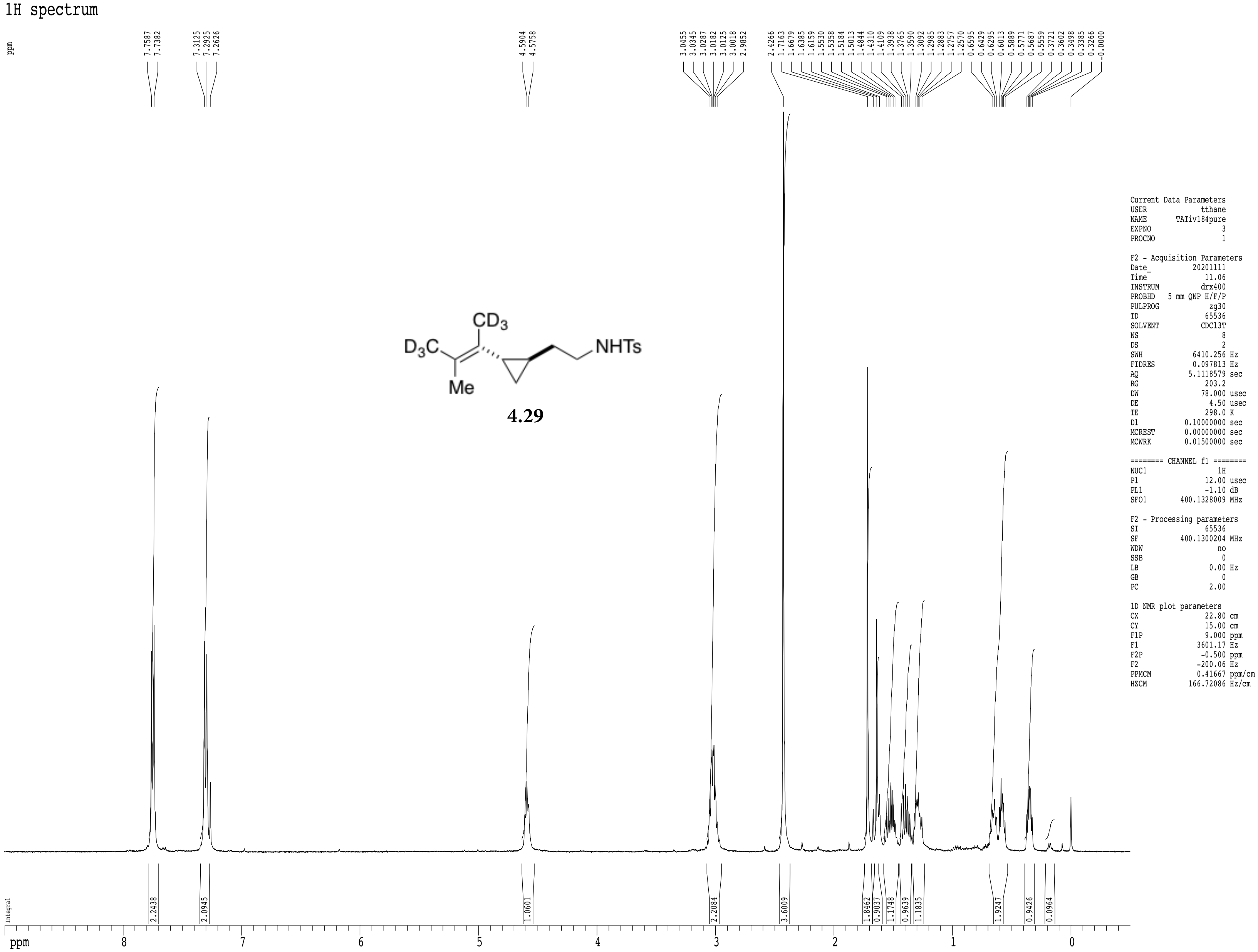


```
Current Data Parameters
USER          nhirbawi
NAME       NH-1-75-crude
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20201028
Time             12.49
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               65536
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG                50.8
DW              78.000 usec
DE                4.50 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300463 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -0.500 ppm
F2             -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```

1H spectrum

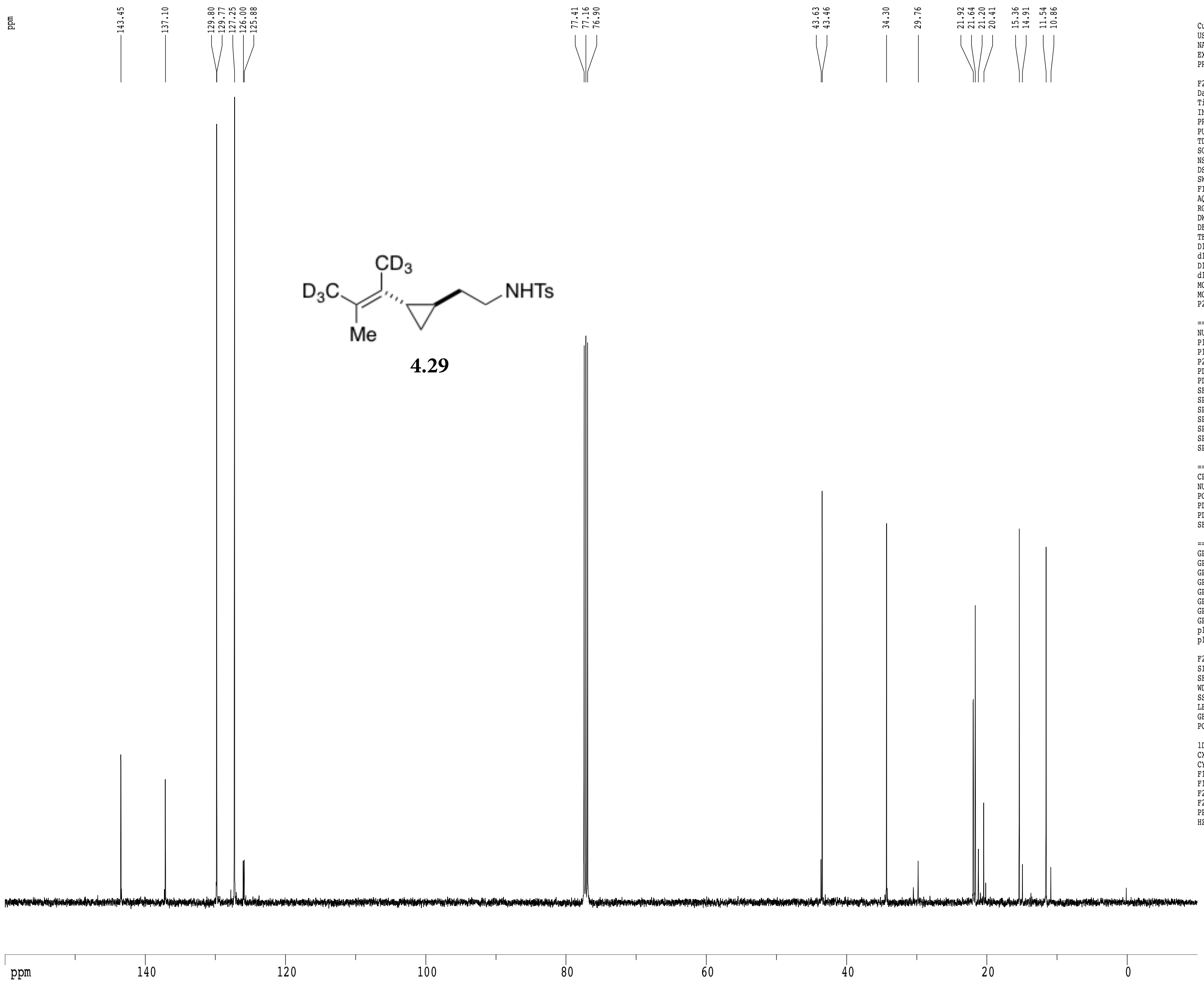


```
Current Data Parameters
USER           khewitt1
NAME        KAH-II-252-1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20191107
Time              17.54
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                406.4
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```


1H spectrum
ppm
7.7587
7.7382
7.3125
7.2925
7.2626
4.5904
4.5758
3.0455
3.0345
3.0287
3.0182
3.0125
3.0018
2.9852
2.4266
1.7163
1.6679
1.6385
1.6159
1.5530
1.5358
1.5184
1.5013
1.4844
1.4310
1.4109
1.3938
1.3765
1.3590
1.3092
1.2985
1.2883
1.2757
1.2570
0.6595
0.6429
0.6295
0.6013
0.5889
0.5771
0.5687
0.5559
0.3721
0.3602
0.3498
0.3385
0.3266
-0.0000
CD3
D3C
Me
NHTs
Current Data Parameters
USER tthane
NAME TATiv184pure
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201111
Time 11.06
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3T
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 203.2
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300204 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Integral
2.2438
2.0945
1.0601
2.2084
3.6009
1.8462
0.9037
1.1748
0.9639
1.1835
1.9247
0.9426
0.0964
ppm
8
7
6
5
4
3
2
1
0

4.29

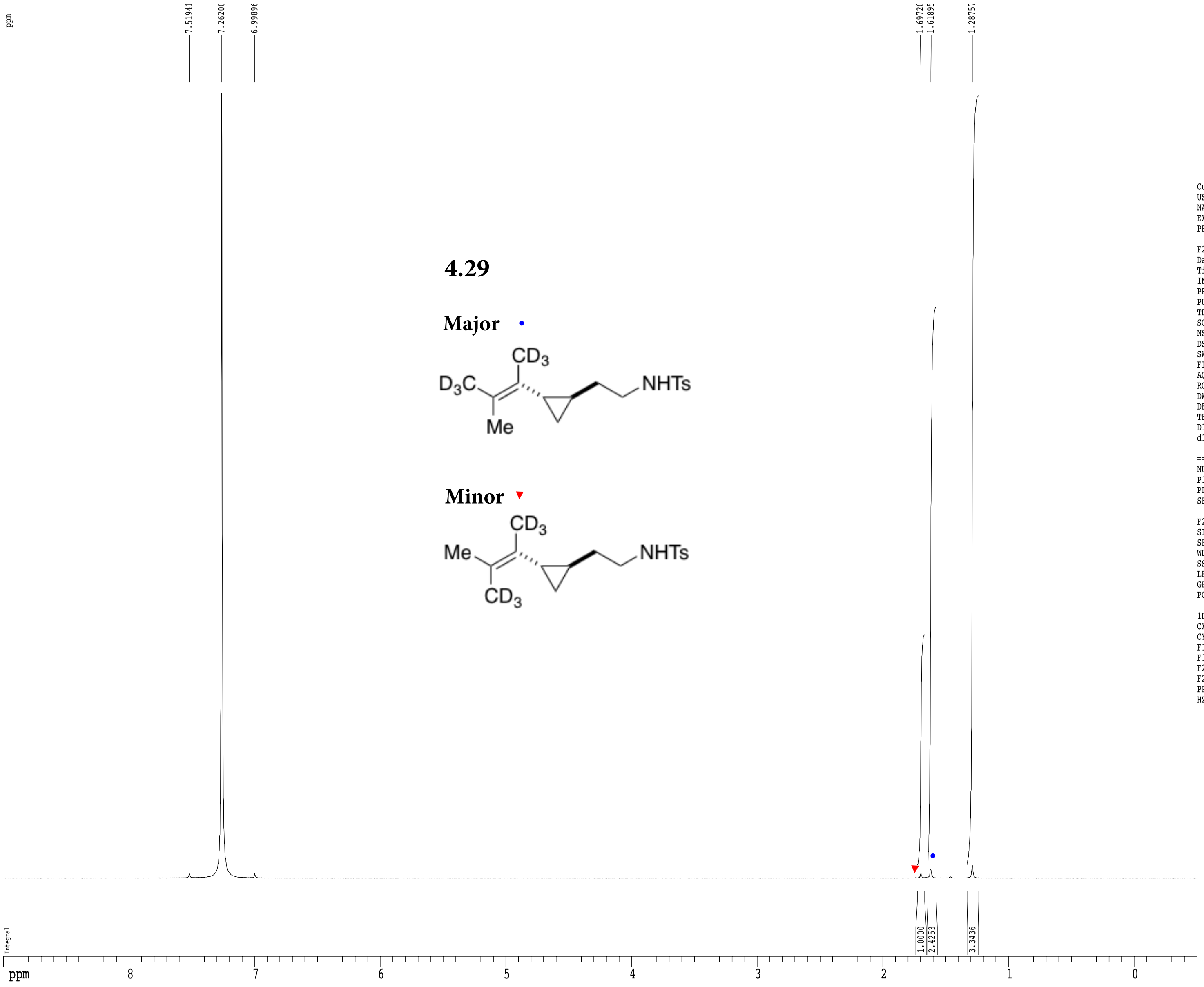
Z-restored spin-echo 13C spectrum with 1H decoupling



4.29

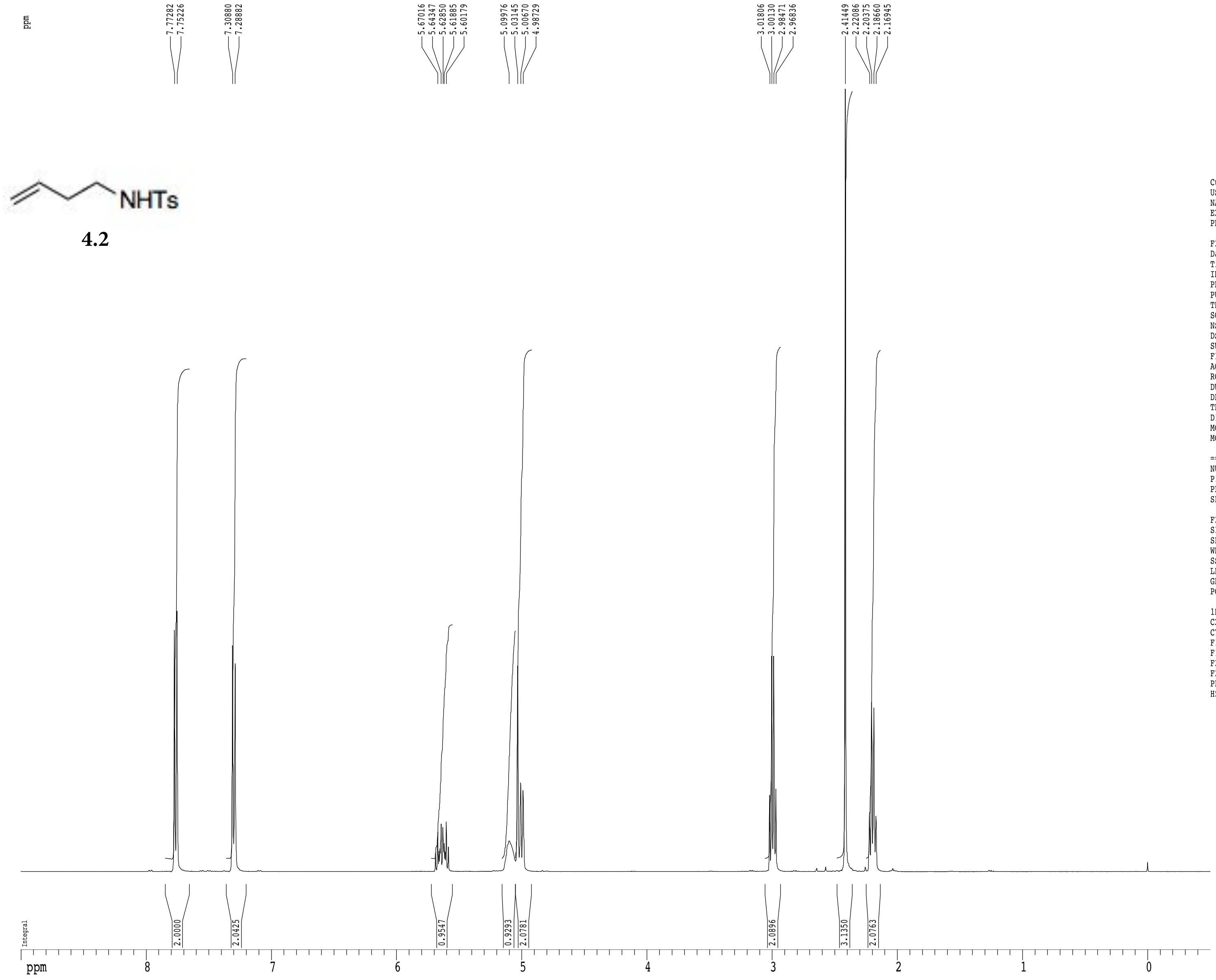
```
Current Data Parameters
USER              tthane
NAME          TATiv184c
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20201111
Time              16.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  598
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804090 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             160.000 ppm
F1             20124.87 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           7.45614 ppm/cm
HZCM          937.83643 Hz/cm
```

2H spectrum (measure via lock channel without changing any cables)



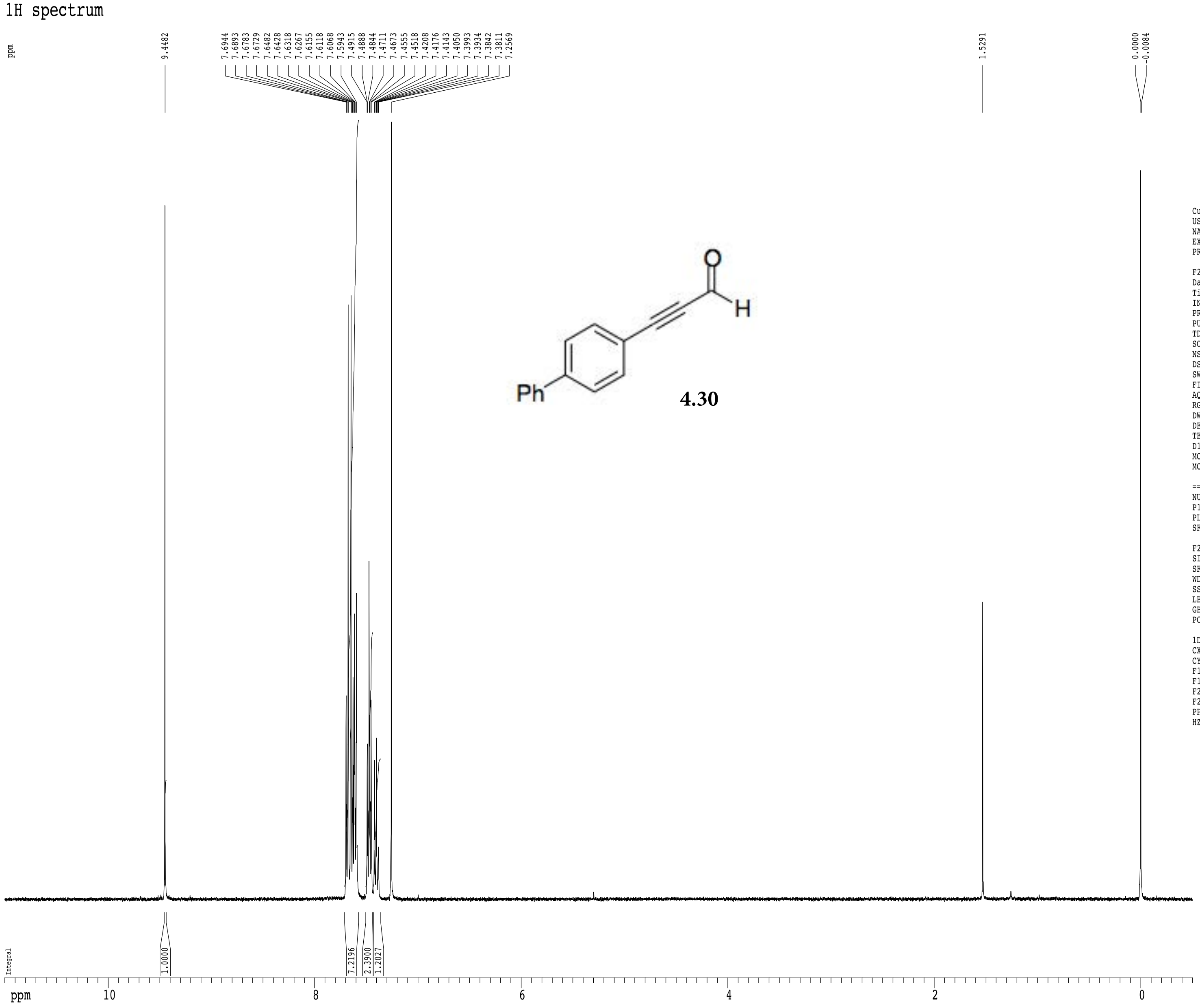
```
Current Data Parameters
USER              tthane
NAME         TATiv184pure
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201111
Time               11.12
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG      zg30h2lock
TD                 10022
SOLVENT            CDCl3
NS                    99
DS                     2
SWH              982.704 Hz
FIDRES          0.098055 Hz
AQ             5.0992436 sec
RG                    64
DW               508.800 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                  2H
P1                 74.00 usec
PL1                -6.00 dB
SFO1          61.4227670 MHz

F2 - Processing parameters
SI                 65536
SF            61.4223340 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1                552.80 Hz
F2P               -0.500 ppm
F2                -30.71 Hz
PPMCM            0.41667 ppm/cm
HZCM            25.59264 Hz/cm
```

1H spectrum



4.2

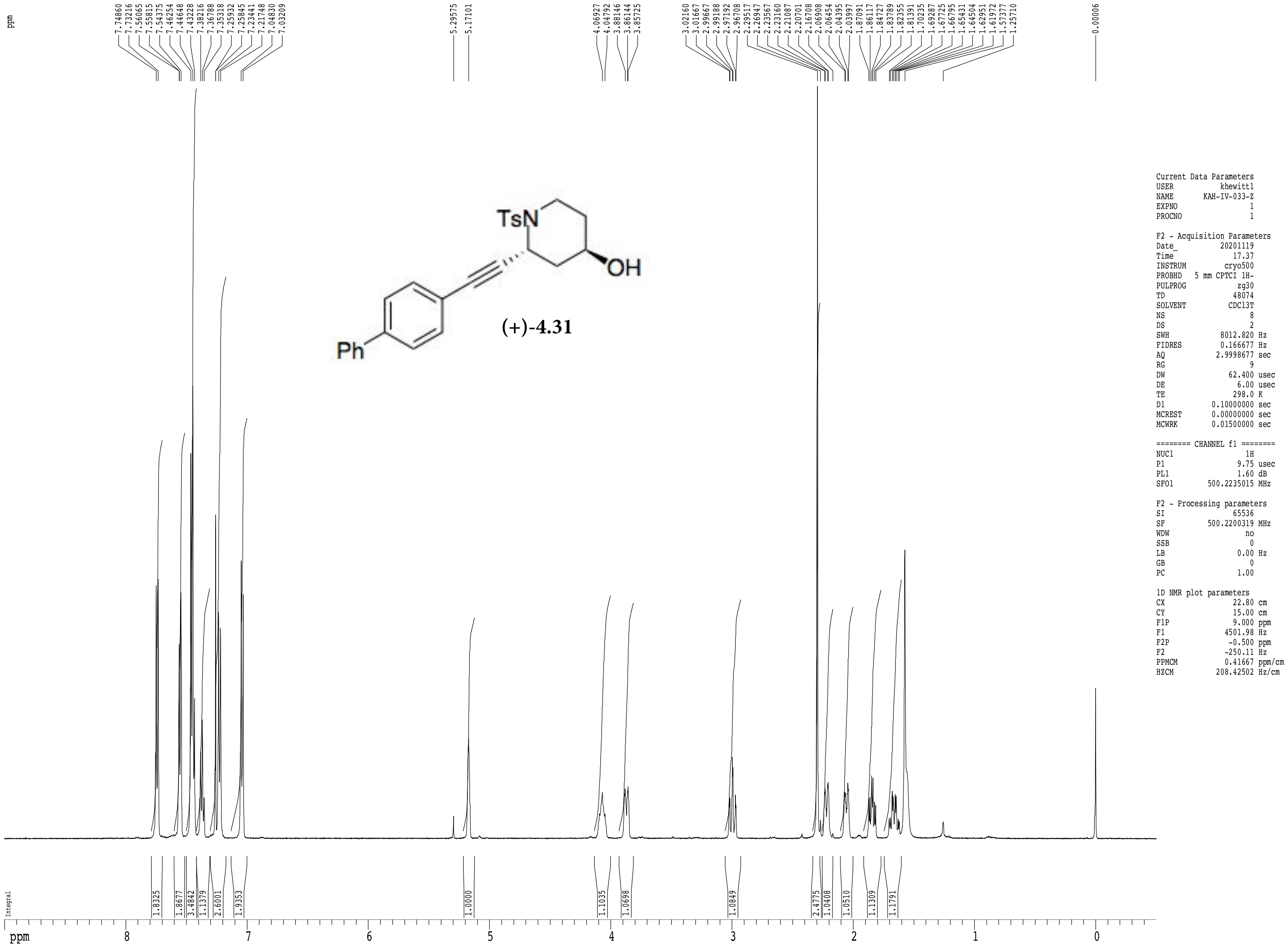
```
Current Data Parameters
USER            khewitt1
NAME           KAH-I-102Z
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20180922
Time                12.03
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG              zg30
TD                  38460
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ              2.9999299 sec
RG                     32
DW                 78.000 usec
DE                   4.50 usec
TE                  297.9 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -1.10 dB
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300086 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                3601.17 Hz
F2P                -0.500 ppm
F2                -200.06 Hz
PPMCM             0.41667 ppm/cm
HZCM            166.72084 Hz/cm
```



4.30

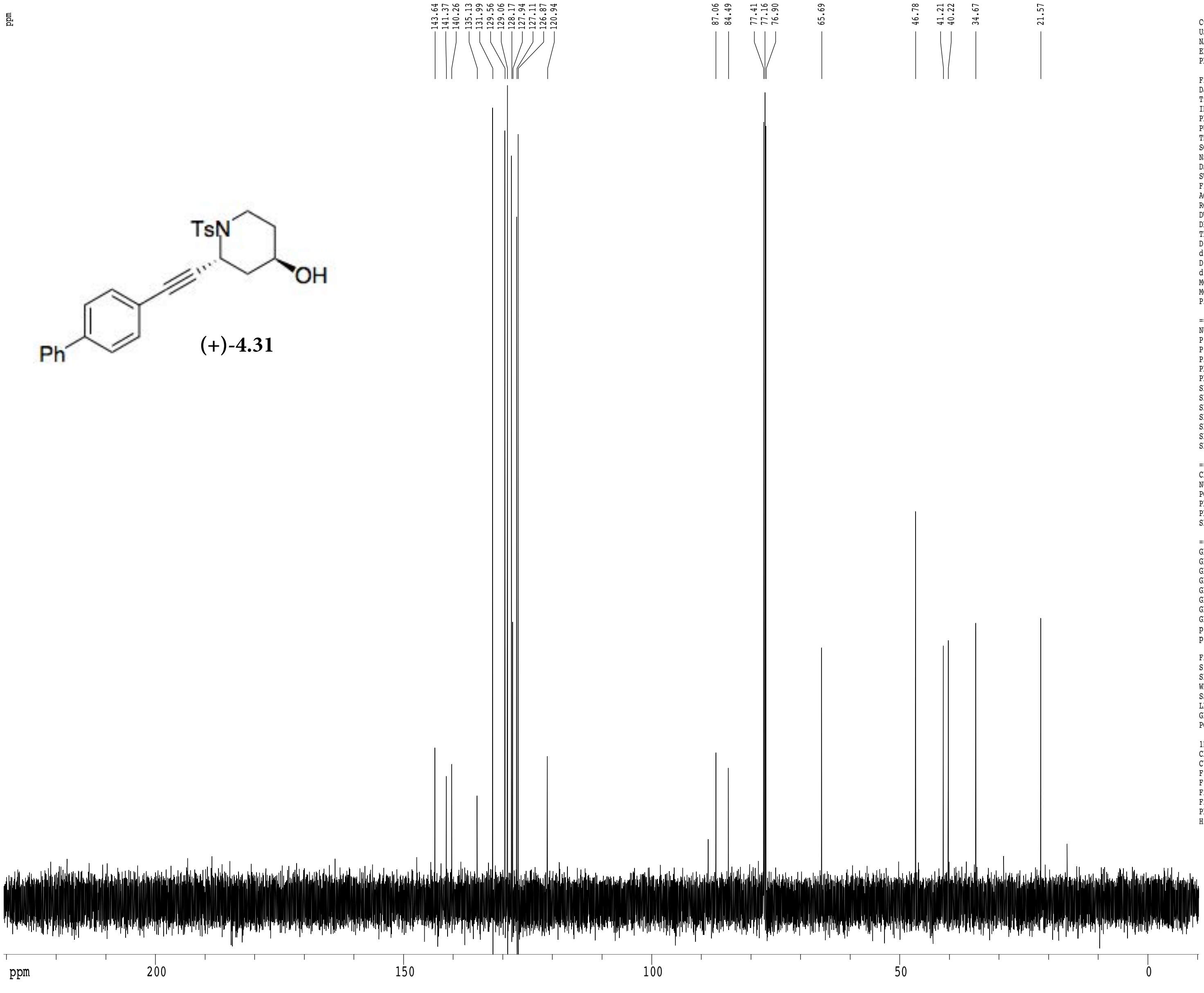
```
Current Data Parameters
USER            khewitt1
NAME         ELL-IV-112
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190218
Time              10.51
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                 1024
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300223 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

1H spectrum



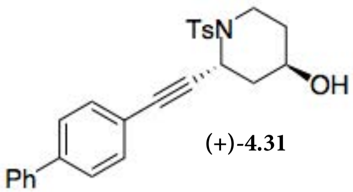
(+)-4.31

Z-restored spin-echo 13C spectrum with 1H decoupling

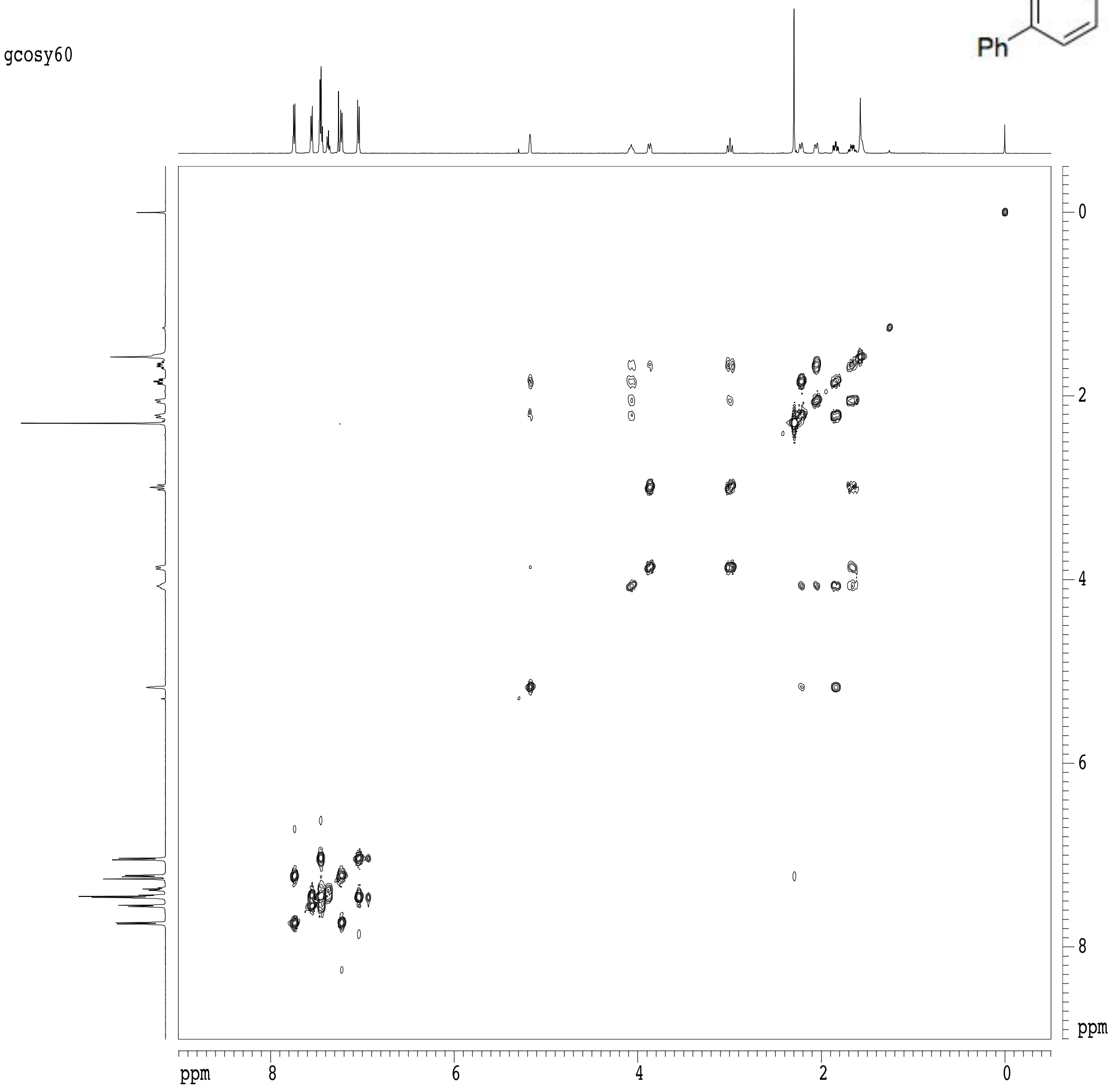


(+)-4.31

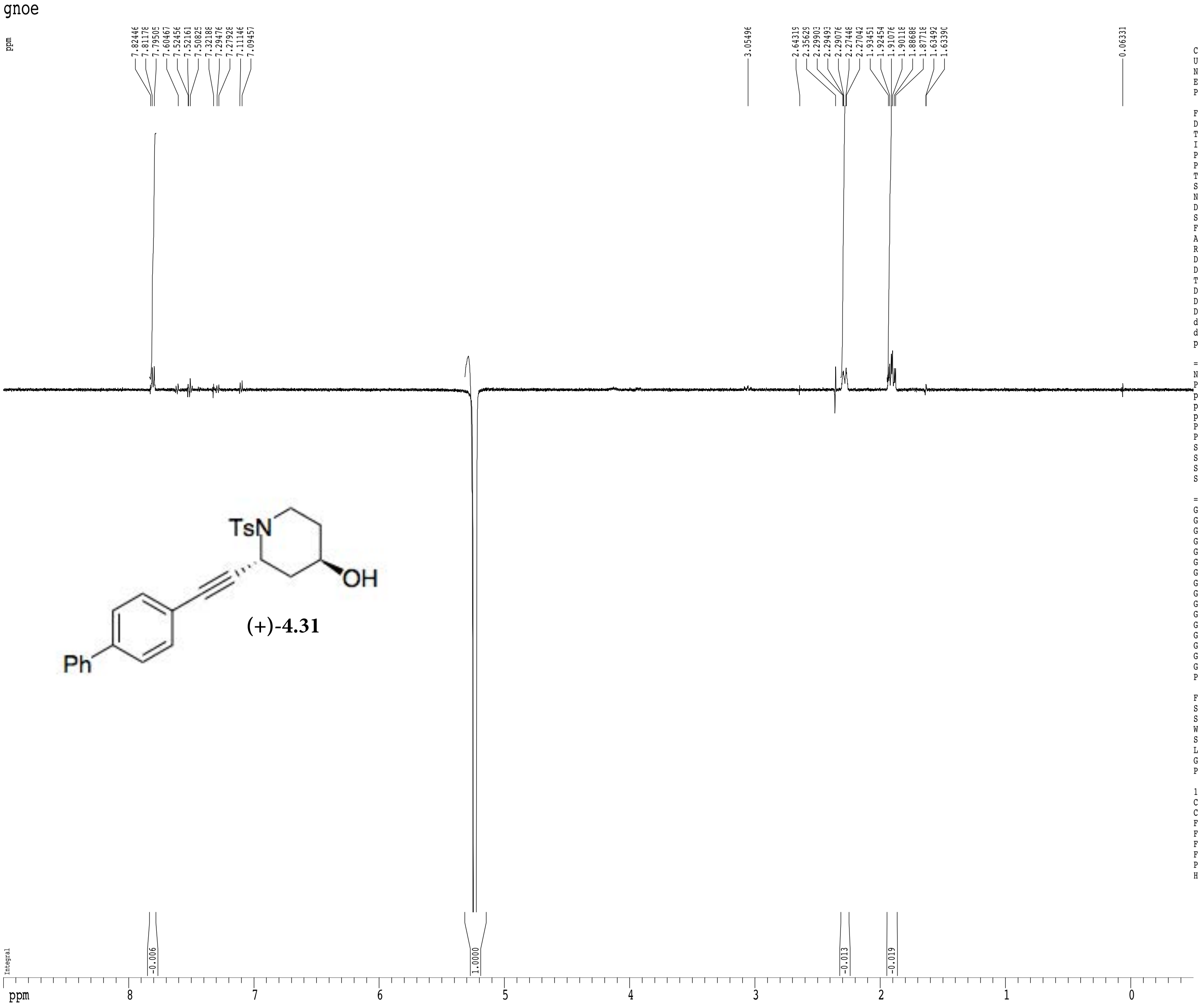
```
Current Data Parameters
USER              khewitt1
NAME          KAH-IV-033-Z
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20201119
Time                 17.53
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     136
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813940 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   37.70 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   18.85 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   1.55 dB
SP4                   1.55 dB
SPNAM2         Crp60comp.4
SPNAM4      Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 22.00 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804076 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                230.637 ppm
F1                29009.68 Hz
F2P                -10.287 ppm
F2                -1293.96 Hz
PPMCM             10.56688 ppm/cm
HZCM            1329.10693 Hz/cm
```



(+)-4.31

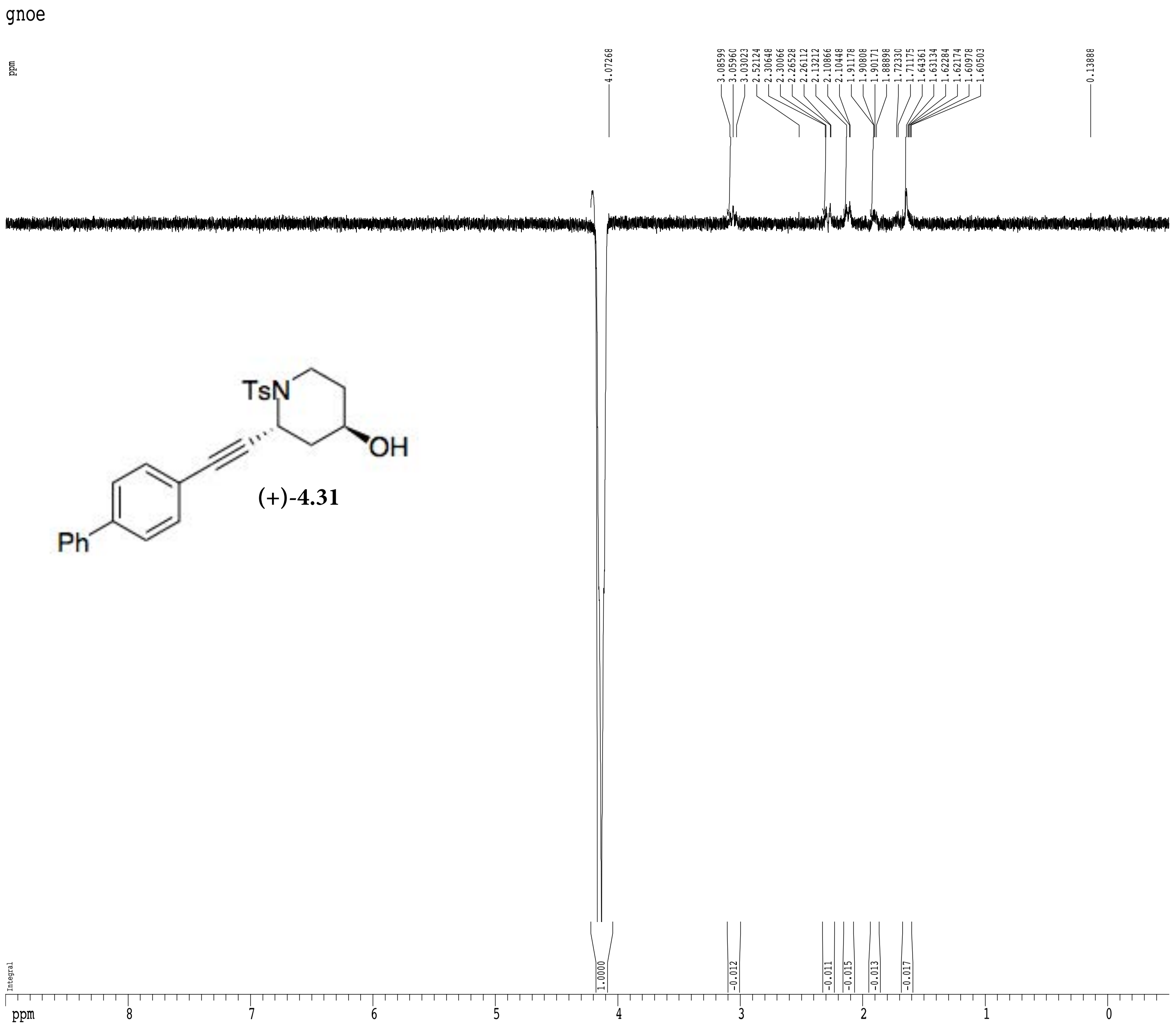


```
        Current Data Parameters
USER              khewitt1
NAME           KAH-IV-033-Z
EXPNO                    6
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20201120
Time                 18.01
INSTRUM              gn500
PROBHD   5 mm broadband
PULPROG      cosygp60.prd
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                      16
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                  5160.6
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
d0              0.00000300 sec
D1              1.00000000 sec
d13             0.00000300 sec
D16             0.00020000 sec
IN0             0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -6.00 dB
SFO1           498.7534913 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 17.00 %
GPZ2                 17.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      1
TD                     256
SFO1              498.7535 MHz
FIDRES           31.300079 Hz
SW                  16.066 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             498.7500325 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             498.7500325 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

        2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                9.006 ppm
F2LO               4491.68 Hz
F2PHI               -0.502 ppm
F2HI               -250.28 Hz
F1PLO                9.006 ppm
F1LO               4491.68 Hz
F1PHI               -0.502 ppm
F1HI               -250.28 Hz
F2PPMCM            0.63385 ppm/cm
F2HZCM           316.13080 Hz/cm
F1PPMCM            0.63385 ppm/cm
F1HZCM           316.13080 Hz/cm
```



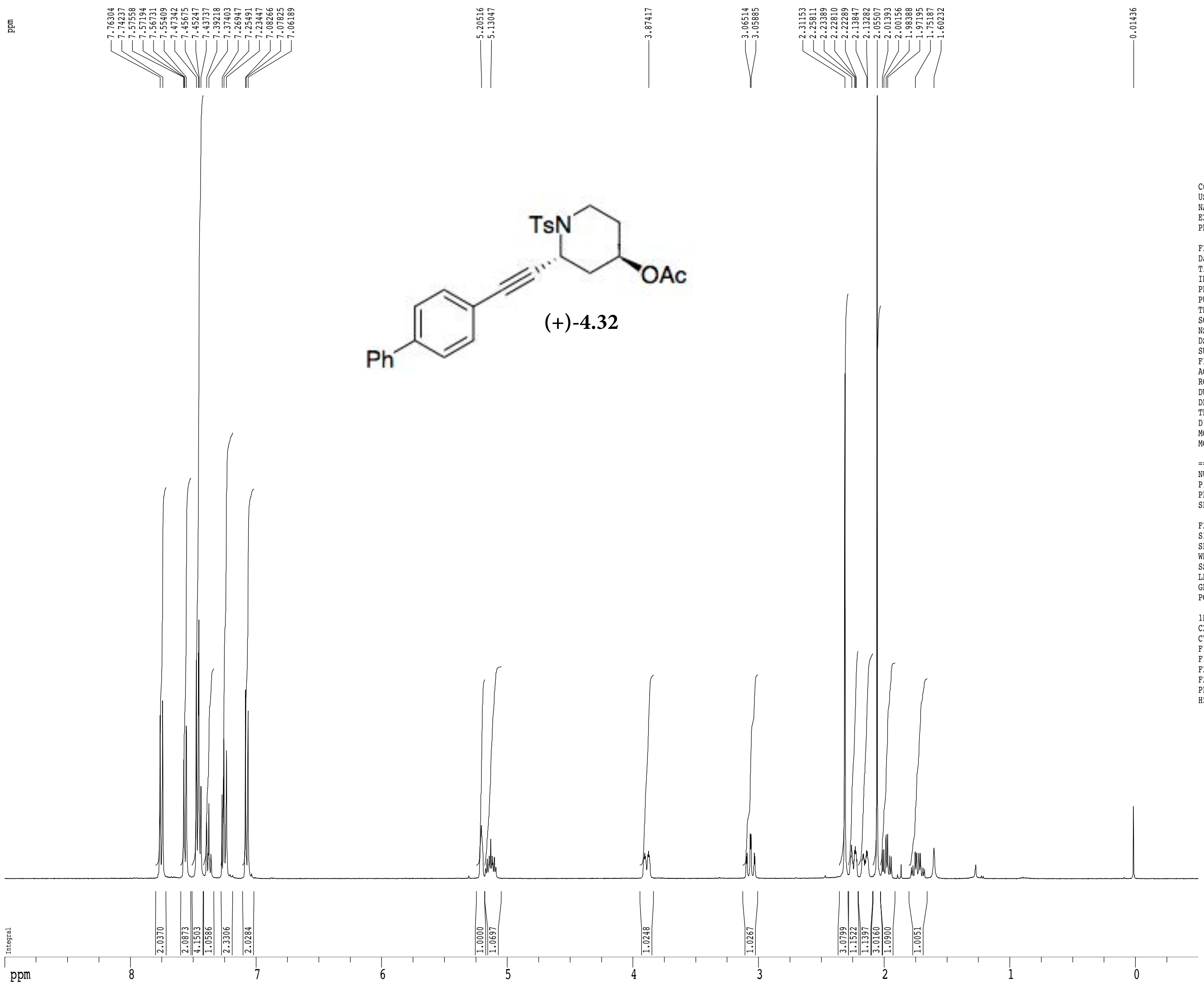
(+)-4.31

```
Current Data Parameters
USER            khewitt1
NAME          KAH-IV-033-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201119
Time               17.52
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   128
DW                62.400 usec
DE                  6.00 usec
TE                 298.1 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33375451 sec
d22           0.16399699 sec
p2                 19.50 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
p3                 29.25 usec
p4                 39.00 usec
p5                 26.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2226183 MHz
SP9                60.00 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPNAM3        SMSQ10.100
GPNAM4        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-033-Z
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20201120
Time              18.20
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG               5160.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33374399 sec
d22          0.16399699 sec
p2                24.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
p3                36.00 usec
p4                48.00 usec
p5                32.00 usec
P29            40000.00 usec
PL1               -6.00 dB
SFO1        498.7520605 MHz
SP9               53.20 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          498.7500000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P               9.000 ppm
F1              4488.75 Hz
F2P              -0.500 ppm
F2              -249.38 Hz
PPMCM           0.47500 ppm/cm
HZCM          236.90625 Hz/cm
```

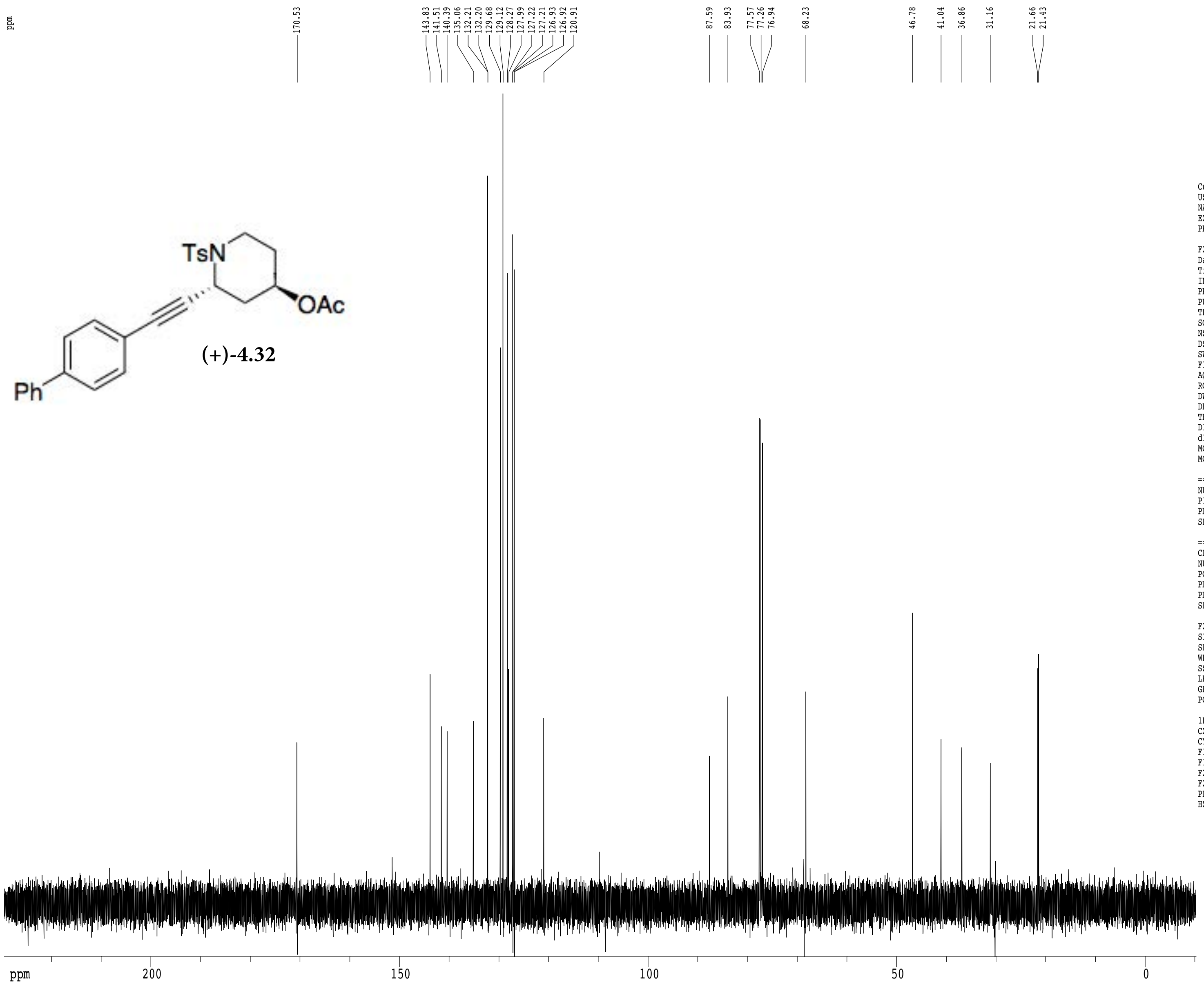
1H spectrum



(+)-**4.32**

```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-035-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20201121
Time              11.51
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                203.2
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

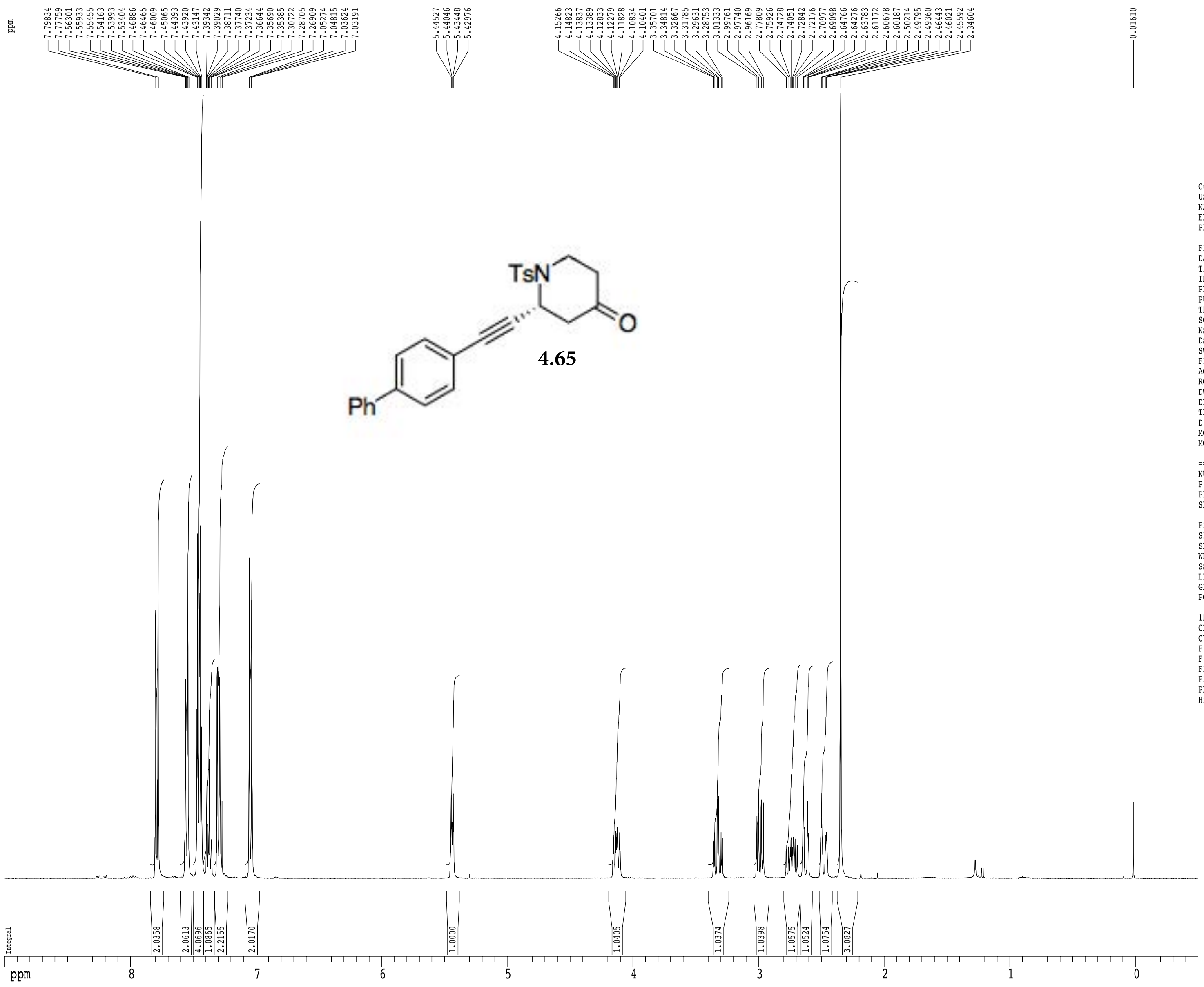
13C spectrum with 1H decoupling



(+)-4.32

```
Current Data Parameters
USER          khewitt1
NAME       KAH-IV-035-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20201121
Time              11.53
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  176
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG               7298.2
DW               20.700 usec
DE                20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.30 usec
PL1               -3.00 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -1.60 dB
PL12              16.50 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          100.6127500 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P             229.496 ppm
F1             23090.21 Hz
F2P             -10.579 ppm
F2             -1064.37 Hz
PPMCM          10.52959 ppm/cm
HZCM         1059.41138 Hz/cm
```

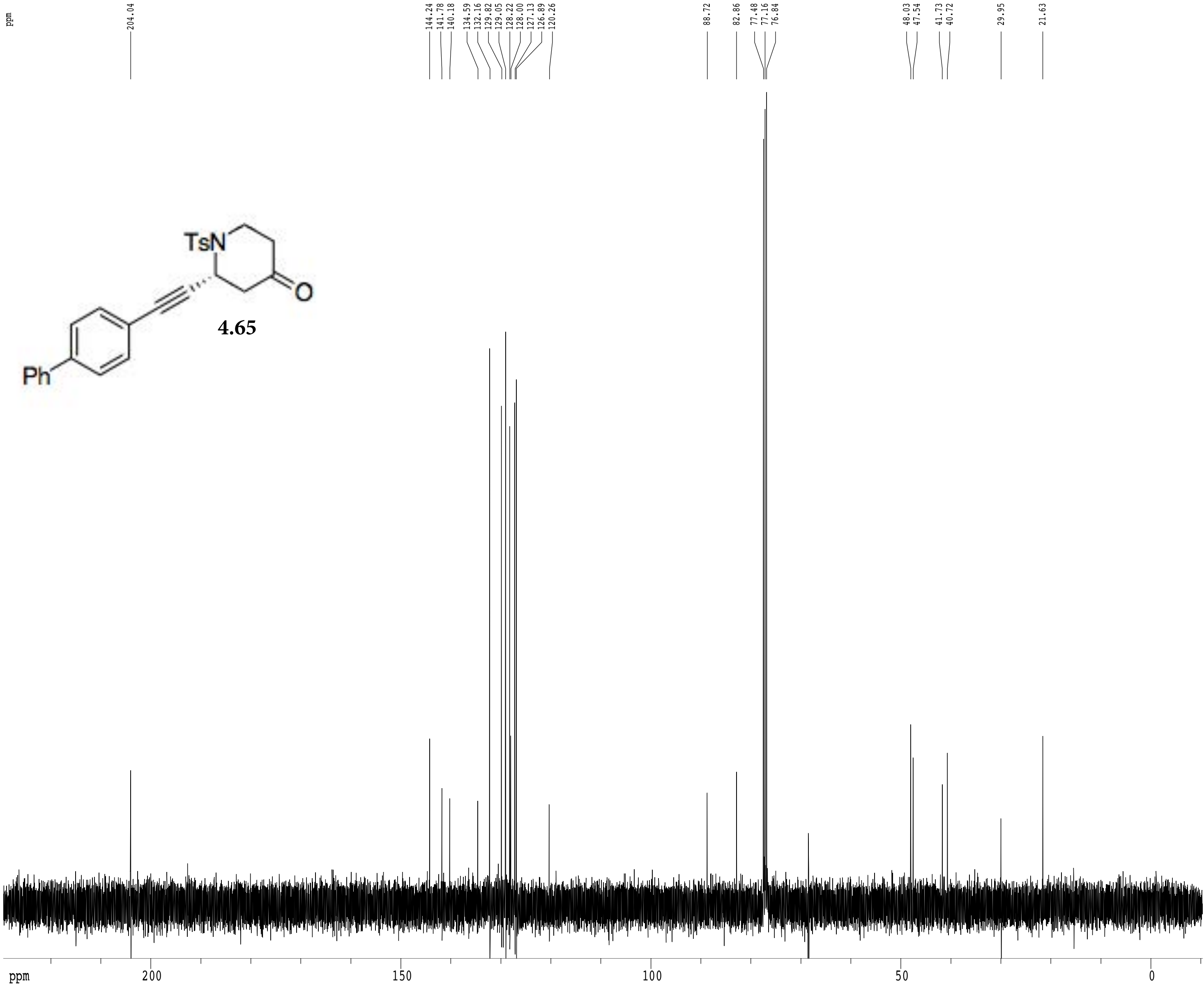
1H spectrum



4.65

```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-048-1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20201123
Time              14.08
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                  128
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

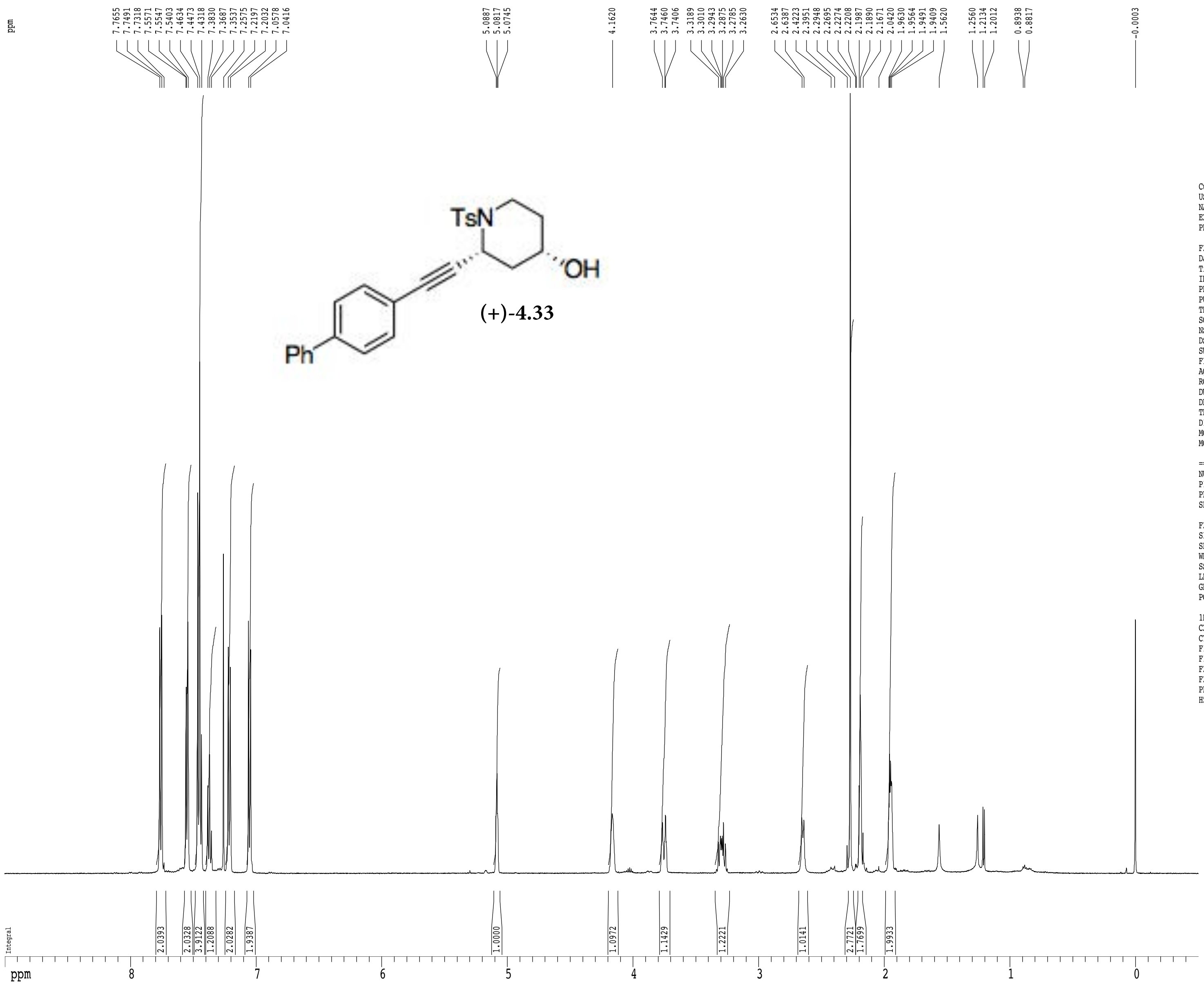
13C spectrum with 1H decoupling



4.65

```
Current Data Parameters
USER            khewitt1
NAME        KAH-IV-040-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201116
Time               10.15
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   408
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                 13004
DW                20.700 usec
DE                 20.39 usec
TE                 297.9 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.82 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.10 dB
PL12               16.80 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127580 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```

1H spectrum



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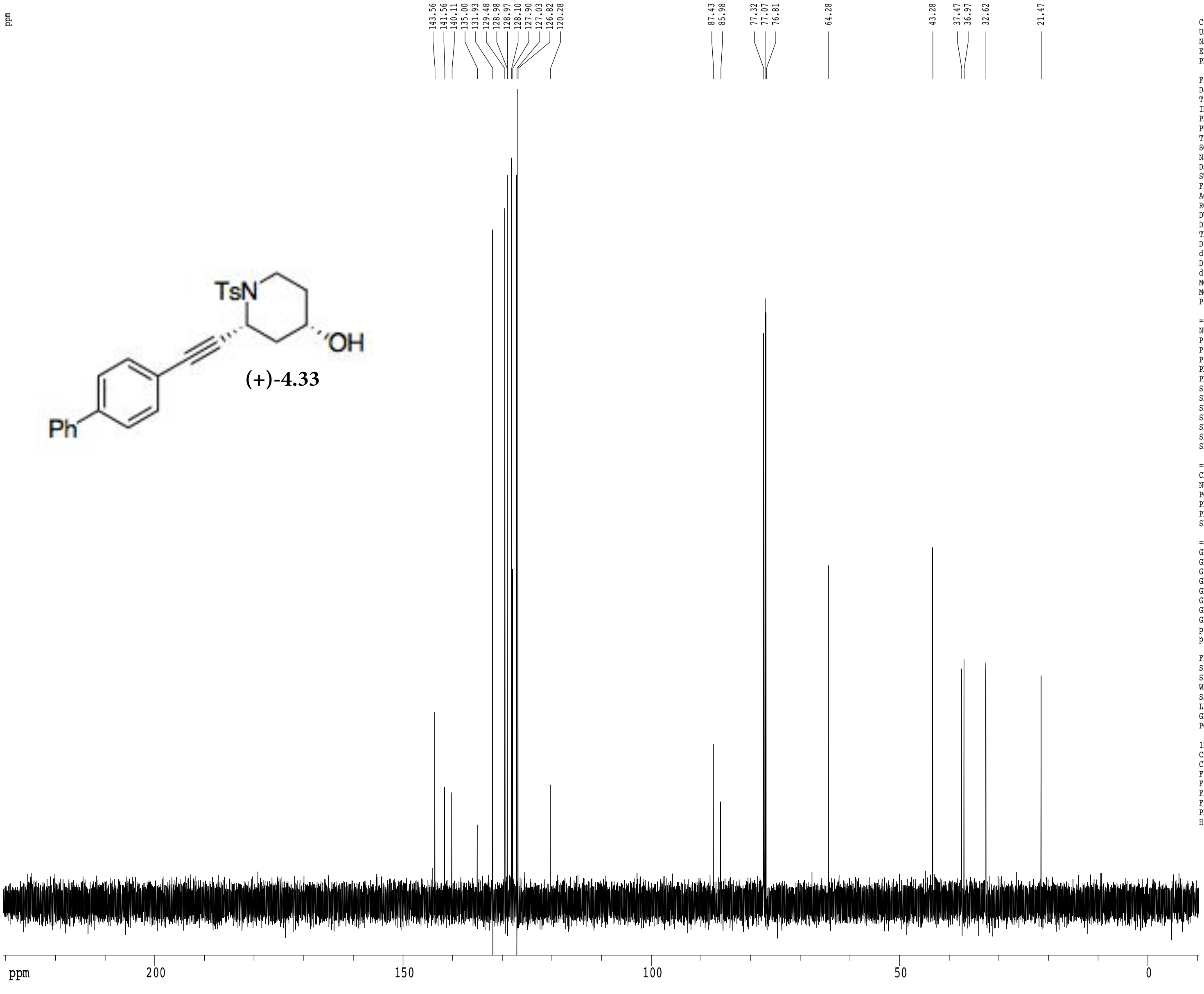
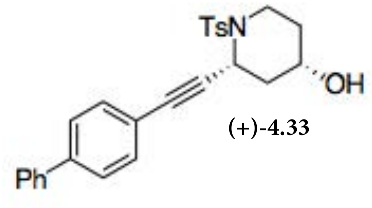
```
Current Data Parameters
USER          khewitt1
NAME       KAH-IV-043-Z
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_         20201127
Time             12.01
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               48074
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH          8012.820 Hz
FIDRES       0.166677 Hz
AQ          2.9998677 sec
RG                 6.3
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1         0.10000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                9.75 usec
PL1               1.60 dB
SFO1     500.2235015 MHz

F2 - Processing parameters
SI               65536
SF       500.2200324 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             4501.98 Hz
F2P             -0.500 ppm
F2             -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling


(+)-4.33

```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-043-Z
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20201127
Time              12.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  144
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```



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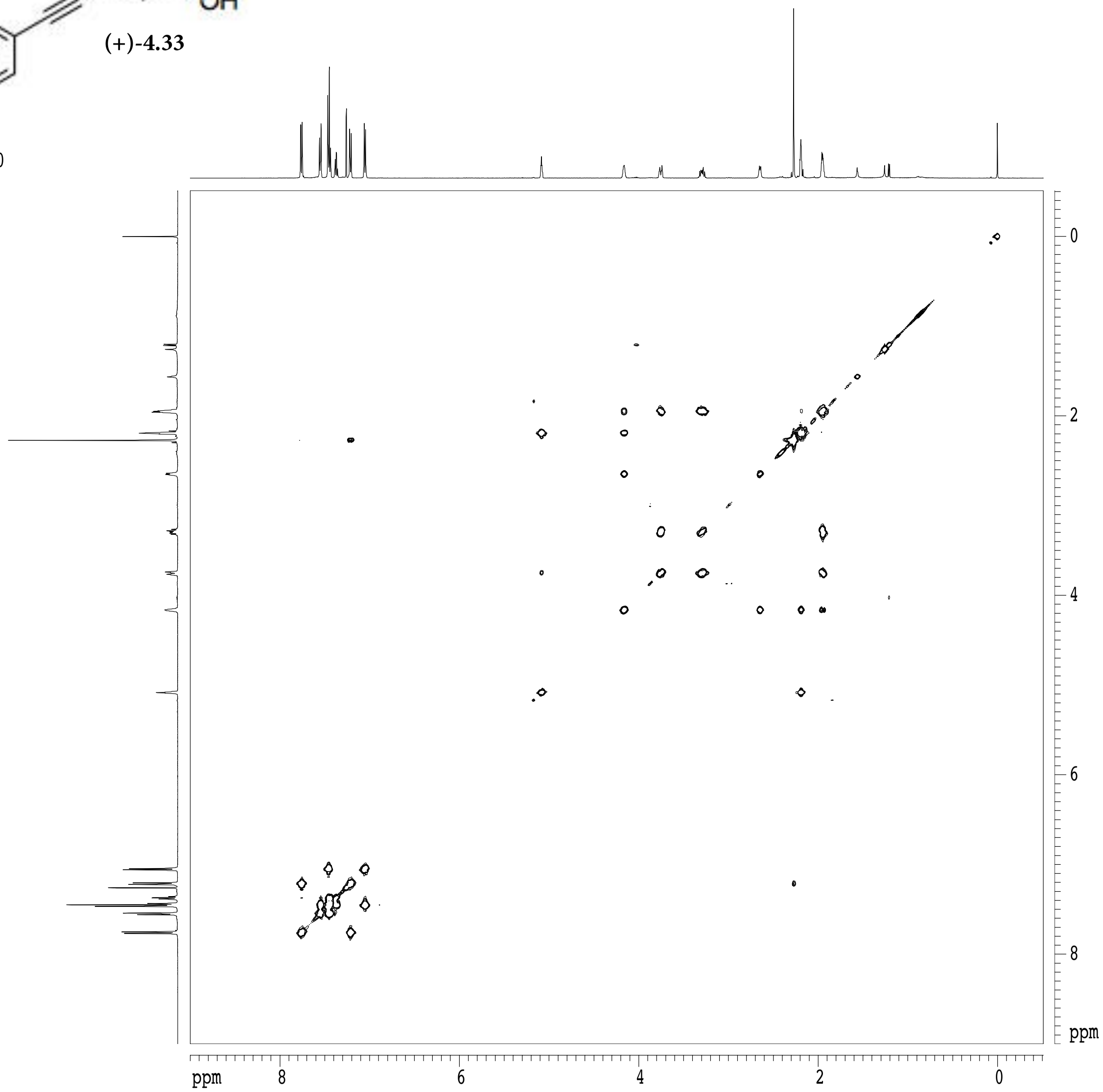
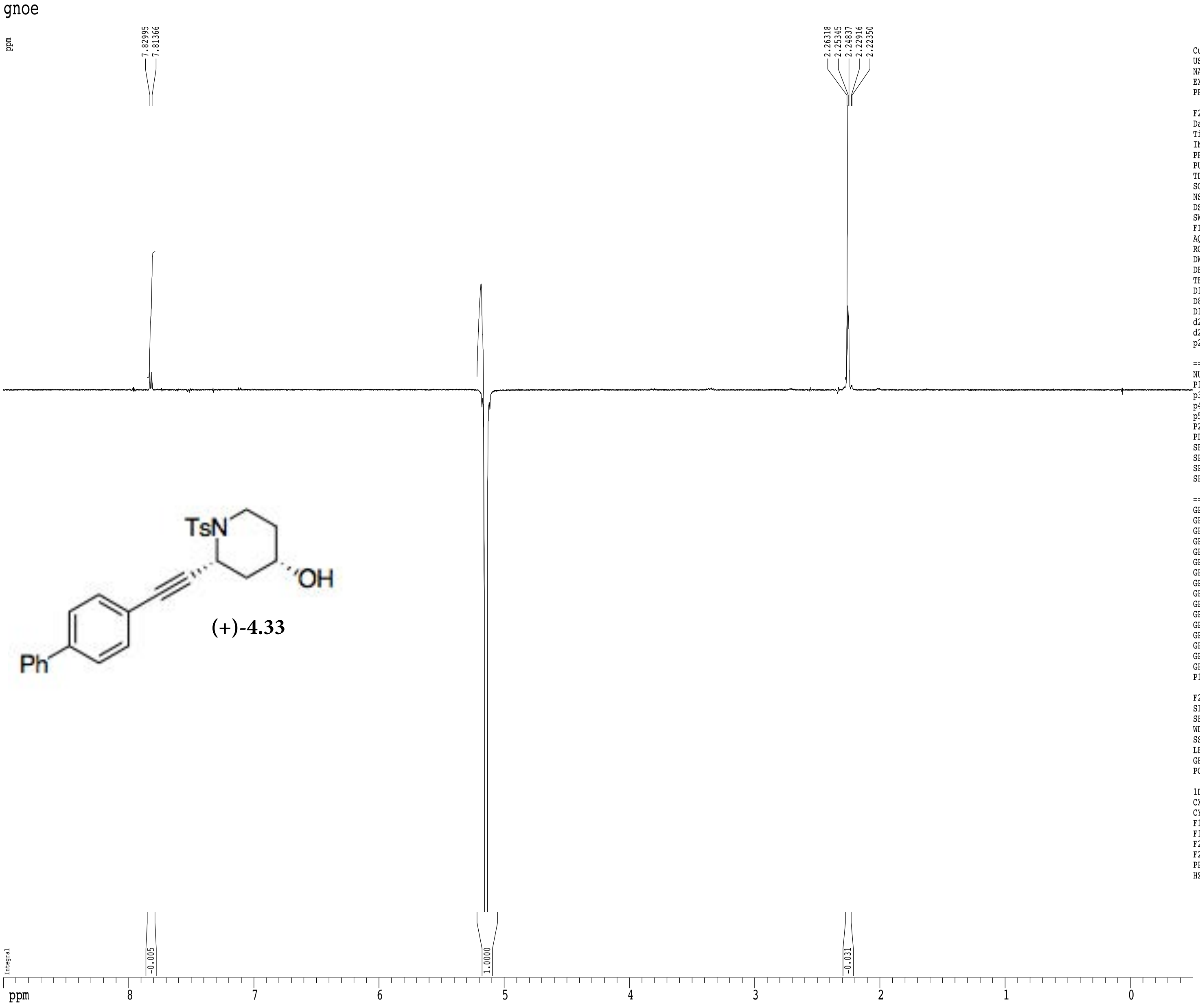
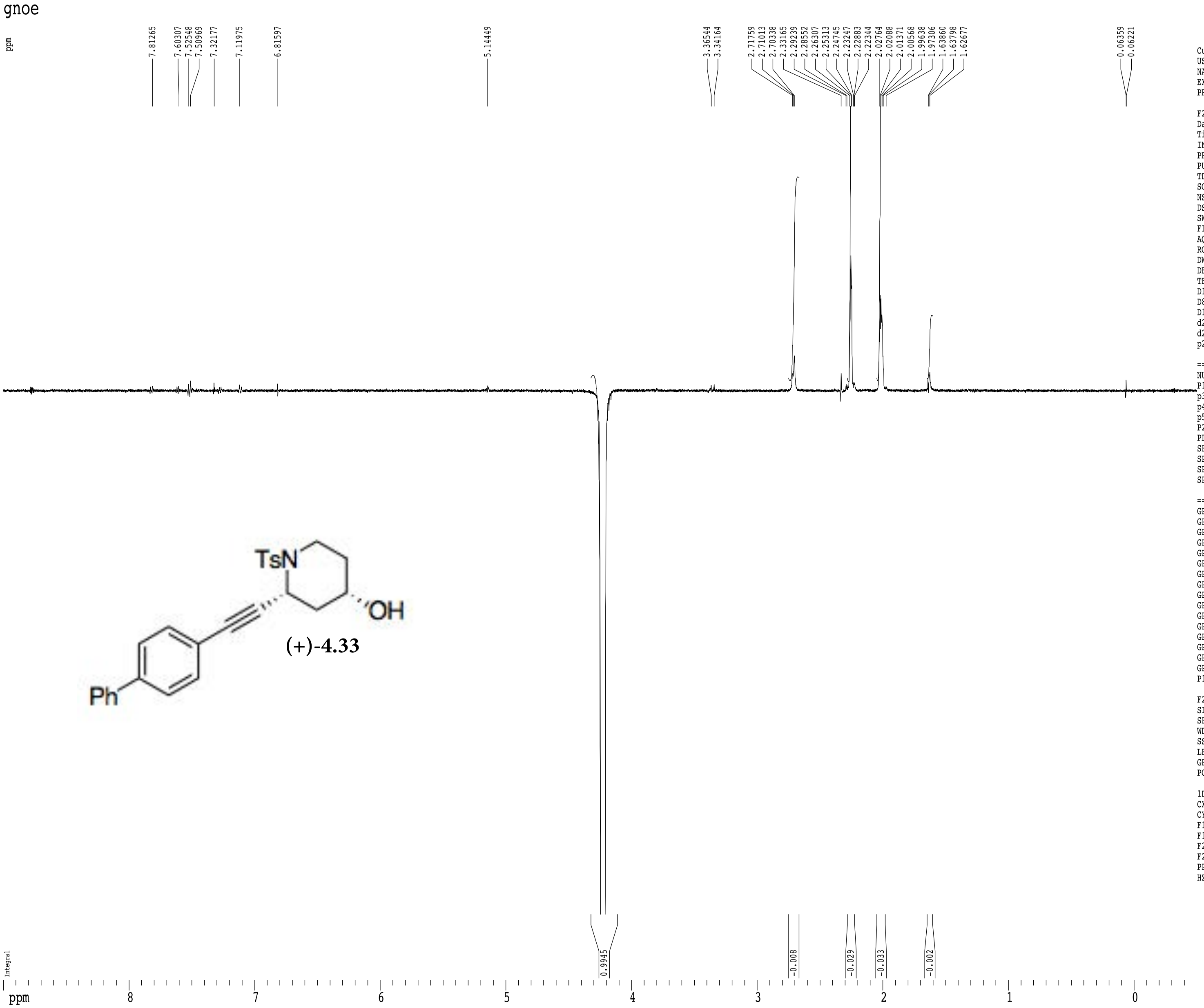
gcosy60



```
        Current Data Parameters
USER            khewitt1
NAME        KAH-IV-043-Z
EXPNO                  6
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20201127
Time               12.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   256
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200324 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200324 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.000 ppm
F2LO             4502.07 Hz
F2PHI             -0.511 ppm
F2HI             -255.54 Hz
F1PLO              9.000 ppm
F1LO             4502.07 Hz
F1PHI             -0.511 ppm
F1HI             -255.54 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```



```
Current Data Parameters
USER            khewitt1
NAME        KAH-IV-043-Z
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201127
Time               12.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  90.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33375451 sec
d22           0.16399699 sec
p2                 19.50 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
p3                 29.25 usec
p4                 39.00 usec
p5                 26.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2225743 MHz
SP9                60.00 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPNAM3       SMSQ10.100
GPNAM4       SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



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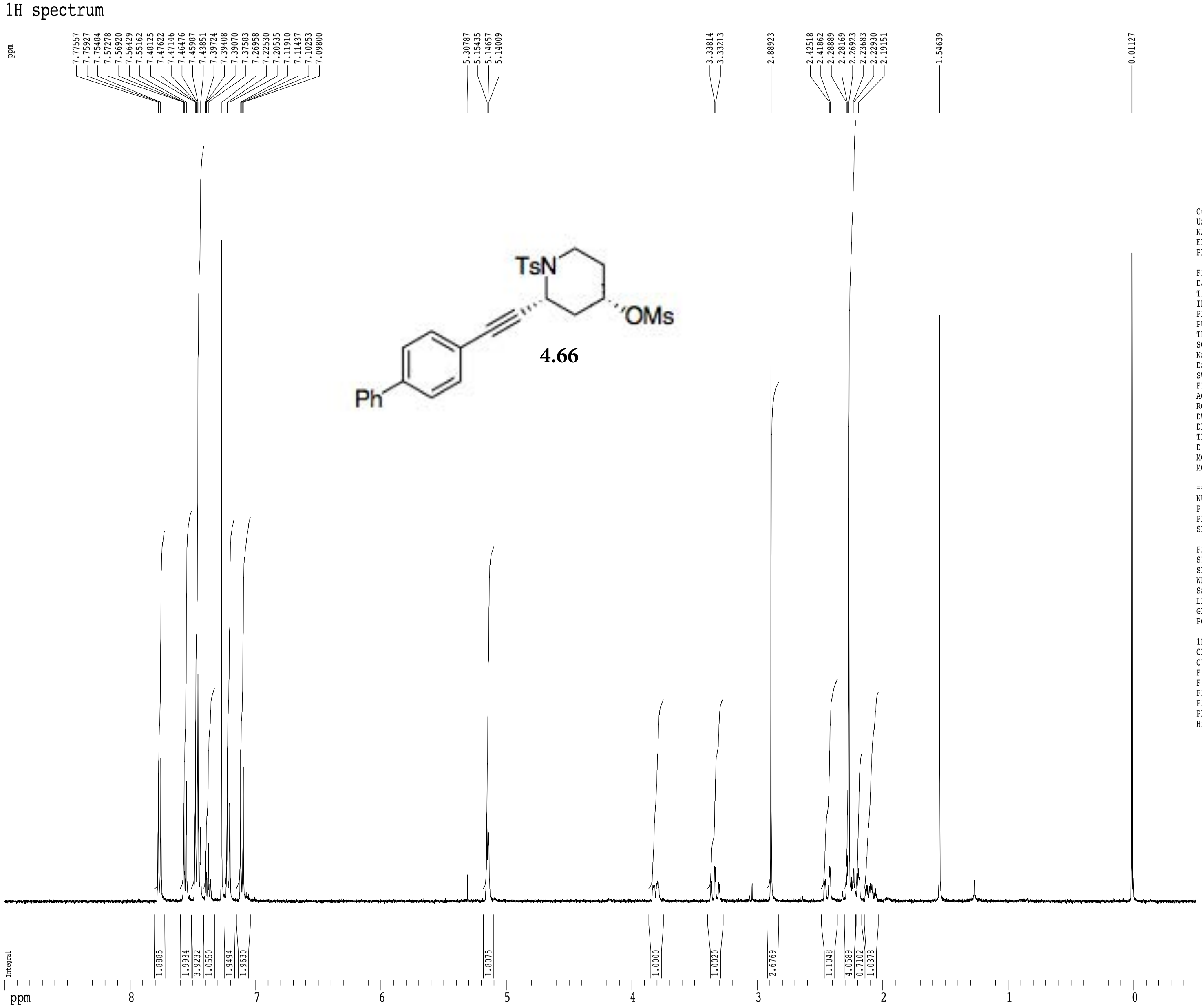
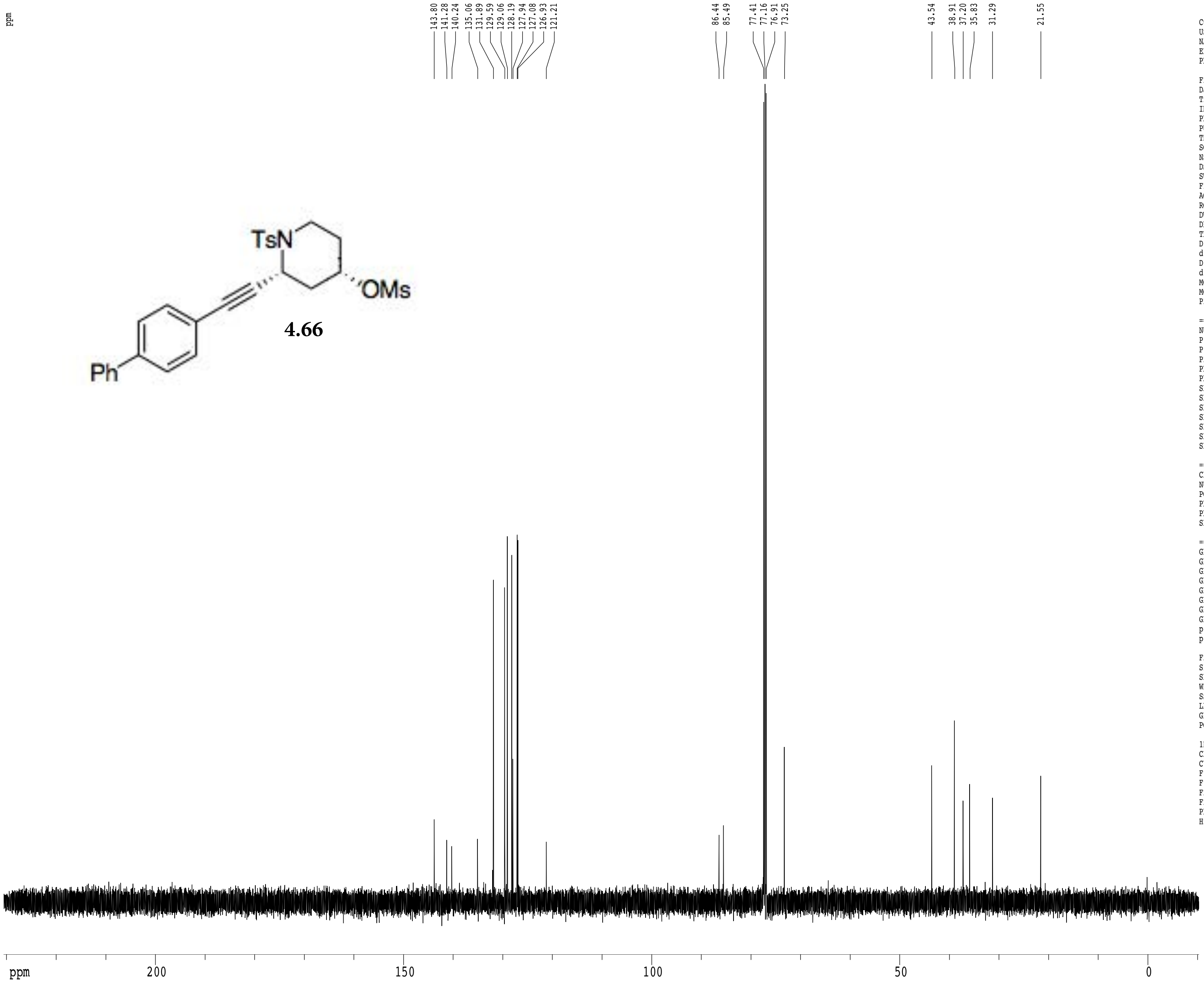
```
Current Data Parameters
USER            khewitt1
NAME       KAH-IV-043-Z
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201127
Time               12.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  80.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33375451 sec
d22           0.16399699 sec
p2                 19.50 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
p3                 29.25 usec
p4                 39.00 usec
p5                 26.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2221143 MHz
SP9                60.00 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPNAM3       SMSQ10.100
GPNAM4       SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



```
Current Data Parameters
USER            khewitt1
NAME       KAH-IV-047-C1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201121
Time               12.05
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                  1024
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

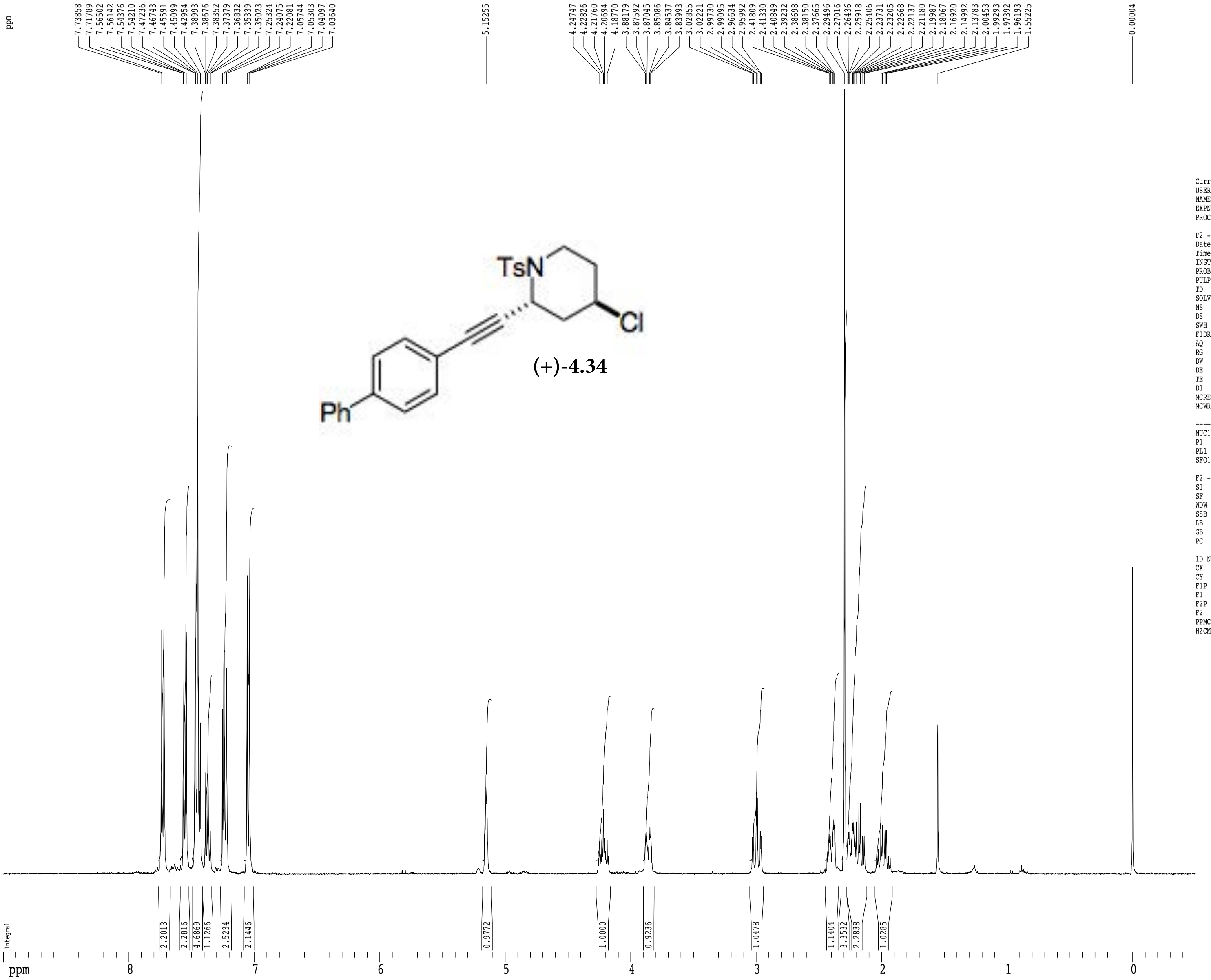
Z-restored spin-echo 13C spectrum with 1H decoupling



4.66

```
Current Data Parameters
USER            khewitt1
NAME         KAH-IV-047-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201121
Time               13.07
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT           CDCl3T
NS                   312
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4     Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804071 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

1H spectrum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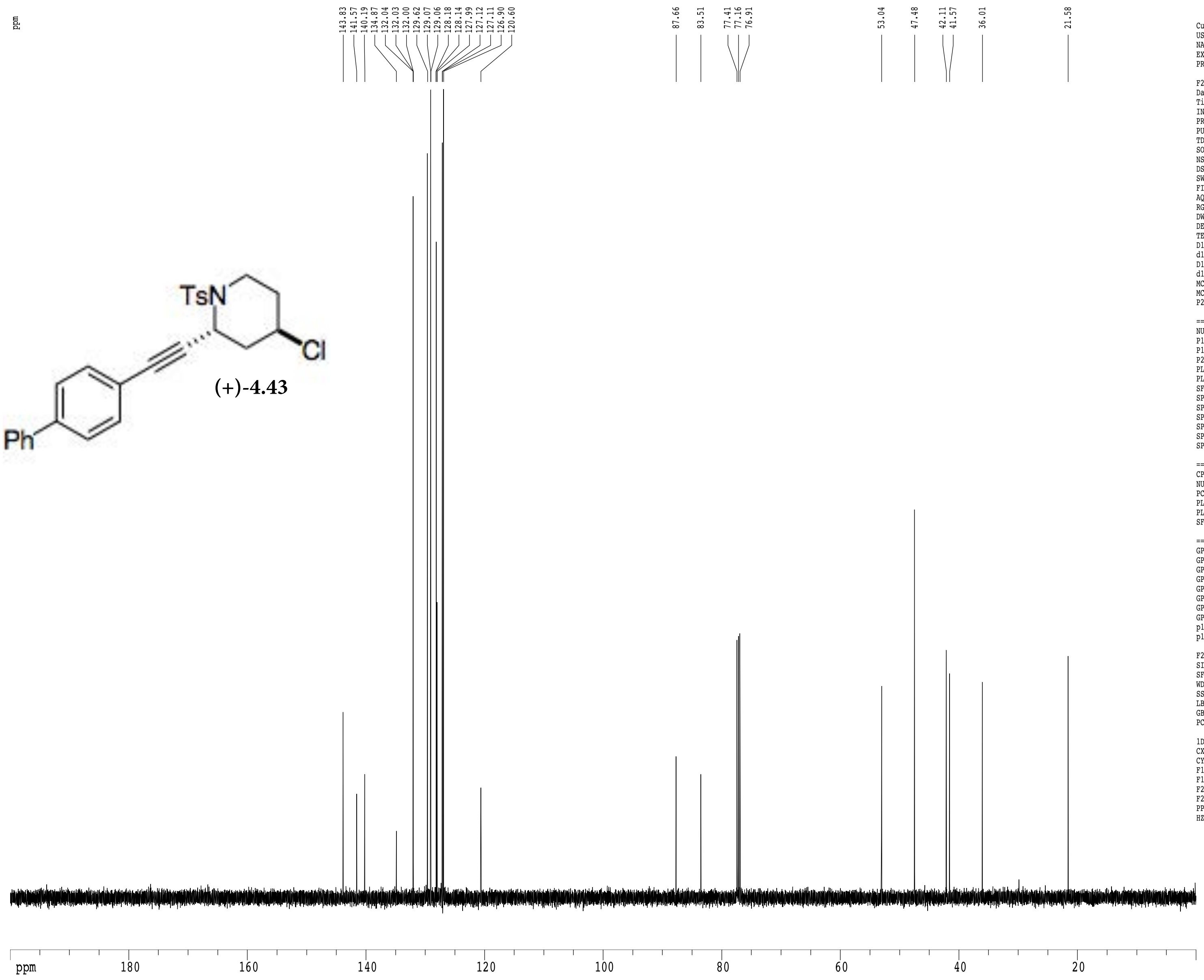
```
Current Data Parameters
USER           khewitt1
NAME     ELL-IV-123-char-grease
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20190613
Time              15.11
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                287.4
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300238 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



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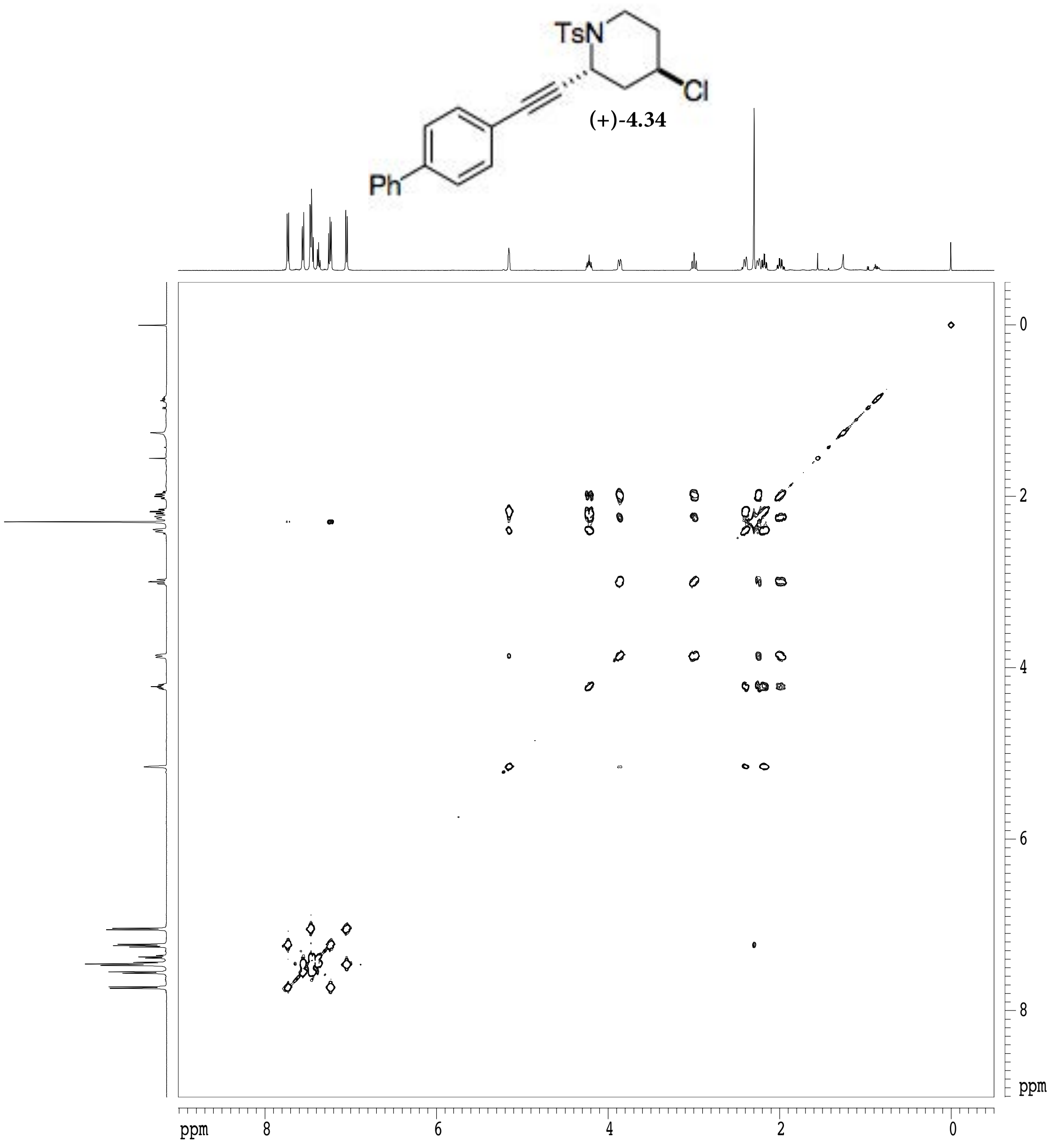
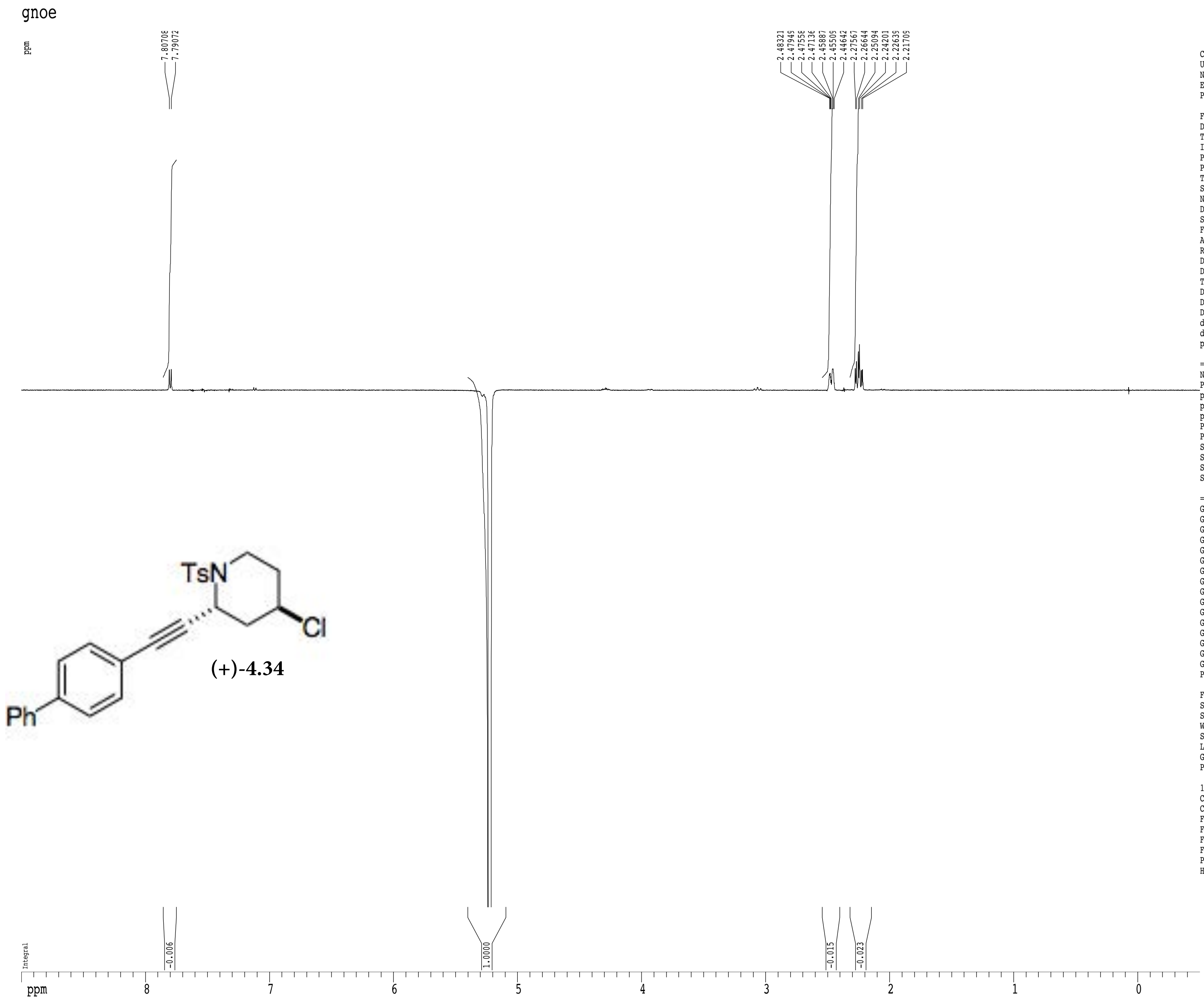
```
Current Data Parameters
USER              khewitt1
NAME            ELL-IV-114
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20190221
Time                 19.18
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     272
DS                      16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                   33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   2.70 dB
SP4                   2.70 dB
SPNAM2         Crp60comp.4
SPNAM4     Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 23.54 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804094 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                200.000 ppm
F1                25156.08 Hz
F2P                  0.000 ppm
F2                    0.00 Hz
PPMCM              8.77193 ppm/cm
HZCM            1103.33691 Hz/cm
```

gcosy60



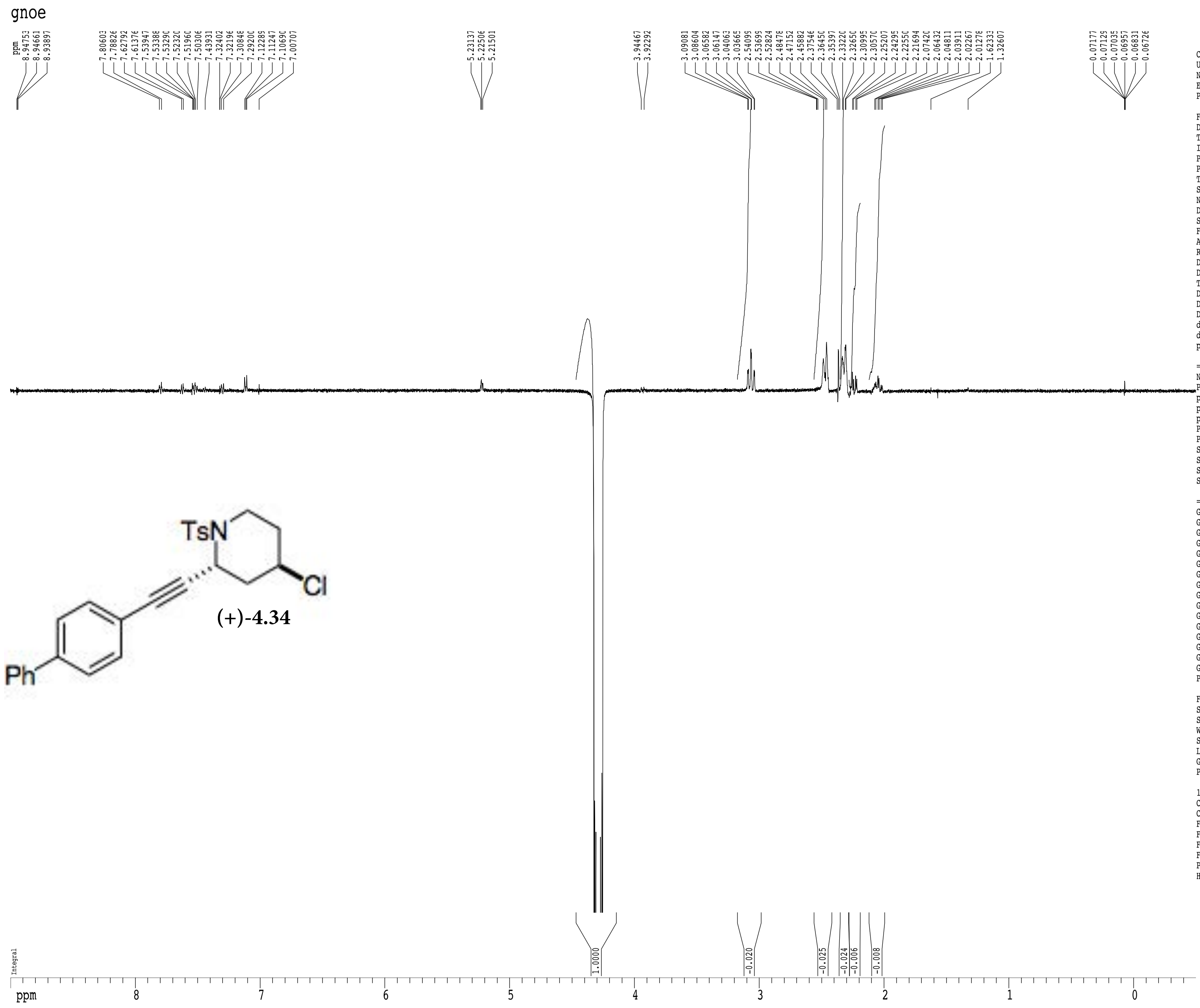
(+)-4.34

```
        Current Data Parameters
USER            khewitt1
NAME          ELL-IV-114
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20190221
Time               19.04
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                 143.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

       F2 - Processing parameters
SI                  1024
SF           500.2200349 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

       F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200349 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

          2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.011 ppm
F2LO             4507.33 Hz
F2PHI             -0.500 ppm
F2HI             -250.28 Hz
F1PLO              9.011 ppm
F1LO             4507.33 Hz
F1PHI             -0.500 ppm
F1HI             -250.28 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```



(+)-4.34

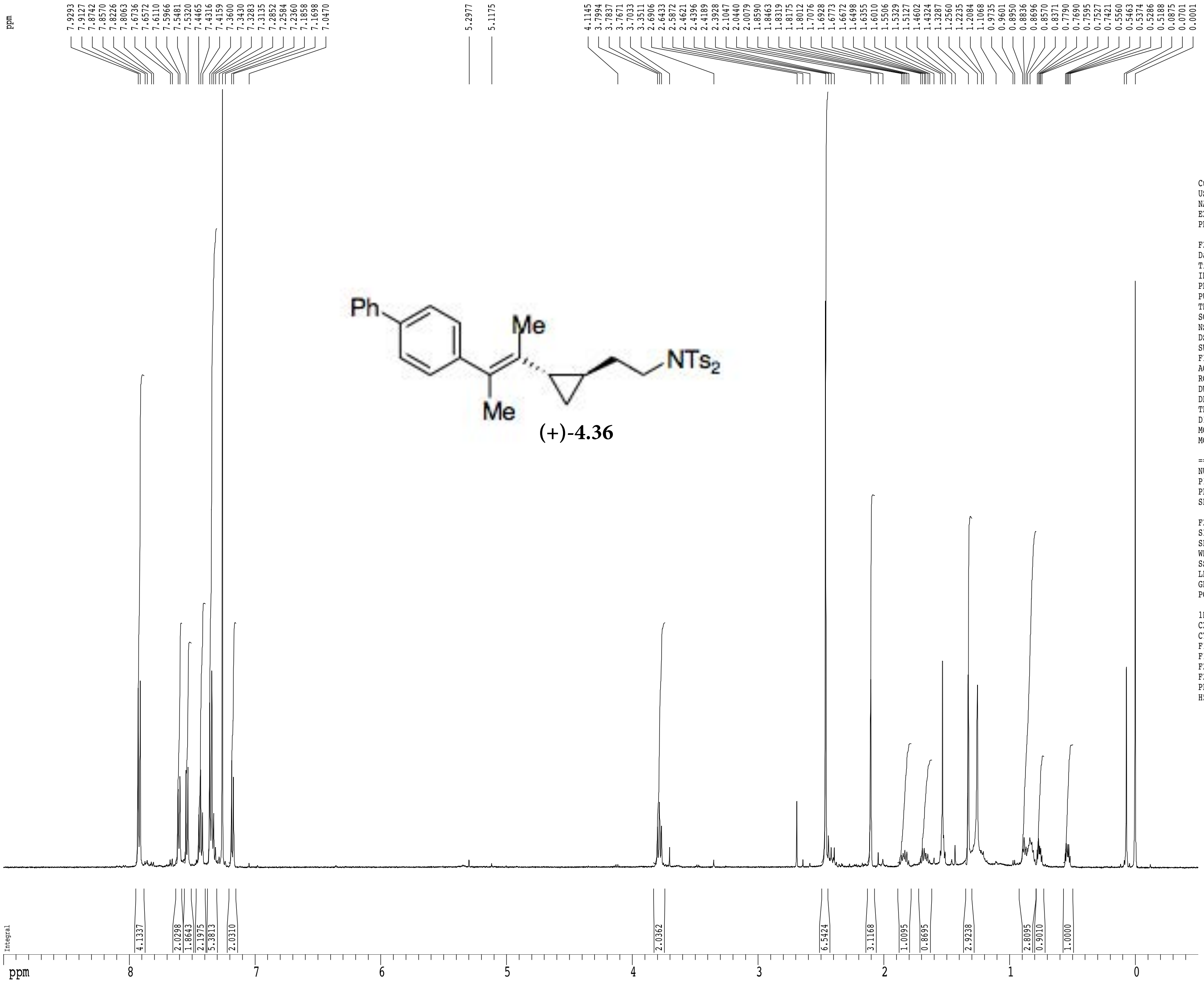
```
Current Data Parameters
USER           khewitt1
NAME         ELL-IV-114
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20190221
Time              19.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                161.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2226128 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



(+)-**4.34**

```
Current Data Parameters
USER            khewitt1
NAME         ELL-IV-114
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20190221
Time              19.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                   24
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                101.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2221450 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

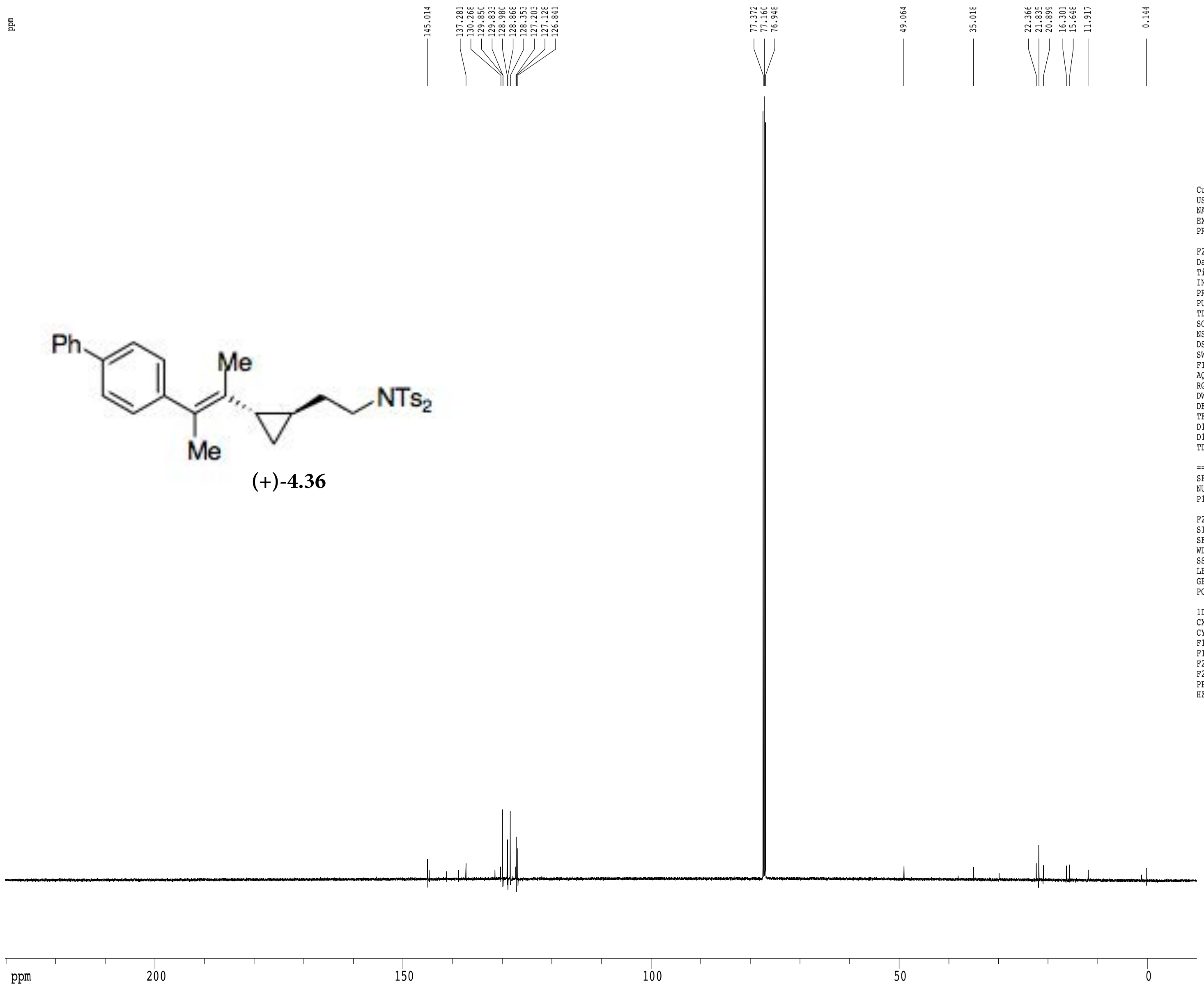
1H spectrum



(+)-4.36

```
Current Data Parameters
USER           khewitt1
NAME     KAH-IV-153-enant
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210323
Time              14.43
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200320 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

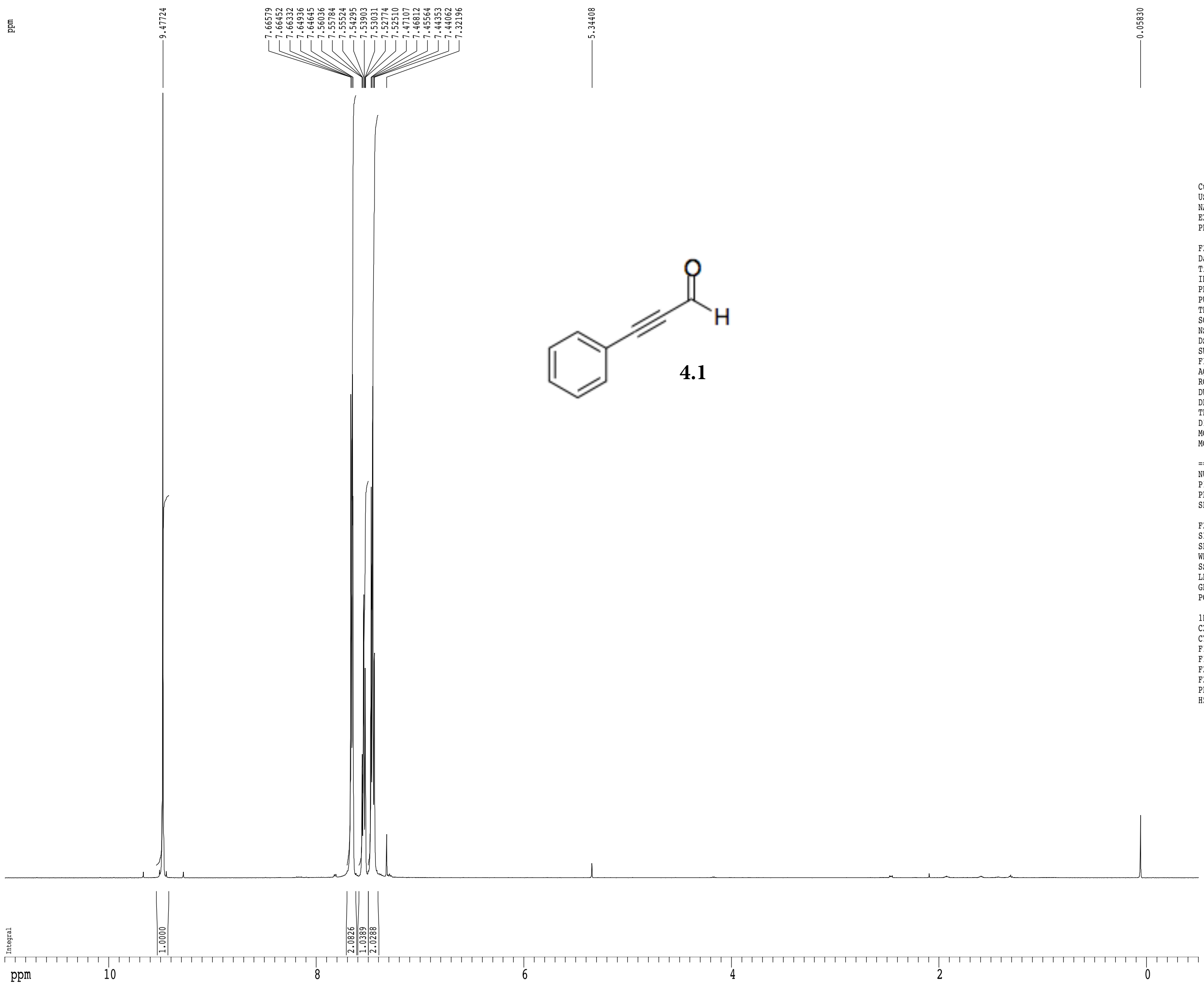
1H spectrum



(+)-4.36

```
Current Data Parameters
USER            khewitt1
NAME     KAH-IV-153-enant
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210323
Time               15.06
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   640
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9027931 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.154 ppm
F1              34730.87 Hz
F2P               -9.947 ppm
F2              -1501.01 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11768 Hz/cm
```

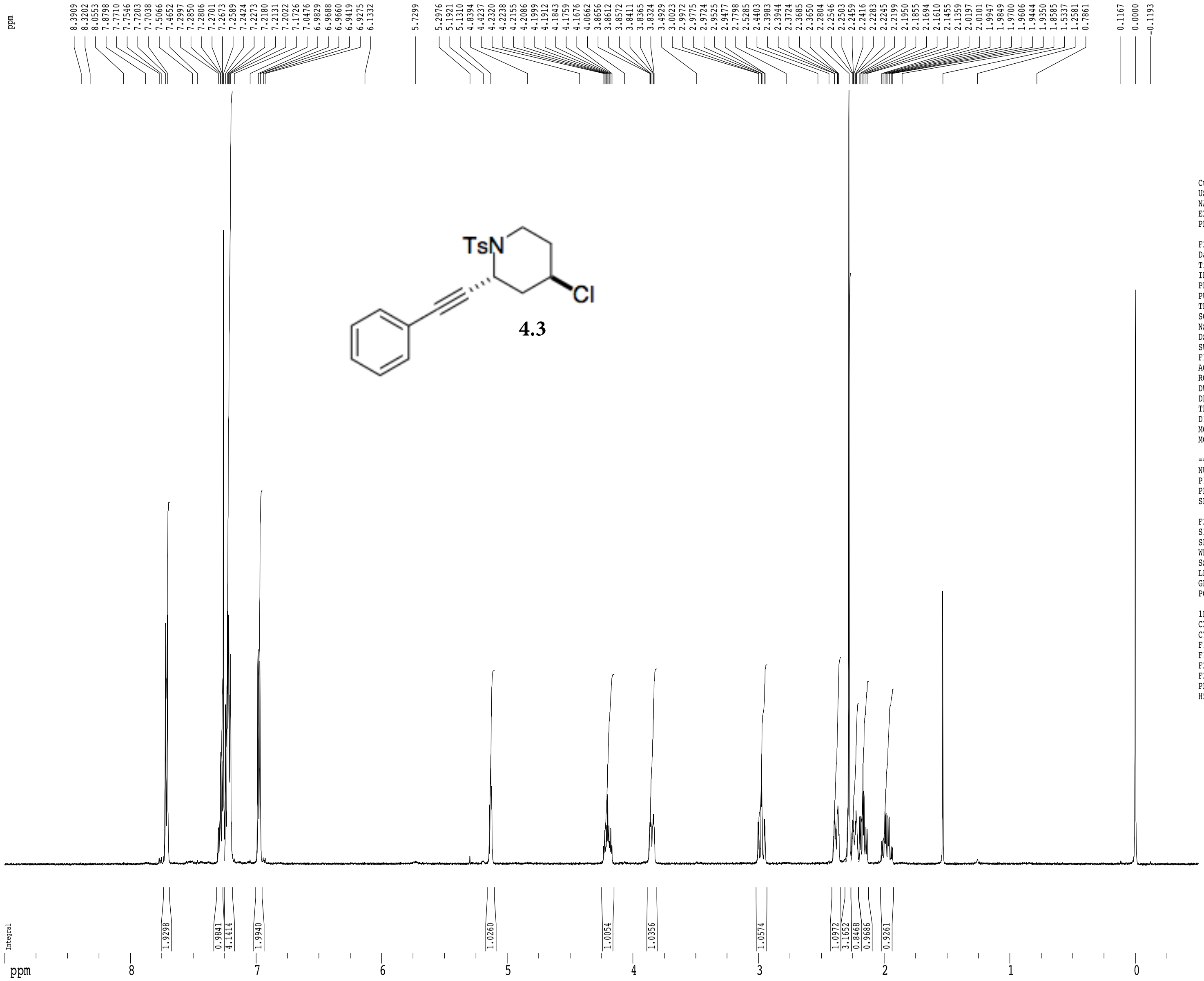
1H spectrum



4.1

```
Current Data Parameters
USER           khewitt1
NAME        KAH-II-282-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200116
Time               16.55
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               11.000 ppm
F1               5502.42 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.50439 ppm/cm
HZCM           252.30396 Hz/cm
```

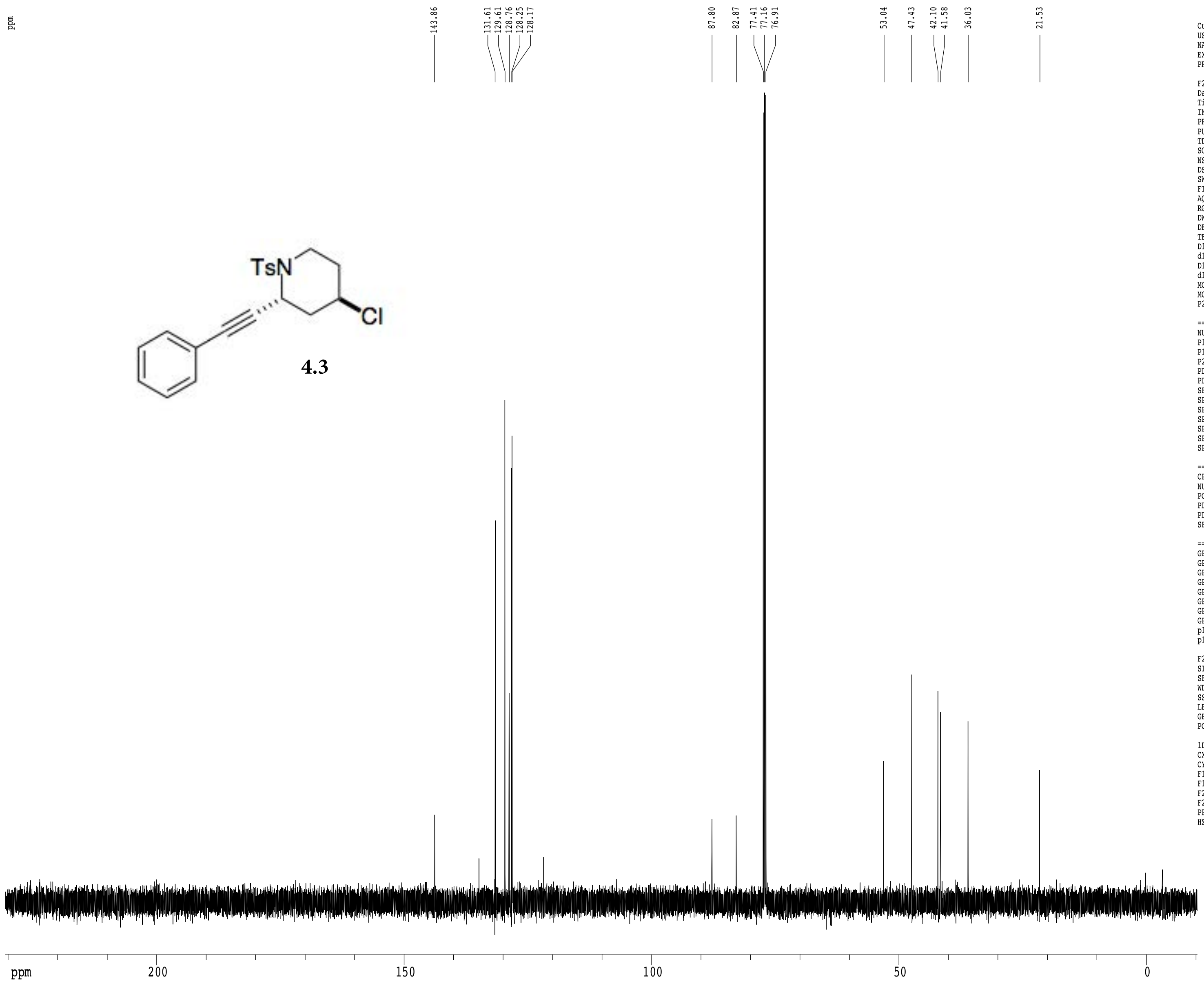
1H spectrum



4.3

```
Current Data Parameters
USER           khewitt1
NAME       KAH-II-283-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20191129
Time              15.38
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200316 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



4.3

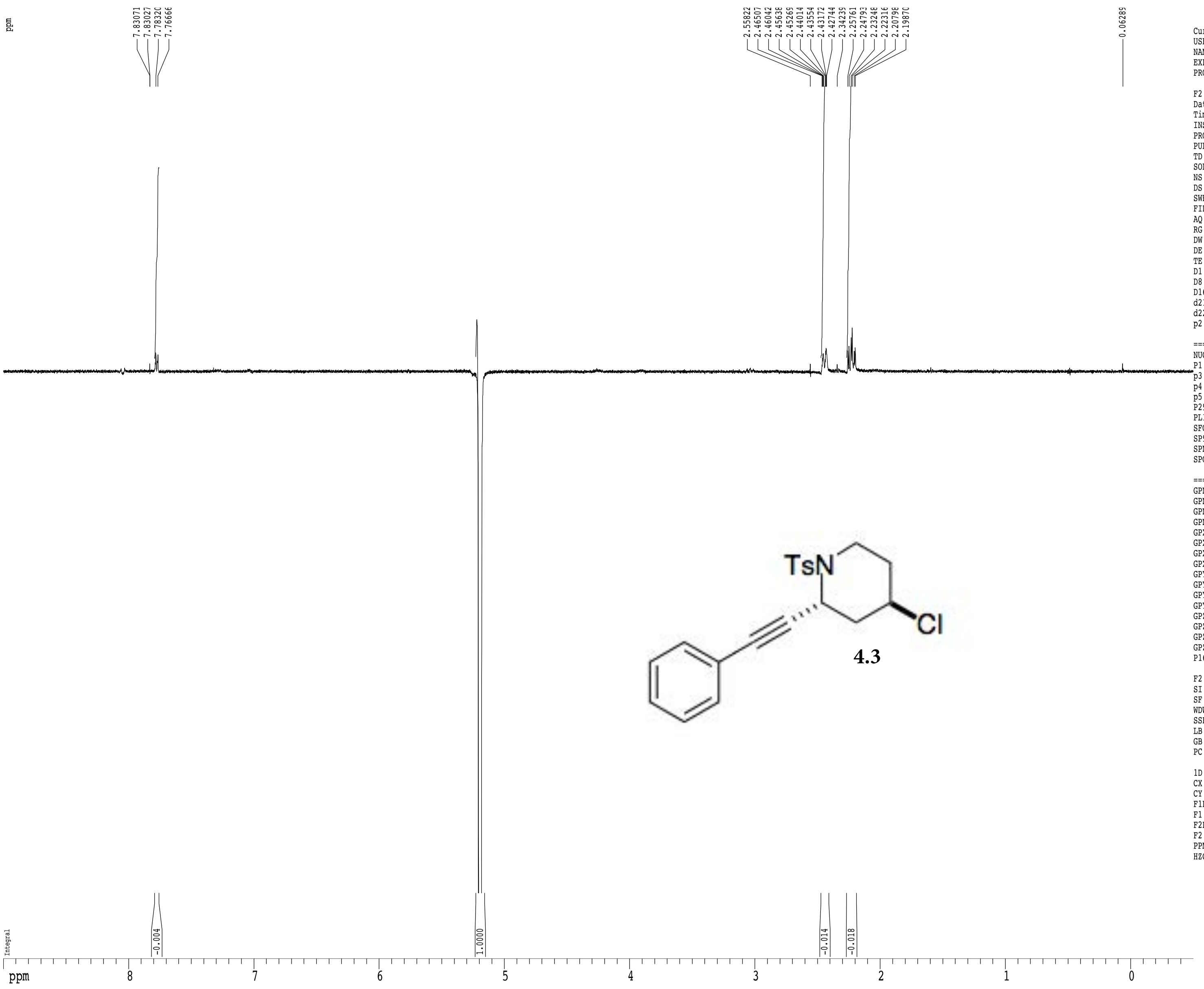
```
Current Data Parameters
USER           khewitt1
NAME        KAH-II-283-Z
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20191129
Time              15.57
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  488
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804057 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```

gcosy60

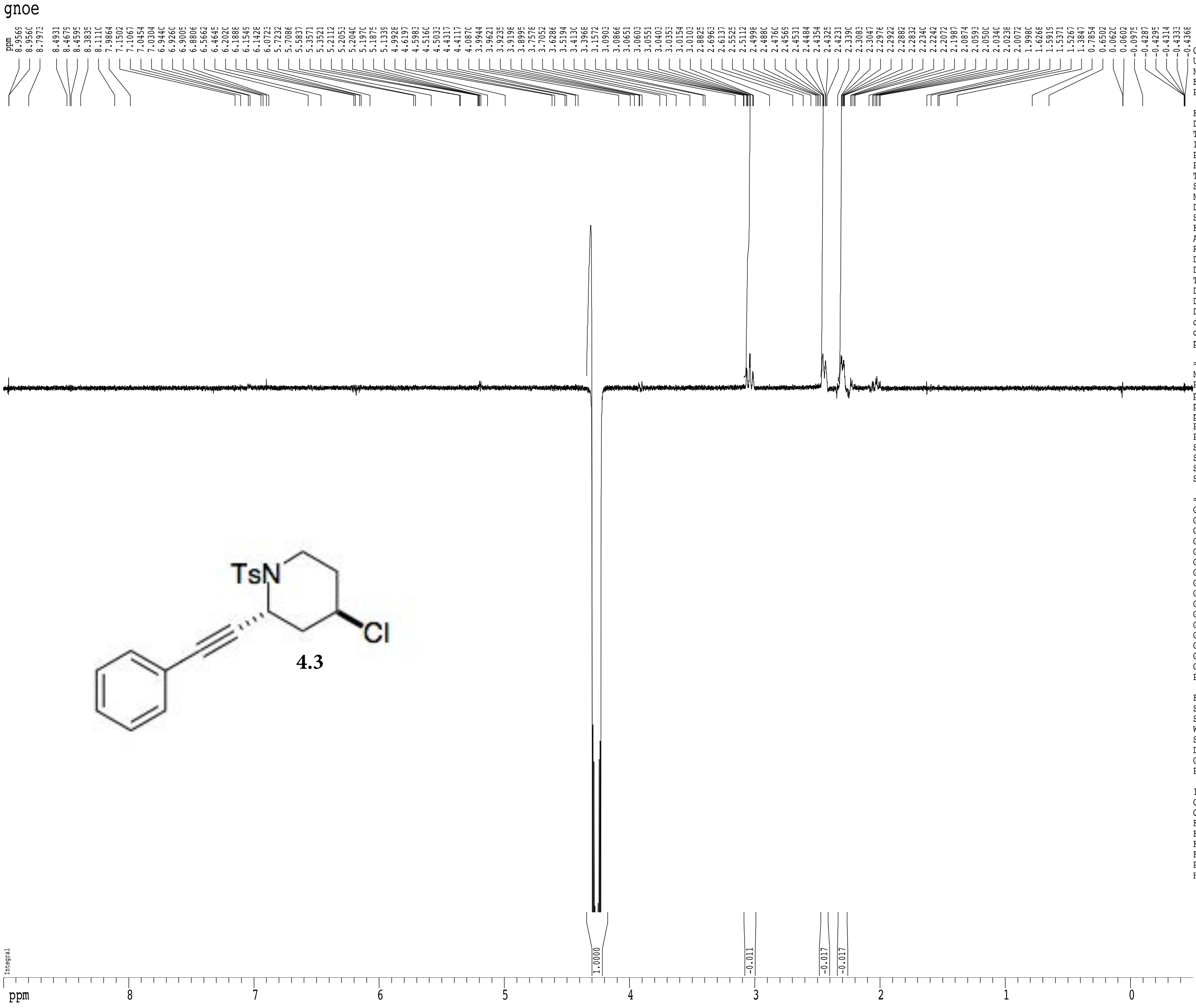
4.3

```
     Current Data Parameters
USER           khewitt1
NAME       KAH-II-283-Z
EXPNO                 2
PROCNO                1

    F2 - Acquisition Parameters
Date_          20191129
Time              15.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                912.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1        sine.100
GPNAM2        sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

    F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

    F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

    F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

      2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.002 ppm
F2LO            4503.14 Hz
F2PHI            -0.524 ppm
F2HI            -262.29 Hz
F1PLO             9.002 ppm
F1LO            4503.14 Hz
F1PHI            -0.509 ppm
F1HI            -254.47 Hz
F2PPMCM         0.63511 ppm/cm
F2HZCM        317.69583 Hz/cm
F1PPMCM         0.63407 ppm/cm
F1HZCM        317.17416 Hz/cm
```

gnoe

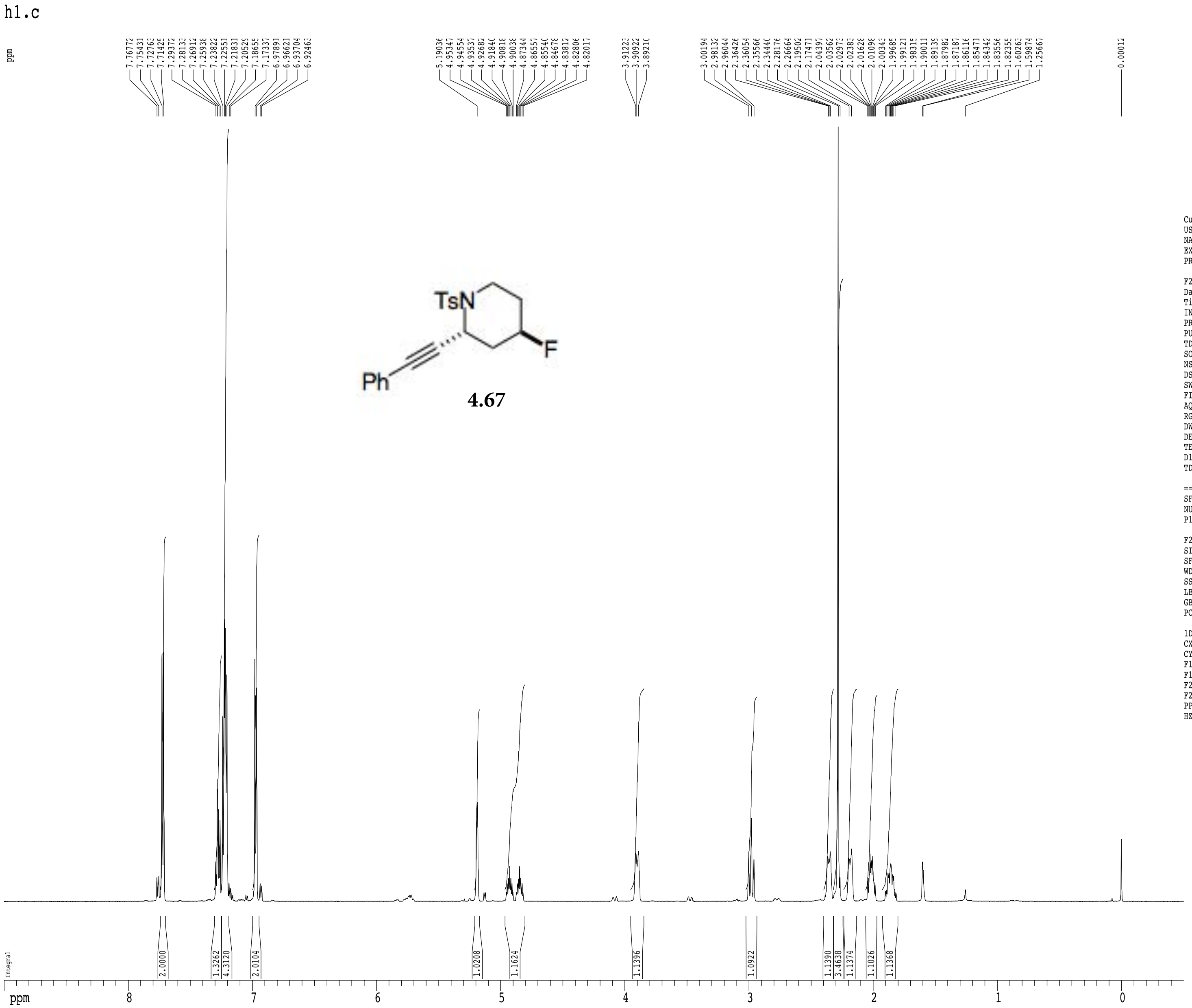


```
Current Data Parameters
USER             khewitt1
NAME          KAH-II-283-Z
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191129
Time                16.19
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                   80.6
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2225982 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```



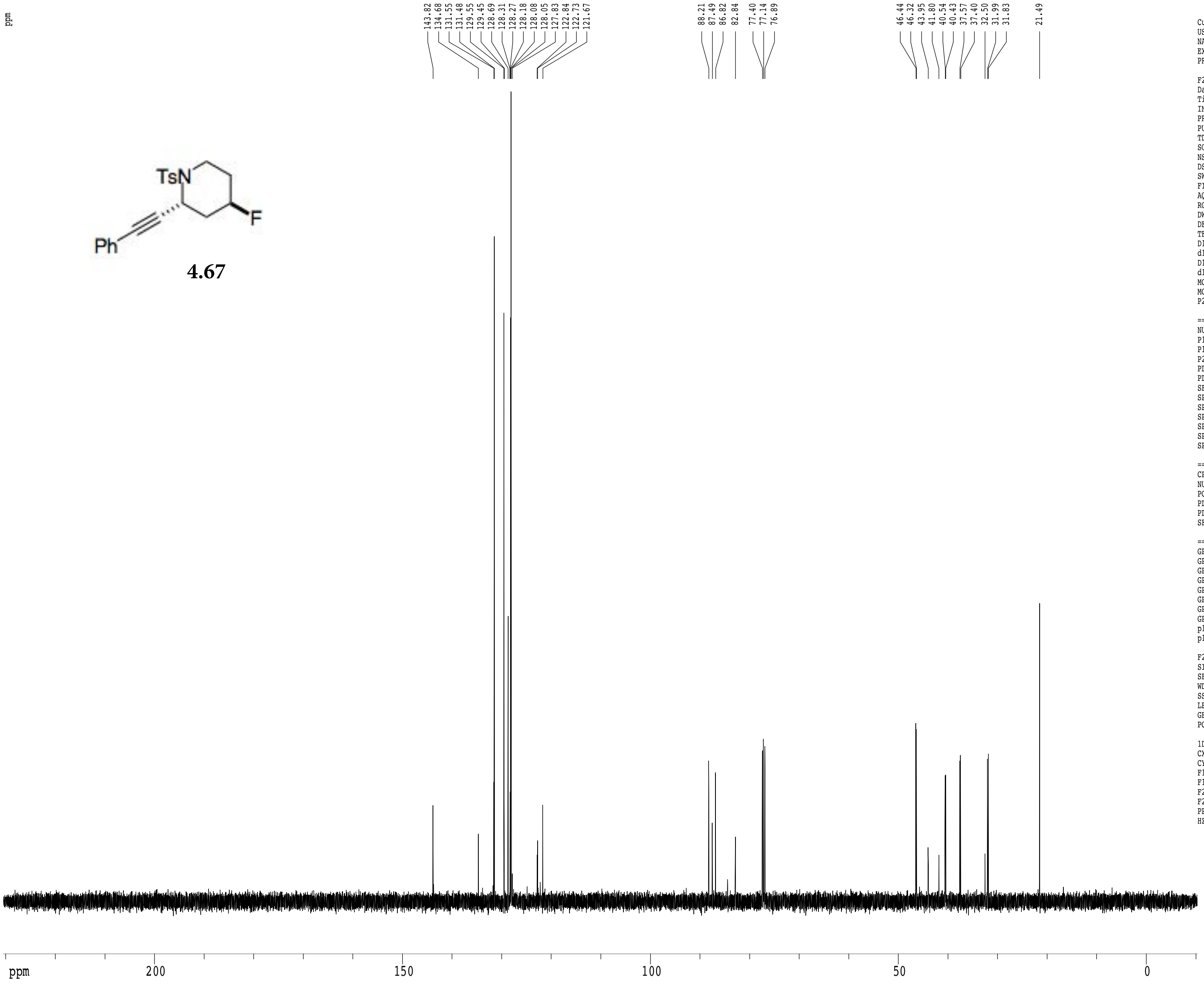
4.3

```
Current Data Parameters
USER              khewitt1
NAME         KAH-II-283-Z
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20191129
Time                 16.35
INSTRUM            cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                    90.5
DW              62.400 usec
DE                6.00 usec
TE                 298.0 K
D1          1.00000000 sec
D8          0.50000000 sec
D16         0.00020000 sec
d21         0.33376500 sec
d22         0.16399699 sec
p2               15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                7.50 usec
p3               22.50 usec
p4               30.00 usec
p5               20.00 usec
P29           40000.00 usec
PL1                1.60 dB
SFO1       500.2221327 MHz
SP9               61.60 dB
SPNAM9         gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                   65536
SF          500.2200000 MHz
WDW                     no
SSB                      0
LB                 0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P              9.000 ppm
F1              4501.98 Hz
F2P             -0.500 ppm
F2              -250.11 Hz
PPMCM       0.41667 ppm/cm
HZCM      208.42500 Hz/cm
```



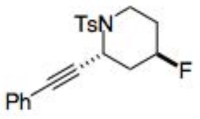
```
Current Data Parameters
USER              khewitt1
NAME      KAH-IV-062-dr-F
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210630
Time                 10.45
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   98074
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998979 sec
RG                      10
DW                  52.000 usec
DE                   14.23 usec
TE                   298.0 K
D1             0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                    1H
P1                    9.50 usec

F2 - Processing parameters
SI                   65536
SF          600.1300349 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 5401.17 Hz
F2P                 -0.500 ppm
F2                 -300.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             250.05418 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



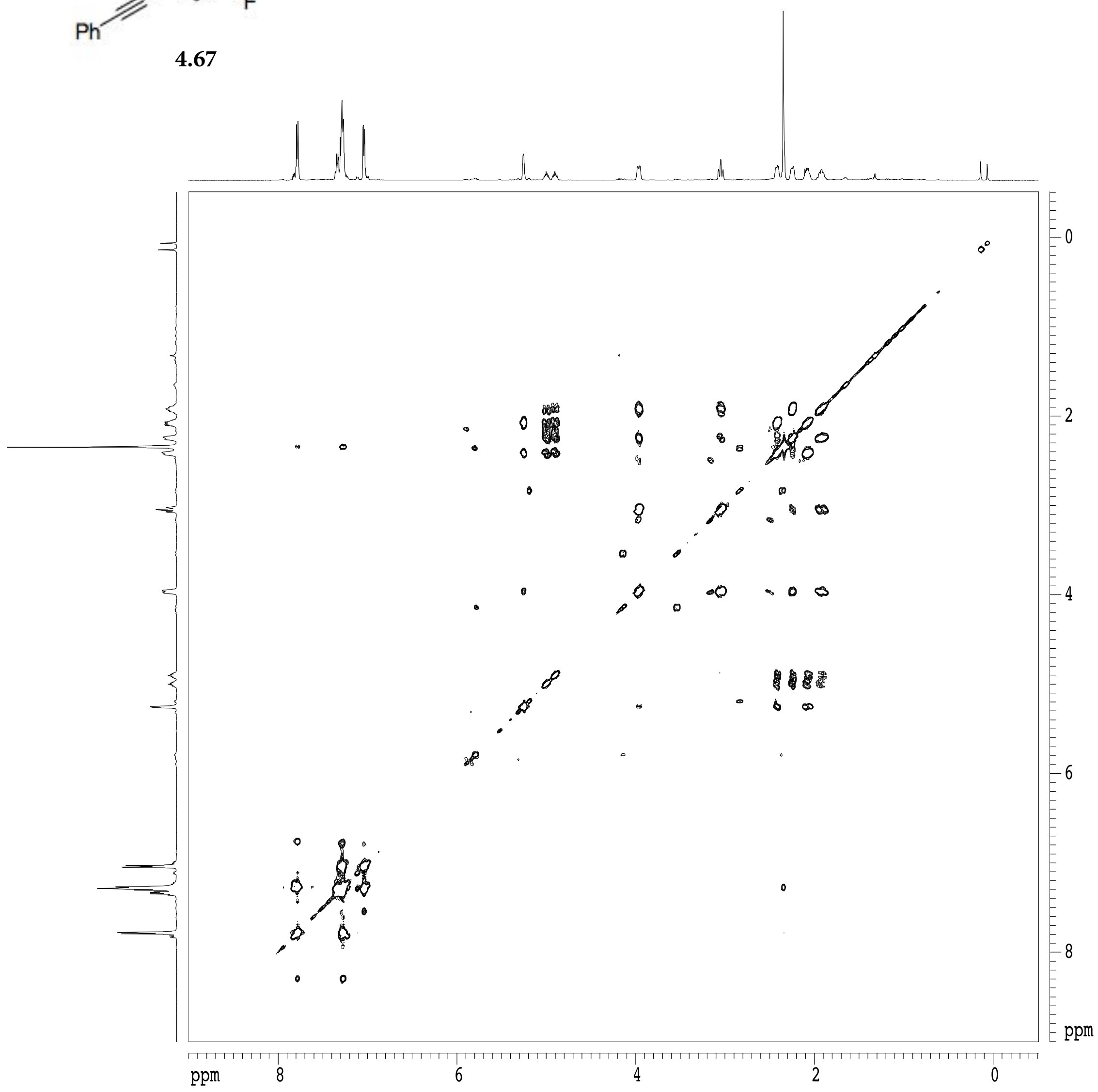
4.67

```
Current Data Parameters
USER              khewitt1
NAME          KAH-IV-062-Z
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20201210
Time                 10.39
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                      48
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813940 sec
RG                  5792.6
DW                  16.500 usec
DE                    6.00 usec
TE                   286.7 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                   37.70 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   18.85 usec
P12                2000.00 usec
P20                 500.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   1.55 dB
SP4                   1.55 dB
SPNAM2         Crp60comp.4
SPNAM4      Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 22.00 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804190 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                230.637 ppm
F1                29009.68 Hz
F2P                -10.287 ppm
F2                -1293.96 Hz
PPMCM             10.56688 ppm/cm
HZCM            1329.10706 Hz/cm
```

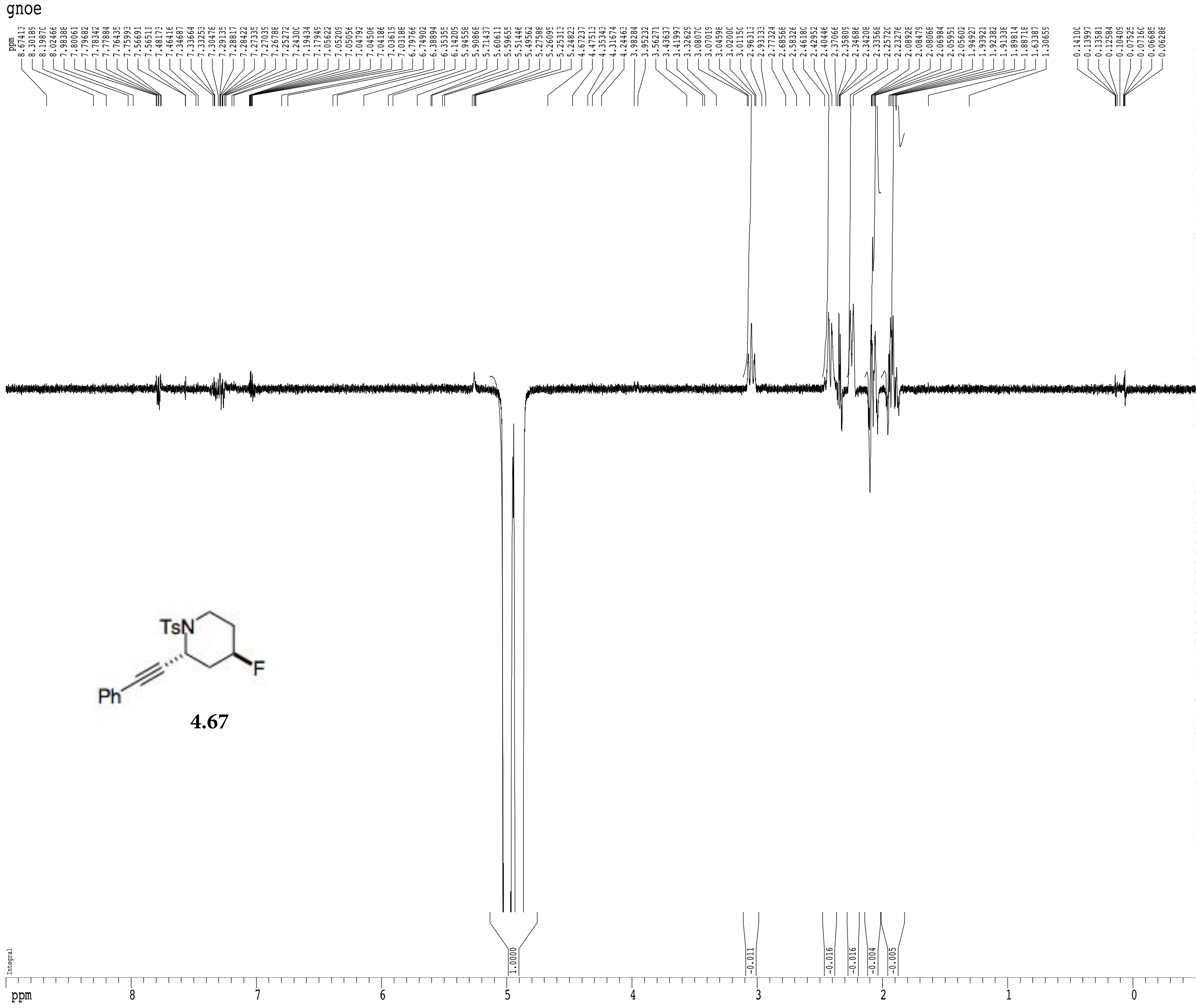


4.67

gcosy60

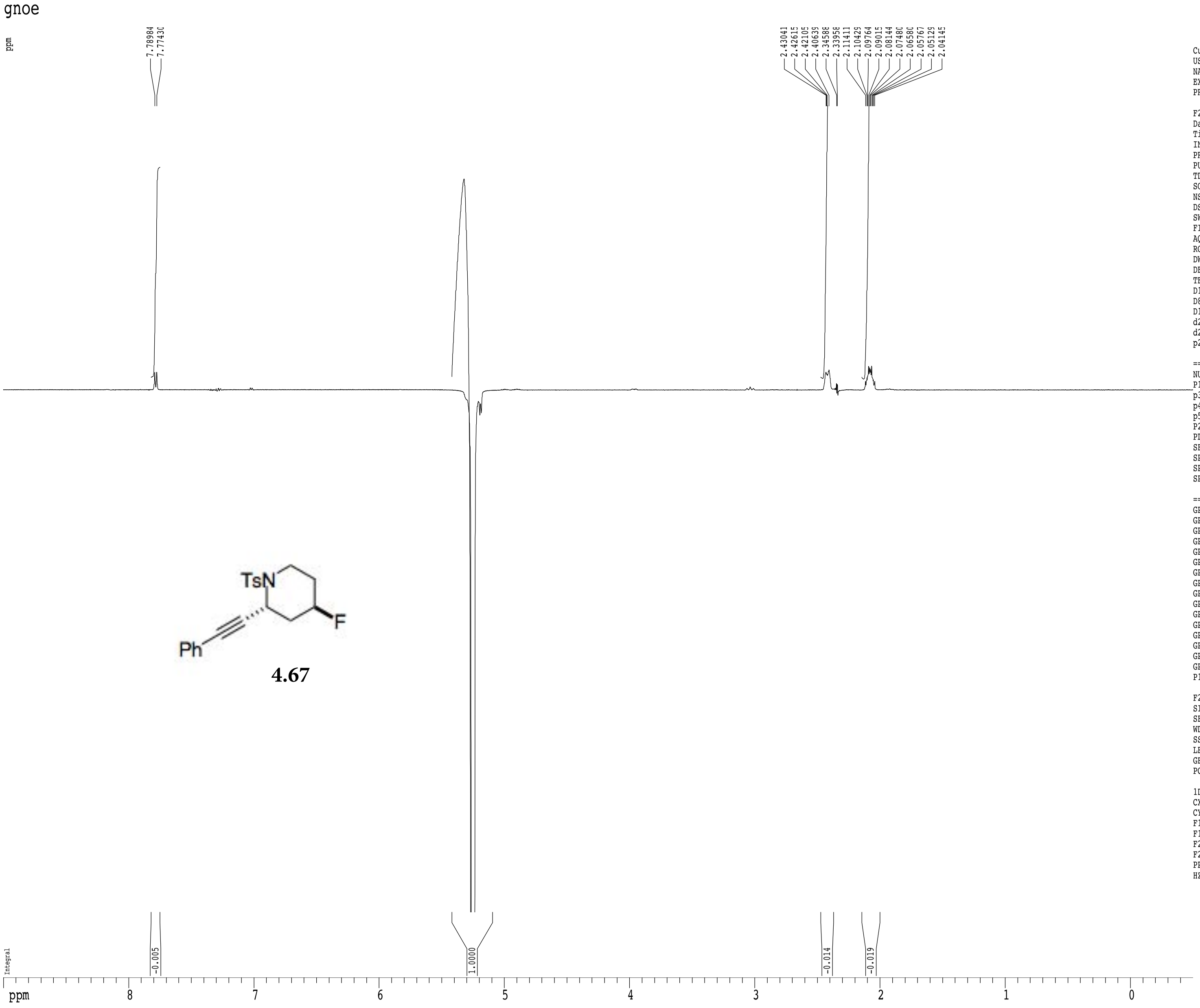


```
        Current Data Parameters
 USER           khewitt1
NAME      KAH-III-098-P1-2D
 EXPNO                  4
 PROCNO                 1

       F2 - Acquisition Parameters
 Date_          20200221
 Time              10.03
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG    cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            8012.820 Hz
 FIDRES         3.912510 Hz
 AQ            0.1278452 sec
 RG                  114
 DW               62.400 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00012480 sec

      ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2235015 MHz

      ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

       F1 - Acquisition parameters
 ND0                   1
 TD                  512
 SFO1           500.2235 MHz
 FIDRES        15.650040 Hz
 SW               16.018 ppm
 FnMODE               QF

       F2 - Processing parameters
 SI                 1024
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

       F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

         2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             9.002 ppm
 F2LO            4503.14 Hz
 F2PHI            -0.509 ppm
 F2HI            -254.47 Hz
 F1PLO             9.002 ppm
 F1LO            4503.14 Hz
 F1PHI            -0.509 ppm
 F1HI            -254.47 Hz
 F2PPMCM         0.63407 ppm/cm
 F2HZCM        317.17416 Hz/cm
 F1PPMCM         0.63407 ppm/cm
 F1HZCM        317.17416 Hz/cm
```



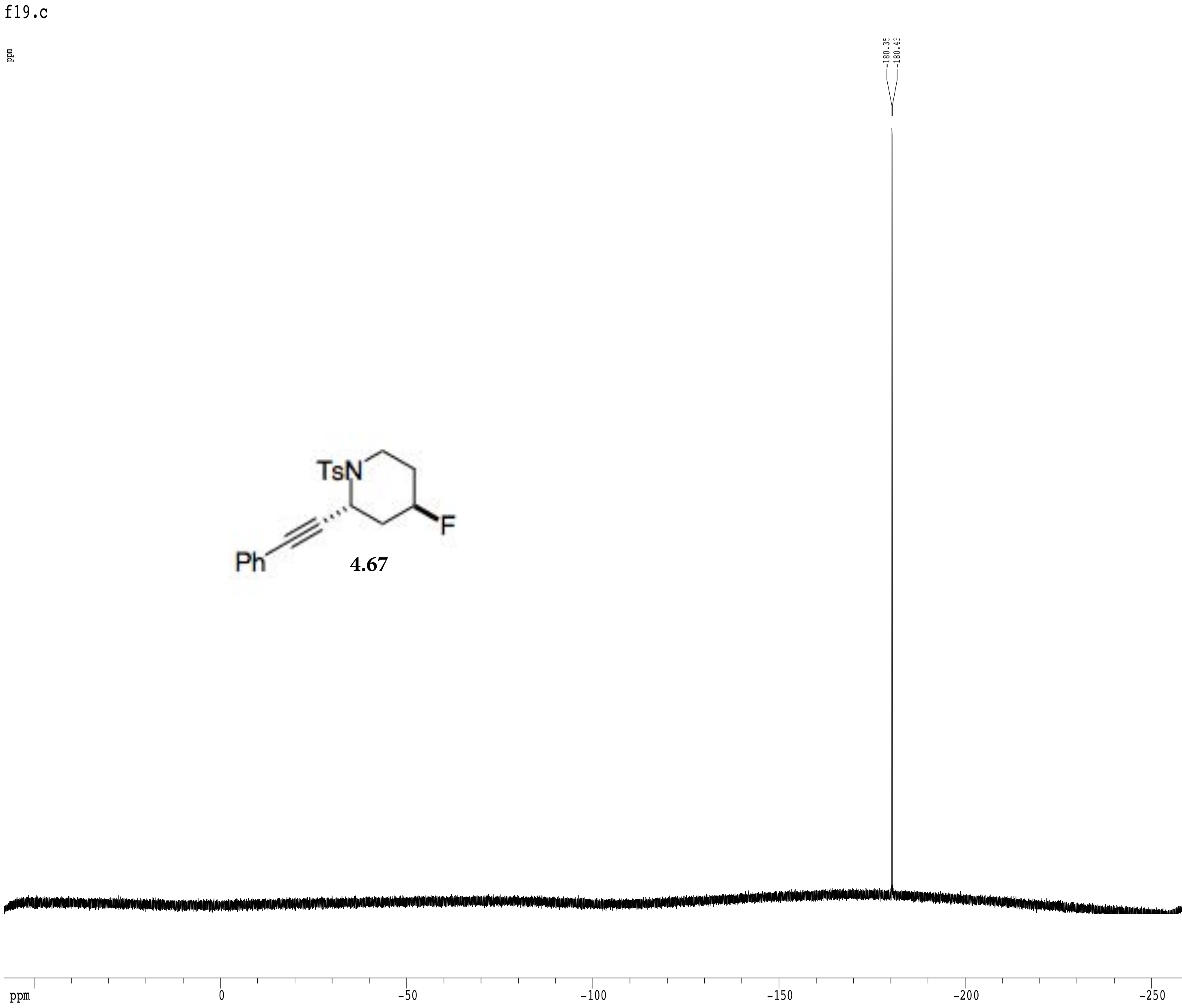
4.67

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-098-P1-2D
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200221
Time                9.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   128
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2224744 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



4.67

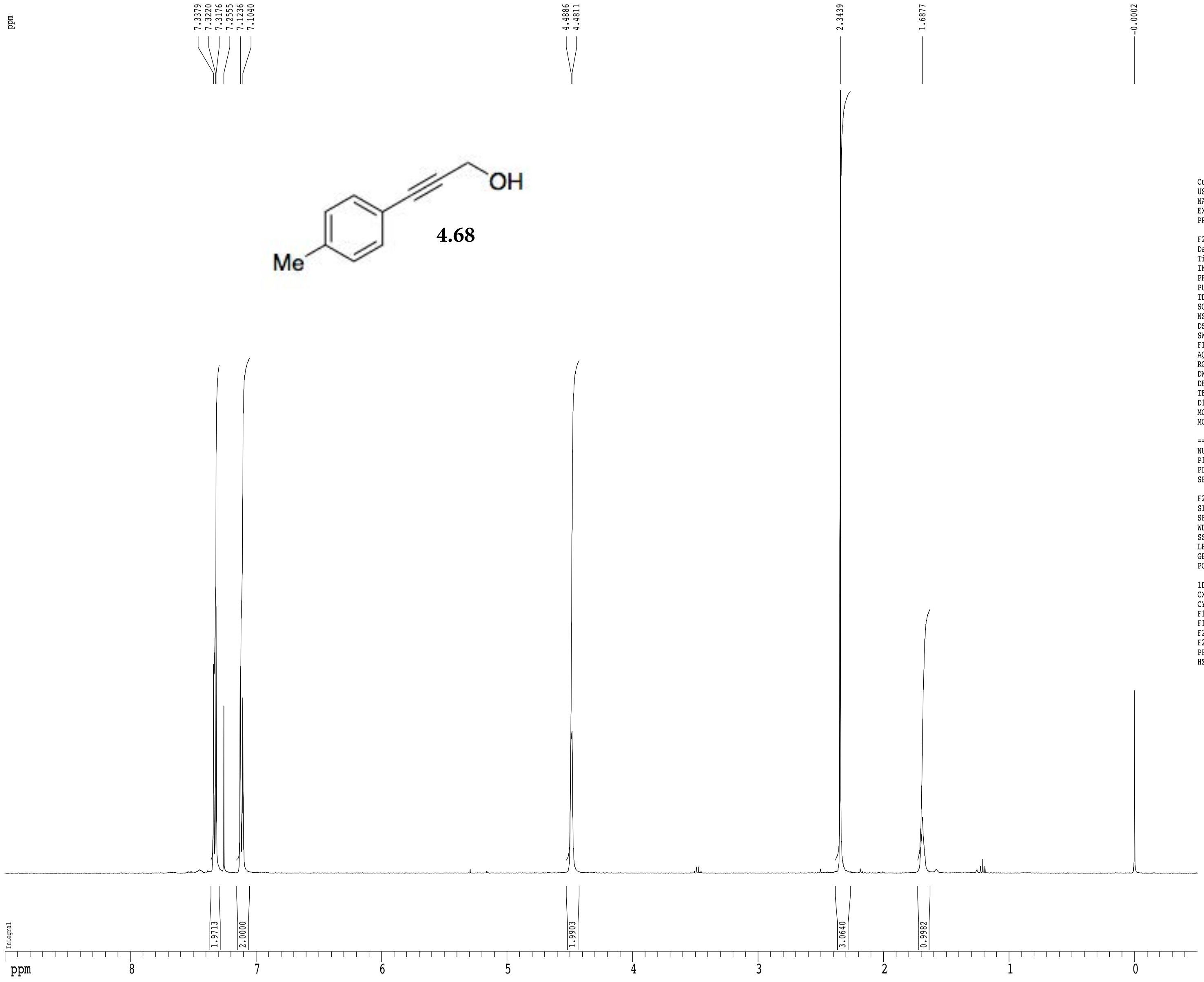
```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-062-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20201210
Time              10.38
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW               62.400 usec
DE                 6.00 usec
TE                286.7 K
D1          1.00000000 sec
D8          0.50000000 sec
D16         0.00020000 sec
d21         0.33375451 sec
d22         0.16399699 sec
p2                19.50 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
p3                29.25 usec
p4                39.00 usec
p5                26.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2226258 MHz
SP9               60.00 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1       SMSQ10.100
GPNAM2       SMSQ10.100
GPNAM3       SMSQ10.100
GPNAM4       SMSQ10.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



4.67

```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-062-F
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210619
Time              15.26
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgflqn30
TD               131072
SOLVENT          CDCl3T
NS                   16
DS                    2
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                  575
DW                2.800 usec
DE                18.00 usec
TE                298.0 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        564.6299196 MHz
NUC1                19F
P1                18.25 usec

F2 - Processing parameters
SI               131072
SF          564.6864212 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              58.057 ppm
F1             32784.16 Hz
F2P            -258.174 ppm
F2           -145787.27 Hz
PPMCM          13.86979 ppm/cm
HZCM         7832.08057 Hz/cm
```

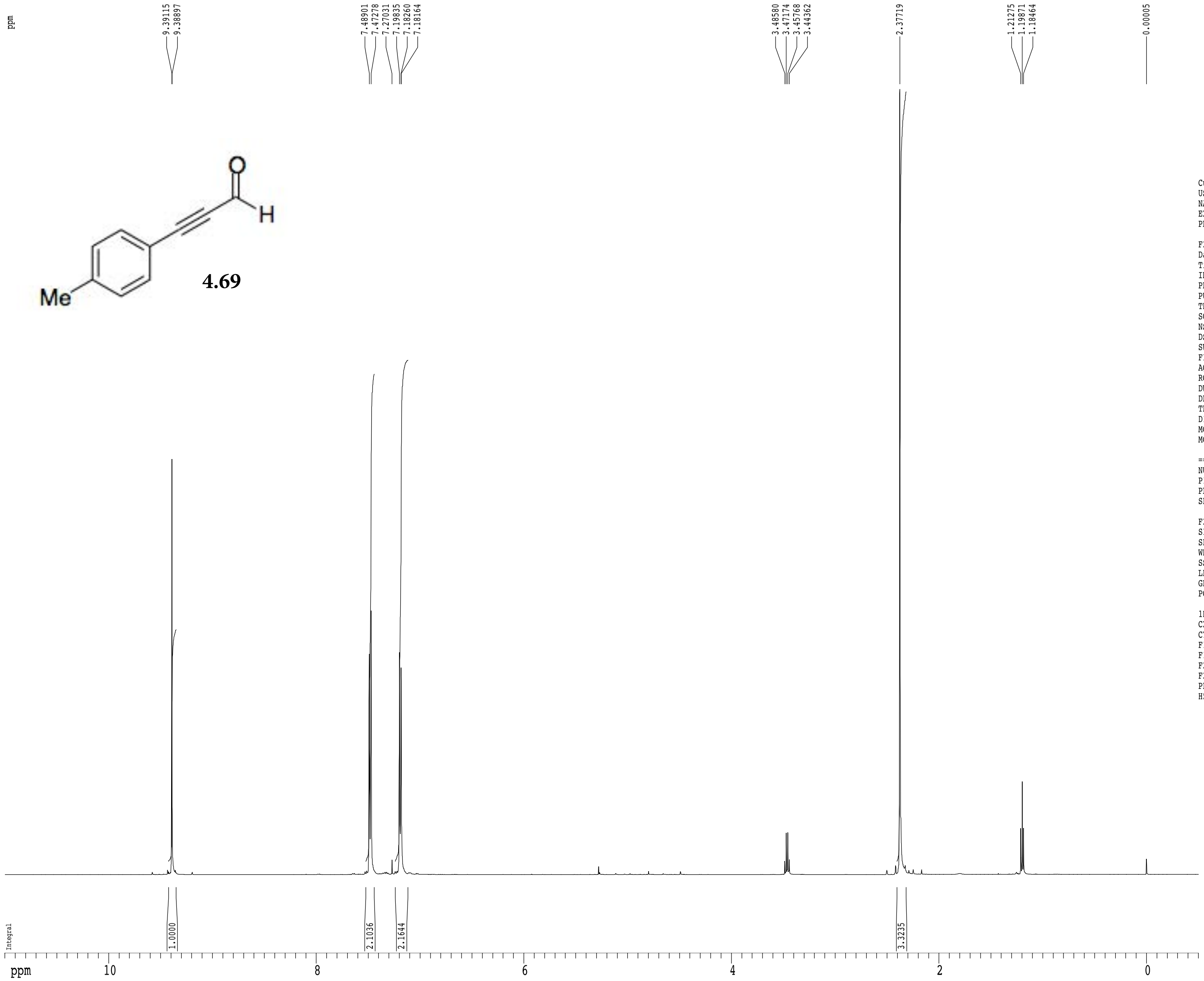
1H spectrum



4.68

```
Current Data Parameters
USER             khewitt1
NAME      ACM-I-152-156-check
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20200206
Time              10.14
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT         CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                406.4
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300233 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

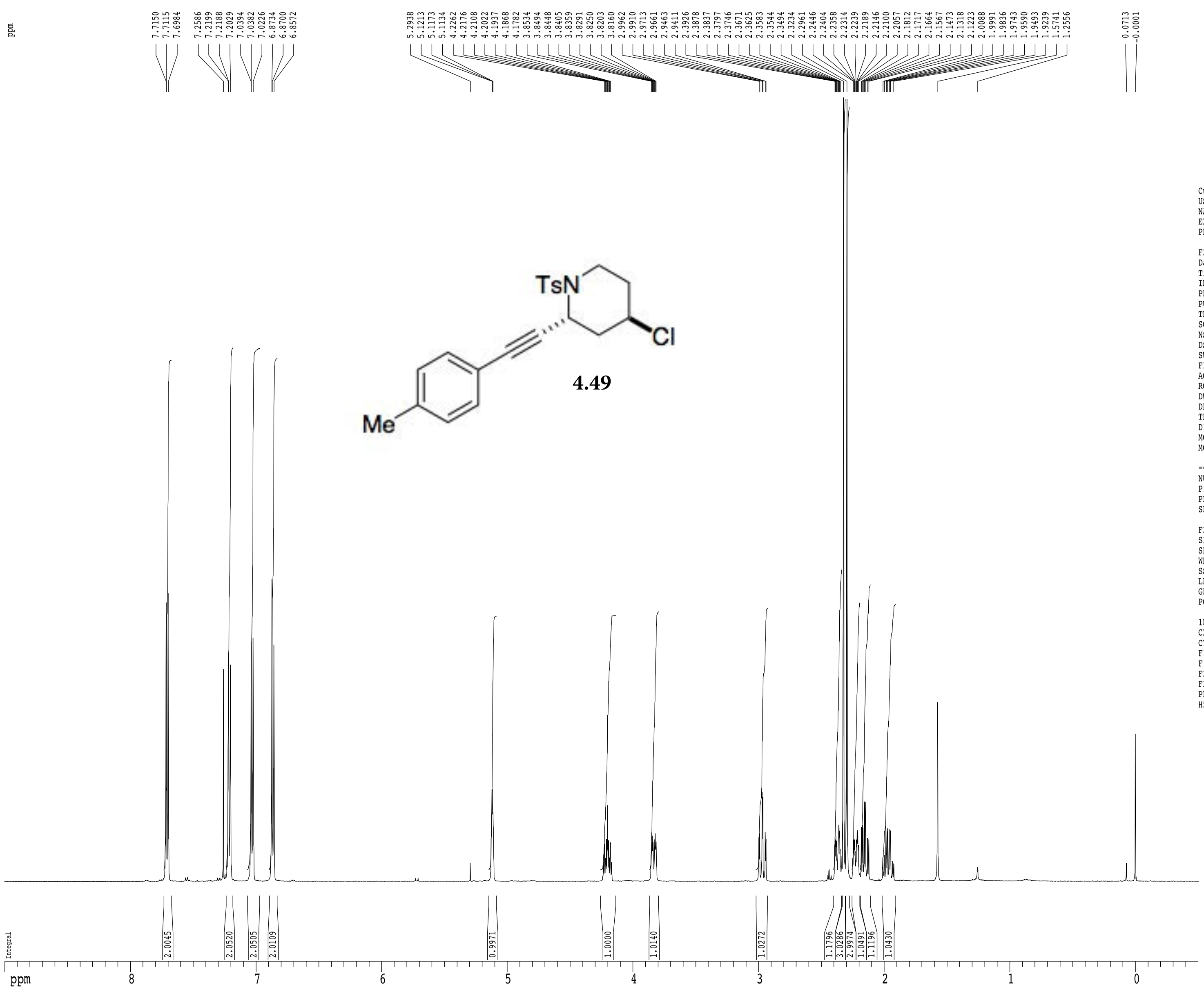
1H spectrum



4.69

```
Current Data Parameters
USER          khewitt1
NAME       ACM-I-159c1
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20200214
Time             15.59
INSTRUM          gn500
PROBHD   5 mm broadband
PULPROG           zg30
TD               81728
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998774 sec
RG                40.3
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -5.00 dB
SFO1       498.8534919 MHz

F2 - Processing parameters
SI               65536
SF         498.8500217 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P             11.000 ppm
F1             5487.35 Hz
F2P             -0.500 ppm
F2             -249.43 Hz
PPMCM          0.50439 ppm/cm
HZCM         251.61296 Hz/cm
```

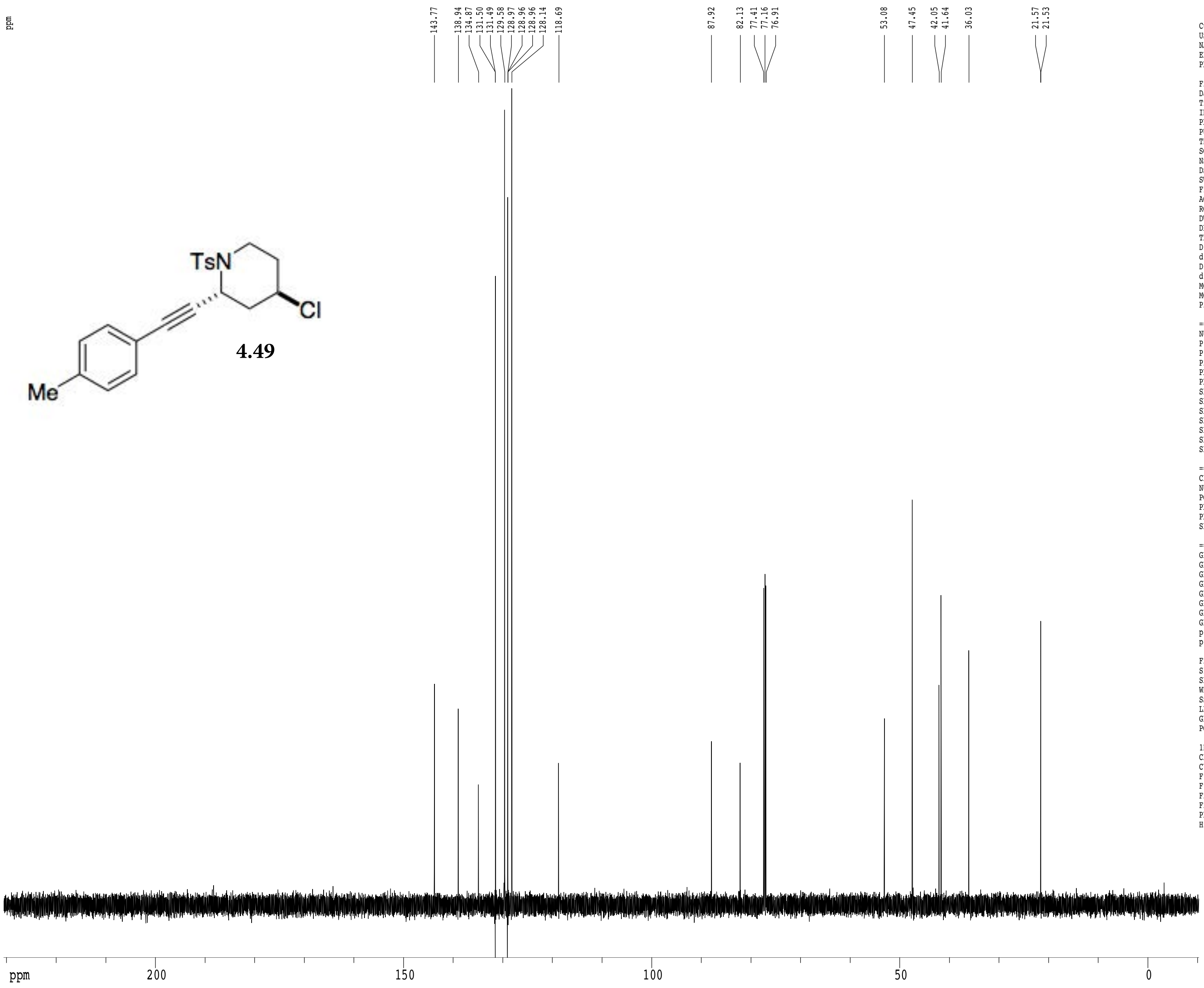
1H spectrum



4.49

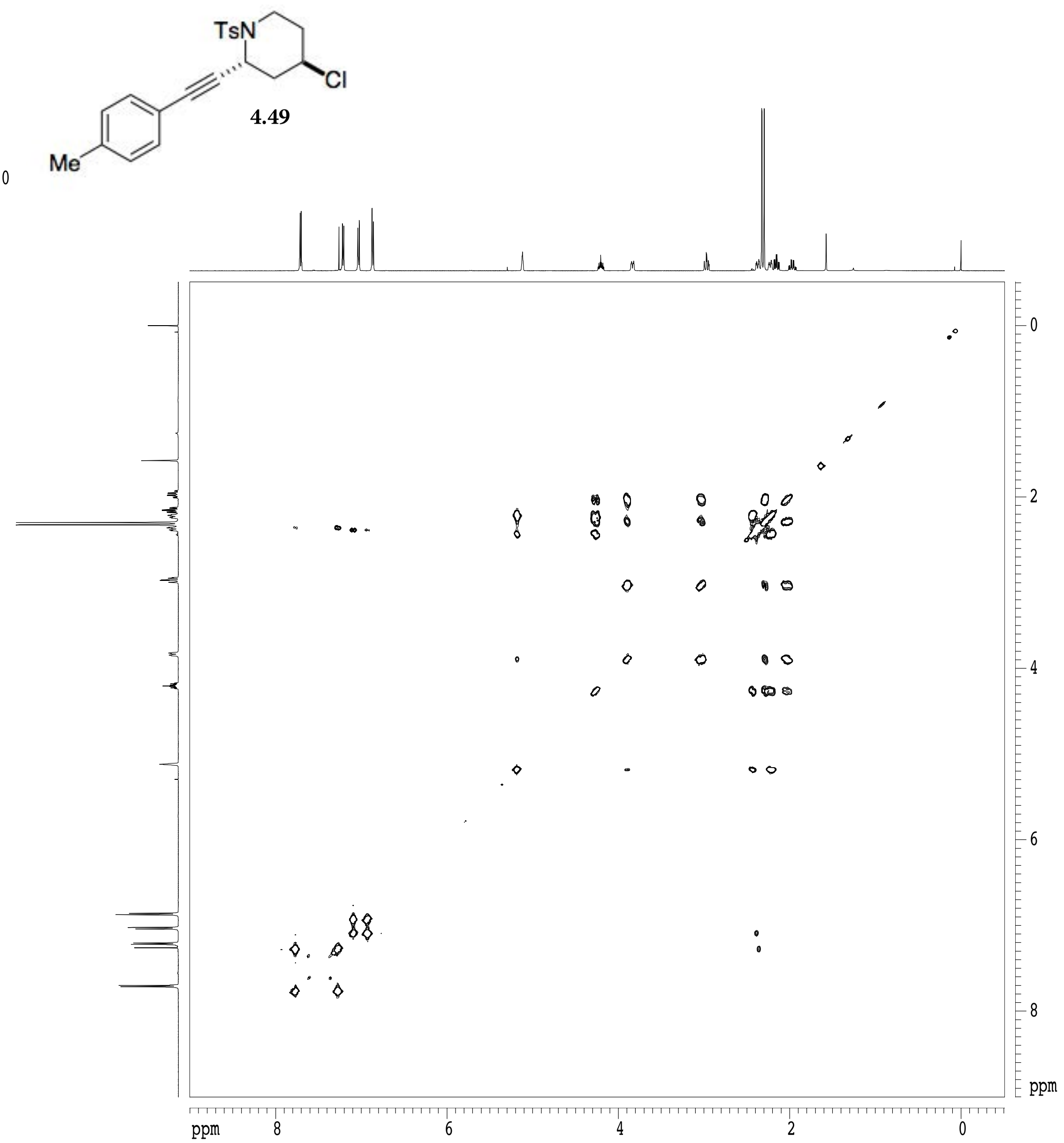
```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-192-SM-Z
EXPNO                5
PROCNO               1

F2 - Acquisition Parameters
Date_          20200716
Time              17.32
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200318 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling

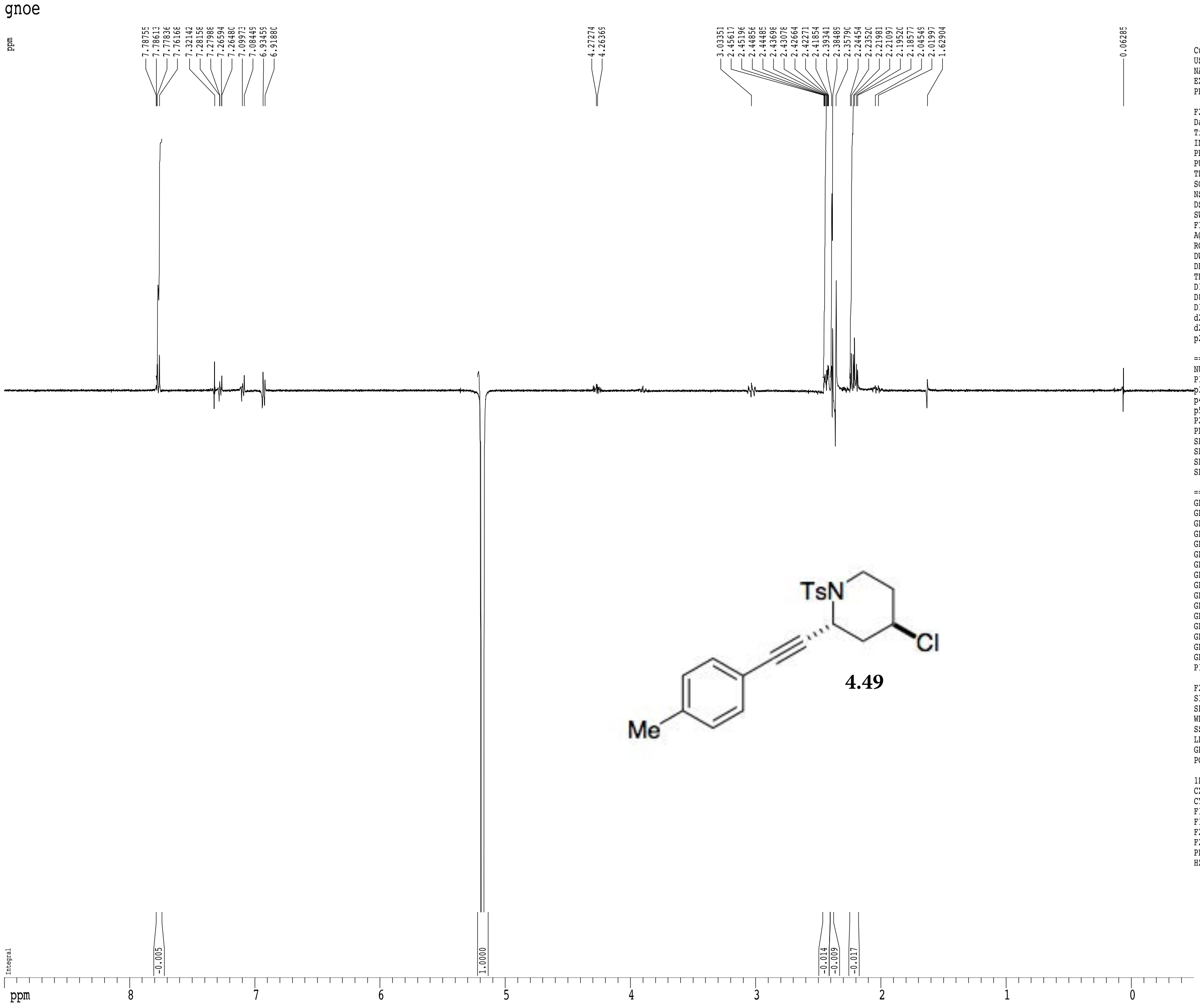


```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-192-SM-Z
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200715
Time               19.55
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

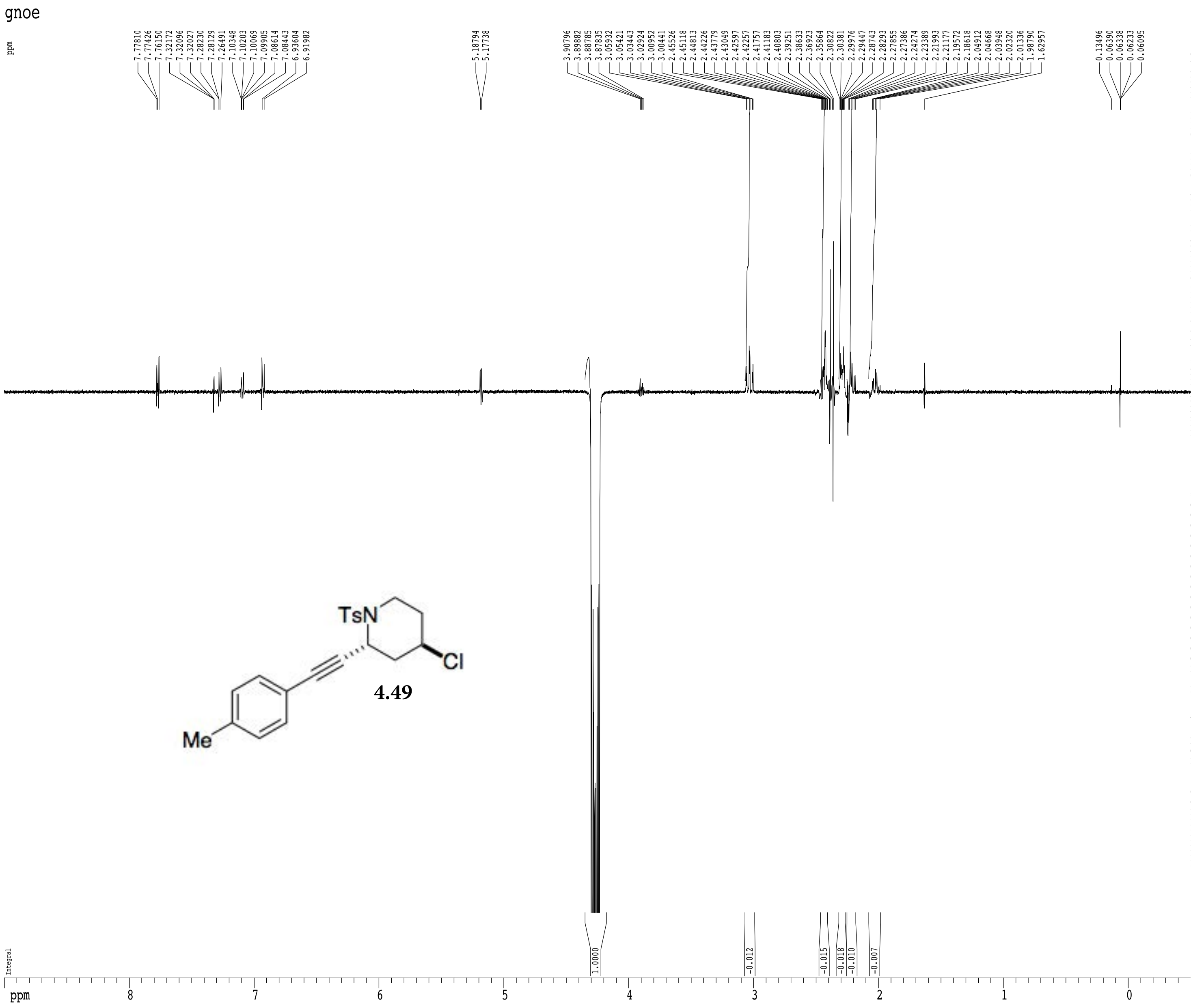
gcosy60


4.49

```
       Current Data Parameters
USER           khewitt1
NAME     KAH-III-192-SM-Z
EXPNO                 6
PROCNO                1

      F2 - Acquisition Parameters
Date_          20200716
Time              17.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                  181
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

       2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.002 ppm
F2LO            4503.14 Hz
F2PHI            -0.509 ppm
F2HI            -254.47 Hz
F1PLO             9.002 ppm
F1LO            4503.14 Hz
F1PHI            -0.509 ppm
F1HI            -254.47 Hz
F2PPMCM         0.63407 ppm/cm
F2HZCM        317.17416 Hz/cm
F1PPMCM         0.63407 ppm/cm
F1HZCM        317.17416 Hz/cm
```



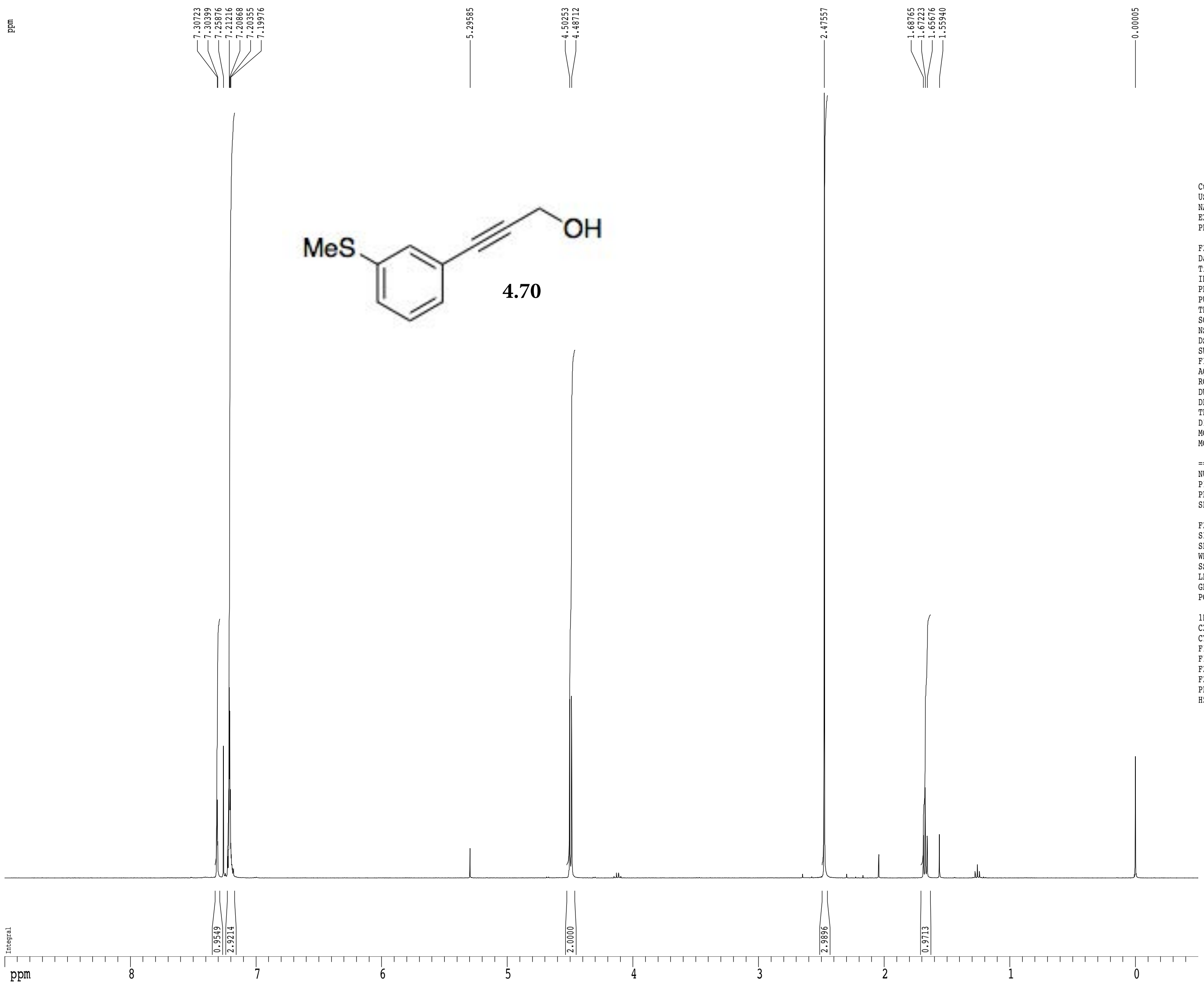
```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-192-SM-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200715
Time               19.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2225919 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



4.49

```
Current Data Parameters
USER             khewitt1
NAME     KAH-III-192-SM-Z
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200715
Time                19.54
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  161.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2221338 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

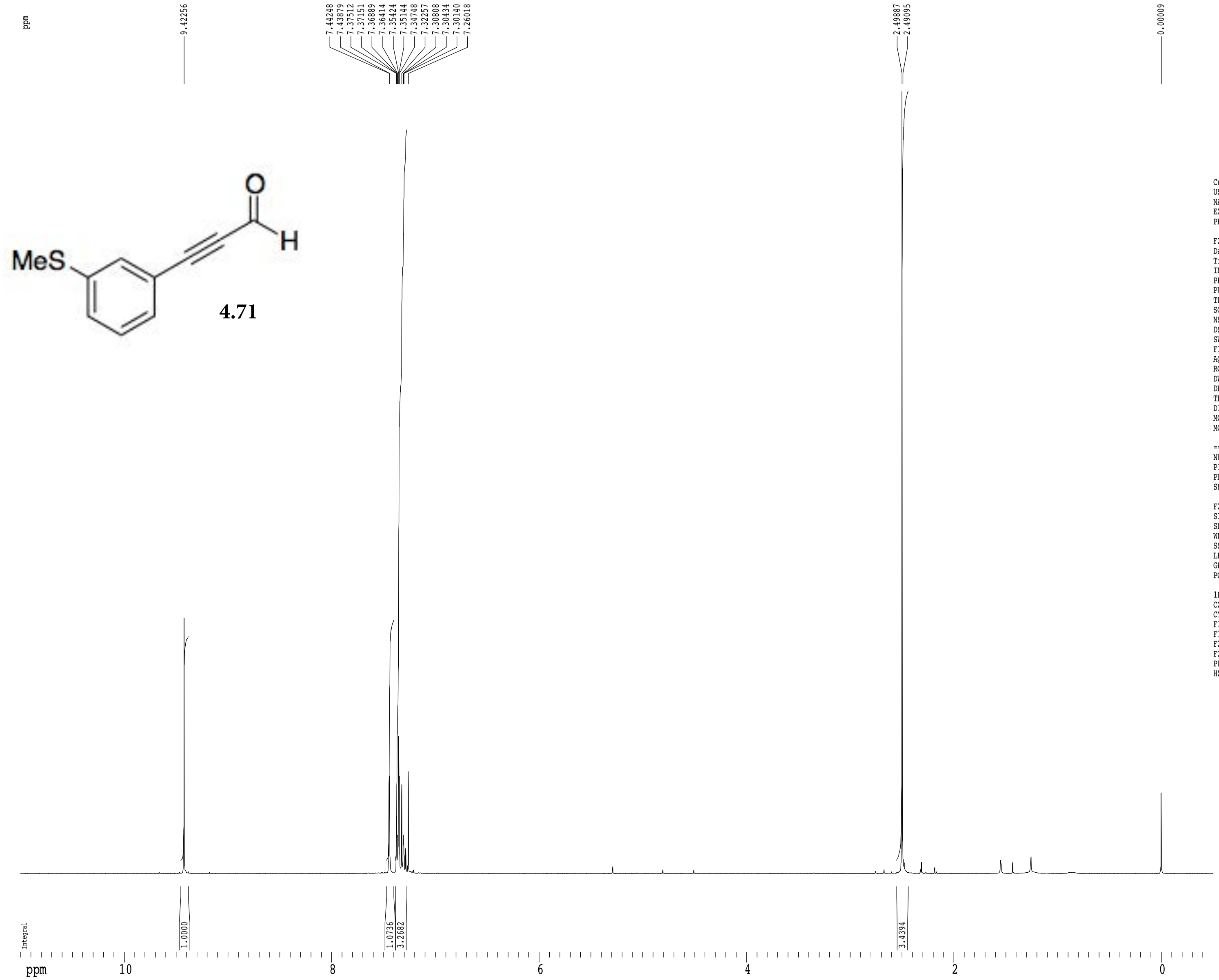
1H spectrum



4.70

```
Current Data Parameters
USER          khewitt1
NAME      ACM-I-164-big
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200306
Time               9.36
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                645.1
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300218 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

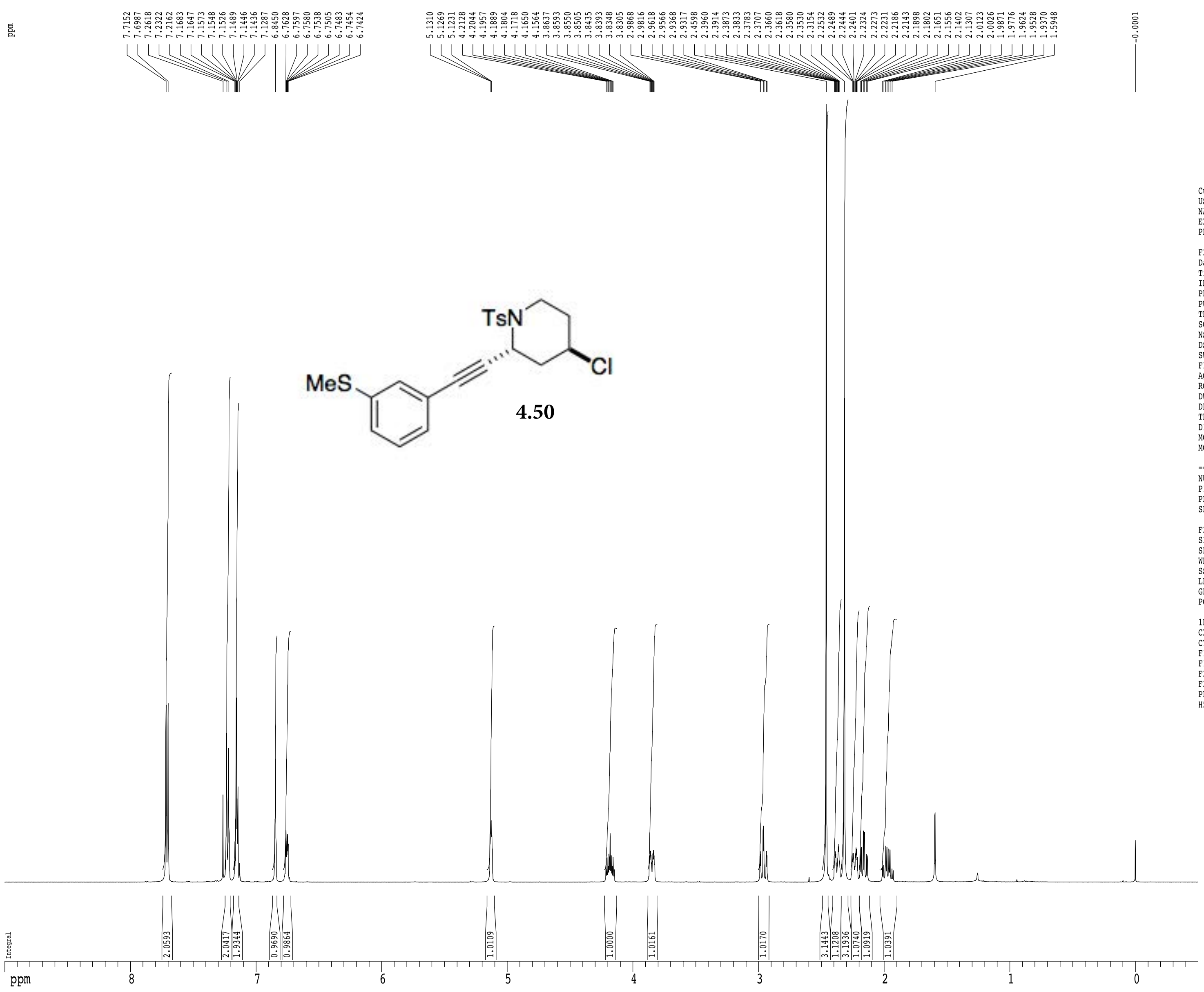
1H spectrum



4.71

```
Current Data Parameters
USER           khewitt1
NAME     ACM-I-169-checking
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200316
Time              18.16
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                574.7
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300214 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

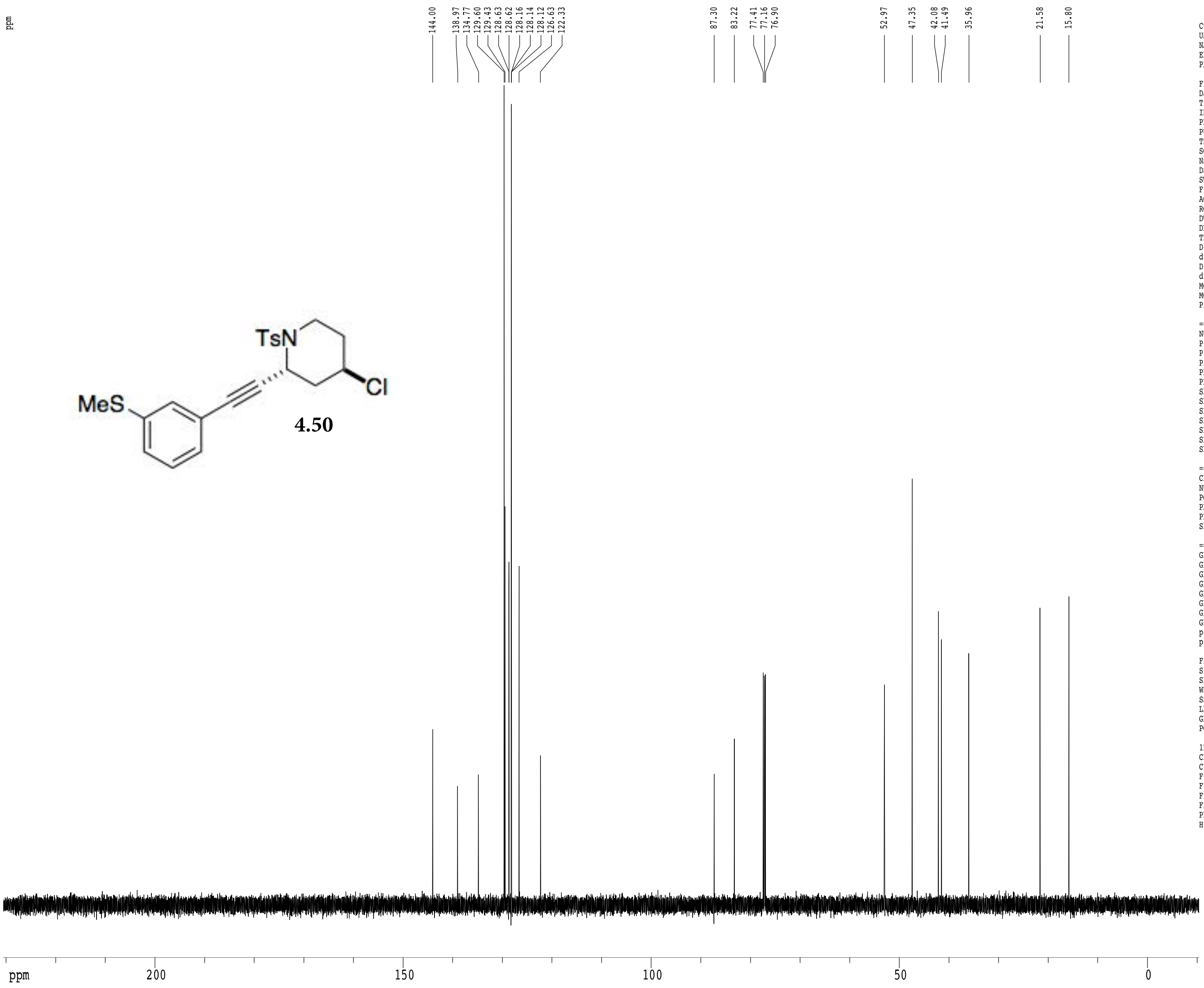
1H spectrum



4.50

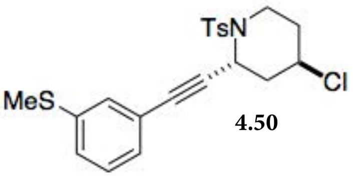
```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-193-SM-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20200711
Time              17.38
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200303 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



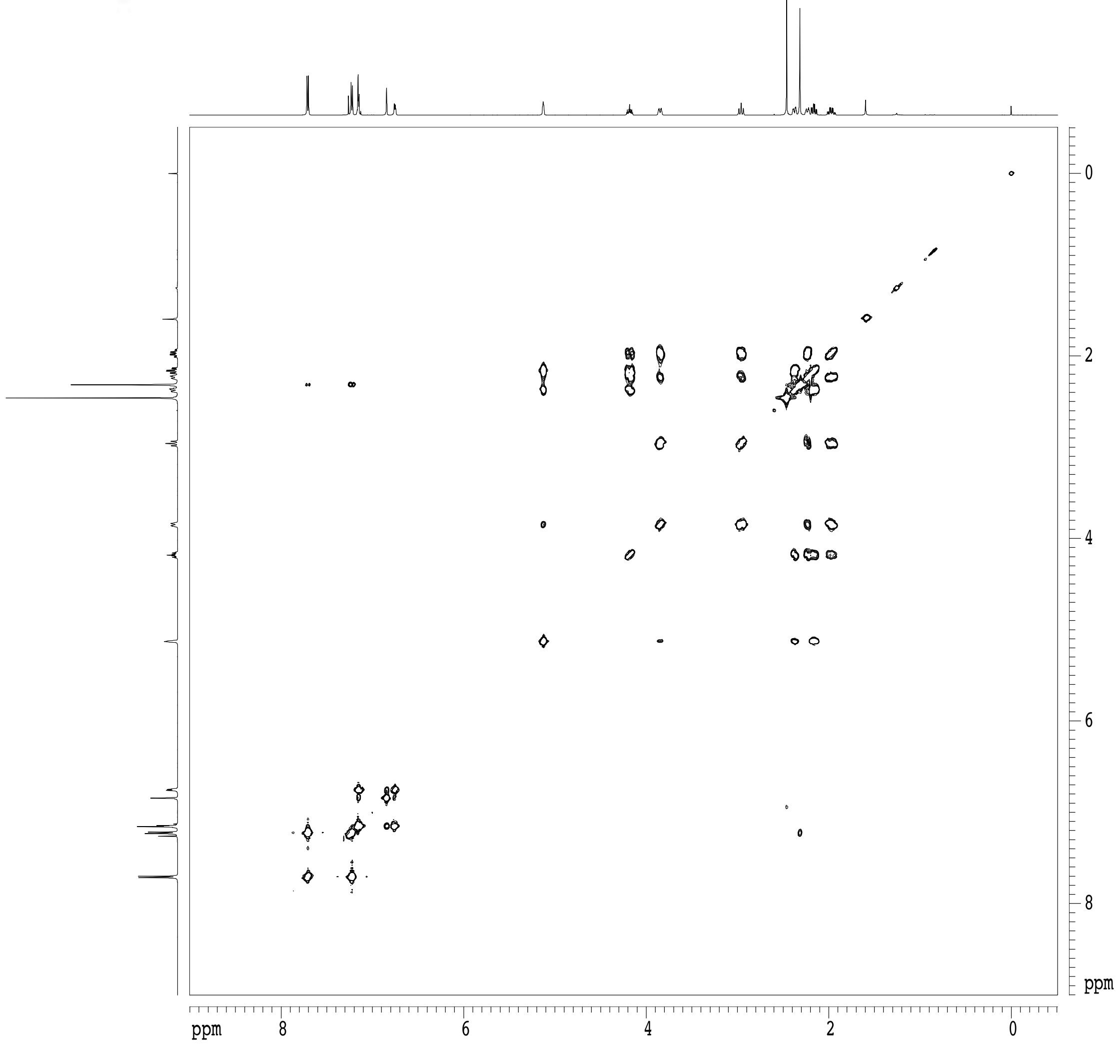
4.50

```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-193-SM-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200710
Time              18.28
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT          CDCl3T
NS                   80
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804103 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.529 ppm
F1             28996.03 Hz
F2P             -10.391 ppm
F2             -1307.00 Hz
PPMCM          10.56667 ppm/cm
HZCM         1329.08032 Hz/cm
```



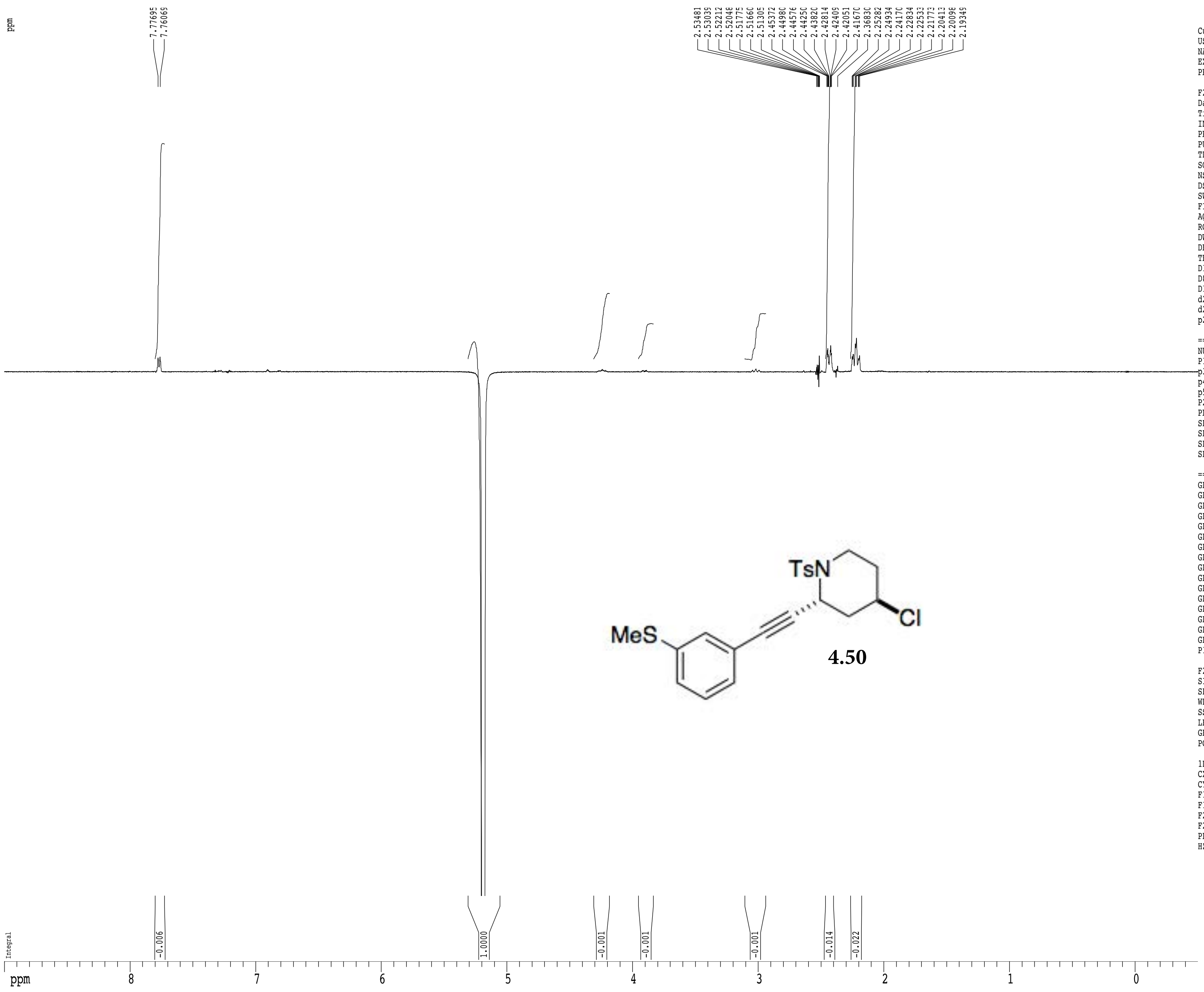
4.50

gcosy



```
        Current Data Parameters
USER            khewitt1
NAME     KAH-III-193-SM-Z
EXPNO                  6
PROCNO                 1

       F2 - Acquisition Parameters
Date_           20200713
Time               18.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                 228.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

       F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

       F2 - Processing parameters
SI                  1024
SF           500.2200309 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

       F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200309 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.003 ppm
F2LO             4503.54 Hz
F2PHI             -0.508 ppm
F2HI             -254.07 Hz
F1PLO              9.003 ppm
F1LO             4503.54 Hz
F1PHI             -0.508 ppm
F1HI             -254.07 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```

gnoe



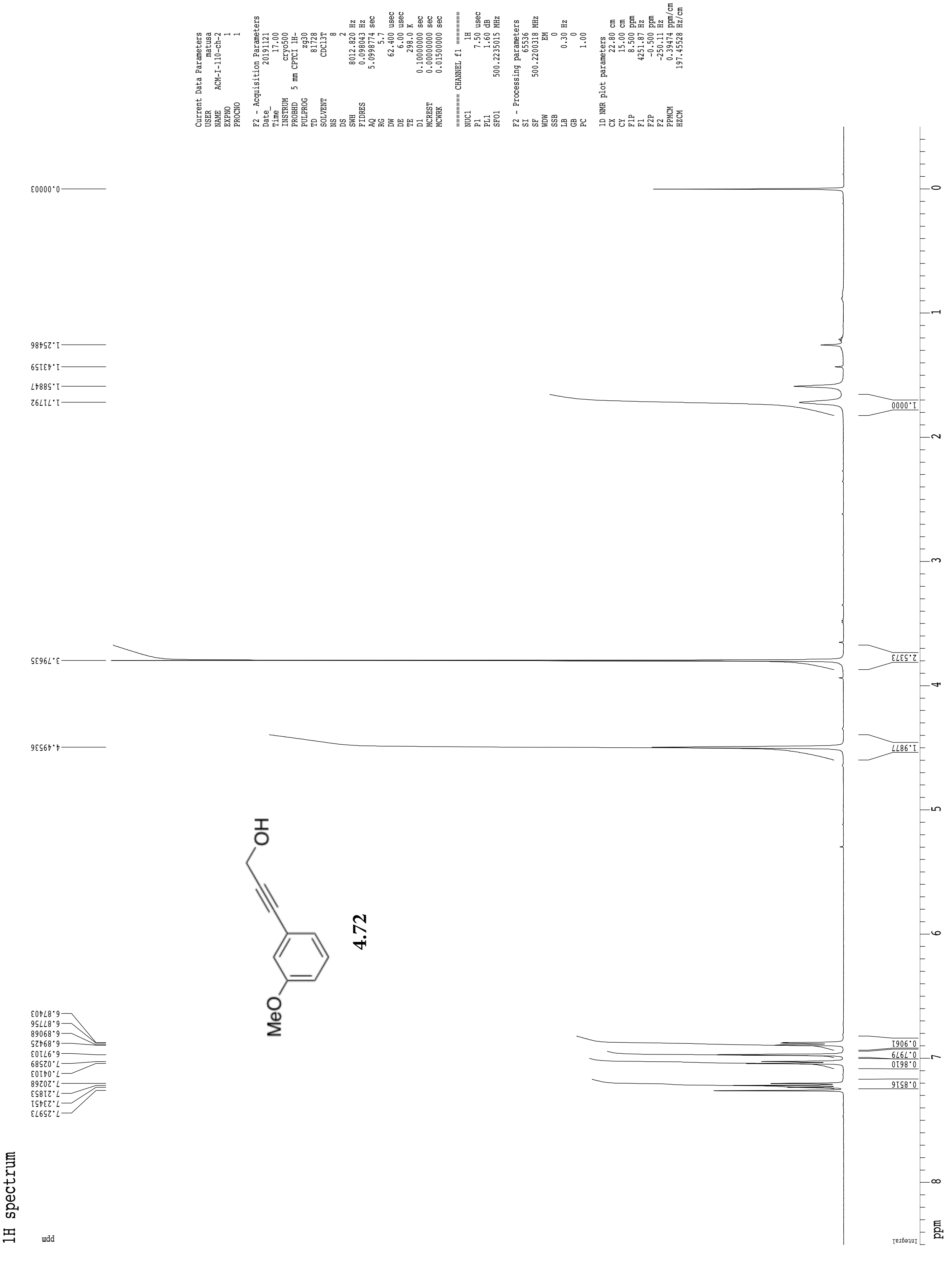
4.50

```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-193-SM-Z
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_         20200713
Time             18.27
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD               65536
SOLVENT          CDCl3
NS                 128
DS                   8
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ           4.0894966 sec
RG                90.5
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          1.00000000 sec
D8          0.50000000 sec
D16         0.00020000 sec
d21         0.33376500 sec
d22         0.16399699 sec
p2               15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2225955 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

gnoe

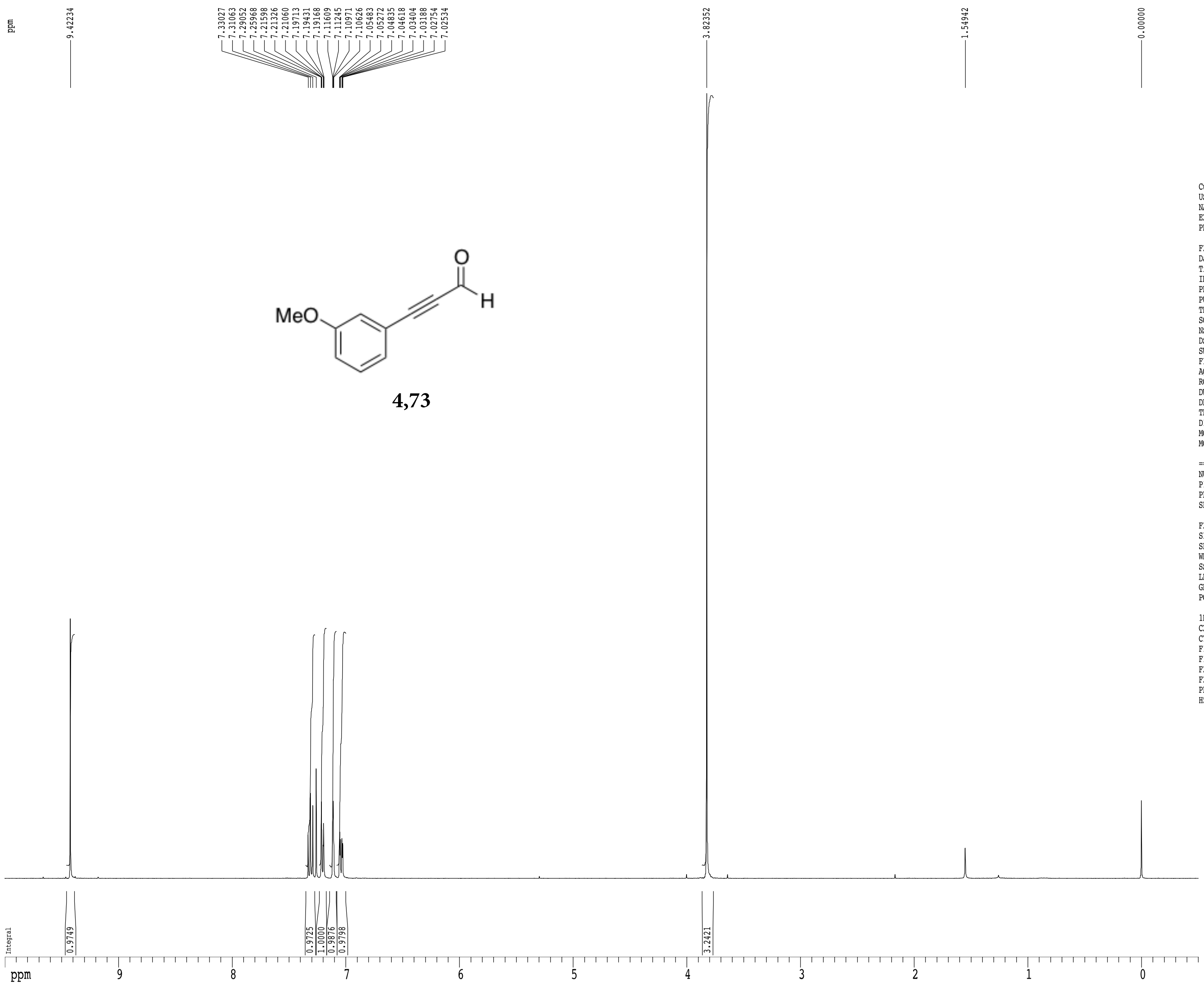
4.50

```
Current Data Parameters
USER              khewitt1
NAME      KAH-III-193-SM-Z
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200713
Time                 18.41
INSTRUM            cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                   161.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2221220 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```


1H spectrum
ppm
0.00003
1.25486
1.43159
1.58847
1.71792
3.79635
4.49536
6.87403
6.87756
6.89068
6.89425
6.97103
7.02589
7.04103
7.20268
7.21853
7.23451
7.25973
Current Data Parameters
USER matusa
NAME ACM-I-110-ch-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191121
Time 17.00
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200318 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 8.500 ppm
F1 4251.87 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.39474 ppm/cm
HZCM 197.45528 Hz/cm
MeO
OH
1.0000
2.5373
1.9877
0.9061
0.7979
0.8610
0.8516
Integral
0
1
2
3
4
5
6
7
8
ppm

4.72

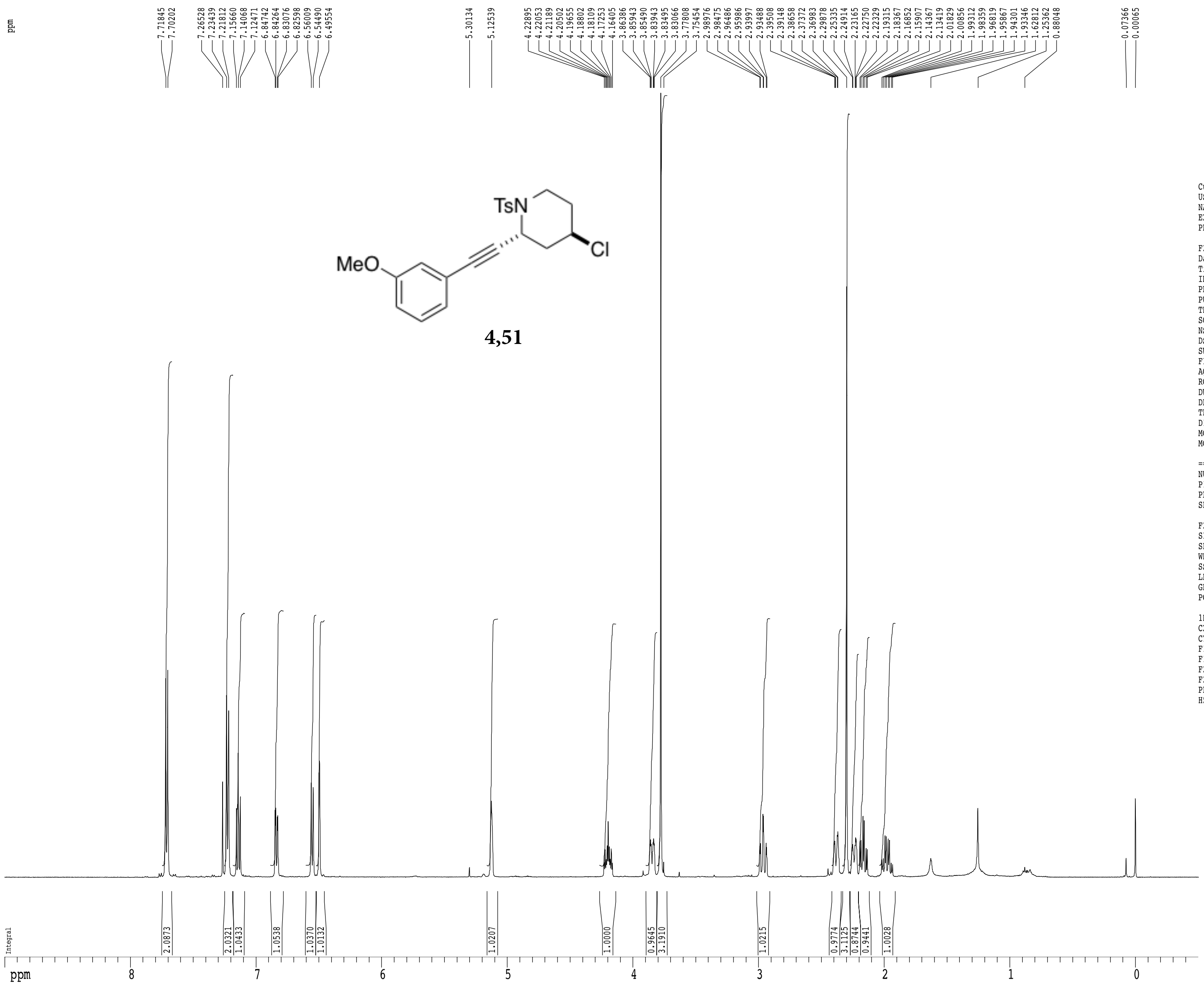
1H spectrum



4,73

```
Current Data Parameters
USER           nhirbawi
NAME     NH-1-44-column
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200821
Time              15.55
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH          6410.256 Hz
FIDRES       0.097813 Hz
AQ          5.1118579 sec
RG                574.7
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300216 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              10.000 ppm
F1              4001.30 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.46053 ppm/cm
HZCM          184.27042 Hz/cm
```

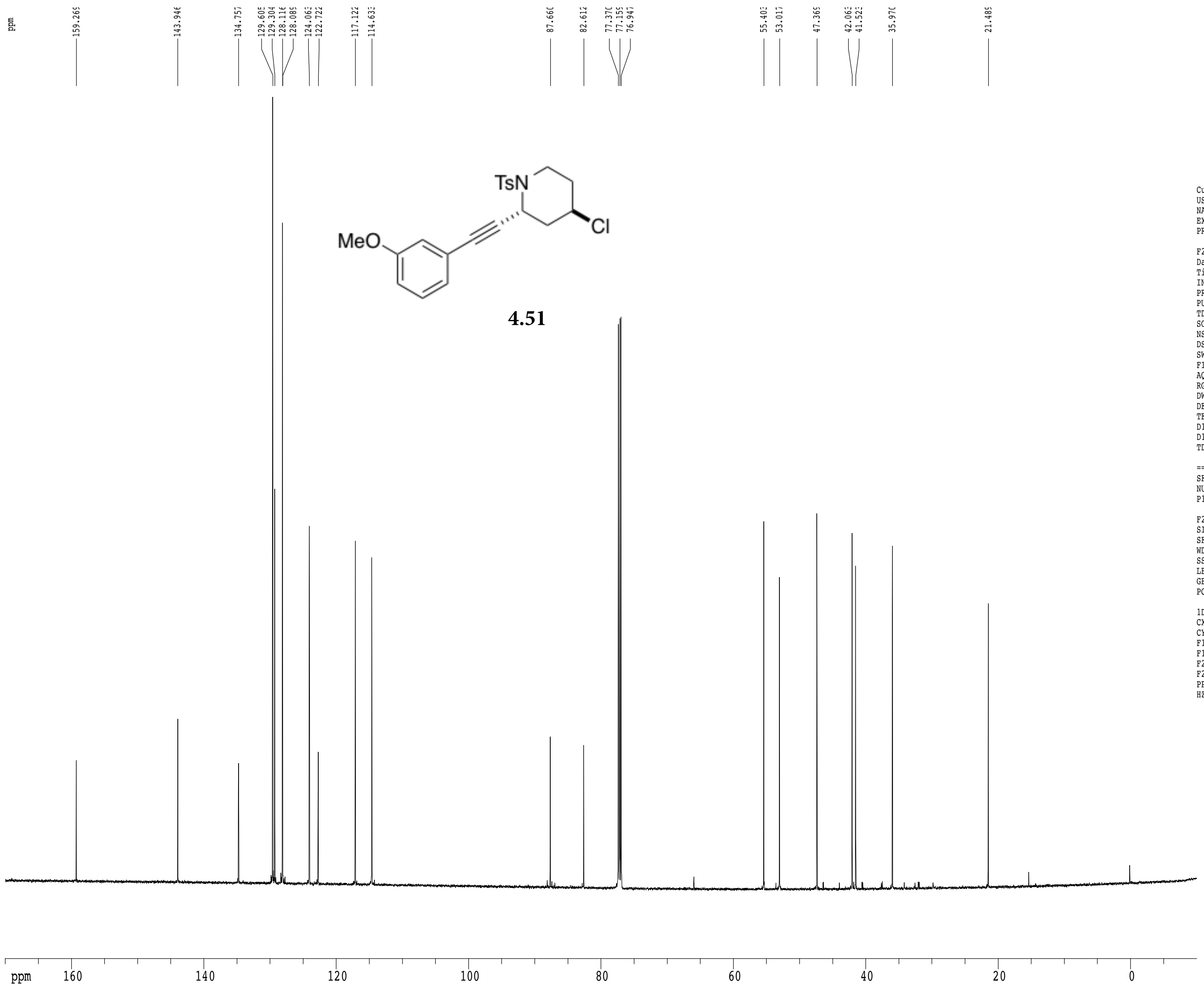
1H spectrum



4,51

```
Current Data Parameters
USER              tthane
NAME          ACM-1-114
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200718
Time               9.03
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                560.9 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200289 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

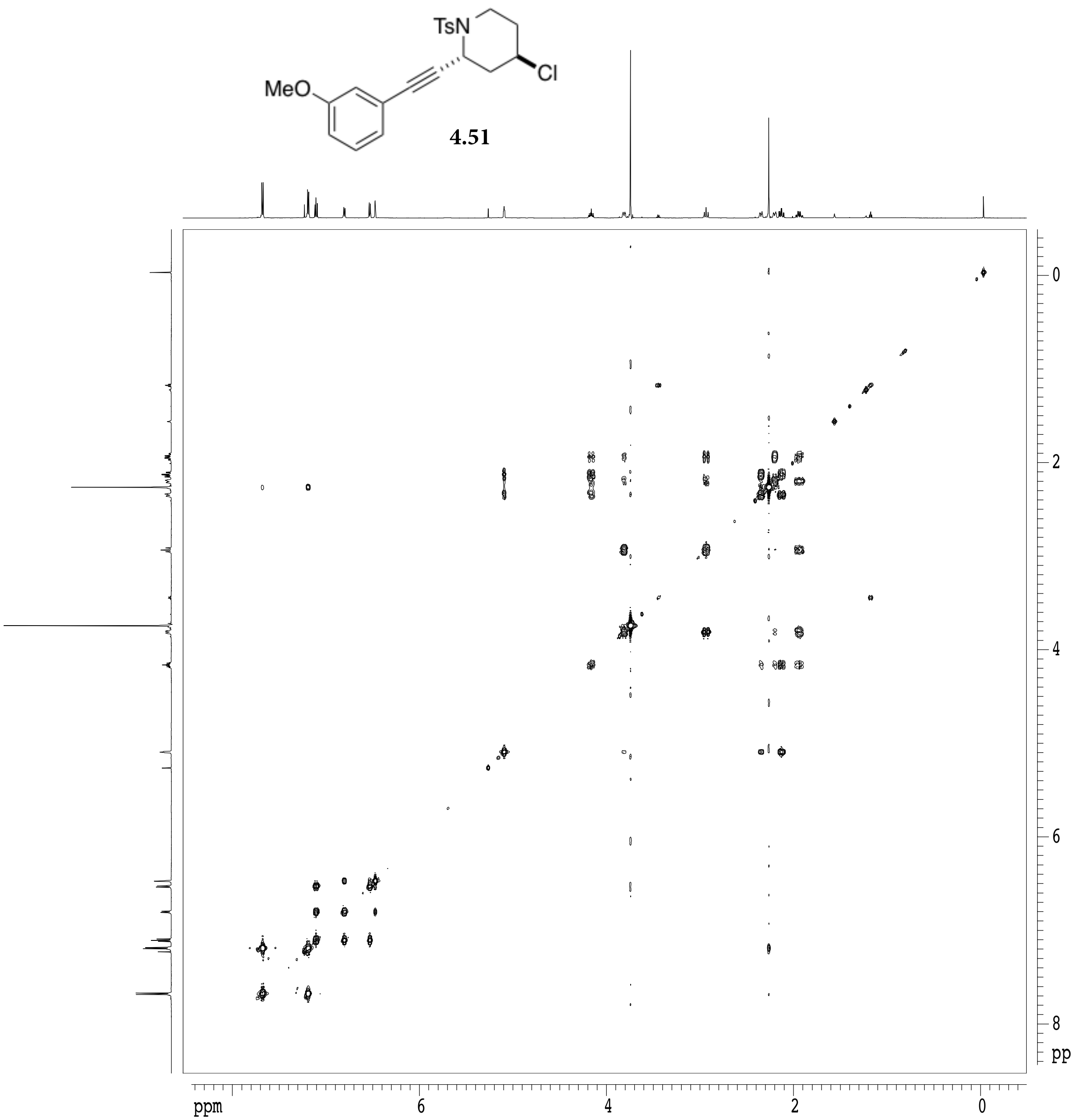
carbon



4.51

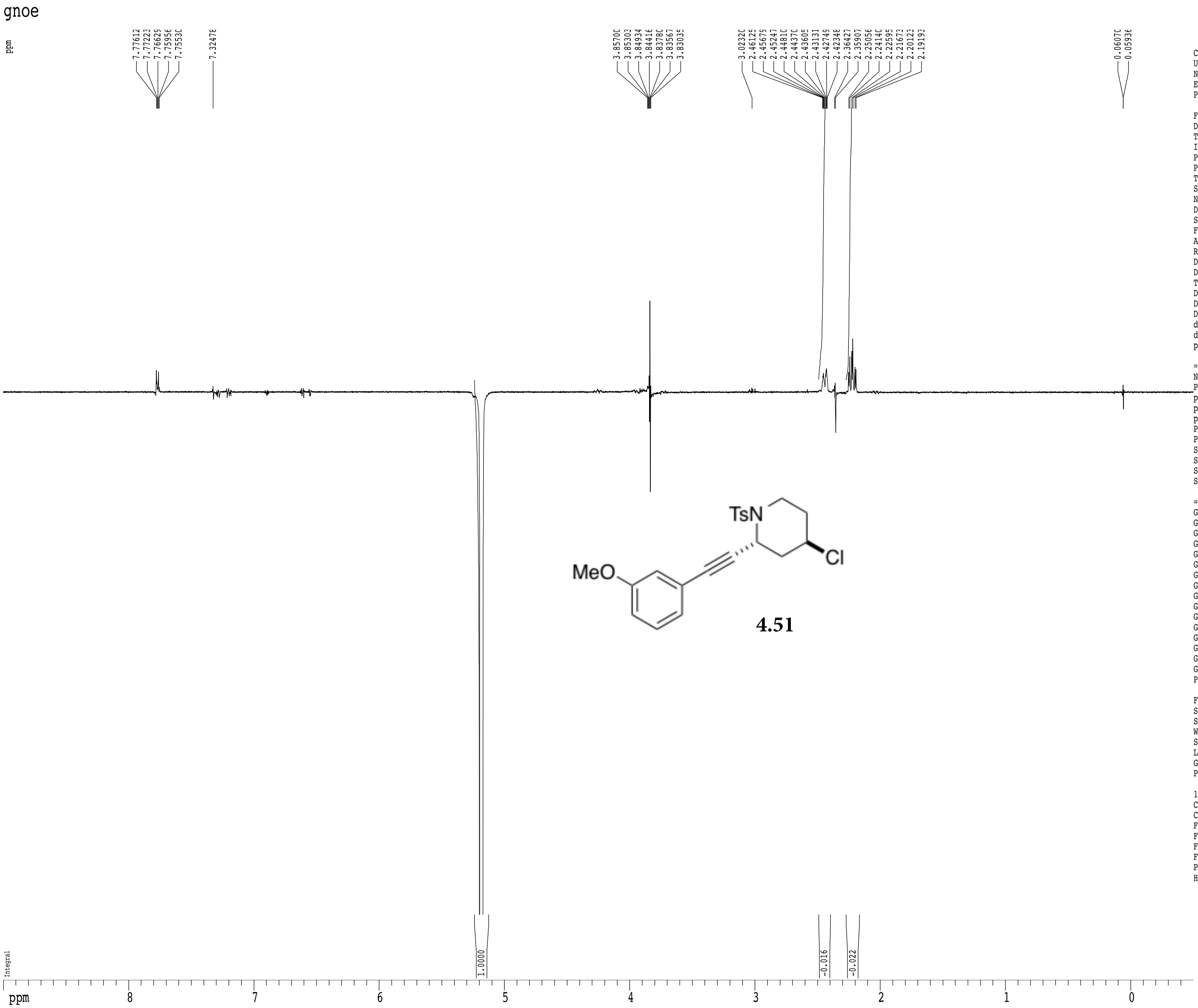
```
Current Data Parameters
USER               matusa
NAME     ACM-I-114-charac
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20191107
Time              18.48
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 504
DS                   4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                2050
DW              13.800 usec
DE               19.63 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1               13C
P1               10.10 usec

F2 - Processing parameters
SI               65536
SF         150.9027981 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P            170.000 ppm
F1            25653.48 Hz
F2P            -10.000 ppm
F2            -1509.03 Hz
PPMCM          7.89474 ppm/cm
HZCM        1191.33789 Hz/cm
```

COSY



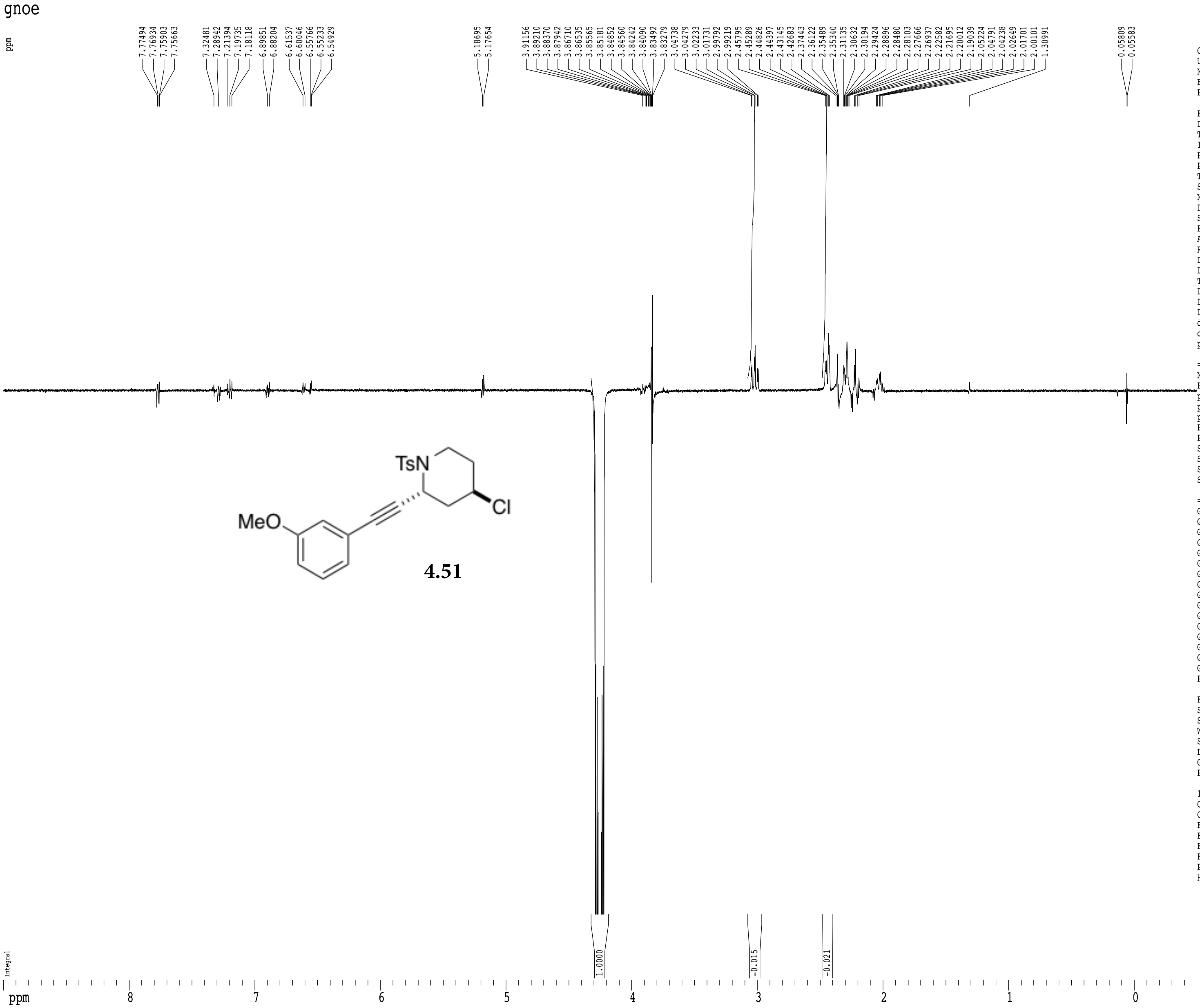
4.51

```
         Current Data Parameters
 USER              matusa
NAME     ACM-I-114-charac
 EXPNO                  4
 PROCNO                 1

      F2 - Acquisition Parameters
 Date_           20191107
 Time               19.03
 INSTRUM            av600
 PROBHD   5 mm CPBBO BB-
 PULPROG         cosygpqf
 TD                  2048
 SOLVENT           CDCl3T
 NS                     1
 DS                    16
 SWH             5411.255 Hz
 FIDRES          2.642215 Hz
 AQ             0.1892852 sec
 RG                   114
 DW                92.400 usec
 DE                 10.00 usec
 TE                 298.0 K
 D0            0.00000300 sec
 D1            1.48689198 sec
 D13           0.00000400 sec
 D16           0.00020000 sec
 IN0           0.00018480 sec

 ======== CHANNEL f1 ========
 SFO1         600.1324113 MHz
 NUC1                  1H
 P0                 12.00 usec
 P1                 12.00 usec

      F1 - Acquisition parameters
 ND0                    1
 TD                   256
 SFO1            600.1324 MHz
 FIDRES         21.137716 Hz
 SW                 9.017 ppm
 FnMODE                QF

      F2 - Processing parameters
 SI                  1024
 SF          600.1300549 MHz
 WDW                 SINE
 SSB                    0
 LB                  0.00 Hz
 GB                     0
 PC                  1.40

      F1 - Processing parameters
 SI                  1024
 MC2                   QF
 SF          600.1300549 MHz
 WDW                 SINE
 SSB                    0
 LB                  0.00 Hz
 GB                     0

      2D NMR plot parameters
 CX2                15.00 cm
 CX1                15.00 cm
 F2PLO              8.526 ppm
 F2LO             5116.95 Hz
 F2PHI             -0.490 ppm
 F2HI             -294.31 Hz
 F1PLO              8.526 ppm
 F1LO             5116.95 Hz
 F1PHI             -0.490 ppm
 F1HI             -294.31 Hz
 F2PPMCM          0.60112 ppm/cm
 F2HZCM         360.75040 Hz/cm
 F1PPMCM          0.60112 ppm/cm
 F1HZCM         360.75040 Hz/cm
```



4.51

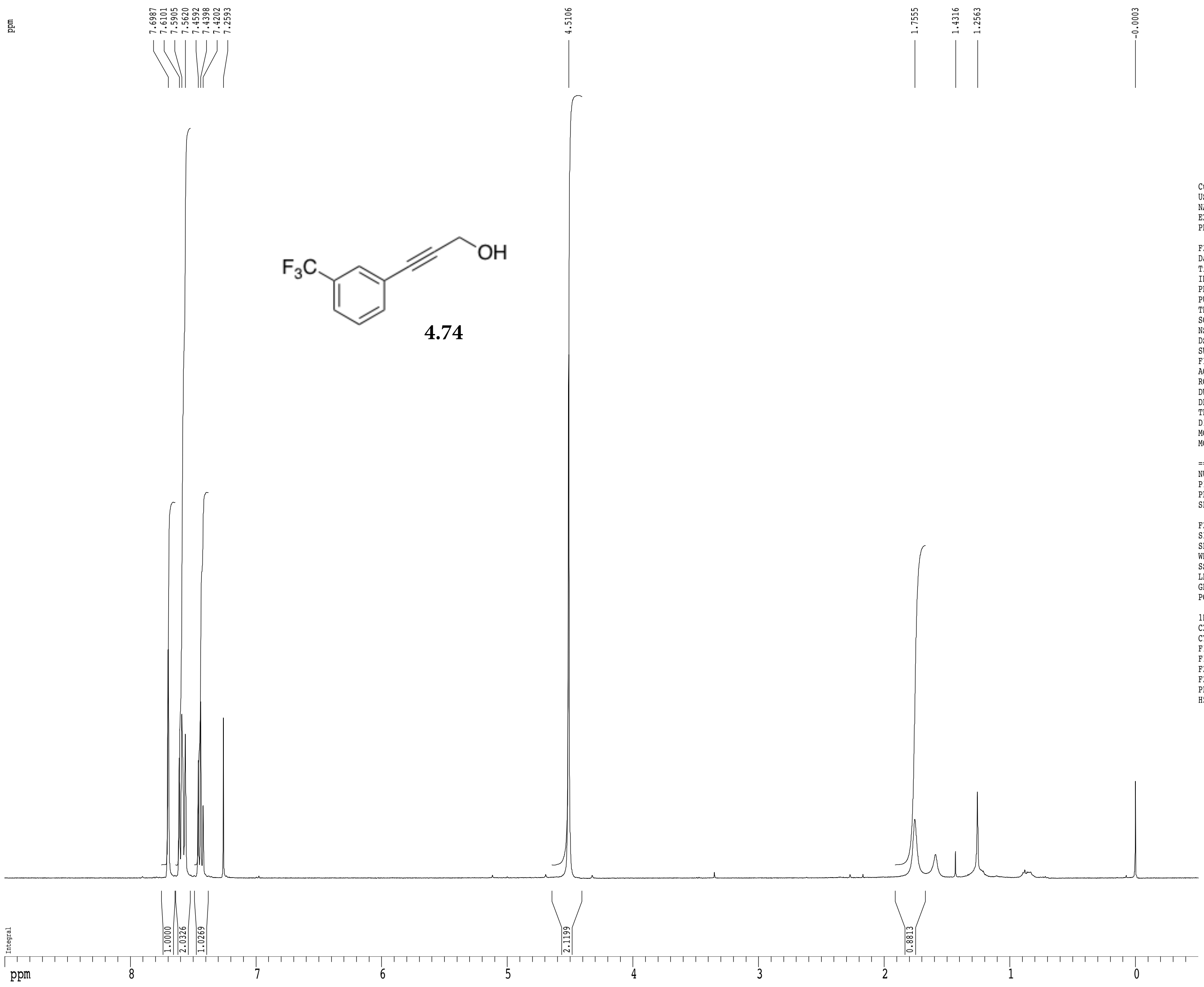
```
Current Data Parameters
USER              tthane
NAME      ACM-1-114NOE1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200718
Time               9.21
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  114
DW               62.400 usec
DE                 6.00 usec
TE                287.9 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2225925 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



4.51

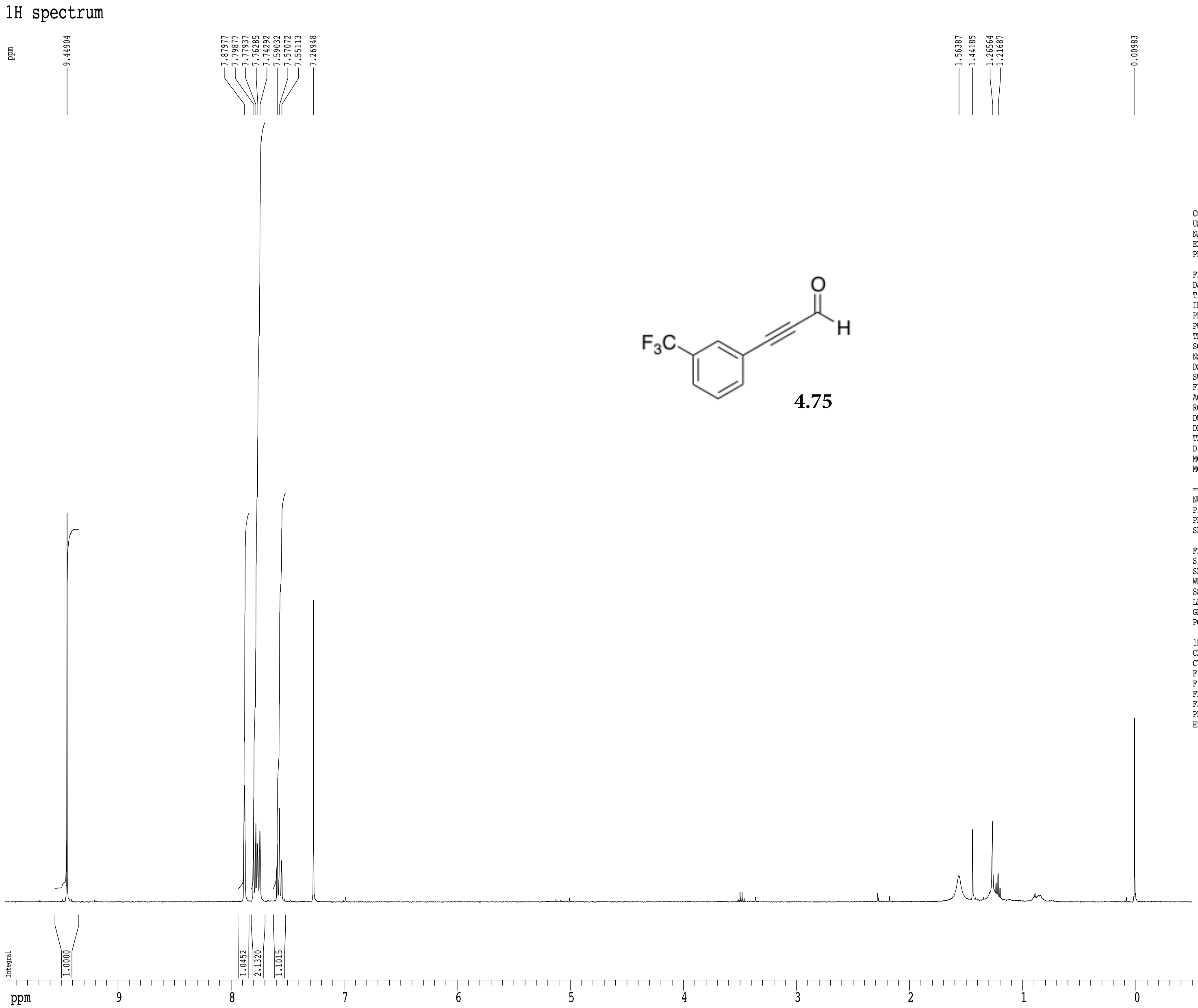
```
Current Data Parameters
USER              tthane
NAME        ACM-1-114NOE2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200718
Time                9.41
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   158
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 288.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2221282 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

1H spectrum



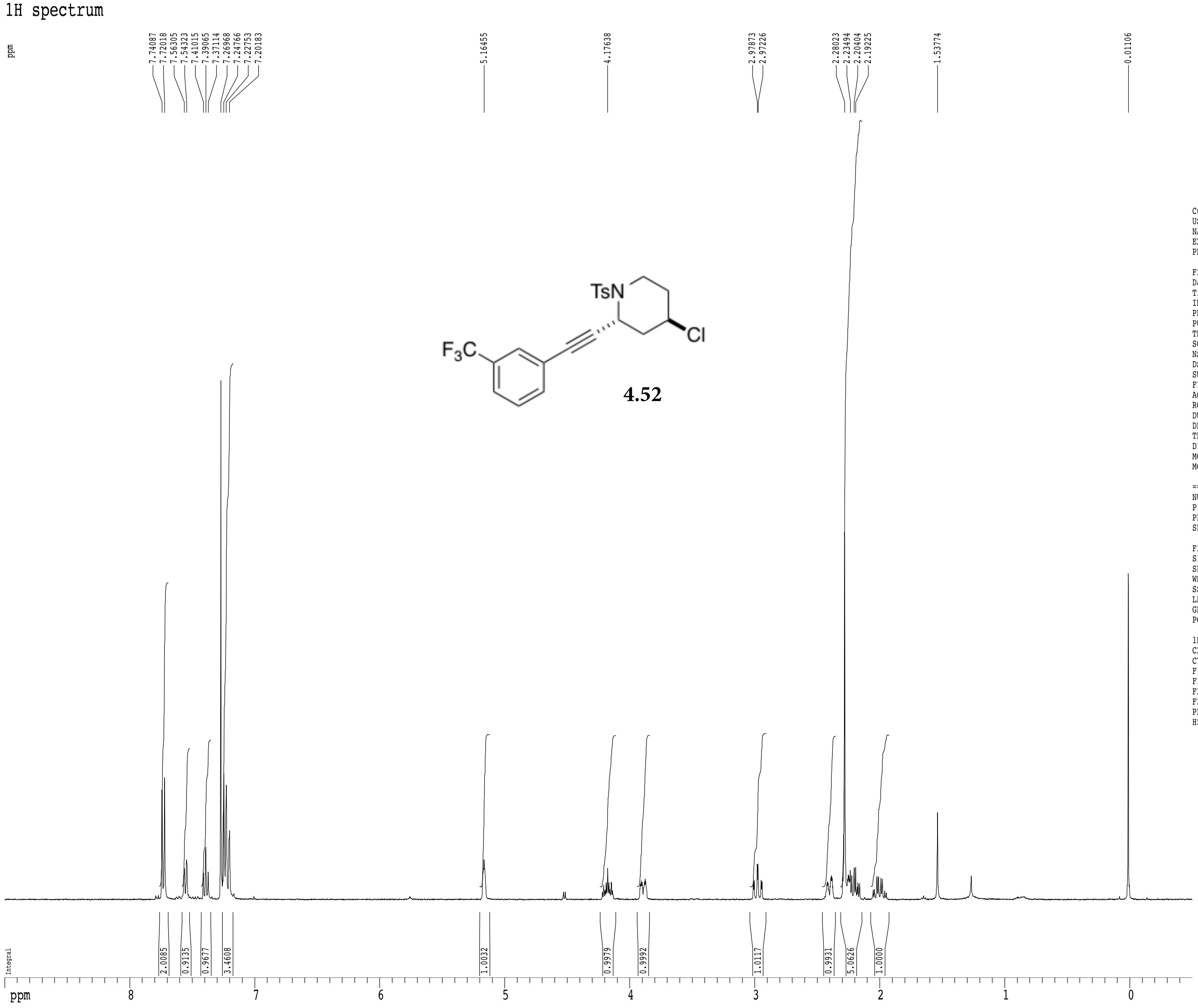
```
Current Data Parameters
USER            nhirbawi
NAME      NH-1-26-dry-1023
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201023
Time               11.34
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                   362
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300216 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 10.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

1H spectrum



4.75

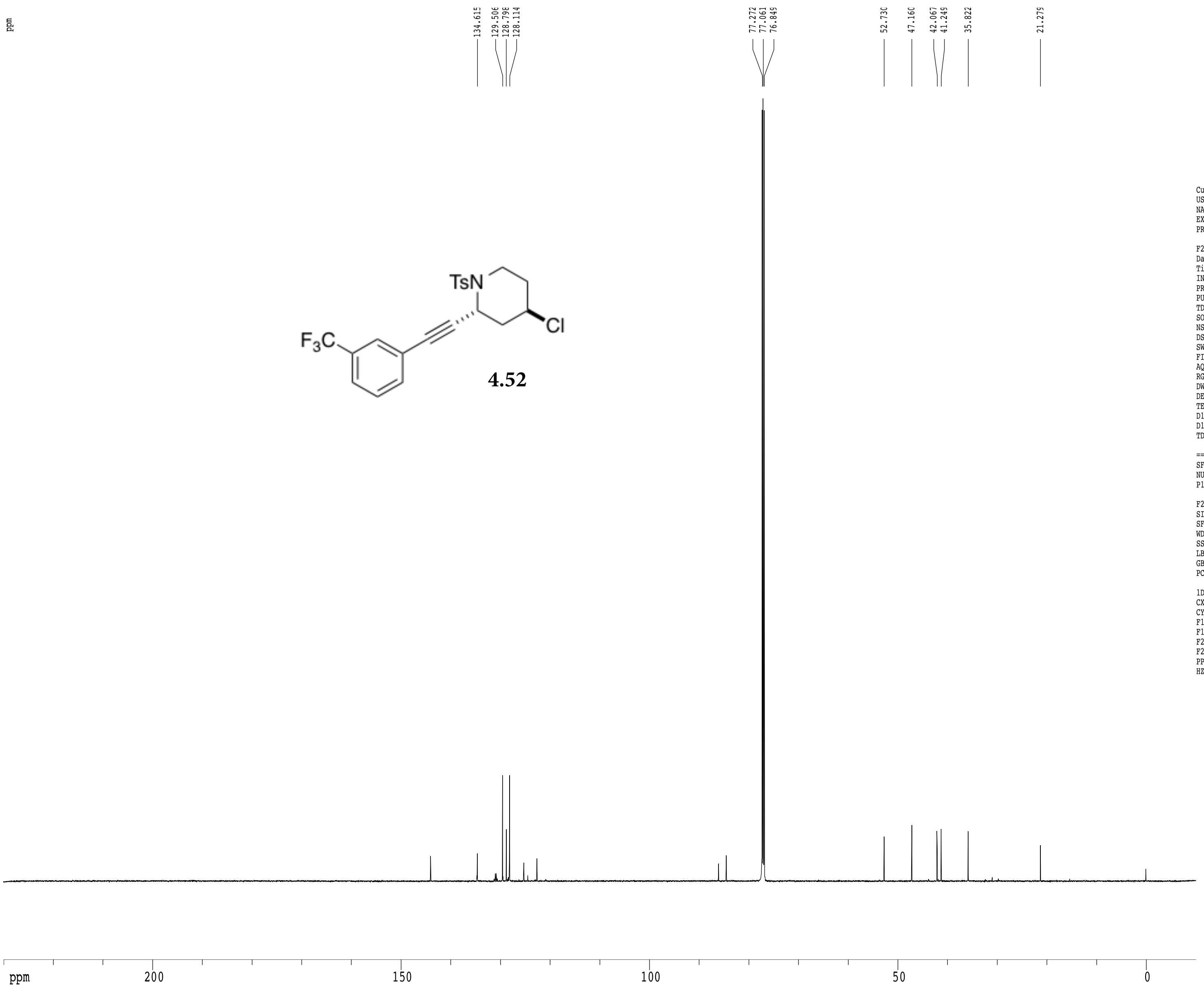
```
Current Data Parameters
USER          nhirbawi
NAME       NH-1-35-dry
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20201022
Time             18.29
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               65536
SOLVENT          CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG               812.7
DW              78.000 usec
DE                4.50 usec
TE               298.0 K
D1         0.10000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300175 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY                7.50 cm
F1P             10.000 ppm
F1             4001.30 Hz
F2P             -0.500 ppm
F2             -200.07 Hz
PPMCM          0.46053 ppm/cm
HZCM         184.27040 Hz/cm
```



4.52

```
Current Data Parameters
USER          nhirbawi
NAME     NH-1-39-on11-19
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201119
Time               16.33
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                1149.4
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 10.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

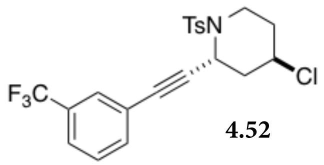
13C spectrum with 1H decoupling



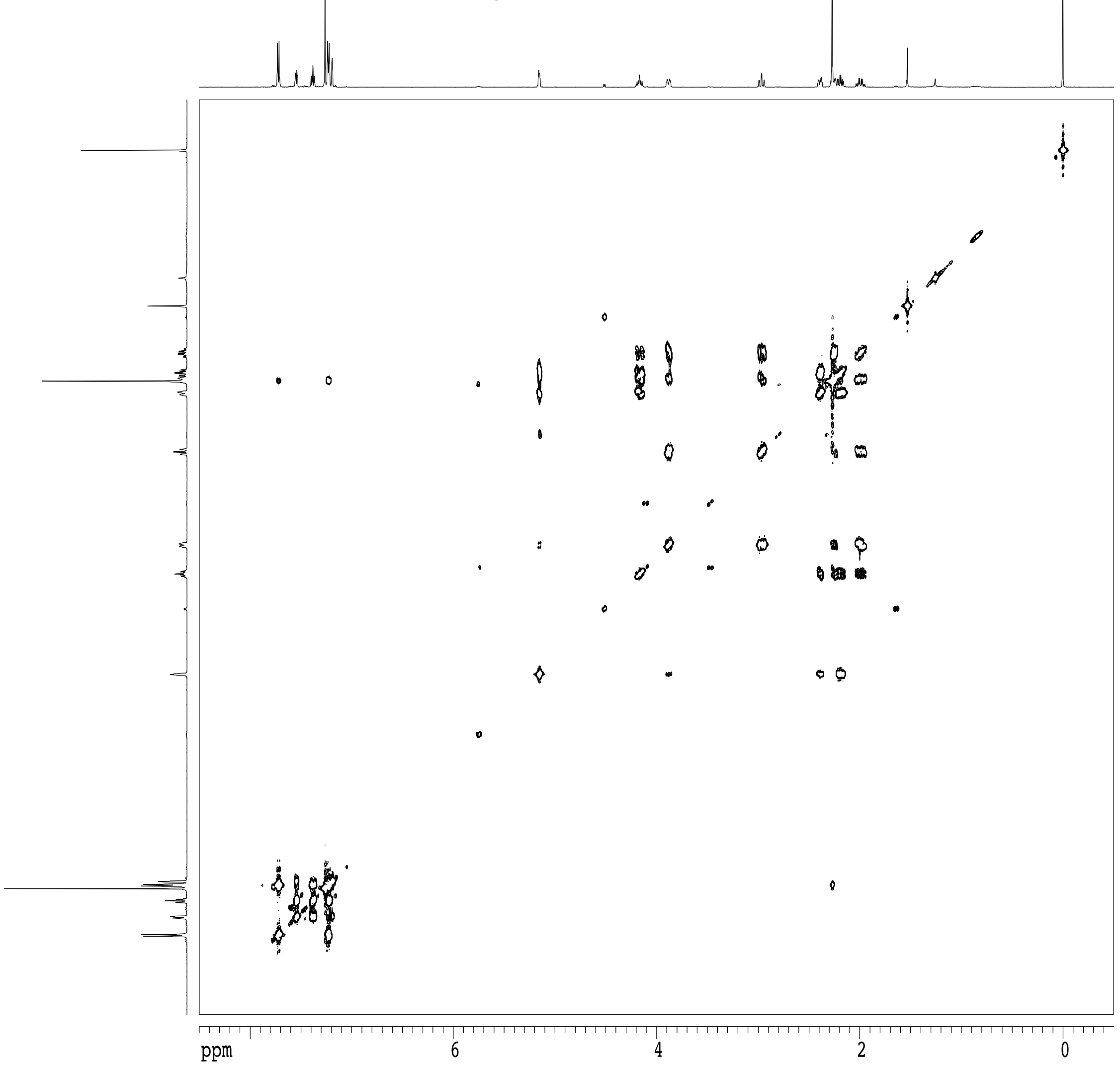
4.52

```
Current Data Parameters
USER           nhirbawi
NAME     NH-1-39-carbon-600
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200819
Time               8.46
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT          CDCl3T
NS                 1024
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                298.0 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9028085 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             230.000 ppm
F1             34707.64 Hz
F2P             -10.000 ppm
F2             -1509.03 Hz
PPMCM          10.52632 ppm/cm
HZCM         1588.45056 Hz/cm
```

gcosy60

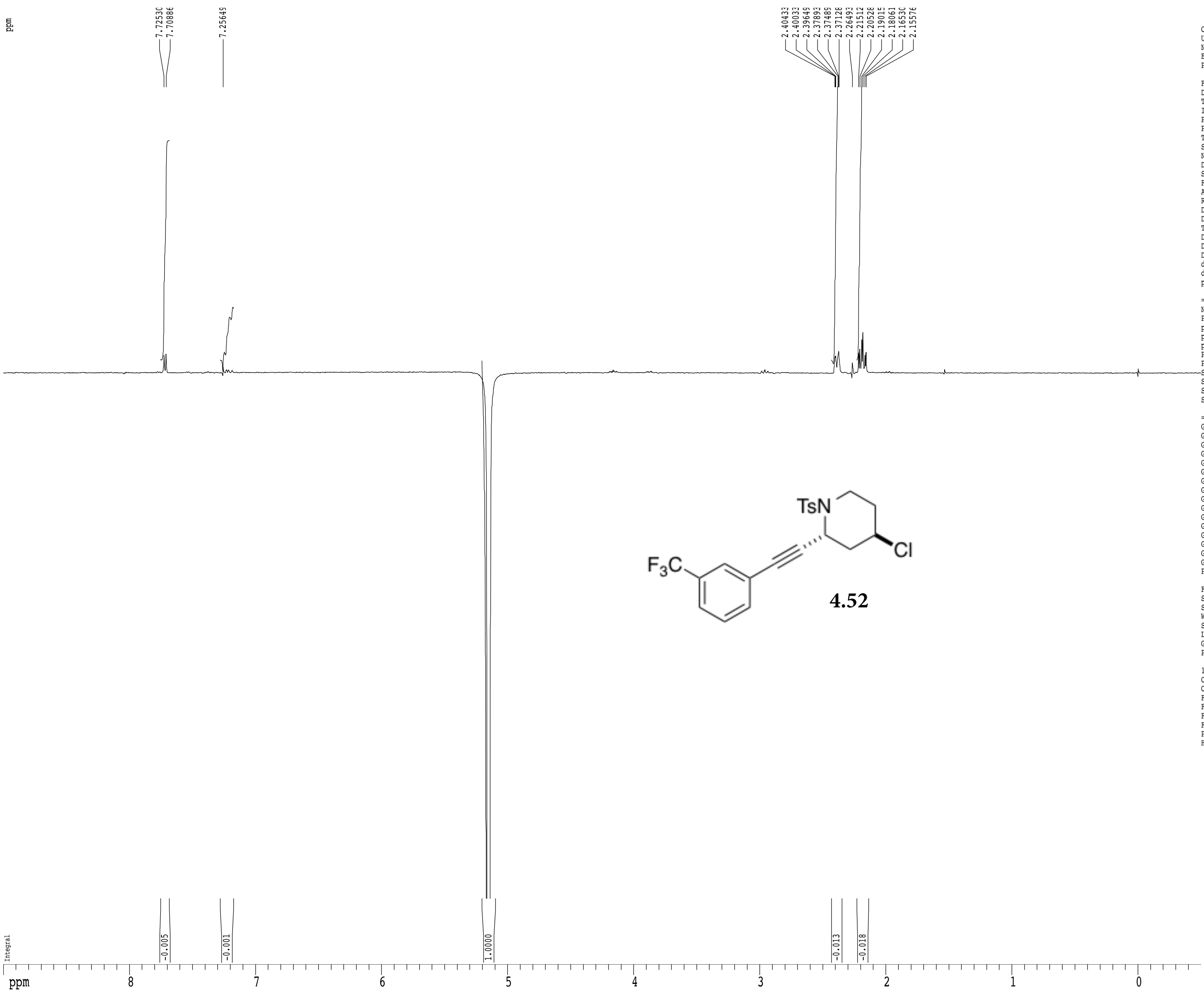


4.52



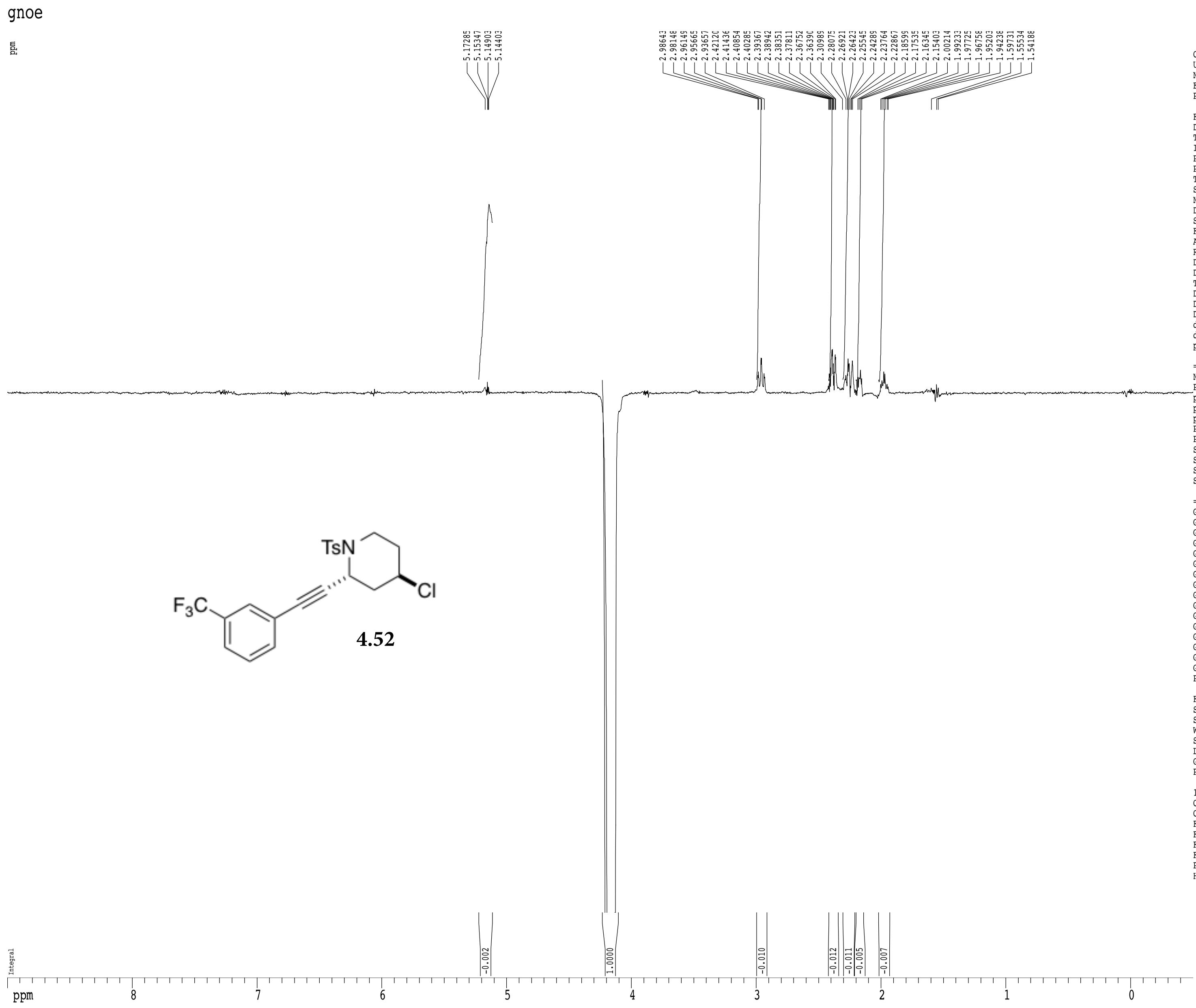
```
        Current Data Parameters
   USER          nhirbawi
NAME     NH-1-39-on11-19-COSY
   EXPNO                2
   PROCNO               1

       F2 - Acquisition Parameters
   Date_           20201119
   Time               17.09
   INSTRUM          cryo500
   PROBHD   5 mm CPTCI 1H-
   PULPROG    cosygp60.prd
   TD                 2048
   SOLVENT          CDCl3T
   NS                    2
   DS                   16
   SWH            5000.000 Hz
   FIDRES         2.441406 Hz
   AQ            0.2048500 sec
   RG               1448.2
   DW              100.000 usec
   DE                 6.00 usec
   TE                298.0 K
   d0           0.00000300 sec
   D1           1.00000000 sec
   d13          0.00000300 sec
   D16          0.00020000 sec
   IN0          0.00020000 sec

      ======== CHANNEL f1 ========
   NUC1                 1H
   P1                 9.75 usec
   PL1                1.60 dB
   SFO1        500.2222827 MHz

      ====== GRADIENT CHANNEL =====
   GPNAM1       SMSQ10.100
   GPNAM2       SMSQ10.100
   GPX1               0.00 %
   GPX2               0.00 %
   GPY1               0.00 %
   GPY2               0.00 %
   GPZ1              17.00 %
   GPZ2              17.00 %
   P16             1000.00 usec

       F1 - Acquisition parameters
   ND0                   1
   TD                  256
   SFO1           500.2223 MHz
   FIDRES        19.531250 Hz
   SW                9.996 ppm
   FnMODE               QF

       F2 - Processing parameters
   SI                 1024
   SF          500.2200318 MHz
   WDW                SINE
   SSB                   0
   LB                 0.00 Hz
   GB                    0
   PC                 1.00

       F1 - Processing parameters
   SI                 1024
   MC2                  QF
   SF          500.2200318 MHz
   WDW                SINE
   SSB                   0
   LB                 0.00 Hz
   GB                    0

         2D NMR plot parameters
   CX2               15.00 cm
   CX1               15.00 cm
   F2PLO             8.500 ppm
   F2LO            4251.87 Hz
   F2PHI            -0.498 ppm
   F2HI            -249.01 Hz
   F1PLO             8.500 ppm
   F1LO            4251.87 Hz
   F1PHI            -0.498 ppm
   F1HI            -249.01 Hz
   F2PPMCM         0.59985 ppm/cm
   F2HZCM        300.05869 Hz/cm
   F1PPMCM         0.59985 ppm/cm
   F1HZCM        300.05869 Hz/cm
```

gnoe



4.52

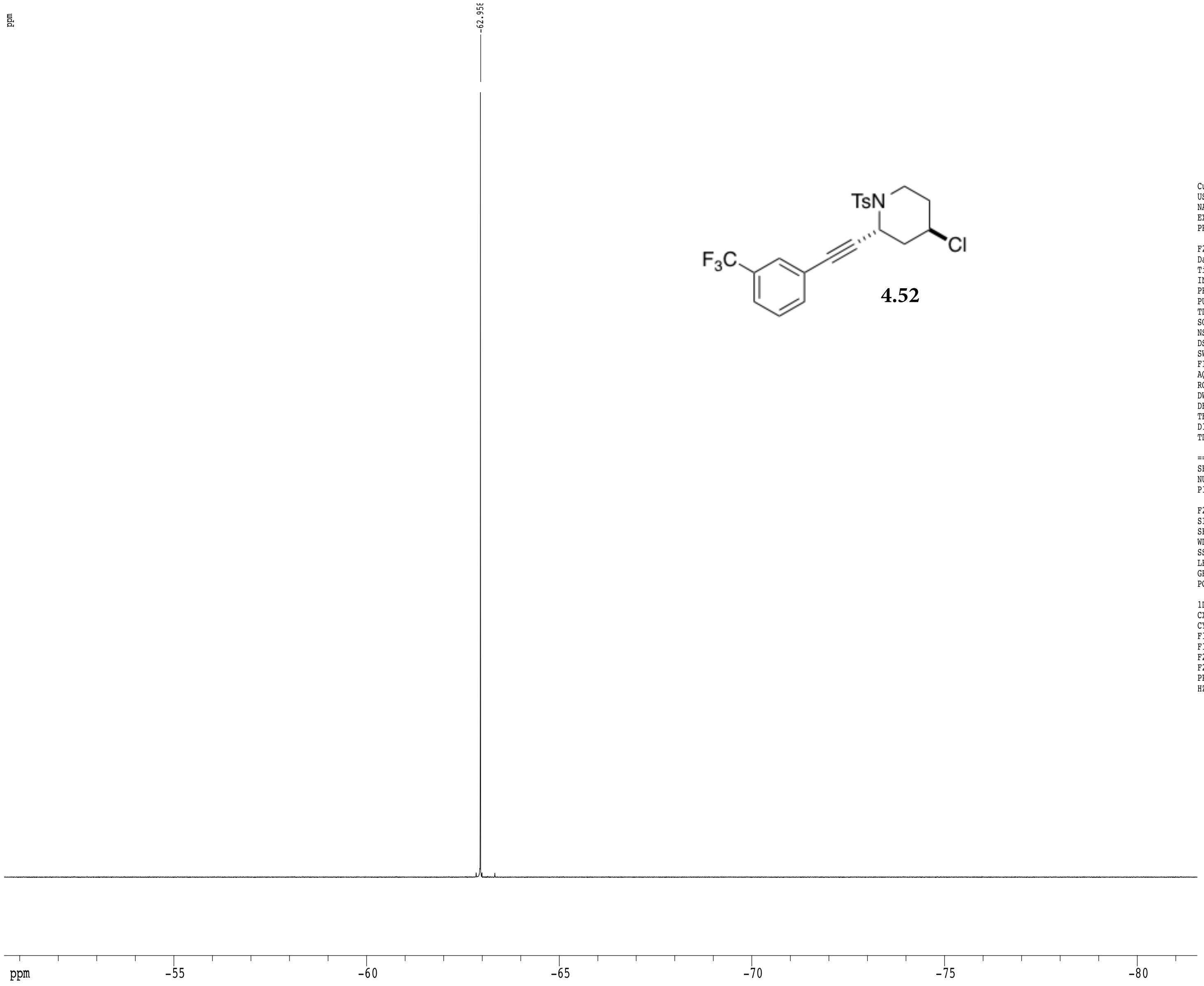
```
Current Data Parameters
USER           nhirbawi
NAME     NH-1-39-HCandCOSYagain
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20200815
Time              16.21
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                   64
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2226092 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200326 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```



4.52

```
Current Data Parameters
USER              nhirbawi
NAME          NH-1-39-NOE2
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200817
Time                 19.13
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     158
DS                       8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                      57
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2221143 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200323 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42502 Hz/cm
```

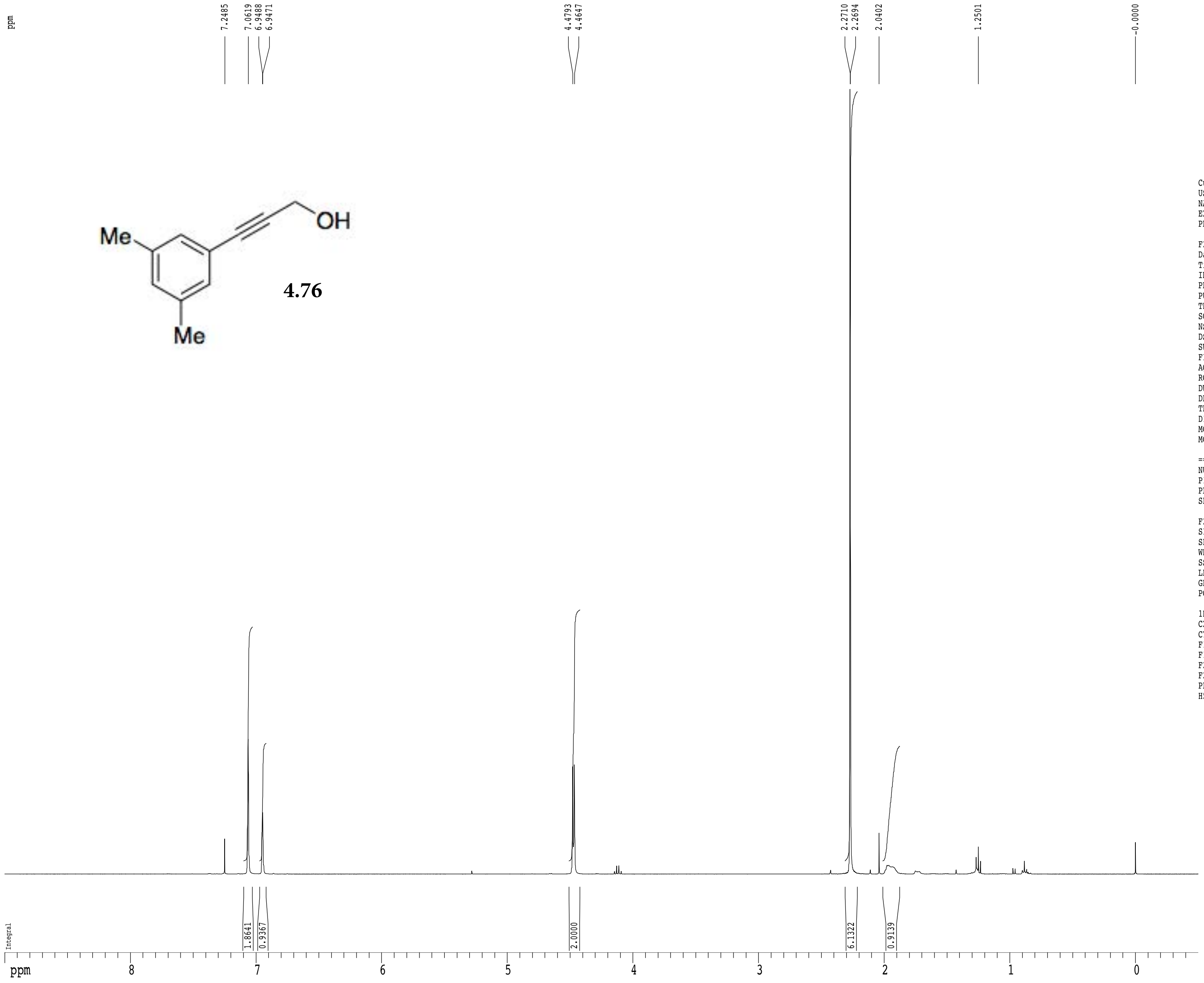
19F spectrum



4.52

```
Current Data Parameters
USER            nhirbawi
NAME         NH-1-39-19F
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200817
Time               17.22
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgflqn30
TD                131072
SOLVENT           CDCl3T
NS                    16
DS                     2
SWH            17482.518 Hz
FIDRES          0.133381 Hz
AQ             3.7487092 sec
RG                  1030
DW                28.600 usec
DE                 18.00 usec
TE                 298.0 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         564.6491091 MHz
NUC1                 19F
P1                 18.25 usec

F2 - Processing parameters
SI                131072
SF           564.6864205 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              -50.595 ppm
F1             -28570.10 Hz
F2P              -81.554 ppm
F2             -46052.62 Hz
PPMCM            1.35788 ppm/cm
HZCM           766.77704 Hz/cm
```

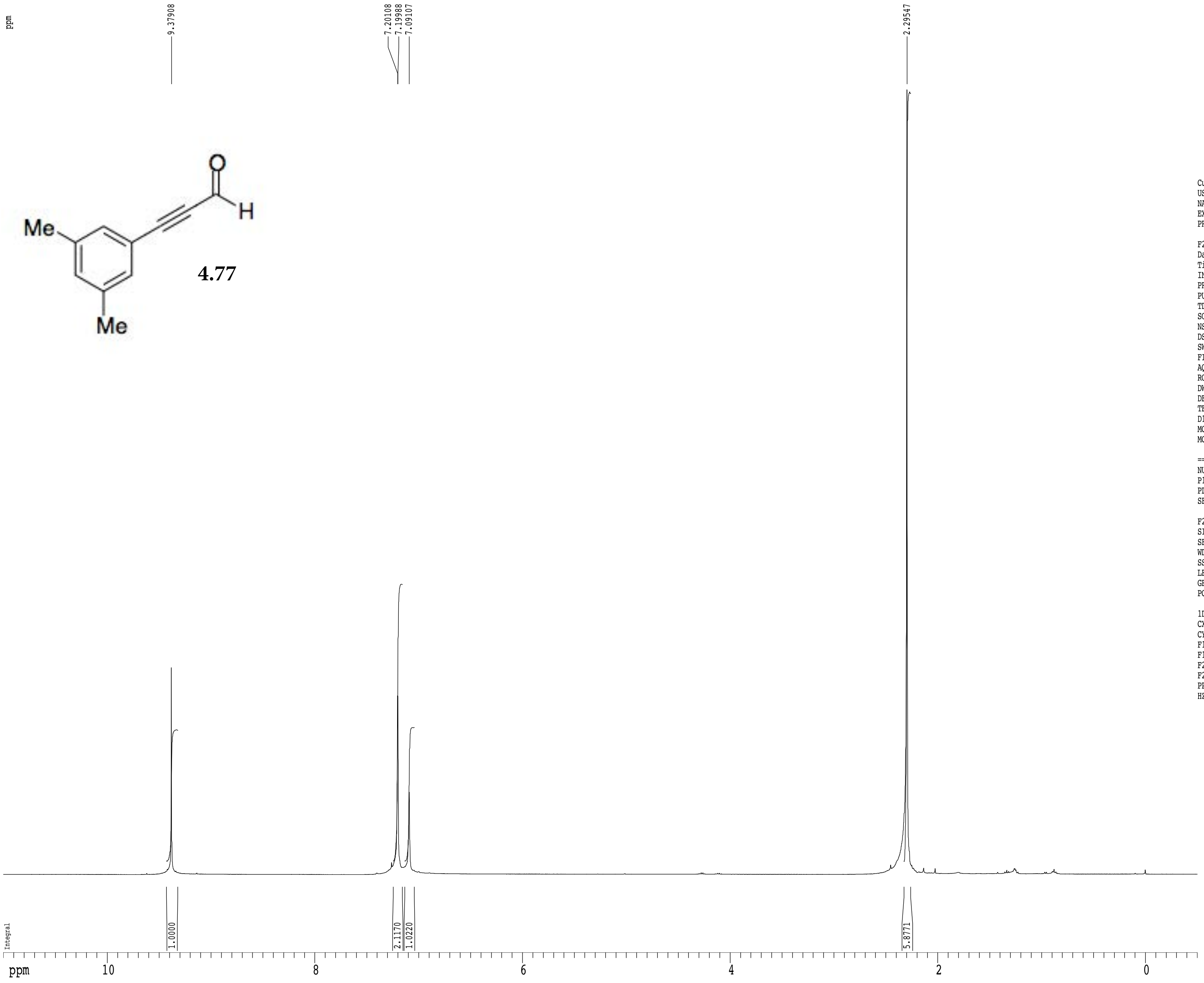
1H spectrum



4.76

```
Current Data Parameters
USER          khewitt1
NAME       KAH-III-254-1
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20200829
Time             17.40
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               38460
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                 114
DW              78.000 usec
DE                4.50 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300259 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -0.500 ppm
F2             -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```

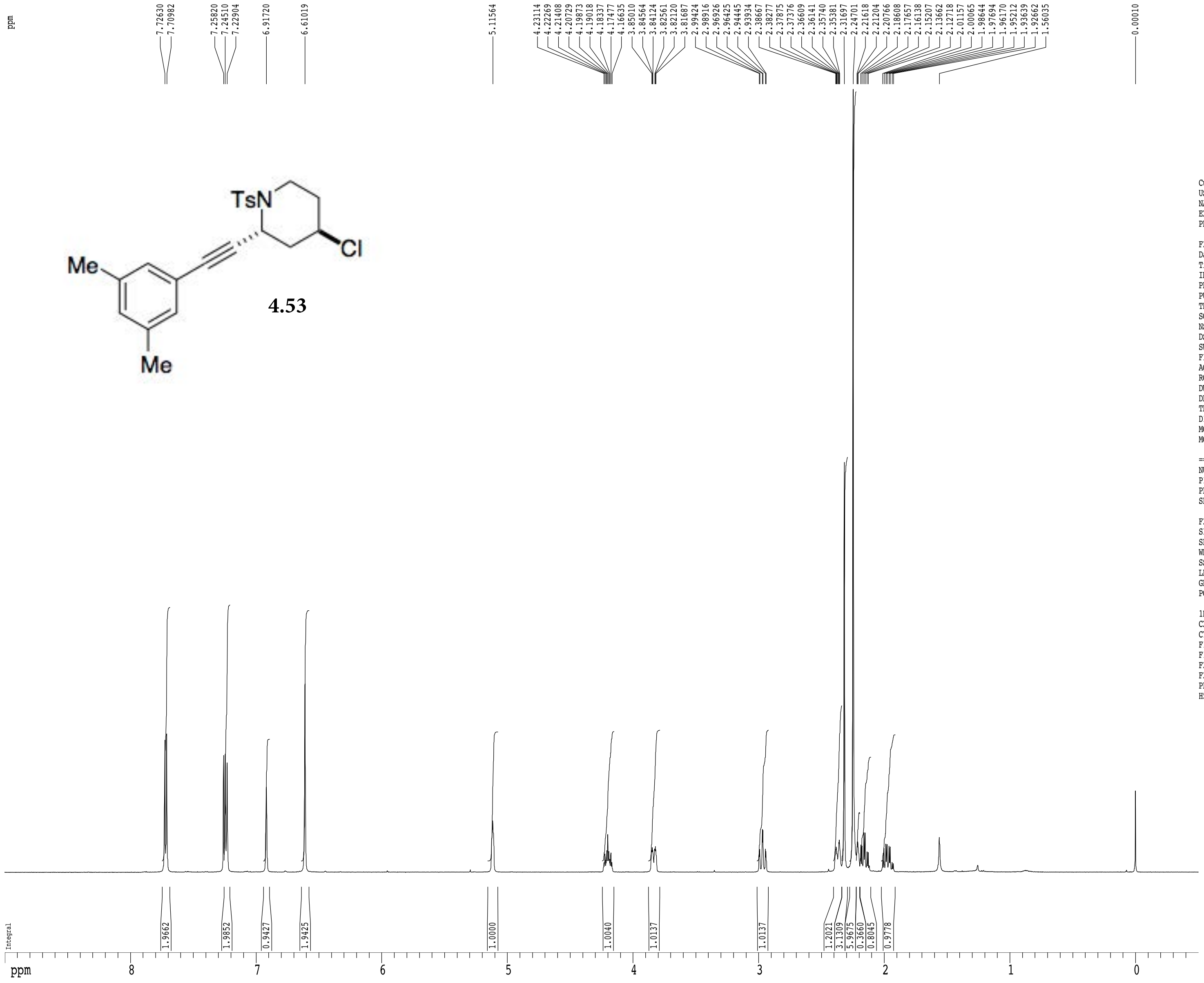
1H spectrum



4.77

```
Current Data Parameters
USER          khewitt1
NAME      KAH-III-259-1
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200902
Time              16.53
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                   32
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300204 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

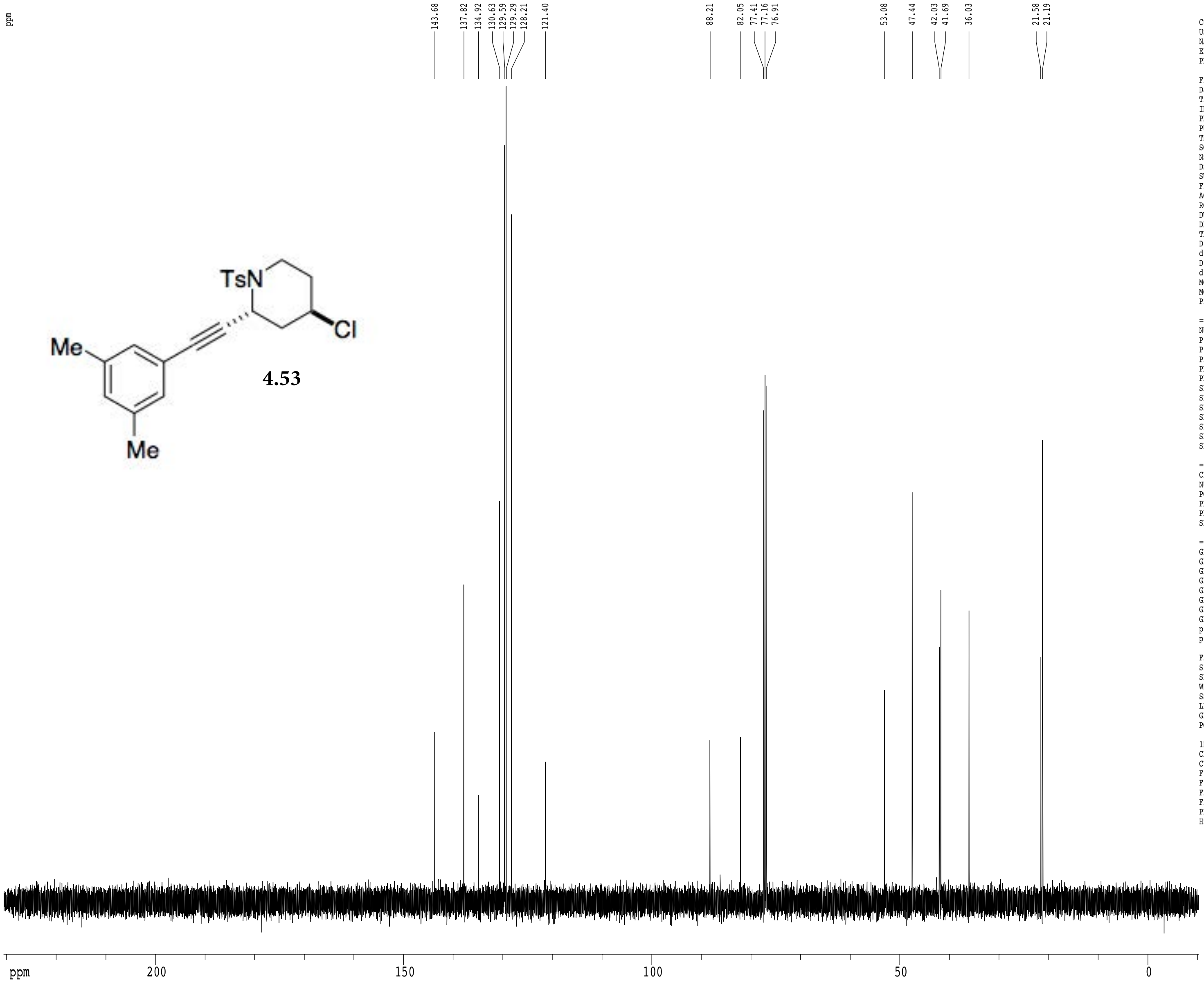
1H spectrum



4.53

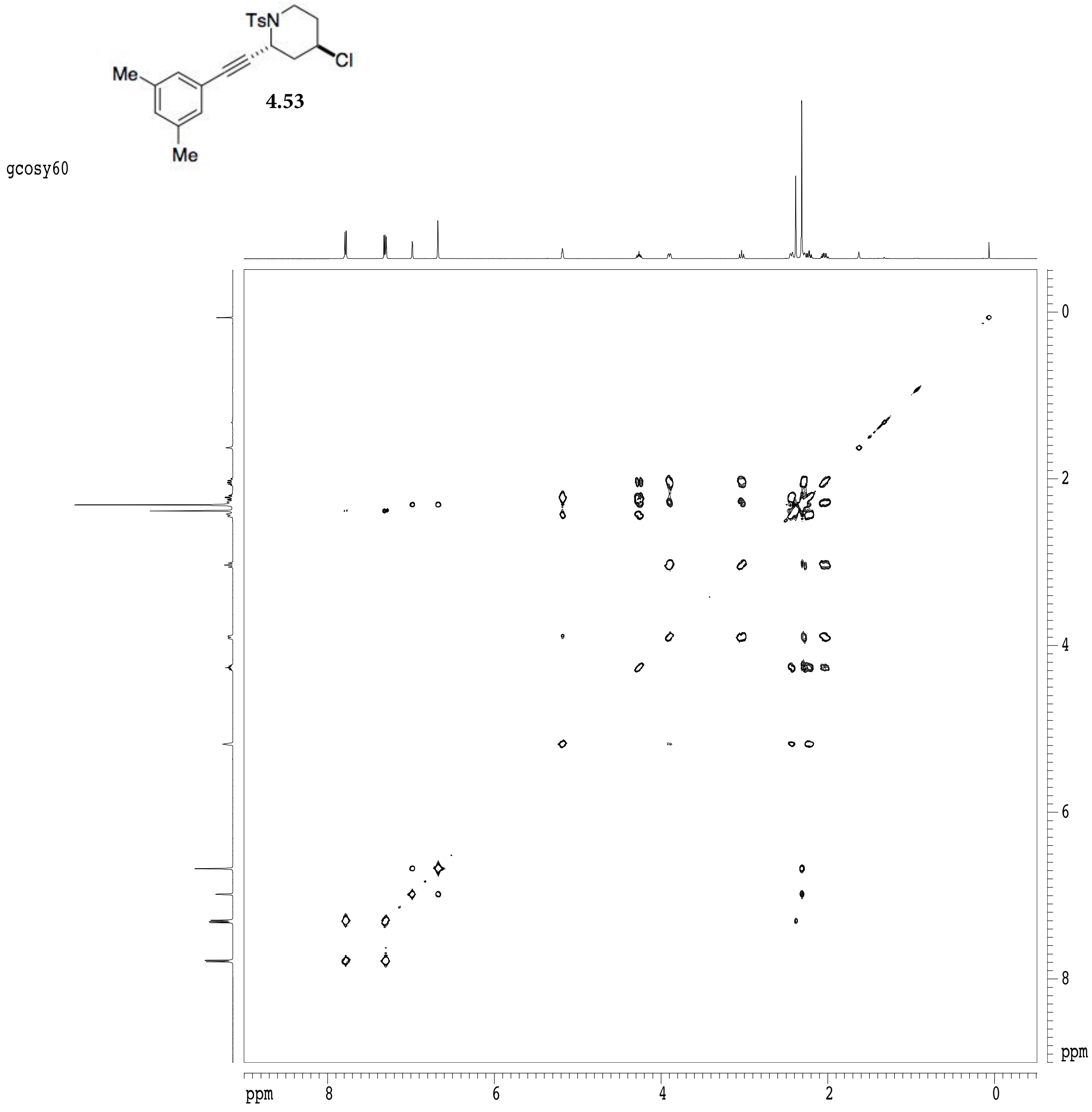
```
Current Data Parameters
USER           khewitt1
NAME        ACM-I-117-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200715
Time              18.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200321 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



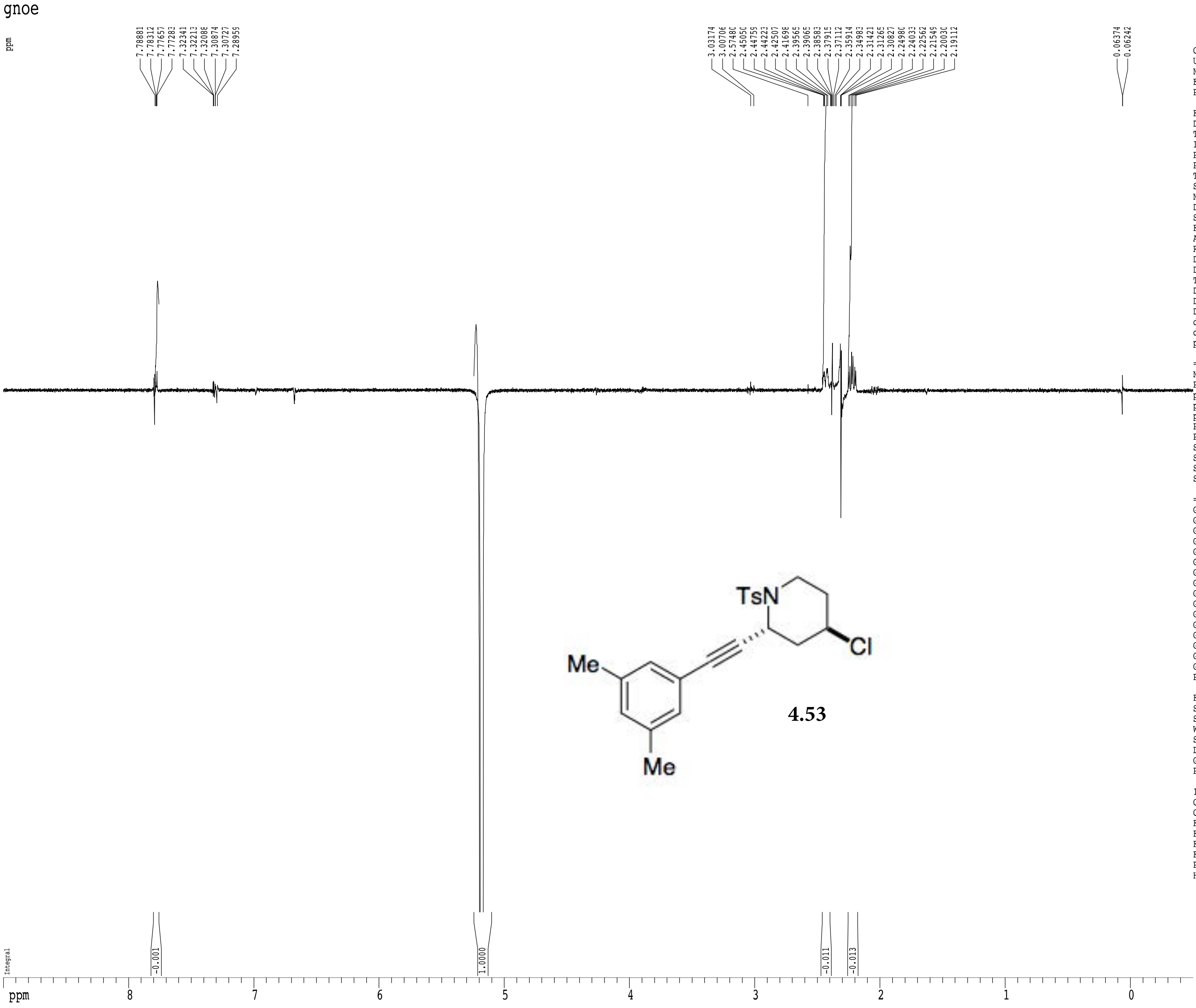
4.53

```
Current Data Parameters
USER          khewitt1
NAME        ACM-I-117-Z
EXPNO                5
PROCNO               1

F2 - Acquisition Parameters
Date_         20200715
Time             19.17
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD               65536
SOLVENT          CDCl3
NS                 208
DS                  16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813940 sec
RG                6502
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P12            2000.00 usec
P20             500.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2            0.00 Hz
SPOFF4            0.00 Hz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPX1              0.00 %
GPX2              0.00 %
GPY1              0.00 %
GPY2              0.00 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7804076 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.65 cm
F1P            230.637 ppm
F1            29009.68 Hz
F2P            -10.287 ppm
F2            -1293.96 Hz
PPMCM         10.56688 ppm/cm
HZCM        1329.10693 Hz/cm
```



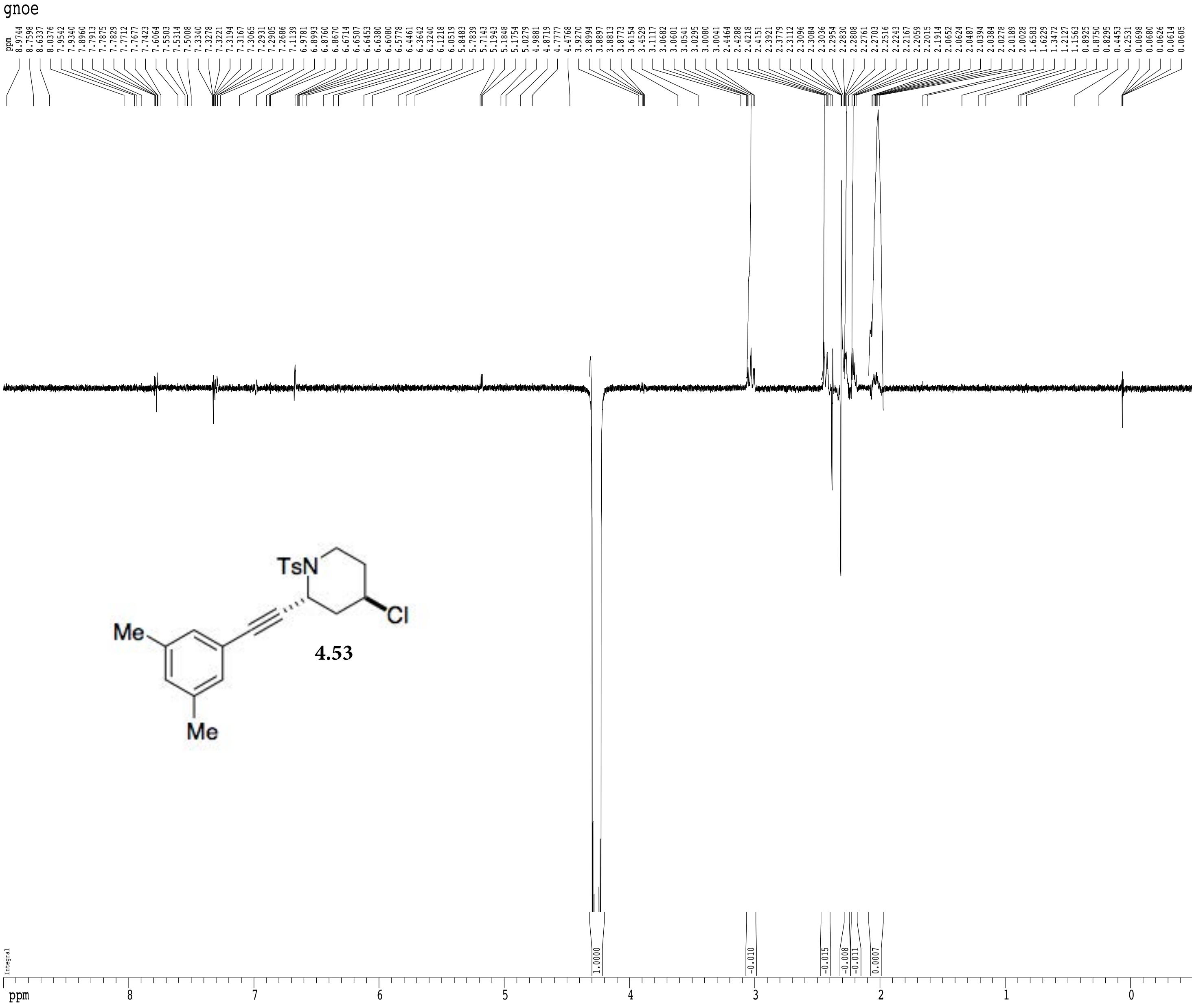
4.53

```
       Current Data Parameters
USER           khewitt1
NAME        ACM-I-117-Z
EXPNO                 4
PROCNO                1

     F2 - Acquisition Parameters
Date_          20200715
Time              19.05
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                228.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

    ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

   ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

     F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

         2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.002 ppm
F2LO            4503.14 Hz
F2PHI            -0.509 ppm
F2HI            -254.47 Hz
F1PLO             9.002 ppm
F1LO            4503.14 Hz
F1PHI            -0.509 ppm
F1HI            -254.47 Hz
F2PPMCM         0.63407 ppm/cm
F2HZCM        317.17416 Hz/cm
F1PPMCM         0.63407 ppm/cm
F1HZCM        317.17416 Hz/cm
```



4.53

```
Current Data Parameters
USER             khewitt1
NAME          ACM-I-117-Z
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200715
Time                18.50
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    114
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2225909 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```



Current Data Parameters
USER khewitt1
NAME ACM-I-117-Z
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200715
Time 19.04
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoe1cc22.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec

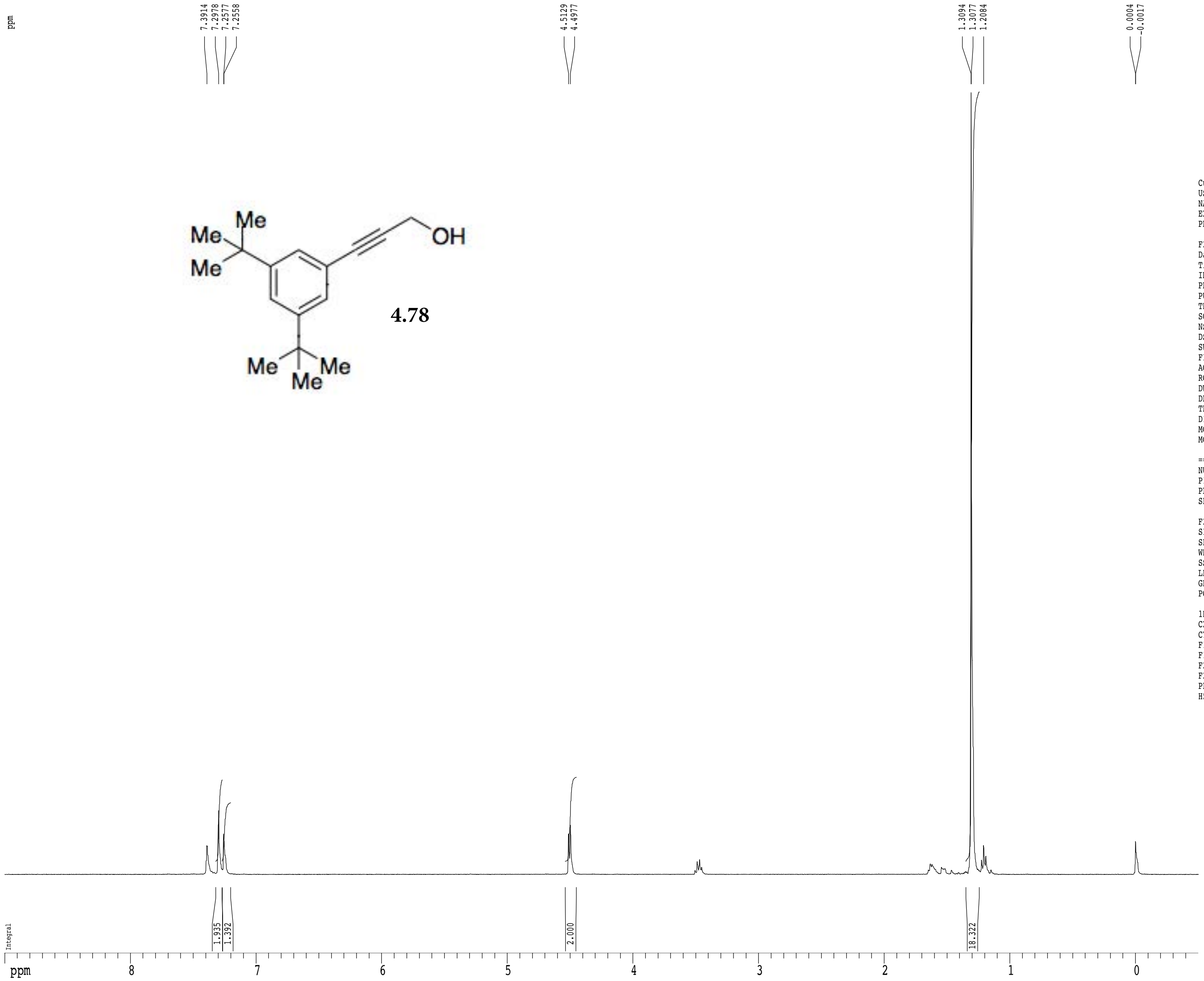
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2221324 MHz
SP9 61.60 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm

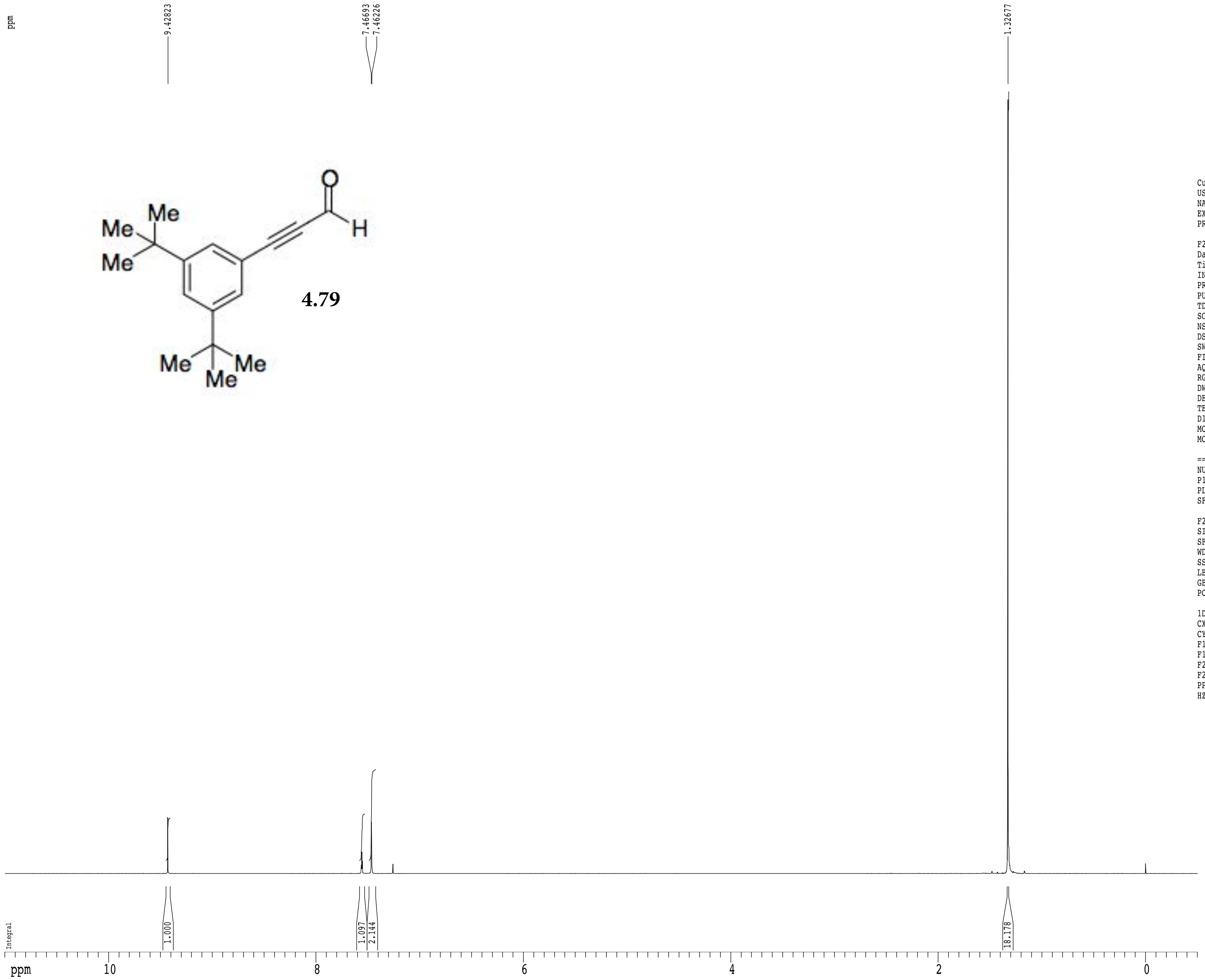
1H spectrum



4.78

```
Current Data Parameters
USER          khewitt1
NAME     ACM-I-150-pdtall
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200121
Time               9.59
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                456.1
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300236 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

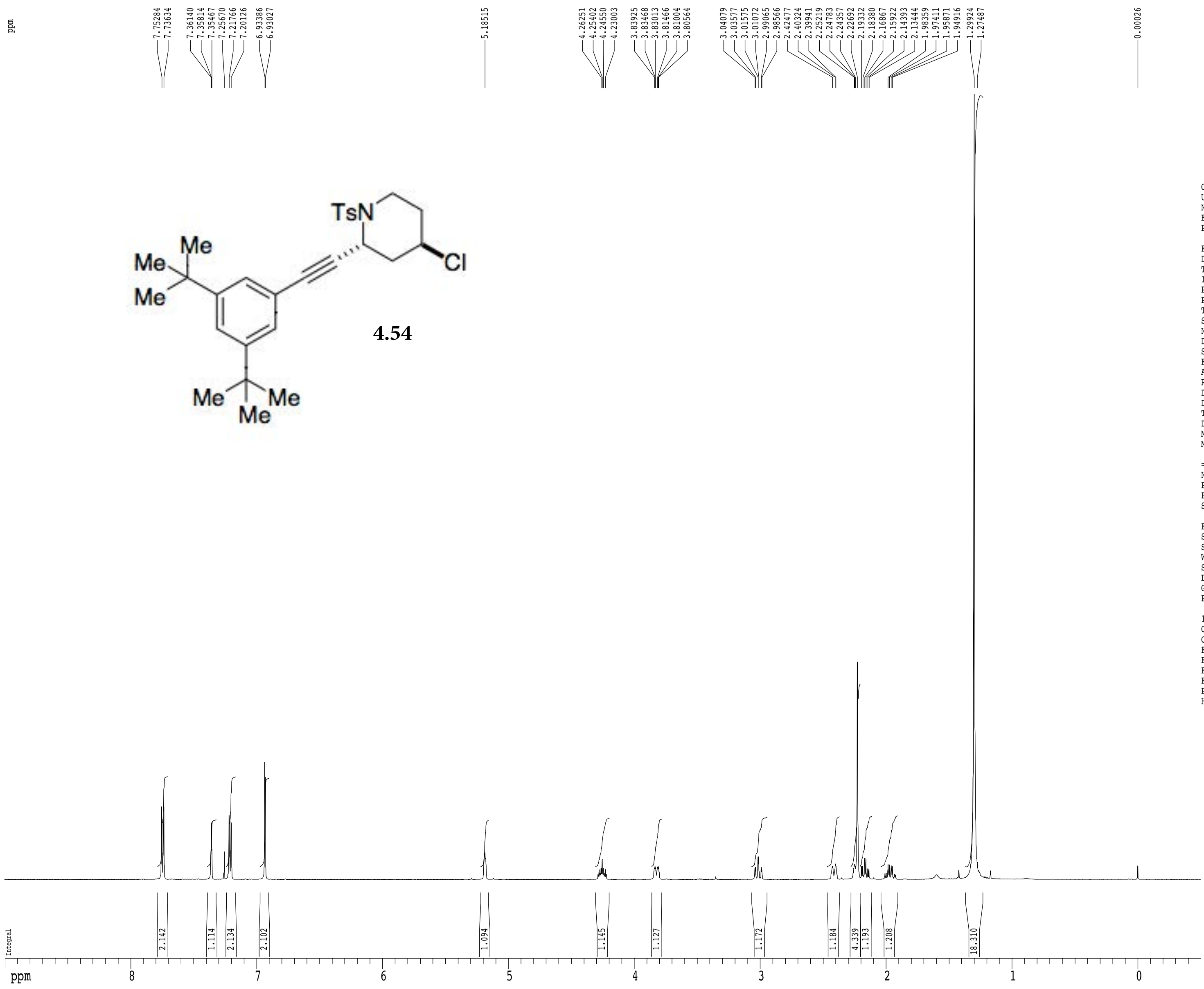
1H spectrum



4.79

```
Current Data Parameters
USER            khewitt1
NAME      ACM-I-151-pdtdry
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20200124
Time              10.14
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                  128
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300224 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

1H spectrum

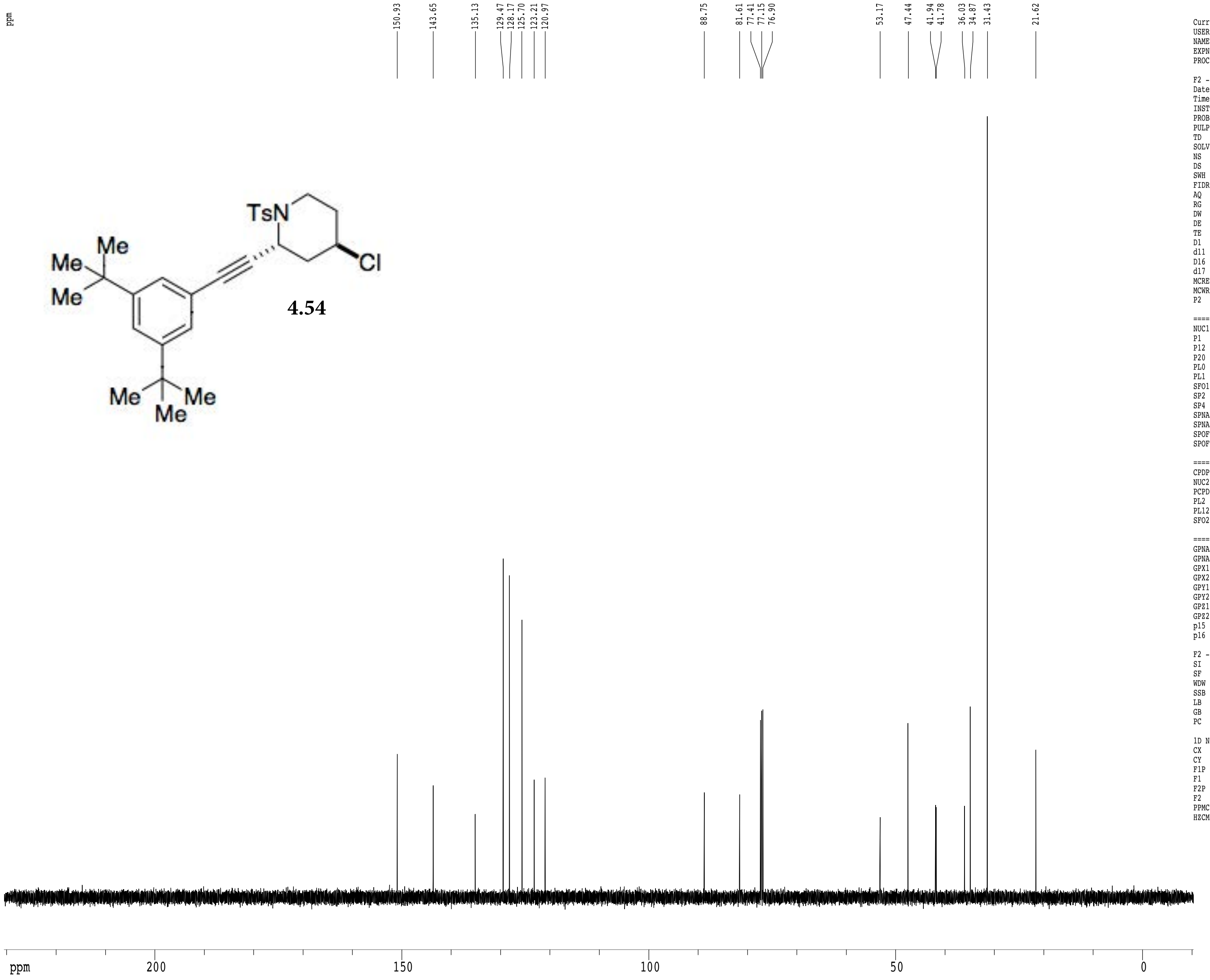


4.54

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-190-SM-Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200711
Time               10.10
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200330 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

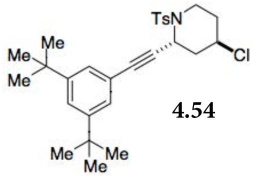
Z-restored spin-echo 13C spectrum with 1H decoupling

4.54

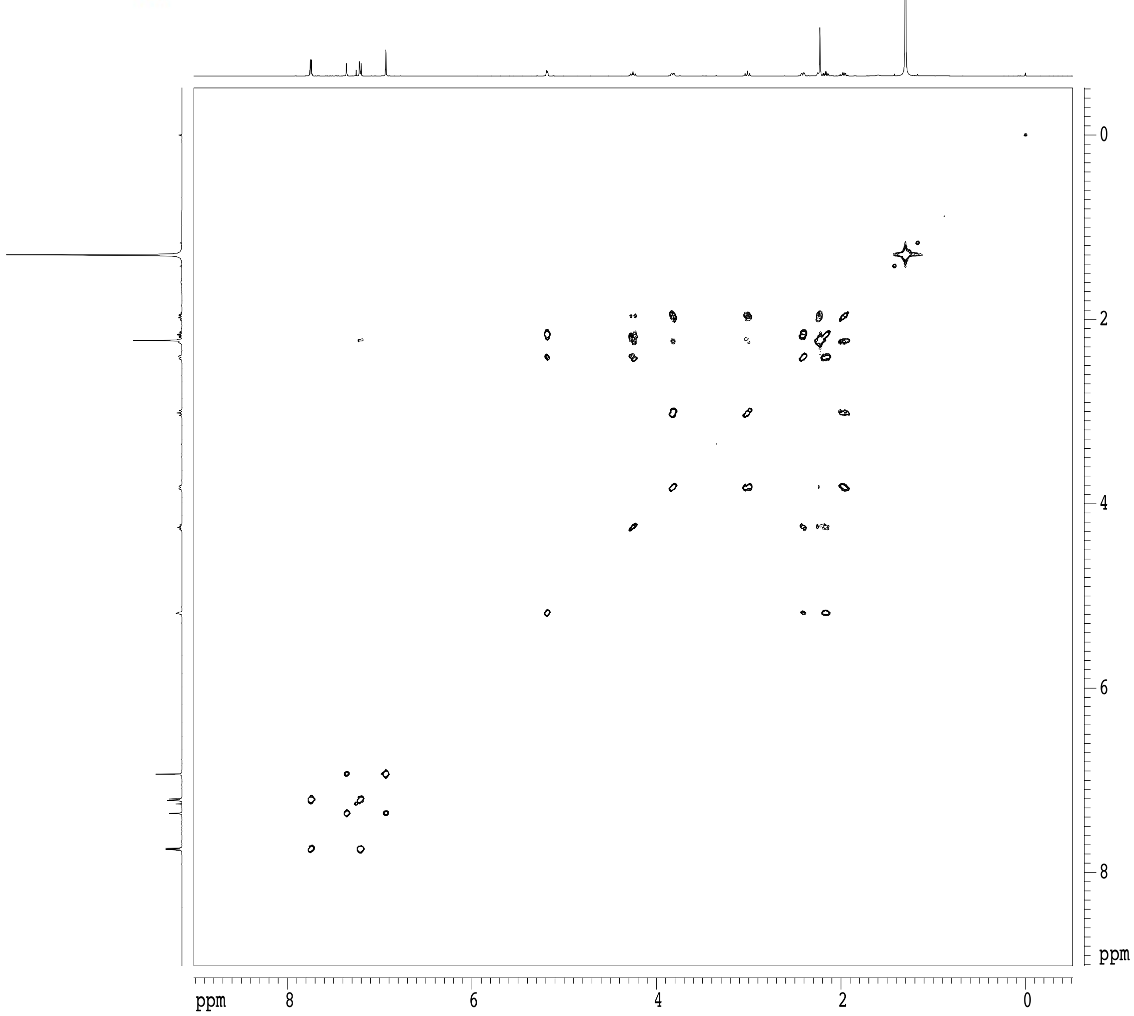


```
Current Data Parameters
USER           khewitt1
NAME      KAH-III-190-SM-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200710
Time              18.16
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD               303026
SOLVENT          CDCl3T
NS                   32
DS                   16
SWH          30303.031 Hz
FIDRES        0.100001 Hz
AQ           4.9999790 sec
RG                 6502
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804103 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```

gcosy60

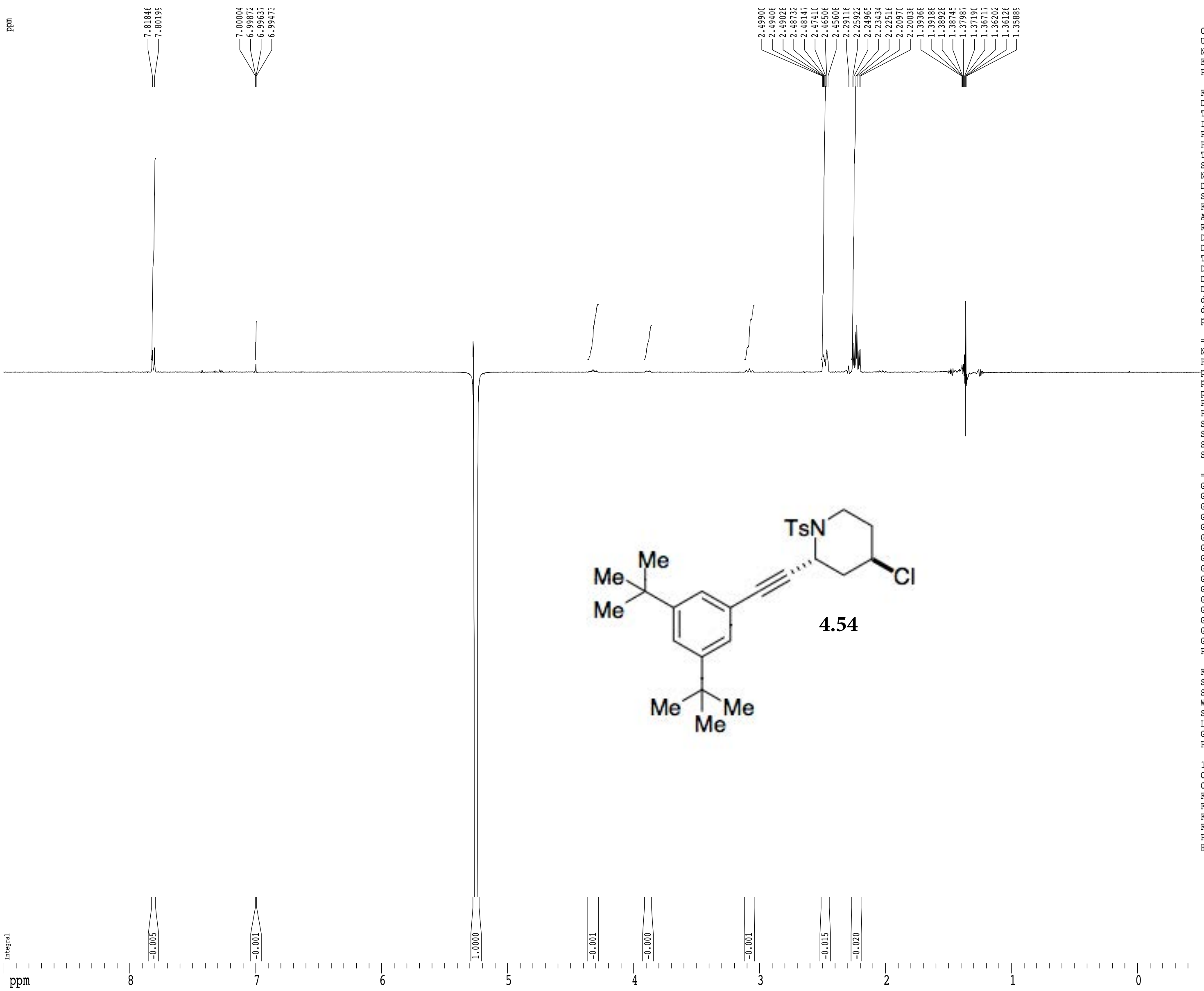


4.54



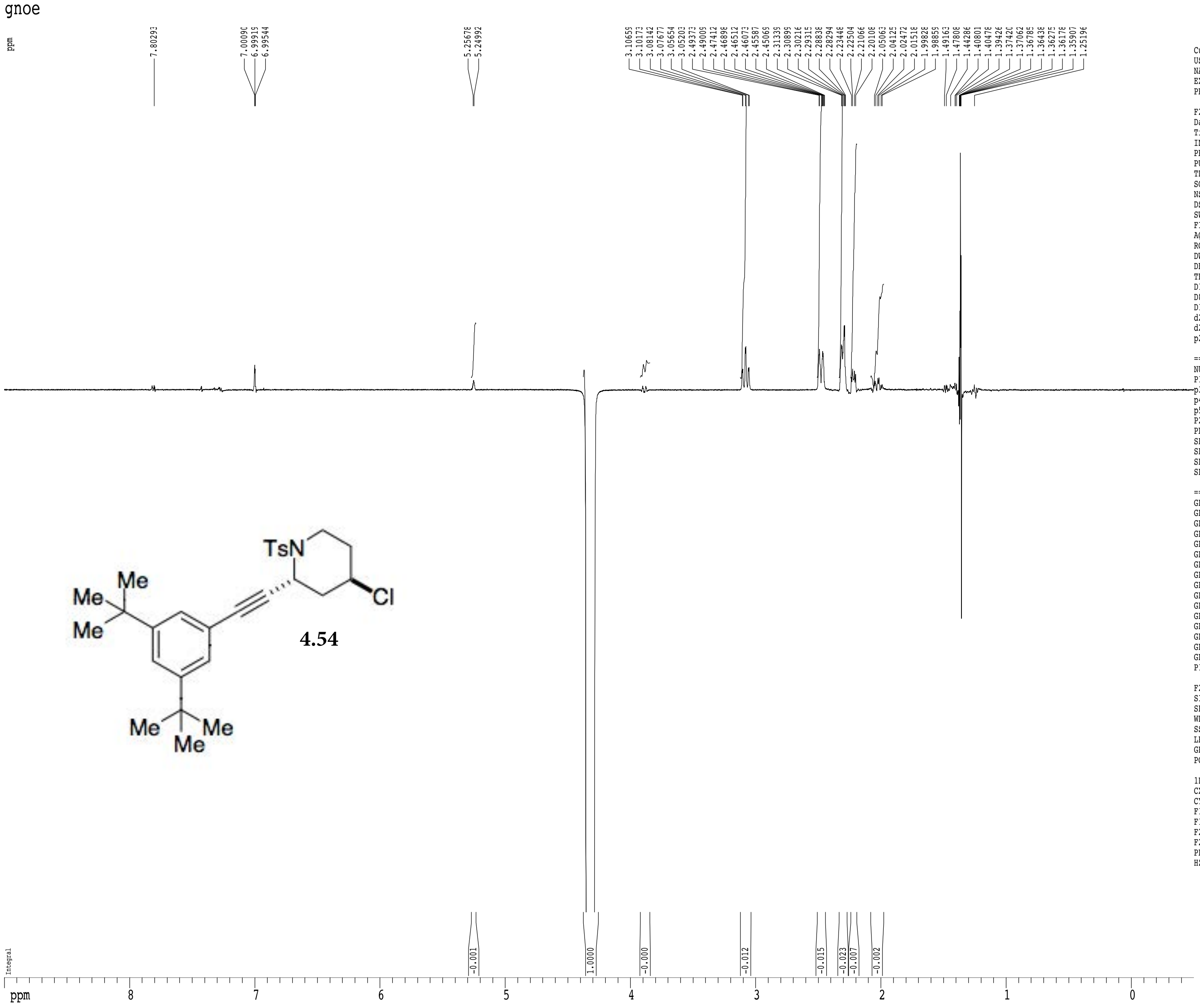
```
        Current Data Parameters
 USER           khewitt1
NAME     KAH-III-190-SM-Z
 EXPNO                 7
 PROCNO                1

      F2 - Acquisition Parameters
 Date_          20200711
 Time              10.45
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG    cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            8012.820 Hz
 FIDRES         3.912510 Hz
 AQ            0.1278452 sec
 RG                   64
 DW               62.400 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00012480 sec

     ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  512
 SFO1           500.2235 MHz
 FIDRES        15.650040 Hz
 SW               16.018 ppm
 FnMODE               QF

      F2 - Processing parameters
 SI                 1024
 SF          500.2200330 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

      F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200330 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

        2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             9.015 ppm
 F2LO            4509.29 Hz
 F2PHI            -0.512 ppm
 F2HI            -256.15 Hz
 F1PLO             9.015 ppm
 F1LO            4509.29 Hz
 F1PHI            -0.512 ppm
 F1HI            -256.15 Hz
 F2PPMCM         0.63511 ppm/cm
 F2HZCM        317.69580 Hz/cm
 F1PPMCM         0.63511 ppm/cm
 F1HZCM        317.69580 Hz/cm
```

gnoe



4.54

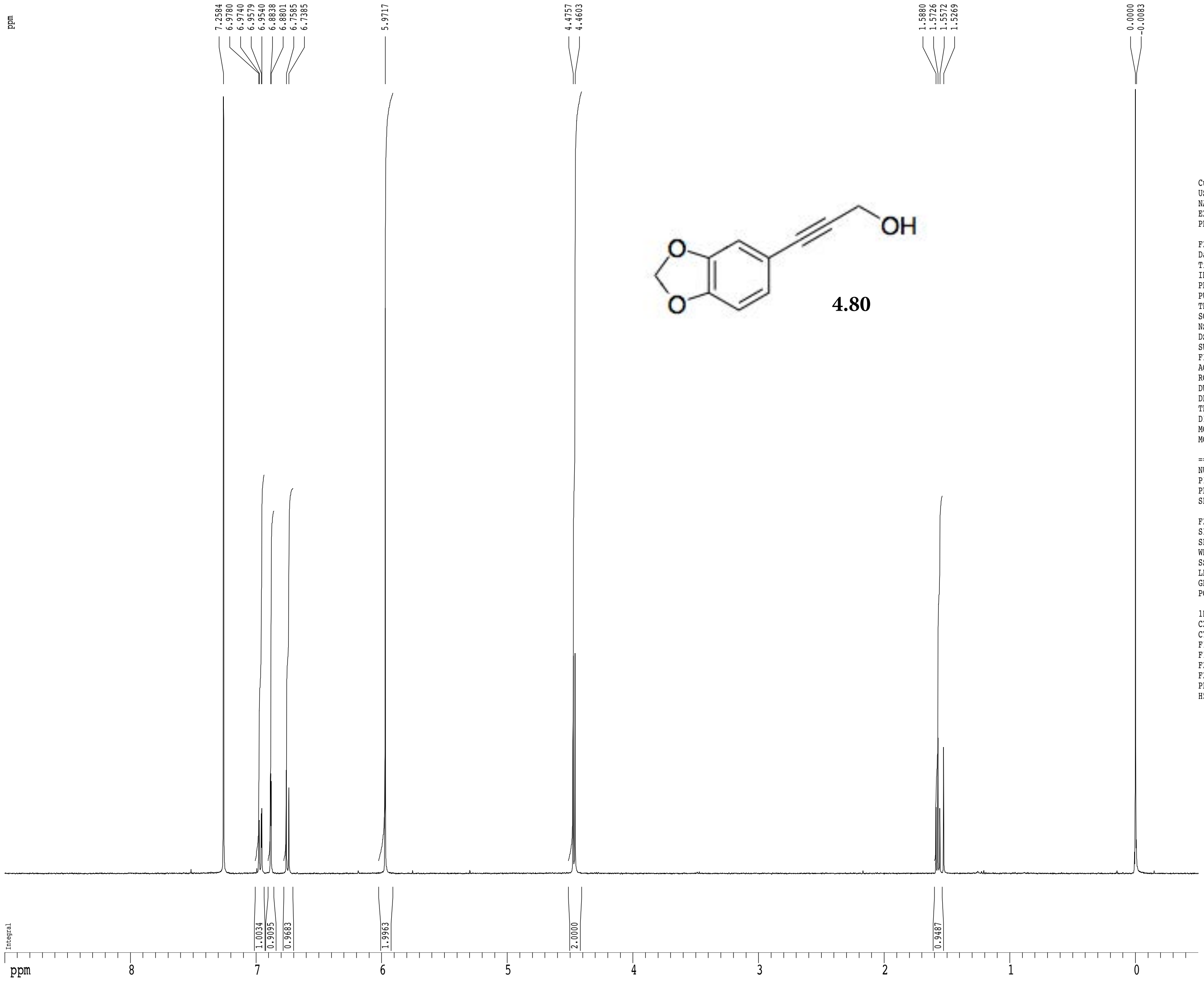
```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-190-SM-Z
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200711
Time               10.26
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  90.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2226267 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



4.54

```
Current Data Parameters
USER              khewitt1
NAME      KAH-III-190-SM-Z
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200711
Time                 10.44
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    90.5
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1          500.2221610 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF          500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

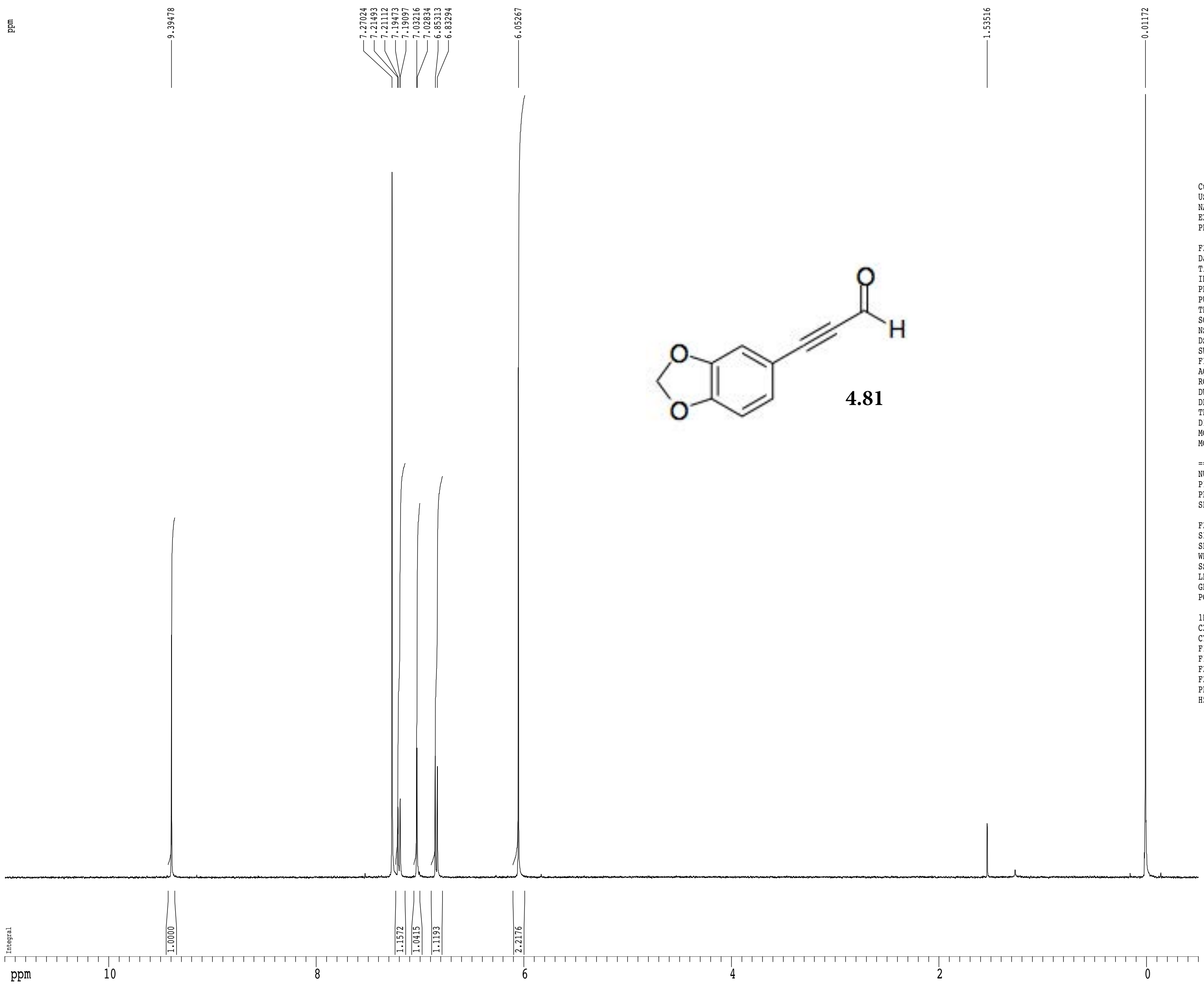
1H spectrum



4.80

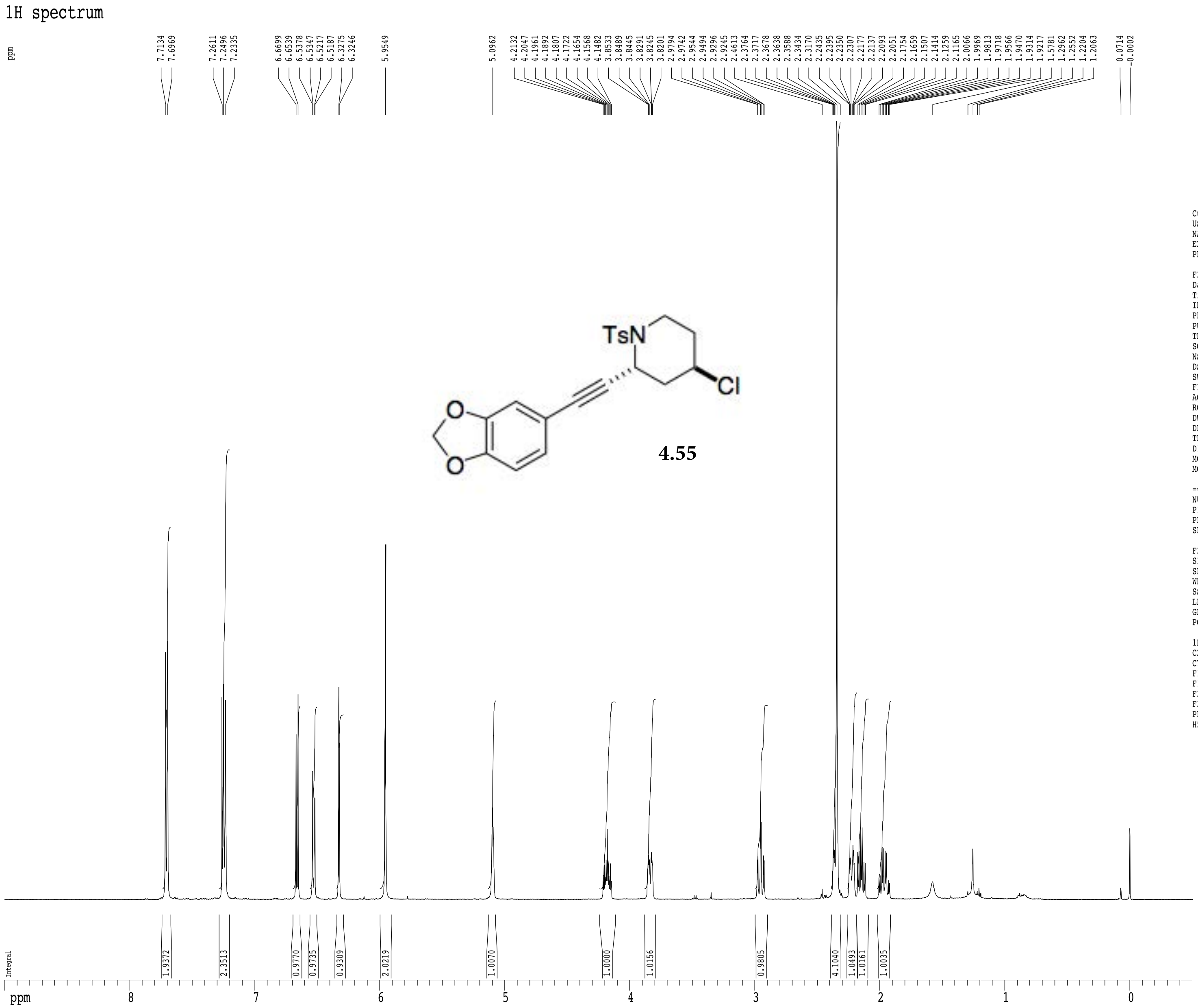
```
Current Data Parameters
USER          khewitt1
NAME      ACM-I-154-big
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200130
Time               9.43
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG               1625.5
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300221 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

1H spectrum



4.81

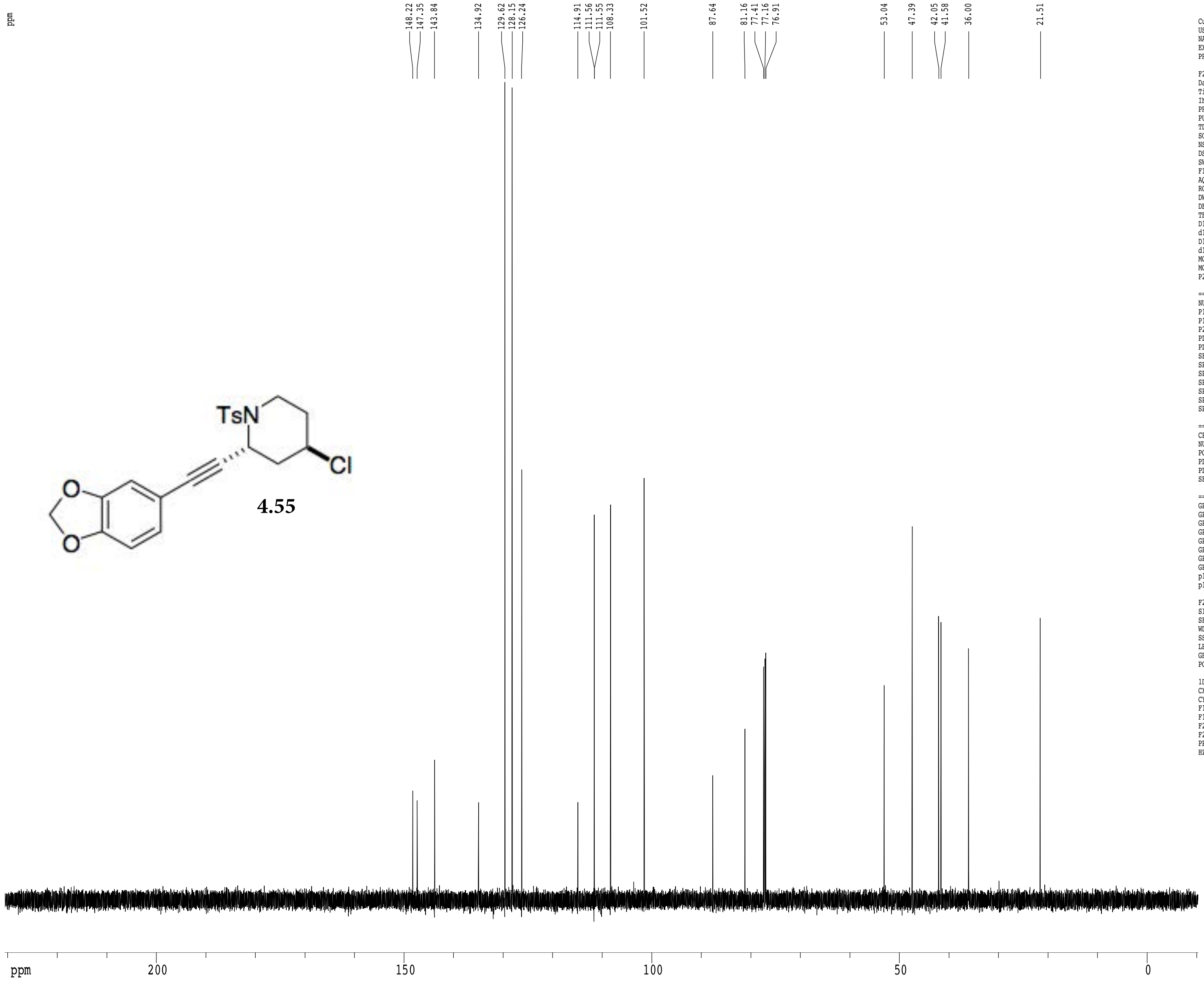
```
Current Data Parameters
USER          khewitt1
NAME     ACM-I-155-c1-pdt
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20200203
Time             16.48
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               65536
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ           5.1118579 sec
RG              1824.6
DW              78.000 usec
DE                4.50 usec
TE               297.9 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300175 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P             11.000 ppm
F1             4401.43 Hz
F2P             -0.500 ppm
F2             -200.07 Hz
PPMCM          0.50439 ppm/cm
HZCM         201.81996 Hz/cm
```



4.55

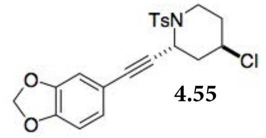
```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-191-SM-Z
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_          20200714
Time              10.41
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200307 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



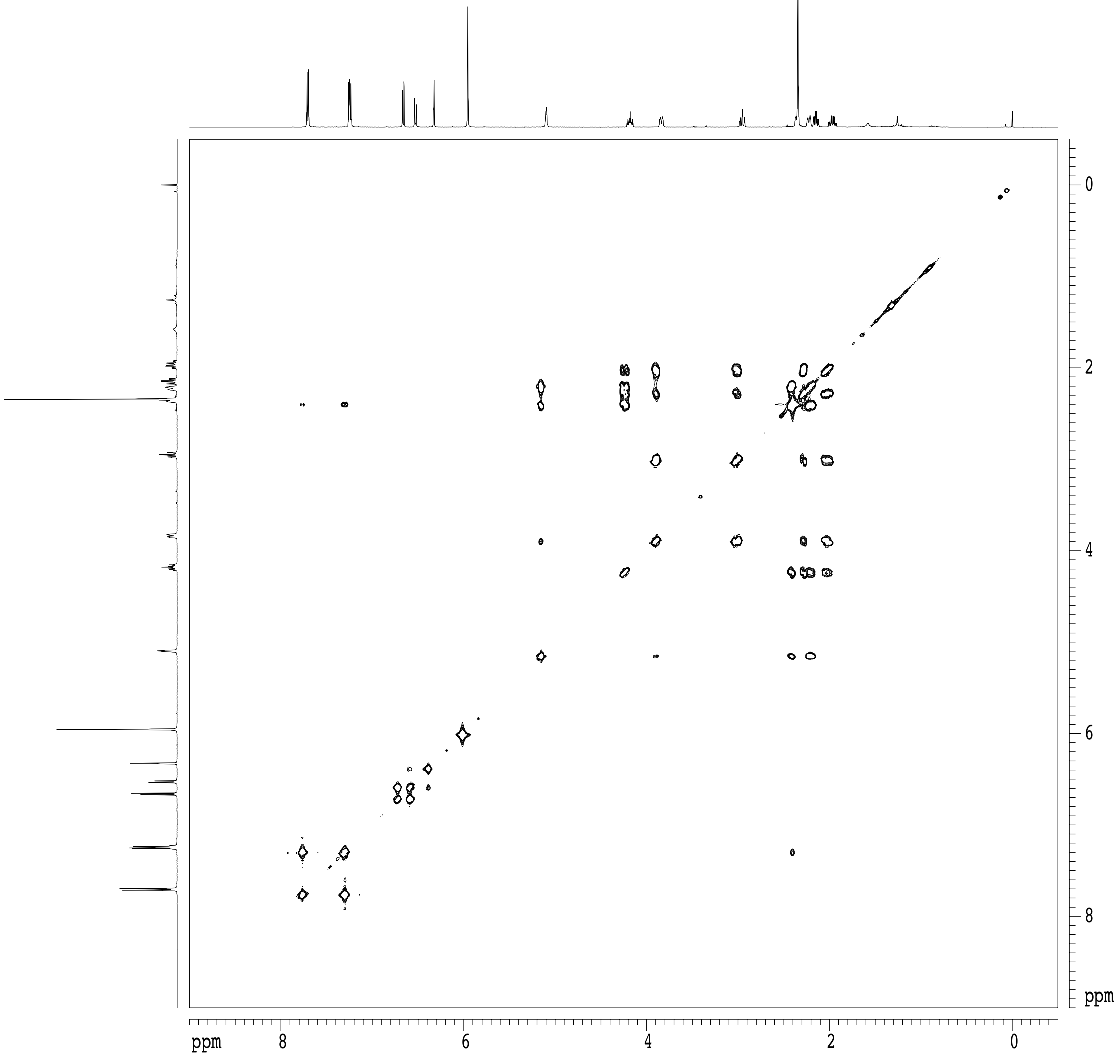
4.55

```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-191-SM-Z-Carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200710
Time               18.23
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT           CDCl3T
NS                    72
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804094 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

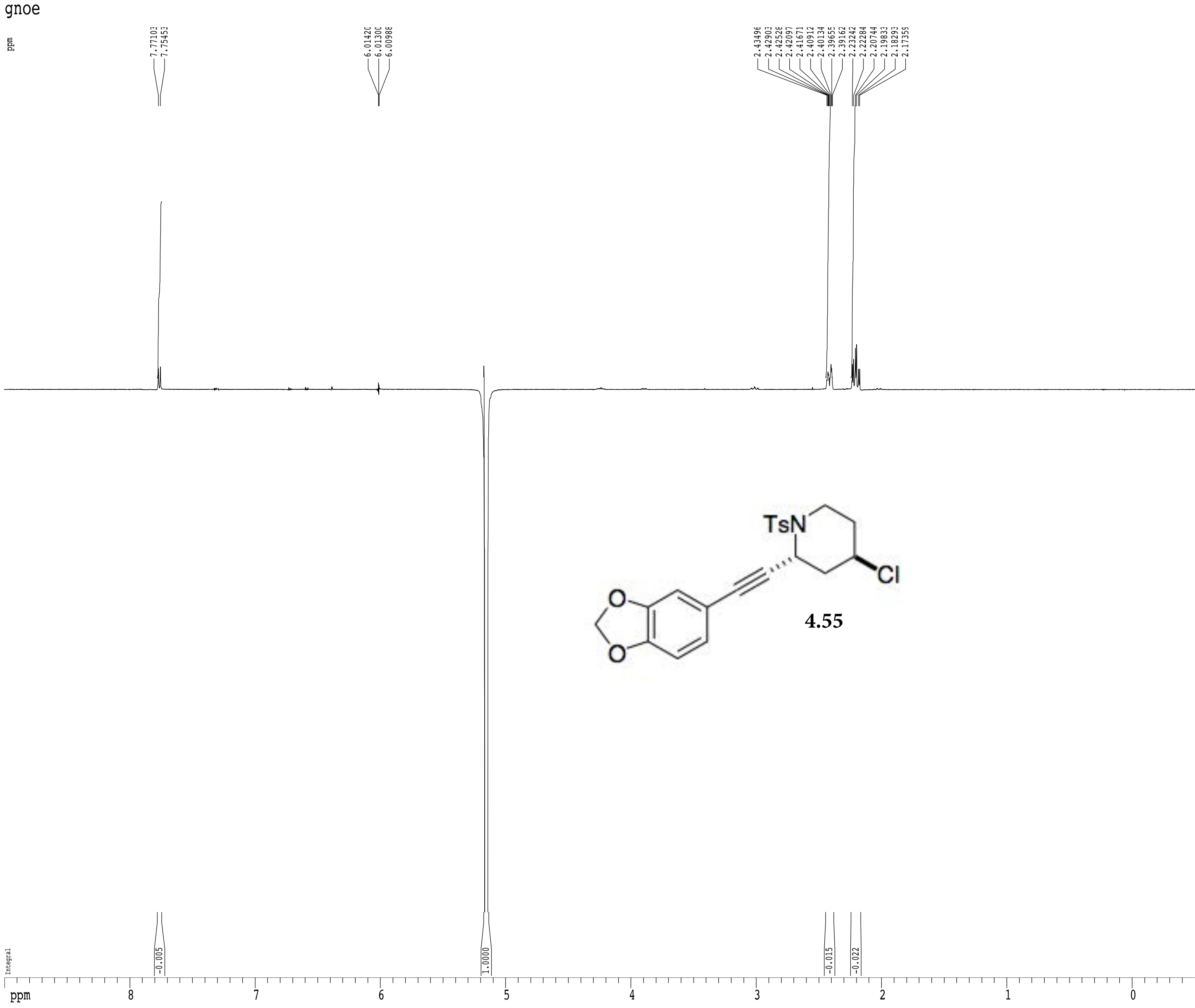


4.55

gcosy60

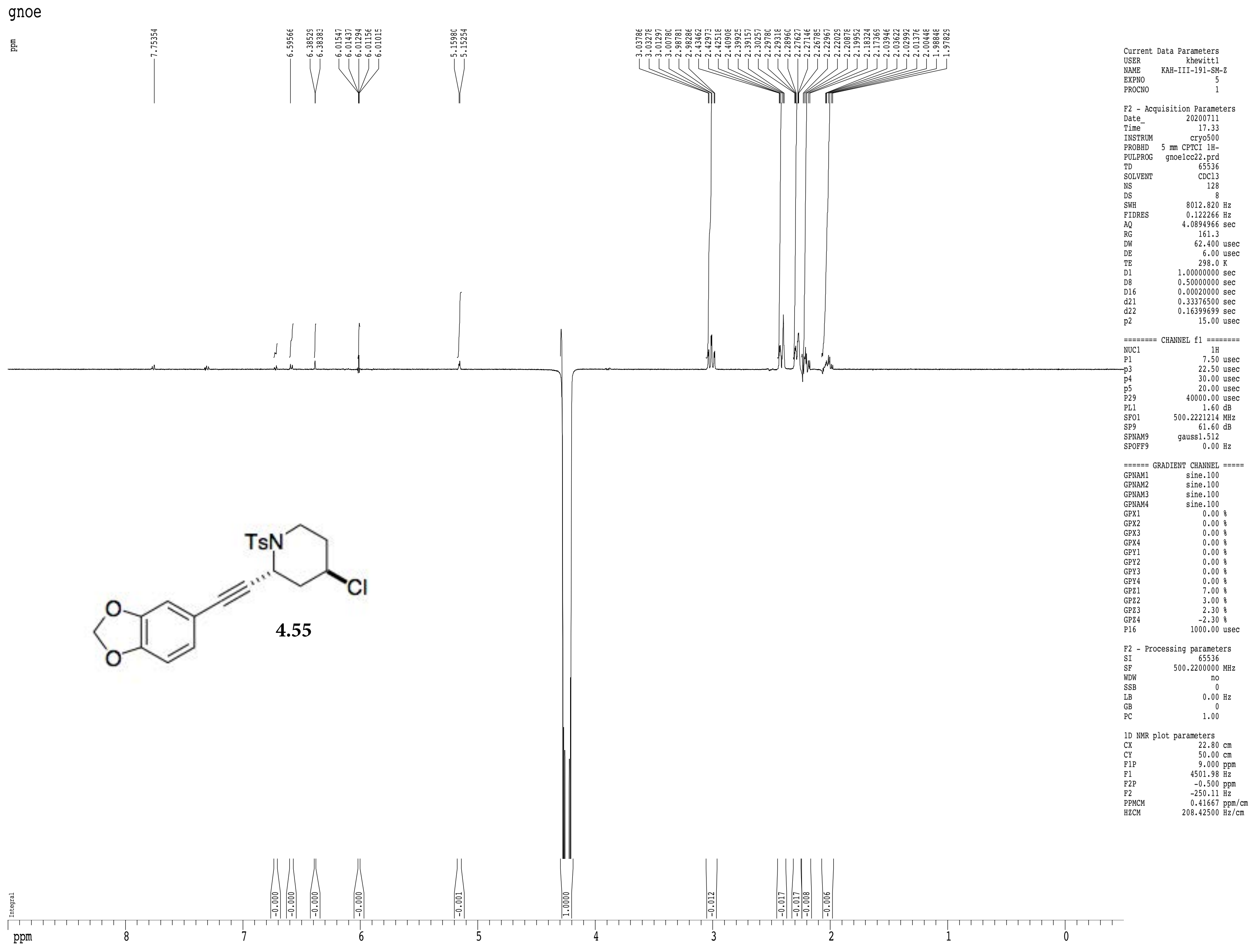


```
        Current Data Parameters
 USER           khewitt1
NAME     KAH-III-191-SM-Z
 EXPNO                 8
 PROCNO                1

      F2 - Acquisition Parameters
 Date_          20200714
 Time              10.42
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG    cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            8012.820 Hz
 FIDRES         3.912510 Hz
 AQ            0.1278452 sec
 RG                  256
 DW               62.400 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00012480 sec

     ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  512
 SFO1           500.2235 MHz
 FIDRES        15.650040 Hz
 SW               16.018 ppm
 FnMODE               QF

       F2 - Processing parameters
 SI                 1024
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

       F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

         2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             9.000 ppm
 F2LO            4501.98 Hz
 F2PHI            -0.500 ppm
 F2HI            -250.11 Hz
 F1PLO             9.000 ppm
 F1LO            4501.98 Hz
 F1PHI            -0.500 ppm
 F1HI            -250.11 Hz
 F2PPMCM         0.63333 ppm/cm
 F2HZCM        316.80600 Hz/cm
 F1PPMCM         0.63333 ppm/cm
 F1HZCM        316.80600 Hz/cm
```



4.55

```
Current Data Parameters
USER             khewitt1
NAME      KAH-III-191-SM-Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200711
Time                 17.19
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    90.5
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2225782 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```


gnoe
ppm
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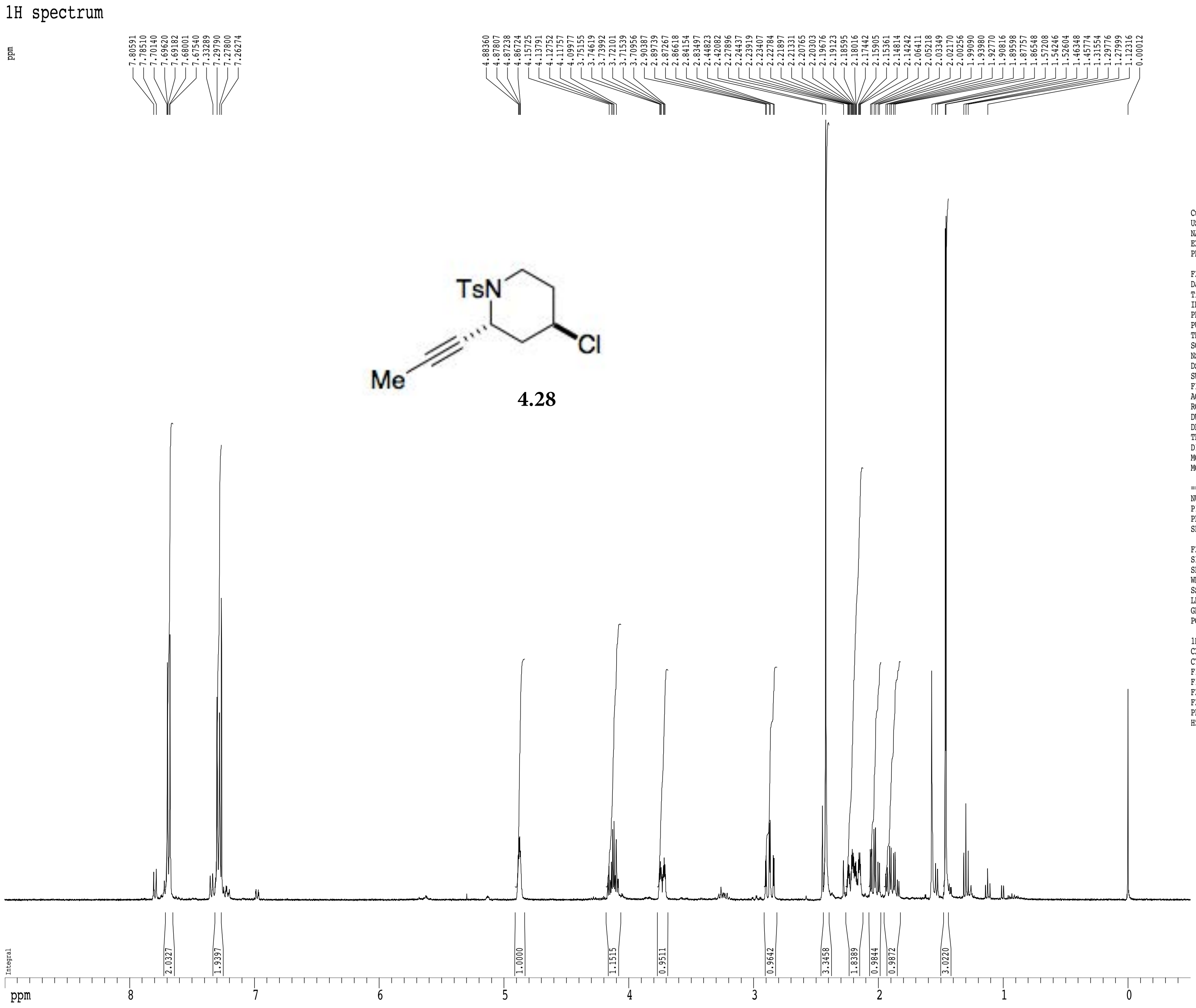
6.59566
6.38529
6.38383
6.01547
6.01437
6.01294
6.01156
6.01015
5.15980
5.15254
3.03786
3.03278
3.01297
3.00780
2.98781
2.98286
2.43462
2.42973
2.42518
2.40908
2.39925
2.39157
2.30257
2.29780
2.29318
2.28960
2.27627
2.27146
2.26785
2.22967
2.22029
2.20878
2.19952
2.18324
2.17369
2.03946
2.03622
2.02992
2.01376
2.00448
1.98848
1.97829
TsN
Cl
O
O
Integral
-0.000
-0.000
-0.000
-0.000
-0.001
1.0000
-0.012
-0.017
-0.017
-0.008
-0.006
ppm
8
7
6
5
4
3
2
1
0
Current Data Parameters
USER khewitt1
NAME KAH-III-191-SM-Z
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200711
Time 17.33
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoe1cc22.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2221214 MHz
SP9 61.60 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz
====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm

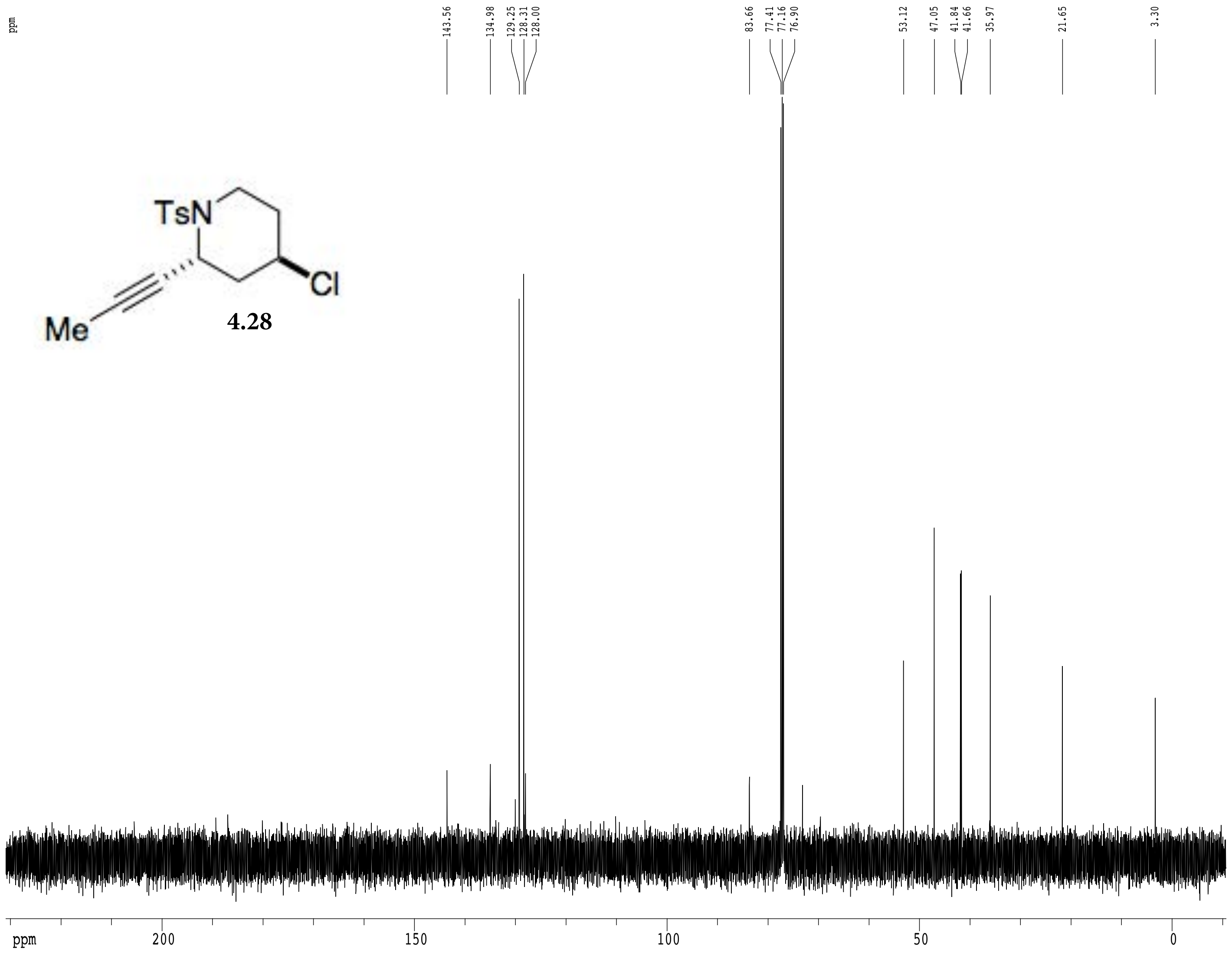
4.55



4.28

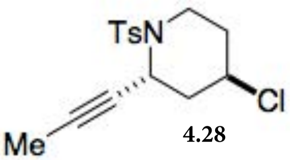
```
Current Data Parameters
USER            khewitt1
NAME         KAH-IV-030-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201104
Time               18.07
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                 406.4
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300204 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

13C spectrum with 1H decoupling



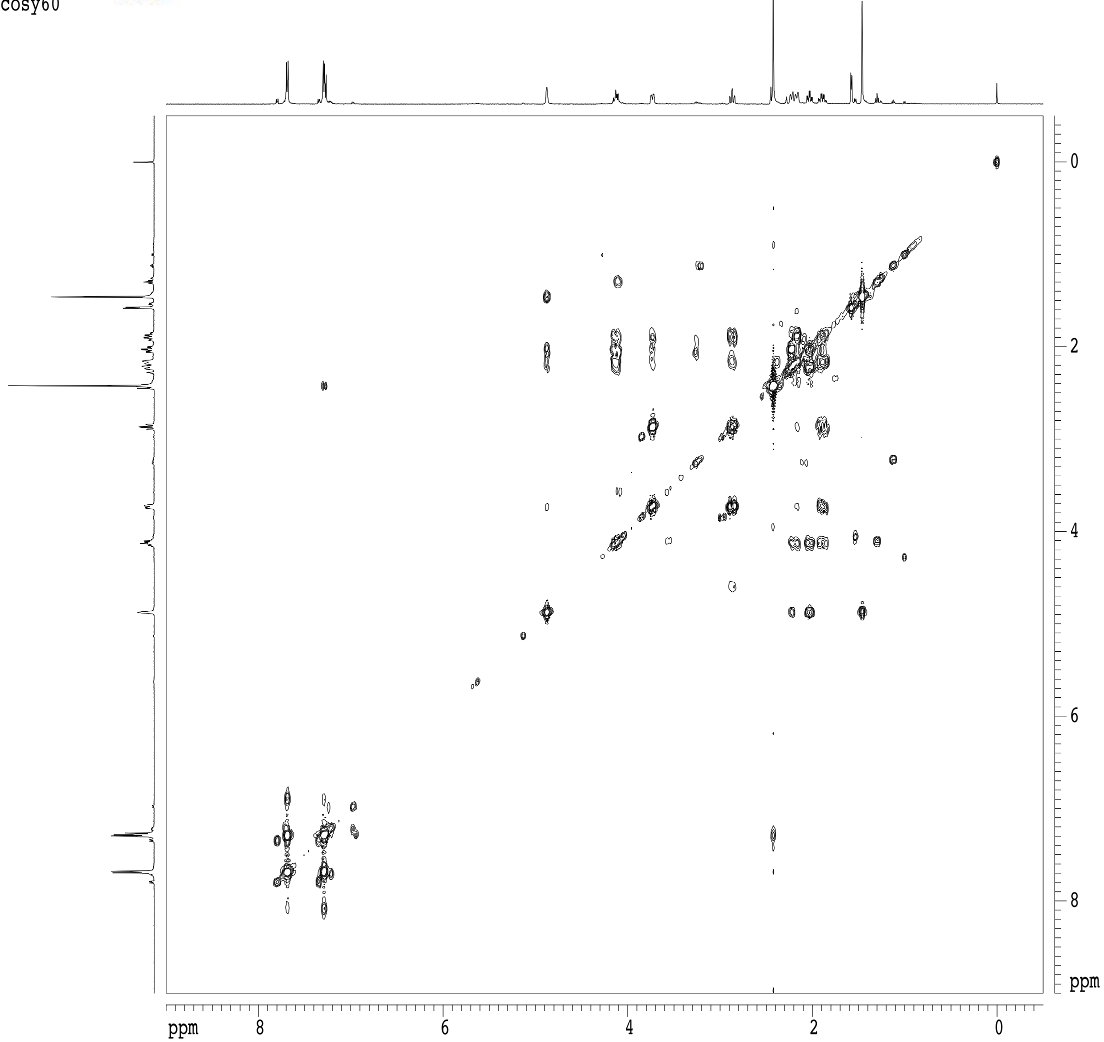
4.28

```
Current Data Parameters
USER             khewitt1
NAME          KAH-IV-030-Z
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201104
Time                19.16
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    224
DS                      4
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 3649.1
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  14.20 usec
PL1                 -6.00 dB
SFO1          125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -6.00 dB
PL12                12.30 dB
SFO2          498.7524937 MHz

F2 - Processing parameters
SI                  65536
SF            125.4107757 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  20.00 cm
CY                  12.50 cm
F1P               230.907 ppm
F1               28958.25 Hz
F2P               -10.723 ppm
F2               -1344.78 Hz
PPMCM            12.08151 ppm/cm
HZCM           1515.15149 Hz/cm
```



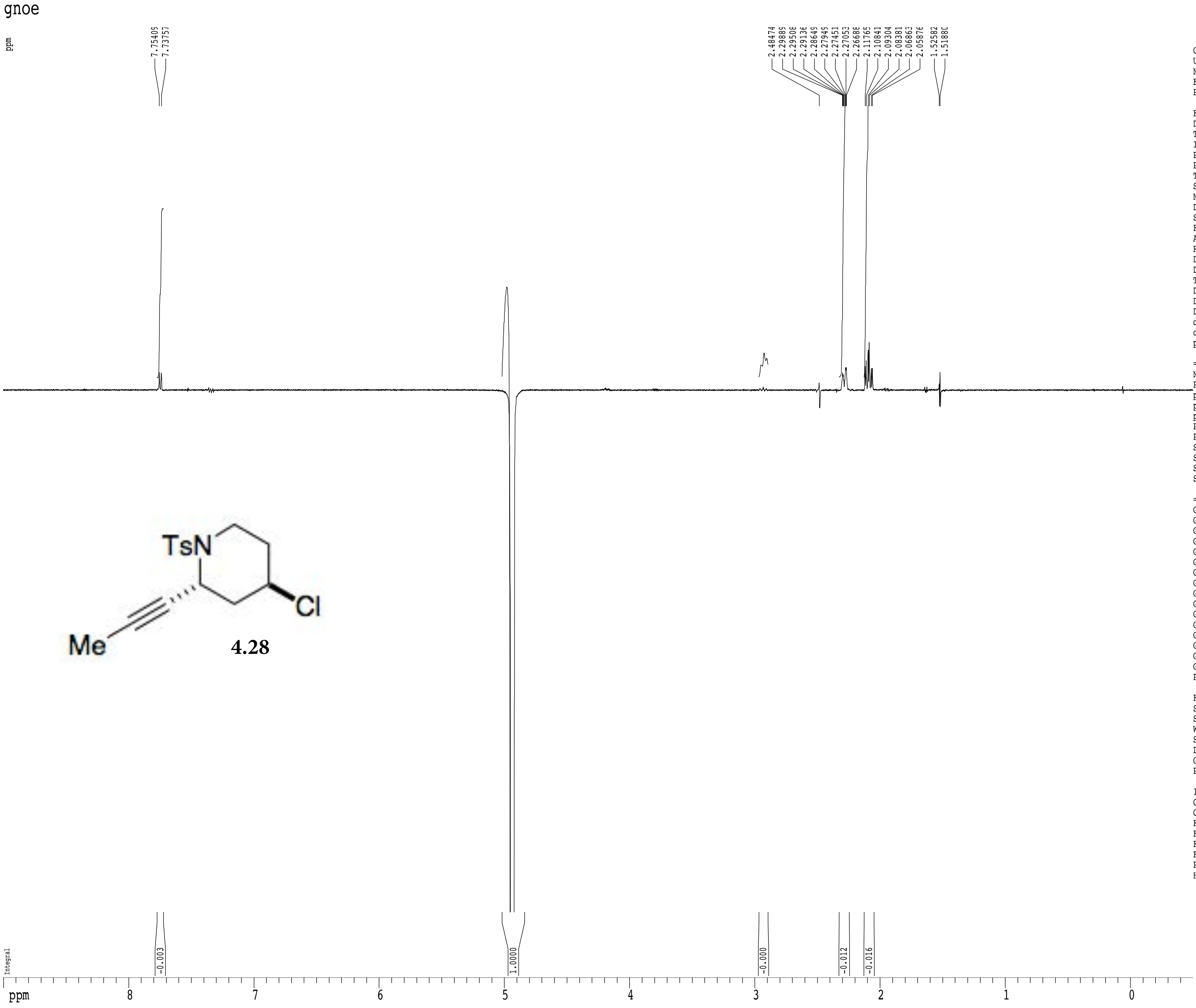
4.28

gcosy60



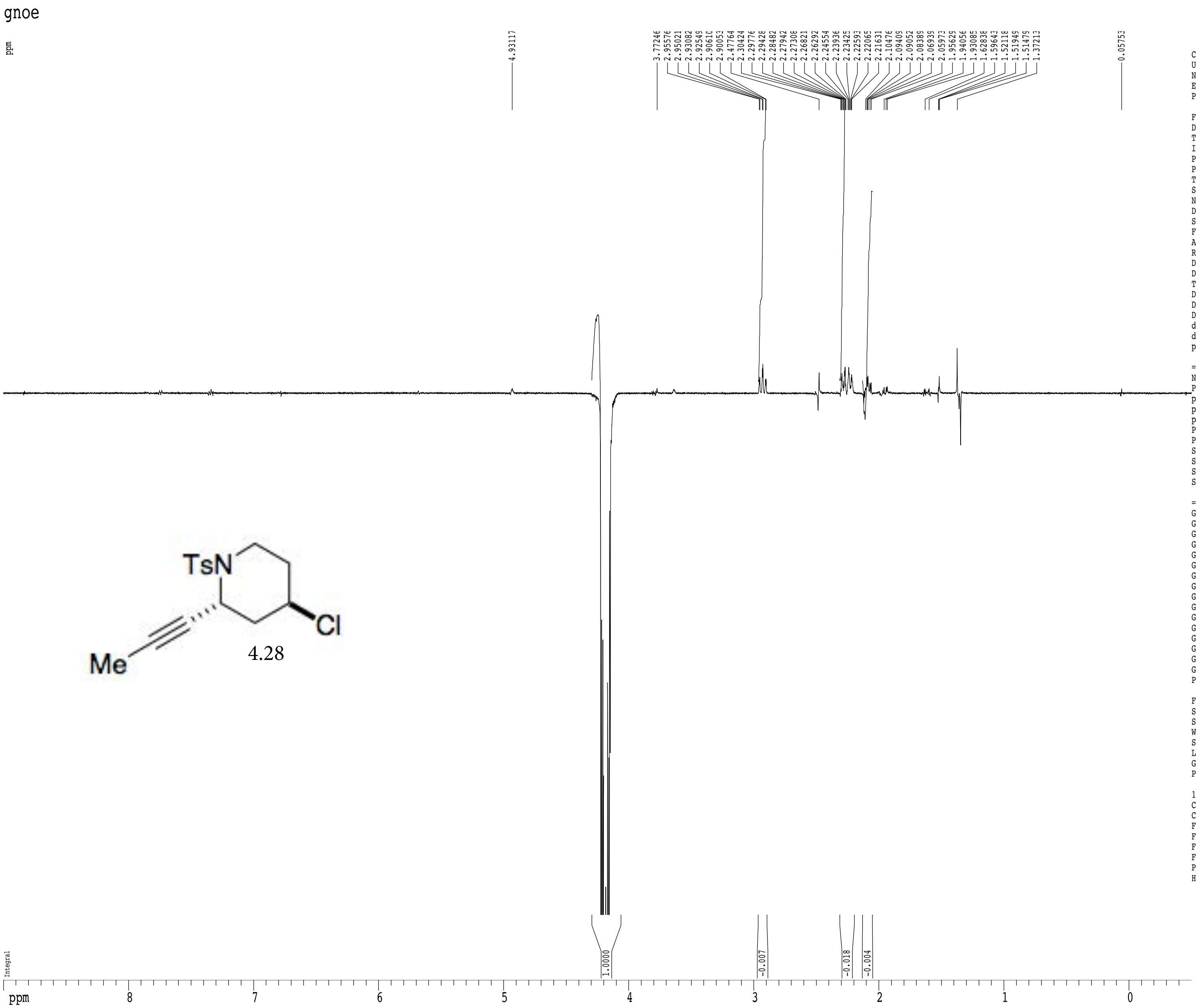
```
         Current Data Parameters
USER            khewitt1
NAME         KAH-IV-030-Z
EXPNO                  7
PROCNO                 1

       F2 - Acquisition Parameters
Date_           20201104
Time               19.05
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                5792.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

       F1 - Acquisition parameters
ND0                    1
TD                   256
SFO1            498.7535 MHz
FIDRES         31.300079 Hz
SW                16.066 ppm
FnMODE                QF

       F2 - Processing parameters
SI                  1024
SF           498.7500295 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

       F1 - Processing parameters
SI                  1024
MC2                   QF
SF           498.7500295 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

         2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.000 ppm
F2LO             4488.75 Hz
F2PHI             -0.500 ppm
F2HI             -249.38 Hz
F1PLO              9.000 ppm
F1LO             4488.75 Hz
F1PHI             -0.500 ppm
F1HI             -249.38 Hz
F2PPMCM          0.63333 ppm/cm
F2HZCM         315.87503 Hz/cm
F1PPMCM          0.63333 ppm/cm
F1HZCM         315.87503 Hz/cm
```

gnoe



4.28

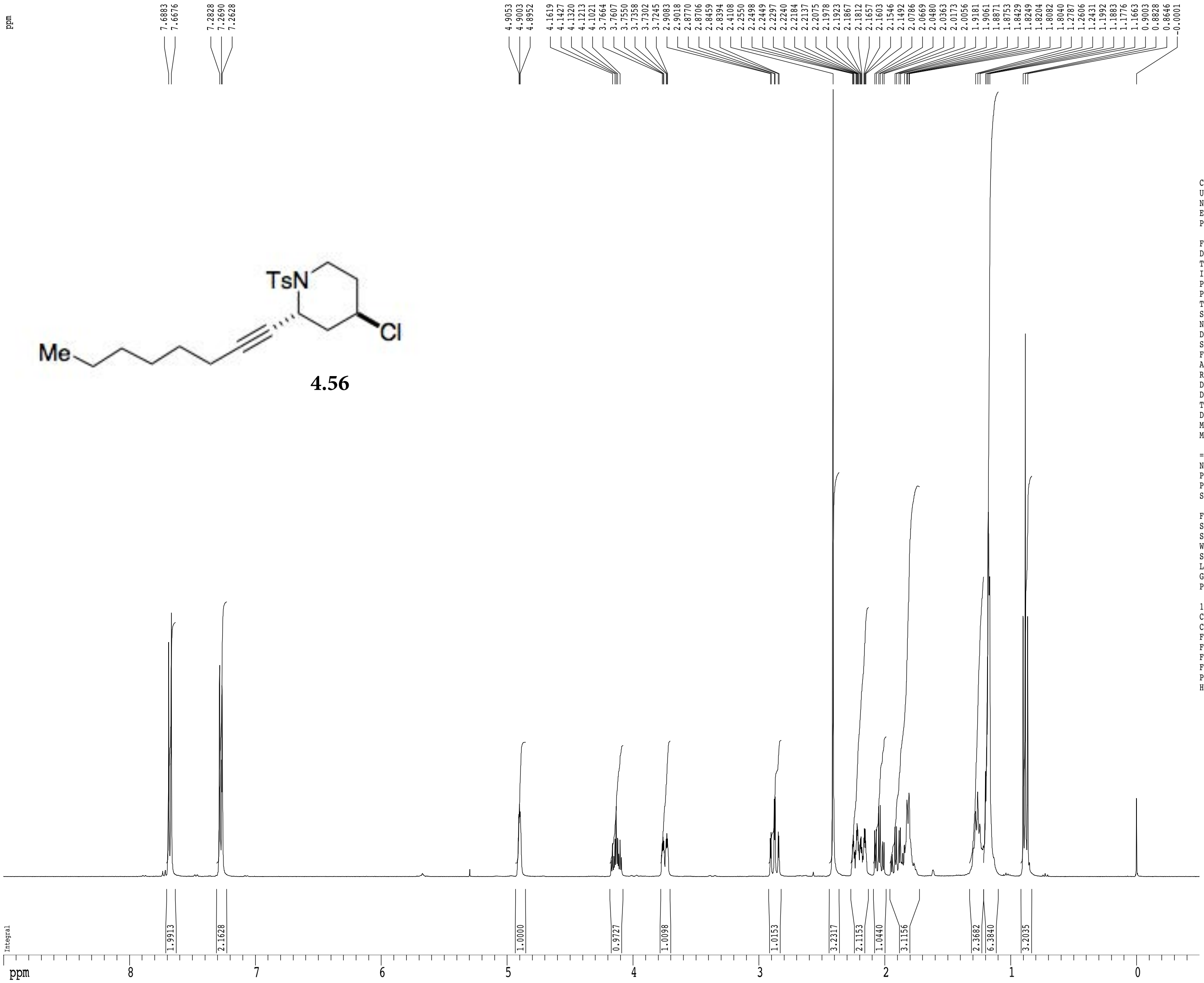
```
Current Data Parameters
USER              khewittl
NAME           KAH-IV-030-Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20201104
Time                 18.42
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    gnoe1cc22.prd
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       8
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    90.5
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
D8              0.50000000 sec
D16             0.00020000 sec
d21             0.33376500 sec
d22             0.16399699 sec
p2                   15.00 usec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
p3                   22.50 usec
p4                   30.00 usec
p5                   20.00 usec
P29               40000.00 usec
PL1                   1.60 dB
SFO1           500.2224686 MHz
SP9                  61.60 dB
SPNAM9          gauss1.512
SPOFF9                0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            sine.100
GPNAM2            sine.100
GPNAM3            sine.100
GPNAM4            sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPX4                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPY4                  0.00 %
GPZ1                  7.00 %
GPZ2                  3.00 %
GPZ3                  2.30 %
GPZ4                 -2.30 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   50.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```



4.28

```
Current Data Parameters
USER            khewitt1
NAME        KAH-IV-030-Z
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201104
Time               18.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  90.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1          1.00000000 sec
D8          0.50000000 sec
D16         0.00020000 sec
d21         0.33376500 sec
d22         0.16399699 sec
p2               15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2220945 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

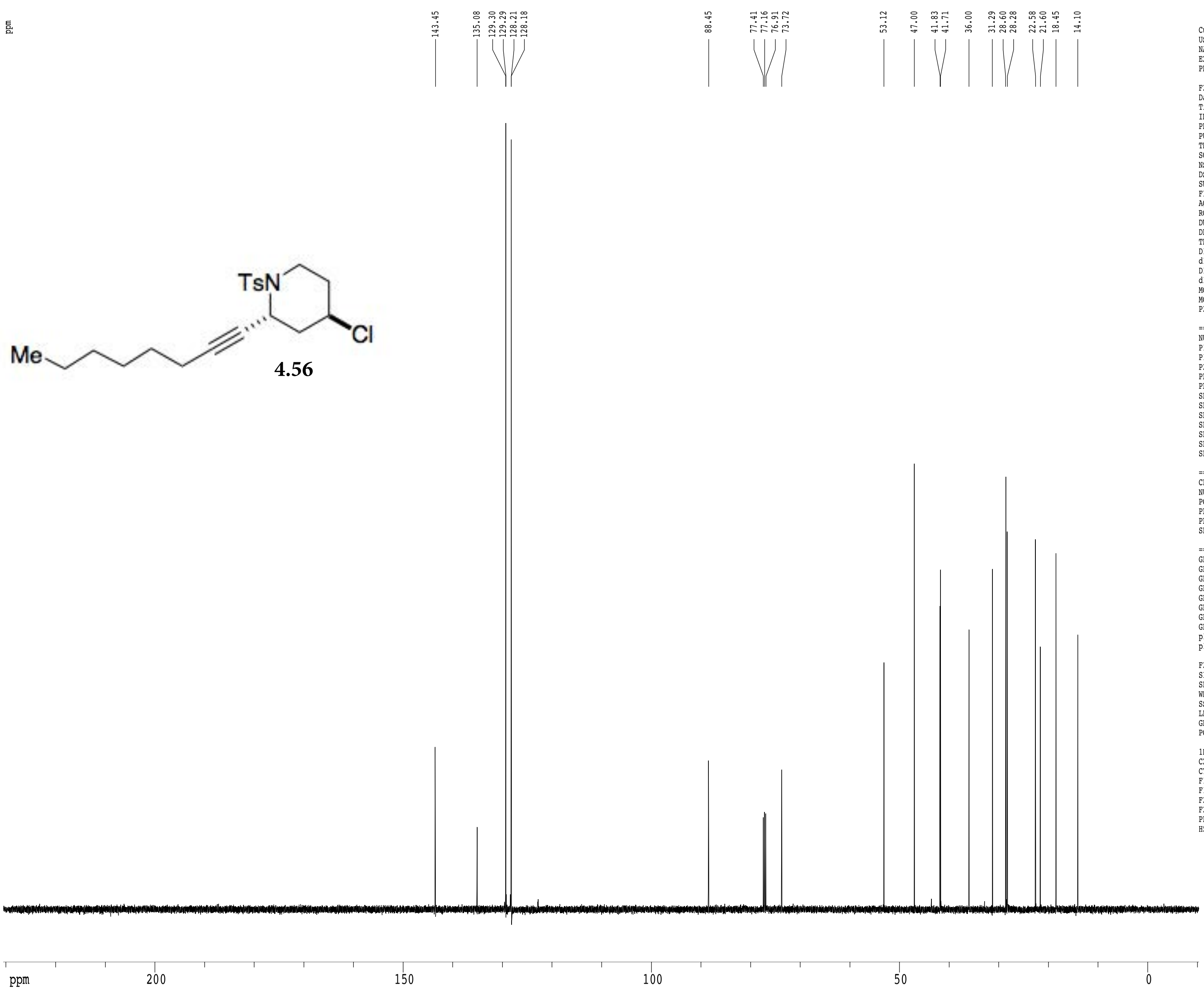
1H spectrum



4.56

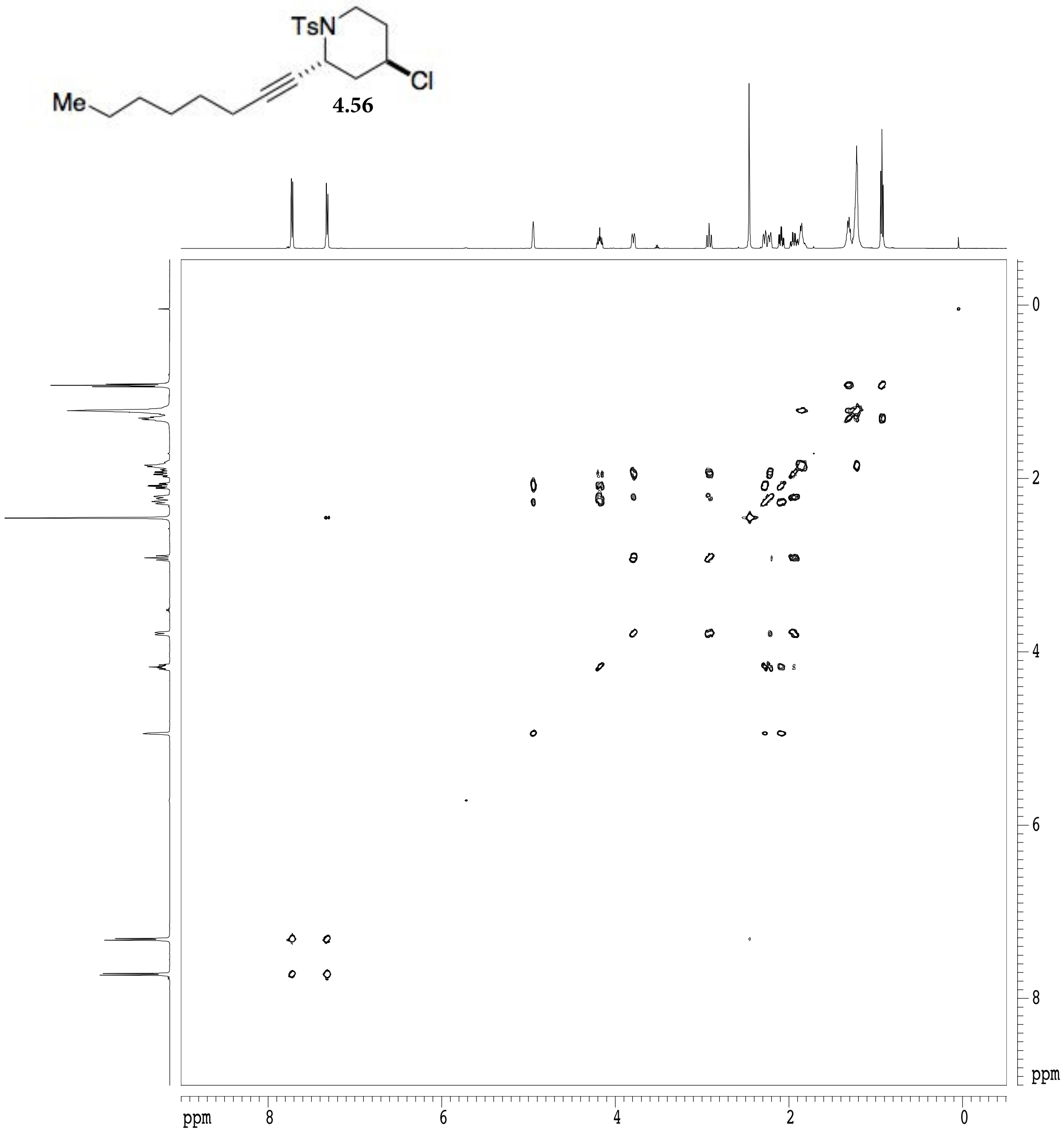
```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-041-check
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200115
Time              11.33
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                 71.8
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300177 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



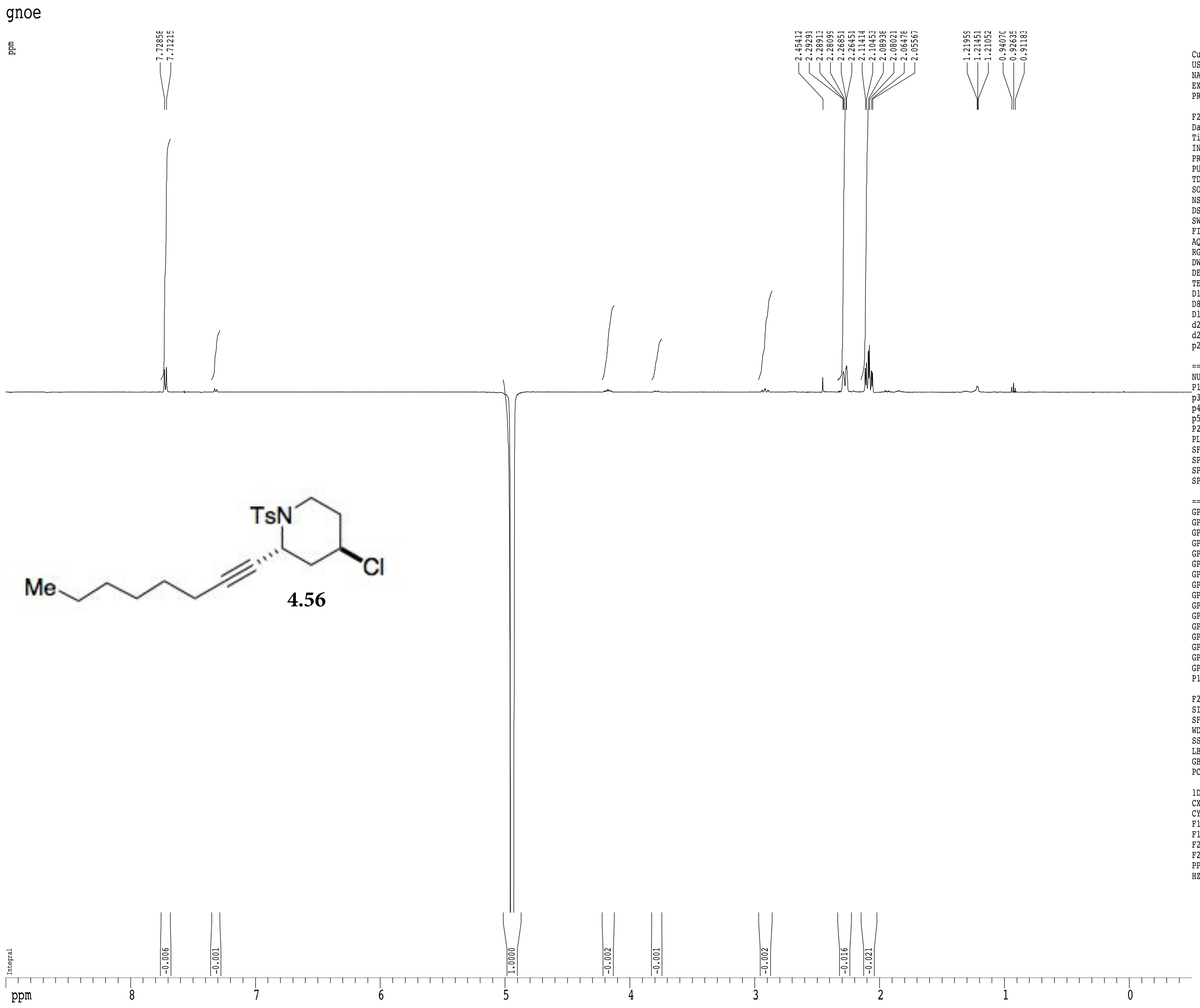
4.56

```
Current Data Parameters
USER            khewitt1
NAME       KAH-III-041-Z
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200116
Time               16.50
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                    96
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804136 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```


4.56

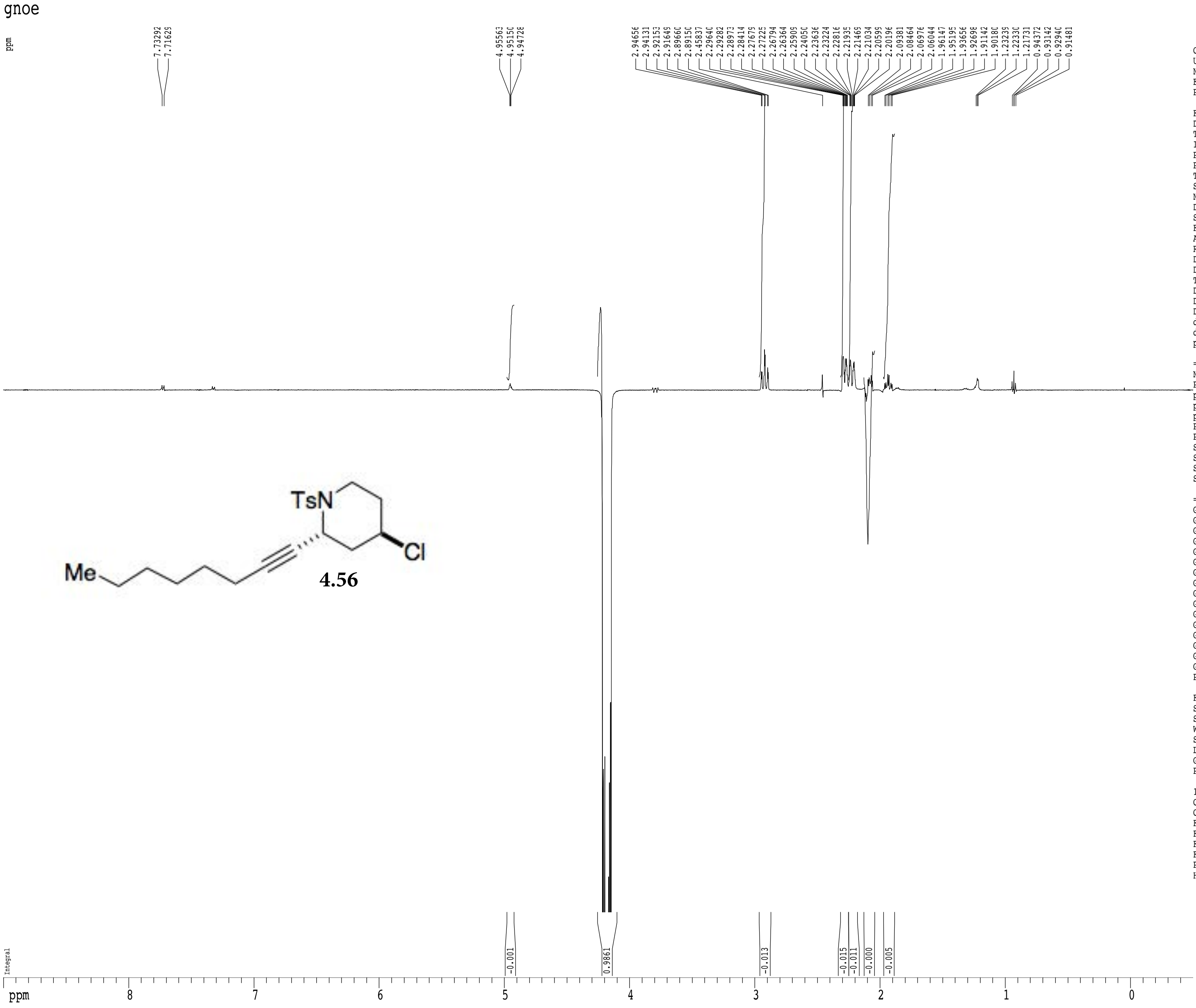
gcosy60

```
        Current Data Parameters
USER            khewitt1
NAME      KAH-III-041-Z
EXPNO                 2
PROCNO                1

      F2 - Acquisition Parameters
Date_          20200115
Time              17.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    1
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                   32
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

      F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.002 ppm
F2LO            4503.14 Hz
F2PHI            -0.509 ppm
F2HI            -254.47 Hz
F1PLO             9.002 ppm
F1LO            4503.14 Hz
F1PHI            -0.524 ppm
F1HI            -262.29 Hz
F2PPMCM         0.63407 ppm/cm
F2HZCM        317.17416 Hz/cm
F1PPMCM         0.63511 ppm/cm
F1HZCM        317.69583 Hz/cm
```



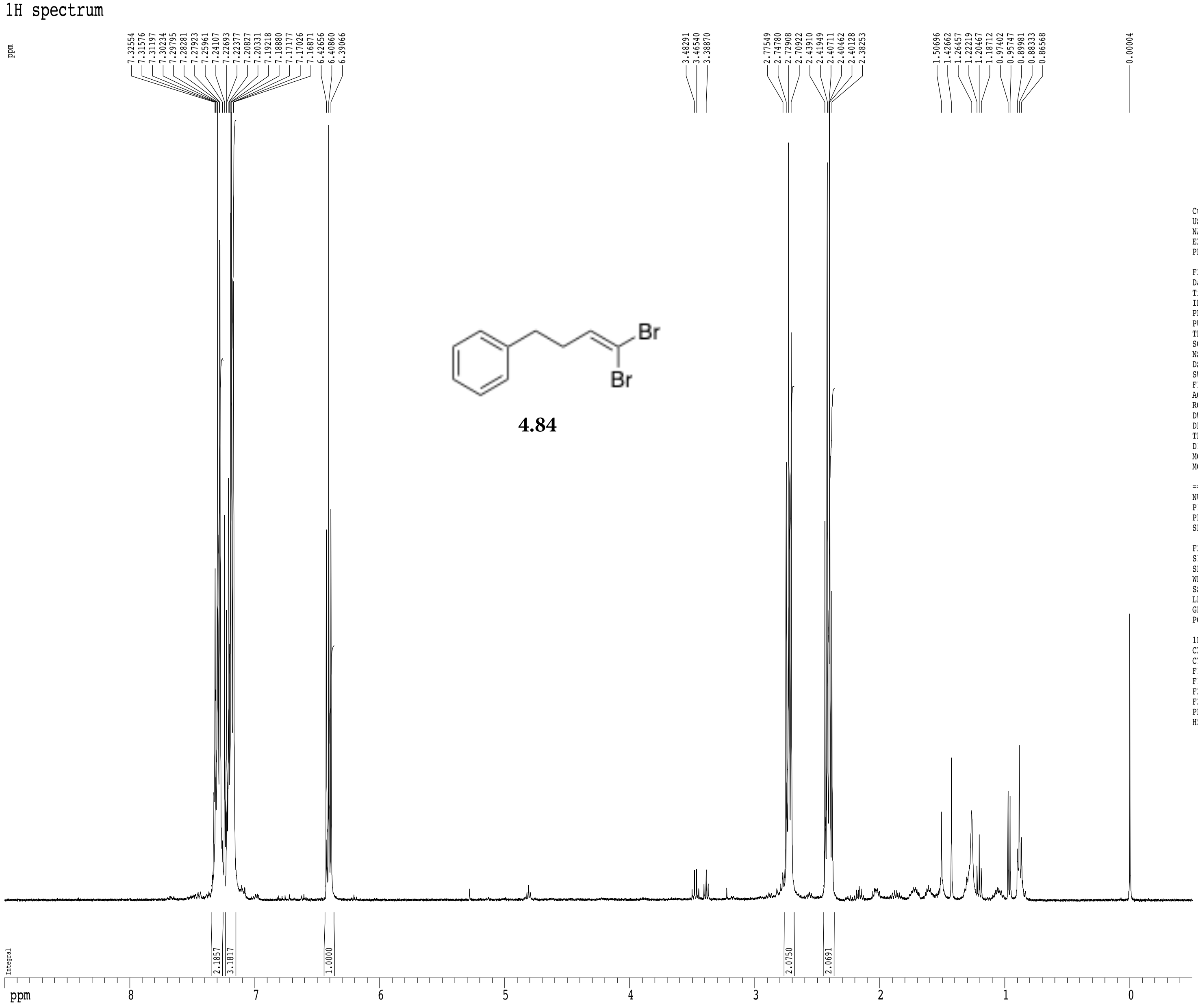
4.56

```
Current Data Parameters
USER          khewitt1
NAME      KAH-III-041-Z
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20200115
Time              17.58
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 35.9
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2224727 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



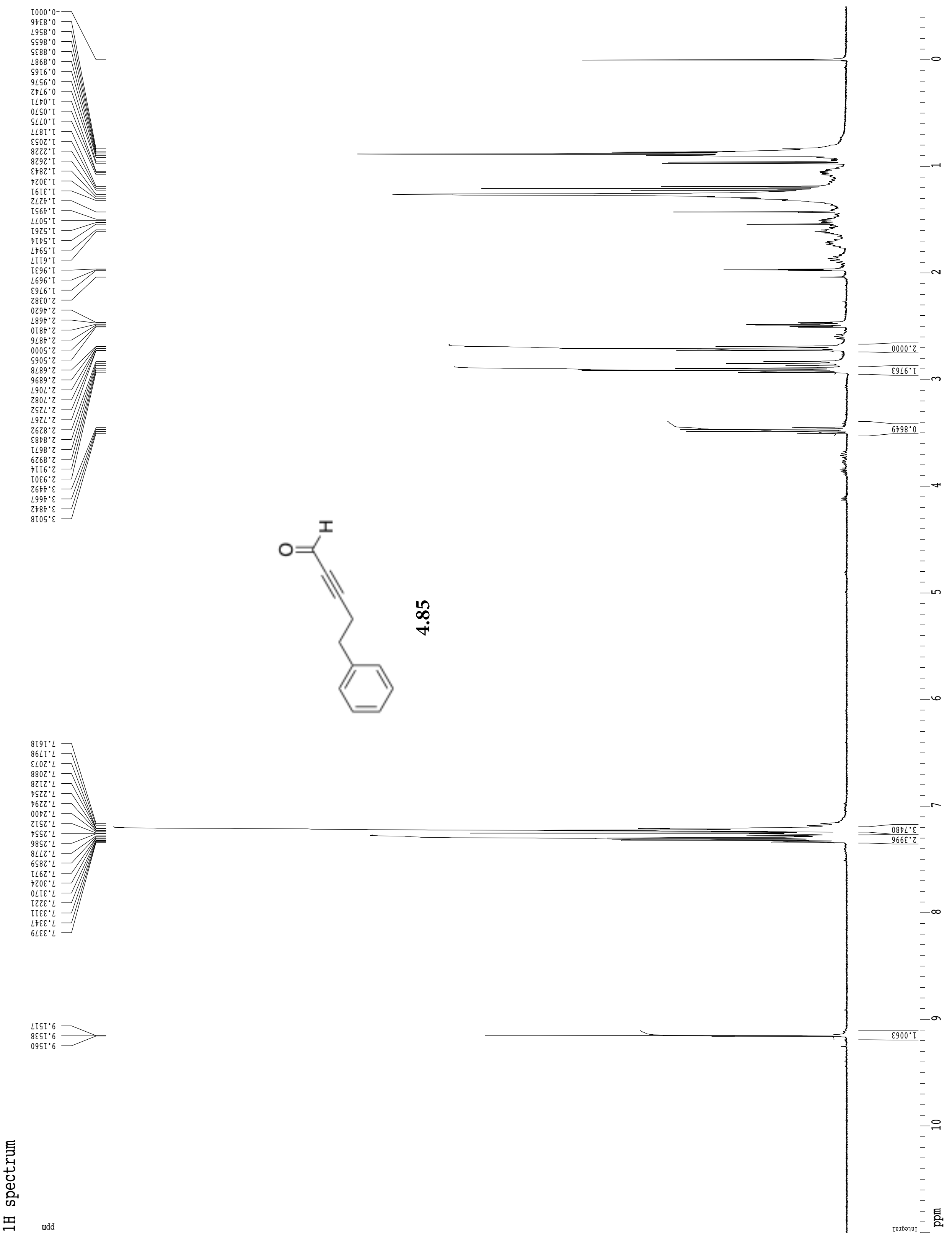
4.56

```
Current Data Parameters
USER              khewitt1
NAME          KAH-III-041-Z
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_          20200116
Time              16.47
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 45.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2220911 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



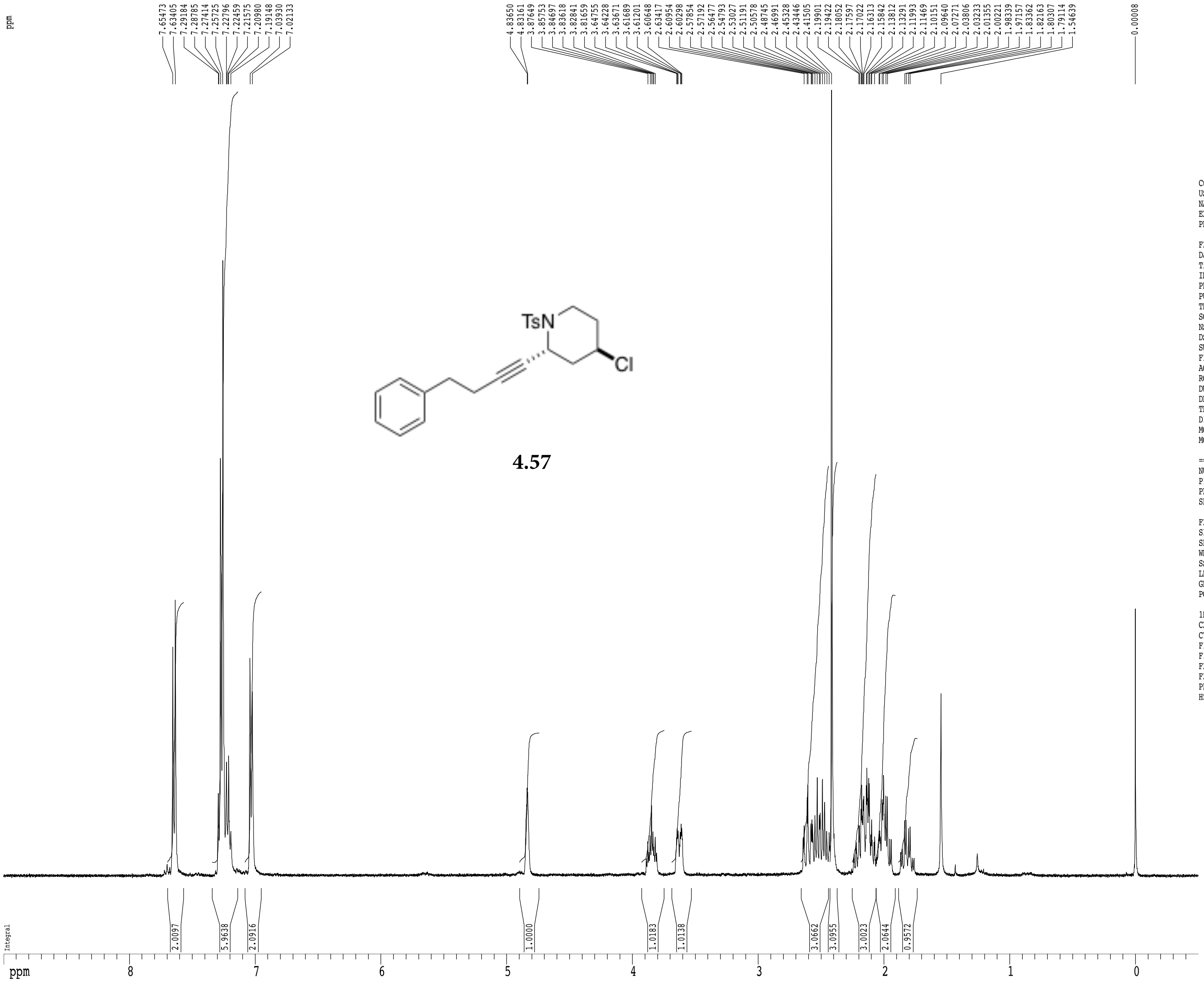
4.84

```
Current Data Parameters
USER              tthane
NAME            TATiv100
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200805
Time                9.32
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                 228.1
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300293 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 18.04 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```


1H spectrum
ppm
-0.0001
0.8346
0.8567
0.8655
0.8835
0.8987
0.9165
0.9576
0.9742
1.0471
1.0570
1.0775
1.1877
1.2053
1.2228
1.2628
1.2843
1.3024
1.3191
1.4272
1.4951
1.5077
1.5261
1.5414
1.5947
1.6117
1.9631
1.9697
1.9763
2.0382
2.4620
2.4687
2.4810
2.4876
2.5000
2.5065
2.6878
2.6896
2.7067
2.7082
2.7252
2.7267
2.8292
2.8483
2.8671
2.8929
2.9114
2.9301
3.4492
3.4667
3.4842
3.5018
7.1618
7.1798
7.2073
7.2088
7.2128
7.2254
7.2294
7.2400
7.2512
7.2554
7.2586
7.2778
7.2859
7.2971
7.3024
7.3170
7.3221
7.3311
7.3347
7.3379
9.1517
9.1538
9.1560
O
H
2.0000
1.9763
0.8649
3.7480
2.3996
1.0063
Integral
0
1
2
3
4
5
6
7
8
9
10
ppm

4.85

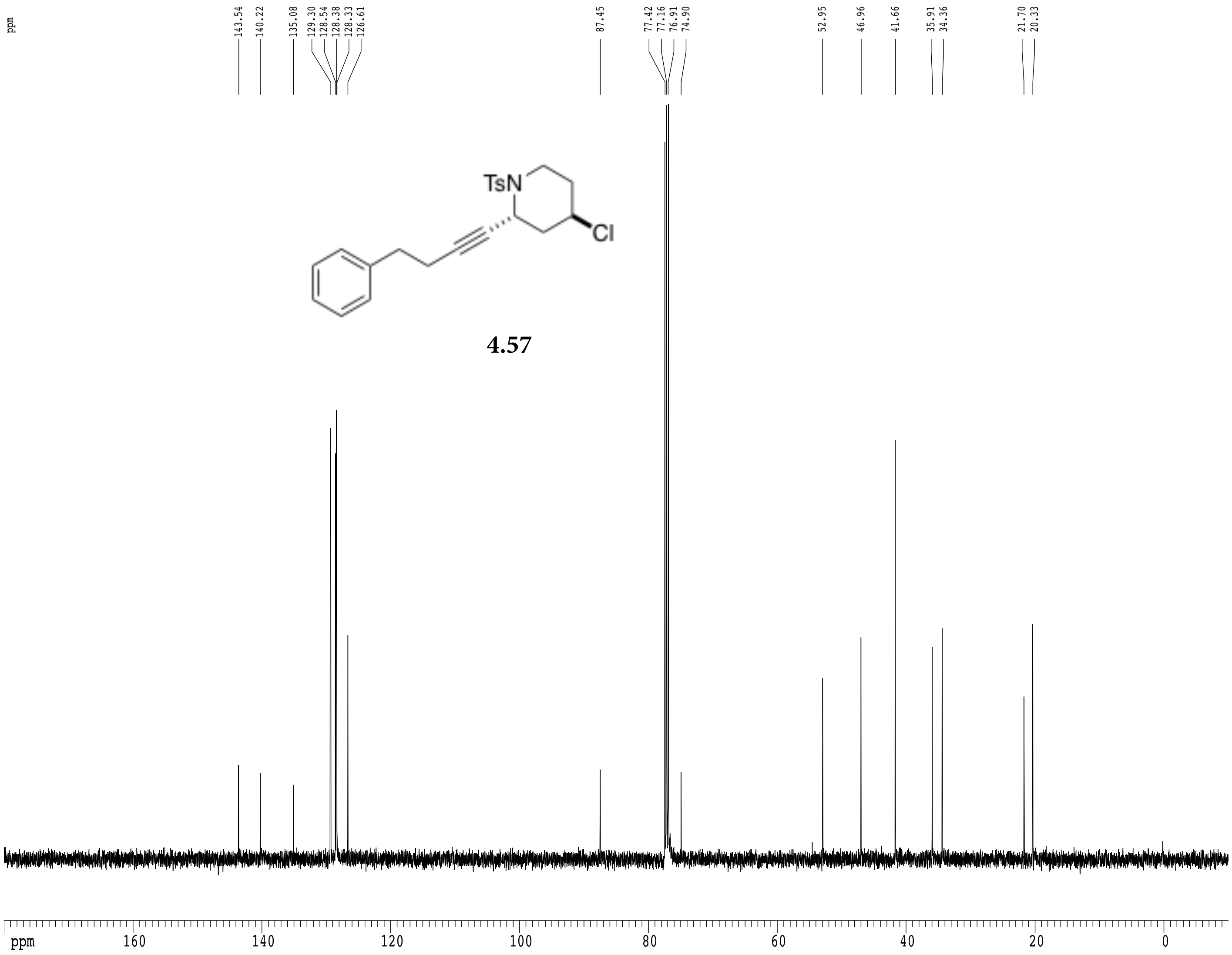
1H spectrum



4.57

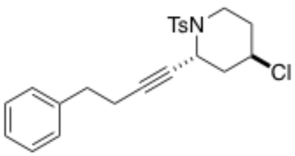
```
Current Data Parameters
USER            tthane
NAME     TATiv116check3
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200908
Time              16.56
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                  362
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300227 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling



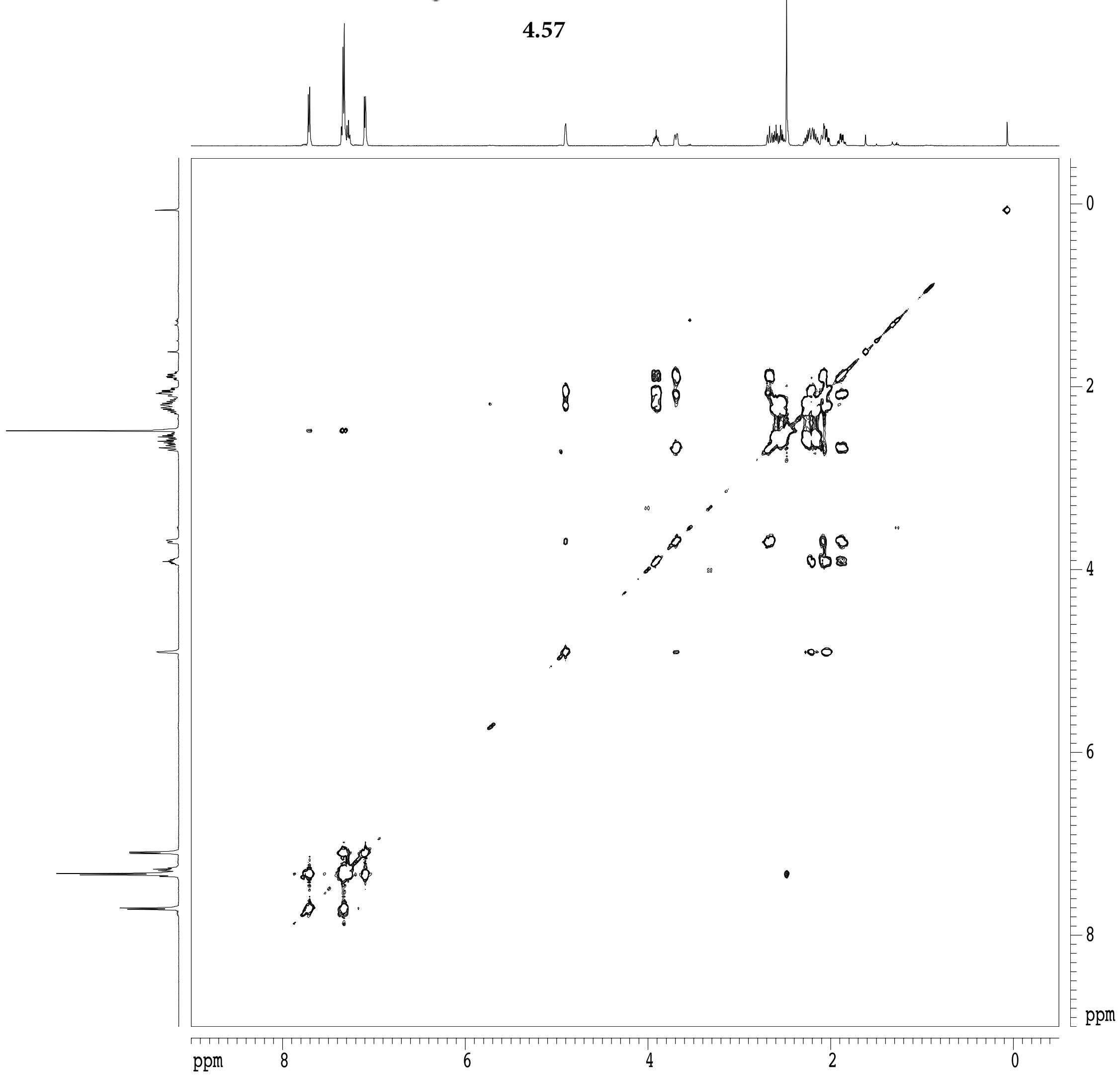
4.57

```
Current Data Parameters
USER              tthane
NAME     TATiv116carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200825
Time               10.06
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   568
DS                     4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 14.20 usec
PL1                -6.00 dB
SFO1        125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.30 dB
SFO2        498.7524937 MHz

F2 - Processing parameters
SI                 65536
SF           125.4107757 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              180.000 ppm
F1              22573.94 Hz
F2P              -10.000 ppm
F2              -1254.11 Hz
PPMCM            9.50000 ppm/cm
HZCM          1191.40234 Hz/cm
```

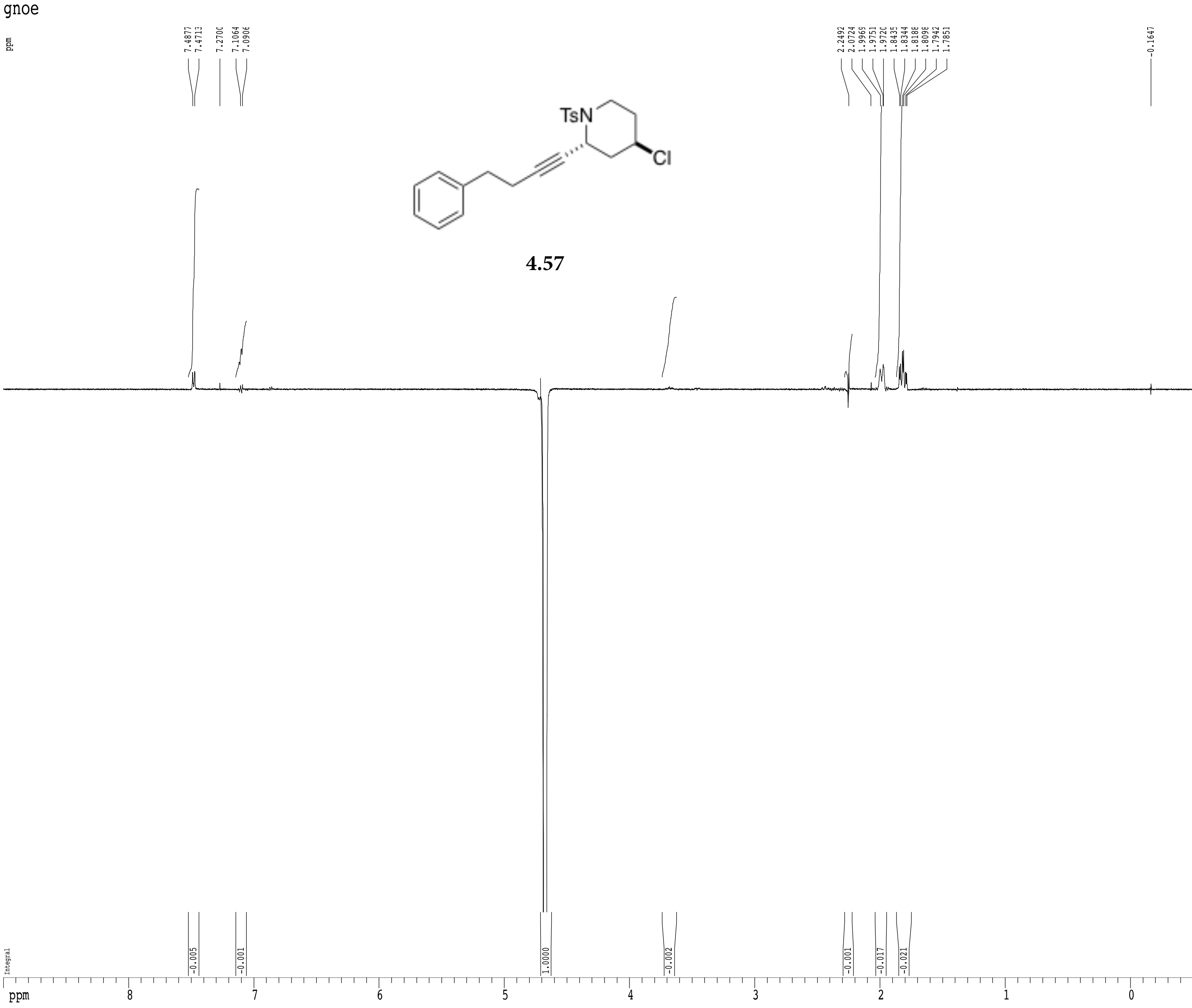


4.57

gcosy60

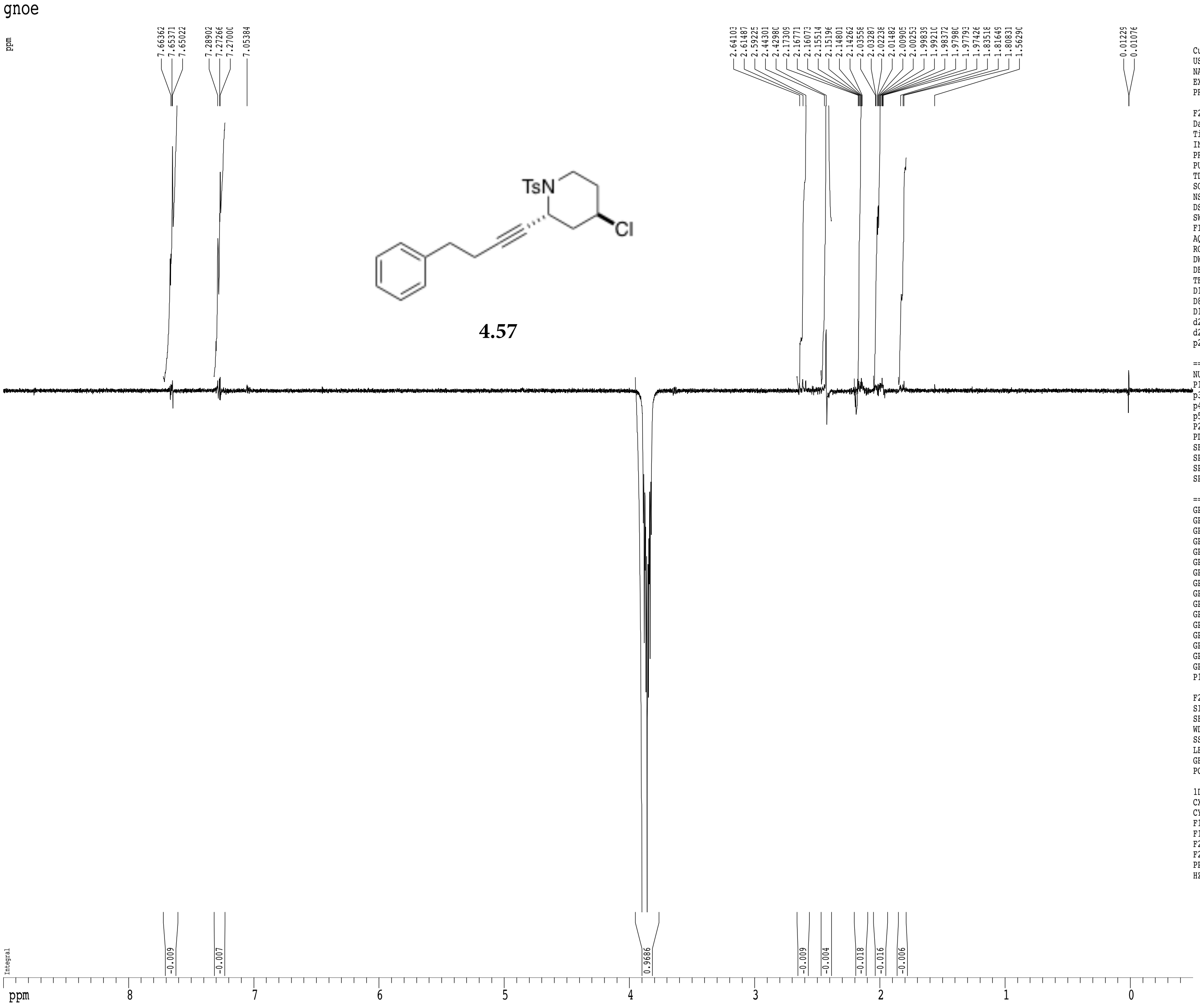


```
       Current Data Parameters
USER             tthane
NAME        TATiv116COSY
EXPNO                 2
PROCNO                1

     F2 - Acquisition Parameters
Date_          20201012
Time              17.47
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    2
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                574.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

    ======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

   ====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

     F1 - Acquisition parameters
ND0                   1
TD                  512
SFO1           500.2235 MHz
FIDRES        15.650040 Hz
SW               16.018 ppm
FnMODE               QF

      F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

      F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

        2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.000 ppm
F2LO            4501.98 Hz
F2PHI            -0.500 ppm
F2HI            -250.11 Hz
F1PLO             9.000 ppm
F1LO            4501.98 Hz
F1PHI            -0.500 ppm
F1HI            -250.11 Hz
F2PPMCM         0.63333 ppm/cm
F2HZCM        316.80600 Hz/cm
F1PPMCM         0.63333 ppm/cm
F1HZCM        316.80600 Hz/cm
```



4.57

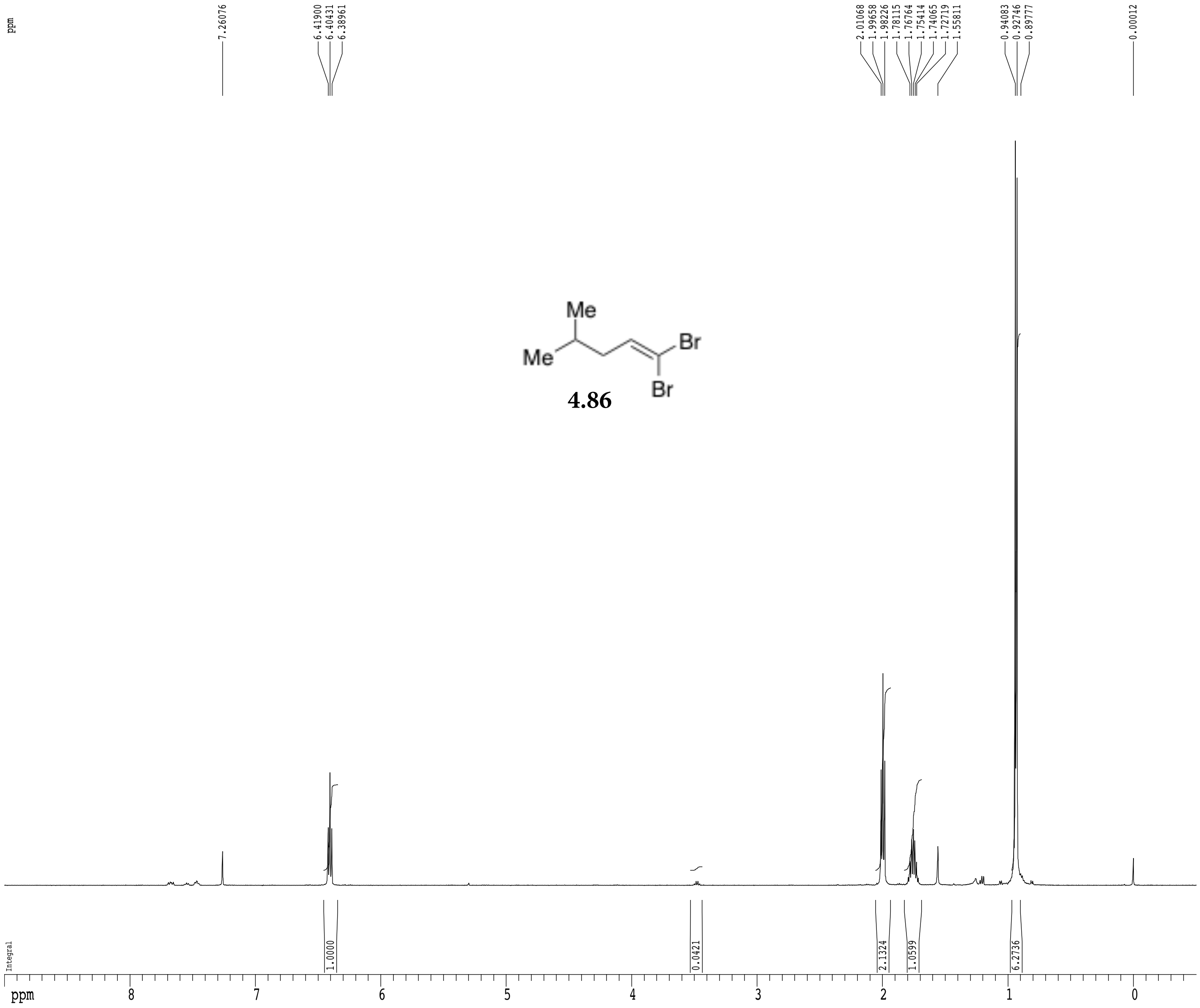
```
Current Data Parameters
USER              tthane
NAME       TATiv116NOE1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20200825
Time              10.00
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 80.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2224525 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2201159 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42506 Hz/cm
```



4.57

```
Current Data Parameters
USER              tthane
NAME        TATiv116NOE2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201012
Time               16.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   158
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 161.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2219567 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200273 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 10.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

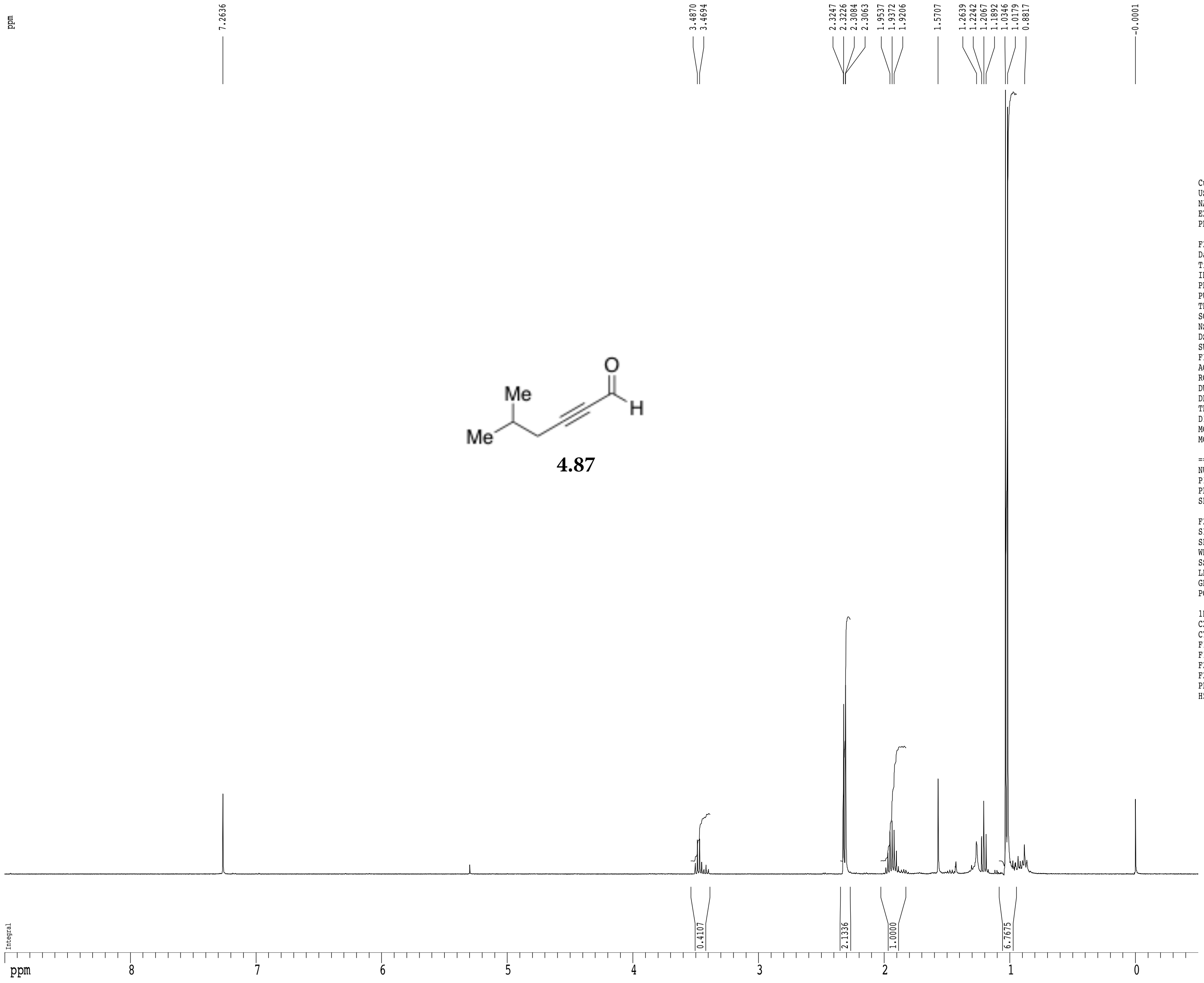
1H spectrum



4.86

```
Current Data Parameters
USER              tthane
NAME            TATiv66c
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200715
Time               11.43
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   512
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500309 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```

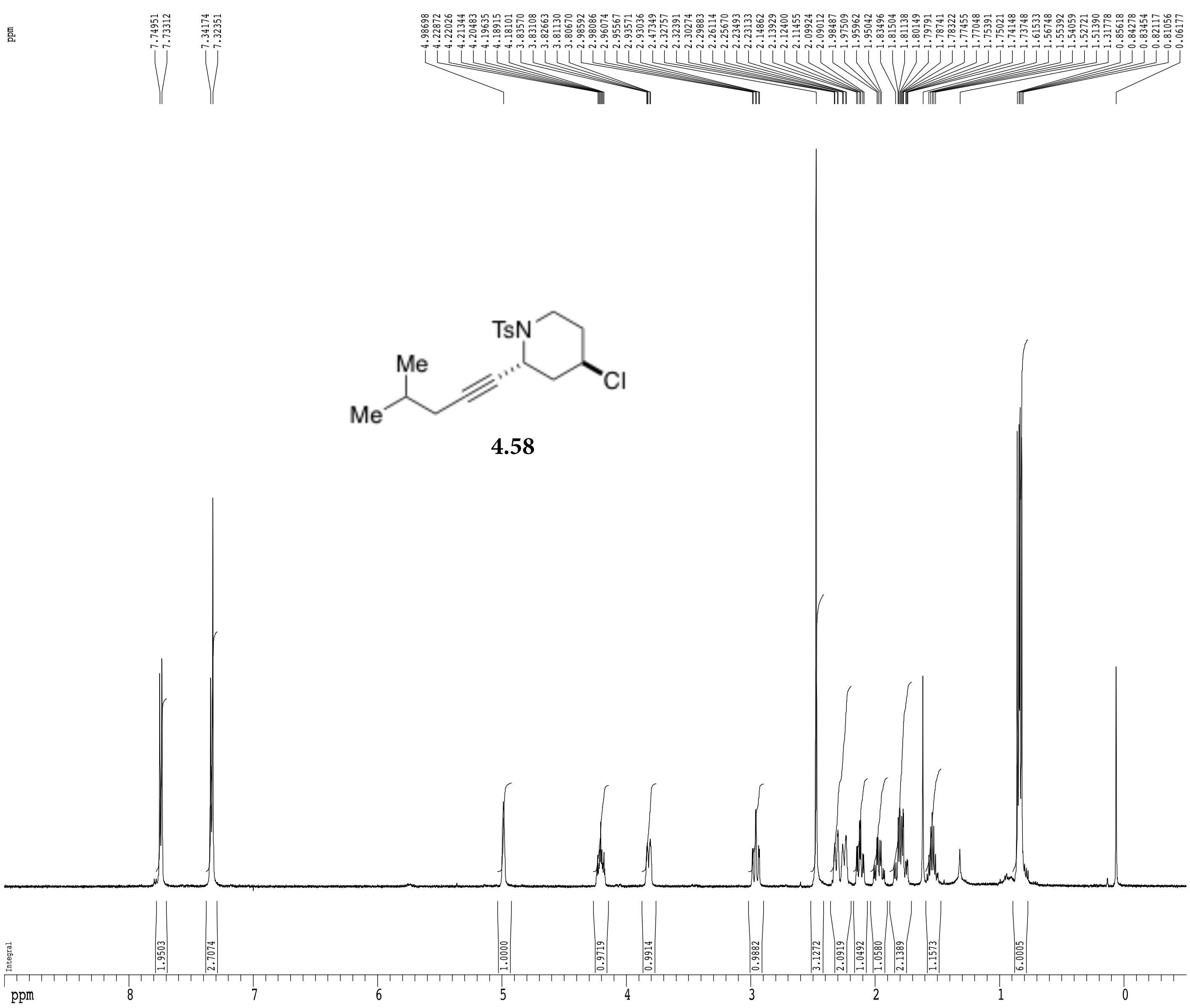
1H spectrum



4.87

```
Current Data Parameters
USER             tthane
NAME        TATiv68pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200711
Time              15.40
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                322.5
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300203 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

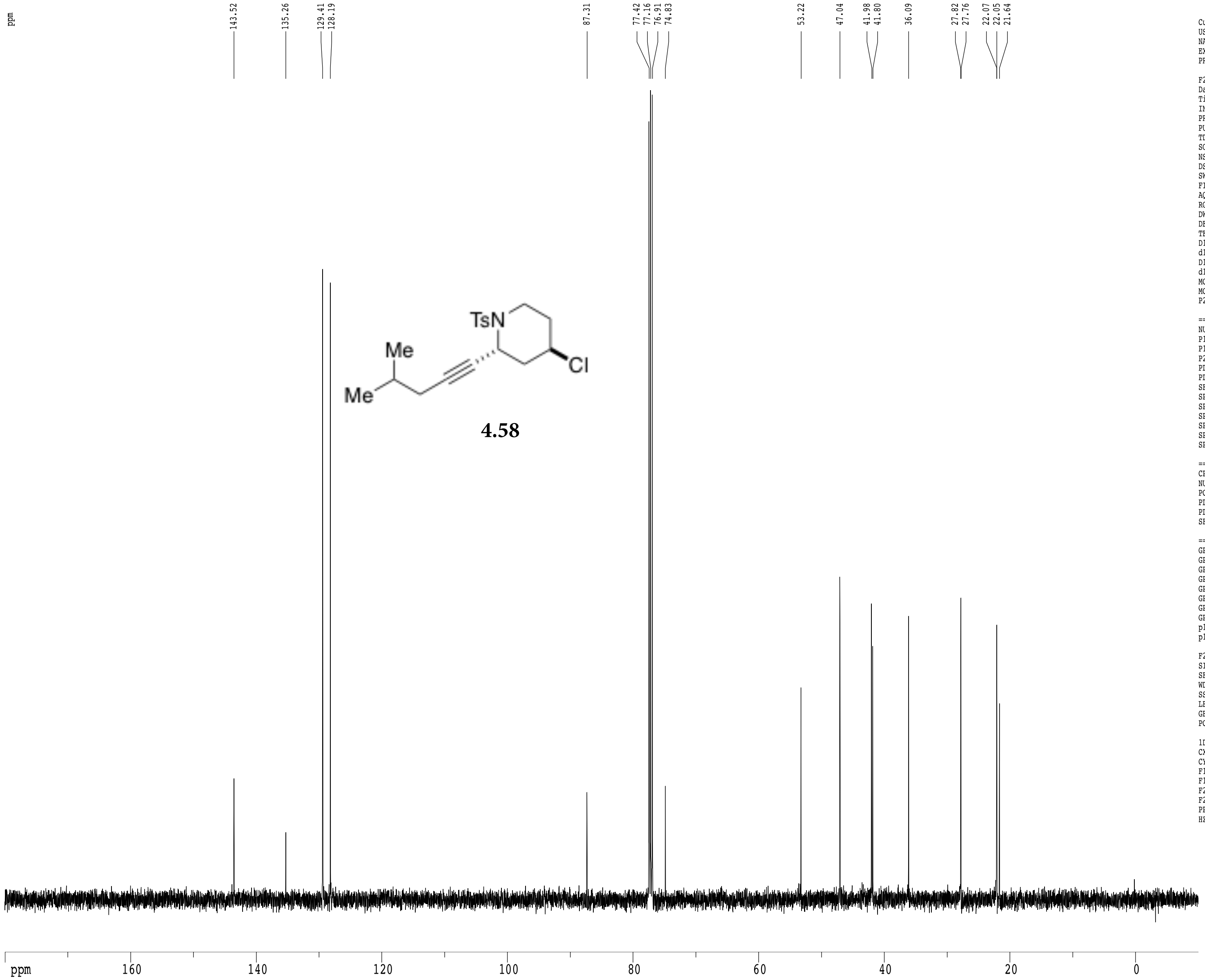
1H spectrum



4.58

```
Current Data Parameters
USER             tthane
NAME           TATiv69c
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200715
Time              11.46
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                912.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -6.00 dB
SFO1        498.7534913 MHz

F2 - Processing parameters
SI                65536
SF          498.7500000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                12.50 cm
F1P               9.000 ppm
F1              4488.75 Hz
F2P              -0.500 ppm
F2              -249.38 Hz
PPMCM           0.47500 ppm/cm
HZCM          236.90625 Hz/cm
```

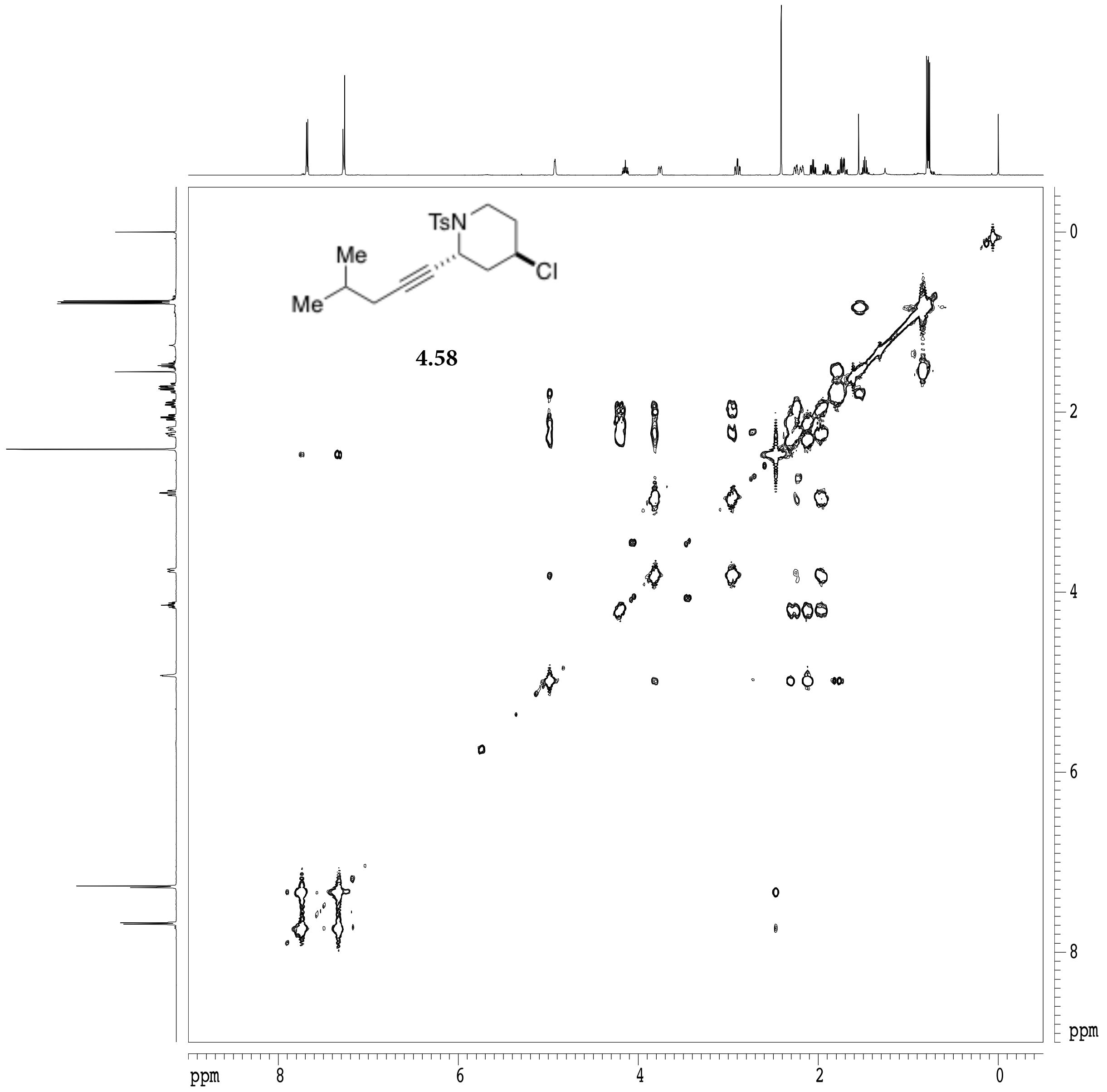
Z-restored spin-echo 13C spectrum with 1H decoupling



4.58

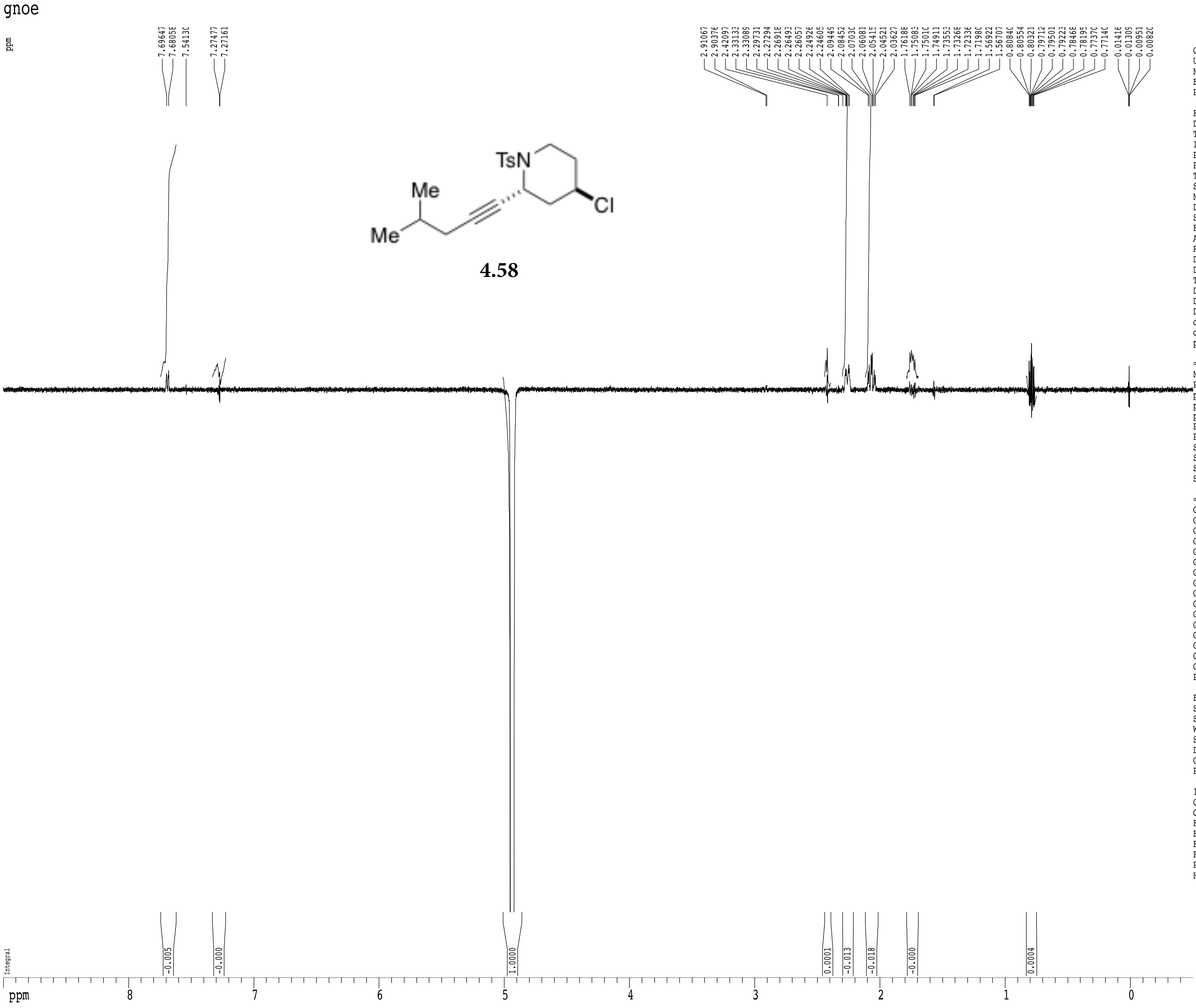
```
Current Data Parameters
USER              tthane
NAME        TATiv69carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200715
Time               15.43
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT           CDCl3T
NS                   408
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804062 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              180.000 ppm
F1              22640.47 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM            8.33333 ppm/cm
HZCM          1048.17004 Hz/cm
```

gcosy60



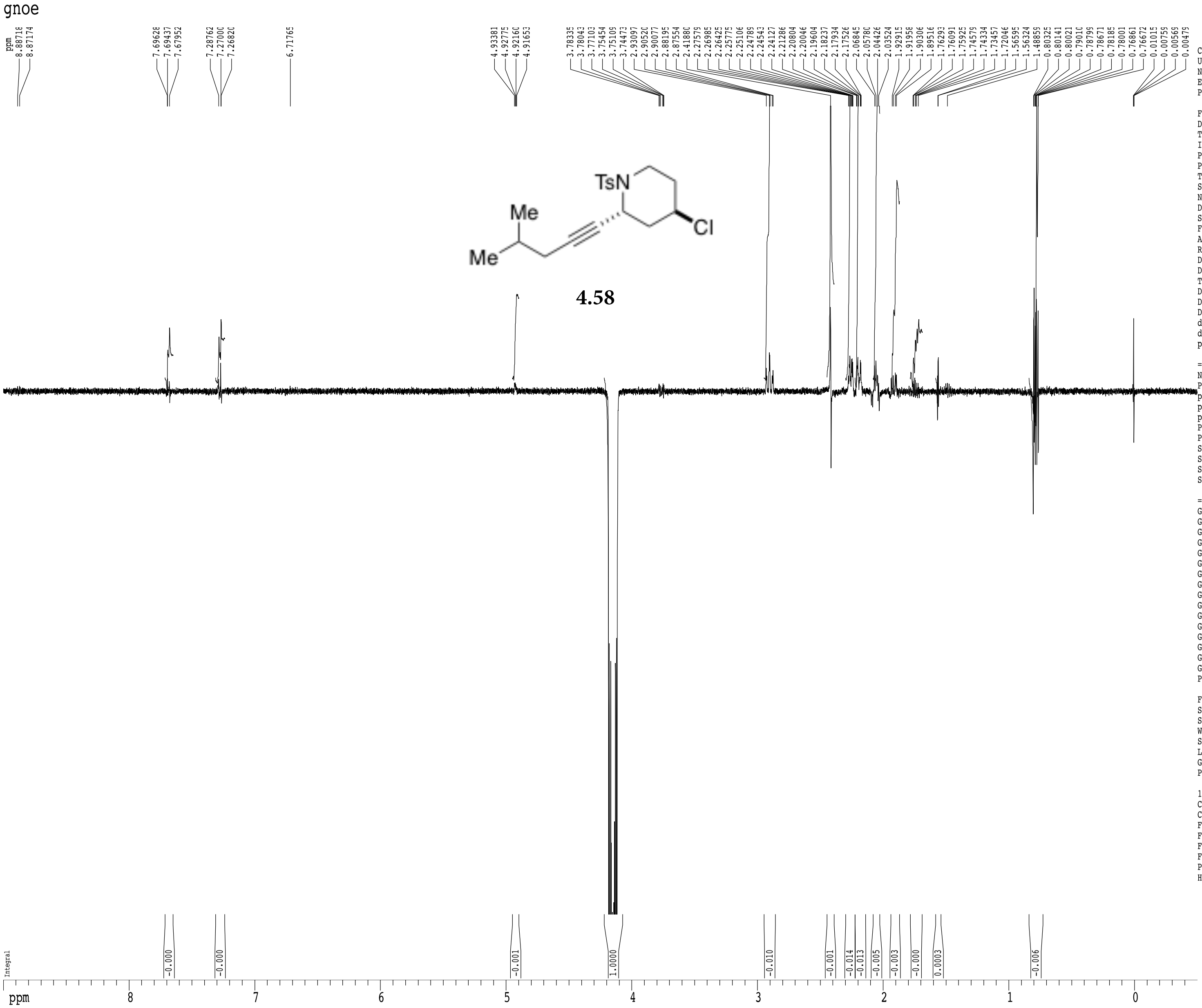
4.58

```
      Current Data Parameters
USER             tthane
NAME        TATiv69cosy
EXPNO                 2
PROCNO                1

     F2 - Acquisition Parameters
Date_          20200715
Time              15.57
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                 2048
SOLVENT           CDCl3
NS                    2
DS                   16
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                456.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
d0           0.00000300 sec
D1           1.00000000 sec
d13          0.00000300 sec
D16          0.00020000 sec
IN0          0.00012480 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              17.00 %
GPZ2              17.00 %
P16             1000.00 usec

     F1 - Acquisition parameters
ND0                   1
TD                  274
SFO1           500.2235 MHz
FIDRES        29.243870 Hz
SW               16.018 ppm
FnMODE               QF

     F2 - Processing parameters
SI                 1024
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

     F1 - Processing parameters
SI                 1024
MC2                  QF
SF          500.2200000 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0

      2D NMR plot parameters
CX2               15.00 cm
CX1               15.00 cm
F2PLO             9.000 ppm
F2LO            4501.98 Hz
F2PHI            -0.500 ppm
F2HI            -250.11 Hz
F1PLO             9.000 ppm
F1LO            4501.98 Hz
F1PHI            -0.500 ppm
F1HI            -250.11 Hz
F2PPMCM         0.63333 ppm/cm
F2HZCM        316.80600 Hz/cm
F1PPMCM         0.63333 ppm/cm
F1HZCM        316.80600 Hz/cm
```



4.58

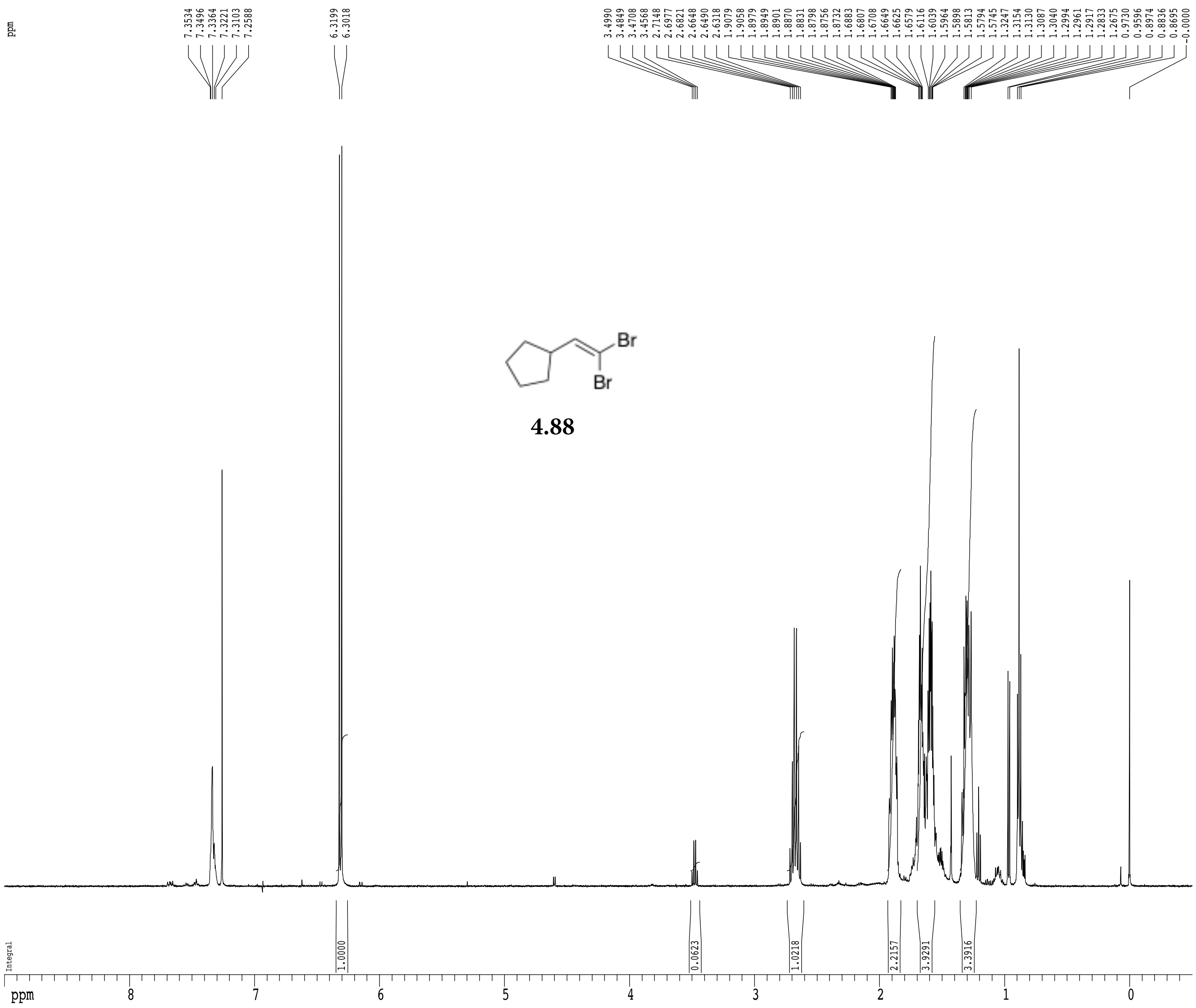
```
Current Data Parameters
USER              tthane
NAME        TATiv69NOE1
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20200716
Time               8.38
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2224946 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200255 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```



4.58

```
Current Data Parameters
USER              tthane
NAME        TATiv69NOE2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200716
Time                8.58
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   152
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 101.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2221031 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200273 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

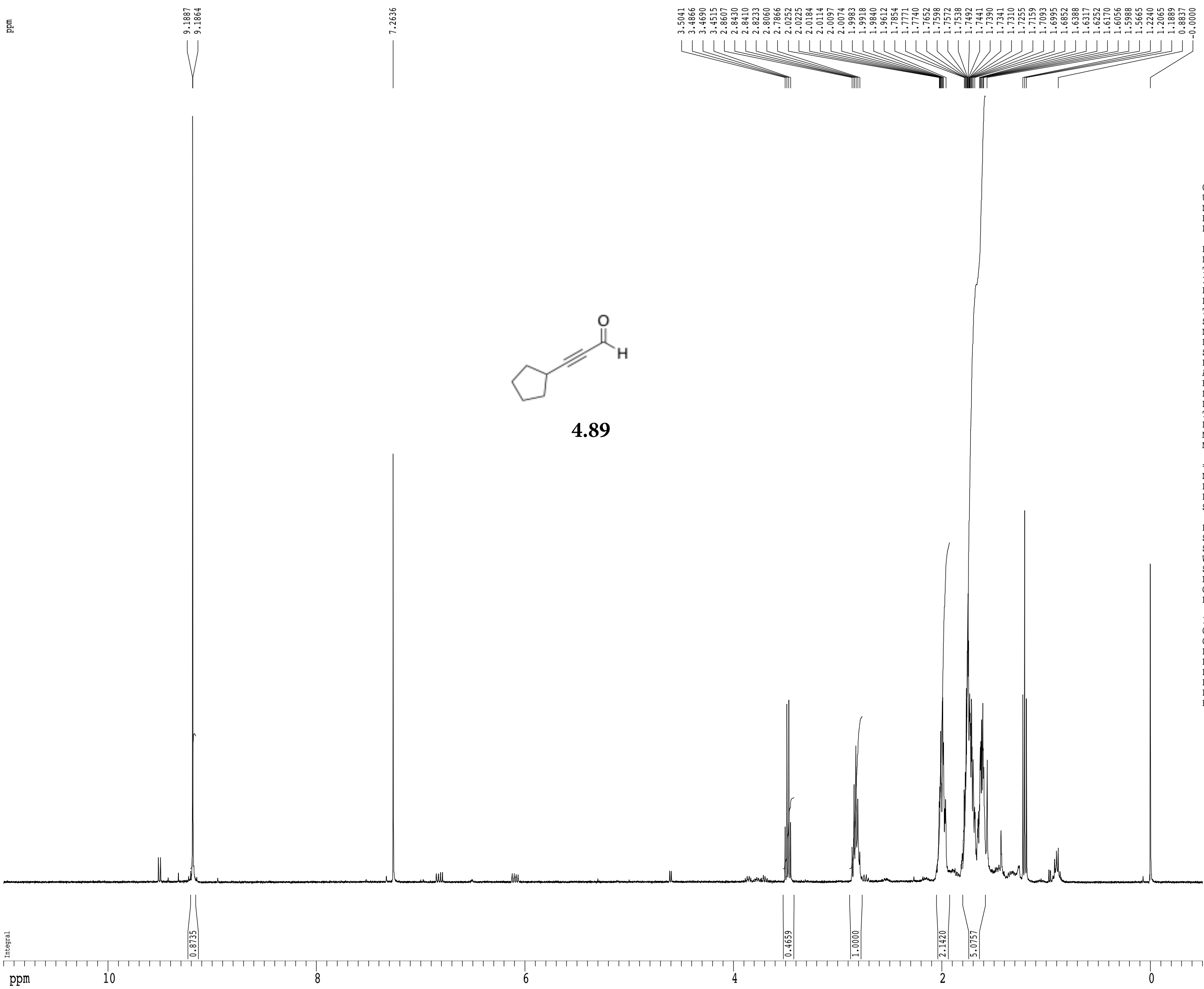
1H spectrum



4.88

```
Current Data Parameters
USER               tthane
NAME          TATiv118-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200826
Time               15.29
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   181
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500319 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```

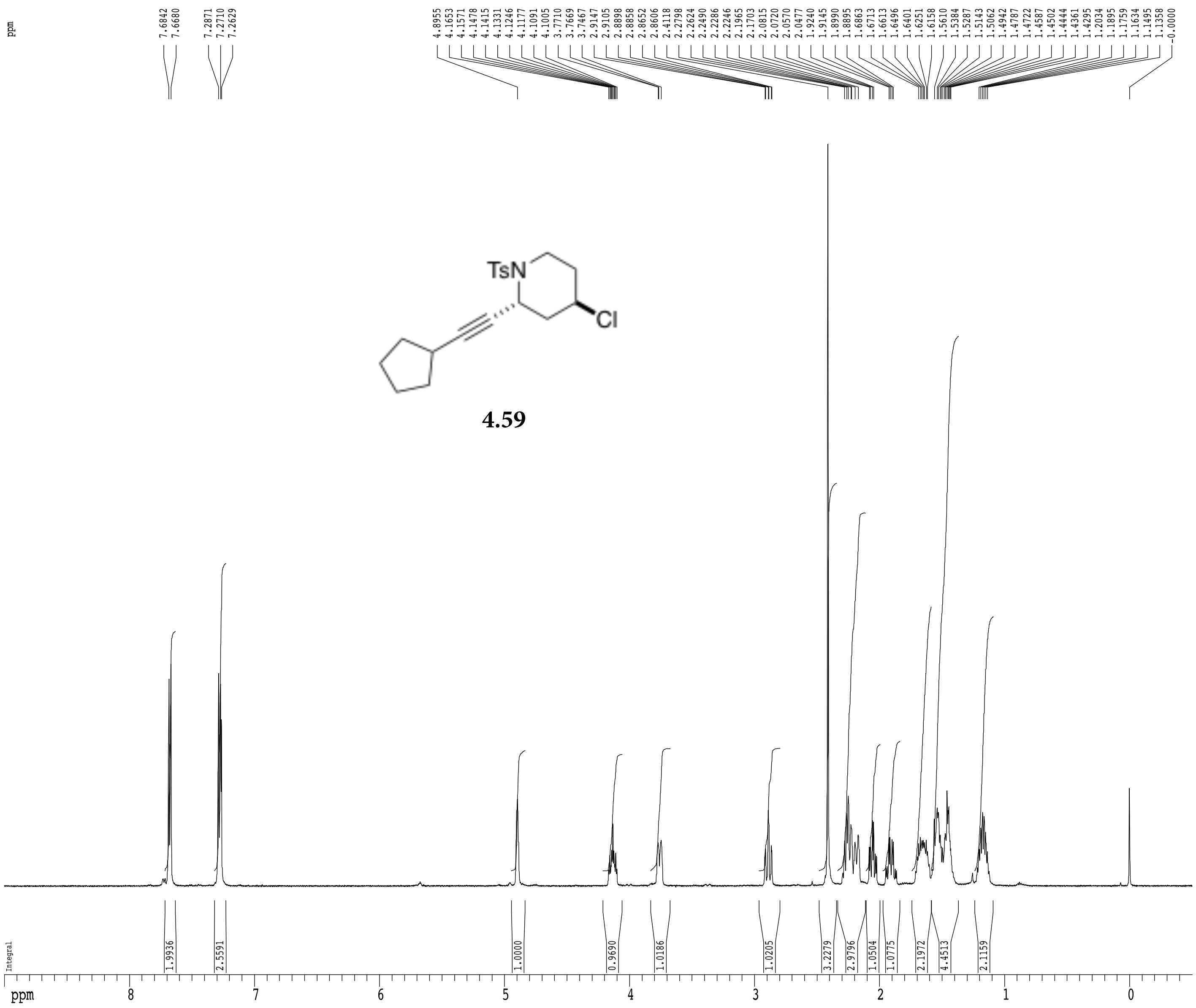
1H spectrum



4.89

```
Current Data Parameters
USER             tthane
NAME        TATiv123pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200827
Time              17.04
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                322.5
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300203 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

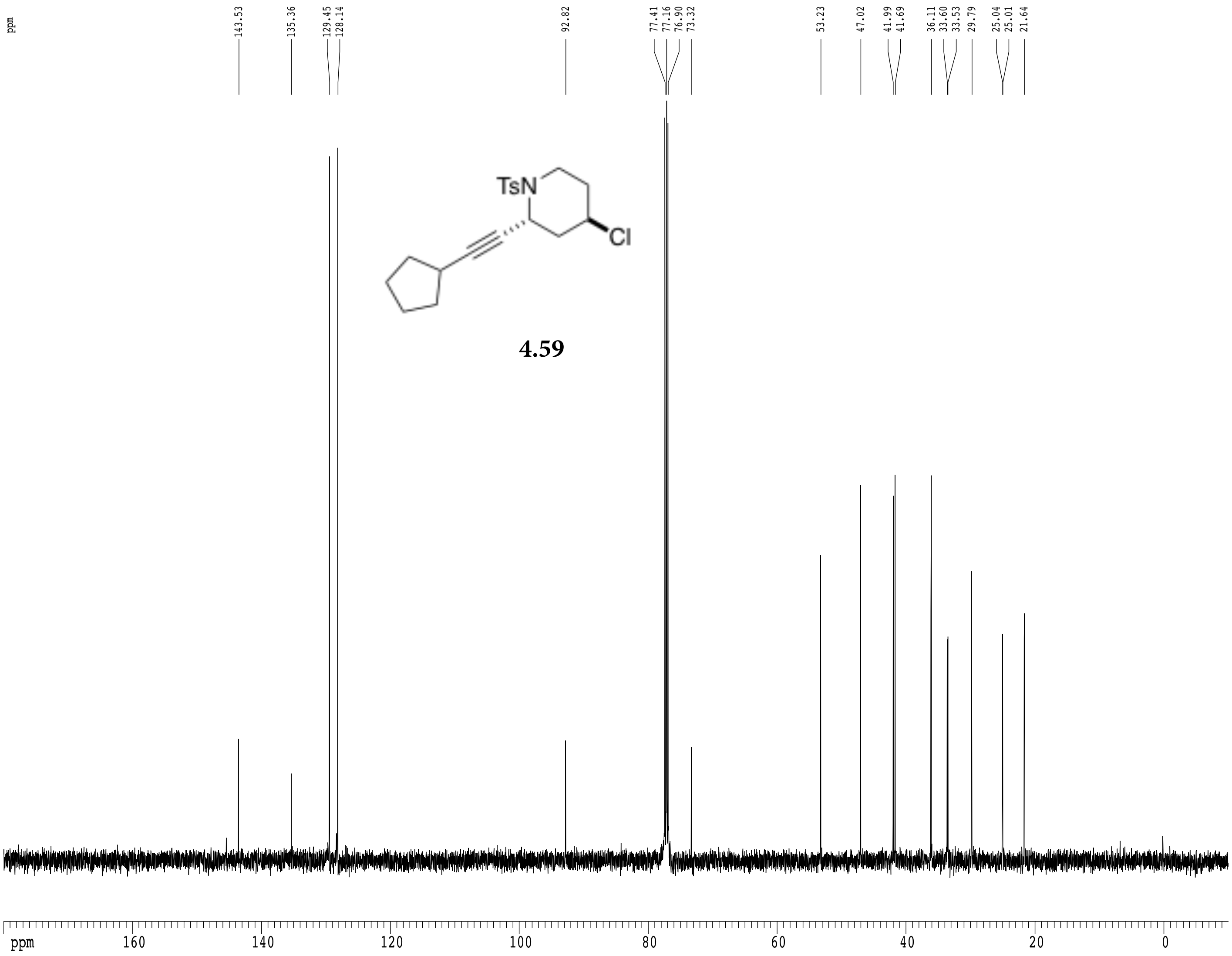
1H spectrum



4.59

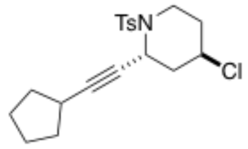
```
Current Data Parameters
USER              tthane
NAME       TATiv129carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201009
Time               15.43
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                 724.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500301 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```

13C spectrum with 1H decoupling



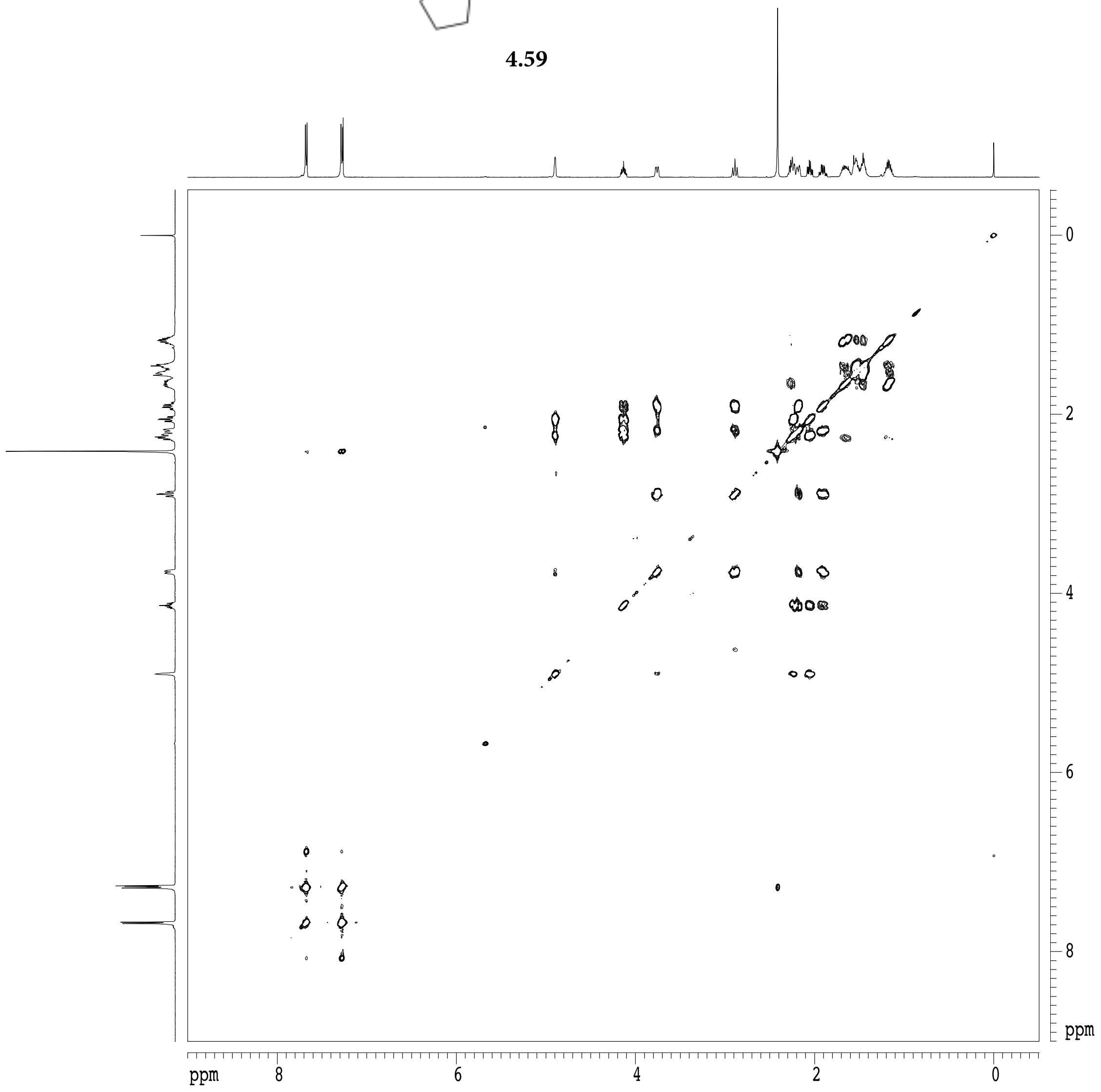
4.59

```
Current Data Parameters
USER              tthane
NAME      TATiv129carbon
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201009
Time               15.45
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                 46341
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 14.20 usec
PL1                -6.00 dB
SFO1         125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.30 dB
SFO2         498.7524937 MHz

F2 - Processing parameters
SI                 65536
SF           125.4107762 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              180.000 ppm
F1              22573.94 Hz
F2P              -10.000 ppm
F2              -1254.11 Hz
PPMCM            9.50000 ppm/cm
HZCM          1191.40234 Hz/cm
```



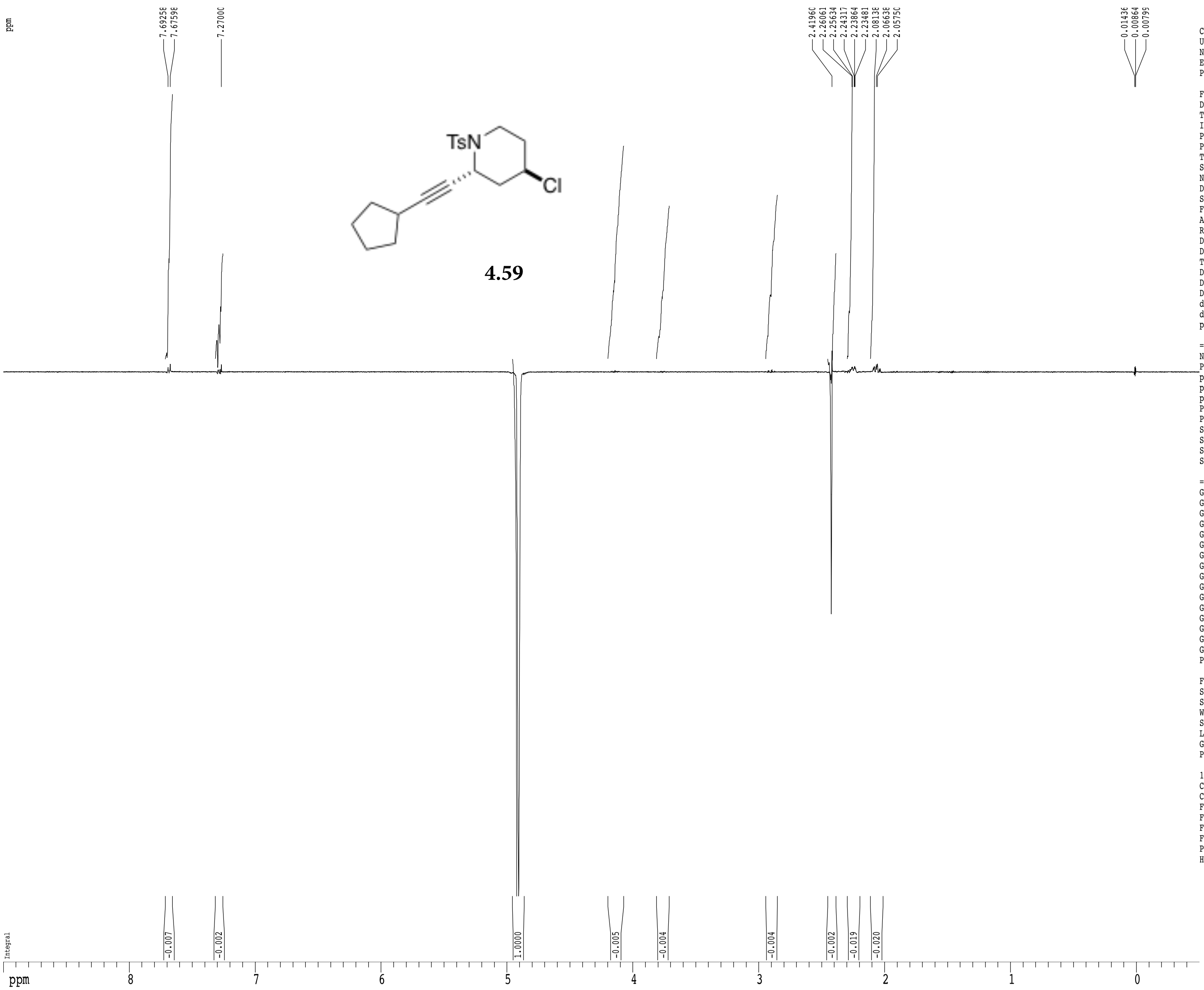
4.59

gcosy60



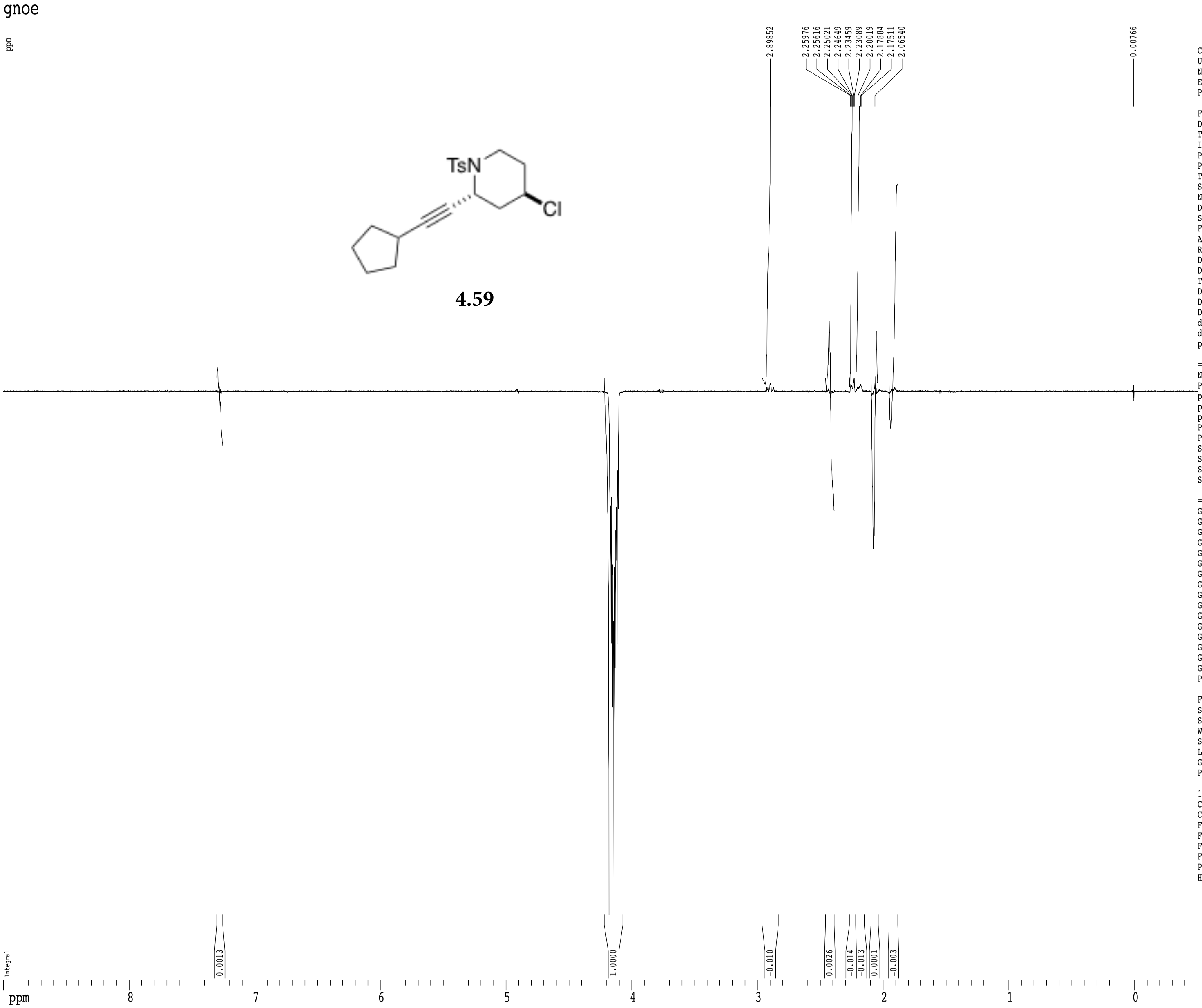
```
       Current Data Parameters
USER              tthane
NAME         TATiv129COSY
EXPNO                  2
PROCNO                 1

     F2 - Acquisition Parameters
Date_           20201010
Time               14.56
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     2
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                 456.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

    ======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

     F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

     F2 - Processing parameters
SI                  1024
SF           500.2200309 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

     F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200309 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.000 ppm
F2LO             4501.98 Hz
F2PHI             -0.508 ppm
F2HI             -254.07 Hz
F1PLO              9.003 ppm
F1LO             4503.54 Hz
F1PHI             -0.508 ppm
F1HI             -254.07 Hz
F2PPMCM          0.63386 ppm/cm
F2HZCM         317.07007 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```

gnoe



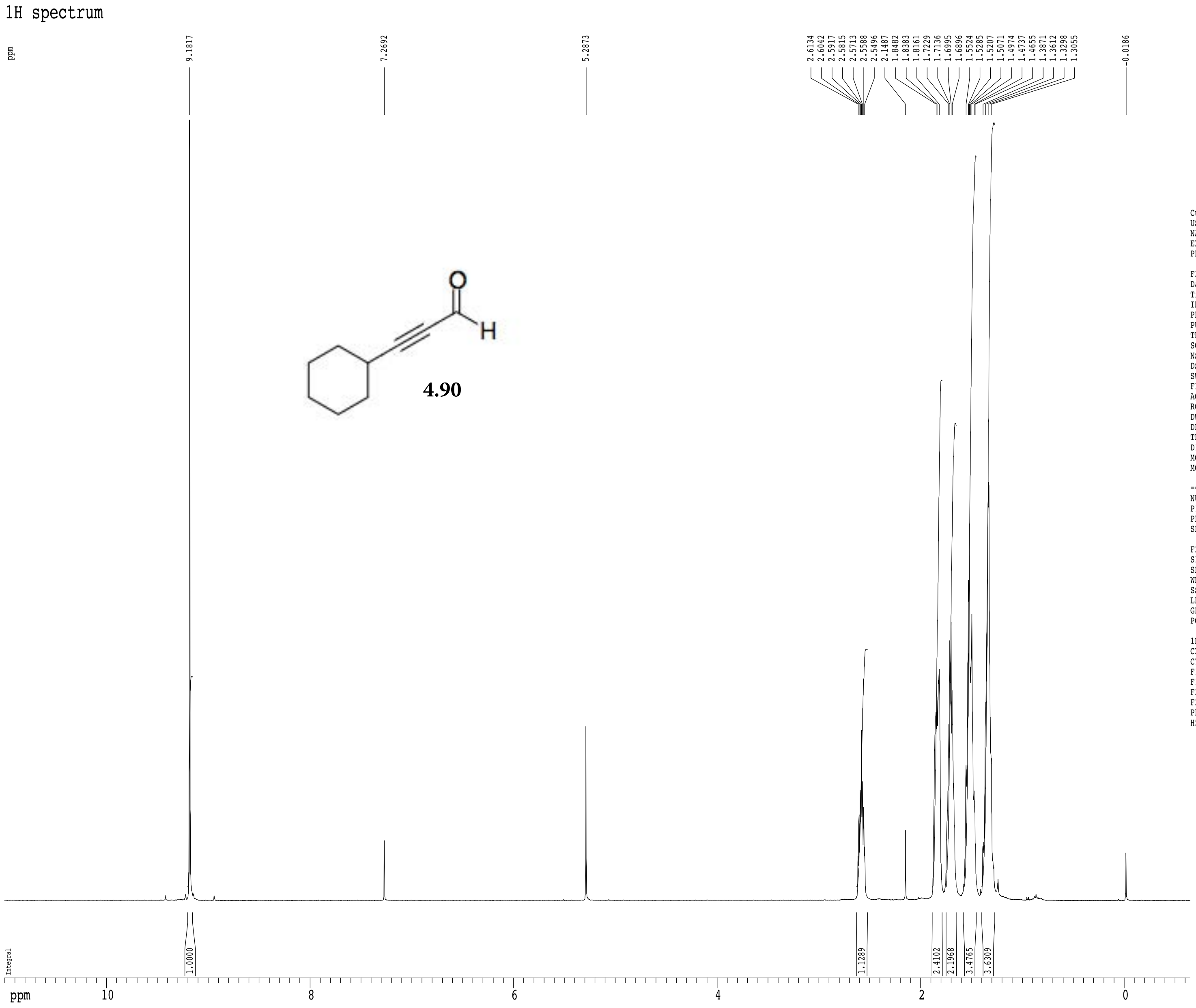
4.59

```
Current Data Parameters
USER               tthane
NAME          TATiv129NOE1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201009
Time                16.48
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                    128
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2224806 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200262 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  10.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42502 Hz/cm
```



4.59

```
Current Data Parameters
USER              tthane
NAME       TATiv129NOE2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20201010
Time              12.20
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                  128
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2220982 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200268 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                10.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

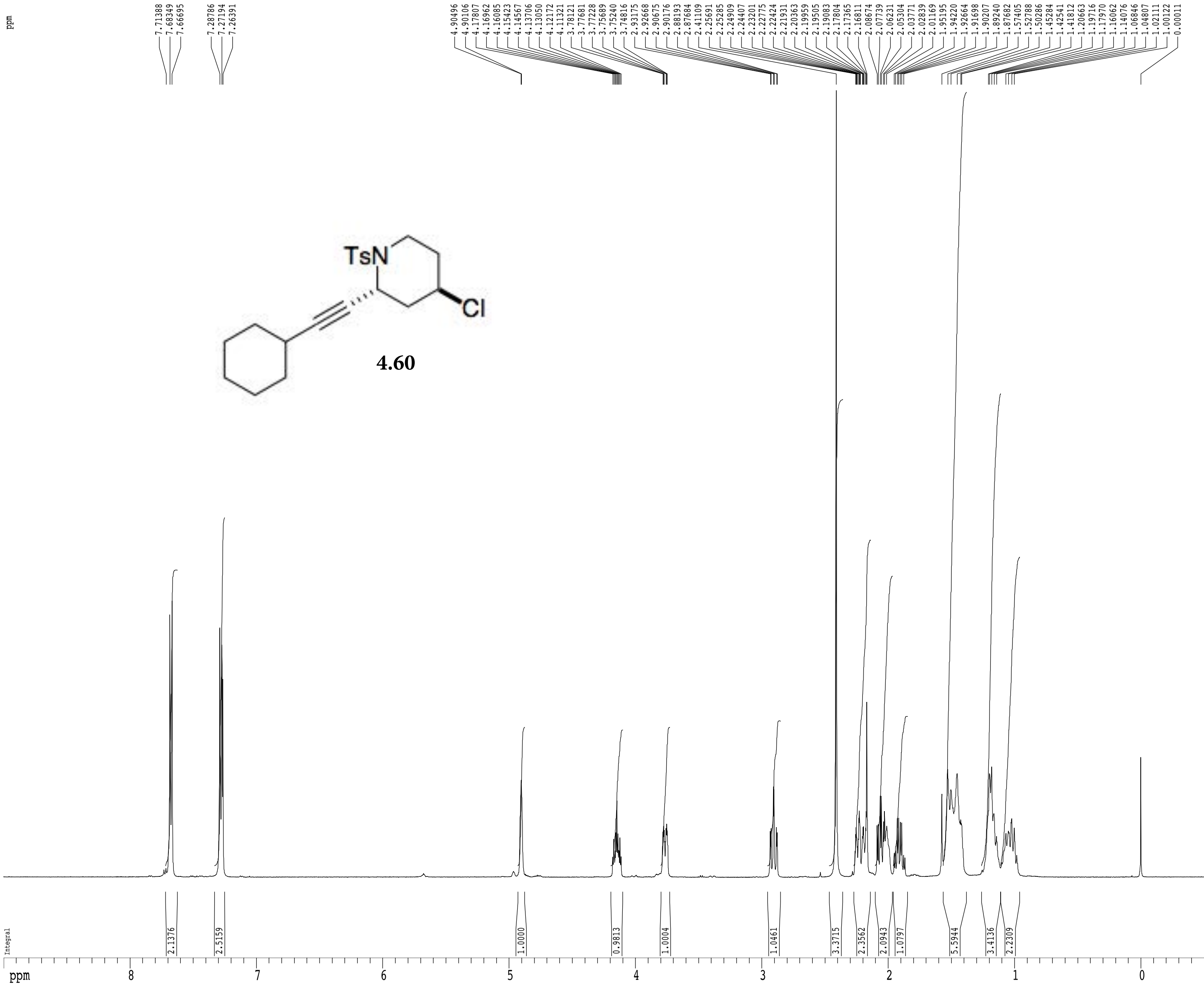


4.90

```
Current Data Parameters
USER           khewitt1
NAME      KAH-III-135-1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200612
Time              13.07
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                   64
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.650 ppm
F2              -260.08 Hz
PPMCM           0.51096 ppm/cm
HZCM          204.45239 Hz/cm
```

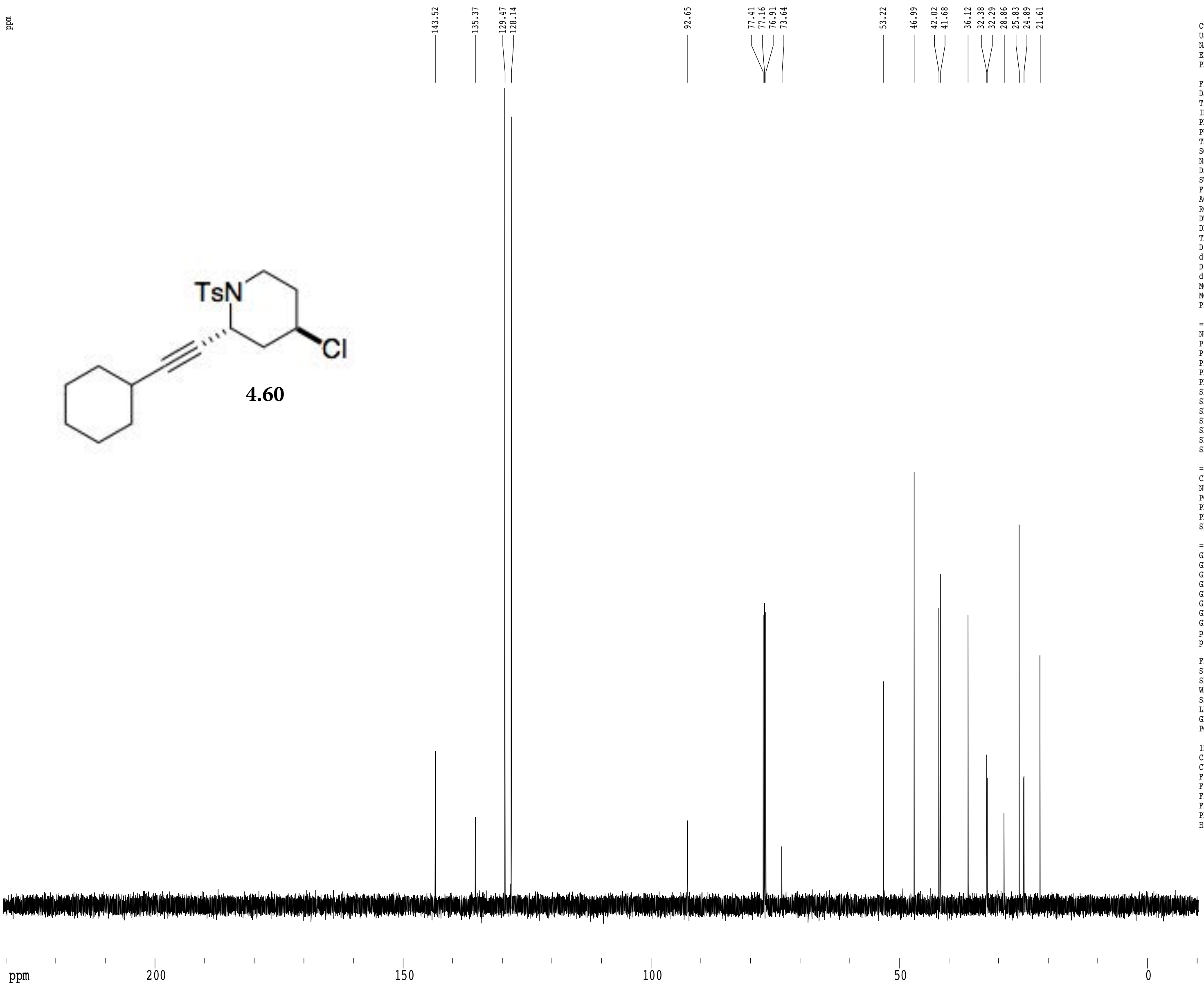
1H spectrum

4.60



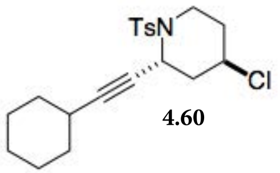
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-132-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200812
Time               16.44
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200294 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



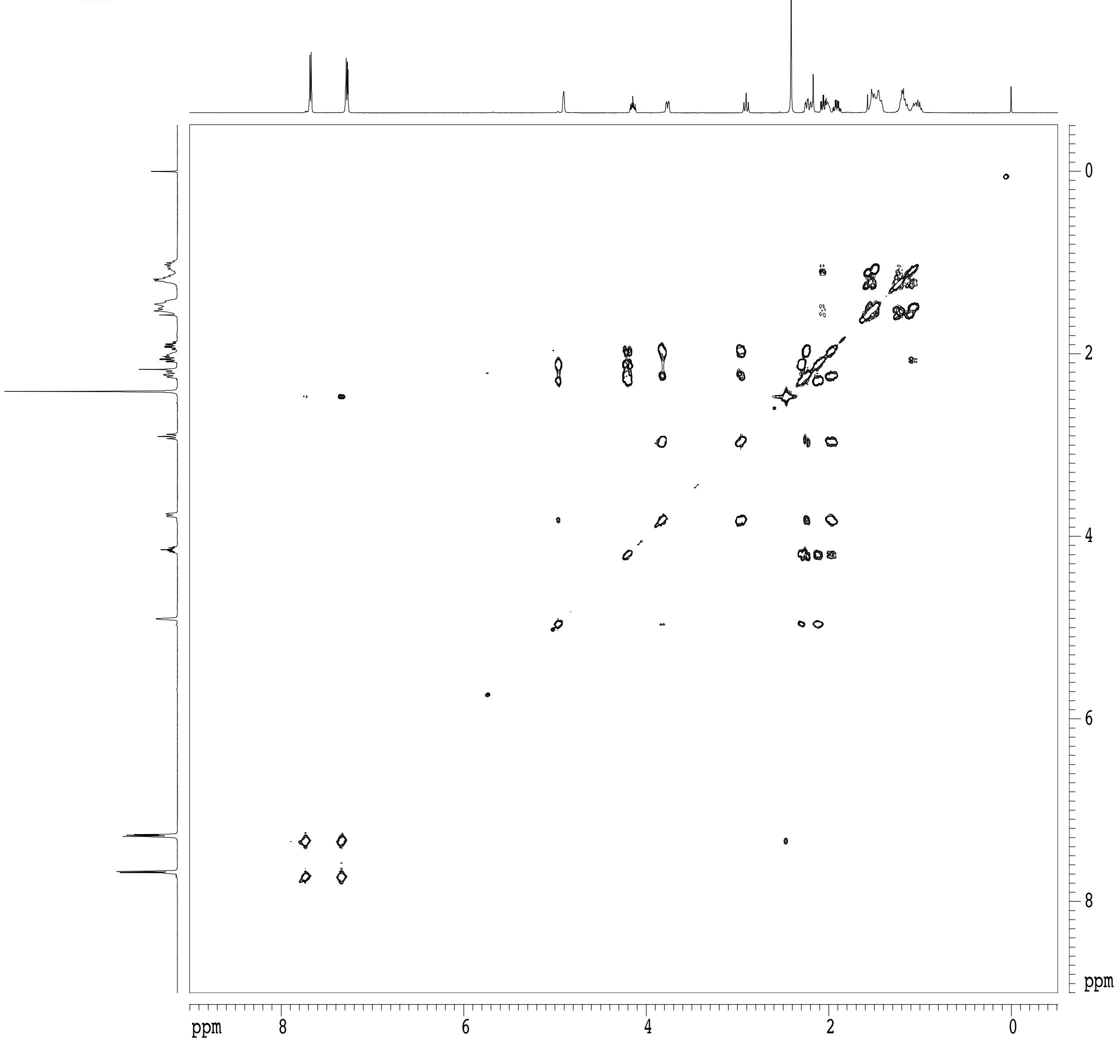
4.60

```
Current Data Parameters
USER           khewitt1
NAME      KAH-III-132-Z
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20200812
Time              16.58
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  192
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                13004
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.547 ppm
F1             28998.34 Hz
F2P             -10.373 ppm
F2             -1304.69 Hz
PPMCM          10.56667 ppm/cm
HZCM         1329.08032 Hz/cm
```

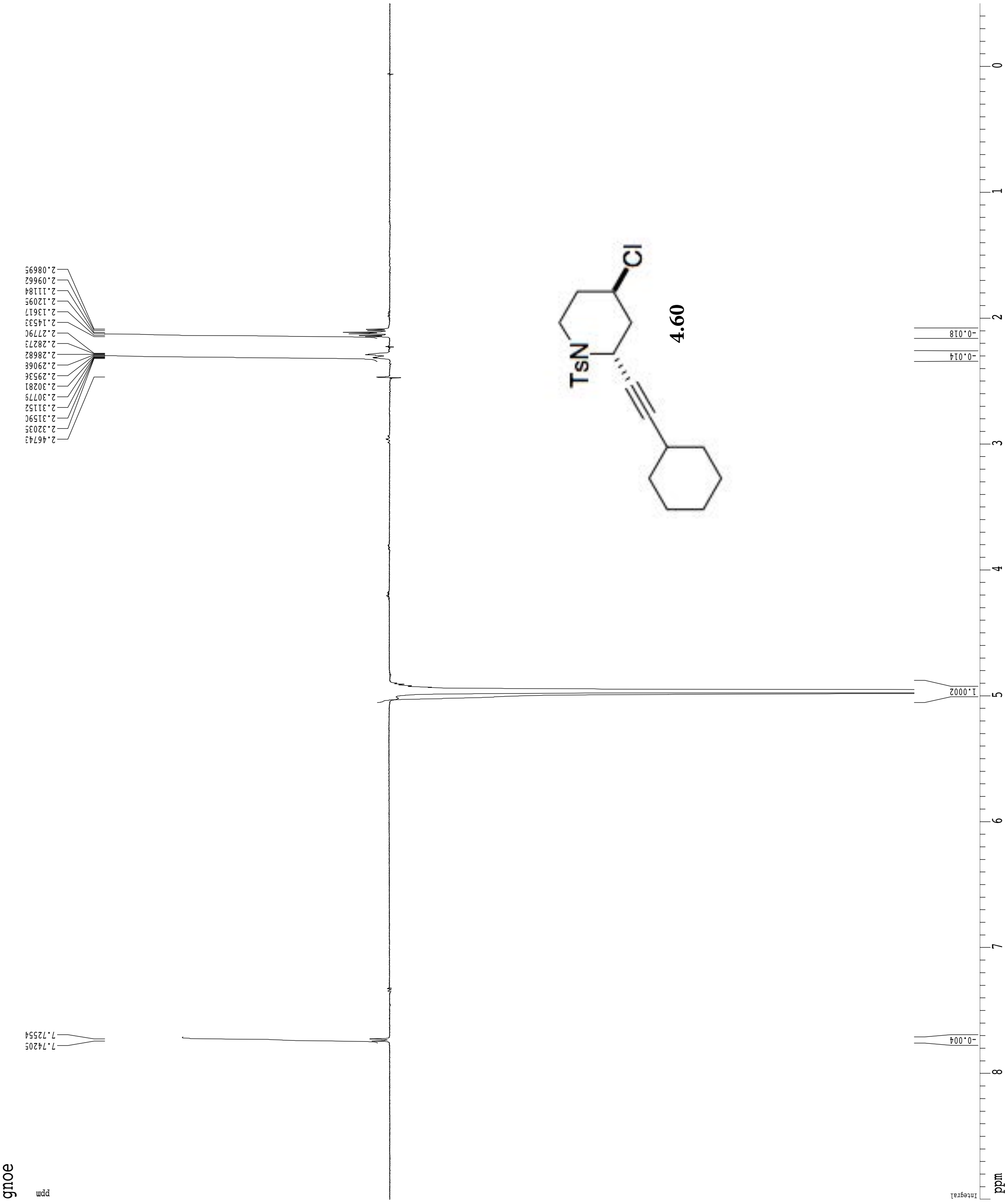


4.60

gcosy60

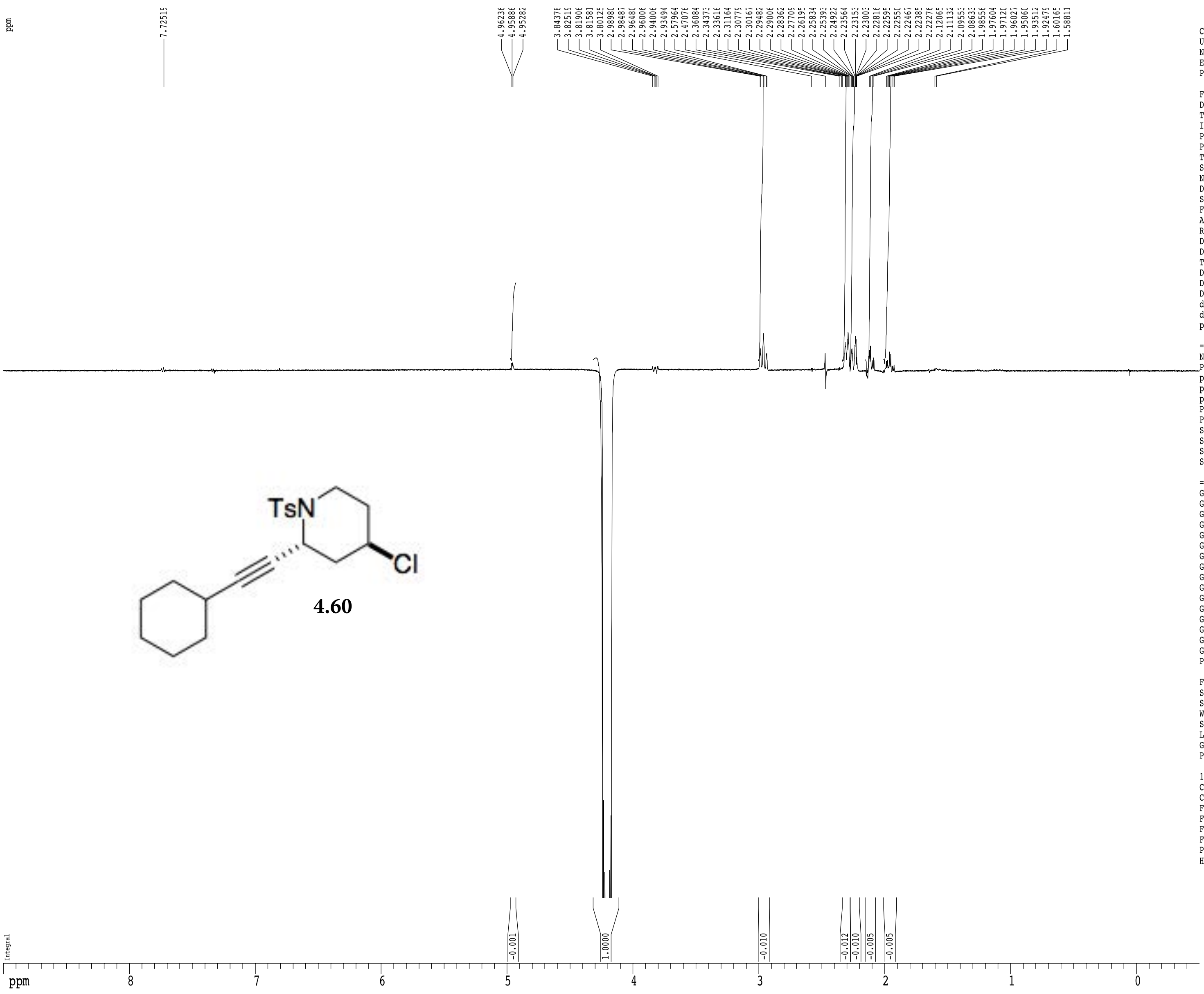


```
        Current Data Parameters
USER            khewitt1
NAME       KAH-III-132-Z
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20200812
Time               16.45
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                   114
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

       2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.002 ppm
F2LO             4503.14 Hz
F2PHI             -0.509 ppm
F2HI             -254.47 Hz
F1PLO              9.002 ppm
F1LO             4503.14 Hz
F1PHI             -0.509 ppm
F1HI             -254.47 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17416 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17416 Hz/cm
```


gnoe
ppm
2.08695
2.09662
2.11184
2.12095
2.13617
2.14533
2.27790
2.28273
2.28682
2.29068
2.29536
2.30281
2.30779
2.31152
2.31590
2.32035
2.46743
7.72554
7.74205
TsN
Cl
-0.018
-0.014
1.0002
-0.004
Integral
0
1
2
3
4
5
6
7
8
ppm

4.60

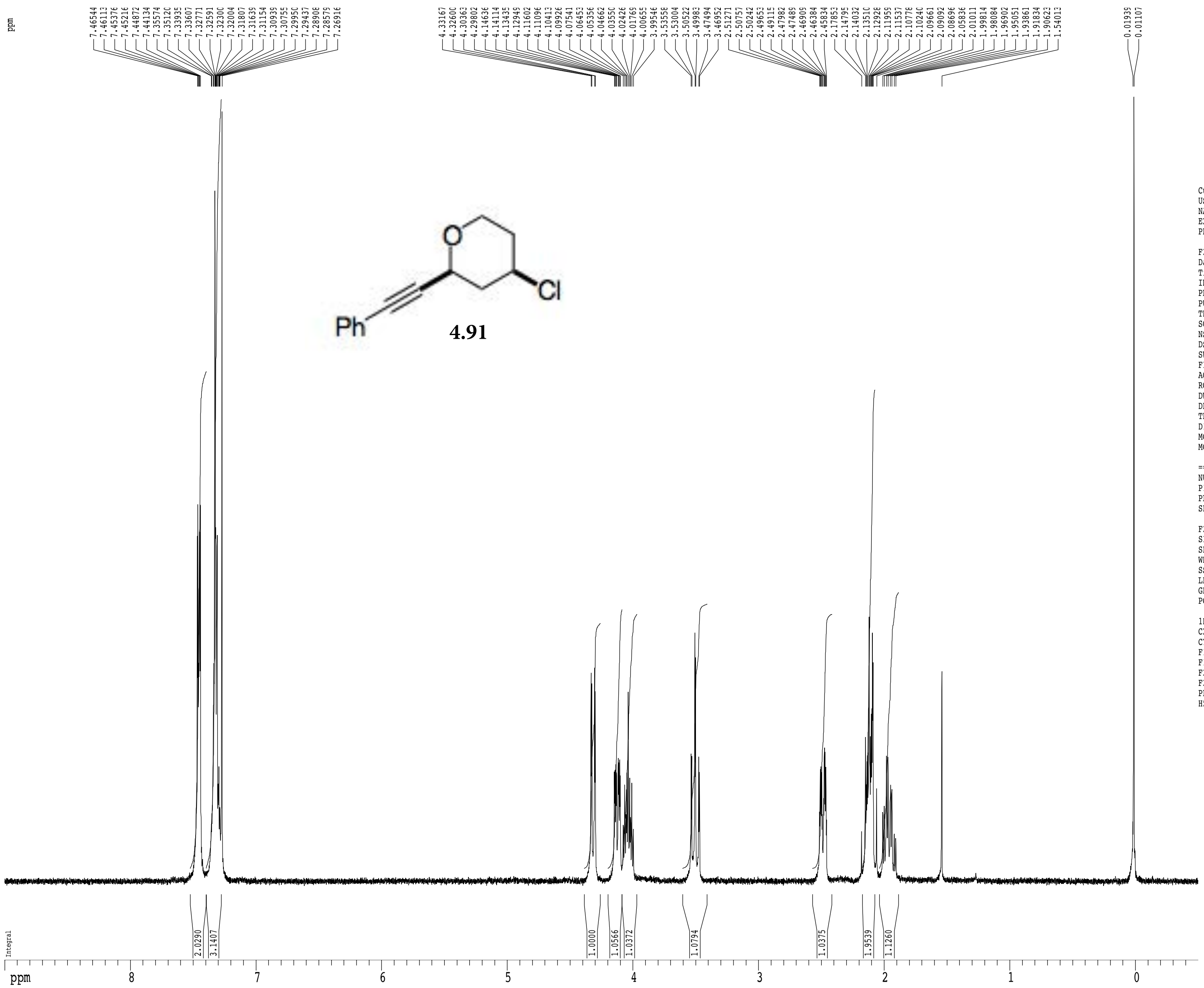
gnoe



4.60

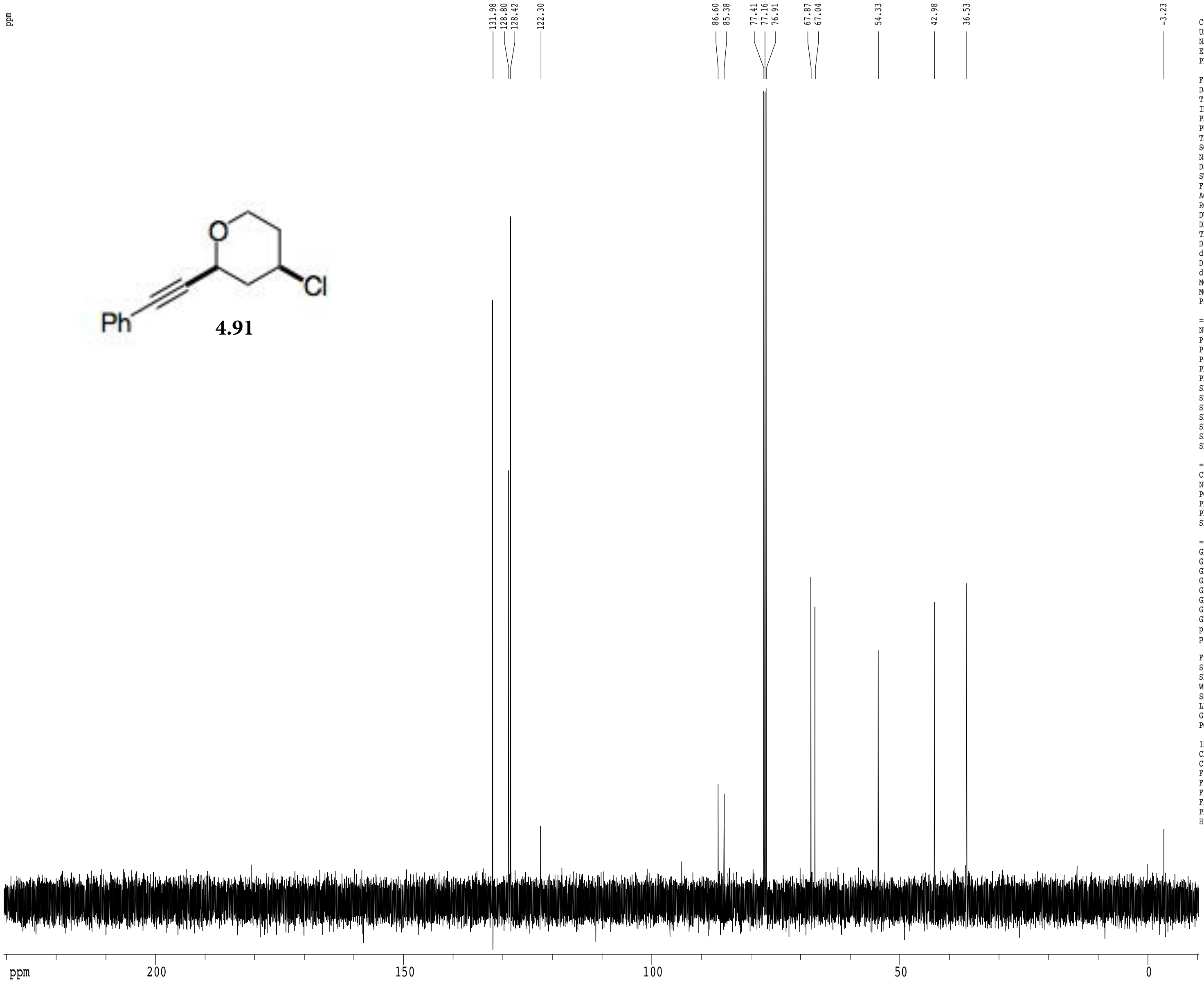
```
Current Data Parameters
USER            khewitt1
NAME       KAH-III-132-Z
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200813
Time               10.45
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                 101.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2221027 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

1H spectrum



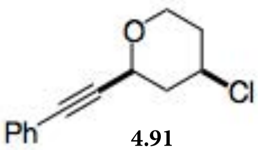
```
Current Data Parameters
USER           khewitt1
NAME     KAH-II-284-check
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20191129
Time              15.22
INSTRUM          drx400
PROBHD   5 mm Multinucl
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                912.3
DW               78.000 usec
DE                 4.50 usec
TE                297.9 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



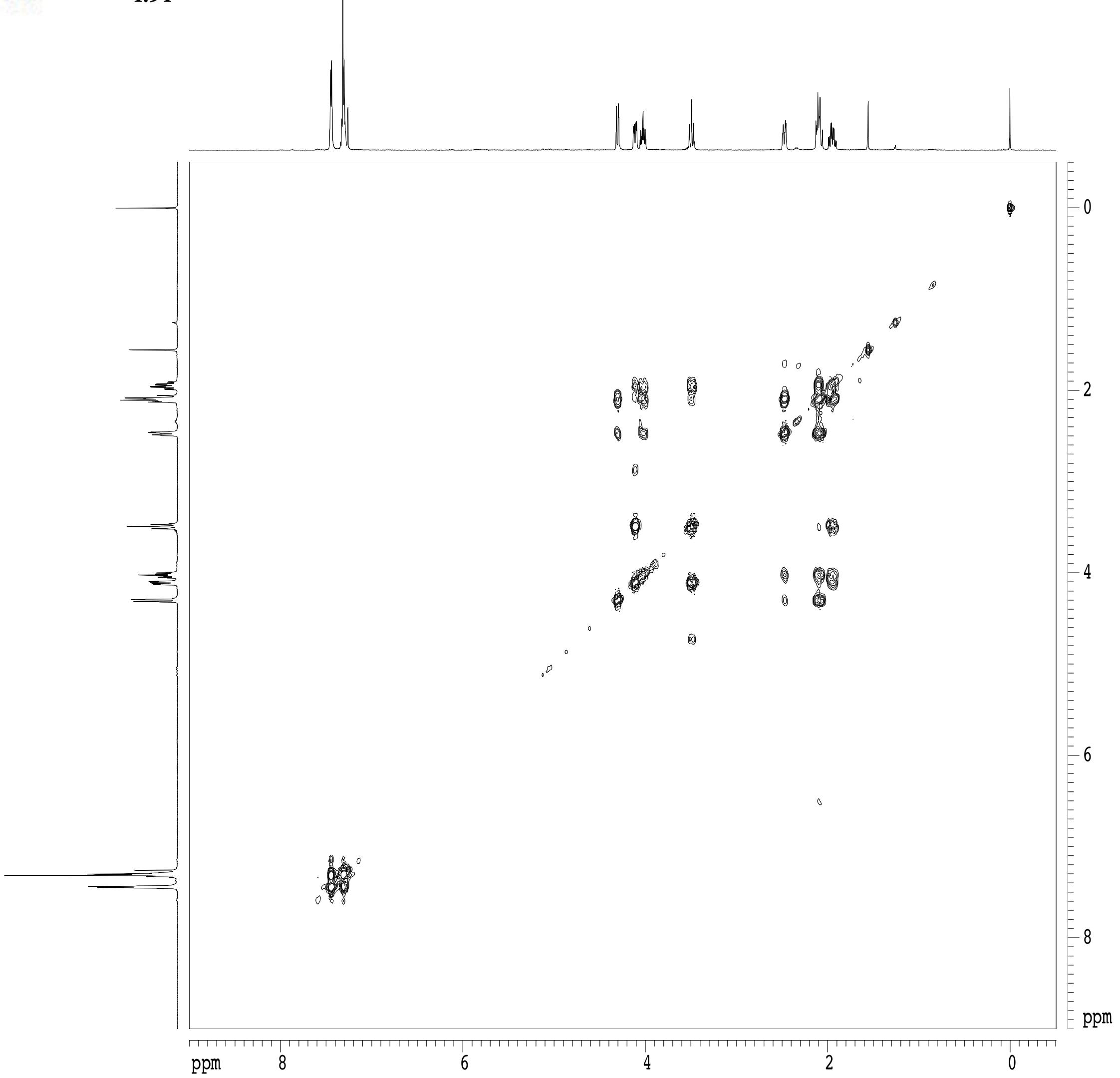
4.91

```
Current Data Parameters
USER            khewitt1
NAME        KAH-II-284-Z
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191129
Time               17.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   264
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                2580.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SP4                 2.70 dB
SPNAM2       Crp60comp.4
SPNAM4     Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804062 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



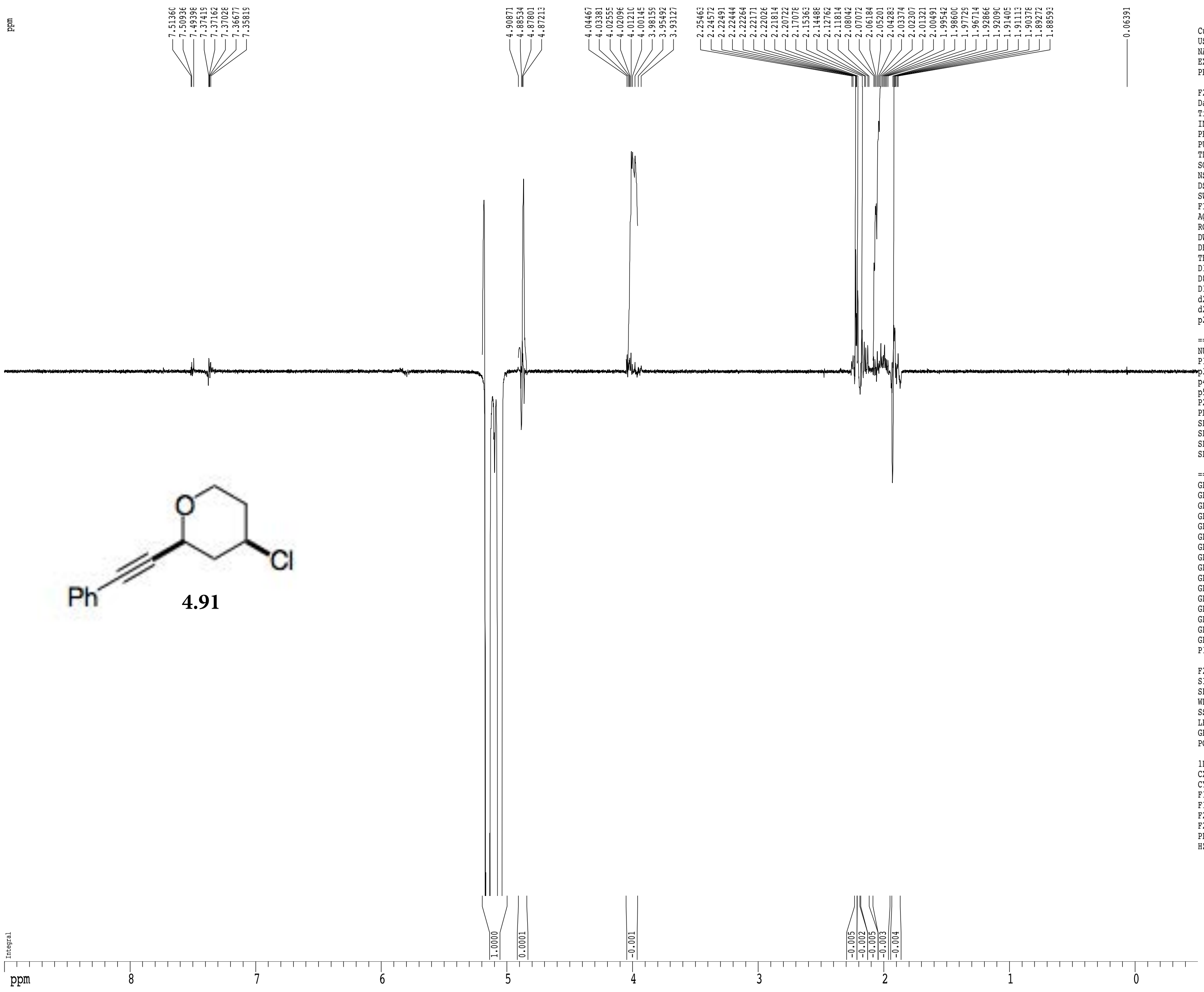
4.91

gcosy60



```
         Current Data Parameters
USER               khewitt1
NAME        KAH-II-196-COSY
EXPNO                     2
PROCNO                    1

       F2 - Acquisition Parameters
Date_              20190930
Time                  17.55
INSTRUM               gn500
PROBHD     5 mm broadband
PULPROG       cosygp60.prd
TD                     2048
SOLVENT               CDCl3
NS                        1
DS                       16
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                   5160.6
DW                   62.400 usec
DE                     6.00 usec
TE                    298.0 K
d0               0.00000300 sec
D1               1.00000000 sec
d13              0.00000300 sec
D16              0.00020000 sec
IN0              0.00012480 sec

      ======== CHANNEL f1 ========
NUC1                     1H
P1                    12.00 usec
PL1                   -5.00 dB
SFO1            498.8534919 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1             SINE.100
GPNAM2             SINE.100
GPX1                   0.00 %
GPX2                   0.00 %
GPY1                   0.00 %
GPY2                   0.00 %
GPZ1                  17.00 %
GPZ2                  17.00 %
P16                 1000.00 usec

       F1 - Acquisition parameters
ND0                       1
TD                      256
SFO1               498.8535 MHz
FIDRES            31.300079 Hz
SW                   16.062 ppm
FnMODE                   QF

        F2 - Processing parameters
SI                     1024
SF              498.8500268 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00

        F1 - Processing parameters
SI                     1024
MC2                      QF
SF              498.8500268 MHz
WDW                    SINE
SSB                       0
LB                     0.00 Hz
GB                        0

          2D NMR plot parameters
CX2                   15.00 cm
CX1                   15.00 cm
F2PLO                 9.001 ppm
F2LO                4490.22 Hz
F2PHI                -0.505 ppm
F2HI                -251.74 Hz
F1PLO                 9.001 ppm
F1LO                4490.22 Hz
F1PHI                -0.505 ppm
F1HI                -251.74 Hz
F2PPMCM             0.63372 ppm/cm
F2HZCM            316.13080 Hz/cm
F1PPMCM             0.63372 ppm/cm
F1HZCM            316.13080 Hz/cm
```

gnoe



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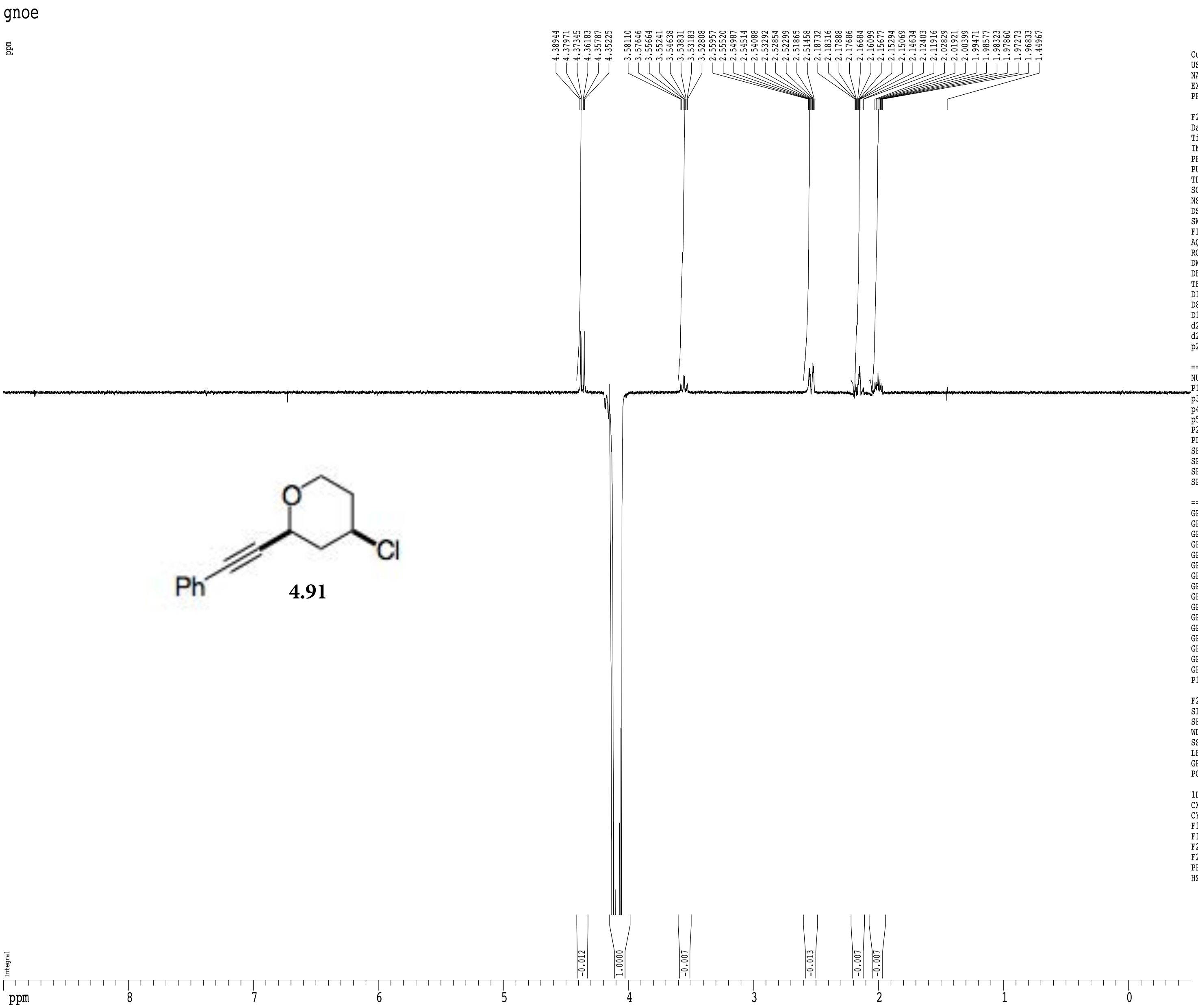
```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-014-1-2D
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191210
Time               12.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  90.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2225530 MHz
SP9                61.60 dB
SPNAM9       gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



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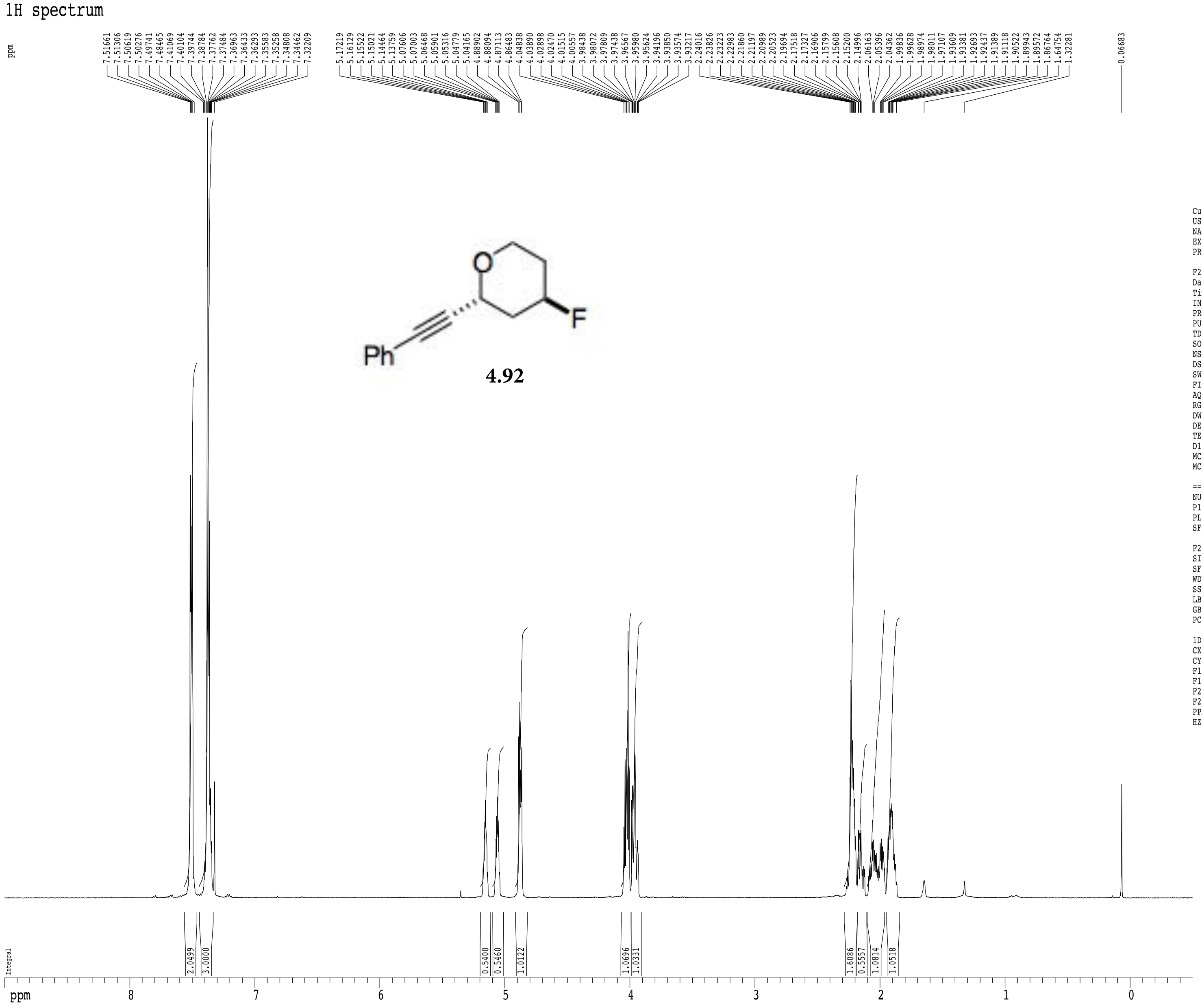
```
Current Data Parameters
USER              khewitt1
NAME           KAH-II-284-Z
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_           20191129
Time               17.37
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2220449 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



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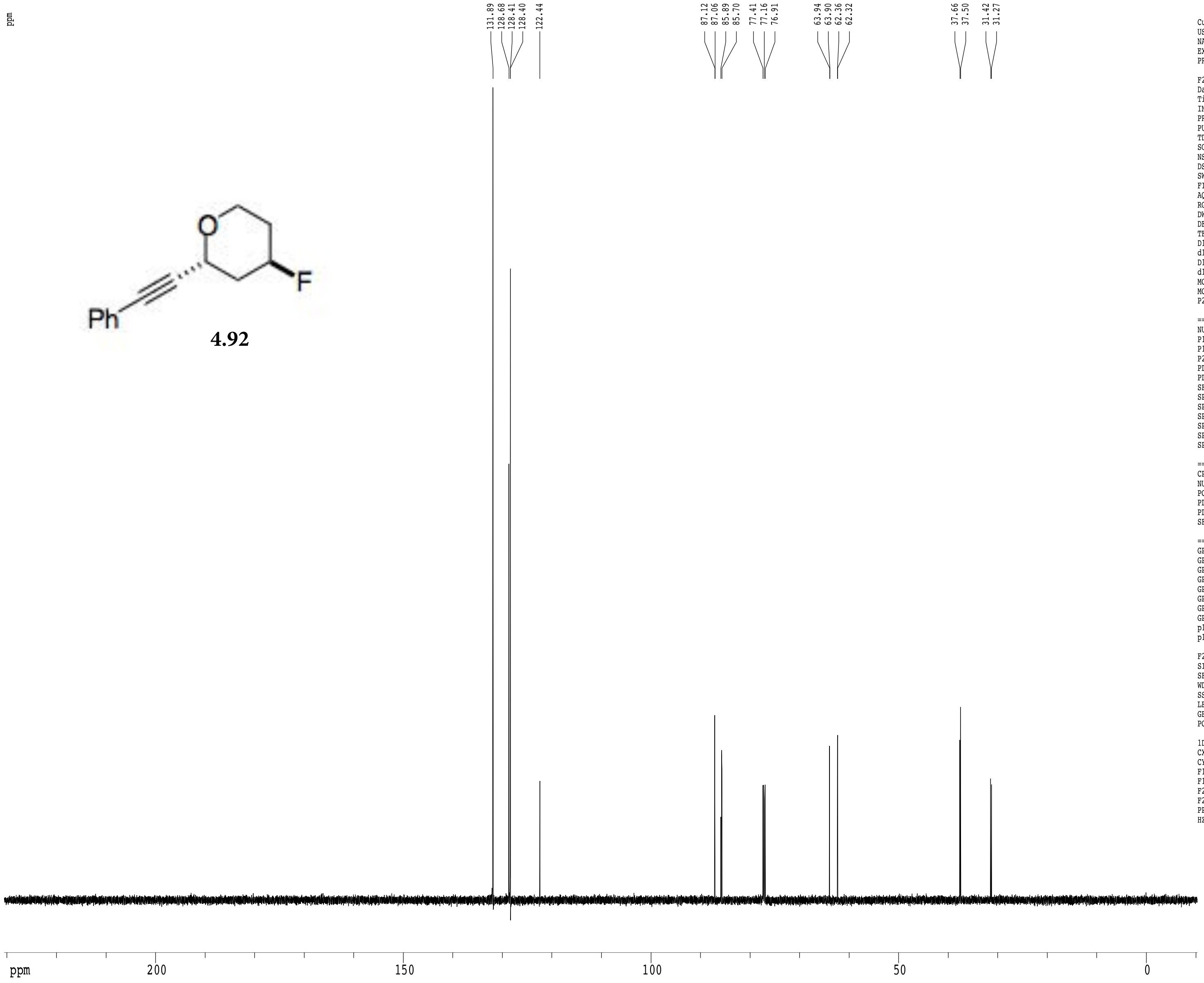
```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-014-1-2D
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20191209
Time              16.45
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



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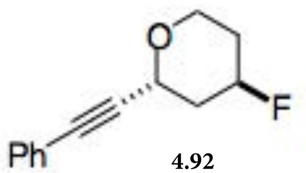
```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-014-1-2D
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20191209
Time              17.01
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  136
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                16384
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804103 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```



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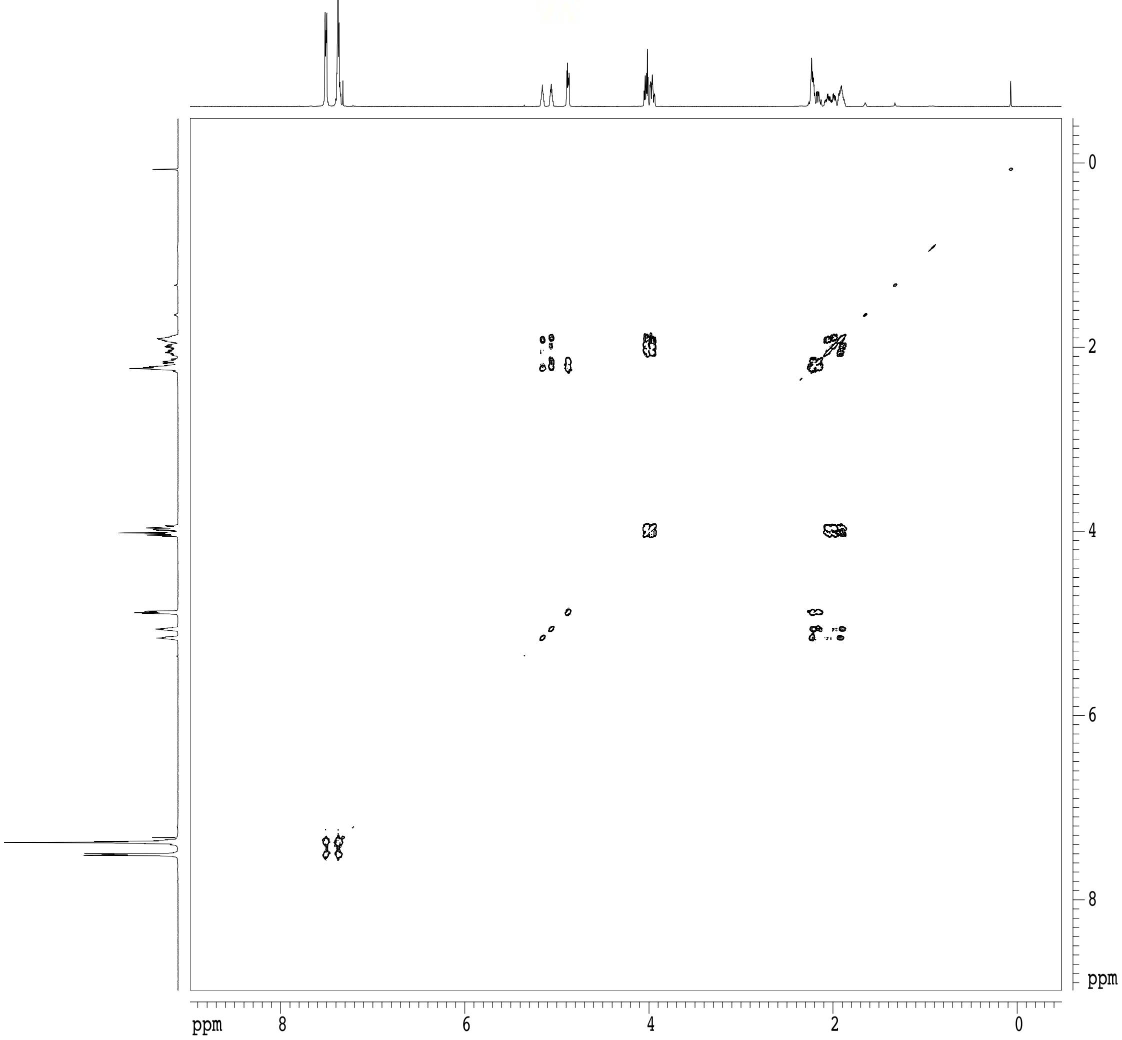
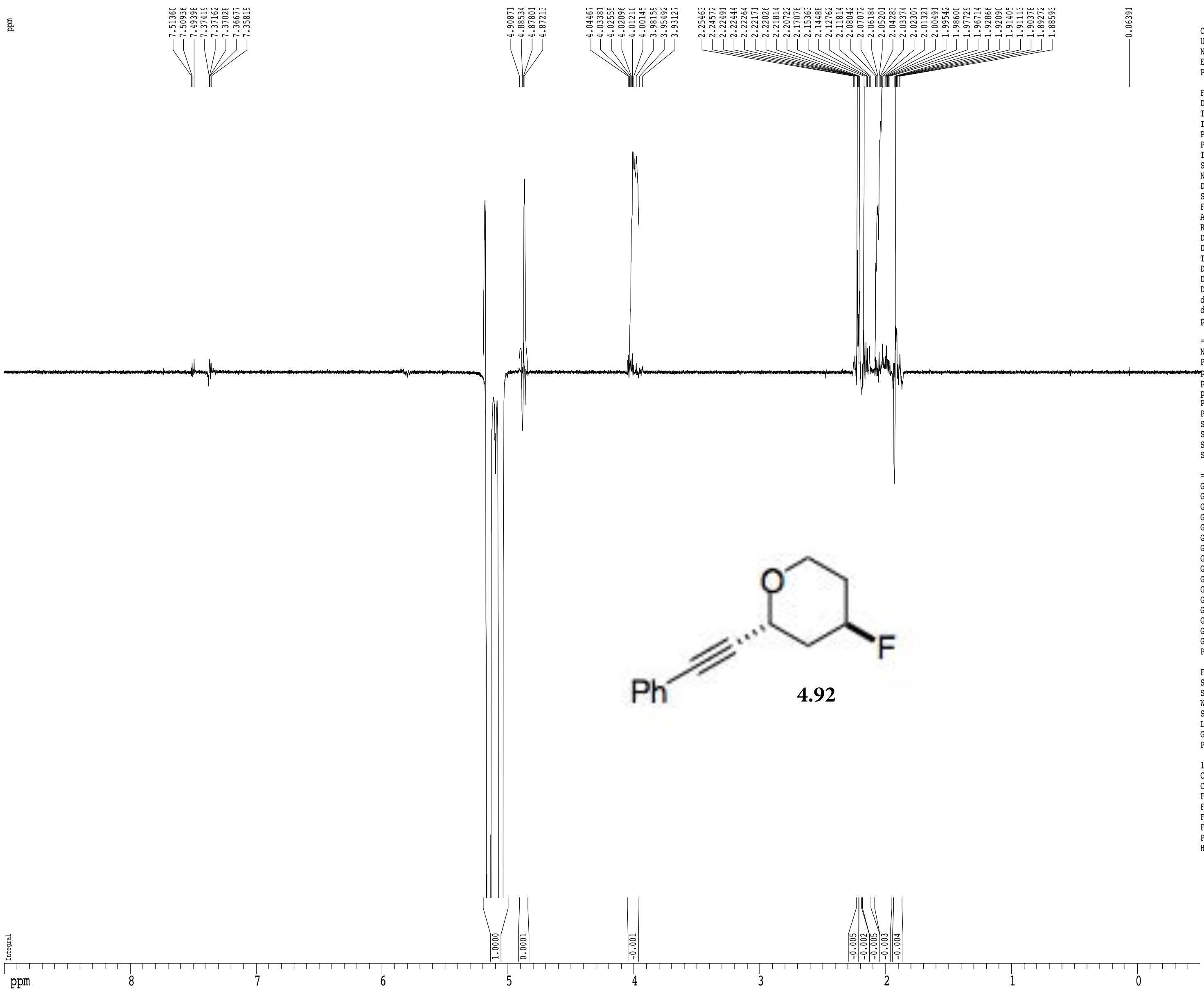
gcosy60



```
        Current Data Parameters
USER                 khewitt1
NAME        KAH-III-014-1-2D
EXPNO                       2
PROCNO                      1

      F2 - Acquisition Parameters
Date_               20191209
Time                   16.48
INSTRUM              cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG        cosygp60.prd
TD                      2048
SOLVENT                CDCl3
NS                         1
DS                        16
SWH                 4734.849 Hz
FIDRES              2.311938 Hz
AQ                 0.2163188 sec
RG                       181
DW                   105.600 usec
DE                      6.00 usec
TE                     298.0 K
d0                0.00000300 sec
D1                1.00000000 sec
d13               0.00000300 sec
D16               0.00020000 sec
IN0               0.00021120 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      7.50 usec
PL1                     1.60 dB
SFO1             500.2221259 MHz

====== GRADIENT CHANNEL =====
GPNAM1              sine.100
GPNAM2              sine.100
GPX1                    0.00 %
GPX2                    0.00 %
GPY1                    0.00 %
GPY2                    0.00 %
GPZ1                   17.00 %
GPZ2                   17.00 %
P16                  1000.00 usec

      F1 - Acquisition parameters
ND0                        1
TD                       512
SFO1                500.2221 MHz
FIDRES              9.247751 Hz
SW                     9.465 ppm
FnMODE                    QF

      F2 - Processing parameters
SI                      1024
SF               500.2200000 MHz
WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00

      F1 - Processing parameters
SI                      1024
MC2                       QF
SF               500.2200000 MHz
WDW                     SINE
SSB                        0
LB                      0.00 Hz
GB                         0

        2D NMR plot parameters
CX2                    15.00 cm
CX1                    15.00 cm
F2PLO                  8.983 ppm
F2LO                 4493.36 Hz
F2PHI                 -0.483 ppm
F2HI                 -241.49 Hz
F1PLO                  8.983 ppm
F1LO                 4493.36 Hz
F1PHI                 -0.483 ppm
F1HI                 -241.49 Hz
F2PPMCM              0.63104 ppm/cm
F2HZCM             315.65659 Hz/cm
F1PPMCM              0.63104 ppm/cm
F1HZCM             315.65659 Hz/cm
```

gnoe



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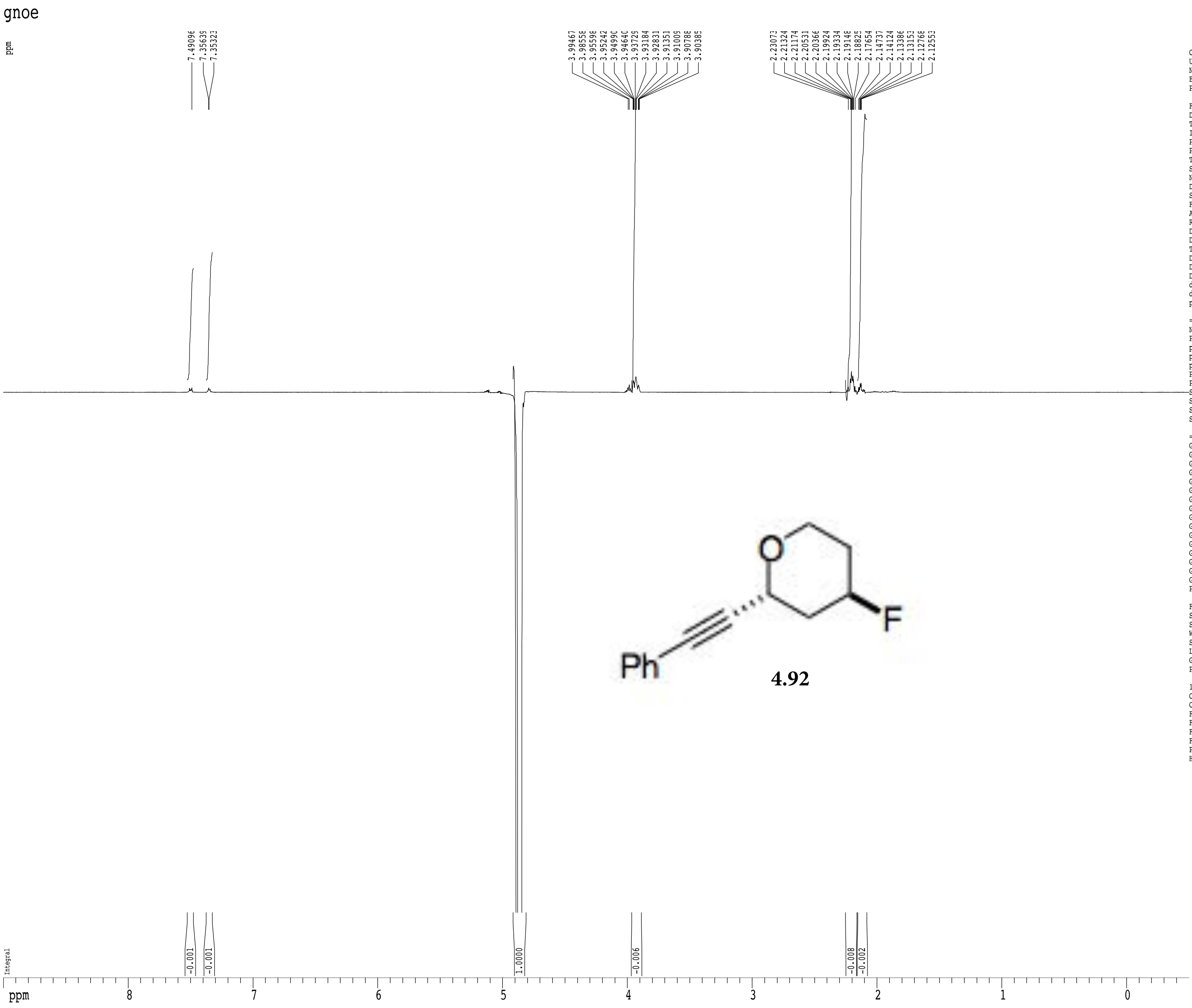
```
Current Data Parameters
USER            khewitt1
NAME     KAH-III-014-1-2D
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191210
Time               12.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  90.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2225530 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



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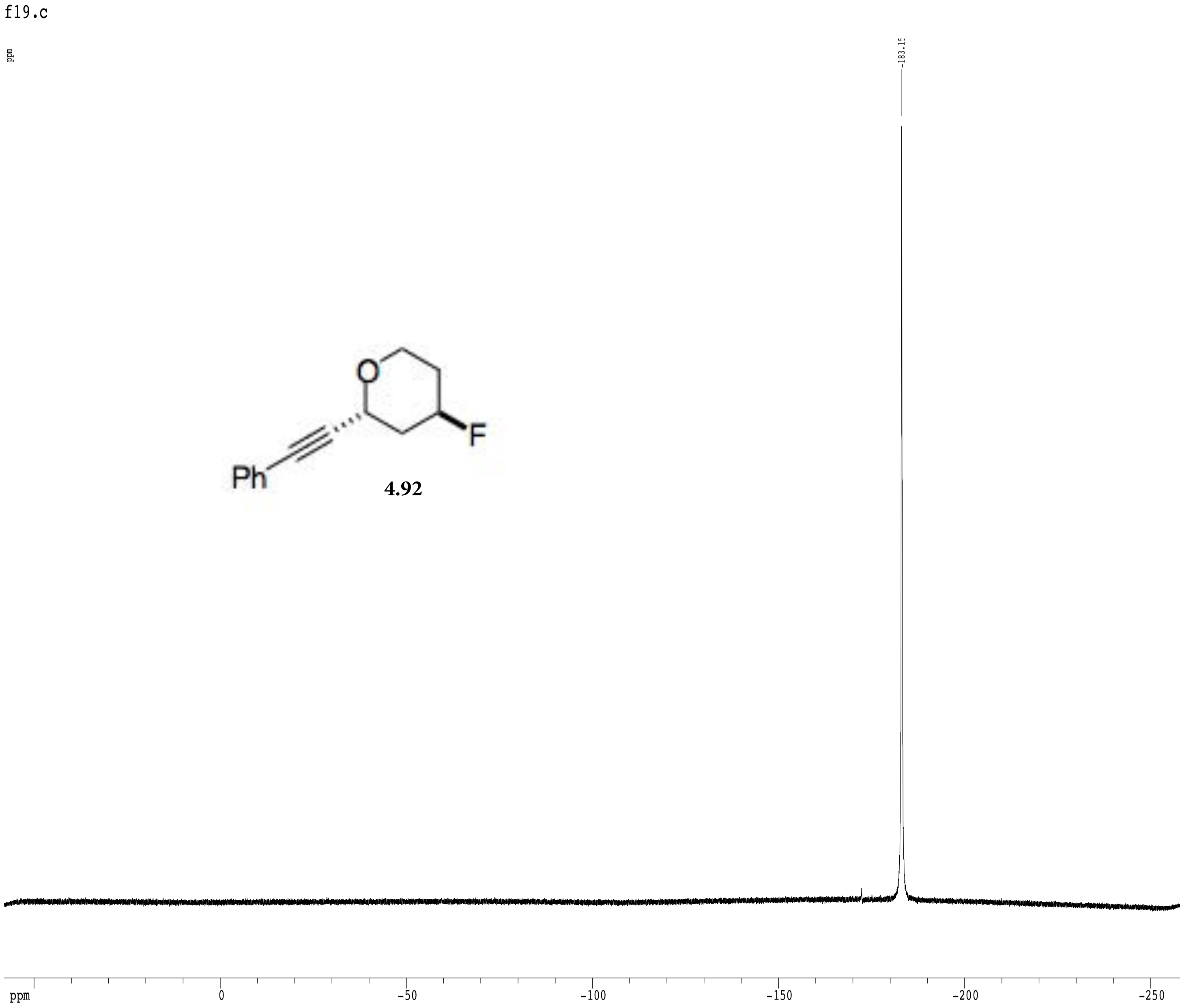
```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-030-trans-cryo
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20200120
Time              15.13
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 20.2
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2224324 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



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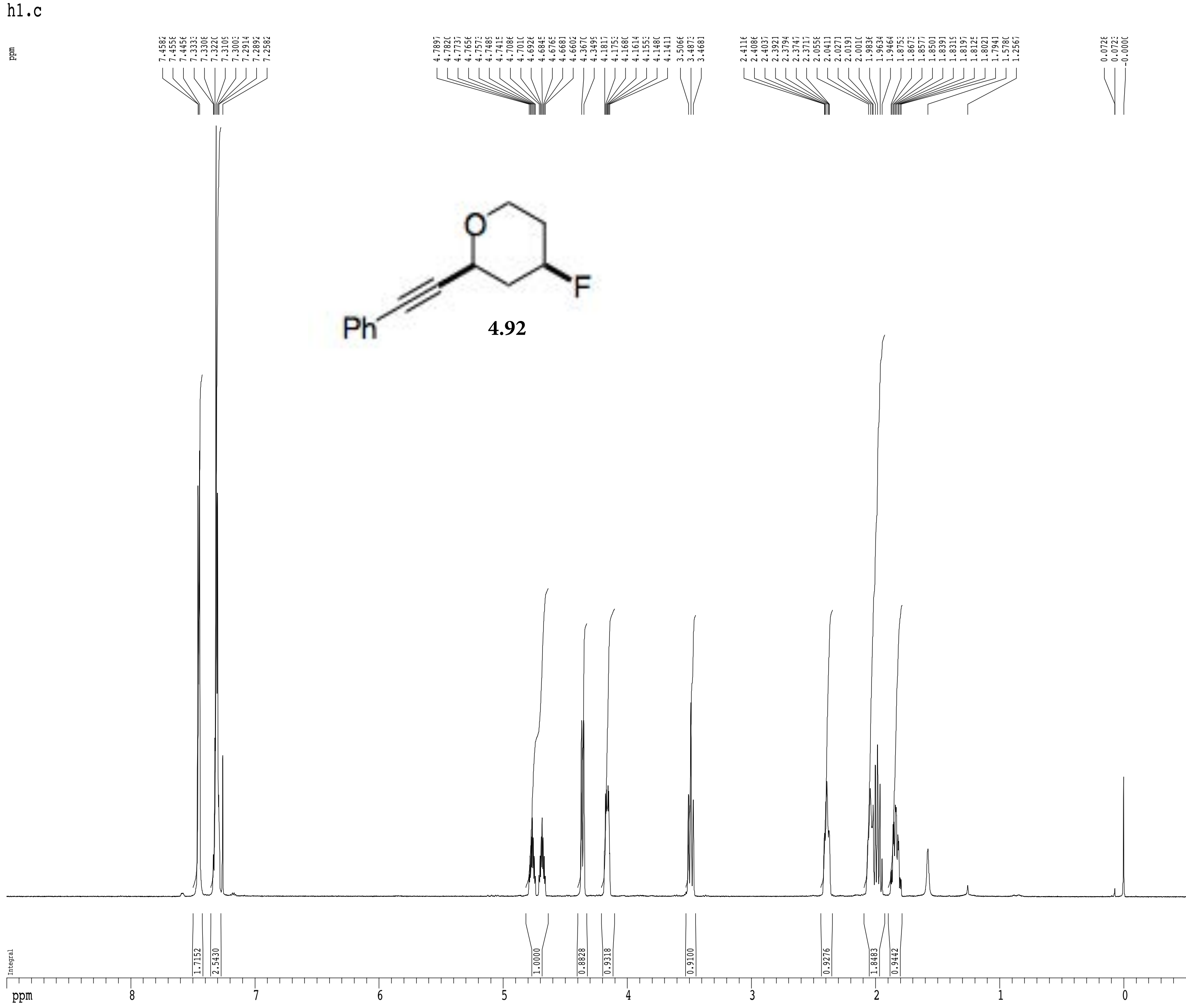
```
Current Data Parameters
USER            khewitt1
NAME        KAH-III-030-F
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210619
Time               15.36
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgflqn30
TD                131072
SOLVENT           CDCl3T
NS                    16
DS                     2
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                   575
DW                 2.800 usec
DE                 18.00 usec
TE                 298.0 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        564.6299196 MHz
NUC1                 19F
P1                 18.25 usec

F2 - Processing parameters
SI                131072
SF          564.6864226 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               58.055 ppm
F1              32782.68 Hz
F2P             -258.176 ppm
F2            -145788.75 Hz
PPMCM           13.86979 ppm/cm
HZCM          7832.08057 Hz/cm
```



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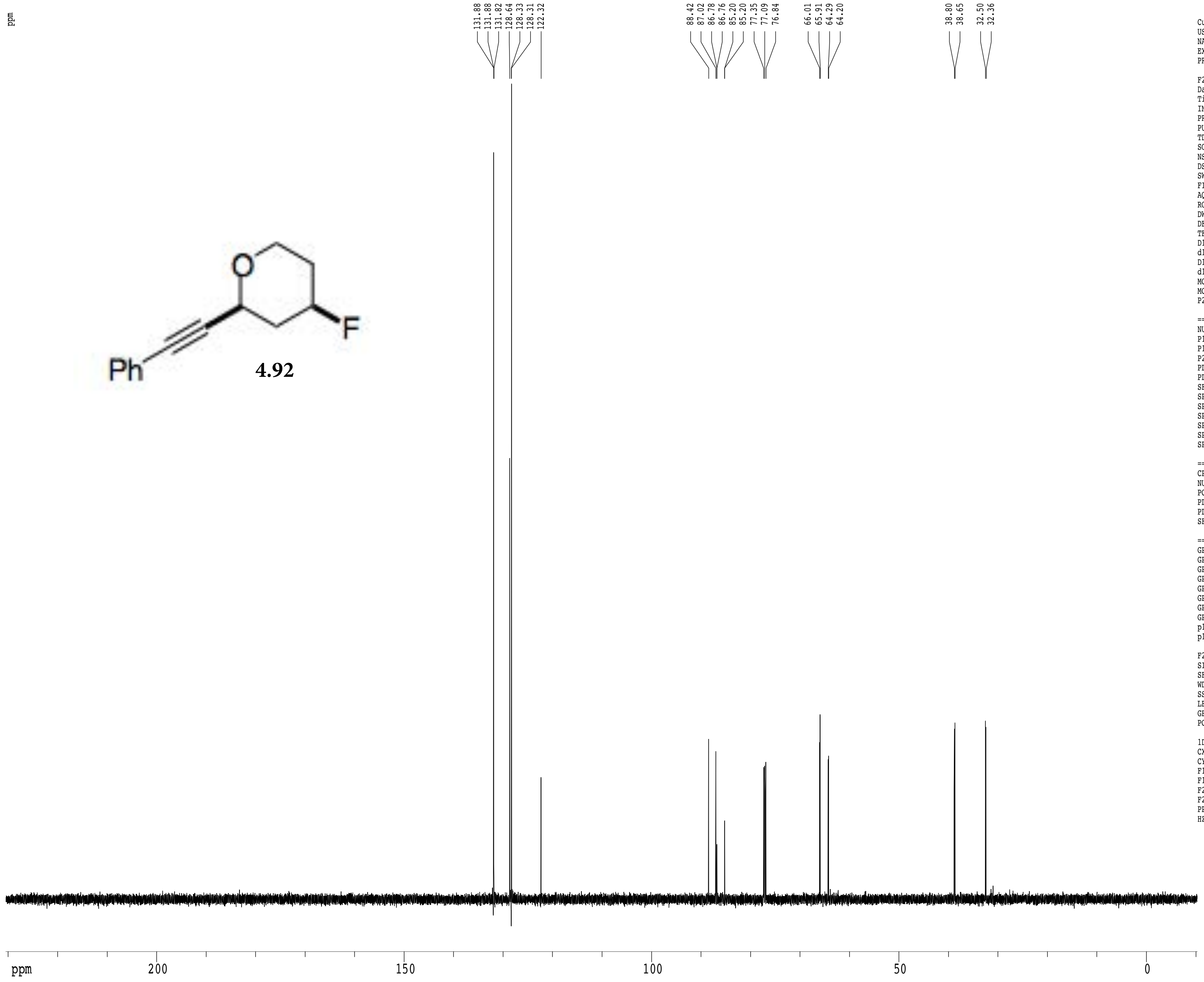
```
Current Data Parameters
USER            khewittl
NAME     KAH-III-030-cis-F
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210630
Time               10.32
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                    10
DW                52.000 usec
DE                 14.23 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                     1H
P1                     9.50 usec

F2 - Processing parameters
SI                 65536
SF          600.1300353 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```

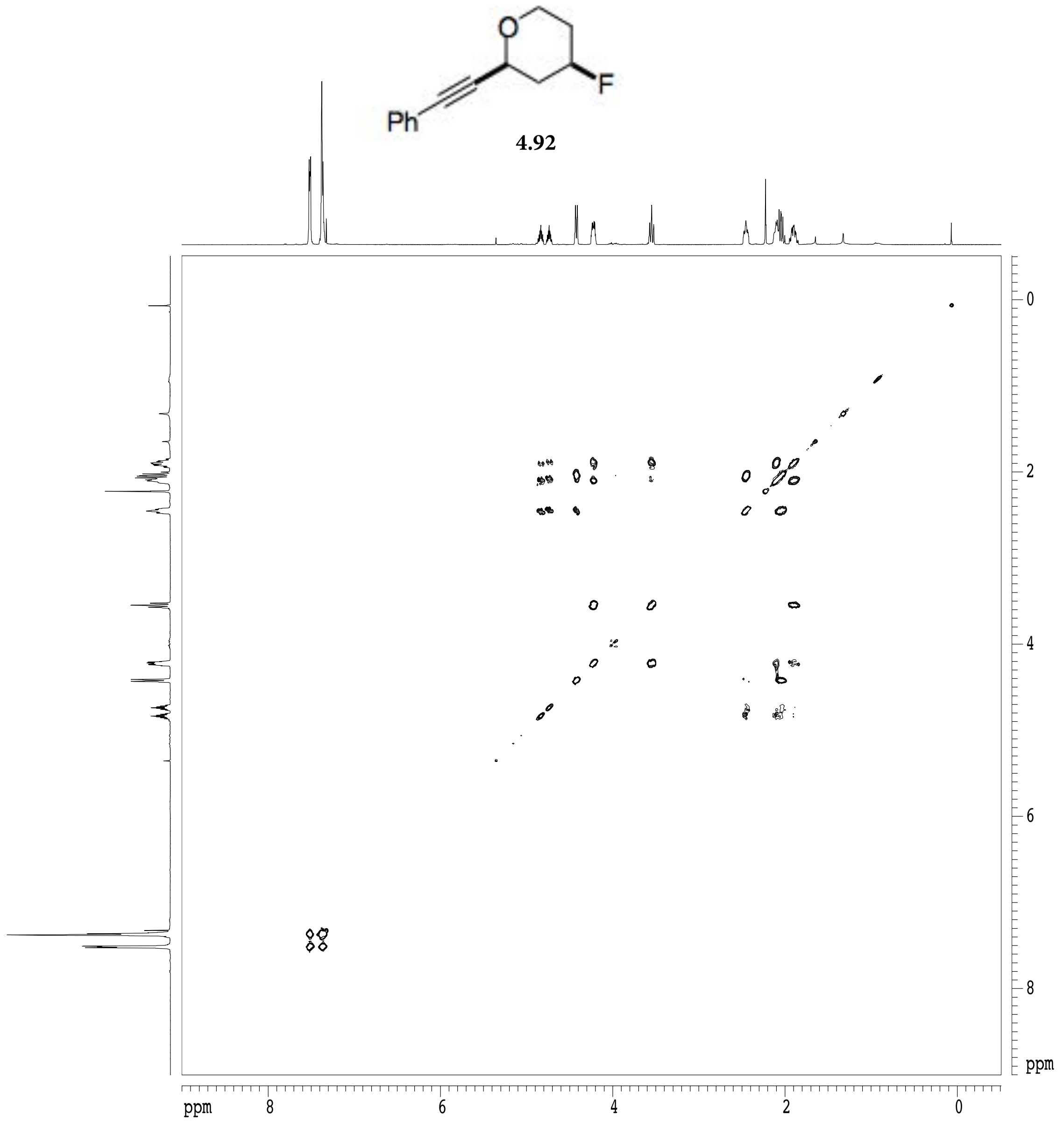
Z-restored spin-echo 13C spectrum with 1H decoupling



4.92

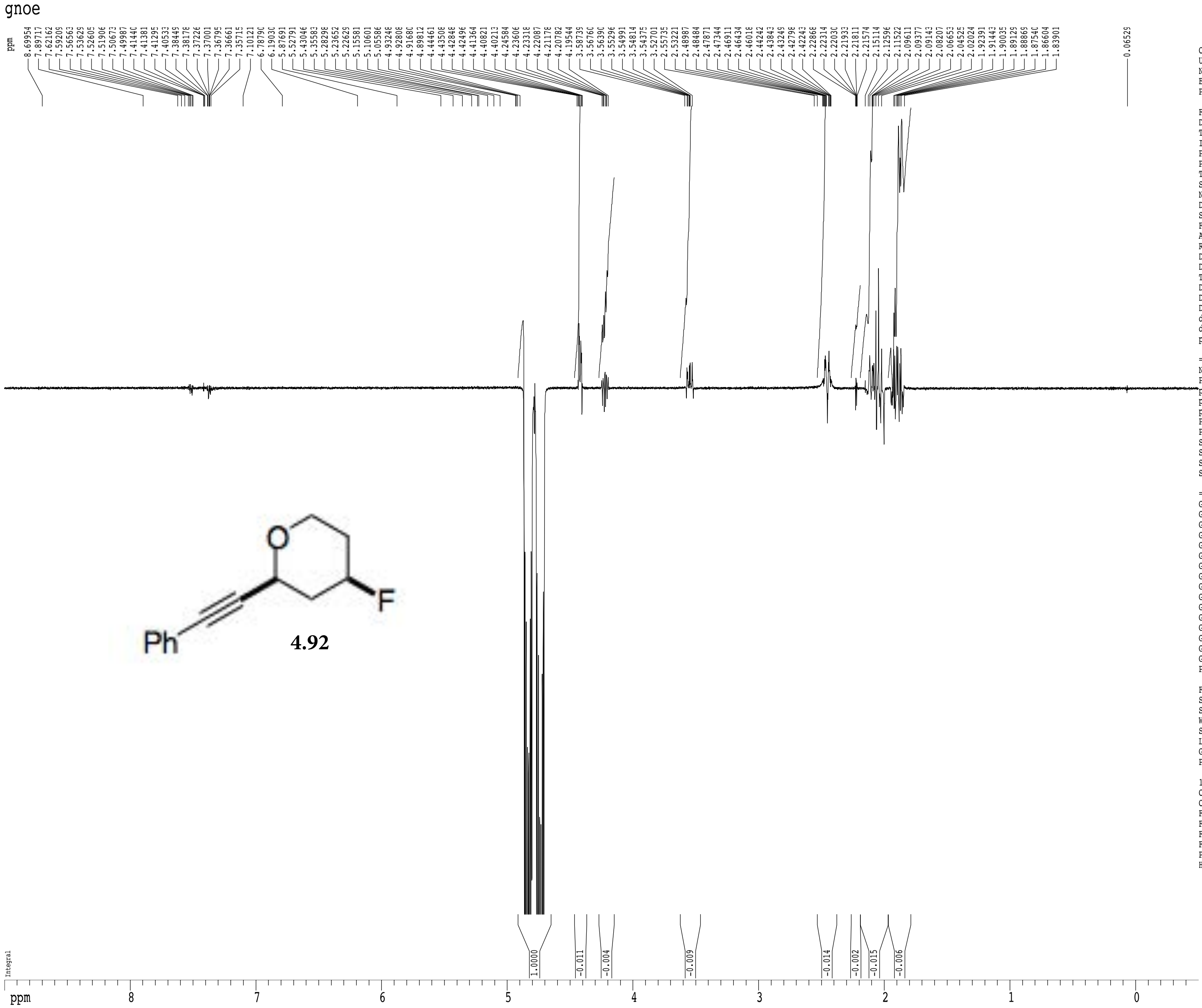
```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-014-2-2D
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20191210
Time              12.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  112
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG              11585.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

gcosy60



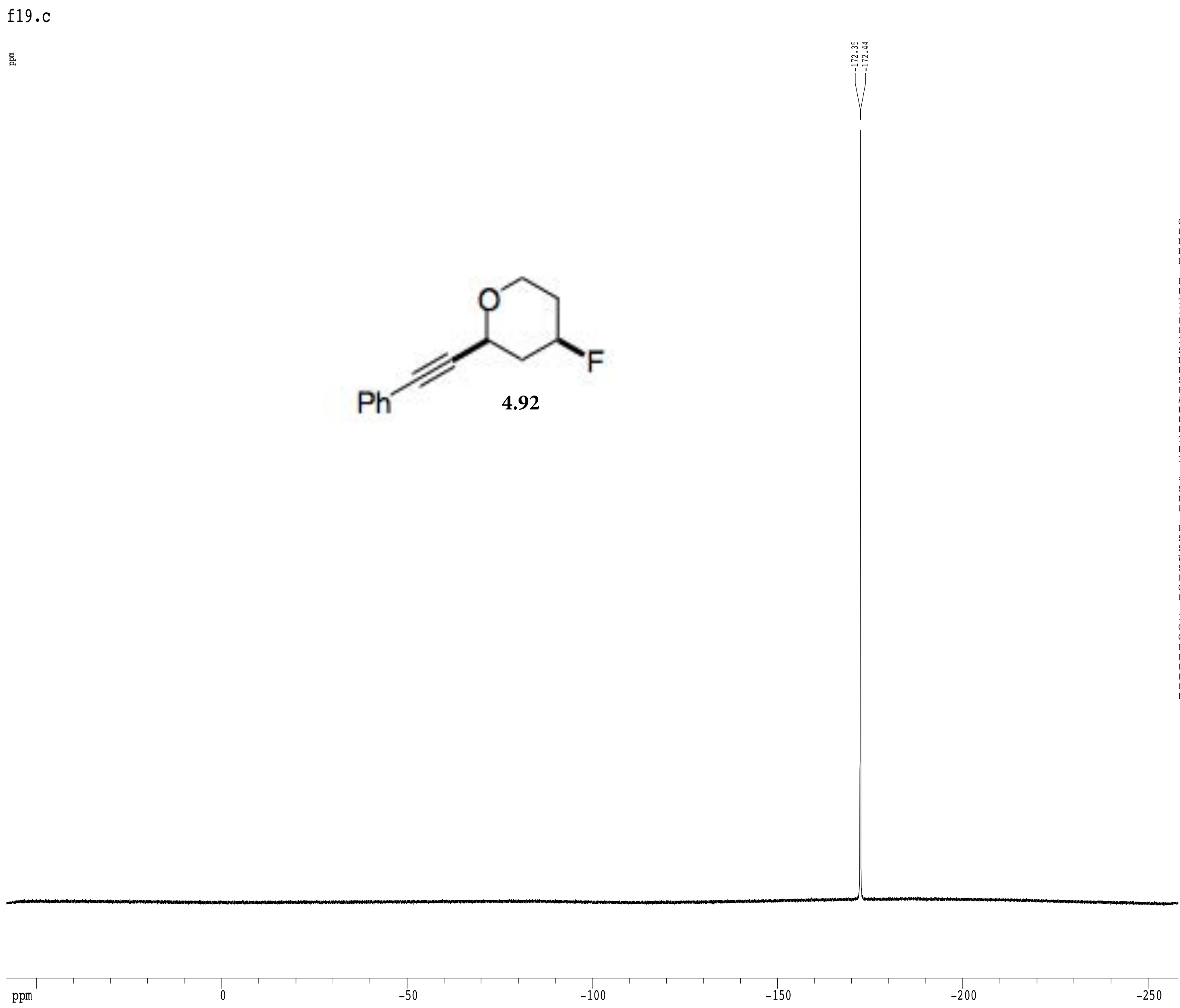
4.92

```
        Current Data Parameters
 USER           khewitt1
NAME     KAH-III-014-2-2D
 EXPNO                 6
 PROCNO                1

      F2 - Acquisition Parameters
 Date_          20191210
 Time              13.25
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG     cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            8012.820 Hz
 FIDRES         3.912510 Hz
 AQ            0.1278452 sec
 RG                143.7
 DW               62.400 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00012480 sec

    ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2235015 MHz

    ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  512
 SFO1           500.2235 MHz
 FIDRES        15.650040 Hz
 SW               16.018 ppm
 FnMODE               QF

      F2 - Processing parameters
 SI                 1024
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

      F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

        2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             9.002 ppm
 F2LO            4503.14 Hz
 F2PHI            -0.509 ppm
 F2HI            -254.47 Hz
 F1PLO             9.002 ppm
 F1LO            4503.14 Hz
 F1PHI            -0.509 ppm
 F1HI            -254.47 Hz
 F2PPMCM         0.63407 ppm/cm
 F2HZCM        317.17416 Hz/cm
 F1PPMCM         0.63407 ppm/cm
 F1HZCM        317.17416 Hz/cm
```

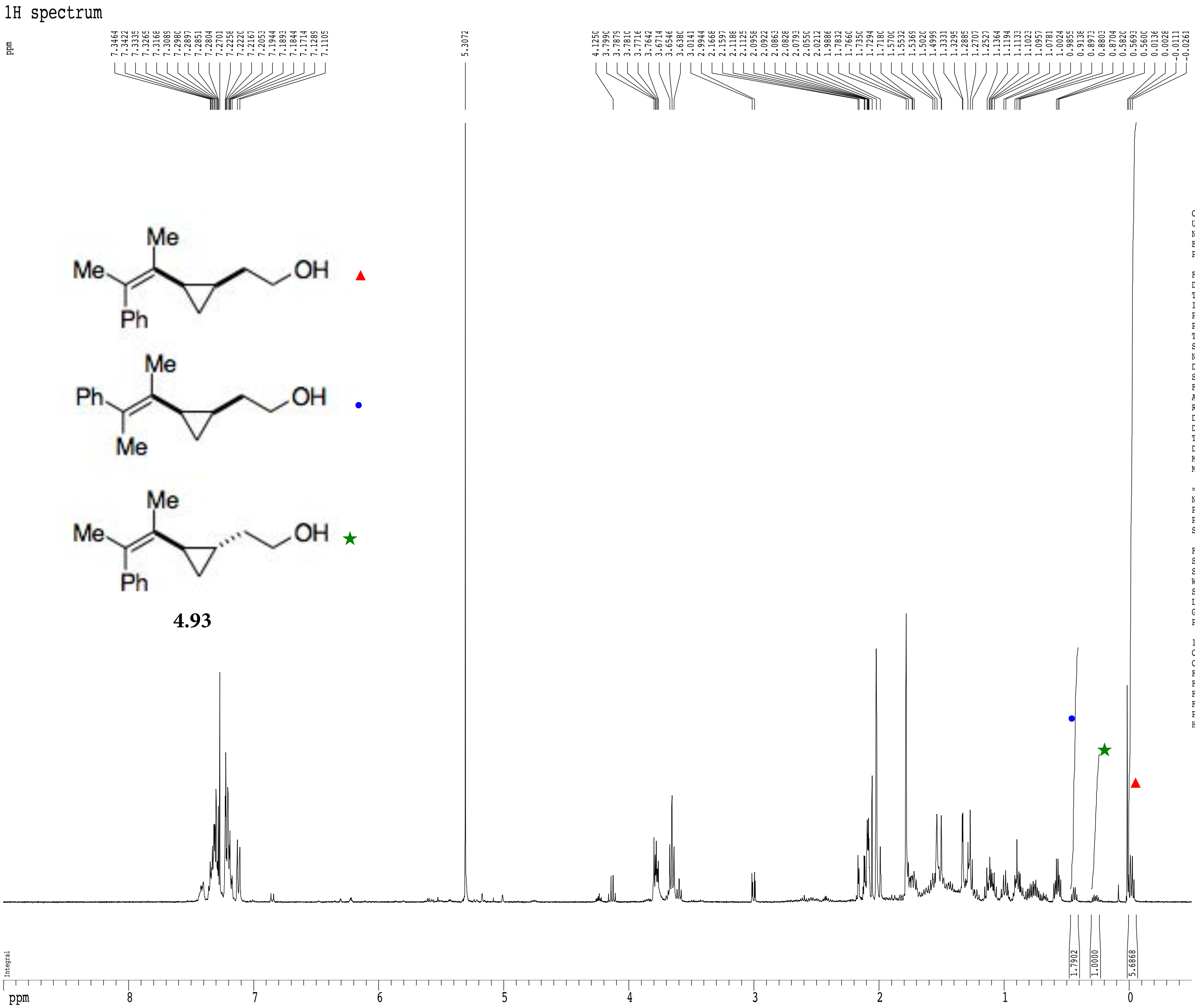


4.92

```
Current Data Parameters
USER             khewitt1
NAME     KAH-III-014-2-2D
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_          20191210
Time              12.51
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                101.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2223920 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

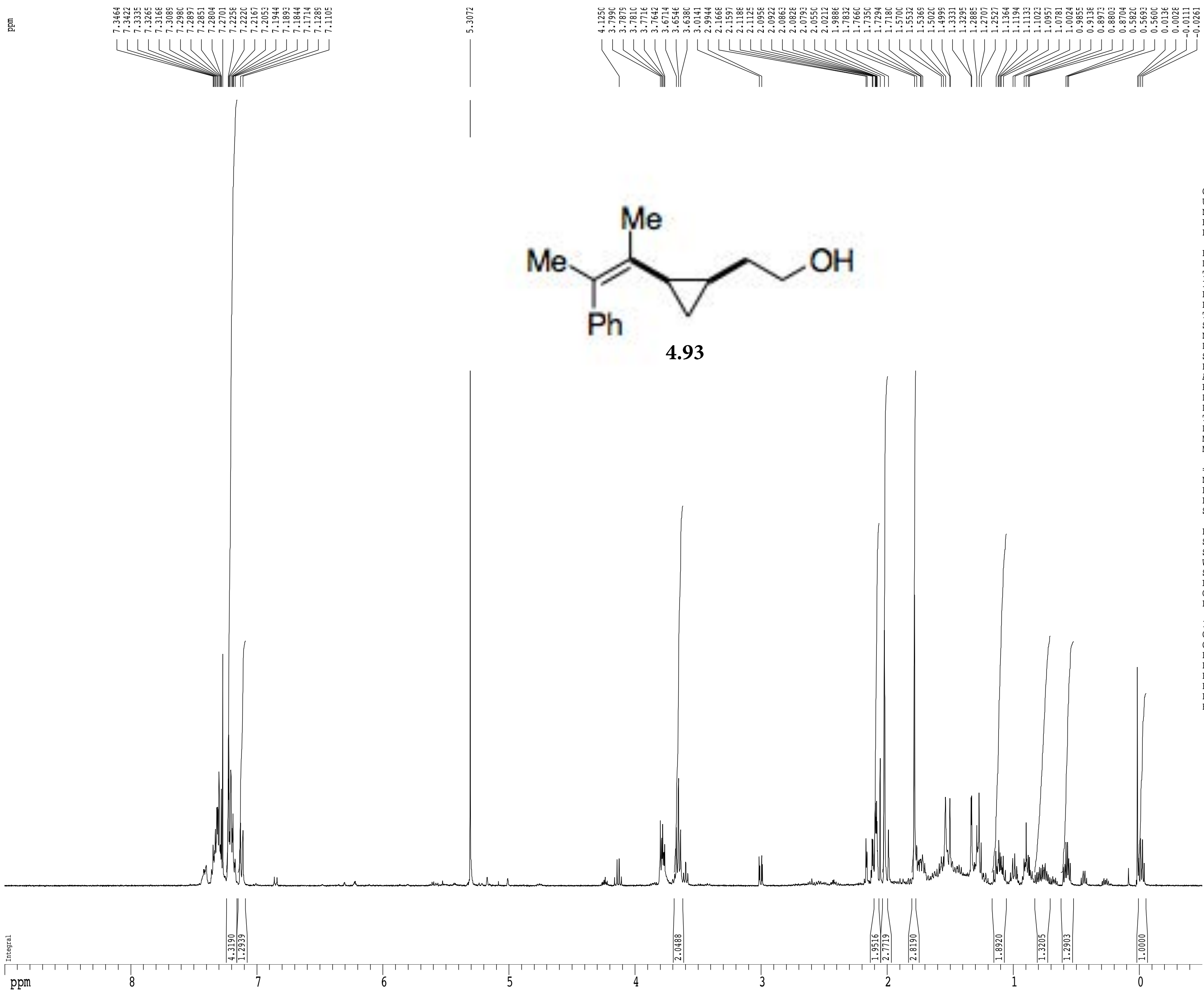


```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-030-cis-F
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20210630
Time              10.38
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgflqn30
TD               131072
SOLVENT          CDCl3T
NS                   16
DS                    2
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                  575
DW                2.800 usec
DE                18.00 usec
TE                298.0 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        564.6299196 MHz
NUC1                19F
P1                18.25 usec

F2 - Processing parameters
SI               131072
SF          564.6864215 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              58.057 ppm
F1             32783.85 Hz
F2P            -258.174 ppm
F2           -145787.58 Hz
PPMCM          13.86979 ppm/cm
HZCM         7832.08057 Hz/cm
```



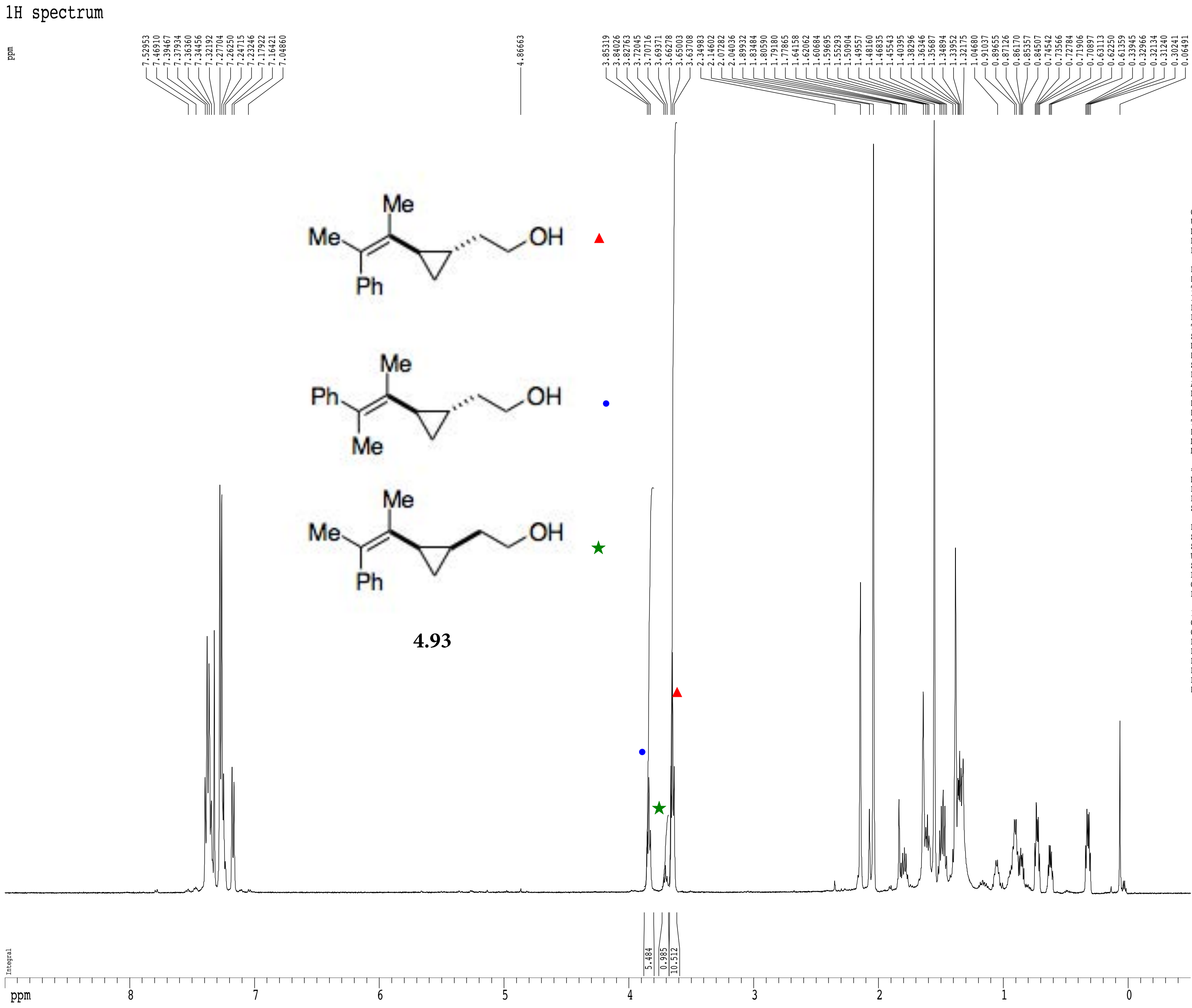
4.93

```
Current Data Parameters
USER            khewitt1
NAME        KAH-II-301-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20191208
Time               14.30
INSTRUM           drx400
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                 322.5
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```


1H spectrum

4.93

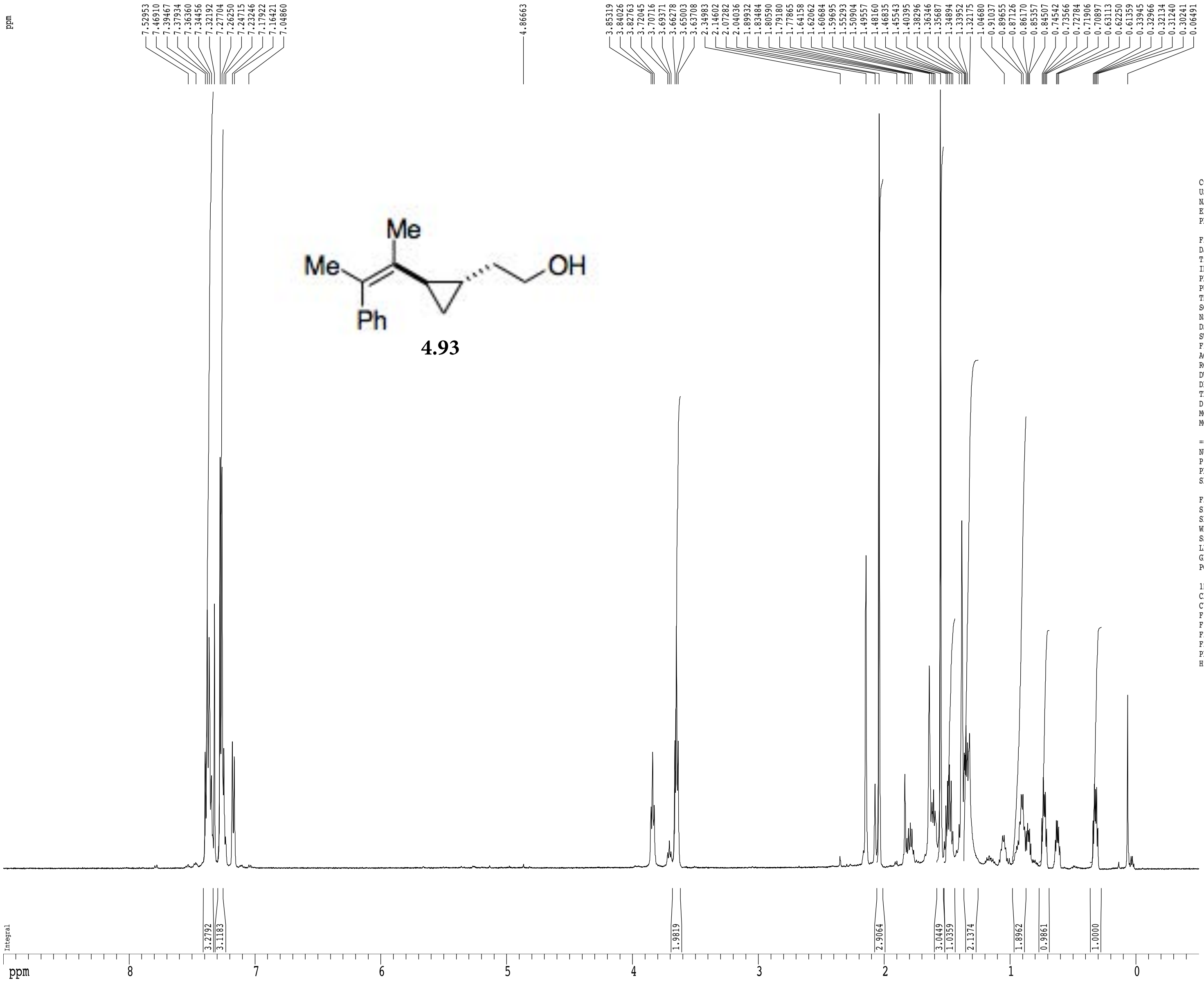
```
Current Data Parameters
USER          khewitt1
NAME       KAH-II-301-1
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20191208
Time             14.30
INSTRUM         drx400
PROBHD   5 mm Multinucl
PULPROG           zg30
TD               38460
SOLVENT         CDCl3T
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG               322.5
DW              78.000 usec
DE                4.50 usec
TE               297.9 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.00 usec
PL1              -1.10 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         400.1300175 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P              9.000 ppm
F1             3601.17 Hz
F2P             -0.500 ppm
F2             -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72084 Hz/cm
```



4.93

```
Current Data Parameters
USER              khewitt1
NAME      KAH-III-053-mix-NOE
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20200302
Time                 17.01
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                   48074
SOLVENT            CDCl3T
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.166677 Hz
AQ               2.9998677 sec
RG                     7.1
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

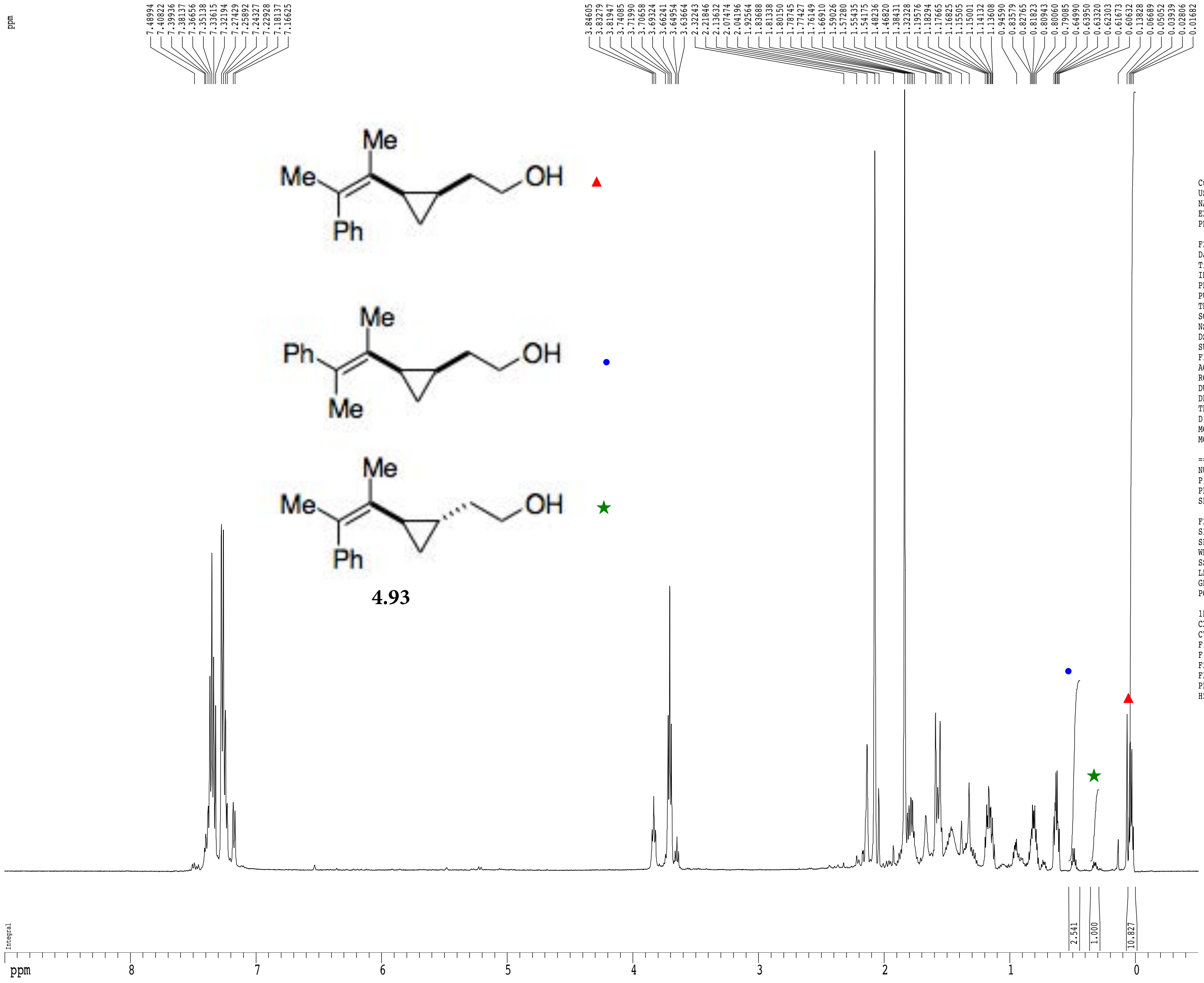
1H spectrum



4.93

```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-053-mix-NOE
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200302
Time              17.01
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH          8012.820 Hz
FIDRES       0.166677 Hz
AQ          2.9998677 sec
RG                  7.1
DW             62.400 usec
DE               6.00 usec
TE              298.0 K
D1         0.10000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

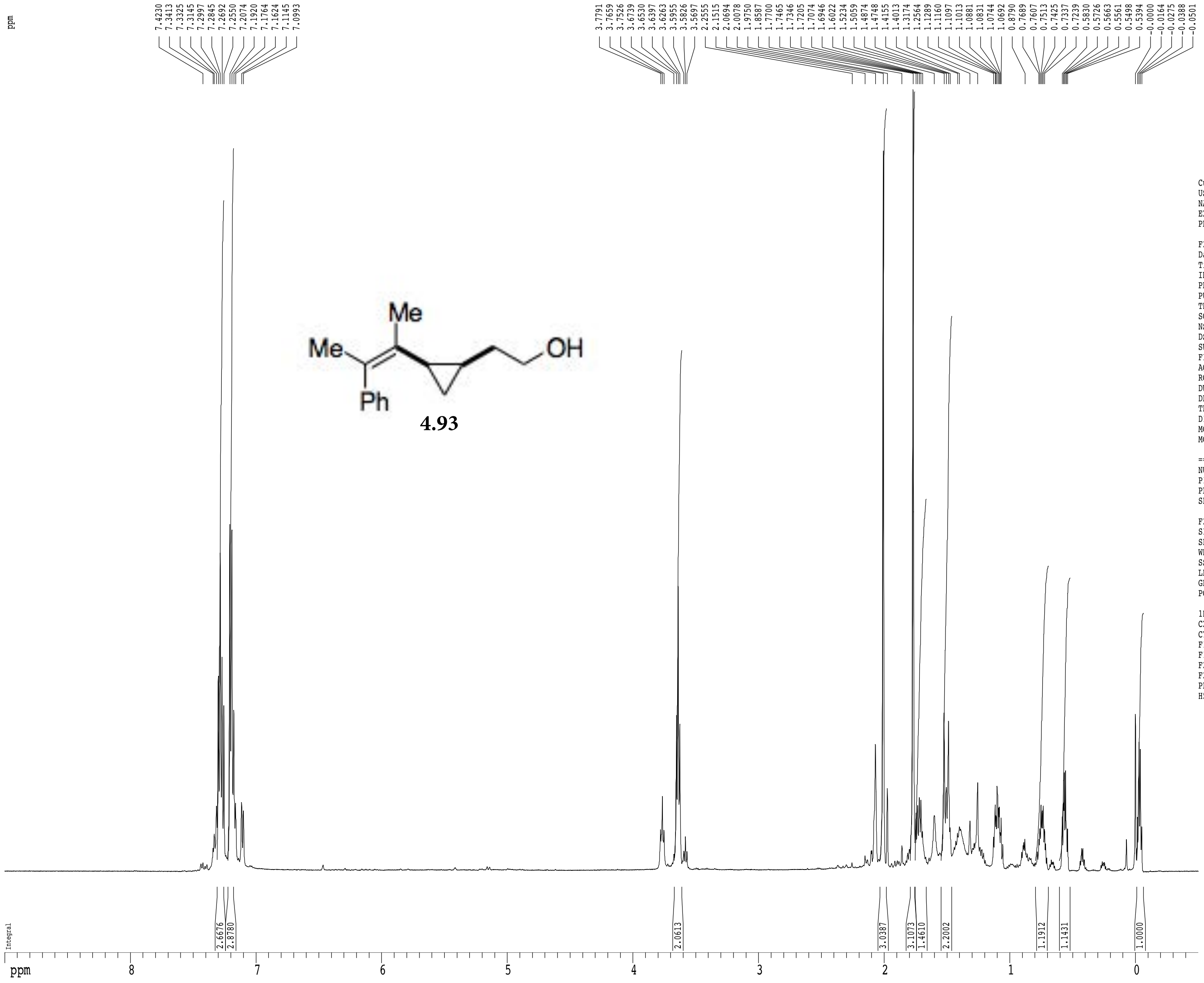
1H spectrum



4.93

```
Current Data Parameters
USER           khewitt1
NAME      KAH-III-052-2D
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200221
Time              17.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

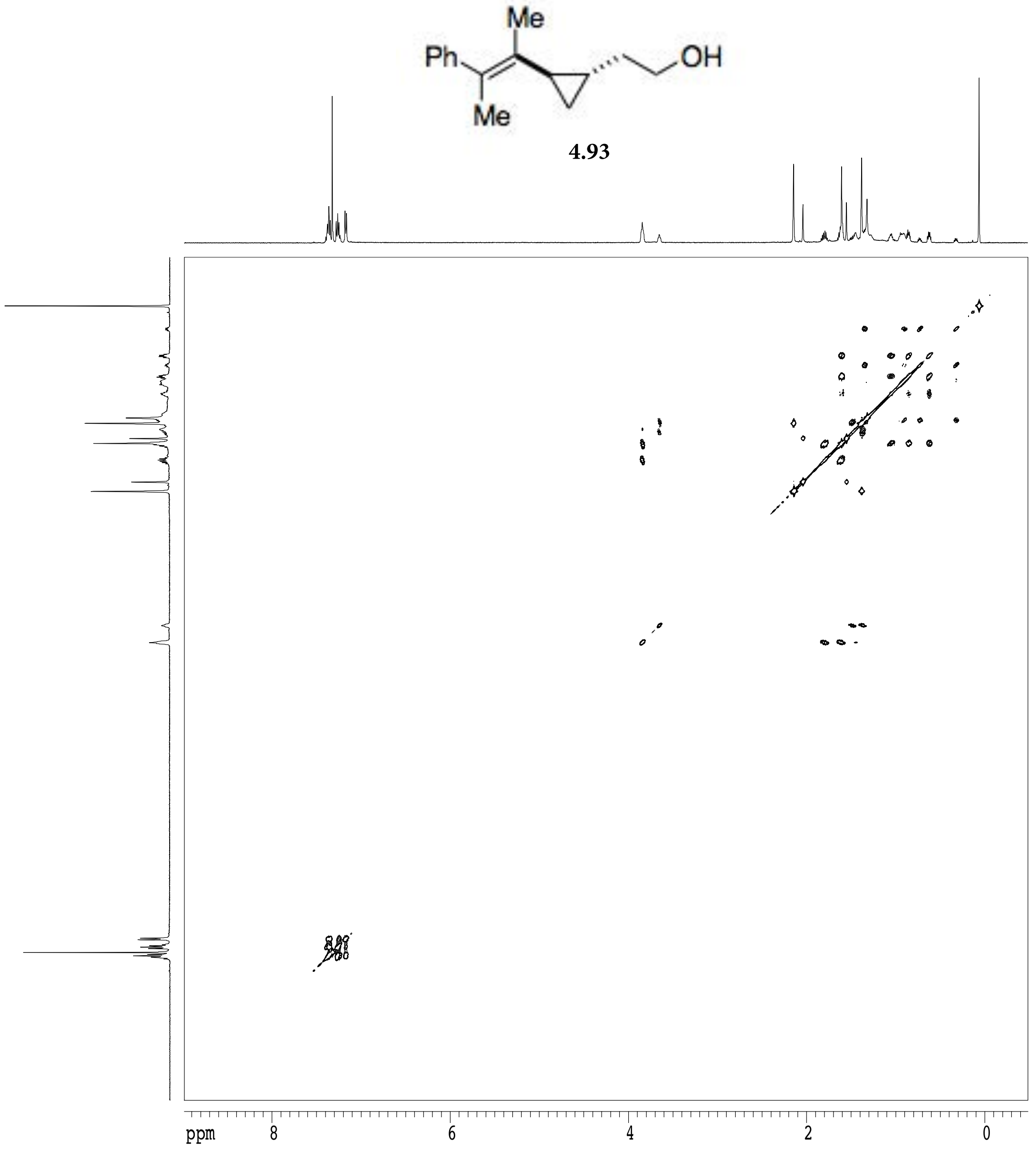
1H spectrum



4.93

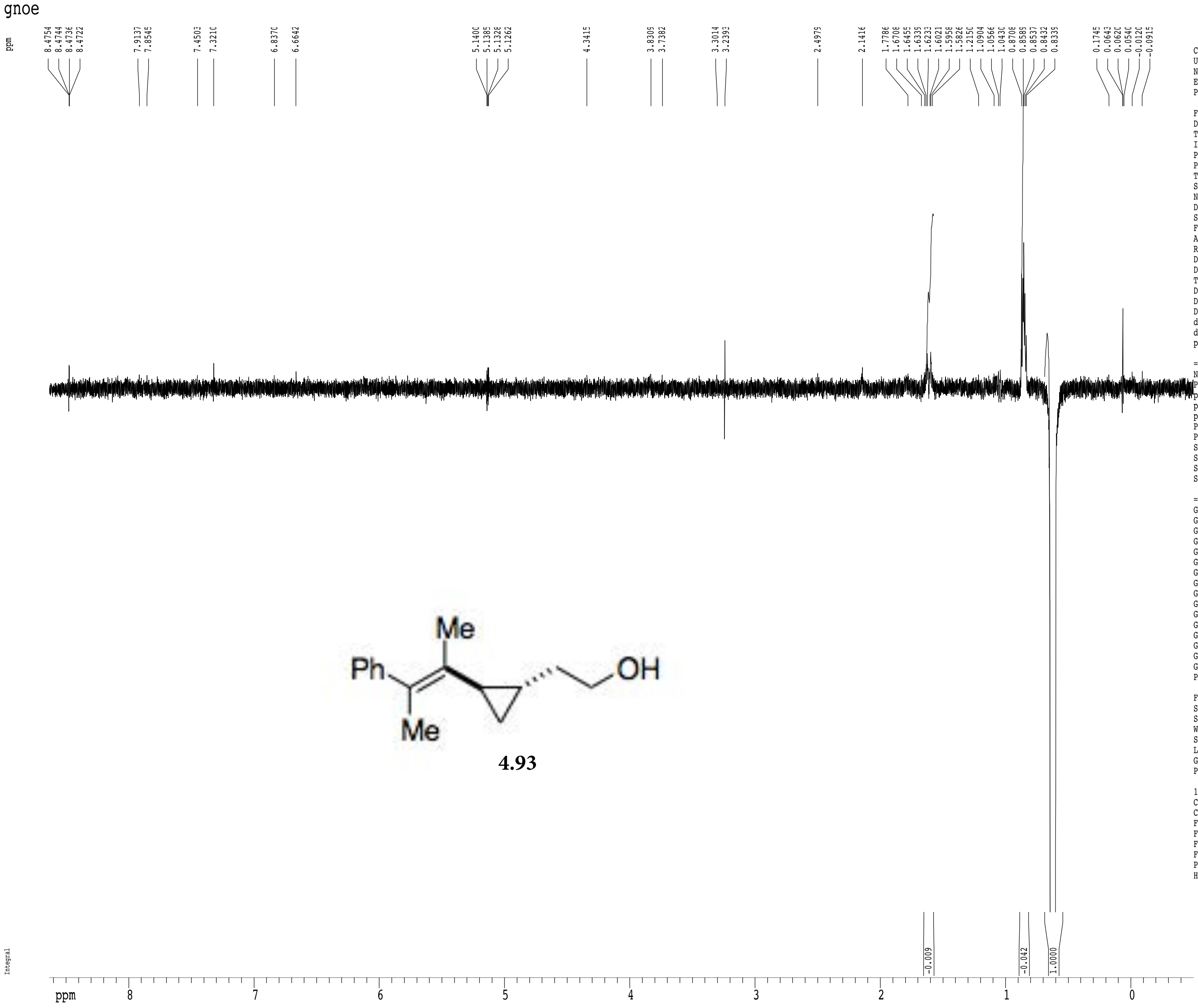
```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-052-2D
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20200221
Time              17.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200335 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

gcosy60



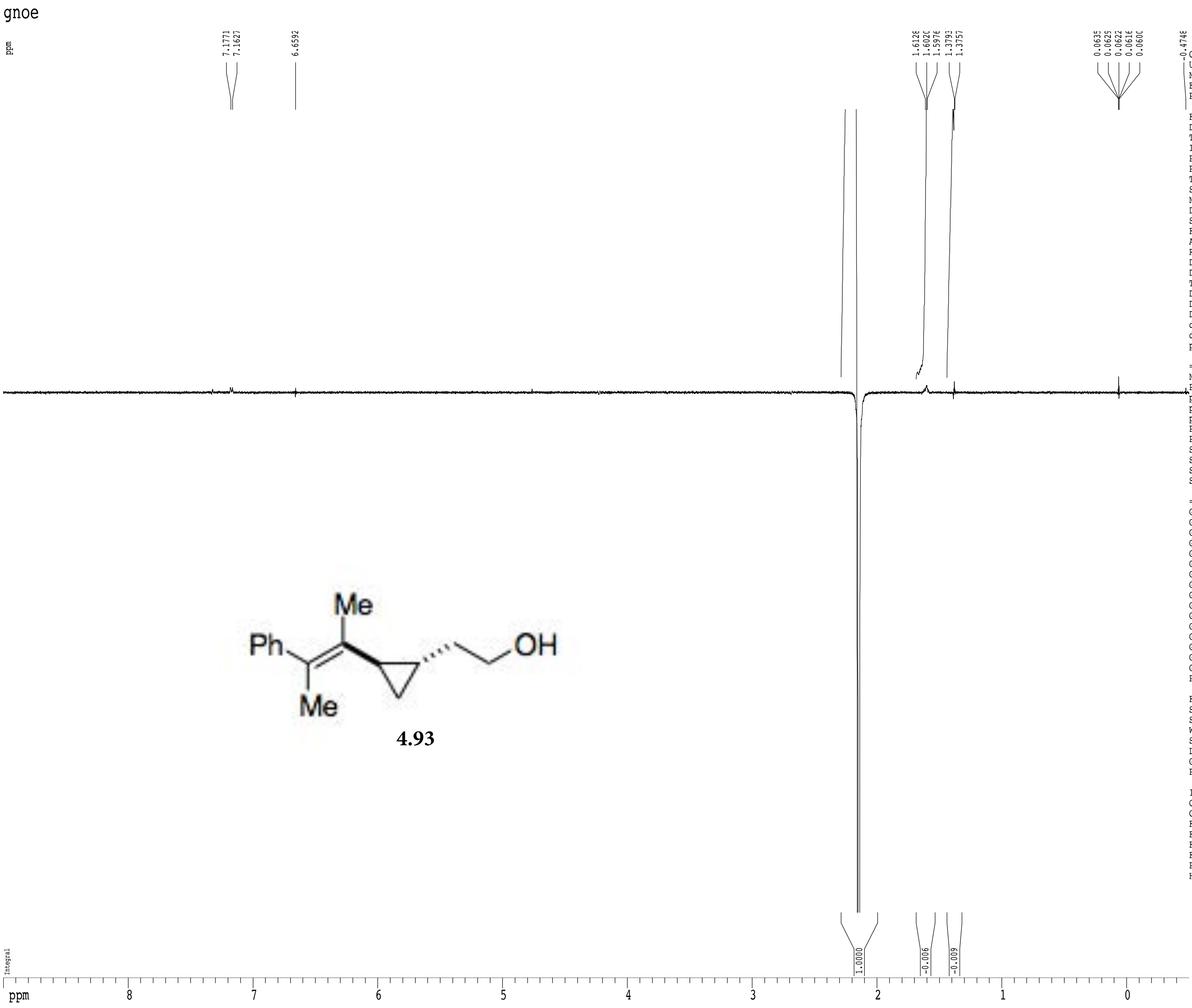
4.93

```
        Current Data Parameters
USER              khewitt1
NAME       KAH-III-053-COSY
EXPNO                    2
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20200219
Time                 11.27
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG     cosygp60.prd
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                      16
SWH               4734.849 Hz
FIDRES            2.311938 Hz
AQ               0.2163188 sec
RG                    1024
DW                 105.600 usec
DE                    6.00 usec
TE                   298.0 K
d0              0.00000300 sec
D1              1.00000000 sec
d13             0.00000300 sec
D16             0.00020000 sec
IN0             0.00021120 sec

    ======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2221259 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 17.00 %
GPZ2                 17.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      1
TD                     512
SFO1              500.2221 MHz
FIDRES            9.247751 Hz
SW                   9.465 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             500.2200000 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.2200000 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

        2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                8.983 ppm
F2LO               4493.36 Hz
F2PHI               -0.483 ppm
F2HI               -241.49 Hz
F1PLO                8.983 ppm
F1LO               4493.36 Hz
F1PHI               -0.483 ppm
F1HI               -241.49 Hz
F2PPMCM            0.63104 ppm/cm
F2HZCM           315.65659 Hz/cm
F1PPMCM            0.63104 ppm/cm
F1HZCM           315.65659 Hz/cm
```



4.93

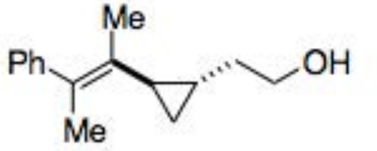
```
Current Data Parameters
USER             khewitt1
NAME         KAH-III-053-2D
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200222
Time                15.48
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG     gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     57
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2203114 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```



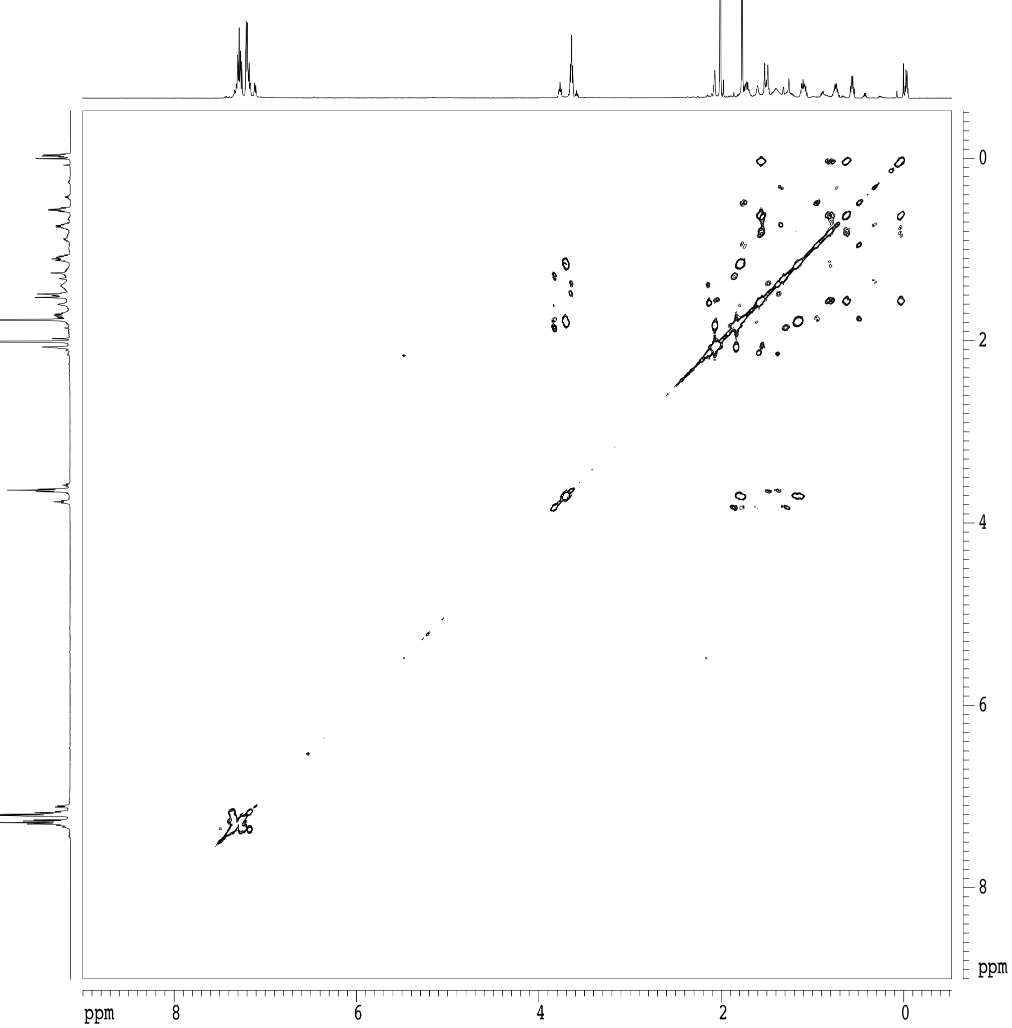
4.93

```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-053-2D
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200222
Time               15.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                    96
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2210722 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

gcosy60

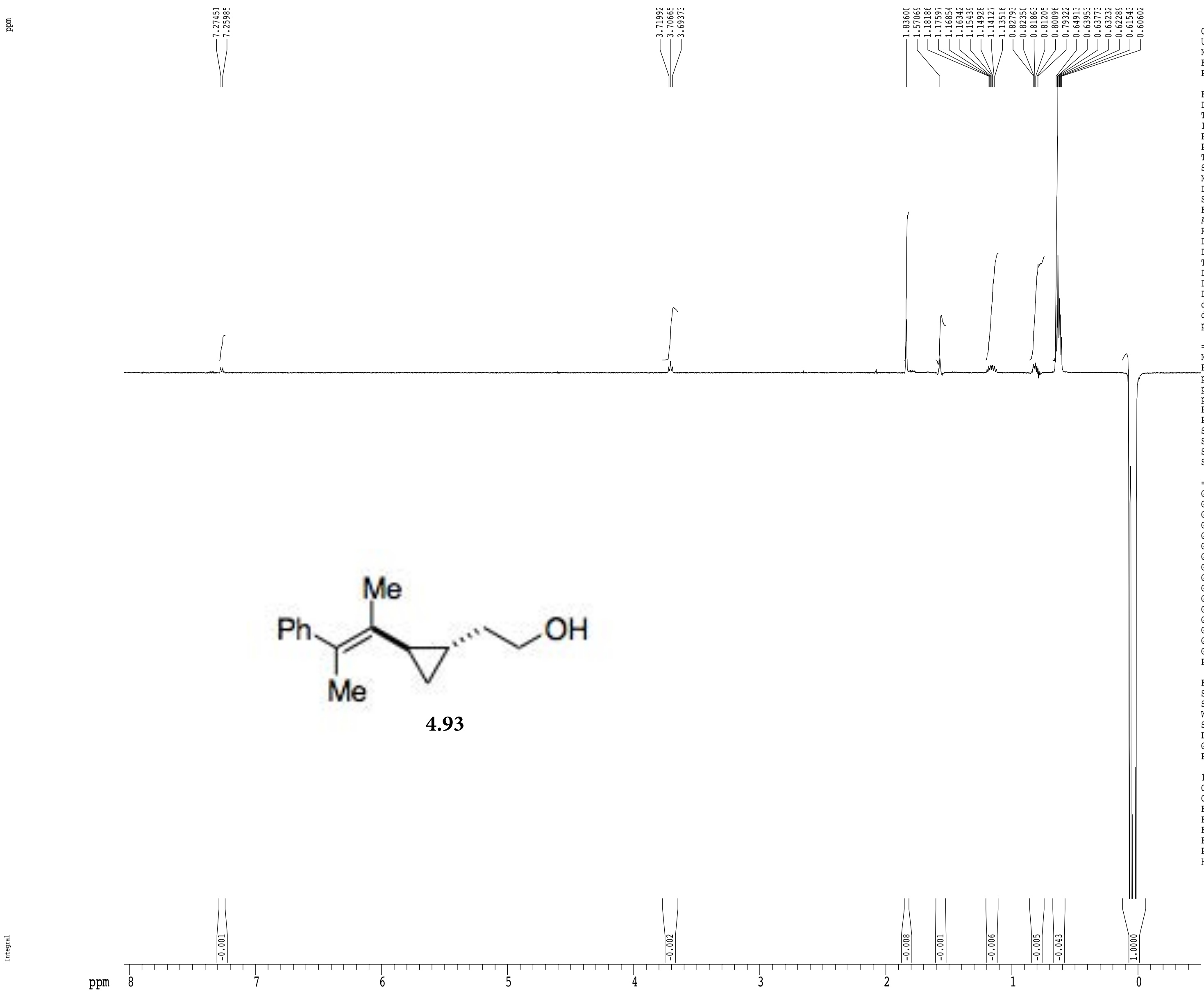


4.93



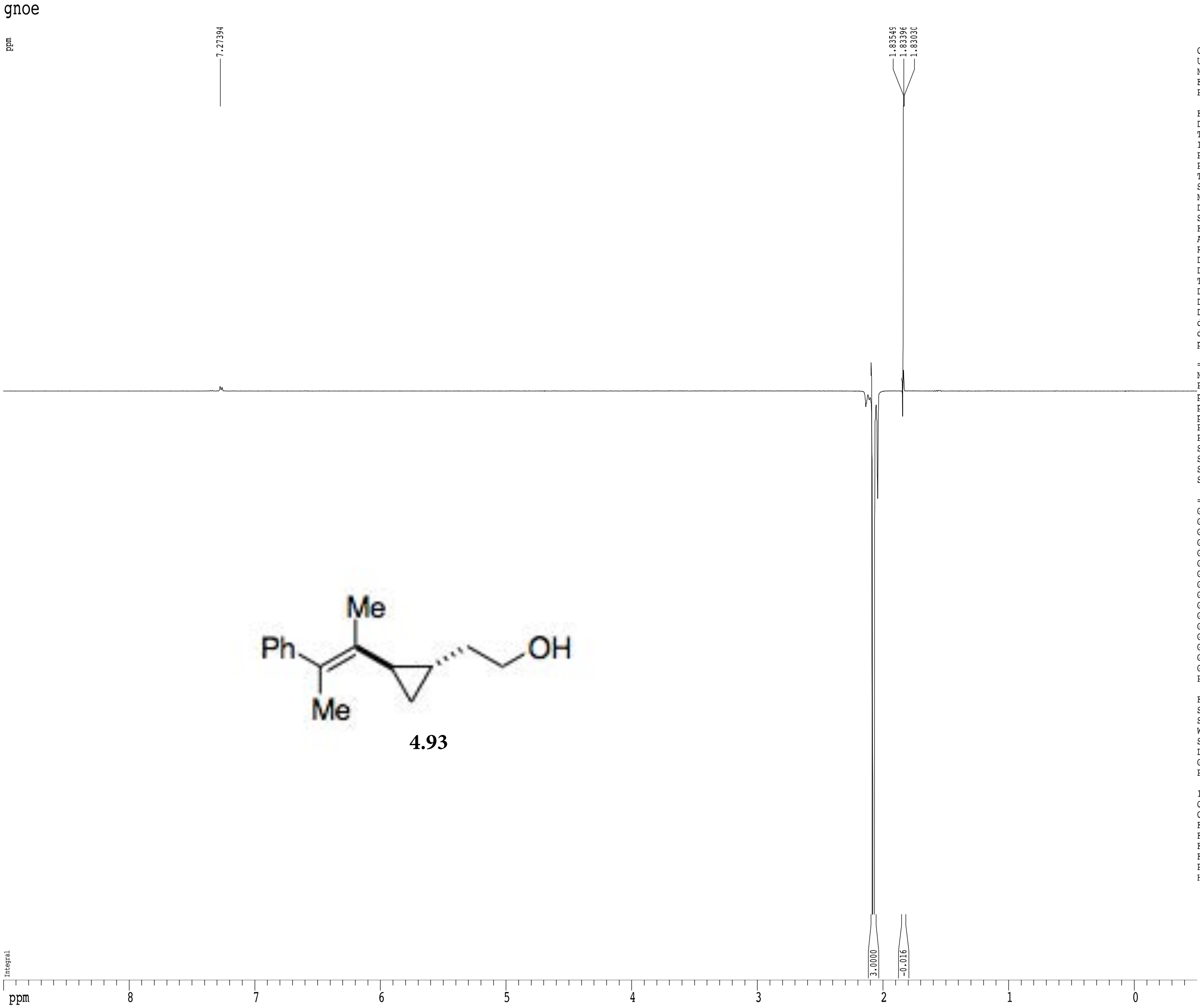
```
        Current Data Parameters
USER             khewitt1
NAME       KAH-III-052-2D
EXPNO                   2
PROCNO                  1

       F2 - Acquisition Parameters
Date_            20200221
Time                17.04
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      cosygp60.prd
TD                   2048
SOLVENT             CDCl3
NS                      1
DS                     16
SWH              8012.820 Hz
FIDRES           3.912510 Hz
AQ              0.1278452 sec
RG                    181
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
d0             0.00000300 sec
D1             1.00000000 sec
d13            0.00000300 sec
D16            0.00020000 sec
IN0            0.00012480 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                17.00 %
GPZ2                17.00 %
P16               1000.00 usec

       F1 - Acquisition parameters
ND0                     1
TD                    512
SFO1             500.2235 MHz
FIDRES          15.650040 Hz
SW                 16.018 ppm
FnMODE                 QF

       F2 - Processing parameters
SI                   1024
SF            500.2200000 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

       F1 - Processing parameters
SI                   1024
MC2                    QF
SF            500.2200000 MHz
WDW                  SINE
SSB                     0
LB                   0.00 Hz
GB                      0

        2D NMR plot parameters
CX2                 15.00 cm
CX1                 15.00 cm
F2PLO               9.002 ppm
F2LO              4503.14 Hz
F2PHI              -0.524 ppm
F2HI              -262.29 Hz
F1PLO               9.002 ppm
F1LO              4503.14 Hz
F1PHI              -0.524 ppm
F1HI              -262.29 Hz
F2PPMCM           0.63511 ppm/cm
F2HZCM          317.69583 Hz/cm
F1PPMCM           0.63511 ppm/cm
F1HZCM          317.69583 Hz/cm
```

gnoe



4.93

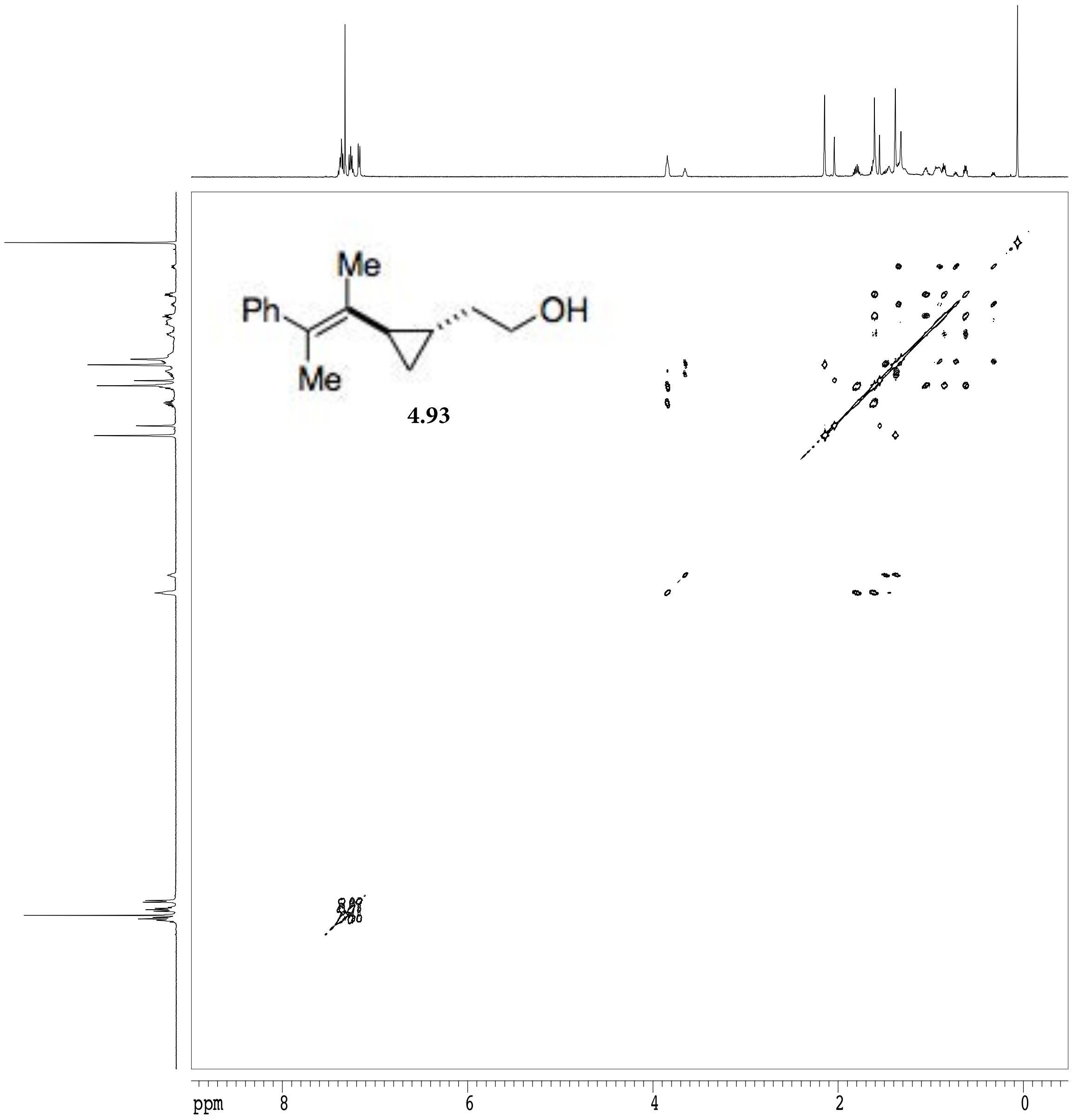
```
Current Data Parameters
USER            khewitt1
NAME      KAH-III-052-2D
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200221
Time               17.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     8
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
D8            0.50000000 sec
D16           0.00020000 sec
d21           0.33376500 sec
d22           0.16399699 sec
p2                 15.00 usec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
p3                 22.50 usec
p4                 30.00 usec
p5                 20.00 usec
P29             40000.00 usec
PL1                 1.60 dB
SFO1         500.2200170 MHz
SP9                61.60 dB
SPNAM9        gauss1.512
SPOFF9              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1          sine.100
GPNAM2          sine.100
GPNAM3          sine.100
GPNAM4          sine.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPX4                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPY4                0.00 %
GPZ1                7.00 %
GPZ2                3.00 %
GPZ3                2.30 %
GPZ4               -2.30 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 50.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```



4.93

```
Current Data Parameters
USER             khewitt1
NAME         KAH-III-052-2D
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200222
Time                14.37
INSTRUM           cryo500
PROBHD     5 mm CPTCI 1H-
PULPROG     gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     57
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2210376 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```

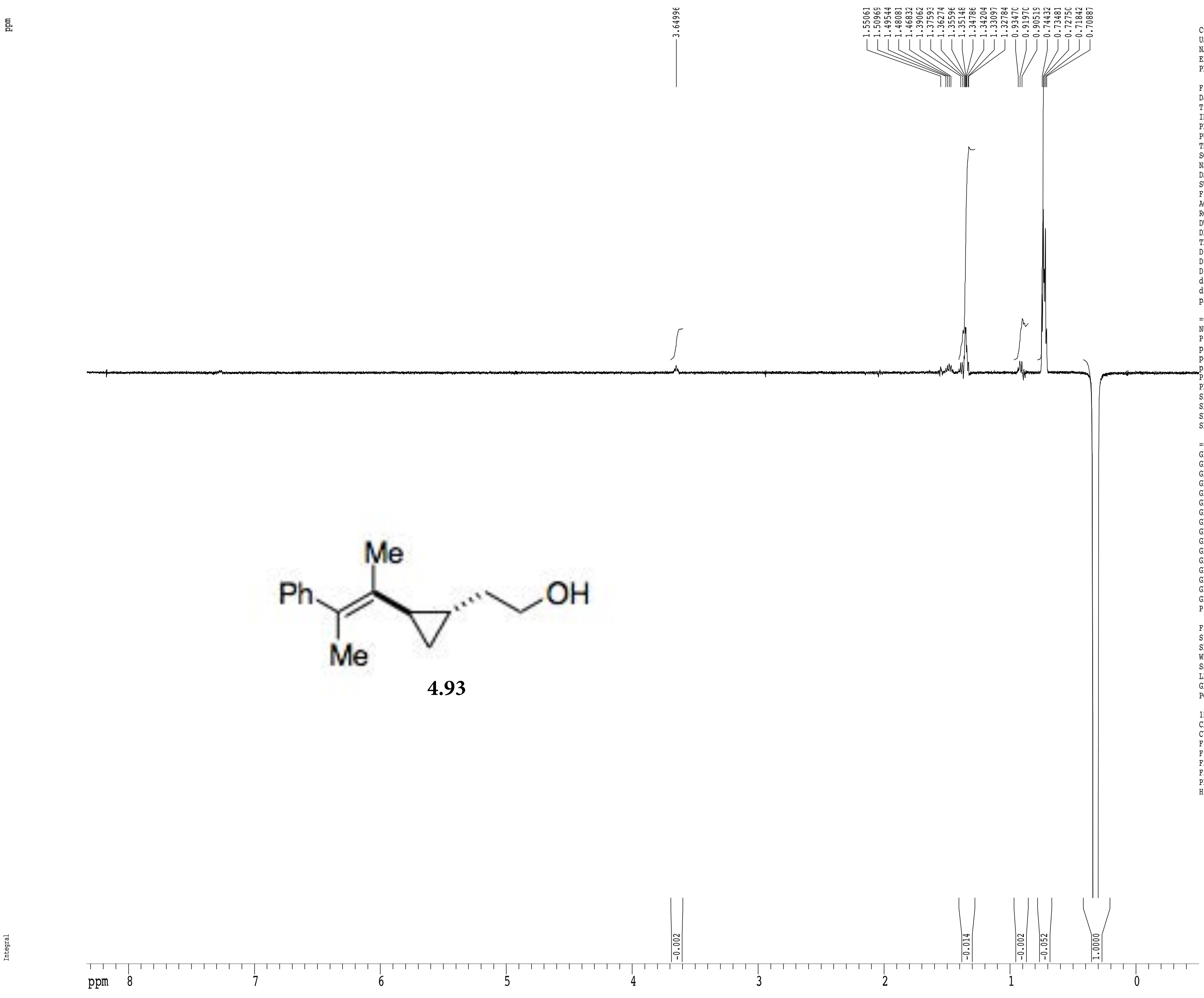
gcosy60



4.93

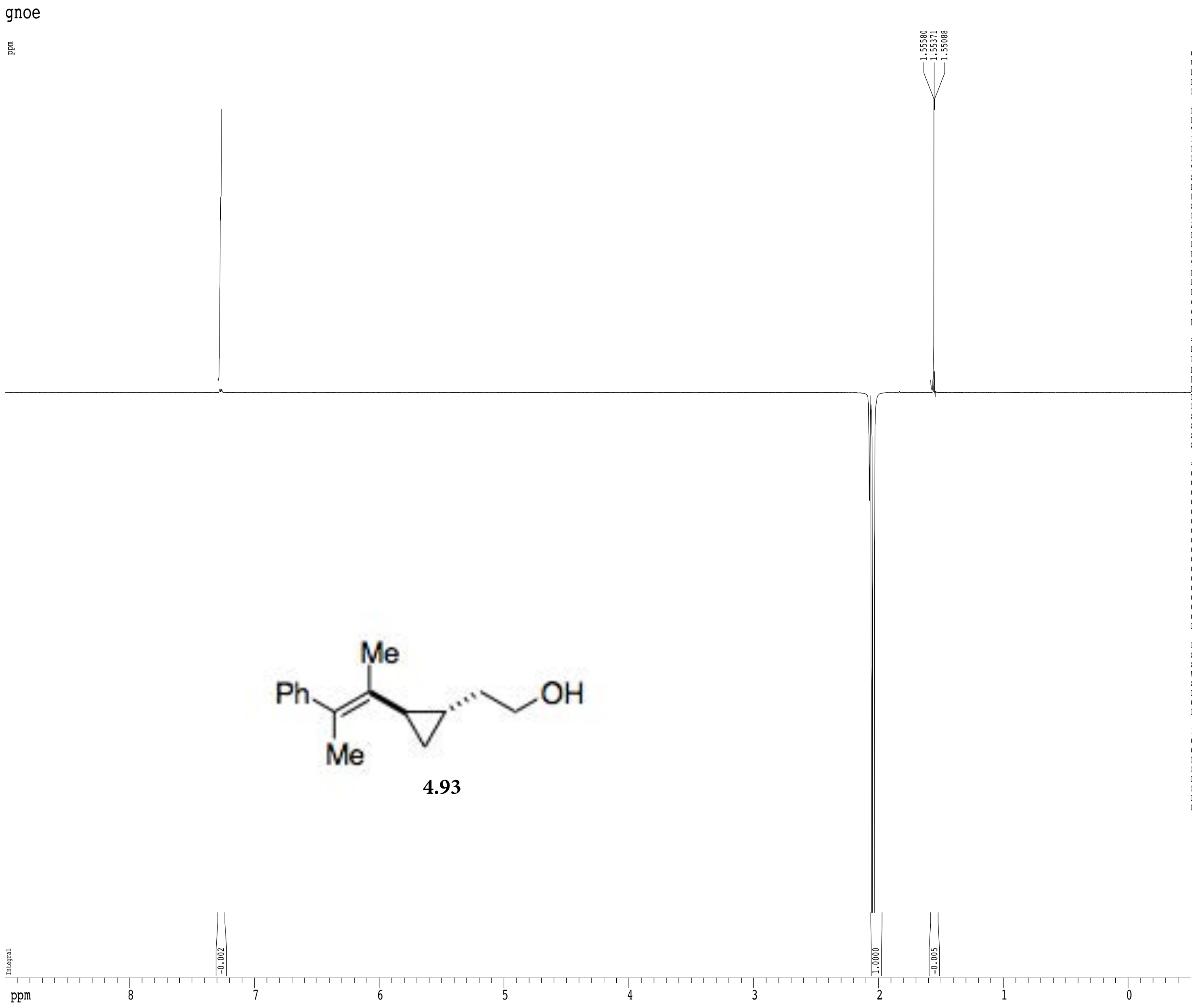
```
        Current Data Parameters
 USER          khewitt1
NAME      KAH-III-053-COSY
 EXPNO                2
 PROCNO               1

      F2 - Acquisition Parameters
 Date_          20200219
 Time              11.27
 INSTRUM         cryo500
 PROBHD   5 mm CPTCI 1H-
 PULPROG     cosygp60.prd
 TD                 2048
 SOLVENT           CDCl3
 NS                    1
 DS                   16
 SWH            4734.849 Hz
 FIDRES         2.311938 Hz
 AQ            0.2163188 sec
 RG                 1024
 DW              105.600 usec
 DE                 6.00 usec
 TE                298.0 K
 d0           0.00000300 sec
 D1           1.00000000 sec
 d13          0.00000300 sec
 D16          0.00020000 sec
 IN0          0.00021120 sec

     ======== CHANNEL f1 ========
 NUC1                 1H
 P1                 7.50 usec
 PL1                1.60 dB
 SFO1        500.2221259 MHz

     ====== GRADIENT CHANNEL =====
 GPNAM1         sine.100
 GPNAM2         sine.100
 GPX1               0.00 %
 GPX2               0.00 %
 GPY1               0.00 %
 GPY2               0.00 %
 GPZ1              17.00 %
 GPZ2              17.00 %
 P16             1000.00 usec

      F1 - Acquisition parameters
 ND0                   1
 TD                  512
 SFO1           500.2221 MHz
 FIDRES         9.247751 Hz
 SW                9.465 ppm
 FnMODE               QF

      F2 - Processing parameters
 SI                 1024
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0
 PC                 1.00

      F1 - Processing parameters
 SI                 1024
 MC2                  QF
 SF          500.2200000 MHz
 WDW                SINE
 SSB                   0
 LB                 0.00 Hz
 GB                    0

        2D NMR plot parameters
 CX2               15.00 cm
 CX1               15.00 cm
 F2PLO             8.983 ppm
 F2LO            4493.36 Hz
 F2PHI            -0.483 ppm
 F2HI            -241.49 Hz
 F1PLO             8.983 ppm
 F1LO            4493.36 Hz
 F1PHI            -0.483 ppm
 F1HI            -241.49 Hz
 F2PPMCM         0.63104 ppm/cm
 F2HZCM        315.65659 Hz/cm
 F1PPMCM         0.63104 ppm/cm
 F1HZCM        315.65659 Hz/cm
```

gnoe



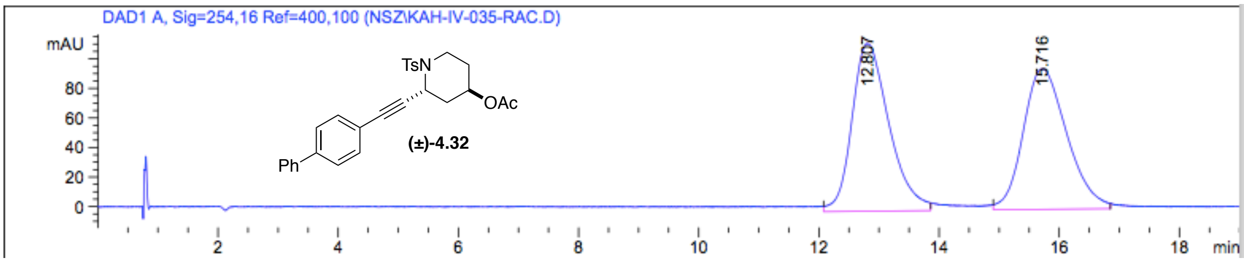
4.93

```
Current Data Parameters
USER             khewitt1
NAME     KAH-III-053-mix-NOE
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20200302
Time                17.15
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG   gnoe1cc22.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      8
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                     64
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
D8             0.50000000 sec
D16            0.00020000 sec
d21            0.33376500 sec
d22            0.16399699 sec
p2                  15.00 usec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
p3                  22.50 usec
p4                  30.00 usec
p5                  20.00 usec
P29              40000.00 usec
PL1                  1.60 dB
SFO1          500.2201607 MHz
SP9                 61.60 dB
SPNAM9         gauss1.512
SPOFF9               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           sine.100
GPNAM2           sine.100
GPNAM3           sine.100
GPNAM4           sine.100
GPX1                 0.00 %
GPX2                 0.00 %
GPX3                 0.00 %
GPX4                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPY3                 0.00 %
GPY4                 0.00 %
GPZ1                 7.00 %
GPZ2                 3.00 %
GPZ3                 2.30 %
GPZ4                -2.30 %
P16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  50.00 cm
F1P                 9.000 ppm
F1                4501.98 Hz
F2P                -0.500 ppm
F2                -250.11 Hz
PPMCM             0.41667 ppm/cm
HZCM            208.42500 Hz/cm
```



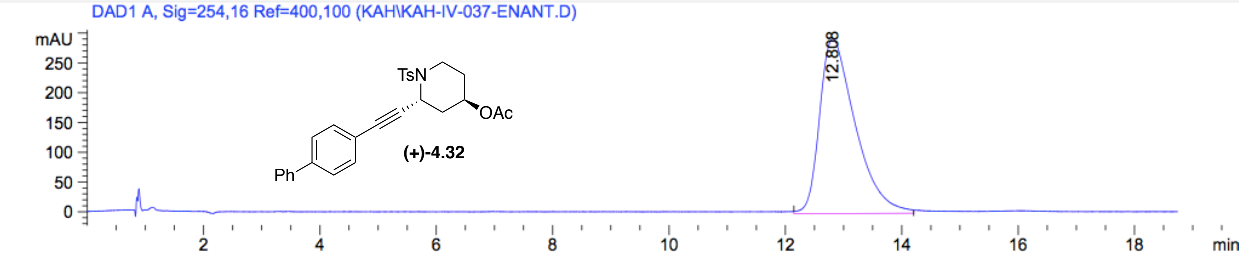
4.93

```
Current Data Parameters
USER          khewitt1
NAME     KAH-III-053-mix-NOE
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20200302
Time              17.30
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  gnoe1cc22.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                 90.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
D8           0.50000000 sec
D16          0.00020000 sec
d21          0.33376500 sec
d22          0.16399699 sec
p2                15.00 usec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
p3                22.50 usec
p4                30.00 usec
p5                20.00 usec
P29            40000.00 usec
PL1                1.60 dB
SFO1        500.2210205 MHz
SP9               61.60 dB
SPNAM9       gauss1.512
SPOFF9             0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1         sine.100
GPNAM2         sine.100
GPNAM3         sine.100
GPNAM4         sine.100
GPX1               0.00 %
GPX2               0.00 %
GPX3               0.00 %
GPX4               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPY3               0.00 %
GPY4               0.00 %
GPZ1               7.00 %
GPZ2               3.00 %
GPZ3               2.30 %
GPZ4              -2.30 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                50.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```



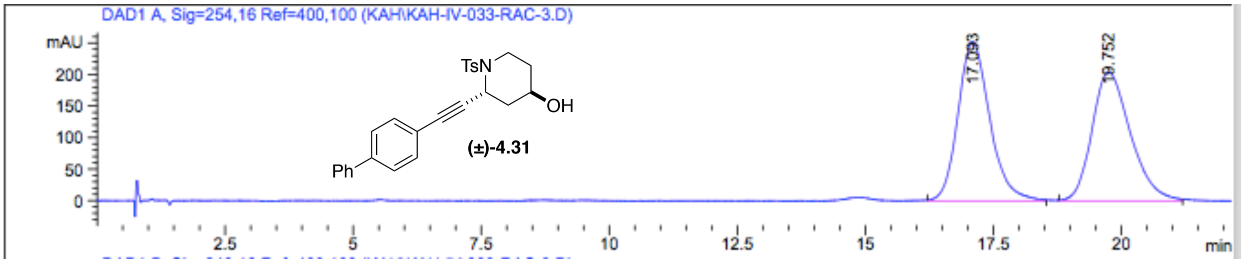
(±)-4.32

```
Signal 1: DAD1 A, Sig=254,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.807 VV     0.5061 4867.51563  113.55048  50.3655
   2  15.716 VV     0.5935 4796.87646   95.08912  49.6345

Totals :                   9664.39209  208.63960
```



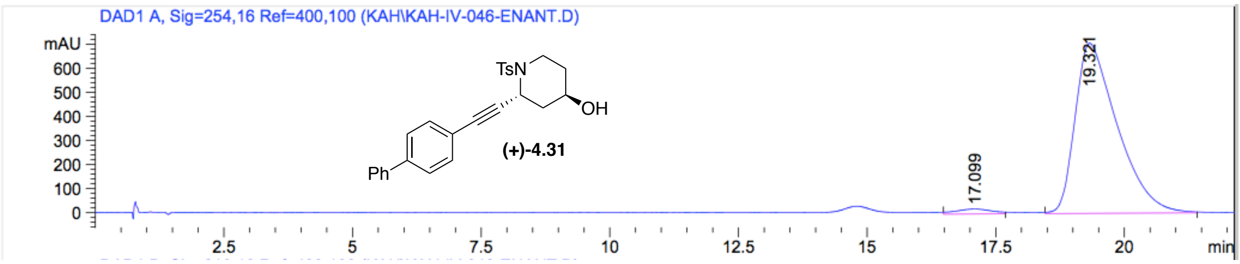
(+)-4.32

```
Signal 1: DAD1 A, Sig=254,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.808 VV     0.5042 1.24940e4  293.16055 100.0000

Totals :                   1.24940e4  293.16055
```

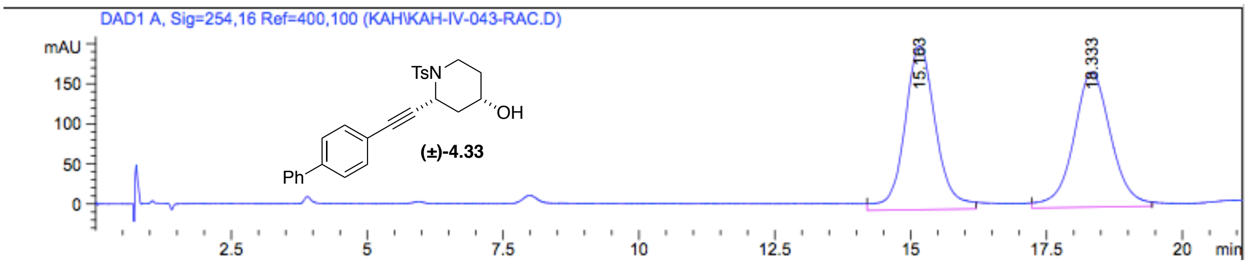


(±)-4.31

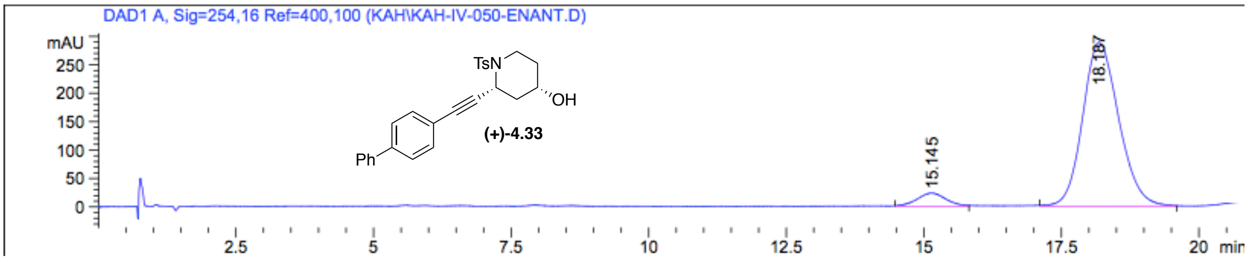
```
Signal 1: DAD1 A, Sig=254,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.093 VV     0.6216 1.09056e4  252.66681  50.5481
   2  19.752 VV     0.7028 1.06691e4  204.44299  49.4519

Totals :                   2.15747e4  457.10980
```



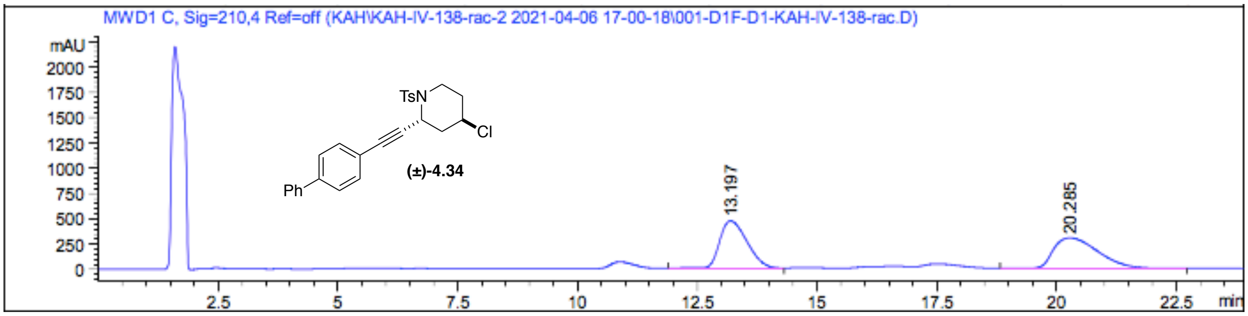
```
Signal 1: DAD1 A, Sig=254,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  17.099 VV    0.5787 1028.28625   20.91209   2.4860
   2  19.321 VB    0.6717 4.03350e4   707.90094  97.5140

Totals :                  4.13632e4   728.81303
```



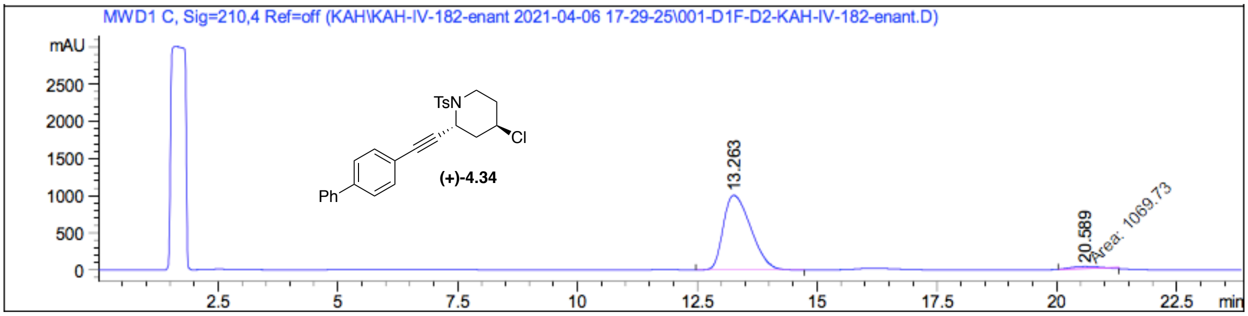
```
Signal 1: DAD1 A, Sig=254,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.163 VB    0.5563 8158.00439  205.00032  50.3242
   2  18.333 VV    0.5825 8052.88818  168.53467  49.6758

Totals :                  1.62109e4   373.53499
```



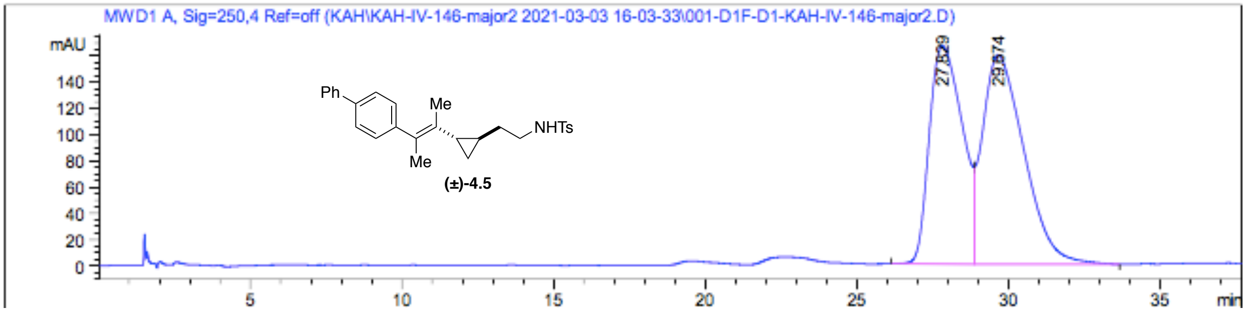
```
Signal 1: DAD1 A, Sig=254,16 Ref=400,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.145 VV    0.4335  856.49738   23.32073   6.1296
   2  18.187 VV    0.6261 1.31167e4   288.13208  93.8704

Totals :                  1.39732e4   311.45281
```



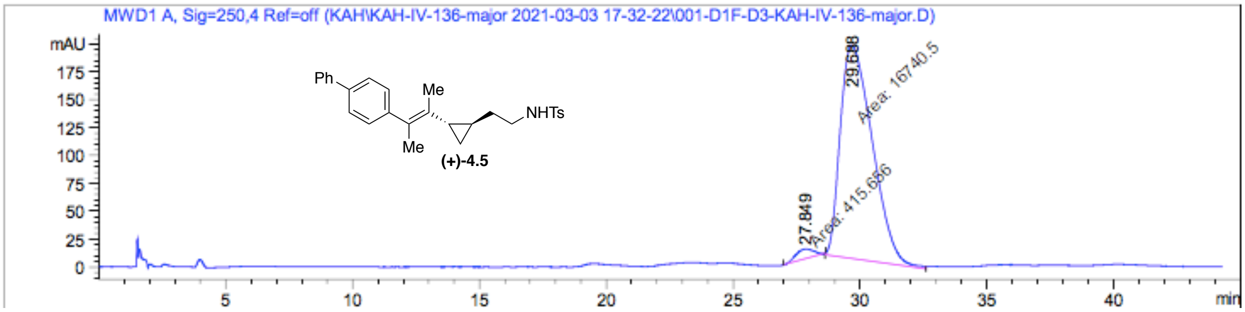
```
Signal 3: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.197 VB R  0.6269 1.85477e4  467.39673  49.0205
   2  20.285 BB    1.0257 1.92889e4  300.15744  50.9795

Totals :                  3.78366e4  767.55417
```



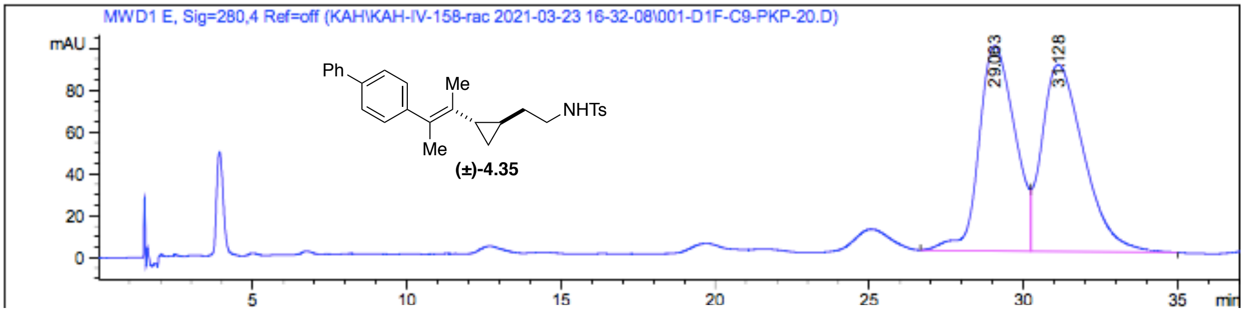
```
Signal 3: MWD1 C, Sig=210,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.263 VB    0.6339 3.99296e4 1004.20569  97.3909
   2  20.589 MM    0.6448 1069.72583  27.65214   2.6091

Totals :                  4.09993e4 1031.85783
```



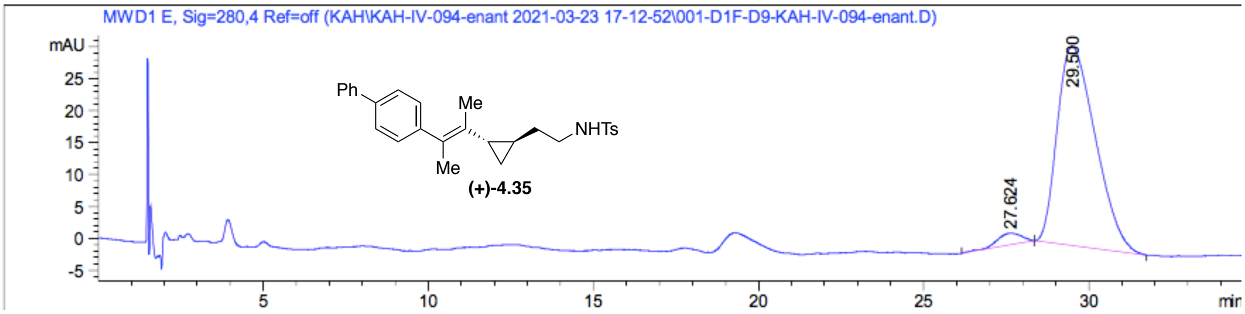
```
Signal 1: MWD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.829 VV R  1.0909 1.25773e4  166.57452  45.1638
   2  29.674 VV R  1.3485 1.52708e4  159.27989  54.8362

Totals :                  2.78481e4  325.85442
```



```
Signal 1: MWD1 A, Sig=250,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.849 MM    0.5898  415.65552    8.55463   2.4228
   2  29.688 MM    1.4600 1.67405e4  191.09866  97.5772

Totals :                  1.71562e4  199.65329
```



```
Signal 5: MWD1 E, Sig=280,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  29.063 BV    1.1694 7931.67773   98.08938  48.2122
   2  31.128 VB    1.3026 8519.92676   89.34296  51.7878

Totals :                   1.64516e4  187.43233
```



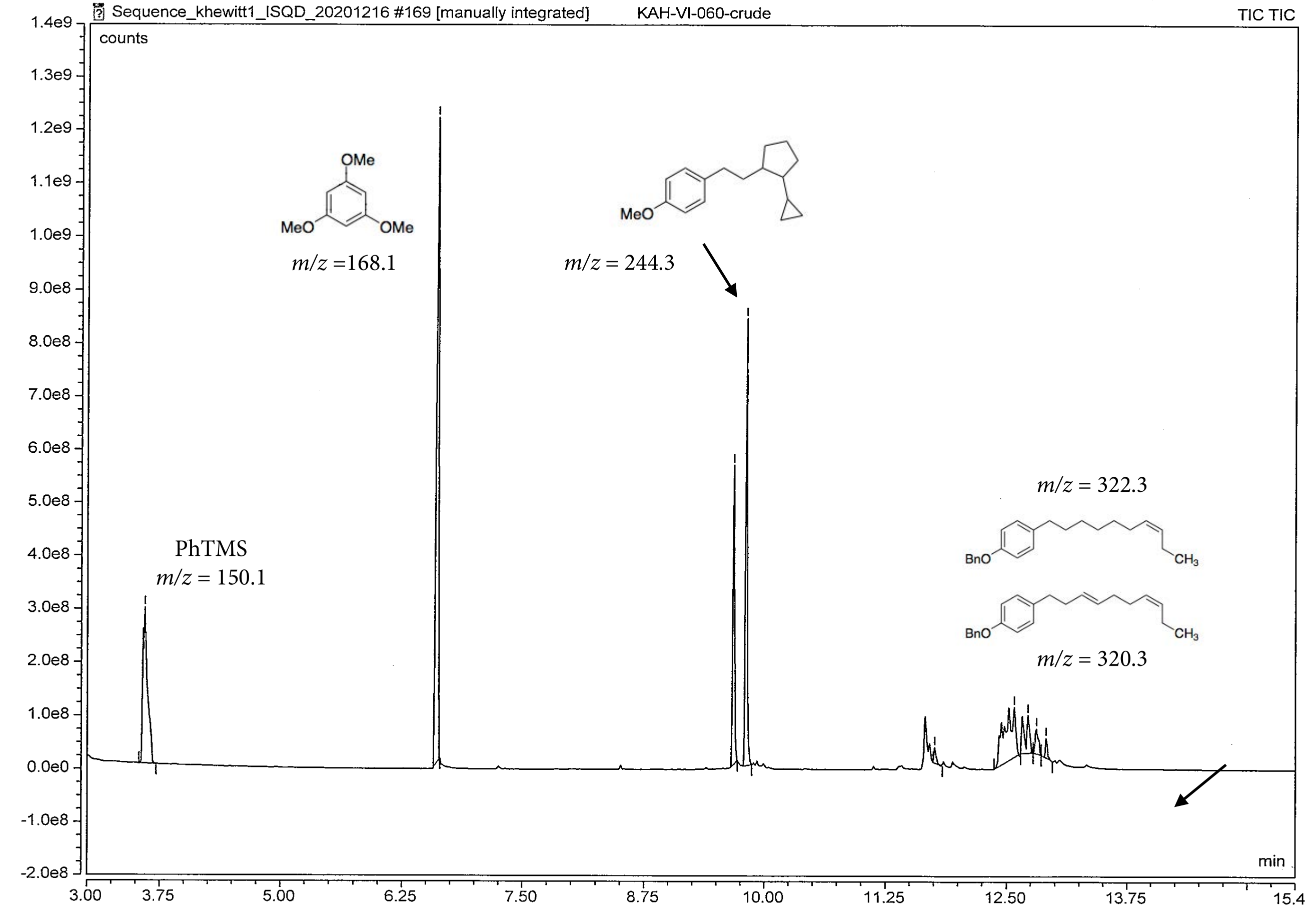
```
Signal 5: MWD1 E, Sig=280,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  27.624 VB R  0.6253   97.29442    1.85081   3.7297
   2  29.500 BB    1.0528 2511.35840   31.27596  96.2703

Totals :                   2608.65282   33.12677
```

APPENDIX A.4

^{1}H, ^{13}C, COSY, HMQC NMR SPECTRA, GCMS SPECTRA FOR CHAPTER 5

Sequence: Sequence_khewitt1_ISQD_20201216
Injection #169: KAH-VI-060-crude

Chromatogram



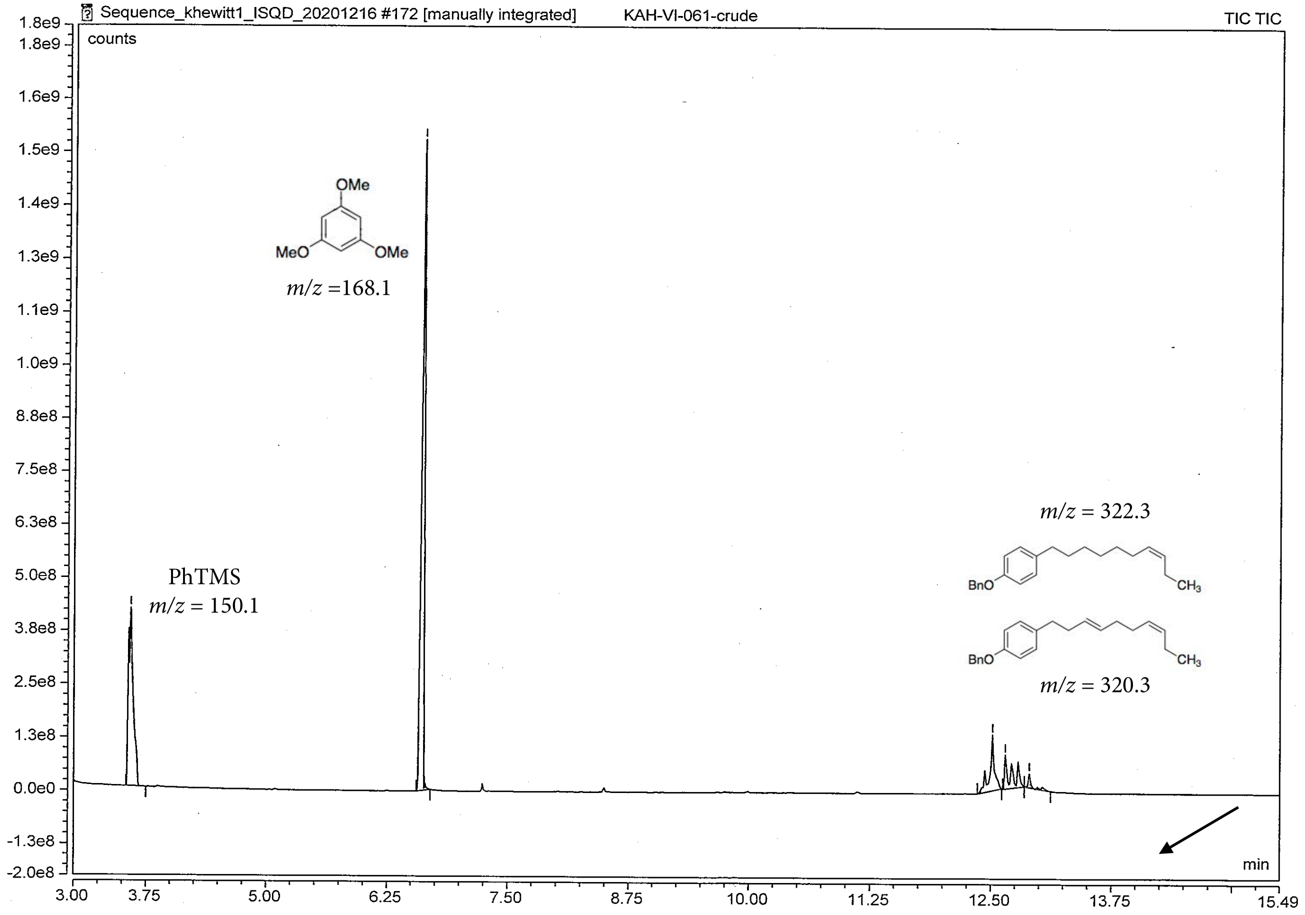
Chromeleon 7,
Version 7.2.9.11323, Thermo Fisher Scientific

Page 1 of 1

Printed by khewitt1
14/04/22 09:34

Sequence: Sequence_khewitt1_ISQD_20201216
Injection #172: KAH-VI-061-crude

Chromatogram



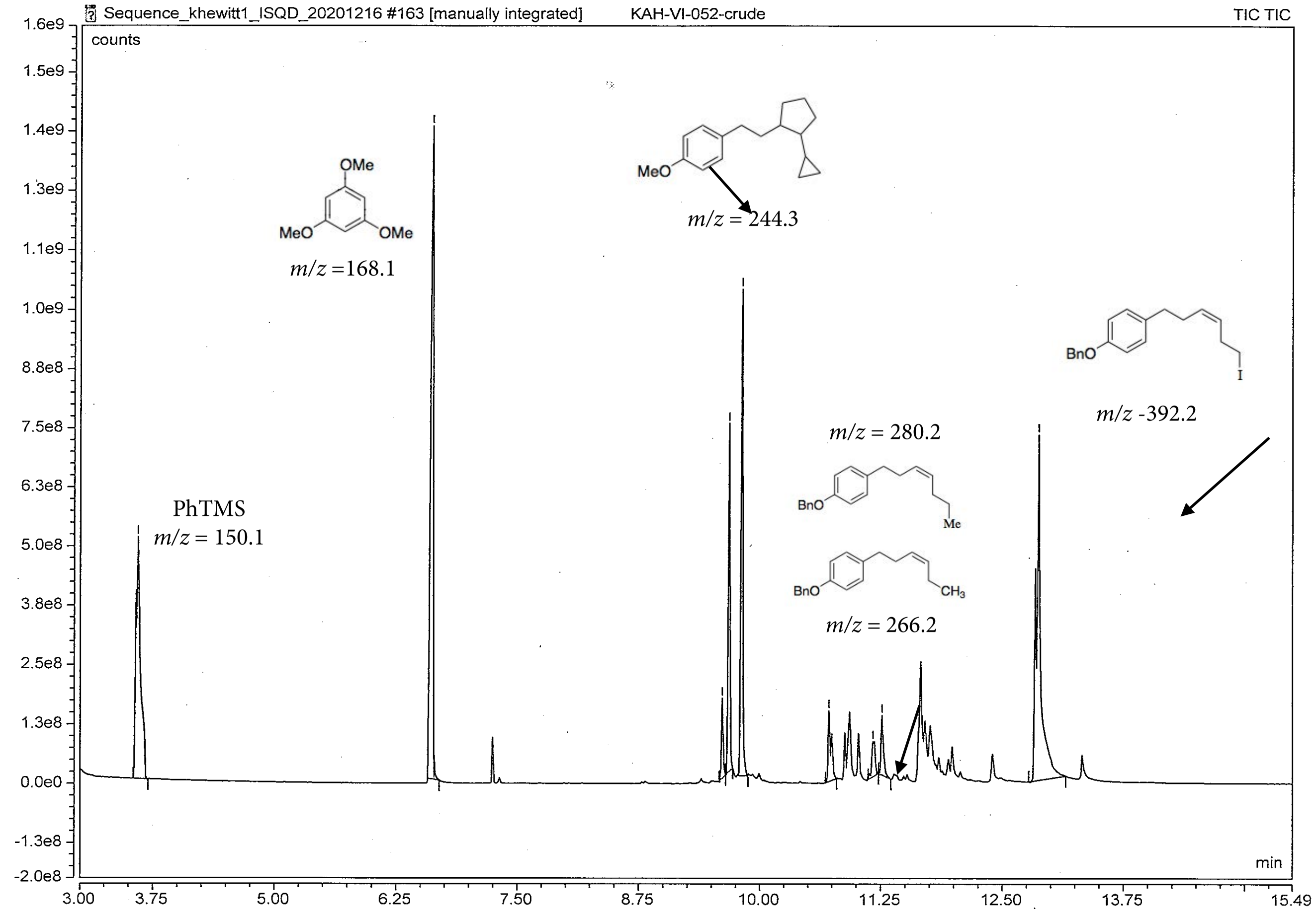
Chromeleon 7,
Version 7.2.9.11323, Thermo Fisher Scientific

Page 1 of 1

Printed by khewitt1
14/04/22 09:30

Sequence: Sequence_khewitt1_ISQD_20201216
Injection #163: KAH-VI-052-crude

Chromatogram



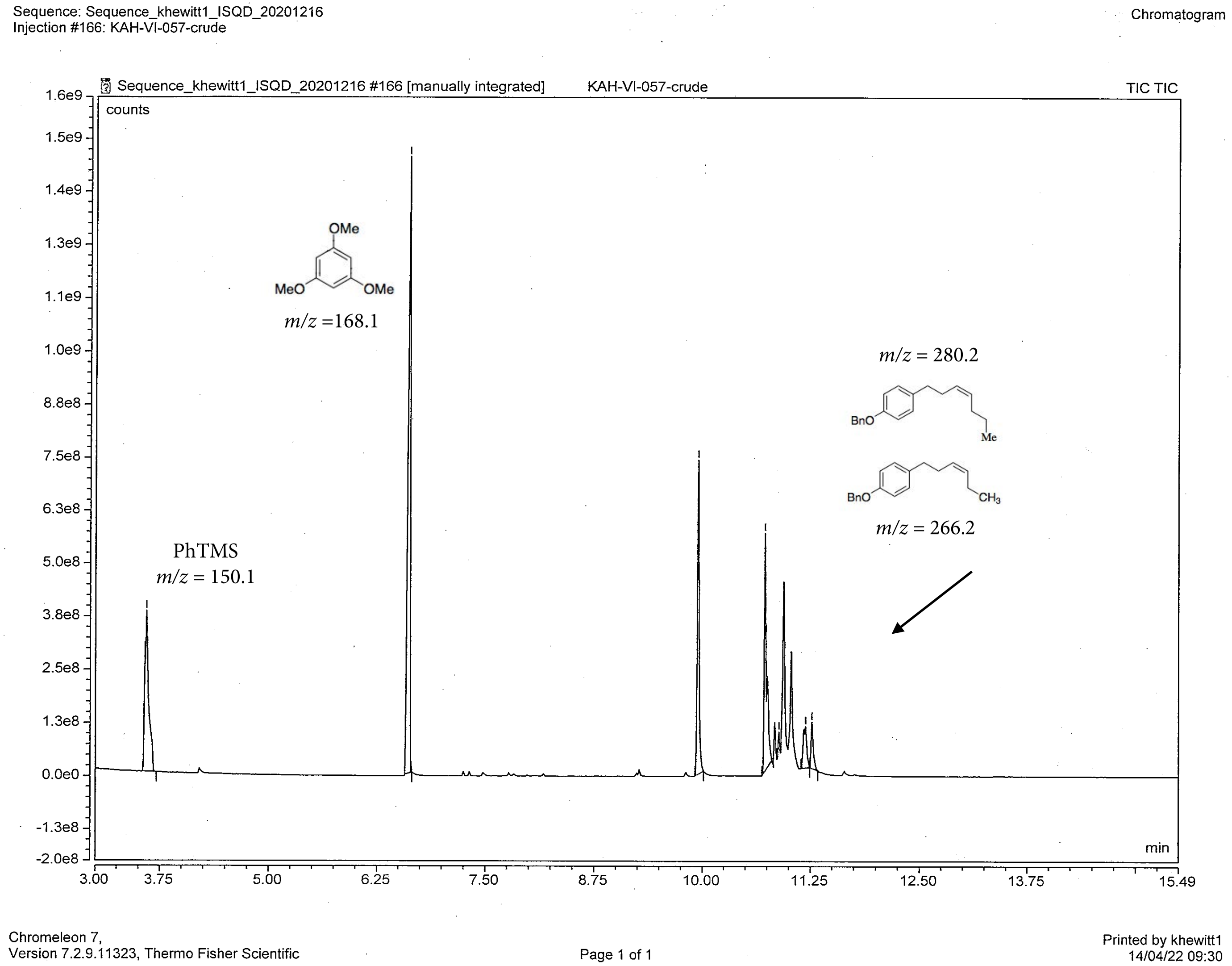
Chromeleon 7,
Version 7.2.9.11323, Thermo Fisher Scientific

Page 1 of 1

Printed by khewitt1
14/04/22 09:31

Sequence: Sequence_khewitt1_ISQD_20201216
Injection #166: KAH-VI-057-crude

Chromatogram

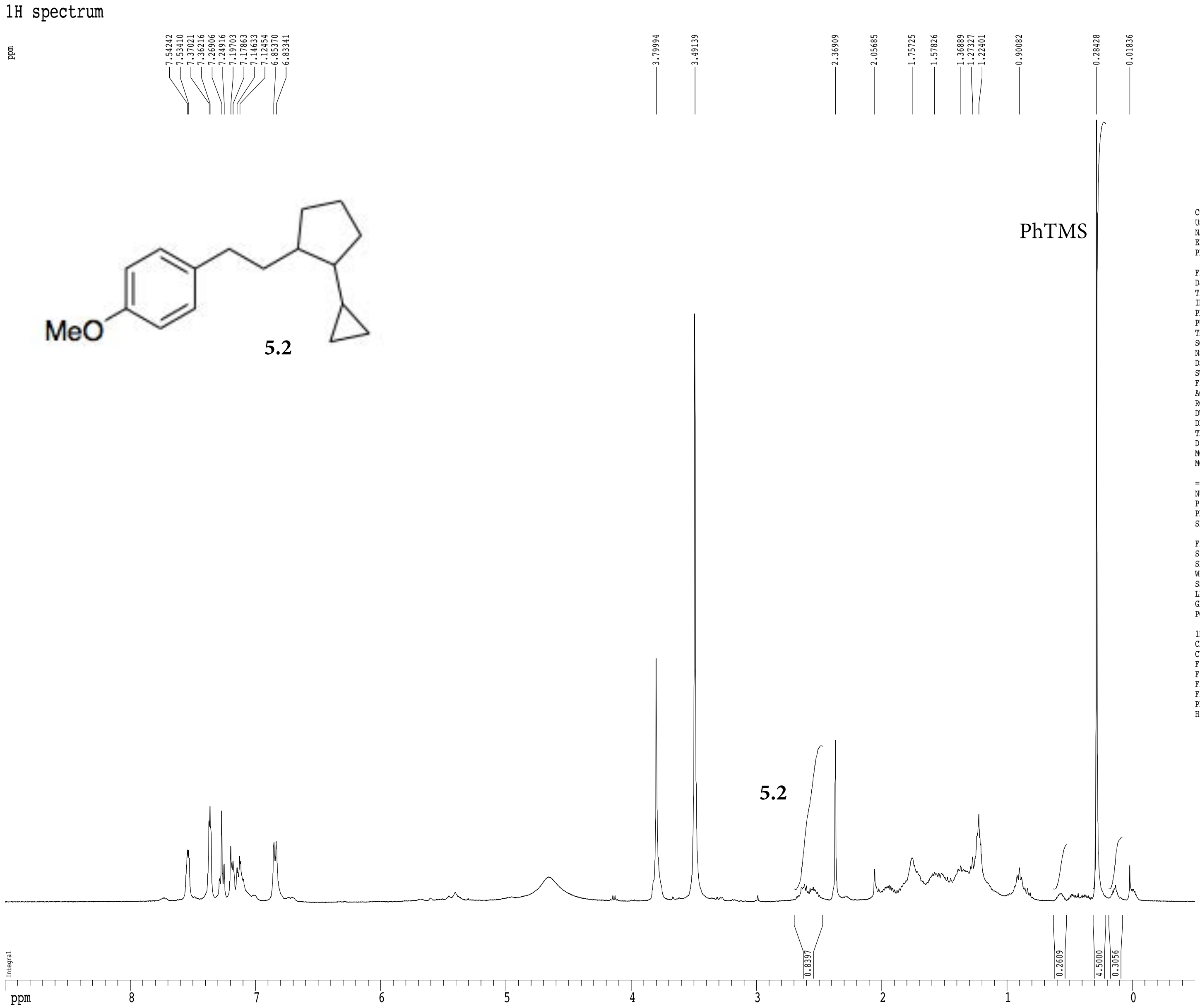


Sequence_khewitt1_ISQD_20201216 #166 [manually integrated] KAH-VI-057-crude TIC TIC

Chromeleon 7,
Version 7.2.9.11323, Thermo Fisher Scientific

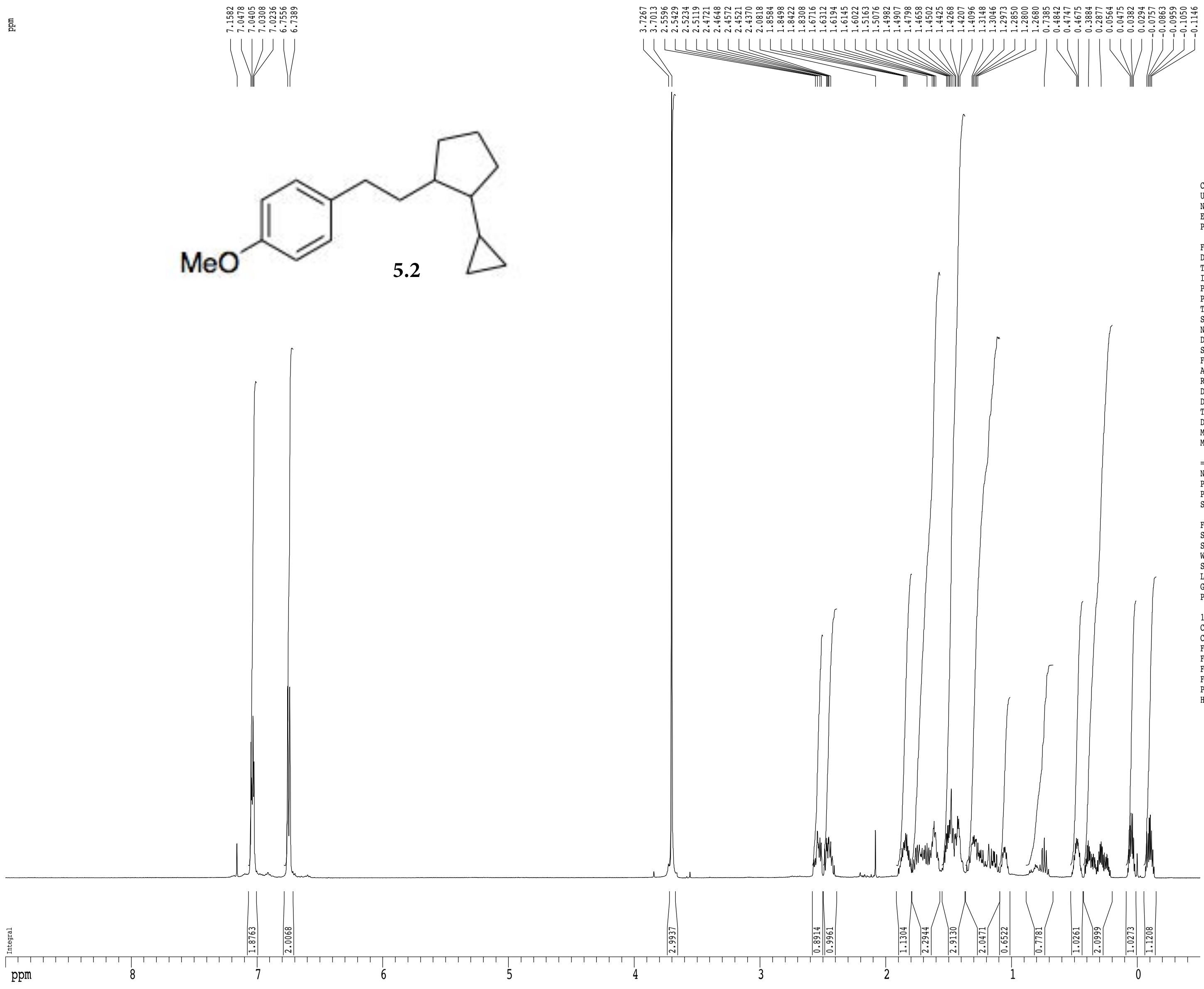
Page 1 of 1

Printed by khewitt1
14/04/22 09:30



```
Current Data Parameters
USER           khewitt1
NAME     KAH-III-064 crude
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20200129
Time              14.31
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                 90.5
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72084 Hz/cm
```

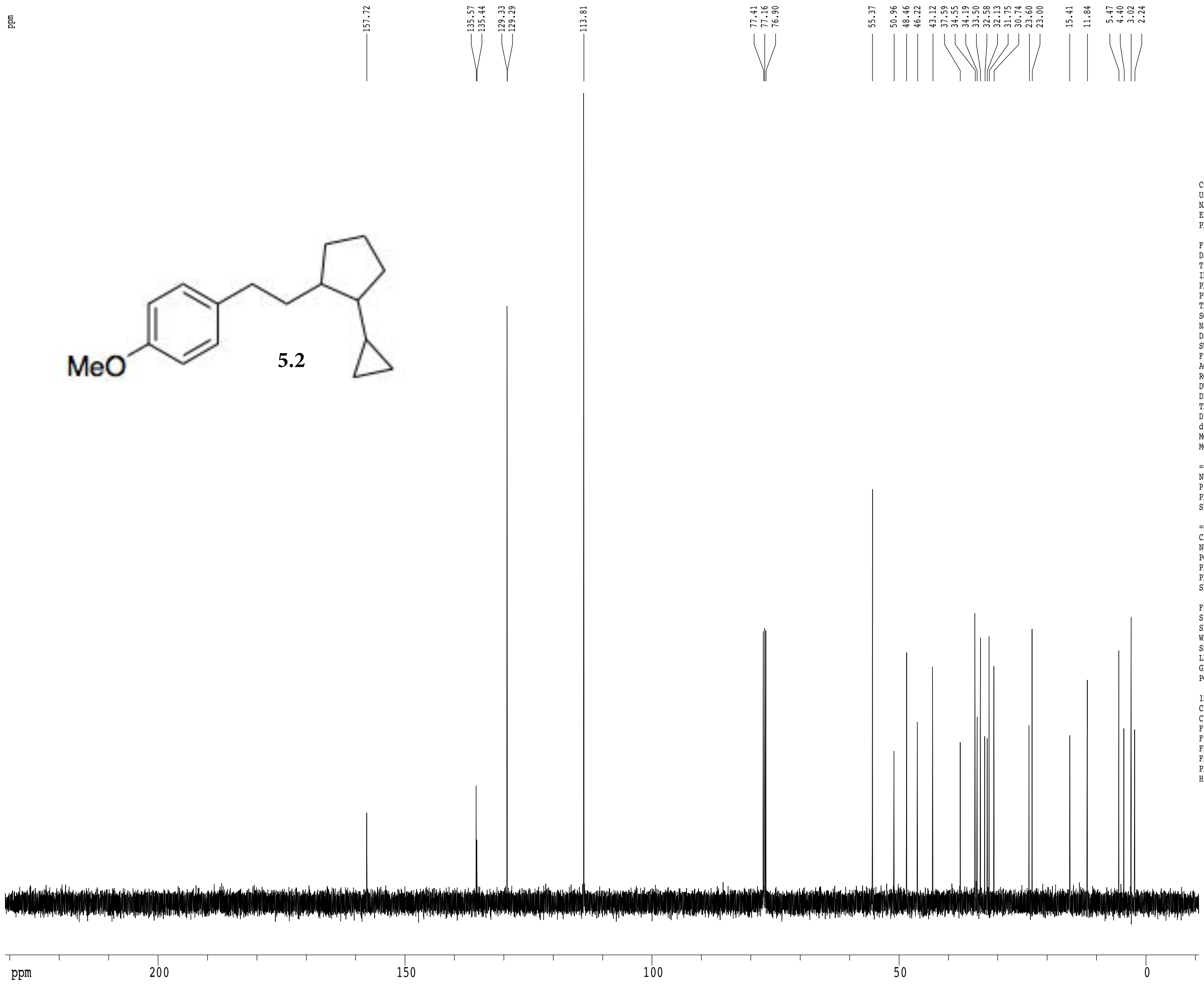
1H spectrum



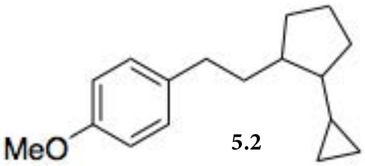
5.2

```
Current Data Parameters
USER              khewitt1
NAME           KAH-V-114-Z
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211001
Time                 14.02
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   48074
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH              8012.820 Hz
FIDRES           0.166677 Hz
AQ              2.9998677 sec
RG                       4
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
PL1                   1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF           500.2200813 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42505 Hz/cm
```

13C spectrum with 1H decoupling

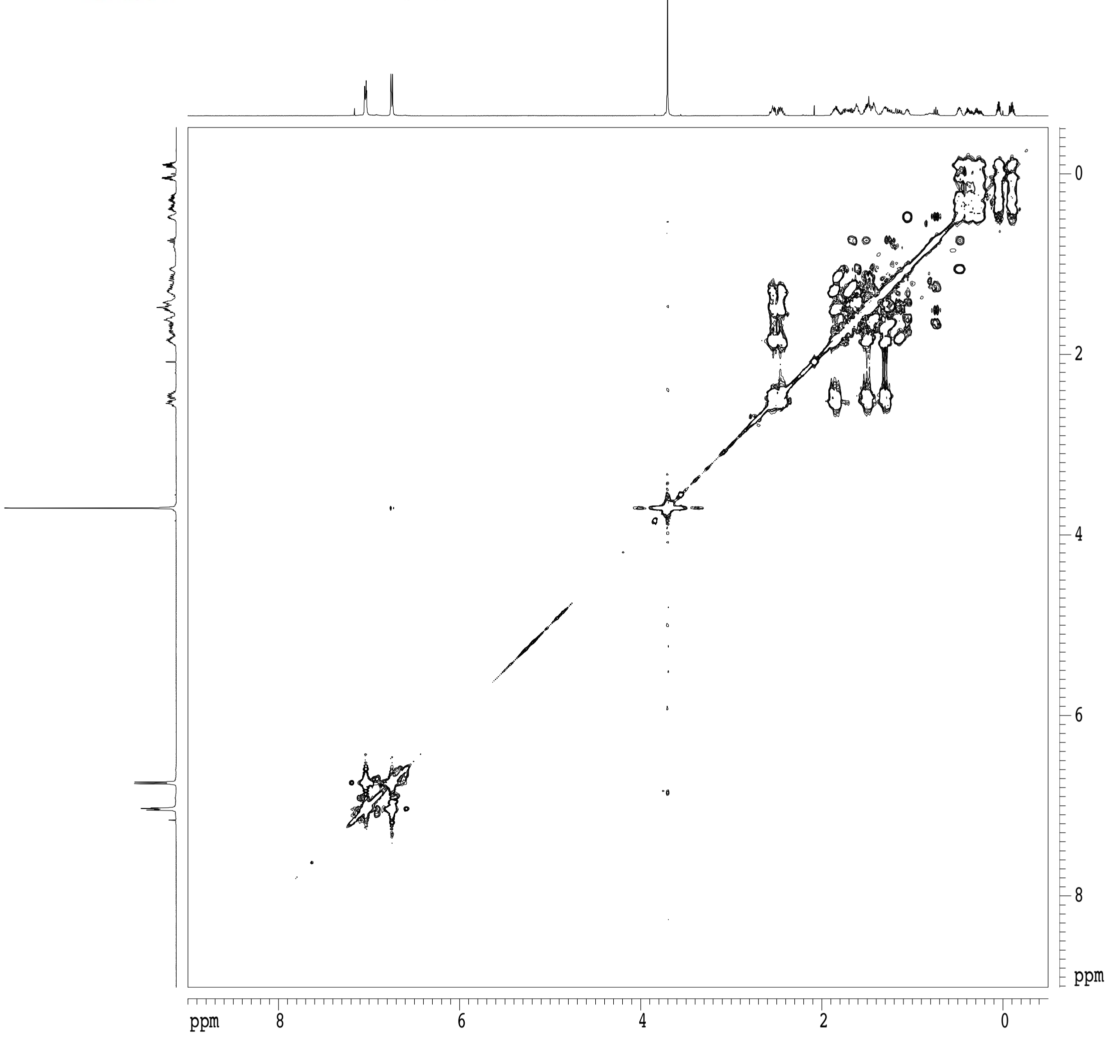


```
Current Data Parameters
USER          khewitt1
NAME     KAH-V-114-115-chk
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_          20210929
Time              16.34
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  120
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                46341
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.20 usec
PL1               -6.00 dB
SFO1        125.3994349 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -6.00 dB
PL12              12.30 dB
SFO2        498.6524933 MHz

F2 - Processing parameters
SI                65536
SF          125.3856329 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.956 ppm
F1             28958.52 Hz
F2P             -10.723 ppm
F2             -1344.51 Hz
PPMCM          10.59994 ppm/cm
HZCM         1329.08032 Hz/cm
```



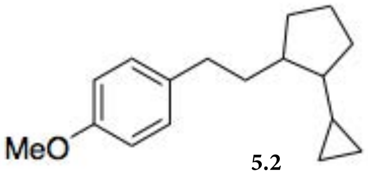
5.2

gcosy60

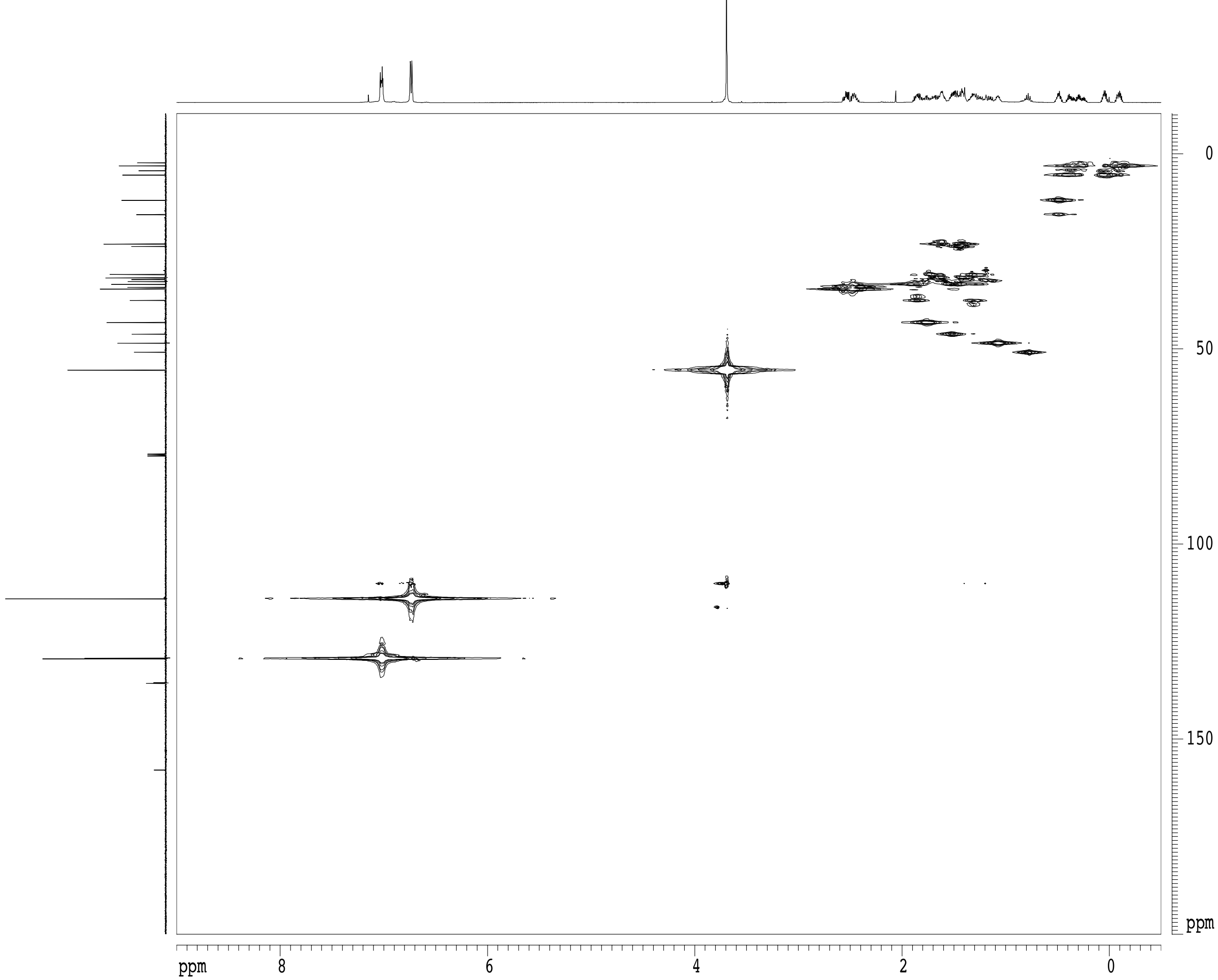


```
      Current Data Parameters
USER            khewitt1
NAME          KAH-V-114-Z
EXPNO                  2
PROCNO                 1

     F2 - Acquisition Parameters
Date_           20211001
Time               14.04
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG     cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                  35.9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

    ======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

     F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200813 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200813 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.000 ppm
F2LO             4501.98 Hz
F2PHI             -0.500 ppm
F2HI             -250.11 Hz
F1PLO              9.012 ppm
F1LO             4507.95 Hz
F1PHI             -0.515 ppm
F1HI             -257.49 Hz
F2PPMCM          0.63333 ppm/cm
F2HZCM         316.80606 Hz/cm
F1PPMCM          0.63511 ppm/cm
F1HZCM         317.69580 Hz/cm
```

ghmqc

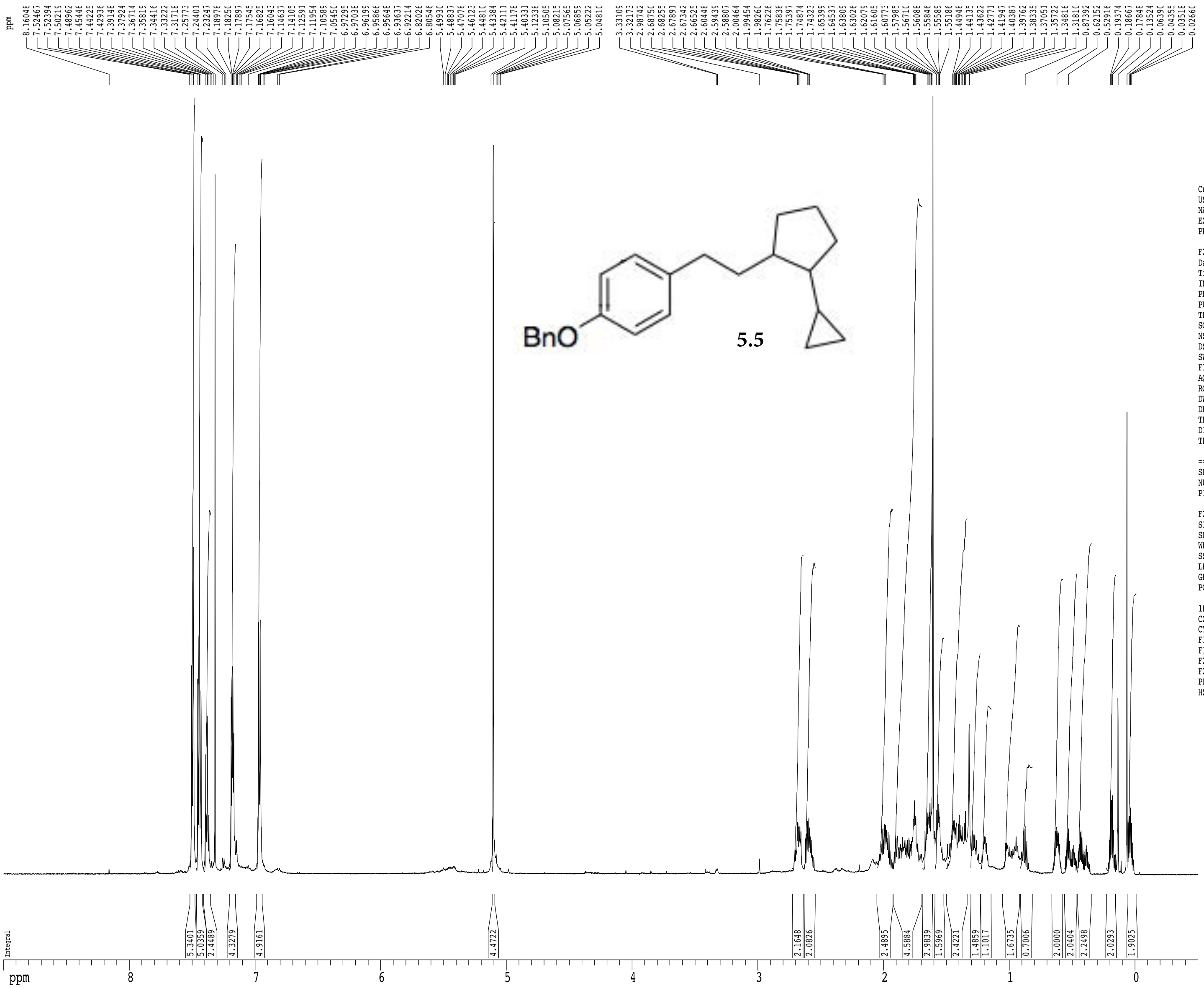


5.2



```
        Current Data Parameters
USER              khewitt1
NAME            KAH-V-114-Z
EXPNO                    6
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20211004
Time                 17.40
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG          inv4gp.wu
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                      16
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                 11585.2
DW                  62.400 usec
DE                    6.50 usec
TE                   323.0 K
CNST2          145.0000000
d0              0.00000300 sec
D1              1.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
d13             0.00000300 sec
D16             0.00020000 sec
d20             0.00242528 sec
IN0             0.00001650 sec

     ======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
p2                   19.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

     ======== CHANNEL f2 ========
CPDPRG2               garp
NUC2                   13C
P3                   18.85 usec
PCPD2                70.00 usec
PL2                  -1.00 dB
PL12                 10.40 dB
SFO2           125.7942548 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1         SMSQ10.100
GPNAM2         SMSQ10.100
GPNAM3         SMSQ10.100
GPX1                  0.00 %
GPX2                  0.00 %
GPX3                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPY3                  0.00 %
GPZ1                 30.00 %
GPZ2                 18.00 %
GPZ3                 24.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      2
TD                     512
SFO1              125.7943 MHz
FIDRES           59.185608 Hz
SW                 240.894 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             500.2200860 MHz
WDW                     EM
SSB                      0
LB                    5.00 Hz
GB                       0
PC                    2.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             125.7804002 MHz
WDW                  QSINE
SSB                      3
LB                    0.00 Hz
GB                       0

         2D NMR plot parameters
CX2                  18.00 cm
CX1                  15.00 cm
F2PLO                9.000 ppm
F2LO               4501.98 Hz
F2PHI               -0.500 ppm
F2HI               -250.11 Hz
F1PLO              200.000 ppm
F1LO              25156.08 Hz
F1PHI              -10.310 ppm
F1HI              -1296.84 Hz
F2PPMCM            0.52778 ppm/cm
F2HZCM           264.00504 Hz/cm
F1PPMCM           14.02069 ppm/cm
F1HZCM          1763.52795 Hz/cm
```

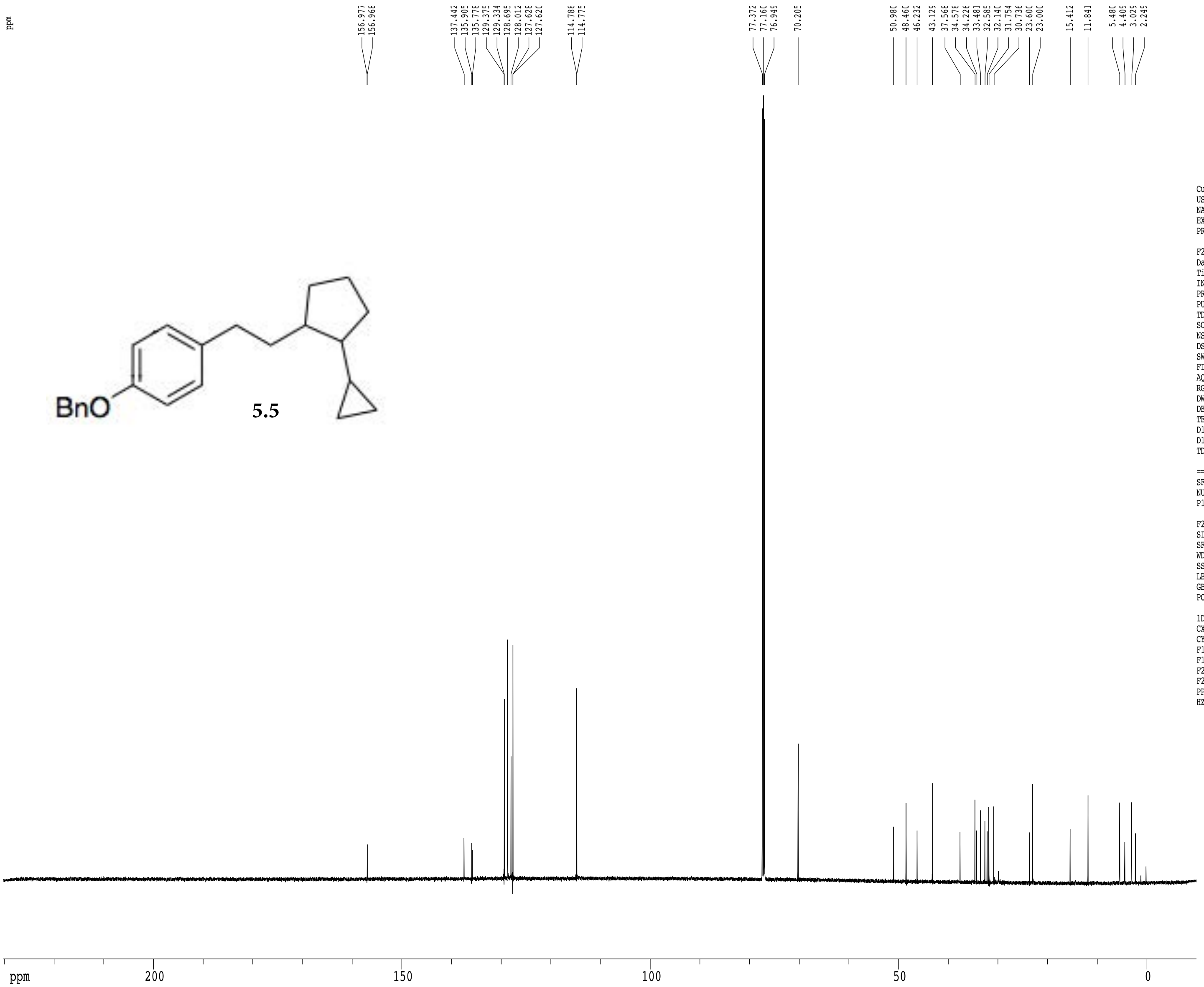
1H spectrum



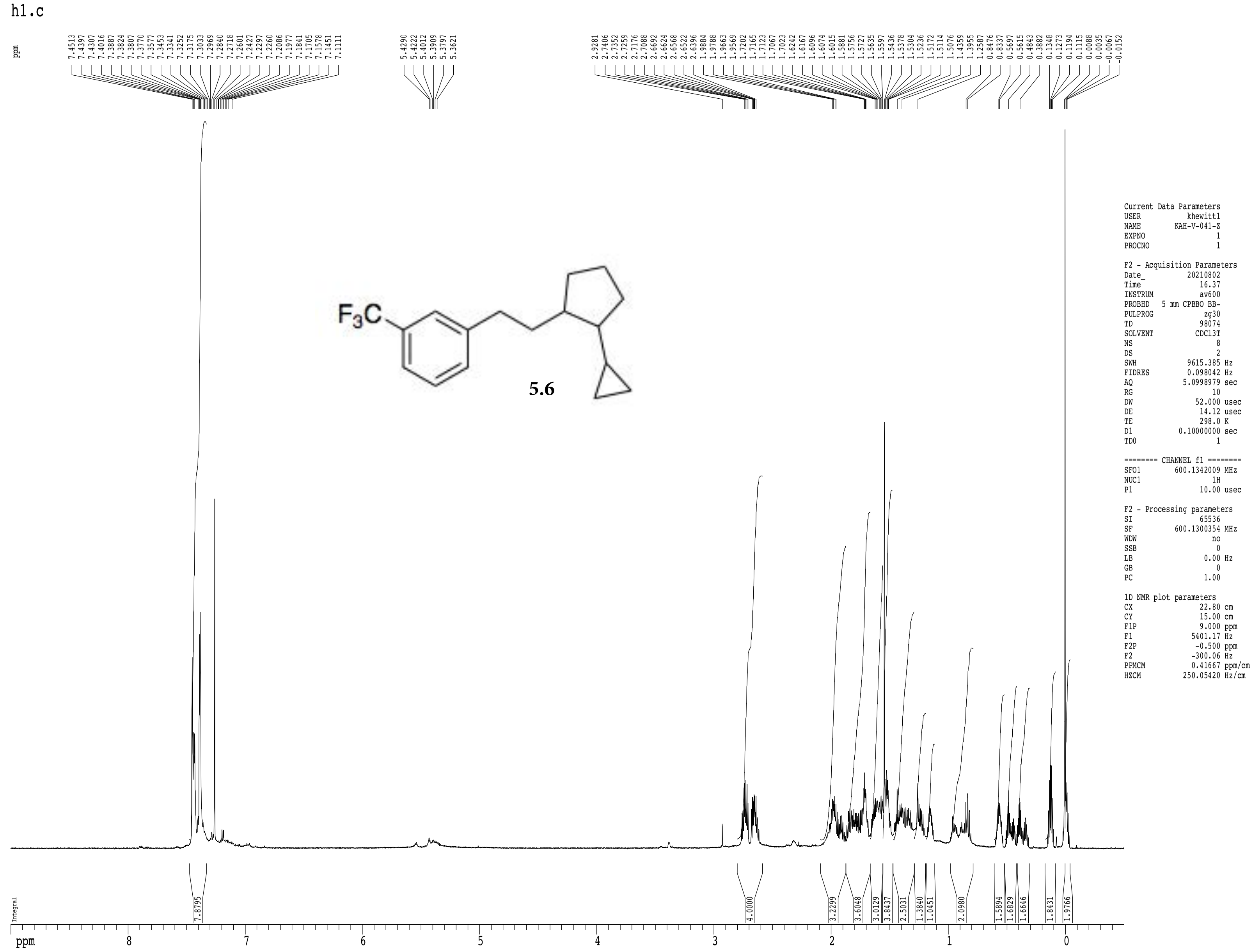
5.5

```
Current Data Parameters
USER          khewitt1
NAME     KAH-V-304-z-600
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220313
Time               16.50
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                    32
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                    10
DW                52.000 usec
DE                 14.23 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.50 usec

F2 - Processing parameters
SI                 65536
SF           600.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```

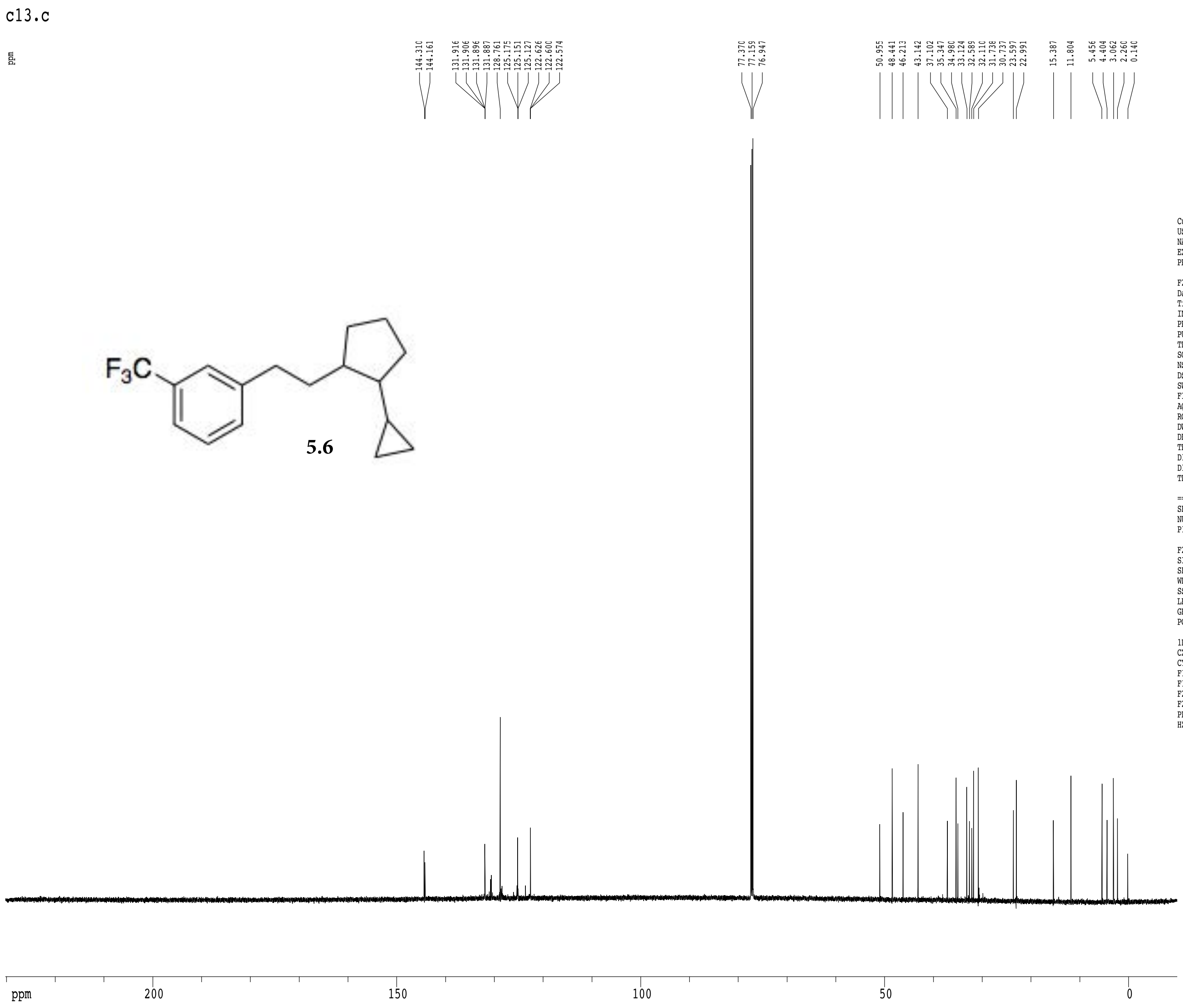
13C spectrum


5.5

```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-304-z-600
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220313
Time               16.56
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   814
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 297.9 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9027942 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.147 ppm
F1              34729.77 Hz
F2P               -9.954 ppm
F2              -1502.12 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11780 Hz/cm
```



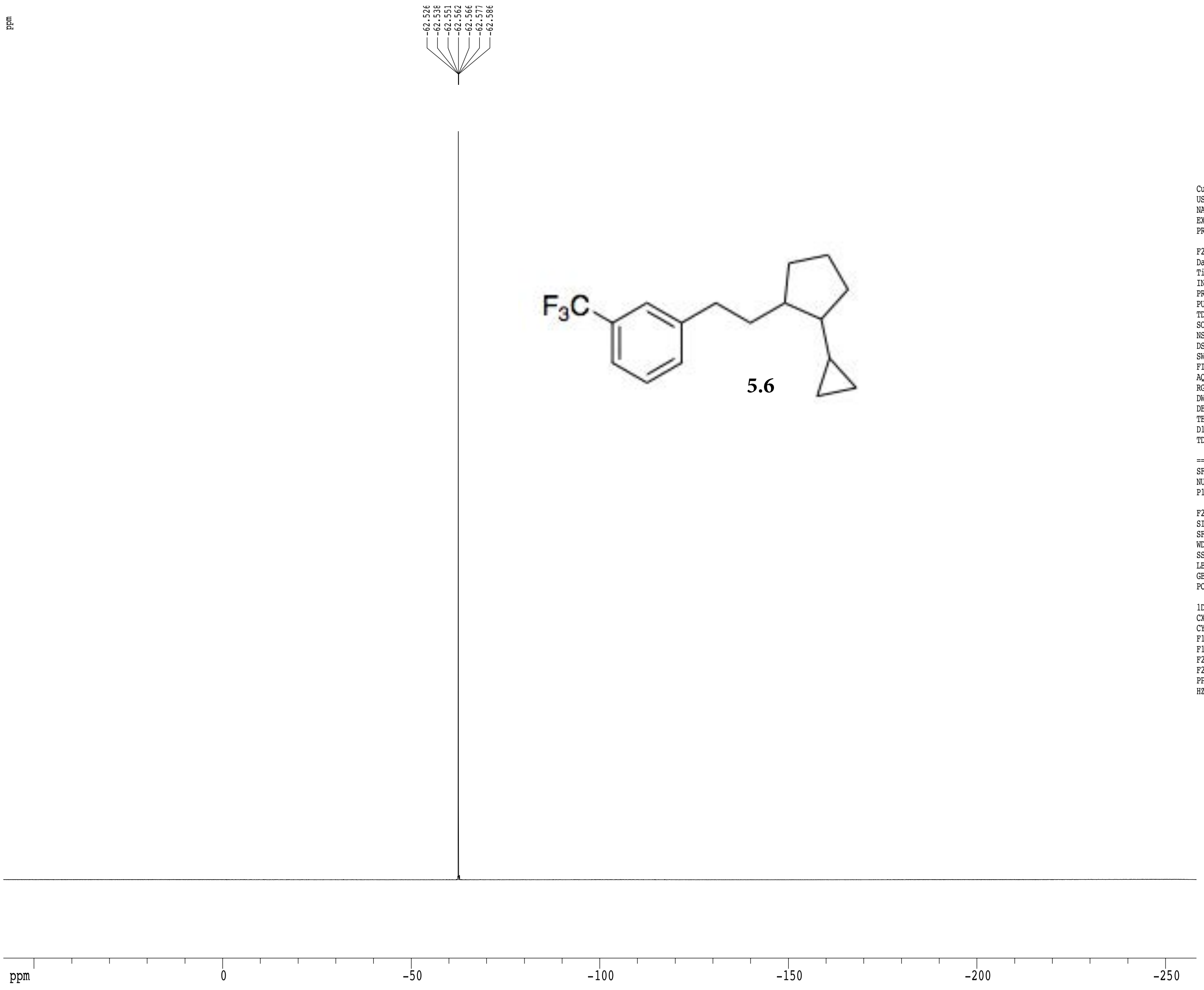
```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-041-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210802
Time               16.37
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                    10
DW                52.000 usec
DE                 14.12 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 10.00 usec

F2 - Processing parameters
SI                 65536
SF           600.1300354 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05420 Hz/cm
```



5.6

```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-041-Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210802
Time               16.48
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   500
DS                     4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                  2050
DW              13.800 usec
DE               19.63 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF         150.9027931 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.154 ppm
F1              34730.87 Hz
F2P               -9.947 ppm
F2              -1501.01 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11768 Hz/cm
```

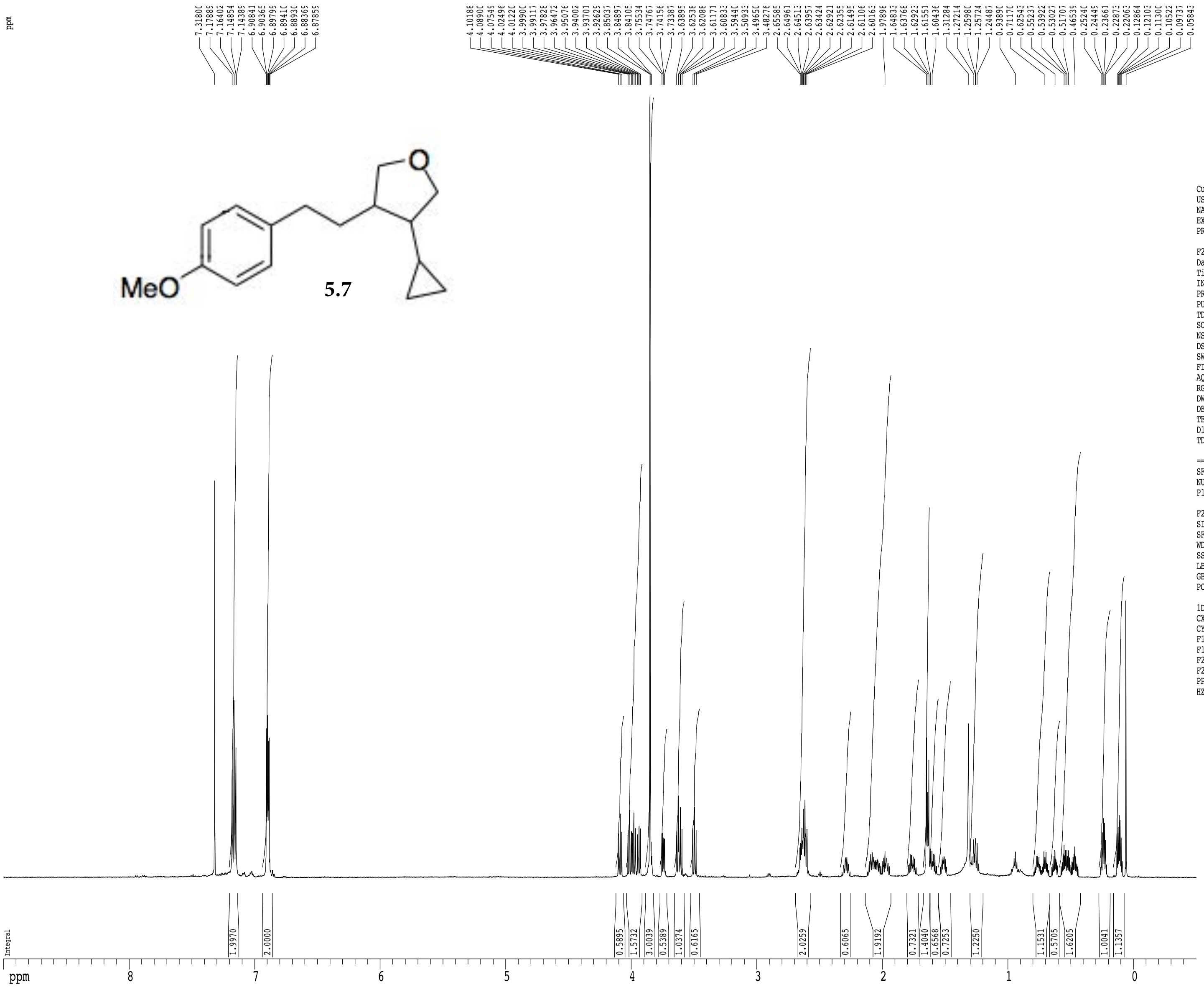
f19.c



5.6

```
Current Data Parameters
USER           khewitt1
NAME        KAH-V-041-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210802
Time              16.43
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgflqn30
TD               131072
SOLVENT          CDCl3T
NS                   16
DS                    2
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                  575
DW                2.800 usec
DE                18.00 usec
TE                298.0 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        564.6299196 MHz
NUC1                19F
P1                18.25 usec

F2 - Processing parameters
SI               131072
SF          564.6864234 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              58.053 ppm
F1             32781.88 Hz
F2P            -258.178 ppm
F2           -145789.55 Hz
PPMCM          13.86979 ppm/cm
HZCM         7832.08008 Hz/cm
```

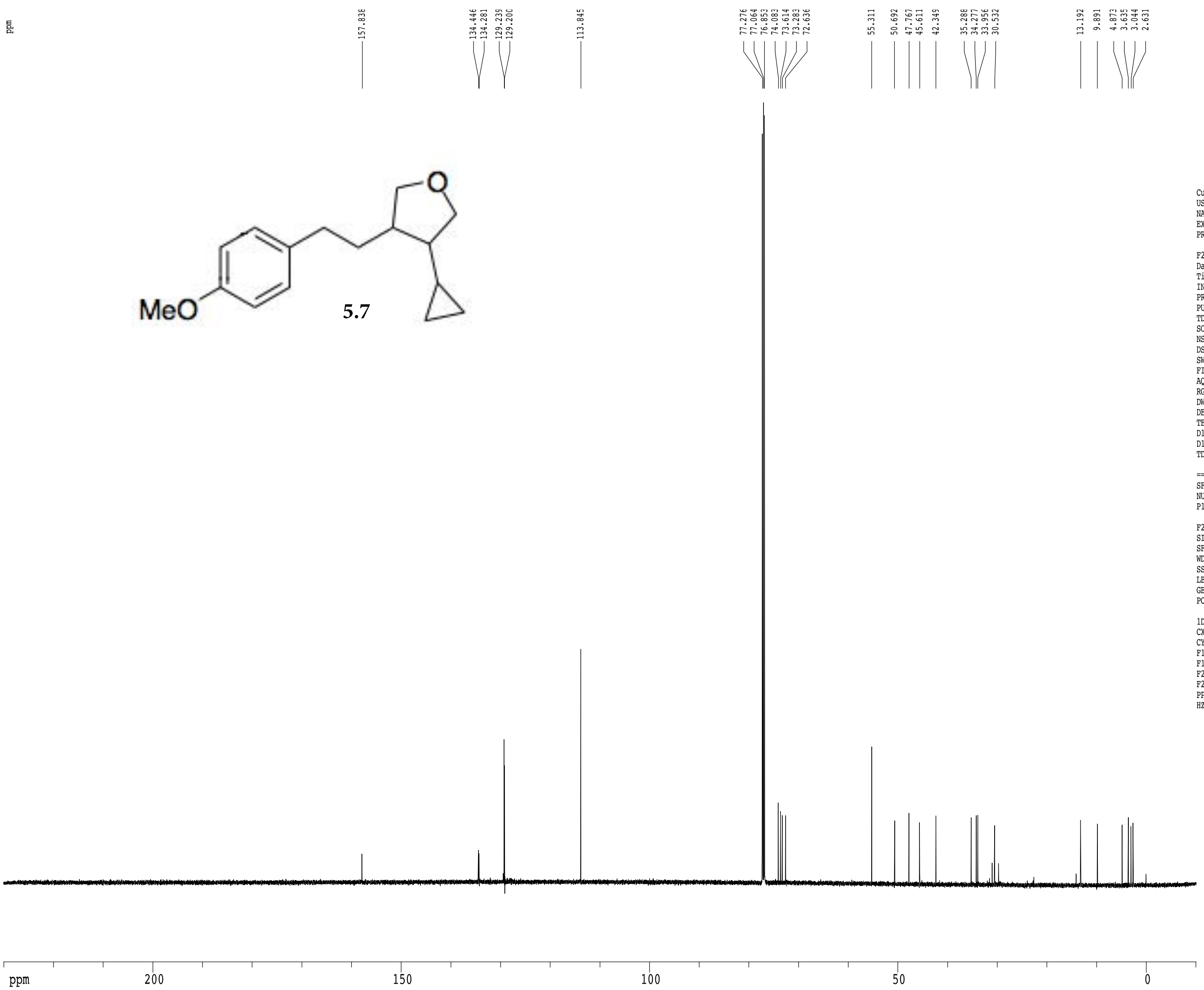
1H spectrum



5.7

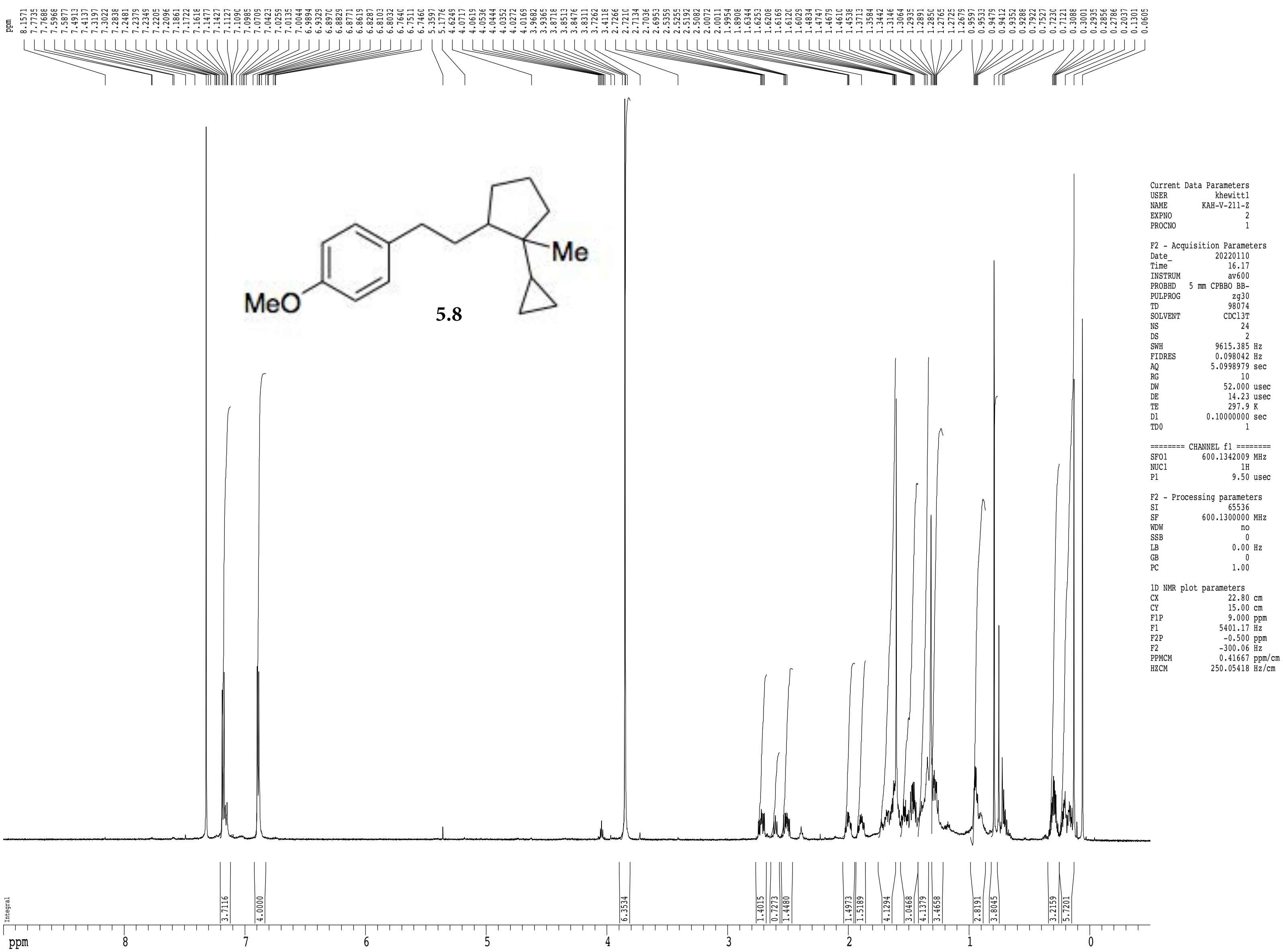
```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-174-Z-600
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211116
Time               13.14
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998979 sec
RG                  20.2
DW                52.000 usec
DE                 14.23 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.50 usec

F2 - Processing parameters
SI                 65536
SF           600.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```

13C spectrum



```
Current Data Parameters
USER           khewitt1
NAME        KAH-V-174-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20211207
Time              12.26
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  283
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                297.9 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9028085 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             230.051 ppm
F1             34715.41 Hz
F2P             -10.049 ppm
F2             -1516.47 Hz
PPMCM          10.53074 ppm/cm
HZCM         1589.11755 Hz/cm
```

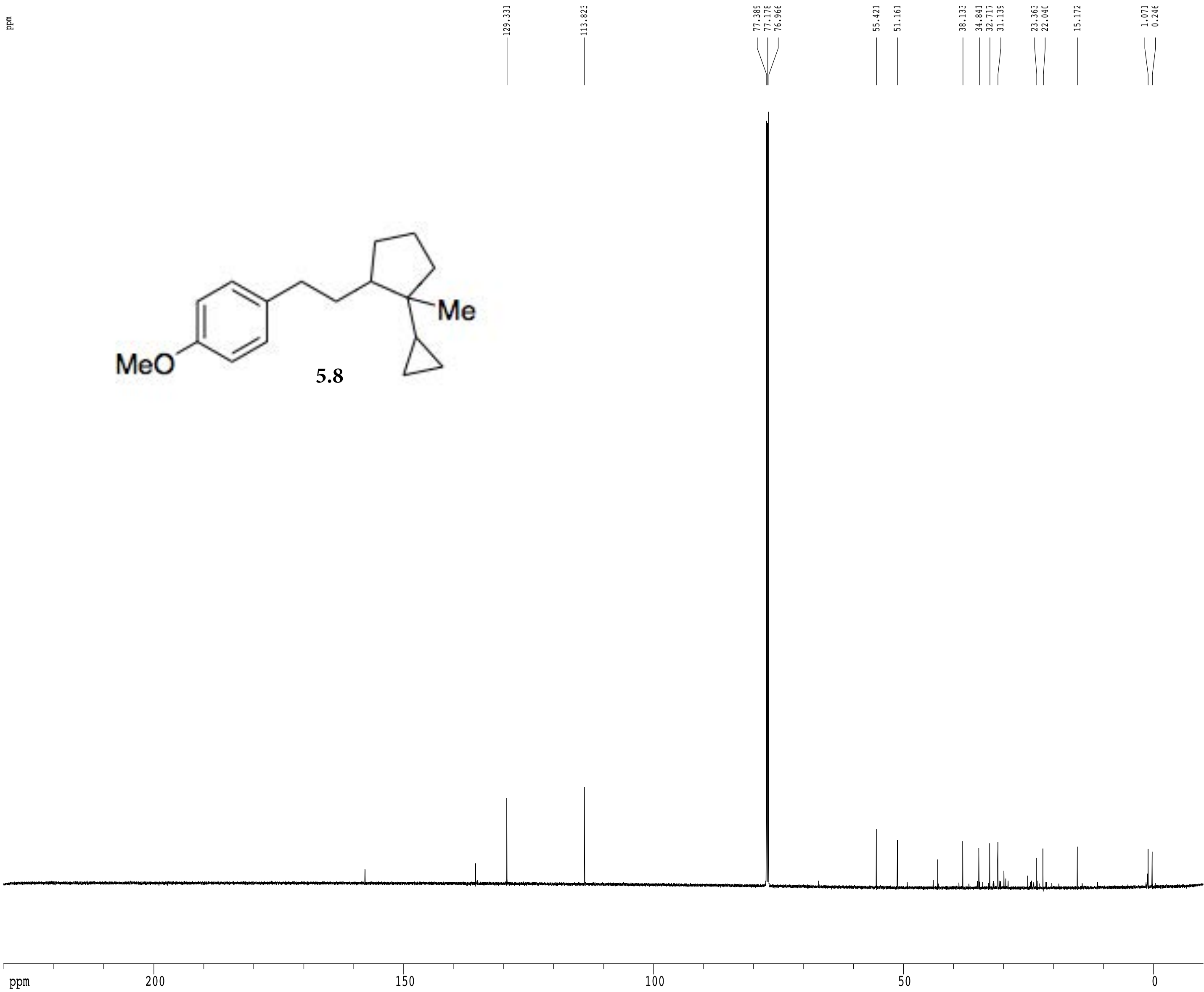
1H spectrum



5.8

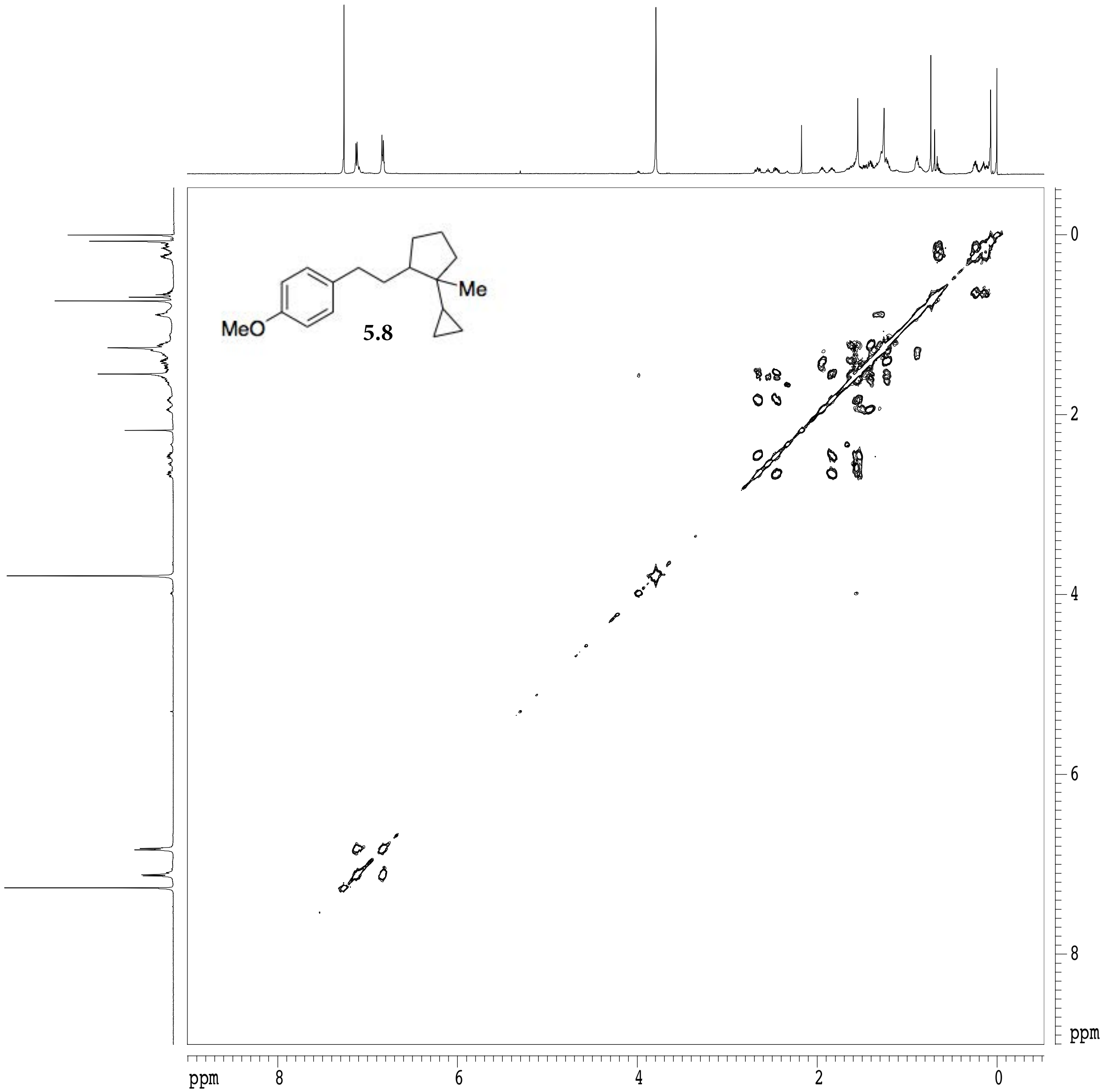
```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-211-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220110
Time               16.17
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                    24
DS                     2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998979 sec
RG                    10
DW                52.000 usec
DE                 14.23 usec
TE                 297.9 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.50 usec

F2 - Processing parameters
SI                 65536
SF          600.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```

13C spectrum

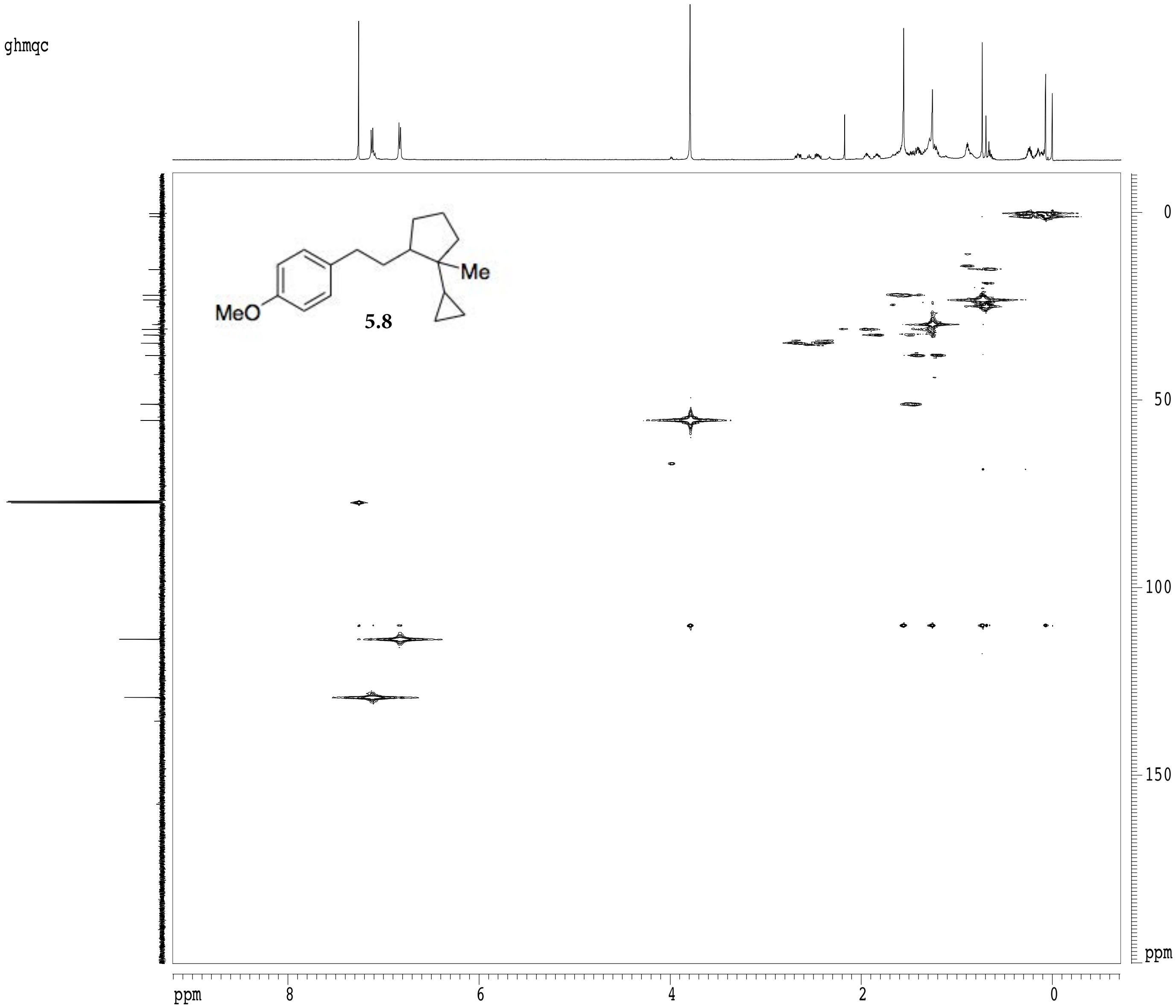

5.8

```
Current Data Parameters
USER           khewitt1
NAME        KAH-V-211-Z
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20220110
Time              16.22
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT          CDCl3T
NS                 1024
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                297.9 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9027907 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             230.051 ppm
F1             34715.41 Hz
F2P             -10.049 ppm
F2             -1516.47 Hz
PPMCM          10.53074 ppm/cm
HZCM         1589.11743 Hz/cm
```

gcosy60


5.8

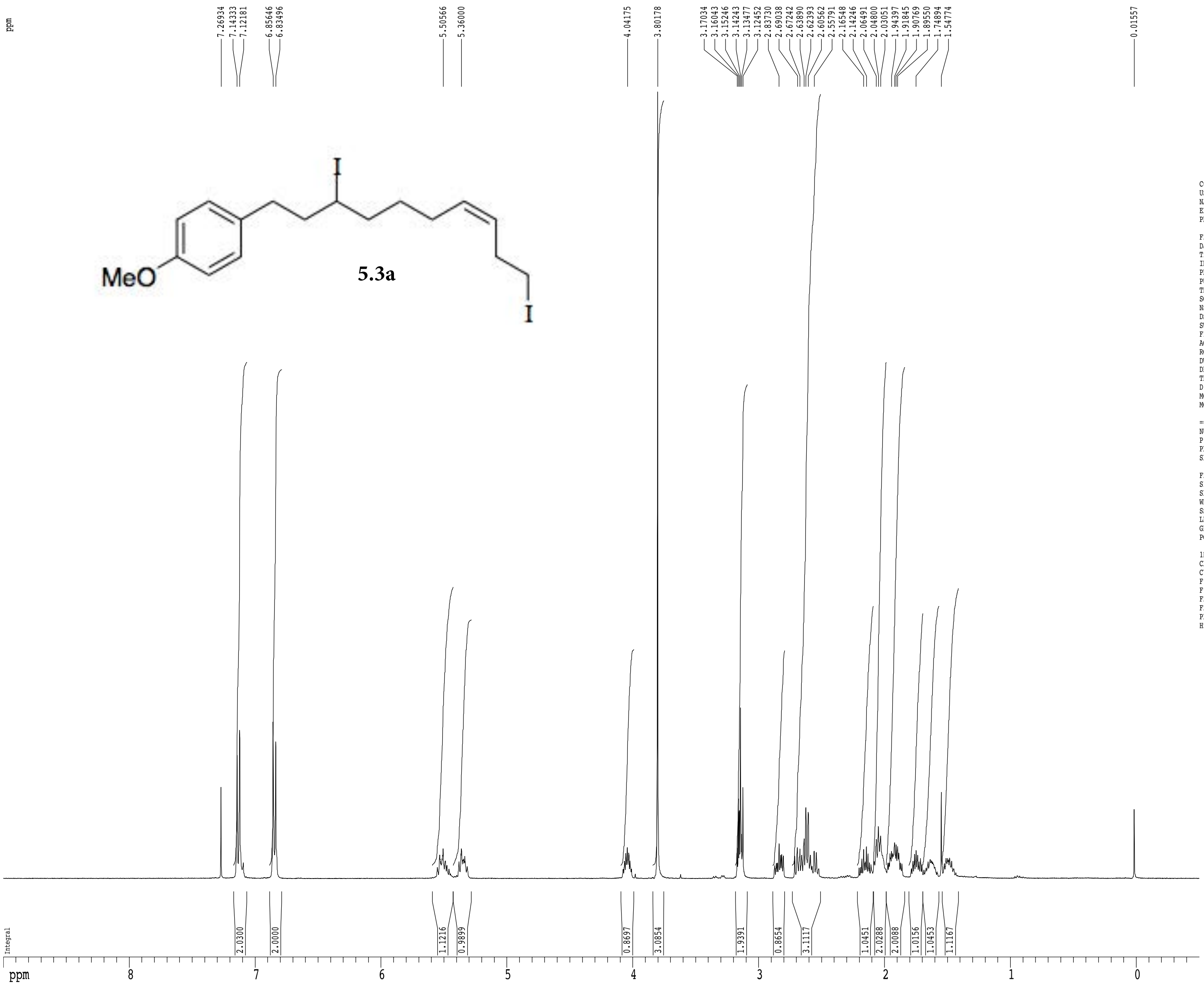
```
        Current Data Parameters
USER              khewitt1
NAME          KAH-V-211-2D
EXPNO                    2
PROCNO                   1

      F2 - Acquisition Parameters
Date_             20220111
Time                 11.06
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG      cosygp60.prd
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                      16
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                   724.1
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
d0              0.00000300 sec
D1              1.00000000 sec
d13             0.00000300 sec
D16             0.00020000 sec
IN0             0.00012480 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SMSQ10.100
GPNAM2          SMSQ10.100
GPX1                  0.00 %
GPX2                  0.00 %
GPY1                  0.00 %
GPY2                  0.00 %
GPZ1                 17.00 %
GPZ2                 17.00 %
P16                1000.00 usec

      F1 - Acquisition parameters
ND0                      1
TD                     512
SFO1              500.2235 MHz
FIDRES           15.650040 Hz
SW                  16.018 ppm
FnMODE                  QF

      F2 - Processing parameters
SI                    1024
SF             500.2200307 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

      F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.2200307 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0

      2D NMR plot parameters
CX2                  15.00 cm
CX1                  15.00 cm
F2PLO                9.004 ppm
F2LO               4503.78 Hz
F2PHI               -0.523 ppm
F2HI               -261.66 Hz
F1PLO                9.004 ppm
F1LO               4503.78 Hz
F1PHI               -0.523 ppm
F1HI               -261.66 Hz
F2PPMCM            0.63511 ppm/cm
F2HZCM           317.69580 Hz/cm
F1PPMCM            0.63511 ppm/cm
F1HZCM           317.69580 Hz/cm
```



5.8

```
        Current Data Parameters
USER            khewitt1
NAME          KAH-V-211-2D
EXPNO                  6
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20220117
Time               16.45
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG       inv4gp.wu
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH            4960.317 Hz
FIDRES         2.422030 Hz
AQ            0.2064884 sec
RG                 26008
DW               100.800 usec
DE                  6.50 usec
TE                 298.0 K
CNST2        145.0000000
d0            0.00000300 sec
D1            1.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
d13           0.00000300 sec
D16           0.00020000 sec
d20           0.00242528 sec
IN0           0.00001650 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
p2                 19.50 usec
PL1                 1.60 dB
SFO1         500.2221566 MHz

     ======== CHANNEL f2 ========
CPDPRG2             garp
NUC2                 13C
P3                 18.85 usec
PCPD2              70.00 usec
PL2                -1.00 dB
PL12               10.40 dB
SFO2         125.7942548 MHz

    ====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPNAM3        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPX3                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPY3                0.00 %
GPZ1               30.00 %
GPZ2               18.00 %
GPZ3               24.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    2
TD                   512
SFO1            125.7943 MHz
FIDRES         59.185608 Hz
SW               240.894 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200307 MHz
WDW                   EM
SSB                    0
LB                  5.00 Hz
GB                     0
PC                  2.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           125.7804071 MHz
WDW                QSINE
SSB                    3
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                18.00 cm
CX1                15.00 cm
F2PLO              9.208 ppm
F2LO             4606.09 Hz
F2PHI             -0.718 ppm
F2HI             -359.07 Hz
F1PLO            200.204 ppm
F1LO            25181.78 Hz
F1PHI            -10.601 ppm
F1HI            -1333.37 Hz
F2PPMCM          0.55144 ppm/cm
F2HZCM         275.84232 Hz/cm
F1PPMCM         14.05367 ppm/cm
F1HZCM        1767.67676 Hz/cm
```

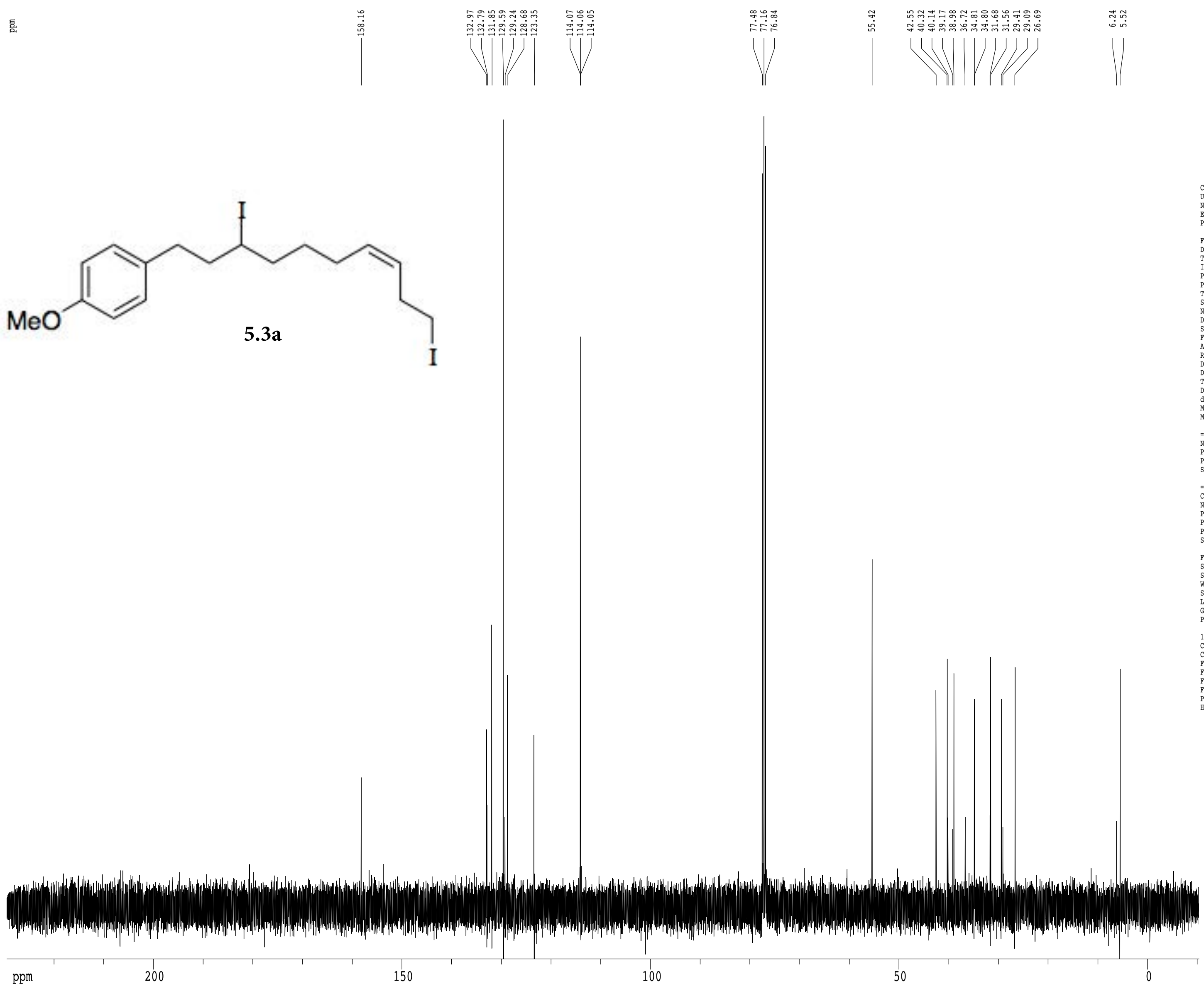
1H spectrum



5.3a

```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-214-greaseextract
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220108
Time               13.33
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                 203.2
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

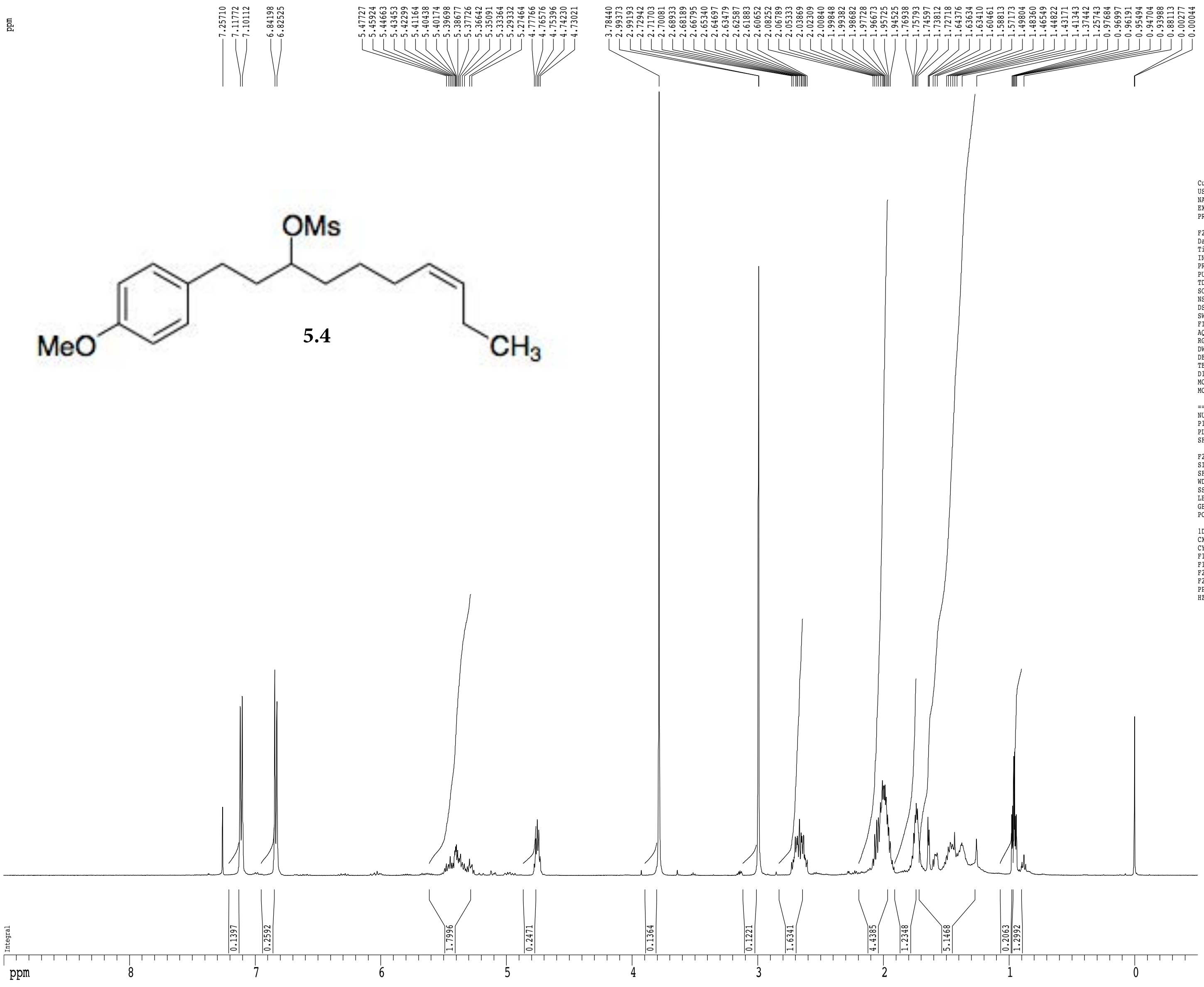
13C spectrum with 1H decoupling



5.3a

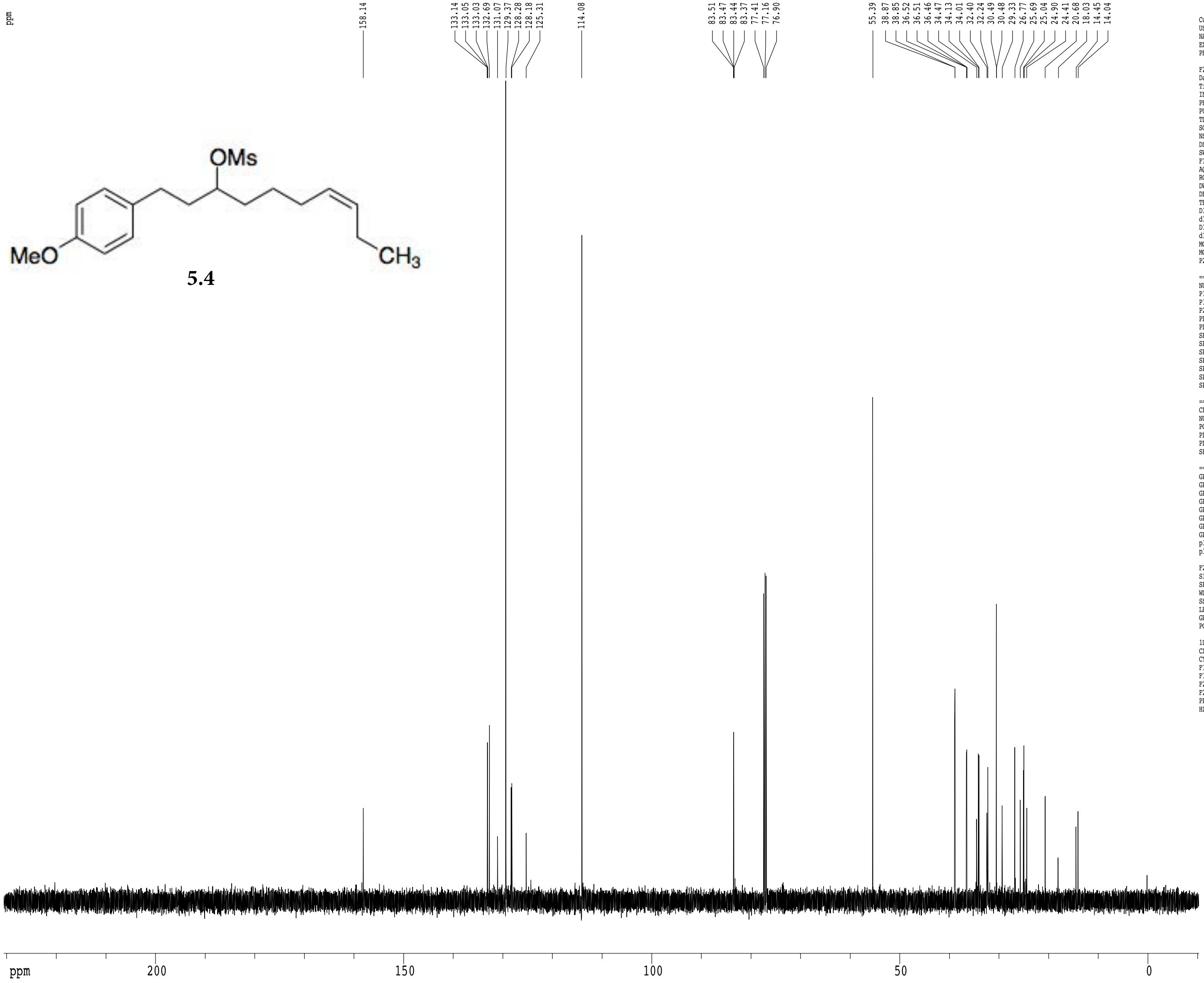
```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-214-greaseextract
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220108
Time               13.37
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   240
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127587 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER          khewitt1
NAME     KAH-V-032-39-(Zn Mn)-dried
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20210725
Time              13.14
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200321 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

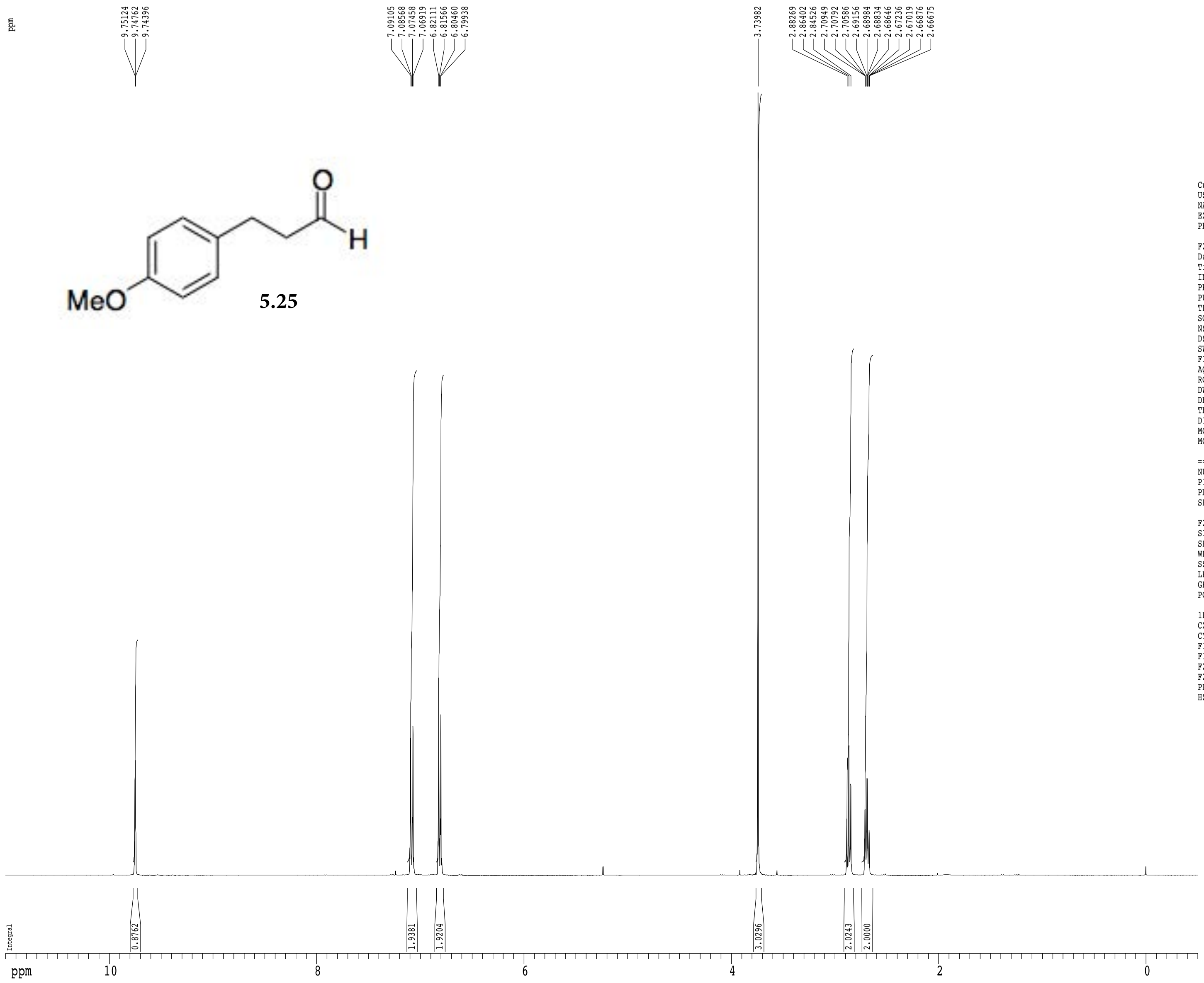
Z-restored spin-echo 13C spectrum with 1H decoupling



5.4

```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-032-39-(Zn Mn)-dried
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210725
Time               13.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   104
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804090 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

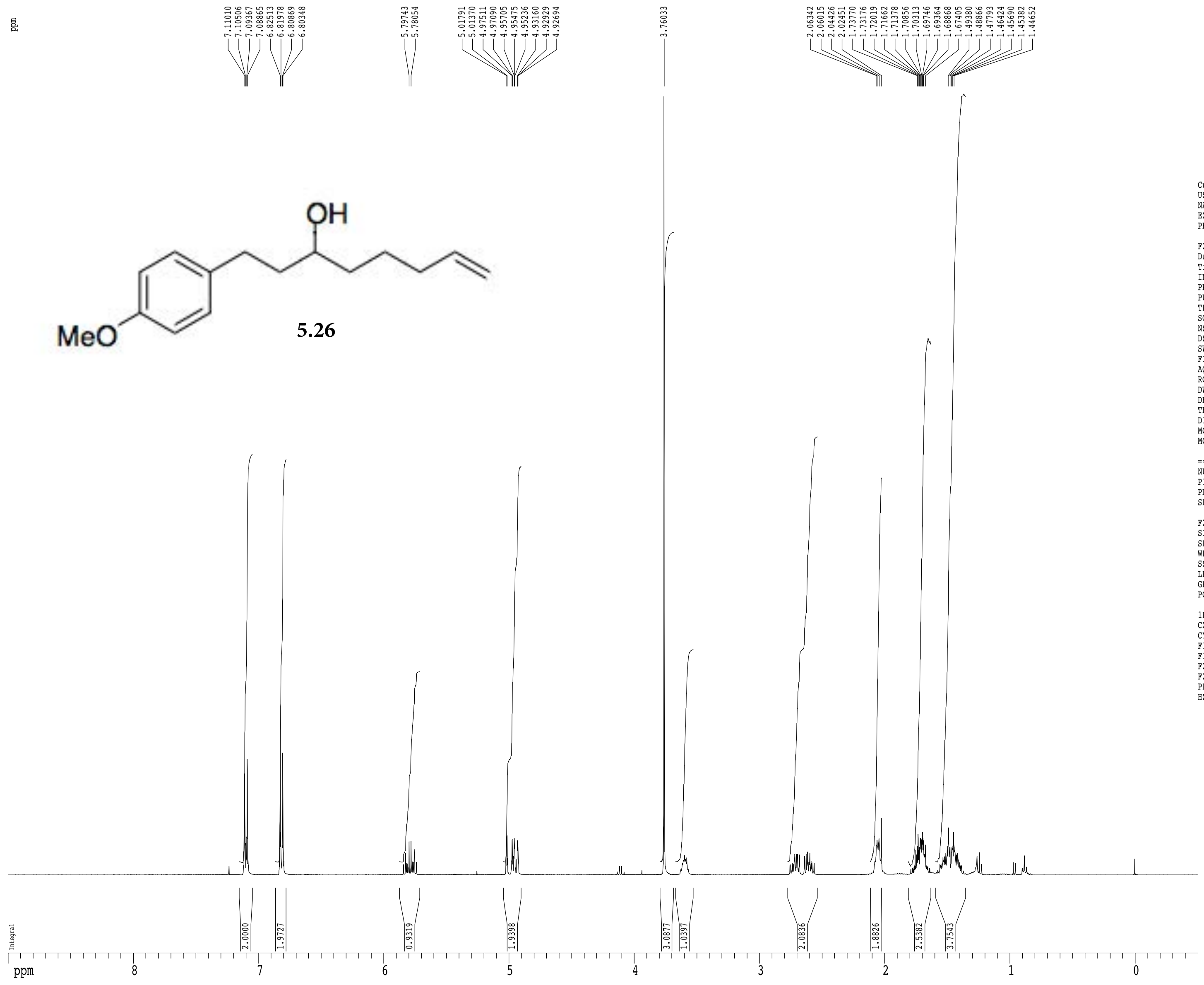
1H spectrum



5.25

```
Current Data Parameters
USER              khewitt1
NAME            KAH-V-054-1
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210805
Time                 15.42
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   38460
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                      32
DW              78.000 usec
DE                4.50 usec
TE                298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1               12.00 usec
PL1               -1.60 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF          400.1300301 MHz
WDW                     no
SSB                      0
LB                 0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81998 Hz/cm
```

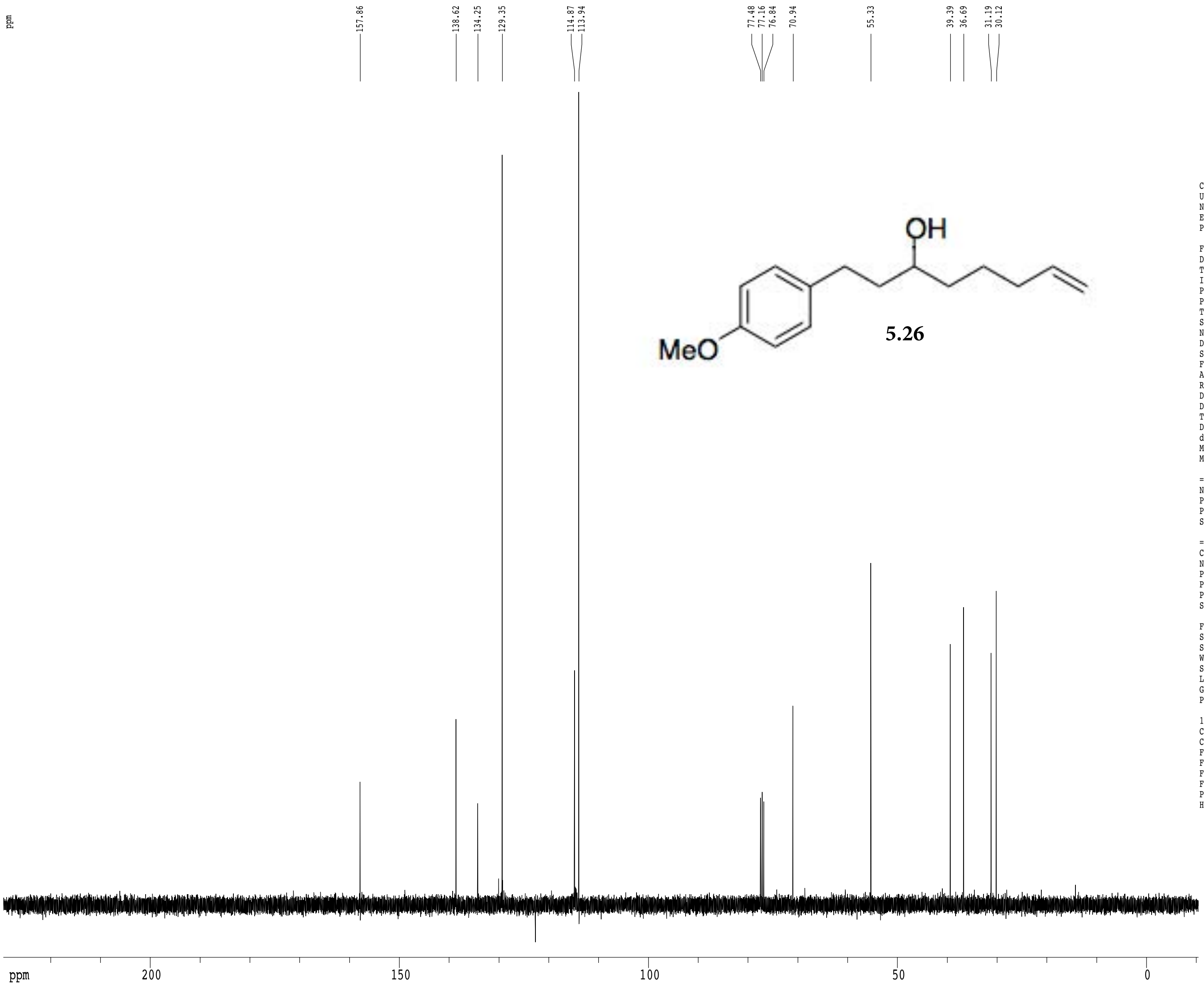
1H spectrum



5.26

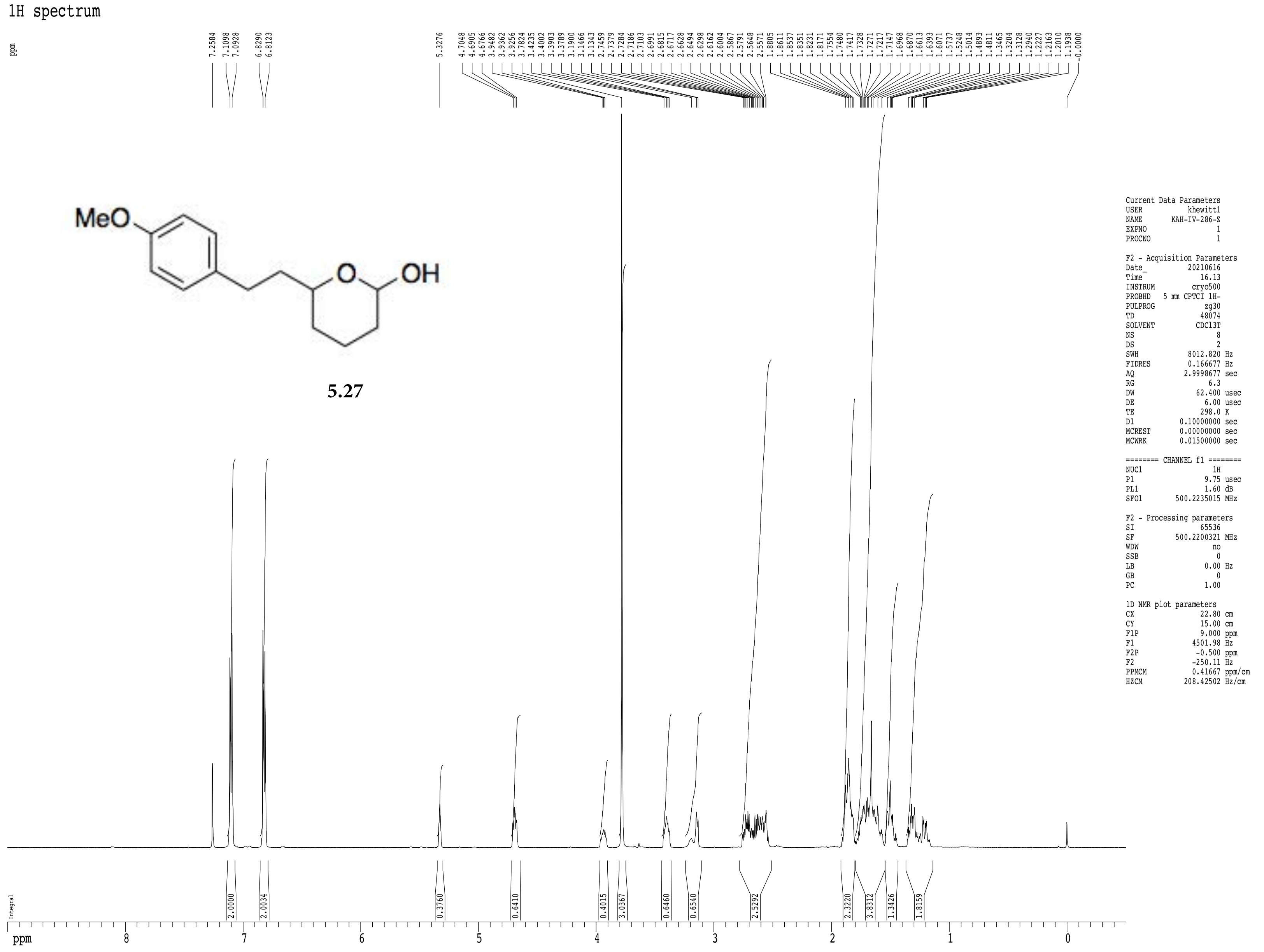
```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-057-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210806
Time               17.51
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    32
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300311 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

13C spectrum with 1H decoupling



5.26

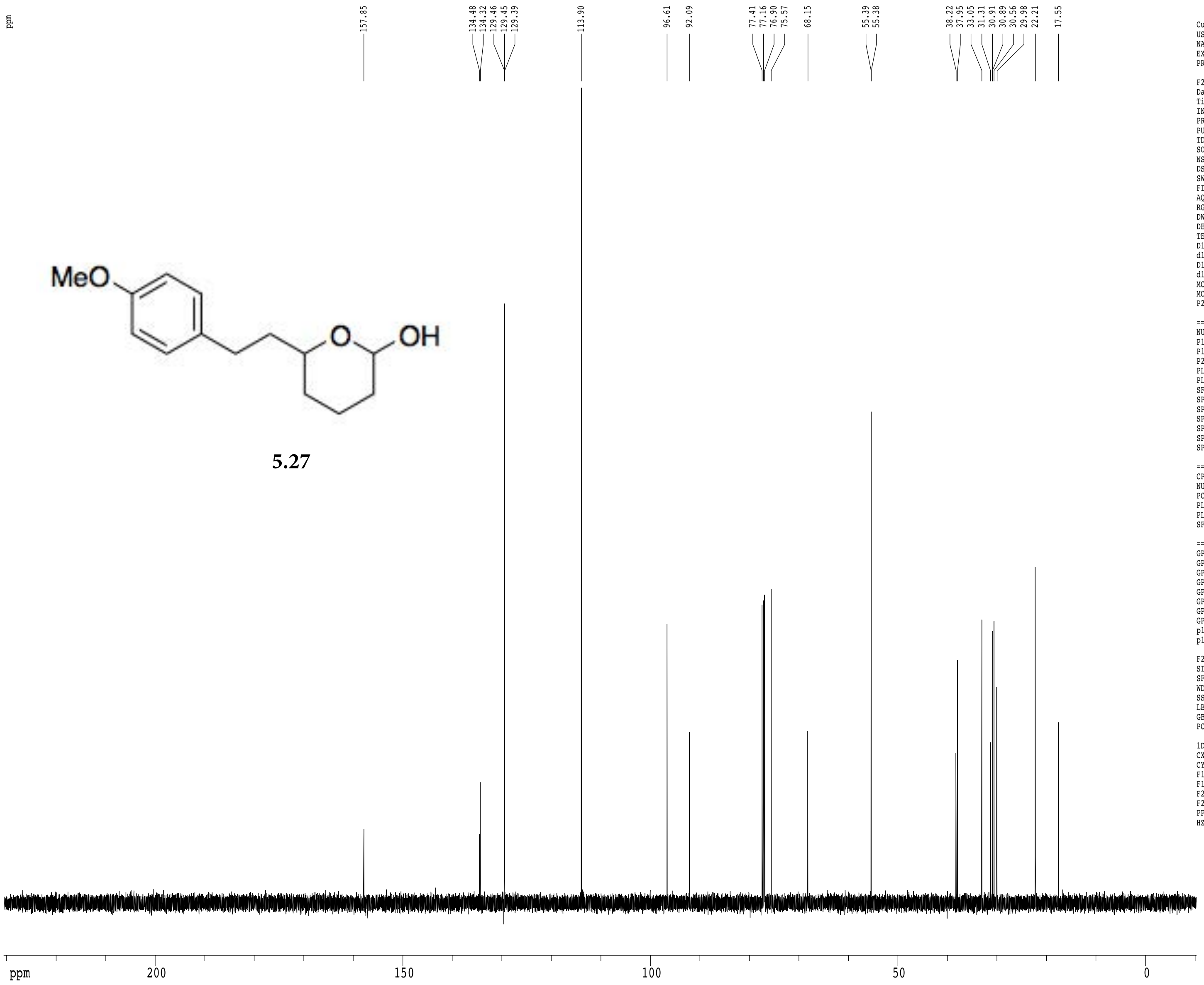
```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-248-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220126
Time               18.37
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127658 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```



5.27

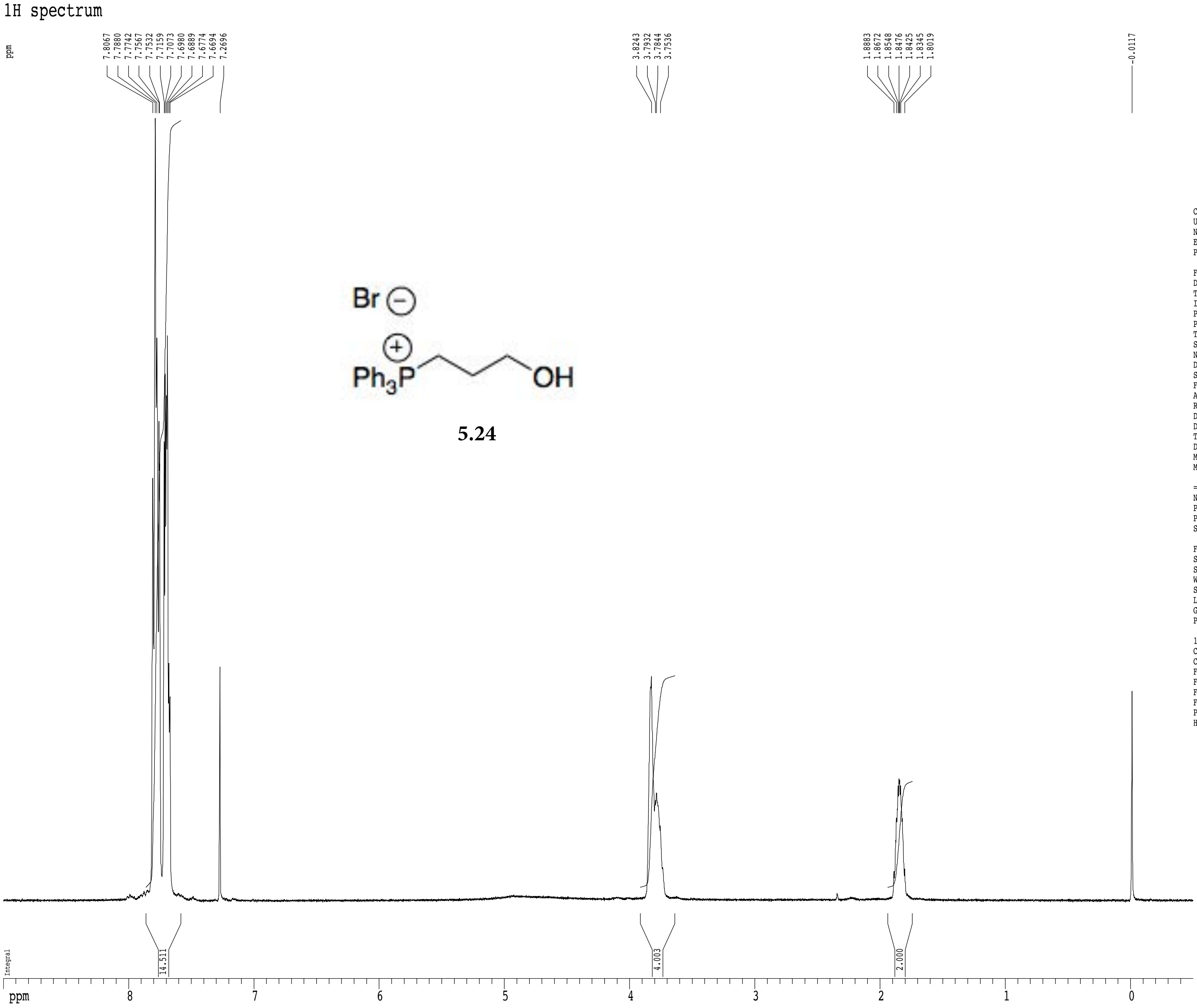
```
Current Data Parameters
USER          khewitt1
NAME       KAH-IV-286-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210616
Time              16.13
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200321 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



5.27

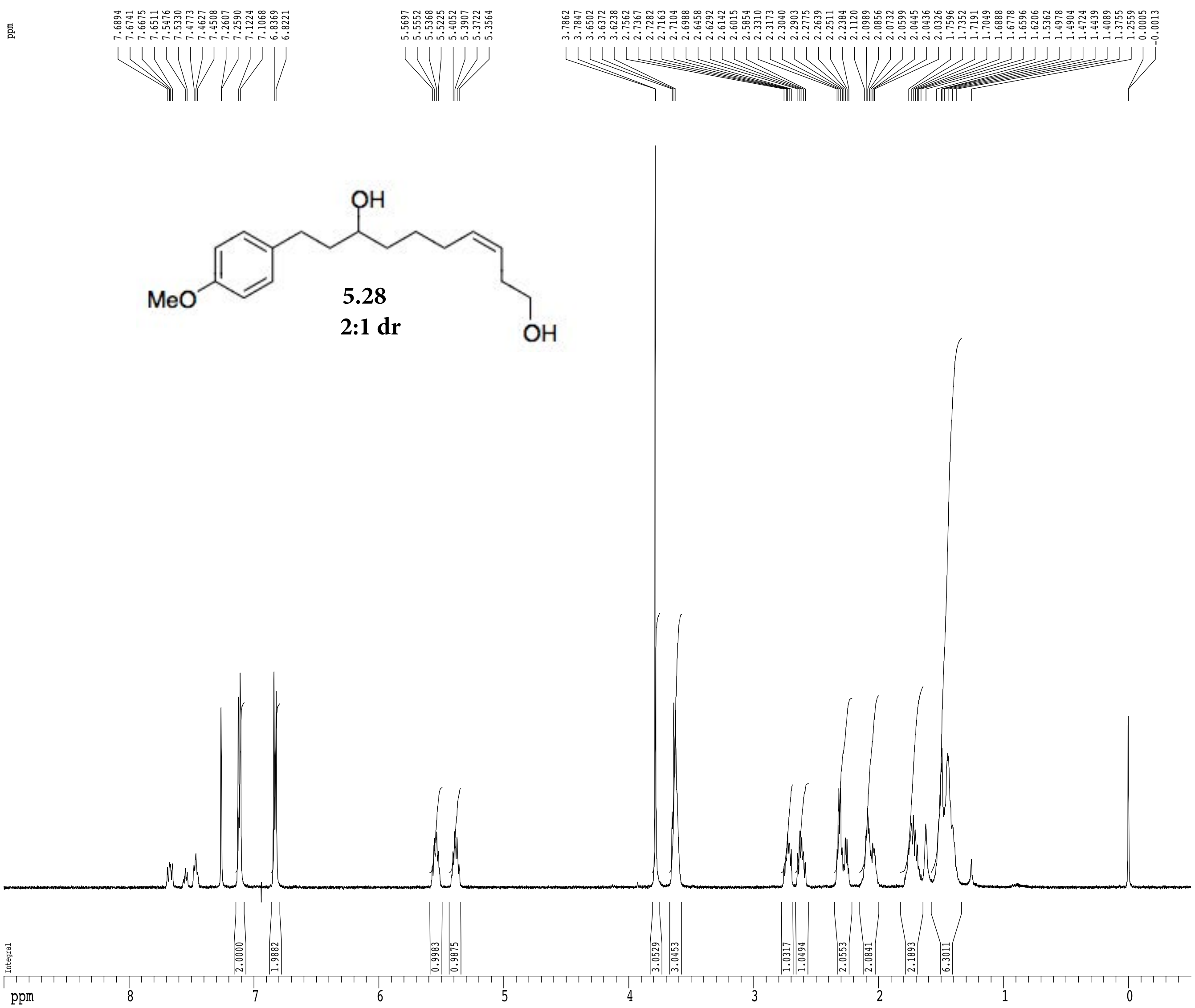
```
Current Data Parameters
USER            khewitt1
NAME         KAH-IV-286-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210616
Time               16.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   144
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804090 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



5.24

```
Current Data Parameters
USER              khewitt1
NAME          KAH-IV-290-1
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210622
Time                 14.37
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   38460
SOLVENT             CDC13T
NS                       8
DS                       2
SWH               6410.256 Hz
FIDRES            0.166673 Hz
AQ               2.9999299 sec
RG                     362
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -1.60 dB
SFO1           400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             166.72084 Hz/cm
```

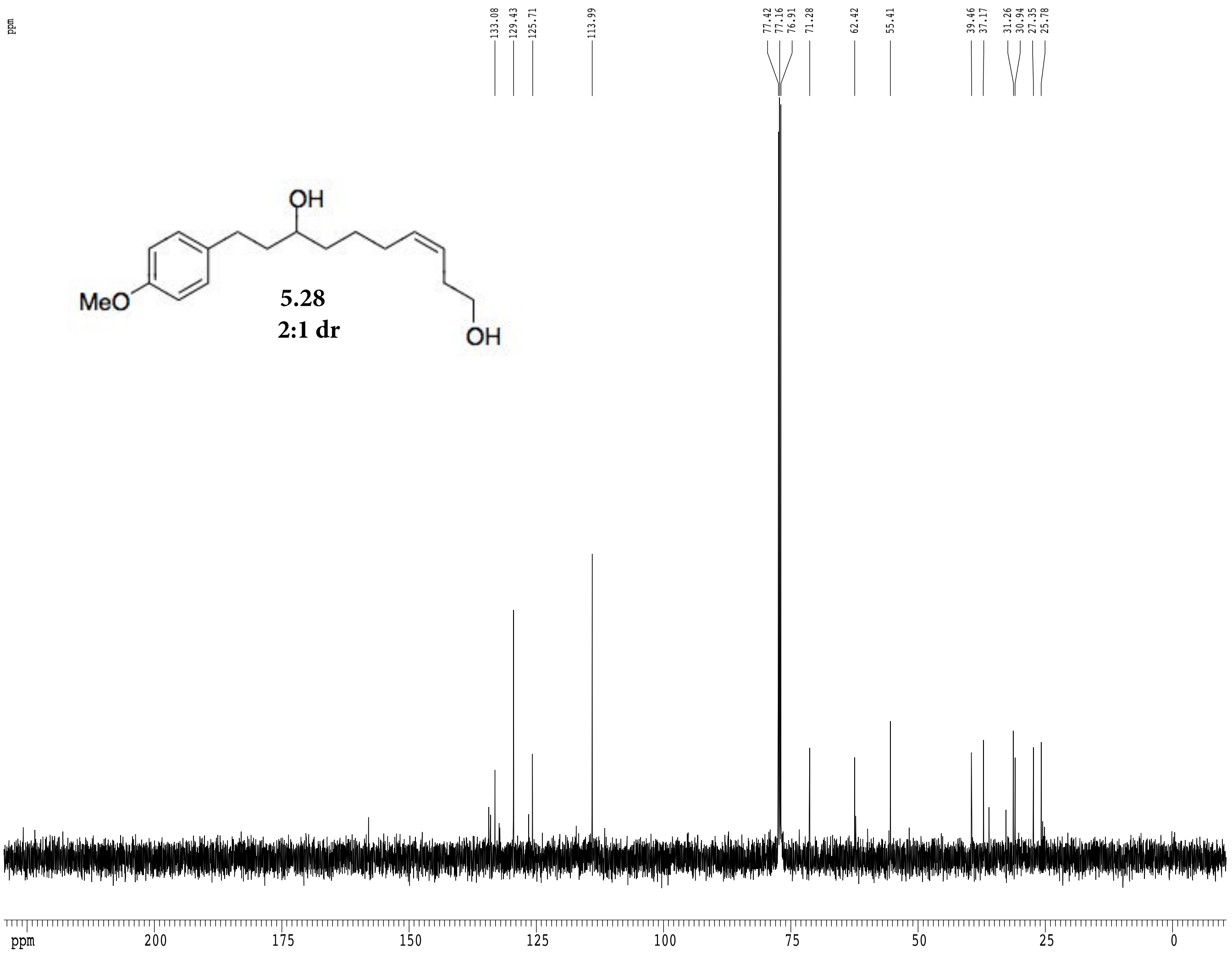
1H spectrum



5.28
2:1 dr

```
Current Data Parameters
USER            khewitt1
NAME      KAH-IV-288-chk
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210621
Time               14.21
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                1448.2
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -6.00 dB
SFO1         498.7534913 MHz

F2 - Processing parameters
SI                 65536
SF           498.7500314 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P                9.000 ppm
F1               4488.75 Hz
F2P               -0.500 ppm
F2               -249.38 Hz
PPMCM            0.47500 ppm/cm
HZCM           236.90627 Hz/cm
```

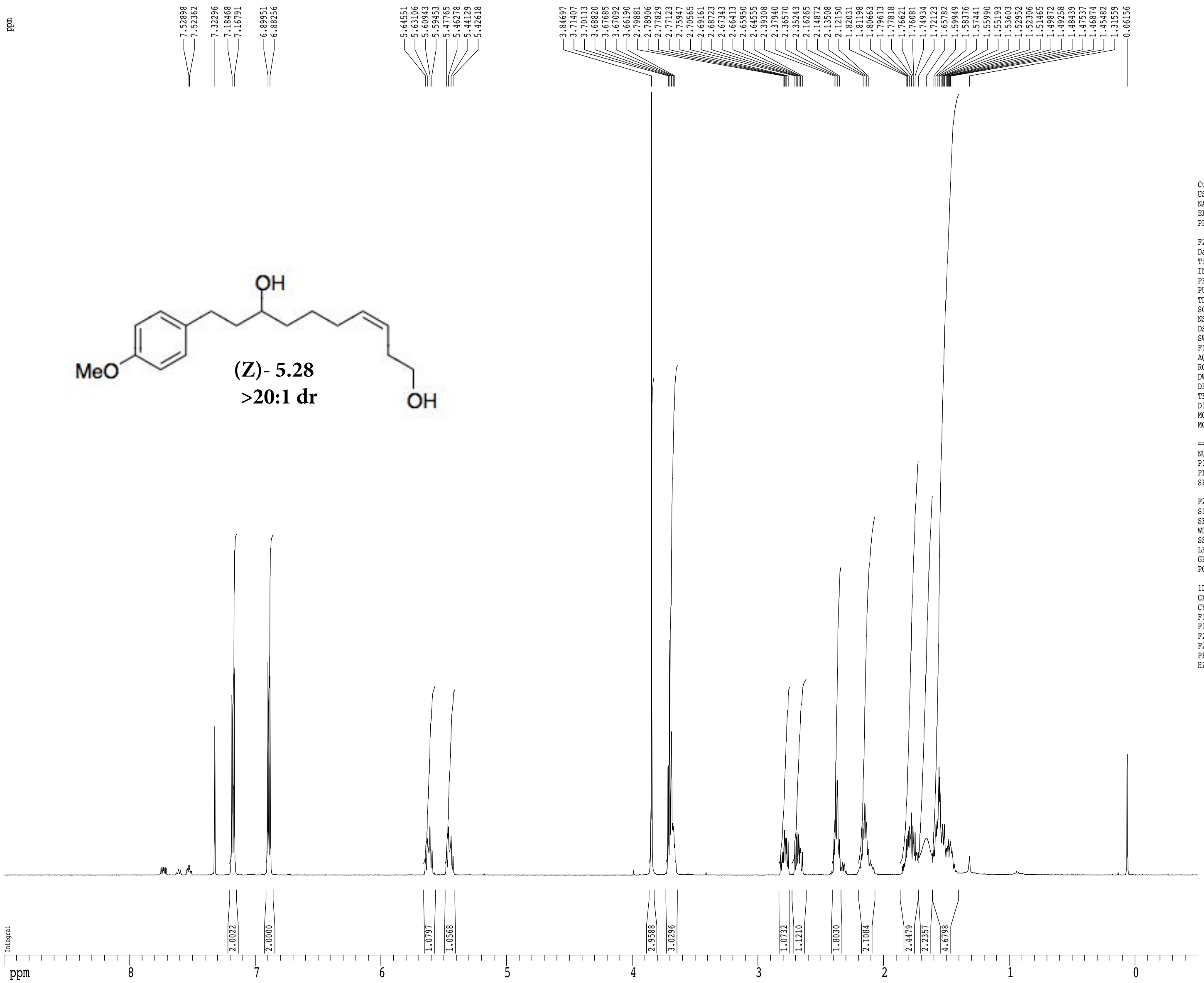
13C spectrum with 1H decoupling



5.28
2:1 dr

```
Current Data Parameters
USER            khewitt1
NAME       KAH-IV-288-chk
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210621
Time                14.23
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG           zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    144
DS                      4
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 5792.6
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  14.20 usec
PL1                 -6.00 dB
SFO1          125.4245824 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -6.00 dB
PL12                12.30 dB
SFO2          498.7524937 MHz

F2 - Processing parameters
SI                  65536
SF            125.4107757 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  20.00 cm
CY                  12.50 cm
F1P               229.520 ppm
F1               28784.24 Hz
F2P               -10.507 ppm
F2               -1317.64 Hz
PPMCM            12.00131 ppm/cm
HZCM           1505.09399 Hz/cm
```

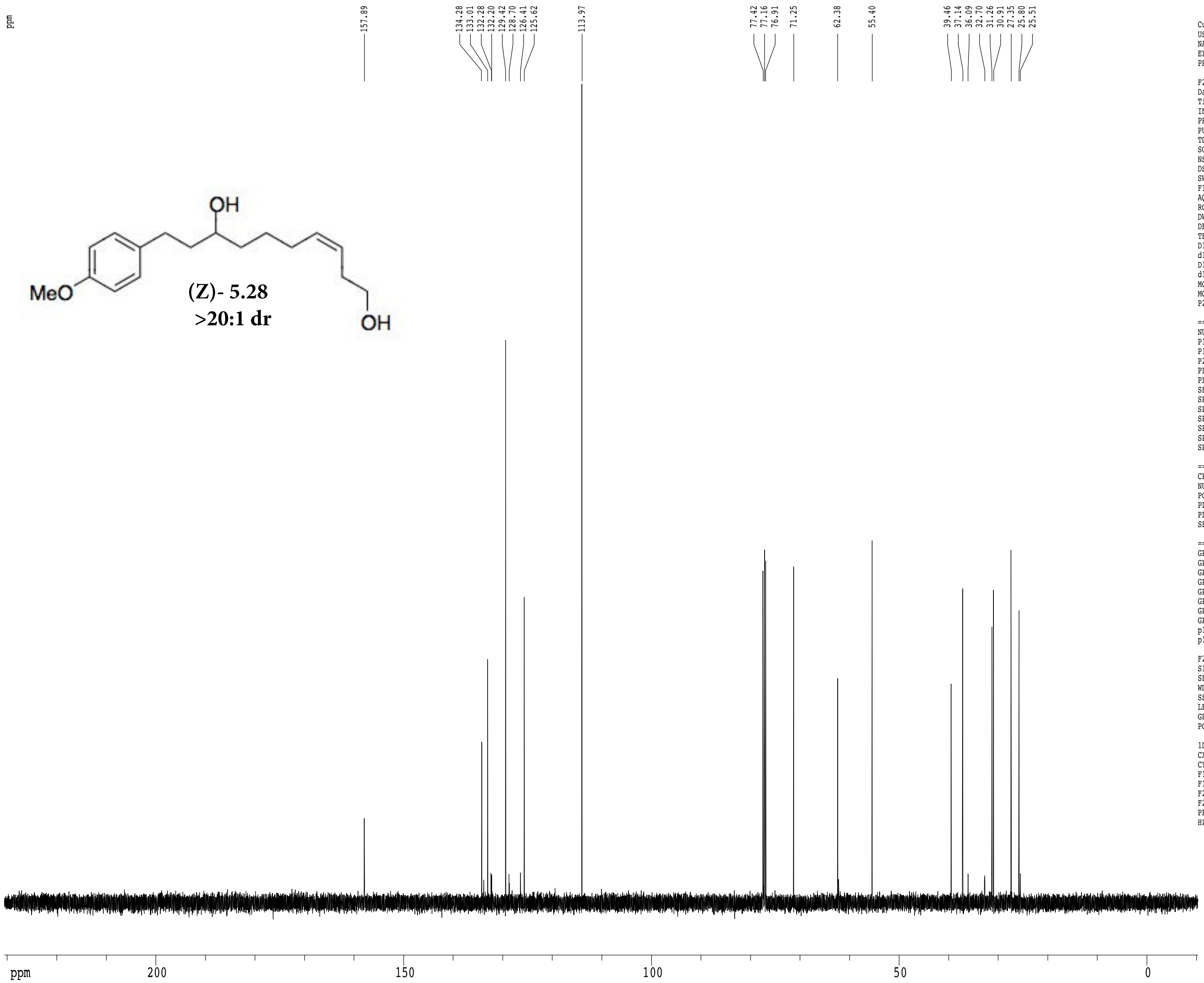
1H spectrum



(Z)- 5.28
>20:1 dr

```
Current Data Parameters
USER              khewitt1
NAME     KAH-V-155-major-Z-Z
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20211105
Time               11.39
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

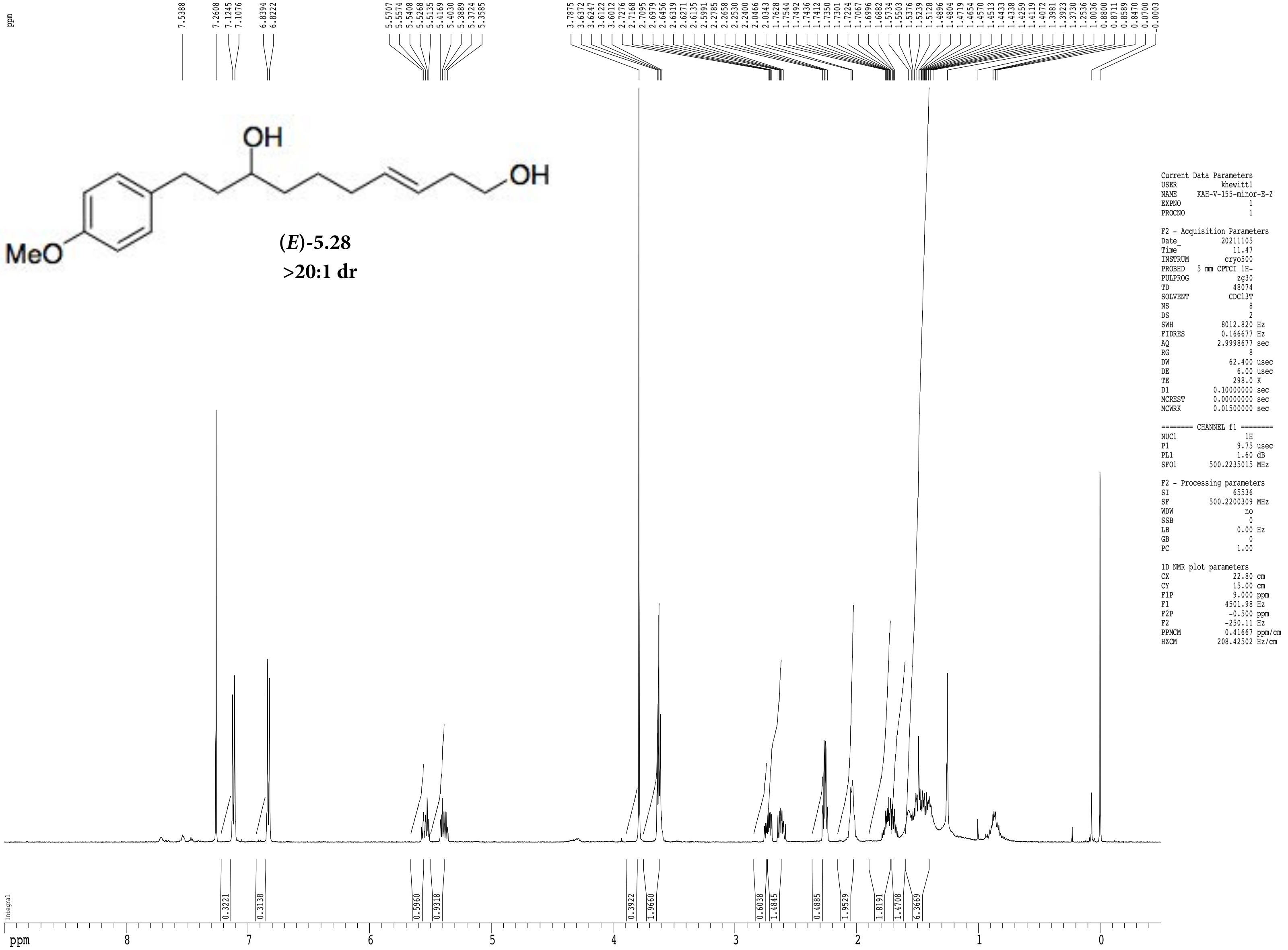
Z-restored spin-echo 13C spectrum with 1H decoupling



(Z)- 5.28
>20:1 dr

```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-155-major-Z-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211105
Time               11.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   184
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                1824.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804090 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```

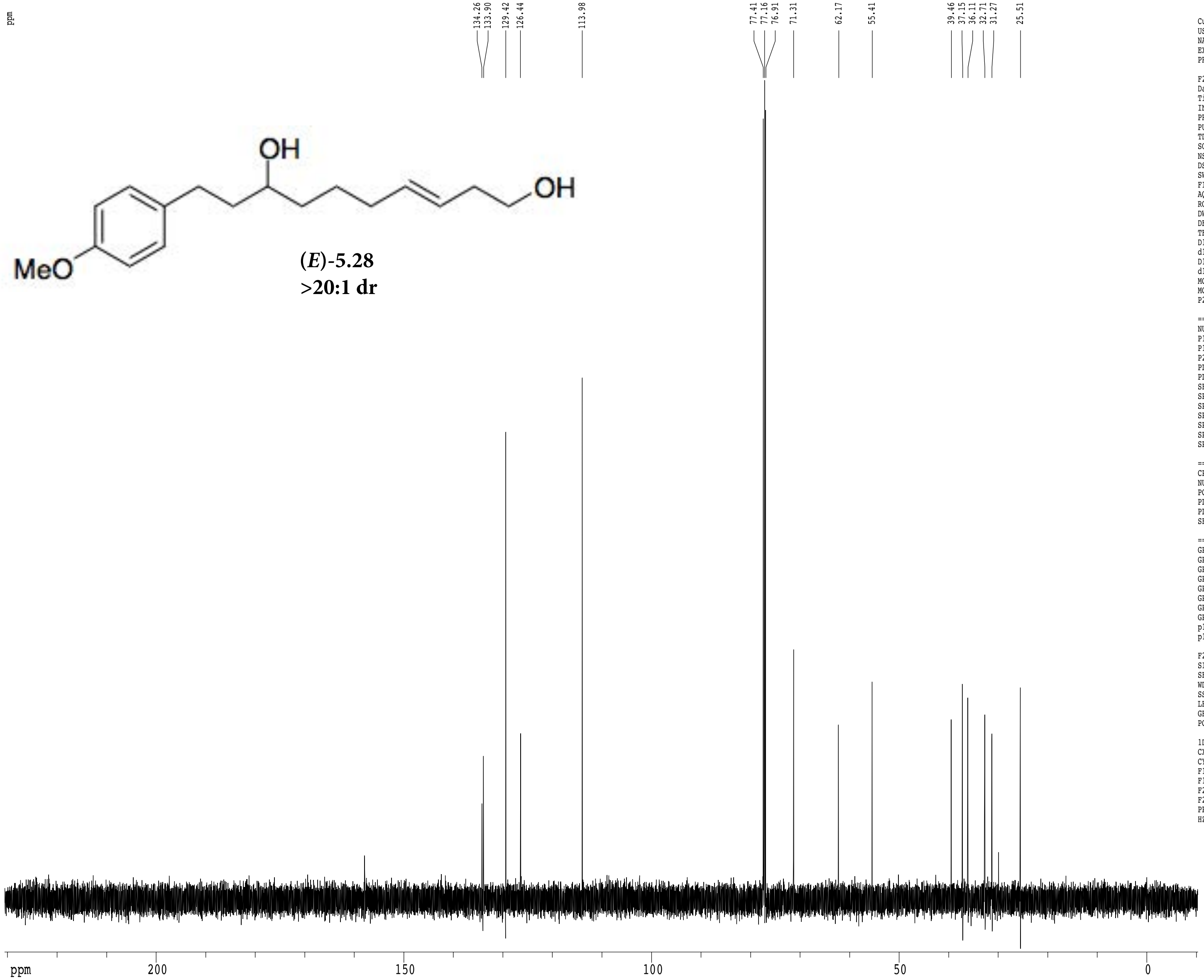
1H spectrum



(*E*)-5.28
>20:1 dr

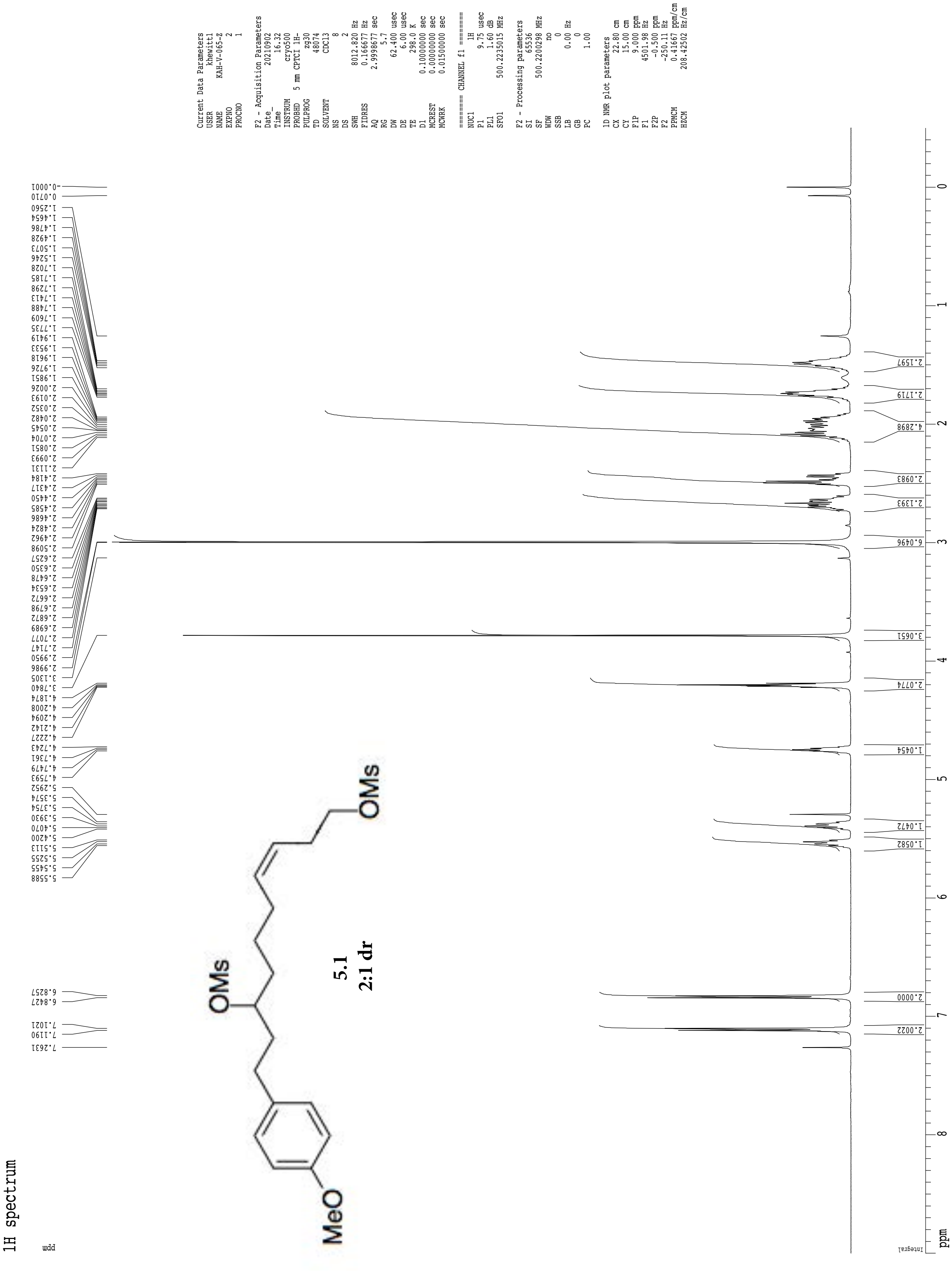
```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-155-minor-E-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211105
Time               11.47
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200309 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



(*E*)-5.28
>20:1 dr

```
Current Data Parameters
USER           khewitt1
NAME     KAH-V-155-minor-E-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20211105
Time              11.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  280
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               2298.8
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804076 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10693 Hz/cm
```


1H spectrum
ppm
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0.0710
1.2560
1.4654
1.4786
1.4928
1.5073
1.5246
1.7028
1.7185
1.7298
1.7413
1.7488
1.7609
1.7735
1.9419
1.9533
1.9618
1.9726
1.9851
2.0026
2.0193
2.0352
2.0482
2.0545
2.0704
2.0851
2.0993
2.1131
2.4184
2.4317
2.4450
2.4585
2.4686
2.4824
2.4962
2.5098
2.6257
2.6350
2.6478
2.6534
2.6672
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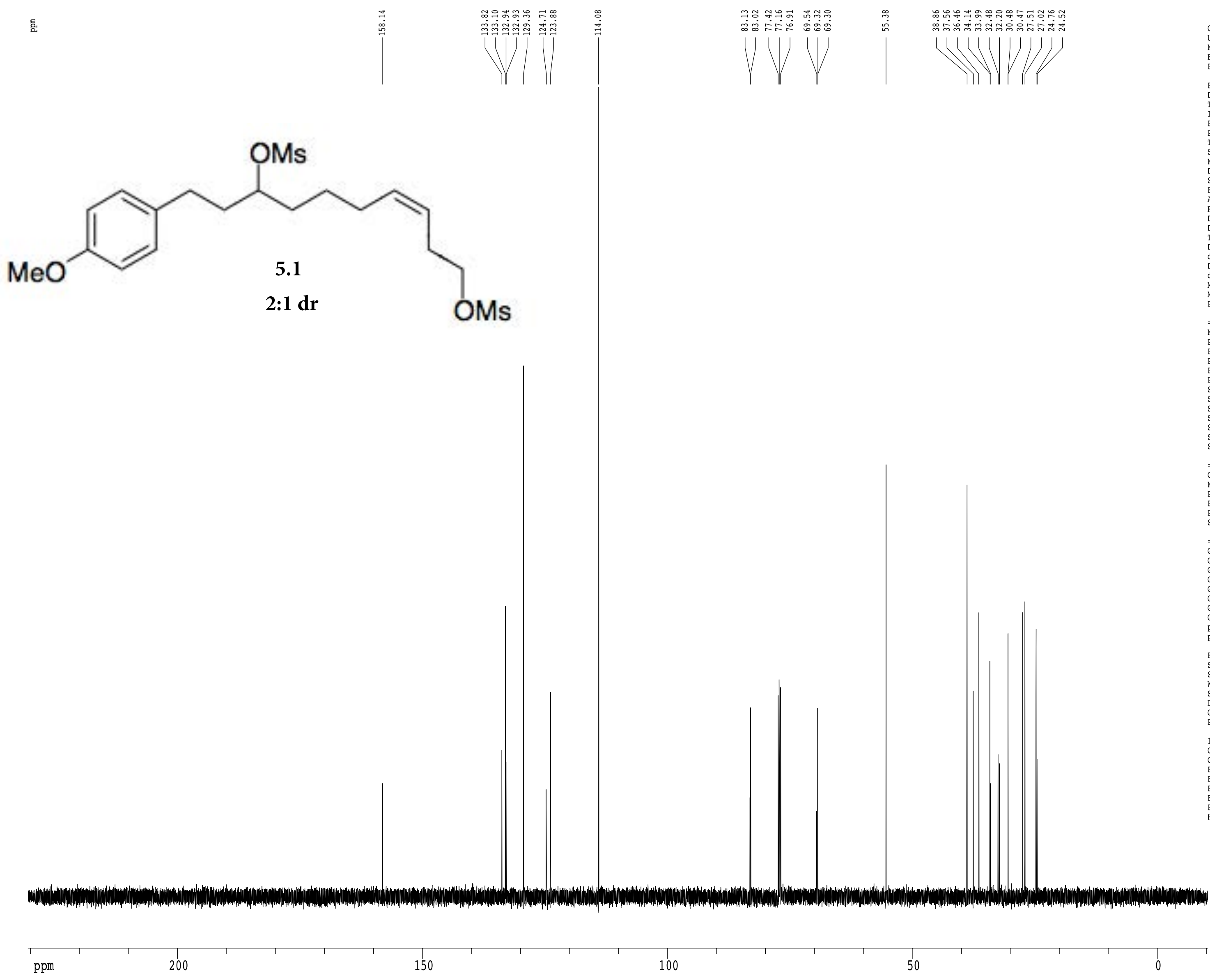
2.7077
2.7147
2.9950
2.9986
3.1305
3.7840
4.1874
4.2008
4.2094
4.2142
4.2227
4.7243
4.7361
4.7479
4.7593
5.2952
5.3574
5.3754
5.3930
5.4070
5.4200
5.5113
5.5255
5.5455
5.5588
6.8257
6.8427
7.1021
7.1190
7.2631
MeO
OMs
OMs
Current Data Parameters
USER khewitt1
NAME KAH-V-065-Z
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210902
Time 16.32
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 48074
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.9998677 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200298 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
2.1597
2.1719
4.2898
2.0983
2.1393
6.0496
3.0651
2.0774
1.0454
1.0472
1.0582
2.0000
2.0022
Integral
0
1
2
3
4
5
6
7
8
ppm

5.1
2:1 dr

Z-restored spin-echo 13C spectrum with 1H decoupling

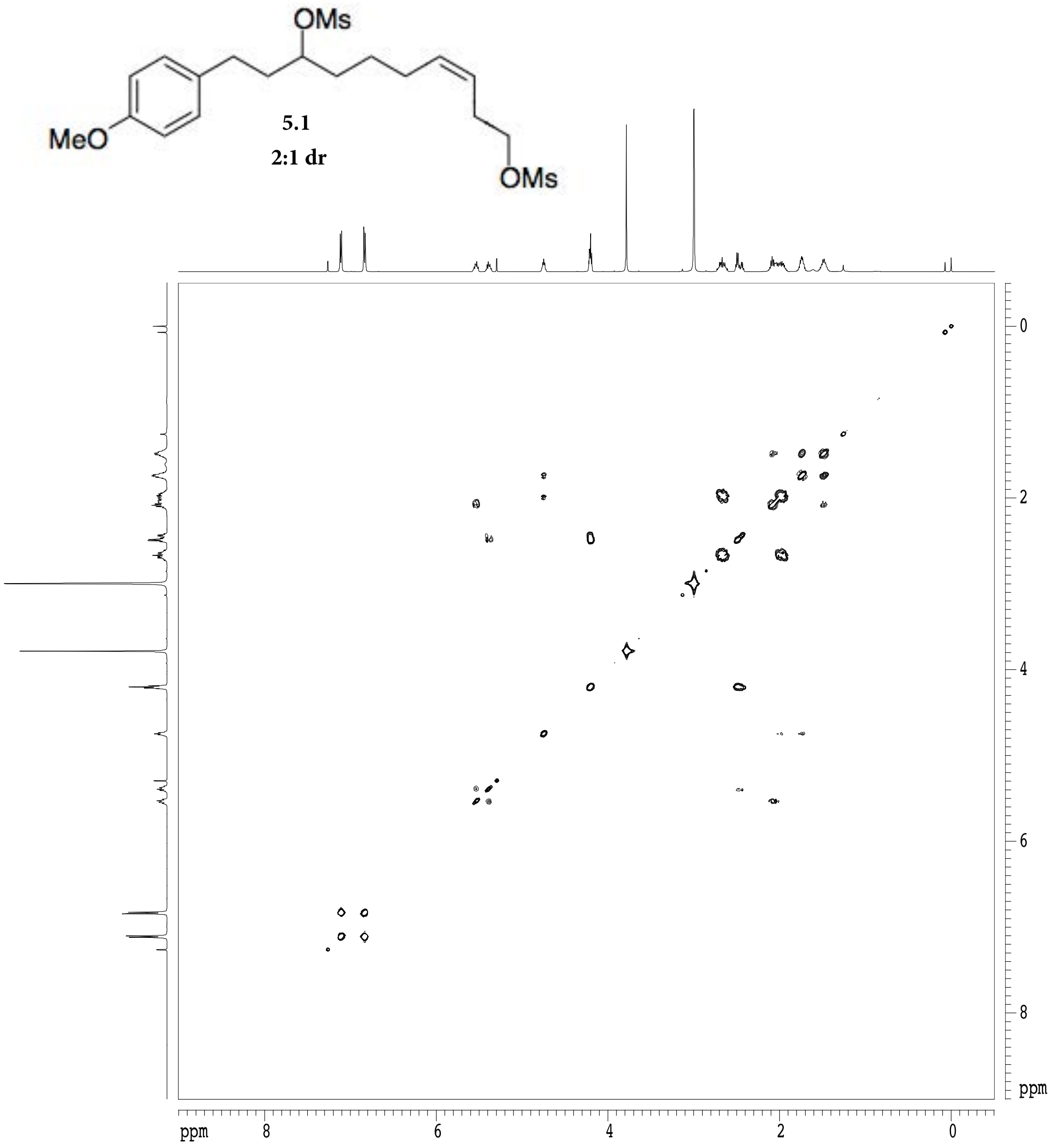


5.1

2:1 dr

```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-065-Z
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20210902
Time                16.46
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT             CDCl3
NS                    104
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813940 sec
RG                 2896.3
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                  37.70 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  18.85 usec
P12               2000.00 usec
P20                500.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP2                  1.55 dB
SP4                  1.55 dB
SPNAM2        Crp60comp.4
SPNAM4     Crp60,0.5,20.1
SPOFF2               0.00 Hz
SPOFF4               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                22.00 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804113 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               230.637 ppm
F1               29009.68 Hz
F2P               -10.287 ppm
F2               -1293.96 Hz
PPMCM            10.56688 ppm/cm
HZCM           1329.10693 Hz/cm
```

gcosy60

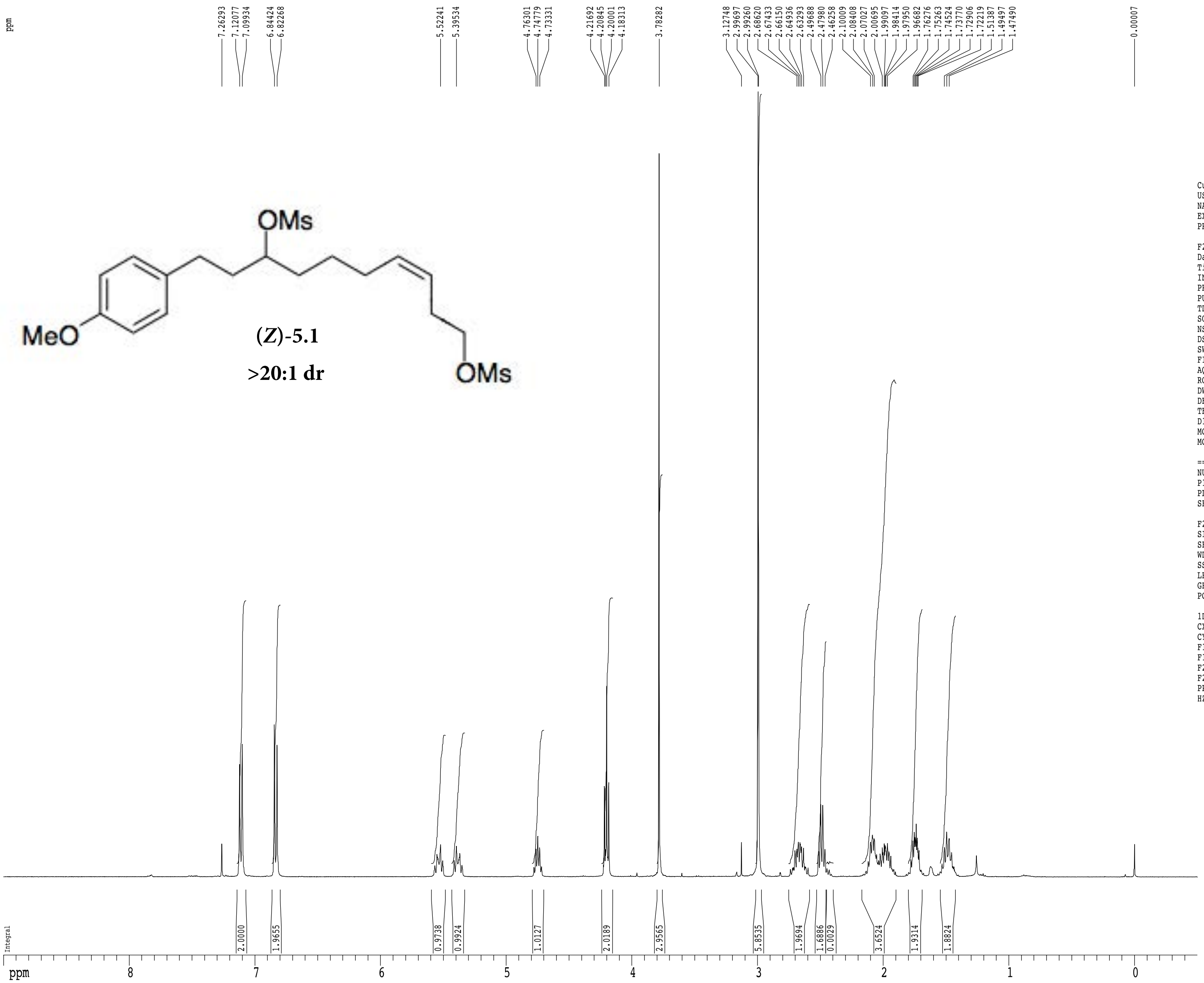


5.1

2:1 dr

```
        Current Data Parameters
USER            khewitt1
NAME         KAH-V-065-Z
EXPNO                  3
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20210902
Time               16.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG     cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                  35.9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00020000 sec
IN0           0.00012480 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               17.00 %
GPZ2               17.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   512
SFO1            500.2235 MHz
FIDRES         15.650040 Hz
SW                16.018 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           500.2200298 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.2200298 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

         2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.005 ppm
F2LO             4504.64 Hz
F2PHI             -0.506 ppm
F2HI             -252.97 Hz
F1PLO              9.005 ppm
F1LO             4504.64 Hz
F1PHI             -0.506 ppm
F1HI             -252.97 Hz
F2PPMCM          0.63407 ppm/cm
F2HZCM         317.17413 Hz/cm
F1PPMCM          0.63407 ppm/cm
F1HZCM         317.17413 Hz/cm
```

1H spectrum

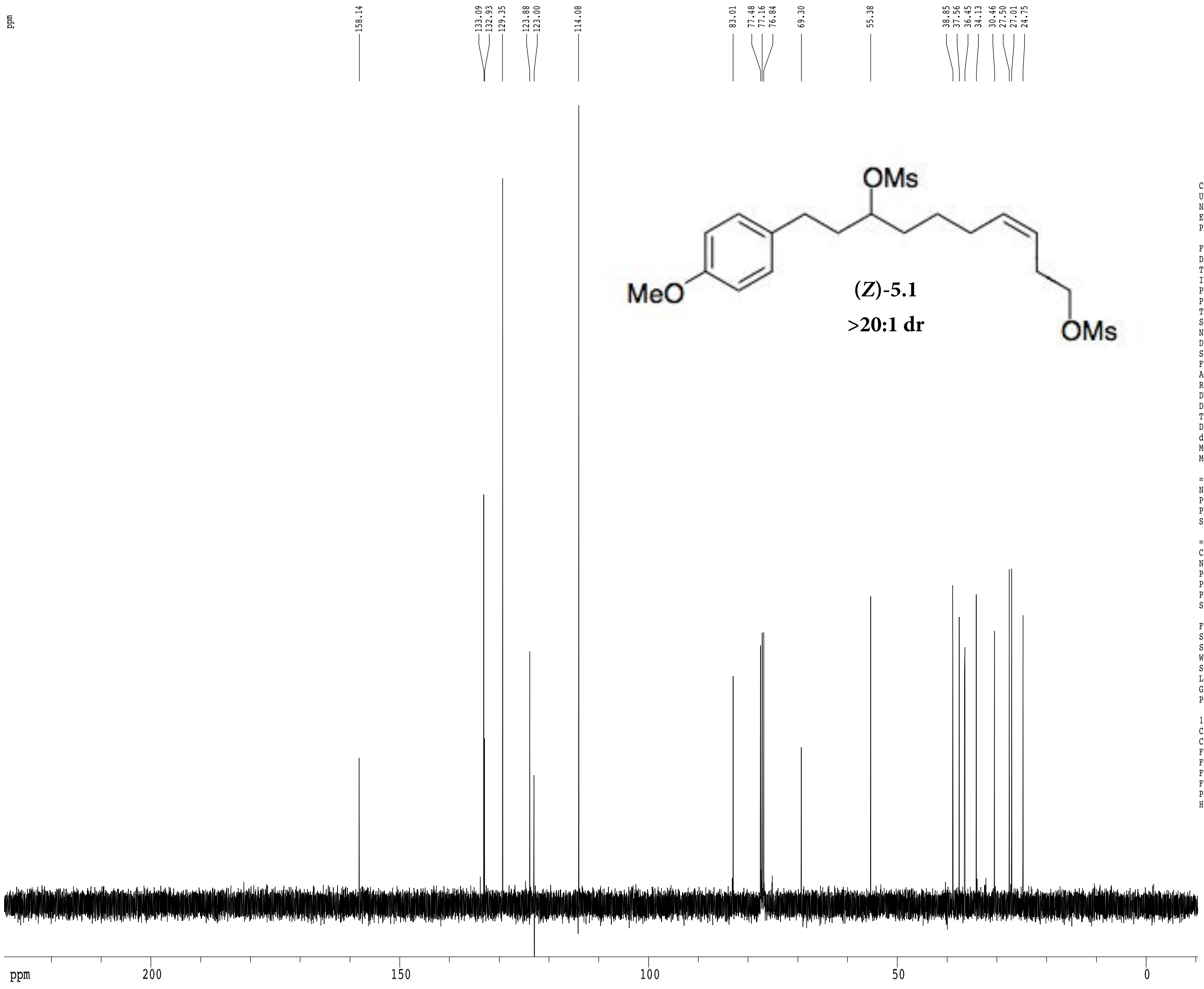


(*Z*)-5.1

>20:1 dr

```
Current Data Parameters
USER          khewitt1
NAME        KAH-V-166-Z
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20211108
Time               9.18
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                  114
DW               78.000 usec
DE                 4.50 usec
TE                298.1 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -0.90 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300202 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling

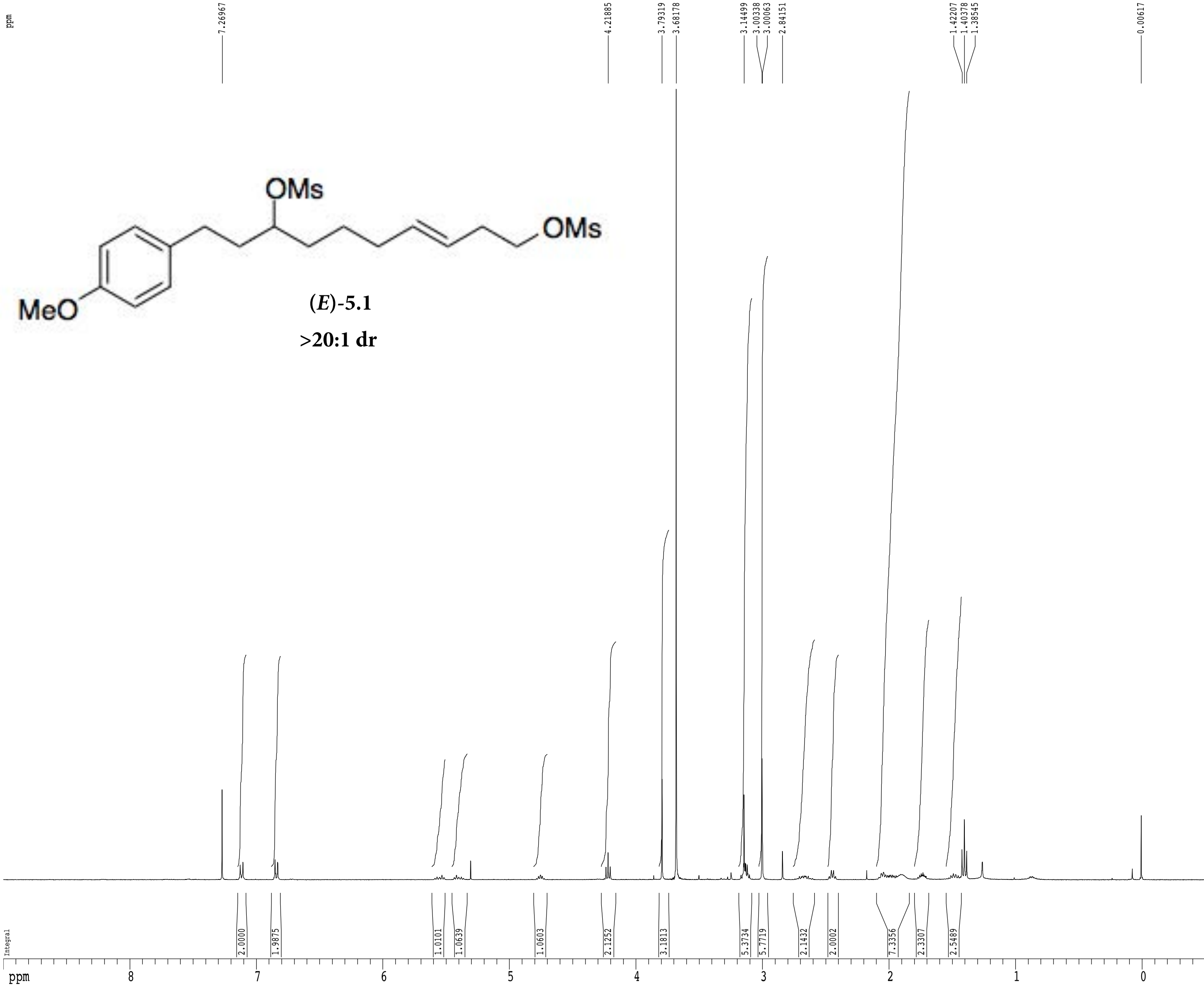


(*Z*)-5.1

>20:1 dr

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-166-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211108
Time                9.25
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   280
DS                     4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG                  8192
DW                20.700 usec
DE                 20.39 usec
TE                 298.1 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF          100.6127621 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```

1H spectrum

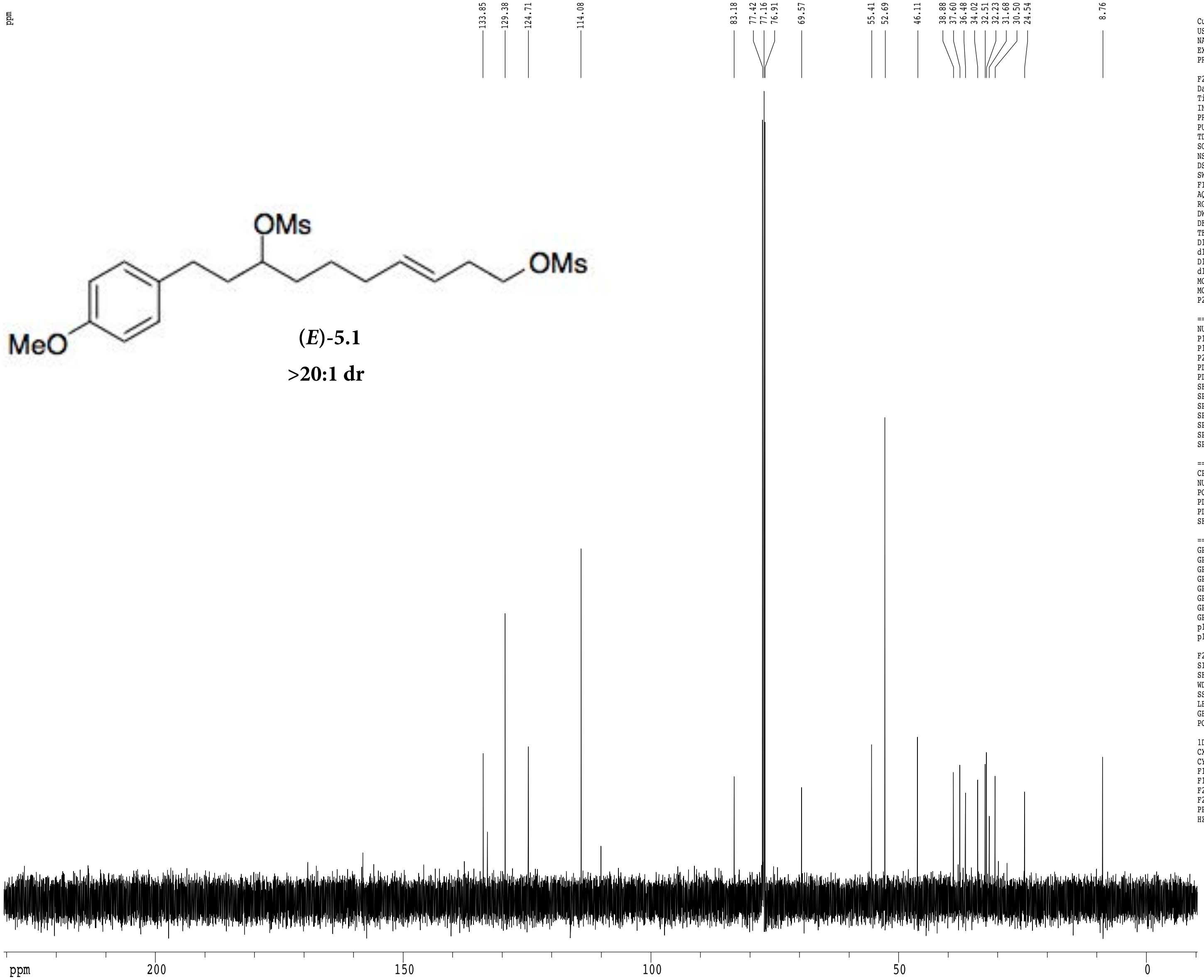


(*E*)-5.1

>20:1 dr

```
Current Data Parameters
USER              khewitt1
NAME            KAH-V-176-Z
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211113
Time                 15.40
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   38460
SOLVENT            CDCl3T
NS                       8
DS                       2
SWH              6410.256 Hz
FIDRES           0.166673 Hz
AQ              2.9999299 sec
RG                     362
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -0.90 dB
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF            400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             166.72084 Hz/cm
```

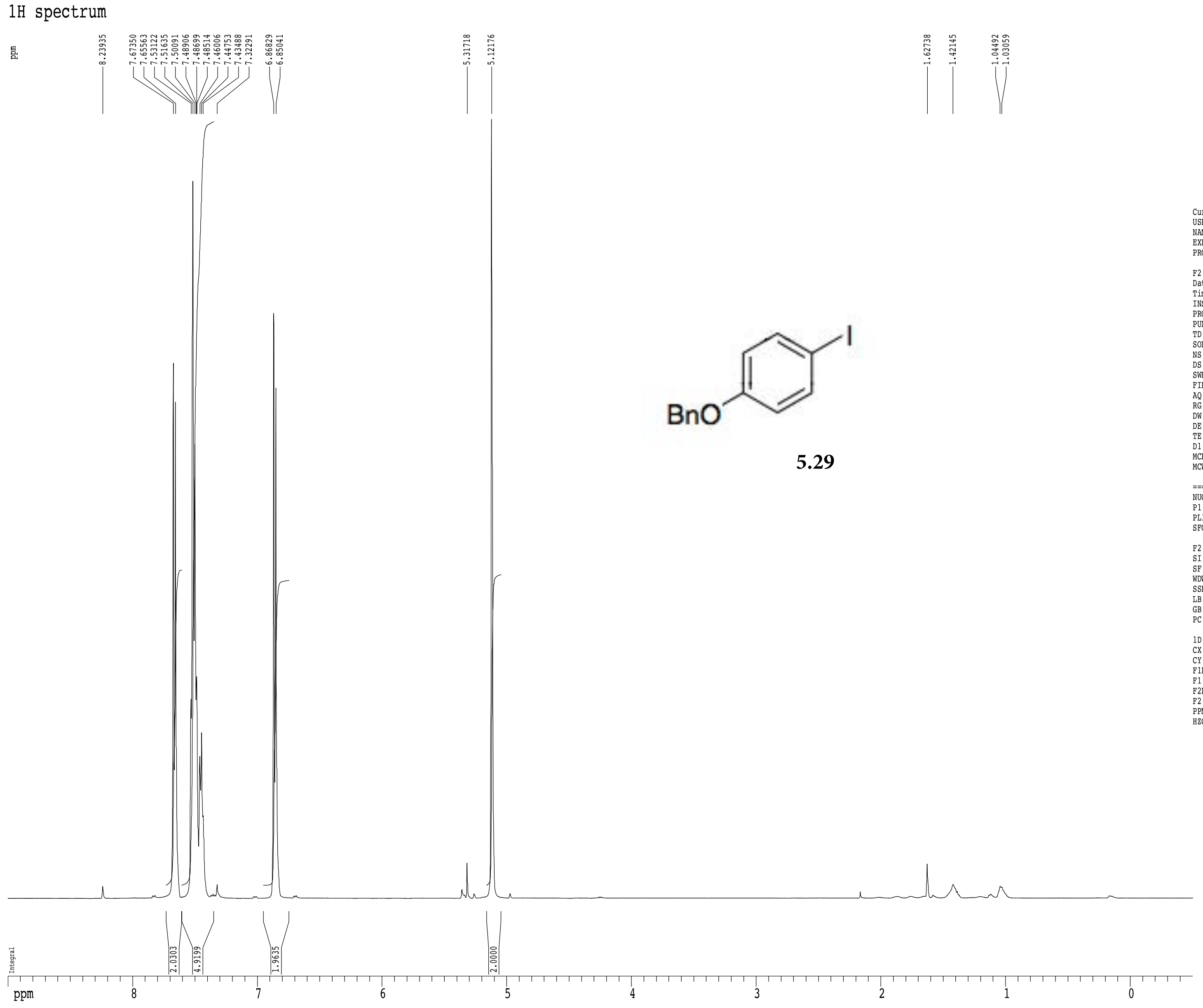
Z-restored spin-echo 13C spectrum with 1H decoupling



(*E*)-5.1

>20:1 dr

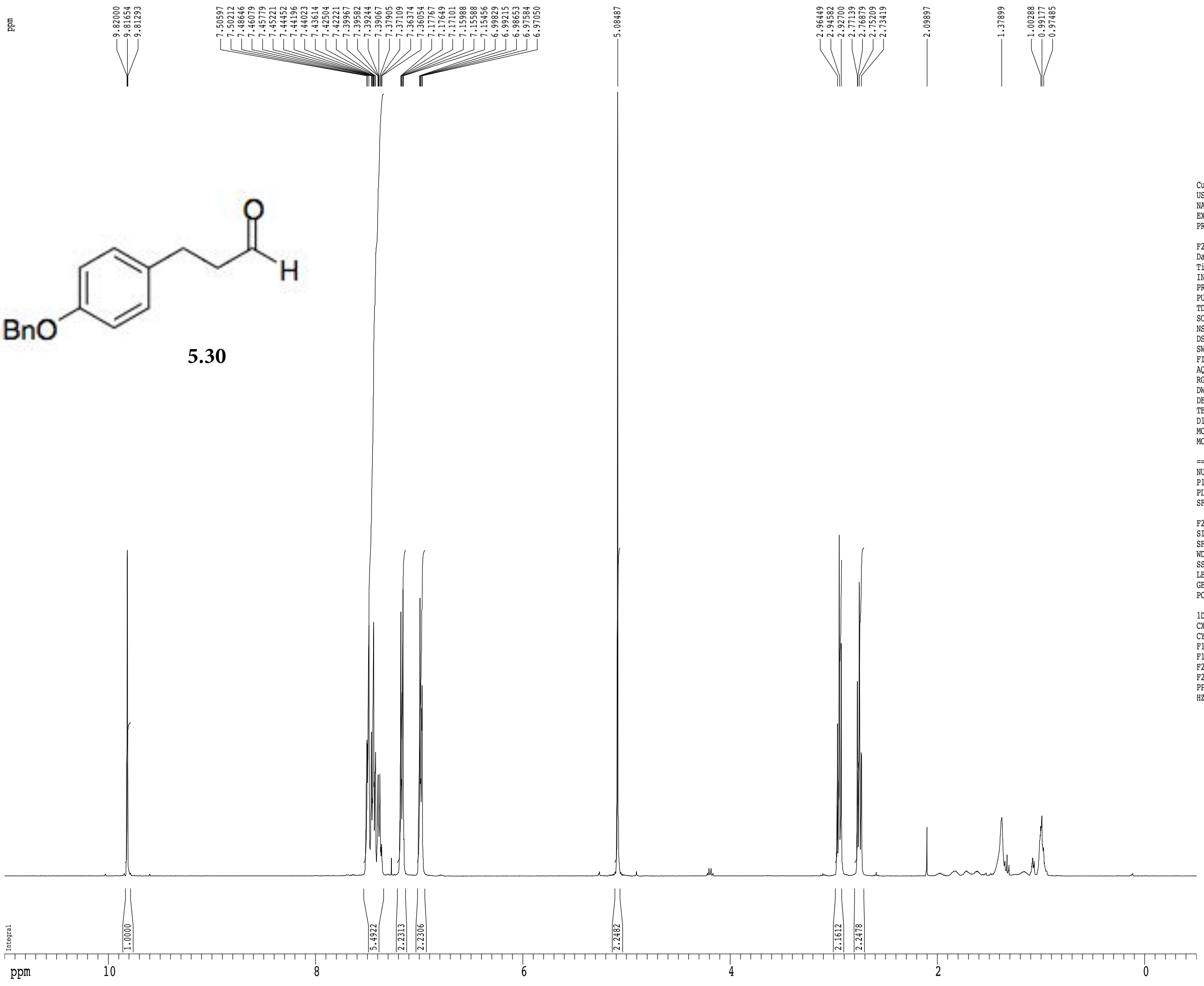
```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-176-Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211113
Time               15.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT           CDCl3T
NS                   120
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                2298.8
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804090 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



5.29

```
Current Data Parameters
USER              khewitt1
NAME           KAH-IV-276-1
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210605
Time                 14.11
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   48074
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.166677 Hz
AQ               2.9998677 sec
RG                     3.6
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
PL1                   1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF           500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

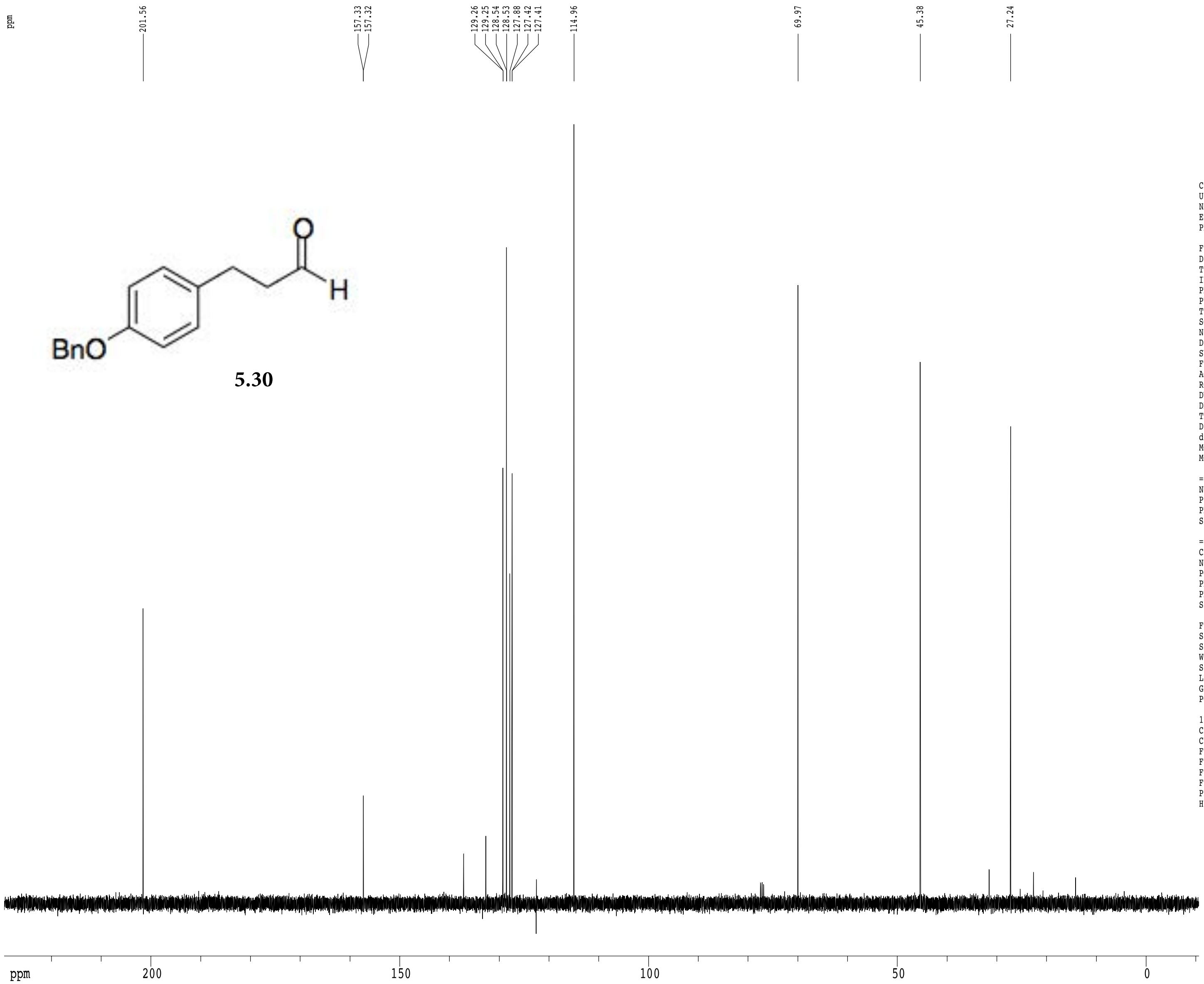
1H spectrum



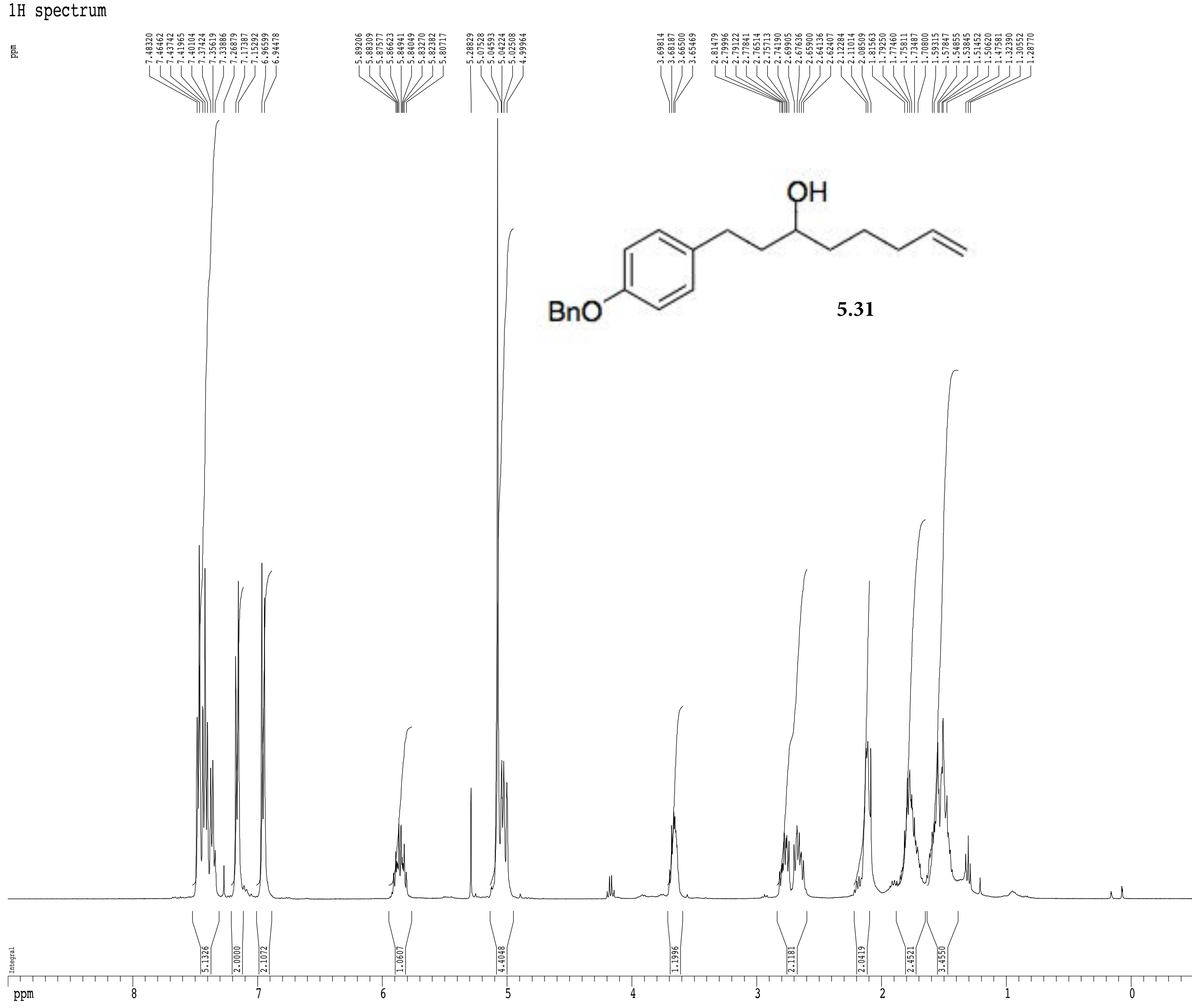
5.30

```
Current Data Parameters
USER              khewitt1
NAME            KAH-V-265-1
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20220205
Time                 16.33
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   65536
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               6410.256 Hz
FIDRES            0.097813 Hz
AQ               5.1118579 sec
RG                      32
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -0.90 dB
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF            400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                 11.000 ppm
F1                 4401.43 Hz
F2P                 -0.500 ppm
F2                 -200.07 Hz
PPMCM              0.50439 ppm/cm
HZCM             201.81996 Hz/cm
```

13C spectrum with 1H decoupling


5.30

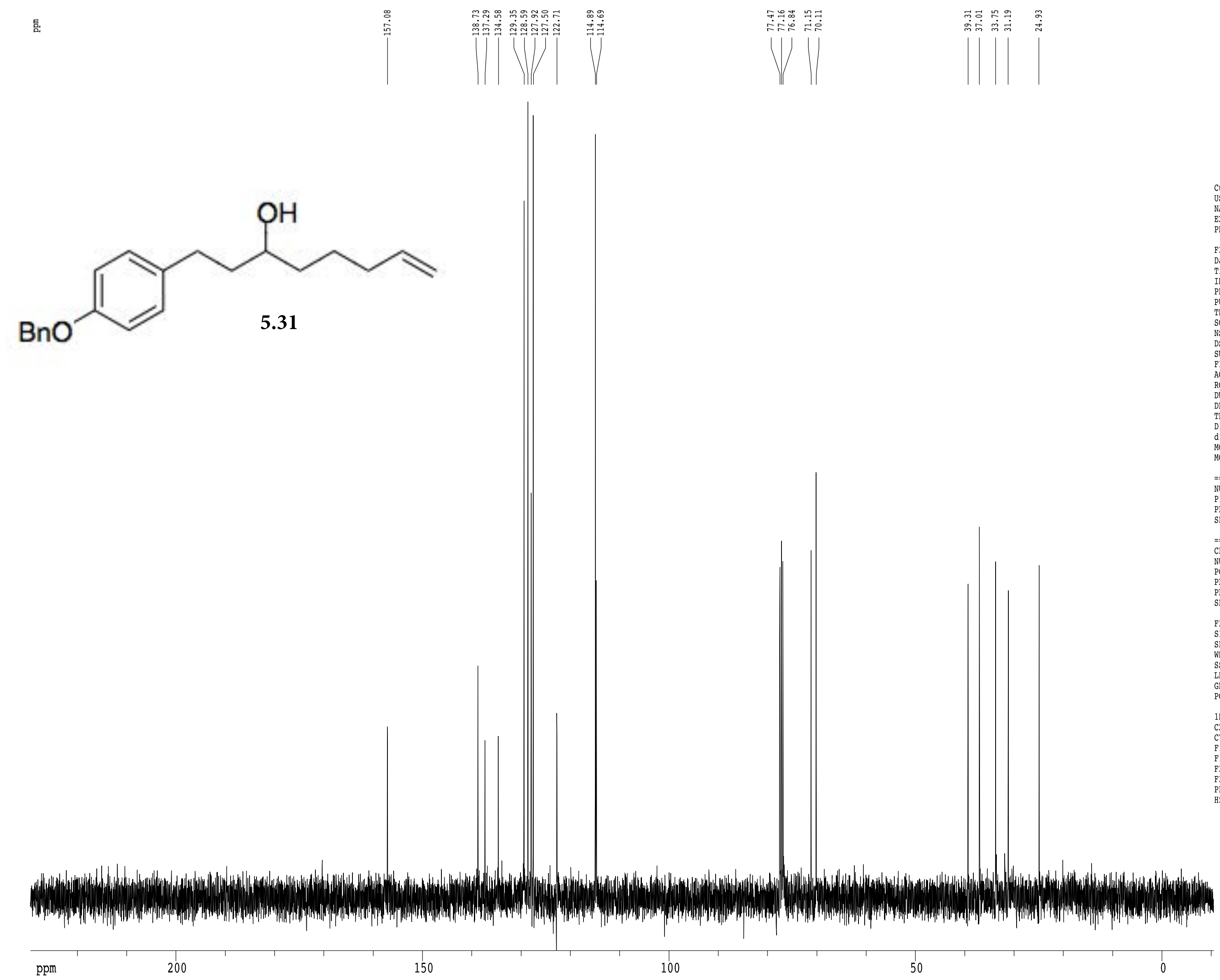
```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-265-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220205
Time               16.34
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                    56
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127838 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.22 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41174 Hz/cm
```



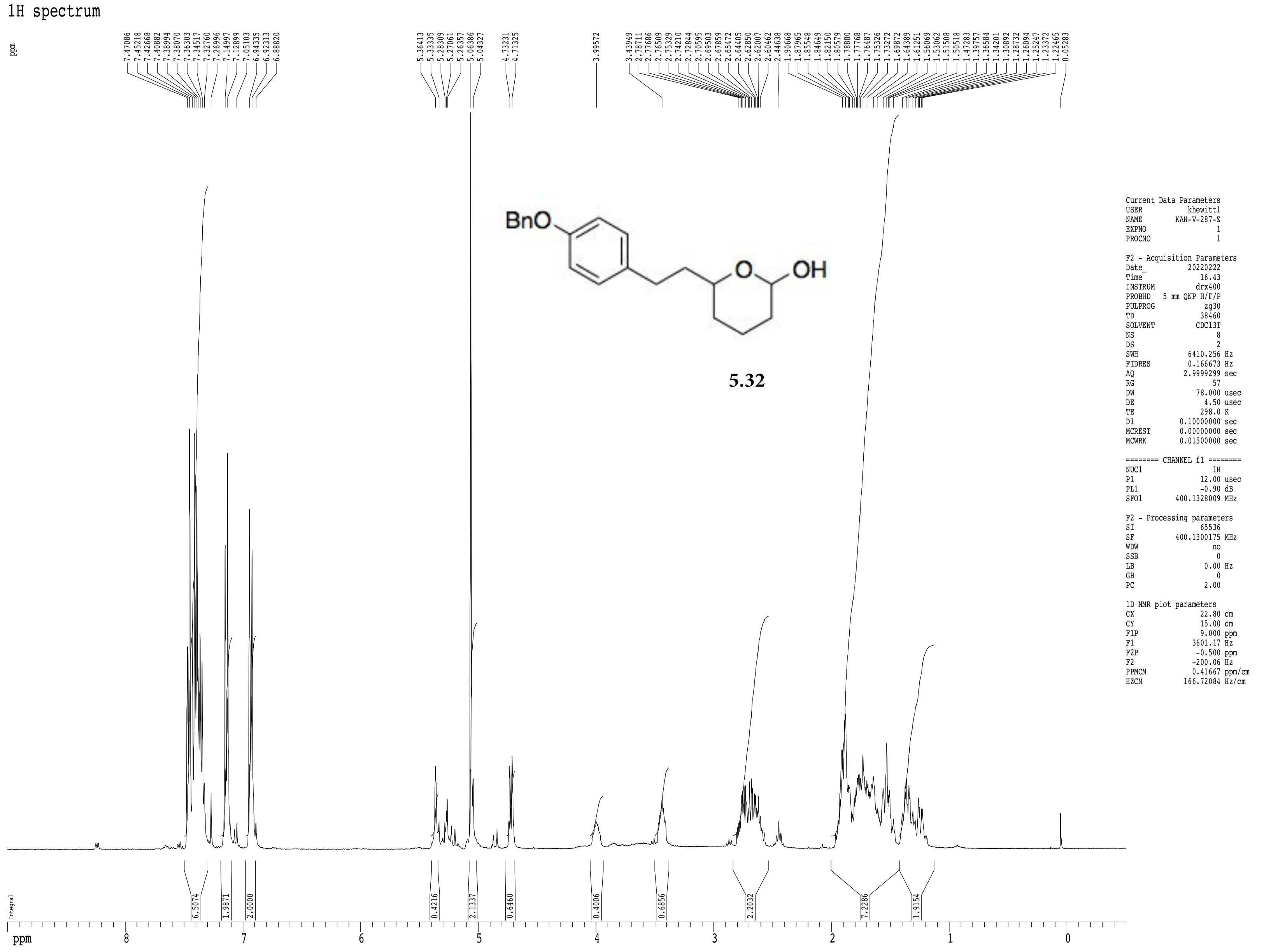
5.31

```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-268-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220207
Time                8.43
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    32
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

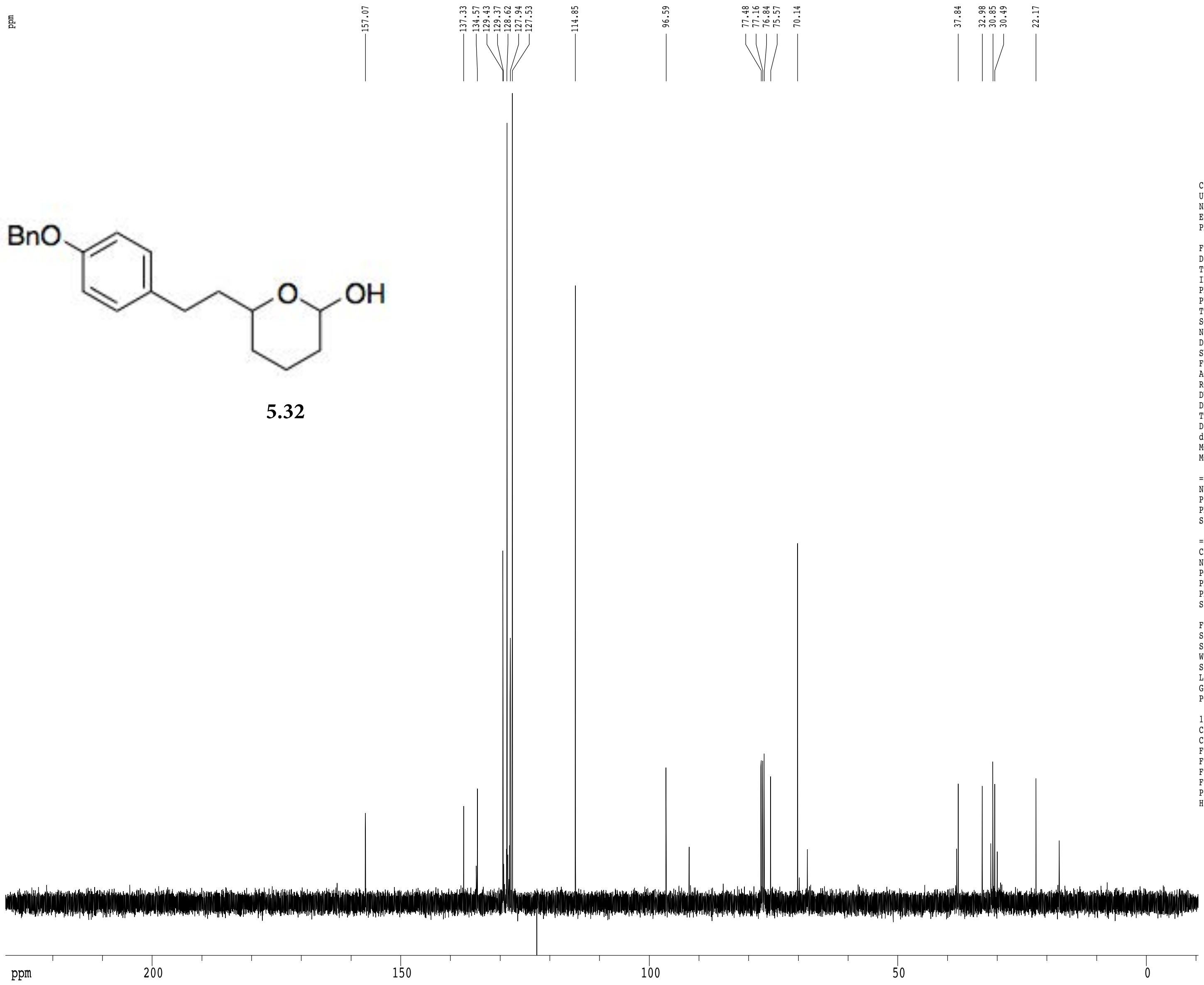
13C spectrum with 1H decoupling


5.31

```
Current Data Parameters
USER             khewitt1
NAME           KAH-V-268-1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220207
Time                 8.44
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      4
SWH             24154.590 Hz
FIDRES           0.368570 Hz
AQ              1.3566452 sec
RG                 9195.2
DW                 20.700 usec
DE                  20.39 usec
TE                  298.0 K
D1             0.10000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   7.90 usec
PL1                 -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -0.90 dB
PL12                17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127731 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.50 cm
F1P               229.496 ppm
F1               23090.22 Hz
F2P               -10.579 ppm
F2               -1064.37 Hz
PPMCM            10.52959 ppm/cm
HZCM           1059.41162 Hz/cm
```


5.32
1H spectrum
ppm
7.47086
7.45218
7.42668
7.40882
7.38994
7.38070
7.36303
7.34517
7.32760
7.26996
7.14997
7.12899
7.05103
6.94335
6.92313
6.88820
5.36413
5.33335
5.28309
5.27061
5.26357
5.06386
5.04327
4.73231
4.71325
3.99572
3.43949
2.78711
2.77686
2.76509
2.75329
2.74210
2.72844
2.70595
2.69503
2.67859
2.65472
2.64405
2.62850
2.62007
2.60462
2.44638
1.90668
1.87965
1.85548
1.84649
1.82150
1.80579
1.78880
1.77768
1.76487
1.75326
1.73272
1.69872
1.64389
1.61251
1.56069
1.53062
1.51508
1.50518
1.47283
1.39757
1.36584
1.34201
1.30892
1.28732
1.26094
1.25247
1.23372
1.22465
0.05283
BnO
O
OH
Current Data Parameters
USER khewitt1
NAME KAH-V-287-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220222
Time 16.43
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3T
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 57
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -0.90 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
Integral
6.5074
1.9871
2.0000
0.4216
2.1337
0.6460
0.4006
0.6856
2.2032
7.2286
1.9154
ppm
8
7
6
5
4
3
2
1
0

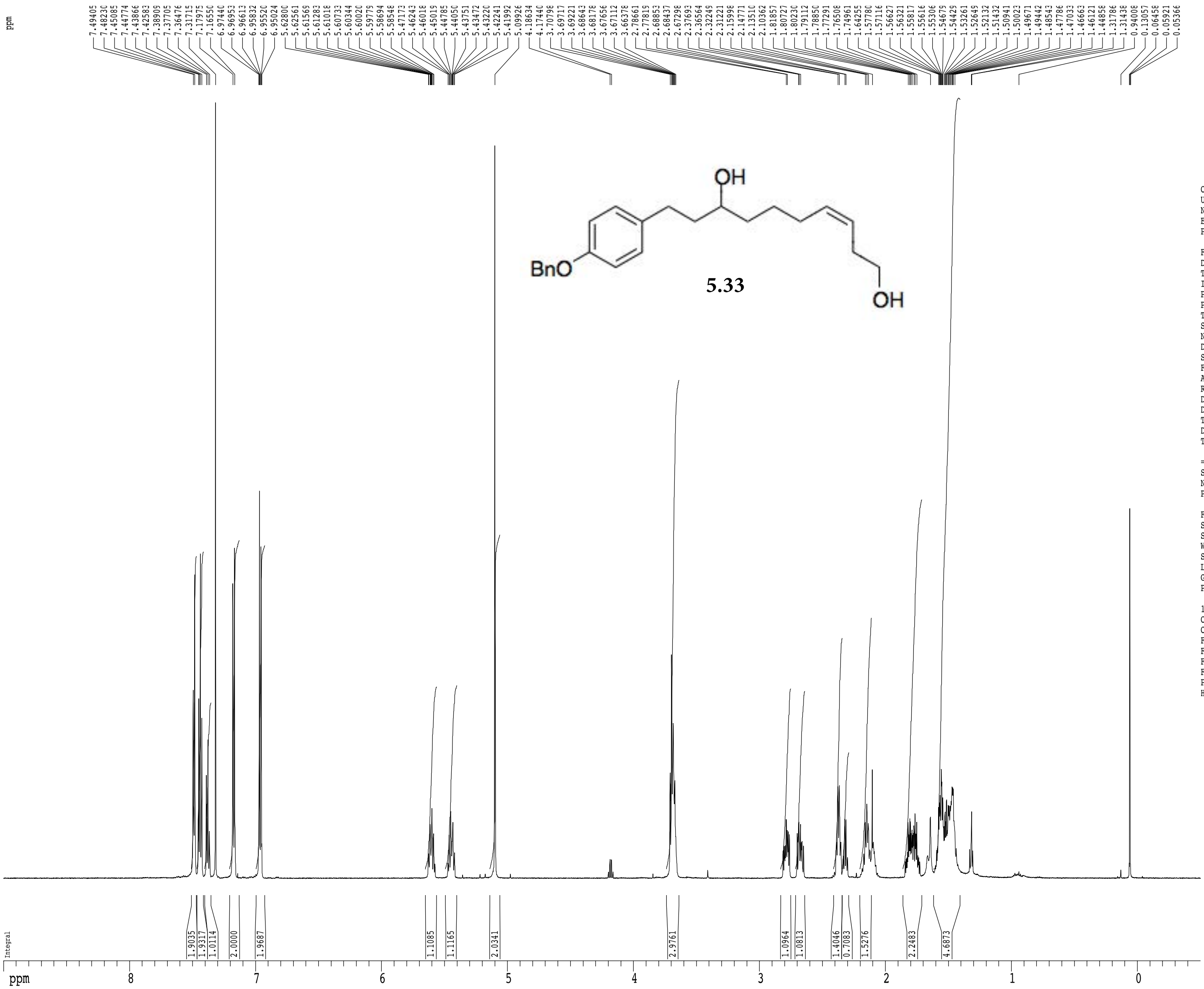
13C spectrum with 1H decoupling



5.32

```
Current Data Parameters
USER              khewitt1
NAME            KAH-V-287-Z
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20220222
Time                 16.44
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                      88
DS                       4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ           1.3566452 sec
RG                   13004
DW              20.700 usec
DE               20.39 usec
TE                 298.0 K
D1          0.10000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                7.90 usec
PL1               -3.00 dB
SFO1       100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            90.00 usec
PL2               -0.90 dB
PL12              17.00 dB
SFO2       400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF         100.6127687 MHz
WDW                     no
SSB                      0
LB                 0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P            229.496 ppm
F1             23090.22 Hz
F2P            -10.579 ppm
F2             -1064.37 Hz
PPMCM       10.52959 ppm/cm
HZCM        1059.41162 Hz/cm
```

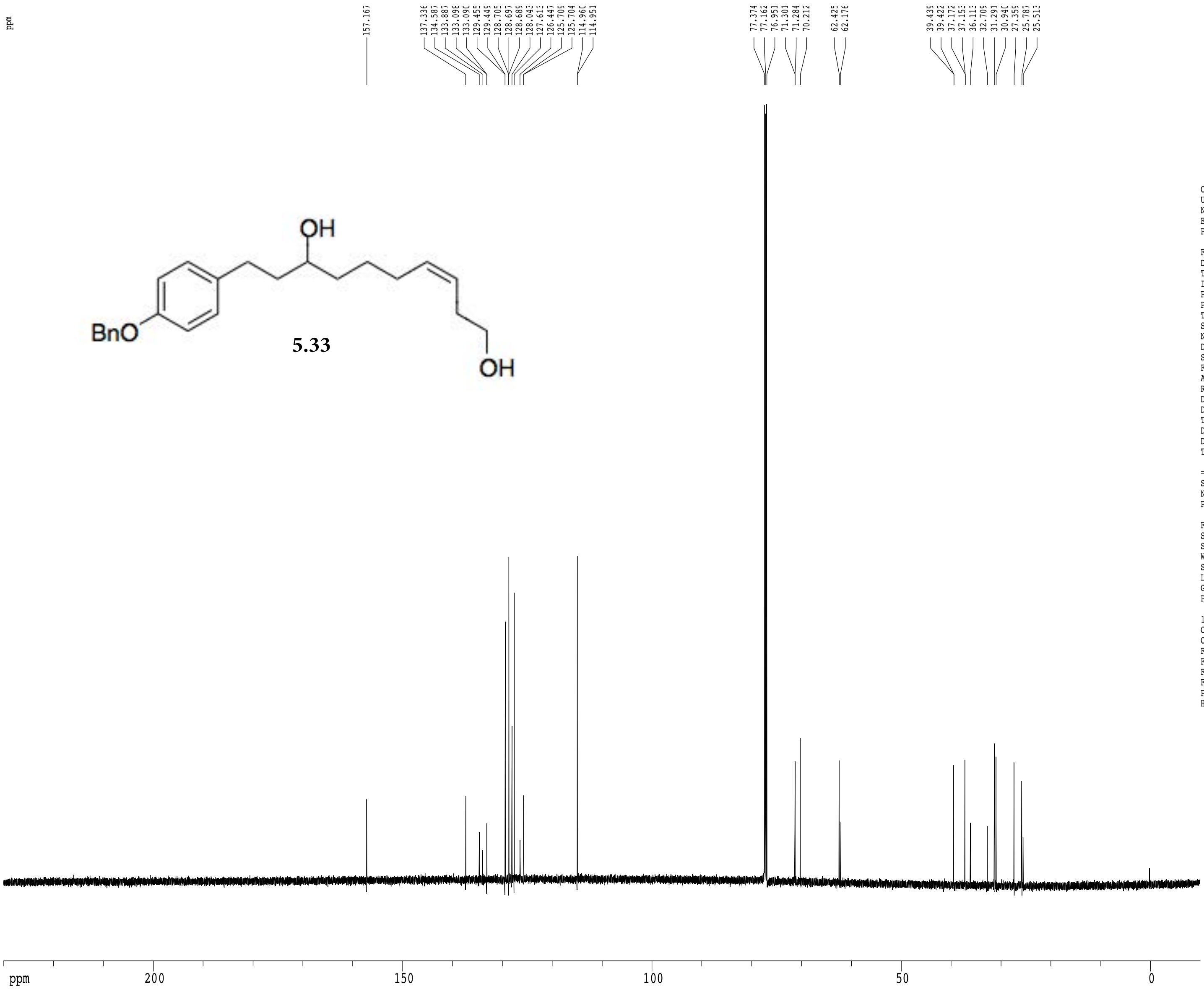
1H spectrum



5.33

```
Current Data Parameters
USER            khewitt1
NAME     KAH-V-291-600-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220225
Time               14.35
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                  25.4
DW                52.000 usec
DE                 14.23 usec
TE                 297.9 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.50 usec

F2 - Processing parameters
SI                 65536
SF          600.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```

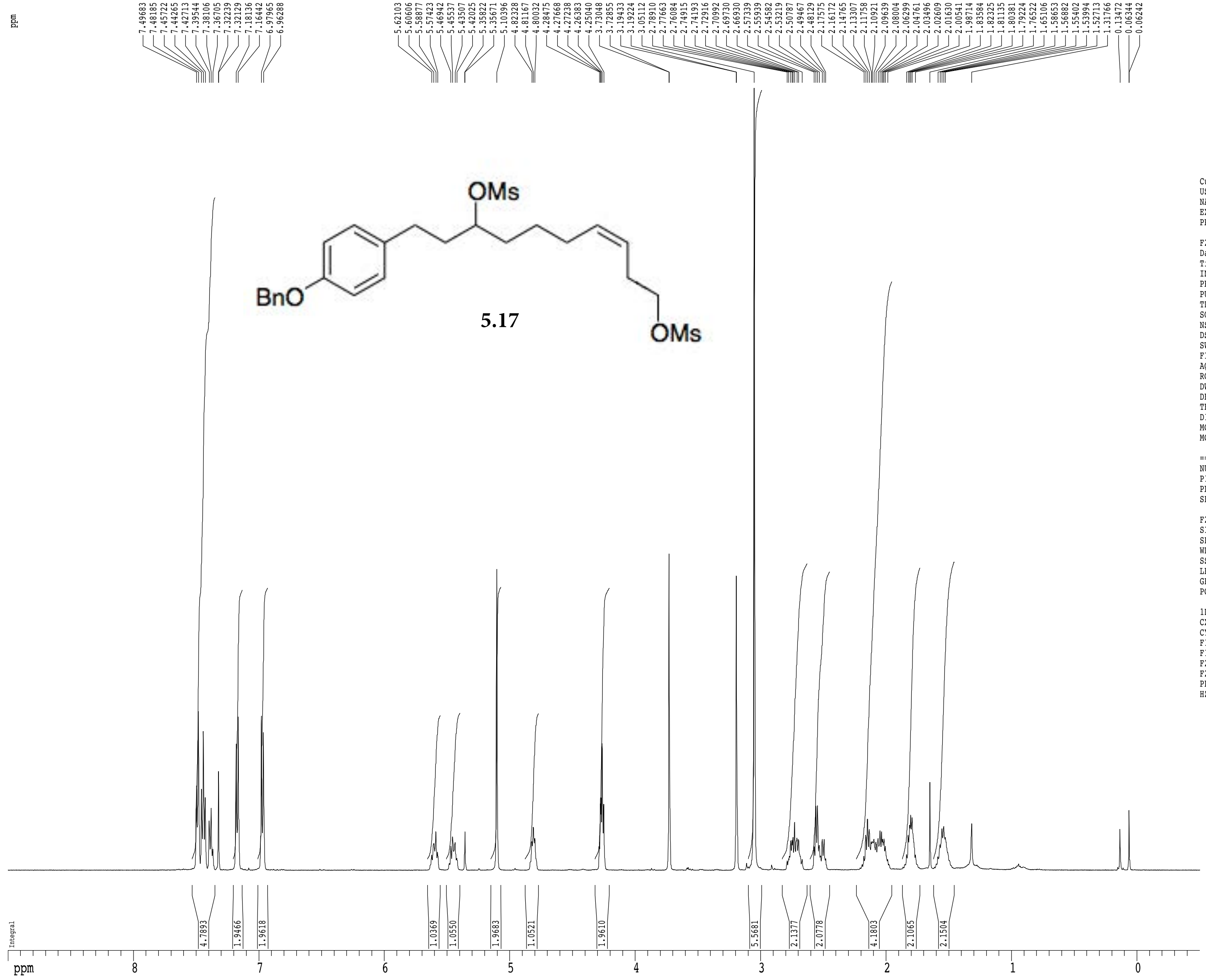
13C spectrum



5.33

```
Current Data Parameters
USER            khewitt1
NAME      KAH-V-291-600-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220225
Time               14.29
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   180
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 297.9 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9027942 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.000 ppm
F1              34707.64 Hz
F2P              -10.000 ppm
F2              -1509.03 Hz
PPMCM           10.52632 ppm/cm
HZCM          1588.45068 Hz/cm
```

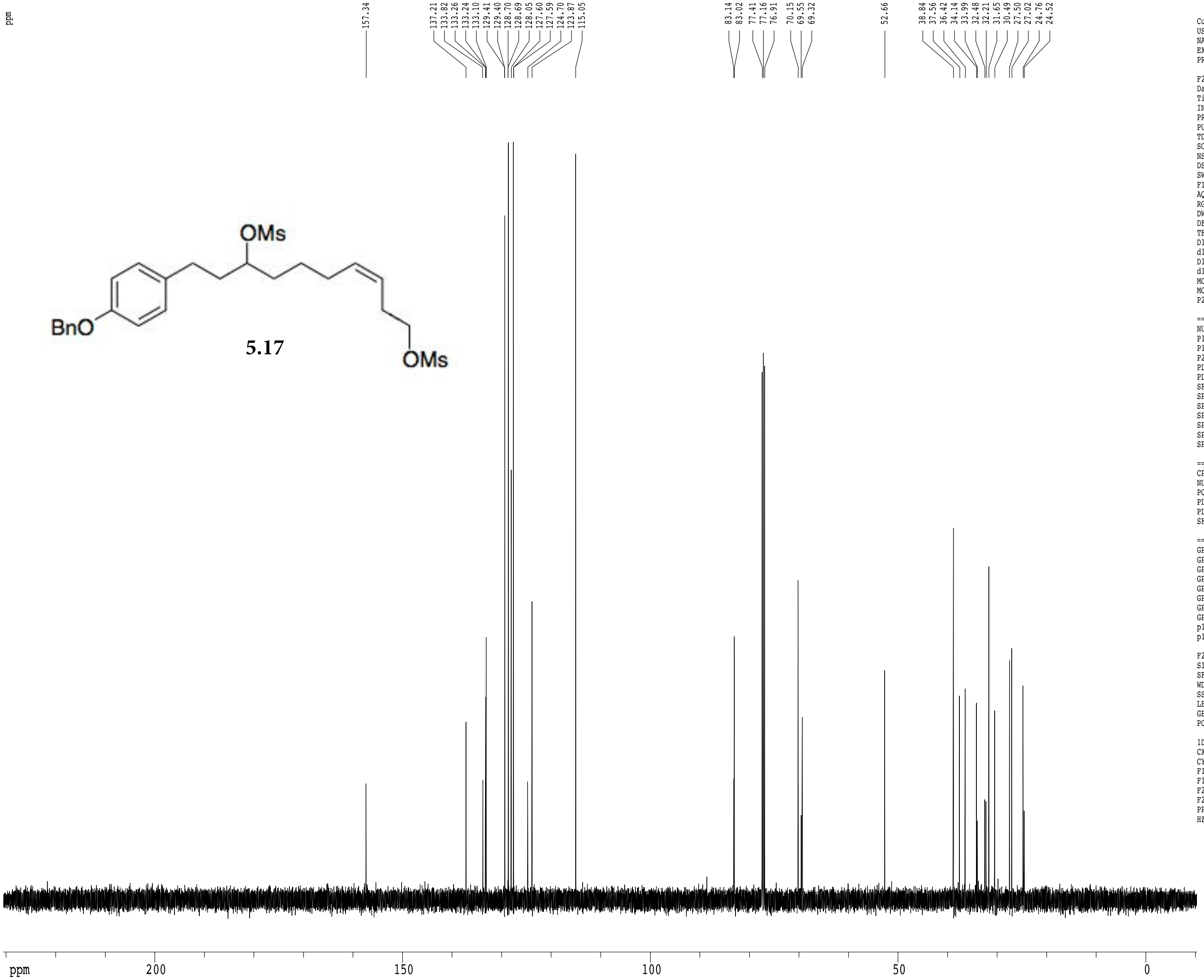
1H spectrum



5.17

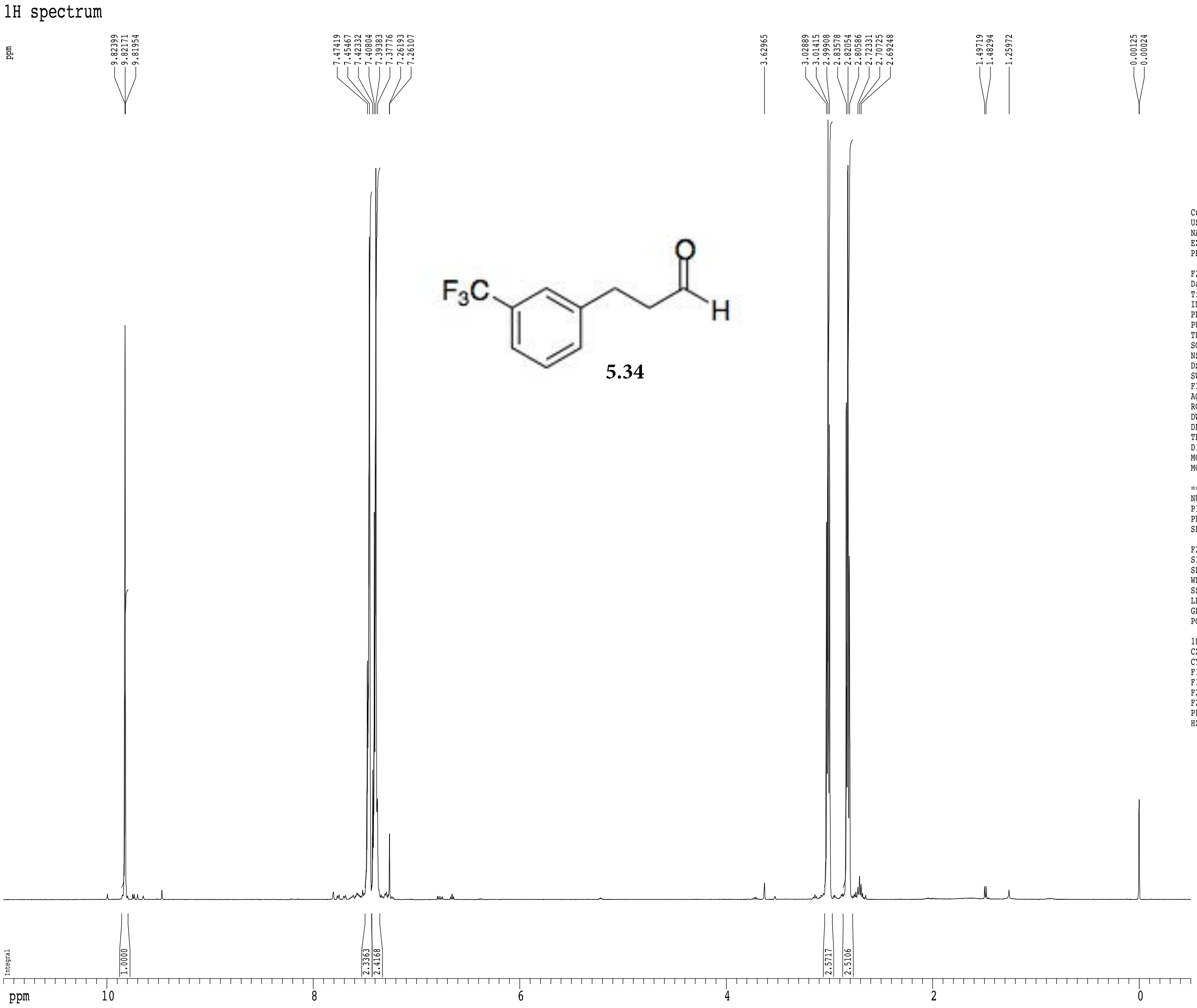
```
Current Data Parameters
USER           khewitt1
NAME        KAH-V-299-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20220226
Time              16.13
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998677 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.75 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42500 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



5.17

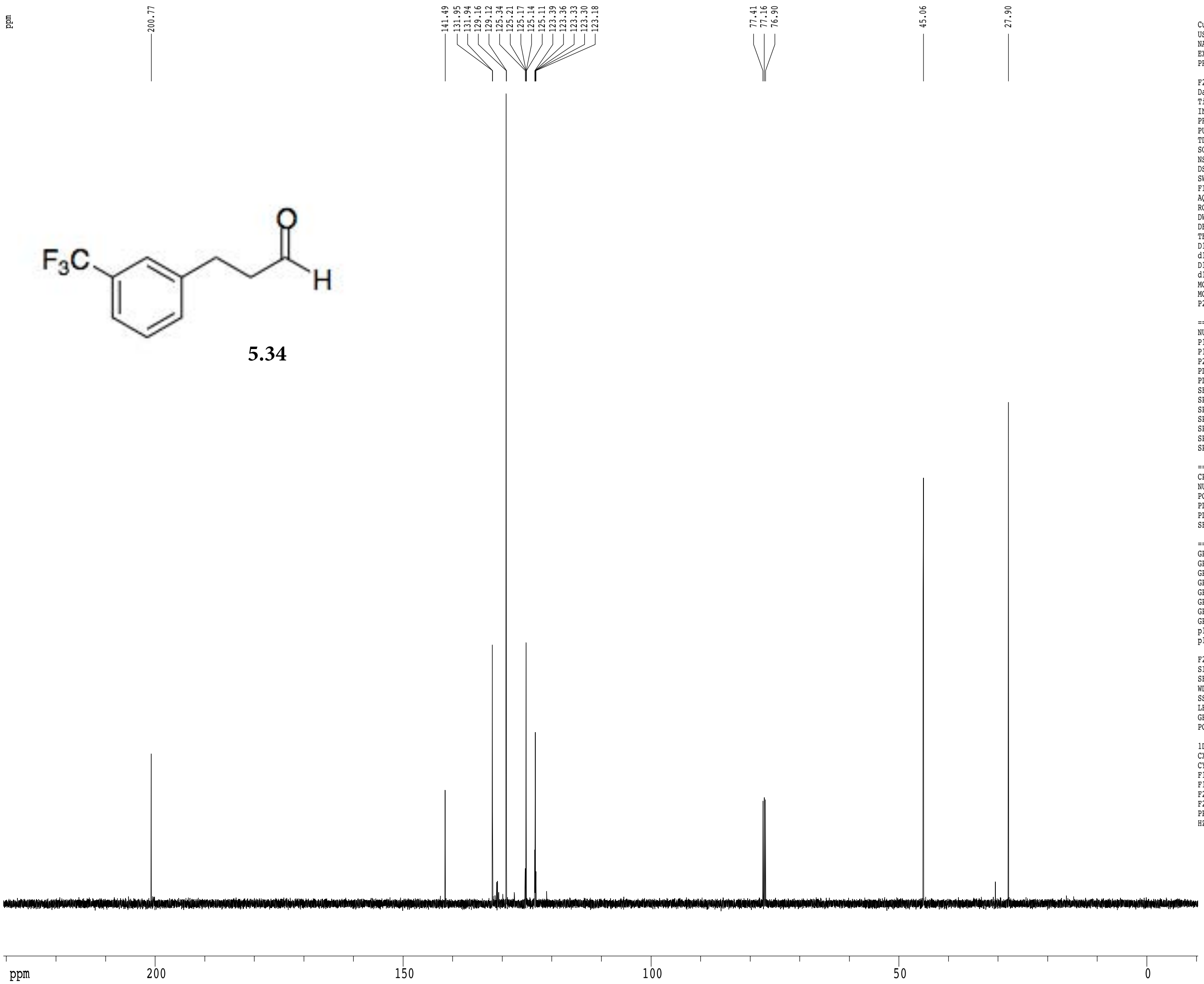
```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-299-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220226
Time               16.16
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   144
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813940 sec
RG                  4096
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804122 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1              29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



5.34

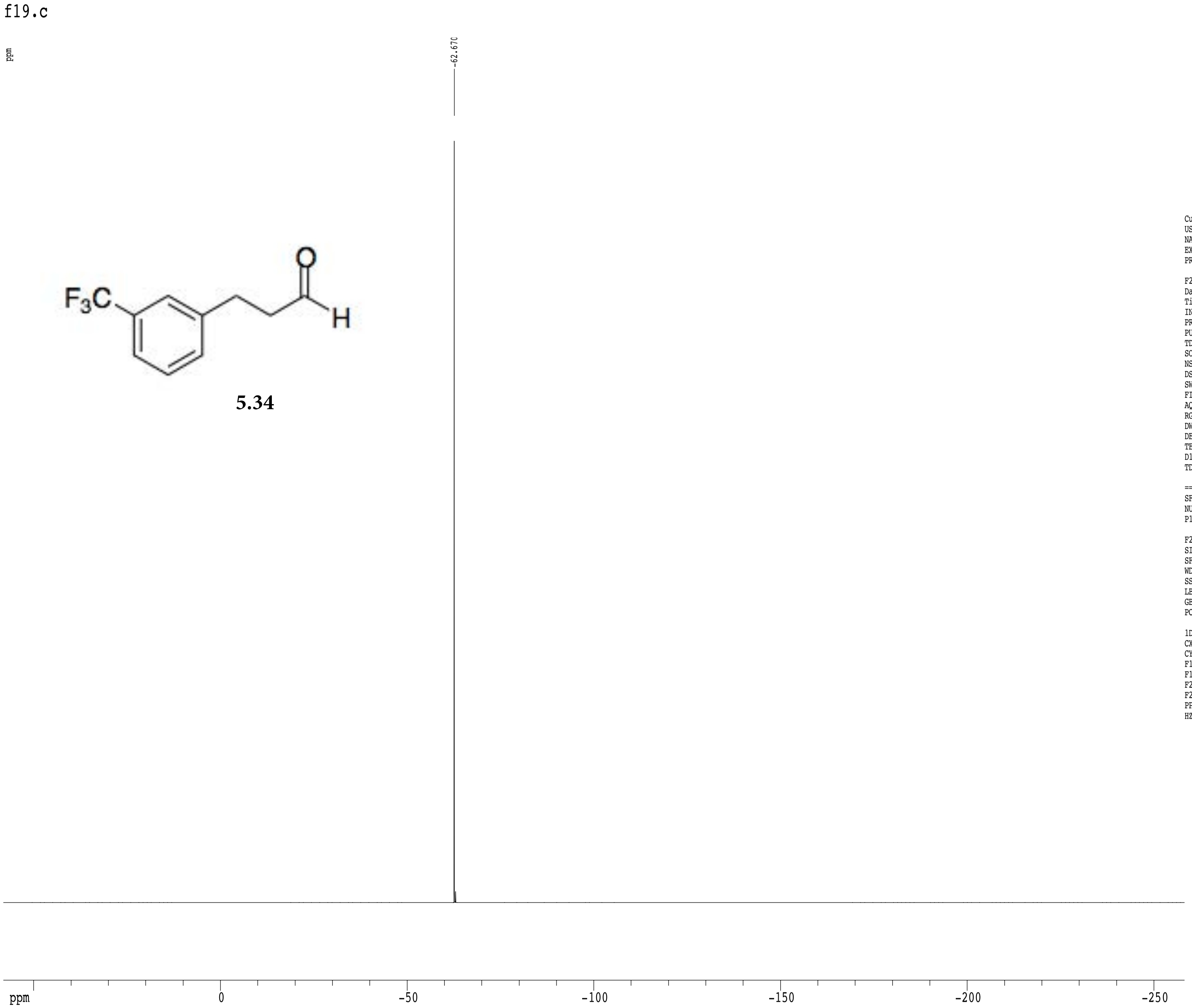
```
Current Data Parameters
USER            khewitt1
NAME        KAH-IV-289-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210621
Time               14.12
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200305 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               11.000 ppm
F1               5502.42 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.50439 ppm/cm
HZCM           252.30397 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



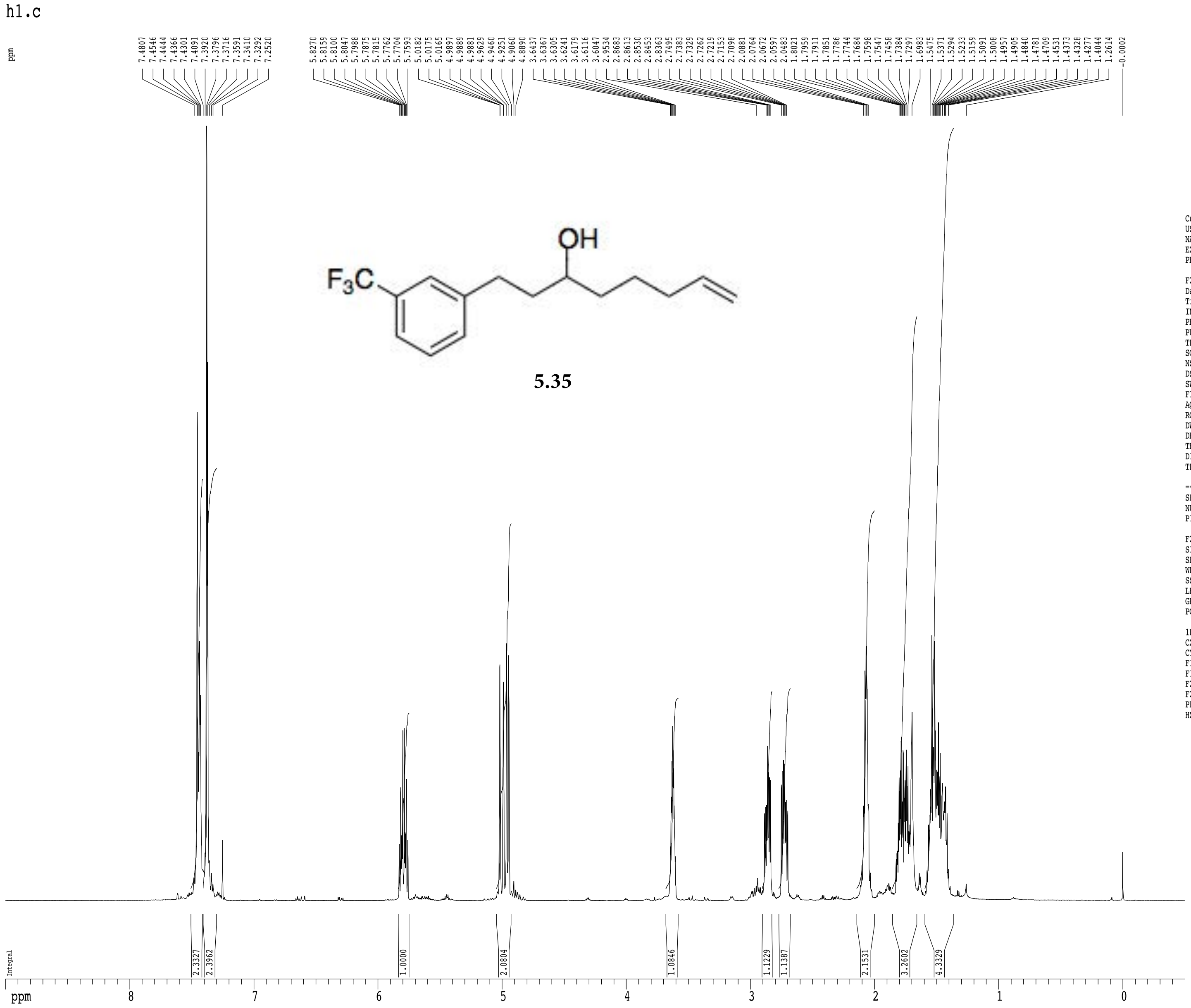
5.34

```
Current Data Parameters
USER            khewitt1
NAME        KAH-IV-289-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210621
Time               14.14
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                 65536
SOLVENT            CDCl3
NS                   176
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 37.70 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 18.85 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 1.55 dB
SP4                 1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               22.00 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              230.637 ppm
F1               29009.68 Hz
F2P              -10.287 ppm
F2              -1293.96 Hz
PPMCM           10.56688 ppm/cm
HZCM          1329.10693 Hz/cm
```



5.34

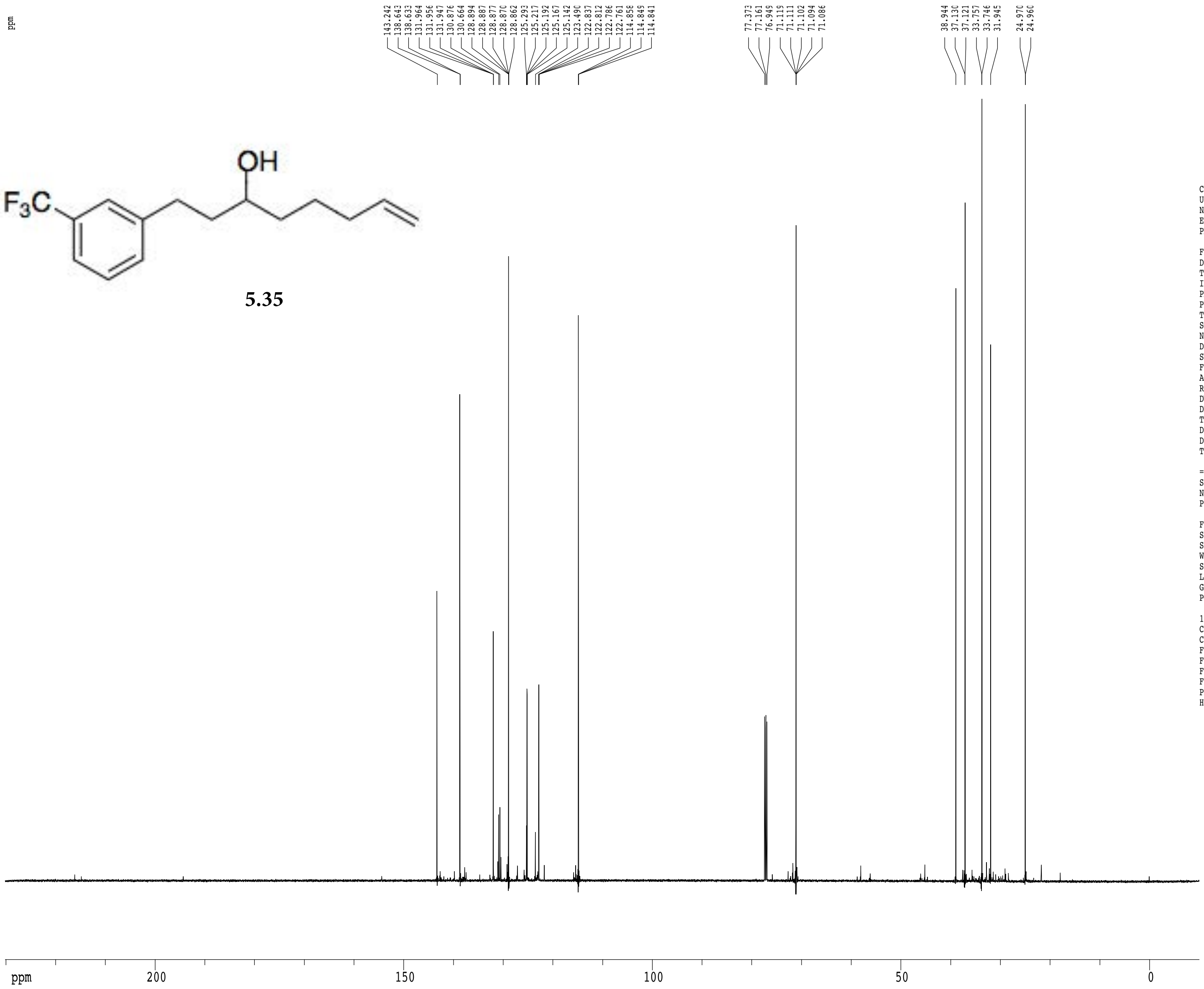
```
Current Data Parameters
USER           khewitt1
NAME        KAH-IV-289-F
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210621
Time               14.54
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgflqn30
TD                131072
SOLVENT           CDCl3T
NS                    16
DS                     2
SWH           178571.422 Hz
FIDRES          1.362392 Hz
AQ             0.3670516 sec
RG                   362
DW                 2.800 usec
DE                 18.00 usec
TE                 298.0 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         564.6299196 MHz
NUC1                 19F
P1                 18.25 usec

F2 - Processing parameters
SI                131072
SF           564.6864196 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               58.060 ppm
F1              32785.75 Hz
F2P             -258.171 ppm
F2            -145785.67 Hz
PPMCM           13.86979 ppm/cm
HZCM          7832.08008 Hz/cm
```



5.35

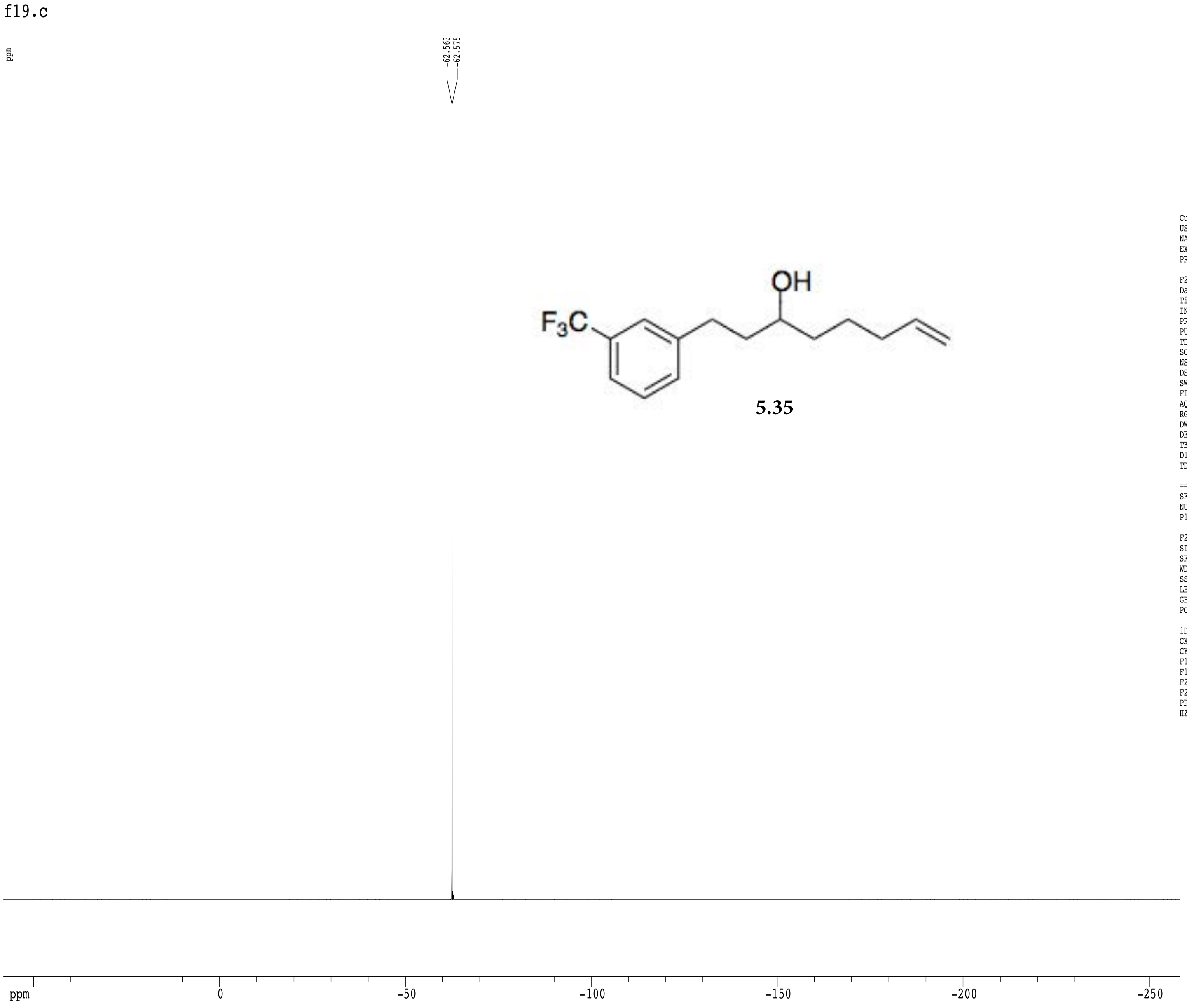
```
Current Data Parameters
USER          khewitt1
NAME       KAH-IV-294-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20210703
Time              12.00
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998979 sec
RG                   10
DW               52.000 usec
DE                14.23 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.50 usec

F2 - Processing parameters
SI                65536
SF          600.1300394 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              5401.17 Hz
F2P              -0.500 ppm
F2              -300.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          250.05420 Hz/cm
```

13C.c



5.35

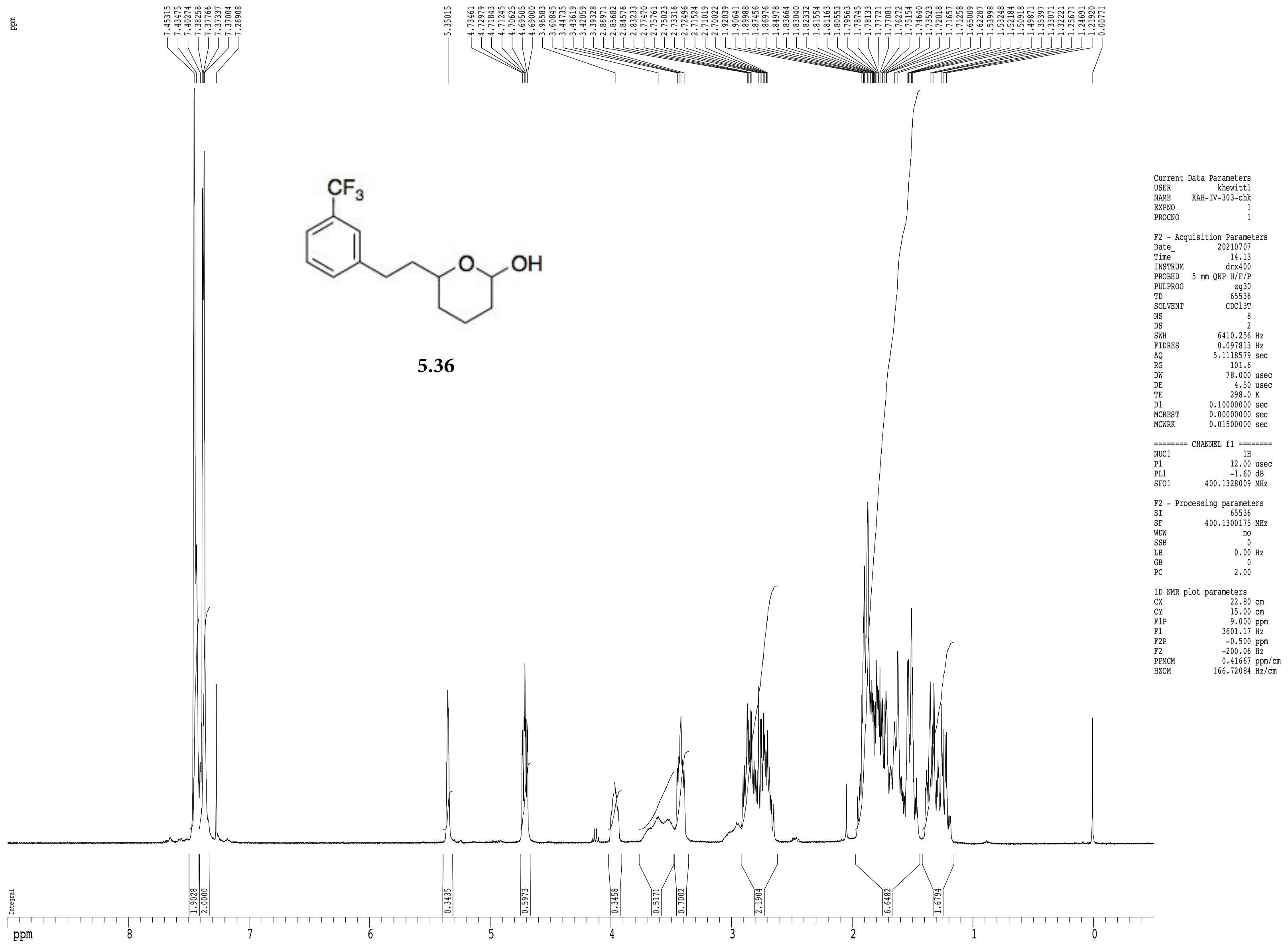
```
Current Data Parameters
USER            khewitt1
NAME         KAH-IV-294-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210703
Time               11.56
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                   157
DS                     4
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF           150.9027986 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.117 ppm
F1              34725.34 Hz
F2P               -9.984 ppm
F2              -1506.54 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11780 Hz/cm
```



5.35

```
Current Data Parameters
USER           khewitt1
NAME       KAH-IV-294-Z
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20210703
Time              12.04
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgflqn30
TD               131072
SOLVENT          CDCl3T
NS                   16
DS                    2
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                  256
DW                2.800 usec
DE                18.00 usec
TE                298.0 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        564.6299196 MHz
NUC1                19F
P1                18.25 usec

F2 - Processing parameters
SI               131072
SF          564.6864253 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              58.050 ppm
F1             32780.04 Hz
F2P            -258.181 ppm
F2           -145791.39 Hz
PPMCM          13.86979 ppm/cm
HZCM         7832.08008 Hz/cm
```

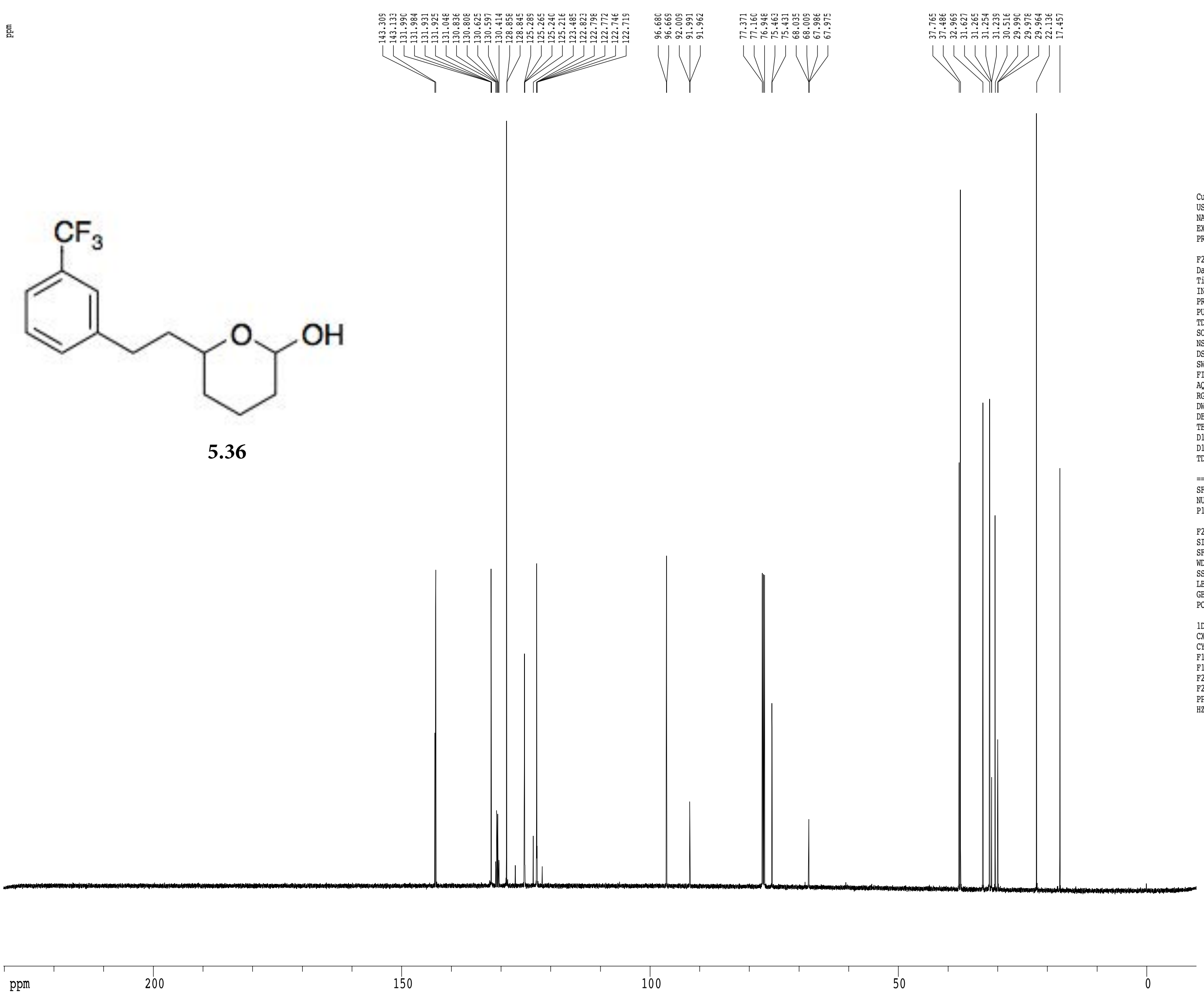
1H spectrum



5.36

```
Current Data Parameters
USER              khewitt1
NAME     KAH-IV-303-chk
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20210707
Time                 14.13
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   65536
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ             5.1118579 sec
RG                   101.6
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -1.60 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF           400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             166.72084 Hz/cm
```

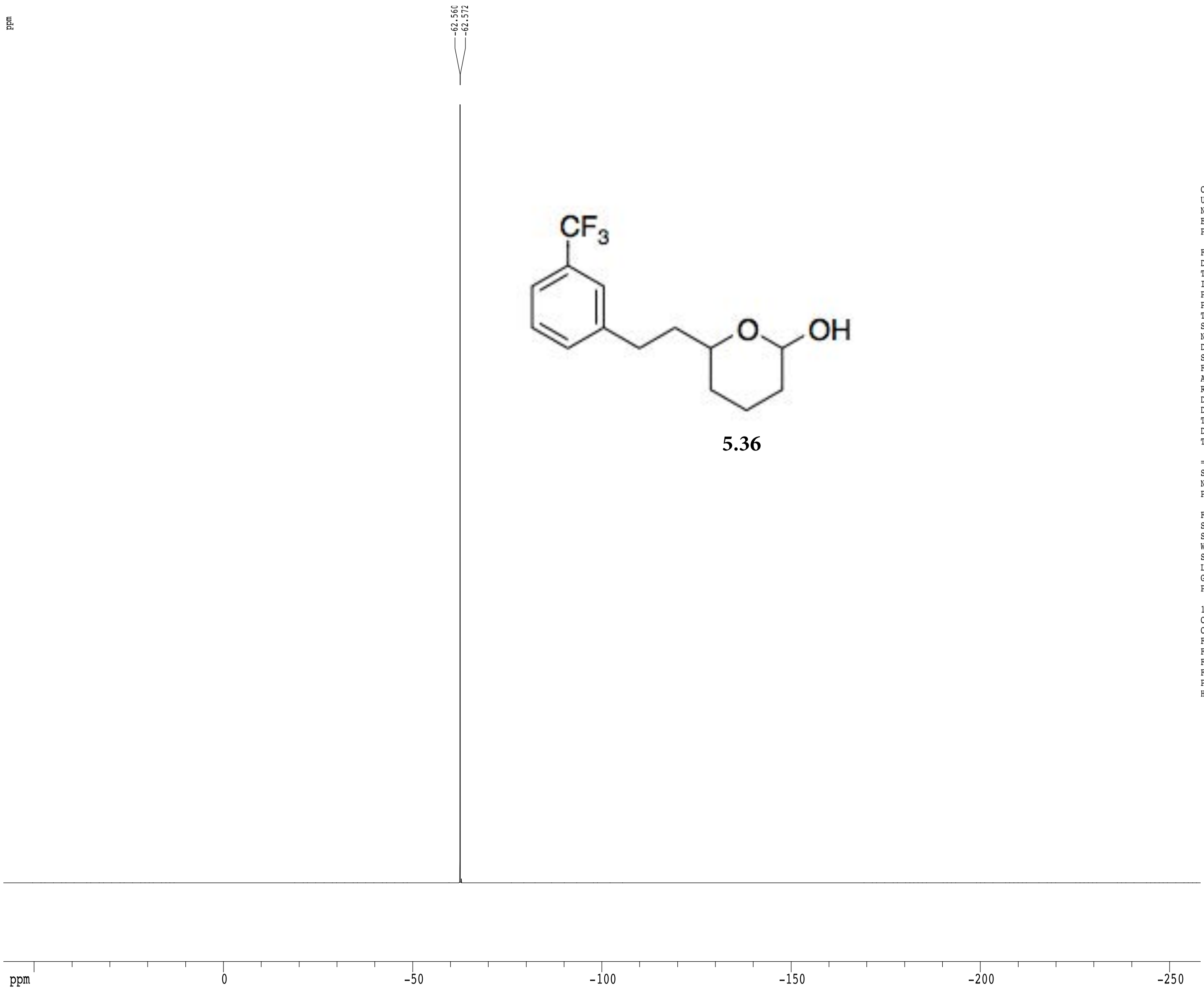
C13.c



5.36

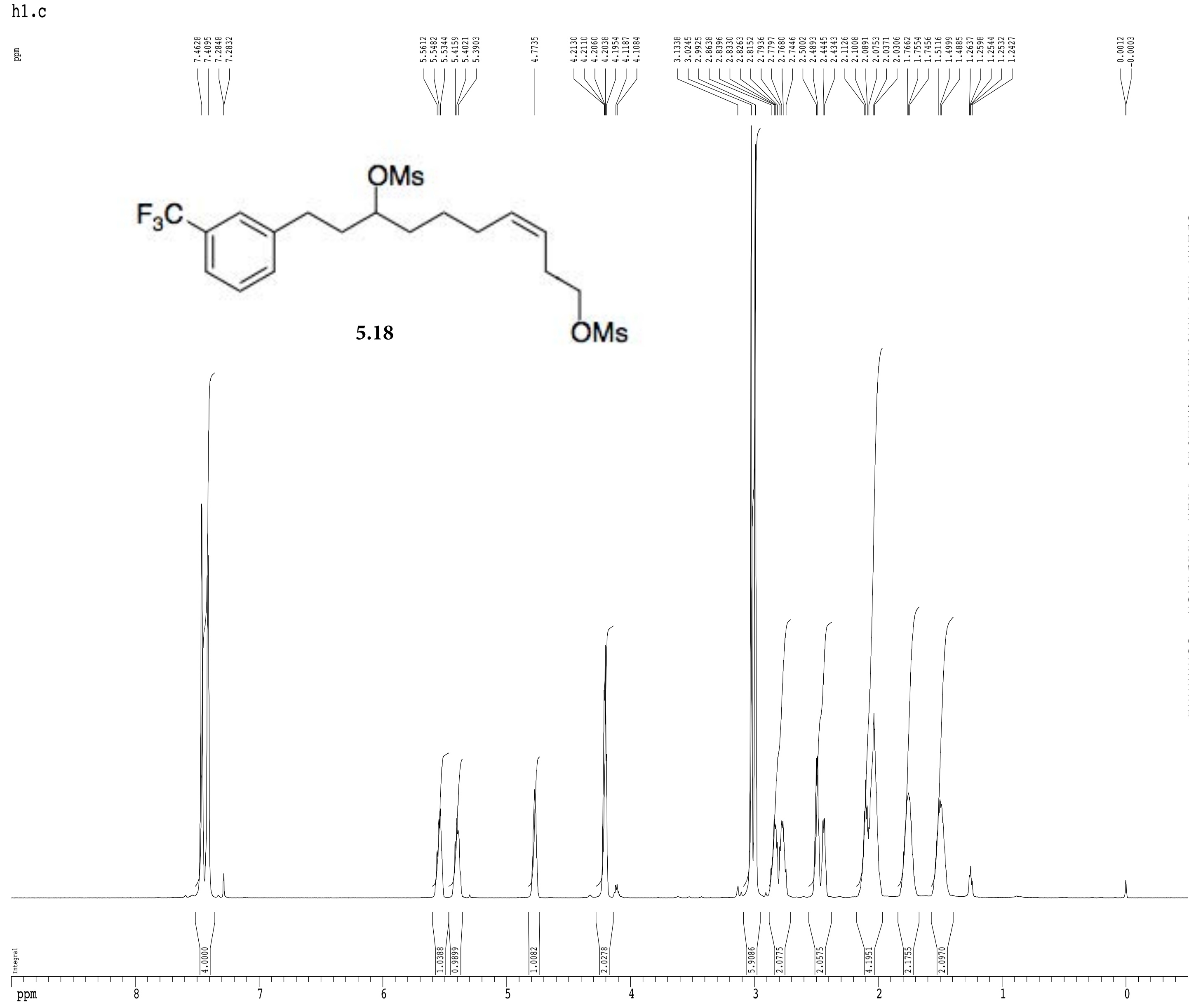
```
Current Data Parameters
USER           khewitt1
NAME        KAH-IV-303-Z
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210707
Time              15.42
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  471
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9027975 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             230.125 ppm
F1             34726.45 Hz
F2P              -9.976 ppm
F2             -1505.43 Hz
PPMCM          10.53074 ppm/cm
HZCM         1589.11780 Hz/cm
```

f19.c



5.36

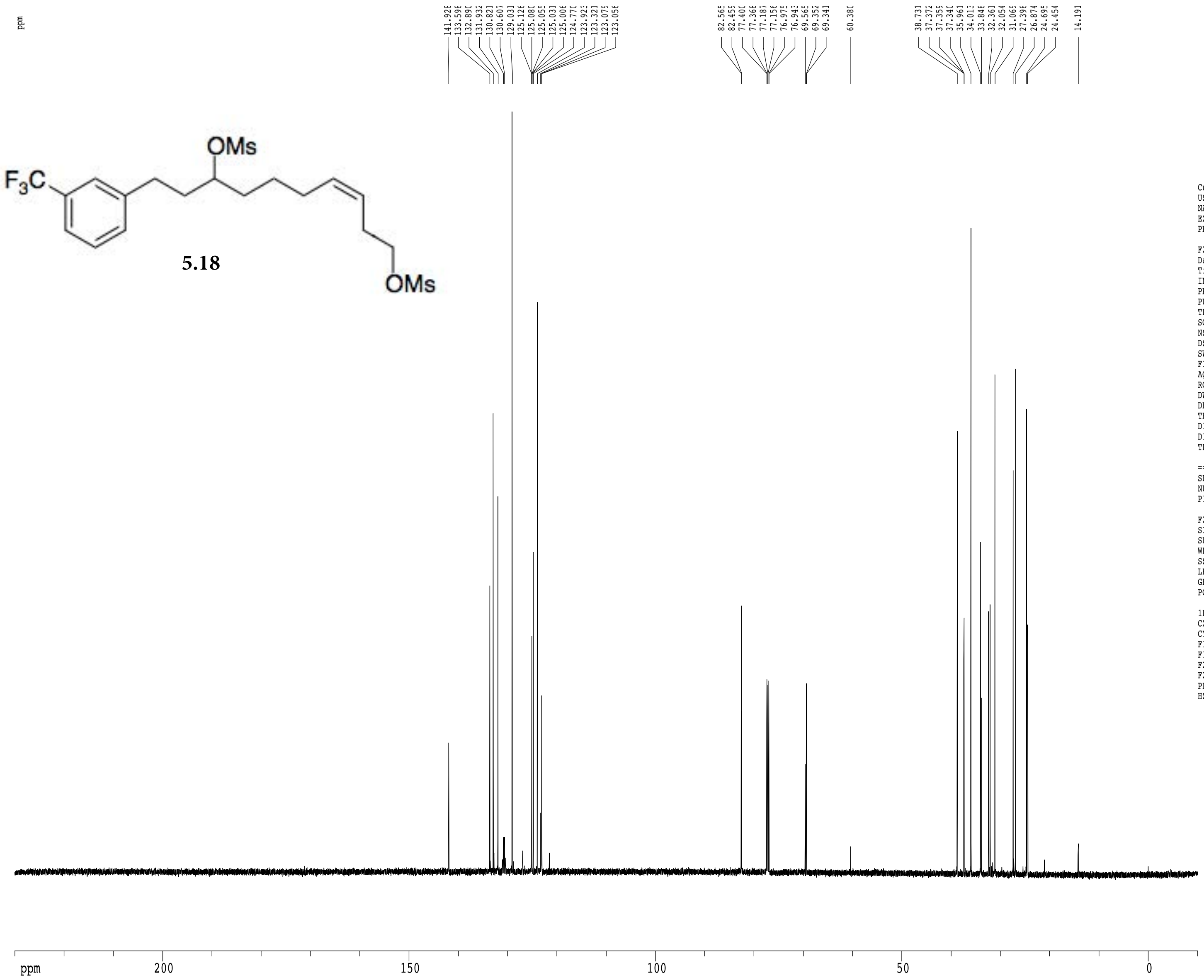
```
Current Data Parameters
USER            khewitt1
NAME         KAH-IV-303-Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210707
Time               15.59
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgflqn30
TD                131072
SOLVENT           CDCl3T
NS                    16
DS                     2
SWH           178571.422 Hz
FIDRES          1.362392 Hz
AQ             0.3670516 sec
RG                   362
DW                 2.800 usec
DE                 18.00 usec
TE                 298.0 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         564.6299196 MHz
NUC1                 19F
P1                 18.25 usec

F2 - Processing parameters
SI                131072
SF           564.6864190 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               58.061 ppm
F1              32786.34 Hz
F2P             -258.170 ppm
F2            -145785.09 Hz
PPMCM           13.86979 ppm/cm
HZCM          7832.08057 Hz/cm
```



5.18

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-025-Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210713
Time               14.04
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                    10
DW                52.000 usec
DE                 14.23 usec
TE                 298.0 K
D1          0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  9.50 usec

F2 - Processing parameters
SI                 65536
SF          600.1300203 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               5401.17 Hz
F2P               -0.500 ppm
F2               -300.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           250.05418 Hz/cm
```

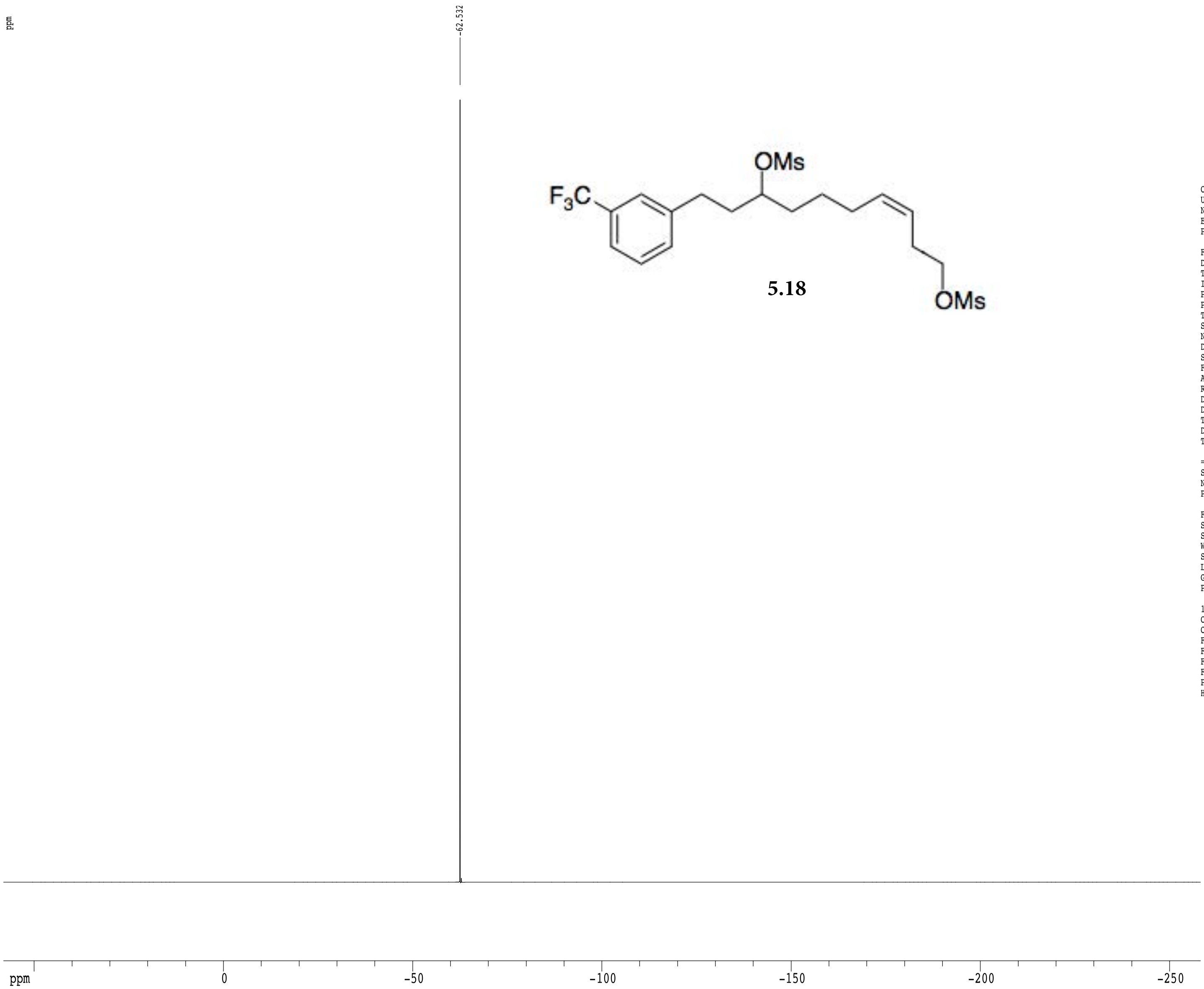
c13.c



5.18

```
Current Data Parameters
USER          khewitt1
NAME        KAH-V-025-Z
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20210713
Time              13.57
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT          CDCl3T
NS                  128
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9044468 sec
RG                 2050
DW               13.800 usec
DE                19.63 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.10 usec

F2 - Processing parameters
SI                65536
SF          150.9028113 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P             230.033 ppm
F1             34712.62 Hz
F2P             -10.068 ppm
F2             -1519.26 Hz
PPMCM          10.53074 ppm/cm
HZCM         1589.11768 Hz/cm
```

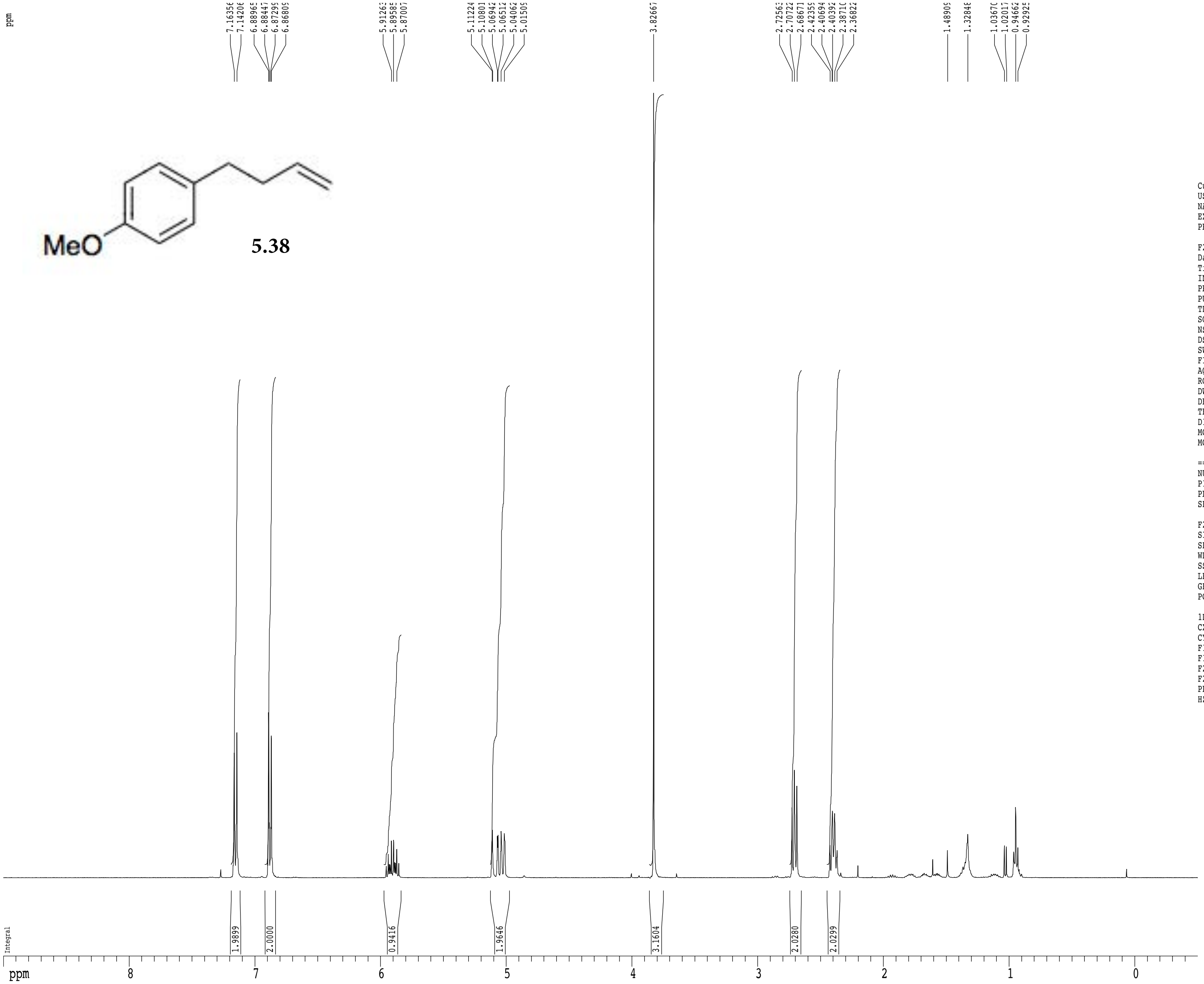
19F Spectrum



5.18

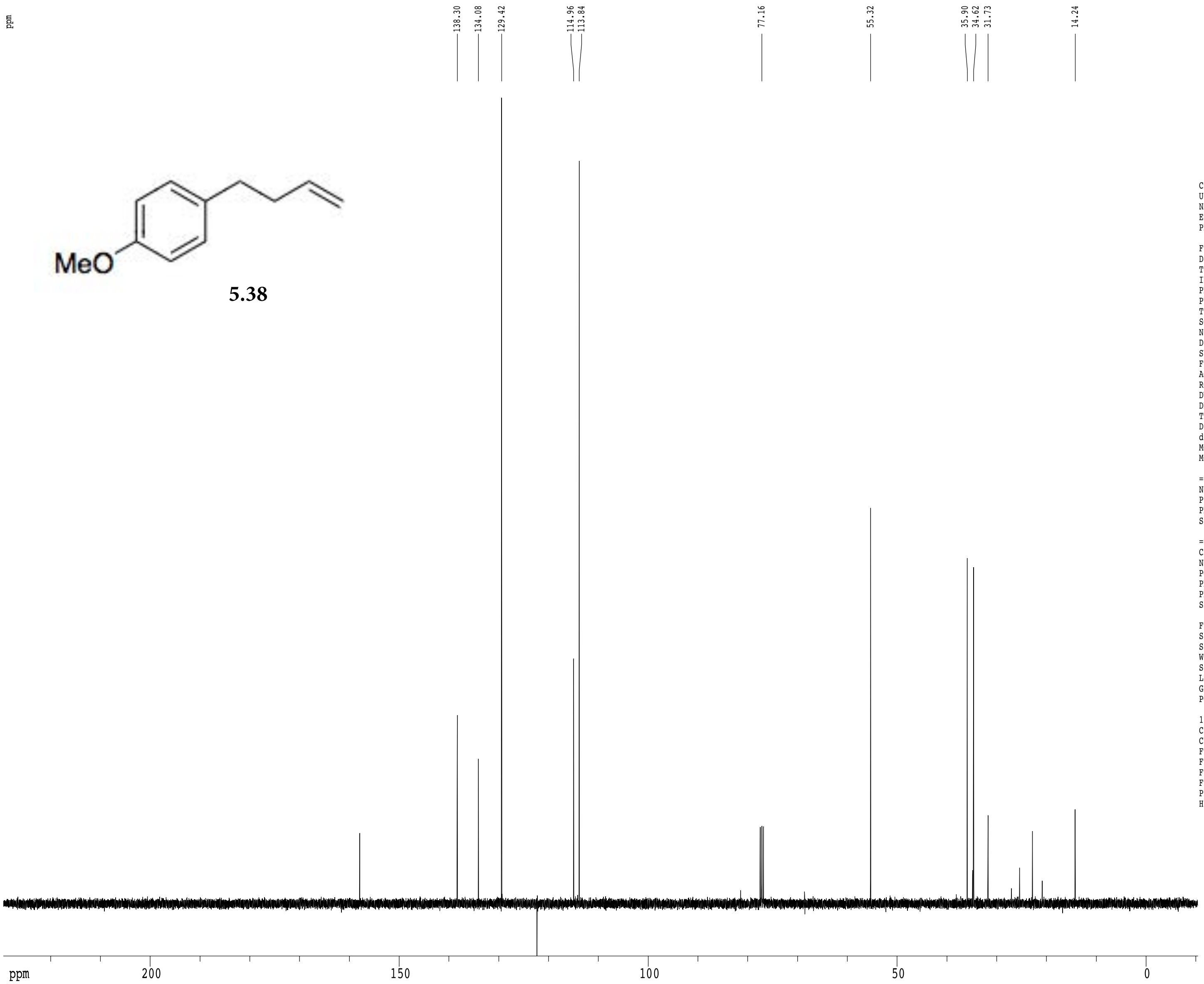
```
Current Data Parameters
USER           khewitt1
NAME        KAH-V-025-F
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20220117
Time              17.13
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgflqn30
TD               131072
SOLVENT          CDCl3T
NS                   16
DS                    2
SWH          178571.422 Hz
FIDRES         1.362392 Hz
AQ            0.3670516 sec
RG                  575
DW                2.800 usec
DE                18.00 usec
TE                298.0 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        564.6299196 MHz
NUC1                19F
P1                18.25 usec

F2 - Processing parameters
SI               131072
SF          564.6864101 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              58.077 ppm
F1             32795.21 Hz
F2P            -258.154 ppm
F2           -145776.22 Hz
PPMCM          13.86979 ppm/cm
HZCM         7832.08057 Hz/cm
```

1H spectrum


5.38

```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-116-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210929
Time               18.03
INSTRUM           drx400
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                  71.8
DW                78.000 usec
DE                  4.50 usec
TE                 297.9 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

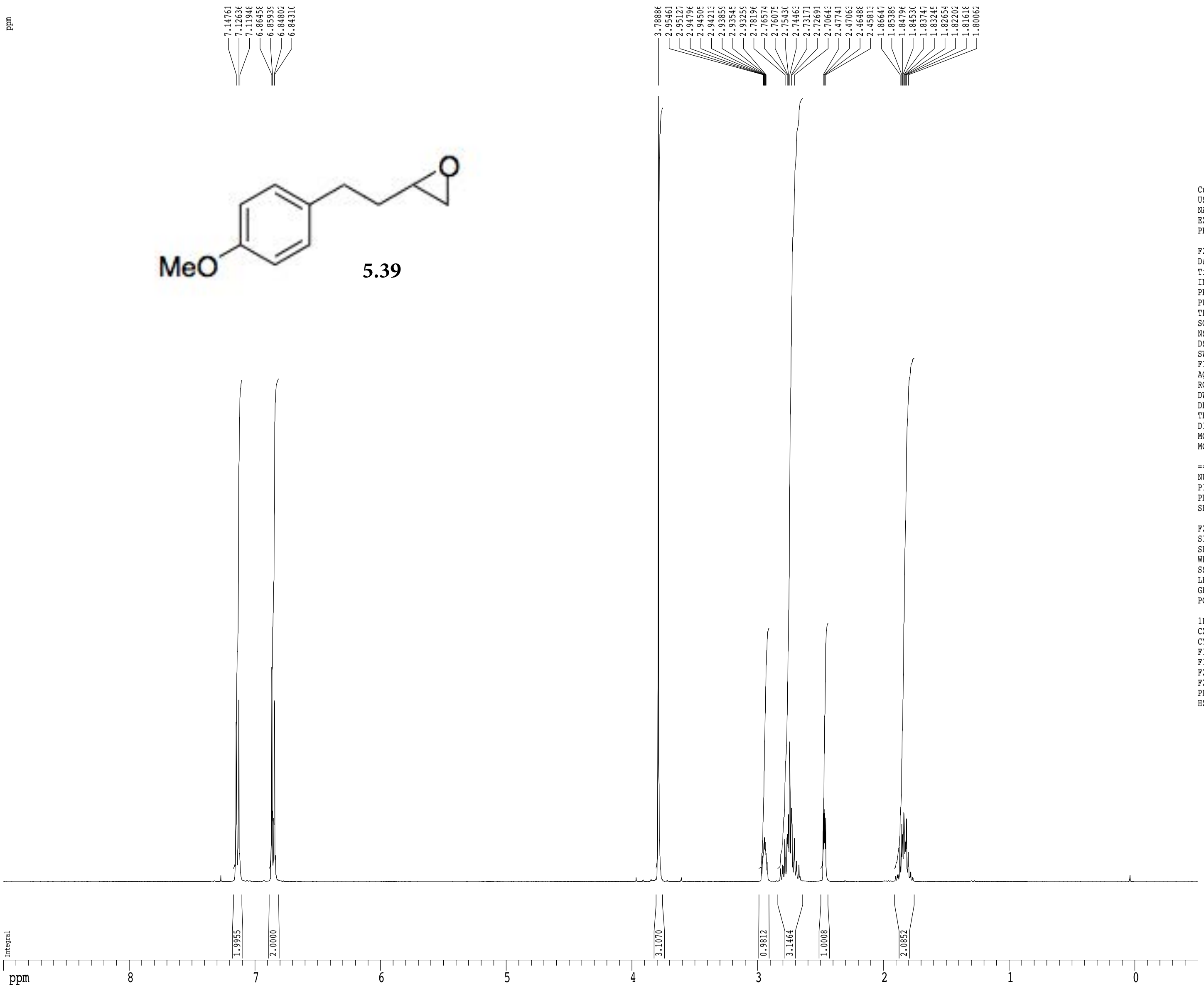
13C spectrum with 1H decoupling



5.38

```
Current Data Parameters
USER              khewitt1
NAME            KAH-V-116-1
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20210929
Time                  18.05
INSTRUM              drx400
PROBHD   5 mm Multinucl
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl3
NS                      136
DS                        4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                   9195.2
DW                  20.700 usec
DE                   20.39 usec
TE                   297.9 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.00 usec
PL1                   -2.50 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -1.10 dB
PL12                  15.60 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                    65536
SF          100.6127632 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    22.80 cm
CY                    15.50 cm
F1P                 229.496 ppm
F1                 23090.21 Hz
F2P                 -10.579 ppm
F2                 -1064.37 Hz
PPMCM              10.52959 ppm/cm
HZCM             1059.41150 Hz/cm
```

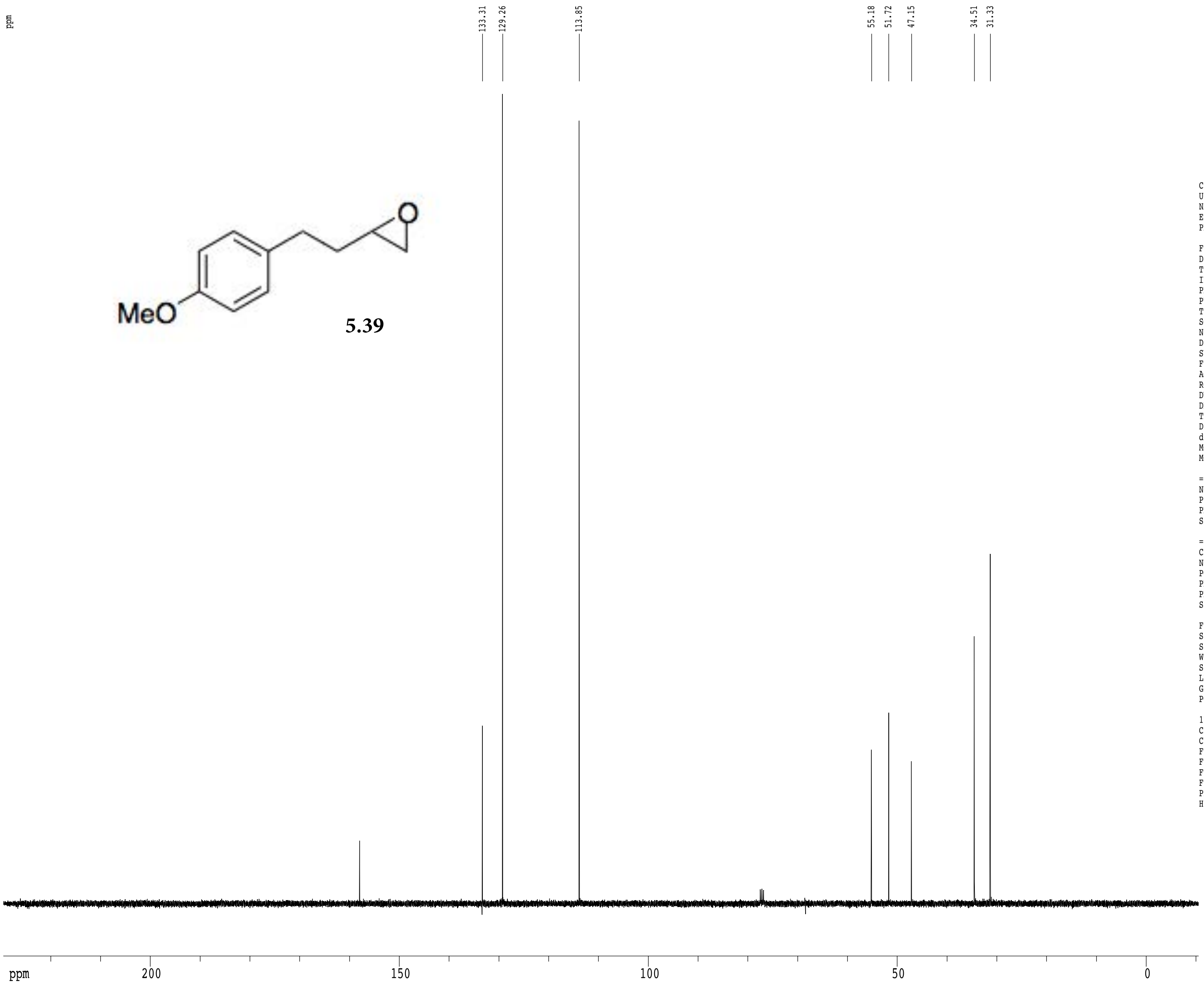
1H spectrum



5.39

```
Current Data Parameters
USER              khewitt1
NAME           KAH-V-117-Z
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211004
Time                 14.24
INSTRUM             drx400
PROBHD   5 mm Multinucl
PULPROG               zg30
TD                   38460
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               6410.256 Hz
FIDRES            0.166673 Hz
AQ               2.9999299 sec
RG                    45.3
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -1.10 dB
SFO1           400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             166.72084 Hz/cm
```

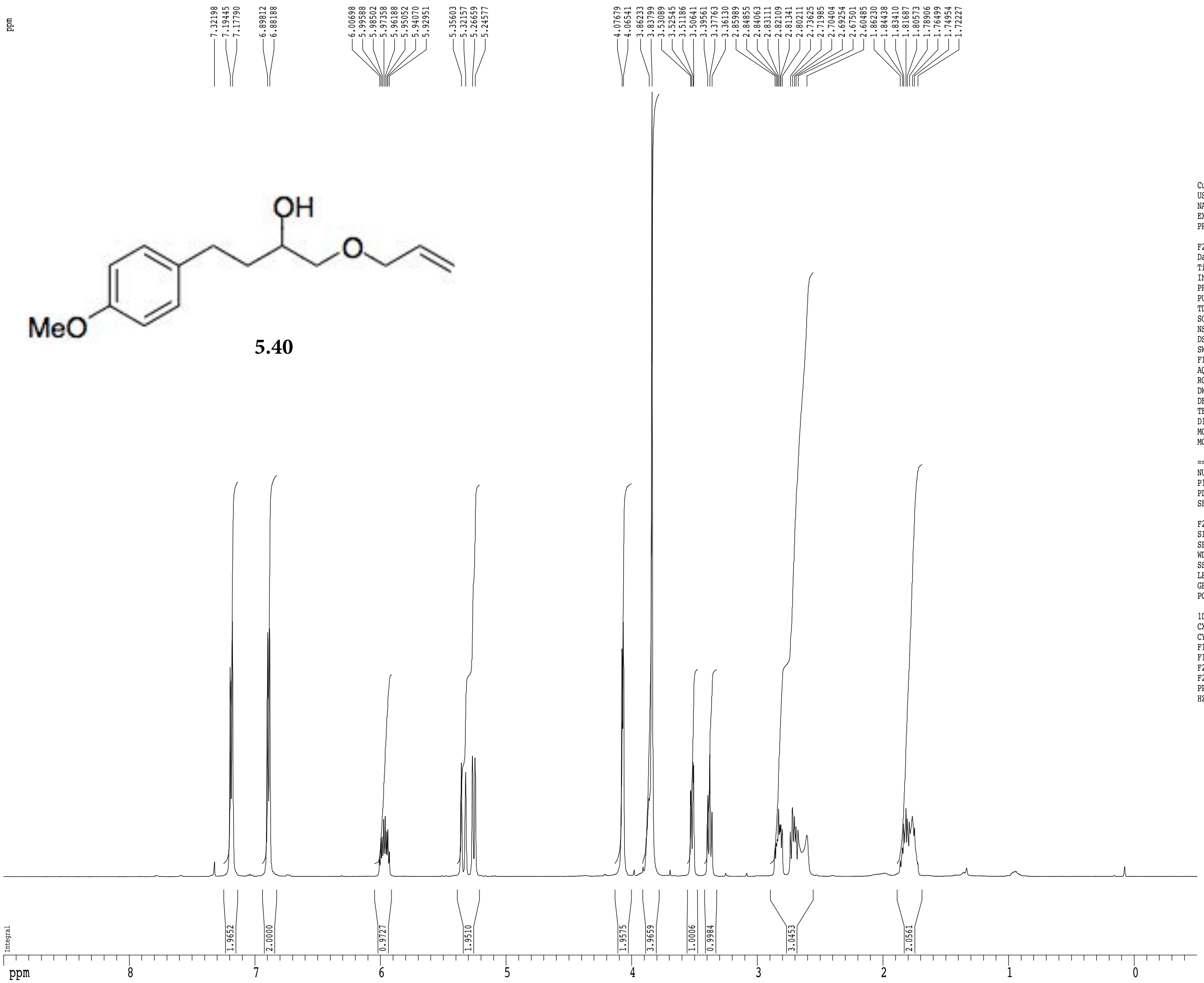
13C spectrum with 1H decoupling



5.39

```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-117-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20211004
Time              14.26
INSTRUM          drx400
PROBHD   5 mm Multinucl
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                   88
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG                13004
DW               20.700 usec
DE                20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.00 usec
PL1               -2.50 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -1.10 dB
PL12              15.60 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          100.6127750 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P             229.496 ppm
F1             23090.22 Hz
F2P             -10.579 ppm
F2             -1064.37 Hz
PPMCM          10.52959 ppm/cm
HZCM         1059.41174 Hz/cm
```

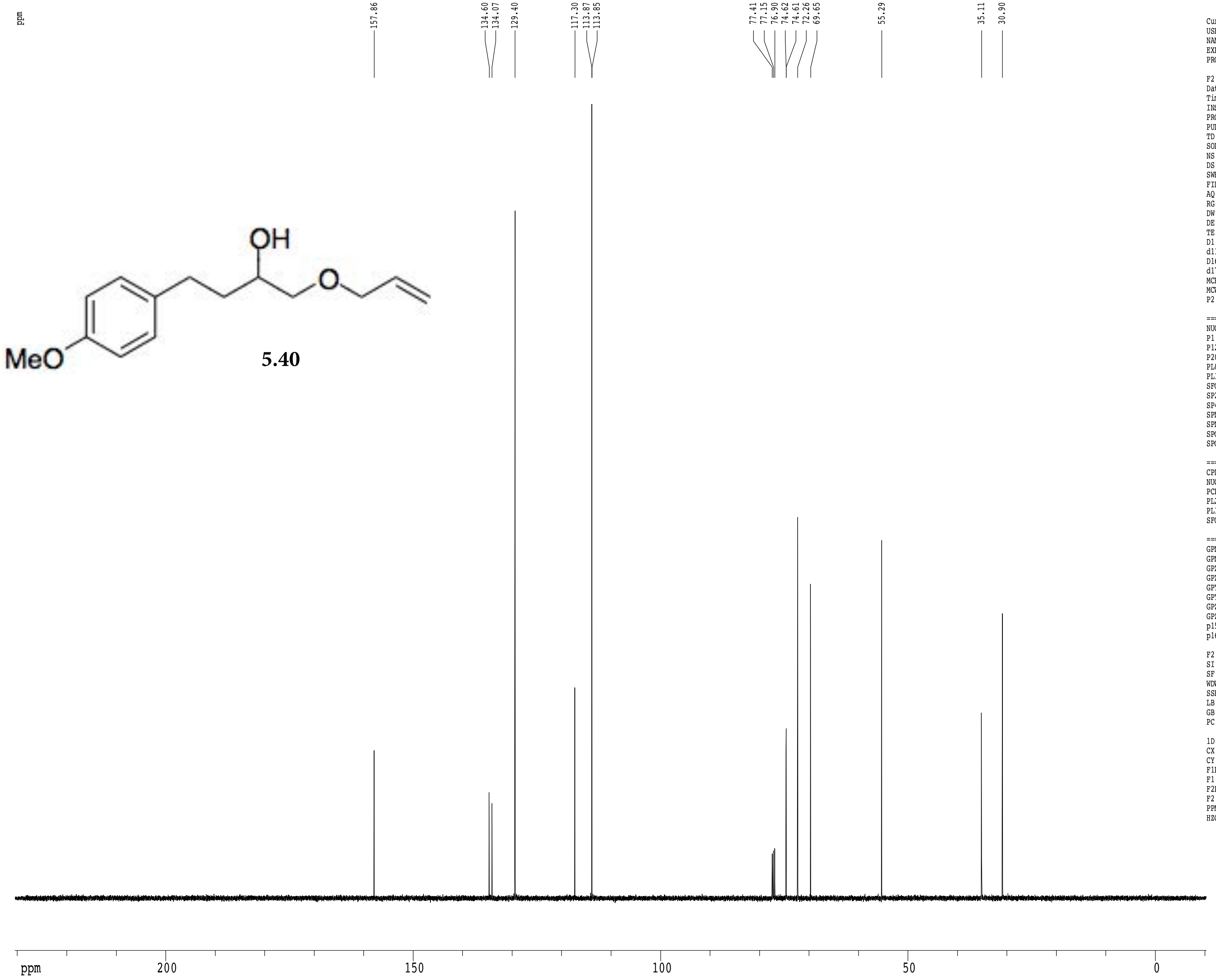
1H spectrum



5.40

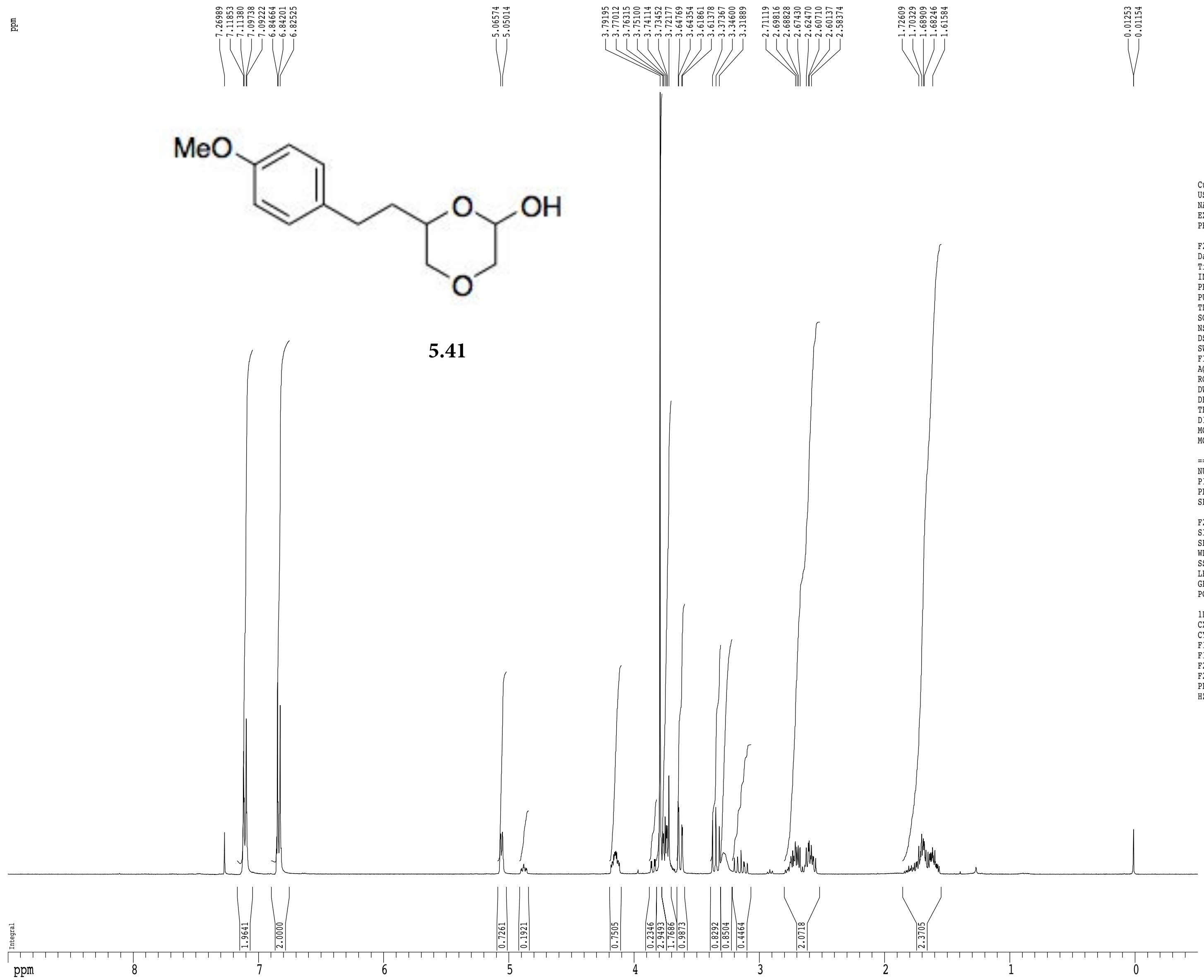
```
Current Data Parameters
USER              khewitt1
NAME           KAH-V-122-Z
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211008
Time                 14.43
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998774 sec
RG                     4.5
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.75 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 4501.98 Hz
F2P                 -0.500 ppm
F2                 -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42500 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling


5.40

```
Current Data Parameters
USER          khewitt1
NAME        KAH-V-122-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20211008
Time              14.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                   88
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

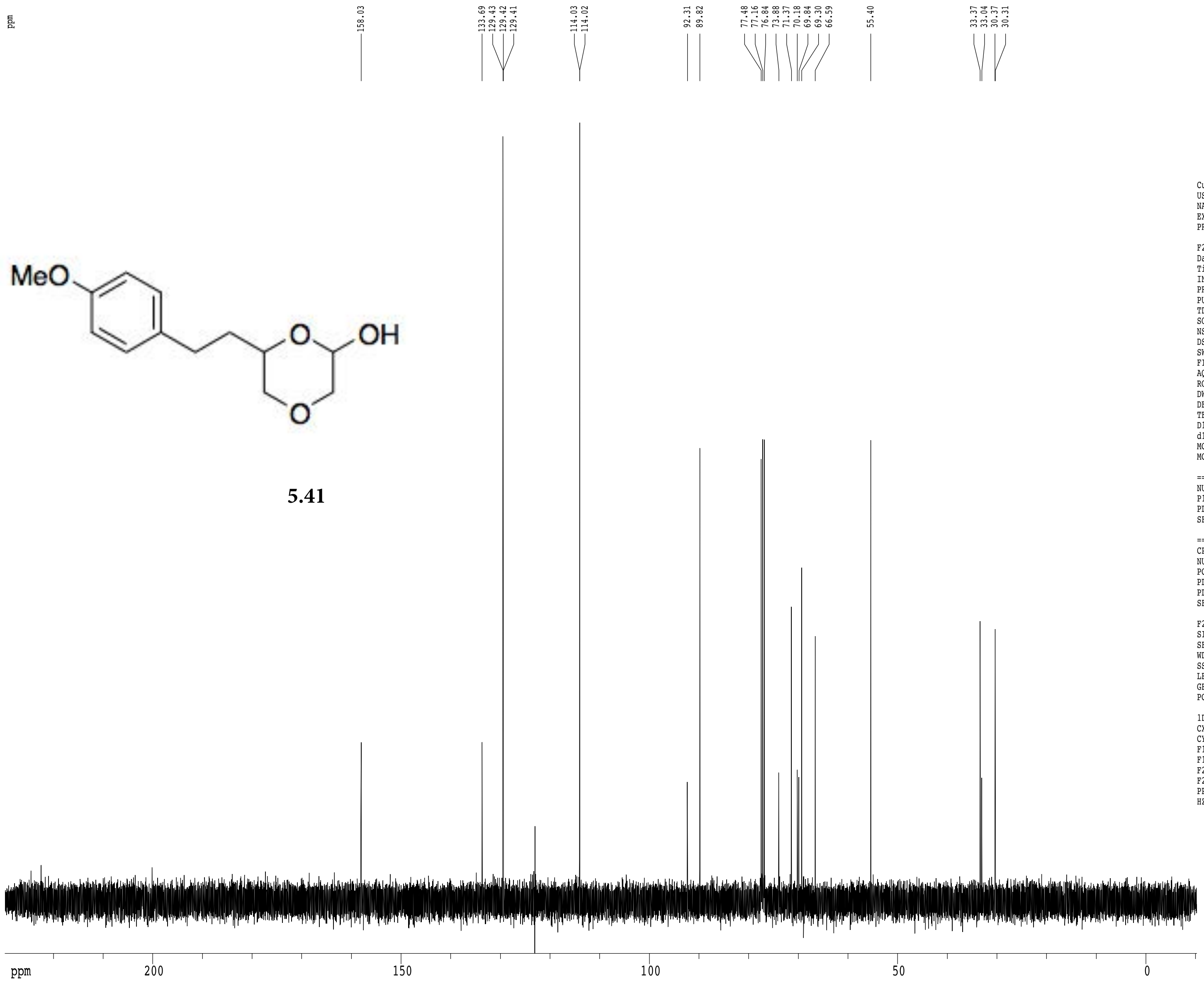
1H spectrum



5.41

```
Current Data Parameters
USER              khewitt1
NAME          KAH-V-153-2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20211027
Time                 15.15
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   38460
SOLVENT              CDCl3T
NS                       8
DS                       2
SWH               6410.256 Hz
FIDRES            0.166673 Hz
AQ               2.9999299 sec
RG                   161.3
DW                  78.000 usec
DE                    4.50 usec
TE                   298.1 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -0.90 dB
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF            400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             166.72084 Hz/cm
```

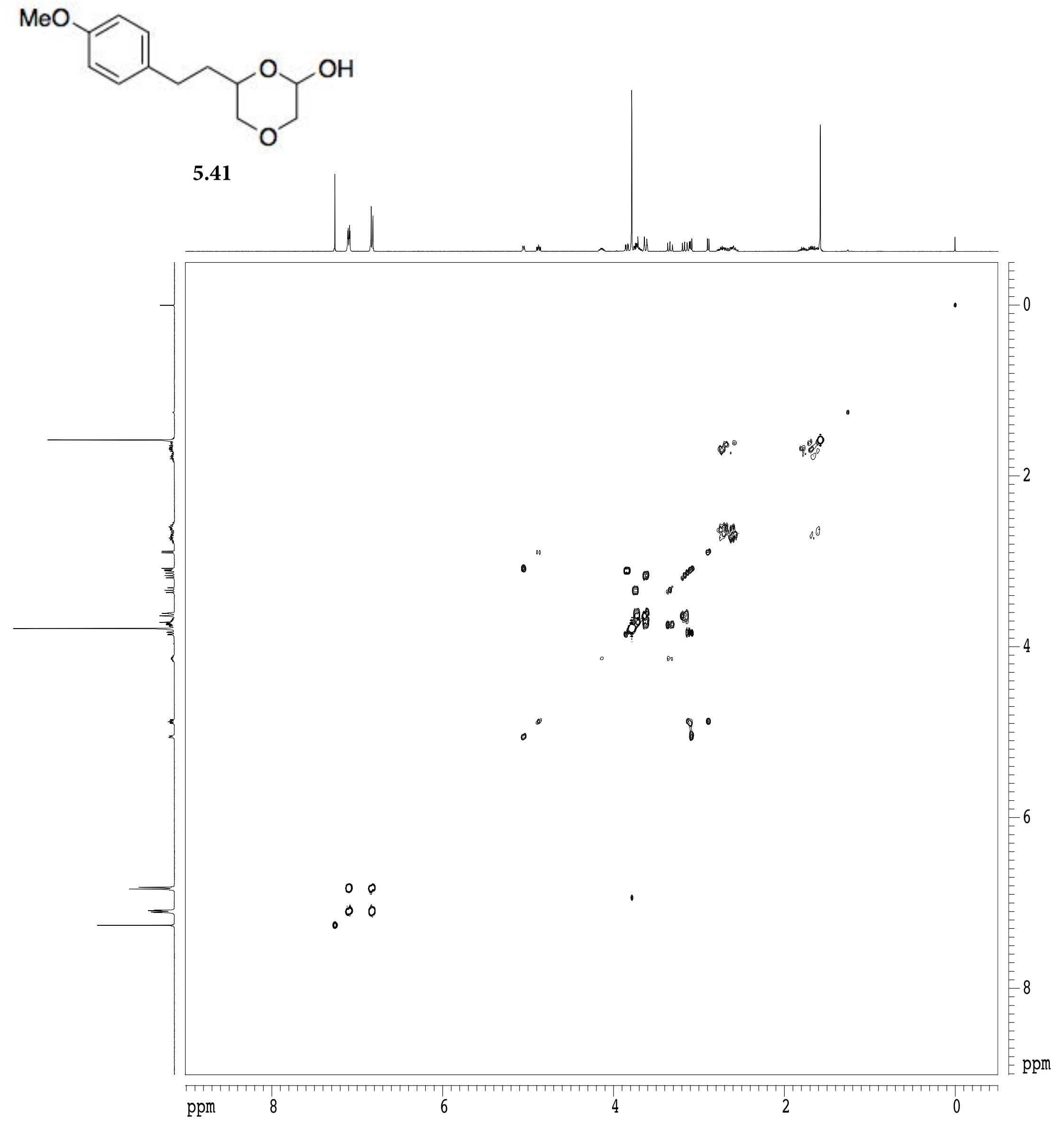
13C spectrum with 1H decoupling



5.41

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-153-Z
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211027
Time               15.17
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   240
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                5160.6
DW                20.700 usec
DE                 20.39 usec
TE                 298.1 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127595 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.829 ppm
F1              23123.72 Hz
F2P              -10.246 ppm
F2              -1030.88 Hz
PPMCM           10.52960 ppm/cm
HZCM          1059.41199 Hz/cm
```

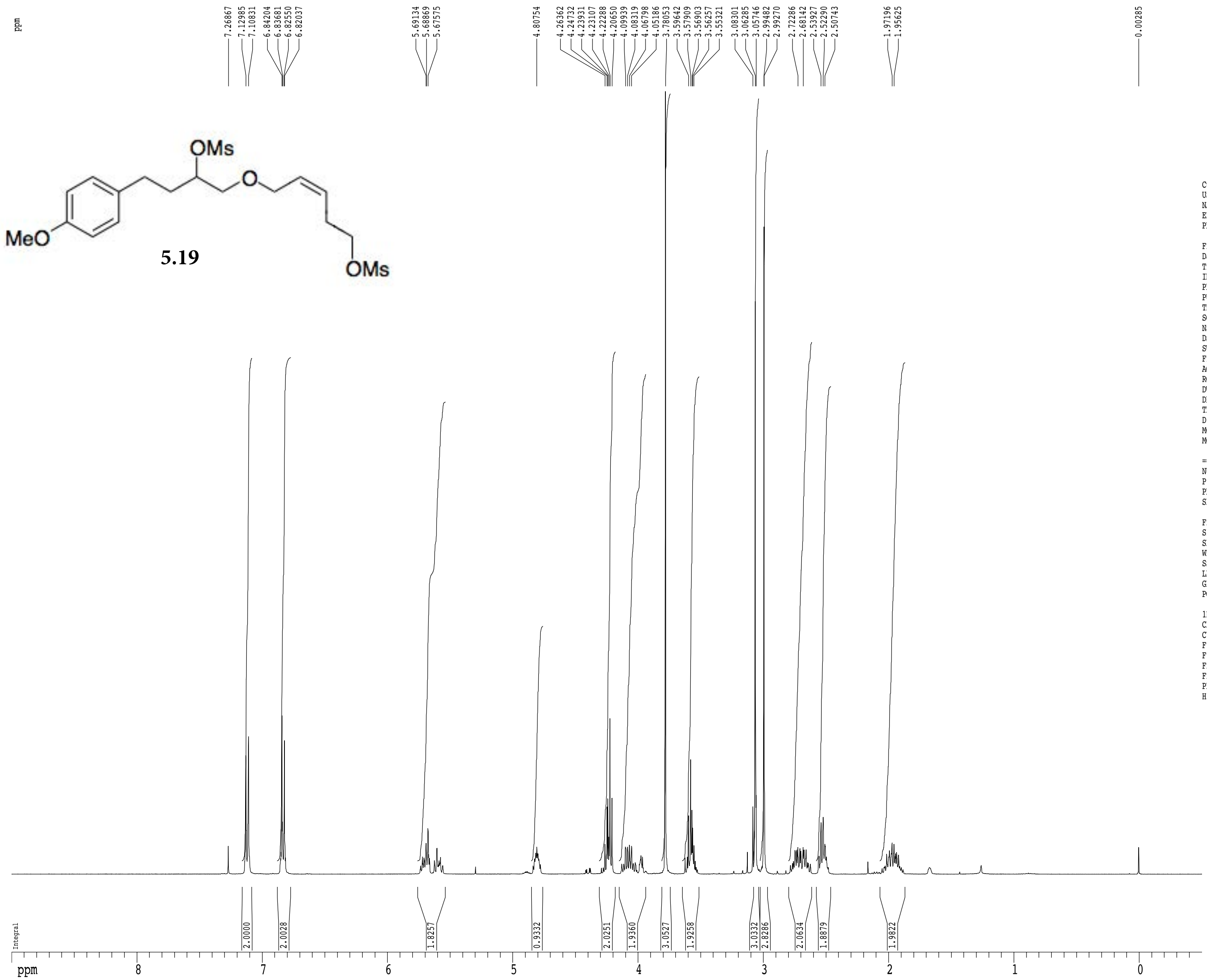
gcosy60



5.41

```
       Current Data Parameters
USER            khewitt1
NAME      KAH-V-164-03-Z
EXPNO                  2
PROCNO                 1

      F2 - Acquisition Parameters
Date_           20211111
Time               14.38
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG    cosygp60.prd
TD                  2048
SOLVENT            CDCl3
NS                     1
DS                    16
SWH             6410.256 Hz
FIDRES          3.130008 Hz
AQ             0.1597940 sec
RG                  2048
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
d0            0.00000300 sec
D1            1.00000000 sec
d13           0.00000300 sec
D16           0.00100000 sec
IN0           0.00015600 sec

     ======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

     ====== GRADIENT CHANNEL =====
GPNAM1        SMSQ10.100
GPNAM2        SMSQ10.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               10.00 %
GPZ2               10.00 %
P16              1000.00 usec

      F1 - Acquisition parameters
ND0                    1
TD                   256
SFO1            400.1328 MHz
FIDRES         25.040064 Hz
SW                16.020 ppm
FnMODE                QF

      F2 - Processing parameters
SI                  1024
SF           400.1300214 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

      F1 - Processing parameters
SI                  1024
MC2                   QF
SF           400.1300214 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0

        2D NMR plot parameters
CX2                15.00 cm
CX1                15.00 cm
F2PLO              9.012 ppm
F2LO             3605.86 Hz
F2PHI             -0.500 ppm
F2HI             -200.23 Hz
F1PLO              9.012 ppm
F1LO             3605.86 Hz
F1PHI             -0.500 ppm
F1HI             -200.23 Hz
F2PPMCM          0.63414 ppm/cm
F2HZCM         253.73933 Hz/cm
F1PPMCM          0.63414 ppm/cm
F1HZCM         253.73933 Hz/cm
```

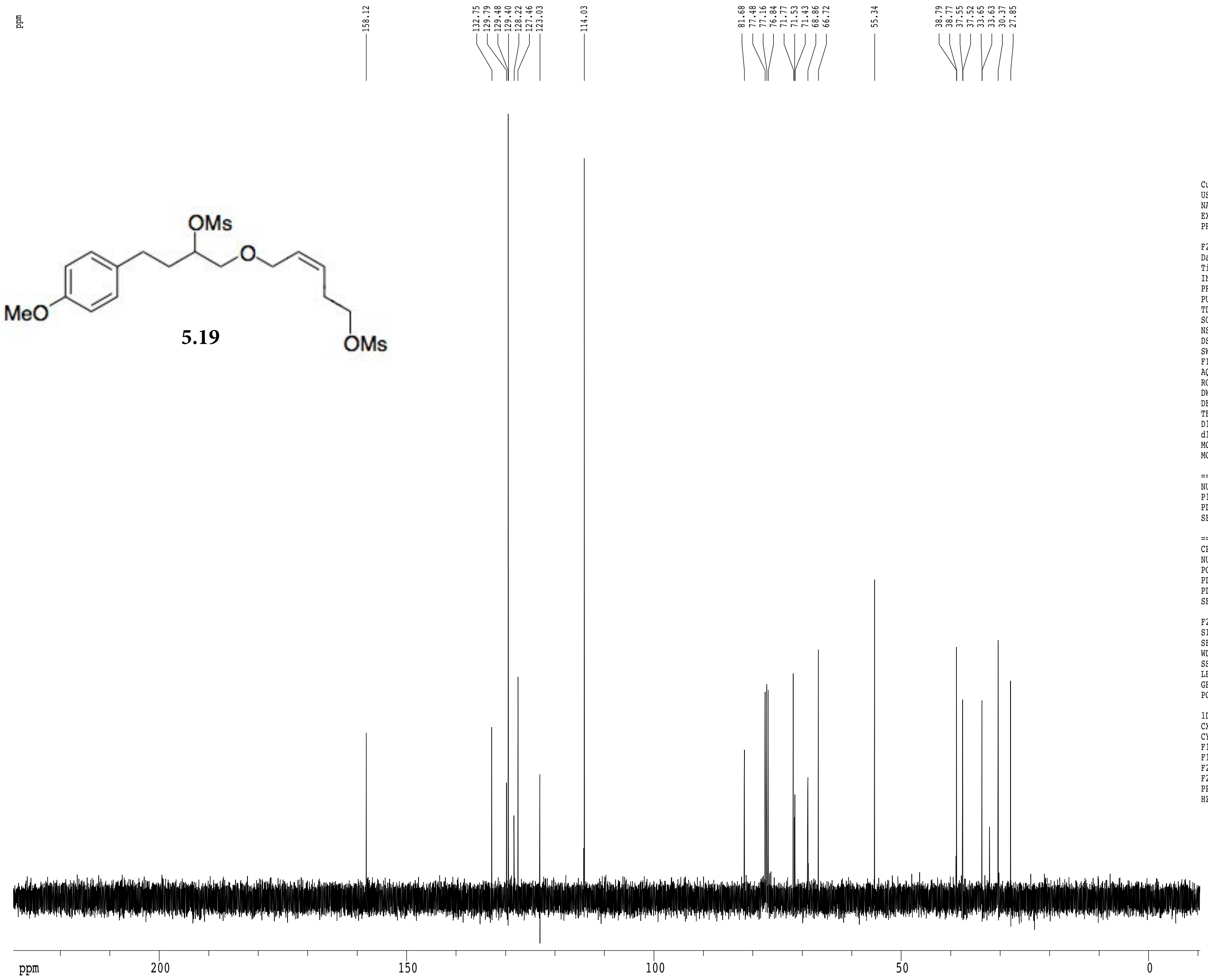
1H spectrum



5.19

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-173-Z
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211112
Time               11.54
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                  90.5
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF          400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

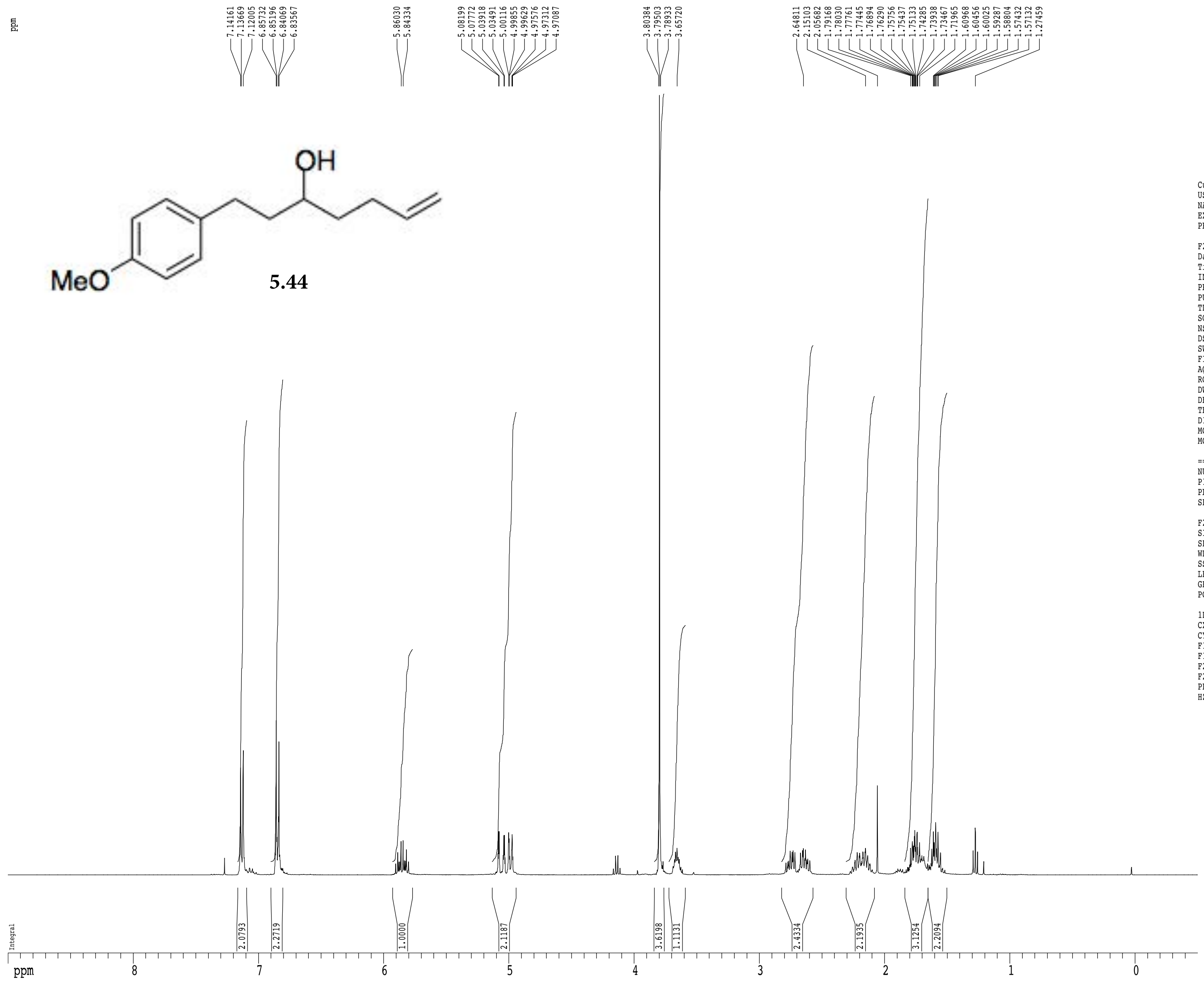
13C spectrum with 1H decoupling



5.19

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-173-Z
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211112
Time               11.57
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   112
DS                     4
SWH          24154.590 Hz
FIDRES        0.368570 Hz
AQ           1.3566452 sec
RG             14596.5
DW              20.700 usec
DE               20.39 usec
TE               298.0 K
D1         0.10000000 sec
d11        0.03000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1       100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2       400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF         100.6127650 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```

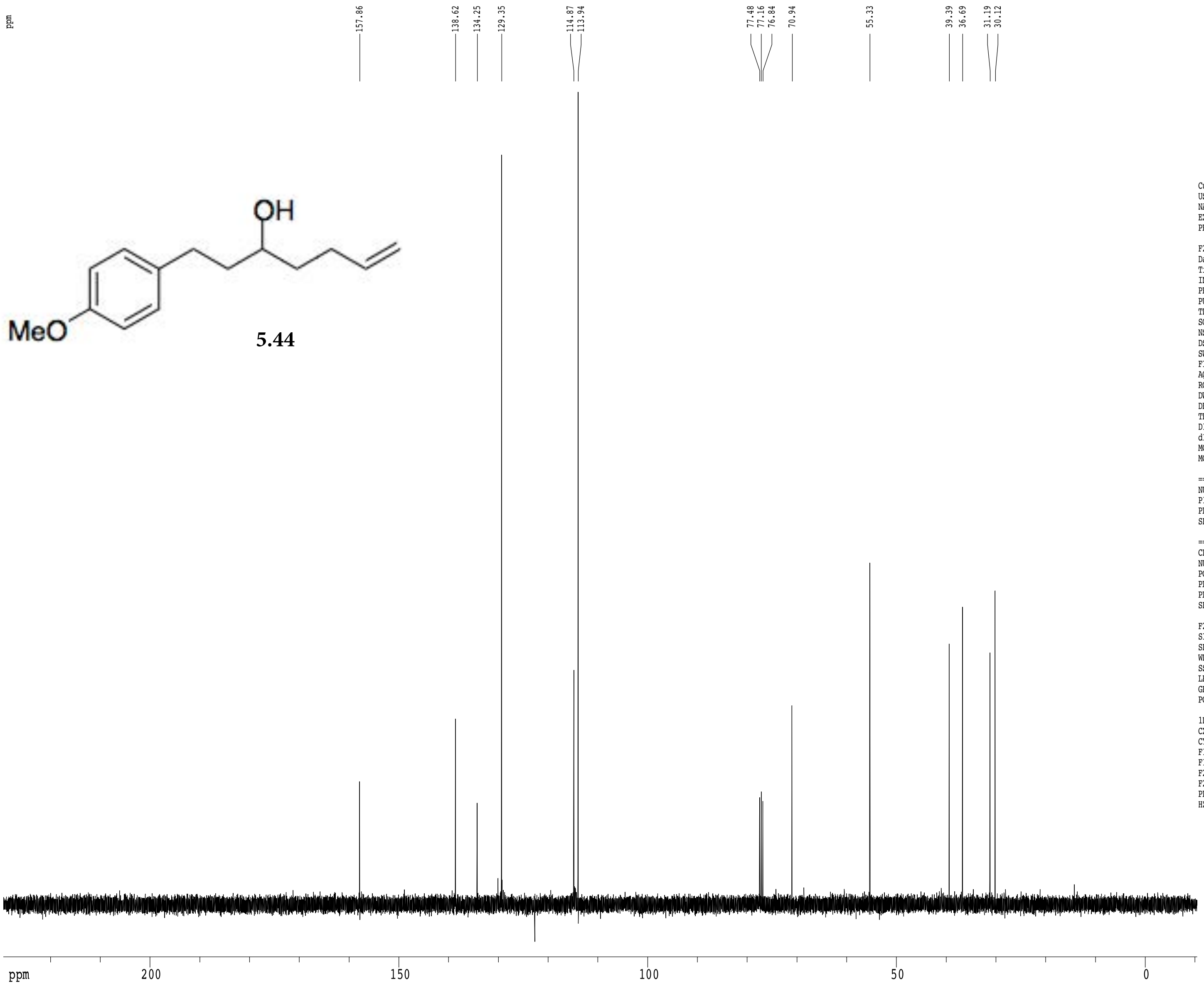
1H spectrum



5.44

```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-248-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220126
Time               18.34
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    57
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

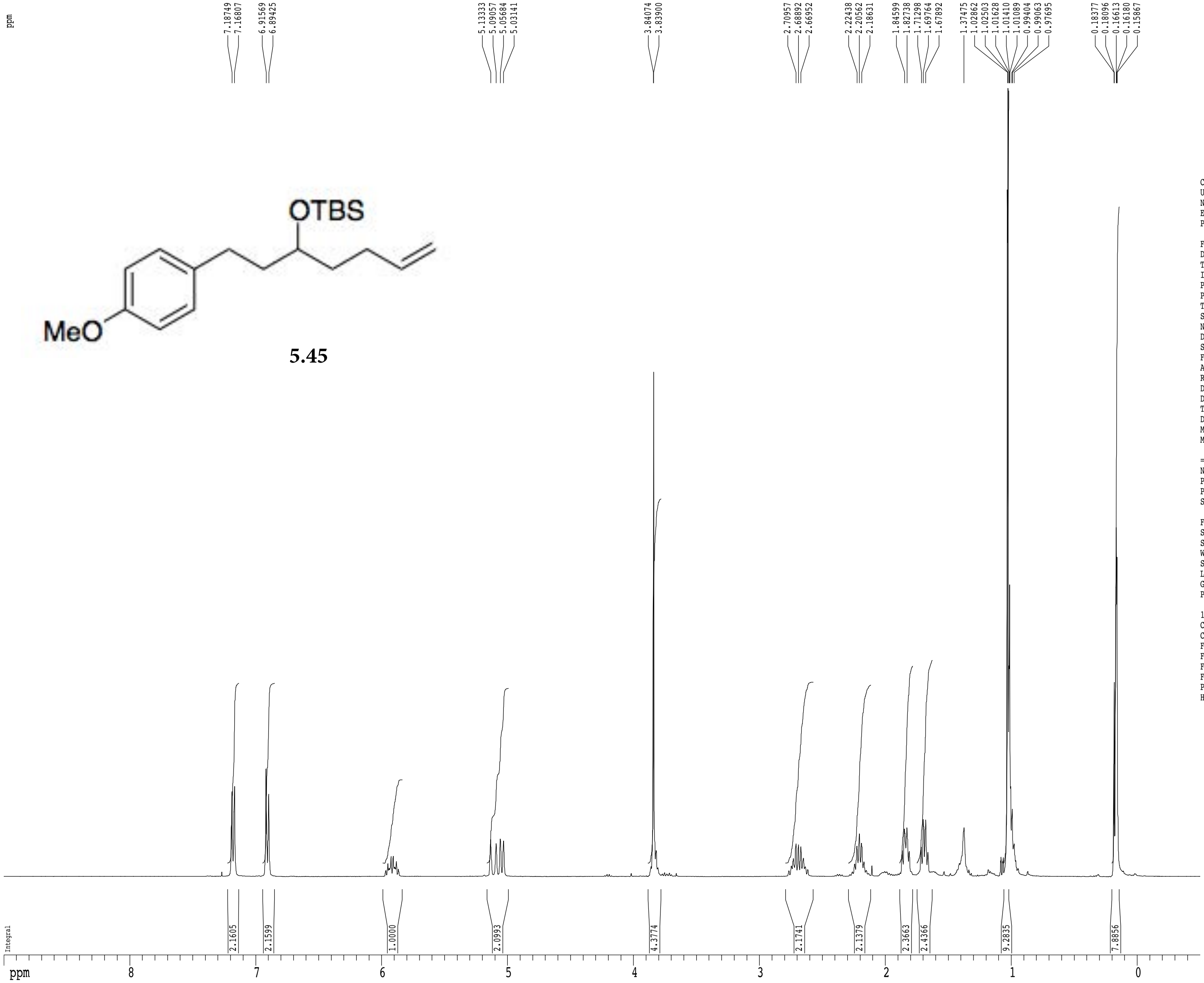
13C spectrum with 1H decoupling


5.44

```
Current Data Parameters
USER          khewitt1
NAME        KAH-V-248-1
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20220126
Time             18.37
INSTRUM         drx400
PROBHD   5 mm QNP H/F/P
PULPROG        zgdc30
TD               65536
SOLVENT          CDCl3
NS                  64
DS                   4
SWH        24154.590 Hz
FIDRES      0.368570 Hz
AQ         1.3566452 sec
RG              9195.2
DW            20.700 usec
DE             20.39 usec
TE             298.0 K
D1        0.10000000 sec
d11       0.03000000 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                7.90 usec
PL1              -3.00 dB
SFO1       100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -0.90 dB
PL12             17.00 dB
SFO2       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         100.6127658 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.50 cm
F1P            229.496 ppm
F1            23090.21 Hz
F2P            -10.579 ppm
F2            -1064.37 Hz
PPMCM         10.52959 ppm/cm
HZCM        1059.41150 Hz/cm
```

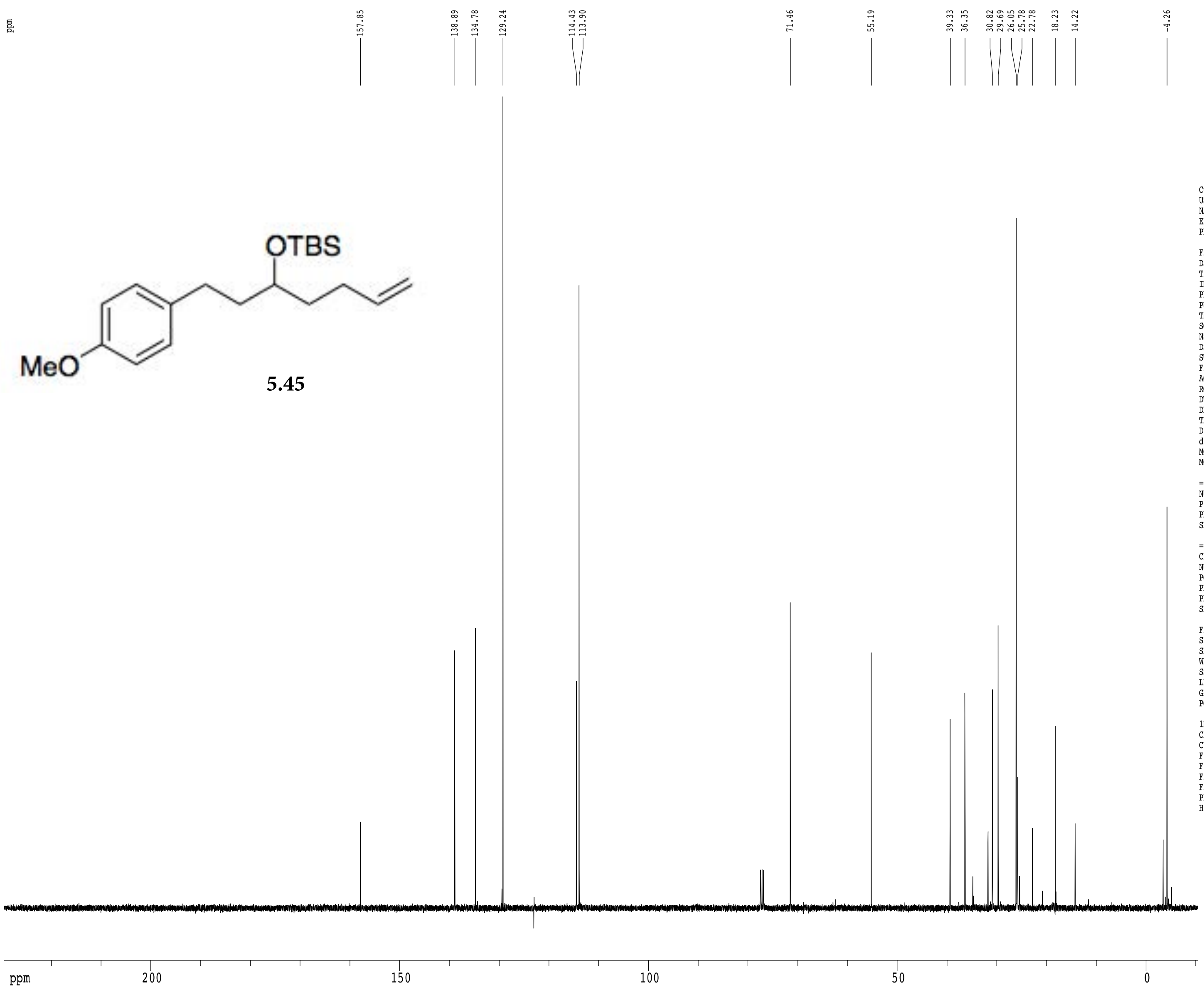
1H spectrum

5.45



```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-159-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211028
Time               18.42
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH          6410.256 Hz
FIDRES       0.166673 Hz
AQ          2.9999299 sec
RG                  11.3
DW            78.000 usec
DE              4.50 usec
TE               298.0 K
D1        0.10000000 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1             12.00 usec
PL1             -0.90 dB
SFO1       400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF         400.1300175 MHz
WDW                   no
SSB                    0
LB               0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX              22.80 cm
CY              15.00 cm
F1P             9.000 ppm
F1            3601.17 Hz
F2P            -0.500 ppm
F2            -200.06 Hz
PPMCM        0.41667 ppm/cm
HZCM        166.72084 Hz/cm
```

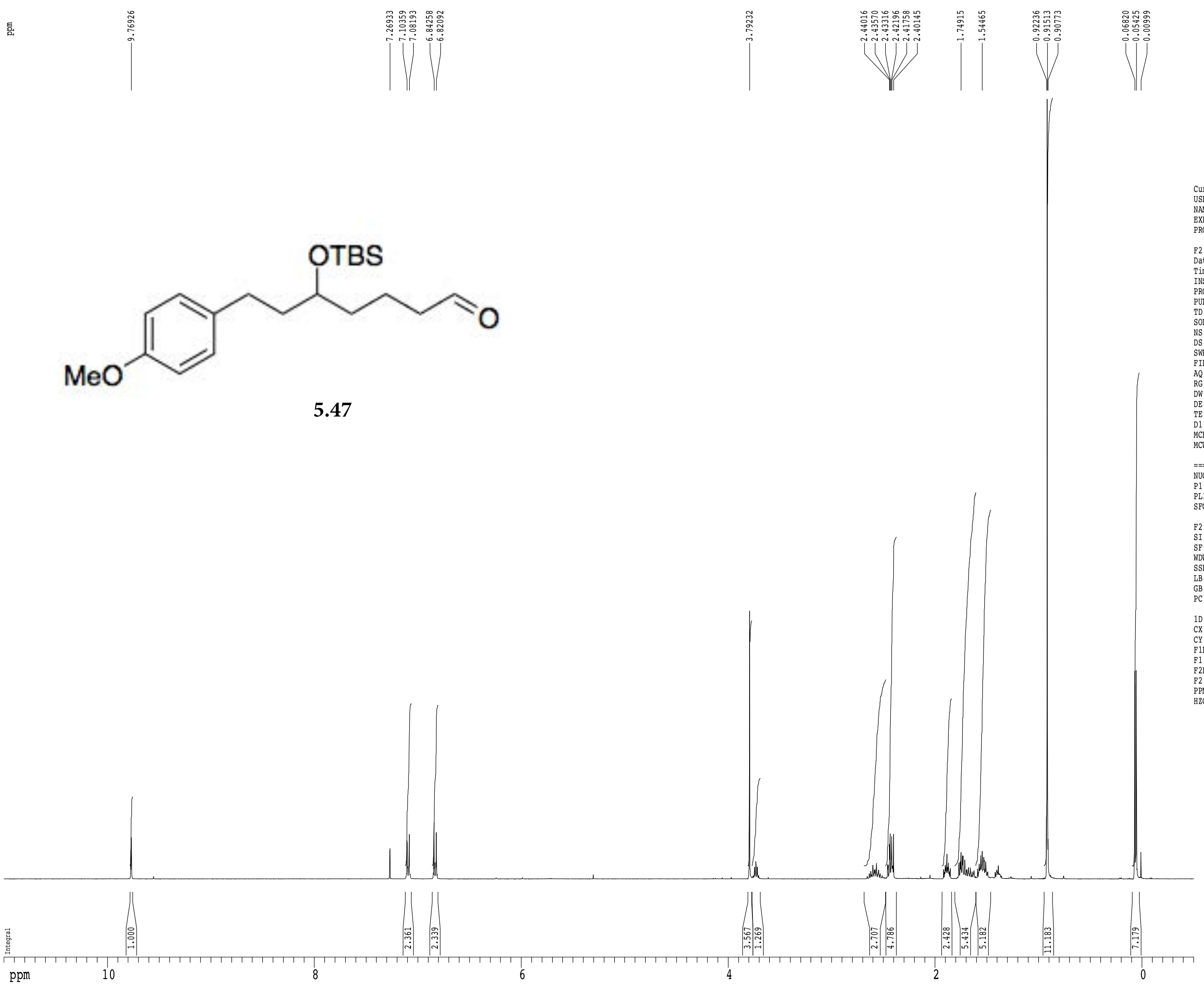
13C spectrum with 1H decoupling



5.45

```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-159-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211028
Time               18.44
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                    80
DS                     4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                 20.39 usec
TE                 298.1 K
D1          0.10000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127680 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.22 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM          10.52959 ppm/cm
HZCM         1059.41162 Hz/cm
```

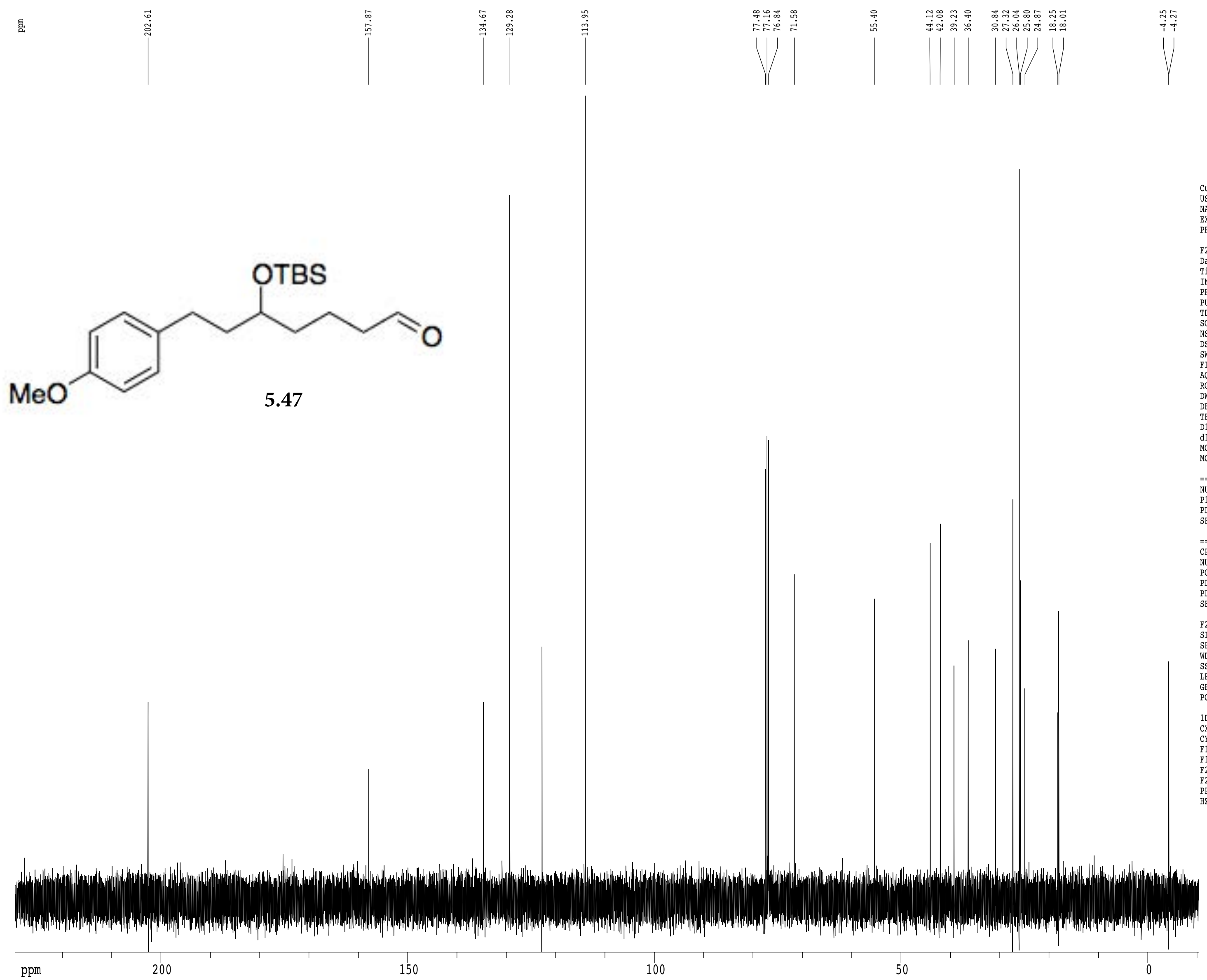
1H spectrum



5.47

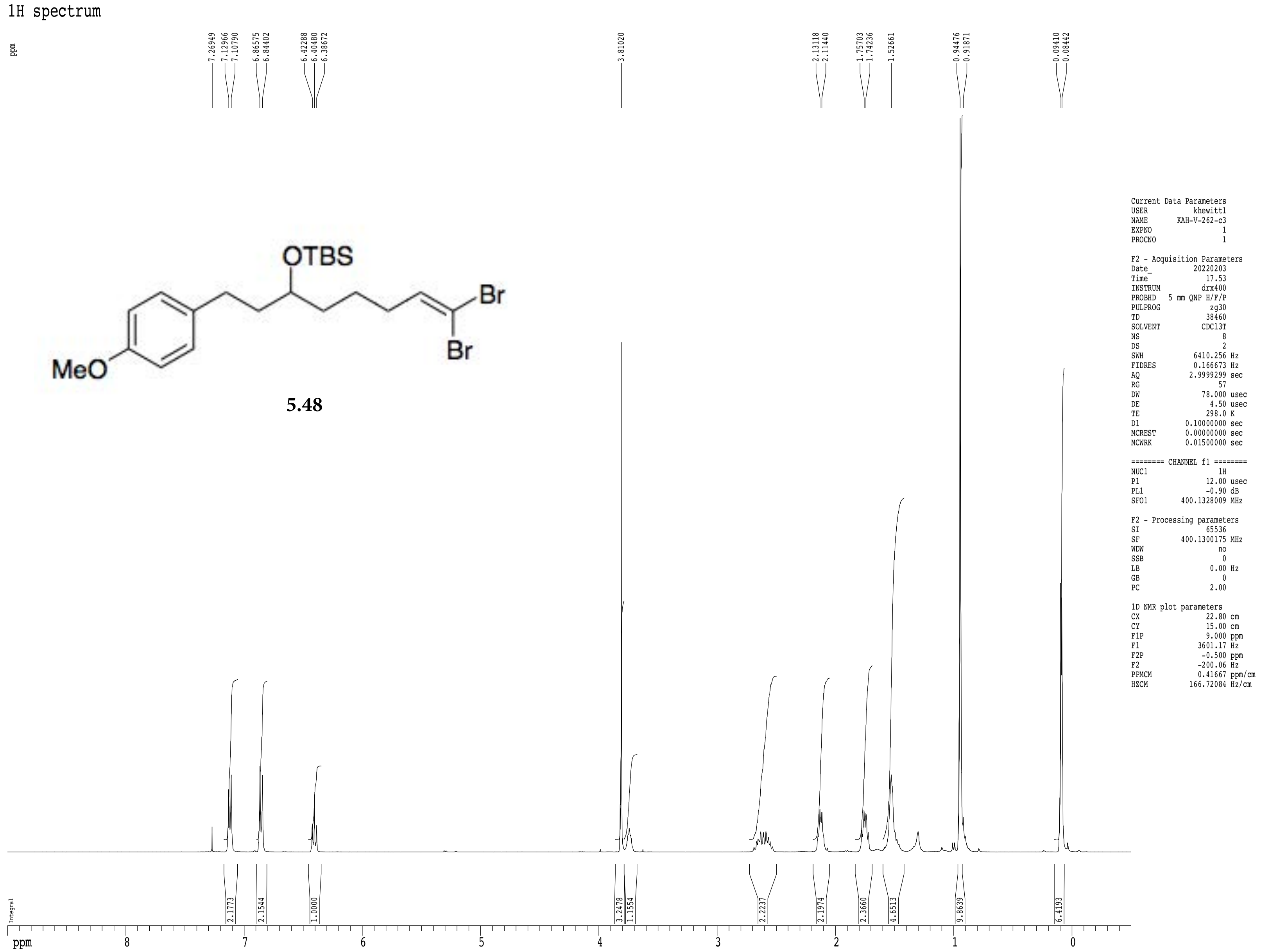
```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-258-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20220202
Time              13.52
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                38460
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ            2.9999299 sec
RG                  114
DW               78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -0.90 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300175 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              11.000 ppm
F1              4401.43 Hz
F2P              -0.500 ppm
F2              -200.07 Hz
PPMCM           0.50439 ppm/cm
HZCM          201.81996 Hz/cm
```

13C spectrum with 1H decoupling



5.47

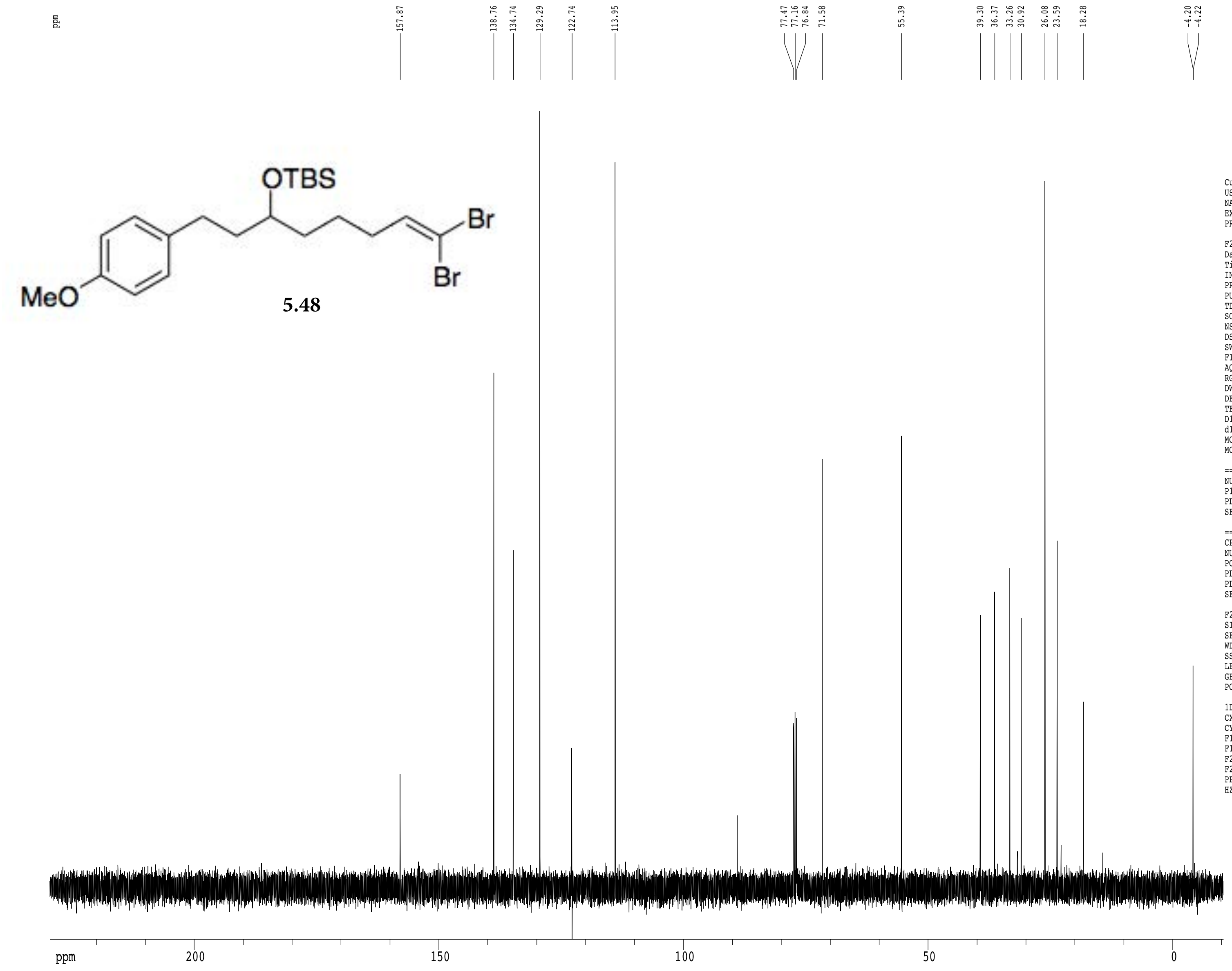
```
Current Data Parameters
USER            khewitt1
NAME         KAH-V-258-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220202
Time               13.56
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                    96
DS                     4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG               10321.3
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127584 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```



5.48

1H spectrum
ppm
7.26949
7.12966
7.10790
6.86575
6.84402
6.42288
6.40480
6.38672
3.81020
2.13118
2.11440
1.75703
1.74236
1.52661
0.94476
0.91871
0.09410
0.08442
OTBS
Br
Br
MeO
Current Data Parameters
USER khewitt1
NAME KAH-V-262-c3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20220203
Time 17.53
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3T
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 57
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -0.90 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
Integral
2.1773
2.1544
1.0000
3.2478
1.1554
2.2237
2.1974
2.3660
4.6513
9.8639
6.4193
ppm
8
7
6
5
4
3
2
1
0

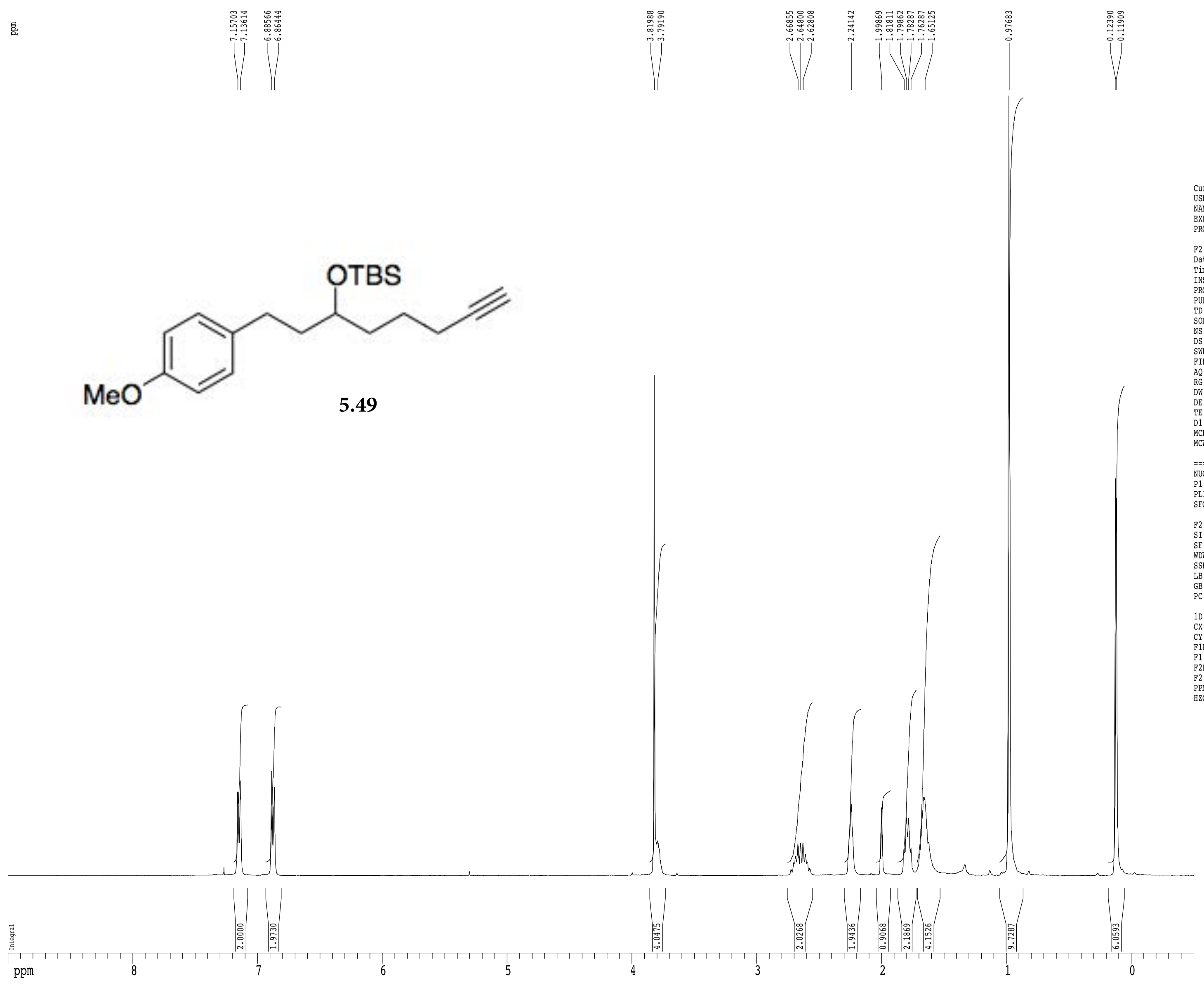
13C spectrum with 1H decoupling



5.48

```
Current Data Parameters
USER              khewitt1
NAME           KAH-V-262-c3
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20220203
Time                 17.55
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                      96
DS                       4
SWH             24154.590 Hz
FIDRES           0.368570 Hz
AQ              1.3566452 sec
RG                  9195.2
DW                  20.700 usec
DE                   20.39 usec
TE                   298.0 K
D1             0.10000000 sec
d11            0.03000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.90 usec
PL1                  -3.00 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -0.90 dB
PL12                 17.00 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF          100.6127602 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.50 cm
F1P                229.496 ppm
F1                23090.21 Hz
F2P                -10.579 ppm
F2                -1064.37 Hz
PPMCM             10.52959 ppm/cm
HZCM            1059.41150 Hz/cm
```

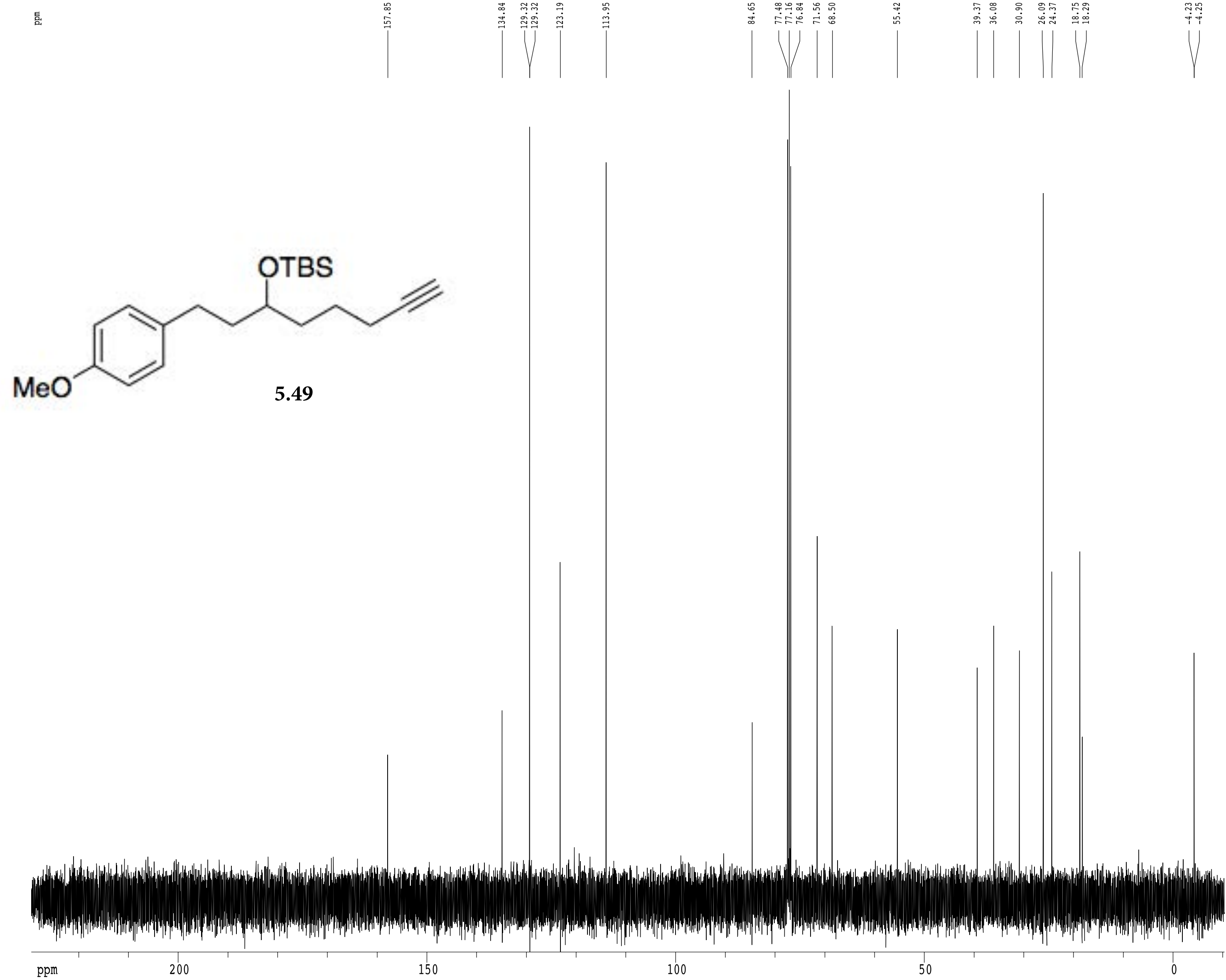
1H spectrum



5.49

```
Current Data Parameters
USER            khewitt1
NAME          KAH-V-185-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211202
Time               17.05
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                    16
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

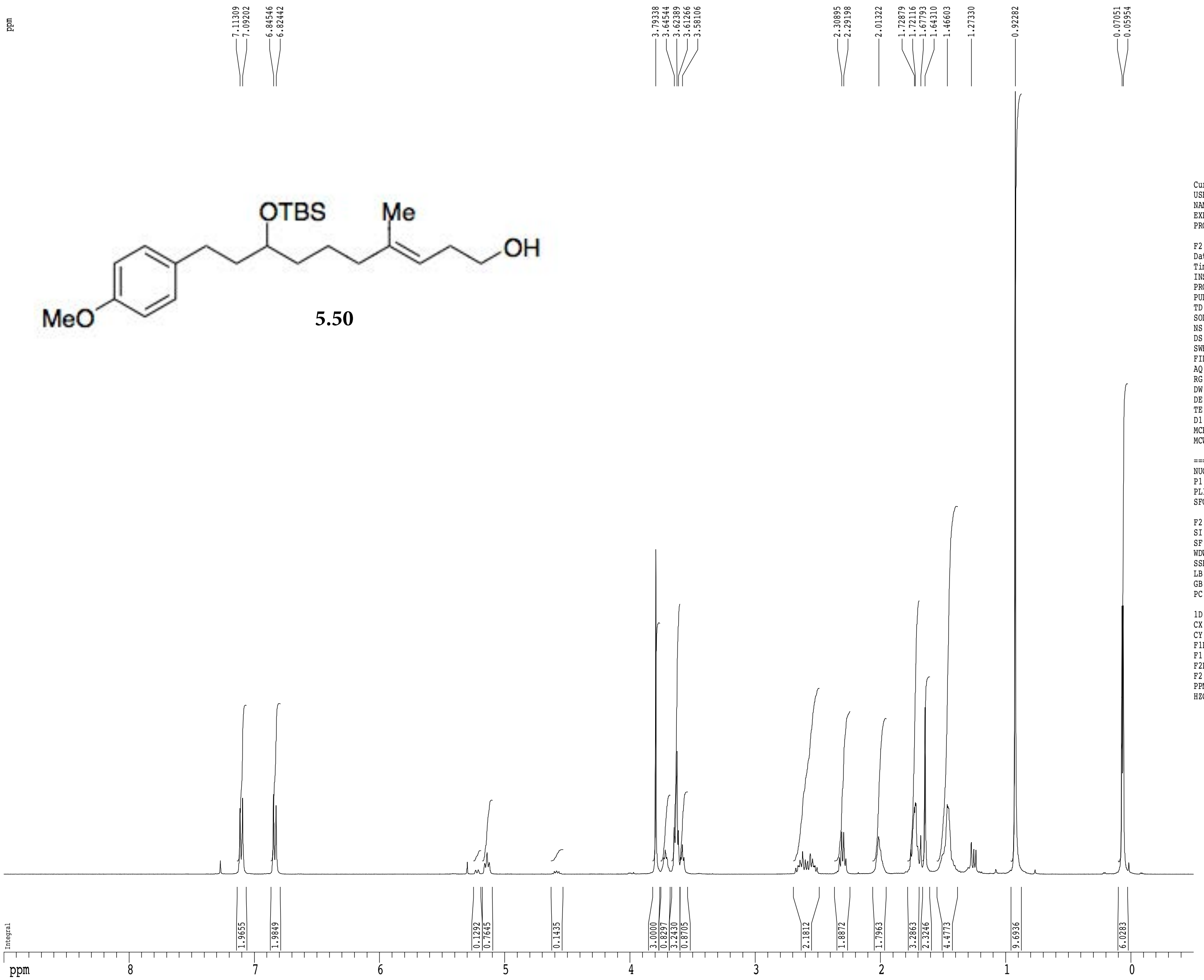
13C spectrum with 1H decoupling



5.49

```
Current Data Parameters
USER              khewitt1
NAME           KAH-V-175-1
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20211122
Time               16.48
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  224
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG               9195.2
DW               20.700 usec
DE                20.39 usec
TE                298.0 K
D1           0.10000000 sec
d11          0.03000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127569 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```

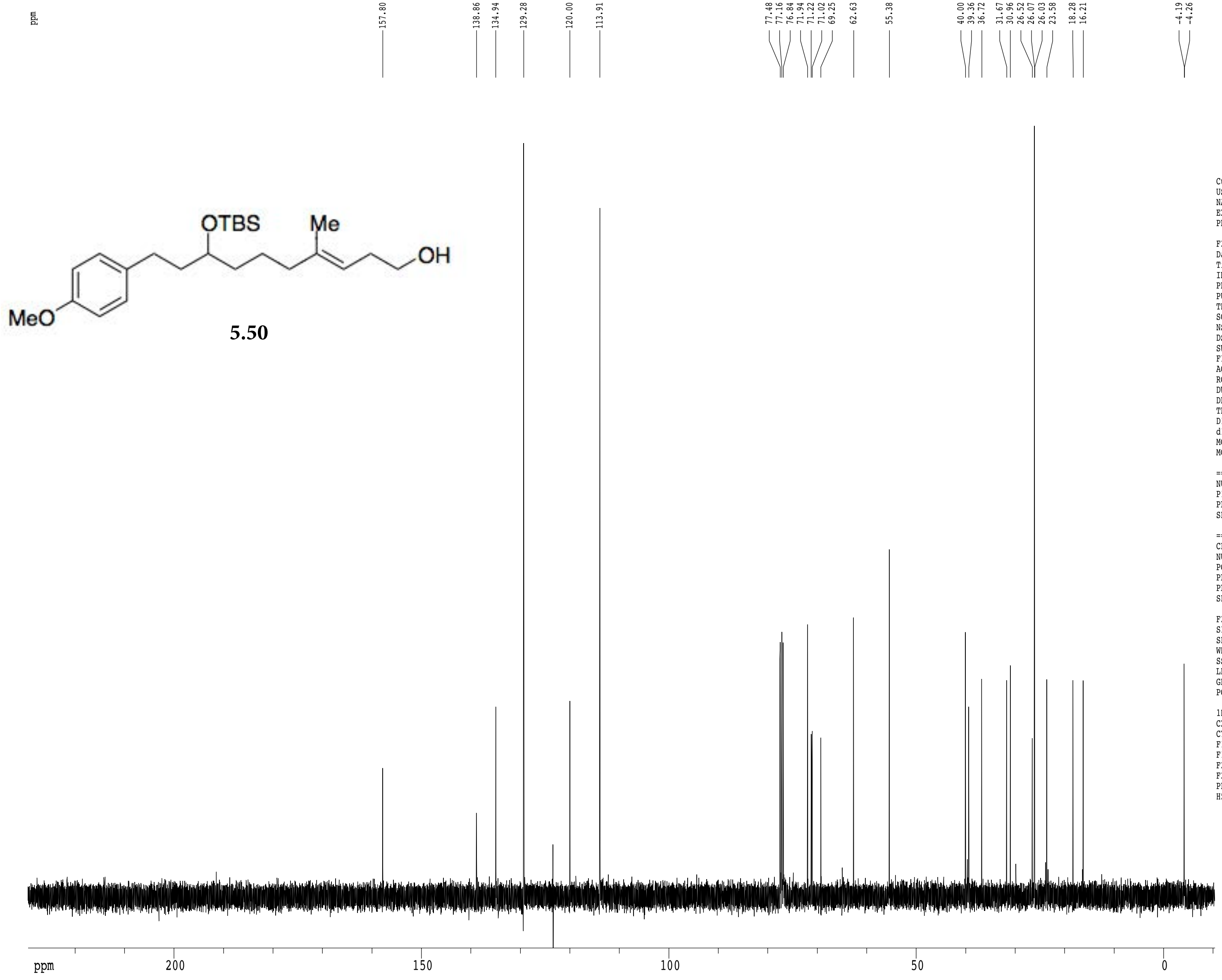
1H spectrum



5.50

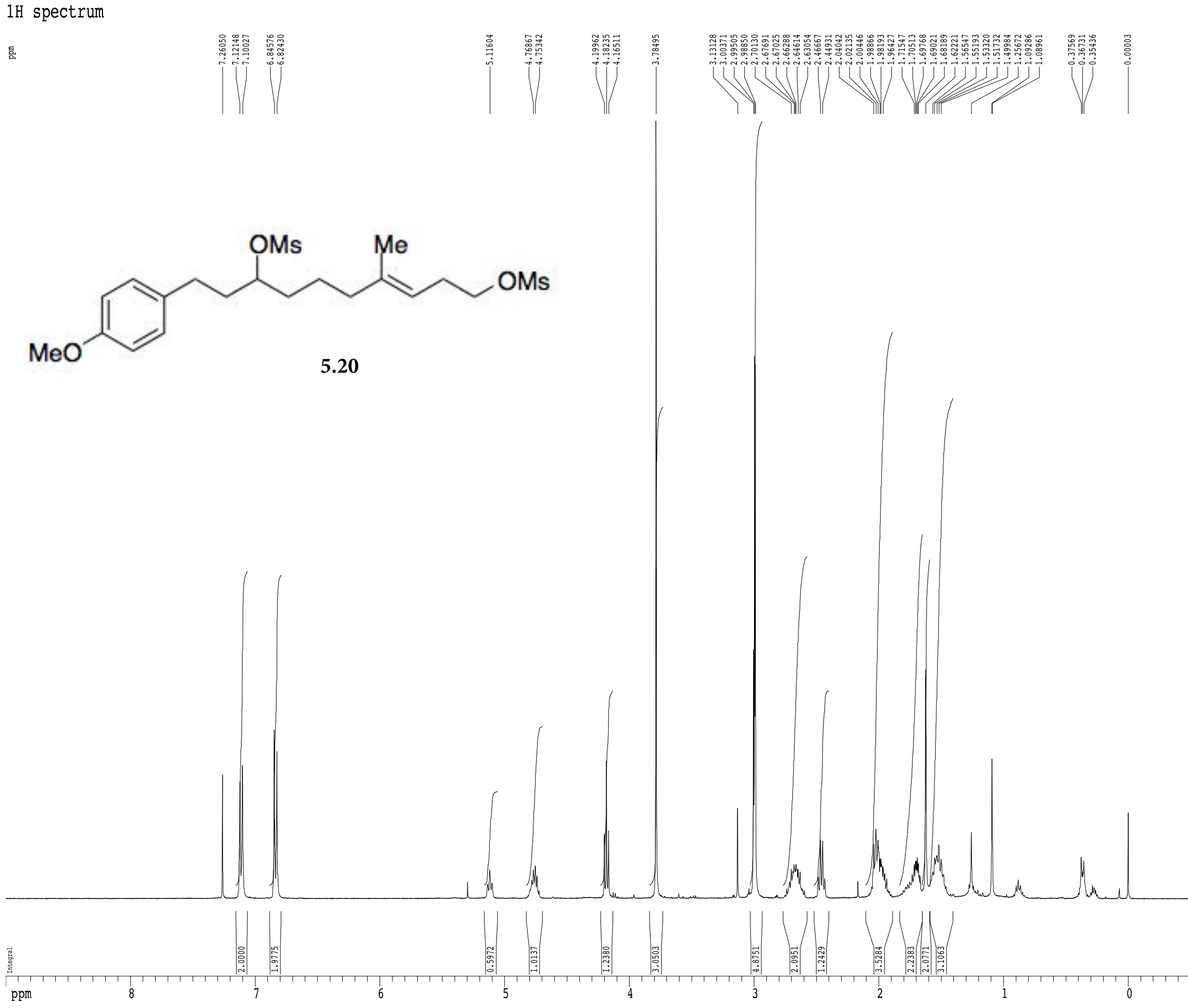
```
Current Data Parameters
USER            khewitt1
NAME       KAH-V-193-chk
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211209
Time               16.41
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDC13T
NS                     8
DS                     2
SWH           6410.256 Hz
FIDRES        0.166673 Hz
AQ           2.9999299 sec
RG                  50.8
DW              78.000 usec
DE                4.50 usec
TE               298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1               12.00 usec
PL1              -0.90 dB
SFO1      400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF        400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

13C spectrum with 1H decoupling



5.50

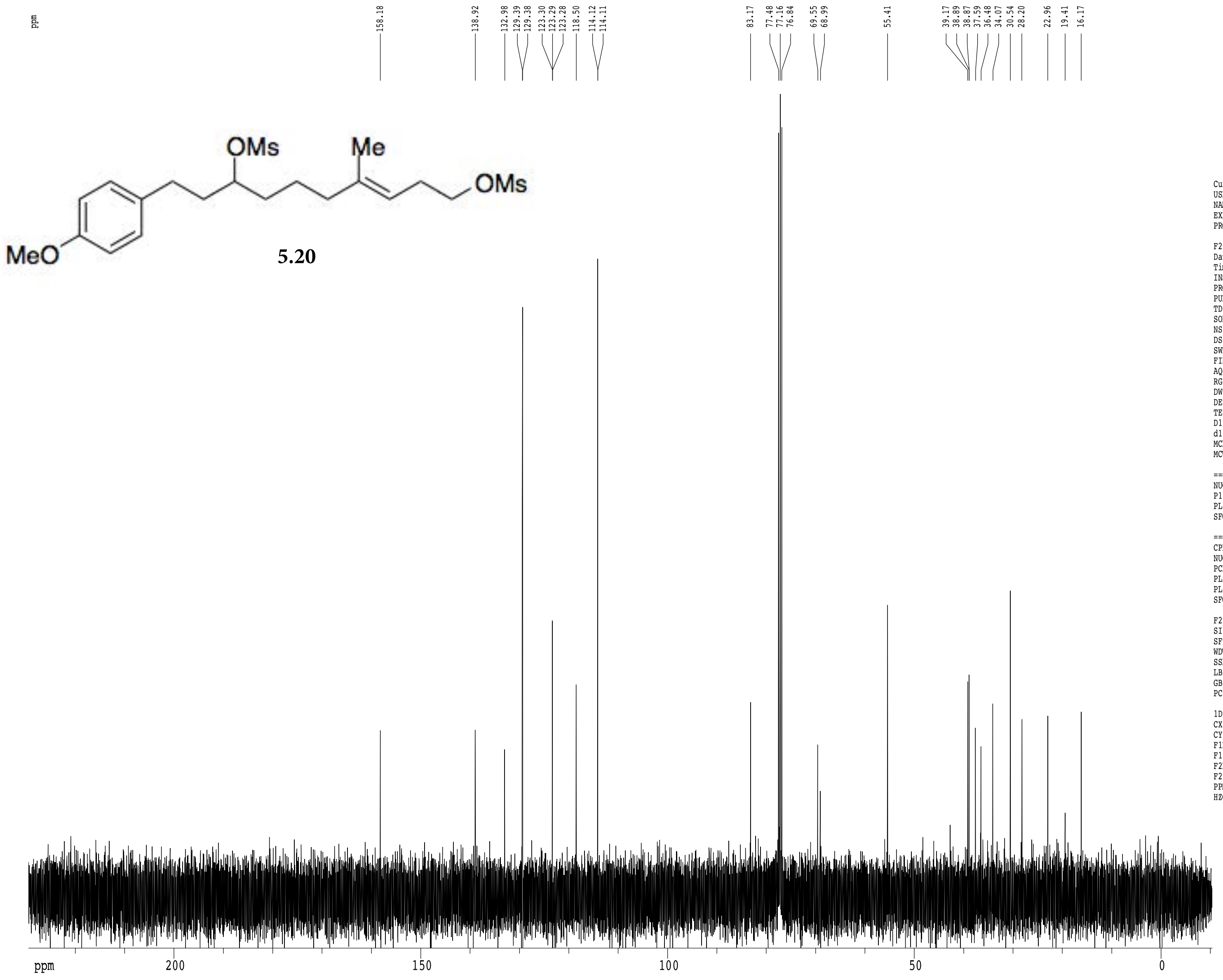
```
Current Data Parameters
USER            khewitt1
NAME      KAH-V-193-chk
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20211209
Time              16.47
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG         zgdc30
TD               65536
SOLVENT           CDCl3
NS                  200
DS                    4
SWH          24154.590 Hz
FIDRES        0.368570 Hz
AQ           1.3566452 sec
RG              9195.2
DW              20.700 usec
DE               20.39 usec
TE               298.0 K
D1          0.10000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                7.90 usec
PL1              -3.00 dB
SFO1       100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -0.90 dB
PL12             17.00 dB
SFO2       400.1328009 MHz

F2 - Processing parameters
SI               65536
SF         100.6127599 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.50 cm
F1P            229.496 ppm
F1            23090.21 Hz
F2P            -10.579 ppm
F2            -1064.37 Hz
PPMCM         10.52959 ppm/cm
HZCM        1059.41150 Hz/cm
```



5.20

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-203-chk
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20211215
Time               16.58
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                   181
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300211 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

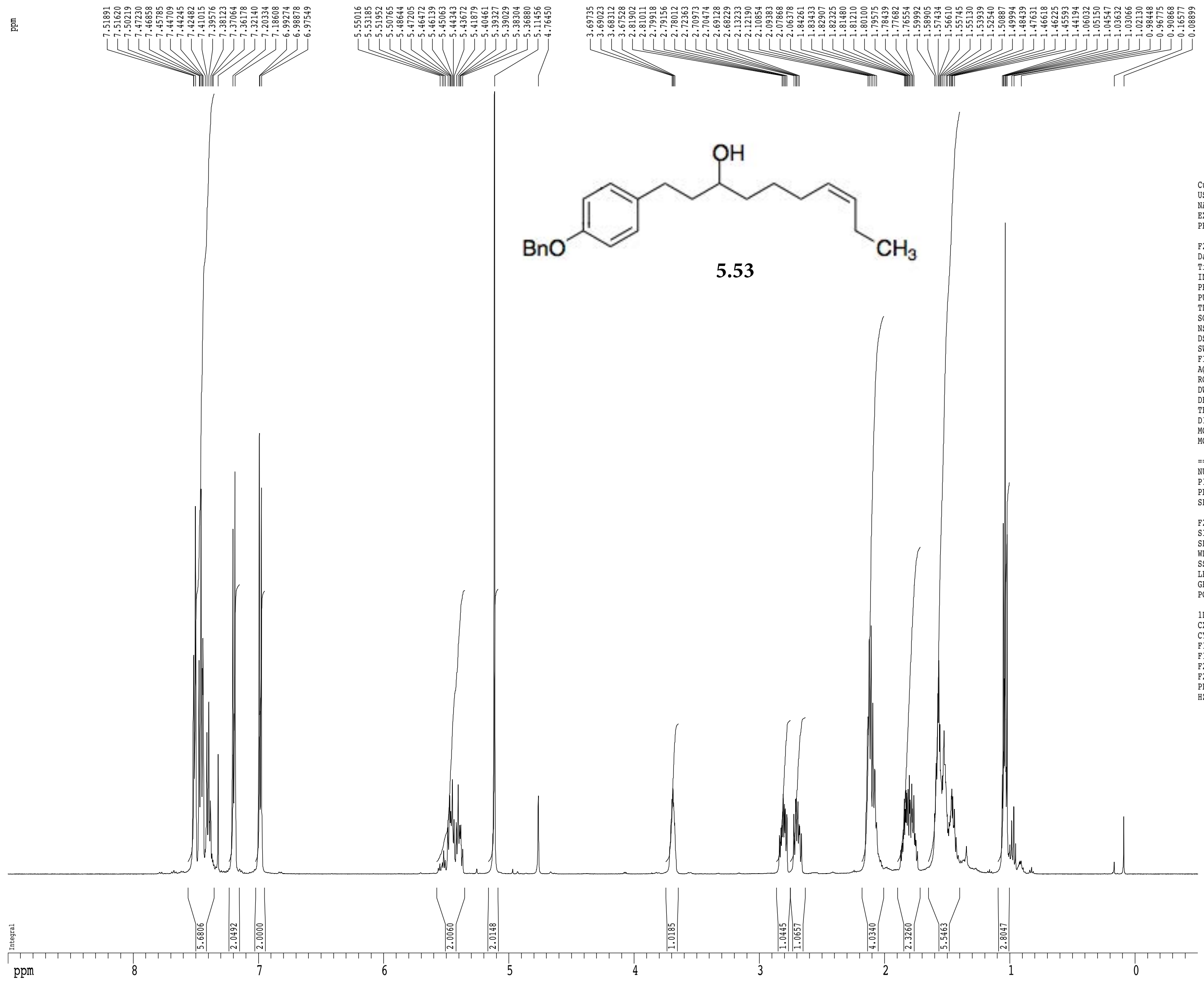
13C spectrum with 1H decoupling



5.20

```
Current Data Parameters
USER              khewitt1
NAME        KAH-V-203-chk
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20211215
Time                17.01
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     4
SWH            24154.590 Hz
FIDRES          0.368570 Hz
AQ             1.3566452 sec
RG                 16384
DW                20.700 usec
DE                 20.39 usec
TE                 298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.90 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -0.90 dB
PL12               17.00 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127587 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.50 cm
F1P              229.496 ppm
F1              23090.21 Hz
F2P              -10.579 ppm
F2              -1064.37 Hz
PPMCM           10.52959 ppm/cm
HZCM          1059.41150 Hz/cm
```

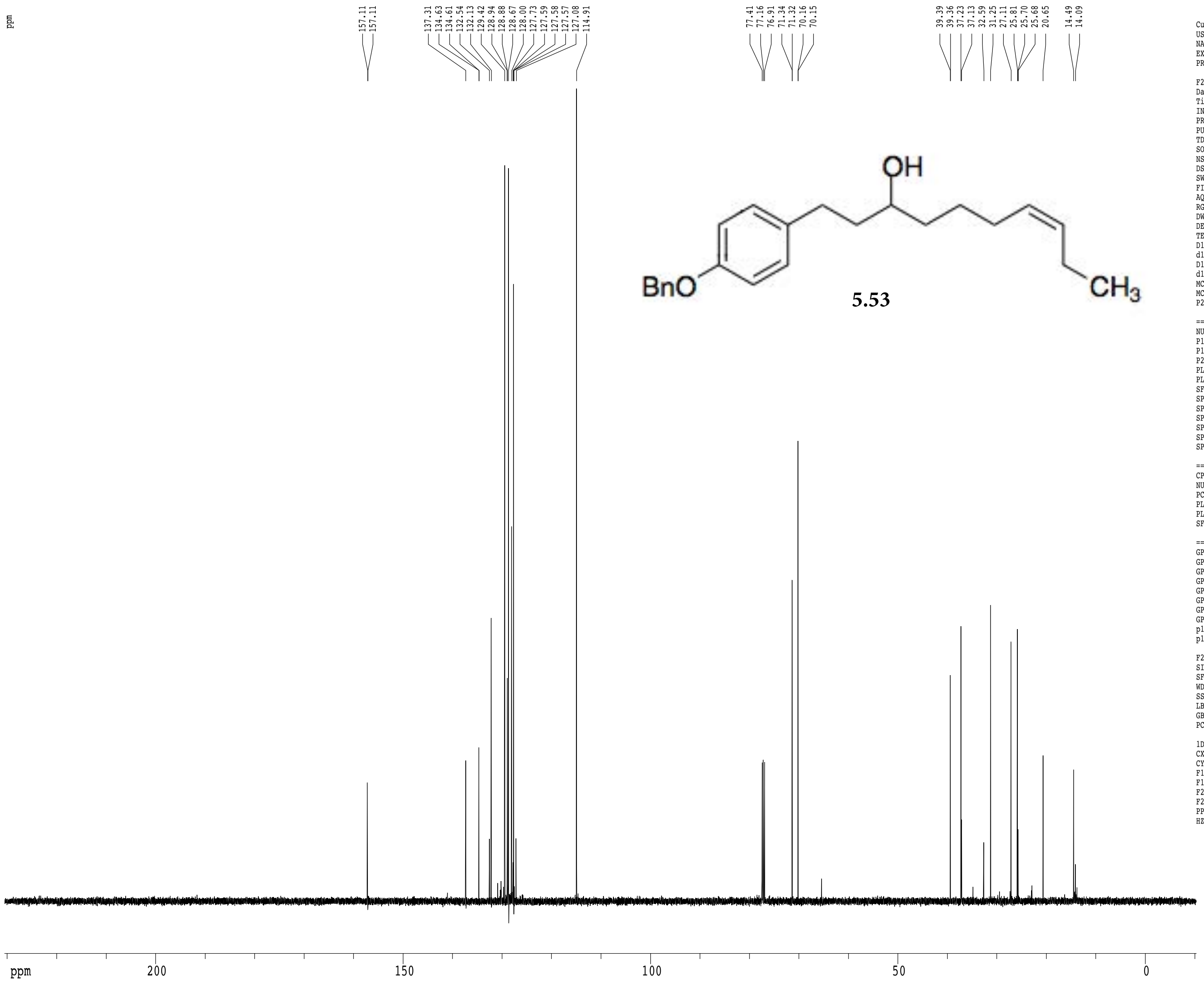
1H spectrum



5.53

```
Current Data Parameters
USER            khewitt1
NAME        KAH-V-294-Z
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220228
Time               10.28
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998677 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.75 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42500 Hz/cm
```

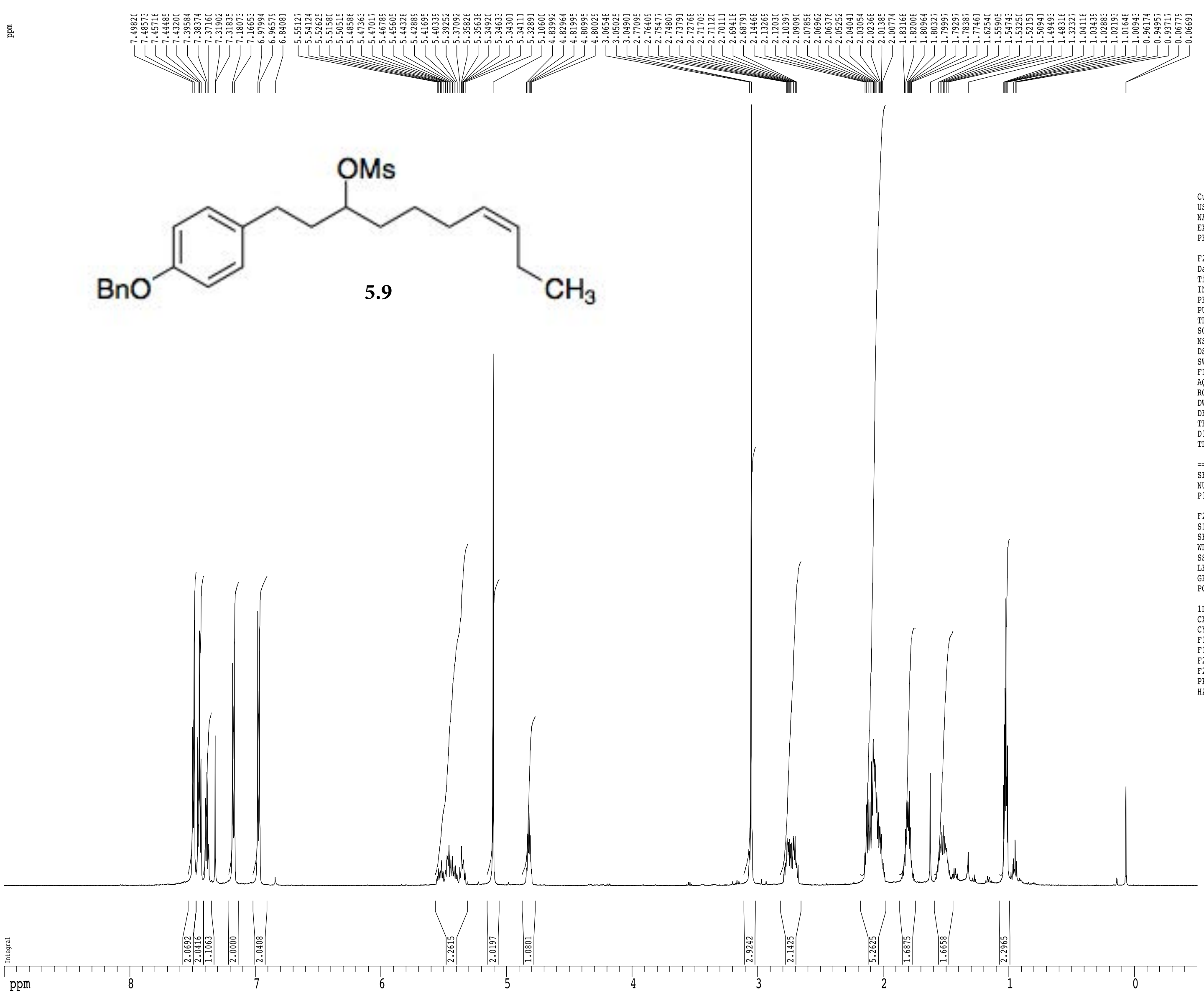
Z-restored spin-echo 13C spectrum with 1H decoupling



5.53

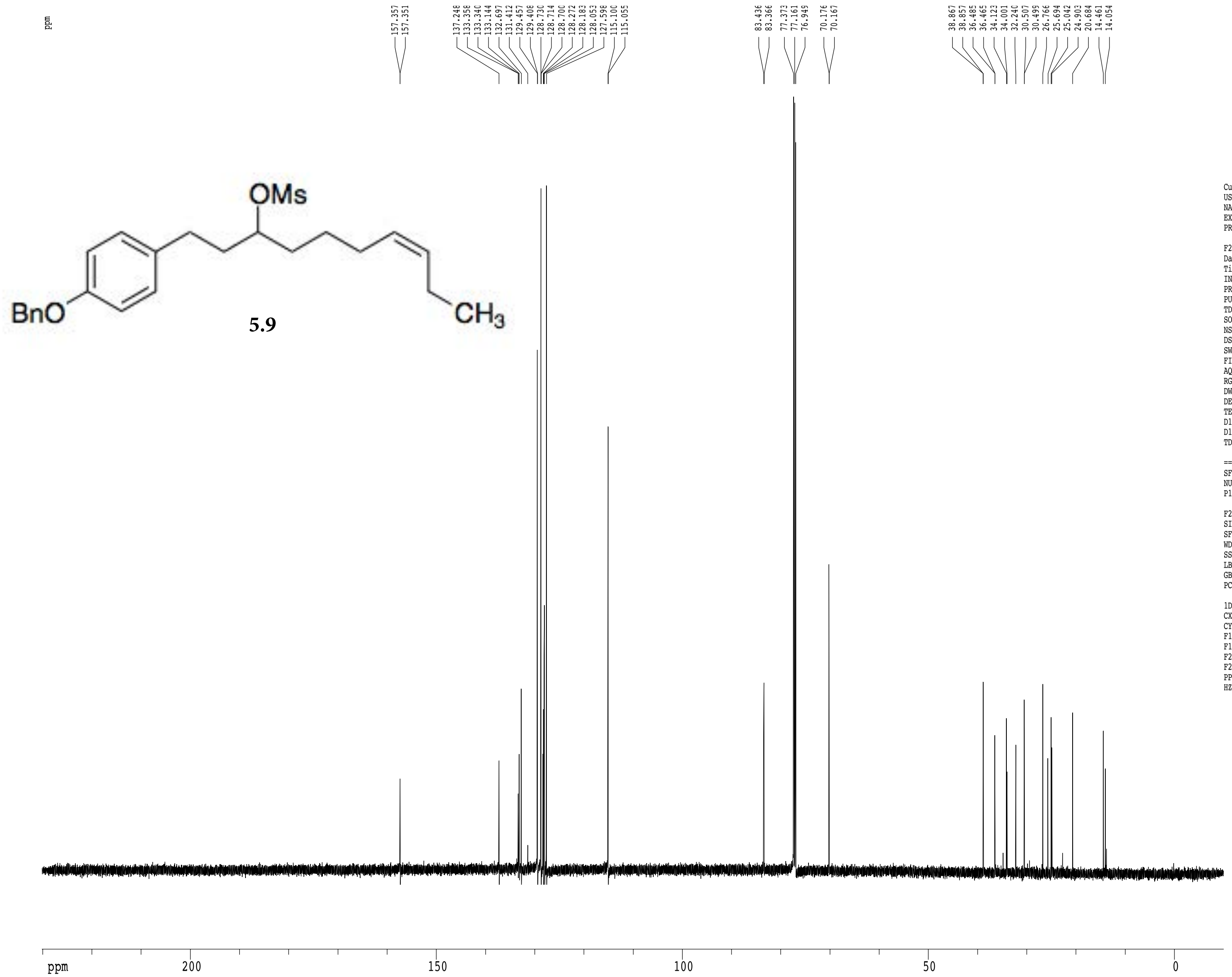
```
Current Data Parameters
USER           khewitt1
NAME         KAH-V-294-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20220228
Time              10.30
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                  168
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                37.70 usec

======== CHANNEL f1 ========
NUC1                13C
P1                18.85 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                1.55 dB
SP4                1.55 dB
SPNAM2      Crp60comp.4
SPNAM4   Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              22.00 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804150 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             230.637 ppm
F1             29009.68 Hz
F2P             -10.287 ppm
F2             -1293.96 Hz
PPMCM          10.56688 ppm/cm
HZCM         1329.10706 Hz/cm
```

1H spectrum



```
Current Data Parameters
USER          khewitt1
NAME     KAH-VI-059-Z-600
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220409
Time                12.38
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG              zg30
TD                  98074
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998979 sec
RG                     10
DW                 52.000 usec
DE                  14.12 usec
TE                  298.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                  10.00 usec

F2 - Processing parameters
SI                  65536
SF           600.1300000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.00 cm
F1P                 9.000 ppm
F1                5401.17 Hz
F2P                -0.500 ppm
F2                -300.06 Hz
PPMCM             0.41667 ppm/cm
HZCM            250.05418 Hz/cm
```

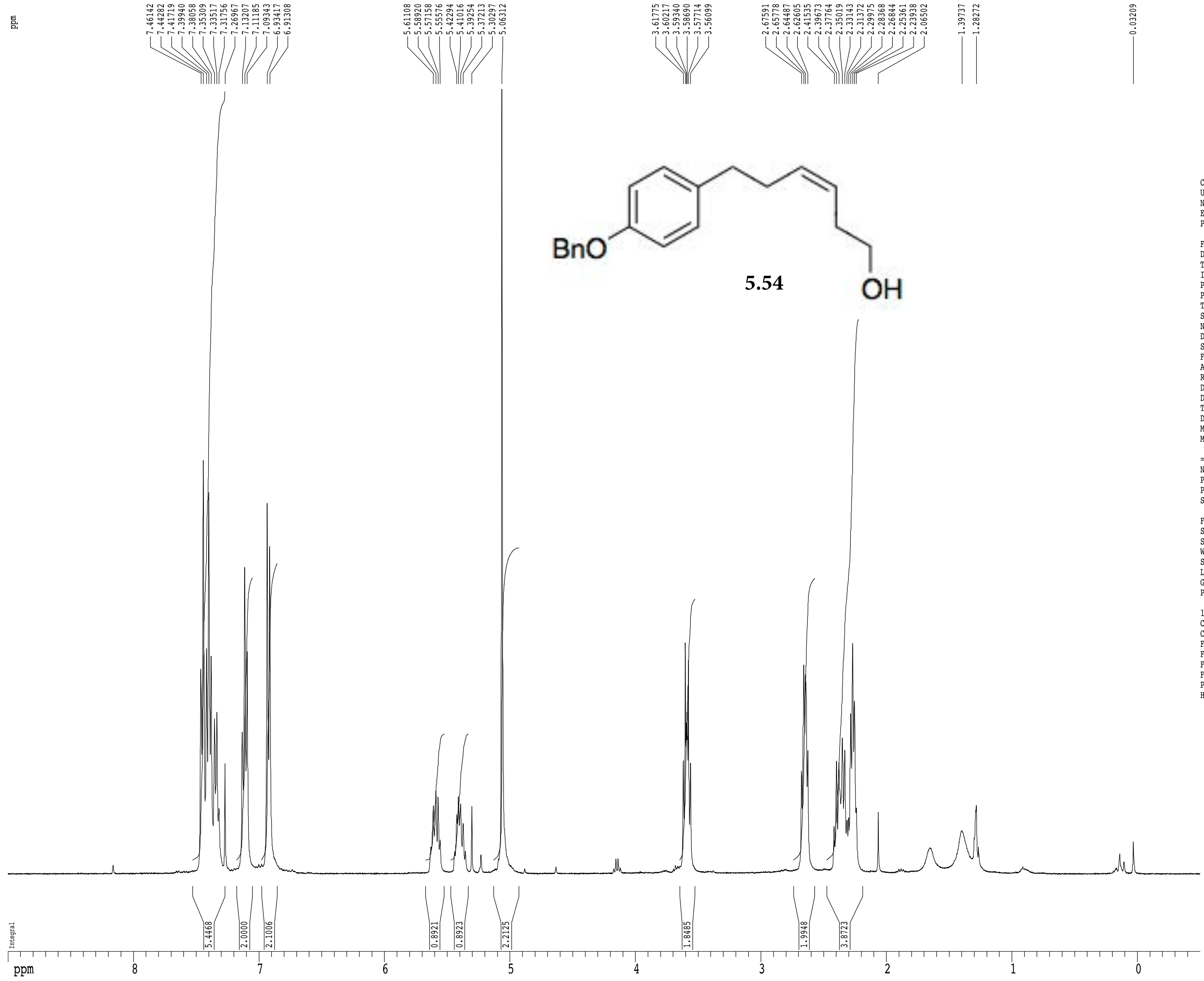
13C spectrum



5.9

```
Current Data Parameters
USER            khewitt1
NAME     KAH-VI-059-Z-600
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220409
Time               12.43
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT           CDCl3T
NS                    86
DS                     4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  2050
DW                13.800 usec
DE                 19.63 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.10 usec

F2 - Processing parameters
SI                 65536
SF          150.9027975 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P              230.125 ppm
F1              34726.45 Hz
F2P               -9.976 ppm
F2              -1505.44 Hz
PPMCM           10.53074 ppm/cm
HZCM          1589.11780 Hz/cm
```

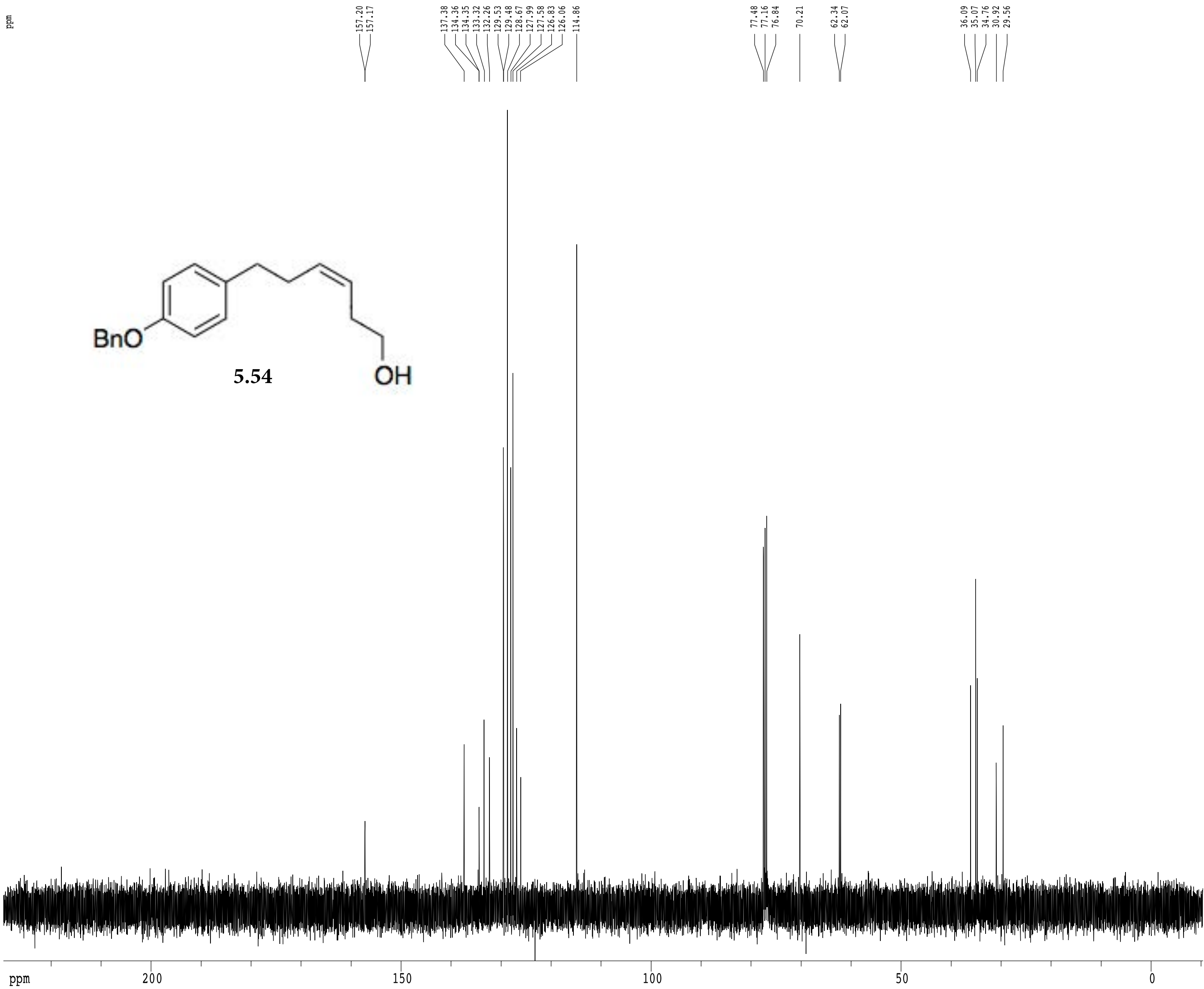
1H spectrum



5.54

```
Current Data Parameters
USER              khewitt1
NAME          KAH-VI-040-Z
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20220330
Time                 16.33
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG               zg30
TD                   38460
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               6410.256 Hz
FIDRES            0.166673 Hz
AQ               2.9999299 sec
RG                     128
DW                  78.000 usec
DE                    4.50 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 usec
PL1                  -0.90 dB
SFO1           400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300175 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.80 cm
CY                   15.00 cm
F1P                  9.000 ppm
F1                 3601.17 Hz
F2P                 -0.500 ppm
F2                 -200.06 Hz
PPMCM              0.41667 ppm/cm
HZCM             166.72084 Hz/cm
```

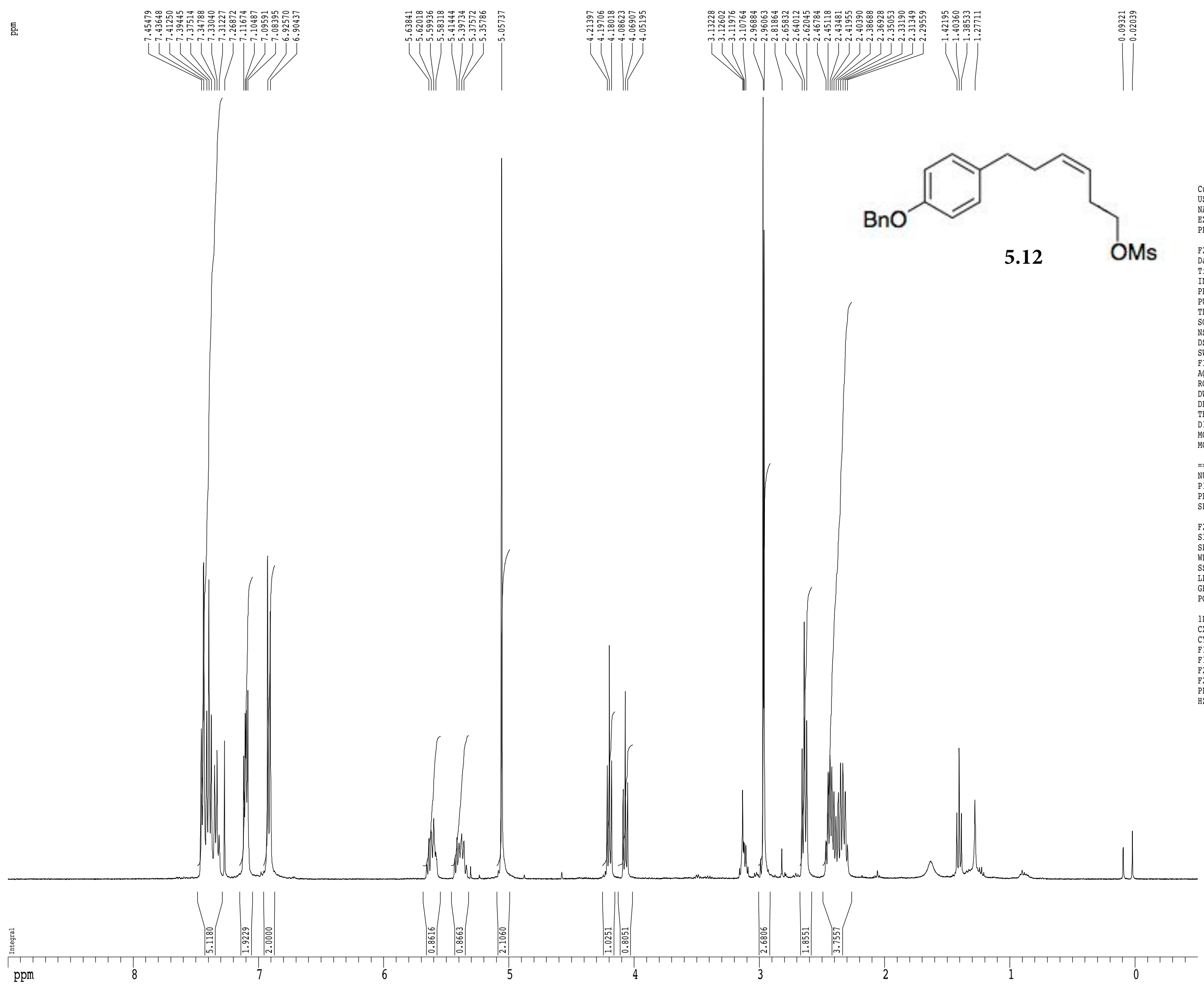
13C spectrum with 1H decoupling



5.54

```
Current Data Parameters
USER           khewitt1
NAME       KAH-VI-040-Z
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20220330
Time              16.35
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG         zgdc30
TD                65536
SOLVENT           CDCl3
NS                  175
DS                    4
SWH          24154.590 Hz
FIDRES        0.368570 Hz
AQ           1.3566452 sec
RG              9195.2
DW              20.700 usec
DE               20.39 usec
TE               298.0 K
D1          0.10000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1               13C
P1                7.90 usec
PL1              -3.00 dB
SFO1       100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            90.00 usec
PL2              -0.90 dB
PL12             17.00 dB
SFO2       400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          100.6127610 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P             229.496 ppm
F1             23090.21 Hz
F2P             -10.579 ppm
F2             -1064.37 Hz
PPMCM          10.52959 ppm/cm
HZCM         1059.41150 Hz/cm
```

1H spectrum

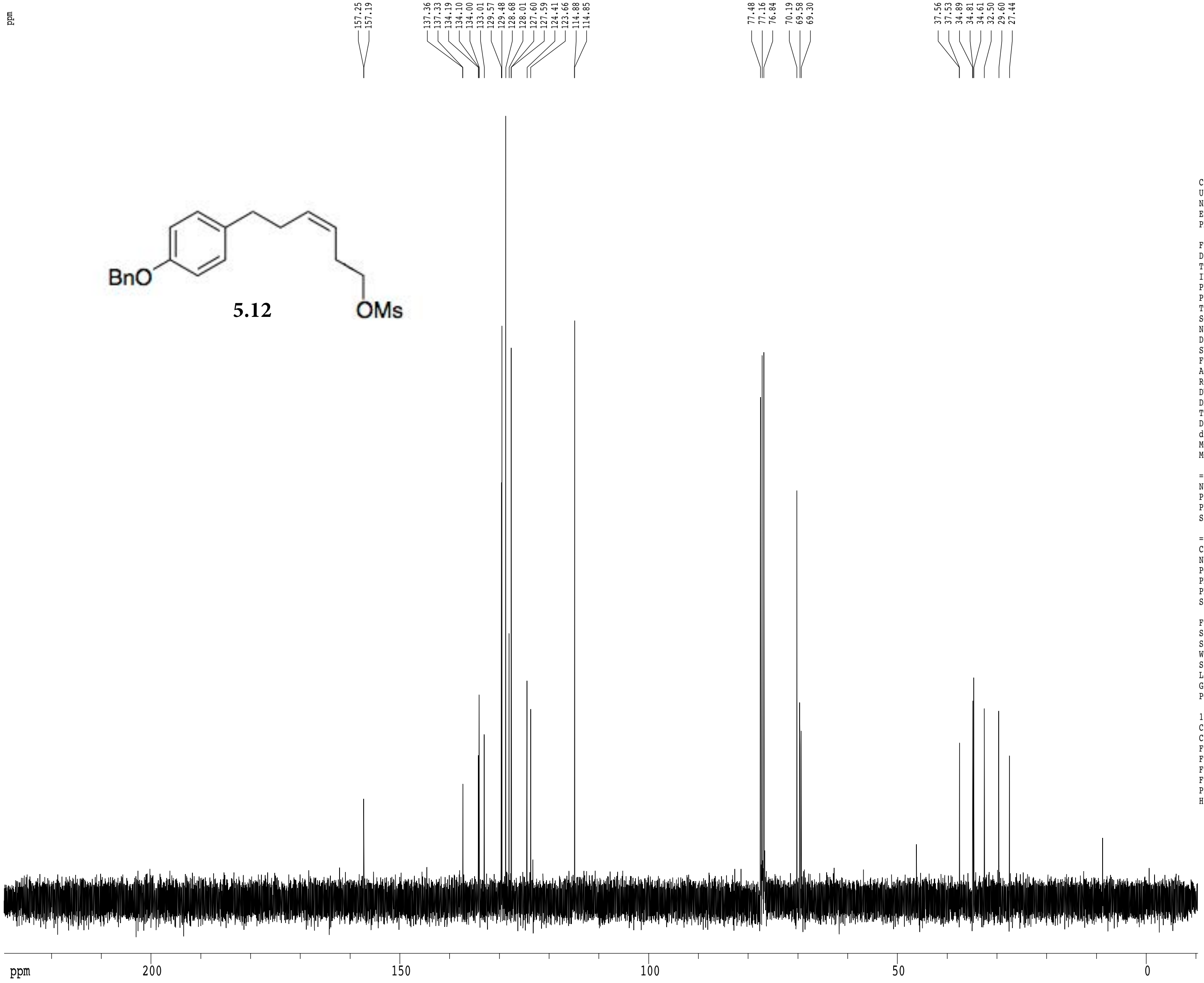


5.12

```
Current Data Parameters
USER            khewitt1
NAME         KAH-VI-041-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220331
Time               10.31
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 38460
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.166673 Hz
AQ             2.9999299 sec
RG                 161.3
DW                78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -0.90 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300175 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P               -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72084 Hz/cm
```

13C spectrum with 1H decoupling

5.12



```
Current Data Parameters
USER              khewitt1
NAME          KAH-VI-041-1
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20220331
Time                 10.33
INSTRUM             drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     288
DS                       4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ            1.3566452 sec
RG                  9195.2
DW              20.700 usec
DE               20.39 usec
TE                 298.0 K
D1          0.10000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                7.90 usec
PL1               -3.00 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            90.00 usec
PL2               -0.90 dB
PL12              17.00 dB
SFO2        400.1328009 MHz

F2 - Processing parameters
SI                   65536
SF          100.6127606 MHz
WDW                     no
SSB                      0
LB                 0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P            229.496 ppm
F1            23090.21 Hz
F2P            -10.579 ppm
F2            -1064.37 Hz
PPMCM       10.52959 ppm/cm
HZCM        1059.41150 Hz/cm
```