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Stereospecific Nickel-Catalyzed Cross-Coupling Reactions

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Aaron George Johnson

Dissertation Committee:
Professor Elizabeth R. Jarvo, Chair
Professor Christopher D. Vanderwal
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2015

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DEDICATION

For my parents
who taught me to never stop learning

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I wish to thank the American Chemical Society Green Chemistry Institute and the National Science Foundation for selecting me as a Green Chemistry Scholar, allowing me to attend and present my research at the 17th annual Green Chemistry and Engineering Conference in Bethesda, Maryland. This experience permanently changed the way I think about chemistry and gave me a solid commitment to minimize the environmental impact of my work.

I would like to thank my Ph.D. advisor, Professor Elizabeth Jarvo, for her mentorship and support. I could not be the scientist I have become without her expert hand. I also wish to thank my undergraduate research advisor, Professor Steven Castle, who welcomed me into his lab and ignited my passion for chemistry.

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CURRICULUM VITAE

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- Stereospecific nickel-catalyzed cross-coupling reactions of alkyl ethers with alkyl and aryl Grignard reagents
- Mechanistic studies of Kumada-type cross-coupling and major side reactions
- Synthesis of either enantiomer of a bioactive triarylmethane

2008-2009 **Undergraduate Research** Brigham Young University; Provo, UT
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PUBLICATIONS:

- **Johnson, A. G.**; Erickson, L. W.; Greene, M. A.; Yonova, I. M.; Taylor, B. L. H.; Jarvo, E. R. “Mechanistic Study of Stereospecific Nickel-Catalyzed Cross-Coupling Reactions.” Manuscript in preparation.
- **Johnson, A. G.**; Tranquilli, M. M.; Harris, M. R.; Jarvo, E. R. “Selective Synthesis of Either Enantiomer of an Anti-Breast Cancer Agent Via a Common Enantioenriched Intermediate.” *Tetrahedron Lett.* **2015**, *56*, 3486.
- **Johnson, A. G.**[‡]; Yonova, I. M.[‡]; Osborne, C. A.; Moore, C. E.; Morrissette, N. S.; Jarvo, E. R. “Stereospecific Nickel-Catalyzed Cross-Coupling Reaction of Alkyl Grignard Reagents and Identification of Selective Anti-Breast-Cancer Agents.” *Angew. Chem. Int. Ed.* **2014**, *53*, 2422–2427.
- **Johnson, A. G.**; Loertscher, B. M.; Moeck, A. R.; Matthews S. S.; Ess, D. H.; Castle, S. L. “Experimental and Theoretical Investigation of the Scope of Enantioselective Ketone Allylations Employing Nakamura’s Allylzinc-bisoxazoline Reagent.” *Bioorg. Med. Chem. Lett.* **2011**, *21*, 2706–2710.

PRESENTATIONS:

- **Johnson, A. G.**; Yonova, I. M.; Erickson, L. W.; Greene, M. A.; Osborne, C. A.; Jarvo E. R. Stereospecific Nickel-Catalyzed Cross-Coupling of Benzylic Ethers and Grignard Reagents. Presented at the 249th National Meeting of the American Chemical Society. Denver, CO, March 25, 2015 (oral presentation).
- **Johnson, A. G.** The Impact of Molecular Handedness on Drug Discovery and Development. Presented at the 2014 UCI Public Impact Fellows Reception. Irvine, CA, February 3, 2014 (oral presentation).
- **Johnson, A. G.**; Yonova, I. M.; Jarvo, E. R. Stereospecific Nickel-Catalyzed Cross-Coupling of Benzylic Ethers with Grignard Reagents. Presented at the 17th Annual ACS Green Chemistry and Engineering Conference. North Bethesda, MD, June, 19, 2013 (poster presentation).
- **Johnson, A. G.**; Yonova, I. M.; Jarvo, E. R. Stereospecific Nickel-Catalyzed Cross-Coupling of Benzylic Ethers with Grignard Reagents. Presented at the University of California, Irvine, Graduate and Postdoctoral Research Symposium. Irvine, CA, February 22, 2013 (oral presentation).
- **Johnson, A. G.**; Moeck, A. R.; Castle, S. L. Asymmetric Allylation of Assorted Ketones Using Nakamura’s Reagent. Presented at the Pacific Northwest Undergraduate Research Symposium on Organic Chemistry and Chemical Biology, Corvallis, OR, August 3-4, 2009 (oral presentation).

ABSTRACT OF DISSERTATION

Stereospecific Nickel-Catalyzed Cross-Coupling Reactions

by

Aaron George Johnson

Doctor of Philosophy in Chemistry

University of California, Irvine, 2015

Professor Elizabeth R. Jarvo, Chair

Transition metal catalyzed cross-coupling reactions have become a staple of organic synthesis and are frequently the most practical strategy for the preparation of medicinal agents and fine chemicals. Catalysts based on the precious metal palladium are commonly used in cross-coupling reactions. Replacing palladium catalysts with nickel catalysts is an active area of research as such advances present significant benefits including increasing the sustainability of transformations and new mechanisms for control of stereochemistry in the construction of C_{sp}³–C_{sp}³ bonds.

In Chapter 1, a stereospecific nickel-catalyzed cross-coupling reaction of secondary benzylic ethers with a variety of aliphatic and aryl Grignard reagents is presented. The method is highly stereospecific and proceeds with inversion at the benzylic carbon. Products prepared by this method were subject to biological testing, and a thiophene-containing product was shown to selectively inhibit the growth of MCF-7 breast cancer cells.

In Chapter 2, mechanistic studies that provide insight into the mechanism of oxidative addition as well as the mechanisms of major side reactions, hydrogenolysis and β-hydride elimination, are presented. Experiments presented provide evidence that the mechanisms of

cross-coupling, hydrogenolysis, and β -hydride elimination reactions all include a step of oxidative addition with inversion at the benzylic center. Hydrogenolysis was also shown to be stereospecific, proceeding with overall inversion at the stereogenic center.

In Chapter 3, the application of nickel-catalyzed cross-coupling reactions to the synthesis of either enantiomer of a bioactive triaryl methane from a single enantiomer of a precursor alcohol is presented. In the key cross-coupling step a Kumada protocol allows for cross-coupling with inversion at the benzylic carbon, while a Suzuki reaction allows for cross-coupling with retention.

Chapter 1

Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Grignard Reagents with Benzylic Ethers

1.1 Introduction

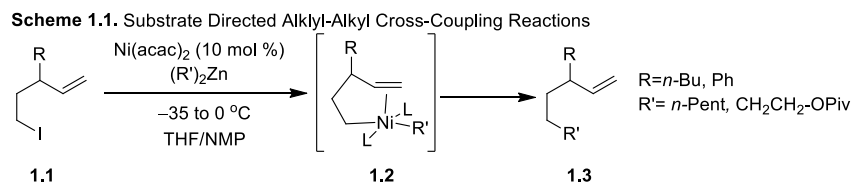
Palladium and nickel catalyzed cross-coupling reactions have revolutionized organic chemistry.¹ For C_{sp^2} – C_{sp^2} bond formation, transition-metal catalyzed cross-coupling reactions are likely the first disconnection a chemist will propose. Nonetheless, these reactions remain underdeveloped in forming C_{sp^3} – C_{sp^3} bonds. Two reasons are commonly cited to explain the difficulty of transition metal mediated alkyl-alkyl cross-coupling reactions: oxidative addition to an alkyl electrophile is slower than oxidative addition to an aryl or vinyl electrophile, and β -hydride elimination often outcompetes reductive elimination.^{1b} The latter challenge is especially pertinent when both coupling partners contain β -hydrogens. Despite these challenges, recent advances have brought the field closer to realizing the potential of transition metal-catalyzed alkyl-alkyl bond formation. Major milestones in nickel-catalyzed alkyl-alkyl cross-coupling research have included reactions between two primary alkyl groups, reactions between primary and secondary alkyl groups, and stereoconvergent reactions.

The Knochel group demonstrated that alkyl-alkyl bonds between two primary coupling partners could be formed in a nickel-catalyzed reaction when they reported the reaction shown in Scheme 1.1.² Reductive elimination to form C_{sp^3} – C_{sp^3} bonds is difficult owing to the electron rich nature of sp^3 carbons. In Knochel's transformation, a pendant olefin promotes reductive elimination by decreasing electron density at the metal center through a backbonding interaction

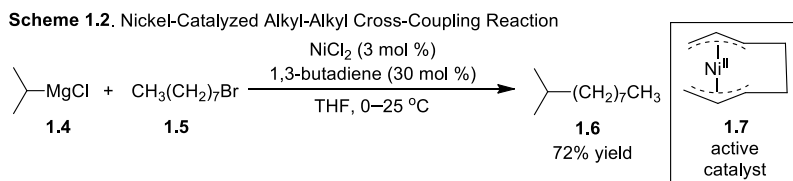
¹ (a) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417. (b) Netherton, M. R.; Fu, G. C. *Adv. Synth. Catal.* **2004**, *346*, 1525. (c) Rudolph, A.; Lautens, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 2656. (d) Johnson, C. R.; De Jong, R. L. *J. Org. Chem.* **1992**, *57*, 594.

² (a) Giovannini, R.; Stüdemann, T.; Devasagayaraj, A.; Dussin, G.; Knochel, P. *J. Org. Chem.* **1999**, *64*, 3544. (b) For a more recent example see: Nielsen, D. K.; Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2013**, *135*, 13605.

(1.2). Other π -accepting functional groups such as ketones, cyanides, or esters also increase reactivity.³ Knochel's work showcased the potential of using nickel catalysts in alkyl-alkyl cross-coupling reactions.



Kambe has shown that nickel complexes can catalyze Kumada-type cross-coupling reactions between primary halides and primary and secondary Grignard reagents.⁴ In the reaction shown in Scheme 1.2, two butadiene molecules dimerize around the metal center to form a bis- π -allyl Ni^{II} complex (**1.7**) that enters a proposed $\text{Ni}^{\text{II}}\text{-Ni}^{\text{IV}}$ catalytic cycle. While initially developed to cross-couple primary alkyl groups, this reaction provides good yields with a secondary Grignard reagent, *i*-PrMgCl (**1.4**).⁵



In recent years, research in the Fu group has shown the power of nickel complexes to catalyze stereocontrolled alkyl-alkyl cross-coupling reactions. The Fu group has developed several methods to prepare enantioenriched tertiary products (Scheme 1.3, structure **1.10**) utilizing secondary alkyl halogens (**1.8**).⁶ Many of these strategies are stereoselective. These

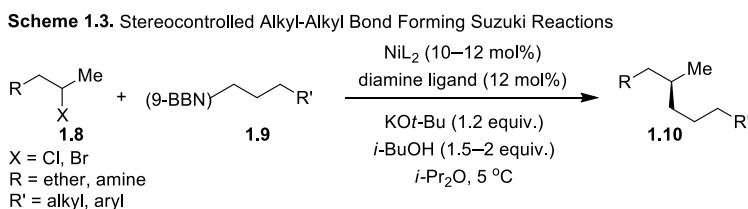
³ (a) Giovannini, R.; Stüdemann, T.; Dussin, G.; Knochel, P. *Angew. Chem. Int. Ed.* **1998**, *37*, 2387. (b) For an example utilizing exogenous dimethyl fumarate see: Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2012**, *134*, 9541.

⁴ Terao, J.; Watanabe, H.; Ikumi, A.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2002**, *124*, 4222.

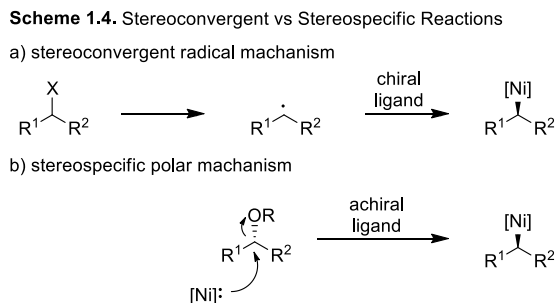
⁵ For a related transformation in which secondary Grignard reagents are coupled to vinyl halides, see: (a) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180. (b) Schwink, L.; Knochel, P. *Chem. Eur. J.* **1998**, *4*, 950.

⁶ (a) Lu, Z.; Wilsily, A.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8154. (b) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726. (c) Lou, S.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 1264. (d) Lundin, P. M.; Fu, G. C. *J. Am.*

reactions are proposed to go through a radical mechanism and rely on a chiral catalyst to set stereochemistry in a stereoconvergent manner.



Stereoconvergent reactions, such as Fu's, represent a strategy that finds high utility when a stereocenter is to be set in a cross-coupling reaction (Scheme 1.4a). However, this strategy is not ideal when stereochemical information is already present at the reactive center of a substrate. In these cases a stereospecific approach, in which stereochemical information is transferred from substrate to product, is desired (Scheme 1.4b). As shown by Fu and others, alkyl halides are expected to go through a radical mechanism of oxidative addition and are not suitable substrates for stereospecific cross-coupling reactions because radical processes scramble stereochemical information.⁷



Ethers are suitable electrophiles for stereospecific nickel catalyzed $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}$ bond formation.⁸ The literature of nickel-catalyzed substitution reactions of allylic ethers shows that

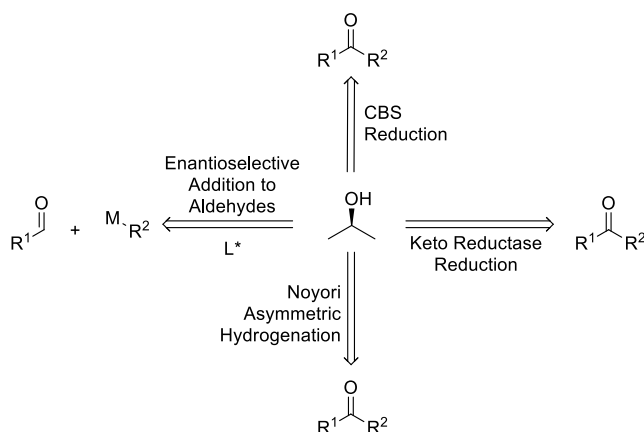
Chem. Soc. **2010**, *132*, 11027. (e) Owston, N. A.; Fu, G. C. *J. Am. Chem. Soc.*, **2010**, *132*, 11908. (f) Saito, B.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 6694.

⁷ (a) Choi, J.; Martín-Gago, P.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 12161. (b) Vechorkin, O.; Csok, Z.; Scopelliti, R.; Hu, X. *Chem. Eur. J.* **2009**, *15*, 3889.; (c) Becker, Y.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 838. (d) Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans* **1980**, 1448.

⁸ For a stereospecific palladium catalyzed reaction, see: He, A.; Falck, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 2524.

the oxidative addition of nickel complexes into C–O bonds may proceed through heterolytic bond cleavage.⁹ Alcohol derivatives are also an attractive electrophile class owing to the variety of robust methods with which enantioenriched alcohols can be prepared (Scheme 1.5).¹⁰ For these reasons, the cross-coupling of ethers with organometallic nucleophiles is a valuable contribution to the cross-coupling literature.

Scheme 1.5. Examples of Asymmetric Alcohol Synthesis



In 2011, the Jarvo lab demonstrated the utility of using ethers in Kumada-type couplings to install a methyl group.^{11,12} An example is shown in Scheme 1.6. First enantioenriched alcohol **1.12** is prepared via a titanium mediated enantioselective addition of diethylzinc to

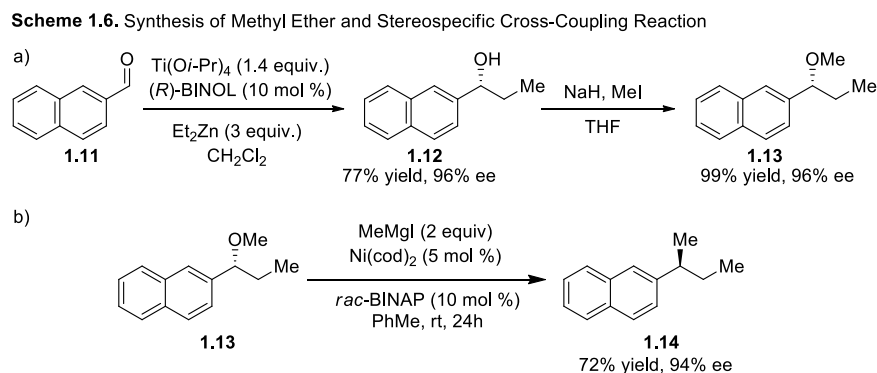
⁹ (a) Consiglio, G.; Morandini, F.; Piccolo, O. *J. Am. Chem. Soc.* **1981**, *103*, 1846. (b) Kobayashi, Y.; Ikeda, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1789. (c) Didiuk, M. T.; Morken, J. P.; Hoveyda, A. H. *Tetrahedron* **1996**, *54*, 1117.

¹⁰ (a) For CBS reduction, see: (i) Corey, E. J. (Nobel Lecture) *Angew. Chem. Int. Ed.* **1991**, *30*, 455. (ii) Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 1986. (iii) “Reductions”: Li, J. J.; Limberakis, C.; Pflum, D. A. in *Modern Organic Synthesis in the Laboratory: A Collection of Standard Experimental Procedures*, Oxford University Press, New York, **2007**, 96–97. (b) for keto reductases, see: Bohren, K. M.; Bullock, B.; Wermuth, B.; Gabbay, K. H. *J. Biol. Chem.* **1989**, *264*, 9547. For Noyori hydrogenation, see: (i) Noyori, R. (Nobel Lecture) *Angew. Chem. Int. Ed.* **2002**, *41*, 2008. (ii) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (d) for asymmetric additions to ketones, see: (i) Zhang, F.-Y.; Yip, C.-W.; Cao, R.; Chan, A. S. C. *Tetrahedron: Asymmetry* **1997**, *8*, 585. (ii) Braga, A. L.; Paixão, M. W.; Westermann, B.; Schneider, P. H.; Wessjohann, L. A. *J. Org. Chem.* **2008**, *73*, 2879.

¹¹ (a) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389. (b) For a variant that does not require an extended π -aromatic system see: Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. *Org. Lett.* **2012**, *14*, 4293.

¹² A similar racemic cross-coupling reaction was reported by Shi, see: Guan, B.-T.; Xiang, S.-K.; Wang, B.-Q.; Sun, Z.-P.; Wang, Y.; Zhao, K.-Q.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 3268.

aldehyde **1.11** (Scheme 1.6a).¹³ Methylation of alcohol **1.12** provides methyl ether **1.13** which is capable of undergoing oxidative addition.¹⁴ Under the influence of an achiral catalyst, ether **1.13** will couple with methyl Grignard reagents with overall inversion at the stereogenic center to form enantioenriched target compound **1.14** (Scheme 1.6b).



The Jarvo lab's initial report established that this nickel-catalyzed cross-coupling method is feasible to install a methyl group to a variety of substrates. Herein are reported my efforts aimed to extend the scope of this methodology to include more complex alkyl and aryl Grignard reagents.¹⁵

1.2 Results and Discussion:

1.2.1 Optimization of Cross-Coupling Reaction

Initial attempts to perform the cross-coupling reaction with a propyl Grignard reagent showed that nickel could catalyze cross-coupling reactions between methyl ether **1.13** and *n*-propylmagnesium iodide to form cross-coupled product **1.15**. Unfortunately, the reaction gave variable yields (14–65%) that seemed to erode proportional to catalyst age (Table 1.1, entry 1).¹⁶

¹³ The competing enantiomer conversion method can be used to assign the absolute configuration of secondary alcohols; see: Wagner, A. J.; Rychnovsky, S. D. *J. Org. Chem.* **2013**, *78*, 4594.

¹⁴ Herrmann, J. M.; König, B. *Eur. J. Org. Chem.* **2013**, 7017.

¹⁵ This chapter will focus on content of the following publication: 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.

¹⁶ Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389.

A time-correlated drop in yield could be explained if a co-catalyst was precipitating out of the Grignard reagent solution as the solution aged. We proposed that such a co-catalyst was present in trace amounts in the magnesium source. This hypothesis was tested through a study on Grignard reagent age. Grignard reagents were prepared from magnesium from two sources: standard purity magnesium from Acros, and ultra-pure magnesium from Alfa Aesar (99.98+% Puratronic grade). Reactions run with aged Grignard reagent were expected to show lower yields than reactions run with fresh reagent. In experiments run with pure magnesium, low yields were expected regardless of Grignard reagent age. Surprisingly, in all experiments, both Grignard reagents afforded between 50% and 60% yield (Table 1.1). It was therefore concluded that a co-catalyst was not responsible for the variable yields. Fortuitously, this study also showed that the reaction was reproducible.

Table 1.1. Effect of Grignard Reagent Age

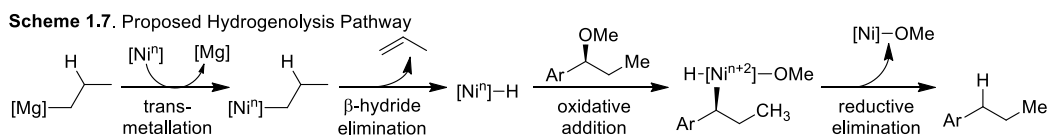
Entry	Mg ^a grade ^b	RMgI age	1.15 yield (%) ^c	1.16 yield (%) ^c	1.17 yield (%) ^c
1 ^a	Standard	variable	14–64	n.d. ^d	n.d. ^d
2	Standard	Fresh	57	31	6
3	Standard	3 Days	61	34	5
4	Standard	6 Days	55	26	5
5	Standard	14 Days	52	39	5
6	Puratronic	Fresh	49	29	<5
7	Puratronic	2 Days	59	15	7
8	Puratronic	5 Days	59	30	7
9	Puratronic	8 Days	54	38	5

^aMultiple experiments run by Buck Taylor ^bAll Grignard reagents were titrated with iodine less than two hours before use. ^cYield determined by ¹H NMR spectroscopy by comparison to an internal standard (1,4-dimethoxybenzene). ^dNot determined.

Although the reproducible yields in these experiments were encouraging, these results showed that the products of β -hydride elimination (**1.16**) and hydrogenolysis (**1.17**) were still problematic.¹⁷ Interestingly, hydrogenolysis product **1.17** was not produced when methyl

¹⁷ See Chapter 2 for in-depth studies on the mechanism of byproduct formation.

Grignard reagent was used. This result suggests that the reduction pathway arises from β -hydride elimination from the nucleophile prior to oxidative addition (Scheme 1.7).



We next sought to identify conditions that would promote the cross-coupling reaction while suppressing formation of the undesired elimination and hydrogenolysis byproducts. The nickel source was briefly studied. First, a nickel-free positive control showed that the cross-coupling reaction was mediated by the metal catalyst (Table 1.2, entry 1). As has already been shown (vide supra), Ni(cod)₂ allows for cross-coupling with an average 56% yield (entry 2). When Ni(acac)₂ is used, the cross-coupling reaction proceeded in a comparable 59% yield (entry 3). Because Ni(acac)₂ is more stable and less expensive than Ni(cod)₂, subsequent studies were performed using Ni(acac)₂. Regardless of the nickel source, greater than 36% of starting material underwent undesired hydrogenolysis or β -hydride elimination.

Table 1.2. Comparison of Nickel Sources

Entry	Nickel Source	1.15 yield (%) ^a	1.16 yield (%) ^a	1.17 yield (%) ^a
1 ^b	no nickel	0	0	0
2 ^c	Ni(cod) ₂	56	30	6
3	Ni(acac) ₂	59	37	7

^a Yield determined by ¹H NMR by comparison to an internal standard (1,4-dimethoxybenzene).

^b 98% starting material recovered. ^c Average of eight experiments.

We postulated that by screening a variety of ligands with varying electronic properties and steric effects, we would be able to improve conversion to desired product **1.15**. To this end we screened a variety of diphosphine ligands (Table 1.3). DPEphos, Xantphos, and racBINAP, all of which give optimal conversion with methyl Grignard reagents, give suboptimal results in reactions with a longer chain Grignard reagent (entries 1–3). Bis-diphenylphosphino ligands

with long carbon-chain linkers (dppoctane and dpppentane) promoted the formation of elimination and hydrogenolysis byproducts (entries 4–5). Use of a ligand with a shorter linker (dppp) resulted in a 62% yield of the desired product with most of the mass balance accounted for by elimination and deoxygenation pathways (entry 6). A ligand with a slightly shorter tether, 1,2-bis(diphenylphosphino)ethane (dppe), proved to be an optimal ligand, providing 80% yield of cross-coupling product with minimal byproduct formation (entry 7). The fact that ligands that contain a short tether (dppe and dppp) best promote the reaction suggests that a strongly coordinating bidentate ligand interaction promotes cross-coupling reactivity.

Table 1.3. Ligand Screen

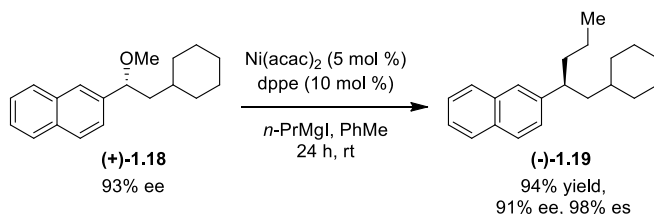
Entry	Ligand	1.13 recovery (%) ^a	1.15 yield (%) ^a	1.16 yield (%) ^a	1.17 yield (%) ^a
1	DPEphos	0	59	37	7
2	Xantphos	77	14	0	0
3	racBINAP	0	0	0	12
4	dppoctane	0	0	68	26
5	dpppentane	0	0	62	24
6	dppp	0	62	19	16
7	dppe	0	80	0	<5

^a Yield determined by ¹H NMR spectroscopy by comparison to an internal standard (1,4-dimethoxybenzene).

Having established that cross-coupling reactions with a long chain Grignard reagent can proceed in high yield, we turned our attention to the enantiospecificity of the reaction. Despite many attempts, enantiomers of product **1.15** were inseparable by SFC and GC analysis. Therefore an alternative substrate **1.18** was investigated (Scheme 1.8). Methyl ether **1.18** is electronically similar to methyl ether **1.13**, but more sterically congested, a property that we expected to improve separation on a chiral SFC column. The cross-coupling reaction with methyl ether **1.18** afforded desired product **1.19** in 94% yield. Enantiomers of product **1.19**

readily separated by chiral column SFC revealing that the reaction proceeds with 98% enantiospecificity.¹⁸

Scheme 1.8. Cross-Coupling Reactions with Cyclohexyl Substrate



Unfortunately, subsequent experiments showed that the cross-coupling protocol shown in Scheme 1.8 is unreliable. In multiple experiments under “identical” conditions, compound **1.18** was either fully consumed, resulting in nearly quantitative conversion to desired product **1.19**, or no reaction was observed, resulting in quantitative recovery of starting material (Table 1.4).

Table 1.4. Variability in Cross-Coupling Results

Entry	(1.18) recovery (%) ^a	(1.19) yield (%) ^a
1	89	0
2	0	89

^aDetermined by ¹H NMR against an internal standard: 1,4-dimethoxybenzene.

This observed *on-off* effect may be due to subtle differences in the stoichiometry of dppe relative to nickel. Such subtle differences could be caused by random error when weighing small quantities on an analytical scale.¹⁹ It is not uncommon for optimal conditions of nickel-catalyzed cross-coupling reactions to be reported with a 2:1 ligand to nickel ratio.²⁰ However, the smaller bite angle of dppe, versus DPEphos, BINAP, or other ligands may allow for two dppe ligands to simultaneously coordinate the nickel center if there is an excess of dppe. Indeed, the bis-dppe-

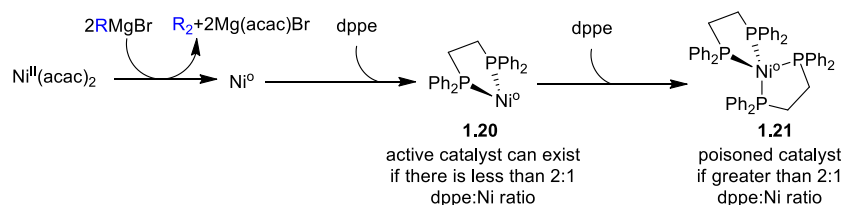
¹⁸ Enantiospecificity (es) = $ee_{\text{product}}/ee_{\text{starting material}}$, see, Denmark, S. E.; Vogler, T. *Chem. Eur. J.* **2009**, *15*, 11737.

¹⁹ Wernerova, M.; Hudlicky, T. *Synlett*, **2010**, 2701.

²⁰ For representative examples, see reference 11 and: (a) Shields, J. D.; Ahneman, D. T.; Graham, T. J. A.; Doyle, A. G. *Org. Lett.* **2014**, *16*, 142. (b) Leowanawat, P.; Zhang, N.; Percec, V. *J. Org. Chem.*, **2012**, *77*, 1018.

nickel complex has been characterized.²¹ We hypothesized that the active catalyst is comprised of one nickel atom ligated to one dppe ligand (**1.20**). Complex **1.20** presumably forms after Grignard reagent reduces nickel (II) to nickel (0) (Scheme 1.9). In the presence of excess dppe, a second ligand will bind the nickel atom resulting in complex **1.21**, which we hypothesized is unreactive in the cross-coupling reaction.²²

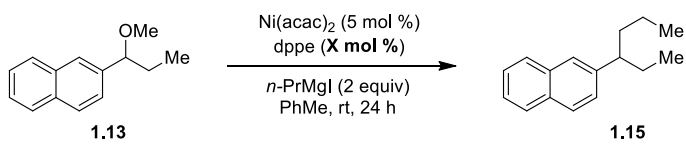
Scheme 1.9. Proposed Formation of Active and Poisoned Catalyst



To test these hypotheses, we carried out the experiments shown in Table 1.5. Cross-coupling reactions were executed with 5 mol % $\text{Ni}(\text{acac})_2$ and varying amounts of dppe. When dppe is used as ligand, conversion to products is efficient if the dppe:nickel ratio is less than 2:1 (entries 1–6). If the dppe:nickel ratio exceeds 2:1, the catalyst presumably coordinates a second dppe ligand rendering an inactive catalyst (entries 9–10). At a 2:1 dppe:nickel ratio, the reaction is unreliable, presumably because the actual ligand to nickel ratio is very slightly above or very slightly below 2:1 (entries 7–8). These results are consistent with the hypotheses that the active catalyst has one and only one dppe ligand bound to the metal atom.

²¹ (a) Fisher, K. J.; Alyea, E. C. *Polyhedron* **1998**, 8, 13. (b) Yamashita, K.-I.; Takeda, H.; Kashiwabara, T.; Hua, R.; Shimada, S.; Tanaka, M. *Tetrahedron Lett.* **2007**, 48, 6655.

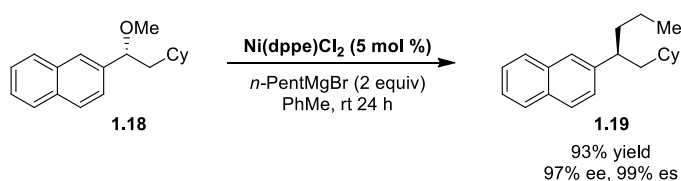
²² Yonova, I. M. Ph.D. Dissertation, University of California, Irvine, 2013.

Table 1.5. Effect of Ligand to Nickel Ratio on Reactivity


Entry	ligand load	[dppe] : [nickel]	1.13 recovery (%) ^a	1.15 yield (%) ^a
1	2.5 mol %	0.5 : 1	3	67
2	2.5 mol %	0.5 : 1	0	72
3	5 mol %	1 : 1	0	89
4	5 mol %	1 : 1	0	87
5	7.5 mol %	1.5 : 1	0	87
6	7.5 mol %	1.5 : 1	0	91
7	10 mol %	2 : 1	0	84
8	10 mol %	2 : 1	95	0
9	12.5 mol %	2.5 : 1	97	0
10	12.5 mol %	2.5 : 1	95	0

^aYield determined by ¹H NMR spectroscopy by comparison to an internal standard (1,4-dimethoxybenzene).

Because the active catalyst has a 1:1 ligand:nickel ratio, a precatalyst that also exhibits this ratio would be advantageous as it would eliminate the possibility of weighing error. Ni(dppe)Cl₂ displays an inherent 1:1 dppe:nickel ratio. Furthermore, it is stable at room temperature and is not air-sensitive, obviating the need for a glovebox. Initial experiments using Ni(dppe)Cl₂ as precatalyst showed the reagent to be as effective as and easier to work with than Ni(acac)₂ (Scheme 1.10). Ni(dppe)Cl₂ was therefore used in all future experiments. With optimized conditions in hand, we turned our attention to reaction scope.

Scheme 1.10. Ni(dppe)Cl₂ as Precatalyst

1.2.2. Reactions with Alkyl Grignard Reagents to Form C_{sp}³-C_{sp}³ bonds.

With regards to scope, we began by studying the scope of alkyl Grignard reagents (Table 1.6). Ni(dppe)Cl₂ catalyzes the coupling of benzylic ethers to a variety of long-chain aliphatic Grignard reagents (entries 1–4). These include functionalized Grignard reagents featuring

aromatic rings and olefins (entries 2–3). A pharmaceutically relevant trifluoromethyl moiety was also tolerated (entry 4). Yields are generally high, but somewhat lower with a sterically encumbered nucleophile (entry 5). In all cases, enantiospecificity is greater than 90%.

Table 1.6. Alkyl Grignard Reagent Scope

entry	product		yield (%) ^a	S.M.ee (%) ^b	prod.ee (%) ^b	es (%) ^c
1		1.22 R ² = <i>n</i> -Pent	91	97	97	>99
2		1.23 R ² = (CH ₂) ₃ Ph	88	97	97	>99
3 ^(d)		1.24 R ² =	81	97	97	>99
4 ^(e)		1.25 R ² = (CH ₂) ₃ CF ₃	67	>99	97	97
5		1.26 R ² = <i>i</i> -Bu	40	97	90	93

6 ^(d)		1.27 R ² = <i>n</i> -Pent	96	>99	96	96
7 ^(d)		1.28 R ² = (CH ₂) ₃ Ph	93	97	97	>99

^aCalculated after silica chromatography. ^bDetermined by chiral SFC chromatography.

^c100 x ee_{product}/ee_{starting material}. ^d[Ni(dppe)Cl₂] (5 mol %). ^e[Ni(dppe)Cl₂] (10 mol %).

Some nucleophiles require mild tuning of reaction conditions to achieve optimal reactivity. In most cases, altering only catalyst loading or temperature is sufficient to realize efficient conversion and high stereospecificity. The cross-coupling reaction with 4,4,4-trifluorobutylmagnesium bromide to form compound **1.25** provides a good example (Table 1.6, entry 4). Most reactions give optimal ee when catalyst loading is 2 mol %; however, inductively electron poor 4,4,4-trifluorobutylmagnesium bromide undergoes poor conversion even at 5 mol % catalyst loading (Table 1.7, entry 1). Heating the reaction boosts yield, but at the expense of ee (entry 2). For the fluorinated nucleophile, optimal results are achieved by doubling catalyst loading to 10 mol % to boost yield while running the reaction at room temperature to maintain high stereochemical fidelity (entry 3). These conditions resulted in an acceptable yield of 68% and an excellent 97% ee. Some Grignard reagents required similar reagent-specific optimization,

but in almost all cases, efficient conversion to cross-coupled product was achieved after slight adjustments of temperature or catalyst loading.²³

Table 1.7. Optimization of Reaction with CF₃ Containing Nucleophile

Entry	Ni(dppe)Cl ₂	Temp	1.18 recovery (%) ^a	1.25 yield (%) ^b	ee/es
1	5 mol %	25 °C	48	37	95/95
2	5 mol %	50 °C	0	68	65/65
3	10 mol %	25 °C	4	68	97/97

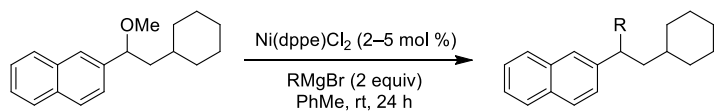
^aDetermined by ¹H NMR against an internal standard, PhTMS. ^bIsolated yield after silica gel flash column chromatography.

Olefin-containing Grignard reagents are exceptionally challenging, and achieving cross-coupling reactivity with them proved more difficult than simply altering concentration or temperature (vide supra, Table 1.6, entry 3). Olefin-containing products are highly attractive as they represent a functional group that can be exploited for further synthetic elaboration. Unfortunately, initial coupling with allyl and terminal olefin-containing Grignard reagents failed to give any cross-coupling product (Table 1.8, entries 1–2). This is not surprising as olefins are known to be ligands for nickel complexes.²⁴ For example, styrenes have been shown by our lab to have a detrimental effect on nickel-catalyzed Kumada reactions.²⁵ Steric bulk around the alkene was expected to prevent coordination and preserve reactivity. Unfortunately, a Grignard reagent containing a bulkier *Z*-substituted olefin failed to promote the reaction (entry 3). Fortunately, a trisubstituted olefin underwent cross-coupling to form compound **1.24** in 81% yield and with 97% ee (entry 4). These results suggest that a high degree of olefin substitution is required to prevent coordination of nickel to double bonds.

²³ See experimental section.

²⁴ See reference 2. See also: Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

²⁵ Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2010**, *133*, 389.

Table 1.8. Effect of Olefin Substitution

Entry	R	yield ^a	ee ^b
1		0	N/A
2		0	N/A
3		0	N/A
4		81 ^c	97/99

^aYield determined by ¹H NMR against an internal standard, 1,4-dimethoxybenzene.

^bee determined by chiral cholum SFC. ^cIsolated yield determined after purification by silica gel flash column chromatography.

1.2.3 Reactions with Aryl Grignard Reagents to Form C_{sp}³–C_{sp}² bonds

The primary focus of the project described in this chapter was to develop a facile method for the stereospecific formation of C_{sp}³–C_{sp}³ bonds. Once optimal conditions for that transformation were identified, we investigated whether or not the same protocol is a general method that could also be applied to the formation of C_{sp}³–C_{sp}² bonds. Such a strategy could be used to prepare diarylalkanes,^{26,27} a class of molecule that has been shown to have significant biological relevance.^{28,29} We therefore investigated if the conditions optimized for C_{sp}³–C_{sp}³

²⁶ For similar disconnections see: (a) López-Pérez, A.; Adrio, J.; Carretero, J. C.; *Org. Lett.* **2009**, *11*, 5514. (b) Imao, D.; Glasspoole, B. W.; Laberge, V. S.; Crudden, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 5024. (c) Li, J.; Burke, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 13774. (d) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 280. (e) Do, H.-Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 16288.

²⁷ For representative alternative strategies for enantioselective synthesis of 1,1-diaryllanes, see: (a) Wang, Z.; Ai, F.; Wang, Z.; Zhao, W.; Zhu, G.; Lin, Z.; Sun, J. *J. Am. Chem. Soc.* **2015**, *137*, 383. (b) Saini, V.; Liao, L.; Wang, Q.; Jana, R.; Sigman, M. S. *Org. Lett.* **2013**, *15*, 5008. (c) Wang, X.; Guram, A.; Caille, S.; Hu, J.; Preston, J. P.; Ronk, M.; Walker, S. *Org. Lett.* **2011**, *13*, 1881. (d) Fessard, T. C.; Andrews, S. P.; Motoyoshi, H.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 9331.

²⁸ Representative Examples: (a) as ligands for nuclear receptors, see: Kainuma, M.; Kasuga, J.-I.; Hosoda, S.; Wakabayashi, K.-I.; Tanatani, A.; Nagasawa, K.; Miyachi, H.; Makishima, M.; Hashimoto, Y. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 3213. (b) as combretastatin analogues for colon cancer, see: Messaoudi, S.; Hamze, A.; Provot, O.; Tréguier, B.; Rodrigo De Losada, J.; Bignon, J.; Liu, J.-M.; Wdzieczak-Bakala, J.; Thoret, S.; Dubois, J.; Brion, J.-D.; Alami, M. *ChemMedChem* **2011**, *6*, 488. (c) prostate cancer: Hu, Q.; Yin, L.; Jagusch, C.; Hille, U. E.; Hartmann, R. W. *J. Med. Chem.* **2010**, *53*, 5049. (d) diabetes: Chang, J.; Kim, R. M.; Lins, A. R.; Parmee, E. R.; Tan, Q.; Yang, C. International Patent WO 2007111864 A2, October 4, 2007.

²⁹ For breast cancer, See: (a) Pathak, T. P.; Gligorich, K. M.; Welm, B. E.; Sigman, M. S. *J. Am. Chem. Soc.* **2010**, *132*, 7870. (b) Pathak, T. P.; Osiak, J. G.; Vaden, R. M.; Welm, B. E.; Sigman, M. S. *Tetrahedron* **2012**, *68*, 5203.

bond formation may represent a general method that is also applicable to stereospecific C_{sp}³–C_{sp}² bond formation.

Experiments run using aryl Grignard reagents showed that the reaction is amenable to alkyl-aryl cross-coupling. Results of experiments run with aryl Grignard reagents are shown in Table 1.9. The reaction works well with electron donating groups (entries 2, 5–6). The reaction does not work well with a strongly electron withdrawn para-trifluoromethylphenylmagnesium bromide (not shown) but does work with a para-fluorinated aryl Grignard reagent (entry 3). A heteroaryl Grignard reagent was also amenable to the reaction (entry 4). Analogous to olefin containing nucleophiles, the reactions with aryl Grignard reagents tolerate trisubstituted olefins in the electrophile (entry 6). These results show that the reaction is a general method amenable to the formation of C_{sp}³–C_{sp}³ bonds as well as C_{sp}³–C_{sp}² bonds.

Table 1.9. Aryl Grignard Reagent Scope

entry	R	Product	Ar	yield (%) ^a	ether ee (%) ^b	prod. ee (%) ^b	es (%) ^c
1	Cy	1.29	Ph	67	>99	92	92
2	Cy	1.30	(4-OMe)C ₆ H ₄	86	>99	97	97
3	Cy	1.31	(4-F)C ₆ H ₄	82	>99	87	88
4 ^d	Cy	1.32		76	>99	93	94
5	Me	1.33	(4-NMe ₂)C ₆ H ₄	80	>99	85	86
6		1.34	(4-OMe)C ₆ H ₄	92	96	88	92

^aIsolated yield after silica gel chromatography. ^bDetermined by chiral SFC chromatography.

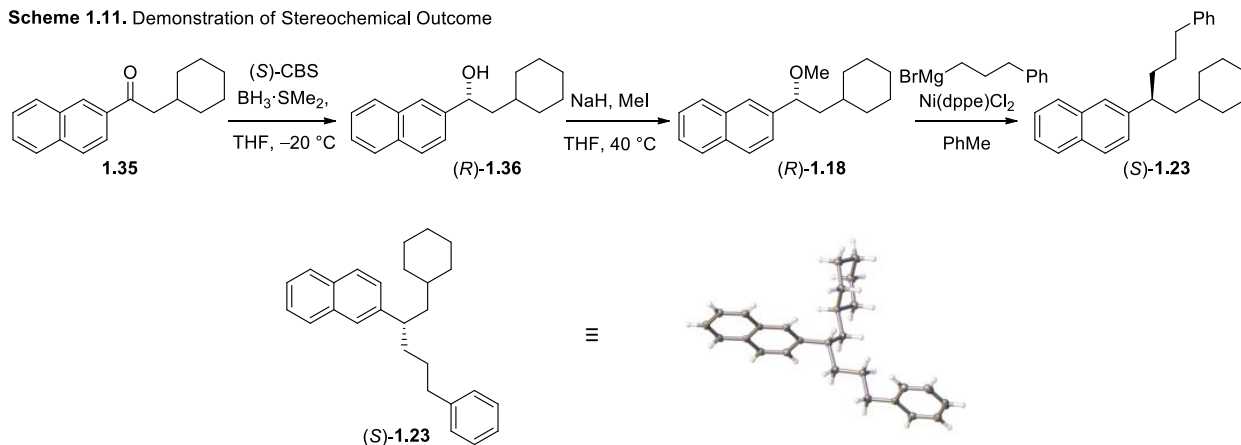
^c100 x ee_{product}/ee_{starting material}. ^d 10 mol % Ni(dppe)Cl₂

1.2.4 Demonstration of Stereochemical Outcome

We wanted to be confident that we knew the absolute stereochemistry of products synthesized by this method. Analogous to previously reported nickel-catalyzed cross-coupling reactions involving methyl Grignard reagents,³⁰ we expected that the Ni(dppe)Cl₂ catalyzed cross-coupling reaction also proceeds with inversion at the benzylic center. Alcohol (*R*)-**1.36** was prepared by CBS reduction of ketone **1.35** (Scheme 1.11). The absolute stereochemistry was assigned as *R* based on the accepted model for CBS reductions³¹ and confirmed by competing enantioselective conversion (CEC).³²

The absolute stereochemistry of the cross-coupled product was confirmed by X-ray crystallography.³³ A crystal of cross-coupled product **1.23** was grown from a methanol/pentane solution by slow evaporation. The x-ray structure was obtained on a Bruker Kappa APEX CCD diffractometer equipped with Cu K α radiation ($\lambda = 1.5478$). The absolute stereochemistry of the crystal structure confirmed that cross-couplings reactions using Ni(dppe)Cl₂ proceed with inversion at the benzylic center.

Scheme 1.11. Demonstration of Stereochemical Outcome



³⁰ See Scheme 1.6.

³¹ Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 1986.

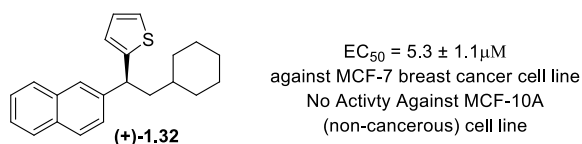
³² (a) Experiment performed by Alexander J. Wagner using the method described in Wagner, A. J.; David, J. G.; Rychnovsky, S. D. *Org. Lett.* **2011**, *13*, 4470. (b) Wagner, A. J.; Rychnovsky, S. D. *J. Org. Chem.* **2013**, *78*, 4594.

³³ X-ray structure solved by Curtis Moore; see, 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.

1.2.5 Biological Studies

As diarylmethanes are a common motif in pharmaceutically relevant molecules, we were interested in seeing if these compounds show biological activity against various cancer cell lines. Several of the compounds exhibited selective inhibition of MCF-7 breast-cancer cell proliferation. The most potent compound tested, (+)-**1.32**, exhibited an EC_{50} of 5.3 μmol (Figure 1.1).³⁴ Fortuitously, this compound had no observed effect on non-cancerous MCF-10A cells.

Figure 1.1. Bioactivity of Compound **1.32**



1.3 Conclusion

In summary, a stereospecific cross-coupling reaction of benzylic ethers with a variety of alkyl and aryl Grignard reagents was developed. It was determined that a 1:1 dppe:nickel ratio was necessary for optimal reactivity; therefore, reaction conditions were optimized using $\text{Ni}(\text{dppe})\text{Cl}_2$ as the precatalyst. The reaction was shown to be amenable to a broad scope of nucleophiles. An X-ray crystal structure confirmed that the reaction proceeds with inversion at the benzylic center. A diarylmethane synthesized by this method was shown to be active against an MCF-7 breast-cancer cell line.

³⁴ Biological assays performed by Charlotte Osborne; see, Yonova, I. M.; Johnson, A. G.; Osborne, C. A.; Moore, C. E.; Morrisette, N. S.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 2422.

1.4 Experimental Section

1.4.1 General Procedures

All reactions were carried out under an atmosphere of N₂ using glassware that was either oven- or flame-dried prior to use. Hexanes, tetrahydrofuran (THF), diethyl ether (Et₂O), and toluene (PhMe), were degassed with argon 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 H₂O. All other solvents utilized were purchased “anhydrous” commercially or purified as described (vide infra). ¹H NMR spectra were recorded on Bruker GN-500 (500 MHz ¹H, 125.7 MHz ¹³C), CRYO-500 (500 MHz ¹H, 125.7 MHz ¹³C) or DRX-400 (400 MHz ¹H, 100 MHz ¹³C) 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), triplet (t), doublet of triplets (dt), doublet of doublet of triplets (ddt), triplet of triplets (tt), quartet (q), quintet (quint), multiplet (m), apparent singlet (ap s), apparent doublet (ap d), apparent quartet (ap q), broad doublet (br d) and broad multiplet (br 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 (CDCl₃, δ 77.16 ppm). Unless otherwise indicated, NMR data were collected at 25 °C. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F₂₅₄ pre-coated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with KMnO₄ solution. Flash chromatography was performed using Silica Gel 60Å (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were obtained on a Mattson Instruments *Galaxy 5000* (thin film) and Perkin-Elmer Spectrum

1000 FT-IR Systems and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Optical rotations were measured with a Rudolph Research Analytical Autopol IV Automatic Polarimeter or a Jasco P-1010 digital polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (OD-H, OJ-H, or AD-H; 100 bar, 50 °C, 215 nm).

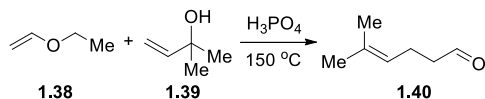
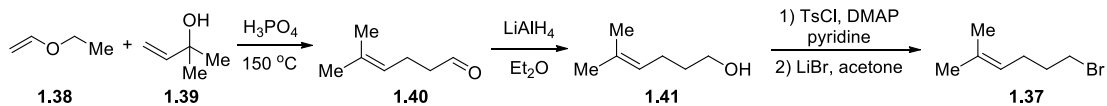
$\text{Ni}(\text{cod})_2$ was purchased from Strem, stored in a glovebox freezer ($-20\text{ }^\circ\text{C}$) under an atmosphere of N_2 , and used as received. $\text{Ni}(\text{acac})_2$ was purchased from Strem, stored in a glovebox under an atmosphere of N_2 , and used as received. 1,2-Bis(diphenylphosphino)ethane (dppe) was purchased from Alfa Aesar, stored in a glovebox under an atmosphere of N_2 , and used as received. 1,2-Bis(diphenylphosphino)ethane nickel (II) chloride ($\text{Ni}(\text{dppe})\text{Cl}_2$) was purchased from Strem and used as received.

Organomagnesium reagents for substrate synthesis were freshly prepared from the halide precursor in THF, and molarities were determined by titration with I_2 .³⁵ All other chemicals were purchased commercially and used as received.

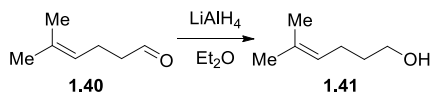
1.4.2 Synthesis of Alkyl and Aryl Halides and Organomagnesium Reagents for Cross-Coupling Reactions

(5-methylhex-4-enyl)magnesium bromide was prepared from **5-methylhex-4-enylbromide (1.37)** which was prepared via the following route:

³⁵ Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890.



5-methylhex-4-enal (1.40) was prepared according to a modified procedure reported by Saucy and co-workers.³⁶ A sealed tube was charged with ethoxyethene (**1.38**) (11.6 mL, 121 mmol), 2-methylbut-3-en-2-ol (**1.39**) (6.40 mL, 60 mmol), and 85% phosphoric acid (59 μ L, 0.60 mmol). The tube was sealed, heated to 150 °C, and allowed to stir for 2.5 h. The reaction mixture was cooled to room temp, opened, and neutralized with triethylamine. Purification by fractional distillation (120 °C, 50 torr) afforded the title compound as a clear, colorless oil (2.41 g, 21.5 mmol, 36%). Analytical data is consistent with literature values.³⁷



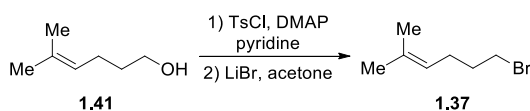
5-methylhex-4-ene-1-ol (1.41) was prepared according to the procedure reported by Heathcock and co-workers.³⁸ A flame dried round bottom flask was charged with LiAlH₄ (1.49 g, 39.4 mmol), put under a nitrogen atmosphere, and cooled to 0 °C. Et₂O (22 mL) was added then aldehyde **1.40** (4.41g, 39.4 mmol) was added as a solution in Et₂O (86 mL). The reaction mixture was allowed to slowly return to room temperature over 3 hours and stirred for an additional 10 hours at which time the reaction mixture was cooled back down to 0 °C. Water (2 mL), 15% NaOH (2 mL), and another aliquot of water (6 mL) were added sequentially. The

³⁶ (a) Marbet, R.; Saucy, G. *Helv. Chim. Acta* **1967**, *50*, 2095. (b) Liu, C.; Kudo, K.; Hashimoto, Y.; Saigo, K. *J. Org. Chem.* **1996**, *61*, 494.

³⁷ Wei, X.; Lorenz, J. C.; Kapadia, S.; Saha, A.; Haddad, N.; Busacca, C. A.; Senanayake, C. H. *J. Org. Chem.* **2007**, *72*, 4250.

³⁸ Wallace, G. A.; Heathcock, C. H. *J. Org. Chem.* **2001**, *66*, 450.

quenched mixture was allowed to return to room temperature. The solid material was filtered and purified by silica gel flash column chromatography to yield the target compound as a clear, colorless oil (3.04g, 26.1 mmol, 68% yield). Analytical data is consistent with literature values.³⁹

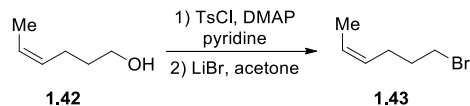


6-Bromo-2-methylhex-2-ene (1.37) was prepared according to a procedure reported by Boyer.⁴⁰

A flame dried round bottom flask was charged with alcohol **1.41** (1.26 g, 11.0 mmol) and DMAP (15.2 mg, 0.125 mmol). Pyridine (11 mL) was added, and the reaction mixture was cooled to 0 °C. Tosyl chloride (232 mg, 12.2 mmol) was added in portions, and the reaction mixture was allowed to stir for 2.5 h at 0 °C. The reaction mixture was poured into ice cold water, and the crude mixture was extracted with Et₂O (3 x 10 mL), washed with 10% HCl, washed with a saturated NaHCO₃ (aq) solution, and washed with brine. The combined organics were dried with MgSO₄ and concentrated in vacuo. With no further purification, the crude tosylate (2.35 g, 9.84 mmol) was loaded into a round bottom flask. LiBr (2.96g, 34.1 mmol) and acetone (23 mL) were added, and the reaction mixture was heated to and stirred at reflux for 1 hour. The reaction mixture was then cooled to room temperature and diluted with a 3:1 mixture of pentane and water. The organic layer was separated and dried with MgSO₄. After filtration and concentration, the crude material was purified by silica gel flash column chromatography (100% hexanes) to yield bromide **1.37** as a clear, colorless oil (0.703g, 3.97 mmol, 36% yield from the alcohol). Analytical data was consistent with literature values.⁴⁰

³⁹ Corey, E. J.; Cheng, H.; Baker, C. H.; Matsuda, S. P. T.; Li, D.; Song, X. *J. Am. Chem. Soc.* **1997**, *119*, 1277.

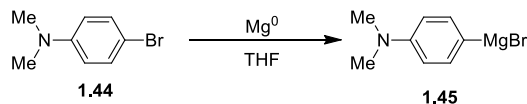
⁴⁰ Boyer, F.-D.; Hanna, I. *Org. Lett.* **2007**, *9*, 2293.



(Z)-6-bromohex-2-ene (1.43) was prepared according to the same procedure as **1.37** but starting from the commercially available alcohol **1.42**. Analytical data were consistent with literature values.⁴¹

All other alkyl and aryl halides were purchased commercially and used as received.

1.4.3 Preparation of Grignard Reagents



***p*-(*N,N*-Dimethylamino)phenylmagnesium bromide (1.45)** was prepared according to a procedure reported by Jarvo and co-workers.⁴² Magnesium turnings (0.18 g, 7.5 mmol) were ground in a mortar and pestle, and then added to a round bottom flask along with one crystal of iodine. The round bottom flask was equipped with a water condenser and put under a nitrogen atmosphere. THF (2.0 mL) was then added. The heterogeneous mixture was heated to reflux, and *p*-(*N,N*-dimethylamino)phenyl bromide (**1.44**) (1.0 g in 0.5 mL THF) was added drop wise. The reaction mixture was allowed to stir for 1 h and cooled to room temperature. The Grignard solution was then carefully transferred by syringe to a Schlenk flask in such a way as to leave left-over magnesium solid behind. The Grignard reagent was then concentrated in vacuo on a Schlenk line. Et₂O (1 mL) was added, and the solution was again concentrated in vacuo by

⁴¹ Burns, N. Z.; Witten, M. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2011**, *133*, 14578.

⁴² Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

Schlenk technique. This process was repeated five times. The solid Grignard reagent was then transferred to a glove box. Grignard reagent **1.45** was stored and dispensed in the same glove box.

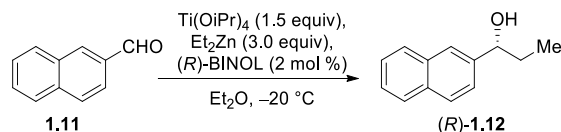
All other Grignard reagents were prepared according to the following general procedure. For satisfactory yields and enantiospecificities in the cross-coupling reactions, the Grignard reagent must be prepared from the alkyl bromide in diethyl ether. In cases where initiation is sluggish, gentle heating by heat gun or oil bath, or the addition of 0.05 mL of 1,2-dibromoethane proved helpful.

General Procedure for Grignard Reagent Preparation: Magnesium turnings (1.08 g, 45.0 mmol) were added to a vacuum flame-dried round-bottom flask equipped with a stir bar and oven-dried condenser. The reaction apparatus was put under a nitrogen atmosphere. Et₂O (5.0 mL) was added to the reaction apparatus, followed by a single crystal of I₂ (ca. 2 mg). The organohalide⁴³ (15.0 mmol) was added portion-wise over 30 min. The reaction was stirred at ambient temperature for an additional two hours. The resulting Grignard reagents were typically between 2.0 and 3.0 M as titrated using Knochel's method,⁴⁴ and could be stored (sealed, under nitrogen) for at least 4 weeks without detrimental effects.

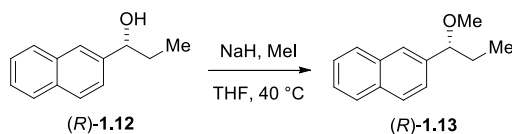
⁴³ All alkyl and arylhalides were commercially available and used as received without any purification unless otherwise noted.

⁴⁴ Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890.

1.4.4 Synthesis and Characterization of Substrates

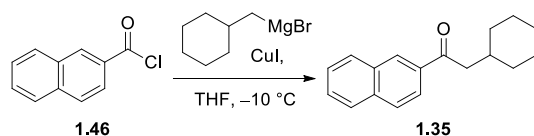


(R)-1-(naphthalen-2-yl)propan-1-ol ((R)-1.12) was prepared according to the procedure reported by Jarvo and co-workers.⁴⁵ Analytical data is consistent with literature values:⁴⁵ ¹H NMR (500 MHz, CDCl₃) δ 7.80 (m, 3H), 7.73 (s, 1H), 7.45 (m, 3H), 4.72 (t, *J* = 6.8 Hz, 1 H), 2.17 (s, 1H), 1.79–1.90 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 142.0, 133.3, 133.1, 128.3, 128.0, 127.8, 126.2, 125.9, 124.8, 124.2, 76.2, 31.8, 10.3; [α]²⁴_D +39.5 (*c* 1.01, CHCl₃), lit. [α]²³_D +41.9 (*c* 1.02, CHCl₃, 96% ee);⁴⁵ SFC analysis (OD-H, 10% IPA, 2.5 mL/min) indicated 95% ee: *t*_R (minor) = 9.1 minutes, *t*_R (major) = 9.9 minutes.

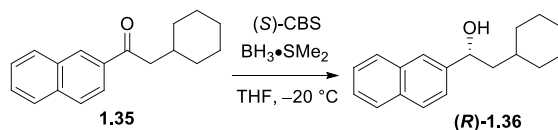


(R)-2-(1-methoxypropyl)naphthalene ((R)-1.13) was Prepared according to the procedure reported by Jarvo and co-workers.⁴⁵ Analytical data is consistent with literature values.⁴⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.83 (m, 3H), 7.70 (s, 1H), 7.45 (m, 3H), 4.17 (t, *J* = 6.6 Hz, 1 H), 3.24 (s, 3H), 1.92 (m, 1H), 1.75 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.8, 133.3, 133.2, 128.4, 128.0, 127.8, 126.17, 126.16, 125.8, 124.7, 85.8, 56.9, 30.9, 10.4; [α]²⁴_D +110.5 (*c* 1.07, CHCl₃), lit. [α]²³_D +92.2 (*c* 1.82, CHCl₃);⁴⁵ SFC analysis (OD-H, 1% IPA, 2.5 mL/min) indicated 95% ee: *t*_R (minor) = 5.8 minutes, *t*_R (major) = 6.2 minutes.

⁴⁵ Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389.



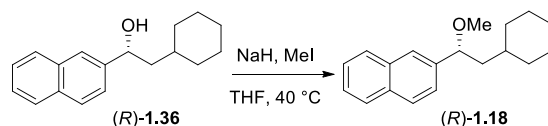
2-cyclohexyl-1-(naphthalen-2-yl)ethanone (1.35) was prepared according to the procedure reported by Jarvo and co-workers.⁴⁶ Analytical data is consistent with literature values:⁴⁶ **¹H NMR** (500 MHz, CDCl₃) δ 8.45 (s, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 9.0 Hz, 2H), 7.46–7.61 (m, 2H), 2.95 (d, *J* = 6.5 Hz, 2H), 2.10–1.97 (m, 1H), 1.85–1.75 (m, 2H), 1.70–1.65 (m, 3H), 1.31–1.26 (m, 2H), 1.22–1.17 (m, 1H), 1.15–1.02 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 200.4, 135.7, 135.0, 132.7, 129.9, 129.7, 128.52, 128.47, 127.9, 126.8, 124.2, 46.4, 34.9, 33.7, 26.4, 26.3.



(R)-2-cyclohexyl-1-(naphthalen-2-yl)ethanol ((R)-1.36) was prepared according to the procedure reported by Jarvo and co-workers.⁴⁶ Analytical data is consistent with literature values:⁴⁶ **¹H NMR** (500 MHz, CDCl₃) δ 7.84–7.83 (m, 3H), 7.78 (s, 1H), 7.49–7.45 (m, 3H), 4.97–4.95 (m, 1H), 1.85–1.77 (m, 4H), 1.71–1.60 (m, 4H), 1.51–1.40 (m, 1H), 1.29–1.13 (m, 3H), 1.04–0.92 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 142.8, 133.5, 133.1, 128.4, 128.1, 127.8, 126.3, 125.9, 124.6, 124.3, 72.4, 47.1, 34.4, 34.1, 33.1, 26.7, 26.4, 26.3; **[α]²⁵_D** +33.3 (*c* 0.17, CHCl₃), lit. **[α]²⁸_D** +23.8 (*c* 1.0, CHCl₃, 87% ee);⁴⁶ **SFC analysis** (AS-H, 3% IPA, 3 mL/min) indicated 96% ee: *t_R* (minor) = 12.2 minutes, *t_R* (major) = 12.8 minutes. Absolute configuration

⁴⁶ Wisniewska, H. M.; Swift, E. C.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 9083.

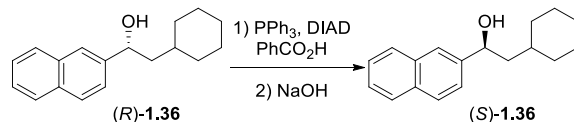
was assigned as *R* based on the accepted model for selectivity in CBS reduction⁴⁷ and confirmed by competing enantioselective conversion (CEC).⁴⁸



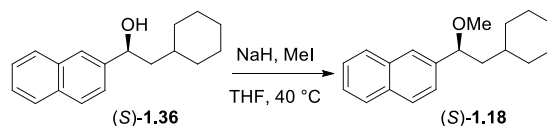
(R)-2-(2-cyclohexyl-1-methoxyethyl)naphthalene ((R)-1.18): To a solution of NaH (0.514 g, 21.4 mmol) in THF (100 mL) was added (*R*)-**1.36** (2.72 g, 10.7 mmol), and the mixture was stirred at 40 °C for 30 min. MeI (2.00 mL, 32.1 mmol) was added, and stirring was continued for 8 h. The reaction was quenched with MeOH, and the solvent was removed in vacuo. The crude mixture was taken up in CH₂Cl₂ (100 mL), washed with sat. NaCO₃, brine, dried over NaSO₄, and concentrated in vacuo. Purification by silica gel flash column chromatography (5% EtOAc in hexanes) afforded the title compound as a white solid (2.85 g, 10.6 mmol, 99%): **m.p.** 43–47 °C; **TLC** *R_f* = 0.4 (5% EtOAc in hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.83–7.82 (m, 3H), 7.70 (s, 1H), 7.49–7.43 (m, 3H), 4.36 (dd, *J* = 8.6, 5.7 Hz, 1H), 3.21 (s, 3H), 1.84–1.76 (m, 3H), 1.69–1.62 (m, 3H), 1.54–1.49 (m, 1H), 1.42–1.37 (m, 1H), 1.25–1.10 (m, 3H), 0.99–0.90 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 140.5, 133.4, 133.2, 128.4, 127.9, 127.8, 126.2, 125.9, 125.8, 124.6, 81.9, 56.8, 46.2, 34.3, 34.0, 33.3, 26.7, 26.4, 26.3; [α]_D²⁵ +63.2 (*c* 1.06, CHCl₃); **HRMS** (TOF MS CI⁺) *m/z* calcd for C₁₉H₂₄O [M]⁺ 268.1827 found 268.1821; **SFC analysis** (OJ-H, 3% IPA, 2.5 mL/min) indicated 97% ee: *t_R* (minor) = 7.1 minutes, *t_R* (major) = 8.8 minutes.

⁴⁷ Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 1986.

⁴⁸ (a) Experiment performed by Alexander J. Wagner using the method described in Wagner, A. J.; David, J. G.; Rychnovsky, S. D. *Org. Lett.* **2011**, *13*, 4470. (b) Wagner, A. J.; Rychnovsky, S. D. *J. Org. Chem.* **2013**, *78*, 4594.



(S)-2-cyclohexyl-1-(naphthalen-2-yl)ethanol ((S)-1.36) was prepared according to a modified procedure reported by Presnell and co-workers.⁴⁹ To a cooled (brine ice bath) solution of (*R*)-**1.36** (0.15 g, 0.59 mmol), benzoic acid (0.29 g, 2.4 mmol), and PPh₃ (0.62 g, 2.4 mmol) in THF (5 mL) was added DIAD (0.46 mL, 2.4 mmol) drop-wise over 30 min. After the addition was complete the reaction was allowed to warm to room temperature and stir for 12 hours, then heated up to 40 °C and stirred for an additional 3 h. The reaction mixture was diluted with Et₂O (10 mL), washed with sat. NaHCO₃, dried over NaSO₄, and concentrated in vacuo. Trituration with hexanes removed the PPh₃ by-products and purification by silica gel flash column chromatography (10% EtOAc in hexanes) afforded the title compound as a white solid (0.112 g, 0.43 mmol, 73%). The product was recrystallized from hexanes to improve enantiopurity. Analytical data is consistent with literature values:⁵⁰ **¹H NMR** (500 MHz, CDCl₃) δ 7.84–7.83 (m, 3H), 7.78 (s, 1H), 7.49–7.45 (m, 3H), 4.97–4.95 (m, 1H), 1.85–1.79 (m, 4H), 1.71–1.60 (m, 4H), 1.51–1.40 (m, 1H), 1.29–1.13 (m, 3H), 1.04–0.92 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 142.8, 133.5, 133.1, 128.4, 128.1, 127.8, 126.3, 125.9, 124.6, 124.3, 72.4, 47.1, 34.4, 34.1, 33.1, 26.7, 26.4, 26.3; [α]_D²⁶ –27.4 (*c* 1.02, CHCl₃); **SFC analysis** (AS-H, 3% IPA, 3 mL/min) indicated 94% ee: *t*_R (major) = 11.8 minutes, *t*_R (minor) = 12.7 minutes.

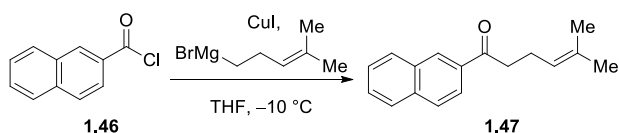


(S)-2-(2-cyclohexyl-1-methoxyethyl)naphthalene ((S)-1.18) was prepared according to the procedure reported above for (*R*)-**1.18**: **¹H NMR** (400 MHz, CDCl₃) δ 7.83–7.82 (m, 3H), 7.70

⁴⁹ Dodge, J. A.; Nissen, J. S.; Presnell, M. *Org. Synth.* **1996**, 73, 110.

⁵⁰ Wisniewska, H. M.; Swift, E. C.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, 135, 9083–9090.

(s, 1H), 7.49–7.43 (m, 3H), 4.36 (dd, $J = 8.6, 5.7$ Hz, 1H), 3.21 (s, 3H), 1.84–1.76 (m, 3H), 1.69–1.62 (m, 3H), 1.54–1.49 (m, 1H), 1.42–1.37 (m, 1H), 1.25–1.10 (m, 3H), 0.99–0.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.5, 133.4, 133.2, 128.4, 127.9, 127.8, 126.2, 125.9, 125.8, 124.6, 81.9, 56.8, 46.2, 34.3, 34.0, 33.3, 26.7, 26.4, 26.3; $[\alpha]^{25}_{\text{D}} -58.1$ (c 1.30, CHCl_3); **SFC analysis** (OJ-H, 3% IPA, 2.5 mL/min) indicated 92% ee: t_{R} (major) = 7.0 minutes, t_{R} (minor) = 8.9 minutes.

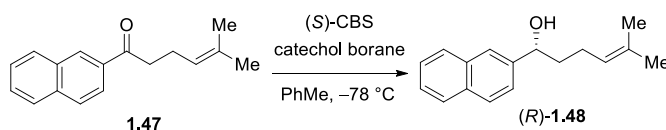


5-methyl-1-(naphthalen-2-yl)hex-4-en-1-one (1.47) was prepared according to a modified procedure reported by Hultzsich and co-workers.⁵¹ To a cooled (brine/ice bath) solution of CuI (0.059 g, 0.31 mmol) and 2-naphthoyl chloride (**1.46**) (1.19 g, 6.25 mmol) in THF (7 mL) was slowly added (4-methylpent-3-enyl)magnesium bromide (10.9 mL, 6.25 mmol, 0.574 M in THF), and the reaction mixture was stirred for 1 h. The reaction was quenched by the addition of MeOH, and the solvent was removed in vacuo. The crude reaction mixture was taken up in EtOAc (30 mL), washed with 1 N HCl (10 mL), sat. NaHCO_3 (10 mL), and brine (10 mL), dried with NaSO_4 , and concentrated in vacuo. Purification by silica gel flash column chromatography (4% EtOAc in hexanes) afforded the title compound as a colorless oil (1.01 g, 4.22 mmol, 68% yield). This compound has been previously reported.⁵² Spectral data is not fully consistent with the reported literature values, therefore full characterization data is provided to support structural assignment shown above: **TLC** $R_f = 0.4$ (10% EtOAc in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 8.46 (s, 1H), 8.03 (d, $J = 8.8$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.86 (t, $J = 7.4$ Hz, 2H), 7.57–7.49 (m, 2H), 5.22 (t, $J = 7.2$ Hz, 1H), 3.12 (t, $J = 7.4$ Hz, 2H), 2.48 (q, $J = 7.4$ Hz, 2H), 1.70 (s,

⁵¹ Gribkov, D. V.; Hultzsich, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748.

⁵² Narender, T.; Sarkar, S.; Rajendar, K.; Tiwari, S. *Org. Lett.* **2011**, *13*, 6140.

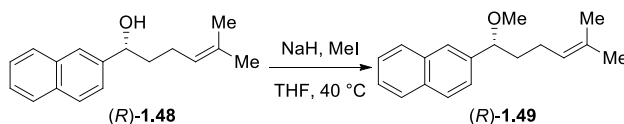
3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.0, 135.6, 134.4, 132.8, 132.6, 129.7, 129.6, 128.43, 128.39, 127.8, 126.8, 124.0, 123.1, 38.9, 25.8, 23.2, 17.8; IR (neat) 3058, 2967, 2913, 1678, 1277, 1180, 1123 cm^{-1} ; HRMS (TOF MS CI^+) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}$ $[\text{M} + \text{H}]^+$ 239.1436, found 239.1429.



(R)-5-methyl-1-(naphthalen-2-yl)hex-4-en-1-ol ((R)-1.48) was prepared according to a modified procedure by Okamura and co-workers.⁵³ A flame dried round bottom flask was charged with (*S*)-2-methyl-CBS-oxazaborolidine (0.12 g, 0.42 mmol), ketone **1.47** (1.01 g, 4.22 mmol), and toluene (20 mL). The mixture was cooled to $-78\text{ }^\circ\text{C}$, and catecholborane (0.90 mL, 8.4 mmol) was added dropwise. The reaction mixture was stirred for 20 h, then quenched by slow addition of MeOH (2 mL) followed by sat. NH_4Cl (10 mL). After warming to room temperature, the quenched mixture was extracted with Et_2O (3 x 20 mL). The combined organics were washed with sat. Na_2CO_3 , then brine and dried over NaSO_4 . Solvent was removed in vacuo. Purification by silica gel flash column chromatography (10–20% EtOAc in hexanes) afforded the title compound as a white solid (0.703 g, 2.91 mmol, 69%). The product was recrystallized from hexanes to improve enantiopurity: **m.p.** 53–55 $^\circ\text{C}$; **TLC** R_f = 0.5 (20% EtOAc in hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 8.0 Hz, 3H), 7.76 (s, 1H), 7.47–7.43 (m, 3H), 5.16 (t, J = 7.0 Hz, 1H), 4.83 (t, J = 5.8 Hz, 1H), 2.12–2.04 (m, 3H), 1.94–1.82 (m, 2H), 1.69 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 142.3, 133.4, 133.1, 132.5, 128.4, 128.1, 127.8, 126.2, 125.9, 124.7, 124.3, 123.9, 74.5, 39.0, 25.9, 24.6, 17.9; IR (neat) 3263, 2924, 2856, 1059, 1016 cm^{-1} ; HRMS (TOF MS CI^+) m/z calcd for $\text{C}_{17}\text{H}_{20}\text{ONH}_4$ $[\text{M} + \text{NH}_4]^+$ 258.1858, found 258.1847;

⁵³ Lee, A. S.; Norman, A. W.; Okamura, W. H. *J. Org. Chem.* **1992**, *57*, 3846.

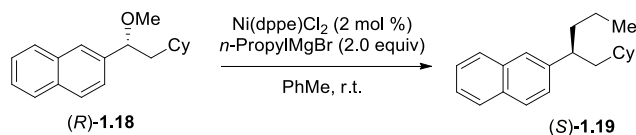
$[\alpha]^{26}_D +4.9$ (c 1.16, CHCl_3); **SFC analysis** (OD-H, 15% IPA, 3 mL/min) indicated 93% ee: t_R (minor) = 4.9 minutes, t_R (major) = 5.3 minutes. Absolute configuration was assigned as *R* based on the accepted model for selectivity in CBS reductions.⁵⁴



(*R*)-2-(1-methoxy-5-methylhex-4-enyl)naphthalene ((*R*)-1.49): To a suspension of NaH (0.032 g, 1.3 mmol) in THF (3 mL) was added a solution of (*R*)-1.48 (0.160 g, 0.67 mmol) in THF (3 mL), and the mixture was stirred at 40 °C for 30 min. MeI (0.124 mL, 2.00 mmol) was added and stirring was continued for 5 h. The reaction was quenched with MeOH, and the solvent was removed in vacuo. The crude mixture was taken up in CH_2Cl_2 (10 mL), filtered, and concentrated in vacuo. Purification by silica gel flash column chromatography (5% EtOAc in hexanes) afforded the title compound as a colorless oil (0.164 g, 0.645 mmol, 96%): **TLC** R_f = 0.5 (10% EtOAc in hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.84 (app d, J = 8.0 Hz, 3H), 7.70 (s, 1H), 7.47–7.43 (m, 3H), 5.12 (t, J = 6.8 Hz, 1H), 4.24 (t, J = 6.6 Hz, 1H), 3.23 (s, 3H), 2.07–2.02 (m, 2H), 1.96–1.91 (m, 1H), 1.74–1.69 (m, 4H), 1.56 (s, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 140.0, 133.4, 133.2, 132.2, 128.4, 128.0, 127.9, 126.2, 126.1, 125.8, 124.6, 124.0, 83.6, 56.8, 38.1, 25.9, 24.5, 17.9; **IR** (neat) 3055, 2966, 2926, 1445, 1099, 745 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{18}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 254.1671, found 254.1652; $[\alpha]^{27}_D +30.2$ (c 1.11, CHCl_3); **SFC analysis** (OD-H, 5% IPA, 2.5 mL/min) indicated 94% ee: t_R (minor) = 4.2 minutes, t_R (major) = 4.6 minutes.

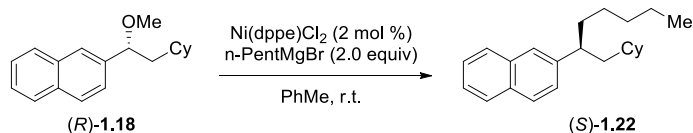
⁵⁴ Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed.* **1998**, 37, 1986.

1.4.5 Representative Procedure for Cross-Coupling Reactions

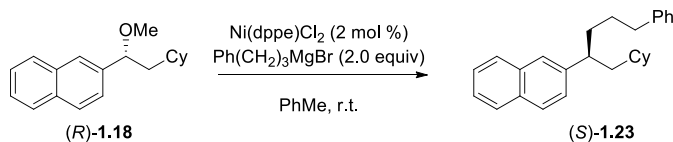


(S)-2-(1-cyclohexylpentan-2-yl)naphthalene ((S)-1.19): A vial was charged with (R)-1.18 (0.134 g, 0.500 mmol) and Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol). The vial was capped, and put under a nitrogen atmosphere. Toluene (3.0 mL) was added, followed by *n*-propylmagnesium bromide (0.44 mL, 1.0 mmol, 2.3 M in Et₂O). The reaction was allowed to stir at room temperature for 24 h, at which point the reaction was quenched by the addition of MeOH (1 mL) and run through a silica plug. The solvents were removed in vacuo, and the crude was purified by silica gel flash column chromatography (100% hexanes). The resulting colorless oil (0.137 g) was a mixture of the title compound (93% calculated yield) and the product of elimination (5% calculated yield). Further purification (100% heptanes) afforded a pure sample of (S)-1.19: **TLC** *R_f* = 0.7 (100% hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.80–7.76 (m, 3H), 7.55 (s, 1H), 7.45–7.39 (dq, *J* = 5.5, 1.2 Hz, 2H), 7.32 (dd, *J* = 8.5, 1.5 Hz, 1H), 2.84–2.79 (dq, *J* = 9.3, 5.5 Hz, 1H), 1.84 (d, *J* = 12.8 Hz, 1H), 1.85–1.47 (m, 8H), 1.26–1.05 (m, 6H), 0.91–0.86 (m, 5H); **¹³C NMR** (500 MHz, CDCl₃) δ 144.1, 133.7, 132.3, 128.0, 127.73, 127.65, 126.4, 126.2, 125.8, 125.1, 44.9, 42.7, 39.9, 35.0, 34.4, 33.0, 26.8, 26.4, 26.3, 20.9, 14.3; **IR** (thin film) 3052, 2661, 1915, 1633, 1600 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₂₁H₂₈ [M]⁺ 280.2191, found 280.2187; **[α]_D²⁹** +17.8 (*c* 1.11, CHCl₃); **SFC** analysis (OJ-H, 2% hexanes, 2.0 mL/min) indicated 97% ee: *t_R* (major) = 11.4 minutes, *t_R* (minor) = 12.3 minutes.

1.4.6 Characterization Data for Cross-Coupling Products

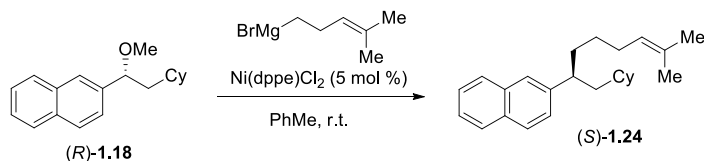


(S)-2-(1-cyclohexylheptan-2-yl)naphthalene ((S)-1.22) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.18** (0.134 g, 0.500 mmol), Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol), *n*-pentylmagnesium bromide (0.50 mL, 1.0 mmol, 2.0 M in Et₂O), and toluene (3.0 mL). Purification by flash column chromatography (100% hexanes) afforded a colorless oil (0.147 g) as a mixture of the title compound (91% calculated yield) and the product of elimination (6% calculated yield). Further purification (100% heptanes) afforded a sample of analytically pure material: **R_f** = 0.3 (100% hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.80–7.75 (m, 3H), 7.55 (s, 1H), 7.44–7.37 (m, 2H), 7.31 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.83–2.75 (m, 1H), 1.84 (d, *J* = 12.8 Hz, 1H), 1.63–1.44 (m, 8H), 1.21–1.04 (m, 10H), 0.89–0.81 (m, 5H); **¹³C NMR** (500 MHz, CDCl₃) δ 144.2, 133.7, 132.3, 128.0, 127.74, 127.67, 126.4, 126.1, 125.8, 125.1, 45.0, 43.0, 37.6, 35.0, 34.4, 33.0, 32.2, 27.5, 26.8, 26.4, 26.3, 22.7, 14.3; **IR** (neat) 3020, 2920, 2850, 815, 744, 697 cm⁻¹; **HRMS** (TOF MS CI+) *m/z* calcd for C₂₃H₃₂ [M]⁺ 308.2504, found 308.2507; **[α]_D²⁷** +9.4 (*c* 1.20, CHCl₃); **SFC** analysis (OJ-H, 2% hexanes, 2.0 mL/min) indicated 97% ee: *t_R* (minor) = 11.4 minutes, *t_R* (major) = 12.3 minutes.



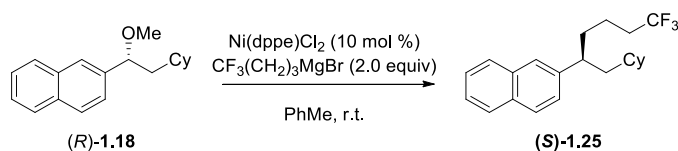
(S)-2-(1-cyclohexyl-5-phenylpentan-2-yl)naphthalene ((S)-1.23) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.18**

(0.401 g, 1.50 mmol), Ni(dppe)Cl₂ (16 mg, 0.030 mmol), (3-phenylpropyl)magnesium bromide (1.59 mL, 1.89 mmol, 1.19 M in Et₂O), and toluene (22 mL). Purification by flash column chromatography (0–5% EtOAc in hexanes) afforded a colorless oil (0.522 g) as a mixture of the title compound (88% calculated yield) and the product of Wurtz coupling of the organomagnesium reagent (1,6-diphenylhexane). Further purification by flash chromatography (100% pentane) afforded a sample of analytically pure material: **m.p.** 81–81 °C; **TLC R_f** = 0.3 (100% hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.54 (s, 1H), 7.46–7.39 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.24–7.20 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 2H), 2.82 (p, *J* = 5.0 Hz, 1H), 2.60–2.48 (m, 2H), 1.82 (d, *J* = 12.5 Hz, 1H), 1.69–1.43 (br m, 10H), 1.11–1.00 (m, 4H), 0.88–0.82 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.7, 142.7, 133.7, 132.3, 128.5, 128.3, 128.0, 127.73, 127.68, 126.4, 126.1, 125.9, 125.7, 125.1, 44.9, 42.9, 37.2, 36.1, 34.9, 34.4, 32.9, 29.6, 26.8, 26.4, 26.3; **IR** (neat) 2918, 2850, 1442, 822, 745, 696 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₂₇H₃₂ [M]⁺ 356.2504, found 356.2509; **[α]²⁰_D** +1.0 (*c* 1.03, CHCl₃); **SFC** analysis (OJ-H, 20% IPA, 2.5 mL/min) indicated 97% ee: *t_R* (minor) = 4.2 minutes, *t_R* (major) = 5.2 minutes. Crystals suitable for X-ray diffraction (vide infra) were grown by slow evaporation of solvent from a solution of the title compound in a mixture of methanol and pentane.



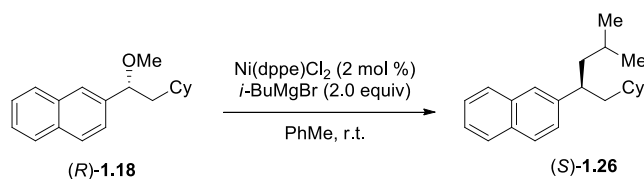
(S)-2-(1-cyclohexyl-7-methyloct-6-en-2-yl)naphthalene ((S)-1.24) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.18** (53.7 mg, 0.200 mmol) and Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol), (5-methylhex-4-enyl)magnesium

bromide (0.48 mL, 0.40 mmol, 0.83 M in Et₂O), and toluene (3.0 mL). The reaction mixture was stirred for 48 h. Purification by silica gel flash column chromatography (100% pentane) afforded a colorless oil (0.054 g) composed of a mixture of the title compound (81% calculated yield) and the product of elimination (12% calculated yield). Further purification by flash chromatography on silver-impregnated silica (0–3% Et₂O in pentane) afforded a sample of analytically pure material: **TLC** *R_f* = 0.4 (100% pentane); **¹H NMR** (400 MHz, CDCl₃) δ 7.81–7.76 (m, 3H), 7.55 (s, 1H), 7.46–7.39 (dp, *J* = 8.4, 1.2 Hz, 2H), 7.31 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.01 (t, *J* = 7.1 Hz, 1H), 2.80 (dq, *J* = 14.8, 5.3 Hz, 1H), 1.96–1.82 (m, 3H), 1.68–1.47 (m, 14H), 1.36–1.18 (m, 2H), 1.16–1.01 (m, 4H), 0.94–0.80 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 144.0, 133.7, 132.3, 131.3, 128.0, 127.7, 127.6, 126.4, 126.1, 125.8, 125.1, 124.9, 44.9, 42.9, 37.2, 35.0, 34.4, 32.9, 28.2, 28.0, 26.8, 26.4, 26.3, 25.8, 17.8; **IR** (neat) 2919, 2850, 1447, 853, 815, 743 cm⁻¹; **HRMS** (TOF MS EI+) *m/z* calcd for C₂₅H₃₄ [M]⁺ 334.2661, found 334.2660; [*α*]_D²⁴ +11.8 (*c* 5.33, CHCl₃); **SFC** analysis (OJ-H, 3% IPA, 2.5 mL/min) indicated 97% ee: *t_R* (minor) = 6.5 minutes, *t_R* (major) = 6.9 minutes.



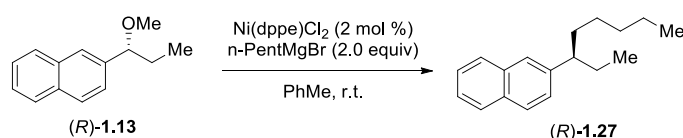
(S)-2-(1-cyclohexyl-6,6,6-trifluorohexan-2-yl)naphthalene ((S)-1.25) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.18** (53.7 mg, 0.200 mmol), Ni(dppe)Cl₂ (10.6 mg, 0.0200 mmol), (4,4,4-trifluorobutyl)magnesium bromide (0.20 mL, 0.40 mmol, 2.0 M in Et₂O), and toluene (3.0 mL). The reaction mixture was stirred for a period of 48 h. Purification by silica gel flash column chromatography (100% pentane) afforded a colorless oil (54 mg) as a mixture of the title compound (67% calculated yield) and the product of elimination (15% calculated yield). Further purification by silica gel

flash column chromatography on silver-impregnated silica (100% pentane) afforded a sample of analytically pure material: **TLC** R_f = 0.4 (100% pentane); **^1H NMR** (400 MHz, CDCl_3) δ 7.82–7.78 (m, 3H), 7.55 (s, 1H), 7.44 (dp, J = 6.9, 1.3 Hz, 2H), 7.29 (dd, J = 8.5, 1.5 Hz, 1H), 2.81 (dq, J = 14.8, 4.9 Hz, 1H), 2.11–1.90 (m, 2H), 1.83 (d, J = 12.9 Hz, 1H), 1.75–1.25 (m, 10H), 1.15–1.01 (m, 4H), 0.93–0.81 (m, 2H); **^{13}C NMR** (125 MHz, CDCl_3) δ 142.9, 133.7, 132.4, 128.3, 127.8, 127.7, 126.4, 126.0, 125.7, 125.3, 44.8, 42.8, 36.5, 34.9, 34.3, 33.9 (q, J = 28.3 Hz, 1C), 32.9, 26.7, 26.7, 26.3, 26.2, 20.3 (q, J = 2.8 Hz, 1C); **IR** (neat) 2920, 2850, 1448, 1253, 1131, 816, 744 cm^{-1} ; **HRMS** (TOF MS EI+) m/z calcd for $\text{C}_{22}\text{H}_{27}\text{F}_3$ $[\text{M}]^+$ 348.2065, found 348.2065; $[\alpha]_D^{26}$ +19.7 (c 1.2, CHCl_3); **SFC** analysis (OJ-H, 10% hexanes, 2.5 mL/min) indicated 97% ee: t_R (major) = 4.7 minutes, t_R (minor) = 5.3 minutes.

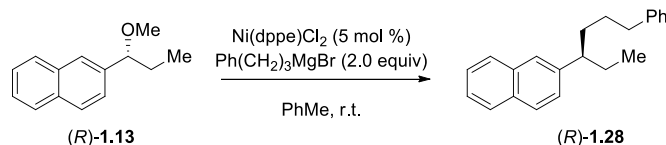


(S)-2-(1-cyclohexyl-4-methylpentan-2-yl)naphthalene ((S)-1.26) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.18** (0.134 g, 0.500 mmol), Ni(dppe)Cl_2 (5.3 mg, 0.010 mmol), *i*-butylmagnesium bromide (0.40 mL, 1.0 mmol, 2.5 M in Et_2O), and toluene (3.0 mL). Purification by flash column chromatography (100% hexanes) afforded a colorless oil (0.067 g) as a mixture of the title compound (40% calculated yield), the product of hydrogenolysis (8% calculated yield), and the product of elimination (7% calculated yield). Further purification (100% heptanes) afforded a sample of analytically pure material: **TLC** R_f = 0.7 (100% hexanes); **^1H NMR** (500 MHz, CDCl_3) δ 7.79 (q, J = 7.5 Hz, 3H), 7.56 (s, 1H), 7.46–7.41 (m, 2H), 7.32 (d, J = 9.0 Hz, 1H), 2.92 (hept, J = 5.0 Hz, 1H), 1.85 (d, J = 12.5 Hz, 1H), 1.66–1.54 (m, 6H), 1.49–1.39 (m, 2H), 1.35–1.33 (m, 1H),

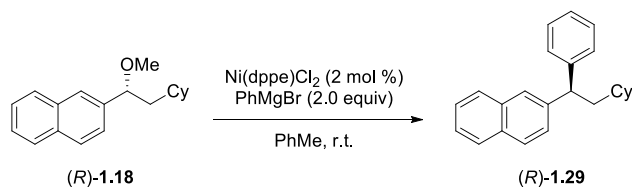
1.14–1.03 (m, 4H), 0.92–0.84 (m, 5H), 0.80 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.2, 133.7, 132.3, 128.0, 127.7, 127.6, 126.3, 126.1, 125.8, 125.1, 46.9, 45.4, 40.5, 34.9, 34.3, 33.0, 26.8, 26.4, 26.3, 25.5, 23.7, 22.0; IR (neat) 2919, 2849, 1447, 853, 813, 743 cm^{-1} ; HRMS (TOF MS EI+) m/z calcd for $\text{C}_{22}\text{H}_{30}$ $[\text{M}]^+$ 294.2347, found 294.2350; $[\alpha]^{27}_{\text{D}} +14.9$ (c 0.80, CHCl_3); SFC analysis (OJ-H, 2% hexanes, 2.0 mL/min) indicated 90% ee: t_{R} (major) = 7.0 minutes, t_{R} (minor) = 8.4 minutes.



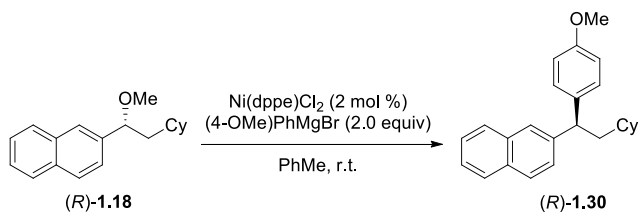
(R)-2-(octan-3-yl)naphthalene ((R)-1.27) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.13** (0.100 g, 0.500 mmol), Ni(dppe)Cl_2 (5.3 mg, 0.010 mmol), n -pentylmagnesium bromide (0.60 mL, 1.0 mmol, 1.7 M in Et_2O), and toluene (3.0 mL). Purification by flash column chromatography (100% hexanes) afforded a colorless oil (0.118 g) as a mixture of the title compound (96% calculated yield), the product of hydrogenolysis (2% calculated yield), and the product of elimination (1% calculated yield). Further purification (100% heptanes) afforded a sample of analytically pure material: TLC $R_f = 0.6$ (100% hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.80–7.76 (m, 3H), 7.56 (s, 1H), 7.46–7.38 (m, 2H), 7.30 (dd, $J = 8.4, 0.8$ Hz, 1H), 2.60–2.52 (m, 1H), 1.78–1.60 (m, 4H), 1.26–1.10 (m, 6H), 0.83–0.76 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.7, 133.7, 132.2, 127.9, 127.7, 127.6, 126.5, 126.2, 125.8, 125.1, 48.2, 36.6, 32.2, 29.8, 27.5, 22.7, 14.2, 12.4; IR (neat) 3056, 2981, 2918, 2850, 1107, 1067 cm^{-1} ; HRMS (TOF MS CI+) m/z calcd for $\text{C}_{18}\text{H}_{24}$ $[\text{M}]^+$ 240.1878, found 240.1871; $[\alpha]^{27}_{\text{D}} -1.6$ (c 1.83, CHCl_3); SFC analysis (OJ-H, 2% hexanes, 2 mL/min) indicated 96% ee: t_{R} (minor) = 10.0 minutes, t_{R} (major) = 10.6 minutes.



(R)-2-(6-phenylhexan-3-yl)naphthalene ((R)-1.28) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.13** (40 mg, 0.20 mmol), Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol), (3-phenylpropyl)magnesium bromide (0.24 mL, 0.40 mmol, 1.7 M in Et₂O), and toluene (3.0 mL). Purification by flash column chromatography (100% heptanes) afforded a colorless oil (0.054 g) as a mixture of the title compound (93% calculated yield) and the product of Wurtz coupling of the organomagnesium reagent (1,6-diphenylhexane). Further purification (flash column chromatography in 100% pentanes) afforded a sample of analytically pure material: **TLC** *R_f* = 0.6 (100% hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.42 (dt, *J* = 17.4, 6.7 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.23–7.20 (m, 2H), 7.14–7.11 (m, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 2.61–2.49 (m, 3H), 1.79–1.59 (m, 4H), 1.57–1.41 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 143.3, 142.7, 133.7, 132.4, 128.5, 128.3, 128.3, 128.0, 127.72, 127.65, 126.6, 126.1, 125.9, 125.7, 125.2, 48.1, 36.23, 36.15, 29.8, 29.6, 12.4; **IR** (neat) 3024, 2928, 2856, 815, 743 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₂₂H₂₄ [M]⁺ 288.1878, found 288.1880; **[α]_D²⁴** -15.1 (*c* 1.08, CHCl₃); **SFC** analysis (OJ-H, 15% IPA, 2.0 mL/min) indicated 97% ee: *t_R* (minor) = 6.3 minutes, *t_R* (major) = 7.8 minutes.

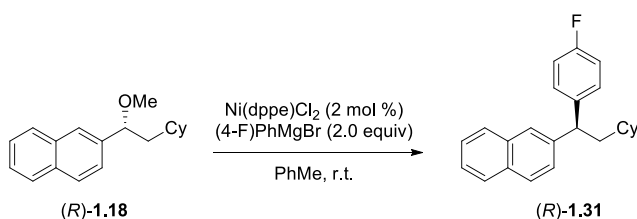


(R)-2-(2-cyclohexyl-1-phenylethyl)naphthalene ((R)-1.29) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(R)-1.18** (0.134 g, 0.500 mmol), Ni(dppe)Cl_2 (5.3 mg, 0.010 mmol), phenylmagnesium bromide (0.37 mL, 1.0 mmol, 2.7 M in Et_2O), and toluene (7.5 mL). The reaction was stirred for a period of 24 h. Purification by flash column chromatography (100% pentane) afforded the title compound as a colorless oil (0.105 g, 0.33 mmol, 67%): **TLC** R_f = 0.2 (100% pentane); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.77 (t, J = 8.1 Hz, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.69 (s, 1H), 7.41 (quintd, J = 6.9, 1.3 Hz, 2H), 7.34 (dd, J = 8.5, 1.6 Hz, 1H), 7.29–7.24 (m, 4H), 7.17–7.14 (m, 1H), 4.23 (t, J = 7.9 Hz, 1H), 2.08–1.95 (m, 2H), 1.80 (t, J = 11.7 Hz, 2H), 1.66–1.58 (m, 3H), 1.26–1.05 (m, 4H), 1.01–0.93 (m, 2H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 145.5, 143.0, 133.7, 132.3, 128.5, 128.1, 127.9, 127.7, 127.0, 126.2, 126.0, 125.4, 48.2, 43.5, 35.0, 33.7, 33.5, 26.8, 26.3; **IR** (neat) 2919, 2849, 1448, 3055, 1490, 743, 698 cm^{-1} ; **HRMS** (TOF MS EI^+) m/z calcd for $\text{C}_{24}\text{H}_{26}$ $[\text{M}]^+$ 314.2035, found 314.2030; **$[\alpha]_D^{25}$** -10.8 (c 1.99, CHCl_3); **SFC** analysis (OJ-H, 15% IPA, 2.5 mL/min) indicated 92% ee: t_R (major) = 6.1 minutes, t_R (minor) = 6.9 minutes.



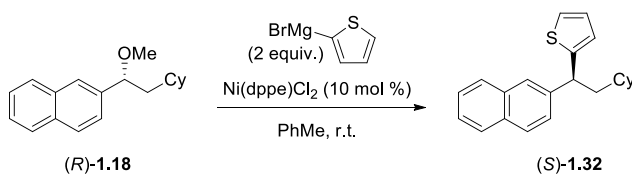
(R)-2-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)naphthalene ((R)-1.30) was prepared according to the representative procedure outlined above using the following amounts of

reagents: (*R*)-**1.18** (0.134 g, 0.500 mmol) and Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol), 4-methoxyphenylmagnesium bromide (0.53 mL, 1.0 mmol, 1.9 M in Et₂O), and toluene (7.5 mL). The reaction mixture was stirred for a period of 24 h. Purification by silica gel flash column chromatography (5% Et₂O in pentane) afforded a mixture of the title compound (86% calculated yield) and the starting material (15% calculated yield) as a colorless oil (0.157 g total mass). Further purification by silica gel flash column chromatography (1–15% benzene in hexanes) afforded a pure sample of the title compound: **TLC** *R_f* = 0.7 (5% EtOAc in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.77 (t, *J* = 9.3 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.66 (s, 1H), 7.45–7.35 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.18 (t, *J* = 7.3 Hz, 1H), 3.74 (s, 3H), 2.02–1.94 (m, 2H), 1.80–1.78 (m, 2H), 1.70–1.55 (m, 3H), 1.23–1.04 (m, 4H), 1.02–0.91 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 157.9, 143.4, 137.6, 133.7, 132.2, 129.0, 128.5, 128.1, 127.8, 127.7, 127.0, 126.0, 125.8, 125.4, 113.9, 55.3, 47.2, 43.7, 35.0, 33.62, 33.57, 26.8, 26.3; **IR** (neat) 2919, 2848, 1509, 1447, 1245, 1177, 1037 cm⁻¹; **HRMS** (TOF MS CI+) *m/z* calcd for C₂₅H₂₈O [M]⁺ 344.2140, found 344.2131; **[α]_D²⁴** –6.3 (*c* 1.17, CHCl₃); **SFC** analysis (AD-H, 15% IPA, 3.0 mL/min) indicated 97% ee: *t_R* (major) = 9.0 minutes, *t_R* (minor) = 9.6 minutes.



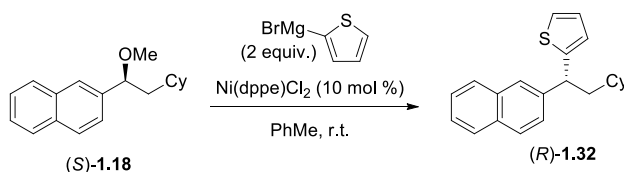
(*R*)-2-(2-cyclohexyl-1-(4-fluorophenyl)ethyl)naphthalene ((*R*)-**1.31**) was prepared according to the representative procedure outlined above using the following amounts of reagents: (*R*)-**1.18** (0.134 g, 0.500 mmol), Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol), 4-fluorophenylmagnesium bromide

(0.46 mL, 1.0 mmol, 2.2 M in Et₂O), and toluene (7.5 mL). The reaction mixture was stirred for a period of 48 h. Purification by silica gel flash column chromatography (100% hexanes) afforded a mixture of the title compound (82% calculated yield) and the product of Wurtz coupling of the organomagnesium reagent as a colorless oil (0.147 g total mass). Further purification by column chromatography (100% pentane) afforded a pure sample of (*R*)-**1.31**: **TLC** *R_f* = 0.8 (5% EtOAc in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.78 (t, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.66 (s, 1H), 7.46–7.40 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.22 (dd, *J* = 8.5, 6.0 Hz, 2H), 6.95 (app t, *J* = 8.5 Hz, 2H), 4.21 (t, *J* = 8.0 Hz, 1H), 2.02 (quint, *J* = 7.1 Hz, 1H), 1.94 (quint, *J* = 7.0 Hz, 1H), 1.79 (t, *J* = 12.3 Hz, 2H), 1.70–1.56 (m, 3H), 1.22–1.04 (m, 4H), 1.01–0.96 (m, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ 161.4 (d, *J* = 242.5 Hz, 1C), 142.8, 141.1 (d, *J* = 3.3 Hz, 1C), 133.7, 132.2, 129.5 (d, *J* = 7.8 Hz, 2C), 128.2, 127.8, 127.7, 126.8, 126.1, 125.9, 125.5, 115.3 (d, *J* = 84.0 Hz, 2C), 47.3, 43.6, 35.0, 33.6, 33.5, 26.7, 26.2; **IR** (neat) 3053, 2920, 2850, 1506, 1222, 793 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₂₄H₂₅F [M]⁺ 332.1940, found 332.1930; [*α*]_D²⁰ -11.1 (*c* 0.91, CHCl₃); **SFC** analysis (OJ-H, 15% IPA, 2.5 mL/min) indicated 87% ee: *t_R* (major) = 4.3 minutes, *t_R* (minor) = 5.6 minutes.



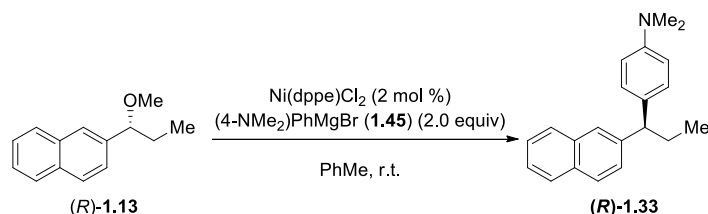
(*S*)-2-(2-cyclohexyl-1-(naphthalen-2-yl)ethyl)thiophene ((*S*)-**1.32**) was prepared according to the representative procedure outlined above using the following amounts of reagents: (*R*)-**1.18** (54 mg, 0.20 mmol), Ni(dppe)Cl₂ (10.6 mg, 0.0200 mmol), 2-thienylmagnesium bromide (0.15 mL, 0.40 mmol, 2.6 M in Et₂O), and toluene (3.0 mL). The reaction mixture was stirred for a period of 48 h. Purification by flash column chromatography (2% Et₂O in pentane) afforded the

title compound as a yellow oil (49 mg, 0.15 mmol, 76%): **TLC** R_f = 0.5 (100% hexanes); **^1H NMR** (400 MHz, CDCl_3) δ 7.78 (t, J = 9.0 Hz, 3H), 7.70 (s, 1H), 7.47–7.38 (m, 3H), 7.12 (d, J = 4.4 Hz, 1H), 6.91 (dd, J = 5.2, 3.2 Hz, 1H), 6.83 (d, J = 3.2 Hz, 1H), 4.45 (t, J = 8.0 Hz, 1H), 2.05 (t, J = 7.4 Hz, 2H), 1.85 (d, J = 12.4 Hz, 1H), 1.73 (d, J = 12.4 Hz, 1H), 1.64–1.50 (m, 3H), 1.30–0.96 (m, 6H); **^{13}C NMR** (150 MHz, CDCl_3) δ 150.2, 142.5, 133.7, 132.5, 128.4, 127.9, 127.8, 126.7, 126.3, 126.2, 126.1, 125.6, 123.9, 123.6, 45.1, 43.9, 35.1, 33.8, 33.1, 26.7, 26.3, 26.2; **IR** (neat) 3026, 2922, 2853, 1453, 743, 697 cm^{-1} ; **HRMS** (TOF MS Cl^+) m/z calcd for $\text{C}_{22}\text{H}_{24}\text{S}$ $[\text{M} + \text{H}]^+$ 321.1677, found 321.1672; $[\alpha]_D^{24}$ +42.4 (c 1.20, CHCl_3); **SFC** analysis (OD-H, 20% hexanes, 3.0 mL/min) indicated 93% ee: t_R (minor) = 14.9 minutes, t_R (major) = 17.5 minutes.



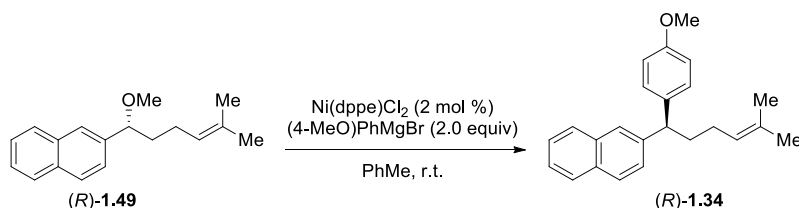
(R)-2-(2-cyclohexyl-1-(naphthalen-2-yl)ethyl)thiophene ((R)-1.32) was prepared according to the representative procedure outlined above using the following amounts of reagents: **(S)-1.18** (39 mg, 0.15 mmol), $\text{Ni}(\text{dppe})\text{Cl}_2$ (7.7 mg, 0.015 mmol), 2-thienylmagnesium bromide (0.17 mL, 0.29 mmol, 2.0 M in Et_2O), and toluene (2.2 mL). The reaction mixture was stirred for a period of 48 h. Purification by flash column chromatography (2% Et_2O in pentane) afforded the title compound as a yellow oil (33 mg, 0.10 mmol, 70%): **^1H NMR** (500 MHz, CDCl_3) δ 7.78 (t, J = 8.6 Hz, 3H), 7.70 (s, 1H), 7.42 (m, 3H), 7.13 (d, J = 5.2 Hz, 1H), 6.91 (dd, J = 5.2, 3.6 Hz, 1H), 6.84 (d, J = 3.6 Hz, 1H), 4.45 (t, J = 8.0 Hz, 1H), 2.05 (t, J = 7.4 Hz, 2H), 1.86 (d, J = 12.8 Hz, 1H), 1.73 (d, J = 12.4 Hz, 1H), 1.64–1.54 (m, 3H), 1.26–0.96 (m, 6H); **^{13}C NMR** (125 MHz, CDCl_3) δ 150.2, 142.5, 133.7, 132.5, 128.4, 127.9, 127.8, 126.7, 126.3, 126.14, 126.09, 125.6,

123.9, 123.6, 45.1, 43.8, 35.1, 33.8, 33.1, 26.7, 26.25, 26.21; $[\alpha]^{24}_{\text{D}} -42.9$ (c 0.98, CHCl_3); **SFC** analysis (OD-H, 20% hexanes, 3.0 mL/min) indicated 92% ee: t_{R} (major) = 14.3 minutes, t_{R} (minor) = 17.5 minutes.



(R)-*N,N*-dimethyl-4-(1-(naphthalen-2-yl)propyl)aniline ((R)-1.33): A 7 mL vial was equipped with a stir bar, flame dried, and pumped into a glove box while still warm. **(R)-1.13** (0.040 g, 0.20 mmol), Ni(dppe)Cl_2 (5.3 mg, 0.010 mmol), and 4-(*N,N*-dimethylamino) phenylmagnesium bromide (**1.45**) (0.133 g, 0.400 mmol) were added. The vial was capped, removed from the glove box and put under a nitrogen atmosphere. Toluene (3 mL) was added and the reaction mixture was stirred for 24 h at which point the reaction was quenched with an excess of methanol. The crude mixture was eluted through a silica plug (100% Et_2O) and concentrated in vacuo. Purification by flash column chromatography (1% Et_3N , 5% Et_2O in pentane) afforded the title compound as a yellow oil (0.047 g, 0.16 mmol, 80% yield). Trace amounts (<5%) of Wurtz coupling product of the organomagnesium reagent could not be separated from the product. **TLC** $R_f = 0.2$ (1% Et_3N , 5% EtOAc in hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.77 (t, $J = 8.0$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.68 (s, 1H), 7.40 (quint, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.14 (d, $J = 8.4$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 3.87 (t, $J = 7.6$ Hz, 1H), 2.89 (s, 6H), 2.17–2.08 (quint, $J = 7.2$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 149.2, 143.6, 133.7, 133.3, 132.2, 128.7, 128.0, 127.8, 127.7, 127.1, 125.9, 125.8, 125.2, 112.9, 52.4, 40.9, 28.6, 13.0; $[\alpha]^{26}_{\text{D}} -3.4$ (c 1.17, CHCl_3); **IR** (neat) 2958, 2928, 2871, 2797, 1613, 1564,

1818, 1345, 811, 780, 747; **HRMS** (TOF MS ES+) m/z calcd for C₂₁H₂₃NH [M + H]⁺ 290.1909, found 290.1903; [α]_D²⁵ -3.4 (c 1.16, CHCl₃); **SFC** analysis (AD-H, 20% IPA, 2.5 mL/min) indicated 85% ee: t_R (major) = 6.1 minutes, t_R (minor) = 7.4 minutes.



(R)-2-(1-(4-methoxyphenyl)-5-methylhex-4-enyl)naphthalene ((R)-1.34): A flame dried 20 mL dram vial was charged with **(R)-1.49** (127 mg, 0.50 mmol) and Ni(dppe)Cl₂ (5.3 mg, 0.010 mmol). The vial was capped and put under a nitrogen atmosphere. Toluene (7.5 mL) was added followed by (4-methoxy)phenylmagnesium bromide (0.57 mL, 1.0 mmol, 1.8 M in Et₂O). The reaction mixture was stirred for a period of 24 h at which point the reaction vessel was briefly opened to air and another 5.3 mg (0.010 mmol) of Ni(dppe)Cl₂ were added. The reaction mixture was then allowed to stir for a second 24 hour period then run through a silica plug (100% Et₂O). Purification of the crude material by silica gel flash column chromatography (2% Et₂O in pentane) yielded a mixture of the title compound (92% calculated yield) and the product of Wurtz coupling of the organomagnesium reagent as an oil (151 mg total mass). Further purification by silica gel flash column chromatography (1% Et₂O in pentane) afforded a pure sample of **(R)-1.34**: **TLC** R_f = 0.7 (2% EtOAc in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.78 (t, J = 8.3 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.45–7.38 (m, 2H), 7.31 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 5.17 (t, J = 7.0 Hz, 1H), 4.02 (t, J = 7.8 Hz, 1H), 3.75 (s, 3H), 2.17–2.11 (m, 2H), 1.97 (app q, J = 7.5 Hz, 2H), 1.69 (s, 3H), 1.48 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 158.0, 143.1, 137.3, 133.7, 132.22, 132.16, 129.1, 128.1, 127.8,

127.7, 126.9, 126.0, 125.9, 125.4, 124.3, 113.9, 55.3, 49.9, 35.8, 26.5, 25.9, 17.9; **IR** (neat) 2925, 1608, 1509, 1440, 1245 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{24}\text{H}_{26}\text{O}$ $[\text{M}]^+$ 330.1984, found 330.1986; $[\alpha]^{20}_{\text{D}}$ -2.7 (c 1.06, CHCl_3); **SFC** analysis (AD-H, 10% IPA, 3.0 mL/min) indicated 88% ee: t_{R} (major) = 8.2 minutes, t_{R} (minor) = 8.9 minutes.

1.4.7 Crystallographic Data⁵⁵

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX CCD diffractometer equipped with Cu K_{α} radiation ($\lambda = 1.5478$). Crystals of the subject compound were grown by slow evaporation of a 1:1 methanol:pentane solution. A 0.217 x 0.095 x 0.053 mm colorless needle was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 90(2) K using ϕ and ω scans. Data was collected at two crystal-to-detector distances, 45mm or 60mm, using variable exposure time (2s-10s) depending on θ with a scan width of 1.0° . Data collection was 98.7% complete to 68.00° in θ . A total of 57312 reflections were collected covering the indices, $-7 \leq h \leq 7$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$. 7355 reflections were found to be symmetry independent, with a R_{int} of 0.0524. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be $P1$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were

⁵⁵ Crystal Structure solved and X-Ray data compiled by Curtis E. Moore at the University of California, San Diego.

constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013. Crystallographic data are summarized in Table 1.10.

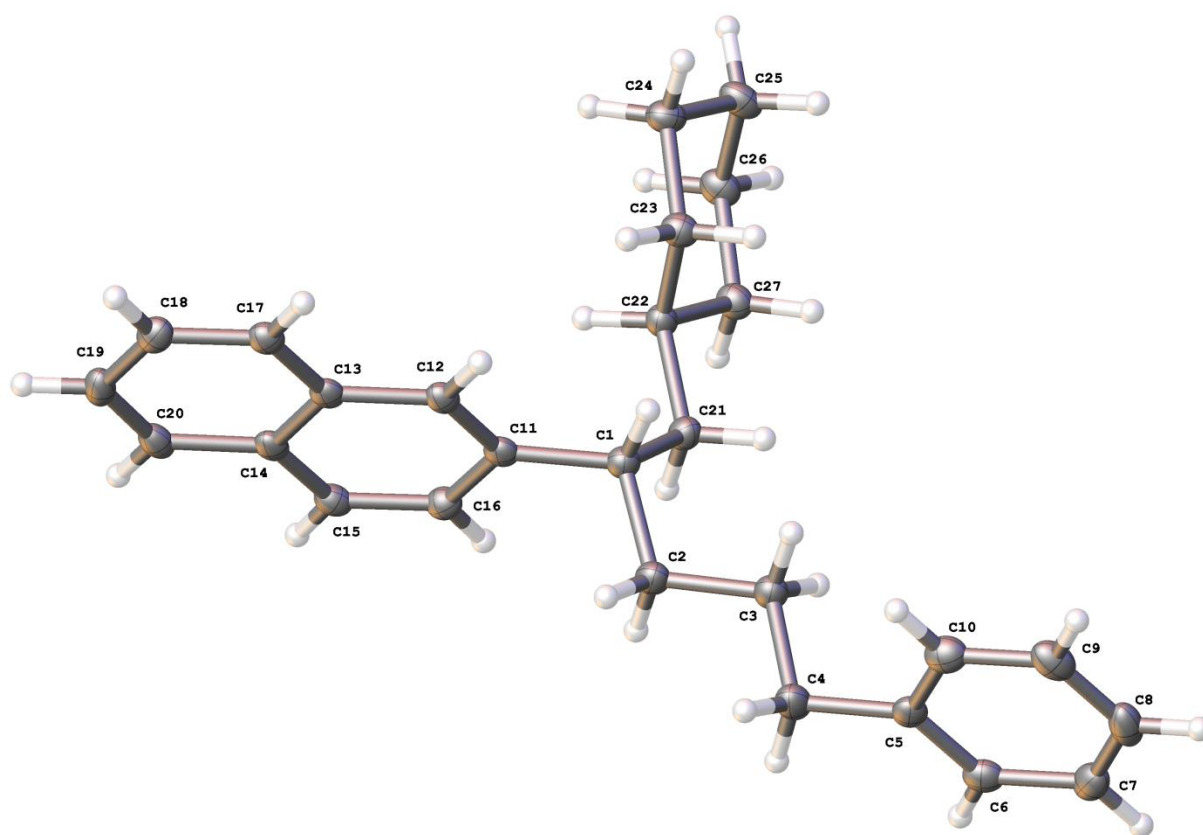


Table 1.10. Crystal Data and Structure Refinement for Jarvo02.

Identification code	ERJ-14	
Empirical formula	C ₂₇ H ₃₂	
Molecular formula	C ₂₇ H ₃₂	
Formula weight	356.52	
Temperature	90 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 5.9031(2) Å	α = 106.3499(15)°.
	b = 13.8552(5) Å	β = 98.3273(14)°.
	c = 14.0936(5) Å	γ = 101.5540(15)°.
Volume	1058.56(7) Å ³	
Z	2	
Density (calculated)	1.119 Mg/m ³	
Absorption coefficient	0.463 mm ⁻¹	
F(000)	388	
Crystal size	0.217 x 0.095 x 0.053 mm ³	
Crystal color, habit	Colorless Needle	
Theta range for data collection	3.345 to 69.358°.	
Index ranges	-7 ≤ h ≤ 7, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17	
Reflections collected	57312	
Independent reflections	7355 [R(int) = 0.0524]	
Completeness to theta = 68.000°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.7017	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7355 / 3 / 487	
Goodness-of-fit on F ²	1.029	
Final R indices [I > 2σ(I)]	R1 = 0.0312, wR2 = 0.0787	
R indices (all data)	R1 = 0.0324, wR2 = 0.0799	
Absolute structure parameter	0.065(347)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.120 and -0.172 e.Å ⁻³	

Table 1.11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Jarvo02. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	8627(3)	2712(2)	9759(1)	20(1)
C(2)	8982(4)	1839(2)	10204(2)	23(1)
C(3)	9335(3)	883(2)	9445(1)	21(1)
C(4)	10054(4)	108(2)	9944(2)	27(1)
C(5)	10507(3)	-808(2)	9186(1)	21(1)
C(6)	8896(3)	-1776(2)	8845(2)	23(1)
C(7)	9312(4)	-2603(2)	8126(2)	27(1)
C(8)	11349(4)	-2473(2)	7748(2)	29(1)
C(9)	12964(4)	-1513(2)	8083(2)	28(1)
C(10)	12546(4)	-689(2)	8797(2)	26(1)
C(11)	8776(3)	3692(2)	10609(1)	18(1)
C(12)	10775(3)	4502(2)	10932(1)	18(1)
C(13)	11023(3)	5399(2)	11773(1)	18(1)
C(14)	9133(3)	5458(2)	12292(1)	19(1)
C(15)	7078(3)	4622(2)	11945(1)	21(1)
C(16)	6901(3)	3768(2)	11136(1)	20(1)
C(17)	13086(3)	6234(2)	12111(1)	20(1)
C(18)	13267(3)	7090(2)	12923(2)	23(1)
C(19)	11385(4)	7148(2)	13438(2)	24(1)
C(20)	9373(4)	6355(2)	13131(2)	22(1)
C(21)	6322(3)	2349(2)	8940(2)	21(1)
C(22)	5748(3)	3152(2)	8446(1)	19(1)
C(23)	7800(3)	3596(2)	8012(2)	22(1)
C(24)	7172(4)	4332(2)	7439(2)	24(1)
C(25)	4963(4)	3801(2)	6602(2)	27(1)
C(26)	2893(3)	3389(2)	7036(2)	25(1)
C(27)	3503(3)	2646(2)	7602(2)	22(1)
C(1')	9460(3)	671(2)	3372(1)	21(1)
C(2')	10172(4)	1568(2)	2946(2)	24(1)
C(3')	11922(4)	2533(2)	3706(2)	23(1)
C(4')	12998(4)	3309(2)	3205(2)	28(1)

C(5')	14500(4)	4307(2)	3977(2)	23(1)
C(6')	13548(4)	5157(2)	4278(2)	25(1)
C(7')	14867(4)	6067(2)	5020(2)	28(1)
C(8')	17162(4)	6145(2)	5474(2)	29(1)
C(9')	18138(4)	5304(2)	5183(2)	28(1)
C(10')	16815(4)	4395(2)	4438(2)	26(1)
C(11')	7920(3)	-281(2)	2526(1)	19(1)
C(12')	8759(3)	-1134(2)	2159(1)	19(1)
C(13')	7410(3)	-2009(2)	1326(1)	18(1)
C(14')	5111(3)	-1999(2)	863(1)	19(1)
C(15')	4255(3)	-1114(2)	1263(2)	21(1)
C(16')	5600(3)	-288(2)	2066(2)	21(1)
C(17')	8279(3)	-2891(2)	942(1)	20(1)
C(18')	6937(4)	-3720(2)	136(2)	23(1)
C(19')	4663(3)	-3706(2)	-327(2)	23(1)
C(20')	3773(3)	-2862(2)	29(2)	22(1)
C(21')	8305(3)	988(2)	4284(2)	22(1)
C(22')	7554(3)	139(2)	4758(1)	19(1)
C(23')	9615(3)	-298(2)	5085(2)	23(1)
C(24')	8856(4)	-1122(2)	5585(2)	26(1)
C(25')	7787(4)	-692(2)	6486(2)	28(1)
C(26')	5719(4)	-262(2)	6172(2)	27(1)
C(27')	6475(3)	559(2)	5667(2)	24(1)

Table 1.12. Bond lengths [\AA] and angles [$^\circ$] for Jarvo02.

C(1)-H(1)	1.0000	C(16)-H(16)	0.9500
C(1)-C(2)	1.546(3)	C(17)-H(17)	0.9500
C(1)-C(11)	1.514(3)	C(17)-C(18)	1.370(3)
C(1)-C(21)	1.542(3)	C(18)-H(18)	0.9500
C(2)-H(2A)	0.9900	C(18)-C(19)	1.415(3)
C(2)-H(2B)	0.9900	C(19)-H(19)	0.9500
C(2)-C(3)	1.523(3)	C(19)-C(20)	1.366(3)
C(3)-H(3A)	0.9900	C(20)-H(20)	0.9500
C(3)-H(3B)	0.9900	C(21)-H(21A)	0.9900
C(3)-C(4)	1.533(3)	C(21)-H(21B)	0.9900
C(4)-H(4A)	0.9900	C(21)-C(22)	1.536(3)
C(4)-H(4B)	0.9900	C(22)-H(22)	1.0000
C(4)-C(5)	1.510(3)	C(22)-C(23)	1.533(3)
C(5)-C(6)	1.388(3)	C(22)-C(27)	1.538(3)
C(5)-C(10)	1.392(3)	C(23)-H(23A)	0.9900
C(6)-H(6)	0.9500	C(23)-H(23B)	0.9900
C(6)-C(7)	1.389(3)	C(23)-C(24)	1.534(3)
C(7)-H(7)	0.9500	C(24)-H(24A)	0.9900
C(7)-C(8)	1.384(3)	C(24)-H(24B)	0.9900
C(8)-H(8)	0.9500	C(24)-C(25)	1.522(3)
C(8)-C(9)	1.382(3)	C(25)-H(25A)	0.9900
C(9)-H(9)	0.9500	C(25)-H(25B)	0.9900
C(9)-C(10)	1.384(3)	C(25)-C(26)	1.526(3)
C(10)-H(10)	0.9500	C(26)-H(26A)	0.9900
C(11)-C(12)	1.373(3)	C(26)-H(26B)	0.9900
C(11)-C(16)	1.424(3)	C(26)-C(27)	1.533(3)
C(12)-H(12)	0.9500	C(27)-H(27A)	0.9900
C(12)-C(13)	1.421(3)	C(27)-H(27B)	0.9900
C(13)-C(14)	1.423(3)	C(1')-H(1')	1.0000
C(13)-C(17)	1.416(3)	C(1')-C(2')	1.539(3)
C(14)-C(15)	1.415(3)	C(1')-C(11')	1.519(3)
C(14)-C(20)	1.420(3)	C(1')-C(21')	1.538(3)
C(15)-H(15)	0.9500	C(2')-H(2'A)	0.9900
C(15)-C(16)	1.366(3)	C(2')-H(2'B)	0.9900

C(2')-C(3')	1.524(3)	C(21')-H(21C)	0.9900
C(3')-H(3'A)	0.9900	C(21')-H(21D)	0.9900
C(3')-H(3'B)	0.9900	C(21')-C(22')	1.531(3)
C(3')-C(4')	1.531(3)	C(22')-H(22')	1.0000
C(4')-H(4'A)	0.9900	C(22')-C(23')	1.533(3)
C(4')-H(4'B)	0.9900	C(22')-C(27')	1.533(3)
C(4')-C(5')	1.505(3)	C(23')-H(23C)	0.9900
C(5')-C(6')	1.391(3)	C(23')-H(23D)	0.9900
C(5')-C(10')	1.392(3)	C(23')-C(24')	1.530(3)
C(6')-H(6')	0.9500	C(24')-H(24C)	0.9900
C(6')-C(7')	1.385(3)	C(24')-H(24D)	0.9900
C(7')-H(7')	0.9500	C(24')-C(25')	1.524(3)
C(7')-C(8')	1.381(3)	C(25')-H(25C)	0.9900
C(8')-H(8')	0.9500	C(25')-H(25D)	0.9900
C(8')-C(9')	1.388(3)	C(25')-C(26')	1.524(3)
C(9')-H(9')	0.9500	C(26')-H(26C)	0.9900
C(9')-C(10')	1.386(3)	C(26')-H(26D)	0.9900
C(10')-H(10')	0.9500	C(26')-C(27')	1.531(3)
C(11')-C(12')	1.369(3)	C(27')-H(27C)	0.9900
C(11')-C(16')	1.425(3)	C(27')-H(27D)	0.9900
C(12')-H(12')	0.9500		
C(12')-C(13')	1.422(3)	C(2)-C(1)-H(1)	107.4
C(13')-C(14')	1.423(2)	C(11)-C(1)-H(1)	107.4
C(13')-C(17')	1.417(3)	C(11)-C(1)-C(2)	109.61(15)
C(14')-C(15')	1.421(3)	C(11)-C(1)-C(21)	113.87(16)
C(14')-C(20')	1.413(3)	C(21)-C(1)-H(1)	107.4
C(15')-H(15')	0.9500	C(21)-C(1)-C(2)	110.96(16)
C(15')-C(16')	1.366(3)	C(1)-C(2)-H(2A)	108.7
C(16')-H(16')	0.9500	C(1)-C(2)-H(2B)	108.7
C(17')-H(17')	0.9500	H(2A)-C(2)-H(2B)	107.6
C(17')-C(18')	1.369(3)	C(3)-C(2)-C(1)	114.19(16)
C(18')-H(18')	0.9500	C(3)-C(2)-H(2A)	108.7
C(18')-C(19')	1.411(3)	C(3)-C(2)-H(2B)	108.7
C(19')-H(19')	0.9500	C(2)-C(3)-H(3A)	109.1
C(19')-C(20')	1.373(3)	C(2)-C(3)-H(3B)	109.1
C(20')-H(20')	0.9500	C(2)-C(3)-C(4)	112.66(16)

H(3A)-C(3)-H(3B)	107.8	C(15)-C(14)-C(13)	118.46(18)
C(4)-C(3)-H(3A)	109.1	C(15)-C(14)-C(20)	122.61(18)
C(4)-C(3)-H(3B)	109.1	C(20)-C(14)-C(13)	118.94(18)
C(3)-C(4)-H(4A)	109.3	C(14)-C(15)-H(15)	119.4
C(3)-C(4)-H(4B)	109.3	C(16)-C(15)-C(14)	121.24(18)
H(4A)-C(4)-H(4B)	107.9	C(16)-C(15)-H(15)	119.4
C(5)-C(4)-C(3)	111.74(16)	C(11)-C(16)-H(16)	119.4
C(5)-C(4)-H(4A)	109.3	C(15)-C(16)-C(11)	121.12(18)
C(5)-C(4)-H(4B)	109.3	C(15)-C(16)-H(16)	119.4
C(6)-C(5)-C(4)	121.28(18)	C(13)-C(17)-H(17)	119.6
C(6)-C(5)-C(10)	118.54(19)	C(18)-C(17)-C(13)	120.76(18)
C(10)-C(5)-C(4)	120.17(19)	C(18)-C(17)-H(17)	119.6
C(5)-C(6)-H(6)	119.8	C(17)-C(18)-H(18)	119.9
C(5)-C(6)-C(7)	120.47(19)	C(17)-C(18)-C(19)	120.16(19)
C(7)-C(6)-H(6)	119.8	C(19)-C(18)-H(18)	119.9
C(6)-C(7)-H(7)	119.8	C(18)-C(19)-H(19)	119.8
C(8)-C(7)-C(6)	120.3(2)	C(20)-C(19)-C(18)	120.5(2)
C(8)-C(7)-H(7)	119.8	C(20)-C(19)-H(19)	119.8
C(7)-C(8)-H(8)	120.2	C(14)-C(20)-H(20)	119.7
C(9)-C(8)-C(7)	119.6(2)	C(19)-C(20)-C(14)	120.66(19)
C(9)-C(8)-H(8)	120.2	C(19)-C(20)-H(20)	119.7
C(8)-C(9)-H(9)	120.0	C(1)-C(21)-H(21A)	108.3
C(8)-C(9)-C(10)	120.0(2)	C(1)-C(21)-H(21B)	108.3
C(10)-C(9)-H(9)	120.0	H(21A)-C(21)-H(21B)	107.4
C(5)-C(10)-H(10)	119.5	C(22)-C(21)-C(1)	116.10(16)
C(9)-C(10)-C(5)	121.0(2)	C(22)-C(21)-H(21A)	108.3
C(9)-C(10)-H(10)	119.5	C(22)-C(21)-H(21B)	108.3
C(12)-C(11)-C(1)	120.95(17)	C(21)-C(22)-H(22)	108.5
C(12)-C(11)-C(16)	118.36(18)	C(21)-C(22)-C(27)	109.54(16)
C(16)-C(11)-C(1)	120.57(18)	C(23)-C(22)-C(21)	111.91(15)
C(11)-C(12)-H(12)	119.0	C(23)-C(22)-H(22)	108.5
C(11)-C(12)-C(13)	121.99(17)	C(23)-C(22)-C(27)	109.80(15)
C(13)-C(12)-H(12)	119.0	C(27)-C(22)-H(22)	108.5
C(12)-C(13)-C(14)	118.84(17)	C(22)-C(23)-H(23A)	109.1
C(17)-C(13)-C(12)	122.18(17)	C(22)-C(23)-H(23B)	109.1
C(17)-C(13)-C(14)	118.98(18)	C(22)-C(23)-C(24)	112.37(15)

H(23A)-C(23)-H(23B)	107.9	C(3')-C(2')-C(1')	114.09(16)
C(24)-C(23)-H(23A)	109.1	C(3')-C(2')-H(2'A)	108.7
C(24)-C(23)-H(23B)	109.1	C(3')-C(2')-H(2'B)	108.7
C(23)-C(24)-H(24A)	109.3	C(2')-C(3')-H(3'A)	109.1
C(23)-C(24)-H(24B)	109.3	C(2')-C(3')-H(3'B)	109.1
H(24A)-C(24)-H(24B)	108.0	C(2')-C(3')-C(4')	112.48(16)
C(25)-C(24)-C(23)	111.43(17)	H(3'A)-C(3')-H(3'B)	107.8
C(25)-C(24)-H(24A)	109.3	C(4')-C(3')-H(3'A)	109.1
C(25)-C(24)-H(24B)	109.3	C(4')-C(3')-H(3'B)	109.1
C(24)-C(25)-H(25A)	109.6	C(3')-C(4')-H(4'A)	109.3
C(24)-C(25)-H(25B)	109.6	C(3')-C(4')-H(4'B)	109.3
C(24)-C(25)-C(26)	110.29(16)	H(4'A)-C(4')-H(4'B)	107.9
H(25A)-C(25)-H(25B)	108.1	C(5')-C(4')-C(3')	111.69(16)
C(26)-C(25)-H(25A)	109.6	C(5')-C(4')-H(4'A)	109.3
C(26)-C(25)-H(25B)	109.6	C(5')-C(4')-H(4'B)	109.3
C(25)-C(26)-H(26A)	109.4	C(6')-C(5')-C(4')	120.02(19)
C(25)-C(26)-H(26B)	109.4	C(6')-C(5')-C(10')	118.34(19)
C(25)-C(26)-C(27)	110.99(16)	C(10')-C(5')-C(4')	121.6(2)
H(26A)-C(26)-H(26B)	108.0	C(5')-C(6')-H(6')	119.5
C(27)-C(26)-H(26A)	109.4	C(7')-C(6')-C(5')	120.91(19)
C(27)-C(26)-H(26B)	109.4	C(7')-C(6')-H(6')	119.5
C(22)-C(27)-H(27A)	109.1	C(6')-C(7')-H(7')	119.9
C(22)-C(27)-H(27B)	109.1	C(8')-C(7')-C(6')	120.3(2)
C(26)-C(27)-C(22)	112.43(17)	C(8')-C(7')-H(7')	119.9
C(26)-C(27)-H(27A)	109.1	C(7')-C(8')-H(8')	120.2
C(26)-C(27)-H(27B)	109.1	C(7')-C(8')-C(9')	119.6(2)
H(27A)-C(27)-H(27B)	107.9	C(9')-C(8')-H(8')	120.2
C(2')-C(1')-H(1')	107.3	C(8')-C(9')-H(9')	120.0
C(11')-C(1')-H(1')	107.3	C(10')-C(9')-C(8')	119.99(19)
C(11')-C(1')-C(2')	109.48(15)	C(10')-C(9')-H(9')	120.0
C(11')-C(1')-C(21')	113.10(16)	C(5')-C(10')-H(10')	119.5
C(21')-C(1')-H(1')	107.3	C(9')-C(10')-C(5')	120.9(2)
C(21')-C(1')-C(2')	112.20(17)	C(9')-C(10')-H(10')	119.5
C(1')-C(2')-H(2'A)	108.7	C(12')-C(11')-C(1')	120.97(17)
C(1')-C(2')-H(2'B)	108.7	C(12')-C(11')-C(16')	118.38(18)
H(2'A)-C(2')-H(2'B)	107.6	C(16')-C(11')-C(1')	120.59(18)

C(11')-C(12')-H(12')	118.9	C(23')-C(22')-H(22')	108.1
C(11')-C(12')-C(13')	122.11(17)	C(23')-C(22')-C(27')	109.76(15)
C(13')-C(12')-H(12')	118.9	C(27')-C(22')-H(22')	108.1
C(12')-C(13')-C(14')	118.90(18)	C(22')-C(23')-H(23C)	109.3
C(17')-C(13')-C(12')	122.20(17)	C(22')-C(23')-H(23D)	109.3
C(17')-C(13')-C(14')	118.90(18)	H(23C)-C(23')-H(23D)	107.9
C(15')-C(14')-C(13')	118.23(18)	C(24')-C(23')-C(22')	111.76(15)
C(20')-C(14')-C(13')	119.09(18)	C(24')-C(23')-H(23C)	109.3
C(20')-C(14')-C(15')	122.68(17)	C(24')-C(23')-H(23D)	109.3
C(14')-C(15')-H(15')	119.4	C(23')-C(24')-H(24C)	109.4
C(16')-C(15')-C(14')	121.23(17)	C(23')-C(24')-H(24D)	109.4
C(16')-C(15')-H(15')	119.4	H(24C)-C(24')-H(24D)	108.0
C(11')-C(16')-H(16')	119.4	C(25')-C(24')-C(23')	111.14(18)
C(15')-C(16')-C(11')	121.13(18)	C(25')-C(24')-H(24C)	109.4
C(15')-C(16')-H(16')	119.4	C(25')-C(24')-H(24D)	109.4
C(13')-C(17')-H(17')	119.6	C(24')-C(25')-H(25C)	109.4
C(18')-C(17')-C(13')	120.72(18)	C(24')-C(25')-H(25D)	109.4
C(18')-C(17')-H(17')	119.6	C(24')-C(25')-C(26')	110.98(17)
C(17')-C(18')-H(18')	119.8	H(25C)-C(25')-H(25D)	108.0
C(17')-C(18')-C(19')	120.34(19)	C(26')-C(25')-H(25C)	109.4
C(19')-C(18')-H(18')	119.8	C(26')-C(25')-H(25D)	109.4
C(18')-C(19')-H(19')	119.9	C(25')-C(26')-H(26C)	109.5
C(20')-C(19')-C(18')	120.27(19)	C(25')-C(26')-H(26D)	109.5
C(20')-C(19')-H(19')	119.9	C(25')-C(26')-C(27')	110.94(17)
C(14')-C(20')-H(20')	119.7	H(26C)-C(26')-H(26D)	108.0
C(19')-C(20')-C(14')	120.68(18)	C(27')-C(26')-H(26C)	109.5
C(19')-C(20')-H(20')	119.7	C(27')-C(26')-H(26D)	109.5
C(1')-C(21')-H(21C)	108.4	C(22')-C(27')-H(27C)	109.2
C(1')-C(21')-H(21D)	108.4	C(22')-C(27')-H(27D)	109.2
H(21C)-C(21')-H(21D)	107.5	C(26')-C(27')-C(22')	112.16(17)
C(22')-C(21')-C(1')	115.48(16)	C(26')-C(27')-H(27C)	109.2
C(22')-C(21')-H(21C)	108.4	C(26')-C(27')-H(27D)	109.2
C(22')-C(21')-H(21D)	108.4	H(27C)-C(27')-H(27D)	107.9
C(21')-C(22')-H(22')	108.1		
C(21')-C(22')-C(23')	112.32(15)		
C(21')-C(22')-C(27')	110.28(16)		

Table 1.13. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Jarvo02. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	23(1)	19(1)	18(1)	7(1)	3(1)	6(1)
C(2)	30(1)	20(1)	18(1)	7(1)	2(1)	7(1)
C(3)	24(1)	20(1)	19(1)	7(1)	3(1)	7(1)
C(4)	38(1)	24(1)	21(1)	9(1)	6(1)	13(1)
C(5)	26(1)	20(1)	17(1)	9(1)	1(1)	9(1)
C(6)	22(1)	27(1)	22(1)	13(1)	2(1)	8(1)
C(7)	34(1)	22(1)	20(1)	6(1)	-4(1)	5(1)
C(8)	41(1)	31(1)	18(1)	5(1)	2(1)	20(1)
C(9)	27(1)	39(1)	24(1)	14(1)	7(1)	16(1)
C(10)	24(1)	28(1)	26(1)	12(1)	1(1)	4(1)
C(11)	21(1)	21(1)	16(1)	9(1)	1(1)	8(1)
C(12)	20(1)	21(1)	16(1)	8(1)	3(1)	9(1)
C(13)	22(1)	21(1)	16(1)	10(1)	2(1)	9(1)
C(14)	24(1)	22(1)	15(1)	10(1)	3(1)	11(1)
C(15)	21(1)	26(1)	20(1)	11(1)	6(1)	9(1)
C(16)	20(1)	21(1)	19(1)	8(1)	1(1)	4(1)
C(17)	21(1)	23(1)	18(1)	10(1)	2(1)	8(1)
C(18)	24(1)	21(1)	21(1)	7(1)	-3(1)	5(1)
C(19)	32(1)	21(1)	16(1)	4(1)	-1(1)	12(1)
C(20)	28(1)	28(1)	16(1)	10(1)	6(1)	15(1)
C(21)	25(1)	18(1)	19(1)	6(1)	1(1)	5(1)
C(22)	22(1)	18(1)	16(1)	6(1)	3(1)	7(1)
C(23)	22(1)	25(1)	21(1)	9(1)	4(1)	7(1)
C(24)	28(1)	26(1)	24(1)	13(1)	7(1)	9(1)
C(25)	30(1)	36(1)	19(1)	13(1)	5(1)	12(1)
C(26)	23(1)	31(1)	21(1)	10(1)	1(1)	9(1)
C(27)	22(1)	25(1)	19(1)	7(1)	2(1)	5(1)
C(1')	24(1)	21(1)	18(1)	8(1)	4(1)	5(1)
C(2')	30(1)	22(1)	18(1)	7(1)	3(1)	4(1)
C(3')	28(1)	22(1)	20(1)	8(1)	4(1)	3(1)

C(4')	36(1)	25(1)	21(1)	9(1)	5(1)	2(1)
C(5')	28(1)	24(1)	19(1)	12(1)	6(1)	3(1)
C(6')	26(1)	29(1)	21(1)	12(1)	2(1)	6(1)
C(7')	37(1)	25(1)	24(1)	10(1)	5(1)	9(1)
C(8')	36(1)	26(1)	19(1)	9(1)	0(1)	-2(1)
C(9')	22(1)	39(1)	22(1)	14(1)	1(1)	2(1)
C(10')	29(1)	30(1)	24(1)	13(1)	10(1)	9(1)
C(11')	21(1)	21(1)	16(1)	10(1)	4(1)	4(1)
C(12')	18(1)	23(1)	17(1)	10(1)	3(1)	4(1)
C(13')	21(1)	21(1)	15(1)	10(1)	5(1)	5(1)
C(14')	19(1)	24(1)	17(1)	11(1)	4(1)	5(1)
C(15')	18(1)	27(1)	20(1)	12(1)	3(1)	8(1)
C(16')	24(1)	21(1)	22(1)	9(1)	7(1)	10(1)
C(17')	20(1)	23(1)	19(1)	9(1)	3(1)	7(1)
C(18')	28(1)	22(1)	21(1)	8(1)	7(1)	8(1)
C(19')	24(1)	24(1)	16(1)	4(1)	0(1)	2(1)
C(20')	20(1)	27(1)	18(1)	9(1)	2(1)	6(1)
C(21')	28(1)	18(1)	19(1)	6(1)	4(1)	6(1)
C(22')	22(1)	18(1)	17(1)	5(1)	4(1)	4(1)
C(23')	23(1)	27(1)	23(1)	11(1)	7(1)	9(1)
C(24')	27(1)	29(1)	26(1)	15(1)	7(1)	10(1)
C(25')	30(1)	36(1)	23(1)	15(1)	8(1)	11(1)
C(26')	27(1)	33(1)	25(1)	12(1)	11(1)	9(1)
C(27')	27(1)	23(1)	22(1)	6(1)	7(1)	8(1)

Table 1.14. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for Jarvo02.

	x	y	z	U(eq)
H(1)	9972	2865	9422	24
H(2A)	10378	2122	10774	27
H(2B)	7583	1624	10479	27
H(3A)	10576	1106	9092	25
H(3B)	7846	532	8931	25
H(4A)	11504	466	10479	32
H(4B)	8780	-144	10268	32
H(6)	7500	-1873	9104	27
H(7)	8192	-3260	7893	32
H(8)	11636	-3041	7260	35
H(9)	14362	-1419	7824	33
H(10)	13667	-32	9025	31
H(12)	12031	4461	10582	22
H(15)	5797	4654	12280	25
H(16)	5504	3215	10921	24
H(17)	14359	6200	11771	24
H(18)	14659	7645	13142	27
H(19)	11522	7743	14001	28
H(20)	8121	6405	13482	27
H(21A)	6416	1730	8401	25
H(21B)	4988	2127	9248	25
H(22)	5437	3736	8972	23
H(23A)	8240	3016	7546	26
H(23B)	9192	3979	8572	26
H(24A)	6906	4953	7920	29
H(24B)	8515	4567	7142	29
H(25A)	5272	3218	6086	32
H(25B)	4559	4303	6268	32
H(26A)	1488	3019	6480	30
H(26B)	2496	3980	7506	30

H(27A)	3735	2022	7114	27
H(27B)	2157	2418	7901	27
H(1')	10945	490	3617	25
H(2'A)	10880	1318	2357	29
H(2'B)	8727	1763	2700	29
H(3'A)	13209	2320	4063	28
H(3'B)	11102	2878	4216	28
H(4'A)	13979	2994	2755	33
H(4'B)	11710	3462	2783	33
H(6')	11971	5113	3971	30
H(7')	14190	6640	5217	34
H(8')	18067	6770	5981	34
H(9')	19713	5351	5495	34
H(10')	17498	3824	4239	31
H(12')	10291	-1142	2470	22
H(15')	2720	-1095	966	25
H(16')	4978	291	2321	25
H(17')	9809	-2908	1246	24
H(18')	7540	-4306	-113	27
H(19')	3744	-4283	-886	27
H(20')	2243	-2859	-289	26
H(21C)	9433	1592	4813	26
H(21D)	6892	1219	4068	26
H(22')	6310	-444	4239	23
H(23C)	10234	-608	4486	28
H(23D)	10908	277	5567	28
H(24C)	7677	-1729	5083	31
H(24D)	10247	-1361	5815	31
H(25C)	9015	-132	7019	34
H(25D)	7232	-1251	6771	34
H(26C)	5121	53	6777	32
H(26D)	4417	-837	5696	32
H(27C)	7651	1167	6169	28
H(27D)	5081	796	5439	28

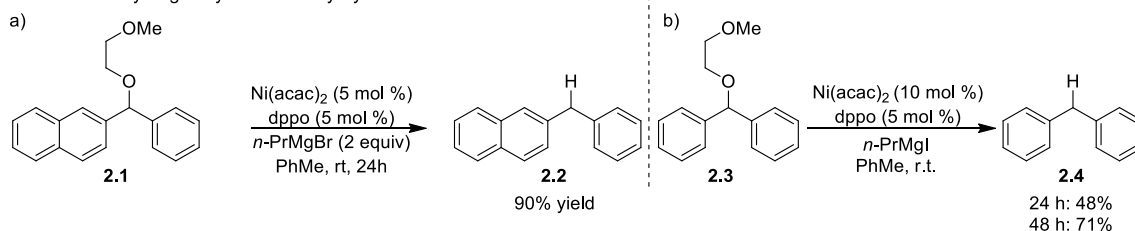
Chapter 2

Studies of Pathways Leading to Side-Products of Kumada-Type Cross-Coupling Reactions

2.1 Introduction

Chapter 1 described a cross-coupling reaction in which Ni(acac)₂ in the presence of dppe catalyzes the cross-coupling of benzylic ethers with aryl and alkyl Grignard reagents. Additionally, Ni(acac)₂ in the presence of a longer-chain ligand, dppe, was shown to promote major side-reactions: hydrogenolysis and elimination.¹ While attempting to identify conditions that were amenable to the cross-coupling of benzhydryl substrates, we saw a similar but more pronounced trend. Ni(acac)₂ in the presence of dppe and *n*-propylmagnesium iodide catalyzes the nearly quantitative hydrogenolysis of substrate **2.1** to form hydrocarbon **2.2** (Scheme 2.1a). The catalytic system also effectively performs hydrogenolysis on substrate **2.3** to form hydrocarbon **2.4** (Scheme 2.1b). If rendered a general method this reaction would be an interesting and useful reaction in its own right. We therefore studied the application of this protocol as a general method for the hydrogenolysis of benzylic ethers.

Scheme 2.1. Hydrogenolysis of Benzhydryl Substrates



One of the most prolific hydrogenolysis protocols is the Barton-McCombie deoxygenation.² This reaction has found ample application in late stage synthesis.³ For example, as shown in Scheme 2.2, Barton-McCombie deoxygenation is the last step in the total synthesis

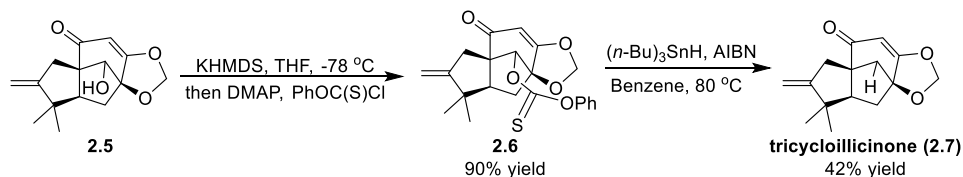
¹ See Table 1.3, entry 4.

² (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574. (b) Hartwig, W. *Tetrahedron* **1983**, *39*, 2609. (c) Hong, F.-T.; Paquette, L. A. *Chemtracts* **1998**, *11*, 67.

³ For representative examples, see (a) Singh, V.; Prathap, S.; Porinchi, M. *J. Org. Chem.*, **1998**, *63*, 4011. (b) Luzzio, F. A.; Fitch, R. W.; *J. Org. Chem.* **1999**, *64*, 5485. (c) Schlessinger, R. H.; Gillman, K. W. *Tetrahedron Lett.* **1996**, *37*, 1331.

of tricycloillicinone (**2.7**).⁴ Barton-McCombie deoxygenations are carried out through a two-step process: first an alcohol is converted to a thiocarbonyl derivative, and second, the intermediate is reduced by a tin hydride reagent in a radical hydrogenolysis reaction. The reaction lends itself to late stage deoxygenation due to its superb functional group tolerance.⁵ The reaction proceeds with primary and tertiary substrates, but works particularly well with secondary alcohols. Unfortunately, the tin reagents are toxic making tin-free alternatives attractive.⁶

Scheme 2.2. Use of Barton-McCombie Deoxygenation in Synthesis of Tricycloillicinone



Among alternatives to the Barton-McCombie deoxygenation, few nickel-catalyzed reactions have been reported. Recent nickel-catalyzed advances that have been reported primarily allow for the deoxygenation of phenols and the hydrogenolysis of aryl ethers (Scheme 2.3a).⁷ Rhodium-based catalysts have been more successful in the hydrogenolysis of alkyl C–O bonds.⁸ For instance rhodium based Wilkinson’s catalyst will promote hydrogenolysis of a benzylic ester (Scheme 2.3b).⁹ Unfortunately, with a commodity price of greater than \$1000 per

⁴ Pettus, T. R. R.; Inoue, M.; Chen, X.-T.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 6160.

⁵ (a) Zard, S. Z. *Angew. Chem. Int. Ed.* **1997**, *36*, 672. (b) Chatgililoglu, C.; Ferreri, C.; *Res. Chem. Intermed.* **1993**, *19*, 755. (c) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C. *J. Org. Chem.* **1993**, *58*, 6838. (d) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. C.; Joseph, C. *Synlett* **1991**, 435. (e) Barton, D. H. R.; Motherwell, W. B.; Stange, A. *Synthesis* **1981**, 743.

⁶ Kimbrough, R. D. *Environ. Health. Perspect.* **1976**, *14*, 51.

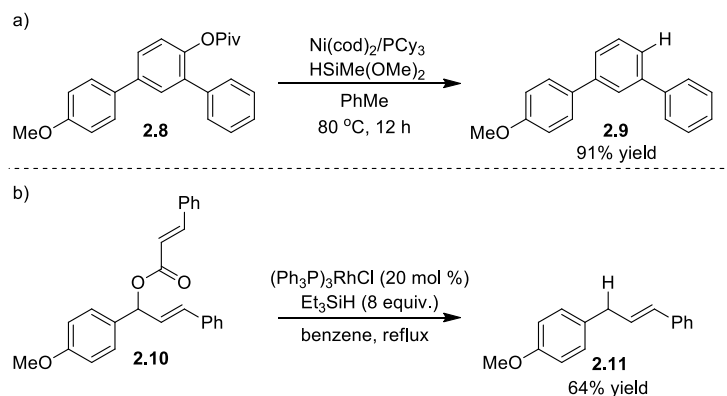
⁷ (a) Sasaki, K.; Sakai, M.; Sakakibara, Y.; Takagi, K. *Chem. Lett.* **1991**, *20*, 2017. (b) Sasaki, K.; Kubo, T.; Sakai, M.; Kuroda, Y. *Chem. Lett.*, **1997**, *26*, 617. (c) Sergeev, A. G.; Hartwig, J. F. *Science* **2011**, *332*, 439. (d) Sergeev, A. G.; Webb, J. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 20226. (e) Tobisu, M.; Yamakawa, K.; Shimasaki, T.; Chatani, N. *Chem. Commun.* **2011**, *47*, 2946. (f) Lipshutz, B. H.; Frieman, B. A.; Butler, T.; Kogan, V. *Angew. Chem. Int. Ed.* **2006**, *45*, 800.

⁸ (a) Maruyama, Y.; Sezaki, T.; Tekawa, M.; Sakamoto, T.; Shimizu, I.; Yamamoto, A. *J. Organomet. Chem.* **1994**, *473*, 257. (b) Kang, S.-K.; Kim, D.-Y.; Rho, H.-S.; Yoon, S.-H.; Ho, P.-S. *Synth. Commun.* **1996**, *26*, 1485.

⁹ Liu, H.-J.; Zhu, B.-Y. *Synth. Commun.* **1990**, *20*, 557.

ounce, rhodium is expensive.¹⁰ In contrast, nickel carries a commodity price of less than \$10 per pound.¹¹ A method of hydrogenolysis catalyzed by an earth-abundant nickel catalyst would be an attractive alternative to rhodium based methods.

Scheme 2.3. Transition Metal-Catalyzed Hydrogenolysis



We envisioned that a catalytic system comprised of Ni(acac)₂ and dppo may be a general catalyst for the hydrogenolysis of benzylic ethers. Analogous to the cross-coupling chemistry discussed in Chapter 1, we envisioned that this reaction would go through a two-electron mechanism. If so, in addition to providing an alternative to the Barton-McCombie reaction, the dppo ligated nickel catalyst may allow for the stereospecific installation of deuterium for labeling studies. In this chapter, I present my efforts to develop a general hydrogenolysis protocol as well as to identify the stereochemical outcome of hydrogenolysis reactions. Although we found that the Ni(acac)₂, dppo catalytic system is not a general method, these studies provided insight into the mechanism of both hydrogenolysis and elimination pathways, and insight into the mechanism of polar cross-coupling reactions in general.

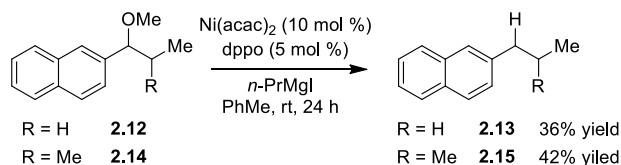
¹⁰ Kitco. <http://www.kitco.com/charts/historicalrhodium.html> (accessed 21 April, 2015).

¹¹ InvestmentMine. Nickel Prices and Nickel Price Charts. <http://www.infomine.com/investment/metal-prices/nickel/> (accessed 21 April, 2015).

2.2 Optimization of Hydrogenolysis Protocol

We set out to investigate if the hydrogenolysis reaction we discovered with benzhydryl ether **2.1** might represent a general method for the hydrogenolysis of alkyl ethers. In particular, we wanted to extend the methodology to benzylic ethers similar to the substrates discussed in Chapter 1. Unfortunately, subjecting benzylic substrates **2.12** and **2.14** to conditions that are identical to those that worked with benzhydryl substrates resulted in less than 50% yield of hydrogenolysis product (Scheme 2.4).

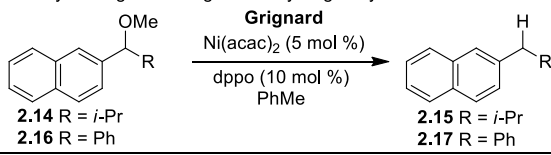
Scheme 2.4. Initial Hydrogenolysis Conditions Applied Simple Benzylic Substrates



Because we had proposed that the Grignard reagent was the hydride source,¹² we hypothesized that certain Grignard reagents may allow for more facile formation of a nickel hydride complex. We therefore studied the effect of various Grignard reagents on hydrogenolysis. Isopropylmagnesium bromide and 2-phenylethylmagnesium bromide were chosen because they were expected to undergo faster β -hydride elimination than *n*-alkyl Grignard reagents. Isopropylmagnesium bromide has six rather than two β -hydrogens, and β -hydride elimination from 2-phenylethylmagnesium bromide would give a stable styrene. As shown in Table 2.1, none of the organomagnesium bromide reagents were effective at performing hydrogenolysis on simple benzylic ethers (entries 1–7) although several were effective at performing hydrogenolysis on benzhydryl ethers (entries 8–11).¹³

¹² See Chapter 1, Scheme 1.7

¹³ With Lucas Erickson

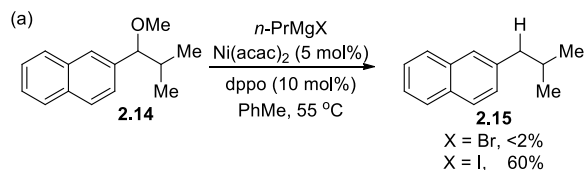
Table 2.1. Efficacy of Grignard Reagents in Hydrogenolysis Reaction


Entry	R	Grignard	Temperature	SM (%) ^a	Hydrogenolysis (%) ^a
1	<i>i</i> -Pr	<i>i</i> -PrMgBr	r.t.	95	0
2	<i>i</i> -Pr	Ph(CH ₂) ₂ Mg Br	r.t.	95	0
4	<i>i</i> -Pr	Ph(CH ₂) ₃ MgBr	60°C	89	0
5	<i>i</i> -Pr	cyclopentylMgBr	60°C	73	9
6	<i>i</i> -Pr	<i>n</i> -OctylMgBr	r.t.	76	0
7	<i>i</i> -Pr	EtMgBr	r.t.	96	0

8	Ph	Ph(CH ₂) ₂ MgBr	r.t.	97	0
9	Ph	Ph(CH ₂) ₃ MgBr	r.t.	7	80
10	Ph	cyclopentylMgBr	r.t.	0	75
11	Ph	<i>n</i> -OctylMgBr	r.t.	0	79

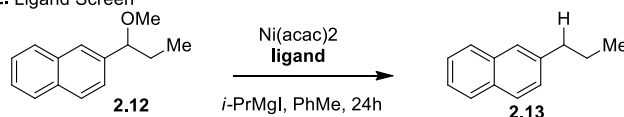
^aDetermined by ¹H NMR against an internal standard, phenyltrimethylsilane (PhTMS)

We wanted to see if the identity of the halogen on the Grignard reagent had any effect on reactivity. Interestingly, *i*-PrMgI was far better at promoting hydrogenolysis from ether **2.14** than *i*-PrMgBr (Scheme 2.5). Therefore, *i*-PrMgI was used in subsequent studies. Unfortunately, with substrate **2.14**, high yield was only accomplished at elevated temperatures.¹⁴

Scheme 2.5. Comparison of Bromine and Iodine Counter Ions in the Hydrogenolysis Reaction

In an attempt to achieve high yields at room temperature, we performed a ligand screen. Bidentate ligands do not efficiently promote hydrogenolysis (Table 2.2, entries 1–6). Bisphosphine ligands with long carbon-chain linkers better promote the hydrogenolysis reaction (entries 7–9). Due to the high degree of freedom of these long linkers, these ligands likely acts as monodentate ligands. Monophosphine ligands were therefore studied and shown to give higher yields of hydrogenolysis product (entries 10–12). Among monodentate ligands, PPh₃ gives the highest yield (33%, entry 12). PPh₃ was therefore used in subsequent studies.

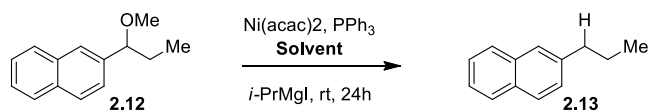
¹⁴ Reactions studying halogen effect run by Lucas Erickson

Table 2.2. Ligand Screen

Entry	ligand	SM (%) ^a	Hydrogenolysis (%) ^a	Elimination (%) ^a
1	DPEPhos	0	10	16
2	racBINAP	54	7	0
3	Xantphos	8	11	13
4	dppf	8	9	6
5	dppe	78	4	7
6	dppp	50	5	32
7	dpppent	0	25	56
8	dpphex	0	25	64
9	dppo	0	24	60
10	Ph ₂ PPr	5	25	52
11	Ph ₂ P <i>i</i> -Pr	0	29	59
12	PPh₃	0	33	44

^aDetermined by ¹H NMR against an internal standard, PhTMS.

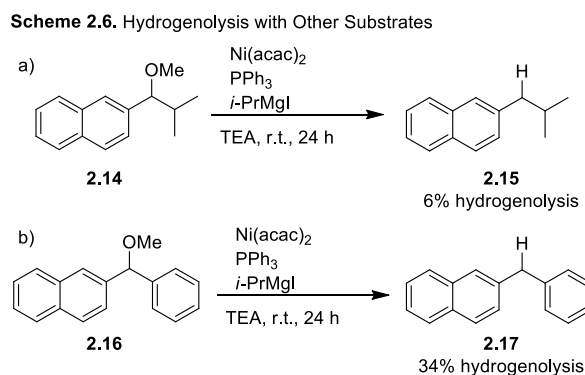
We were interested in seeing what solvent effects might be at play in this reaction. A study of solvent effects is shown in Table 2.3. The reaction does not proceed in the presence of THF and DCM (entries 1–3). Hydrocarbon solvents, toluene and *n*-hexane, both provide hydrogenolysis product in 33% yield (entries 4–5). The use of diethyl ether improved yield to 42% (entry 6). The best result, 51% yield, was achieved with triethylamine (TEA) (entry 7). A small ligand screen run in TEA showed that regardless of solvent, hydrogenolysis is most efficient when PPh₃ is used as ligand (entries 7–10).

Table 2.3. Solvent Effects

Entry	Solvent	ligand	Hydrogenolysis (%) ^a	Elimination (%) ^a	SM (%) ^a
1	THF	PPh ₃	3	1	86
2	1:1 THF: Tol	PPh ₃	3	1	91
3	DCM	PPh ₃	0	0	88
4	Tol	PPh ₃	33	44	0
5	<i>n</i> -hexane	PPh ₃	33	40	0
6	Et ₂ O	PPh ₃	42	43	4
7	TEA	PPh₃	51	27	18
8	TEA	Ph ₂ PPr	29	59	0
9	TEA	dpphexane	25	64	0
10	TEA	dppo	24	60	0

^aDetermined by ¹H NMR against an internal standard, PhTMS.

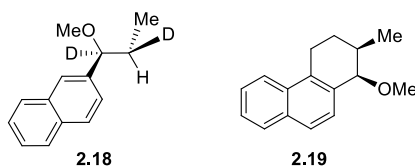
We wanted to see if we were converging on a general hydrogenolysis method that could be applied to compounds other than ether **2.12**. To test for generality, we ran the optimized reaction against benzylic substrate **2.14** and benzhydryl substrate **2.16** (Scheme 2.6). Unfortunately, the optimized conditions for hydrogenolysis of **2.12** proved to be suboptimal for the other two ethers. Because we did not appear to be converging on a general method, we shifted our focus to mechanistic studies.



2.3 Mechanistic Studies

From the inception of this project we sought to develop a stereospecific method for deuterium incorporation. To test for stereospecificity, we needed to design molecules that would allow for the differentiation of deuterated diastereomers. Ethers **2.18** and **2.19** were selected because diastereomers of the products of hydrogenolysis were expected to give discernable differences in *J*-coupling as defined by the Karplus equation.¹⁵ Additionally, experiments run with these compounds provided evidence for a mechanism of oxidative addition with inversion at the benzylic center.

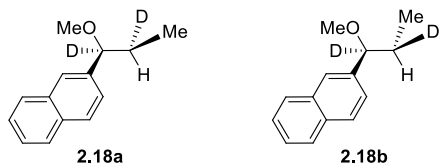
Figure 2.1. Mechanistic Probes



¹⁵ Karplus, M. *J. Chem. Phys.* **1959**, 30, 11

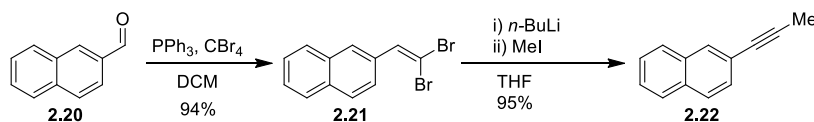
2.3.1 Stereochemical and Mechanistic Studies with Compound 2.18

Figure 2.2. Diastereomers of Compound 2.18



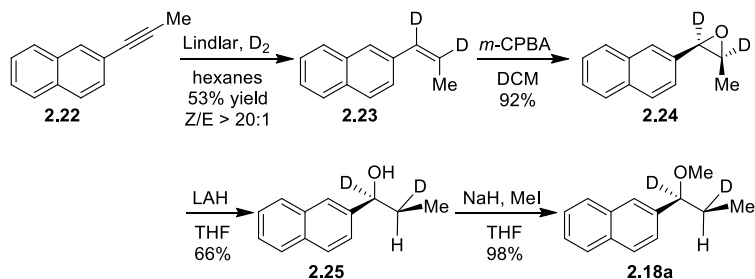
Studies on diastereomeric compounds **2.18a** and **2.18b** (Figure 2.2) provided insight into both the mechanism of oxidative addition and the stereochemical course of hydrogenolysis. These compounds were prepared as shown in Schemes 2.7–2.9. Synthesis of both **2.18a** and **2.18b** went through common alkynyl intermediate **2.22** which was prepared by a Corey-Fuchs protocol (Scheme 2.7).¹⁶ Trapping the acetylide with MeI allowed for the facile synthesis of the methylated alkyne.

Scheme 2.7. Preparation of Alkynyl Naphthalene



Ether **2.18a** was prepared from acetylene **2.22** as shown in Scheme 2.8. *Syn*-deuteration was achieved by treatment with Lindlar catalyst under a D₂ atmosphere. *m*-CPBA epoxidation to form epoxide **2.24** followed by ring-opening with LAH afforded alcohol **2.25**.¹⁷ Finally, *o*-methylation of **2.25** in the presence of NaH and MeI yielded the desired mechanistic probe **2.18a**.

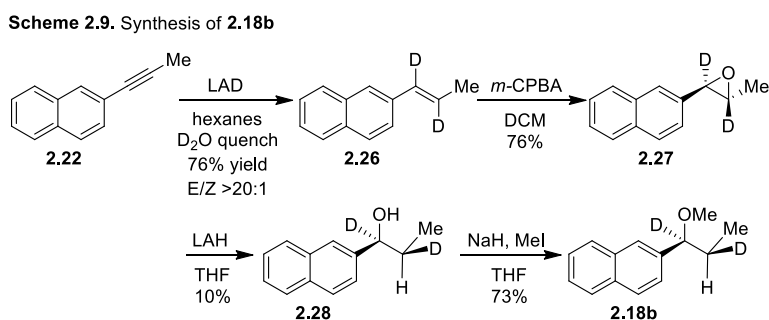
Scheme 2.8. Synthesis of 2.18a



¹⁶ Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 13, 3769.

¹⁷ Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, 135, 3307.

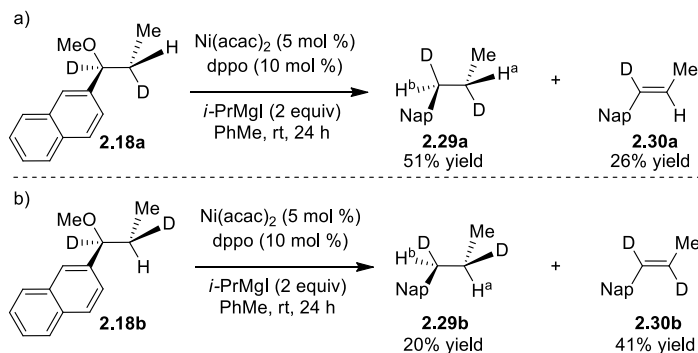
Compound **2.18b** was prepared by a similar procedure, differing primarily in the deuteration of the alkyne (Scheme 2.9). Treatment of **2.22** with lithium aluminum deuteride afforded the desired *trans* olefin in 76% yield with a greater than 20:1 E/Z ratio.¹⁸ To achieve high deuterium incorporation at the benzylic position, it was important that this step was quenched with D₂O from a freshly opened ampule. The remainder of the synthesis of **2.18b** is analogous to the procedures used for **2.18a**. Oddly, epoxide opening with LAH is far less effective on *trans*-epoxide **2.27** than with *cis*-epoxide **2.24**. Ring opening of epoxide **2.27** suffers from attack at the benzylic position resulting in formation of the homobenzylic alcohol as the major product.



With deuterated compounds **2.18a** and **2.18b** in hand, we were ready to perform studies on the stereochemical outcome of the hydrogenolysis reaction. The outcome of experiments run with **2.18a** and **2.18b** in the presence of Ni(acac)₂ and dppo are shown in Scheme 2.10. A discussion of the mechanistic implications of these results follows. In the presence of Ni(acac)₂ and dppo, diastereomers of **2.18** undergo both hydrogenolysis and elimination processes. The mechanistic implications of these processes will each be discussed in turn.

¹⁸ Magoon, E. F.; Slaugh, L. H. *Tetrahedron*, **1967**, 23, 4509.

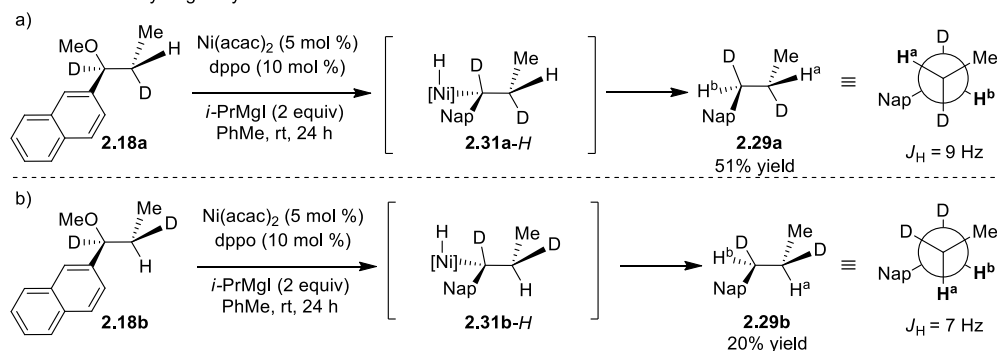
Scheme 2.10. Results with Ethers **2.18a** and **2.18b**



Mechanistic insights gained from hydrogenolysis will be discussed first. An explanation of the results of hydrogenolysis using both diastereomers of ether **2.18** is provided in Scheme 2.11. Oxidative addition with inversion into diastereomer **2.18a** followed by reductive elimination from **2.31a-H** was expected to result in deuterated hydrocarbon **2.29a** (Scheme 2.11a). In its most stable *s*-trans conformation, **2.29a** bears hydrogen atoms, H^a and H^b, which are anti to each other and should therefore exhibit a large $J_{H^a-H^b}$ coupling (see Newman projection). If diastereomer **2.18b** were subject to the same reaction, product **2.29b** would exhibit hydrogens that, in the *s*-trans conformation, exhibit H^a and H^b in a gauche orientation (Scheme 2.11b). Diastereomer **2.29b** would therefore be expected to exhibit a smaller $J_{H^a-H^b}$ coupling value than **2.29a**. A *J*-coupling of 8 Hz or greater is indicative of protons on adjacent carbons that are predominantly in a trans orientation relative to one another, and a *J*-coupling value of 7 Hz or less is typical of a gauche orientation.¹⁹ As expected **2.29a** gave a *J*-coupling value greater than 8 Hz and **2.29b** gave a *J*-coupling value of 7 Hz. These results show that the hydrogenolysis process delivers a hydride stereospecifically with inversion at the benzylic center.

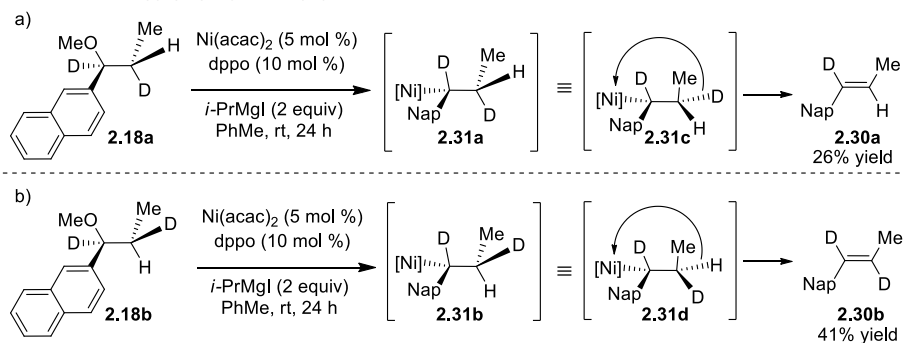
¹⁹ (a) Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds*, 7th ed; John Wiley and Sons: Hoboken, NJ, 2005; 171–172. (b) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (c) Whitesides, G. M.; Sevenair, J. P.; Goetz, R. W. *J. Am. Chem. Soc.* 1967, *89*, 1135. For similar experiments, see: (d) Ridgway, B. H.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 458. (e) Matos, K.; Soderquist, J. A. *J. Org. Chem.* **1998**, *63*, 461. (f) Taylor, B. L. H.; Jarvo, E. R. *J. Org. Chem.* **2011**, *76*, 7573.

Scheme 2.11. Hydrogenolysis with Inversion



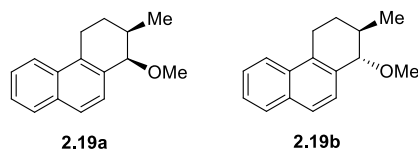
Under the conditions used in this experiment, the product of β -hydride elimination was also a major product (vide supra, Scheme 2.10). Interestingly, both diastereomers underwent elimination to give very different yields. This difference in yield can be explained by a kinetic isotope effect that is consistent with a mechanism of oxidative addition with inversion followed by β -hydride elimination. When diastereomer **2.18a** undergoes oxidative addition with inversion, intermediate **2.31a** forms (Scheme 2.12a). To avoid a steric interaction between the methyl and naphthyl groups, reductive elimination will proceed from rotamer **2.31c**. Because β -deuteride elimination proceeds from this rotamer, a slow rate is expected and observed. In contrast, when diastereomer **2.18b** is subject to eliminating conditions, oxidative addition leads to intermediate **2.31b** (Scheme 2.12b). Sterics are minimized in rotamer **2.31d** from which β -hydride elimination can occur. The kinetic isotope effect is seen as β -deuteride elimination from **2.31c** proceeds slower than β -hydride elimination from **2.31d**. These results provide evidence that elimination and hydrogenolysis mechanisms begin with a polar $S_{\text{N}}2$ -like mechanism of oxidative addition which proceeds with inversion at the reactive center.

Scheme 2.12. Mechanism of Elimination



2.3.2 Stereochemical and Mechanistic Studies with Compound 2.19

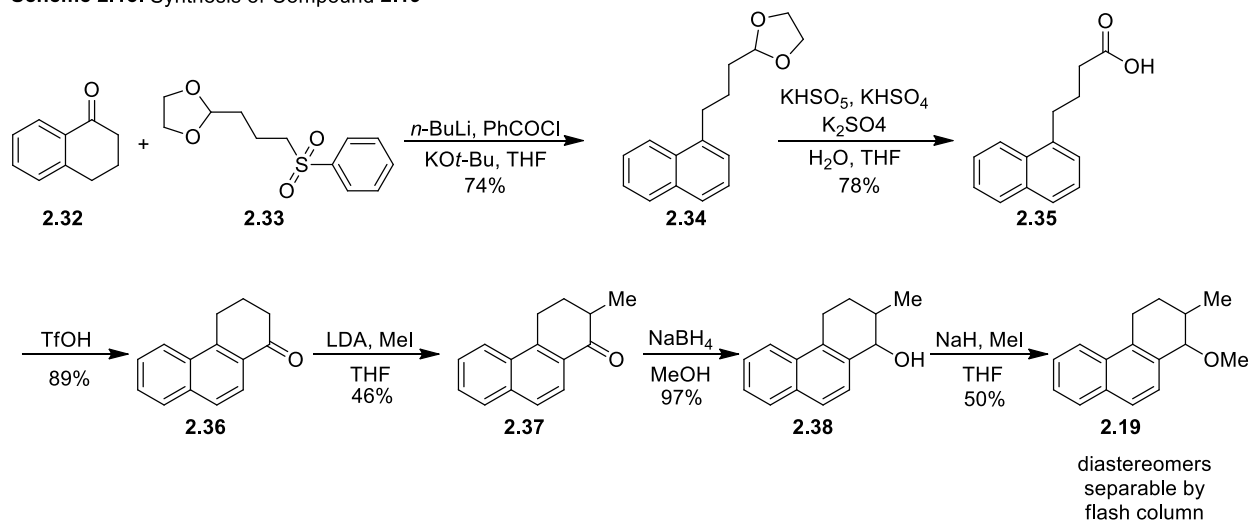
Figure 2.3. Diastereomers of 2.19



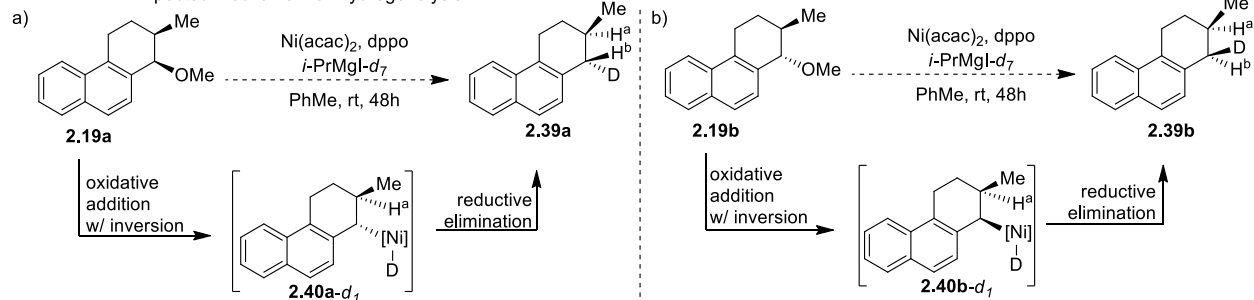
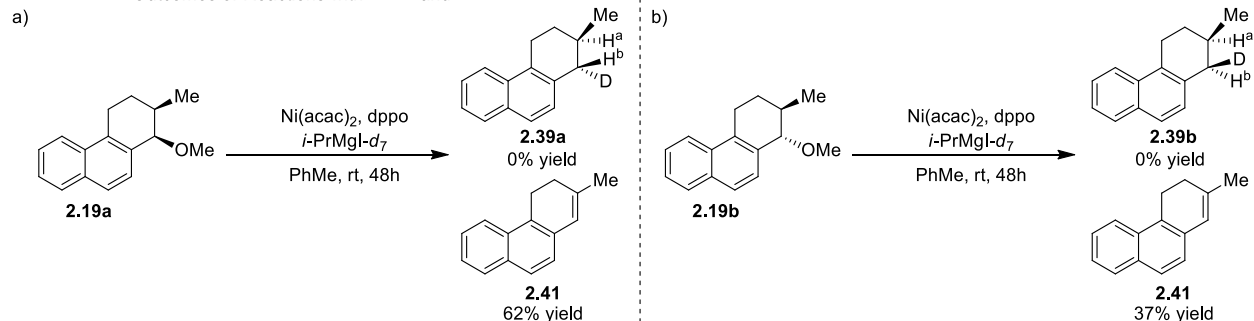
Diastereomers of compound **2.19** (Figure 2.3) were also designed to probe the stereochemical outcome of hydrogenolysis and the mechanism of β -hydride elimination. Both diastereomers of compound **2.19** were obtained via the synthesis outlined in Scheme 2.13. Addition of deprotonated sulfone **2.33** into ketone **2.32** resulted in dioxolane **2.34**. Oxidizing conditions revealed carboxylic acid **2.35**. A Friedel-Crafts type cyclization gave tetralone **2.36**.²⁰ Reaction of the enolate of **2.36** with methyl iodide resulted in methylated ketone **2.37** which could be reduced to alcohol **2.38**. Finally, *o*-methylation of alcohol **2.38** completed the synthesis of the desired mechanistic probe **2.19** as a mixture of diastereomers which were readily separated by silica gel flash column chromatography.

²⁰ Orita, A.; Yaruva, J.; *Angew. Chem. Int. Ed.* **1999**, 38, 2267.

Scheme 2.13. Synthesis of Compound 2.19



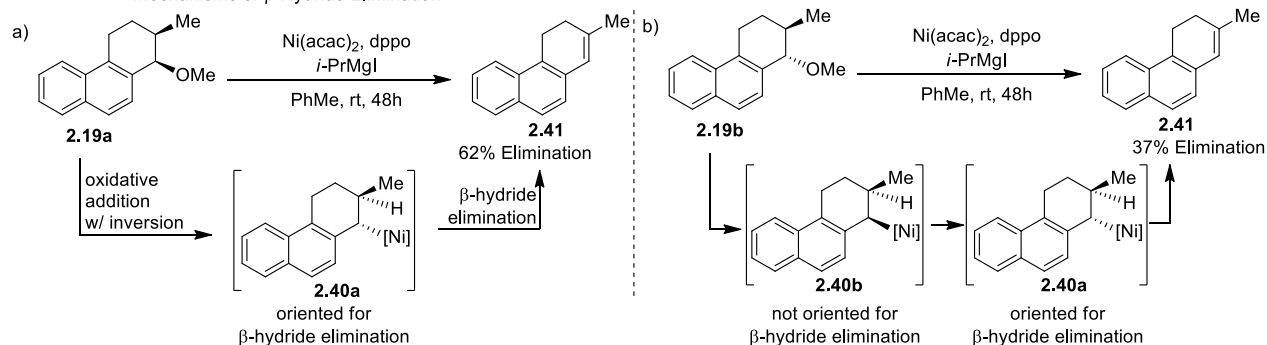
Compound **2.19** was chosen to study the hydrogenolysis stereochemical course because hydrogenolysis of the diastereomers of **2.19** were expected to yield diastereomeric products **2.39a** or **2.39b**, which should exhibit distinct differences in the magnitude $J_{\text{H}^{\text{a}}-\text{H}^{\text{b}}}$ -couplings (Scheme 2.14). Starting from **2.19a**, oxidative addition with inversion would give intermediate **2.40a-d₁**, which could undergo reductive elimination to give hydrogenolysis product **2.39a** (Scheme 2.14a). In its most stable conformation, compound **2.39a** would present hydrogen H^{a} anti to hydrogen H^{b} , and would be expected to give a large value for the $J_{\text{H}^{\text{a}}-\text{H}^{\text{b}}}$ coupling. Hydrogenolysis of **2.19b** should give product **2.39b** in which H^{a} is gauche to H^{b} (Scheme 2.14b). This confirmation would be expected to exhibit a small value for the $J_{\text{H}^{\text{a}}-\text{H}^{\text{b}}}$ coupling. Unexpectedly, no hydrogenolysis product was observed with either of these substrates. Rather, the major observed product was that of β -hydride elimination (Scheme 2.15).

Scheme 2.14. Expected Mechanism of Hydrogenolysis**Scheme 2.15.** Outcomes of Reactions with **2.19a** and **2.19b**

Although the stereochemical course of hydrogenolysis could not be determined in the above studies, experiments using the diastereomers of **2.19** provided valuable insight into the mechanisms of oxidative addition and subsequent elimination processes. The conformational rigidity of **2.19** would be expected to define β -hydride elimination reactivity. Oxidative addition with inversion into diastereomer **2.19a** would result in a nickel complex (**2.40a**) in which nickel is in a syn orientation to the only adjacent hydride (Scheme 2.16a). In this orientation, complex **2.40a** should readily undergo β -hydride elimination to form elimination product **2.41**. Indeed, elimination is observed at 62% yield. In contrast, if diastereomer **2.19b** is used, oxidative addition with inversion would result in complex **2.40b** in which nickel is anti to the only adjacent hydride (Scheme 2.16b). β -hydride elimination should not be possible from complex **2.40b**. When we ran experiments with **2.19b** we were surprised to observe 37% yield of the elimination product. This result can be explained, however, if after oxidative addition with inversion to form complex **2.40b**, a second nickel complex attacks **2.40b**, again with inversion, resulting in complex **2.40a**. Complex **2.40a** can then undergo β -hydride elimination. In support of this

bimetallic mechanism, we have shown that there is an inverse correlation between nickel catalyst concentration and cross-coupled product ee.²¹ These results are consistent with an overall oxidative addition with inversion, followed by β -hydride elimination. Taken together, the results of all mechanistic studies discussed in this report provide evidence that cross-coupling, hydrogenolysis, and elimination mechanisms all include a fundamental mechanistic step of S_N2 -like oxidative addition with inversion at the benzylic carbon.

Scheme 2.16. Mechanisms of β -Hydride Elimination



2.4 Conclusion

In conclusion, we sought to identify a general method for the hydrogenolysis of benzylic and benzhydryl ethers. With dppo as ligand, the reaction works well with benzhydryl ethers, but provides marginal conversion with simple benzylic ethers. Attempts to optimize the hydrogenolysis reaction with ether **2.12** showed that in the presence of PPh_3 and with triethylamine as solvent, compound **2.12** undergoes hydrogenolysis at 51% yield. Unfortunately, these optimized conditions are not applicable to a broad range of substrates.

Studies were conducted to better understand the polar mechanism of these reactions. Deuterium labeling studies showed that the nickel-catalyzed hydrogenolysis reaction delivers a hydride in a stereospecific manner with inversion at the benzylic center. Additionally, results of

²¹ 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.

elimination reactions are consistent with a mechanism of oxidative addition with inversion followed by β -hydride elimination.

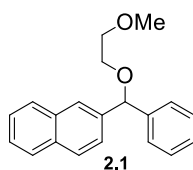
2.5 Experimental Section

2.5.1 General Procedures

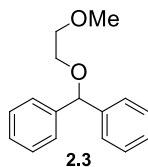
All reactions were carried out under an atmosphere of N₂ using glassware that was either oven- or flame-dried prior to use. Methanol (MeOH) was purchased commercially and used without further purification. *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF), and toluene (PhMe) were degassed with argon 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 H₂O. All other solvents utilized were purchased “anhydrous” commercially, or purified as described (vide infra). ¹H NMR spectra were recorded on Bruker GN-500 (500 MHz ¹H, 125.7 MHz ¹³C), CRYO-500 (500 MHz ¹H, 125.7 MHz ¹³C) or DRX-400 (400 MHz ¹H, 100 MHz ¹³C) 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), triplet (t), quartet (q), quintet (quin), sextet, septet (sep), multiplet (m), doublet of doublets (dd), doublet of triplets (dt), apparent doublet (ap d), apparent triplet (ap t), apparent septet (ap sep), apparent quintet (ap q), apparent doublet of doublets (ap dd), apparent quintet of doublets, (ap quin)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard (CDCl₃, δ 77.16 ppm). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F₂₅₄ pre-coated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp. Flash chromatography was performed using Silica Gel 60Å (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were obtained on a Nicolet™ iS™5 FT-IR spectrometer system

and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Optical rotations were measured with a Rudolph Research Analytical Autopol IV Automatic Polarimeter or a Jasco P-1010 digital polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (AD-H; 100 bar, 50 °C, 254 nm).

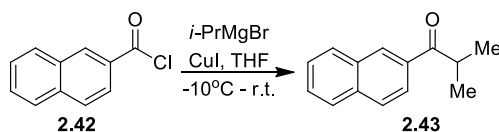
2.5.2 Preparation of Hydrogenolysis Substrates



2-((2-Methoxyethoxy)(phenyl)methyl)naphthalene (2.1) was prepared as described by Jarvo.²²



((2-Methoxyethoxy)methylene)dibenzene (2.3) was prepared as described by Jarvo.²³

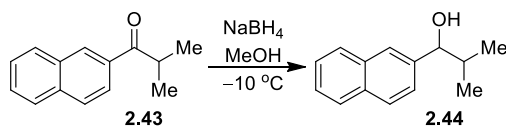


2-Methyl-1-(naphthalen-2-yl)propan-1-one (2.43): In a glove box, a flame-dried round bottom flask was charged with CuI (0.141 g, 0.711 mmol, 0.551 equiv.), then removed and 2-naphthoyl chloride **2.42** (2.46 g, 12.9 mmol, 1.00 equiv.) was added as a solution in THF (25 mL). The reaction mixture was cooled to -10°C and isopropylmagnesium bromide (1.52 M in THF, 8.50

²² Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

²³ Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. *Org. Lett.* **2012**, *14*, 4293.

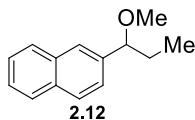
mL, 12.9 mmol, 1.00 equiv.) was added dropwise. The mixture was warmed to room temperature and stirred for 1 h. The crude mixture was concentrated in vacuo then quenched with HCl (20 mL, 1M) and extracted with Et₂O (3 x 20 mL). The crude mixture was then washed with brine (20 mL) and dried over MgSO₄. Purification by flash column chromatography (5% EtOAc in hexanes) yielded **2.43** as a yellow oil (2.23 g, 11.2 mmol, 87% yield). Spectral data are consistent with literature values.²⁴



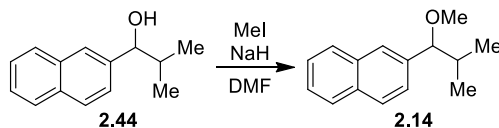
2-Methyl-1-(naphthalen-2-yl)propan-1-ol (2.44): A round bottom flask was charged with sodium borohydride (0.303 g, 8.0 mmol) and cooled to $-10\text{ }^\circ\text{C}$. **2.43** (0.793 g, 4.0 mmol) and methanol (80 mL) were added to the reaction flask, and the reaction mixture was stirred for 1 h. The reaction was quenched with NaHCO₃ (20 mL), extracted with EtOAc (3 x 30 mL), washed with brine (40 mL), and dried over Na₂SO₄. The crude mixture was then concentrated in vacuo and purified by flash column chromatography (20% Et₂O in hexanes) to afford the title compound as a yellow oil (0.375 g, 1.87 mmol, 47% yield). Analytical data are consistent with literature values:²⁵ **TLC** $R_f = 0.3$ (20% Et₂O in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (m, 3H), 7.74 (s, 1H), 7.46 (m, 3H), 4.52 (d, $J = 6.8$ Hz, 1H), 2.06 (sx, $J = 6.6$ Hz, 1H), 1.96 (s, 1H), 1.03 (d, $J = 6.5$ Hz, 3H), 0.83 (d, $J = 6.7$ Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 141.4, 133.5, 133.3, 128.3, 128.2, 128.0, 126.4, 126.1, 125.7, 125.0, 80.5, 35.5, 19.5, 18.6.

²⁴ Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 4852.

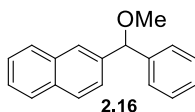
²⁵ Kulasegaram, S.; Kulawiec, R. J. *J. Org. Chem.* **1997**, *62*, 6547.



2-(1-Methoxypropyl)naphthalene (2.12) was prepared as described by Jarvo.²⁶



2-(1-Methoxy-2-methylpropyl)naphthalene (2.14): A round bottom flask was charged with NaH (348 mg, 14.5 mmol, 1.8 equiv.). Alcohol **2.44** (1.61 g, 8.05 mmol, 1.00 equiv.) was then added as a solution in THF (25 mL), and the reaction mixture was allowed to stir for 1 h. MeI (0.85 mL, 14 mmol, 1.7 equiv.) was added and the reaction mixture was allowed to stir overnight. The reaction was quenched with saturated aqueous NH_4Cl , extracted with EtOAc (3 x 20 mL), washed with brine, and dried over MgSO_4 . The crude mixture was then concentrated in vacuo. Purification of the crude mixture by silica gel flash column chromatography (2% Et_2O in pentanes) yielded **2.14** as a clear, colorless oil (1.51 g, 7.06 mmol, 88% yield): **TLC** R_f = 0.6 (2% Et_2O in pentanes); **^1H NMR** (500 MHz, CDCl_3) δ 7.82 (d, J = 6.4 Hz, 3H), 7.67 (s, 1H), 7.48–7.40 (m, 2H), 7.41 (d, J = 8.1 Hz, 1H), 3.89 (d, J = 7.3 Hz, 1H), 3.22 (s, 3H), 2.02 (sextet, J = 6.8 Hz, 1H), 1.05 (d, J = 6.8 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H); **^{13}C NMR** δ (125 MHz, CDCl_3) δ 138.8, 133.21, 133.18, 128.04, 127.96, 127.8, 126.9, 126.1, 125.8, 125.3, 90.1, 57.2, 34.8, 19.23, 19.20; **IR** (neat) 3055, 2957, 2927, 2919, 1468, 1383, 1135, 1089, 815, 773 cm^{-1} ; **HRMS** (TOF MS Cl^+) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{ONH}_4$ [$\text{M} + \text{NH}_4$] $^+$ 232.1701, found 232.1704.

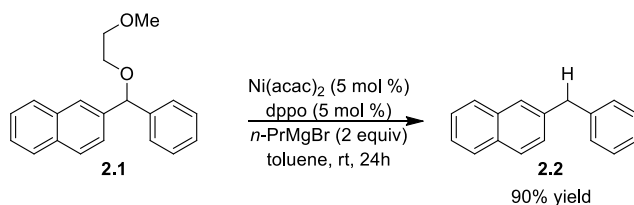


2-(Methoxy(phenyl)methyl)naphthalene (2.16) was prepared as described by Jarvo.²²

²⁶ Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2011**, 133, 389.

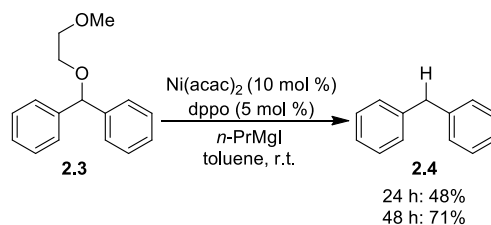
2.5.3 Hydrogenolysis Reactions

Hydrogenolysis Representative Procedure A

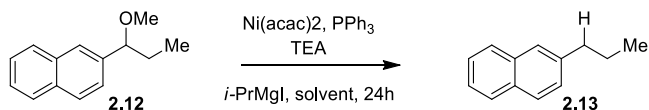


2-Benzyl-naphthalene (2.2): In a glove box, a flame-dried 7 mL vial was charged with 1,8-bis(diphenylphosphino)octane (dppo) (4.8 mg, 0.010 mmol, 0.10 equiv.). Ni (acac)₂ (1.3 mg, 0.0050 mmol, 0.050 equiv.) was added as a stock solution in toluene (1 mL, 5.06 x 10⁻³ M). The vial was capped and removed from the box but kept under a nitrogen atmosphere. Ether **2.1** (28 mg, 0.10 mmol, 1.0 equiv.) was also added from a stock solution in toluene (0.5 mL, 0.191 M). *n*-Propylmagnesium bromide (0.090 mL, 0.20 mmol, 2.2 M, 2.2 equiv.) was added, and the reaction mixture was allowed to stir for 24 h. The reaction was quenched with MeOH and run through a silica plug (100% Et₂O as eluent). Analysis by ¹H NMR with an internal standard (1,2-dimethoxybenzene) revealed that the reaction proceeded to give 19 mg of hydrogenolysis product (0.087 mmol, 87% yield). Purification by silica gel flash column chromatography (20% DCM in hexanes) yielded a pure sample. Analytical data is consistent with literature values:²⁷ **TLC** R_f = 0.7 (20% DCM in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.77 (m, 3H), 7.64 (s, 1H), 7.44 (quint, *J* = 7.5 Hz, 2H), 7.30 (quint, *J* = 7.3 Hz, 3H), 7.23 (m, 3H), 4.15 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 141.3, 138.9, 133.9, 132.4, 129.4, 128.8, 128.4, 127.97, 127.95, 127.8, 127.4, 126.5, 126.3, 125.7, 42.4.

²⁷ Cho, C.-H.; Sun, M.; Seo, Y.-S.; Kim, C.-B.; Park, K. *J. Org. Chem.* **2005**, *70*, 1482.



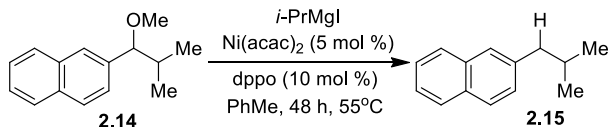
Diphenylmethane (2.4) was prepared according to Representative Procedure A described above using the following amounts of reagents: **2.3** (23 μL , 0.010 mmol, 1 equiv.), Ni(acac)_2 (1.3 mg, 0.0049 mmol, 0.050 equiv.), dppo (4.7 mg, 0.010 mmol, 0.10 equiv.), $n\text{-PrMgI}$ (0.079 mL, 0.20 mmol, 2.0 equiv.), and toluene (1.5 mL). Analysis by $^1\text{H NMR}$ with an internal standard (PhTMS) revealed 71% conversion to the product of hydrogenolysis. Analytical data are consistent with literature values.²⁸



2-Propylnaphthalene (2.13) was prepared according to Representative Procedure A using the following amounts of reagents: ether **2.12** (40 mg, 0.20 mmol, 1.0 equiv.), Ni(acac)_2 (2.6 mg, 0.010 mmol, 0.050 equiv.), PPh_3 (5.3 mg, 0.020 mmol, 0.10 equiv.), $i\text{-PrMgI}$ (0.26 mL, 0.40 mmol, 1.5 M, 2.0 equiv.), and TEA (1.5 mL). Analysis by $^1\text{H NMR}$ with an internal standard (PhTMS) revealed 51% conversion to the product of hydrogenolysis. Analytical data was consistent with literature values.²⁹

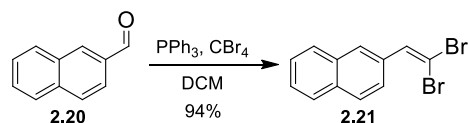
²⁸ Peña-López, M.; Ayán-Varela, M.; Sarandeses, L. A.; Sestelo, J. P. *Chem. Eur. J.* **2010**, *16*, 9905.

²⁹ Guan, B.-T.; Xiang, S.-K.; Wang, B.-Q.; Sun, Z.-P.; Wang, Y.; Zhao, K.-Q.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 3268.



2-Isobutylnaphthalene (2.15) was prepared according to Representative Procedure A outlined above with the follow reagents: **2.14** (43 mg, 0.20 mmol, 1.00 equiv.), Ni(acac)₂ (2.6 mg, 0.010 mmol, 0.050 equiv.), dppo (9.7 mg, 0.020 mmol, 0.10 equiv.), *i*-PrMgI (1.43 M in ether, 0.28 mL, 0.40 mmol, 2.0 equiv.) and toluene (1.5 mL). The crude mixture was purified by silica gel flash column chromatography (20% DCM in hexanes) to give **2.15** as a clear colorless oil (27 mg, 0.15 mmol, 71% yield). Spectral data are consistent with literature values:³⁰ **TLC** *R_f* = 0.9 (20% DCM in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.79 (t, *J* = 8.7 Hz, 2H), 7.59 (s, 1H), 7.49–7.38 (m, 2H), 7.32 (dd, *J* = 8.4, 1.5 Hz, 1H), 2.65 (d, *J* = 7.3 Hz, 2H), 2.00 (septet, *J* = 6.7 Hz, 1H), 0.97 (d, *J* = 6.6 Hz, 6H); **¹³C NMR** (125 MHz, CDCl₃) δ 139.6, 133.9, 132.3, 128.3, 127.93, 127.90, 127.8, 127.5, 126.1, 125.3, 46.0, 30.5, 22.8.

2.5.4 Preparation of Mechanistic Probes

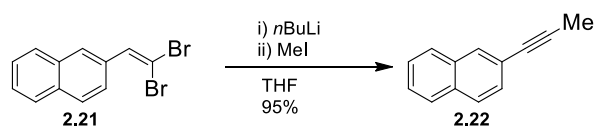


2-(2,2-Dibromovinyl)naphthalene (2.21) was prepared according to a modified procedure as described by Rao.³¹ A flame dried round bottom flask was charged with triphenylphosphine (13.4 g, 51.2 mmol, 4.00 equiv.) and put under a nitrogen atmosphere. Dichloromethane (DCM, 46 mL) was added, and the reaction mixture was cooled to 0 °C. Tetrabromomethane (8.5g, 26 mmol, 2.0 equiv.) was then added as a solution in DCM (12 mL). The reaction mixture was allowed to stir for 3 min, and 2-naphthaldehyde (**2.20**) (2.00 g, 12.8 mmol, 1.00 equiv.) was

³⁰ Limmert, M. E.; Roy, A. H.; Hartwig, J. F. *J. Org. Chem.* **2005**, *70*, 9364

³¹ Rao, M. L. N.; Jadhav, D. N.; Dasgupta, P. *Org. Lett.* **2010**, *12*, 2048.

added as a solution in DCM (11 mL). The reaction mixture was stirred for 10 additional min then run through a silica plug. Purification by silica gel flash column chromatography (5–50% EtOAc in hexanes) yielded the title compound as a white solid (3.47g, 11.1 mmol, 94% yield). Spectral data are consistent with literature values:³² **m.p.** = 103–105 °C; **TLC R_f** = 0.8 (10% EtOAc in hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.84–7.79 (m, 3H), 7.64–7.62 (m, 2H), 7.52–7.46 (m, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 137.1, 133.12, 133.11, 132.9, 128.4, 128.3, 128.1, 127.8, 126.9, 126.6, 125.8, 90.0; **IR** (neat) 3011, 1595, 1506, 1272, 834 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₁₂H₈Br₂ [M]⁺ 309.8993, found 309.8995.

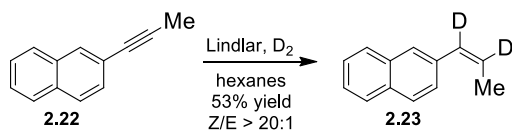


2-(Prop-1-yn-1-yl)naphthalene (2.22) was prepared by Corey-Fuchs protocol.³³ A flame dried round bottom flask was charged with dibromide **2.21** (2.90 g, 9.15 mmol, 1.00 equiv.) and put under a nitrogen atmosphere. THF was added, and the reaction vessel was cooled to –78 °C. *n*-BuLi (12.3 mL, 18.3 mmol, 1.49 M in Et₂O, 2.00 equiv.) was added, and the reaction mixture was stirred for 1 hour at –78 °C. The reaction mixture was heated to room temperature, and the reaction was allowed to stir for an additional 1 h. Methyl iodide (1.25 mL, 20.1 mmol, 2.20 equiv.) was added dropwise followed by an excess of MeOH, also added dropwise. An excess of H₂O was added, and the aqueous layer was separated from the organic layer. The aqueous layer was extracted with Et₂O (3 x 30 mL). The combined organics layers were dried with MgSO₄, filtered, and purified by silica gel flash column chromatography (100% hexanes) to yield the title compound as a reluctant solid (1.39 g, 8.57 mmol, 94% yield): **m.p.** = 28–29 °C; **TLC R_f** = 0.4 (100% hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.80–7.73 (m, 3H); 7.46–7.43 (m,

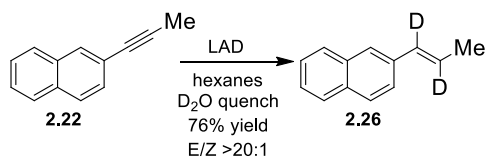
³² Rao, M. L. N.; Jadhav, D. N.; Dasgupta, P. *Org. Lett.* **2010**, *12*, 2048.

³³ Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769.

3H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 133.2, 132.6, 131.1, 128.8, 128.0, 127.8, 127.7, 126.5, 126.4, 121.5, 86.4, 80.2, 4.6; IR (neat) 3056, 2914, 2235, 1596, 1500 cm^{-1} ; HRMS (TOF MS CI^+) m/z calcd for $\text{C}_{13}\text{H}_{10}$ $[\text{M}]^+$ 184.1126, found 184.1122.



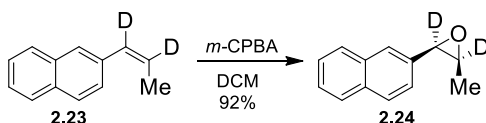
d_2 -(Z)-2-(Prop-1-en-1-yl)naphthalene (2.23): In a glove box, a flame-dried 7 mL vial was loaded with acetylene **2.22** (50 mg, 0.30 mmol, 1.0 equiv.) and Lindlar catalyst (5% pd, 3.0 mg, 0.0010 mmol Pd, 0.0050 equiv.). The vial was capped and connected to a Schlenk line. The reaction vessel was evacuated and back filled with D_2 gas (x 5). The reaction mixture was stirred under a deuterium atmosphere for 7 h at which point the reaction vessel was again evacuated and back filled with nitrogen (x 6). The reaction mixture was filtered through Celite to yield the title compound as a clear colorless oil (163 mg, 0.959 mmol, 53% yield): TLC R_f = 0.6 (100% hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.81–7.78 (m, 3H), 7.73 (s, 1H), 7.47–7.41 (m, 3H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.2, 133.5, 132.2, 129.6 (t, J = 23.6 Hz, 1C), 128.0, 127.71, 127.69, 127.59, 127.4, 126.9 (t, J = 23.6 Hz, 1C), 126.1, 125.8, 14.8; IR (neat) 3053, 2938, 2243, 1503, 1372 cm^{-1} ; HRMS (TOF MS CI^+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{D}_2$ $[\text{M}]^+$ 170.1064, found 170.1069.



(E) -2-(1,2-Dideuterioprop-1-enyl)naphthalene (2.26) was prepared according to a modified procedure reported by Magoon.³⁴ In a glove box, a flame-dried round bottom flask was charged with lithium aluminum deuteride (141 mg, 3.35 mmol, 1.70 equiv.). The reaction vessel was

³⁴ Magoon, E. F.; Slaugh, L. H. *Tetrahedron* **1967**, 23, 4509.

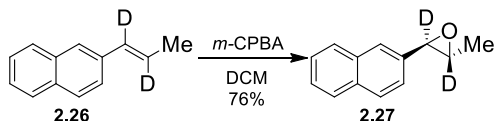
fitted with a water condenser, capped, removed from the glove box, and kept under a nitrogen atmosphere. Alkyne **2.22** (327 mg, 1.97 mmol, 1.00 equiv.) was added as a solution in dry THF (6 mL). The reaction mixture was heated to a gentle reflux and allowed to stir for 24 h. The reaction was quenched with D₂O (1.40 mL, 19.4 mmol, 9.85 equiv.) from a sealed ampule. The reaction mixture was run down a silica plug with 100% Et₂O as eluent. The crude material was purified by silica gel flash column chromatography (100% hexanes) to yield the title compound as a white solid (255 mg, 1.50 mmol, 76% yield, 97% D incorporation, > 20:1 *E/Z*): **m.p.** 43–44 °C; **TLC** *R_f* = 0.6 (100% hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.78–7.74 (m, 3H), 7.65 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.41 (ap quin, *J* = 8.1 Hz, 2H), 1.93 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 135.5, 133.9, 132.7, 130.9 (t, *J* = 23.1 Hz, 1C), 128.2, 128.0, 127.8, 126.2, 125.9 (t, *J* = 22.7 Hz, 1C), 125.5, 125.3, 123.6, 18.6; **IR** (neat) 3051, 2906, 2846, 2226, 1508, 1445 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₁₃H₁₀D₂NH₄ [M + NH₄]⁺ 188.1408 found 188.1409.



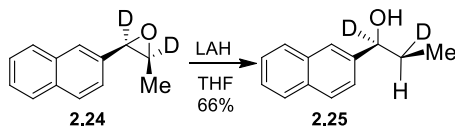
(*cis*)-2-Methyl-1,2-dideutero-3-(naphthalen-2-yl)oxirane (2.24) was prepared according to a modified procedure as reported by Watson.³⁵ A round bottom flask was charged with a stir bar and *m*-CPBA (898 mg, 4.01 mmol, 1.20 equiv.) then put under a nitrogen atmosphere. DCM (25 mL) was added followed by olefin **2.23** (562 mg, 3.34 mmol, 1.00 equiv.) as a solution in DCM (13 mL). The reaction mixture was stirred for 35 min then quenched with saturated Na₂SO₄. The crude mixture was diluted with brine and the organic layer was separated from the aqueous layer. The organic layer was dried with Na₂SO₄, filtered, and purified by flash column chromatography (5% Et₂O in hexanes) to give the product as a clear colorless oil (568 mg, 3.08

³⁵ Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307.

mmol, 92% yield): **TLC** R_f = 0.2 (2% EtOAc in hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.85–7.82 (m, 3H), 7.76 (s, 1H), 7.51–7.41 (m, 3H), 1.11 (s, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 133.11, 133.10, 133.0, 128.0, 127.9, 127.8, 126.4, 126.0, 125.6, 124.6, 57.4 (t, J = 26.4 Hz, 1C), 55.1 (t, J = 26.4 Hz, 1C), 12.5; **IR** (neat) 3055, 2963, 2927, 2207, 1602, 1389 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{D}_2\text{ONH}_4$ [$\text{M} + \text{NH}_4$] $^+$ 204.1357, found 204.1366.



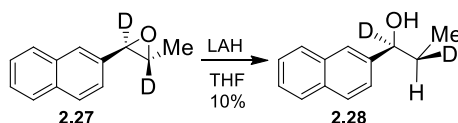
(trans)-2-Methyl-1,2-dideutero-3-(naphthalen-2-yl)oxirane (2.27) was prepared according to the same epoxidation procedure as compound **2.24** (vide supra) using the following amounts of reagents: *m*-CPBA (363 mg, 1.62 mmol, 1.40 equiv.), **2.26** (197 mg, 1.16 mmol, 1.00 equiv. in 5 mL DCM), and 10 additional mL of DCM. Purification by flash column chromatography (5% Et_2O in hexanes) yielded the title compound as a white solid (165 mg, 0.886 mmol, 76% yield): **m.p.** 51–53 $^\circ\text{C}$; **TLC** R_f = 0.2 (2% EtOAc in hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.81 (ap d, J = 8.15 Hz, 3H), 7.76 (s, 1H), 7.49–7.44 (m, 2H), 7.32 (dd, J = 7.0, 1.5 Hz, 1H), 1.49 (s, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 135.3, 133.4, 133.3, 128.4, 127.9, 126.4, 126.1, 125.1, 123.1, 59.4 (t, J = 26.8 Hz, 1C), 58.8 (t, J = 26.4 Hz, 1C), 17.9; **IR** (neat) 3055, 2974, 2926, 2226, 1600, 1505 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{D}_2\text{ONH}_4$ [$\text{M} + \text{NH}_4$] $^+$ 204.1357, found 204.1345.



threo-1-(Naphthalen-2-yl)-1,2-dideuteropropan-1-ol (2.25) was prepared according to a modified procedure reported by Watson.³⁶ A flame-dried round bottom flask was charged with

³⁶ Zhou, Qi; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307.

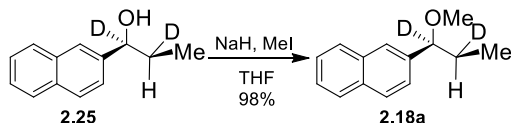
LiAlH₄ (524 mg, 13.7 mmol, 4.50 equiv.) and put under a nitrogen atmosphere. Dry THF (20 mL) was added and the vessel was cooled to 0 °C. Epoxide **2.24** (568 mg, 3.05 mmol, 1.00 equiv) was then added dropwise as a solution in THF (5 mL). The reaction mixture was allowed to return to room temperature and stirred for an additional 2 h. The reaction was quenched with saturated aqueous NH₄Cl and washed with brine. The organic layer was dried with MgSO₄ and purified by silica gel flash column chromatography (17% Et₂O in hexanes) to yield the title compound as a white solid (376 mg, 2.00 mmol, 66% yield): **m.p.** 31–32 °C; **TLC** R_f = 0.6 (20% EtOAc in hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.84–7.82 (m, 3H), 7.78 (s, 1H), 7.45–7.44 (m, 3H), 1.92–1.85 (m, 2H), 0.93 (d, *J* = 7.3 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 142.0, 133.3, 133.1, 128.3, 128.0, 127.8, 126.2, 125.9, 124.8, 124.2, 75.7 (t, *J* = 21.7, 1C), 31.3 (t, *J* = 19.4 Hz, 1C), 10.12; **IR** (neat) 3254, 3052, 2967, 1600, 1452 cm⁻¹; **HRMS** (TOF MS CI⁺) *m/z* calcd for C₁₃H₁₂D₂O [M]⁺ 188.1170, found 188.1174.



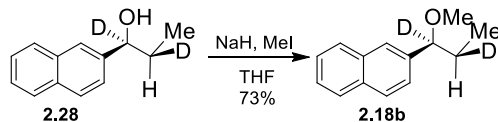
erythro-1-(Naphthalen-2-yl)-1,2-dideuteropropan-1-ol (2.28) was prepared according to a modified procedure reported by Watson.³⁷ In a glove box, a flame-dried round bottom flask was charged with lithium aluminum hydride (117 mg, 3.09 mmol, 4.50 equiv.) and dry THF (1 mL). The reaction vessel was capped, removed from the glove box, and kept under a nitrogen atmosphere. Epoxide **2.27** (128 mg, 0.687 mmol, 1.00 equiv) was added as a solution in THF (4 mL). The reaction mixture was allowed to stir for 4 h at room temperature and then quenched with H₂O and run through a silica plug. Purification by silica gel flash column chromatography (10% EtOAc in hexanes) yielded the title compound as an oil (13 mg, 0.069 mmol, 10% yield):

³⁷ Zhou, Qi; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307.

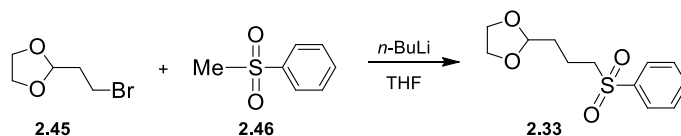
TLC R_f = 0.6 (20% EtOAc in Hexanes); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.84–7.82 (m, 3H), 7.77 (s, 1H), 7.49–7.44 (m, 3H), 1.90–1.80 (m, 2H), 0.93 (d, J = 7.5 Hz, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 142.0, 133.4, 133.1, 128.4, 128.1, 127.8, 126.2, 125.9, 124.9, 124.3, 75.8 (t, J = 21.7 Hz, 1C), 31.4 (t, J = 19.4 Hz, 1C), 10.1; **IR** (neat) 3352, 3054, 2963, 2937, 1127, 1018 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{D}_2\text{O}$ $[\text{M}]^+$ 188.1170, found 188.1306.



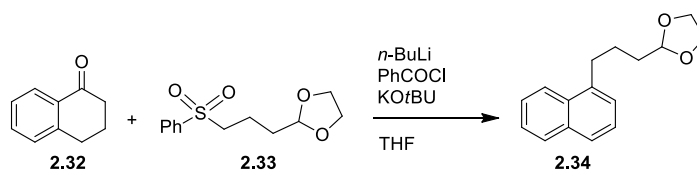
***threo*-2-(1-Methoxy-1,2-dideuteropropyl)naphthalene (2.18a)**: In a glove box, a flame-dried round bottom flask was charged with NaH (82 mg, 3.4 mmol, 1.8 equiv.). The reaction vessel was capped, removed from the glove box, and put under a nitrogen atmosphere. THF (5 mL) was added, followed by alcohol **2.25** (360 mg, 1.91 mmol, 1.00 equiv.) as a solution in THF (4 mL). The reaction mixture was stirred for 1 h, at which point MeI (0.202 mL, 3.25 mmol, 1.78 equiv.) was added. The reaction mixture was stirred overnight then the reaction was quenched with an excess of saturated aqueous NH_4Cl . The aqueous phase was extracted with EtOAc (4 x 10 mL), and the combined organics were dried with MgSO_4 , filtered, and concentrated in vacuo. The crude material was purified by silica gel flash column chromatography to yield the title compound as a clear, colorless oil (380 mg, 1.88 mmol, 98% yield): **TLC** R_f = 0.7 (10% EtOAc in hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.85–7.83 (m, 3H), 7.71 (ap d, J = 1.4 Hz, 1H), 7.49–7.43 (m, 3H), 3.25 (s, 3H), 1.89 (q, J = 7.4 Hz, 1H), 0.89 (d, J = 7.3 Hz, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 139.7, 133.3, 133.2, 128.4, 128.0, 127.9, 126.18, 126.16, 125.8, 124.7, 85.3 (t, J = 21.7 Hz, 1C), 56.8, 30.4 (t, J = 19.4 Hz, 1C), 10.3; **IR** (neat) 3055, 2971, 2929, 2816, 1460 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{D}_2\text{O}$ $[\text{M}]^+$ 202.1327, found 202.1325.



erythro-2-(1-Methoxy-1,2-dideuteropropyl)naphthalene (2.18b) was prepared by the same procedure as **2.18a** with the following amounts of reagents: NaH (7.2 mg, 0.30 mmol, 4.0 equiv.), alcohol **2.28** (14 mg, 0.07 mmol, 1.0 equiv.), MeI (0.050 mL, 0.82 mmol, 11 equiv.). Purification by silica gel flash column chromatography (10% EtOAc in hexanes) afforded the title compound as an oil (11 mg, 0.050 mmol, 73% yield): **TLC** R_f = 0.7 (10% EtOAc in hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.85–7.82 (m, 3H), 7.71 (s, 1H), 7.49–7.43 (m, 3H), 3.25 (s, 3H), 1.73 (q, J = 7.4 Hz, 1H), 0.88 (d, J = 7.4 Hz, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 139.7, 133.3, 133.2, 128.4, 128.0, 127.9, 126.2 (2C), 125.8, 124.7, 85.3 (t, J = 21.7 Hz, 1C), 56.8, 30.4 (t, J = 19.4 Hz, 1C), 10.2; **IR** (neat) 3055, 2969, 2929, 2817, 1454, 1086 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{D}_2\text{O}$ $[\text{M}]^+$ 202.1327, found 202.1323.



2-(3-(Phenylsulfonyl)propyl)-1,3-dioxolane (2.33) was prepared according to the procedure reported by LeBel.³⁸

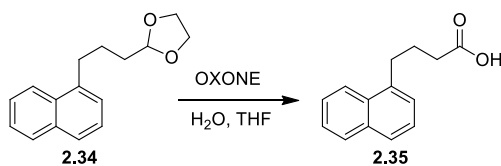


2-(3-(Naphthalen-1-yl)propyl)-1,3-dioxolane (2.34) was prepared according to a modified procedure reported by Otera.³⁹ A flame-dried round bottom flask was charged with sulfone **2.33** (1.95g, 7.61 mmol, 1.40 equiv.) and put under a nitrogen atmosphere. THF (31 mL) was added,

³⁸ LeBel, N. A.; Balasubramanian, N. *J. Am. Chem. Soc.* **1989**, *111*, 3363.

³⁹ Orita, A.; Yaruva, J.; Otera, J. *Angew. Chem. Int. Ed.* **1999**, *38*, 2267.

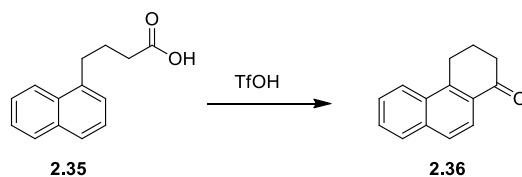
and the vessel was cooled to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (4.2 mL, 6.5 mmol, 1.6 M in hexanes, 1.2 equiv.) was added and the reaction mixture was stirred for 30 min. α -Tetralone (**2.32**) (795 mg, 5.44 mmol, 1.00 equiv.) and benzoyl chloride (0.95 mL, 8.2 mmol, 1.5 equiv.) were then added. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Potassium *tert*-butoxide (3.05 g, 27.2 mmol, 5.00 equiv.) was added and the reaction mixture was stirred at reflux for another 3 h. The reaction was quenched with saturated aqueous NH_4Cl . The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried with Na_2SO_4 , filtered through a fritted funnel, and concentrated in vacuo. The crude mixture was purified by flash chromatography (5% Et_2O in Hexanes) to yield **2.34** as a yellow oil (608 mg, 2.51 mmol, 46% yield): **TLC** $R_f = 0.1$ (3% EtOAc in Hexanes); **^1H NMR** (500 MHz, CDCl_3) δ 7.99 (d, $J = 8.2$ Hz, 1H), 7.77 (d, $J = 7.9$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.42 (t, $J = 7.25$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 6.8$ Hz, 1H), 4.81 (t, $J = 4.4$ Hz, 1H), 3.84–3.77 (m, 2H), 3.71–3.64 (m, 2H), 3.05 (t, $J = 7.6$ Hz, 2H), 1.85 (quin, $J = 7.6$ Hz, 2H), 1.77–1.73 (m, 2H); **^{13}C NMR** (125 MHz, CDCl_3) δ 138.4, 134.0, 132.0, 128.9, 126.7, 126.1, 125.9, 125.6, 125.5, 124.0, 104.6, 65.0 (2C), 33.9, 32.9, 25.1; **IR** (neat) 2924, 1733, 1394, 1133, 1029 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 242.1307, found 242.1302.



4-(Naphthalen-1-yl)butanoic acid (2.35) was prepared according to a modified procedure reported by Otera.⁴⁰ A flame-dried round bottom flask was charged with dioxolane **2.34** (54 mg, 0.22 mmol, 1.0 equiv.) and THF (0.67 mL). In a second flame-dried round bottom flask was

⁴⁰ Orita, A.; Yaruva, J.; Otera, J. *Angew. Chem. Int. Ed.* **1999**, 38, 2267.

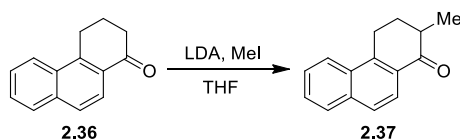
prepared a solution of potassium peroxymonosulfate (OXONE[®]) (205 mg, 0.67 mmol, 3 equiv.) in H₂O (0.7 mL). The OXONE[®] solution was added to the solution of dioxolane **2.34**, and the resulting mixture was stirred for 12 h. The reaction was quenched by a mixture of H₂O and EtOAc. The organic layer was separated, and the aqueous layer was washed three times with EtOAc. The organic layer was separated, and the aqueous layer was washed three times with EtOAc. The combined organic layers were dried with Na₂SO₄, filtered, and concentrated in vacuo. The crude material was purified by flash column chromatography (30% EtOAc in hexanes) to yield the title compound as a white solid (705 mg, 3.29 mmol; 78% yield): **m.p.** 109–110 °C; **TLC** *R_f* = 0.2 (30% EtOAc in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 11.33 (br s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 1H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.11 (quin, *J* = 7.4 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 179.6, 137.4, 134.0, 131.9, 128.9, 127.1, 126.4, 126.1, 125.7, 125.6, 123.8, 33.7, 32.3, 25.6; **IR** (neat) 2951, 1705, 1428, 1408 cm⁻¹; **HRMS** (TOF MS ES⁻) *m/z* calcd for C₁₄H₁₃O₂ [M-H]⁻ 213.0916, found 213.0909.



3,4-Dihydrophenanthren-1(2H)-one (2.36) was prepared according to a modified procedure reported by Otera and coworkers.⁴¹ A flamed dried round bottom flask was charged with carboxylic acid **2.35** (705mg, 3.29 mmol, 1.00 equiv) and cooled to 0 °C. Trifluoromethanesulfonic acid (3.29 mL, 37.2 mmol, 11.3 equiv.) was then added. The reaction mixture was slowly allowed to warm to room temperature over 2 h while stirring. Ice-cold H₂O

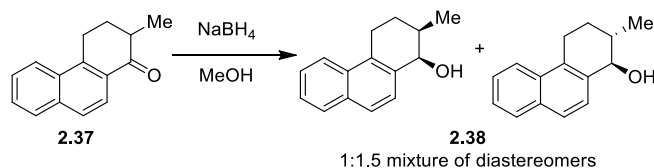
⁴¹ Orita, A.; Yaruva, J.; Otera, J. *Angew. Chem. Int. Ed.* **1999**, 38, 2267.

was added and the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organics were washed with brine, dried over Na₂SO₄, and purified by silica gel flash column chromatography (10% EtOAc in hexanes) to yield the title compound as a white solid (577 mg, 2.94 mmol, 89% yield): **m.p.** 89–90 °C; **TLC R_f** = 0.4 (10% EtOAc in hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 8.16–8.11 (m, 2H), 7.88–7.86 (m, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.64–7.57 (m, 2H), 3.40 (t, *J* = 6.2 Hz, 2H), 2.75 (ap t, *J* = 6.7 Hz, 2H), 2.31 (quin, *J* = 6.4 Hz, 2H); **¹³C NMR** (125 Hz, CDCl₃) δ 198.7, 143.1, 135.9, 131.6, 130.2, 128.9, 128.4, 127.1, 126.8, 125.0, 122.9, 38.5, 25.8, 22.9; **I.R.** (neat) 2947, 1668, 1618, 1460, 1105 cm⁻¹; **HRMS** (TOF MS ES⁺) *m/z* calcd for C₁₄H₁₂ONa [M + Na]⁺ 219.0786, found 219.0781.



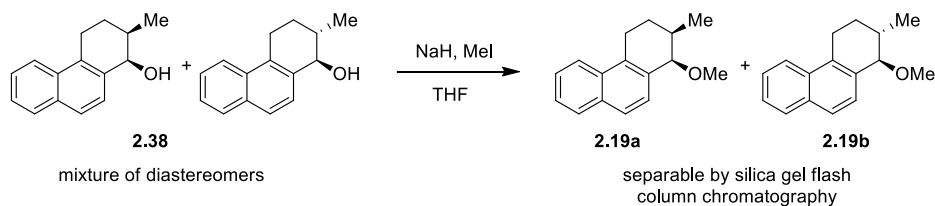
3,4-Dihydrophenanthren-1(2H)-one (2.37): A flame-dried round bottom flask was charged with distilled diisopropyl amine (0.33 mL, 2.4 mmol, 1.0 equiv.) and dry THF (4.7 mL). The reaction was cooled to –78 °C, and a solution of *n*-BuLi (1.6 mL, 2.4 mmol, 1.5 M in hexanes, 1.0 equiv.) was added. The reaction mixture was warmed to 0 °C and stirred for 1 h. The reaction mixture was again cooled to –78 °C and ketone **2.36** (462 mg, 2.35 mmol, 1.00 equiv.) was added as a solution in THF. The reaction mixture was warmed to 0 °C and stirred for 3 h, at which point methyl iodide (0.29 mL, 4.7 mmol, 2.0 equiv.) was added. The reaction mixture was stirred for an additional 2 h at 0 °C, and the reaction was quenched with saturated aqueous NaHCO₃. The aqueous layer was extracted with Et₂O (3 x 10 mL) and the combined organics were washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (2% EtOAc in hexanes) to yield the title compound as a white solid (495 mg, 2.35 mmol, 46% yield): **m.p.** 67–68 °C; **TLC R_f** =

0.2 (2% EtOAc in hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 8.11–8.08 (m, 2H), 7.83 (ap dd, *J* = 6.4, 2.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.59–7.53 (m, 2H), 3.50 (dt, *J* = 17.4, 4.2 Hz, 1H), 3.27–3.19 (m, 1H), 2.66 (ap sep, *J* = 5.9 Hz, 1H), 2.38–2.32 (m, 1H), 2.02–1.95 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 201.1, 142.4, 135.6, 131.5, 129.8, 128.8, 128.2, 127.0, 126.7, 124.8, 123.2, 41.7, 30.8, 25.1, 15.4; **IR** (neat) 3060, 2930, 2862, 1674 cm⁻¹; **HRMS** (TOF MS ES+) *m/z* calcd for C₁₅H₁₄ONa [M + Na]⁺ 233.0942, found 233.0951.



2-Methyl-1,2,3,4-tetrahydrophenanthren-1-ol (2.38): In a glove box, a flame-dried round bottom flask was charged with ketone **2.37** (219 mg, 1.04 mmol, 1.00 equiv.) and NaBH₄ (79 mg, 2.1 mmol, 2.0 equiv.). The flask was removed from the glove box and kept under a nitrogen atmosphere. The reaction vessel was cooled to –10 °C and methanol (21 mL) was added. The reaction was stirred for 25 min at –10 °C. The reaction was quenched with a mixture of saturated aqueous NaHCO₃. Dichloromethane was added, and the aqueous and organic layers were separated. The aqueous layer was extracted with dichloromethane (3 x 25 mL) and the combined organic layers were dried with MgSO₄ then filtered through a fritted funnel. The crude mixture was purified by silica gel flash column chromatography to yield **2.38** as a white solid. The product was an inseparable mixture of diastereomers (215 mg, 1.01 mmol, 97% yield): **m.p.** 84–92 °C.; **TLC R_f** = 0.3 (10% EtOAc in hexanes); **¹H NMR** (400 MHz, CDCl₃) δ 7.96 (t, *J* = 9.3 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.68 (ap t, *J* = 7.0 Hz, 2H), 7.62 (ap d, *J* = 8.6 Hz, 1H), 7.52–7.42 (m, 5H), 4.64 (d, *J* = 3.1 Hz, 1H), 4.43 (d, *J* = 7.3 Hz, 1H), 3.29 (dt, *J* = 17.4, 4.2 Hz, 1H), 3.17–2.91 (m, 3H), 2.13–2.06 (m, 1H), 1.98–1.80 (m, 5H), 1.70–1.60 (m, 2H), 1.17 (d, *J* = 6.8

Hz, 3H), 1.14 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.8, 135.6, 133.3, 132.9, 132.5, 132.2, 132.1, 132.0, 128.6, 128.5, 128.1, 126.8, 126.7, 126.21 (2C), 126.17, 125.9, 125.7, 123.7, 123.6, 75.5, 72.1, 37.0, 33.9, 27.7, 25.8, 24.7, 24.6, 18.1, 17.1; IR (neat) 3312, 2955, 2926, 2872 cm^{-1} ; HRMS (TOF MS Cl^+) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 212.1201, found 212.1199.



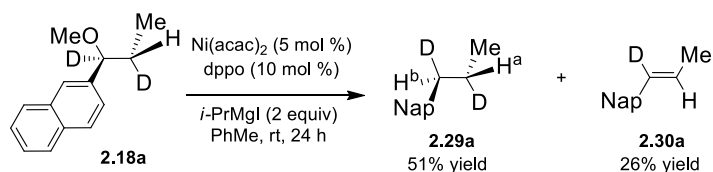
1-Methoxy-2-methyl-1,2,3,4-tetrahydrophenanthrene (2.19): In a glove box, a flame-dried round bottom flask was charged with alcohol **2.38** as a mixture of diastereomers (270 mg, 1.27 mmol, 1.00 equiv.). NaH (55 mg, 2.3 mmol, 1.8 equiv) was added, and the reaction vessel was capped, removed from the glove box, and kept under a nitrogen atmosphere. Dry THF (3.8 mL) was added, and the reaction was stirred for 1 h. Methyl iodide (0.13 mL, 2.2 mmol, 1.7 equiv.) was then added, and the reaction mixture was stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl , extracted with ethyl acetate (3 x 5 mL), and washed with brine. The crude mixture was dried over MgSO_4 , filtered through a fritted funnel and concentrated in vacuo. Purification by silica gel flash column chromatography (2–5% Et_2O in pentane) yielded each diastereomer pure, both as clear, colorless oils (85% combined yield).

2.19a (100 mg, 0.442 mmol, 35% yield): TLC $R_f = 0.5$ (5% Et_2O in pentane); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.2$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.50–7.42 (m, 3H), 4.23 (d, $J = 3.3$ Hz, 1H), 3.51 (s, 3H), 3.27 (dt, $J = 17.6, 5.6$ Hz, 1H), 3.03 (dt, $J = 17.6, 7.6$ Hz, 1H), 2.16–2.13 (m, 1H), 2.09–2.00 (m, 1H), 1.89–1.81 (m, 1H), 1.11 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.9, 133.2, 132.4, 132.2, 128.5, 127.6, 126.0, 125.9,

125.6, 123.7, 81.4, 57.9, 32.2, 25.5, 24.6, 15.8; **IR** (neat) 3049, 2927, 2817, 1457, 1088, 818 cm^{-1} ;
HRMS (TOF MS ES+) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{ONa}$ $[\text{M} + \text{Na}]^+$ 249.1255, found 249.1249.

2.19b (145 mg, 0.642 mmol, 50% yield): **TLC** $R_f = 0.4$ (5% Et_2O in pentane); **^1H NMR** (400MHz, CDCl_3) δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.50–7.44 (m, 3H), 4.21 (d, $J = 6.3$ Hz, 1H), 3.36 (s, 3H), 3.10 (t, $J = 6.4$ Hz, 2H), 2.24–2.15 (m, 2H), 1.70–1.67 (m, 1H), 1.06 (d, $J = 6.8$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 133.2, 133.01, 132.98, 132.2, 128.5, 127.1, 126.3, 126.0, 125.6, 123.5, 83.2, 55.2, 30.9, 26.7, 23.7, 17.3; **IR** (neat) 3052, 2926, 1508, 1456, 1083, 815 cm^{-1} ; **HRMS** (TOF MS ES+) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{ONa}$ $[\text{M} + \text{Na}]^+$ 249.1255, found 249.1248.

2.5.5 Representative Mechanistic Experiments

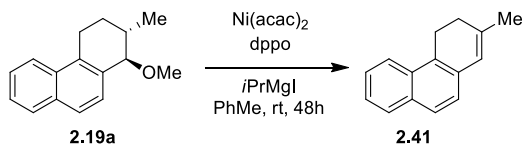


2-(1,2-Dideuteropropyl)naphthalene (2.29a) and (E)-2-(prop-1-en-1-yl-1-d)naphthalene

(2.30a): In a glove box, a flame-dried 7mL vial was charged with $\text{Ni}(\text{acac})_2$ (2.5 mg, 0.010 mmol, 0.050 equiv.), dppo (9.8 mg, 0.020 mmol, 0.10 equiv.), and ether **2.18a** (41.0 mg, 0.200 mmol, 1.00 equiv.). Toluene (1.5 mL) was then added. The reaction vessel was removed from the glove box and kept under a nitrogen atmosphere. The reaction mixture was stirred for 10 min, then isopropylmagnesium iodide (0.25 mL, 1.7M, 0.41 mmol, 2.0 equiv.) was added. The reaction mixture was allowed to stir for 24 hours, quenched with methanol, then run down a silica plug (100% Et_2O as eluent). Purification by silica gel flash column chromatography (100% pentanes) yielded **2.29a** as an oil and **2.30a** as a white solid.

2.29a (18 mg, 0.095 mmol, 51% yield): **TLC** R_f = 0.6 (100% pentane); **^1H NMR** (400 MHz, CDCl_3) δ 7.81–7.75 (m, 3H), 7.61 (s, 1H), 7.42 (ap quin, J = 7.5, 1.3 Hz, 2H), 7.33 (dd, J = 8.4, 1.5 Hz, 1H), 2.72 (d, J = 8.6 Hz, 1 H), 1.71 (quin, J = 7.4 Hz, 1H), 0.96 (d, J = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl_3) δ 140.3, 133.8, 132.1, 127.8, 127.7, 127.6, 127.5, 126.5, 125.9, 125.1, 37.9 (t, J = 19.4 Hz, 1C), 24.1 (J = 19.4 Hz, 1C), 13.9; **IR** (neat) 3050, 2957, 2910, 2871, 1507 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{D}_2$ $[\text{M}]^+$ 172.1221, found 172.1216.

2.30a (8.9 mg, 0.052 mmol, 26% yield): **m.p.** 40–42 °C; **TLC** R_f = 0.5 (100% pentane); **^1H NMR** (500 MHz, CDCl_3) δ 7.78–7.74 (m, 3H), 7.65 (s, 1H), 7.56 (dd, J = 8.6, 1.6 Hz, 1H), 7.45–7.38 (m, 2H), 6.36 (qt, J = 6.6, 2.2 Hz, 1H), 1.93 (d, J = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl_3) δ 135.5, 133.9, 132.8, 131.0 (t, J = 23.1 Hz, 1C), 128.2, 128.0, 127.8, 126.24, 126.23, 125.5, 125.3, 123.6, 18.7; **IR** (thin film) 3052, 2906, 2847, 2225, 1596, 1507, 1445 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{D}$ $[\text{M}]^+$ 169.1002, found 169.1004.



2-Methyl-3,4-dihydrophenanthrene (2.41): In a glove box, a flame-dried 7 mL vial was charged with $\text{Ni}(\text{acac})_2$ (2.6 mg, 0.010 mmol, 0.050 equiv.), dppo (9.7 mg, 0.020 mmol, 0.10 equiv.), and **2.19a** (45.3 mg, 0.200 mmol, 1.00 equiv.). The reaction vessel was capped, removed from the glove box and kept under a nitrogen atmosphere. Toluene (1.5 mL) was added and the reaction mixture was stirred for 10 min. Isopropylmagnesium iodide (0.23 mL, 1.7M, 0.40 mmol, 2.0 equiv.) was added then the reaction mixture was stirred for 48 h. The reaction was quenched with an excess of methanol and run through a silica plug (100% Et_2O). Analysis by ^1H NMR with an internal standard (PhTMS) revealed 62% yield of product. Purification by

silica-gel flash column chromatography provided a small amount of analytically pure material: **TLC** $R_f = 0.4$ (100% hexanes); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.6$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.64 (d, $J = 8.2$ Hz, 1H), 7.47 (ap t, $J = 7.6$ Hz, 1H), 7.37 (ap t, $J = 7.5$ Hz, 1H), 7.17 (d, $J = 8.3$ Hz, 1H), 6.31 (s, 1H), 3.24 (t, $J = 8.7$ Hz, 2H), 2.40 (t, $J = 8.7$ Hz, 2H), 1.98 (s, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 138.1, 132.9, 132.2, 131.5, 128.7, 128.4, 126.4, 126.0, 125.3, 124.6, 123.4, 123.3, 28.9, 23.5, 23.3; **IR** (thin film in CDCl_3) 3047, 2960, 2920, 2828, 1434 cm^{-1} ; **HRMS** (TOF MS CI^+) m/z calcd for $\text{C}_{14}\text{H}_{15}$ $[\text{M} + \text{H}]^+$ 195.1174, found 195.1080.

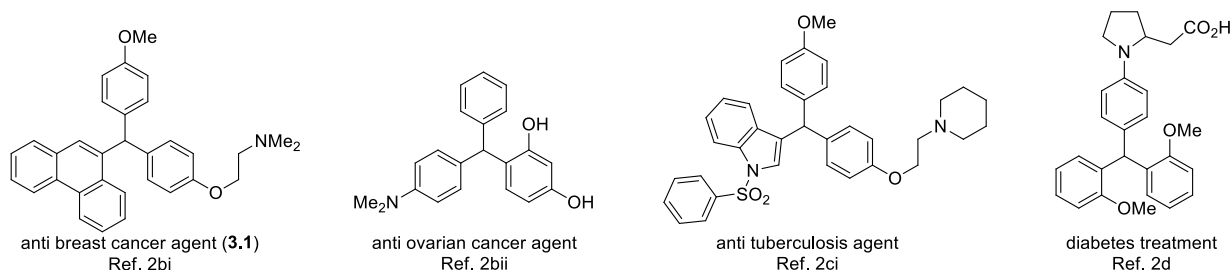
Chapter 3

Selective Synthesis of Either Enantiomer of an Anti Breast Cancer Agent from a Common Enantioenriched Intermediate

3.1. Introduction

Triarylmethanes are important targets owing to their application in materials¹ and medicinal chemistry (Figure 3.1).² In particular, the triarylmethane motif is found in anti-cancer lead compounds.^{2b} One such compound is anti breast cancer agent **3.1**.^{2bi} In 2006, (±)-**3.1** was shown by Panda and co-workers to inhibit proliferation of the MCF-7 breast cancer cell line, with an in vitro IC₅₀ of 3.88 μM. In vivo, (±)-**3.1** was shown to inhibit tumor growth and induce significant regression of mammary tumors in mice. Synthetic access to enantioenriched samples of triarylmethanes is critical for their evaluation as medicinal agents and in determining three-dimensional structure-activity relationships.

Figure 3.1. Bioactive Triarylmethanes



¹ (a) Duxbury, D. F. *Chem. Rev.* **1993**, 93, 381. (b) Shchepinov, M. S.; Korshun, V. A. *Chem. Soc. Rev.* **2003**, 32, 170. (c) Xu, Y.-Q.; Lu, J.-M.; Li, N.-J.; Yan, F.; Xia, X.-W.; Xu, Q.-F. *Eur. Polym. J.* **2008**, 44, 2404. (d) Herron, N.; Johansson, G. A.; Radu, N. S.; US Patent Application 2005/0187364A1, Aug 25, 2005.

² (a) For an overview of synthesis and medicinal properties of triarylmethanes, see: Mondal, F. S.; Panda, G. *RSC Adv.* **2014**, 4, 28317. (b) Anti-cancer: (i) Shagufta; Srivastava, A. K.; Sharma, R.; Mishra, R.; Balapure, A. K.; Murthy, P. S. R.; Panda, G. *Bioorg. Med. Chem.* **2006**, 14, 1497. (ii) Finer, J. T.; Chabala, J. C.; Lewis, E. US Patent Application 2004/0132830 A1, Jul 8, 2004. (iii) Palchaudhuri, R.; Nesterenko, V.; Hergenrother, P. J. *J. Am. Chem. Soc.* **2008**, 130, 10274. (c) Anti-tuberculosis: (i) Panda, G.; Parai, M. K.; Das, S. K.; Shagufta; Manish, S.; Chaturvedi, V.; Srivastava, A. K.; Manju, Y. S.; Gaikwad, A. N.; Sinha, S. *Eur. J. Med. Chem.* **2007**, 42, 410. (ii) Parai, M. K.; Panda, G.; Chaturvedi, V.; Manju, Y. K.; Sinha, S. *Bioorg. Med. Chem. Lett.* **2008**, 18, 289. (d) Anti-diabetes: Ellsworth, B. A.; Ewing, W. R.; Jurica, E. U.S. Patent Application 2011/0082165 A1, Apr 7, 2011. (e) Anti-implantation: Srivastava, N.; Sangita; Ray, S.; Singh, M. M.; Dwivedi, A.; Kumar, A. *Bioorg. Med. Chem.* **2004**, 12, 1011.

Traditional syntheses of triarylmethanes, including **3.1**, have relied on Friedel-Crafts reactions that lead to racemic products.^{3,4} To broaden substrate scope beyond electron-rich aromatic compounds, access alternative regioisomers, and achieve stereocontrol, new methods have been developed.^{5,6} Recent advances include methods that utilize chiral Brønsted acids and C–H bond activation.⁷ Approaches that develop Suzuki and Kumada cross-coupling reactions have further increased access to enantioenriched triarylmethanes. Crudden and co-workers have demonstrated a palladium-catalyzed Suzuki reaction of enantioenriched boronic esters and aryl iodides.⁸ Our group has developed the umpolung approach in which benzylic ethers or esters are coupled with arylmetal reagents.⁹

The contributions of the Jarvo laboratory provide a strategy to prepare both enantiomers of a triarylmethane from a common enantiomer of an alcohol intermediate (Scheme 3.1). In 2012, our group reported a stereospecific nickel-catalyzed Kumada cross-coupling reaction that allows for the preparation of optically active triarylmethanes from enantioenriched benzylic ethers such as **3.3**. The reaction proceeds with inversion at the benzylic center. This Kumada

³ (a) Nair, V.; Thomas, S.; Mathew, S. C.; Abhilash, K. G. *Tetrahedron* **2006**, *62*, 6731. (b) Pratt, E. F.; Green, L. Q. *J. Am. Chem. Soc.* **1953**, *75*, 275. (c) Muthyala, R.; Katritzky, A. R.; Lan, X. *Dyes Pigm.* **1994**, *25*, 303.

⁴ For more recent advances in transition-metal catalyzed Friedel-Crafts reactions, see: (a) Lin, S.; Lu, X. *J. Org. Chem.* **2007**, *72*, 9757. (b) Esquivias, J.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 629. (c) Iovel, I.; Mertins, K.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3913.

⁵ (a) Nambo, M.; Crudden, C. M. *Angew. Chem., Int. Ed.* **2014**, *53*, 742. (b) Xia, Y.; Hu, F.; Liu, Z.; Qu, P.; Ge, R.; Ma, C.; Zhang, Y.; Wang, J. *Org. Lett.* **2013**, *15*, 1784.

⁶ For cross-coupling strategies that provide racemic products, see: (a) Molander, G. A.; Elia, M. D. *J. Org. Chem.* **2006**, *71*, 9198. (b) Yu, J.-Y.; Kuwano, R. *Org. Lett.* **2008**, *10*, 973. (c) Tabuchi, S.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2014**, *79*, 5401.

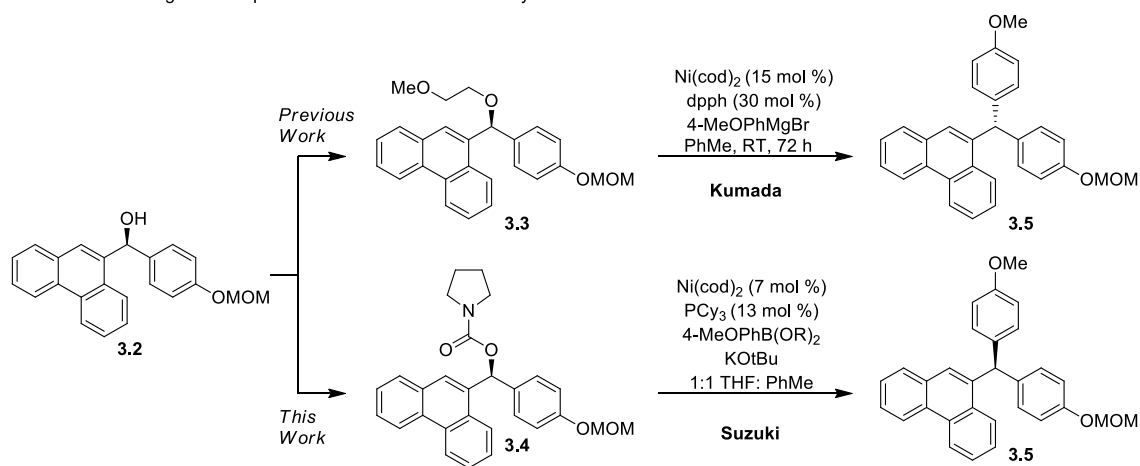
⁷ (a) Sun, F.-L.; Zheng, X.-J.; Gu, Q.; He, Q.-L.; You, S.-L. *Eur. J. Org. Chem.* **2010**, 47. (b) Zhuo, M.-H.; Jiang, Y.-J.; Fan, Y.-S.; Gao, Y.; Liu, S.; Zhang, S. *Org. Lett.* **2014**, *16*, 1096. (c) Saha, S.; Alamsetti, S. K.; Schneider, C. *Chem. Commun.* **2015**, *51*, 1461. (d) Shi, B.-F.; Maugel, N.; Zhang, Y.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 4882. (e) Li, Y.-Z.; Li, B.-J.; Lu, X.-Y.; Lin, S.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2009**, *48*, 3817. (f) McGrew, G. I.; Temaismithi, J.; Carroll, P. J.; Walsh, P. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 5541. (g) Zhang, J.; Bellomo, A.; Creamer, A. D.; Dreher, S. D.; Walsh, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 13765. (h) Zhang, J.; Bellomo, A.; Trongsirawat, N.; Jia, T.; Carroll, P. J.; Dreher, S. D.; Tudge, M. T.; Yin, H.; Robinson, J. R.; Schelter, E. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 6276. (i) Niwa, T.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*, 2373.

⁸ Mathew, S. C.; Glasspoole, B. W.; Eisenberger, P.; Crudden, C. M. *J. Am. Chem. Soc.* **2014**, *136*, 5828.

⁹ (a) Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 7790. (b) Harris, M. R.; Hanna, L. E.; Greene, M. A.; Moore, C. E.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 3303. (c) For a related transformation, see: Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307.

method was employed in an enantioselective synthesis of **3.1**.¹⁰ In 2013 our group reported a nickel-catalyzed stereospecific Suzuki-Miyaura reaction of enantioenriched diaryl carbamates, such as **3.4**, with arylboronic esters.¹¹ In contrast to the Kumada protocol, the Suzuki reaction can proceed with retention of configuration at the benzylic center if tricyclohexylphosphine is used as ligand or inversion if SIMes is employed. Together, the Kumada and Suzuki reactions provide complementary methods to synthesize both enantiomers of **3.1** from the same enantiomer of alcohol **3.2**. Herein we report the synthesis of the opposite enantiomer of **3.1** via the Suzuki reaction.¹²

Scheme 3.1. Strategies to Prepare Both Enantiomers of a Triarylmethane from a Common Enantioenriched Intermediate



3.2. Synthesis of a Bioactive Triarylmethane

The synthesis was carried out as described in Scheme 3.2. Enantioenriched alcohol **3.2** was prepared from commercially available boronic acid **3.6** and phenanthrene-9-carboxaldehyde **3.7** via an asymmetric arylation using chiral aziridine catalyst **3.8**.^{9a,13} Alcohol **3.2** is the common intermediate for both the Kumada and Suzuki protocols. The Kumada protocol requires

¹⁰ Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 7790.

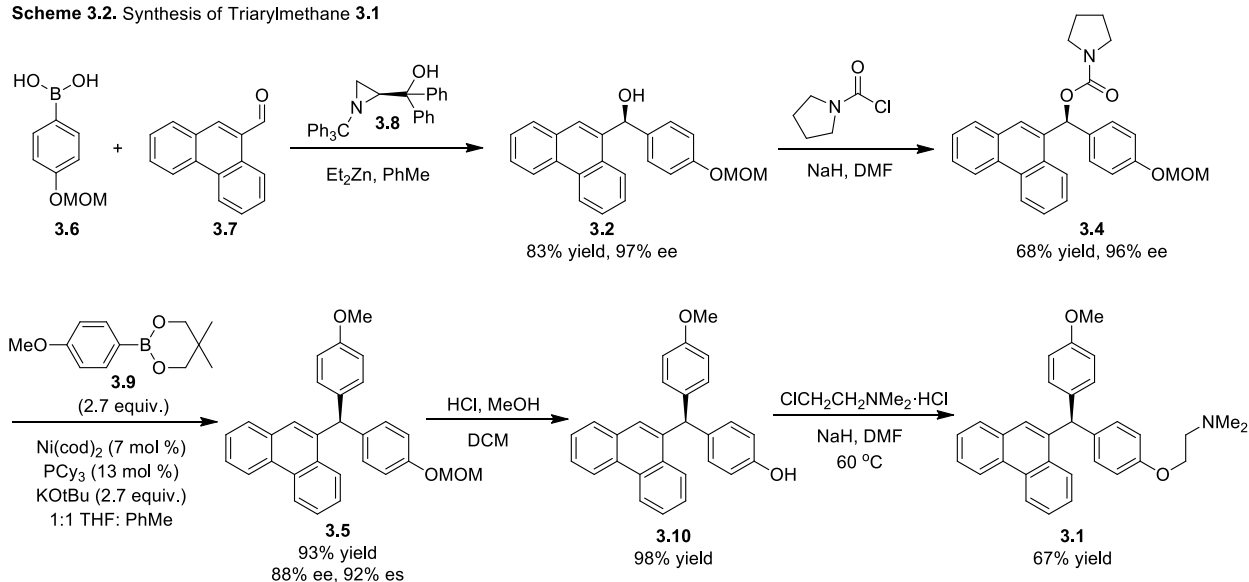
¹¹ Harris, M. R.; Hanna, L. E.; Greene, M. A.; Moore, C. E.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 3303.

¹² This chapter will focus on content from the following publication: Johnson, A. G.; Tranquilli, M. M.; Harris, M. R.; Jarvo, E. R. *Tetrahedron Lett.* **2015**, [online early access]. DOI: 10.1016/j.tetlet.2015.02.121. Published Online: March 2, 2015. <http://www.sciencedirect.com/science/article/pii/S0040403915004141> (accessed May 4, 2015).

¹³ (a) Braga, A. L.; Paixão, M. W.; Westermann, B.; Schneider, P. H.; Wessjohann, L. A. *J. Org. Chem.* **2008**, *73*, 2879. (b) Bolm, C.; Rudolph, J. *J. Am. Chem. Soc.* **2002**, *124*, 14850.

that the alcohol be converted into a methoxyethyl ether leaving group. The Suzuki reaction is more efficient if the alcohol is converted to an electron-withdrawing carbamate. The carbamate is installed by treatment of **3.2** with sodium hydride and 1-pyrrolidinecarbonyl chloride resulting in compound **3.4**.

Scheme 3.2. Synthesis of Triarylmethane **3.1**



With carbamate **3.4** in hand, we were poised to test the key step, the stereospecific Suzuki cross-coupling reaction. Subjection of **3.4** to Suzuki conditions with tricyclohexylphosphine as ligand led to the efficient formation of triarylmethane **3.5** in 93% yield and 88% ee (92% es).¹⁴ Importantly, analysis of the reaction product by chiral SFC chromatography and comparison to material obtained by the Kumada route confirmed that the Suzuki reaction proceeds with overall retention. To achieve the highest yield, **3.4** was recrystallized prior to the cross-coupling reaction, as residual alcohol **3.2** diminishes the yield in the Suzuki coupling. Interestingly, when PCy₃ is replaced with SIMes, compound **3.4** provides low yields of the desired Suzuki product.¹⁵

¹⁴ es = enantiospecificity = (ee starting material)/(ee product) see, Denmark, S. E.; Vogler, T. *Chem. Eur. J.* **2009**, *15*, 11737.

¹⁵ Although effective with many benzhydryl carbamates, subjection of carbamate **3.4** to cross-coupling conditions using a catalyst prepared in situ from Ni(cod)₂ and SIMes resulted in only 10% yield of triarylmethane **3.5**. See reference 11.

Completion of the synthesis was achieved by introduction of the requisite side chain. In the penultimate step of the synthesis the MOM group was removed under acidic conditions to form phenol **3.10**. Finally, alkylation of the phenol by treatment with sodium hydride and 2-dimethylaminoethylchloride hydrochloride afforded target compound **3.1**.¹⁶ This synthesis allowed for the preparation of **3.1** in 34% overall yield and 88% ee.

3.3. Conclusion

In summary, either enantiomer of anti-cancer triarylmethane **3.1** can be synthesized using a complementary pair of nickel-catalyzed cross-coupling reactions from a common enantiomer of a chiral alcohol intermediate. For the synthesis of anti-cancer agent **3.1**, when the Kumada protocol is followed, the reaction occurs with inversion at the benzylic stereogenic center. When the Suzuki protocol is followed, the reaction occurs with retention at the benzylic stereogenic center, providing the opposite enantiomer of **3.1**. These syntheses allow for efficient and selective preparation of either enantiomer of triarylmethanes for biological testing. With the exception of the alcohol protection and the subsequent nickel-catalyzed cross-coupling steps, both syntheses are identical and provide optically active **3.1** in five synthetic steps from commercially available starting materials.

¹⁶ McCague, R.; Leclercq, G.; Jordan, V. C. *J. Med. Chem.* **1988**, *31*, 1285.

3.4. Experimental Section

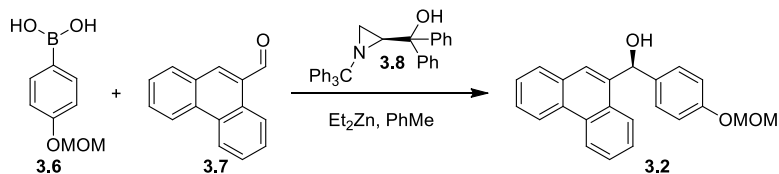
3.4.1. General Procedures

All reactions were carried out under an atmosphere of N₂ using glassware that was either oven- or flame-dried prior to use. Methanol (MeOH) was purchased commercially and used without further purification. *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and toluene (PhMe) were degassed with argon 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 H₂O. All other solvents utilized were purchased anhydrous commercially, or purified as described (vide infra). ¹H NMR spectra were recorded on Bruker GN-500 (500 MHz ¹H, 125.7 MHz ¹³C), CRYO-500 (500 MHz ¹H, 125.7 MHz ¹³C) or DRX-400 (400 MHz ¹H, 100 MHz ¹³C) 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), triplet (t), multiplet (m), apparent doublet (ap d), apparent triplet (ap t)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard (CDCl₃, δ 77.16 ppm). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F₂₅₄ pre-coated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp. Flash chromatography was performed using Silica Gel 60Å (170-400 mesh) from Fisher Scientific. Melting points (m.p.) were obtained using a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were obtained on a Nicolet™ iST™5 FT-IR spectrometer system and are reported in terms of frequency of absorption (cm⁻¹). High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. Optical rotations were measured with a Rudolph Research Analytical

Autopol IV Automatic Polarimeter or a Jasco P-1010 digital polarimeter. SFC determinations of enantiopurity were performed on a Berger Analytical instrument using a Daicel™ Chiralpak® column (AD-H; 100 bar, 50 °C, 254 nm).

(*S*)- α,α -diphenyl-1-(triphenylmethyl)-2-aziridinemethanol (**3.8**) was prepared according to a procedure described by Braga.¹⁷ *p*-[(Methoxymethyl)oxy]phenylboronic acid (**3.6**) was prepared from the corresponding methoxymethyl protected aryl bromide.¹⁸ 2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**3.9**) was prepared from the corresponding boronic acid and 2,2-dimethylpropane-1,3-diol.¹⁹ 4-Methoxymethoxybenzaldehyde was prepared from the corresponding 4-hydroxybenzaldehyde and chloromethyl methyl ether.²⁰ Ni(cod)₂ was purchased from Strem, stored in a glove box freezer (−20 °C) under an atmosphere of N₂, and used as received. Tricyclohexylphosphine (PCy₃) was purchased from Strem, stored in a glove box, and used as received. All other chemicals were purchased commercially and used as received.

3.4.2. Preparation and Characterization of Products



(4-(Methoxymethoxy)phenyl)(phenanthren-9-yl)methanol (**3.2**) was prepared according to a procedure reported by Jarvo modified from a procedure developed by Braga.²¹ A flame-dried

¹⁷ Braga, A. L.; Paixão, M. W.; Westermann, B.; Schneider, P. H.; Wessjohann, L. A. *J. Org. Chem.* **2008**, *73*, 2879.

¹⁸ Choshi, T.; Yamada, S.; Sugino, E.; Kuwada, T.; Hibino, S. *J. Org. Chem.* **1995**, *60*, 5899.

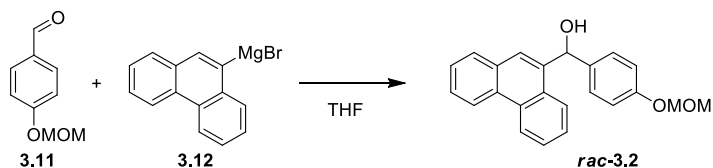
¹⁹ Tivola, P. B.; Deagostino, A.; Prandi, C.; Venturello, P. *Org. Lett.* **2002**, *4*, 1275.

²⁰ Fruit, C.; Turck, A.; Plé, N.; Mojovic, L.; Quéguiner, G. *Tetrahedron* **2001**, *57*, 9435.

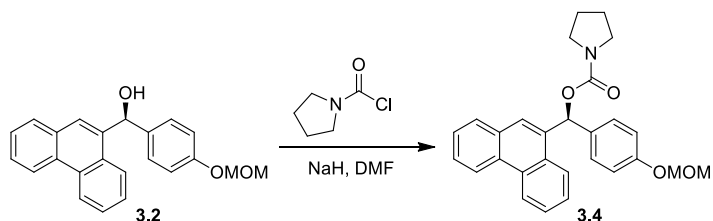
²¹ Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

round bottom flask was charged with boronic acid **3.6** (717 mg, 3.94 mmol, 1.63 equiv.). Toluene (6.5 mL) was added, followed by a solution of Et₂Zn in PhMe (22.3 mL, 22.3 mmol 1.00 M, 9.20 equiv.). The reaction mixture was heated to 60 °C and allowed to stir for 12 hours, then cooled to room temperature. A solution of (*S*)- α,α -diphenyl-1-(triphenylmethyl)-2-aziridinemethanol (**3.8**) (113 mg, 0.240 mmol, 0.100 equiv.) in toluene (5 mL) was added and the reaction was stirred for 15 minutes. A solution of phenanthrene-9-carbaldehyde **3.7** (499 mg, 2.42 mmol, 1.00 equiv.) in toluene (4.8 mL) was added and the reaction was stirred for 14 hours at room temperature. The reaction was quenched with an excess of 1 M HCl. The crude mixture was extracted with EtOAc (3 x 30 mL), washed with brine, dried over Na₂SO₄, and purified by silica gel flash column chromatography (1% EtOAc/benzene) to afford the target compound as a white solid (820 mg, 2.38 mmol, 98% yield, 94% ee): $[\alpha]^{23}_{\text{D}} +79.1$ (*c* 1.35, CHCl₃). The product was recrystallized in a mixture of 20:1 Et₂O:H₂O to improve ee. After recrystallization, SFC analysis indicated 97% ee (689 mg, 2.00 mmol, 83% yield, 97% ee). Analytical data are consistent with literature values:²² **¹H NMR** (400 MHz, CDCl₃) δ 8.73 (d, *J* = 8.2 Hz, 1H), 8.67 (d, *J* = 8.1 Hz, 1H), 8.01 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.68–7.59 (m, 3H), 7.51 (t, *J* = 7.1 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 3.4 Hz, 1H), 5.14 (s, 2H), 3.45 (s, 3H), 2.31 (d, *J* = 3.8 Hz, 1H); **SFC** analysis (AD-H, 35% MeOH, 3.5 mL/min, 254 nm) indicated 97% ee: *t*_R (major) = 4.4 min, *t*_R (minor) = 6.2 min.

²² Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.



racemic-4-(Methoxymethoxy)phenyl(phenanthren-9-yl)methanol (rac-3.2) was prepared according to a procedure reported by Jarvo.²³ To a solution of 4-(methoxymethoxy)benzaldehyde **3.11** (1.66 g, 10.0 mmol, 1.00 equiv.) in THF (10 mL) was added 9-phenanthrenylmagnesium bromide **3.12** (12 mL, 12 mmol, 1.0 M in THF, 1.2 equiv.) at 0 °C. The mixture was warmed to room temperature and stirred for 4 hours. Saturated aqueous NH₄Cl was added, and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The crude reaction mixture was purified by silica gel flash column chromatography (10–20% EtOAc/hexanes) to afford the title compound as a white solid (1.80 g, 5.23 mmol, 52% yield). Analytical data are consistent with the values listed above for compound **3.2**.

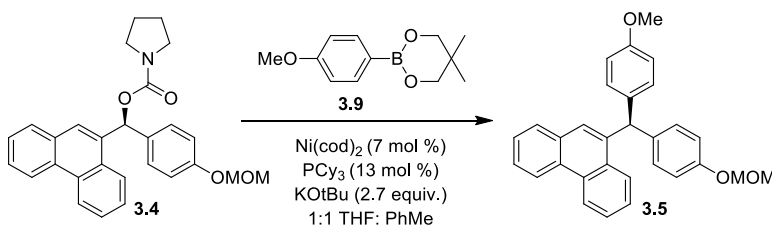


4-(Methoxymethoxy)phenyl(phenanthren-9-yl)methyl pyrrolidine-1-carboxylate (3.4) was prepared according to a modified procedure reported by Ishihara and co-workers.²⁴ A flame-dried round bottom flask was charged with NaH (86 mg, 3.6 mmol, 1.8 equiv.) and alcohol **3.2** (689 mg, 2.00 mmol, 1.00 equiv.) and cooled to 0 °C. DMF (3 mL) was added to the reaction vessel at 0 °C, and the reaction mixture was allowed to stir for 1 hour at 0 °C. 1-

²³ Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

²⁴ Ishihara, K.; Kosugi, Y.; Umemura, S; Sakakura, A. *Org. Lett.* **2008**, *10*, 3191.

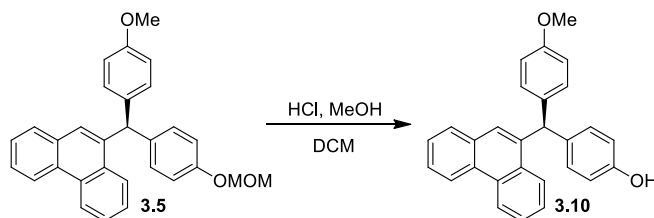
Pyrrolidinecarbonyl chloride (0.243 mL, 2.20 mmol, 1.10 equiv.) was then added. The reaction mixture was stirred for an additional 3 hours at room temperature and quenched with an excess of saturated aqueous NH₄Cl. The crude mixture was extracted with EtOAc (4 x 5 mL), and the combined organic layers were washed with brine and dried over Na₂SO₄. Silica gel flash column chromatography (20% EtOAc/hexanes) followed by recrystallization from hexanes afforded the target compound as a white solid (604 mg, 1.37 mmol, 68% yield, 96% ee): **m.p.** = 54–57 °C; **TLC** R_f = 0.5 (30% EtOAc in hexanes); **¹H NMR** (500 MHz, CDCl₃) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.90–7.87 (m, 2H), 7.67–7.58 (m, 3H), 7.53–7.50 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.14 (s, 2H), 3.56–3.40 (m, 7H), 1.92–1.83 (m, 4H); **¹³C NMR** (125 MHz, CDCl₃) δ 157.0, 154.4, 134.5, 133.9, 131.3, 131.0, 130.6, 129.9, 129.1, 129.0, 127.0, 126.8, 126.74, 126.70, 126.4, 125.5, 123.2, 122.6, 116.2, 94.5, 75.3, 56.2, 46.5, 46.0, 25.9, 25.1; **IR** (neat) 2951, 2876, 1696, 1409, 1509, 1078 cm⁻¹; **HRMS** (TOF MS ES+) *m/z* calcd for C₂₈H₂₇NO₄Na [M + Na]⁺ 464.1838, found 464.1830; [α]_D²⁵ +52.9 (c 5.00, CDCl₃); **SFC** analysis (AD-H 30% MeOH, 2.5 mL/min, 254 nm) indicated 96% ee: t_R (major) = 7.8 min, t_R (minor) = 8.7 min.



9-((4-(Methoxymethoxy)phenyl)(4-methoxyphenyl)methyl)phenanthrene (3.5) was prepared according to a modified procedure reported by Jarvo.²⁵ In a glove box, a 7 mL vial was charged with carbamate **3.4** (200 mg, 0.450 mmol, 1.00 equiv.), boronic ester **3.9** (266 mg, 1.21 mmol, 2.66 equiv.), and KOt-Bu (135 mg, 1.21 mmol, 2.66 equiv.). PCy₃ as a solution in 1:1

²⁵ Harris, M. R.; Hanna, L. E.; Greene, M. A.; Moore, C. E.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 3303.

THF:PhMe (0.020 M, 3.0 mL, 0.060 mmol, 0.13 equiv.) was added followed by Ni(cod)₂ as a solution in 1:1 THF:PhMe (0.010 M, 3.0 mL, 0.030 mmol, 0.070 equiv.). The reaction was then stirred for 24 h in the glove box. The reaction vessel was removed from the glove box, and the crude mixture was passed through a silica plug with 1:1 Et₂O:hexanes. Silica gel flash column chromatography (100% benzene) afforded a mixture of desired product and boronic ester. A second flash column (100% benzene) afforded a pure sample of the target compound as a white solid (182 mg, 0.419 mmol, 93% yield, 88% ee). NMR data are consistent with the values previously reported by Jarvo:²⁶ ¹H NMR (400 MHz, CDCl₃) δ 8.72, (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 1.5 Hz, 2 H), 7.60–7.47 (m, 2H), 7.16 (s, 1H), 7.07 (apt d, *J* = 8.5 Hz, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.15 (s, 1H), 5.15 (s, 2H), 3.78 (s, 3H) 3.48 (s, 3H); [α]²³_D –3.3 (*c* 3.8, CHCl₃)²⁷; SFC analysis (AD-H, 10% MeOH, 3.5 mL/min, 254 nm) indicated 88% ee, 92% es: *t*_R (major) = 13.3 min, *t*_R (minor) = 14.0 min.



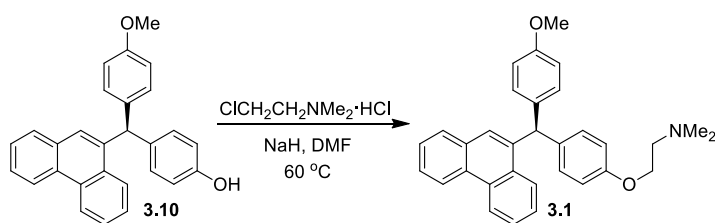
4-((4-Methoxyphenyl)(phenanthren-9-yl)methyl)phenol (3.10) was prepared according to a procedure reported by Jarvo.²⁸ To a solution of triarylmethane **3.5** (182 mg, 0.419 mmol, 1.00 equiv.) in DCM (12.1 mL) was added a solution of HCl in MeOH (2.00 M, 12.1 mL). The reaction mixture was stirred overnight and then quenched with an excess of NaHCO₃. The crude

²⁶ Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

²⁷ Optical rotation data are inconsistent with literature values (ref. 26). SFC data, however, are consistent with formation of the opposite enantiomer (vide infra).

²⁸ See reference 26.

mixture was extracted with EtOAc (3 x 30 mL), washed with brine, and dried over Na₂SO₄. Purification by silica gel flash column chromatography (30% EtOAc/hexanes) yielded the target compound as a white solid (160 mg, 0.410 mmol, 98% yield, 88% ee). NMR data are consistent with literature values:²⁹ ¹H NMR (500 MHz, CDCl₃) δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.63–7.57 (m, 2H), 7.54–7.46 (m, 2H), 7.15 (s, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.14 (s, 1H), 4.65 (br s, 1H), 3.77 (s, 3H); [α]_D²³ -2.6 (*c* 1.5, CDCl₃)³⁰; SFC analysis (AD-H, 25% MeOH, 2.5 mL/min, 254 nm) indicated 88% ee: *t*_R (major) = 9.0 min, *t*_R (minor) = 11.0 min.



2-(4-((4-Methoxyphenyl)(phenanthren-9-yl)methyl)phenoxy)-*N,N*-dimethylethanamine (**3.1**)

was prepared according to a procedure reported by Jarvo, adapted from McCague.^{31,32} In a glove box, a flame dried round bottom flask was charged with NaH (129 mg, 5.38 mmol, 15.0 equiv.). The reaction vessel was removed from the box and phenol **3.10** (140 mg, 0.359 mmol, 1.00 equiv.) was added as a solution in DMF (7.0 mL). The reaction mixture was heated to 60 °C and stirred for 10 min. The reaction mixture was allowed to cool to room temperature before addition of 2-dimethylaminoethylchloride hydrochloride (211 mg, 1.47 mmol, 4.10 equiv.) as a slurry in DMF (7.0 mL; a large gauge needle is recommended to prevent clogging of the syringe).

²⁹ Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

³⁰ Optical rotation data are inconsistent with literature values (ref. 29). SFC data, however, are consistent with formation of the opposite enantiomer (vide infra).

³¹ See reference 29.

³² McCague, R.; Leclercq, G.; Jordan, V. C. *J. Med. Chem.* **1988**, *31*, 1285.

The reaction mixture was again heated to 60 °C and stirred for 4 hours, at which time the mixture was allowed to cool to room temperature. The reaction was then quenched with an excess of isopropanol. The crude mixture was diluted with H₂O, and extracted with EtOAc (4 x 10 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. Purification by silica gel flash column chromatography (3% Et₃N/EtOAc) yielded the target compound as an off-white solid (110 mg, 0.239 mmol, 67% yield). NMR data are consistent with reported values:³³ **¹H NMR** (400 MHz, CDCl₃) δ 8.72 (d, *J* = 8.1 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.1 Hz, 2H), 7.58–7.48 (m, 2H), 7.15 (s, 1H), 7.07–7.04 (m, 4H), 6.83 (apt t, *J* = 8.2 Hz, 4H), 6.14 (s, 1H), 4.04 (t, *J* = 5.8 Hz, 2H), 3.78 (s, 3H), 2.71 (t, *J* = 5.8 Hz, 2H), 2.32 (s, 6H); [α]_D²⁵ –0.06 (*c* 8.83 CHCl₃).³⁴

³³ Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790.

³⁴ Optical rotation data are inconsistent with literature values (ref. 33). SFC data, however, are consistent with formation of the opposite enantiomer (*vide infra*).

APPENDIX A

^1H and ^{13}C NMR Spectra


```

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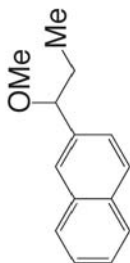
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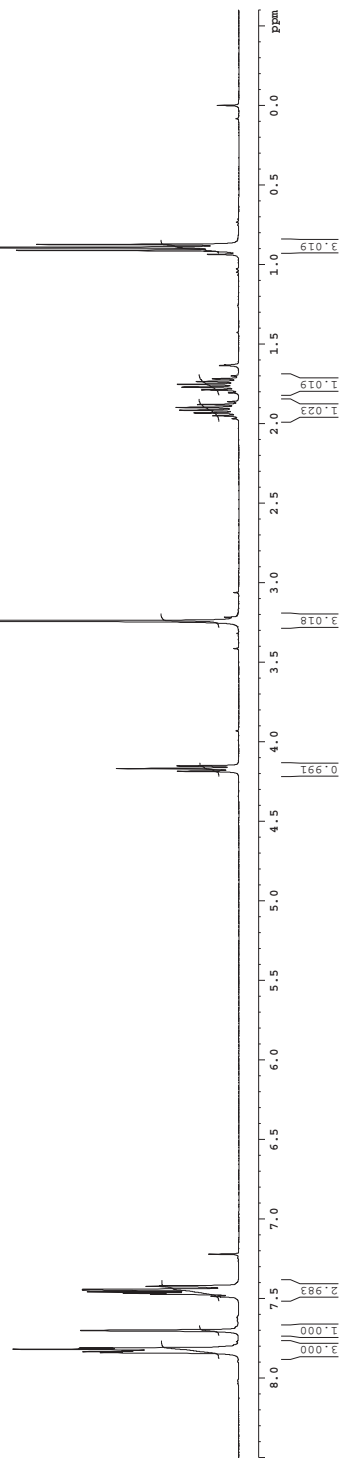
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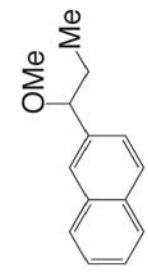
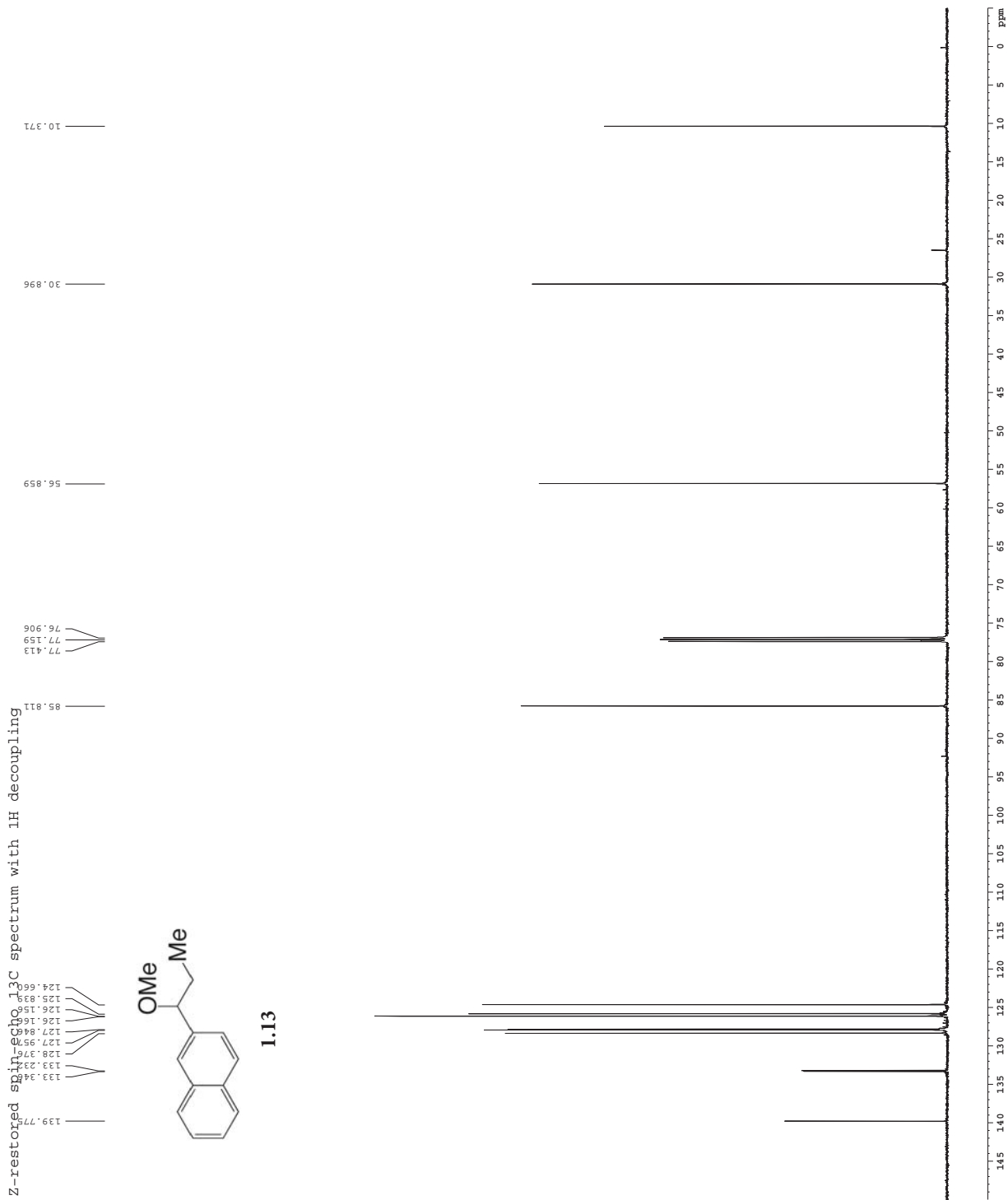


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SS           16
SF           101.625136
FIDRES       0.0003688
AQ           1.0813940
RG           327.680
DM           16.500
DE           6.00
D1           0.25000000
d11          0.03000000
d17          0.00156000
MCWPRG      CPMASK
PCWPRG      CPMASK
===== CHANNEL f1 =====
NUC1          13C
P1           12.00
P2           500.00
P3           2000.00
P4           -1.00
P5           -1.00
P6           125.7945280
P7           2.00
P8           0.00
P9           0.00
P10          0.00
P11          0.00
P12          0.00
P13          0.00
P14          0.00
P15          0.00
P16          0.00
P17          0.00
P18          0.00
P19          0.00
P20          0.00
P21          0.00
P22          0.00
P23          0.00
P24          0.00
P25          0.00
P26          0.00
P27          0.00
P28          0.00
P29          0.00
P30          0.00
P31          0.00
P32          0.00
P33          0.00
P34          0.00
P35          0.00
P36          0.00
P37          0.00
P38          0.00
P39          0.00
P40          0.00
P41          0.00
P42          0.00
P43          0.00
P44          0.00
P45          0.00
P46          0.00
P47          0.00
P48          0.00
P49          0.00
P50          0.00
===== CHANNEL f2 =====
NUC2          1H
P1           10.00
P2           500.00
P3           2000.00
P4           -1.00
P5           -1.00
P6           125.7945280
P7           2.00
P8           0.00
P9           0.00
P10          0.00
P11          0.00
P12          0.00
P13          0.00
P14          0.00
P15          0.00
P16          0.00
P17          0.00
P18          0.00
P19          0.00
P20          0.00
P21          0.00
P22          0.00
P23          0.00
P24          0.00
P25          0.00
P26          0.00
P27          0.00
P28          0.00
P29          0.00
P30          0.00
P31          0.00
P32          0.00
P33          0.00
P34          0.00
P35          0.00
P36          0.00
P37          0.00
P38          0.00
P39          0.00
P40          0.00
P41          0.00
P42          0.00
P43          0.00
P44          0.00
P45          0.00
P46          0.00
P47          0.00
P48          0.00
P49          0.00
P50          0.00
===== GRADIENT CHANNEL =====
CPDPRG2      WALTZ16
NUC2          13C
P1           10.00
P2           500.00
P3           2000.00
P4           -1.00
P5           -1.00
P6           125.7945280
P7           2.00
P8           0.00
P9           0.00
P10          0.00
P11          0.00
P12          0.00
P13          0.00
P14          0.00
P15          0.00
P16          0.00
P17          0.00
P18          0.00
P19          0.00
P20          0.00
P21          0.00
P22          0.00
P23          0.00
P24          0.00
P25          0.00
P26          0.00
P27          0.00
P28          0.00
P29          0.00
P30          0.00
P31          0.00
P32          0.00
P33          0.00
P34          0.00
P35          0.00
P36          0.00
P37          0.00
P38          0.00
P39          0.00
P40          0.00
P41          0.00
P42          0.00
P43          0.00
P44          0.00
P45          0.00
P46          0.00
P47          0.00
P48          0.00
P49          0.00
P50          0.00
===== Processing parameters =====
SI           65536
SF           125.7804188
WDW          EM
SSB          0
GB           0
PC           2.00

```

Z-restored spin-echo ¹³C spectrum with 1H decoupling



1.13

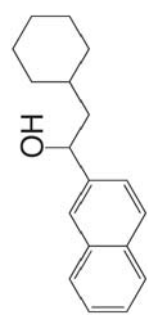
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Current Data Parameters
NAME      AG_1_Nsp_Cy_OH
PROCNO    1
Date_    20120502
Time     11:11:11
PROBHD    5 mm CPYCI 1H-
PULPROG   zgpg30
TD         83728
SOLVENT    CDCl3
DS         2
AQ         0.028453 Hz
FIDRES    0.038943 Hz
AQ         5.0998774 sec
DM         62.400 usec
DE         6.00 usec
DI         0.10000000 sec
MCNST     0.00000000 sec
PCPRG1    0.03000000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL1        0.00 dB
SFO1       500.2335015 MHz
===== CHANNEL f2 =====
NUC2       13C
P2         7.50 usec
PL2        0.00 dB
SFO2       125.7613500 MHz
===== CHANNEL f3 =====
NUC3       13C
P3         7.50 usec
PL3        0.00 dB
SFO3       125.7613500 MHz
===== CHANNEL f4 =====
NUC4       13C
P4         7.50 usec
PL4        0.00 dB
SFO4       125.7613500 MHz
===== CHANNEL f5 =====
NUC5       13C
P5         7.50 usec
PL5        0.00 dB
SFO5       125.7613500 MHz
===== CHANNEL f6 =====
NUC6       13C
P6         7.50 usec
PL6        0.00 dB
SFO6       125.7613500 MHz
===== CHANNEL f7 =====
NUC7       13C
P7         7.50 usec
PL7        0.00 dB
SFO7       125.7613500 MHz
===== CHANNEL f8 =====
NUC8       13C
P8         7.50 usec
PL8        0.00 dB
SFO8       125.7613500 MHz
===== CHANNEL f9 =====
NUC9       13C
P9         7.50 usec
PL9        0.00 dB
SFO9       125.7613500 MHz
===== CHANNEL f10 =====
NUC10      13C
P10        7.50 usec
PL10       0.00 dB
SFO10      125.7613500 MHz
===== CHANNEL f11 =====
NUC11      13C
P11        7.50 usec
PL11       0.00 dB
SFO11      125.7613500 MHz
===== CHANNEL f12 =====
NUC12      13C
P12        7.50 usec
PL12       0.00 dB
SFO12      125.7613500 MHz
===== CHANNEL f13 =====
NUC13      13C
P13        7.50 usec
PL13       0.00 dB
SFO13      125.7613500 MHz
===== CHANNEL f14 =====
NUC14      13C
P14        7.50 usec
PL14       0.00 dB
SFO14      125.7613500 MHz
===== CHANNEL f15 =====
NUC15      13C
P15        7.50 usec
PL15       0.00 dB
SFO15      125.7613500 MHz
===== CHANNEL f16 =====
NUC16      13C
P16        7.50 usec
PL16       0.00 dB
SFO16      125.7613500 MHz
===== CHANNEL f17 =====
NUC17      13C
P17        7.50 usec
PL17       0.00 dB
SFO17      125.7613500 MHz
===== CHANNEL f18 =====
NUC18      13C
P18        7.50 usec
PL18       0.00 dB
SFO18      125.7613500 MHz
===== CHANNEL f19 =====
NUC19      13C
P19        7.50 usec
PL19       0.00 dB
SFO19      125.7613500 MHz
===== CHANNEL f20 =====
NUC20      13C
P20        7.50 usec
PL20       0.00 dB
SFO20      125.7613500 MHz
===== CHANNEL f21 =====
NUC21      13C
P21        7.50 usec
PL21       0.00 dB
SFO21      125.7613500 MHz
===== CHANNEL f22 =====
NUC22      13C
P22        7.50 usec
PL22       0.00 dB
SFO22      125.7613500 MHz
===== CHANNEL f23 =====
NUC23      13C
P23        7.50 usec
PL23       0.00 dB
SFO23      125.7613500 MHz
===== CHANNEL f24 =====
NUC24      13C
P24        7.50 usec
PL24       0.00 dB
SFO24      125.7613500 MHz
===== CHANNEL f25 =====
NUC25      13C
P25        7.50 usec
PL25       0.00 dB
SFO25      125.7613500 MHz
===== CHANNEL f26 =====
NUC26      13C
P26        7.50 usec
PL26       0.00 dB
SFO26      125.7613500 MHz
===== CHANNEL f27 =====
NUC27      13C
P27        7.50 usec
PL27       0.00 dB
SFO27      125.7613500 MHz
===== CHANNEL f28 =====
NUC28      13C
P28        7.50 usec
PL28       0.00 dB
SFO28      125.7613500 MHz
===== CHANNEL f29 =====
NUC29      13C
P29        7.50 usec
PL29       0.00 dB
SFO29      125.7613500 MHz
===== CHANNEL f30 =====
NUC30      13C
P30        7.50 usec
PL30       0.00 dB
SFO30      125.7613500 MHz
===== CHANNEL f31 =====
NUC31      13C
P31        7.50 usec
PL31       0.00 dB
SFO31      125.7613500 MHz
===== CHANNEL f32 =====
NUC32      13C
P32        7.50 usec
PL32       0.00 dB
SFO32      125.7613500 MHz
===== CHANNEL f33 =====
NUC33      13C
P33        7.50 usec
PL33       0.00 dB
SFO33      125.7613500 MHz
===== CHANNEL f34 =====
NUC34      13C
P34        7.50 usec
PL34       0.00 dB
SFO34      125.7613500 MHz
===== CHANNEL f35 =====
NUC35      13C
P35        7.50 usec
PL35       0.00 dB
SFO35      125.7613500 MHz
===== CHANNEL f36 =====
NUC36      13C
P36        7.50 usec
PL36       0.00 dB
SFO36      125.7613500 MHz
===== CHANNEL f37 =====
NUC37      13C
P37        7.50 usec
PL37       0.00 dB
SFO37      125.7613500 MHz
===== CHANNEL f38 =====
NUC38      13C
P38        7.50 usec
PL38       0.00 dB
SFO38      125.7613500 MHz
===== CHANNEL f39 =====
NUC39      13C
P39        7.50 usec
PL39       0.00 dB
SFO39      125.7613500 MHz
===== CHANNEL f40 =====
NUC40      13C
P40        7.50 usec
PL40       0.00 dB
SFO40      125.7613500 MHz
===== CHANNEL f41 =====
NUC41      13C
P41        7.50 usec
PL41       0.00 dB
SFO41      125.7613500 MHz
===== CHANNEL f42 =====
NUC42      13C
P42        7.50 usec
PL42       0.00 dB
SFO42      125.7613500 MHz
===== CHANNEL f43 =====
NUC43      13C
P43        7.50 usec
PL43       0.00 dB
SFO43      125.7613500 MHz
===== CHANNEL f44 =====
NUC44      13C
P44        7.50 usec
PL44       0.00 dB
SFO44      125.7613500 MHz
===== CHANNEL f45 =====
NUC45      13C
P45        7.50 usec
PL45       0.00 dB
SFO45      125.7613500 MHz
===== CHANNEL f46 =====
NUC46      13C
P46        7.50 usec
PL46       0.00 dB
SFO46      125.7613500 MHz
===== CHANNEL f47 =====
NUC47      13C
P47        7.50 usec
PL47       0.00 dB
SFO47      125.7613500 MHz
===== CHANNEL f48 =====
NUC48      13C
P48        7.50 usec
PL48       0.00 dB
SFO48      125.7613500 MHz
===== CHANNEL f49 =====
NUC49      13C
P49        7.50 usec
PL49       0.00 dB
SFO49      125.7613500 MHz
===== CHANNEL f50 =====
NUC50      13C
P50        7.50 usec
PL50       0.00 dB
SFO50      125.7613500 MHz
===== CHANNEL f51 =====
NUC51      13C
P51        7.50 usec
PL51       0.00 dB
SFO51      125.7613500 MHz
===== CHANNEL f52 =====
NUC52      13C
P52        7.50 usec
PL52       0.00 dB
SFO52      125.7613500 MHz
===== CHANNEL f53 =====
NUC53      13C
P53        7.50 usec
PL53       0.00 dB
SFO53      125.7613500 MHz
===== CHANNEL f54 =====
NUC54      13C
P54        7.50 usec
PL54       0.00 dB
SFO54      125.7613500 MHz
===== CHANNEL f55 =====
NUC55      13C
P55        7.50 usec
PL55       0.00 dB
SFO55      125.7613500 MHz
===== CHANNEL f56 =====
NUC56      13C
P56        7.50 usec
PL56       0.00 dB
SFO56      125.7613500 MHz
===== CHANNEL f57 =====
NUC57      13C
P57        7.50 usec
PL57       0.00 dB
SFO57      125.7613500 MHz
===== CHANNEL f58 =====
NUC58      13C
P58        7.50 usec
PL58       0.00 dB
SFO58      125.7613500 MHz
===== CHANNEL f59 =====
NUC59      13C
P59        7.50 usec
PL59       0.00 dB
SFO59      125.7613500 MHz
===== CHANNEL f60 =====
NUC60      13C
P60        7.50 usec
PL60       0.00 dB
SFO60      125.7613500 MHz
===== CHANNEL f61 =====
NUC61      13C
P61        7.50 usec
PL61       0.00 dB
SFO61      125.7613500 MHz
===== CHANNEL f62 =====
NUC62      13C
P62        7.50 usec
PL62       0.00 dB
SFO62      125.7613500 MHz
===== CHANNEL f63 =====
NUC63      13C
P63        7.50 usec
PL63       0.00 dB
SFO63      125.7613500 MHz
===== CHANNEL f64 =====
NUC64      13C
P64        7.50 usec
PL64       0.00 dB
SFO64      125.7613500 MHz
===== CHANNEL f65 =====
NUC65      13C
P65        7.50 usec
PL65       0.00 dB
SFO65      125.7613500 MHz
===== CHANNEL f66 =====
NUC66      13C
P66        7.50 usec
PL66       0.00 dB
SFO66      125.7613500 MHz
===== CHANNEL f67 =====
NUC67      13C
P67        7.50 usec
PL67       0.00 dB
SFO67      125.7613500 MHz
===== CHANNEL f68 =====
NUC68      13C
P68        7.50 usec
PL68       0.00 dB
SFO68      125.7613500 MHz
===== CHANNEL f69 =====
NUC69      13C
P69        7.50 usec
PL69       0.00 dB
SFO69      125.7613500 MHz
===== CHANNEL f70 =====
NUC70      13C
P70        7.50 usec
PL70       0.00 dB
SFO70      125.7613500 MHz
===== CHANNEL f71 =====
NUC71      13C
P71        7.50 usec
PL71       0.00 dB
SFO71      125.7613500 MHz
===== CHANNEL f72 =====
NUC72      13C
P72        7.50 usec
PL72       0.00 dB
SFO72      125.7613500 MHz
===== CHANNEL f73 =====
NUC73      13C
P73        7.50 usec
PL73       0.00 dB
SFO73      125.7613500 MHz
===== CHANNEL f74 =====
NUC74      13C
P74        7.50 usec
PL74       0.00 dB
SFO74      125.7613500 MHz
===== CHANNEL f75 =====
NUC75      13C
P75        7.50 usec
PL75       0.00 dB
SFO75      125.7613500 MHz
===== CHANNEL f76 =====
NUC76      13C
P76        7.50 usec
PL76       0.00 dB
SFO76      125.7613500 MHz
===== CHANNEL f77 =====
NUC77      13C
P77        7.50 usec
PL77       0.00 dB
SFO77      125.7613500 MHz
===== CHANNEL f78 =====
NUC78      13C
P78        7.50 usec
PL78       0.00 dB
SFO78      125.7613500 MHz
===== CHANNEL f79 =====
NUC79      13C
P79        7.50 usec
PL79       0.00 dB
SFO79      125.7613500 MHz
===== CHANNEL f80 =====
NUC80      13C
P80        7.50 usec
PL80       0.00 dB
SFO80      125.7613500 MHz
===== CHANNEL f81 =====
NUC81      13C
P81        7.50 usec
PL81       0.00 dB
SFO81      125.7613500 MHz
===== CHANNEL f82 =====
NUC82      13C
P82        7.50 usec
PL82       0.00 dB
SFO82      125.7613500 MHz
===== CHANNEL f83 =====
NUC83      13C
P83        7.50 usec
PL83       0.00 dB
SFO83      125.7613500 MHz
===== CHANNEL f84 =====
NUC84      13C
P84        7.50 usec
PL84       0.00 dB
SFO84      125.7613500 MHz
===== CHANNEL f85 =====
NUC85      13C
P85        7.50 usec
PL85       0.00 dB
SFO85      125.7613500 MHz
===== CHANNEL f86 =====
NUC86      13C
P86        7.50 usec
PL86       0.00 dB
SFO86      125.7613500 MHz
===== CHANNEL f87 =====
NUC87      13C
P87        7.50 usec
PL87       0.00 dB
SFO87      125.7613500 MHz
===== CHANNEL f88 =====
NUC88      13C
P88        7.50 usec
PL88       0.00 dB
SFO88      125.7613500 MHz
===== CHANNEL f89 =====
NUC89      13C
P89        7.50 usec
PL89       0.00 dB
SFO89      125.7613500 MHz
===== CHANNEL f90 =====
NUC90      13C
P90        7.50 usec
PL90       0.00 dB
SFO90      125.7613500 MHz
===== CHANNEL f91 =====
NUC91      13C
P91        7.50 usec
PL91       0.00 dB
SFO91      125.7613500 MHz
===== CHANNEL f92 =====
NUC92      13C
P92        7.50 usec
PL92       0.00 dB
SFO92      125.7613500 MHz
===== CHANNEL f93 =====
NUC93      13C
P93        7.50 usec
PL93       0.00 dB
SFO93      125.7613500 MHz
===== CHANNEL f94 =====
NUC94      13C
P94        7.50 usec
PL94       0.00 dB
SFO94      125.7613500 MHz
===== CHANNEL f95 =====
NUC95      13C
P95        7.50 usec
PL95       0.00 dB
SFO95      125.7613500 MHz
===== CHANNEL f96 =====
NUC96      13C
P96        7.50 usec
PL96       0.00 dB
SFO96      125.7613500 MHz
===== CHANNEL f97 =====
NUC97      13C
P97        7.50 usec
PL97       0.00 dB
SFO97      125.7613500 MHz
===== CHANNEL f98 =====
NUC98      13C
P98        7.50 usec
PL98       0.00 dB
SFO98      125.7613500 MHz
===== CHANNEL f99 =====
NUC99      13C
P99        7.50 usec
PL99       0.00 dB
SFO99      125.7613500 MHz
===== CHANNEL f100 =====
NUC100     13C
P100       7.50 usec
PL100      0.00 dB
SFO100     125.7613500 MHz

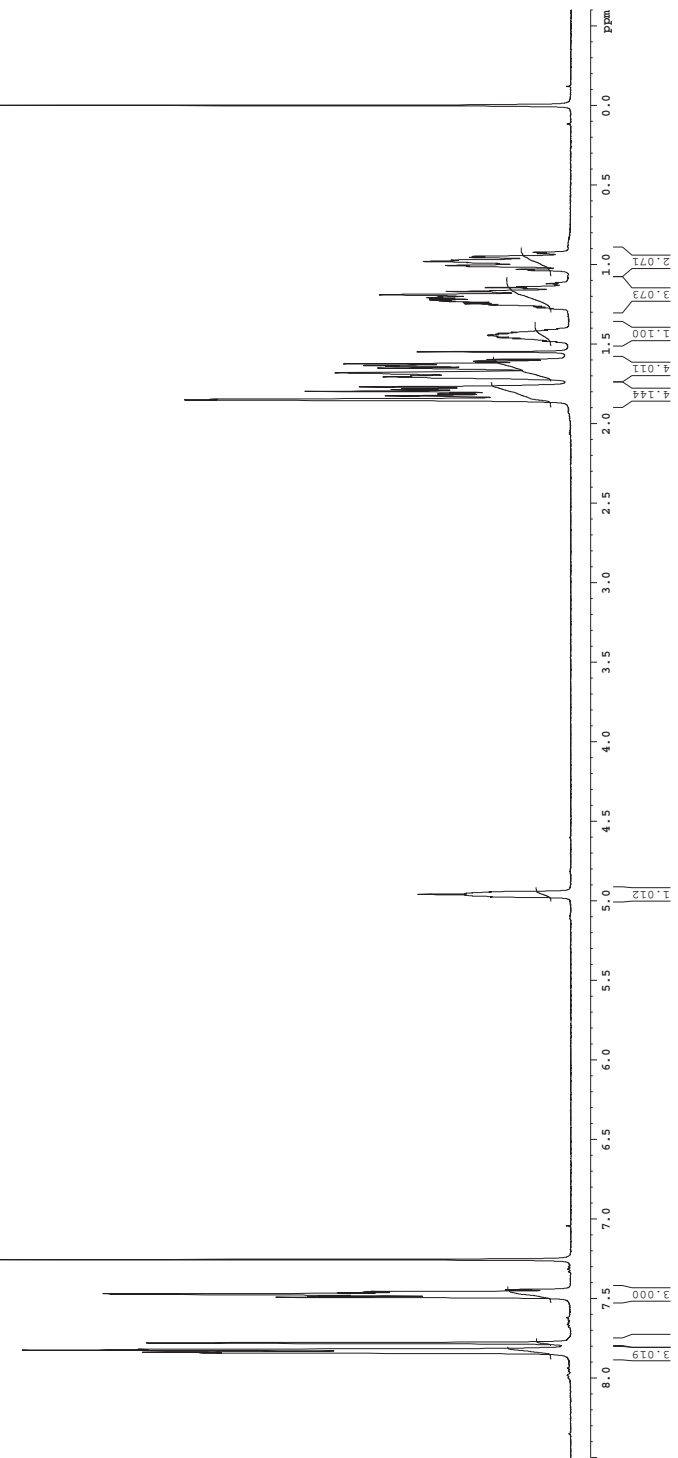
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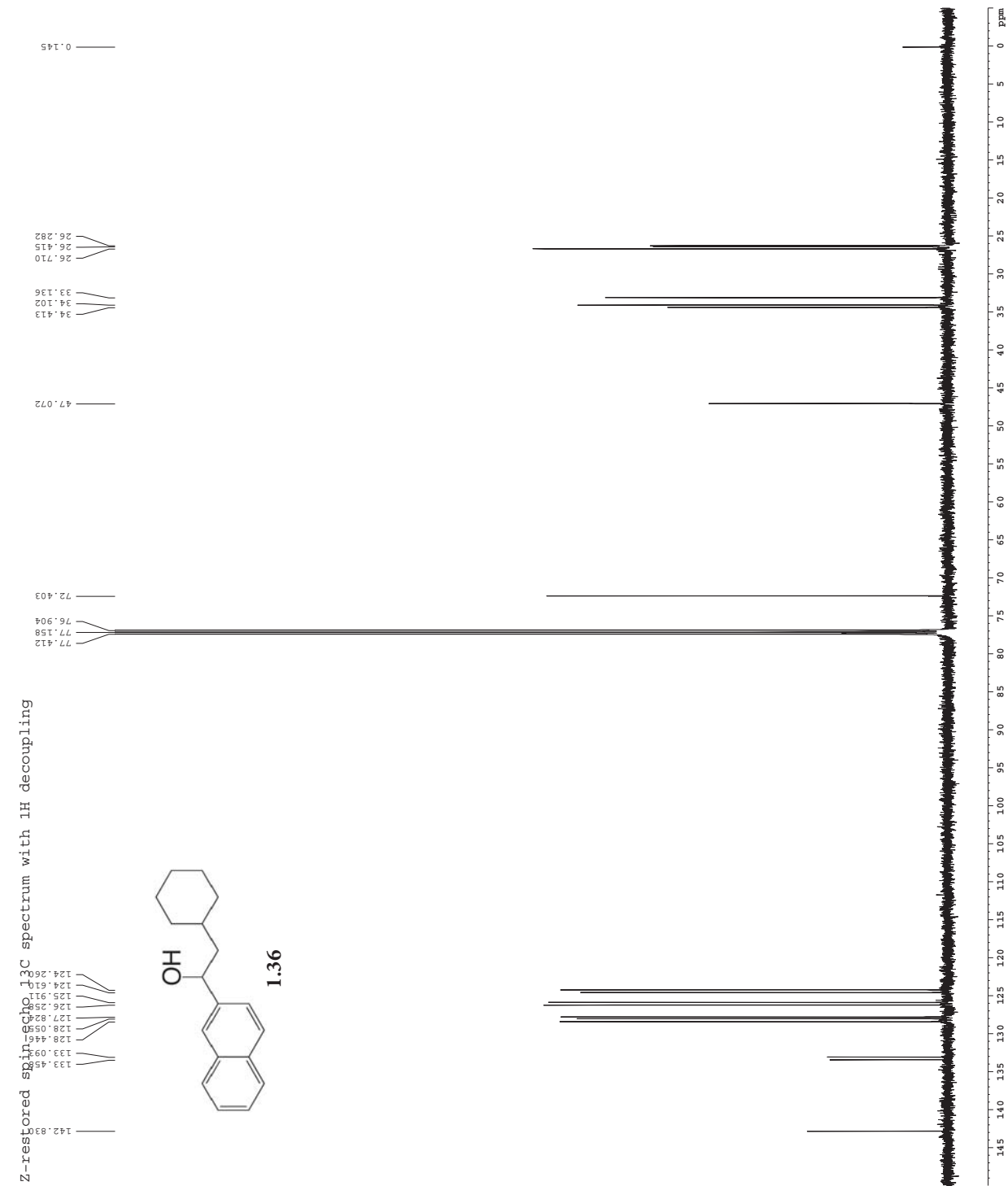
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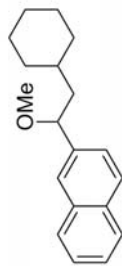
Z-restored spin echo ¹³C spectrum with 1H decoupling

```

Current Data Parameters
NAME      AQ_1_NBP_Cy_OH
PROCNO    1
Date_     20120502
INSTRUM   cryo500
PROBHD    5 mm CPCL1H-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         16
SF         125.7611716 MHz
FIDRES    0.0003688 Hz
AQ         1.0813940 sec
RG         327.500
DM         16.500 usec
DE         6.00 usec
D1         0.25000000 sec
d11        0.03000000 sec
d17        0.00156000 sec
KICKOFF   0.03000000 sec
KICKOFF2  0.03000000 sec
P2         31.00 usec
***** CHANNEL f1 *****
NUC1       13C
P1         12C
P11        500.00 usec
P12        2000.00 usec
PL1        -1.00 dB
PL2        -1.00 dB
SFO1       125.7945280 MHz
SFO2       500.225011 MHz
SP2        CP160
SP2A1      0.5
SP2A2      3.20 dB
SP2A3      CP160CCP-4
SFOFF1     0.00 Hz
SFOFF2     0.00 Hz
***** CHANNEL f2 *****
CPDPRG2   zgpg30
NUC2       1H
P2         12H
P21        100.00 usec
P22        10.00 usec
P23        24.60 dB
P24        24.60 dB
SFO2       500.225011 MHz
***** GRADIENT CHANNEL *****
GNAME1     SINE100
GPA1       0.00 %
GPA2       0.00 %
GPA3       0.00 %
GPA4       0.00 %
GPA5       0.00 %
GPA6       30.00 %
GPA7       30.00 %
GPA8       50.00 %
GPA9       1000.00 usec
P16        1000.00 usec
P17        1000.00 usec
P18        1000.00 usec
P19        1000.00 usec
P20        1000.00 usec
F2 - Processing Parameters
SI         65536
SF         125.7804000 MHz
WDW        EM
SSB        0
GB         1.0 Hz
PC         2.00
  
```



13C spectrum with 1H decoupling



140.459
133.397
133.199
128.441
127.938
127.842
126.155
125.853
125.808
124.636

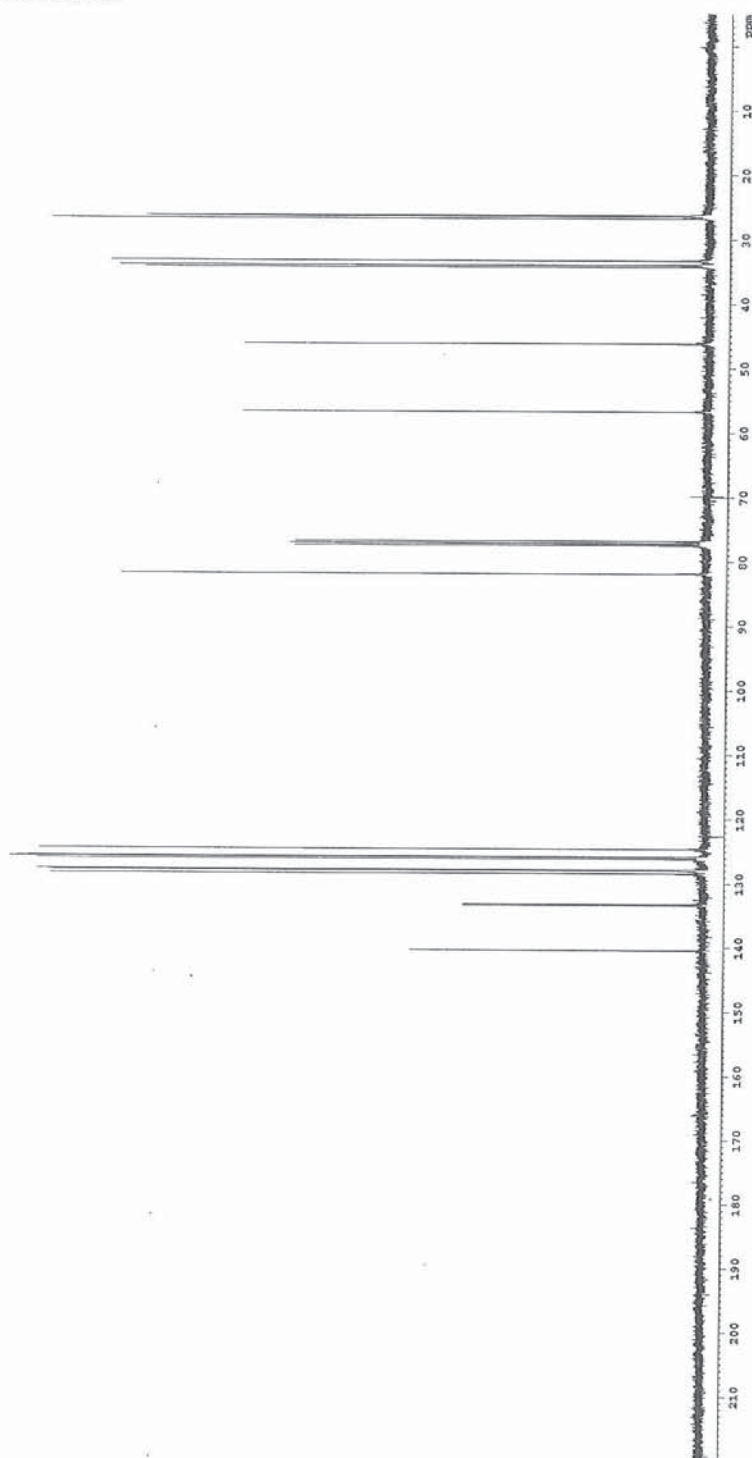
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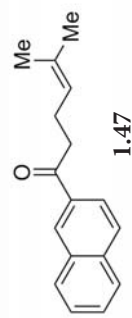
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Current Data Parameters
=====
USER          : ascon1
EXPNO         : 1
PROCNO       : 1
F2 - Acquisition Parameters
=====
Date_         : 20120423
Time         : 11.00
INSTRUM      : dr4540
PROBHD       : 5 mm QNP 1H/13
PULPROG      : zgpg30
TD           : 65536
SOLVENT      : CDCl3
NS           : 1311
DS           : 4
SWH           : 24151.444 Hz
FIDRES       : 0.326970 Hz
AQ           : 1.7756432 sec
RG           : 327.500
DW           : 29.700 uS
DE           : 2.75 uS
TE           : 300.2 K
NUC1         : 13C
NUC2         : 13C
MAGNET       : 400.128000 MHz
MCW1        : 0.0150000 sec
MCW2        : 0.0150000 sec
===== CHANNEL f1 =====
NUC1         : 13C
P1           : 11.300 uS
PL1         : 0.00 dB
SFO1        : 100.623764 MHz
===== CHANNEL f2 =====
CPDPRG2     : waltz16
NUC2         : 13C
PCPD2       : 80.00 uS
PL12        : 18.00 dB
PL13        : 18.00 dB
SFO2        : 400.128000 MHz
F2 - Processing parameters
=====
SI           : 32768
SF           : 100.623764 MHz
WDW          : EM
SSB          : 0
LB           : 1.00 Hz
GB           : 0
PC           : 2.00
    
```



1H spectrum

8.537
8.023
8.001
7.920
7.898
7.859
7.839
7.827
7.574
7.557
7.537
7.510
7.499



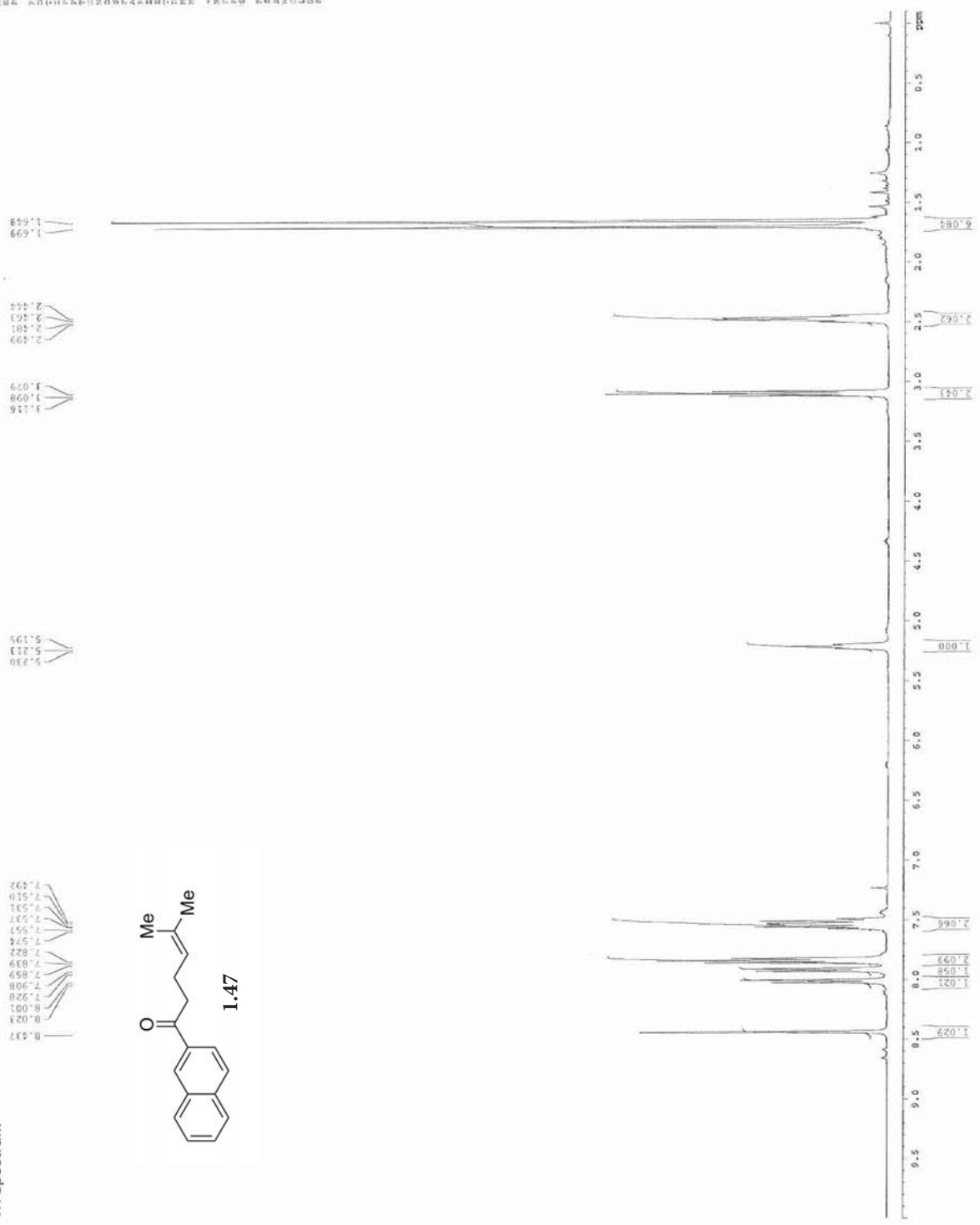
5.230
5.213
5.199

3.116
3.098
3.079

2.499
2.481
2.463
2.444

1.699
1.681

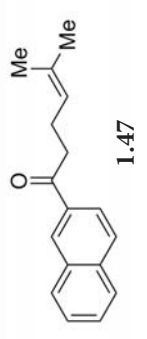
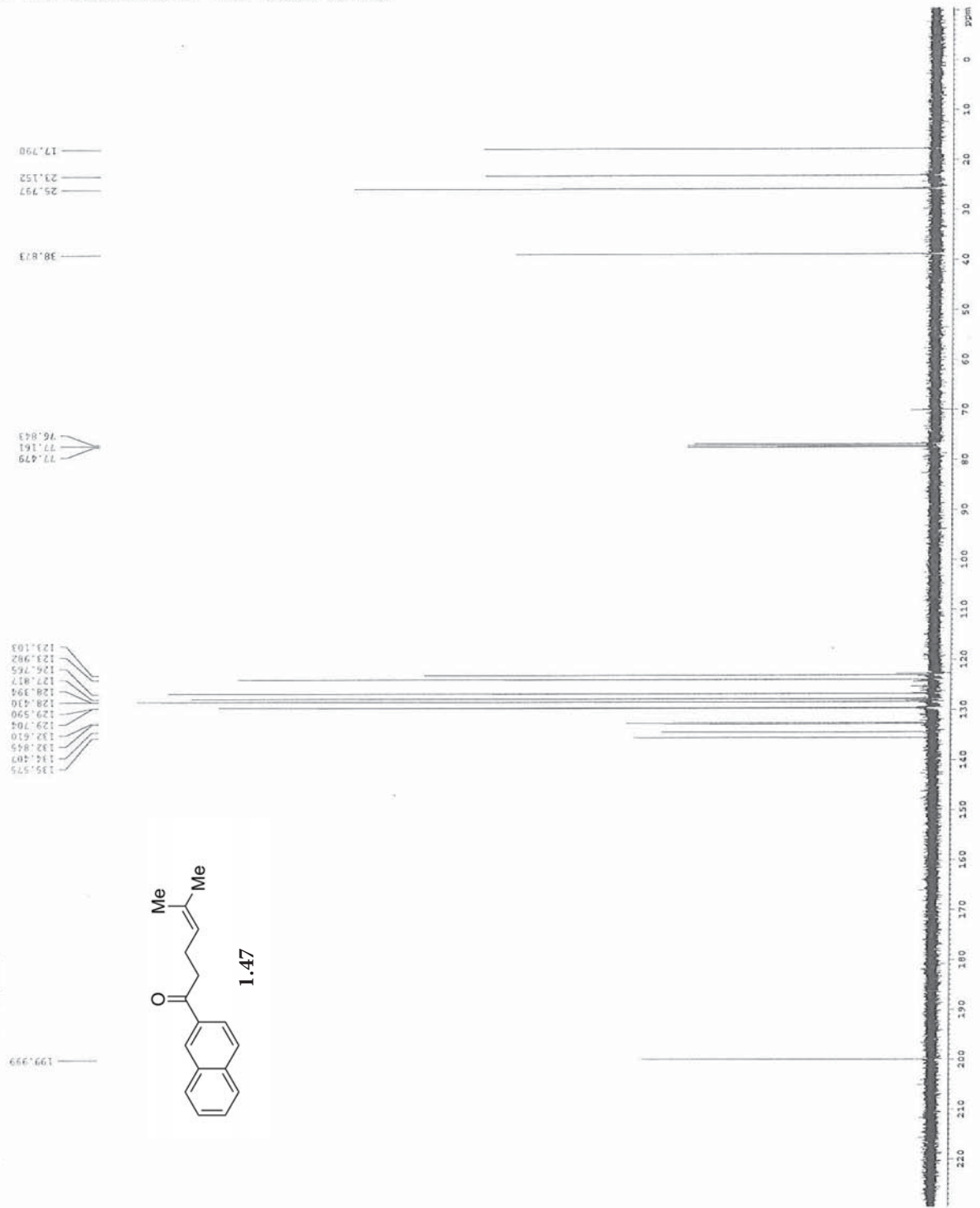
Current Data Parameters
 Date_ Time_ Day_ - MM-DD-YY
 11/01/00 11:51:13 11-01-00
 F1 F2 - Acquisition Parameters
 Date_ Time_ Day_ - MM-DD-YY
 11/01/00 11:51:13 11-01-00
 INSTRUM 5 mm QNP 700D
 PULPROG zgpg30
 TO 65.516
 SOLVENT CDCl3
 NS 8
 DS 4
 SWH 610.342 MHz
 FIDRES 0.1078813 Hz
 AQ 5.1118532 sec
 RG 327.5
 ZW 78.000 umsec
 ZD 0.000000 sec
 DE 1.000000 sec
 TE 298.1 K
 D0 0.000000 sec
 EQU 0.000000 sec
 FIDRES 0.01590000 Hz
 ***** CHANNEL f1 *****
 NUCL1 13C LAC
 P1 10.00 usec
 PL 0.00 dB
 PR 400.132825 MHz
 SF 400.132825 MHz
 F2 - Processing parameters
 Date_ Time_ Day_ - MM-DD-YY
 11/01/00 11:51:13 11-01-00
 INSTRUM 5 mm QNP 700D
 PULPROG zgpg30
 TO 65.516
 SOLVENT CDCl3
 NS 8
 DS 4
 SWH 610.342 MHz
 FIDRES 0.1078813 Hz
 AQ 5.1118532 sec
 RG 327.5
 ZW 78.000 umsec
 ZD 0.000000 sec
 DE 1.000000 sec
 TE 298.1 K
 D0 0.000000 sec
 EQU 0.000000 sec
 FIDRES 0.01590000 Hz
 ***** CHANNEL f2 *****
 NUCL2 1H LAC
 P1 10.00 usec
 PL 0.00 dB
 PR 400.132825 MHz
 SF 400.132825 MHz
 F2 - Processing parameters
 Date_ Time_ Day_ - MM-DD-YY
 11/01/00 11:51:13 11-01-00
 INSTRUM 5 mm QNP 700D
 PULPROG zgpg30
 TO 65.516
 SOLVENT CDCl3
 NS 8
 DS 4
 SWH 610.342 MHz
 FIDRES 0.1078813 Hz
 AQ 5.1118532 sec
 RG 327.5
 ZW 78.000 umsec
 ZD 0.000000 sec
 DE 1.000000 sec
 TE 298.1 K
 D0 0.000000 sec
 EQU 0.000000 sec
 FIDRES 0.01590000 Hz



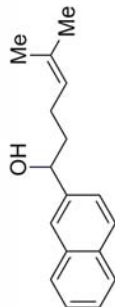
¹³C spectrum with ¹H decoupling

```

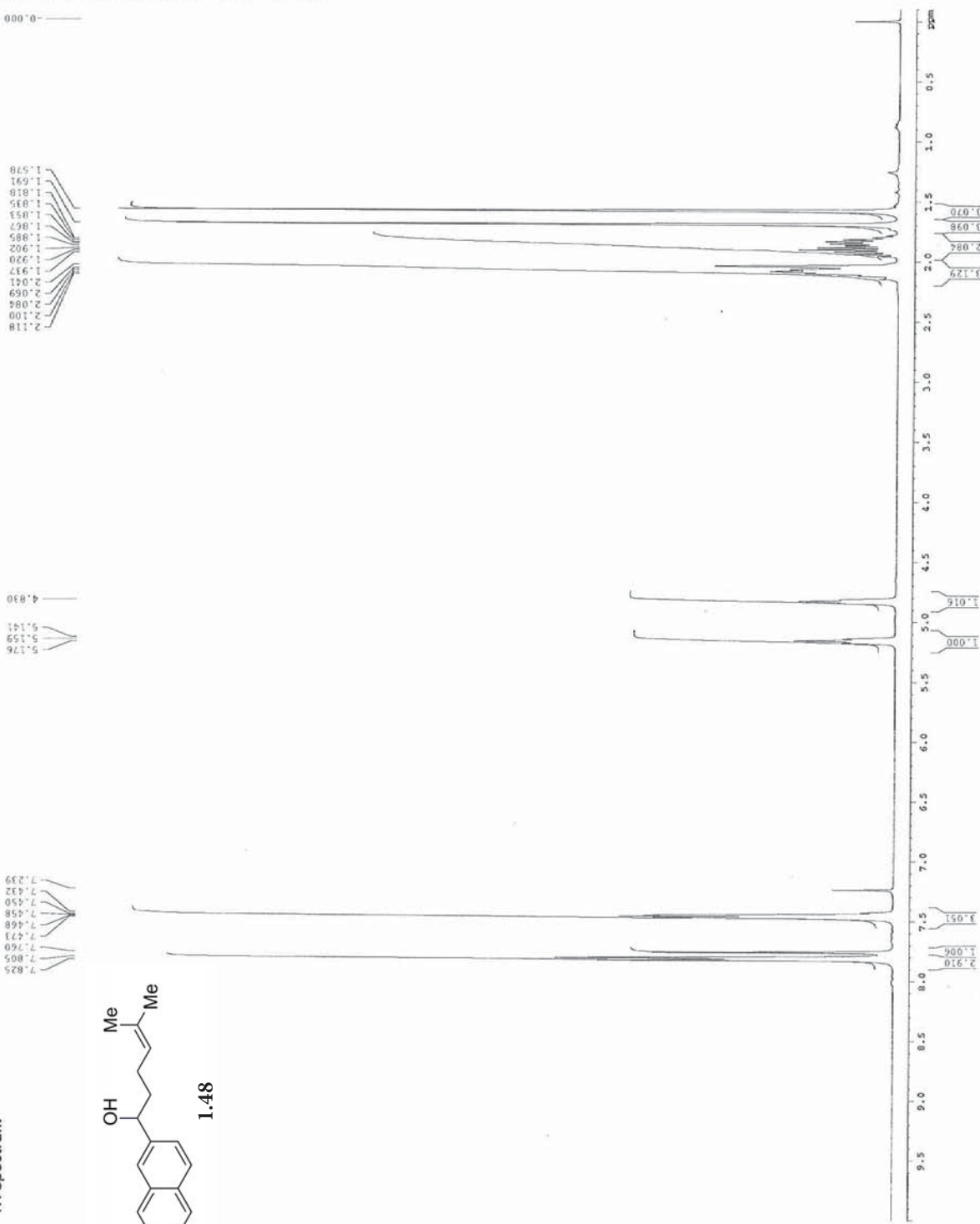
Current Data Parameters
NAME: 1993 - ACS-145
PROCNO: 1
Date_: 2010011
Time: 16:05:00
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
AQ: 0.19519
RG: 327.5
SI: 3275
SF: 125.760
WDW: EM
SSB: 0
GB: 0
PC: 1.00
===== CHANNEL f1 =====
NUC1: 13C
P1: 12.00
PL1: 0.00
SFO1: 100.627764 MHz
===== CHANNEL f2 =====
NUC2: 1H
P2: 80.00
PL2: 0.00
SFO2: 400.128001 MHz
F2 - Processing parameters
SI: 3275
SF: 100.617764 MHz
WDW: EM
SSB: 0
GB: 0
PC: 1.00
  
```



1H spectrum



Current Data Parameters
 Date_ 20100111
 Time_ 11:21
 ExpNO 1
 F2 - Acquisition Parameters
 Date_ 20100111
 Time_ 11:21
 INSTRUM spect
 PROCNO 5
 PULPROG zgpg30
 TD 65536
 SFO 400
 US 2
 CQ 1
 RG 641
 B2 2
 FIDRES 0.107813 Hz
 AQ 5.1118579 sec
 RG 78.000 USAC
 DW 4.75 usec
 DE 2.00 usec
 DI 0.1000000 EVC
 SFO 400.1328000 MHz
 NUC1 1H
 CHANSEL f1
 P1 12.00 usec
 PL 0.00 dB
 PR 400.1328000 MHz
 P2 - Hydroline parameters
 SI 65536
 SF 400.1328000 MHz
 SFO 400.1328000 MHz
 DS 0
 GB 0.00 Hz
 GR 2.00




```

Current Data Parameters
=====
USER      AG_1_propyl_6-7
PRCNO    1
Date_    20110830
INSTRUM  spect
PROBHD   5 mm QNP 1H/1
TD       65536
SOLVENT  CDCl3
DS       2
AQ       0.100000 sec
FIDRES   0.100753 Hz
AQ       5.111879 sec
DM       78.000 usec
DE       4.50 usec
D1       0.10000000 sec
MCHEST   0.00000000 sec
PCPRGR   0.03000000 sec
=====
NUC1     CHANNEL f1 1H
P1       12.00 usec
SFO1     400.1328009 MHz
=====
F2 - Processing Parameters
SI       65536
SF       400.1300464 MHz
SFO2     0.00000000 MHz
SSB      0
GB       0
PC       2.00

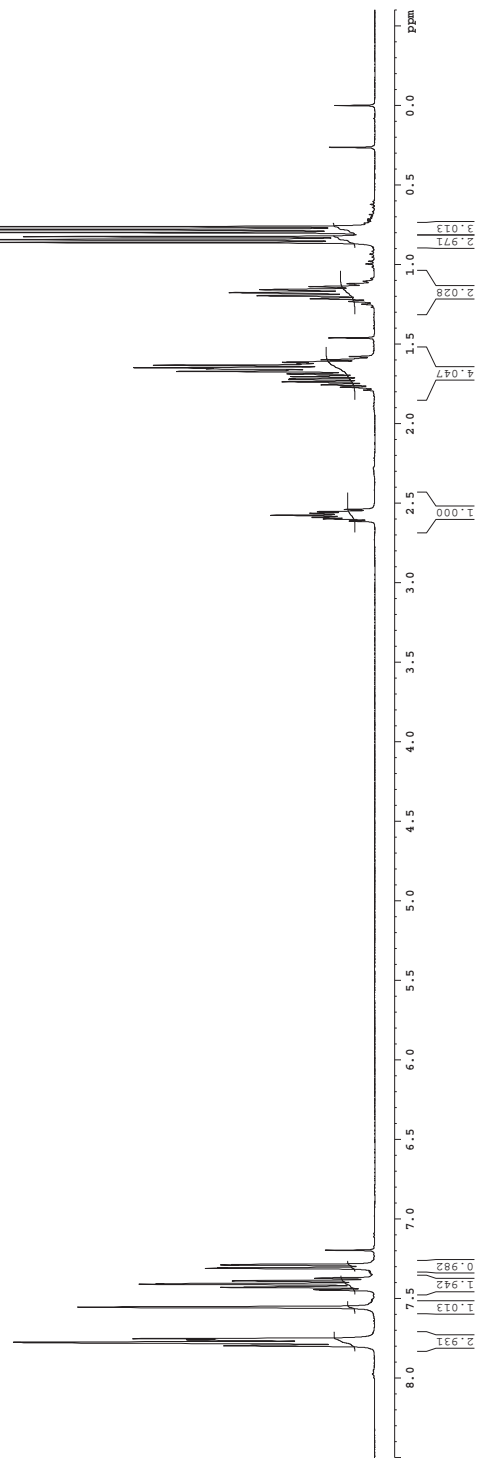
```

0.000
0.264
0.762
0.781
0.799
0.825
0.844
0.862
1.121
1.139
1.158
1.177
1.197
1.216
1.232
1.461
1.579
1.600
1.615
1.621
1.626
1.634
1.650
1.657
1.665
1.673
1.688
1.705
1.719
1.724
1.738
1.757
1.771
2.541
2.554
2.564
2.577
2.590
2.600
2.614

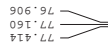
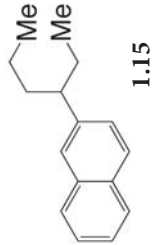
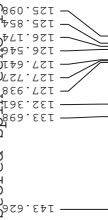
7.198
7.288
7.291
7.309
7.312
7.372
7.375
7.391
7.409
7.412
7.449
7.449
7.754
7.762
7.777
7.799



1.15

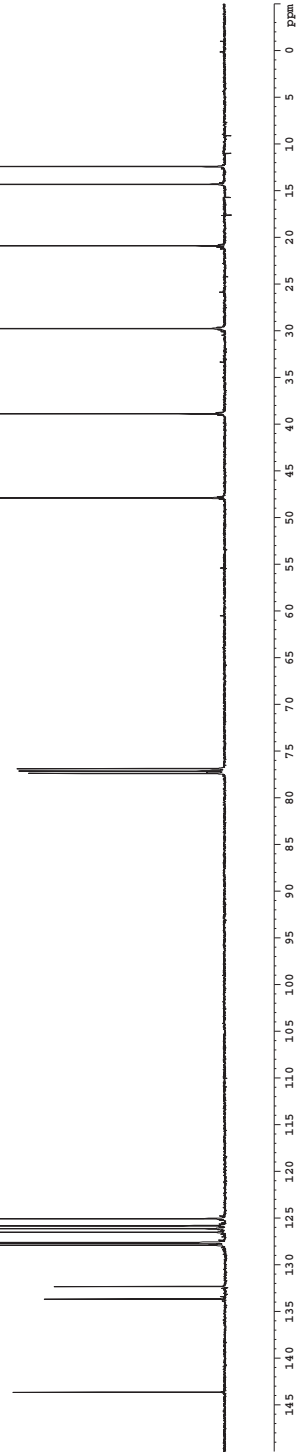


Z-restored spin-echo 13C spectrum with 1H decoupling

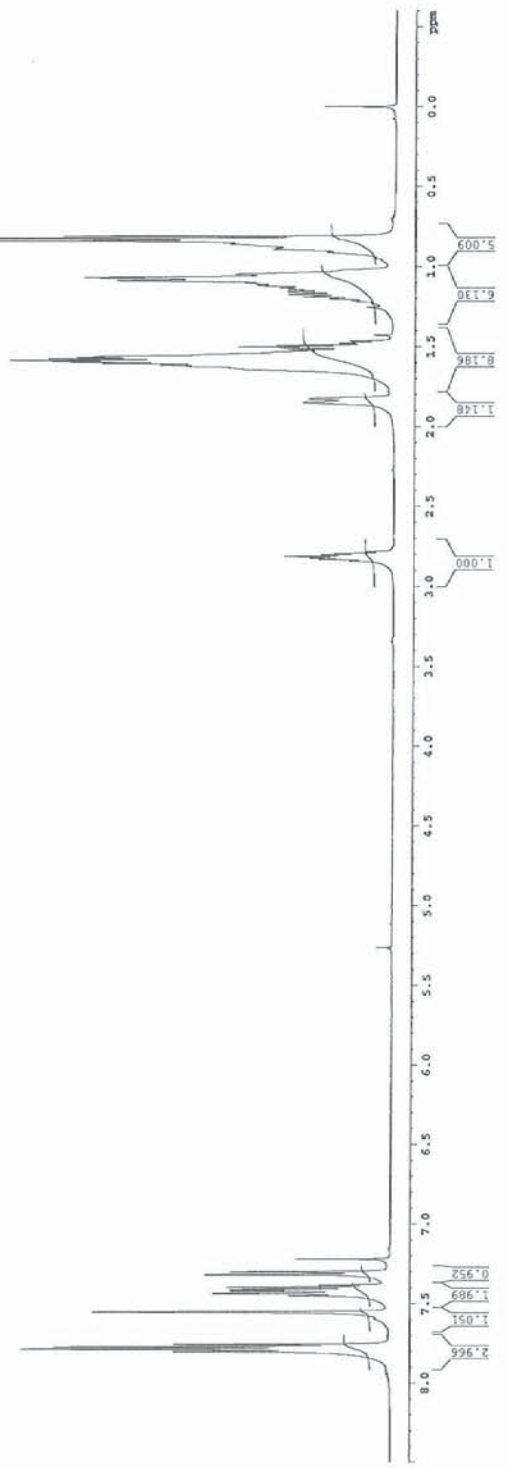
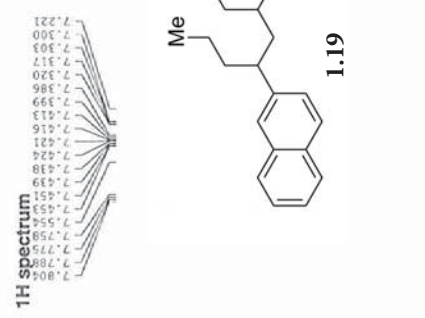
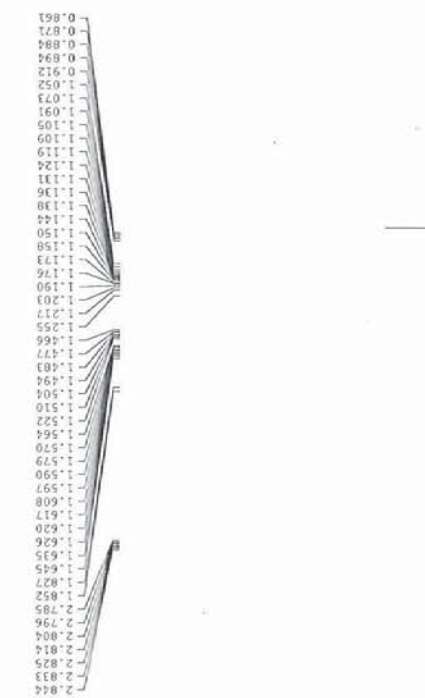


```

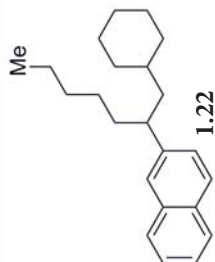
Current Data Parameters
USER          AG3_1_pcp_1
EXPNO        1
PROCNO       1
F2 - Acquisition Parameters
Date_         2011.07
Time          11.07
INSTRUM      spect
PROBHD       5 mm cryo500
PULPROG      zgpg30
TD           65536
AQ           0.0019600
RG           327.5
WDW          EM
SSB          0
GB           0
PC           2.00
===== CHANNEL f1 =====
NUC1          13C
P1            15.50 usec
PL1           0.00 dB
PR1           1.00 usec
RG1           327.5
RF1           125.76011 MHz
SFO1          500.1363011 MHz
SP1           3.20 dB
SFO2          500.1363011 MHz
SFO3          500.2224011 MHz
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          13C
P2            100.00 usec
PL2           0.00 dB
PR2           1.00 usec
RG2           327.5
RF2           125.76011 MHz
SFO2          500.2224011 MHz
SFO3          500.2224011 MHz
===== GRADIENT CHANNEL =====
GPMAX1       SINE.100
GPMAX2       SINE.100
GEX1         0.00 %
GEX2         0.00 %
GPR1         0.00 %
GPR2         0.00 %
GPR3         0.00 %
GPR4         0.00 %
GPR5         0.00 %
GPR6         0.00 %
P15          1000.00 usec
P16          1000.00 usec
F2 - Processing parameters
SI           65536
SF           125.76011 MHz
WDW          EM
SSB          0
GB           0
PC           2.00
  
```



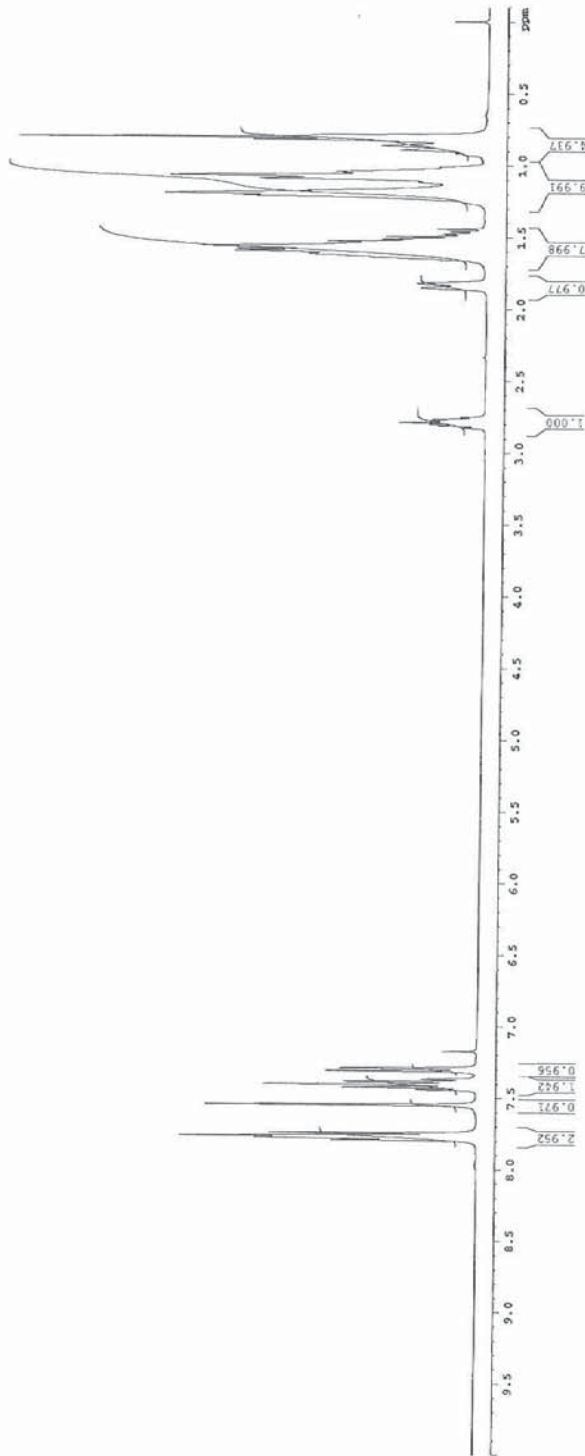
Current Data Parameters
 USER: aarcmj
 NAME: Ac_1_10
 PACNO: 1
 DATE_: 20120522
 TIME: 11:50
 INSTRUM: spect
 PULPROG: zgpg30
 PROCNO: 5
 DS: 2
 SWH: 10000.000
 F2: 500.1362618
 AQ: 0.1000000
 RG: 62.400
 DW: 6.00
 DE: 5.00
 TE: 300.2
 ACQU: 0.1000000
 CHMOD: 0.0100000
 ===== CHANNEL f1 =====
 NU1: 1
 PR1: 7.50
 PL1: 0.00
 SFO1: 500.1362618
 =====
 F4 - Predefined parameters
 PR: 0
 PL: 0
 SFO: 500.1362618
 DS: 2
 SW: 10000.000
 F2: 500.1362618
 AQ: 0.1000000
 RG: 62.400
 DW: 6.00
 DE: 5.00
 TE: 300.2
 ACQU: 0.1000000
 CHMOD: 0.0100000



1H spectrum

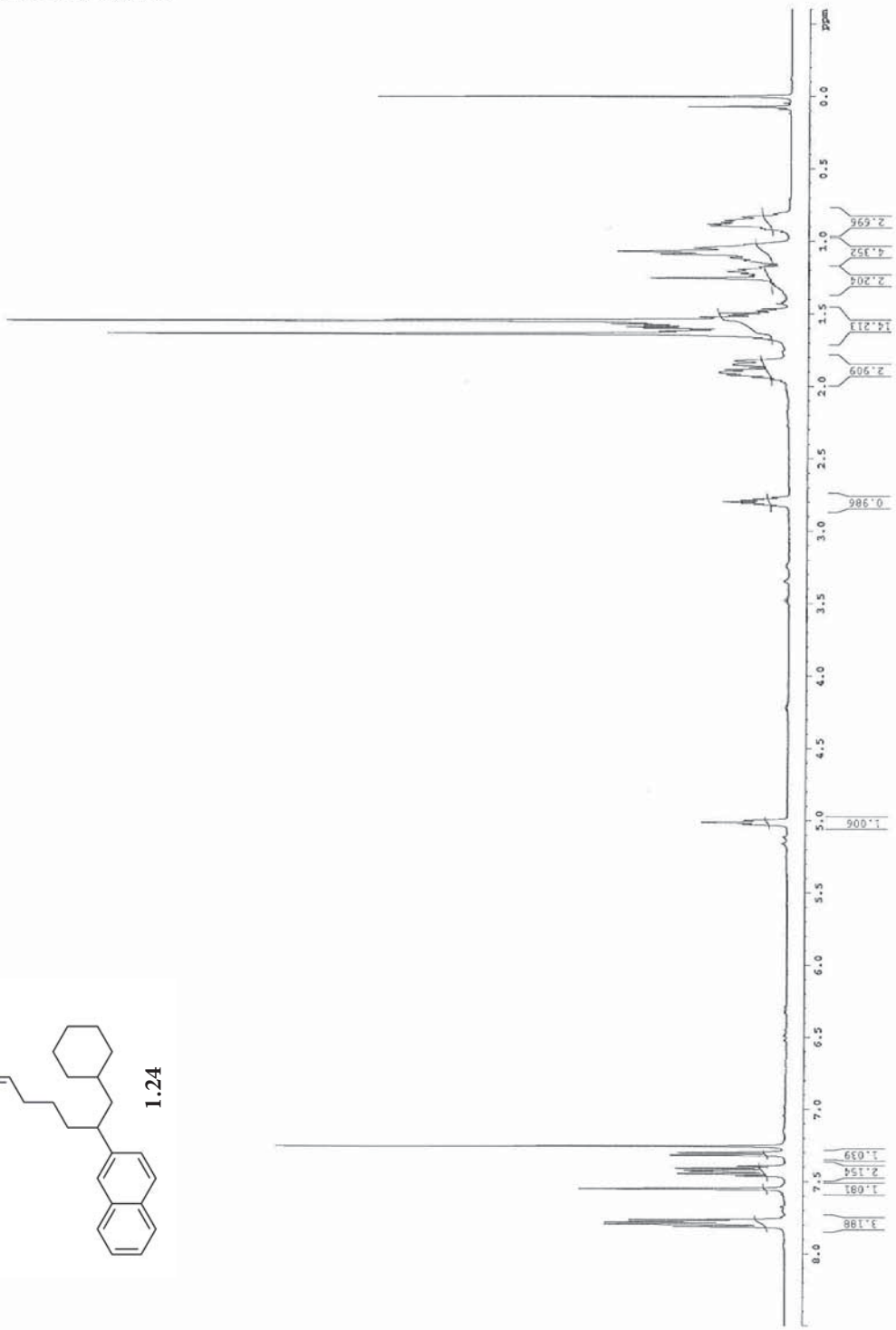
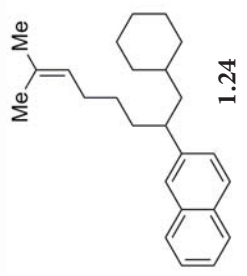


Current Data Parameters
 F2 - Acquisition Parameters
 Date_ 20111209
 Time_ 08:24:20
 Program 5 mm QNP 77YP
 TO 1000 65.36
 SOLVENT ccdcl3
 DS 2
 AS 2
 PS 640.228 Hz
 FID 12.00 usec
 AQ 5.111879 sec
 SFO 400.1328000 MHz
 ZW 78.000 usec
 DE 4.00 usec
 DI 0.1000000 sec
 D1 0.0000000 sec
 D2 0.0000000 sec
 D3 0.0000000 sec
 P1 12.00 usec
 P2 0.0000000 sec
 P3 400.1328000 MHz
 PFO 400.1328000 MHz
 PZ - Processing parameters
 SI 65536
 SF 400.1305400 MHz
 SD 0
 SFO 400.1305400 MHz
 AS 0
 PS 12.00 usec
 PZ 2.00

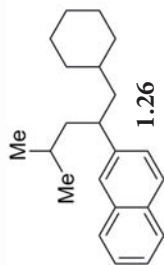



```

Current Data Parameters
=====
USER          : user1
EXPNO         : 1
PROCNO       : 1
PROBHD       : 5 mm CPY-130
P2 - Acquisition Parameters
=====
Date_         : 20101020
Time         : 11:24
INSTRUM      : spect
TD           : 65536
SOLVENT      : CDCl3
NUC1         : 13C
NUC2         : 13C
AQ           : 0.05000000 sec
RG           : 62.400 usec
SI           : 288.00 usec
SF           : 0.13000000 sec
AQ           : 0.05000000 sec
SI           : 288.00 usec
SF           : 0.13000000 sec
===== CHANNEL f1 parameters =====
NUC1         : 13C
P1           : 7.50 usec
PL1         : 0.00000000 dB
SFO1        : 500.2225015 MHz
P2 - Processing parameters
=====
SI           : 65536
SF           : 500.2225015 MHz
WDW         : EM
SSB         : 0
GB          : 0
PC          : 4.00
  
```



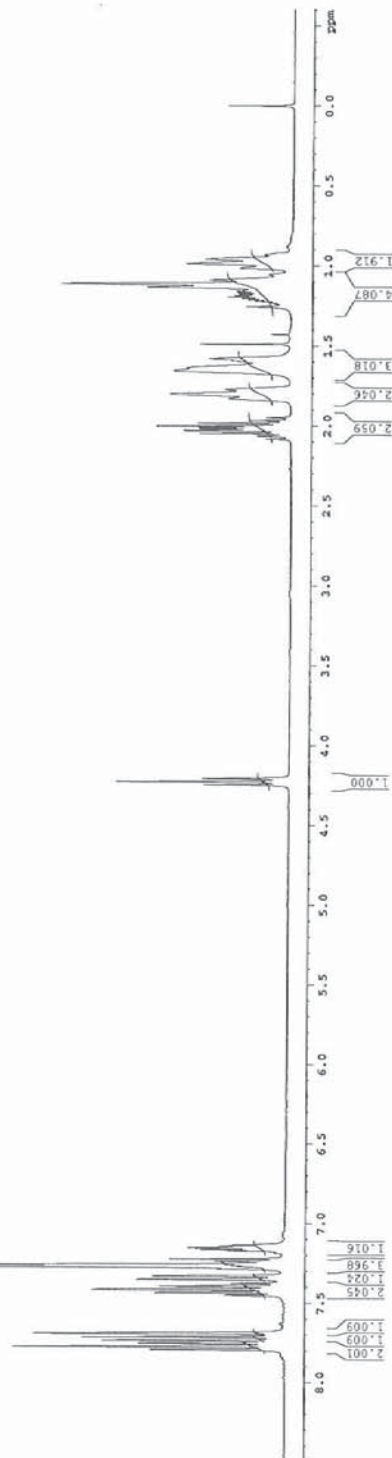
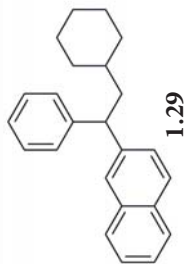
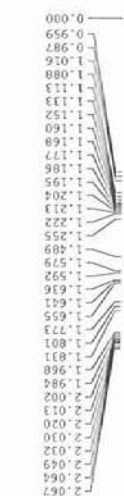
1H spectrum



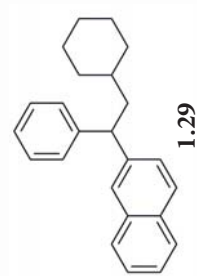
***** CHANNEL f1 *****
 F1 - Processing parameters
 F2 - Processing parameters
 F3 - Processing parameters
 F4 - Processing parameters
 F5 - Processing parameters
 F6 - Processing parameters
 F7 - Processing parameters
 F8 - Processing parameters
 F9 - Processing parameters
 F10 - Processing parameters
 F11 - Processing parameters
 F12 - Processing parameters
 F13 - Processing parameters
 F14 - Processing parameters
 F15 - Processing parameters
 F16 - Processing parameters
 F17 - Processing parameters
 F18 - Processing parameters
 F19 - Processing parameters
 F20 - Processing parameters
 F21 - Processing parameters
 F22 - Processing parameters
 F23 - Processing parameters
 F24 - Processing parameters
 F25 - Processing parameters
 F26 - Processing parameters
 F27 - Processing parameters
 F28 - Processing parameters
 F29 - Processing parameters
 F30 - Processing parameters
 F31 - Processing parameters
 F32 - Processing parameters
 F33 - Processing parameters
 F34 - Processing parameters
 F35 - Processing parameters
 F36 - Processing parameters
 F37 - Processing parameters
 F38 - Processing parameters
 F39 - Processing parameters
 F40 - Processing parameters
 F41 - Processing parameters
 F42 - Processing parameters
 F43 - Processing parameters
 F44 - Processing parameters
 F45 - Processing parameters
 F46 - Processing parameters
 F47 - Processing parameters
 F48 - Processing parameters
 F49 - Processing parameters
 F50 - Processing parameters
 F51 - Processing parameters
 F52 - Processing parameters
 F53 - Processing parameters
 F54 - Processing parameters
 F55 - Processing parameters
 F56 - Processing parameters
 F57 - Processing parameters
 F58 - Processing parameters
 F59 - Processing parameters
 F60 - Processing parameters
 F61 - Processing parameters
 F62 - Processing parameters
 F63 - Processing parameters
 F64 - Processing parameters
 F65 - Processing parameters
 F66 - Processing parameters
 F67 - Processing parameters
 F68 - Processing parameters
 F69 - Processing parameters
 F70 - Processing parameters
 F71 - Processing parameters
 F72 - Processing parameters
 F73 - Processing parameters
 F74 - Processing parameters
 F75 - Processing parameters
 F76 - Processing parameters
 F77 - Processing parameters
 F78 - Processing parameters
 F79 - Processing parameters
 F80 - Processing parameters
 F81 - Processing parameters
 F82 - Processing parameters
 F83 - Processing parameters
 F84 - Processing parameters
 F85 - Processing parameters
 F86 - Processing parameters
 F87 - Processing parameters
 F88 - Processing parameters
 F89 - Processing parameters
 F90 - Processing parameters
 F91 - Processing parameters
 F92 - Processing parameters
 F93 - Processing parameters
 F94 - Processing parameters
 F95 - Processing parameters
 F96 - Processing parameters
 F97 - Processing parameters
 F98 - Processing parameters
 F99 - Processing parameters
 F100 - Processing parameters



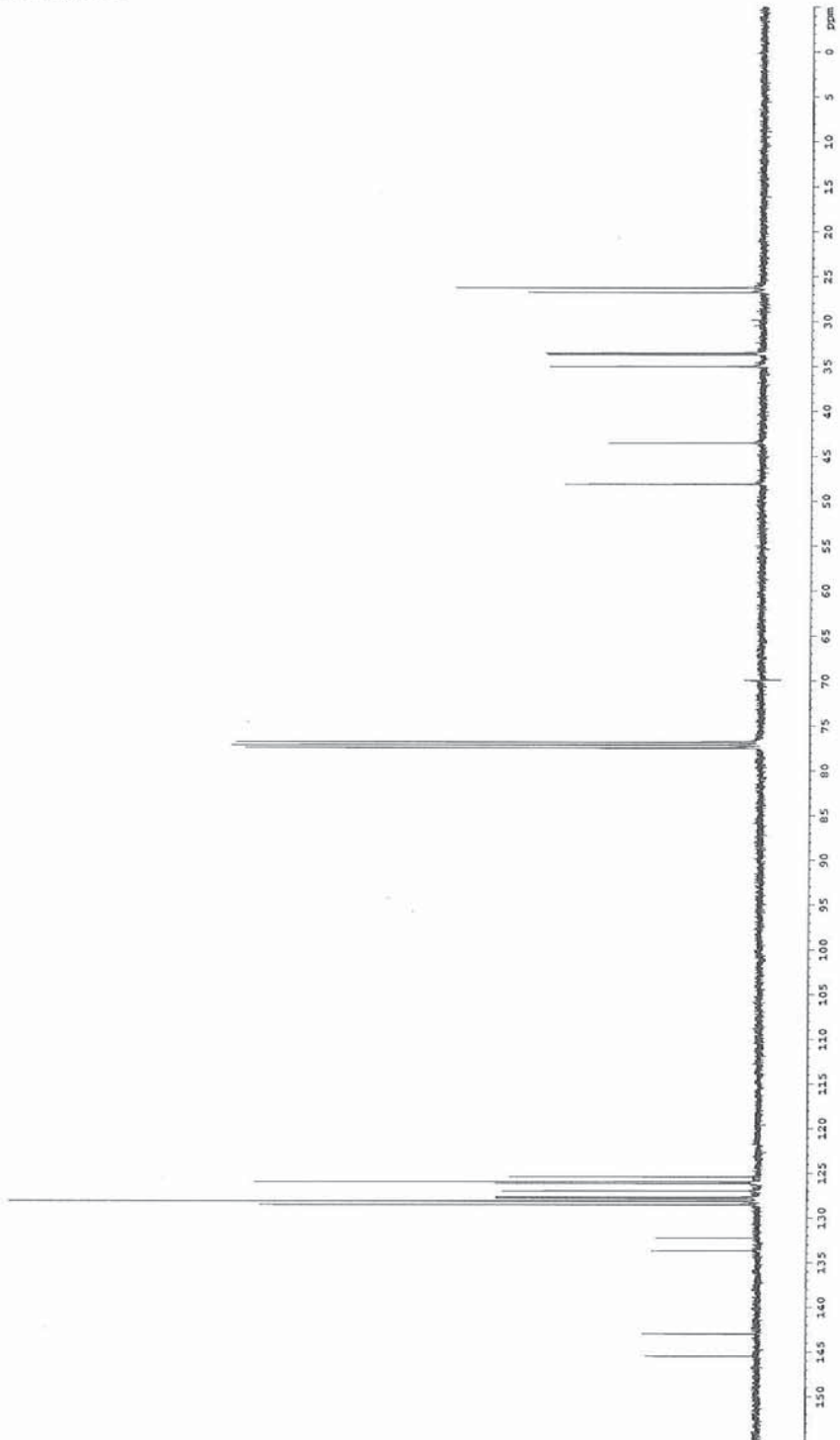
Current Data Parameters
 NAME: AGC_2_231
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20130105
 Time: 11:37
 INSTRUM: 5 mm QNP 1H/13
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 DS: 2
 SWH: 6420.256 MHz
 FIDRES: 0.118972 MHz
 AQRES: 5.118972 MHz
 RG: 78.118 MHz
 DE: 4.50 MHz
 TE: 300.2 K
 D1: 0.10000000 sec
 d11: 0.00000000 sec
 d12: 0.00000000 sec
 d13: 0.01000000 sec
 ===== CHANNEL f1 =====
 P1: 12.00 MHz
 PL1: -0.02 dB
 PR1: 400.130000 MHz
 FFO1: 400.130000 MHz
 ===== CHANNEL f2 =====
 P2: 1.00 MHz
 PL2: 0.00 dB
 PR2: 600.130000 MHz
 FFO2: 600.130000 MHz
 ===== Processing parameters =====
 SI: 32768
 SF: 600.130000 MHz
 DF: 600.130000 MHz
 LB: 0.30 MHz
 GB: 0.00 MHz
 PC: 2.00



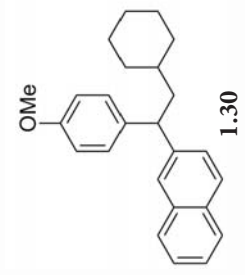
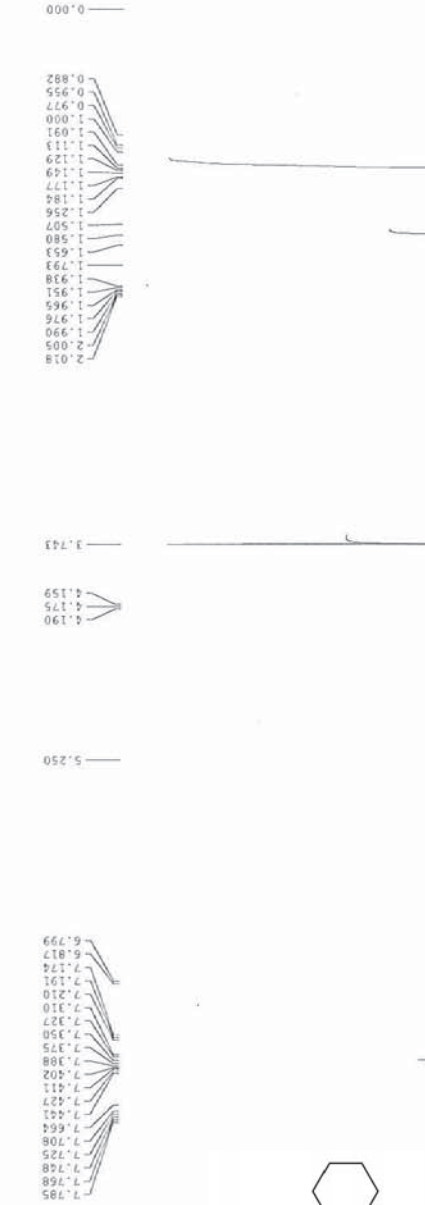
¹³C spectrum with ¹H decoupling



Current Data Parameters
 UZDIR: /usr/local/chem
 NAME: AC_2_31
 PRG/NO: 1
 F2 - Acquisition Parameters
 Date_: 20101001
 Time: 11:00:00
 INSTRUM: spect
 PFRQID: 5 mm QNP 1H/13C
 PFRQF0: 125.761 MHz
 PFRQF1: 500.136099 MHz
 SOLVENT: CDCl3
 NS: 64
 DS: 4
 SWH: 26176.000 Hz
 FWHM: 1.3100000 Hz
 AQ BRGS: 1.3100000 Hz
 SFO: 100.627764 MHz
 IM: 32.100 uSAC
 RE: 20.39 uSAC
 SI: 0.10000000000000000
 d11: 0.01000000000000000
 d12: 0.01000000000000000
 d13: 0.01000000000000000
 d14: 0.01000000000000000
 ***** CHANNEL f1 *****
 P1: 1.30
 PL1: 0.00 dB
 P2: 1.00
 PL2: 0.00 dB
 P3: 1.00
 PL3: 0.00 dB
 P4: 1.00
 PL4: 0.00 dB
 ***** CHANNEL f2 *****
 P1: 1.00
 PL1: 0.00 dB
 P2: 1.00
 PL2: 0.00 dB
 P3: 1.00
 PL3: 0.00 dB
 P4: 1.00
 PL4: 0.00 dB
 ***** CHANNEL f3 *****
 P1: 1.00
 PL1: 0.00 dB
 P2: 1.00
 PL2: 0.00 dB
 P3: 1.00
 PL3: 0.00 dB
 P4: 1.00
 PL4: 0.00 dB
 ***** CHANNEL f4 *****
 P1: 1.00
 PL1: 0.00 dB
 P2: 1.00
 PL2: 0.00 dB
 P3: 1.00
 PL3: 0.00 dB
 P4: 1.00
 PL4: 0.00 dB



Current Data Parameters
 NAME: 14975 - 4912-272
 F2 - Acquisition Parameters
 PULPROG zgpg30
 PROCNO 5
 F2 - Processing parameters
 SI 327
 SF 500.136094 MHz
 DS 4
 AS 0.10 sec
 LA 0
 GB 0
 PC 2.00

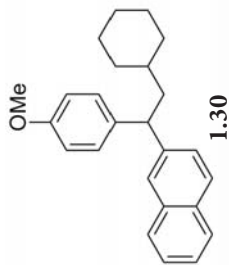
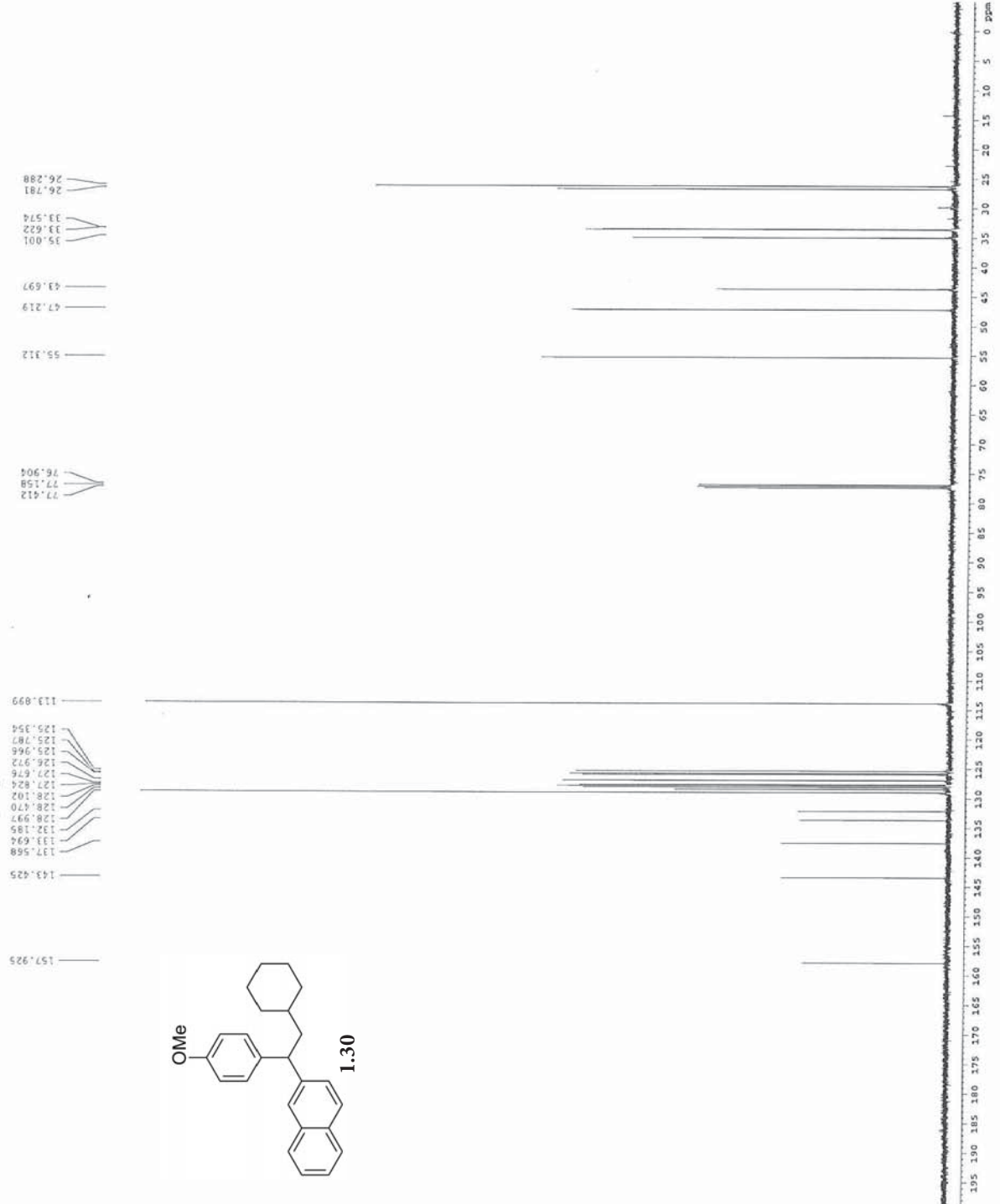


Z-restored spin-echo 13C spectrum with 1H decoupling

```

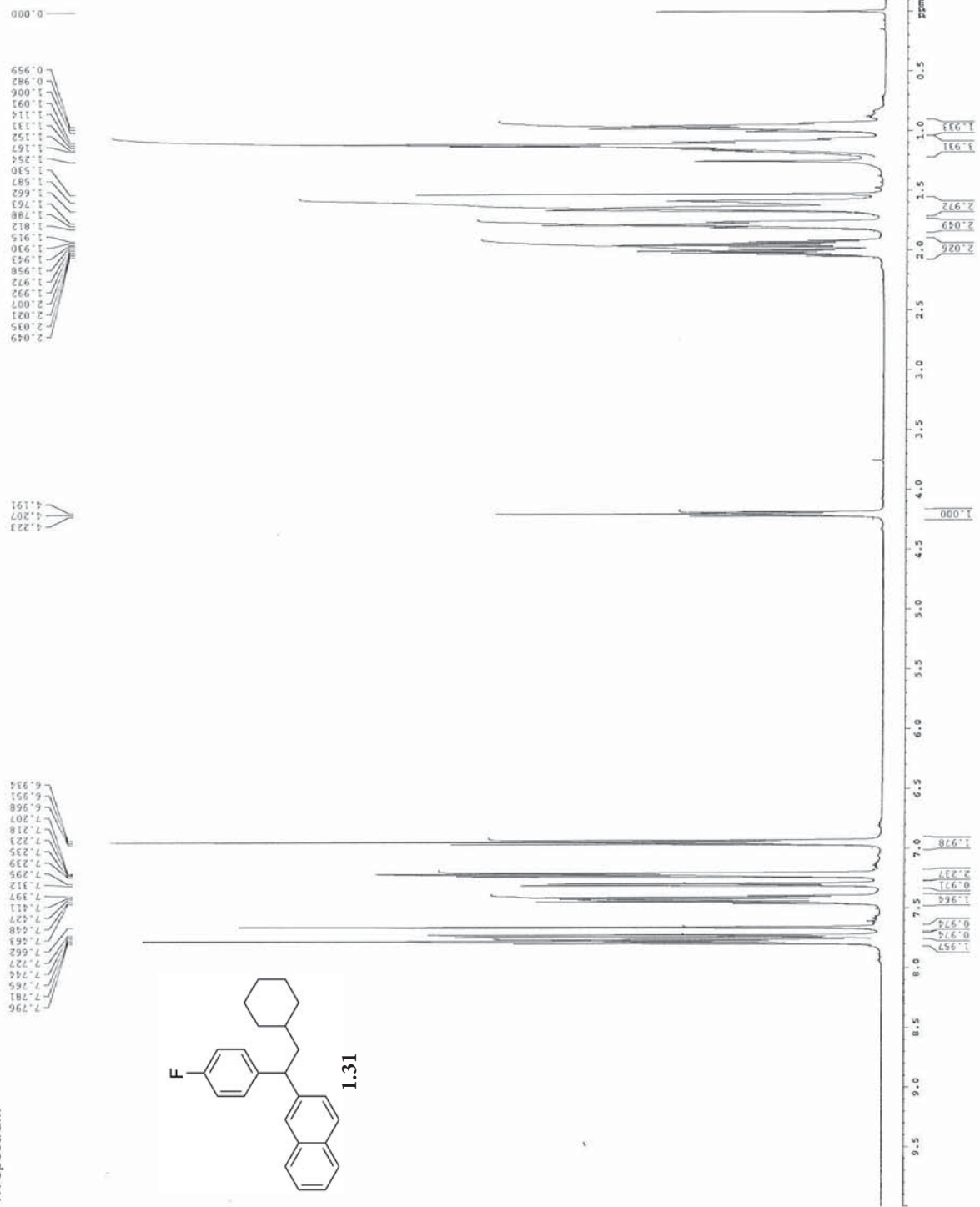
Current Data Parameters
Date_ 20130224
Time_ 09:52:22
INSTRUM spect
PROBHD 5 mm QNP1H1
P1 12.00
PC 4.00
===== CHANNEL f1 =====
NUC1 13C
P1 12.00
PC 4.00
===== CHANNEL f2 =====
NUC2 1H
P1 1.00
PC 4.00
===== CHANNEL f3 =====
NUC3 13C
P1 12.00
PC 4.00
===== CHANNEL f4 =====
NUC4 1H
P1 1.00
PC 4.00
===== CHANNEL f5 =====
NUC5 13C
P1 12.00
PC 4.00
===== CHANNEL f6 =====
NUC6 1H
P1 1.00
PC 4.00
===== CHANNEL f7 =====
NUC7 13C
P1 12.00
PC 4.00
===== CHANNEL f8 =====
NUC8 1H
P1 1.00
PC 4.00
===== CHANNEL f9 =====
NUC9 13C
P1 12.00
PC 4.00
===== CHANNEL f10 =====
NUC10 1H
P1 1.00
PC 4.00
===== CHANNEL f11 =====
NUC11 13C
P1 12.00
PC 4.00
===== CHANNEL f12 =====
NUC12 1H
P1 1.00
PC 4.00
===== CHANNEL f13 =====
NUC13 13C
P1 12.00
PC 4.00
===== CHANNEL f14 =====
NUC14 1H
P1 1.00
PC 4.00
===== CHANNEL f15 =====
NUC15 13C
P1 12.00
PC 4.00
===== CHANNEL f16 =====
NUC16 1H
P1 1.00
PC 4.00
===== CHANNEL f17 =====
NUC17 13C
P1 12.00
PC 4.00
===== CHANNEL f18 =====
NUC18 1H
P1 1.00
PC 4.00
===== CHANNEL f19 =====
NUC19 13C
P1 12.00
PC 4.00
===== CHANNEL f20 =====
NUC20 1H
P1 1.00
PC 4.00
===== CHANNEL f21 =====
NUC21 13C
P1 12.00
PC 4.00
===== CHANNEL f22 =====
NUC22 1H
P1 1.00
PC 4.00
===== CHANNEL f23 =====
NUC23 13C
P1 12.00
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NUC98 1H
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PC 4.00
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PC 4.00
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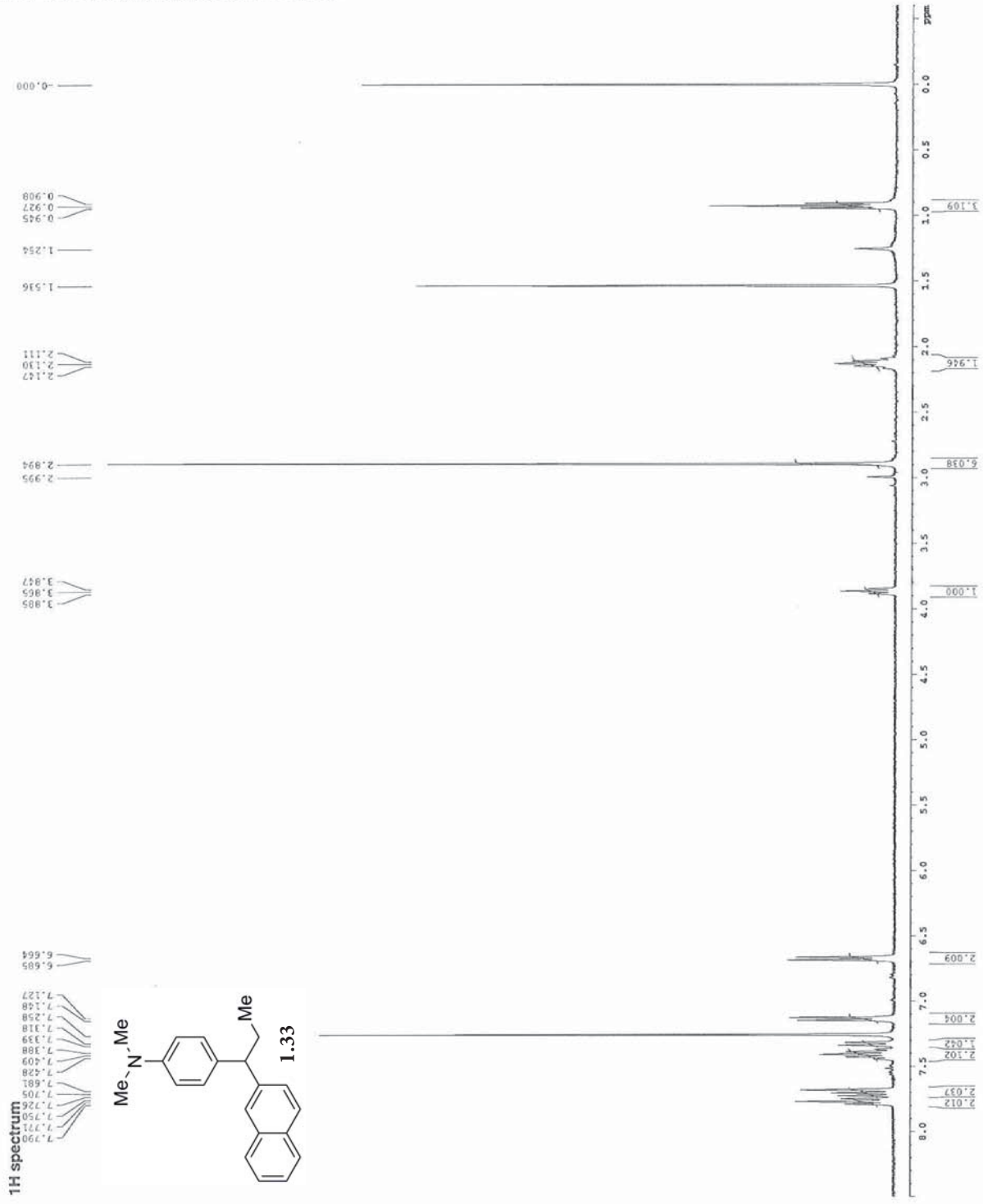
1H spectrum

Current Data Parameters
 NAME: Yonova
 EXPNO: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_ : 20130211
 Time: 11:00:00
 INSTRUM: spect
 PULPROG: zgpg30
 PRGNAME: 3 90c c13c1 21c
 F2: 100.626130
 AQ: 0.1278
 SOLVENT: CDCl3
 NS: 2
 DS: 4
 SWH: 8672.142 Hz
 FIDRES: 0.088621 Hz
 AQ: 5.088939 sec
 DE: 67.400 usec
 TE: 300.2 K
 SH: 0.000000 sec
 SI: 32768
 SF: 0.1000000 sec
 D1: 0.1000000 sec
 d11: 0.000000 sec
 DECI: 0.0150000 sec
 AROMATIC: 0.0150000 sec
 ===== CHANNEL f1 =====
 NUC1: 13C
 P1: 1.20 usec
 PL1: 0 dB
 SFO1: 100.626130 MHz
 F2 - Processing parameters
 SI: 32768
 SF: 100.626130 MHz
 MDW: 0.000000 sec
 SSB: 0.000000 sec
 GB: 0.000000 sec
 CH: 0.000000 sec
 PC: 2.00

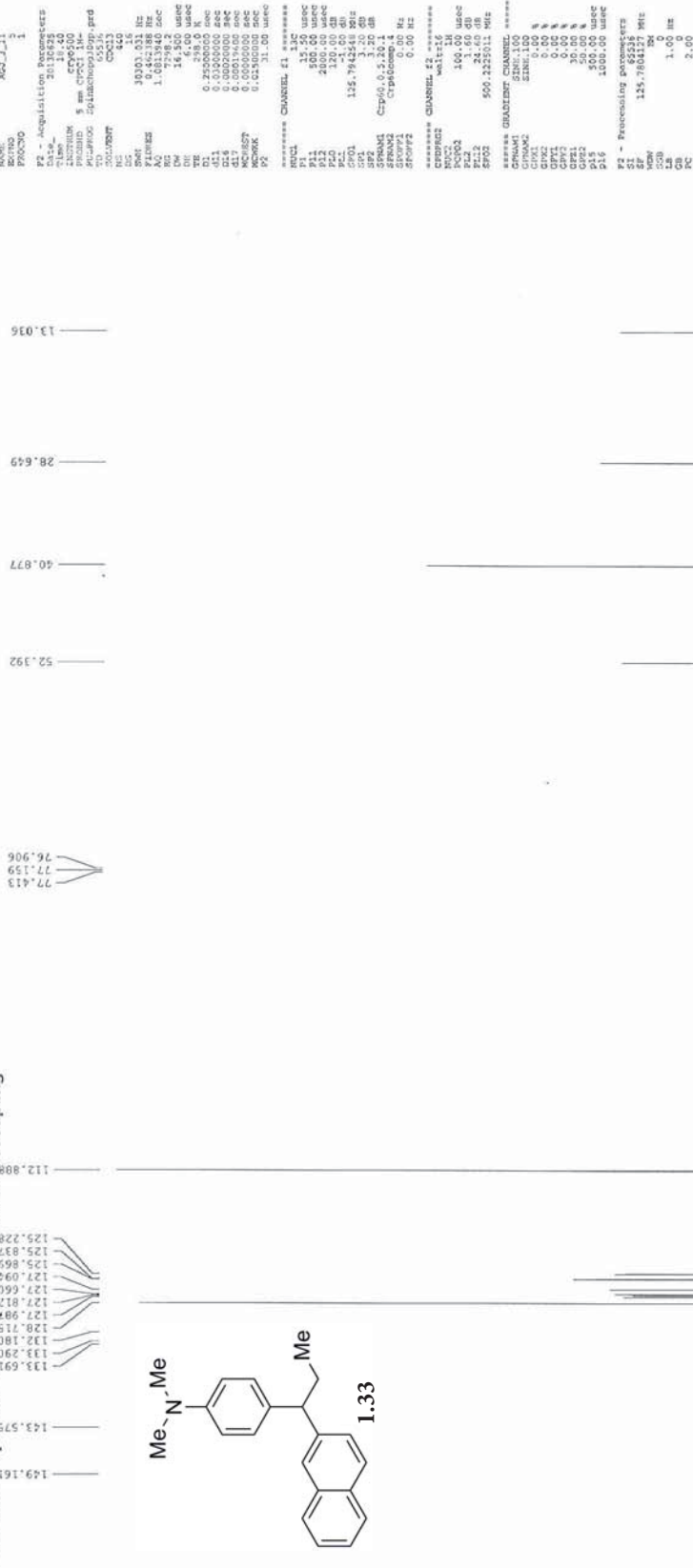


Current Data Parameters
 DIR: 40001
 EXPNO: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20171221
 Time: 05:40:00
 INSTRUM: spect
 PULPROG: zgpg30
 TD: 65536
 SFO: 400.1326000
 ACQ: 2
 PC: 8
 CQ: 2
 SI: 6410.262
 SF: 0.959513 Hz
 FIDRES: 5.1110379 Hz
 AQ: 78.000 usac
 SFO: 400.1326000
 SI: 2877.0
 SC: 2877.0
 DC: 0.1000000 Hz
 SFO: 400.1326000
 SI: 0.0150000 Hz
 SC: 0.0150000 Hz
 PC: 2.00

***** CHANNEL f1 *****
 NUCL1: 1H
 P1: 12.00 usac
 PL1: 0.00 dB
 SFO1: 400.1326000 MHz
 F2 - Processing parameters
 SI: 65536
 SFO: 400.1326000 MHz
 SC: 0.0150000 Hz
 PC: 2.00



Z-restored spin-echo ¹³C spectrum with ¹H decoupling



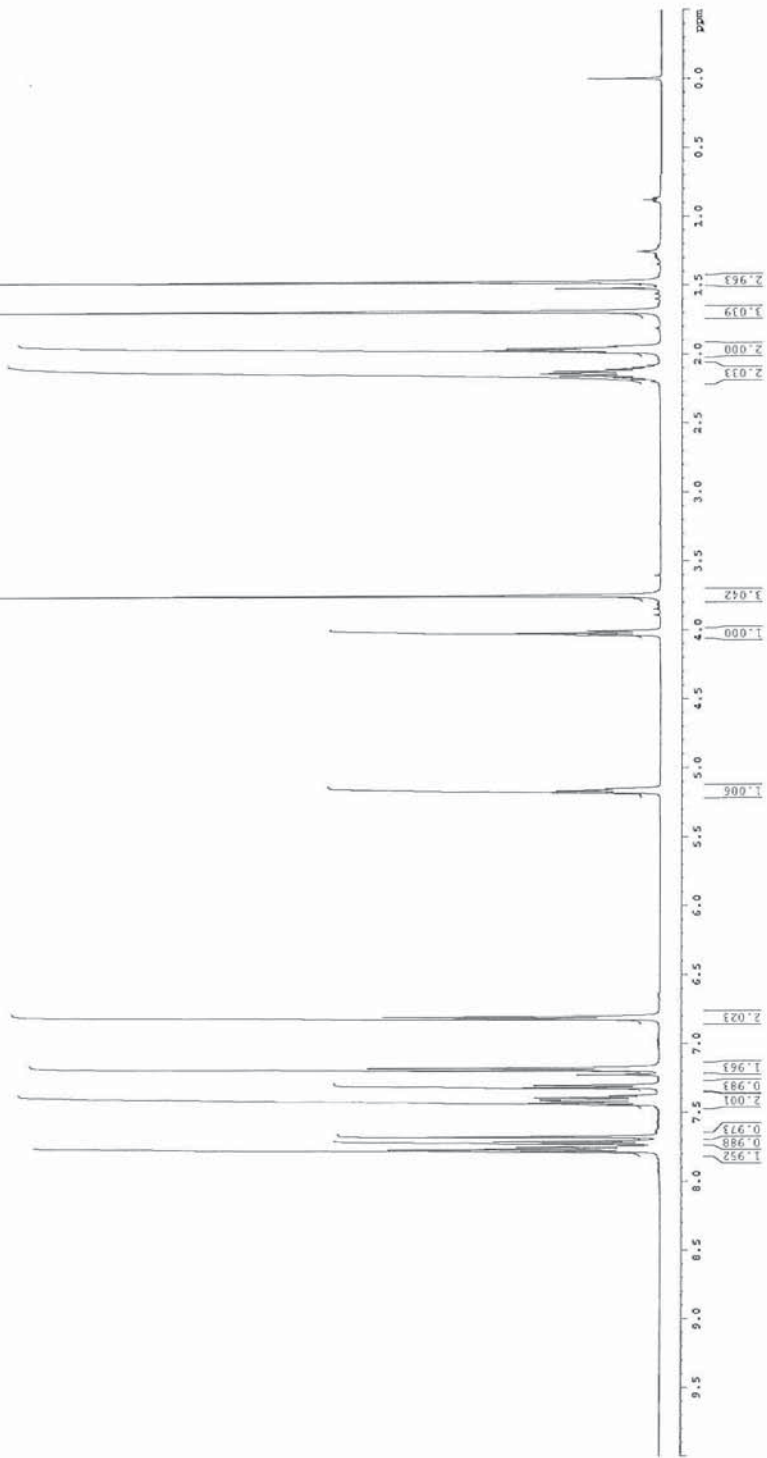
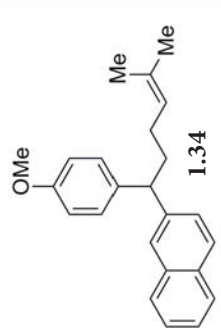
¹H spectrum

Current Data Parameters
 USDF YPOVA
 IDVNO 1073 - 40111
 PRGNO 11
 P2 - Acquisition Parameters
 DATE_ 201112
 TIME_ 20:21:12
 INSTRUM 5 IN CPY010
 NUC1 13C
 PULPROG zgpg30
 TO F2
 ACQ 1278
 NO 8
 NS 8
 DS 4
 SWH 1031.462 MHz
 F2 101.625 MHz
 P2 0.09841 sec
 SFO1 500.1360513 MHz
 AQC 5.09997 sec
 RG 6.3 sec
 ZW 62.500 MHz
 TE 298.0 K
 D1 0.10000000 sec
 DELT 0.10000000 sec
 ADEL 0.10000000 sec
 MCHN1 0.01300000 sec
 ***** CHANNEL F1 *****
 NUC1 1H
 PULPROG zgpg30
 TO F1
 ACQ 1.765 sec
 NO 8
 DS 4
 SWH 500.2235013 MHz
 F2 500.1360513 MHz
 P2 0.09841 sec
 SFO1 500.2235013 MHz
 AQC 5.09997 sec
 RG 6.3 sec
 ZW 62.500 MHz
 TE 298.0 K
 D1 0.10000000 sec
 DELT 0.10000000 sec
 ADEL 0.10000000 sec
 MCHN1 0.01300000 sec

2.171
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2.143
2.124
2.109
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5.179
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5.151

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7.176
7.162
6.804



Current Data Parameters
 USER LME-1-fy-niet-zh
 NAME lucase
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 2011120
 Time_ 11.00
 INSTRUM crys400
 PROBMG 5 mm CPY1.1H-
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 DS 2
 SWH 812.56 Hz
 FIDRES 0.220026 Hz
 AQ 1.9958451 sec
 RM 0.00000000
 DM 62.400 usec
 DE 6.00 usec
 DI 0.10000000 sec
 D1 0.00000000 sec
 MCHSET 0.00000000 sec
 MONR 0.03000000 sec
 NUC1 ***** CHANNEL f1 *****
 P1 7.50 usec
 PL1 0.00 dB
 SFO1 500.2335015 MHz
 F2 - Processing Parameters
 SI 65536
 SF 500.2335015 MHz
 SSF 0.00000000
 SSB 0 Hz
 GB 0 Hz
 PC 4.00

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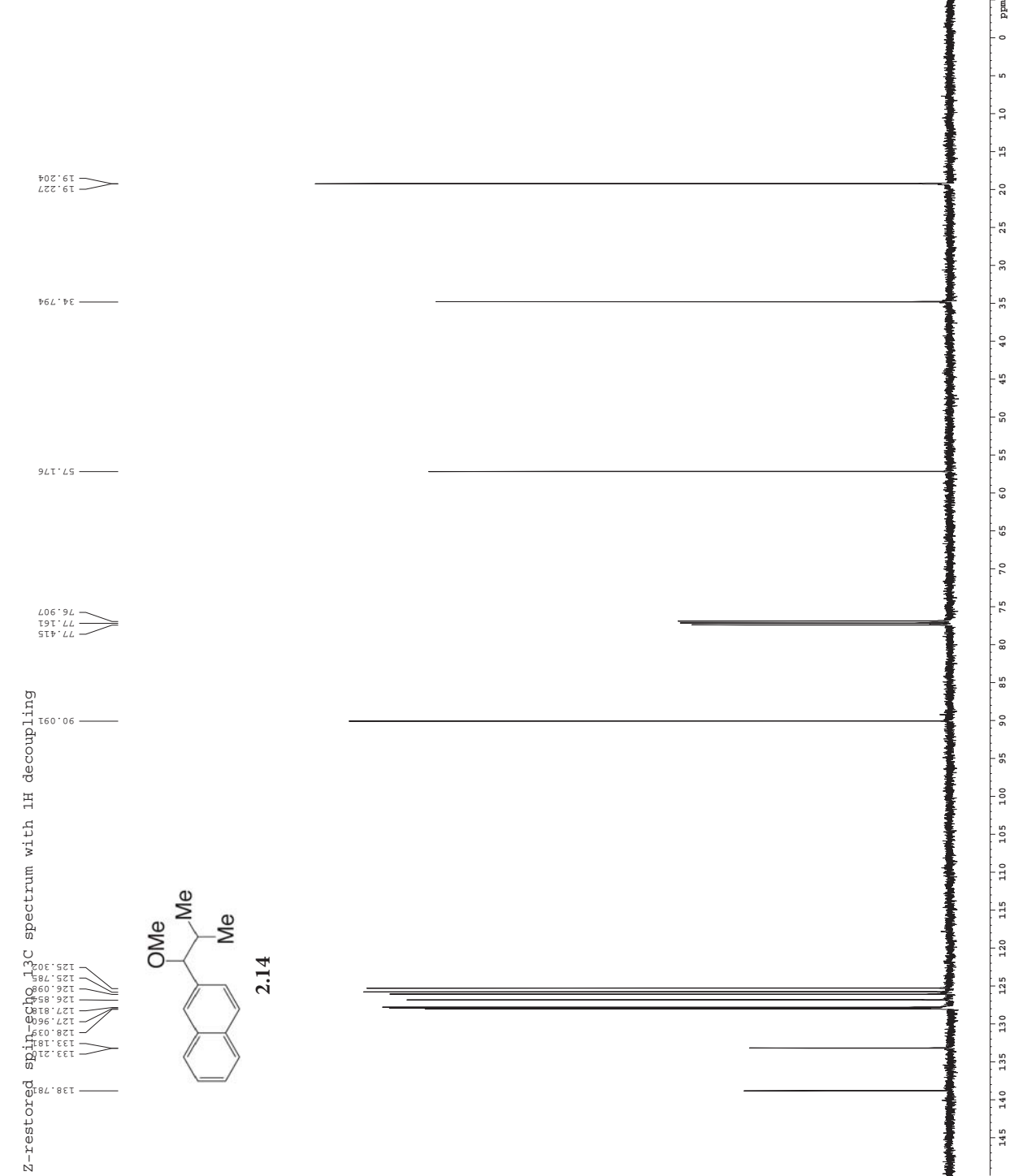
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Current Data Parameters
USER      LME-1-fy-het-2c
NAME      LME-1-fy-het-2c
PROCNO    1
F2 - Acquisition Parameters
Date_     2011120
Time      16:55:00
INSTRUM   crys500
PROBHD    5 mm CPCL1H-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         8
SS         3192.488
AQ         0.092388 Hz
RG         1.0813940 sec
DM         16.500 usec
DE         6.00 usec
DI         0.25000000 sec
D11        0.03000000 sec
d17        0.00116600 sec
MCKBKT     0.03000000 sec
MCKWBK     0.03000000 sec
P2         31.00 usec
***** CHANNEL f1 *****
NUC1       13C
P1         12C
P11        500.00 usec
P12        2000.00 usec
P13        -1.00 dB
P14        -1.00 dB
SFO1       125.7945280 MHz
SFO2       500.2225011 MHz
SFO3       500.2225011 MHz
SFO4       500.2225011 MHz
SFO5       500.2225011 MHz
SFO6       500.2225011 MHz
SFO7       500.2225011 MHz
SFO8       500.2225011 MHz
SFO9       500.2225011 MHz
SFO10      500.2225011 MHz
SFO11      500.2225011 MHz
SFO12      500.2225011 MHz
SFO13      500.2225011 MHz
SFO14      500.2225011 MHz
SFO15      500.2225011 MHz
SFO16      500.2225011 MHz
SFO17      500.2225011 MHz
SFO18      500.2225011 MHz
SFO19      500.2225011 MHz
SFO20      500.2225011 MHz
SFO21      500.2225011 MHz
SFO22      500.2225011 MHz
SFO23      500.2225011 MHz
SFO24      500.2225011 MHz
SFO25      500.2225011 MHz
SFO26      500.2225011 MHz
SFO27      500.2225011 MHz
SFO28      500.2225011 MHz
SFO29      500.2225011 MHz
SFO30      500.2225011 MHz
SFO31      500.2225011 MHz
SFO32      500.2225011 MHz
SFO33      500.2225011 MHz
SFO34      500.2225011 MHz
SFO35      500.2225011 MHz
SFO36      500.2225011 MHz
SFO37      500.2225011 MHz
SFO38      500.2225011 MHz
SFO39      500.2225011 MHz
SFO40      500.2225011 MHz
SFO41      500.2225011 MHz
SFO42      500.2225011 MHz
SFO43      500.2225011 MHz
SFO44      500.2225011 MHz
SFO45      500.2225011 MHz
SFO46      500.2225011 MHz
SFO47      500.2225011 MHz
SFO48      500.2225011 MHz
SFO49      500.2225011 MHz
SFO50      500.2225011 MHz
SFO51      500.2225011 MHz
SFO52      500.2225011 MHz
SFO53      500.2225011 MHz
SFO54      500.2225011 MHz
SFO55      500.2225011 MHz
SFO56      500.2225011 MHz
SFO57      500.2225011 MHz
SFO58      500.2225011 MHz
SFO59      500.2225011 MHz
SFO60      500.2225011 MHz
SFO61      500.2225011 MHz
SFO62      500.2225011 MHz
SFO63      500.2225011 MHz
SFO64      500.2225011 MHz
SFO65      500.2225011 MHz
SFO66      500.2225011 MHz
SFO67      500.2225011 MHz
SFO68      500.2225011 MHz
SFO69      500.2225011 MHz
SFO70      500.2225011 MHz
SFO71      500.2225011 MHz
SFO72      500.2225011 MHz
SFO73      500.2225011 MHz
SFO74      500.2225011 MHz
SFO75      500.2225011 MHz
SFO76      500.2225011 MHz
SFO77      500.2225011 MHz
SFO78      500.2225011 MHz
SFO79      500.2225011 MHz
SFO80      500.2225011 MHz
SFO81      500.2225011 MHz
SFO82      500.2225011 MHz
SFO83      500.2225011 MHz
SFO84      500.2225011 MHz
SFO85      500.2225011 MHz
SFO86      500.2225011 MHz
SFO87      500.2225011 MHz
SFO88      500.2225011 MHz
SFO89      500.2225011 MHz
SFO90      500.2225011 MHz
SFO91      500.2225011 MHz
SFO92      500.2225011 MHz
SFO93      500.2225011 MHz
SFO94      500.2225011 MHz
SFO95      500.2225011 MHz
SFO96      500.2225011 MHz
SFO97      500.2225011 MHz
SFO98      500.2225011 MHz
SFO99      500.2225011 MHz
SFO100     500.2225011 MHz
***** GRADIENT CHANNEL *****
GPNAM1     SINE.100
GPNAM2     SINE.100
GPNAM3     SINE.100
GPNAM4     SINE.100
GPNAM5     SINE.100
GPNAM6     SINE.100
GPNAM7     SINE.100
GPNAM8     SINE.100
GPNAM9     SINE.100
GPNAM10    SINE.100
GPNAM11    SINE.100
GPNAM12    SINE.100
GPNAM13    SINE.100
GPNAM14    SINE.100
GPNAM15    SINE.100
GPNAM16    SINE.100
GPNAM17    SINE.100
GPNAM18    SINE.100
GPNAM19    SINE.100
GPNAM20    SINE.100
GPNAM21    SINE.100
GPNAM22    SINE.100
GPNAM23    SINE.100
GPNAM24    SINE.100
GPNAM25    SINE.100
GPNAM26    SINE.100
GPNAM27    SINE.100
GPNAM28    SINE.100
GPNAM29    SINE.100
GPNAM30    SINE.100
GPNAM31    SINE.100
GPNAM32    SINE.100
GPNAM33    SINE.100
GPNAM34    SINE.100
GPNAM35    SINE.100
GPNAM36    SINE.100
GPNAM37    SINE.100
GPNAM38    SINE.100
GPNAM39    SINE.100
GPNAM40    SINE.100
GPNAM41    SINE.100
GPNAM42    SINE.100
GPNAM43    SINE.100
GPNAM44    SINE.100
GPNAM45    SINE.100
GPNAM46    SINE.100
GPNAM47    SINE.100
GPNAM48    SINE.100
GPNAM49    SINE.100
GPNAM50    SINE.100
GPNAM51    SINE.100
GPNAM52    SINE.100
GPNAM53    SINE.100
GPNAM54    SINE.100
GPNAM55    SINE.100
GPNAM56    SINE.100
GPNAM57    SINE.100
GPNAM58    SINE.100
GPNAM59    SINE.100
GPNAM60    SINE.100
GPNAM61    SINE.100
GPNAM62    SINE.100
GPNAM63    SINE.100
GPNAM64    SINE.100
GPNAM65    SINE.100
GPNAM66    SINE.100
GPNAM67    SINE.100
GPNAM68    SINE.100
GPNAM69    SINE.100
GPNAM70    SINE.100
GPNAM71    SINE.100
GPNAM72    SINE.100
GPNAM73    SINE.100
GPNAM74    SINE.100
GPNAM75    SINE.100
GPNAM76    SINE.100
GPNAM77    SINE.100
GPNAM78    SINE.100
GPNAM79    SINE.100
GPNAM80    SINE.100
GPNAM81    SINE.100
GPNAM82    SINE.100
GPNAM83    SINE.100
GPNAM84    SINE.100
GPNAM85    SINE.100
GPNAM86    SINE.100
GPNAM87    SINE.100
GPNAM88    SINE.100
GPNAM89    SINE.100
GPNAM90    SINE.100
GPNAM91    SINE.100
GPNAM92    SINE.100
GPNAM93    SINE.100
GPNAM94    SINE.100
GPNAM95    SINE.100
GPNAM96    SINE.100
GPNAM97    SINE.100
GPNAM98    SINE.100
GPNAM99    SINE.100
GPNAM100   SINE.100
F2 - Processing parameters
SI         65536
SF         125.7804136 MHz
WDW        EM
SSB        0
GB         0
CB         0
PC         2.00

```

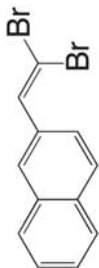


Current Data Parameters
 USER AOL_3_26_01
 PROCNO 1
 Date_ 2010414
 Time 11:06
 INSTRUM 5 mm QNP H/P/P
 PROBHD 65536
 TD 65536
 SOLVENT CDCl3
 DS 2
 SWH 610.000 Hz
 FIDRES 0.107853 Hz
 AQ 5.1118579 sec
 INJ 1.0000000 sec
 DM 78.000 usec
 DE 4.50 usec
 D1 0.10000000 sec
 MCHSET 0.00000000 sec
 PCHPR 0.03000000 sec
 NUC1 ***** CHANNEL f1 1H *****
 P1 12.00 usec
 SFO1 400.1328009 MHz
 P2 Processing Parameters
 S1 6.5536
 SF 400.1300339 MHz
 SSF 0
 CB 0 Hz
 PC 2.00

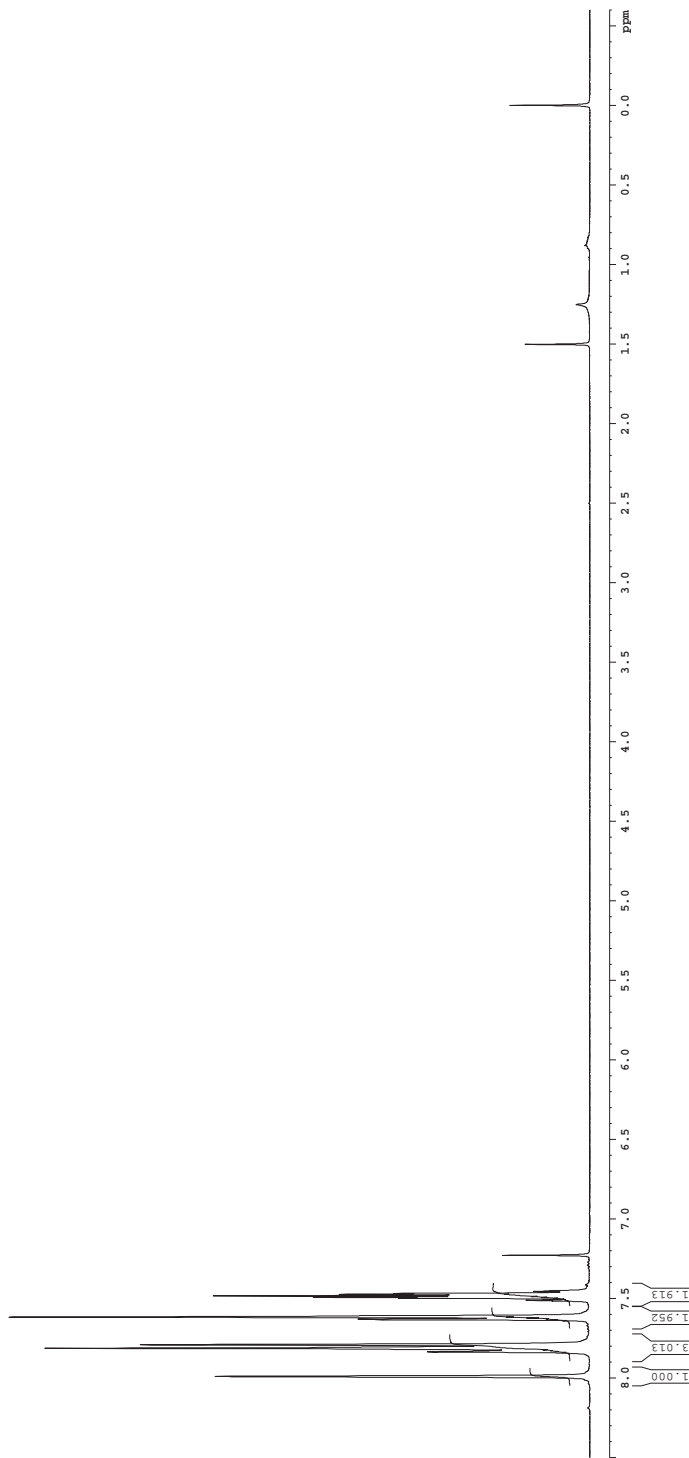
0.00

1.502

1H spectrum
 7.230
 7.457
 7.470
 7.476
 7.485
 7.493
 7.500
 7.517
 7.519
 7.619
 7.631
 7.635
 7.739
 7.837
 7.989



2.21




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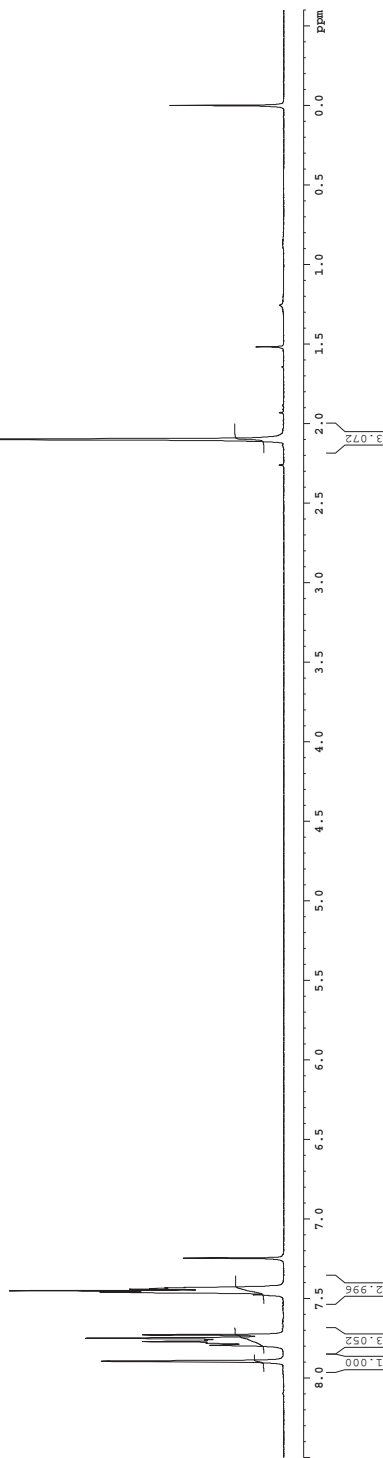
Current Data Parameters
=====
USER      ACL_3_26_01
NAME
PROCNO    1
Date_     2010415
Time      16:00
INSTRUM   5 mm QNP H/P/P
PROBHD    5 mm QNP H/P/P
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         2
SWH        610.000 Hz
FIDRES     0.107853 Hz
AQ         5.1118579 sec
RG         327.680
DM         78.000 usec
DE         2.50 usec
TE         300.2 K
MCHRES    0.1000000 sec
MCHRES    0.0000000 sec
MCHRES    0.0000000 sec
===== CHANNEL f1 =====
NUC1       13C
P1         12.00 usec
PL1        0.00 dB
SFO1       400.1328009 MHz
===== CHANNEL f2 =====
NUC2       1H
P2         12.00 usec
PL2        0.00 dB
SFO2       400.1328009 MHz
===== Processing Parameters =====
SI         65536
SF         400.1300266 MHz
WDW        EM
SSB        0
GB         0
PC         2.00
  
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0.00

2.099

1H spectrum

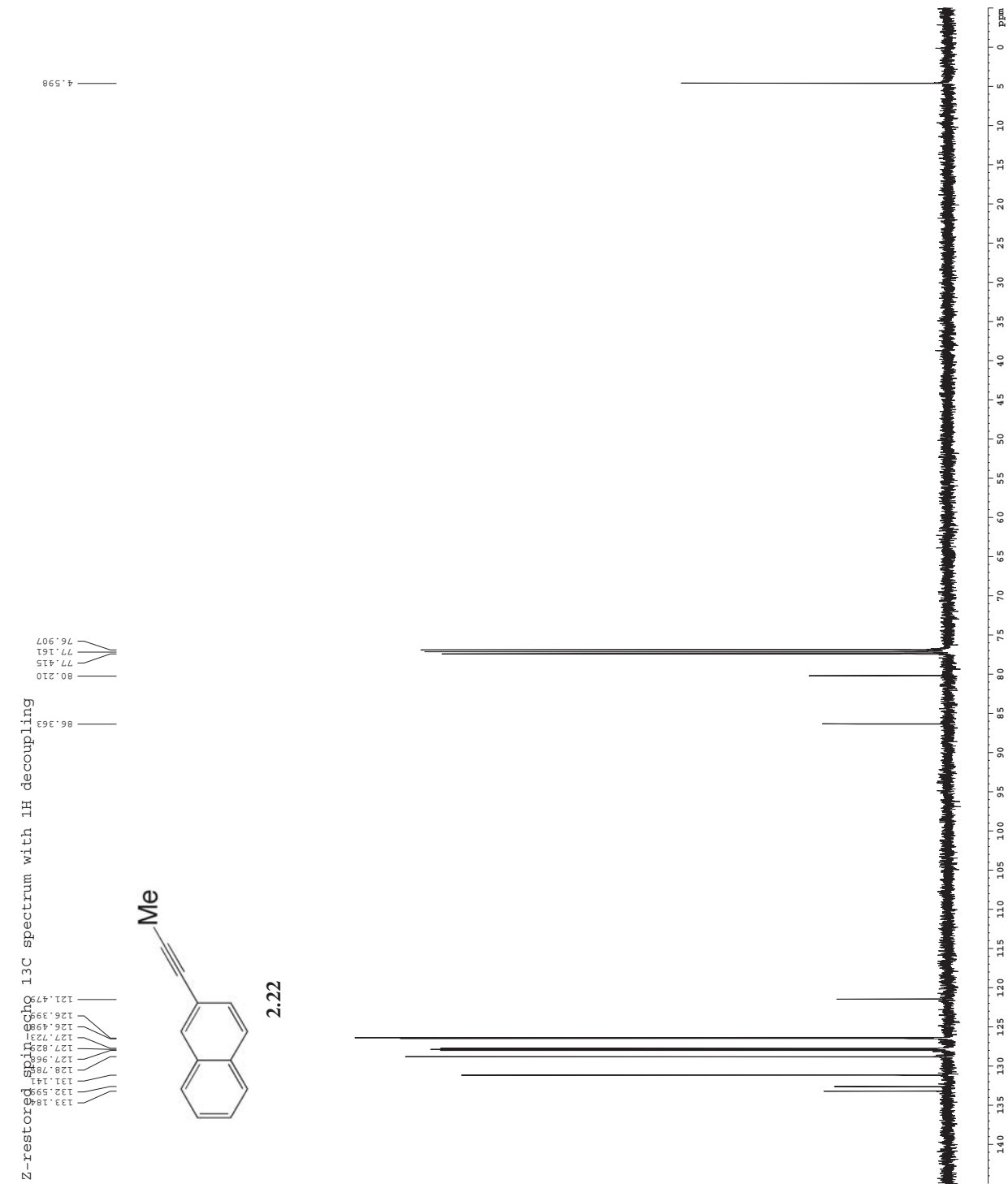
7.896
7.796
7.782
7.772
7.766
7.751
7.730
7.710
7.696
7.682
7.453
7.443
7.439
7.436
7.432
7.248



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Current Data Parameters
NAME          AXL_263_01
PROCNO       1
Date_        2010415
Time_        07:55:00
INSTRUM      5 mm CPCL 1H-
PROBHD       5 mm QNP1HPC
TD           65536
SOLVENT      CDCl3
DS           4
AQ           1.000000 sec
FIDRES       0.000368 Hz
AQ           1.0813940 sec
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00136000 sec
MCWPRG       0.000000 sec
MCWPRG2      0.000000 sec
P2           31.00 usec
***** CHANNEL f1 *****
NUC1         13C
P1           1.00 usec
P11          500.00 usec
P12          2000.00 usec
P13          2000.00 usec
P14          -1.00 dB
P15          -1.00 dB
P16          125.794520 MHz
P17          2.00 dB
P18          125.794520 MHz
P19          2.00 dB
P20          0.000000 sec
P21          0.000000 sec
P22          0.00136000 sec
P23          0.00136000 sec
P24          0.000000 sec
P25          0.000000 sec
P26          0.000000 sec
P27          0.000000 sec
P28          0.000000 sec
P29          0.000000 sec
P30          0.000000 sec
P31          0.000000 sec
P32          0.000000 sec
P33          0.000000 sec
P34          0.000000 sec
P35          0.000000 sec
P36          0.000000 sec
P37          0.000000 sec
P38          0.000000 sec
P39          0.000000 sec
P40          0.000000 sec
P41          0.000000 sec
P42          0.000000 sec
P43          0.000000 sec
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P46          0.000000 sec
P47          0.000000 sec
P48          0.000000 sec
P49          0.000000 sec
P50          0.000000 sec
P51          0.000000 sec
P52          0.000000 sec
P53          0.000000 sec
P54          0.000000 sec
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P56          0.000000 sec
P57          0.000000 sec
P58          0.000000 sec
P59          0.000000 sec
P60          0.000000 sec
P61          0.000000 sec
P62          0.000000 sec
P63          0.000000 sec
P64          0.000000 sec
P65          0.000000 sec
P66          0.000000 sec
P67          0.000000 sec
P68          0.000000 sec
P69          0.000000 sec
P70          0.000000 sec
P71          0.000000 sec
P72          0.000000 sec
P73          0.000000 sec
P74          0.000000 sec
P75          0.000000 sec
P76          0.000000 sec
P77          0.000000 sec
P78          0.000000 sec
P79          0.000000 sec
P80          0.000000 sec
P81          0.000000 sec
P82          0.000000 sec
P83          0.000000 sec
P84          0.000000 sec
P85          0.000000 sec
P86          0.000000 sec
P87          0.000000 sec
P88          0.000000 sec
P89          0.000000 sec
P90          0.000000 sec
P91          0.000000 sec
P92          0.000000 sec
P93          0.000000 sec
P94          0.000000 sec
P95          0.000000 sec
P96          0.000000 sec
P97          0.000000 sec
P98          0.000000 sec
P99          0.000000 sec
P100         0.000000 sec
***** CHANNEL L2 *****
CPDPRG2      WALTZ16
NUC2         1H
P101         1.00 usec
P102         100.60 usec
P103         100.60 usec
P104         100.60 usec
P105         100.60 usec
P106         100.60 usec
P107         100.60 usec
P108         100.60 usec
P109         100.60 usec
P110         100.60 usec
P111         100.60 usec
P112         100.60 usec
P113         100.60 usec
P114         100.60 usec
P115         100.60 usec
P116         100.60 usec
P117         100.60 usec
P118         100.60 usec
P119         100.60 usec
P120         100.60 usec
P121         100.60 usec
P122         100.60 usec
P123         100.60 usec
P124         100.60 usec
P125         100.60 usec
P126         100.60 usec
P127         100.60 usec
P128         100.60 usec
P129         100.60 usec
P130         100.60 usec
P131         100.60 usec
P132         100.60 usec
P133         100.60 usec
P134         100.60 usec
P135         100.60 usec
P136         100.60 usec
P137         100.60 usec
P138         100.60 usec
P139         100.60 usec
P140         100.60 usec
P141         100.60 usec
P142         100.60 usec
P143         100.60 usec
P144         100.60 usec
P145         100.60 usec
P146         100.60 usec
P147         100.60 usec
P148         100.60 usec
P149         100.60 usec
P150         100.60 usec
***** GRADIENT CHANNEL *****
GPNAM1       SINE.100
GPNAM2       SINE.100
G1          0.00 Hz
G2          0.00 Hz
G3          0.00 Hz
G4          0.00 Hz
G5          0.00 Hz
G6          0.00 Hz
G7          0.00 Hz
G8          0.00 Hz
G9          0.00 Hz
G10         0.00 Hz
G11         0.00 Hz
G12         0.00 Hz
G13         0.00 Hz
G14         0.00 Hz
G15         0.00 Hz
G16         0.00 Hz
G17         0.00 Hz
G18         0.00 Hz
G19         0.00 Hz
G20         0.00 Hz
G21         0.00 Hz
G22         0.00 Hz
G23         0.00 Hz
G24         0.00 Hz
G25         0.00 Hz
G26         0.00 Hz
G27         0.00 Hz
G28         0.00 Hz
G29         0.00 Hz
G30         0.00 Hz
G31         0.00 Hz
G32         0.00 Hz
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G51         0.00 Hz
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G89         0.00 Hz
G90         0.00 Hz
G91         0.00 Hz
G92         0.00 Hz
G93         0.00 Hz
G94         0.00 Hz
G95         0.00 Hz
G96         0.00 Hz
G97         0.00 Hz
G98         0.00 Hz
G99         0.00 Hz
G100        0.00 Hz
***** Processing Parameters *****
SI           65536
SF           125.7604000 MHz
WDW          EM
SSB          0
GB           0
PC           2.00

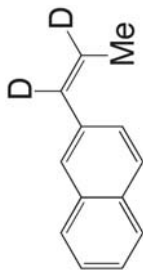
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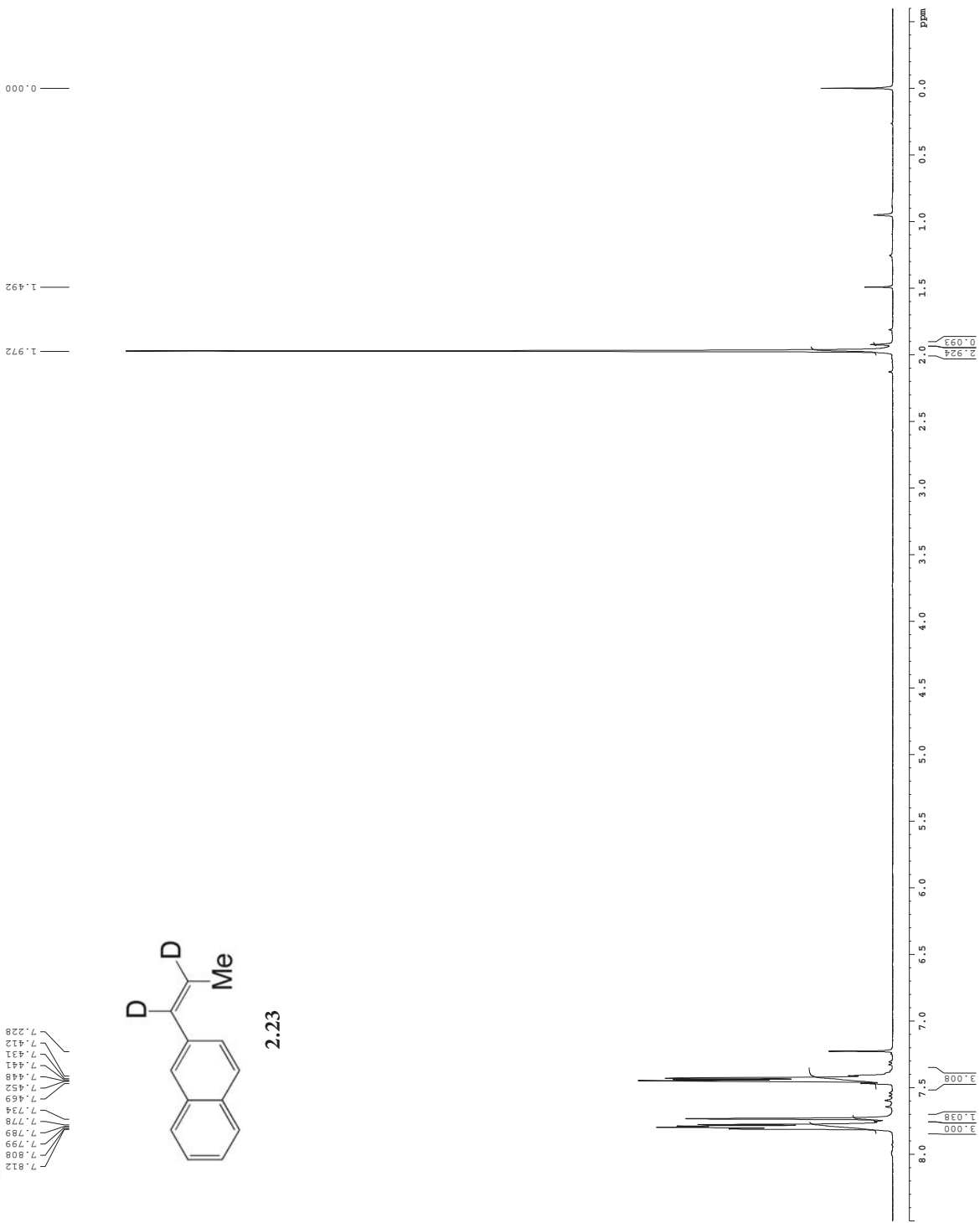
Current Data Parameters
 USER AG_3_24_c1_1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 2010419
 Time_ 11:24:00
 INSTRUM 5 mm QNP H/P/P
 PROBHD 5 mm QNP H/P/P
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 DS 2
 SWH 610.000 MHz
 FIDRES 0.100000 Hz
 AQ 5.1118579 sec
 SFO1 400.1328009 MHz
 DM 78.000 usec
 DE 4.50 usec
 D1 0.1000000 sec
 MCHSET 0.0000000 sec
 PCPRG 0.0300000 sec
 NUC1 CHANNEL f1 1H
 P1 12.00 usec
 SFO2 400.1328009 MHz
 F2 - Processing Parameters
 SI 65536
 SF 400.1300348 MHz
 DF 1000
 SSB 0
 CB 0 Hz
 PC 2.00

1H spectrum

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2.23



```

Current Data Parameters
USER          ACL_3_26_01
PROCNO       1
Date_        2010422
INSTRUM      CPY6540
PROBHD       5 mm CPCL1H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           16
AQ           3.992388 Hz
FIDRES       1.0813940 sec
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00136000 sec
MORPH        0.00000000 sec
MCWPRG       0.00000000 sec
PC           31.00 usec

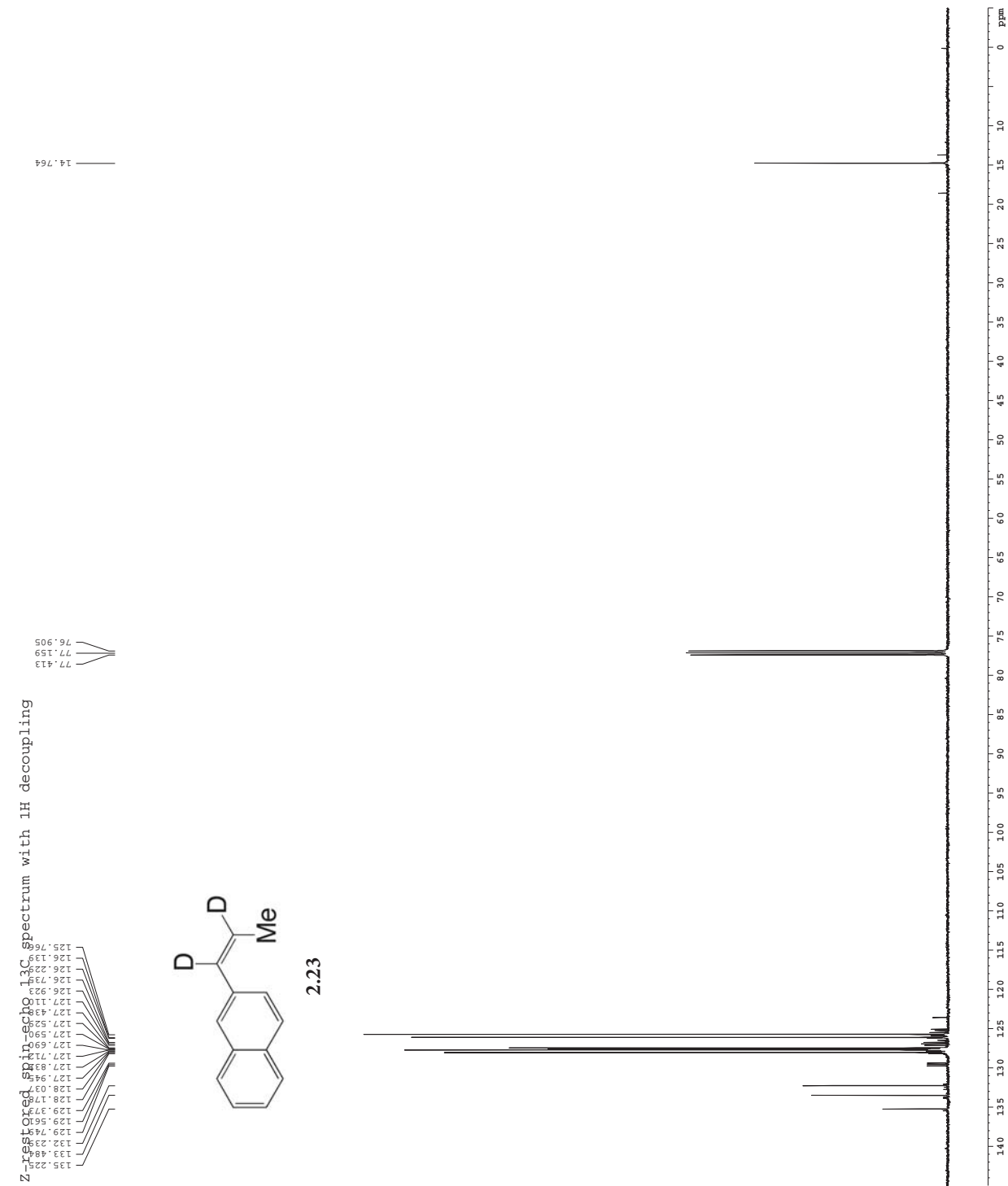
***** CHANNEL f1 *****
NUC1          13C
P11           500.00 usec
P21           2000.00 usec
PL1          -1.00 dB
SFO1         125.7945280 MHz
SE1          3.20 dB
SFO2         0.00000000 MHz
SFO3         0.00000000 MHz
SFO4         0.00000000 MHz
SFO5         0.00000000 MHz
SFO6         0.00000000 MHz
SFO7         0.00000000 MHz
SFO8         0.00000000 MHz
SFO9         0.00000000 MHz
SFO10        0.00000000 MHz
SFO11        0.00000000 MHz
SFO12        0.00000000 MHz
SFO13        0.00000000 MHz
SFO14        0.00000000 MHz
SFO15        0.00000000 MHz
SFO16        0.00000000 MHz
SFO17        0.00000000 MHz
SFO18        0.00000000 MHz
SFO19        0.00000000 MHz
SFO20        0.00000000 MHz
SFO21        0.00000000 MHz
SFO22        0.00000000 MHz
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SFO85        0.00000000 MHz
SFO86        0.00000000 MHz
SFO87        0.00000000 MHz
SFO88        0.00000000 MHz
SFO89        0.00000000 MHz
SFO90        0.00000000 MHz
SFO91        0.00000000 MHz
SFO92        0.00000000 MHz
SFO93        0.00000000 MHz
SFO94        0.00000000 MHz
SFO95        0.00000000 MHz
SFO96        0.00000000 MHz
SFO97        0.00000000 MHz
SFO98        0.00000000 MHz
SFO99        0.00000000 MHz
SFO100       0.00000000 MHz

***** GRADIENT CHANNEL *****
GPNAM1       SINE.100
GPNAM2
GPNAM3
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GPNAM98
GPNAM99
GPNAM100

***** CHANNEL L2 *****
CPDPRG2      zgpg30
NUC2          1H
P22           10.00 usec
PL2           0.00 dB
SFO2         500.2225011 MHz

***** GRADIENT CHANNEL *****
GPNAM1       SINE.100
GPNAM2
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GPNAM100

***** Processing Parameters *****
SI           65536
SF           125.7804159 MHz
RG           0
GB           0
CB           1.00 Hz
PC           2.00
  
```



```

Current Data Parameters
=====
USER      AGL_297_c2
PRCNO    1
Date_    2010528
Time     11:54:00
INSTRUM  cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  zgpg30
TD       83728
SOLVENT  CDCl3
DS       2
AQ       0.13000000 sec
FIDRES   0.1038643 Hz
SFO1     500.2335015 MHz
AQ       5.0998774 sec
DE       62.400 usec
DM       2.00 usec
DE       6.00 usec
D1       0.10000000 sec
D2       0.00000000 sec
MCREST  0.00000000 sec
PCPRG1   0.13000000 sec
=====
NUC1     13C
P1       7.50 usec
PL1     -2.00 dB
SFO1     500.2335015 MHz
=====
F2 - Processing Parameters
=====
SI       65536
SF       500.2200409 MHz
RG       0
SRB      0
CH       0
PC       4.00

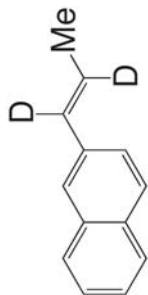
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0.00

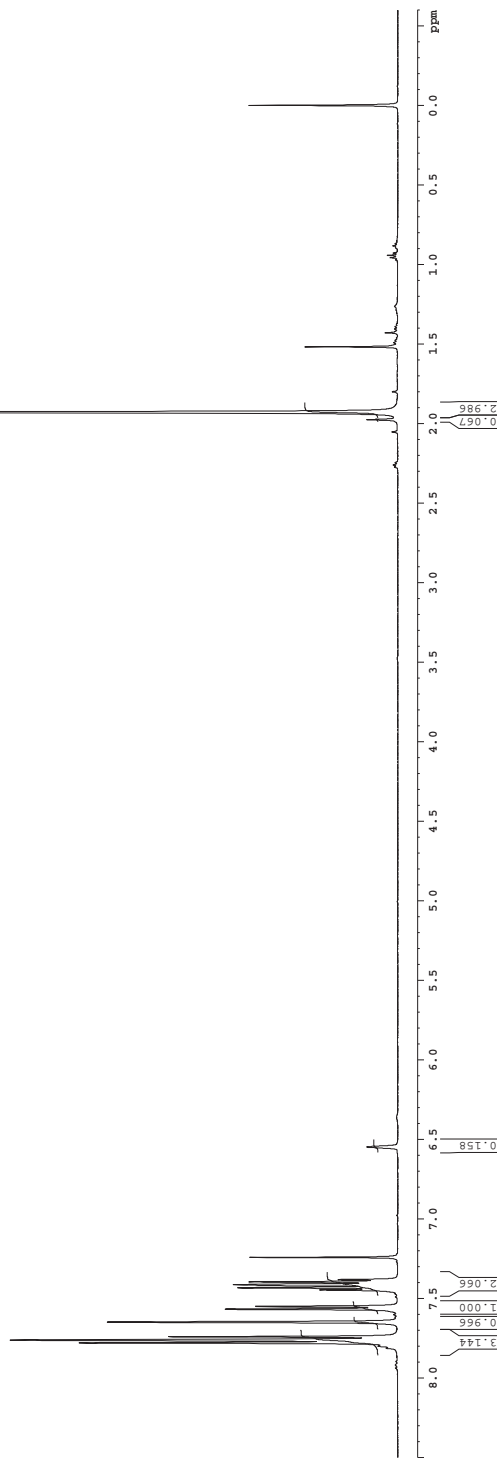
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1.929

7.781
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7.755
7.750
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Z-Isotopolog Spin Echo 13C spectrum with 1H decoupling

```

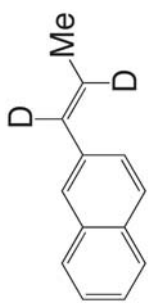
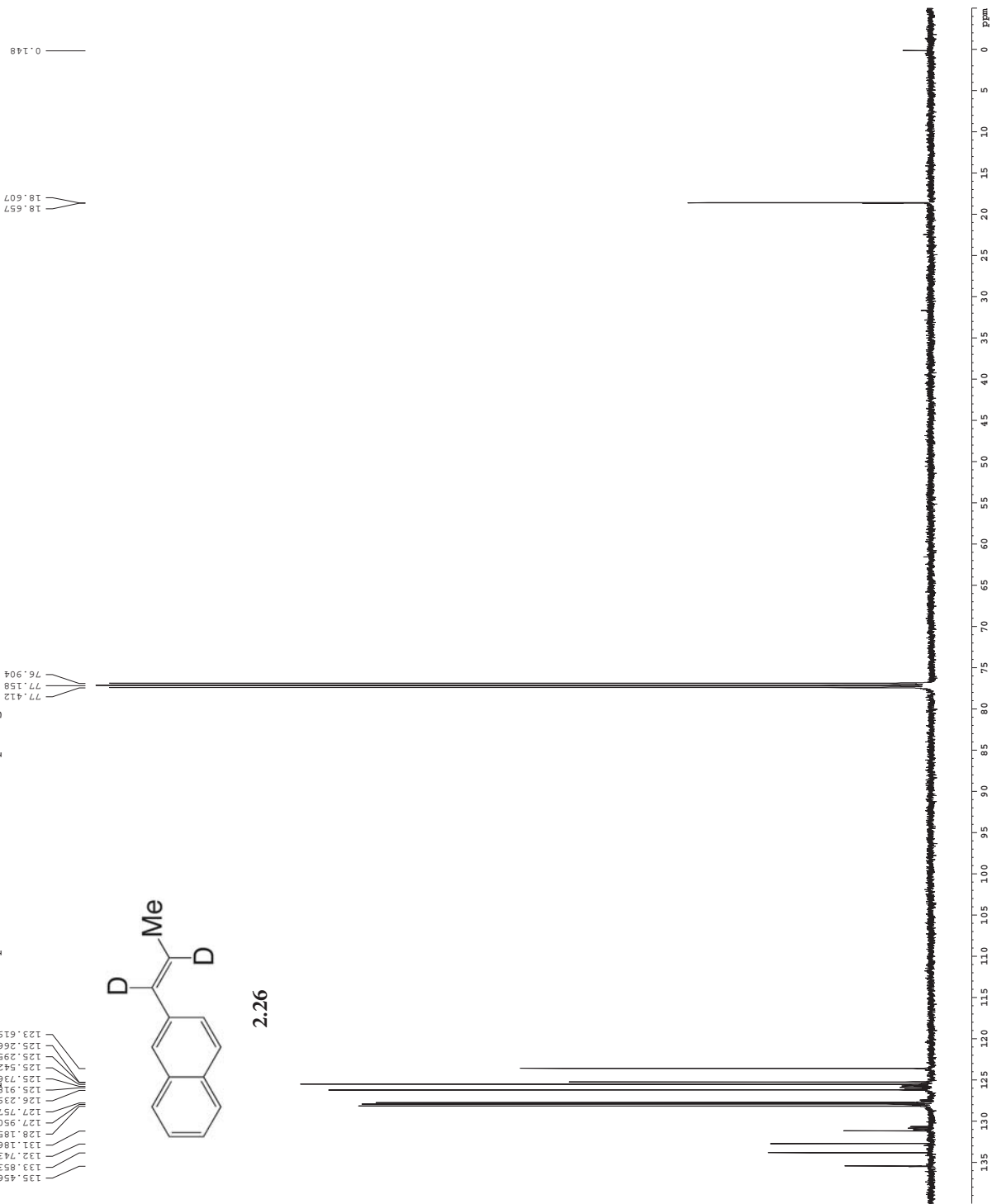
Current Data Parameters
NAME      ACL_3_29_52
PROCNO    1
Date_     2010528
INSTRUM   cryo500
PROBHD    5 mm CPTCL1H-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         16
SF         500.1362688 MHz
AQ         1.0813940 sec
RG         655.360
DM         16.500 usec
DE         6.00 usec
D1         0.25000000 sec
d11        0.03000000 sec
d17        0.00136000 sec
MCKBKT     0.00000000 sec
MCKWBK     0.00000000 sec
P2         31.00 usec

***** CHANNEL f1 *****
NUC1       13C
P1         12.00 usec
P11        500.00 usec
P12        2000.00 usec
P13        1.00 usec
P14        -1.00 dB
P15        125.7945200 MHz
P16        0.00 dB
P17        0.00 dB
P18        0.00 dB
P19        0.00 dB
P20        0.00 dB
P21        0.00 dB
P22        0.00 dB
P23        0.00 dB
P24        0.00 dB
P25        0.00 dB
P26        0.00 dB
P27        0.00 dB
P28        0.00 dB
P29        0.00 dB
P30        0.00 dB
P31        0.00 dB
P32        0.00 dB
P33        0.00 dB
P34        0.00 dB
P35        0.00 dB
P36        0.00 dB
P37        0.00 dB
P38        0.00 dB
P39        0.00 dB
P40        0.00 dB
P41        0.00 dB
P42        0.00 dB
P43        0.00 dB
P44        0.00 dB
P45        0.00 dB
P46        0.00 dB
P47        0.00 dB
P48        0.00 dB
P49        0.00 dB
P50        0.00 dB
P51        0.00 dB
P52        0.00 dB
P53        0.00 dB
P54        0.00 dB
P55        0.00 dB
P56        0.00 dB
P57        0.00 dB
P58        0.00 dB
P59        0.00 dB
P60        0.00 dB
P61        0.00 dB
P62        0.00 dB
P63        0.00 dB
P64        0.00 dB
P65        0.00 dB
P66        0.00 dB
P67        0.00 dB
P68        0.00 dB
P69        0.00 dB
P70        0.00 dB
P71        0.00 dB
P72        0.00 dB
P73        0.00 dB
P74        0.00 dB
P75        0.00 dB
P76        0.00 dB
P77        0.00 dB
P78        0.00 dB
P79        0.00 dB
P80        0.00 dB
P81        0.00 dB
P82        0.00 dB
P83        0.00 dB
P84        0.00 dB
P85        0.00 dB
P86        0.00 dB
P87        0.00 dB
P88        0.00 dB
P89        0.00 dB
P90        0.00 dB
P91        0.00 dB
P92        0.00 dB
P93        0.00 dB
P94        0.00 dB
P95        0.00 dB
P96        0.00 dB
P97        0.00 dB
P98        0.00 dB
P99        0.00 dB
P100       0.00 dB

***** CHANNEL L2 *****
CPDPRG2   zgpg30
NUC2       13C
P1         12.00 usec
P11        500.00 usec
P12        2000.00 usec
P13        1.00 usec
P14        -1.00 dB
P15        125.7945200 MHz
P16        0.00 dB
P17        0.00 dB
P18        0.00 dB
P19        0.00 dB
P20        0.00 dB
P21        0.00 dB
P22        0.00 dB
P23        0.00 dB
P24        0.00 dB
P25        0.00 dB
P26        0.00 dB
P27        0.00 dB
P28        0.00 dB
P29        0.00 dB
P30        0.00 dB
P31        0.00 dB
P32        0.00 dB
P33        0.00 dB
P34        0.00 dB
P35        0.00 dB
P36        0.00 dB
P37        0.00 dB
P38        0.00 dB
P39        0.00 dB
P40        0.00 dB
P41        0.00 dB
P42        0.00 dB
P43        0.00 dB
P44        0.00 dB
P45        0.00 dB
P46        0.00 dB
P47        0.00 dB
P48        0.00 dB
P49        0.00 dB
P50        0.00 dB
P51        0.00 dB
P52        0.00 dB
P53        0.00 dB
P54        0.00 dB
P55        0.00 dB
P56        0.00 dB
P57        0.00 dB
P58        0.00 dB
P59        0.00 dB
P60        0.00 dB
P61        0.00 dB
P62        0.00 dB
P63        0.00 dB
P64        0.00 dB
P65        0.00 dB
P66        0.00 dB
P67        0.00 dB
P68        0.00 dB
P69        0.00 dB
P70        0.00 dB
P71        0.00 dB
P72        0.00 dB
P73        0.00 dB
P74        0.00 dB
P75        0.00 dB
P76        0.00 dB
P77        0.00 dB
P78        0.00 dB
P79        0.00 dB
P80        0.00 dB
P81        0.00 dB
P82        0.00 dB
P83        0.00 dB
P84        0.00 dB
P85        0.00 dB
P86        0.00 dB
P87        0.00 dB
P88        0.00 dB
P89        0.00 dB
P90        0.00 dB
P91        0.00 dB
P92        0.00 dB
P93        0.00 dB
P94        0.00 dB
P95        0.00 dB
P96        0.00 dB
P97        0.00 dB
P98        0.00 dB
P99        0.00 dB
P100       0.00 dB

***** GRADIENT CHANNEL *****
GPNAM1     SINE.100
GPNAM2     SINE.100
GPA1       0.00 %
GPA2       0.00 %
GPA3       0.00 %
GPA4       0.00 %
GPA5       0.00 %
GPA6       0.00 %
GPA7       0.00 %
GPA8       0.00 %
GPA9       0.00 %
GPA10      0.00 %
GPA11      0.00 %
GPA12      0.00 %
GPA13      0.00 %
GPA14      0.00 %
GPA15      0.00 %
GPA16      0.00 %
GPA17      0.00 %
GPA18      0.00 %
GPA19      0.00 %
GPA20      0.00 %
GPA21      0.00 %
GPA22      0.00 %
GPA23      0.00 %
GPA24      0.00 %
GPA25      0.00 %
GPA26      0.00 %
GPA27      0.00 %
GPA28      0.00 %
GPA29      0.00 %
GPA30      0.00 %
GPA31      0.00 %
GPA32      0.00 %
GPA33      0.00 %
GPA34      0.00 %
GPA35      0.00 %
GPA36      0.00 %
GPA37      0.00 %
GPA38      0.00 %
GPA39      0.00 %
GPA40      0.00 %
GPA41      0.00 %
GPA42      0.00 %
GPA43      0.00 %
GPA44      0.00 %
GPA45      0.00 %
GPA46      0.00 %
GPA47      0.00 %
GPA48      0.00 %
GPA49      0.00 %
GPA50      0.00 %
GPA51      0.00 %
GPA52      0.00 %
GPA53      0.00 %
GPA54      0.00 %
GPA55      0.00 %
GPA56      0.00 %
GPA57      0.00 %
GPA58      0.00 %
GPA59      0.00 %
GPA60      0.00 %
GPA61      0.00 %
GPA62      0.00 %
GPA63      0.00 %
GPA64      0.00 %
GPA65      0.00 %
GPA66      0.00 %
GPA67      0.00 %
GPA68      0.00 %
GPA69      0.00 %
GPA70      0.00 %
GPA71      0.00 %
GPA72      0.00 %
GPA73      0.00 %
GPA74      0.00 %
GPA75      0.00 %
GPA76      0.00 %
GPA77      0.00 %
GPA78      0.00 %
GPA79      0.00 %
GPA80      0.00 %
GPA81      0.00 %
GPA82      0.00 %
GPA83      0.00 %
GPA84      0.00 %
GPA85      0.00 %
GPA86      0.00 %
GPA87      0.00 %
GPA88      0.00 %
GPA89      0.00 %
GPA90      0.00 %
GPA91      0.00 %
GPA92      0.00 %
GPA93      0.00 %
GPA94      0.00 %
GPA95      0.00 %
GPA96      0.00 %
GPA97      0.00 %
GPA98      0.00 %
GPA99      0.00 %
GPA100     0.00 %

F2 - Processing Parameters
SI         65536
SF          125.7804103 MHz
RG          655.360
DM          16.500
DE          6.000
D1          0.250
MCKBKT      0.000
MCKWBK      0.000
PC          2.000
    
```



2.26

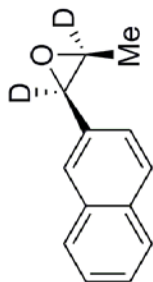
```

Current Data Parameters
=====
USER          ACL_3_268_C1
NAME          ACL_3_268_C1
PROCNO       1
Date_         20100423
Time         12:22:00
INSTRUM      5 mm QNP H/P/P
PROBHD       5 mm QNP H/P/P
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
SWH           610.000 MHz
F2           0.10000000 sec
AQ           0.10000000 sec
RG           5.1118579 sec
DM           78.000 usec
DE           4.50 usec
DI           0.10000000 sec
MCNST       0.00000000 sec
PCNST       0.00000000 sec
===== CHANNEL f1 =====
NUC1         1H
P1           12.00 usec
PL1         -2.00 dB
SFO1         400.1328009 MHz
===== CHANNEL f2 =====
NUC2         13C
P2           12.00 usec
PL2         -2.00 dB
SFO2         100.6281500 MHz
=====
F2 - Processing Parameters
SI           65536
SF           400.1300243 MHz
WDW          EM
SSB          0
GB           0
PC           2.00

```

1.542
1.111
-0.000

7.848
7.844
7.833
7.825
7.813
7.761
7.507
7.494
7.487
7.479
7.470
7.451
7.437
7.433
7.415
7.317
7.256



2.24

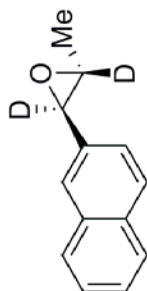



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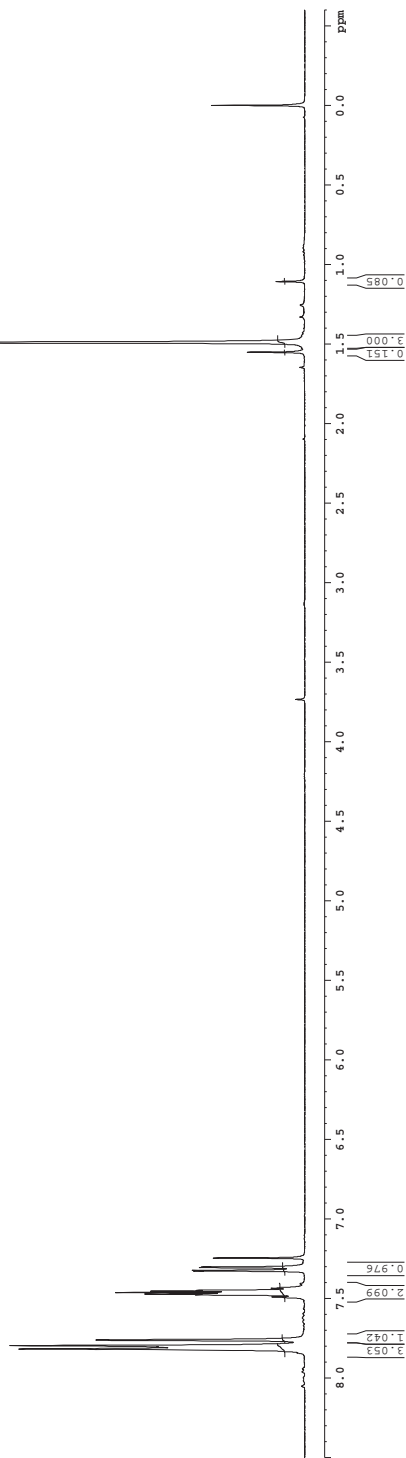
Current Data Parameters
=====
USER      ACL_29_01
PROCNO    1
Date_     2010620
Time      12.00
INSTRUM   5 mm QNP 1H/1
PROBHD    5 mm QNP 1H/1
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         2
AQ         5.118793 sec
RG         0.107853 Hz
AQ         5.118793 sec
RG         0.107853 Hz
DM         78.000 usec
DE         4.50 usec
DI         0.1000000 sec
MCREST    0.0000000 sec
PCPRG1    0.0000000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         12.00 usec
PL1        0 dB
SFO1       400.1328009 MHz
===== CHANNEL f2 =====
NUC2       13C
P2         12.00 usec
PL2        0 dB
SFO2       100.6281500 MHz
===== Processing Parameters =====
SI         65536
SF         400.1300258 MHz
WDW        EM
SSB        0
GB         0
PC         2.00
  
```

0.00
1.52
1.491

1H spectrum
7.819
7.798
7.786
7.762
7.492
7.479
7.474
7.455
7.450
7.437
7.329
7.325
7.307
7.247



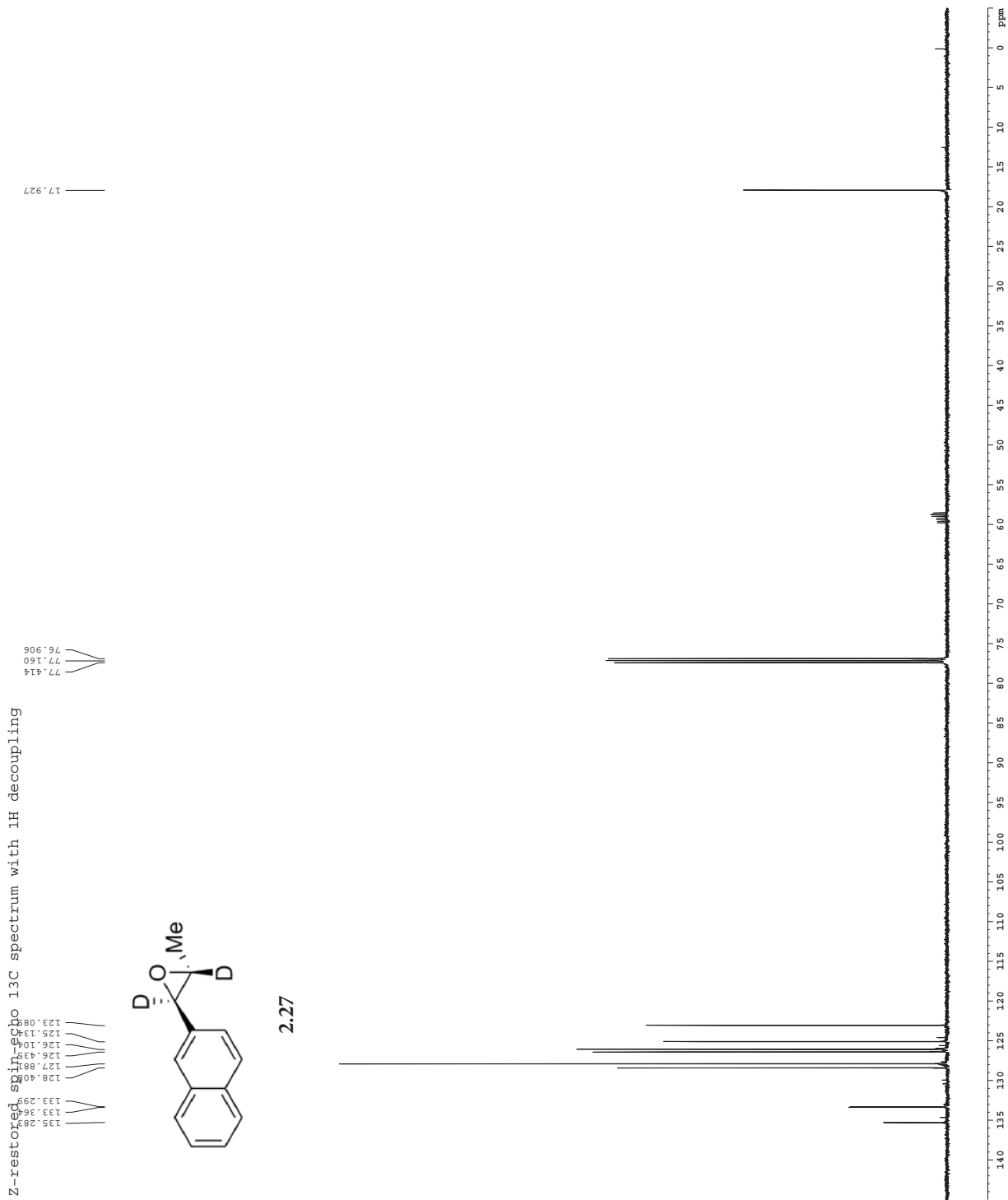
2.27



```

Current Data Parameters
=====
USER          ACL_29_51
NAME          ACL_29_51
PROCNO       1
Date_         20140610
Time_         17:05:00
INSTRUM      CPY5000
PROBHD       5 mm CPYCL 1H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           16
AQ           3.921368 Hz
FIDRES       1.0813940 sec
RG           16.500 usec
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00196000 sec
MCWPRG      0.00000000 sec
MCWPRK      0.00000000 sec
P2           31.00 usec
===== CHANNEL f1 =====
NUC1          13C
P1           12.00 usec
P11          500.00 usec
P12          2000.00 usec
P13          0.00 usec
P14          -1.00 dB
P15          0.00 dB
P16          125.7945200 MHz
P17          0.00 usec
P18          0.00 usec
P19          0.00 usec
P20          0.00 usec
P21          0.00 usec
P22          0.00 usec
P23          0.00 usec
P24          0.00 usec
P25          0.00 usec
P26          0.00 usec
P27          0.00 usec
P28          0.00 usec
P29          0.00 usec
P30          0.00 usec
P31          0.00 usec
P32          0.00 usec
P33          0.00 usec
P34          0.00 usec
P35          0.00 usec
P36          0.00 usec
P37          0.00 usec
P38          0.00 usec
P39          0.00 usec
P40          0.00 usec
P41          0.00 usec
P42          0.00 usec
P43          0.00 usec
P44          0.00 usec
P45          0.00 usec
P46          0.00 usec
P47          0.00 usec
P48          0.00 usec
P49          0.00 usec
P50          0.00 usec
P51          0.00 usec
P52          0.00 usec
P53          0.00 usec
P54          0.00 usec
P55          0.00 usec
P56          0.00 usec
P57          0.00 usec
P58          0.00 usec
P59          0.00 usec
P60          0.00 usec
P61          0.00 usec
P62          0.00 usec
P63          0.00 usec
P64          0.00 usec
P65          0.00 usec
P66          0.00 usec
P67          0.00 usec
P68          0.00 usec
P69          0.00 usec
P70          0.00 usec
P71          0.00 usec
P72          0.00 usec
P73          0.00 usec
P74          0.00 usec
P75          0.00 usec
P76          0.00 usec
P77          0.00 usec
P78          0.00 usec
P79          0.00 usec
P80          0.00 usec
P81          0.00 usec
P82          0.00 usec
P83          0.00 usec
P84          0.00 usec
P85          0.00 usec
P86          0.00 usec
P87          0.00 usec
P88          0.00 usec
P89          0.00 usec
P90          0.00 usec
P91          0.00 usec
P92          0.00 usec
P93          0.00 usec
P94          0.00 usec
P95          0.00 usec
P96          0.00 usec
P97          0.00 usec
P98          0.00 usec
P99          0.00 usec
P100         0.00 usec
===== CHANNEL L2 =====
CPYPRG      zgpg30
NUC2          13C
P1           12.00 usec
P11          500.00 usec
P12          2000.00 usec
P13          0.00 usec
P14          -1.00 dB
P15          0.00 dB
P16          125.7945200 MHz
P17          0.00 usec
P18          0.00 usec
P19          0.00 usec
P20          0.00 usec
P21          0.00 usec
P22          0.00 usec
P23          0.00 usec
P24          0.00 usec
P25          0.00 usec
P26          0.00 usec
P27          0.00 usec
P28          0.00 usec
P29          0.00 usec
P30          0.00 usec
P31          0.00 usec
P32          0.00 usec
P33          0.00 usec
P34          0.00 usec
P35          0.00 usec
P36          0.00 usec
P37          0.00 usec
P38          0.00 usec
P39          0.00 usec
P40          0.00 usec
P41          0.00 usec
P42          0.00 usec
P43          0.00 usec
P44          0.00 usec
P45          0.00 usec
P46          0.00 usec
P47          0.00 usec
P48          0.00 usec
P49          0.00 usec
P50          0.00 usec
P51          0.00 usec
P52          0.00 usec
P53          0.00 usec
P54          0.00 usec
P55          0.00 usec
P56          0.00 usec
P57          0.00 usec
P58          0.00 usec
P59          0.00 usec
P60          0.00 usec
P61          0.00 usec
P62          0.00 usec
P63          0.00 usec
P64          0.00 usec
P65          0.00 usec
P66          0.00 usec
P67          0.00 usec
P68          0.00 usec
P69          0.00 usec
P70          0.00 usec
P71          0.00 usec
P72          0.00 usec
P73          0.00 usec
P74          0.00 usec
P75          0.00 usec
P76          0.00 usec
P77          0.00 usec
P78          0.00 usec
P79          0.00 usec
P80          0.00 usec
P81          0.00 usec
P82          0.00 usec
P83          0.00 usec
P84          0.00 usec
P85          0.00 usec
P86          0.00 usec
P87          0.00 usec
P88          0.00 usec
P89          0.00 usec
P90          0.00 usec
P91          0.00 usec
P92          0.00 usec
P93          0.00 usec
P94          0.00 usec
P95          0.00 usec
P96          0.00 usec
P97          0.00 usec
P98          0.00 usec
P99          0.00 usec
P100         0.00 usec
===== GRADIENT CHANNEL =====
GPNAM1       SINE.100
GPNAM2
GPNAM3
GPNAM4
GPNAM5
GPNAM6
GPNAM7
GPNAM8
GPNAM9
GPNAM10
GPNAM11
GPNAM12
GPNAM13
GPNAM14
GPNAM15
GPNAM16
GPNAM17
GPNAM18
GPNAM19
GPNAM20
GPNAM21
GPNAM22
GPNAM23
GPNAM24
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GPNAM76
GPNAM77
GPNAM78
GPNAM79
GPNAM80
GPNAM81
GPNAM82
GPNAM83
GPNAM84
GPNAM85
GPNAM86
GPNAM87
GPNAM88
GPNAM89
GPNAM90
GPNAM91
GPNAM92
GPNAM93
GPNAM94
GPNAM95
GPNAM96
GPNAM97
GPNAM98
GPNAM99
GPNAM100
===== Processing Parameters =====
SI           65536
SF           125.7804133 MHz
WDW          EM
SSB          0
GB           0
PC           2.00

```

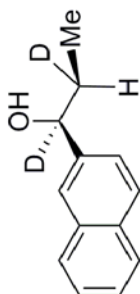



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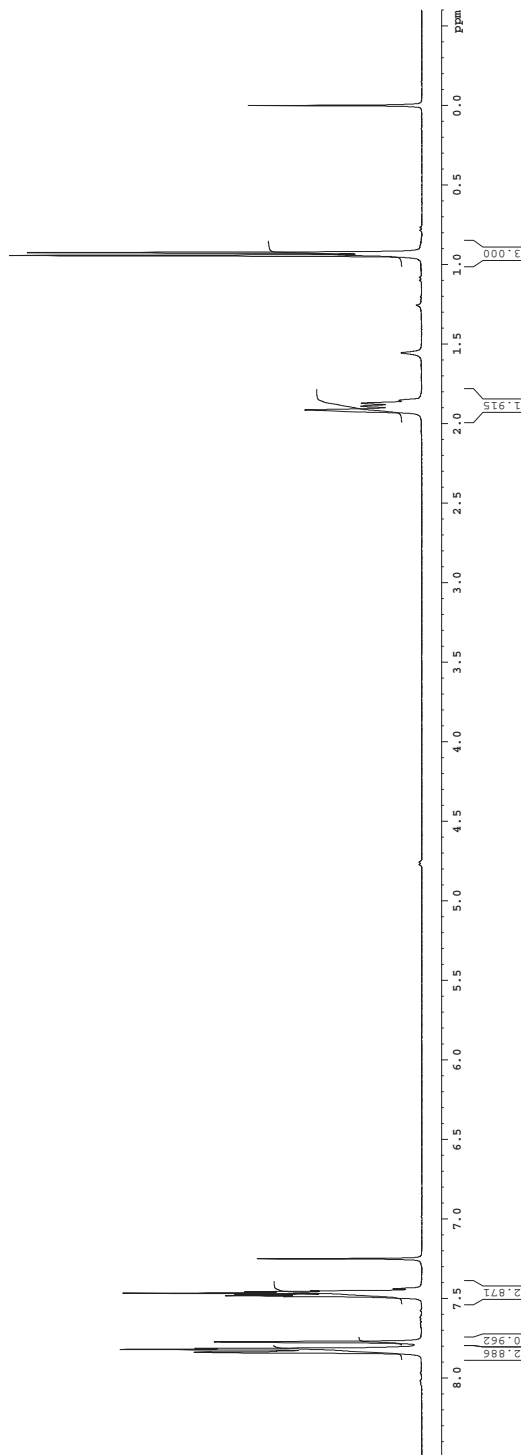
Current Data Parameters
=====
USER          ACL_3_269_c1
NAME
PROCNO       1
Date_        2010425
Time        01:00
INSTRUM     5 mm QNP H/P/P
PROBHD      5 mm QNP 1H/13
PULPROG     zgpg30
TD          65536
SOLVENT     CDCl3
DS          2
AQ          0.100000 sec
F2         513.000000 MHz
F1         0.100000 MHz
AQ         5.1118579 sec
RG         327.680000
DM         78.0000 usec
DE         4.50 usec
DI         0.100000000 sec
MCREST     0.000000000 sec
PCPRG1     0.030000000 sec
===== CHANNEL f1 =====
NUC1        13C
P1          12.00 usec
PL1         0.00 dB
SFO1        400.1326009 MHz
===== CHANNEL f2 =====
NUC2        1H
P2          12.00 usec
PL2         0.00 dB
SFO2        400.1326009 MHz
===== Processing Parameters =====
SI          65536
SF          400.1300252 MHz
WDW         EM
SSB         0
GB          0
PC          2.00
  
```

1.915
1.891
1.873
1.854
1.556
0.944
0.926
0.000

7.839
7.833
7.822
7.812
7.799
7.789
7.784
7.777
7.768
7.759
7.748
7.741
7.725



2.25



```

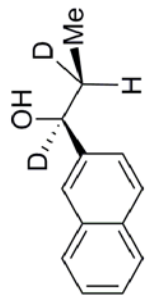
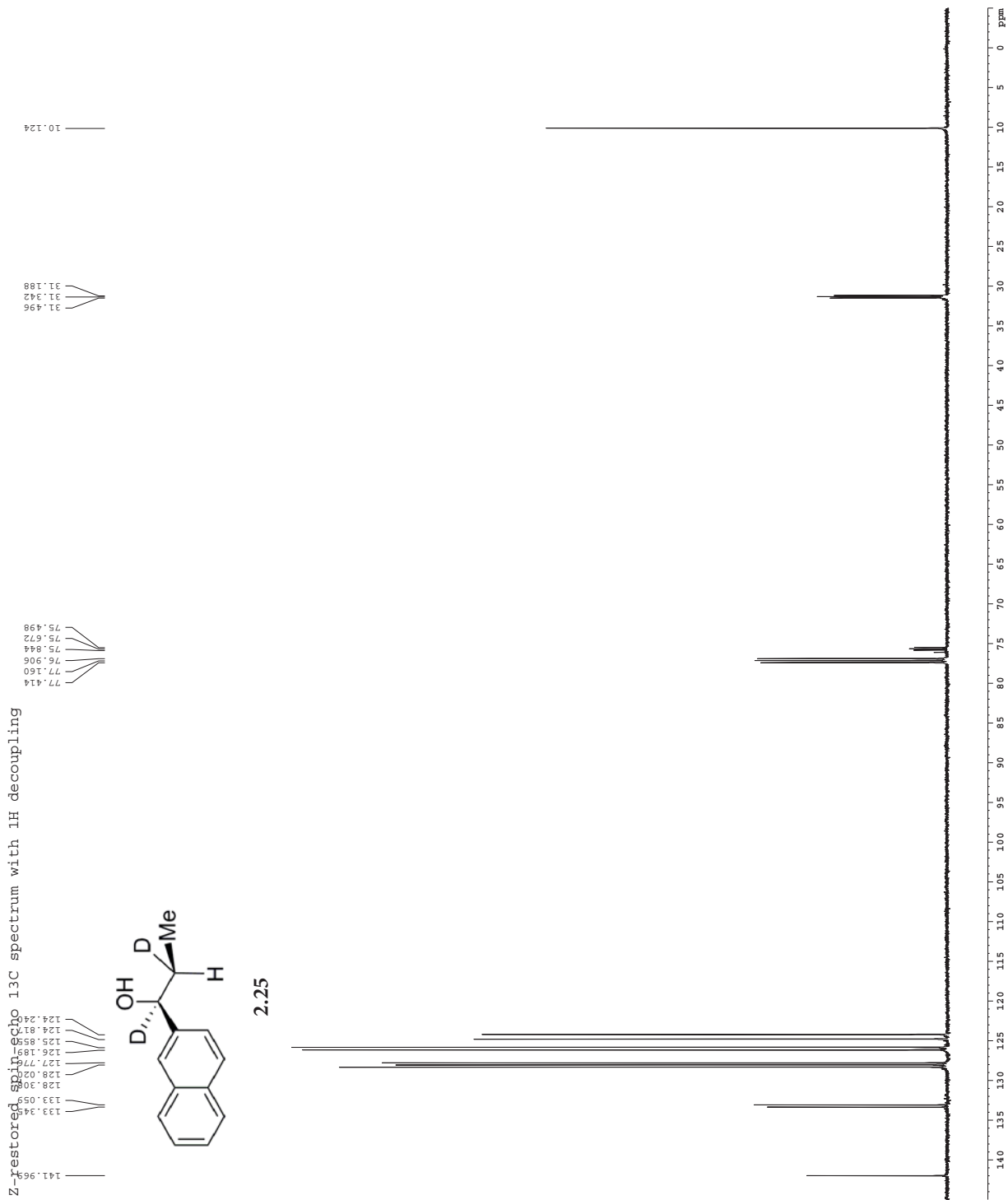
Current Data Parameters
=====
USER          AAL_3_269_01
PROCNO       1
Date_         2010425
Time_         16:55:00
INSTRUM      crys500
PROBHD       5 mm CPCL1H1-
PULPROG      zgpg30
TD            65536
SOLVENT      CDCl3
DS            4
AQ            1.000000 sec
FIDRES       0.092388 Hz
AQ           1.0813940 sec
RG           327.680
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00136000 sec
MCKMT        0.00000000 sec
MCKMK        0.00000000 sec
P2           31.00 usec

===== CHANNEL f1 =====
NUC1          13C
P1            12C
P11           500.00 usec
P12           2000.00 usec
P13           1.00000000 sec
P14           -1.00 dB
P15           125.7945200 MHz
P16           2.00 dB
P17           0.00000000 sec
P18           0.00000000 sec
P19           0.00000000 sec
P20           0.00000000 sec
P21           0.00000000 sec
P22           0.00000000 sec
P23           0.00000000 sec
P24           0.00000000 sec
P25           0.00000000 sec
P26           0.00000000 sec
P27           0.00000000 sec
P28           0.00000000 sec
P29           0.00000000 sec
P30           0.00000000 sec
P31           0.00000000 sec
P32           0.00000000 sec
P33           0.00000000 sec
P34           0.00000000 sec
P35           0.00000000 sec
P36           0.00000000 sec
P37           0.00000000 sec
P38           0.00000000 sec
P39           0.00000000 sec
P40           0.00000000 sec
P41           0.00000000 sec
P42           0.00000000 sec
P43           0.00000000 sec
P44           0.00000000 sec
P45           0.00000000 sec
P46           0.00000000 sec
P47           0.00000000 sec
P48           0.00000000 sec
P49           0.00000000 sec
P50           0.00000000 sec
P51           0.00000000 sec
P52           0.00000000 sec
P53           0.00000000 sec
P54           0.00000000 sec
P55           0.00000000 sec
P56           0.00000000 sec
P57           0.00000000 sec
P58           0.00000000 sec
P59           0.00000000 sec
P60           0.00000000 sec
P61           0.00000000 sec
P62           0.00000000 sec
P63           0.00000000 sec
P64           0.00000000 sec
P65           0.00000000 sec
P66           0.00000000 sec
P67           0.00000000 sec
P68           0.00000000 sec
P69           0.00000000 sec
P70           0.00000000 sec
P71           0.00000000 sec
P72           0.00000000 sec
P73           0.00000000 sec
P74           0.00000000 sec
P75           0.00000000 sec
P76           0.00000000 sec
P77           0.00000000 sec
P78           0.00000000 sec
P79           0.00000000 sec
P80           0.00000000 sec
P81           0.00000000 sec
P82           0.00000000 sec
P83           0.00000000 sec
P84           0.00000000 sec
P85           0.00000000 sec
P86           0.00000000 sec
P87           0.00000000 sec
P88           0.00000000 sec
P89           0.00000000 sec
P90           0.00000000 sec
P91           0.00000000 sec
P92           0.00000000 sec
P93           0.00000000 sec
P94           0.00000000 sec
P95           0.00000000 sec
P96           0.00000000 sec
P97           0.00000000 sec
P98           0.00000000 sec
P99           0.00000000 sec
P100          0.00000000 sec

===== CHANNEL L2 =====
CPDPRG2      zgpg30
NUC2          13C
P101          12C
P102          100.620 usec
P103          1.00000000 sec
P104          1.00000000 sec
P105          1.00000000 sec
P106          1.00000000 sec
P107          1.00000000 sec
P108          1.00000000 sec
P109          1.00000000 sec
P110          1.00000000 sec
P111          1.00000000 sec
P112          1.00000000 sec
P113          1.00000000 sec
P114          1.00000000 sec
P115          1.00000000 sec
P116          1.00000000 sec
P117          1.00000000 sec
P118          1.00000000 sec
P119          1.00000000 sec
P120          1.00000000 sec
P121          1.00000000 sec
P122          1.00000000 sec
P123          1.00000000 sec
P124          1.00000000 sec
P125          1.00000000 sec
P126          1.00000000 sec
P127          1.00000000 sec
P128          1.00000000 sec
P129          1.00000000 sec
P130          1.00000000 sec
P131          1.00000000 sec
P132          1.00000000 sec
P133          1.00000000 sec
P134          1.00000000 sec
P135          1.00000000 sec
P136          1.00000000 sec
P137          1.00000000 sec
P138          1.00000000 sec
P139          1.00000000 sec
P140          1.00000000 sec
P141          1.00000000 sec
P142          1.00000000 sec
P143          1.00000000 sec
P144          1.00000000 sec
P145          1.00000000 sec
P146          1.00000000 sec
P147          1.00000000 sec
P148          1.00000000 sec
P149          1.00000000 sec
P150          1.00000000 sec
P151          1.00000000 sec
P152          1.00000000 sec
P153          1.00000000 sec
P154          1.00000000 sec
P155          1.00000000 sec
P156          1.00000000 sec
P157          1.00000000 sec
P158          1.00000000 sec
P159          1.00000000 sec
P160          1.00000000 sec
P161          1.00000000 sec
P162          1.00000000 sec
P163          1.00000000 sec
P164          1.00000000 sec
P165          1.00000000 sec
P166          1.00000000 sec
P167          1.00000000 sec
P168          1.00000000 sec
P169          1.00000000 sec
P170          1.00000000 sec
P171          1.00000000 sec
P172          1.00000000 sec
P173          1.00000000 sec
P174          1.00000000 sec
P175          1.00000000 sec
P176          1.00000000 sec
P177          1.00000000 sec
P178          1.00000000 sec
P179          1.00000000 sec
P180          1.00000000 sec
P181          1.00000000 sec
P182          1.00000000 sec
P183          1.00000000 sec
P184          1.00000000 sec
P185          1.00000000 sec
P186          1.00000000 sec
P187          1.00000000 sec
P188          1.00000000 sec
P189          1.00000000 sec
P190          1.00000000 sec
P191          1.00000000 sec
P192          1.00000000 sec
P193          1.00000000 sec
P194          1.00000000 sec
P195          1.00000000 sec
P196          1.00000000 sec
P197          1.00000000 sec
P198          1.00000000 sec
P199          1.00000000 sec
P200          1.00000000 sec

===== GRADIENT CHANNEL =====
GPMAX2       0.00 G
GPRG2        0.00 G
GPRG3        0.00 G
GPRG4        0.00 G
GPRG5        0.00 G
GPRG6        0.00 G
GPRG7        0.00 G
GPRG8        0.00 G
GPRG9        0.00 G
GPRG10       0.00 G
GPRG11       0.00 G
GPRG12       0.00 G
GPRG13       0.00 G
GPRG14       0.00 G
GPRG15       0.00 G
GPRG16       0.00 G
GPRG17       0.00 G
GPRG18       0.00 G
GPRG19       0.00 G
GPRG20       0.00 G
GPRG21       0.00 G
GPRG22       0.00 G
GPRG23       0.00 G
GPRG24       0.00 G
GPRG25       0.00 G
GPRG26       0.00 G
GPRG27       0.00 G
GPRG28       0.00 G
GPRG29       0.00 G
GPRG30       0.00 G
GPRG31       0.00 G
GPRG32       0.00 G
GPRG33       0.00 G
GPRG34       0.00 G
GPRG35       0.00 G
GPRG36       0.00 G
GPRG37       0.00 G
GPRG38       0.00 G
GPRG39       0.00 G
GPRG40       0.00 G
GPRG41       0.00 G
GPRG42       0.00 G
GPRG43       0.00 G
GPRG44       0.00 G
GPRG45       0.00 G
GPRG46       0.00 G
GPRG47       0.00 G
GPRG48       0.00 G
GPRG49       0.00 G
GPRG50       0.00 G
GPRG51       0.00 G
GPRG52       0.00 G
GPRG53       0.00 G
GPRG54       0.00 G
GPRG55       0.00 G
GPRG56       0.00 G
GPRG57       0.00 G
GPRG58       0.00 G
GPRG59       0.00 G
GPRG60       0.00 G
GPRG61       0.00 G
GPRG62       0.00 G
GPRG63       0.00 G
GPRG64       0.00 G
GPRG65       0.00 G
GPRG66       0.00 G
GPRG67       0.00 G
GPRG68       0.00 G
GPRG69       0.00 G
GPRG70       0.00 G
GPRG71       0.00 G
GPRG72       0.00 G
GPRG73       0.00 G
GPRG74       0.00 G
GPRG75       0.00 G
GPRG76       0.00 G
GPRG77       0.00 G
GPRG78       0.00 G
GPRG79       0.00 G
GPRG80       0.00 G
GPRG81       0.00 G
GPRG82       0.00 G
GPRG83       0.00 G
GPRG84       0.00 G
GPRG85       0.00 G
GPRG86       0.00 G
GPRG87       0.00 G
GPRG88       0.00 G
GPRG89       0.00 G
GPRG90       0.00 G
GPRG91       0.00 G
GPRG92       0.00 G
GPRG93       0.00 G
GPRG94       0.00 G
GPRG95       0.00 G
GPRG96       0.00 G
GPRG97       0.00 G
GPRG98       0.00 G
GPRG99       0.00 G
GPRG100      0.00 G

===== Processing Parameters =====
SI            65536
SF            125.7804187 MHz
WDW           EM
SSB           0
GB            0
PC            2.00
  
```



2.25


```

Current Data Parameters
=====
USER          AQ_1_53
NAME          AQ_1_53
PROCNO       1
F2 - Acquisition Parameters
=====
Date_        2010730
Time         16:55:00
INSTRUM     CY5500
PROBHD      5 mm CPCL1H-
PULPROG     zgpg30
TD          65536
SOLVENT     CDCl3
DS          4
SS          16
SF          101.625 MHz
FIDRES      0.092688 Hz
AQ          1.0813940 sec
RG          167.500 usec
DM          167.500 usec
DE          6.00 usec
D1          0.25000000 sec
d11         0.03000000 sec
d17         0.00196000 sec
d18         0.00196000 sec
d19         0.00196000 sec
d20         0.00196000 sec
d21         0.00196000 sec
d22         0.00196000 sec
d23         0.00196000 sec
d24         0.00196000 sec
d25         0.00196000 sec
d26         0.00196000 sec
d27         0.00196000 sec
d28         0.00196000 sec
d29         0.00196000 sec
d30         0.00196000 sec
===== CHANNEL f1 =====
NUC1         13C
P1           12.00 usec
PL1          0.00 dB
P2           500.00 usec
PL2          0.00 dB
P3           2000.00 usec
PL3          0.00 dB
P4           -1.00 dB
PL4          0.00 dB
P5           125.7945200 dB
PL5          0.00 dB
SFO1         125.7945200 MHz
SFO2         500.1362800 MHz
SFO3         500.1362800 MHz
SFO4         500.1362800 MHz
SFO5         500.1362800 MHz
SFO6         500.1362800 MHz
SFO7         500.1362800 MHz
SFO8         500.1362800 MHz
===== CHANNEL f2 =====
CPDPRG2     zgpg30
NUC2         13C
P1           12.00 usec
PL1          0.00 dB
P2           500.00 usec
PL2          0.00 dB
P3           2000.00 usec
PL3          0.00 dB
P4           -1.00 dB
PL4          0.00 dB
P5           125.7945200 dB
PL5          0.00 dB
SFO1         125.7945200 MHz
SFO2         500.1362800 MHz
SFO3         500.1362800 MHz
SFO4         500.1362800 MHz
SFO5         500.1362800 MHz
SFO6         500.1362800 MHz
SFO7         500.1362800 MHz
SFO8         500.1362800 MHz
===== GRADIENT CHANNEL =====
GPNAM1      SINE.100
GPNAM2      SINE.100
GPA1        0.00 %
GPA2        0.00 %
GPA3        0.00 %
GPA4        0.00 %
GPA5        0.00 %
GPA6        0.00 %
GPA7        0.00 %
GPA8        0.00 %
GPA9        0.00 %
GPA10       0.00 %
GPA11       0.00 %
GPA12       0.00 %
GPA13       0.00 %
GPA14       0.00 %
GPA15       0.00 %
GPA16       0.00 %
===== Processing parameters =====
SI           65536
SF           125.7804094 MHz
WDW          EM
SSB          0
GB           0
CB           0
PC           2.00

```

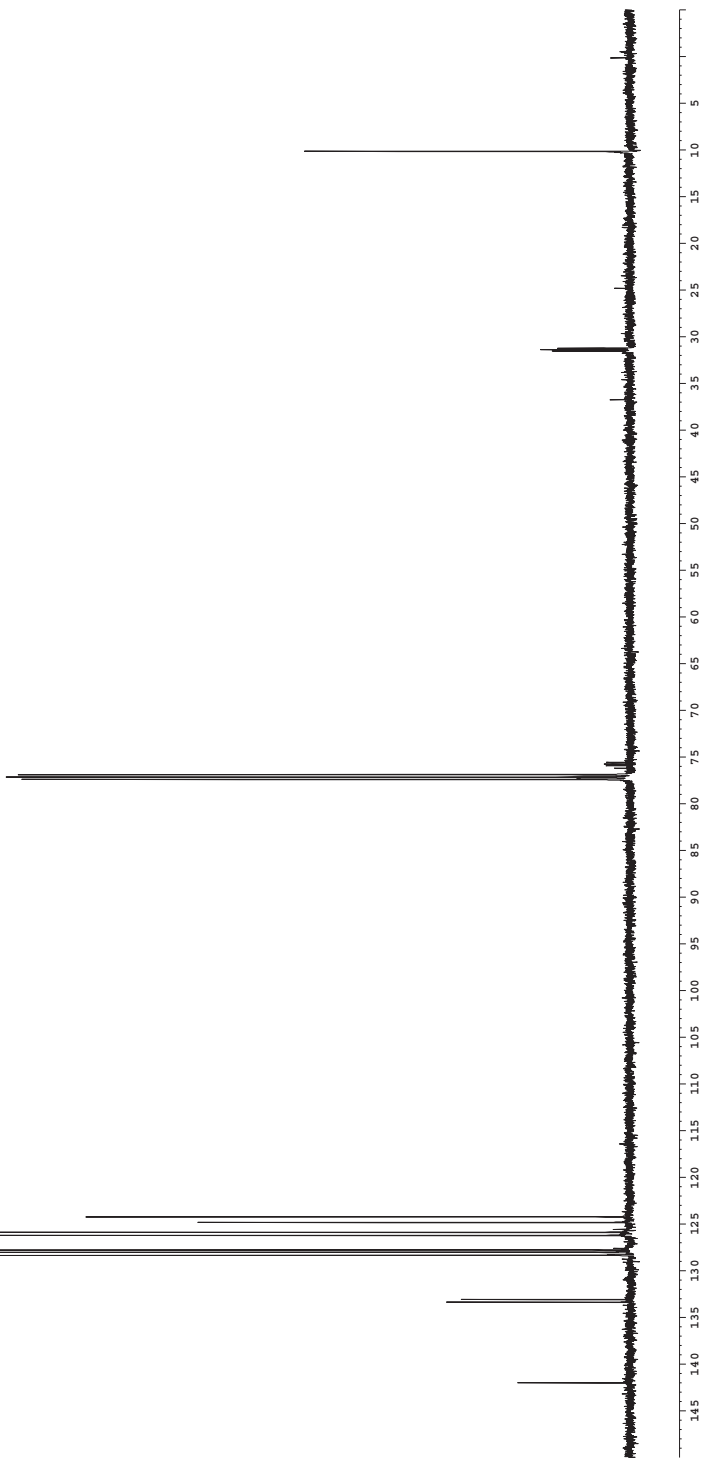
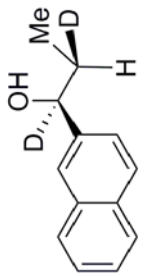
10.146

31.234
31.389
31.544

75.764
76.905
77.159
77.413

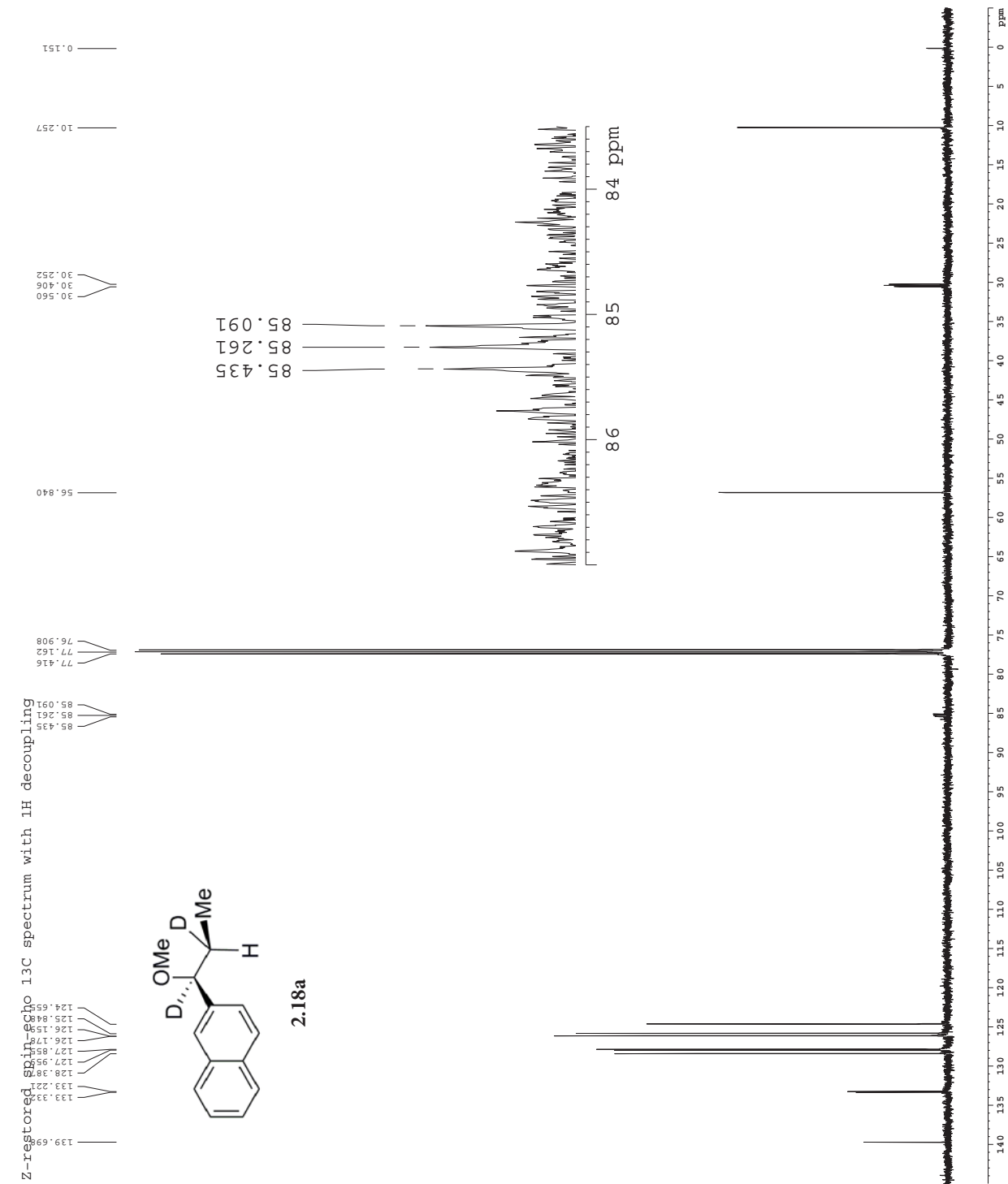
Z-restored spin-echoed ¹³C spectrum with 1H decoupling

141.98
133.39
133.11
133.37
128.37
128.05
127.81
126.24
125.91
125.91
124.86
124.26




```

Current Data Parameters
USER          ACL_3_270_01
PROCNO       1
Date_        20140426
INSTRUM      cryo500
PROBHD       5 mm CPCL1H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           4
AQ           1.013940 sec
FIDRES       0.092688 Hz
AQ           1.013940 sec
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00156000 sec
MCWPRG       CPMAS
MCWPRG2      CPMAS2
PC           31.00 usec
***** CHANNEL f1 *****
NUC1          13C
P1           12.00 usec
P11          500.00 usec
P2           2000.00 usec
P21          1.00 dB
P22          -1.00 dB
P23          125.794520 MHz
P24          30.00 dB
P25          30.00 dB
P26          30.00 dB
P27          30.00 dB
P28          30.00 dB
P29          30.00 dB
P30          30.00 dB
P31          30.00 dB
P32          30.00 dB
P33          30.00 dB
P34          30.00 dB
P35          30.00 dB
P36          30.00 dB
P37          30.00 dB
P38          30.00 dB
P39          30.00 dB
P40          30.00 dB
P41          30.00 dB
P42          30.00 dB
P43          30.00 dB
P44          30.00 dB
P45          30.00 dB
P46          30.00 dB
P47          30.00 dB
P48          30.00 dB
P49          30.00 dB
P50          30.00 dB
P51          30.00 dB
P52          30.00 dB
P53          30.00 dB
P54          30.00 dB
P55          30.00 dB
P56          30.00 dB
P57          30.00 dB
P58          30.00 dB
P59          30.00 dB
P60          30.00 dB
P61          30.00 dB
P62          30.00 dB
P63          30.00 dB
P64          30.00 dB
P65          30.00 dB
P66          30.00 dB
P67          30.00 dB
P68          30.00 dB
P69          30.00 dB
P70          30.00 dB
P71          30.00 dB
P72          30.00 dB
P73          30.00 dB
P74          30.00 dB
P75          30.00 dB
P76          30.00 dB
P77          30.00 dB
P78          30.00 dB
P79          30.00 dB
P80          30.00 dB
P81          30.00 dB
P82          30.00 dB
P83          30.00 dB
P84          30.00 dB
P85          30.00 dB
P86          30.00 dB
P87          30.00 dB
P88          30.00 dB
P89          30.00 dB
P90          30.00 dB
P91          30.00 dB
P92          30.00 dB
P93          30.00 dB
P94          30.00 dB
P95          30.00 dB
P96          30.00 dB
P97          30.00 dB
P98          30.00 dB
P99          30.00 dB
P100         30.00 dB
***** CHANNEL L2 *****
CPDPRG2      waltz16
NUC2          1H
P1           12.00 usec
P11          500.00 usec
P2           2000.00 usec
P21          1.00 dB
P22          -1.00 dB
P23          125.794520 MHz
P24          30.00 dB
P25          30.00 dB
P26          30.00 dB
P27          30.00 dB
P28          30.00 dB
P29          30.00 dB
P30          30.00 dB
P31          30.00 dB
P32          30.00 dB
P33          30.00 dB
P34          30.00 dB
P35          30.00 dB
P36          30.00 dB
P37          30.00 dB
P38          30.00 dB
P39          30.00 dB
P40          30.00 dB
P41          30.00 dB
P42          30.00 dB
P43          30.00 dB
P44          30.00 dB
P45          30.00 dB
P46          30.00 dB
P47          30.00 dB
P48          30.00 dB
P49          30.00 dB
P50          30.00 dB
P51          30.00 dB
P52          30.00 dB
P53          30.00 dB
P54          30.00 dB
P55          30.00 dB
P56          30.00 dB
P57          30.00 dB
P58          30.00 dB
P59          30.00 dB
P60          30.00 dB
P61          30.00 dB
P62          30.00 dB
P63          30.00 dB
P64          30.00 dB
P65          30.00 dB
P66          30.00 dB
P67          30.00 dB
P68          30.00 dB
P69          30.00 dB
P70          30.00 dB
P71          30.00 dB
P72          30.00 dB
P73          30.00 dB
P74          30.00 dB
P75          30.00 dB
P76          30.00 dB
P77          30.00 dB
P78          5.00 dB
P79          5.00 dB
P80          5.00 dB
P81          5.00 dB
P82          5.00 dB
P83          5.00 dB
P84          5.00 dB
P85          5.00 dB
P86          5.00 dB
P87          5.00 dB
P88          5.00 dB
P89          5.00 dB
P90          5.00 dB
P91          5.00 dB
P92          5.00 dB
P93          5.00 dB
P94          5.00 dB
P95          5.00 dB
P96          5.00 dB
P97          5.00 dB
P98          5.00 dB
P99          5.00 dB
P100         5.00 dB
***** GRADIENT CHANNEL *****
GPNAM1       SINE.100
GPNAM2       SINE.100
GPA1         0.00 Hz
GPA2         0.00 Hz
GPA3         0.00 Hz
GPA4         0.00 Hz
GPA5         0.00 Hz
GPA6         0.00 Hz
GPA7         0.00 Hz
GPA8         0.00 Hz
GPA9         0.00 Hz
GPA10        0.00 Hz
GPA11        0.00 Hz
GPA12        0.00 Hz
GPA13        0.00 Hz
GPA14        0.00 Hz
GPA15        0.00 Hz
GPA16        0.00 Hz
GPA17        0.00 Hz
GPA18        0.00 Hz
GPA19        0.00 Hz
GPA20        0.00 Hz
GPA21        0.00 Hz
GPA22        0.00 Hz
GPA23        0.00 Hz
GPA24        0.00 Hz
GPA25        0.00 Hz
GPA26        0.00 Hz
GPA27        0.00 Hz
GPA28        0.00 Hz
GPA29        0.00 Hz
GPA30        0.00 Hz
GPA31        0.00 Hz
GPA32        0.00 Hz
GPA33        0.00 Hz
GPA34        0.00 Hz
GPA35        0.00 Hz
GPA36        0.00 Hz
GPA37        0.00 Hz
GPA38        0.00 Hz
GPA39        0.00 Hz
GPA40        0.00 Hz
GPA41        0.00 Hz
GPA42        0.00 Hz
GPA43        0.00 Hz
GPA44        0.00 Hz
GPA45        0.00 Hz
GPA46        0.00 Hz
GPA47        0.00 Hz
GPA48        0.00 Hz
GPA49        0.00 Hz
GPA50        0.00 Hz
GPA51        0.00 Hz
GPA52        0.00 Hz
GPA53        0.00 Hz
GPA54        0.00 Hz
GPA55        0.00 Hz
GPA56        0.00 Hz
GPA57        0.00 Hz
GPA58        0.00 Hz
GPA59        0.00 Hz
GPA60        0.00 Hz
GPA61        0.00 Hz
GPA62        0.00 Hz
GPA63        0.00 Hz
GPA64        0.00 Hz
GPA65        0.00 Hz
GPA66        0.00 Hz
GPA67        0.00 Hz
GPA68        0.00 Hz
GPA69        0.00 Hz
GPA70        0.00 Hz
GPA71        0.00 Hz
GPA72        0.00 Hz
GPA73        0.00 Hz
GPA74        0.00 Hz
GPA75        0.00 Hz
GPA76        0.00 Hz
GPA77        0.00 Hz
GPA78        0.00 Hz
GPA79        0.00 Hz
GPA80        0.00 Hz
GPA81        0.00 Hz
GPA82        0.00 Hz
GPA83        0.00 Hz
GPA84        0.00 Hz
GPA85        0.00 Hz
GPA86        0.00 Hz
GPA87        0.00 Hz
GPA88        0.00 Hz
GPA89        0.00 Hz
GPA90        0.00 Hz
GPA91        0.00 Hz
GPA92        0.00 Hz
GPA93        0.00 Hz
GPA94        0.00 Hz
GPA95        0.00 Hz
GPA96        0.00 Hz
GPA97        0.00 Hz
GPA98        0.00 Hz
GPA99        0.00 Hz
GPA100       0.00 Hz
***** Processing parameters *****
SI           65536
SF           125.7804085 MHz
WDW          EM
SSB          0
GB           0
PC           1.30
  
```



```

Current Data Parameters
=====
USER          AG_A_5_1
NAME          AG_A_5_1
PROCNO       1
Date_         20100804
Time_         12:24:00
INSTRUM      5 mm QNP H/P/P
PROBHD       5 mm QNP 1H/13
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
AQ           5.118753 sec
RG           0.107853 Hz
AQ           5.118753 sec
RG           0.107853 Hz
DM           78.000 usec
DE           4.50 usec
DI           0.10000000 sec
MCNST       0.00000000 sec
PCNST       0.00000000 sec
=====
NUC1         13C
NUC2         1H
P1           12.00 usec
PL1         -2.00 dB
SFO1         400.1328009 MHz
SFO2         400.1328009 MHz
SFO3         400.1328009 MHz
SFO4         400.1328009 MHz
=====
F2 - Acquisition Parameters
=====
SI           65536
SF          400.1300007 MHz
RG           0.107853 Hz
DE           4.50 usec
DI           0.10000000 sec
PC           2.00
=====
F2 - Processing Parameters
=====
SI           65536
SF          400.1300007 MHz
RG           0.107853 Hz
DE           4.50 usec
DI           0.10000000 sec
PC           2.00
=====

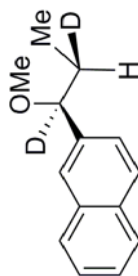
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0.893
0.874

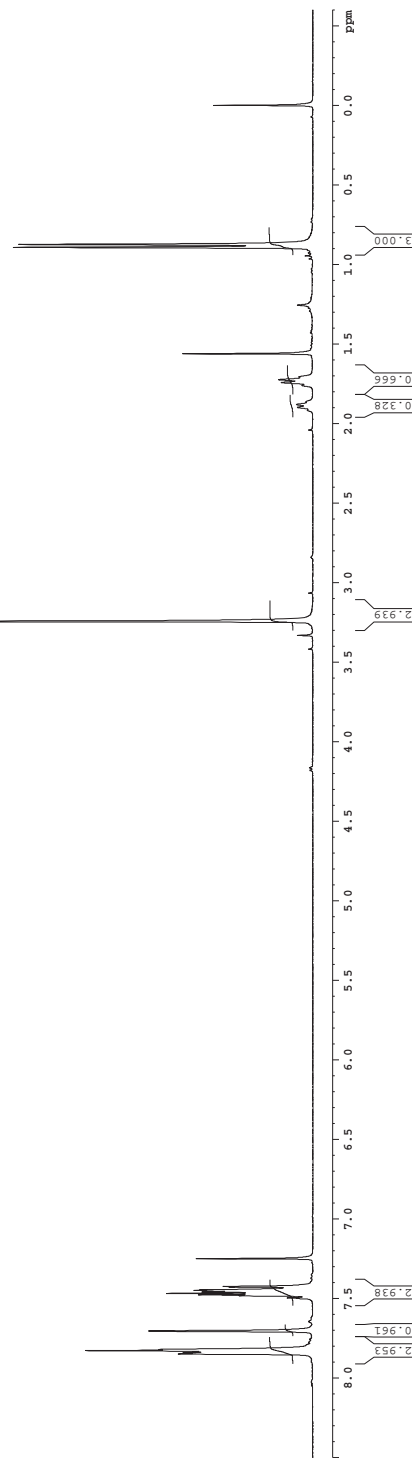
1.743
1.725
1.562

3.245

1H spectrum
7.850
7.845
7.837
7.832
7.822
7.806
7.788
7.770
7.751
7.747
7.745
7.742
7.726
7.725



2.18b



```

Current Data Parameters
=====
USER          AC_1_5_01
PRCNO        1
Date_         20100804
Time_        07:55:00
INSTRUM      CPY500
PROBHD       5 mm CPYCL1H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
SS           16
SPRES        3032.888 Hz
AQ           1.0813940 sec
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00136000 sec
MCKBKT       0.03000000 sec
MCKWBK       0.03000000 sec
P2           31.00 usec

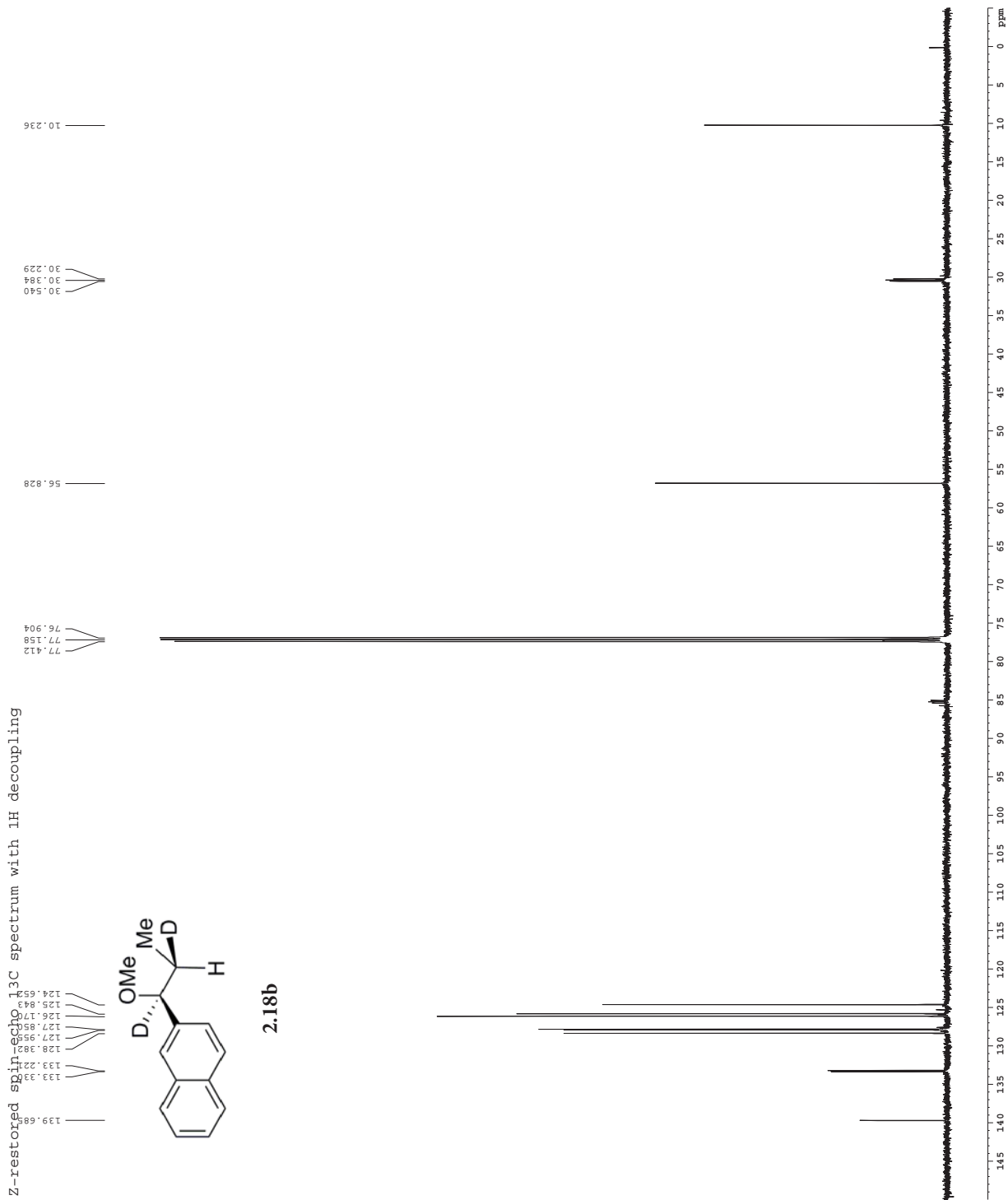
===== CHANNEL f1 =====
NUC1          13C
P1            12C
P11           500.00 usec
P12           2000.00 usec
P13           1.00 dB
P14           -1.00 dB
P15           125.7945200 MHz
P16           0.00 Hz
P17           0.00 Hz
P18           0.00 Hz
P19           0.00 Hz
P20           0.00 Hz
P21           0.00 Hz
P22           0.00 Hz
P23           0.00 Hz
P24           0.00 Hz
P25           0.00 Hz
P26           0.00 Hz
P27           0.00 Hz
P28           0.00 Hz
P29           0.00 Hz
P30           0.00 Hz
P31           0.00 Hz
P32           0.00 Hz
P33           0.00 Hz
P34           0.00 Hz
P35           0.00 Hz
P36           0.00 Hz
P37           0.00 Hz
P38           0.00 Hz
P39           0.00 Hz
P40           0.00 Hz
P41           0.00 Hz
P42           0.00 Hz
P43           0.00 Hz
P44           0.00 Hz
P45           0.00 Hz
P46           0.00 Hz
P47           0.00 Hz
P48           0.00 Hz
P49           0.00 Hz
P50           0.00 Hz
P51           0.00 Hz
P52           0.00 Hz
P53           0.00 Hz
P54           0.00 Hz
P55           0.00 Hz
P56           0.00 Hz
P57           0.00 Hz
P58           0.00 Hz
P59           0.00 Hz
P60           0.00 Hz
P61           0.00 Hz
P62           0.00 Hz
P63           0.00 Hz
P64           0.00 Hz
P65           0.00 Hz
P66           0.00 Hz
P67           0.00 Hz
P68           0.00 Hz
P69           0.00 Hz
P70           0.00 Hz
P71           0.00 Hz
P72           0.00 Hz
P73           0.00 Hz
P74           0.00 Hz
P75           0.00 Hz
P76           0.00 Hz
P77           0.00 Hz
P78           0.00 Hz
P79           0.00 Hz
P80           0.00 Hz
P81           0.00 Hz
P82           0.00 Hz
P83           0.00 Hz
P84           0.00 Hz
P85           0.00 Hz
P86           0.00 Hz
P87           0.00 Hz
P88           0.00 Hz
P89           0.00 Hz
P90           0.00 Hz
P91           0.00 Hz
P92           0.00 Hz
P93           0.00 Hz
P94           0.00 Hz
P95           0.00 Hz
P96           0.00 Hz
P97           0.00 Hz
P98           0.00 Hz
P99           0.00 Hz
P100          0.00 Hz

===== CHANNEL L2 =====
CPYPRG2      zgpg30
NUC2          13C
P101          12C
P102          500.00 usec
P103          2000.00 usec
P104          1.00 dB
P105          -1.00 dB
P106          125.7945200 MHz
P107          0.00 Hz
P108          0.00 Hz
P109          0.00 Hz
P110          0.00 Hz
P111          0.00 Hz
P112          0.00 Hz
P113          0.00 Hz
P114          0.00 Hz
P115          0.00 Hz
P116          0.00 Hz
P117          0.00 Hz
P118          0.00 Hz
P119          0.00 Hz
P120          0.00 Hz
P121          0.00 Hz
P122          0.00 Hz
P123          0.00 Hz
P124          0.00 Hz
P125          0.00 Hz
P126          0.00 Hz
P127          0.00 Hz
P128          0.00 Hz
P129          0.00 Hz
P130          0.00 Hz
P131          0.00 Hz
P132          0.00 Hz
P133          0.00 Hz
P134          0.00 Hz
P135          0.00 Hz
P136          0.00 Hz
P137          0.00 Hz
P138          0.00 Hz
P139          0.00 Hz
P140          0.00 Hz
P141          0.00 Hz
P142          0.00 Hz
P143          0.00 Hz
P144          0.00 Hz
P145          0.00 Hz
P146          0.00 Hz
P147          0.00 Hz
P148          0.00 Hz
P149          0.00 Hz
P150          0.00 Hz
P151          0.00 Hz
P152          0.00 Hz
P153          0.00 Hz
P154          0.00 Hz
P155          0.00 Hz
P156          0.00 Hz
P157          0.00 Hz
P158          0.00 Hz
P159          0.00 Hz
P160          0.00 Hz
P161          0.00 Hz
P162          0.00 Hz
P163          0.00 Hz
P164          0.00 Hz
P165          0.00 Hz
P166          0.00 Hz
P167          0.00 Hz
P168          0.00 Hz
P169          0.00 Hz
P170          0.00 Hz
P171          0.00 Hz
P172          0.00 Hz
P173          0.00 Hz
P174          0.00 Hz
P175          0.00 Hz
P176          0.00 Hz
P177          0.00 Hz
P178          0.00 Hz
P179          0.00 Hz
P180          0.00 Hz
P181          0.00 Hz
P182          0.00 Hz
P183          0.00 Hz
P184          0.00 Hz
P185          0.00 Hz
P186          0.00 Hz
P187          0.00 Hz
P188          0.00 Hz
P189          0.00 Hz
P190          0.00 Hz
P191          0.00 Hz
P192          0.00 Hz
P193          0.00 Hz
P194          0.00 Hz
P195          0.00 Hz
P196          0.00 Hz
P197          0.00 Hz
P198          0.00 Hz
P199          0.00 Hz
P200          0.00 Hz

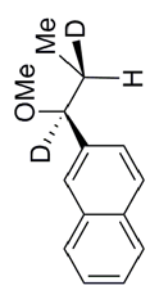
===== GRADIENT CHANNEL =====
GPNAM2       SINE.100
GPA1         0.00 Hz
GPA2         0.00 Hz
GPA3         0.00 Hz
GPA4         0.00 Hz
GPA5         0.00 Hz
GPA6         0.00 Hz
GPA7         0.00 Hz
GPA8         0.00 Hz
GPA9         0.00 Hz
GPA10        0.00 Hz
GPA11        0.00 Hz
GPA12        0.00 Hz
GPA13        0.00 Hz
GPA14        0.00 Hz
GPA15        0.00 Hz
GPA16        0.00 Hz
GPA17        0.00 Hz
GPA18        0.00 Hz
GPA19        0.00 Hz
GPA20        0.00 Hz
GPA21        0.00 Hz
GPA22        0.00 Hz
GPA23        0.00 Hz
GPA24        0.00 Hz
GPA25        0.00 Hz
GPA26        0.00 Hz
GPA27        0.00 Hz
GPA28        0.00 Hz
GPA29        0.00 Hz
GPA30        0.00 Hz
GPA31        0.00 Hz
GPA32        0.00 Hz
GPA33        0.00 Hz
GPA34        0.00 Hz
GPA35        0.00 Hz
GPA36        0.00 Hz
GPA37        0.00 Hz
GPA38        0.00 Hz
GPA39        0.00 Hz
GPA40        0.00 Hz
GPA41        0.00 Hz
GPA42        0.00 Hz
GPA43        0.00 Hz
GPA44        0.00 Hz
GPA45        0.00 Hz
GPA46        0.00 Hz
GPA47        0.00 Hz
GPA48        0.00 Hz
GPA49        0.00 Hz
GPA50        0.00 Hz
GPA51        0.00 Hz
GPA52        0.00 Hz
GPA53        0.00 Hz
GPA54        0.00 Hz
GPA55        0.00 Hz
GPA56        0.00 Hz
GPA57        0.00 Hz
GPA58        0.00 Hz
GPA59        0.00 Hz
GPA60        0.00 Hz
GPA61        0.00 Hz
GPA62        0.00 Hz
GPA63        0.00 Hz
GPA64        0.00 Hz
GPA65        0.00 Hz
GPA66        0.00 Hz
GPA67        0.00 Hz
GPA68        0.00 Hz
GPA69        0.00 Hz
GPA70        0.00 Hz
GPA71        0.00 Hz
GPA72        0.00 Hz
GPA73        0.00 Hz
GPA74        0.00 Hz
GPA75        0.00 Hz
GPA76        0.00 Hz
GPA77        0.00 Hz
GPA78        0.00 Hz
GPA79        0.00 Hz
GPA80        0.00 Hz
GPA81        0.00 Hz
GPA82        0.00 Hz
GPA83        0.00 Hz
GPA84        0.00 Hz
GPA85        0.00 Hz
GPA86        0.00 Hz
GPA87        0.00 Hz
GPA88        0.00 Hz
GPA89        0.00 Hz
GPA90        0.00 Hz
GPA91        0.00 Hz
GPA92        0.00 Hz
GPA93        0.00 Hz
GPA94        0.00 Hz
GPA95        0.00 Hz
GPA96        0.00 Hz
GPA97        0.00 Hz
GPA98        0.00 Hz
GPA99        0.00 Hz
GPA100       0.00 Hz

===== Processing Parameters =====
SI           65536
SF           125.7804085 MHz
RG           0
WDW           EM
SSB           0
GB           0
PC           2.00

```



Z-restored spin echo ¹³C spectrum with 1H decoupling

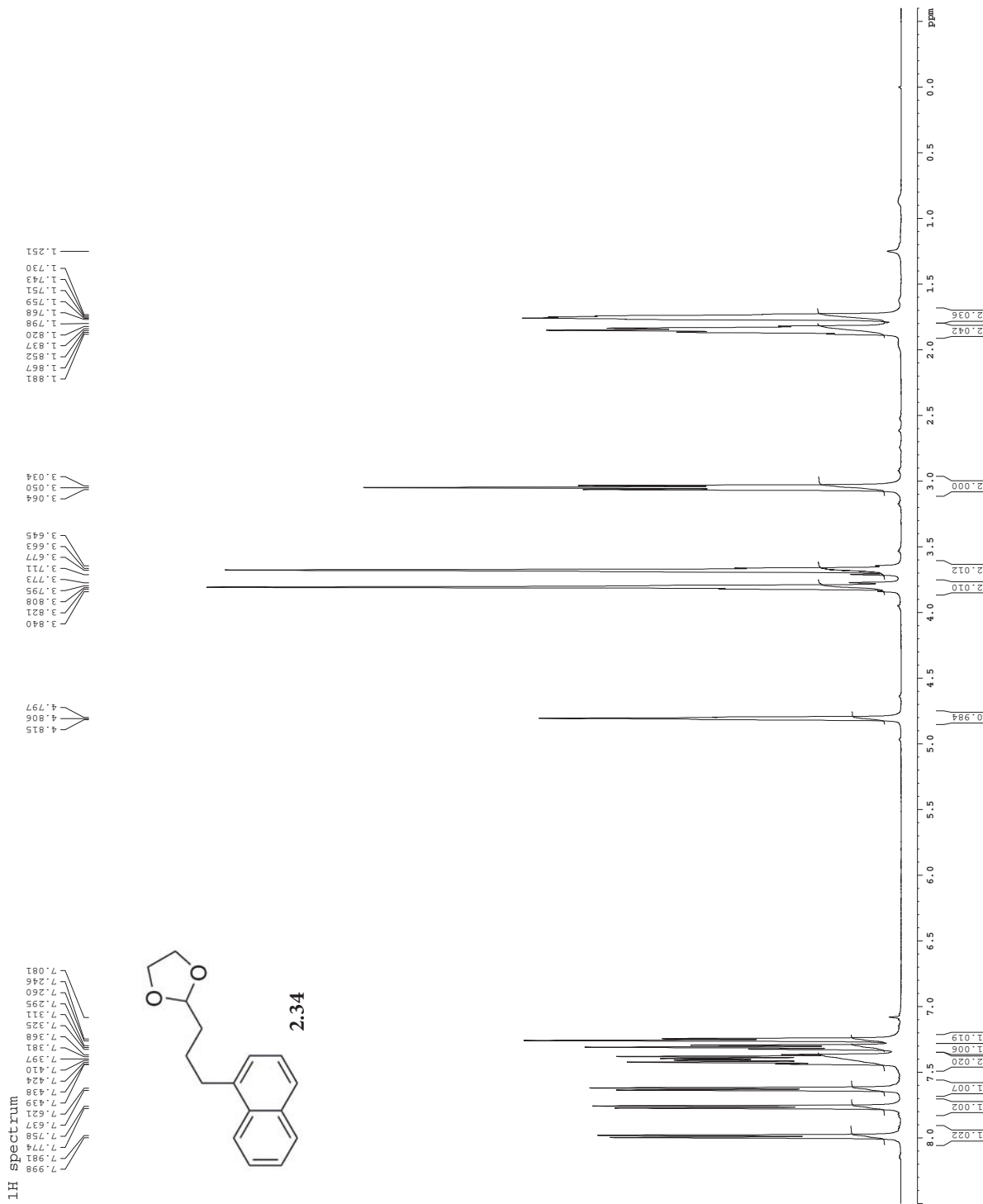


2.18b


```

Current Data Parameters
=====
NAME      AGL_3_17_C1
PROCNO    1
Date_     2011105
Time      01500
INSTRUM   5 mm broadband
PULPROG   zgpg30
TD         83728
SOLVENT   CDCl3
DS         2
AQ         5.000000 sec
RG         0.038943 Hz
AQ         5.0998774 sec
DM         62.400 usec
DE         6.00 usec
DI         0.10000000 sec
MCNST     0.00000000 sec
PCPRG1    0.03000000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         12.20 usec
SFO1       499.9934950 MHz
F2 - Acquisition Parameters
SI         65536
SF         499.9901165 MHz
SSB        0
GB         0
PC         1.00

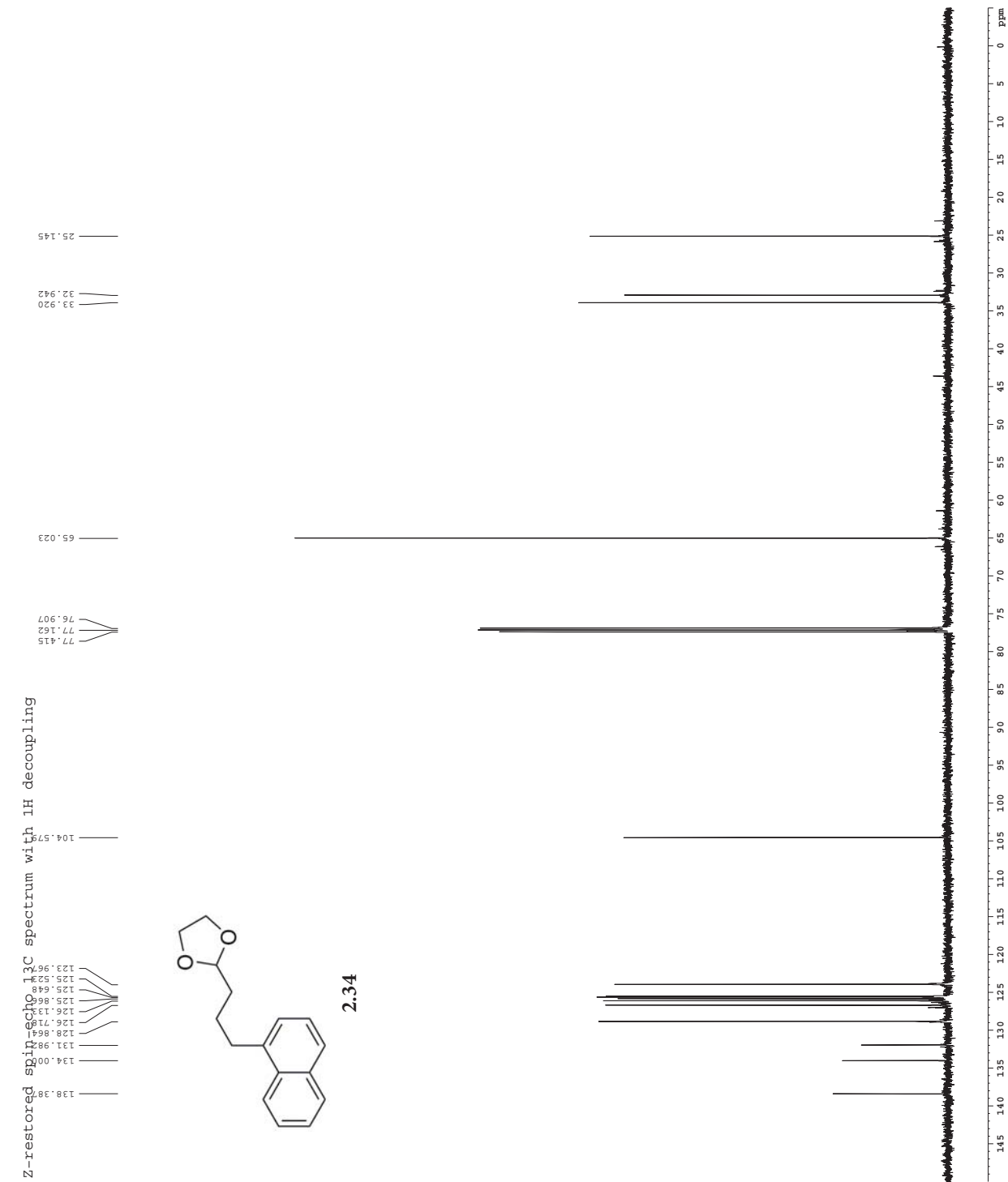
```



```

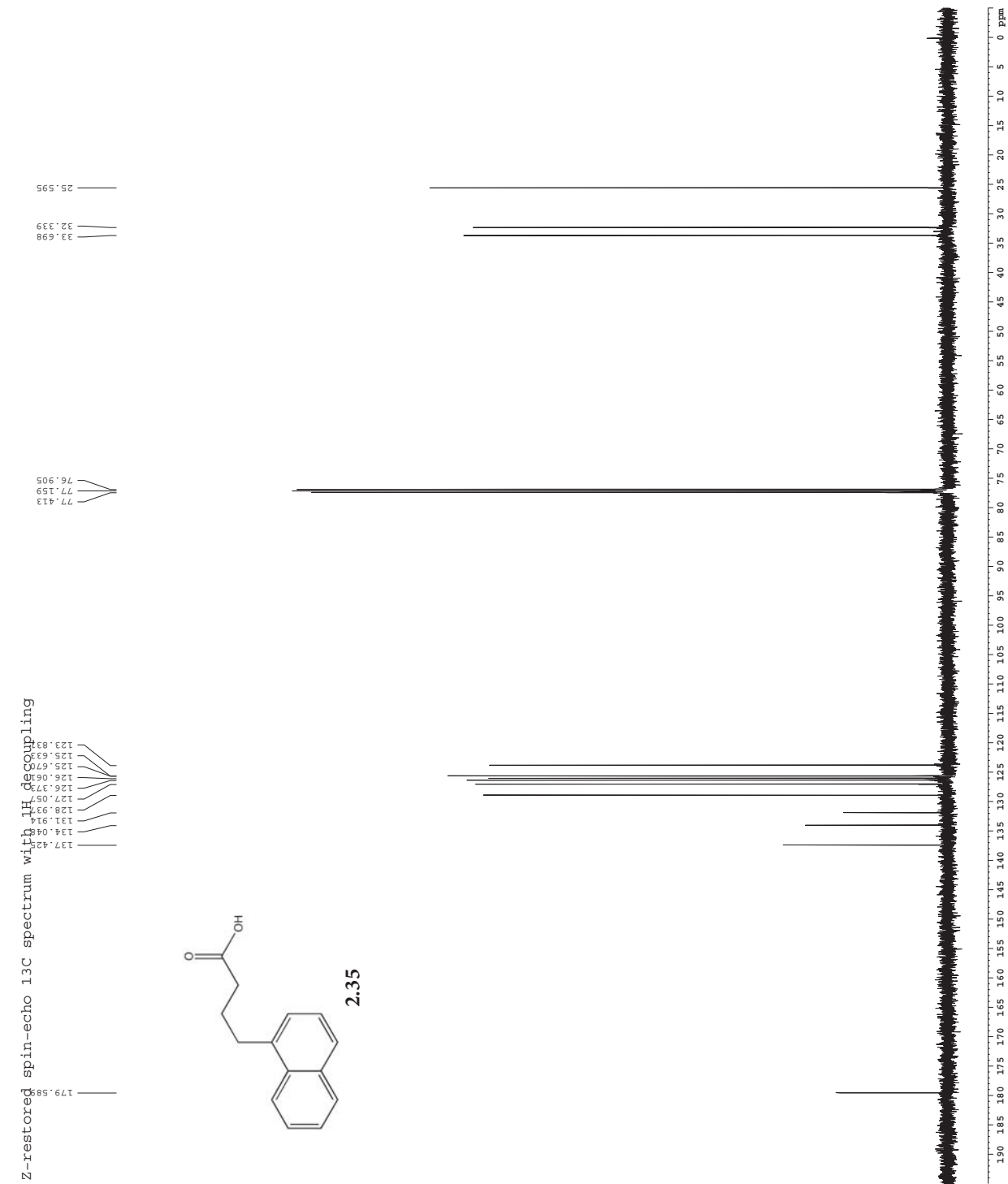
Current Data Parameters
=====
USER          AG3_3_diox
PRCNO        1
Date_        2010331
Time_        12:00:00
INSTRUM      cryso500
PROBHD       5 mm CPTCL 1H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           16
SF          500.136
AQ           3.000000 sec
RG           1.0813940 sec
DM           16.500 usec
DE           6.00 usec
DI           0.25000000 sec
D11          0.03000000 sec
d17          0.0019600 sec
MCKBKT       0.03000000 sec
MCKWBK       0.03000000 sec
P2           31.00 usec
===== CHANNEL f1 =====
NUC1         13C
P1           1.00 usec
P11          500.00 usec
P12          2000.00 usec
P13          -1.00 dB
P14          -1.00 dB
SFO1         125.794520 MHz
SFO2         125.794520 MHz
SP2         CPD60 0.5 3.20 dB
SPNAM2       CP60CCP-4
SFOFF1       0.00 Hz
SFOFF2       0.00 Hz
===== CHANNEL f2 =====
CPDPRG2      zgpg30
NUC2         13C
P2           1.00 usec
P21          500.00 usec
P22          2000.00 usec
P23          -1.00 dB
P24          -1.00 dB
SFO2         125.794520 MHz
SFO3         125.794520 MHz
SP2         CPD60 0.5 3.20 dB
SPNAM2       CP60CCP-4
SFOFF1       0.00 Hz
SFOFF2       0.00 Hz
===== GRADIENT CHANNEL =====
GPNAM2       G LINE.100
GPA1         0.00 %
GPA2         0.00 %
GPA3         0.00 %
GPA4         0.00 %
GPA5         0.00 %
GPA6         0.00 %
GPA7         30.00 %
GPA8         50.00 %
GPA9         1000.00 usec
===== Processing Parameters =====
SI           65536
SF           125.7804099 MHz
MKM          0
SBN          0
GB           1.0 Hz
PC           2.00

```




```

Current Data Parameters
USER      AQ_3_carboxacid
NAME      AQ_3_carboxacid
PROCNO    1
Date_     2010402
Time      12:55:00
INSTRUM   cryo500
PROBHD    5 mm CPTCL1H-
PULPROG   spinachis
TD         65536
SOLVENT   CDCl3
DS         4
AQ        16
FIDRES    0.092688 Hz
AQ        1.0813940 sec
DM         16.500 usec
DE         6.00 usec
D1         0.25000000 sec
d11        0.03000000 sec
d17        0.00196000 sec
MORPH     0.03000000 sec
MORPH     0.03000000 sec
PC        31.00 usec
***** CHANNEL f1 *****
NUC1       13C
P1         12.00 usec
P11        500.00 usec
P2         2000.00 usec
P21        -1.00 dB
P22        -1.00 dB
SFO1       125.7942500 MHz
SFO2       500.2225011 MHz
SP1        0.00 Hz
SP2        0.00 Hz
SFOFF1     0.00 Hz
SFOFF2     0.00 Hz
***** CHANNEL f2 *****
CPDPRG2   waltz16
NUC2       1H
P2         10.00 usec
P21        10.00 dB
P22        24.60 dB
SFO2       500.2225011 MHz
***** GRADIENT CHANNEL *****
SFOG1      0.00 Hz
SFOG2      0.00 Hz
SFOG3      0.00 Hz
SFOG4      0.00 Hz
SFOG5      0.00 Hz
SFOG6      0.00 Hz
SFOG7      0.00 Hz
SFOG8      0.00 Hz
SFOG9      0.00 Hz
SFOG10     0.00 Hz
SFOG11     0.00 Hz
SFOG12     0.00 Hz
SFOG13     0.00 Hz
SFOG14     0.00 Hz
SFOG15     0.00 Hz
SFOG16     0.00 Hz
SFOG17     0.00 Hz
SFOG18     0.00 Hz
SFOG19     0.00 Hz
SFOG20     0.00 Hz
***** Processing parameters *****
SI         65536
SF          125.7804000 MHz
WDW         0
SSB         0
GB          0
CB          0
PC          2.00
  
```



```

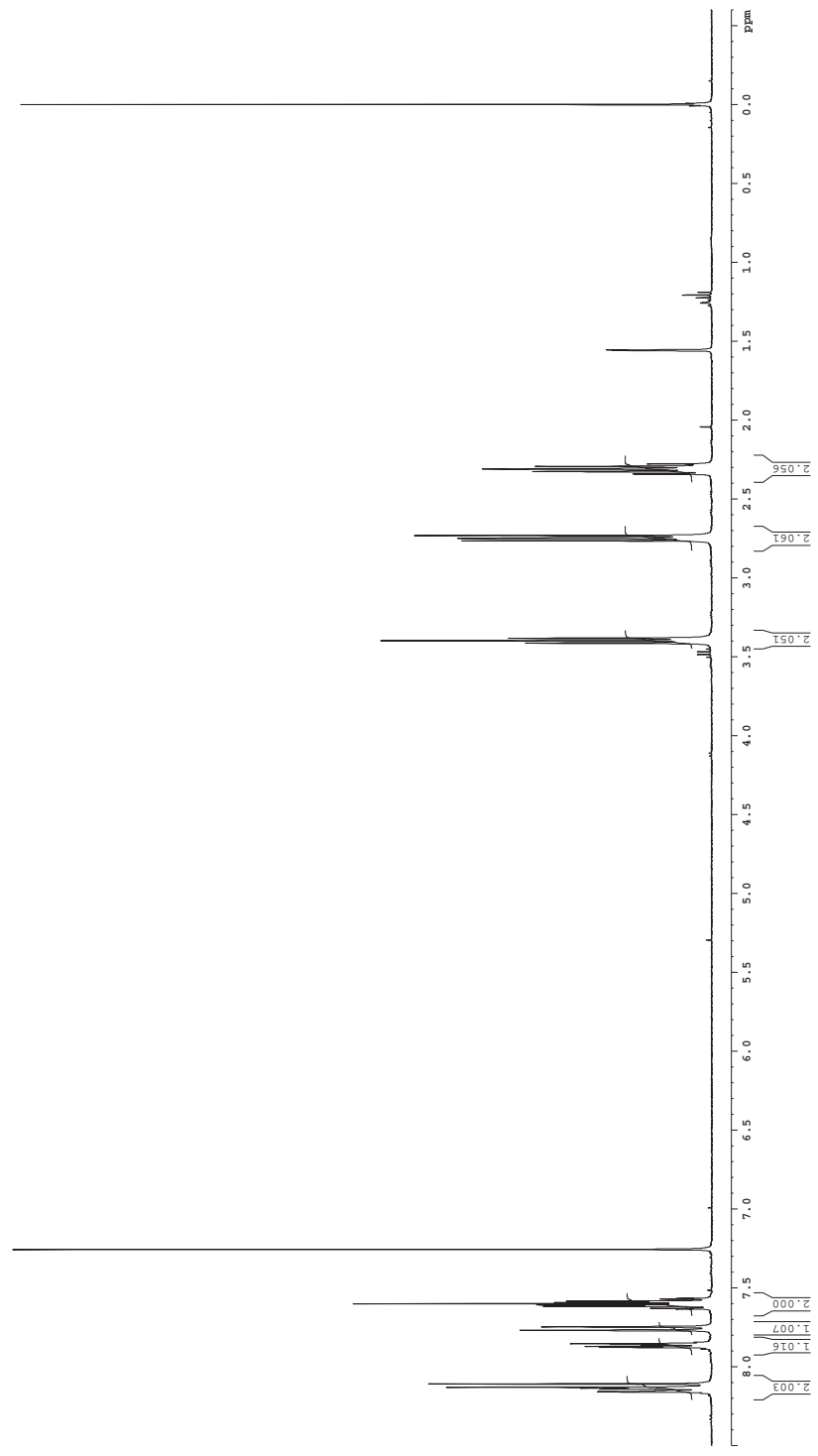
Current Data Parameters
USER      ACL_3_12_01
NAME      ACL_3_12_01
PROCNO    1
Date_     2011109
Time      12:00:00
INSTRUM   5 mm QNP H/P/P
PROBHD    5 mm QNP H/P/P
TD         65536
SOLVENT   CDCl3
DS         2
AQ         5.118793 sec
RG         0.1000000 sec
RG2        0.1000000 sec
DM         78.000 usec
DE         4.50 usec
DI         0.1000000 sec
MCREST    0.0000000 sec
PCPRGR    0.0300000 sec
NUC1      13C
NUC2      1H
P1         12.00 usec
SFO1       400.1328009 MHz
SFO2       400.1328009 MHz
P2         Processing Parameters
SI         65536
SF         400.1300225 MHz
RG         0.1000000 sec
SSB        0
GB         0
PC         2.00
  
```

0.000
 0.008
 1.208
 1.558
 1.558
 2.278
 2.294
 2.310
 2.326
 2.337
 2.343
 2.352
 2.746
 2.750
 2.766
 3.184
 3.199
 3.414

7.258
 7.569
 7.573
 7.585
 7.590
 7.595
 7.602
 7.610
 7.614
 7.619
 7.631
 7.636
 7.745
 7.771
 7.855
 7.864
 7.879
 8.107
 8.123



2.36



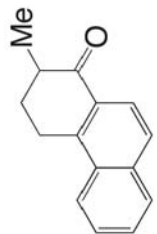

```

Current Data Parameters
=====
USER          Ag_3_125
NAME
PROCNO       1
Date_         201113
Time_         11:44:00
INSTRUM      5 mm QNP H/P/P
PROBHD       5 mm QNP 1H/13
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
AQ           5.115000 sec
RG           0.100000 Hz
AQ           5.111879 sec
RG           0.100000 Hz
DM           78.000 usec
DE           2.50 usec
DI           0.10000000 sec
MCNSTP      0.00000000 sec
PCNSTP      0.00000000 sec
=====
NUC1          CHANNEL f1 13C
P1           12.00 usec
PL1          0.00 dB
SFO1         400.1328009 MHz
=====
F2 - Processing Parameters
SI           65536
SF           400.1300289 MHz
RG           0.10000000 sec
DE           2.50 usec
DI           0.10000000 sec
PC           0.00000000 sec
=====

```

0.00

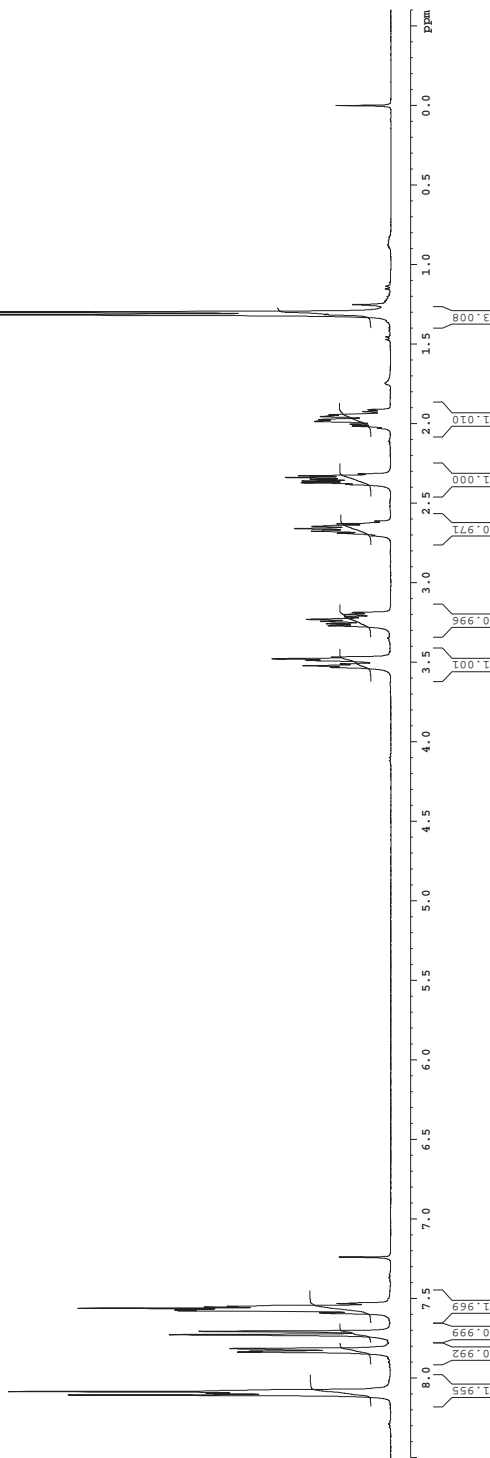
1.253
1.298
1.315
1.946
1.957
1.976
1.987
2.004
2.016
2.017
2.317
2.328
2.339
2.350
2.361
2.373
2.384
2.631
2.647
2.661
2.673
2.678
2.689
3.189
3.201
3.216
3.231
3.244
3.260
3.272
3.459
3.479
3.490
3.512
3.523
3.533



2.37

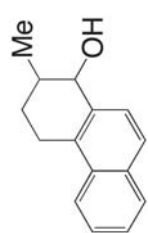
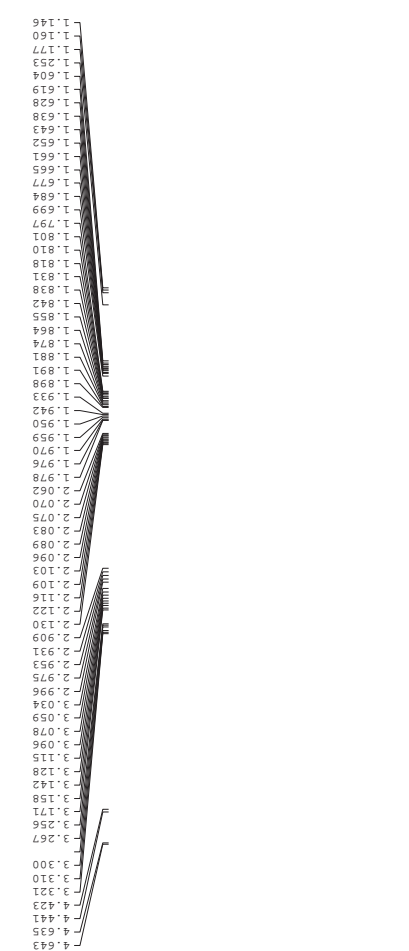
1H spectrum

8.106
8.084
8.096
8.088
7.817
7.730
7.708
7.579
7.570
7.563
7.556
7.551
7.546
7.241
7.533




```

Current Data Parameters
=====
USER          user_3_136
NAME
PROCNO       1
F2 - Acquisition Parameters
Date_        2011114
TIME
INSTRUM     d13400
PROBHD      5 mm QNP H/P/P
PULPROG     zgpg30
TD           65536
SOLVENT     CDCl3
DS           2
AQ           5.118793 sec
FIDRES      0.100753 Hz
AQ          5.118793 sec
RG           78.000 usec
DE           4.50 usec
DI           0.10000000 sec
MCNST      0.00000000 sec
PCPRG1      0.03000000 sec
===== CHANNEL f1 =====
NUC1         13C
P1           12.00 usec
PL1          0 dB
SFO1         400.1328009 MHz
F2 - Processing Parameters
SI           65536
SF           400.1300361 MHz
WDW          EM
SSB          0
GB           0
PC           2.00
  
```



2.38

Current Data Parameters
 USER AG_3_28_C1_1
 NAME AG_3_28_C1_1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 201121
 Time_ 7:11:21
 INSTRUM gmsd0
 PROBHD 5 mm broadband
 PULPROG zgpg30
 TD 83728
 SOLVENT CDCl3
 DS 2
 SWH 191.245 MHz
 FWH 0.038643 Hz
 AQ 5.0958774 sec
 RM 0.0000000 sec
 DM 62.400 usec
 DE 6.00 usec
 DI 0.1000000 sec
 MCHSET 0.0000000 sec
 MONPR 0.0300000 sec
 NUC1 ***** CHANNEL f1 *****
 P1 12.20 usec
 PL1 0.00 dB
 SFO1 499.9934950 MHz
 F2 - Processing Parameters
 SI 65536
 SF 499.990583 MHz
 DF 0 Hz
 SSB 0 Hz
 CB 0 Hz
 PC 1.00

0.000

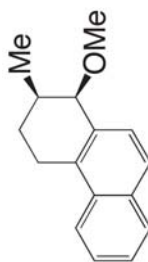
1.102
1.115
1.128
1.198
1.212
1.255
1.544
1.834
1.850
1.859
1.988
2.006
2.024
2.035
2.048
2.048
2.064
2.139
2.146
2.152

2.993
3.009
3.027
3.044
3.059
3.237
3.248
3.271
3.283
3.467
3.510

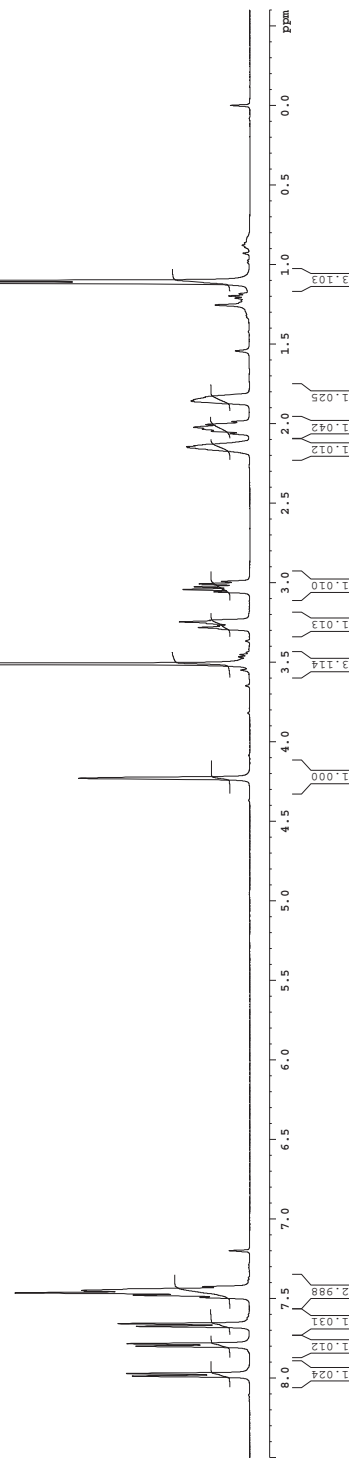
4.231

1H spectrum

7.990
7.973
7.801
7.786
7.677
7.660
7.494
7.481
7.466
7.455
7.451
7.442
7.442
7.428
7.201



2.19a

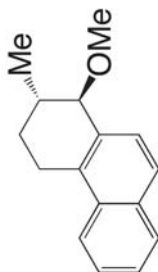



```

Current Data Parameters
=====
USER      AG_3_28_c1_2
PROCNO    1
Date_     2011120
Time      11:46
INSTRUM   5 mm QNP H/P/P
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         2
AQ         6.150000 sec
FIDRES    0.100000 Hz
AQRES     5.1118579 sec
SFO1      400.1328009 MHz
SFO2      101.2548515 MHz
DM         78.000 usec
DE         2.50 usec
DI         0.10000000 sec
MCREST    0.00000000 sec
PCPRGR    0.03000000 sec
NUC1      13C
===== CHANNEL f1 =====
P1         12.00 usec
PL1        0.00 dB
SFO1      400.1328009 MHz
===== CHANNEL f2 =====
P2         12.00 usec
PL2        0.00 dB
SFO2      101.2548515 MHz
===== Processing Parameters =====
SI         65536
SF         400.1300456 MHz
WDW        EM
SSB        0
GB         0
CB         0
PC         2.00
  
```

1H spectrum

7.970
7.950
7.798
7.779
7.775
7.692
7.671
7.496
7.482
7.476
7.463
7.459
7.455
7.439
7.436

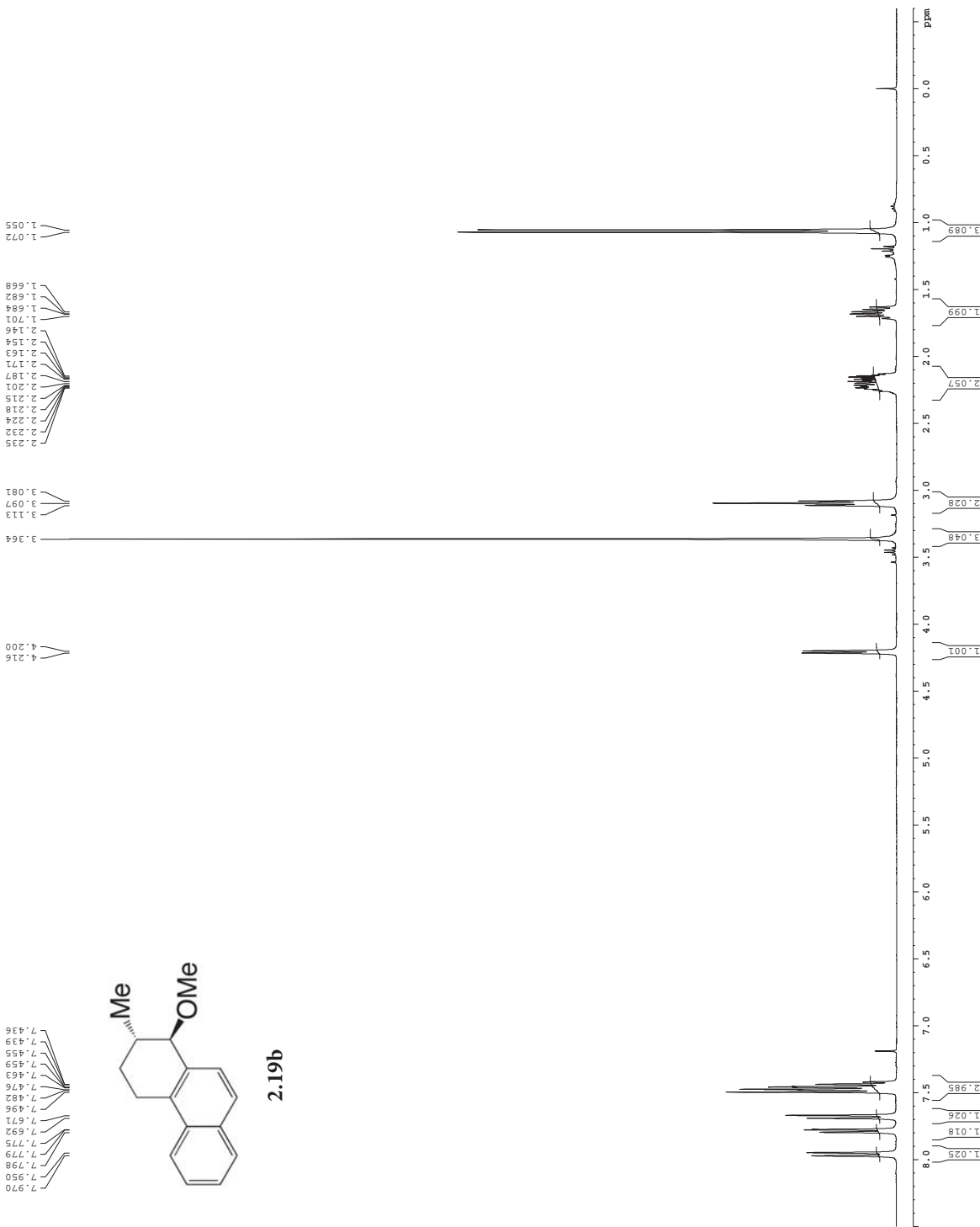


2.19b

2.235
2.232
2.224
2.218
2.215
2.205
2.187
2.171
2.163
2.154
2.146
1.701
1.684
1.682
1.668

3.081
3.097
3.113
3.364

4.200
4.216




```

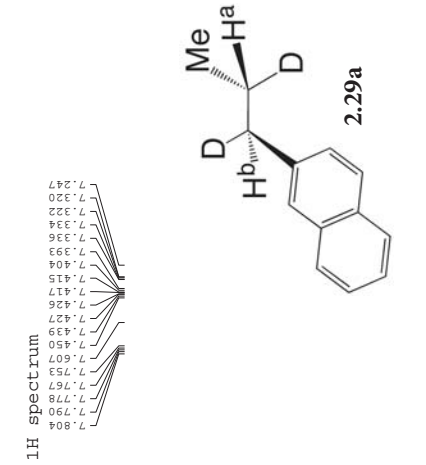
Current Data Parameters
=====
USER          Agt_3_271
NAME
PROCNO       1
Date_         2010501
Time_         11:43
INSTRUM      spect
PROBHD       5 mm TBI 1H/13
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
AQ           0.038462 sec
RG           0.038462 Hz
SFO1         600.1342009 MHz
PC           1.00
===== CHANNEL f1 =====
NUC1         13C
P1           8.00 usec
=====
F2 - Processing Parameters
SI           65536
SF           600.1300415 MHz
SR           0
SSB          0
CB           0
PC           1.00

```

```

F2 - Acquisition Parameters
=====
Date_         2010501
Time_         11:43
INSTRUM      spect
PROBHD       5 mm TBI 1H/13
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
AQ           0.038462 sec
RG           0.038462 Hz
SFO1         600.1342009 MHz
PC           1.00
===== CHANNEL f1 =====
NUC1         13C
P1           8.00 usec
=====
F2 - Processing Parameters
SI           65536
SF           600.1300415 MHz
SR           0
SSB          0
CB           0
PC           1.00

```

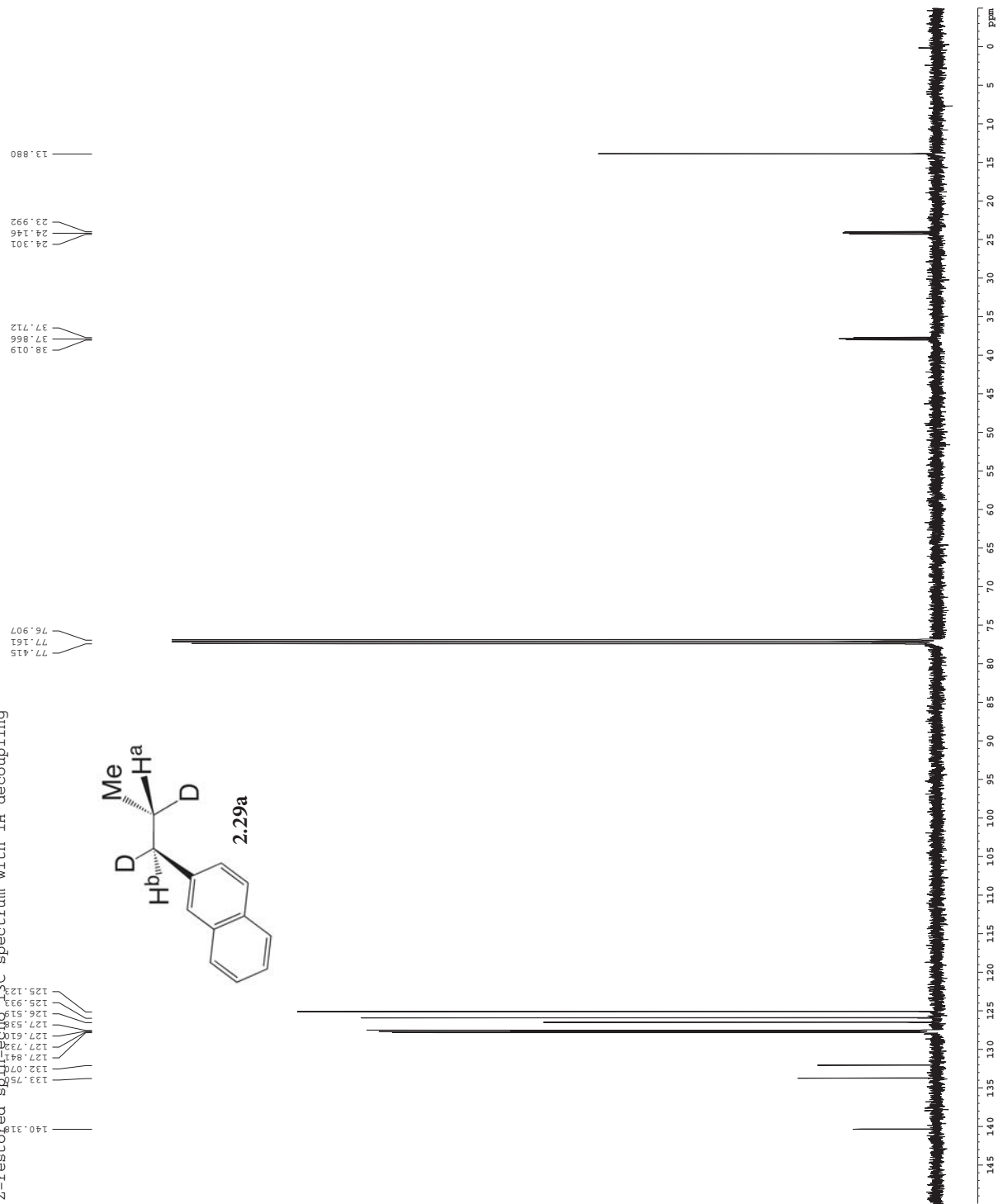


```

Current Data Parameters
=====
USER          ACL_271_c1
NAME          ACL_271_c1
PROCNO       1
Date_        2010501
Time_        14:56:00
INSTRUM      CPY5000
PROBHD       5 mm CPCL1.H
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           4
SS           16
SF           300.135
FIDRES       0.392688
AQ           1.081394
RG           167.500
DM           167.500
DE           6.00
D1           0.25000000
D11          0.03000000
d17          0.00136800
MORPHY       0.00000000
MORPHY2      0.00000000
MORPHY3      0.00000000
MORPHY4      0.00000000
MORPHY5      0.00000000
MORPHY6      0.00000000
MORPHY7      0.00000000
MORPHY8      0.00000000
MORPHY9      0.00000000
MORPHY10     0.00000000
MORPHY11     0.00000000
MORPHY12     0.00000000
MORPHY13     0.00000000
MORPHY14     0.00000000
MORPHY15     0.00000000
MORPHY16     0.00000000
MORPHY17     0.00000000
MORPHY18     0.00000000
MORPHY19     0.00000000
MORPHY20     0.00000000
MORPHY21     0.00000000
MORPHY22     0.00000000
MORPHY23     0.00000000
MORPHY24     0.00000000
MORPHY25     0.00000000
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MORPHY27     0.00000000
MORPHY28     0.00000000
MORPHY29     0.00000000
MORPHY30     0.00000000
MORPHY31     0.00000000
MORPHY32     0.00000000
MORPHY33     0.00000000
MORPHY34     0.00000000
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MORPHY41     0.00000000
MORPHY42     0.00000000
MORPHY43     0.00000000
MORPHY44     0.00000000
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MORPHY47     0.00000000
MORPHY48     0.00000000
MORPHY49     0.00000000
MORPHY50     0.00000000
MORPHY51     0.00000000
MORPHY52     0.00000000
MORPHY53     0.00000000
MORPHY54     0.00000000
MORPHY55     0.00000000
MORPHY56     0.00000000
MORPHY57     0.00000000
MORPHY58     0.00000000
MORPHY59     0.00000000
MORPHY60     0.00000000
MORPHY61     0.00000000
MORPHY62     0.00000000
MORPHY63     0.00000000
MORPHY64     0.00000000
MORPHY65     0.00000000
MORPHY66     0.00000000
MORPHY67     0.00000000
MORPHY68     0.00000000
MORPHY69     0.00000000
MORPHY70     0.00000000
MORPHY71     0.00000000
MORPHY72     0.00000000
MORPHY73     0.00000000
MORPHY74     0.00000000
MORPHY75     0.00000000
MORPHY76     0.00000000
MORPHY77     0.00000000
MORPHY78     0.00000000
MORPHY79     0.00000000
MORPHY80     0.00000000
MORPHY81     0.00000000
MORPHY82     0.00000000
MORPHY83     0.00000000
MORPHY84     0.00000000
MORPHY85     0.00000000
MORPHY86     0.00000000
MORPHY87     0.00000000
MORPHY88     0.00000000
MORPHY89     0.00000000
MORPHY90     0.00000000
MORPHY91     0.00000000
MORPHY92     0.00000000
MORPHY93     0.00000000
MORPHY94     0.00000000
MORPHY95     0.00000000
MORPHY96     0.00000000
MORPHY97     0.00000000
MORPHY98     0.00000000
MORPHY99     0.00000000
MORPHY100    0.00000000
=====
Channel f1
=====
NUC1       13C
P1         12.00 usec
P2         500.00 usec
P3         2000.00 usec
P4         10.00 usec
P5         1.00 usec
P6         1.00 usec
P7         1.00 usec
P8         1.00 usec
P9         1.00 usec
P10        1.00 usec
P11        1.00 usec
P12        1.00 usec
P13        1.00 usec
P14        1.00 usec
P15        1.00 usec
P16        1.00 usec
P17        1.00 usec
P18        1.00 usec
P19        1.00 usec
P20        1.00 usec
P21        1.00 usec
P22        1.00 usec
P23        1.00 usec
P24        1.00 usec
P25        1.00 usec
P26        1.00 usec
P27        1.00 usec
P28        1.00 usec
P29        1.00 usec
P30        1.00 usec
P31        1.00 usec
P32        1.00 usec
P33        1.00 usec
P34        1.00 usec
P35        1.00 usec
P36        1.00 usec
P37        1.00 usec
P38        1.00 usec
P39        1.00 usec
P40        1.00 usec
P41        1.00 usec
P42        1.00 usec
P43        1.00 usec
P44        1.00 usec
P45        1.00 usec
P46        1.00 usec
P47        1.00 usec
P48        1.00 usec
P49        1.00 usec
P50        1.00 usec
P51        1.00 usec
P52        1.00 usec
P53        1.00 usec
P54        1.00 usec
P55        1.00 usec
P56        1.00 usec
P57        1.00 usec
P58        1.00 usec
P59        1.00 usec
P60        1.00 usec
P61        1.00 usec
P62        1.00 usec
P63        1.00 usec
P64        1.00 usec
P65        1.00 usec
P66        1.00 usec
P67        1.00 usec
P68        1.00 usec
P69        1.00 usec
P70        1.00 usec
P71        1.00 usec
P72        1.00 usec
P73        1.00 usec
P74        1.00 usec
P75        1.00 usec
P76        1.00 usec
P77        1.00 usec
P78        1.00 usec
P79        1.00 usec
P80        1.00 usec
P81        1.00 usec
P82        1.00 usec
P83        1.00 usec
P84        1.00 usec
P85        1.00 usec
P86        1.00 usec
P87        1.00 usec
P88        1.00 usec
P89        1.00 usec
P90        1.00 usec
P91        1.00 usec
P92        1.00 usec
P93        1.00 usec
P94        1.00 usec
P95        1.00 usec
P96        1.00 usec
P97        1.00 usec
P98        1.00 usec
P99        1.00 usec
P100       1.00 usec
=====
Channel f2
=====
NUC2       1H
P1         12.00 usec
P2         500.00 usec
P3         2000.00 usec
P4         10.00 usec
P5         1.00 usec
P6         1.00 usec
P7         1.00 usec
P8         1.00 usec
P9         1.00 usec
P10        1.00 usec
P11        1.00 usec
P12        1.00 usec
P13        1.00 usec
P14        1.00 usec
P15        1.00 usec
P16        1.00 usec
P17        1.00 usec
P18        1.00 usec
P19        1.00 usec
P20        1.00 usec
P21        1.00 usec
P22        1.00 usec
P23        1.00 usec
P24        1.00 usec
P25        1.00 usec
P26        1.00 usec
P27        1.00 usec
P28        1.00 usec
P29        1.00 usec
P30        1.00 usec
P31        1.00 usec
P32        1.00 usec
P33        1.00 usec
P34        1.00 usec
P35        1.00 usec
P36        1.00 usec
P37        1.00 usec
P38        1.00 usec
P39        1.00 usec
P40        1.00 usec
P41        1.00 usec
P42        1.00 usec
P43        1.00 usec
P44        1.00 usec
P45        1.00 usec
P46        1.00 usec
P47        1.00 usec
P48        1.00 usec
P49        1.00 usec
P50        1.00 usec
P51        1.00 usec
P52        1.00 usec
P53        1.00 usec
P54        1.00 usec
P55        1.00 usec
P56        1.00 usec
P57        1.00 usec
P58        1.00 usec
P59        1.00 usec
P60        1.00 usec
P61        1.00 usec
P62        1.00 usec
P63        1.00 usec
P64        1.00 usec
P65        1.00 usec
P66        1.00 usec
P67        1.00 usec
P68        1.00 usec
P69        1.00 usec
P70        1.00 usec
P71        1.00 usec
P72        1.00 usec
P73        1.00 usec
P74        1.00 usec
P75        1.00 usec
P76        1.00 usec
P77        1.00 usec
P78        1.00 usec
P79        1.00 usec
P80        1.00 usec
P81        1.00 usec
P82        1.00 usec
P83        1.00 usec
P84        1.00 usec
P85        1.00 usec
P86        1.00 usec
P87        1.00 usec
P88        1.00 usec
P89        1.00 usec
P90        1.00 usec
P91        1.00 usec
P92        1.00 usec
P93        1.00 usec
P94        1.00 usec
P95        1.00 usec
P96        1.00 usec
P97        1.00 usec
P98        1.00 usec
P99        1.00 usec
P100       1.00 usec
=====
===== GRADIENT CHANNEL =====
GPNAM1     SINE.100
GPNAM2     SINE.100
GPNAM3     SINE.100
GPNAM4     SINE.100
GPNAM5     SINE.100
GPNAM6     SINE.100
GPNAM7     SINE.100
GPNAM8     SINE.100
GPNAM9     SINE.100
GPNAM10    SINE.100
GPNAM11    SINE.100
GPNAM12    SINE.100
GPNAM13    SINE.100
GPNAM14    SINE.100
GPNAM15    SINE.100
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GPNAM17    SINE.100
GPNAM18    SINE.100
GPNAM19    SINE.100
GPNAM20    SINE.100
GPNAM21    SINE.100
GPNAM22    SINE.100
GPNAM23    SINE.100
GPNAM24    SINE.100
GPNAM25    SINE.100
GPNAM26    SINE.100
GPNAM27    SINE.100
GPNAM28    SINE.100
GPNAM29    SINE.100
GPNAM30    SINE.100
GPNAM31    SINE.100
GPNAM32    SINE.100
GPNAM33    SINE.100
GPNAM34    SINE.100
GPNAM35    SINE.100
GPNAM36    SINE.100
GPNAM37    SINE.100
GPNAM38    SINE.100
GPNAM39    SINE.100
GPNAM40    SINE.100
GPNAM41    SINE.100
GPNAM42    SINE.100
GPNAM43    SINE.100
GPNAM44    SINE.100
GPNAM45    SINE.100
GPNAM46    SINE.100
GPNAM47    SINE.100
GPNAM48    SINE.100
GPNAM49    SINE.100
GPNAM50    SINE.100
GPNAM51    SINE.100
GPNAM52    SINE.100
GPNAM53    SINE.100
GPNAM54    SINE.100
GPNAM55    SINE.100
GPNAM56    SINE.100
GPNAM57    SINE.100
GPNAM58    SINE.100
GPNAM59    SINE.100
GPNAM60    SINE.100
GPNAM61    SINE.100
GPNAM62    SINE.100
GPNAM63    SINE.100
GPNAM64    SINE.100
GPNAM65    SINE.100
GPNAM66    SINE.100
GPNAM67    SINE.100
GPNAM68    SINE.100
GPNAM69    SINE.100
GPNAM70    SINE.100
GPNAM71    SINE.100
GPNAM72    SINE.100
GPNAM73    SINE.100
GPNAM74    SINE.100
GPNAM75    SINE.100
GPNAM76    SINE.100
GPNAM77    SINE.100
GPNAM78    SINE.100
GPNAM79    SINE.100
GPNAM80    SINE.100
GPNAM81    SINE.100
GPNAM82    SINE.100
GPNAM83    SINE.100
GPNAM84    SINE.100
GPNAM85    SINE.100
GPNAM86    SINE.100
GPNAM87    SINE.100
GPNAM88    SINE.100
GPNAM89    SINE.100
GPNAM90    SINE.100
GPNAM91    SINE.100
GPNAM92    SINE.100
GPNAM93    SINE.100
GPNAM94    SINE.100
GPNAM95    SINE.100
GPNAM96    SINE.100
GPNAM97    SINE.100
GPNAM98    SINE.100
GPNAM99    SINE.100
GPNAM100   SINE.100
=====
Processing parameters
=====
SI         65536
SF          125.7604094
WDW         EM
SSB         0
GB          0
PC          2.00

```

Z-restored spin-echo ¹³C spectrum with 1H decoupling




```

Current Data Parameters
NAME      AGL_4_176_C1
PROCNO    1
Date_     20100527
INSTRUM   spect
PROBHD    5 mm CPTCI 1H-
PULPROG   zgpg30
TD         83728
SOLVENT   CDCl3
DS         2
AQ         0.10000000 sec
FIDRES    0.10000000 Hz
AQ        5.0998774 sec
DM        62.400 usec
DE        6.00 usec
D1        0.10000000 sec
D2        0.00000000 sec
MCNST     0.00000000 sec
PCPRG1    0.00000000 sec
NUC1      13C
NUC2      13C
P1        7.50 usec
SFO1      500.2235015 MHz
P2        7.50 usec
SFO2      500.2235015 MHz
P3        7.50 usec
SFO3      500.2235015 MHz
PCPRG2    0.00000000 sec
PCPRG3    0.00000000 sec
PCPRG4    0.00000000 sec
PCPRG5    0.00000000 sec
PCPRG6    0.00000000 sec
PCPRG7    0.00000000 sec
PCPRG8    0.00000000 sec
PCPRG9    0.00000000 sec
PCPRG10   0.00000000 sec
PCPRG11   0.00000000 sec
PCPRG12   0.00000000 sec
PCPRG13   0.00000000 sec
PCPRG14   0.00000000 sec
PCPRG15   0.00000000 sec
PCPRG16   0.00000000 sec
PCPRG17   0.00000000 sec
PCPRG18   0.00000000 sec
PCPRG19   0.00000000 sec
PCPRG20   0.00000000 sec
PCPRG21   0.00000000 sec
PCPRG22   0.00000000 sec
PCPRG23   0.00000000 sec
PCPRG24   0.00000000 sec
PCPRG25   0.00000000 sec
PCPRG26   0.00000000 sec
PCPRG27   0.00000000 sec
PCPRG28   0.00000000 sec
PCPRG29   0.00000000 sec
PCPRG30   0.00000000 sec
PCPRG31   0.00000000 sec
PCPRG32   0.00000000 sec
PCPRG33   0.00000000 sec
PCPRG34   0.00000000 sec
PCPRG35   0.00000000 sec
PCPRG36   0.00000000 sec
PCPRG37   0.00000000 sec
PCPRG38   0.00000000 sec
PCPRG39   0.00000000 sec
PCPRG40   0.00000000 sec
PCPRG41   0.00000000 sec
PCPRG42   0.00000000 sec
PCPRG43   0.00000000 sec
PCPRG44   0.00000000 sec
PCPRG45   0.00000000 sec
PCPRG46   0.00000000 sec
PCPRG47   0.00000000 sec
PCPRG48   0.00000000 sec
PCPRG49   0.00000000 sec
PCPRG50   0.00000000 sec
PCPRG51   0.00000000 sec
PCPRG52   0.00000000 sec
PCPRG53   0.00000000 sec
PCPRG54   0.00000000 sec
PCPRG55   0.00000000 sec
PCPRG56   0.00000000 sec
PCPRG57   0.00000000 sec
PCPRG58   0.00000000 sec
PCPRG59   0.00000000 sec
PCPRG60   0.00000000 sec
PCPRG61   0.00000000 sec
PCPRG62   0.00000000 sec
PCPRG63   0.00000000 sec
PCPRG64   0.00000000 sec
PCPRG65   0.00000000 sec
PCPRG66   0.00000000 sec
PCPRG67   0.00000000 sec
PCPRG68   0.00000000 sec
PCPRG69   0.00000000 sec
PCPRG70   0.00000000 sec
PCPRG71   0.00000000 sec
PCPRG72   0.00000000 sec
PCPRG73   0.00000000 sec
PCPRG74   0.00000000 sec
PCPRG75   0.00000000 sec
PCPRG76   0.00000000 sec
PCPRG77   0.00000000 sec
PCPRG78   0.00000000 sec
PCPRG79   0.00000000 sec
PCPRG80   0.00000000 sec
PCPRG81   0.00000000 sec
PCPRG82   0.00000000 sec
PCPRG83   0.00000000 sec
PCPRG84   0.00000000 sec
PCPRG85   0.00000000 sec
PCPRG86   0.00000000 sec
PCPRG87   0.00000000 sec
PCPRG88   0.00000000 sec
PCPRG89   0.00000000 sec
PCPRG90   0.00000000 sec
PCPRG91   0.00000000 sec
PCPRG92   0.00000000 sec
PCPRG93   0.00000000 sec
PCPRG94   0.00000000 sec
PCPRG95   0.00000000 sec
PCPRG96   0.00000000 sec
PCPRG97   0.00000000 sec
PCPRG98   0.00000000 sec
PCPRG99   0.00000000 sec
PCPRG100  0.00000000 sec

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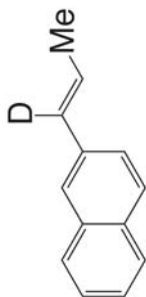
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1.928

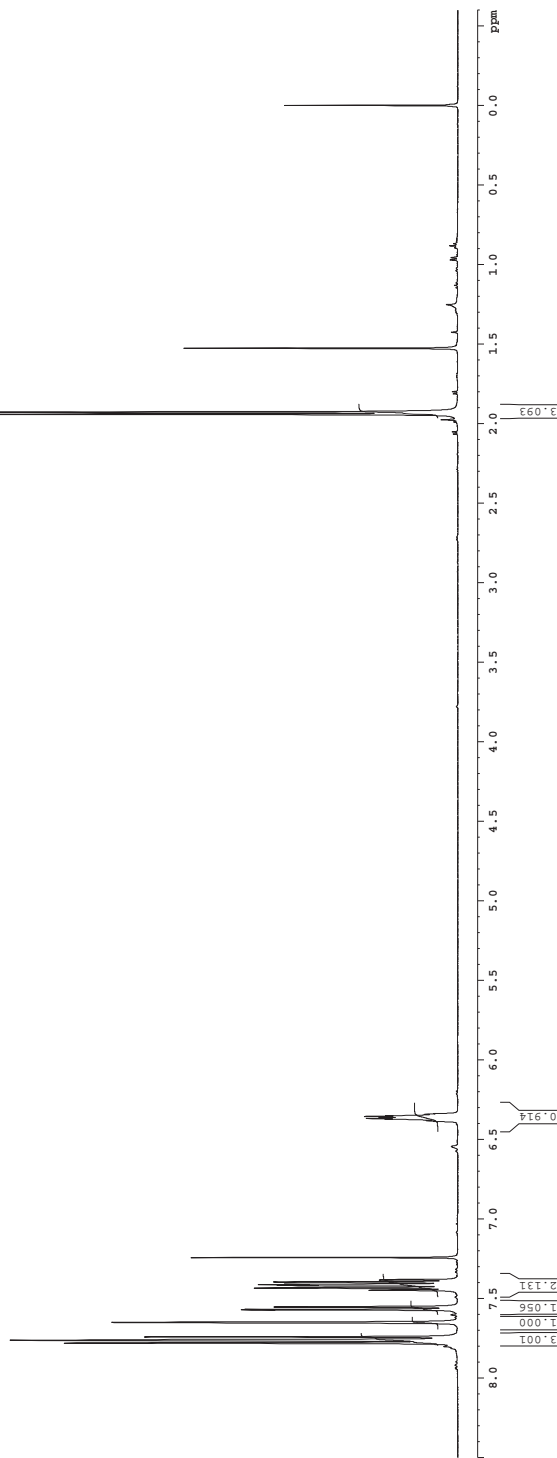
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1H spectrum

7.782
7.764
7.743
7.743
7.573
7.573
7.570
7.556
7.553
7.450
7.436
7.421
7.418
7.415
7.398
7.385
7.383
7.244
7.244
6.375
6.370
6.366
6.361
6.357
6.353
6.344



2.30a



```

Current Data Parameters
USER          ACL_4_176_01
PROCNO       1
Date_         20100527
Time         07:55:00
INSTRUM      CPY5000
PROBHD       5 mm CPCL1H1-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           2
AQ           30.92146 sec
RG           30.92146 sec
AQ           1.0813940 sec
DM           16.500 usec
DE           6.00 usec
D1           0.25000000 sec
d11          0.03000000 sec
d17          0.00136000 sec
MCWMT       0.03000000 sec
MCWBK       0.03000000 sec
P2           33.10 usec

***** CHANNEL f1 *****
NUC1         13C
P1           12.00 usec
P11          500.00 usec
P12          2000.00 usec
P13          1.00 usec
P14          -1.00 dB
P15          125.794250 MHz
P16          0.00 usec
P17          0.00 usec
P18          0.00 usec
P19          0.00 usec
P20          0.00 usec
P21          0.00 usec
P22          0.00 usec
P23          0.00 usec
P24          0.00 usec
P25          0.00 usec
P26          0.00 usec
P27          0.00 usec
P28          0.00 usec
P29          0.00 usec
P30          0.00 usec
P31          0.00 usec
P32          0.00 usec
P33          0.00 usec
P34          0.00 usec
P35          0.00 usec
P36          0.00 usec
P37          0.00 usec
P38          0.00 usec
P39          0.00 usec
P40          0.00 usec
P41          0.00 usec
P42          0.00 usec
P43          0.00 usec
P44          0.00 usec
P45          0.00 usec
P46          0.00 usec
P47          0.00 usec
P48          0.00 usec
P49          0.00 usec
P50          0.00 usec
P51          0.00 usec
P52          0.00 usec
P53          0.00 usec
P54          0.00 usec
P55          0.00 usec
P56          0.00 usec
P57          0.00 usec
P58          0.00 usec
P59          0.00 usec
P60          0.00 usec
P61          0.00 usec
P62          0.00 usec
P63          0.00 usec
P64          0.00 usec
P65          0.00 usec
P66          0.00 usec
P67          0.00 usec
P68          0.00 usec
P69          0.00 usec
P70          0.00 usec
P71          0.00 usec
P72          0.00 usec
P73          0.00 usec
P74          0.00 usec
P75          0.00 usec
P76          0.00 usec
P77          0.00 usec
P78          0.00 usec
P79          0.00 usec
P80          0.00 usec
P81          0.00 usec
P82          0.00 usec
P83          0.00 usec
P84          0.00 usec
P85          0.00 usec
P86          0.00 usec
P87          0.00 usec
P88          0.00 usec
P89          0.00 usec
P90          0.00 usec
P91          0.00 usec
P92          0.00 usec
P93          0.00 usec
P94          0.00 usec
P95          0.00 usec
P96          0.00 usec
P97          0.00 usec
P98          0.00 usec
P99          0.00 usec
P100         0.00 usec

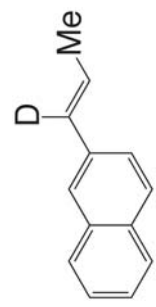
***** CHANNEL f2 *****
CPDPRG2     zgpg30
NUC2         13C
P1           12.00 usec
P11          500.00 usec
P12          2000.00 usec
P13          1.00 usec
P14          -1.00 dB
P15          125.794250 MHz
P16          0.00 usec
P17          0.00 usec
P18          0.00 usec
P19          0.00 usec
P20          0.00 usec
P21          0.00 usec
P22          0.00 usec
P23          0.00 usec
P24          0.00 usec
P25          0.00 usec
P26          0.00 usec
P27          0.00 usec
P28          0.00 usec
P29          0.00 usec
P30          0.00 usec
P31          0.00 usec
P32          0.00 usec
P33          0.00 usec
P34          0.00 usec
P35          0.00 usec
P36          0.00 usec
P37          0.00 usec
P38          0.00 usec
P39          0.00 usec
P40          0.00 usec
P41          0.00 usec
P42          0.00 usec
P43          0.00 usec
P44          0.00 usec
P45          0.00 usec
P46          0.00 usec
P47          0.00 usec
P48          0.00 usec
P49          0.00 usec
P50          0.00 usec
P51          0.00 usec
P52          0.00 usec
P53          0.00 usec
P54          0.00 usec
P55          0.00 usec
P56          0.00 usec
P57          0.00 usec
P58          0.00 usec
P59          0.00 usec
P60          0.00 usec
P61          0.00 usec
P62          0.00 usec
P63          0.00 usec
P64          0.00 usec
P65          0.00 usec
P66          0.00 usec
P67          0.00 usec
P68          0.00 usec
P69          0.00 usec
P70          0.00 usec
P71          0.00 usec
P72          0.00 usec
P73          0.00 usec
P74          0.00 usec
P75          0.00 usec
P76          0.00 usec
P77          0.00 usec
P78          0.00 usec
P79          0.00 usec
P80          0.00 usec
P81          0.00 usec
P82          0.00 usec
P83          0.00 usec
P84          0.00 usec
P85          0.00 usec
P86          0.00 usec
P87          0.00 usec
P88          0.00 usec
P89          0.00 usec
P90          0.00 usec
P91          0.00 usec
P92          0.00 usec
P93          0.00 usec
P94          0.00 usec
P95          0.00 usec
P96          0.00 usec
P97          0.00 usec
P98          0.00 usec
P99          0.00 usec
P100         0.00 usec

***** GRADIENT CHANNEL *****
GPNAM2      SINE100
G1          0.00 usec
G2          0.00 usec
G3          0.00 usec
G4          0.00 usec
G5          0.00 usec
G6          0.00 usec
G7          0.00 usec
G8          0.00 usec
G9          0.00 usec
G10         0.00 usec
G11         0.00 usec
G12         0.00 usec
G13         0.00 usec
G14         0.00 usec
G15         0.00 usec
G16         0.00 usec
G17         0.00 usec
G18         0.00 usec
G19         0.00 usec
G20         0.00 usec
G21         0.00 usec
G22         0.00 usec
G23         0.00 usec
G24         0.00 usec
G25         0.00 usec
G26         0.00 usec
G27         0.00 usec
G28         0.00 usec
G29         0.00 usec
G30         0.00 usec
G31         0.00 usec
G32         0.00 usec
G33         0.00 usec
G34         0.00 usec
G35         0.00 usec
G36         0.00 usec
G37         0.00 usec
G38         0.00 usec
G39         0.00 usec
G40         0.00 usec
G41         0.00 usec
G42         0.00 usec
G43         0.00 usec
G44         0.00 usec
G45         0.00 usec
G46         0.00 usec
G47         0.00 usec
G48         0.00 usec
G49         0.00 usec
G50         0.00 usec
G51         0.00 usec
G52         0.00 usec
G53         0.00 usec
G54         0.00 usec
G55         0.00 usec
G56         0.00 usec
G57         0.00 usec
G58         0.00 usec
G59         0.00 usec
G60         0.00 usec
G61         0.00 usec
G62         0.00 usec
G63         0.00 usec
G64         0.00 usec
G65         0.00 usec
G66         0.00 usec
G67         0.00 usec
G68         0.00 usec
G69         0.00 usec
G70         0.00 usec
G71         0.00 usec
G72         0.00 usec
G73         0.00 usec
G74         0.00 usec
G75         0.00 usec
G76         0.00 usec
G77         0.00 usec
G78         0.00 usec
G79         0.00 usec
G80         0.00 usec
G81         0.00 usec
G82         0.00 usec
G83         0.00 usec
G84         0.00 usec
G85         0.00 usec
G86         0.00 usec
G87         0.00 usec
G88         0.00 usec
G89         0.00 usec
G90         0.00 usec
G91         0.00 usec
G92         0.00 usec
G93         0.00 usec
G94         0.00 usec
G95         0.00 usec
G96         0.00 usec
G97         0.00 usec
G98         0.00 usec
G99         0.00 usec
G100        0.00 usec

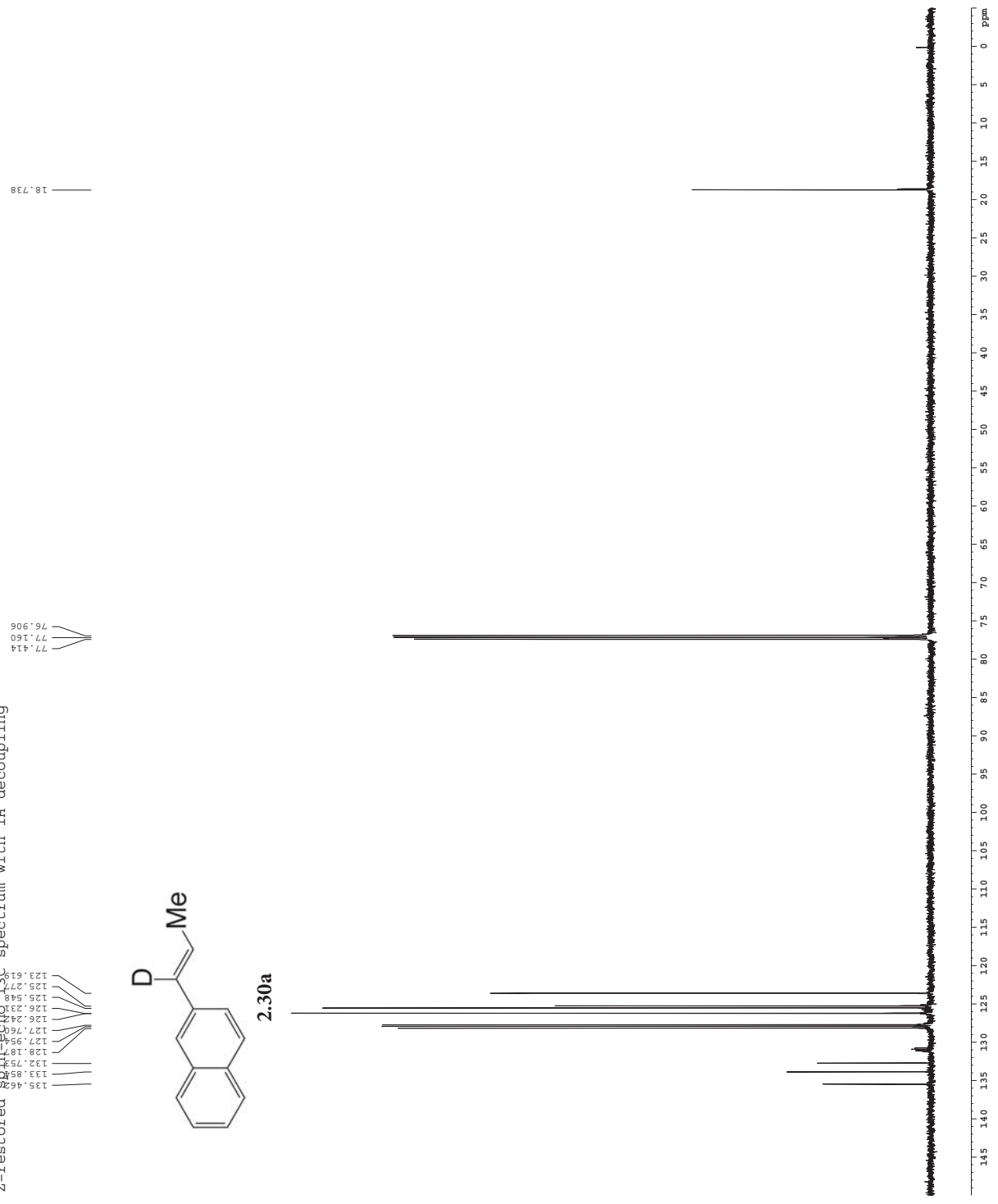
***** Processing Parameters *****
SI           65536
SF           125.7804094 MHz
WDW          EM
SSB          0
GB           0
CB           0
PC           2.00
  
```

Z-restored spin-echo ¹³C spectrum with 1H decoupling

123.61
123.27
125.21
125.54
126.23
126.26
127.76
127.95
128.18
132.75
133.85
135.46



2.30a

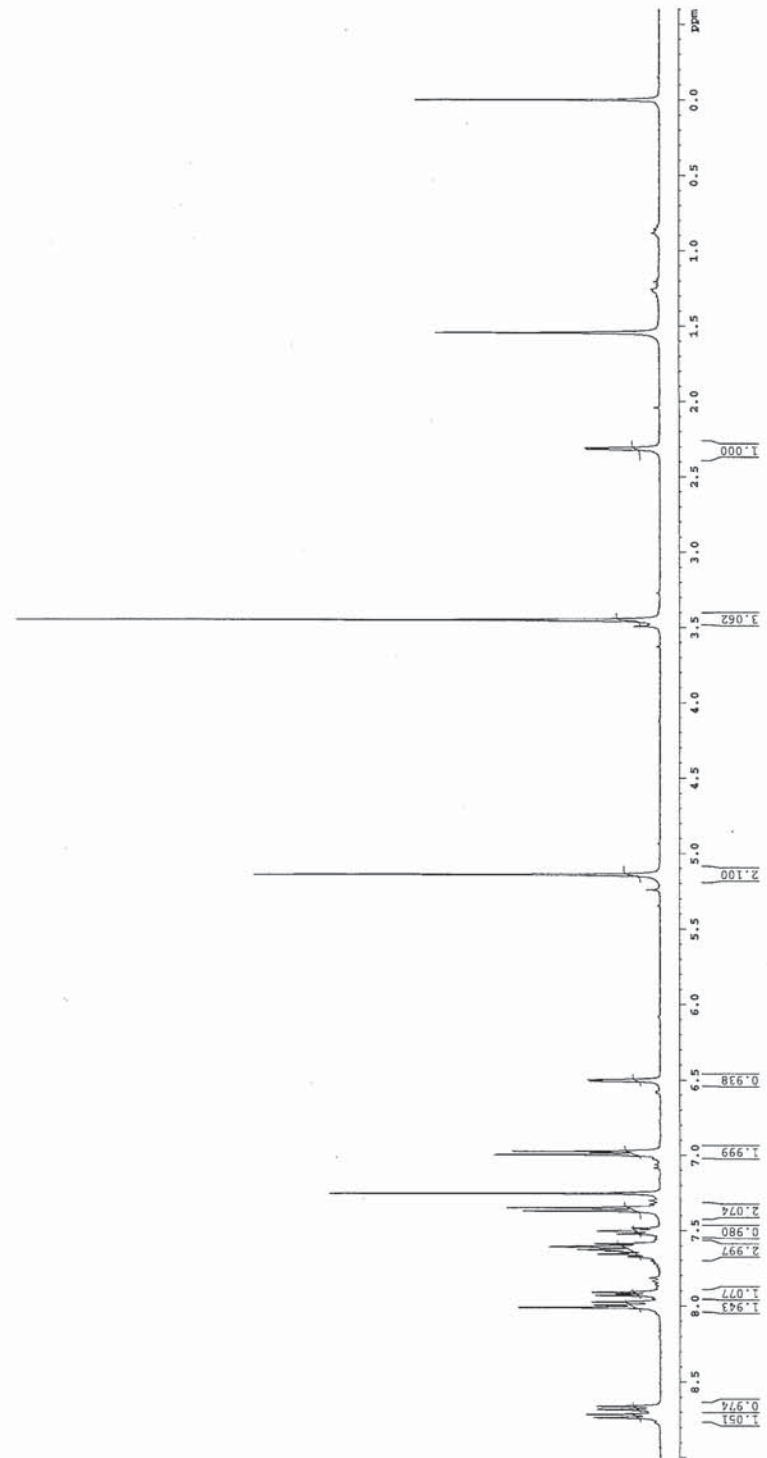
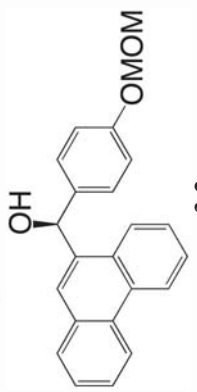


```

Current Data Parameters
=====
USER      ACL_3_25_04
PRCNO    1
Date_    2010411
INSTRUM  spect
PROBHD   5 mm QNP H/P/P
TD       65536
SOLVENT  CDCl3
DS       2
AQ       0.100000 sec
FIDRES   0.100000 Hz
AQ       5.111879 sec
RG       327.680
DM       28.000 usec
DE       4.50 usec
DI       0.1000000 sec
MCREST   0.0000000 sec
PCPRGR   0.0000000 sec
===== CHANNEL f1 =====
NUC1     1H
P1       12.00 usec
SFO1     400.1328009 MHz
F2 - Processing Parameters
SI       65536
SF       400.1328009 MHz
SSB      0
GB       0
PC       4.00
  
```



Current Data Parameters
 USER: AGL_5_Bent...
 NAME: AGL_5_Bent...
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20111229
 Time: 11:25:00
 INSTRUM: spect
 PROBHD: 5 mm QNP 1H/13
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 2
 DS: 4
 SWH: 6418.24 Hz
 FIDRES: 0.037833 Hz
 AQ: 5.118979 sec
 RG: 327.5
 EQ: 78.000 usec
 DE: 3.850 usec
 DI: 0.1000000 sec
 D1: 0.0500000 sec
 INJECT: 0.0150000 sec
 INJPRG: CHAMEL f1
 NUC1: 1H
 P1: 12.00 usec
 PL1: 0 dB
 RFPO: 400.1328009 MHz
 F2 - Processing parameters
 SI: 65536
 SF: 400.1300224 MHz
 SFO2: 0 MHz
 GB: 0 Hz
 CB: 0 Hz
 PC: 2.00



```

Current Data Parameters
=====
NAME          azax07
EXPNO         1
PROCNO        1
PROCDS        1
F2 - Acquisition Parameters
=====
Date_         20141128
Time         14.00
PROBHD        5 mm CYC1 1H-
PULPROG       zgpg30
TD            65536
SFO1          500.136261 MHz
AQ            0.0150000 sec
RG            655.36
DE            2.00 usec
TE            300.2 K
D1            0.10000000 sec
DELTA         0.01500000 sec
PCYCLE        1
MCOPI        0.01500000 sec
=====
===== CHANNEL f1 =====
NUC1          1H
P1            7.50 usec
SFO1          500.136261 MHz
F2 - Processing parameters
=====
SI            32768
SF            500.136261 MHz
WDW           EM
SSB           0
GB            0
PC            4.00
  
```

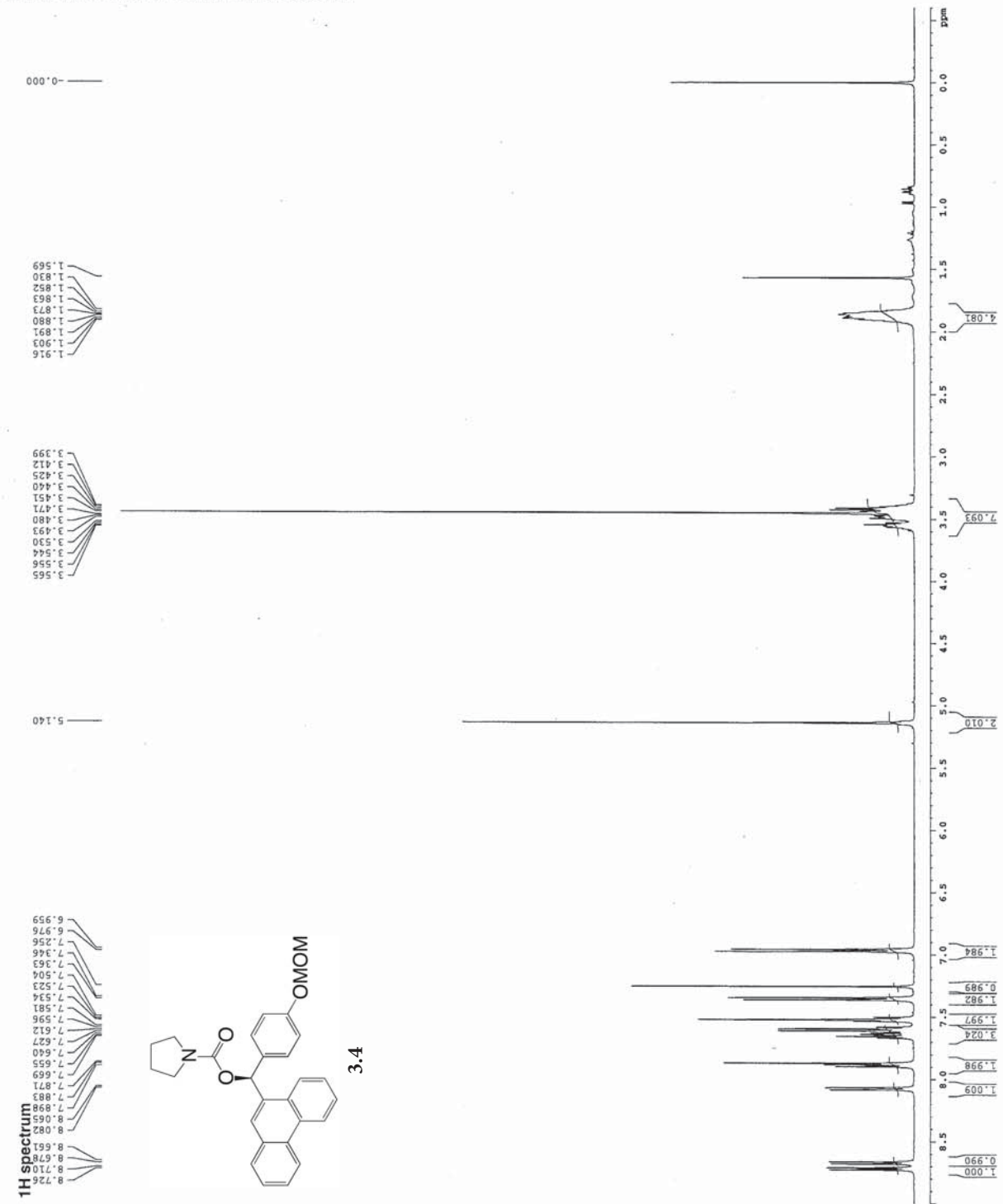
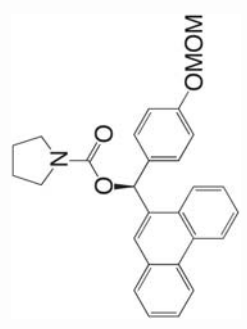
0.000

1.916
1.903
1.891
1.880
1.873
1.863
1.852
1.830
1.569

3.565
3.556
3.544
3.530
3.493
3.480
3.471
3.451
3.440
3.425
3.412
3.399

5.140

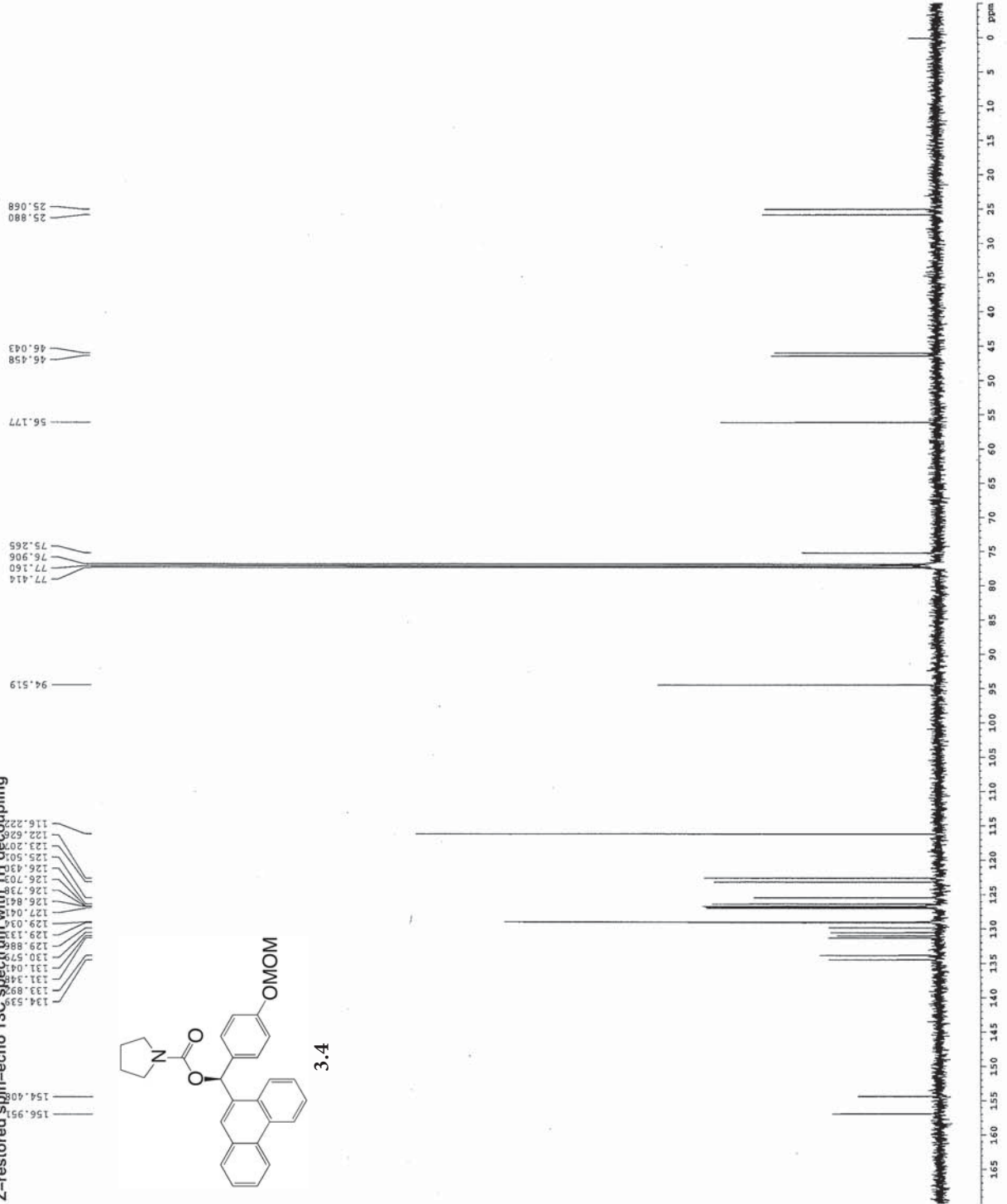
9.724
9.716
9.678
9.661
8.082
8.063
7.998
7.883
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7.659
7.655
7.640
7.627
7.612
7.596
7.581
7.534
7.523
7.504
7.363
7.346
7.256
6.976
6.959



Z-restored spin-echo 13C spectrum with 1H decoupling

```

Current Data Parameters
NAME      AG2_4_105_F3
PROCNO    1
Date_ Acquisition  20181128
Time       16.44
INSTRUM   spect
PROBHD    5 mm CryoCI 1H-
PULPROG   zgpg30
SOLVENT   CDCl3
DS         316
ZS         16
ZOH        3030.031 Hz
AQ         1.0841305 sec
RG         2896.00 usec
RG2        6.00 usec
DE         0.25000000 sec
d11        0.01000000 sec
d17        0.00010000 sec
d18        0.00010000 sec
d19        0.00010000 sec
d20        0.00010000 sec
d21        0.00010000 sec
d22        0.00010000 sec
===== CHANNEL F1 =====
NUC1       13C
P1         100.00 usec
PL1        0.00 dB
P2         2000.00 usec
PL2        1.00 dB
P3         1.00 usec
PL3        1.00 dB
SFO1       125.764248 MHz
SF2        2.70 MHz
SFO1M1     Cp60, 0.5, 20.1
CPDPRG2    0.00 Hz
SFOFF1     0.00 Hz
SFOFF2     0.00 Hz
===== CHANNEL F2 =====
NUC2       13C
P2         100.00 usec
PL2        0.00 dB
P3         24.50 usec
PL3        24.50 dB
SFO2       500.1225011 MHz
===== GRABBIT CHANNEL =====
SFO1M1     0.00 Hz
SFO1M2     0.00 Hz
SFO1M3     0.00 Hz
SFO1M4     0.00 Hz
SFO1M5     0.00 Hz
SFO1M6     0.00 Hz
SFO1M7     0.00 Hz
SFO1M8     0.00 Hz
SFO1M9     0.00 Hz
SFO1M10    0.00 Hz
SFO1M11    0.00 Hz
SFO1M12    0.00 Hz
SFO1M13    0.00 Hz
SFO1M14    0.00 Hz
SFO1M15    0.00 Hz
SFO1M16    0.00 Hz
SFO1M17    0.00 Hz
SFO1M18    0.00 Hz
SFO1M19    0.00 Hz
SFO1M20    0.00 Hz
SFO1M21    0.00 Hz
SFO1M22    0.00 Hz
SFO1M23    0.00 Hz
SFO1M24    0.00 Hz
SFO1M25    0.00 Hz
SFO1M26    0.00 Hz
SFO1M27    0.00 Hz
SFO1M28    0.00 Hz
SFO1M29    0.00 Hz
SFO1M30    0.00 Hz
SFO1M31    0.00 Hz
SFO1M32    0.00 Hz
SFO1M33    0.00 Hz
SFO1M34    0.00 Hz
SFO1M35    0.00 Hz
SFO1M36    0.00 Hz
SFO1M37    0.00 Hz
SFO1M38    0.00 Hz
SFO1M39    0.00 Hz
SFO1M40    0.00 Hz
SFO1M41    0.00 Hz
SFO1M42    0.00 Hz
SFO1M43    0.00 Hz
SFO1M44    0.00 Hz
SFO1M45    0.00 Hz
SFO1M46    0.00 Hz
SFO1M47    0.00 Hz
SFO1M48    0.00 Hz
SFO1M49    0.00 Hz
SFO1M50    0.00 Hz
SFO1M51    0.00 Hz
SFO1M52    0.00 Hz
SFO1M53    0.00 Hz
SFO1M54    0.00 Hz
SFO1M55    0.00 Hz
SFO1M56    0.00 Hz
SFO1M57    0.00 Hz
SFO1M58    0.00 Hz
SFO1M59    0.00 Hz
SFO1M60    0.00 Hz
SFO1M61    0.00 Hz
SFO1M62    0.00 Hz
SFO1M63    0.00 Hz
SFO1M64    0.00 Hz
SFO1M65    0.00 Hz
SFO1M66    0.00 Hz
SFO1M67    0.00 Hz
SFO1M68    0.00 Hz
SFO1M69    0.00 Hz
SFO1M70    0.00 Hz
SFO1M71    0.00 Hz
SFO1M72    0.00 Hz
SFO1M73    0.00 Hz
SFO1M74    0.00 Hz
SFO1M75    0.00 Hz
SFO1M76    0.00 Hz
SFO1M77    0.00 Hz
SFO1M78    0.00 Hz
SFO1M79    0.00 Hz
SFO1M80    0.00 Hz
SFO1M81    0.00 Hz
SFO1M82    0.00 Hz
SFO1M83    0.00 Hz
SFO1M84    0.00 Hz
SFO1M85    0.00 Hz
SFO1M86    0.00 Hz
SFO1M87    0.00 Hz
SFO1M88    0.00 Hz
SFO1M89    0.00 Hz
SFO1M90    0.00 Hz
SFO1M91    0.00 Hz
SFO1M92    0.00 Hz
SFO1M93    0.00 Hz
SFO1M94    0.00 Hz
SFO1M95    0.00 Hz
SFO1M96    0.00 Hz
SFO1M97    0.00 Hz
SFO1M98    0.00 Hz
SFO1M99    0.00 Hz
SFO1M100   0.00 Hz
===== Processing parameters =====
SF         125.764039 MHz
AQ         1.0841305 sec
RG         2896.00 usec
RG2        6.00 usec
DE         0.25000000 sec
d11        0.01000000 sec
d17        0.00010000 sec
d18        0.00010000 sec
d19        0.00010000 sec
d20        0.00010000 sec
d21        0.00010000 sec
d22        0.00010000 sec
=====
PC
  
```



Current Data Parameters
 USER: aarof
 NAME: AQ_110_C2
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 201125
 TIME: 11:00
 INSTRON: QNP400
 PROBHD: 5 mm QNP 1H/13
 TOUPOG: 65536
 SOLVENT: CDCl3
 NS: 2
 DS: 4
 SWH: 6448.42 Hz
 FIDRES: 0.107813 Hz
 AQ: 5.1118579 sec
 RG: 78.000
 EQ: 78.000 usec
 DE: 3.50 usec
 DI: 0.1000000 sec
 D1: 0.0500000 sec
 DELT: 0.0500000 sec
 ACQNO: 1
 CHANNEL f1: 1H
 P1: 12.00 usec
 PL: 0.00 dB
 SFO1: 400.1328009 MHz
 F2 - Processing parameters
 SI: 65536
 SF: 400.1360516 MHz
 DSF: 0.0000000
 SSB: 0.0
 GB: 0.0
 PC: 2.00

0.000
 0.003

1.527

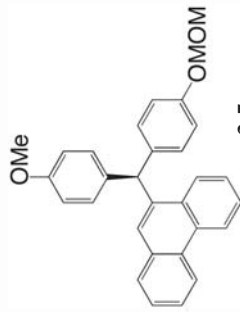
3.478

3.778

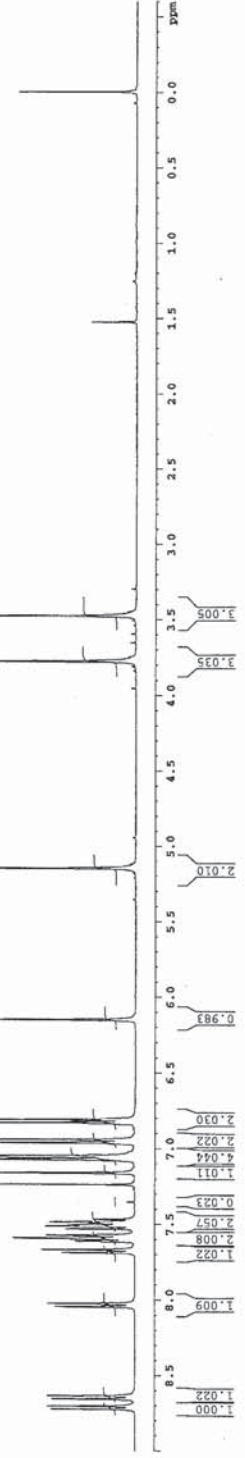
5.152

6.152

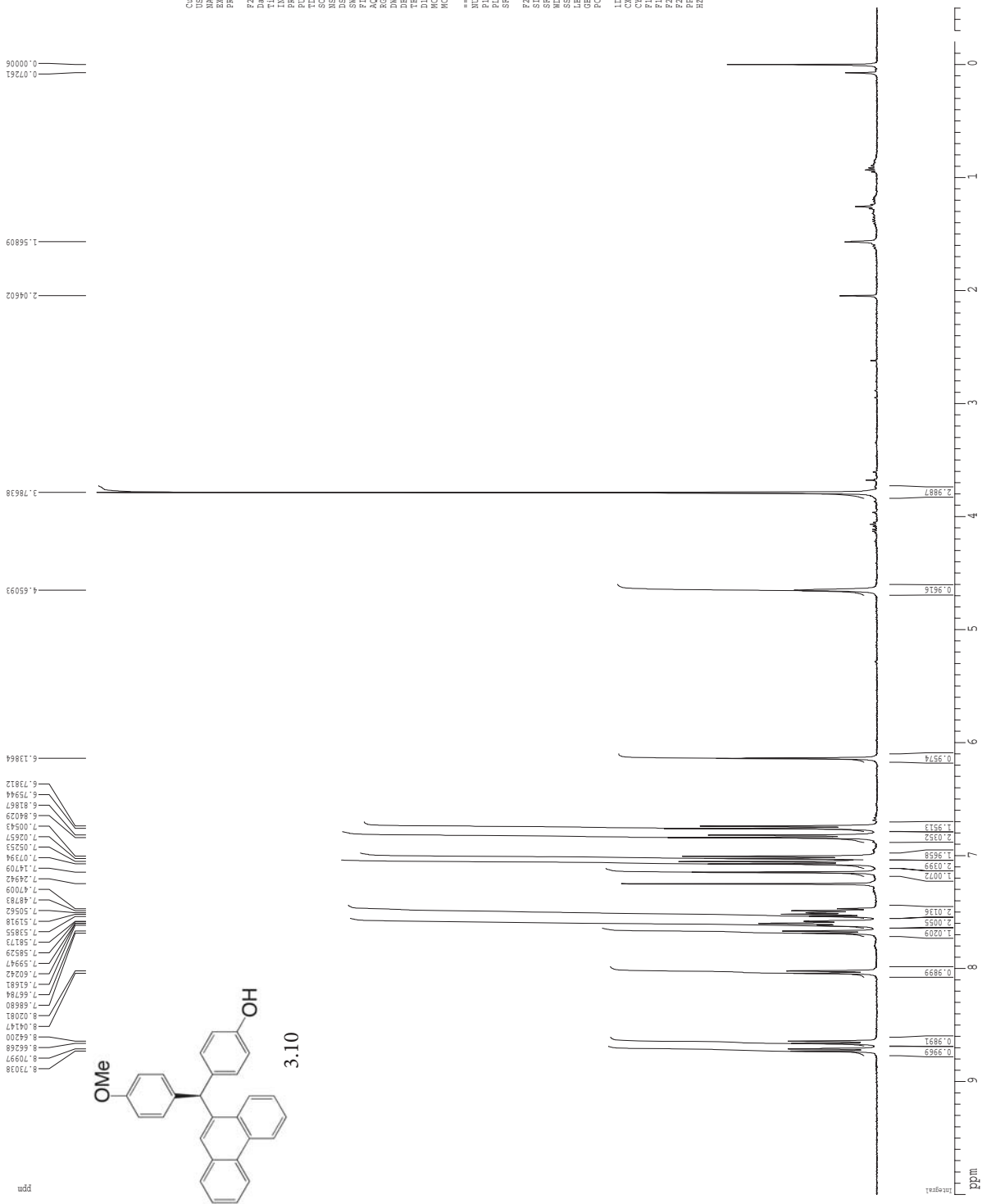
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1H spectrum

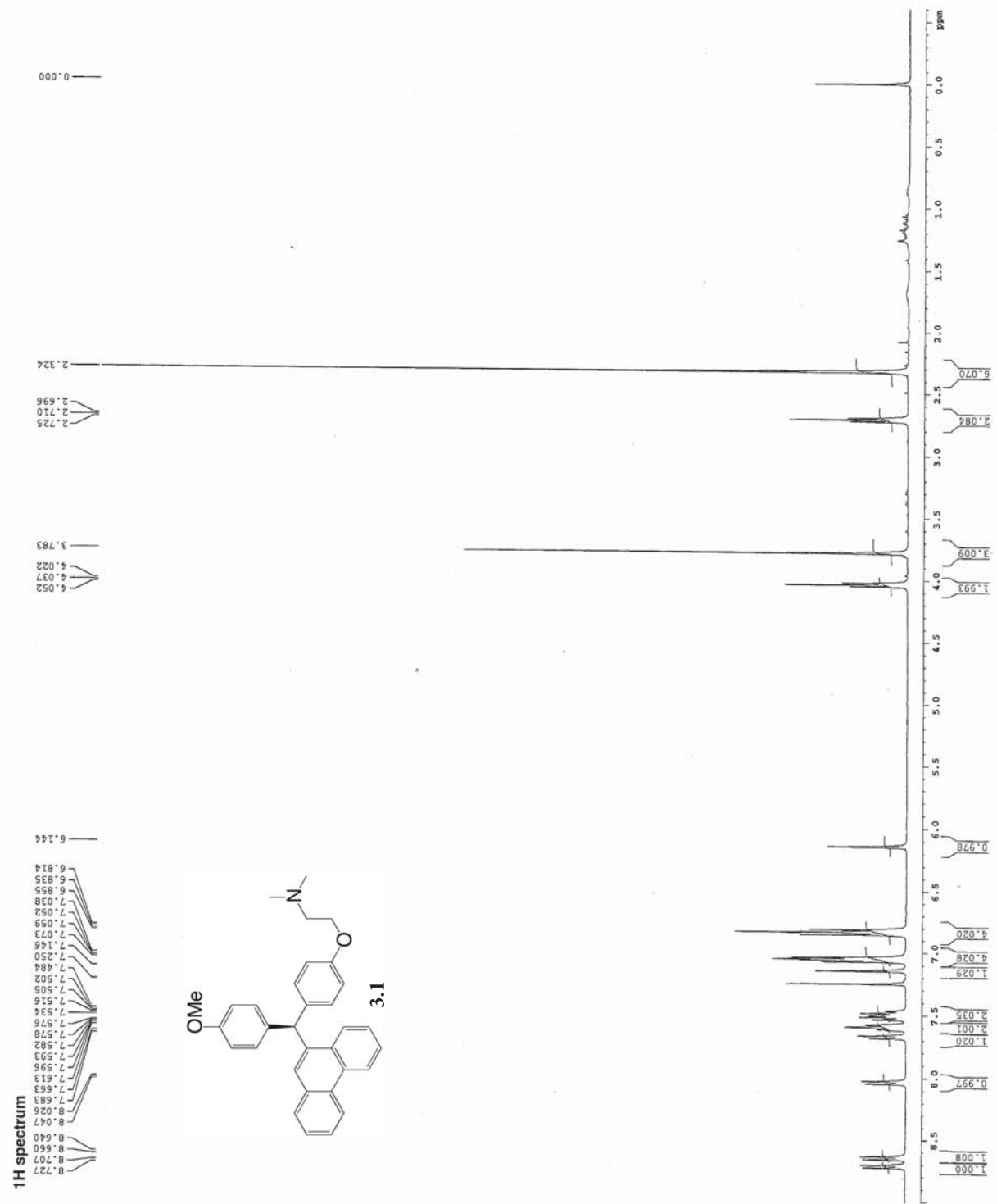


1H spectrum



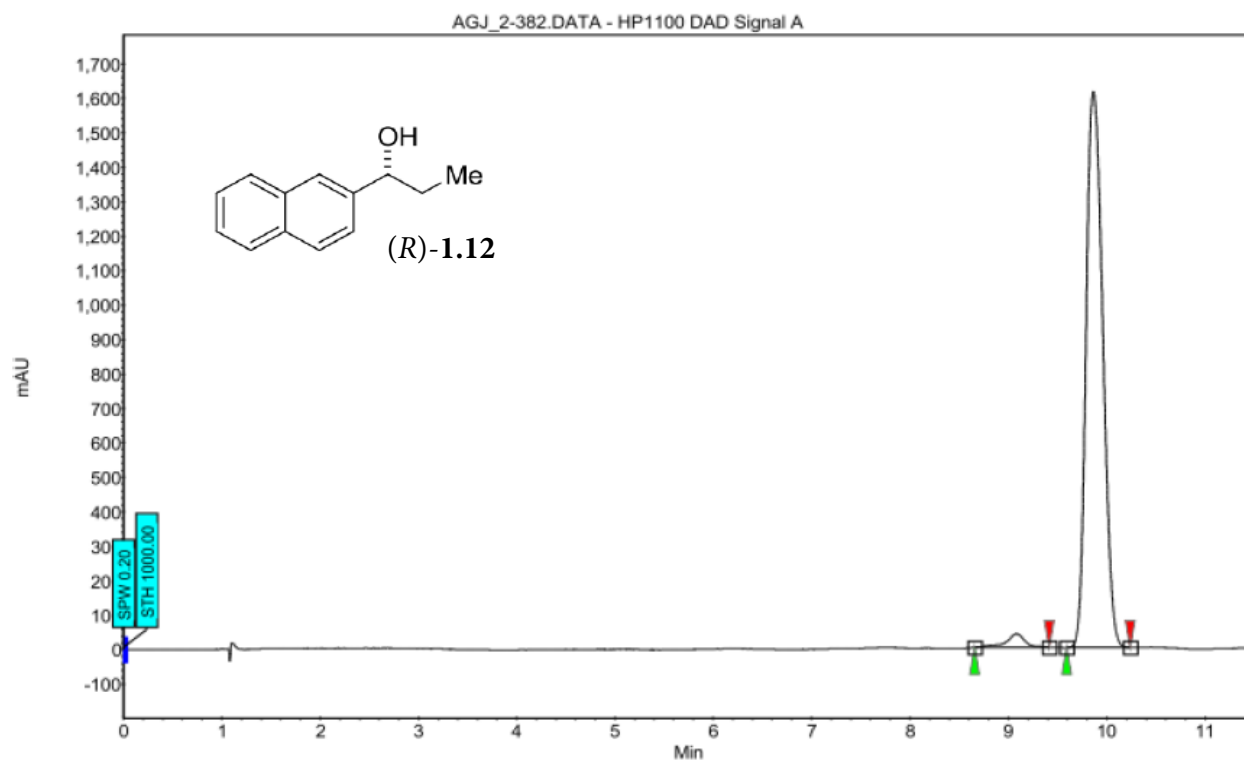
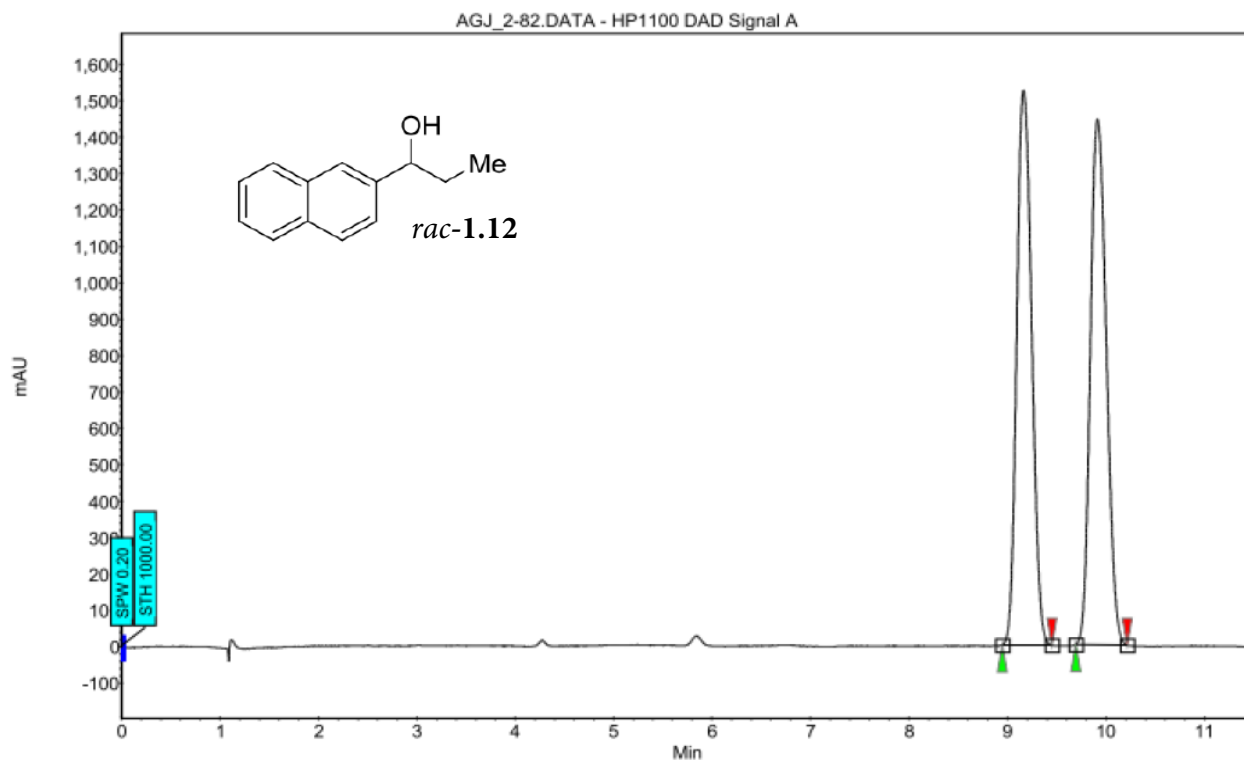
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 NAME BUT-6-014-A
 EXPNO 4
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20220113
 Time 13.03
 INSTRUM spect
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 DS 2
 SWH 640.256 Hz
 FIDRES 0.097813 Hz
 AQ 5.1118579 sec
 RG 327.5
 DN 78.000 uSAC
 DE 4.50 uSAC
 TE 298.0 K
 D0 0.11000000 sec
 MCKEY 0.01000000 sec
 MONEK 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 12.01 uSAC
 P1 12.00 uSAC
 PL1 -0.60 dB
 SFO1 400.1328009 MHz
 F2 - Processing parameters
 SI 65536
 SF 400.1300259 MHz
 DM 327.5
 SFO 400.1300259 MHz
 LB 0.30 Hz
 GB 0
 PC 2.00
 LD VWR p10r parameters
 CX 22.80 cm
 CY 15.00 cm
 F1P 100.000 ppm
 F2P -9.500 ppm
 F2 -200.07 Hz
 PRGM 0.46052 ppm/cm
 HZCN 184.27042 Hz/cm

Current Data Parameters
 NAME A07_4_133_03
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ Time 04/11/2008 11:43
 Operator
 PULPROG zgpg30
 PROGRAM 5 mm QNP H/1D
 SOLVENT CDCl3
 DS 8
 SWH 6410.256 Hz
 FWHM 12.000 Hz
 AQ 5.118577 sec
 RG 287.4
 DE 4.50 umsec
 TE 298.0 K
 DT 0.10000000 sec
 MCOREST 0.00000000 sec
 MCHRGK 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 13C
 P1 12.00 umsec
 PL1 0.00 dB
 SFO1 400.1326000 MHz
 F2 - Processing parameters
 SF 400.1300244 MHz
 DSF 80
 SFO 400.1300244 MHz
 LB 0.30 Hz
 GB 0
 PC 2.00

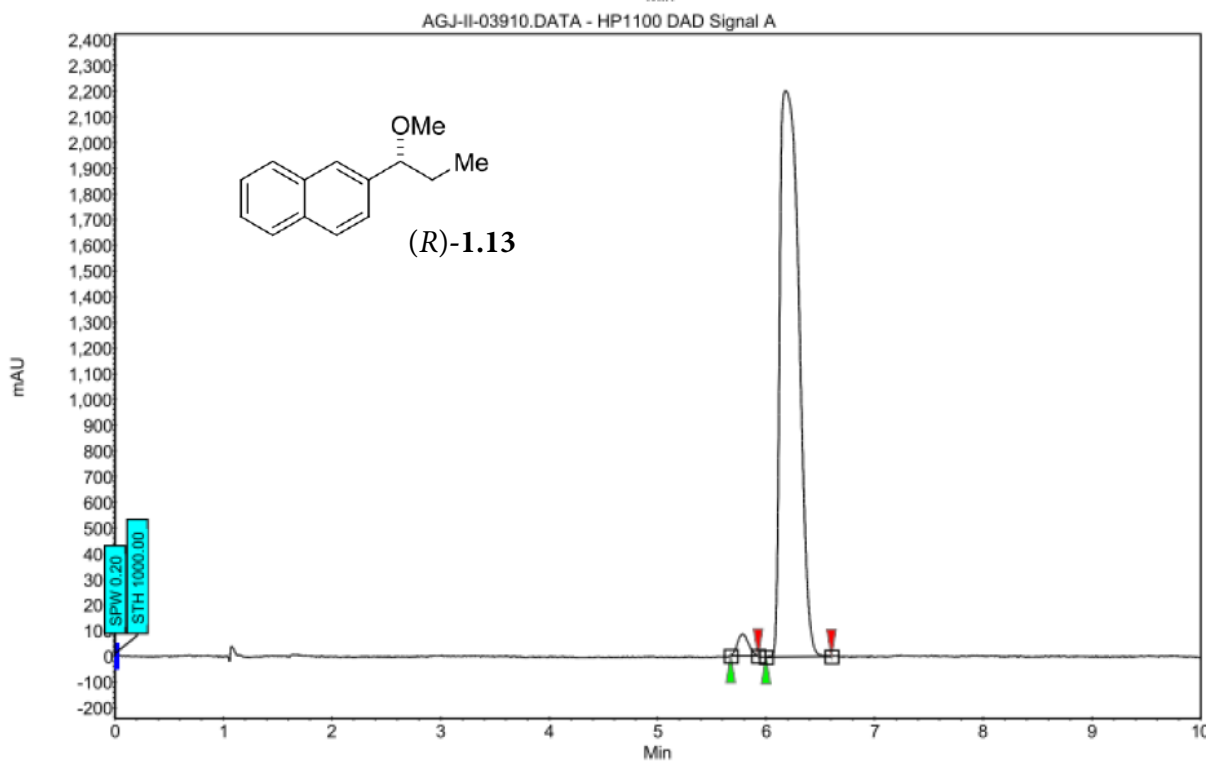
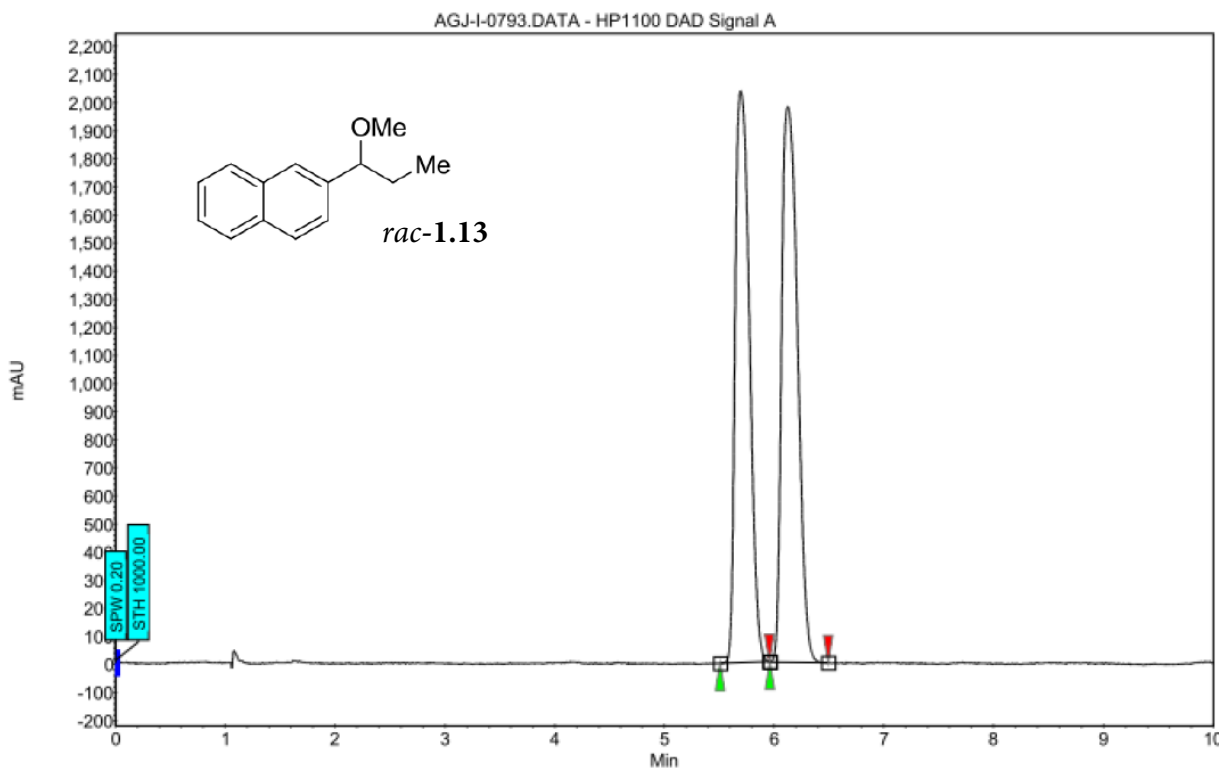


APPENDIX B

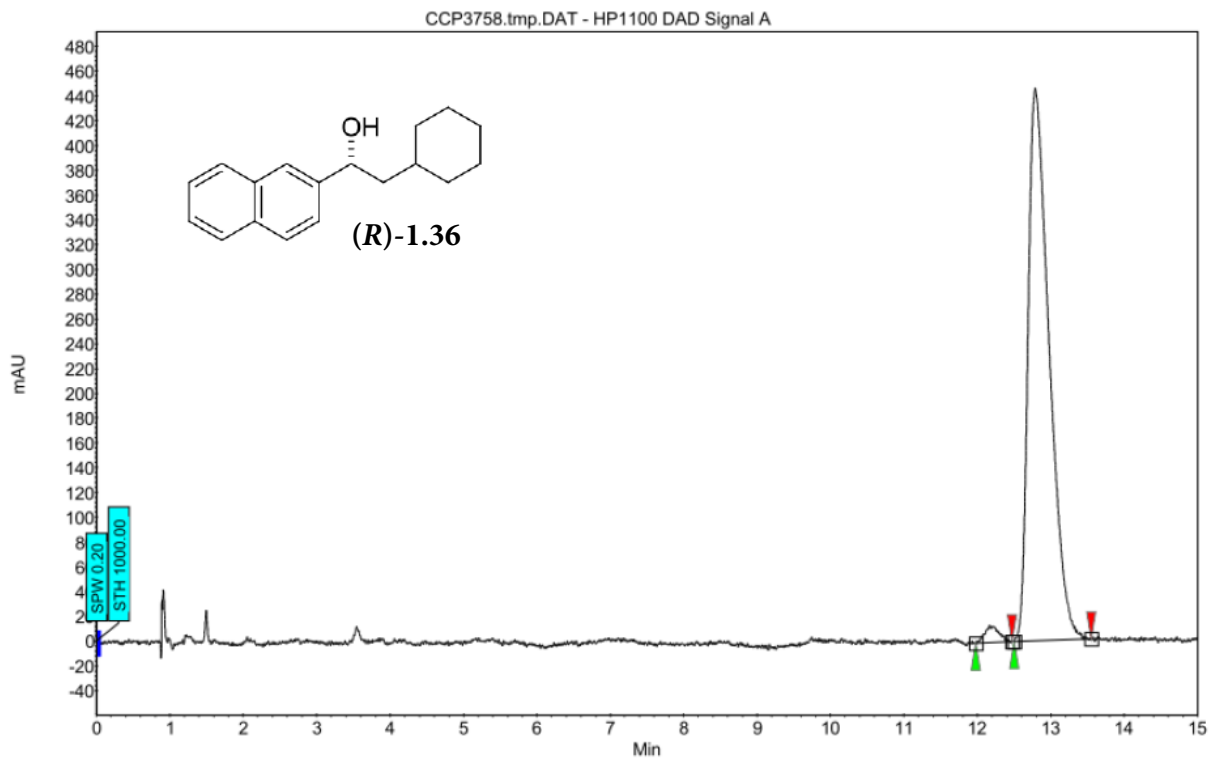
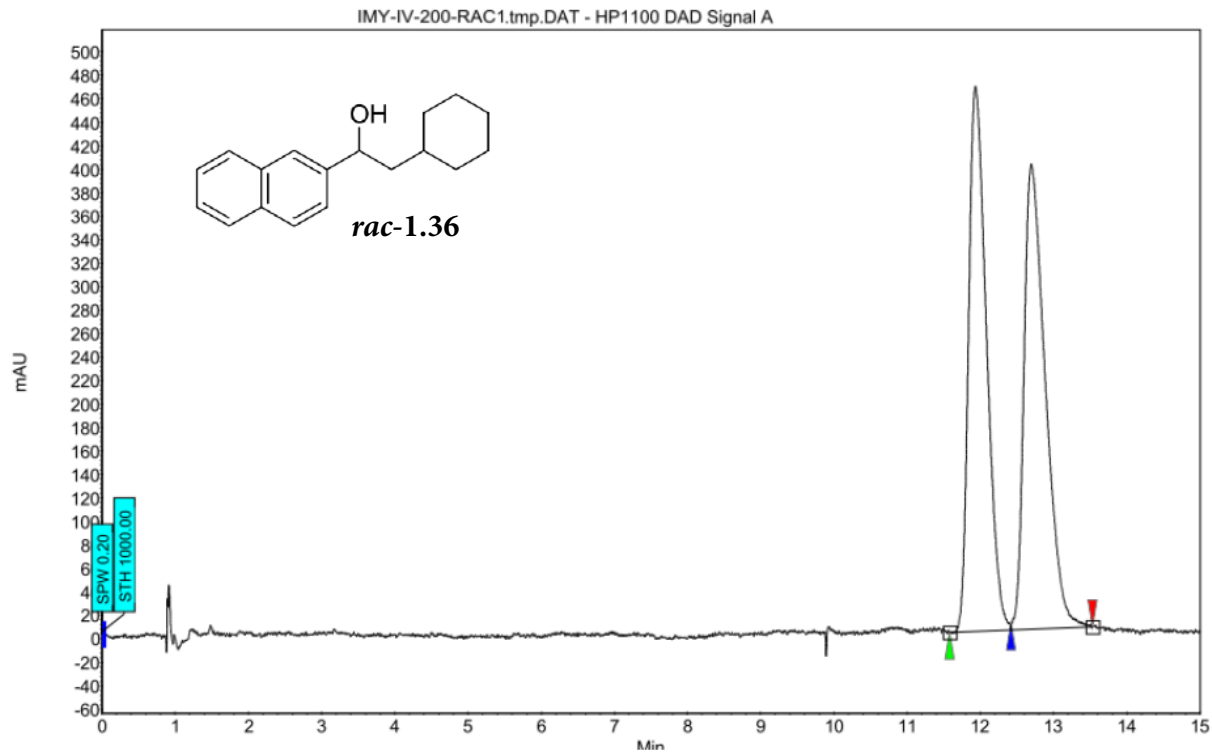
SFC Traces



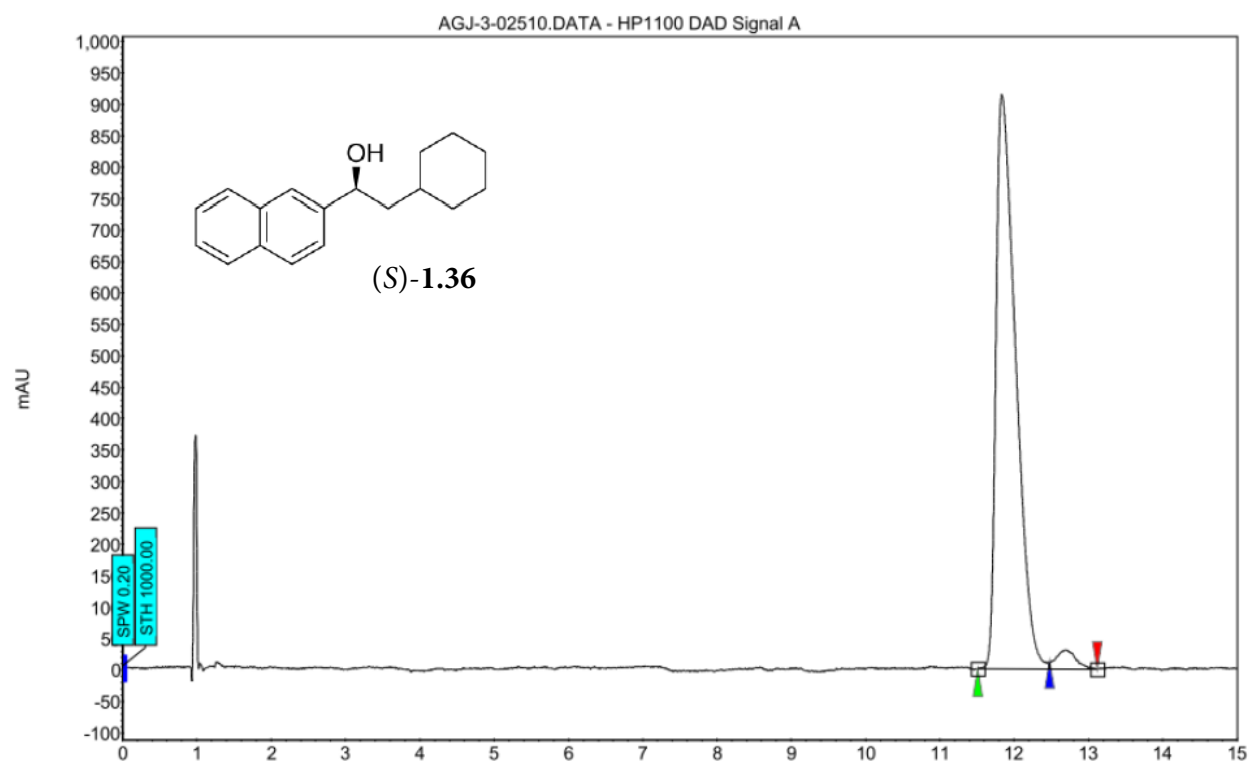
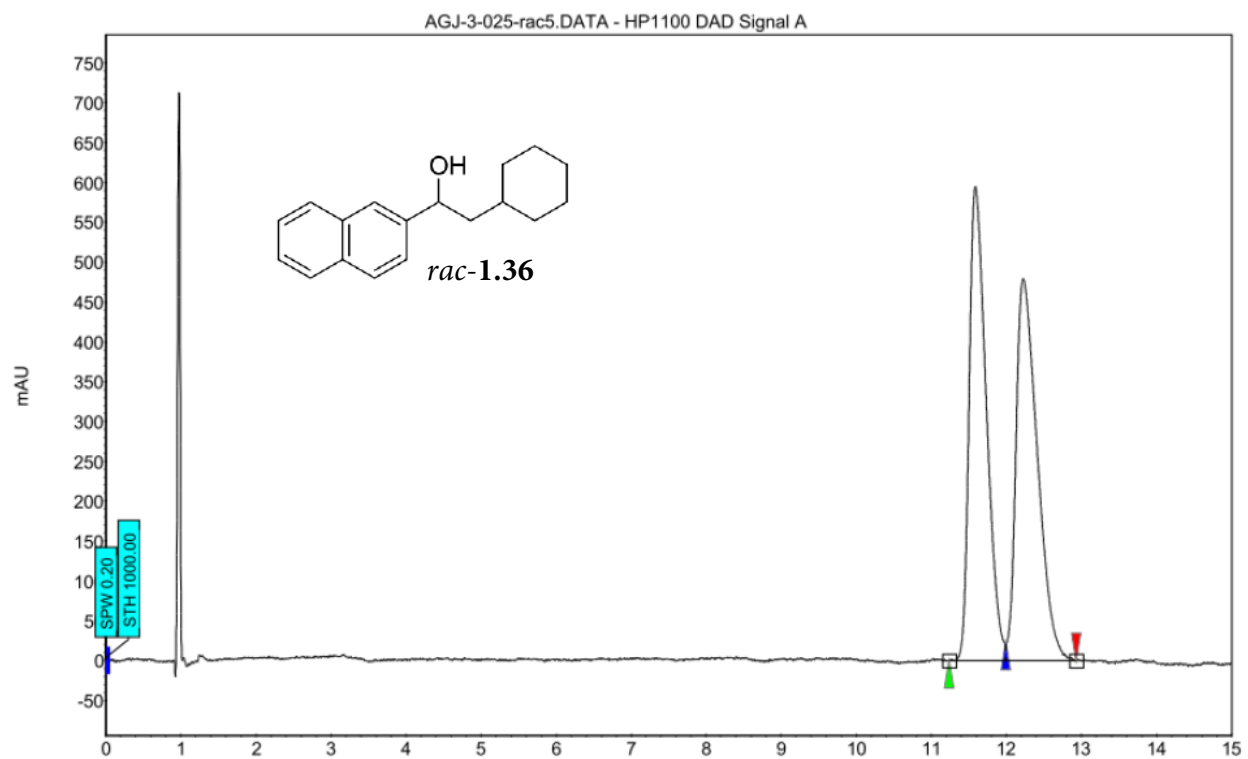
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
2	UNKNOWN	8.66	9.08	9.42	0.00	2.69	39.6	8.8	2.691
1	UNKNOWN	9.60	9.86	10.24	0.00	97.31	1613.2	316.9	97.309
Total						100.00	1652.8	325.7	100.000



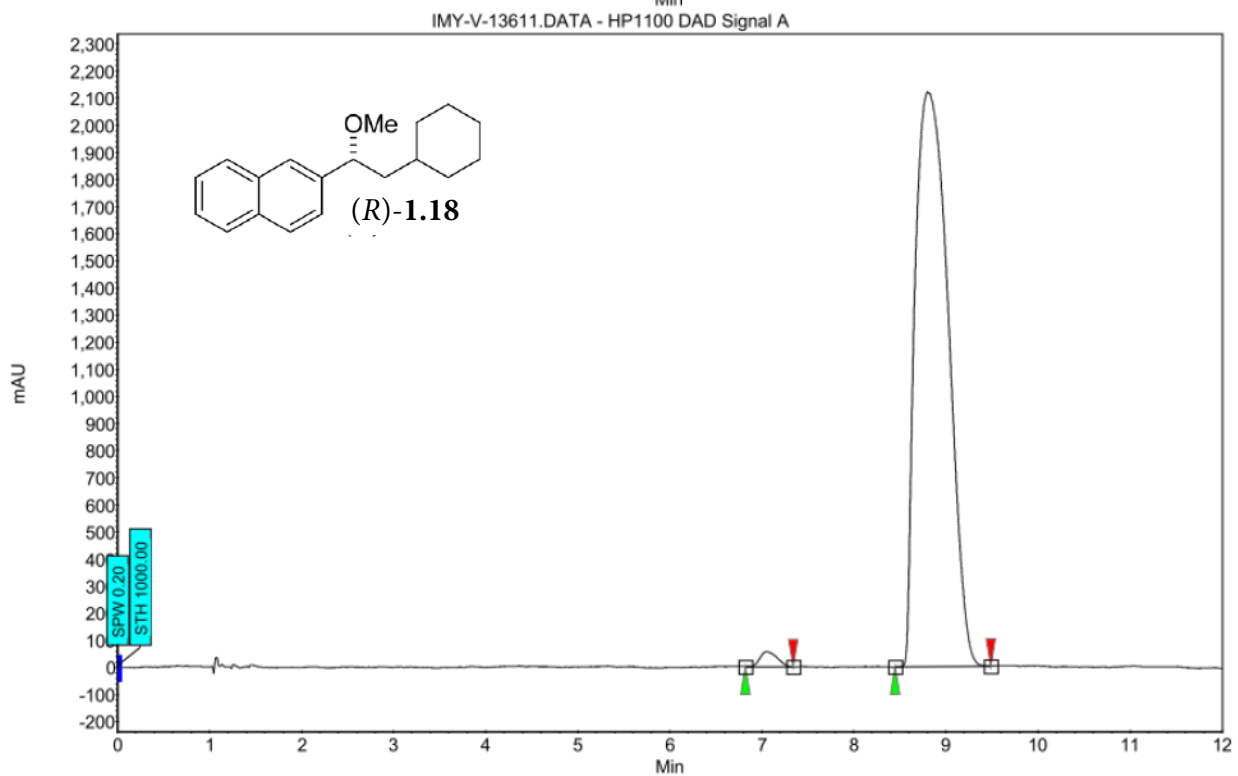
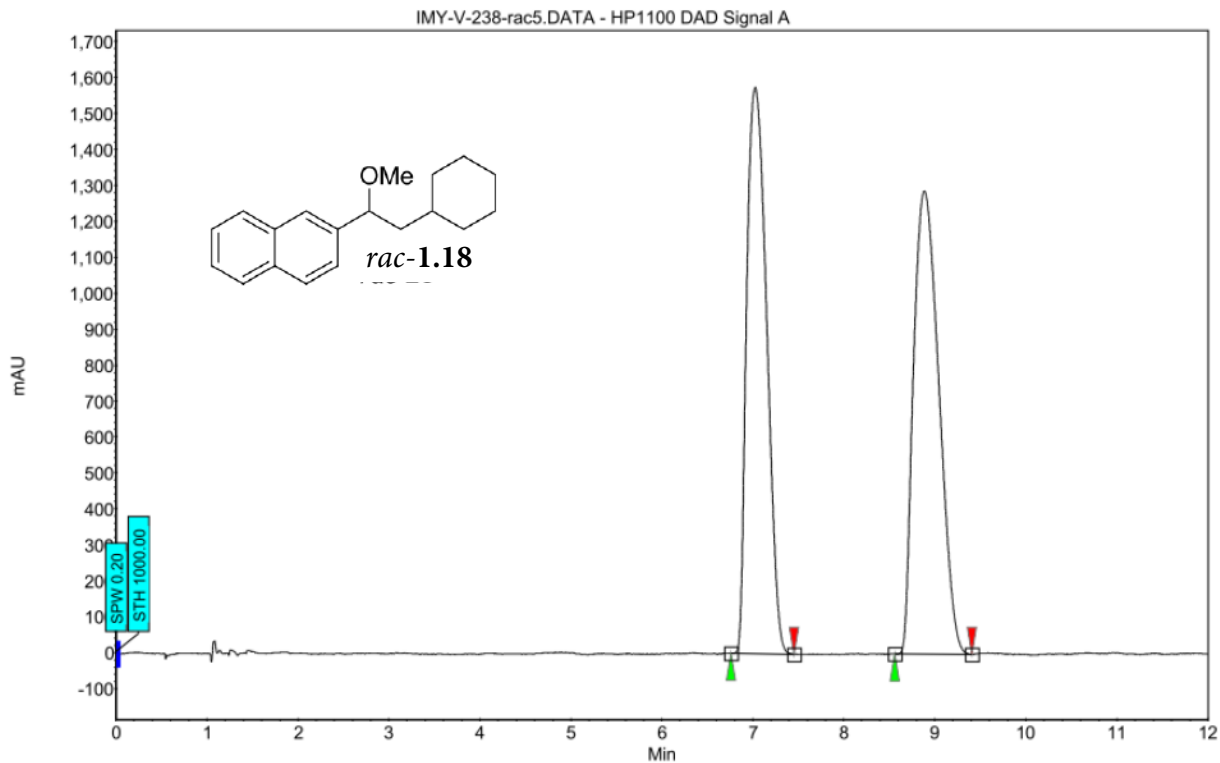
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
2	UNKNOWN	5.67	5.78	5.93	0.00	2.19	84.6	10.0	2.186
1	UNKNOWN	6.00	6.18	6.60	0.00	97.81	2204.3	445.6	97.814
Total						100.00	2288.8	455.6	100.000



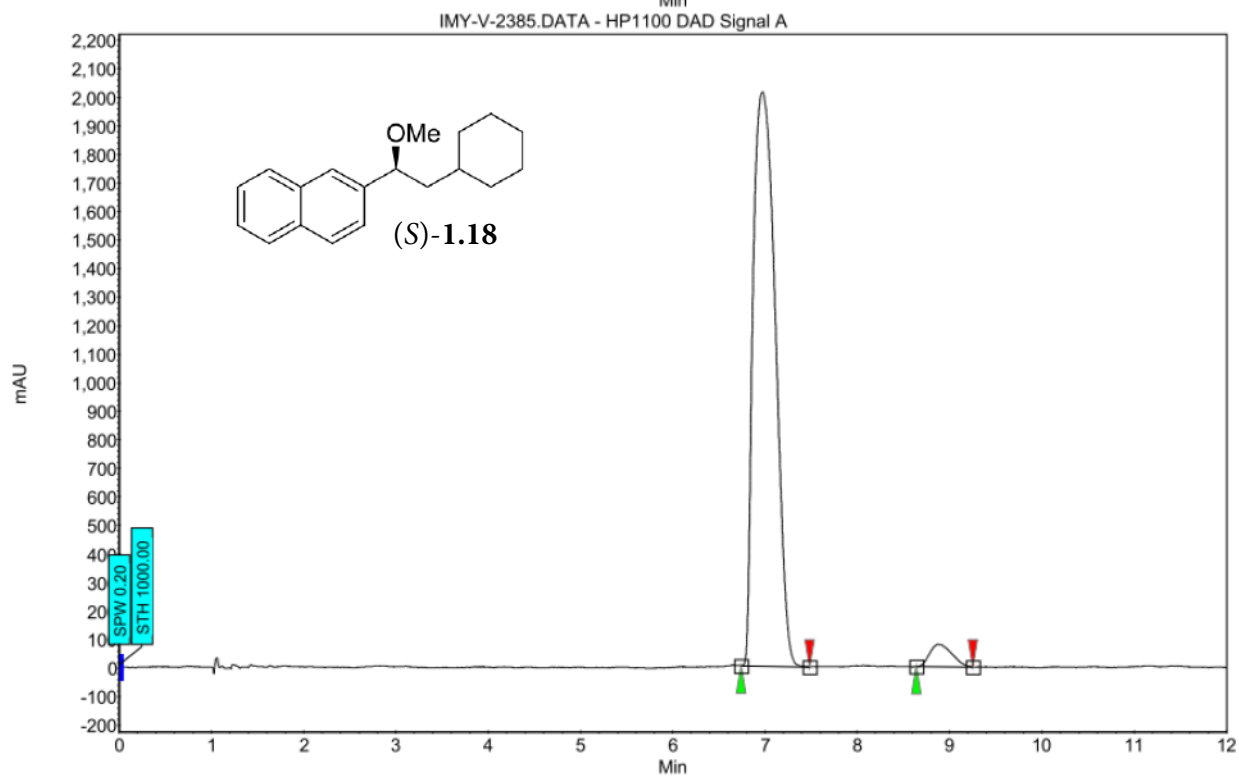
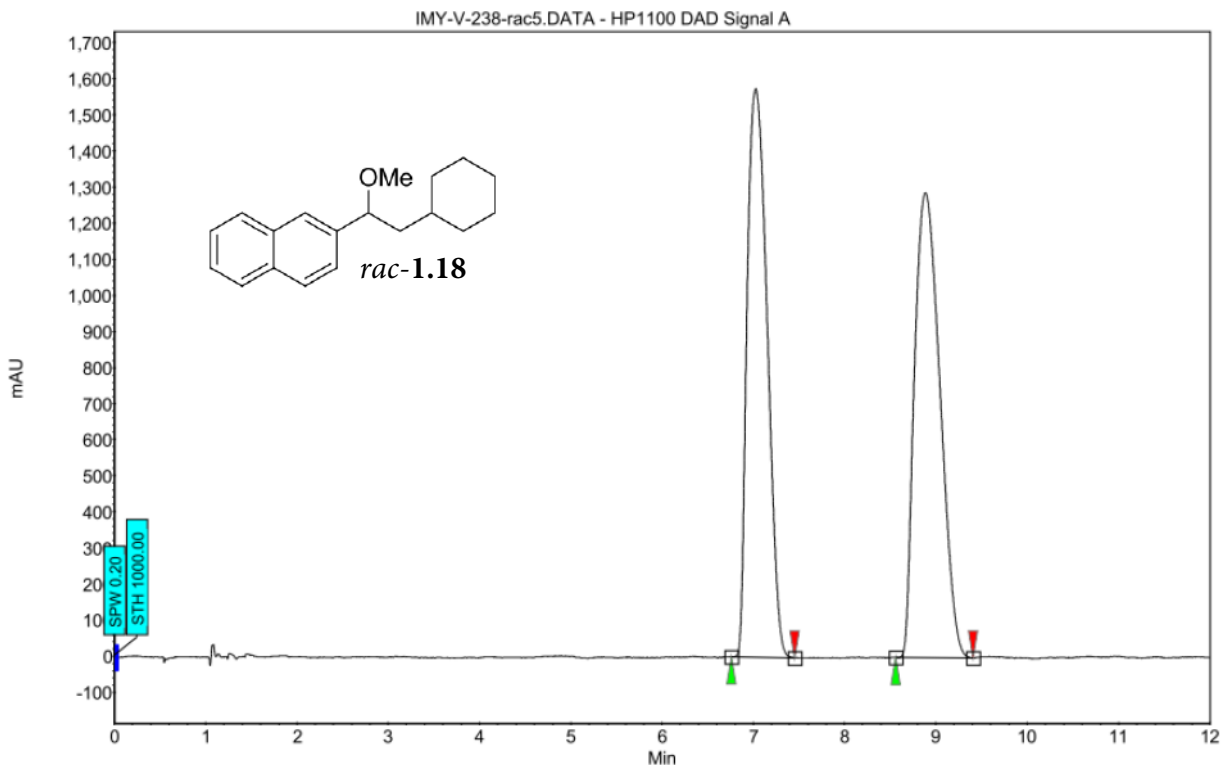
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μ V]	Area [μ V.Min]	Area [%]
1	UNKNOWN	11.98	12.17	12.47	0.00	2.01	13.9	3.0	2.010
2	UNKNOWN	12.50	12.79	13.55	0.00	97.99	445.8	147.3	97.990
Total						100.00	459.7	150.3	100.000



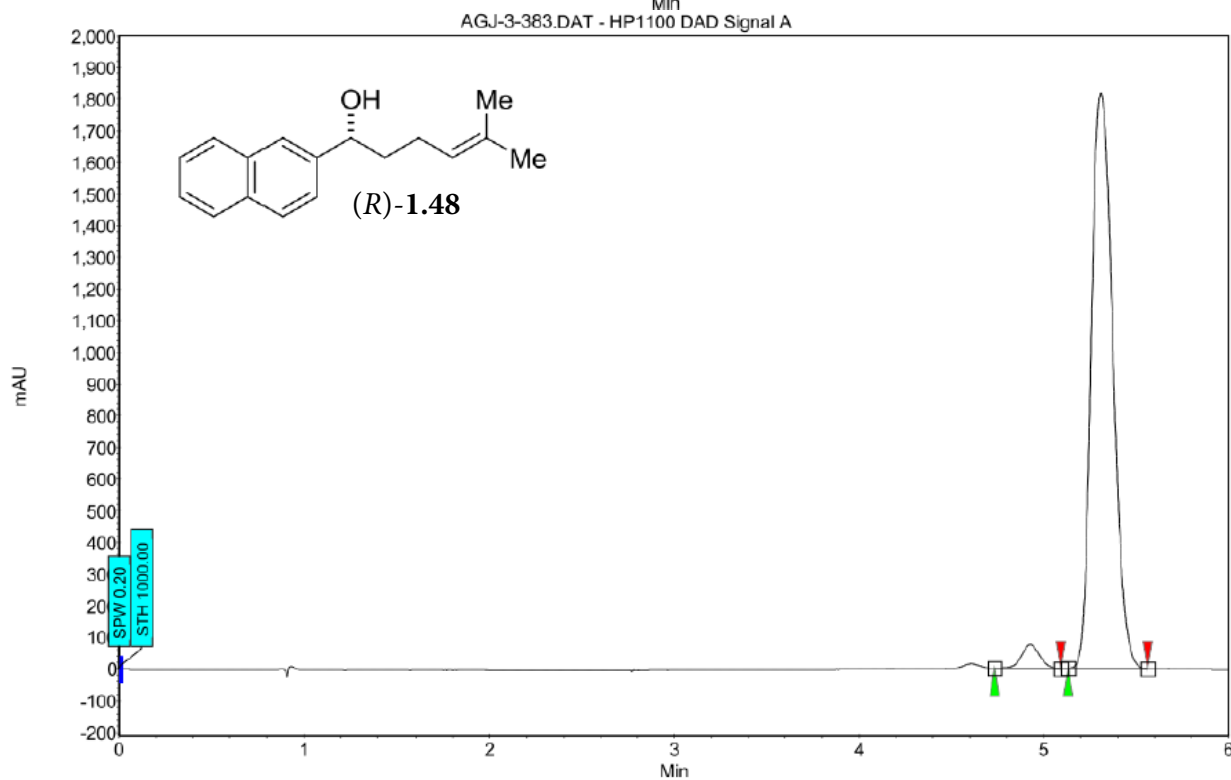
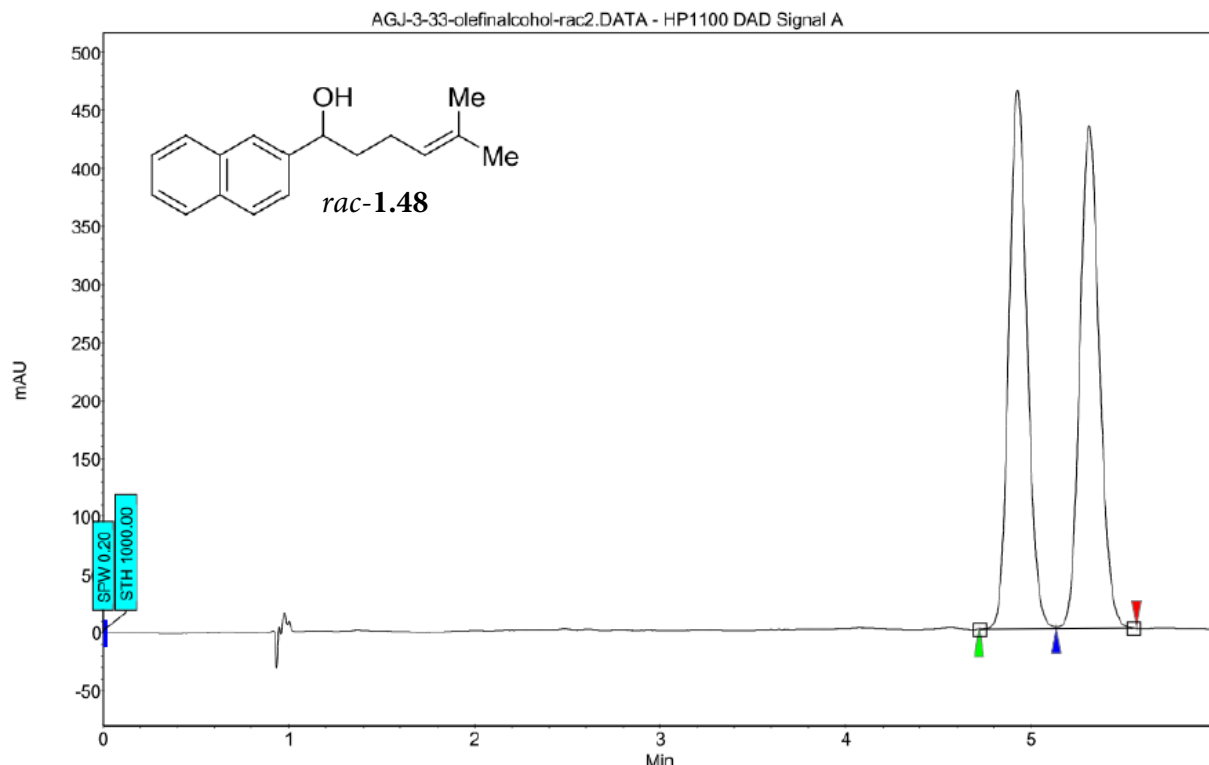
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	11.51	11.83	12.47	0.00	96.72	913.1	279.8	96.723
2	UNKNOWN	12.47	12.70	13.11	0.00	3.28	30.9	9.5	3.277
Total						100.00	944.0	289.3	100.000



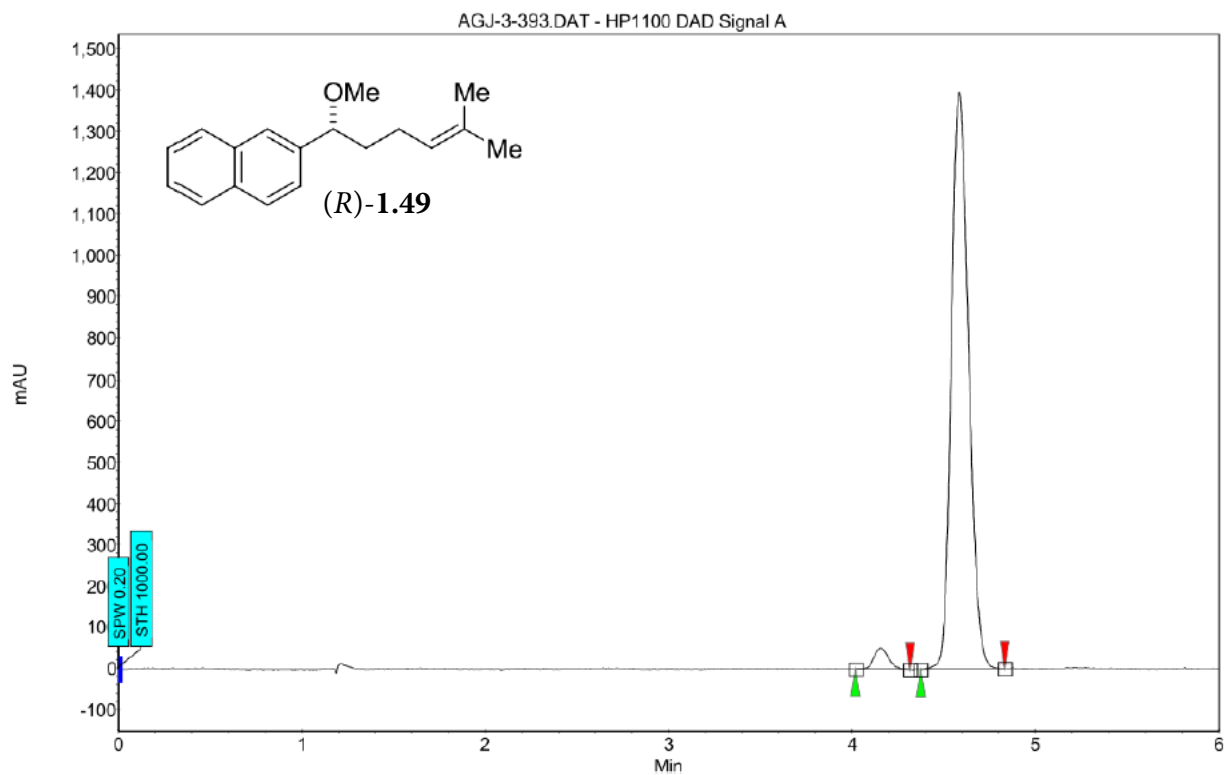
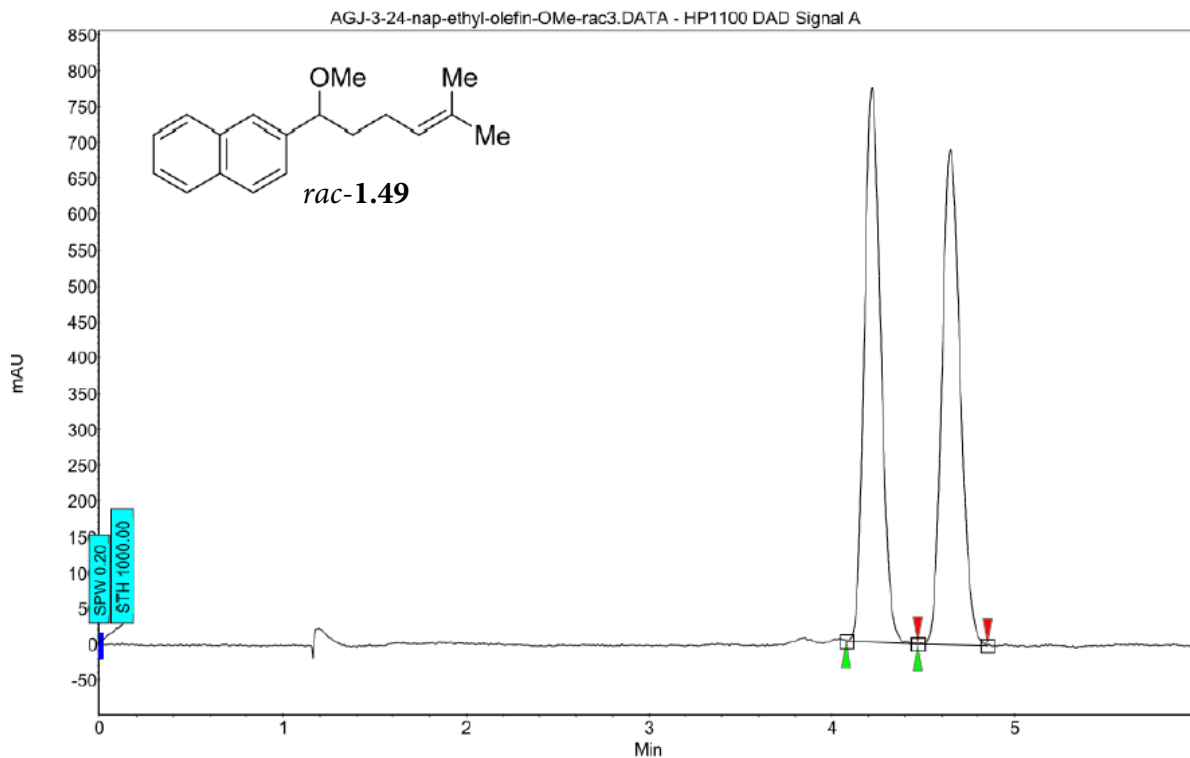
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
2	UNKNOWN	6.82	7.05	7.34	0.00	1.35	56.2	12.1	1.352
1	UNKNOWN	8.45	8.80	9.49	0.00	98.65	2120.6	879.3	98.648
Total						100.00	2176.8	891.4	100.000



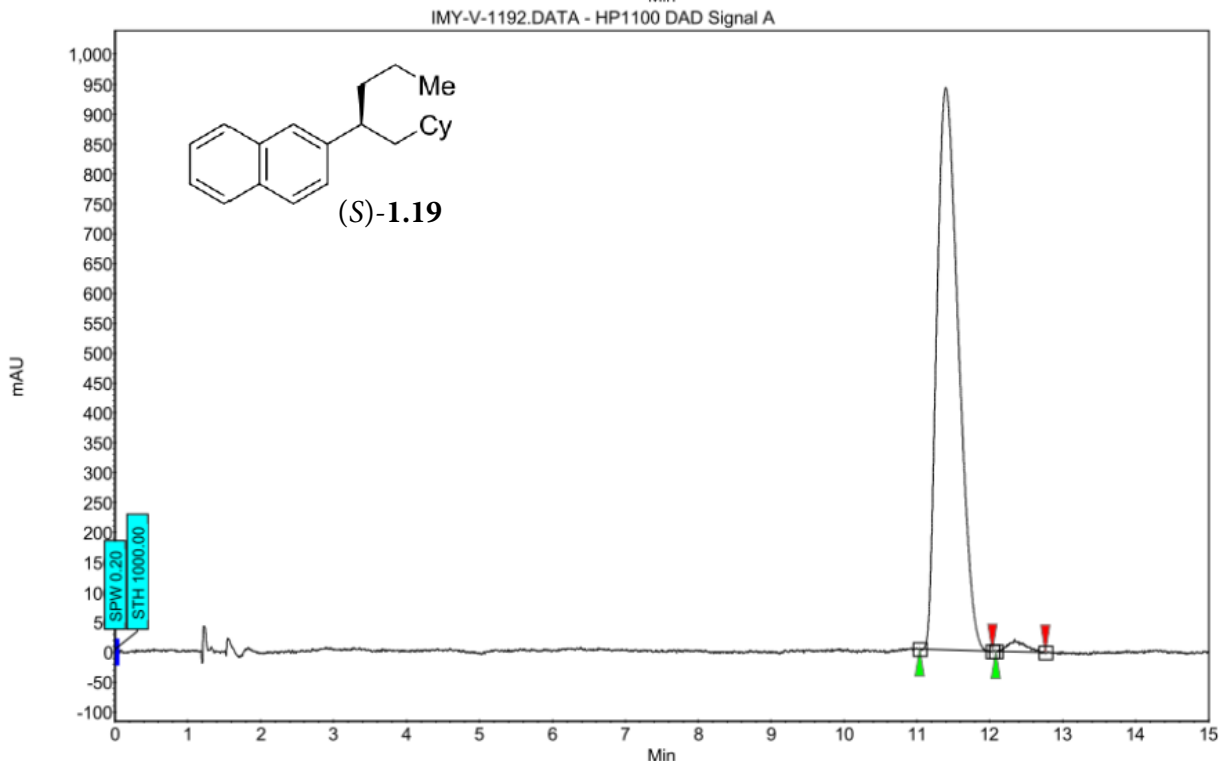
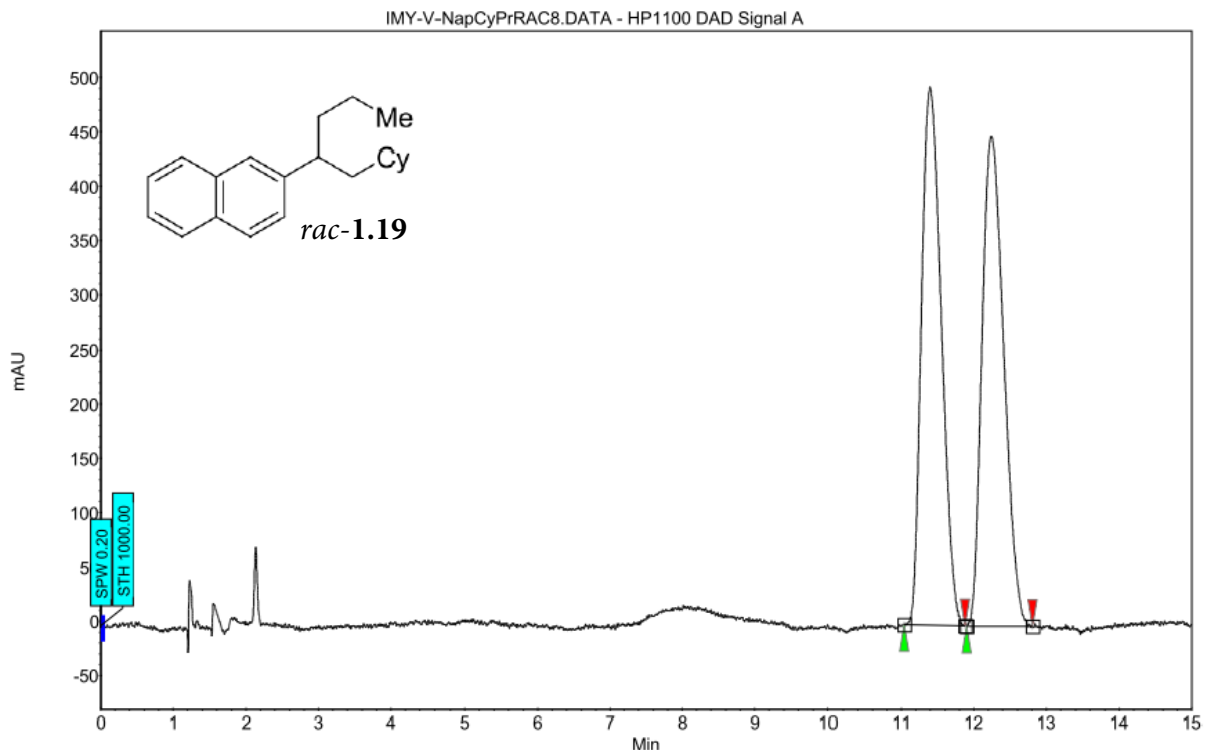
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	6.75	6.98	7.49	0.00	96.23	2011.3	558.6	96.229
2	UNKNOWN	8.64	8.87	9.25	0.00	3.77	78.5	21.9	3.771
Total						100.00	2089.9	580.5	100.000



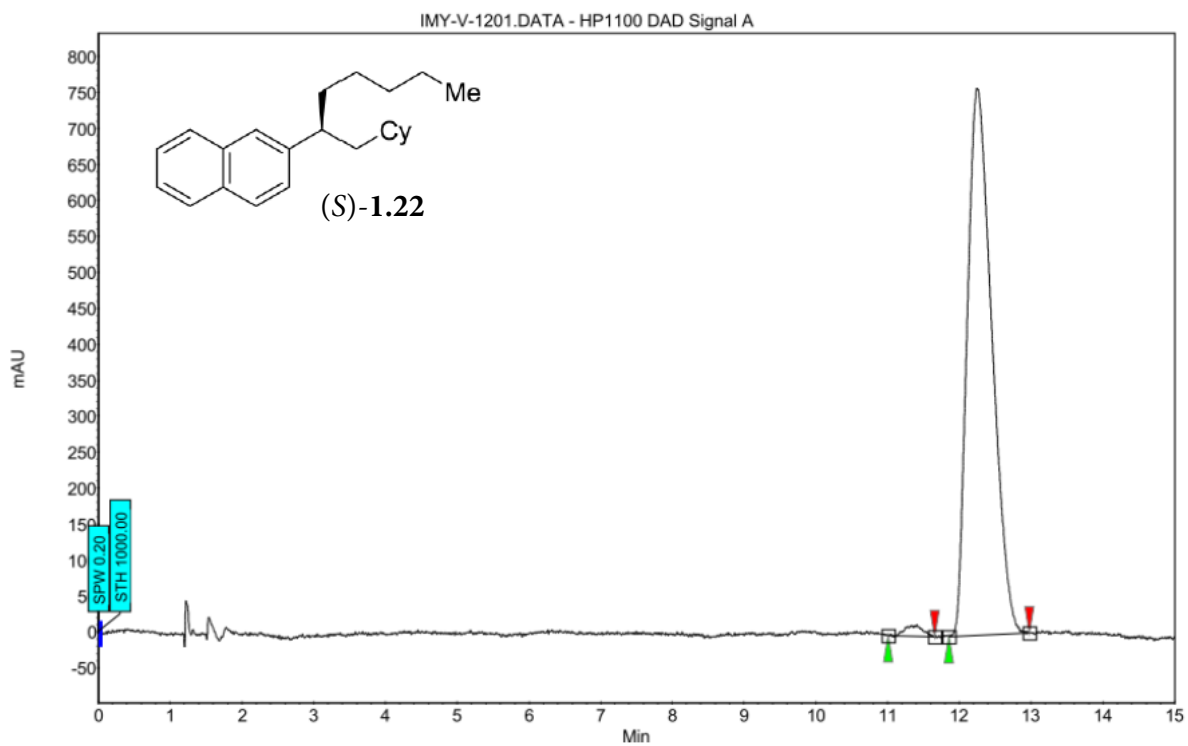
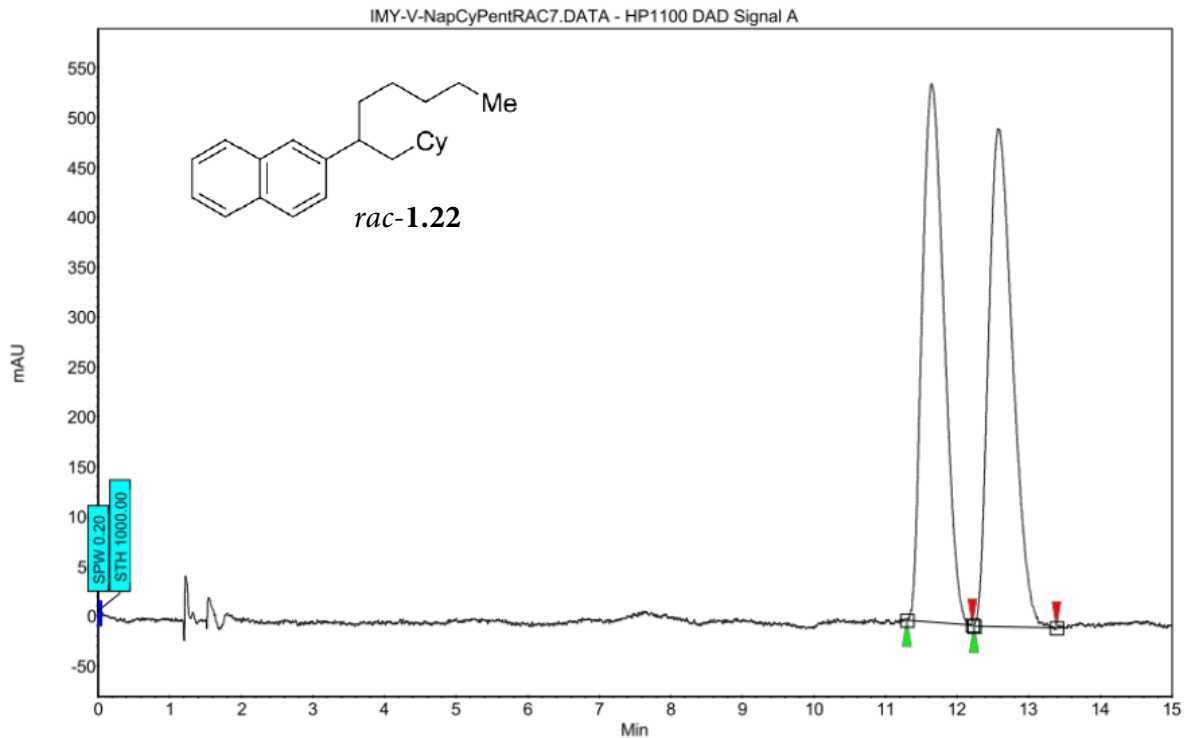
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
2	UNKNOWN	4.73	4.93	5.09	0.00	3.37	75.0	8.6	3.373
1	UNKNOWN	5.13	5.31	5.56	0.00	96.63	1816.9	245.2	96.627
Total						100.00	1891.9	253.8	100.000



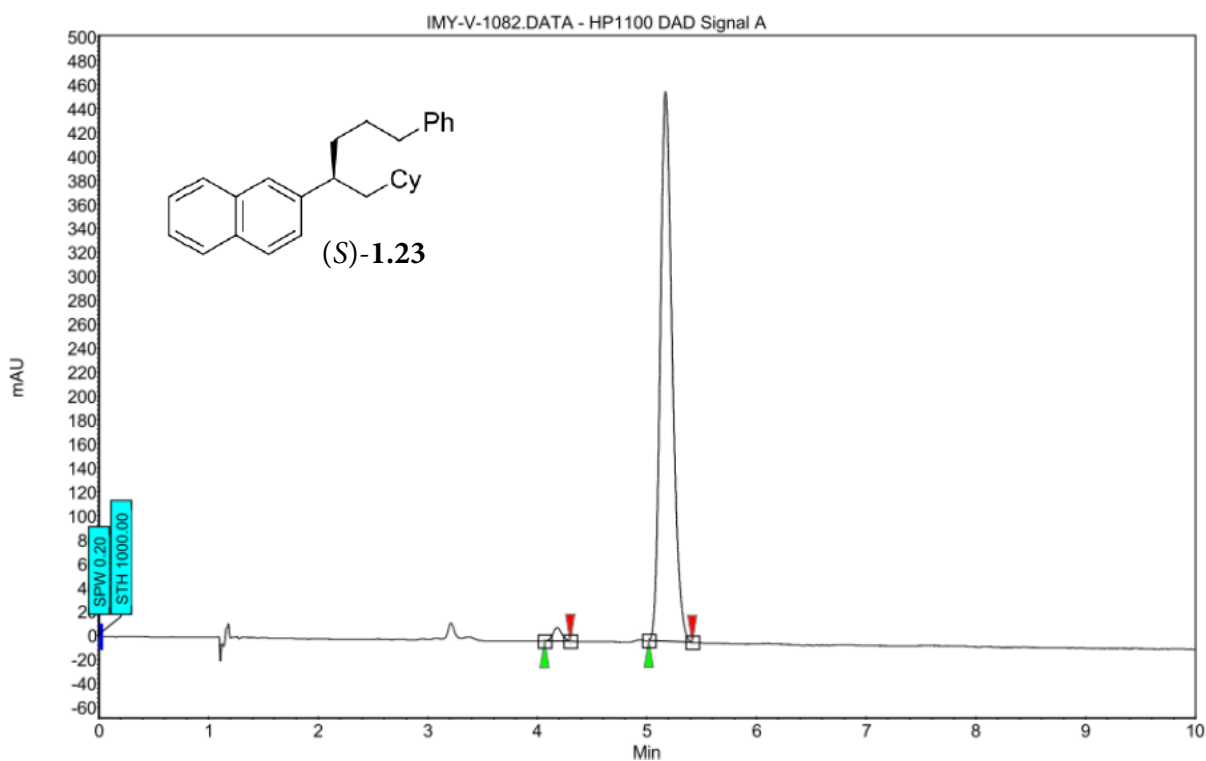
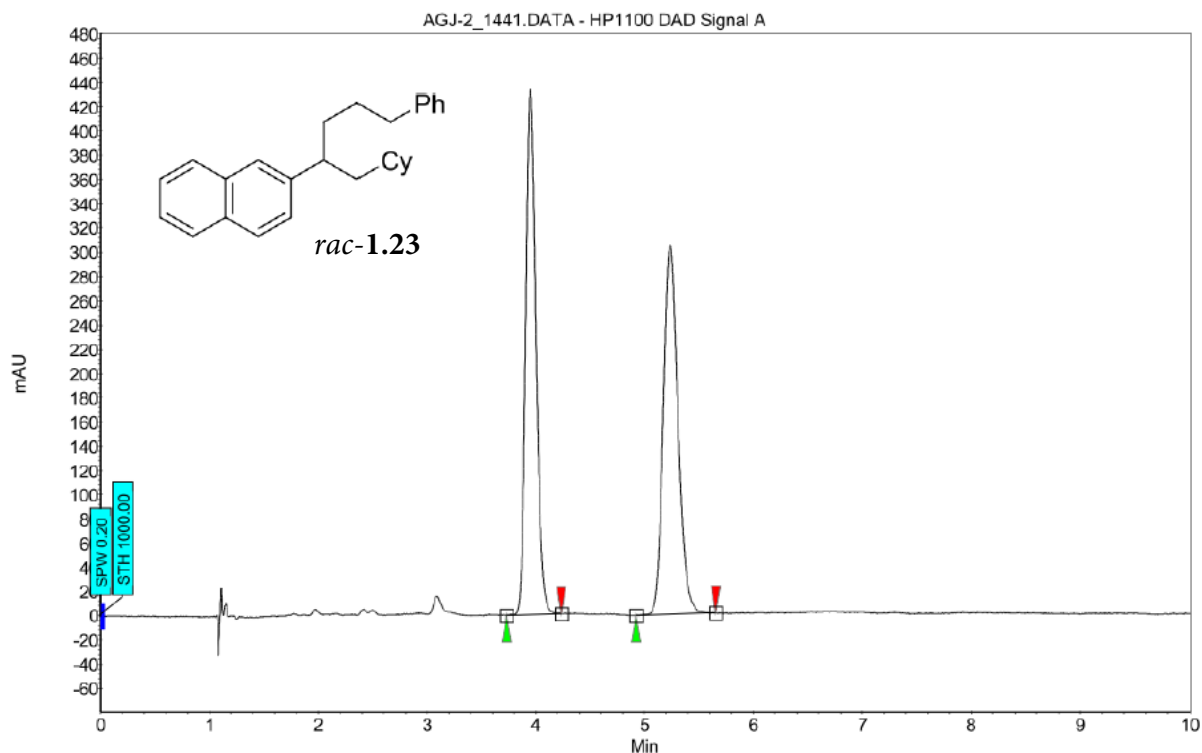
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
2	UNKNOWN	4.02	4.16	4.32	0.00	3.08	51.8	4.9	3.080
1	UNKNOWN	4.37	4.58	4.83	0.00	96.92	1396.8	153.4	96.920
Total						100.00	1448.6	158.2	100.000



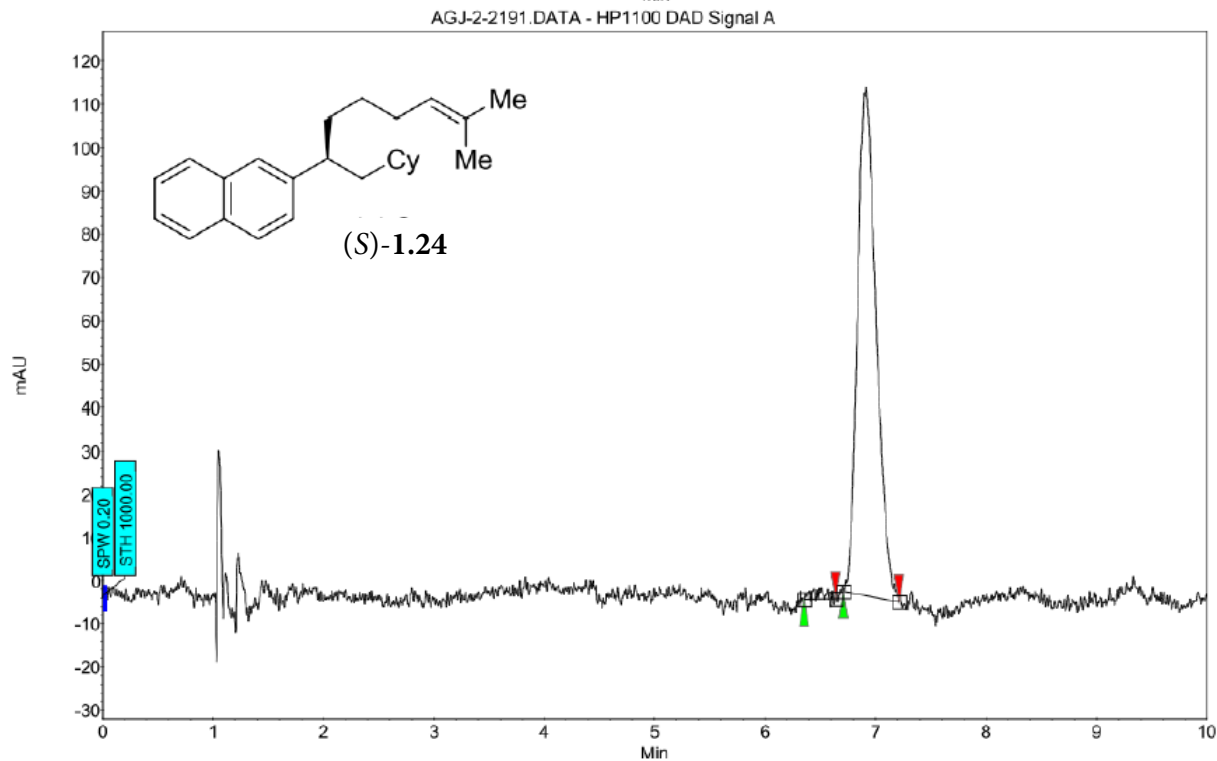
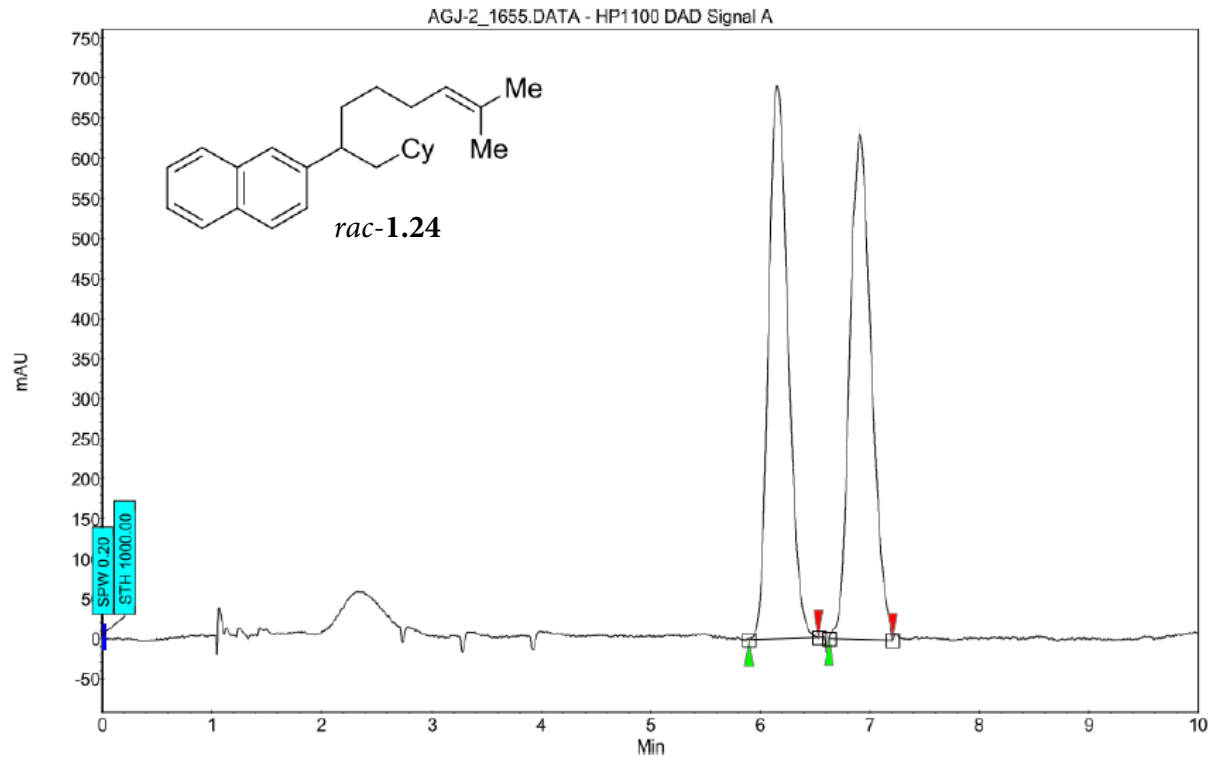
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	11.04	11.40	12.03	0.00	98.37	939.8	323.2	98.367
2	UNKNOWN	12.08	12.34	12.76	0.00	1.63	20.8	5.4	1.633
Total						100.00	960.6	328.6	100.000



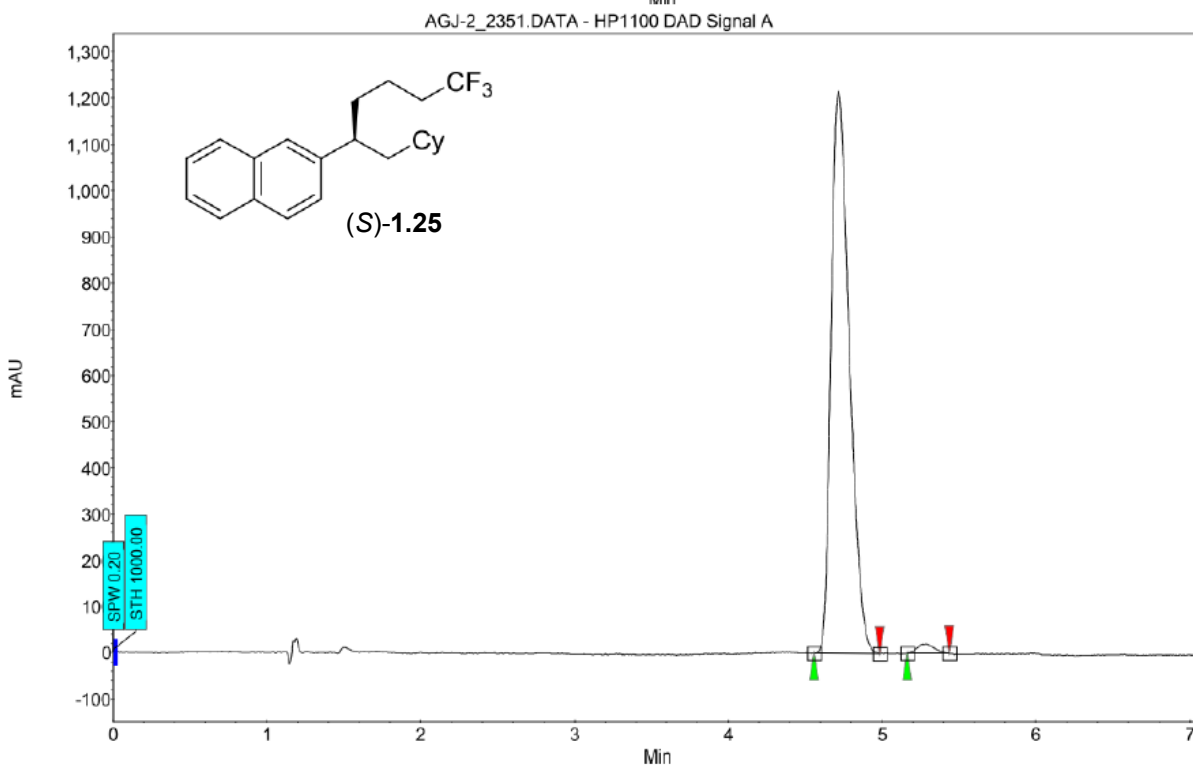
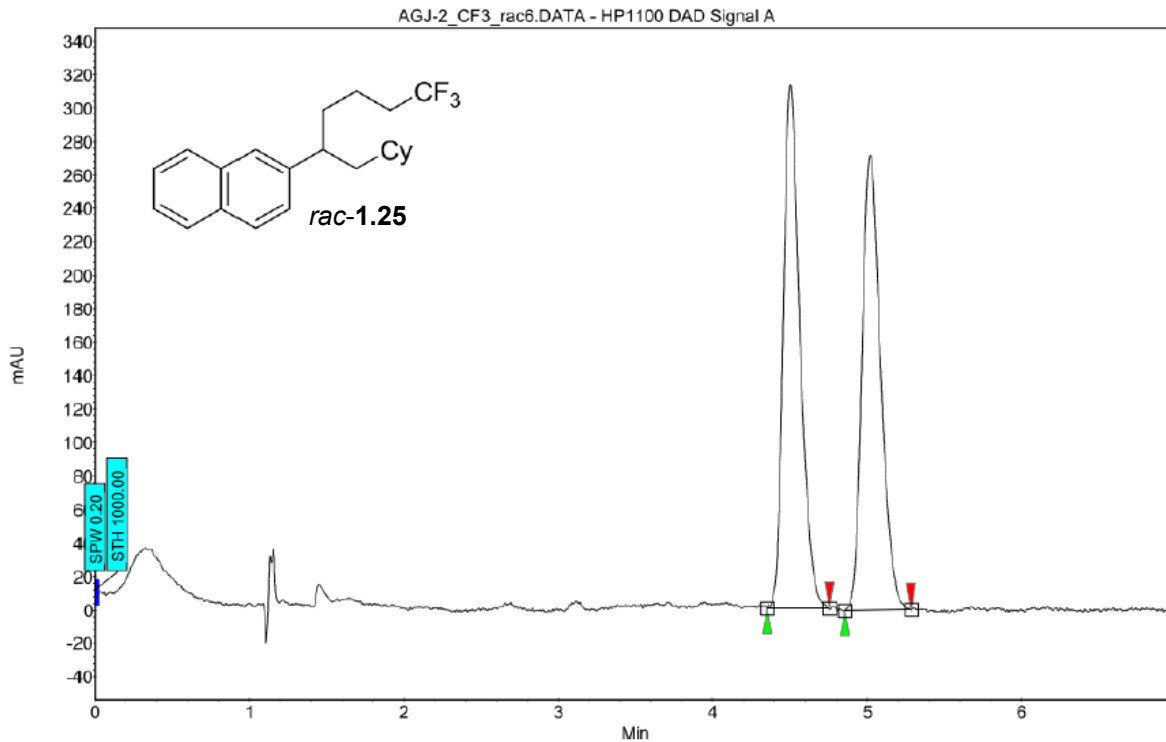
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
2	UNKNOWN	11.01	11.41	11.66	0.00	1.44	16.2	4.4	1.435
1	UNKNOWN	11.85	12.25	12.98	0.00	98.56	759.8	301.9	98.565
Total						100.00	776.0	306.3	100.000



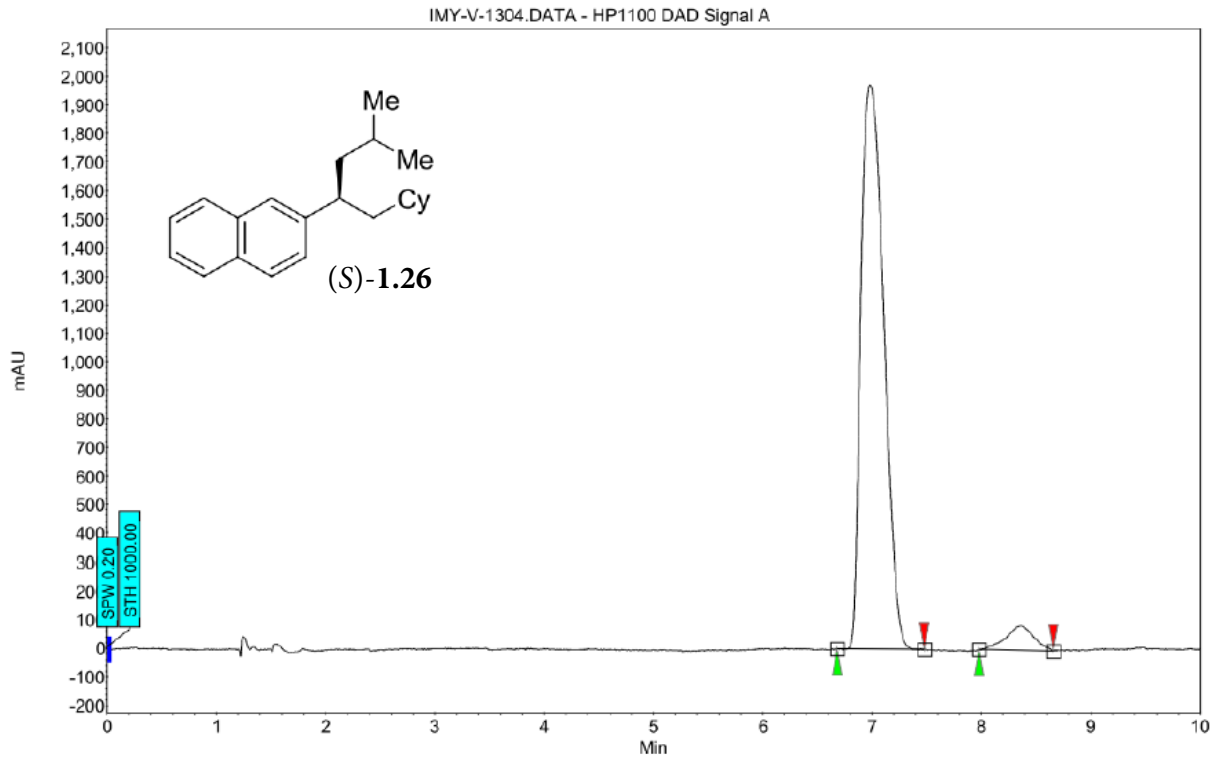
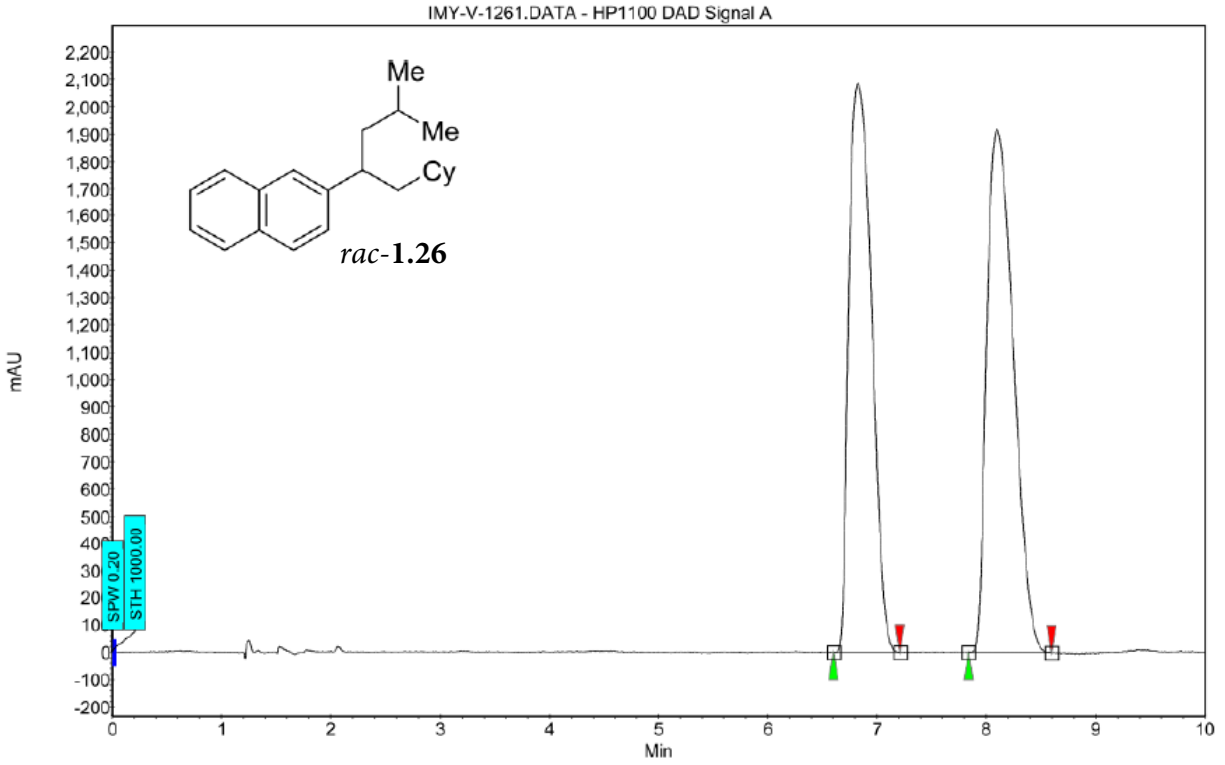
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	4.07	4.18	4.30	0.00	1.74	11.2	1.0	1.735
2	UNKNOWN	5.02	5.17	5.42	0.00	98.26	458.7	58.1	98.265
Total						100.00	469.9	59.1	100.000



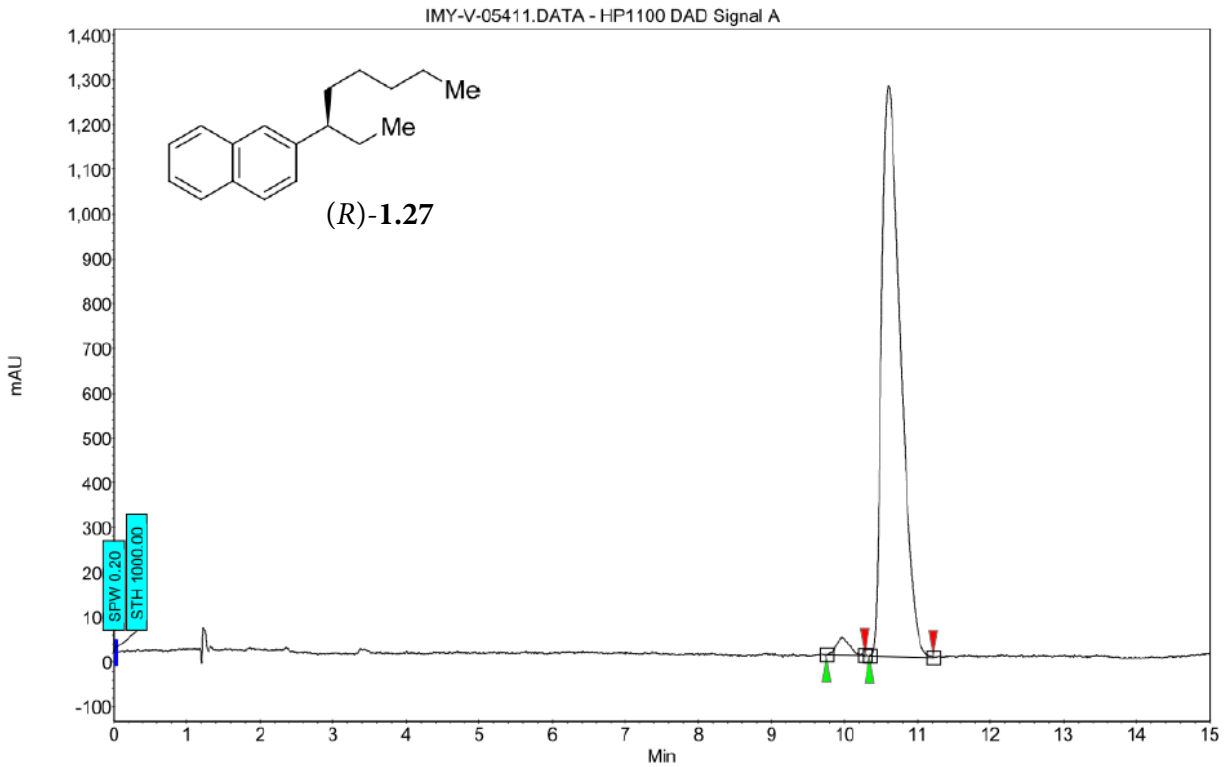
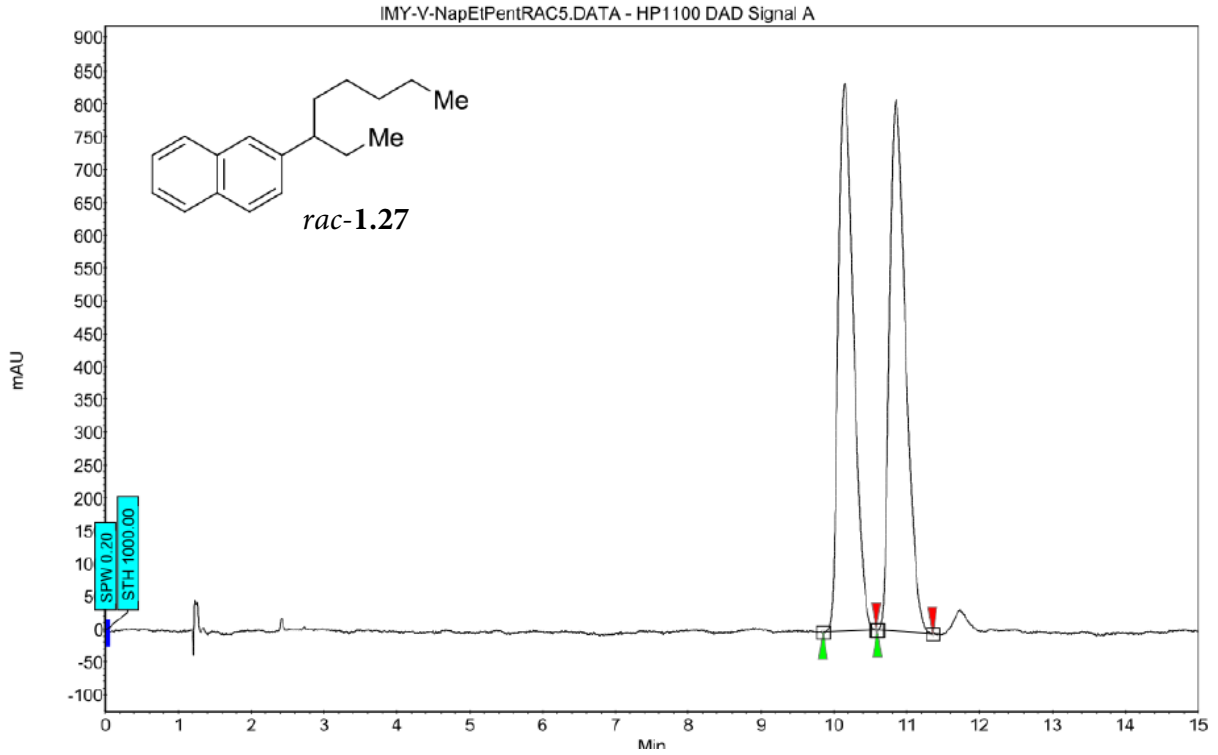
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μ V]	Area [μ V.Min]	Area [%]
2	UNKNOWN	6.35	6.49	6.64	0.00	1.12	2.2	0.3	1.119
1	UNKNOWN	6.71	6.92	7.21	0.00	98.88	117.2	23.0	98.881
Total						100.00	119.4	23.3	100.000



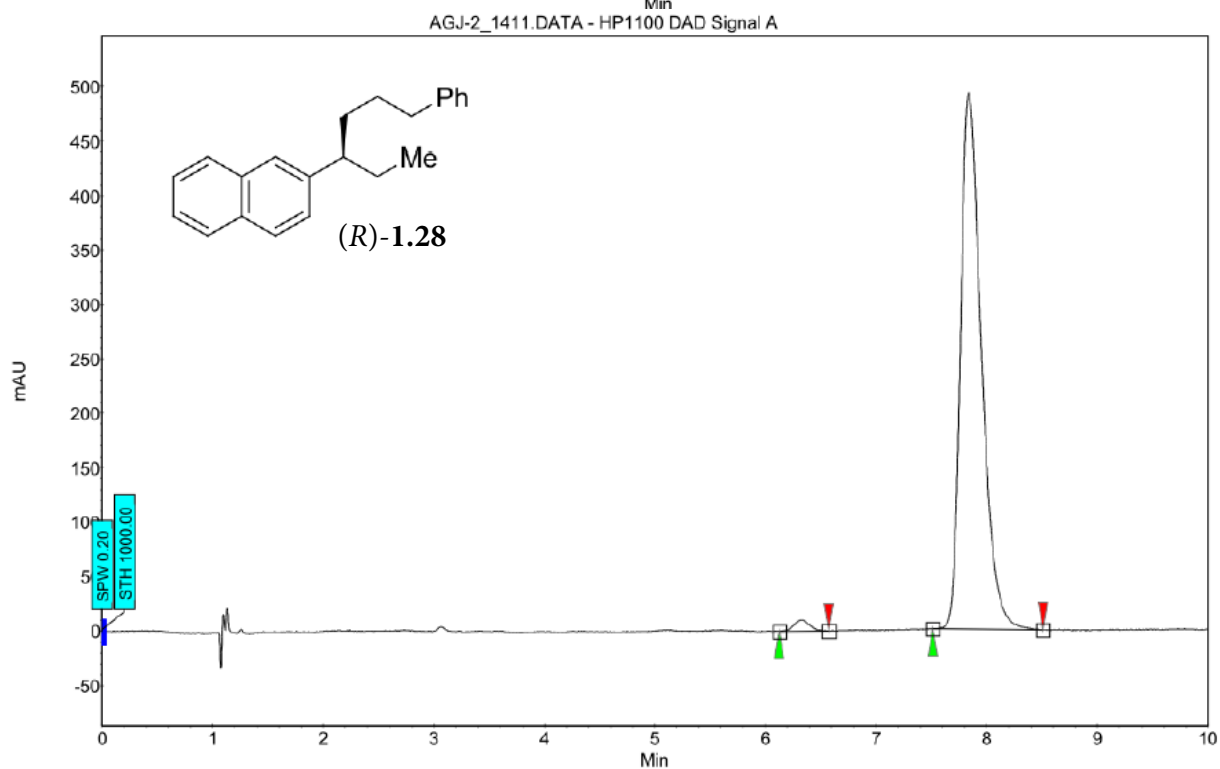
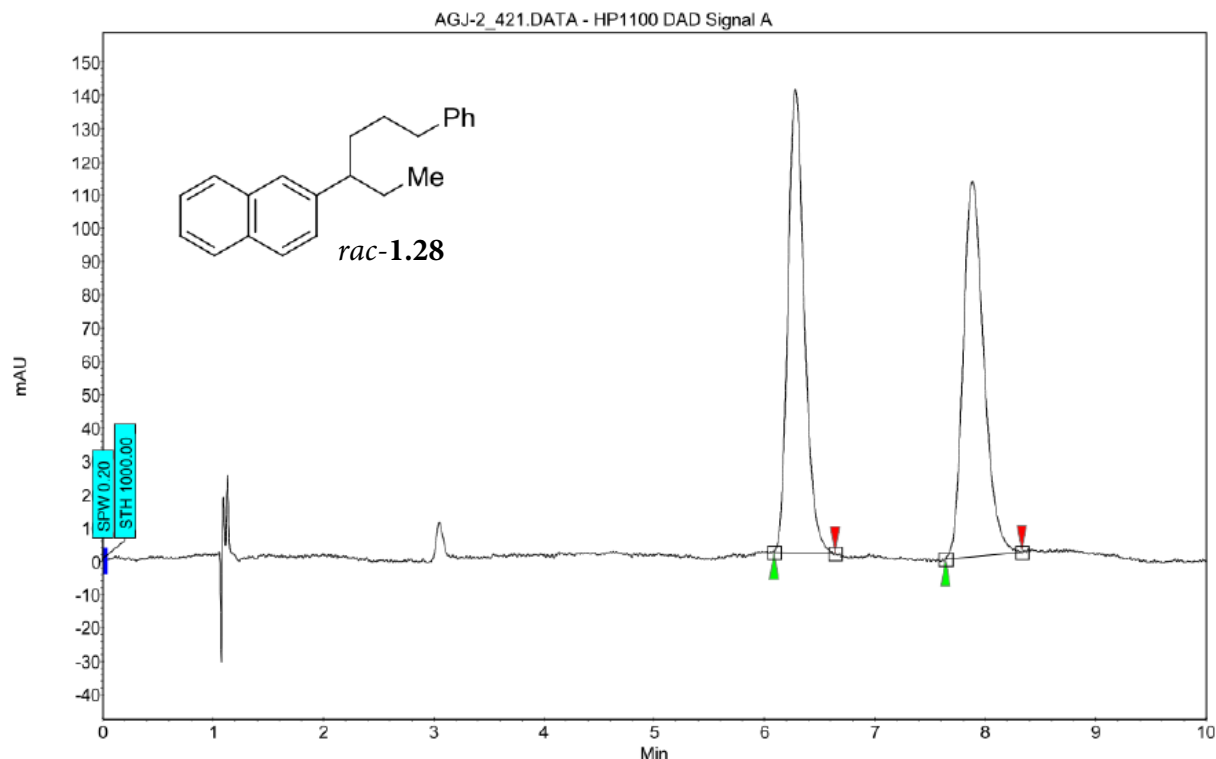
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	4.56	4.72	4.99	0.00	98.50	1215.7	167.4	98.504
2	UNKNOWN	5.16	5.29	5.44	0.00	1.50	20.2	2.5	1.496
Total						100.00	1235.9	169.9	100.000



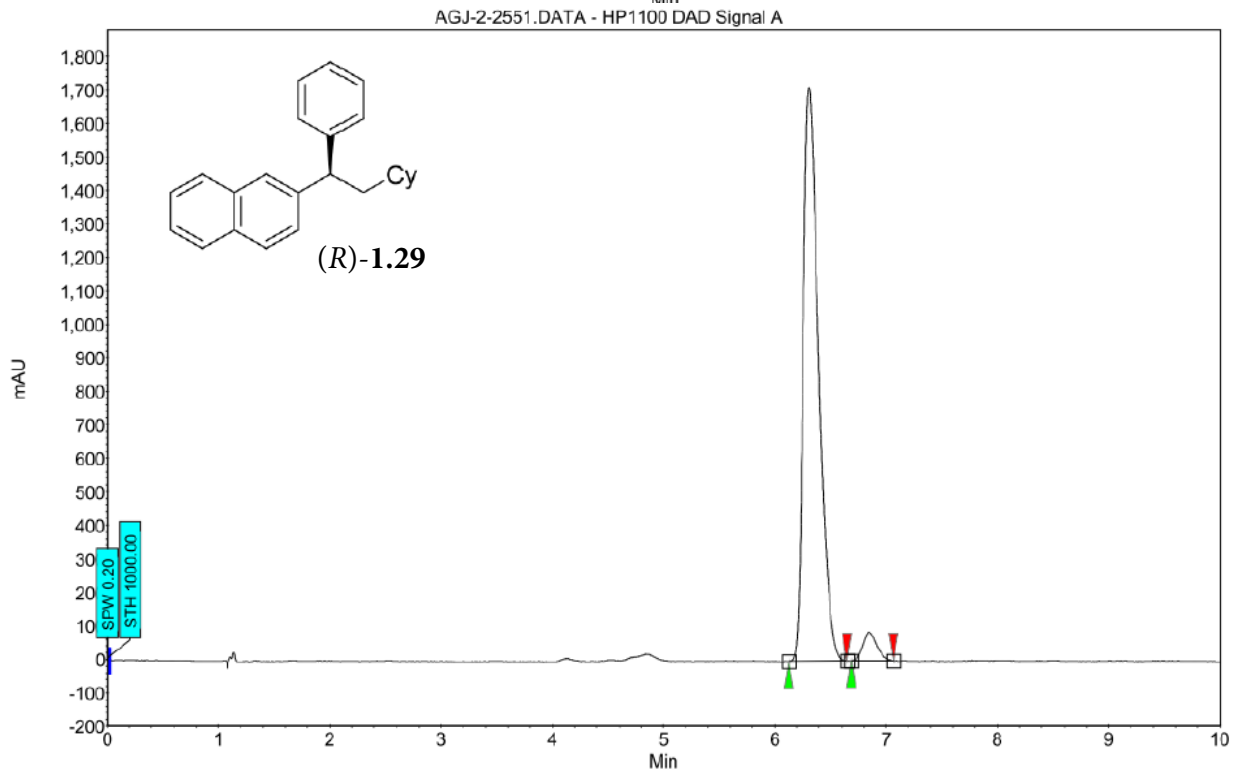
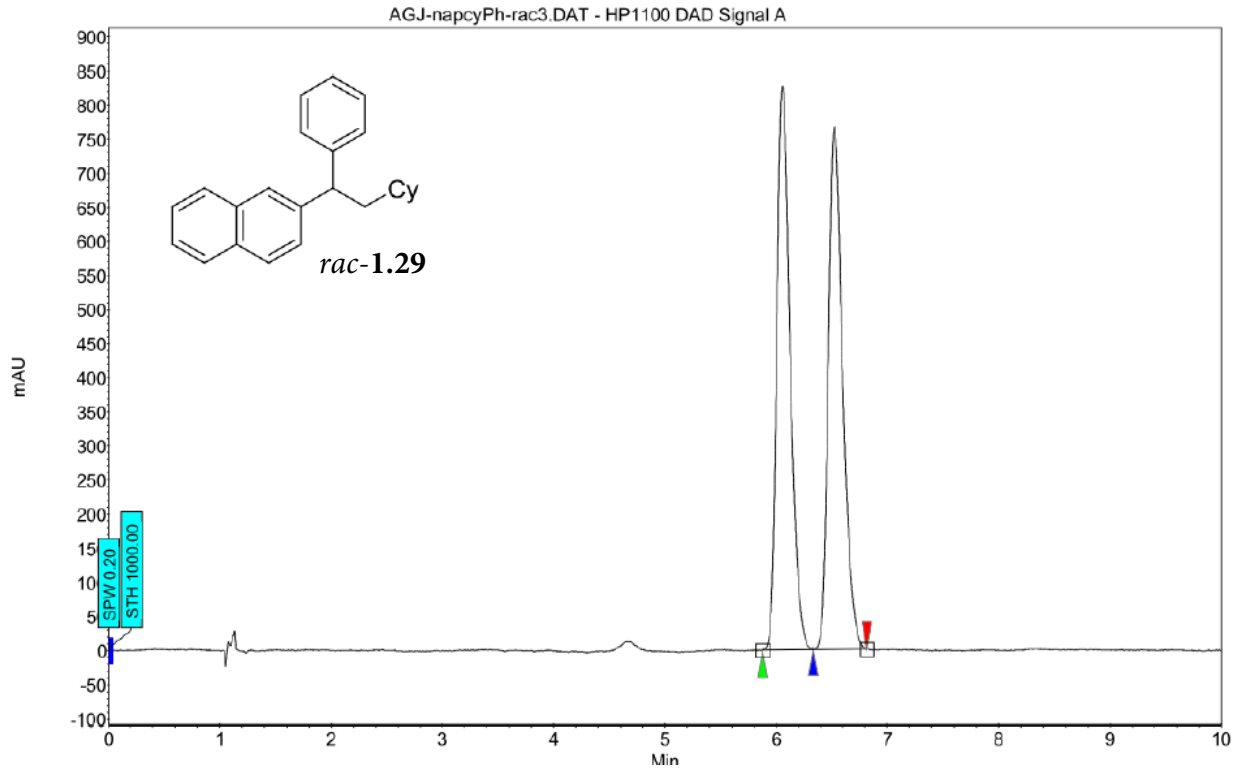
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	6.68	6.98	7.48	0.00	94.98	1972.0	477.3	94.985
2	UNKNOWN	7.98	8.36	8.66	0.00	5.02	86.7	25.2	5.015
Total						100.00	2058.6	502.5	100.000



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	9.76	9.97	10.28	0.00	1.97	38.7	7.7	1.972
2	UNKNOWN	10.34	10.61	11.22	0.00	98.03	1272.5	380.8	98.028
Total						100.00	1311.2	388.5	100.000

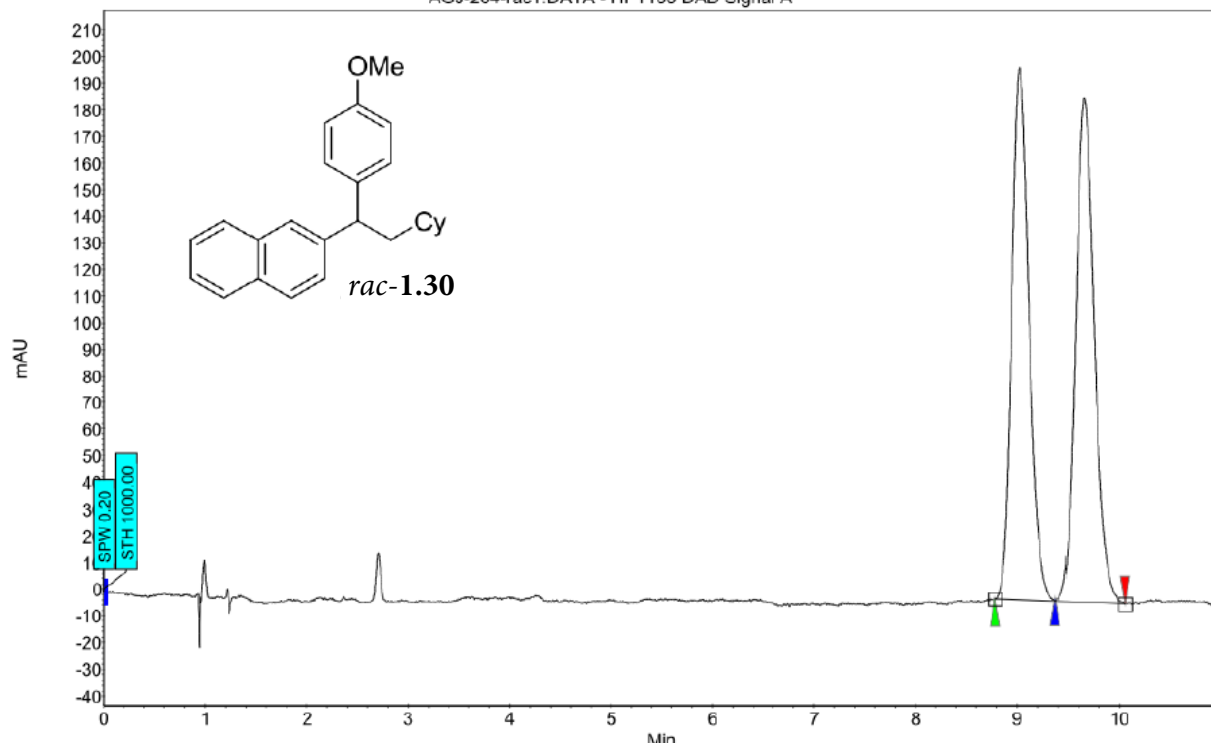


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	6.12	6.32	6.57	0.00	1.49	10.0	1.6	1.489
2	UNKNOWN	7.51	7.84	8.51	0.00	98.51	492.5	107.7	98.511
Total						100.00	502.5	109.3	100.000

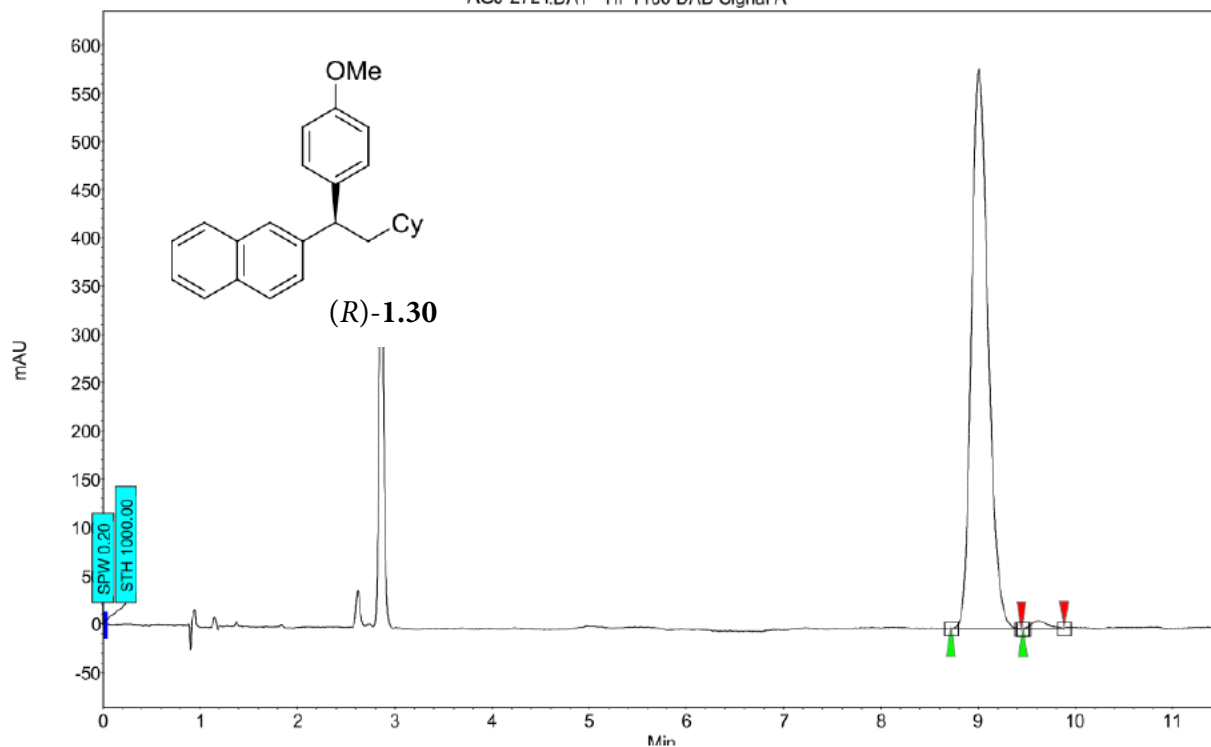


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	6.13	6.31	6.65	0.00	95.60	1711.1	272.1	95.596
2	UNKNOWN	6.69	6.85	7.07	0.00	4.40	85.5	12.5	4.404
Total						100.00	1796.6	284.6	100.000

AGJ-264-rac1.DAT - HP1100 DAD Signal A

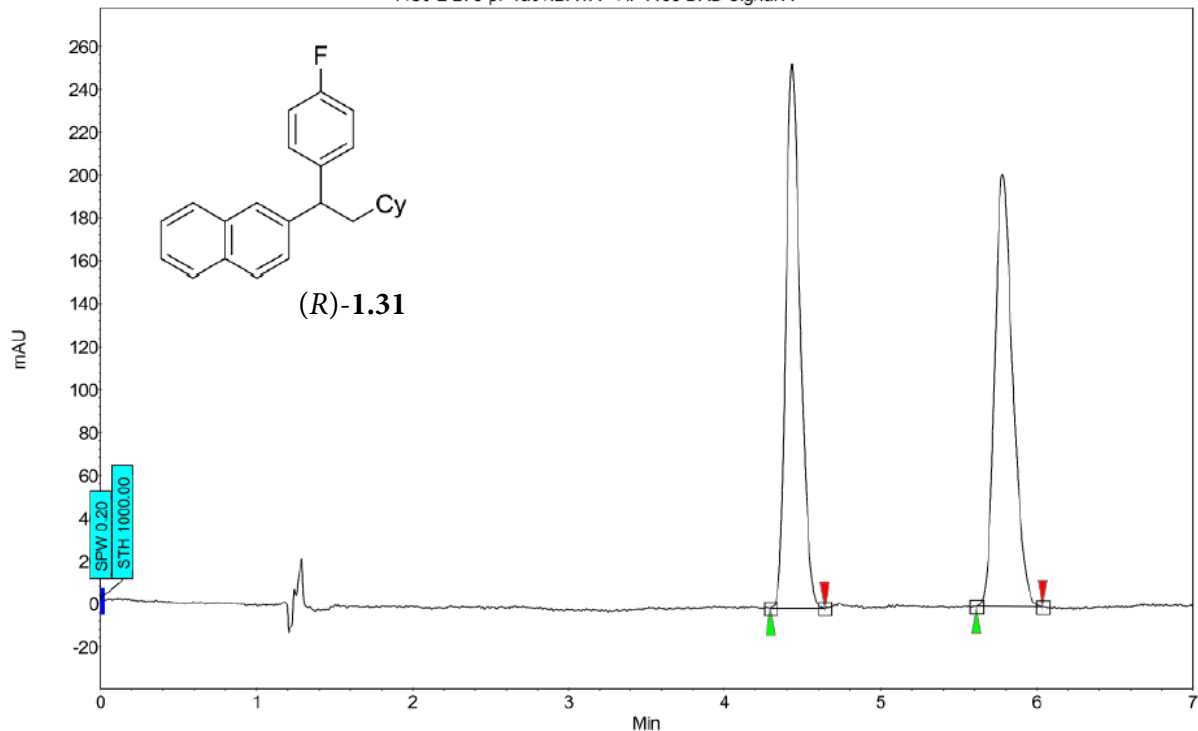


AGJ-2721.DAT - HP1100 DAD Signal A

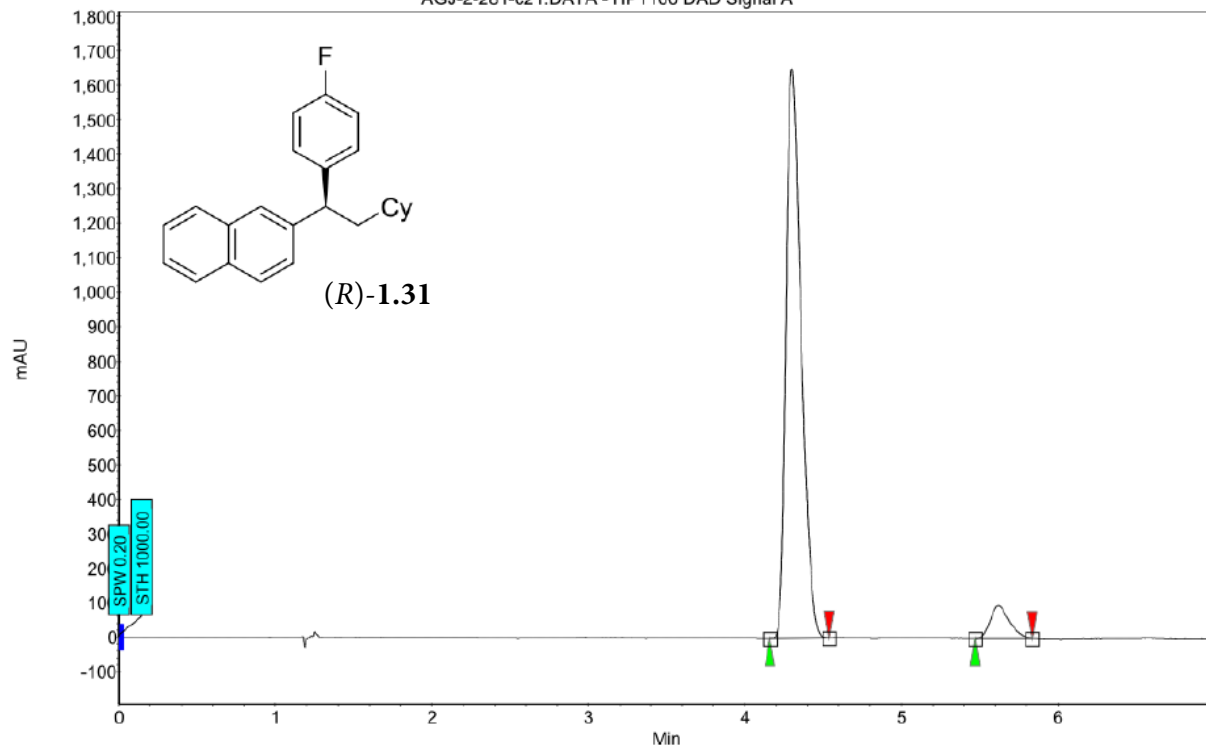


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	8.72	9.01	9.44	0.00	98.68	579.9	115.5	98.681
2	UNKNOWN	9.46	9.63	9.88	0.00	1.32	8.0	1.5	1.319
Total						100.00	587.9	117.0	100.000

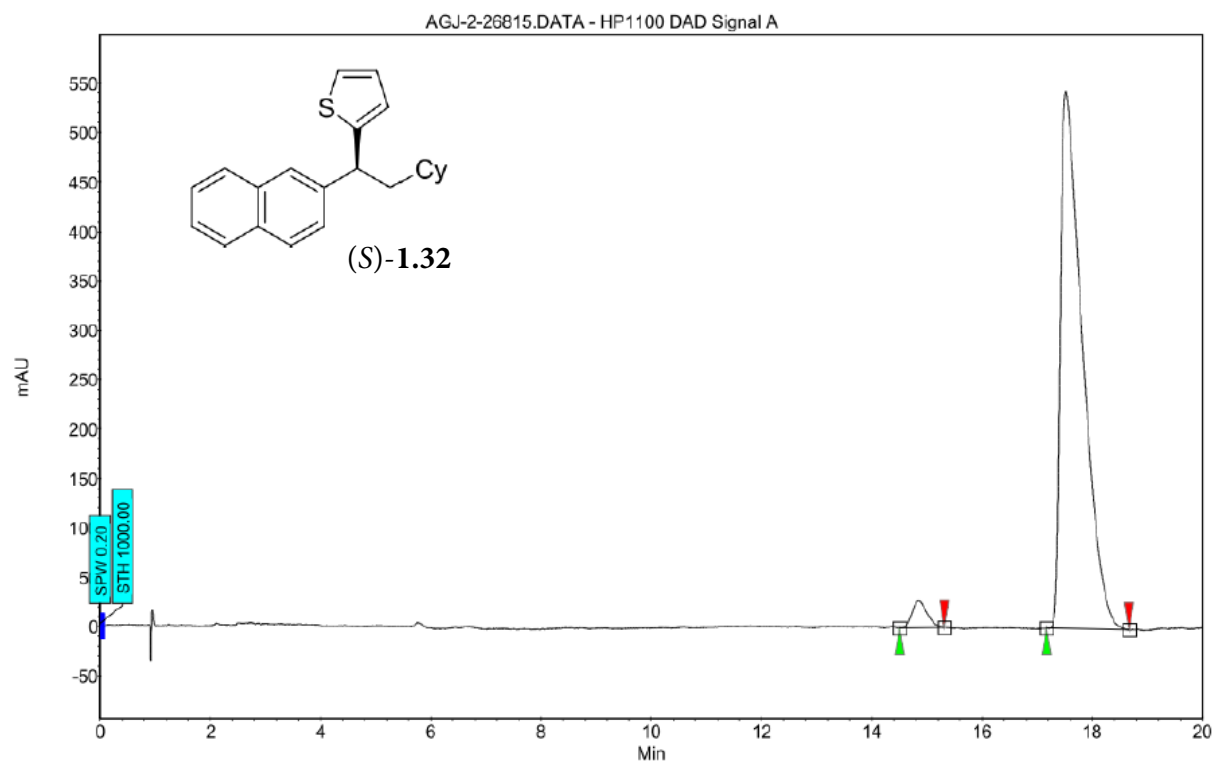
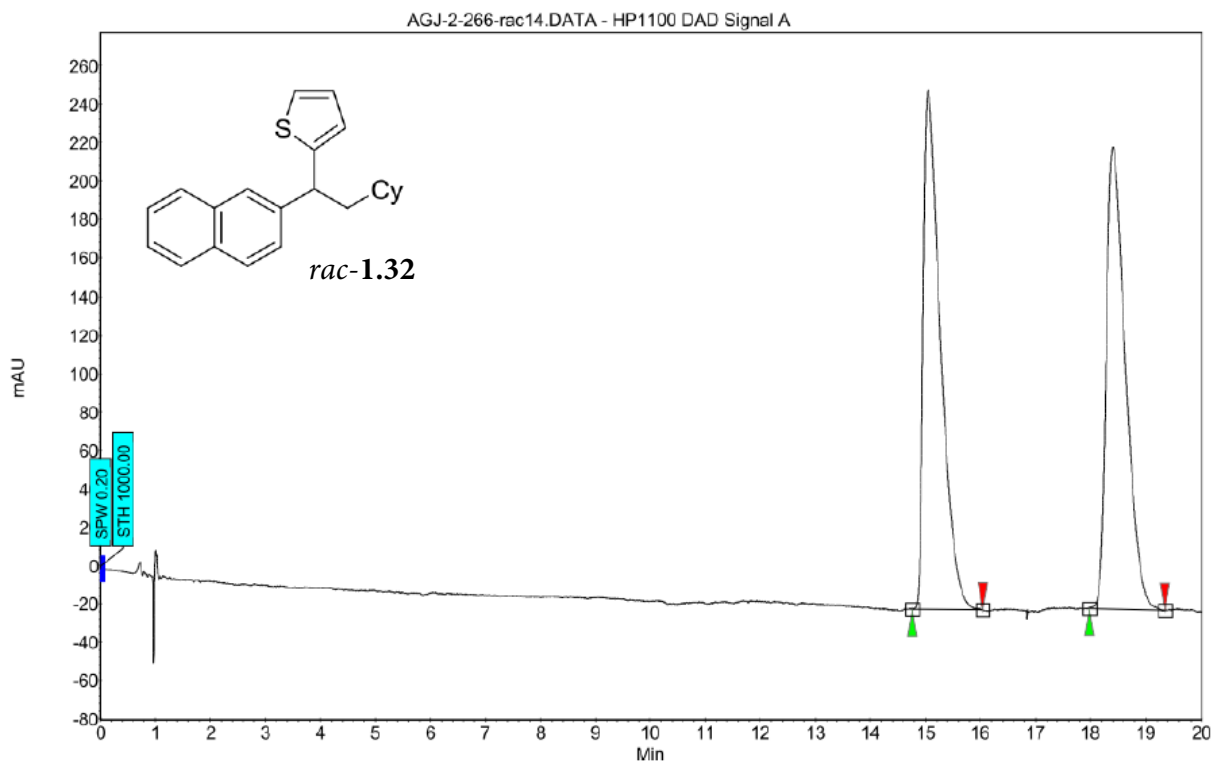
AGJ-2-276-pF-rac1.DATA - HP1100 DAD Signal A



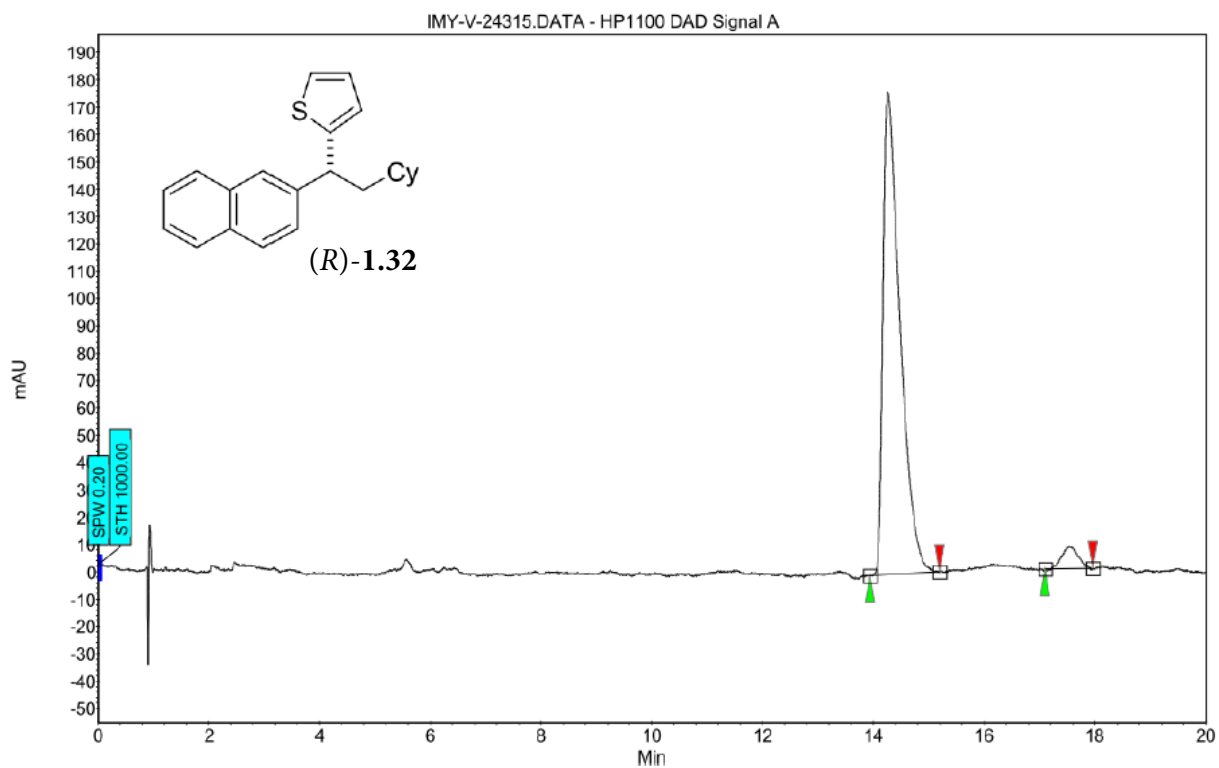
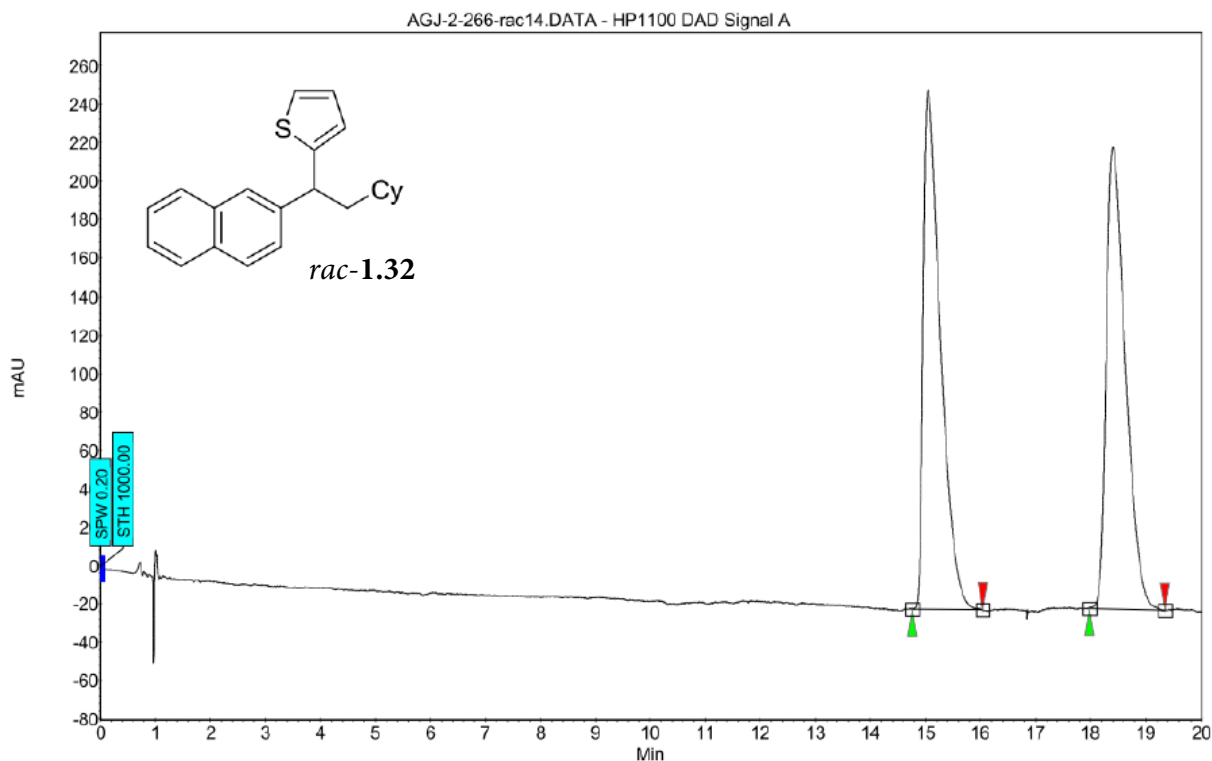
AGJ-2-281-c21.DATA - HP1100 DAD Signal A



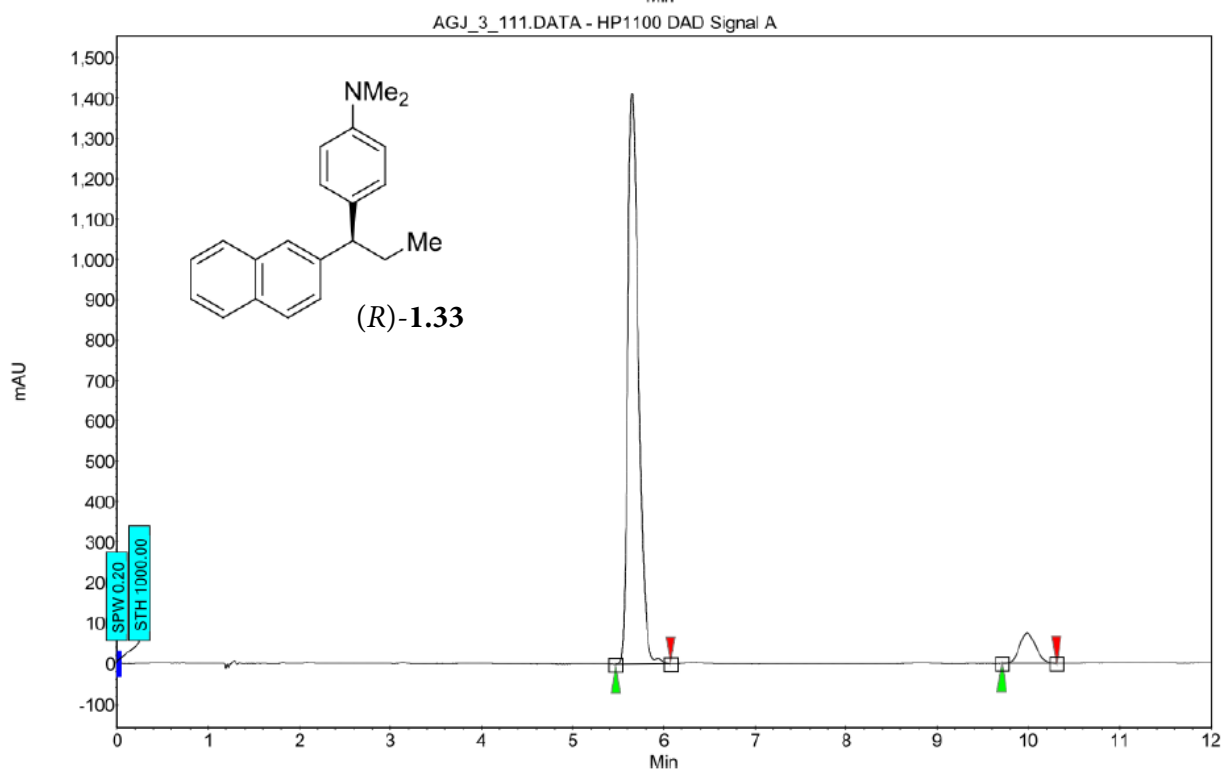
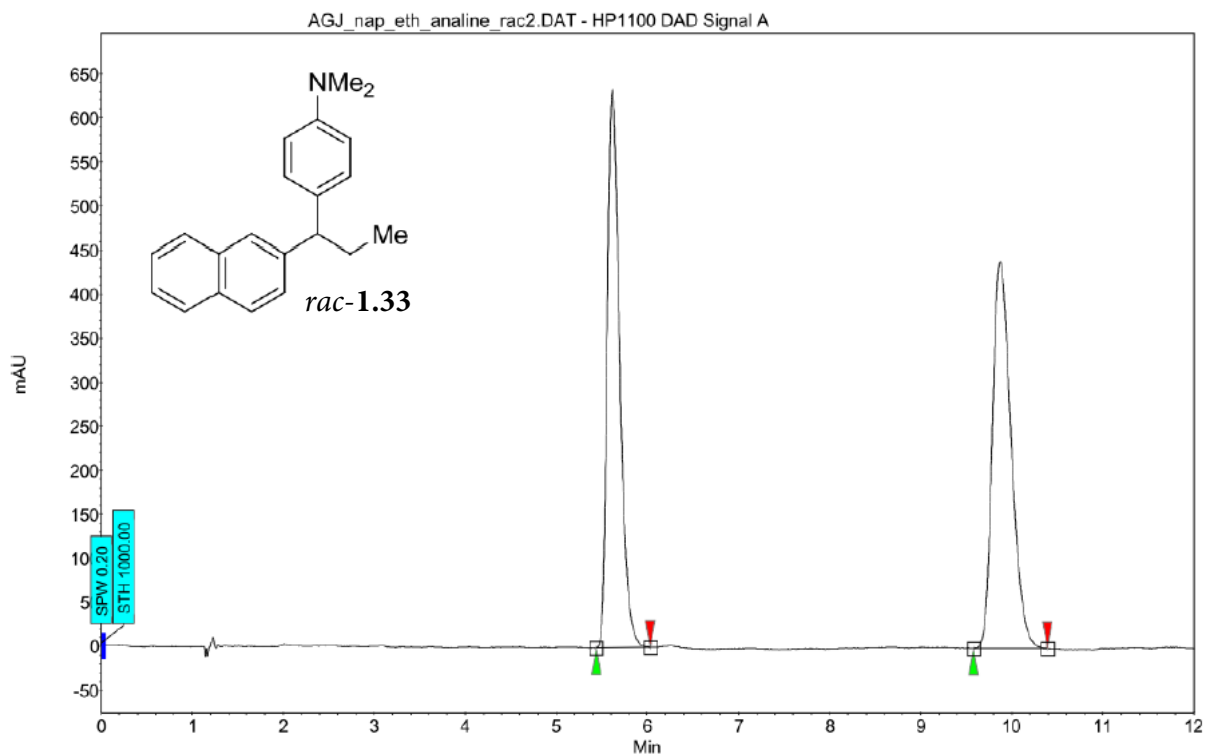
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	4.16	4.30	4.54	0.00	93.26	1651.3	185.9	93.264
2	UNKNOWN	5.47	5.62	5.84	0.00	6.74	94.7	13.4	6.736
Total						100.00	1746.0	199.4	100.000



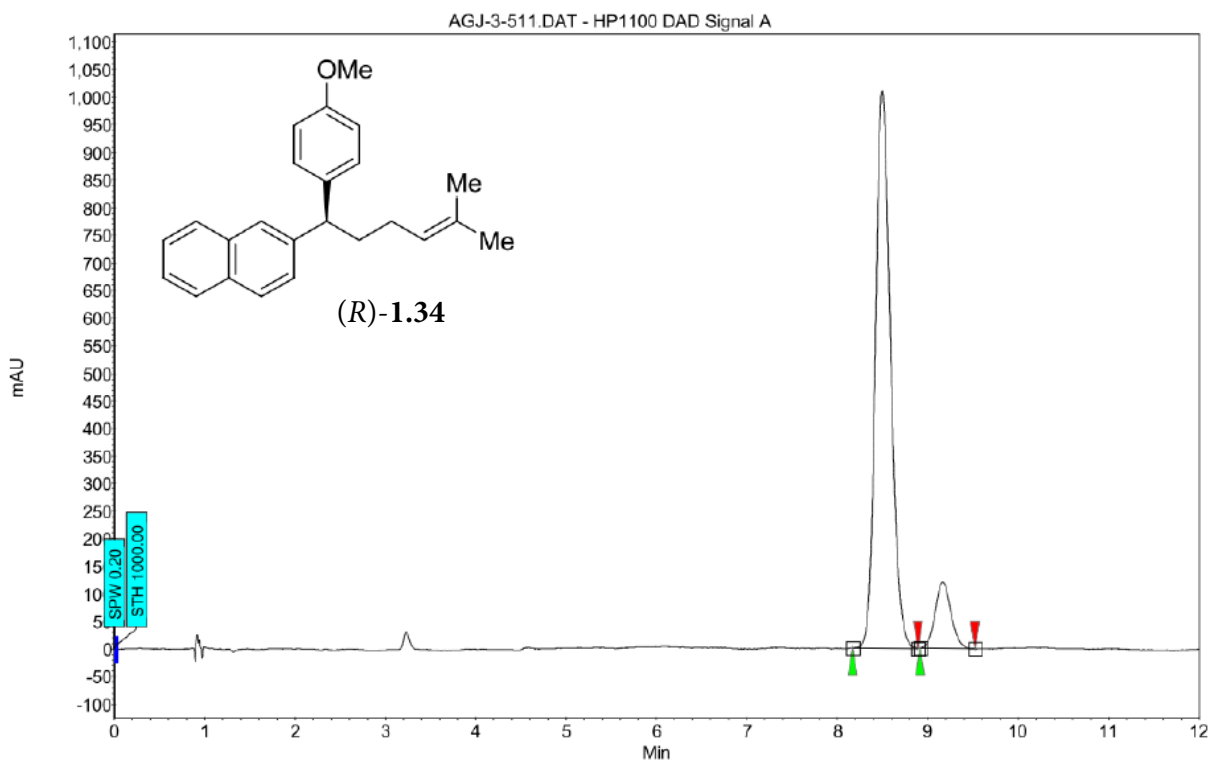
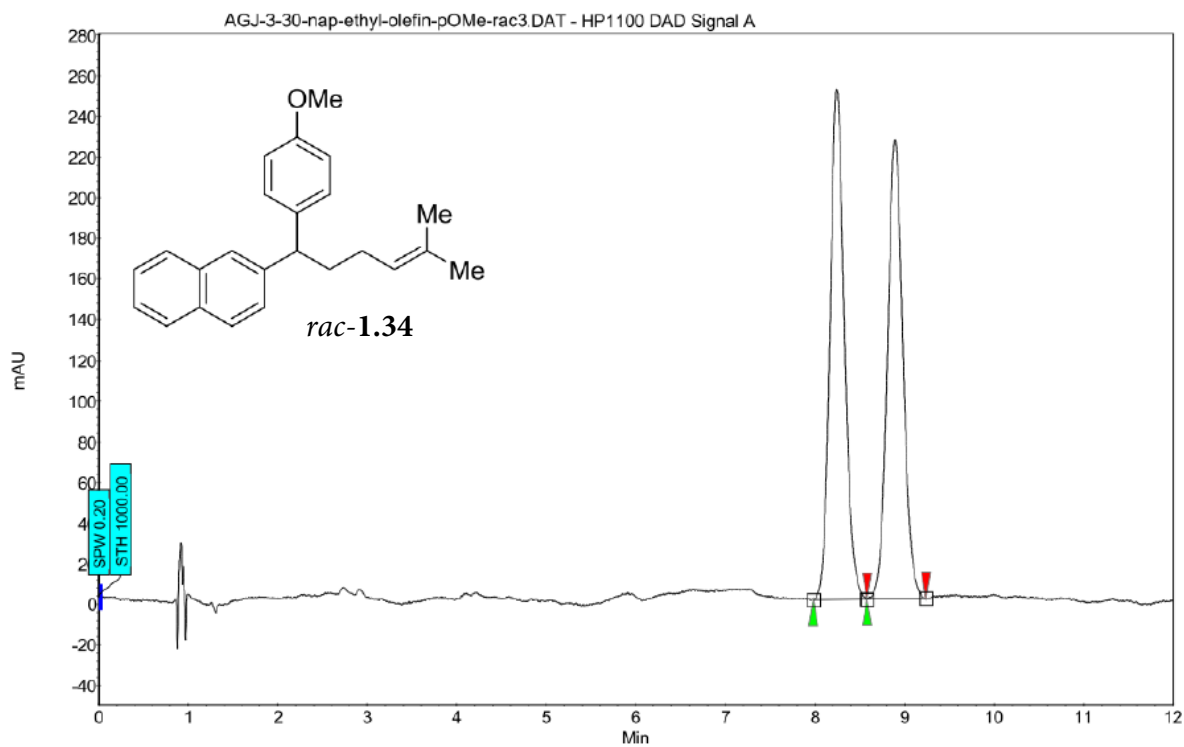
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
2	UNKNOWN	14.50	14.85	15.31	0.00	3.24	26.9	8.4	3.236
1	UNKNOWN	17.17	17.52	18.67	0.00	96.76	543.4	252.1	96.764
Total						100.00	570.3	260.5	100.000



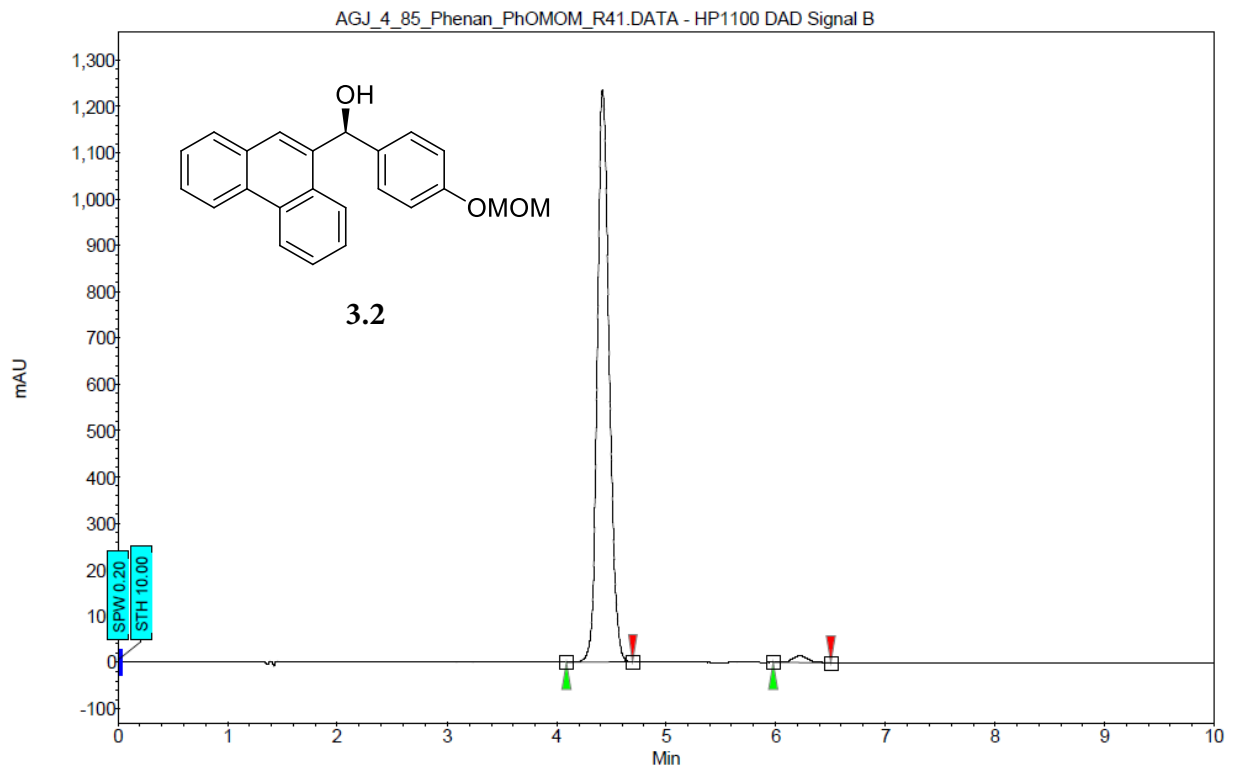
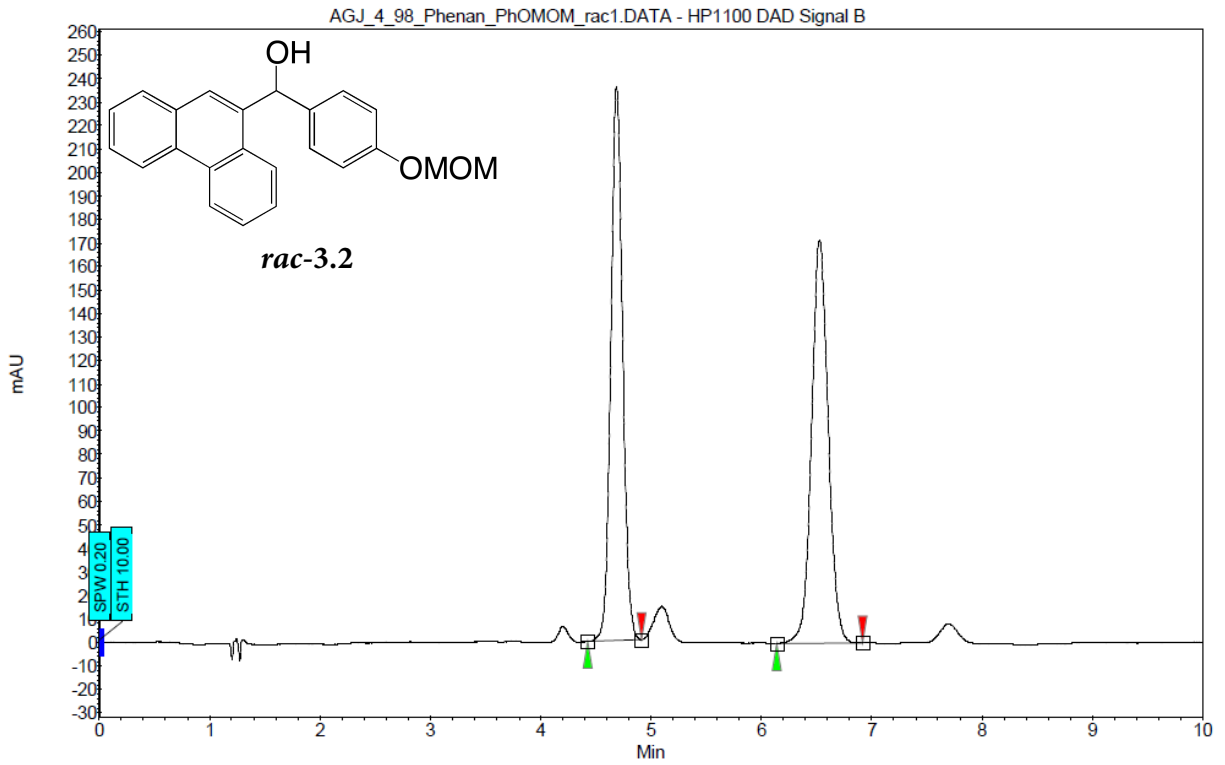
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	13.94	14.26	15.20	0.00	95.79	176.7	62.8	95.788
2	UNKNOWN	17.10	17.53	17.96	0.00	4.21	8.4	2.8	4.212
Total						100.00	185.2	65.6	100.000



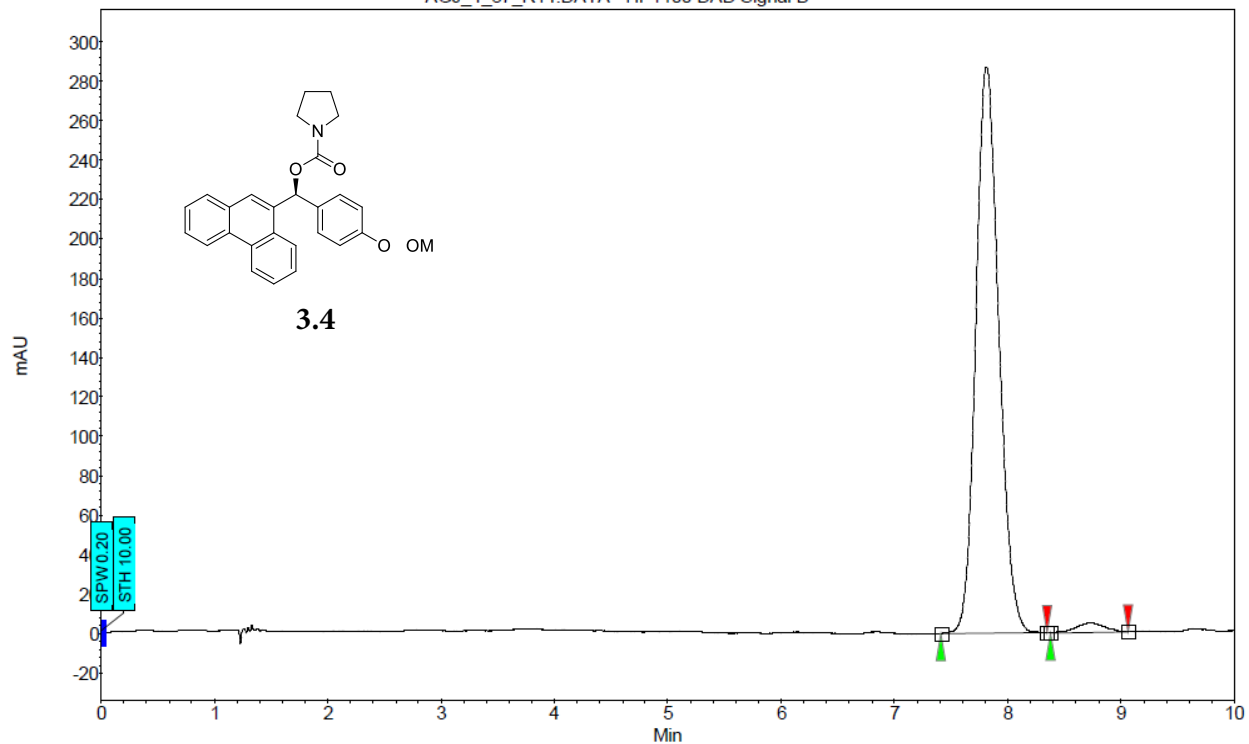
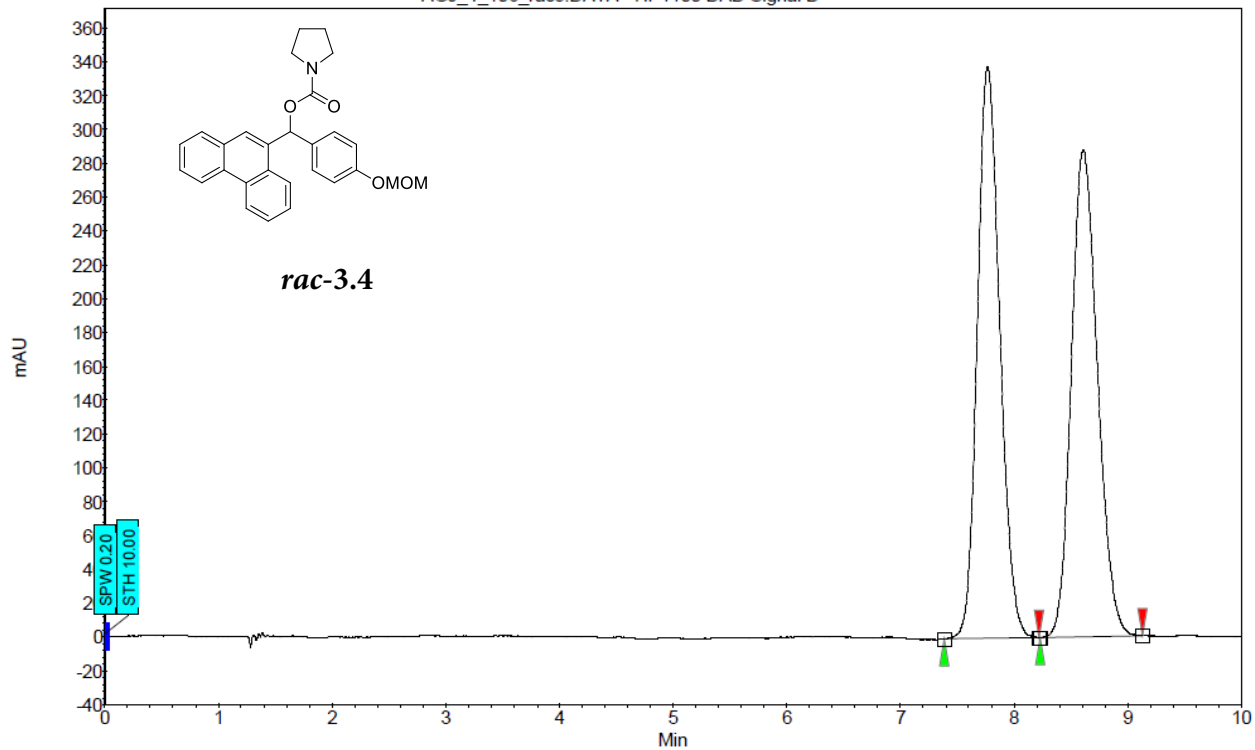
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	5.47	5.65	6.08	0.00	92.72	1414.5	200.0	92.717
2	UNKNOWN	9.71	9.98	10.31	0.00	7.28	75.1	15.7	7.283
Total						100.00	1489.6	215.7	100.000



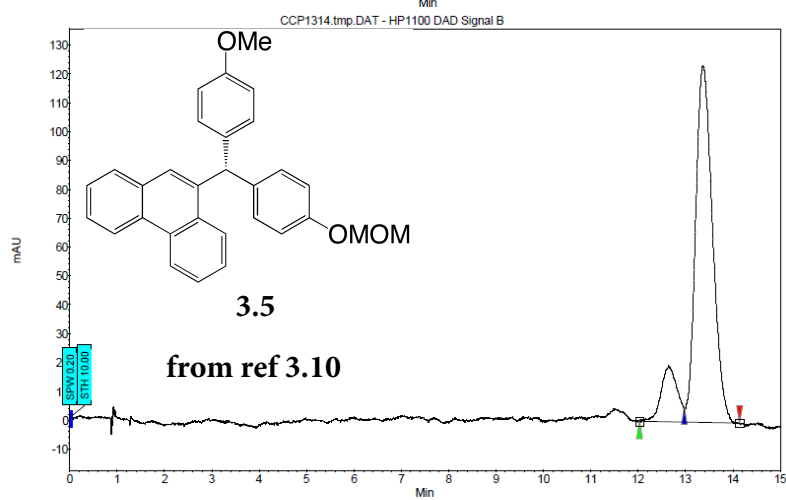
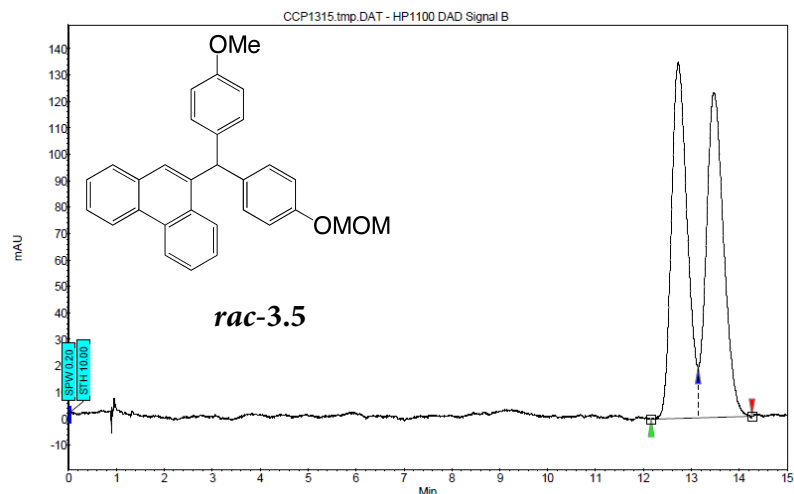
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	8.17	8.50	8.89	0.00	89.04	1009.3	195.4	89.036
2	UNKNOWN	8.91	9.17	9.52	0.00	10.96	119.6	24.1	10.964
Total						100.00	1128.9	219.5	100.000



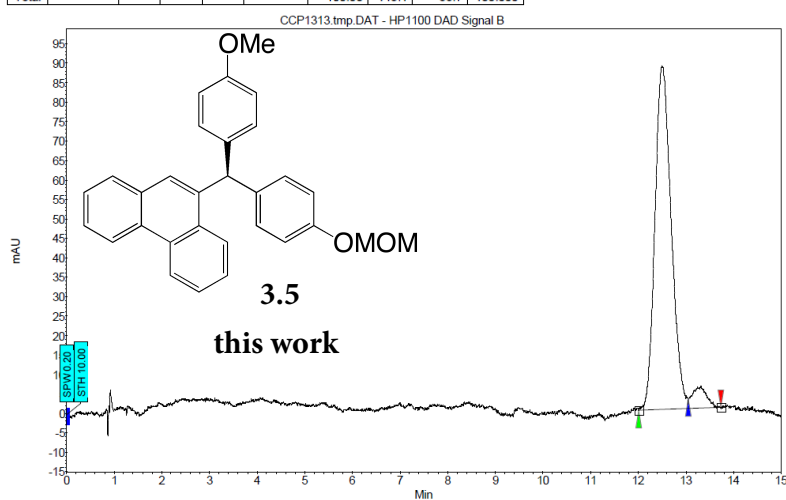
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	4.09	4.42	4.69	0.00	98.41	1236.6	155.9	98.410
2	UNKNOWN	5.98	6.22	6.50	0.00	1.59	14.7	2.5	1.590
Total						100.00	1251.3	158.4	100.000



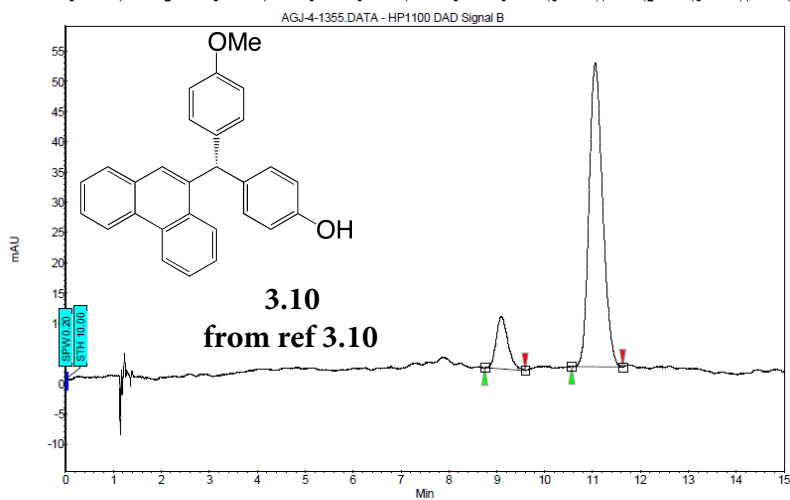
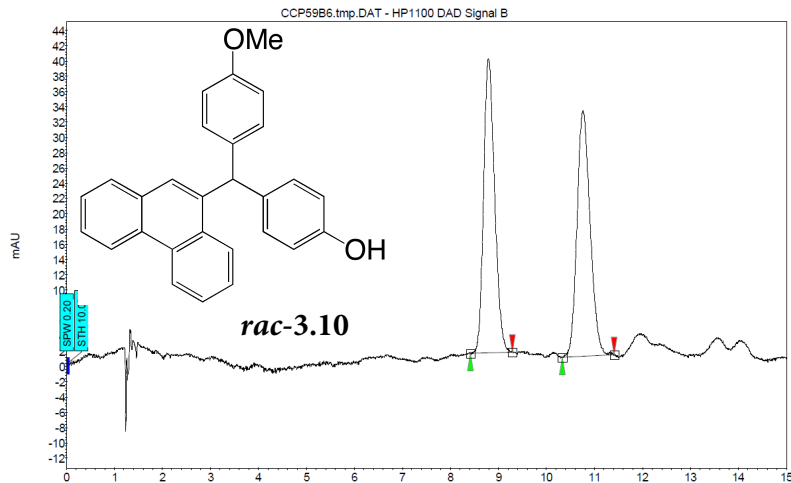
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[μ V]	[μ V.Min]	[%]
1	UNKNOWN	7.41	7.81	8.35	0.00	97.94	286.9	67.5	97.943
2	UNKNOWN	8.37	8.70	9.06	0.00	2.06	4.9	1.4	2.057
Total						100.00	291.7	68.9	100.000



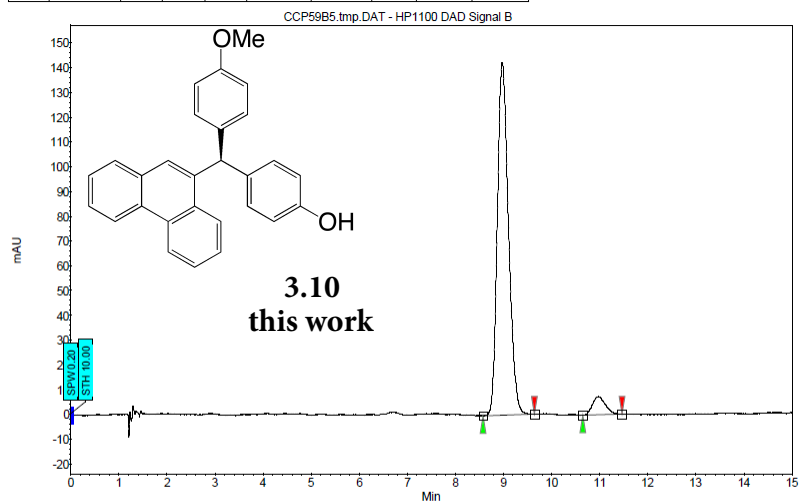
Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	12.03	12.64	12.97	0.00	12.98	19.4	7.6	12.978
2	UNKNOWN	12.97	13.37	14.14	0.00	87.02	123.8	51.0	87.022
Total						100.00	143.1	58.7	100.000



Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	12.01	12.50	13.05	0.00	94.82	88.3	34.9	94.824
2	UNKNOWN	13.05	13.32	13.73	0.00	5.18	5.6	1.9	5.176
Total						100.00	93.9	36.8	100.000



Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	8.75	9.09	9.60	0.00	13.00	8.7	2.5	12.997
2	UNKNOWN	10.57	11.06	11.63	0.00	87.00	50.2	16.5	87.003
Total						100.00	58.9	18.9	100.000



Index	Name	Start [Min]	Time [Min]	End [Min]	RT Offset [Min]	Quantity [% Area]	Height [μV]	Area [μV.Min]	Area [%]
1	UNKNOWN	8.58	8.98	9.65	0.00	94.42	142.5	38.3	94.421
2	UNKNOWN	10.65	10.98	11.47	0.00	5.58	7.4	2.3	5.579
Total						100.00	149.9	40.5	100.000