Title

Development of Visible-Light Photoredox Catalyzed Transformations and Applications in Total Syntheses of Natural Products

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Development of Visible-Light Photoredox Catalyzed Transformations and Applications in Total Syntheses of Natural Products

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Yuriy Slutskyy

Dissertation Committee:
Distinguished Professor Larry E. Overman, Chair
Assistant Professor Sergey Pronin
Professor Scott D. Rychovsky

2018

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Garnsey, M. R.; Slutskyy, Y.; Jamison, C. R.; Zhao, P.; Lee, J.; Rhee, Y. H.; Overman, L. E. *J. Org. Chem.* **2018**, *ASAP*. DOI: 10.1021/acs.joc.7b02458. © 2018 American Chemical Society.
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Tao, D. J.; Muuronen, M.; Slutskyy, Y.; Le, A.; Furche, F.; Overman, L. E. *Chem. Eur. J.* **2016**, *22*, 8786–8790. © 2016 John Wiley and Sons.
Tao, D. J.; Slutskyy, Y.; Muuronen, M.; Le, A.; Kohler, P.; Overman, L. E. *J. Am. Chem. Soc.* **2018**, *ASAP*. DOI: 10.1021/jacs.7b13799. © 2018 American Chemical Society.

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EDUCATION

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PUBLICATIONS

10. "Total Synthesis of (–)-Chromodorolide B By a Computationally-Guided Radical Addition/Cyclization/Fragmentation Cascade." Tao, D. J.; Slutskky, Y.; Muuronen, M.; Le, A.; Kohler, P.; Overman, L. E. *J. Am. Chem. Soc.* **2018**, *ASAP*. DOI: 10.1021/jacs.7b13799.

9. "Short Enantioselective Total Syntheses of Cheloviolenes A and B and Dendrillolide C via Convergent Fragment Coupling Using a Tertiary Carbon Radical." Garnsey, M. R.; Slutskyy, Y.; Jamison, C. R.; Zhao, P.; Lee, J.; Rhee, Y. H.; Overman, L. E. *J. Org. Chem.* **2018**, *ASAP*. DOI: 10.1021/acs.joc.7b02458.

8. "Fragment Coupling and Formation of Quaternary Carbons by Visible-Light Photoredox Catalyzed Reaction of *tert*-Alkyl Hemioxalate Salts and Michael Acceptors." Jamison, C. R.; Slutskyy, Y.; Overman, L. E. *Org. Synth.* **2017**, *94*, 167–183.

7. "Versatile Construction of 6-Substituted *cis*-2,8-Dioxabicyclo[3.3.0]octan-3-ones: Short Enantioselective Total Syntheses of Cheloviolenes A and B and Dendrillolide C." Slutskyy, Y.; Jamison, C. R.; Zhao, P.; Lee, J.; Rhee, Y. H.; Overman, L. E. *J. Am. Chem. Soc.* **2017**, *139*, 7192–7195.

6. "Short Enantioselective Total Syntheses of *trans*-Clerodane Diterpenoids: Convergent Fragment Coupling Using a *trans*-Decalin Tertiary Radical Generated from a Tertiary Alcohol Precursor." Slutskyy, Y.; Jamison, C. R.; Lackner, G. L.; Müller, D. S.; Dieskau, A. P.; Untiedt, N. L.; Overman, L. E. *J. Org. Chem.* **2016**, *81*, 7029–7035.

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4. “Diastereoselective Coupling of Chiral Acetonide Trisubstituted Radicals with Alkenes.” Tao, D. J.; Muuronen, M.; Slutskyy, Y.; Le, A.; Furche, F.; Overman, L. E. *Chem. Eur. J.* **2016**, *22*, 8786–8790.

3. “Total Synthesis of (–)-Chromodorolide B.” Tao, D. J.; Slutskyy, Y.; Overman, L. E. *J. Am. Chem. Soc.* **2016**, *138*, 2186–2189.

2. “Oxalates as Activating Groups for Alcohols in Visible Light Photoredox Catalysis: Formation of Quaternary Centers by Redox-Neutral Fragment Coupling.” Nawrat, C. C.; Jamison, C. R.; Slutskyy, Y.; MacMillan, D. W. C.; Overman. L. E. *J. Am. Chem. Soc.* **2015**, *137*, 11270–11273.

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PRESENTATIONS

7. Slutskyy, Y.; Overman, L. E. “Synthesis of Natural Products via Late-Stage Fragment Coupling Strategy Utilizing Carbon Radicals.” Presented at the 25th International Symposium: Synthesis in Organic Chemistry, Oxford, United Kingdom, July 2017.

6. Slutskyy, Y.; Jamison, C. R.; Nawrat, C. C.; MacMillan, D. W. C.; Overman, L. E. “Photoredox Catalyzed Formation of Quaternary Centers via 3° Oxalates.” Presented at the Royal Society ISACS19: Challenges in Organic Chemistry Symposium, Irvine, CA, March 2016.

5. Slutskyy, Y. “Formation of Quaternary Carbon Stereocenters via Redox-Neutral Fragment Coupling.” Presented at the UC Irvine Chemistry Department Graduate Student and Postdoctoral Scholar Symposium, Irvine, CA, February 2016.

4. Slutskyy, Y.; Jamison, C. R.; Nawrat, C. C.; MacMillan, D. W. C.; Overman, L. E. “Photoredox Catalyzed Formation of Quaternary Centers via 3° Oxalates.” Presented at the 2015 National Organic Symposium, College Park, MD, July 2015.

3. Slutskyy, Y.; Lucero, C.G. “Syntheses of (–)-Tatarinoid A and (±)-Tatarinoid B, Efforts Towards the Total Synthesis of (–)-Tatarinoid B.” Presented at the CIMERA Event, Sacramento, CA, February 2013.

2. Slutskyy, Y.; Lucero, C.G. “Syntheses of (–)-Tatarinoid A, (±)-Tatarinoid B, and (–)-Tatarinoid C.” Presented at the 25th Annual CSU Biotechnology Symposium, Anaheim, CA, January 2013.

1. Slutskyy, Y.; Lucero, C. G. “Total Synthesis of (±)-Tatarinoid B.” Presented at the 244th American Chemical Society National Meeting, Philadelphia, PA, August 2012.

GRANTS AND AWARDS

7. 2017 Joan Rowland Award – UC Irvine. (May 2017)

6. Ruth L. Kirschstein National Research Service Award (NRSA) Individual Predoctoral Fellowship, "Fragment-Coupling at Tertiary Carbons: Macrocarpal and Eucalyptin A Derivatives." – UC Irvine. (June 2015 to March 2018)

5. 2014 National Science Foundation Graduate Research Foundation Fellowship Program Honorable Mention – UC Irvine. (April 2014)

4. 2013 F. S. Rowland Fund Scholar – UC Irvine. (July 2013 to June 2014)

3. 2013 Outstanding Undergraduate Chemistry Scholar Award – CSU Sacramento. (May 2013)

2. 2013 Doris A. Howell Foundation – CSUPERB Research Scholar Award, "Total Synthesis of Jomthonic Acid A." – CSU Sacramento. (December 2012 to May 2013)

1. CSU Program for Education and Research in Biotechnology (Presidents' Commission Scholars Grant Program), "Total Synthesis of (–)-Tatarinoid B." – CSU Sacramento. (June 2012 to August 2012)

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May 2016 to March 2018	**University of California, Irvine** (Irvine, CA) *Larry E. Overman Group Coordinator*

ABSTRACT OF THE DISSERTATION

Development of Visible-Light Photoredox Catalyzed Transformations and Applications in Total Syntheses of Natural Products

By

Yuriy Slutskyy

Doctor of Philosophy in Chemistry

University of California, Irvine, 2018

Professor Larry E. Overman, Chair

In Chapter 1, alkyl oxalates are described as new bench-stable alcohol activating groups for radical generation under visible light photoredox conditions. Using these precursors, the first net redox-neutral coupling of tertiary and secondary alcohols with electron-deficient alkenes is achieved.

In Chapter 2, visible light photoredox-catalyzed fragmentation of methyl *N*-phthalimidoyl oxalates is described for the direct construction of a 1,4-dicarbonyl structural motif by a conjugate addition of the methoxycarbonyl radical to Michael acceptors. The regioselectivity of the addition of this alkoxyacyl radical species to electron-deficient olefins is found to be influenced by the electronic nature of the acceptor, behavior similar to that exhibited by nucleophilic alkyl radicals.

In Chapter 3, the evolution of a convergent fragment-coupling strategy for the enantioselective total synthesis of *trans*-clerodane diterpenoids is described. The key bond construction is accomplished by 1,6-addition of a *trans*-decalin tertiary radical with 4-vinylfuran-2-one. The tertiary radical is optimally generated from the hemioxalate salt of

the corresponding tertiary alcohol upon activation by visible light and an Ir(III) photoredox catalyst. The synthetic strategy described in this chapter allows a number of *trans*-clerodane diterpenoids to be synthesized in enantioselective fashion by synthetic sequences of 10 steps or less.

In Chapter 4, the development of a convergent fragment-coupling strategy for the enantioselective total syntheses of a group of rearranged spongian diterpenoids that harbor the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one unit is described. The key bond disconnection relies on a late-stage fragment coupling between a tertiary carbon radical and an electron-deficient alkene to unite two ring systems and form two new stereocenters, one of which is quaternary, in a stereoselective and efficient manner. This strategy is applied towards 14–15 step syntheses of three diterpenoids, cheloviolenes A and B and dendrillolide C.

In Chapter 5, the first total synthesis of a chromodorolide marine diterpenoid is described. The core of the natural product is constructed by a bimolecular radical addition/cyclization/fragmentation cascade that unites two complex fragments and forms two C–C bonds and four contiguous stereogenic centers of (–)-chromodorolide B in a single step. Computational studies guided the development of this transformation and provide insight into the origin of the observed stereoselectivity.

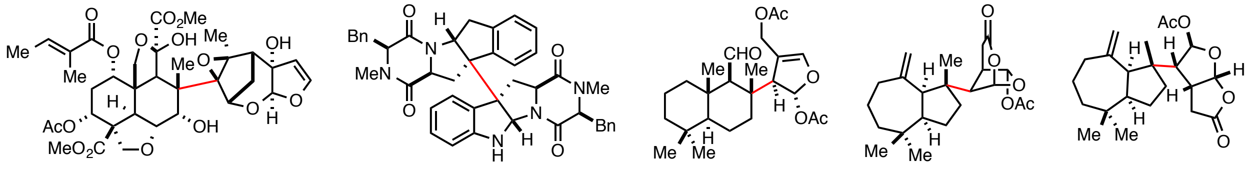
Chapter 1: Fragment Coupling and Formation of Quaternary Carbons by Visible-Light Photoredox Catalyzed Reaction of *tert*-Alkyl Hemioxalate Salts and Michael Acceptors

1.1 Introduction

Synthetic strategies that rely on independent syntheses of fragments, followed by their late-stage union are key to efficient preparation of complex molecules. The major drawback of this convergent approach is the small pool of privileged reactions that are reliable, chemoselective, and high-yielding. Some of the most widely used methods having these properties are Diels-Alder reactions, transition metal-catalyzed cross couplings, Nozaki–Hiayama–Kishi couplings, and olefin metathesis.[1]

The union of complex fragments is particularly challenging when the coupling results in the formation of sp^3–sp^3 σ bonds and two stereocenters, especially when the two stereocenters reside in different rings. The challenge is further enhanced when one of the newly formed stereocenters is quaternary.[2] Bonds highlighted in red, connecting complex fragments found in azadirachtin (**1.1**),[3] ditryptophenaline (**1.2**),[4] tyrinnal (**1.3**),[5] aplyviolene (**1.4**),[6] and dendrillolide A (**1.5**),[7] illustrate this synthetic difficulty (Figure 1.1). The challenges associated with the synthesis of azadirachtin are legendary, featuring a common synthetic tactic that utilized an intramolecular sigmatropic rearrangement[8] to achieve the formation of the key bond.

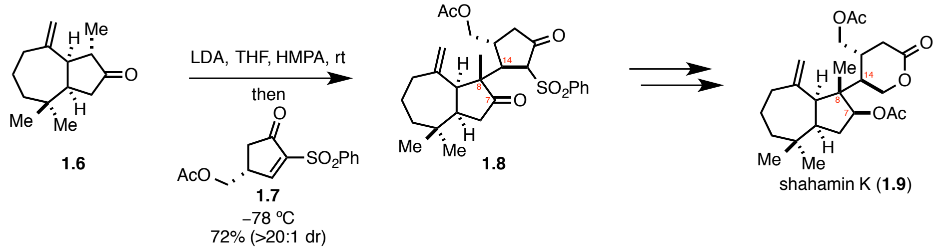
Figure 1.1. Natural products with ring systems joined via stereogenic carbons.



azadirachtin (**1.1**) ditryptophenaline (**1.2**) tyrinnal (**1.3**) aplyviolene (**1.4**) dendrillolide A (**1.5**)

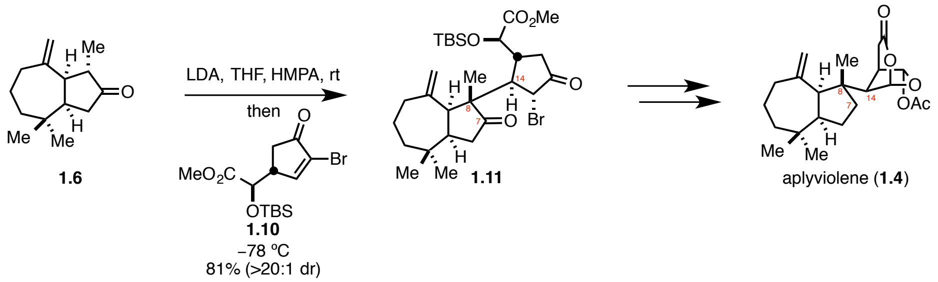
A much less common approach for the formation of sterically congested bonds is the use of bimolecular couplings of two complex fragments to form two new stereocenters, one of which is quaternary.[9,10] One of the early examples is Overman's total synthesis of shahamin K (**1.9**).[10] The construction of the C8-C14 bond of diterpenoid **1.9** featured a Michael addition of the thermodynamic enolate of hydroazulenone **1.6** to a doubly activated enantiopure cyclopentenone **1.7** (Figure 1.2). The desired coupling product **1.8** was obtained as a single diastereomer at the two newly formed stereocenters in 72% yield.

Figure 1.2. Key fragment coupling in the total synthesis of shahamin K (**1.9**).



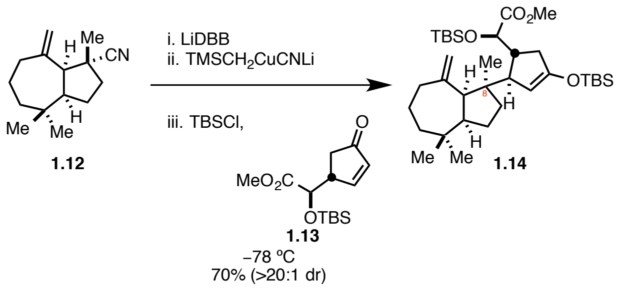
The first-generation synthesis of aplyviolene (**1.4**) utilized the same key bond disconnection as was used in the synthesis of shahamin K (**1.9**).[11] In this case, the same thermodynamic enolate underwent diastereoselective coupling with bromocyclopentenone **1.10** to provide adduct **1.11** in 81% yield. One noteworthy difference between the two diterpenoids **1.4** and **1.9** is the oxygen functionality at C-7. In the synthesis of shahamin K (**1.9**), the ketone functionality is transformed into the acetoxy group found in the natural product. Since aplyviolene (**1.4**) lacks oxygenation at C-7, the ketone functionality needed to be removed over three steps.[11] This undesirable multi-step redox manipulation lowered the overall efficiency of the synthetic sequence and highlighted the importance of coupling the hydroazulene unit in the correct oxidation state.

Figure 1.3. Key fragment coupling in the first-generation synthesis of aplyviolene.



The initial approach for the formation of C8-C14 bond proposed by the Overman group was an intramolecular coupling between an unstabilized tertiary anion and an electron-deficient olefin, such as **1.13**. To investigate the possibility of the desired bond construction in this manner, a method to access tertiary organocuprates by reductive lithiation of tertiary nitrile precursors followed by transmetalation to copper was developed.[12] When applied to the synthesis of aplyviolene (**1.4**), the tertiary organocuprate, generated from nitrile **1.12**, underwent diastereoselective conjugate addition to cyclopentenone **1.13** to deliver **1.14** in 70% yield (Equation 1.1). Unexpectedly, the stereochemistry at C-8 was opposite to the one observed in the couplings of the enolate derived from **1.6** to Michael acceptors **1.7** and **1.10**. The result suggested that the intermediate organocuprate underwent highly stereoselective addition to enone **1.13** from the less sterically favorable concave face of the bicycle. Computational studies by the Houk group suggested that the intermediate organocuprate reacted preferentially from the more sterically hindered face in order to minimize torsional strain effects within the hydroazulene framework.[12]

Equation 1.1

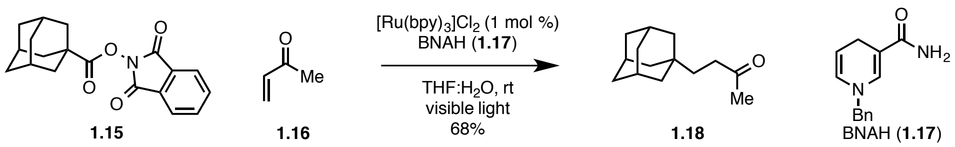


An alternative approach for the diastereoselective formation of the quaternary carbon stereocenter at C-8 was envisaged by intermolecular addition of a nucleophilic tertiary carbon radical to an electron-deficient olefin.[13] Formation of sterically congested sp^3–sp^3 σ bonds by such a method is attractive for several reasons: the early transition state with a long forming bond (~2.5 Å) reduces the enthalpic penalty of bringing two bulky fragments together;[14] the high rates of addition[15] and stereoselection[15a,16] realized in additions of tertiary radicals to Michael acceptors often leads to efficient fragment-couplings with reliable stereochemical outcomes. Despite the aforementioned appealing features of the Giese reaction of tertiary carbon radicals, which were known since the 1980s,[15a,17] bimolecular radical reactions have not been used to unite complex fragments because of the large excesses (commonly 3–10-fold) of one of the coupling components often required.

The side reactions, leading to low yields of coupled products, associated with bimolecular radical reactions of highly functionalized partners are often a consequence of the harsh reaction conditions required for radical generation (e.g., high temperatures, stoichiometric tin reagent, or high-energy light). As a result, the selection of the radical precursor for the formation of the requisite tertiary radical was nontrivial. Commonly used tertiary alkyl halide precursors,[18] are difficult to prepare, purify, and handle making them undesirable for the use in complex molecule synthesis. Another large class of radical precursors are derived from more stable carboxylic acids. The most commonly used carboxylic acid-based thiohydroxamate esters,[19] Barton esters, were initially investigated to achieve the desired fragment coupling. However, upon preparation of a series of tertiary Barton esters, the Overman group deemed them unfit as candidates for the desired union of the hydroazulene and cyclopentenone fragments due to decomposition of these radical precursors upon exposure to light.

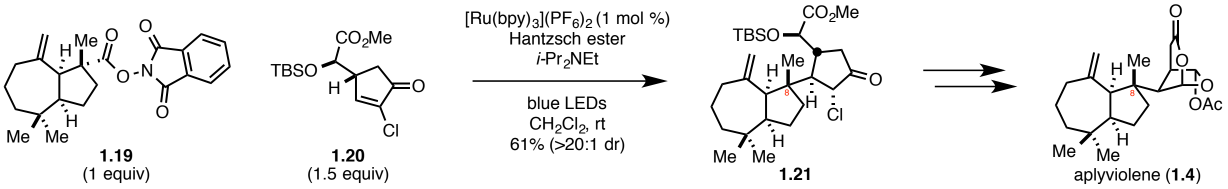
The recent advent of visible-light photoredox catalysis to generate carbon radicals under mild conditions,[20] a method that is compatible with most polar functional groups, led to a resurgence of radical-based approaches for convergent construction of complex molecules.[21] One of the earliest examples of generating nucleophilic carbon-centered radicals under photoredox reaction conditions is the method developed by Okada in 1991, that relies on the use of crystalline *N*-acyloxyphthalimides that are prepared directly from corresponding carboxylic acids.[22] In his seminal work, Okada suggested that single-electron transfer (SET) from the reduced photocatalyst, $[Ru(bpy)_3]Cl_2$, to *N*-acyloxyphthalimide substrate such as **1.15** induces fragmentation of the homolytically weak N–O bond, followed by decarboxylation to release the key nucleophilic carbon-centered radical intermediate (Equation 1.2). Upon addition of the radical to conjugate acceptor, methyl vinyl ketone (**1.16**), the resulting α-acyl radical is terminated via a hydrogen atom transfer (HAT) from 1-benzyl-1,4-dihydronicotinamide (BNAH, **1.17**) to form the desired product **1.18**. Despite the fact that the only example of a tertiary *N*-acyloxyphthalimide in Okada's initial report was derived from the 1-adamantanecarboxylic acid, the crystallinity of these radical precursors and mild conditions utilized for the transformation suggested that the use of this methodology may be applicable for the proposed complex fragment coupling in the second-generation synthesis of aplyviolene (**1.4**).

Equation 1.2



Utilizing Okada's method for generation and coupling of tertiary radicals, hydroazulene-containing *N*-acyloxyphthalimide **1.19** underwent reductive fragmentation, under slightly modified reaction conditions,[23] to release a nucleophilic radical that was intercepted by an enantiopure chlorocyclopentenone **1.20** to provide the desired product **1.21** as a single diastereomer at both newly formed stereocenters in 61% yield (Figure 1.4).[13] Single-crystal X-ray diffraction analysis indicated that the coupling proceeded in high stereoselectivity from the desired convex face of the hydroazulene bicyclic unit to provide the correct stereochemistry at C-8, found in aplyviolene (**1.4**). It is notable that only a slight excess of the cyclopentenone coupling partner **1.20** (0.5 equiv) was required to realize the desired transformation, serving as a further testament to the robustness of Okada's redox-active *N*-acyloxyphthalimides in the complex molecule synthesis setting and the mildness of the reaction conditions enabled by visible-light photoredox catalysis.

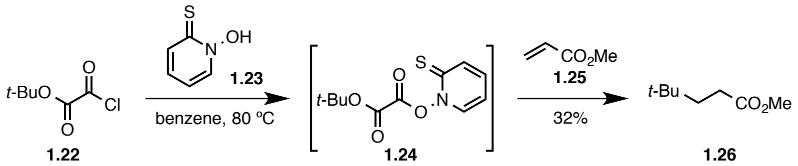
Figure 1.4. Radical fragment coupling in the second-generation synthesis of aplyviolene.



The success of the complex fragment coupling during the second-generation synthesis of aplyviolene (**1.4**), achieved via a conjugate addition of a nucleophilic tertiary radical to an electron-deficient olefin, indicated that such an approach may be useful in other total synthesis settings. Nonetheless, the major drawback of carboxylic acid-based radical precursors that hinders their general use in total synthesis is the requirement for the incorporation of the carbon-carbon bond in the starting material that is cleaved during the decarboxylation event. Thus, a quaternary carbon must be formed in starting material in order to construct the desired quaternary carbon in the product. This limitation can often lead to cumbersome late-stage manipulations of hindered tertiary functional groups, decreasing the efficiency of the overall synthetic sequence. As a result, the Overman group hypothesized that utilizing a radical precursor derived from tertiary alcohols would be advantageous in a complex synthesis setting because of their relative ease of preparation, i.e. additions of carbon nucleophiles to carbonyls, epoxide ring-openings, and selective C-H oxidation methodologies.

The most widely used alcohol-based precursors of carbon radicals are xanthate esters.[24] The scope of the transformation has been largely limited to deoxygenations of secondary alcohols, as tertiary variants tend to undergo rapid elimination. As an alternative, Barton reported generation of nucleophilic carbon radicals from thiohydroxamate oxalates (Barton oxalates), derived from corresponding alcohols (Figure 1.5).[25] Upon exposure to heat or high-energy light, precursors such as **1.24** undergo homolysis of the N–O bond. In contrast to Okada's *N*-acyloxyphthalimides, fragmentation is followed by two stepwise decarboxylation events to release a carbon radical. The loss of an additional molecule of CO_2 activates the C–O bond, allowing the generation of nucleophilic radicals from alcohols.

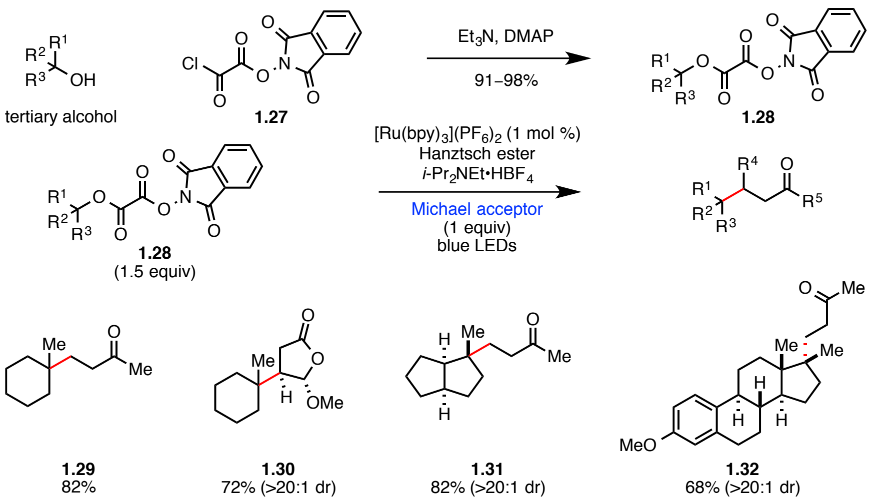
Figure 1.5. Generation of tertiary radicals from a thiohydroxamate oxalate.



Barton described the trapping of several radicals, generated from thiohydroxamate oxalates, with electron-deficient olefins. However, the yields of the desired products such as **1.26** were low. One possible explanation for the low efficiency is the high sensitivity of these radical precursors. Barton oxalates must be prepared from corresponding chlorooxoacetates such as **1.22** and coupled *in situ* without isolation. The inability to purify and characterize structurally complex activated alcohols in multistep total synthesis applications is the likely reason that the Barton oxalate method has not been widely adopted. The instability of thiohydroxamate oxalates stands in stark contrast to Okada's *N*-acyloxyphthalimides which are generally stable to aqueous workup, chromatography, and ambient light. Additionally, these redox-active esters are often crystalline solids, allowing for isolation of complex intermediates in pure form, easy handling, and prolonged storage at room temperature.

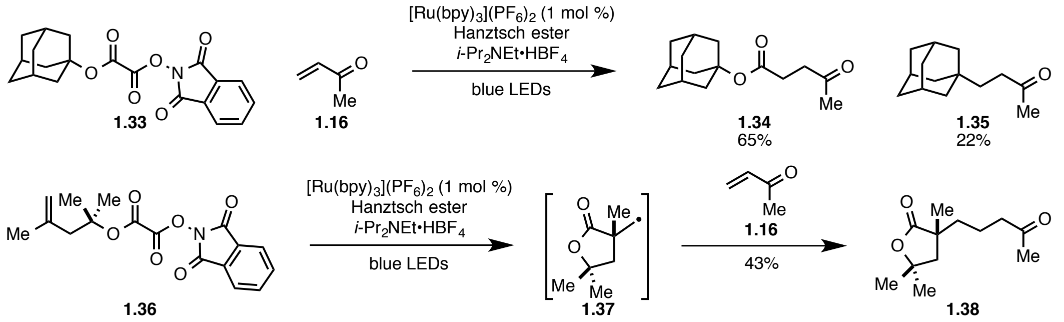
The Overman group proposed that the desirable properties of *N*-acyloxyphthalimide esters may be conferred to a previously unreported alkyl *N*-phthalimidoyl oxalate radical precursors to reductively generate tertiary carbon radicals from alcohols under visible-light photoredox reaction conditions. As shown in Figure 1.6, *tert*-alkyl *N*-phthalimidoyl oxalates **1.28**, which are generated upon acylation of tertiary alcohols with *N*-phthalimidoyl chlorooxoacetate (**1.27**), undergo the desired fragmentation under visible-light photoredox conditions.[26] These radical precursors are isolable by filtration, are typically solids, and are not light-sensitive. However, they are unstable toward aqueous workup and flash chromatography on silica gel. Subjection of a slight excess *tert*-alkyl *N*-phthalimidoyl oxalates **1.28** (1.5 equiv), to photoredox reaction conditions in the presence of catalytic $[Ru(bpy)_3]PF_6$, Hantzsch ester, and a Michael acceptor (1 equiv) resulted in the efficient coupling of tertiary radicals with alkenes upon irradiation with blue light-emitting diodes (LEDs). As expected, excellent levels of diastereocontrol were observed, with addition occurring exclusively from the least sterically hindered faces of the carbon radicals. Efficient coupling with 5-methoxybutenolide to deliver coupled product **1.30** as a single diastereomer indicated that such an approach may be applicable to syntheses of spongian diterpenoids such as tyrinnal (**1.3**), aplyviolene (**1.4**), and dendrillolide A (**1.5**). Preparation of estrone analogue **1.32** was particularly noteworthy as the fragment coupling led to the formation of synthetically demanding contiguous quaternary stereocenters.[27]

Figure 1.6. Selected examples of the preparation of *tert*-alkyl *N*-phthalimidoyl oxalates and their subsequent coupling with Michael acceptors.



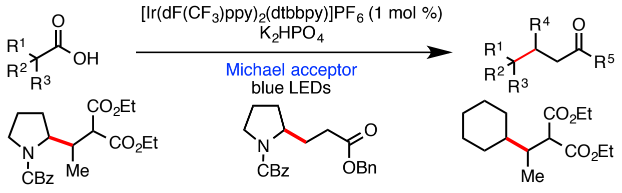
In two cases, an intermediate alkoxycarbonyl radical was trapped prior to a second decarboxylation event (Scheme 1.1). In the first example, coupling of an adamantyl-containing oxalate **1.33** with methyl vinyl ketone (**1.16**) led to a 3:1 mixture of products **1.34** and **1.35** in an 87% combined yield. The observed product distribution likely stemmed from the higher energy of the non-planar adamantyl radical in comparison to other tertiary counterparts generated in Figure 1.6, leading to a lower rate of the second decarboxylation.[28] In the second example, SET reduction of oxalate **1.36** induced N–O bond homolysis, followed by an intramolecular 5-*exo* radical cyclization onto a pendant olefin, prior to the second decarboxylation, forming a primary alkyl radical that was intercepted by the acceptor **1.16** to deliver lactone **1.38** in 43% yield.

Scheme 1.1. Trapping of an intermediate alkoxycarbonyl radicals.



Although the *tert*-alkyl *N*-phthalimidoyl oxalates **1.28** were useful for generating nucleophilic radicals from tertiary alcohols, we pursued additional activation strategies because of the relative instability of these radical precursors and formation of stoichiometric amounts of byproducts, phthalimide and pyridine (the oxidation product of Hantzsch ester). After our initial disclosure of *tert*-alkyl *N*-phthalimidoyl oxalates, the MacMillan group described the use of carboxylic acids as general precursors of carbon-centered radicals.[29] As shown in Figure 1.7, MacMillan and co-workers reported photoredox-mediated oxidation of carboxylate salts, followed by decarboxylation and trapping of resulting radicals with Michael acceptors. Notably, the developed method did not utilize any external oxidants or reductants. Just as in the case of Okada's *N*-acyloxyphthalimides, the major drawback of the reaction was the requirement for the incorporation of a C–C bond in the starting material that is cleaved during the decarboxylation event. This report led to a collaboration with the MacMillan lab wherein we aimed developed a hybrid method that would possess the following characteristics: (1) radical generation from tertiary alcohols; (2) easy to prepare and handle bench-stable precursor; (3) minimal waste generation.

Figure 1.7. Radical generation from carboxylic acids and coupling with Michael acceptors.



1.39
92%

1.40
75%

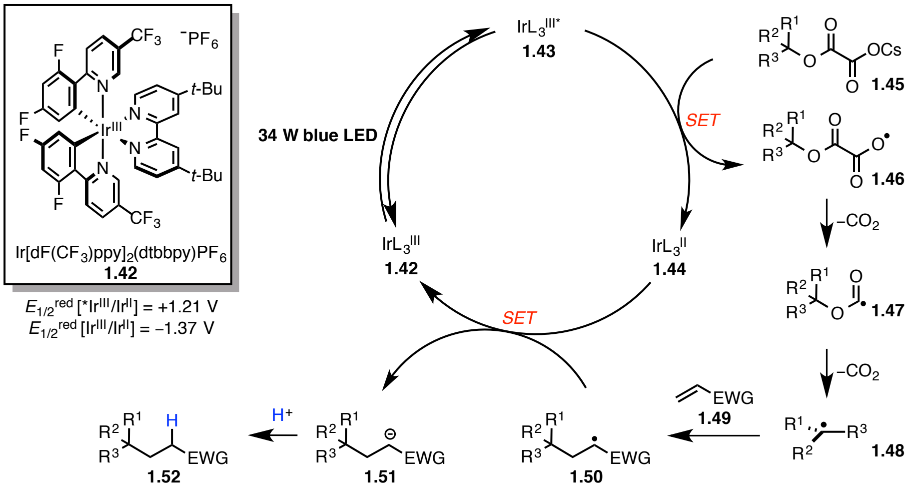
1.41
75%

1.2 Results and Discussion

The mechanistic details of the proposed coupling reaction are outlined in Scheme 1.2. It has been shown that irradiation of heteroleptic photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**1.42**) [$dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtbbpy = 4,4'-di-*tert*-butyl-2,2′-bipyridine] with visible light leads to the formation of a long-lived (τ = 2.3 μs) excited state $^*Ir^{III}$ **1.43**, which is a strong oxidant ($E_{1/2}^{red}$ [$^*Ir^{III}/Ir^{II}$] = +1.21 V vs. SCE in CH_3CN).[30] On this basis, we hypothesized that oxidation of the conjugate base of alkyl oxalate **1.45** ($E_{1/2}^{red}$ = +1.28 V vs. SCE in MeCN for *t*-$BuOCOCO_2Cs$)[31] by $^*Ir^{III}$ (**1.43**) via single-electron transfer should be thermodynamically feasible, generating alkyl radical **1.48** following the stepwise loss of two molecules of

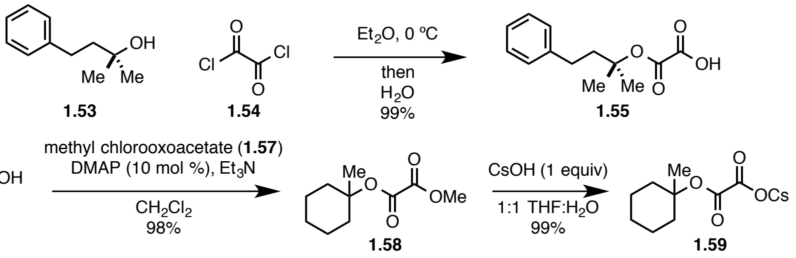
CO_2.[25b,26] This nucleophilic carbon-centered radical **1.48** should rapidly undergo addition to electron-deficient alkenes **1.49**. Finally, we expected that reduction of the resulting adduct radical **1.50** ($E_{1/2}^{red}$ = −0.59 to −0.73 V vs. SCE in MeCN)[32] by SET from the available Ir^{II} species **1.44** ($E_{1/2}^{red}$ [Ir^{III}/Ir^{II}] = –1.37 V vs. SCE in MeCN)[30] should give after protonation coupled product **1.52** and regenerate ground state photocatalyst **1.42**, completing the proposed catalytic cycle.

Scheme 1.2. Proposed mechanism for redox-neutral radical coupling reaction using alkyl oxalates and Michael acceptors.



Initially two robust routes to *tert*-alkyl hemioxalate radical precursors were developed (Scheme 1.3). The first route relied on activation of a tertiary alcohol such as **1.53** with oxalyl chloride **1.54** at 0 °C in Et_2O, followed by aqueous workup to hydrolyze the intermediate chlorooxoacetate, providing the corresponding tertiary oxalic acid derivative **1.55** in excellent yield. Alternatively, the alcohol could be activated with methyl chlorooxoacetate **1.57** at room temperature under mildly basic conditions to generate the mixed methyl *tert*-alkyl oxalates such as **1.58**, which were stable toward aqueous workup and silica gel chromatography. Typically, these intermediates were isolated and subsequently hydrolyzed with 1 equiv of aqueous base to provide the corresponding metal hemioxalates **1.59** in nearly quantitative yields following simple concentration on a rotary evaporator.

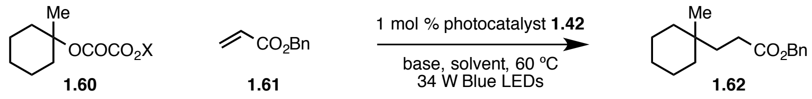
Scheme 1.3. Preparation of *tert*-alkyl oxalic acids and hemioxalate salts.



With streamlined access to the new radical precursors, we first explored the proposed decarboxylative alkylation reaction using the alkyl hydrogen oxalate derived from 1-methylcyclohexanol **1.60** in the presence of benzyl acrylate **1.61** as an archetypal Michael acceptor (Table 1.1). Using Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (**1.42**) as photocatalyst and dipotassium phosphate as base,[29] we were delighted to obtain the desired product in moderate yield (entry 1). Further optimization revealed cesium fluoride to be a more competent base and a 3:1 mixture of DME:DMF to be the optimal solvent (entries 2–4).

Although *tert*-alkyl hydrogen oxalates clearly function as viable radical precursors, many were observed to be intrinsically unstable species that disproportionated into a mixture of the corresponding dialkyl oxalate and oxalic acid, even during storage at –18 °C.[33] Furthermore, it was apparent that the presence of a highly acidic hydrogen oxalate would likely preclude the preparation of substrates containing sensitive functional groups. Fortunately, it was found that the preformed cesium salts of the starting acids were also competent in the reaction (entry 5). In contrast to the parent acid (and, indeed, most activating groups for tertiary alcohols used for radical generation), we found alkyl cesium oxalates to be bench-stable, non-hygroscopic and easy to isolate and handle. The addition of 10 equiv of water was found to be highly beneficial when utilizing the pre-formed oxalate salt, giving the coupled product **1.62** in an excellent 95% yield (entry 6). Presumably, the water both assists in solubilizing the oxalate salt and provides a proton source to quench the intermediate cesium enolate after radical coupling and reduction. Additionally, oxalates bearing other alkali counterions, such as lithium (entry 7), performed comparably to cesium oxalates in the reaction.[34] The use of a 26 W CFL bulb in place of the 34 W blue LED lamp resulted in a diminished but still useful yield (entry 8). Finally, it was observed that control experiments run in the absence of photocatalyst **1.42** or a visible-light source did not generate any of the desired 1,4-addition product **1.62** (entries 9 and 10).

Table 1.1. Initial studies and reaction optimization.

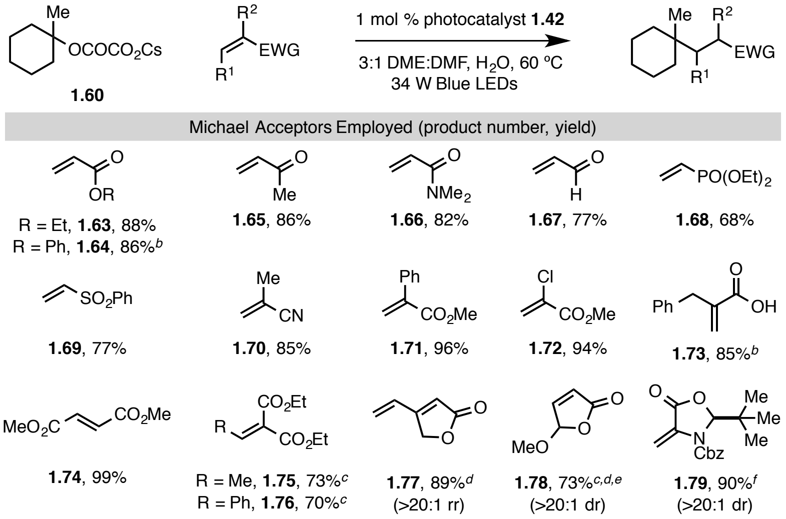


entry	X	solvent	base	yield[a]
1	H	DMF	K_2HPO_4	64%
2	H	DMF	CsF	74%
3	H	DME	CsF	82%
4	H	3:1 DME:DMF	CsF	91%
5	Cs	3:1 DME:DMF	none	65%
6[b]	Cs	3:1 DME:DMF	none	95%
7[b]	Li	3:1 DME:DMF	none	93%
8[b,c]	Cs	3:1 DME:DMF	none	66%
9[b,d]	Cs	3:1 DME:DMF	none	0%
10[b,e]	Cs	3:1 DME:DMF	none	0%

[a]Reactions on 0.2 mmol scale using 1.0 equiv acceptor and 1.1 equiv oxalate. Yields determined by ^{1}H NMR using mesitylene as an internal standard. [b]10 equiv water added. [c]Reaction performed with 26W CFL. [d]Reaction performed without photocatalyst. [e]Reaction performed in the absence of light.

Having identified optimal conditions, we examined the scope of the acceptor component. As shown in Table 1.2, a wide range of electron-deficient alkenes can be used in the reaction. As expected, various acrylates proved to be capable acceptors in the reaction (products **1.63** and **1.64**, 88 and 86% yield respectively), and the presence of α-substitution was well tolerated (products **1.70–1.73** 85–96% yield). Moreover, α,β-unsaturated acids can also be used as coupling partners, owing to the low basicity of the oxalate salt (product **1.73**, 85% yield). This procedure could be applied to a range of other electron-deficient alkenes, including enones, enals, acrylamides, vinyl phosphonates, and vinyl sulfones (products **1.65–1.69**, 68–86% yield). Surprisingly, under standard conditions acrylonitrile produced little product (11% yield),[35] whereas methacrylonitrile proved to be a much more capable acceptor (product **1.70**, 85% yield). Substitution at the β-position was tolerated for more electron-deficient alkenes such as dimethyl fumarate and dimethyl ethylidene- and benzylidenemalonate, furnishing the desired adducts with good efficiency (products **1.74–1.76**; 70–99% yield). As expected, 4-vinylfuran-2-one gave exclusively the 1,6-addition product in excellent yield (product **1.77**, 89% yield). In the case of acceptors harboring existing stereogenic centers, high levels of diastereoselectivity were obtained (products **1.78** and **1.79**, 73–90% yield, >20:1 dr).

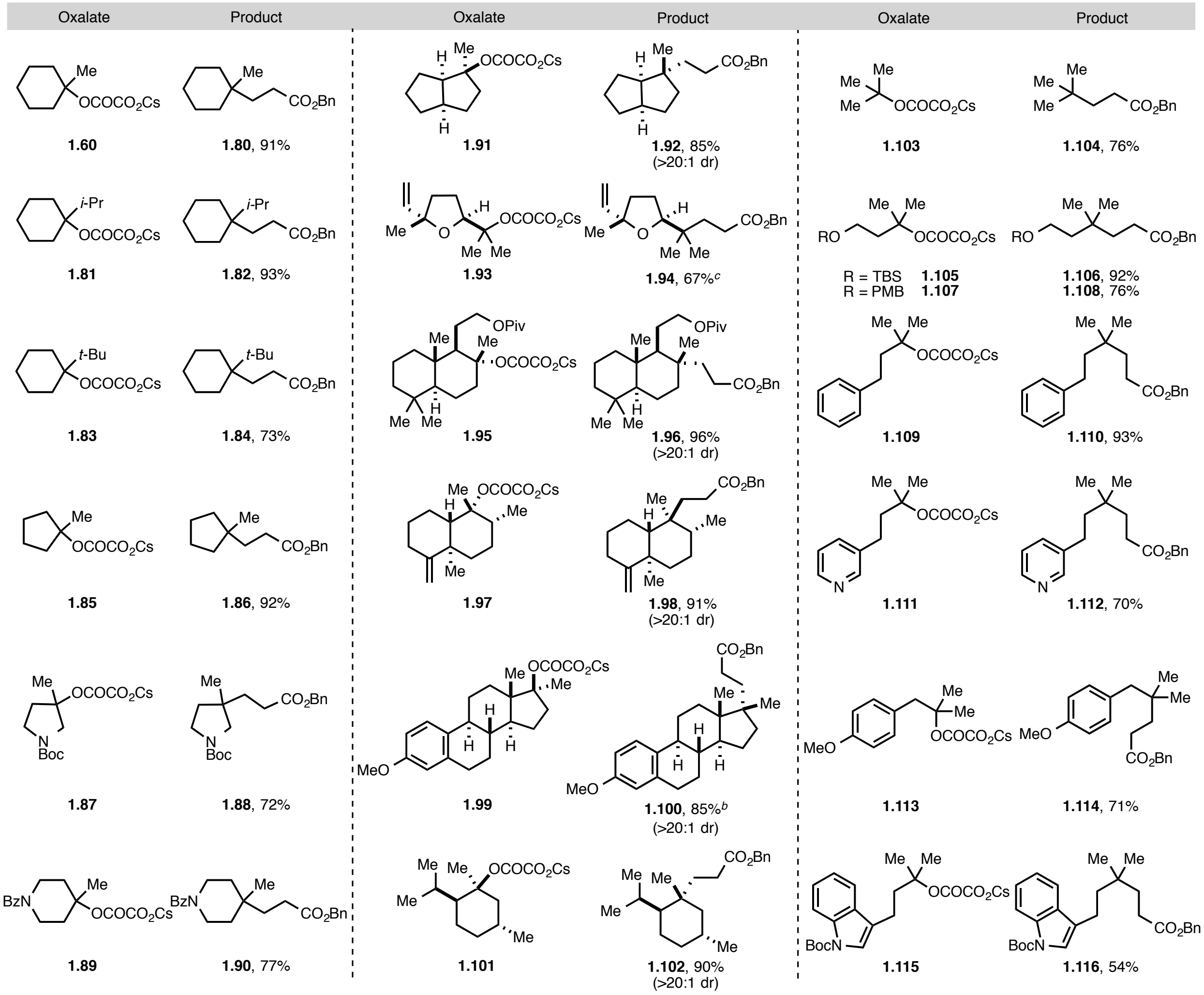
Table 1.2. Acceptor scope with alkyl cesium oxalate **1.60**.[a]



[a]Isolated yields using optimized conditions from Table 1.1 with 1.0 equiv acceptor and 1.1 equiv oxalate (see Experimental Information). [b]Performed with 1.5 equiv of cesium oxalate. [c]Performed in 100% DME. [d]Run at 22 °C. [e]Product **1.78** isolated as *trans*-isomer. [f]Product **1.78** isolated as *cis*-isomer.

Next, we turned our attention to the investigation of the cesium oxalate scope (Table 1.3). Owing to the long forming bond (2.2–2.5 Å) in the transition state of carbon radical conjugate addition[14] and the poor solvation of carbon radicals,[17a] the reaction proved to be quite insensitive to steric hindrance around the site of radical generation, with adjacent isopropyl and *tert*-butyl groups not greatly reducing the efficiency of the reaction (products **1.82** and **1.84**, 73–93% yield). Cyclopentanol-derived oxalates also underwent coupling in good yield (products **1.86** and **1.92**, 85–92% yield), although very low conversion was observed for 1-methylcyclopropanol- and 1-methylcyclobutanol-derived oxalates. Heterocycles including pyrrolidines, piperidines, tetrahydrofurans, pyridines, and indoles were well tolerated in the reaction (products **1.88**, **1.90**, **1.94**, **1.112**, and **1.116**, 54–77% yield). Underscoring the utility of this method for the constructing quaternary stereocenters in complex molecules, natural product-derived oxalates also performed well, with good levels of diastereoselectivity being observed (products **1.96**, **1.98**, **1.100**, and **1.102**, 67–96% yield). Indeed, high yields were obtained even for the formation of vicinal quaternary stereocenters (product **1.100**, 85% yield). In addition, a number of acyclic *tert*-alkyl oxalates also undergo the coupling with high levels of efficiency (products **1.104**–**1.116**, 54–93% yield). Unsurprisingly, attempts to couple benzyl acrylate (**1.61**) with *tert*-alkyl hemioxalates that would yield stabilized benzylic or allylic radicals[18a,b] upon double decarboxylation failed to produce the desired product.[36]

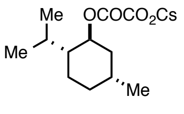
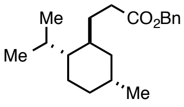
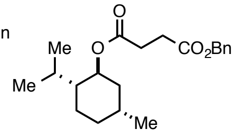
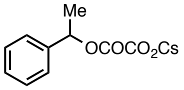
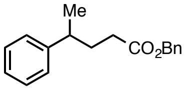
Table 1.3. Scope of *tert*-alkyl cesium hemioxalates with benzyl acrylate as the acceptor.[a]



[a]Isolated yields using optimized conditions from Table 1.1 with 1.0 equiv acceptor and 1.1 equiv oxalate (see Experimental Information). [b]Performed with 1.5 equiv of oxalate. [c]Using 100% DME.

The reaction was examined with several secondary cesium oxalates, and two representative examples are shown in Table 1.4. Although still synthetically useful, lower yields of the desired coupled products were obtained with these substrates and the product of trapping of the intermediate alkoxycarbonyl radical was also isolated (products **1.118** and **1.119**). Because of the faster rate of the second decarboxylation to form a more stabilized benzylic radical,[28] these side products were not observed with oxalate **1.120** although the yields remained moderate (product **1.121**). Further optimization of the coupling of secondary hemioxalate salts was not carried out because of the variety of existing precursors for the generation of secondary radicals, such as alkyl halides.[18]

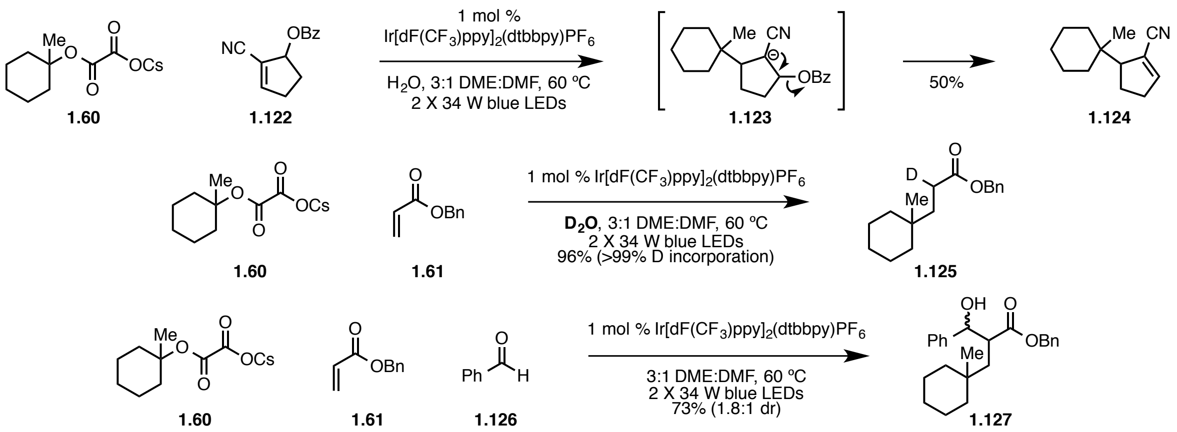
Table 1.4. Examples of secondary oxalate salts.[a]

Oxalate	Product	
 **1.117**	 **1.118**, 51%	 **1.119**, 29%
 **1.120**	 **1.121**, 57%	

[a]Isolated yields using optimized conditions from Table 1.1 with 1.0 equiv acceptor and 1.5 equiv oxalate (see Experimental Information).

To gain a further insight into the catalytic cycle of the reaction depicted in Scheme 1.2 and probe the formation of the enolate **1.51** via SET from the reduced photocatalyst **1.44** to an α-acyl radical intermediate we performed the series of reactions shown in Scheme 1.4. Upon exposure of 1-methylcyclohexanol cesium oxalate (**1.60**) to the reaction conditions in the presence of nitrile **1.122**,[26b] bearing a benzyloxy β leaving group, a single cyclopentenenitrile product **1.124** was isolated in 50% yield. We believe that the observed product arose from a heterolytic cleavage of the strong C–O bond upon formation of the nitrile-stabilized anion intermediate **1.123**. Additionally, deuterium labeling experiments, performed in the presence of D_2O in place of H_2O, led to exclusive deuterium incorporation at the α position of the product **1.125**, providing further evidence for the proposed radical-polar crossover event.[37] Taking advantage of the polar intermediate formed under the reaction conditions, we were able to perform a three-component coupling reaction between cesium oxalate **1.60**, benzyl acrylate (**1.61**) and benzaldehyde (**1.126**) to provide a 1.8:1 diastereomeric mixture of alcohols **1.127** in 73% combined yield.

Scheme 1.4. Experimental evidence of the radical-polar crossover event and three-component coupling.



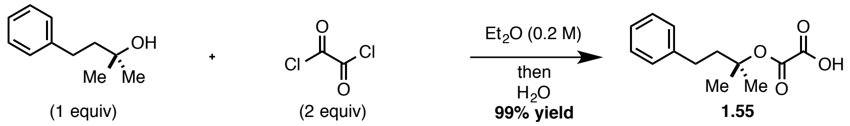
1.3 Conclusion

In summary, a new method for the formation of quaternary carbon stereocenters via the coupling of tertiary radicals, generated via photoredox-catalyzed oxidation of *tert*-alkyl hemioxalate salts, to Michael acceptors was developed. The new class of bench-stable radical precursors are readily prepared from corresponding tertiary alcohols by a two-step acylation/saponification procedure in high yields. The redox-neutral coupling proceeds under mild conditions without the requirement for external oxidants and reductants in nearly 1:1 stoichiometry of the coupling partners, making it particularly suited for the late-stage union of structurally elaborate fragments. The radical-polar crossover nature of the catalytic cycle enables for three component couplings between an intermediate enolate, generated upon SET reduction of an α-acyl radical, and a polar electrophile, such as benzaldehyde. Taken together, these characteristics make this the current state-of-the-art method for the synthesis of quaternary stereocenters from tertiary alcohols.[38]

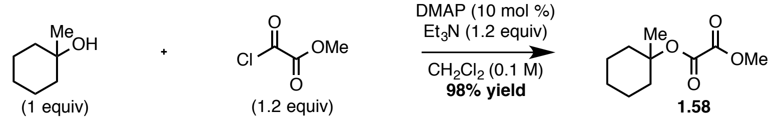
1.4 Experimental Information

Materials and Methods:

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received. Methyl vinyl ketone, acrolein, methacrylonitrile, methyl methacrylate and cyclopentenone were distilled prior to use. Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$[39] was prepared according to literature procedures. All alcohols whose synthesis is not described were either obtained from commercial suppliers or prepared using the referenced literature procedures. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 50 F$_{254}$ pre-coated plates (0.25 mm) or Analtech Uniplate (0.25 mm), and visualized by exposure to UV light (254 nm) and potassium permanganate (KMnO$_4$) staining. EMD silica gel 60 (particle size 0.040–0.063 mm) or Fluka (200–400 mesh) was used for flash column chromatography. ^{1}H NMR spectra were recorded at 500 or 600 MHz. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded at 126 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. NMR spectra are internally referenced to residual proton solvent signals (note: CDCl$_3$ referenced at 7.26 for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). IR spectra of oils and solids were recorded on a FT-IR and ATR-FTIR spectrometers, respectively, and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from the Princeton University and UC Irvine Mass Spectrometry Facilities. Optical rotations were measured with a polarimeter. Kessil KSH150B LED Grow Light 150, Blue was purchased from http://www.amazon.com.

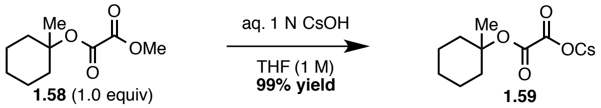


Preparation of oxalic acid 1.55: A round-bottom flask was charged with 2-methyl-4-phenylbutan-2-ol (10.4 g, 63.4 mmol 1.0 equiv) followed by the addition of Et_2O (320 mL, 0.2 M). The solution was cooled to 0 °C. Next, oxalyl chloride (11 mL, 127 mmol, 2 equiv) was added dropwise. The homogeneous reaction mixture was warmed to 23 °C and maintained at that temperature for 18 h. The reaction was cooled to 0 °C and quenched by slow addition of H_2O (200 mL). The resulting mixture was transferred to a separatory funnel with Et_2O (100 mL). The resulting biphasic mixture was extracted with Et_2O (3 x 100 mL) and the organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure to yield **1.55** (14.8 g, 99% yield) as a brown solid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.32–7.29 (m, 2H), 7.23–7.20 (m, 3H), 2.17 (t, *J* = 5.4 Hz, 2H), 2.17 (t, *J* = 4.8 Hz, 2H), 1.65 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.5, 157.1, 141.4, 128.7, 128.5, 126.3, 88.7, 42.3, 30.4, 25.9; IR (thin film): 3215, 2983, 1766, 1722, 1195 cm^{-1}; HRMS-ESI (*m*/*z*) $[M-H]^-$ calculated for $C_{13}H_{15}O_4$, 235.0970; found, 235.0962.

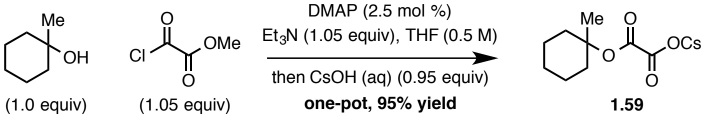


Preparation of methyl oxalate 1.58: A round-bottom flask was charged with 1-methylcyclohexan-1-ol (2.3 g, 20 mmol, 1.0 equiv) and CH_2Cl_2 (DCM) (200 mL, 0.1M). Triethylamine (3.4 mL, 24 mmol, 1.2 equiv) and DMAP (250 mg, 2 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (2.2 mL, 24 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH_4Cl (aq)

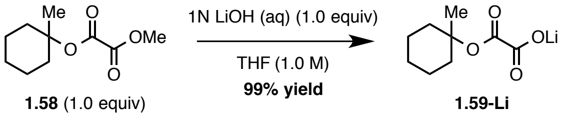
(100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et_2O) to give **1.58** as clear oil (3.9 g, 98% yield). R_f 0.45 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 3.88 (s, 3H), 2.23–2.21 (m, 2H), 1.60–1.49 (m, 10H), 1.32–1.28 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3, 156.9, 87.0, 53.5, 36.5, 25.3, 25.2, 22.1; IR (thin film): 2936, 1736, 1734, 1200, 1138 cm^{-1}; HRMS-ESI (*m/z*) $[M+Na]^+$ calculated for $C_{10}H_{16}O_4Na$, 223.0946; found, 223.0943.



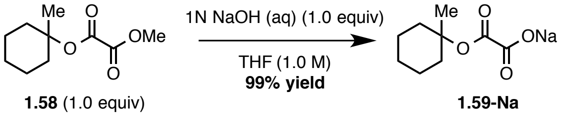
Preparation of cesium oxalate 1.59: A round-bottom flask was charged with methyl (1-methylcyclohexyl) oxalate **1.58** (3.9 g, 19.5 mmol, 1.0 equiv) followed by the addition of THF (19.5 mL, 1 M). To this solution, 1 N aq. CsOH (19.5 mL, 19.5 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.59** as a colorless solid (6.2 g, 99% yield). ^1H NMR (600 MHz, DMSO-d_6): δ 2.01 (app d, *J* = 15.6 Hz, 2H), 1.52–1.44 (m, 3H), 1.36–1.33 (m, 7H), 1.26–1.20 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 168.0, 164.0, 79.8, 36.7, 25.8, 25.5, 21.9; IR (thin film): 3441, 2932, 1713, 1635, 1202 cm^{-1}; HRMS-ESI (*m/z*) $[M-Cs]^-$ calculated for $C_9H_{13}O_4$, 185.0814; found, 185.0816.



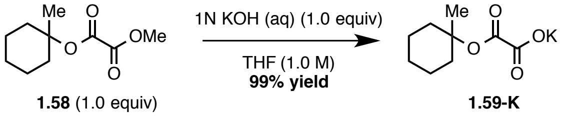
One-pot preparation of cesium oxalate 1.59: 1-methylcyclohexan-1-ol (2.28 g, 20 mmol, 1.0 equiv) was dissolved in THF (40 mL, 0.5 M). Triethylamine (2.9 mL, 21 mmol, 1.05 equiv) and DMAP (61 mg, 0.5 mmol, 0.025 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (1.9 mL, 21 mmol, 1.05 equiv). The reaction was stirred for 1 hour at room temperature, then quenched with sat. brine (50 mL). The layers were separated and the organic extracts washed again with 50% sat. brine (50 mL). The organic extracts were then treated with 1 M CsOH (aq) (19 mL, 19 mmol, 0.95 equiv), and the mixture was shaken until the intermediate methyl oxalate was consumed as judged by TLC (<5 min). Hexanes (75 mL) were added, and the aqueous phase was collected. The organic extracts were washed with a second portion of water (10 mL), and the combined aqueous phases were concentrated under reduced pressure to give **1.59** as a colorless solid (6.07 g, 95% yield). Spectral data were consistent with reported data from the 2-step procedure for preparing **1.59**, and the material prepared in this way performed as well in the photoredox coupling reaction.



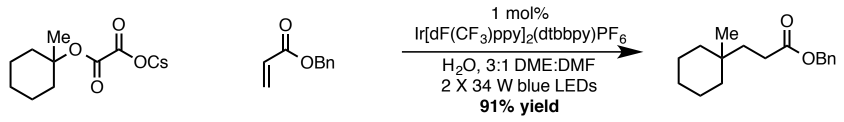
Preparation of lithium oxalate 1.59-Li: A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **1.58** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N LiOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.59-Li** as a colorless solid (190 mg, 99% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.02 (app d, *J* = 13.0 Hz, 2H), 1.54–1.32 (m, 10H), 1.27–1.16 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.3, 163.4, 79.6, 36.2, 25.3, 25.0, 21.5; IR (thin film): 2931, 2862, 1705, 1655, 1409, 1268, 1240, 1107 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_9H_{13}O_4Li$ ([M–Li]$^-$) 185.0814; found 185.0816.



Preparation of sodium oxalate 1.59-Na: A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **1.58** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N NaOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.59-Na** as a colorless solid (206 mg, 99% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.02 (app d, *J* = 13.0 Hz, 2H), 1.54–1.32 (m, 10H), 1.28–1.17 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.3, 163.7, 79.6, 36.2, 25.3, 25.0, 21.5; IR (thin film): 2930, 2861, 1733, 1709, 1659, 1659, 1405, 1265, 1218 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_9H_{13}O_4Na$ ([M–Na]$^-$) 185.0814; found 185.0807.



Preparation of potassium oxalate 1.59-K: A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **1.58** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N KOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.59-K** as a colorless solid (221 mg, 99% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.02 (app d, *J* = 13.2 Hz, 2H), 1.54–1.31 (m, 10H), 1.27–1.16 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.5, 163.6, 79.3, 36.2, 25.3, 25.0, 21.5; IR (thin film): 2933, 2863, 1720, 1710, 1642, 1413, 1201, 1145 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_9H_{13}O_4K$ ([M–K]$^-$) 185.0814; found 185.0807.



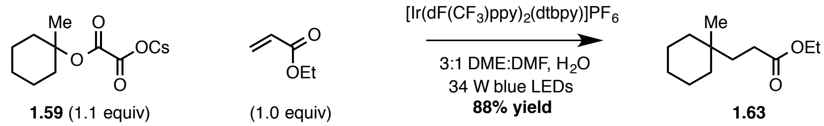
1.59 (1.1 equiv)

(1.0 equiv)

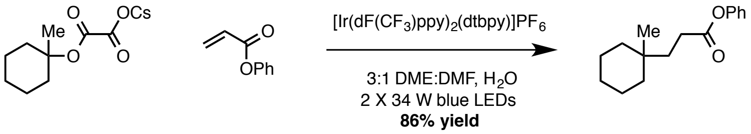
1.62

Preparation of ester 1.62: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **1.62** as a yellow oil (118 mg, 91% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39–7.32 (m, 5H), 5.12, (s, 2H), 2.34 (t, *J* = 6.0 Hz, 2H), 1.61 (t, *J* = 6.0 Hz, 2H), 1.48–1.40 (m, 5H), 1.34–1.30 (m, 1H), 1.27–1.22 (m, 4H), 0.86 (s, 3H); ^{13}C NMR

(126 MHz, $CDCl_3$): δ 174.6, 136.2, 128.7, 128.4, 128.3, 66.3, 37.6, 36.8, 32.4, 29.1, 26.5, 24.6, 22.1; IR (thin film): 2923, 2850, 1730, 1157, 696 cm^{-1}; HRMS-ESI (*m/z*) $[M+Na]^+$ calculated for $C_{17}H_{24}O_2Na$, 283.1674; found, 283.16748.

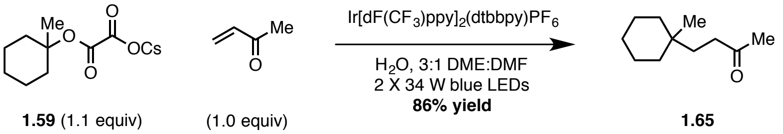


Preparation of ester 1.63: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and ethyl acrylate (50 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to give **1.63** as a yellow oil (87 mg, 88% yield): R_f = 0.30 (95:5 hexanes:ethyl acetate, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 4.12 (q, *J* = 7.1 Hz, 2H), 2.27–2.21 (m, 2H), 1.59–1.54 (m, 2H), 1.49–1.20 (m, 13H), 0.84 (s, 3H;. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 60.4, 37.6, 36.8, 32.4, 29.2, 26.6, 24.6, 22.1, 14.4; IR (KBr disk): 2927, 2859, 1738, 1452, 1375, 1302, 1176, 1039 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{22}O_2$ ($[M+Na]^+$) 221.1517; found 221.1523.

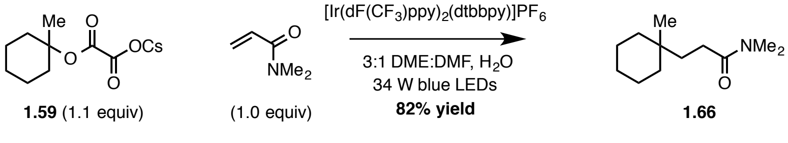


1.59 (1.5 equiv) (1.0 equiv) **1.64**

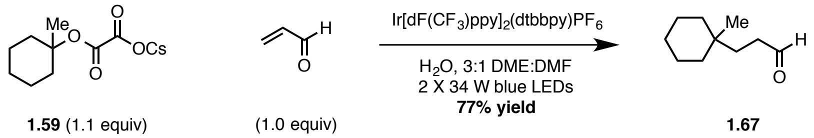
Preparation of ester 1.64: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (238 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and phenyl acrylate (69 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **1.64** as a pale yellow oil (106 mg, 86% yield): R_f = 0.57 (9:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.24–7.21 (m, 1H), 7.09–7.07 (m, 2H), 2.53–2.50 (m, 2H), 1.73–1.70 (m, 2H), 1.51–1.44 (m, 5H), 1.35–1.26 (m, 5H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 150.9, 129.5, 125.8, 121.7, 37.7, 32.6, 29.3, 26.5, 22.1; IR (ATR): 2970, 2924, 2854, 1752, 1370, 1229, 1216, 1196, 1161, 1120 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{16}H_{23}O_2^+$ ($[M+H]^+$) 247.1693; found 247.1692.



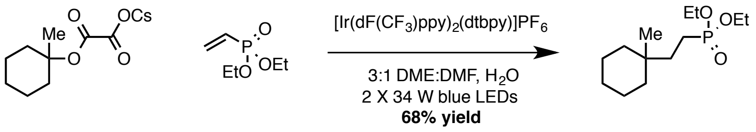
Preparation of ketone 1.65: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and methyl vinyl ketone (42 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. Li Cl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **1.65** as a yellow oil (72 mg, 86% yield). R$_f$ = 0.3 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 2.36 (t, *J* = 8.2 Hz, 2H), 2.15 (s, 3H), 1.50 (t, *J* = 8.3 Hz, 2H), 1.46–1.39 (m, 5H), 1.32–1.29 (m, 1H), 1.25–1.20 (m, 4H), 0.84 (s, 3H). Spectral data match those previously reported.[26a]



Preparation of amide 1.66: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and *N*,*N*-dimethylacrylamide (50 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (50:50 hexanes:EtOAc) to give **1.66** as a yellow oil (81 mg, 82% yield). Spectral data were consistent with previously reported data.[26a]



Preparation of aldehyde 1.67: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.67**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and acrolein (34 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et$_2$O) to give **1.67** as a yellow oil (59 mg, 77% yield). R$_f$ = 0.4 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 9.79 (t, J = 2.4 Hz, 1H), 2.39 (t, J = 1.8 Hz, 2H), 1.57 (t, J = 3.6 Hz, 2H), 1.48–1.41 (m, 5H), 1.33–1.30 (m, 1H), 1.29–1.21 (m, 4H), 0.86 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 203.6, 38.9, 37.7, 33.9, 32.4, 30.5, 26.6, 24.7, 22.1; IR (thin film): 2923, 2713, 1730, 1454, 1378 cm^{-1}; HRMS-ESI (m/z) [M + Na]$^+$ calculated for C$_{10}$H$_{18}$ONa, 177.1255; found, 177.1257.

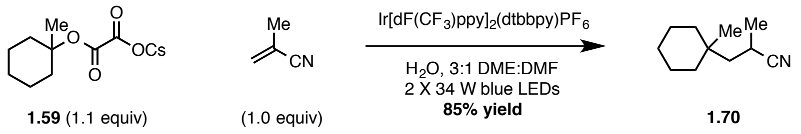


1.59 (1.1 equiv) (1.0 equiv) **1.68**

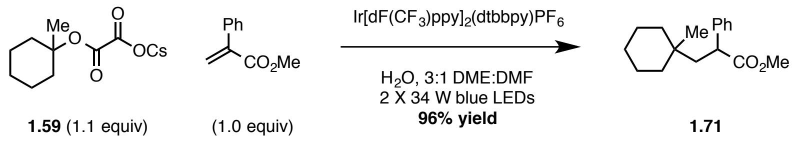
Preparation of phosphonate 1.58: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and diethyl vinyl phosphonate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 hexanes:acetone) to give **1.68** as a yellow oil (89 mg, 68% yield). R$_f$ = 0.3 (7:3

hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 4.14–4.04 (m, 4H), 1.71–1.63 (m, 2H), 1.56–1.39 (m, 7H), 1.33 (app t, *J* = 7.0 Hz, 7H), 1.25–1.19 (m, 4H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 61.6 (d, J_{C-P}=6.4), 37.4, 34.0, 26.6, 24.4, 22.1, 20.7, 19.6, 16.7 (d, J_{C-P}=6.0); IR (thin film): 2925, 1456, 1231, 1080, 957 cm^{-1}; HRMS-ESI (*m*/*z*) $[M + Na]^+$ calculated for $C_{13}H_{27}O_3PNa$, 285.1595; found, 285.1596.

Preparation of sulfone 1.69: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and phenyl vinyl sulfone (84 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (95:5 hexanes:EtOAc) to give **16.9** as a yellow oil (102 mg, 77% yield). Spectral data were consistent with previously reported data.[26a]

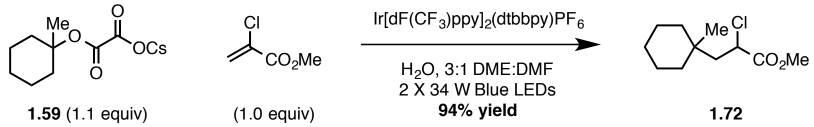


Preparation of nitrile 1.70: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and methacrylonitrile (34 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **1.70** as a yellow oil (70 mg, 85% yield). R$_f$ = 0.45 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 2.63–2.60 (m, 1H), 1.79 (dd, *J*=13.8, 9.6, 1H), 1.57–1.44 (m, 6H), 1.38–1.25 (m, 10H), 0.99 (s, 3H). Spectral data match those previously reported.[40]

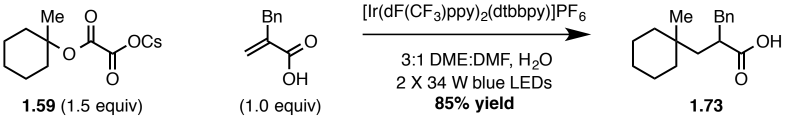


Preparation of ester 1.71: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005

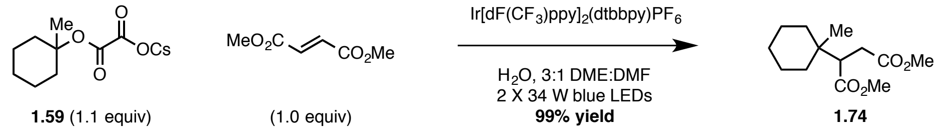
mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and methyl 2-phenylacrylate[41] (81 mg, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:EtOAc) to give **1.71** as a yellow oil (125 mg, 96% yield). R_f = 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.26 (m, 5H), 3.72 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.67 (s, 3H), 2.34 (dd, *J* = 14.0, 9.0 Hz, 1H), 1.65 (dd, *J* = 14.0, 4.0 Hz, 1H), 1.50–1.42 (m, 5H), 1.34–1.24 (m, 5H), 0.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.6, 141.4, 128.8, 128.0, 127.2, 52.2, 47.2, 46.4, 38.0, 37.9, 33.6, 26.5, 24.5, 22.2, 22.1; IR (thin film): 2933, 1735, 1453, 1152, 670 cm^{-1}; HRMS-CI (*m/z*) $[M + NH_4]^+$ calculated for $C_{17}H_{28}NO_2$, 278.2120; found, 278.2122.



Preparation of ester 1.72: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and α-chloro methacrylate (51 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **1.72** as a yellow oil (102 mg, 94% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.36–4.34 (m, 1H), 3.78 (s, 3H), 2.18 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.90 (dd, *J* = 12.7, 5.4 Hz, 1H) 1.47–1.44 (m, 6H), 1.29 (t, *J* = 5.4 Hz, 2H), 1.27–1.24 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 53.7, 53.1, 47.3, 38.0, 37.9, 33.6, 26.3, 24.7, 22.0, 21.0; IR (thin film): 2926, 1742, 1437, 1161, 687 cm^{-1}; HRMS-CI (*m*/*z*) $[M + NH_4]^+$ calculated for $C_{11}H_{23}ClNO_2$, 236.1417; found, 236.1415.

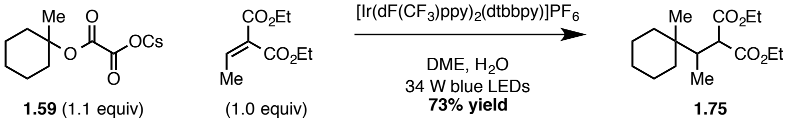


Preparation of acid 1.73: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (239 mg, 0.75 mmol, 1.5 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and 2-benzylacrylic acid (81 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and 1 N HCl (aq) (2 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (94:5:1 hexanes:THF:AcOH) to give **1.73** as a yellow oil (110 mg, 85% yield): Rf = 0.45 (75:25 hexanes:ethyl acetate, stained with $KMnO_4$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.23–7.16 (m, 3H), 2.96 (dd, *J* = 12.7, 7.0 Hz, 1H), 2.75–2.65 (m, 2H), 1.83 (dd, *J* = 14.3, 9.2 Hz, 1H), 1.44–1.13 (m, 11H), 0.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 139.0, 129.1, 128.5, 126.6, 43.8, 43.1, 40.9, 37.9, 37.8, 33.2, 26.4, 24.5, 22.02, 21.97; IR (KBr disk) 2928, 2860, 2671, 1705, 1453, 1419, 1291 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{17}H_{24}O_2$ ($[M–H]^-$) 259.1698; found 259.1690.

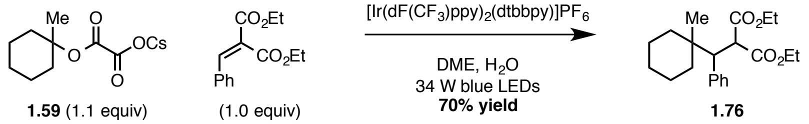


Preparation of diester 1.74: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and dimethyl fumarate (72 mg, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **1.74**

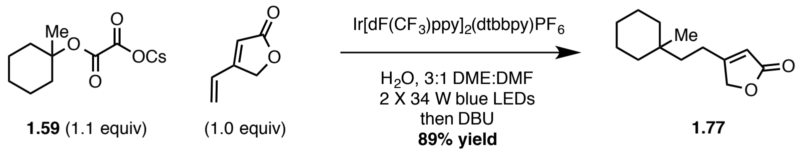
as a yellow oil (120 mg, 99% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.66 (s, 3H), 2.83−2.76 (m, 2H), 2.47 (d, *J* = 14.1 Hz, 1H), 1.62−1.57 (m, 1H), 1.52−1.37 (m, 6H), 1.31−1.22 (m, 3H), 0.92 (s, 3H). Spectral data match those previously reported.[26a]



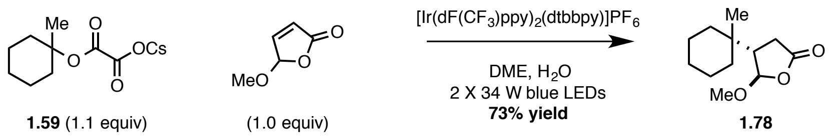
Preparation of diester 1.75: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and diethyl ethylidenemalonate (93 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 48 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (97:3 hexanes:EtOAc) to give **1.75** as a yellow oil (104 mg, 73% yield): R_f = 0.20 (95:5 hexanes:ethyl acetate, stained with KMnO4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22–4.12 (m, 4H), 3.55 (d, *J* = 4.7 Hz, 1H), 2.36–2.28 (m, 1H), 1.55–1.16 (m, 16H), 0.99 (d, *J* = 7.3 Hz, 3H), 0.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 169.9, 61.5, 61.0, 52.4, 42.1, 36.3, 35.94, 35.92, 26.3, 22.02, 21.96, 19.5, 14.2, 11.1; IR (KBr disk) 2982, 2931, 2858, 1747, 1725, 1463, 1371, 1301, 1151 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{16}H_{28}O_4$ ([M+Na]$^+$) 307.1885; found 307.1894.



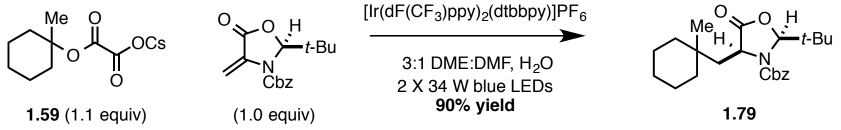
Preparation of diester 1.76: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and diethyl benzylidenemalonate (124 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 48 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (95:5 hexanes:EtOAc) to give **1.76** as a yellow oil (121 mg, 70% yield): $R_f = 0.20$ (95:5 hexanes:ethyl acetate, stained with KMnO4). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24–7.12 (m, 5H), 4.27–4.14 (m, 2H), 4.00 (d, *J* = 10.6 Hz, 1H), 3.74–3.64 (m, 2H), 3.50 (d, *J* = 10.6 Hz, 1H), 1.56–1.01 (m, 13H), 0.95 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.8, 168.5, 139.7, 127.4, 126.6, 61.8, 61.3, 56.0, 54.6, 37.2, 36.9, 35.9, 26.1, 22.1, 22.0, 19.2, 14.1, 13.5; IR (thin film) 2929, 2860, 1759, 1728, 1464, 1299, 1149, 1033, 910 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{30}O_4$ ([M+Na]$^+$) 369.2042; found 369.2048.



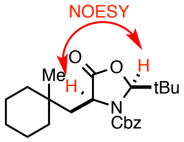
Preparation of butenolide 1.77: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (124 mg, 0.38 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (4.0 mg, 0.0035 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (7 mL, 0.05 M) was added, followed by water (63 µL, 3.5 mmol, 10 equiv), and vinyl butenolide[42] (39 mg, 0.35 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h. Air was blown over the reaction vessel to maintain the temperate at 23 °C. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The residue was redissolved in CH$_2$Cl$_2$ (9 mL, 0.04 M) and DBU (63 µL, 0.42 mmol, 1.2 equiv) was added. The solution was maintained at 23 °C for 10 min. The reaction was diluted with CH$_2$Cl$_2$ (10 mL), washed with 2 N aq. HCl (3 x 10 mL). Combined organic phases were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (4:1 hexanes:EtOAc) to yield **1.77** (64 mg, 88% yield) as a yellow oil. R_f = 0.3 (4:1 hexanes:EtOAc); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.89 (s, 1H), 4.80 (s, 2H), 2.40 (t, *J* = 7.8 Hz, 2H), 1.57–1.50 (m, 7H), 1.41–1.28 (m, 5H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 174.4, 171.7, 115.1, 73.3, 39.6, 37.7, 32.7, 26.5, 24.6, 23.1, 22.1; IR (thin film): 2923, 1778, 1744, 1636, 884 cm^{-1}; HRMS-CI (*m/z*) [M + NH$_4$]$^+$ calculated for C$_{13}$H$_{24}$NO$_2$, 226.1807; found, 226.1803.

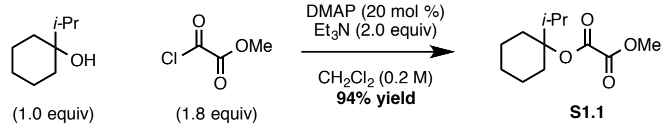


Preparation of lactone 1.78: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and 5-methoxy butenolide[43] (57 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 36 h maintaining ambient temperature via cooling with a flow of air from a fan. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (90:10 hexanes:EtOAc) to give **1.78** as a yellow oil (77 mg, 73% yield). Spectral data were consistent with previously reported data.[26a]

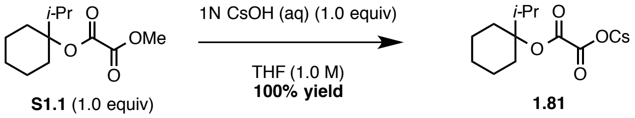


Preparation of oxooxazolidine 1.79: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate[44] (145 mg, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (95:5 hexanes:EtOAc) to give **1.79** as a yellow oil (175 mg, 90% yield): R_f = 0.30 (90:10 hexanes:ethyl acetate, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.32 (m, 5H), 5.55 (s, 1H), 5.19 (d, *J* = 11.8 Hz, 1H), 5.13 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 6.3 Hz, 1H), 1.90 (dd, *J* = 14.3, 8.2 Hz, 1H), 1.67 (dd, *J* = 14.3, 2.8 Hz, 1H), 1.50–1.15 (m, 10H), 0.96 (app s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 155.9, 135.3, 129.1, 128.85, 128.80, 96.2, 68.5, 53.7, 47.8, 38.1, 37.8, 37.0, 33.4, 26.4, 25.1, 24.3, 22.05, 22.04; IR (KBr disk) 2930, 2863, 1791, 1711, 1455, 1396, 1318, 1192 cm^{-1}; $[\alpha]^{23}_{589}$ +36.2, $[\alpha]^{23}_{577}$ +37.9, $[\alpha]^{23}_{546}$ +43.3, $[\alpha]^{23}_{435}$ +77.5, $[\alpha]^{23\cdot}_{405}$ +98.1 (*c* = 1.0, $CHCl_3$). HRMS (ESI–TOF) *m/z* calculated for $C_{23}H_{33}NO_4$ ($[M+Na]^+$) 410.2307; found 410.2315. Product stereochemistry was confirmed by a NOESY correlation:

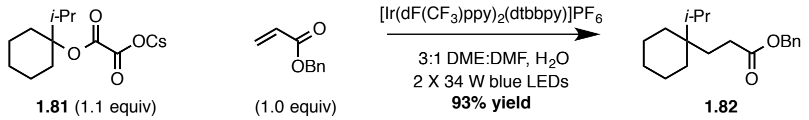




Preparation of methyl oxalate S1.1: 1-isopropylcyclohexan-1-ol (380 mg, 2.68 mmol, 1.0 equiv) was dissolved in CH$_2$Cl$_2$ (13 mL, 0.2 M). Triethylamine (750 µL, 5.4 mmol, 2.0 equiv) and DMAP (66 mg, 0.54 mmol, 0.2 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (440 µL, 4.83 mmol, 1.8 equiv). The reaction was stirred for 8 hours at 35 °C, then quenched with sat. NH$_4$Cl (aq) (20 mL). The aqueous phase was extracted with CH$_2$Cl$_2$ (40 mL), and the organic extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (90:10 hexanes:EtOAc) to give **S1.1** as a clear oil (576 mg, 94% yield): R$_f$ = 0.40 (90:10 hexanes:ethyl acetate, stained with KMnO4). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.87 (s, 3H), 2.65 (hept, *J* = 6.9 Hz, 1H), 2.26 (app d, *J* = 11.5 Hz, 2H), 1.72–1.57 (m, 3H), 1.54–1.39 (m, 4H), 1.26–1.13 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.4, 156.8, 93.4, 53.3, 33.3, 30.0, 25.6, 21.6, 17.4; IR (thin film) 2938, 2866, 1763, 1733, 1449, 1323, 1200, 1136 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for C$_{12}$H$_{20}$O$_4$ ([M+Na]$^+$) 251.1259; found 251.1251.

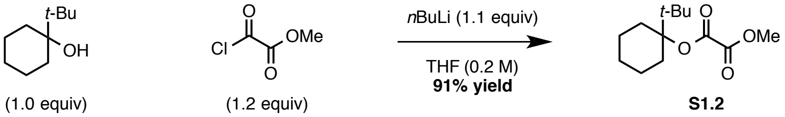


Preparation of cesium oxalate 1.81: A round-bottom flask was charged with 1-isopropylcyclohexyl methyl oxalate **S1.1** (563 mg, 2.47 mmol, 1 equiv) followed by the addition of THF (2.5 mL, 1 M). To this solution, 1 N CsOH (aq) (2.5 mL, 2.5 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.81** as a colorless solid (855 mg, 100% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.56 (hept, *J* = 7.0 Hz, 1H), 2.06 (app d, *J* = 12.8 Hz, 2H), 1.56 (app d, *J* = 12.7 Hz, 1H), 1.53–1.39 (m, 4H), 1.29 (td, *J* = 12.9, 4.7 Hz, 2H), 1.17–1.06 (m, 1H), 0.83 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 167.6, 163.7, 84.9, 32.9, 29.7, 25.4, 21.0, 17.1; IR (thin film) 2967, 2934, 1707, 1698, 1654, 1368, 1193, 1141, 946 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{11}H_{17}O_4Cs$ ([M–Cs]$^-$) 213.1127; found 213.1129.

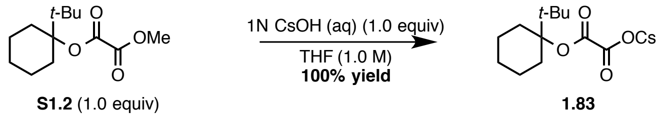


Preparation of ester 1.82: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.81** (190 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to give **1.82** as a yellow oil (134 mg, 93% yield): Rf = 0.35 (95:5 hexanes:ethyl acetate, stained with KMnO4). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41–7.29 (m, 5H), 5.12 (s, 2H), 2.29–2.23 (m, 2H), 1.74–1.69 (m, 2H), 1.65 (hept, *J*

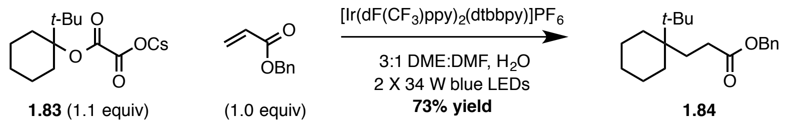
= 6.9 Hz, 1H), 1.52–1.15 (m, 10H), 0.82 (d, *J*=7.0 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.7, 136.3, 128.7, 128.32, 128.29, 66.3, 36.6, 31.8, 31.2, 28.8, 27.6, 26.5, 21.5, 16.8. IR (KBr disk) 2933, 2866, 1729, 1456, 1388, 1216, 1163 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{19}H_{28}O_2$ ([M+Na]$^+$) 311.1987; found 311.1982.



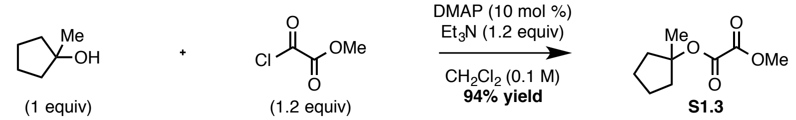
Preparation of methyl oxalate S1.2: A round-bottom flask was charged with 1-(*tert*-butyl)cyclohexan-1-ol (234 mg, 1.5 mmol, 1.0 equiv) and THF (7.5 mL, 0.2 M) under an atmosphere of argon. The solution was stirred and cooled to –78 °C before a 2.5M solution of *n*-BuLi in hexanes (660 µL, 1.65 mmol, 1.1 equiv) was added drop-wise. The solution was stirred for 5 min, then methyl chlorooxoacetate (160 µL, 1.8 mmol, 1.2 equiv) was added drop-wise. The reaction was stirred for 1 hour, then warmed to room temperature and quenched with sat. NaHCO$_3$(aq) (20 mL). The aqueous phase was extracted with EtOAc (40 mL), and the organic extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (97:3 hexanes:EtOAc) to give **S1.2** as a clear oil (331 mg, 91% yield): R$_f$ = 0.45 (90:10 hexanes:ethyl acetate, stained with KMnO4). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.87 (s, 3H), 2.59–2.49 (m, 2H), 1.72–1.62 (m, 3H), 1.44–1.32 (m, 4H), 1.21–1.09 (m, 1H), 1.00 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.8, 157.6, 97.0, 53.3, 39.5, 30.1, 26.5, 25.1, 22.4; IR (thin film) 2941, 2870, 1764, 1735, 1450, 1324, 1216, 1122 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{22}O_4$ ([M+Na]$^+$) 265.1416; found 265.1420.



Preparation of cesium oxalate 1.83: A round-bottom flask was charged with 1-(*tert*-butyl)cyclohexyl methyl oxalate **S1.2** (311 mg, 1.29 mmol, 1 equiv) followed by the addition of THF (1.3 mL, 1 M). To this solution, 1 N CsOH (aq) (1.3 mL, 1.3 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.83** as a colorless solid (467 mg, 100% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 2.34 (app d, *J* = 12.3 Hz, 2H), 1.57–1.36 (m, 5H), 1.24 (td, *J* = 13.0, 4.3 Hz, 2H), 1.14–1.04 (m, 1H), 0.91 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 168.1, 164.1, 88.3, 38.8, 29.8, 26.3, 25.0, 21.8; IR (thin film) 2940, 2872, 1709, 1623, 1612, 1397. 1196, 1127 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{19}O_4Cs$ ([M–Cs]$^-$) 227.1283; found 227.1273.

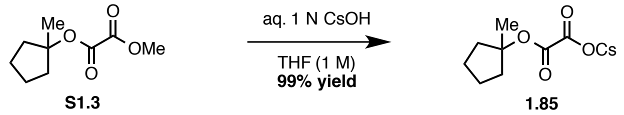


Preparation of ester 1.84: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.83** (198 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to give **1.84** as a yellow oil (110 mg, 73% yield): Rf = 0.40 (95:5 hexanes:ethyl acetate, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.29 (m, 5H), 5.12 (s, 2H), 2.46–2.39 (m, 2H), 1.86–1.80 (m, 2H), 1.63 (app d, *J* = 13.0 Hz, 1H), 1.53 (app d, *J* = 13.3 Hz, 2H), 1.43–1.24 (m, 6H), 1.09–0.99 (m, 1H), 0.86 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 136.3, 128.7, 128.32, 128.31, 66.3, 38.9, 37.3, 31.2, 29.7, 26.7, 26.1, 25.7, 22.5; IR (thin film) 2934, 2868, 1734, 1455, 1370, 1294, 1135, 1079 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{20}H_{30}O_2$ ($[M+Na]^+$) 325.2144; found 325.2133.

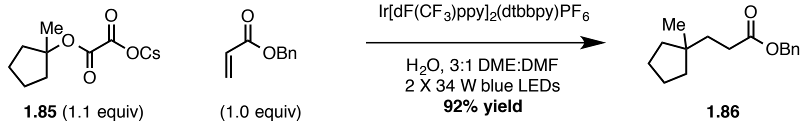


Preparation of methyl oxalate S1.3: A round-bottom flask was charged with 1-methylcyclopentan-1-ol (620 mg, 6.2 mmol, 1.0 equiv) and CH_2Cl_2 (62 mL, 0.1M). Triethylamine (1.0 mL, 7.5 mmol, 1.2 equiv) and DMAP (76 mg, 0.62 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.7 mL, 7.5 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (9:1 hexanes:EtOAc) to give **S1.3** as a clear oil (1.1 g, 94% yield). R_f = 0.5 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 3.87 (s, 3H), 2.22–2.20 (m, 2H), 1.78–1.75 (m, 4H), 1.69–1.64 (m, 5H); ^{13}C NMR (126 MHz,

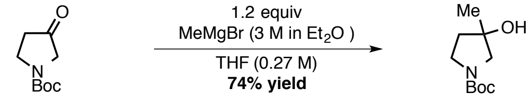
$CDCl_3$): δ 159.2, 157.2, 94.5, 53.5, 39.0, 24.1, 23.9; IR (thin film): 2958, 1762, 1735, 1151, 789 cm^{-1}; HRMS-CI (*m/z*) [M + NH_4]$^+$ calculated for $C_9H_{18}NO_4$, 204.1236; found, 204.1233.



Preparation of cesium oxalate 1.85: A round-bottom flask was charged with methyl (1-methylcyclopentyl) oxalate (**S1.3**) (1.0 g, 5.4 mmol, 1.0 equiv) followed by the addition of THF (5.4 mL, 1 M). To this solution, 1 N aq. CsOH (5.4 mL, 5.4 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.85** as a colorless solid (1.6 g, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 1.98–1.95 (m, 2H), 1.63–1.54 (m, 6H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.6, 87.2, 38.6, 24.3, 23.3; IR (thin film): 3430, 2957, 1723, 1637, 1173 cm^{-1}; HRMS-ESI (*m/z*) [M−Cs]$^-$ calculated for $C_8H_{11}O_4$, 171.0657; found, 171.0661.



Preparation of ester 1.86: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate (**1.85**) (170 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **1.86** as a yellow oil (113 mg, 92% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 7.39–7.32 (m, 5H), 5.12, (s, 2H), 2.37 (t, *J* = 4.2 Hz, 2H), 1.70–1.59 (m, 6H), 1.40–1.32 (m, 4H), 0.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.5, 136.3, 128.8, 128.5, 128.4, 66.4, 41.8, 39.3, 37.1, 31.1, 25.7, 24.6; IR (thin film): 2951, 1733, 1455, 1159, 696 cm^{-1}; HRMS-CI (m/z) $[M + NH_4]^+$ calculated for $C_{16}H_{26}NO_2$, 264.1964; found, 264.1967.

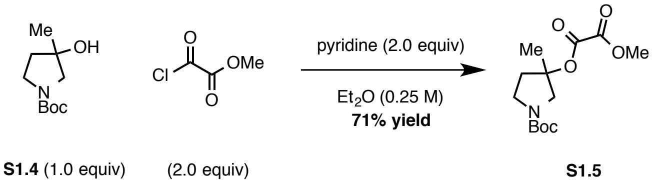


(1.0 equiv)

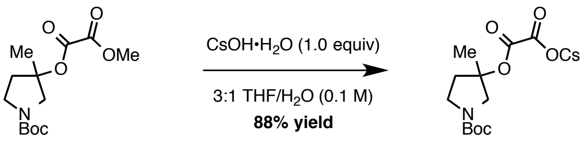
S1.4

Preparation of alcohol S1.4: A solution of methyl magnesium bromide (3 M in Et_2O; 10.8 mL, 32.39 mmol, 1.2 equiv) was added dropwise to *tert*-butyl 3-oxopyrrolidine-1-carboxylate (5.0 g, 26.99 mmol, 1.0 equiv) in THF (100 mL) at 0 °C over 5 min. The resulting solution was warmed to room temperature overnight quenched with saturated aqueous NH_4Cl solution (50 mL) and diluted with Et_2O (100 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined ethereal extracts were washed with brine (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (3:7 → 1:1 EtOAc:hexanes) to give **S1.4**[45] as a beige solid (4.02 g, 74% yield): R_f = 0.17 (2:1

hexanes:EtOAc, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) 3:1 mixture of rotamers (major given) δ 3.53–3.44 (m, 2H), 3.41–3.33 (m, 1H), 3.27–3.20 (m, 1H), 1.92–1.81 (m, 2H), 1.68 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers (both given) δ 154.8, 79.5, 59.1, 58.8, 45.1, 44.7, 39.6, 39.1, 28.7, 25.5; IR (ATR): 3384, 2970, 2908, 1716, 1656, 1417, 1367, 1156, 1144, 1105 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{10}H_{20}NO_3^+$ ($[M+H]^+$) 202.1438; found 202.1436.

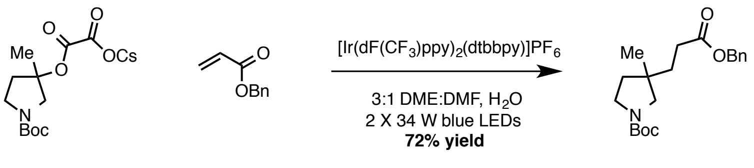


Preparation of methyl oxalate S1.5: Methyl chlorooxoacetate (920 µL, 9.94 mmol, 2.0 equiv) was added to a solution of *tert*-butyl 3-hydroxy-3-methylpyrrolidine-1-carboxylate **S.14** (1.0 g, 4.97 mmol, 1.0 equiv) and pyridine (760 µL, 9.94 mmol, 2.0 equiv) in Et_2O (20 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 20 mL) and saturated aqueous $NaHCO_3$ solution (20 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:9 → 1:4) EtOAc:hexanes) to give **S.15** as a clear oil (1.03 g, 71% yield): R_f = 0.32 (2:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 3.91–3.83 (m, 1H), 3.88 (s, 3H), 3.50–3.41 (m, 3H), 2.49–2.46 (m, 1H), 2.04–1.99 (m, 1H), 1.69 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 158.3, 156.8, 156.7, 154.3, 89.5, 88.8, 79.8, 79.7, 56.0, 53.5, 44.2, 43.7, 37.0, 36.6, 28.5, 21.3; IR (ATR): 2974, 2907, 2848, 1740, 1715, 1692, 1635, 1397, 1207, 1160, 1125, 1102 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{22}NO_6^+$ ($[M+H]^+$) 288.1442, found 288.1439.



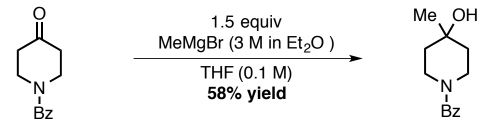
S1.5 (1.0 equiv) **1.87**

Preparation of cesium oxalate 1.87: CsOH•H_2O (175 mg, 1.04 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S.15** (300 mg, 1.04 mmol, 1.0 equiv) in THF (10 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 5 mL) and dried *in vacuo* to give **1.87** as a colorless solid that was used without further purification (370 mg, 88% yield). ^{1}H NMR (500 MHz, D_2O) δ 3.81–3.71 (m, 1H), 3.40–3.32 (m, 3H), 2.38 (dt, *J* = 12.3, 5.8 Hz, 1H), 1.99 (dt, *J* = 14.2, 8.9 Hz, 1H), 1.55 (s, 3H), 1.35 (s, 9H); Mixture of 2 rotamers: ^{13}C NMR (126 MHz, D_2O) δ 164.3, 163.7, 156.32, 55.8, 55.2, 44.3, 43.7, 36.3, 35.8, 27.6, 20.1; IR (ATR): 2975, 2908, 2848, 1716, 1685, 1628, 1403, 1205, 1175, 1102 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{18}NO_6^-$ ($[M-Cs]^-$) 272.1140; found 272.1137.



1.87 (1.1 equiv) (1.0 equiv) **1.88**

Preparation of ester 1.88: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.87** (304 mg, 0.75 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et$_2$O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 → 9:1 hexanes:EtOAc) to give **1.88** as a colorless film (126 mg, 72% yield): R_f = 0.29 (19:1 hexanes:EtOAc, stained with KMnO$_4$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39–7.31 (m, 5H), 5.11 (s, 2H), 3.46–3.30 (m, 2H), 3.14–3.08 (m, 1H), 3.07–3.02 (m, 1H), 2.39–2.35 (m, 2H), 1.77–1.73 (m, 2H), 1.68–1.57 (m, 2H), 1.45 (s, 9H), 1.01 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) mixture of rotamers δ 173.5, 173.4, 154.8, 154.7, 135.9, 135.8, 128.6, 128.34, 128.31, 79.2, 66.5, 66.4, 57.6, 57.0, 44.8, 44.5, 41.1, 40.2, 37.5, 36.7, 34.3, 34.2, 30.4, 30.3, 28.6, 22.9; IR (ATR): 2968, 2874, 1736, 1690, 1397, 1364, 1154, 1100 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for C$_{20}$H$_{29}$NaNO$_4^+$ ([M+Na]$^+$) 370.1989; found 370.1992.

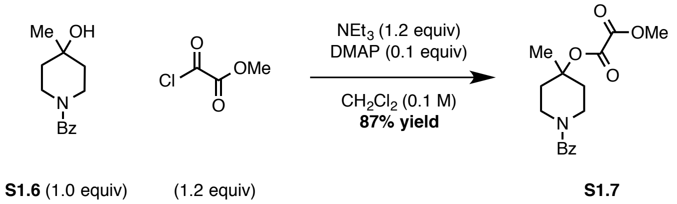


(1.0 equiv)

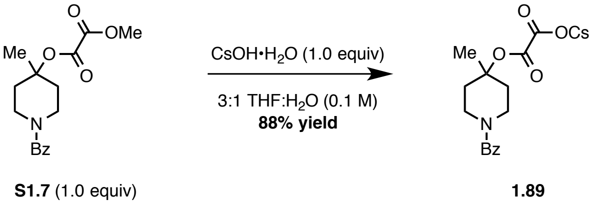
S1.6

Preparation of alcohol S1.6: A solution of methyl magnesium bromide (3 M in Et$_2$O; 4.92 mL, 14.76 mmol, 1.5 equiv) was added dropwise to 1-benzoyl-4-piperidone (2.0 g, 9.84

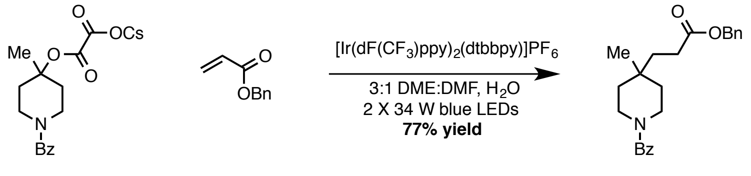
mmol, 1.0 equiv) in THF (100 mL) at 0 °C over 5 min. The resulting solution was warmed to room temperature over 1 h, stirred for a further 1 hour and then quenched with 1 M hydrochloric acid (50 mL). The resulting aqueous mixture was extracted with Et_2O (4 x 50 mL) and the combined ethereal extracts were washed with brine (50 mL), dried over $MgSO_4$, and concentrated. The crude material was purified by flash column chromatography on silica gel (4:1 – 1:0 EtOAc:hexanes) to give **S1.6** as a viscous, clear oil (1.24 g, 58% yield): R_f = 0.47 (EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.37 (m, 5H), 4.33–4.31 (m, 1H), 3.46–3.33 (m, 3H), 1.67–1.55 (m, 4H), 1.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 170.4, 136.3, 129.6, 128.6, 126.9, 68.2, 44.2, 39.2, 38.6, 38.4, 30.4; IR (film)3323, 2964, 2901, 1601, 1575, 1447, 1257, 1109 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{18}NO_2^+$ ([M+H]$^+$) 220.1332; found 220.1331.



Preparation of methyl oxalate S1.7: Methyl chlorooxoacetate (373 μL, 4.05 mmol, 1.2 equiv) was added to a solution of (4-hydroxy-4-methylpiperidin-1-yl)(phenyl)methanone **S1.6** (740 mg, 3.37 mmol, 1.0 equiv), triethylamine (564 μL, 4.05 mmol, 1.2 equiv) and DMAP (42 mg, 0.34 mmol, 0.1 equiv) in CH_2Cl_2 (30 mL) and the resulting yellow solution was maintained at room temperature for 6 hours. Water (50 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were washed with water (50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 EtOAc:hexanes) to give **S1.7** as a sticky colorless foam (894 mg, 87% yield): R$_f$ = 0.42 (1:4 hexanes:EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.40 (m, 5H), 4.44 (br s, 1H), 3.91 (s, 3H), 3.59 (br s, 1H), 3.34 (br s, 1H), 3.24 (br s, 1H), 2.41 (br s, 1H), 2.28 (br s, 1H), 1.77 (br s, 1H), 1.66 (s, 3H), 1.63 (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 170.5, 158.5, 156.6 135.7, 129.8, 128.5, 126.9, 83.8, 53.5, 43.6, 37.96, 36.3, 35.4, 24.8; IR (ATR): 3003, 2981, 2940, 2913, 1761, 1628, 1438, 1325, 1261, 1209, 1166, 1139 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{16}H_{20}NO_5^+$ ([M+H]$^+$) 306.1336; found 306.1335.

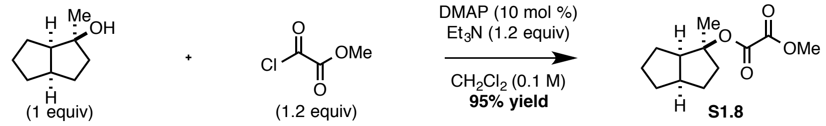


Preparation of cesium oxalate 1.89: CsOH•H$_2$O (407 mg, 2.42 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.7** (740 mg, 2.42 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 5 mL) and dried *in vacuo* to give **1.89** as a colorless solid that was used without further purification (952 mg, 93% yield). ^{1}H NMR (500 MHz, D_2O) δ 7.53–7.46 (m, 3H), 7.40–7.38 (m, 2H), 4.22–4.19 (m, 2H), 3.52–3.49 (m, 1H), 3.37–3.26 (m, 2H), 2.39–2.34 (m, 1H), 2.19–2.16 (m, 1H), 1.82–1.76 (m, 1H), 1.72–1.65 (m, 1H), 1.57 (s, 3H); ^{13}C NMR (126 MHz, D_2O) mixture of rotamers δ 172.3, 164.8, 163.9, 134.5, 130.3, 128.7, 126.4, 82.2, 60.9, 44.1, 38.6, 35.4, 34.8, 23.8; IR (ATR): 2934, 2910, 1714, 1616, 1575, 1438, 1203, 1171, 1138, 966 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{15}H_{16}NO_5^-$ ([M–Cs]$^-$) 290.1034; found 290.1037.



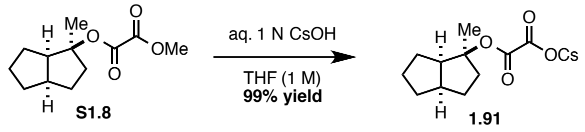
1.89 (1.1 equiv) (1.0 equiv) **1.90**

Preparation of ester 1.90: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.89** (232 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et$_2$O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **1.90** as a colorless film (141 mg, 77% yield): R$_f$ = 0.30 (2:1 hexanes:EtOAc, stained with KMnO$_4$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42–7.29 (m, 10H), 5.14 (s, 2H), 4.02 (br s, 1H), 3.44 (br s, 2H), 3.27 (br s, 1H), 2.38–2.35 (m, 2H), 1.73–1.70 (m, 2H), 1.49 (br s, 2H), 1.35–1.28 (m, 2H), 2.99 (3H, s); ^{13}C NMR (126 MHz, CDCl$_3$) mixture of rotamers δ 173.7, 170.3, 136.3, 135.9, 129.5, 128.6, 128.4, 128.34, 128.33, 126.8, 66.4, 44.0, 40.0, 38.3, 37.3, 36.3, 31.5, 28.8, 23.0; HRMS (ESI–TOF) *m/z* calculated for $C_{23}H_{28}NO_3^+$ ([M+H]$^+$) 366.2064; found 366.2066.

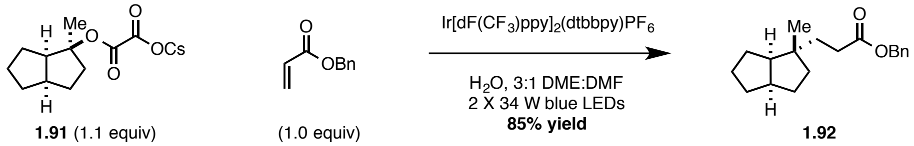


S1.8

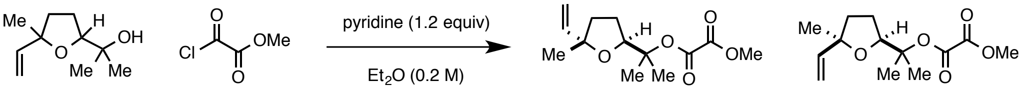
Preparation of methyl oxalate S1.8: A round-bottom flask was charged with (1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-ol[46] (280 mg, 2.0 mmol, 1.0 equiv) and CH_2Cl_2 (20 mL, 0.1M). Triethylamine (0.35 mL, 2.4 mmol, 1.2 equiv) and DMAP (25 mg, 0.2 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.22 mL, 2.4 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et_2O) to give **S1.8** as a clear oil (430 mg, 95% yield). R_f = 0.4 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.85 (s, 3H), 2.58–2.54 (m, 1H), 2.51–2.48 (m, 1H), 2.12–2.08 (m, 1H), 1.89–1.84 (m, 2H), 1.81–1.75 (m, 1H), 1.70–1.61 (m, 2H), 1.56 (s, 3H), 1.53–1.49 (m, 1H), 1.47–1.40 (m, 1H), 1.34–1.24 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 156.9, 93.6, 53.5, 53.3, 41.6, 36.5, 35.5, 29.0, 28.7, 27.2, 24.0; IR (thin film): 2952, 1766, 1738, 1160, 732 cm^{-1}; HRMS-CI (*m/z*) [M + NH_4]$^+$ calculated for $C_{12}H_{22}NO_4$, 244.1549; found, 244.1544.



Preparation of cesium oxalate 1.91: A round-bottom flask was charged with methyl ((1*S*, 3*R*, 6*R*)-1-methyloctahydropentaien-1-yl) oxalate (**S1.8**) (390 mg, 1.7 mmol, 1.0 equiv) followed by the addition of THF (1.7 mL, 1 M). To this solution, 1 N aq. CsOH (1.7 mL, 1.7 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.91** as a colorless solid (590 mg, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 2.47–2.37 (m, 2H), 1.88–1.74 (m, 2H), 1.72–1.64 (m, 2H), 1.58–1.51 (m, 1H), 1.50–1.40 (m, 2H), 1.38 (s, 3H), 1.36–1.28 (m, 1H), 1.25–1.16 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.0, 163.4, 86.9, 52.7, 40.7, 36.4, 35.2, 28.3, 28.1, 26.6, 24.2; IR (thin film): 2947, 1722, 1635, 1210, 1121 cm^{-1}; HRMS-ESI (*m/z*) [M–Cs]$^-$ calculated for $C_{11}H_{15}O_4$, 211.0970; found, 211.0970.

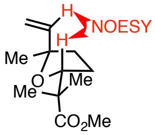


Prepartion of ester 1.92: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-(((1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-yl)oxy)-2-oxoacetate (**1.91**) (190 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **1.92** as a yellow oil (122 mg, 85% yield). R_f = 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.34 (m, 5H), 5.12, (s, 2H), 2.49–2.46 (m, 1H), 2.34 (t, *J* = 8.0 Hz, 2H), 1.96 (q, *J* = 8.5 Hz, 1H), 1.87–1.79 (m, 2H), 1.65–1.59 (m, 3H), 1.58–1.51 (m, 1H), 1.41–1.32 (m, 3H), 1.28–1.22 (m, 2H), 1.16–1.11 (m, 1H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.6, 136.3, 128.8, 128.4, 128.3, 66.4, 53.6, 43.7, 42.9, 38.0, 36.7, 35.2, 31.6, 30.5, 29.4, 28.1, 21.3; IR (thin film): 2944, 2861, 1732, 1653, 1154 cm^{-1}; HRMS-CI (*m/z*) $[M+NH_4]^+$ calculated for $C_{19}H_{30}NO_2$, 304.2277; found, 204.2266.

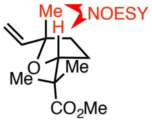


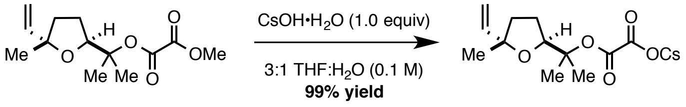
S1.9 (30% yield) **S1.10 (32% yield)**

Preparation of methyl oxalate S1.9: Methyl chlorooxoacetate (1.30 mL, 14.10 mmol, 1.2 equiv) was added to a solution of linalool oxide (purchased from Aldrich as a mixture of isomers; 2.0 g, 11.75 mmol, 1.0 equiv) and pyridine (1.41 mL, 14.10 mmol, 1.2 equiv) in Et_2O (50 mL) and the resulting white suspension was stirred at room temperature for 16 hours. The reaction mixture was quenched with water (50 mL) and the organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 ml), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:19 → 1:9 EtOAc:hexanes) to give two diastereomers as clear oils. Eluted first was the desired *trans* isomer **S1.9** (973 mg, 30% yield): R_f = 0.24 (19:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.18 (dd, *J* = 17.3, 1.5 Hz, 1H), 4.99 (dd, *J* = 10.7, 1.5 Hz, 1H), 4.06 (dd, *J* = 7.4, 6.2 Hz, 1H), 3.85 (s, 3H), 2.04–1.76 (m, 4H), 1.58 (s, 3H), 1.55 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 156.7, 143.6, 111.6, 87.5, 83.92, 83.89, 53.4, 37.0, 26.60, 26.56, 22.4, 21.45; IR (ATR): 2979, 2881, 1765, 1740, 1327, 1203, 1174, 1147, 1128 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{21}O_5^+$ ($[M+H]^+$) 257.1384, found 257.1386 The *trans* stereochemistry was confirmed by an observed NOESY correlation between the vinyl group and the methine:



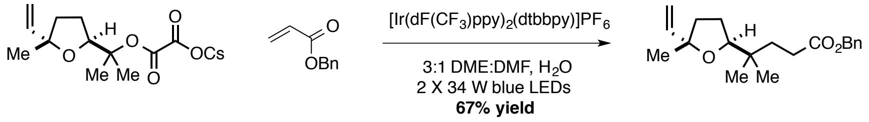
Eluted second was a fraction containing predominantly the *cis* isomer (**S1.10**) (1.04 g, 32% yield): R_f = 0.21 (19:1 hexanes:EtOAc, stained with $KMnO_4$) ^1H NMR (500 MHz, $CDCl_3$) δ 5.99 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.19 (dd, *J* = 17.3, 1.5 Hz, 1H), 4.97 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.11 (t, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 2.01–1.72 (m, 4H), 1.57 (s, 3H), 1.54 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 156.8, 144.0, 111.7, 87.4, 83.8, 83.6, 53.4, 37.7, 26.8, 25.7, 22.5, 21.6; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{21}O_5^+$ ($[M+H]^+$) 257.1384, found 257.1382. The *cis* stereochemistry was confirmed by an observed NOESY correlation between the methyl and methine groups:





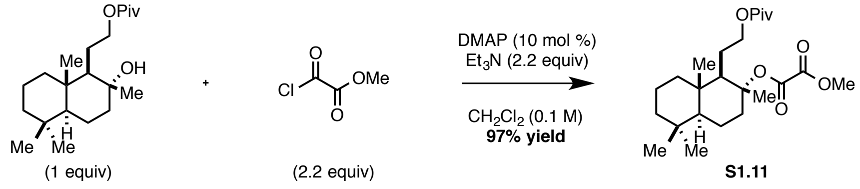
S1.9 (1.0 equiv) **1.93**

Preparation of cesium oxalate 1.93: CsOH•H_2O (328 mg, 1.95 mmol, 1.0 equiv) in water (5 mL) was added to linalool oxide-derived mixed oxalate **S1.9** (500 mg, 1.95 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for a further 5 min after addition had complete then concentrated to give the **1.93** as a colorless semi-solid that was not purified further (729 mg, 99% yield). ^{1}H NMR (500 MHz, D_2O) δ 5.93 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.19 (d, *J* = 17.4 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.29 (t, *J* = 6.8 Hz, 1H), 2.11–1.79 (4H, m), 1.51 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (126 MHz, D_2O) δ 165.3, 164.1, 143.12 142.8, 111.9, 107.8, 86.62, 84.62, 83.9, 67.7, 36.4, 26.1, 25.0, 21.4, 20.0; IR (ATR): 2977, 1719, 1627, 1385, 1371, 1213, 1121, 1096, 1027 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{17}O_5^-$ ([M–Cs]$^-$) 241.1082; found 241.1079.

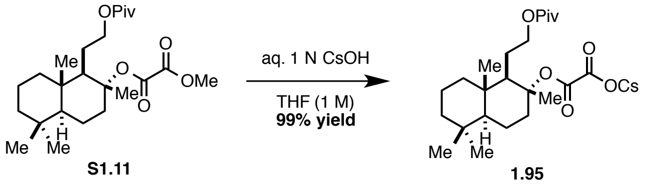


1.93 (1.1 equiv) (1.0 equiv) **1.94**

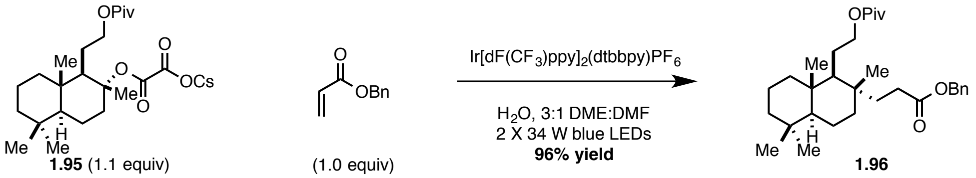
Preparation of ester 1.94: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.93** (281 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **1.94** as a pale yellow oil (105 mg, 67% yield): R_f = 0.51 (24:1 hexanes:EtOAc, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 5H), 5.85 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.16 (dd, *J* = 17.3, 1.6 Hz, 1H), 5.11 (s, 2H), 4.96 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.68 (t, *J* = 7.2 Hz, 1H), 2.45–2.35 (m, 2H), 1.87–1.60 (m, 6H), 1.27 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 144.3, 136.2, 128.7, 128.4, 128.3, 111.1, 85.7, 82.4, 66.3, 37.4, 35.9, 34.2, 29.7, 27.0, 26.4, 23.0, 22.3; IR (ATR): 2966, 2872, 1734, 1366, 1295, 1150, 1025 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{20}H_{29}O_3^+$ ($[M+H]^+$) 317.2111; found 317.2111.



Preparation of methyl oxalate 1.11: A round-bottom flask was charged with 2-((1*R*,2*R*,4*S*,8*S*)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate[26a] (340 mg, 1.0 mmol, 1.0 equiv) and CH_2Cl_2 (10 mL, 0.1M). Triethylamine (0.17 mL, 1.2 mmol, 1.2 equiv) and DMAP (12 mg, 0.1 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.11 mL, 1.2 mmol, 1.2 equiv). The homogeneous reaction mixture was maintained at 23 °C for 1 h. Additional triethylamine (140 µL, 1.0 mmol, 1.0 equiv) and methyl chlorooxalate (90 µL, 1.0 mmol 1.0 equiv) were added. The reaction was warmed to 35 °C and maintained at that temperature for 4 h. The reaction was quenched by slow addition of saturated aq. NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (10 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (9:1 hexanes:Et_2O) to give **S1.11** as colorless solid (410 mg, 97% yield). $R_f = 0.4$ (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 4.22 (qd, *J*= 8.0, 1.9 Hz, 1H), 4.11 (qd, *J* = 8.0, 1.9 Hz, 1H), 3.86 (s, 3H), 2.83−2.81 (m, 1H), 1.62 (s, 3H), 1.59 (br s, 2H), 1.49−1.46 (m, 1H), 1.40 (app d, *J* = 13.3 Hz, 1H), 1.29 (qd, *J* = 12.5, 3.1 Hz, 1H), 1.21 (s, 9H), 1.18 (td, *J* = 13.5, 4.1 Hz, 1H), 1.01 (dd, *J* = 14.1, 1.5 Hz, 1H), 0.96 (dd, *J* = 11.4, 3.6 Hz, 1H), 0.89 (s, 3H), 0.86 (s, 3H), 0.80 (S, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.8, 159.1, 156.2, 92.4, 65.8, 55.8, 55.5, 53.5, 42.0, 39.6, 39.3, 38.9, 33.5, 33.4, 27.5, 25.1, 21.6, 20.1, 18.5, 15.8; IR (thin film): 2935, 1762, 1733, 1721, 1164, 1127 cm^{-1}; $[\alpha]^{23}_{D}$ −2.83, $[\alpha]^{23}_{577}$ −3.12, $[\alpha]^{23}_{546}$ −3.78, $[\alpha]^{23}_{435}$ −6.30, $[\alpha]^{23}_{405}$ −7.96 (*c* = 1.00, MeOH); HRMS-ESI (*m/z*) $[M+Na]^+$ calculated for $C_{24}H_{40}O_6Na$, 447.2722; found, 447.2708.

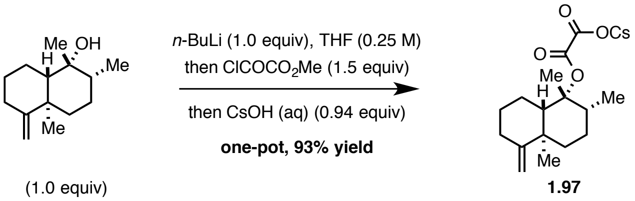


Preparation of cesium oxalate 1.95: A round-bottom flask was charged with methyl ((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy)ethyl)decahydronaphthalen-2-yl) oxalate (**S1.11**) (420 mg, 1.0 mmol, 1.0 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N aq. CsOH (1.0 mL, 1.0 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.95** as a colorless solid (540 mg, 99% yield). ^1H NMR (600 MHz, DMSO-d_6): δ 4.05–4.03 (m, 2H), 2.55–2.52 (m, 1H), 1.70–1.55 (m, 5H), 1.52–1.46 (m, 2H), 1.41 (s, 3H), 1.39–1.32 (m, 2H), 1.30–1.24 (m, 2H), 1.13 (s, 9H), 1.00–0.91 (m, 2H), 0.86 (app s, 4H), 0.76 (app d, *J* = 5.1 Hz, 5H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 177.4, 167.0, 163.1, 84.9, 65.6, 55.1, 54.3, 41.4, 38.4, 38.3, 38.1, 33.2, 32.8, 27.0, 24.6, 21.3, 20.3, 19.4, 17.9, 15.2; IR (thin film): 2956, 1762, 1718, 1635, 1161, cm^{-1} $[\alpha]^{23}_{D}$ −2.48, $[\alpha]^{23}_{577}$ −2.75, $[\alpha]^{23}_{546}$ −3.09, $[\alpha]^{23}_{435}$ −5.15, $[\alpha]^{23}_{405}$ −6.17 (*c* = 1.0, MeOH); HRMS-ESI (*m/z*) [M−Cs]$^-$ calculated for $C_{23}H_{37}O_6$, 409.2590; found, 409.2599.



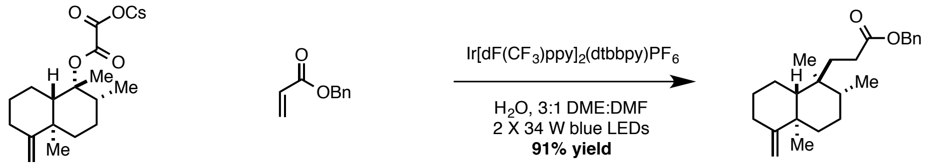
Preparation of ester 1.96: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy) ethyl) decahydro-naphthalen-2-yl)oxy)acetate (**1.95**) (209 mg, 0.39 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.0035 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (3.5 mL, 0.1M) was added, followed by water (54 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (54 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **1.96** as a yellow oil (162 mg, 96%

yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$; ^1H NMR (600 MHz, $CDCl_3$): δ 7.37−7.33 (m, 5H), 5.11 (s, 2H), 4.07−4.02 (m, 1H), 3.93−3.88 (m, 1H), 2.32 (t, *J* = 7.7 Hz, 2H), 1.81−1.75 (m, 1H), 1.68 (app d, *J* = 12.6 Hz, 1H), 1.60−1.55 (m, 2H), 1.53−1.50 (m, 2H), 1.43−1.38 (m, 3H), 1.33−1.26 (m, 3H), 1.20 (s, 9H), 1.14 (td, *J* = 12.9, 3.3 Hz, 2H), 0.90−0.88 (m, 1H), 0.87 (s, 3H), 0.85 (S, 3H), 0.83 (s, 3H), 0.80 (s, 3H), 0.72 (t, *J* = 3.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.8, 174.5, 136.3, 128.8, 128.5, 128.4, 66.5, 66.4, 56.5, 56.1, 42.2, 40.2, 39.3, 39.1, 38.8, 37.4, 33.5, 29.0, 27.5, 25.4, 22.6, 21.8, 19.3, 18.7, 18.5, 16.3, 14.3; $[\alpha]^{23}_{D}$ +1.16, $[\alpha]^{23}_{577}$ +1.67, $[\alpha]^{23}_{546}$ +1.82, $[\alpha]^{23}_{435}$ +3.45, $[\alpha]^{23}_{405}$ +4.02 (*c* = 1.0, MeOH); IR (thin film): 2921, 1734, 1720, 1252, 1166 cm^{-1}; HRMS-CI (*m/z*) $[M+NH_4]^+$ calculated for $C_{31}H_{52}NO_4$, 502.3896; found, 502.3884.



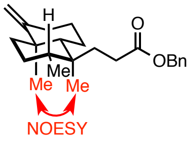
Preparation of (*rac*)-cesium oxalate 1.97: A round-bottom flask was charged with 3° alcohol[47] (233 mg, 1.12 mmol, 1.0 equiv) and THF (4.5 mL, 0.25 M) under an atmosphere of argon. The solution was stirred and cooled to –78 °C before a 2.5 M solution of *n*-BuLi in hexanes (450 µL, 1.12 mmol, 1.0 equiv) was added drop-wise. The solution was stirred for 15 min, then methyl chlorooxoacetate (160 µL, 1.68 mmol, 1.5 equiv) was added drop-wise. The reaction was stirred for 1 hour at –78 °C, then at cryogenic temperature as the dry ice bath slowly warmed to room temperature (2–3 h). The reaction was diluted with 5 mL of THF, and the organic extracts were washed (2X) with sat. $NaHCO_3$ (aq) (5 mL), then 1 X with 50% sat. brine (5 mL). The organic extracts were then treated with 0.5 M CsOH (aq)

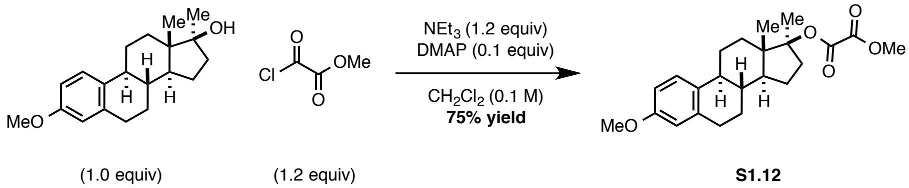
(2.1 mL, 1.05 mmol, 0.94 equiv), and the mixture was shaken until the intermediate methyl oxalate was consumed as judged by TLC (<5 min). Hexanes (10 mL) were added, and the aqueous phase was collected. The organic extracts were washed with a second portion of water (5 mL), and the combined aqueous phases were concentrated under reduced pressure to give **1.97** as a colorless solid (427 mg, 93% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 4.52 (d, *J* = 10.0 Hz, 2H), 2.30 (td, *J* = 16.2, 5.8 Hz, 1H), 2.05 (app d, *J* = 14.9 Hz, 1H), 1.93–1.86 (m, 2H), 1.65 (qd, *J* = 15.7 Hz, 3.4, 1H), 1.60–1.49 (m, 6H), 1.39–1.31 (m, 2H), 1.19 (qt, *J* = 15.9, 4.8 Hz, 1H), 1.10 (s, 3H), 1.04 (dd, *J* = 14.9, 2.9 Hz, 1H), 0.88 (d, *J* = 7.9 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.7, 158.8, 103.6, 83.9, 54.0, 43.2, 39.0, 36.7, 32.3, 27.9, 26.6, 22.8, 22.7, 20.2, 16.5; IR (thin film): 2394, 1670, 1608, 1214, 1160 cm^{-1}; HRMS-ESI (*m/z*) [M–Cs]$^-$ calculated for $C_{16}H_{23}O_4$, 279.1596; found, 279.1590.



1.97 (1.1 equiv) (1.0 equiv) **1.98**

Preparation of (*rac*)-ester 1.98: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*R*,8*S*)-1,2,4a-trimethyl-5-methylenedecahydronaphthalen-1-yl)oxy)acetate (**1.97**) (137 mg, 0.39 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.9 mg, 0.0035 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (3.5 mL, 0.1M) was added, followed by water (63 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (54 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **1.98** as a yellow oil (113 mg, 91% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.33 (m, 5H), 5.11 (s, 2H), 4.50 (s, 2H), 2.31–2.21 (m, 2H), 2.16–2.09 (m, 2H), 1.88–1.85 (m, 1H), 1.74–1.64 (m, 2H), 1.63–1.55 (m, 2H), 1.51–1.47 (m, 1H), 1.46–1.42 (m, 1H), 1.37–1.31 (m, 1H), 1.29–1.24 (m, 1H), 1.05 (s, 3H), 0.96 (dd, *J* = 14.8, 2.7 Hz, 1H), 0.88–0.83 (m, 2H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 160.6, 136.3, 128.8, 128.5, 128.4, 102.8, 66.4, 49.0, 40.2, 39.2, 37.4, 37.0, 33.2, 32.9, 28.8, 28.5, 27.6, 21.8, 21.0, 18.1, 16.2; IR (thin film): 2924, 1734, 1456, 1158, 889 cm^{-1}; HRMS-CI (*m*/*z*) $[M+NH_4]^+$ calculated for $C_{24}H_{38}NO_2$, 372.2903; found, 372.2893. Product stereochemistry was confirmed by a NOESY correlation:

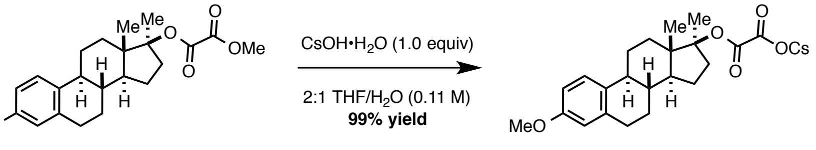




S1.12

Preparation of methyl oxalate S1.12: Methyl chlorooxoacetate (514 µL, 4.19 mmol, 1.2 equiv) was added to a solution of the known sterol[26a] (1.05 g, 3.50 mmol, 1.0 equiv), triethylamine (424 µL, 4.19 mmol, 1.2 equiv), and DMAP (43 mg, 0.35 mmol, 0.1 equiv) in CH_2Cl_2 (35 mL) and the resulting yellow solution was maintained at room temperature for

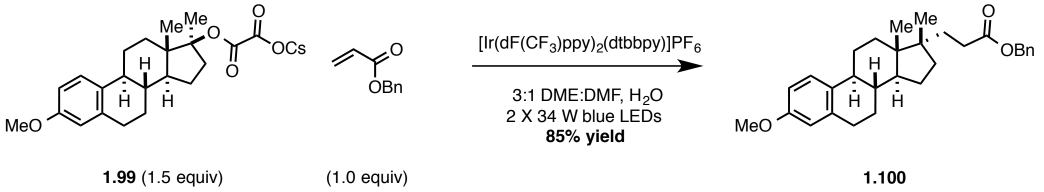
5 hours. Water (50 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were washed with water (50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:9 → 1:4 EtOAc:hexanes) to give **S1.12** as a sticky colorless foam (1.01 g, 75% yield): R_f = 0.49 (9:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 2.92–2.81 (m, 2H), 2.37–2.31 (m, 1H), 2.25–1.16 (m, 3H), 1.92–1.88 (s, 2H), 1.79–1.71 (m, 1H), 1.62 (dt, *J* = 12.7, 3.8 Hz, 1H), 1.56 (3H, s), 1.54–1.47 (m, 2H), 1.45–1.37 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 157.5, 157.0, 137.9, 132.3, 126.3, 113.8, 111.5, 95.0, 55.2, 53.3, 48.2, 47.1, 43.7, 39.3, 36.3, 32.0, 29.8, 27.5, 26.2, 23.3, 21.2, 14.3; IR (ATR): 2989, 2942, 2877, 2841, 2808, 1757, 1738, 1323, 1205, 1171, 1144, 1037 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{23}H_{31}O_5^+$ ($[M+H]^+$) 387.2166, found 387.2164.



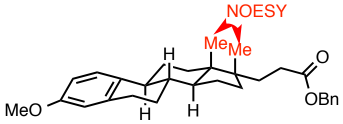
S1.12 (1.0 equiv)

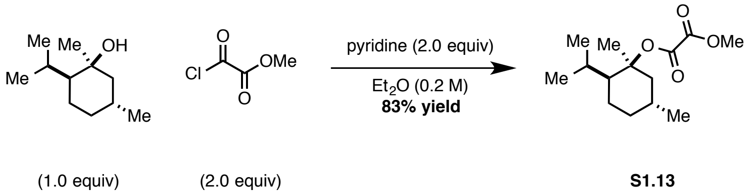
1.99

Preparation of cesium oxalate 1.99: $CsOH \bullet H_2O$ (367 mg, 2.24 mmol, 1.0 equiv) in water (5 mL) was added to estrone-derived mixed oxalate **S1.12** (867 mg, 2.24 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for a further 5 min after addition had completed then concentrated to give **1.99** as an off-white solid that was dried *in vacuo* but not purified further (1.13 g, 99% yield). ^1H NMR (500 MHz, DMSO-*d6*) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.61 (d, *J* = 2.7Hz, 1H), 3.69 (s, 3H), 2.84–2.74 (m, 2H), 2.32–2.29 (m, 1H), 2.15–2.12 (m, 1H), 2.01 (t, *J* = 7.7 Hz, 2H), 1.83–1.80 (m, 1H), 1.74 (dt, *J* = 12.1, 2.9 Hz, 1H), 1.64 (dq, *J* = 13.6, 6.0 Hz, 1H), 1.55 (td, *J* = 12.8, 3.8 Hz, 1H), 1.40 (s, 3H), 1.39–1.27 (m, 5H), 0.81 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d6*) δ 167.4, 163.6, 157.0, 137.4, 132.1, 126.2, 113.4, 111.5, 88.8, 54.9, 47.7, 46.4, 43.1, 39.8, 39.0, 36.6, 31.9, 29.3, 27.0, 26.0, 22.9, 21.4, 14.0; IR (ATR): 2977, 2939, 2867, 1705, 1610, 1227, 1209, 1148, 1039 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{22}H_{27}O_5^-$ ([M–Cs]$^-$) 371.1864; found 371.1863.

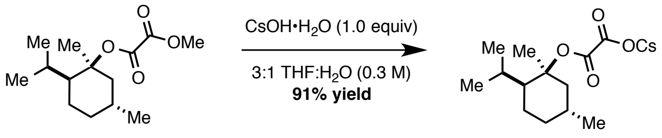


Preparation of ester 1.100: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.99** (378 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et$_2$O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **1.100** as an off-white solid (190 mg, 85% yield): R$_f$ = 0.45 (12:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.27–7.20 (m, 5H), 7.10 (d, *J* = 8.6 Hz, 1H), 6.60 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.52 (d, *J* = 2.6 Hz, 1H), 5.02 (s, 2H), 3.66 (s, 3H), 2.80–2.70 (m, 2H), 2.33–2.22 (m, 2H), 2.20–2.16 (m, 1H), 2.09–2.04 (m, 1H), 1.79–1.75 (m, 1H), 1.64–1.33(m, 9H), 1.31–1.21 (m, 2H), 1.18–1.09 (m, 1H), 0.77 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 157.3, 138.0, 136.0, 132.9, 128.5, 128.2, 128.1, 126.2, 113.7, 111.3, 66.2, 55.1, 49.3, 45.8, 45.3, 43.6, 39.4, 33.2, 31.7, 31.6, 30.5, 29.9, 28.1, 26.2, 24.6, 20.4, 16.1; IR (ATR): 2933, 2869, 1733, 1608, 1298, 1279, 1254, 1235, 1154, 1037 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{30}H_{39}O_3^+$ ($[M+H]^+$) 447.2894; found 447.2895. The configuration at the newly formed stereocenter was determined by NOESY experiments where a strong interaction between the two methyl groups was observed:[48]



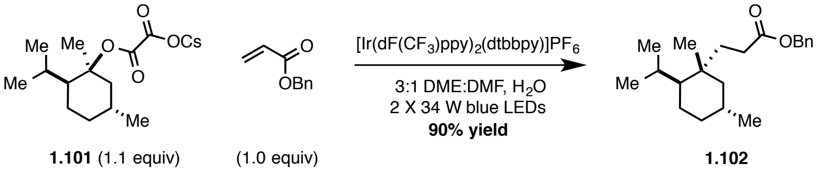


Preparation of methyl oxalate S1.13: Methyl chlorooxoacetate (1.08 mL, 11.74 mmol, 2 equiv) was added to a solution of the known alcohol[49] (4:1 mixture of diastereomers; major shown; 1.00 g, 5.87 mmol, 1.0 equiv) and pyridine (0.95 mL, 11.74 mmol, 2 equiv) in Et_2O (50 mL) and the resulting yellow solution was stirred at room temperature for 2 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:24 EtOAc:hexanes) to give **S1.13** as a clear oil (4:1 mixture of diastereomers; 1.23 g, 83% yield): R$_f$ = 0.51 (19:1 hexanes:EtOAc, stained with KMnO$_4$). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.88 (s, 3H), 2.76 (dt, *J* = 14.4, 2.9 Hz, 1H), 2.25–2.18 (m, 1H), 1.83–1.77 (m, 1H), 1.63 (s, 3H), 1.60–1.45 (m, 4H), 1.08 (ddd, *J* = 11.7, 4.3, 1.8 Hz, 1H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.92 (dd, *J* = 12.5, 4.7 Hz, 1H) 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 159.0, 156.5, 89.2, 53.2, 52.6, 43.8, 34.8, 28.0, 26.1, 24.22, 23.8, 22.0, 17.6; IR (ATR): 2954, 2871, 1765, 1738, 1201, 1172, 1101 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{14}H_{25}O_4^+$ ([M+H]$^+$) 257.1747; found 257.1746.

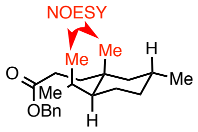


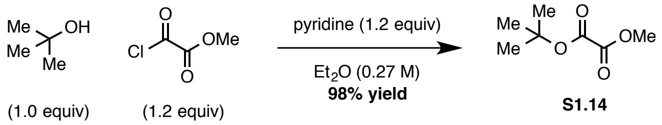
S1.13 (1.0 equiv) **1.101**

Preparation of cesium oxalate 1.101: CsOH•H$_2$O (1.05 g, 6.24 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.13** (1.60 g, 6.24 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 10 mL) and dried *in vacuo* to give **1.101** as a colorless solid that was used without further purification (1.56 g, 91% yield). ^{1}H NMR (500 MHz, D$_2$O) δ 2.56–2.55 (m, 1H), 2.22–2.14 (m, 1H), 1.76–1.73 (m, 1H), 1.56 (s, 3H), 1.53–1.37 (m, 4H), 1.14–1.11 (m, 1H), 1.04 (t, *J* = 12.4 Hz, 1H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz), 0.82 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, D$_2$O) δ 166.7, 165.6, 88.47, 88.46, 51.8, 43.8, 40.0, 34.3, 30.4, 27.7, 25.9, 25.5, 23.8, 22.9, 21.4, 20.2, 17.1; IR (thin film) 2952, 2868, 1711, 1629, 1153, 1190, 1153 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{21}O_4^-$ ([M–Cs]$^-$) 241.1445; found 241.1446.

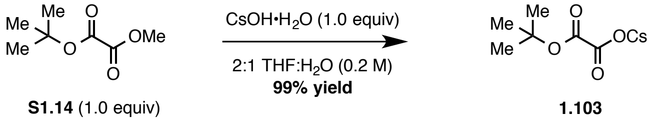


Preparation of ester 1.102: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.101** (206 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **1.102** as a pale yellow oil (142 mg, 90% yield): R_f = 0.59 (19:1 hexanes:EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 5H), 5.12 (s, 2H), 2.33–2.26 (m, 2H), 1.95–1.87 (m, 1H), 1.79–1.59 (m, 3H), 1.53–1.43 (m, 2H), 1.31–1.21 (m, 2H), 1.11–0.92 (m, 2H), 0.90–0.87 (7H, m), 0.81 (d, *J* = 6.4 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 136.2, 128.7, 128.4, 128.3, 66.3, 48.9, 48.0, 37.4, 35.9, 28.9, 28.3, 25.3, 24.9, 23.1, 21.9, 20.6, 18.6; IR (ATR): 2951, 2923, 2866, 1735, 1455, 1157 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{33}O_2^+$ ([M+H]$^+$) 317.2475; found 317.2475. Product stereochemistry was confirmed by a NOESY correlation:

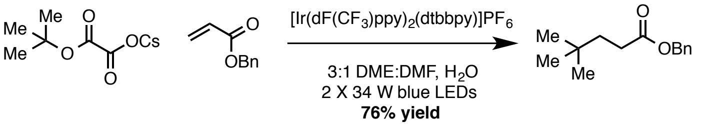




Preparation of methyl oxalate S1.14: Methyl chlorooxoacetate (2.98 mL, 32.38 mmol, 1.2 equiv) was added to a solution of *tert*-butanol (2.56 mL, 26.98 mmol, 1.0 equiv) and pyridine (3.24 mL, 32.38 mmol, 1.2 equiv) in Et_2O (100 mL) and the resulting yellow solution was maintained at room temperature for 4 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:19 – 1:9 Et_2O:hexanes) to give **S1.14** as a clear oil (4.26 g, 98% yield): $R_f = 0.41$ (10:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 156.9, 85.2, 53.4, 27.8; IR (ATR): 1981, 1760, 1737, 1371, 1327, 1211, 1137 cm^{-1}. Data match those previously reported.[50]

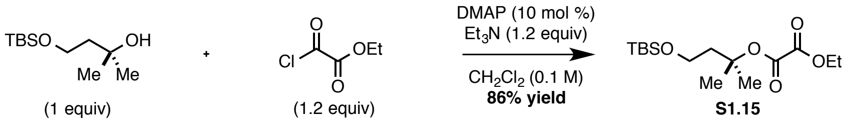


Preparation of cesium oxalate 1.103: $CsOH•H_2O$ (1.05 g, 6.24 mmol, 1.0 equiv) in water (10 mL) was added to *tert*-butyl methyl oxalate **S1.14** (1.00 g, 6.24 mmol, 1.0 equiv) in THF (20 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was dried *in vacuo* to give **1.103** that was used without further purification (1.73 g, 99% yield). ^{1}H NMR (500 MHz, D_2O) δ 1.50 (s, 9H); ^{13}C NMR (126 MHz, D_2O) δ 165.4, 164.1, 84.2, 27.0; IR (ATR): 2975, 1721, 1634, 1364, 1222, 1148, 1033 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_6H_9O_4^-$ ([M–Cs]$^-$) 145.0506; found 145.0506.

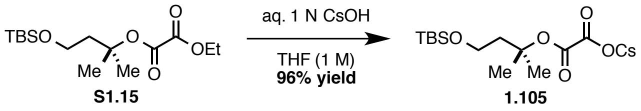


1.103 (1.1 equiv) (1.0 equiv) **1.104**

Preparation of ester 1.104: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with *tert*-butyl cesium oxalate **1.103** (153 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **1.104** as a pale yellow oil (84 mg, 76% yield): R_f = 0.48 (19:1 hexanes:EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.23 (m, 5H), 5.03 (s, 2H), 2.26 (t, *J* = 8.5 Hz, 2H), 1.50 (t, *J* = 8.5 Hz, 2H), 0.81 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 136.1, 128.6, 128.3, 128.2, 66.2, 38.5, 30.1, 29.0; IR (ATR): 3035, 2955, 2867, 1734, 1138 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{14}H_{20}NaO_2^+$ ([M+Na]$^+$) 243.1356; found 243.1355. Data match those previously reported in the literature.[51]

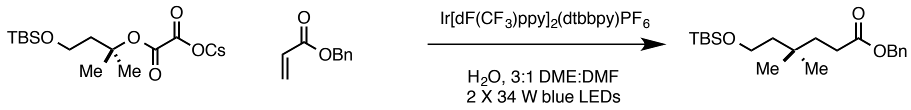


Preparation of ethyl oxalate S1.15: A round-bottom flask was charged with 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-ol[26a] (2.4 g, 11 mmol, 1.0 equiv) and CH_2Cl_2 (110 mL, 0.1M). Triethylamine (0.35 mL, 2.4 mmol, 1.2 equiv) and DMAP (25 mg, 0.62 mmol, 0.1 equiv) were added followed by drop-wise addition of ethyl chlorooxoacetate (1.5 mL, 13 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (9:1 hexanes:EtOAc) to give **S1.15** as clear oil (3.0 g, 86% yield). R_f = 0.55 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 4.32 (q, *J* = 7.2 Hz, 2H), 3.76 (t, *J* = 6.6 Hz, 2H), 2.11 (t, *J* = 6.6 Hz, 2H), 1.58 (s, 6H), 1.36 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7, 157.2, 86.5, 63.0, 59.1, 43.1, 26.4, 26.1, 18.4, 14.1; IR (thin film): 2930, 1764, 1739, 1186, 834 cm^{-1}; HRMS-ESI (*m/z*) [M+H]$^+$ calculated for $C_{15}H_{31}O_5Si$, 319.1941; found, 319.1933.



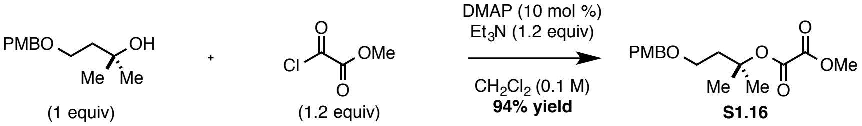
Preparation of cesium oxalate 1.105: A round-bottom flask was charged with 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**S1.15**) (1.6 g, 5.0 mmol, 1.0

equiv) followed by the addition of THF (5.0 mL, 1 M). To this solution, 1 N aq. CsOH (5.0 mL, 5.0 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.105** as a colorless solid (2.1 g, 96% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 3.65 (t, *J* = 7.2 Hz, 2H), 1.94 (t, *J* = 6.6 Hz, 2H), 1.37 (s, 6H), 0.86 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.4, 163.4, 79.4, 58.7, 42.6, 26.5, 25.8, 17.8, −5.3; IR (thin film): 2930, 1722, 1633, 1207, 770 cm^{-1}; HRMS-ESI (*m/z*) [M−Cs]$^-$ calculated for $C_{13}H_{25}O_5Si$, 289.1471; found, 289.1464.



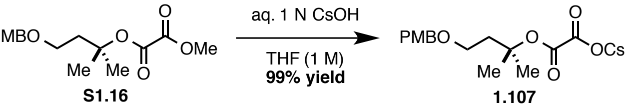
1.105 (1.1 equiv) (1.0 equiv) **1.106**

Preparation of ester 1.106: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**1.106**) (233 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et$_2$O) to give **1.106** as a yellow oil (167 mg, 92% yield). R$_f$ = 0.5 (9:1 hexanes:acetone); visualized with KMnO$_4$. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.38–7.35 (m, 5H), 5.12 (s, 2H), 3.66 (t, *J* = 7.5 Hz, 2H), 2.35 (t, *J* = 8.5 Hz, 2H), 1.60 (t, *J* = 6.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 2H), 0.89 (s, 15H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 136.3, 128.8, 128.5, 128.4, 66.4, 60.1, 44.1, 37.1, 32.1, 29.8, 27.3, 26.2, 18.5, −5.1; IR (thin film): 2955, 2928, 1737, 1091, 834 cm^{-1}; HRMS-CI (*m*/*z*) $[M+H]^+$ calculated for $C_{21}H_{37}O_3Si$, 365.2512; found, 365.2515.

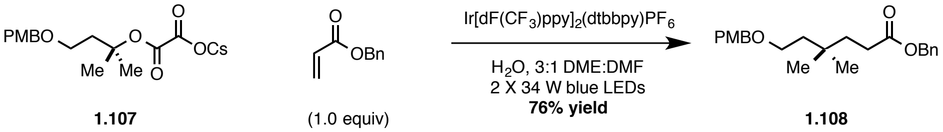


S1.16

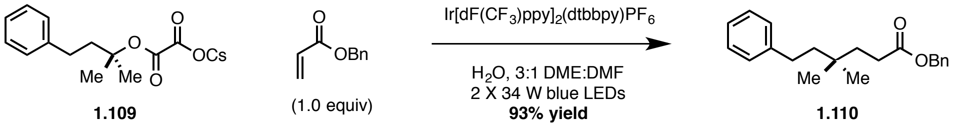
Preparation of methyl oxalate S1.16: A round-bottom flask was charged with 4-((4-methoxybenzyl)oxy)-2-methylbutan-2-ol[26a] (1.9 g, 8.3 mmol, 1.0 equiv) and CH_2Cl_2 (83 mL, 0.1M). Triethylamine (1.4 mL, 9.9 mmol, 1.2 equiv) and DMAP (100 mg, 0.83 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.9 mL, 9.9 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (4:1 hexanes:Et_2O) to give **S1.16** as a clear oil (2.4 g, 95% yield). R_f = 0.4 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 (d, *J* = 10.2 Hz, 2H), 6.88 (d, *J* = 10.2 Hz, 2H), 4.42 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H), 3.58 (t, *J* = 7.8 Hz, 2H), 2.19 (t, *J* = 7.8 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3, 159.1, 156.9, 130.5, 129.4, 114.0, 86.4, 72.9, 66.0, 55.5, 53.5, 39.9, 26.4; IR (thin film): 1762, 1738, 1512, 1203, 1131 cm^{-1}; HRMS-ESI (*m*/*z*) $[M+Na]^+$ calculated for $C_{16}H_{22}O_6Na$, 333.1314; found, 333.1326.



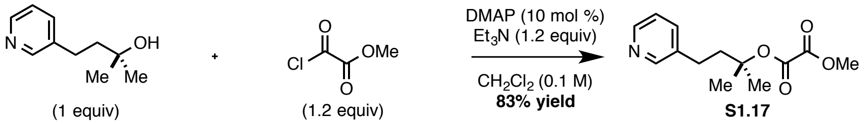
Preparation of cesium oxalate 1.107: A round-bottom flask was charged with methyl 4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl methyl oxalate (**S1.16**) (2.3 g, 7.4 mmol, 1.0 equiv) followed by the addition of THF (7.4 mL, 1 M). To this solution, 1 N aq. CsOH (7.4 mL, 7.4 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.107** as a colorless solid (2.7 g, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.23 (d, *J* = 10.2 Hz, 2H), 6.89 (d, *J* = 10.2 Hz, 2H), 4.35 (s, 2H), 3.73 (s, 3H), 3.48 (t, *J* = 8.4 Hz, 2H), 2.01 (t, *J* = 8.4 Hz, 2H), 1.38 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.4, 163.4, 158.6, 130.5, 129.1, 113.6, 79.4, 71.6, 65.6, 55.0, 39.6, 26.4; IR (thin film): 1720, 1634, 1513, 1243, 1139 cm^{-1}; HRMS-ESI (*m*/*z*) [M−Cs]$^-$ calculated for $C_{15}H_{19}O_6$, 295.1182; found, 295.1183.



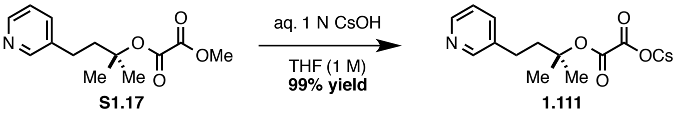
Preparation of ester 1.108: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**1.107**) (236 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv) and benzyl acrylate (77 μL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **1.108** as a yellow oil (140 mg, 76% yield). R_f = 0.4 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 7.37–7.34 (m, 5H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 5.12, (s, 2H), 4.42 (s, 2H), 3.81 (s, 3H), 3.51 (t, *J* = 6.6 Hz, 2H), 2.35 (t, *J* = 7.8 Hz, 2H), 1.61 (t, *J* = 8.4 Hz, 2H), 1.58–1.56 (m, 2H), 0.91 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3, 159.3, 136.2, 130.8, 129.4, 128.8, 128.4, 114.0, 72.9, 67.1, 66.4, 55.5, 40.9, 37.1, 32.1, 29.8, 27.3; IR (thin film): 2955, 1733, 1512, 1245, 1033 cm^{-1}; HRMS-CI (*m/z*) $[M+NH_4]^+$ calculated for $C_{23}H_{34}NO_4$, 388.2488; found, 388.2482.



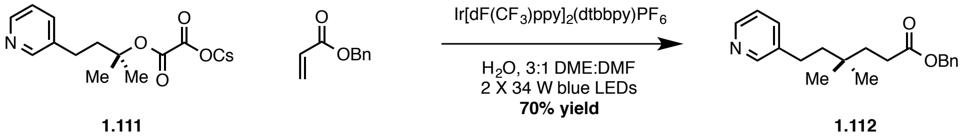
Preparation of ester 1.110: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetate (**1.109**) (167 mg, 0.55 mmol, 1.1 equiv) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et_2O) to give **1.110** as a yellow oil (113 mg, 93% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38−7.34 (m, 5H), 7.30−7.27 (m, 2H), 7.19−7.17 (m, 3H), 5.13 (s, 2H), 2.57 (t, *J* = 5.0 Hz, 2H), 2.37 (t, *J* = 8.0 Hz, 2H), 1.67 (t, *J* = 8.5 Hz, 2H), 1.51 (t, *J* = 5.0 Hz, 2H), 0.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 143.3, 136.2, 128.8, 128.6, 128.5, 128.46, 128.4, 125.8, 66.5, 44.2, 36.5, 32.9, 32.9, 30.8, 29.8, 26.9; IR (thin film): 2955, 1733, 1258, 1151, 656 cm^{-1}; HRMS-CI (*m/z*) $[M+Na]^+$ calculated for $C_{21}H_{26}O_2Na$, 333.1830; found, 333.1838.



Preparation of methyl oxalate S1.17: A round-bottom flask was charged with 2-methyl-4-(pyridin-3-yl)butan-2-ol(120 mg, 0.73 mmol, 1.0 equiv) and CH_2Cl_2 (7.5 mL, 0.1M). Triethylamine (0.12 mL, 0.88 mmol, 1.2 equiv) and DMAP (9 mg, 0.073 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.08 mL, 0.88 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH_4Cl (aq) (20 mL). The aqueous phase was extracted with CH_2Cl_2 (20 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 CH_2Cl_2:MeOH) to give **S1.17** as a clear oil (150 mg, 83% yield). R_f = 0.3 (19:1 CH_2Cl_2:MeOH); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 8.45 (s, 2H), 7.49 (br s, *J* = 6.6 Hz, 1H), 7.20 (d, *J* = 4.8 Hz, 1H), 3.86 (s, 3H), 2.70−2.67 (m, 2H), 2.15−2.12 (m, 2H), 1.60 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2, 157.1, 150.3, 148.0, 137.1, 136.2, 123.8, 86.7, 53.7, 42.4, 27.7, 26.1; IR (thin film): 3406, 2954, 1764, 1740, 1201 cm^{-1}; HRMS-ESI (*m/z*) [M+Na]$^+$ calculated for $C_{13}H_{17}NO_4Na$, 274.1055; found, 274.1048.

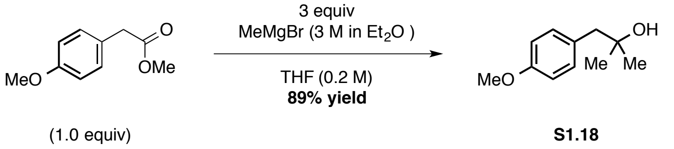


Preparation of cesium oxalate 1.111: A round-bottom flask was charged with methyl (2-methyl-4-(pyridin-3-yl)butan-2-yl) oxalate (**S1.17**) (190 mg, 0.74 mmol, 1.0 equiv) followed by the addition of THF (0.75 mL, 1 M). To this solution, 1 N aq. CsOH (0.75 mL, 0.75 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.111** as a beige solid (270 mg, 99% yield). ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 8.41 (d, *J* = 1.8 Hz, 1H), 8.38 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.29 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.50 (t, *J* = 1.8 Hz, 2H), 2.00 (t, *J* = 4.8 Hz, 2H), 1.42 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.4, 149.5, 147.1, 137.6, 135.6, 123.5, 79.7, 41.6, 26.6, 26.1; IR (thin film): 3430, 2974, 1739, 1721, 1189 cm^{-1}; HRMS-ESI (*m/z*) [M−Cs]$^-$ calculated for $C_{12}H_{14}NO_4$, 236.0923; found, 236.0922.

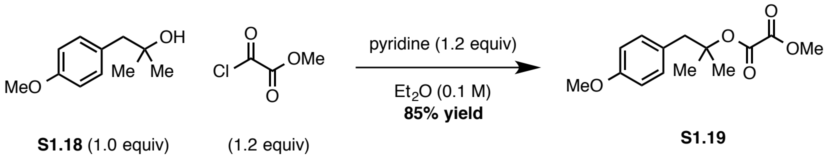


Preparation of ester 1.112: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((2-methyl-4-(pyridin-3-yl)butan-2-yl)oxy)-2-oxoacetate (**1.111**) (120 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (5.6

mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 hexanes:Et_2O) to give **1.112** as a yellow oil (76 mg, 70% yield). R_f = 0.4 (1:1 hexanes:EtOAc); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, *J* = 5.5 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.45–7.28 (m, 5H), 7.27 (dd, *J* = 8.0, 5.0 Hz, 1H), 5.20 (s, 2H), 2.63 (t, *J* = 5.0 hz, 2H), 2.43 (t, *J* = 8.5 Hz, 2H), 1.75 (t, *J* = 6.0 Hz, 2H), 1.56 (t, *J* = 8.5 Hz, 2H), 1.03, (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.2, 150.0, 147.4, 138.4, 136.1, 135.9, 128.8, 128.5, 128.4, 123.5, 66.5, 43.9, 36.4, 32.9, 29.8, 28.0, 26.8; IR (thin film): 3430, 2960, 1739, 1569, 1233, 1090 cm^{-1}; HRMS-CI (*m/z*) $[M+H]^+$ calculated for $C_{20}H_{26}NO_2$, 312.1964; found, 312.1953.

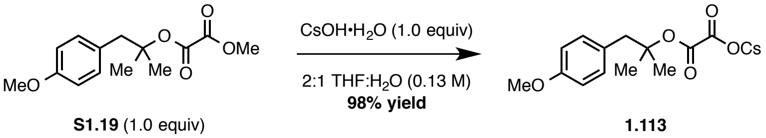


Preparation of tertiary alcohol S1.18: A solution of methyl phenylacetate (1.75 mL, 11.09 mmol, 1.0 equiv) in THF (50 mL) was added dropwise to a 0 °C solution of methyl magnesium bromide (3 M in Et_2O; 11.0 mL, 33.29 mmol, 3 equiv) over 20 min. After addition had completed, the resulting yellow solution was warmed to rt, stirred for 6 hours, quenched with saturated aqueous NH_4Cl solution (50 mL) and diluted with Et_2O (50 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined ethereal extracts were washed with brine (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (3:7 EtOAc:hexanes) to give **S1.18** as a colorless oil (1.78 g, 89% yield): R_f = 0.21 (4:1 hexanes:EtOAc, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 2.73 (s, 2H), 1.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 131.4, 129.8, 113.6, 70.8, 55.2, 48.8, 29.1; IR (ATR): 3351, 2970, 2908, 2847, 1715, 1632, 1211, 1181, 1051 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{11}H_{17}O_2^+$ ($[M+H]^+$) 181.1223; found 181.1224.

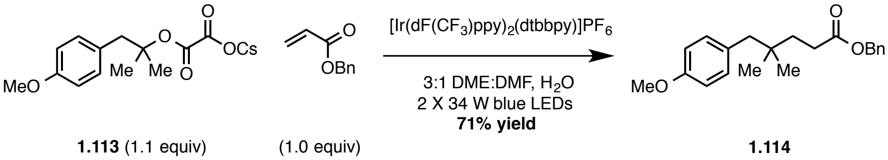


Preparation of methyl oxalate S1.19: Methyl chlorooxoacetate (1.02 mL, 11.05 mmol, 1.2 equiv) was added to a solution of 1-(4-methoxyphenyl)-2-methylpropan-2-ol **S1.18** (1.77 g, 9.21 mmol, 1.0 equiv) and pyridine (1.11 mL, 11.05 mmol, 1.2 equiv) in Et_2O (100 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:9 EtOAc:hexanes) to give **S1.19** as a colorless oil (2.08 g, 85% yield): R_f = 0.34 (9:1 hexanes:EtOAc, stained with $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.79

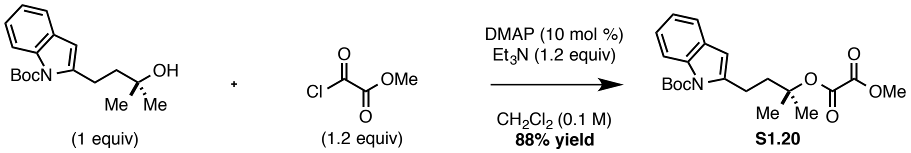
(s, 3H), 3.04 (s, 2H), 1.52 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 158.5, 156.7, 313.6, 128.3, 113.5, 55.2, 53.3, 45.8, 25.3; IR (ATR): 2907, 2847, 1716, 1632, 1210, 1199, 1051 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{11}H_{17}O_2^+$ ([M+H]$^+$) 267.1227, found 267.1230.



Preparation of cesium oxalate 1.113: CsOH•H_2O (315 mg, 1.88 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.19** (500 mg, 1.88 mmol, 1.0 equiv) in THF (10 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure to give **1.113** as a colorless solid that was used without further purification (522 mg, 98% yield). ^{1}H NMR (500 MHz, D_2O) δ 7.21–7.19 (m, 2H), 6.94–6.92 (m, 2H), 3.79 (s, 3H), 3.08 (s, 2H), 1.45 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 164.3, 157.5, 131.7, 129.7, 113.6, 85.8, 55.3, 43.9, 25.1; IR (ATR): 2907, 2847, 1715, 1632, 1210, 1188, 1051 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{13}H_{15}O_5^-$ ([M–Cs]$^-$) 251.0925; found 251.0925.

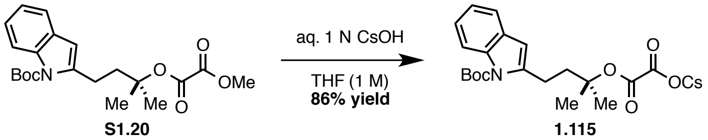


Preparation of ester 1.114: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.113** (211 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 – 9:1 hexanes:EtOAc) to give **1.114** as a colorless film (116 mg, 71% yield): R_f = 0.67 (19:1 hexanes:EtOAc, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.35 (m, 5H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.12 (s, 2H), 3.79 (s, 3.79), 2.45 (s, 2H), 2.39 (t, *J* = 8.4 Hz, 2H), 1.60 (t, *J* = 8.4 Hz, 2H), 0.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 157.9, 136.1, 131.4, 130.8, 128.6, 128.2, 113.2, 66.3, 55.2, 47.4, 36.5, 33.9, 29.8, 26.3; IR (ATR): 3005, 2970, 2954, 1736, 1510, 1368, 1230, 1216 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{27}O_3^+$ ($[M+H]^+$) 327.1955, found 327.1956.

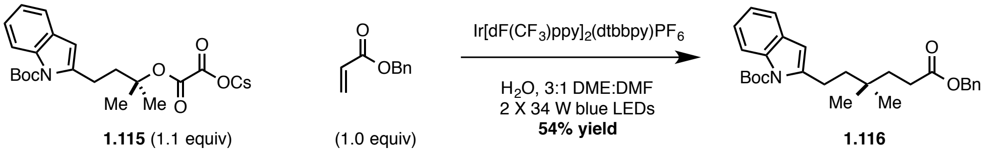


Preparation of methyl oxalate S1.20: A round-bottom flask was charged with *tert*-butyl 2-(3-hydroxy-3-methylbutyl)-1*H*-indole-1-carboxylate[26a] (930 mg, 3.1 mmol, 1.0 equiv) and CH_2Cl_2 (31 mL, 0.1M). Triethylamine (0.51 mL, 3.7 mmol, 1.2 equiv) and DMAP (37 mg, 0.31 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.34 mL, 3.7 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23

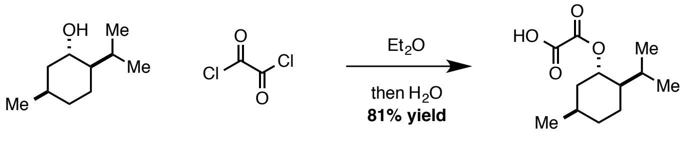
°C, then quenched with sat. NH_4Cl (aq) (100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the organic extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et_2O) to give **S1.20** as a colorless oil (2.4 g, 95% yield). R_f = 0.3 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.38 (br s, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 3.89 (s, 3H), 2.28 (t, *J* = 8.5 Hz, 2H), 2.25 (t, *J* = 8.5 Hz, 2H), 1.68–1.66 (app d, 15H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 156.9, 150.0, 135.8, 130.6, 124.6, 122.6, 122.4, 120.4, 119.1, 115.5, 86.9, 83.6, 53.5, 40.4, 28.4, 25.8, 19.5; IR (thin film): 1754, 1733, 1721, 1451, 1117 cm^{-1}; HRMS-ESI (*m*/*z*) $[M+Na]^+$ calculated for $C_{21}H_{27}NO_6Na$, 412.1736; found, 412.1748.



Preparation of cesium oxalate 1.115: A round-bottom flask was charged with 4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl methyl oxalate (**S1.20**) (1.0 g, 2.6 mmol, 1.0 equiv) followed by the addition of THF (2.6 mL, 1 M). To this solution, 1 N aq. CsOH (2.6 mL, 2.6 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.115** as a colorless solid (1.1 g, 86% yield). ^1H NMR (600 MHz, DMSO-d_6): δ 8.04 (d, *J* = 9.6 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.41 (s, 1H), 7.31 (t, *J* = 9.0 Hz, 1H), 7.24 (t, *J* = 9.0 Hz, 1H), 2.67 (t, *J* = 10.2 Hz, 2H), 2.09 (t, *J* = 10.8 Hz, 2H), 1.61 (s, 9H), 1.45 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 167.7, 163.5, 149.1, 134.9, 130.2, 124.3, 122.4, 122.0, 120.9, 119.4, 114.7, 83.4, 79.8, 39.4, 27.7, 26.1, 18.7; IR (thin film): 2986, 1754, 1722, 1206, 1152, 748 cm^{-1}; HRMS-ESI (*m/z*) [M−Cs]$^-$ calculated for $C_{20}H_{24}NO_6$, 374.1604; found, 374.1608.

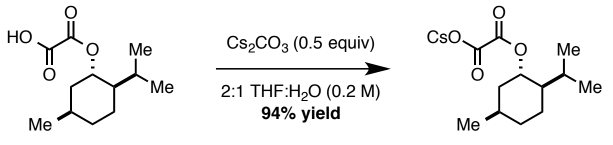


Preparation of ester 1.116: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**1.115**) (195 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et_2O) to give **1.116** as a yellow oil (85 mg, 54% yield). R_f = 0.2 (9:1 hexanes:acetone); visualized with $KMnO_4$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (br s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.38–7.30 (m, 7H), 7.25–7.23 (m, 1H), 5.13, (s, 2H), 2.64 (t, *J* = 8.5 Hz, 2H), 2.38 (t, *J* = 8.0 Hz, 2H), 1.71 (t, *J* = 8.5 Hz, 2H), 1.68 (s, 9H), 1.61 (t, *J* = 9.0 Hz, 2H), 1.00 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3, 150.0, 136.2, 130.8, 128.8, 128.6, 128.5, 128.4, 124.4, 122.5, 122.1, 121.8, 119.0, 115.5, 83.4, 66.5, 41.4, 36.5, 32.8, 29.8, 28.5, 26.8, 19.7; IR (thin film): 2955, 1727, 1452, 1368, 1153 cm^{-1}; HRMS-CI (*m*/*z*) [M–Boc+H]$^+$ calculated for $C_{23}H_{28}NO_2$, 350.2120; found, 350.2129.



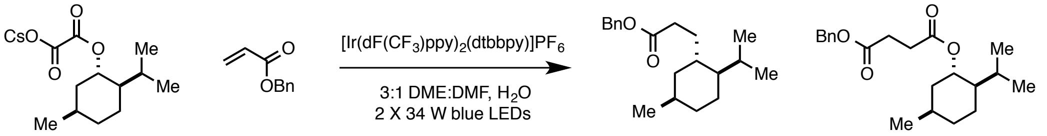
S1.21

Preparation of acid S1.21: (+)-Isomenthol (2.0 g, 12.80 mmol, 1.0 equiv) in Et_2O (100 mL) was added dropwise over 20 min to a 0 °C solution of oxalyl chloride (2.17 mL, 25.60 mmol, 2.0 equiv) in Et_2O. The resulting pale yellow solution was stirred at 0 °C for 2 hours then concentrated under reduced pressure. Unreacted oxalyl chloride was removed *in vacuo* and the resulting yellow oil was redissolved in Et_2O (50 mL) and carefully treated with water (50 mL). The biphasic reaction mixture was stirred vigorously for 1 hour and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 50 mL) and the combined ethereal extracts were washed with water (2 x 100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated to give **S1.21** as a clear oil that was used without further purification (2.36 g, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (br s, 1H), 5.23–5.19 (m, 1H), 1.99–1.93 (m, 1H), 1.80–1.71 (m, 2H), 1.68–1.62 (m, 1H), 1.60–1.45 (m, 4H), 1.30–1.21 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 157.8, 77.3, 45.4, 35.3, 29.7, 27.4, 26.2, 20.8, 20.6, 20.3, 18.9; IR (ATR): 2956, 2872, 1751, 1732, 1185, 1138 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{21}O_4^+$ ([M+H]$^+$) 229.1434; found 229.1435.



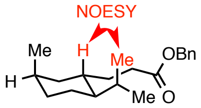
S1.21 (1.0 equiv) **1.117**

Preparation of cesium oxalate 1.117: Cs_2CO_3 (928 mg, 2.85 mmol, 0.5 equiv) in water (5 mL) was added dropwise to acid **S1.21** (1.30 g, 5.69 mmol, 1 equiv) in THF (10 mL). The resulting solution was stirred for 10 min then concentrated under reduced pressure to give **1.117** as a white powder that was washed with toluene (2 x 5 mL) and dried *in vacuo* (1.93 g, 94% yield). ^{1}H NMR (500 MHz, D_2O) δ 7.55–7.51 (m, 1H), 4.42 (br s, 1H), 4.23 (dp, *J* = 13.4, 6.8 Hz, 1H), 4.15–1.03 (m, 3H), 3.98–3.89 (m, 3H), 3.82–3.76 (m, 1H), 3.41 (d, *J* = 6.8 Hz, 3H), 3.38 (d, *J* = 6.8 Hz, 3H), 3.29 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, D_2O) δ 164.6, 74.9, 45.7, 35.5, 29.5, 27.3, 25.9, 20.00, 19.8, 19.0, 17.7; IR (ATR): 2958, 2932, 2869, 1716, 1223, 1644, 1368, 1383, 1198 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{12}H_{19}O_4^-$ ([M–Cs]$^-$) 227.1289; found 227.1291.

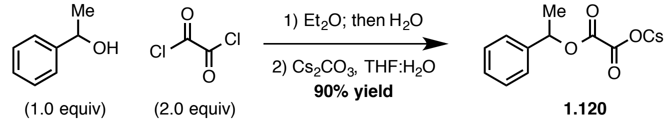


1.117 (1.1 equiv) (1.0 equiv) **1.118 (51% yield)** **1.119 (29% yield)**

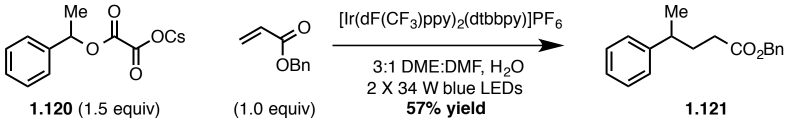
Preparation of esters 1.118 and 1.119: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.117** (270 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **1.118** and **1.119**, both obtained as pale yellow oils. Eluted first was **1.118** (79 mg, 51% yield): R_f = 0.35 (24:1 hexanes:EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 5H), 5.12 (s, 2H), 2.40–2.28 (m, 2H), 1.90–1.78 (m, 2H), 1.75–1.70 (m, 1H), 1.66–1.61 (m, 2H), 1.44–1.40 (m, 3H), 1.35–1.19 (m, 3H), 0.95–0.90 (m, 1H), 0.86 (d, *J* = 6.8 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 136.2, 128.7, 128.4, 128.3, 66.2, 45.5, 35.7, 33.7, 32.3, 30.9, 28.4, 27.1, 26.6, 21.7, 21.0, 20.8, 18.8;); IR (ATR): 2953, 2925, 2869, 1735, 1455, 1161 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{33}O_2^+$ ([M+H]$^+$) 317.2475; found 317.2475. Product stereochemistry was confirmed by NOESY correlation:



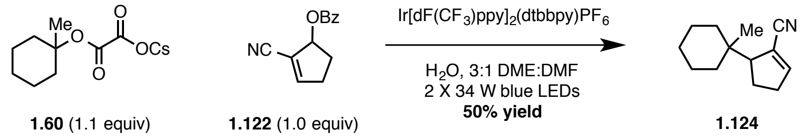
Eluted second was the isomenthol alkoxylcarbonyl radical adduct (**1.119**) (50 mg, 29% yield): R_f = 0.30 (24:1 hexanes:EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 5H), 5.15 (s, 2H), 5.09–5.06 (m, 1H), 2.72–2.69 (m, 2H), 2.68–2.65 (m, 2H), 1.91–1.85 (m, 1H), 1.78–1.71 (m, 1H), 1.61–1.55 (m, 2H), 1.56–1.52 (m, 3H), 1.35–1.26 (m, 2H), 0.94 (app t, *J* = 7.4 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 171.6, 135.8, 128.6, 128.3, 128.2, 72.3, 66.5, 45.6, 35.7, 29.9, 29.6, 29.3, 27.5, 26.3, 20.9, 20.8, 20.6, 19.1. IR (ATR): 2955, 2927, 2871, 1730, 1212, 1154, 1140 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{21}H_{31}O_4^+$ ([M+H]$^+$) 347.2217; found 347.2213.



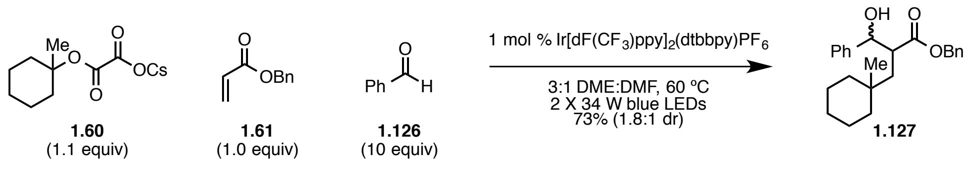
Preparation of cesium oxalate 1.120: 1-phenylethanol (7.9 mL, 65.5 mmol, 1.0 equiv) in Et_2O (100 mL) was added dropwise over 20 min to a 0 °C solution of oxalyl chloride (11.08 mL, 131 mmol, 2.0 equiv) in Et_2O (300 mL). The resulting pale yellow solution was stirred at 0 °C for 2 hours then concentrated under reduced pressure. Unreacted oxalyl chloride was removed *in vacuo* and the resulting yellow oil was redissolved in Et_2O (100 mL) and carefully treated with water (100 mL). The biphasic reaction mixture was stirred vigorously for 1 hour and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL) and the combined ethereal extracts were washed with water (2 x 100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated to give the crude acid as a colorless oil that was redissolved in THF (200 mL). Cs_2CO_3 (10.67 g, 32.75 mmol, 0.5 equiv) in water (50 mL) was added dropwise and the resulting solution was stirred for 10 min then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3 x 50 mL) to give **1.120** as a colorless solid that was dried *in vacuo* but not purified further (19.36 g, 90% yield). ^{1}H NMR (500 MHz, D_2O) δ 1.47–1.37 (m, 5H), 5.90–5.86 (m, 1 H), 1.60 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, D_2O) δ 173.5, 163.9, 141.1, 128.8, 128.3, 125.9, 75.1, 21.3; IR (ATR): 3035, 2992, 1719, 1634, 1602, 1371, 1192, 1050 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{10}H_9O_4^-$ ([M–Cs]$^-$) 193.0506; found 193.0506.



Preparation of ester 1.121: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.120** (244 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF_3)ppy)]$_2$(dtbpy)PF_6 (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and benzyl acrylate (77 µL, 0.5 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with water (25 mL) and the aqueous phase was extracted with Et_2O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:EtOAc) to give **1.121** as a pale yellow oil (89 mg, 57% yield): R_f = 0.61 (24:1 hexanes:EtOAc, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 7H), 7.20–7.14 (m, 3H), 5.09 (d, *J* = 12.4, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 2.75–2.67 (1H, m), 2.30–2.19 (m, 2H), 2.00–1.87 (m, 2H), 1.26 (d, *J* = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 146.2, 136.0, 128.6, 128.5, 128.22, 128.20, 127.0, 126.2, 66.1, 39.4, 33.2, 32.5, 22.2; IR (ATR): 3029, 2960, 1735, 1454, 1157 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{18}H_{21}O_2^+$ ([M+H]$^+$) 269.1536; found 269.1537.



Preparation of nitrile 1.124: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.60**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 µL, 5.0 mmol, 10 equiv), and 2-cyanocyclopent-2-en-1-yl benzoate (**1.122**)[26b] (107 mg, 0.50 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na$_2$SO$_4$ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et$_2$O) to give 5-(1-methylcyclohexyl)cyclopent-1-ene-1-carbonitrile (**1.124**) as a yellow oil (47 mg, 50% yield). R$_f$ = 0.5 (9:1 hexanes:acetone); visualized with KMnO$_4$. Spectral data match those previously reported.[26b]



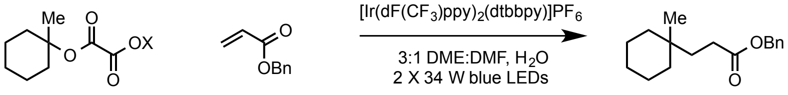
Preparation of alcohol 1.127: A flame-dried 4 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.60**) (70 mg, 0.22 mmol, 1.1 equiv) and

Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (2.2 mg, 0.002 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (2 mL, 0.1M) was added, followed by benzyl acrylate (**1.61**) (31 μL, 0.2 mmol, 1.0 equiv) and freshly distilled benzaldehyde (**1.126**) (200 μL, 2 mmol, 10 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et_2O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was purified by flash column chromatography on silica gel (1:0 hexanes:EtOAc → 9:1 hexanes:EtOAc) to provide the major diastereomer as a colorless solid (34 mg, 47% yield) (R_f = 0.17, 9:1 hexanes:EtOAc; visualized with $KMnO_4$) and the minor diastereomer as a clear oil (19 mg, 26% yield) (R_f = 0.09, 9:1 hexanes:EtOAc; visualized with $KMnO_4$).

Characterization data for the major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.30 (m, 8H), 7.18 (dd, *J* = 7.2, 2.4 Hz, 2H), 5.01–4.96 (m, 1H), 4.96–4.89 (m, 1H), 4.86 (d, *J* = 5.5 Hz, 1H), 2.80 (ddd, *J* = 10.3, 5.6, 1.6 Hz, 1H), 2.54 (s, 1H), 1.84 (dd, *J* = 14.2, 10.3 Hz, 1H), 1.65 (dd, *J* = 14.2, 1.6 Hz, 1H), 1.40–1.00 (m, 10H), 0.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 141.8, 135.9, 128.9, 128.73, 128.72, 128.2, 126.8, 75.6, 67.1, 49.4, 39.1, 38.2, 38.1, 33.0, 26.7, 24.9, 22.3, 22.2; IR (ATR): 3493, 2922, 1728, 1713, 1153 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{24}H_{30}O_3Na^+$ ([M+Na]$^+$) 389.2093; found 389.2082.

Characterization data for the minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.28 (m, 8H), 7.26–7.23 (m, 2H), 5.34–4.98 (m, 2H), 4.71 (dd, *J* = 7.6, 4.4 Hz, 1H), 2.90 (ddd, *J* = 9.8, 7.5, 2.0 Hz, 1H), 2.68 (d, *J* = 6.0 Hz, 1H), 1.89–1.77 (m, 1H), 1.36–1.24 (m, 5H), 1.20–1.03 (m, 5H), 0.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 142.3, 135.8, 128.71, 128.66, 128.6, 128.4, 128.4, 126.7, 77.4, 66.7, 48.9, 41.8, 37.9, 37.8, 33.1, 26.4, 24.7, 22.03, 21.96; IR (ATR): 3485, 2924, 1724, 1157, 906 cm^{-1}; HRMS (ESI–TOF) *m/z* calculated for $C_{24}H_{30}O_3Na^+$ ([M+Na]$^+$) 389.2093; found 389.2100.

Table S1.1. Effects of counterions on the efficiency of coupling of methyl cyclohexyl oxalate salts **1.60** with benzyl acrylate (**1.61**).^{a}

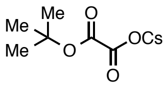


1.60 (1.1 equiv) **1.61** (1.0 equiv) **1.80**

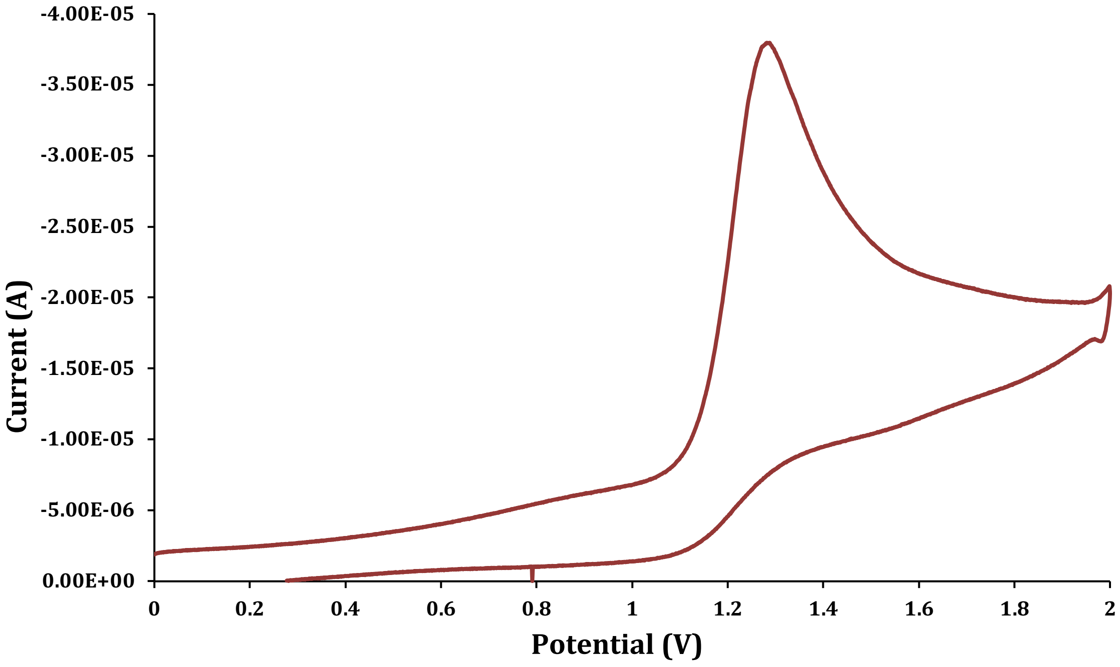
counterion	trial 1	trial 2
Li	93% yield	92% yield
Na	86% yield	88% yield
K	90% yield	95% yield
Cs	97% yield	92% yield

^{a}Yield based on ^{1}H NMR analysis of crude reaction mixture with 1,2-dibromo-4,5-(methylenedioxy)benzene as internal standard.

Figure S1.1. Cyclic voltammetry data for *tert*-butyl cesium oxalate **1.103**.



1.103



Instrument Model	CHI600E
Init E (V)	0
High E (V)	2
Low E (V)	0
Final E (V)	0
Init P/N	P
Scan Rate (V/s)	0.1
Segment	2
Sample Interval (V)	0.001
Quiet Time (sec)	2
Sensitivity (A/V)	0.001 A/V
Ep	1.282 V
Eh	1.202 V
ip	$-2.789e^{-5}$ A
Ah	$-2.398e^{-5}$ C

1.5 References and Notes:

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35. The yield of the coupling reaction with acrylonitrile can be increased to 90% by performing the reaction in 10:1 DME:water.

36. Only dimerization products of benzylic radicals were observed.

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48. Utilizing DFT calculations, the distance between hydrogen atoms on the 17α-methyl and the angular 18-methyl (steroid numbering) was found to be 4.3 Å. As a result, no NOE signal would be observed. In contrast, the distance between hydrogen atoms on the 17β-methyl and the angular 18-methyl was found to be 1.7 Å, leading to the observed NOE signal.

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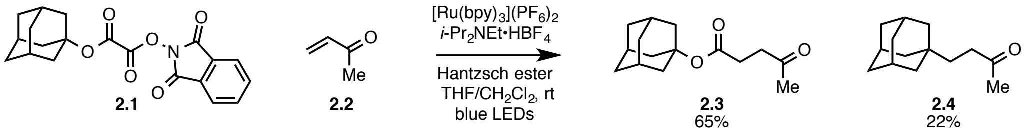
Chapter 2: Generation of the Methoxycarbonyl Radical by Visible-Light Photoredox Catalysis and Its Conjugate Addition with Electron-Deficient Olefins

2.1 Introduction

The normal reactivity of carbonyl compounds renders 1,3- or 1,5-dicarbonyl functionality much easier to incorporate into organic molecules than 1,4-dicarbonyl motif.[1] The 1,4-addition of acyl-anion equivalents to α,β-unsaturated carbonyl compounds is a general approach for constructing 1,4-dicarbonyl products. However, several steps are needed to introduce an alkoxycarbonyl group in this way.[1] Transition-metal catalyzed alkoxycarbonylation is a widely practiced and immensely important method to incorporate carbonyl functionality into alkenes;[2] however the use of this chemistry to alkoxycarbonylate electron-deficient alkenes has not been widely developed.[3] A potentially attractive approach for preparing γ-ketoesters would be the direct 1,4-addition of an alkoxycarbonyl radical to α,β-unsaturated carbonyl compounds.[4] Although intramolecular additions of alkoxycarbonyl radicals to alkenes are well known and used productively to construct 5- and 6-membered lactones,[5] there are only a few examples of synthetically useful bimolecular coupling reactions of alkoxycarbonyl radicals with alkenes.[6] In these cases, the alkoxycarbonyl radical is generated by either Fe- or Pd-catalyzed oxidation of carbazate precursors.

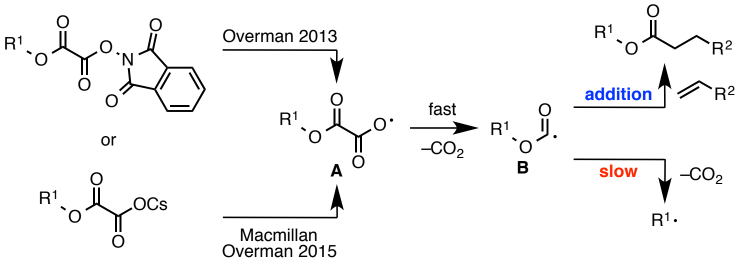
Computational studies suggest that alkoxycarbonyl radicals are less-nucleophilic than acyl radicals, leading them to be termed either as ambiphilic or in some contexts electrophilic radicals.[7] These studies raise concern about whether an alkoxycarbonyl radical would be sufficiently nucleophilic to add efficiently to an electron-deficient C–C π-bond. However, in our recent investigations on the generation of tertiary radicals from tertiary alkyl *N*-phthalimidoyl oxalate precursors, we observed that the intermediate alkoxycarbonyl radical formed from adamantanol precursor **2.1** reacted efficiently with methyl vinyl ketone (**2.2**) to give γ-ketoester **2.3** as the major product in 65% yield (Equation 2.1).[8,9]

Equation 2.1



Following our initial report on tertiary alkyl *N*-phthalimidoyl oxalates, we became interested in the possibility of using a similar oxalate precursor and visible-light photoredox catalysis to conveniently generate alkoxycarbonyl radicals in the context of their conjugate addition to α,β-unsaturated carbonyl compounds and related electron-deficient alkenes. Two potential precursors for producing alkoxycarbonyl radicals by visible-light photoredox catalysis would be alkyl *N*-phthalimidoyl oxalates[8] or an alkyl hemioxalate salt (Scheme 2.1).[10,11] For this method to be successful, β-scission of the alkoxycarbonyl radical **B** to give an alkyl radical must be slower than its reaction with the radical acceptor.[12] The rate of decarboxylation of alkoxycarbonyl radicals is known to reflect the stability of the forming alkyl radical with the rate of decarboxylation of the *tert*-butoxycarbonyl radical estimated to be ~500 times faster than that of a primary alkoxycarbonyl radical.[13] As the methoxycarbonyl radical would be expected to decarboxylate even more slowly, our studies focused on developing a convenient method to generate this carbon radical and surveying its reactivity with alkenes.

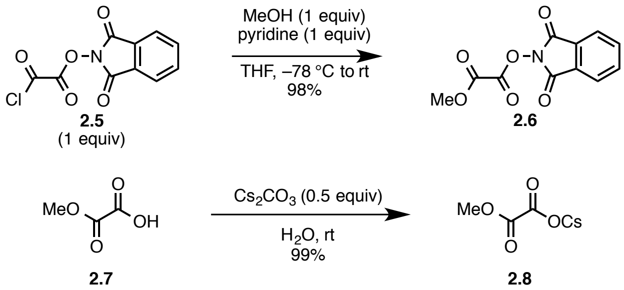
Scheme 2.1. Two potential precursors of alkoxycarbonyl radicals.



2.2 Results and Discussion

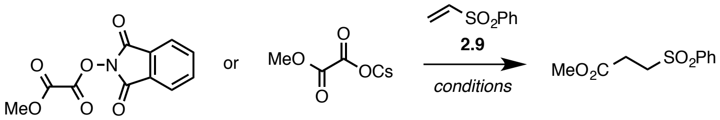
Methyl *N*-phthalimidoyl oxalate (**2.6**) was obtained by acylation of methanol with *N*-phthalimidoyl chlorooxalate (**2.5**) using a modification of a procedure developed earlier in our laboratory for the preparation of *tert*-alkyl *N*-phthalimidoyl oxalates (Scheme 2.2).[8] The reaction was carried out in the absence of DMAP at 0 °C to prevent formation of dimethyl oxalate. Additionally, the use of pyridine in place of Et_3N led to more reproducible results. Phthalimidoyl oxalate **2.6** was not stable to silica gel chromatography; however, upon careful trituration it was isolated on multigram scale as a colorless solid in high yield and acceptable purity. Reagent **2.6** is stable to light and can be stored in the −20 °C freezer for prolonged periods of time without observable decomposition. Cesium methyl oxalate **2.8** was generated from commercially available methyl hemioxalate **2.7** upon reaction with 0.5 equiv of Cs_2CO_3 in water, followed by concentration to give **2.8** as a colorless solid.

Scheme 2.2. Preparation of methyl *N*-phthalimidoyl oxalate (**2.6**) and cesium methyl oxalate (**2.8**).



Using conditions optimized earlier for the coupling of tertiary radicals generated from related precursors with electron-deficient alkenes,[8,10] the reaction of radical precursors **2.6** and **2.8** with phenyl vinyl sulfone (**2.9**) was examined (Table 2.1). Coupling of *N*-phthalimidoyl oxalate **2.6** (1.5 equiv) with phenyl vinyl sulfone in the presence of 1.5 mol % of $[Ru(bpy)_3](PF_6)_2$, 1.5 equiv of diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch ester, **2.11**), and 1 equiv of *i*-$Pr_2NEt·HBF_4$ in 1:1 THF:CH_2Cl_2 with irradiation at room temperature with low-intensity blue LEDs gave product **2.10** in 50% yield (Table 1, entry 1). In contrast, the reaction of methyl cesium oxalate **2.8** (1.5 equiv) with phenyl vinyl sulfone in the presence of 2 mol % of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 10 equiv of water in 3:1 DME:DMF irradiated with 2 X 34 W blue LEDs provided adduct **2.10** in only 2% yield (Table 1, entry 2). As low yields were also obtained in further screening of the reaction of oxalate salt **2.8** with benzyl acrylate,[14] we chose to focus on optimizing the coupling of phthalimidoyl oxalate **2.6** with acceptor **2.9**. The major by-product of the reaction of entry 1 was identified as the product of addition of the 2-tetrahydrofuryl radical to phenyl vinyl sulfone (~30% yield). To suppress this unwanted reactivity, a solvent screen was performed, which identified CH_2Cl_2 as the optimal solvent (entry 3). The choice of a polar aprotic solvent was important, as reactions run in nonpolar solvents such as benzene led to lower yields, likely because of the low solubility of Hantzsch ester **7** (entry 4). Employing alternative reductive quenchers such as 1,3-dimethyl-2-arylbenzimidazolines,[15] or 2-phenylbenzothiazoline,[16] led to greatly diminished yields of addition product **2.10**. The yield of **2.10** was improved substantially by increasing the amounts of phthalimidoyl oxalate **2.6** and Hantzsch ester **2.11** to 3 equiv (entry 5). Raising the temperature of the reaction proved to be detrimental (entry 6), whereas omission of the ammonium additive resulted in a slight increase in yield (entry 7). Finally, by varying the concentration of the reaction mixture, we were able to reduce the excess of the radical precursor **2.6** and the Hantzsch ester **2.11** from 3 to 2 equiv without compromising the isolated yield of **2.10** (entry 8). In the absence of visible light, no product was formed (entry 9), whereas reactions carried out in absence of the photocatalyst or for 6 h instead of 18 h led to greatly reduced formation of coupled product **2.10** (entries 10,11).[17]

Table 2.1. Initial studies and reaction optimization.



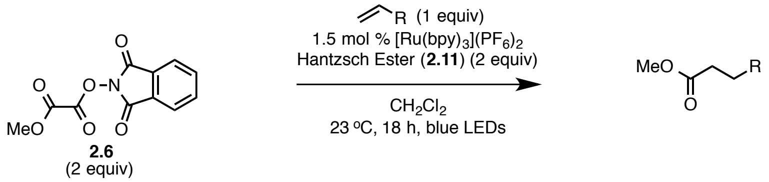
2.6 **2.8** **2.10**

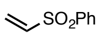
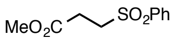
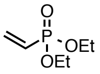
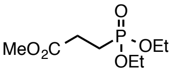
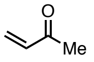
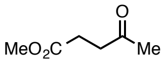
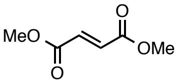
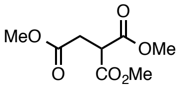
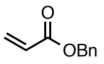
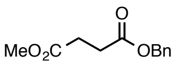
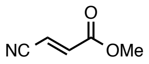
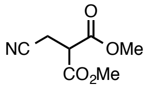
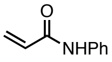
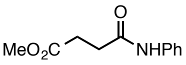
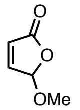
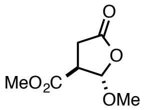
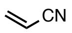
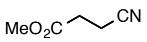
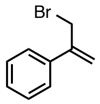
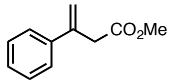
entry[a]	radical precursor (equiv)	solvent (M)	*t* (°C)	**2.11** (equiv)	yield (%)[b]
1[c]	**2.6** (1.5)	1:1 CH_2Cl_2:THF (0.1)	23	1.5	50
2	**2.8** (1.5)	3:1 DME:DMF (0.1)	60	-	2
3[c]	**2.6** (1.5)	CH_2Cl_2 (0.1)	23	1.5	55
4[c]	**2.6** (1.5)	benzene (0.1)	23	1.5	38
5[c]	**2.6** (3.0)	CH_2Cl_2 (0.1)	23	3.0	90
6[c]	**2.6** (3.0)	CH_2Cl_2 (0.1)	80	3.0	50
7	**2.6** (3.0)	CH_2Cl_2 (0.1)	23	3.0	94[d]
8	**2.6** (2.0)	**CH_2Cl_2 (0.6)**	**23**	**2.0**	**94**[d]
9[e]	**2.6** (2.0)	CH_2Cl_2 (0.6)	23	2.0	0
10[f]	**2.6** (2.0)	CH_2Cl_2 (0.6)	23	2.0	16
11[g]	**2.6** (2.0)	CH_2Cl_2 (0.6)	23	2.0	56

[a] Reaction conditions for radical precursor **2.6**: 1 equiv **2.9**, 1.5 mol % $[Ru(bpy)_3](PF_6)_2$, low-intensity blue LEDs, 18 h; reaction conditions for radical precursor **2.8**: 1 equiv **2.9**, 2 mol % $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, 2 X 34 W blue LEDs, 18 h. [b] Yield determined by ^1H NMR analysis of the crude reaction mixture using 1,4-dimethoxybenzene as an internal standard. [c] Reaction was performed in the presence of *i*-$Pr_2NEt{\bullet}HBF_4$ (1 equiv) as an additive. [d] Isolated yield after silica gel chromatography. [e] Reaction performed in the absence of visible light. [f] Reaction performed in the absence of photocatalyst. [g] Reaction was stopped after 6 h.

With optimal reaction conditions identified, the scope of the conjugate addition of the methoxycarbonyl radical to a range of alkene coupling partners was investigated (Table 2.2). Acceptors containing a terminal double bond activated by sulfone, ketone, ester, amide, nitrile, or phosphonate functional groups performed best in the reaction, furnishing the corresponding products in moderate to high yields (entries 1–6). However, introduction of either an α-methyl or α-phenyl substituent to methyl vinyl ketone resulted in no detectable formation of the coupled product, as did incorporation of such substituents into benzyl acrylate.[18] Cyclopent-2-en-1-one was a poor coupling partner, providing the desired product in 27% yield. Whereas 5-oxocyclopent-1-ene-1-carbonitrile underwent conjugate hydride reduction by the Hantzsch ester **2.11**.[18] However, acyclic enones containing a second electron-withdrawing substituent at the β-carbon, such as dimethyl fumarate (**2.22**) or *trans*-3-cyanoacrylate **2.24**, did react in high yield (entries 7, 8). The outcome of the latter reaction is noteworthy, as acceptor **2.24** possessing two electron-withdrawing groups of different steric and electronic properties underwent exclusive addition α to the methyl ester substituent. This sense of regioselectivity, which was attributed by Giese to a larger LUMO coefficient at C-2,[4a] has been observed previously; however, in these reported cases the magnitude of regioselection was much lower 5–6:1.[20] 5-Methoxybutenolide (**2.26**), which was shown previously to react in good yield with a nucleophilic tertiary carbon radical,[8,10] coupled in low yield under these conditions (entry 9). Coupling of the methoxycarbonyl radical with 2-phenylallyl bromide (**2.28**) gave allylic substitution product **2.29** in 47% yield. To our surprise, methyl 2-(bromomethyl)acrylate was found to be unreactive.[18]

Table 2.2. Acceptor scope with *N*-phthalimidoyl oxalate **2.6**.

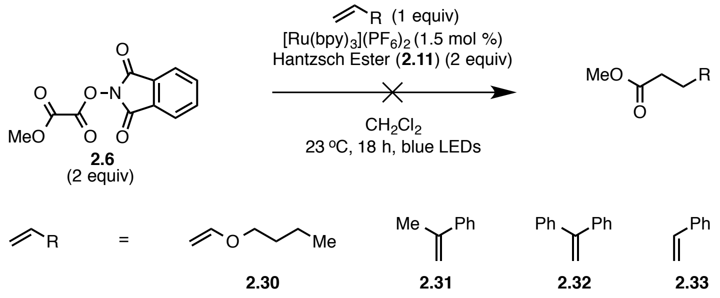


entry[a]	acceptor	product	yield (%)	entry[a]	acceptor	product	yield (%)
1	 **2.9**	 **2.10**	94	6	 **2.20**	 **2.21**	66
2	 **2.12**	 **2.13**	74	7	 **2.22**	 **2.23**	80
3	 **2.14**	 **2.15**	89	8	 **2.24**	 **2.25**	91
4	 **2.16**	 **2.17**	60	9	 **2.26**	 **2.27**	28
5	 **2.18**	 **2.19**	74	10	 **2.28**	 **2.29**	47

[a]Reaction performed using the optimized conditions (see Experimental Information). All yields are yields of pure products isolated after silica gel chromatography.

As alkoxycarbonyl radicals had been suggested to be ambiphilic or electrophilic, we examined the reactivity of the methoxycarbonyl radical generated from *N*-phthalimidoyl oxalate **2.6** with electron-rich alkenes and styrenes (Scheme 2.3).[18] For example, performing the reaction in the presence of a prototypical electron-rich alkene, butyl vinyl ether (**2.30**), led to no detectable coupled product. Reactions carried out in the presence of styrene derivatives (**2.31–2.33**) led to broad peaks in ^{1}H NMR spectra of crude reaction mixtures, indicating likely polymerization of the intermediate stabilized benzylic radicals formed upon addition of the methoxycarbonyl radical.

Scheme 2.3. Coupling of *N*-phthalimidoyl oxalate **2.6** with electron-rich alkenes and styrenes.



2.3 Conclusion

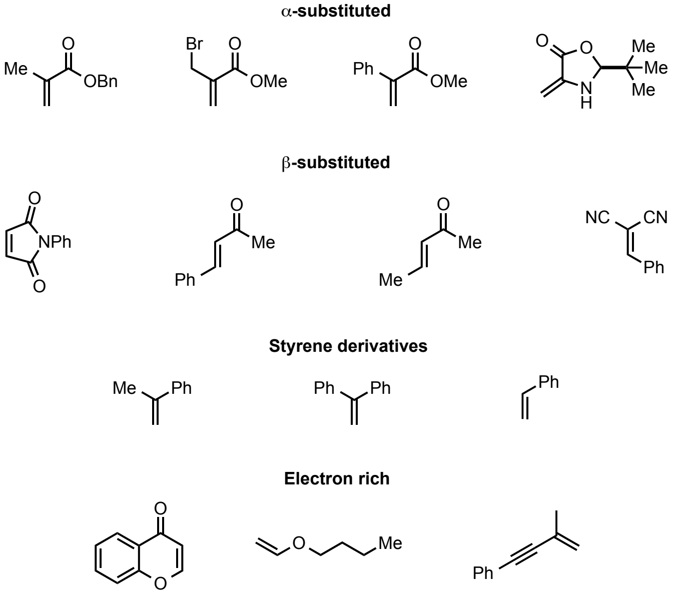
In summary, methyl *N*-phthalimidoyl oxalate (**2.6**) was shown to be a convenient precursor of the methoxycarbonyl radical under visible-light photoredox conditions. It reacts in good yield with terminal alkenes harboring a variety of electron-withdrawing substituents, thus providing a convenient method for the direct construction of γ-ketoesters and related products. It also reacts in high yield with 1,2-disubstituted alkenes activated by two electron-withdrawing substituents, and in one relevant case with regioselectivity higher than that of alkyl radicals. We attribute the somewhat limited scope of reactivity of the methoxycarbonyl radical to its reduced nucleophilicity in comparison to alkyl carbon radicals. No indication that the methoxycarbonyl radical shows ambiphilic reactivity was observed.[21]

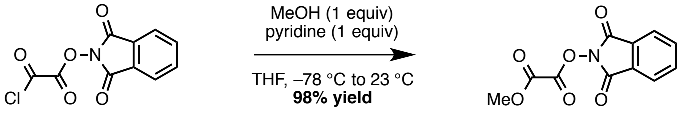
2.4 Experimental Information

Materials and Methods.

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). For all photoredox reactions, solvents were sparged with argon for five minutes prior to use. All commercially obtained reagents were used as received. $[Ru(bpy)_3](PF_6)_2$ was obtained from Sigma Aldrich. Methyl potassium oxalate was obtained from AK Scientific. Methyl vinyl ketone, acrylonitrile, and benzyl acrylate were distilled neat prior to use. Hantzsch ester,[22] *i*-Pr_2NEt•HBF_4,[23] chloro *N*-phthalimidoyl oxalate,[8a] β-cyanoacrylate **2.24**,[24] and (bromomethyl)styrene **2.28**[25] were prepared according to literature procedures. Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 50 F_{254} pre-coated plates, (0.25 mm), and visualized by exposure to UV light (254 nm) and potassium permanganate ($KMnO_4$) staining. EMD silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^1H NMR spectra were recorded on Bruker spectrometers (at 500 or 600 MHz) and are reported relative to deuterated solvent signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on a Bruker Spectrometer at 126 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on Varian 640-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from UC Irvine Mass Spectrometry Facility with a Micromass LCT spectrometer. Low-intensity blue LEDs were purchased from http://ww.creativelightings.com (product code CL-FRS5050-12WP-12V) and powered by eight AA batteries. Kessil KSH150B 34 W LED Grow Light 150, Blue was purchased from http://www.amazon.com.

Figure S2.1. List of failed methoxycarbonyl radical acceptors.

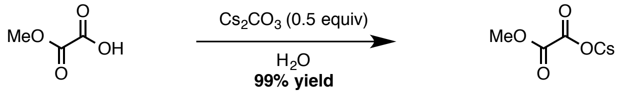




2.5 (1 equiv)

2.6

Preparation of *N*-phthalimidoyl oxalate 2.6: A round-bottom flask was charged with **2.5** (11.4 g, 45.0 mmol, 1.0 equiv) followed by the addition of THF (1.5 L, 0.030 M). The mixture was cooled to −78 °C and a solution of MeOH (1.8 mL, 45 mmol, 1.0 equiv), pyridine (3.6 mL, 45 mmol, 1.0 equiv) in THF (5 mL) was added dropwise. The resulting heterogeneous mixture was warmed to 0 °C and allowed to stir for 1 h. The reaction was then allowed to warm to 23 °C and stirred for another 30 min. The reaction mixture was concentrated under reduced pressure, and the resulting crude residue was dissolved in CH_2Cl_2 (100 mL) and washed with sat. aq. $CuSO_4$ (3 x 100 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude residue was dissolved in CH_2Cl_2 (125 mL) then poured into pentanes (250 mL). The resulting heterogeneous mixture was filtered through a cotton plug that was then washed with pentanes (2 x 75 mL). The filtrate was concentrated under reduced pressure to yield oxalate **4** as a colorless solid (11 g, 44 mmol, 98% yield). ^1H NMR (600 MHz, $CDCl_3$): δ 7.95–7.94 (m, 2H), 7.85–7.84 (m, 2H), 4.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.0, 154.9, 153.8, 135.4, 128.9, 124.6, 54.8; IR (thin film): 3155, 2985, 1793, 1751, 1097 cm^{-1}; HRMS (CI) calculated for $C_{11}H_{11}N_2O_6$ (M+NH_4) 267.0617, found 267.0618.



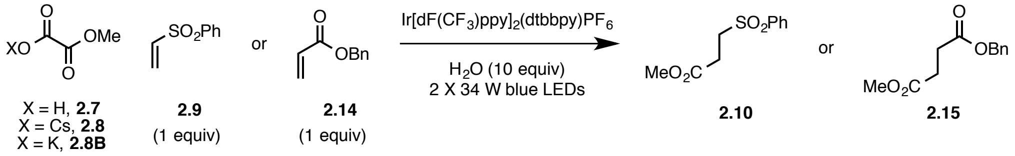
2.7 (1 equiv) **2.8**

Preparation of cesium oxalate 2.8: A round-bottom flask was charged with **2.7** (4.0 g, 38 mmol, 1.0 equiv) followed by the addition of H_2O (38 mL, 1 M) and Cs_2CO_3 (6.2 g, 19 mmol, 0.5 equiv). The resulting mixture was stirred vigorously for 5 min at 23 °C. The solution was concentrated under reduced pressure to yield oxalate salt **2.8** as a colorless solid (9.0 g, 38 mmol, 99% yield). ^1H NMR (500 MHz, DMSO-d_6): δ 3.50 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 168.1, 162.8, 50.4; IR (thin film): 3019, 2961, 2865, 1731, 1225 cm^{-1}; HRMS (ESI) calculated for $C_3H_3O_4$ (M−Cs) 103.0031, found 103.0035.

Reaction Optimization Studies with Oxalic Acid Monomethyl Derivatives

A 1-dram vial equipped with a Teflon septum and magnetic stir bar was charged with one of the oxalic acid monomethyl derivative (**2.7**, **2.8**, **2.8B**) and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$. Solvent was added, followed by water (10 equiv) and an acceptor (**2.9** or **2.14**). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h. The reaction mixture was diluted with sat. aq. LiCl (5 mL) and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. Next, the internal standard (1,2-dibromo-4,5-methylenedioxybenzene) was added. The mixture was then diluted in $CDCl_3$ and analyzed by ^1H NMR. Ratios of the desired addition product **2.10** or **2.15** to internal standard were used to determine yield (%) of reactions. Results of the studies are summarized in Table S2.1.

Table S2.1. Optimization of coupling of oxalic acid derivatives with Michael acceptors.

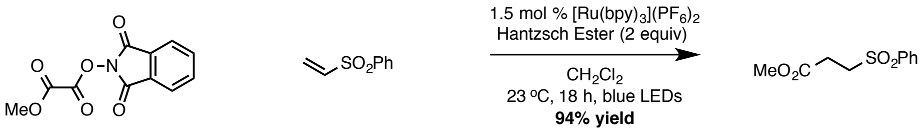


entry	X	base	oxalate equiv	acceptor	solvent (M)	mol % cat.	Result (^1H NMR)
1	H	K_2HPO_4	1.1	**2.14**	3:1 DME:DMF (0.1 M)	1	4% **2.15** 14% **2.14** remaining
2	H	CsF	1.1	**2.14**	3:1 DME:DMF (0.5 M)	1	8% **2.15**
3	H	CsF	1.1	**2.14**	3:1 DME:DMF (0.1 M)	1	20% **2.15**
4	H	CsF	2.0	**2.14**	3:1 DME:DMF (0.1 M)	1	25% **2.15**
5	H	CsF	1.1	**2.14**	3:1 DME:DMF (0.1 M)	2	32% **2.15** 28% **2.14** remaining
6	H	CsF	1.1	**2.14**	3:1 DME:DMF (0.1 M)	2	35% **2.15** 30% **2.14** remaining
7	H	CsF	2.0	**2.14**	3:1 DME:DMF (0.1 M)	2	36% **2.15** 1% **2.14** remaining
8	Cs	none	1.1	**2.14**	3:1 DME:DMF (0.1 M)	1	25% **2.15**
9	Cs	none	1.5	**2.9**	3:1 DME:DMF (0.1 M)	2	2% **2.10**
10	Cs	none	2.0	**2.9**	3:1 DME:DMF (0.1 M)	2	2% **2.10**
11	K	none	1.5	**2.14**	3:1 DME:DMF (0.1 M)	2	0% **2.15**
12	K	none	1.5	**2.14**	10:1 acetone:H_2O (0.1 M)	2	0% **2.15**
13	K	none	1.5	**2.14**	10:1 CH_3CN:H_2O (0.1 M)	2	0% **2.15** 19% **2.14** remaining
14	K	none	1.0	**2.14**	CH_2Cl_2 (0.1 M)	2	0% **2.15** 52% **2.14** remaining
15	K	none	1.0	**2.14**	CH_3CN (0.1 M)	2	0% **2.15** 56% **2.14** remaining
16	K	none	1.0	**2.14**	acetone (0.1 M)	2	2% **2.15** 42% **2.14** remaining
17	K	none	1.5	**2.14**	DMF (0.1 M)	2	5% **2.15** 77% **2.14** remaining

Coupling of Methyl *N*-Phthalimidoyl Oxalate with Various Acceptors

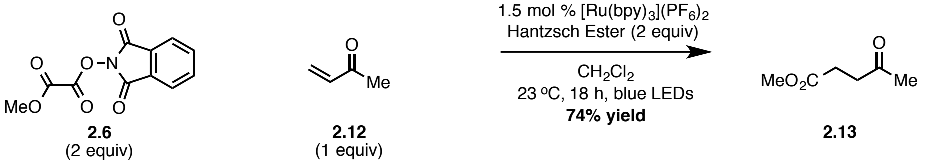
General procedure for the coupling of methyl N-phthalimidoyl oxalate with various acceptors:

A 1-dram vial was charged with methyl *N*-phthalimidoyl oxalate (**2.6**) (130 mg, 0.53 mmol, 2.0 equiv), $[Ru(bpy)_3](PF_6)_2$ (4 mg, 0.004 mmol, 0.015 equiv), Hantzsch ester (**2.11**) (140 mg, 0.53 mmol, 2.0 equiv), and a magnetic stir bar. CH_2Cl_2 (0.5 mL, 0.6 M, sparged with Ar for 5 min) was added followed by an acceptor (0.27 mmol, 1.0 equiv). The heterogeneous reaction mixture was placed in the center of a 30-cm loop of blue LEDs and allowed to stir at 23 °C for 18 h. The reaction was filtered through a pad of silica gel, washed with CH_2Cl_2 (10 mL), and the filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel to yield corresponding addition products.

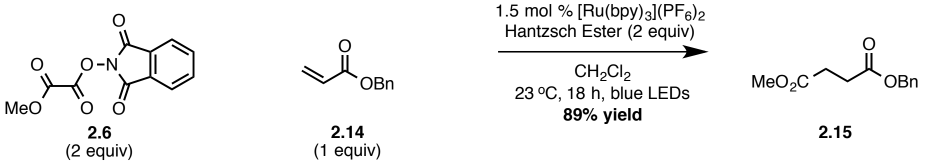


2.6 (2 equiv) **2.9** (1 equiv) **2.10**

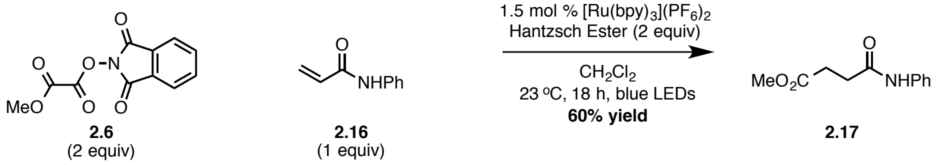
Preparation of sulfone 2.10: According to general procedure, phenyl vinyl sulfone (**2.9**) (45 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (7:3 hexanes:EtOAc) to yield sulfone **2.10** (56 mg, 0.25 mmol, 94% yield) as a colorless solid. $R_f = 0.35$ (3:2 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 3.65 (s, 3H), 3.45 (t, *J* = 4.8 Hz, 2H), 2.77 (t, *J* = 4.2 Hz, 2H). Spectral data match those previously reported.[26]



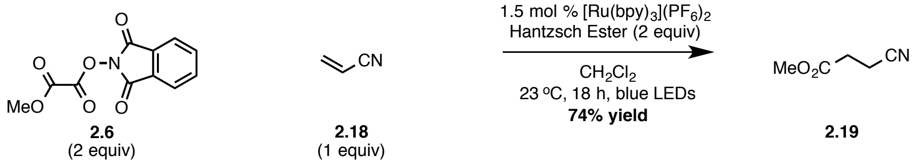
Preparation of ketone 2.13: According to general procedure, methyl vinyl ketone (**2.12**) (22 µL, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:1 hexanes:EtOAc) to yield ketone **2.13** (29 mg, 0.20 mmol, 74% yield) as a clear oil. R_f = 0.22 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 3.69 (s, 3H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.1 (s, 3H). Spectral data match those previously reported.[27]



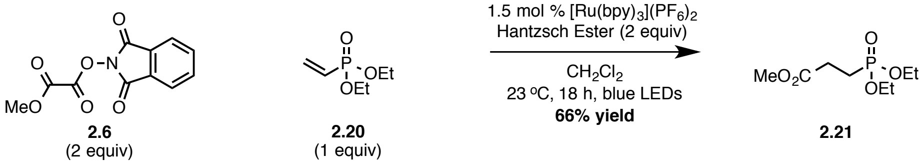
Preparation of ester 2.15: According to general procedure, benzyl acrylate (**2.14**) (40 µL, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (9:1 hexanes:EtOAc) to yield ester **2.15** (53 mg, 0.24 mmol, 89% yield) as a clear oil. R_f = 0.55 (3:2 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (500 MHz, $CDCl_3$): δ 7.39–7.33 (m, 5H), 5.15 (s, 2H), 3.68 (s, 3H), 2.72–2.64 (m, 4H). Spectral data match those previously reported.[28]



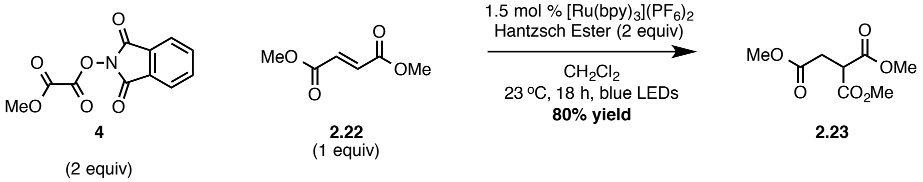
Preparation of amide 2.17: According to general procedure, *N*-phenylacrylamide (**2.16**) (40 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (65:35 hexanes:EtOAc) to yield amide **2.17** (33 mg, 0.16 mmol, 60% yield) as a colorless solid. R_f = 0.30 (3:2 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 7.81 (br s, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.10−7.10 (m, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.67 (t, *J* = 6.0, 2H). Spectral data match those previously reported.[29]



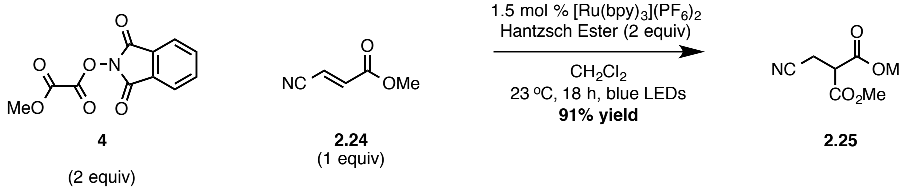
Preparation of nitrile 2.19: According to general procedure, acrylonitrile (**2.18**) (18 µL, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:1 hexanes:EtOAc) to yield nitrile **2.19** (22 mg, 0.20 mmol, 74% yield) as a clear oil. R_f = 0.30 (3:2 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 3.80 (s, 3H), 2.72−2.70 (m, 2H), 2.67−2.65 (m, 2H). Spectral data match those previously reported.[30]



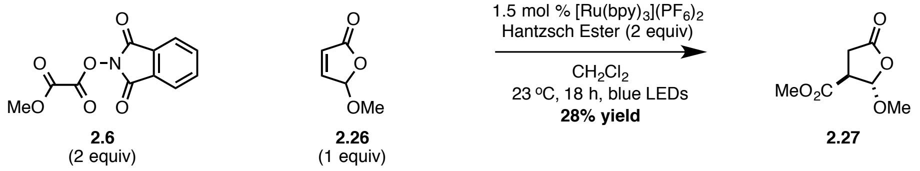
Preparation of phosphonate 2.21: According to general procedure, diethyl vinylphosphonate (**2.20**) (42 µL, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:2 hexanes:acetone) to yield phosphonate **2.21** (39 mg, 0.18 mmol, 66% yield) as a clear oil. R_f = 0.22 (7:3 hexanes:acetone); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 4.14–4.07 (m, 4H), 3.7 (s, 3H), 2.63–2.58 (m, 2H), 2.11–2.05 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 6H). Spectral data match those previously reported.[31]



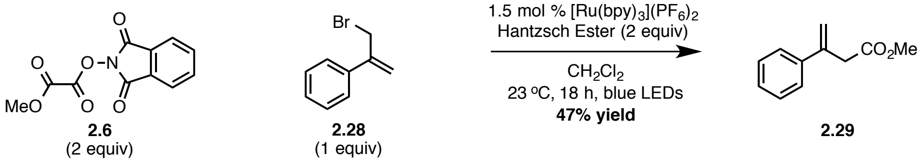
Preparation of ester 2.23: According to general procedure, dimethyl fumarate (**2.22**) (38 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (4:1 hexanes:EtOAc) to yield malonate ester **2.23** (43 mg, 0.22 mmol, 80% yield) as a colorless solid. R_f = 0.20 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 3.83 (s, 6H), 3.75 (t, *J* = 7.5 Hz, 1H), 2.94 (d, *J* = 7.8 Hz, 2H). Spectral data match those previously reported.[32]



Preparation of diester 2.25: According to general procedure, β-cyanomethylacrylate (**2.24**) (30 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:1 hexanes:EtOAc) to yield cyanomalonate **2.25** (42 mg, 0.25 mmol, 91% yield) as a colorless oil. R$_f$ = 0.20 (3:1 hexanes:EtOAc); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 3.78 (s, 6H), 3.73 (t, *J* = 8.8 Hz, 1H), 2.89 (d, *J* = 7.2 Hz, 2H). Spectral data match those previously reported.[33]



Preparation of lactone 2.27: According to general procedure, butenolide **2.26** (30 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:1 hexanes:EtOAc) to yield lactone **2.27** (13 mg, 0.076 mmol 28% yield) as a clear oil. R$_f$ = 0.33 (3:2 hexanes:EtOAc); visualized with KMnO$_4$. ^{1}H NMR (600 MHz, CDCl$_3$): δ 5.56 (d, *J* = 1.8 Hz, 1H), 3.79 (s, 3H), 3.54 (s, 3H), 3.26 (dd, *J* = 6.0, 1.8 Hz, 1H), 2.88 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 174.4, 170.9, 105.9, 57.6, 53.4, 47.2, 30.7; IR (thin film): 3155, 2983, 1793, 1742, 1381, 1168, 1111 cm^{-1}; HRMS (ESI) calculated for $C_7H_{14}NO_5$ (M+NH$_4$) 192.0872, found 192.0868.



Preparation of styrene 2.29: According to general procedure, styrene **2.28** (53 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (95:5 hexanes:EtOAc) to yield styrene **2.29** (22 mg, 0.13 mmol, 47% yield) as a clear oil. R_f = 0.55 (4:1 hexanes:EtOAc); visualized with $KMnO_4$. ^1H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 5.57 (s, 1H), 5.25 (s, 1H), 3.67 (s, 3H), 3.54 (s, 2H). Spectral data match those previously reported.[34]

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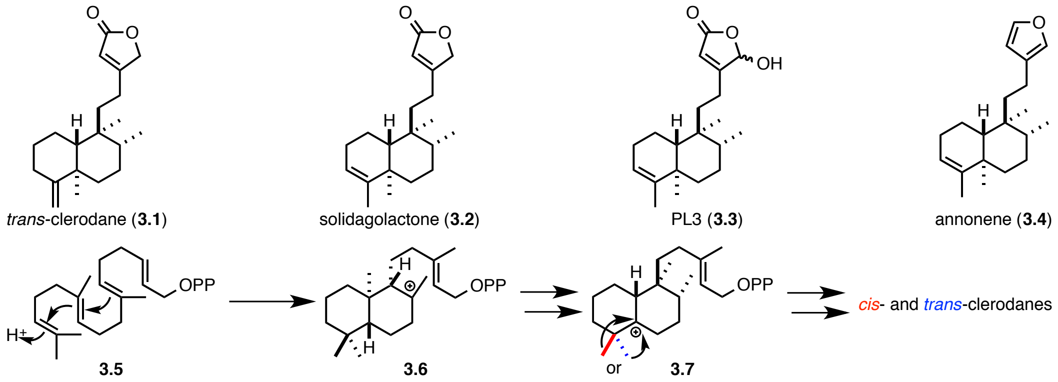
Chapter 3: Enantioselective Total Syntheses of *trans*-Clerodane Diterpenoids via a Convergent Fragment-Coupling Strategy

3.1 Introduction

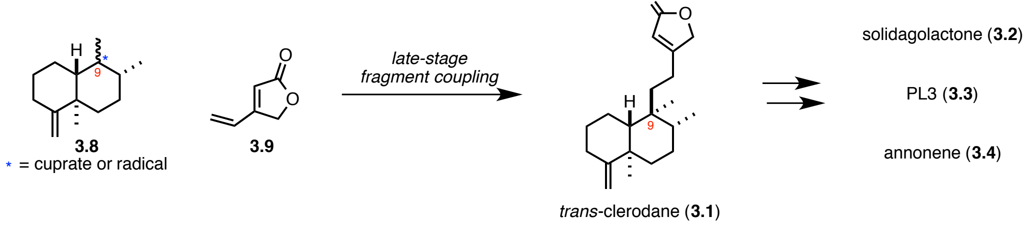
The clerodane family of diterpenoid natural products is comprised of more than 650 secondary metabolites isolated from various plant sources.[1] Many clerodane diterpenoids are known to exhibit antifeedant activity,[1] whereas the biological activity reported for certain members is much more extensive.[2] The *trans*-clerodane subset of this family of natural products, represented by **3.1**,[3] solidagolactone (**3.2**),[3] 16-hydroxycleroda-3,13-dien-15,16-olide (**3.3**, referred to as PL3 or HCD),[2,4] and annonene (**3.4**)[5] (Figure 3.1), is structurally characterized by a *trans*-decalin core harboring four contiguous stereocenters, two of which are 1,3-related quaternary carbons. The decalin core **3.6** is believed to originate from a series of enzymatic cyclizations of geranylgeranyl pyrophosphate (**3.5**). The proposed biosynthetic intermediate **3.6** provides a point of divergence for clerodane and labdane diterpenoids.[1a] A series of hydride and methyl migrations leads to a tertiary cation intermediate **3.7** from which both *cis*- and *trans*-clerodanes may be formed, depending on the orientation of the geminal migrating methyl group.[1a]

Figure 3.1. Four representative *trans*-clerodane diterpenoids and proposed biosynthetic origin of *cis*- and *trans*-clerodanes.



Early total syntheses of *trans*-clerodanes, including those of (–)-PL3 (**3.3**)[6] and (±)-annonene (**3.4**),[7] required lengthy sequences to install the contiguous stereocenters and fashion the C-9 quaternary stereocenter.[8] At the onset of our studies, we conjectured that 1,6-addition of a *trans*-decalin cuprate or nucleophilic tertiary radical intermediates **3.8** to 4-vinylfuran-2-one (**3.9**) could be employed to join the decalin and side chain fragments and fashion the C-9 quaternary stereocenters of *trans*-clerodane **3.1** (Figure 3.2). Straightforward manipulation of **3.1** would then secure the total syntheses of diterpenoids **3.2–3.4**. We hoped to employ methods recently developed by the Overman group for the generation of tertiary cuprates from corresponding nitriles[9] and tertiary radicals from tertiary alcohols via visible-light photoredox catalyzed fragmentation of *tert*-alkyl *N*-phthalimidoyl oxalates[10] or cesium hemioxalates[11] to achieve the desired late-stage fragment coupling.

Figure 3.2. Proposed fragment-coupling strategy for the synthesis of *trans*-clerodane diterpenoids.

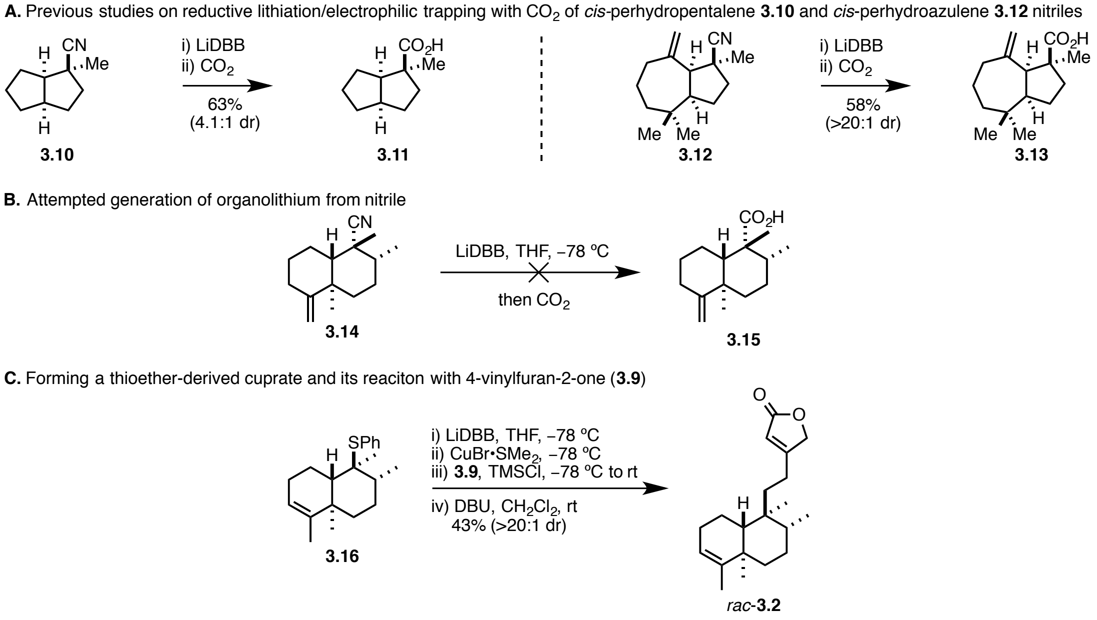


3.2 Results and Discussion

Our preliminary investigations focused on identifying viable precursors for generating either the tertiary organocuprate or tertiary radical intermediates **3.8**. We postulated that a tertiary organometallic reagent could be most easily formed by reductive lithiation of a tertiary nitrile[12] or phenyl thioether,[13] followed by transmetalation to copper. We elected to compare the reductive lithiation of the tertiary nitrile **3.14** and thioether

3.16,[14] which were prepared readily as racemates using chemistry largely developed by Piers (Figure 3.3).[15] We were surprised to observe that the reductive lithiation of tertiary nitrile **3.14** at –78 °C was inefficient, as subjection of **3.14** to 2.2 equiv of lithium 4,4'-(di-*tert*-butyl)biphenylide (LiDBB) in THF at –78 °C, followed by attempted trapping of the organolithium with CO_2, resulted in nearly quantitative recovery of the tertiary nitrile (Figure 3.3B). In contrast, reductive lithiation of tertiary thioether **3.16** took place readily under identical conditions. Thus, treatment of **3.16** with 2.2 equiv of LiDBB in THF at –78 °C, followed successively by transmetalation with 1 equiv of $CuBr•SMe_2$ and addition to 4-vinylfuran-2-one (**3.9**) in the presence of TMSCl gave exclusively the product of 1,6-addition as a mixture of double bond isomers. The isomeric products converged to form racemic (±)-solidagolactone (*rac*-**3.2**) in 43% overall yield from thioether **3.16** upon exposure of the crude mixture to DBU in dichloromethane (Figure 3.3C).[14] The coupling of the tertiary organocuprate with the conjugate acceptor **3.9** occurred with high stereoselectivity exclusively from the less-hindered β-face of the *trans*-octahydronapthalene nucleophile. This outcome contrasts with the coupling reactions of *cis*-perhydropentalene and *cis*-perhydroazulene cuprates generated from tertiary nitriles **3.10** and **3.12** that we had studied earlier, which reacted with CO_2 preferentially from the more-hindered concave face to yield tertiary carboxylic acids **3.11** and **3.13** (Figure 3.3A).[9] We attribute the stereoselection observed in forming *rac*-**3.2** as arising from the severe steric impediment for the coupling to take place from the face proximal to the α-oriented angular methyl group. The coupling partner, 4-vinylfuran-2-one (**3.9**), is commercially available on scale,[16a] or can be prepared in two steps from tetronic acid following a literature procedure.[16b]

Figure 3.3. Previous studies on reductive lithiation of nitriles. Comparison of a nitrile and a phenylsulfide as precursors of a tertiary cuprate intermediate for the synthesis of *rac*-**3.2**.



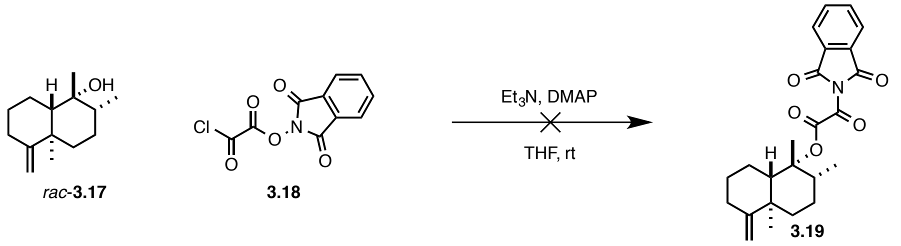
A. Previous studies on reductive lithiation/electrophilic trapping with CO_2 of *cis*-perhydropentalene **3.10** and *cis*-perhydroazulene **3.12** nitriles

B. Attempted generation of organolithium from nitrile

C. Forming a thioether-derived cuprate and its reaciton with 4-vinylfuran-2-one (**3.9**)

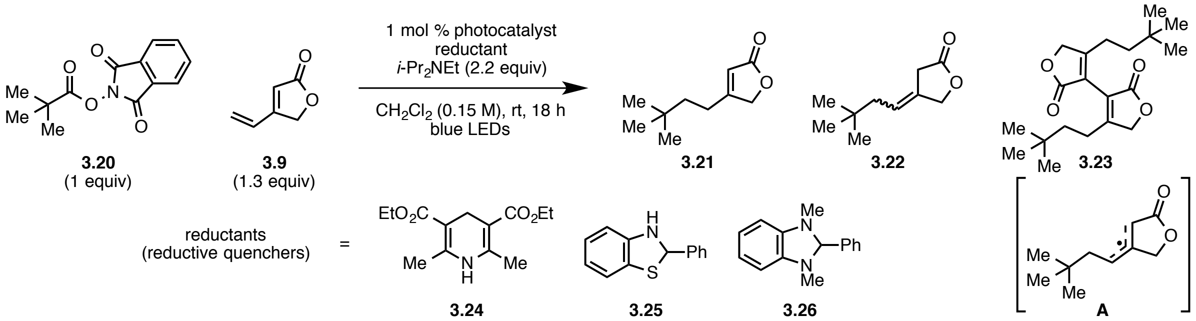
We next examined potential precursors from which the alternative tertiary radical intermediate could be generated and coupled with 4-vinylfuran-2-one (**3.9**). Our recent introduction of *tert*-alkyl *N*-phthalimidoyl oxalate precursors of tertiary carbon radicals suggested that the radical coupling might be accomplished using such an activating group.[10] However, we found that attempted acylation of tertiary alcohol *rac*-**3.17** with *N*-phthalimidoyl chlorooxoacetate (**3.18**) in the presence of Et_3N and catalytic DMAP to form the desired radical precursor **3.19** returned only the starting alcohol (Equation 3.1). A brief survey of more forcing conditions, including preformation of various tertiary alkoxide intermediates from alcohols and their reaction with *N*-phthalimidoyl chlorooxoacetate (**3.18**), resulted in substantial decomposition of the sensitive *N*-phthalimidoyl oxalate products. We then elected to perform the fragment coupling using the visible-light photoredox catalyzed method pioneered by Okada for generating tertiary radicals from carboxylic acid-derived *N*-acyloxyphthalimides,[17] since recent studies from our laboratory had shown that the reductive coupling of these substrates with electron-deficient alkenes is especially robust.[18]

Equation 3.1



As high-yielding 1,6-addition of carbon radicals to electron-deficient 1,3-dienes appears to be extremely rare,[19,20] in contrast to the well-established 1,6-addition of organocuprate intermediates,[20,21] we chose to initially explore this approach using the simpler *N*-acyloxyphthalimide **3.20** derived from trimethylacetic acid. Salient results of our optimization of the 1,6-coupling of the *tert*-butyl radical generated from **3.20** with 4-vinylfuran-2-one (**3.9**) are summarized in Table 3.1. Using conditions that we had optimized for the 1,4-addition of tertiary radicals to electron-deficient alkenes,[18b] **3.20** did provide the coupled product **3.21** accompanied by trace amounts of β,γ-unsaturated lactones **3.22** (entry 1). This product distribution would be inconsequential, as treatment with base had been shown previously to converge regioisomeric products of this type. More problematic was the formation of a significant amount of a product **3.23** containing two *tert*-butyl butenolide fragments. Such a product would arise from dimerization of the delocalized allylic radical intermediate **A** at the carbon adjacent to the carbonyl group, followed by isomerization of the double bonds into conjugation with the lactone carbonyl group. Speculating that the reduction potential of the catalyst might affect the termination sequence,[22] we screened several common visible-light photoredox catalysts in an attempt to minimize the formation of **3.23**. Of the iridium photocatalysts examined, *fac*-Ir(ppy)$_3$ did not promote the reaction, whereas Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ provided primarily radical dimer **3.23** (entries 2–4). [Ru(bpz)$_3$](BF$_4$)$_2$, whose +1 oxidation state is a much poorer reductant than Ru(bpy)$_3^{1+}$, also promoted no reactivity (entry 5). We also examined in addition to Hantzsch ester **3.24**, the use of two other reductive quenchers, **3.25**[23] and **3.26**,[24] with [Ru(bpy)$_3$](BF$_4$)$_2$. Both reduced the formation of product **3.23** (entries 6 and 7), with **3.26** delivering a 75% overall yield of 1,6-addition products. Ultimately, we found that the highest yields of adducts **3.21** and **3.22** were obtained, while avoiding the formation radical dimer **3.23**, by conducting the reaction at higher dilution (0.02 M) using an excess of the dihydropyridine reductant **3.24** (entry 9).[25]

Table 3.1. Optimization of the 1,6-addition of the *tert*-butyl radical generated from *N*-acyloxyphthalimide **3.20** with 4-vinylfuran-2-one (**3.9**).

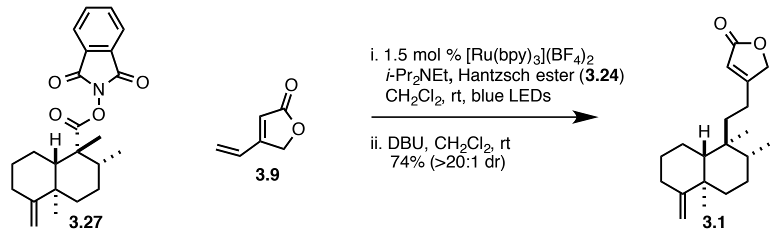


entry[a]	photocatalyst	reductant (equiv)	yield **3.21** (%)[b]	yield **3.22** (%)[b]	yield **3.23** (%)[b]
1	[Ru(bpy)$_3$](BF$_4$)$_2$	**3.24** (1.5)	36	<5	30
2[c]	*fac*-Ir(ppy)$_3$	**3.24** (1.5)	0	0	0
3	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	**3.24** (1.5)	24	0	42
4[c]	[Ir(dtbbpy)ppy$_2$]PF$_6$	**3.24** (1.5)	25	0	33
5	[Ru(bpz)$_3$](PF$_6$)$_2$	**3.24** (1.5)	0	0	0
6	[Ru(bpy)$_3$](BF$_4$)$_2$	**3.25** (1.5)	27	20	9
7	[Ru(bpy)$_3$](BF$_4$)$_2$	**3.26** (1.5)	66	9	<5
8	[Ru(bpy)$_3$](BF$_4$)$_2$	**3.24** (5.0)	46	<5	34
9[d]	**[Ru(bpy)$_3$](BF$_4$)$_2$**	**3.24 (5.0)**	**25**	**75**	**0**

[a]Conditions unless otherwise noted: **3.20** (1 equiv), **3.9** (1.3 equiv), photocatalyst (0.01 equiv), *i*-Pr$_2$NEt (2.2 equiv), reductant (1.5 or 5 equiv), 0.15 M (with respect to **3.20**) in CH$_2$Cl$_2$, rt, 18 h, blue LEDs. [b]Determined by ^{1}H NMR integration relative to an internal standard (1,4-dimethoxybenzene). [c]A compact fluorescent light was used in place of blue LEDs.[d] The concentration of **3.20** was 0.02 M.

Fortunately, the direct application of these conditions to the coupling of decalin tertiary radical formed from enantioenriched *N*-acyloxyphthalimide **3.27**, gave in high yield the desired 1,6-adducts as a mixture of double bond isomers (Equation 3.2).[14] Equilibration of these crude products with DBU afforded the *trans*-clerodane diterpenoid **3.1**, as a single stereoisomer at the newly formed C-9 quaternary carbon stereocenter. As expected,[18] this coupling took place exclusively from the less-hindered β-face of the *trans*-decalin tertiary radical intermediate. In addition, the yield of the coupled product **3.1** was significantly higher than that realized in the coupling of an organocuprate intermediate (Figure 3.3C).

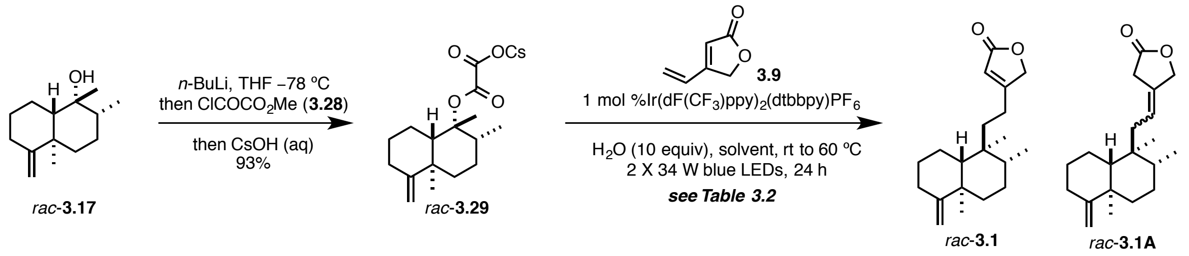
Equation 3.2



Although we successfully executed our fragment-coupling strategy utilizing *N*-acyloxyphthalimide **3.27** as a radical precursor, the approach suffered from five extra steps involved in introducing the carboxyl functionality, stemming from our inability to form (*N*-phthalimidoyl)oxalate **3.19** from the readily available tertiary alcohol *rac*-**3.17** (Equation 3.1). As a result of the relative stability of cesium salts of tertiary hemioxalates, it seemed likely that the method recently introduced from our and the MacMillan laboratories for generating tertiary radicals from cesium oxalate derivatives of tertiary alcohols under visible-light photoredox conditions might be successful with *trans*-decalin alcohol **3.17**.[11]

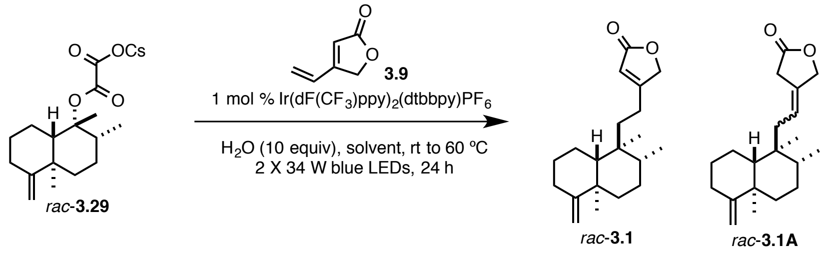
This possibility was initially pursued in the racemic series (Scheme 3.1). Although the highly hindered, axial tertiary alcohol *rac*-**3.17** did not react with methyl chlorooxoacetate (**3.28**) in the presence of DMAP and triethylamine,[11] initial deprotonation of *rac*-**3.17** in THF with *n*-BuLi at –78 °C, followed by the addition of 1.5 equiv of **3.28** and allowing the reaction to warm to room temperature generated the mixed oxalate diester in nearly quantitative yield. Exposure of a THF solution of this crude intermediate to just less than 1 equiv of aqueous CsOH provided cesium salt *rac*-**3.29** in 93% yield upon concentration of the aqueous layer.

Scheme 3.1. Synthesis of cesium oxalate *rac*-**3.29** and its photoredox coupling with 4-vinylfuran-2-one (**3.9**).



Optimization of the 1,6-conjugate addition of the tertiary carbon radical, generated from alkyl cesium oxalate *rac*-**3.29**, to 4-vinylfuran-2-one (**3.9**) was explored next (Table 3.2). Guided by the results from our previous studies with *N*-acyloxyphthalimide **3.27**, the coupling of *rac*-**3.29** with **3.9** was performed under high dilution to avoid dimerization of the intermediate allylic radical, leading to the formation of the desired coupling product *rac*-**3.1** in 63% yield (entry 1). Utilization of an excess of the radical precursor *rac*-**3.29** had minor effect on the efficiency of the reaction with respect to the more valuable coupling partner (entry 2). Solvent combinations that proved to be advantageous in other reactions utilizing *tert*-alkyl cesium oxalates were investigated next (entries 3–7), identifying a 3:1 mixture of DME:THF to be optimal for this transformation. Under these reaction conditions the double bond regioisomers, *rac*-**3.1** and *rac*-**3.1A**,[26] were formed and subsequently equilibrated with DBU in the final step of the synthesis (*vide infra*). Attempts to further increase the efficiency of the coupling via changes in concentration of the reaction mixture (entries 8, 9) or employing an excess of 4-vinylfuran-2-one (**3.9**) (entry 10) were unsuccessful.

Table 3.2. Optimization of the 1,6-addition of the *trans*-decalin radical generated from alkyl cesium oxalate *rac*-**3.29** with 4-vinylfuran-2-one (**3.9**).

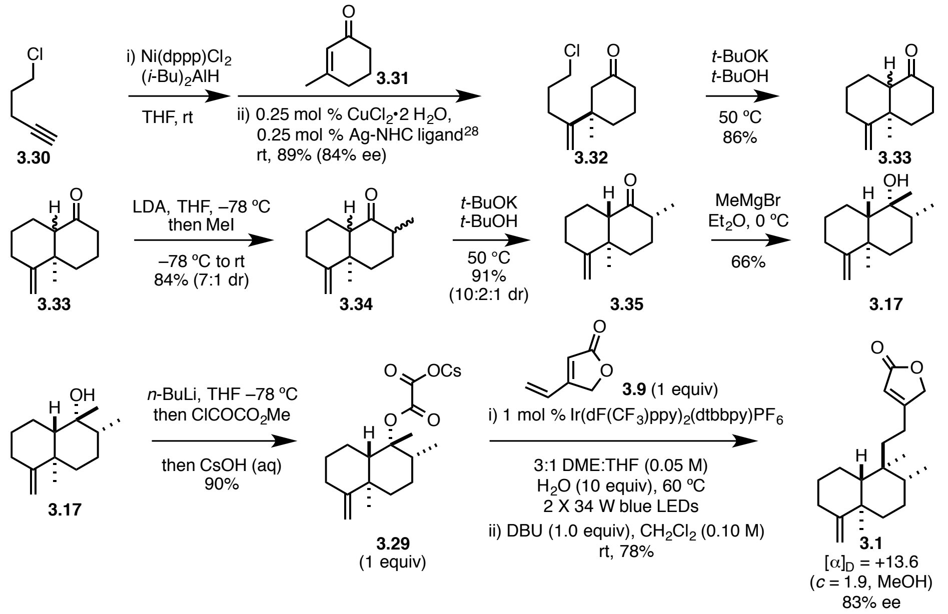


entry	solvent (M)^a	*rac*-**3.29** (equiv)	**6** (equiv)	yield *rac*-**3.1** (%)^b	yield *rac*-**3.1A** (%)^b
1	3:1 DME:DMF (0.05 M)	1.1	1	63 (57)^c	30
2	3:1 DME:DMF (0.05 M)	1.5	1	98 (65)^c	0
3	3:1 DMF:CH$_3$CN (0.05 M)	1	1	48	42
4	3:1 DMF:THF (0.05 M)	1	1	52	33
5	3:1 DME:CH$_3$CN (0.05 M)	1	1	66	0
6	**3:1 DME:THF (0.05 M)**	**1**	**1**	**70**	**10**
7	3:1 THF:DME (0.05 M)	1	1	47	10
8	3:1 DME:THF (0.01 M)	1	1	65	11
9	3:1 DME:THF (0.2 M)	1	1	41	8
10	3:1 DME:THF (0.01 M)	1	2	66	8

^{a}Concentration is reported with respect to cesium oxalate *rac*-**3.29**. ^{b}Determined by ^{1}H NMR integration relative to an internal standard (1,2-dibromo-4,5-methylenedioxybenzene). ^{c}Yield with respect to cesium oxalate *rac*-**3.29**.

Scheme 3.2 summarizes the use of the visible-light photoredox reaction of a *trans*-decalin cesium hemioxalate **3.29** with 4-vinylfuran-2-one (**3.9**) to achieve a short enantioselective total synthesis of *trans*-clerodane diterpenoid **3.1**. The synthesis begins with the enantioselective construction of *trans*-decalone **3.35** following the general lines outlined much earlier by Piers in the racemic series.[15] To render this sequence enantioselective, the first intermediate, 3,3-disubstituted (*R*)-cyclohexanone **3.32**, was prepared by catalytic enantioselective conjugate addition of a vinylcuprate to 3-methyl-2-cyclohexenone (**3.31**).[27] Specifically, two methods pioneered by Hoveyda were utilized: Ni-catalyzed regioselective hydroalumination of chloroalkyne **3.30**,[28] and Cu-NHC catalyzed 1,4-addition of the internal vinylalane intermediate to 3-methyl-2-cyclohexenone (**3.31**)[29] to furnish (*R*)-cyclohexanone **3.32** in 89% yield and 84% ee. Cyclization of **3.32** with *t*-BuOK provided decalone **3.33**, as a 2.8:1 mixture of *trans*:*cis* stereoisomers, in 77% overall yield from enone **3.31**. Methylation of decalone **3.33**, followed by *t*-BuOK-catalyzed equilibration provided **3.35** as a 10:2:1 mixture of diastereomers. Reaction of **3.35** with methylmagnesium bromide delivered *trans*-decalin alcohol **3.17**, which could be isolated in diastereomeric purity in 66% yield from **3.35**. Next, the one-pot acylation/saponification procedure described earlier provided oxalate salt **3.29** in 90% yield. The pivotal coupling of *trans*-decalin cesium oxalate **3.29** and butenolide **3.9** was carried out with equimolar amounts of the two coupling partners using the optimized visible-light photoredox conditions identified in our exploratory study (Table 3.2) to give **3.1** and its β,γ–unsaturated isomer as single epimers at the newly formed C-9 quaternary carbon stereocenter. Exposure of the crude product mixture to DBU at room temperature furnished *trans*-clerodane **3.1**, $[\alpha]_D$ +12.9 (*c* = 0.43, $CHCl_3$) and +13.6 (*c* = 1.9, MeOH), in 78% yield.[30] NMR data of synthetic (+)-**3.1** was identical to that observed earlier by us[14] and fully consistent with data described for natural **3.1**, whose rotation at the sodium D line was reported to be +15.2 (*c* = 1.9, MeOH).[3]

Scheme 3.2. Seven-step enantioselective synthesis of *trans*-clerodane diterpenoid **3.1**.



3.3 Conclusion

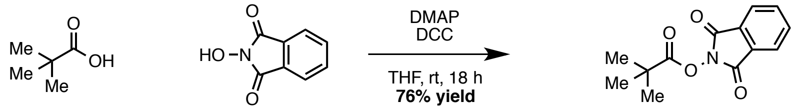
The enantioselective total synthesis of (+)-*trans*-clerodane diterpenoid **3.1** described in detail herein, and our earlier synthesis of (+)-**3.1** and congeners **3.2–3.4**,[14] illustrate a powerful tactic in organic synthesis in which a target structure is disconnected at a quaternary carbon stereocenter to yield fragments of comparable complexity, which are united in the synthesis by conjugate addition of a tertiary radical to a fragment harboring alkene–or in this case diene–functionality.[31] The selection of the precursor for generating the tertiary carbon radical intermediate is an important consideration. The short enantioselective total synthesis of (+)-clerodane diterpenoid **3.1** summarized in Scheme 3.2 exploits the use of tertiary alcohols as convenient precursors of tertiary carbon radicals upon activation by visible-light and photoredox catalysis.[11] Of critical importance, the coupling of *trans*-decalin cesium oxalate **3.29** and vinyl butenolide **3.9** was carried out in 78% yield using equimolar amounts of the two coupling partners. This enantioselective total synthesis of (+)-**3.1** was accomplished in seven steps from 3-methyl-2-cyclohexenone (**3.31**). As the *trans*-clerodane diterpenoids (–)-solidagolactone (**3.2**), (–)-PL3 (**3.3**) and (–)-annonene (**3.4**) have previously been prepared from (+)-**3.1** in 1–3 additional steps,[14] the synthetic strategy described in this report provides enantioselective access to a number of *trans*-clerodane diterpenoids by short sequences of 10 steps or less.[32]

3.4 Experimental Information

Materials and methods.

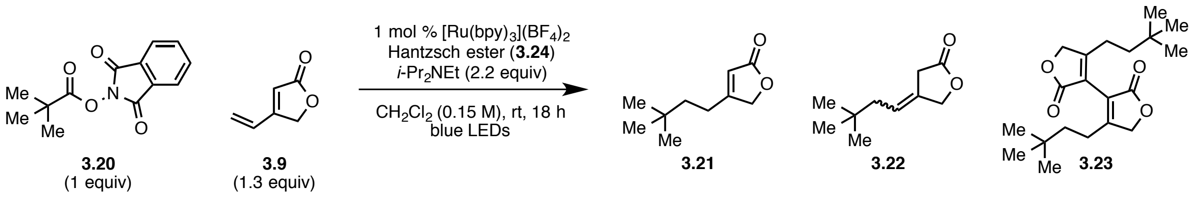
Experimental procedures and characterization data for, **3.1–3.4**, **3.14**, **3.16**, *rac*-**3.17**, **3.27**, and **3.32–3.34** have been reported previously.[14] The synthesis of *rac*-**20** and its characterization data has also been reported.[11a] A procedure for the radical addition reported in Table 3.2 has also been described previously in the racemic series.[10] Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of argon using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, ceric ammonium molybdate, or potassium permanganate. Flash chromatography was performed using 40–63 μm EMD Chemicals Silica Gel 60 Å Geduran silica gel. ^1H NMR spectra were recorded at 500 or 600 MHz and chemical shifts are reported relative to deuterated solvent signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded at 126 or 151 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on an FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility. Blue LEDs (30 cm, 1 watt) were purchased from http://www.creativelightings.com (product code CL-FRS5050-12WP-12V) and were powered by 8 AA batteries. Kessil KSH150B LED Grow Light 150, Blue LEDs, used in cesium oxalate couplings, were purchased from http://www.amazon.com. See JOC Standard Abbreviations and Acronyms for abbreviations. Available at:

http://pubs.acs.org/userimages/ContentEditor/1218717864819/joceah_abbreviations.pdf.



3.20

Preparation of *N*-acyloxyphthalimide 3.20: Pivalic acid (2.00 g, 19.6 mmol, 1 equiv) and *N*-hydroxyphthalimide (4.80 g, 29.4 mmol, 1.5 equiv) were dissolved in THF (200 mL) under an argon atmosphere. After sequential addition of dicyclohexylcarbodiimide (6.07 g, 29.4 mmol, 1.5 equiv) and DMAP (120 mg, 0.98 mmol, 0.05 equiv), the reaction mixture was stirred for 18 h at rt. The mixture was concentrated under reduced pressure, the resulting residue was suspended in Et_2O (200 mL) and transferred to a separatory funnel. The organic layer was washed with saturated aqueous NH_4Cl solution (3 x 150 mL) and brine (2 x 150 mL) and was dried over $MgSO_4$. The drying agent was removed by filtration and the filtrate was concentrated under reduced pressure. The crude residue obtained was purified by silica gel chromatography (7:93 EtOAc:hexanes) to provide the *N*-acyloxyphthalimide **3.20** (3.68 g, 14.9 mmol, 76% yield) as a colorless solid. Characterization data matched that previously reported.[33]

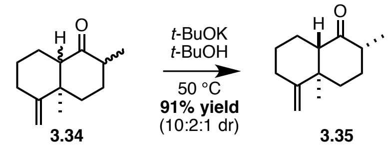


Preparation of lactones 3.21, 3.22, and 3.23 (Table 3.1, entry 1 is described): A solution of 4-vinylfuran-2-one (**3.9**)[34] in Et_2O (0.53 M, 610 µL, 0.34 mmol, 1.3 equiv) was added to a 1-dram vial and the solution was concentrated under reduced pressure. The residue was immediately dissolved in CH_2Cl_2 (1.5 mL, previously sparged with Ar for 5 min) under an argon atmosphere. After sequential addition of *N*-acyloxyphthalimide **3.20** (64 mg, 0.26 mmol, 1 equiv), Hantzsch ester **3.24**[35] (100 mg, 0.39 mmol, 1.5 equiv), *i*-Pr_2NEt (100 µL, 0.57 mmol, 2.2 equiv) and a solution of $[Ru(bpy)_3](BF_4)_2$[18] in CH_2Cl_2 (0.01 M, 260 µL, 0.003 mmol, 0.01 equiv) under Ar, the 1-dram vial was capped and placed in the center of a 30-cm loop of blue LEDs. The reaction mixture was stirred at rt under visible light irradiation for 18 h, after which time a solution of 1,4-dimethoxybenzene (36 mg, 0.26 mmol, 1 equiv) in CH_2Cl_2 (1 mL) was added. The reaction mixture was stirred for 1 min and a small aliquot was removed and concentrated under reduced pressure. ^{1}H NMR analysis of the residue and comparison of relative peak integrations using 1,4-dimethoxybenzene as an internal standard was used to determine the yield of products obtained. Silica gel chromatography (10:90 acetone:hexanes) of the crude mixture provided analytically pure samples of **3.21**, **3.22**, and **3.23**.

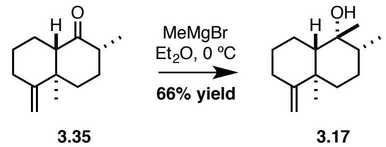
4-(3,3-Dimethylbutyl)furan-2(5H)-one (**3.21**): R_f = 0.16 (10:90 acetone:hexanes). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.80–5.83 (m, 1H), 4.74 (s, 2H), 2.32–2.38 (m, 2H), 1.43–1.48 (m, 2H), 0.93 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 171.4, 115.1, 73.2, 41.2, 30.4, 29.2, 24.2; IR (thin film) 2955, 2868, 1781, 1748, 1638, 1027 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{16}O_2Na$, $(M+Na^+)$ 191.1048, found 191.1054.

***E*- and *Z*- 4-(3,3-Dimethylbutylidene)dihydrofuran-2(3*H*)-one** (**3.22**, a 2.6:1 mixture of double-bond isomers): R_f = 0.3 (10:90 acetone:hexanes). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of isomers) δ 5.50–5.60 (m, 1H, major and minor isomers), 4.85–4.88 (m, 2H, major and minor isomers), 3.22–3.25 (m, 2H, major isomer), 3.13–3.15 (m, 2H, minor isomer), 1.90 (d, *J* = 7.5 Hz, 2H, minor isomer), 1.82 (d, *J* = 7.5 Hz, 2H, major isomer), 0.91 (s, 9H, major and minor isomers); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of isomers): δ 175.9, 175.8, 130.1, 129.6, 122.7, 122.2, 72.5, 70.7, 43.9, 42.6, 34.0, 31.9, 31.73, 31.68, 29.34, 29.29; IR (thin film) 2955, 1785, 1364, 1163, 1028 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{16}O_2Na$, (M+Na$^+$) 191.1048, found 191.1057.

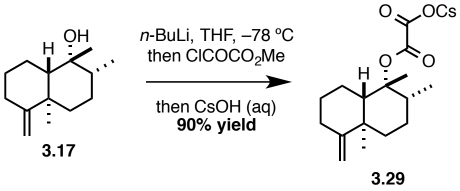
4,4'-bis(3,3-Dimethylbutyl)-[3,3'-bifuran]-2,2'(5*H*,5'*H*)-dione (**3.23**): R$_f$ = 0.12 (10:90 acetone:hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (s, 4H), 2.45–2.50 (m, 4H), 1.38–1.44 (m, 4H), 0.91 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 169.7, 117.3, 72.2, 41.6, 30.7, 29.1, 24.4; IR (thin film) 2955, 1756, 1620, 1157, 1030 cm^{-1}; HRMS (ESI-TOF) *m/z* calcd for $C_{20}H_{30}O_4Na$, (M+Na$^+$) 357.2042, found 357.2043.



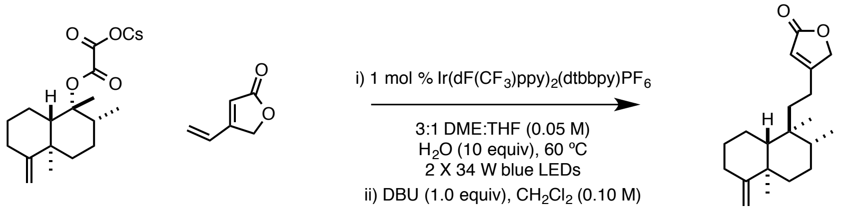
Preparation of ketone 3.35: A round-bottom flask was charged with ketone **3.34**[14] (844 mg, 4.39 mmol), *t*-BuOH (8.8 mL), and *t*-BuOK (985 mg, 8.78 mmol). The resulting solution was maintained at 50 °C for 2 h. The vessel was allowed to cool down to rt and the reaction was quenched with a saturated aqueous NH_4Cl (10 mL). The resulting mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to yield a colorless oil, which was purified by flash column chromatography on silica gel (98:2 hexanes:EtOAc) to yield **3.35** as a clear oil (770 mg, 91% yield, 10:2:1 dr). R$_f$ = 0.37 (19:1 hexanes:ethyl acetate). ^{1}H NMR (500 MHz, $CDCl_3$) of the major diastereomer: δ 4.71 (s, 2H), 2.41–2.22 (m, 3H), 2.18–2.09 (m, 2H), 1.98 (td, *J* = 13.5, 4.5 Hz, 1H), 1.91–1.84 (m, 2H), 1.67–1.56 (m, 3H), 1.30–1.21 (m, 1H), 1.03 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) of the major diastereomer: δ 213.5, 156.1, 105.8, 58.2, 45.4, 44.8, 36.1, 32.4, 32.0, 26.8, 21.2, 19.2, 14.6; IR (thin film) 2931, 2865, 1710, 1639, 1240 cm^{-1}; $[\alpha]^{19}_{D}$ +63.2, $[\alpha]^{19}_{577}$ +63.3, $[\alpha]^{19}_{546}$ +74.1, $[\alpha]^{19}_{435}$ +148, $[\alpha]^{19}_{405}$ +194 (*c* = 0.6, CH_2Cl_2); HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{20}ONa$ (M+Na$^+$) 215.1412, found 215.1403.



Preparation of alcohol 3.17: A round-bottom flask was charged with 13 mL of Et_2O and a solution of MeMgBr (2.5 mL, 7.5 mmol, 3.0 M solution in Et_2O) under an atmosphere of argon. The solution was stirred and cooled to 0 °C before a solution of ketone **3.35** (730 mg, 3.8 mmol, 10:2:1 mixture of three stereoisomers from the previous step) and Et_2O (3.0 mL) was added over 3 min. The reaction mixture was stirred for another 15 min at 0 °C and then was allowed to warm to rt. After 1 h at rt, the reaction mixture was poured into a saturated aqueous NH_4Cl (20 mL). The organic phase was separated and the aqueous phase was extracted with Et_2O (2 x 15 mL). The combined organic phases were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (98:2 hexanes:Et_2O) to yield, as a the single stereoisomer, **3.17** (524 mg, 2.52 mmol, 66% yield, 86% yield based on major diastereomer of **3.35**) as a clear oil that solidified to a colorless solid upon standing: R_f = 0.40 (10:1 hexanes:ethyl acetate, stained with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54–4.53 (m, 1H), 4.52 (s, 1H), 2.37 (td, *J* = 13.7, 5.2 Hz, 1H), 2.13–2.07 (m, 1H), 1.96–1.89 (m, 1H), 1.86–1.79 (m, 1H), 1.67–1.49 (m, 4H), 1.49–1.41 (m, 1H), 1.38–1.24 (m, 2H), 1.15 (s, 3H), 1.14 (s, 3H), 1.02 (dd, *J* = 12.5, 2.8 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 103.3, 74.4, 53.3, 41.5, 40.0, 37.0, 32.7, 28.4, 27.3, 26.7, 21.3, 20.1, 15.7; IR (thin film) 3619, 2931, 2859, 1634, 1447, 1372, 1180, 895 cm^{-1}; $[\alpha]^{21}_{D}$ +79.3, $[\alpha]^{21}_{577}$ +82.8, $[\alpha]^{21}_{546}$ +93.6, $[\alpha]^{21}_{435}$ +156, $[\alpha]^{21}_{405}$ +187 (*c* = 1.2, $CHCl_3$); HRMS (GC-CI-TOF) *m/z* calcd for $C_{14}H_{24}O$, $(M+NH_4^+)$ 226.2171, found 226.2173.



Preparation of cesium oxalate 3.29: A round-bottom flask was charged with alcohol **3.17** (478 mg, 2.30 mmol, 1.0 equiv) and THF (9.0 mL, 0.25 M) under an atmosphere of argon. The solution was cooled to –78 °C before a 2.5 M solution of *n*-BuLi in hexanes (930 μL, 2.3 mmol, 1.0 equiv) was added dropwise with stirring. The solution was stirred for an additional 15 min, then methyl chlorooxoacetate (320 μL, 3.5 mmol, 1.5 equiv) was added dropwise. The reaction was stirred at –78 °C for an additional 1 h, then was allowed to slowly warm to rt over 2–3 h as the dry ice/acetone bath slowly warmed to rt. The reaction was diluted with 20 mL of THF, and the organic phase was washed with saturated aqueous $NaHCO_3$ (2 x 10 mL), then with 50% sat. brine (10 mL). Aqueous 0.5 M CsOH (4.2 mL, 2.1 mmol, 0.9 equiv) was added to the separatory funnel and the mixture was shaken until the intermediate methyl oxalate was consumed as judged by TLC analysis (<5 min). Hexanes (30 mL) were added, and the aqueous phase was separated. The organic phase was washed with a second portion of water (10 mL), and the combined aqueous phases were concentrated under reduced pressure to give the product **3.29** as a colorless solid (849 mg, 90% yield). ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 4.52 (d, *J* = 8.3 Hz, 2H), 2.30 (td, *J* = 13.5, 4.8 Hz, 1H), 2.05 (app d, *J* = 12.4 Hz, 1H), 1.93–1.86 (m, 2H), 1.65 (qd, *J* = 13.1, 2.8 Hz, 1H), 1.60–1.49 (m, 6H), 1.39–1.31 (m, 2H), 1.19 (qt, *J* = 13.3, 4.0 Hz, 1H), 1.10 (s, 3H), 1.04 (dd, *J* = 12.4, 2.4 Hz, 1H), 0.88 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 167.6, 163.7, 158.8, 103.6, 83.9, 54.0, 43.2, 39.0, 36.7, 32.3, 27.9, 26.6, 22.8, 22.7, 20.2, 16.5; IR (thin film): 2832, 1715, 1635, 1218, 1163, 1038 cm^{-1}; $[\alpha]^{22}_{D}$ +43.5, $[\alpha]^{22}_{577}$ +44.7, $[\alpha]^{22}_{546}$ +51.0, [α⍰]$^{22}_{435}$ +85.8, $[\alpha]^{22}_{405}$ +101.6 (*c* = 1.0, MeOH); HRMS (ESI-TOF) *m/z* calcd for C$_{16}$H$_{23}$O$_4$, (M−Cs$^+$) 279.1596, found 279.1588.



3.29 (1 equiv) **3.9** (1 equiv) **3.1**

Preparation of *trans*-clerodane 3.1: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate salt **3.29** (106 mg, 0.300 mmol, 1.0 equiv) and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (3.4 mg, 0.0030 mmol, 0.01 equiv). A 3:1 mixture of DME:THF (6.0 mL, 0.05 M) was added, followed by water (54 μL, 3.0 mmol, 10 equiv) and 4-vinylfuran-2-one (**3.9**) (33 mg, 0.30 mmol, 1.0 equiv). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h with the reaction temperature rising to 60 °C because of heat given off from the LEDs. The reaction mixture was diluted with saturated aqueous LiCl (25 mL) and the aqueous phase was extracted with Et$_2$O (2 x 25 mL). The combined ethereal extracts were dried over Na_2SO_4 and concentrated. The crude material was filtered through silica gel (4:1 hexanes:EtOAc) to give a 1.3:1 mixture of α,β:β,γ-double bond isomers[36] (71 mg, 0.23 mmol). The mixture was dissolved in CH_2Cl_2 (2.5 mL, 0.10 M), followed by the addition of DBU (15 mg, 0.10 mmol, 1.0 equiv with respect to *β,γ*-double bond isomer). The homogenous solution was maintained at 23 °C for 15 min and loaded directly onto silica gel column, eluting with 4:1 hexanes:EtOAc to yield (+)-**3.1** as a colorless solid (71 mg, 0.23 mmol, 78% yield). R_f = 0.4 (4:1 hexanes:EtOAc); visualized with $KMnO_4$; $[\alpha]^{21}_{D}$ +12.9, $[\alpha]^{21}_{546}$ +12.6, $[\alpha]^{21}_{435}$ +17.9, $[\alpha]^{21}_{405}$ +13.1 (*c* = 0.43, $CHCl_3$); $[\alpha]^{21}_{D}$ +13.6, $[\alpha]^{21}_{577}$ +13.9, $[\alpha]^{21}_{546}$ +15.2, $[\alpha]^{21}_{435}$ +21.0 (*c* = 1.9, MeOH). Other characterization data acquired for (+)-**3.1** matched that previously reported.[3,14]

3.5 References and Notes:

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2. For example, a broad spectrum of bioactivity has been reported for *trans*-clerodane diterpenoid **3.3**. See: (a) Habtemariam, S.; Gray, A. I.; Waterman, P. G. *Planta Med.* **1992**, *58*, 109–110. (b) Gupta, V. K.; Verma, S.; Pal, A.; Srivastava, S. K.; Srivastava, P. K.; Darokar, M. P. *Appl. Microbiol. Biot.* **2013**, *97*, 9121–9131. (c) Misra, P.; Sashidhara, K. V.; Singh, S. P.; Kumar, A.; Gupta, R.; Chaudhaery, S. S.; Gupta, S. S.; Majumder, H. K.; Saxena, A. K.; Dube, A. *Brit. J. Pharmacol.* **2010**, *159*, 1143–1150. (d) Sashidhara, K. V.; Singh, S. P.; Srivastava, A.; Puri, A.; Chhonker, Y. S.; Bhatta, R. S.; Shah, P.; Siddiqi, M. I. *Eur. J. Med. Chem.* **2011**, *46*, 5206–5211. (e) Chen, C.-Y.; Chang, F.-R.; Shih Y.-C.; Hsieh, T.-J.; Chia, Y.-C.; Tseng, H.-Y.; Chen H.-C.; Chen S.-J.; Hsu, M.-C.; Wu, Y.-C. *J. Nat. Prod.* **2000**, *63*, 1475–1478. (f) Chang, F.-R.; Hwang, T.-L.; Yang, Y.-L.; Li, C.-E.; Wu, C.-C.; Issa, H.-H., Hsieh, W.-B.; Wu, Y.-C. *Planta Med.* **2006**, *72*, 1344–1347. (g) Lin, Y.-H.; Lee, C.-C.; Chang, F.-R.; Chang, W.-H.; Wu, Y.-C.; Chang, J.-G. *Life Sciences* **2011**, *89*, 886–895. (h) Lin, Y.-H.; Lee, C.-C.; Chan, W.-L.; Chang, W.-H.; Wu, Y.-C.; Chang, J.-G. *Toxicology* **2011**, *285*, 72–80. (i) Phadnis, A. P.; Patwardhan, S. A.; Dhaneshwar, N. N.; Tavale, S. S.; Row, T. N. G. *Phytochemistry* **1988**, *27*, 2899–2901.

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22. Termination by both hydrogen-atom transfer and single-electron reduction followed by protonation are possible, see: Lackner, G. L.; Quasdorf, K. W.; Pratsch, G.; Overman, L. E. *J. Org. Chem.* **2015**, *80*, 6012–6024, and reference 18b.

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25. Hantzsch ester **3.24** was ultimately chosen as the reductant for these conditions as it is more easily prepared than **3.25** and **3.26**.

26. Compound *rac*-**3.1A** was not isolated in pure form. Upon exposure of the mixture of addition products to DBU in CH_2Cl_2, equilibration of *rac*-**3.1A** to *rac*-**3.1** was observed (see the Experimental Information for details).

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30. Carrying out this coupling in a similar fashion in 3:1 DME:DMF (0.05 M) using 1.5 equiv of *trans*-decalin cesium oxalate **3.29** (160 mg) gave directly (+)-**3.1** in 98% yield (65% yield from **3.29**). Under these conditions, the β,γ-unsaturated lactone isomer of **3.1** was not detected.

31. For an early example of the use of this strategy, see reference 18a.

32. The text describing the reactions depicted in Figures 3.1–3.3, Equations 3.1–3.2, Tables 3.1–3.2, and Schemes 3.1–3.2 is taken verbatim from a previous publication, see: Slutskyy, Y.; Jamison, C. R.; Lackner, G. L.; Müller, D. S.; Dieskau, A. P.; Untiedt, N. L.; Overman, L. E. *J. Org. Chem.* **2016**, *81*, 7029–7035.

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35. Eey, S. T. C.; Lear, M. J. *Org. Lett.* **2010**, *12*, 5510–5513.

36. The β,γ-unsaturated lactones exist as a 1:1 mixture of *cis*- and *trans*-double bond isomers.

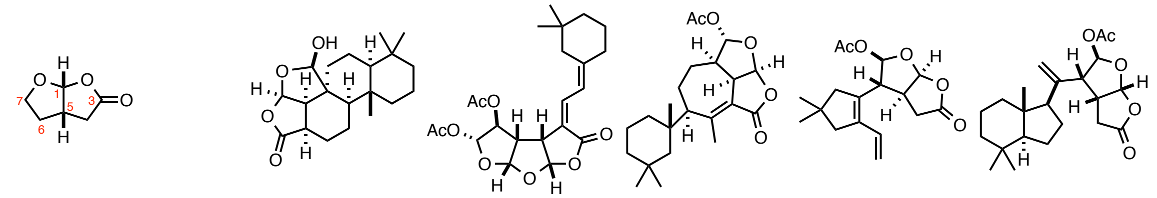
Chapter 4: Short Enantioselective Total Syntheses of Cheloviolenes A and B and Dendrillolide C via Convergent Fragment Coupling Using a Tertiary Carbon Radical

4.1 Introduction

More than 100 natural products harbor a *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one (**4.1**) fragment (Figure 4.1).[1] The marine diterpenoids dendrillol 1 (**4.2**),[2] gracilin C (**4.3**),[3] and darwinolide (**4.4**)[4] exemplify members of this group in which the dioxabicyclooctanone unit is fused to a larger polycyclic ring system. In others, such as the fungal sesquiterpenoid **4.5**,[5] the dioxabicyclic unit is isolated and joined by a single bond to a second cyclic or polycyclic fragment. Among these is a subset of rearranged spongian diterpenoids of marine origin, illustrated by **4.6–4.11**, having the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment joined at C-6 to a fourteen-carbon bicyclic hydrocarbon fragment.[6] The first member of this diterpenoid group to be reported was norissolide (**4.6**), whose structure and relative configuration were established by single-crystal X-ray diffraction analysis.[7] In the more common members of this group depicted in Figure 4.1B, the dioxabicyclo[3.3.0]octan-3-one fragment is joined by a single bond to a quaternary carbon of the hydrocarbon unit. The hydrocarbon fragment of these diterpenoids can reside on either the convex or concave face of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment, as exemplified respectively by cheloviolene A (**4.7**)[8,9] and macfarlandin C (**4.9**).[10] A freely rotating single bond having three staggered conformers of roughly similar energies characterizes this group of rearranged spongian diterpenoids. As a result of this structural feature, relating the configurations of the two chiral bicyclic fragments is notably challenging in the absence of X-ray structures. Only the relative configurations of macfarlandin C (**4.9**) and cheloviolene A (**4.7**) are known with certainty by virtue of single-crystal X-ray analyses.[8,10] The relative configurations of the other diterpenoids in this family are proposed to be as depicted in Figure 4.1B as a result of their presumed biosynthesis from precursors having a spongian skeleton **4.12** (see Figure 4.1C).[3,11] Absolute configurations for these natural products have not been established experimentally and are also proposed on the basis of this biosynthetic hypothesis.[12]

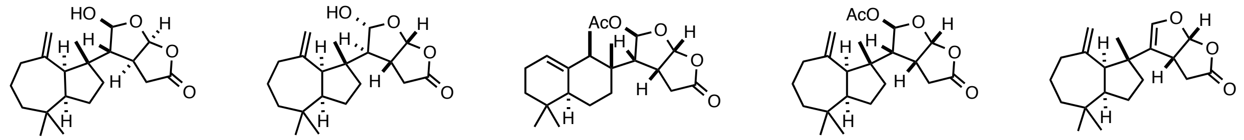
Figure 4.1. Representative natural products that harbor the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system and proposed biogenesis of rearranged spongian diterpenoids.

A. The *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system and representative structurally diverse natural products harboring this structural fragment.



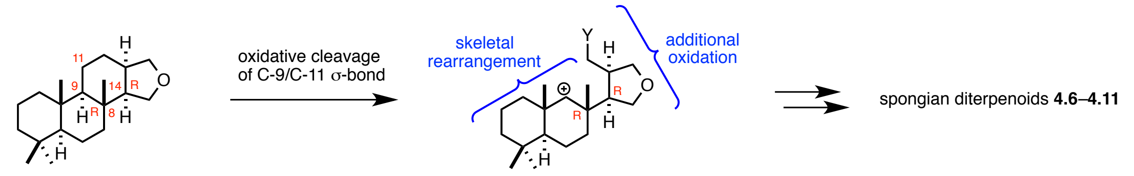
cis-2,8-dioxabicyclo[3.3.0]octan-3-one (**4.1**) dendrillol 1 (**4.2**) gracilin C (**4.3**) darwinolide (**4.4**) dermalactone (**4.5**) norissolide (**4.6**)

B. Rearranged spongian diterpenoids having a *cis*-dioxabicyclo[3.3.0]octan-3-one fragment attached to a quaternary carbon of a hydrocarbon fragment.



cheloviolene A (**4.7**) cheloviolene B (**4.8**) (corrected structure) macfarlandin C (**4.9**) dendrillolide A (**4.10**) dendrillolide C (**4.11**)

C. Proposed biogenesis of rearranged spongian diterpenoids such as **4.6**–**4.11** from a precursor having the spongian diterpenoid skeleton.

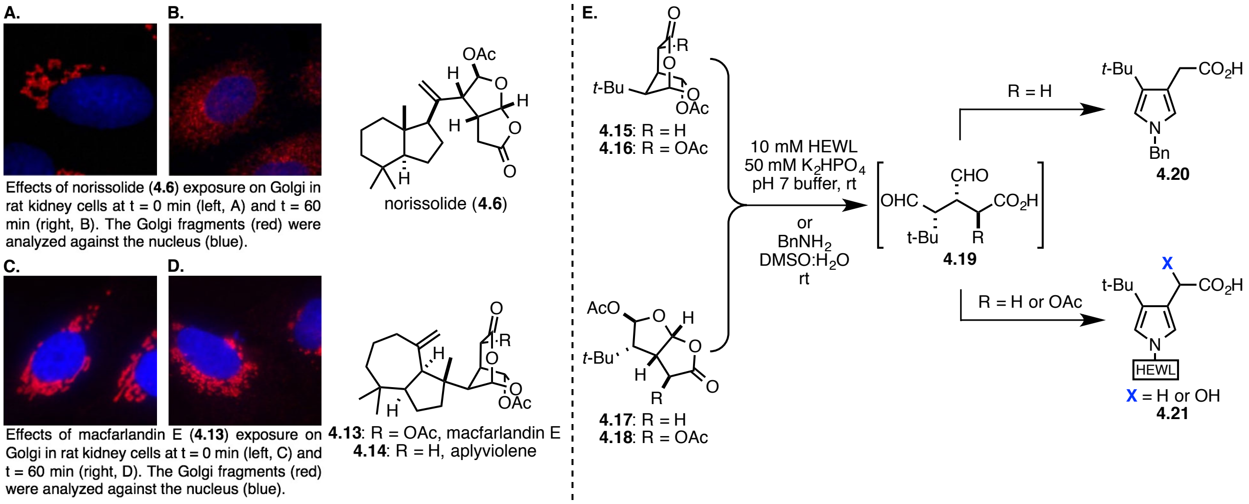


spongian skeleton (**4.12**) (e.g., Y = CO_2H)

The biological activity of rearranged spongian diterpenoids of marine origin has been little explored.[9,10,13] Our recent interest in the group of natural products exemplified in Figure 4.1B was stimulated by Sütterlin's observations from a screen of small molecule marine natural products that macfarlandin E (**4.13**, Figure 4.2), a rearranged spongian diterpenoid harboring a 2,7-dioxabicyclo[3.2.1]octan-3-one fragment, exhibits unique Golgi-altering activity.[14] Macfarlandin E (**4.13**) induces irreversible fragmentation of the

Golgi apparatus with the fragments remaining in the pericentriolar region of the cell (Figure 4.2C and 4.2D). This phenotype contrasts with the effects of other natural products such as brefeldin A,[15] ilimaquinone,[16] and norissolide (**4.6**),[17] which cause Golgi fragmentation with the resulting fragments being delocalized throughout the cytosol (Figure 4.2A and 4.2B). In our initial studies, we prepared racemic *tert*-butyl analogues **4.15–4.18** of the rearranged spongian diterpenoids macfarlandin E (**4.13**), aplyviolene (**4.14**) and dendrillolide A (**4.10**) and explored their chemical reactivity and effects on the Golgi apparatus (Figure 4.2E).[14,18] Both the bridged and fused dioxabicyclooctanone ring systems were found to react with primary amines to form pyrrole products (e.g., **4.20**), presumably via the intermediacy of 1,4-dialdehyde **4.19** generated upon cleavage of the anomeric acetoxy group. Under physiologically relevant conditions, *tert*-butyl analogues **4.15–4.18** reacted with lysine chains of hen egg white lysozyme (HEWL) to form pyrrole conjugates **4.21**, a reaction that could be the origin of the effects of these agents on the Golgi. The presence of an acetoxy substituent adjacent to the lactone carbonyl group in analogues **4.16** and **4.18** increased the extent of the lysine to pyrrole conversion and was important for induction of the macfarlandin E Golgi phenotype.[18] To further elucidate the mechanism by which dioxabicyclooctanones **4.15–4.18** trigger Golgi fragmentation, a more efficient preparation of these molecules was necessary as our initial route required many steps.[18]

Figure 4.2. Comparison of Golgi phenotypes induced by norissolide (**4.6**) and macfarlandin E (**4.13**) and proposed origin of the bioactivity of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one and 2,7-dioxabicyclo[3.2.1]octan-3-one fragments.

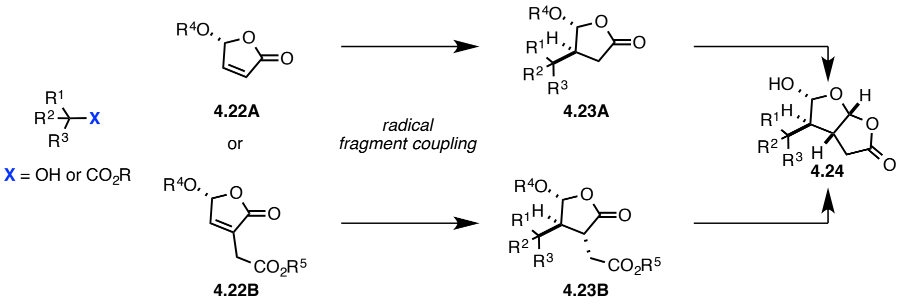


Effects of norissolide (**4.6**) exposure on Golgi in rat kidney cells at t = 0 min (left, A) and t = 60 min (right, B). The Golgi fragments (red) were analyzed against the nucleus (blue).

Effects of macfarlandin E (**4.13**) exposure on Golgi in rat kidney cells at t = 0 min (left, C) and t = 60 min (right, D). The Golgi fragments (red) were analyzed against the nucleus (blue).

As analogues having the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system were expected to be easier to access by chemical synthesis than their 2,7-dioxabicyclo[3.2.1]octan-3-one counterparts, our studies in this area focused on developing a short and versatile synthesis of 6-substituted *cis*-2,8-dioxabicyclo[3.3.0]octan-3-ones. Our plan was to employ fragment coupling reactions of tertiary carbon radicals generated from alcohol or carboxylic acid precursors by visible-light photoredox catalysis[19] to unite tertiary carbon fragments with an unsubstituted 5-alkoxybutenolide **4.22A** or a butenolide such as **4.22B** containing the additional two carbons of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one product **4.24** (Scheme 4.1). In the former instance, alkylation of the coupled product **4.23A** with a haloacetate electrophile would be employed to append the additional two carbons. In either case, coupling of a tertiary radical with butenolides **4.22A** and **4.22B** was expected to proceed with high stereoselectivity from the face opposite to the 5-alkoxy substituent.[28] The task of relating the configurations of the hydrocarbon and dioxabicyclooctanone fragments in total syntheses of the rearranged spongian diterpenoids depicted in Figure 4.1B would be addressed by uniting enantiopure butenolide and tertiary hydrocarbon fragments to form the demanding bond joining the two attached ring systems.[21,22] The sequence delineated in Scheme 4.1 could potentially access a wide variety of dioxabicyclooctanones **4.24** in 3–4 steps, representing a significant improvement on our earlier synthesis of **4.17** which required 14 steps.[18,23]

Scheme 4.1. Proposed fragment coupling strategy for the synthesis of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system



4.2 Results and Discussion

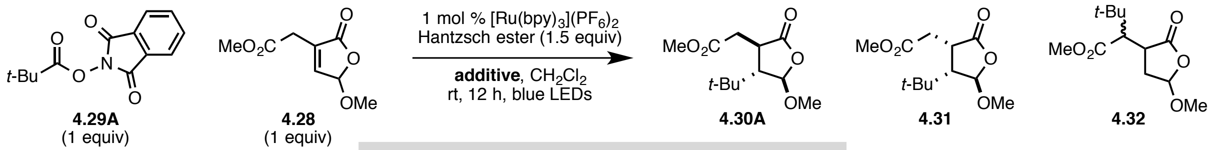
We examined the proposed sequence initially with 5-methoxybutenolide **4.28** containing all the carbon atoms of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system (Scheme 4.2). A ring closing metathesis route was developed for preparing racemic **4.28**.[24] The sequence starts with itaconic acid (**4.25**), which after converting selectively to the monomethyl ester by a known procedure,[25] was allylated to yield diester **4.26**. After examining several metathesis catalysts, the Stewart–Grubbs catalyst was found to be uniquely proficient at promoting the desired transformation to form butenolide **4.27**.[26] Optimization studies showed that reaction concentrations as high as 0.03 M could be employed before side products resulting from bimolecular metathesis were observed. The 5-methoxy substituent was introduced by initial bromination of **4.27** with NBS, followed by methanolysis[27] to deliver butenolide **4.28** in five steps from commercially available itaconic acid (**4.25**).

Scheme 4.2. Synthesis of butenolide **4.28**.

The fragment coupling was explored initially with the *N*-hydroxyphthalimide (NHP) ester of pivalic acid **4.29A** as the precursor of *tert*-butyl radical (Scheme 4.3). Using the modification of Okada's conditions[28] developed during our first studies in this area,[22] the Ru(bpy)$_3$-catalyzed reaction of equimolar amounts of activated ester **4.29A** and butenolide **4.28** in the presence of low-intensity blue LEDs, 1.5 equiv of a Hantzsch ester (diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate), and 1 equiv of *i*-Pr$_2$NEt proceeded to give the expected stereoisomeric products **4.30A** and **4.31** in a 10:1 ratio favoring the formation of the desired all-*trans* adduct **4.30A** (isolated in 72% yield).[29] The relative configuration of these stereoisomers was assigned initially on the basis of vicinal coupling constants and ^{1}H NOE data.[30,31] In addition to products **4.30A** and **4.31**, lactone **4.32**, which would arise from base-promoted isomerization of the double bond prior to radical coupling, was formed in ~5% yield. As would be expected, increasing the amount of *i*-Pr$_2$NEt enhanced the formation of byproduct **4.32**, whereas replacing *i*-Pr$_2$NEt with *i*-Pr$_2$NEt•HBF$_4$ led to **4.32** being produced in trace amounts only. To our initial surprise, stereoselection was reduced significantly (to 2:1) in coupling reactions conducted in the presence of *i*-Pr$_2$NEt•HBF$_4$. Although not understood at the time these experiments were carried out, our recent investigations suggest that in the presence of the basic amine the *α*-acyloxy radical produced upon conjugate addition is terminated by single-electron transfer

(SET) followed by protonation of the lactone enolate, whereas hydrogen-atom transfer (HAT) predominates in presence of *i*-$Pr_2NEt•HBF_4$.[32] It would not be surprising that the former termination process is more stereoselective.[33] Control experiments established that product ratios did not change with time and that adducts **4.30A** and **4.31** did not equilibrate at room temperature in the presence of excess *i*-Pr_2NEt.[34] In the hope of enchancing the formation of the minor adduct **4.31**, we examined a number of variables reported to affect stereoselection in HAT;[35] however, no conditions were identified that led to this product in useful yield.

Scheme 4.3. Coupling of *N*-acyloxyphthalimide **4.29A** with butenolide **4.28**.

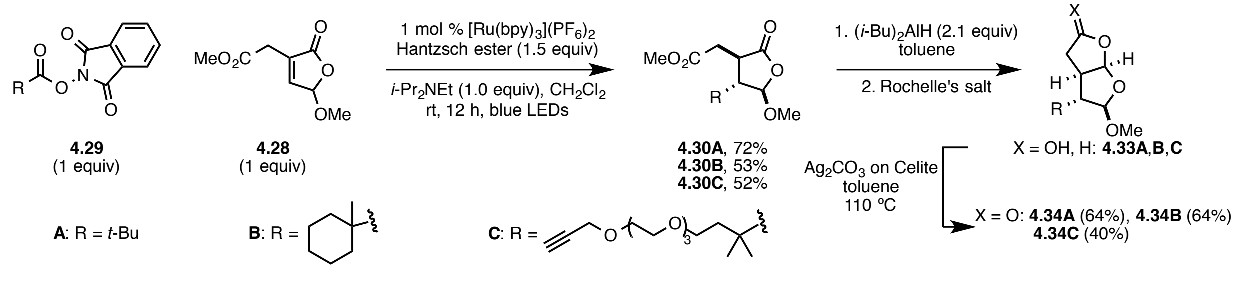


additive (equiv)	ratio **4.30A**:**4.31**:**4.32**[a]	yield of **4.30A**[b]
i-Pr_2NEt (1.0)	10:1:1	72%
i-Pr_2NEt (2.2)	10:1:2	ND
i-$Pr_2NEt•HBF_4$ (1.0)	2:1:ND	40%

[a]Determined by ^1H NMR integration of the crude reaction mixture. [b]Isolated yield.

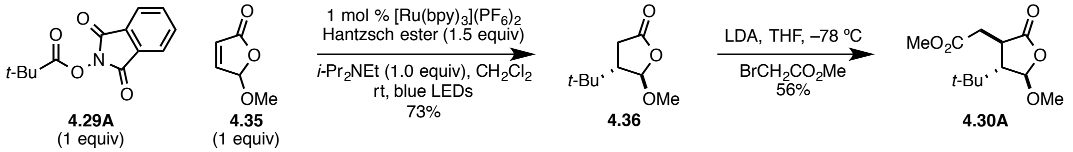
The salient results of our efforts to explore the scope of the fragment coupling step and to elaborate the conjugate-addition products to *cis*-2,8-dioxabicyclo[3.3.0]octan-3-ones are summarized in Scheme 4.4. The NHP esters **4.29B** and **4.29C**, the latter harboring a side chain chosen for use in future studies to pursue Golgi molecular targets, underwent stereoselective (dr = 5–10:1) reductive photoredox coupling with butenolide **4.28** in the presence of 1 equiv of *i*-Pr_2NEt to yield the all-*trans* trisubstituted products **4.30B** and **4.30C** in respectively 53% and 52% yield after purification on silica gel. In initial scouting studies, butyrolactone **4.30A** was allowed to react with 1 equiv of (i-Bu)$_2$AlH (DIBALH) at –78 °C in the hope that the lactone carbonyl could be selectively reduced to give, after intramolecular lactonization, *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one **4.34A**. However, this reaction did not afford **4.34A**, but gave rise to a 1:1 mixture of the starting lactone ester **4.30A** and dioxabicyclic lactol **4.33A**, suggesting that intramolecular lactonization of the diisobutylaluminum lactol intermediate was faster than reduction of the starting butyrolactone. After screening several reductants and reaction conditions with only modest success, we turned to accomplishing the desired conversion in two steps. A quick survey showed that several oxidants, including Br_2, PCC, acetone (via Oppenhauer oxidation), and Ag_2CO_3 supported on Celite could transform **4.33A** to dioxabicyclooctanone **4.34A**, the latter leading to the highest yield of the desired product. The final sequence involved reduction of the coupled products **4.30** with 2.1 equiv of (*i*-Bu)$_2$AlH at –78 °C and isolation of the crude mixture of lactol epimers **4.33A–C** after workup with an aqueous solution of Rochelle's salt. This crude mixture of lactol intermediates was then directly oxidized with Ag_2CO_3/Celite in refluxing toluene to give *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one **4.34A–C** in 40–64% yield.

Scheme 4.4. Synthesis of analogues containing the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system via a radical fragment coupling strategy.



Although the convergent construction of *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one was appealing, the yield of the all-*trans* product from the addition of tertiary radicals to butenolide **4.28** was compromised by the formation of the two additional isomeric products **4.31** and **4.32** depicted in Scheme 4.3. As a result, we examined the alternate sequence in which an unsubstituted 5-alkoxybutenolide would be the radical acceptor, an approach that could be advantageous because of the commercial availability of several butenolides of this type in high enantiomeric purity.[36] As summarized in Scheme 4.5, reductive photoredox-catalyzed coupling of the *tert*-NHP ester **4.29A** with racemic 5-methoxybutenolide (**4.35**) gave exclusively the *trans* product **4.36** in 73% yield. The reaction proceeded in identical yield, also with complete stereoselectivity, when *i*-Pr_2NEt•HBF_4 was substituted for *i*-Pr_2NEt. Alkylation of the lithium enolate of **4.36** with methyl bromoacetate occurred stereoselectively to give a single product **4.30A** in 56% yield. Although the transformations summarized in Schemes 4.3–4.5 likely could be further optimized, we chose to move forward to explore the application of this chemistry for the synthesis of rearranged-spongian diterpenoids that harbor a *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment.

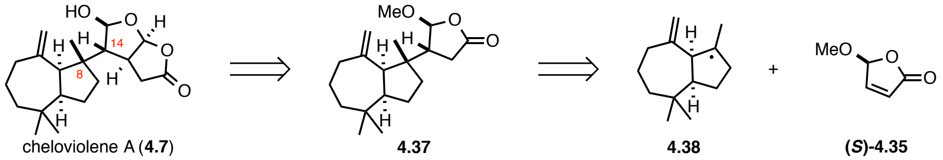
Scheme 4.5. Two-step synthesis of lactone **4.30A** via coupling of *tert*-NHP ester **4.29A** with unsubstituted butenolide **4.35**, followed by alkylation with methyl bromoacetate.



The plan for synthesis of (+)-cheloviolene A (**4.7**) using the approach developed in our exploratory studies is outlined in retrosynthetic format in Scheme 4.6. The decisive step would be the Giese coupling of *cis*-perhydroazulene radical **4.38** with butenolide **(*S*)-4.35** to form tricyclic adduct **4.37**. The configuration of the C-8 and C-14 stereocenters of the attached chiral bicyclic rings of (+)-cheloviolene A (**4.7**) would derive from the expected high preference for this union to take place from the convex face of the *cis*-

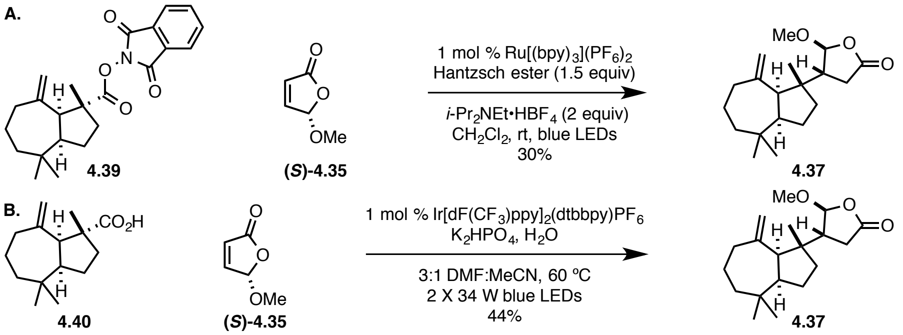
perhydroazulene radical[22] and the face opposite the methoxy substituent of butenolide **(*S*)-4.35** to form coupled product **4.37**.

Scheme 4.6. Proposed fragment-coupling strategy for the synthesis of cheloviolene A (**4.7**).



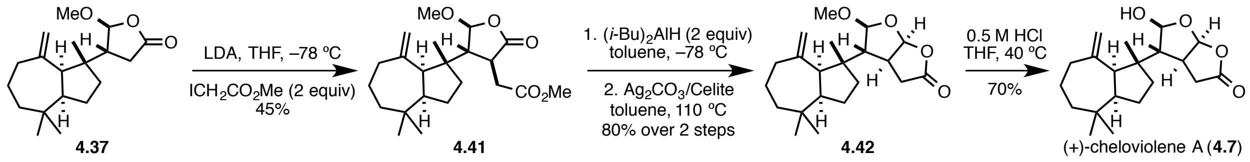
The pivotal radical coupling was examined initially using the enantiopure *cis*-perhydroazulene NHP ester **4.39**, which we had prepared earlier in 14 steps from (+)-fenchone.[22] Exposure of the activated ester **4.39** and butenolide **4.35** to Ni-catalyzed Giese reaction conditions did not lead to the formation of the desired product **4.37**.[37,38] In contrast, when equimolar amounts of coupling partners **4.39** and **4.35** were subjected to photoredox reaction conditions the desired lactone **4.37** was obtained as a single stereoisomer (Equation 4.1A). However, the efficiency of the reaction was poor, resulting in a modest 30% yield of coupled product **4.37**. The major byproducts were derived from premature reduction of the tertiary radical generated upon reductive cleavage of *N*-acyloxyphthalimide **4.39**. We hypothesized that the presence of Hantzsch ester, a known hydrogen atom donor,[39] was largely responsible for the undesired reduction of the intermediate tertiary radical. To circumvent premature reduction of the tertiary radical, we examined the coupling of *cis*-perhydroazulene carboxylic acid **4.40** with 1 equiv of **(*S*)-4.35** using the Ir(III)-catalyzed photoredox conditions developed by MacMillan[40] in which no external reductants or hydrogen atom sources are required. In this case, the desired product **37** was isolated in 44% yield (Equation 4.1B). Once again premature reduction of the tertiary radical was observed,[41] suggesting that a more activated acceptor would be required to efficiently trap sterically encumbered *cis*-perhydroazulene radical **4.38**.

Equation 4.1



Despite modest yields of the key coupling step, we turned our attention to elaboration of the lactone fragment of addition product **4.37** to a *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one to conclude a first-generation total synthesis of (+)-cheloviolene A (**4.7**) (Scheme 4.7). Deprotonation of lactone **4.37** with LDA at –78 °C, followed by addition of methyl iodoacetate furnished methyl ester **4.41**, as a single stereoisomer, in 45% yield. Next, reduction of **4.41** with excess DIBALH at –78 °C, followed by direct oxidation of the resulting epimeric mixture of dioxabicyclic lactols under Fétizon oxidation conditions provided tetracyclic intermediate **4.42** in 80% yield. Finally, hydrolysis of **4.42** with dilute aqueous HCl at 40 °C furnished (+)-cheloviolene A (**4.7**), mp: 157–158 °C, in 70% yield. Synthetic **4.7** exhibits a higher optical rotation from the one reported in literature, synthetic: $[\alpha]_D^{22}$ +49 (*c* 0.11, $CHCl_3$), literature: $[\alpha]_D$ +4.5 (*c* 0.11, $CHCl_3$).[8] However, the spectroscopic data for synthetic 4.**7** compared well with those reported for the natural product isolated from the New Zealand sponge *Chelonaplysilla violacea*, leaving little doubt as to their identity.[9] In addition, the structure of synthetic (+)-cheloviolene A was confirmed by single-crystal X-ray analysis.[42a]

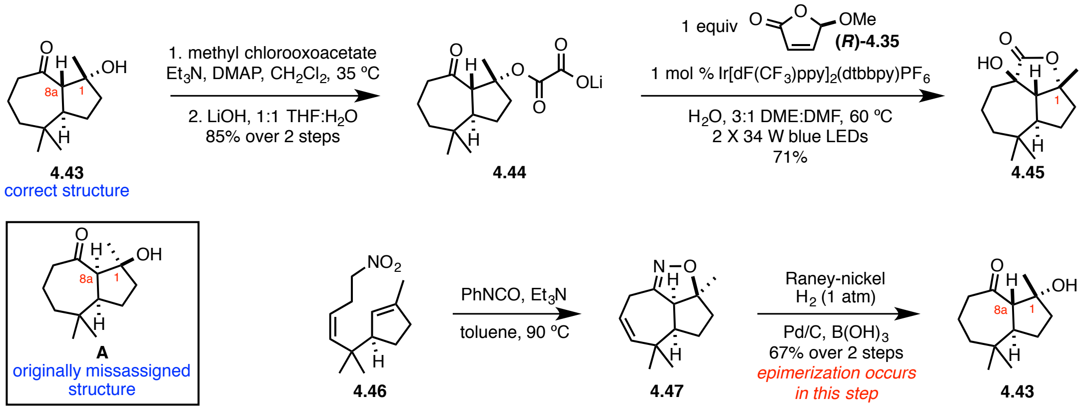
Scheme 4.7. First-generation synthesis of (+)-cheloviolene A (**4.7**).



Completion of the synthesis of (+)-cheloviolene A (**4.7**) validated our strategy and identified several problems that needed to be addressed to secure a more concise approach to the family of spongian diterpenoids containing a *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment. First, the efficiency of the radical fragment-coupling step had to be improved, which would likely necessitate use of a more activated butenolide radical acceptor. Second, a shorter synthesis of a precursor of the *cis*-perhydroazulene tertiary radical **4.38** would be needed, as our earlier preparation of carboxylic acid **4.40** required 13 steps.[22] The recent development of convenient methods to generate tertiary radicals from tertiary alcohols[43,44] directed our attention to the use of a tertiary *cis*-perhydroazulene alcohol as the radical precursor.

A *cis*-perhydroazulene tertiary alcohol, which at the time was assigned structure **A** (Scheme 4.8), was an intermediate in our earlier synthesis of *cis*-perhydroazulene carboxylic acid **4.40**.[22] As this alcohol was accessed on gram-scale in only eight steps from (+)-fenchone, we initially examined whether it, or potentially an exomethylene analogue, could be utilized in the crucial radical coupling event. To test the feasibility of this approach, alcohol **4.43** was acylated with methyl chlorooxoacetate and the resulting diester selectively saponified with 0.95 equiv of LiOH to provide *cis*-perhydroazulene lithium oxalate salt **4.44** in 85% yield. Upon attempted coupling of oxalate salt **4.44** with (*R*)-butenolide **(*R*)-35** using the Ir(III)-catalyzed photoredox conditions developed earlier,[43,44] no coupling product was observed, rather a tricyclic lactone **4.45**, whose structure was unambiguously established via single-crystal X-ray analysis of the 4-nitrobenzoate derivative, was isolated in 71% yield.[42b] To our surprise, the perhydroazulene fragment of **4.45** is *trans*-fused and the configuration at C-1 is opposite to that expected from a precursor of structure **A**. Single-crystal X-ray analysis of the phenylhydrazone derivative of **4.43** confirmed that tertiary alcohol **4.43** has the stereostructure depicted in Scheme 4.8, with the C-1 and C-8a stereocenters opposite to those found in the originally misassigned structure **A**.[42c] To the best of our knowledge, the addition of an alkoxyacyl radical to a ketone carbonyl group is without precedent.

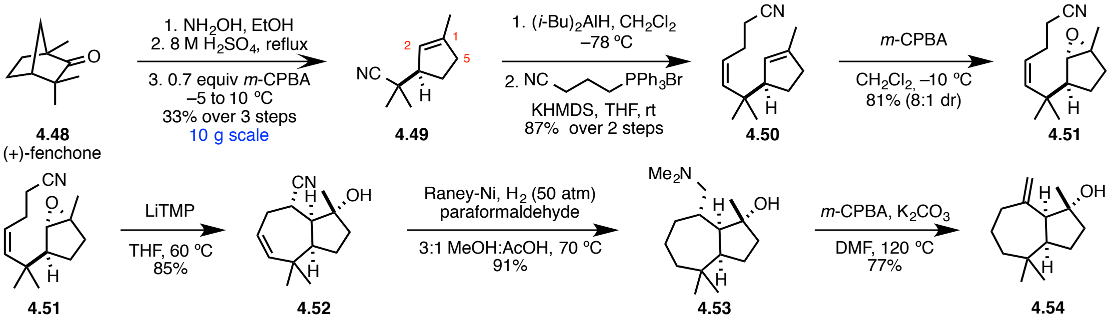
Scheme 4.8. Unexpected intramolecular 5-*exo* cyclization of the intermediate alkoxycarbonyl radical and correct stereochemical assignment of tertiary alcohol **4.43**.



Brief comment on our original assignment of structure **A** to the perhydroazulenol intermediate used to prepare *cis*-perhydroazulene carboxylic acid **4.40** is warranted. First, this structural misassignment was not detected in our earlier studies because the next step in the synthesis of **4.40**, dehydration of tertiary alcohol **4.43** to form the corresponding conjugated enone, removed the C-1 and C-8a stereocenters of **4.43**.[22] In this earlier synthesis, the perhydroazulene ring was constructed by intramolecular nitrile oxide cycloaddition of nitro precursor **4.46** to yield an isoxazoline intermediate, whose structure was assigned as **4.47** on the basis of excellent precedent.[45] Extensive 2D NMR experiments confirm the relative configuration of cycloadduct **4.47**. Thus, epimerization of the ring fusion and alcohol stereocenter in route to **4.43** must occur during reduction of isoxazoline **4.47** under acidic conditions.[46] This epimerization, which undoubtedly arises by a retro aldol/aldol sequence, has precedent in the unmasking of related tricyclic isoxazolines in the presence of boric acid.[47–49]

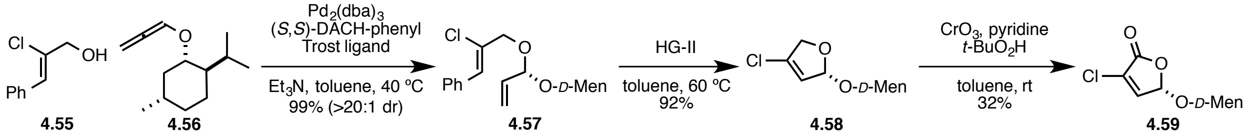
It was clear at this point that a new route to a *cis*-perhydroazulenol intermediate would be required. We conjectured in addition that the tertiary alcohol should reside on the convex face of the *cis*-perhydroazulene ring to avoid the possibility of unwanted cyclization of a transiently generated alkoxyacyl radical onto a proximal carbonyl or exomethylene functional group. Our development of a short enantioselective route to access such an intermediate, *cis*-perhydroazulenol **4.54**, is summarized in Scheme 4.9. The synthesis began with inexpensive (+)-fenchone (**4.48**), whose oxime derivative underwent a known Beckmann fragmentation when heated at reflux with aqueous sulfuric acid to give cyclopentene nitrile **4.49** and its $\Delta^{1,5}$ isomer in near-equal amounts.[50] Although these double-bond regioisomers can be separated by careful chromatography on silver nitrate-impregnated silica gel,[22] we found it more convenient on scale to selectively epoxidize the less-hindered $\Delta^{1,5}$ isomer of this mixture thereby allowing pure **4.49** to be obtained reliably on 10 g scales by simple flash chromatography on silica gel. Conventional reduction of nitrile **4.49** and Wittig olefination of the aldehyde product gave dienyl nitrile **4.50** in 87% yield over two steps. As the prelude to forming the seven-membered ring, the trisubstituted double bond of **4.50** was selectively epoxidized by reaction with 1 equiv of *m*-CPBA at –10 °C in CH_2Cl_2 to give an 8:1 mixture of stereoisomers from which the major isomer **4.51** was isolated after chromatographic purification in 81% yield. Deprotonation of **4.51** with 1 equiv of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) induced stereospecific cyclization to form *cis*-perhydroazulenol **4.52** in 85% yield.[51,52] To our knowledge, this is the first example of forming a seven-membered ring by Stork epoxy-nitrile cyclization,[53] an outcome undoubtedly assisted by the *cis*-double bond in the tether and the presence of *gem*-dimethyl substitution. After examining several non-conventional methods for transforming the nitrile substituent to an exomethylene group in one step, this transformation was ultimately realized in high yield by a two-step sequence. First, reaction of **4.52** with Raney-Ni and hydrogen (50 atm) in the presence of paraformaldehyde delivered amino alcohol **4.53** in 91% yield. Formation of the corresponding *N*-oxide and heating this crude intermediate to 120 °C in DMF occasioned clean Cope elimination to provide alcohol **4.54** in 77% yield.[54]

Scheme 4.9. Synthesis of *cis*-perhydroazulene tertiary alcohol **4.54**.



In addition to developing an expedited route to a precursor of *cis*-perhydroazulene radical **4.38**, both the conjugate addition step and the elaboration of the butenolide fragment of the coupled product to a *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one would need to be optimized significantly in order to define an efficient route to (+)-cheloviolene A (**4.7**) and congeners. Initially we wished to evaluate whether incorporation of a radical-stabilizing group at the α-position of a 5-alkoxybutenolide would increase the efficiency of the fragment-coupling step. An obvious choice would be a chlorine substituent.[22,55] Undoubtedly reflecting the sensitivity of the allylic acetal functionality, our attempts to directly introduce chlorine at C-3 of a 5-alkoxybutenolide led to either decomposition or, when attempted with enantiopure 5-alkoxybutenolides, partial racemization.[56] As a result, our efforts shifted to the development of a new route to 3-chloro-5-alkoxybutenolides that would exploit Rhee's recent method for enantioselective synthesis of acetals (Scheme 4.10).[57] The sequence began with palladium-catalyzed enantioselective alkoxylation of (*D*)-menthol-derived allene **4.56** with allylic alcohol **4.55** to deliver mixed acetal **4.57** in 99% yield as a single detectable diastereomer by ^{1}H NMR analysis.[58] Subjection of diene **4.57** to the Hoveyda-Grubbs second-generation catalyst in toluene at 60 °C gave rise to dihydrofuran **4.58** in excellent yield on gram-scale. Incorporation of the phenyl group in the alkenyl chloride fragment was crucial to the success of this ring-closing metathesis as reported by Dorta.[59,60] After much experimentation, we found that the demanding allylic oxidation of **4.58** could be accomplished with CrO_3 and *tert*-butylhydroperoxide[61] to reliably give butenolide **4.59** in 32% yield.[70–72] The opposite enantiomer of butenolide **4.59** was readily accessible on gram-scale by the same sequence, starting from (*L*)-menthol and employing the opposite enantiomer of the Trost ligand.

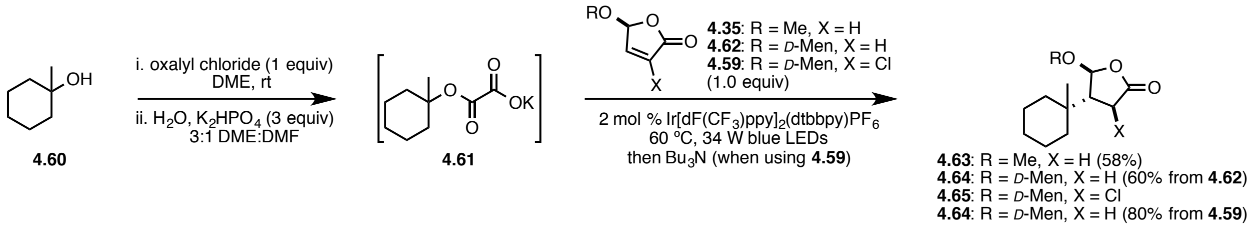
Scheme 4.10. Synthesis of chlorobutenolide **4.59**.



Our exploratory studies, summarized in Scheme 4.11, aimed at developing a one-pot sequence for directly transforming a tertiary alcohol to a coupled product and optimizing the coupling with a 5-alkoxybutenolide. We eventually found that reaction of 1-

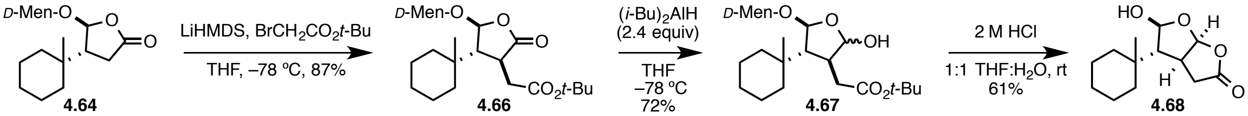
methylcyclohexanol (**4.60**) with 1 equiv of oxalyl chloride at room temperature in DME, followed by addition of water and 3 equiv of K_2HPO_4 cleanly generated the potassium hemioxalate intermediate **4.61** *in situ*. Direct addition of 1 equiv of 5-methoxybutenolide (**4.35**) in DMF, followed by photoredox-catalyzed coupling as described previously[43] provided *trans* adduct **4.63** as a single stereoisomer in 58% yield.[65] Using menthyloxybutenolide **4.62**,[66] coupled product **4.64** was generated, again as a single stereoisomer, in this case in 60% yield. The analogous coupling with butenolide **4.59** harboring a 3-chloro substituent was much more efficient delivering a 3:1 mixture of **4.65** and dechlorinated analogue **4.64** in 78% combined yield. Addition of 10 equiv of tri-*n*-butylamine to the reaction mixture following the initial fragment coupling with butenolide **4.59** and allowing the subsequent photocatalytic dechlorination[67] to proceed for 4 h gave conjugate addition product **4.64** in 80% yield in one-step from alcohol **4.60**.

Scheme 4.11. One-step activation and coupling of 1-methylcyclohexanol with butenolides.



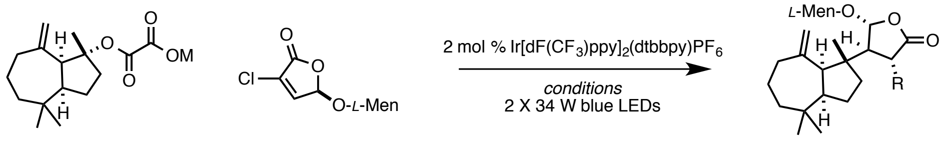
In our first-generation synthesis of (+)-cheloviolene A (**4.7**), a four-step sequence proceeding in 25% yield was used to fashion the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one moiety from the butyrolactone fragment of the coupled product (Scheme 4.7). We anticipated that this elaboration could be shortened by one step by introducing the acetic ester side chain as a *tert*-butyl ester. This sequence in the 1-methylcyclohexyl model series is summarized in Scheme 4.12. Enolization of coupled product **4.64** with LiHMDS, followed by trapping with *tert*-butyl bromoacetate took place stereoselectively to give *tert*-butyl ester **4.66** in high yield. As expected, the steric bulk of the *tert*-butyl ester simplified chemoselective reduction of the lactone carbonyl group of **4.66** such that reaction with 2.4 equiv of $(i\text{-Bu})_2AlH$ in toluene at –78 °C delivered lactol **4.67** in 72% yield. Finally, exposure of this intermediate to 2 M HCl formed the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one moiety and cleaved the menthyl acetal to provide tricyclic product **4.68** in 61% yield. This expedited sequence furnished **4.68** in 38% yield over three steps from coupled product **4.64**.

Scheme 4.12. Improved synthesis of *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one **4.68** from the radical coupling product **4.64**.



Our studies aimed at second-generation total syntheses of rearranged spongian diterpenoids **4.7**, **4.8**, and **4.11** began by optimizing the efficiency of the fragment-coupling reaction between butenolide ***ent*-4.59** and *cis*-perhydroazulene oxalate salts **4.69**. In this study, the oxalate salt intermediates were generated by selective hydrolysis of the mixed oxalate diester formed from *cis*-perhydroazulenol **4.54** and methyl chlorooxalate (Table 4.1).[43] An initial solvent screen revealed DME and THF to be superior to other solvents, with the Ir(III)-catalyzed visible-light photocatalytic reaction yielding mixtures of coupled product **4.70** and its dechlorinated analogue **4.71** in ~40% combined yield (entries 1–4).[68] We utilized THF in our further optimization experiments because of the overall cleaner reaction profile and lower amounts of dechlorinated product **4.71** in this solvent. Increasing the amount of water in the reaction was deleterious to reaction efficiency (entry 5). The yield of the transformation could be increased somewhat by using 1.5 equiv of the butenolide radical acceptor (entry 6). However, since our objective was to optimize the coupling step using equimolar amounts of the addends, 1 equiv of the butenolide was used in subsequent experiments.

Table 4.1. Optimization of the coupling between oxalate **4.69** and butenolide ***ent*-4.59**.



4.69
(1 equiv)

***ent*-4.59**
(1 equiv)

4.70: R = Cl
4.71: R = H

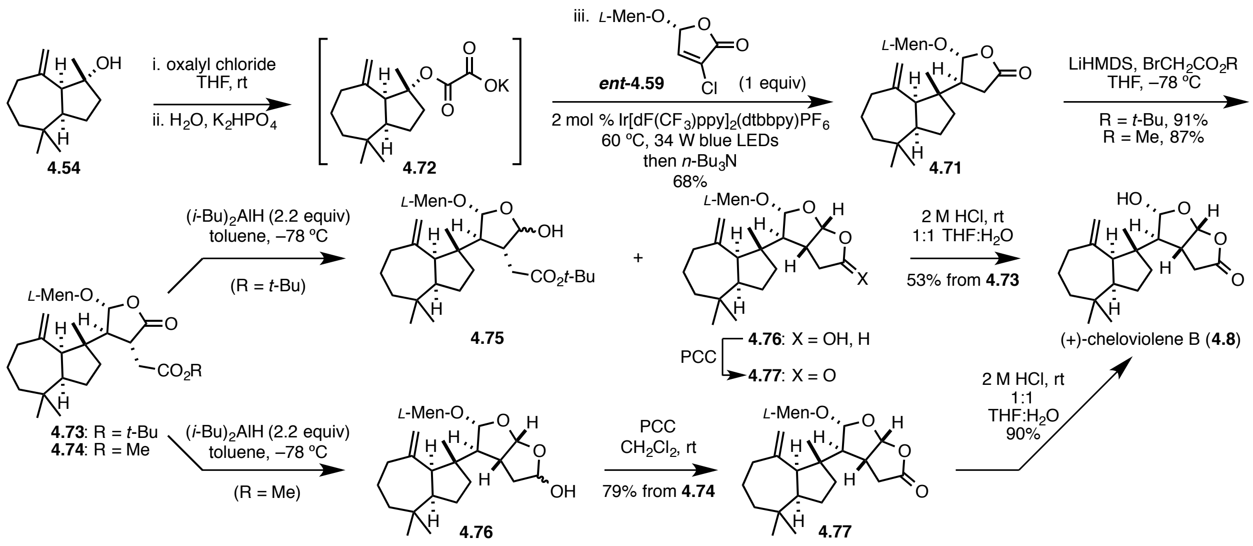
entry	M	conditions	**4.70**, yield (%)[a]	**4.71**, yield (%)[a]
1	Li	MeCN (0.05 M), H_2O (10 equiv)	0	0
2	Li	DMF (0.05 M), H_2O (10 equiv)	24	0
3	Li	DME (0.05 M), H_2O (10 equiv)	29	13
4	Li	THF (0.05 M), H_2O (10 equiv)	34	5
5	Li	THF (0.05 M), H_2O (100 equiv)	17	12
6[b]	Li	THF (0.05 M), H_2O (10 equiv)	48	0
7	**Li**	THF (0.6 M), H_2O (5 equiv)	73[c]	<5%
8[d]	**Li**	**THF (0.6 M), H_2O (5 equiv)**	**0**	**75[d]**
9	K	THF (0.6 M), H_2O (5 equiv)	72[c]	<5%

[a] Determined by ^1H NMR integration relative to an internal standard (1,2-dibromo-4,5-methylenedioxybenzene). [b] 1.5 equiv of butenolide ***ent*-4.59** was utilized. [c] Isolated yield. [d] *n*-Bu_3N (10 equiv) was added after coupling.

The yield of the conjugate addition was dramatically enhanced when the concentration of the reaction was increased from 0.05 M to 0.6 M, providing coupled product **4.70** in 73% isolated yield (entry 7).[69] Notably, only minor amounts of the dechlorinated product **4.71** were formed under these reaction conditions. Resubjection of **4.70** to the reaction conditions in the presence of *n*-Bu_3N led to a quantitative conversion of **4.70** to **4.71**.[67] Finally, we were able to perform the desired radical fragment coupling and dechlorination in one step to deliver **4.71** in 75% isolated yield by adding of *n*-Bu_3N after 18 h and allowing the subsequent dechlorination to proceed for 4 h (entry 8). As expected from our earlier studies,[43] the yield of the Ir(III) photoredox-mediated fragment coupling under optimized conditions was essentially identical when the oxalate counter ion was switched from Li to K. (entry 9).

With reaction conditions for the pivotal fragment coupling step optimized, we turned to investigate accomplishing this union in one step from *cis*-perhydroazulenol **4.54** and butenolide ***ent*-4.59** (Scheme 4.13). To this end, a THF solution of tertiary alcohol **4.54** was allowed to react with 1 equiv of oxalyl chloride at room temperature for 6 h and then water and 3 equiv of K_2HPO_4 were added to generate potassium oxalate intermediate **4.72**. Addition of butenolide ***ent*-4.59** (1 equiv), the photocatalyst and irradiation with high-intensity blue LEDs for 18 h at 60 °C, followed by addition of excess *n*-Bu_3N and irradiation for an additional 4 h gave the desired product **4.71** in 68% yield after purification. This radical fragment coupling is noteworthy for several reasons: (1) it is the first example of a one-step coupling of an alcohol-derived tertiary radical with a Michael acceptor; (2) equimolar amounts of the two coupling partners are utilized; (3) the desired product **4.71** is obtained as a single diastereomer at both newly formed stereocenters; and (4) the reaction conditions allowed for selective isolation of either the direct coupling product, or its dehalogenated congener **4.71**.[31]

Scheme 4.13. Synthesis of (+)-cheloviolene B (**4.8**).

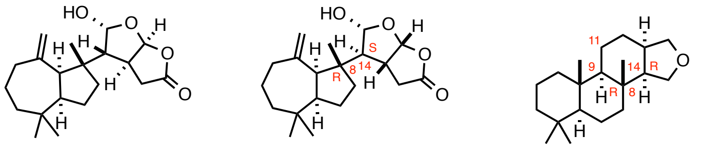


Elaboration of coupled product **4.71** to (+)-cheloviolene B (**4.8**) began with alkylation of the lactone fragment of **4.71** with *tert*-butyl bromoacetate to deliver ester **4.73** in 91% yield. In contrast to our earlier results in the model series, reduction of **4.73** with 2.2 equiv of DIBALH at – 78 °C in toluene did not lead exclusively to the desired tricyclic lactol product **4.75**, but rather to a 2:1 mixture of **4.75** and **4.76**, both as mixtures of lactol epimers. Attempts to modify the reduction conditions to furnish **4.75** selectively were met with no success. To converge these products, **4.76** was oxidized with PCC to give tetracyclic product **4.77** harboring the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one moiety. At this point, **4.75** and **4.77** were combined and exposed to 2 M HCl in THF:H_2O at room temperature to give what turned out to be (+)-cheloviolene B (**4.8**), mp: 189–190 °C, $[\alpha]^{21}_{D}$ +26.6, in 53% overall yield from intermediate **4.73.**

As the oxidation step in route to (+)-cheloviolene B (**4.8**) could not be avoided by introducing the two-carbon side chain as a *tert*-butyl ester, and processing both intermediates **4.75** and **4.76** was cumbersome, a more efficient route was developed to access (+)-cheloviolene B. In this sequence, the fragment-coupling product **4.71** was alkylated in high yield with methyl bromoacetate to give lactone ester **4.74**. In this methyl ester series, lactonization of the initially formed tricyclic lactol alkoxide intermediate generated upon exposure of **4.74** to excess DIBALH was sufficiently rapid at –78 °C that tetracyclic lactol product **4.76** was formed in high yield. Without purification, this mixture of lactol epimers was directly oxidized with PCC to give **4.77** in 79% yield over the two steps. Exposure of **4.77** to 2 M HCl in THF:H_2O then afforded (+)-cheloviolene B (**4.8**). Using this four-step sequence, fragment-coupling product **4.71** was transformed to (+)-cheloviolene B (**4.8**) in 62% overall yield.

The relative configuration of synthetic (+)-cheloviolene B (**8**) was confirmed by single-crystal X-ray analysis,[42e] whereas its absolute configuration follows rigorously from the absolute configuration of precursors **4.54** and ***ent*-4.59**. Structure **4.8** was originally proposed by Bobzin and Faulkner for a diterpenoid isolated from the marine sponge *Chelonaplysilla sp.* collected in Pohnpei, Federated States of Micronesia, and called chelonaplysin B.[9] Two years later, Taylor and coworkers reported that the ^{1}H NMR spectra of so-called chelonaplysin B was identical to that of (+)-cheloviolene A (**4.7**), one of a series of diterpenoids isolated from the sponge *Chelonaplysilla violacea* collected from coastal waters of New Zealand.[8] In addition to (+)-cheloviolene A (**4.7**), whose structure was confirmed by X-ray analysis, these workers isolated a related diterpenoid, (+)-cheloviolene B, which they assigned as the lactol epimer of cheloviolene A **4.78** (Figure 4.3).[8b] It is this sponge isolate whose reported ^{1}H and ^{13}C NMR spectra are indistinguishable from synthetic **4.8**. The structure of (+)-cheloviolene B must therefore be revised to be **4.8**.

Figure 4.3. Comparison of the originally proposed structure of (+)-cheloviolene B **4.78** and the revised structure **4.8**.



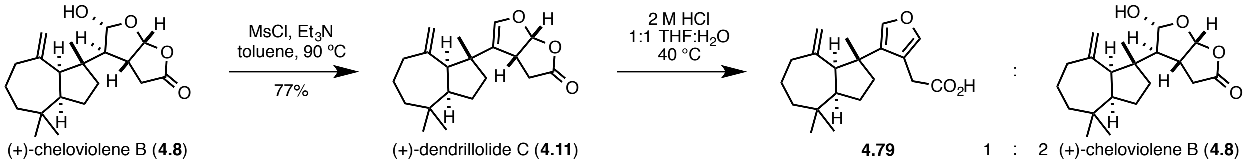
4.78
originally proposed
incorrect structure
of (+)-cheloviolene B

(+)-cheloviolene B (**4.8**)
(corrected structure)

spongian skeleton (**4.12**)

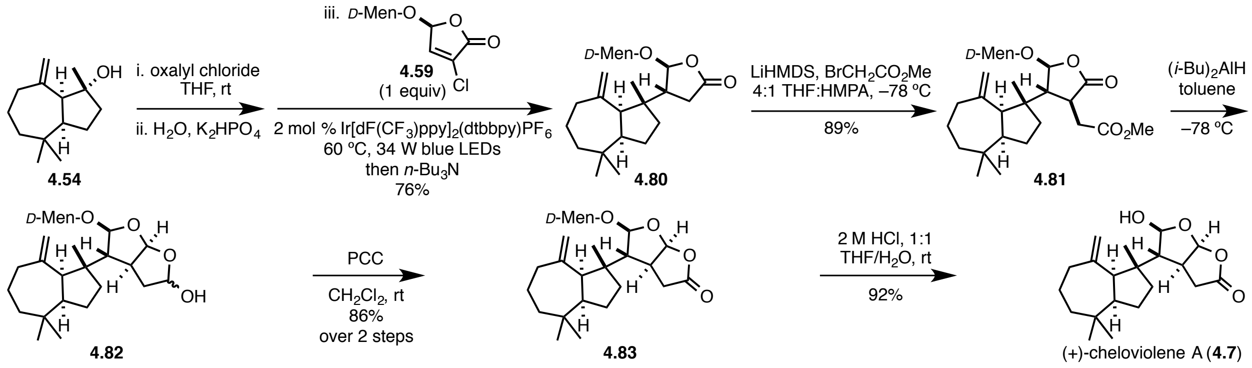
As first pointed out by Faulkner, a diterpenoid of structure **4.8** would be an outlier in the group of rearranged spongian diterpenoids exemplified in Figure 4.1B, because the relative configuration of its attached carbons, C-8 and C-14, differs at C-14 from that expected from a precursor having the spongian skeleton **4.12** (see Figure 4.1).[9] They suggested that the unexpected *S* configuration at C-14 of a diterpenoid of structure **4.8** might arise by hydration of the corresponding enol ether double bond of another spongian diterpenoid, dendrillolide C, which this research group had isolated earlier from the sponge *Dendrilla sp.* obtained from a marine lake of Palau and assigned structure **4.11**.[70] To confirm the structure of dendrillolide C, establish its absolute configuration, and pursue Faulkner's suggestion for the origin of the unexpected stereostructure of cheviolene B (**4.8**), we carried out the experiments summarized in Scheme 4.14. Reaction of **4.8** with 2.5 equiv of MsCl and excess Et_3N in toluene at 90 °C provided (+)-dendrillolide C (**4.11**), $[\alpha]^{21}_{D}$ +133, in 77% yield. ^1H NMR and optical rotation data of synthetic dendrillolide C (**4.11**) were indistinguishable from those reported for the diterpenoid isolated from the sponge *Dendrilla sp*.[70] Exposing synthetic dendrillolide C (**4.11**) to 2 M HCl in $THF:H_2O$ at 40 °C led to the formation of a 1.2:1 mixture of cheloviolene B (**4.8**) and tricyclic furan **4.79**. Careful analysis of the ^1H NMR spectra of this crude product mixture showed that stereoisomers of **4.8** were not present in significant amounts.[31] Other acidic conditions (both Lewis and protic) that we investigated resulted in exclusive formation of furan **4.79** or intractable mixtures of products. That (+)-dendrillolide C (**4.11**) undergoes protonation at C-14 preferentially from the *Si* face is consistent with the Faulkner initial proposal and with torsional effects dictating the stereochemical outcome of the hydration reaction *in vitro*.[71]

Scheme 4.14. Conversion of (+)-cheloviolene B (**4.8**) to (+)-denrillolide C (**4.11**) and stereoselective hydration of enol ether **4.11** to lactol **4.8**.



Besides efficiency, the ability to access analogues by varying the structure of late-stage fragments is a distinct advantage of convergent synthesis strategies. The second-generation total synthesis of (+)-cheloviolene A (**4.7**) illustrates this point (Scheme 4.15). In this case, the fragment coupling step employed butenolide **4.59**, which trapped the tertiary radical generated from *cis*-pehydroazulenol **4.54** to give tricyclic lactone **4.80** as the only detectable stereoisomer in 76% yield. The 10% higher yield of this step than the analogous one employing ***ent*-4.59** (Scheme 4.13) reflects a match of the chirality of the enantiopure fragments combining to yield **4.80**. Processing of this product by the identical four-step sequence used to prepare (+)-cheloviolene B (**4.8**) gave (+)-cheloviolene A (**4.7**) in 70% overall yield from intermediate **4.80**.

Scheme 4.15. Second-generation total synthesis of (+)-cheloviolene A (**4.7**).



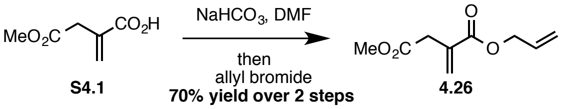
4.3 Conclusions

Enantioselective total syntheses of rearranged spongian diterpenoids **4.7**, **4.8**, and **4.11** exemplify advantages of convergent synthesis strategies based upon late-stage fragment coupling between a tertiary carbon radical and an electron-deficient alkene to unite two ring systems and form two new stereocenters, one of which is quaternary, in a stereoselective and efficient manner. (+)-Cheloviolene A (**4.7**) and (+)-cheloviolene B (**4.8**) were prepared in 11 steps from the known cyclopentene nitrile **4.49**[50] in respectively 22% and 18% overall yield, and in 14 steps and 5–7% overall yield from (+)-fenchone (**4.48**). These short synthetic sequences are made possible in part by the one-step generation of tertiary radical **4.38** from tertiary alcohol **4.54** and its *in situ* trapping with chlorobutenolides **4.59** and ***ent*-4.59**. Of critical importance, these fragment unions were accomplished using equimolar amounts of the two coupling partners. It should be noted that while this strategy has allowed us to access diterpenoids such as (+)-cheloviolenes A (**4.7**) and B (**4.8**) that bear the fourteen-carbon hydrophobic fragment on the convex face of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one unit, we have so far been unsuccessful in developing a complimentary stereoselective approach to diterpenoids such as dendrillolide A (**4.10**) in which the *cis*-perhydroazulene resides on the concave face.[72] We anticipate that the convergent strategy described in this chapter, namely late-stage union of a structurally complex tertiary carbon radical with an acceptor, will find applications in future syntheses of a variety of stereochemically elaborate natural products.[73]

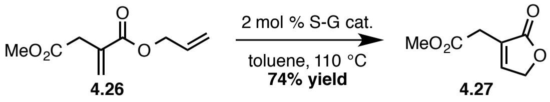
4.4 Experimental Information

Materials and methods.

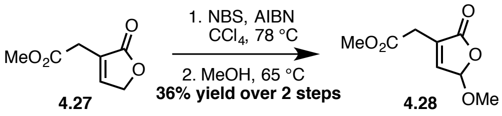
Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon. Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), dimethylformamide (DMF), toluene, dichloromethane, methanol (MeOH), *N,N*-diisopropylethylamine (*i*-Pr_2NEt), and triethylamine (Et_3N) were dried by passage through activated alumina. Methyl bromoacetate and *tert*-butyl bromoacetate were distilled under reduced pressure and stored in a Schlenk flask. All other commercial reagents were used as received unless otherwise noted. Reaction temperatures were controlled using a temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or by *p*-anisaldehyde, ceric ammonium molybdate, and potassium permanganate staining ($KMnO_4$). Silica gel 60 (particle size 0.040–0.063mm) was used for flash column chromatography. ^1H NMR spectra were recorded at 500 or 600 MHz and are reported relative to deuterated solvent signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded at 126 or 151 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained with an LCT spectrometer. Optical rotation readings were obtained using JASCO P-1010 polarimeter. Kessil KSH150B LED Grow Light 150, Blue (34 W blue LED lamps) was purchased from http://www.amazon.com. Low-intensity blue LEDs (30 cm, 1 watt) were purchased from http://www.creativelightings.com (product code CL-FRS5050-12WP-12V) and were powered by 8 AA batteries. See JOC Standard Abbreviations and Acronyms for abbreviations (available at http://pubs.acs.org/paragonplus/submission/joceah/joceah_abbreviations.pdf).



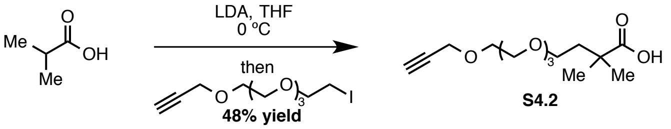
Preparation of Ester 4.26: A round-bottom flask was charged with 4-methyl 2-methylenesuccinate (**S4.1**) (3.0 g, 21 mmol, 1.0 equiv),[25] DMF (15 mL, 2.0 M), and a magnetic stir bar under an atmosphere of argon. Next, sodium bicarbonate (3.53 g, 42.0 mmol, 2.0 equiv) was added portionwise to the solution and the resulting heterogeneous mixture was stirred at rt for 1 h. After 1 h, allyl bromide (2.7 mL, 31 mmol, 1.5 equiv) was added dropwise to the mixture that was then stirred vigorously at rt for 12 h. After 12 h, H_2O (50 mL) was added to the reaction mixture and the resulting solution was transferred to a separatory funnel and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with H_2O (3 x 50 mL), dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash chromatography on silica gel using 10:90 ethyl acetate:hexanes to yield ester **4.26** as a clear oil (3.0 g, 16 mmol, 78% yield): R_f = 0.35 (10:90 ethyl acetate:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.38 (s, 1H), 5.94 (dddd, *J* = 22.4, 16.2, 10.7, 5.4 Hz, 1H), 5.75 (s, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 5.5 Hz, 2H), 3.71 (s, 3H), 3.37 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 165.9, 133.8, 132.0, 128.9, 118.3, 65.8, 52.2, 37.7; IR (thin film) 1744, 1642 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_{12}O_4Na$ 207.0633; Found 207.0637.



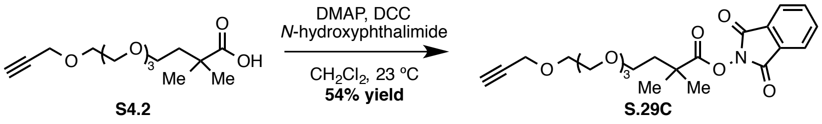
Preparation of Butenolide 4.27: A round-bottom flask was charged with diene **4.26** (800 mg, 4.3 mmol, 1.0 equiv), toluene (440 mL, 0.01 M), and a magnetic stir bar under an atmosphere of argon. Next, Stewart-Grubbs catalyst (50 mg, 0.09 mmol, 0.02 equiv)[26] was added to the reaction mixture and the resulting solution was heated to 110 °C for 18 h. After 18 h, the solution was allowed to cool to rt and concentrated by use of a rotary evaporator to yield a brown oil. The residue was purified by flash column chromatography on silica gel using 20:80 ethyl acetate:hexanes → 40:60 ethyl acetate:hexanes as eluent to yield butenolide **4.27** as a brown oil (500 mg, 3.2 mmol, 74% yield): R_f = 0.29 (50:50 ethyl acetate:hexanes, stained with $KMnO_4$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 4.87 (s, 2H), 3.75 (s, 3H), 3.38 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.7, 170.1, 148.1, 127.1, 70.8, 52.5, 30.5; IR (thin film) 2955, 2871, 1737, 1657, 1438, 1349, 1223, 1078, 1049 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_7H_8O_4Na$ 179.0320; Found 179.0312.



Preparation of Butenolide 4.28: A round-bottom flask was charged with butenolide **4.27** (490 mg, 3.1 mmol, 1.0 equiv), CCl_4 (21 mL, 0.15 M), *N*-bromosuccinimide (1.7 g, 9.4 mmol, 3.0 equiv), AIBN (52 mg, 0.31 mmol, 0.1 equiv), and a magnetic stir bar under an atmosphere of argon. The mixture was irradiated with a 100 W compact fluorescent light bulb and heated to 75 °C for 3 h. After 3 h, additional *N*-bromosuccinimide (560 mg, 3.1 mmol, 1.0 equiv) and AIBN (52 mg, 0.31 mmol, 0.1 mmol) were added. The mixture was stirred at 75 °C for 1 h, at which point TLC analysis indicated complete consumption of starting material **4.27**. The reaction was then cooled to 0 °C, vacuum filtered and concentrated by use of a rotary evaporator to yield the crude 5-bromo analogue as a yellow oil. Diagnostic ^{1}H NMR shifts (600 MHz, CDCl$_3$) δ 7.59 (d, *J* = 1.2 Hz, 1H), 6.90 (d, *J* = 1.2 Hz, 1H), 3.76 (s, 3H), 3.44 (br s, 2H). A round-bottom flask was charged with the crude intermediate, MeOH (7 mL, 0.45 M), and a magnetic stir bar under an atmosphere of argon. The solution was heated to 70 °C for 12 h. After 12 h the solution was allowed to cool to rt and concentrated by use of a rotary evaporator. The residue was purified by flash chromatography on silica gel using 10:90 ethyl acetate:hexanes → 25:75 ethyl acetate:hexanes as eluent to yield butenolide **4.28** as a yellow oil (210 mg, 1.1 mmol, 36% yield over 2 steps): R$_f$ = 0.28 (30:70 ethyl acetate:hexanes); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.16 (d, *J* = 1.2 Hz, 1H), 5.83 (d, *J* = 1.2 Hz, 1H), 3.74 (s, 3H), 3.57 (s, 3H), 3.38 (d, *J* = 1.2 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 170.7, 169.5, 145.6, 131.2, 103.0, 57.1, 52.6, 30.4; IR (thin film) 1780, 1750 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_8H_{10}O_5Na$ 209.0426; Found 209.0418.

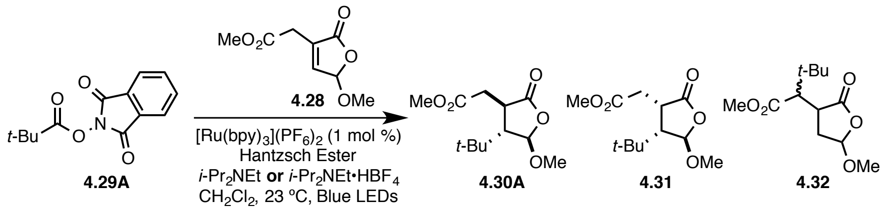


Preparation of Carboxylic Acid S4.2: A round-bottom flask was charged with *i*-Pr$_2$NH (9.0 mL, 68 mmol, 2.6 equiv), THF (200 mL, 0.13 M), and a magnetic stir bar under an atmosphere of argon. After cooling the solution to –78 °C, 2.4 M *n*-BuLi in hexanes (27 mL, 65 mmol, 2.5 equiv) was added dropwise. The resulting solution was then warmed to 0 °C stirred for 30 min. Next, isobutyric acid (2.4 mL, 26 mmol, 1.0 equiv) was added dropwise at 0 °C. The reaction was maintained at 0 °C for 20 min, followed by a dropwise addition of a solution of 1-iodo-3,6,9,12-tetraoxapentadec-14-yne (10.2 g, 28.6 mmol, 1.1 equiv)[74] in THF (60 mL, 0.43 M). The resulting heterogeneous mixture was allowed to warm to rt and stirred vigorously for 12 h. After 12 h, the reaction was quenched via addition of H_2O (50 mL). The resulting biphasic mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (2 x 200 mL). The aqueous layer was acidified with sat. NH_4Cl (aq) and extracted with CH_2Cl_2 (2 x 300 mL). The combined organic layers, resulting from extracting the acidified aqueous layer, were dried over $MgSO_4$ and concentrated by use of a rotary evaporator to yield **S4.2** as a clear oil (3.8 g, 13 mmol, 48% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (d, *J* = 2.3 Hz, 2H), 3.73–3.56 (m, 14H), 2.43 (br s, 1H), 1.87 (t, *J* = 5.9 Hz, 2H), 1.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.5, 79.7, 74.7, 70.9, 70.6, 70.4, 70.3, 70.2, 69.2, 67.8, 58.5, 40.4, 40.0, 25.5; IR (thin film) 3251, 1728, 1700, 1103 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{15}H_{26}O_6Na$ 325.1627; Found 325.1636.



Preparation of NHP Ester 4 . 29C: A round-bottom flask was charged with acid **S4.2** (1.9 g, 7.4 mmol, 1.0 equiv), CH_2Cl_2 (50 mL, 0.2 M), DCC (2.0 g, 9.6 mmol, 1.3 equiv), DMAP (180 mg, 1.5 mmol, 0.2 equiv), and a magnetic stir bar under an atmosphere of argon. The resulting heterogeneous mixture was stirred at rt for 15 min. Next, *N*-hydroxyphthalimide (1.4 g, 8.8 mmol, 1.2 equiv) was added in one portion and the mixture was stirred at rt for 16 h. After 16 h, the reaction was quenched via addition of sat. NH_4Cl (aq). The resulting biphasic mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash chromatography on silica gel using 50:50 ethyl acetate:hexanes as eluent to yield *N*-acyloxyphthalimide **4.29C** as a clear oil (1.6 g, 4.0 mmol, 54% yield): R_f = 0.35 (50:50 ethyl acetate:hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.6, 4.7 Hz, 2H), 7.79 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.20 (d, *J* = 2.4 Hz, 2H), 3.71–3.61 (m, 14H), 2.43–2.42 (m, 1H), 2.06 (t, *J* = 7.0 Hz, 2H), 1.44 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 162.2, 134.8, 129.2, 124.0, 79.8, 74.6, 70.8, 70.7, 70.5, 70.4, 69.2, 67.7, 58.5, 40.9, 39.7, 25.6; IR (thin film) 3273, 1782, 1743 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{23}H_{29}NO_8Na$ 470.1791; Found 470.1777.

General Procedure for the Photoredox-mediated Couplings of 4.29A–C with 4.28: A 1-dram scintillation vial was charged with *N*-acyloxyphthalimide **4.29A–C** (1.0 equiv), butenolide 28 (1.0 equiv), Hantzsch ester (1.5 equiv),[75] $[Ru(bpy)_3](PF_6)_2$ (0.01 equiv), followed by either *i*-Pr_2NEt (1.0 equiv) or *i*-$Pr_2NEt•HBF_4$ (2.2 equiv),[76] and a magnetic stir bar. The vial was sealed with a screw cap bearing a Teflon septum and CH_2Cl_2 (0.15 M, sparged with argon for 10 min) was added. Next, the vial was placed in the center of a 30 cm loop of low-intensity blue LEDs. Heterogeneous reaction mixture was irradiated by low intensity blue LEDs and stirred vigorously at rt for 18 h. The mixture was filtered over silica gel using Et_2O as eluent and concentrated by use of a rotary evaporator to yield a yellow residue



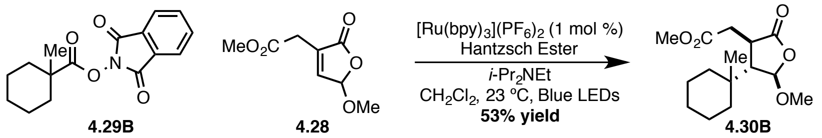
Preparation of Lactone 30a: Following the general procedure, *N*-acyloxyphthalimide **4.29A** (27 mg, 0.11 mmol, 1.0 equiv) and butenolide **4.28** (20 mg, 0.11 mmol, 1.0 equiv) were coupled in the presence of *i*-Pr$_2$NEt (19 µL, 0.11 mmol, 1.0 equiv), [Ru(bpy)$_3$](PF$_6$)$_2$ (1 mg, 0.001 mmol, 0.01 equiv), and Hantzsch ester (41 mg, 0.16 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (0.75 mL). Purification of the crude residue by flash chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent yielded **4.30A** as a clear oil (19 mg, 0.076 mmol, 72% yield): R$_f$ = 0.45 (10:90 ethyl acetate:hexanes, stained with KMnO$_4$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.17 (d, *J* = 2.3 Hz, 1H), 3.71 (s, 3H), 3.51 (s, 3H), 2.85–2.73 (m, 3H), 1.95 (app s, *J* = 1.9 Hz, 1H), 0.94 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 177.8, 171.3, 106.5, 57.2, 56.6, 52.1, 38.7, 36.9, 31.8, 27.1; IR (thin film) 1644, 1633 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{12}H_{20}O_5Na$ 267.1208; Found 267.1209.

The reaction performed in the presence of *i*-Pr$_2$NEt•HBF$_4$ (53 mg, 0.24 mmol, 2.2 equiv) in place of *i*-Pr$_2$NEt led to product **4.30A** (17 mg, 0.69 mmol, 66% yield) that was isolated after purification by flash chromatography on silica gel. The product ratios shown in Scheme 4.3 arise from ^{1}H and ^{13}C NMR analysis of crude reaction mixtures.

Lactone 4.31 was isolated in 22% yield from the above reaction when *i*-Pr$_2$NEt•HBF$_4$ was used: R$_f$ = 0.47 (10:90 ethyl acetate:hexanes, stained with KMnO$_4$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.27 (s, 1H), 3.74 (s, 3H), 3.63–3.59 (m, 1H), 3.48 (s, 3H), 2.97 (dd, *J* = 17.5, 6.1 Hz, 1H), 2.74 (dd, *J* = 17.5, 9.3 Hz, 1H), 2.36 (d, *J* = 8.2 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (126 MHz,

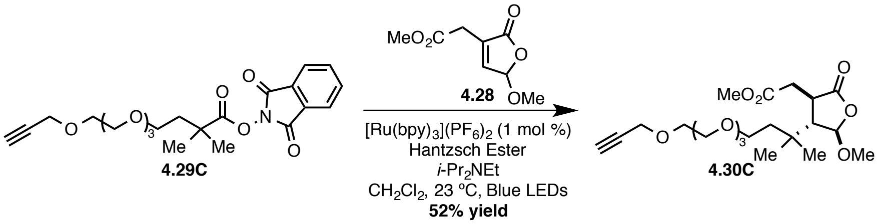
$CDCl_3$) δ 177.8, 172.0, 105.9, 56.6, 54.2, 52.3, 38.3, 32.3, 32.0, 28.3; IR (thin film) 2956, 2922, 1783, 1742 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{12}H_{20}O_5Na$ 267.1208; Found 267.1201.

Lactone 4.32 was isolated in 1% yield as a 1.5:1 mixture of diastereomers from the above reaction when *i*-Pr_2NEt was used: R_f = 0.42 (10:90 ethyl acetate:hexanes, stained with $KMnO_4$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.40 (app t, *J* = 5.8 Hz, 1H), 5.36 (dd, *J* = 6.9, 5.2 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H), 3.57 (s, 3H), 3.54 (s, 3H), 3.11 (ddd, *J* = 11.8, 10.5, 9.3 Hz, 1H), 3.01 (d, *J* = 3.1 Hz, 1H), 2.88 (dd, *J* = 9.5, 3.0 Hz, 1H), 2.69 (ddd, *J* = 13.9, 9.0, 5.2 Hz, 1H), 2.57 (ddd, *J* = 13.7, 10.4, 6.2 Hz, 1H), 2.45 (d, *J* = 10.3 Hz, 1H), 2.38 (ddd, *J* = 14.6, 9.3, 5.7 Hz, 1H), 2.00 (app dt, *J* = 12.0, 6.9 Hz, 1H), 1.06 (s, 9H), 1.03 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 175.2, 173.8, 172.6, 104.5, 103.9, 58.1, 57.7, 55.8, 54.1, 51.6, 51.5, 41.3, 39.8, 35.9, 33.1, 32.3, 28.6, 28.5, 15.4; IR (thin film) 1770, 1644 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{12}H_{20}O_5Na$ 267.1208; Found 267.1199.



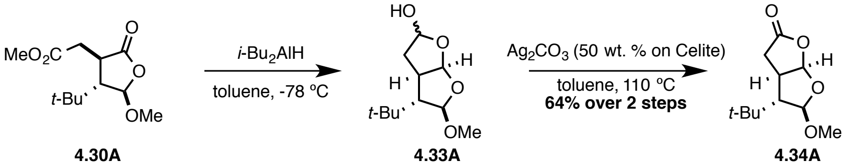
Preparation of Lactone 4.30B: Synthesized according to the general procedure from the *N*-acyloxyphthalimide **4.29B** (77 mg, 0.27 mmol, 1.0 equiv),[32] butenolide **4.28** (50 mg, 0.27 mmol, 1.0 equiv), *i*-Pr_2NEt (47 μL, 0.27 mmol, 1.0 equiv), $[Ru(bpy)_3](PF_6)_2$ (2 mg, 0.003 mmol, 0.01 equiv) and Hantzsch ester (100 mg, 0.4 mmol, 1.5 equiv) in CH_2Cl_2 (1.8 mL). Purification of the crude residue by flash chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent yielded **4.30B** (41 mg, 0.14 mmol, 53% yield) as a colorless solid:

R_f = 0.61 (30:70 diethyl ether:pentanes, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.21 (d, *J* = 2.1 Hz, 1H), 3.71 (s, 3H), 3.50 (s, 3H), 2.89–2.72 (m, 3H), 2.06 (br s, 1H), 1.60–1.21 (m, 10H), 0.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 171.4, 106.0, 57.2, 52.2, 37.9, 37.0, 35.43, 35.38, 34.4, 26.1, 21.53, 21.47; IR (thin film) 2929, 2855, 1777, 1738 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{24}O_5Na$ 307.1521; Found 307.1523.



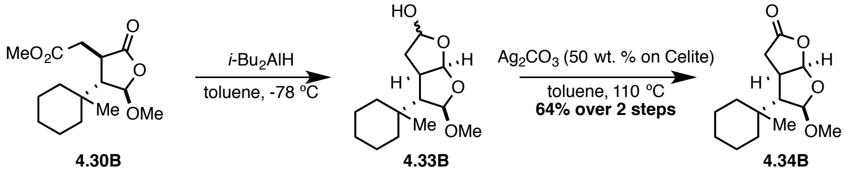
Preparation of Lactone 4.30C: Synthesized according to the general procedure from *N*-acyloxyphthalimide **4.29C** (30 mg, 0.07 mmol, 1.0 equiv), butenolide **4.28** (13 mg, 0.07 mmol, 1.0 equiv), *i*-Pr_2NEt (12 μL, 0.07 mmol, 1.0 equiv), $[Ru(bpy)_3](PF_6)_2$ (0.6 mg, 0.0007 mmol, 0.01 equiv) and Hantzsch ester (25 mg, 0.10 mmol, 1.5 equiv) in CH_2Cl_2 (0.45 mL). Purification of the crude residue by flash chromatography on silica gel using 10:90 acetone:hexanes as eluent yielded **4.30C** (16 mg, 0.036 mmol, 52% yield) as a clear oil: R_f = 0.40 (70:30 ethyl acetate:hexanes, stained with $KMnO_4$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.20 (d, *J* = 2.3 Hz, 1H), 4.21 (d, *J* = 2.4 Hz, 2H), 3.76–3.45 (m, 20H), 2.89–2.74 (m, 3H), 2.43 (app t, *J* = 2.4 Hz, 1H), 2.06 (dd, *J* = 4.5, 2.3 Hz, 1H), 1.58 (app t, *J* = 7.0 Hz, 2H), 0.94 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 171.3, 106.2, 79.8, 74.7, 70.8, 70.7, 70.6, 70.4, 69.2, 67.6, 58.6, 57.2, 55.8, 52.2, 39.1, 38.4, 36.9, 33.7, 24.6, 24.2; IR (thin film) 3267, 2932, 2873, 1775, 1739, 1440, 1364, 1111, 939 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{36}O_9Na$ 467.2257; Found 467.2248.

General Procedure for the Reduction/Cyclization/Oxidation to Generate Dioxabicyclo[3.3.0]octanones 4.34A–C: A round-bottom flask was charged with the coupled product **4.30A–C** (1.0 equiv), toluene (0.1 M), and a magnetic stir bar under an atmosphere of argon. After cooling the solution to –78 °C, *i*-Bu_2AlH (2.1 equiv, 1 M in toluene) was added dropwise. The solution was maintained at –78 °C for 30 min. The reaction was quenched by the addition of saturated solution of Rochelle's salt (aq) (0.1 M) at –78 °C. The mixture was allowed to warm to rt and stirred at rt for 1 h. The biphasic mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by use of a rotary evaporator to yield a crude mixture of bicyclic lactol epimers **4.33A–C**. A 1-dram scintillation vial was charged with this crude mixture of bicyclic lactol epimers **4.33A–C** (1.0 equiv), toluene (0.1 M), Ag_2CO_3 (50 wt. % on Celite, 3.0 equiv), and a magnetic stir bar under an atmosphere of argon. The reaction vessel was capped and heated to 110 °C. After 1 h, the black suspension was allowed to cool to rt, filtered over Celite and concentrated by use of a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel to yield bicyclic lactones **4.34A–C**.

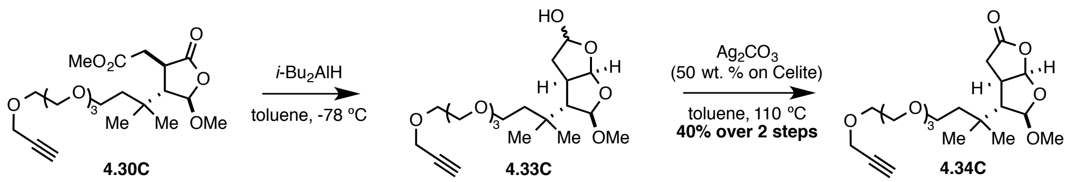


Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.34A: Synthesized according to the general procedure described above from **4.30A** (50 mg, 0.21 mmol, 1.0 equiv) and 1 M solution of *i*-Bu_2AlH in toluene (430 µL, 0.43 mmol, 2.2 equiv) in toluene (2 mL, 0.1 M).

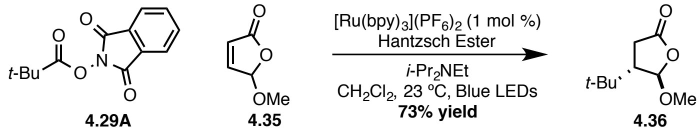
Diagnostic data for lactol intermediate **4.33A**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (d, *J* = 12.1 Hz, 1H, OH confirmed by D_2O exchange); MS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{11}H_{20}O_4Na$ 239.1; Found 239.1. Conversion of lactol **4.33A** to lactone **4.34A** was achieved with Ag_2CO_3 (340 mg, 0.62 mmol, 3.0 equiv) in toluene (2 mL, 0.1 M). Purification of the crude residue by flash chromatography on silica gel using 20:80 ethyl acetate:hexanes as eluent yielded **4.34A** (28 mg, 0.13 mmol, 64% yield; 73% based on recovered starting material) as a colorless solid: R_f = 0.45 (30:70 ethyl acetate:hexanes, stained with ceric ammonium molybdate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (d, *J* = 6.1 Hz, 1H), 5.04 (s, 1H), 3.36 (s, 3H), 2.97–2.93 (m, 1H), 2.86 (dd, *J* = 18.1, 11.2 Hz, 1H), 2.62 (dd, *J* = 18.1, 3.6 Hz, 1H), 1.95 (d, *J* = 1.4 Hz, 1H) 0.93 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 109.1, 108.7, 64.4, 55.0, 39.2, 36.6, 31.5, 27.5; IR (thin film) 1784 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{11}H_{18}O_4Na$ 237.1103; Found 237.1110.



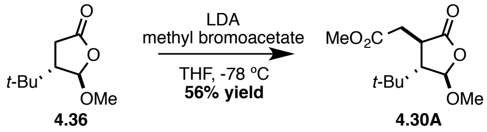
Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.34B: Synthesized according to the general procedure described above from **4.30B** (33 mg, 0.12 mmol, 1.0 equiv) and 1 M solution of *i*-Bu_2AlH in toluene (240 μL, 0.24 mmol, 2.2 equiv) in toluene (1.2 mL, 0.1 M). Diagnostic data for lactol intermediate **4.33B**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (d, *J* = 12.0 Hz, 1H, OH confirmed by D_2O exchange). Conversion of lactol **4.33B** to lactone **4.34B** was achieved with Ag_2CO_3 (190 mg, 0.35 mmol, 3.0 equiv) in toluene (1.2 mL, 0.1 M). Purification of the crude residue by flash chromatography on silica gel using 15:85 ethyl acetate:hexanes as eluent yielded **4.34B** (18 mg, 0.071 mmol, 64% yield) as a colorless solid: R_f = 0.45 (30:70 ethyl acetate:hexanes, stained with ceric ammonium molybdate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (d, *J* = 6.1 Hz, 1H), 5.07 (s, 1H), 3.35 (s, 3H), 3.01–2.95 (m, 1H), 2.86 (dd, *J* = 18.1, 11.0 Hz 1H), 2.61 (dd, *J* = 18.1, 3.5 Hz, 1H), 2.04 (br s, 1H), 1.56–1.19 (m, 10H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 109.2, 108.3, 55.0, 38.4, 36.8, 35.8, 35.7, 33.9, 26.2, 21.6, 20.8; IR (thin film) 1785 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{22}O_4Na$ 277.1416; Found 277.1417.



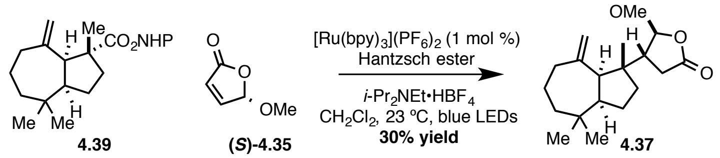
Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.34C: Synthesized according to the general procedure described above from **4.30C** (94 mg, 0.21 mmol, 1.0 equiv) and 1 M solution of *i*-Bu_2AlH in toluene (460 μL, 0.46 mmol, 2.2 equiv) in toluene (2.1 mL, 0.1 M). Conversion of lactol **4.33C** to lactone **4.34C** was achieved with Ag_2CO_3 (340 mg, 0.63 mmol, 3.0 equiv) in toluene (2.1 mL, 0.1 M). Purification of the crude residue by flash chromatography on silica gel using 30:70 ethyl acetate:hexanes as eluent yielded **4.34C** (35 mg, 0.08 mmol, 40% yield) as a colorless solid: R_f = 0.30 (30:70 ethyl acetate:hexanes, stained with ceric ammonium molybdate); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (d, *J* = 6.1 Hz, 1H), 5.03 (s, 1H), 4.21 (d, *J* = 2.3 Hz, 2H), 3.72–3.50 (m, 14H), 3.00–2.95 (m, 1H), 2.86 (dd, *J* = 18.3, 11.2 Hz, 1H), 2.63 (dd, *J* = 18.3, 3.8 Hz, 1H), 2.43 (t, *J* = 2.3 Hz, 1H), 2.10 (s, 1H), 1.65–1.48 (m, 2H), 0.95 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 109.0, 108.5, 79.8, 74.7, 70.7, 70.6, 70.5, 69.2, 67.8, 63.1, 58.6, 54.9, 39.9, 39.1, 36.6, 33.4, 25.2, 24.9; IR (thin film) 1781 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{21}H_{34}O_8Na$ 437.2151; Found 437.2149.



Preparation of Lactone 4.36: Synthesized according to the general fragment coupling procedure from *N*-acyloxyphthalimide **4.29A** (150 mg, 0.6 mmol, 1.0 equiv), butenolide **4.35** (69 mg, 0.60 mmol, 1.0 equiv), *i*-Pr_2NEt (100 μL, 0.6 mmol, 1.0 equiv), $[Ru(bpy)_3](PF_6)_2$ (5 mg, 0.006 mmol, 0.01 equiv) and Hantzsch ester (230 mg, 0.90 mmol, 1.5 equiv) in CH_2Cl_2 (4 mL). Purification of the crude residue by flash chromatography on silica gel using 5:95 ethyl acetate:hexanes → 10:90 ethyl acetate:hexanes as eluent yielded **4.36** (75 mg, 0.44 mmol, 73% yield) as a clear oil: R_f = 0.27 (10:90 ethyl acetate:hexanes; stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.19 (d, *J* = 2.5 Hz, 1H), 3.49 (s, 3H), 2.65 (dd, *J* = 18.5, 10.0 Hz, 1H), 2.35 (dd, *J* = 18.5, 5.5 Hz, 1H), 2.14 (ddd, *J* = 10.0, 5.5, 3.0 Hz, 1H), 0.92 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 107.4, 57.0, 51.7, 31.5, 30.0, 27.0; IR (thin film) 2965, 1779, 1175, 1115 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_9H_{16}O_3Na$ 195.0997; Found 195.0993.

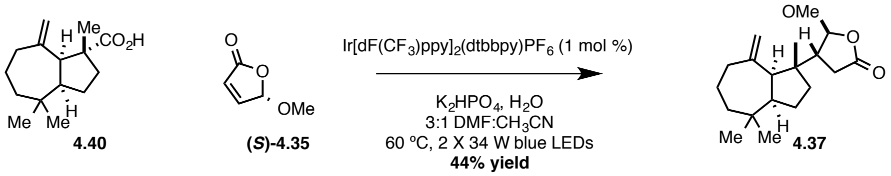


Preparation of Ester 4.30A: A round-bottom flask was charged with *i*-Pr_2NH (110 μL, 0.75 mmol, 3.8 equiv), THF (4.6 mL, 0.1 M), and a magnetic stir bar under an atmosphere of argon. After cooling the solution to –78 °C, 1.93 M *n*-BuLi in hexanes (260 μL, 0.50 mmol, 2.5 equiv) was added dropwise. The resulting solution was then warmed to 0 °C and stirred for 30 min. Next, an aliquot of the LDA solution (3 mL, 0.3 mmol, 1.5 equiv) was added dropwise to a solution of **4.36** (34 mg, 0.20 mmol, 1.0 equiv) in THF (2 mL, 0.1 M) at –78 °C. After 1 h at –78 °C, a solution of methyl bromoacetate (45 mg, 0.30 mmol, 1.5 equiv) in THF (0.3 mL) was added dropwise. The reaction was allowed to warm to rt, H_2O (5 mL) was added, and the resulting biphasic mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated by use of a rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using 5:95 ethyl acetate:hexanes as eluent to yield **4.30A** (27 mg, 0.11 mmol, 56% yield) as a clear oil: R_f = 0.45 (10:90 ethyl acetate:hexanes; stained with $KMnO_4$).

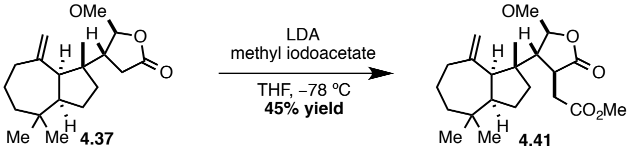


Preparation of Lactone 4.37 from 4.39: A 1-dram scintillation vial was charged with *N*-acyloxyphthalimide **4.39** (25 mg, 0.066 mmol, 1.0 equiv), butenolide **(*S*)-4.35** (8 mg, 0.07 mmol, 1.0 equiv), Hantzsch ester (25 mg, 0.11 mmol, 1.5 equiv), $[Ru(bpy)_3](PF_6)_2$ (0.6 mg, 0.0007 mmol, 0.01 equiv), *i*-Pr_2NEt•HBF_4 (29 mg, 0.13 mmol, 2.2 equiv), and a magnetic stir bar. The vial was sealed with a screw cap bearing a Teflon septum and CH_2Cl_2 (0.1 M, sparged with argon for 10 min) was added. Next, the vial was placed in the center of a 30 cm loop of low-intensity blue LEDs. Heterogeneous reaction mixture was irradiated by low intensity blue LEDs and stirred vigorously at rt for 18 h. The mixture was filtered over silica gel using

Et_2O as eluent and concentrated by use of a rotary evaporator. The resulting yellow residue was purified by flash chromatography on silica gel using 5:95 ethyl acetate:hexanes as eluent to yield **4.37** (12 mg, 0.039 mmol, 30% yield) as a clear oil: R_f = 0.30 (10:90 ethyl acetate:hexanes; stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.21 (d, *J* = 1.7 Hz, 1H), 4.83 (d, *J* = 1.7 Hz, 1H), 4.60 (br s, 1H), 3.50 (s, 3H), 2.75 (dd, *J* = 19.6, 11.2 Hz, 1H), 2.51 (d, *J* = 8.7 Hz, 1H), 2.46–2.47 (m, 1H), 2.43–2.41 (m, 1H), 2.35 (dd, *J* = 12.5, 5.2 Hz, 1H), 1.97–1.91 (m, 1H), 1.82–1.73 (m, 4H), 1.64 (dd, *J* = 13.9, 4.1 Hz, 1H), 1.61–1.56 (m, 2H), 1.45–1.34 (m, 1H), 1.28–1.25 (m, 1H), 0.98 (s, 3H), 0.94 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 153.5, 114.9, 107.6, 66.1, 57.0, 56.2, 54.3 52.0, 47.1, 37.9, 37.7, 37.0, 36.4, 34.6, 28.9, 26.2, 25.9, 20.9, 15.5; IR (thin film) 1787 cm^{-1}; $[\alpha]^{23}_{D}$ +90.8, $[\alpha]^{23}_{577}$ +93.2, $[\alpha]^{23}_{546}$ +106, $[\alpha]^{23}_{435}$ +181 (*c* = 1.0, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{30}O_3Na$ 329.2093; Found 329.2099.

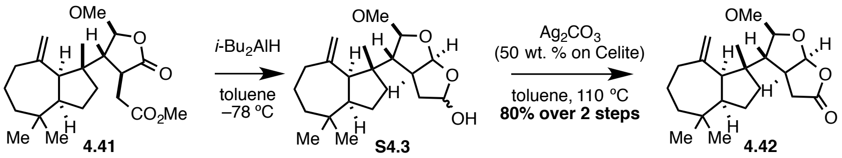


Preparation of Lactone 4.37 from 4.40: A 1-dram scintillation vial was charged with **4.40** (47 mg, 0.2 mmol, 1.0 equiv), K_2HPO_4 (38 mg, 0.22 mmol, 1.1 equiv), ($Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5 mg, 0.004 mmol, 0.02 equiv), 3:1 DMF:CH_3CN (0.5 mL, 0.4 M), H_2O (36 μL, 2.0 mmol, 10 equiv), **(*S*)-4.35** (23 mg, 0.2 mmol, 1.0 equiv), and a magnetic stir bar. The vial was then sealed with a screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. The reaction was allowed to cool to rt and transferred to a separatory funnel and extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 5:95 ethyl acetate:hexanes as eluent to yield **4.37** (27 mg, 0.088 mmol, 44% yield) as a clear oil.



Preparation of Ester 4.41: A round-bottom flask was charged with *i*-Pr_2NH (280 μL, 2.0 mmol, 13 equiv), THF (3 mL, 0.05 M), and a magnetic stir bar under an atmosphere of argon. After cooling the solution to –78 °C, 2.3 M *n*-BuLi in hexanes (800 μL, 1.8 mmol, 12 equiv) was added dropwise. The resulting solution was then warmed to 0 °C and stirred for 30 min. Next, an aliquot of the LDA solution (550 μL, 0.22 mmol, 1.5 equiv) was added dropwise to a solution of **4.37** (46 mg, 0.149 mmol, 1.0 equiv) in THF (1.5 mL, 0.1 M) at –78

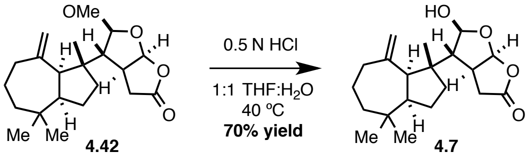
°C. After 1 h at –78 °C, a solution of methyl iodoacetate (60 mg, 0.3 mmol, 2.0 equiv) in THF (0.3 mL) was added dropwise. The reaction was allowed to warm to rt, H_2O (5 mL) was added, and the resulting biphasic mixture was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated by use of a rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using 5:95 ethyl acetate:hexanes as eluent to yield **4.41** (26 mg, 0.069 mmol, 45% yield) as a clear oil: R_f = 0.30 (10:90 ethyl acetate:hexanes; stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.20 (s, 1H), 4.84 (d, *J* = 1.8 Hz, 1H), 4.70 (br s, 1H), 3.74 (s, 3H), 3.50 (s, 3H), 2.94–2.90 (m, 1H), 2.81–2.78 (m, 2H), 2.63 (d, *J* = 8.5 Hz, 1H), 2.34 (dd, *J* = 12.8, 5.7 Hz, 1H), 2.19 (br d, *J* = 2.1 Hz, 1H), 1.95–1.89 (m, 1H), 1.83–1.70 (m, 3H), 1.65 (dd, *J* = 13.9, 4.0 Hz, 1H), 1.61–1.58 (m, 2H), 1.43–1.35 (m, 1H), 1.27–1.25 (m, 2H), 1.00 (s, 3H), 0.94 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 171.3, 153.4, 115.0, 107.2, 57.1, 57.0, 54.9, 54.1, 52.3, 47.4, 39.6, 37.82, 37.79, 37.0, 36.4, 34.5, 29.0, 26.1, 25.8, 21.2; IR (thin film) 1781, 1742 cm^{-1}; $[\alpha]^{23}_{D}$ +73.0, $[\alpha]^{23}_{577}$ +76.4, $[\alpha]^{23}_{546}$ +86.1, $[\alpha]^{23}_{435}$ +146 (*c* = 1.0, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{34}O_5Na$ 401.2304; Found 401.2295.



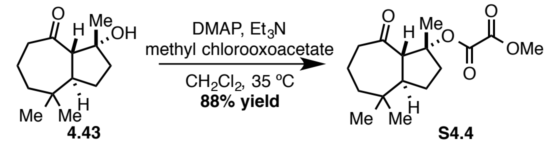
Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.42: A round-bottom flask was charged with **4.41** (4 mg, 0.01 mmol, 1.0 equiv), toluene (0.1 mL, 0.1 M), and a magnetic stir bar under an atmosphere of argon. After cooling the solution to –78 °C, 1 M solution of *i*-Bu_2AlH in toluene (22 μL, 0.022 mmol, 2.2 equiv) was added dropwise. The solution was maintained at −78 °C for 30 min. The reaction was quenched by the slow addition of sutured solution of Rochelle's salt (aq) (0.1 mL) at −78 °C. The mixture was allowed to warm to rt and stirred at rt for 1 h. Biphasic mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by use of a rotary evaporator to yield a crude mixture of biyclic lactol epimers **S4.3**. Diagnostic chemical shifts of the lactol intermediate **S4.3**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.86 (d, *J* = 6.0 Hz, 1H), 5.75 (d, *J* = 12.0 Hz, 1H), 5.47 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.96 (s, 1H), 4.85 (d, *J* = 2.4 Hz, 1H), 4.64 (d, *J* = 1.8 Hz, 1H), 3.50 (s, 3H).

A 1-dram scintillation vial was charged with crude mixture of bicyclic lactol epimers **S4.3,** toluene (0.1 mL, 0.1 M), Ag_2CO_3 (50 wt. % on Celite, 17 mg, 0,03 mmol, 3.0 equiv), and a magnetic stir bar under an atmosphere of argon. The reaction vessel was capped and heated to 110 °C. After 1 h, the black suspension was allowed to cool to rt, filtered over Celite and concentrated by use of a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to yield lactone **4.42** (3.5 mg, 0.01 mmol, 80% yield) as a clear oil: R_f = 0.30 (10:90 ethyl acetate:hexanes; stained with $KMnO_4$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.06 (d, *J* = 6.6 Hz, 1H), 4.98 (s, 1H), 4.84 (d, *J* =1.8 Hz, 1H), 4.62 (br s, 1H), 3.36 (s, 3H), 3.07–3.05 (m, 1H), 2.90 (dd, *J* = 18.6, 11.4 Hz, 1H), 2.66 (dd, *J* = 18.6, 3.6 Hz, 1H), 2.53 (d, *J* = 9.0 Hz, 1H), 2.37–2.34 (m, 1H), 2.22 (s, 1H), 1.96–1.91 (m, 1H), 1.85–1.80 (m, 1H), 1.80–1.71 (m, 3H), 1.63 (dt, *J* = 13.8, 4.2 Hz, 1H), 1.59–1.56 (m, 2H), 1.44–1.38 (m, 1H), 1.31–1.23 (m, 1H), 1.00 (s, 3H), 0.95 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 154.1, 114.6, 109.4, 109.3, 66.0, 56.6, 55.0, 54.5, 47.0, 39.9, 38.7, 37.8, 37.0, 36.8, 36.3, 34.6, 28.9, 26.4, 25.8, 21.2; IR (thin film) 2929, 2865, 1787, 1175, 1074, 1003, 932 cm^{-1}; $[\alpha]^{23}_{D}$ +73.9, $[\alpha]^{23}_{577}$ +77.2,

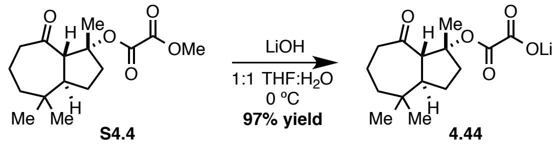
$[\alpha]^{23}_{546}$ +89.4, $[\alpha]^{23}_{435}$ +153 (*c* = 1.0, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{32}O_4Na$ 371.2198; Found 371.2193.



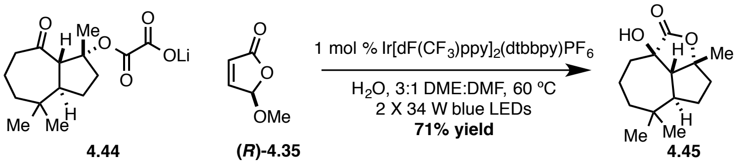
Preparation of (+)-Cheloviolene A (4.7) from 4.42: A 1-dram scintillation vial was charged with lactone **4.42** (13 mg, 0.036 mmol, 1.0 equiv), 1:1 1N HCl (aq):THF (1.4 mL, 0.025 M), and a magnetic stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at 40 °C for 12 h. The reaction mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 20:80 ethyl acetate:hexanes as eluent to yield (+)-cheloviolene A (**4.7**) as a colorless solid (9 mg, 0.026 mmol, 70% yield): R_f = 0.30 (20:80 ethyl acetate:hexanes, stained with $KMnO_4$). Recrystallization of the solid from hexanes:ethyl acetate afforded (+)-cheloviolene A (**4.7**) as a colorless crystalline solid. The ^1H and ^{13}C NMR data in $CDCl_3$ matched that of the isolation data.[8b] IR (thin film) 3430, 2951, 2923, 2867, 1789, 1365 cm^{-1}; $[\alpha]^{22}_{D}$ +53 (isolation: +4.5),[9] $[\alpha]^{22}_{577}$ +60, $[\alpha]^{22}_{546}$ +65, $[\alpha]^{22}_{435}$ +113 (*c* = 0.11, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{30}O_4Na$ 357.2042; Found 357.2048; mp: 155 – 156 °C (recrystallized from hexanes:ethyl acetate).



Preparation of methyl oxalate S4.4: A round-bottom flask was charged with **4.43** (146 mg, 0.694 mmol, 1.0 equiv), CH_2Cl_2 (7 mL, 0.1 M), DMAP (170 mg, 1.4 mmol, 2.0 equiv), Et_3N (210 mg, 2.1 mmol, 3.0 equiv), methyl chlorooxoacetate (190 µL, 2.1 mmol, 3.0 equiv), and a magnetic stir bar under ambient atmosphere. The resulting solution was heated to 35 °C and maintained at that temperature for 30 min. After 30 min, the reaction was allowed to cool to rt, quenched with H_2O, transferred to a separatory funnel, and extracted with CH_2Cl_2 (3 x 10 mL). Combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to yield **S4.4** (181 mg, 0.61 mmol, 88% yield) as a clear oil: R_f = 0.12 (10:90 ethyl acetate:hexanes; stained with *p*-anisaldehyde); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 2.79 (td, *J* = 12.2, 3.2 Hz, 1H), 2.48–2.32 (m, 3H), 2.18 (d, *J* = 12.5 Hz, 1H), 1.98 (ddd, *J* = 15.2, 10.0, 2.9 Hz, 1H), 1.88–1.72 (m, 2H), 1.75 (s, 3H), 1.61–1.43 (m, 3H), 1.44–1.30 (m, 1H), 0.97 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.5, 158.5, 156.3, 95.8, 63.2, 53.6, 49.1, 45.1, 44.1, 36.3, 34.3, 30.8, 25.2, 24.0, 20.8, 19.4; IR (thin film) 3021, 2964, 2873, 1742, 1646, 1216, 1161 cm^{-1}; $[\alpha]^{23}_{D}$ –104, $[\alpha]^{23}_{577}$ –113, $[\alpha]^{23}_{546}$ –131, $[\alpha]^{23}_{435}$ –247 (*c* = 0.4, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{24}O_5Na$ 319.1521; Found 319.1522.



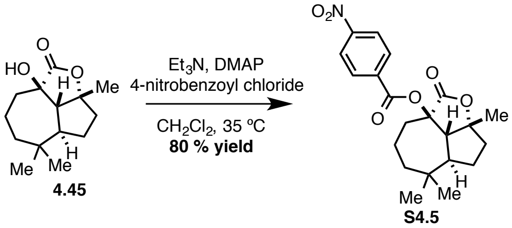
Preparation of lithium oxalate 4.44: A round-bottom flask was charged with **S4.4** (177 mg, 0.597 mmol, 1.0 equiv), 1:1 THF:H_2O (6 mL, 0.1 M), and a magnetic stir bar under ambient atmosphere. After cooling the biphasic mixture to 0 °C, 0.5 N LiOH (aq) (1.1 mL, 0.57 mmol, 0.95 equiv) was added dropwise. The mixture was then vigorously stirred at 0 °C for 5 min. Next, the homogenous solution was concentrated by use of a rotary evaporator (50 °C, 12 torr). The resulting colorless solid was washed with pentanes (3 x 5 mL) and dried further under high vacuum (rt, 0.5 torr) to yield **4.44** as a colorless solid (158 mg, 0.547 mmol, 97% yield): ^{1}H NMR (600 MHz, CD_3OD) δ 2.92 (td, *J* = 12.1, 3.3 Hz, 1H), 2.60 (td, *J* = 12.0, 6.8 Hz, 1H), 2.42 (dt, *J* = 15.0, 8.7 Hz, 1H), 2.32 (ddd, *J* = 12.3, 6.9, 2.5 Hz, 1H), 2.14 (dd, *J* = 12.5, 1.9 Hz, 1H), 1.92 (ddd, *J* = 15.0, 10.2, 3.0 Hz, 1H), 1.88–1.78 (m, 2H), 1.70 (s, 3H), 1.63–1.41 (m, 3H), 1.40–1.30 (m, 1H), 0.99 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 215.7, 166.7, 166.1, 94.0, 65.2, 46.1, 45.1, 37.6, 35.1, 31.2, 26.2, 24.5, 22.1, 19.6; IR (thin film) 3513, 2900, 2819, 1694, 1448, 1420, 1050 cm^{-1}; $[\alpha]^{21}_{D}$ –95.8, $[\alpha]^{21}_{577}$ –101, $[\alpha]^{21}_{546}$ –116, $[\alpha]^{21}_{435}$ –199 (*c* = 0.6, CH_3OH); HRMS (ESI-TOF) m/z: $[M]^-$ Calcd for $C_{15}H_{21}O_5$ 281.1389; Found 281.1388.



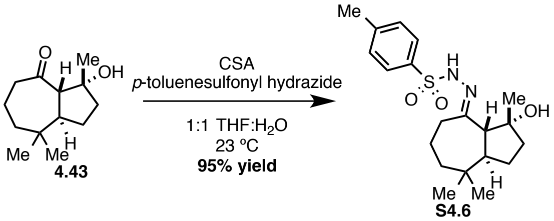
Preparation of lactone 4.45: A 1-dram scintillation vial was charged with **4.44** (29 mg, 0.1 mmol, 1.0 equiv), (Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (2 mg, 0.002 mmol, 0.02 equiv), 3:1

DME:DMF (2 mL, 0.05 M), H_2O (18 µL, 1.0 mmol, 10 equiv), ***(R)*-4.35** (11 mg, 0.1 mmol, 1.0 equiv), and a magnetic stir bar. The vial was then sealed with a screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. The reaction was allowed to cool to rt and transferred to a separatory funnel and extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes → 15:85 ethyl acetate:hexanes as eluent to yield **4.45** (17 mg, 0.071 mmol, 71% yield) as a colorless solid: R_f = 0.30 (20:80 ethyl acetate:hexanes; stained with *p*-anisaldehyde); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.13 (d, *J* = 11.9 Hz, 2H), 1.99–1.85 (m, 3H), 1.72 (dddd, *J* = 24.7, 12.7, 8.8, 5.6 Hz, 4H), 1.64–1.50 (m, 2H), 1.56 (s, 3H), 1.34 (qd, *J* = 12.2, 8.3 Hz, 1H), 1.25 (td, *J* = 13.4, 13.0, 2.6 Hz, 1H), 0.91 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 93.1, 79.6, 56.5, 51.0, 46.5, 38.6, 37.5, 35.0, 31.6, 28.0, 27.7, 19.6, 19.0; IR (thin film) 3419, 1754, 1651, 1644, 1289, 1130 cm^{-1}; $[\alpha]^{21}_{D}$ +55.6,

$[\alpha]^{23}_{577}$ +52.2, $[\alpha]^{23}_{546}$ +57.5, $[\alpha]^{23}_{435}$ +85.6 (*c* = 0.2, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{22}O_3Na$ 261.1467; Found 261.1466.

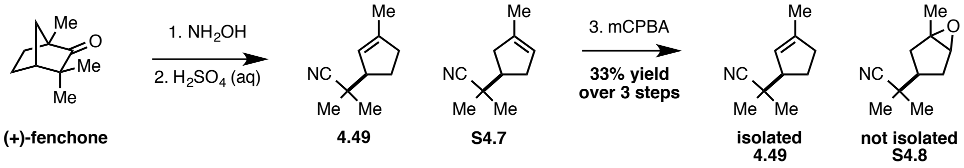


Preparation of benzoate ester S4.5: **Preparation of Benzoate Ester S4.5**: A 1-dram scintillation flask was charged with **4.45** (17 mg, 0.71 mmol, 1.0 equiv), CH_2Cl_2 (1.4 mL, 0.05 M), DMAP (9 mg, 0.07 mmol, 1.0 equiv), Et_3N (25 μL, 0.18 mmol, 2.5 equiv), 4-nitrobenzoyl chloride (16 mg, 0.085 mmol, 1.2 equiv), and a magnetic stir bar under an atmosphere of argon at rt. The flask was capped and heated to 35 °C for 18 h. The reaction was quenched with addition of sat. $NaHCO_3$ (aq). The resulting biphasic mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to yield **S4.5** (22 mg, 0.057 mmol, 80% yield) as a colorless solid: R_f = 0.27 (10:90 ethyl acetate:hexanes; stained with *p*-anisaldehyde). Recrystallization of the solid from hot hexanes afforded a crystal suitable for single-crystal X-ray diffraction analysis. ^1H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H), 2.58 (d, *J* = 11.9 Hz, 1H), 2.47 (ddd, *J* = 15.8, 6.0, 3.1 Hz, 1H), 2.11–1.85 (m, 5H), 1.79 (dq, *J* = 11.2, 5.7, 5.3 Hz, 2H), 1.64–1.57 (m, 1H), 1.56 (s, 3H), 1.41–1.30 (m, 2H), 0.99 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 162.7, 151.0, 135.4, 131.1, 123.9, 92.0, 87.2, 55.4, 52.4, 44.2, 40.0, 34.9, 34.3, 30.3, 27.1, 27.0, 21.1, 20.0; IR (thin film) 2958, 2934, 2869, 1771, 1731, 1530, 1348, 1281 cm^{-1}; $[\alpha]^{22}_{D}$ +38.7, $[\alpha]^{22}_{577}$ +40.5, $[\alpha]^{22}_{546}$ +45.4, $[\alpha]^{22}_{435}$ +80.8 (*c* = 0.8, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{25}NO_6Na$ 410.1580; Found 410.1599; mp: 135–137 °C (recrystallized from hexanes).



Preparation of hydrazone S4.6: A 1-dram vial was charged with **4.43** (10 mg, 0.05 mmol, 1.0 equiv), 1:1 THF:H_2O (0.5 mL, 0.1 M), *p*-toluenesulfonyl hydrazide (28 mg, 0.15 mmol, 3.0 equiv), CSA (3 mg, 0.02 mmol, 0.3 equiv), and a magnetic stir bar under ambient atmosphere at rt. The resulting biphasic mixture was stirred vigorously for 18 h at rt. The mixture was transferred to a separatory funnel, diluted with H_2O (5 mL), and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated by use of a rotary evaporator. The resulting residue was purified by flash column chromatography on silica gel using 20:80 ethyl acetate:hexanes as eluent to yield **S4.6** (18 mg, 0.048 mmol, 95% yield) as a colorless solid: R_f = 0.2 (20:80 ethyl acetate:hexanes; stained with $KMnO_4$). Recrystallization of the solid from benzene and pentanes via a vapor diffusion method afforded a crystal suitable for single-crystal X-ray diffraction analysis. ^1H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.39–2.34 (m, 1H), 2.32 (d, *J* = 9.9 Hz, 1H), 2.19 (ddd, *J* = 18.4, 10.1, 6.1 Hz, 1H), 2.02–1.88 (m, 2H), 1.67–1.52 (m, 4H), 1.51–1.43 (m, 1H), 1.26 (ddd, *J* = 12.9, 11.4, 9.1

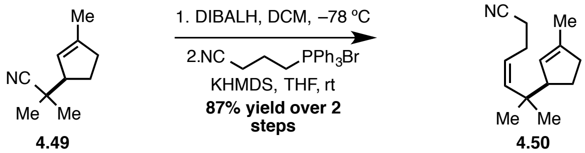
Hz, 1H), 1.13 (s, 3H), 1.07 (ddd, *J* = 13.7, 9.1, 4.7 Hz, 1H), 0.87 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.5, 144.7, 135.1, 130.1, 128.4, 81.2, 52.5, 51.9, 44.6, 40.7, 35.0, 31.9, 31.6, 26.1, 25.3, 21.8, 18.9, 18.8; IR (thin film) 3426, 3224, 2964, 1633, 1598, 1455, 1336, 1166 cm^{-1}; $[\alpha]^{23}_{D}$ –79.2, $[\alpha]^{23}_{577}$ –81.1, $[\alpha]^{23}_{546}$ –105, $[\alpha]^{23}_{435}$ –183 (*c* = 1.3, CHCl$_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{20}H_{30}N_2O_3S$ [M+Na]$^+$ 401.1875; observed 401.1868; mp: 153–156 °C (recrystallized benzene and pentanes via a vapor diffusion method).



Preparation of nitrile 4.49: The original procedure reported by Kreiser has been modified to completely resolve the mixture of alkene regioisomers **4.49** and **S4.7**.[50] A round-bottom flask was charged with (+)-fenchone (30.0 g, 197 mmol, 1.0 equiv), hydroxylamine hydrochloride (23.0 g, 335 mmol, 1.7 equiv), sodium acetate trihydrate (53.6 g, 394 mmol, 2.0 equiv), ethanol (360 mL, 0.55 M), and a magnetic stir bar under ambient atmosphere. The mixture was stirred and heated to reflux for 36 h and then allowed to cool to rt. The mixture was concentrated to 1/4 volume by use of a rotary evaporator and water (300 mL) was added. The suspension was vacuum filtered, and the solids were thoroughly washed with water and allowed to dry on the filter. The solids were collected and dried *in vacuo* to yield 31.1 g of the crude oxime as a colorless solid.

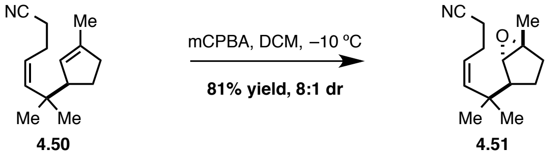
The crude oxime (31.1 g) was added to a round-bottom flask along with 8 M H$_2$SO$_4$ (aq) (300 mL), and a magnetic stir bar under ambient atmosphere. The round-bottom flask was placed into a preheated oil bath and vigorously stirred at 120 °C for 30 min. The flask was then removed from the oil bath and immediately cooled to 0 ºC with an ice bath. A portion of pentanes (300 mL) was added to the mixture, and the layers were separated. The organic layer was washed with sat. $NaHCO_3$ (aq). The organic layer was dried over Na_2SO_4 and gently concentrated by use of a rotary evaporator (12 torr, rt) to yield a crude mixture of regioisomeric alkenes **4.49** and **S4.7** as a clear oil (25.9 g, 90% pure with a 1:1 ratio of alkenes as measured by ^1H NMR analysis of a 15 mg aliquot of the crude material to which 1,2-dibromo-4,5-methylenedioxybenzene was added as an internal standard; the ^1H NMR resonances for the olefinic protons at 5.30 ppm and 5.27 ppm were used for the measurement).

A round-bottom flask was charged with the crude mixture of alkenes **4.49** and **S4.7** (25.9 g, 90% pure, 157 mmol, 1.0 equiv), dichloromethane (300 mL, 0.5 M), and a magnetic stir bar. The solution was stirred in a large –10 °C brine/ice bath under ambient atmosphere. A portion of 74% *m*-CPBA (25.5 g, 110 mmol, 0.7 equiv) was added, and the mixture was stirred for 16 h with the temperature of the bath gradually rising to 5 °C as the ice melted over the course of the reaction. Hexanes (300 mL) was added and the crude mixture was flushed through a plug of silica gel. The product was eluted with additional dichloromethane:hexanes (50:50), and the solvent front was discarded. The filtrate was gently concentrated by use of a rotary evaporator (12 torr, rt) to yield the desired olefin isomer **4.49** as a clear oil (9.7 g, 65 mmol, 33% yield combined over 3 steps. The ratio of alkene regioisomers is >20:1 by ^1H NMR analysis): R_f = 0.42 (50:50 dichloromethane:hexanes, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.31–5.28 (m, 1H), 2.79–2.73 (m, 1H), 2.39–2.30 (m, 1H), 2.28–2.19 (m, 1H), 2.10 (dtd, *J* = 13.6, 8.9, 4.7 Hz, 1H), 1.81–1.72 (m, 4H), 1.30 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 125.2, 123.0, 55.1, 36.7, 36.6, 26.8, 24.8, 24.6, 16.9; IR (thin film) 3046, 2976, 2232, 1659, 988, 826 cm^{-1}; $[\alpha]^{22}_{D}$ +83.9, $[\alpha]^{22}_{577}$ +87.8, $[\alpha]^{22}_{546}$ +98.8, $[\alpha]^{22}_{435}$ +167, $[\alpha]^{22}_{405}$ +200 (c = 1.0, $CHCl_3$); HRMS (GC-CI/TOF) m/z calculated for $C_{10}H_{15}N$ $[M + NH_4]^+$ 167.1548, observed 167.1542.

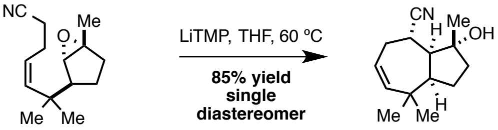


Preparation of diene 4.50: A round-bottom flask was charged with nitrile **4.49** (7.8 g, 52 mmol, 1.0 equiv), dichloromethane (350 mL, 0.15 M), and a magnetic stir bar under an argon atmosphere. The solution was stirred and cooled to –78 °C, and a portion of neat (i-Bu)$_2$AlH (14 mL, 78 mmol, 1.5 equiv) was added via syringe over 5 min. After the addition was complete, the round-bottom flask was removed from the cooling bath, allowed to warm to rt, and maintained for 2 h at rt. A portion of 2N HCl (aq) (200 mL) was added, and the mixture was stirred vigorously overnight. The two phases were separated and the aqueous layer was extracted with dichloromethane (200 mL). The combined organic layers were washed with sat. $NaHCO_3$ (aq) (200 mL). The organic phase was dried over $MgSO_4$ and gently concentrated by use of a rotary evaporator (12 torr, rt) to yield the crude aldehyde product as a clear oil (crude mass: 7.5 g).

A round-bottom flask was charged with KHMDS (16.6 g, 83.0 mmol, 1.7 equiv), tetrahydrofuran (490 mL, 0.10 M), and a magnetic stir bar under an argon atmosphere. The solution was stirred and cooled to 0 °C, and (3-cyanopropyl)triphenylphosphonium bromide[77] (34 g, 83 mmol, 1.7 equiv) was added. After the addition was complete, the round-bottom flask was removed from the cooling bath and stirred for 30 min at rt. The crude aldehyde (7.5 g, 49 mmol, 1.0 equiv) dissolved in tetrahydrofuran (50 mL) was added via syringe over 5 min. The solution was maintained at rt for 1 h and was then quenched with water (300 mL). The mixture was extracted with Et_2O (2 x 200 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was flushed through a plug of silica gel with toluene and was then concentrated by use of a rotary evaporator to yield product **4.50** as a clear oil (9.1 g, 45 mmol, 87% yield over 2 steps): R_f = 0.50 (100% toluene, stained with $KMnO_4$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 (dt, *J* = 12.1, 1.8 Hz, 1H), 5.24 (hept, *J* = 1.7 Hz, 1H), 5.17 (dt, *J* = 12.1, 7.3 Hz, 1H), 2.64 (ddp, *J* = 8.7, 6.6, 2.2 Hz, 1H), 2.55 (qd, *J* = 7.3, 1.8 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.22–2.14 (m, 2H), 1.95–1.87 (m, 1H), 1.72 (s, 3H), 1.62–1.53 (m, 1H), 1.07 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 141.5, 125.8, 124.5, 119.6, 57.9, 39.9, 36.9, 26.60, 26.58, 26.3, 24.7, 18.0, 16.9; IR (thin film) 3040, 3005, 2962, 2245, 1656, 1445, 986, 827, 733 cm^{-1}; $[\alpha]^{23}_{D}$ +65.6, $[\alpha]^{23}_{577}$ +68.0, $[\alpha]^{23}_{546}$ +78.1, $[\alpha]^{23}_{435}$ +130, $[\alpha]^{23}_{405}$ +159 (*c* = 1.0, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{21}N$ [M + Na]$^+$ 226.1572, observed 226.1574.

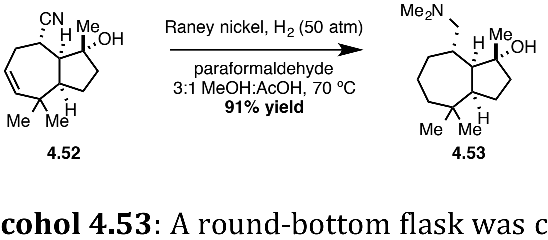


Preparation of epoxide 4.51: A round-bottom flask was charged with **4.50** (9.00 g, 44.3 mmol, 1.0 equiv), dichloromethane (150 mL, 0.3 M), and a magnetic stir bar. The solution was stirred in a large –10 °C brine/ice bath under ambient atmosphere. A portion of 70% *m*-CPBA (11.3 g, 45.6 mmol, 1.03 equiv) was added, and the mixture was stirred for 3 h at –10 °C. The reaction was quenched with sat. $NaHCO_3$ (aq) (300 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (2 x 200 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The epoxidation proceeded to give an 8:1 mixture of epoxide stereoisomers, from which pure **4.51** was isolated after chromatography. The crude product was purified by flash column chromatography on silica gel using 15:85 ethyl acetate:hexanes as eluent to yield epoxide **4.51** as a clear oil (7.90 g, 36.1 mmol, 81% yield): $R_f = 0.28$ (20:80 ethyl acetate:hexanes, stained with $KMnO_4$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 (dt, *J* = 12.2, 1.8 Hz, 1H), 5.22 (dt, *J* = 12.2, 7.3 Hz, 1H), 3.16 (s, 1H), 2.56 (qd, *J* = 7.3, 1.8 Hz, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 2.19 (dd, *J* = 7.9, 2.1 Hz, 1H), 1.88–1.80 (m, 1H), 1.64 – 1.51 (m, 3H), 1.44 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 125.0, 119.3, 66.5, 66.2, 51.0, 38.7, 31.9, 27.0, 26.6, 24.6, 24.0, 18.0, 17.8; IR (thin film) 3010, 2961, 2245, 1648, 1421, 996, 904, 827, 733 cm^{-1}; $[\alpha]^{23}_{D}$ –1.6, $[\alpha]^{23}_{577}$ –1.7, $[\alpha]^{23}_{546}$ –1.8, $[\alpha]^{23}_{435}$ –2.4, $[\alpha]^{23}_{405}$ –2.6 (*c* = 0.85, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{21}NO$ $[M + Na]^+$ 242.1521, observed 242.1511.



4.51 4.52

Preparation of cyclized product 4.52: A round-bottom flask was charged with 2,2,6,6-tetramethylpiperidine hydrobromide[78] (5.90 g, 26.6 mmol, 1.05 equiv), tetrahydrofuran (400 mL, 0.063 M), and a magnetic stir bar under an argon atmosphere. The solution was stirred and cooled to 0 °C, and 2.3 M *n*-BuLi (23.0 mL, 53.0 mmol, 2.1 equiv) was added. After the addition was complete, the mixture was stirred for 10 min at 0 °C, then a solution of epoxide **4.51** (5.50 g, 25.1 mmol, 1.0 equiv) in tetrahydrofuran (50 mL) was added via syringe. The solution was maintained at 0 °C for 10 min, then the round-bottom flask was placed into a preheated oil bath and stirred at 60 °C for 2 h. The flask was then removed from the oil bath and cooled to 0 °C with an ice bath. Portions of sat. NH_4Cl (aq) (300 mL) and hexanes (200 mL) were added and the layers were separated. The aqueous phase was extracted with hexanes (2 x 200 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 20:80 ethyl acetate:hexanes as eluent to yield product **4.52** as a clear oil that solidified to a colorless solid during storage at –20 °C (4.65 g, 21.3 mmol, 85% yield as a single diastereomer): R_f = 0.28 (30:70 ethyl acetate:hexanes, stained with $KMnO_4$); ^1H NMR (500 MHz, CD_3OD) δ 5.56–5.50 (m, 1H), 5.47–5.41 (m, 1H), δ 2.91 (ddd, *J* = 9.4, 8.0, 2.8 Hz, 1H), 2.68–2.59 (m, 1H), 2.55 (dddd, *J* = 16.6, 9.3, 5.5, 1.7 Hz, 1H), 2.50–2.42 (m, 1H), 2.29 (t, *J* = 7.6 Hz, 1H), 1.89–1.80 (m, 1H), 1.79–1.69 (m, 2H), 1.60–1.50 (m, 1H), 1.41 (s, 3H), 1.25 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 142.4, 124.7, 124.6, 82.8, 55.4, 51.5, 39.3, 38.8, 31.7, 31.4, 29.8, 29.3, 25.9, 25.4; IR (thin film) 3453, 3016, 2962, 2236, 1660, 1469, 1379, 736 cm^{-1}; $[\alpha]^{23}_{D}$ +25.9, $[\alpha]^{23}_{577}$ +27.3, $[\alpha]^{23}_{546}$ +29.7, $[\alpha]^{23}_{435}$ +49.0, $[\alpha]^{23}_{405}$ +59.2 (*c* = 1.2, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{21}NO$ [M + Na]$^+$ 242.1521, observed 242.1510.

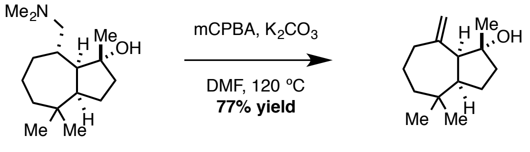


4.52

4.53

Preparation of amino alcohol 4.53: A round-bottom flask was charged with **4.52** (1.00 g, 4.56 mmol, 1.0 equiv), paraformaldehyde (1.38 g, 46.0 mmol, 10 equiv), Raney nickel (2.0 g, 200 wt %), 3:1 methanol:acetic acid (46 mL, 0.10 M), and a magnetic stir bar under ambient atmosphere. The round-bottom flask was placed inside a Parr bomb, and the bomb was evacuated then pressurized to 50 atm with H_2. The bomb was placed on a stir plate, and the solution inside was vigorously stirred at room temperature for 30 min. The bomb was then placed into a heating bath on the stir plate and heated to 70 °C for 5 h with vigorous stirring. The bomb was removed from the heating bath and was allowed to cool to rt before being depressurized. The crude reaction mixture was filtered to remove the solid Raney nickel. The round-bottom flask and solids on the filter were washed with portions of MeOH (3 x 50 mL), and care was taken to not allow the Raney nickel to fully dry on the filter. The combined filtrate was concentrated to 1/10 volume by use of a rotary evaporator, and the Raney nickel was carefully destroyed with 1 M HCl (aq). The concentrated filtrate was diluted with ethyl acetate (200 mL) and shaken in a separatory funnel with sat. K_2CO_3 (aq) (200 mL). The layers were separated, and the aqueous phase was extracted with ethyl acetate (100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 6:94 methanol:dichloromethane as eluent to yield product **4.53** as a clear oil (1.06 g, 4.2 mmol, 91% yield): R_f = 0.30 (10:90 methanol:dichloromethane, stained with $KMnO_4$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 2.42 (dd, *J* = 12.7, 8.8 Hz, 1H), 2.27–2.19 (m, 7H), 2.15 (d, *J* = 12.9 Hz, 1H), 1.91–1.80 (m, 2H), 1.78–1.38 (m, 8H), 1.29–1.21 (m, 2H), 1.18 (s, 3H), 0.92 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 77.9, 71.4, 61.9, 50.3, 47.8, 45.6, 41.1, 37.6, 37.4, 37.2, 32.6, 26.6, 26.4, 23.9, 22.6; IR (thin film) 3389, 3190, 2871, 1458, 1153, 1001 cm^{-1}; $[\alpha]^{21}_{D}$ –29.3, $[\alpha]^{21}_{577}$ –

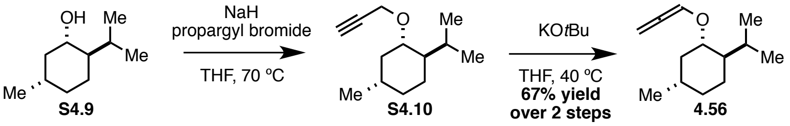
31.9, $[\alpha]^{21}_{546}$ –37.2, $[\alpha]^{21}_{435}$ –60.1, $[\alpha]^{21}_{405}$ –69.7 (*c* = 1.2, MeOH); HRMS (ESI/TOF) *m*/*z* calculated for $C_{16}H_{31}NO$ $[M + Na]^+$ 276.2303, observed 276.2300.



4.53 **4.54**

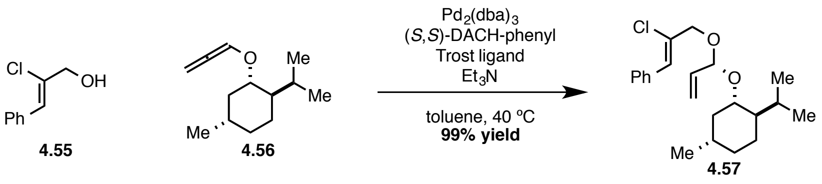
Preparation of tertiary alcohol 4.54: A round-bottom flask was charged with **4.53** (1.00 g, 3.95 mmol, 1.0 equiv), K_2CO_3 (815 mg, 5.92 mmol, 1.5 equiv), DMF (40 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. A portion of 70% *m*-CPBA (972 mg, 3.95 mmol, 1.0 equiv) was added, and the mixture was stirred vigorously for 20 min at rt, then at 120 °C for 12 h. The reaction was allowed to cool to rt and then was diluted with water (150 mL). The solution was extracted with Et_2O (2 x 100 mL). The combined organic layers were then washed with brine (100 mL), dried over Na_2SO_4, and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to yield product **4.54** as a clear oil (630 mg, 3.03 mmol, 77% yield): R_f = 0.43 (20:80 ethyl acetate:hexanes, stained with $KMnO_4$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.80 (d, *J* = 2.5 Hz, 1H), 4.69 (d, *J* = 2.2 Hz, 1H), 2.57 (d, *J* = 7.9 Hz, 1H), 2.54–2.46 (m, 1H), 2.25 (dd, *J* = 12.6, 5.7 Hz, 1H), 1.91 (tdd, *J* = 10.8, 8.9, 7.1 Hz, 1H), 1.81–1.61 (m, 6H), 1.36 (qdd, *J* = 13.0, 3.8, 2.1 Hz, 1H), 1.30 (s, 1H), 1.23 (dt, *J* = 14.4, 3.5 Hz, 1H), 1.17 (s, 3H), 0.98 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 114.9, 83.9, 62.0, 51.1, 39.5, 37.6, 36.2, 35.4, 33.8, 28.8, 26.8, 26.2, 24.5; IR (thin film) 3351, 3066, 2865, 1628, 1451, 922, 890 cm^{-1}; $[\alpha]^{23}_{D}$ +70.5, $[\alpha]^{23}_{577}$ +73.1, $[\alpha]^{23}_{546}$ +82.6, $[\alpha]^{23}_{435}$ +147,

$[\alpha]^{23}_{405}$ +180 (c = 1.1, $CHCl_3$); HRMS (GC-CI/TOF) m/z calculated for $C_{14}H_{24}O$ $[M]^+$ 208.1827, observed 208.1828.

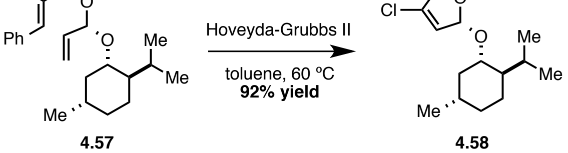


Preparation of allene 4.56: The procedure for the preparation of allene **4.56** was a slight modification of a literature procedure.[79] A round-bottom flask was charged with (*D*)-menthol (**S4.9**) (20.0 g, 128 mmol), tetrahydrofuran (210 mL, 0.6 M), and a magnetic stir bar under an atmosphere of argon. Next, 60% NaH (10.2 g, 256 mmol, 2.0 equiv) was added in one portion at rt. The resulting heterogeneous mixture was stirred vigorously and heated to 70 °C over a period of 30 min. After being stirred at 70 °C for 2 h, the reaction was allowed to cool to rt. Next, an 80 wt% solution of propargyl bromide in toluene (36 mL, 320 mmol, 2.5 equiv) was added at rt. The mixture was then heated to reflux for 18 h. The reaction was allowed to cool to rt, quenched with ice (~5 g), and concentrated to ~50 mL by use of a rotary evaporator. The resulting slurry was diluted with 100 mL hexanes and filtered over silica gel (200 mL SiO_2, 500 mL 5:94.8:0.2 diethyl ether:hexanes:triethylamine) into 125 mL Erlenmeyer flasks by applying a mild vacuum. Fractions containing product **S4.10** [R_f = 0.48 (5:95 diethyl ether:hexanes, stained with *p*-anisaldehyde)] were combined and concentrated by use of a rotary evaporator. *Note: minor amounts of (D)-menthol (**S4.9**) [R_f = 0.10 (5:95 diethyl ether:hexanes, stained with p-anisaldehyde)] can be present in later fractions, depending on the rate of filtration and silica gel column height. This impurity does not affect the overall yield as it is usually completely removed during the second silica gel filtration following alkyne isomerization.*

A round-bottom flask was charged with crude **S4.10**, tetrahydrofuran (250 mL, 0.5 M), and a magnetic stir bar under an argon atmosphere. Next, KO*t*Bu (14.4 g, 128 mmol, 1.0 equiv) was added in one portion at rt. The resulting heterogeneous mixture was placed in a preheated 40 °C oil bath and stirred at 40 °C for 1 h. The reaction was allowed to cool to rt, concentrated to ~30 mL by use of a rotary evaporator. The resulting slurry was diluted with 100 mL hexanes and filtered over silica gel (200 mL SiO_2, 500 mL 2:97.8:0.2 diethyl ether:hexanes:triethylamine) into 125 mL Erlenmeyer flasks by applying a mild vacuum. Fractions containing allene **4.56** [R_f = 0.83 (5:95 diethyl ether:hexanes, stained with *p*-anisaldehyde)] were combined and concentrated by use of a rotary evaporator. The resulting red oil was further purified by distillation (oil bath temperature: 65 °C; bp: 40 °C, 0.32 torr) to yield **4.56** as a clear oil (16.7 g, 85.8 mmol, 67% yield). Spectral data were consistent with reported values.[78]



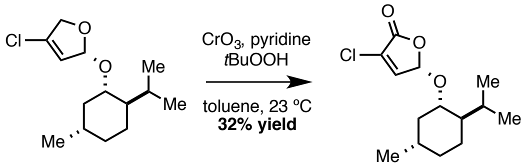
Preparation of acetal 4.57: A round-bottom flask was charged with $Pd_2(dba)_3$ (184 mg, 0.201 mmol, 0.015 equiv), (*S,S*)-DACH-phenyl Trost ligand (278 mg, 0.402 mmol, 0.03 equiv), toluene (27 mL, 0.5 M), Et_3N (2.8 mL, 20 mmol, 1.5 equiv), and a magnetic stir bar under an argon atmosphere. Next, allene **4.56** (3.9 g, 20 mmol, 1.5 equiv) and alcohol **4.55** (2.3 g, 13.5 mmol, 1.0 equiv) were added sequentially. The reaction was placed in a preheated 40 °C oil bath and stirred at 40 °C for 40 min, at which point TLC analysis indicated complete consumption of the starting material **4.55** [R_f = 0.24 (20:80 ethyl acetate:hexanes, stained with $KMnO_4$)]. The reaction mixture was allowed to cool to rt and diluted with pentanes (75 mL). The resulting heterogeneous mixture was filtered over Celite (125 mL, 400 mL pentanes) by applying a mild vacuum. The filtrate was concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:99.8:0.2 diethyl ether:hexanes:triethylamine → 2:97.8:0.2 diethyl ether:hexanes:triethylamine as eluent to yield product **4.57** as a clear oil (4.85 g, 13.4 mmol, 99% yield): R_f = 0.60 (5:95 diethyl ether:hexanes, stained with $KMnO_4$); ^1H NMR (500 MHz, C_6D_6) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.88 (s, 1H), 5.91 (ddd, *J* = 17.4, 10.5, 4.8 Hz, 1H), 5.40 (d, *J* = 17.4 Hz, 1H), 5.16 (d, *J* = 4.8 Hz, 1H), 5.10 (d, *J* = 10.7 Hz, 1H), 4.26–4.20 (m, 2H), 3.61 (td, *J* = 10.7, 4.4 Hz, 1H), 2.56 (pd, *J* = 7.0, 2.1 Hz, 1H), 2.08–2.03 (m, 1H), 1.58–1.50 (m, 2H), 1.40–1.33 (m, 1H), 1.23–1.13 (m, 1H), 0.98 (d, *J* = 7.3 Hz, 3H), 0.94 (d, *J* = 7.3 Hz, 3H), 0.92–0.88 (m, 2H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.75 (qd, *J* = 12.8, 3.4 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 136.6, 135.2, 131.1, 129.9, 128.9, 128.6, 125.7, 118.7, 98.9, 75.7, 68.8, 48.9, 41.4, 35.1, 32.0, 26.0, 23.8, 22.9, 21.9, 16.7; IR (thin film) 2960, 2926, 2868, 1454, 1023 cm^{-1}; $[\alpha]^{22}_{D}$ +95, $[\alpha]^{22}_{577}$ +100, $[\alpha]^{22}_{546}$ +113, $[\alpha]^{22}_{435}$ +189 (*c* = 1.0, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{22}H_{31}ClO_2$ $[M + Na]^+$ 385.1910, observed 385.1897.



4.57

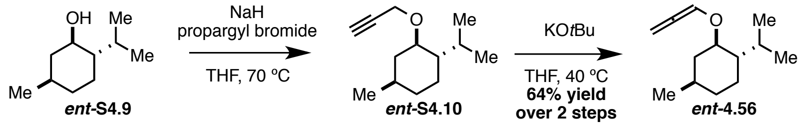
4.58

Preparation of dihydrofuran 4.58: A round-bottom flask was charged with **4.57** (4.8 g, 13.2 mmol, 1.0 equiv), toluene (66 mL, 0.2 M), and a magnetic stir bar under an argon atmosphere. A solution of Hoveyda-Grubbs 2nd generation catalyst (446 mg, 0.66 mmol, 0.05 equiv) in toluene (66 mL, 0.2 M) was added to the solution of acetal **4.57** in toluene. The resulting solution was placed in a preheated 60 °C oil bath and stirred at 60 °C for 1 h. After 1 h at 60 °C, the reaction was allowed to cool to rt and diluted with 150 mL pentanes. The resulting suspension was filtered over Celite (125 mL Celite, 400 mL pentanes) by applying a mild vacuum. The filtrate was concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:99.8:0.2 diethyl ether:hexanes:triethylamine → 2:97.8:0.2 diethyl ether:hexanes:triethylamine as eluent to yield a yellow oil that was further purified by Kugelrohr short-pass distillation (195 °C, 0.6 torr) to yield **4.58** as a clear oil (3.6 g, 13.6 mmol, 92% yield): R_f = 0.65 (5:95 diethyl ether:hexanes, stained with $KMnO_4$); ^1H NMR (500 MHz, C_6D_6) δ 5.75 (d, *J* = 4.1 Hz, 1H), 5.49 (br, 1H), 4.44 (ddd, *J* = 13.0, 4.4, 2.3 Hz, 1H), 4.16 (d, *J* = 13.0, 1H), 3.45 (td, *J* = 10.5, 4.3 Hz, 1H), 2.38 (p, *J* = 6.9, 1H), 1.87 (d, *J* = 11.9, 1H), 1.55–1.46 (m, 2H), 1.26 (t, *J* = 11.1, 1H), 1.11–1.04 (m, 1H), 0.94–0.91 (m, 6H), 0.89–0.85 (m, 2H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.76–0.67 (m, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 134.8, 123.6, 105.6, 76.2, 74.6, 48.7, 41.6, 35.1, 32.0, 26.1, 24.0, 22.8, 21.6, 16.6; IR (thin film) 2953, 2919, 2867, 1638, 1454, 1316, 1024 cm^{-1}; $[\alpha]^{23}_{D}$ +117, $[\alpha]^{23}_{577}$ +120, $[\alpha]^{23}_{546}$ +135, $[\alpha]^{23}_{435}$ +213 (*c* = 1.0, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{23}ClO_2$ $[M + H]^+$ 259.1465, observed 259.1472.



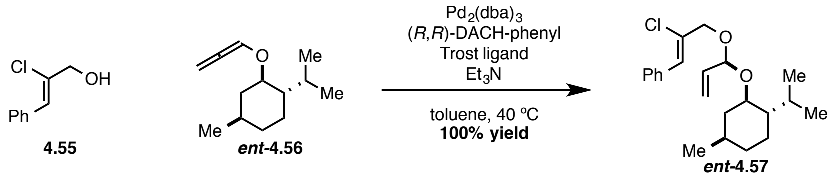
4.58 **4.59**

Preparation of butenolide 4.59: A round-bottom flask was charged with **4.58** (2.1 g, 8.0 mmol, 1.0 equiv), benzene (80 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, pyridine (260 μL, 3.2 mmol, 0.4 equiv), CrO_3 (160 mg, 1.6 mmol, 0.2 equiv), and a 5 M solution of *t*BuOOH in *n*-decane (11 mL, 56 mmol, 7.0 equv) were added sequentially. The reaction was removed from an ice bath, allowed to warm to rt and stirred for 3 h at rt. The heterogeneous mixture was then cooled to 0 °C and additional pyridine (260 μL, 3.2 mmol, 0.4 equiv), CrO_3 (160 mg, 1.61 mmol, 0.2 equiv), and a 5 M solution of *t*-BuO_2H in *n*-decane (11 mL, 56 mmol, 7.0 equv) were added sequentially. The reaction was removed from an ice bath, allowed to warm to rt and stirred for 18 h at rt. The mixture was filtered over silica gel (50 mL SiO_2, 200 mL 99.8:0.2 diethyl ether:triethylamine) by applying a mild vacuum. The filtrate was concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:99.8:0.2 diethyl ether:hexanes:triethylamine → 5:94.8:0.2 diethyl ether:hexanes:triethylamine as eluent to provide a colorless solid that was further purified by crystallization from hot pentanes at –20 °C to yield **4.59** as colorless large prisms (673 mg, 2.56 mmol, 32% yield after 2 rounds of crystallization): R_f = 0.29 (10:90 diethyl ether:hexanes, stained with *p*-anisaldehyde). ^1H NMR (600 MHz, C_6D_6) δ 6.03 (s, 1H), 5.17 (s, 1H), 3.36 (td, *J* = 10.8, 4.2 Hz, 1H), 2.17 (q, *J* = 7.0 Hz, 1H), 1.71–1.66 (m, 1H), 1.45–1.39 (m, 2H), 1.14 (t, *J* = 10.9, 1H), 1.03–0.95 (m, 1H), 0.83–0.79 (m, 9H), 0.77–0.68 (m, 2H), 0.65–0.58 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ 165.4, 142.9, 129.1, 98.3, 79.2, 47.3, 40.7, 34.6, 31.8, 25.9, 23.6, 22.7, 21.3, 16.2; IR (thin film) 2957, 2922, 2864, 1770, 1343 cm^{-1}; $[\alpha]^{23}_{D}$ +139, $[\alpha]^{23}_{577}$ +144, $[\alpha]^{23}_{46}$ +163, $[\alpha]^{23}_{435}$ +267 (c = 1.0, $CHCl_3$); HRMS (ESI/TOF) m/z calculated for $C_{14}H_{21}ClO_3$ $[M + Na]^+$ 295.1077 observed 295.1074; mp: 70–71 °C (recrystallized from hot pentanes).

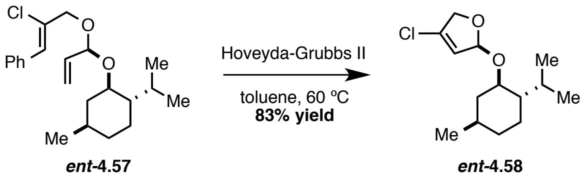


Preparation of allene *ent*-4.56: The procedure for the preparation of allene ***ent*-4.56** was a slight modification from the literature procedure.[79] A round-bottom flask was charged with (*L*)-menthol (***ent*-S4.9**) (20 g, 128 mmol), tetrahydrofuran (210 mL, 0.6 M), and a magnetic stir bar under an atmosphere of argon. Next, 60% NaH (10.2 g, 256 mmol, 2.0 equiv) was added in one portion at rt. After being stirring at 70 °C for 2 h, the reaction was allowed to cool to rt. Next, an 80 wt% solution of propargyl bromide in toluene (36 mL, 320 mmol, 2.5 equiv) was added at rt. The mixture was then heated to reflux for 18 h. The reaction was allowed to cool to rt, quenched with ice (~5 g), and concentrated to ~50 mL by use of a rotary evaporator. The resulting slurry was diluted with 100 mL hexanes and filtered over silica gel (200 mL SiO_2, 500 mL 5:94.8:0.2 diethyl ether:hexanes:triethylamine) into 125 mL Erlenmeyer flasks by applying a mild vacuum. Fractions containing product ***ent*-S4.10** [R_f = 0.48 (5:95 diethyl ether:hexanes, stained with *p*-anisaldehyde)] were combined and concentrated by use of a rotary evaporator. *Note: minor amounts of (L)-menthol (**ent-S4.9**) [R_f = 0.10 (5:95 diethyl ether:hexanes, stained with p-anisaldehyde)] can be present in later fractions, depending on the rate of filtration and* *silica gel column height. This does not affect the overall yield as it is usually completely removed during the second silica gel filtration following alkyne isomerization*.

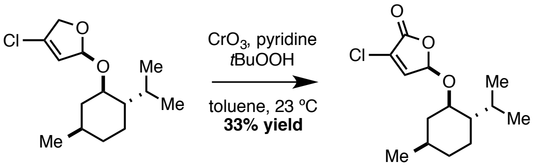
A round-bottom flask was charged with crude ***ent*-S4.10**, tetrahydrofuran (260 mL, 0.5 M), and a magnetic stir bar under an argon atmosphere. Next, KO*t*Bu (14.4 g, 128 mmol, 1.0 equiv) was added in one portion at rt. The resulting heterogeneous mixture was placed in a preheated 40 °C oil bath and stirred at 40 °C for 1 h. The reaction was allowed to cool to rt, concentrated to ~30 mL by use of a rotary evaporator. The resulting slurry was diluted with 100 mL hexanes and filtered over silica gel (200 mL SiO_2, 500 mL 2:97.8:0.2 diethyl ether:hexanes:triethylamine) into 125 mL Erlenmeyer flasks by applying a mild vacuum. Fractions containing allene ***ent*-4.56** [R_f = 0.83 (5:95 diethyl ether:hexanes, stained with *p*-anisaldehyde)] were combined and concentrated by use of a rotary evaporator. The resulting red oil was further purified by distillation (oil bath temperature: 65 °C; bp: 40 °C, 0.32 torr) to yield ***ent*-4.56** as a clear oil (15.9 g, 81.8 mmol, 64% yield). Spectral data were consistent with reported values.[78]



Preparation of acetal *ent*-4.57: A round-bottom flask was charged with $Pd_2(dba)_3$ (370 mg, 0.40 mmol, 0.015 equiv), (*R*,*R*)-DACH-phenyl Trost ligand (560 mg, 0.40 mmol, 0.03 equiv), toluene (54 mL, 0.5 M), Et_3N (5.7 mL, 40 mmol, 1.5 equiv), and a magnetic stir bar under an argon atmosphere. Next, allene ***ent*-4.56** (7.9 g, 40 mmol, 1.5 equiv) and alcohol **4.55** (4.5 g, 27 mmol, 1.0 equiv) were added sequentially. The reaction was placed in a preheated 40 °C oil bath and stirred at 40 °C for 40 min, at which point TLC analysis indicated complete consumption of the starting material **4.55** [R_f = 0.24 (20:80 ethyl acetate:hexanes, stained with $KMnO_4$)]. The reaction mixture was allowed to cool to rt and diluted with pentanes (150 mL). The resulting heterogeneous mixture was filtered over Celite (125 mL, 400 mL pentanes) by applying a mild vacuum. The filtrate was concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:99.8:0.2 diethyl ether:hexanes:triethylamine → 2:97.8:0.2 diethyl ether:hexanes:triethylamine as eluent to yield product ***ent*-4.57** as a clear oil (9.8 g, 27 mmol, 100% yield): R_f = 0.60 (5:95 diethyl ether:hexanes, stained with $KMnO_4$); ^1H NMR (600 MHz, C_6D_6) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 5.90 (ddd, *J* = 17.3, 10.5, 4.7 Hz, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.16 (d, *J* = 4.8 Hz, 1H), 5.10 (d, *J* = 10.6 Hz, 1H), 4.25–4.17 (m, 2H), 3.60 (td, *J* = 10.6, 4.2 Hz, 1H), 2.55 (pd, *J* = 7.0, 2.5 Hz, 1H), 2.07–1.97 (m, 1H), 1.58–1.44 (m, 2H), 1.16 (tdt, *J* = 12.0, 6.6, 3.5 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.92–0.84 (m, 2H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.73 (qd, *J* = 12.4, 3.2 Hz, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 136.4, 135.1, 131.0, 129.8, 128.9, 128.5, 125.6, 118.5, 98.8, 75.6, 68.7, 48.8, 41.2, 34.9, 31.8, 25.8, 23.6, 22.7, 21.6, 16.5; IR (thin film) 2960, 2925, 2870, 1645, 1215 cm^{-1}; $[\alpha]^{22}_{D}$ –92.9, $[\alpha]^{22}_{577}$ –100, $[\alpha]^{22}_{546}$ –112, $[\alpha]^{22}_{435}$ –184 (*c* = 0.7, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{22}H_{31}ClO_2$ $[M + Na]^+$ 385.1910, observed 385.1903.

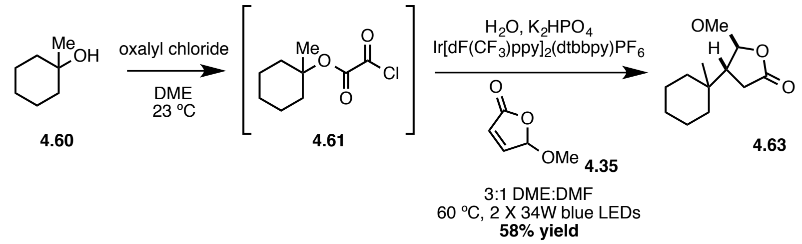


Preparation of dihydrofuran *ent*-4.58: A round-bottom flask was charged with ***ent*-4.57** (9.8 g, 27 mmol, 1.0 equiv), toluene (135 mL, 0.2 M), and a magnetic stir bar under an argon atmosphere. A solution of Hoveyda-Grubbs 2nd generation catalyst (840 mg, 1.3 mmol, 0.05 equiv) in toluene (135 mL, 0.2 M) was added to the solution of acetal ***ent*-4.57** in toluene. The resulting solution was placed in a preheated 60 °C oil bath and stirred at 60 °C for 1 h. After 1 h at 60 °C, the reaction was allowed to cool to rt and diluted with 200 mL pentanes. The resulting suspension was filtered over Celite (125 mL Celite, 400 mL pentanes) by applying a mild vacuum. The filtrate was concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:99.8:0.2 diethyl ether:hexanes:triethylamine → 2:97.8:0.2 diethyl ether:hexanes:triethylamine as eluent to yield a yellow oil that was further purified by Kugelrohr short-pass distillation (195 °C, 0.6 torr) to yield ***ent*-4.58** as a clear oil (5.8 g, 22.4 mmol, 83% yield): R_f = 0.65 (5:95 diethyl ether:hexanes, stained with $KMnO_4$); ^{1}H NMR (500 MHz, C_6D_6) δ 5.75 (d, *J* = 4.3 Hz, 1H), 5.49 (d, *J* = 1.7 Hz, 1H), 4.44 (ddd, *J* = 13.0, 4.3, 2.4 Hz, 1H), 4.16 (dd, *J* = 13.0, 2.0 Hz, 1H), 3.46 (td, *J* = 10.6, 4.3 Hz, 1H), 2.40 (pd, *J* = 7.0, 2.5 Hz, 1H), 1.87 (dtd, *J* = 12.3, 3.9, 1.9 Hz, 1H), 1.62–1.41 (m, 2H), 1.27 (ddt, *J* = 13.4, 10.5, 3.1 Hz, 1H), 1.16–1.00 (m, 1H), 0.94 (d, *J* = 3.6 Hz, 3H), 0.93 (d, *J* = 3.5 Hz, 3H), 0.88 (dd, *J* = 12.9, 2.6 Hz, 2H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.78 – 0.62 (m, 1H);^{13}C NMR (126 MHz, C_6D_6) δ 135.8, 124.6, 106.6, 77.2, 75.6, 49.7, 42.5, 36.0, 32.9, 27.1, 25.0, 23.8, 22.6, 17.4; IR (thin film) 2953, 2920, 2867, 1638, 1455, 1317, 1024 cm^{-1}; $[\alpha]^{22}_{D}$ −118, $[\alpha]^{22}_{577}$ −124, $[\alpha]^{22}_{546}$ −139, $[\alpha]^{22}_{435}$ −217 (*c* = 1.4, $CHCl_3$); HRMS (ESI/TOF) *m*/*z* calculated for $C_{14}H_{23}ClO_2$ [M + Na]$^+$ 281.1284, observed 281.1277.

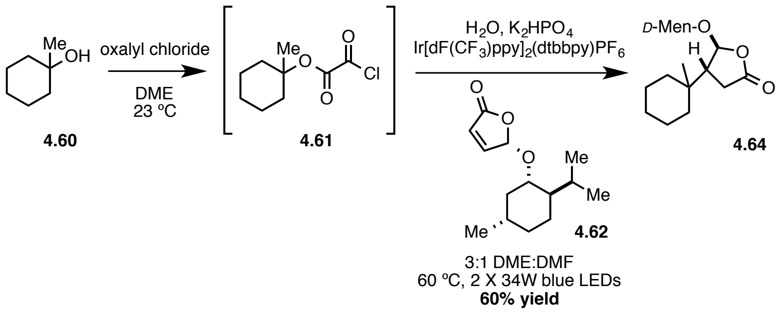


***ent*-4.58** ***ent*-4.59**

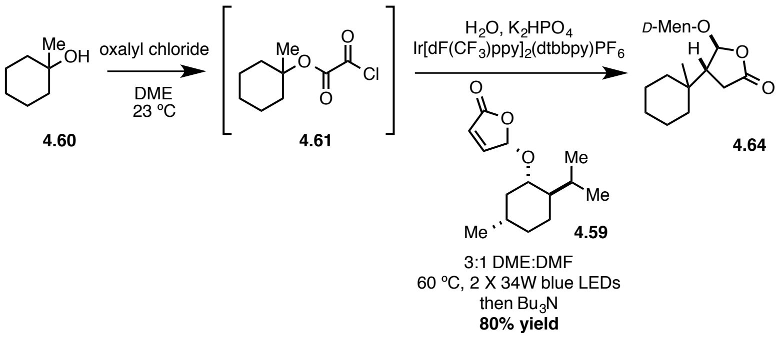
Preparation of butenolide *ent*-4.59: A round-bottom flask was charged with ***ent*-4.58** (5.8 g, 22.4 mmol, 1.0 equiv), benzene (225 mL, 0.1 M), and a magentic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, pyridine (0.7 mL, 9.0 mmol, 0.4 equiv), CrO_3 (450 mg, 4.5 mmol, 0.2 equiv), and a 5.5 M solution of *t*BuOOH in *n*-decane (28 mL, 157 mmol, 7.0 equv) were added sequentially. The reaction was removed from an ice bath, allowed to warm to rt and stirred for 3 h at rt. The heterogeneous mixture was then cooled to 0 °C and additional pyridine (0.7 mL, 9.0 mmol, 0.4 equiv), CrO_3 (450 mg, 4.5 mmol, 0.2 equiv), and a 5.5 M solution of *t*BuOOH in *n*-decane (28 mL, 157 mmol, 7.0 equv) were added sequentially. The reaction was removed from an ice bath, allowed to warm to rt and stirred for 18 h at rt. The mixture was filtered over silica gel (100 mL SiO_2, 500 mL 99.8:0.2 diethyl ether:triethylamine) by applying a mild vacuum. The filtrate was concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:99.8:0.2 diethyl ether:hexanes:triethylamine → 5:94.8:0.2 diethyl ether:hexanes:triethylamine as eluent to provide a colorless solid that was further purified by crystallization from hot pentanes at −20 °C to yield ***ent*-4.59** as colorless large prisms (2.0 g, 7.3 mmol, 33% yield after 3 rounds of crystallization). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, *J* = 1.5 Hz, 1H), 6.05 (d, *J* = 1.5 Hz, 1H), 3.66 (td, *J* = 10.7, 4.3 Hz, 1H), 2.19–1.96 (m, 2H), 1.84–1.61 (m, 2H), 1.40 (dddt, *J* = 12.1, 9.5, 6.5, 3.2 Hz, 1H), 1.25 (ddt, *J* = 13.4, 10.4, 3.1 Hz, 1H), 1.13–0.96 (m, 2H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.91–0.83 (m, 4H), 0.78 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 142.6, 129.1, 98.5, 79.5, 47.8, 40.4, 34.2, 31.6, 25.4, 23.2, 22.3, 21.0, 15.8; IR (thin film) 2957, 2922, 2865, 1769, 1343 cm^{-1}; $[\alpha]^{23}_{D}$ –101, $[\alpha]^{23}_{577}$ –108, $[\alpha]^{23}_{546}$ –124, $[\alpha]^{23}_{435}$ –212 (*c* = 0.5, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{21}ClO_3$ $[M + Na]^+$ 295.1077 observed 295.1066; mp: 68–70 °C (recrystallized from hot pentanes).



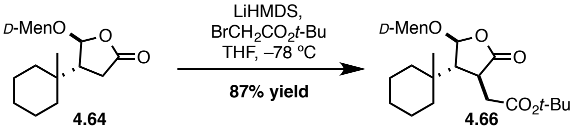
Preparation of *rac*-lactone 4.63: A 1-dram scintillation vial was charged with **4.60** (34 mg, 0.3 mmol, 1.0 equiv), DME (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C and oxalyl chloride (26 µL, 0.3 mmol, 1.0 equiv) was added dropwise. The needle connected to the argon line was removed from the septum to prevent corrosion by HCl generated during the reaction, and the solution was allowed to warm to rt and maintained at rt. After 6 h, H_2O (54 µL, 3.0 mmol, 10 equiv), K_2HPO_4 (160 mg, 0.9 mmol, 3.0 equiv), DME (1.7 mL, 0.17 M) and DMF (0.75 mL, 0.4 M) were added sequentially. The mixture was stirred vigorously for 1 min. Next, racemic **4.35** (34 mg, 0.3 mmol, 1.0 equiv) and ($Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7 mg, 0.006 mmol, 0.02 equiv) were added. The vial was then sealed with a new screw cap bearing a Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box. The temperature of the reaction mixture rose to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. The reaction was allowed to cool to rt and transferred to a separatory funnel with Et_2O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:100 ethyl acetate:hexanes → 10:90 ethyl acetate:hexanes as eluent to yield product **4.63** as a thick colorless foam (37 mg, 0.17 mmol, 58% yield): $R_f = 0.30$ (10:90 ethyl acetate:hexanes, stained with $KMnO_4$). Spectral data match those previously reported.[20]



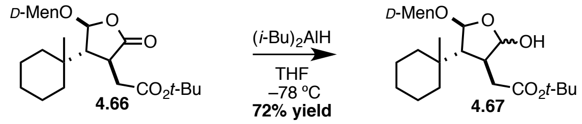
Preparation of lactone 4.64: Using an identical procedure, alcohol **4.60** (34 mg, 0.3 mmol, 1.0 equiv), and butenolide **4.62** (72 mg, 0.3 mmol, 1.0 equiv) were coupled and the product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield product **4.64** as a thick colorless foam (60 mg, 0.178 mmol, 60% yield): R_f = 0.25 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.55 (d, *J* = 2.4 Hz, 1H), 3.51 (td, *J* = 10.7, 4.2 Hz, 1H), 2.63 (dd, *J* = 18.4, 10.0 Hz, 1H), 2.36 (dd, *J* = 18.3, 4.8 Hz, 1H), 2.26 (ddd, *J* = 9.0, 5.0, 2.3 Hz, 1H), 2.08 (dq, *J* = 10.0, 3.5, 2.7 Hz, 2H), 1.69–1.60 (m, 2H), 1.54 (dt, *J* = 13.4, 4.9 Hz, 2H), 1.50–1.13 (m, 10H), 0.99 (qd, *J* = 13.1, 12.6, 3.1 Hz, 1H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.91–0.81 (m, 8H), 0.77 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.7, 101.8, 76.9, 50.3, 47.8, 39.8, 35.30, 35.28, 34.3, 33.9, 31.4, 29.1, 26.0, 25.4, 23.1, 22.3, 21.34, 21.31, 20.9, 20.2, 15.6; IR (thin film) 2951, 2925, 1788, 1455, 1102 cm^{-1}; $[\alpha]^{22}_{D}$ +111, $[\alpha]^{22}_{577}$ +112, $[\alpha]^{22}_{546}$ +125, $[\alpha]^{22}_{435}$ +199 (*c* = 0.3, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{21}H_{36}O_3$ [M + Na]$^+$ 359.2562, observed 359.2574.



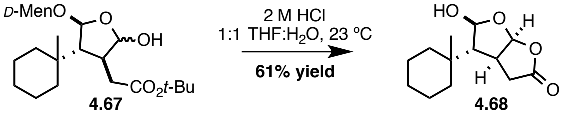
Preparation of lactone 4.64: A 1-dram scintillation vial was charged with **4.60** (34 mg, 0.3 mmol, 1.0 equiv), DME (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, oxalyl chloride (26 μL, 0.3 mmol, 1.0 equiv) was added dropwise. Needle connected to the argon line was removed from the septum, to prevent corrosion by HCl generated during the reaction, and the solution was allowed to warm to rt and maintained at rt for 6 h. After 6 h, H_2O (54 μL, 3.0 mmol, 10 equiv), K_2HPO_4 (160 mg, 0.9 mmol, 3.0 equiv), DME (1.7 mL, 0.17 M) and DMF (0.75 mL, 0.4 M) were added sequentially. The mixture was stirred vigorously for 1 min. Next, **4.59** (82 mg, 0.3 mmol, 1.0 equiv) and (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (7 mg, 0.006 mmol, 0.02 equiv) were added. The vial was then sealed with a new screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. After 18 h, degassed Bu_3N (0.7 mL, 3 mmol, 10 equiv) was added via syringe. The sample was irradiated by lamps for additional 4 h inside the closed box. The reaction was allowed to cool to rt and transferred to a separatory funnel with Et_2O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield the desired product **4.64** as a thick colorless foam (81 mg, 0.238 mmol, 80% yield): R_f = 0.25 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde).



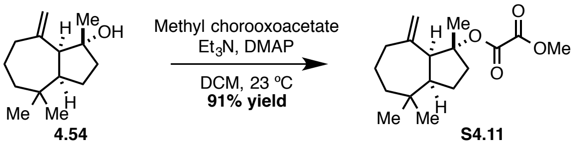
Preparation of ester 4.66: A round-bottom flask was charged with lactone **4.64** (58 mg, 0.17 mmol, 1.0 equiv), tetrahydrofuran (1.7 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to –78 °C and a 1 M solution of LiHMDS in tetrahydrofuran (210 µL, 0.21 mmol, 1.2 equiv) was added dropwise. After stirring the reaction mixture for 1 h at –78 °C, *tert*-butyl bromoacetate (38 µL, 0.26 mmol, 1.5 equiv) was added dropwise. After 1 h at –78 °C, the reaction was quenched by addition of sat. NH_4Cl (aq) (5 mL). The resulting mixture was allowed to warm to rt and transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 5:95 ethyl acetate:hexanes as eluent to yield product **4.66** as a clear oil (67 mg, 0.15 mmol, 87% yield): R_f = 0.19 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.53 (d, *J* = 1.9 Hz, 1H), 3.51 (td, *J* = 10.7, 4.1 Hz, 1H), 2.88 (dt, *J* = 9.0, 4.8 Hz, 1H), 2.67 (dd, *J* = 15.4, 5.4 Hz, 1H), 2.59 (dd, *J* = 15.4, 8.1 Hz, 1H), 2.12 (dtd, *J* = 22.4, 13.1, 11.4, 5.5 Hz, 2H), 1.99 (t, *J* = 2.9 Hz, 1H), 1.68–1.60 (m, 2H), 1.60–1.15 (m, 22H), 0.98 (dt, *J* = 10.4, 6.7 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.91–0.79 (m, 8H), 0.76 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 170.2, 101.0, 81.4, 77.2, 56.4, 47.9, 39.7, 38.9, 38.3, 35.5, 35.3, 34.6, 31.6, 28.2, 26.2, 25.4, 23.0, 22.5, 21.6, 21.5, 21.2, 20.3, 15.5; IR (thin film) 2953, 2929, 1770, 1727, 1369, 1151 cm^{-1}; $[\alpha]^{21}_{D}$ +78.5, $[\alpha]^{21}_{577}$ +82.1, $[\alpha]^{21}_{546}$ +88.5, $[\alpha]^{21}_{435}$ +138 (*c* = 0.27, $CHCl_3$); HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{27}H_{46}O_5Na$ 473.3243; Found 473.3250.



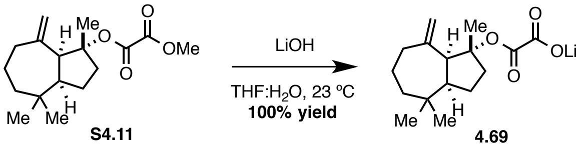
Preparation of lactol 4.67: A round-bottom flask was charged with **4.66** (64 mg, 0.14 mmol, 1.0 equiv), THF (1.2 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. After 30 min at –78 °C, TLC analysis of the reaction (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated presence of the starting material and additional 1M solution of DIBALH in toluene (85 µL, 0.085 mmol, 0.6 equiv) was added, followed by another portion of 1M solution of DIBALH in toluene (85 µL, 0.085 mmol, 0.6 equiv) after 30 min (total 1M solution of DIBALH in toluene added: 340 µL, 0.34 mmol, 2.4 equiv). After 30 min at –78 °C, TLC analysis of the reaction (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated complete consumption the starting material and the reaction was quenched by addition of 100 μL of MeOH, followed by the addition of saturated solution of Rochelle's salt (aq) (5 mL) at –78 °C. The reaction was allowed to warm to rt and stirred at rt for 30 min. Biphasic mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to yield a 2.1:1 mixture of lactol epimers **4.67** as a colorless solid (46 mg, 0.10 mmol, 72% yield): R_f = 0.21 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate); ^1H NMR (600 MHz, C_6D_6) δ 5.84 (t, *J* = 6.3 Hz, 1H), 5.53 (s, 2H), 5.37 (d, *J* = 2.3 Hz, 2H), 5.34 (d, *J* = 2.6 Hz, 1H), 3.65 (qd, *J* = 10.9, 3.9 Hz, 3H), 3.23 (d, *J* = 5.5 Hz, 2H), 2.97–2.80 (m, 2H), 2.69–2.62 (m, 1H), 2.62–2.46 (m, 8H), 2.41 (dt, *J* = 9.9, 4.9 Hz, 2H), 2.21 (d, *J* = 12.3 Hz, 1H), 2.16 (d, *J* = 11.9 Hz, 2H), 2.05–1.98 (m, 1H), 1.85–1.74 (m, 2H), 1.60–1.07 (m, 71H), 1.03 (d, *J* = 6.9 Hz, 6H), 1.01 (d, *J* = 7.1 Hz, 6H), 0.98–0.87 (m, 16H), 0.85 (d, *J* = 6.5 Hz, 6H), 0.83 (d, *J* = 6.5 Hz, 4H), 0.80–0.71 (m, 6H); ^{13}C NMR (151 MHz, C_6D_6) δ 172.8, 172.3, 104.7, 103.2, 102.0, 101.0, 80.9, 80.4, 75.6, 75.4, 61.1, 58.9, 49.2, 49.1, 44.8, 41.5, 40.9, 40.8, 40.5, 37.7, 37.6, 37.2, 36.8, 36.7, 35.4, 35.3, 32.2, 32.1, 28.7, 28.6, 27.1, 27.0, 25.8, 23.9, 23.6, 23.1, 22.52, 22.47, 22.45, 22.4, 22.03, 21.95, 21.4, 21.1, 16.54, 16.46; IR (thin film) 3463, 3438, 2924, 2867, 1704, 1636, 1367, 1152 cm^{-1}; $[\alpha]^{21}_{D}$ +101, $[\alpha]^{21}_{577}$ +101, $[\alpha]^{21}_{546}$ +112, $[\alpha]^{21}_{435}$ +159 (*c* = 0.15, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{48}O_5Na$ 475.3399; Found 475.3395.



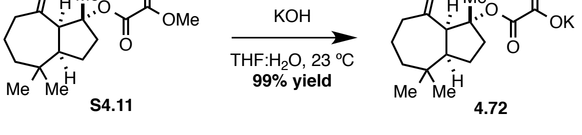
Preparation of dioxabicyclo[3.3.0]octan-3-one 4.68: A 2-dram scintillation vial was charged with lactol **4.67** (34 mg, 0.075 mmol, 1.0 equiv), 1:1 4 M HCl (aq):THF (3 mL, 0.025 M), and a magnetic stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at rt for 30 min. The reaction mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes → 25:75 ethyl acetate:hexanes as eluent to yield product **4.68** as a colorless solid (11 mg, 0.046 mmol, 61% yield): R_f = 0.30 (30:70 ethyl acetate:hexanes, stained with ceric ammonium molybdate). ^1H NMR (600 MHz, $CDCl_3$) δ 6.05 (d, *J* = 6.1 Hz, 1H), 5.60 (s, 1H), 3.23 (d, *J* = 2.9 Hz, 1H), 3.01 (ddd, *J* = 9.9, 6.3, 3.0 Hz, 1H), 2.89 (dd, *J* = 18.4, 10.9 Hz, 1H), 2.69 (dd, *J* = 18.4, 3.6 Hz, 1H), 2.07 (s, 1H), 1.63–1.39 (m, 5H), 1.34 (dt, *J* = 9.5, 4.4 Hz, 3H), 1.27–1.17 (m, 2H), 0.85 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 109.5, 102.4, 64.2, 39.0, 37.0, 35.9, 35.7, 34.0, 26.2, 21.7, 20.8; IR (thin film) 3433, 2927, 2854, 1782, 1367, 987 cm^{-1}; $[\alpha]^{22}_{D}$ +27.2, $[\alpha]^{22}_{577}$ +27.8, $[\alpha]^{22}_{546}$ +30.2, $[\alpha]^{22}_{435}$ +47.9 (*c* = 1.1, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{13}H_{20}O_4$ $[M + Na]^+$ 263.1259, observed 263.1259.



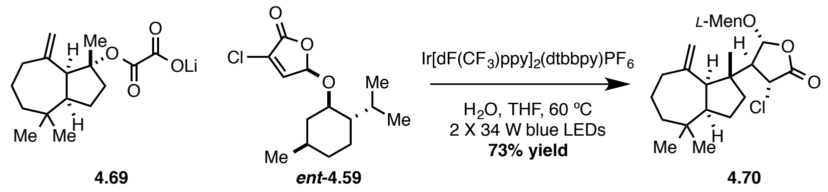
Preparation of methyl oxalate S4.11: A round-bottom flask was charged with **4.54** (560 mg, 2.7 mmol, 1.0 equiv), DMAP (33 mg, 0.27 mmol, 0.1 equiv), dichloromethane (13 mL, 0.20 M), and a stir bar under ambient atmophere. Next, Et_3N (0.45 mL, 3.2 mmol, 1.2 equiv) and methyl chlorooxoacetate (0.30 mL, 3.2 mmol, 1.2 equiv) were added sequentially. The resulting yellow solution was maintained at rt for 10 min, at which point TLC analysis (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde) indicated complete consumption of the starting material. The reaction was quenched via addition of sat. NH_4Cl (aq) (15 mL). The resulting biphasic mixture was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 25 mL). Combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 5:95 ethyl acetate:hexanes as eluent to yield the desired product **S4.11** as a clear oil (720 mg, 2.45 mmol, 91% yield): R_f = 0.43 (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^1H NMR (500 MHz, $CDCl_3$) δ 4.92 (d, *J* = 2.3 Hz, 1H), 4.86 (d, *J* = 2.3 Hz, 1H), 3.88 (s, 3H), 3.20 (dd, *J* = 8.1, 1.7 Hz, 1H), 2.44 (dddd, *J* = 12.0, 10.1, 3.4, 1.6 Hz, 1H), 2.38–2.26 (m, 2H), 1.92–1.72 (m, 4H), 1.69–1.59 (m, 2H), 1.49 (s, 3H), 1.45–1.31 (m, 1H), 1.25 (dt, *J* = 14.3, 3.5 Hz, 1H), 0.98 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 157.1, 150.2, 117.2, 99.7, 57.7, 53.5, 50.9, 37.6, 37.3, 36.2, 35.9, 33.9, 28.7, 26.1, 24.3, 21.7; IR (thin film) 2953, 2937, 2867, 1766, 1739, 1154 cm^{-1}; $[\alpha]^{23}_D$ +11.5, $[\alpha]^{23}_{577}$ +13.6, $[\alpha]^{23}_{546}$ +14.4, $[\alpha]^{23}_{435}$ +29.1 (*c* = 1.0, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{26}O_4Na$ 317.1729; Found 317.1732.



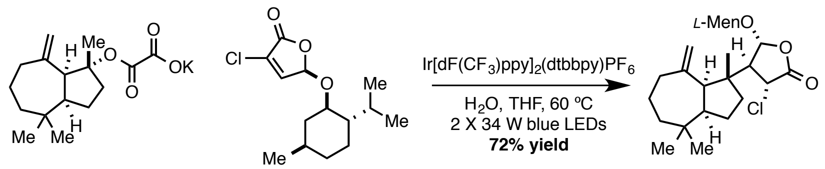
Preparation of lithium oxalate 4.69: A round-bottom flask was charged with **S4.11** (700 mg, 2.38 mmol, 1.0 equiv), 1:1 THF:H_2O (4.8 mL, 0.5 M), and a stir bar under ambient atmosphere. The resulting biphasic mixture was cooled to 0 °C. Next, 0.5N LiOH (aq) (4.8 mL, 1.0 equiv) was added dropwise. The mixture was then stirred vigorously at 0 °C for 5 min. The stir bar was removed and homogeneous solution was concentrated by use of a rotary evaporator with water bath warmed gradually from rt to 45 °C. The resulting colorless solid was washed with pentanes (3 x 5 mL) and dried further under high vacuum to yield product **4.69** as a colorless solid (680 mg, 2.38 mmol, 100% yield); ^{1}H NMR (500 MHz, CD_3OD) δ 4.91 (d, *J* = 2.6 Hz, 1H), 4.86 (d, *J* = 2.6 Hz, 1H), 2.51–2.37 (m, 2H), 2.35–2.27 (m, 1H), 1.95–1.84 (m, 1H), 1.84–1.67 (m, 5H), 1.46 (s, 3H), 1.43–1.34 (m, 1H), 1.31–1.15 (m, 1H), 1.00 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 167.0, 166.3, 152.7, 116.8, 97.0, 58.5, 51.9, 38.6, 38.5, 37.0, 36.9, 34.2, 29.8, 26.4, 25.1, 22.2; IR (thin film) 2954, 2935, 2865, 1710, 1693, 1667, 1251, 1161 cm^{-1}; $[\alpha]^{23}_{D}$ +20.9, $[\alpha]^{23}_{577}$ +22.7, $[\alpha]^{23}_{546}$ +21.4, $[\alpha]^{23}_{435}$ +40.4 (*c* = 0.6, MeOH); HRMS (ESI-TOF) m/z: $[M]^-$ Calcd for $C_{16}H_{23}O_4$ 279.1596; Found 279.1595.



Preparation of potassium oxalate 4.72: A round-bottom flask was charged with **S4.11** (81 mg, 0.28 mmol, 1.0 equiv), 1:1 THF:H_2O (1.4 mL, 0.2 M), and a stir bar under ambient atmosphere. The resulting biphasic mixture was cooled to 0 °C. Next, 0.85N KOH (aq) (320 µL, 1.0 equiv) was added dropwise. The mixture was then stirred vigorously at 0 °C for 5 min. The stir bar was removed and homogeneous solution was concentrated by use of a rotary evaporator with water bath warmed gradually from rt to 45 °C. The resulting colorless solid was washed with pentanes (3 x 5 mL) and dried further under high vacuum to yield product **4.72** as a colorless solid (86 mg, 0.28 mmol, 99% yield); ^{1}H NMR (600 MHz, CD_3OD) 4.93–4.89 (m, 2H), 2.49–2.38 (m, 2H), 2.31 (d, *J* = 12.9 Hz, 1H), 1.93–1.84 (m, 1H), 1.84–1.69 (m, 5H), 1.48–1.44 (m, 3H), 1.41 (q, *J* = 12.3, 11.4 Hz, 1H), 1.25 (d, *J* = 13.8 Hz, 1H), 1.00 (t, *J* = 2.5 Hz, 3H), 0.95–0.91 (m, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 166.9, 166.5, 152.8, 117.0, 97.2, 58.7, 52.0, 38.7, 38.6, 37.2, 37.1, 34.3, 30.0, 26.5, 25.3, 22.4; IR (thin film) 3608, 1713, 1663, 1641, 1233, 893 cm^{-1}; $[\alpha]^{23}_{D}$ +14.6, $[\alpha]^{23}_{577}$ +14.9, $[\alpha]^{23}_{546}$ +16.7, $[\alpha]^{23}_{435}$ +31.2 (*c* = 1.7, MeOH); HRMS (ESI-TOF) m/z: $[M]^-$ Calcd for $C_{16}H_{23}O_4$ 279.1596; Found 279.1598.

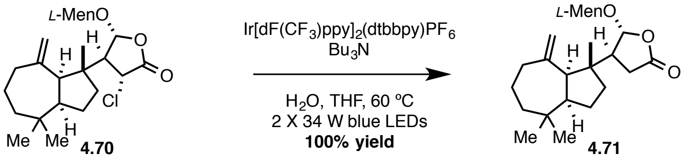


Preparation of lactone 4.70 from 4.69: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.69** (86 mg, 0.30 mmol, 1.0 equiv), ***ent*-4.59** (82 mg, 0.30 mmol, 1.0 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7 mg, 0.006 mmol, 0.02 equiv), tetrahydrofuran (500 µL, 0.6 M), H_2O (27 µL, 1.5 mmol, 5 equiv), and a stir bar. The vial was then sealed with screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. The reaction was allowed to cool to rt, diluted with Et_2O (1 mL) and filtered over $MgSO_4$. The filtrate was concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield the desired product **4.70** as a thick colorless foam (102 mg, 0.22 mmol, 73% yield): R_f = 0.33 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^1H NMR (600 MHz, $CDCl_3$) δ 5.59 (d, *J* = 3.3 Hz, 1H), 4.87 (s, 1H), 4.62 (s, 1H), 3.59 (td, *J* = 10.7, 4.7 Hz, 1H), 2.68–2.59 (m, 2H), 2.36 (dd, *J* = 12.3, 5.4 Hz, 1H), 2.26–2.17 (m, 1H), 2.14 (d, *J* = 11.1 Hz, 1H), 2.05 (q, *J* = 9.8 Hz, 1H), 1.83–1.73 (m, 5H), 1.73–1.57 (m, 5H), 1.45–1.34 (m, 2H), 1.28 (dd, *J* = 12.4, 6.7 Hz, 2H), 1.03–0.97 (m, 4H), 0.97–0.92 (m, 7H), 0.92–0.86 (m, 4H), 0.84 (s, 3H), 0.80 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 153.4, 115.2, 101.9, 77.7, 60.9, 55.7, 53.7, 52.2, 48.1, 47.9, 40.0, 37.7, 37.4, 37.0, 36.5, 34.5, 31.6, 28.9, 25.8, 25.7, 25.4, 23.2, 22.5, 21.2, 21.1, 15.7; IR (thin film) 2953, 2922, 2868, 1789, 1364 cm^{-1}; $[\alpha]^{23}_{D}$ –52.0, $[\alpha]^{23}_{577}$ –54.3, $[\alpha]^{23}_{546}$ –65.8, $[\alpha]^{23}_{435}$ –104 (*c* = 0.6, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{45}ClO_3Na$ 487.2955; Found 487.2971.



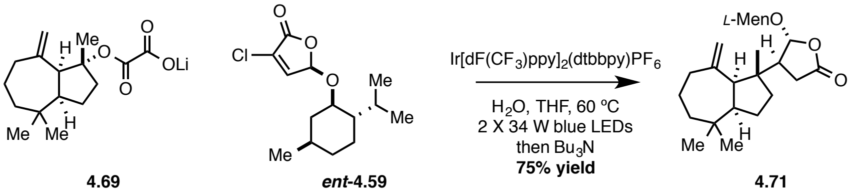
4.72 ***ent*-4.59** **4.70**

Preparation of lactone 4.70 from 4.72: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.72** (63 mg, 0.20 mmol, 1.0 equiv), ***ent*-4.59** (55 mg, 0.20 mmol, 1.0 equiv), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (5 mg, 0.004 mmol, 0.02 equiv), tetrahydrofuran (330 µL, 0.6 M), H$_2$O (18 µL, 1.0 mmol, 5 equiv), and a stir bar. The vial was then sealed with screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. The reaction was allowed to cool to rt, diluted with Et$_2$O (1 mL) and filtered over MgSO$_4$. The filtrate was concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield the desired product **4.70** as a thick colorless foam (67 mg, 0.14 mmol, 72% yield): R_f = 0.33 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde).



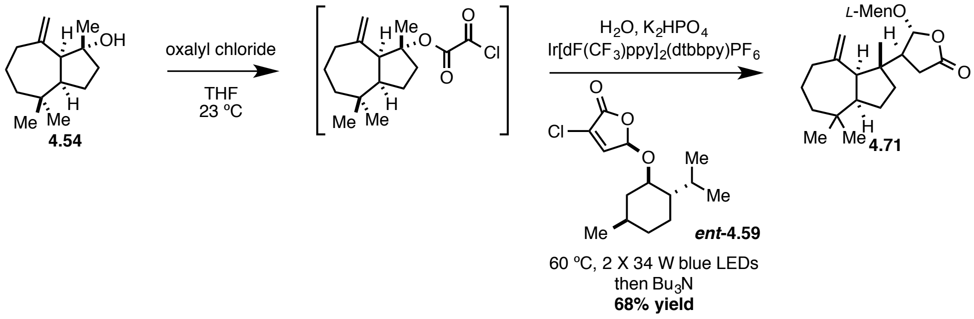
Preparation of lactone 4.71 from 4.70: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.70** (86 mg, 0.18 mmol, 1.0 equiv), Bu_3N (44 μL, 1.8 mmol, 10 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4 mg, 0.004 mmol, 0.02 equiv), tetrahydrofuran (1.8 mL, 0.1 M), H_2O (33 μL, 1.8 mmol, 10 equiv), and a stir bar. The vial was then sealed with screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 4 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. The reaction was allowed to cool to rt and transferred to a separatory funnel with Et_2O (10 mL). The solution was then sequentially washed with 1N

HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield the desired product **4.71** as a thick colorless foam (79 mg, 0.18 mmol, 100% yield): R_f = 0.28 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde). ^1H NMR (600 MHz, $CDCl_3$) δ 5.58 (s, 1H), 4.85 (s, 1H), 4.62 (s, 1H), 3.55 (td, *J* = 10.6, 4.7 Hz, 1H), 2.75 (dd, *J* = 18.3, 9.6 Hz, 1H), 2.65–2.60 (m, 1H), 2.43–2.32 (m, 3H), 2.18–2.12 (m, 1H), 2.11–2.05 (m, 1H), 2.03–1.97 (m, 1H), 1.82–1.72 (m, 3H), 1.72–1.60 (m, 4H), 1.49–1.37 (m, 4H), 1.26–1.20 (m, 2H), 1.03–0.97 (m, 4H), 0.96–0.91 (m, 7H), 0.91–0.86 (m, 4H), 0.81 (s, 3H), 0.78 (d, *J* = 10.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 154.3, 115.0, 103.1, 77.1, 56.3, 54.2, 51.7, 48.3, 48.0, 40.5, 38.1, 38.0, 37.2, 36.7, 34.79, 34.75, 31.8, 30.9, 29.3, 26.2, 26.1, 25.9, 23.5, 22.8, 21.4, 21.1, 16.1; IR (thin film) 2952, 2924, 2868, 1788, 1364 cm^{-1}; $[\alpha]^{23}_D$ –47.5, $[\alpha]^{23}_{577}$ –49.3, $[\alpha]^{23}_{546}$ –56.5, $[\alpha]^{23}_{435}$ –87.7 (*c* = 1.1, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{28}H_{46}O_3$ $[M + Na]^+$ 453.3345, observed 453.3352.

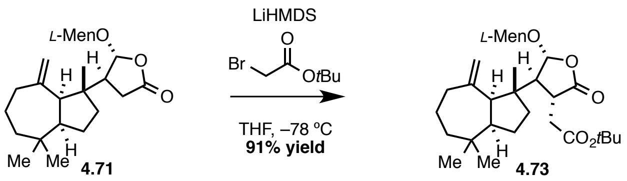


4.69 *ent*-**4.59** **4.71**

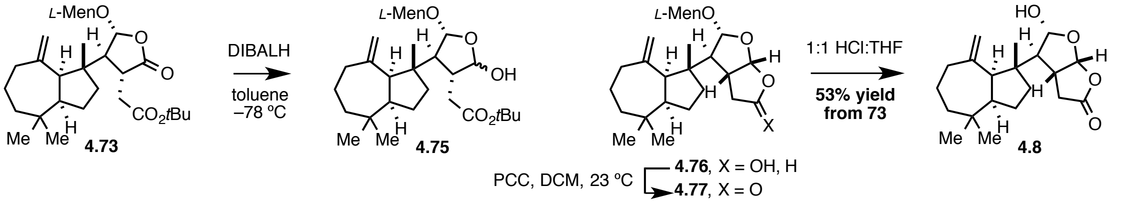
Preparation of lactone 4.71 from 4.69: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.69** (86 mg, 0.30 mmol, 1.0 equiv), ***ent*-4.59** (82 mg, 0.30 mmol, 1.0 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7 mg, 0.006 mmol, 0.02 equiv), tetrahydrofuran (500 µL, 0.6 M), H_2O (27 µL, 1.5 mmol, 5 equiv), and a stir bar. The vial was then sealed with screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. After 18 h, a degassed solution of Bu_3N (0.7 mL, 3 mmol, 10 equiv) in tetrahydrofuran (2.5 mL, 0.12 M) was added via syringe. The sample was irradiated by lamps for additional 4 h inside the closed box. The reaction was allowed to cool to rt and transferred to a separatory funnel with Et_2O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield the desired product **4.71** as a thick colorless foam (97 mg, 0.23 mmol, 75% yield): R_f = 0.28 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde).



Preparation of lactone 4.71 from 4.54: A 1-dram scintillation vial was charged with **4.54** (62 mg, 0.3 mmol, 1.0 equiv), tetrahydrofuran (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, oxalyl chloride (26 μL, 0.3 mmol, 1.0 equiv) was added dropwise. Needle connected to the argon line was removed from the septum, to prevent corrosion by HCl generated during the reaction, and the solution was allowed to warm to rt and maintained at rt for 6 h. After 6 h, H_2O (33 μL, 1.8 mmol, 6.0 equiv) and K_2HPO_4 (160 mg, 0.9 mmol, 3.0 equiv) were added sequentially. The mixture was stirred vigorously for 1 min. Next, ***ent*-4.59** (82 mg, 0.3 mmol, 1.0 equiv) and (Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7 mg, 0.006 mmol, 0.02 equiv) were added. The vial was then sealed with a new screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. After 18 h, a degassed solution of Bu_3N (0.7 mL, 3 mmol, 10 equiv) in tetrahydrofuran (2.5 mL, 0.12 M) was added via syringe. The sample was irradiated by lamps for additional 4 h inside the closed box. The reaction was allowed to cool to rt and transferred to a separatory funnel with Et_2O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield product **4.71** as a thick colorless foam (88 mg, 0.20 mmol, 68% yield): R_f = 0.28 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde). ^1H NMR (600 MHz, $CDCl_3$) δ 5.58 (s, 1H), 4.85 (s, 1H), 4.62 (s, 1H), 3.55 (td, *J* = 10.6, 4.7 Hz, 1H), 2.75 (dd, *J* = 18.3, 9.6 Hz, 1H), 2.65–2.60 (m, 1H), 2.43–2.32 (m, 3H), 2.18–2.12 (m, 1H), 2.11–2.05 (m, 1H), 2.03–1.97 (m, 1H), 1.82–1.72 (m, 3H), 1.72–1.60 (m, 4H), 1.49–1.37 (m, 4H), 1.26–1.20 (m, 2H), 1.03–0.97 (m, 4H), 0.96–0.91 (m, 7H), 0.91–0.86 (m, 4H), 0.81 (s, 3H), 0.78 (d, *J* = 10.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 154.3, 115.0, 103.1, 77.1, 56.3, 54.2, 51.7, 48.3, 48.0, 40.5, 38.1, 38.0, 37.2, 36.7, 34.79, 34.75, 31.8, 30.9, 29.3, 26.2, 26.1, 25.9, 23.5, 22.8, 21.4, 21.1, 16.1; IR (thin film) 2952, 2924, 2868, 1788, 1364 cm^{-1}; $[\alpha]^{23}_{D}$ –47.5, $[\alpha]^{23}_{577}$ –49.3, $[\alpha]^{23}_{546}$ –56.5, $[\alpha]^{23}_{435}$ –87.7 (*c* = 1.1, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{28}H_{46}O_3$ $[M + Na]^+$ 453.3345, observed 453.3352.



Preparation of ester 4.73: A round-bottom flask was charged with **4.71** (420 mg, 0.98 mmol, 1.0 equiv), tetrahydrofuran (10 mL, 0.1 M), and a stir bar under an argon atmosphere. The solution was cooled to –78 °C. Next, a 1M solution of LiHMDS in tetrahydrofuran (1.2 mL, 1.2 mmol, 1.2 equiv) was added dropwise. After stirring the reaction mixture for 15 min at –78 °C, *tert*-butyl bromoacetate (220 μL, 1.5 mmol, 1.5 equiv) was added dropwise. After 1 h at –78 °C, the reaction was quenched via addition of sat. NH_4Cl (aq) (10 mL). The resulting mixture was allowed to warm to rt and transferred to a separatory funnel and extracted with Et_2O (3 x 25 mL). Combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield the desired product **4.73** as a clear oil (480 mg, 2.45 mmol, 91% yield): R_f = 0.31 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.58 (d, *J* = 1.3 Hz, 1H), 4.85 (d, *J* = 2.2 Hz, 1H), 4.62 (d, *J* = 2.1 Hz, 1H), 3.55 (td, *J* = 10.7, 4.2 Hz, 1H), 2.86 (ddd, *J* = 8.6, 5.3, 2.8 Hz, 1H), 2.72 (dd, *J* = 15.3, 5.3 Hz, 1H), 2.62 (d, *J* = 8.8 Hz, 1H), 2.60 (d, *J* = 9.0 Hz, 1H), 2.37–2.30 (m, 1H), 2.18–2.08 (m, 3H), 2.02 (dt, *J* = 11.2, 8.0 Hz, 1H), 1.82–1.71 (m, 3H), 1.71–1.60 (m, 5H), 1.47 (s, 9H), 1.46–1.42 (m, 2H), 1.38 (dt, *J* = 13.7, 3.3 Hz, 2H), 1.25 (dd, *J* = 10.4, 3.3 Hz, 2H), 1.03–0.95 (m, 4H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.92 (s, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.89–0.82 (m, 2H), 0.79 (s, 3H), 0.77 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 179.1, 170.5, 154.2, 114.9, 102.4, 81.7, 57.0, 56.3, 53.8, 48.3, 48.1, 40.2, 40.0, 39.5, 38.0, 37.5, 37.2, 36.7, 34.74, 34.70, 31.8, 29.3, 28.49, 28.46, 26.00, 25.95, 25.8, 23.2, 22.7, 21.5, 21.3, 15.7; IR (thin film) 2953, 2924, 2869, 1780, 1732, 1456, 1367, 1152 cm^{-1}; $[\alpha]^{23}_{D}$ –41.9, $[\alpha]^{23}_{577}$ –45.2, $[\alpha]^{23}_{546}$ –52.6, $[\alpha]^{23}_{435}$ –83.9 (c = 0.9, $CHCl_3$); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{56}O_5Na$ 567.4025; Found 567.4030.

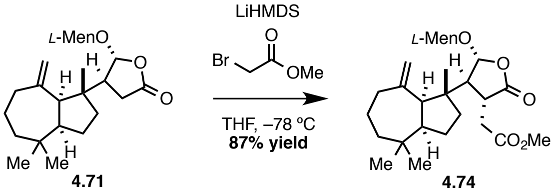


Preparation of (+)-cheloviolene B (4.8) from 4.73: A round-bottom flask was charged with **4.73** (278 mg, 0.51 mmol, 1.0 equiv), toluene (5.1 mL, 0.1 M), and a stir bar under an argon atmosphere. The solution was cooled to to –78 °C. Next, a 1M solution of DIBALH in toluene (610 µL, 0.61 mmol, 1.2 equiv) was added dropwise. After 1 h, TLC analysis of the reaction (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated presence of the starting material and additional 1M solution of DIBALH in toluene (300 µL, 0.3 mmol, 0.5 equiv) was added, followed by another portion of 1M solution of DIBALH in toluene (300 µL, 0.3 mmol, 0.5 equiv) after 30 min (total 1M solution of DIBALH in toluene added: 1.2 mL, 1.2 mmol). After 30 min, TLC analysis indicated complete consumption of the starting material and the reaction was quenched via addition of 100 µL of MeOH, followed by the addition of saturated solution of Rochelle's salt (aq) (10 mL) at –78 °C. The reaction was allowed to warm to rt and stirred at rt for 30 min. Biphasic mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 25 mL). Combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was quickly passed though a pH 7 silica gel[80] column using 5:95 ethyl acetate:hexanes to elute crude lactol epimers **4.75** as a clear oil [crude mass: 155 mg; 1.1:1

dr; R_f minor = 0.45; R_f major = 0.3 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate); diagnostic ^{1}H NMR shifts (600 MHz, $CDCl_3$): major: δ 5.26 (t, *J* = 4.6 Hz, 1H), 5.23 (d, *J* = 1.5 Hz, 1H), 4.82 (d, *J* = 2.3 Hz, 1H), 4.65 (d, *J* = 2.3 Hz, 1H); minor: δ 5.52 (dd, *J* = 7.9, 5.7 Hz, 1H), 5.20 (d, *J* = 2.3 Hz, 1H), 4.81 (d, *J* = 2.2 Hz, 1H), 4.60 (d, *J* = 2.3 Hz, 1H)] and 10:90 ethyl acetate:hexanes to elute crude bicyclic lactol epimers **4.76** a a clear oil [crude mass: 72 mg; 1.7:1 dr; R_f = 0.15 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate); diagnostic ^{1}H NMR shifts (600 MHz, $CDCl_3$): major: δ 5.81 (d, *J* = 6.0 Hz, 1H), 5.46 (dd, *J* = 11.1, 5.5 Hz, 1H), 5.25 (s, 1H), 4.84 (s, 1H), 4.60 (s, 1H); minor: δ 5.89 (d, *J* = 5.8 Hz, 1H), 5.67–5.62 (m, 1H), 5.35 (s, 1H), 4.82 (s, 1H), 4.61 (s, 1H)].

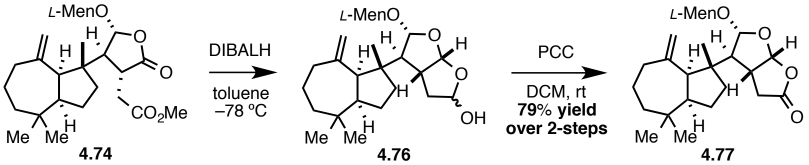
A 2-dram scintillation vial was charged with crude bicyclic lactol epimers **4.76** (72 mg, 0.15 mmol, 1.0 equiv), dichloromethane (1.5 mL, 0.1 M), and a stir bar under ambient atmosphere. Next, PCC (65 mg, 0.30 mmol, 2.0 equiv) was added in one portion at rt. Heterogeneous reaction mixture was stirred vigorously at rt for 6 h, at which point TLC analysis (10:90 ethyl acetate:hexane, stained with ceric ammonium molybdate) indicated complete consumption of the starting material. The reaction mixture was filtered over pH 7 silica gel plug using 10:90 ethyl acetate:hexanes and concentrated by use of a rotary evaporator to yield crude bicyclic lactone **4.77** as a clear oil [crude mass: 70 mg; R_f = 0.24 (10:90 ethyl acetate: hexanes, stained with ceric ammonium molybdate); diagnostic ^{1}H NMR shifts (600 MHz, $CDCl_3$) δ 6.03 (d, *J* = 6.0 Hz, 1H), 5.42 (s, 1H), 4.84 (d, *J* = 2.1 Hz, 1H), 4.61 (d, *J* = 2.1 Hz, 1H)].

A 20 mL scintillation vial was charged with crude lactol epimers **4.75** (155 mg, 0.28 mmol, 1.0 equiv), crude bicyclic lactone **4.77** (70 mg, 0.15 mmol, 1.0 equiv), 1:1 4N HCl (aq):THF (17 mL, 0.025 M), and a stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at rt for 24 h. The reaction mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 25 mL). Combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes → 20:80 ethyl acetate:hexanes as eluent to yield (+)-cheloviolene B (**4.8**) as a colorless solid (90 mg, 0.27 mmol, 53% yield from **4.73**): R_f = 0.15 (20:80 ethyl acetate:hexanes, stained with ceric ammonium molybdate). Recrystallization of the solid from hot pentanes afforded a crystal suitable for single-crystal X-ray diffraction analysis. The ^1H and ^{13}C NMR data in $(CD_3)_2CO$ matched that reported for the natural product.[8b] ^1H NMR (500 MHz, $CDCl_3$) δ 6.09 (d, *J* = 6.0 Hz, 1H), 5.64 (s, 1H), 4.83 (d, *J* = 2.0 Hz, 1H), 4.61 (d, *J* = 2.0 Hz, 1H), 2.98 (dddd, *J* = 11.4, 5.9, 3.1, 2.1 Hz, 1H), 2.85 (br s, 1H), 2.92 (dd, *J* = 17.6, 11.1 Hz, 1H), 2.65 (d, *J* = 8.8 Hz, 1H), 2.61 (dd, *J* = 17.5, 2.9 Hz, 1H), 2.35 (dd, *J* = 13.3, 5.8 Hz, 1H), 2.24 (d, *J* = 1.5 Hz, 1H), 1.99 (dt, *J* = 12.0, 8.2 Hz, 1H), 1.83 (dd, *J* = 13.1, 2.3 Hz, 1H), 1.80–1.72 (m, 2H), 1.72–1.64 (m, 1H), 1.60 (dd, *J* = 13.9, 4.1 Hz, 1H), 1.57–1.52 (m, 1H), 1.51–1.46 (m, 1H), 1.43–1.34 (m, 1H), 1.25 (dt, *J* = 14.3, 3.3 Hz, 1H), 0.99 (s, 3H), 0.94 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 153.9, 114.9, 109.7, 103.2, 66.3, 56.6, 54.3, 47.4, 40.6, 39.0, 37.9, 37.2, 37.0, 36.4, 34.6, 29.0, 26.2, 25.8, 21.5; IR (thin film) 3430, 2951, 2937, 2866, 1783, 1771, 1633 cm^{-1}; $[\alpha]^{21}_{D}$ +26.6, $[\alpha]^{21}_{577}$ +29.4, $[\alpha]^{21}_{546}$ +33.4, $[\alpha]^{21}_{435}$ +60.2, $[\alpha]^{21}_{405}$ +73.7 (*c* = 0.7, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{20}H_{30}O_4$ $[M + Na]^+$ 357.2042, observed 357.2032; mp 189–190 °C (recrystallized from hot pentanes).



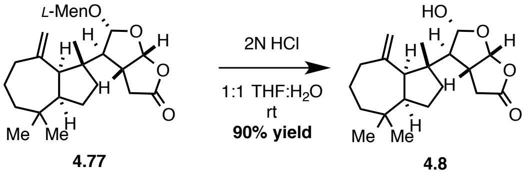
Preparation of ester 4.74: A round-bottom flask was charged with **4.71** (100 mg, 0.23 mmol, 1.0 equiv), tetrahydrofuran (2.3 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to –78 °C. Next, a 1 M solution of LiHMDS in tetrahydrofuran (280 µL, 0.28 mmol, 1.2 equiv) was added dropwise. After stirring the reaction mixture for 1 h at –78 °C, methyl bromoacetate (33 µL, 3.5 mmol, 1.5 equiv) was added dropwise. After 1 h at –78 °C, the reaction was quenched by addition of sat. NH_4Cl (aq) (5 mL). The resulting mixture was allowed to warm to rt and transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 4:96 ethyl acetate:hexanes as eluent to yield product **4.74** as a clear oil (100 mg, 0.20 mmol, 87% yield): R_f = 0.35 (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (d, *J* = 1.1 Hz, 1H), 4.83 (d, *J* = 2.1 Hz, 1H), 4.59 (d, *J* = 2.1 Hz, 1H), 3.70 (s, 3H), 3.53 (td, *J* = 10.6, 4.1 Hz, 1H), 2.89–2.77 (m, 2H), 2.71 (dd, *J* = 15.4, 9.4 Hz, 1H), 2.59 (d, *J* = 8.5 Hz, 1H), 2.37–2.29 (m, 1H), 2.19–1.90 (m, 4H), 1.80–1.55 (m, 8H), 1.50–1.38 (m, 1H), 1.41–1.34 (m, 2H), 1.28–1.19 (m, 3H), 0.97 (s, 4H), 0.93–0.90 (m, 6H), 0.89–0.83 (m, 4H), 0.77 (s, 3H), 0.75 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.4, 171.3, 153.8, 114.6, 102.3, 77.1, 56.4, 55.9, 53.6, 52.0, 47.9, 47.7, 39.9, 39.5, 37.6, 36.9, 36.8, 36.3, 34.3, 31.4, 28.8, 25.59, 25.57, 25.5, 22.8, 22.3, 21.1, 21.0, 15.3; IR (thin film) 2953, 2924, 1781, 1744, 1454, 1366, 1172 cm^{-1};

$[\alpha]^{21}_{D}$ −56.1, $[\alpha]^{21}_{577}$ −60.1, $[\alpha]^{21}_{546}$ −69.7, $[\alpha]^{21}_{435}$ −112 (*c* = 0.18, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{31}H_{50}O_5$ $[M + Na]^+$ 525.3556, observed 525.3560.



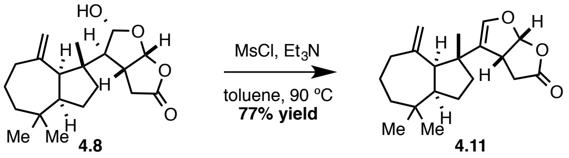
Preparation of lactone 4.77: A round-bottom flask was charged with **4.74** (80 mg, 0.16 mmol, 1.0 equiv), toluene (1.6 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to to −78 °C. Next, a 1 M solution of DIBALH in toluene (350 μL, 0.35 mmol, 2.2 equiv) was added dropwise. After 1 h at −78 °C, TLC analysis of the reaction (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated complete consumption the starting material and the reaction was quenched by addition of 100 μL of MeOH, followed by the addition of saturated solution of Rochelle's salt (aq) (10 mL) at −78 °C. The reaction was allowed to warm to rt and stirred at rt for 30 min. The biphasic mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by use of a rotary evaporator to yield a crude mixture of biyclic lactole epimers **4.76** [R_f = 0.13 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate); diagnostic ^1H NMR shifts (500 MHz, C_6D_6): major: δ 6.04 (d, *J* = 5.9 Hz, 1H), 5.58 (s, 1H), 4.82 (d, *J* = 2.4 Hz, 1H), 4.76 (d, *J* = 2.3 Hz, 1H); minor: δ 5.80 (d, *J* = 6.0 Hz, 1H), 5.37 (d, *J* = 1.6 Hz, 1H), 4.81 (d, *J* = 2.3 Hz, 1H), 4.67 (d, *J* = 2.2 Hz, 1H)].

A 2-dram scintillation vial was charged with a crude mixture of bicyclic lactol epimers **4.76**, dichloromethane (1.6 mL, 0.1 M), and a magnetic stir bar under ambient atmosphere. Next, PCC (70 mg, 0.32 mmol, 2.0 equiv) was added in one portion at rt. The heterogeneous reaction mixture was stirred vigorously at rt for 9 h, at which point TLC analysis (10:90 ethyl acetate:hexane, stained with *p*-anisaldehyde) indicated complete consumption of the starting material. The reaction mixture was filtered over Celite and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 5:95 ethyl acetate:hexanes → 10:90 ethyl acetate:hexanes as eluent to yield product **4.77** as a clear oil (60 mg, 0.127 mmol, 79% yield): R_f = 0.23 (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.02 (d, *J* = 5.9 Hz, 1H), 5.41 (s, 1H), 4.82 (d, *J* = 2.2 Hz, 1H), 4.60 (d, *J* = 2.2 Hz, 1H), 3.50 (td, *J* = 10.6, 4.1 Hz, 1H), 2.94–2.80 (m, 2H), 2.67 (dd, *J* = 17.6, 3.8 Hz, 1H), 2.60 (d, *J* = 8.5 Hz, 1H), 2.37–2.29 (m, 1H), 2.22–2.06 (m, 3H), 2.04–1.97 (m, 1H), 1.82–1.45 (m, 10H), 1.44–1.10 (m, 4H), 0.98 (s, 4H), 0.93 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88–0.83 (m, 4H), 0.79–0.72 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 154.0, 114.6, 109.7, 105.4, 75.9, 64.4, 56.3, 53.7, 48.1, 48.0, 40.5, 40.2, 38.5, 37.8, 36.9, 36.7, 36.4, 34.6, 31.6, 29.0, 25.9, 25.7, 24.9, 22.9, 22.6, 21.4, 21.3, 15.5; IR (thin film) 2953, 2928, 2868, 1785, 1456, 1364, 1180 cm^{-1}; $[\alpha]^{22}_{D}$ –92.7, $[\alpha]^{22}_{577}$ –97.4, $[\alpha]^{22}_{546}$ –110, $[\alpha]^{22}_{435}$ –176 (*c* = 0.8, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{30}H_{48}O_4$ [M + Na]$^+$ 495.3450, observed 495.3457.

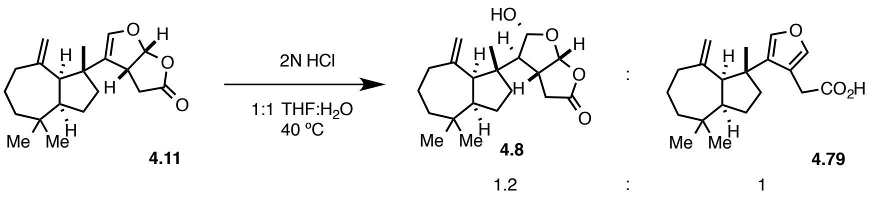


4.77 **4.8**

Preparation of (+)-cheloviolene B (4.8) from 4.77: A 20 mL scintillation vial was charged with lactone **4.77** (69 mg, 0.15 mmol, 1.0 equiv), 1:1 4 M HCl (aq):THF (5.8 mL, 0.025 M), and a magnetic stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at rt for 72 h. The reaction mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes → 20:80 ethyl acetate:hexanes as eluent to yield (+)-cheloviolene B (**4.8**) as a colorless solid (44 mg, 0.13 mmol, 90% yield): R_f = 0.15 (20:80 ethyl acetate:hexanes, stained with ceric ammonium molybdate).

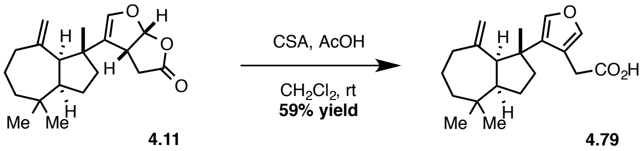


Preparation of (+)-dendrillolide C (4.11): A round-bottom flask was charged with **4.8** (40 mg, 0.12 mmol, 1.0 equiv), toluene (6 mL, 0.025 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C, and Et_3N (83 µL, 0.60 mmol, 5.0 equiv) and MsCl (23 µL, 0.30 mmol, 2.5 equiv) were added sequentially. The resulting solution was stirred at 0 °C for 20 min. After 20 min at 0 °C, the mixture became heterogeneous and was placed in a preheated to 90 °C oil bath. After vigorous stirring for 40 min at 90 °C, TLC analysis (30:70 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated complete consumption of the starting material. The reaction was cooled to rt and quenched by addition of H_2O (5 mL). The biphasic mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 5:95 ethyl acetate:hexanes → 10:90 ethyl acetate:hexanes as eluent to yield (+)-dendrillolide C (**4.11**) as a clear oil (29 mg, 0.09 mmol, 77% yield): R_f = 0.25 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate). The ^{1}H NMR data in CCl_4 matched that reported for the natural product.[9] ^{13}C NMR (151 MHz, CCl_4) δ 172.3, 152.5, 140.1, 125.5, 115.4, 107.6, 57.1, 52.7, 46.6, 43.4, 38.9, 38.1, 37.1, 36.5, 34.4, 33.4, 29.0, 27.1, 26.5, 25.6; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.36 (d, *J* = 6.8 Hz, 1H), 6.19 (d, *J* = 1.6 Hz, 1H), 4.85 (d, *J* = 2.2 Hz, 1H), 4.57 (d, *J* = 2.2 Hz, 1H), 3.68 (dddd, *J* = 8.8, 6.4, 3.9, 1.7 Hz, 1H), 2.84 (dd, *J* = 18.3, 9.1 Hz, 1H), 2.79 (dd, *J* = 18.3, 3.9 Hz, 1H), 2.55 (d, *J* = 7.9 Hz, 1H), 2.34 (dd, *J* = 13.0, 5.6 Hz, 1H), 1.99 (q, *J* = 9.4 Hz, 1H), 1.86 (ddd, *J* = 13.1, 8.4, 4.7 Hz, 1H), 1.81–1.71 (m, 4H), 1.70–1.63 (m, 1H), 1.63–1.56 (m, 1H), 1.41–1.35 (m, 1H), 1.25 (dd, *J* = 10.8, 3.8 Hz, 1H), 1.01 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 152.5, 139.9, 125.7, 115.1, 108.3, 57.0, 52.4, 46.4, 43.5, 38.7, 37.8, 36.9, 36.3, 34.0, 33.6, 28.9, 26.9, 26.3, 25.3; IR (thin film) 2953, 2931, 1792, 1640, 1452, 1031 cm^{-1}; $[\alpha]^{22}_{D}$ +133 (isolation: 130.90),[9] $[\alpha]^{22}_{577}$ +134, $[\alpha]^{22}_{546}$ +152, $[\alpha]^{22}_{435}$ +253 (*c* = 0.3, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{20}H_{38}O_3$ $[M + Na]^+$ 339.1936, observed 339.1924.



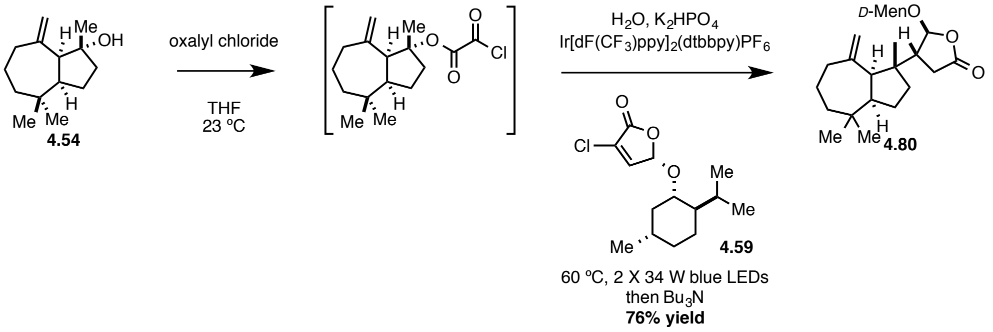
Acid-catalyzed hydration of (+)-dendrillolide C (4.11): A 1-dram scintillation vial was charged with **4.11** (9 mg, 0.028 mmol, 1 equiv), 1:1 4 M HCl (aq):THF (0.6 mL, 0.025 M), and a magnetic stir bar. The resulting heterogeneous mixture was stirred vigorously at 40

°C for 18 h. The reaction mixture was diluted with H_2O (1 mL) and extracted with Et_2O (3 x 2 mL). Organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. Integration of ^1H NMR spectrum [$CDCl_3$, 600 MHz: shifts corresponding to **4.8**: δ 6.09 (d, *J* = 6.0 Hz, 1H), 5.64 (s, 1H), 4.83 (d, *J* = 2.0 Hz, 1H), 4.61 (d, *J* = 2.0 Hz, 1H); shifts corresponding to **4.79**: δ 7.42 (d, *J* = 1.6 Hz, 1H), 7.21(d, *J* = 1.7 Hz, 1H), 4.89 (d, *J* = 2.2 Hz, 1H), 4.71 (d, *J* = 2.1 Hz, 1H), 3.63 (s, 2H)] of the crude reaction mixture was used to establish the ratio of the two products formed, 1.2 : 1 (+)-cheloviolene B (**4.8**) : furan **4.79**.



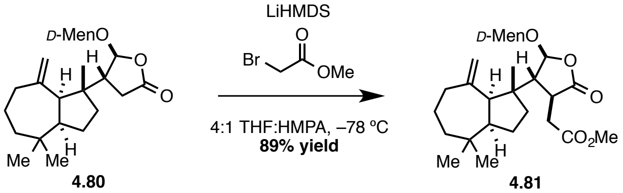
Preparation of furan 4.79: A 1-dram scintillation vial was charged with **4.11** (11 mg, 0.035 mmol, 1 equiv), CSA (40 mg, 0.17 mmol, 5.0 equiv), acetic acid (20 µL, 0.35 mmol, 10 equiv), dichloromethane (0.7 mL, 0.05 M), and a magnetic stir bar. The resulting heterogeneous mixture was stirred vigorously at rt for 48 h. Green solution was then washed sequentially with sat. $NaHCO_3$ (aq) (1 mL), H_2O (1 mL), 4N HCl (aq) (1 mL), and brine (1 mL). Organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:100 methanol:dichloromethane → 2:98 methanol:dichloromethane as eluent to yield product **4.79** as a colorless solid (6.5 mg, 0.0205 mmol, 59% yield): R_f = 0.15 (2:98 methanol:dichloromethane, stained with ceric ammonium molybdate); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 1.6 Hz, 1H), 7.21 (d, *J* = 1.7 Hz, 1H), 4.89 (d, *J* = 2.2 Hz, 1H), 4.71 (d, *J* = 2.1 Hz, 1H), 3.63 (s, 2H), 2.75 (d, *J* = 7.6 Hz, 1H), 2.36 (dd, *J* = 13.0, 5.6 Hz, 1H), 2.10 (dt, *J* =

12.8, 6.0 Hz, 1H), 2.01 (q, *J* = 9.5 Hz, 1H), 1.89–1.56 (m, 7H), 1.45–1.32 (m, 2H), 1.27–1.17 (m, 1H), 1.10 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 153.0, 143.4, 139.3, 133.5, 115.4, 114.8, 57.6, 51.4, 46.2, 38.6, 37.8, 37.0, 36.2, 33.8, 30.5, 29.1, 26.4, 26.0, 24.9; IR (thin film) 3408, 2963, 2927, 1714, 1452 cm^{-1}; $[\alpha]^{22}_{D}$ +1.84, $[\alpha]^{22}_{577}$ +1.98, $[\alpha]^{22}_{546}$ +2.89, $[\alpha]^{22}_{435}$ +6.38 (*c* = 0.5, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{20}H_{28}O_3$ [M – H]$^-$ 315.1960, observed 315.1960.

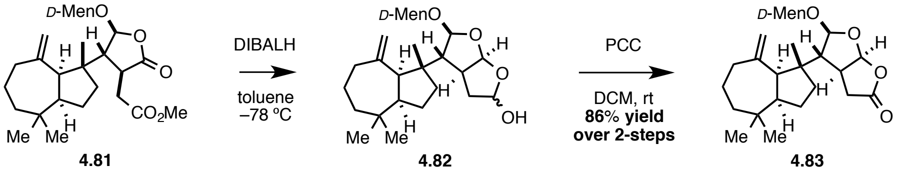


Preparation of lactone 4.80 from 4.54: A 1-dram scintillation vial was charged with **4.54** (62 mg, 0.3 mmol, 1.0 equiv), tetrahydrofuran (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, oxalyl chloride (26 μL, 0.3 mmol, 1.0 equiv) was added dropwise. The needle connected to the argon line was removed from the septum, to prevent corrosion by HCl generated during the reaction, and the solution was allowed to warm to rt and maintained at rt for 6 h. After 6 h, H_2O (33 μL, 1.8 mmol, 6.0 equiv) and K_2HPO_4 (160 mg, 0.9 mmol, 3.0 equiv) were added sequentially. The mixture was stirred vigorously for 1 min. Next, **4.59** (82 mg, 0.3 mmol, 1.0 equiv) and (Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7 mg, 0.006 mmol, 0.02 equiv) were added. The vial was then sealed with a new screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5" needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h inside the closed box, allowing the temperature of the reaction mixture to rise to 60 °C and the air inside the box to 40–45 °C because of heat given off from the LEDs. After 18 h, a degassed solution of *n*-Bu_3N (0.7 mL, 3 mmol, 10 equiv) in tetrahydrofuran (2.5 mL, 0.12 M) was added via syringe. The sample was irradiated by lamps for additional 4 h inside the closed box. The reaction was allowed to cool to rt and transferred to a separatory funnel with Et_2O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield product **4.80** as a thick colorless foam (93 mg, 0.20 mmol, 76% yield): R_f = 0.28 (5:95 ethyl acetate:hexanes, stained with *p*-anisaldehyde). ^1H NMR (600 MHz, $CDCl_3$) δ 5.52 (s, 1H), 4.82 (s, 1H), 4.60 (s, 1H), 3.53 (td, *J* = 10.7, 4.1 Hz, 1H), 2.75 (dd, *J* = 18.0, 9.6 Hz, 1H), 2.53 (d, *J* = 8.8 Hz, 1H), 2.47–2.38 (m, 2H), 2.34 (dd, *J* = 12.2, 4.7 Hz, 1H), 2.09 (td, *J* = 10.9, 9.5, 3.6 Hz, 2H), 1.92 (dd, *J* = 13.7, 6.2 Hz, 1H), 1.87–1.70 (m, 4H), 1.71–1.61 (m, 3H), 1.60–1.47 (m, 2H), 1.41–1.34 (m, 2H), 1.28–1.19 (m, 2H), 1.00 (dd, *J* = 13.1, 3.2 Hz, 1H), 0.97 (s, 3H), 0.94 (d, *J* = 4.5 Hz, 6H), 0.91 (d, *J* = 12.1 Hz, 1H), 0.89–

0.86 (m, 3H), 0.84 (d, *J* = 2.5 Hz, 1H), 0.82 (s, 3H), 0.79 (dd, *J* = 6.9, 1.6 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 177.0, 153.6, 114.9, 102.9, 77.1, 55.9, 54.5, 51.9, 48.1, 47.5, 40.2, 38.0, 37.6, 37.1, 36.34, 34.61, 34.55, 31.6, 30.9, 28.9, 26.4, 25.9, 25.7, 23.3, 22.5, 21.1, 15.9; IR (thin film) 2952, 2923, 2868, 1790, 1453 cm^{-1}; $[\alpha]^{23}_{D}$ +137, $[\alpha]^{23}_{577}$ +143, $[\alpha]^{23}_{546}$ +162, $[\alpha]^{23}_{435}$ +269 (*c* = 1.0, CHCl$_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{28}H_{46}O_3$ [M + Na]$^+$ 453.3345, observed 453.3352.



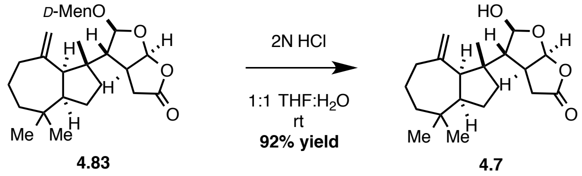
Preparation of ester 4.81: A round-bottom flask was charged with **4.80** (52 mg, 0.12 mmol, 1.0 equiv), tetrahydrofuran:hexamethylphosphoramide (4:1) (1.2 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to –78 °C. Next, a 1 M solution of LiHMDS in tetrahydrofuran (145 µL, 0.15 mmol, 1.2 equiv) was added dropwise. After stirring the reaction mixture for 1 h at –78 °C, methyl bromoacetate (17 µL, 0.18 mmol, 1.5 equiv) was added dropwise. After 1 h at –78 °C, the reaction was quenched by addition of sat. NH$_4$Cl (aq) (5 mL). The resulting mixture was allowed to warm to rt and transferred to a separatory funnel and extracted with Et$_2$O (3 x 10 mL). The combined organic layers were dried over MgSO$_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 4:96 ethyl acetate:hexanes as eluent to yield product **4.81** as a clear oil (54 mg, 0.11 mmol, 89% yield): R$_f$ = 0.35 (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.52 (s, 1H), 4.83 (s, 1H), 4.71 (s, 1H), 3.73 (s, 3H), 3.53 (td, *J* = 10.7, 4.1 Hz, 1H), 2.96–2.91 (m, 1H), 2.83 (dd, *J* = 15.4, 5.2 Hz, 1H), 2.73 (dd, *J* = 15.4, 9.4 Hz, 1H), 2.66 (d, *J* = 8.8 Hz, 1H), 2.37–2.31 (m, 1H), 2.17–2.05 (m, 3H), 1.94–1.87 (m, 1H), 1.84–1.51 (m, 9H), 1.44–1.32 (m, 2H), 1.29–1.21 (m, 2H), 0.99 (s, 3H), 0.96–0.92 (m, 6H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.88–0.83 (m, 1H), 0.82 (s, 3H), 0.78 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 178.6, 171.4, 153.5, 115.0, 102.4, 77.4, 57.0, 54.7, 54.3, 52.2, 47.9, 47.8, 39.89, 39.87, 37.9, 37.7, 37.1, 36.4, 34.6, 34.5, 31.6, 28.9, 26.3, 25.8, 25.6, 23.0, 22.5, 21.28, 21.26, 15.3; IR (thin film) 3466, 2360, 2101, 1644, 1366 cm^{-1}; $[\alpha]^{21}_{D}$ +102, $[\alpha]^{21}_{577}$ +106, $[\alpha]^{21}_{546}$ +120, $[\alpha]^{21}_{435}$ +196 (*c* = 0.7, CHCl$_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{31}H_{50}O_5$ [M + Na]$^+$ 525.3556, observed 525.3568.



Preparation of lactone 4.83: A round-bottom flask was charged with **4.81** (54 mg, 0.11 mmol, 1.0 equiv), toluene (1.1 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to to –78 °C and a 1 M solution of DIBALH in toluene (240 μL, 0.24 mmol, 2.2 equiv) was added dropwise. After 1 h at –78 °C, TLC analysis of the reaction (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated complete consumption the starting material and the reaction was quenched by addition of 100 μL of MeOH, followed by the addition of saturated solution of Rochelle's salt (aq) (10 mL) at –78 °C. The reaction was allowed to warm to rt and stirred at rt for 30 min. The biphasic mixture was transferred to a separatory funnel and extracted with Et$_2$O (3 x 25 mL). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated by use of a rotary evaporator to yield a crude mixture of biyclic lactol epimers **4.82** [R_f = 0.13 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate); diagnostic ^{1}H NMR shifts (500 MHz, C_6D_6): major: δ 5.91 (d, *J* = 6.1 Hz, 1H), 5.69 (s, 1H), 4.85 (br, 1H), 4.67 (d, *J* = 2.4 Hz, 1H); minor: δ 5.85 (d, *J* = 6.0 Hz, 1H), 4.87 (br, 1H), 4.71 (br, 1H)].

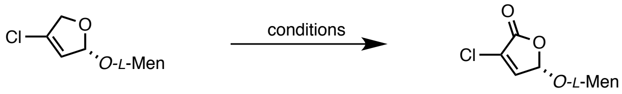
A 2-dram scintillation vial was charged with a crude mixture of bicyclic lactol epimers **4.82**, dichloromethane (1.6 mL, 0.1 M), and a magnetic stir bar under ambient atmosphere. Next, PCC (47 mg, 0.22 mmol, 2.0 equiv) was added in one portion at rt. The heterogeneous reaction mixture was stirred vigorously at rt for 9 h, at which point TLC analysis (10:90 ethyl acetate:hexane, stained with *p*-anisaldehyde) indicated complete consumption of the starting material. The reaction mixture was filtered over Celite and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 5:95 ethyl acetate:hexanes → 10:90 ethyl acetate:hexanes as eluent to yield product **4.83** as a clear oil (44 mg, 0.092 mmol, 86% yield): R_f = 0.23 (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (d, *J* = 6.2 Hz, 1H), 5.34 (s, 1H), 4.82 (d, *J* = 2.3 Hz, 1H), 4.61 (d, *J* = 2.3 Hz, 1H), 3.49 (td, *J* = 10.6, 4.1 Hz, 1H), 3.03–2.97 (m, 1H), 2.87 (dd, *J* = 18.2, 10.6 Hz, 1H), 2.70 (dd, *J* = 18.2, 4.3 Hz, 1H), 2.56 (d, *J* = 8.9 Hz, 1H), 2.39–2.34 (m, 1H), 2.20–2.09 (m, 3H), 2.95–1.62 (m, 8H), 1.60–1.48 (m, 3H), 1.44–1.23 (m, 4H), 1.20–1.14 (m, 1H), 0.99 (s, 3H), 0.96 (s, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.86–0.82 (m, 4H), 0.79 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 154.1, 114.6, 109.8, 105.5, 76.1, 65.1, 56.5, 54.9, 48.2, 47.6, 40.6, 39.9, 38.1, 38.0, 37.2, 36.7, 36.4, 34.7, 31.6, 28.9, 26.6, 25.9, 24.9, 22.9, 22.6, 21.6, 21.4, 15.6; IR (thin film) 3458, 2952, 2925, 2868, 1789, 1644 cm^{-1}; $[\alpha]^{22}_D$ +140,

$[\alpha]^{22}_{577}$ +146, $[\alpha]^{22}_{546}$ +166, $[\alpha]^{22}_{435}$ +273 (c = 0.9, $CHCl_3$); HRMS (ESI/TOF) *m*/*z* calculated for $C_{30}H_{48}O_4$ $[M + Na]^+$ 495.3450, observed 495.3457.



Preparation of (+)-cheloviolene A (4.7) from 4.83: A 20 mL scintillation vial was charged with lactone **4.83** (16 mg, 0.035 mmol, 1.0 equiv), 1:1 4N HCl (aq):THF (1.4 mL, 0.025 M), and a magnetic stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at rt for 24 h. The reaction mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 10:90 ethyl acetate:hexanes → 20:80 ethyl acetate:hexanes as eluent to yield (+)-cheloviolene A (**4.7**) as a colorless solid (11 mg, 0.032 mmol, 92% yield): R_f = 0.15 (20:80 ethyl acetate:hexanes, stained with ceric ammonium molybdate).

Table S4.1. Summary of unsuccessful allylic oxidation reaction conditions for the conversion of **4.58** to **4.59**.



4.58 **4.59**

conditions	result[a]
Fe(acac)$_3$ (10 mol %), *t*BuOOH (7.5 equiv) benzene (0.025 M), 80 °C, 18 h	0% **4.59**
SeO$_2$ (3 equiv), *t*BuOOH (5 equiv) CH$_2$Cl$_2$ (0.2 M), 23 °C, 18 h	0% **4.59**
Cr(CO)$_6$ (50 mol %), *t*BuOOH (3 equiv) CH$_3$CN (0.2 M), 80 °C, 1 h	0% **4.59**
*t*BuOOH (5 equiv) K$_2$CO$_3$ (2 equiv) PDC (10 mol %) toluene (0.5 M), 23 °C, 18 h	75% **4.58**
Pd(OH)$_2$ (5 mol %), Cs$_2$CO$_3$ (1 equiv) *t*BuOOH (5 equiv) O$_2$ (1 atm), CH$_2$Cl$_2$ (0.2 M), 23 °C, 18 h	15% **4.58** 3% **4.59**
CuCl (1.1 equiv), *t*BuOOH (7 equiv) DBU (1.5 equiv) CH$_3$CN (0.05 M), 23 °C, 18 h	39% **4.58** 12% **4.59**
*t*BuOOH (5 equiv) PDC (10 mol %) toluene (0.5 M), 23 °C, 18 h	13% **4.59**
CuCl (1.1 equiv), *t*Bu peroxybenzoate (7 equiv) DBU (1.5 equiv) CH$_3$CN (0.05 M), 23 °C, 18 h	17% **4.59**
CrO$_3$ (15 equiv) 3,5-dimethylpyrazole (15 equiv) CH$_2$Cl$_2$ (0.05 M), −20 °C, 2 h, 0 °C, 18 h	15% **4.58** 17% **4.59**

[a] Determined by ^{1}H NMR integration relative to an internal standard (1,2-dibromo-4,5-methylenedioxybenzene).

Scheme S4.1. Summary of unsuccessful approaches for the preparation of 6-*endo*-substituted *cis*-2,8-dioxabicyclo[3.3.0]octan-3-ones.

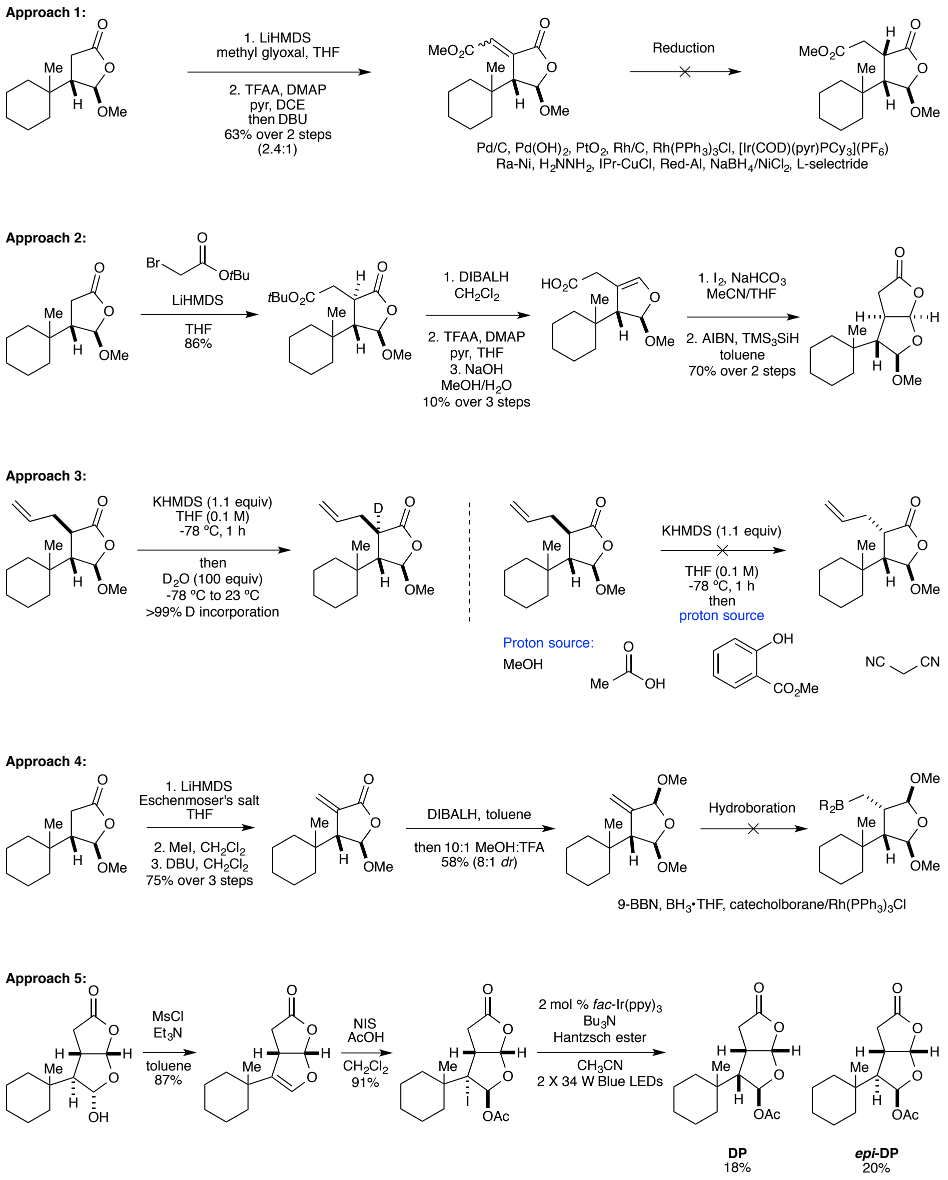
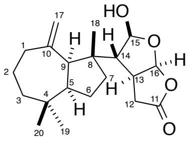


Table S4.2. Comparison table for synthetic and natural cheloviolene A.

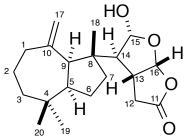


cheloviolene A

^{1}H (500 MHz) and ^{13}C (126 MHz) Data   Solvent: CDCl$_3$

Atom	**^{1}H Shift Exp.**	**^{1}H Shift Lit.**[8b]	**^{13}C Shift Exp.**	**^{13}C Shift Lit.**[8b]
1a	2.36 (dd, 12.0, 4.8 Hz)	2.35 (br dd, 13.0, 5.0 Hz)	37.0	37.0
1b	1.83 (br t, 12.6 Hz)	1.84 (br t, 13.0 Hz)	37.0	37.0
2a	1.42-1.35 (m)	1.39 (br dd, 13.5, 13.0 Hz)	28.9	28.8
2b	1.79-1.70 (m)	1.80-1.70 (m)	28.9	28.8
3a	1.29-1.26 (m)	1.27 (br d, 14 Hz)	37.9	37.8
3b	1.63 (dt, 13.8, 4.2 Hz)	1.63 (m)	37.9	37.8
4	N/A	N/A	36.3	36.1
5	1.96-1.91 (m)	1.93 (ddd, 11.0, 9.0, 8.0 Hz)	54.5	54.3
6a	1.79-1.70 (m)	1.80-1.70 (m)	26.3	26.3
6b	1.79-1.70 (m)	1.80-1.70 (m)	26.3	26.3
7a	1.79-1.70 (m)	1.80-1.70 (m)	38.6	38.4
7b	1.59-1.57 (m)	1.58 (m)	38.6	38.4
8	N/A	N/A	47.0	46.9
9	2.56 (d, 9.0 Hz)	2.55 (d, 9.0 Hz)	56.6	56.5
10	N/A	N/A	154.1	153.9
11	N/A	N/A	175.6	175.5
12a	2.74 (dd, 18.0, 3.6 Hz)	2.73 (ddd, 18.4, 3.9, 0.5 Hz)	37.0	36.8
12b	2.94 (dd, 11.4, 18.6 Hz)	2.94 (dd, 18.4, 11.0 Hz)	37.0	36.8
13	3.12-3.09 (m)	3.10 (dddd, 11.0, 6.2, 3.9, 2.2 Hz)	40.3	40.2
14	2.25 (s)	2.25 (br d, 2.2 Hz)	66.2	66.0
15	5.52 (d, 1.8 Hz)	5.52 (br s)	103.3	103.1
16	6.07 (d, 6.6 Hz)	6.07 (d, 6.2 Hz)	109.7	109.6
17a	4.84 (d, 1.8 Hz)	4.83 (ddd, 2.30, 0.8. 0.7 Hz)	114.6	114.4
17b	4.63 (br s)	4.62 (dd, 2.30, 0.8 Hz)	114.6	114.4
18	0.82 (s)	0.81 (s)	21.2	21.2
19	0.96 (s)	0.95 (s)	34.6	34.4
20	1.00 (s)	0.99 (s)	25.8	25.7
OH	2.83 (br s)	3.07 (br s)	N/A	N/A

Table S4.3. Comparison table for synthetic and natural cheloviolene B.



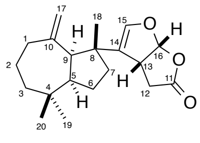
cheloviolene B
(corrected structure)

^{1}H (500 MHz) and ^{13}C (126 MHz) Data Solvent: $(CD_3)_2CO$

Atom	^{1}H Shift Exp.	^{1}H Shift Lit.[8b]	^{13}C Shift Exp.	^{13}C Shift Lit.[8b]
1a	2.35 (dd, 12.5, 5.1 Hz)	2.41 (br dd, 12.6, 5.4 Hz)	39.3	39.3
1b	1.90 (td, 12.9, 2.3 Hz)	1.90 (br t, 13 Hz)	39.3	39.3
2a	1.75 (m)	1.51-1.84 (m)	31.5	“32”
2b	1.39 (m)	1.39 (ddd, 13, 4, 2 Hz)	31.5	“32”
3a	1.25 (dt, 14.4, 3.6 Hz)	1.25 (br d, 14 Hz)	40.2	40.2
3b	1.69 (m)	1.51-1.84 (m)	40.2	40.2
4	N/A	N/A	38.6	38.7
5	2.12 (dt, 11.8, 8.2 Hz)	2.12 (ddd, 11.7, 8.8, 7.8 Hz)	56.4	56.4
6a	1.77 (m)	1.51-1.84 (m)	28.5	28.5
6b	1.77 (m)	1.51-1.84 (m)	28.5	28.5
7a	1.55 (ddd, 12.7, 8.5, 4.0)	1.51-1.84 (m)	40.8	40.8
7b	1.64 (m)	1.51-1.84 (m)	40.8	40.8
8	N/A	N/A	49.9	49.9
9	2.75 (d, 8.7 Hz)	2.75 (d, 8.8 Hz)	59.0	59.0
10	N/A	N/A	157.1	157.1
11	N/A	N/A	177.7	177.7
12a	2.95 (dd, 18.2, 11.0 Hz)	2.96 (dd, 18.1, 11.0 Hz)	39.4	**68.4***
12b	2.61 (dd, 18.2, 3.6 Hz)	2.61 (ddd, 18.1, 3.6, 0.5 Hz)	39.4	**68.4***
13	3.10 (dddd, 11.0, 6.2, 3.6, 2.6 Hz)	3.10 (dddd, 11.0, 6.2, 3.6, 2.6 Hz)	43.0	43.1
14	2.25 (d, 2.5 Hz)	2.25 (ddd, 2.6, 1.0, 0.5 Hz)	68.5	68.5
15	5.62 (d, 3.3 Hz)	5.61 (d, 1.0 Hz)	105.6	105.6
16	6.06 (d, 6.2 Hz)	6.06 (d, 6.2 Hz)	112.1	112.1
17a	4.84 (d, 2.4 Hz)	4.84 (2.4 Hz)	116.6	116.6
17b	4.68 (d, 2.4 Hz)	4.68 (d, 2.4 Hz)	116.6	116.6
18	0.79 (s)	0.79 (s)	23.4	23.4
19	0.95 (s)	0.95 (s)	36.6	36.6
20	1.01 (s)	1.01 (s)	27.8	27.9
OH	5.64 (d, 3.3 Hz)	2.85	N/A	N/A

*Likely an impurity in the sample. The signal for C-12 is likely not resolved from that of C-1.

Table S4.4. Comparison table for synthetic and natural dendrillolide C.



dendrillolide C

^{1}H (600 MHz) and ^{13}C (151 MHz) Data   Solvent: CCl$_4$

Atom	**^{1}H Shift Exp.**	**^{1}H Shift Lit.**[9]	**^{13}C Shift Exp.**
1a	2.34 (dd, 13.0 5.6 Hz)	2.34 (m)	38.9
1b	1.88 (m)	1.85 (m)	38.9
2a	1.76 (m)	1.77 (m)	29.0
2b	1.40 (m)	1.40 (m)	29.0
3a	1.66 (m)	1.64 (m)	37.1
3b	1.26 (m)	1.28 (m)	37.1
4	N/A	N/A	38.1
5	2.00 (q, 9.4 Hz)	2.00 (m)	52.6
6a	1.76 (m)	1.77 (m)	25.6
6b	1.76 (m)	1.77 (m)	25.6
7a	1.76 (m)	1.77 (m)	36.5
7b	1.76 (m)	1.77 (m)	36.5
8	N/A	N/A	46.6
9	2.56 (d, 7.9 Hz)	2.58 (d, 8.0 Hz)	57.1
10	N/A	N/A	152.5
11	N/A	N/A	172.3
12a	2.71 (dd, 18.0, 9.4 Hz)	2.68 (dd, 17.4, 9.0 Hz)	33.4
12b	2.63 (dd, 18.0, 3.8 Hz)	2.64 (17.4, 4.0 Hz)	33.4
13	3.58 (m)	3.57 (m)	43.4
14	N/A	N/A	125.5
15	6.14 (s)	6.14 (d, 1.0 Hz)	140.0
16	6.24 (d, 6.9 Hz)	6.24 (d, 6.8 Hz)	107.6
17a	4.83 (d, 2.1 Hz)	4.88 (d, 2.0 Hz)	115.4
17b	4.57 (d, 2.1 Hz)	4.58 (d, 2.0 Hz)	115.4
18	1.02 (s)	1.01 (s)	27.1
19	0.98 (s)	0.96 (s)	26.5
20	0.92 (s)	0.91 (s)	34.4

4.5 References and Notes:

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Chapter 5: Total Synthesis of (–)-Chromodorolide B via a Radical Addition/Cyclization/Fragmentation Cascade

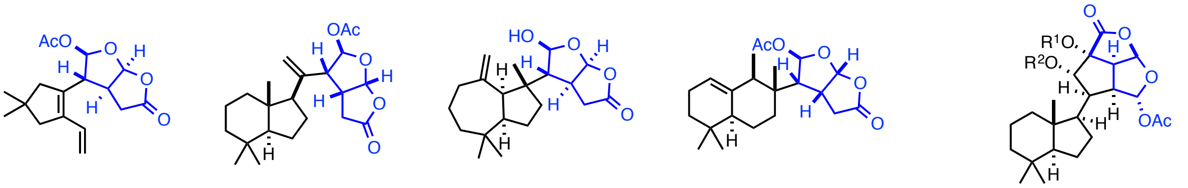
5.1 Introduction

Convergent strategies where advanced fragments of a target molecule are prepared in parallel and joined together at the latest possible stage in a synthesis are nearly always more efficient than linear strategies.[1] A corollary of this fact is the importance of reactions that are capable of combining complex molecules efficiently with high regio- and stereoselectivity. Recent investigations have shown that bimolecular-coupling reactions of tertiary carbon radicals can unite advanced synthesis fragments of structurally complex natural products in an efficient fashion.[2,3] Cascade reactions in which an intermediate produced in a bond-forming reaction propagates to construct additional bonds of a target molecule also typically increase efficiency in a chemical synthesis.[4] Radical cascade reactions, in particular intramolecular radical cascades, have long played a significant role in the efficient construction of complex molecules.[4,5] Much less developed are strategies in which a bimolecular radical coupling reaction initiates a further bond-forming cascade sequence.[6] The discovery of such a stereoselective sequence, whose optimization was guided by computational analysis, led to the first total synthesis of a chromodorolide diterpenoid and is the subject of this chapter.

The rearranged spongian diterpenoids are a large and structurally diverse family of natural products, which have been isolated largely from marine sources (Figure 5.1).[7] Distinct members of this group are characterized by the presence of a hydrophobic unit connected by a single bond to a highly oxygenated *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment, as exemplified by dermalactone (**5.1**),[8] norrisolide (**5.2**),[9] cheloviolene A (**5.3**),[10] macfarladin C (**5.4**),[11] or a 2,7-dioxabicyclo[3.2.1]octan-3-one fragment as found in aplyviolene (**5.5**),[12] macfarlandin E (**5.6**),[11] shahamin F (**5.7**),[13] verrielactone (**5.8**),[14] and norrlandin (**5.9**).[15] In chromodorolides A–E (**5.10–5.14**),[16–18] these bicyclic frameworks are appended to an additional oxygenated cyclopentane ring.

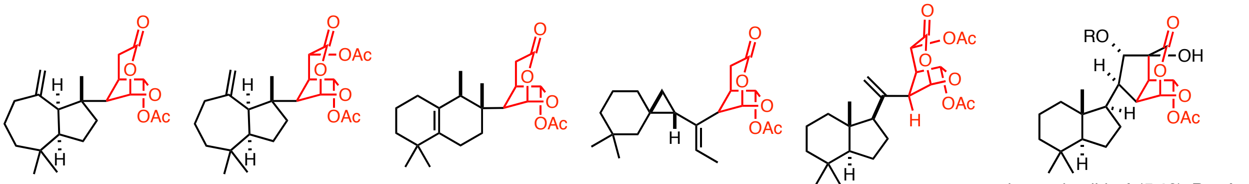
Figure 5.1. Representative rearranged spongian diterpenes harboring the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one or the 2,7-dioxabicyclo[3.2.1]octan-3-one fragments.

A. Representative structurally diverse rearranged spongian diterpenes that harbor the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one (blue) ring system.



dermalactone (**5.1**)
norrisolide (**5.2**)
cheloviolene A (**5.3**)
macfarlandin C (**5.4**)
chromodorolide B (**5.11**): R¹, R² = Ac
chromodorolide C (**5.12**): R¹=H, R² = Ac
chromodorolide E (**5.14**): R¹, R² = H

B. Representative structurally diverse rearranged spongian diterpenes that harbor the *cis*-2,7-dioxabicyclo[3.2.1]octan-3-one (red) ring system.



aplyviolene (**5.5**)
macfarlandin E (**5.6**)
shahamin F (**5.7**)
verrielactone (**5.8**)
norrlandin (**5.9**)
chromodorolide A (**5.10**): R = Ac
chromodorolide D (**5.13**): R = H

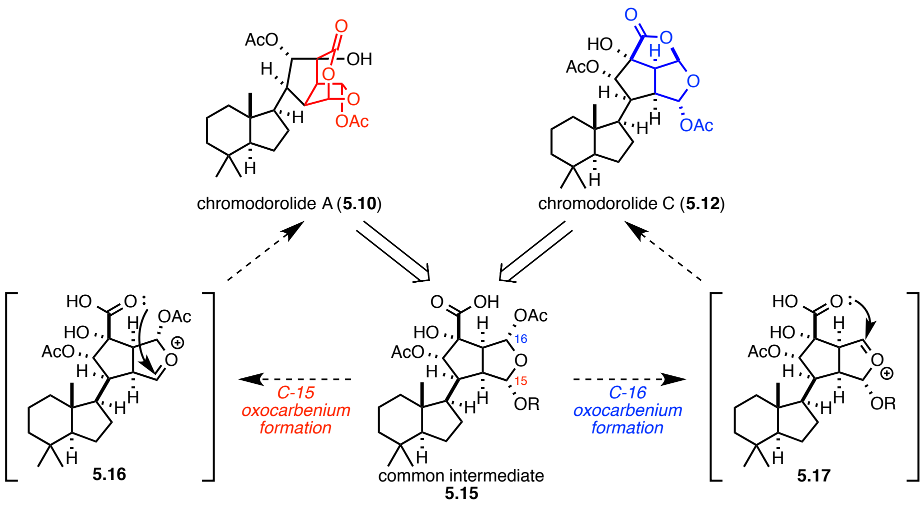
The chromodorolides have been isolated from nudibranchs in the genus *Chromodoris* and from encrusting sponges on which these nudibranchs potentially feed. Chromodorolide A (**5.10**) was first reported in 1989 by Anderson and Clardy, with its novel structure being revealed by X-ray crystallography.[16a] Two years later these workers described a second diterpenoid found in skin extracts of the tropical dorid nudibranch *Chromodoris cavae*, which showed a high frequency carbonyl stretching band at 1812 cm^{-1} in its IR spectrum.[16b] Detailed analyses of ^{1}H and ^{13}C NMR spectra indicated that this diterpenoid, chromodorolide B (**5.11**), had the same chromodorane carbon skeleton as chromodorolide A, but the bridging lactone ring in this case was 5-membered. Analogues of **5.10** and **5.11**, chromodorolides C–E (**5.12–5.14**) that display different degrees of acetylation of the vicinal hydroxyl substituents were isolated subsequently from two different marine sponges.[17,18] The chromodorolides are the most structurally intricate of the spongian diterpenoids, with 10 contiguous stereocenters arrayed upon their pentacyclic ring systems. Prior to our investigations, the absolute configuration of the chromodorolides was proposed upon the basis of their presumed biosynthesis from diterpenoids having the spongian ring system.[19]

Modest *in vitro* antitumor, nematocidal and antimicrobial activities have been reported for various chromodorolides.[16b,17,18a] Because of their structural relationship to molecules such as norrisolide (**5.2**), cheloviolene A (**5.3**) and macfarlandin E (**5.6**),[20,21] which have pronounced effects on the Golgi apparatus, the activity of the chromodorolides on the structure and function of the Golgi apparatus is potentially more significant. In our own investigations of analogues harboring 2,7-dioxabicyclo[3.2.1]octan-3-one or *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragments, we have identified conjugation of these ring systems with lysine side chains of proteins to form pyrrole adducts as potentially involved in the biological activities of diterpenoids such as those depicted in Figure 5.1.[21] As a result of the little-studied biological activity of the chromodorolides, and the challenge apparent in assembling these densely functionalized diterpenoids, we initiated studies to develop chemical syntheses of the chromodorolides.

5.2 Results and Discussion

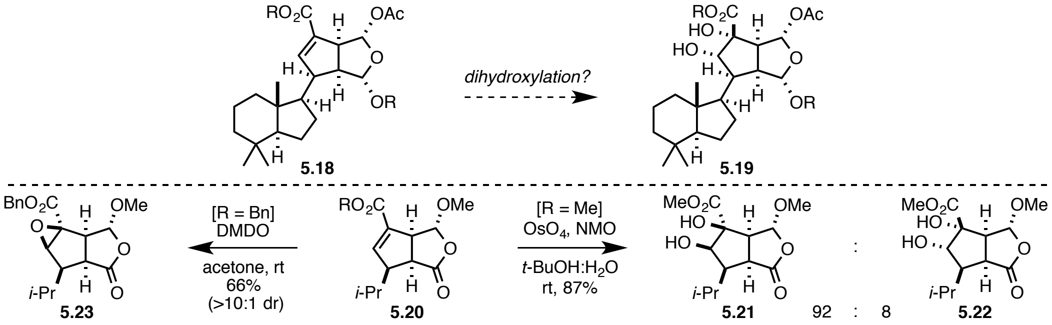
Retrosynthetically, we envisioned disconnecting the lactone bonds in **5.10** and **5.12** to arrive at a common tetracyclic acid intermediate **5.15** (Scheme 5.1). We hypothesized that both bridged and fused tricyclic frameworks could be prepared from acid **5.15** by site-selective oxocarbenium ion formation, followed by intramolecular lactonization. The *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment of chromodorolide C (**5.12**) is likely to be accessed most readily, as kinetically favored 5-membered ring closure of **5.17** could dominate even if oxocarbenium ion formation were unselective yet reversible.[21] In contrast, to construct the 2,7-dioxabicyclo[3.2.1]octan-3-one fragment found in chromodorolide A (**5.10**) regioselective activation at C-15 undoubtedly would be required to permit less-kinetically favored lactonization of oxocarbenium ion **5.16**.

Scheme 5.1. Common tetracyclic intermediate to access both bridged and fused chromodorolides.



Our initial thoughts on accessing the highly oxygenated bicyclic motif found in **5.15** envisaged late-stage dihydroxylation of an alkene precursor (Scheme 5.2). We expected that oxidation of an intermediate such as **5.18** would take place from the convex face opposite the bulky hydrindane fragment to generate **5.19**. As this step would occur late in the synthesis, we examined this conversion initially in a model system harboring an isopropyl group in place of the hydrindane fragment.[22] *cis*-Oxabicyclo[3.3.0]octenone **5.20** was readily assembled from an allenoate precursor by a diastereoselective phosphine-promoted (3+2) annulation.[23] To our surprise, dihydroxylation of **5.20** took place with high stereoselectivity from the concave face to give mainly diol **5.21**. Other oxidants such as *m*-chloroperoxybenzoic acid or dimethyl dioxorane behaved similarly, giving crystalline epoxide **5.23** as the predominant product.[24,25a] Computational studies by the Houk group suggested that the contrasteric selectivity for dihydroxylation of the enoate **5.20** arose from torsional effects.[22,26] Torsional, electrostatic and steric effects can all influence stereoselection in dihydroxylations of *cis*-bicyclo[3.3.0]octenes, and a more general discussion of this issue has been published.[22]

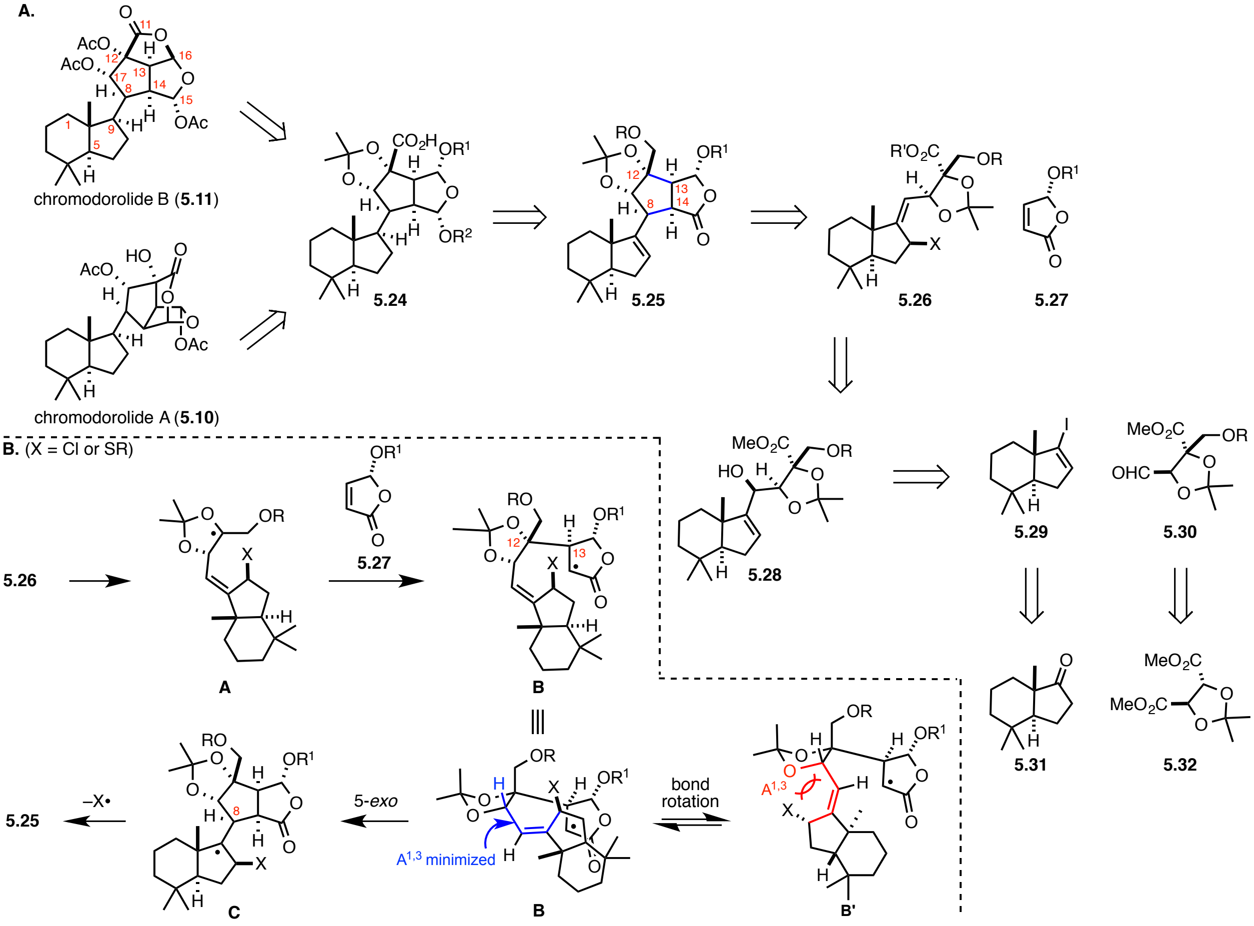
Scheme 5.2. Early attempts to introduce oxygenation via late-stage dihydroxylation or epoxidation of enoate **5.20**.



As installation of the *cis*-diol functionality did not appear to be feasible from a *cis*-oxabicyclo[3.3.0]octenone precursor, we turned to a plan wherein the *cis*-diol would be incorporated early in the synthetic sequence (Figure 5.2A). Disconnection of the lactone ring of chromodorolides A or B series leads to intermediate **5.24**. Further simplification leads to hydrindene **5.25**, with the expectation that late-stage hydrogenation of its double bond would take place from the face opposite the angular methyl substituent to install the C-9 stereocenter. We were attracted to a carbon radical-based approach to construct **5.25**, which we expected to be compatible with pre-installed oxygen functionalities at C-11, C-12 and C-17.[27,28] The cyclopentane ring of key intermediate **5.25**, we saw arising in one step from the union of tricyclic acetonide carboxylate **5.26** and (*R*)-5-alkoxybutenolide **5.27**.[29]

We envisioned the *trans*-hydrindane acetonide **5.26** arising from allylic alcohol **5.28**, which in turn would result from the addition of a vinylic nucleophile generated from vinyl iodide **5.29** and aldehyde **5.30**. As (*S*,*S*)-trimethylhydrindanone **5.31**[30] is the obvious precursor of iodide **5.29**, and (*R*,*R*)-tartaric acid derived acetonide **5.32** of aldehyde **5.30**,[31] the plan outlined in Figure 5.2A projects assembling the chromodorolides from three well-known enantiopure starting materials: **5.27**, **5.31**, and **5.32**.

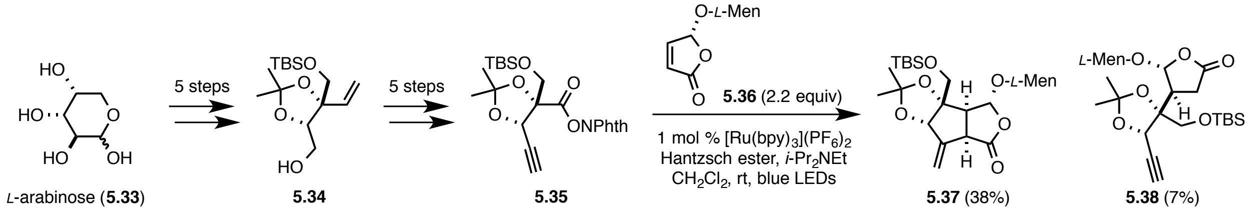
Figure 5.2. A. Plan for the proposed syntheses of chromodorolide A and chromodorolide B. **B.** Mechanistic analysis of the central radical addition/cyclization/fragmentation cascade to form pentacyclic intermediate **5.25**.



In the projected cascade sequence,[5] chiral acetonide (2,2-dimethyl-1,3-dioxolane) radical **A**, formed from oxidative decarboxylation of precursor **5.26**, would couple with butenolide **5.27** to generate alkoxyacyl radical **B** which would undergo 5-*exo* cyclization with the proximal alkene to generate intermediate **C** (Figure 5.2B). The radical cascade would then be terminated by *β*-fragmentation of the C–X bond (X = Cl or SR) of this intermediate to yield pentacyclic product **5.25**. If successful, the proposed bimolecular radical addition/cyclization/fragmentation (ACF) cascade would form two C–C bonds and four contiguous stereocenters of the chromodorolides in a single step. The stereochemical outcome of two steps would be critical to the successful outcome of the proposed cascade sequence (Figure 5.2B). First, the Giese reaction to unite acetonide radical **A** with butenolide **5.27** would have to correctly set the C-12 and C-13 stereocenters.[32,34] Ample precedent existed that this union would take place from the butenolide face opposite to the methoxy group to correctly set the C-13 stereocenter.[34] Less certain would be the facial selectivity of the reaction of trisubstituted acetonide radical **A**. To correctly form the C-12 stereocenter, this coupling would have to take place from the face proximal to the vinylic β-substituent. As few C–C bond-forming reactions of 2,2-dimethyl-1,3-dioxolane trisubstituted radicals had been described with both *syn*- and *anti*-addition being observed,[35] it was uncertain at the outset from which face radical intermediate **A** would couple. We took some encouragement from the report by Renaud that a bulky β-substituent (*tert*-butyl) favored bond formation *cis* to the substituent, although in these precedents the alkene was unsubstituted at its bond-forming terminus.[35a] The second step whose stereochemical outcome would be critical was the 5-*exo* cyclization of tetracyclic radical intermediate **B**. We expected that this conversion would take place as depicted in Figure 5.2B by a conformation that minimizes destabilizing $A^{1,3}$ interactions.

As we had most concern about the facial selectivity in the bimolecular radical coupling step, particularly with regard to facial selectivity of the reaction of a trisubstituted acetonide radical, we chose to examine this aspect of the ACF cascade in a model system having a terminal alkyne substituent at the β carbon of the acetonide radical (Scheme 5.3). Starting with *L*-arabinose (**5.33**), enantiopure *N*-acyloxyphthalimide **5.35** was prepared in 10 steps by way of the known acetonide alcohol **5.34**.[36,37] Using a slight modification[38] of visible-light photoredox conditions pioneered by Okada for generating radicals from *N*-acyloxyphthalimides,[39] the coupling of **5.35** with 2.2 equiv of enantiopure (*R*)-5-*L*-menthoxybutenolide (**5.36**)[29b,c] gave the crystalline tricyclic lactone **5.37** in 38% yield. X-ray analysis of **5.37** confirmed that the coupling step had taken place as desired.[25b] The other isolable product, formed in 7% yield, was **5.38**. ^{1}H NMR NOE analysis confirmed that this product formed from coupling of the trisubstituted acetonide radical from the face opposite to the alkyne substituent, resulting in the coupled radical being quenched rather than undergoing 5-*exo* cyclization with the *trans*-oriented alkyne substituent. In subsequent studies discussed later in the chapter, the coupling of a broad selection of trisubstituted acetonide radicals harboring β-substituents was studied both experimentally and computationally.[40] The origin of the observed *syn* stereoselection for the addition of the trisubstituted radical formed from **5.35** to butenolides such as **5.36** is ascribed to destabilizing non-covalent interactions between the alkynyl substituent and silyl-protected hydroxymethyl substituent in the transition state.[35a,40] Since the β-substituent of the trisubstituted radical **A** (Figure 5.2B) in the proposed ACF cascade is certainly larger than an alkyne, we were encouraged to proceed ahead to assemble the fragments to examine this pivotal step in our synthesis plan.

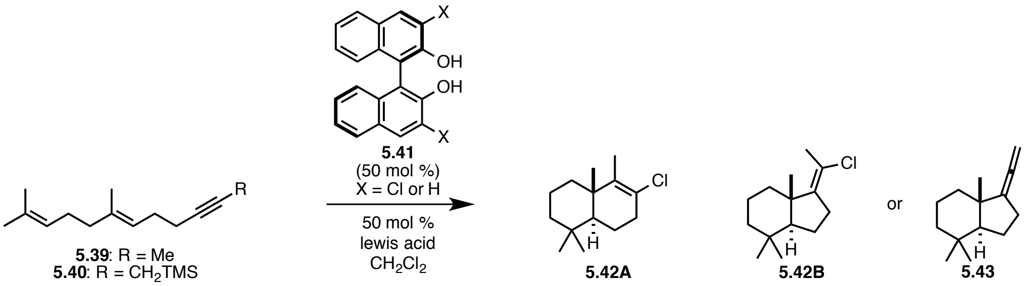
Scheme 5.3. Model system for the study of the facial selectivity of the reaction of a trisubstituted acetonide radical with butenolide **5.36**.



Several syntheses of enantioenriched *trans*-hydrindanone **5.31** have been reported.[30] We initially examined the short route reported by Granger and Snapper to prepare this ketone from 2-methylcyclopenten-2-one and prenylmagnesium bromide.[30b] After slight modification, this approach provided initial quantities of (*S*,*S*)-*trans*-hydrindanone **5.31** for our early studies. However, this route was deemed impractical for a large-scale preparation of **5.31** because its modest overall yield (20%) and scalability issues in several steps.[36]

We turned to examine a biomimetically inspired polyene cyclization route to *trans*-hydrindanone **5.31**.[41] Based on the reports from the Yamamoto[42] and Corey[43] laboratories, we conjectured that dienyne **5.39**, obtained in two steps from geranyl chloride,[36] would undergo enantioselective proton-initiated polyene cyclization upon exposure to a chiral BINOL derivative in the presence of a strong Lewis acid, forming the alkylidene *trans*-hydrindane **5.42B** (Scheme 5.4).[44] In our hands, subjection of dienyne **5.39** to the reaction conditions reported by Corey,[43] using $SbCl_5$ in combination with *o,o'*-dichloro-(*R*)-BINOL **5.41** (X = Cl) led to a 1:3 mixture of two regioisomeric bicyclic products **5.42A** and **5.42B** in 35% combined yield (entry 1). Ozone-mediated cleavage of the exocyclic double bond of **5.42B** provided racemic *trans*-hydrindanone **5.31**. Examination of other Lewis acids (entries 2 and 3) revealed $SnCl_4$ to be superior in terms of reaction efficiency and enantioinduction. Unfortunately, further variation of reaction temperatures and the use of unsubstituted BINOL (**5.41**, X = H) led to no appreciable improvements in enantioselectivity or selectivity in forming **5.42B** (entries 4–6). Unable to eliminate formation of the *trans*-decalin product **5.42A**, we examined cyclization of propargylic silane **5.40**.[45] However, reactions of this precursor gave **5.43** in low yield only (e.g., entry 7).[46]

Scheme 5.4. Attempted enantioselective proton-initiated polyene cyclization route for the synthesis of *trans*-hydrindanone **5.31**.

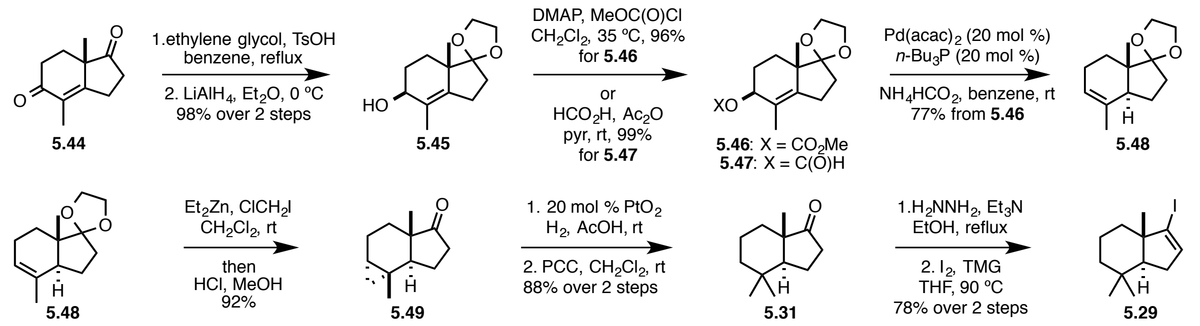


entry	Lewis acid	R	X	T (°C)	yield[a] (ratio **5.42A**:**5.42B**)[b]	**5.31**, %*ee*[c]
1	$SbCl_5$	Me	Cl	–78	35% (1.0:3.0)	0%
2	$TiCl_4$	Me	Cl	–78	<5% (*ND*)	*ND*
3	$SnCl_4$	Me	Cl	–78	55% (1.0:1.5)	18%
4	$SnCl_4$	Me	Cl	–90	53% (1.0:1.1)	20%
5	$SnCl_4$	Me	Cl	–50	12% (0:1.0)	*ND*
6	$SnCl_4$	Me	H	–78	53% (1.1:1.0)	13%
7	$SnCl_4$	CH_2TMS	Cl	–78	23% (0:1.0)	*ND*

[a] Isolated combined yield of **5.42A** and **5.42B**. [b] Determined by ^1H NMR integration of the crude reaction mixture. [c] Hydrindanone **5.31** was obtained by ozonolysis of **5.42B** or **5.43**. Enantioselective HPLC analysis of a hydrazone derivative was used to establish enantiopurity of **5.31**.[36]

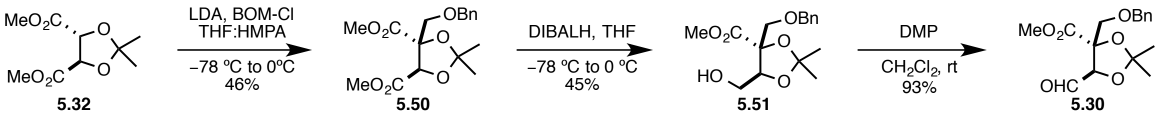
The scalable route we finally developed to provide (*S*,*S*)-*trans*-hydrindanone **5.31** is summarized in Scheme 5.5. This sequence hinged on stereospecific reductive transposition of an allylic alcohol intermediate to set the thermodynamically disfavored *trans* ring fusion of **5.31**.[47,48] The preparation begins with commercially available (*S*)-enedione **5.44**,[49] which alternatively can be obtained reliably in 98% *ee* on >20 g scales in two steps from 2-methylcyclopentane-1,3-dione.[50] Selective ketalization of **5.44**, followed by stereoselective 1,2-reduction of the enone provided allylic alcohol **5.45** in 98% yield after a simple distillation. A number of approaches were investigated to convert allylic alcohol **5.45** to the desired *trans*-hydrindene ketal **5.48**. Reaction of **5.45** with *o*-nitrobenzenesulfonylhydrazine followed by warming of the reaction to room temperature, as described by Myers,[51] led to the desired *trans*-fused ketal **5.48** as a minor component of a complex mixture of product. Unable to perform the desired transformation in a single step, we turned to examine Tsuji's palladium-mediated stereospecific reductive transpositions of *β*-allylic carbonates and formates.[48] Carbonate **5.46** readily underwent the desired reductive transposition upon treatment with Pd(acac)$_2$, (n-Bu)$_3$P, and finely crushed NH_4HCO_2 to provide *trans*-hydrindene ketal **5.48** in 77% yield. The choice of phosphine was critical to the success of the reaction, as the use of other phosphines (Cy$_3$P, t-Bu$_3$P, Ph$_3$P) led largely to recovery of starting carbonate **5.46**. The more commonly used allylic formate **5.47** was to our surprise found to be inert under our reaction conditions. Stereoselective cyclopropanation of the trisubstituted double bond of **5.48** was achieved by reaction with diethylzinc and chloroiodomethane,[52] which after acidic workup delivered cyclopropyl ketone **5.49** in 92% yield. It was important to use chloroiodomethane in this reaction, as use of diiodomethane led largely to recovery of the starting alkene. Hydrogenolysis of cyclopropane **5.49** using PtO_2 in acetic acid,[53] followed by PCC oxidation of the resulting secondary alcohol gave *trans*-hydrindanone **5.31** in 88% yield over two steps. This sequence delivered (*S*,*S*)-*trans*-hydrindanone **5.31** (98% ee) in 7 steps and 59% overall yield from enone **5.44**. Using the method of Barton,[54] hydrindanone **5.31** was converted to the known vinyl iodide **5.29**[30a] in 78% yield. The sequence summarized in Scheme 5.5 readily provided 7 g of the light-sensitive iodide **5.29** in a single pass.

Scheme 5.5. Synthesis of vinyl iodide **5.29**.



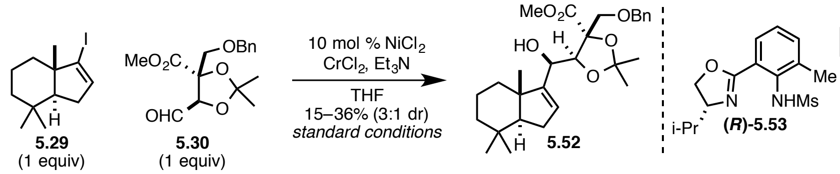
With streamlined access to vinyl iodide **5.29** in hand, we turned our attention to the synthesis of the aldehyde coupling partner **5.30** (Scheme 5.6). The sequence began with tartrate-derived acetonide **5.32**, which was desymmetrized by LDA-mediated alkylation with BOM-Cl, as reported by Crich, to give benzyl ether **5.50** in 46% yield.[31,55] Selective reduction of the less hindered ester group of **5.50** with DIBALH provided primary alcohol **5.51** in 45% yield along with 36% of recovered starting material **5.50**. All our attempts to improve the efficiency of this conversion were unsuccessful, as the use of alternate reductants (e.g., $LiAlH_4$, Red-Al) or extra equivalents of DIBALH led to complex mixtures of various reduction products. Oxidation of primary alcohol **5.51** to aldehyde **5.30** could be achieved by a number of conventional methods; however, purification of **5.30** proved to be challenging. We ultimately elected to oxidize alcohol **5.51** with the Dess-Martin reagent (DMP) in CH_2Cl_2 and filter the resulting mixture with *n*-hexanes over Celite to remove the insoluble byproducts and give aldehyde **5.30** in 93% yield and high purity.[56] As a result of its unexpected instability, aldehyde **5.30** was used immediately in the ensuing coupling step (*vide infra*).[57] This approach proved to be a short and scalable approach to aldehyde coupling partner **5.30**, with >8 g being readily prepared in a single pass, albeit in modest overall yield.

Scheme 5.6. Synthesis of aldehyde **5.30**.



Next, we focused on uniting the *trans*-hydrindene and aldehyde fragments. Early attempts to directly couple the vinyllithium intermediate formed from vinyl iodide **5.29** with aldehyde **5.30** provided only low yields (<20% yields) of adducts as an equimolar mixture of allylic alcohol epimers. We turned to the use of the Nozaki-Hiyama-Kishi (NHK) reaction to achieve the desired fragment-coupling (Scheme 5.7).[58] NHK conditions that had been employed earlier to couple this iodide[59] led to the formation of adduct **5.52** in low yields and 3:1 stereoselectivity. To accelerate the rate of NHK coupling and improve stereoselection, we elected to employ the oxazoline ligands developed by the Kishi group.[60] To our delight, use of ligand (*R*)-**5.53** resulted in the formation of adduct **5.52** as a single diastereomer in 28% yield. The identical reaction using the enantiomeric ligand, led to inversion of diastereoselectivity, giving the allylic alcohol epimer in 18% yield and 4:1 dr. Upon further optimization of the reaction with ligand (*R*)-**5.53**, we discovered that employing the sensitive aldehyde **5.30** in a slight excess (1.6 equiv) and performing the reaction on a larger scale (3 mmol) led to the formation of the desired product **5.52** in 66% isolated yield.[61]

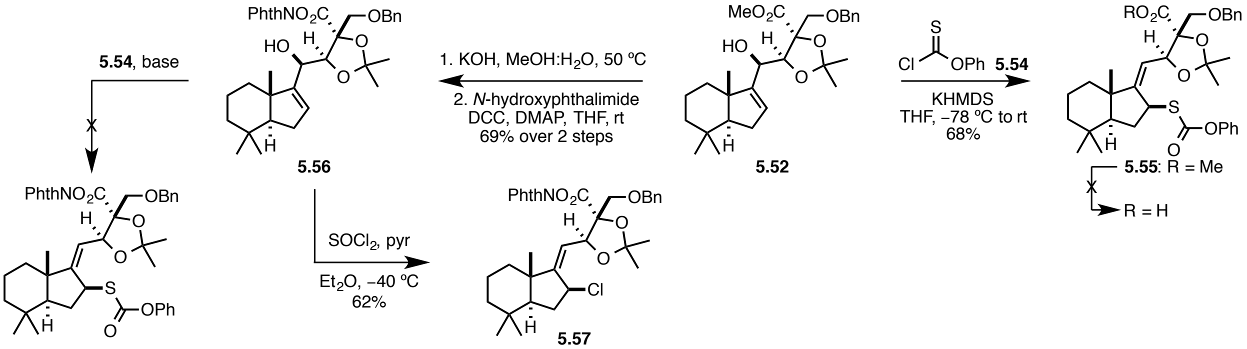
Scheme 5.7. Optimization of the NHK coupling of vinyl iodide **5.29** to aldehyde **5.30**.



deviation from standard conditions	yield (dr)
addition of **(*R*)-5.53**	28% (>20:1)
addition of **(*R*)-5.53** **5.30** (1.6 equiv)	66% (>20:1)

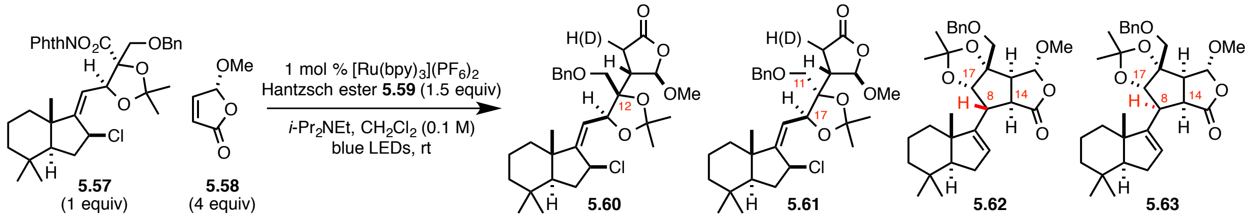
Having forged all of the C–C bonds of the radical cascade precursor, we were faced with the need to allylically transpose the alcohol functionality to a heteroatom capable of undergoing radical β-cleavage, while setting the required *E*-configuration of the exocyclic double bond of the product (Scheme 5.8). We first investigated the possibility of performing a [3,3]-sigmatropic rearrangement to an allylic thiocarbonate.[62,63] To this end, deprotonation of alcohol **5.52** with KHMDS at –78 °C, followed by addition of phenyl chlorothionoformate (**5.54**) resulted in thioacylation and spontaneous [3,3]-sigmatropic rearrangement upon warming to room temperature to give allylic thiocarbonate **5.55** as a single stereoisomer in 68% yield. However, we were unable to selectively cleave the methyl ester group of **5.55** in the presence of the sensitive thiocarbonate functionality under a variety of classical saponification, S_N2 demethylation,[64] or other non-basic methods.[65] To circumvent this selectivity issue, the order of transformations was reversed. Saponification of methyl ester **5.52** and subsequent esterification with *N*-hydroxyphthalimide (NHP) provided the crystalline NHP ester **5.56** in 69% yield, whose structure was confirmed by single-crystal X-ray analysis.[25c] Unfortunately, subjection of allylic alcohol **5.56** to the reaction conditions that were successful for thioacylation of **5.52** led to immediate decomposition of the *N*-acyloxyphthalimide functionality.[66] Deprotonation of **5.56** with LiHMDS or NaHMDS followed by reaction with **5.54** led to recovery of the starting material, whereas reaction of **5.56** with other potassium bases uniformly resulted in instantaneous decomposition. Unable to selectively activate hindered allylic alcohol **5.56** for thioacylation with phenyl chlorothionoformate (**5.54**), we investigated allylic OH → Cl transformations. Reaction of alcohol **5.56** with 2 equiv of $SOCl_2$ in a 10:1 mixture of Et_2O:pyridine at –40 °C[67] induced the desired suprafacial rearrangement to deliver crystalline *N*-acyloxyphthalimide radical precursor **5.57**, whose structure was confirmed by single-crystal X-ray analysis,[25d] in 62% yield on gram-scale. This stereoselective conversion could also be accomplished on the product of the NHK coupling **5.52**, followed by saponification to the corresponding carboxylic acid. However, in contrast to NHP ester **5.57**, the non-crystalline acid produced was difficult to purify.

Scheme 5.8. Synthesis of radical precursor **5.57** from NHK coupling product **5.52**.



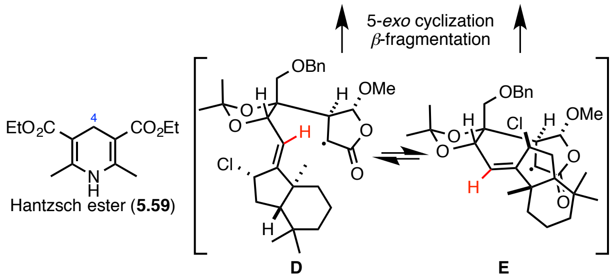
Exposure of *N*-acyloxyphthalimide **5.57** to standard reductive photoredox reaction conditions[38] in the presence of 4 equiv of enantioenriched (89% *ee*) (*R*)-5-methoxybutenolide (**5.58**)[29a,c] gave a mixture of four products accounting for 95% of the mass balance (Scheme 5.9, entry 1). Pentacyclic products **5.62** (35%) and **5.63** (25%) arose from the desired ACF cascade reaction. Initial structural assignments of products **5.62** and **5.63** were based on detailed analyses of their NMR spectra. Particularly useful were ^{1}H NOE correlations between the C-8, C-17, and C-14 methine hydrogens.[36] Further confirmation of the structures of these two C-8 epimers was obtained by eventual conversion of cascade product **5.63** to (–)-chromodorolide B (**5.11**). The stereochemical relationship of lactone and hydrophobic fragments in the two tetracyclic products was assigned based on a strong ^{1}H NOE correlation between the C-17 methine hydrogen and the C-11 hydrogens of the benzyloxymethyl substituent of isomer **5.61**. Products **5.61**, **5.62** and **5.63** are derived from the desired *syn* addition of butenolide **5.58** to the acetonide radical formed from **5.57**. In contrast, tetracyclic lactone **5.60** arose from coupling of the dioxolane radical with acceptor **5.57** *anti* to the vicinal hydrophobic fragment. The resulting *R* configuration at C-12 prevents ensuing 5-*exo* cyclization.[68]

Scheme 5.9. First-generation ACF cascade.



entry	deviation from above	yield[a] 5.60	5.61	5.62	5.63
1	none	11%	29%	35%	20%
2	no *i*-Pr$_2$NEt	7%	14%	34%	18%
3	no *i*-Pr$_2$NEt, CH$_2$Cl$_2$ (0.02 M)	6%	3%	29%	16%
4	no *i*-Pr$_2$NEt, d$_2$-**5.59**	10% (d$_1$)	6% (d$_1$)	45%	25%
5	no *i*-Pr$_2$NEt, d$_2$-**5.59**, MeCN (0.1 M)	13% (d$_1$)	8% (d$_1$)	37%	27%[b]

[a]Determined by ^{1}H NMR integration relative to an internal standard (1,4-dimethoxybenzene). [b]Isolated yield.



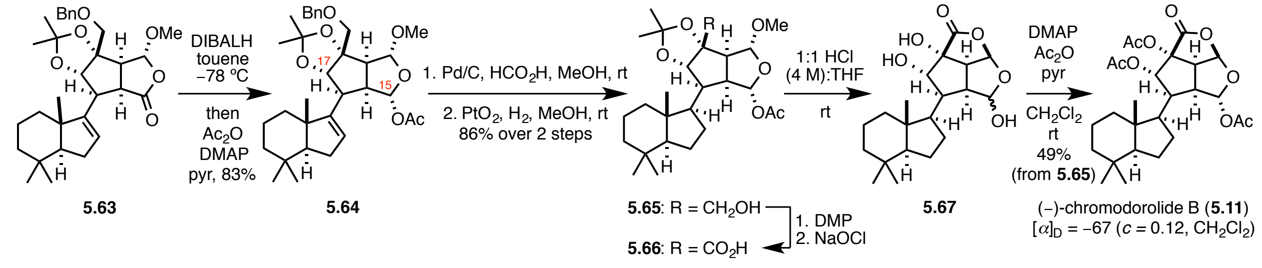
Although the initial coupling of dioxolane radical to butenolide **5.58** occurred with 7.6:1 diastereoselectivity favoring the desired adduct, minimizing premature reduction of the α-acyl radical intermediate leading to the significant byproduct, lactone **5.61**, would be important for optimizing the efficiency of the ACF cascade. Formation of product **5.61** indicated that quenching of the α-acyl radical produced in the Giese coupling step by either single-electron transfer (SET) to form an enolate followed by protonation or by hydrogen atom abstraction from Hantzsch ester **5.59** was competitive with 5-*exo* cyclization.[38] In an attempt to minimize the SET pathway,[38] *i*-Pr$_2$NEt was omitted from the reaction mixture, significantly decreasing the yield of product **5.61** to 14% (entry 2). To further reduce premature quenching of the radical intermediate, we performed the reaction at higher dilution, resulting in a further decrease in the yield of product **5.61** to 3% (entry 3). However, these more dilute conditions also resulted in less efficient coupling of the dioxolane radical and butenolide **5.58** leading to lower yields of pentacyclic products **5.62** and **5.63**. To attenuate hydrogen atom abstraction by the α-acyl radical in reactions carried out at higher concentration, we employed 4,4-dideuterio analogue of Hantzsch ester **5.59** (entry 4). Under these conditions, the combined yield of cyclization products **5.62** and **5.63** increased to 70%, with tetracyclic lactone **5.61** being formed in only 6% yield.

Having attenuated premature quenching of the α-acyl radical intermediate, we sought to explore the effects of temperature, solvent, and structural modifications of butenolide **5.58** on diastereoselection of the of 5-*exo* cyclization. As illustrated in Scheme 5.9, the major pentacyclic product **5.62** arose from cyclization taking place by a transition state related to radical conformer **D**, not by way of a transition structure related to conformer **E**. Varying the temperature of the reaction (0 °C to 40 °C) did not have a significant impact on the ratio of the epimeric products **5.62** and **5.63**. Likewise, using butenolides harboring acetoxy or menthoxy substituents at the acetal stereocenter, led to no improvement in the yield of the desired tetracyclic product **5.63**. The ratio was slightly enhanced in reactions conducted in acetonitrile, allowing the desired epimer **5.63** to be isolated in 27% yield (entry 5). Unable to further increase the yield of the desired ACF product **5.63**, we advanced the pentacycle forward to validate our post fragment-coupling strategy.

Product **5.63** of the ACF cascade was converted to (–)-chromodorolide B (**5.11**) by way of two isolated and purified intermediates, **5.64** and **5.65** (Scheme 5.10). Reduction of **5.63** with DIBALH at –78 °C and *in situ* acetylation with Ac_2O and DMAP afforded diacetal

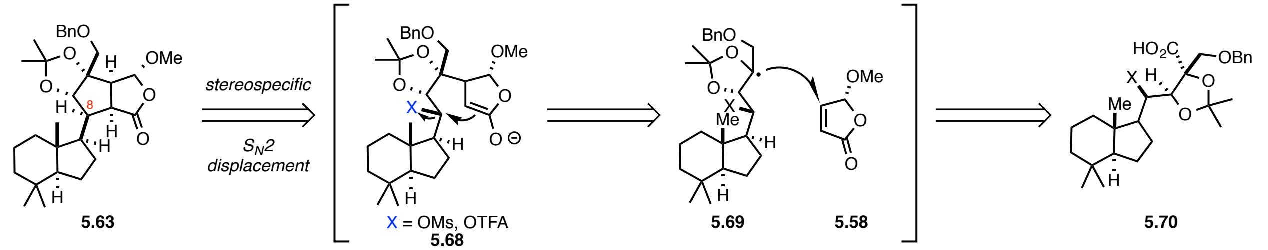
5.64 as a single epimer at C-15,[69] which was assigned the α-orientation on the basis of ^{1}H NOE correlations between the C-15 and C-17 methines. We speculate that stereoselection in this reduction resulted from prior coordination of DIBALH with the benzyl ether substituent. Following unsuccessful attempts to accomplish reduction of the alkene and deprotection of the benzyl ether in one step, we first unveiled the primary alcohol under transfer-hydrogenation conditions, followed by conventional PtO_2-mediated hydrogenation. The latter step proceeded exclusively from the alkene face opposite the angular methyl group to afford a single product **5.65** in 86% yield. Without purifying subsequent intermediates, the primary alcohol of **5.65** was oxidized to carboxylic acid **5.66**, which upon exposure of the crude reaction mixture to 1:1 solution of 4 M HCl and THF for 72 h at room temperature delivered pentacyclic intermediate **5.67** as a mixture of lactol epimers. Reaction of a pyridine solution of this intermediate with a large excess of acetic anhydride in the presence of DMAP gave (–)-chromodorolide B (**5.11**) as a colorless solid in 49% overall yield from tetracyclic alcohol precursor **5.65**. Spectroscopic data for synthetic **5.11** compared well with that reported for the natural product.[16b] The magnitude of the levorotatory rotation, $[\alpha]_D = -67$ ($c = 0.12$, CH_2Cl_2), was somewhat less than that reported, $[\alpha]_D = -95$ ($c = 0.12$, CH_2Cl_2), for a non-crystalline sample of the natural product.[16b] Recrystallization of synthetic (–)-chromodorolide B (**5.11**) provided single crystals, mp = 236–238 °C, allowing its structure to be rigorously confirmed by X-ray analysis.[25e]

Scheme 5.10. Synthesis of (–)-chromodorolide B (**5.11**) from ACF product **5.63**.



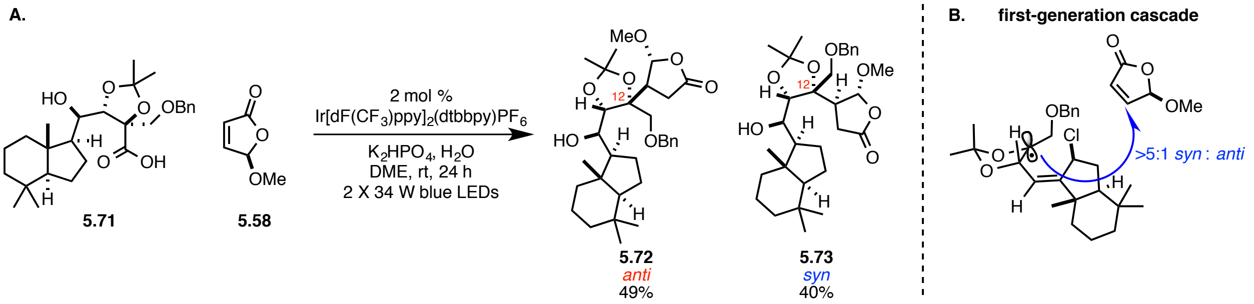
Upon completion of the synthesis of (–)-chromodorolide B (**5.11**), we shifted our focus back to optimization of the ACF cascade. As discussed earlier, we predicted that the 5-*exo* cyclization, to construct the C-8 stereocenter of diterpenoid **5.11**, would occur preferentially from a conformation wherein $A^{1,3}$ interactions would dictate which face of the alkene would be attacked. Unfortunately, the major product of the ACF cascade was epimeric at C-8. Since the initial coupling of the dioxolane radical to butenolide **5.58** was efficient and proceeded with 5.5:1 diastereoselectivity to set the desired stereochemistry at C-12 we decided to modify the cyclization step of the cascade (Figure 5.3). We proposed a stereospecific displacement of a leaving group at C-8, such as a mesylate or a trifluoroacetate, by an enolate to secure the desired stereochemistry at C-8. The enolate intermediate **5.68** would be formed upon SET reduction of an α-acyl radical by a photocatalyst, following the initial coupling of the dioxolane radical **5.69** to butenolide **5.58**. We elected to generate the trisubstituted radical **5.69** from the corresponding carboxylic acid **5.70** following MacMillan's protocol for visible-light photoredox catalyzed oxidation of carboxylates.[40,70]

Figure 5.3. Proposed stereospecific S_N2 displacement of a leaving group to set the C-8 stereocenter of (–)-chromodorolide B (**5.11**).



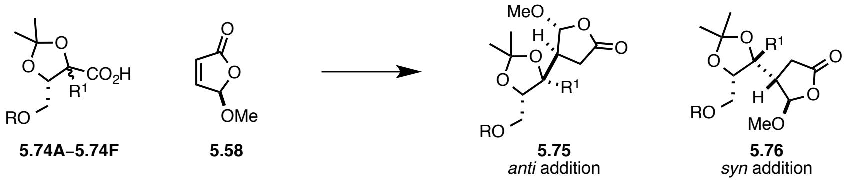
To test the feasibility of the modified cascade sequence, we prepared a simplified carboxylic acid **5.71** in two steps from the NHK product **5.52**,[36] bearing a secondary alcohol in place of a leaving group. To our surprise, upon subjection of the acid **5.71** to the photoredox reaction conditions in the presence of (*R*)-5-methoxybutenolide (**5.58**) we obtained a 1.2:1 mixture of C-12 epimeric products **5.72** and **5.73** in 89% combined yield (Scheme 5.11A). Although the efficiency of the transformation was high, the major product **5.72** was formed as a result of the undesired *anti* addition of the acetonide radical to butenolide **5.58**. This unexpected outcome stood in stark contrast to the high degree of stereoselection observed during the first-generation ACF cascade in which the desired C-12 epimer, formed by *syn* addition, was obtained in 5.5:1 dr (Scheme 5.11B). High degree of sensitivity of stereoselection for the addition of trisubstituted acetonide radicals to butenolide **5.58**, coupled to limited previous related studies,[35] prompted us to undertake a systematic study of diastereoselection in radical coupling reaction of this type, involving both experimental and computational analysis in collaboration with the Furche group.

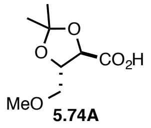
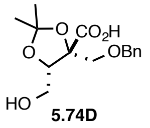
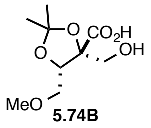
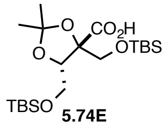
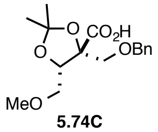
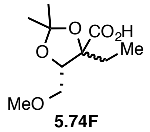
Scheme 5.11. Results of the coupling of a dioxolane radical bearing an sp^3-hybridized substituent and comparison to the first-generation cascade that involved a dioxolane radical substituted with an sp^2-hybridized carbon.



Our initial studies focused on radical additions of structurally simple acetonide radicals, prepared from primary alcohol **5.51**,[36] to chiral butenolide **5.58**. We first examined the coupling of the disubstituted radical generated from acid **5.74A**. As expected, addition occurred preferentially *anti* to the adjacent methoxymethyl substituent (Table 5.1, entry 1).[71,72] We then turned our attention to precursors that would yield trisubstituted radical intermediates. In entries 2–5, the radical center bore a hydroxymethyl or protected-hydroxymethyl substituent, and addition occurred with low stereoselectivity *syn* to the β substituent. Only when the substituent at the radical center was an ethyl group was *syn* stereoselectivity high (9.3:1, entry 6). The relative configurations of products **5.75** and **5.76** were assigned by ^{1}H NOE experiments and confirmed in the case of the major product **5.76F** by single-crystal X-ray analysis.[73, 25f]

Table 5.1. Coupling of acetonide radicals generated by decarboxylation of acetonide acids **5.74A–5.74F** with (*R*)-5-methoxybutenolide (**5.58**).

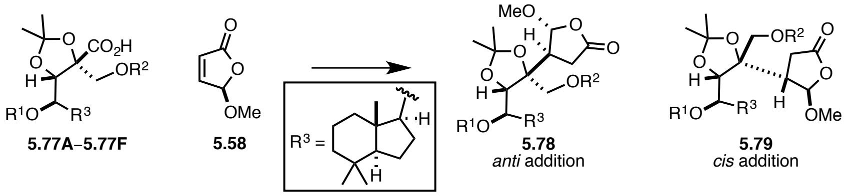


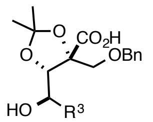
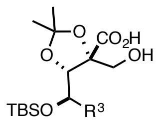
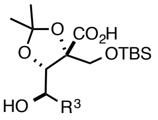
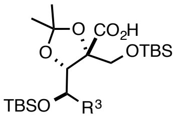
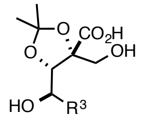
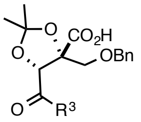
entry[a]	acid	*anti* : *syn*[b] (% yield)[c]	entry[a]	acid	*anti* : *syn*[b] (% yield)[c]
1	 **5.74A**	3.5:1 (37%)	4	 **5.74D**	1:2.6 (66%)
2	 **5.74B**	1:3.3 (54%)	5	 **5.74E**	1:2.2 (67%)
3	 **5.74C**	1:2.8 (64%, 84%[d])	6	 **5.74F**	1:9.3 (68%)

[a]Reaction conditions: 1.0 equiv of **5.74A–5.74F**, 1.1 equiv of **5.58**, 2 mol % of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$, 1.1 equiv of K$_2$HPO$_4$, 10 equiv of H$_2$O in DME (0.1 M) at rt for 18 h with 2 X 34 W blue LEDs. [b]Diastereoselectivity determined by ^{1}H NMR analysis of the crude reaction mixture using an internal standard. [c]Isolated yield after silica gel chromatography. [d]Concentration was 0.4 M.

Having confirmed that trisubstituted acetonide radicals in this series react with butenolide **5.58** preferentially in a *syn* fashion, which is required for the synthesis of (–)-chromodorolide B (**5.11**), we turned to examine structurally more elaborate substrates that harbored the trimethylhydrindane fragment found in **5.11** (Table 5.2). Because of the scarcity of the more elaborate radical precursors in this series and limited solubility of diol carboxylic acid precursor **5.77C**, the coupling reactions reported in Tables 5.1 and 5.2 were performed under identical conditions at a concentration of 0.1 M in DME. It should be recognized that a higher reaction concentration typically improves the yield of bimolecular radical coupling reactions of this type.[2b] For example, carrying out the coupling reactions of precursors **5.74C** and **5.77E** at 0.4 M instead of 0.1 M increased the yield of the coupled products by more than 30%.

Table 5.2. Coupling of acetonide radicals generated by decarboxylation of trimethylhydrindane-bearing acids **5.77A–5.77F** with (*R*)-5-methoxybutenolide (**5.58**).



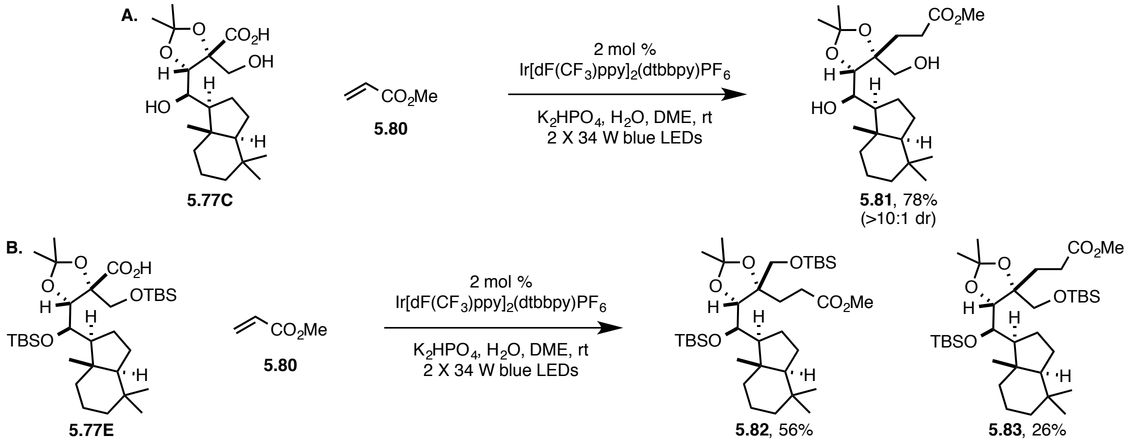
entry^a	acid	*anti* : *syn*^{b} (% yield)^c	entry^a	acid	*anti* : *syn*^{b} (% yield)^c
1	 **5.77A**	1.2:1 (49%)^d	4	 **5.77D**	1:7.0 (22%)^d
2	 **5.77B**	1.3:1 (71%)	5	 **5.77E**	1:8.2^e (37%, 50%^{g})
3	 **5.77C**	9.8:1^e (45%)^f	6	 **5.77F**	1:2.6 (43%)

[a]Reaction conditions: 1.0 equiv of **5.77A–5.77F**, 1.1 equiv of **5.58**, 2 mol % of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$, 1.1 equiv of K$_2$HPO$_4$, 10 equiv of H$_2$O in DME (0.1 M) at rt for 18 h with 2 X 34 W blue LEDs. [b]Diastereoselectivity determined by ^{1}H NMR analysis of the crude reaction mixture using an internal standard. [c]Isolated yield after silica gel chromatography. [d]Yield of the major product only. [e]Within experimental uncertainty, the isomer ratio was constant over time: **5.77C** 9.4:1 at 3 h, 9.3:1 at 6h; **5.77E** 1:8.5 at 3 h, 1:8.6 at 6 h. [f]45% combined yield by ^{1}H NMR analysis using an internal standard. The major diastereoisomer was isolated in 27% yield. [g]Concentration was 0.4 M.

We anticipated that the greater bulk of the trimethylhydrindane fragment would result in enhanced *syn* stereoselection in the reactions reported in Table 5.2.[35] However, we found that depending upon the nature of the oxygen substituents R^1 and R^2 of the acetonide carboxylic acid precursors **5.77**, either high *anti* or *syn* stereoselectivity was observed. When both oxygen substituents were alcohols (entry 3), *anti* stereoselection was 9.8:1; whereas when these substituents are *tert*-butyldimethylsiloxy groups, formation of the *syn* stereoisomer was favored by 8.2:1 (entry 5).

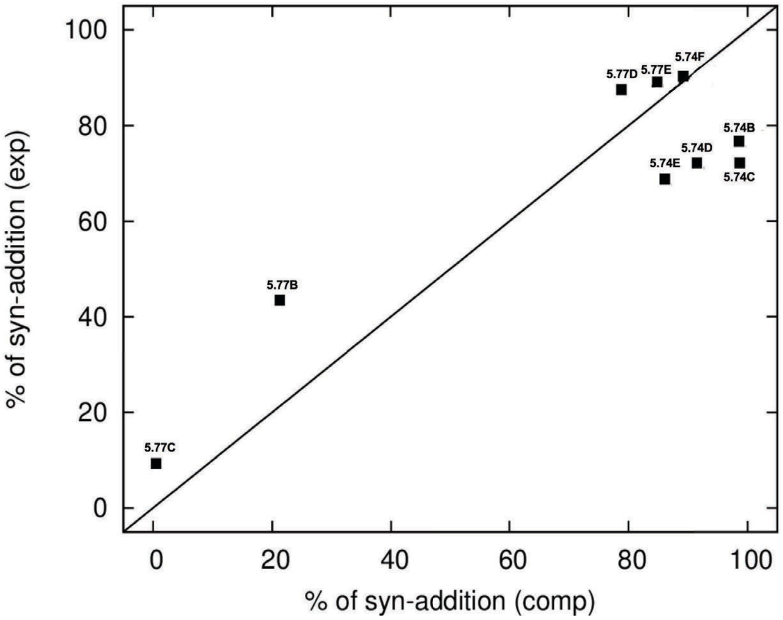
To validate that the dramatic reversal in stereoselectivity between the trisubstituted acetonide radicals generated from **5.77C** and **5.77E** was not unique to butenolide radical acceptor **5.58**, these acids were also coupled with methyl acrylate (**5.80**). In this case, product **5.81** was formed in high yield and >10:1 *anti* stereoselectivity from diol acid **5.77C** (Scheme 5.12A) whereas the bis-TBS precursor **5.77E** provided preferentially product **5.82** resulting from *syn* addition with 2.2:1 stereoselectivity (Scheme 5.12B).

Scheme 5.12. Comparison of observed stereoselectivities for the addition of trisubstituted acetonide radicals formed from carboxylic acids **5.77C** and **5.77E** to methyl acrylate (**5.80**).



Since the stereoselectivities reported in Table 5.2 could not be explained by simple steric arguments, extensive electronic structure calculations were performed to develop a rationale for the observed results. Our best theoretical estimates achieved excellent agreement with the experimental results observed in the reaction of trisubstituted acetonide radicals derived from carboxylic acid precursors **5.74** and **5.78** with butenolide **5.58** (Figure 5.4). The computational methodology included extensive sampling of conformational freedom, thermal corrections within the quasi rigid-rotor harmonic-oscillator approximation,[74] geometry optimization using the TPSS-D3[75–77] functional, and single-point calculations at the random-phase approximation (RPA) level.

Figure 5.4. Correlation plot of experimental and computed (using RPA/def2-TZVP/TPSS-D3-def2-TZVP) diastereoselectivities of the reaction of trisubstituted acetonide radicals formed from carboxylic acids **5.74** and **5.77** with (*R*)-5-methoxybutenolide (**5.58**).



The observed selectivity arose from the free energy difference between two transition states (TS), **TS-*anti*** and **TS-*syn*** (Figure 5.5), which led to the products of *anti* and *syn* addition respectively. In **TS-*anti***, the R^1 and R^2 substituents were *cis* to each other, and the butenolide **5.58** was on the sterically less hindered side of the acetonide radical; in **TS-*syn***, the R substituents were in a *trans* orientation and the butenolide **5.58** was on the sterically less favorable side of the radical.

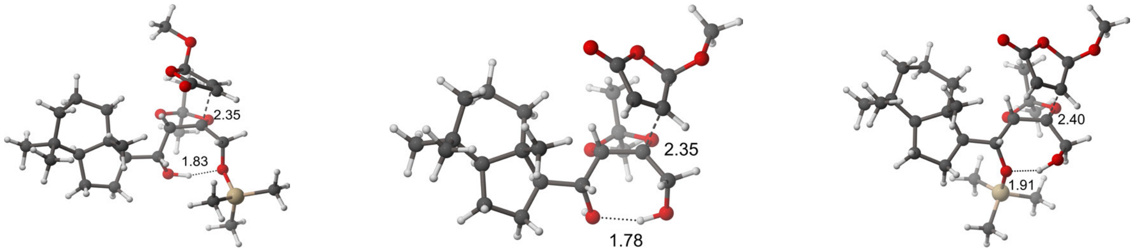
Figure 5.5. Transition state (TS) models for anti (**TS-*anti***) and syn (**TS-*syn***) additions. The arrow indicates non=covalent interactions, which can be attractive or repulsive.

Our results suggested that the selectivity was mainly determined by two effects: (1) non-covalent interactions between R^1 and R^2; and (2) non-covalent interactions between the acetonide radical and the butenolide **5.58**. The magnitude and sign of these interactions depended strongly on the size and functionalization of R^1 and R^2 on the acetonide radical.

For the reactions of trisubstituted acetonide radicals reported in Table 5.1, the repulsion between R^1 and R^2 dominated (effect 1) and *syn* stereoselectivity was observed. This conclusion was also supported by Renaud's experiments showing mostly *syn* addition when R^1 was a bulky *tert*-butyl group.[35a] Effect (2) was less important in these cases, because the butenolide **5.58** was at a distance of ~2.4 Å from the acetonide radical in the TS according to our computations. This result was also experimentally supported by the stereoselectivities observed in the reaction of acetonide radicals formed from **5.77C** and **5.77E**, which did not change qualitatively when (*R*)-5-methoxybutenolide (**5.58**) was replaced by methyl acrylate (**5.80**).

For the reactions of certain radicals reported in Table 5.2, hydrogen bonding could significantly stabilize **TS-*anti***.[78] This effect was illustrated by the lowest-energy **TS-*anti*** conformers for the coupling of radicals formed from **5.77B**, **5.77C** and **5.77D** (Figure 5.6), where the R-groups interact by a hydrogen-bond to form a seven-membered ring. The length of the H-bond correlated with the selectivity: it was the shortest for **5.77C**, which also had the highest *anti*-selectivity; and longest for **5.77D**, which favored *syn*-selectivity. In transition structure **5.77D-*anti***, the structure was also in general sterically more crowded, which explained the large *syn*-selectivity. However, apart from hydrogen bonding, other noncovalent interactions such as electrostatic, induction and dispersion interactions also affected the reaction stereoselectivity. Thus, quantitative predictions of reaction stereoselectivities required accurate computations of the energy and entropy of both proposed transition states. The computational analysis reported here rationalized all observed results for trisubstituted acetonide radicals, including why hydrogen bonding contributed significantly for **5.77C** but not for **5.77B** and **5.77D**.

Figure 5.6. The anti-transition states for reactions of acetonide radicals formed from **5.77B**, **5.77C**, and **5.77D** with butenolide **5.58** and their *anti*:*syn* selectivities.

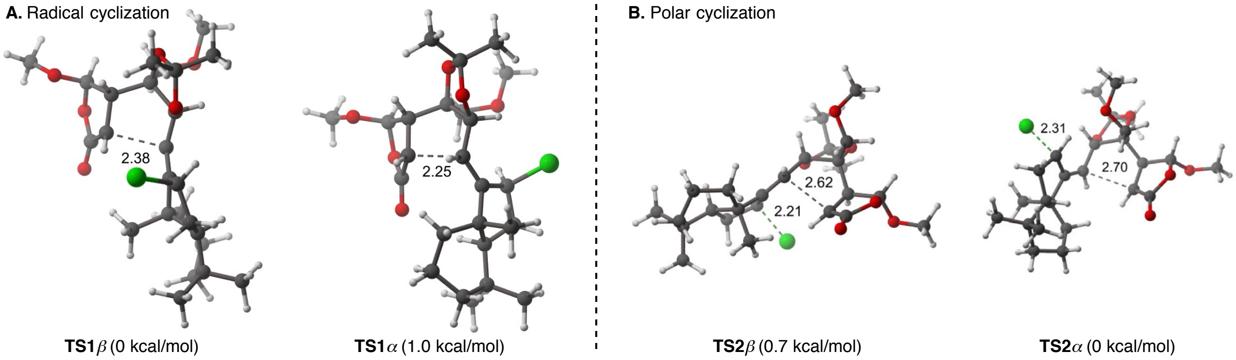


acid:	**5.77B**	**5.77C**	**5.77D**
length of H-bond:	1.83 Å	1.78 Å	1.91 Å
anti : *syn*:	1.3:1	9.1:1	1:7.0

The structures were optimized using TPSS-D3/def2-TZVP. The TBS-groups were replaced TMS-groups for computational simplicity.

With an accurate computational model for the addition of trisubstituted acetonide radicals to (*R*)-5-methoxybutenolide (**5.58**) in hand, we attempted to gain insight into the undesired selectivity of the 5-*exo* cyclization observed during the first-generation ACF cascade.[79] Two mechanistic scenarios for the 5-*exo* cyclization were considered: (1) direct cyclization of an α-acyl radical onto the pendant alkene (the scenario outlined in Figure 5.2 and Scheme 5.9), and (2) initial SET to the radical intermediate formed in the bimolecular coupling step, to form a lactone enolate that undergoes S_N2' cyclization. To identify the most likely pathway, energies and structures of diastereomeric transition states for both modes of cyclization were computed using the TPSS[72] functional and def2-TZVP basis sets[80] in combination with the BJ-damped D3-disperion correction (Figure 5.7).[75,77] In the case of the radical pathway, transition state **TS1β**, leading to the undesired C-8 epimer **5.62**, was found to be 1.0 kcal/mol (in CH_2Cl_2) or 0.5 kcal/mol (in MeCN) lower in energy than **TS1α** leading to epimer **5.63** having the C-8 configuration of (–)-chromodorolide B (**5.11**). The computed ratio of cyclized products **5.62**:**5.63** of 2.5:1 in MeCN agreed well with the experimentally observed ratio of 1.4:1 (Scheme 5.9, entry 5). In contrast, computed diastereomeric transition states for the alternative polar reaction pathway (enolate formation followed by S_N2' cyclization) found the alternate transition state (**TS2*α***) to be 0.7 kcal/mol (in MeCN) or 0.5 kcal/mol (in CH_2Cl_2) lower in energy than **TS2*β***, qualitatively disagreeing with experimental results. Although the energy differences of the computed diastereoisomeric transitions states in the two mechanisms are small, the radical pathway, which we considered the most plausible, was more consistent with the observed reaction outcome. As a result, further computational studies focused on this pathway.

Figure 5.7. Structures and energies of diastereoisomeric transition states of the 5-*exo* cyclization step of the ACF cascade.



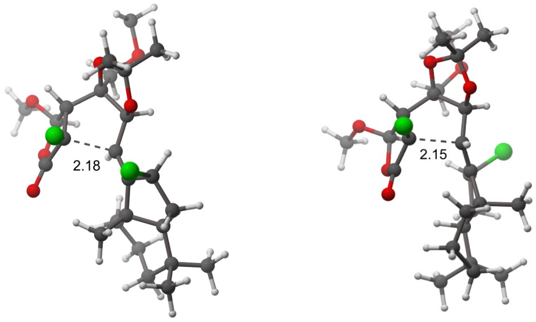
TS1*β* (0 kcal/mol) **TS1***α* (1.0 kcal/mol) **TS2***β* (0.7 kcal/mol) **TS2***α* (0 kcal/mol)

Values enclosed in parentheses are relative energies computed using the TPSS functional and def2-TZVP basis set (CH_2Cl_2 solvent); the values by the dotted line are the lengths of the forming C–C bond in Å. Diastereomeric transition structures labeled α lead to the formation of the configuration at C-8 found in (–)-chromodorolide B (**5.11**). Benzyloxy substituent at C-11 was replaced with methoxy group for computational simplicity.

Examination of the transition structures of the two diastereomeric transition states of the radical pathway (Figure 5.7A) was instructive. The lower-energy diastereomeric transition structure, **TS1*β***, had a longer forming bond (2.38 Å vs 2.25 Å) and a somewhat helical shape. Further analysis suggested a potential destabilizing steric interaction between the chloride of the hydrindane fragment and a substituent larger than hydrogen at the α-carbon of the butenolide fragment in a transition structure analogous to **TS1*β***. If the α-carbon of the butenolide carried a chloride or bromide substituent, the halogen substituents would clash in a helical structure such as **TS1*β***, yet would point in opposite directions in a structure such as **TS1*α***. In addition, introduction of a halogen atom would shift the transition states later by decreasing the nucleophilicity of the butenolide radical, which could further increase a destabilizing halogen-halogen interaction.

The computationally predicted lowest energy transition structures of the 5-*exo* radical cyclization step with (*R*)-3-chloro-5-methoxybutenolide are shown in Figure 5.8. As envisioned, the **TS3*β*** was affected significantly, with the forming C–C bond distance decreased from 2.38 Å to 2.18 Å. As a consequence, the kinetic barrier for forming the undesired *β*-configured product was increased from 7.9 kcal/mol to 11.3 kcal/mol. The forming bond in **TS3*α*** was also shortened slightly (from 2.25 Å to 2.15 Å) and the kinetic barrier slightly was increased from 8.9 kcal/mol to 9.4 kcal/mol. The transition state that would lead to the ACF product having the C-8 configuration of (–)-chromodorolide B (**5.11**), **TS3*α***, was predicted to be more stable by 2.0 kcal/mol.

Figure 5.8. Structures and energies of diastereoisomeric transition states of the 5-*exo* cyclization step of the ACF cascade when (*R*)-3-chloro-5-methoxybutenolide is employed.

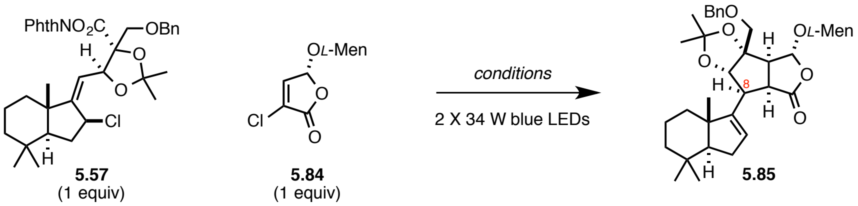


TS3*β* (2.0 kcal/mol) **TS3*α*** (0 kcal/mol)

Values enclosed in parentheses are relative energies computed using the TPSS functional and def2-TZVP basis set (CH_2Cl_2 solvent); the values by the dotted line are the lengths of the forming C–C bond in Å. Benzyloxy substituent at C-11 was replaced with methoxy group for computational simplicity.

We turned to explore this computational prediction by utilizing a 3-chlorobutenolide in the radical coupling step.[81] This possibility was particularly attractive, as we have shown previously that the addition of a 3-Cl substituent to a butenolide increases the yields of radical coupling reactions. Furthermore, the α-chloride substituent in a coupled product can be removed directly in the photoredox-catalyzed coupling step.[2b] Salient results of our investigation of the use of enantiopure 3-chlorobutenolide **5.84**[2b] in the ACF cascade are summarized in Table 5.3. Using the reaction conditions optimized earlier (entry 5, Scheme 5.9) and carrying out the reaction with 1 equiv of both *N*-acyloxyphthalimide **5.57** and chlorobutenolide **5.84**, followed by addition of *n*-Bu_3N and additional irradiation,[2b,77] provided a chlorinated ACF cascade product. Hypothesizing that under these conditions the dechlorination step was slow, the crude product after aqueous extraction was isolated and re-subjected to dechlorination using *n*-Bu_3N and, in place of $[Ru(bpy)_3](PF_6)_2$, the iridium photocatalyst, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$. This sequence provided a single ACF cascade product **5.85** in 41% yield (Table 5.3, entry 1). The pentacyclic C-8 epimer of **5.85** was not detectable by NMR analysis. Increasing the concentration of the reaction to 0.6 M led to ACF product **5.85** being formed in 58% yield (entry 2). We eventually found that the desired cascade sequence and dechlorination of the product could be accomplished in a single step utilizing $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as the sole photocatalyst (entry 3). The yield of **5.85** was similar using Hantzsch ester **5.59** (entry 4), which was expected as by-products resulting from premature quenching of the α-acyloxy radical intermediate had not been observed. In addition, we were able to use an organic photocatalyst, 4CzIPN,[83–85] in place of the Ir catalyst, giving the desired ACF cascade product in 54% isolated yield (entry 5). Thus, the computationally-guided structural modification of the butenolide coupling partner doubled the yield of the pivotal pentacyclic intermediate **5.85** and decreased the amount of butenolide acceptor required in this step by four-fold.

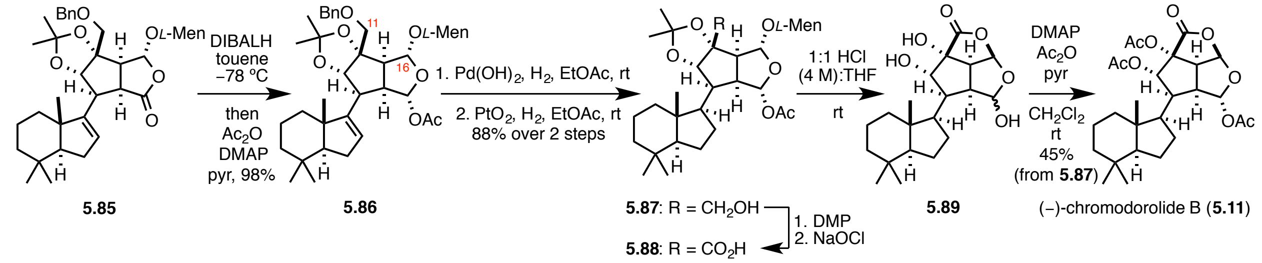
Table 5.3. Optimization of the fragment coupling between **5.57** and **5.84**.



entry	conditions	isolated yield
1	i. 2 mol % $[Ru(bpy)_3](PF_6)_2$, d_2-Hantzsch ester **5.59**, MeCN (0.1 M) ii. 2 mol % $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, *n*-$Bu_3N$, THF (0.1 M)	41%
2	i. 2 mol % $[Ru(bpy)_3](PF_6)_2$, d_2-Hantzsch ester **5.59**, MeCN (0.6 M) ii. 2 mol % $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, *n*-$Bu_3N$, THF (0.1 M)	58%
3	2 mol % $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, d_2-Hantzsch ester **5.59,** THF (0.6 M), then Bu_3N	56%
4	2 mol % $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, Hantzsch ester **5.59,** THF (0.6 M), then Bu_3N	57%
5	2 mol % 4CzIPN, Hantzsch ester **5.59**, THF (0.6 M), then Bu_3N	54%

With sufficient amounts of lactone **5.85** in hand, we elaborated it to (–)-chromodorolide B (**5.11**) by a seven-step sequence that paralleled the final steps of our first-generation synthesis (Scheme 5.13). Reduction of lactone functionality of **5.85** and *in situ* acetylation of the resulting aluminum hemiacetal intermediate with Ac_2O proceeded smoothly to deliver diacetal **5.86** in 98% yield. Deprotection of the primary alcohol proved challenging once again. Debenzylation of **5.86** employing the acidic transfer hydrogenolysis conditions developed during our first-generation synthesis of **5.11**, led to cyclization of the newly unveiled C-11 alcohol onto C-16 forming a bridging tetrahydrofuran ring. We were able to suppress this undesired cyclization by performing the reaction with basic $Pd(OH)_2$ and H_2.[86] Without purification, the trisubstituted alkene was reduced stereoselectively with PtO_2 to deliver saturated-pentacyclic product **5.87** in 88% over two steps. Finally, we successfully converted **5.87** to (–)-chromodorolide B (**5.11**) in 45% yield over four steps by the sequence of transformations employed in our first-generation synthesis.

Scheme 5.13. Synthesis of (–)-chromodorolide B (**5.11**) from ACF product **5.85**.



5.3 Conclusion

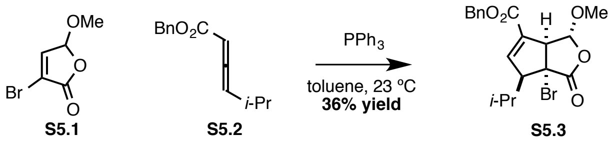
The structurally intricate marine diterpenoid (–)-chromodorolide B (**5.11**), which harbors 10 contiguous stereocenters and two ring fragments, has been synthesized for the first time. This total synthesis established the absolute configuration of the diterpenoid, which had previously been proposed on biogenetic grounds. The synthetic sequence featured a novel late-stage radical addition/cyclization/fragmentation (ACF) cascade that united two chiral fragments by forming two C–C bonds and four contiguous stereocenters in a single, highly stereoselective step. A notable feature of this late-stage fragment union was the use of the two coupling partners in equimolar amounts. The coupling step was initiated by visible-light photocatalytic fragmentation of a redox-active ester, which could be accomplished in the presence of 2 mol % of an iridium photocatalyst or 2 mol % of a less-precious electron-rich dicyanobenzene photocatalyst. The high degree of stereocontrol eventually realized in the cascade sequence was made possible by in-depth DFT computational modeling of the 5-*exo* cyclization step of the ACF cascade. Our second-generation total synthesis of (–)-chromodorolide B (**5.11**) proceeds in in 21 steps from commercially available (*S*)-enedione **5.44** in 3% overall yield. We anticipate that the results delineated in this chapter will find applications in future syntheses of other structurally intricate natural products.[87,88]

5.4 Experimental Information

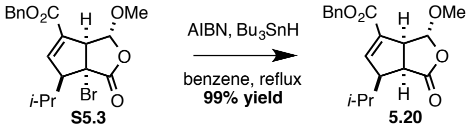
Materials and methods.

Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon. Tetrahydrofuran (THF), dichloromethane, methanol (MeOH), toluene, diethyl ether, toluene, benzene, triethylamine (Et_3N), and pyridine were dried by passage through activated alumina. Acetic anhydride (Ac_2O), tributyphsphine (*n*-Bu_3P), TBSOTf, and 2,6-lutidine were distilled under reduced pressure and stored in a Schlenk flask. Benzyloxymethyl chloride (BOM-Cl) distilled under Ar from CaH directly before use. 1,1,3,3-Tetramethylguanidine was distilled under Ar from barium oxide directly before use. Thionyl chloride was distilled from quinoline under Ar. All other commercial reagents were used as received unless otherwise noted. Hantzsch ester[89a] and its 4-dideutero derivative[89b] were prepared according to literature procedures. Reaction temperatures were controlled using a temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with silica gel 60 F254 pre-coated plates, (0.25 mm) and visualized by exposure to UV light (254 nm) or by *p*-anisaldehyde, ceric ammonium molybdate, and potassium permanganate staining ($KMnO_4$). Silica gel 60 (particle size 0.040–0.063mm) was used for flash column chromatography. ^1H NMR spectra were recorded at 500 or 600 MHz and are reported relative to deuterated solvent signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded at 126 or 151 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained with an LCT spectrometer. Optical rotation readings were obtained using JASCO P-1010 polarimeter. Blue LEDs (30 cm, 1 watt) were purchased from http://www.creativelightings.com (product code CL-FRS5050-12WP-12V) and powered by 8 AA batteries. Kessil KSH150B LED Grow Light 150, Blue (34 W blue LED lamps) was purchased from http://www.amazon.com. See JOC Standard Abbreviations and Acronyms for abbreviations (available at http://pubs.acs.org/paragonplus/submission/joceah/joceah_abbreviations.pdf).

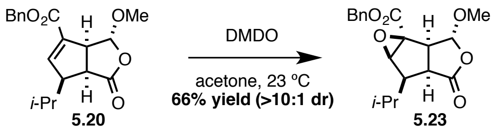
Preparation of the model system for initial dihydroxylation studies



Preparation of (*rac*)-lactone S5.3: A round-bottom flask was charged with **S5.1**[22,90] (1.88 g, 9.73 mmol, 1 equiv), benzene (40 mL, 0.24 M), **S5.2**[91] (3.20 g, 14.8 mmol, 1.5 equiv), and a magnetic stir bar under an atmosphere of argon. The resulting orange mixture was stirred vigorously for 30 min at 23 °C. The reaction mixture was then concentrated by use of a rotary evaporator and purified by flash chromatography on silica gel using 5:95 ethyl acetate:hexanes → 10:90 ethyl acetate:hexanes as eluent to afford lactone **S5.3** (1.44 g, 3.51 mmol, 36% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 6.87 (t, *J* = 2.0 Hz, 1H), 5.42 (d, *J* = 0.8 Hz, 1H), 5.32 (d, *J* = 12.3 Hz, 1H), 2.33 (oct., *J* = 6.6 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 162.3, 146.1, 135.1, 131.4, 128.7, 128.6, 128.4, 105.1, 66.9, 66.7, 64.0, 57.3, 53.4, 27.3, 23.3, 20.4; IR (thin film) 2962, 2934, 2872, 1786, 1716, 1640, 1456, 1388, 1350, 1269, 1247, 1219, 1173, 1111, 947 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{19}H_{21}O_5Br$ $[M+Na]^+$ 433.0452; observed 433.0446.

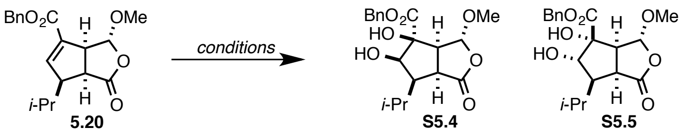


Preparation of (*rac*)-enoate 5.20: A round-bottom flask was charged with **S5.3** (1.44 g, 3.52 mmol, 1 equiv), benzene (35 mL, 0.1 M), *n*-Bu$_3$SnH (1.25 mL, 4.65 mmol, 1.3 equiv), AIBN (61 mg, 0.37 mmol, 0.1 equiv), and a magnetic stir bar under an atmosphere of argon. The resulting solution was heated to reflux for 15 min. The reaction mixture was then concentrated by use of a rotary evaporator and purified by flash chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to afford lactone **5.20** (1.15 g, 3.5 mmol, 99% yield) as a pale yellow solid. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40–7.34 (m, 5H), 6.96 (t, *J* = 2.1 Hz, 1H), 5.44 (d, *J* = 0.5 Hz, 1H), 5.29 (d, *J* = 12.3 Hz, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 3.66 (dt, *J* = 7.5, 2.5 Hz, 1H), 3.46 (s, 3H), 3.39 (dd, *J* = 8.6, 7.6, Hz, 1H), 2.82 (tdd, *J* = 8.8, 2.7, 2.2 Hz, 1H), 2.22–2.16 (m, 1H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 175.7, 163.7, 148.5, 135.7, 132.7, 128.8, 128.6, 128.4, 105.0, 66.8, 56.8, 56.2, 63.5, 43.0, 27.2, 23.2, 21.4; IR (thin film) 2959, 2925, 2870, 1777, 1713, 1628, 1456, 1348, 1270, 1154, 1108, 951 cm^{-1}; HMRS (ESI/TOF) *m/z* calculated for C$_{19}$H$_{22}$O$_5$ [M+Na]$^+$ 353.1365; observed 353.1351.



Preparation of (*rac*)-epoxide 5.23: A round-bottom flask was charged with **5.20** (51 mg, 0.156 mmol, 1 equiv), freshly prepared DMDO solution[92] (9 mL, 0.45 mmol, 0.05 M in acetone, 3 equiv), and a magnetic stir bar under an atmosphere of argon. The resulting solution was maintained at 23 °C for 4 h. The reaction mixture was then concentrated by use of a rotary evaporator and purified by flash chromatography on silica gel using 15:95 ethyl acetate:hexanes → 20:80 ethyl acetate:hexanes as eluent to afford epoxide **5.23** (36 mg, 0.11 mmol, 66% yield) as a clear oil. Crystallization of the oil from MeOH by slow evaporation afforded a crystal suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.34 (m, 5H), 5.38 (s, 1H), 5.28 (d, *J* = 12.3 Hz, 1H), 5.20 (d, *J* = 12.2 Hz, 1H), 3.85 (s, 1H), 3.47 (s, 3H), 3.25 (d, *J* = 7.8 Hz, 1H), 3.06 (t, *J* = 8.1 Hz, 1H), 2.43–2.35 (m, 1H), 2.09 (t, *J* = 9.9 Hz, 1H), 1.14 (d, *J* = 6.5 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 167.3, 134.9, 128.9, 128.5, 102.5, 67.9, 64.9, 61.4, 56.6, 52.0, 47.0, 39.0, 24.9, 23.2, 22.0; IR (thin film) 2961, 2921, 2870, 1779, 1732, 1456, 1284, 1247, 1159, 1112, 1050, 952, 758 cm^{-1}; HMRS (ESI/TOF) *m/z* calculated for $C_{19}H_{22}O_6$ $[M+Na]^+$ 369.1314; observed 369.1311; mp: 78–79 °C (crystallized from MeOH).

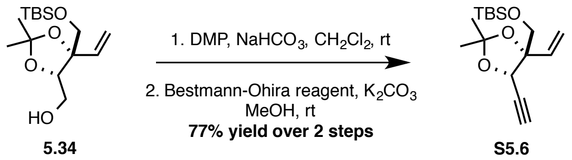
Table S5.1. Summary of reaction conditions for dihydroxylation of **5.20**.



entry	conditions	yield (**S5.4**:**S5.5**)[a]
1	OsO_4 (5 mol %), NMO or Me_3NO, various solvents	65–94% (85:15–95:5)
2	AD-mix α, $K_2Os_2(OH)_4$, $(DHQ)_2PHAL$	45% (>20:1)
3	$RuCl_3$, $NaIO_4$	100% (>20:1)
4	AgOAC, I_2, H_2O, AcOH, 90 °C	0% (NR)
5	$PhI(OAc)_2$, TfOH, AcOH	0% (acetal hydrolysis)
6	$KMnO_4$, NaOAc, MeOH	50% (>20:1)

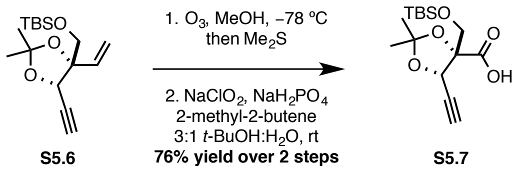
[a]Determined by ^{1}H NMR integration relative to an internal standard.

Preparation of the model system for the study of the facial selectivity of the reaction of a trisubstituted acetonide radical with butenolide 5.36

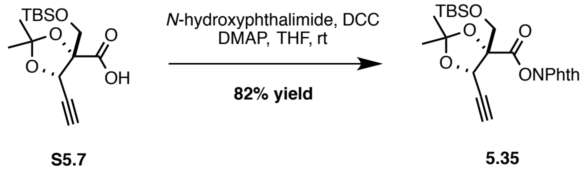


Preparation of alkyne S5.6: To a suspension of known alcohol **5.34**[37b] (732 mg, 2.42 mmol) and solid $NaHCO_3$ (1.01 g, 12.1 mmol) in CH_2Cl_2 (4 mL) was added Dess-Martin periodinane (1.23 g, 2.90 mmol). The reaction was vigorously stirred for 2 h, at which point the suspension was filtered through Celite and concentrated *in vacuo*. The residue was then washed with pentanes (4 x 8 mL), and the combined organic washes were filtered through Celite and concentrated *in vacuo* to afford the crude aldehyde as a yellow oil which was carried forward immediately.

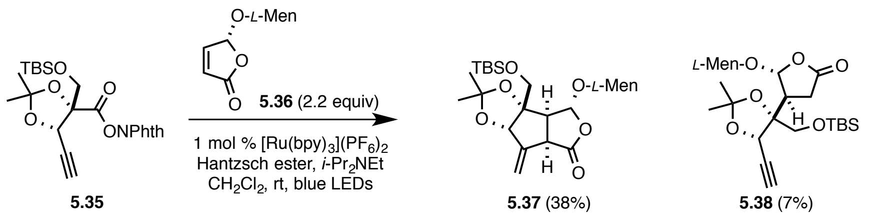
The crude aldehyde and dimethyl (1-azoacetonyl)phosphonate (0.558 g, 2.90 mmol) were dissolved in MeOH (9 mL). Solid K_2CO_3 (670 mg, 4.84 mmol) was then added, and the suspension was vigorously stirred for 2 h. Celite (~5 g) was added to the reaction vessel, and the reaction was concentrated *in vacuo.* Purification by flash column chromatography (5% EtOAc in hexanes to 7% EtOAc in hexanes) afforded alkyne **S5.6** (0.550 g, 1.86 mmol, 77% yield) as a clear oil, which solidified upon standing. R_f = 0.90 (20% EtOAc in hexanes; visualized with $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.53 (dd, *J* = 17.5, 1.6 Hz, 1H), 5.30 (dd, *J* = 10.9, 1.6 Hz, 1H), 4.99 (d, *J* = 2.1 Hz, 1H), 3.58 (d, *J* = 10.6 Hz, 1H), 3.55 (d, *J* = 10.7 Hz, 1H), 2.60 (d, *J* = 2.2 Hz, 1H), 1.54 (s, 3H), 1.43 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 116.7, 110.3, 85.8, 79.3, 77.1, 69.7, 65.4, 27.9, 27.0, 26.0, 18.4, –5.2, –5.5; IR (thin film) 3312, 2988, 2955, 2858, 1741, 1378, 1253 cm^{-1}; $[\alpha]^{25}_{D}$ +0.79 (c = 2.5, CH_2Cl_2); HRMS (ESI) calculated for $C_{16}H_{29}O_3Si$ (M+H) 297.1887, observed 297.1890; mp 39–41 °C.



Preparation of carboxylic acid S5.7: A solution of alkyne **S5.6** (0.553 g, 1.87 mmol) in methanol (8 mL) was cooled to –78 °C. Ozone from an ozone generator was bubbled through the solution until a pale blue color was observed (~5 min). The solution was then sparged with oxygen until the pale blue color disappeared. Dimethyl sulfide (0.31 mL, 4.3 mmol) was added to the solution, which was maintained at –78 °C for 1 h. The reaction vessel was allowed to warm to 23 °C and concentrated *in vacuo*. The residue was then redissolved in a 3:1 solution of *t*-BuOH:H_2O (8 mL). A solution of 2-methyl-2-butene (2.0 mL, 19 mmol) was added to the mixture, followed by NaH_2PO_4 (1.80 g, 15.0 mmol) and $NaClO_2$ (0.845 g, 9.35 mmol). The reaction was maintained at 23 °C for 2 h, at which point H_2O (4 mL) was added. This mixture was washed with EtOAc (3 x 10 mL), and the combined organic layers were washed with aq. NaOH (5 mL of 0.5 M soln). The aqueous layer was then acidified with aq. HCl (7 mL of 0.5 M soln). The aqueous layer was then washed with EtOAc (3 x 10 mL), and the combined organic layers were washed with brine (1 x 10 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to provide acid **S5.7** as a clear oil (0.450 g, 1.43 mmol, 76% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 4.97 (d, *J* = 2.3 Hz, 1H), 3.94 (d, *J* = 11.0 Hz, 1H), 3.92 (d, *J* = 11.0 Hz, 1H), 2.63 (d, *J* = 2.2 Hz, 1H), 1.67 (s, 3H), 1.47 (s, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 113.3, 88.2, 77.7, 69.0, 63.6, 26.99, 26.97, 26.0, 18.5, 14.3, –5.3, –5.5; IR (thin film) 3505, 3277, 2990, 2931, 2858, 1731, 1379 cm^{-1}; $[\alpha]^{25}_{D}$ –30.0 (c = 2.1, CH_2Cl_2); HRMS (ESI) calculated for $C_{15}H_{25}O_5Si$ (M–H) 313.1471, observed 313.1467.



Preparation of *N*-acyloxyphthalimide 5.35: Acid **S5.7** (0.453 g, 1.44 mmol) was charged into a flask with THF (8 mL). Next, *N*-hydroxyphthalimide (0.399 g, 2.45 mmol), *N,N*'-dicycylohexylcarbodiimide (0.446 g, 2.16 mmol), and 4-dimethylaminopyridine (9 mg, 0.07 mmol) were added to the reaction vessel, which was maintained at 23 °C for 20 h. Hexanes (5 mL) was added to the reaction, and the resulting suspension was filtered through Celite. The yellow filtrate was concentrated *in vacuo* and then purified by flash column chromatography (10% EtOAc in hexanes to 15% EtOAc in hexanes) to provide *N*-acyloxyphthalimide **5.35** (0.539 g, 1.18 mmol, 82% yield) as a colorless crystalline solid. R_f = 0.25 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (m, 2H), 7.78 (m, 2H), 5.14 (d, *J* = 2.2 Hz, 1H), 4.10 (d, *J* = 11.5 Hz, 1H), 4.07 (d, *J* = 11.3 Hz, 1H), 2.78 (d, *J* = 2.2 Hz, 1H), 1.71 (s, 3H), 1.50 (s, 3H), 0.93 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 161.4, 134.9, 129.1, 124.1, 113.5, 88.1, 78.8, 76.3, 68.8, 62.8, 26.7, 26.6, 26.0, 18.5, –5.2, –5.5; IR (thin film) 3283, 2930, 2855, 2360, 2340, 2118, 1789, 1748 cm^{-1}; $[\alpha]^{25}_{D}$ +38.3 (c = 2.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{23}H_{29}NO_7SiNa$(M+Na) 482.1611, observed 482.1612; mp 105–109 °C.

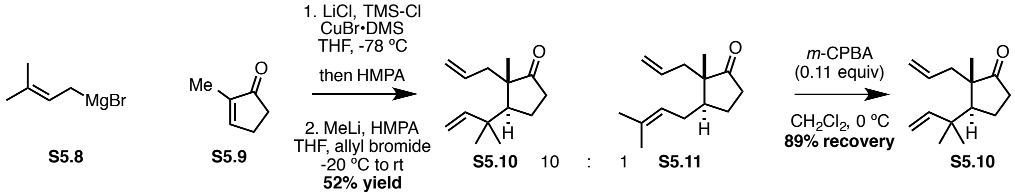


Preparation of lactones 5.37 and 5.38: To a 1-dram vial charged with *N*-acyloxyphthalimide **5.35** (100 mg, 0.218 mmol) was added CH_2Cl_2 (2 mL) that had been separately sparged with argon. Next, butenolide **S3**[29] (78 mg, 0.33 mmol), Hantzsch ester (82 mg, 0.63 mmol), $Ru(bpy)_3(PF_6)_2$ (2 mg, 0.02 mmol), and Hünig's base (80 µL, 0.48 mmol) were added to the reaction. The vial was then vigorously stirred while being irradiated by a single strip of blue LED lights (450 nm) at 23 °C. After 6 h, the reaction mixture was diluted with hexanes (2 mL) and filtered through Celite. The resulting solution was then concentrated *in vacuo* and separated by flash column chromatography (3% EtOAc in hexanes to 5% EtOAc in hexanes) to provide lactone **5.37** (42 mg, 0.083 mmol, 38% yield) as a colorless, crystalline solid and addition product **5.38** (7.5 mg, 0.015 mmol, 7% yield) as a clear oil. A single crystal X-ray structure of lactone **5.37** was obtained after recrystallization in MeOH:hexanes to confirm structural assignment.[25b] R_f for **5.37**: 0.65 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate). R_f for **5.38**: 0.60 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate).

5.37: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (d, *J* = 2.6 Hz, 1H), 5.62 (dd, *J* = 2.3, 1.0 Hz, 1H), 5.50 (dd, *J* = 2.7, 0.8 Hz, 1H), 4.73 (app s, 1H), 3.96–3.92 (m, 1H), 3.86 (d, *J* = 10.7 Hz, 1H), 3.77 (d, *J* = 10.8 Hz, 1H), 3.51 (dt, *J* = 10.6, 4.3 Hz, 1H), 3.07 (dd, *J* = 10.3, 2.3 Hz, 1H), 2.14–2.03 (m, 2H), 1.69–1.60 (m, 2H), 1.47 (s, 3H), 1.40–1.32 (m, 4H), 1.27–1.16 (m, 2H), 1.04–0.93 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.90–0.80 (m, 13H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1, 143.3, 116.6, 112.7, 99.7, 90.8, 86.9, 77.2, 64.4, 57.4, 48.2, 47.9, 40.0, 34.4, 31.5, 28.4, 27.0, 25.9, 25.5, 23.2, 22.4, 21.0, 18.4, 15.8, –5.4, –5.5; IR (thin film) 2953, 2929, 2858, 1779, 1461 cm^{-1}; $[\alpha]^{25}_{D}$ –133 (c = 1.9, CH_2Cl_2); HRMS (ESI) calculated for $C_{28}H_{48}O_6SiNa$ (M+Na) 531.3118, observed 531.3126; mp 136–142 °C.

5.38: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (d, J = 2.2 Hz, 1H), 4.59 (d, J = 2.2 Hz, 1H), 3.98 (d, J = 10.7 Hz, 1H), 3.75 (d, J = 10.7 Hz, 1H), 3.52 (dt, J = 10.9, 4.4 Hz, 1H), 2.82–2.65 (m, 3H), 2.58 (d, J = 2.3 Hz, 1H), 2.17–2.04 (m, 2H), 1.69–1.59 (m, 2H), 1.50 (s, 3H), 1.38 (s, 3H), 1.37–1.32 (m, 1H), 1.27–1.17 (m, 2H), 0.99 (app qd, J = 12.5, 3.3 Hz, 1H), 0.91 (d, J = 6.9 Hz, 3H), 0.90 (s, 9H), 0.87 (d, J = 7.0 Hz, 3H), 0.86–0.81 (m, 1H), 0.77 (d, J = 7.0 Hz, 3H), 0.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 110.0, 100.8, 83.8, 78.8, 77.2, 76.7, 71.6, 64.4, 47.9, 46.9, 39.9, 34.5, 31.5, 29.8, 28.2, 27.1, 26.0, 25.6, 23.2, 22.4, 21.0, 18.4, 15.8, –5.4, –5.5; IR (thin film) 3311, 3262, 2955, 2929, 2858, 1791, 1462, 1374, 1252 cm^{-1}; $[\alpha]^{25}_{D}$ –93.7 (c = 1.2, CH_2Cl_2); HRMS (ESI) calculated for $C_{28}H_{48}O_6SiNa$ (M+Na) 531.3118, observed 531.3131.

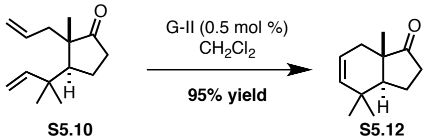
Modified Snapper route to hydrindanone (+)-5.31



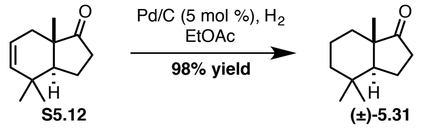
Preparation of (*rac*)-ketone S5.10: The procedure for preparation of **S5.10** was a modification from the literature.[30a] A round-bottom flask was charged with CuBr•DMS (14.4 g, 75.5 mmol, 1.5 equiv), anhydrous LiCl (4.26 g, 101 mmol, 2 equiv), THF (130 mL, 0.4 M), and a magnetic stir bar under an atmosphere of argon. After maintaining the solution at 23 °C for 15 min, the flask was cooled to –78 °C. A solution of prenyl magnesium bromide[93] **S5.8** (63 mmol, 290 mL, 0.22 M in THF, 1.25 equiv) was added slowly over 15 min. After maintaining the reaction at –78 °C for 15 min, TMS-Cl (12.7 mL, 101 mmol, 2 equiv) was added dropwise, followed immediately by 2-methyl-cyclopent-2-enone **S5.9** (4.84 g, 50.3 mmol, 1 equiv) in THF (5 mL). The reaction was maintained at –78 °C for 1 h, and then HMPA (17.5 mL, 101 mmol, 2 equiv) was added. After 1 h, Et_3N (15.4 mL, 111 mmol, 2.2 equiv) was added, and the reaction was then warmed to 0 °C over 1 h. The reaction was diluted with Et_2O (200 mL), and ice-cold 10% aq. NH_4Cl solution (200 mL) was added. Upon separation of the mixture, the organic layer was washed with ice-cold 10% aq. NH_4Cl solution (3 x 100 mL). The organic layer was then dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator to provide enoxysilane as a yellow oil.

A round-bottom flask was charged with crude enoxysilane, THF (150 mL, 0.33 M), and a magnetic stir bar under an atmosphere of argon. Upon cooling the resulting solution to –20 °C, MeLi (33.5 mL, 50.3 mmol, 1.50 M in hexanes, 1 equiv) was added at a rate which kept the reaction temperature below –10 °C. The reaction was then allowed to warm to 23 °C over 1 h. Upon cooling the reaction to –78 °C, HMPA (35 mL, 201 mmol, 4 equiv) was added and the reaction was maintained at –78 °C for 15 min. Freshly distilled allyl bromide (21.8 mL, 252 mmol, 5 equiv) was added to the reaction flask, which was allowed to warm to 23 °C over 6 h. The reaction was quenched with sat. aq. NH_4Cl (200 mL), and the resulting aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine (150 mL), dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator. Purification of the resulting residue by flash chromatography on silica gel using 0:100 diethyl ether:hexanes → 3:97 diethyl ether:hexanes as eluent to provide a mixture of ketones **S5.10** and **S5.11** as a clear oil (5.38 g, 26.1 mmol, 10:1 ratio, 52% yield).

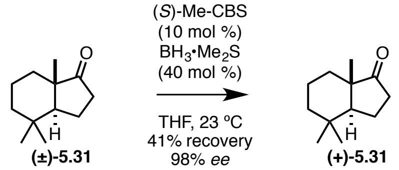
A round-bottom flask was charged with ketones **S5.10** and **S5.11** (14.9 g, 72.1 mmol, 10:1 ratio, 1 equiv), CH_2Cl_2 (150 mL, 0.5 M), and a magnetic stir bar under an atmosphere of argon. Upon cooling to 0 °C, *m*-CPBA (1.83 g, 7.93 mmol, 0.11 equiv) was added. The reaction was maintained at 0 °C for 1 h. The reaction was the concentrated by use of a rotary evaporator and directly purified by flash chromatography on silica gel using 6:94 diethyl ether:hexanes as eluent to afford ketone **S5.10** (13.3 g, 64.6 mmol, 89% recovery) as a clear oil. Spectral data was consistent with reported values.[30a]



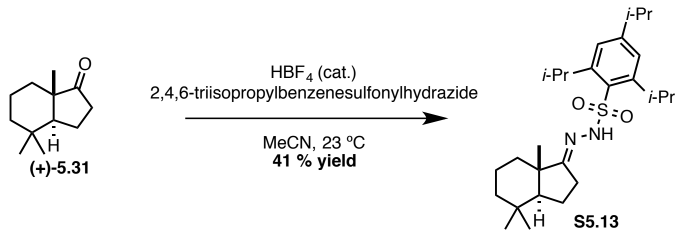
Preparation of (*rac*)-ketone S5.12: The procedure for preparation of **S5.12** was a slight modification from the literature.[30a] A round-bottom flask was charged with **5.10** (3.26 g, 15.8 mmol, 1 equiv), CH_2Cl_2 (80 mL, 0.2 M), Grubb's GII catalyst (67 mg, 0.079 mmol, 0.005 equiv), and a magnetic stir bar under an atmosphere of argon. The reaction was maintained for 16 h, at which point silica gel (~3 g) was added. Upon stirring for 30 min, the suspension was concentrated by use of a rotary evaporator and filtered over Celite with Et_2O (20 mL). Concentration by use of a rotary evaporator and distillation (195 °C, 10 torr) provided ketone **S5.12** (2.68 g, 15.0 mmol, 95% yield) as a clear oil. Spectral data was consistent with reported values.[30a]



Preparation of (*rac*)-ketone 5.31: The procedure for preparation of (±)-**5.31** was a slight modification from the literature.[30a] A round bottom-flask was charged with 10% Pd/C (1.59 g, 1.50 mmol, 0.1 equiv), ketone **S5.12** (2.68 g, 15.0 mmol, 1 equiv), EtOAc (60 mL), and a magnetic stir bar. The reaction vessel was evacuated and backfilled with H_2 (3x). The reaction was maintained at 23 °C for 20 h before purging the vessel of H_2. The black suspension was filtered over Celite with EtOAc (30 mL). Upon concentration, (±)-**5.31** (2.65 g, 14.7 mmol, 98% yield) was isolated as a colorless, amorphous solid. Spectral data was consistent with reported values.[30a]

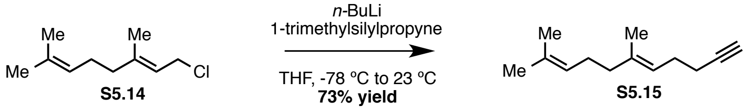


Preparation of (+)-ketone 5.31: The procedure for preparation of (+)-**5.31** was a slight modification from the literature.[30a] A round-bottom flask was charged with (*S*)-1-methyl-3,3-diphenyl-tetrahydro-pyrrolo[1,2*c*][1,3,2]oxazaborole (0.86 mL, 0.86 mmol, 1.0 M in toluene, 0.1 equiv), THF (40 mL, 0.22 M), BH_3•Me_2S (325 μL, 3.44 mmol, 0.4 equiv), and a magnetic stir bar under an atmosphere of argon. After 15 min at 23 °C, (±)-**5.31** (1.55 g, 8.60 mmol, 1 equiv) in THF (40 mL, 0.22 M) was added rapidly in a single potion. After 2 min, MeOH (40 mL) and aq. HCl (40 mL of 1 M soln) were added to quench the reaction, followed by Et_2O (100 mL) and H_2O (50 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator. Purification by flash chromatography on silica gel using 5:95 diethyl ether:hexanes → 15:85 diethyl ether:hexanes as eluent afforded ketone (+)-**5.31** (650 mg, 3.6 mmol, 98% *ee*, 42% recovery) as a colorless, amorphous solid. Spectral data was consistent with reported values.[30a] *ee* was determined by chiral HPLC analysis of corresponding hydrazone **S5.13** (*vide infra*).

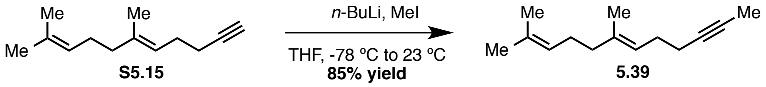


Preparation of hydrazone S5.13: The procedure for preparation of hydrazone **S5.13** was repeated from literature.[30a] A round-bottom flask was charged with (+)-**5.31** (105 mg, 0.582 mmol, 1 equiv) 2,4,6-triisopropylbenzenesulfonylhydrazide (182 mg, 0.611 mmol, 1.05 equiv), MeCN (3 mL, 0.2 M), and a magnetic stir bar under an atmosphere of argon. The suspension was vigorously stirred for 15 min before one drop of HBF_4 was added to the suspension (which immediately became a homogeneous solution). The reaction was maintained for 14 h before addition of Et_2O (2 mL). The crude reaction mixture was dried over silica gel (~2 g) and purified by flash column chromatography on silica gel using 10:90 diethyl ether:hexanes → 20:80 diethyl ether:hexanes to provide hydrazone **S5.13** as a colorless solid (0.110 g, 0.238 mmol, 41% yield). Spectral data was consistent with reported values.[30a] HLPC analysis was used to determine enantiomeric ratios to be 99:1 (Chiracel OD-H column; flow: 1.0 mL/min, 1% isopropanol:*n*-hexane; λ = 254 nm; minor enantiomer t_R = 13.65 min, major enantiomer t_R = 21.34 min).

Enantioselective proton-initiated polycyclization route to hydrindanone (+)-5.31

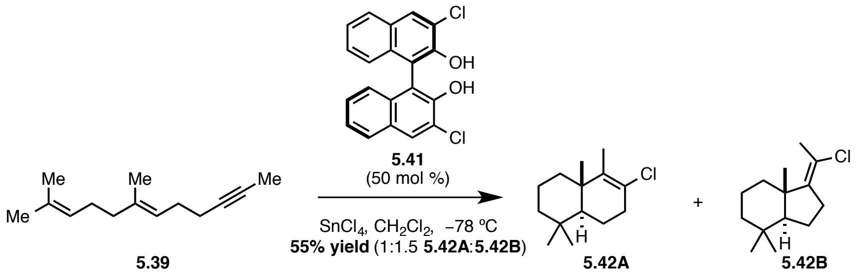


Preparation of dieneyne S5.15: The procedure for preparation of **S5.15** was a modification from the literature.[94] A round-bottom flask was charged with 1-trimethylsilyl-propyne (2.96 g, 26.4 mmol, 1.2 equiv), THF (100 mL, 0.22M), and a magnetic stir bar under an atmosphere of argon. Upon cooling the solution to –78 °C, *n*-BuLi (30.8 mmol, 11.8 mL, 2.5 M in hexanes, 1.4 equiv) was added slowly, and the reaction was then warmed to 0 °C over 1 h. The reaction was cooled to –78 °C, and geranyl chloride **S5.14** (3.8 g, 22 mmol, 1 equiv) was added. The reaction was allowed to warm to 23 °C over 16 h. The reaction vessel was then cooled to –78 °C, and TBAF (28.6 mmol, 28.6 mL, 1.0 M in THF, 1.3 equiv) was then added. The reaction was allowed to warm to 23 °C before diluting with H_2O (50 mL). The aqueous layer was extracted with hexanes (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator. The resulting oil was purified by flash chromatography on silica gel using 100% hexanes as eluent to provide **S5.15** as a clear oil (2.85 g, 16.1 mmol, 73% yield). Spectral data was consistent with reported values.[94]

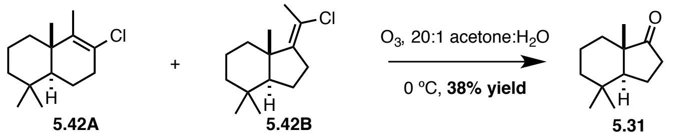


Preparation of dieneyne 5.39: A round-bottom flask was charged with dieneyne **S5.15** (2.17 g, 12.3 mmol, 1 equiv), THF (120 mL, 0.1 M), and a magnetic stir bar under an atmosphere of argon. Upon cooling the solution to –78 °C, *n*-BuLi (18.5 mmol, 7.10 mL, 2.5

M in hexanes, 1.5 equiv) was added slowly to the reaction, which was then warmed to 0 °C. After 10 min, the reaction was cooled to –78 °C, and methyl iodide (8.73 g, 61.5 mmol, 5 equiv) was added. The reaction was then allowed to warm to 23 °C over 2 h. The reaction was quenched with saturated aq. NH_4Cl (50 mL). The aqueous layer was extracted with hexanes (3 x 50 mL), and the combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator. The resulting residue was purified by flash chromatography on silica gel using 100% hexanes as eluent to provide dieneyne **5.39** as a clear oil (1.99 g, 10.5 mmol, 85% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 5.16 (dt, *J* = 6.6, 1.2 Hz, 1H), 5.09 (tt, *J* = 6.9, 1.3 Hz,1H), 2.20–2.10 (m, 4H), 2.09–2.02 (m, 2H), 2.01–1.94 (m, 2H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.68 (s, 3H), 1.61 (app s, 3H), 1.60 (app s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 131.5, 124.4, 123.1, 79.4, 75.5, 39.8, 27.9, 26.8, 25.8, 19.4, 17.8, 16.2, 3.6; IR (thin film) 2966, 2918, 2855, 1443, 1377 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{22}$ $[M+NH_4]^+$ 207.0633; observed 208.2067.



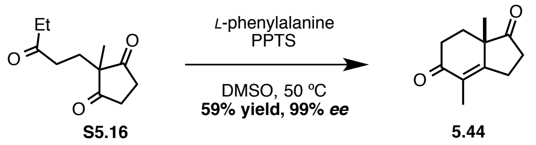
Preparation of vinyl chlorides 5.42A and 5.42B: (Procedure for entry 3 from Scheme 5.4). To a solution of *o,o'*-dichloro-(*R*)-BINOL **5.41**[95] (357 mg, 1.25 mmol, 0.5 equiv) in CH_2Cl_2 (6.5 mL, 0.38 M) at –78 °C was added $SnCl_4$ (1.25 mL, 1.25 mmol, 1.0 M in CH_2Cl_2, 0.5 equiv) dropwise. After 15 min, a solution of dieneyne **5.39** (475 mg, 2.49 mmol, 1 equiv) in CH_2Cl_2 (6.5 mL, 0.38 M) cooled to –78 °C was added via cannula to the reaction. Upon full consumption of dieneyne **5.39** (monitored by TLC), saturated aq. NH_4Cl (5 mL) was added, and the reaction was allowed to warm to 23 °C. The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator. The resulting residue was concentrated over silica gel (~1 g) and then purified by flash column chromatography on silica gel using 100% hexanes as eluent to provide an inseparable mixture of vinyl chlorides **5.42A** and **5.42B** as a clear oil (310 mg, 1.37 mmol, 55% yield) in a 1:1.5 ratio by ^{1}H NMR. Diagnostic peaks for 6-*endo* product **5.42A** in ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.72 (app t, *J* = 2.1 Hz, 3H), 1.01 (s, 3H); diagnostic peaks for 6-*endo* product **5.42A** in ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.3, 127.1; diagnostic peaks for 5-*exo* product **5.42B** in ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (app t, *J* = 2.0 Hz, 3H), 0.99 (s, 3H); diagnostic peaks for 5-*exo* product **5.42B** in ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 120.8. IR (thin film) 2949, 2866, 1665, 1458, 1378 cm^{-1}; HRMS (ESI/TOF) *m/z* calculated for $C_{14}H_{23}Cl$ $[M^+]^+$ 226.1488; observed 226.1497.



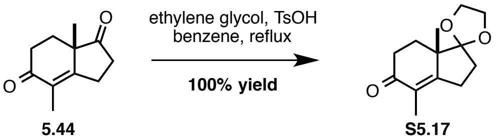
Preparation of ketone 5.31 from vinyl chlorides 5.42A and 5.42B: A 1:1.5 mixture of vinyl chlorides **5.42A** and **5.42B** (303 mg, 1.42 mmol, 1 equiv) were dissolved in acetone (10 mL, 0.14 M) and H_2O (0.5 mL, 2.84 M) and cooled to 0 °C. Ozone was passed through the solution until TLC analysis indicated complete consumption of starting material. The solution was sparged with O_2 and then concentrated over silica gel (~1 g) by use of a rotary evaporator. Purification by flash column chromatography on silica gel using 5:95 diethyl ether:hexanes → 15:85 diethyl ether:hexanes as eluent provided ketone **5.31** as a clear oil

(91 mg, 0.50 mmol, 38% yield). Spectral data was consistent with reported values.[30a] *ee* was determined to be –18% by chiral HPLC of corresponding hydrazone **S5.13**.[30a]

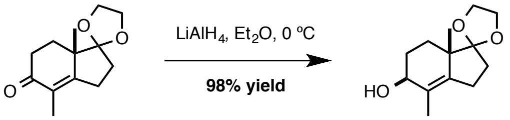
Experimental procedures for the first-generation synthesis of (–)-chromodorolide B



Preparation of ketone 5.44: (*S*)-enone was prepared according to a literature procedure.[50] A 100 mL round-bottom flask was charged with 2-methyl-2-(3-oxopentyl)cyclopetane-1,3-dione **S5.16** (39.6 g, 202 mmol), followed by the addition of *L*-phenylalanine (10 g, 61 mmol), PPTS (25.3 g, 101 mmol), and DMSO (14 mL, 200 mmol). The heterogeneous reaction mixture was then sonicated for 36 h at 50 °C. The mixture was transferred into a separatory funnel with EtOAc (500 mL), followed by the addition of H_2O (500 mL). The two layers were separated and the aqueous phase was extracted with EtOAc (3 x 500 mL). The combined organic extracts were washed sequentially with aq. HCl (1 x 500 mL of 1 M soln), sat. aq. $NaHCO_3$ (1 x 500 mL), and brine (1 x 500 mL). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo* to yield a viscous red oil. The resulting oil was filtered through a silica gel plug (100 g SiO_2) with 30% EtOAc in hexanes (1 L) to afford 32.7 g of crude (+)-**5.44** as an orange oil. R_f = 0.23 (30% EtOAc in hexanes; visualized with *p*-anisaldehyde). The resulting oil was crystallized from Et_2O (23 mL) at –20 °C utilizing a seed crystal (obtained via crystallization from Et_2O:benzene at –20 °C) to provide (+)-**5.44** as an off-white crystalline solid (21.3 g, 120 mmol, 59% yield, 99% *ee*). Spectral data were consistent with reported values.[50] The enantiomeric excess was determined by chiral stationary-phase HPLC analysis (Chiracel OB-H column; flow: 2.0 mL/min, 20% isopropanol:*n*-hexane; λ = 254 nm; minor enantiomer t_R = 5.86 min, major enantiomer t_R = 7.25 min).

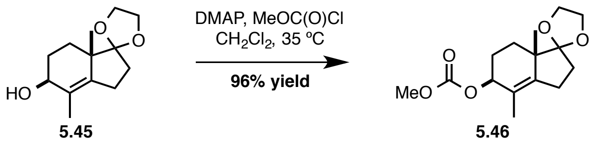


Preparation of ketal S5.17: A 2 L round-bottom flask was charged with enone (+)-**5.44** (7.7 g, 43 mmol), followed by the addition of benzene (860 mL), ethylene glycol (2.9 mL, 52 mmol), and *p*-TsOH•H_2O (1.6 g, 8.6 mmol). A Dean-Stark apparatus was fitted to the flask, and the homogeneous reaction mixture was maintained at reflux overnight. Upon completion of the reaction, as indicated by TLC analysis (40% EtOAc in hexanes; visualized with *p*-anisaldehyde), the mixture was cooled to 0 °C and sat. aq. $NaHCO_3$ (300 mL) was added. The resulting biphasic mixture was separated and the aqueous layer was extracted with Et_2O (3 x 200 mL). The combined organic layers were washed with brine (1 x 500 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow oil. The crude residue was purified by flash column chromatography (20% EtOAc in hexanes) to yield **S5.17** as a yellow oil (9.6 g, 43 mmol, 100% yield). R_f = 0.45 (40% EtOAc in hexanes; visualized with *p*-anisaldehyde). ^1H NMR (600 MHz, $CDCl_3$) δ 4.04–3.91 (m, 4H), 2.58–2.51 (m, 2H), 2.43 (dd, *J* = 5.4, 3.6 Hz, 1H), 2.28 (td, *J* = 13.2, 5.4 Hz, 1H), 2.20–2.16 (m, 1H), 1.95–1.91 (m, 1H), 1.68 (s, 3H), 1.61–1.58 (m, 1H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 167.1, 129.0, 118.0, 65.9, 65.1, 47.7, 33.2, 31.9, 26.8, 26.0, 20.5, 10.8; IR (thin film) 2953, 2881, 1660, 1451, 1153 cm^{-1}; $[\alpha]^{21}_D$ −7.79 (*c* = 1.6, CH_2Cl_2); HRMS (ESI) calculated for $[C_{13}H_{18}O_3Na]^+$ (M+Na) 245.1154, observed 245.1163.

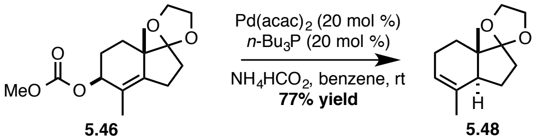


S5.17 **5.45**

Preparation of allylic alcohol 5.45: A 1 L round-bottom flask was charged with enone **S5.17** (9.6 g, 43 mmol), followed by the addition of Et$_2$O (310 mL). The solution was cooled to –78 °C. A solution of LiAlH$_4$ (65 mL of 1 M in Et$_2$O, 65 mmol) was added dropwise. The homogeneous solution was warmed to 0 °C and maintained at that temperature until TLC analysis (40% EtOAc in hexanes; visualized with *p*-anisaldehyde) indicated complete consumption of the starting material, typically 10–20 min. Upon completion of the reaction, sat. aq. Rochelle's salt (150 mL) was slowly added. The biphasic mixture was stirred vigorously for 30 min at 0 °C. The solution was then transferred to a separatory funnel and extracted with Et$_2$O (3 x 150 mL). Combined organic layers were washed with brine (1 x 500 mL), dried over MgSO$_4$, and concentrated *in vacuo* to yield a colorless solid. The crude residue was purified by flash column chromatography (30% EtOAc in hexanes) to yield **5.45** as a colorless, crystalline solid (9.5 g, 42 mmol, 98% yield). R_f = 0.25 (40% EtOAc in hexanes; visualized with *p*-anisaldehyde). ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.14–4.12 (m, 1H), 3.96–3.86 (m, 4H), 2.33–2.30 (m, 2H), 2.13–2.06 (m, 2H), 1.87–1.78 (m, 2H), 1.71–1.62 (m, 4H), 1.35–1.31 (m, 2H), 1.14 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 141.4, 127.9, 118.5, 71.7, 65.7, 64.9, 46.7, 32.1, 30.1, 26.6, 24.0, 22.5, 14.6; IR (thin film) 3411, 2947, 2873, 1642, 1149 cm^{-1}; $[\alpha]^{21}_D$ –32.0 (*c* = 1.8, CH$_2$Cl$_2$); HRMS (ESI) calculated for [C$_{13}$H$_{20}$O$_3$] (M) 224.1413, observed 224.1406; mp 86–88 °C.

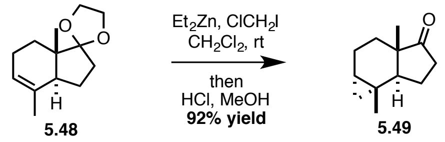


Preparation of allylic carbonate 5.46: A 1 L round-bottom flask was charged with allylic alcohol **5.45** (9.5 g, 42 mmol), followed by the addition of DMAP (15.0 g, 126 mmol), CH_2Cl_2 (420 mL), and methyl chloroformate (13 mL, 170 mmol). The resulting homogeneous solution was maintained at 35 °C until TLC analysis (30% EtOAc in hexanes; visualized with *p*-anisaldehyde) indicated complete consumption of the starting material, typically 30–90 min. Upon completion of the reaction, the mixture was cooled to room temperature, followed by the addition of sat. aq. NH_4Cl (200 mL). Next, the solution was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 200 mL). The combined organic layers were washed with brine (1 x 500 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a colorless solid. The crude residue was purified by flash column chromatography (10% EtOAc in hexanes) to yield **5.46** as a colorless, crystalline solid (11.4 g, 40.4 mmol, 96% yield). R_f = 0.35 (20% EtOAc in hexanes; visualized with *p*-anisaldehyde). ^1H NMR (600 MHz, $CDCl_3$) δ 5.19 (app t, *J* = 7.8 Hz, 1H), 3.96–3.87 (m, 4H), 3.79 (s, 3H), 2.34 (t, *J* = 7.8 Hz, 2H), 2.24–2.20 (m, 1H), 2.12–2.07 (m, 1H), 1.89 (td, *J* = 14.4, 3.0 Hz, 1H), 1.84–1.77 (m, 2H), 1.57 (s, 3H), 1.36 (dt, *J* = 12.7, 3.8 Hz, 1H), 1.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 144.2, 123.9, 118.4, 78.7, 65.8, 64.9, 54.8, 46.5, 31.9, 26.3, 25.8, 24.1, 22.2, 14.7; IR (thin film) 2954, 2878, 1742, 1442, 1260 cm^{-1}; $[\alpha]^{22}_D$ –41.32 (*c* = 1.1, CH_2Cl_2); HRMS (ESI) calculated for $[C_{15}H_{22}O_5Na]^+$ (M+Na) 305.1365, observed 305.1370; mp 56–58 °C.



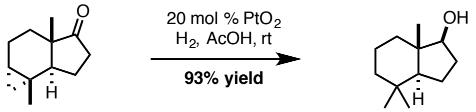
Preparation of olefin 5.48: A 200 mL round-bottom flask was charged with Pd(acac)$_2$ (490 mg, 1.6 mmol), followed by the addition of benzene (21 mL), PBu$_3$ (0.4 mL, 1.6 mmol). The homogeneous mixture was maintained at room temperature for 5 min. Ammonium formate (4.2 g, 67 mmol) was finely crushed with a mortar and pestle and added to the reaction mixture in one portion. The resulting heterogeneous solution was stirred vigorously for 10 min. Next, a solution of carbonate **5.46** (3.0 g, 10.6 mmol) in benzene (32 mL) was added dropwise. The heterogeneous mixture was stirred vigorously overnight at room temperature. Upon completion of the reaction, as indicated by TLC analysis (10% EtOAc in hexanes; visualized with *p*-anisaldehyde), the mixture was filtered through a silica gel plug (10% EtOAc in hexanes) to provide a brown oil. The crude residue was purified by flash column chromatography (350 g SiO$_2$, 1 L 100% hexanes, 1 L 0.5% EtOAc in hexanes, 5 L 1% EtOAc in hexanes) to yield **5.48** (1.72 g, 8.26 mmol, 78% yield) as a yellow oil that contained ~1% tributylphosphine oxide as an impurity. R$_f$ = 0.2 (2% EtOAc in hexanes, visualized with *p*-anisaldehyde). *Note*: It is helpful to develop the TLC plate 2 times to visualize two more polar impurities with similar R$_f$ values. If desired, the yellow oil can be purified further by Kugelrohr short-pass distillation (135 °C, 0.6 torr) to yield **5.48** (1.69 g, 8.11 mmol, 77% yield) as a clear oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.20 (s 1H), 3.94–3.84 (m, 4H), 2.46 (br s, 1H), 2.10–2.05 (m, 3H), 1.91–1.84 (m, 1H), 1.78–1.69 (m, 2H), 1.62 (s, 3H), 1.46–1.40 (m, 2H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 134.9, 120.0, 119.4, 65.4, 64.7, 46.4, 45.7, 35.2, 28.5, 24.1, 22.0, 20.5, 13.8; IR (thin film) 2944, 2878, 1436, 1376, 1044 cm^{-}

^{1}; $[\alpha]^{21}_{D}$ –62.3 (c = 1.0, CH_2Cl_2); HRMS (ESI) calculated for $[C_{13}H_{20}O_2]$ (M) 208.1463, observed 208.1460.



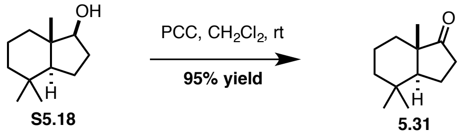
Preparation of cyclopropane 5.49: A 500 mL round-bottom was charged with ketal **5.48** (6.2 g, 30 mmol), followed by the addition of CH_2Cl_2 (150 mL). The solution was cooled to 0 °C, and a solution of Et_2Zn (60 mL of 1 M in hexanes, 60 mmol) was added dropwise. After 10 min at 0 °C, chloroidomethane (8.7 mL, 120 mmol) was added. After 2 h at 0 °C, the heterogeneous mixture was allowed to warm to room temperature and stirred overnight while shielded from light. Upon cooling the reaction mixture to 0 °C, conc. HCl (7.6 mL) in MeOH (115 mL) was added dropwise. Upon complete deprotection of the ketal (typically 10–30 min), as indicated by TLC analysis (5% EtOAc in hexanes, visualized with *p*-anisaldehyde), the mixture was transferred to a separatory funnel. H_2O (150 mL) was added, and the resulting biphasic mixture was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic layers were washed with brine (1 x 500 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow oil. The crude residue was purified by flash column chromatography (0% to 2% EtOAc in hexanes) to yield cyclopropane **5.49** as a clear oil (4.9 g, 28 mmol, 92% yield). R_f = 0.15 (5% EtOAc in hexanes; visualized with *p*-anisaldehyde). Alternatively, cyclopropane **5.49** can be purified by Kugelrohr short-pass distillation (100 °C, 0.4 torr). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50–2.45 (m, 1H), 2.10–2.04 (m, 2H), 2.01–1.97 (m, 1H), 1.91–1.85 (m, 1H), 1.81 (dd, J = 14.4, 6.9 Hz, 1H), 1.66 (dd, J = 13.4, 7.8 Hz, 1H), 1.37 (dd, J = 13.3, 6.0 Hz, 1H), 1.10 (s, 3H), 0.90–0.85 (m, 4H), 0.67–0.64 (m, 1H), 0.56 (dd, J

= 9.5, 4.3 Hz, 1H), 0.01 (app t, *J* = 5.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.2, 50.7, 47.3, 36.6, 28.0, 23.3, 23.0, 22.2, 19.7, 17.8, 16.3, 13.3; IR (thin film) 3051, 2945, 2864, 1737, 1445, 1024 cm^{-1}; $[\alpha]^{22}_{D}$ +118 (*c* = 1.0, CH_2Cl_2); HRMS (ESI) calculated for $[C_{12}H_{18}O]$ (M) 178.1358, observed 178.1358.

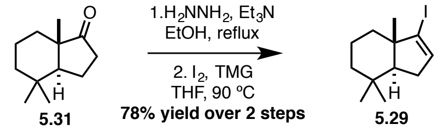


5.49 **S5.18**

Preparation of alcohol S5.18: A 20 mL vial was charged with ketone **5.49** (1.1 g, 6.0 mmol), followed by the addition of AcOH (6.0 mL), $PtO_2•H_2O$ (270 mg, 1.2 mmol). The flask was then placed in a Parr high pressure vessel that was subsequently filled with H_2 (10 atm). The vessel was placed on top of an IKA magnetic plate and stirred overnight. The reaction mixture was filtered through Celite into a separatory funnel, followed by the addition of EtOAc (50 mL). The resulting solution was washed with H_2O (3 x 50 mL), sat. aq. $NaHCO_3$ (1 x 50 mL), and brine (1 x 50 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo* to yield a colorless solid. The crude residue was purified by flash column chromatography (2% to 6% EtOAc in hexanes) to yield **S5.18** as a colorless solid (1.02 g, 5.59 mmol, 93% yield) that contained ~5% of an impurity. R_f = 0.20 (10% EtOAc in hexanes; visualized with *p*-anisaldehyde). Recrystallization from hot *n*-hexanes (50 mL) yielded **S5.18** as colorless needles (820 mg, 4.5 mmol, 81% recovery). Spectral data were consistent with reported values.[95]

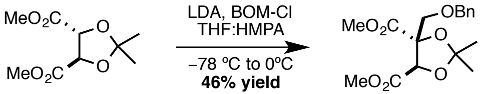


Preparation of ketone 5.31: A 100 mL round-bottom flask was charged with alcohol **S5.18** (0.80 g, 4.4 mmol), followed by the addition of PCC (2.0 g, 9.4 mmol), Celite (2.0 g), and CH_2Cl_2 (22 mL). The resulting heterogeneous solution was stirred vigorously at room temperature, until TLC analysis (10% EtOAc in hexanes, visualized with *p*-anisaldehyde) indicated complete consumption of the starting material (typically 60–90 min). Hexanes (22 mL) was added to the reaction mixture, which was subsequently gravity filtered. The reaction vessel and filtrate were washed with 10% EtOAc in hexanes (4 x 25 mL). The combined organic washes were concentrated *in vacuo* to yield an orange oil. The crude residue was purified by flash column chromatography (0% to 2% EtOAc in hexanes) to provide **5.31** (0.75 g, 4.2 mmol, 95% yield, 98.5% *ee*) as a clear oil, which solidified upon standing. R_f = 0.29 (5% EtOAc in hexanes, visualized with *p*-anisaldehyde). Alternatively, ketone **5.31** can be purified by Kugelrohr short-pass distillation (130 °C, 0.8 torr). Spectral data were consistent with reported values.[30a] The enantiomeric excess of the corresponding trisyl hydrazone[30a] was determined by chiral stationary-phase HPLC analysis (Chiracel OD-H column; flow: 1.0 mL/min, 1% isopropanol:*n*-hexane; λ = 254 nm; minor enantiomer t_R = 13.65 min, major enantiomer t_R = 21.34 min). *Note*: The reaction is readily scalable. In a separate experiment, crude alcohol **S5.18** (4.46 g, 24.5 mmol) was oxidized according to the above procedure to yield ketone **5.31** (4.33 g, 24.0 mmol, 96% yield) as a clear oil. The material contained ~5% impurity that was carried through from the previous step. Therefore, it is important to recrystallize alcohol **S5.18** prior to oxidation to obtain pure ketone **5.31**.



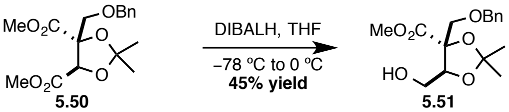
Preparation of vinyl idodide 5.29: Hydrazine hydrate (20 mL) and NEt_3 (16.3 mL, 118 mmol) were added to a solution of ketone **5.31** (1.06 g, 5.88 mmol) in EtOH (45 mL). The reaction was heated to reflux for 20 h; upon cooling to 23 °C, CH_2Cl_2 (100 mL) and H_2O (150 mL) were added. The aqueous layer was washed with CH_2Cl_2 (3 x 100 mL), and the combined organic layers were dried over Mg_2SO_4, filtered, and concentrated *in vacuo*. The remaining white solid (excess hydrazine) was removed by filtration using hexanes. Concentration *in vacuo* provided the crude hydrazone as a yellow oil, which was carried forward without further purification.

A solution of 1,1,3,3-tetramethylguanidine (5.15 mL, 41.2 mmol) in THF (30 mL) was added dropwise over 10 min to a solution of I_2 (3.28 g, 12.9 mmol) in THF (30 mL). The hydrazone (5.88 mmol) in THF (6 mL) was then added dropwise over 10 min, and the reaction was maintained for 30 min. The dark red solution was then concentrated *in vacuo*, and the resulting red oil was heated neat at 90 °C for 5 h with a reflux condenser attached. The reaction was then cooled to 23 °C, diluted with Et_2O (60 mL), and concentrated *in vacuo* over silica gel (~10 g). Purification by flash column chromatography (100% hexanes) provided light-sensitive vinyl iodide **5.29** (1.33 g, 4.58 mmol, 78% yield) as a colorless, crystalline solid. Spectral data were consistent with reported values.[30a,96]

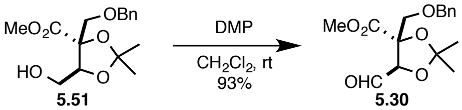


5.32 **5.50**

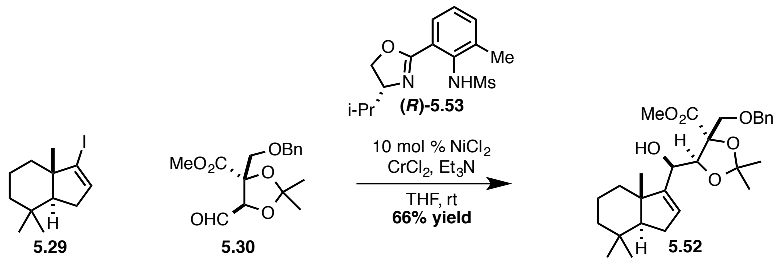
Preparation of diester 5.50: The procedure for the preparation of diester **5.50** was a slight modification from the literature procedure.[31] Dimethyl 2,3,-*O*-isopropylidene-*L*-tartrate (3.83 g, 17.6 mmol) was dissolved in THF (67 mL) and cooled to −78 °C. HMPA (13 mL) was added, followed by BOM-Cl (5.6 mL, 40 mmol). Freshly prepared LDA (17.7 mmol) in THF (50 mL) was then added to the reaction flask via cannula over ~30 min. The reaction was maintained for 5 h at −78 °C, before warming to 0 °C. After 3 h, the reaction was quenched with sat. aq. NH_4Cl solution (50 mL). The organic layer was washed with H_2O (3 x 40 mL) and brine (1 x 40 mL), dried over $MgSO_4$, and concentrated *in vacuo.* Unreacted dimethyl 2,3,-*O*-isopropylidene-*L*-tartrate was distilled from the crude product (120 °C, 0.3 torr). The remaining oil was purified by flash column chromatography (8% EtOAc in hexanes to 15% EtOAc in hexanes) to provide diester **5.50** (2.75 g, 8.14 mmol, 46% yield) as a light-yellow oil. This reaction could be run on larger scale (~5x) with similar yields (41–43% yield). R_f = 0.80 (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.23 (m, 5H), 5.12 (s, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 3.82 (s, 3H), 3.73 (d, *J* = 9.8 Hz, 1H), 3.70 (d, *J* = 9.8 Hz, 1H), 3.63 (s, 3H), 1.59 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 168.8, 137.6, 128.4, 127.8, 127.5, 112.7, 85.3, 77.6, 73.7, 70.1, 53.2, 52.4, 27.4, 26.0; IR (thin film) 2989, 2950, 1743, 1442, 1436, 1391, 1382, 1256, 1211 cm^{-1}; $[\alpha]^{25}_D$ −33.8 (c = 1.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{17}H_{22}O_7Na$ (M+Na) 361.1263, observed 361.1271.



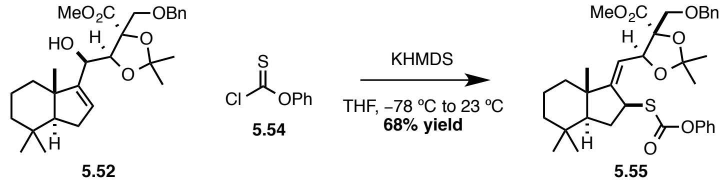
Preparation of alcohol 5.51: The procedure for the preparation of alcohol **5.51** was a slight modification from the literature procedure.[31] Diester **5.50** (17.7 g, 52.3 mmol) was dissolved in THF (450 mL) and cooled to –78 °C. DIBALH (14 mL, 79 mmol) was added dropwise to the reaction. After 5 min, the reaction was warmed to 0 °C. After 1 h, a saturated solution of Rochelle's salt (250 mL) and EtOAc (100 mL) were added. The reaction was allowed to warm to 23 °C, and the heterogeneous mixture was extracted with EtOAc (4 x 150 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was then purified by flash column chromatography (20% EtOAc in hexanes to 50% EtOAc in hexanes) to provide recovered diester **5.50** (6.34 g, 18.6 mmol, 36% recovery) as a light-yellow oil and alcohol **5.51** (7.44 g, 23.9 mmol, 46% yield) as a clear oil. R_f = 0.35 (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5H), 4.56–4.51 (m 3H), 3.91 (dd, *J* = 12.1, 5.3 Hz, 1H), 3.85 (dd, *J* = 12.2, 5.5 Hz, 1H), 3.80 (s, 3H), 3.72 (d, *J* = 9.4 Hz, 1H), 3.65 (d, *J* = 9.4 Hz, 1H), 2.37 (bs, 1H), 1.47 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 137.2, 128.7, 128.1, 127.9, 110.2, 83.8, 73.9, 70.5, 60.7, 52.9, 27.8, 25.3; IR (thin film) 3500, 2989, 2937, 2871, 1743, 1454, 1380 cm^{-1}; $[\alpha]^{25}_D$ –2.17 (c = 1.2); HRMS (ESI) calculated for $C_{16}H_{22}O_6NH_4$ (M+NH_4) 328.1760, observed 328.1754.



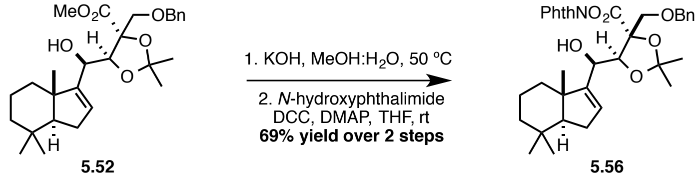
Preparation of aldehyde 5.30: To a stirring suspension of alcohol **5.51** (4.80 g, 15.5 mmol) and $NaHCO_3$ (6.50 g, 77.4 mmol) in CH_2Cl_2 (40 mL) was added Dess-Martin periodinane (7.87 g, 18.6 mmol) in two portions over 5 min. After 2 h, the reaction mixture was diluted with Et_2O (40 mL) and filtered through a cotton plug to remove solid $NaHCO_3$. The filtrate was concentrated *in vacuo*, resulting in a white solid. The solid was then washed with hexanes (6 x 30 mL), and the combined hexane washes were filtered through Celite. Upon concentration, aldehyde **5.30** (4.33 g, 14.0 mmol, 91% yield) was obtained as a clear oil. Notes: 1) Aldehyde **5.30** was found to decompose within 14 h upon its formation (at room temperature or in the freezer), possibly due to self-aldol polymerization. Therefore, it was always carried forward *immediately* into the next reaction. 2) Aldehyde **5.30** did not appear unstable to column chromatography, but it could not be purified in that manner. 3) Aqueous washes diminished the yields, possibly from hydrate formation. ^1H NMR (500 MHz, $CDCl_3$) δ 9.69 (s, 1H); 7.36–7.24 (m, 5H), 4.89 (s, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.82 (s, 3H), 3.66 (d, *J* = 10.0 Hz, 1H), 3.63 (d, *J* = 10.0 Hz, 1H), 1.59 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 170.7, 137.2, 128.5, 127.8, 127.7, 112.8, 86.3, 83.0, 73.5, 69.3, 53.3, 27.3, 25.8; IR (thin film) 2991, 2937, 2868, 1740, 1454, 1374 cm^{-1}; $[\alpha]^{25}_D$ –2.37 (c = 2.5, CH_2Cl_2); HRMS (ESI) calculated for $[C_{16}H_{20}O_6NH_4]^+$ (M+NH_4) 326.1604, observed 326.1612.



Preparation of allylic alcohol 5.52: *L*-Oxazoline **5.53**[60] (2.86 g, 9.65 mmol) and CrCl$_2$ (1.19 g, 9.65 mmol) were dissolved in THF (20 mL) in the glove box, and NEt$_3$ (1.34 mL, 9.65 mmol) was then added. The suspension was vigorously stirred for 6 h, and then NiCl$_2$ (36 mg, 0.28 mmol) was added, followed by a solution of vinyl iodide **5.29** (0.80 g, 2.8 mmol) and aldehyde **5.30** (1.30 g, 4.21 mmol) in THF (10 mL). Vigorous stirring was maintained for 20 h before removing the flask from the glovebox and cooling the solution to 0 °C. Ethylene diamine (2 mL) was added to quench the reaction. After stirring for 30 min, H$_2$O (40 mL) and Et$_2$O (40 mL) were added. The aqueous layer was extracted with EtOAc (4 x 20 mL), and the combined organic layers were washed with sat. aq. NaHCO$_3$ solution (40 mL) and brine (1 x 40 mL), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (5% EtOAc in hexanes to 11% EtOAc in hexanes) provided a single diastereomer, alcohol **5.52** (0.860 g, 1.82 mmol, 66% yield) as a clear oil. *L*-Oxazoline **5.53** was recovered during flash column chromatography (60–80% recovery) and recrystallized from Et$_2$O:hexanes for reuse. R$_f$ = 0.50 for **5.52** (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.36–7.24 (m, 5H), 5.78–5.74 (m, 1H), 4.61 (d, *J* = 12.6 Hz, 1H), 4.55 (d, *J* = 12.6 Hz, 1H), 4.44 (d, *J* = 9.0 Hz, 1H), 4.37 (s, 1H), 3.97 (d, *J* = 9.8 Hz, 1H), 3.80 (d, *J* = 9.8 Hz, 1H), 3.77 (s, 3H), 2.58 (d, *J* = 9.0 Hz, 1H), 2.12–1.99 (m, 2H), 1.74–1.70 (m, 2H), 1.58–1.56 (m, 1H), 1.54 (s, 3H), 1.50–1.43 (m, 2H), 1.42 (s, 3H), 1.25–1.19 (m, 1H), 1.11–1.01 (m, 1H), 0.98 (s, 3H), 0.95 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 155.1, 137.9, 128.4, 127.8, 127.7, 126.0, 110.2, 80.4, 73.7, 71.9, 65.5, 60.0, 52.7, 41.5, 35.5, 33.3, 33.0, 28.8, 27.6, 25.5, 21.5, 20.2, 18.2; IR (thin film) 3527, 2989, 2926, 2848, 1741, 1454, 1380 cm^{-1}; $[\alpha]^{25}_{D}$ –4.85 (c = 1.5, CH_2Cl_2); HRMS (ESI) calculated for $C_{28}H_{40}O_6NH_4$ (M+NH_4) 490.3169, observed 490.3165.

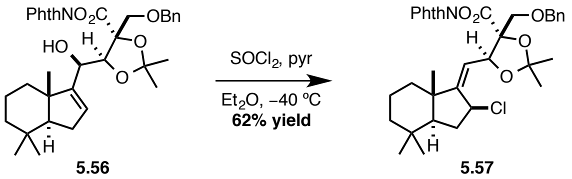


Preparation of thiocarbonate 5.55: A round-bottom flask was charged with **5.52** (58 mg, 0.123 mmol, 1 equiv), THF (1.5 mL, 0.08 M), and a magnetic stir bar under an atmosphere of argon. Upon cooling the solution to –78 °C, KHMDS (49 mg, 0.246 mmol, 2 equiv) was added as a solution in THF (0.3 mL, 0.41 M). After 1 h at –78 °C, **5.54** (70 μL, 0.51 mmol, 4 equiv) was added dropwise. The solution was maintained at –78 °C for 30 min and then allowed to warm to 23 °C over 1 h. The reaction was quenched with sat. NH_4Cl (aq) (3 mL). The solution was transferred to a separatory funnel and extracted with Et_2O (3 x 5 mL). The organic layers were dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The residue was purified by flash chromatography on silica gel using 10:90 ethyl acetate:hexanes as eluent to provide the desired product **5.55** as a yellow oil (51 mg, 0.084 mmol, 68% yield): R_f = 0.11 (10:90 ethyl acetate:hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.34 (m, 2H), 7.33–7.27 (m, 5H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17–7.13 (m, 2H), 5.30 (d, *J* = 9.5 Hz, 1H), 5.18 (dd, *J* = 9.5, 2.2 Hz, 1H), 4.56 (app q, *J* = 12.3 Hz, 2H), 4.52–4.43 (m, 1H), 3.78 (s, 3H), 3.69 (d, *J* = 9.6 Hz, 1H), 3.54 (d, *J* = 9.6 Hz, 1H), 2.55 (ddd, *J* = 12.6, 8.4, 6.1 Hz, 1H), 1.74 (dt, *J* = 13.1, 3.9 Hz, 2H), 1.62 (dd, *J* = 15.6, 12.1 Hz, 2H), 1.54 (s, 4H), 1.45 (s, 3H), 1.02–0.99 (m, 5H), 0.90–0.86 (m, 4H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 170.1, 157.9, 151.4, 129.6, 128.4, 127.73, 127.70, 126.3, 121.4, 114.9, 110.5, 85.4, 76.1, 73.6, 71.4, 55.6, 52.9, 45.3, 42.1, 41.3, 36.9, 33.4, 33.3, 32.9, 27.8, 25.3, 21.1, 20.5, 19.7; IR (thin film) 2953, 2924, 1751, 1724, 1491, 1458, 1188, 1101, 905 cm^{-1}; $[\alpha]^{21}_{D}$ 45.5, $[\alpha]^{21}_{577}$ 46.7, $[\alpha]^{21}_{546}$ 51.4, $[\alpha]^{21}_{435}$ 84.4 (*c* = 0.45, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{35}H_{44}O_7S$ $[M+Na]^+$ 631.2706; observed 631.2710.

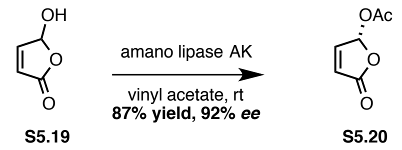


Preparation of *N*-acyloxyphthalimide 5.56: Alcohol **5.52** (0.850 g, 1.80 mmol) was dissolved in a mixture of MeOH (10 mL) and H_2O (10 mL). Potassium hydroxide pellets (0.807 g, 14.4 mmol) were then added, and the reaction was warmed to 50 °C. After 3 h, TLC analysis confirmed starting material was consumed; and the reaction was cooled to 23 °C. Aqueous HCl (18 mL of 1 M soln) was added to the flask, and the heterogeneous mixture was extracted with EtOAc (5 x 15 mL). The combined organic layers were washed with brine (1 x 20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to provide the crude acid as a clear oil which was carried forward without further purification.

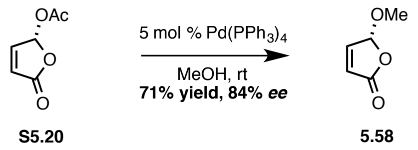
The crude acid was dissolved in THF (20 mL) to which *N*-hydroxyphthalimide (0.881 g, 5.40 mmol), DCC (0.483 g, 2.34 mmol), and DMAP (11 mg, 0.090 mmol) were added. The reaction was maintained for 3 h at 23 °C, at which point Celite (~2 g) was added. The reaction mixture was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using pH 7 silica gel[97] (10% EtOAc in hexanes to 20% EtOAc in hexanes) to provide *N*-acyloxyphthalimide **5.56** as a colorless solid. Recrystallization from acetone:hexanes afforded *N*-acyloxyphthalimide **5.56** (0.750 g, 1.24 mmol, 69% yield) as colorless needles. R_f = 0.25 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91–7.88 (2H, m), 7.81–7.78 (2H, m), 7.42–7.26 (m, 5H), 5.80 (s, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 4.71 (d, *J* = 12.4 Hz, 1H), 4.69 (s, 1H), 4.49 (d, *J* = 9.7 Hz, 1H), 4.14 (d, *J* = 9.9 Hz, 1H), 3.97 (d, *J* = 10.1 Hz, 1H), 2.47 (d, *J* = 9.6 Hz, 1H), 2.11–2.00 (m, 2H), 1.74–1.64 (m, 2H), 1.59 (s, 3H), 1.56–1.51 (m, 2H), 1.54 (s, 3H), 1.43 (app d, *J* = 13.3 Hz, 1H), 1.27 (app td, *J* = 12.5, 3.7 Hz, 1H), 1.13 (app td, *J* = 13.5, 4.3 Hz, 1H), 0.98 (s, 3H), 0.95 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 161.6, 154.8, 137.7, 134.9, 129.1, 128.5, 128.0, 127.8, 126.3, 124.2, 111.3, 85.1, 80.6, 74.2, 71.8, 65.6, 59.9, 47.3, 41.5, 35.4, 33.3, 32.9, 28.8, 27.4, 25.1, 21.5, 20.1, 18.2; IR (thin film) 3524, 2989, 2928, 2862, 1813, 1788, 1747, 1454, 1373 cm^{-1}; $[\alpha]^{25}_D$ –7.60 (*c* = 1.6, CH_2Cl_2); HRMS (ESI) calculated for $C_{35}H_{41}NO_8Na$ (M+Na) 626.2730, observed 626.2712; mp 139–141 °C.



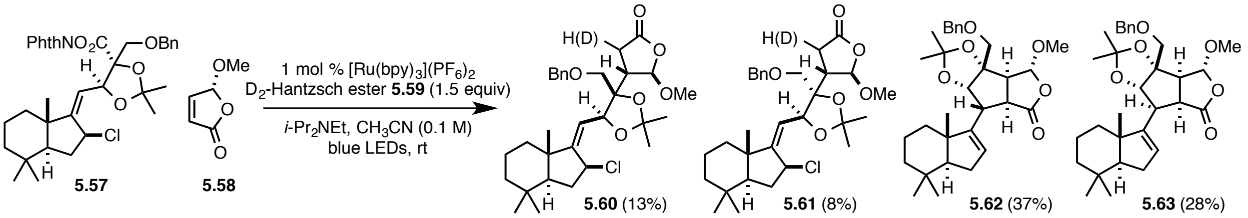
Preparation of allylic chloride 5.57: *N*-acyloxyphthalimide **5.56** (0.223 g, 0.369 mmol) was dissolved in a 10:1 mixture of Et_2O:pyridine (3.5 mL) and cooled to –45 °C. A solution of $SOCl_2$ (54 μL, 0.74 mmol) in a 10:1 mixture of Et_2O:pyridine (0.5 mL) was then added dropwise to the reaction over 5 min. The reaction was maintained at –45 °C until full conversion of starting material was observed by TLC analysis (~45 min). Saturated aq. $NaHCO_3$ solution (2 mL) was added, and the reaction was allowed to warm to 23 °C. The mixture was then diluted with H_2O (2 mL) and washed with EtOAc (3 x 3 mL). The combined organic layers were washed with brine (1 x 2 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* onto Celite (~1 g). Purification by flash column chromatography using pH 7 silica gel[97] (5% EtOAc in hexanes to 11% EtOAc in hexanes) provided allylic chloride **5.57** as a colorless solid. Recrystallization from acetone:hexanes afforded allylic chloride **5.57** (0.143 g, 0.229 mmol, 62%) as colorless needles. R_f = 0.40 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 7.95–7.88 (m, 2H), 7.83–7.78 (m, 2H), 7.40–7.26 (m, 5H), 5.59 (d, *J* = 9.6 Hz, 1H), 5.18 (d, *J* = 9.6 Hz, 1H), 4.96 (app t, *J* = 7.6 Hz, 1H), 4.70 (d, *J* = 12.3 Hz, 1H), 4.64 (d, *J* = 12.3 Hz, 1H), 3.78 (d, *J* = 10.0 Hz, 1H), 3.71 (d, *J* = 10.0 Hz, 1H), 2.32 (app quint, *J* = 6.4 Hz, 1H), 1.84 (td, *J* = 13.7 Hz, 7.5 Hz, 1H), 1.74 (app d, *J* = 12.6 H, 1H), 1.67–1.59 (m, 1H), 1.59 (s, 6H), 1.55–1.48 (m, 1H), 1.41 (app d, *J* = 13.6 Hz, 1H), 1.13 (s, 3H), 0.99–0.84 (m, 3H), 0.87 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 161.7, 161.3, 137.6, 135.0, 129.1, 128.5, 128.0, 127.8, 124.3, 114.3, 111.6, 85.0, 76.4, 74.0, 71.1, 54.6, 54.1, 45.1, 41.2, 37.0, 34.1, 32.2, 32.8, 27.6, 24.8, 21.3, 21.1, 19.5; IR (thin film) 2986, 2928, 2866, 2350, 2336, 1813, 1787, 1747, 1459 cm^{-1}; $[\alpha]^{25}_D$ +83.2 (*c* = 1.8, CH_2Cl_2); HRMS (ESI) calculated for $C_{35}H_{40}ClNO_7Na$ (M+Na) 644.2391, observed 644.2383; mp 154–158 °C.



Preparation of butenolide S5.20: The procedure for preparation of acetoxy butenolide **S5.20** was a slight modification from the literature procedure.[98] 5-Hydroxyfuran-2(5H)-one[29a] (2.90 g, 28.9 mmol) was dissolved in vinyl acetate (30 mL). Amano lipase AK (2.00 g) was then added, and the suspension was stirred for 8 days at 23 °C. The suspension was then filtered through Celite, and the filtrate was concentrated *in vacuo.* Purification of the residue by flash column chromatography (40% EtOAc in hexanes) provided (*R*)-5-acetoxyfuran-2(5H)-one **S5.20** (3.58 g, 25.3 mmol, 87% yield) as a yellow oil. R_f = 0.35 (40% EtOAc in hexanes; visualized with $KMnO_4$). Spectral data were consistent with reported values.[98] The enantiomeric excess was determined to be 92% *ee* by known methods.[98]



Preparation of butenolide 5.58: Acetoxy butenolide **S5.20** (1.23 g, 8.65 mmol) was dissolved in MeOH (35 mL), and $Pd(PPh_3)_4$ (0.500 g, 0.433 mmol) was added to the solution. The solution, which turned a deep red, was maintained at 23 °C for 50 min. Upon TLC analysis confirming consumption of starting material (TLC, 10% acetone in hexanes and running the TLC plate 3x), the reaction solution was directly filtered through a silica gel plug (250 mL of 40% acetone in hexanes). The eluent was concentrated *in vacuo*, and the residue was distilled (0.8 torr, 110 °C) to provide methoxy butenolide **5.58** and a trace amount of AcOH. Removal of AcOH upon further concentration *in vacuo* afforded methoxy butenolide **5.58** (0.705 g, 6.18 mmol, 71% yield) as a clear oil. Spectral data were consistent with reported values.[99] HLPC analysis was used to determine the enantiomeric ratio to be 92:8 (Chiracel AS column; flow: 2.0 mL/min, 10% isopropanol:*n*-hexane; λ = 210 nm; major enantiomer t_R = 8.70 min, minor enantiomer t_R = 11.60 min); $[\alpha]^{25}_{D}$ –124 (*c* = 1.2, CH_2Cl_2).



Preparation of lactones 5.60, 5.61, 5.62, and 5.63: Allylic chloride **5.57** (70 mg, 0.11 mmol), methoxy butenolide **5.58** (51 mg, 0.45 mmol), D_2-Hantzsch ester (43 mg, 0.17 mmol), and $[Ru(bpy)_3](PF_6)_2$ (1 mg, 0.001 mmol) were charged into a vial. Acetonitrile (1.1 mL) was added, and the solution was sparged with Ar. The vial was then vigorously stirred while being irradiated by a single strip of blue LED lights (450 nm) at 23 °C. After 6 h, the reaction mixture was concentrated *in vacuo*, and the residue was dissolved in EtOAc (1 mL) and washed with aq. HCl (4 x 2 mL of 4 M soln) followed by H_2O (2 x 2 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. ^{1}H NMR analysis of the crude residue using an internal standard (1,4-dimethoxybenzene) showed 28% yield of **5.63**, 37% yield of **5.62**, 8% yield of **5.61**, and 13% yield of **5.60**. Purification of the crude residue by flash column chromatography (0% acetone in hexanes to 5% acetone in hexanes) provided **5.63** (15 mg, 0.030 mmol, 27% yield) as a clear oil. R_f for **5.63** = 0.55 (20% acetone in hexanes; visualized with ceric ammonium molybdate). Flash column chromatography under separate conditions of the remaining mixed fractions from the first purification (4% EtOAc in hexanes to 10% EtOAc in hexanes) provided epimeric product **5.62** (20 mg, 0.039 mmol, 35% yield) as a clear oil. R_f for **5.62** = 0.45 (20% acetone in hexanes; visualized with ceric ammonium molybdate).

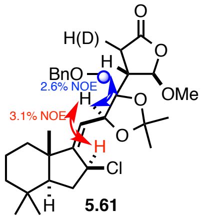
Desired ACF product **5.63** for ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 5.48 (app s, 1H), 5.38 (app s, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.41 (d, *J* = 7.5 Hz, 1H), 3.64 (d, *J* = 10.5 Hz, 1H), 3.50 (d, *J* = 10.3 Hz, 1H), 3.43 (app t, *J* = 8.7 Hz, 1H), 3.38 (s, 3H), 3.07 (app d, *J* = 8.7 Hz, 1H), 3.00 (app t, *J* = 8.2 Hz, 1H), 2.10 (ddd, *J* = 14.9, 6.3, 3.0 Hz, 1H), 2.02 (app t, *J* = 13.3 Hz, 1H), 1.76 (dd, *J* = 11.7, 6.3 Hz, 1H), 1.60–1.50 (m, 2H), 1.58 (s, 3H), 1.50 (s, 3H), 1.45–1.39 (m, 1H), 1.19 (td, *J* = 13.2, 3.4 Hz, 1H), 0.95 (s, 3H), 0.92–0.82 (m, 2H), 0.89 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 150.7, 137.2, 128.7, 128.4, 128.3, 124.7, 113.2, 103.6, 90.0, 86.8, 74.0, 70.8, 58.2, 56.8, 55.1, 47.8, 45.9, 43.7, 41.5, 34.7, 33.1, 32.9, 20.2, 29.4, 29.2, 21.5, 20.2, 17.7; $[\alpha]^{25}_D$ –84.9 (*c* = 1.0, CH_2Cl_2); IR (thin film) 2993, 2934, 2862, 1785, 1636, 1455, 1371, 1234, 1215 cm^{-1}; HRMS (ESI) calculated for $C_{31}H_{42}O_6NH_4$ (M+NH_4) 528.3325, observed 528.3331.

Epimer **5.62**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.29 (m, 5H), 5.75 (app s, 1H), 5.53 (d, *J* = 4.8 Hz, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.55 (d, *J* = 12.3 Hz, 1H), 4.47 (d, *J* = 3.7 Hz, 1H), 3.82 (d, *J* = 9.6 Hz, 1H), 3.61 (d, *J* = 9.7 Hz, 1H), 3.50 (app t, *J* = 10.8 Hz, 1H), 3.41 (s, 3H), 2.88 (dd, *J* = 9.7, 4.8 Hz, 1H), 2.72 (app d, *J* = 11.3 Hz, 1H), 2.13–2.06 (m, 2H), 1.76–1.65 (m, 1H), 1.61–1.52 (m, 2H), 1.43 (s, 3H), 1.36–1.27 (m, 1H), 1.28 (s, 3H), 1.15 (td, *J* = 13.6, 4.1 Hz, 1H), 0.96 (s, 3H), 0.92–0.81 (m, 2H), 0.89 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 148.5, 137.1, 128.7, 128.3, 128.1, 127.3, 111.6, 105.0, 89.6, 87.4, 73.8, 72.1, 59.3, 58.1, 57.6, 47.7, 47.5, 45.8, 41.6, 35.7, 33.1, 33.0, 29.2, 27.8, 26.0, 21.5, 20.2, 17.4;

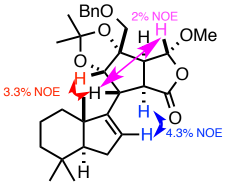
$[\alpha]^{25}_{D}$ –88.2 (*c* = 2.0, CH_2Cl_2); IR (thin film) 2988, 2929, 2861, 1775, 1454, 1373, 1246 cm^{-1}; HRMS (ESI) calculated for $C_{31}H_{42}O_6Na$ (M+Na) 533.2879, observed 533.2897.

An analytical sample of clean product **5.61** was obtained from flash column chromatography (0% acetone in hexanes to 4% acetone in hexanes). R_f = 0.60 (20% acetone in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 5.61 (s, 1H), 5.18 (d, *J* = 9.6, 1H), 5.09 (dd, *J* = 9.6, 1.6 Hz, 1H), 4.57 (td, *J* = 8.0 Hz, 1.6 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 4.41 (d. *J* = 10.4 Hz, 1H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.53 (d, *J* = 9.6 Hz, 1H), 3.51 (s, 3H), 2.68 (d, *J* = 2.1 Hz, 1H), 2.50 (d, *J* = 2.1 Hz, 1H), 1.93–1.86 (m, 1H), 1.76–1.51 (m, 4H), 1.48 (s, 3H), 1.42 (s, 3H), 1.09 (s, 3H), 1.04–0.95 (m, 2H), 0.91–0.83 (m, 1H), 0.85 (s, 3H), 0.74 (s, 3H), 0.60 (dd, *J* = 14.4, 6.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 159.7, 137.0, 128.7, 128.3, 128.3, 115.6, 109.0, 106.8, 82.6, 78.2, 74.5, 74.4, 56.9, 54.6, 54.5, 45.2, 44.9, 41.2, 36.7, 33.9, 33.2, 33.0, 29.9, 27.6, 26.2, 21.5, 21.2, 19.5; $[\alpha]^{25}_{D}$ +109.1 (*c* = 0.57, CH_2Cl_2); IR (thin film) 2986, 2931, 2864, 2359, 2342, 1787, 1455, 1370, 1252 cm^{-1}; HRMS (ESI) calculated for $C_{31}H_{42}DClO_6Na$ (M+Na) 570.2709, observed 570.2702.

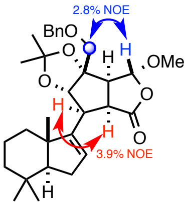
Diagnostic peaks of addition product **5.60**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.43 (d, *J* = 2.9 Hz, 1H), 5.21 (d, *J* = 9.6, 1.7 Hz, 1H), 4.75 (d, *J* = 9.6 Hz, 1H), 4.59 (app t, *J* = 7.0 Hz, 1H).



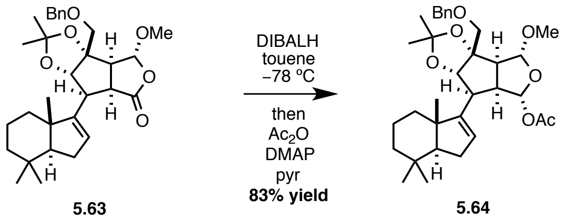
5.61



5.62

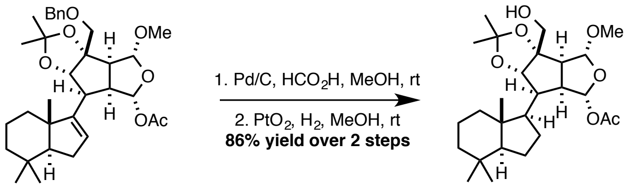


5.63



Preparation of diacetal 5.64: Product **5.63** (40 mg, 0.078 mmol) was charged into a flask with toluene (1.4 mL) and then cooled to –78 °C. A solution of DIBALH (18 μL, 0.10 mmol) in toluene (0.2 mL) was added dropwise to the reaction vessel, keeping the temperature near –78 °C. After 45 min, TLC analysis showed some remaining starting material, and an additional solution of DIBALH (5 μL, 0.03 mmol) in toluene (0.05 mL) was added. After 45 min, a solution of DMAP (19 mg, 0.16 mmol), pyridine (20 μL, 0.23 mmol), and CH$_2$Cl$_2$ (0.2 mL) was added, followed by Ac$_2$O (44 μL, 0.47 mmol). The reaction was maintained at –78 °C for 12 h, at which point it was allowed to warm to 23 °C. An aqueous solution saturated with Rochelle's salt (3 mL) was added, and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. Purification of the residue by flash column chromatography (6% EtOAc in hexanes to 10% EtOAc in hexanes) provided a single diastereomer, diacetal **5.64** (36 mg, 0.065 mmol, 83% yield), as a clear oil. R$_f$ = 0.35 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38–7.27 (m, 5H), 5.92 (d, *J* = 4.1 Hz, 1H), 5.60 (app s, 1H), 5.17 (s, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 4.58 (d, *J* = 12.3 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H), 3.60 (d, *J* = 10.4 Hz, 1H), 3.54 (d, *J* = 10.5 Hz, 1H), 3.27 (s, 3H), 3.20 (app td, *J* = 7.8, 4.0 Hz, 1H), 3.03 (d, *J* = 8.0 Hz, 1H), 2.92 (app t, *J* = 8.1 Hz, 1H), 2.05 (s, 3H), 2.06–2.00 (m, 2H), 1.72–1.51 (m, 2H), 1.51 (s, 3H), 1.46 (app d, *J* = 13.6 Hz, 1H), 1.35 (s, 3H), 1.28–1.24 (m, 1H), 1.20 (td, *J* = 12.7, 3.9 Hz, 1H), 0.98 (td, *J* =

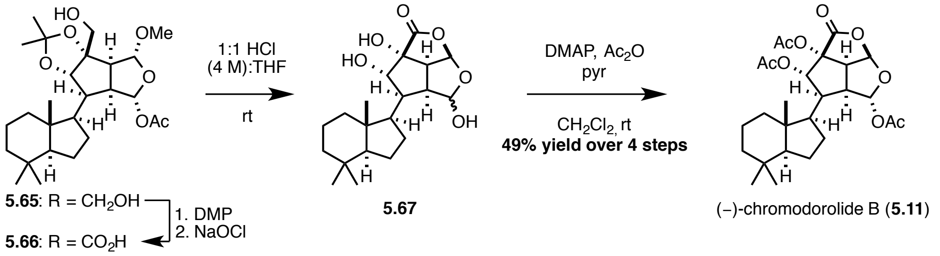
13.7, 4.4 Hz, 1H), 0.93 (s, 3H), 0.90–0.85 (m, 1H), 0.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 151.8, 137.5, 128.6, 128.4, 128.1, 125.0, 113.3, 107.8, 99.7, 90.2, 85.9, 73.8, 70.5, 50.9, 47.6, 43.3, 42.1, 36.8, 35.6, 33.3, 33.0, 31.7, 30.6, 29.7, 29.0, 24.8, 22.8, 21.3, 21.2, 20.1, 17.2, 14.3; $[\alpha]^{25}_{D}$ −46.3 (*c* = 2.1, CH_2Cl_2); IR (thin film) 2991, 2930, 2861, 1748, 1455, 1367 cm^{-1}; HRMS (ESI) calculated for $C_{33}H_{46}O_7Na$ (M+Na) 577.3141, observed 577.3127.



5.64 **5.65**

Preparation of alcohol 5.65: Diacetal **5.64** (28 mg, 0.050 mmol) and 10% Pd/C (28 mg) were charged into a flask with MeOH (1.0 mL). The reaction vessel was then evacuated and refilled with Ar (3x). Formic acid (50 μL) was then added dropwise to the vigorously stirring suspension. After 2 h, TLC analysis showed full consumption of starting material. The reaction mixture was diluted with MeOH (1 mL), filtered through Celite, and concentrated *in vacuo* to provide the crude alcohol, which was carried forward to the subsequent step.

To a flask containing the crude alcohol (0.050 mmol) was added PtO_2 (12 mg, 0.050 mmol) and EtOAc (1.0 mL). The reaction vessel was then evacuated and refilled with H_2 (3x, 1 atm H_2). The reaction was maintained under 1 atm of H_2 for 12 h at 23 °C, at which point the reaction vessel was refilled first with Ar and then air. Filtration of the suspension through Celite, concentration of the filtrate *in vacuo*, and purification of the residue by flash column chromatography (30% EtOAc in hexanes) provided alcohol **5.65** (20 mg, 0.043 mmol, 86% yield) as a clear oil. R$_f$ 0.25 (30% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.13 (d, *J* = 3.5 Hz, 1H), 5.31 (s, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.65 (bs, 2H), 3.31 (s, 3H), 3.19 (app td, *J* = 7.4, 3.6 Hz, 1H), 2.87 (app d, *J* = 7.6 Hz, 1H), 2.30 (app dt, *J* = 10.1, 7.3 Hz, 1H), 2.16 (bs, 1H), 2.05 (s, 3H), 1.80–1.66 (m, 2H), 1.63–1.56 (m, 2H), 1.53 (s, 3H), 1.43 (s, 6H), 1.36–1.28 (m, 1H), 1.11–0.93 (m, 2H), 0.90–0.86 (m, 1H), 0.85 (s, 3H), 0.83 (s, 3H), 0.76 (s, 3H), 0.76–0.69 (m, 1H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.8, 112.7, 106.8, 97.7, 91.0, 88.1, 63.6, 57.7, 56.0, 54.9, 52.3, 50.7, 45.0, 42.9, 41.4, 40.0, 33.6, 33.3, 30.7, 30.5, 29.8, 25.8, 21.2, 21.0, 20.9, 20.2, 13.9; [α]$^{25}_{D}$ –17.6 (*c* = 1.7, CH$_2$Cl$_2$); IR (thin film) 3490, 2951, 2931, 2873, 1745, 1459, 1368 cm^{-1}; HRMS (ESI) calculated for C$_{26}$H$_{42}$O$_7$Na (M+Na) 489.2828, observed 489.2813.



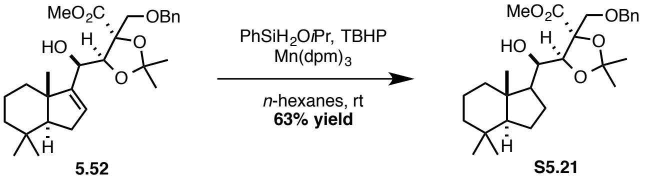
Preparation of (–)-chromodorolide B (5.11): Alcohol **5.65** (9.0 mg, 0.019 mmol) and Dess-Martin periodinane (12 mg, 0.029 mmol) were charged into a flask with CH$_2$Cl$_2$ (0.3 mL). The reaction mixture was maintained at 23 °C for 5 h, at which point it was diluted with hexanes (0.5 mL), filtered through Celite, and concentrated *in vacuo*. The residue was dissolved in hexanes (1 mL) and filtered through Celite. The filtrate was then concentrated *in vacuo* to afford the crude aldehyde which was carried forward into the next step.

To a solution of aldehyde in THF (0.1 mL) was added *t*-BuOH (0.1 mL), H$_2$O (0.1 mL), 2-methyl-2-butene (50 μL), NaH$_2$PO$_4$ (25 mg, 0.21 mmol), and NaClO$_2$ (14 mg, 0.15 mmol). The reaction was maintained at 23 °C for 12 h and then diluted with H$_2$O (1 mL). The solution was washed with EtOAc (3 x 1 mL); and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to provide crude carboxylic acid **5.66**.

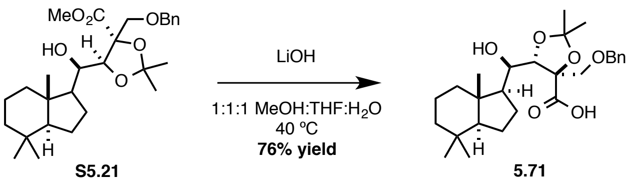
This crude acid **5.66** was then dissolved in a solution of THF (0.3 mL) and aq. HCl (0.3 mL of 4 M soln), which was maintained at 23 °C for 72 h. The reaction was then diluted with H_2O (1 mL), and the solution was washed with EtOAc (3 x 1 mL). The combined organic layers were washed with brine (1 x 1 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford crude lactol **5.67**.

Crude lactol **5.67** was then dissolved in CH_2Cl_2 (0.3 mL). Next, DMAP (2 mg, 0.019 mmol) and pyridine (31 μL, 0.38 mmol) were added, followed by Ac_2O (28 μL, 0.29 mmol). The reaction was maintained at 23 °C for 24 h, at which point it was diluted with H_2O (2 mL), and the heterogeneous solution was washed with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 3 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (20% EtOAc in hexanes to 30% EtOAc in hexanes) provided **5.11** (4.7 mg, 0.010 mmol, 49% yield over 4 steps) as a colorless solid. Recrystallization of the solid from acetone:hexanes afforded colorless needles. The NMR data matched that of the isolation data.[16b] $[\alpha]^{25}_{D}$ –66.8 (c = 0.12, CH_2Cl_2) compared to isolation sample $[\alpha]^{25}_{D}$ –95 (c = 0.10, CH_2Cl_2)[16b]; IR (thin film) 2948, 2876, 1813, 1752, 1370, 1214, 1093, 1000, 964 cm^{-1}; HRMS (ESI) calculated for $C_{26}H_{36}O_9Na$ (M+Na) 515.2257, observed 515.2260; mp 236–238 °C (decomp).

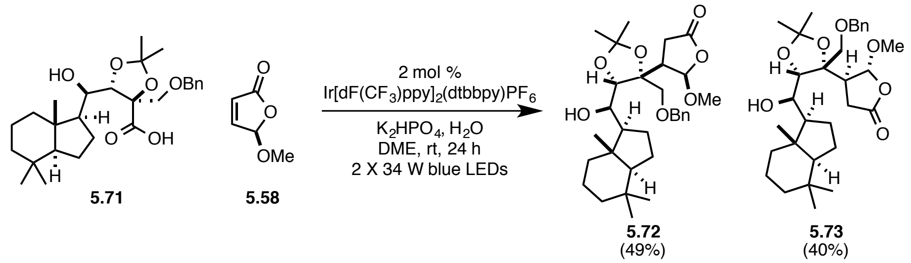
Experimental procedures for studies on the origin of diastereoselectivity for additions of trisubstituted acetonide radicals to electron-deficient olefins



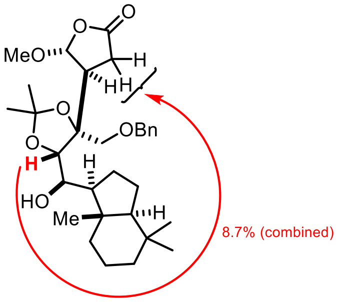
Preparation of alcohol S5.21: A 4 mL scintillation vial was charged with **5.52** (130 mg, 0.275 mmol), followed by the addition of *n*-hexanes (0.55 mL, 0.5 M). To this stirring solution, $PhSiH_2O$*i*Pr (69 mg, 0.41 mmol), and a solution of TBHP in hexanes (75 μL mL of 5.5 M soln, 0.41 mmol) were added and the resulting mixture was degassed by sparging with argon for 10 min. Next, $Mn(dpm)_3$ (17 mg, 0.028 mmol) was added in one portion and the reaction was then further degassed for an additional 30 seconds. The resulting mixture was allowed to stir at 23 °C for 1 h. Upon complete consumption of the starting material, as indicated by TLC analysis (10% EtOAc in hexanes; visualized with ceric ammonium molybdate), the reaction was transferred directly onto a silica gel column and purified by flash column chromatography (5% EtOAc in hexanes to 8% EtOAc in hexanes), yielding ester **S5.21** as a clear oil (83 mg, 0.18 mmol, 63% yield). R_f = 0.40 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.23 (m, 5H), 4.58 (d, *J* = 12.5 Hz, 1H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.31 (s, 1H), 3.94 (d, *J* = 9.5 Hz, 1H), 3.85 (t, *J* = 8.5 Hz, 1H), 3.78–3.76 (m, 4H), 2.20 (d, *J* = 9.5 Hz, 1H), 1.88–1.82 (m, 1H), 1.70–1.68 (m, 1H), 1.62–1.50 (m, 4H), 1.48 (s, 3H), 1.47–1.43 (m, 2H), 1.42–1.35 (m, 4H), 1.12–1.02 (m, 3H), 0.85 (s, 3H), 0.84 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 138.0, 128.5, 127.81, 127.76, 109.9, 85.3, 80.2, 73.7, 72.3, 70.0, 58.5, 55.6, 52.7, 42.3, 41.5, 39.7, 33.7, 33.3, 27.7, 25.3, 25.2, 20.9, 20.7, 19.2, 13.8; IR (thin film) 2923, 1765, 1727, 1598, 1382 cm^{-1}; $[\alpha]^{23}_{D}$ +19.1 (*c* = 0.4, CH_2Cl_2); HRMS (ESI) calculated for $C_{28}H_{42}O_6Na$ (M+Na) 497.2879, observed 497.2855.

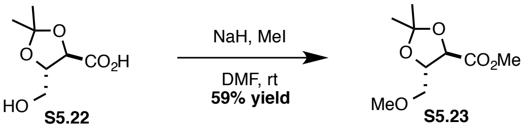


Preparation of carboxylic acid 5.71: A 20 mL scintillation vial was charged with ester **S5.21** (76 mg, 0.16 mmol), followed by the addition of 1:1:1 MeOH:THF:H_2O (4.9 mL, 0.033 M). Next, LiOH•H_2O (42 mg, 1.0 mmol) was added. The resulting heterogeneous mixture was stirred vigorously at 40 °C for 72 h. Upon allowing reaction mixture to cool down to 23 °C, the solution was treated with aq. HCl (1 mL of 1 N soln) and EtOAc (1 mL). The resulting biphasic mixture was extracted with EtOAc (3 x 2 mL). Combined organic layers washed with brine (1 x 10 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield acid **5.71** as a clear oil (55 mg, 0.12 mmol, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5H), 4.58 (s, 2H), 4.27 (s, 1H), 3.94 (d, *J* = 10.5 Hz, 1H), 3.87–3.83 (m, 2H), 1.85–1.83 (m, 1H), 1.68–1.66 (m, 1H), 1.68–1.53 (m, 4H), 1.45 (s, 3H), 1.43–1.40 (m, 7H), 1.11–0.99 (m, 3H), 0.85 (s, 3H), 0.83 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 137.7, 128.6, 127.9, 127.8, 110.6, 85.8, 80.4, 74.0, 72.2, 70.2, 58.6, 55.6, 42.3, 41.5, 39.6, 33.7, 33.3, 27.8, 25.6, 25.0, 21.0, 20.7, 19.9, 13.9; IR (thin film) 1943, 2924, 1737, 1383, 1217 cm^{-1}; $[\alpha]^{23}_{D}$ +27.8 (*c* = 2.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{27}H_{40}O_6Na$ (M+Na) 483.2722, observed 483.2706.

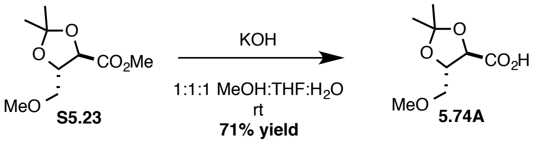


Preparation of lactones 5.72 and 5.73: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.71** (32 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.70 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure to yield a yellow oil. ^1H NMR analysis of the crude residue displayed a 1.2:1 ratio of **5.72**:**5.73**.The crude residue was purified by flash column chromatography (4% EtOAc in hexanes to 8% EtOAc in hexanes) to yield **5.72** as a clear oil (18 mg, 0.34 mmol, 49% yield). Minor diastereomer **5.73** could not be isolated in pure form by column chromatography. R_f = 0.26 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 5.42 (d, *J* = 4.0, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 3.86 (d, *J* = 10.0 Hz, 1H), 3.81 (br s, 1H), 3.65 (s, 1H), 3.47 (s, 3H), 3.30 (d, *J* = 10.0 Hz, 1H), 2.88–2.81 (m, 2H), 2.65–2.62 (m, 2H), 1.80–1.75 (m, 1H), 1.66–1.57 (m, 5H), 1.43–1.38 (m, 5H), 1.35–1.28 (m, 4H), 1.10–0.96 (m, 3H), 0.84 (s, 3H), 0.83 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.0, 137.5, 129.0, 128.6, 128.5, 108.4, 106.8, 81.72, 81.70, 74.3, 69.9, 68.3, 58.6, 57.6, 55.0, 45.0, 42.6, 41.7, 40.1, 33.9, 33.5, 30.4, 29.0, 27.1, 24.4, 21.2, 21.0, 20.2, 14.8; IR (thin film) 2924, 2873, 1789, 1454, 1382 cm^{-1}; $[\alpha]^{23}_{D}$ +12.17 (c = 1.2, CH_2Cl_2); HRMS (ESI) calculated for $C_{31}H_{46}O_7Na$ (M+Na) 553.3141, observed 553.3146.

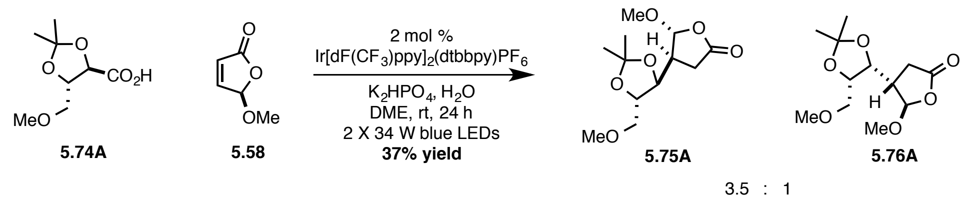




Preparation of methyl ester S5.23: A solution of **S5.22**[100] (1.06 g, 5.57 mmol) in DMF (40 mL) was cooled to 0 °C, and methyl iodide (1.7 mL, 28 mmol) was added. NaH (60% dispersion in mineral oil, 0.234 g, 5.85 mmol) was then added at 0 °C, and the reaction vessel was allowed to slowly warm to 23 °C over 4 h. Sat. aq. NH_4Cl soln (50 mL) and EtOAc (50 mL) were then added, and the resulting layers were separated. The aqueous phase was extracted with EtOAc (3 x 50 mL), and the combined organic layers were washed with brine (1 x 100 mL). The organic phase was dried over Na_2SO_4 and concentrated *in vacuo.* The crude residue was purified by flash column chromatography (20% EtOAc in hexanes to 25% EtOAc in hexanes) to yield ester **S5.23** as a clear oil (0.671 g, 3.29 mmol, 59% yield). R_f = 0.30 (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 4.32–4.26 (m, 2H), 3.77 (s, 3H), 3.66 (dd, J = 10.6, 2.7 Hz, 1H), 3.54 (dd, J = 10.6, 5.4 Hz, 1H), 3.40 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 111.7, 78.2, 75.5, 72.6, 59.6, 52.6, 27.0, 25.7; IR (thin film) 2990, 2938, 2892, 1762, 1439, 1383 cm^{-1}; $[\alpha]^{25}_{D}$ –15.5 (*c* = 2.5, CH_2Cl_2); HRMS (ESI) calculated for $C_9H_{16}O_5Na$ (M+Na) 227.0895, observed 227.0900.

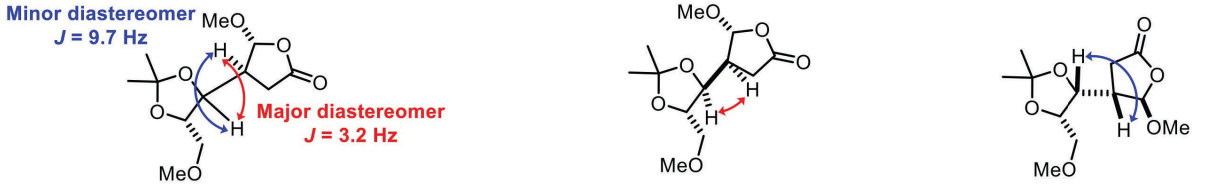


Preparation of carboxylic acid 5.74A: Ester **S5.23** (0.104 g, 0.509 mmol) was dissolved in 1:1:1 THF:H_2O:MeOH (1.5 mL), and KOH pellets (43 mg, 0.76 mmol) were added. The resulting homogeneous solution was maintained at 23 °C for 3 h before Et_2O (2 mL) and H_2O (2 mL) were added. The resulting organic layer was discarded, and the remaining aqueous layer was acidified with HCl (0.5 mL of 4 M soln) and then washed with EtOAc (3 x 2 mL). The combined organic layers were then washed with brine (3 mL) and dried over Na_2SO_4. Concentration *in vacuo* afforded acid **5.74A** (69 mg, 0.36 mmol, 71% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39 (app d, *J* = 7.9 Hz, 1H), 4.37–4.31 (m, 1H), 3.73 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.64 (dd, *J* = 10.6, 5.5 Hz, 1H), 3.46 (s, 3H), 1.51 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 112.2, 77.9, 75.3, 72.4, 59.8, 27.0, 25.7; IR (thin film) 3504, 2991, 2938, 1737, 1384, 1215 cm^{-1}; $[\alpha]^{25}_{D}$ –1.2 (*c* = 4.2, CH_2Cl_2); HRMS (ESI) calculated for $C_8H_{14}O_5Na$ (M+Na) 213.0739, observed 213.0741.



Preparation of lactones 5.75A and 5.76A: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74A** (18 mg, 0.094 mmol), K_2HPO_4 (18 mg, 0.10 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (2 mg, 0.002 mmol). Next, DME (0.9 mL, 0.1 M) was added, followed by water (17 µL, 0.94 mmol), and butenolide **5.58** (12 mg, 0.10 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^{1}H NMR analysis of the crude residue displayed a 3.5:1 ratio of **5.75A**:**5.76A**. The crude residue was purified by flash column chromatography (10% EtOAc in hexanes to 25% EtOAc in hexanes) to yield an inseparable mixture of lactones **5.75A** and **5.76A** as a yellow oil (9 mg, 0.03 mmol, 37% yield). R_f = 0.35 (30% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **5.75A** (500 MHz, $CDCl_3$) 5.31 (d, *J* = 2.7 Hz, 1H), 4.02 (dd, *J* = 8.2, 2.8 Hz, 1H), 3.79–3.74 (m, 1H), 3.55 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.51 (s, 3H), 3,46 (dd, *J* = 9.7, 5.4 Hz, 1H), 3.38 (s, 3H), 2.67 (dd, *J* = 18.5, 10.3 Hz, 1H), 2.59–2.51 (m, 2H), 1.39 (app s, 6H); ^{13}C NMR for major diastereomer **5.75A** (126 MHz, $CDCl_3$) δ 175.2, 109.9, 107.5, 77.6, 77.6, 73.0, 59.7, 57.3, 43.4, 28.6, 27.1, 27.0; IR (thin film) 2987, 2936, 1789, 1585, 1451, 1381 cm^{-1}; $[\alpha]^{25}_D$ –96.7 (*c* = 0.8, CH_2Cl_2); HRMS (ESI) calculated for $C_{12}H_{20}O_6Na$ (M+Na) 283.1158, observed 283.1160.

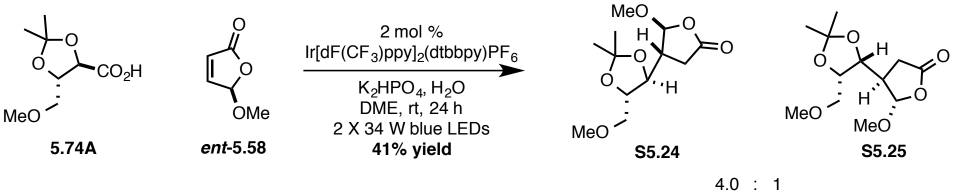
^{1}H NMR NOE studies were unsuccessful to assign diastereomers **5.75A** and **5.76A**. The distinctive vicinal coupling constant of the methine hydrogens noted below was 3.2 Hz for the major product and 9.7 Hz for the minor product. Conformer populations of **5.75A** and **5.76A** were generated by molecular mechanics, and low energy conformations were optimized by DFT calculations at the B3LYP/631-G* level. Calculations and predictions of Boltzmann-weighted vicinal coupling constants for low-energy conformers were done using Spartan '14 (Wavefunction, Inc.).



Observed Coupling Constants on 600 MHz ^{1}H NMR ($CDCl_3$)

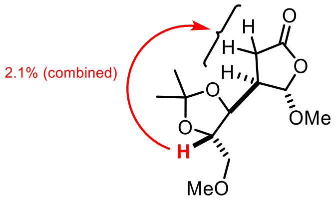
Computational Prediction: J = 2.4 Hz

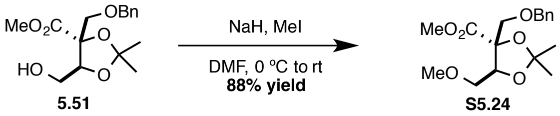
Computational Prediction: J = 10.0 Hz



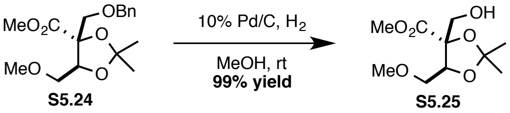
Preparation of lactones S5.24 and S5.25: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74A** (18 mg, 0.094 mmol), K_2HPO_4 (18 mg, 0.10 mmol), and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2 mg, 0.002 mmol). Next, DME (0.9 mL, 0.1 M) was added, followed by water (17 μL, 0.94 mmol), and *ent*-butenolide **5.58** (12 mg, 0.10 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^{1}H NMR analysis of the crude residue displayed a 4.0:1 ratio of **S5.24**:**S5.25**. The crude residue was purified by flash column chromatography (0% acetone in hexanes to

12% acetone in hexanes) to yield lactone **S5.24** as a clear oil (10 mg, 0.038 mmol, 41% yield). R_f = 0.20 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **S5.24** (500 MHz, C_6D_6) δ 5.33 (d, *J* = 1.9 Hz, 1H), 3.67 (ddd, *J* = 7.3, 6.3, 4.3 Hz, 1H), 3.61 (app t, *J* = 6.3 Hz, 1H), 3.19 (dd, *J* = 9.9, 4.3 Hz, 1H), 3.10–3.07 (m, 1H), 3.08 (s, 3H), 2.95 (s, 3H), 2.36–2.21 (m, 3H), 1.27 (s, 3H), 1.25 (s, 3H); ^{13}C NMR for major diastereomer **S5.24** (126 MHz, C_6D_6) δ 174.2, 109.3, 106.0, 78.9, 78.2, 73.3, 59.0, 56.3, 44.6, 30.3, 27.3, 27.1; IR (thin film) 2986, 2922, 2851, 1787, 1454, 1371, 1240 cm^{-1}; $[\alpha]^{25}_D$ +51.0 (c = 1.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{12}H_{20}O_6Na$ (M+Na) 283.1158, observed 283.1150.



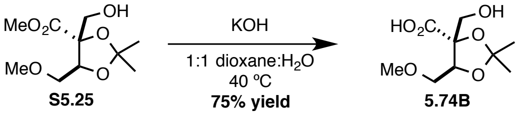


Preparation of methyl ether S5.24: A 25 mL round-bottom flask was charged with **5.51** (500 mg, 1.61 mmol), followed by the addition of DMF (11 mL, 0.15 M). The resulting mixture was cooled down to 0 °C. Next, the solution was treated with NaH (60% dispersion in mineral oil, 77 mg, 1.9 mmol). After 15 min at 0 °C, MeI (0.5 mL, 8 mmol) was added dropwise. After 1 h at 0 °C, the heterogeneous reaction mixture was allowed to warm to 23 °C over 2 h. Upon complete consumption of the starting material, as indicated by TLC analysis (30% EtOAc in hexanes; visualized with ceric ammonium molybdate), the reaction was quenched via dropwise addition of sat. aq. NH_4Cl soln. (10 mL). The mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (1 x 100 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield a yellow oil. The crude residue was purified by flash column chromatography (10% EtOAc in hexanes to 15% EtOAc in hexanes) to yield methyl ether **S5.24** as a clear oil (468 mg, 1.41 mmol, 88% yield). R_f = 0.20 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5H), 4.57–4.50 (m, 3H), 3.79 (s, 3H), 3.76 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.65 (d, *J* = 9.5 Hz, 1H), 3.56–3.52 (m, 2H), 3.40 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 137.8, 128.6, 127.9, 127.8, 110.8, 83.9, 78.7, 73.8, 70.8, 70.6, 59.6, 52.9, 27.9, 25.4; IR (thin film) 2988, 2874, 1742, 1454, 1103 cm^{-1}; $[\alpha]^{23}_D$ –3.65 (*c* = 6.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{17}H_{24}O_6Na$ (M+Na) 347.1471, observed 347.1464.

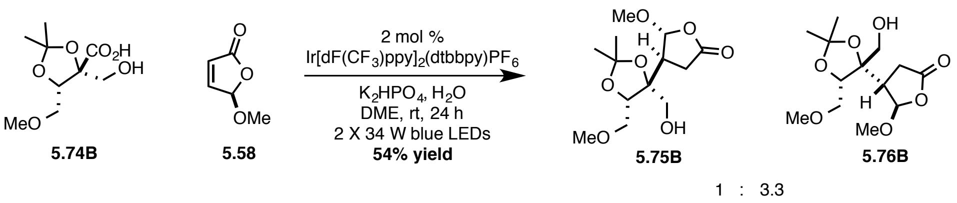


Preparation of alcohol S5.25: A 4 mL scintillation vial was charged with ester **S5.24** (200 mg, 0.616 mmol), followed by the addition of MeOH (1.8 mL, 0.14 M). Next, 10% Pd/C (200 mg) was added. The reaction vessel was then evacuated and refilled with Ar (3x). The heterogeneous mixture was then treated with formic acid (90 μL) and stirred vigorously for 18 h at 23 °C. The reaction mixture was filtered through Celite, and evaporated under reduced pressure to provide ester **S5.25** (143 mg, 0.610 mmol, 99% yield) as a clear oil. ^1H NMR (600 MHz, $CDCl_3$) δ 4.50 (dd, *J* = 6.6, 4.2 Hz, 1H), 3.82 (s, 3H), 3.79–3.76 (m, 3H), 3.71 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.45 (s, 3H), 2.62 (br s, 1H), 1.53 (s, 3H), 1.44 (s, 3H); ^{13}C NMR

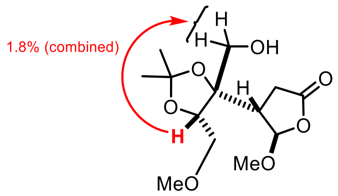
(126 MHz, $CDCl_3$) δ 172.1, 110.7, 84.7, 78.5, 70.3, 63.7, 59.8, 53.1, 27.9, 25.4; IR (thin film) 3472, 2938, 1741, 1383, 1098 cm^{-1}; $[\alpha]^{21}_D$ −4.44 (*c* = 3.4, CH_2Cl_2); HRMS (ESI) calculated for $C_{10}H_{18}O_6Na$ (M+Na) 257.1001, observed 257.0997.

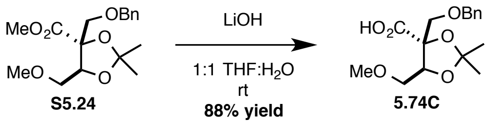


Preparation of carboxylic acid 5.74B: A 4 mL scintillation vial was charged with ester **S5.25** (80 mg, 0.34 mmol), followed by the addition of 1:1 dioxane:H_2O (2 mL, 0.17 M). Next, KOH (76 mg, 1.4 mmol) was added. The resulting biphasic mixture was stirred vigorously at 40 °C for 18 h. Upon allowing reaction mixture to cool down to 23 °C, aq. HCl (1 mL of 1 N soln) and EtOAc (1 mL) were added. The resulting biphasic mixture was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield acid **5.74B** (56 mg, 0.25 mmol, 75% yield) as a clear oil. ^1H NMR (600 MHz, $CDCl_3$) δ 4.46 (dd, *J* = 6.0, 3.6 Hz, 1H), 3.84–3.77 (m, 3H), 3.72–3.66 (m, 2H), 3.45 (s, 3H), 1.53 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 110.0, 77.2, 68.9, 66.1, 62.5, 58.7, 26.7, 24.2; IR (thin film) 3509, 2984, 1740, 1377, 1091 cm^{-1}; $[\alpha]^{21}_D$ +3.69 (*c* = 1.9, CH_2Cl_2); HRMS (ESI) calculated for $C_9H_{16}O_6Na$ (M+Na) 243.0845, observed 243.0845.

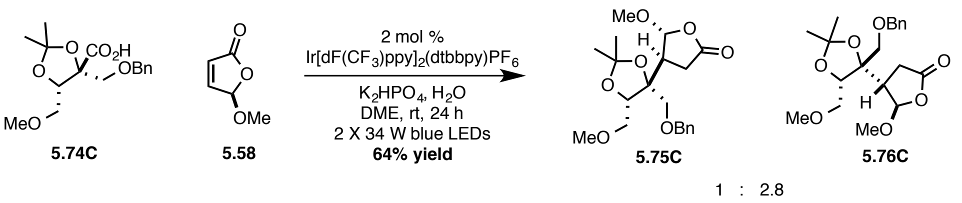


Preparation of lactones 5.75B and 5.76B: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with acid **5.74B** (16 mg, 0.070 mmol), K$_2$HPO$_4$ (13 mg, 0.77 mmol), and Ir[dF(CF$_3$)ppy)]$_2$(dtbbpy)PF$_6$ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.70 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through MgSO$_4$, and evaporated under reduced pressure to yield a yellow oil. ^{1}H NMR analysis of the crude residue displayed a 1:3.3 ratio of **5.75B**:**5.76B**. The crude residue was purified by flash column chromatography (20% EtOAc in hexanes to 35% EtOAc in hexanes) to yield an inseparable mixture of **5.75B** and **5.76B** as a clear oil (11 mg, 0.38 mmol, 54% yield). R$_f$ = 0.2 (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **5.76B** (500 MHz, CDCl$_3$) δ 5.61 (s, 1H), 4.31 (dd, *J* = 7.5, 5.5 Hz, 1H), 3.69 (dd, *J* = 9.5, 5.5 Hz, 1H), 3.62–3.60 (m, 2H), 3.58–3.52 (m, 1H), 3.49 (s, 3H), 3.42 (s, 3H), 2.75–2.67 (m, 2H), 2.54 (d, *J* = 15.0 Hz, 1H), 2.36 (br s, 1H), 1.45 (s, 3H), 1.39 (s, 3H); ^{13}C NMR for major diastereomer **5.76B** (126 MHz, CDCl$_3$) δ 176.4, 109.3, 106.5, 83.9, 78.9, 69.4, 65.0, 59.7, 57.0, 43.6, 29.3, 27.1, 26.3; IR (thin film) 2986, 2925, 1785, 1375, 1108 cm^{-1}; $[\alpha]^{22}_D$ –10.5 (*c* = 1.3, CH$_2$Cl$_2$); HRMS (ESI) calculated for C$_{13}$H$_{22}$O$_7$Na (M+Na) 313.1263, observed 313.1262.

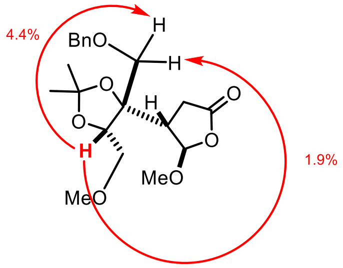




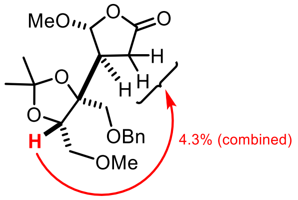
Preparation of carboxylic acid 5.74C: A 4 mL scintillation vial was charged with ester **S5.24** (100 mg, 0.308 mmol), followed by the addition of 1:1 THF:H_2O (1.8 mL, 0.17 M). Next, LiOH•H_2O (26 mg, 0.62 mmol) was added. The resulting biphasic mixture was stirred vigorously at 23 °C for 18 h. The reaction was then treated with aq. HCl (1 mL of 1 N soln) and EtOAc (1 mL). The resulting biphasic mixture was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield acid **5.74C** (84 mg, 0.27 mmol, 88% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (br s, 1 H), 7.32–7.28 (m, 5H), 4.57 (app s, 2 H), 4.46 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.75–3.71 (m, 2H), 3.60–3.54 (m, 2H), 3.38 (s, 3H), 1.50, (s, 3H), 1.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 136.2, 127.3, 126.8, 126.6, 110.0, 82.9, 77.2, 72.7, 69.2, 69.1, 58.3, 26.6, 24.1; IR (thin film) 2989, 2934, 1738, 1375, 1099 cm^{-1}; $[\alpha]^{23}_{D}$ +10.4 (*c* = 3.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{16}H_{22}O_6Na$ (M+Na) 333.1314, observed 333.1303.

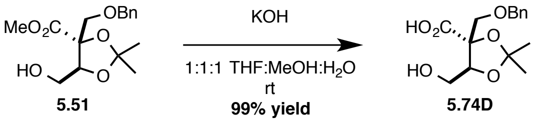


Preparation of lactones 5.75C and 5.76C: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74C** (22 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.70 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure to yield a yellow oil. ^{1}H NMR analysis of the crude residue displayed a 1:2.8 ratio of **5.75C**:**5.76C**. The crude residue was purified by flash column chromatography (10% EtOAc in hexanes to 17.5% EtOAc in hexanes) to yield **5.76C** as a clear oil (13 mg, 0.33 mmol, 47% yield) and **5.75C** as a clear oil (4 mg, 0.1 mmol, 17% yield). R_f of **5.76C** = 0.33 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate); R_f of **5.75C** = 0.27 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **5.76C** (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 5.64 (s, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.53 (t, *J* = 4.0 Hz, 1H), 3.67–3.56 (m, 2H), 3.49–3.48 (m, 5H), 3.38 (s, 3H), 2.60–2.58 (m, 2H), 2.45–2.41 (m, 1H), 1.46 (s, 3H), 1.36 (s, 3H); ^{13}C NMR for major diastereomer **5.76C** (126 MHz, $CDCl_3$) δ 176.4, 137.3, 128.7, 128.2, 128.0, 109.5, 106.9, 82.4, 80.4, 74.0, 73.5, 70.6, 59.6, 57.01 44.4, 29.7, 27.2, 26.3; IR (thin film) 2986, 2927, 1785, 1598, 1106 cm^{-1}; $[\alpha]^{23}_{D}$ –20.1 (*c* = 1.2, CH_2Cl_2); HRMS (ESI) calculated for $C_{20}H_{28}O_7Na$ (M+Na) 403.1733, observed 403.1727.

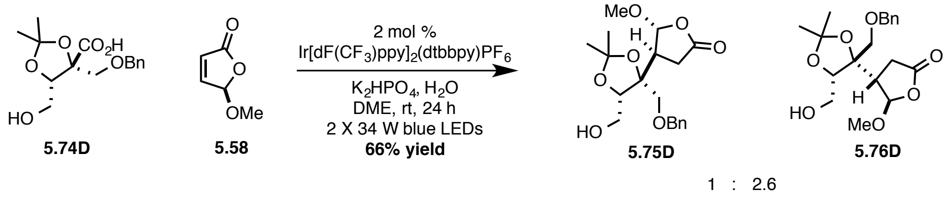


^{1}H NMR for minor diastereomer **5.75C** (500 MHz, CDCl$_3$) δ 7.38–7.28 (m, 5H), 5.41 (d, *J* = 2.5 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 3.92 (dd *J* = 7.5, 3.5 Hz, 1 H), 3.61 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.58–3.55 (m, 1H), 3.52–3.50 (m, 1H), 3.46 (s, 3H), 3.35 (s, 3H), 3.30 (d, *J* = 9.5 Hz, 1H), 2.86–2.83 (m, 1H), 2.73–2.68 (m, 1H), 2.62–2.57 (m, 1H), 1.40 (s, 3H), 1.37 (s, 3H); ^{13}C NMR for minor diastereomer **5.75C** (126 MHz, CDCl$_3$) δ 175.2, 137.6, 128.7, 128.2, 128.1, 109.2, 106.4, 81.4, 79.8, 73.8, 70.6, 69.6, 59.6, 57.2, 44.2, 29.8, 28.8, 26.7; IR (thin film) 2985, 2923, 1787, 1598, 1107 cm^{-1}; $[\alpha]^{23}_{D}$ –19.4 (*c* = 0.4, CH$_2$Cl$_2$); HRMS (ESI) calculated for $C_{20}H_{28}O_7Na$ (M+Na) 403.1733, observed 403.1740.



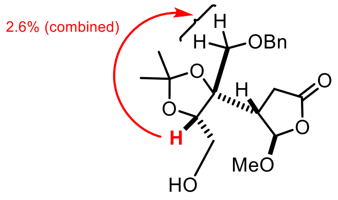


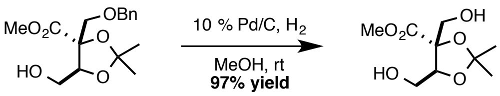
Preparation of carboxylic acid 5.74D: A 4 mL scintillation vial was charged **5.51** (200 mg, 0.644 mmol), followed by the addition of 1:1:1 THF:MeOH:H$_2$O (2.0 mL, 0.32 M). Next, KOH (72 mg, 1.3 mmol) was added. The resulting biphasic mixture was stirred vigorously at 23 °C for 18 h. The reaction was then treated with aq. HCl (1 mL of 1 N soln) and EtOAc (1 mL). The resulting biphasic mixture was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 10 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield acid **5.74D** (188 mg, 0.634 mmol, 99% yield) as a clear oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.35–7.30 (m, 5H), 4.59 (app s, 2H), 4.43 (t, *J* = 3.2 Hz, 1H), 3.92 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.85 (dd, *J* = 12.0, 5.4 Hz, 1H), 3.79 (d, *J* = 9.6 Hz, 1H), 3.69 (d, *J* = 9.0 Hz, 1 H), 1.51 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 137.2, 128.7, 128.2, 128.0, 111.0, 84.4, 79.4, 74.2, 70.5, 60.4, 27.8, 25.5; IR (thin film) 3457, 2989, 2937, 1738, 1382, 1100 cm^{-1}; $[\alpha]^{22}_D$ +9.53 (*c* = 4.3, CH_2Cl_2); HRMS (ESI) calculated for $C_{15}H_{20}O_6Na$ (M+Na) 319.1158, observed 319.1157.



Preparation of lactones 5.75D and 5.76D: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74D** (21 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.70 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure to yield a yellow oil. ^1H NMR analysis of the crude residue displayed a 1:2.6 ratio of **5.75D**:**5.76D**.The crude residue was purified by flash column chromatography (20%

EtOAc in hexanes to 32% EtOAc in hexanes) to yield an inseparable mixture of lactones **5.75D** and **5.76D** as a clear oil (17 mg, 0.46 mmol, 66% yield). R_f = 0.25 (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **5.76D** (600 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 5.57 (s, 1H), 4.48–4.46 (m, 2H), 4.21 (t, *J* = 4.0 Hz, 1H), 3.88–3.82 (m, 2H), 3.54 (d, *J* = 9.0 Hz, 1H), 3.40 (s, 3H), 3.31 (d, *J* = 9.6 Hz, 1H), 2.67–2.60 (m, 2H), 2.43 (dd, *J* = 17.4, 2.4 Hz, 1 H), 2.28 (m, 1H), 1.53 (s, 3H), 1.46 (s, 3H); ^{13}C NMR for major diastereomer **5.76D** (126 MHz, $CDCl_3$) δ 176.4, 136.8, 128.9, 128.5, 128.3, 109.4, 106.5, 83.0, 82.0, 74.2, 73.5, 60.5, 57.0, 44.3, 29.7, 27.2, 26.3; IR (thin film) 3468, 2986, 2935, 1784, 1373 cm^{-1}; $[\alpha]^{22}_D$ −21.7 (*c* = 1.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{19}H_{26}O_7Na$ (M+Na) 389.1576, observed 389.1576.

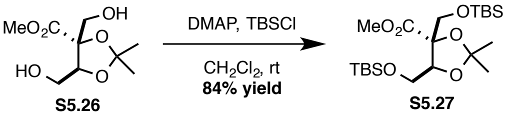




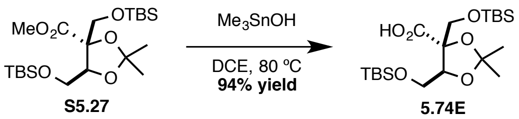
5.51 **S5.26**

Preparation of diol S5.26: A reaction vessel was charged with methyl **5.51** (0.250 g, 0.806 mmol) and 10% Pd/C (0.200 g). The vessel was then evacuated and refilled with Ar (3x) before MeOH (4 mL) was added followed by formic acid (0.2 mL). The suspension was then vigorously stirred for 4 h at 23 °C before filtering through Celite. Upon concentration *in vacuo*, ester **S5.26** was isolated (0.172 g, 0.781 mmol, 97% yield) as a colorless solid. R_f = 0.25 (60% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (t, *J* = 5.1 Hz, 1H), 3.98 (dd, *J* = 12.3, 5.1 Hz, 1H), 3.94 (dd, *J* = 12.3, 5.1

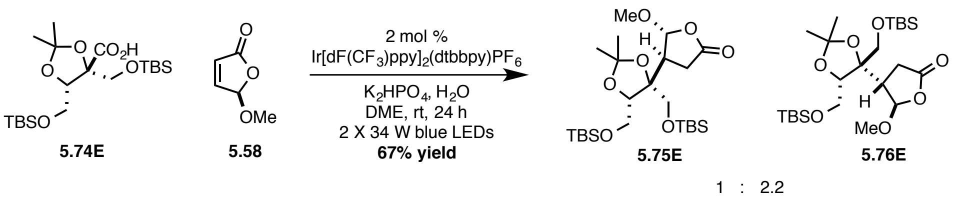
Hz, 1H), 3.84–3.77 (m, 2H), 3.81 (s, 3H), 2.97 (bs, 1H), 2.82 (bs, 1H), 1.50 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 110.4, 84.5, 79.4, 63.5, 60.2, 53.1, 27.8, 25.3; IR (thin film) 3426, 2990, 2954, 2886, 1742, 1457, 1438, 1384 cm^{-1}; $[\alpha]^{25}_{D}$ +6.1 (*c* = 2.6, CH_2Cl_2); HRMS (ESI) calculated for $C_9H_{16}O_6Na$ (M+Na) 243.0845, 243.0842.



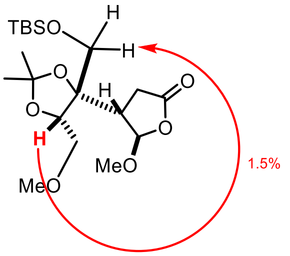
Preparation of ester S5.27: To a solution of ester **S5.26** (0.108 g, 0.490 mmol) in CH_2Cl_2 (2.5 mL) at 23 °C was added imidazole (0.167 g, 2.45 mmol) followed by DMAP (3 mg, 0.03 mmol) and then TBSCl (0.222 g, 1.47 mmol). The reaction was maintained for 2 h before quenching with H_2O (2 mL), and the heterogeneous solution was concentrated *in vacuo* over Celite (~2 g). The resulting solid was purified by flash column chromatography (8% EtOAc in hexanes) to yield ester **S5.27** as a clear oil (0.185 g, 0.412 mmol, 84% yield). R_f = 0.80 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (dd, *J* = 7.5, 3.0 Hz, 1H), 4.11 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.85–3.80 (m, 2H), 3.76 (s, 3H), 3.71 (d, *J* = 9.5 Hz, 1 H), 1.47 (s, 3H), 1.38 (s, 3H), 0.91 (s, 9H), 0.85 (s, 9H), 0.09 (s, 6H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 110.0, 84.5, 80.7, 64.3, 62.2, 52.5, 28.1, 26.2, 25.9, 25.6, 18.7, 18.3, –4.98, –5.00, –5.4, –5.6; IR (thin film) 2930, 2857, 1747, 1472, 1381 cm^{-1}; $[\alpha]^{22}_{D}$ –7.84 (c = 4.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{21}H_{44}O_6Si_2Na$ (M+Na) 471.2574, observed 471.2574.



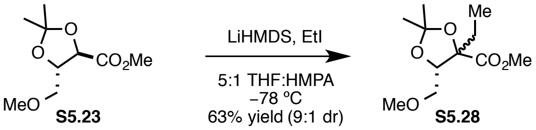
Preparation of carboxylic acid 5.74E: The procedure for the preparation of **5.74E** was a slight modification from the literature procedure.[65b] A 4 mL scintillation vial was charged with ester **S5.27** (80 mg, 0.18 mmol), followed by the addition of DCE (1.1 mL, 0.16 M). Next, Me_3SnOH (225 mg, 1.25 mmol) was added. The resulting heterogeneous mixture was stirred vigorously at 80 °C for 48 h. Upon allowing reaction mixture to cool down to 23 °C, the solution was treated with aq. HCl (1 mL of 1 N soln) and CH_2Cl_2 (1 mL). The resulting biphasic mixture was extracted with aq. HCl (5 x 1 mL of 1 N soln). The organic layer was washed with brine (1 x 5 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield a clear oil. The crude residue was purified by flash column chromatography (20% acetone in hexanes) to yield **5.74E** as a clear oil (72 mg, 0.17 mmol, 94% yield). $R_f = 0.5$ (20% acetone in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (600 MHz, $CDCl_3$) δ 4.30 (t, *J* = 9.6 Hz, 1H), 4.02 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.94 (d, *J* = 10.2 Hz, 1H), 3.87 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.80 (d, *J* = 10.8 Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 0.91 (s, 9H), 0.88 (s, 9H), 0.09 (s, 6H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 110.8, 86.0, 80.0, 65.0, 61.6, 28.2, 26.3, 26.2, 25.8, 18.8, 18.7, –4.9, –5.0, –5.1; IR (thin film) 2954, 2858, 1726, 1472, 1382 cm^{-1}; $[\alpha]^{22}_D$ +2.70 (*c* = 1.3, CH_2Cl_2); HRMS (ESI) calculated for $C_{20}H_{42}O_6Si_2Na$ (M+Na) 457.2418, observed 457.2430.



Preparation of lactones 5.75E and 5.76E: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74E** (30 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.70 mmol), and butenolide **5.58** (9 mg, 0.077 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure to yield a yellow oil. ^1H NMR analysis of the crude residue displayed a 1:2.2 ratio of **5.75E**:**5.76E**. The crude residue was purified by flash column chromatography (0% EtOAc in hexanes to 4% EtOAc in hexanes) to yield **5.76E** as a clear oil (16 mg, 0.32 mmol, 45% yield) and **5.75E** as a clear oil (8 mg, 0.2 mmol, 22% yield). R_f of **5.76E** = 0.18 (5% EtOAc in hexanes; visualized with ceric ammonium molybdate); R_f of **5.75E** = 0.13 (5% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR for major diastereomer **5.76E** (600 MHz, $CDCl_3$) δ 5.65 (s, 1H), 4.07 (t, *J* = 6.0 Hz, 1H), 3.85 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.75–3.60 (m, 2H), 3.59 (d, *J* = 10.2 Hz, 1H), 3.48 (s, 3H), 2.63 (dd, *J* = 18.6, 11.4 Hz, 1H), 2.58–2.55 (m, 2H), 1.43 (s, 3H), 1.36 (s, 3H), 0.90–0.89 (m, 18H), 0.08–0.06 (m, 12H); ^{13}C NMR for major diastereomer **5.76E** (126 MHz, $CDCl_3$) δ 176.6, 108.9, 107.2, 83.8, 80.5, 66.9, 61.3, 57.0, 44.1, 30.0, 27.4, 26.6, 26.1, 18.6, 18.5, –5.1, –5.2, –5.4, –5.5; IR (thin film) 2954, 2930, 1790, 1254, 1104 cm^{-1}; $[\alpha]^{22}_D$ –18.0 (*c* = 1.4, CH_2Cl_2); HRMS (ESI) calculated for $C_{24}H_{48}O_7Si_2Na$ (M+Na) 527.2836, observed 527.2828.

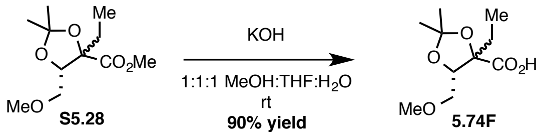


^{1}H NMR for minor diastereomer **5.75E** (600 MHz, $CDCl_3$) δ 5.43 (d, *J* = 3.0 Hz, 1H), 3.92 (d, *J* = 2.4 Hz, 1H), 3.80–3.75 (m, 2H), 3.73 (d, *J* = 10.2 Hz, 1H), 3.46 (s, 3H), 3.41 (d, *J* = 10.2, 1H), 2.83 (t, *J* = 2.0 Hz, 1H), 2.69 (dd, *J* = 17.4, 9.0 Hz, 1H), 2.58 (dd, *J* = 17.4, 6.0 Hz, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 0.91–0.88 (m, 18H), 0.08–0.05 (m, 12H); ^{13}C NMR for minor diastereomer **5.75E** (126 MHz, $CDCl_3$) δ 175.6, 108.7, 106.4, 82.2, 82.1, 62.6, 62.0, 57.0, 43.4, 29.7, 29.0, 26.6, 26.3, 25.9, 18.7, 18.2, –4.9, –5.0, –5.6, –5.7; IR (thin film) 2954, 2930, 1795, 1253, 1098 cm^{-1}; $[\alpha]^{23}_D$ –19.7 (*c* = 0.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{24}H_{48}O_7Si_2Na$ (M+Na) 527.2836, observed 527.2825.

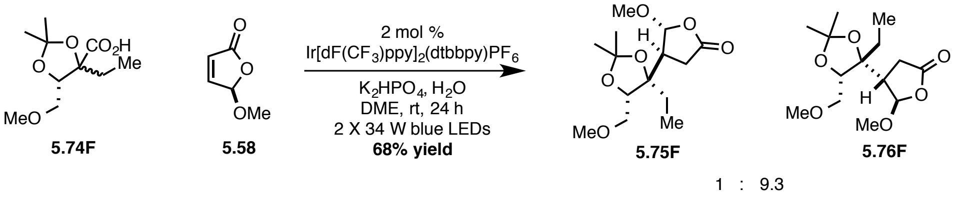


Preparation of ester S5.28: Ester **S5.23** (0.151 g, 0.739 mmol) was dissolved in a mixture of THF (3 mL) and HMPA (0.6 mL). The solution was then cooled to –78 °C, and ethyl iodide (0.24 mL, 3.0 mmol) was added followed by LiHMDS (0.8 mL of 1.0 M soln in THF, 0.8 mmol). The reaction was maintained for 1 h at –78 °C before sat. aq. NH_4Cl soln (2 mL) was added. The vessel was then allowed to warm to 23 °C, and Et_2O (2 mL) was added. The resulting aqueous layer was extracted with Et_2O (3 x 3 mL), and the combined organic layers were washed with brine (1 x 5 mL). The organic phases were dried over $MgSO_4$ and concentrated *in vacuo.* The crude residue was purified by flash column chromatography

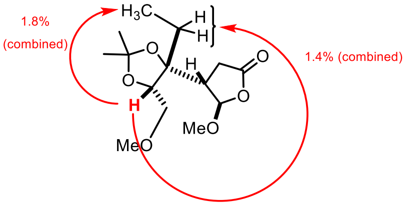
(0% EtOAc in hexanes to 8% EtOAc in hexanes) to afford ester **S5.28** as a clear oil as a 9:1 mixture of diastereomers (0.108 g, 0.465 mmol, 63% yield). R_f = 0.25 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for **S5.28**'s major diastereomer (500 MHz, CDCl$_3$) δ 4.27 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.75 (s, 3H), 3.66 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.54 (dd, *J* = 10.1, 8.6 Hz, 1H), 3.39 (s, 3H), 1.75–1.66 (m, 1H), 1.62–1.55 (m, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR for **S5.28**'s major diastereomer (126 MHz, CDCl$_3$) δ 172.8, 110.2, 85.2, 79.3, 71.2, 59.5, 52.6, 28.0, 26.2, 25.4, 8.1; IR (thin film) 2987, 2938, 2883, 1759, 1731, 1458, 1381 cm^{-1}; $[\alpha]^{25}_D$ +10.1 (*c* = 1.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{11}H_{20}O_5Na$ (M+Na) 255.1208, observed 255.1218.

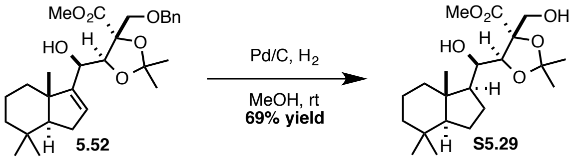


Preparation of acid 5.74F: Ester **S5.28** (59 mg, 0.25 mmol) was dissolved in 1:1:1 MeOH:THF:H$_2$O (0.9 mL), and KOH pellets (29 mg, 0.51 mmol) were added to the solution. The reaction was maintained at 23 °C for 14 h, at which point the reaction was diluted with H$_2$O (1 mL) and Et$_2$O (1 mL). The aqueous layer was washed with Et$_2$O (3 x 1 mL), and the combined organic layers were discarded. The aqueous layer was then acidified with aq. HCl (0.5 mL of 4 M soln) and then extracted with EtOAc (3 x 1 mL). The combined organic phases were washed with brine (1 x 3 mL), dried over MgSO$_4$, and concentrated *in vacuo* to provide acid **5.74F** as a colorless solid in a 9:1 mixture of diastereomers (50 mg, 0.23 mmol, 90% yield). ^{1}H NMR for **5.74F**'s major diastereomer (500 MHz, CDCl$_3$) δ 4.32 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.72 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.63 (app t, *J* = 8.9 Hz, 1H), 3.43 (s, 3H), 1.83–1.75 (m, 1H), 1.70–1.62 (m, 1H), 1.52 (s, 3H), 1.48 (s, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR for **5.74F**'s major diastereomer (126 MHz, $CDCl_3$) δ 174.6, 110.8, 85.3, 78.9, 70.8, 59.6, 27.3, 25.6, 25.6, 7.9; IR (thin film) 3472, 3180, 2988, 2939, 2884, 1731, 1459, 1381, 1247 cm^{-1}; $[\alpha]^{25}_{D}$ +37.8 (*c* = 1.1, CH_2Cl_2); HRMS (ESI) calculated for $C_{10}H_{18}O_5Na$ (M+Na) 241.1052, observed 241.1054.

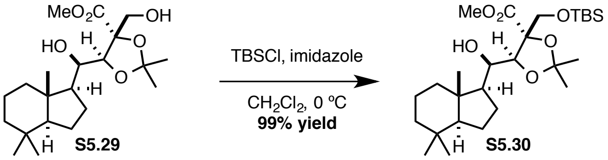


Preparation of lactones 5.75F and 5.76F: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74F** (20 mg, 0.092 mmol), K_2HPO_4 (18 mg, 0.10 mmol), and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2 mg, 0.002 mmol). Next, DME (0.9 mL, 0.1 M) was added, followed by water (17 μL, 0.94 mmol), and butenolide **5.58** (12 mg, 0.10 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^1H NMR analysis of the crude residue displayed a 1:9.3 ratio of **5.75F**:**5.76F**. The crude residue was purified by flash column chromatography (20% EtOAc in hexanes) to afford an inseparable mixture of lactones **5.75F** and **5.76F** as a yellow solid (18 mg, 0.062 mmol, 68% yield). R_f = 0.20 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). Recrystallization from acetone and hexanes afforded yellow crystals suitable for single crystal X-ray diffraction of **5.76F**.[25f] ^1H NMR (500 MHz, $CDCl_3$) δ 5.53 (d, *J* = 1.1 Hz, 1H), 4.19 (app t, *J* = 6.2 Hz, 1H), 3.56 (dd, *J* = 10.0, 6.5 Hz, 1H), 3.48 (s, 3H), 3.41 (dd, *J* = 10.0, 5.8 Hz, 1H), 3.38 (s, 3H), 2.68 (dd, *J* = 18.0, 10.3 Hz, 1H), 2.61–2.57 (m, 1H), 2.44 (dd, *J* = 18.1, 2.7 Hz, 1H), 1.68–1.59 (m, 1H), 1.58–1.50 (m, 1H), 1.44 (s, 3H), 1.37 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.7, 108.2, 106.9, 83.8, 78.5, 70.4, 59.6, 56.9, 45.5, 29.4, 27.6, 26.4, 25.8, 7.9; IR (thin film) 2975, 2937, 2900, 2812, 1780, 1459, 1382 cm^{-1}; $[\alpha]^{25}_{D}$ –17.7 (*c* = 1.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{14}H_{24}O_6Na$ (M+Na) 311.1471, observed 311.1474; mp 105–113 °C.

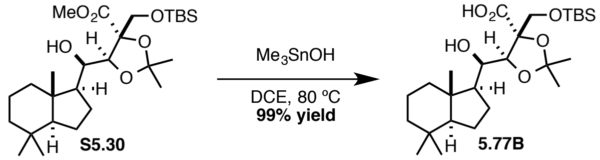




Preparation of diol S5.29: To a suspension of 10% Pd/C (0.207 g, 0.195 mmol) in MeOH (4 mL) was added **5.52** (0.230 g, 0.487 mmol) in a solution of MeOH (0.5 mL). The reaction vessel was then evacuated and refilled with H_2 (3x). The reaction was then vigorously stirred at 23 °C for 18 h, at which point the reaction vessel was purged with Ar to remove remaining H_2. The suspension was then filtered through Celite and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (20% EtOAc in hexanes to 40% EtOAc in hexanes) to yield diol ester **S5.29** as a colorless solid (0.127 g, 0.330 mmol, 69% yield). R_f = 0.40 (50% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 (s, 1H), 3.98 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 2H), 3.82 (s, 3H), 2.82–1.98 (bs, 2H), 1.94–1.85 (m, 1H), 1.76–1.56 (m, 5H), 1.54–1.34 (m, 3H), 1.52 (s, 3H), 1.42 (s, 3H), 1.19–1.11 (m, 2H), 1.04 (td, *J* = 13.4, 4.0 Hz, 1H), 0.87 (s, 3H), 0.85 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 109.7, 84.9, 79.6, 70.2, 64.0, 58.5, 55.5, 52.8, 42.3, 41.4, 39.6, 33.6, 33.2, 27.8, 25.6, 25.3, 20.9, 20.6, 19.9, 13.7; IR (thin film) 3415, 2985, 2963, 2875, 1739, 1457 cm^{-1}; $[\alpha]^{25}_{D}$ +40.1 (c = 1.3, CH_2Cl_2); HRMS (ESI) calculated for $C_{21}H_{36}O_6Na$ (M+Na) 407.2410, observed 407.2393.

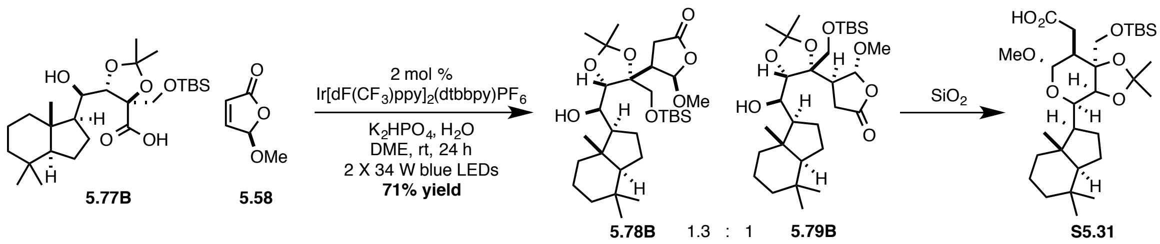


Preparation of ester S5.30: To a solution of **S5.29** (80 mg, 0.21 mmol) in CH_2Cl_2 (2.5 mL) at 0 °C was added imidazole (85 mg, 1.3 mmol), followed by TBSCl (94 mg, 0.62 mmol). The reaction was stirred at 0 °C until starting material was consumed as monitored by TLC (about 45 min). H_2O (1 mL) was added to the solution, and the aqueous layer was extracted with CH_2Cl_2 (3 x 1 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (5% EtOAc in hexanes) to yield ester **S5.30** as a light yellow oil (0.104 g, 0.209 mmol, 99% yield). R_f = 0.50 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 4.47 (s, 1H), 4.14 (d, J = 10.0 Hz, 1H), 3.98 (app t, J = 8.6 Hz, 1H), 3.81 (d, J = 10.0 Hz, 1H), 3.78 (s, 3H), 2.53 (d, J =8.7 Hz, 1H), 1.95–1.84 (m, 1H), 1.79 (dt, J = 12.2, 3.0 Hz, 1H), 1.67–1.58 (m, 3H), 1.49 (s, 3H), 1.45–1.38 (m, 1H), 1.36 (s, 3H), 1.32–1.23 (m, 3H), 1.18–1.10 (m, 1H), 1.09–1.08 (m, 1H), 0.96 (d, J = 6.8 Hz, 1H), 0.89–0.81 (m, 18H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 109.2, 85.1, 79.4, 69.4, 64.8, 58.5, 55.6, 52.4, 42.2, 41.5, 39.6, 33.7, 33.2, 27.7, 25.8, 25.5, 25.4, 20.9, 20.6, 20.0, 18.2, 13.7, –5.4, –5.6; IR (thin film) 3568, 2952, 2929, 2858, 1742, 1462 cm^{-1}; $[\alpha]^{25}_{D}$ +23.0 (c = 2.9, CH_2Cl_2); HRMS (ESI) calculated for $C_{27}H_{50}O_6SiNa$ (M+Na) 521.3275, observed 521.3280.



S5.30 → **5.77B**

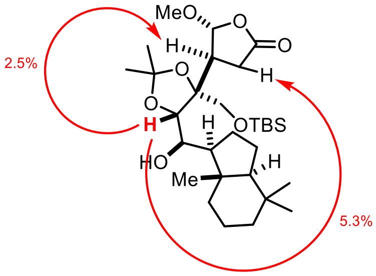
Preparation of carboxylic acid 5.77B: The procedure for the preparation of **5.77B** was a slight modification from the literature procedure.[65b] A 4 mL scintillation vial was charged with ester **S5.30** (94 mg, 0.19 mmol), followed by the addition of DCE (1.2 mL, 0.16 M). Next, Me_3SnOH (170 mg, 0.94 mmol) was added. The resulting heterogeneous mixture was stirred vigorously at 80 °C for 36 h. Upon allowing reaction mixture to cool down to 23 °C, the solution was treated with aq. HCl (1 mL of 1 N soln) and CH_2Cl_2 (1 mL). The resulting biphasic mixture was extracted with aq. HCl (5 x 1 mL of 1 N soln). Organic layer was washed with brine (1 x 5 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield acid **5.77B** as a clear oil (91 mg, 0.19 mmol, 99% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 4.34 (s, 1H), 4.09 (d, *J* = 10.5 Hz, 1H), 3.92 (d, *J* = 10.5 Hz, 1H), 3.87 (d, *J* = 8.0 Hz, 1H), 1.92–1.84 (m, 1H), 1.75–1.69 (m, 1H), 1.64–1.55 (m, 4H), 1.53 (s, 3H), 1.49–1.22 (m, 7H), 1.14–0.94 (m, 3H), 0.87–0.84 (m, 15H), 0.80 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 110.1, 86.3, 79.8, 70.1, 65.7, 58.6, 55.7, 42.3, 41.5, 39.6, 33.7, 33.3, 27.8, 26.0, 25.5, 25.3, 21.0, 20.7, 20.0, 18.4, 13.8, –5.29, –5.31; IR (thin film) 3322, 2922, 2613, 1734, 1073 cm^{-1}; $[\alpha]^{23}_D$ +24.4 (c = 2.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{26}H_{48}O_6SiNa$ (M+Na) 507.3118, observed 507.3131.



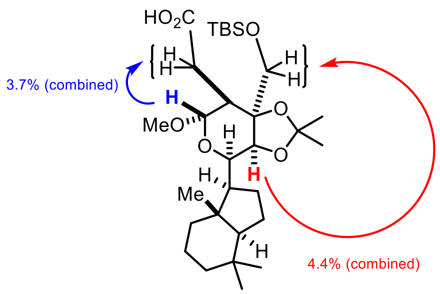
Preparation of lactone 5.78B and acid S5.31: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77B** (32 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.67 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^{1}H NMR analysis of the crude residue displayed a 1.3:1 ratio of **5.78B**:**5.79B**. The crude residue was purified by flash column chromatography (5% EtOAc in hexanes to 30% EtOAc in hexanes) to yield lactone **5.78B** as a yellow oil (15 mg, 0.027 mmol, 41% yield) and acid **S5.31** from SiO_2-mediated rearrangement of **5.79B** (11 mg, 0.020 mmol, 30% yield) as a yellow oil. R_f of **5.78B** = 0.40 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). R_f of **S5.31** = 0.20 (50% EtOAc in hexanes; visualized with ceric ammonium molybdate).

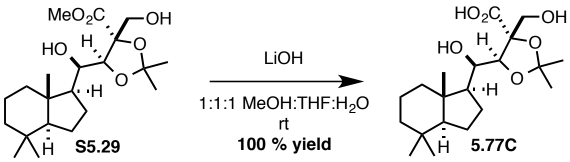
^{1}H NMR for major diastereomer **5.78B** (500 MHz, $CDCl_3$) δ 5.48 (d, *J* = 3.1 Hz, 1H), 4.08 (d, *J* = 10.5 Hz, 1H), 3.82 (app t, *J* = 6.9 Hz, 1H), 3.68 (s, 1H), 3.49 (s, 3H), 3.43 (d, *J* = 10.5 Hz, 1H), 2.88 (app d, *J* = 7.1 Hz, 1H), 2.83–2.79 (m, 1H), 2.71 (dd, *J* = 17.3, 9.4 Hz, 1H), 2.57 (dd, *J* = 17.3, 6.0 Hz, 1H), 1.94–1.85 (m, 1H), 1.65–1.45 (m, 7H), 1.44–1.40 (m, 1H), 1.42 (s, 3H), 1.36–1.32 (m, 1H), 1.34 (s, 3H), 1.18–1.08 (m, 1H), 1.04 (app td, *J* = 13.1, 4.2 Hz, 1H), 0.91

(s, 9H), 0.85 (s, 3H), 0.84 (s, 3H), 0.75 (s, 3H), 0.10 (s, 6H); ^{13}C NMR for major diastereomer **5.78B** (126 MHz, CDCl$_3$) δ 175.3, 108.3, 106.3, 82.3, 81.3, 67.6, 62.3, 58.4, 57.0, 55.8, 44.4, 42.1, 41.4, 40.0, 33.6, 33.2, 30.0, 28.9, 27.0, 25.8, 24.9, 20.9, 20.6, 19.9, 18.2, 14.3, –5.6, –5.8; IR (thin film) 3568, 2953, 2929, 2858, 1794, 1463, 1382 cm^{-1}; $[\alpha]^{25}_{D}$ –1.7 (*c* = 2.5, CH$_2$Cl$_2$); HRMS (ESI) calculated for C$_{30}$H$_{54}$O$_7$SiNa (M+Na) 577.3536, observed 577.3520.

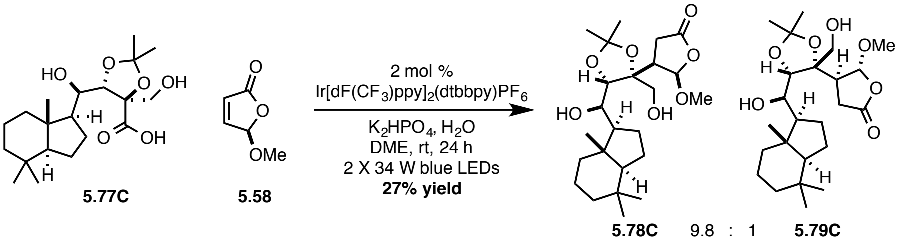


^{1}H NMR for minor diastereomer **S5.31** (500 MHz, CDCl$_3$) δ 4.54 (d, *J* = 7.3 Hz, 1H), 4.20 (app s, 1H), 3.66 (d, *J* = 10.2 Hz, 1H), 3.58 (app d, *J* = 8.7 Hz, 1H), 3.48 (d, *J* = 10.3 Hz, 1H), 3.36 (s, 3H), 2.66 (dd, *J* = 14.6, 4.1 Hz, 1H), 2.41 (app td, *J* = 8.1, 4.2 Hz, 1H), 2.33 (dd, *J* = 14.5, 8.7 Hz, 1H), 1.97–1.90 (m, 1H), 1.78–1.67 (m, 2H), 1.63–1.46 (m, 4H), 1.45–1.39 (m, 1H), 1.43 (s, 3H), 1.35 (s, 3H), 1.34–1.30 (m, 1H), 1.22–1.14 (m, 2H), 1.09–1.02 (m, 1H), 0.88 (s, 9H), 0.86 (s, 3H), 0.85 (s, 3H), 0.76 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR for minor diastereomer **S5.31** (126 MHz, CDCl$_3$) δ 177.5, 110.5, 102.0, 82.2, 79.4, 72.0, 65.6, 58.3, 55.3, 51.0, 42.0, 41.6, 39.5, 37.8, 33.7, 33.4, 33.2, 29.2, 27.4, 26.0, 25.4, 20.9, 20.8, 20.0, 18.3, 14.2, –5.4, –5.5; IR (thin film) 2928, 2858, 1712, 1463, 1366 cm^{-1}; $[\alpha]^{25}_{D}$ +45.1 (*c* = 1.2, CH$_2$Cl$_2$); HRMS (ESI) calculated for C$_{30}$H$_{54}$O$_7$Na (M+Na) 577.3536, observed 577.3536.

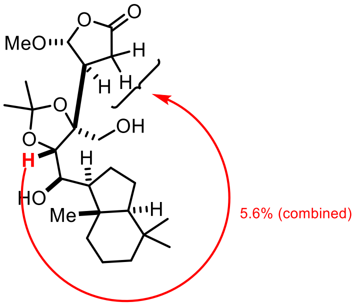


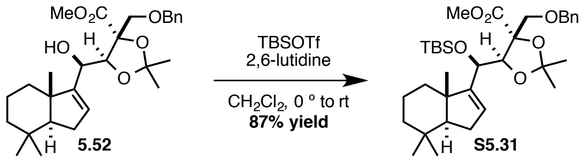


Preparation of carboxylic acid 5.77C: A 20mL scintillation vial was charged with ester **S5.29** (82 mg, 0.21 mmol), followed by the addition of 1:1:1 MeOH:THF:H_2O (3.6 mL, 0.06 M). Next, LiOH•H_2O (18 mg, 0.42 mmol) was added. The resulting heterogeneous mixture was stirred vigorously at 23 °C for 18 h. Next, the solution was treated with aq. HCl (1 mL of 1 N soln) and EtOAc (1 mL). The resulting biphasic mixture was extracted with EtOAc (3 x 2 mL). Combined organic layers washed with brine (1 x 10 mL), dried over $MgSO_4$, and evaporated under reduced pressure to yield acid **5.77C** as a clear oil (77 mg, 0.21 mmol, 100% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62–4.43 (br s, 2H), 4.31 (s, 1H), 3.98–3.88 (m, 3H), 1.92–1.85 (m, 1H), 1.73–1.54 (m, 8H), 1.48–1.35 (m, 6H), 1.14–1.00 (m, 3H), 0.84 (s, 3H), 0.80 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 110.3, 85.0, 79.9, 70.4, 63.8, 58.6, 55.5, 42.4, 41.4, 39.6, 33.7, 33.3, 27.6, 25.6, 25.3, 20.9, 20.6, 19.9, 13.8; IR (thin film) 3418, 2932, 1733, 1373, 763 cm^{-1}; $[\alpha]^{23}_{D}$ +22.6 (*c* = 1.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{20}H_{34}O_6Na$ (M+Na) 393.2253, observed 393.2256.



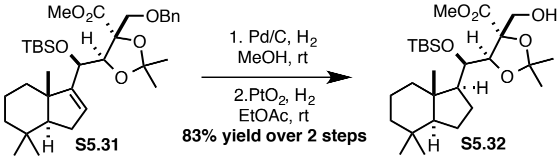
Preparation of lactones 5.78C and 5.79C: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77C** (25 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 μL, 0.67 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 ºC. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^{1}H NMR analysis of the crude residue displayed a 9.8:1 ratio of **5.78C**:**5.79C**. The crude residue was purified by flash column chromatography using pH 7 buffered silica gel[97] (15% EtOAc in hexanes to 23% EtOAc in hexanes) to yield lactone **5.78C** as a clear oil (8 mg, 0.02 mmol, 27% yield). Minor diastereomer **5.79C** could not be isolated in pure form by column chromatography. R_f = 0.25 (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (d, *J* = 5.3 Hz, 1H), 3.92 (d, *J* = 12.5 Hz, 1H), 3.79 (d, *J* = 8.9 Hz, 1H), 3.62–3.58 (m, 1H), 3.59 (s, 3H), 3.33 (d, *J* = 12.5 Hz, 1H), 2.85 (td, *J* = 9.4, 5.4 Hz, 1H), 2.71 (dd, *J* = 16.9, 9.1 Hz, 1H), 2.62 (dd, *J* = 16.9, 9.3 Hz, 1H), 1.95–1.85 (m, 1H), 1.75–1.49 (m, 7H), 1.49 (s, 3H), 1.34 (s, 3H), 1.20–1.11 (m, 2H), 1.08–1.00 (m, 1H), 0.91–0.83 (m, 1H), 0.86 (s, 3H), 0.85 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 108.3, 106.4, 81.7, 80.3, 69.0, 61.7, 58.5, 57.9, 55.0, 43.6, 42.3, 41.2, 39.9, 33.6, 33.0, 30.1, 28.7, 26.9, 25.3, 20.9, 20.5, 19.9, 14.3; IR (thin film) 3453, 2927, 1790, 1460, 1382 cm^{-1}; $[\alpha]^{25}_{D}$ +37.0 (*c* = 0.7, CH_2Cl_2); HRMS (ESI) calculated for $C_{24}H_{40}O_7Na$ (M+Na) 463.2672, observed 463.2667.





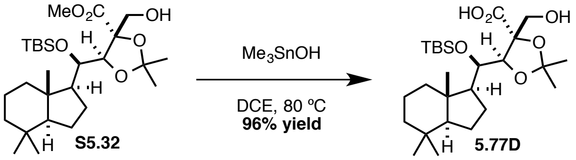
Preparation of ester S5.31: To a solution at 0 °C of **5.52** (0.132 g, 0.279 mmol), in CH_2Cl_2 (2 mL), and 2,6-lutidine (0.10 mL, 1.1 mmol) was added TBSOTf (160 μL, 0.56 mmol). The reaction was maintained at 0 °C for 15 min before allowing to warm to 23 °C for 6 h, at which point H_2O (1 mL) was added to the reaction. The aqueous layer was extracted with CH_2Cl_2 (3 x 1 mL), and the combined organic layers were then dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (0% EtOAc in hexanes to 8% EtOAc in hexanes) to afford ester **S5.31** as a yellow oil (0.142 g, 0.242 mmol, 87% yield). R_f = 0.70 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.23 (m, 5H), 5.68 (app s, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 4.54 (d, *J* = 12.6 Hz, 1H), 4.38 (app s, 1H), 4.25 (d, *J* = 2.4 Hz, 1H), 3.85 (d, *J* = 9.8 Hz, 1H), 3.78 (d, *J* = 9.8 Hz, 1H), 3.74 (s, 3H), 2.04 (ddd, *J* = 15.2, 6.4, 3.2 Hz, 1H), 1.94 (app t, *J* = 11.9 Hz, 1H), 1.69 (app qt, *J* = 12.9, 3.2 Hz, 1H), 1.60–1.43 (m, 2H), 1.55 (s, 3H), 1.41 (s, 3H), 1.32–1.14 (m, 2H), 1.10 (td, *J* = 13.4, 4.6 Hz, 1H), 1.03 (dd, *J* = 14.4, 7.6

Hz, 1H), 0.94 (s, 6H), 0.86 (s, 3H), 0.85 (s, 9H), –0.03 (s, 3H), –0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 153.1, 138.2, 128.4, 127.7, 127.6, 127.4, 110.4, 85.5, 82.2, 73.6, 71.8, 67.0, 59.7, 52.5, 47.3, 41.6, 35.6, 32.3, 32.9, 28.5, 27.7, 26.3, 25.9, 21.5, 20.2, 18.4, 18.1, –2.8, –4.4; IR (thin film) 2987, 2950, 2855, 1744, 1461, 1379 cm^{-1}; $[\alpha]^{25}_{D}$ –27.9 (c = 2.2, CH_2Cl_2); HRMS (ESI) calculated for $C_{34}H_{54}O_6SiNa$ (M+Na) 609.3588, observed 609.3602.

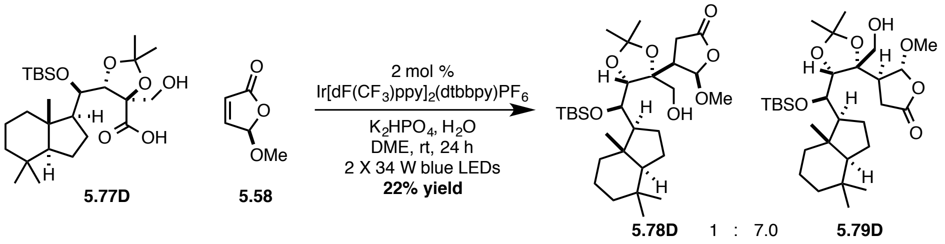


Preparation of alcohol S5.32: Ester **S5.31** (32 mg, 0.055 mmol) and 10% Pd/C (12 mg, 0.011 mmol) were charged into a flask with MeOH (1.0 mL). The reaction vessel was then evacuated and refilled with H_2 (3x). The reaction was then vigorously stirred at 23 °C for 12 h, at which point the reaction vessel was purged with Ar to remove remaining H_2. The reaction mixture was filtered through Celite, concentrated *in vacuo*, and then dissolved EtOAc (1 mL). To the solution was added PtO_2 (25 mg, 0.11 mmol) which was then placed in a Parr high pressure vessel and subsequently filled with H_2 (10 atm). The vessel was placed on top of an IKA magnetic plate and stirred for 3 h before being removed. The resulting suspension was filtered through Celite and concentrated *in vacuo*. The afforded residue was then purified by flash column chromatography (20% EtOAc in hexanes) provided alcohol **S5.32** (23 mg, 0.046 mmol, 83% yield) as a colorless solid. R_f = 0.30 (30% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (d, J = 9.2 Hz, 1H), 4.06 (d, J = 9.2 Hz, 1H), 4.01 (dd, J = 11.6, 8.1 Hz, 1H), 3.81 (s, 3H), 3.63 (dd, J = 11.6, 5.8 Hz, 1H), 2.17 (dd, J = 7.9, 5.8 Hz, 1H), 2.06–1.98 (m, 1H), 1.71 (dt, J =

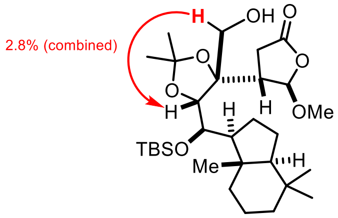
12.1, 3.2 Hz, 1H), 1.66–1.40 (m, 4H), 1.52 (s, 3H), 1.47 (s, 3H), 1.39–1.23 (m, 3H), 1.08–0.92 (m, 3H), 0.87 (s, 9H), 0.84 (s, 6H), 0.80 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 172.2, 109.7, 84.3, 83.4, 68.5, 62.4, 58.3, 53.1, 52.6, 43.0, 41.8, 39.6, 33.7, 33.2, 28.1, 26.8, 25.0, 21.1, 21.0, 19.8, 19.5, 19.2, 16.1, –2.2, –3.2; IR (thin film) 3491, 2928, 2899, 2856, 1738, 1469, 1383 cm^{-1}; $[\alpha]^{25}_{D}$ +23.7 (*c* = 1.4, CH$_2$Cl$_2$); HRMS (ESI) calculated for $C_{27}H_{50}O_6SiNa$ (M+Na) 521.3275, observed 521.3281.

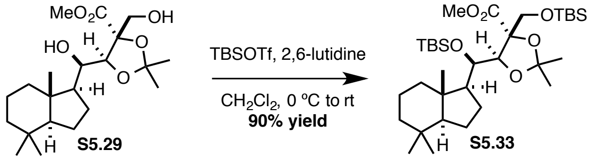


Preparation of carboxylic acid 5.77D: The procedure for the preparation of **5.77D** was a slight modification from the literature procedure.[65b] To a solution of ester **S5.32** (61 mg, 0.12 mmol) in DCE (0.5 mL) was added Me$_3$SnOH (0.110 g, 0.608 mmol). The heterogeneous mixture was then heated to 80 °C for 24 h, at which point TLC analysis confirmed full consumption of starting material. The reaction was cooled to 23 °C and diluted with CH$_2$Cl$_2$ (1 mL) and aq. HCl (1 mL of 1 M soln). The organic layer was washed with aq. HCl (5 x 1 mL of 4 M soln) and brine (1 x 2 mL) before being dried over Na$_2$SO$_4$. Upon concentration *in vacuo*, acid **5.77D** was obtained (57 mg, 0.12 mmol, 96% yield) as a colorless solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.19 (d, *J* = 8.6 Hz, 1H), 4.06 (d, *J* = 8.6 Hz, 1H), 4.02 (d, *J* = 11.8 Hz, 1H), 3.68 (d, *J* = 11.7 Hz, 1H), 2.01 (app q, *J* = 11.0 Hz, 1H), 1.69 (app d, *J* = 11.8 Hz, 1H), 1.63–1.22 (m, 6H), 1.54 (s, 3H), 1.47 (s, 3H), 1.10–0.91 (m, 4H), 0.88 (s, 9H), 0.84 (s, 6H), 0.80 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.3, 109.9, 84.4, 82.6, 68.8, 62.5, 58.0, 52.3, 43.0, 41.7, 39.5, 33.6, 33.2, 28.0, 26.8, 25.0, 21.1, 21.0, 20.0, 19.6, 19.2, 16.1, –2.2, –3.1; IR (thin film) 3454, 2951, 2927, 2896, 1734, 1461 cm^{-1}; $[\alpha]^{25}_{D}$ +32.7 (c = 1.0, CH_2Cl_2); HRMS (ESI) calculated for $C_{26}H_{48}O_6SiNa$ (M+Na) 507.3118, observed 507.3113.



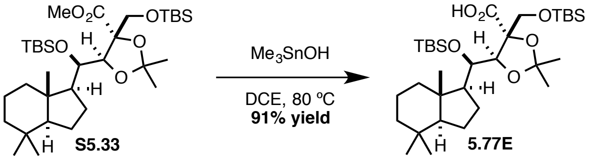
Preparation of lactones 5.78D and 5.79D: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77D** (32 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.70 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^{1}H NMR analysis of the crude residue displayed a 1:7.0 ratio of **5.78D**:**5.79D**. The crude residue was purified by flash column chromatography (10% EtOAc in hexanes to 20% EtOAc in hexanes) to yield acid **5.79D** as a clear oil (8 mg, 0.01 mmol, 22% yield). Minor diastereomer **5.78D** could not be isolated in pure form by column chromatography. R_f = 0.20 (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **5.79D** (500 MHz, $CDCl_3$) δ 5.90 (s, 1H), 4.19 (d, J = 9.8 Hz, 1H), 4.17 (d, J = 9.9 Hz, 1H), 3.63 (dd, J = 12.2, 4.0 Hz, 1H), 3.51 (s, 3H), 3.47 (dd, J = 12.2, 8.4 Hz, 1H), 2.70 (dd, J = 18.2, 10.0 Hz, 1H), 2.60 (dd, J = 18.1, 3.0 Hz, 1H), 2.43 (dd, J = 9.9, 3.0 Hz, 1H), 2.17–2.10 (m, 1H), 1.87 (app dd, *J* = 8.3, 4.2 Hz, 1H), 1.78 (dt, *J* = 12.5, 3.3 Hz, 1H), 1.65–1.58 (m, 2H), 1.53–1.44 (m, 3H), 1.47 (s, 3H), 1.37 (s, 3H), 1.30–1.22 (m, 2H), 1.06–0.91 (m, 2H), 0.90 (s, 9H), 0.86 (s, 6H), 0.85 (s, 3H), 0.81–0.77 (m, 1H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR for major diastereomer **5.79D** (126 MHz, CDCl$_3$) δ 176.5, 107.4, 105.9, 83.4, 81.2, 68.5, 65.2, 58.5, 56.7, 53.2, 44.4, 43.1, 41.8, 40.0, 33.7, 33.2, 29.2, 26.8, 26.5, 25.9, 21.1, 21.0, 19.9, 19.18, 19.16, 16.5, –1.7, –2.8; IR (thin film) 3473, 2952, 2927, 2855, 1781, 1462, 1384 cm^{-1}; [α]$^{25}_{D}$ +11.7 (*c* = 0.7, CH$_2$Cl$_2$); HRMS (ESI) calculated for C$_{30}$H$_{54}$O$_7$SiNa (M+Na) 577.3536, observed 577.3541.



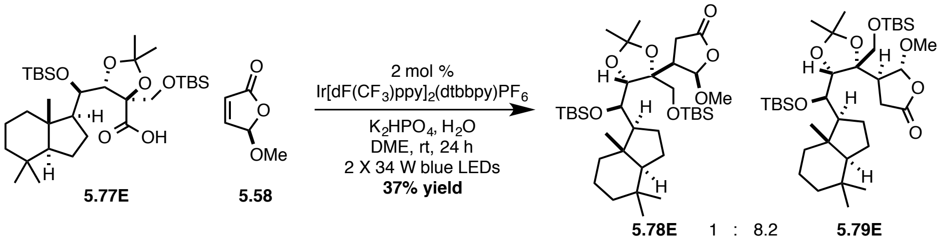


Preparation of ester S5.33: To a solution of **S5.29** (0.117 g, 0.304 mmol) in CH$_2$Cl$_2$ (2 mL) at 0 °C was added 2,6-lutidine (170 μL, 1.8 mmol) followed by TBSOTf (260 μL, 0.91 mmol). The reaction was then allowed to warm to 23 °C over 12 h before H$_2$O (2 mL) was added. Celite (3 g) was then added to the heterogeneous mixture, and the suspension was concentrated *in vacuo*. The resulting crude residue suspending on Celite was then purified by flash column chromatography (0% EtOAc in hexanes to 4% EtOAc in hexanes) to yield ester **S5.33** as a clear oil (0.168 g, 0.274 mmol, 90% yield). R$_f$ = 0.60 (5% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.27 (app d, *J* =

8.7 Hz, 1H), 4.16 (d, *J* = 8.7 Hz, 1H), 4.02 (d, *J* = 10.8 Hz, 1H), 3.87 (d, *J* = 10.8 Hz, 1H), 3.82 (s, 3H), 2.11–2.02 (m, 1H), 1.80 (dt, *J* = 12.1, 3.0 Hz, 1H), 1.71–1.47 (m, 4H), 1.58 (s, 3H), 1.49 (s, 3H), 1.45–1.30 (m, 3H), 1.16–1.01 (m, 3H), 0.96 (s, 9H), 0.94 (s, 9H), 0.91 (s, 6H), 0.87 (s, 3H), 0.16 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 172.7, 109.1, 85.1, 82.6, 69.4, 63.9, 58.2, 52.7, 52.3, 42.9, 41.8, 39.7, 33.7, 33.2, 27.5, 26.9, 26.2, 24.9, 21.2, 21.0, 19.9, 19.8, 19.3, 18.6, 16.0, –2.0, –2.9, –5.1, –5.2; IR (thin film) 2953, 2928, 2857, 1736, 1462, 1379 cm^{-1}; $[\alpha]^{25}_{D}$ +24.4 (*c* = 1.2, CH$_2$Cl$_2$); HRMS (ESI) calculated for C$_{33}$H$_{64}$O$_6$Si$_2$Na (M+Na) 635.4139, observed 635.4146.

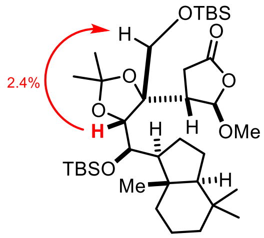


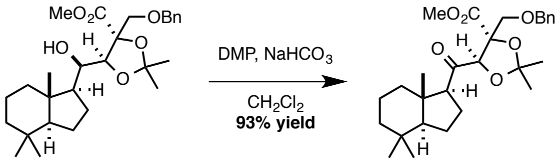
Preparation of carboxylic acid 5.77E: The procedure for the preparation of **5.77E** was a slight modification from the literature procedure.[65b] To a solution of ester **S5.33** (0.122 g, 0.199 mmol) in DCE (1.2 mL) was added Me$_3$SnOH (0.252 g, 1.39 mmol). The heterogeneous mixture was then heated to 80 °C for 48 h, at which point TLC analysis confirmed full consumption of starting material. The reaction was cooled to 23 °C and diluted with CH$_2$Cl$_2$ (2 mL) and aq. HCl (2 mL of 1 M soln). The organic layer was washed with aq. HCl (5 x 2 mL of 1 M soln) and brine (1 x 4 mL) before being dried over Na$_2$SO$_4$. Upon concentration *in vacuo*, acid **5.77E** was obtained (0.109 g, 0.182 mmol, 91% yield) as a colorless foam. ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.17 (d, *J* = 8.7 Hz, 1H), 4.05–3.99 (m, 2H), 3.72 (d, *J* = 10.6 Hz, 1H), 1.99 (app q, *J* = 10.7 Hz, 1H), 1.75 (t, *J* = 9.4 Hz, 1H), 1.70–1.56 (m, 3H), 1.53 (s, 3H), 1.52–1.45 (m, 2H), 1.43 (s, 3H), 1.38–1.28 (m, 1H), 1.10–0.94 (m, 4H), 0.89 (s, 9H), 0.87 (s, 9H), 0.84 (s, 6H), 0.80 (s, 3H), 0.09 (s, 6H), 0.08 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 109.2, 85.0, 81.3, 69.2, 64.1, 57.7, 51.9, 42.8, 41.7, 39.8, 33.5, 33.1, 27.7, 26.7, 25.9, 24.9, 21.03, 20.97, 19.8, 19.7, 19.2, 18.4, 16.0, –2.1, –3.0, –5.3, –5.34; IR (thin film) 2953, 2928, 2857, 1717, 1462, 1381 cm^{-1}; $[\alpha]^{25}_{D}$ +31.6 (*c* = 2.5, CH_2Cl_2); HRMS (ESI) calculated for $C_{32}H_{62}O_6Si_2Na$ (M+Na) 621.3983, observed 621.3972.



Preparation of lactones 5.78E and 5.79E: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77E** (40 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.67 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^{1}H NMR analysis of the crude residue displayed a 1:8.2 ratio of **5.78E**:**5.79E**. The crude residue was purified by flash column chromatography (0% EtOAc in hexanes to 5% EtOAc in hexanes) to yield an inseparable mixture of lactones **5.78E** and **5.79E** as a clear oil (17 mg, 0.025 mmol, 37% yield). R_f = 0.50 (10% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR for major diastereomer **5.79E** (500 MHz, $CDCl_3$) δ 5.84 (s, 1H), 4.12 (d, *J* = 9.8 Hz, 1H), 4.08 (d, *J* = 9.7 Hz, 1H), 3.64 (s, 2H), 3.51 (s, 3H), 2.70 (dd, *J* =

17.9, 9.9 Hz, 1H), 2.57 (dd, *J* = 10.1, 2.1 Hz, 1H), 2.43 (dd, *J* = 17.8, 2.4 Hz, 1H), 2.18–2.08 (m, 1H), 1.77 (dt, *J* = 12.4, 3.1 Hz, 1H), 1.65–1.43 (m, 4H), 1.42 (s, 3H), 1.41–1.23 (m, 2H), 1.29 (s, 3H), 1.07–0.94 (m, 4H), 0.91 (s, 9H), 0.89 (s, 9H), 0.85 (s, 3H), 0.84 (s, 3H), 0.83 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.08 (app s, 6H); ^{13}C NMR for major diastereomer **5.79E** (126 MHz, $CDCl_3$) δ 176.9, 106.7, 106.2, 84.1, 83.7, 68.6, 68.1, 58.0, 56.6, 51.8, 43.4, 43.0, 41.8, 39.6, 33.6, 33.2, 29.5, 26.8, 26.3, 26.2, 25.8, 21.1, 21.0, 19.9, 19.2, 19.0, 18.7, 16.6, –1.7, –2.8, –5.2, –5.4; IR (thin film) 2953, 2930, 2857, 1794, 1471, 1385, 1253 cm^{-1}; $[\alpha]^{25}_{D}$ +10.2 (*c* = 1.6, CH_2Cl_2); HRMS (ESI) calculated for $C_{36}H_{68}O_7Si_2Na$ (M+Na) 691.4401, observed 691.4407.

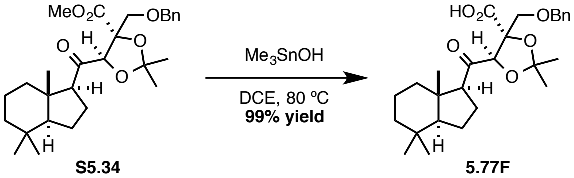




S5.21 **S5.34**

Preparation of ketone S5.34: To a stirring suspension of alcohol **S.521** (10 mg, 0.02 mmol) and $NaHCO_3$ (7 mg, 0.08 mmol) in CH_2Cl_2 (0.4 mL) was added Dess-Martin periodinane (12 mg, 0.03 mmol). After 2 h, the reaction mixture was diluted with Et_2O (3 mL) and filtered through a silica gel plug. The filtrate was concentrated *in vacuo* to provide **S5.34** as a clear oil (9.6 mg, 0.20 mmol, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.23 (m, 5H), 4.66 (s, 1H), 4.44 (d, *J* = 12.5 Hz, 1H), 4.37 (d, *J* = 12.5 Hz, 1H), 3.77 (s, 3H), 3.66 (d,

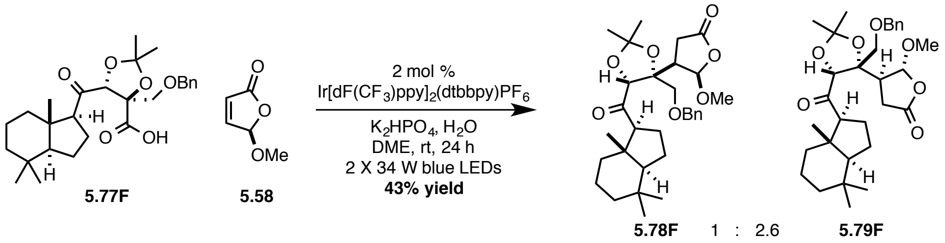
J = 10.2 Hz, 1H), 3.62 (d, J = 10.2 Hz, 1H), 3.21 (t, J = 9.3 Hz, 1H), 2.11–2.02 (m, 1H), 1.72 (dt, J = 12.5, 3.3 Hz, 1H), 1.59 (s, 3H), 1.58–1.45 (m, 2H), 1.44 (s, 3H), 1.43–1.22 (m, 3H), 0.92 (s, 3H), 0.90–0.78 (m, 1H), 0.83 (s, 6H), 0.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.1, 171.1, 138.0, 128.4, 127.6, 127.2, 111.6, 86.3, 83.7, 73.2, 69.9, 59.4, 58.9, 53.0, 45.6, 41.4, 39.6, 33.6, 33.5, 27.1, 25.5, 21.8, 21.3, 20.9, 20.1, 15.3; IR (thin film) 2948, 2865, 1746, 1701, 1453, 1380 cm^{-1}; $[\alpha]^{25}_D$ +63.8 (c = 0.8, CH_2Cl_2); HRMS (ESI) calculated for $C_{28}H_{40}O_6Na$ (M+Na) 495.2722, observed 495.2704.



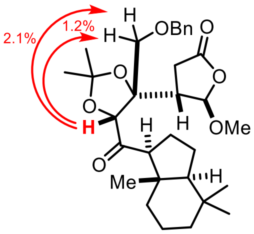
S5.34 **5.77F**

Preparation of carboxylic acid 5.77F: The procedure for the preparation of **5.77F** was a slight modification from the literature procedure.[65b] To a solution of ester **S5.34** (32 mg, 0.068 mmol) in DCE (0.7 mL) was added Me_3SnOH (61 mg, 0.34 mmol). The heterogeneous mixture was then heated to 80 °C for 18 h, at which point TLC analysis confirmed full consumption of starting material. The reaction was cooled to 23 °C and diluted with CH_2Cl_2 (1 mL) and aq. HCl (1 mL of 1 M soln). The organic layer was washed with aq. HCl (5 x 1 mL of 4 M soln) and brine (1 x 2 mL) before being dried over Na_2SO_4. Upon concentration *in vacuo*, acid **5.77F** was obtained (31 mg, 0.067 mmol, 99% yield) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 4.52 (s, 1H), 4.47 (d, J = 12.2 Hz, 1H), 4.42 (d, J = 12.2 Hz, 1H), 3.64 (s, 2H), 3.28 (t, J = 9.3 Hz, 1H), 2.14–2.06 (m, 1H), 1.70 (dt, J = 12.7, 3.2 Hz, 1H), 1.62 (s, 3H), 1.61–1.49 (m, 4H), 1.46 (s, 3H), 1.45–1.36 (m, 1H), 1.31–1.25 (m, 3H), 1.09 (td, J = 13.6, 4.4 Hz, 1H), 0.86 (s, 3H), 0.71 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (126 MHz,

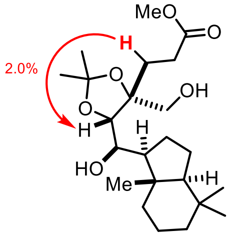
$CDCl_3$) δ 211.5, 172.5, 137.5, 128.5, 127.8, 127.4, 111.9, 86.3, 82.9, 73.5, 70.2, 59.5, 59.1, 46.2, 41.3, 39.6, 33.60, 33.56, 27.0, 25.3, 21.7, 21.3, 20.9, 20.1, 15.4; IR (thin film) 3440, 2926, 2866, 1787, 1722, 1455, 1380 cm^{-1}; $[\alpha]^{25}_{D}$ +63.3 (c = 0.8, CH_2Cl_2); HRMS (ESI) calculated for $C_{27}H_{38}O_6Na$ (M+Na) 481.2566, observed 481.2562.

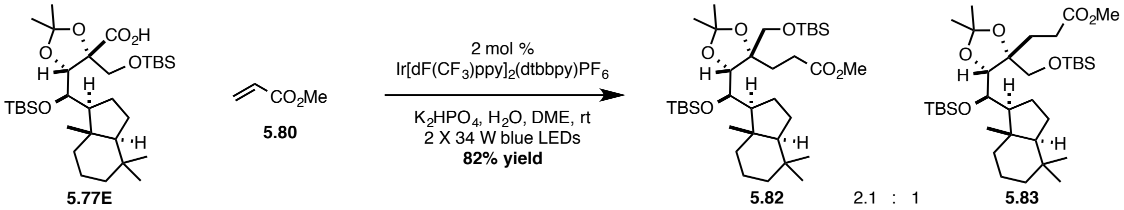


Preparation of lactones 5.78F and 5.79F: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77F** (31 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 μL, 0.67 mmol), and butenolide **5.58** (9 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. ^1H NMR analysis of the crude residue displayed a 1:2.6 ratio of **5.78F**:**5.79F**. The crude residue was purified by flash column chromatography (5% EtOAc in hexanes to 8% EtOAc in hexanes) to yield an inseparable mixture of lactones **5.78F** and **5.79F** as a clear oil (15 mg, 0.028 mmol, 43% yield). R_f = 0.75 (30% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR for major diastereomer **5.79F** (500 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 5.37 (d, J = 2.5 Hz, 1H), 4.60 (d, J = 12.1 Hz, 1H), 4.53 (d, J = 12.1 Hz, 1H), 4.41 (s, 1H), 3.63 (d, J = 10.5 Hz, 1H), 3.56 (d, J = 10.5 Hz, 1H), 3.40 (s, 3H), 3.23–3.16 (m, 1H), 2.77–2.43 (m, 3H), 2.24–2.14 (m, 1H), 1.72–1.63 (m, 2H), 1.62–1.42 (m, 5H), 1.52 (s, 3H), 1.42 (s, 3H), 1.39–1.32 (m, 2H), 1.13–1.05 (m, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.67 (s, 3H); ^{13}C NMR for major diastereomer **5.79F** (126 MHz, $CDCl_3$) δ 208.7, 175.8, 137.6, 128.6, 128.0, 127.7, 109.3, 106.4, 84.4, 82.7, 73.9, 72.5, 60.3, 59.1, 56.9, 47.5, 46.1, 44.2, 41.3, 39.5, 33.6, 30.2, 26.8, 25.7, 21.3, 21.3, 20.9, 20.1, 15.4; IR (thin film) 2928, 2866, 1792, 1702, 1454, 1382 cm^{-1}; $[\alpha]^{25}_{D}$ +54.9 (*c* = 1.4, CH_2Cl_2); HRMS (ESI) calculated for $C_{31}H_{44}O_7Na$ (M+Na) 551.2985, observed 551.2964.

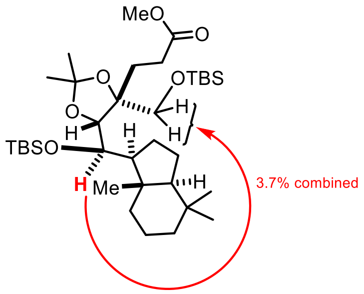


Preparation of ester 5.81: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77C** (26 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 μL, 0.67 mmol), and methacrylate (6 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure to yield a yellow oil. The crude residue was purified by flash column chromatography (20% EtOAc in hexanes to 30% EtOAc in hexanes) to yield ester **5.81** as a clear oil (22 mg, 0.053 mmol, 78% yield). R_f = 0.23 (30% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^{1}H NMR (500 MHz, CD_3OD) δ 3.82 (s, 1H), 3.75 (d, *J* = 8.5 Hz, 1H), 3.70–3.68 (m, 3H), 3.36–3.33 (m, 1H), 2.52–2.48 (m, 2H), 2.18–2.13 (m, 1H), 1.94–1.85 (m, 1H), 1.83–1.64 (m, 7H), 1.54–1.51 (m, 2H), 1.48–1.42 (m, 5H), 1.34–1.32 (m, 4H), 1.34–1.20 (m, 3H), 0.93 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 176.6, 109.4, 84.8, 84.3, 70.9, 64.7, 60.6, 56.6, 53.1, 44.1, 43.4, 41.9, 34.92, 34.89, 31.2, 30.5, 29.5, 27.9, 27.0, 22.3, 22.1, 21.6, 15.3; IR (thin film) 3434, 2925, 1741, 1438, 1051 cm^{-1}; $[\alpha]^{23}_D$ +20.5 (*c* = 1.6, CH_2Cl_2); HRMS (ESI) calculated for $C_{23}H_{40}O_6Na$ (M+Na) 435.2722, observed 435.2729.

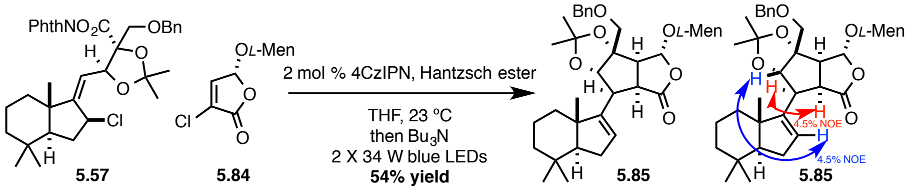




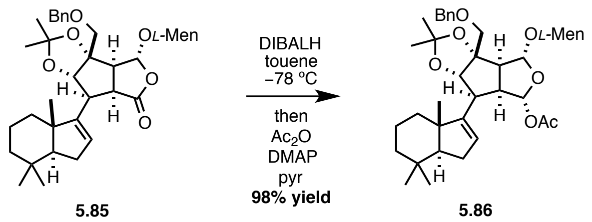
Preparation of esters 5.82 and 5.83: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77E** (40 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and Ir[dF(CF_3)ppy)]$_2$(dtbbpy)PF_6 (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 µL, 0.67 mmol), and methacrylate (6 mg, 0.08 mmol). The reaction mixture was degassed by sparging with argon for 15 min and the vial was sealed and irradiated (2 x 34 W blue LED lamps) for 24 h at 23 °C. The reaction mixture was filtered through $MgSO_4$, and concentrated under reduced pressure. ^1H NMR analysis of the crude residue displayed a 2.1:1 ratio of **5.82**:**5.83**. The crude residue was purified by flash column chromatography (2% EtOAc in hexanes to 4% EtOAc in hexanes) to yield an inseparable mixture of esters **5.82** and **5.83** as a clear oil (35 mg, 0.055 mmol, 82% yield). R_f = 0.5 (5% EtOAc in hexanes; visualized with ceric ammonium molybdate). ^1H NMR for major diastereomer **5.82** (500 MHz, $CDCl_3$) δ 3.99 (d, *J* = 10.0 Hz, 1H), 3.97 (d, *J* = 10.0 Hz, 1H), 3.67–3.63 (m, 4H), 3.53 (d, *J* = 11.0 Hz, 1H), 2.57–2.47 (m, 1H), 2.35–2.27 (m, 1H), 2.15–2.05 (m, 1H), 1.92–1.82 (m, 1H), 1.76–1.67 (m, 2H), 1.65–1.41 (m, 5H), 1.40 (s, 3H), 1.39–1.21 (m, 2H), 1.29 (s, 3H), 1.09–0.94 (m, 3H), 0.91 (s, 9H), 0.88 (s, 9H), 0.87 (s, 3H), 0.84 (s, 3H), 0.82 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 6H); ^{13}C NMR for major diastereomer **5.82** (126 MHz, $CDCl_3$) δ 174.5, 105.7, 83.2, 81.2, 69.4, 66.3, 58.2, 52.1, 51.7, 42.8, 41.9, 39.5, 33.6, 33.2, 28.5, 28.2, 26.9, 26.3, 26.3, 26.1, 21.0, 20.9, 19.9, 19.3, 19.1, 18.6, 16.3, –1.9, –3.2, –5.3, –5.4; IR (thin film) 2953, 2857, 1744, 1463, 1379, 1252 cm^{-1}; $[\alpha]^{25}_D$ +30.8 (*c* = 2.5, CH_2Cl_2); HRMS (ESI) calculated for $C_{35}H_{68}O_6Si_2Na$ (M+Na) 663.4452, observed 663.4431.



Experimental procedures for the second-generation synthesis of (–)-chromodorolide B

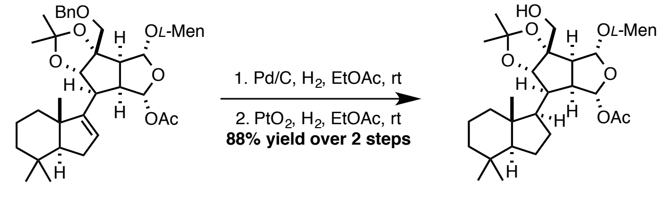


Preparation of lactone 5.85: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **5.57** (93 mg, 0.15 mmol, 1 equiv), **5.84**[2b] (41 mg, 0.15 mmol, 1 equiv), 4CzIPN[83] (2.4 mg, 0.003 mmol, 0.02 equiv), tetrahydrofuran (250 µL, 0.6 M), and a magnetic stir bar. The vial was then sealed with screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5'' needle that was inserted just barely through the septum with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3'' needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging with argon for 15 min. Both needles were removed, and the sealed vial was then placed on a stir plate equipped with 2 x 34 W blue LED lamps and a rack to hold the vial inside of a cardboard box to block light pollution from entering the lab. The vial was placed approximately 4 cm from the lamps and stirred vigorously. The sample was irradiated by the lamps for 18 h. The vial cooled by a stream of air to keep the temperature of the reaction at 23 °C. After 18 h, a degassed solution of Bu_3N (350 µL, 1.5 mmol, 10 equiv) in tetrahydrofuran (1 mL, 0.15 M) was added via syringe. The sample was irradiated by lamps for additional 8 h at 23 °C. The reaction was transferred to a separatory funnel with Et_2O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H_2O (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 0:100 ethyl acetate:hexanes → 4:96 ethyl acetate:hexanes as eluent to yield the desired product **5.85** as a thick colorless foam (51 mg, 0.08 mmol, 54% yield): R_f = 0.13 (5:95 ethyl acetate:hexanes, stained with ceric ammonium molybdate). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39–7.28 (m, 5H), 5.71 (s, 1H), 5.50–5.47 (m, 1H), 4.62 (d, *J* = 2.3 Hz, 2H), 4.38 (d, *J* = 7.9 Hz, 1H), 3.66 (d, *J* = 10.6 Hz, 1H), 3.52 (d, *J* = 10.5 Hz, 1H), 3.44–3.35 (m, 2H), 3.06 (d, *J* = 8.3 Hz, 1H), 3.01–2.91 (m, 1H), 2.10 (ddd, *J* = 15.0, 6.5, 3.2 Hz, 1H), 2.05–1.95 (m, 3H), 1.79 (dd, *J* = 11.7, 6.4 Hz, 1H), 1.74–1.51 (m, 7H), 1.50 (s, 3H), 1.43–1.39 (m, 2H), 1.37 (s, 3H), 1.27–1.11 (m, 3H), 1.02–0.96 (m, 1H), 0.96 (s, 3H), 0.89 (s, 4H), 0.88 (d, *J* = 3.6 Hz, 4H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 12.2 Hz, 1H), 0.74 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 174.8, 150.5, 137.2, 128.7, 128.5, 128.3, 124.8, 113.3, 99.5, 90.1, 86.7, 77.5, 74.2, 71.2, 58.3, 55.4, 47.88, 47.85, 46.1, 43.9, 41.4, 40.4, 36.8, 34.7, 34.5, 33.1, 33.0, 31.5, 30.4, 29.5, 29.2, 25.7, 24.9, 23.3, 22.4, 21.5, 21.1, 20.3, 17.7, 15.8; IR (thin film) 3019, 2956, 1779, 1656, 1457, 1215, 1090 cm^{-1}; $[\alpha]^{21}_{D}$ –116, $[\alpha]^{21}_{577}$ –119, $[\alpha]^{21}_{546}$ –134, $[\alpha]^{21}_{435}$ –225 (*c* = 0.15, CHCl$_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{40}H_{58}O_6$ [M+Na]$^+$ 657.4131; observed 657.4108.



Preparation of diacetal 5.86: A round-bottom flask was charged with **5.85** (143 mg, 0.225 mmol 1 equiv) toluene (4.1 mL, 0.055 M), a magnetic stir bar under an atmosphere of argon and then cooled to –78 °C. A solution of DIBALH (300 μL, 1 M in toluene, 0.292 mmol, 1.3 equiv) was added dropwise to the reaction vessel, keeping the temperature near –78 °C. After 1 h, TLC analysis indicated remaining starting material, and an additional portion of DIBALH (150 μL, 0.15 mmol, 0.65 equiv) was added. After 30 min, a solution of DMAP (55 mg, 0.45 mmol, 2 equiv), pyridine (55 μL, 0.68 mmol, 3 equiv) in CH_2Cl_2 (0.6 mL, 0.4 M) was added, followed by Ac_2O (130 μL, 1.35 mmol, 6 equiv). The reaction was maintained at –78 °C for 8 h, at which point it was allowed to warm to 23 °C. An aqueous solution saturated with Rochelle's salt (5 mL) was added, and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (1 x 5 mL), dried over $MgSO_4$, filtered, and concentrated by use of a rotary evaporator. The crude product was purified by flash column chromatography on silica gel using 0:100 ethyl acetate:hexanes → 8:92 ethyl acetate:hexanes as eluent to yield the desired product **5.86** as a thick colorless foam (150 mg, 0.221 mmol, 98% yield): R_f = 0.26 (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.29 (m, 5H), 5.84 (d, *J* = 4.5 Hz, 1H), 5.59 (d, *J* = 2.3 Hz, 1H), 5.53 (s, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.31 (d, *J* = 8.7 Hz, 1H), 3.61 (s, 2H), 3.31 (td, *J* = 10.6, 4.1 Hz, 1H), 3.22 (td, *J* = 7.6, 4.6 Hz, 1H), 2.97 (d, *J* = 7.8 Hz, 1H), 2.89 (t, *J* = 8.1 Hz, 1H), 2.22 (pd, *J* = 7.2, 2.5 Hz, 1H), 2.03–2.00 (m, 6H), 1.71–1.57 (m, 6H), 1.50 (s, 3H), 1.46 (d, *J* = 3.9 Hz, 1H), 1.45–1.38 (m, 1H), 1.36 (s, 3H), 1.31–1.15 (m, 5H), 0.99 (ddd, *J* = 24.7, 12.9, 3.8 Hz, 2H), 0.94 (s, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.87–0.76 (m, 11H), 0.69 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 151.7, 137.3, 128.4, 128.3, 128.0, 124.4, 113.3, 104,7, 99.6, 90.4, 86.0, 76.8, 73.9, 71.0, 60.3, 57.4, 51.1, 47.6, 47.5, 43.3, 42.0, 40.9, 36.6, 35.2, 34.4, 33.2, 32.8, 31.4, 30.4, 29.6, 28.8, 24.8, 24.7, 22.8, 22.2, 21.1, 21.0, 21.0, 19.9, 17.1, 15.6; IR (thin film) 3019, 1734, 1652, 1214 cm^{-1};

$[\alpha]^{21}_{D}$ –43.2, $[\alpha]^{21}_{577}$ –47.3, $[\alpha]^{21}_{546}$ –56.0, $[\alpha]^{21}_{435}$ –92.3 (*c* = 0.2, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{42}H_{62}O_7$ $[M+Na]^+$ 701.4393; observed 701.4374.

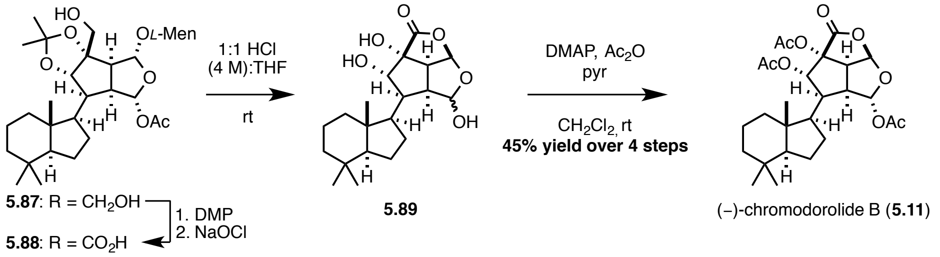


5.86

5.87

Preparation of alcohol 5.87: A 1-dram vial was charged with diacetal **5.86** (37 mg, 0.054 mmol, 1 equiv), $Pd(OH)_2$ (37 mg, 100 wt%), EtOAc (1.1 mL, 0.05 M), and a magnetic stir bar. The reaction vessel was then evacuated and refilled with H_2 (3x). After the resulting suspension was vigorously stirred at rt for 2 h, TLC analysis indicated full consumption of starting material. The reaction mixture was diluted with EtOAc (1 mL), filtered over Celite, and concentrated by use of a rotary evaporator to provide the crude alcohol.

A 1-dram vial was charged with crude alcohol (0.054 mmol), PtO_2 (37 mg, 100 wt%) EtOAc (1.1 mL, 0.05 M), and a magnetic stir bar. The reaction vessel was then evacuated and refilled with H_2 (3 x). The resulting suspension was stirred for 18 h at 23 °C, at which point the reaction vessel was refilled first with Ar and then air. Filtration of the suspension over Celite, concentration of the filtrate by use of a rotary evaporator, and purification of the residue by flash column chromatography on silica gel using 0:100 ethyl acetate:hexanes → 15:85 ethyl acetate:hexanes as eluent provided the desired product **5.87** as a thick colorless foam (28 mg, 0.047 mmol, 88% yield): R_f = 0.35 (20:80 ethyl acetate:hexanes, stained with ceric ammonium molybdate). ^1H NMR (600 MHz, $CDCl_3$) δ 6.05 (d, *J* = 4.2 Hz, 1H), 5.61 (s, 1H), 3.89 (d, *J* = 9.3 Hz, 1H), 3.73–3.61 (m, 2H), 3.36 (td, *J* = 10.6, 4.1 Hz, 1H), 3.22 (td, *J* = 7.1, 4.2 Hz, 1H), 2.81 (d, *J* = 7.5 Hz, 1H), 2.35–2.19 (m, 3H), 2.07 (d, *J* = 11.6 Hz, 1H), 2.03 (s, 3H), 1.83–1.77 (m, 1H), 1.73 (td, *J* = 9.9, 9.1, 5.5 Hz, 2H), 1.62 (tdd, *J* = 11.9, 7.2, 3.1 Hz, 4H), 1.53 (s, 3H), 1.46–1.38 (m, 6H), 1.32 (dtd, *J* = 13.5, 10.2, 9.6, 4.5 Hz, 2H), 1.24–1.18 (m, 1H), 1.08 (s, 2H), 1.04–0.93 (m, 3H), 0.89 (d, *J* = 6.1 Hz, 6H), 0.85 (s, 3H), 0.84 (s, 3H), 0.76 (s, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 112.9, 104.2, 98.0, 91.3, 88.1, 78.3, 64.0, 57.9, 57.2, 52.2, 51.1, 47.8, 45.0, 43.0, 41.6, 41.1, 40.3, 34.6, 33.7, 33.3, 31.6, 30.7, 30.5, 25.7, 25.0, 23.0, 22.4, 21.3, 21.0, 20.3, 15.7, 13.9; IR (thin film) 3383, 2994, 1620 cm^{-1}; $[\alpha]^{22}_{D}$ –56.2, $[\alpha]^{22}_{577}$ –57.2, $[\alpha]^{22}_{546}$ –60.0, $[\alpha]^{22}_{435}$ –105 (*c* = 0.1, $CHCl_3$); HRMS (ESI/TOF) *m/z* calculated for $C_{35}H_{58}O_7$ [M+Na]$^+$ 613.4080; observed 613.4068.



Preparation of (–)-chromodorolide B (5.11): A 1-dram vial was charged with alcohol **5.87** (14 mg, 0.024 mmol, 1 equiv), Dess-Martin periodinane (15 mg, 0.035 mmol, 1.5 equiv), CH_2Cl_2 (0.4 mL, 0.06 M), and a magnetic stir bar. The reaction mixture was maintained at 23 °C for 3.5 h, at which point it was diluted with hexanes (0.5 mL), filtered over Celite, and concentrated by use of a rotary evaporator. The residue was dissolved in hexanes (1 mL) and filtered over Celite. The filtrate was then concentrated by use of a rotary evaporator to afford the crude aldehyde.

A 1-dram vial was charged with crude aldehyde, THF (125 μL, 0.2 M), *t*-BuOH (125 μL, 0.2 M), H_2O (125 μL, 0.2 M), 2-methyl-2-butene (65 μL, 0.4 M), NaH_2PO_4 (36 mg, 0.26 mmol, 10 equiv), $NaClO_2$ (17 mg, 0.19 mmol, 8 equiv), and a magnetic stir bar. The reaction was maintained at 23 °C for 12 h and then diluted with H_2O (1 mL). The solution was washed with EtOAc (3 x 1 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by use of a rotatory evaporator to provide crude acid **5.88**.

A 1-dram vial was charged with crude acid **5.88**, THF (0.4 mL, 0.06 M), 4N HCl (aq) (0.4 mL, 0.06 M), and a magnetic stir bar. The reaction was maintained at 23 °C for 5 days. The reaction was then diluted with H_2O (1 mL), and the solution was washed with EtOAc (3 x 1 mL). The combined organic layers were washed with brine (1 x 1 mL), dried over Na_2SO_4, filtered, and concentrated by use of a rotary evaporator to afford crude lactol **5.89**.

A 1-dram vial was charged with crude lactol **5.89**, CH_2Cl_2 (0.4 mL, 0.06 M), DMAP (3 mg, 0.024 mmol, 1 equiv), pyridine (38 μL, 0.47 mmol, 20 equiv), Ac_2O (33 μL, 0.35 mmol, 15 equiv), and a magnetic stir bar under an atmosphere of argon. The reaction was maintained at 23 °C for 24 h, at which point it was diluted with H_2O (2 mL). The biphasic mixture was extracted with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 3 mL), dried over Na_2SO_4, filtered, and concentrated by use of a rotary evaporator. Purification of the residue by flash column chromatography on silica gel using 20:80 ethyl acetate:hexanes → 30:70 ethyl acetate:hexanes as eluent provided the desired product **5.11** as a colorless solid (5.2 mg, 0.01 mmol, 45% yield). Spectral data were consistent with reported values.[16b]

Computational details for determination of the origin of diastereoselection in additions of trisubstituted acetonide radicals to electron-deficient olefins

To model the reactive radical species, the Furche group developed a multi-level computational approach that included extensive sampling of conformational freedom, thermal corrections within the quasi rigid-rotor harmonic-oscillator approximation,[74] geometry optimization using the TPSS-D3 functional,[75,76] and single-point calculations at the random-phase approximation (RPA) level. RPA is comparable in computational cost to conventional second-order Møller-Plesset (MP2) theory but more reliable for weak interactions,[101] especially for the radical species considered in these diastereoselectivity studies.

All force-field computations were performed using Maestro 2015 with the OPLS-2005 force field.[102,103] The relaxed potential energy surfaces (PES) were optimized using Orca 3.0.3 with additional settings "Grid4" and "TightSCF".[104] Other computations were performed using Turbomole 7.0 with grid *m4*.[105] All structures were optimized using the TPSS[76] functional with def2-SVP or def2-TZVP basis sets[80] as described in the text in combination with the BJ-damped D3-dispersion correction, denoted -D3 in the following.[75] The resolution-of-the-identity approximation for Coulomb term (RI-J)[106] or multipole-accelerated RI-J (MARI-J)[107] were used with the corresponding auxiliary basis sets[108] in Orca and Turbomole, respectively. Solvation effects were taken into account using the COSMO solvation model with a dielectric constant of 8.9 (dichloromethane).[109] Pictures of the computed structures were generated using CYLview.[110]

The experimentally observed differences in the diastereoselectivities are raised by very small energy differences, e.g., 1 kcal/mol error in the computation is enough to change the selectivity from 2.3:1 to 1:2.3. Thus, we used TPSS-D3/def2-TZVP structures to further compute single-point energies with TPSSh-D3[111] and resolution-of-identity random phase approximation (RI-RPA)[112] with corresponding auxiliary basis sets.[113] We also calculated single-point energies using the TPSS functional without dispersion corrections for comparison. For RPA, solvated PBE[114] orbitals were used, and the core orbitals were kept frozen for computation of correlation energy.

Harmonic vibrational frequencies were computed numerically for all studied transition states (TS) at the level of optimization (TPSS-D3/def2-TZVP/COSMO). The chemical potentials (c.p.), which are needed to study the Gibbs free energies (G = E(0) + c.p.), were then calculated using two variations: (i) the standard rigid-rotor harmonic-oscillator (RRHO) approximation and (ii) the quasi-RRHO approach proposed by Grimme.[74] In the quasi-RRHO approach the vibrational entropy is replaced by the free-rotor entropy for all modes with frequencies less than 100 cm^{-1}. Method (ii) is considered more reliable for systems with many vibrational modes below 100 cm^{-1}.[74]

We chose the TPSS functional for the optimizations because of its solid performance across the periodic table.[115] TPSS can be combined efficiently with RI-approximation, which significantly sped up the computations (approx. by factor of 10) and enabled the use of triple-ζ basis set for large set of transition states. The hybrid variant of TPSS, TPSSh, was used for single-point energies. TPSSh contains 10% of Hartree-Fock exchange, which reduces the self-interaction error (SIE), and therefore we consider it to be more accurate to describe interaction between the nucleophilic acetonide radical and electron deficient olefin. These functionals were further coupled with the atom-pairwise D3 dispersion correction. RPA was chosen because it captures the non-pairwise-additive nature of long-range interactions accurately[107] and from first principles. In our preliminary study for radical **5.74D**, we also employed MP2/def2-QZVP to study the selectivity. The wave-functions were, however, spin-contaminated at Hartree-Fock level (the total spin expectation value was ~1 instead of 0.75) and the norm of the T_2 amplitudes was high (>1).

This suggested that the reliability of MP2 for these systems is questionable, and therefore MP2 was not used further. The basis-set convergence of RPA was tested for radicals **4.74A** and **4.74C** by extrapolating the correlation energy to the complete basis-set (CBS) limit using a two-point extrapolation scheme[101,116] with Dunning's cc-pVXZ[117] basis-sets, where X=3,4 (Table S5.2)

Table S5.2. The RPA energy differences between **TS-*anti*** and **TS-syn** for different basis-sets in kcal/mol.

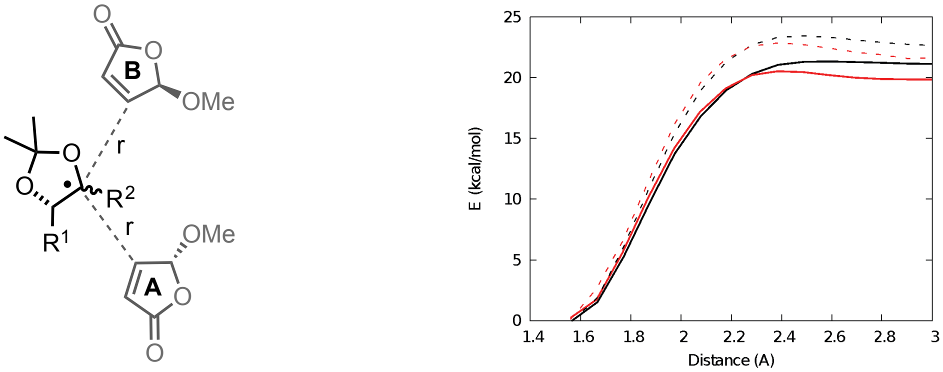
Basis set	ΔΔE(**5.74A-*anti*** – **5.74A-*syn***)	ΔΔE(**5.74C-*anti*** – **5.74C-*syn***)
def2-TZVP	0.12	3.26
cc-pVTZ	-0.08	3.01
cc-pVQZ	0.13	3.24
CBS(3,4)	0.13	3.30

Protocol for selectivities

To explain the experimentally observed selectivities, diastereoselectivities were computed to radicals **5.74A**–**5.74F**, and **5.77B**–**5.77E**. The OBn and OTBS-groups were simplified to OMe and OTMS, respectively.

We started by studying the reaction profile for the radical addition for radical **5.74D.** First, the lowest energy conformer of the addition products was located, and then the relaxed PES was optimized (Figure S5.1). The PES was studied for different values for bond distance r with TPSS-D3 and TPSSh-D3 using def2-SVP basis sets and in the gas-phase.

Figure S5.1. The PES using different r values to describe the C-C bond formation step for radical **5.74D**. Solid lines = TPSS-D3/def2-SVP; dashed lines = TPSSh-D3/def2-SVP; black = syn; red = anti.



The two functionals provided slightly different PESs: TPSS-D3 predicted lower activation energy barriers than TPSSh-D3, and the PES for *syn*-reaction was found to be barrierless, which might be an artifact due to SIE. However, both methods agreed that the interaction between radical and the olefin starts at approximately r = 2.5 Å. Thus, this distance was used in the conformational sampling of the transition states. The C–C bond formation step is very exothermic (by ~20-25 kcal/mol, Figure S5.1) and as a result was considered irreversible.

Next, the selectivity was studied using a multi-level protocol. First, the preliminary TSs were formed for all studied radicals by freezing r at 2.5 Å and optimizing the *syn* and *anti* TSs with TPSS-D3/def2-SVP in the gas-phase. Then, the lowest energy conformers were determined at this distance. For conformers within 1 kcal/mol, the PES was studied using TPSS-D3/def2-TZVP with COSMO for bond distances of r = 2.3–2.5 Å in 0.05 Å steps. These optimized structures were then used to compute the PES with TPSS, TPSS-D3, TPSSh-D3 and RPA. All methods employed COSMO and def2-TZVP basis sets. The PES scan was extended up to 2.7 Å if the PES was not converged at the RPA level.

The maximum of the PES was taken as the as the absolute energy of the TS and used to determine the selectivity. The PESs for different methods are shown in Figure S5.4 Thermal corrections were calculated for the transition states according to RPA, i.e., we chose the TPSS-D3/def2-TZVP optimized structure, which has the highest energy in the RPA PES.

Conformational search

To perform a conformational search using molecular mechanics methods, the constrained TS structure was first optimized with TPSS-D3/def2-SVP to obtain the correct relative position for C^1 and C^2, which were set 2.5 Å apart. In Maestro, a long bond of 2.5 Å was inserted between the respected atoms and the electrophile was modified to be an enolate anion instead of a radical (Figure S5.2A) because we did not have access to force field, which is parameterized for sp^3 carbon radicals. The Cartesian coordinates of C^1 and C^2 were kept frozen during the conformational search. Systematic torsional sampling was employed using the OPLS-2005 force field with the following settings: Torsion sampling options "Intermediate"; maximum number of steps "2000"; steps per rotatable bond "4"; energy window for saving structures "6 kcal/mol".

Figure S5.2. Maestro Computational Search. **A.** In force field calculations, the system was modified to be an enolate anion. **B.** In quantum chemical computations, the system was treated as radical. In both cases, the bond distance r was fixed at 2.5 Å.

All structures within 6 kcal/mol were then re-optimized using TPSS-D3/def2-SVP in gas-phase. The bond length was kept fixed at 2.5 Å, but unlike in the force field optimization, the relative orientation of C^1 and C^2 was allowed to relax freely instead of fixing the Cartesian coordinates. The system was treated as a radical instead of enolate anion (Figure S5.2B), which was not possible in the force field computations as explained above. The conformers below 1 kcal/mol where then visually inspected and taken to PES study if the structures differed from each other. Optimization of all conformers of radical **5.74D** with COSMO and computing single-point energies with TPSSh-D3/def2-SVP leads to identical lowest energy conformer confirming the validity of our approach.

Correlation between theory and experiment

The computed energy difference between *syn*- and *anti*-TSs was used to calculate the diastereoselectivity using the Boltzmann distribution at 298 K. The correlation between experiment and theory was studied using three approaches:

(i) Selectivity was determined according to ΔE values (Table S5.3)

(ii) Thermal corrections were added to the ΔE values using the RRHO-approximation (Table S5.4)

(iii) Thermal corrections were added to the ΔE values using the quasi-RRHO approach (Table S5.5)

Approach (iii) was found to be most realistic for the following reasons: First, the selectivities arise from very small energy differences and thus the thermal corrections are important. Second, small errors in low-lying frequencies cause significant error in the vibrational entropy; for example, the *syn*-selectivity of radical **5.77E** is underestimated using approach (ii) with RPA (experiment 89%; theory 60%) whereas with approach (iii) the correlation is quantitative with the experiment (experiment 89%; theory 85%). Approaches (i) and (ii) are only shown for comparison.

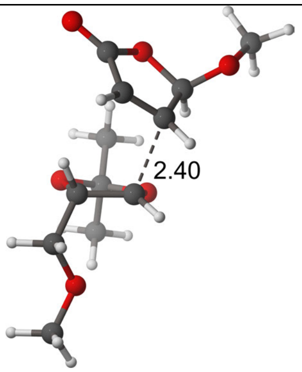
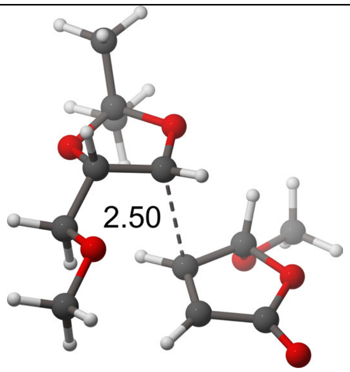
With approach (iii), the correlation between the experiment and theory is semi-quantitative for most studied radicals when TPSS-D3, TPSSh-D3 or RPA is used, whereas the result is worse with non-dispersion corrected TPSS, which illustrates the importance of medium- and long-range non-covalent interactions. The correlation is best for TPSSh-D3 and RPA. The *anti*-selectivity of radical **5.74A** was not reproduced but this originates from very small energy error (1-2 kcal/mol) and is within the error margin of the methods used here. All methods except RPA also produce the *anti*-selectivity qualitatively correctly at ΔE-level. The *syn*-selectivity is overestimated slightly for most radicals with prefix **5.74**, whereas the more complex with prefix **5.77** are computed with quantitative accuracy using TPSSh-D3 and RPA.

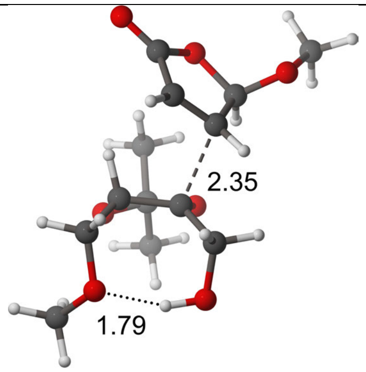
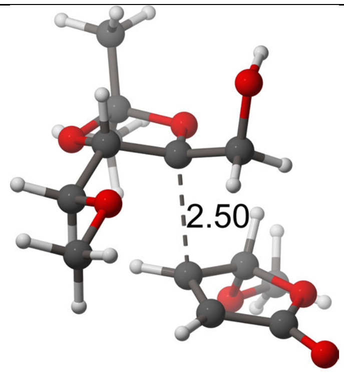
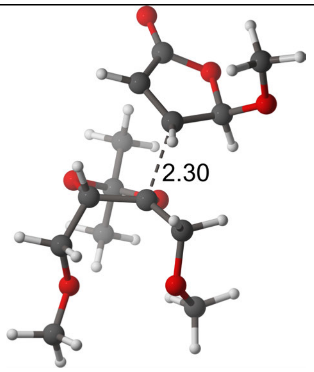
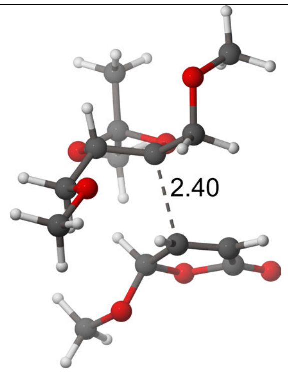
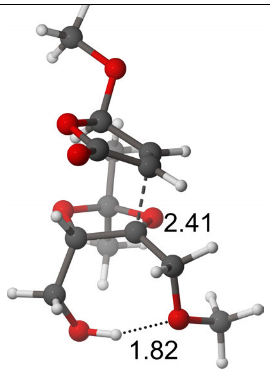
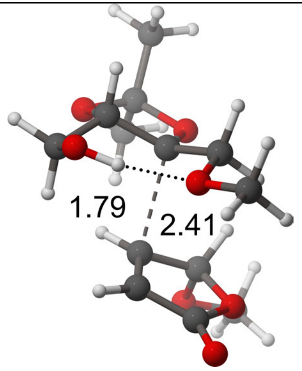
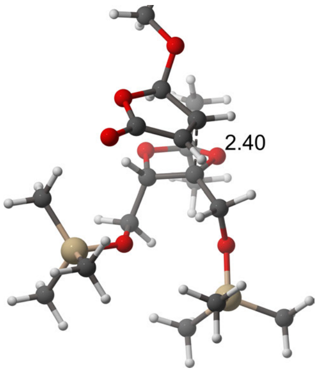
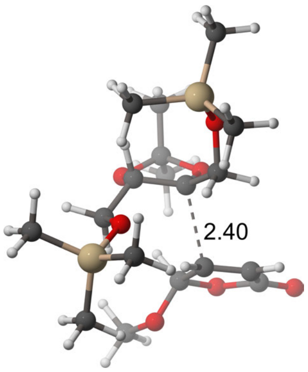
The effect of entropy on the selectivity can be assessed by comparing approaches (i) and (iii) (Table S5.3 and Table S5.5). In most cases, the correlation is still qualitative but not quantitative for approach (i). Thus, the effect of entropy on these results is significant. The standard RRHO-approximation predicts too high entropies especially for larger complexes (**5.77**) with more low-lying frequencies whereas the smaller complexes (**5.74**) are not affected much.

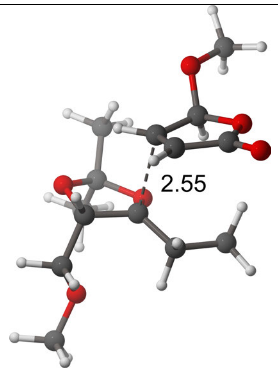
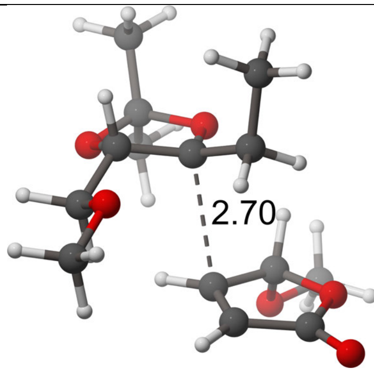
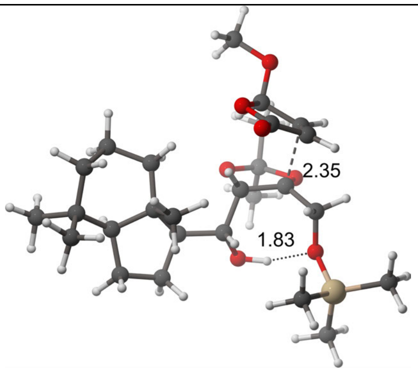
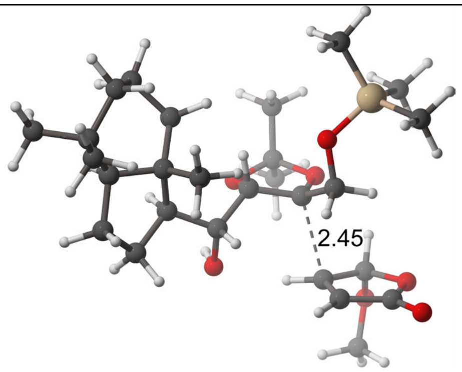
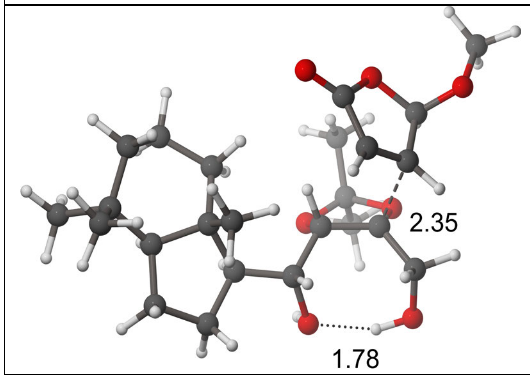
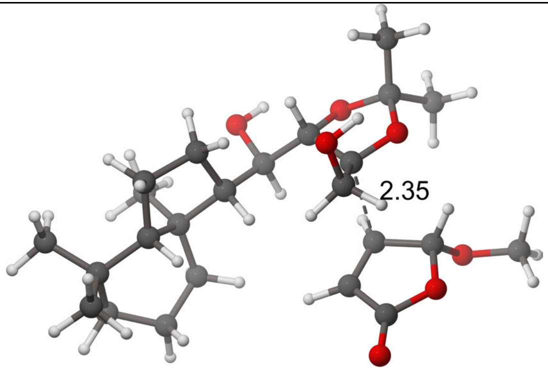
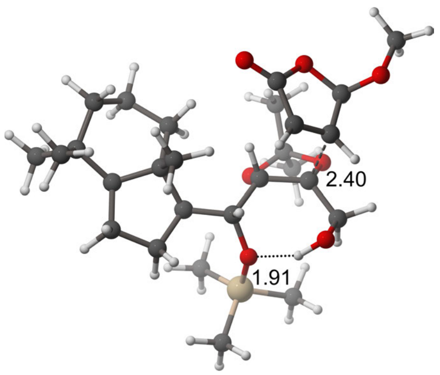
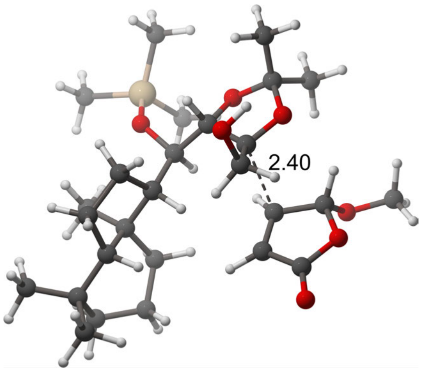
In summary, the selectivity of the radical addition can be computed with high accuracy if the following aspects are carefully taken into account: For large molecules, the conformational freedom causes much larger deviation to the energy than is needed to induce the selectivity. In addition, the computational method needs to accurately account for dispersive interactions between the different functional groups of the radical and between the radical and the approaching olefin. Especially for large complexes thermal effects should be computed with the quasi-RRHO-approximation.

Computational figures and transition state figures

Figure S5.3. RPA/def2-TZVP/COSMO Transition State Structures Optimized Using TPSS-D3/def2-TZVP/COSMO.

	
5.74A-*anti*	**5.74A-*syn***

	
5.74B-*anti*	**5.74B-*syn***
	
5.74C-*anti*	**5.74C-*syn***
	
5.74D-*anti*	**5.74D-*syn***
	
5.74E-*anti*	**5.74E-*syn***

	
5.74F-*anti*	**5.74F-*syn***
	
5.77A-*anti*	**5.77A-*syn***
	
5.77B-*anti*	**5.77B-*syn***
	
5.77C-*anti*	**5.77C-*syn***

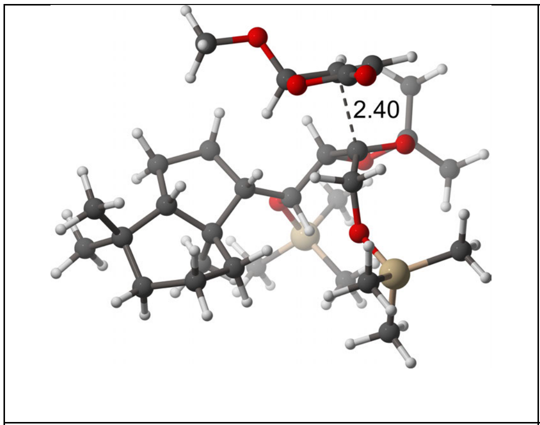
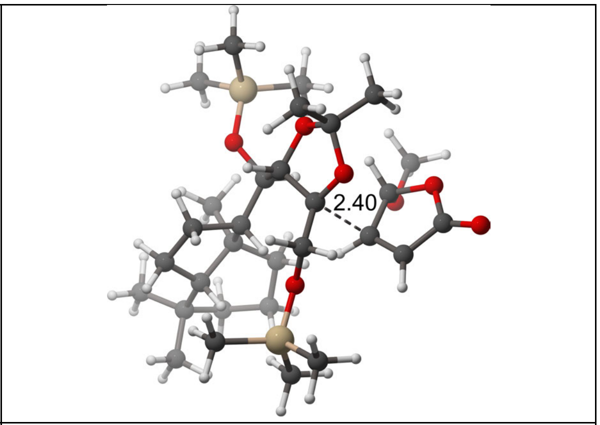
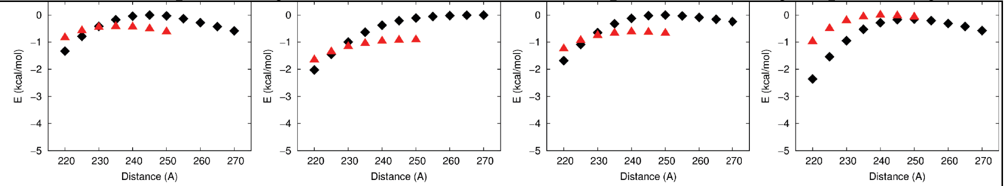
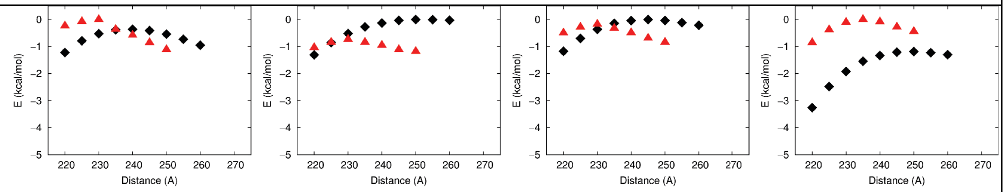
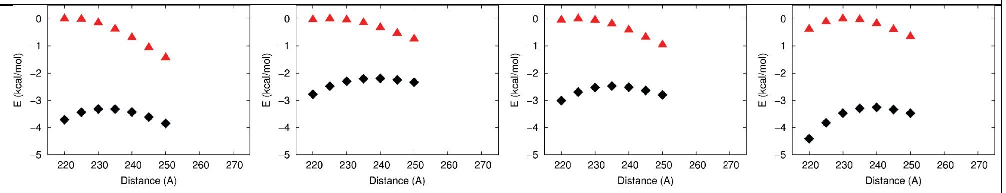
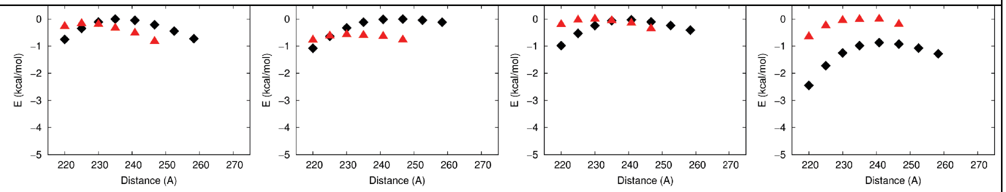
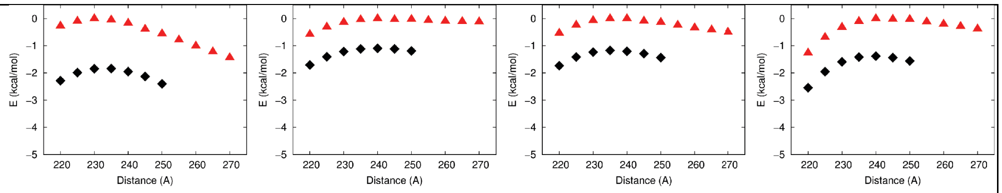
	
5.77D-*anti*	**5.77D-*syn***

Figure S5.4. The PES's for the studied radicals computed using different methods. The geometries were relaxed at TPSS-D3/def2-TZVP/COSMO level and different methods were used for single-point energies with def2-TZVP basis set and COSMO. The red-triangles represent the *anti*-pathway and black diamonds represent the *syn*-pathway.

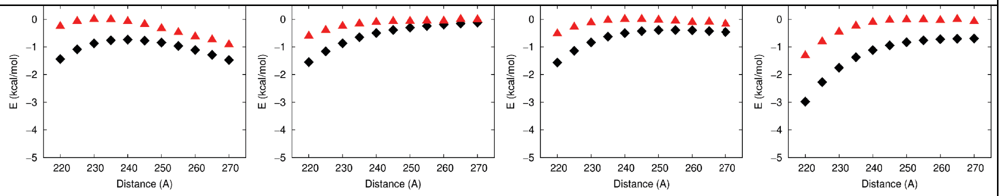
5.74A	 (a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA
5.74B	 (a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA
5.74C	 (a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA
5.74D	 (a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

5.74E



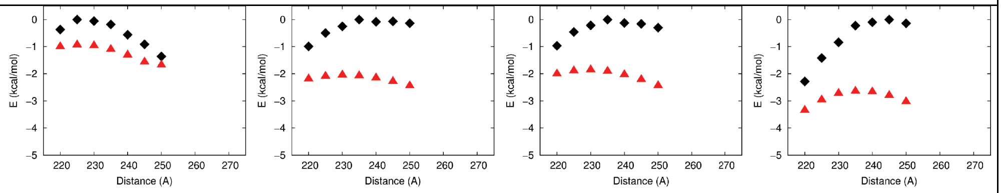
(a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

5.74F



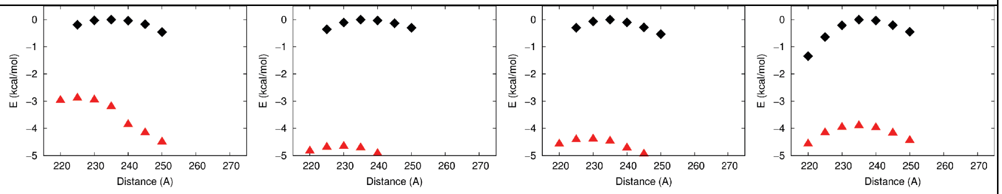
(a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

5.77B



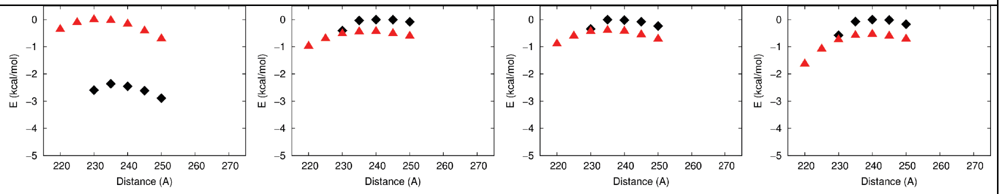
(a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

5.77C



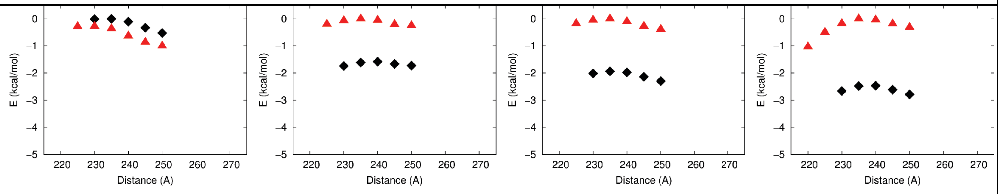
(a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

5.77D



(a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

5.77E



(a) TPSS (b) TPSS-D3 (c) TPSSh-D3 (d) RPA

Table S5.3. The energy difference (ΔE) between TS-*anti* and TS-*syn* computed with several methods in kcal/mol. The %-values represent the computed amount of *syn*-product which is calculated from the ΔE values using the Boltzmann distribution at 298 K.

	TPSS		TPSS-D3		TPSSh-D3		RPA		Exp
Radical	ΔE	%	ΔE	%	ΔE	%	ΔE	%	%
5.74A	-0.4	33	-0.9	18	-0.6	26	0.1	55	22
5.74B	0.4	65	-0.7	22	-0.2	43	1.2	88	77
5.74C	3.3	100	2.2	98	2.5	98	3.3	100	72
5.74D	-0.2	43	-0.6	28	0.0	51	0.9	81	72
5.74E	1.8	96	1.1	86	1.2	88	1.4	91	69
5.74F	0.7	77	0.1	55	0.4	66	0.7	76	90
5.77B	-0.9	17	-2.0	3	-1.9	4	-2.6	1	43
5.77C	-2.9	1	-4.7	0	-4.4	0	-3.9	0	9
5.77D	2.4	98	-0.4	32	-0.4	34	-0.5	29	88
5.77E	-0.3	39	1.6	93	1.9	96	2.5	98	89

Table S5.4. The energy difference (ΔG 298) between TS-*anti* and TS-*syn* computed with several methods in kcal/mol. The %-values present the computed amount of *syn*-product, which is calculated from the ΔG values using the Boltzmann distribution at 298 K. Thermal corrections are accounted using standard RRHO-approximation.

	TPSS		TPSS-D3		TPSSh-D3		RPA		Exp
Radical	ΔG	%	ΔG	%	ΔG	%	ΔG	%	%
5.74A	0.5	70	0.0	50	0.3	62	1.0	85	22
5.74B	2.1	97	1.0	85	1.6	94	2.9	99	77
5.74C	2.7	99	1.5	93	1.8	96	2.6	99	72
5.74D	0.6	74	0.2	59	0.8	80	1.7	94	72
5.74E	1.5	93	0.8	78	0.8	80	1.0	85	69
5.74F	1.9	96	1.2	89	1.5	93	1.8	96	90
5.77B	1.2	88	0.1	53	0.3	61	-0.5	29	43
5.77C	-1.9	4	-3.7	0	-3.5	0	-3.0	1	9
5.77D	3.9	100	1.1	87	1.2	88	1.0	85	88
5.77E	-2.5	1	-0.6	25	-0.3	38	0.2	60	89

Table S5.5. The energy difference (ΔG 298) between TS-*anti* and TS-*syn* computed with several methods in kcal/mol. The %-values present the computed amount of *syn*-product, which is calculated from the ΔG values using the Boltzmann distribution at 298 K. Thermal corrections are accounted using quasi-RRHO approach.

	TPSS		TPSS-D3		TPSSh-D3		RPA		Exp
Radical	ΔG	%	ΔG	%	ΔG	%	ΔG	%	%
5.74A	0.3	62	-0.2	41	0.1	54	0.8	80	22
5.74B	1.7	95	0.6	74	1.2	88	2.5	99	77
5.74C	2.6	99	1.5	93	1.8	95	2.6	99	72
5.74D	0.4	65	0	49	0.6	72	1.4	91	72
5.74E	1.5	93	0.8	79	0.9	81	1.1	86	69
5.74F	1.3	90	0.7	76	1	83	1.3	89	90
5.77B	0.9	83	-0.2	43	0	51	-0.8	21	43
5.77C	-2.2	3	-3.9	0	-3.7	0	-3.2	0	9
5.77D	3.7	100	0.9	82	0.9	83	0.8	79	88
5.77E	-1.7	5	0.1	56	0.5	70	1	85	89

Table S5.6. Absolute energies for transition states in *Hartrees*.

	TPSS	TPSS-D3	TPSSh-D3	RPA
5.74A-*anti*	-920.475563	-920.525971	-920.418546	-919.972228
5.74A-*syn*	-920.474888	-920.524515	-920.41756	-919.97242
5.74B-*anti*	-1035.07049	-1035.13179	-1035.01093	-1034.51537
5.74B-*syn*	-1035.07107	-1035.13062	-1035.01065	-1034.51726
5.74C-*anti*	-1074.3841	-1074.45138	-1074.32649	-1073.81699
5.74C-*syn*	-1074.38939	-1074.45488	-1074.33043	-1073.82218
5.74D-*anti*	-1035.07171	-1035.13381	-1035.01282	-1034.51728
5.74D-*syn*	-1035.07145	-1035.1329	-1035.01287	-1034.51866
5.74E-*anti*	-1813.36302	-1813.46534	-1813.31944	-1811.93735
5.74E-*syn*	-1813.36596	-1813.46708	-1813.32131	-1811.93955
5.74F-*anti*	-999.147161	-999.210532	-999.096534	-998.624269
5.74F-*syn*	-999.14832	-999.210717	-999.097153	-998.625353
5.77B-*anti*	-1874.12141	-1874.2673	-1874.09605	-1872.97609
5.77B-*syn*	-1874.11993	-1874.26405	-1874.0931	-1872.97188
5.77C-*anti*	-1465.3137	-1465.43771	-1465.28123	-1464.61189
5.77C-*syn*	-1465.3091	-1465.43028	-1465.27423	-1464.60567
5.77D-*anti*	-1874.10962	-1874.26208	-1874.09122	-1872.97076
5.77D-*syn*	-1874.11339	-1874.26139	-1874.09059	-1872.96991
5.77E-*anti*	-2282.91775	-2283.09017	-2282.90445	-2281.33148
5.77E-*syn*	-2282.91731	-2283.09269	-2282.90754	-2281.33541

Table S5.7. TPSS-D3/def2-TZVP/COSMO chemical potentials (c.p. in kJ/mol) for all transition states using RRHO and quasi-RRHO approximations and imaginary-frequencies ν_{im} in cm^{-1}.

	c.p.(RRHO) kJ/mol	c.p.(quasi-RRHO) kJ/mol	ν_{im} (cm^{-1})
5.74A-*anti*	656.93	663.44	91.03
5.74A-*syn*	653.1	660.484	86.54
5.74B-*anti*	736.35	743.378	122.91
5.74B-*syn*	729	737.74	-
5.74C-*anti*	800.13	807.942	129.47
5.74C-*syn*	802.88	810.821	107.26
5.74D-*anti*	736.93	743.257	66.41
5.74D-*syn*	733.65	740.999	136.35
5.74E-*anti*	1141.97	1158.31	74.16
5.74E-*syn*	1143.42	1159.57	100.48
5.74F-*anti*	788.59	797.36	-
5.74F-*syn*	783.89	794.98	-
5.77B-*anti*	1635.21	1652.98	94.68
5.77B-*syn*	1626.38	1645.16	74.42
5.77C-*anti*	1400.76	1412.39	121.61
5.77C-*syn*	1396.82	1409.37	146.72
5.77D-*anti*	1645.36	1659.31	92.47
5.77D-*syn*	1638.8	1653.8	135.18
5.77E-*anti*	1866.89	1891.22	73.36
5.77E-*syn*	1876.19	1897.28	113.09

Computational details for determination of the mechanism of 5-*exo* cyclization event during the ACF cascade and modifications of the butenolide coupling partner.

Structures were optimized in solution using the TPSS[76] functional and def2-TZVP basis sets[80] in combination with the BJ-damped D3-dispersion correction, denoted with –D3.[75] Solvation effects were accounted for using the COSMO[109] model for dichloromethane (ε = 8.9) unless otherwise noted, and for acetonitrile, dielectric constant of 37.5 was used. Chemical potentials (c.p.) and the Gibbs free energies (G = E(0) + c.p.) were computed at 298.15 K from the harmonic vibrational frequencies using the quasi rigid-rotor harmonic oscillator (quasi-RRHO) approach where the free-rotor entropy was used instead of vibrational entropy for all modes less than 100 cm^{-1}.[74] For comparison, we also computed single-point energies for the optimized structures using the TPSSh-D3[111] hybrid functional to exclude computational artifacts originating from the self-interaction error (SIE) of density functional theory (DFT).

All computations were performed using Turbomole 7.1 program package[118] with default settings except finer integration grid *m4* was used. The multipole-accelerated resolution-of-the-identity approximation (MARI-J)[107] was used with the corresponding auxiliary basis sets to significantly speedup computation of the Coulomb energy.[108] Structures were visualized using CYLview.[110]

Mechanism of 5-*exo* Cyclization

Two mechanistic scenarios were considered for the intramolecular 5-*exo* cyclization: In (**a**), the α-acyloxy radical intermediate cyclizes directly, and in (**b**), the radical intermediate is first reduced to enolate anion prior the S_N2-type cyclization. The α-acyloxy radical intermediate exists in two conformers, **Int1-*cis*** and **Int1-*trans***, yielding *cis* and *trans* products via two diastereomeric transition states (TSs) **TS-*cis*** and **TS-*trans***, see Figure S5.5. Both ground states are thermodynamically accessible within energy window of 1.8 kcal/mol favoring *cis* ground state. Kinetic barriers for the *cis* and *trans* additions are 8.9 and 7.9 kcal/mol, respectively, and are in accordance with *trans* product being observed as the main product. Overall, the reactions are exergonic by 7.9-9.3 kcal/mol and considered irreversible.

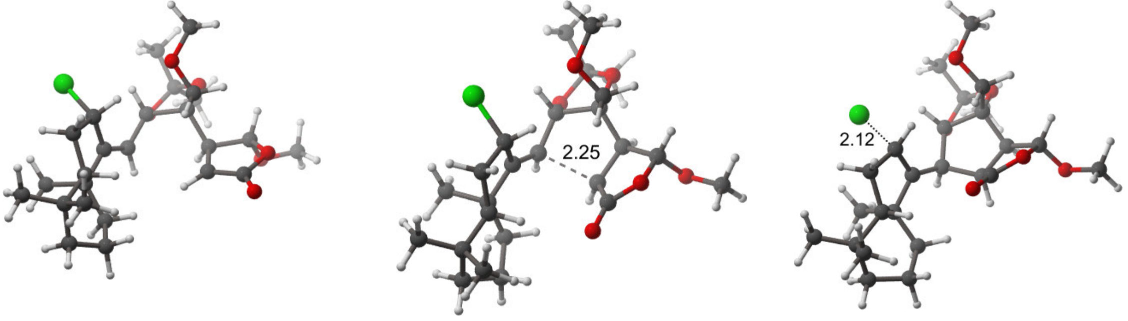
Computed reaction profiles are energetically similar for the radical (**a**) and enolate (**b**) pathways; see Figure S5.6 for (**b**). Enolate S_N2 TSs are earlier than the corresponding radical TSs: The C-C bond distances in the radical pathway are 2.25 and 2.38 Å for **TS-*cis*** and **TS-*trans***, while they are 2.70 and 2.62 Å in the enolate pathway. The kinetic barriers are 8.1 and 8.6 kcal/mol for the enolate **TS-*cis*** and **TS-*trans***, respectively.

The operative pathway was concluded from the computed and experimental diastereomeric ratios, see Table S5.8. For the radical pathway, computed *cis*:*trans* ratio is 1:5.6 in dichloromethane (DCM) and 1:2.5 in acetonitrile (MeCN). These agree well with the experimentally obtained ratios, 1:1.8 in DCM and 1:1.3 in MeCN. The **TS-*cis*** is slightly favored over the **TS-*trans*** in the enolate pathway, yielding *cis*:*trans* ratios of 2.3:1 in DCM and 3.4:1 in MeCN, qualitatively disagreeing with experiment. The computed diastereomeric ratios of the radical pathway are consistent with the experimental values and also reproduce the correct solvation effect where *cis*-isomer forms slightly more in MeCN than in DCM.

Table S5.8. The relative Gibbs free energies and populations of **TS-*cis*** and **TS-*trans*** for radical and enolate pathways.

	Computed radical pathway		Experimental	Computed enolate pathway	
	ΔG(*cis*-*trans*)	*cis*:*trans*	*cis*:*trans*	ΔG(*cis*-*trans*)	*cis*:*trans*
Dichloromethane	**1.0**	1:5.6	1:1.8	**-0.5**	2.3:1
Acetonitrile	**0.5**	1:2.5	1:1.3	**-0.7**	3.4:1

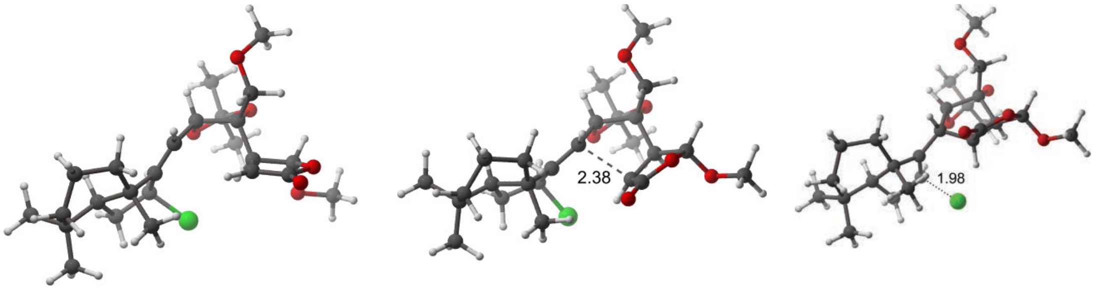
Figure S5.5. *Cis* and *trans* 5-*exo* cyclizations from the α-acyloxy radical intermediate. The Gibbs free energies are in kcal/mol.



0.0
Int1-*cis*

8.9
TS-*cis*

-7.9
Int2-*cis*

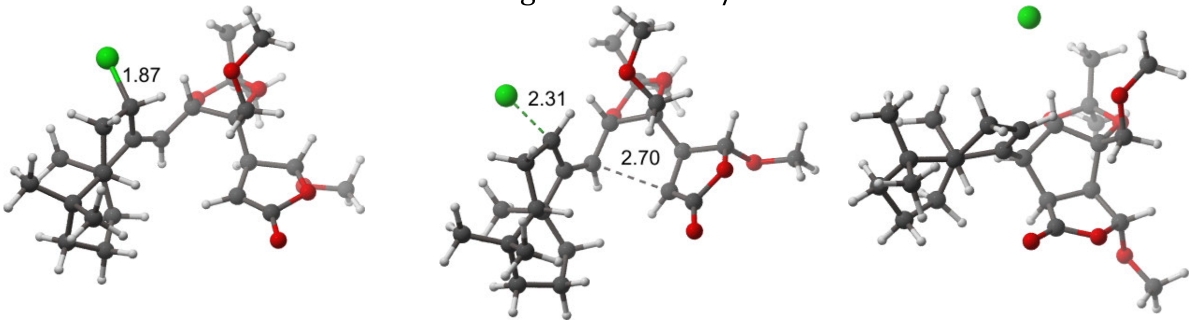


1.8 Int1-*trans*

7.9 TS-*trans*

-9.3 Int2-*trans*

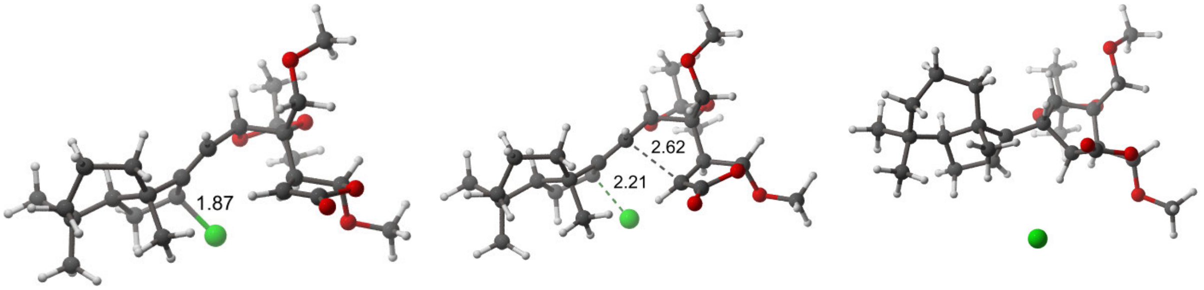
Figure S5.6. *Cis* and *trans* 5-*exo* cyclizations from the enolate intermediate. The Gibbs free energies are in kcal/mol.



0.0 Int1-*cis*

8.1 TS-*cis*

-34.8 Int2-*cis*



2.5 Int1-*trans*

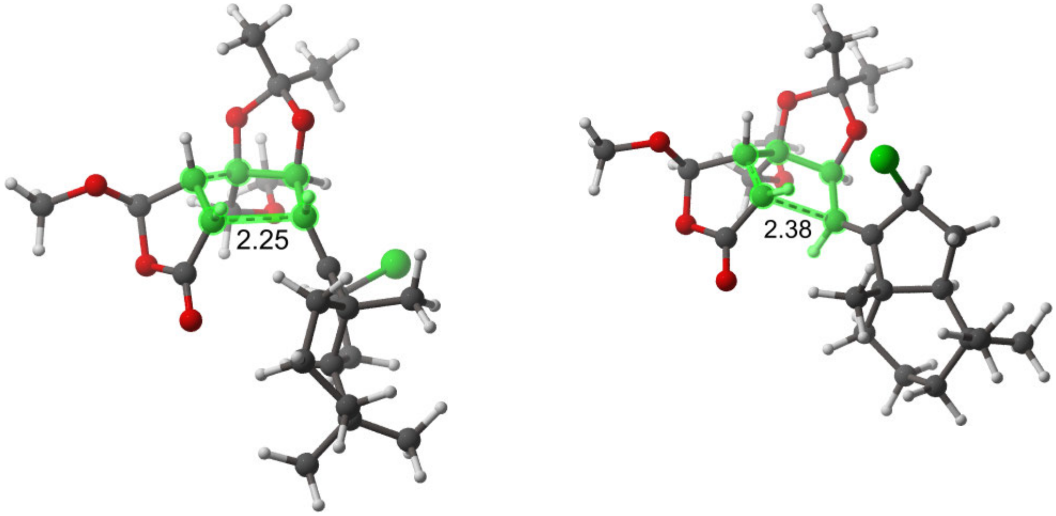
8.6 TS-*trans*

-36.9 Int2-*trans*

Predicted Substrate Modifications

The **TS-*trans*** is stabilized by helical structure similar to enantioselective Rautenstrauch rearrangement,[119] and is 0.5-1.0 kcal/mol more stable than the **TS-*cis***, see Figure S5.7 and Table S5.8. For similar TSs,[120] larger C-X substituents on bond forming carbons destabilize *cis* TSs, whereas the helical shaped *trans* TSs are not affected much. In this system, however, we envisioned that the helicity of the **TS-*trans*** may be distorted by halogenating the butenolide α-CH bond to cause halogen-halogen repulsion with the chlorohydrindane chloride substituent. In **TS-*cis*** the chloride points to opposite direction and the modification would mainly affect the **TS-*trans***. Additionally, halogenation would shift the TSs later by decreasing the nucleophilicity of the butenolide radical, which could affect the earlier **TS-*trans*** more than the later **TS-*cis***.

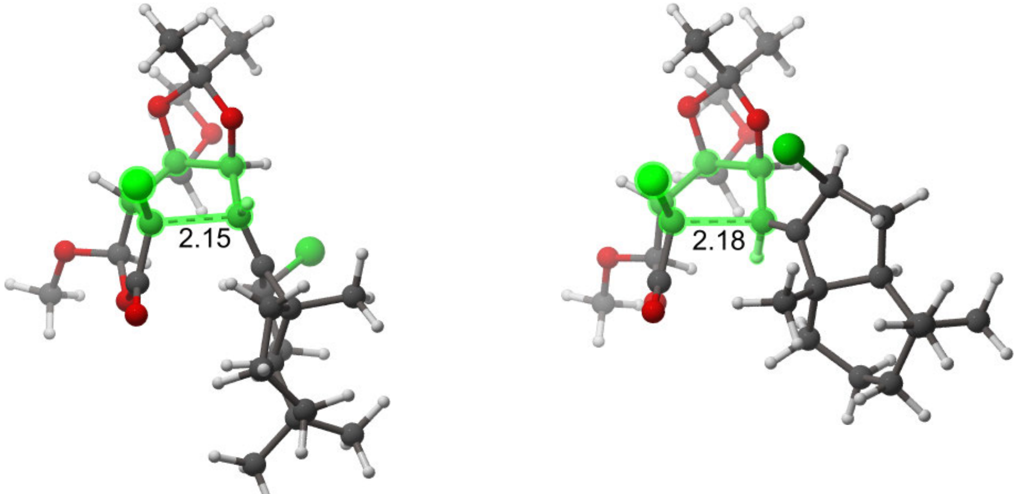
Figure S5.7. The optimized diastereomeric transition states **TS-*cis*** and **TS-*trans*** for the butenolide substrate.



TS-*cis*, R = H **TS-*trans***, R = H

The predicted TSs for the chloride analogue are shown in Figure S5.8. As envisioned, the **TS-*trans*** is affected significantly: The C-C bond distance is decreased from 2.38 Å to 2.18 Å and the helicity is distorted. As a consequence, the kinetic barrier for the *trans* product is increased from 7.9 kcal/mol to 11.3 kcal/mol (Figure S5.9). The **TS-*cis*** is also shifted slightly, from 2.25 Å to 2.15 Å, and the kinetic barrier is increased from 8.9 kcal/mol to 9.4 kcal/mol. The **TS-*cis*** is now predicted more stable than the **TS-*trans*** by 2 kcal/mol, which should yield almost complete *cis* selectivity, see Table S5.9. For bromide analogue, the selectivity is predicted to be even slightly higher, see Table S5.9 and Figure S5.10.

Figure S5.8. The optimized diastereomeric transition states **TS-*cis*** and **TS-*trans*** for the chlorobutenolide substrate.



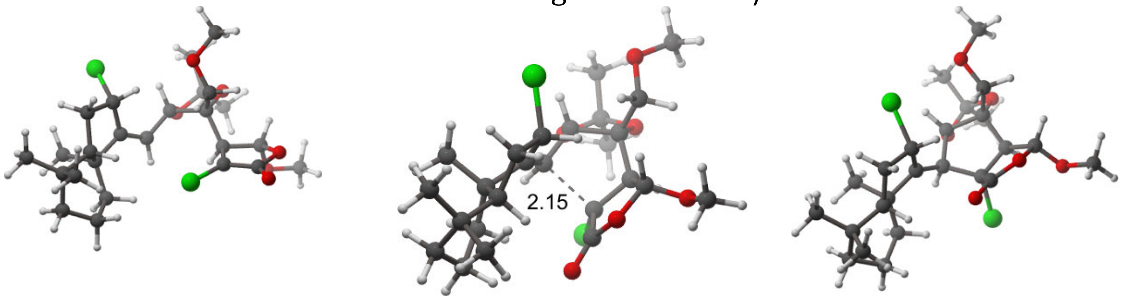
TS-*cis*, R = Cl

TS-*trans*, R = Cl

Table S5.9. The relative Gibbs free energies and populations of **TS-*cis*** and **TS-*trans*** for α-H, α-Cl and α-Br butenolide substrates.

	R = H		R = Cl		R = Br	
Functional	ΔG(*cis*-*trans*)	*cis*:*trans*	ΔG(*cis*-*trans*)	*cis*:*trans*	ΔG(*cis*-*trans*)	*cis*:*trans*
TPSS-D3	**1.0**	1:5.6	**-2.0**	32:1	**-2.5**	46:1
TPSSh-D3	**1.1**	1:5.7	**-2.1**	32:1	**-2.5**	46:1

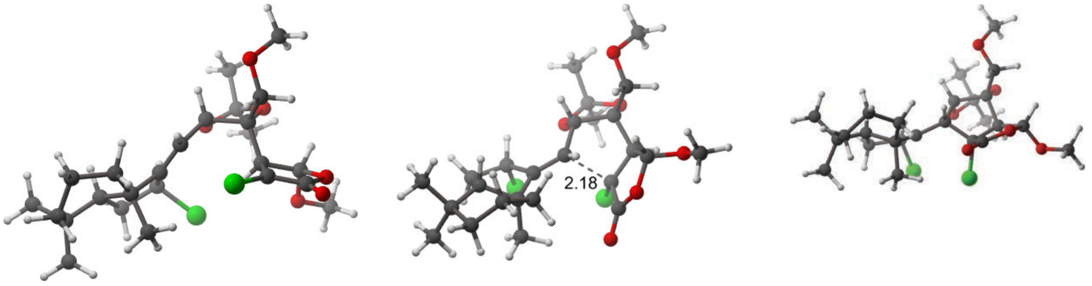
Figure S5.9. *Cis* and *trans* 5-*exo* cyclizations for the chlorobutenolide analogue. The Gibbs free energies are in kcal/mol.



0.0
Int1-*cis*

9.4
TS-*cis*

-1.9
Int2-*cis*

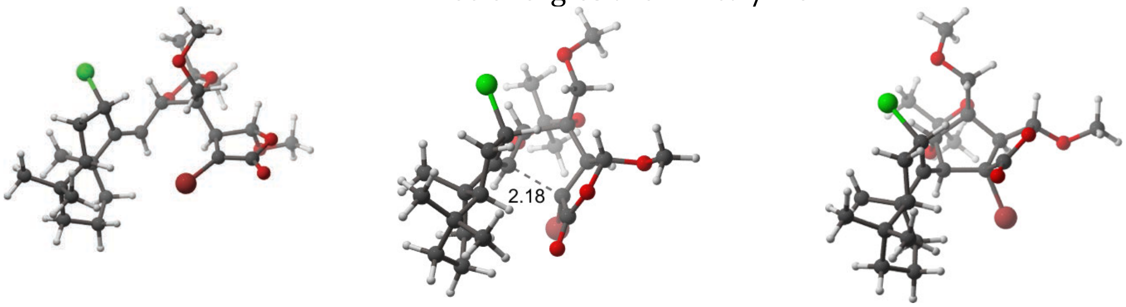


3.1
Int1-*trans*

11.3
TS-*trans*

0.3
Int2-*trans*

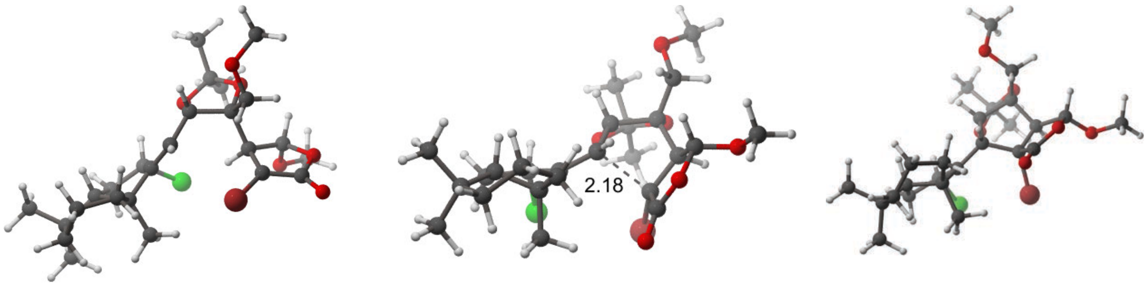
Figure S5.10. *Cis* and *trans* 5-*exo* cyclizations for the bromobutenolide analogue. The Gibbs free energies are in kcal/mol.



0.0
Int1-*cis*

8.1
TS-*cis*

-3.8
Int2-*cis*



2.2
Int1-*trans*

10.5
TS-*trans*

-0.9
Int2-*trans*

Cartesian Coordinates

The TPSS-D3/def2-TZVP/COSMO optimized coordinates are given for all RPA TS's.

5.74A-*anti*				**5.74A-*syn***			
C	0.01261364669752	0.01272813864658	-0.00298164486521	C	0.08853627960581	-0.08808280046886	-0.01150427439277
C	2.41252795923541	-0.00708081383874	-0.00730677582753	C	2.58659716721781	0.00848454047020	-0.03064286247445
C	2.84299353711932	1.28980532565561	0.00042571904059	C	3.00937772784375	1.29813398776755	-0.02183936722186
C	3.19968167887584	1.68453458747556	-1.35143089854895	C	3.30729755105475	1.71388410966637	-1.38566796431879
O	3.03475225176581	0.58279361276444	-2.18756054948773	O	3.09194028893765	0.63295940503231	-2.23210521810081
C	2.65519524068466	-0.57574894748282	-1.37946936004221	C	2.71791109450096	-0.53209984080804	-1.42984893977026
O	-0.45290043829258	-0.61215318837732	-1.10567658697681	O	-0.15920191227784	-1.32834794026702	-0.51048290302105
C	-1.06507933225690	0.38513004531885	-2.01753507615616	C	-0.45977525712113	-2.23395039676988	0.62805135701206
O	-0.84913286541024	1.64449696631896	-1.37827983629261	O	-0.20158625844862	-1.44202058096034	1.78994098756313
C	-0.38629924504575	1.45698281020217	-0.02301307223438	C	-0.37640719447329	-0.05974051515333	1.41223120833380
C	-1.42234822696767	1.84854034579359	1.02712595602732	C	0.38709060971083	0.81664763688486	2.39343384557267
O	-2.48266896843947	0.89852138861804	1.04615736822442	O	0.22417377214411	2.16147388089643	1.95293726899204
C	-3.52171917567985	1.27673984911740	1.95461245615998	C	0.86096927345558	3.08960205067112	2.83848517077239
C	-0.33536084167968	0.36013613161307	-3.34841171006641	C	-1.92686029473091	-2.62043452879031	0.51641646021483
C	-2.54366918258919	0.04635949841716	-2.11822798731588	C	0.50493338787975	-3.40041786898341	0.59513503597022
O	3.69673072190532	-1.51168625743146	-1.32480082260376	O	3.72012124844857	-1.50979278937826	-1.46055126229913
C	3.87940762134708	-2.21961790716644	-2.57156033782384	C	3.78071992919299	-2.21577377891908	-2.72014928435297
O	3.58607079014507	2.75116226915314	-1.80267739532402	O	3.68297009828485	2.78637809484461	-1.83015269430007
H	0.47835209702947	2.12117850605218	0.11178507044941	H	-1.44560926679260	0.21564342455102	1.45704437282677
H	0.71478710161926	0.62609996221627	-3.21307369373053	H	-2.56125276848029	-1.73167500212970	.56558678700200
H	-0.80069874036818	1.08428475777448	-4.02300415919379	H	-2.18727449173935	-3.29415769633368	1.33782561758635
H	-0.41176195752227	-0.63360639045690	-3.79937548119621	H	-2.10778332738756	-3.13355133982171	0.43230460188807
H	-2.99711029629281	0.08547665072580	-1.12610654664059	H	1.53530565045890	-3.03742865246726	0.62190093269932
H	-2.67060007754702	-0.95131803661443	-2.54853115645816	H	0.35053078229725	-3.98842152074236	-0.31344451501570
H	-3.03151100559942	0.77508806171914	-2.77204398830926	H	0.32804043732801	-4.04280909773311	1.46238010702068
H	-0.92407672824899	1.88876101470363	2.00963676772934	H	-0.03106274482137	0.68480493419048	3.40249105900682
H	-1.80520539669577	2.85302468682405	0.79294766960787	H	1.44920998242038	0.53765225792356	2.41858921335254
H	0.01786901337643	-0.59891308038053	0.89221422348306	H	-0.02109939110885	0.72323181395245	0.72207288547577
H	2.92235335258655	1.96277679846958	0.84361270527071	H	3.11676467355118	1.96391535371392	0.82282463742993
H	1.77721530913962	-1.01046837603622	-1.86912802763608	H	1.79459482526896	-0.92003554544644	-1.87202766068478
H	4.62668257842981	-2.98907501780812	-2.37496078869487	H	4.50665490725276	-3.01760888364320	-2.58141558200479
H	4.23612807007319	-1.53878215707846	-3.35110329623328	H	4.10811304192437	-1.54551544200761	-3.52126949163092
H	2.93557340390576	-2.68302790742089	-2.88493877948942	H	2.79735938700102	-2.63599312934084	-2.96489511809809
H	2.31106207910362	-0.65863366510370	0.85051096863707	H	2.46867560623215	-0.65483602816404	0.81545602698861
H	-3.13922901236238	1.33715126734135	2.98331877693764	H	1.93980075940750	2.88839746004634	2.90570206176280
H	-3.95086325991882	2.24867358619157	1.67273960788699	H	0.69815496252184	4.08414401469117	2.41948483317286
H	-4.29033772563058	0.50343139165372	1.89234165899354	H	0.42141012045040	3.03154144928846	3.84361304732220

5.74B-*anti*				**5.74B-*syn***			
C	0.03755589987802	0.00832760849879	-0.01441008403501	C	-0.01427717169175	0.00255287786292	0.00708013496819
C	2.38752443428107	-0.00116190719495	-0.00682155611993	C	2.48569554156605	0.01136444299837	-0.00057763425124
C	2.48216986174061	1.50160712922310	0.00023016620206	C	2.94763879039437	1.28751518168901	-0.01188081770428
O	3.84670340015462	1.94556538626006	-0.01200759610004	C	3.30742896912735	1.65455765561253	-1.37583454380174
C	2.75981042164829	-0.91485056312161	1.14940293134119	O	3.09321802404253	0.55460302982251	-2.19799917768672
O	3.77791848319924	-1.76117743584817	0.57626253780438	C	2.64848296084335	-0.57315952453028	-1.37828244626906
C	3.54194556216404	-1.84905464193986	-0.82516258871286	C	-0.44216756771825	-0.06198028106502	1.44896398101558
O	2.83473183400656	-0.58384136813507	-1.15052639294204	O	-0.26203833082223	-1.46162914262076	.74470034896094
C	-0.40882332966993	-0.65356865702353	1.09892827639576	C	-0.55402684423053	-2.18542161281582	0.54751543798494
C	-0.80509970630856	-2.00237586310850	0.73312178373093	O	-0.25724407960110	-1.22508796390408	0.54228276657260
O	-0.65536990130262	-2.14362450405843	0.64376927336128	C	-0.21350298249064	1.17040220578826	-0.89750983039575
C	-0.23337317731942	-0.86231792081410	1.21414872488214	O	-1.62055112642102	1.46689273904123	1.09557283943692
O	-1.25383646291613	-0.29325469717575	1.98364351679065	O	3.61251881706758	-1.58715991709597	-1.34545295589293
C	-1.44454906743130	-0.96393340064060	3.24997459285368	C	3.67532113409454	-2.34472634286583	-2.57507321314235

O	-1.21259060509835	-2.93266780322439	1.41100075513240
C	3.27147673936485	-0.27535046214933	2.43636950435068
O	4.42317801055238	0.56664509663424	2.27611638424404
C	5.68483249616626	-0.12459522870473	2.41555430995674
C	2.65027778631291	-3.02860948119086	-1.17988516773233
C	4.86842125444183	-1.82318576054943	-1.55601217897065
H	1.88433846609971	-1.52251845217450	1.43486564042361
H	1.73265655738489	-3.01775644173199	-0.58947614904231
H	3.19228428828479	-3.95623746774013	-0.97463018374778
H	2.39140119472817	-3.00069021471284	-2.24169645323876
H	5.41411974274583	-0.91228065847055	-1.29758403572463
H	4.70265390218295	-1.85683700142445	-2.63591116587479
H	5.45861148019198	-2.69606793274849	-1.26201844924602
H	2.47641778618052	0.35683834206272	2.84491860928155
H	3.49152328384977	-1.06695204761166	3.16169804141361
H	0.63965976646763	-1.08522227767703	-1.83735244743197
H	-2.17162156968936	-0.36633234721043	3.80076096250207
H	-1.83038496802022	-1.97639405022236	3.09422024781170
H	-0.49658756691851	-1.00506396716642	3.80069434286400
H	0.10083480704167	1.08245911229980	-0.12776699360366
H	1.94640784146831	1.89667264200092	0.87364676599856
H	2.01985930081111	1.90335925709540	-0.90521132229935
H	-0.47700588414818	-0.28196436585774	2.11251359318027
H	5.82188603501427	-0.85419720588404	1.61323356133603
H	6.45592109462176	0.64586842108595	2.36709466779230
H	5.72216698448832	-0.62761878277827	3.38894672522055
H	4.24749586271120	1.57722751111806	0.81247937888561

O	3.72672436319102	2.70329847078340	-1.83577386664466
C	-2.02903745312687	-2.54293974154925	0.44309341481985
C	0.39101090745951	-3.36289448638026	0.43360774261546
C	0.33907700982560	0.74853207026088	2.47323476076916
O	0.16131036386623	2.12228375492635	2.14231049349458
C	0.82780472839243	2.98223718596570	3.07318200090321
H	-1.50815531793510	0.21435911067608	1.52763986230706
H	-2.64815416258962	-1.64820299445847	0.54705711546994
H	-2.28697537325364	-3.25174523024280	1.23518152263814
H	-2.23454236772412	-3.00566031055132	0.52626963519727
H	1.42736085881464	-3.01692473837077	0.45612768049455
H	0.20806803445569	-3.90097922525968	-0.50036331680630
H	0.22190685460840	-4.04641717514609	1.27035279608159
H	-0.05841942676701	0.53634267215932	3.47693183611145
H	1.40328805339548	0.47767638125413	2.45934383372913
H	1.72663075257526	-0.94013451658739	-1.84099918459814
H	4.37096364568298	-3.16340624478909	-2.38913511255723
H	4.04126665426923	-1.71793710296294	-3.39446708235093
H	2.68354876217081	-2.74191382721484	-2.82391308047628
H	2.32004869336851	-0.62658666480755	0.85658008679006
H	0.21393088490496	2.05840445170204	-0.43204028419630
H	0.27416909701934	0.99270928613043	-1.86289637661287
H	3.04467653785946	1.97380968990054	0.81782722261892
H	-1.99645808301058	0.74372784837795	1.62496106317350
H	0.42542754355267	2.84446445622238	4.08625934211861
H	1.90895123210955	2.78176559245682	3.08496515492589
H	0.64672034410421	4.00518444128972	2.73852556945352

5.74C-*anti*

C	0.03046738854703	0.00076715362467	-0.00697832546452
C	2.33045190234167	-0.00410059245984	-0.00009646367982
C	2.42675522986880	1.49909027706750	-0.00036432659528
O	3.75102409512618	2.02469999542314	0.15679908170975
C	4.58438000396951	1.88122175887608	-1.00291476519436
C	-0.25006786792159	0.25031298008937	-1.47633069252632
O	-0.83596003675582	-1.00059864145569	1.94654793294218
C	-1.01436190579120	-1.86482414565455	0.86810559192997
C	-0.49706577787634	-1.22389199445635	0.32311569106415
C	2.63487296833881	-0.89839648896044	1.17874911682107
O	2.86373704678538	-2.17921570354125	0.55941087202112
C	3.12346410639735	-2.02107842627384	-0.84029538033922
O	2.73765754398686	-0.62207704366287	-1.13543747941288
C	3.77848018670959	-0.45760700663542	2.09370882804929
O	5.00803663907894	-0.41299515693501	1.38673498880680
C	6.02230431562782	0.27124309318782	2.12571956218878
C	2.23522727148308	-2.96162893947065	-1.63101279821115
C	4.59815432945122	-2.17192059523368	-1.17897119868085
O	-1.09689561996077	1.33608742996643	1.75329682050147
C	-2.35365506885606	1.33355479023550	-1.03892962378948
O	-1.54787032183362	-2.95228491452796	1.03146370141008
H	1.19245686895129	-2.84027087743705	-1.34027686864689
H	2.53970420938054	-3.99274507889669	-1.42919982683560
H	2.34317018497819	-2.76754518055396	-2.70186471618706
H	5.19266704465350	-1.48903040297193	-0.57242890428136
H	4.75565394871918	-1.97006307391664	-2.24271015629442
H	4.90335754914491	-3.20185841369370	-0.97106168121303
H	1.75453115146203	-1.00576432935775	1.82380774670550
H	3.84644019832891	-1.16377834433755	2.93602238233511
H	3.52544072052789	0.53549355449012	2.49660667034703
H	6.92722395244917	0.24425495094150	1.51517705537947
H	6.21232857931231	-0.22718337717436	3.08693857965456
H	5.72782121938329	1.31379236937216	2.30760316608716
H	1.87048999159769	1.89081562456282	0.85441056207257
H	1.98024794881259	1.88972300092864	-0.92589478264681

5.74C-*syn*

C	0.01913454061731	0.00141504545321	0.00997496576968
C	2.41909285787648	0.01008789866705	-0.00119166204335
C	2.62532549432449	1.50396126020661	-0.00352600347178
O	2.98569491425585	1.82791992008380	1.37217943307105
C	3.12677850170913	0.64527631713774	2.09270889538573
C	2.81426236810829	-0.46842724002892	1.21223354075686
C	-0.47989271291224	0.67690353822733	-1.25111813806824
O	-0.66080489473013	2.04063962778650	0.82259719393531
C	-1.03235554005375	1.99149341511196	0.55511556831551
O	-0.31808449931253	0.79824875559902	1.06740195234031
C	-0.09888539101635	-1.47457611366941	0.23579115488020
O	-1.48202780481391	-1.87550741922256	.35649691413379
C	-1.95093209676690	-1.86478963547155	1.71502124896386
C	0.43391127656434	0.69436529725522	-2.47227715606774
O	0.70988773438643	-0.65926693117622	-2.82261768800410
C	1.52258810563891	-0.73751123992439	-4.00296497973781
C	-2.52527796257632	1.74576704367664	0.72885874879050
C	-0.52186397921404	3.22413335011244	1.26792977765763
O	3.65693889848907	1.83324858445983	-0.89249327520317
C	3.78895818669428	3.25869247726062	-1.09172836236976
O	3.46917558795515	0.67113215146003	3.26347477988650
H	-2.82910586096009	0.83040233987631	0.21411466224825
H	-3.08030027812798	2.59141307639366	0.31232726924137
H	-2.76765496239640	1.65090902385627	1.79044693721341
H	0.56207786070386	3.30684497006943	1.16453190249988
H	-0.77585903873862	3.16857480835842	2.32937517086952
H	-0.99610112030981	4.11102529926260	0.83938989109080
H	1.73261128506889	2.09921021298361	-0.22340667481962
H	2.89121069389310	-1.49856415609265	1.53155605898739
H	-1.44505085173705	0.22939552119227	1.54279329254185
H	1.36546713581789	1.23508456511705	-2.25738143456244
H	-0.07880464929563	1.21077987066209	3.29661265815650
H	1.69189807632613	-1.79769813194016	-4.19577618459397
H	2.48352993526673	-0.22887809298119	-3.84652882233561
H	1.00615055244725	-0.27927720180775	-4.85735246054392

H	4.06055800170529	2.23979464068552	-1.89965176641311	H	0.45397268560826	-1.77087197900211	1.13444059890303
H	4.88840636266227	0.84009407803667	-1.14469212971799	H	0.30307379831621	-1.99936560950164	-0.63332371611249
H	5.46606757150415	2.49844290656169	-0.81948423042807	H	4.53593926178467	3.38608713755445	-1.87589204086952
H	-0.57476495406725	-1.67677111074350	1.30229401596319	H	4.12275772710316	3.74633210346032	-0.17039284866653
H	0.13417827970591	0.82848278835637	0.68385899125307	H	2.83042012672981	3.68530121671737	-1.41338676797836
H	0.63880183187763	0.41977640242780	-2.08651303612664	H	-2.99100792613248	-2.19511540573077	1.68285847860093
H	-2.90146204657379	2.19814310218805	1.41476714970815	H	-1.89601688374419	-0.86035375066333	.14945183504483
H	-2.19281672003483	1.43315288594482	0.03994424356284	H	-1.35800766892649	-2.55707228271994	.32768200779712
H	-2.91639075946106	0.41852216757011	1.24919405084701	H	2.32692971536343	-0.54752730204553	-0.92470113235977

5.74D-*anti*				**5.74D-*syn***			
C	-0.01876307719750	-0.00390654795868	0.00305056831922	C	-0.03895214672368	0.00015928655387	-0.00749378398161
C	2.38955409320844	-0.00855378240124	0.00446180664363	C	2.36937762855751	-0.00198755068698	-0.00393844347050
C	2.69116743102550	1.47055175358280	0.00573832549589	C	2.71363617729949	1.45556978381702	-0.00098824736783
O	3.16341749324614	1.74558417808335	1.36136790949298	O	2.20555824772292	2.06208940747653	-1.18955436320155
C	3.29505473486242	0.54148896737579	2.04842875713585	C	2.49204219392225	3.47054283879765	-1.24578334817842
C	2.84448478480768	-0.53334689269714	1.17809506458577	O	2.60995571417566	-0.60457828393479	1.19777076721277
C	-0.38938349232116	1.25495298167014	0.73968280782949	C	2.85309392747340	-2.05193608968168	0.96354999491414
O	-0.55356002551275	2.21047399840759	0.33185007128429	O	2.52916970007594	-2.23972276509156	-0.41290300942056
C	-0.75835841397718	1.53239921898376	-1.57784710233532	C	2.77088982543405	-0.98442278389591	-1.08248299204204
O	-0.34240121889320	0.13995858337117	1.31588040510254	C	-0.19649274370935	0.57105321173021	1.37800499389527
C	-0.12585943676560	-1.38900835807205	0.54440318416968	O	-0.58891311480595	1.96155038477759	1.15275308875085
O	-1.50255806223080	-1.85865583362069	0.62602251816806	C	-0.83611959789611	2.14598193521612	-0.20457639243783
C	-1.95599255173104	-2.50572637537918	0.58339030277425	C	-0.53094450844527	0.90578662887980	-0.89914555772038
O	3.73025239525542	0.52165282064395	3.18743791354683	O	-1.23348315671297	3.22150011280195	-0.62120661886455
O	3.68348285828340	1.73920692454671	-0.94443366512552	O	-1.19764172634046	-0.13280034811204	2.06057471367560
C	3.92990212770802	3.15434974457040	-1.11300067055140	C	-1.27567842855742	0.21634957148224	3.46060623437652
C	0.15612883343313	2.12073895834400	-2.63697169959828	C	4.32576256869675	-2.30951967974718	1.24615304747115
C	-2.22369031411129	1.51413585554849	-1.98013642418172	C	1.89965743290717	-2.85647204459820	1.82055533653360
C	-1.60603235833553	1.16311978701998	1.67998766193202	C	2.01632518073783	-0.98412128674727	-2.41089051888510
O	-2.76468287410802	0.55788891987853	1.11364664397085	O	2.33506012202762	0.17026060563470	-3.18635626308875
H	0.43886091156604	1.61577632588798	1.36485321266235	H	3.84806397274651	-0.86473299218286	-1.30036095723069
H	1.20382144258959	2.00657983389411	-2.34990000732451	H	4.95526807510965	-1.71524865290087	0.57931833618168
H	-0.07141966199911	3.18332512869323	2.75763182888139	H	4.54275986596494	-3.37049830455767	1.09232167626228
H	-0.00743183897786	1.61558051974763	3.59252374595300	H	4.55900397772711	-2.04677491149240	2.28147822387962
H	-2.82560010691465	1.10802855039220	1.16489177529637	H	0.86647243081153	-2.56900389650905	1.61173761034358
H	-2.35483289543764	0.90998008853192	2.88222623278391	H	2.11576680092738	-2.68774914983262	2.87912085029053
H	-2.54661406481198	2.53742063201274	2.19255373553287	H	2.02752046943913	-3.92076182259812	1.60191804046529
H	-1.28067718076660	0.62650780047732	2.58388119805636	H	2.34103502282563	-1.85373440102038	-2.98825168937393
H	-1.88050818364967	2.18147914565314	1.96805855387534	H	0.93775078530137	-1.06931940683143	-2.23236679946370
H	-2.52254049653994	-0.38519203899330	0.95250871836010	H	2.21435859060020	0.95670461503467	-2.60353076075841
H	1.83273874416809	2.13494713542526	-0.14629178218977	H	0.71644593306810	0.60674960952385	1.98112571653488
H	4.61527842016553	3.24165243161880	-1.95652416797587	H	-2.00687910666050	-0.46233378018401	3.90055428212433
H	4.38486588944411	3.57400911048987	-0.21062233420821	H	-1.60529111804325	1.25338613960200	3.58054003536910
H	2.99146747843735	3.67806020096179	-1.33417619360941	H	-0.29817403052135	0.07860244736921	3.93951563668735
H	2.22009016389506	-0.53617203256943	-0.92492861789106	H	0.08217545753209	-1.06443540330981	-0.15819001734789
H	0.25526920247789	-1.40222052150287	1.56734625223871	H	2.28810677640537	1.94253250475087	0.88741534227493
H	0.44941503623695	-2.09432444368612	-0.06509652551104	H	3.81205823771621	1.58019207589834	0.04229367758087
H	-1.29801556242608	-3.34979457943408	0.81980836794649	H	2.06478655521652	3.83429086454778	-2.18028651466895
H	-1.97489675296426	-1.80328543029887	1.42318469232574	H	3.57569250295895	3.64292494505572	-1.23210305170404
H	-2.96431588657179	-2.86473482960541	0.37337560890763	H	2.02225592127934	3.98135519451499	-0.39695122059065
H	2.88757566825977	-1.57295974857836	1.47279401941155	H	-0.65196382706349	0.79827885457552	-1.96809510129254

5.74E-*anti*				**5.74E-*syn***			
C	0.03032851409726	0.00185660405943	-0.00989226444122	C	0.01451739860466	0.00658465556964	0.00013174414864
C	2.43029484790984	-0.00897169635639	-0.00324738447590	C	2.41444858618953	-0.01158876274380	-0.00025544947355
O	2.76557208969525	1.31042455084014	0.00317070630579	C	2.82582969893240	1.28739880563578	0.00234799664671
C	3.41701674855190	1.65433219819376	-1.27098578020218	C	3.17588681681766	1.68657795073478	-1.35152910098314
O	3.10739373865302	0.55487701630685	-2.13525160464840	O	3.03096585624044	0.58289538240185	-2.18659821644835

C	2.80988286497327	-0.60635884739217	-1.33309042023936	C	2.62971096096764	-0.56842984627555	-1.38475655391242
C	-0.40976230467907	-1.26009429574737	0.26614818227395	O	-0.32224080551659	0.71226200171172	1.11747093598985
C	-0.79059062507496	-1.92043415056742	0.97034755740050	C	-1.04546808189225	-0.18624174500791	2.04515010333281
O	-0.63441849866614	-1.01309702149307	2.01779636166662	O	-0.67669837069941	-1.49481068544252	1.60467711702499
C	-0.21988860500752	0.27860990204955	-1.47072009383004	C	-0.49019130730635	-1.40809584390272	0.17904136546631
C	2.53532939381447	-0.69978720623125	1.31680174720863	C	-0.09647377341987	0.75741583952080	1.28912276718948
O	3.92238863138420	-0.78697483801662	1.68482478282811	O	-1.49036406070087	0.95335930494381	1.61459041969627
Si	4.62618257000422	-2.04235717429703	2.55000701663520	Si	-2.18919400204754	0.41579510491822	3.04537557278014
C	3.36095449159165	-3.38018684467888	2.91001008465631	C	-3.85428423580403	1.26919205712365	3.08195990388252
O	-1.23563507057358	1.23318604877384	1.59817168287936	O	3.63589351360040	-1.54150209518761	-1.34526433141224
C	-1.42863357605754	1.66717515928053	-2.96378248036075	C	3.76100562774674	-2.27122304657033	-2.58634050690908
O	-1.18623196098055	-3.05362013749851	1.18767371272526	O	3.55318690523368	2.75687190276425	-1.79961186622308
C	3.95926027561827	-1.63399148665164	-1.31550851408497	C	0.42839518559481	-2.54367364090066	0.26371807217822
O	3.44799274013578	-2.83553526814793	-0.74057656622176	O	0.75340703780911	-2.30743302786790	1.63202235501479
Si	3.07825143576809	-4.19224481106948	-1.66181628644871	Si	1.53826849881426	-3.42895598777159	2.60881571991081
C	2.06986980757588	-3.70423720766648	-3.16904178858095	C	3.17792323359557	-3.89754613279510	1.82701304203794
C	2.78909623285048	2.91793270408745	-1.82318295538397	C	-2.53447593540693	0.07612701055489	-1.86185902108399
C	4.91146077416328	1.76873287019879	-1.00538510952090	C	-0.54296858860046	0.03802543820308	-3.45373926257383
C	5.27849542073280	-1.30145073436938	4.14720012859466	C	-1.11595652665708	0.91839518553176	4.50299590468095
C	6.05340712707163	-2.71639211117778	1.53793526970415	C	-2.39590086361574	-1.45022001329863	3.03698209915993
C	2.09255268369321	-5.28932135391965	-0.51352730920208	C	0.45349408680942	-4.94512516448575	2.81829879949338
C	4.67928272739276	-5.00854659808599	-2.20515968009734	C	1.76524770063566	-2.51580768021538	4.22527420548344
H	1.70900967133315	2.78843236125950	-1.92655601616982	H	-2.82339933664703	-0.07024532619789	0.81752384812853
H	3.22129855012263	3.14001830500801	-2.80234862665875	H	-3.10512115881743	-0.60820676772379	2.49562705812165
H	2.98872120908041	3.75724936307245	-1.15217535608231	H	-2.76907703596575	1.10514550813294	2.14683820061934
H	5.28604467922071	0.85195517496574	-0.54426661928823	H	0.53759661748134	-0.11299022501011	-3.50354065520884
H	5.10876712904089	2.60696682349244	-0.33132798402053	H	-0.77611727399101	1.05764118345626	3.77050073813222
H	5.43567277182600	1.93878195139716	-1.94989537223746	H	-1.03900490641982	-0.66186666594966	4.13117738141888
H	1.96101844902320	-1.11387289328162	-1.80494459264276	H	1.73379349030767	-0.96831980291509	-1.87079479364277
H	4.80222136849933	-1.29199158326967	-0.71183800137267	H	2.89689477521365	1.96449944107147	0.84270841507862
H	4.29554583622167	-1.77836275124872	-2.35064717033142	H	-1.45384103158770	-1.51558413678601	0.34363331432045
H	2.08821391523369	-1.69306452509318	1.22929907990803	H	1.33457784849989	-2.56449928603765	-0.35150399178395
H	1.99623010127039	-0.12420996048100	2.07914140899515	H	-0.09710306071889	-3.49886385656540	0.13751215300082
H	-0.47807226993359	-1.74774968175147	1.22871245468982	H	0.36812695052124	1.74151861312484	1.18124120569274
H	0.16741988100839	0.81506253381051	0.69079985191413	H	0.42051527589718	0.19727125500470	2.07467393297064
H	0.65624309920490	0.57920563426555	-2.05761439880673	H	4.47961855516139	-3.06876841099927	-2.39587300260800
H	-2.15206195334539	2.48193056770924	2.92095777742426	H	4.12745954859001	-1.61594157633144	-3.38299464852511
H	-1.81815222126728	0.84727575426389	3.57538108257532	H	2.79186965527604	-2.69862116702959	-2.87240239259655
H	-0.48115176960227	2.02658937890453	3.38392605060238	H	2.30227166727979	-0.66653519631149	0.85425404586807
H	6.62477203973171	-3.45027840509285	2.12041914117224	H	-0.51698462560216	-4.67909589309793	3.25319706099819
H	6.74170660249852	-1.91444494879193	1.24415434342311	H	0.27075248315319	-5.44619724095005	1.86040215079589
H	5.68675103767305	-3.20785119176383	0.63095939929260	H	0.93386654914134	-5.67226207976135	3.48531896014354
H	2.94253150082797	-3.79148659165814	1.98579006236938	H	3.80634930767130	-3.01501988639586	1.65949889997424
H	2.53494181291004	-3.00624851070671	3.52697720858646	H	3.03147261615404	-4.39448708096020	0.86042936286906
H	3.83749448760291	-4.20339564878185	3.45698174695321	H	3.72902105594504	-4.58964118224345	2.47621820488054
H	5.80764517882264	-2.05809355464467	4.74084512035640	H	0.79740684512083	-2.23730079311962	4.65718848066276
H	5.98150437305421	-0.48531456426753	3.93964730133024	H	2.29179639606240	-3.14261584438658	4.95526382765050
H	4.46250107902900	-0.89951660298641	4.75998556050463	H	2.35174985173020	-1.60054001318852	4.08267043519876
H	5.27854768634118	-4.33121718981595	-2.82666456080556	H	-1.59610793318942	0.62348408312029	5.44462687632269
H	5.28637638108623	-5.30054319693626	-1.33990193798089	H	-0.13307353019364	0.43408988098310	4.47294228358782
H	4.47511490802257	-5.90950545014478	-2.79672536474820	H	-0.95933818835525	2.00313511239187	4.52784724820455
H	2.67846084508620	-5.57832770412810	0.36637532929142	H	-3.74111093207309	2.35923427214039	3.10679679577491
H	1.78850469680563	-6.20805238685889	-1.02917908202794	H	-4.44704267747884	1.00697986851597	2.19700993436440
H	1.18403554167686	-4.77906302289075	-0.17445401587310	H	-4.42504512758190	0.96556450767124	3.96878270746150
H	1.87875821458225	-4.58780705392870	-3.79125109740857	H	-3.07529324917153	-1.77723591954244	2.24054988499570
H	1.09950604019839	-3.28208665847427	-2.88613950901212	H	-2.81621556768599	-1.78670351734624	3.99356248511880
H	2.59579824208499	-2.97216243687364	-3.79499542992872	H	-1.43611687294627	-1.95752958469831	2.89416710974641

5.74F-*anti*				**5.74F-*syn***			
C	0.03545381199772	0.01634529999071	-0.00962603116520	C	-0.01003091182991	-0.00970548123101	0.00168115924533
C	2.58540178735279	0.00571270037018	0.00270601354174	C	2.68989995320317	-0.00072169638427	0.01878106758505
O	2.89474490887900	1.32841344632424	-0.00417031578683	C	2.76773588505240	1.49893724579693	0.00158179848859
C	2.97899230946149	1.81092290601436	-1.39335426687377	O	3.18167586372021	1.85348751907013	1.36094663932557
O	2.71117210107506	0.65723234497195	-2.20354024100271	C	3.40156382969379	0.68902038842719	2.08328027680342

C	2.73829070256609	-0.53581187631643	-1.39274200247610	C	3.10738359819708	-0.45197481031922	1.22022934803560
C	-0.20627741585396	1.16291286022400	0.93195462732587	C	-0.41903209922684	-1.30858821230058	-0.63450080314489
O	-0.67662723456239	0.52809773120273	2.16197273126459	O	-0.20973814489286	-1.03354570453354	-2.03476891749534
C	-0.81696507585329	-0.84002700625642	1.94020805997063	C	-0.48856292498310	0.35486729904629	-2.23365150061381
C	-0.39508453281770	-1.12962645117332	0.57833592609637	O	-0.20654799424585	0.98007840553273	-0.92673403635909
C	2.88377609410010	-0.77197457996835	1.24081222605543	C	-0.19234974256006	0.37493509707979	1.42774829252666
C	2.81872995786761	0.03533453011120	2.54204438077921	C	-1.67692189558672	0.53902380372570	1.82730211247382
O	-1.23617974876554	-1.56974535287315	2.82449920513227	C	0.36835964452589	-2.56129912900225	-0.27511006673094
O	-1.18191925479630	2.01642571739923	0.39948293854135	O	0.09714222707072	-2.85371158169590	1.09271609534424
C	-1.33297569430992	3.23901012093144	1.15506144985364	C	0.78651851776431	-4.03188309602777	1.52436859303091
C	3.97988131604023	-1.39814225786792	-1.63432341709324	C	-1.95934794005034	0.59641887853551	-2.54544903552893
O	5.14019952251767	-0.76549355284212	-1.10677025291553	C	0.46903607401098	0.91156312129814	-3.26660221610197
C	6.32518286067268	-1.52486282947482	-1.37041892030662	O	3.71335878905749	1.91719139332661	-0.94089842498926
C	1.89784061752849	2.85215237799662	-1.62681225389267	C	3.68405656854698	3.34317149002980	-1.17521905728811
C	4.38699614430505	2.34057133962060	-1.61155028008398	O	3.77492202673360	0.73487058979022	3.24317166701549
H	0.90820370068795	2.43621453472139	-1.42845585121490	H	-2.59166661533891	0.15930635374971	-1.76797913917707
H	1.93998857854386	3.18364413578820	-2.66816450838621	H	-2.20825643639015	0.13809122196211	-3.50674919276176
H	2.06382982405560	3.71616935409663	-0.97789280871743	H	-2.15853812466462	1.66987986081648	-2.60094251191154
H	5.11055806118597	1.54435345568329	-1.43006068489023	H	1.50193851969813	0.74073257438263	-2.95311709029745
H	4.57669938882701	3.18025832104089	-0.93665168427478	H	0.30071926904848	1.98439641945034	-3.39190886657024
H	4.48100079921650	2.69184539432206	-2.64352037692382	H	0.29908258504790	0.41514313805737	-4.22601046810050
H	0.22995947307582	0.18724815636621	-1.05963983802413	H	2.50434520614794	-0.56437005024782	-0.88473302995847
H	0.68779675139995	1.73523819679114	1.20665788509766	H	1.81087679170885	2.00605291274966	-0.16648548516788
H	-0.44137530502447	-2.12364555536590	0.15471412930152	H	3.21977866840752	-1.47419485923946	1.55388294754853
H	1.88056786155406	-1.15154219993664	-1.69118588169522	H	-1.48925774334788	-1.51217940914993	-0.44427391242304
H	4.08667824149303	-1.56321765735438	-2.71712809625612	H	1.44365475645522	-2.40542416861617	-0.43328228831223
H	3.82292975896803	-2.37590263905775	-1.15089832541369	H	0.03682690734311	-3.38904728043859	-0.92035239021555
H	7.15757551136717	-0.96764231935494	-0.93725747035725	H	0.52716690960570	-4.18064683413543	2.57385270371332
H	6.47914327182539	-1.64223490436393	-2.45226480394350	H	1.87434243025647	-3.90637836880579	1.42534896761225
H	6.26306777059654	-2.51818454528506	-0.90473036833950	H	0.47039956535702	-4.90454671085747	0.93567400993397
H	3.89289842339880	-1.20004998805737	1.13128684099414	H	0.27554841232006	-0.39523379141038	2.04884348204741
H	2.19031431173207	-1.62194073698273	1.28151118815840	H	0.33680103985253	1.31738098054742	1.61108111982605
H	-1.75078848789916	3.02954011086921	2.14477040478401	H	2.66986947777328	3.65950713454887	-1.44815387999678
H	-2.01911793611018	3.86446871696091	0.58296081515786	H	4.36920051150103	3.52652009703375	-2.00342102178669
H	-0.36278251774779	3.74099979922614	1.25839838290134	H	4.01670777264258	3.88616370236091	-0.28467719915290
H	3.51405867454892	0.87878626674635	2.51231448086944	H	-1.74824362499213	0.84557062020938	2.87567333800465
H	3.09083764519881	-0.60747944131278	3.38420792054242	H	-2.22156201305391	-0.40287599561139	1.70829590526688
H	1.81473235136255	0.42317922147818	2.72676105347467	H	-2.16110997469805	1.30179369408982	1.20942104257822

5.77B-*anti*				**5.77B-*syn***			
C	0.03122720348144	0.00392209199330	-0.00845728803428	C	0.01140290019458	-0.06676666054596	0.02523761852962
C	2.38118374742870	-0.00957634845568	-0.00373915110757	C	2.46061580042581	-0.00569281296156	0.01399556244784
O	2.74638229873762	1.29663187119257	0.00513817464984	C	2.55240939151244	1.48647223573985	-0.00949852887199
C	3.06438524782225	1.72969171890810	-1.36981960820987	O	3.93307671255935	1.86870235421052	-0.14319346332057
O	2.87516135818955	0.55589359797855	-2.17282320117694	Si	4.72624487570984	2.84717559826509	0.96788001215948
C	2.73585963783995	-0.61030666877122	-1.33709834829404	C	6.48540685173932	2.90210154969164	0.33381763421675
C	-0.42024112828973	-1.19181955337860	0.48541094366277	C	3.06554294782719	-0.82139868430412	-1.09816154060374
C	-0.84302443470404	-2.04391830877643	0.61147647394031	O	3.26140606397892	-2.10978246747702	-0.48176456063009
O	-0.72060472689737	-1.32186682317616	1.79772247167666	C	3.48528661631176	-1.88489980206296	0.90993121955706
C	-0.29271226239769	0.03926960556518	-1.48487086535780	O	2.78828691210220	-0.60905592401873	1.19280162469934
C	2.49884042893468	-0.70986431530556	1.30925156947453	C	-0.48333823738224	1.07029507271291	-0.53662491721217
O	3.89296903675462	-0.86251747143498	1.67196308123840	C	-0.87705663178807	1.99596072161983	0.51545067899869
Si	4.38526669767387	-2.03622127317613	2.79228674926802	O	-0.66850912413307	1.37804899242905	1.74277423567767
C	3.50059264586885	-1.73704272553843	4.41637414074243	C	-0.17841713809499	0.01506834244861	1.52179950806630
O	-1.32298648551677	0.96082223738816	-1.71053936838876	O	-1.06566427698936	-0.92726594933376	2.06592048723429
C	-1.58411366667652	1.16526156866658	-3.11824192713873	C	-2.34651402098623	-1.02665602621747	1.40246136526990
O	-1.24722052429330	-3.19484999653089	-0.62615175948908	O	-1.32144033125857	3.13169740292096	0.45901094988436
C	3.96847060491555	-1.54232360927777	-1.35273865102166	C	2.27970840254993	-1.02408145553329	-2.39871037136758
O	5.12899916447751	-0.91919748252750	-0.79307570791688	O	1.17598371241831	-1.92097012603884	-2.17630695070039
C	2.07044551874223	2.79927379469432	-1.78814158566684	C	4.96217109227484	-1.66483249526946	1.20487660854818
C	4.50737000097917	2.20261039323239	-1.39005932784919	C	2.83367480007740	-2.98969268754366	1.71190800501490
C	6.22940965220130	-1.77223264349932	2.92226904417215	C	3.92678051029665	4.54566562928196	0.97529954818168
C	3.97594692204392	-3.73756207752115	2.11589881695073	C	4.63223776543606	2.09534819198668	2.68557980927201
C	4.32379551848038	-2.01945955358248	-2.75697896524114	C	3.15609845445908	-1.53561361182136	-3.54659090287003

C	3.23242208371742	-2.80735826502294	-3.54542372228538
C	4.12979838562606	-3.41861042860448	-4.65598384216661
C	5.35053289828281	-3.96639399201715	-3.90302975573743
C	5.55484877643794	-2.96775483654060	-2.73361556807000
C	3.42516018107907	-4.32791866165712	-5.69923974706408
C	1.96987333194958	-3.81704254259067	-5.89591945533687
C	1.86613083756276	-2.30496444952281	-5.67504871943099
C	2.13461382704813	-1.92346940844015	-4.20237308501166
C	2.58426529203820	-3.87743583457869	-2.64581408738169
C	3.40443883267828	-5.81659432263848	-5.31557539896548
C	4.18479749115157	-4.18977567373828	-7.03378605542360
H	1.04394316655897	2.45332462554634	-1.64935282787857
H	2.22785398171595	3.03948062450045	-2.84317582697865
H	2.22418326286726	3.70410377204777	-1.19451436848156
H	5.16884904917560	1.37843368878677	-1.11928230220974
H	4.63487446111083	3.03626943136419	-0.69356919114064
H	4.75260129348338	2.54738937497301	-2.39902507236645
H	-0.46969847387792	-1.51006960231036	1.51769111123672
H	2.01746164285009	-1.69048533261984	1.22461511013188
H	1.99032504778464	-0.12997547658613	2.08699302225135
H	4.92124028179949	-0.79095423563051	0.16076250592398
H	3.69121626091178	-2.41430508311440	-0.73725575111789
H	4.56892564111342	-1.12831265504251	-3.34924917099938
H	5.60980131007260	-3.49274027902644	-1.77327046324693
H	6.48138543642311	-2.39751428970578	-2.83287227870791
H	6.23288189306509	-4.04318060629504	-4.54633507266523
H	5.14735546606281	-4.96942757963801	-3.51448359101548
H	2.42093237157029	-0.86771083002038	-4.15204512484006
H	1.20037690108476	-2.02506582284048	-3.63667862576277
H	2.58737061991302	-1.79656387821750	-6.32865802116890
H	0.87485747423279	-1.94142139607275	-5.96980150679661
H	1.63296884942630	-4.08504897788815	-6.90522516235930
H	1.29504658903178	-4.32936103843277	-5.19771974872694
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H	2.94173301484719	-5.98393410216796	-4.33849346885012
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H	2.82872347412921	-6.37895821164744	-6.06083055471596
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H	5.24165960356493	-4.45360843093816	-6.91160025036629
H	3.32800839718981	-4.53069882893515	-2.17620801477657
H	1.89071512260400	-4.50271576658982	-3.21192101935864
H	2.00046401752084	-3.40806210979247	-1.84584801981010
H	0.54676420957726	0.24707813424579	-2.15727532531625

C	4.38085520355586	-0.66048513485016	-3.96223981660306
C	4.64562003130686	-1.25046235333761	-5.37531993054127
C	3.25744384500373	-1.32638157329692	-6.02165850431499
C	2.32158435425970	-1.71295458849381	-4.84849817376382
C	5.81451494395602	-0.62656308664355	-6.18411089255579
C	6.91060453402423	-0.16144522894792	-5.18433285103041
C	6.93531859577794	-1.03645875210552	-3.92735302255477
C	5.65157907531188	-0.85939832923711	-3.08621726431052
C	3.98588488993607	0.82894403162735	-3.99212626911813
C	5.39224295674164	0.54971172859090	-7.07966603418285
C	6.40114243285122	-1.72666645304791	-7.08985727586858
H	5.34861751599802	-0.83691580265850	0.60415048544569
H	5.51844689163205	-2.57495337032965	0.96300014259442
H	5.10478926340553	-1.43176982743201	2.26298181537180
H	1.77207310521618	-3.05554908348114	1.46199984302760
H	2.94456519277050	-2.78925592934354	2.78109716068963
H	3.31962687147185	-3.94192947433884	1.48173533290244
H	0.21116098415616	-0.99883308746059	-0.48914625861864
H	0.73749504982632	-0.09307241899122	2.10259545098859
H	-0.58496897342182	1.30855183447504	-1.58715113382068
H	4.03630487582907	-0.36868861065540	-1.34418379088505
H	2.00256627632851	1.87359551312921	-0.87371121060072
H	2.10102339955997	1.90404389969032	0.89873643753307
H	-2.23027055178451	-1.40646397798656	0.38188709764553
H	-2.85117757185502	-0.05546852980042	1.38445132544544
H	-2.92590309542798	-1.73214718042060	1.99875859563591
H	1.55199031150893	-2.68911982974455	-1.70810184283270
H	1.82481485837104	-0.06764686617765	-2.67821600662835
H	3.55329596457552	-2.51296578598479	-3.24151505132493
H	1.43342438079615	-1.07262435824325	-4.82321250236058
H	1.96440801145939	-2.74183329454208	-4.93520977677473
H	3.21879924037820	-2.04806305218657	-6.84375535578340
H	2.97101554409857	-0.35300698101421	-6.43195641151337
H	5.52732974405876	-1.73249984244454	-2.43415225321585
H	5.78076365773292	0.01153689773247	-2.42988869342471
H	7.04233125245731	-2.08800541921289	-4.22426780144023
H	7.80948329119912	-0.79894333466402	-3.31041827996130
H	7.88511431743471	-0.18159607048864	-5.68883116999252
H	6.73420267621382	0.88242028954071	-4.89290401320197
H	4.94621470266362	-2.29105799410667	-5.17333485804338
H	4.89972026560097	1.34506105353843	-6.51365841798145
H	4.70767837207094	0.22159598839313	-7.86993471402593
H	6.27928486823885	0.97835984897977	-7.56166592063872
H	6.82123719764629	-2.54387717339964	-6.49125255051073

5.77C-*anti*

C	0.08655832090475	0.16432393240688	-0.03976950649872
C	2.43364146551782	0.04794389548523	-0.02727375974309
C	2.56762525958800	1.54883940986764	-0.05039504113069
O	3.93471476175773	1.97383292209102	-0.12676915947286
C	-0.39920609198524	-0.31740920045976	1.14698719553343
C	-0.84876047250500	-1.68631999362505	0.96557037848668
O	-0.67689836600962	-2.02701688966442	-0.37529800796891
C	-0.22502566181707	-0.84631660583892	-1.11218293453432
C	2.78895153486730	-0.86324078005514	1.13903385811532
O	3.74970405050217	-1.77164604013397	0.55501367524500
C	3.49041294512522	-1.86283148324624	-0.84197234392719
O	2.83904909532128	-0.57056348761279	-1.16991531500012
C	2.54425705502078	-3.00983560169898	-1.16140971516848
C	4.80512007505804	-1.91024313297539	-1.59216868017667
C	3.45197308428178	-0.24801086534433	2.37606241836578
O	4.67710687491471	0.42891126983827	1.99036105822531
O	-1.30904545634229	-2.49401127993183	1.75610281970156
O	-1.24092239909342	-0.35087187415933	-1.93823052275325
C	-1.47583648600553	-1.18464035324996	-3.09519100623265

5.77C-*syn*

C	0.01132808860699	-0.07136371085792	0.06648197455398
C	2.35944000523041	0.00923014356128	0.01774917010823
C	2.53799588001467	1.49631425794795	0.01607007113588
O	3.93231903930979	1.86604202429577	-0.04898353736379
C	-0.54337564071354	0.98825015940138	-0.60161250567582
C	-0.95267691951244	2.00482282811950	0.35189589198543
O	-0.69391651757676	1.53297152488295	1.63399700868863
C	-0.18059308514702	0.16580336740931	1.54539338716710
C	2.85315148886988	-0.92232056249448	-1.06625077750032
O	2.74380436694440	-2.20473581751374	-0.39893362226101
C	3.07234757266005	-1.99307178385102	0.96974697575024
O	2.68302037846827	-0.57996577570900	1.20947889142460
C	2.15799991839085	-1.06980610035674	-2.42565995183215
O	2.82699027713446	-2.14536237900072	-3.10915861157382
C	4.56792760863261	-2.09617772337991	1.22853486095936
C	2.21963684342922	-2.89474173076497	1.83609786552051
O	-1.10682987571949	-0.75675695103606	2.04597757734815
C	-1.20386362469474	-0.72732308447327	3.48798893774576
O	-1.44495323494399	3.10893695947360	0.18295852246196

C	3.76950396785748	-1.28185931576191	3.46123127735420
C	2.58225674545955	-2.06662780950949	4.09571852177428
C	3.30919256518945	-2.64741196558762	5.33937844379159
C	4.09292415549291	-1.45912319644257	5.91502942174192
C	4.50647191382290	-0.63366292344948	4.66750252742626
C	2.44991849530635	-3.51346375772504	6.30055307212879
C	1.36358946147186	-4.24703686855527	5.46356432315476
C	1.84254301377137	-4.53684352209272	4.03750175372696
C	2.03737784402024	-3.23514851677197	3.22804959156920
C	1.44717174306963	-1.09387192140289	4.46340046576571
C	1.77771698765262	-2.71239742594685	7.42786024969965
C	3.37597748258325	-4.56137027162011	6.94657958985478
H	1.63879834315529	-2.95343711260256	-0.55352692613152
H	3.05214858040367	-3.95474003805262	-0.94841106385979
H	2.26912238020400	-2.99096394459861	-2.21935226380276
H	5.40096715205676	-1.02623579670868	-1.35141121809998
H	4.62106812736723	-1.94435702487499	-2.66906691592058
H	5.35443171211491	-2.80998174585776	-1.29962316642013
H	1.89443028792951	-1.41439696751318	1.46204013824962
H	4.95691307820381	-1.78042184187084	6.50497236282931
H	3.45783711066361	-0.85922139766160	6.57364379745003
H	2.71765200956694	-3.43111476097702	2.39076622868703
H	1.07161178368695	-2.94681695268855	2.79669648035026
H	2.78757094354523	-5.09368120573299	4.08287927272740
H	1.12597984697465	-5.18253861138245	3.51710856308099
H	1.08928728995997	-5.17848096644699	5.97515297746738
H	0.45245070755979	-3.63720150475004	5.41873717572069
H	4.05816750134357	-3.33305399783131	4.91213176529193
H	1.16295239966884	-1.89398101898857	7.04346677651170
H	2.52051203005373	-2.28852820930398	8.11322917030559
H	1.12732244348228	-3.37705582023411	8.00991271488891
H	3.79333410929523	-5.23434992315677	6.18759070932117
H	2.82414820922471	-5.16740336647059	7.67555432737216
H	4.21165287859496	-4.07883751288413	7.46650269643261
H	1.79478630077151	-0.27416429679253	5.10154084035790
H	0.63163283064764	-1.60663383432276	4.97718456891646
H	1.02117933803272	-0.65377984602803	3.55560480279353
H	4.20989541313530	0.41569563420442	4.77409999370955
H	5.58794559598152	-0.64100557326317	4.50888969226932
H	2.80664024957446	0.54137028160414	2.77286576240254
H	4.43092279671439	-2.03059790527469	3.00384360872585
H	5.24591704220756	-0.25550931288316	1.59124188383634
H	4.37977298392731	1.56744653630107	0.65663593640787
H	2.07068311258262	1.96529630653496	0.83641890502860
H	2.07862405934168	1.94507460254843	-0.94420677093188
H	0.62952750605304	-1.17061074383470	-1.71411594351654
H	0.19627778620146	1.20864004216901	-0.29739864197796
H	-2.19127212299052	-0.64448675973465	-3.71613792588798
H	-1.89218035321739	-2.15060020931428	-2.79361834007347

C	2.23658560827729	0.20738357630869	-3.25644804506013
C	1.51717729355451	0.25116842057015	-4.63813515855432
C	2.01550079166535	1.65166467410026	-5.09073326863546
C	3.52860105791729	1.61624767290623	-4.81742910996409
C	3.66817834513106	0.72381540518962	-3.55054662871046
C	1.50343820557265	2.16574305155518	-6.46174093282810
C	0.06537155894125	1.61111096190084	-6.68313642708235
C	-0.67572111011703	1.38224976194920	-5.35978265533260
C	-0.03052876220184	0.23883685867891	-4.54781504938944
C	1.98458696415369	-0.87384473474832	-5.58015301711675
C	2.39810921508787	1.78177892881881	-7.65204340040059
C	1.43975463035275	3.70352390350867	-6.39145426615677
H	5.12206241731966	-1.43158788564189	0.56084401378471
H	4.89318093175041	-3.12638390490697	1.05771202112272
H	4.78818891292248	-1.82319267776085	2.26405705811450
H	1.16017874213894	-2.73493911428600	1.61954231678783
H	2.41180548574742	-2.68910442991169	2.89279187801880
H	2.47357259315712	-3.93900313017876	1.63150535147746
H	0.14080312381601	-1.07726932060708	-0.31074728683233
H	0.73345764220366	0.15062942791743	2.14619049431806
H	-0.68570316348543	1.10799924253102	1.66583352135196
H	3.91561966907204	-0.70021369557334	-1.26195339796032
H	-1.63444661182567	0.22094486202838	3.82499163091863
H	-0.21197992495846	-0.86543128813030	3.93581671797061
H	-1.85810014378259	-1.55498832657948	3.76343636384548
H	3.94256910875734	2.61708745026021	-4.66347781835822
H	4.06648894052806	1.16931047984053	-5.65862442179256
H	-0.35386181226275	0.30551535215050	3.50274000419760
H	-0.40523751401187	-0.72152539987428	4.92195720543139
H	-0.66191836542855	2.31109094959727	4.77471210319466
H	-1.72999549867199	1.14889341185263	5.54690110217437
H	-0.49087696572826	2.31119854269746	7.31958588583751
H	0.11443001045995	0.66220835089548	-7.23253193864889
H	1.58696635594097	2.34153486385777	-4.34693589580341
H	2.54656608335082	0.70100239694270	-7.72575564886066
H	3.38246989400240	2.25661754752965	-7.57817564371397
H	1.93270783338662	2.12393097632879	-8.58439503666308
H	0.72567572491690	4.02980291443597	-5.62546997297466
H	1.12542449443561	4.12292005187757	-7.35467687682258
H	2.42016710954849	4.12546541466310	-6.14062536343745
H	3.07276512827352	-0.89759840006658	-5.69480826844238
H	1.53829584062586	-0.74772449547484	-6.56995537756143
H	1.67170710890851	-1.84335016642123	-5.18781025681404
H	4.33955463462102	-0.12016101733482	-3.73639386722225
H	4.07045613946628	1.28031685237937	-2.69945027990857
H	1.10534252573891	-1.34178302555833	-2.26313264654200
H	1.71772889676257	0.96694969459464	-2.65499111831077
H	2.83324282587963	-2.90103573132121	-2.49609000576781
H	4.33564689557526	1.63683593538011	0.80515835685264

5.77D-*anti*

C	0.01027690297860	0.00183471381443	-0.00338502853882
C	2.41024121274122	0.00329969352530	-0.01639693692345
C	2.63254812779756	1.49221246976387	0.01490500945603
O	3.04117106201614	1.76660938542429	1.39375298939103
C	3.25689418171119	0.55634398079369	2.05182349654522
C	2.88498456822070	-0.52228527854135	1.15027925023677
O	-0.44632345633433	1.25754315601504	0.28852750274318
C	-1.19206824365135	1.78190512242551	0.89409218062029
O	-1.45465877056842	0.61626405489007	1.65981222763298
C	-0.33455496717885	-0.27414234088974	1.44978270548653
C	-0.13312165928826	-0.92719824912741	1.18813532923080
O	0.34135739318192	-2.24710815702638	-0.95264544818672
O	3.68419467849185	0.54056204770420	3.19423551643119
O	3.64906819666374	1.83219116309885	-0.88670077985462
C	3.80041014227694	3.26045536142020	-1.04662528813490
C	-0.68718472461409	-1.68961792790409	1.89316975915687

5.77D-*syn*

C	0.03810162125915	0.01494946030597	0.01351002488465
C	2.43794053494121	0.00275587008276	-0.01148403477624
O	2.74494652085390	1.33525771785110	-0.01402416458572
C	3.25976760374501	1.72576288149422	1.32375473164298
O	2.97531176396098	0.60021265762425	2.13463956139064
C	2.98184272565526	-0.56654042263792	1.28592337575706
C	-0.17416863308922	1.37622317234789	-0.60199114710400
O	-0.66295009147755	1.09605201805218	-1.95298673162559
C	-0.87867844070876	-0.26945943325682	-2.08278471814049
C	-0.47367489888756	-0.91703709911925	-0.84517342686953
C	2.59847467269524	-0.63529764359009	-1.35896252286318
O	3.99159132380320	-0.83101015578731	-1.68856032767395
O	-1.33783591168231	-0.73354939183637	-3.11384447913826
O	-1.12591803694474	2.08006271017415	0.14540115303787
C	-1.25167863366077	3.46168671600347	-0.26259951996163
C	2.26793920249738	-1.68637732429045	2.05770156487476

C	-1.14543351757695	-1.76857705271158	3.35219818539099	C	1.93959690073413	-2.87864058952234	1.16488178754611
C	-0.11885772947150	-1.34797274383602	4.45100046083024	C	0.98849249483092	-3.97630361880428	1.71865542876386
C	-0.84693504261182	-1.93029222727750	5.69252441827642	C	1.08792733881264	-4.96012208765934	0.52107028129918
C	-1.25306434743398	-3.34724605725323	5.26294788026760	C	2.59989642780218	-5.06691420584552	0.24936705868861
C	-1.55548627054526	-3.21313214802325	3.74669941433454	C	3.15786220734845	-3.66272355333112	0.62443380542843
C	-0.14172816283594	-1.73985273558810	7.06320987698615	C	0.23391663186556	-6.25123091885017	0.60508177051134
C	0.65321666051049	-0.40356100282558	7.02807797165437	C	-1.06728976084176	-5.92156490177541	1.39371446616032
C	-0.00772882926716	0.62547467815191	6.10604600973319	C	-1.48722064153205	-4.45498247876387	1.22880859423105
C	0.05364806922347	0.18598779702300	4.62729708184571	C	-0.47725796491017	-3.50564925917885	1.90705338943505
C	-0.31421236234702	2.78034356729799	1.63495332055317	C	4.75382093682562	1.97212757712974	1.16805383402612
C	-2.49730009945332	2.36054418985246	0.39300853843401	C	2.47331272419837	2.91686650420645	1.83041604231185
C	1.24395923574449	-2.01396589370474	4.19627287600258	C	1.50246818804647	-4.58537970652579	3.03437851918742
C	0.80233425238680	-2.89246342086502	7.44392787744313	C	0.95785911738048	-7.43837239892094	1.26109217832334
C	-1.23386539442871	-1.64181848770019	8.14551605537034	C	-0.14421353014963	-6.65874240235206	-0.83257871118896
O	-1.63223083338497	-2.29724327794981	.98970358879646	O	3.12903804771453	-2.08557659260664	3.12297294246624
Si	-3.30676838631048	-2.29565483753238	0.82644226998936	Si	3.30041325888533	-1.42055960676531	4.64815697699645
C	-3.82927713205814	-4.09707169956034	0.85071985898322	C	3.57291756086874	-2.88290643733735	5.79298853347637
C	-4.23355094142628	-1.31315191772293	2.12846591786733	C	4.82014348991803	-0.32044660146130	4.72219536952046
C	-3.71000228687991	-1.58706404973052	0.86472119491455	C	1.75180489211949	-0.47329967744529	5.12866696264083
H	0.59403194994958	2.30783053599769	2.01499197499995	H	5.25613612078867	1.06972919184038	0.80935170823910
H	-0.87603891433097	3.19168677627609	2.47794634223946	H	5.17695939304536	2.25248444895822	2.13669530016846
H	-0.03363099459596	3.59876092595506	0.96652959375777	H	4.92919158386420	2.78336930533955	0.45638448544604
H	-3.05261976641707	1.60344005658919	0.16412473092986	H	1.41120421062731	2.66666973660852	1.88632569973221
H	-2.30163412501706	3.21947714636371	0.25387281530509	H	2.61667489337041	3.77311856375628	1.16646412273275
H	-3.09577945082467	2.69142997287700	1.24663881466024	H	2.82968829915890	3.18466096452015	2.82877781244072
H	0.50976946492095	0.04802468644860	2.07973251232511	H	0.17262389524056	-0.08773857714485	1.08200517294894
H	-2.11327277707377	-3.72096890004538	5.82676370927009	H	0.73133191352526	1.97586191592716	-0.73371636249585
H	-0.43170575387569	-4.05198414071436	5.42461980292380	H	-0.59036082372319	-1.98046857644735	-0.69355964052945
H	-0.71872605855145	0.71808101112006	4.06211295962318	H	4.01757660569120	-0.90398182859115	1.11060679214733
H	1.02269458492185	0.48990431228925	4.21106341083419	H	-1.67230576811085	3.52724446078178	-1.27099343051502
H	-1.05415748430141	0.76078333226247	6.41072412616210	H	-0.27217685718249	3.95474109703915	-0.23506354565590
H	0.47506688859793	1.60304128638283	6.21453712341548	H	-1.92619009012072	3.92742651841453	0.45637461449730
H	0.73464992853105	-0.01241234251709	8.05017339087535	H	2.81120539776037	-5.32978804381358	-0.79138671076700
H	1.67926119604385	-0.58583173084851	6.68347100455490	H	3.05665440009949	-5.83690677859177	0.87781718469247
H	-1.77807444107420	-1.34590325633896	5.75373974689286	H	-0.61020846376175	-2.48756839414043	1.51968482959350
H	1.56425222654486	-3.07124232274052	6.68056829724609	H	-0.70271010931544	-3.45162234329608	2.97879933974680
H	0.25026809865605	-3.82614010937017	7.59984265312804	H	-1.56593286844854	-4.22161618994128	0.15860465205926
H	1.31541629703219	-2.64825815889645	8.38232605294626	H	-2.48510858885180	-4.29313083436515	1.65230336658013
H	-1.86879049071812	-0.76215745333864	7.98231104453910	H	-1.86718509218873	-6.59174396836092	1.05450004632168
H	-0.78418470903593	-1.55982996874105	9.14234693983008	H	-0.91844016208855	-6.12898082825355	2.46165187079066
H	-1.87813671311701	-2.52944663557606	8.13423560061098	H	0.66798637203250	-4.39335422468468	-0.32506802626578
H	1.16240473506522	-3.10132499290643	4.08976150832227	H	1.31941418919690	-7.19744602255802	2.26444509766462
H	1.94708051060924	-1.79854936169022	5.00314716129853	H	1.81464402429732	-7.76137472105611	0.65858771328881
H	1.69192773466290	-1.61758214304116	3.28033818974225	H	0.26896822195998	-8.28773264242624	1.34454726081716
H	-0.98708016475488	-3.94404020254638	3.16206133455152	H	-0.76000812442429	-5.88571509381753	-1.30806805627029
H	-2.61116230298013	-3.39162322949382	3.52991212616581	H	-0.71182161338938	-7.59714304450140	-0.83122328878434
H	0.22926913724359	-2.28002758759239	1.78077369388815	H	0.75247377846280	-6.80181776147187	-1.44709585212074
H	-2.00856537391280	-1.10524432711104	3.46805602484335	H	2.54047582836727	-4.92185310582950	2.96464005477878
H	-0.32313234077353	-2.64749667364886	0.35053810512936	H	0.88106103964763	-5.43420737233323	3.33091694329788
H	0.42485672861457	-0.51861076246959	-2.03679040426376	H	1.44886708061955	-3.84142250502714	3.83251253204142
H	-1.19459841275610	-0.94109258714216	1.47522221319656	H	3.92073905369179	-3.73664156691194	1.40486533440762
H	1.74273734628761	2.10440652050866	-0.16418684687692	H	3.61495747069220	-3.15704384238383	-0.23145011484014

5.77E-*anti*				**5.77E-*syn***			
C	-0.00339978791374	0.00100206498169	-0.02848949180007	C	0.01421877547615	0.00325731841489	0.00761529671752
C	2.39648518835391	0.00978789130954	-0.00669494758910	C	2.41403810520431	0.01631140883681	-0.01877871092347
C	2.56566674963704	1.49821837110891	-0.00392222298160	C	2.69571999400827	1.49585281030052	0.00186475691135
O	3.96219622021201	1.80138407603242	0.09620374296493	O	3.01787006231663	1.78606289318367	1.39638755559146
Si	4.74043528416929	2.95739159733798	-0.83677034024993	C	3.07774662282759	0.58907426504691	2.10457646940850
C	4.56353377880408	2.52461752638095	-2.65440393597438	C	2.74244549907796	-0.49634890828194	1.19854584763635
C	-0.34957875002325	0.70387351421019	-1.14521062832356	C	-0.58071763142234	0.81144065967892	-1.13578016888432
C	-0.80262442906666	2.03006941600158	-0.75874700754200	O	-0.65645891215884	2.12703863839384	-0.54831337640551
O	-0.79035059309284	2.10892369541703	0.63417888069065	C	-0.94524849797278	1.95084669471889	0.83022759149633

C	-0.40849408460086	0.81094279013980	1.17815930543329	O	-0.25587540014739	0.68541942425234	1.16443887876824
C	2.83871353034584	-0.96688553883371	1.07545416932018	C	-0.16571909199562	-1.48169570317264	0.20446853956837
O	3.64684811328174	-1.90269120102746	0.33124294338270	O	0.68867471022629	-2.24277962942423	-0.63761223916109
C	3.20779054757294	-1.90309589702491	-1.01756984497730	Si	0.72819618180174	-3.91910489683253	-0.69106670628237
O	2.68683231028005	-0.53851973074597	-1.21714081633031	C	2.31667187978578	-4.29848159466527	-1.60303367008451
C	2.08775292133297	-2.90744383309970	-1.25464938680423	C	0.11916070388995	0.96529333131972	-2.49818205590881
C	4.40147624277114	-2.07693435043819	-1.93342165253531	C	0.31245022675911	-0.38356228557052	-3.19158000359184
C	3.70036345349517	-0.41791784339243	2.23817703036674	C	1.26495723750235	-0.44233837183323	-4.42148595911378
C	2.82307908653999	0.36037440302585	3.22543398173463	C	0.89875018922735	-1.86341455018097	-4.92785334797708
C	3.51980551095085	1.36956028052719	4.17983657517170	C	-0.63569154058409	-1.88417313906265	-4.91357542103735
C	2.31763391090337	1.67816947292415	5.11101150294596	C	-1.01095822318282	-1.04135108261592	-3.66494790289473
C	1.73624010903042	0.29589133410291	5.44563843856609	C	1.64977857766380	-2.37013030853653	-6.18658191101592
C	1.94484311596201	-0.52862666400431	4.14550961922416	C	3.07920545967695	-1.75510521319115	-6.18543207551374
C	2.56746469345232	2.69334885163176	6.25626149160423	C	3.59092596245393	-1.49425218927666	-4.76365209019622
C	3.61602021790722	3.73307164011747	5.76430614827322	C	2.77045798180557	-0.39732655442430	-4.04819694666468
C	3.55211482400974	3.94077059098141	4.24616067631389	C	-2.43324403155641	1.74362248033115	1.08774637158678
C	3.98830542194834	2.67296529283738	3.47903202567264	C	-0.33649930153271	3.08216970522737	1.62948264198567
O	-1.15013304092126	2.98812116668301	-1.42794456745801	O	3.78183202966876	1.76942652663981	-0.83764254902204
O	-1.48242892617761	0.18953802922689	1.82438305158698	C	4.08234361160559	3.17879538608469	-0.93402998227934
C	-1.83353753695818	0.83507102217486	3.06970136597991	O	3.38150675680876	0.58460229292877	3.28653020501746
C	4.70569440071378	0.71775319409181	4.90893027319281	C	0.95897345211131	0.66073402869957	-5.44826388294618
C	3.04998199929540	2.04548791225978	7.56465933390976	C	0.94002378816867	-2.03770848883146	-7.50965625857529
C	1.23800399300277	3.41823420208182	6.54280667965851	C	1.76456920216348	-3.90263789685228	-6.07929327523032
C	6.51965509654475	2.86247926047719	-0.26906283664598	O	-0.71558432684335	1.80159049680808	-3.29726786293605
C	3.98618496949257	4.64192445165054	-0.49142819837573	Si	-0.83331736233521	3.46224324464569	-3.40621419428651
O	4.31251680387993	-1.52649317859984	2.89733785887270	C	-1.01453368961759	3.82384958671914	-5.24059903084445
Si	5.83090560764661	-2.16312517009919	2.58358041120724	C	0.75213585072030	-4.60123569325971	1.05670016254965
C	6.66297525479011	-2.36100852959860	4.25736192075284	C	-0.76741187197643	-4.56195063527369	-1.62435935685409
C	6.81926219932135	-0.99826455356484	1.49154250847815	C	-2.38153826426388	4.07158573161390	-2.53595051829450
C	5.68489294577420	-3.87132039045222	1.81884620714546	C	0.70637460632815	4.29145494613808	-2.72433481246233
H	1.28961237258929	-2.78131058709905	-0.51824919573155	H	-2.82513784859057	0.92528364296835	0.47774695187919
H	2.48758529064672	-3.92097174067364	-1.16042264506460	H	-2.97532093955307	2.66071506225635	0.83978006701020
H	1.67128659599066	-2.78228364821677	-2.25776649041632	H	-2.59881762229039	1.50798214021606	2.14213827125598
H	5.13171438399977	-1.28823956601693	-1.73877364256568	H	0.73833053798628	3.14210028002299	1.44989679481541
H	4.08383589635942	-2.03214955586200	-2.97854874406767	H	-0.51246433282994	2.91933901806905	2.69620492356409
H	4.86330302088019	-3.05119268159661	-1.74885013150025	H	-0.80829865804321	4.02416476989317	1.33661848259007
H	1.97554613391962	-1.49689788670319	1.50647268407094	H	2.31207626763119	-0.53417721908981	-0.94187748095891
H	2.04111474872186	1.96258560718805	0.83628870687233	H	1.84420419055299	2.14117888113767	-0.24585466296262
H	2.13422080248380	1.88694164571443	-0.93424284408319	H	2.74086553326192	-1.53315732095172	1.50496902847433
H	4.46437495620222	0.24077123621715	1.81299416643683	H	-1.59896759911881	0.43463197566822	-1.34400006142183
H	2.15754773314970	0.98214189984995	2.61331039690391	H	0.03725551964868	-1.69640913561364	1.26080135433125
H	2.46126095373652	-1.46843416079524	4.35175890680745	H	-1.22313207913933	-1.73165498628173	0.00563578269204
H	0.99331862989153	-0.78096367714075	3.66651008861651	H	4.83452487476480	3.27322180465587	-1.71793423833365
H	0.68406855717730	0.34794197663287	5.74263061379991	H	4.47711372839308	3.55234510722711	0.01583737041801
H	2.28320914446868	-0.16192892792390	6.27508137453918	H	3.18254177798043	3.74195832615422	-1.20856689618626
H	3.60660107467762	2.71272916434731	2.45375315626685	H	1.09302587470569	1.45008162304844	-2.33866347741033
H	5.08147008657087	2.66193349689406	3.39154985956290	H	0.76334319717354	-1.04483663090486	-2.44508406899670
H	2.52615857776918	4.21177581856681	3.96395506822853	H	-1.74737060545389	-0.27297105735072	-3.91275576684773
H	4.18587714397995	4.78488167738811	3.94990591913507	H	-1.43535059214122	-1.66453263306399	-2.87147006938352
H	3.45076876364187	4.68160462304687	6.29114351250467	H	-1.03923943539774	-2.90073659369044	-4.86755385566223
H	4.62575533430921	3.39936711231650	6.03614123998180	H	-1.03629450998363	-1.42004365215153	-5.81964894819482
H	1.58596094887301	2.16561618657691	4.44522649506471	H	2.89949249545111	-0.50746784764470	-2.96447767618487
H	3.95479738133704	1.44856227009923	7.41892158815991	H	3.17986200497829	0.58753328250675	-4.30497473644232
H	2.27871544456707	1.39560028804035	7.99379170787778	H	3.53919642977679	-2.42908033899324	-4.19016728285028
H	3.27489468673289	2.82789337497538	8.29955460182242	H	4.64829411574033	-1.20672061672476	-4.78563114856293
H	0.90589897136651	3.98574767896785	5.66534314885334	H	3.75790490069888	-2.43305818065607	-6.71892860124490
H	1.35158628764453	4.11677004578165	7.38067778985220	H	3.07777735042859	-0.81198651194104	-6.74568676338518
H	0.44963891812546	2.70096778112548	6.79980636539203	H	1.21808508058779	-2.52695411033545	-4.10888994177760
H	4.42898234756800	-0.21149050069630	5.41495466376697	H	0.75757556233104	-0.96528076193798	-7.62079013457260

Int1-*cis* enolate pathway (R=H)				**Int1-*trans* enolate pathway (R=H)**			
C	-0.4026288	2.0508611	-0.8578679	C	-1.0650789	2.2656716	0.7468192
C	1.1525807	2.1432520	-0.9301138	C	0.4728468	2.4855483	0.6863050
C	1.6332905	3.6054467	-0.8236154	C	0.8190896	3.9767762	0.8623227
O	2.2303490	3.7730997	0.4522608	O	1.3617223	4.1415595	2.1655985

C	2.5041463	2.4404439	1.0059741
C	1.9182815	1.5017393	0.1900956
C	-0.9555573	0.7271795	-1.4335315
O	-0.8836407	0.9737169	-2.8568437
C	-1.2730499	2.3455659	-3.0400027
O	-1.0024432	3.0019145	-1.7807946
C	-0.9056236	2.3375635	0.5559495
O	-2.3126635	2.1295439	0.7368742
C	-3.1050859	3.3036555	0.5239954
C	-0.2019329	-0.5154037	-1.1108704
C	-0.5982699	-1.4211982	-0.2106508
C	0.1747512	-2.6479514	0.2499211
C	-0.1519131	-2.5927228	1.7713284
C	-1.6567481	-2.2838538	1.8146969
C	-1.8372720	-1.2955541	0.6491106
C	0.3965125	-3.7563222	2.6375286
C	1.7449047	-4.2227996	2.0155695
C	2.4741278	-3.0811108	1.2970731
C	1.7085514	-2.6087371	0.0408499
C	-2.7708670	2.4466877	-3.3199606
C	-0.4140043	2.9425271	-4.1452256
O	2.5800463	3.8300628	-1.8710123
C	3.0188752	5.1916417	-1.9153366
O	3.1699410	2.4287319	2.0672716
C	-0.4241354	-3.8807004	-0.4717405
Cl	-3.3876161	-1.6830782	-0.3166364
C	-0.5663633	-4.9490841	2.7495373
C	0.6577977	-3.2095466	4.0538570
H	-3.3335938	1.9392237	-2.5313566
H	-3.0053503	1.9833279	-4.2834181
H	-3.0765068	3.4971420	-3.3494966
H	0.6386834	2.9033511	-3.8558398
H	-0.6986904	3.9857057	-4.3127927
H	-0.5607573	2.3854154	-5.0760660
H	0.8333750	4.3499935	-0.9207743
H	1.9150744	0.4458094	0.4195714
H	-0.3919473	1.6462378	1.2291895
H	-0.6314784	3.3598246	0.8483058
H	3.5558075	5.4632058	-0.9987716
H	2.1615338	5.8692370	-2.0456304
H	3.6876930	5.2793371	-2.7745299
H	-3.0203329	3.6601388	-0.5071555
H	-4.1386319	3.0206611	0.7376862
H	-2.7946584	4.1039048	1.2115979
H	-2.0315799	-0.2752096	0.9735695
H	-1.9882116	-1.8493627	2.7611712
H	-2.2440559	-3.1874340	1.6358360
H	2.0337004	-1.5957115	-0.2160408
H	1.9718911	-3.2488877	-0.8094111
H	2.5990543	-2.2401078	1.9915053
H	3.4839367	-3.3953850	1.0104068
H	2.3747523	-4.6413069	2.8107664
H	1.5621827	-5.0370014	1.3022956
H	0.3637836	-1.6862643	2.1220323
H	-0.8509432	-5.3411731	1.7690763
H	-1.4810776	-4.6736523	3.2866486
H	-0.0818089	-5.7586121	3.3088304
H	1.4216569	-2.4233687	4.0335106
H	1.0062742	-4.0102159	4.7171197
H	-0.2554842	-2.7822289	4.4843875
H	-1.5010341	-3.9761300	-0.3041733
H	0.0627443	-4.8052387	-0.1500561
H	-0.2612694	-3.7690084	-1.5490645
H	0.7418540	-0.6472068	-1.6359133
H	-2.0044150	0.6420125	-1.1281714
H	1.4234894	1.7834069	-1.9325361

C	1.7674905	2.8184174	2.6553182
C	1.2737265	1.8666447	1.7948866
C	-1.5052509	0.8973870	0.1674022
O	-1.5622141	1.1483355	-1.2408286
C	-2.0305886	2.4961516	-1.4056517
O	-1.7320560	3.1740043	-0.1689198
C	-1.6128954	2.4999555	2.1574087
O	-3.0358516	2.3457546	2.2549916
C	-3.7504489	3.5814960	2.1344532
C	-0.6552088	-0.2743236	0.5198579
C	0.0886627	-1.0802798	-0.2481879
C	0.8210019	-2.3229720	0.2567557
C	0.5322293	-3.2905862	-0.9255468
C	0.7516803	-2.4267734	-2.1760430
C	0.2461845	-1.0334110	-1.7491181
C	1.2140946	-4.6833325	-0.8563971
C	1.3372278	-5.0879360	0.6413342
C	0.2137492	-4.4885112	1.4948214
C	0.2860561	-2.9443588	1.5687437
C	-3.5442840	2.5151598	-1.6086784
C	-1.2572255	3.1276962	-2.5538042
O	1.7721356	4.3300383	-0.1412294
C	2.0952902	5.7234259	-0.1070435
O	2.4371345	2.8214842	3.7159324
C	2.3183990	-1.9611684	0.4130199
Cl	1.4735929	0.2646445	-2.2963571
C	2.6001154	-4.7272420	-1.5196805
C	0.3020063	-5.6944660	-1.5771495
H	-4.0357639	2.0082138	-0.7734703
H	-3.8057506	2.0102463	-2.5440776
H	-3.9036402	3.5479827	-1.6528296
H	-0.1900788	3.1147202	-2.3238196
H	-1.5859991	4.1614870	-2.6971535
H	-1.4350052	2.5695845	-3.4784295
H	-0.0401889	4.6531962	0.7719674
H	1.4550194	0.8078697	1.9106759
H	-1.1606391	1.7583589	2.8211830
H	-1.3142018	3.4944120	2.5132557
H	2.5859150	5.9927067	0.8358616
H	1.1873488	6.3339356	-0.2278605
H	2.7741627	5.9101426	-0.9423615
H	-3.5880783	4.0395751	1.1537991
H	-4.8089007	3.3410324	2.2629619
H	-3.4374457	4.2830267	2.9215827
H	-0.6591753	-0.7118027	-2.2531649
H	0.2157260	-2.7910651	-3.0569065
H	1.8126901	-2.3766660	-2.4294543
H	-0.7148719	-2.5571217	1.7880361
H	0.9314076	-2.6436446	2.4023488
H	-0.7525967	-4.7892052	1.0688032
H	0.2451840	-4.9038956	2.5084812
H	1.3282223	-6.1831784	0.7135062
H	2.3064767	-4.7592482	1.0363707
H	-0.5497952	-3.4802746	-0.8576998
H	3.2768210	-3.9742128	-1.1064046
H	2.5300167	-4.5675759	-2.6015546
H	3.0519032	-5.7133657	-1.3564863
H	-0.6660642	-5.7780627	-1.0687875
H	0.7665950	-6.6876559	-1.5960497
H	0.1147586	-5.3851671	-2.6122709
H	2.7469253	-1.5794094	-0.5178423
H	2.9071281	-2.8212220	0.7429745
H	2.4150100	-1.1749897	1.1686237
H	-0.6976085	-0.4958268	1.5855052
H	-2.5223064	0.7058708	0.5487769
H	0.7834666	2.1764390	-0.3194250

TS-*cis* enolate pathway (R=H, DCM)				**TS-*trans* enolate pathway (R=H, DCM)**			
C	-2.1480136	-0.9832867	-0.5059973	C	-2.3561586	0.1325788	-0.1798237
C	0.5499789	-0.8294447	-0.6099088	C	0.2183464	-0.1223090	-0.6066335
C	1.1034154	0.4211269	-0.6068374	C	-2.2528576	1.5599125	-0.6134218
C	1.1881485	1.3553059	-1.8135446	C	-1.1350280	1.7951258	-1.6770512
C	1.0882266	2.7256330	-1.0865453	C	0.2168257	1.2472362	-1.1862340
C	1.9321811	2.5343496	0.1883432	O	-0.8449096	3.2081025	-1.7998751
C	1.6669482	1.0822122	0.5282992	C	0.2932691	3.5236892	-0.9522063
C	0.5943104	-1.7306382	0.5692333	O	0.6698289	2.2913923	-0.3165413
C	-0.6933713	-1.8847355	1.4019273	C	-3.4526541	-0.4736033	-0.7921068
C	-1.9435624	-2.0838860	0.4855618	O	-4.1260328	0.5247670	-1.6156243
O	0.8300592	-3.1046963	0.1787867	C	-3.6504446	1.8083528	-1.1952448
C	0.5610950	-3.8758977	1.3615456	C	0.7549970	-0.5612820	0.5695010
O	-0.4095332	-3.1023493	2.1275512	C	0.9041959	-2.0416915	0.9381020
C	-3.1611326	-0.1270589	-0.0739263	C	2.2002898	-1.9585943	1.7902577
O	-3.6911080	-0.6462856	1.1773004	C	2.0310048	-0.6662107	2.6096994
C	-3.2440525	-2.0022539	1.2977873	C	1.2472356	0.2322849	1.6617122
C	1.2942276	3.9816864	-1.9669207	C	2.6357292	-3.2639987	2.5016267
C	0.7195390	3.6632515	-3.3796934	C	2.2312317	-4.4583326	1.5868162
C	-0.4297022	2.6465569	-3.3248163	C	2.2254845	-4.0759997	0.1001191
C	0.0308203	1.2512250	-2.8349723	C	1.1504488	-3.0130332	-0.2405850
C	-0.8672083	-0.7160029	2.3767713	C	-0.3554110	-2.4718045	1.7258199
O	0.3156057	-0.4023095	3.1192549	Cl	-0.4343759	0.9686862	2.8884188
C	0.4062827	-1.0764936	4.3803013	C	2.0219101	-3.4442951	3.8991278
O	-4.1824375	-2.9065454	0.7367143	C	4.1693032	-3.2397786	2.6481220
C	-5.4259743	-2.9147994	1.4526984	C	-1.4948380	1.2201042	-3.0523359
O	-3.6647134	0.9230589	-0.5012124	O	-0.4252609	1.2994688	-4.0044389
C	1.8201461	-4.0273370	2.2117770	C	-0.4959549	2.4640948	-4.8374769
C	-0.0358576	-5.2090723	0.9406864	C	1.4197293	4.0374911	-1.8460515
C	2.5480881	1.0912255	-2.5007357	C	-0.1079388	4.5102645	0.1329653
Cl	3.7545489	0.1853111	0.9368254	O	-4.4732291	2.3556525	-0.1753122
C	2.7619039	4.4221657	-2.0829078	C	-5.8033964	2.6273201	-0.6370676
C	0.4896838	5.1387958	-1.3447276	O	-3.9444305	-1.6142358	-0.7949295
H	2.2513424	-3.0461238	2.4277431	H	-2.0569135	2.2535209	0.2079296
H	2.5594133	-4.6333893	1.6789790	H	1.6956132	3.2730126	-2.5775842
H	1.5742054	-4.5196185	3.1575924	H	2.2950691	4.2880581	-1.2387117
H	-0.9429759	-5.0472494	0.3537407	H	1.0930093	4.9339219	-2.3821044
H	-0.2838288	-5.7993685	1.8275734	H	-0.8940602	4.0775575	0.7552750
H	0.6874738	-5.7681050	0.3389994	H	-0.4712118	5.4356034	-0.3236010
H	-3.1459684	-2.2139213	2.3699786	H	0.7559602	4.7443094	0.7627881
H	-1.8400023	-1.0156890	-1.5384770	H	-3.6935148	2.4684388	-2.0712760
H	-1.1072114	0.1681050	1.7775101	H	-1.9144339	-0.2438987	0.7270279
H	-1.6969447	-0.9012658	3.0679128	H	-1.7247657	0.1586668	-2.9169640
H	-5.9214526	-1.9397820	1.3874883	H	-2.3826788	1.7150423	-3.4599017
H	-5.2593697	-3.1684332	2.5097303	H	-6.3159137	1.7017927	-0.9220979
H	-6.0486713	-3.6799272	0.9853917	H	-5.7803468	3.3098604	-1.4995194
H	0.4497052	-2.1619095	4.2489406	H	-6.3299297	3.1024405	0.1929817
H	1.3249031	-0.7202166	4.8517033	H	-0.4248913	3.3811447	-4.2442633
H	-0.4554542	-0.8196014	5.0133695	H	0.3476163	2.4006758	-5.5290036
H	1.4163707	0.7889322	1.5391334	H	-1.4363741	2.4699048	-5.4074315
H	1.6506003	3.1991382	1.0111462	H	1.5676412	1.2472282	1.4813318
H	2.9968110	2.6907886	-0.0099891	H	2.9805433	-0.2069437	2.9038665
H	-0.8212870	0.7404954	-2.3756544	H	1.4583560	-0.8484988	3.5223519
H	0.3518603	0.6441955	-3.6903452	H	1.4760625	-2.4526416	-1.1251855
H	-1.2094664	3.0273557	-2.6528009	H	0.2095048	-3.5082150	-0.5083481
H	-0.8957939	2.5522016	-4.3122213	H	3.2180464	-3.6899121	-0.1671334
H	0.3772432	4.5983453	-3.8415846	H	2.0674867	-4.9682611	-0.5165340
H	1.5170081	3.2732929	-4.0244096	H	2.9267996	-5.2897076	1.7608000
H	0.0415543	2.7636531	-0.7497102	H	1.2365085	-4.8224395	1.8706511
H	3.4042232	3.6174520	-2.4508582	H	2.9856247	-1.7465564	1.0487840
H	3.1532482	4.7559430	-1.1151050	H	0.9303752	-3.3895733	3.8773448
H	2.8391466	5.2637162	-2.7825020	H	2.3885304	-2.6810392	4.5949616
H	-0.5826456	4.9100254	-1.3402563	H	2.3043409	-4.4253757	4.3011986
H	0.6416941	6.0637275	-1.9140916	H	4.6546951	-3.2172751	1.6648477
H	0.8009937	5.3203098	-0.3091715	H	4.5206055	-4.1300931	3.1838324
H	3.3814338	1.2148511	-1.8020022	H	4.4958158	-2.3543963	3.2065884
H	2.7051769	1.7434210	-3.3642875	H	-0.5193925	-1.8334364	2.5989842

H	2.5630761	0.0541973	-2.8555749	H	-0.2967133	-3.5138416	2.0517413
H	0.2259225	-1.2694037	-1.5470299	H	-1.2283443	-2.3759014	1.0712286
H	1.3912163	-1.4062116	1.2486360	H	-0.0439742	-0.8728090	-1.3482349
H	-1.8520929	-3.0787411	0.0418832	H	0.8683445	1.2082814	-2.0759484

Int2-*cis* enolate pathway (R=H)				**Int2-*trans* enolate pathway (R=H)**			
C	-1.6598136	-0.9818775	-0.4351699	C	-1.9136263	0.2604935	-0.4518748
C	-0.0889629	-0.8149868	-0.4582217	C	-0.3635635	0.0923606	-0.5614527
C	0.4398973	0.5911043	-0.4064386	C	-2.2238927	1.7566517	-0.3528272
C	0.8985298	1.3159117	-1.6739097	C	-0.9694449	2.4764546	-0.9348957
C	0.9121892	2.7756636	-1.1516538	C	0.1807467	1.5342165	-0.5365266
C	1.3648822	2.6440623	0.3140581	O	-0.6913046	3.6972187	-0.2316084
C	0.7651135	1.3050553	0.6804168	C	0.3254032	3.4153937	0.7761873
C	0.3951042	-1.7124823	0.6868435	O	0.4638453	1.9912687	0.7962550
C	-0.7662687	-1.9629163	1.6570669	C	-2.6625318	-0.1706717	-1.6895049
C	-2.0076010	-1.9518275	0.7056640	O	-3.5811189	0.7855390	-2.0491556
O	0.5716467	-3.0534977	0.1562152	C	-3.5465856	1.9090054	-1.0984471
C	0.4154421	-3.9523135	1.2584251	C	0.2434880	-0.8383542	0.4546740
O	-0.5083198	-3.2799674	2.1729283	C	0.9627452	-2.1223442	0.0437116
C	-2.4890776	0.2552738	-0.1364149	C	1.6959676	-2.4548821	1.3695841
O	-3.3531676	0.0049841	0.9012140	C	0.7252370	-1.9824827	2.4665475
C	-3.3225238	-1.4167551	1.2645118	C	0.0817948	-0.7975524	1.7842350
C	1.5415766	3.8266566	-2.0943699	C	2.3774363	-3.8405293	1.4332459
C	1.2201106	3.3969883	-3.5581291	C	2.9074533	-4.1659383	0.0032474
C	-0.0871201	2.5956518	-3.6585870	C	3.2553777	-2.8997755	-0.7961111
C	-0.0058272	1.2315946	-2.9287024	C	2.0162537	-2.0115908	-1.0858111
C	-0.8995321	-0.9797697	2.8250065	C	-0.1505486	-3.1212439	-0.3549996
O	0.3258093	-0.6160282	3.4446169	Cl	-3.3823175	-1.5615365	2.1386301
C	0.7723973	-1.5141359	4.4677108	C	1.4526656	-4.9663121	1.9222404
O	-4.3831106	-2.0887094	0.6497974	C	3.5719992	-3.7435224	2.4014084
C	-5.6735498	-1.7120404	1.1730953	C	-1.0328889	2.7540074	-2.4383499
O	-2.4868273	1.3336288	-0.6846961	O	0.2062203	3.2446153	-2.9548390
C	1.7415845	-4.1808443	1.9756165	C	0.2422516	4.6733064	-3.0825038
C	-0.2208002	-5.2344843	0.7454295	C	1.6276391	4.0913273	0.3526953
C	2.2975639	0.7341662	-1.9950058	C	-0.1713020	3.8626355	2.1399047
Cl	3.8219553	-1.0376597	1.7983192	O	-4.5945375	1.8104866	-0.1859897
C	3.0589427	3.9942632	-1.9170139	C	-5.8923545	1.9825388	-0.7863912
C	0.8701200	5.1841798	-1.8114948	O	-2.5339851	-1.1770732	-2.3547338
H	2.2367834	-3.2258263	2.1821776	H	-2.3538997	2.0918164	0.6759646
H	2.4014494	-4.7799293	1.3390868	H	1.9413636	3.7212826	-0.6268369
H	1.5710118	-4.7240926	2.9108640	H	2.4119559	3.8822021	1.0868084
H	-1.1754596	-5.0149815	0.2603222	H	1.4830718	5.1740522	0.2884972
H	-0.3915069	-5.9230416	1.5782400	H	-1.1030042	3.3457954	2.3822948
H	0.4457052	-5.7173617	0.0242494	H	-0.3465646	4.9422541	2.1364413
H	-3.4342480	-1.4332881	2.3529597	H	0.5769670	3.6309906	2.9038297
H	-2.0079858	-1.3484362	-1.4051211	H	-3.6586875	2.8023579	-1.7228939
H	-1.3281295	-0.0443557	2.4512105	H	-2.3272404	-0.3177512	0.3941331
H	-1.5932905	-1.4005465	3.5678557	H	-1.2479795	1.8186908	-2.9678166
H	-5.9009593	-0.6696624	0.9280826	H	-1.8392121	3.4635149	-2.6619471
H	-5.6939079	-1.8506787	2.2615845	H	-6.1177025	1.1531261	-1.4644507
H	-6.3981132	-2.3743371	0.6983562	H	-5.9338845	2.9325966	-1.3356680
H	0.9652827	-2.5125389	4.0689564	H	-6.6070728	1.9949740	0.0369901
H	1.6993578	-1.0892215	4.8559651	H	0.1077629	5.1600312	-2.1115485
H	0.0225328	-1.5790237	5.2705871	H	1.2252220	4.9200159	-3.4898392
H	0.7016764	0.9539948	1.7056363	H	-0.5384204	5.0151507	-3.7768133
H	1.0101914	3.4660964	0.9475293	H	-0.5085870	-0.0604333	2.3161196
H	2.4600945	2.6090476	0.4148264	H	1.2311847	-1.7267522	3.4054707
H	-1.0166532	0.9232682	-2.6458846	H	-0.0417804	-2.7341301	2.7045156
H	0.3914381	0.4720457	-3.6138747	H	2.3443704	-0.9701252	-1.1963331
H	-0.9013789	3.1912102	-3.2255574	H	1.5648834	-2.3051297	-2.0416313
H	-0.3490476	2.4354872	-4.7112512	H	3.9944586	-2.3195279	-0.2284275
H	1.1636029	4.2941204	-4.1887706	H	3.7409697	-3.1748225	-1.7397511
H	2.0445912	2.7916370	-3.9551031	H	3.7925953	-4.8100540	0.0886935
H	-0.1567525	3.0269926	-1.0912253	H	2.1561486	-4.7450943	-0.5468068
H	3.5921222	3.0483454	-2.0437221	H	2.5168510	-1.7210953	1.3941926

H	3.2982997	4.3896312	-0.9232627	H	0.5508212	-5.0486936	1.3103673
H	3.4438449	4.7029647	-2.6614338	H	1.1455038	-4.7990038	2.9608645
H	-0.2047056	5.1386591	-2.0250502	H	1.9817397	-5.9269064	1.8793270
H	1.3111398	5.9726741	-2.4338614	H	4.3114437	-3.0200717	2.0366765
H	0.9934169	5.4698540	-0.7599801	H	4.0669244	-4.7170153	2.5060001
H	2.9890044	0.8716747	-1.1581886	H	3.2437621	-3.4186095	3.3958797
H	2.7278407	1.1756483	-2.8987524	H	-0.8486882	-3.2791135	0.4734803
H	2.2054804	-0.3449679	-2.1704463	H	0.2517513	-4.0860811	-0.6779885
H	0.2646944	-1.2689071	-1.3892654	H	-0.7227028	-2.7021146	-1.1906874
H	1.3182372	-1.3610518	1.1615657	H	-0.1334714	-0.3029466	-1.5582618
H	-2.1660224	-2.9699917	0.3535670	H	1.0626245	1.6529098	-1.1753897

TS-*cis* enolate pathway (R=H, MeCN)				**TS-*trans* enolate pathway (R=H, MeCN)**			
C	-2.1702581	-0.9614451	-0.5028274	C	-2.4105528	0.0474408	-0.2691131
C	0.5606360	-0.8324362	-0.6218257	C	0.2573670	-0.1621491	-0.6608765
C	1.1103072	0.4192078	-0.6190389	C	-2.2317972	1.4910202	-0.6125764
C	1.1940456	1.3578942	-1.8226770	C	-1.1396953	1.7423392	-1.6965110
C	1.0968980	2.7260737	-1.0908366	C	0.2288733	1.2081970	-1.2314092
C	1.9428377	2.5285360	0.1823878	O	-0.8687596	3.1577176	-1.8136600
C	1.6697773	1.0792704	0.5186481	C	0.2736540	3.4869081	-0.9765583
C	0.5949576	-1.7303529	0.5595439	O	0.6814365	2.2506668	-0.3622212
C	-0.6971721	-1.8723056	1.3893856	C	-3.5619818	-0.4472228	-0.8745680
C	-1.9473102	-2.0714269	0.4745337	O	-4.2013599	0.6330248	-1.6035706
O	0.8228955	-3.1060724	0.1746200	C	-3.6239038	1.8635041	-1.1380268
C	0.5478141	-3.8720595	1.3624517	C	0.7495024	-0.5926857	0.5383781
O	-0.4228371	-3.0879080	2.1194847	C	0.9327093	-2.0702139	0.9086299
C	-3.1921774	-0.1279116	-0.0584382	C	2.1930537	-1.9480417	1.8090981
O	-3.7109470	-0.6606781	1.1859439	C	1.9529981	-0.6611059	2.6208221
C	-3.2427345	-2.0147201	1.2975902	C	1.1924460	0.2090967	1.6377307
C	1.3046032	3.9851956	-1.9665572	C	2.6421636	-3.2399270	2.5356033
C	0.7288326	3.6722087	-3.3802250	C	2.3103570	-4.4441734	1.6043073
C	-0.4220747	2.6572726	-3.3280883	C	2.3489016	-4.0581541	0.1190102
C	0.0372926	1.2590030	-2.8452992	C	1.2534675	-3.0299748	-0.2614270
C	-0.8641466	-0.6981450	2.3591033	C	-0.3402658	-2.5401135	1.6496985
O	0.3164146	-0.4026576	3.1120738	Cl	-0.6250651	0.9050762	2.8460452
C	0.3749246	-1.0653830	4.3835448	C	1.9829952	-3.4411421	3.9093197
O	-4.1742100	-2.9246515	0.7404242	C	4.1677535	-3.1666466	2.7387016
C	-5.4005903	-2.9791925	1.4887034	C	-1.5285319	1.1778520	-3.0675643
O	-3.7155259	0.9216910	-0.4762280	O	-0.4776652	1.2527105	-4.0388841
C	1.8022945	-4.0228798	2.2180481	C	-0.5463896	2.4272444	-4.8616226
C	-0.0535349	-5.2039372	0.9465083	C	1.3783749	4.0319818	-1.8769920
C	2.5533454	1.0944928	-2.5115043	C	-0.1319080	4.4505095	0.1268423
Cl	3.7680616	0.1588020	0.9307379	O	-4.3823840	2.4128843	-0.0740984
C	2.7729839	4.4238098	-2.0809100	C	-5.6882826	2.8369097	-0.4967370
C	0.5012725	5.1405652	-1.3394884	O	-4.1276254	-1.5568013	-0.9248687
H	2.2333547	-3.0418582	2.4356193	H	-1.9696526	2.1127095	0.2472064
H	2.5427423	-4.6320399	1.6906717	H	1.6686826	3.2778060	-2.6137021
H	1.5506567	-4.5130285	3.1632671	H	2.2516845	4.3032388	-1.2758703
H	-0.9573513	-5.0420737	0.3542971	H	1.0240786	4.9217265	-2.4062929
H	-0.3074693	-5.7880091	1.8357059	H	-0.9159935	4.0035496	0.7418244
H	0.6699252	-5.7702856	0.3520446	H	-0.4993378	5.3825434	-0.3122410
H	-3.1321552	-2.2269754	2.3678116	H	0.7318981	4.6775870	0.7591525
H	-1.8443537	-0.9636017	-1.5303617	H	-3.6399500	2.5627285	-1.9833594
H	-1.0849876	0.1876934	1.7544226	H	-1.9410060	-0.4287517	0.5745019
H	-1.7030709	-0.8690288	3.0425403	H	-1.7635176	0.1174991	-2.9322996
H	-5.9207166	-2.0156014	1.4559137	H	-2.4209497	1.6835974	-3.4521423
H	-5.1988737	-3.2501556	2.5343948	H	-6.2863285	1.9832680	-0.8344904
H	-6.0160992	-3.7489461	1.0200325	H	-5.6082157	3.5707505	-1.3112525
H	0.4029988	-2.1523324	4.2627384	H	-6.1609947	3.3001146	0.3712289
H	1.2913825	-0.7193761	4.8663029	H	-0.4423228	3.3370824	-4.2628361
H	-0.4927326	-0.7871993	4.9982296	H	0.2783228	2.3528228	-5.5740378
H	1.4269352	0.7790932	1.5293682	H	-1.5005974	2.4551419	-5.4065390
H	1.6692998	3.1934205	1.0075502	H	1.4449316	1.2476929	1.4919890
H	3.0074419	2.6794116	-0.0210889	H	2.8735932	-0.1737490	2.9580604
H	-0.8148686	0.7450010	-2.3894769	H	1.3442085	-0.8595536	3.5068123

H	0.3586527	0.6567304	-3.7035744	H	1.5936435	-2.4578615	-1.1329295
H	-1.2000405	3.0376842	-2.6534469	H	0.3397678	-3.5552753	-0.5640423
H	-0.8890480	2.5676547	-4.3153781	H	3.3374101	-3.6390342	-0.1099647
H	0.3873959	4.6091137	-3.8383669	H	2.2429805	-4.9530087	-0.5046284
H	1.5248379	3.2832368	-4.0271058	H	3.0255451	-5.2526693	1.8028117
H	0.0509616	2.7653426	-0.7516658	H	1.3181997	-4.8418320	1.8499393
H	3.4136715	3.6209864	-2.4559219	H	2.9985725	-1.7097338	1.0982221
H	3.1655825	4.7507613	-1.1112582	H	0.8915637	-3.4278656	3.8473729
H	2.8507899	5.2699096	-2.7745973	H	2.2952205	-2.6641323	4.6163761
H	-0.5709913	4.9108033	-1.3325478	H	2.2866500	-4.4103824	4.3238591
H	0.6503376	6.0662178	-1.9079827	H	4.6881060	-3.1268938	1.7740769
H	0.8155722	5.3207164	-0.3046090	H	4.5264974	-4.0464895	3.2862140
H	3.3875974	1.2156495	-1.8133862	H	4.4449485	-2.2725611	3.3096895
H	2.7098698	1.7507308	-3.3716127	H	-0.5612572	-1.9024619	2.5109333
H	2.5667213	0.0593558	-2.8718088	H	-0.2562854	-3.5769759	1.9848051
H	0.2268194	-1.2686575	-1.5577297	H	-1.1898005	-2.4815313	0.9605740
H	1.3902450	-1.4101754	1.2426144	H	0.0254578	-0.9168927	-1.4087431
H	-1.8477087	-3.0600272	0.0186061	H	0.8643605	1.1810636	-2.1331801

Int1-*cis* radical pathway (R=H)				**Int1-*trans* radical pathway (R=H)**			
C	-0.4044753	2.0695882	-0.8626460	C	-1.0930014	2.2595613	0.7803706
C	1.1731098	2.1690432	-0.9202472	C	0.4723384	2.4465603	0.7090076
C	1.6513055	3.6342883	-0.8763052	C	0.8704137	3.9342281	0.7551917
O	2.2994840	3.8147567	0.4264599	O	1.5458151	4.1394524	2.0424459
C	2.5296781	2.5822366	1.0129524	C	1.8466044	2.9166615	2.6160209
C	1.8898596	1.5652136	0.2168197	C	1.2369288	1.8738608	1.8296943
C	-0.9185883	0.7280474	-1.4347879	C	-1.5357311	0.8969323	0.1878739
O	-0.8216926	0.9792029	-2.8518125	O	-1.5479674	1.1732368	-1.2142454
C	-1.2619668	2.3305587	-3.0438146	C	-2.0315818	2.5139439	-1.3703489
O	-0.9603573	3.0082081	-1.7810873	O	-1.7094748	3.1831963	-0.1139175
C	-0.8966053	2.3621318	0.5562301	C	-1.5944177	2.5049850	2.2062914
O	-2.2946728	2.1689658	0.7155432	O	-2.9983661	2.3300533	2.3406674
C	-3.0721982	3.3689235	0.5694705	C	-3.7430913	3.5567103	2.2576402
C	-0.1562046	-0.5027688	-1.0869196	C	-0.7091639	-0.2902911	0.5504381
C	-0.5561556	-1.3979242	-0.1764548	C	0.0769625	-1.0702323	-0.2022995
C	0.2051636	-2.6324189	0.2779504	C	0.7730972	-2.3334548	0.3005048
C	-0.1644027	-2.6207840	1.7902953	C	0.5715354	-3.2508533	-0.9391693
C	-1.6696544	-2.3148432	1.7979884	C	0.8818229	-2.3372114	-2.1330371
C	-1.8131488	-1.2827041	0.6661319	C	0.3237714	-0.9699489	-1.6929729
C	0.3601661	-3.8102876	2.6362348	C	1.2504853	-4.6457507	-0.8780568
C	1.7233905	-4.2618140	2.0361247	C	1.2700183	-5.1098104	0.6071459
C	2.4747139	-3.1012071	1.3728515	C	0.0862309	-4.5472229	1.4016754
C	1.7439274	-2.5909875	0.1106256	C	0.1491915	-3.0076931	1.5456236
C	-2.7679312	2.3994906	-3.2650131	C	-3.5457870	2.5377981	-1.5397661
C	-0.4500114	2.9492389	-4.1673779	C	-1.2740339	3.1671766	-2.5122596
O	2.5654577	3.8341169	-1.9087366	O	1.7427750	4.1953671	-0.2988558
C	2.9527069	5.2160315	-2.0658293	C	2.0428917	5.5981756	-0.4538560
O	3.1693850	2.4866587	2.0509849	O	2.5150261	2.8475410	3.6388494
C	-0.3764380	-3.8416366	-0.4975097	C	2.2545823	-1.9759307	0.5748264
Cl	-3.3383641	-1.5979427	-0.3424607	Cl	1.5471499	0.3701067	-2.1107084
C	-0.6080735	-5.0027828	2.6882508	C	2.6788300	-4.6633278	-1.4460481
C	0.5846761	-3.3045109	4.0738880	C	0.3919118	-5.6254413	-1.7006341
H	-3.2959196	1.8865752	-2.4566388	H	-4.0272908	2.0183323	-0.7067598
H	-3.0238615	1.9262541	-4.2174796	H	-3.8213375	2.0481239	-2.4784359
H	-3.0931003	3.4434950	-3.2902011	H	-3.9022364	3.5716502	-1.5628441
H	0.6125590	2.9372366	-3.9133732	H	-0.2028409	3.1574156	-2.3010371
H	-0.7686133	3.9826280	-4.3298796	H	-1.6117252	4.1997690	-2.6375894
H	-0.6083152	2.3842352	-5.0906497	H	-1.4621981	2.6203623	-3.4408448
H	0.8496853	4.3767800	-0.9110600	H	0.0293723	4.6328756	0.7516749
H	1.9551687	0.5126394	0.4526243	H	1.3611920	0.8241501	2.0542090
H	-0.3949189	1.6541849	1.2293668	H	-1.1092698	1.7703179	2.8623015
H	-0.6060194	3.3781166	0.8550346	H	-1.2952401	3.5075626	2.5405545
H	3.5107436	5.5611593	-1.1897681	H	2.6078125	5.9692929	0.4072399
H	2.0630636	5.8409993	-2.2120004	H	1.1140893	6.1715341	-0.5655206
H	3.5863841	5.2531960	-2.9520845	H	2.6443074	5.6804141	-1.3594717

H	-2.9668183	3.7843414	-0.4374067	H	-3.6188970	4.0251954	1.2764613
H	-4.1096632	3.0820385	0.7495773	H	-4.7896822	3.2892364	2.4149682
H	-2.7596290	4.1160057	1.3112068	H	-3.4174426	4.2524034	3.0426204
H	-1.9864961	-0.2724825	1.0327788	H	-0.5603554	-0.6550448	-2.2379607
H	-2.0329046	-1.9170363	2.7484135	H	0.4241435	-2.6692927	-3.0683309
H	-2.2486815	-3.2109808	1.5645019	H	1.9594073	-2.2665428	-2.2954222
H	2.0793272	-1.5724108	-0.1132204	H	-0.8658946	-2.6302231	1.7105507
H	2.0292618	-3.2053099	-0.7508710	H	0.7346461	-2.7429316	2.4338969
H	2.5817668	-2.2826470	2.0967228	H	-0.8461278	-4.8286449	0.8950916
H	3.4909386	-3.4090668	1.1037033	H	0.0456391	-5.0034613	2.3969055
H	2.3313322	-4.7050946	2.8343385	H	1.2597908	-6.2066441	0.6342211
H	1.5589512	-5.0537394	1.2942747	H	2.2079148	-4.7974028	1.0830110
H	0.3401118	-1.7255285	2.1849102	H	-0.5120505	-3.4417786	-0.9585403
H	-0.8681308	-5.3664229	1.6902582	H	3.3259126	-3.9292205	-0.9577041
H	-1.5354795	-4.7403426	3.2095691	H	2.6826170	-4.4602749	-2.5227912
H	-0.1397248	-5.8290161	3.2362346	H	3.1196312	-5.6555918	-1.2923866
H	1.3507648	-2.5203836	4.0966938	H	-0.6088929	-5.7286714	-1.2646983
H	0.9135197	-4.1246985	4.7226239	H	0.8587545	-6.6170478	-1.7268705
H	-0.3389428	-2.8875699	4.4921753	H	0.2769056	-5.2748565	-2.7330077
H	-1.4583997	-3.9361202	-0.3679196	H	2.7423100	-1.5364248	-0.2997150
H	0.0960029	-4.7755372	-0.1832238	H	2.8249288	-2.8529322	0.8896893
H	-0.1768429	-3.7021859	-1.5650831	H	2.2989536	-1.2420397	1.3865948
H	0.7824749	-0.6500899	-1.6182889	H	-0.8226131	-0.5575201	1.6009540
H	-1.9696278	0.6349509	-1.1409674	H	-2.5625632	0.7232214	0.5460989
H	1.4579501	1.7277383	-1.8826924	H	0.7725636	2.0163106	-0.2552042

TS-*cis* radical pathway (R=H, DCM)				**TS-*trans* radcial pathway (R=H, DCM)**			
C	-1.6612706	-1.0267807	-0.5194087	C	-2.2342063	0.3174854	-0.3041455
C	0.5829301	-0.9070877	-0.5237627	C	0.1409725	0.2499805	-0.3222136
C	1.0529025	0.3874966	-0.5246050	C	-2.3577000	1.7974521	-0.4051532
C	1.1657047	1.2844594	-1.7411482	C	-0.9729138	2.5493311	-0.6044686
C	0.7964068	2.6524887	-1.0977654	C	0.1734617	1.7106559	-0.0113015
C	1.5484723	2.6471043	0.2426366	O	-0.9369409	3.7242113	0.2141698
C	1.4684626	1.1740207	0.6837867	C	-0.2370436	3.4142277	1.4600409
C	0.7120981	-1.8426192	0.6430967	O	0.0747681	2.0167390	1.3807877
C	-0.5355467	-2.0282229	1.5287774	C	-2.7090347	-0.2916244	-1.5269697
C	-1.8124517	-1.9999578	0.6047295	O	-3.1854107	0.7163521	-2.3664615
O	0.9011897	-3.1820792	0.1435304	C	-3.3532080	1.9310231	-1.5751474
C	0.6219216	-4.0595042	1.2432108	C	0.4816134	-0.7919959	0.4869487
O	-0.3367358	-3.3362044	2.0773045	C	0.7659760	-2.2089347	0.0148560
C	-2.3898188	0.1883700	-0.1776304	C	1.9525565	-2.5518524	0.9635587
O	-3.0861797	-0.0299381	1.0098453	C	1.5047065	-2.0123835	2.3304962
C	-3.0802131	-1.4669332	1.2932311	C	0.7279325	-0.7324171	1.9702720
C	0.9192472	3.8956122	-2.0176657	C	2.4948031	-4.0044831	0.8787425
C	0.5820136	3.4516618	-3.4711698	C	2.3283860	-4.4982170	-0.5879139
C	-0.4011750	2.2752831	-3.5041501	C	2.4032726	-3.3466643	-1.5969129
C	0.2110507	0.9813732	-2.9211639	C	1.2201518	-2.3592273	-1.4566777
C	-0.6097435	-1.0223651	2.6854298	C	-0.5000068	-3.0667375	0.2728358
O	0.6408142	-0.8470777	3.3441979	Cl	-0.8815275	-0.6737435	2.9309975
C	0.7753946	-1.6171207	4.5482683	C	1.7984661	-4.9822991	1.8387734
O	-4.1871372	-2.0879795	0.7093865	C	3.9942591	-3.9675350	1.2304486
C	-5.4364961	-1.7147493	1.3281128	C	-0.7061944	2.9541669	-2.0611114
O	-2.4440522	1.2723361	-0.7318650	O	0.6126579	3.4637992	-2.2529980
C	1.8743341	-4.3181036	2.0739409	C	0.6743196	4.8995177	-2.2623284
C	-0.0136235	-5.3261613	0.6980783	C	1.0301064	4.2603649	1.5134548
C	2.6390229	1.1968131	-2.2251855	C	-1.1589669	3.6267359	2.6475065
Cl	3.1410797	0.5868218	1.3041686	O	-4.6415751	1.9918303	-1.0323570
C	2.3053555	4.5586993	-1.9836336	C	-5.6652866	2.1928617	-2.0290373
C	-0.1246782	4.9284748	-1.5520027	O	-2.7227208	-1.4559050	-1.8969719
H	2.3178822	-3.3724191	2.3964155	H	-2.8040584	2.2362087	0.4880234
H	2.6057767	-4.8731520	1.4791142	H	1.6836171	4.0179111	0.6711896
H	1.6194087	-4.9067409	2.9599368	H	1.5637367	4.0711374	2.4495459
H	-0.9013590	-5.0788728	0.1108867	H	0.7714786	5.3220117	1.4626653
H	-0.2999801	-5.9814806	1.5252350	H	-2.0422068	2.9906993	2.5547815
H	0.7007037	-5.8570419	0.0618318	H	-1.4680087	4.6745653	2.6943908

H -3.1213214 -1.5477050 2.3825636	H -0.6344123 3.3725017 3.5730619
H -1.6362873 -1.3355503 -1.5551335	H -3.1946418 2.7556931 -2.2734668
H -0.9080653 -0.0451483 2.2915514	H -2.2015016 -0.2253692 0.6283572
H -1.3719398 -1.3440019 3.4043509	H -0.8091126 2.0692573 -2.7001876
H -5.6443580 -0.6524801 1.1659018	H -1.4404654 3.7010535 -2.3820675
H -5.4029183 -1.9276796 2.4040761	H -5.7524564 1.3134260 -2.6748121
H -6.2039432 -2.3239692 0.8501689	H -5.4332257 3.0776208 -2.6354694
H 0.6825486 -2.6885354 4.3456981	H -6.5947105 2.3490740 -1.4808498
H 1.7704482 -1.3967490 4.9396849	H 0.3474341 5.3142499 -1.3038247
H 0.0154815 -1.3147098 5.2820218	H 1.7190599 5.1587539 -2.4448848
H 0.8450876 1.0095573 1.5597489	H 0.0483098 5.3018608 -3.0703403
H 1.1088856 3.3086072 0.9931123	H 1.2060603 0.1913050 2.2826484
H 2.5923747 2.9388027 0.1089046	H 2.3350146 -1.7941248 3.0068839
H -0.6025564 0.3287523 -2.5948899	H 0.8436934 -2.7228427 2.8308067
H 0.7626469 0.4457628 -3.7026696	H 1.5277869 -1.3884105 -1.8611938
H -1.2962834 2.5373408 -2.9276720	H 0.3736822 -2.7010753 -2.0626135
H -0.7329651 2.0875989 -4.5315826	H 3.3486205 -2.8081740 -1.4505752
H 0.1662031 4.3100561 -4.0136137	H 2.4277004 -3.7393725 -2.6194302
H 1.5033493 3.1705067 -3.9970752	H 3.1079165 -5.2406889 -0.7999554
H -0.2718866 2.5526019 -0.8643777	H 1.3682812 -5.0167230 -0.6999716
H 3.1049042 3.8553638 -2.2328493	H 2.7717547 -1.9029731 0.6194246
H 2.5195182 4.9851234 -0.9970893	H 0.7155574 -5.0043350 1.6902271
H 2.3369564 5.3765409 -2.7135958	H 1.9960906 -4.7234895 2.8850400
H -1.1404648 4.5297711 -1.6572357	H 2.1829965 -5.9950790 1.6681743
H -0.0509606 5.8455078 -2.1484715	H 4.5507664 -3.3637557 0.5037488
H 0.0274543 5.1929202 -0.4989429	H 4.4143211 -4.9801606 1.2287590
H 3.3493409 1.4791977 -1.4434617	H 4.1537795 -3.5333929 2.2244774
H 2.8000473 1.8374982 -3.0957480	H -0.8002806 -3.0478356 1.3241568
H 2.8534302 0.1639656 -2.5199803	H -0.3326728 -4.1051918 -0.0230594
H 0.5159800 -1.4052178 -1.4872724	H -1.3235128 -2.6713774 -0.3286640
H 1.5505544 -1.5508544 1.2850217	H 0.1465087 0.0590162 -1.3939487
H -1.9829723 -3.0212983 0.2648608	H 1.1114258 2.1153105 -0.4227674

Int2-*cis* radical pathway (R=H)	**Int2-*trans* radical pathway (R=H)**
C -1.5135897 -0.7429230 -0.2716863	C -1.8512371 0.2458747 -0.5391598
C 0.0583408 -0.7986963 -0.3507831	C -0.2805173 0.1491697 -0.5059572
C 0.7495123 0.5244393 -0.4189542	C -2.2344189 1.7248808 -0.4711972
C 1.0194584 1.2516311 -1.7160903	C -0.9577419 2.5090793 -0.9050296
C 1.0113601 2.7202878 -1.2074329	C 0.1893002 1.6137642 -0.4004441
C 1.6978875 2.6544360 0.1694849	O -0.8154960 3.7219781 -0.1549250
C 1.3196428 1.2619653 0.6725349	C 0.1020556 3.4774842 0.9514808
C 0.4623425 -1.7328958 0.8078350	O 0.3202115 2.0585591 0.9564171
C -0.7757383 -2.0485512 1.6663147	C -2.4498703 -0.2232278 -1.8508342
C -1.9631656 -1.8588060 0.6750966	O -3.3349921 0.7052910 -2.3228135
O 0.7812733 -3.0265153 0.2595528	C -3.4716420 1.8175465 -1.3605892
C 0.5094457 -3.9808757 1.2939095	C 0.2743021 -0.8139245 0.4903944
O -0.6192399 -3.4243474 2.0345702	C 0.7848506 -2.1871462 0.1142864
C -2.1415344 0.5007415 0.3358016	C 1.7573138 -2.4464667 1.2989255
O -3.1293295 0.1425301 1.2078433	C 1.0036356 -1.9000973 2.5204395
C -3.2780686 -1.3292362 1.2371338	C 0.2909327 -0.6677761 1.9484511
C 1.4492630 3.7942582 -2.2330517	C 2.3910543 -3.8595770 1.3623307
C 0.9675750 3.3233318 -3.6382649	C 2.5883701 -4.3544731 -0.1011677
C -0.2899120 2.4466474 -3.5613221	C 2.8137427 -3.1956347 -1.0819067
C -0.0385928 1.0998446 -2.8385526	C 1.5746499 -2.2754779 -1.2155300
C -0.8597016 -1.1860273 2.9316395	C -0.4442685 -3.1381611 0.0719392
O 0.3265520 -1.2801484 3.7154859	Cl -1.5319993 -0.5954453 2.7056674
C 0.1907967 -2.1523806 4.8481405	C 1.5551810 -4.8779007 2.1536212
O -4.3181770 -1.7237142 0.4032194	C 3.7678929 -3.7314934 2.0414198
C -5.6230808 -1.3464078 0.8966489	C -0.8720002 2.8182671 -2.4019062
O -1.8776799 1.6650103 0.1303566	O 0.3942596 3.3668668 -2.7646559
C 1.7020376 -4.1269399 2.2337523	C 0.3821839 4.7982886 -2.8846421
C 0.0837091 -5.2840934 0.6439000	C 1.4008654 4.2302747 0.6813189
C 2.3984050 0.7445315 -2.2257615	C -0.5617568 3.8566503 2.2627053
Cl 3.1408416 0.3514766 1.2543249	O -4.6046717 1.6352830 -0.5736268
C 2.9632849 4.0555515 -2.2582704	C -5.8407505 1.7857199 -1.3056255

C	0.7351823	5.1105482	-1.8711444	O	-2.2148547	-1.2380891	-2.4703234
H	1.9647131	-3.1566763	2.6623917	H	-2.4933535	2.0443860	0.5376538
H	2.5601541	-4.5240714	1.6831459	H	1.8364244	3.9012645	-0.2659264
H	1.4540797	-4.8153949	3.0468111	H	2.1134340	4.0466368	1.4910613
H	-0.7661897	-5.1071709	-0.0200598	H	1.2026043	5.3043568	0.6216944
H	-0.2036125	-6.0047722	1.4144553	H	-1.4737754	3.2709056	2.3999612
H	0.9133588	-5.7022464	0.0664567	H	-0.8105299	4.9214696	2.2575313
H	-3.4959806	-1.5642539	2.2831306	H	0.1192122	3.6599226	3.0959993
H	-1.9469382	-0.8457579	-1.2703719	H	-3.5639178	2.7120265	-1.9842515
H	-0.9782750	-0.1326529	2.6523491	H	-2.3001125	-0.3389096	0.2664807
H	-1.7342109	-1.4737649	3.5274587	H	-0.9923972	1.8885409	-2.9705043
H	-5.7328806	-0.2576322	0.8983128	H	-1.6786880	3.5012462	-2.6946866
H	-5.7681908	-1.7390405	1.9104804	H	-5.9538273	0.9813572	-2.0390693
H	-6.3440834	-1.7950353	0.2133853	H	-5.8613467	2.7586916	-1.8120007
H	-0.0790275	-3.1658284	4.5342330	H	-6.6379989	1.7317026	-0.5642325
H	1.1637820	-2.1639511	5.3433417	H	0.1072314	5.2710180	-1.9366384
H	-0.5694331	-1.7648434	5.5402263	H	1.3961950	5.0897415	-3.1658384
H	0.8846158	1.1645410	1.6619287	H	-0.3205059	5.1094055	-3.6698733
H	1.3551965	3.4289108	0.8611819	H	0.6269420	0.2979612	2.3111777
H	2.7833165	2.7423271	0.0846146	H	1.6528991	-1.6361102	3.3589975
H	-0.9887325	0.7476265	-2.4272506	H	0.2681147	-2.6239199	2.8794228
H	0.3003819	0.3465611	-3.5587900	H	1.9102352	-1.2777942	-1.5238251
H	-1.0764740	2.9995651	-3.0326013	H	0.9146615	-2.6468158	-2.0073992
H	-0.6741981	2.2495323	-4.5682430	H	3.6723016	-2.6043582	-0.7387835
H	0.7720451	4.2065736	-4.2589984	H	3.0836428	-3.5848264	-2.0698605
H	1.7687617	2.7660615	-4.1388539	H	3.4423749	-5.0427662	-0.1291889
H	-0.0492622	2.9095433	-1.0045456	H	1.7137634	-4.9345325	-0.4194464
H	3.5362359	3.1419224	-2.4381270	H	2.5904182	-1.7523197	1.1133274
H	3.3067635	4.4946341	-1.3148314	H	0.5373050	-4.9665299	1.7645010
H	3.1994841	4.7650610	-3.0605577	H	1.4941270	-4.6036045	3.2128101
H	-0.3531018	4.9960087	-1.9412164	H	2.0271123	-5.8659150	2.0918244
H	1.0406592	5.9139209	-2.5518812	H	4.4362043	-3.0925222	1.4518198
H	0.9771696	5.4201546	-0.8476537	H	4.2384121	-4.7162290	2.1454887
H	3.1930245	0.9378148	-1.5010062	H	3.6732929	-3.2911142	3.0409735
H	2.6573426	1.2113762	-3.1791087	H	-0.9801061	-3.1484366	1.0259270
H	2.3429547	-0.3380952	-2.3878591	H	-0.1463342	-4.1603360	-0.1753052
H	0.2877862	-1.3368414	-1.2773178	H	-1.1320219	-2.7912326	-0.7054733
H	1.2956825	-1.3508598	1.4005859	H	0.0408026	-0.1983960	-1.4939312
H	-2.1360176	-2.8079190	0.1685529	H	1.1226197	1.7759483	-0.9494806

TS-*cis* radical pathway (R=H, MeCN)				**TS-*trans* radcial pathway (R=H, MeCN)**			
C	-1.6636193	-1.0180339	-0.5181092	C	-2.2427641	0.3187646	-0.3028628
C	0.5845983	-0.9030635	-0.5242438	C	0.1373812	0.2466348	-0.3195407
C	1.0550250	0.3910203	-0.5261369	C	-2.3593396	1.7989876	-0.4066463
C	1.1703521	1.2861180	-1.7438707	C	-0.9724163	2.5474382	-0.6042739
C	0.7964636	2.6545785	-1.1039870	C	0.1710780	1.7069172	-0.0085717
C	1.5453048	2.6531398	0.2382438	O	-0.9365064	3.7223395	0.2137422
C	1.4636760	1.1812101	0.6819927	C	-0.2385309	3.4126784	1.4611589
C	0.7127575	-1.8397066	0.6419396	O	0.0705297	2.0141431	1.3833135
C	-0.5355318	-2.0280862	1.5265900	C	-2.7206555	-0.2901103	-1.5232909
C	-1.8142220	-1.9927189	0.6045528	O	-3.1912485	0.7169381	-2.3656931
O	0.9059121	-3.1778918	0.1404929	C	-3.3539536	1.9355759	-1.5770726
C	0.6236612	-4.0591740	1.2374788	C	0.4753490	-0.7959241	0.4893652
O	-0.3404066	-3.3391875	2.0680397	C	0.7623519	-2.2121662	0.0164284
C	-2.3902696	0.1962742	-0.1739119	C	1.9517594	-2.5512393	0.9632363
O	-3.0824345	-0.0196776	1.0145544	C	1.5040953	-2.0140485	2.3312369
C	-3.0788047	-1.4590488	1.2985103	C	0.7231810	-0.7363071	1.9724034
C	0.9185587	3.8965025	-2.0256657	C	2.4996606	-4.0017323	0.8774387
C	0.5876512	3.4490110	-3.4794611	C	2.3323450	-4.4961166	-0.5889254
C	-0.3930500	2.2705703	-3.5133266	C	2.4007288	-3.3443384	-1.5982138
C	0.2208265	0.9789943	-2.9269684	C	1.2142763	-2.3611675	-1.4559064
C	-0.6042383	-1.0283555	2.6889447	C	-0.5006302	-3.0735205	0.2767160
O	0.6456046	-0.8769065	3.3558670	Cl	-0.8861959	-0.6818173	2.9339392
C	0.7540288	-1.6480941	4.5628948	C	1.8099549	-4.9824965	1.8391653
O	-4.1897185	-2.0749470	0.7186600	C	3.9998890	-3.9581638	1.2257244

C	-5.4343372	-1.7142113	1.3570600	C	-0.7021769	2.9501881	-2.0610562
O	-2.4478050	1.2807850	-0.7297605	O	0.6178771	3.4581961	-2.2500185
C	1.8727098	-4.3166221	2.0731123	C	0.6819705	4.8943654	-2.2624798
C	-0.0071504	-5.3252972	0.6863027	C	1.0300609	4.2563109	1.5154556
C	2.6456852	1.2005908	-2.2223407	C	-1.1622652	3.6284010	2.6466402
Cl	3.1344540	0.5962655	1.3150304	O	-4.6427365	2.0019564	-1.0356683
C	2.3025265	4.5637754	-1.9879540	C	-5.6653675	2.2042860	-2.0344230
C	-0.1301411	4.9269332	-1.5651870	O	-2.7438496	-1.4569530	-1.8900073
H	2.3097363	-3.3707473	2.4040018	H	-2.8050650	2.2401248	0.4857180
H	2.6096692	-4.8651274	1.4789667	H	1.6847168	4.0110406	0.6748301
H	1.6156475	-4.9118955	2.9539759	H	1.5614006	4.0676154	2.4529363
H	-0.8988541	-5.0788454	0.1046714	H	0.7735935	5.3183954	1.4624296
H	-0.2858416	-5.9882245	1.5100082	H	-2.0462299	2.9932377	2.5533317
H	0.7077700	-5.8477497	0.0437383	H	-1.4699978	4.6767438	2.6911174
H	-3.1161552	-1.5391241	2.3875736	H	-0.6396200	3.3755027	3.5736512
H	-1.6361150	-1.3247217	-1.5543604	H	-3.1913631	2.7578632	-2.2769671
H	-0.8871656	-0.0445326	2.2997821	H	-2.2099509	-0.2227900	0.6303902
H	-1.3741332	-1.3437748	3.4019223	H	-0.8041934	2.0644430	-2.6991383
H	-5.6526798	-0.6530362	1.2017278	H	-1.4347949	3.6972320	-2.3850438
H	-5.3827204	-1.9311209	2.4311214	H	-5.7558298	1.3228912	-2.6772780
H	-6.2034806	-2.3275728	0.8873389	H	-5.4286939	3.0859607	-2.6434660
H	0.6545775	-2.7185100	4.3583948	H	-6.5948292	2.3663396	-1.4876347
H	1.7448721	-1.4372628	4.9699845	H	0.3537364	5.3116223	-1.3056163
H	-0.0146329	-1.3385092	5.2840486	H	1.7275519	5.1515123	-2.4429737
H	0.8354458	1.0190469	1.5548757	H	0.0585610	5.2959251	-3.0726690
H	1.1040274	3.3160680	0.9863411	H	1.1992163	0.1886129	2.2842394
H	2.5893813	2.9447008	0.1054819	H	2.3345854	-1.7933685	3.0064799
H	-0.5915076	0.3232838	-2.6035131	H	0.8459779	-2.7270855	2.8319543
H	0.7768245	0.4447564	-3.7061199	H	1.5173023	-1.3893386	-1.8614235
H	-1.2901531	2.5321390	-2.9394656	H	0.3679433	-2.7069209	-2.0601502
H	-0.7215029	2.0804721	-4.5413738	H	3.3442668	-2.8020691	-1.4539305
H	0.1722947	4.3055552	-4.0251609	H	2.4244973	-3.7372471	-2.6207172
H	1.5113373	3.1680884	-4.0012326	H	3.1143900	-5.2355406	-0.8025299
H	-0.2721502	2.5527039	-0.8728924	H	1.3739044	-5.0184657	-0.6990037
H	3.1045917	3.8625949	-2.2352785	H	2.7678259	-1.8990776	0.6181937
H	2.5126896	4.9906229	-1.0007154	H	0.7266486	-5.0096759	1.6931397
H	2.3333577	5.3816665	-2.7179047	H	2.0089091	-4.7223823	2.8848904
H	-1.1444450	4.5256963	-1.6761831	H	2.1989467	-5.9935415	1.6677925
H	-0.0555166	5.8440792	-2.1613627	H	4.5520707	-3.3518367	0.4977747
H	0.0158615	5.1913602	-0.5112403	H	4.4242606	-4.9690781	1.2228933
H	3.3524905	1.4871336	-1.4388751	H	4.1597505	-3.5233309	2.2194277
H	2.8082726	1.8396898	-3.0937352	H	-0.7991835	-3.0554541	1.3285476
H	2.8633301	0.1675815	-2.5141488	H	-0.3310166	-4.1116017	-0.0194016
H	0.5149944	-1.4007329	-1.4878327	H	-1.3262477	-2.6800236	-0.3233062
H	1.5495046	-1.5477668	1.2860197	H	0.1426651	0.0559845	-1.3913214
H	-1.9876891	-3.0127313	0.2620772	H	1.1104427	2.1097612	-0.4184804

Int1-*cis* radical pathway (R=Cl)				**Int1-*trans* radical pathway (R=Cl)**			
C	-0.3693152	2.1437262	-0.7354491	C	-1.0994551	2.2458415	0.9137097
C	1.2101607	2.3239082	-0.7246130	C	0.4747450	2.4474187	0.9460617
C	1.6231305	3.7839331	-1.0233104	C	0.8791216	3.9104424	0.6543163
O	2.1412191	4.3513932	0.2335570	O	1.4425399	4.4639086	1.9015448
C	2.4219196	3.3444581	1.1237805	C	1.7075768	3.4534281	2.7902144
C	1.9046607	2.1082987	0.5680620	C	1.1559713	2.2283080	2.2440770
C	-0.8220381	0.7748785	-1.3053929	C	-1.5106751	0.8795507	0.2895118
O	-0.6986587	1.0093429	-2.7244543	O	-1.5115904	1.1713625	-1.1087568
C	-1.1930713	2.3321442	-2.9482803	C	-2.0043899	2.5033921	-1.2622386
O	-0.9360007	3.0403552	-1.6931037	O	-1.6750849	3.1704971	-0.0078350
C	-0.9448948	2.4526737	0.6506697	C	-1.7007228	2.4907270	2.3035579
O	-2.3453803	2.2275860	0.7333929	O	-3.1157153	2.3490856	2.3207616
C	-3.1408673	3.4084059	0.5368757	C	-3.8205198	3.5980098	2.2228832
C	-0.0642435	-0.4613146	-0.9662996	C	-0.6787654	-0.3127438	0.6233981
C	-0.5069590	-1.3996415	-0.1227080	C	0.1138815	-1.0622410	-0.1545309
C	0.2015932	-2.6858355	0.2679793	C	0.8013147	-2.3511962	0.2922571
C	-0.1498499	-2.7173094	1.7843070	C	0.5828221	-3.2126056	-0.9849847

C	-1.6422636	-2.3510162	1.8219500	C	0.9128691	-2.2526001	-2.1370866
C	-1.7641914	-1.2848437	0.7179771	C	0.3709849	-0.8996024	-1.6381288
C	0.3349861	-3.9570388	2.5802775	C	1.2362274	-4.6213105	-0.9845721
C	1.6704469	-4.4433611	1.9458388	C	1.2529214	-5.1486833	0.4793494
C	2.4602643	-3.2937075	1.3085066	C	0.0842030	-4.5974965	1.3035292
C	1.7367035	-2.7226081	0.0697150	C	0.1812088	-3.0680712	1.5149416
C	-2.6977685	2.3364493	-3.1900754	C	-3.5199740	2.5210830	-1.4234225
C	-0.3923521	2.9649288	-4.0722049	C	-1.2547233	3.1629374	-2.4056956
O	2.6202432	3.7669179	-1.9916682	O	1.8407556	3.9093316	-0.3467495
C	2.9627978	5.0837121	-2.4797165	C	2.1501840	5.2295634	-0.8430484
O	2.9891761	3.5481257	2.1828862	O	2.2914308	3.6459404	3.8433271
C	-0.4538096	-3.8333550	-0.5428744	C	2.2919967	-2.0297090	0.5628161
Cl	-3.2960421	-1.5416839	-0.3005136	Cl	1.6074441	0.4503104	-1.9741612
C	-0.6809812	-5.1099552	2.6044248	C	2.6617857	-4.6424570	-1.5593322
C	0.5993233	-3.5120856	4.0311960	C	0.3561494	-5.5490668	-1.8439580
H	-3.2171757	1.8314120	-2.3714520	H	-3.9951523	2.0098730	-0.5819692
H	-2.9220462	1.8226396	-4.1293290	H	-3.7983975	2.0204883	-2.3554174
H	-3.0617742	3.3658395	-3.2547607	H	-3.8797802	3.5534589	-1.4562084
H	0.6728686	2.9469343	-3.8291498	H	-0.1801088	3.1142956	-2.2174120
H	-0.7135232	3.9997412	-4.2198830	H	-1.5668522	4.2067633	-2.5002926
H	-0.5583295	2.4112886	-5.0009088	H	-1.4778192	2.6441977	-3.3425934
H	0.7936521	4.4326355	-1.3070837	H	0.0406995	4.5636922	0.4093431
Cl	2.1728744	0.6378823	1.3636657	Cl	1.3814603	0.7582534	3.0576146
H	-0.4721255	1.7783540	1.3735147	H	-1.2940427	1.7455654	2.9959090
H	-0.6972011	3.4849823	0.9326620	H	-1.4064099	3.4868783	2.6606151
H	3.4387996	5.6729267	-1.6902382	H	2.6501297	5.8236169	-0.0718150
H	2.0620670	5.5964023	-2.8383804	H	1.2314213	5.7341093	-1.1664156
H	3.6588440	4.9266780	-3.3035334	H	2.8158288	5.0819636	-1.6934675
H	-2.9877494	3.8240876	-0.4635837	H	-3.5914320	4.1061031	1.2813144
H	-4.1799647	3.0972873	0.6580006	H	-4.8832970	3.3523562	2.2660948
H	-2.8901519	4.1646053	1.2927723	H	-3.5576807	4.2489147	3.0675255
H	-1.9189271	-0.2820897	1.1114514	H	-0.5049669	-0.5506600	-2.1742997
H	-1.9740902	-1.9623989	2.7876534	H	0.4532540	-2.5360449	-3.0874414
H	-2.2612537	-3.2169060	1.5776822	H	1.9918540	-2.1919596	-2.2932960
H	2.1218969	-1.7217256	-0.1460726	H	-0.8229255	-2.6783537	1.7140313
H	1.9693491	-3.3440078	-0.8026329	H	0.7857303	-2.8555821	2.4044286
H	2.6070231	-2.5016298	2.0552887	H	-0.8559220	-4.8362622	0.7893530
H	3.4613675	-3.6324119	1.0199854	H	0.0376673	-5.0965872	2.2777883
H	2.2693890	-4.9389182	2.7197977	H	1.2215566	-6.2452781	0.4595422
H	1.4627593	-5.2014872	1.1796421	H	2.1987388	-4.8746408	0.9631837
H	0.3937120	-1.8581980	2.2052121	H	-0.5039494	-3.3826892	-1.0144043
H	-0.9676650	-5.4270085	1.5978271	H	3.3254152	-3.9445710	-1.0411838
H	-1.5904729	-4.8284900	3.1469937	H	2.6657776	-4.3912624	-2.6258689
H	-0.2406766	-5.9735234	3.1170026	H	3.0824064	-5.6495446	-1.4524522
H	1.3983652	-2.7620656	4.0698055	H	-0.6447649	-5.6518432	-1.4081819
H	0.9019075	-4.3673329	4.6466261	H	0.8039563	-6.5472815	-1.9144749
H	-0.3000450	-3.0714295	4.4770669	H	0.2438609	-5.1526667	-2.8599450
H	-1.5359210	-3.8851767	-0.3938647	H	2.7818472	-1.5828648	-0.3066671
H	-0.0172981	-4.7990268	-0.2756666	H	2.8436165	-2.9277808	0.8506782
H	-0.2690714	-3.6602574	-1.6082312	H	2.3576874	-1.3137876	1.3869091
H	0.8844580	-0.5974707	-1.4820350	H	-0.8016192	-0.6204750	1.6598869
H	-1.8781329	0.6661016	-1.0362595	H	-2.5389996	0.6875165	0.6336365
H	1.6063246	1.6842749	-1.5203167	H	0.8866937	1.8087336	0.1541961

TS-*cis* radical pathway (R=Cl, DCM)				**TS-*trans* radcial pathway (R=Cl, DCM)**			
C	-1.6997561	-0.6816632	-0.2643371	C	-2.4410226	-0.2030328	-0.2158841
C	0.2145768	-0.1363911	-1.0818455	C	-0.2598437	-0.1725385	-0.1351977
C	0.7391587	1.0126758	-0.4954566	C	0.3358675	1.0794906	-0.0983413
C	0.5464986	2.4142313	-1.0401154	C	0.6117515	1.8856826	1.1590729
C	0.4476147	3.2122649	0.2908954	C	2.0800643	2.3106136	0.8494624
C	1.5558009	2.6000921	1.1623109	C	2.0446438	2.7223700	-0.6306508
C	1.4994224	1.1081993	0.7892840	C	1.0129119	1.7606062	-1.2543746
C	0.7705688	-1.5354949	-0.9100791	C	-2.8340278	0.1020038	1.1683847
C	0.1499740	-2.3776602	0.2414713	O	-2.7542046	-1.0490058	1.9078338
C	-1.1998043	-1.7334179	0.6886228	C	-2.5255335	-2.2146293	1.0420701

O	0.3958001	-2.2529610	-2.0950192	C	-2.4545835	-1.6936802	-0.4148904
C	0.3008137	-3.6395993	-1.7555693	C	-0.1308740	-1.1483634	-1.2772489
O	-0.1382540	-3.6418050	-0.3727671	C	-1.2514895	-2.2202205	-1.2591641
C	-2.1932335	0.4714462	0.5085871	O	-0.2953025	-0.4913499	-2.5304712
O	-1.7148841	0.3697030	1.7879319	C	-0.8256108	-1.4486488	-3.4502423
C	-1.1910517	-0.9810436	2.0417617	O	-1.6627389	-2.3099423	-2.6299690
C	0.3638416	4.7563172	0.1610611	C	2.7410479	3.2771453	1.8713709
C	-0.3867436	5.0860516	-1.1622062	C	2.1589716	2.9683615	3.2807812
C	-1.3948534	3.9955303	-1.5451189	C	1.7471668	1.4995937	3.4257830
C	-0.7014328	2.6671717	-1.9206987	C	0.5628294	1.1229259	2.5045675
C	1.1072137	-2.5949057	1.4330747	C	-0.7764911	-3.5979748	-0.7496198
O	2.2401417	-3.3802045	1.0921114	O	0.1579052	-4.2255054	-1.6178100
C	2.1139978	-4.7582356	1.4809891	C	-0.4443937	-5.1886178	-2.4986321
O	-2.0146479	-1.6577716	2.9284358	O	-3.5804298	-3.1083390	1.1477830
C	-1.9386571	-1.1525217	4.2832159	C	-3.6163197	-3.8078385	2.4138712
O	-2.8669614	1.4160562	0.1538792	O	-3.1575964	1.1589002	1.6728969
Cl	-2.6822500	-1.1225156	-1.6301185	Cl	-3.0666254	0.8692978	-1.4140803
C	1.6550592	-4.3274844	-1.9017173	C	0.2970033	-2.2433211	-4.1123661
C	-0.7825675	-4.2772823	-2.6064028	C	-1.7058746	-0.7286944	-4.4544381
C	1.8282539	2.7328129	-1.8617311	C	-0.3734294	3.0850432	1.1928656
Cl	3.2288319	0.3910090	0.6298112	Cl	-0.1734985	2.7229814	-2.3306882
C	1.7339943	5.4524657	0.1720999	C	2.5365654	4.7642801	1.5408801
C	-0.4586089	5.2823334	1.3526839	C	4.2543481	2.9874866	1.8768372
H	2.4034183	-3.8328510	-1.2796820	H	0.9148115	-2.7365386	-3.3595860
H	1.9660391	-4.2901073	-2.9501913	H	0.9148135	-1.5625811	-4.7057991
H	1.5782362	-5.3748283	-1.5957650	H	-0.1231841	-3.0046900	-4.7759284
H	-1.7277585	-3.7526341	-2.4560311	H	-2.4872577	-0.1756094	-3.9324639
H	-0.8988980	-5.3279447	-2.3262658	H	-2.1596988	-1.4570574	-5.1324714
H	-0.5013143	-4.2277013	-3.6621926	H	-1.0997961	-0.0332374	-5.0415009
H	-0.2085459	-0.8081512	2.4871787	H	-1.6021751	-2.6557349	1.4282771
H	1.4972469	-1.6279067	1.7661039	H	-0.2585382	-3.4613315	0.2060498
H	0.5576791	-3.0545828	2.2653313	H	-1.6443934	-4.2495922	-0.5827872
H	-2.3817385	-0.1542694	4.3427966	H	-3.8480261	-3.1139941	3.2271740
H	-0.8928062	-1.1205773	4.6111478	H	-2.6517967	-4.2957781	2.5994478
H	-2.5041124	-1.8538816	4.8960752	H	-4.4036935	-4.5554162	2.3207030
H	1.2588940	-5.2302944	0.9876290	H	-1.1959088	-4.7194795	-3.1407707
H	3.0393611	-5.2485322	1.1728226	H	0.3653030	-5.5949054	-3.1077130
H	2.0013160	-4.8341710	2.5709049	H	-0.9077611	-5.9954611	-1.9148016
H	1.0851219	0.4931005	1.5855817	H	1.4309106	1.0532477	-1.9662061
H	1.4060129	2.7457579	2.2344630	H	3.0139856	2.6358333	-1.1280534
H	2.5322460	3.0125860	0.8998208	H	1.7047131	3.7538161	-0.7396593
H	-1.4243016	1.8530125	-1.8186266	H	0.5912072	0.0398794	2.3416182
H	-0.3956752	2.6955993	-2.9727947	H	-0.3856818	1.3405911	3.0071108
H	-2.0774953	3.8208308	-0.7050197	H	2.6105825	0.8641583	3.1893669
H	-2.0131982	4.3290146	-2.3858587	H	1.4788019	1.2808479	4.4652279
H	-0.8951778	6.0512064	-1.0458386	H	2.9106702	3.2281153	4.0366601
H	0.3367200	5.2134416	-1.9777552	H	1.2905546	3.6096851	3.4744295
H	-0.5107659	2.8950980	0.7256335	H	2.6523337	1.3729703	0.9072095
H	2.3965076	5.0709482	-0.6099787	H	1.4786617	5.0231416	1.4450153
H	2.2366226	5.3281918	1.1378792	H	3.0434311	5.0403842	0.6094737
H	1.5979645	6.5272984	0.0029414	H	2.9620544	5.3764441	2.3451571
H	-1.4821377	4.8907762	1.3223088	H	4.4552590	1.9640544	2.2153902
H	-0.5082996	6.3772102	1.3313896	H	4.7750429	3.6797269	2.5488696
H	-0.0079399	4.9791293	2.3051047	H	4.6794205	3.1018348	0.8728041
H	2.7415217	2.6194888	-1.2712504	H	-0.2883290	3.7075803	0.2985931
H	1.7888896	3.7507312	-2.2575198	H	-0.1913920	3.7069568	2.0724690
H	1.8836281	2.0410619	-2.7086446	H	-1.3971151	2.7069540	1.2482352
H	-0.2104874	0.0090391	-2.0725647	H	-0.3215958	-0.6759364	0.8300669
H	1.8618325	-1.5093176	-0.8014284	H	0.8518880	-1.6432598	-1.2227439
H	-1.9183586	-2.5516978	0.7883647	H	-3.3692884	-2.0206983	-0.9192556

Int2-*cis* radical pathway (R=Cl)				**Int2-*trans* radical pathway (R=Cl)**			
C	-1.6752433	-0.7249434	-0.1993299	C	-1.9802623	0.2968725	-0.3430438
C	-0.1073669	-0.7017654	-0.3764566	C	-0.4102398	0.1881964	-0.1800000
C	0.5395340	0.6474819	-0.3902216	C	-2.3032858	1.7746430	-0.6049197

C	1.1417250	1.2663366	-1.6324907
C	0.8500352	2.7662574	-1.3432585
C	1.1309413	2.9243030	0.1591032
C	0.7089010	1.5646511	0.7411002
C	0.3998775	-1.7139938	0.6780449
C	-0.7320276	-2.0475930	1.6713644
C	-2.0373301	-1.7729957	0.8555112
O	0.5875525	-2.9745242	0.0105285
C	0.4043685	-3.9950823	1.0007111
O	-0.5953637	-3.4521201	1.9141587
C	-2.3326049	0.5689595	0.3053018
O	-3.1128696	0.2965654	1.3796653
C	-3.2294845	-1.1672952	1.5965966
C	1.4621409	3.7829705	-2.3399167
C	1.4653231	3.1190731	-3.7486184
C	0.3291881	2.1013771	-3.9133787
C	0.4897643	0.8753264	-2.9816079
C	-0.6268931	-1.2986229	3.0046717
O	0.6061919	-1.5696465	3.6589022
C	0.4851309	-2.5299417	4.7197569
O	-4.4060914	-1.6397930	1.0422985
C	-5.5909943	-1.2094249	1.7514967
O	-2.2092017	1.6853183	-0.1400210
C	1.6950695	-4.2556133	1.7699779
C	-0.1599401	-5.2268775	0.3184896
C	2.6500595	0.8930010	-1.6462253
Cl	2.1246700	0.9628445	1.9565363
C	2.8832292	4.2379743	-1.9723889
C	0.5478466	5.0226501	-2.3689463
H	2.0472846	-3.3328451	2.2374936
H	2.4618770	-4.6355980	1.0882516
H	1.5178219	-4.9990661	2.5524821
H	-1.0754360	-4.9672261	-0.2189681
H	-0.3841166	-5.9928959	1.0657697
H	0.5715039	-5.6304562	-0.3876055
H	-3.2277270	-1.2757472	2.6840616
Cl	-2.5041769	-1.0565910	-1.7896468
H	-0.6755783	-0.2173878	2.8241082
H	-1.4650693	-1.5715919	3.6563302
H	-5.7340184	-0.1308138	1.6377137
H	-5.5050730	-1.4674404	2.8138721
H	-6.4224394	-1.7488282	1.2985795
H	0.1188860	-3.4905932	4.3434999
H	1.4873676	-2.6515708	5.1355735
H	-0.1927097	-2.1555104	5.4992298
H	-0.1060003	1.6011789	1.4600791
H	0.5726201	3.7415409	0.6225707
H	2.1928367	3.0942073	0.3491078
H	-0.4966259	0.4310311	-2.8156604
H	1.1039756	0.1127204	-3.4745427
H	-0.6265209	2.5974490	-3.7015515
H	0.2750802	1.7596975	-4.9529441
H	1.3826237	3.9047060	-4.5100022
H	2.4266913	2.6200489	-3.9224492
H	-0.2385419	2.8433008	-1.4601542
H	3.5705029	3.3945096	-1.8634076
H	2.8894355	4.8079963	-1.0364804
H	3.2740762	4.8910074	-2.7620593
H	-0.4543084	4.7600112	-2.7281031
H	0.9610418	5.7896915	-3.0345264
H	0.4449279	5.4585451	-1.3683165
H	3.1646543	1.2457185	-0.7482235
H	3.1496311	1.3036809	-2.5275037
H	2.7465991	-0.1979690	-1.6853087
H	0.0884732	-1.1633208	-1.3470282
H	1.3143202	-1.3897717	1.1786838
H	-2.3400267	-2.7166751	0.4057203
C	-0.9347333	2.5099674	-0.8052054
C	0.0426611	1.6362447	-0.0056167
O	-0.9254185	3.7607411	-0.1109849
C	-0.3409548	3.5442849	1.2136141
O	-0.1754440	2.1240846	1.3214319
C	-2.4789908	-0.4340337	-1.5965356
O	-3.1026702	0.4423541	-2.4260146
C	-3.2878841	1.7576108	-1.7751342
C	0.1923410	-0.8284258	0.7344070
C	0.5570917	-2.2449674	0.3196042
C	1.9111178	-2.4021361	1.0765122
C	1.6570619	-1.7425966	2.4347019
C	0.7621954	-0.5457684	2.0757880
C	2.5588967	-3.8119402	1.0407770
C	2.2106543	-4.4651185	-0.3274371
C	2.0281583	-3.4171177	-1.4313423
C	0.8076021	-2.4957342	-1.1887761
C	-0.5663360	-3.1852628	0.8350910
Cl	-0.5277859	-0.3357438	3.4642746
C	2.1102893	-4.7285281	2.1902162
C	4.0857487	-3.6290489	1.1369953
C	-0.5325263	2.7279780	-2.2639045
O	0.8191770	3.1617975	-2.3903480
C	0.9519747	4.5840922	-2.5499884
C	1.0021967	4.2636306	1.2684526
C	-1.3150199	3.9882910	2.2888862
O	-4.5802339	1.8719570	-1.2867982
C	-5.5802011	1.9822516	-2.3254269
O	-2.3367561	-1.5989550	-1.8821673
H	-2.7909844	2.2313838	0.2532582
H	1.6687492	3.8810471	0.4908676
H	1.4649022	4.1103738	2.2478328
H	0.8574019	5.3361707	1.1094613
H	-2.2534153	3.4368056	2.1941854
H	-1.5122550	5.0594674	2.1921945
H	-0.8876893	3.7956635	3.2770476
H	-3.1002201	2.4806746	-2.5738484
Cl	-2.9308799	-0.3808245	1.0327460
H	-0.6174289	1.7768366	-2.8051049
H	-1.2092406	3.4500314	-2.7371244
H	-5.6551941	1.0457190	-2.8860783
H	-5.3263271	2.8063471	-3.0031773
H	-6.5201069	2.1906766	-1.8148286
H	0.5512982	5.1173265	-1.6824125
H	2.0213938	4.7807324	-2.6477412
H	0.4320931	4.9154073	-3.4591984
H	1.2528719	0.4236376	2.1379765
H	2.5667245	-1.4217304	2.9487510
H	1.1167840	-2.4205808	3.0990944
H	0.9908562	-1.5494934	-1.7117217
H	-0.0903970	-2.9300030	-1.6365529
H	2.9400410	-2.8091503	-1.4934753
H	1.9190499	-3.9074984	-2.4050331
H	3.0102502	-5.1656815	-0.5990605
H	1.2949545	-5.0616886	-0.2356377
H	2.5995318	-1.7412156	0.5283255
H	1.0234693	-4.8417949	2.2267768
H	2.4473638	-4.3449601	3.1597665
H	2.5491015	-5.7244986	2.0550985
H	4.4672311	-3.0691592	0.2747224
H	4.5883904	-4.6030659	1.1632561
H	4.3590021	-3.0794911	2.0454246
H	-0.7245391	-3.0727131	1.9116294
H	-0.3359854	-4.2313860	0.6186570
H	-1.4986406	-2.9291340	0.3251825
H	-0.0705796	-0.0792069	-1.1921630
H	1.0839985	1.7753554	-0.3162047

Int1-*cis* radical pathway (R=Br)				**Int1-*trans* radical pathway (R=Br)**			
C	-0.3680018	2.1588712	-0.7184781	C	-1.1084006	2.2466789	0.9233108
C	1.2130743	2.3494006	-0.7026660	C	0.4688692	2.4530357	0.9629245
C	1.6211464	3.8003755	-1.0527814	C	0.8753680	3.9069616	0.6287582
O	2.1011946	4.4232125	0.1910209	O	1.3561286	4.5189463	1.8813741
C	2.3866938	3.4531368	1.1214295	C	1.6281976	3.5411339	2.8062780
C	1.8992943	2.1887752	0.6027969	C	1.1349725	2.2837830	2.2768532
C	-0.8103383	0.7849467	-1.2851096	C	-1.5101189	0.8786564	0.2956790
O	-0.6870596	1.0158414	-2.7049869	O	-1.5128731	1.1725160	-1.1019659
C	-1.1916665	2.3334131	-2.9333079	C	-2.0068037	2.5037942	-1.2556426
O	-0.9412196	3.0470893	-1.6797577	O	-1.6889705	3.1681499	0.0029073
C	-0.9509392	2.4683951	0.6644978	C	-1.7181508	2.4858433	2.3105006
O	-2.3495578	2.2310239	0.7429734	O	-3.1320546	2.3332509	2.3194862
C	-3.1551315	3.4039002	0.5407483	C	-3.8458175	3.5772936	2.2242467
C	-0.0495629	-0.4497696	-0.9468513	C	-0.6707957	-0.3089698	0.6274274
C	-0.4985826	-1.3962043	-0.1155584	C	0.1179830	-1.0577096	-0.1556056
C	0.2030002	-2.6890708	0.2653267	C	0.8126314	-2.3450348	0.2846085
C	-0.1489274	-2.7287873	1.7812982	C	0.5758584	-3.2086962	-0.9880610
C	-1.6399627	-2.3567369	1.8207976	C	0.8927410	-2.2508022	-2.1459427
C	-1.7579841	-1.2844397	0.7221584	C	0.3604790	-0.8959223	-1.6416658
C	0.3312646	-3.9743632	2.5706627	C	1.2279125	-4.6181339	-0.9939904
C	1.6640298	-4.4635745	1.9329224	C	1.2661004	-5.1420650	0.4707758
C	2.4587304	-3.3146527	1.3005175	C	0.1096033	-4.5886972	1.3106140
C	1.7374370	-2.7342676	0.0652487	C	0.2113583	-3.0591231	1.5181207
C	-2.6962472	2.3259750	-3.1759179	C	-3.5211994	2.5192737	-1.4272368
C	-0.3948463	2.9682739	-4.0589012	C	-1.2503508	3.1665713	-2.3930389
O	2.6435805	3.7501742	-1.9942068	O	1.8968865	3.8695806	-0.3115294
C	2.9910448	5.0486192	-2.5259038	C	2.2334598	5.1708828	-0.8390478
O	2.9350662	3.7087850	2.1790784	O	2.1711486	3.7860799	3.8701028
C	-0.4594890	-3.8272984	-0.5528662	C	2.3075012	-2.0238333	0.5308057
Cl	-3.2874781	-1.5338170	-0.3016724	Cl	1.5959450	0.4521965	-1.9871681
C	-0.6896686	-5.1229601	2.5898920	C	2.6445521	-4.6422339	-1.5904183
C	0.5986819	-3.5372561	4.0233873	C	0.3339706	-5.5469904	-1.8377297
H	-3.2119939	1.8161355	-2.3579524	H	-4.0006915	2.0071344	-0.5887765
H	-2.9159678	1.8112146	-4.1157360	H	-3.7923016	2.0179588	-2.3610114
H	-3.0682868	3.3525174	-3.2399396	H	-3.8825751	3.5510235	-1.4626867
H	0.6705037	2.9572750	-3.8158642	H	-0.1769343	3.1239103	-2.1959744
H	-0.7228074	4.0003377	-4.2107245	H	-1.5679569	4.2081888	-2.4934643
H	-0.5565580	2.4100857	-4.9856222	H	-1.4608209	2.6439341	-3.3306816
H	0.7939888	4.4284910	-1.3847671	H	0.0473784	4.5386614	0.3052766
Br	2.2400256	0.6235714	1.5327857	Br	1.4331203	0.7147092	3.2188918
H	-0.4743203	1.8012104	1.3911901	H	-1.3091101	1.7430579	3.0038149
H	-0.7131945	3.5039892	0.9428202	H	-1.4333859	3.4837831	2.6699076
H	3.4385732	5.6739929	-1.7476514	H	2.6592526	5.8058114	-0.0559662
H	2.0979446	5.5385292	-2.9323717	H	1.3404649	5.6472591	-1.2621254
H	3.7129176	4.8637932	-3.3212681	H	2.9710820	4.9953098	-1.6221295
H	-2.9996779	3.8206413	-0.4589123	H	-3.6093517	4.0955713	1.2900633
H	-4.1919256	3.0827956	0.6553373	H	-4.9070354	3.3227676	2.2521447
H	-2.9165161	4.1628688	1.2978158	H	-3.5985611	4.2226008	3.0778517
H	-1.9119836	-0.2834920	1.1204780	H	-0.5198488	-0.5448439	-2.1690239
H	-1.9698884	-1.9713925	2.7884773	H	0.4194373	-2.5344128	-3.0895476
H	-2.2625566	-3.2189247	1.5726951	H	1.9696360	-2.1931493	-2.3169866
H	2.1283932	-1.7345722	-0.1463467	H	-0.7889030	-2.6679608	1.7330816
H	1.9655889	-3.3534935	-0.8097942	H	0.8305350	-2.8458258	2.3972482
H	2.6093134	-2.5269606	2.0515396	H	-0.8379618	-4.8272932	0.8101300
H	3.4584898	-3.6559039	1.0104684	H	0.0763137	-5.0861546	2.2862741
H	2.2612087	-4.9658343	2.7038830	H	1.2342465	-6.2387291	0.4538511
H	1.4522953	-5.2166944	1.1629000	H	2.2189645	-4.8671733	0.9401500
H	0.3974313	-1.8737214	2.2069294	H	-0.5114260	-3.3773763	-1.0030807
H	-0.9782980	-5.4336417	1.5818362	H	3.3161838	-3.9420172	-1.0858601
H	-1.5975808	-4.8402028	3.1344027	H	2.6321338	-4.3959413	-2.6580427
H	-0.2528340	-5.9910123	3.0978296	H	3.0666697	-5.6488999	-1.4853256
H	1.4013043	-2.7911483	4.0648413	H	-0.6604863	-5.6474243	-1.3868466
H	0.8978097	-4.3965171	4.6348717	H	0.7794907	-6.5459526	-1.9123911
H	-0.2982279	-3.0942512	4.4718245	H	0.2070221	-5.1529831	-2.8529436
H	-1.5418373	-3.8738549	-0.4042354	H	2.7822011	-1.5735405	-0.3451839
H	-0.0284320	-4.7970287	-0.2914718	H	2.8643612	-2.9226014	0.8061124

H	-0.2736182	-3.6487691	-1.6171307	H	2.3863718	-1.3105520	1.3560924
H	0.9009862	-0.5825186	-1.4600639	H	-0.7850560	-0.6145716	1.6655091
H	-1.8662155	0.6715369	-1.0172468	H	-2.5373194	0.6794229	0.6393062
H	1.6183710	1.6839377	-1.4716181	H	0.8887287	1.7898816	0.1966121

TS-*cis* radical pathway (R=Br, DCM)				**TS-*trans* radcial pathway (R=Br, DCM)**			
C	-1.6593192	-1.2380899	-0.6284333	C	-2.3931489	-0.2329540	-0.1396589
C	0.5041809	-0.9935811	-0.4947319	C	-0.2127416	-0.1955121	-0.1272458
C	0.8708373	0.3451281	-0.4478708	C	0.3726804	1.0630581	-0.1036672
C	1.2487131	1.1699724	-1.6620963	C	0.6232669	1.8893894	1.1457961
C	0.6518963	2.5467765	-1.2550235	C	2.0954755	2.3157897	0.8596627
C	1.0285239	2.6807040	0.2289267	C	2.0930944	2.6962799	-0.6291003
C	0.8798135	1.2407931	0.7516949	C	1.0692843	1.7288877	-1.2580267
C	0.6103637	-1.9748862	0.6522458	C	-2.7387623	0.0309980	1.2658801
C	-0.6437810	-2.1092268	1.5619674	O	-2.6447287	-1.1459145	1.9653003
C	-1.8961889	-1.5285484	0.8282869	C	-2.4868230	-2.2863138	1.0564848
O	0.7274658	-3.2717703	0.0482936	C	-2.4214325	-1.7170380	-0.3843406
C	0.2321152	-4.2317826	0.9858392	C	-0.1068270	-1.1637355	-1.2767551
O	-0.8194774	-3.5277109	1.6965169	C	-1.2334739	-2.2297715	-1.2583168
C	-2.2168725	0.0830332	-0.9586647	O	-0.2772936	-0.4944613	-2.5224022
O	-2.4648465	0.7505136	0.2147438	C	-0.8283557	-1.4373713	-3.4451345
C	-2.4400692	-0.1751636	1.3528875	O	-1.6684377	-2.2927767	-2.6227236
C	0.9470967	3.7315372	-2.2126505	C	2.7287240	3.3075526	1.8747657
C	1.0410730	3.1658134	-3.6599975	C	2.1164567	3.0257653	3.2769221
C	0.1714826	1.9174792	-3.8540215	C	1.7107806	1.5576682	3.4452197
C	0.6818377	0.7152613	-3.0287045	C	0.5535873	1.1489042	2.5027158
C	-0.4583349	-1.4914615	2.9638957	C	-0.7558623	-3.6188365	-0.7776863
O	0.5476511	-2.1481506	3.7213245	O	0.1291803	-4.2564452	-1.6882136
C	0.0199282	-3.0797661	4.6798739	C	-0.5295095	-5.1959425	-2.5540212
O	-3.7243197	-0.3782150	1.8394391	O	-3.5836643	-3.1330715	1.1468946
C	-4.2745247	0.7840234	2.5029513	C	-3.6705898	-3.8253075	2.4141672
O	-2.4112654	0.6058528	-2.0361695	O	-3.0317084	1.0709229	1.8211106
Br	-1.9543145	-2.5712194	-1.9513831	Br	-3.1567658	0.9770596	-1.3752785
C	1.3362329	-4.6772754	1.9407023	C	0.2780139	-2.2402962	-4.1247444
C	-0.3904929	-5.3872502	0.2236294	C	-1.7050225	-0.6967906	-4.4374559
C	2.8029107	1.1575597	-1.7175468	C	-0.3705407	3.0821534	1.1375674
Cl	2.2713481	0.8078335	1.9312242	Cl	-0.0862128	2.6845831	-2.3727904
C	2.2325792	4.4998614	-1.8676408	C	2.5247063	4.7862438	1.5074608
C	-0.2410496	4.7084478	-2.1286869	C	4.2428959	3.0265715	1.9205041
H	1.7544795	-3.8185678	2.4691357	H	0.8981776	-2.7471336	-3.3833200
H	2.1248384	-5.1764546	1.3694642	H	0.8969129	-1.5618024	-4.7198325
H	0.9349012	-5.3820729	2.6746390	H	-0.1588352	-2.9912365	-4.7893180
H	-1.1653258	-5.0129826	-0.4476316	H	-2.5232564	-0.2024527	-3.9128761
H	-0.8297572	-6.0972607	0.9298975	H	-2.1077301	-1.3998213	-5.1720795
H	0.3776964	-5.9045255	-0.3582495	H	-1.1060738	0.0537622	-4.9604149
H	-1.8239805	0.3326825	2.0986698	H	-1.5800026	-2.7846378	1.4101052
H	-0.1332503	-0.4509120	2.8648233	H	-0.1962875	-3.4943149	0.1559820
H	-1.4164604	-1.5080908	3.5002026	H	-1.6254084	-4.2590877	-0.5772845
H	-4.4273962	1.5964692	1.7867578	H	-3.8214466	-3.1126129	3.2299383
H	-3.6007808	1.1109607	3.3042805	H	-2.7568776	-4.4070540	2.5871152
H	-5.2291438	0.4655636	2.9209047	H	-4.5296312	-4.4908156	2.3324678
H	-0.5687516	-3.8603157	4.1879662	H	-1.3285024	-4.7124697	-3.1241227
H	0.8818740	-3.5240604	5.1812196	H	0.2355444	-5.5750525	-3.2341485
H	-0.6033978	-2.5535667	5.4155161	H	-0.9434482	-6.0254654	-1.9646744
H	0.0054439	1.1159882	1.3877425	H	1.4983492	1.0100283	-1.9515155
H	0.3912867	3.3716561	0.7854801	H	3.0722449	2.5950769	-1.1040062
H	2.0630778	3.0116608	0.3420241	H	1.7609448	3.7269014	-0.7662636
H	-0.1420391	0.0086666	-2.8933706	H	0.6008884	0.0638895	2.3582874
H	1.4674483	0.1913632	-3.5850735	H	-0.4093608	1.3611726	2.9785812
H	-0.8596662	2.1440124	-3.5586887	H	2.5850198	0.9239640	3.2468729
H	0.1389887	1.6393591	-4.9133110	H	1.4170472	1.3614570	4.4822830
H	0.7409227	3.9519327	-4.3639870	H	2.8492080	3.3067980	4.0437494
H	2.0847011	2.9212471	-3.8957771	H	1.2401317	3.6654247	3.4370102
H	-0.4354242	2.3922199	-1.2948403	H	2.6703913	1.3824324	0.9509361
H	3.1093227	3.8465499	-1.8431920	H	1.4690714	5.0346097	1.3687979

H	2.1501921	4.9994332	-0.8957624	H	3.0621884	5.0478267	0.5890873
H	2.4099007	5.2725029	-2.6252600	H	2.9168538	5.4178411	2.3136372
H	-1.1663863	4.2255389	-2.4639015	H	4.4415459	2.0115658	2.2848008
H	-0.0621598	5.5859946	-2.7607692	H	4.7448846	3.7355441	2.5893565
H	-0.3932135	5.0542458	-1.0993812	H	4.6898574	3.1226013	0.9240769
H	3.2563698	1.5280178	-0.7940228	H	-0.2892010	3.6730497	0.2217149
H	3.1637824	1.7616267	-2.5538422	H	-0.1938793	3.7360368	1.9946820
H	3.1410246	0.1276167	-1.8719821	H	-1.3907602	2.6972386	1.2067900
H	0.6572881	-1.4788651	-1.4558604	H	-0.2561369	-0.7004981	0.8379938
H	1.4892895	-1.7540663	1.2704272	H	0.8727014	-1.6671606	-1.2371037
H	-2.6968884	-2.2600598	0.9649310	H	-3.3413703	-2.0248937	-0.8901962

Int2-*cis* radical pathway (R=Br)				**Int2-*trans* radical pathway (R=Br)**			
C	-1.6815991	-0.7229282	-0.1899599	C	-1.9921770	0.3000540	-0.3552687
C	-0.1169754	-0.7002500	-0.3830937	C	-0.4283295	0.1802492	-0.1657822
C	0.5304329	0.6493916	-0.3928203	C	-2.3087391	1.7784905	-0.6113921
C	1.1479315	1.2661022	-1.6289030	C	-0.9327561	2.5032461	-0.8053894
C	0.8459049	2.7656412	-1.3476529	C	0.0296984	1.6267176	0.0086919
C	1.1093101	2.9292606	0.1573472	O	-0.9199989	3.7575080	-0.1184060
C	0.6885053	1.5688252	0.7386931	C	-0.3560901	3.5418254	1.2156057
C	0.3955021	-1.7136101	0.6696947	O	-0.2016102	2.1209455	1.3309558
C	-0.7285887	-2.0441899	1.6728603	C	-2.4826273	-0.4248416	-1.6109000
C	-2.0405985	-1.7692110	0.8657251	O	-3.1188341	0.4523925	-2.4319958
O	0.5748034	-2.9744657	0.0013438	C	-3.2915221	1.7696899	-1.7838947
C	0.3975555	-3.9944967	0.9932467	C	0.1725013	-0.8372440	0.7502038
O	-0.5927434	-3.4486173	1.9151226	C	0.5475074	-2.2513232	0.3305288
C	-2.3411460	0.5691206	0.3037609	C	1.9117244	-2.3966977	1.0719650
O	-3.1246364	0.2991309	1.3782795	C	1.6679944	-1.7386460	2.4319447
C	-3.2294906	-1.1614953	1.6117068	C	0.7706275	-0.5428694	2.0786022
C	1.4644152	3.7826342	-2.3400641	C	2.5712865	-3.8008506	1.0307996
C	1.4874921	3.1150041	-3.7467747	C	2.2149707	-4.4584545	-0.3330778
C	0.3586697	2.0908734	-3.9215573	C	2.0111378	-3.4124244	-1.4350122
C	0.5178434	0.8680982	-2.9858647	C	0.7849346	-2.5018624	-1.1803127
C	-0.6140837	-1.2950043	3.0049122	C	-0.5605007	-3.2036976	0.8559273
O	0.6215640	-1.5697797	3.6526778	Cl	-0.4806567	-0.3076482	3.4928238
C	0.5031682	-2.5314504	4.7126780	C	2.1429632	-4.7196206	2.1862260
O	-4.4081815	-1.6493852	1.0744637	C	4.0973737	-3.6041598	1.1109780
C	-5.5894075	-1.2123298	1.7851698	C	-0.5176820	2.7079435	-2.2621300
O	-2.2152356	1.6871639	-0.1381063	O	0.8392184	3.1270179	-2.3820473
C	1.6942342	-4.2575965	1.7514489	C	0.9883053	4.5474407	-2.5443004
C	-0.1761500	-5.2249790	0.3166006	C	0.9908641	4.2524598	1.2866230
C	2.6580908	0.8998814	-1.6210054	C	-1.3421833	3.9961718	2.2754682
Cl	2.0974569	0.9730639	1.9638397	O	-4.5833408	1.9012613	-1.2985755
C	2.8786189	4.2462802	-1.9570250	C	-5.5798995	2.0166510	-2.3394240
C	0.5439615	5.0173576	-2.3832855	O	-2.3217502	-1.5834752	-1.9138729
H	2.0470609	-3.3373975	2.2235610	H	-2.7942820	2.2428897	0.2436358
H	2.4571430	-4.6300916	1.0613085	H	1.6659871	3.8618872	0.5204770
H	1.5246128	-5.0075479	2.5294438	H	1.4383539	4.1004116	2.2732254
H	-1.0890636	-4.9605075	-0.2229326	H	0.8556274	5.3252079	1.1208529
H	-0.4072684	-5.9849908	1.0678580	H	-2.2832194	3.4512460	2.1692714
H	0.5523041	-5.6385185	-0.3868202	H	-1.5303268	5.0684270	2.1729040
H	-3.2164501	-1.2588175	2.7002788	H	-0.9303159	3.8033398	3.2701389
Br	-2.6105665	-1.0947597	-1.9170825	H	-3.0935526	2.4898673	-2.5830391
H	-0.6603884	-0.2137407	2.8238413	Br	-3.0800868	-0.4404479	1.1181488
H	-1.4496178	-1.5652682	3.6610641	H	-0.6082262	1.7540569	-2.7975816
H	-5.7286954	-0.1335395	1.6686949	H	-1.1838797	3.4333230	-2.7450998
H	-5.5020641	-1.4678716	2.8480987	H	-5.6654579	1.0772961	-2.8938357
H	-6.4239942	-1.7496488	1.3355795	H	-5.3150164	2.8329389	-3.0225081
H	0.1220118	-3.4871145	4.3385898	H	-6.5180983	2.2399685	-1.8319510
H	1.5090912	-2.6651061	5.1156920	H	0.5904962	5.0870565	-1.6793694
H	-0.1608604	-2.1515448	5.5013492	H	2.0601762	4.7319241	-2.6387550
H	-0.1312987	1.6039405	1.4518356	H	0.4752562	4.8824212	-3.4560384
H	0.5407672	3.7442593	0.6122743	H	1.2705365	0.4234852	2.1158357
H	2.1679275	3.1062670	0.3586763	H	2.5808104	-1.4176511	2.9402094
H	-0.4670330	0.4151437	-2.8327955	H	1.1317109	-2.4169737	3.0993651

H	1.1448706	0.1100577	-3.4695569
H	-0.6021444	2.5815929	-3.7205105
H	0.3172470	1.7466780	-4.9608715
H	1.4097932	3.8981511	-4.5112268
H	2.4532474	2.6201545	-3.9079434
H	-0.2416926	2.8372159	-1.4768218
H	3.5682156	3.4066924	-1.8336026
H	2.8700130	4.8221563	-1.0247159
H	3.2768112	4.8961385	-2.7456379
H	-0.4524905	4.7484303	-2.7534806
H	0.9609793	5.7847495	-3.0460635
H	0.4269918	5.4553867	-1.3851330
H	3.1572908	1.2498474	-0.7133555
H	3.1688081	1.3179924	-2.4923213
H	2.7602060	-0.1903866	-1.6649668
H	0.0828549	-1.1597884	-1.3534257
H	1.3148662	-1.3898648	1.1618173
H	-2.3461102	-2.7163891	0.4258429
H	0.9542509	-1.5553251	-1.7072157
H	-0.1136551	-2.9445762	-1.6181536
H	2.9168653	-2.7964024	-1.5069543
H	1.8959807	-3.9039357	-2.4074408
H	3.0183625	-5.1514263	-0.6128251
H	1.3060853	-5.0637668	-0.2315577
H	2.5880657	-1.7303305	0.5154135
H	1.0577018	-4.8429722	2.2342071
H	2.4863182	-4.3311027	3.1515993
H	2.5896488	-5.7116984	2.0483481
H	4.4648838	-3.0421247	0.2440591
H	4.6088774	-4.5736511	1.1332845
H	4.3751397	-3.0509641	2.0158193
H	-0.7149189	-3.0894818	1.9328678
H	-0.3188733	-4.2476302	0.6414530
H	-1.4988498	-2.9603772	0.3507347
H	-0.0801829	-0.0895834	-1.1748990
H	1.0753967	1.7584250	-0.2901885

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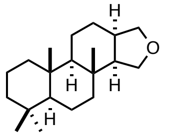

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79. Stereospecific S_N2 displacement of a leaving group to set the C-8 stereocenter of (–)-chromodorolide B (**5.11**) proposal depicted in Figure 5.3 was abandoned because of the lengthy low-yielding synthetic sequences required to prepare acids such as **5.70** from **5.51**. Additionally, no S_N2 displacement was observed in the preliminary experiments that utilized substrates with secondary mesylate and trifluoroacetate leaving groups.

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81. Computational studies suggested that employing α-bromobutenolide would also favor the desired α-transition state in this case by 2.4 kcal/mol. However, this prediction could not be verified experimentally because of decomposition of the bromide-containing butenolide upon irradiation with blue LEDs.[36]

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86. Use of other transfer hydrogenation reagents such as 1,4-cyclohexadiene or ammonium formate did not result in debenzylation of **5.86**.

87. The text describing the reactions depicted in Figures 5.1–5.2, 5.7–5.8, Schemes 5.1–5.10, 5.13, and Table 5.3 is taken verbatim from a previous publication, see: Tao, D. J.; Slutskyy, Y.; Muuronen, M.; Le, A.; Kohler, P.; Overman, L. E. *J. Am. Chem. Soc.* **2018**, *ASAP*. DOI: 10.1021/jacs.7b13799.

88. The text describing the reactions depicted in Tables 5.1–5.2, Scheme 5.12, Figures 5.4–5.6 is taken verbatim from a previous publication, see: Tao, D. J.; Muuronen, M.; Slutskyy, Y.; Le, A.; Furche, F.; Overman, L. E. *Chem. Eur. J.* **2016**, *22*, 8786–8790.

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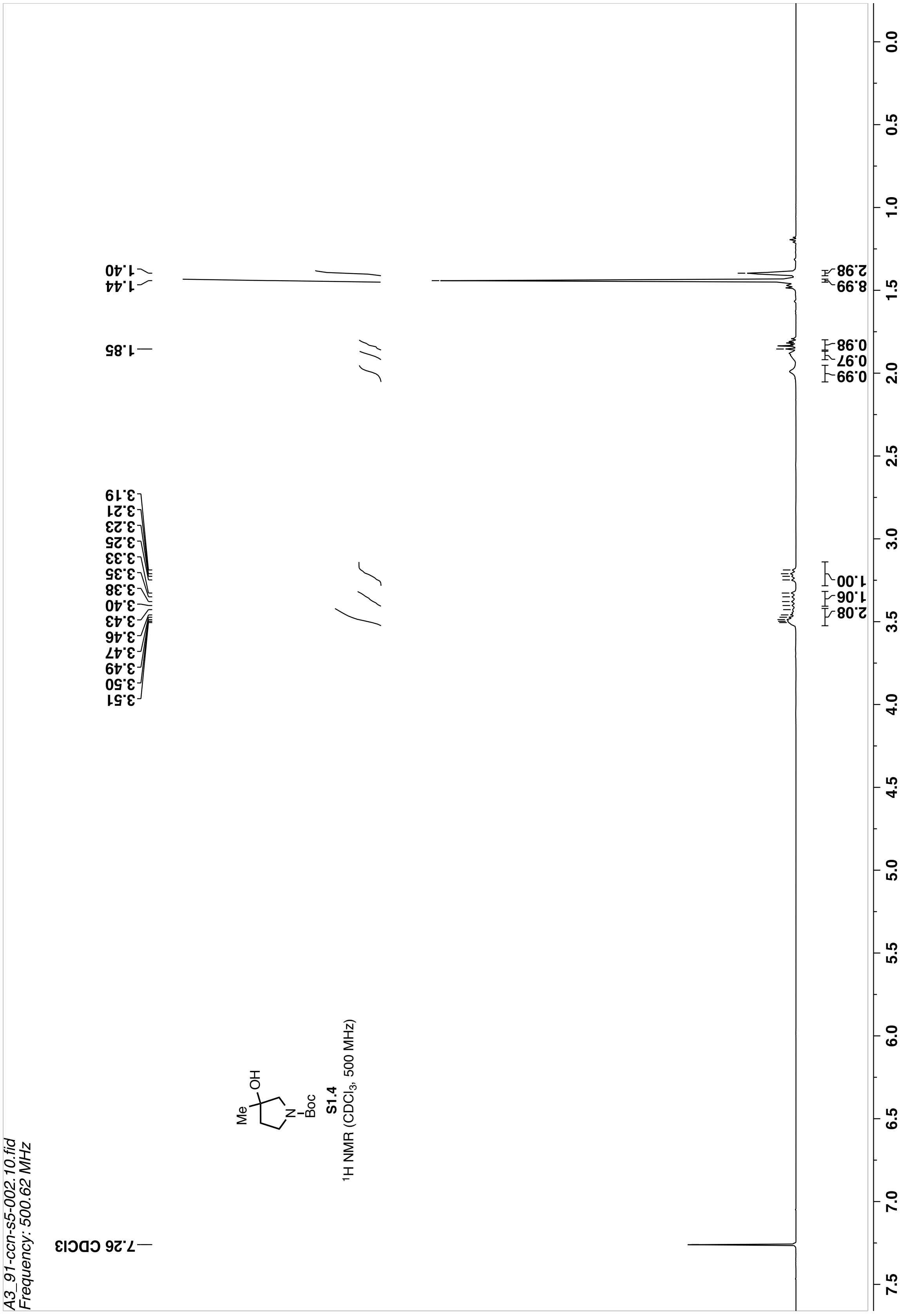
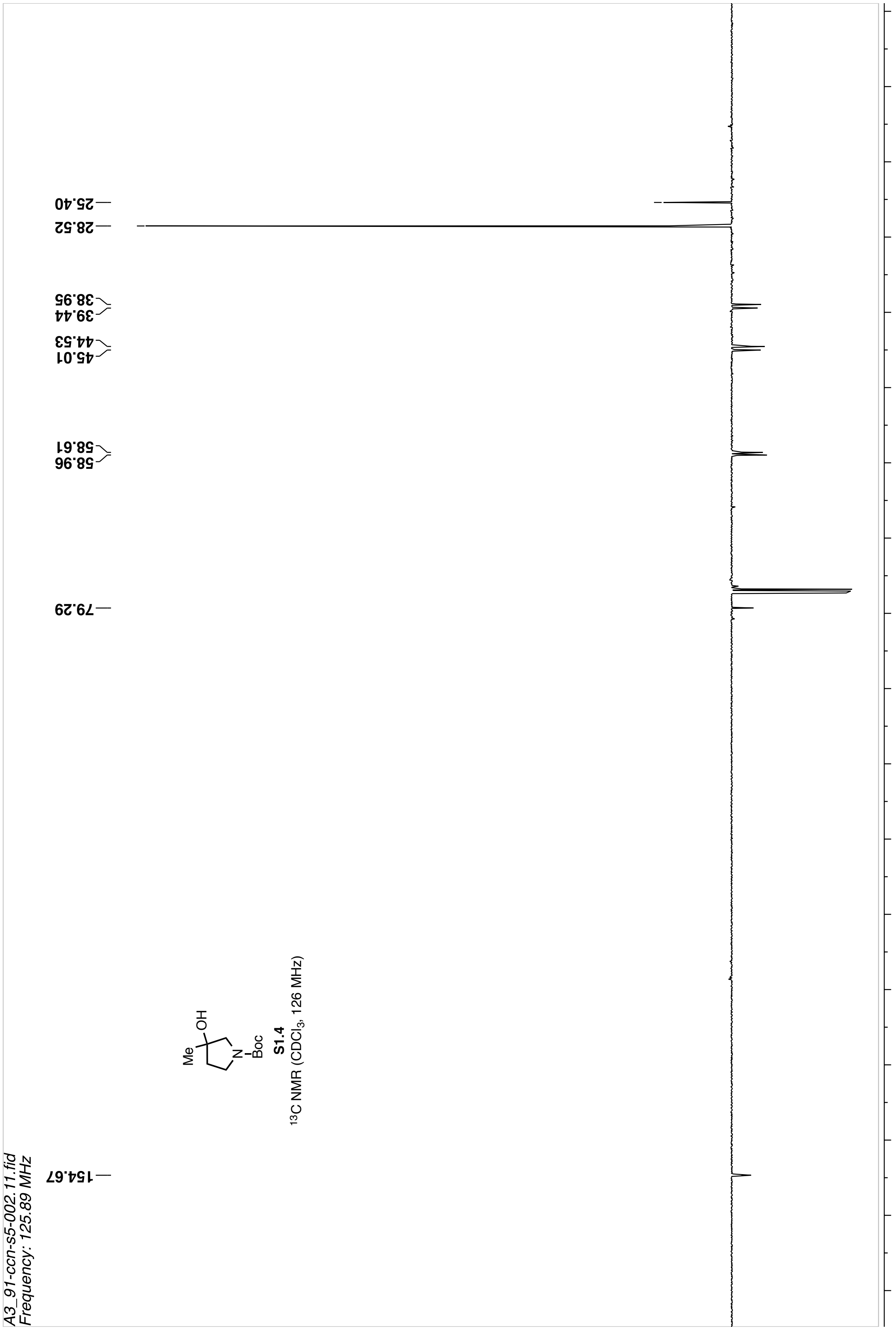
Appendix A: Chapter 1 NMR Spectra



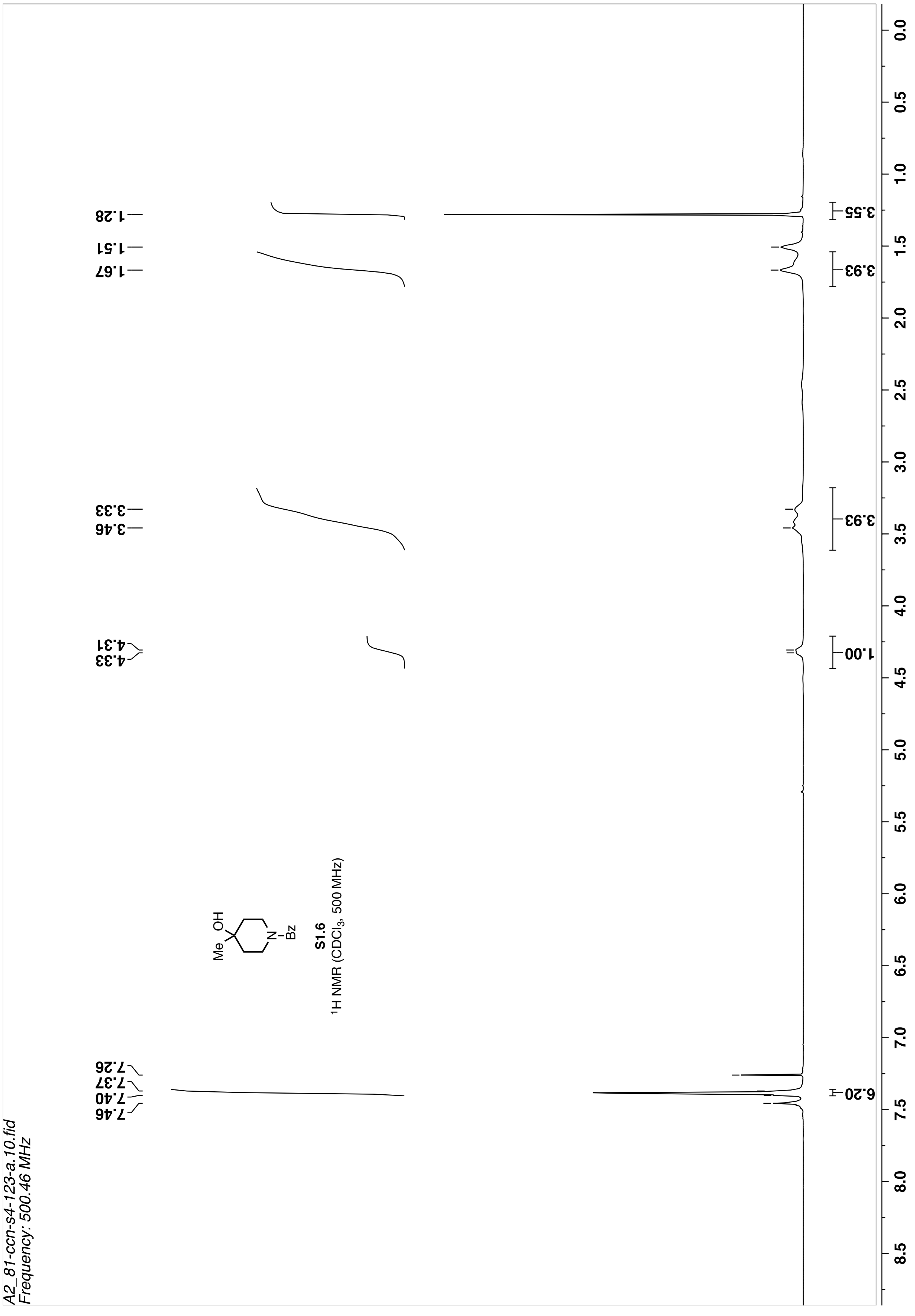
S1.4

^{1}H NMR (CDCl$_3$, 500 MHz)



S1.4

^{13}C NMR (CDCl$_3$, 126 MHz)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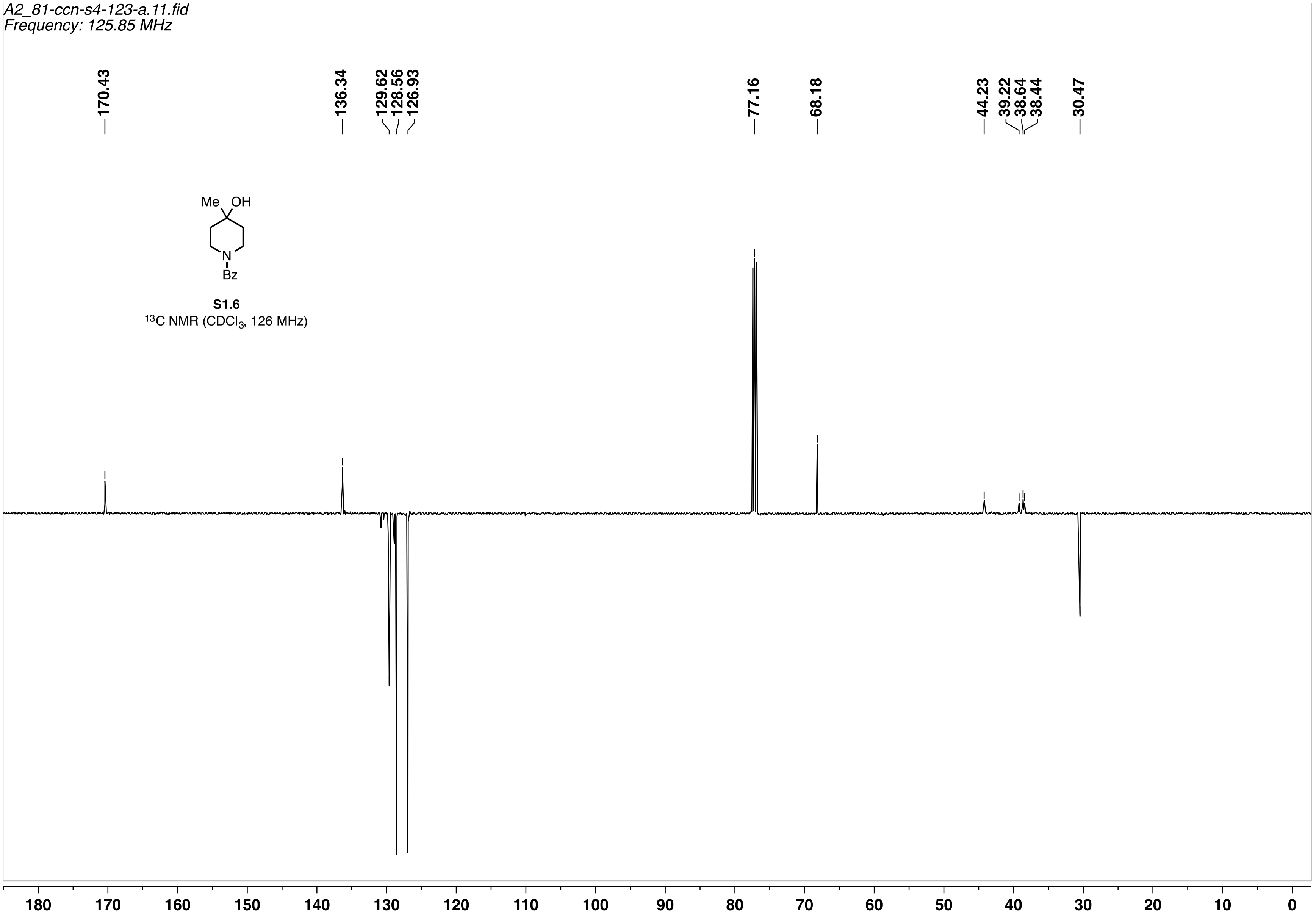
7.40
7.37
7.26
4.33
4.31
3.46
3.33
1.67
1.51
1.28
Me
OH
N
Bz
S1.6
¹H NMR (CDCl₃, 500 MHz)
6.20
1.00
3.93
3.93
3.55
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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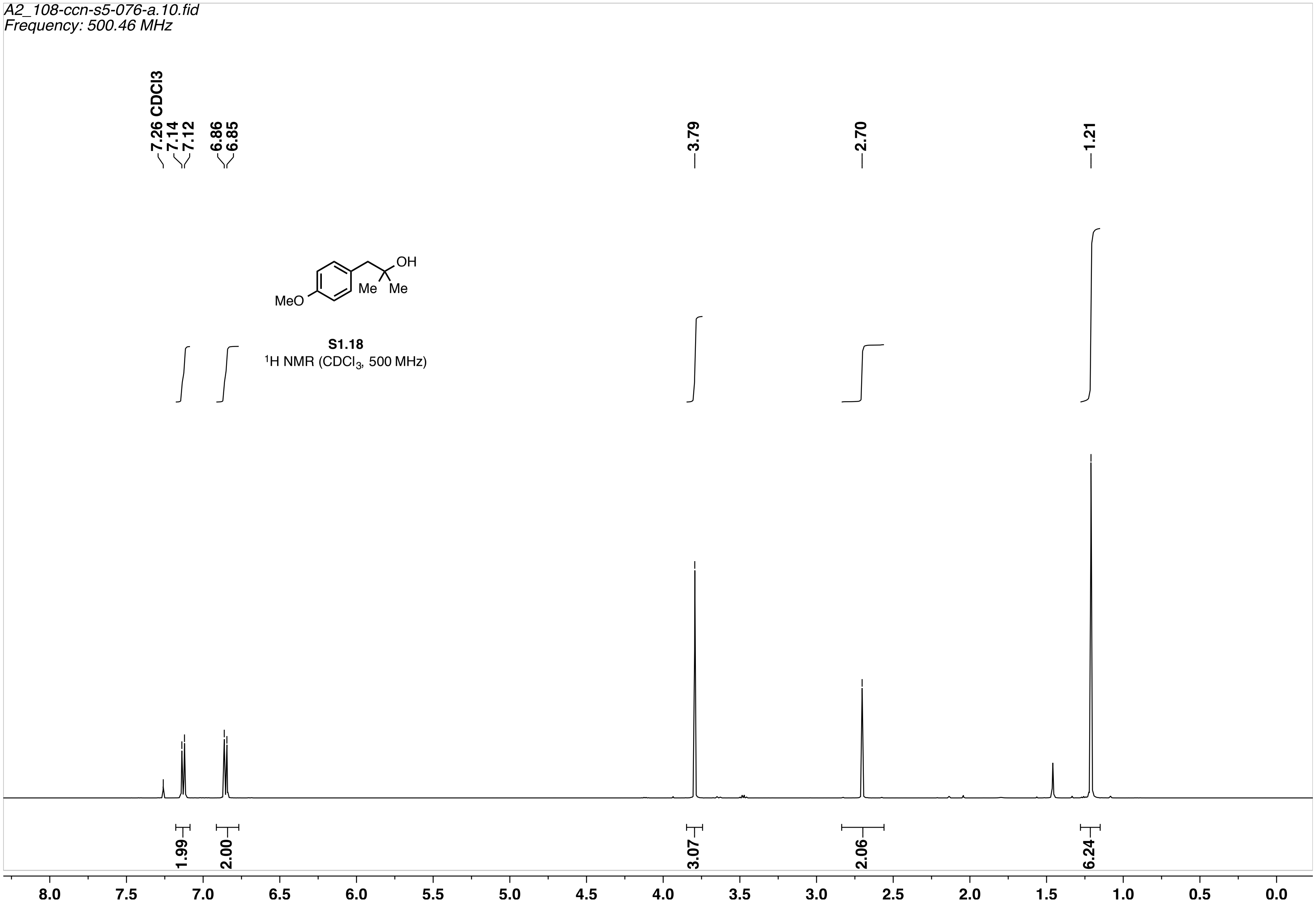
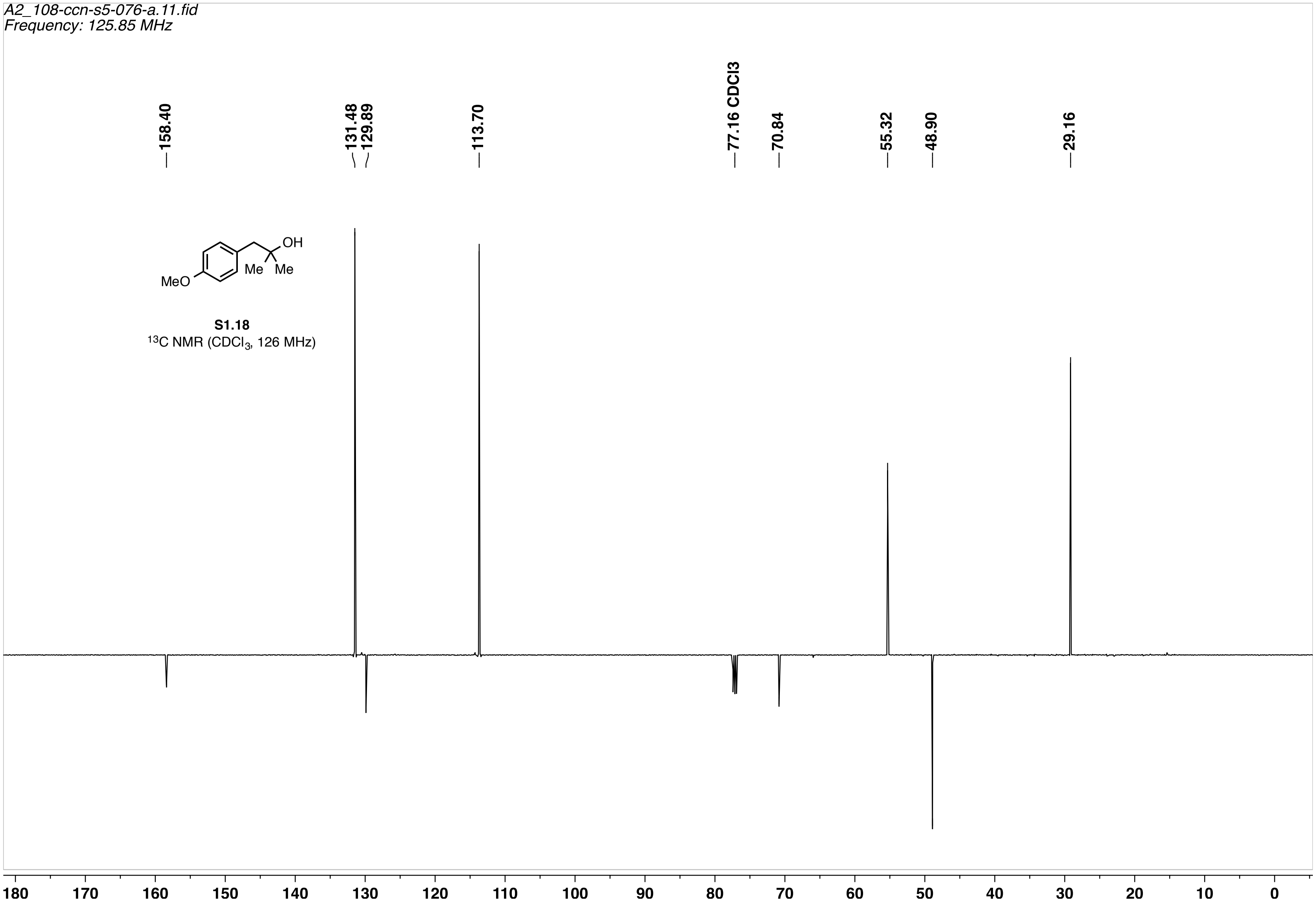
170.43
136.34
129.62
128.56
126.93
77.16
68.18
44.23
39.22
38.64
38.44
30.47
Me
OH
N
Bz
S1.6
^{13}C NMR (CDCl$_3$, 126 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

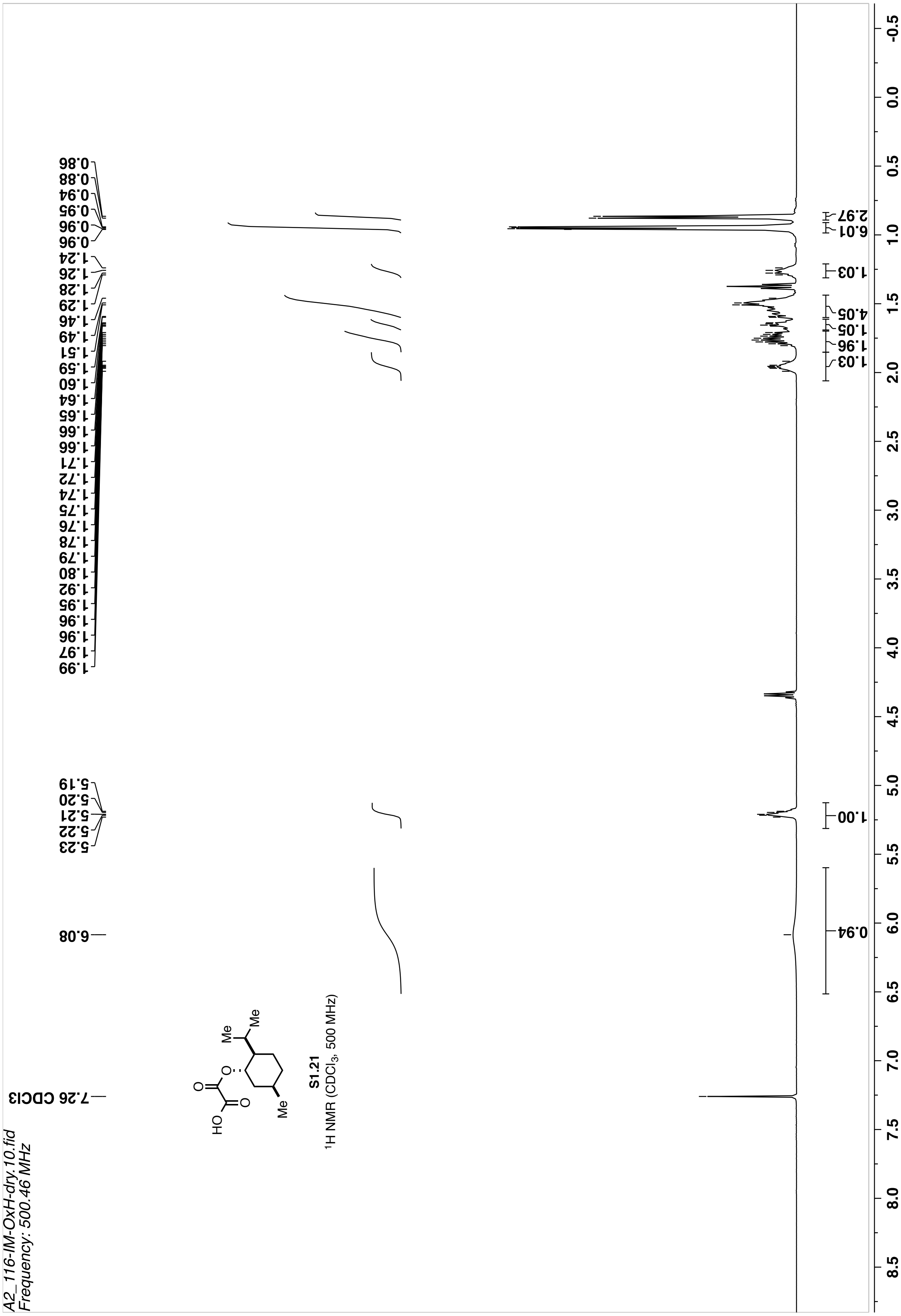


S1.18
^{1}H NMR ($CDCl_3$, 500 MHz)



S1.18

^{13}C NMR (CDCl$_3$, 126 MHz)



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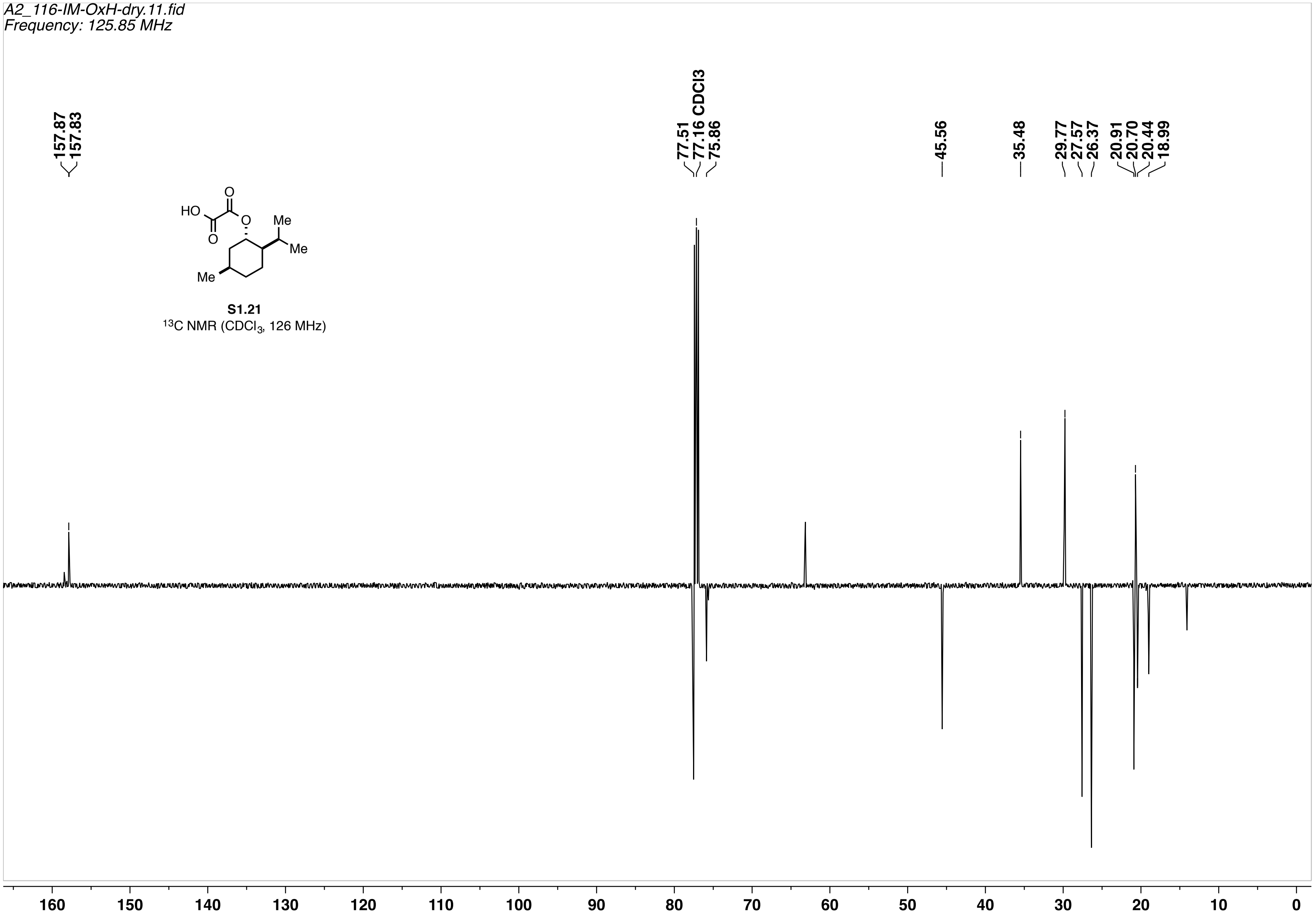
^{1}H NMR (CDCl$_3$, 500 MHz)

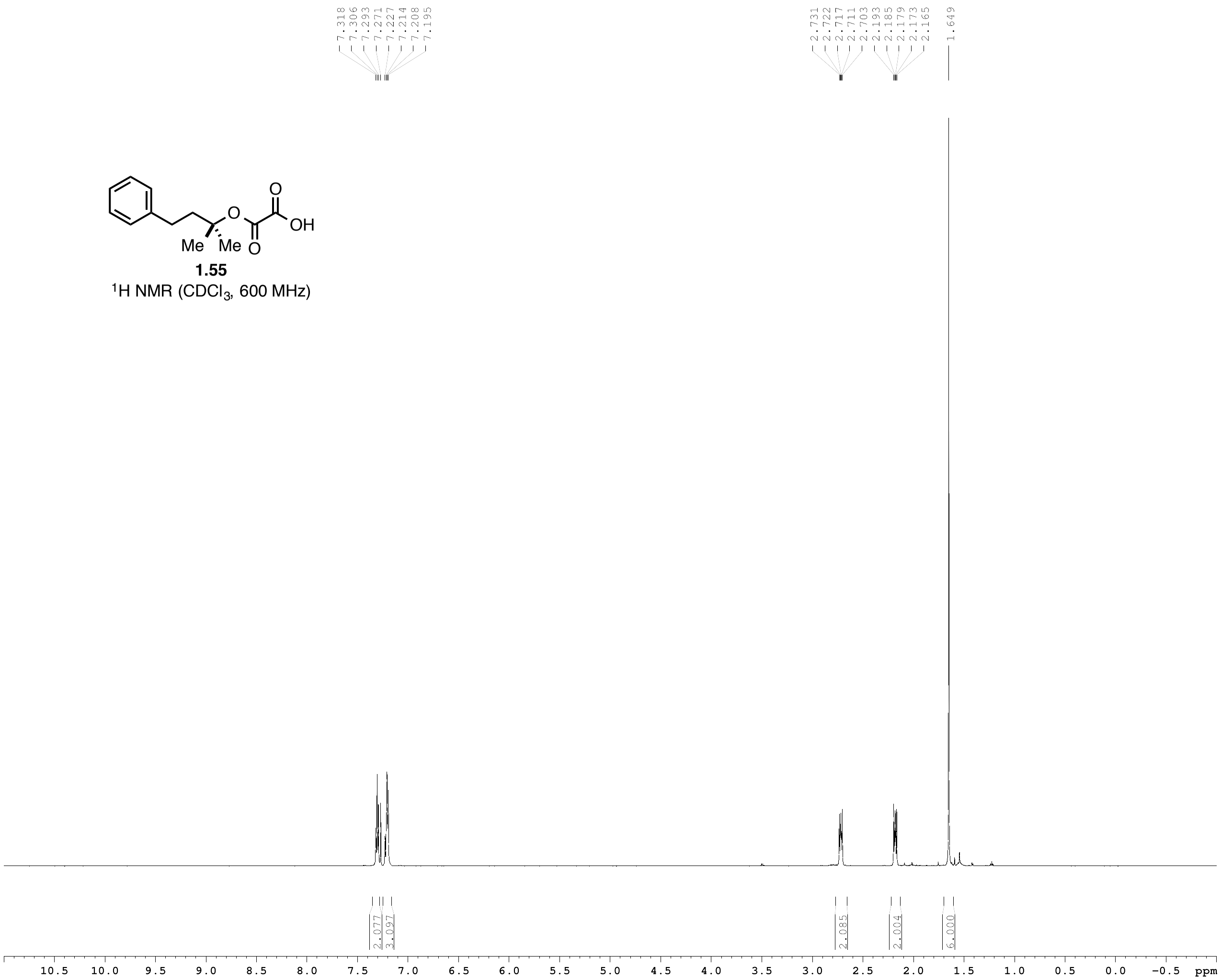


S1.21
^{13}C NMR (CDCl$_3$, 126 MHz)

YS-II-149

1.55

^{1}H NMR (CDCl$_3$, 600 MHz)



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TD                19228
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DS                    2
SWH            9615.385 Hz
FIDRES         0.500072 Hz
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RG                  724
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DE                14.54 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

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NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

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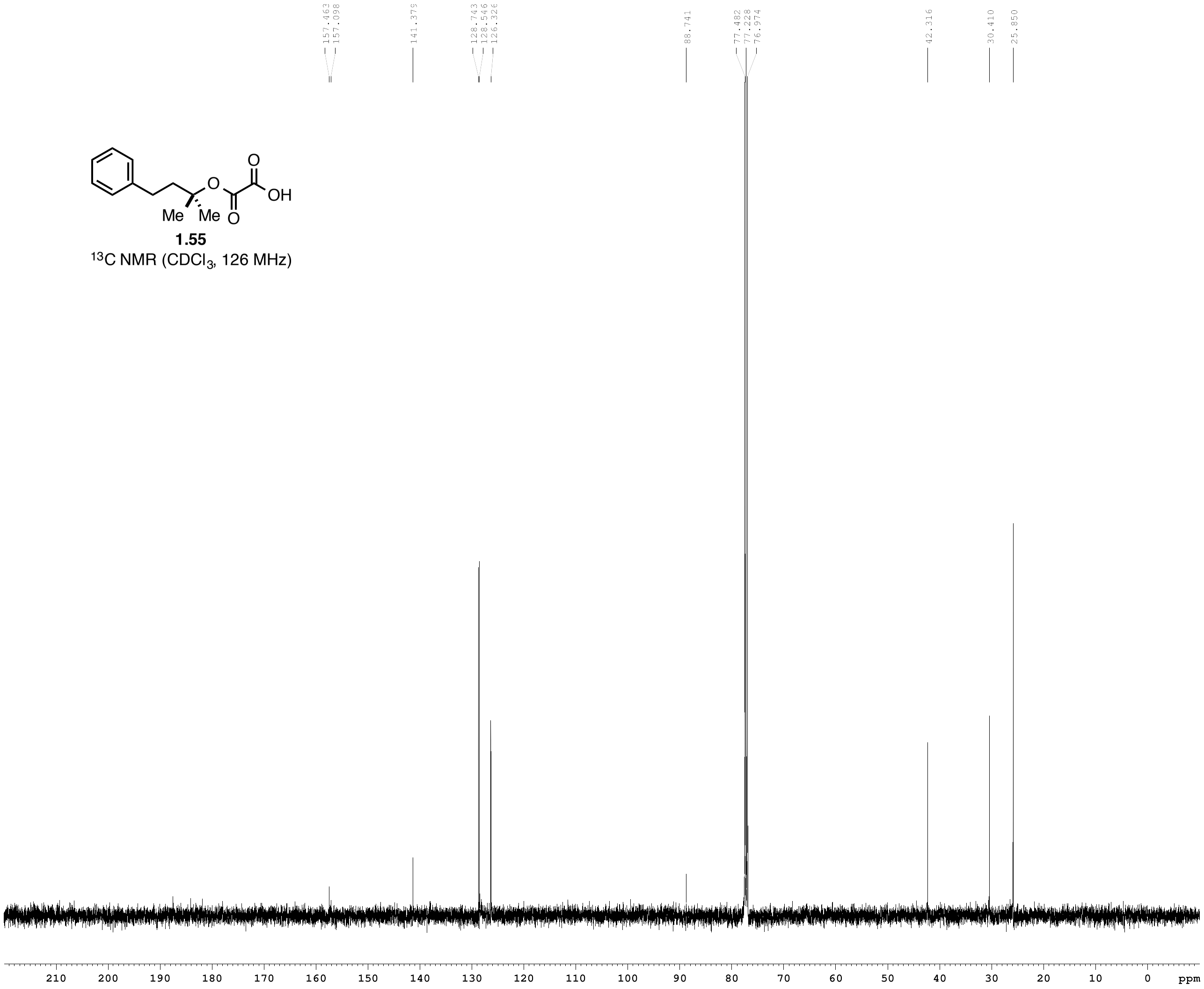
YS-II-152



1.55

^{13}C NMR (CDCl$_3$, 126 MHz)

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PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  552
DS                   16
SWH           30303.031 Hz
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AQ            1.0813440 sec
RG              14596.5
DW               16.500 usec
DE                 6.00 usec
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d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
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MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
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SPNAM[2]    Crp60comp.4
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SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

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GPNAM[2]       SINE.100
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GPX2     0 %
GPY1     0 %
GPY2     0 %
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GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

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WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
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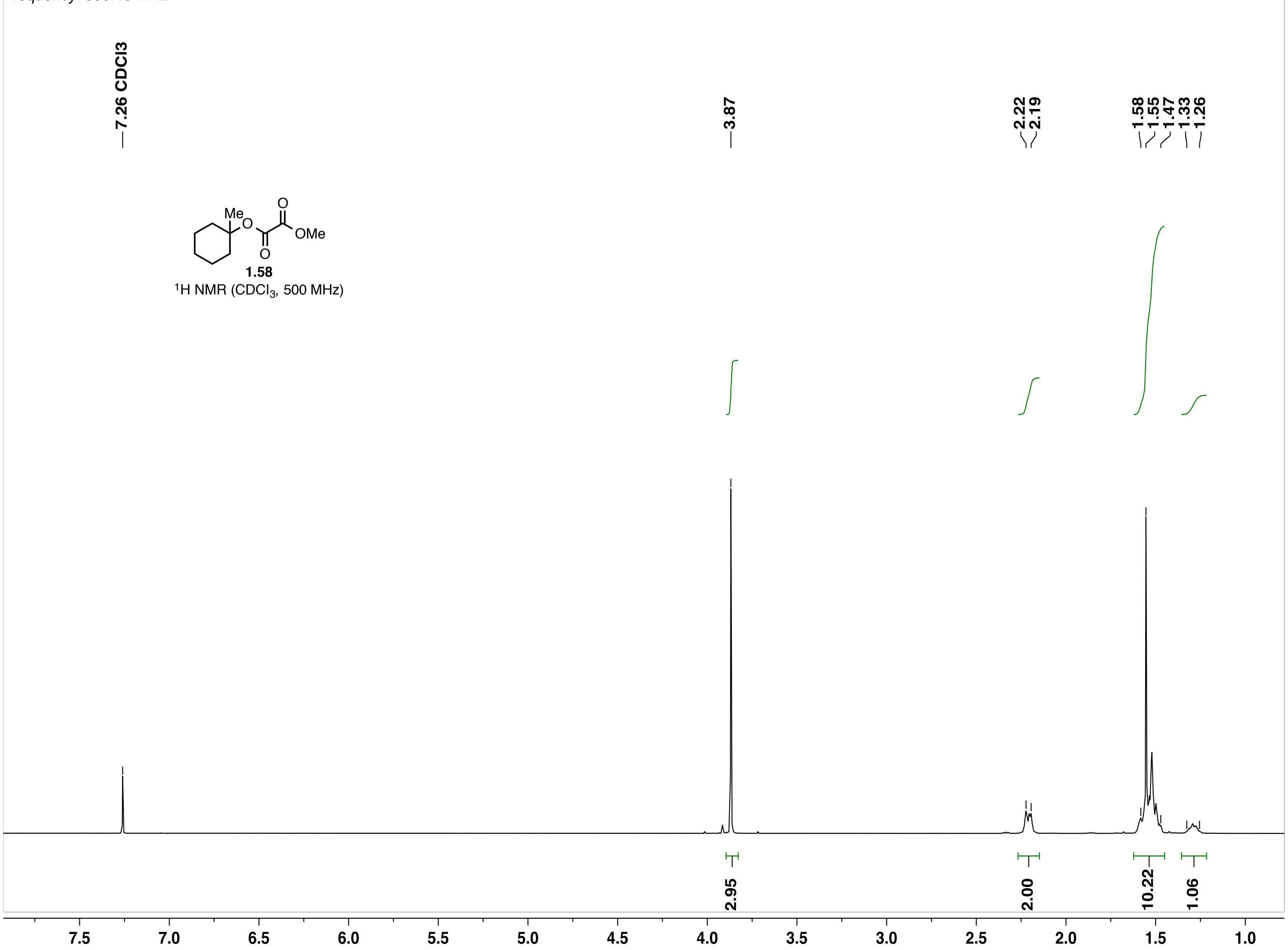
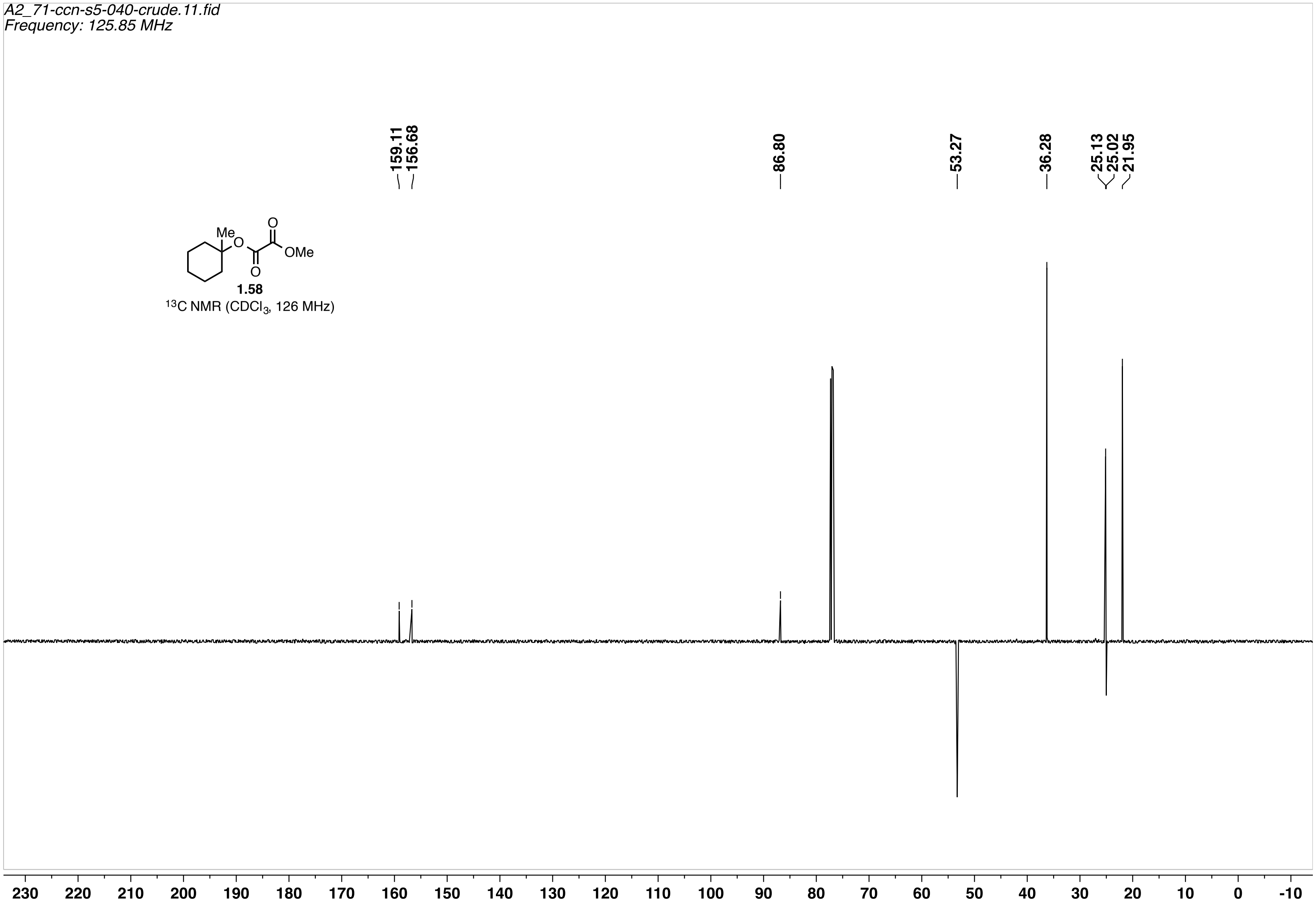


1.58

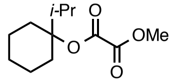
^{1}H NMR (CDCl$_3$, 500 MHz)



1.58

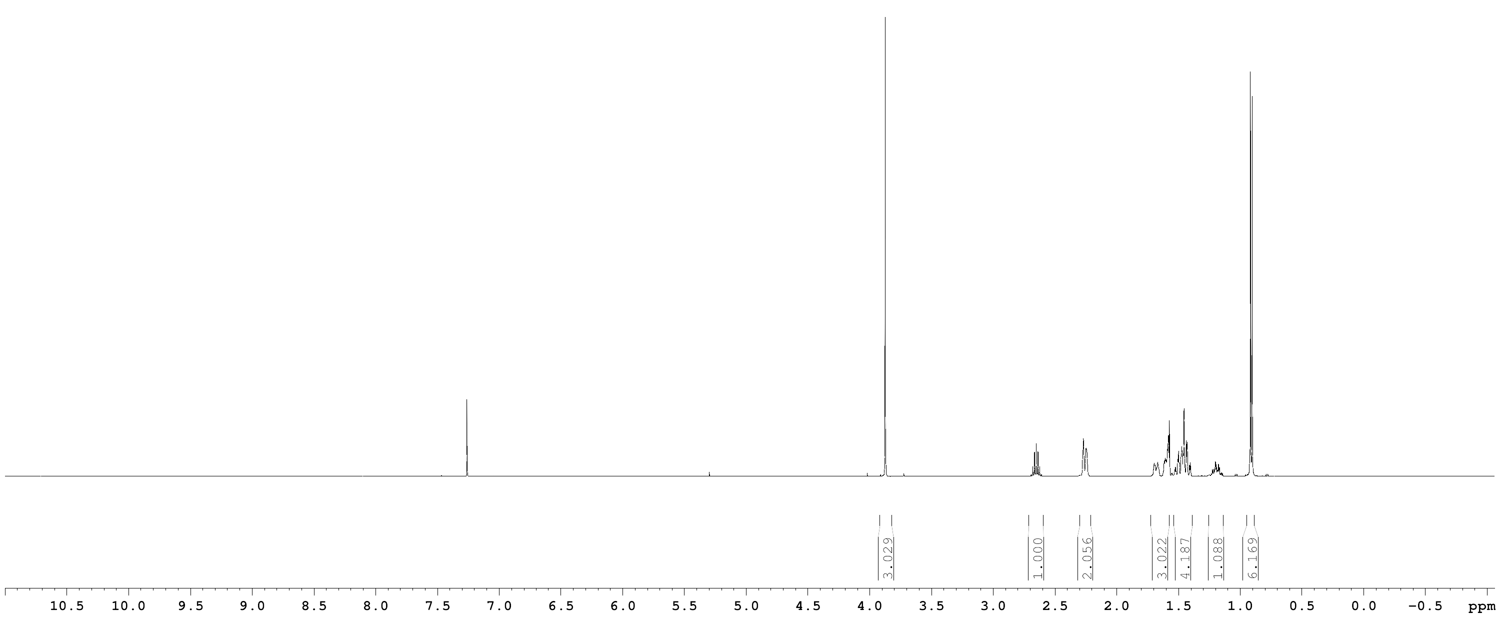
^{13}C NMR (CDCl$_3$, 126 MHz)

1H spectrum



S1.1

^{1}H NMR ($CDCl_3$, 500 MHz)



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DS                     2
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FIDRES          0.166677 Hz
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RG                   5.7
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MCWRK         0.01500000 sec

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F2 - Processing parameters
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GB       0
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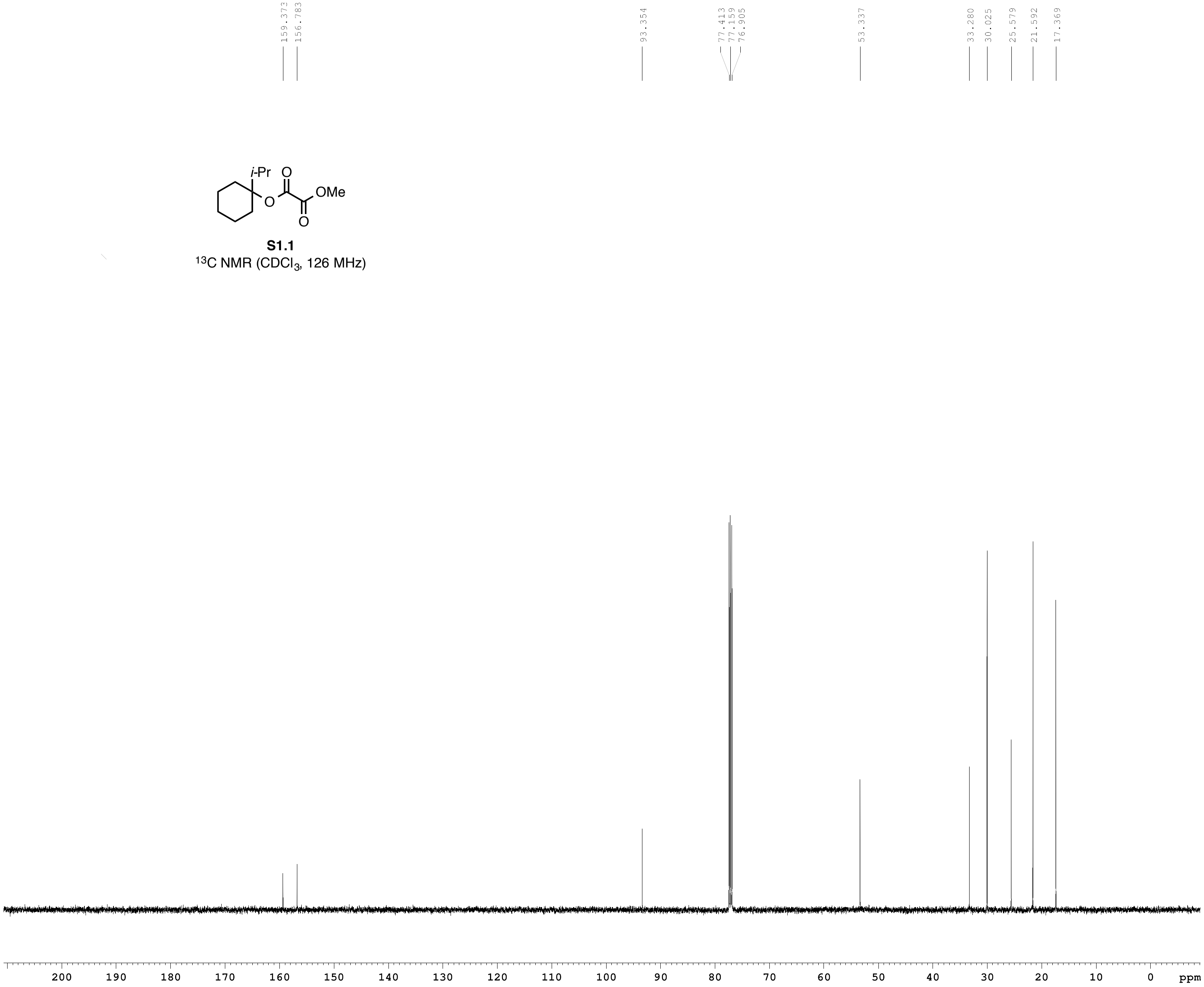
```

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



S1.1

^{13}C NMR (CDCl$_3$, 126 MHz)

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FIDRES         0.462388 Hz
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RG               5792.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
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PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

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GPNAM[2]       SINE.100
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GPX2      0 %
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GPY2      0 %
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GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
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WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum

S1.2

^{1}H NMR (CDCl$_3$, 500 MHz)

```
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PROCNO                1

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DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
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P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
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SF          500.2200311 MHz
WDW                  no
SSB      0
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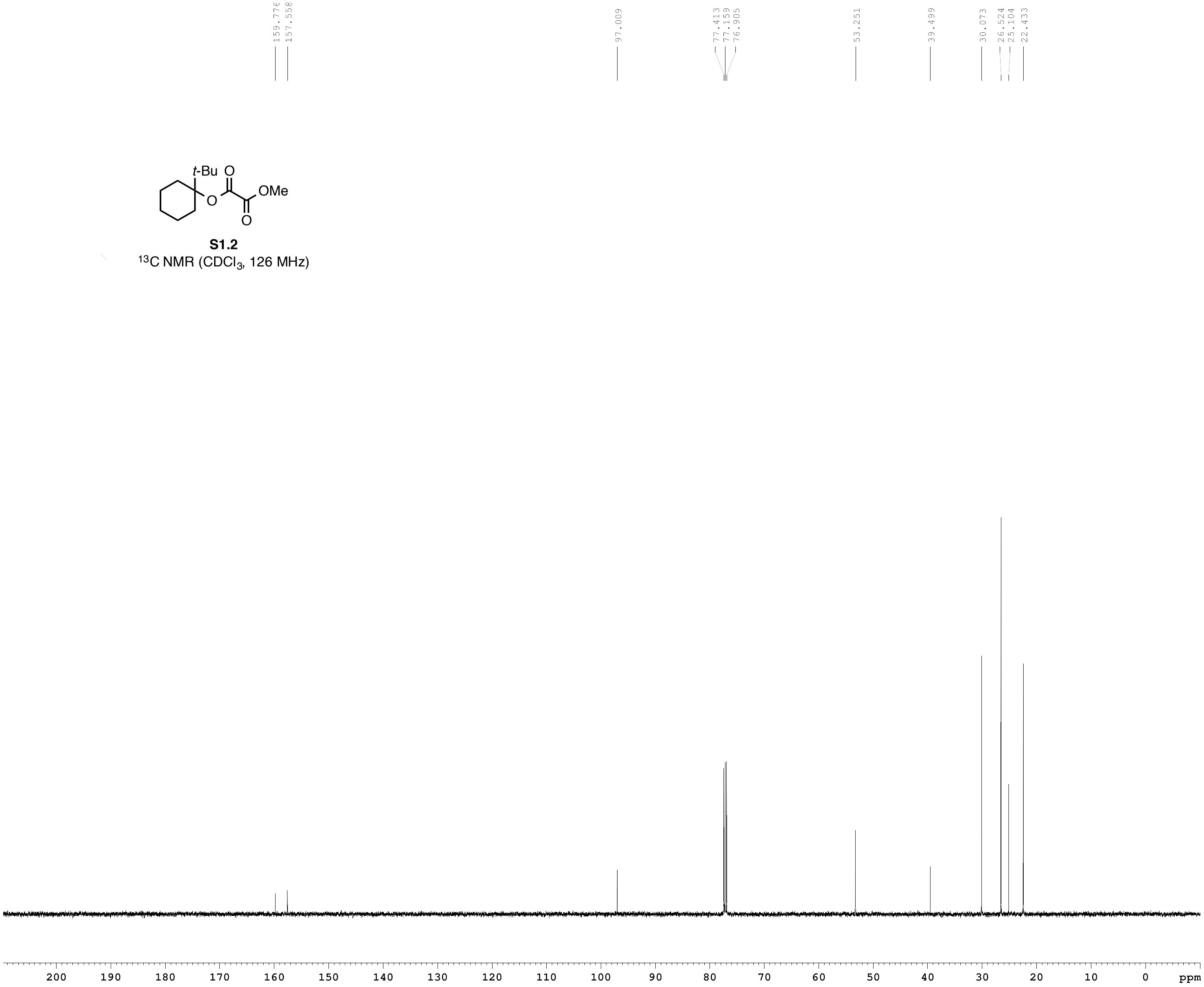
Z-restored spin-echo 13C spectrum with 1H decoupling

S1.2

^{13}C NMR (CDCl$_3$, 126 MHz)



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PROCNO                1

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TD                65536
SOLVENT           CDCl3
NS                   72
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1         1.00000000 sec
d11        0.03000000 sec
D16        0.00020000 sec
d17        0.00019600 sec
MCREST   0 sec
MCWRK      0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
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GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
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SSB      0
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PC                 2.00
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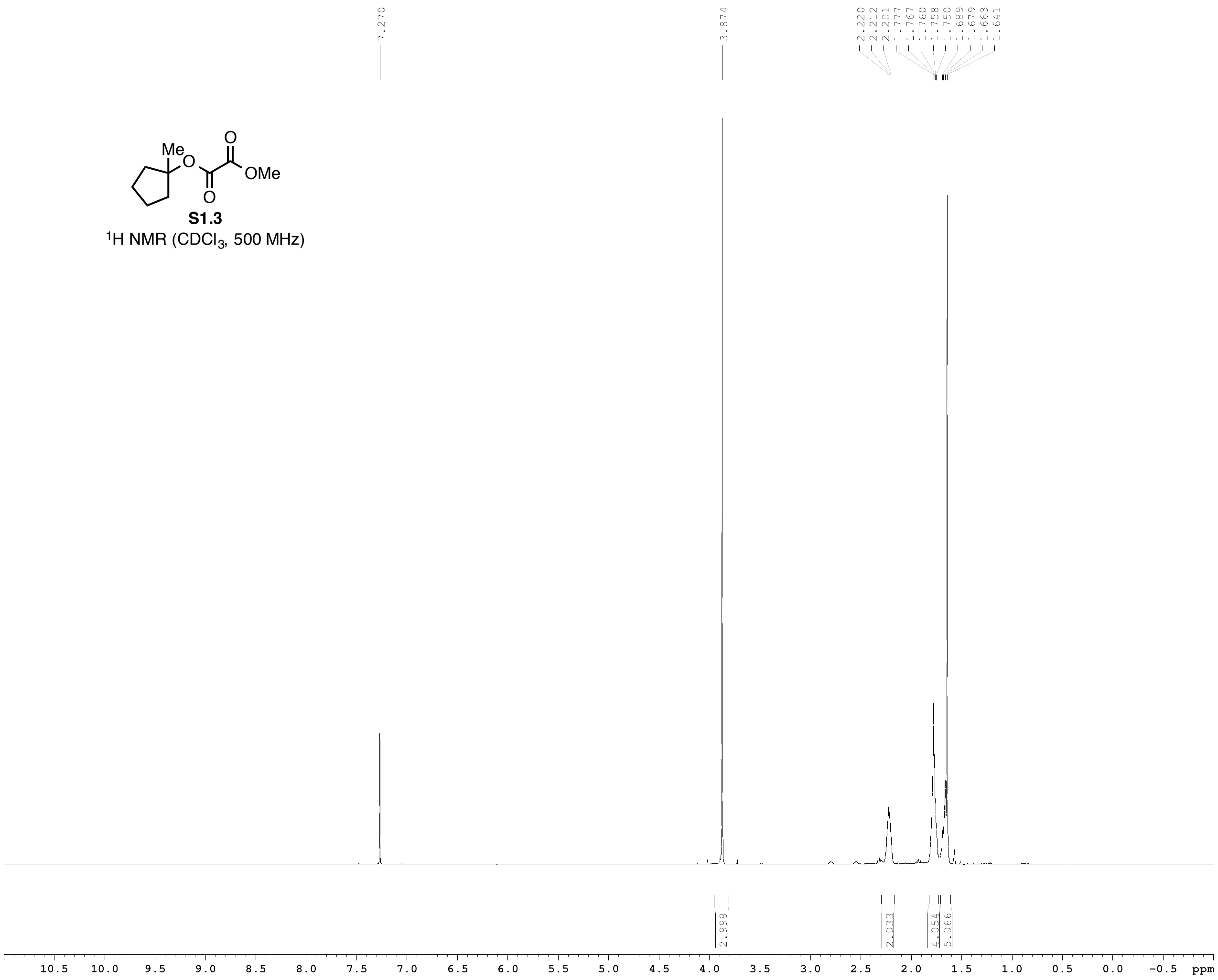
YS-II-240



S1.3

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
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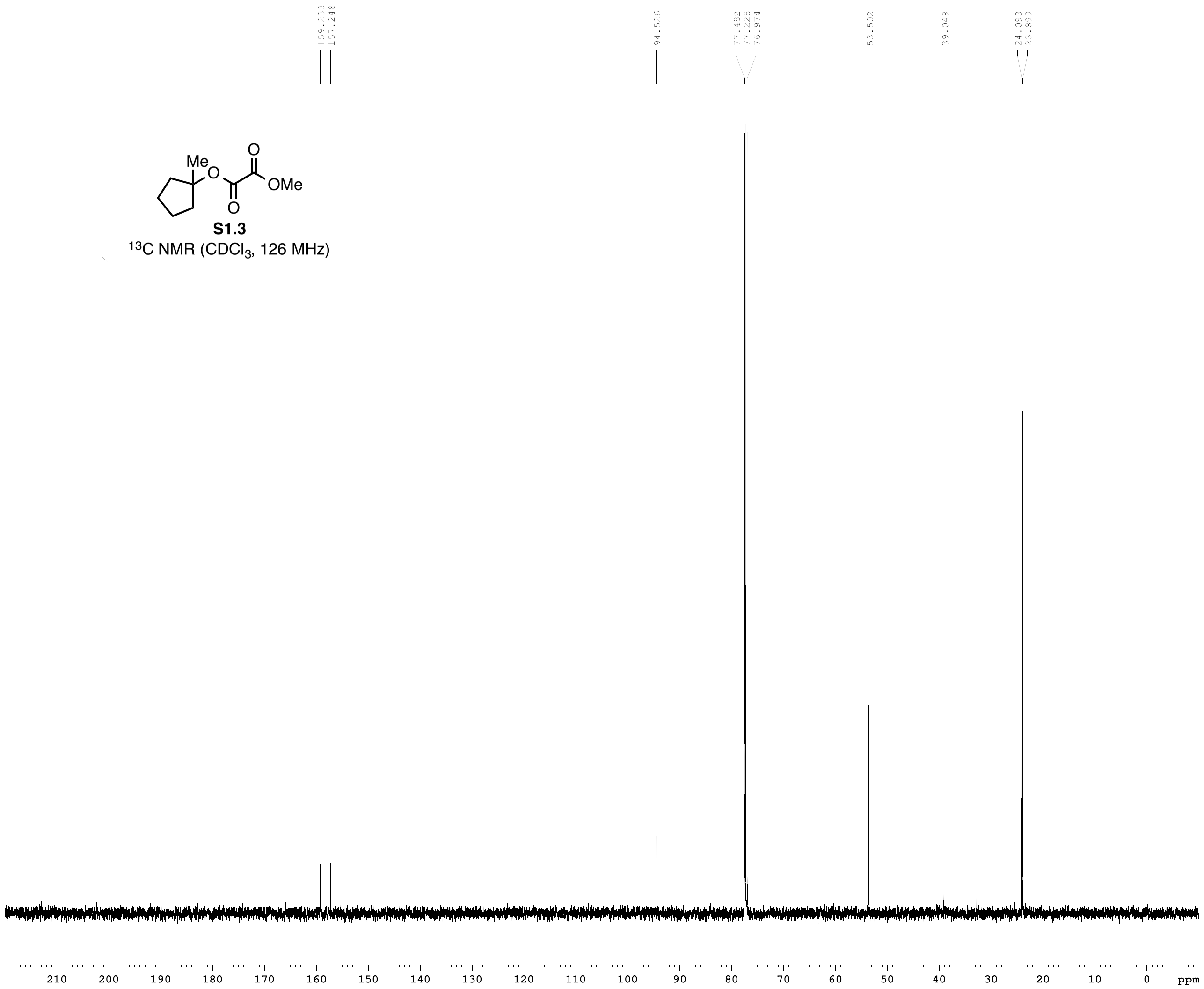
PROCNO                1

F2 - Acquisition Parameters
Date_          20150212
Time              10.09
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200258 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-240



S1.3

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-240
EXPNO                 3
PROCNO                1

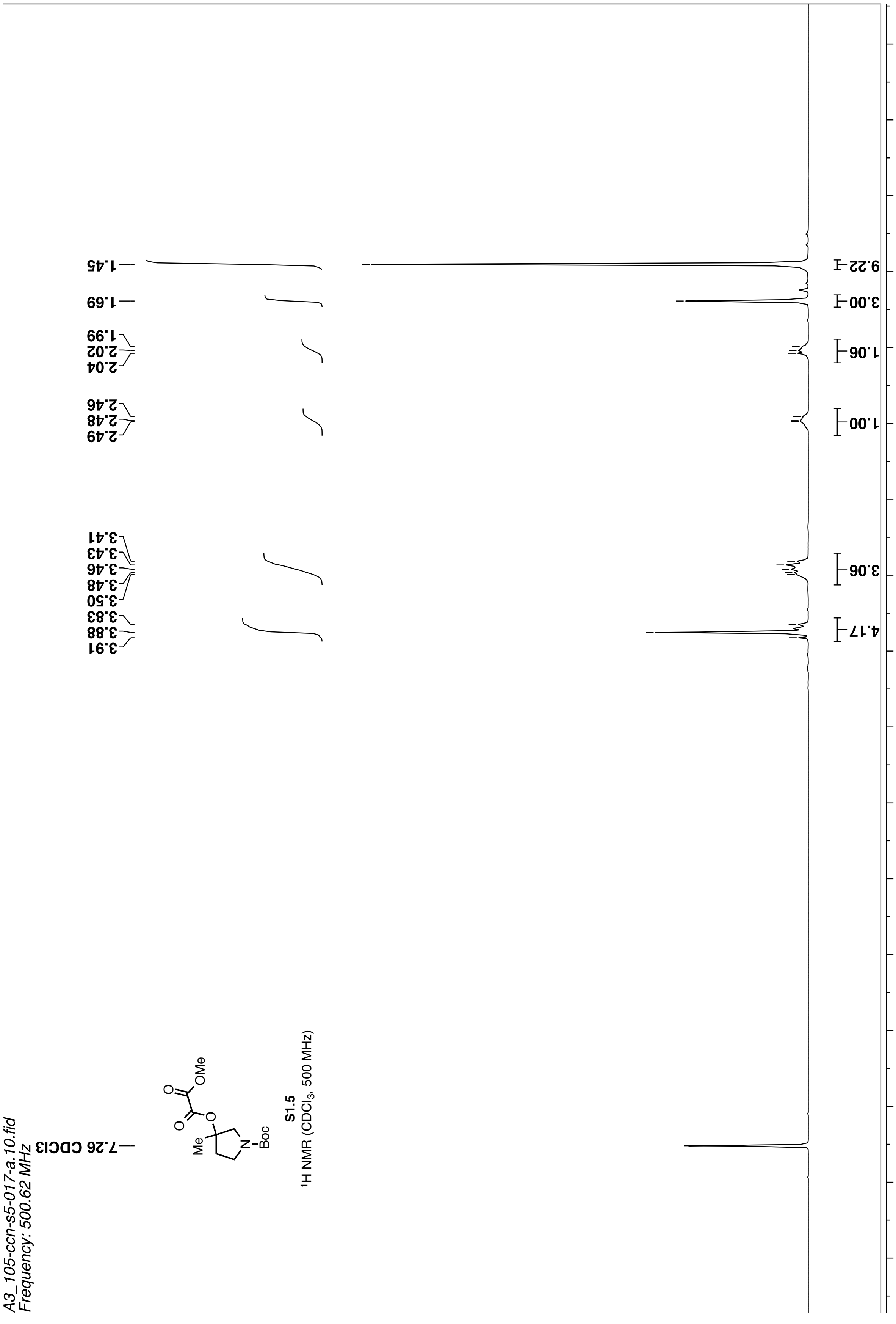
F2 - Acquisition Parameters
Date_          20150212
Time              10.13
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  312
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

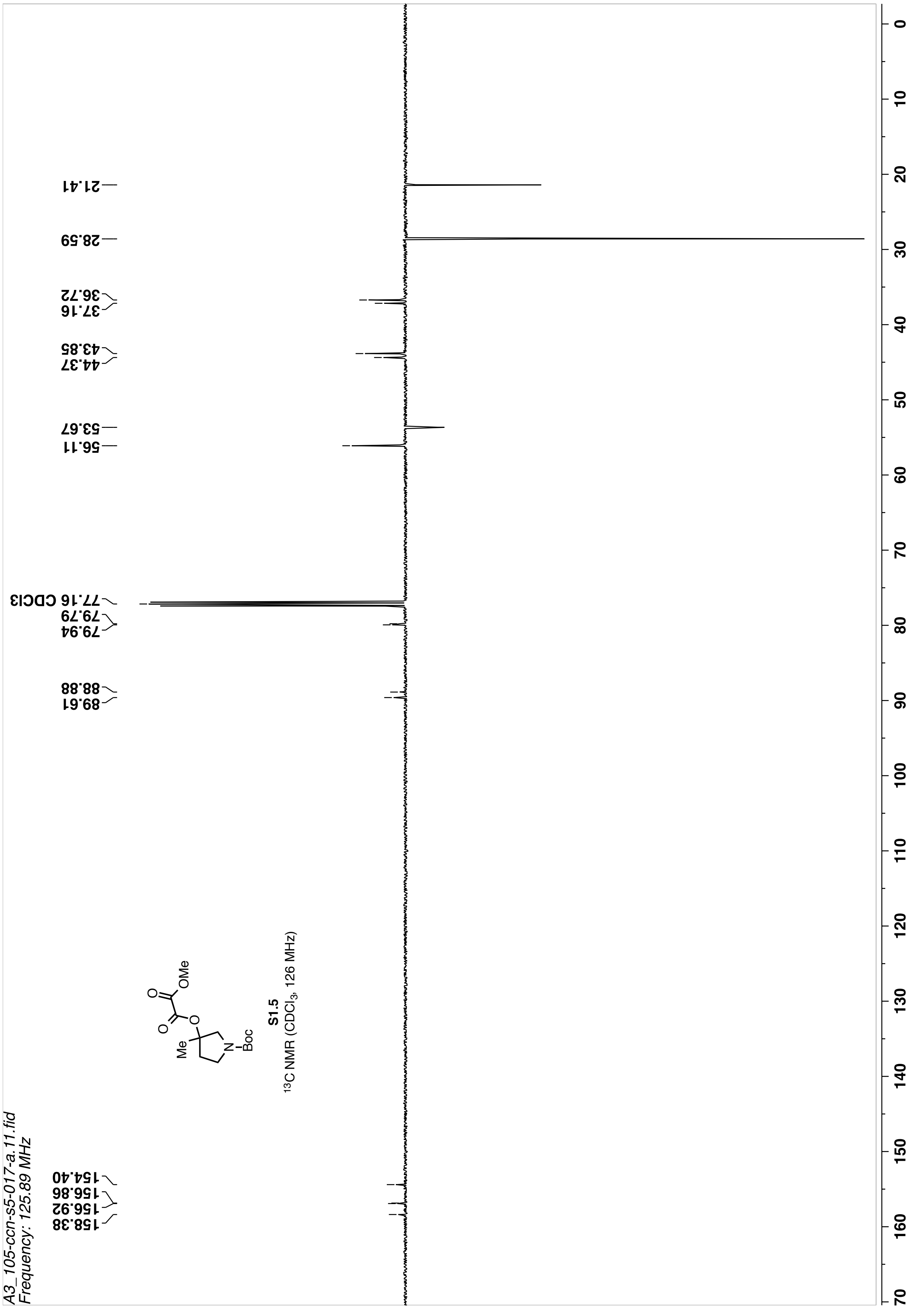
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803987 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



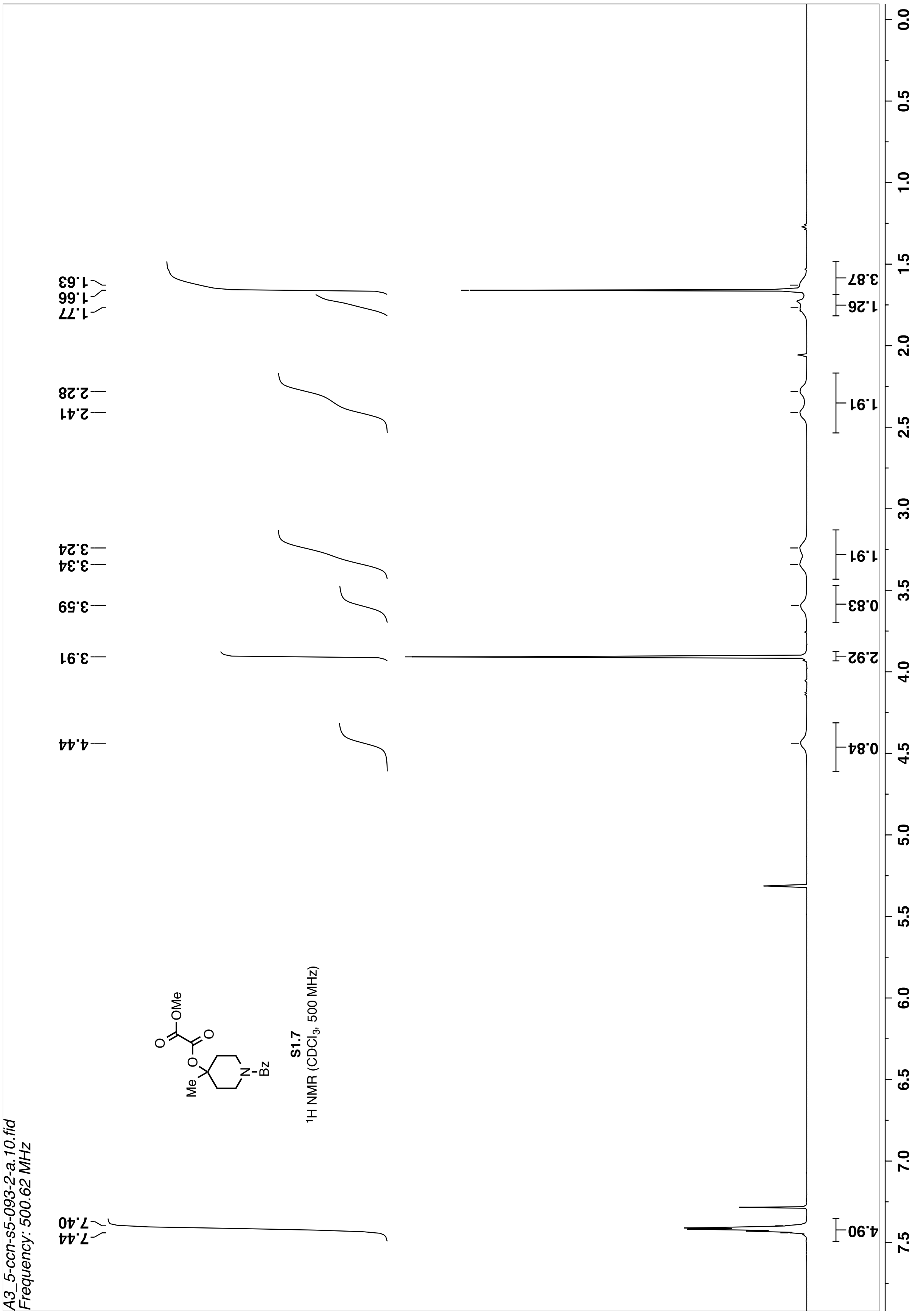
S1.5

^{1}H NMR (CDCl$_3$, 500 MHz)

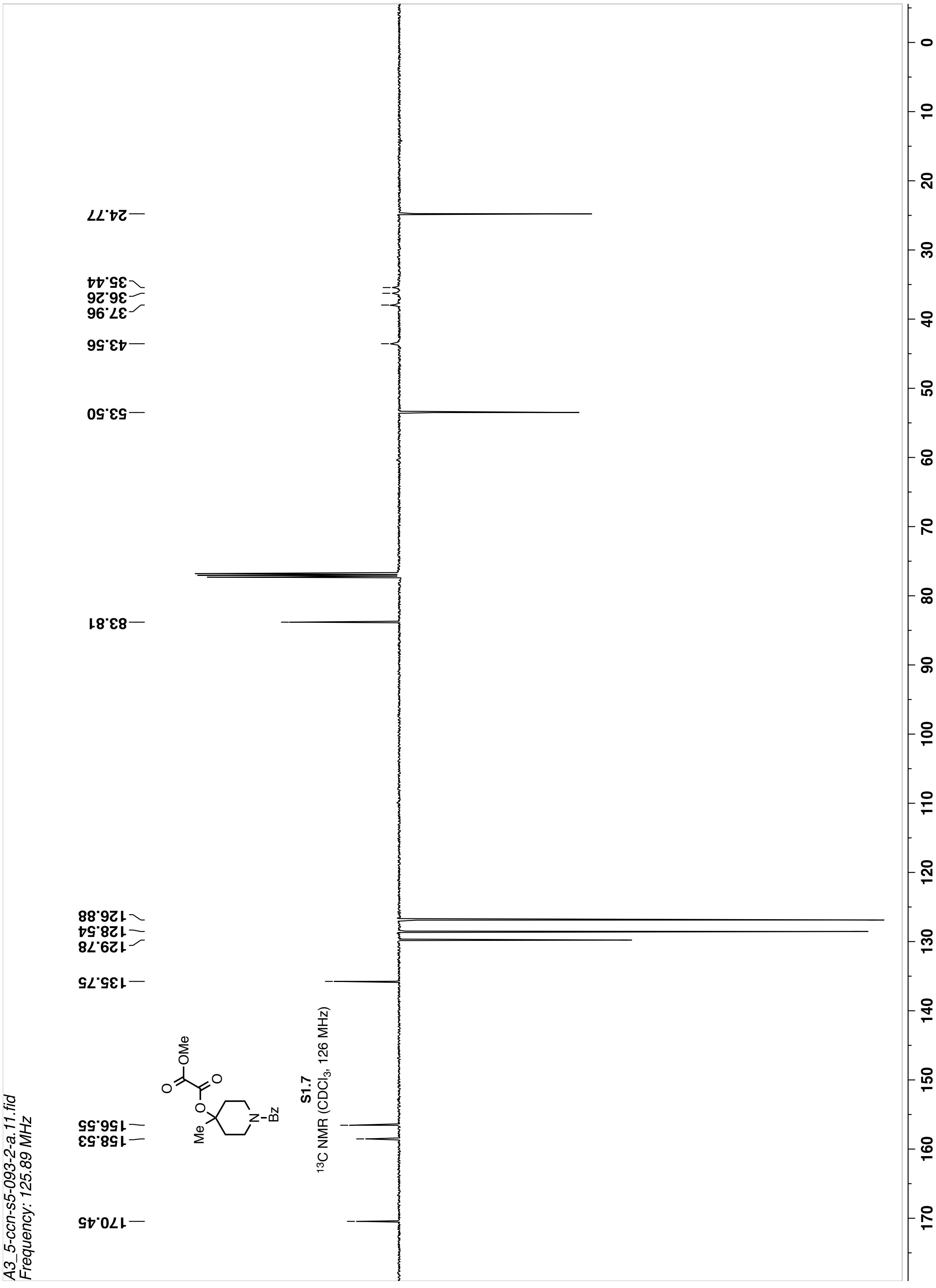


S1.5

^{13}C NMR (CDCl$_3$, 126 MHz)



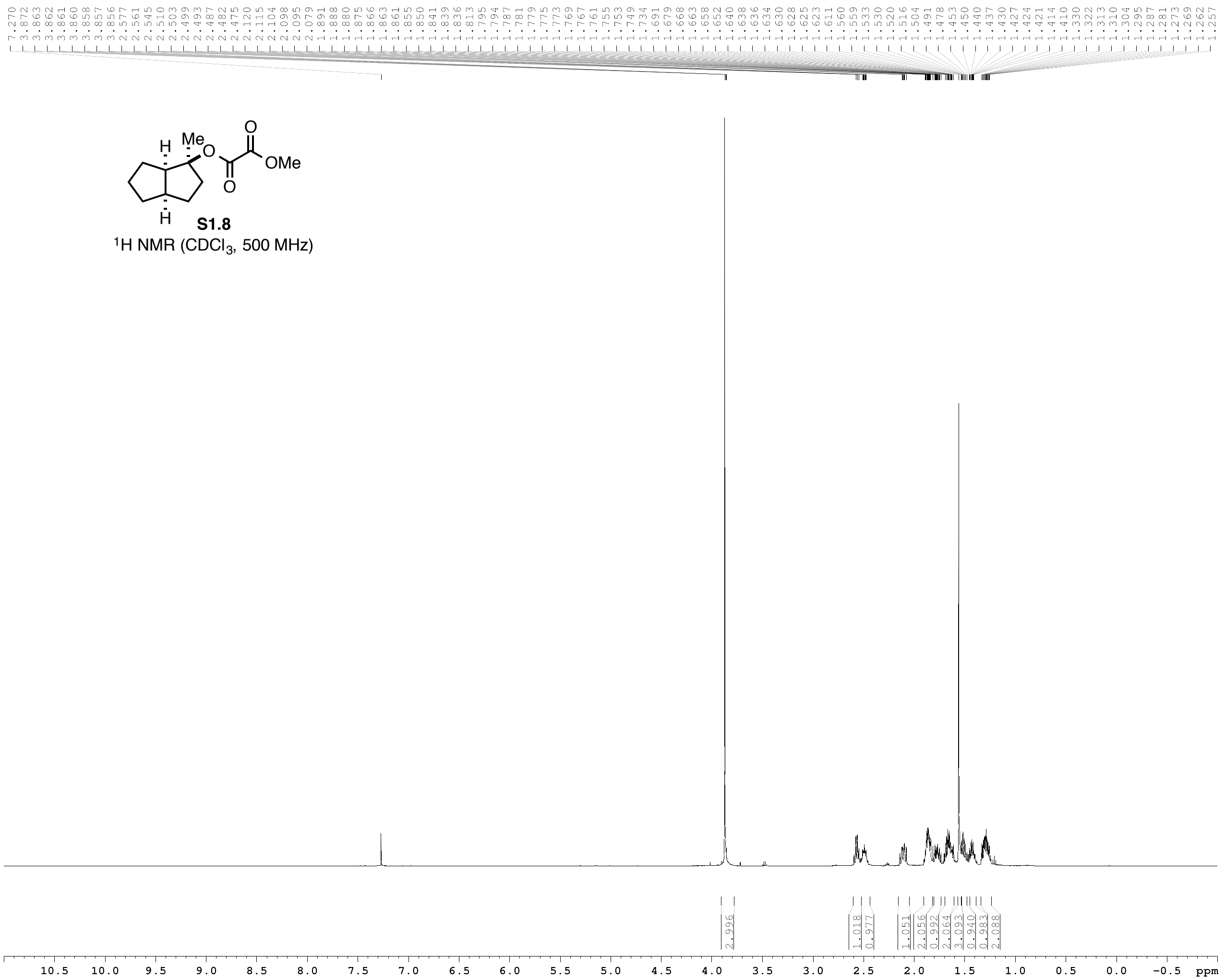
S1.7
^{1}H NMR (CDCl$_3$, 500 MHz)



S1.7

^{13}C NMR (CDCl$_3$, 126 MHz)

YS-II-286



S1.8

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME           YS-II-286
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150306
Time               17.55
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 32048
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                 101.6
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

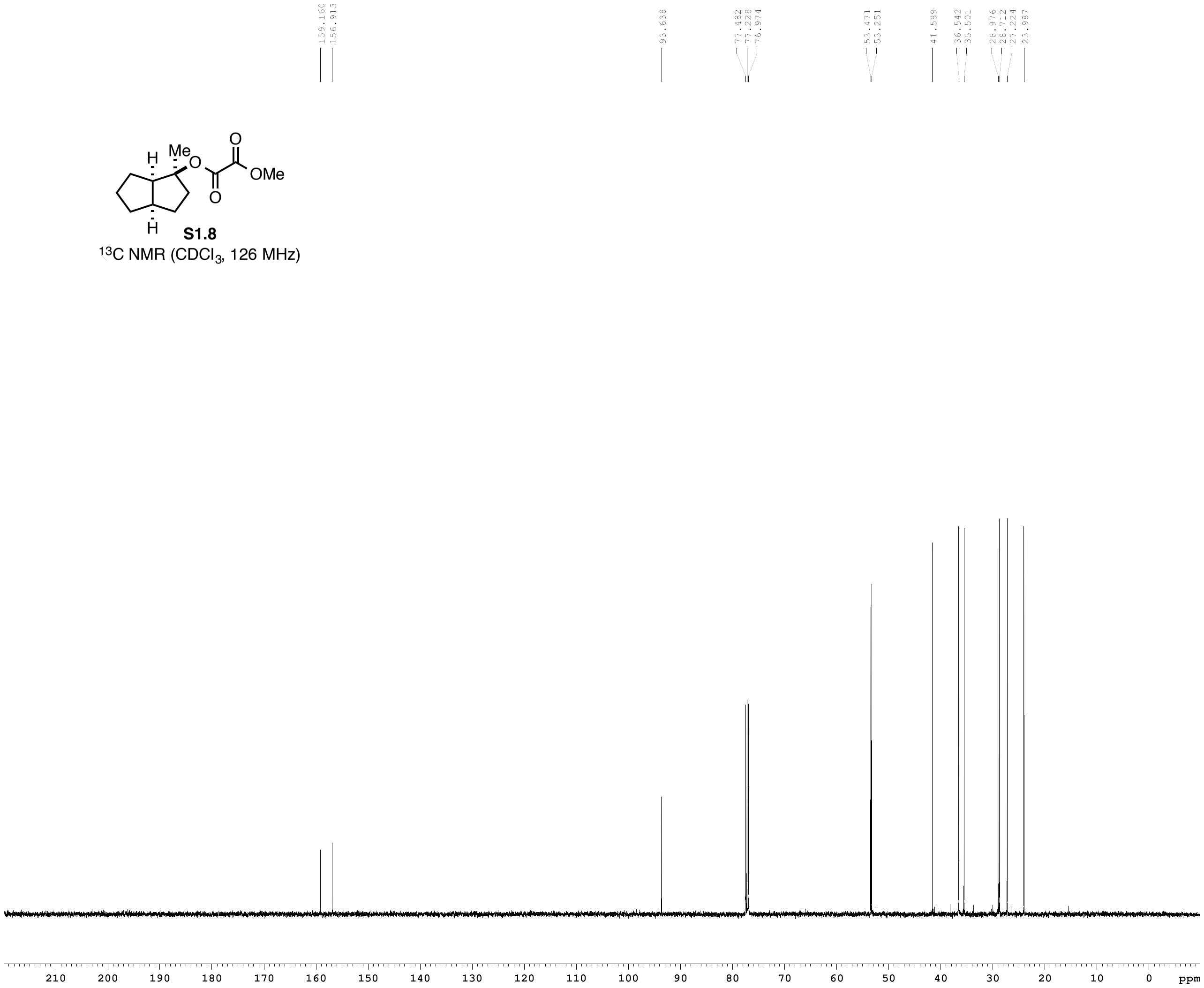
======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -5.80 dB
SFO1         499.1834943 MHz

F2 - Processing parameters
SI                 65536
SF           499.1800217 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-286

S1.8

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          YS-II-286
EXPNO                 3
PROCNO                1

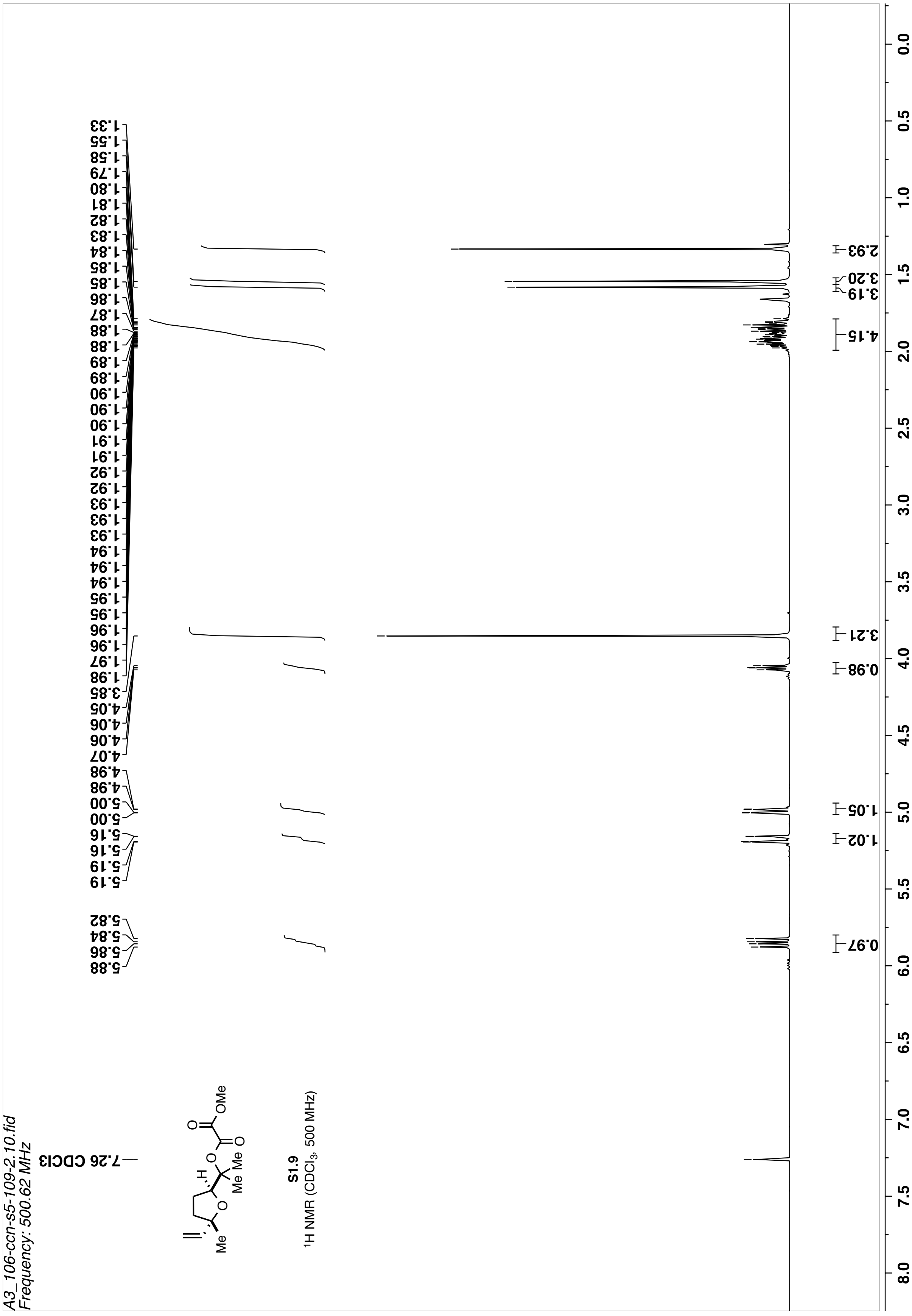
F2 - Acquisition Parameters
Date_          20150309
Time              10.51
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  144
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

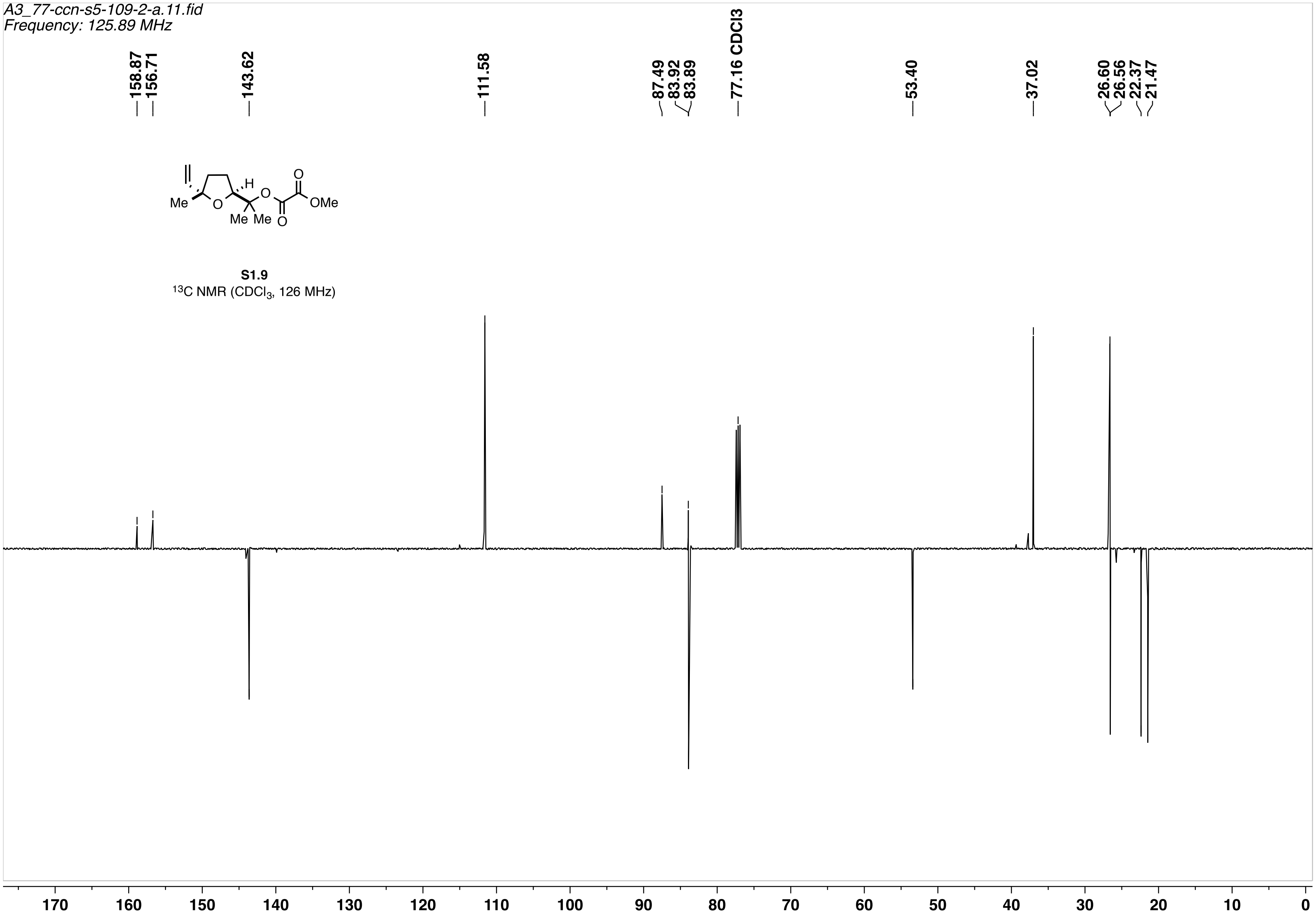
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803334 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



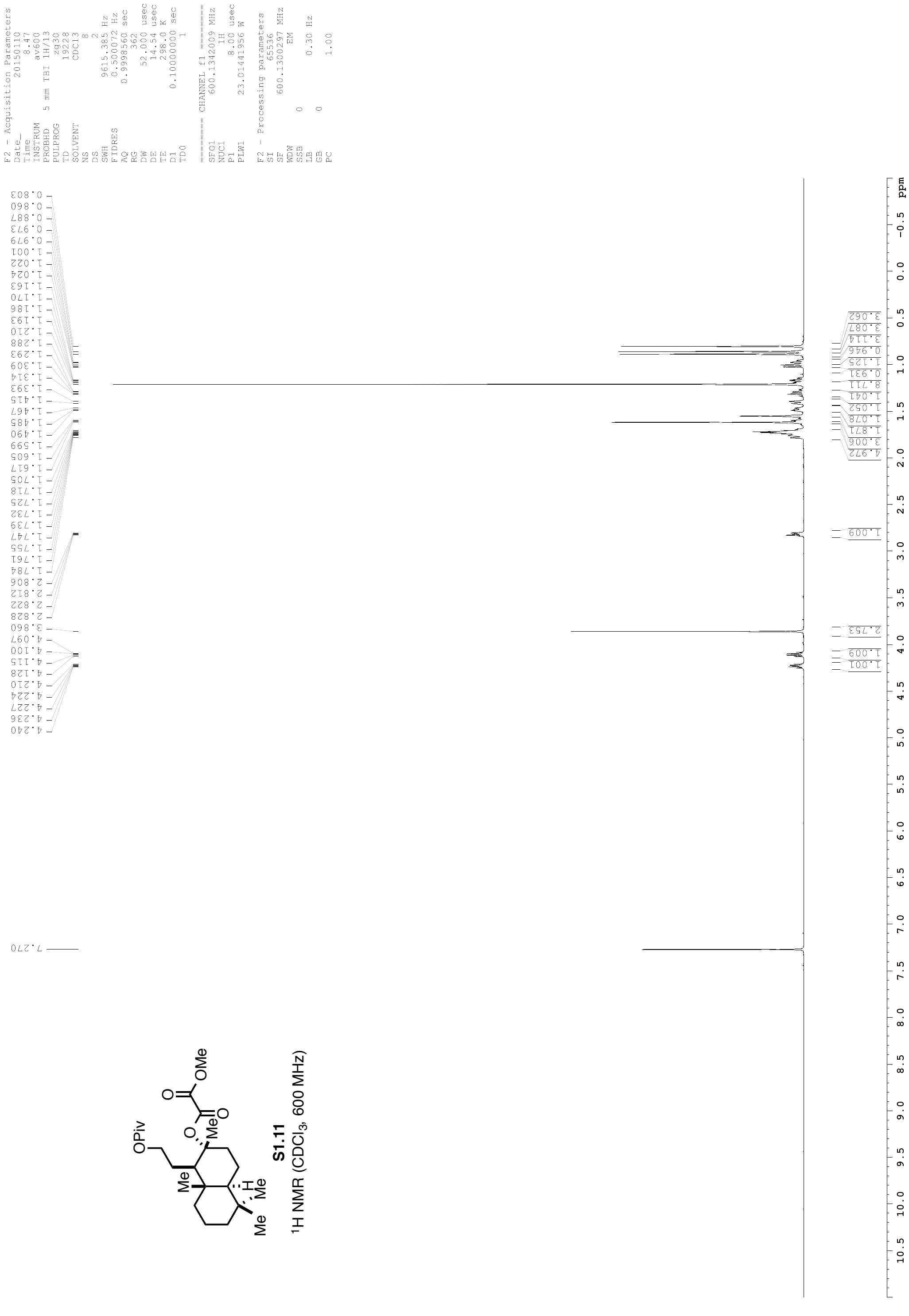
S1.9

^{1}H NMR (CDCl$_3$, 500 MHz)



S1.9
^{13}C NMR (CDCl$_3$, 126 MHz)

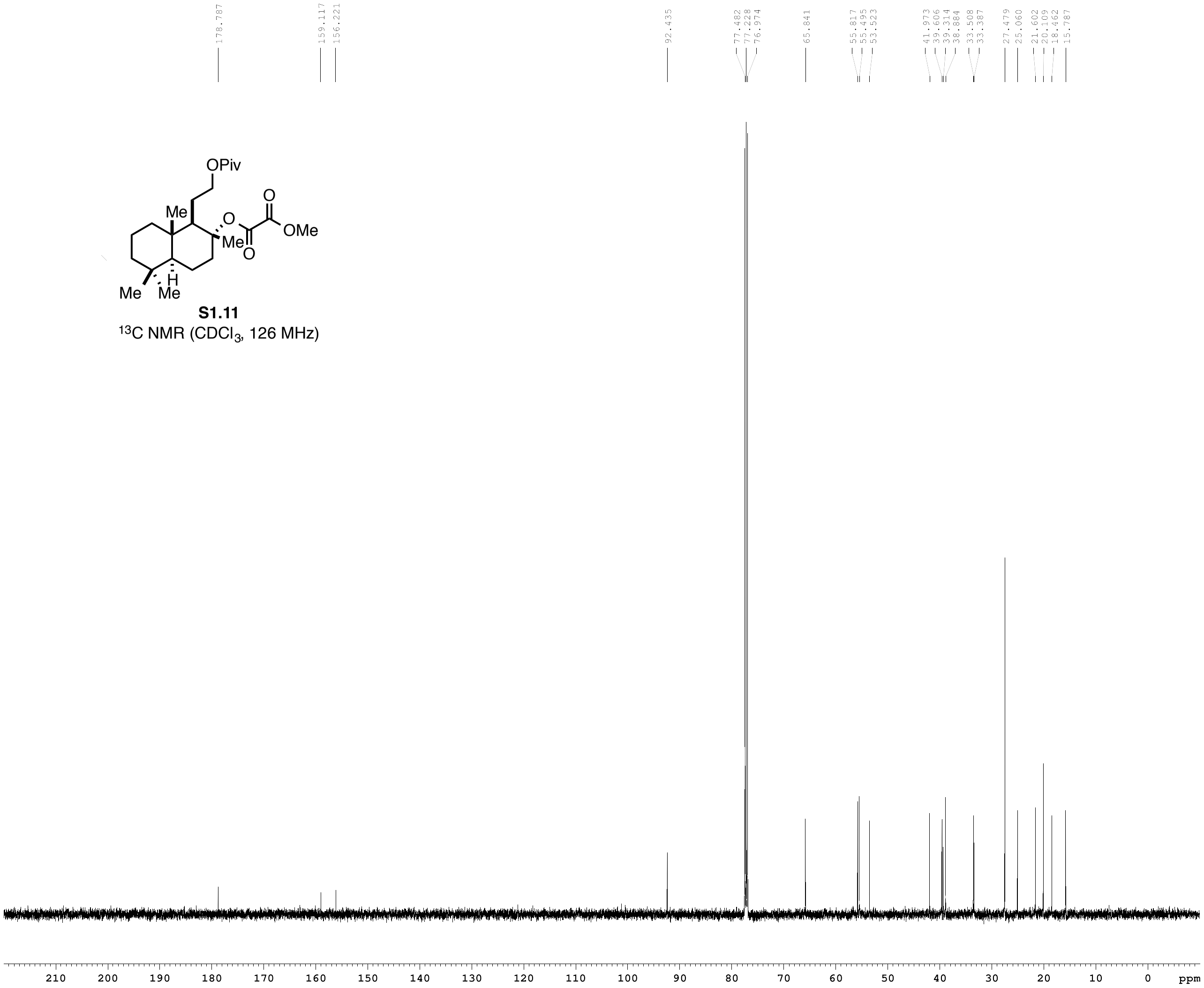
YS-II-169



S1.11

^{1}H NMR (CDCl$_3$, 600 MHz)

YS-II-169



S1.11

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME           YS-II-169
EXPNO                  2
PROCNO                 1

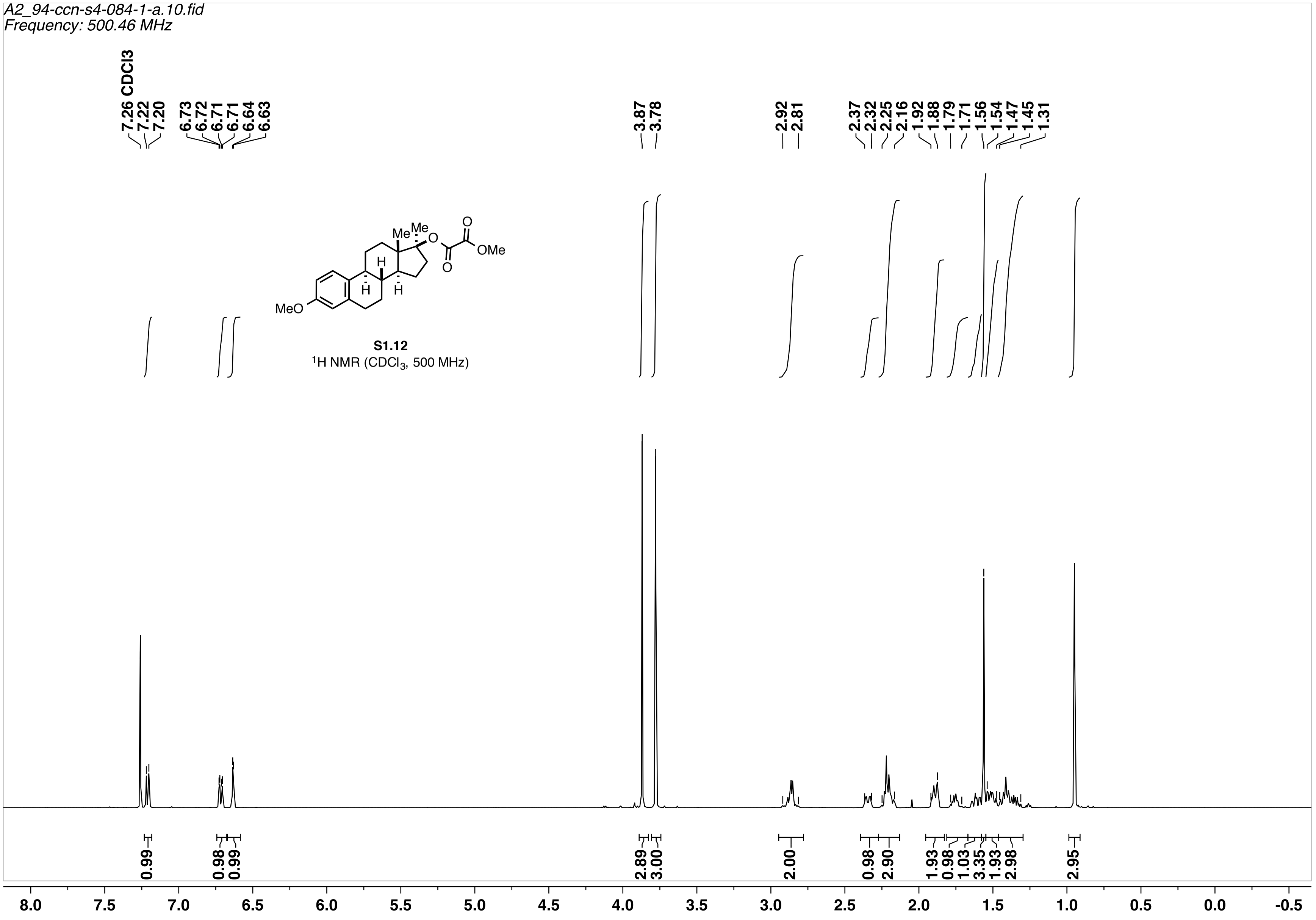
F2 - Acquisition Parameters
Date_           20150110
Time                9.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

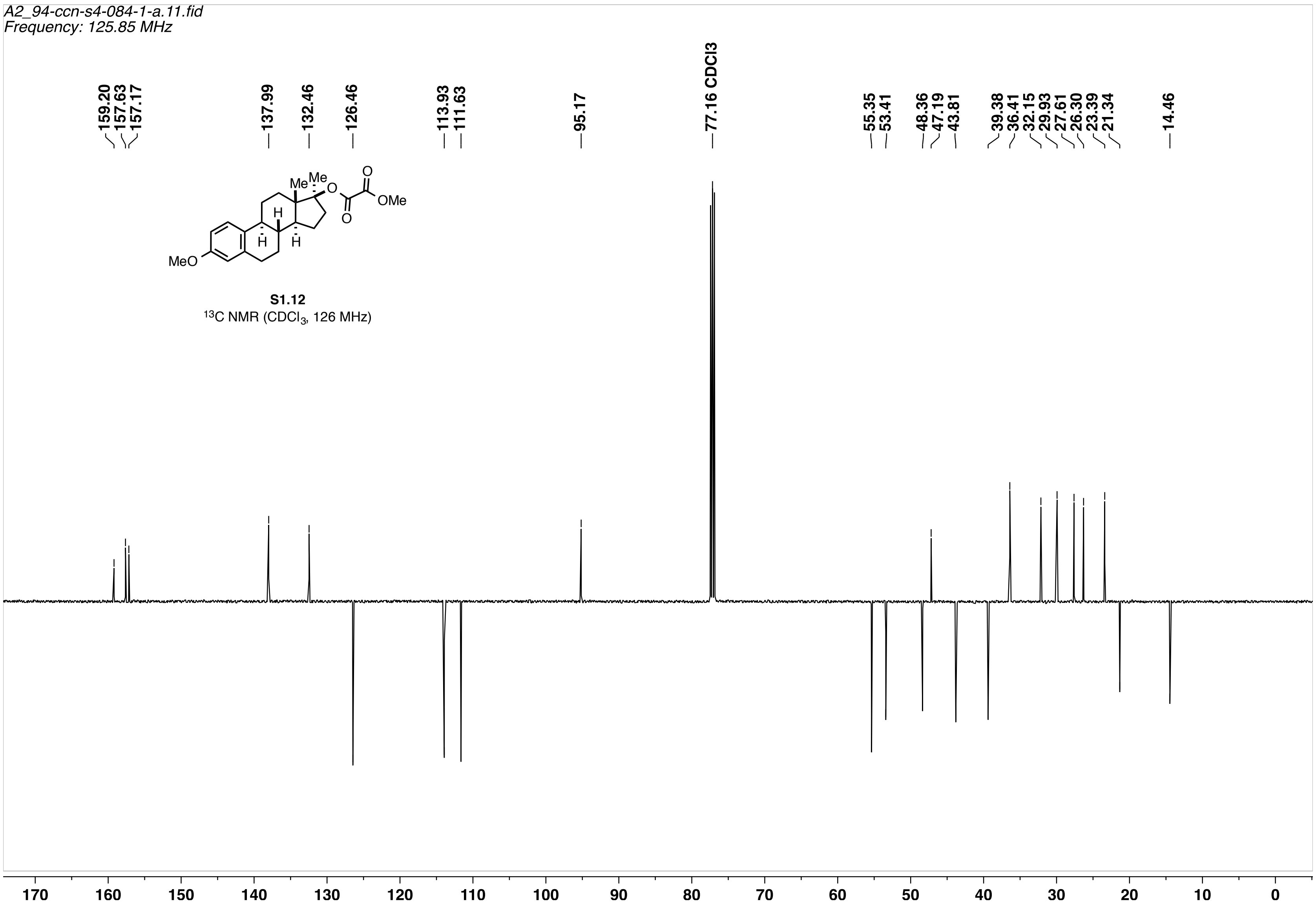
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803825 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



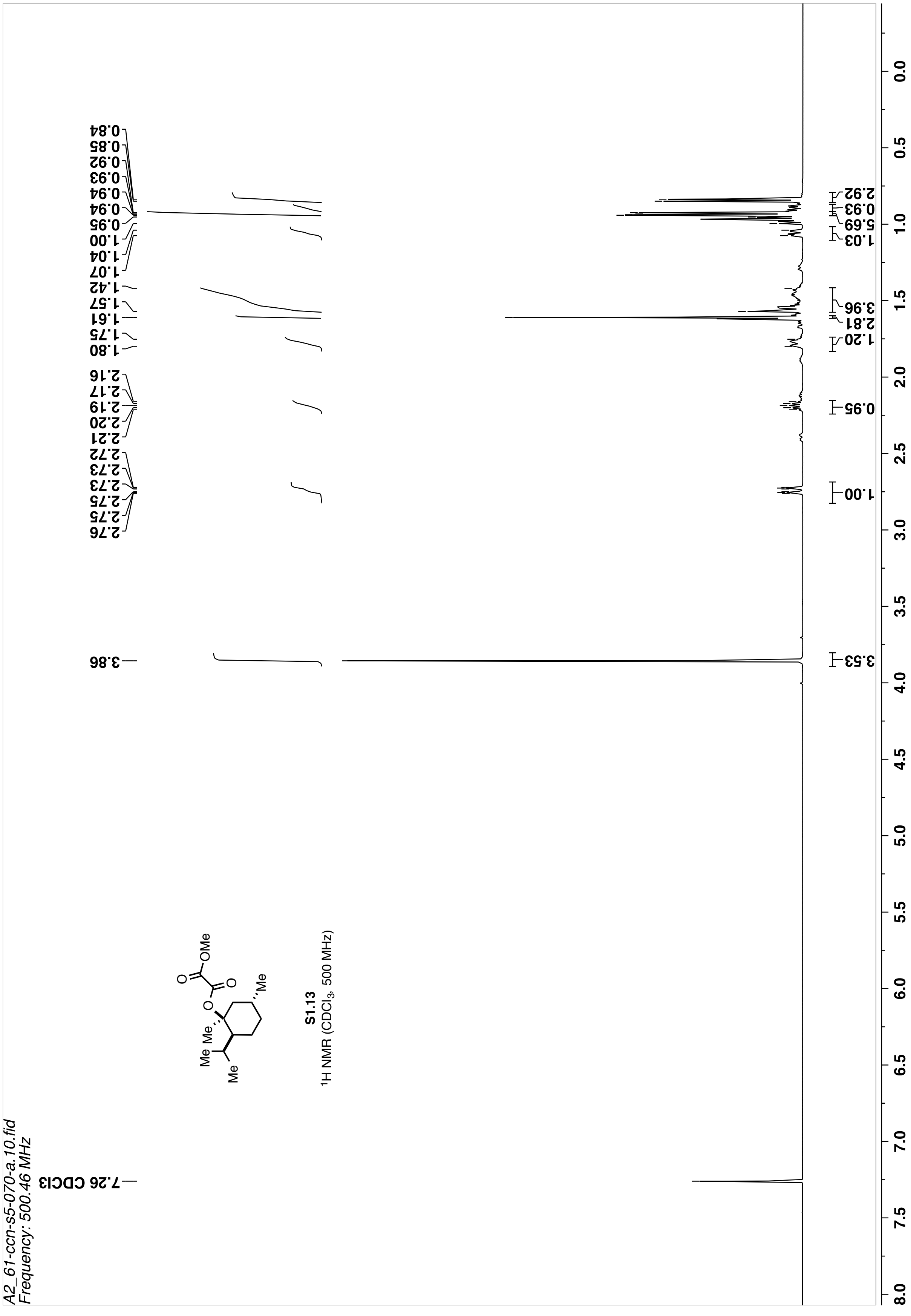
S1.12

^{1}H NMR (CDCl$_3$, 500 MHz)



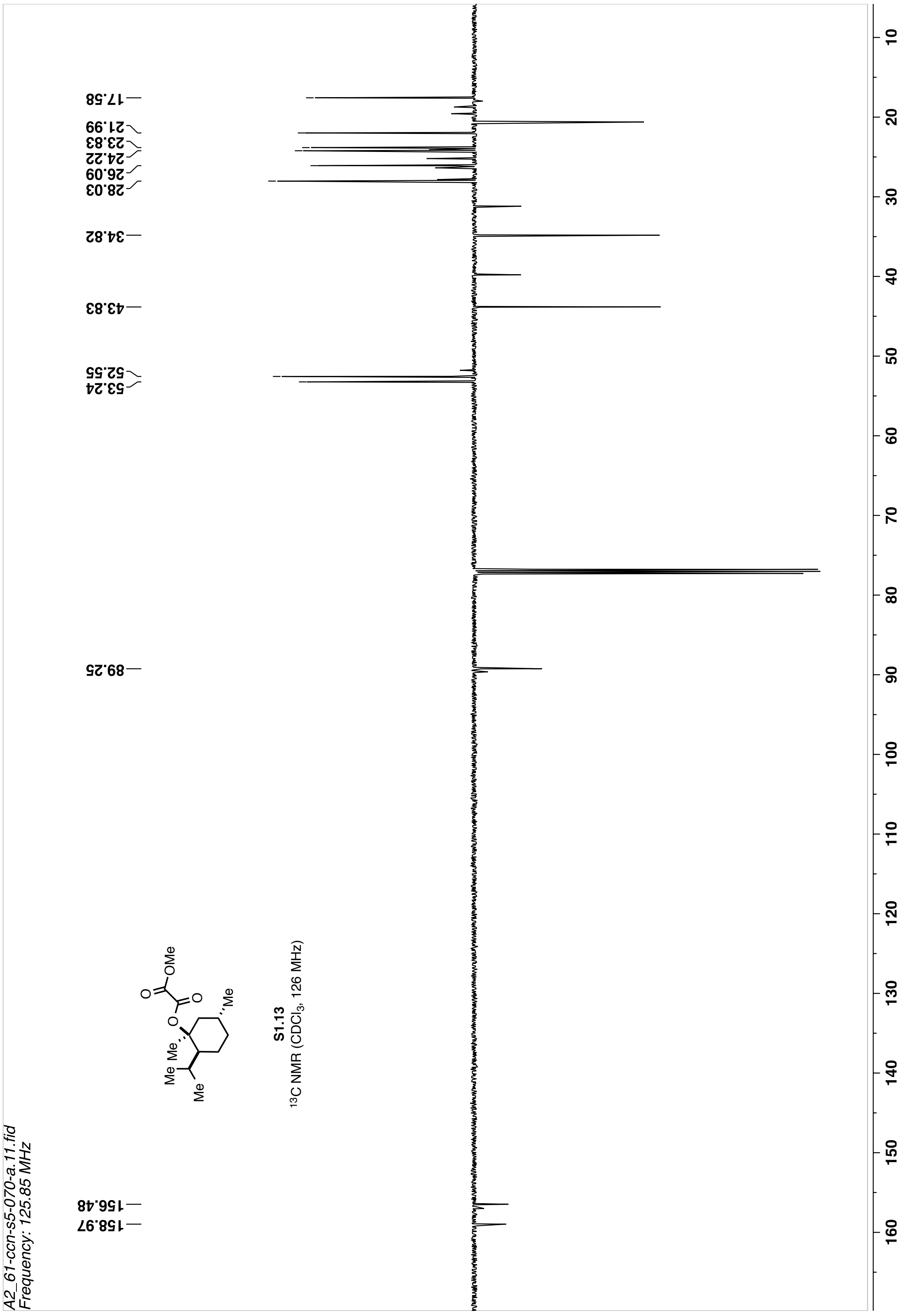
S1.12

^{13}C NMR (CDCl$_3$, 126 MHz)



S1.13

^{1}H NMR ($CDCl_3$, 500 MHz)



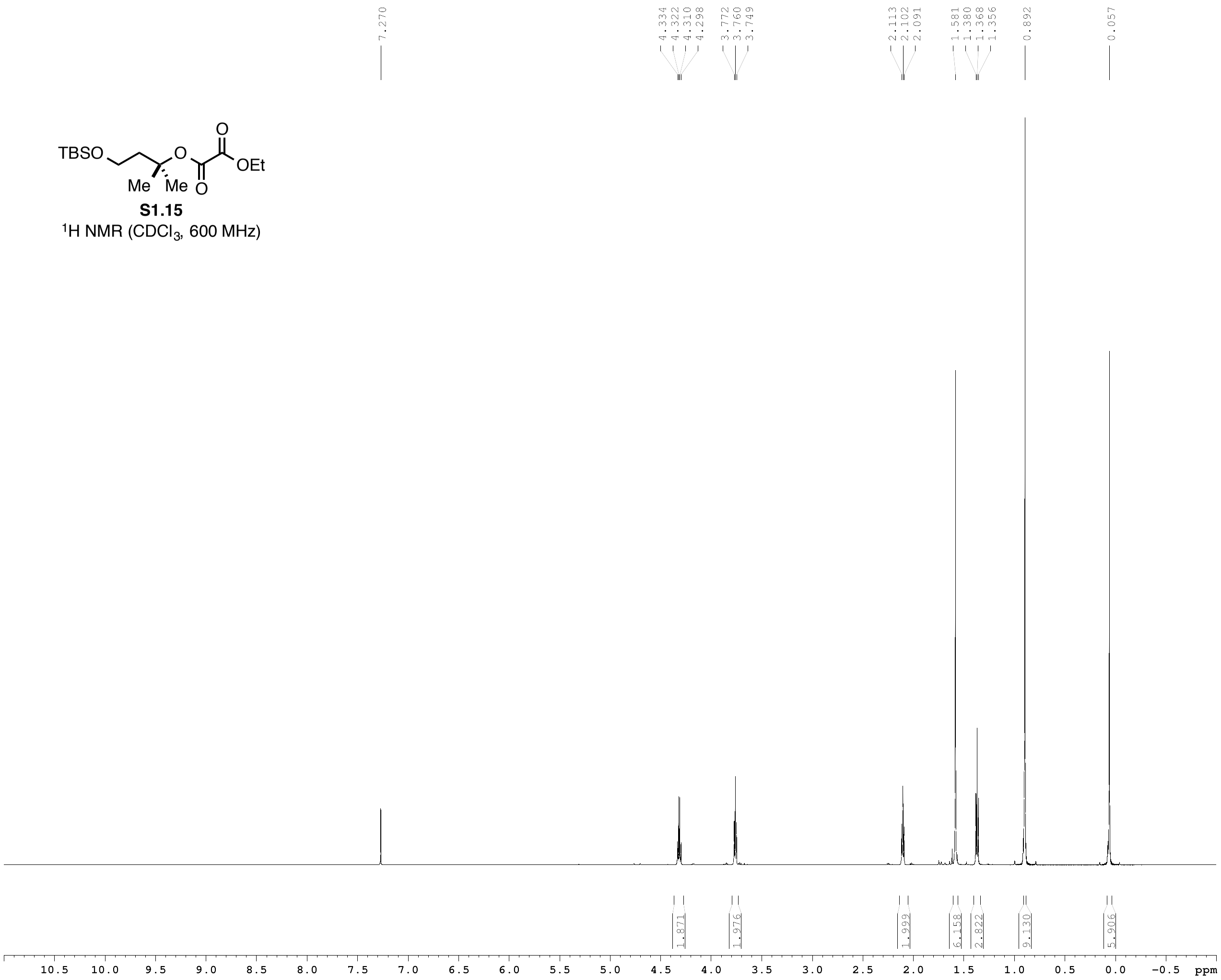
S1.13

^{13}C NMR (CDCl$_3$, 126 MHz)

YS-II-199

S1.15

^{1}H NMR (CDCl$_3$, 600 MHz)



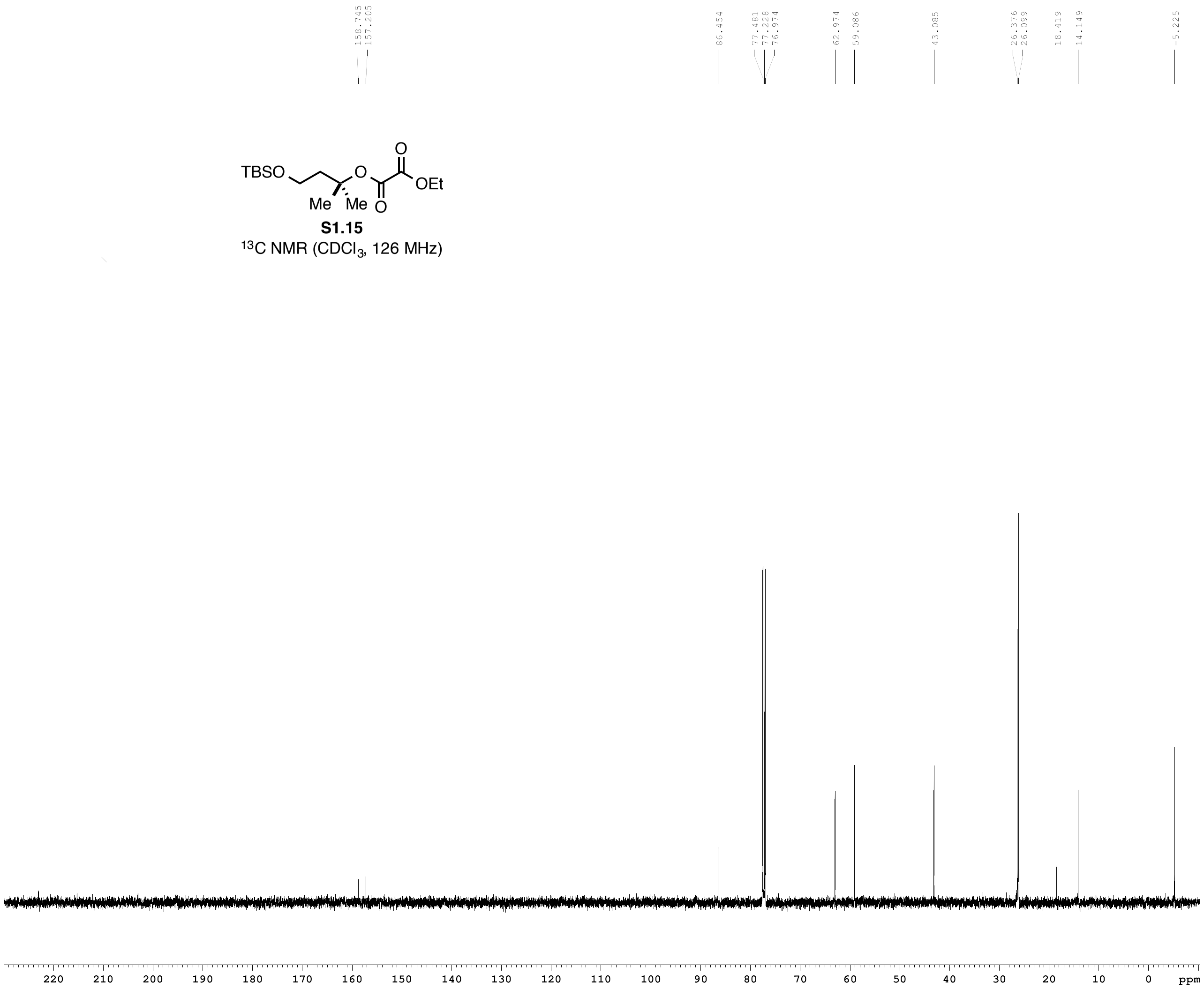
```
Current Data Parameters
NAME          YS-II-199
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150123
Time              17.08
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                19228
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           9615.385 Hz
FIDRES        0.500072 Hz
AQ           0.9998560 sec
RG                  181
DW               52.000 usec
DE                14.54 usec
TE                298.2 K
D1          0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300296 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-199



S1.15

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-199
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150425
Time               9.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  248
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                13004
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803988 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-259

S1.16

^{1}H NMR ($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME         YS-II-259
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20150220
Time               8.52
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST  0 sec
MCWRK        0.01500000 sec

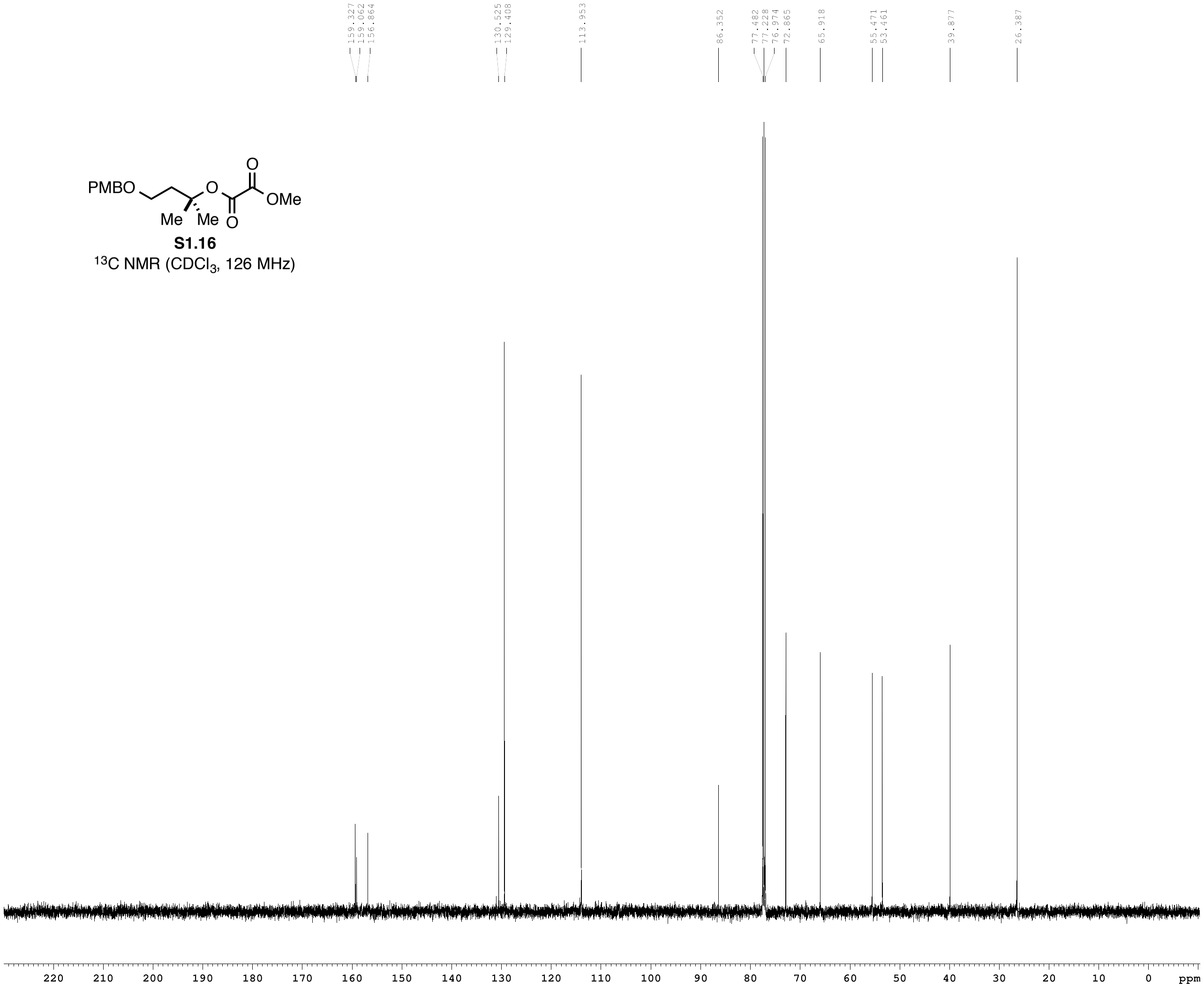
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200271 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-259

S1.16

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          YS-II-259
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150220
Time               8.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              10321.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804006 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-54

S1.17

^{1}H NMR (CDCl$_3$, 600 MHz)

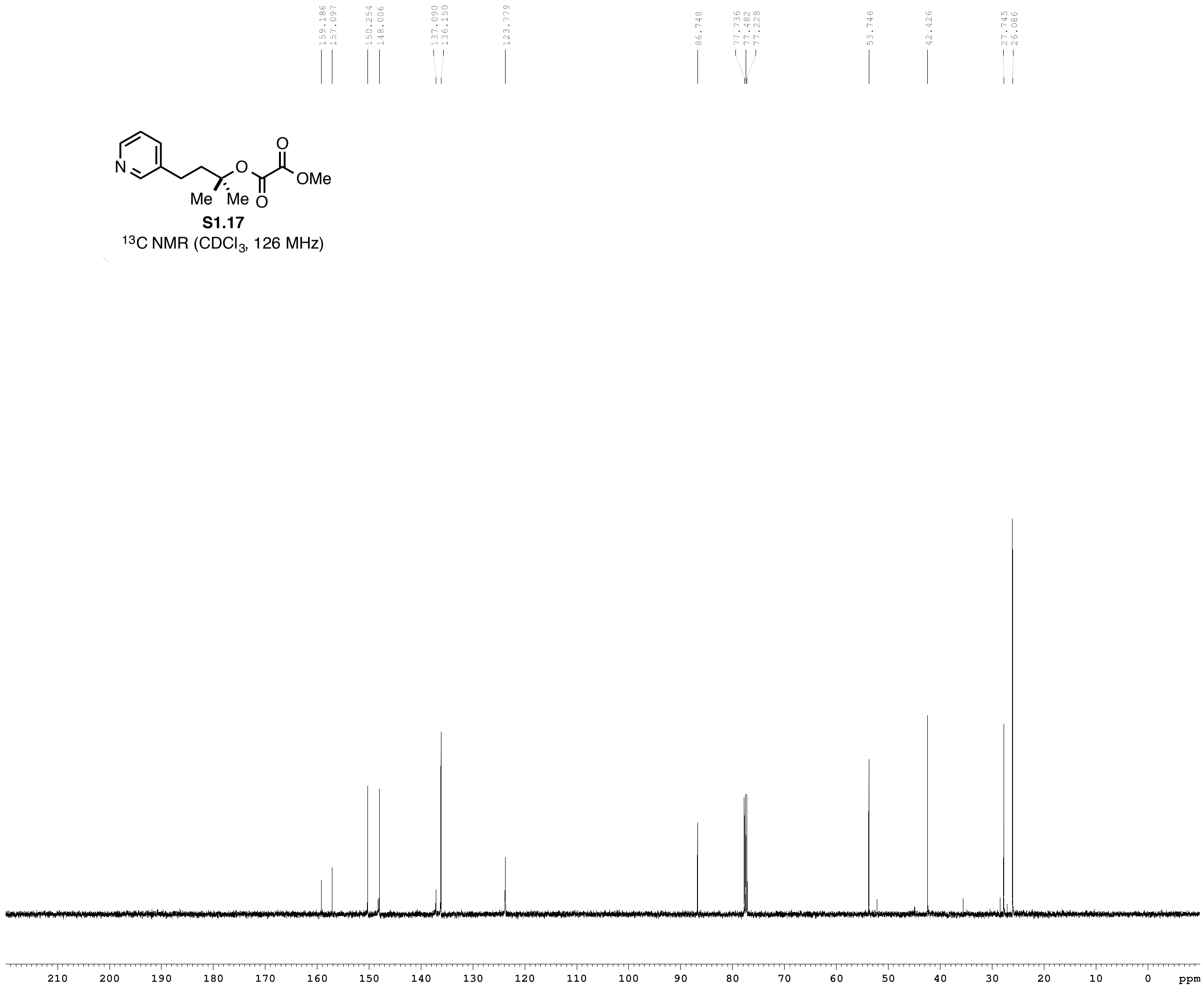
```
Current Data Parameters
NAME          YS-III-54
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150429
Time               8.29
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                  161
DW               52.000 usec
DE                14.33 usec
TE                298.4 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.00 usec
PLW1        60.25600052 W

F2 - Processing parameters
SI                65536
SF          600.1300273 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-III-54



S1.17

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-54
EXPNO                 3
PROCNO                1

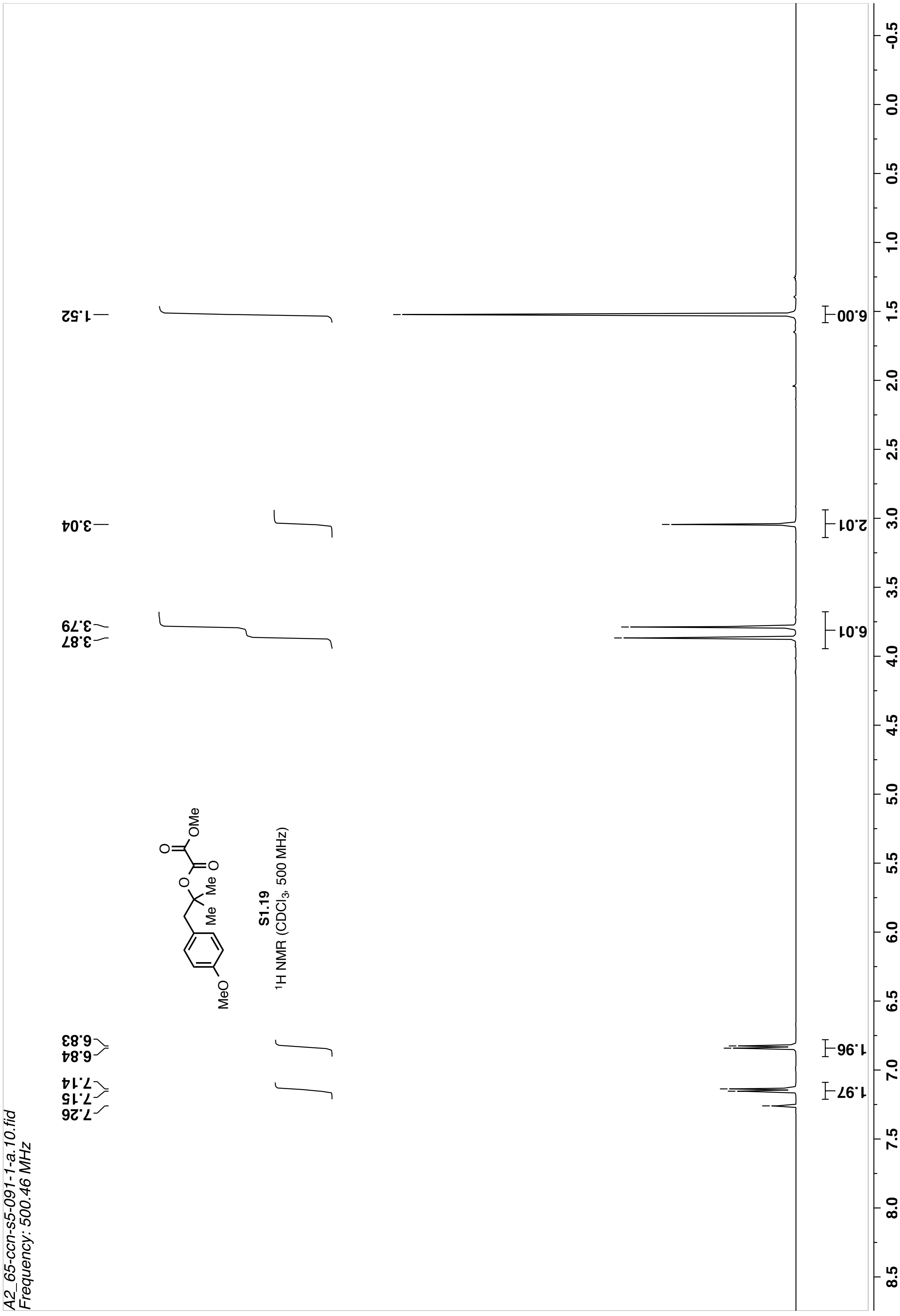
F2 - Acquisition Parameters
Date_          20150429
Time               8.22
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   56
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 4096
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

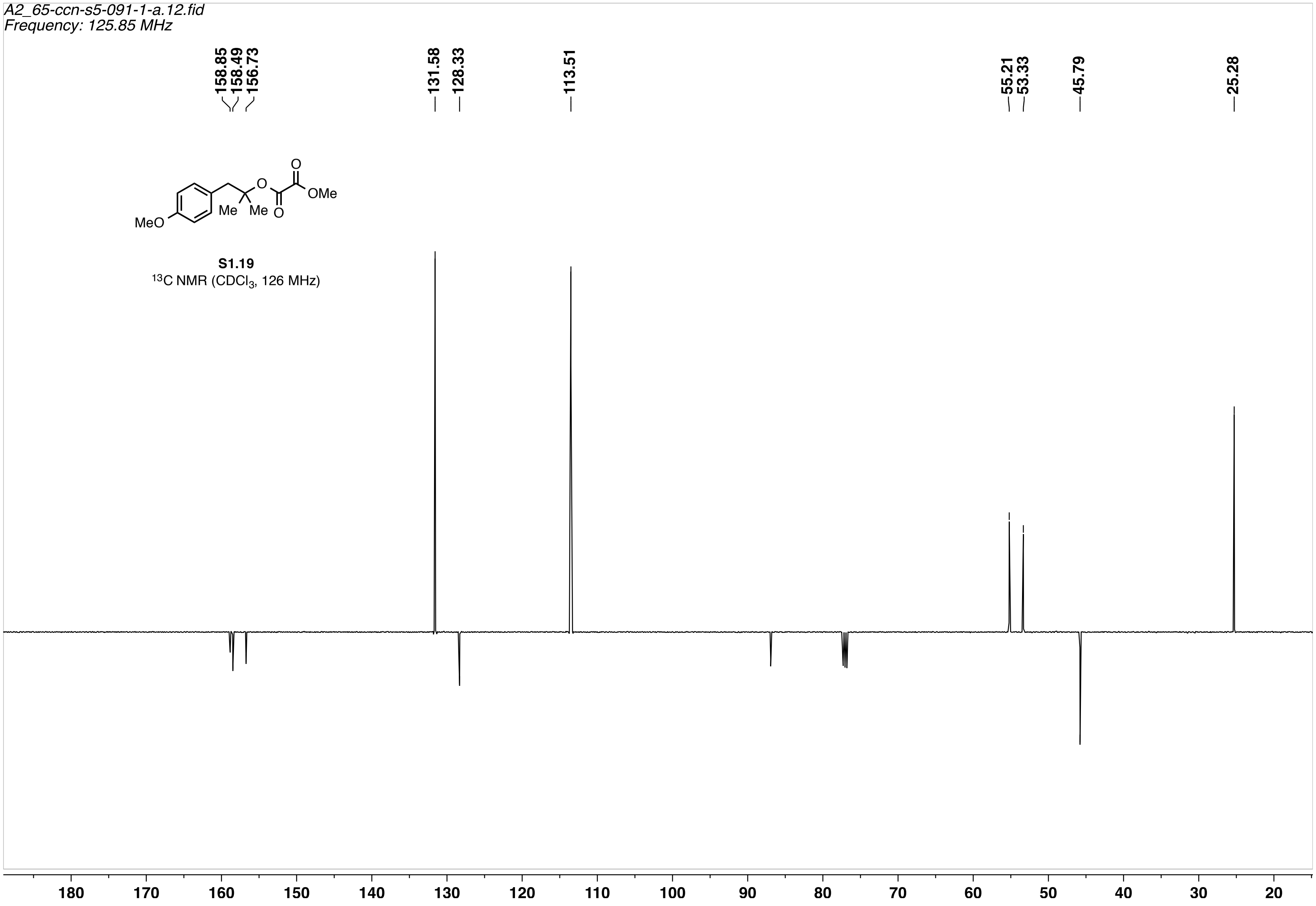
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803737 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



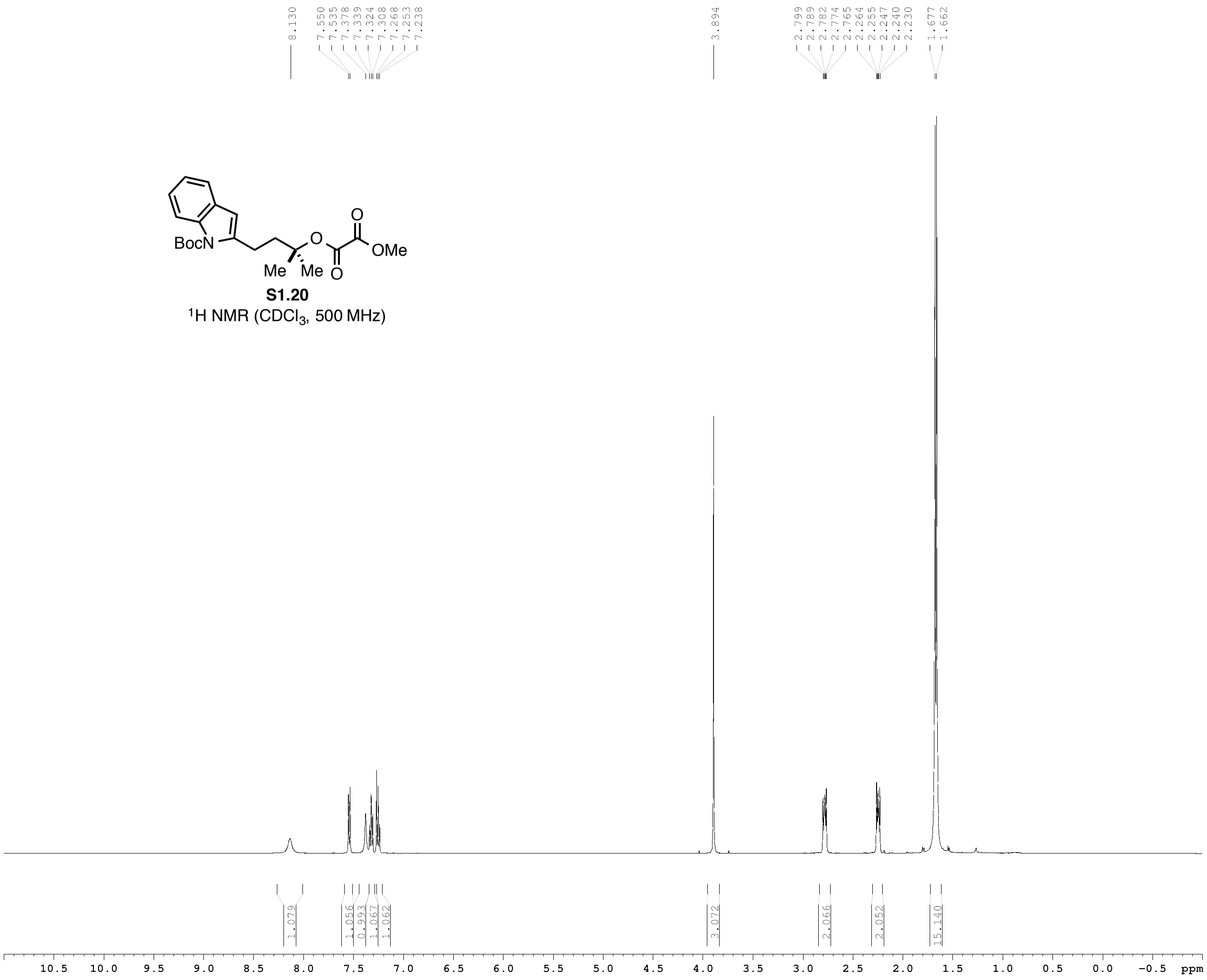
S1.19

^{1}H NMR (CDCl$_3$, 500 MHz)



S1.19
^{13}C NMR (CDCl$_3$, 126 MHz)

YS-II-247



S1.20

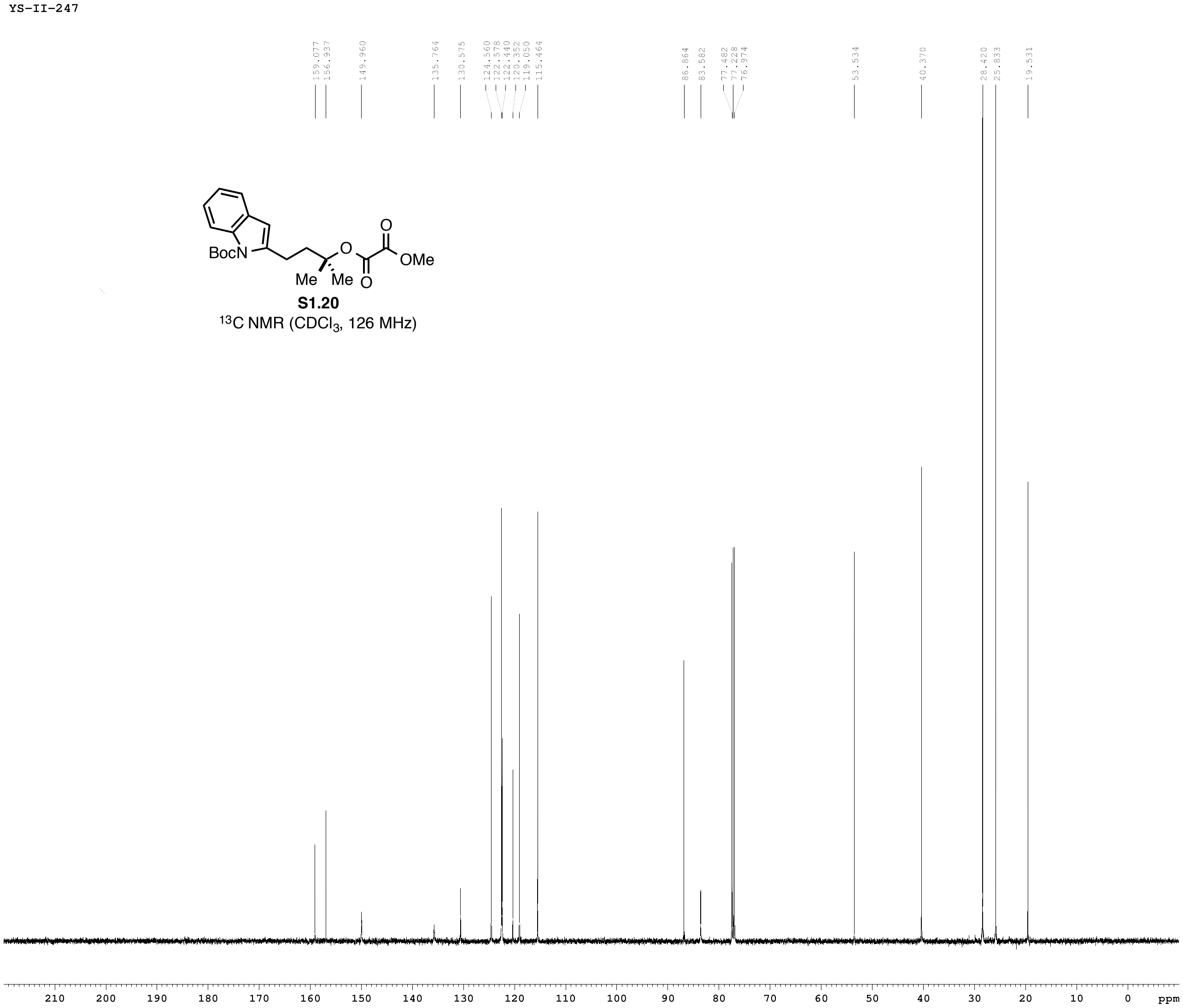
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          YS-II-247
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150216
Time              13.21
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200265 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```



S1.20

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-247
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150216
Time              13.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  584
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

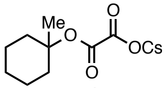
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

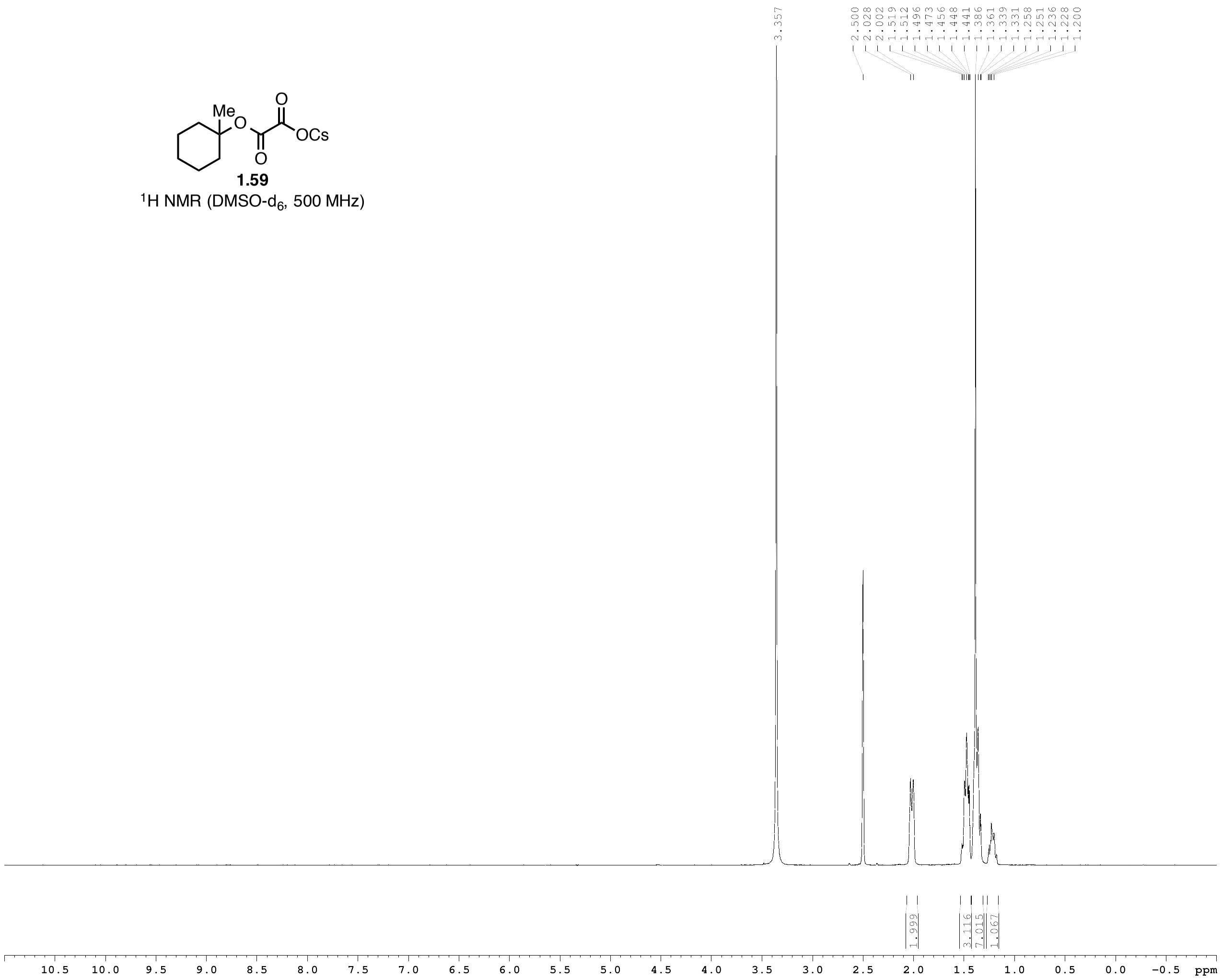
F2 - Processing parameters
SI                65536
SF          125.7804026 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-192



1.59

^{1}H NMR (DMSO-d$_6$, 500 MHz)



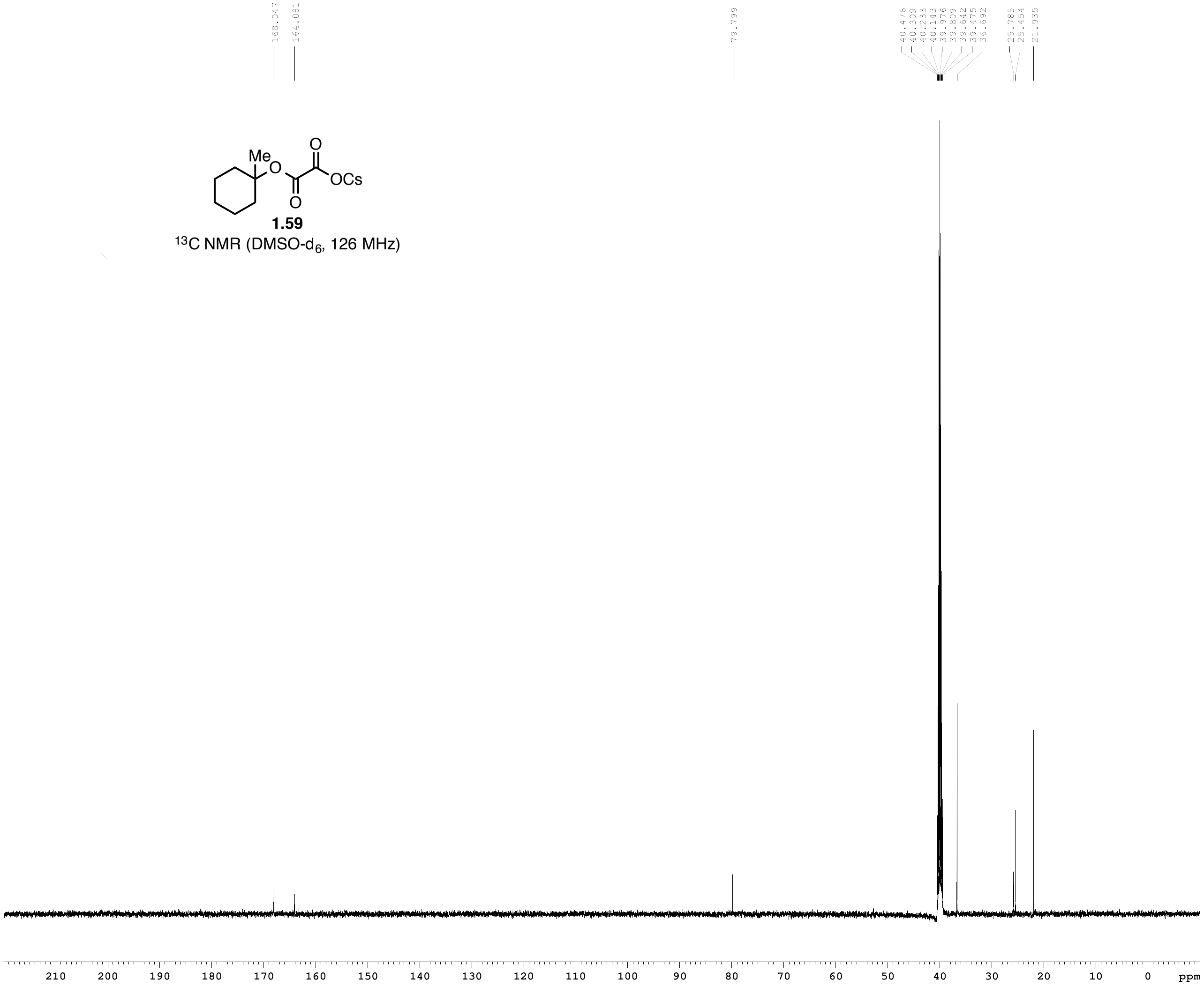
```
Current Data Parameters
NAME          YS-II-192
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150120
Time              14.17
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                16022
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.500114 Hz
AQ            0.9997728 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                297.8 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200134 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-192



1.59

^{13}C NMR (DMSO-d_6, 126 MHz)

```
Current Data Parameters
NAME          YS-II-192
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150120
Time              14.19
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  232
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                297.9 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

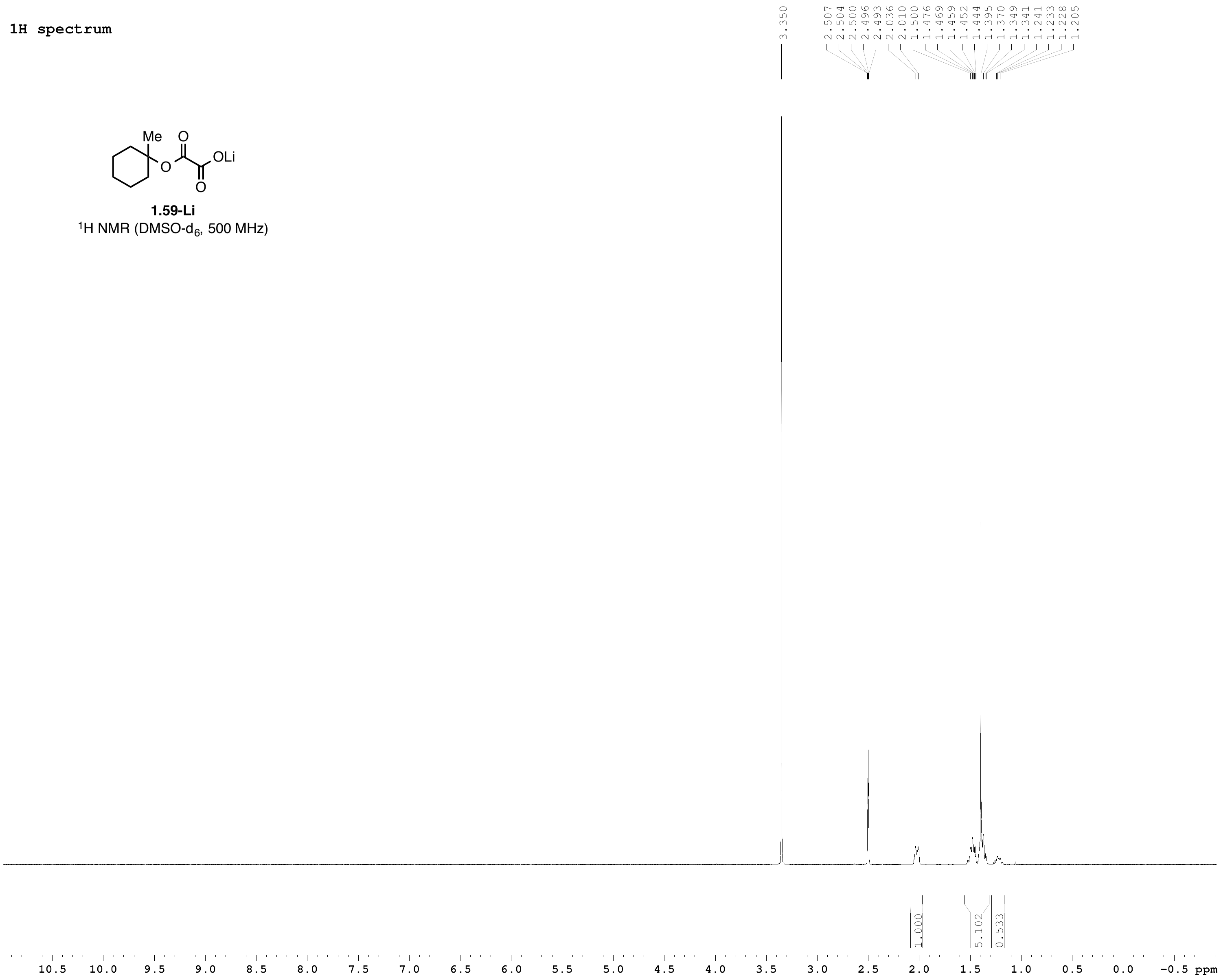
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804190 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum

1.59-Li

^{1}H NMR (DMSO-d_6, 500 MHz)



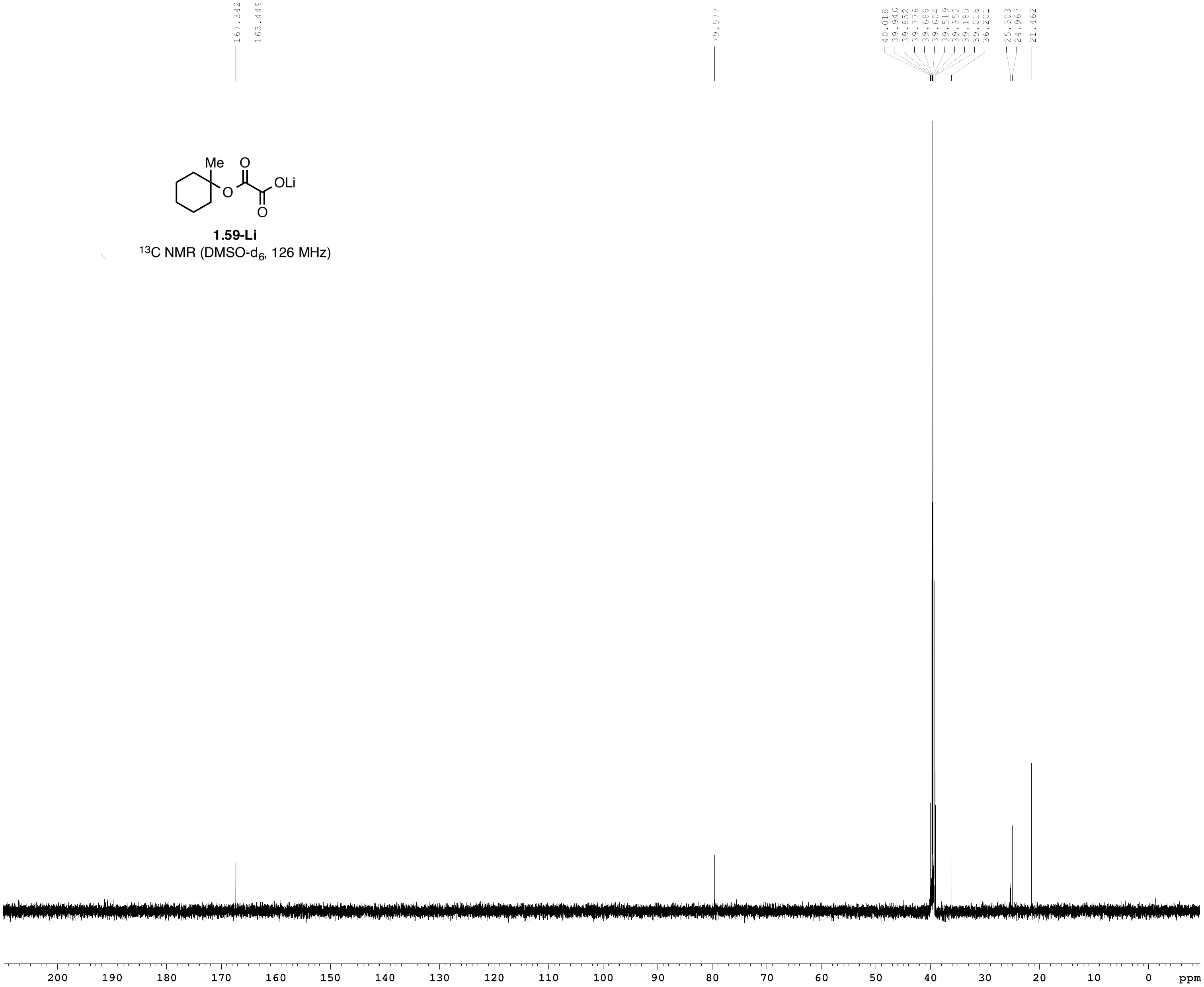
```
Current Data Parameters
NAME        CRJ1-177-Li
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150401
Time              14.03
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                 14.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200122 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

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



1.59-Li

^{13}C NMR (DMSO-d_6, 126 MHz)

```
Current Data Parameters
NAME         CRJ1-177-Li
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20150401
Time              14.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2580.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

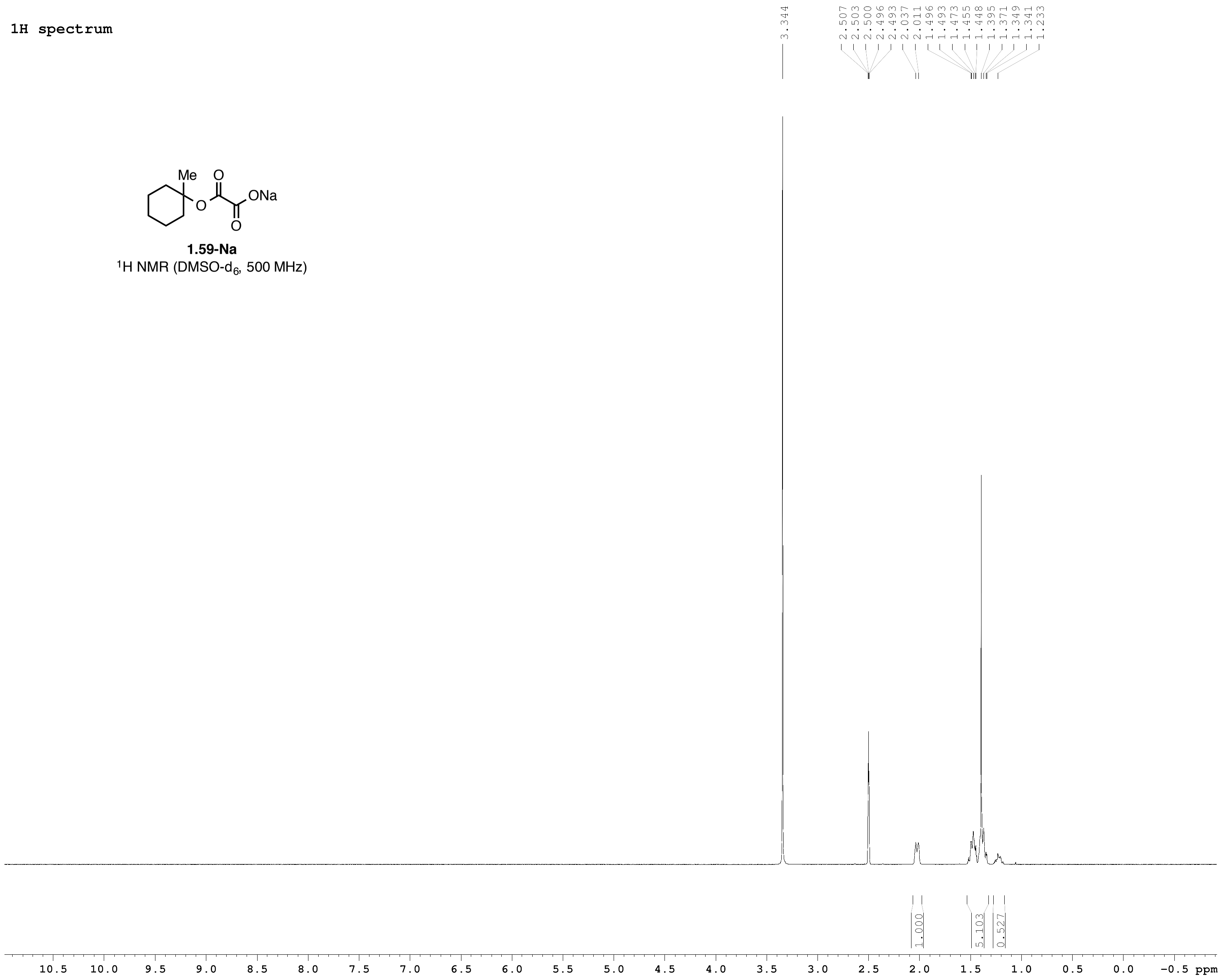
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804773 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 2.00
```

1H spectrum



1.59-Na

^{1}H NMR (DMSO-d_6, 500 MHz)

```
Current Data Parameters
NAME        CRJ1-177-Na
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150401
Time              14.11
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                   18
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

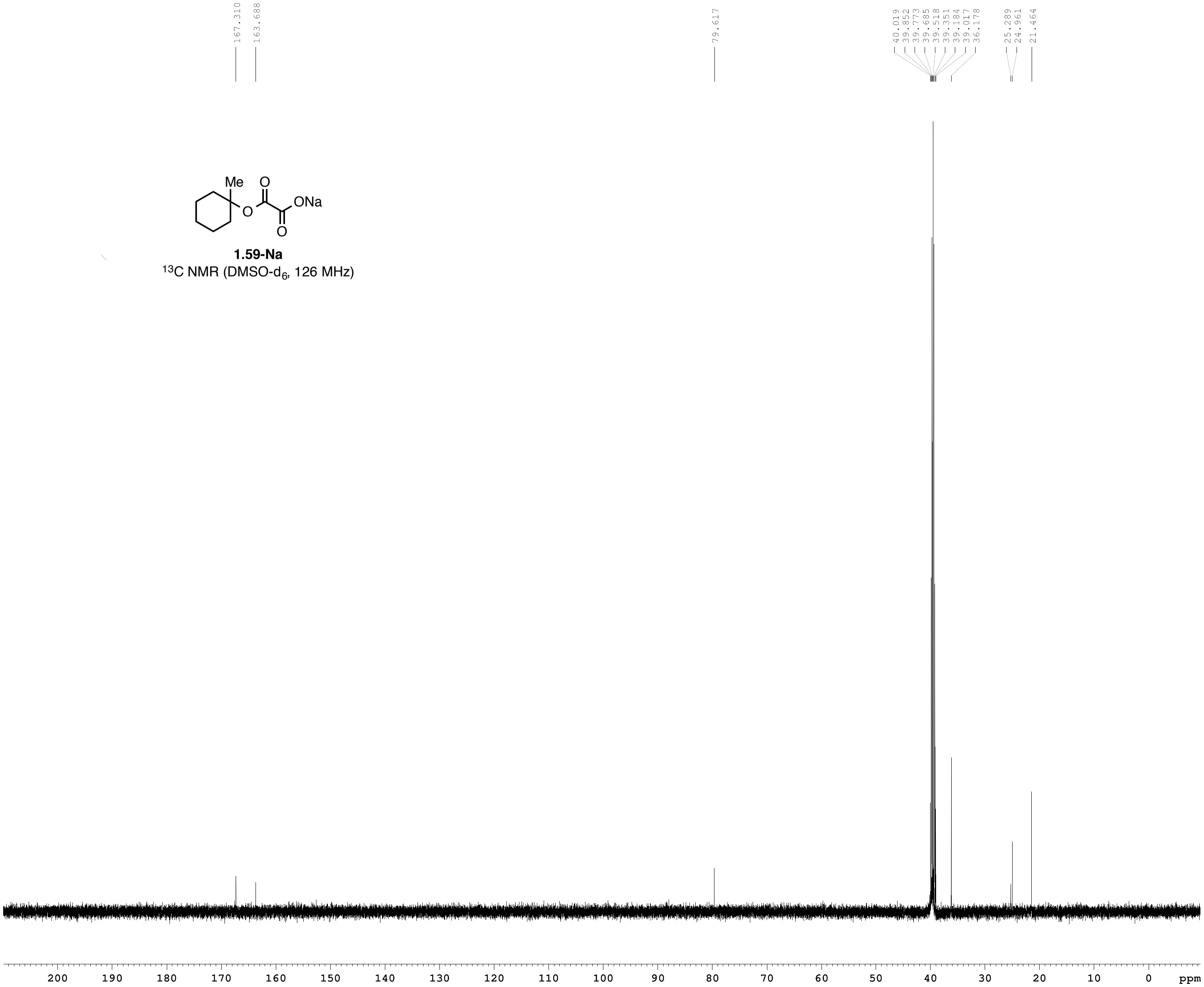
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200122 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

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

1.59-Na

^{13}C NMR (DMSO-d_6, 126 MHz)



```
Current Data Parameters
NAME          CRJ1-177-Na
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150401
Time                14.12
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      2
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   8192
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             1.00000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

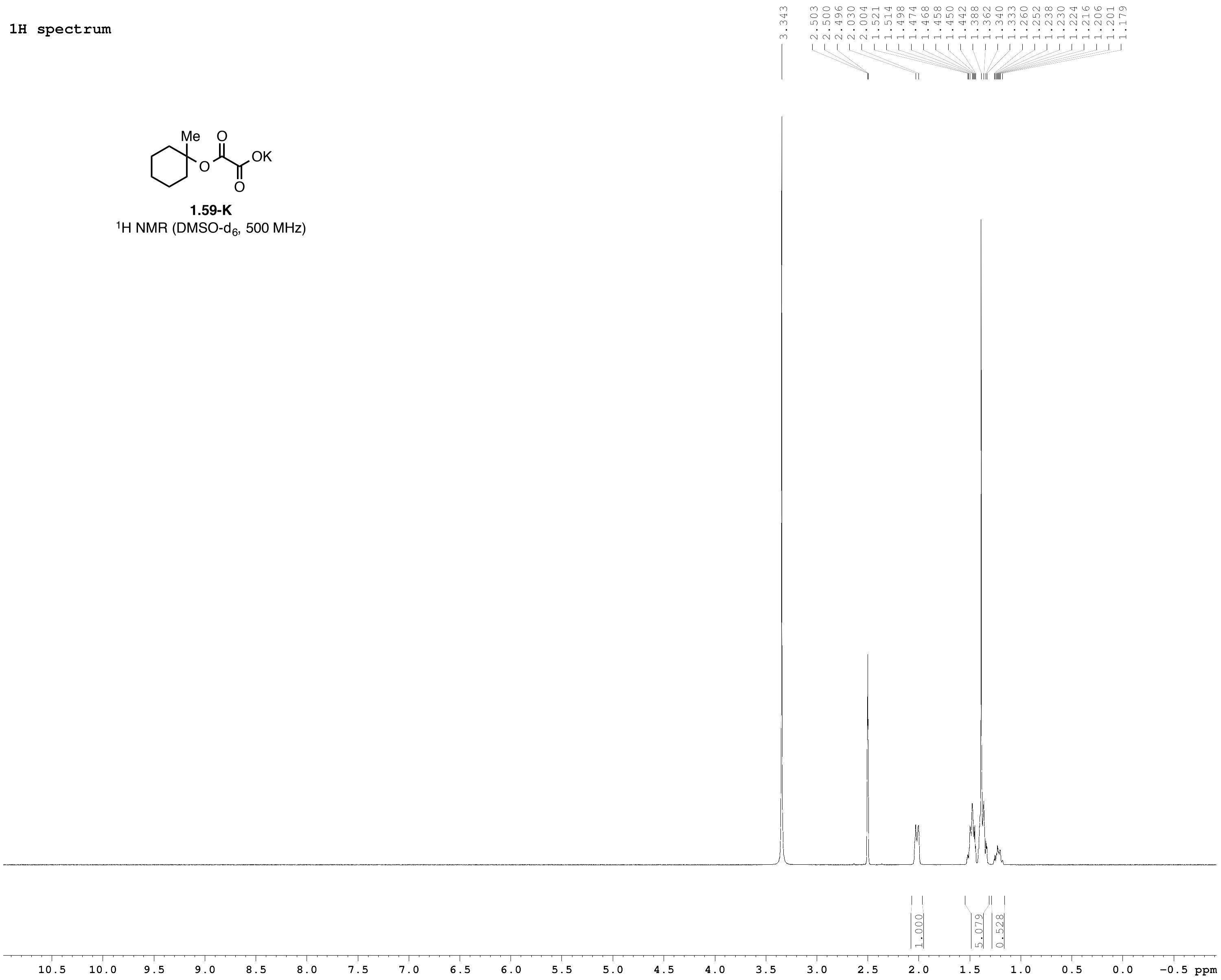
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804777 MHz
WDW                    no
SSB       0
LB        0 Hz
GB        0
PC                   2.00
```

1H spectrum

1.59-K
^{1}H NMR (DMSO-d_6, 500 MHz)



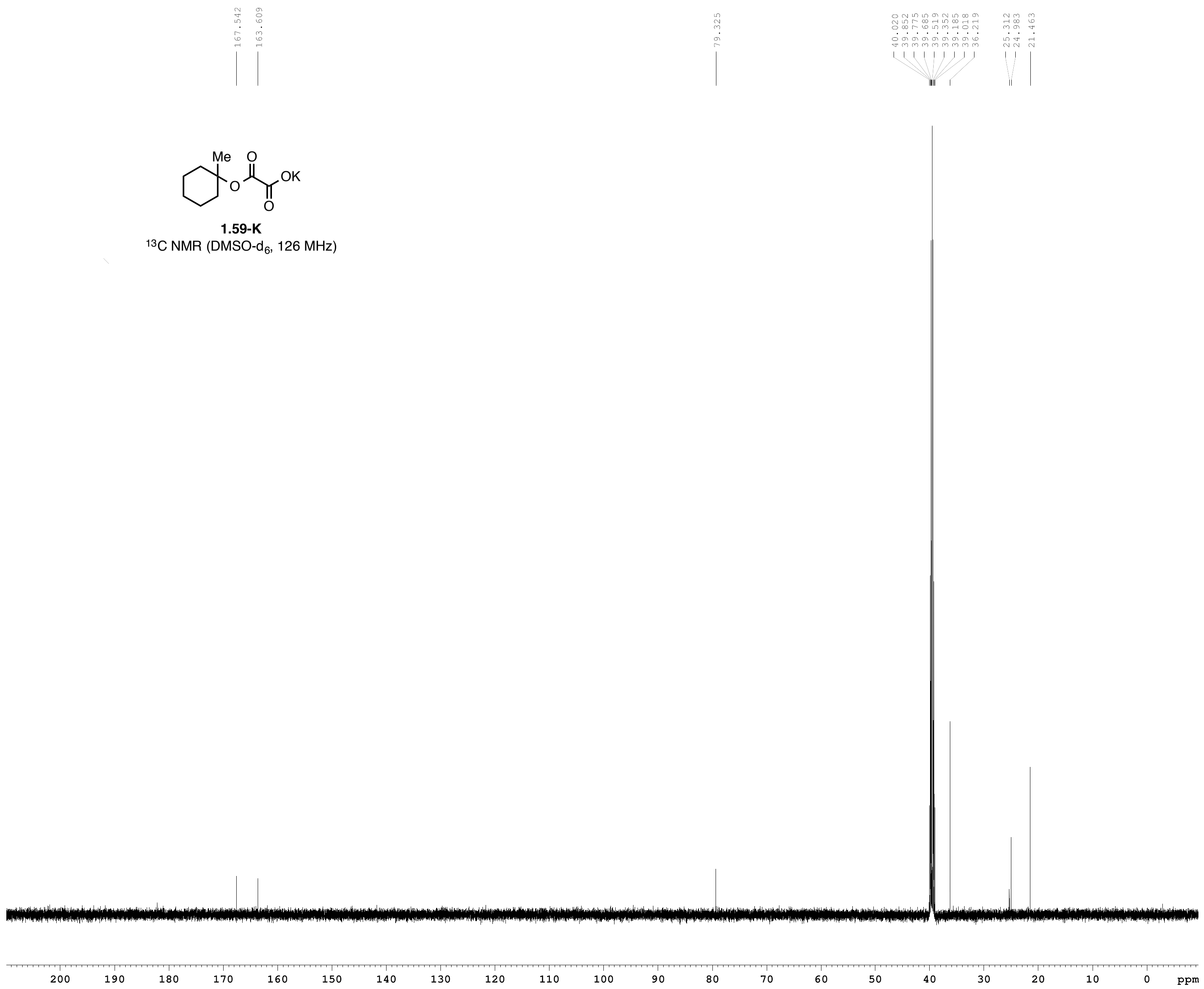
```
Current Data Parameters
NAME          CRJ1-177-K
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150401
Time               14.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                  20.2
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200121 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

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



1.59-K

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME          CRJ1-177-K
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150401
Time               14.18
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    80
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

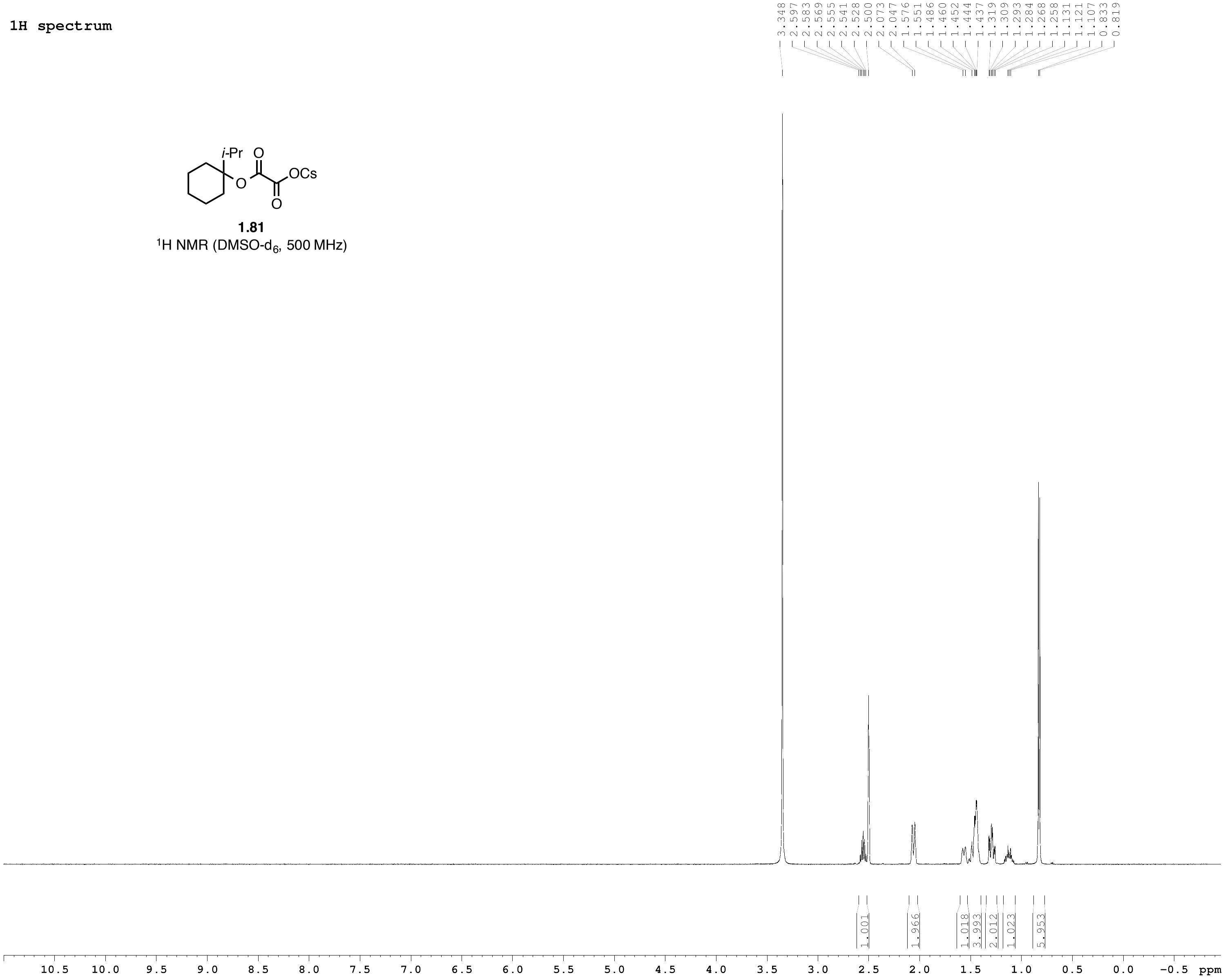
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804779 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  2.00
```

1H spectrum

1.81

^{1}H NMR (DMSO-d$_6$, 500 MHz)



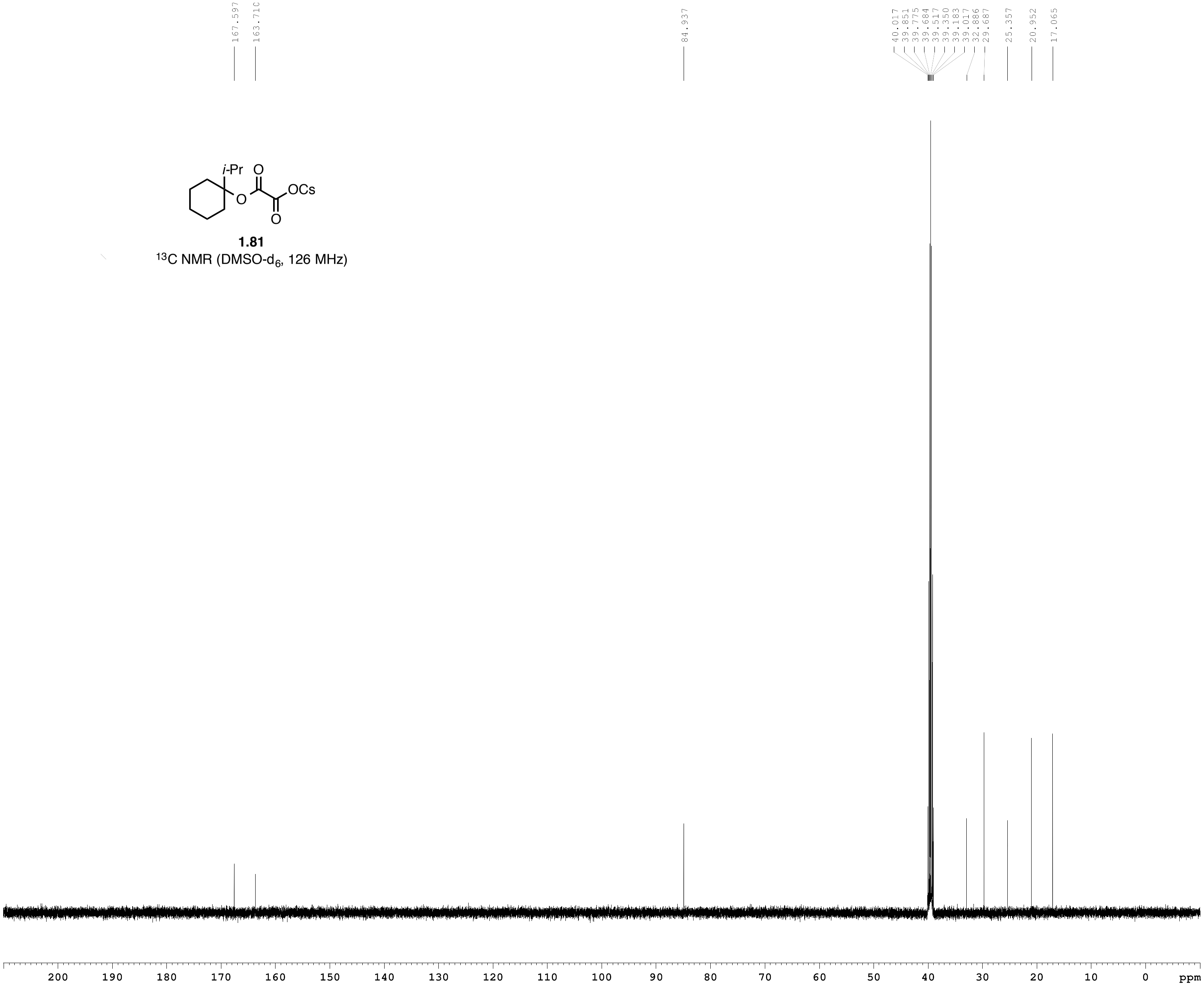
```
Current Data Parameters
NAME          CRJ1-094-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150223
Time               13.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                  10.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            3.00000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200136 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

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



1.81

^{13}C NMR (DMSO-d_6, 126 MHz)

```
Current Data Parameters
NAME          CRJ1-094-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150223
Time               13.21
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804783 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  2.00
```

1H spectrum

1.83

^{1}H NMR (DMSO-d_6, 500 MHz)

```
Current Data Parameters
NAME      CRJ1-127-pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time              11.16
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

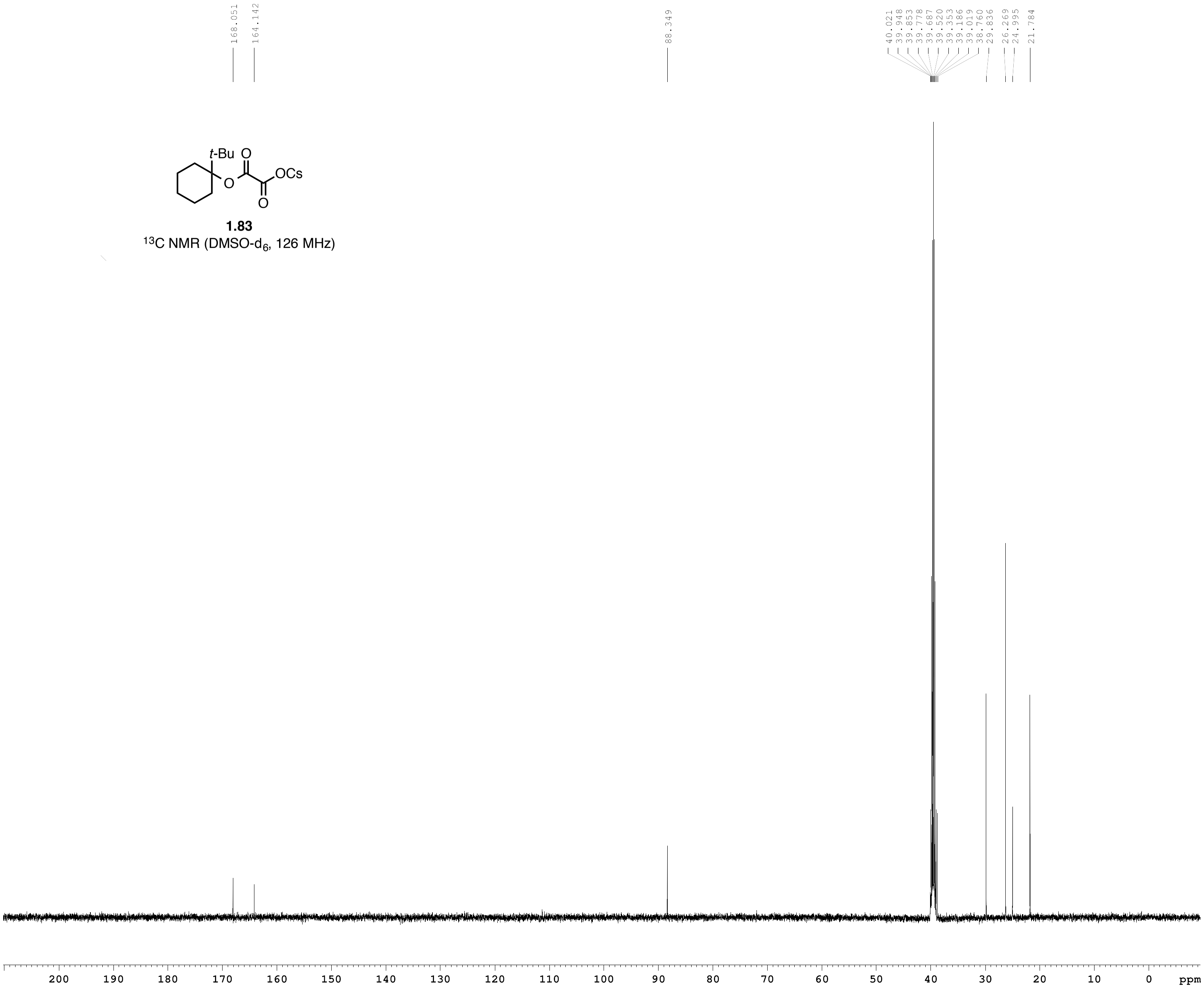
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200127 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

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

1.83

^{13}C NMR (DMSO-d_6, 126 MHz)



```
Current Data Parameters
NAME      CRJ1-127-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time              11.18
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

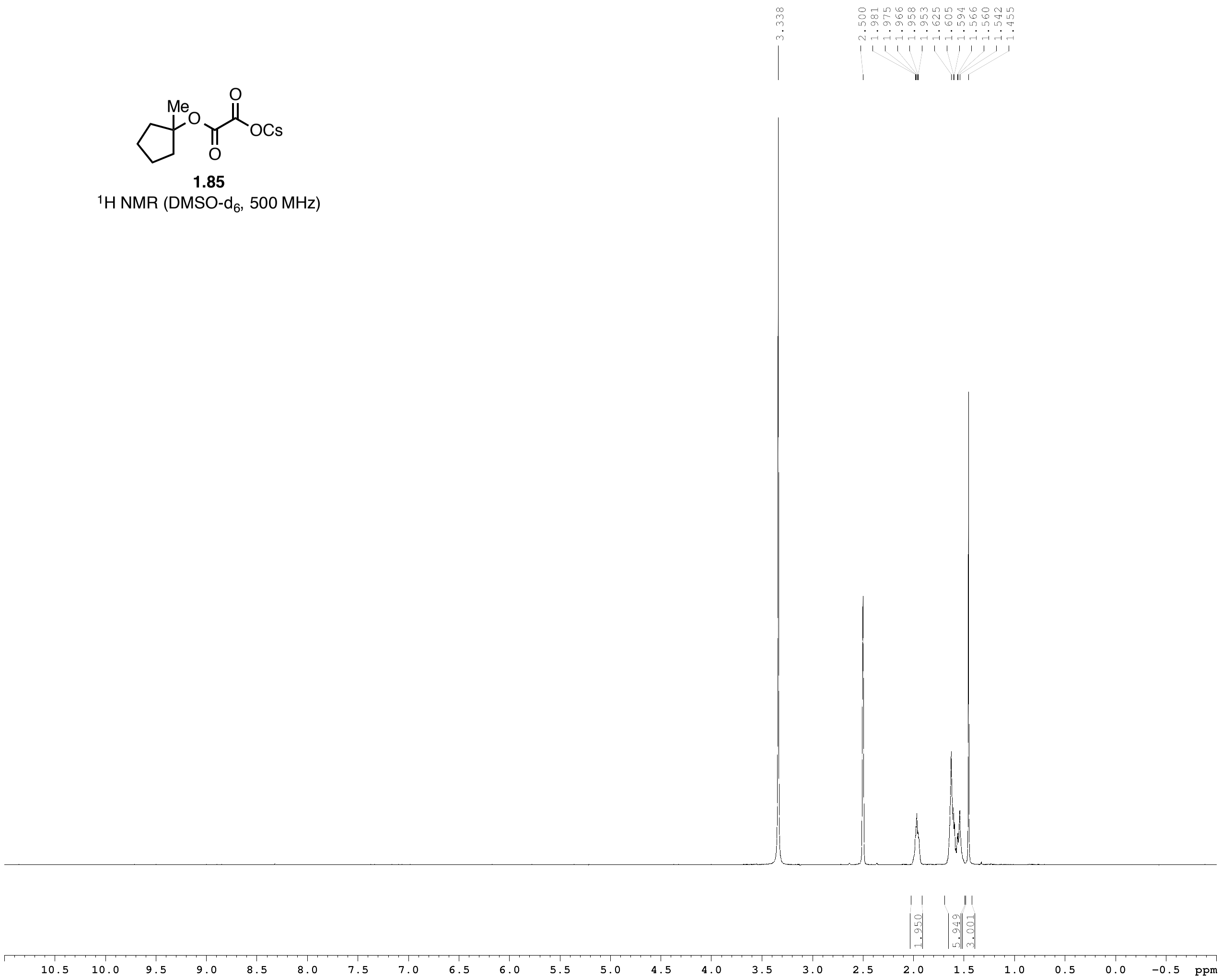
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804769 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-243

1.85

^{1}H NMR (DMSO-d$_6$, 500 MHz)



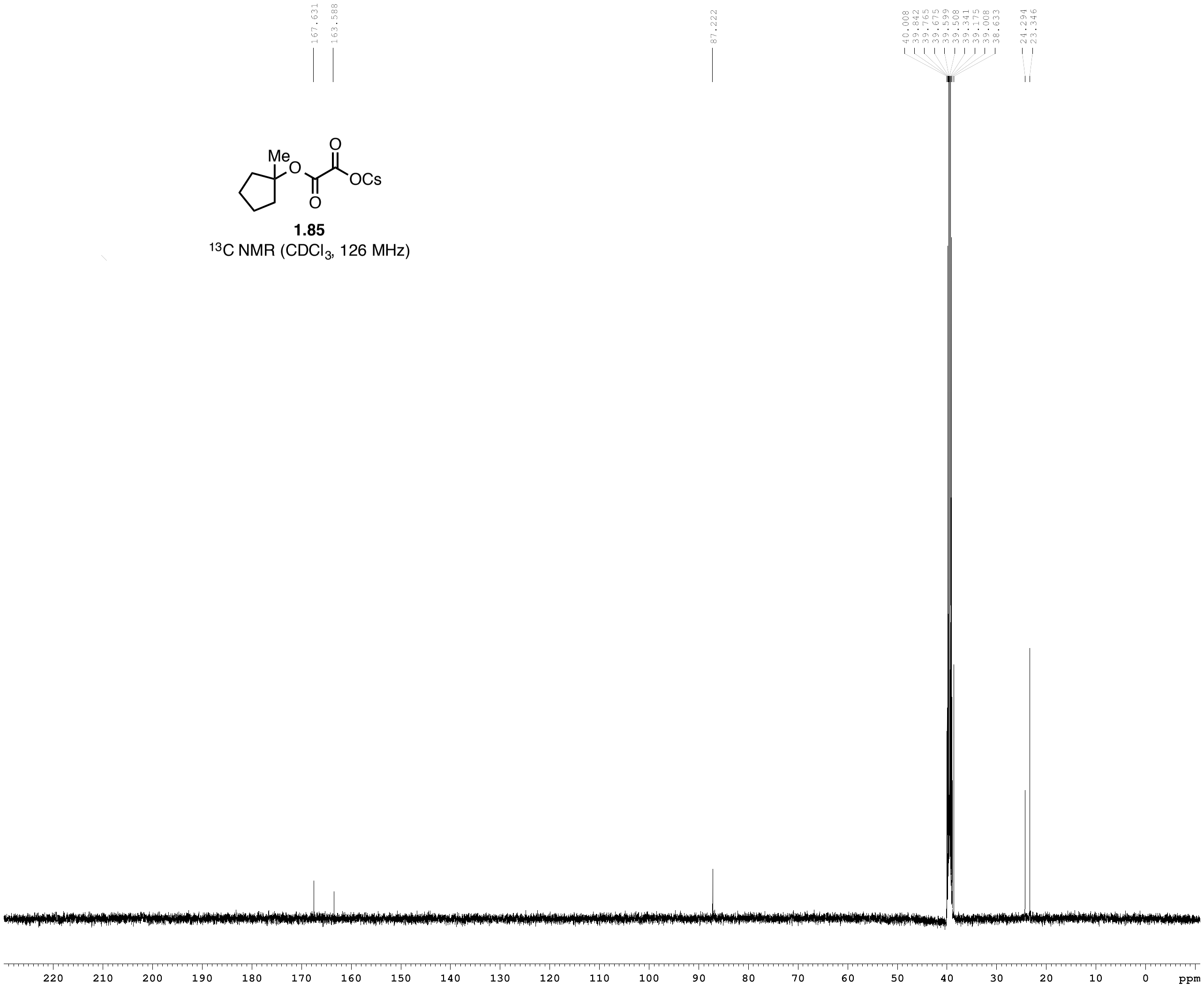
```
Current Data Parameters
NAME          YS-II-243
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150213
Time               8.59
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                 10.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200119 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-243



1.85

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-243
EXPNO                 2
PROCNO                1

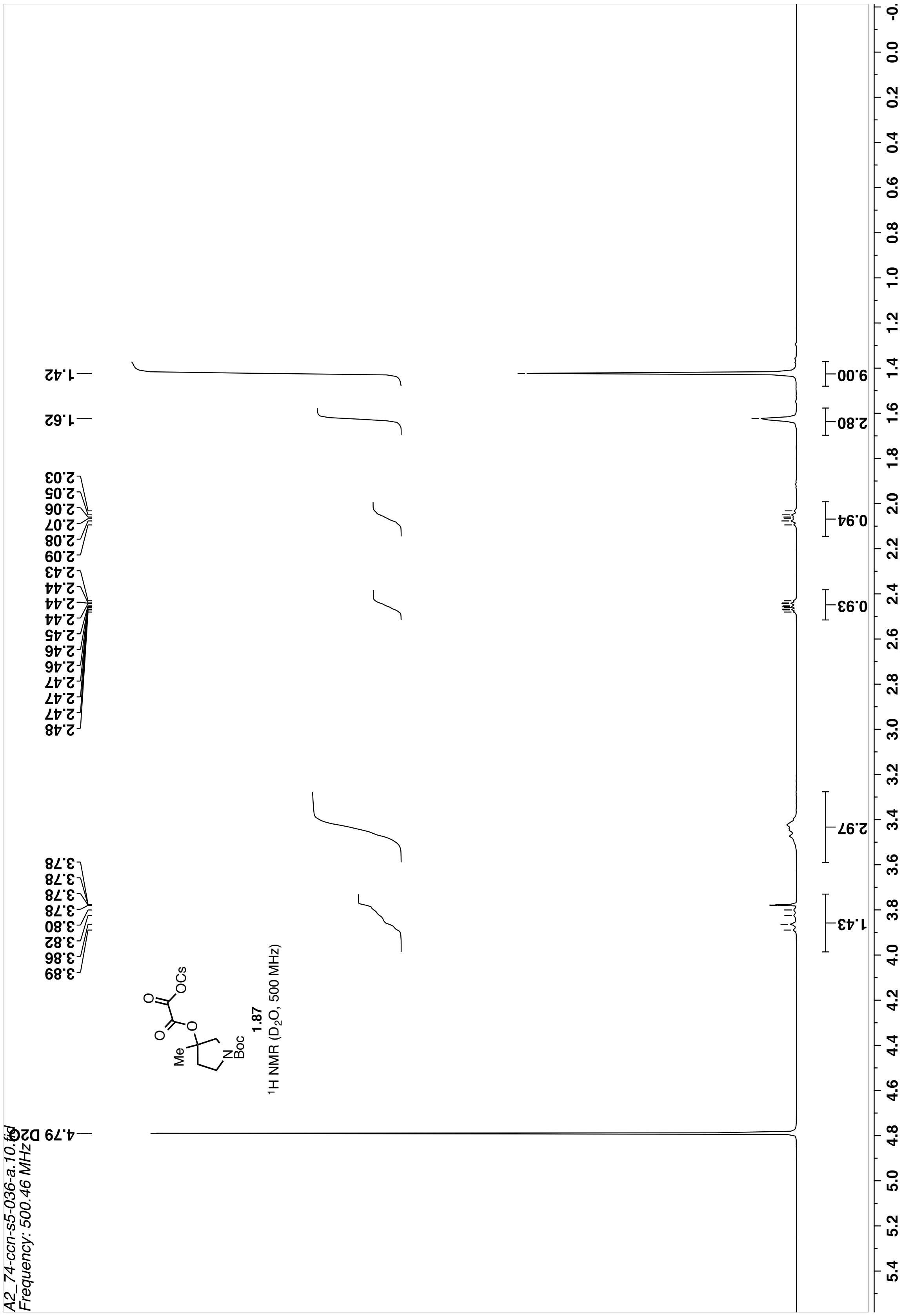
F2 - Acquisition Parameters
Date_          20150213
Time               9.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  400
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5792.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

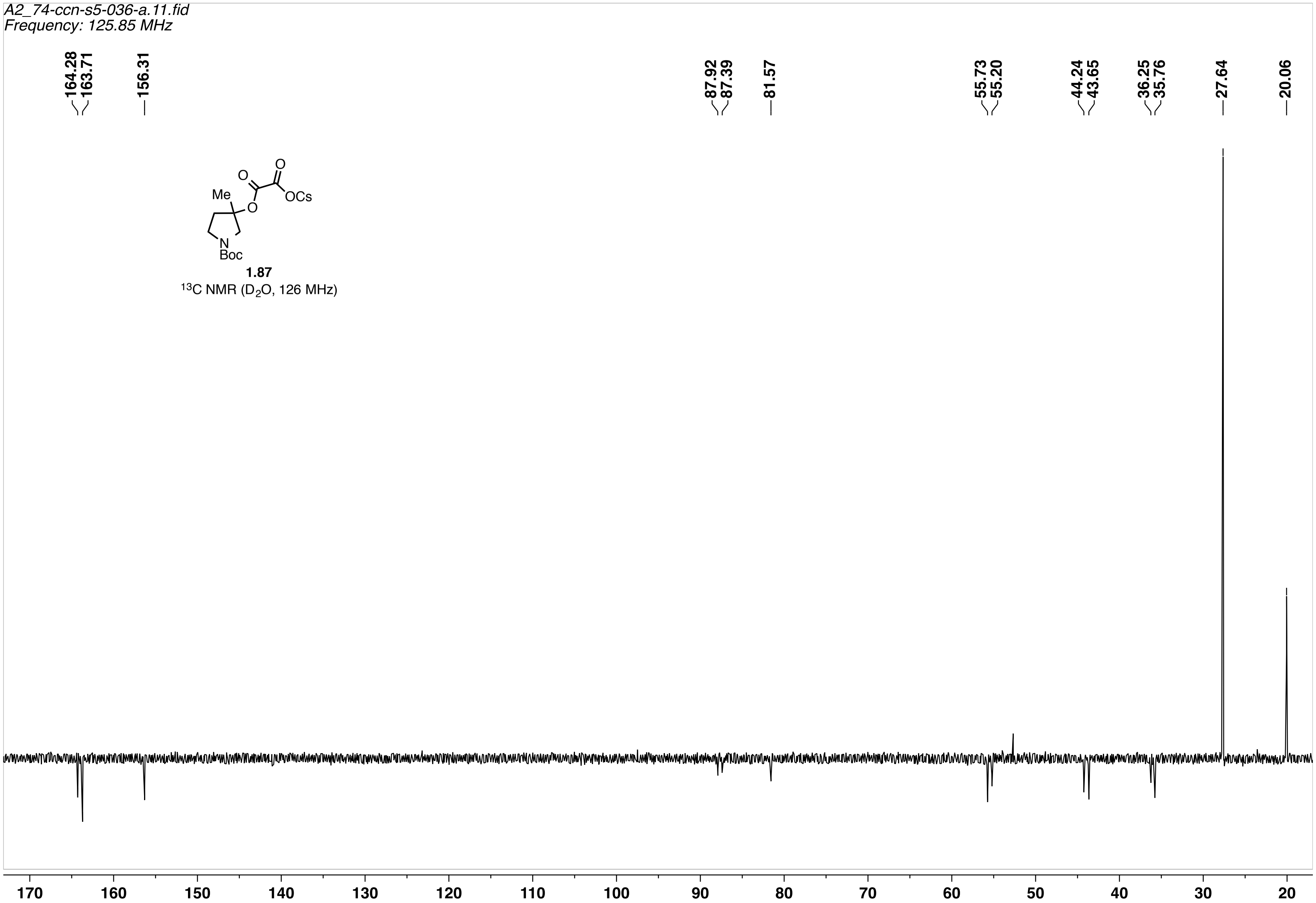
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804792 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



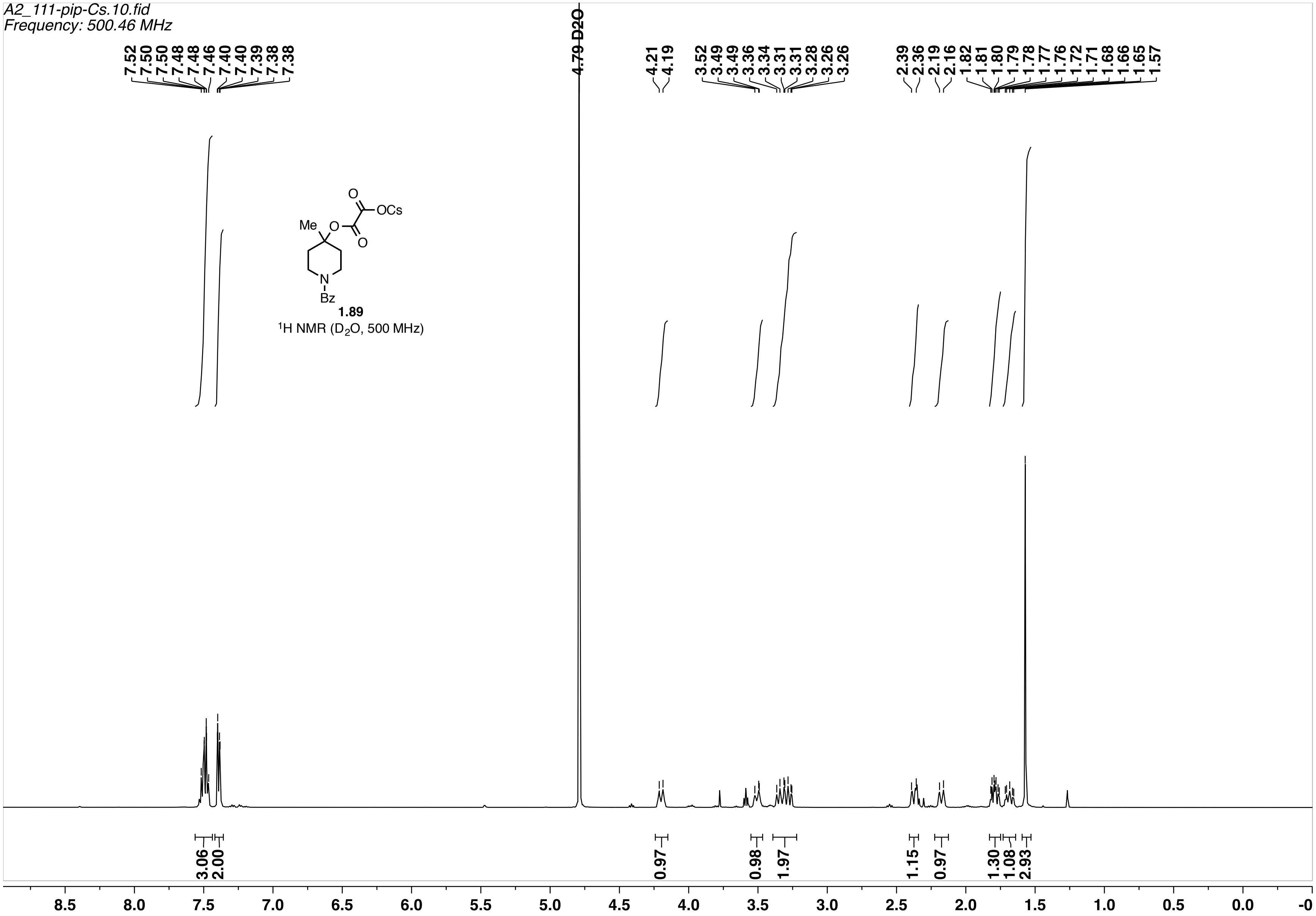
1.87

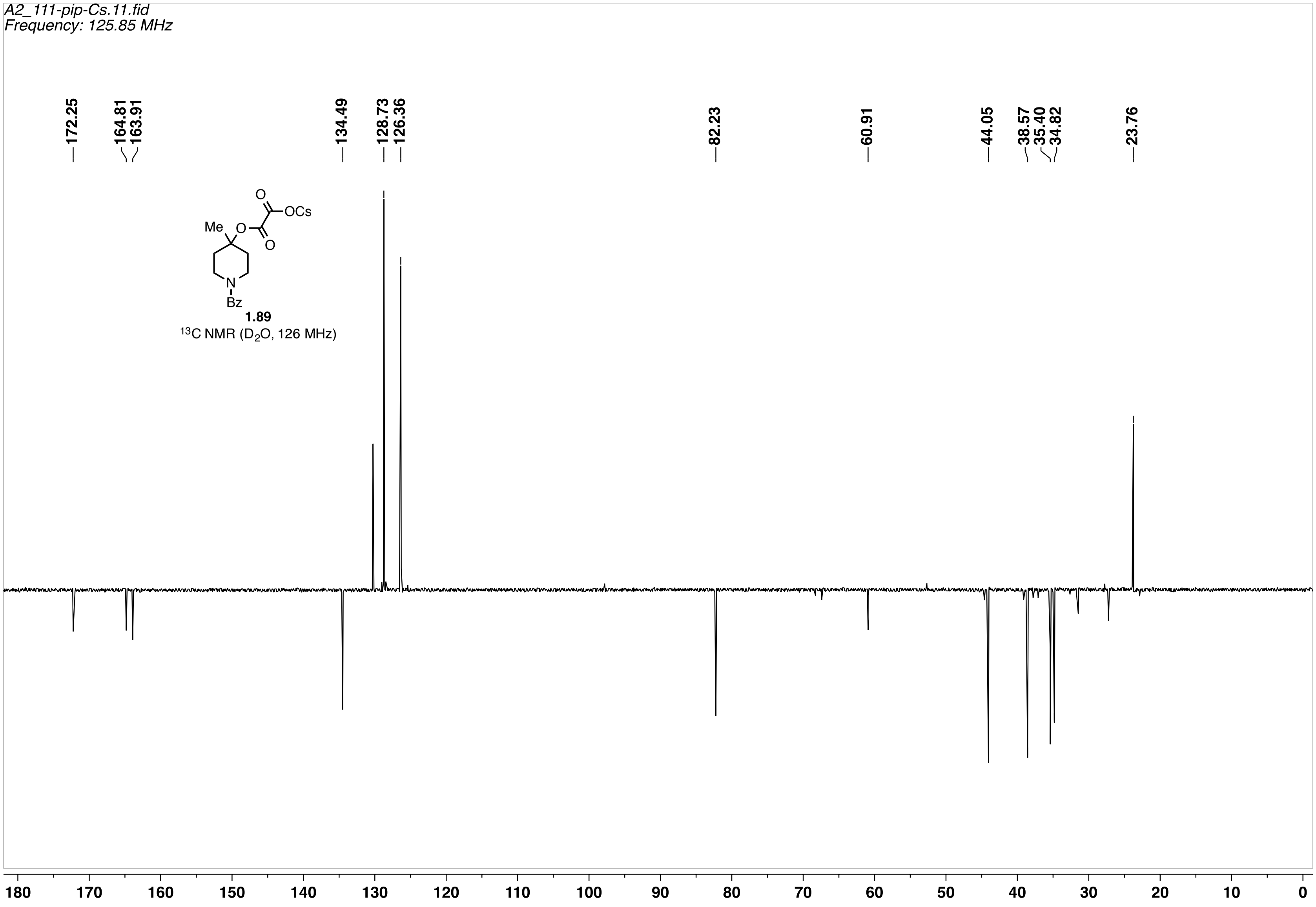
^{1}H NMR (D_2O, 500 MHz)



1.87

^{13}C NMR (D_2O, 126 MHz)


A2_111-pip-Cs.10.fid
Frequency: 500.46 MHz
7.52
7.50
7.50
7.48
7.48
7.46
7.40
7.40
7.39
7.38
7.38
4.79 D2O
4.21
4.19
3.52
3.49
3.49
3.36
3.34
3.31
3.31
3.28
3.26
3.26
2.39
2.36
2.19
2.16
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.72
1.71
1.68
1.66
1.65
1.57
Me
O
O
OCs
O
N
Bz
1.89
^{1}H NMR (D_2O, 500 MHz)
3.06
2.00
0.97
0.98
1.97
1.15
0.97
1.30
1.08
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0


A2_111-pip-Cs.11.fid
Frequency: 125.85 MHz

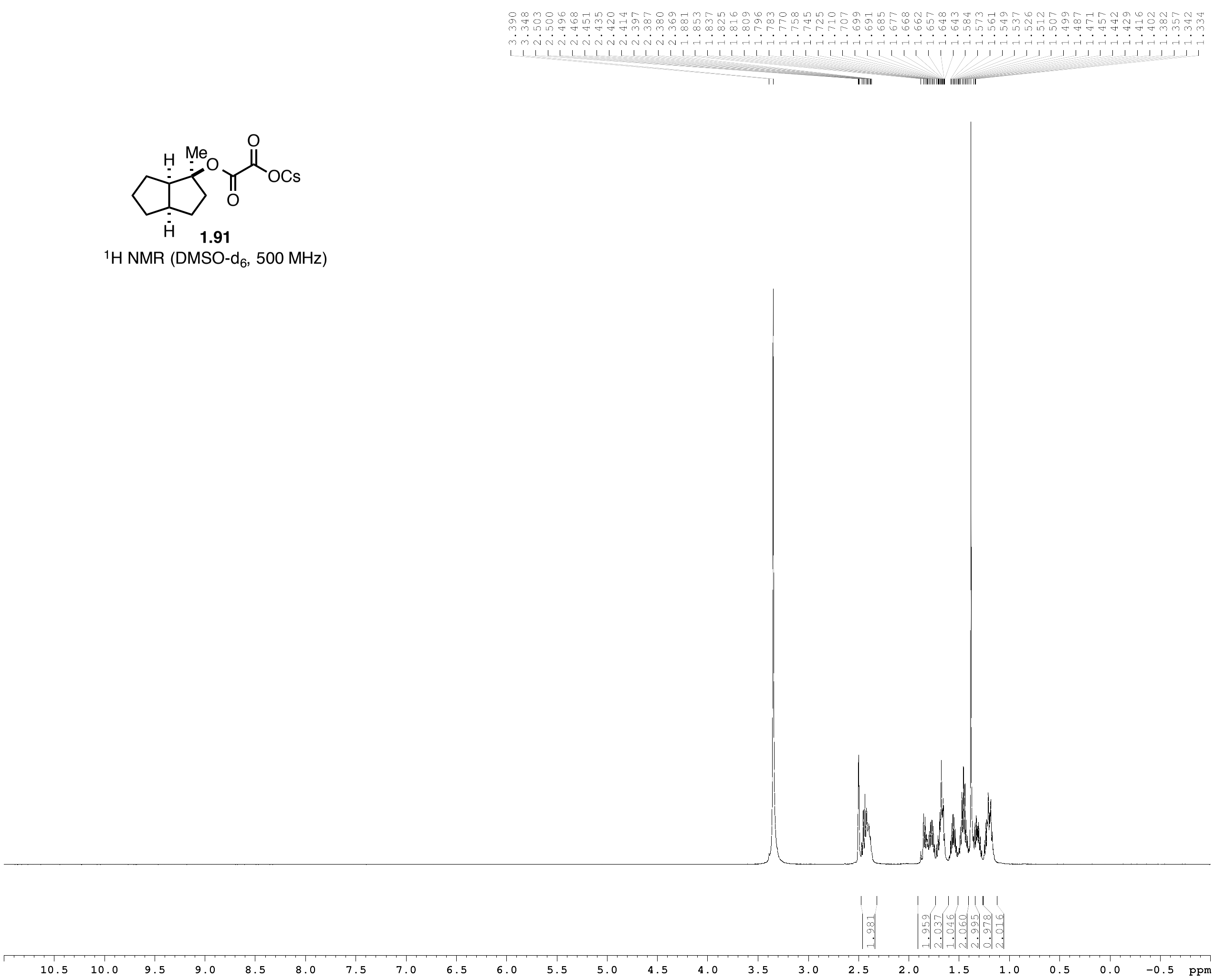
1.89

^{13}C NMR (D_2O, 126 MHz)

YS-II-288

1.91

^{1}H NMR (DMSO-d$_6$, 500 MHz)



```
Current Data Parameters
NAME          YS-II-288
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150306
Time              18.00
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                574.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

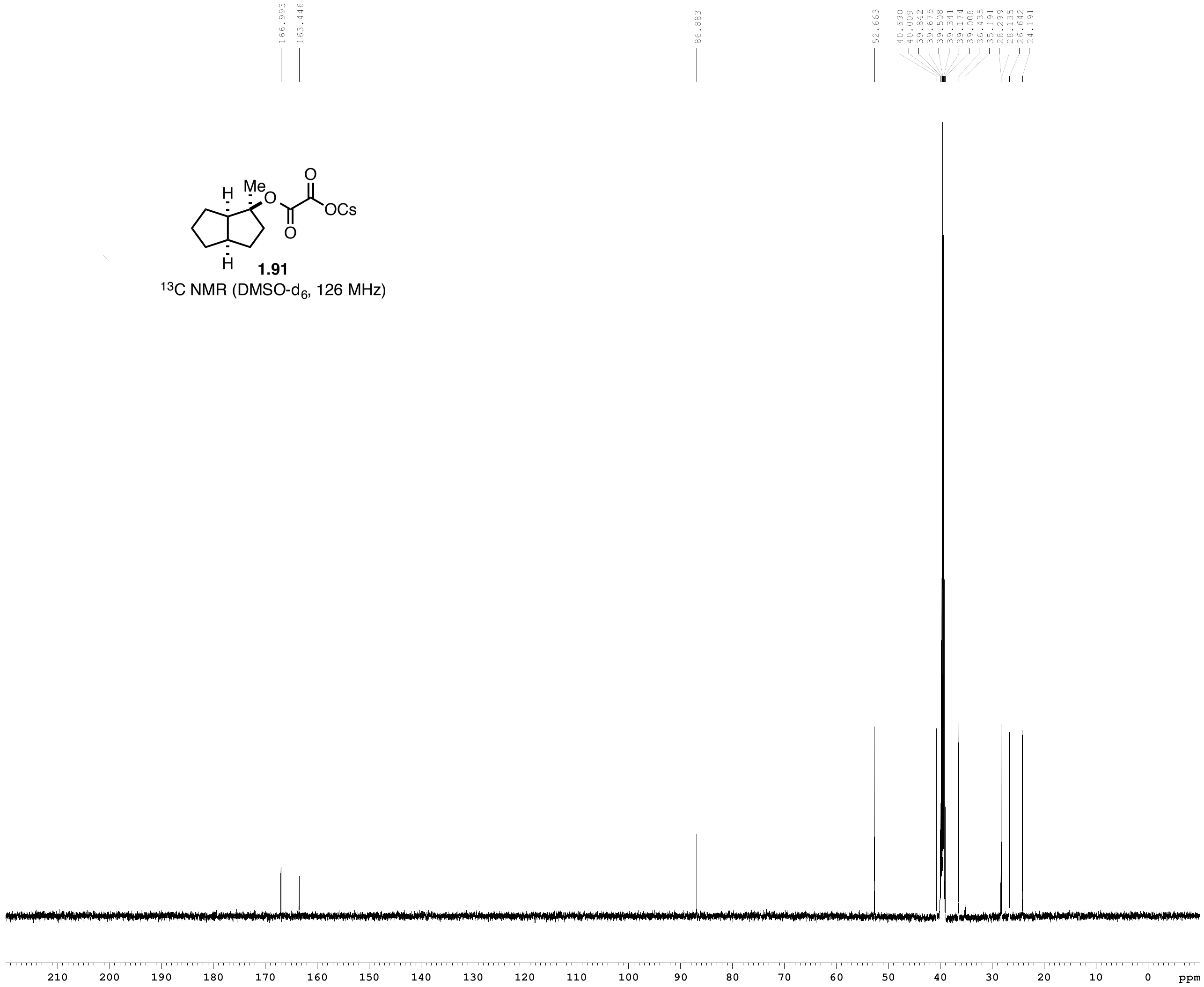
======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -5.80 dB
SFO1        499.1834943 MHz

F2 - Processing parameters
SI                65536
SF          499.1800085 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-288

1.91

^{13}C NMR (DMSO-d_6, 126 MHz)



```
Current Data Parameters
NAME          YS-II-288
EXPNO                 2
PROCNO                1

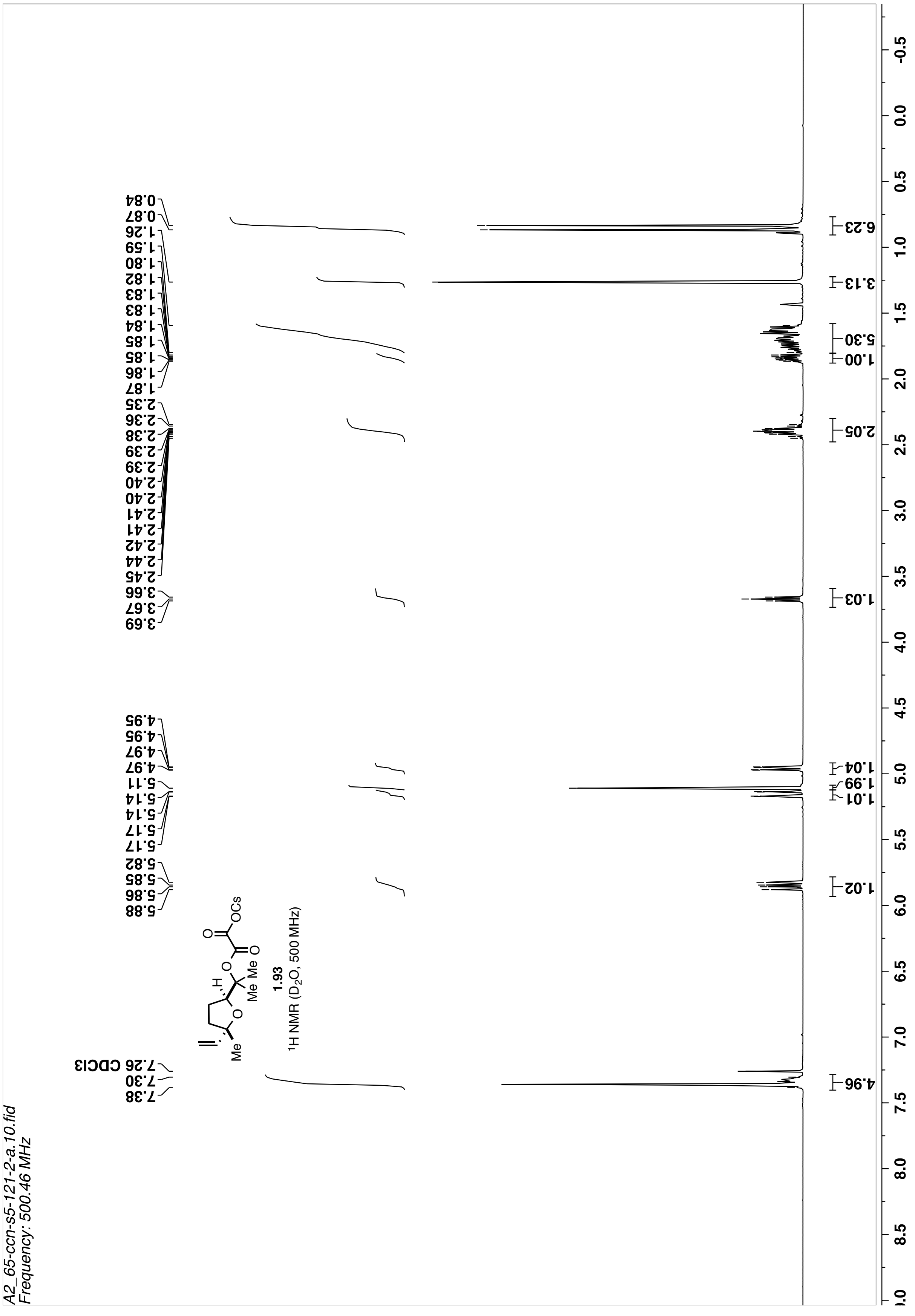
F2 - Acquisition Parameters
Date_          20150309
Time              10.56
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  248
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              10321.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

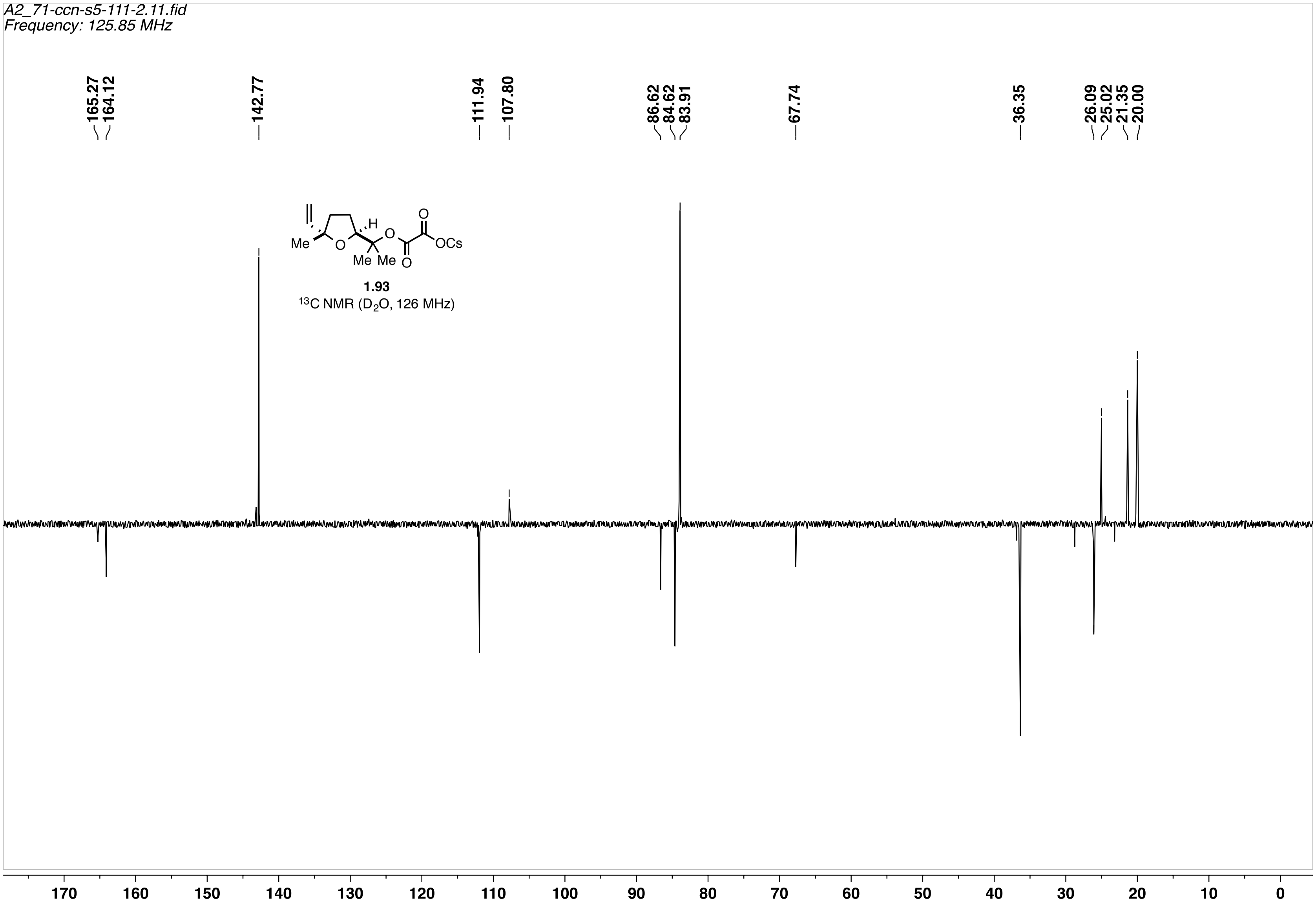
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804793 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

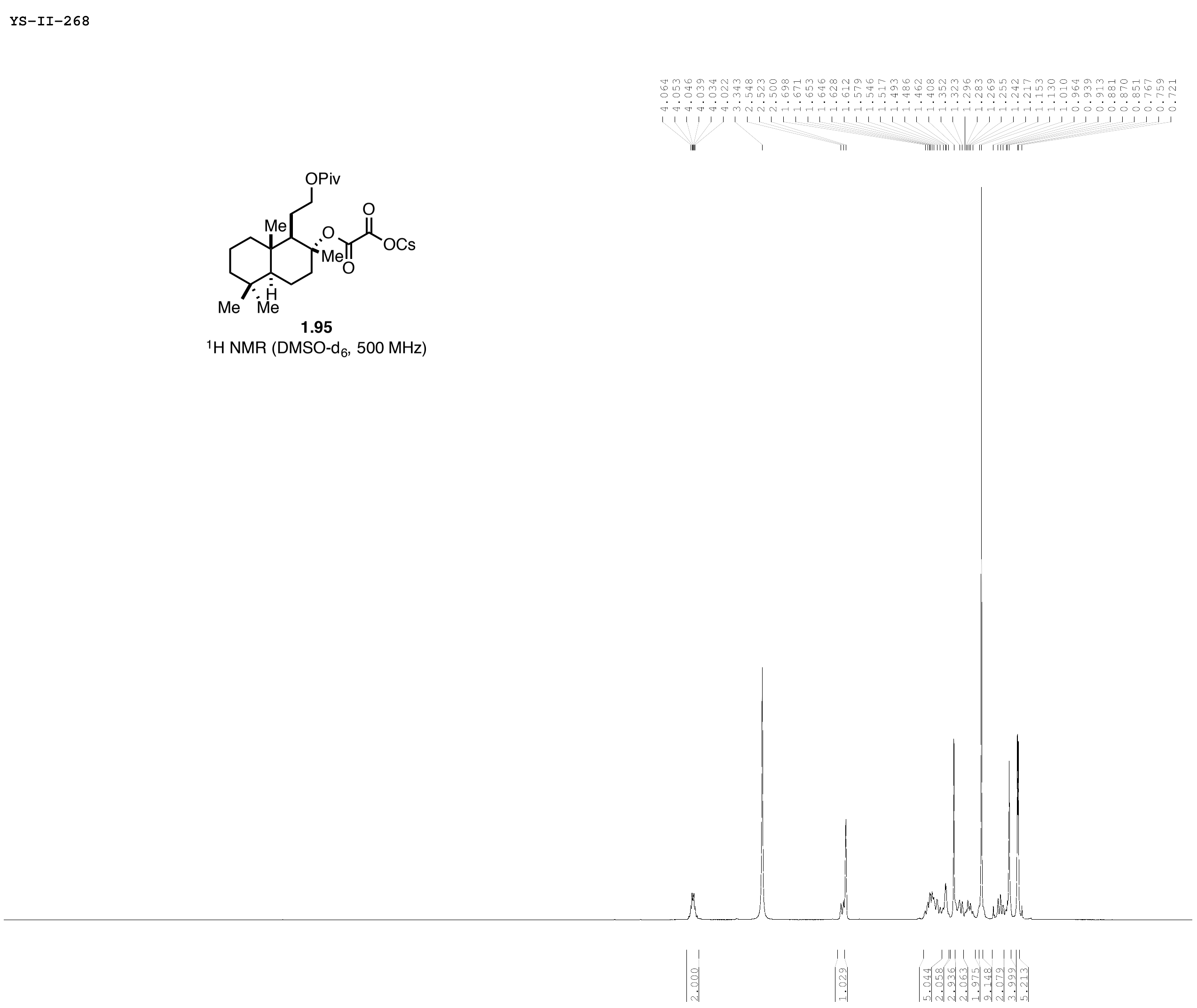

A2_65-ccn-s5-121-2-a.10.fid
Frequency: 500.46 MHz
1.93
1H NMR (D2O, 500 MHz)
OCs
Me
Me Me
H
O
7.38
7.30
7.26 CDCl3
5.88
5.86
5.85
5.82
5.17
5.17
5.14
5.14
5.11
4.97
4.97
4.95
4.95
3.69
3.67
3.66
2.45
2.44
2.42
2.41
2.41
2.40
2.40
2.39
2.39
2.38
2.36
2.35
1.87
1.86
1.85
1.85
1.84
1.83
1.83
1.82
1.80
1.59
1.26
0.87
0.84
4.96
1.02
1.01
1.99
1.04
1.03
2.05
1.00
5.30
3.13
6.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



1.93

^{13}C NMR (D_2O, 126 MHz)

YS-II-268



1.95

^{1}H NMR (DMSO-d$_6$, 500 MHz)

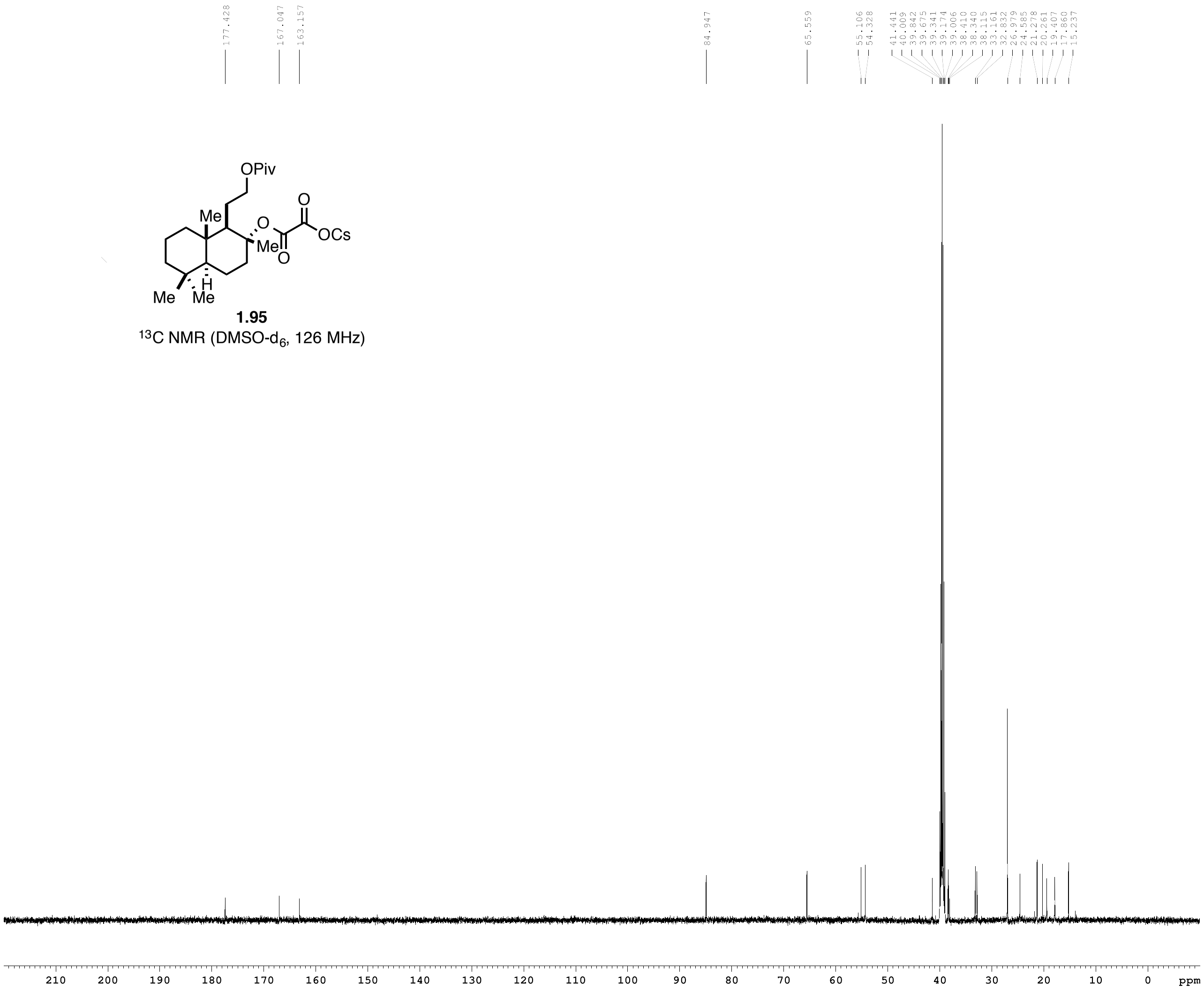
```
Current Data Parameters
NAME          YS-II-268
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150225
Time               9.44
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH           8012.820 Hz
FIDRES        0.250026 Hz
AQ           1.9997952 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200128 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-268



1.95

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-268
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150225
Time               9.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  352
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

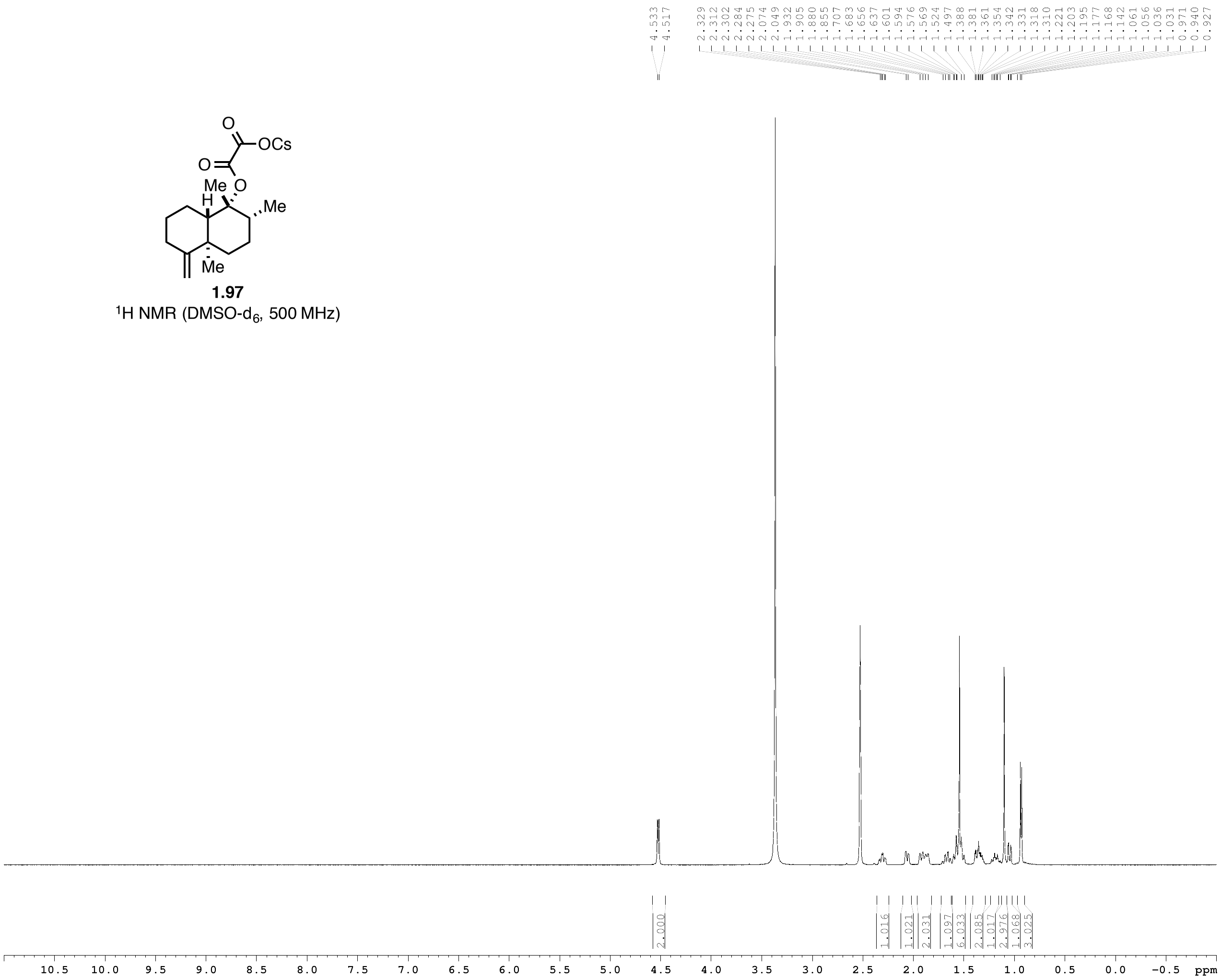
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804795 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-284

1.97

^{1}H NMR (DMSO-d$_6$, 500 MHz)



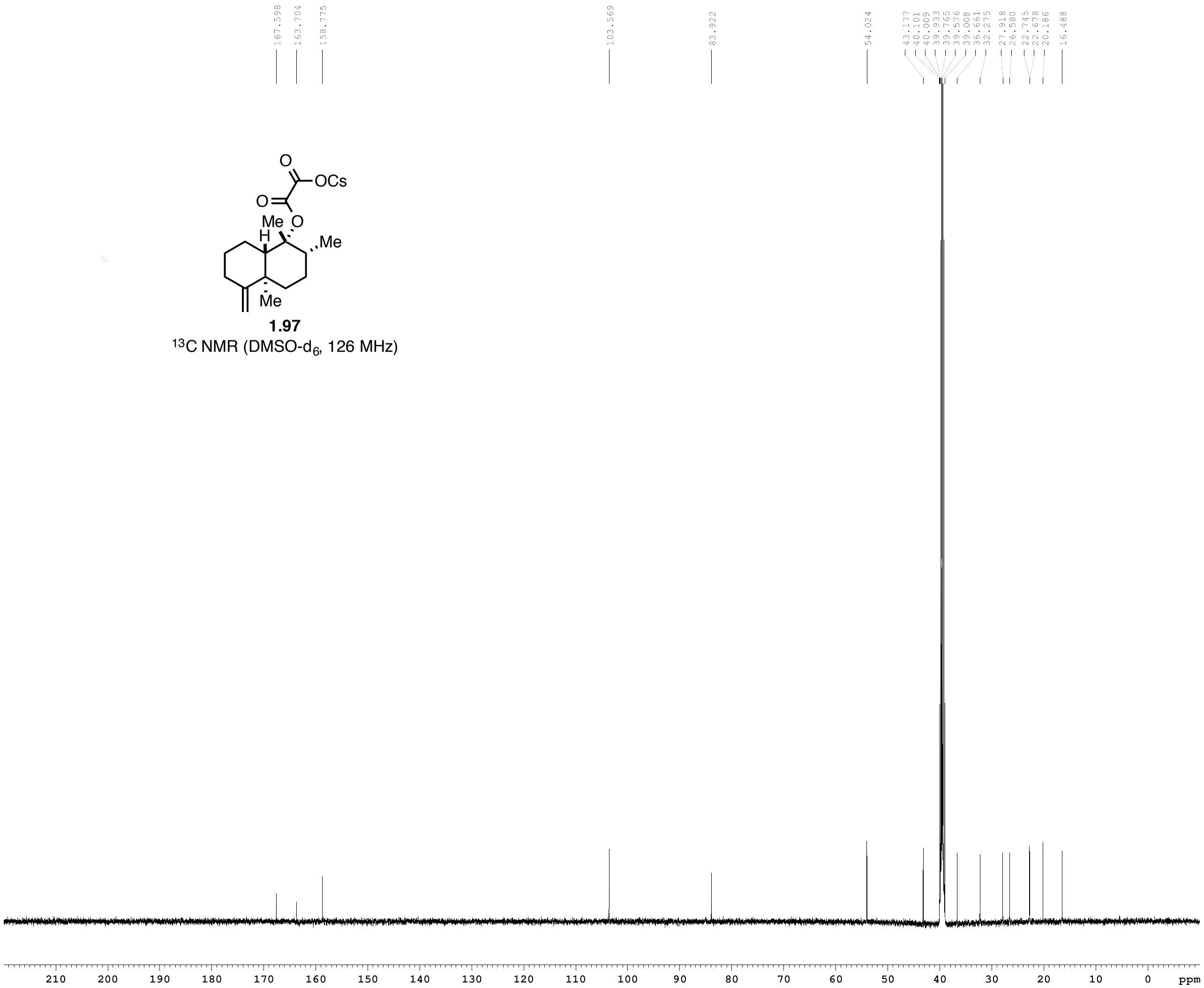
```
Current Data Parameters
NAME          YS-II-284
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150306
Time               8.44
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200000 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-284



1.97

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-284
EXPNO                 3
PROCNO                1

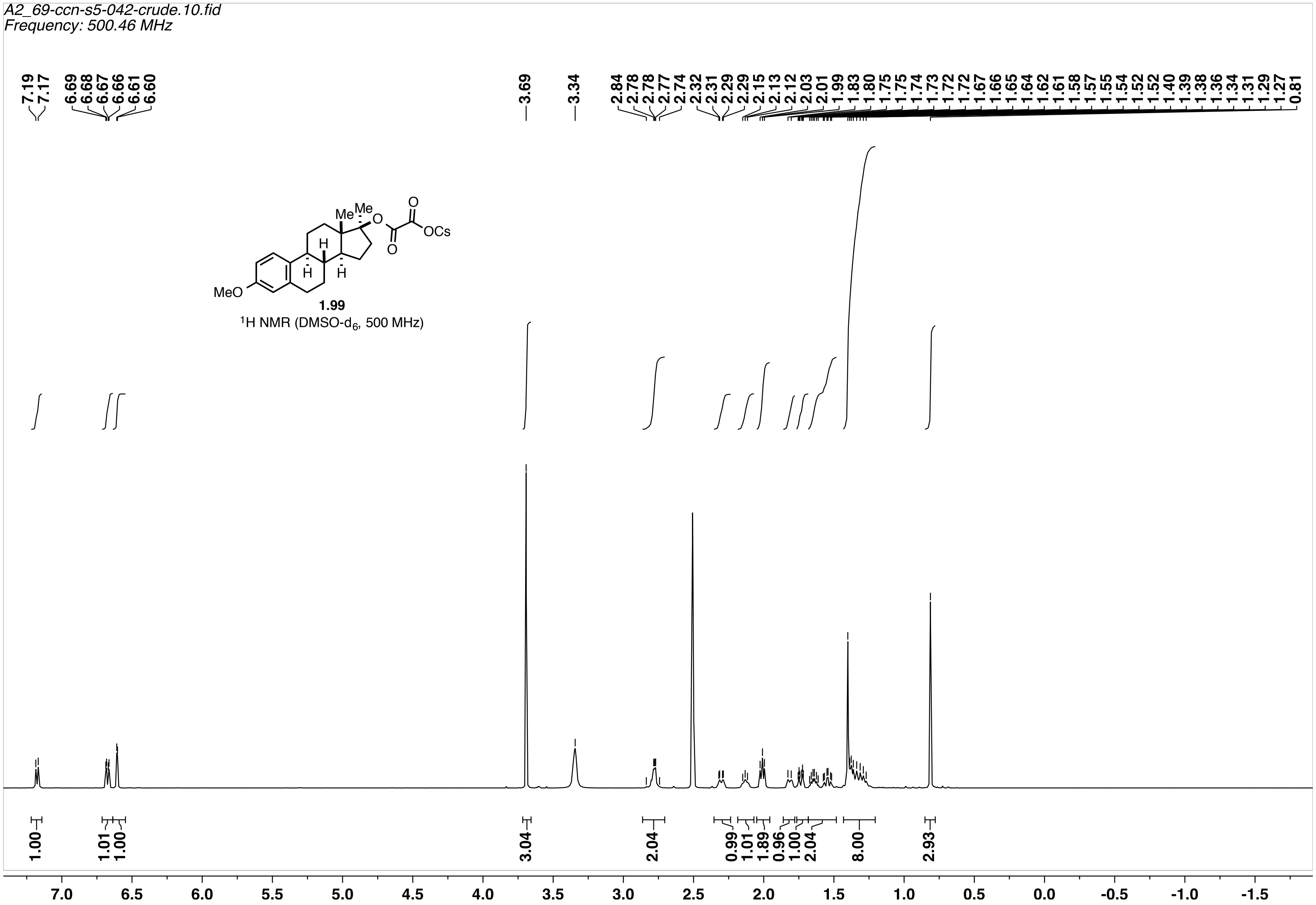
F2 - Acquisition Parameters
Date_          20150306
Time               8.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

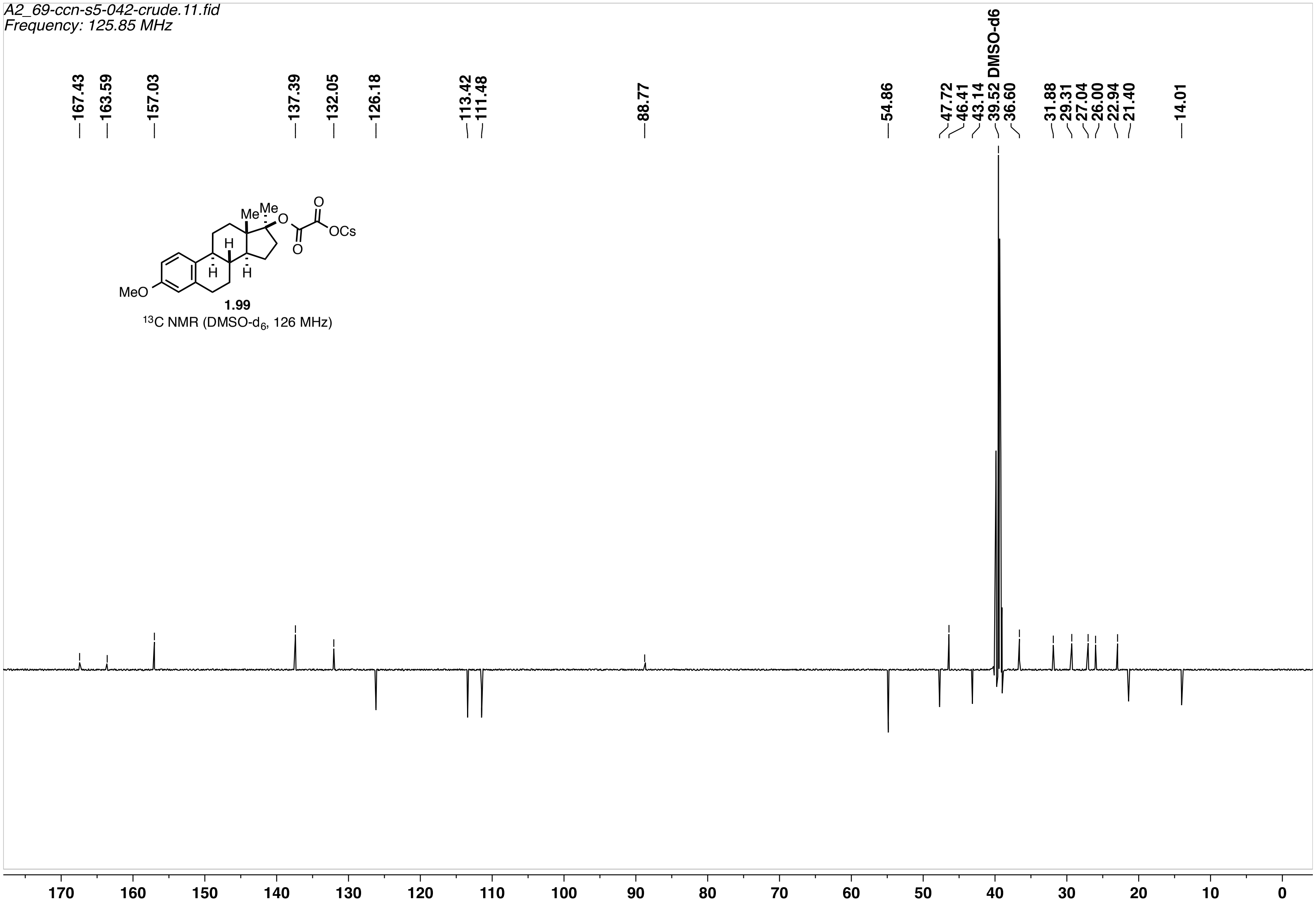
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804793 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



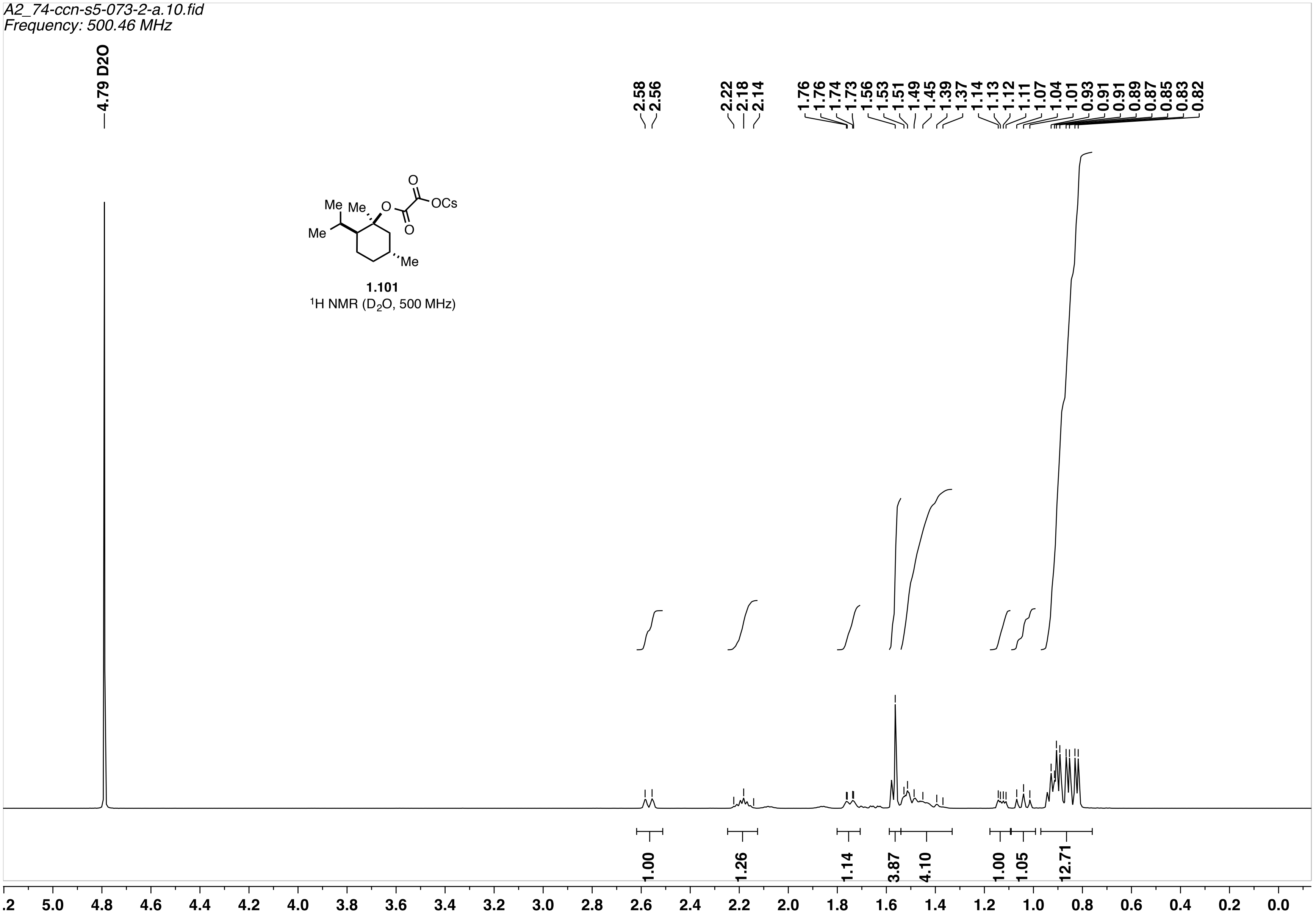
1.99

^{1}H NMR (DMSO-d_6, 500 MHz)



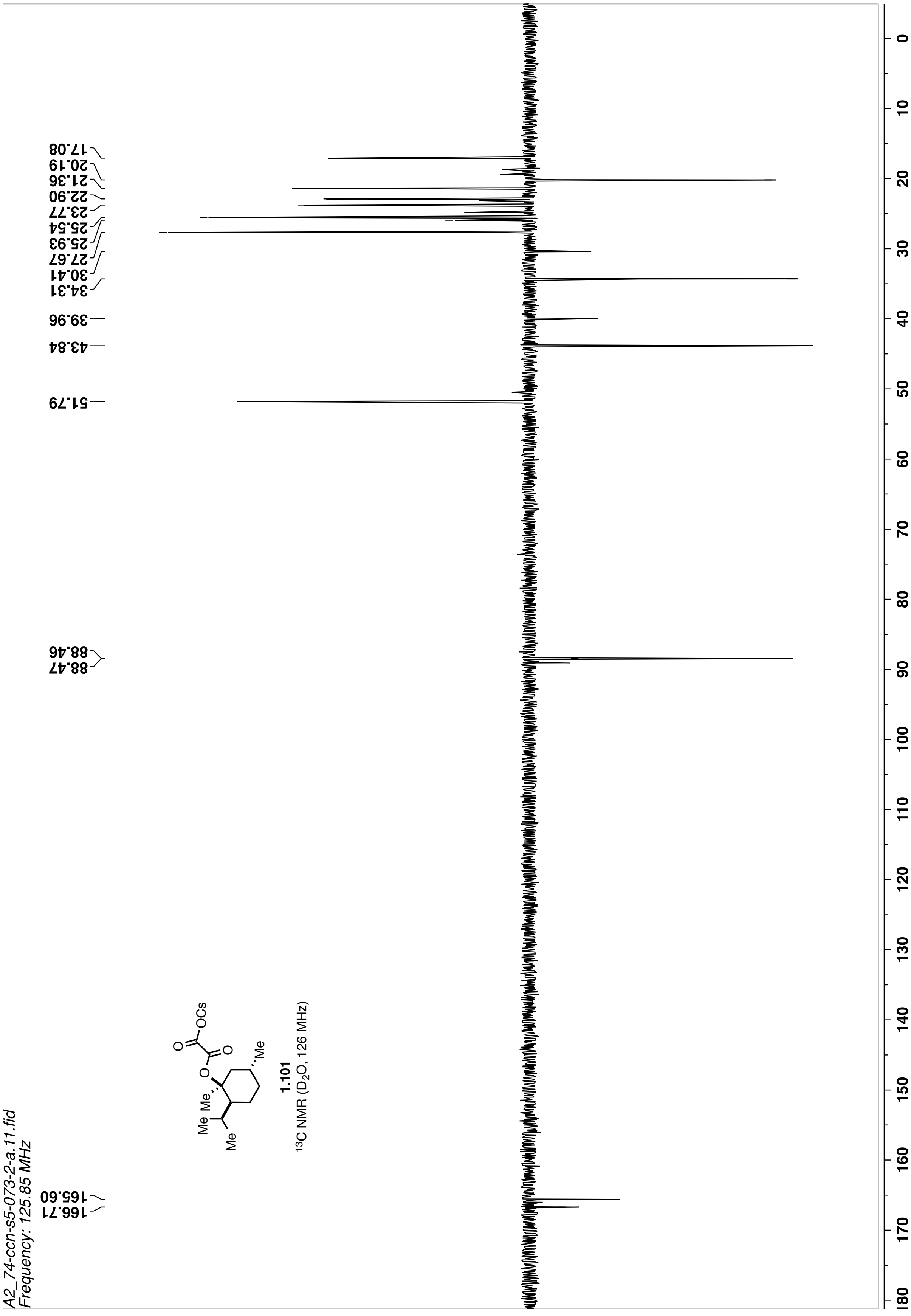
1.99

^{13}C NMR (DMSO-d_6, 126 MHz)



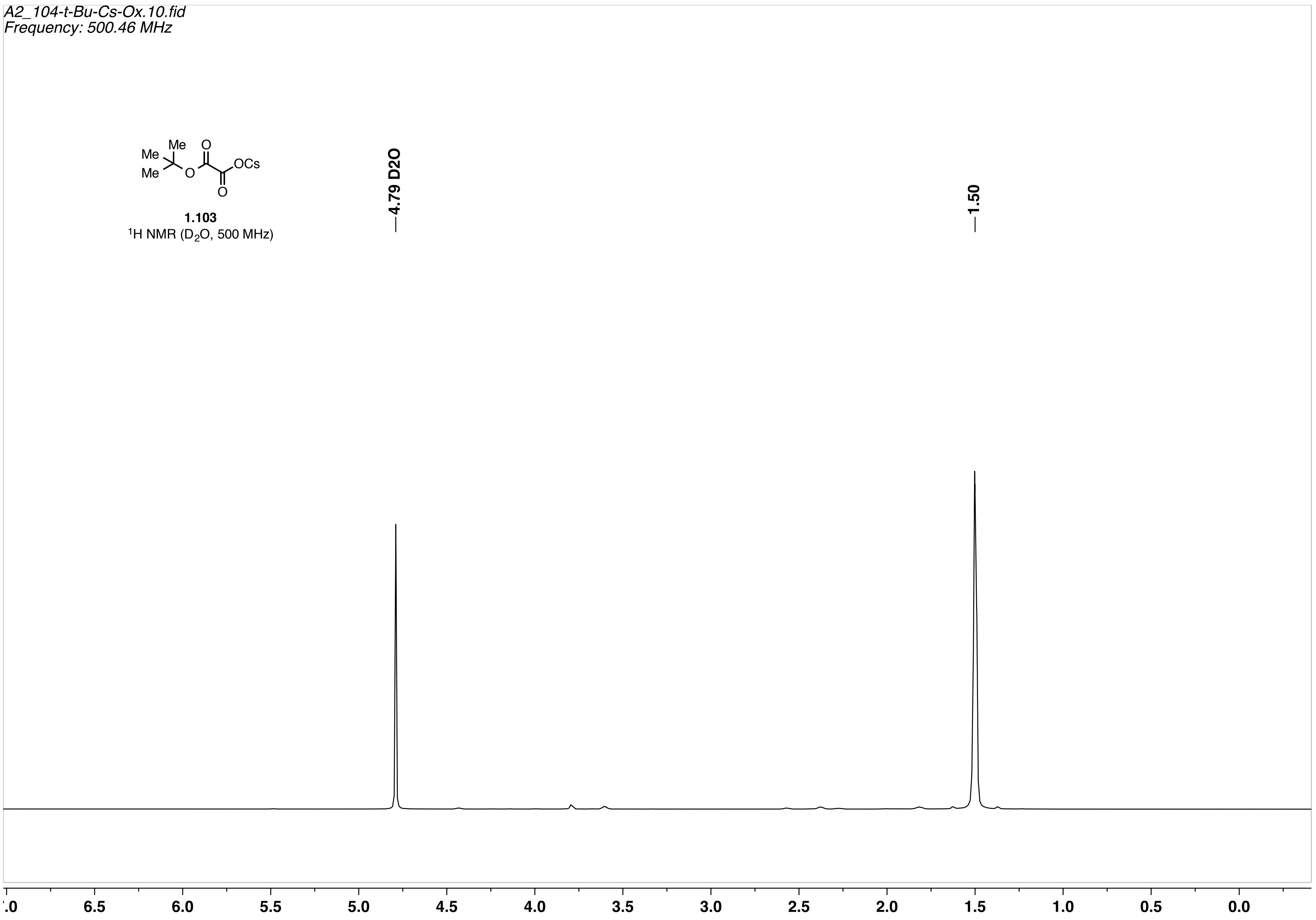
1.101

^{1}H NMR (D_2O, 500 MHz)



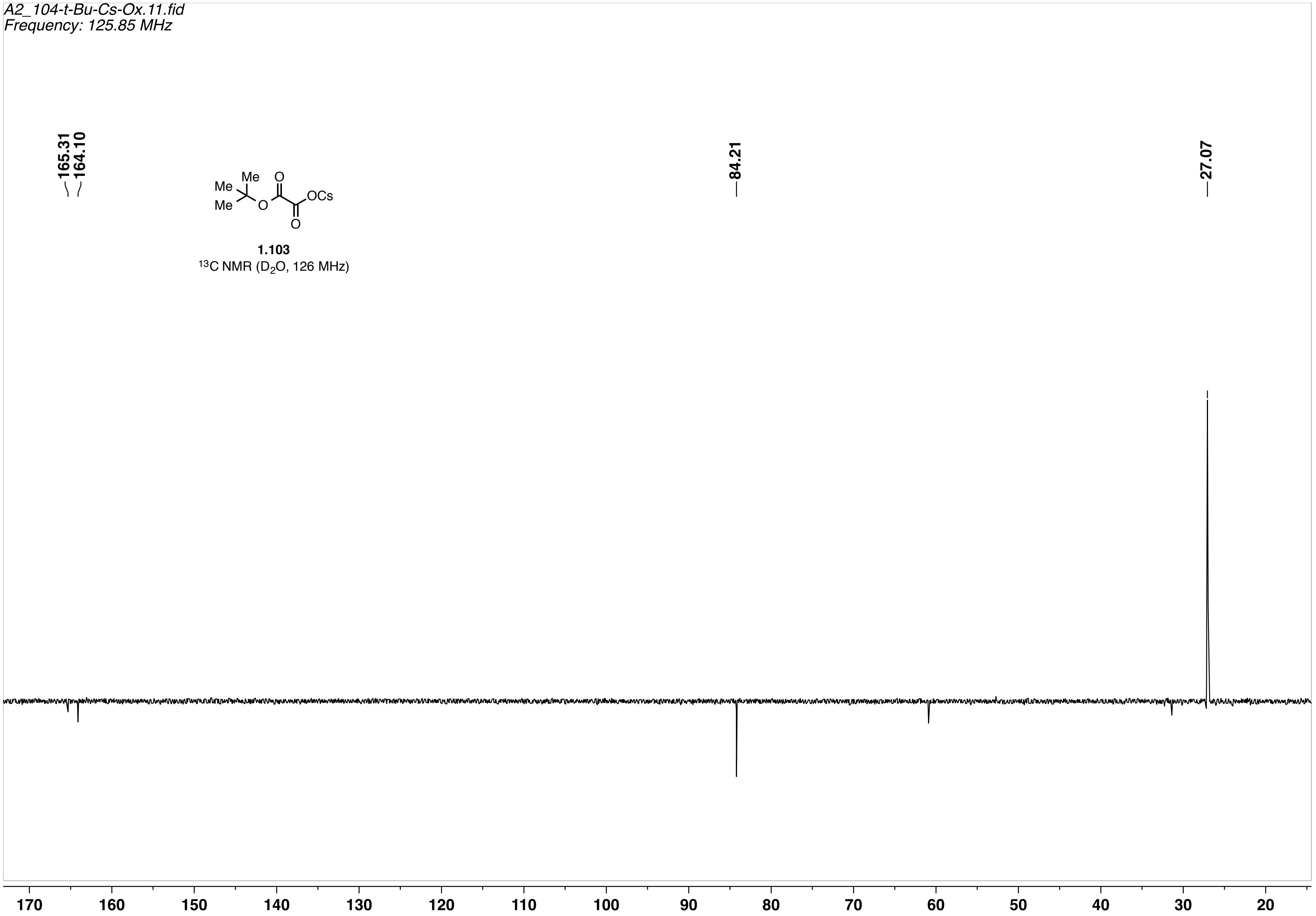
1.101

^{13}C NMR (D_2O, 126 MHz)



1.103

^{1}H NMR (D_2O, 500 MHz)



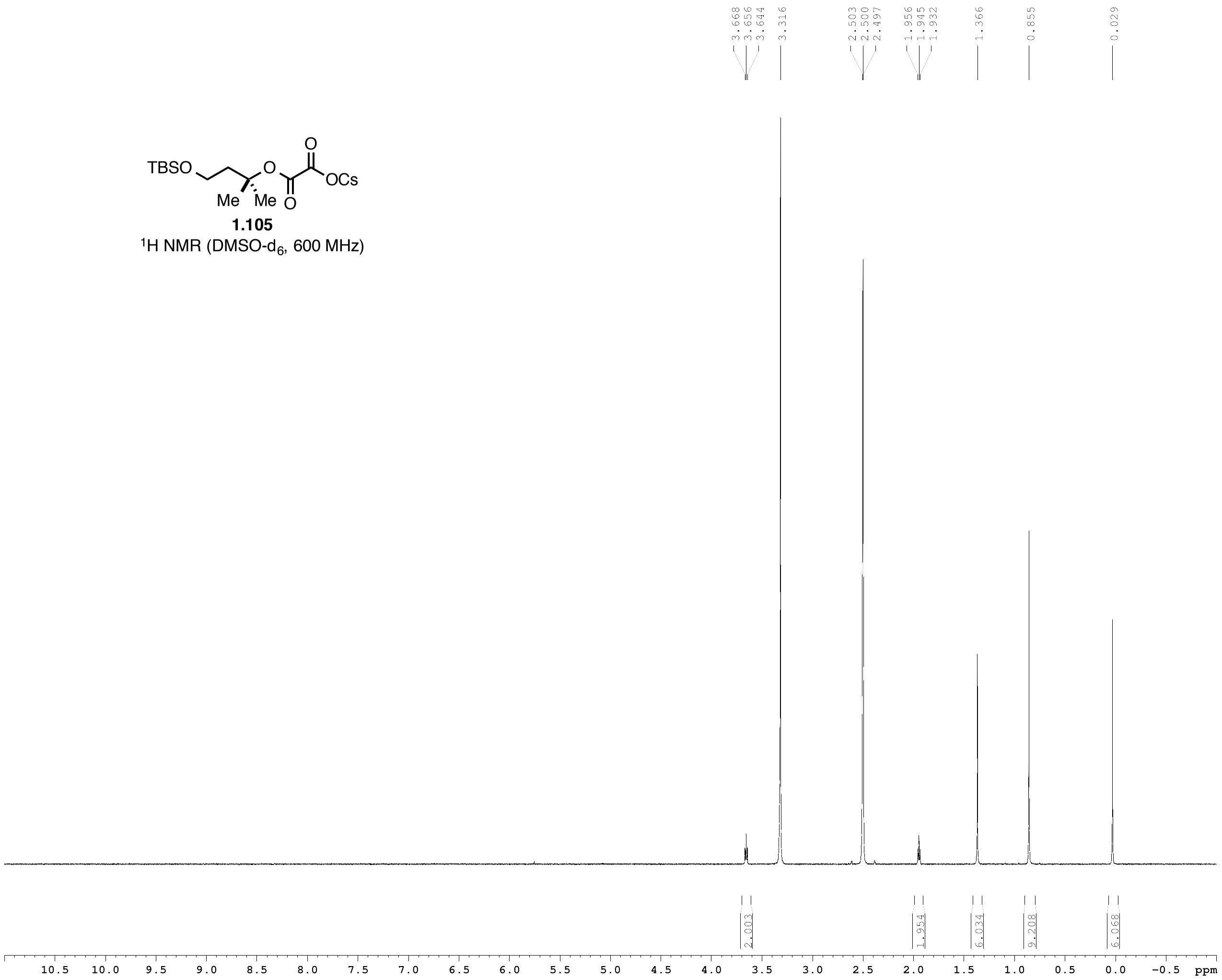
1.103

^{13}C NMR (D_2O, 126 MHz)

YS-II-202

1.105

^{1}H NMR (DMSO-d$_6$, 600 MHz)



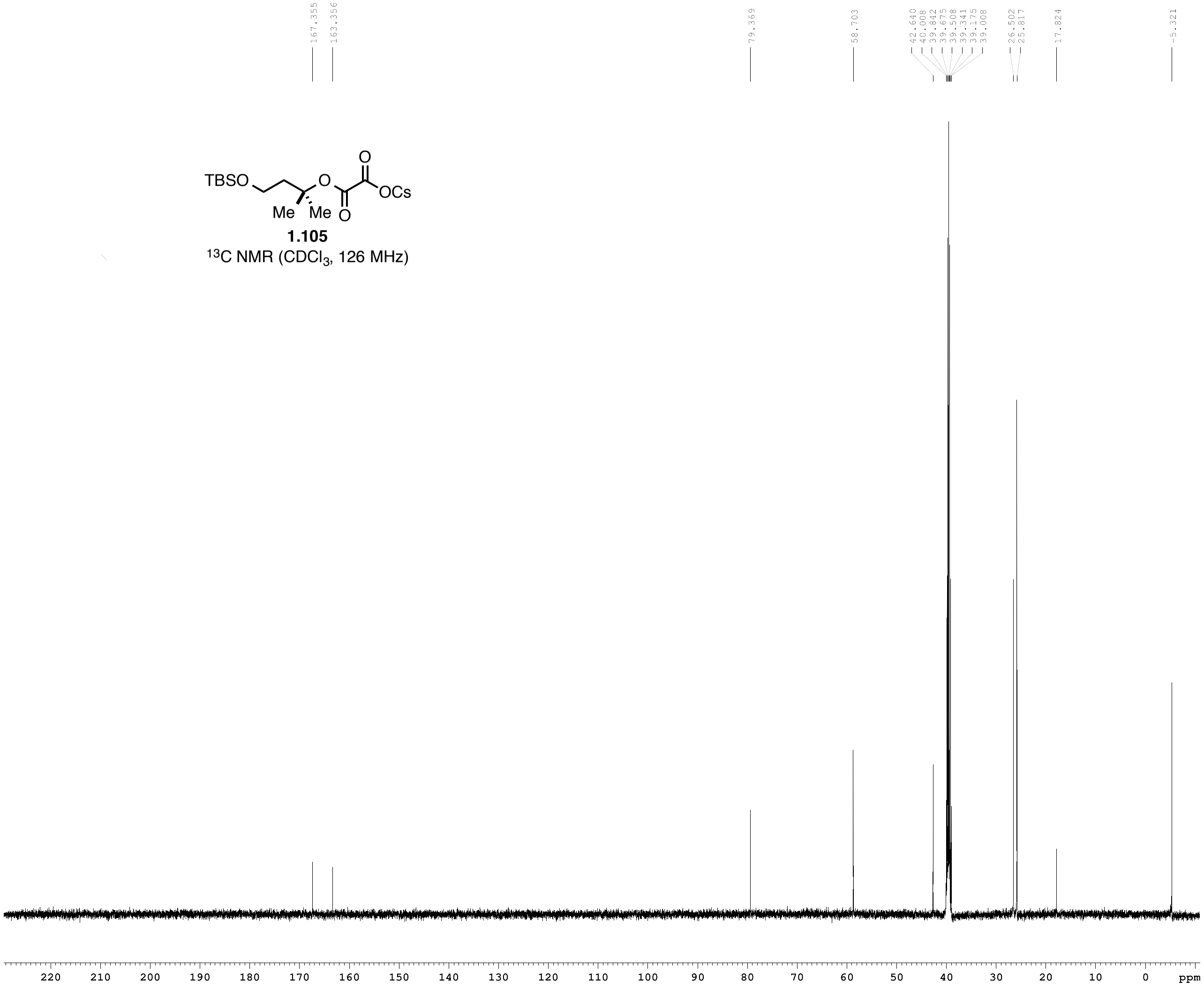
```
Current Data Parameters
NAME          YS-II-202
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150127
Time               8.49
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                98074
SOLVENT            DMSO
NS                    8
DS                    2
SWH           9615.385 Hz
FIDRES        0.098042 Hz
AQ           5.0998478 sec
RG                 2050
DW               52.000 usec
DE                14.54 usec
TE                298.0 K
D1          0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300134 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-202



1.105

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-202
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20150425
Time               9.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  144
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              11585.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

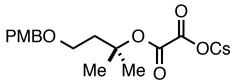
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

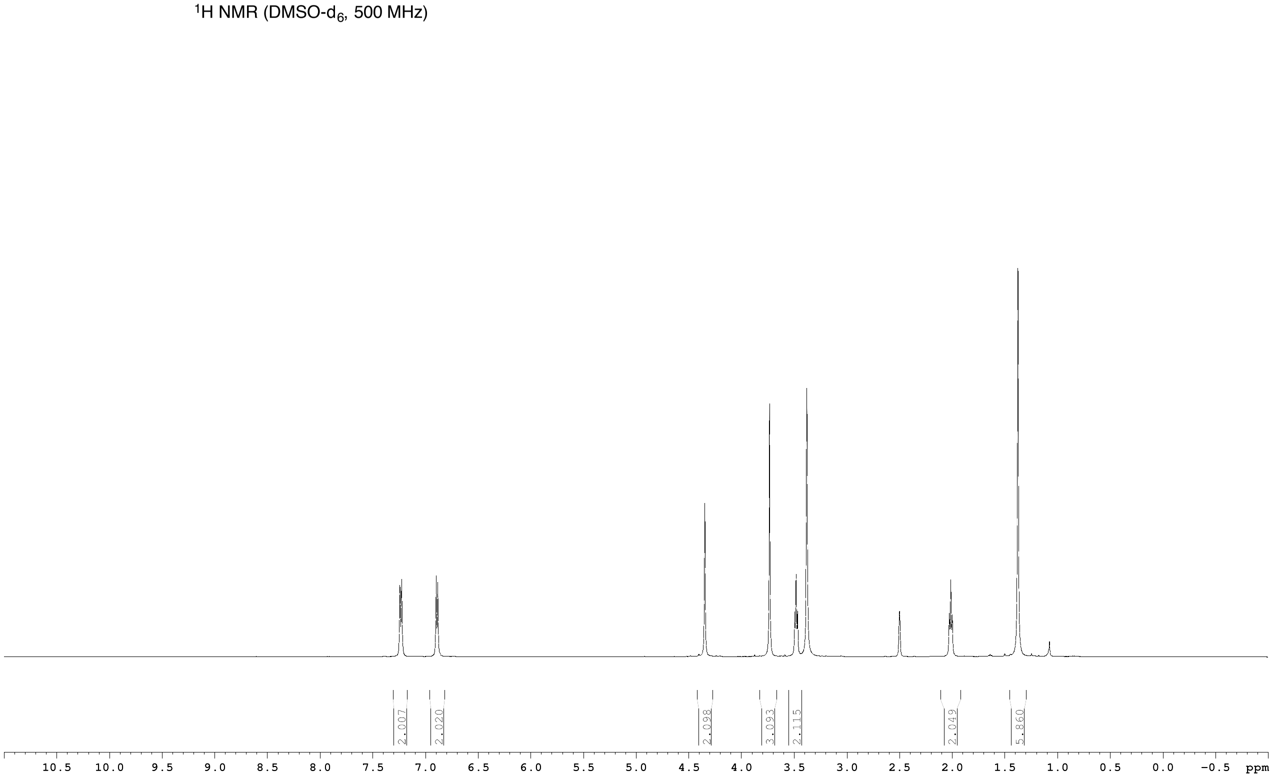
F2 - Processing parameters
SI                65536
SF          125.7805484 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-260



1.107

^{1}H NMR (DMSO-d_6, 500 MHz)



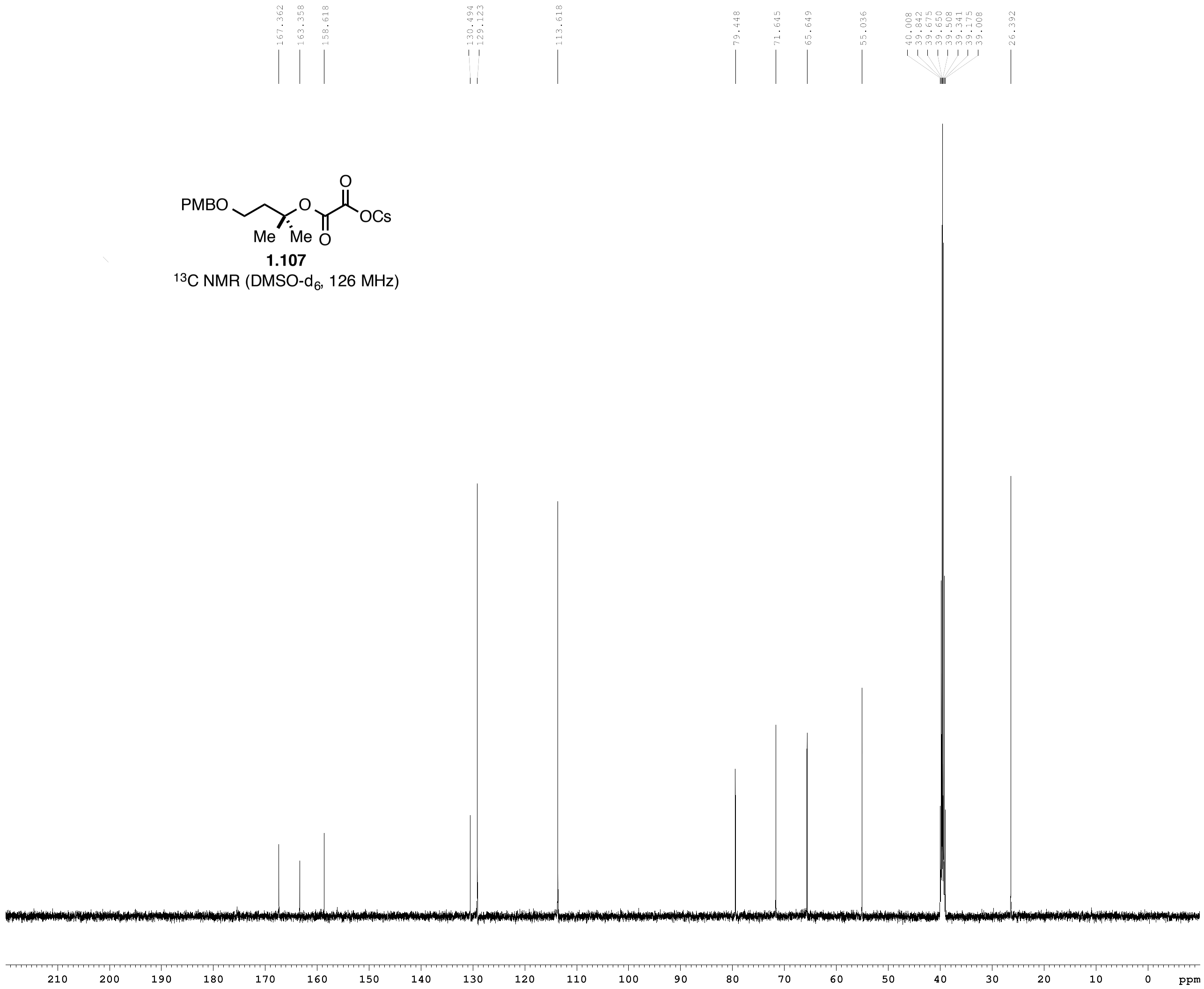
```
Current Data Parameters
NAME          YS-II-260
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150220
Time              13.25
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH           8012.820 Hz
FIDRES        0.250026 Hz
AQ           1.9997952 sec
RG                  5.7
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST   0 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200138 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-260



1.107

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-260
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150220
Time              13.29
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  128
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

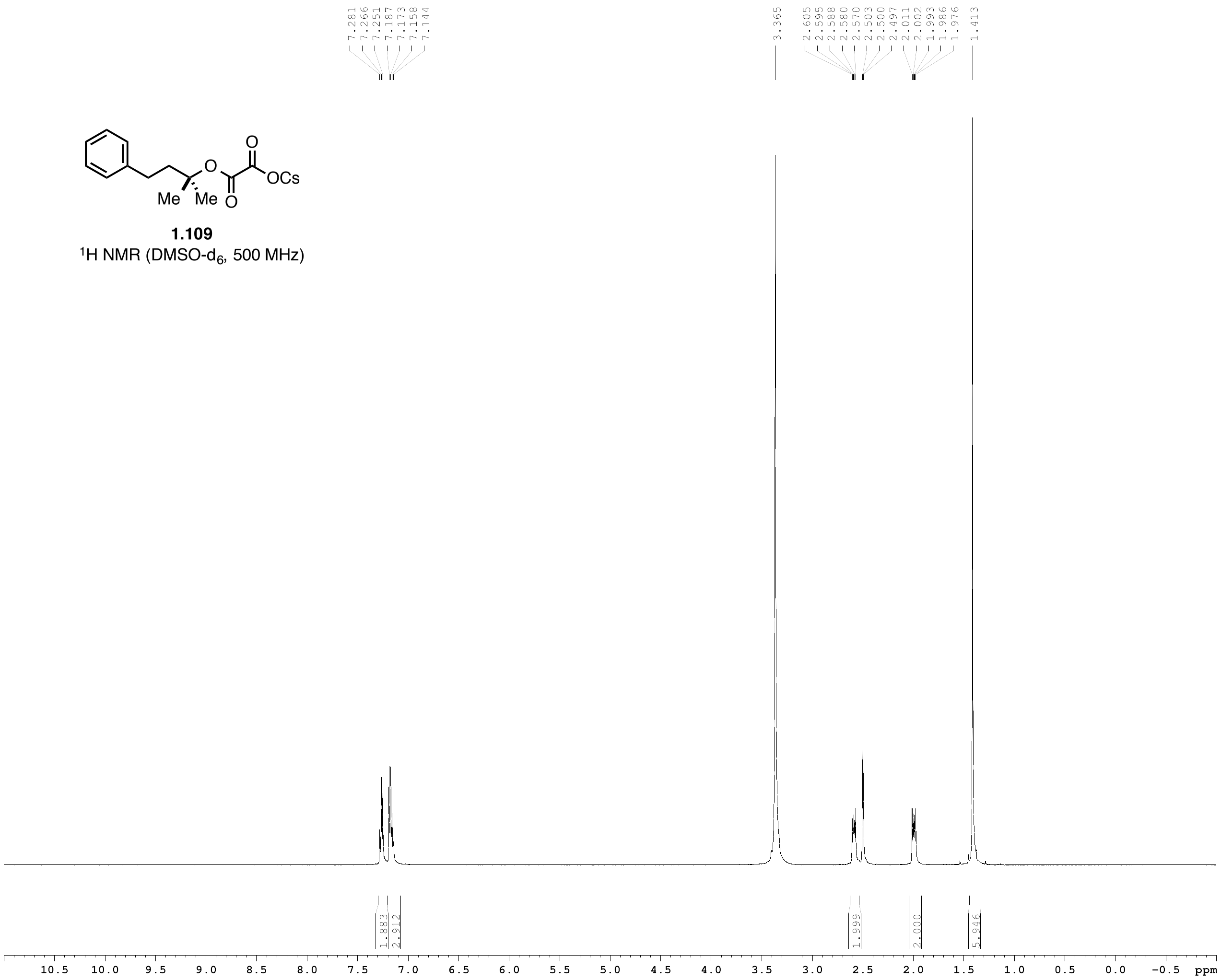
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804781 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-195

1.109

^{1}H NMR (DMSO-d_6, 500 MHz)



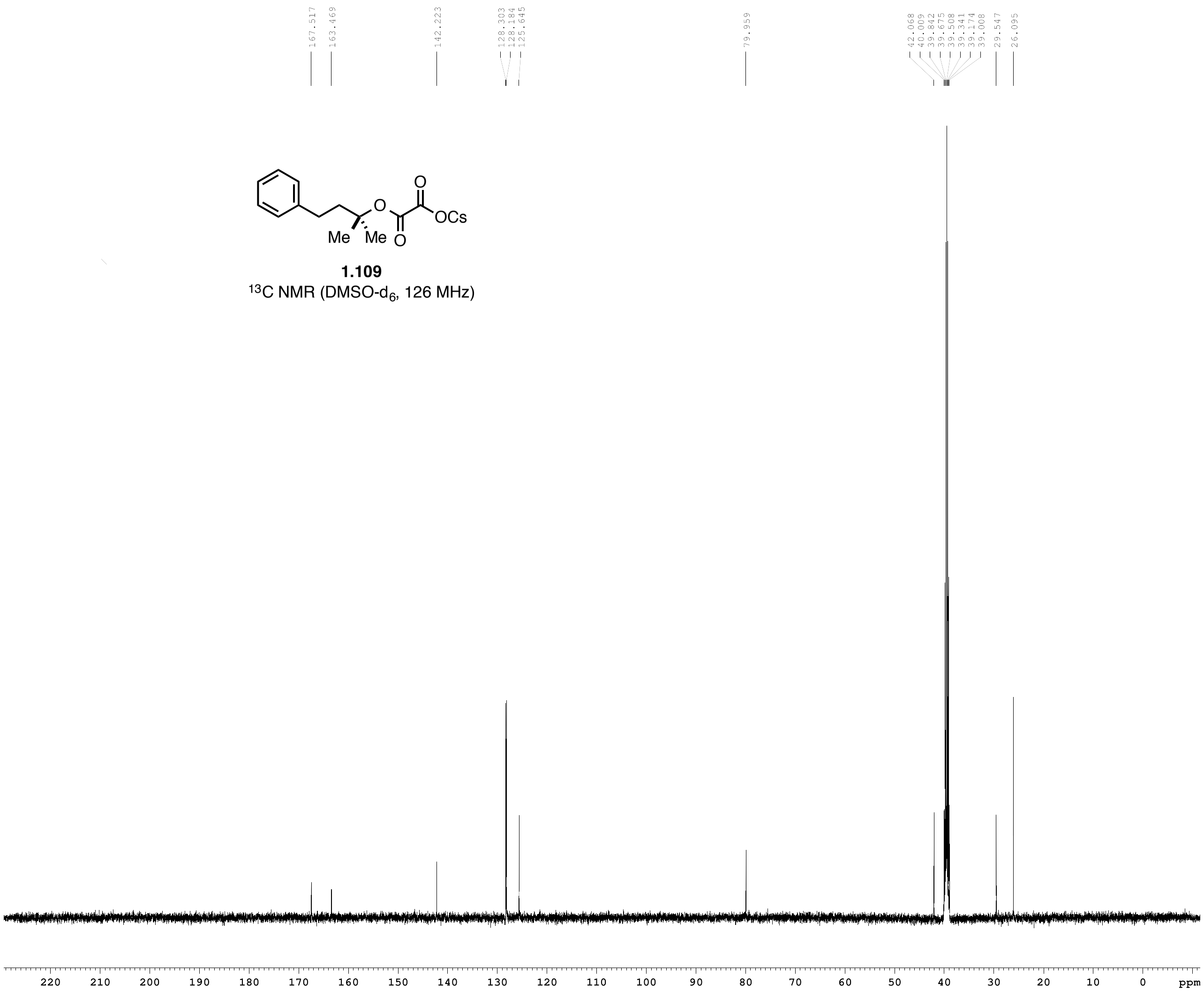
```
Current Data Parameters
NAME          YS-II-195
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150502
Time              14.16
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                32048
SOLVENT            DMSO
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                912.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -5.80 dB
SFO1        499.1834943 MHz

F2 - Processing parameters
SI                65536
SF          499.1800087 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-195



1.109

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-195
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150425
Time               9.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  160
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

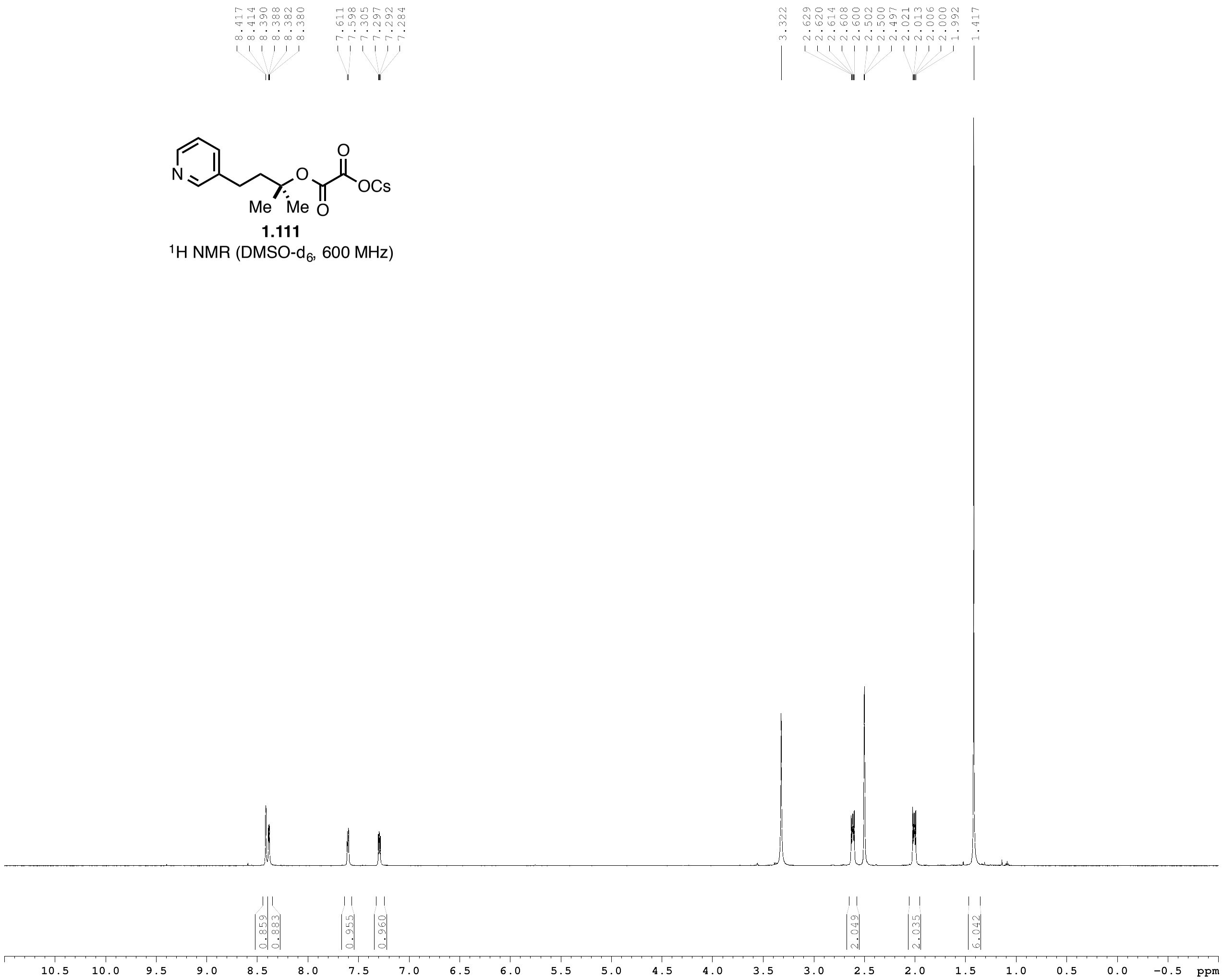
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7805494 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-41



1.111

^{1}H NMR (DMSO-d_6, 600 MHz)

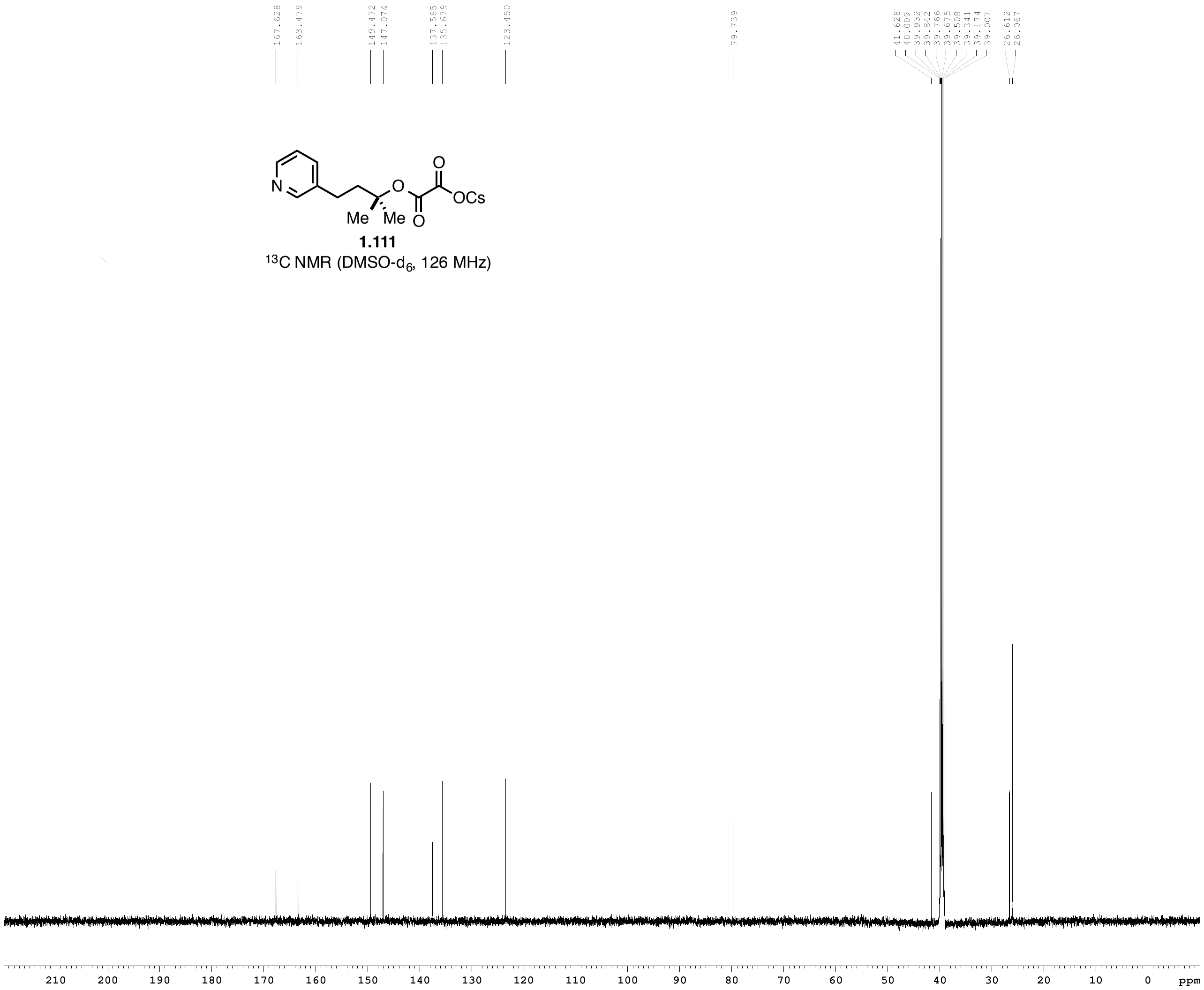
```
Current Data Parameters
NAME          YS-III-41
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150404
Time              14.53
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                38460
SOLVENT            DMSO
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                  512
DW               52.000 usec
DE                14.33 usec
TE                298.1 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.00 usec
PLW1        60.25600052 W

F2 - Processing parameters
SI                65536
SF          600.1300122 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-III-41



1.111

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-41
EXPNO                 2
PROCNO                1

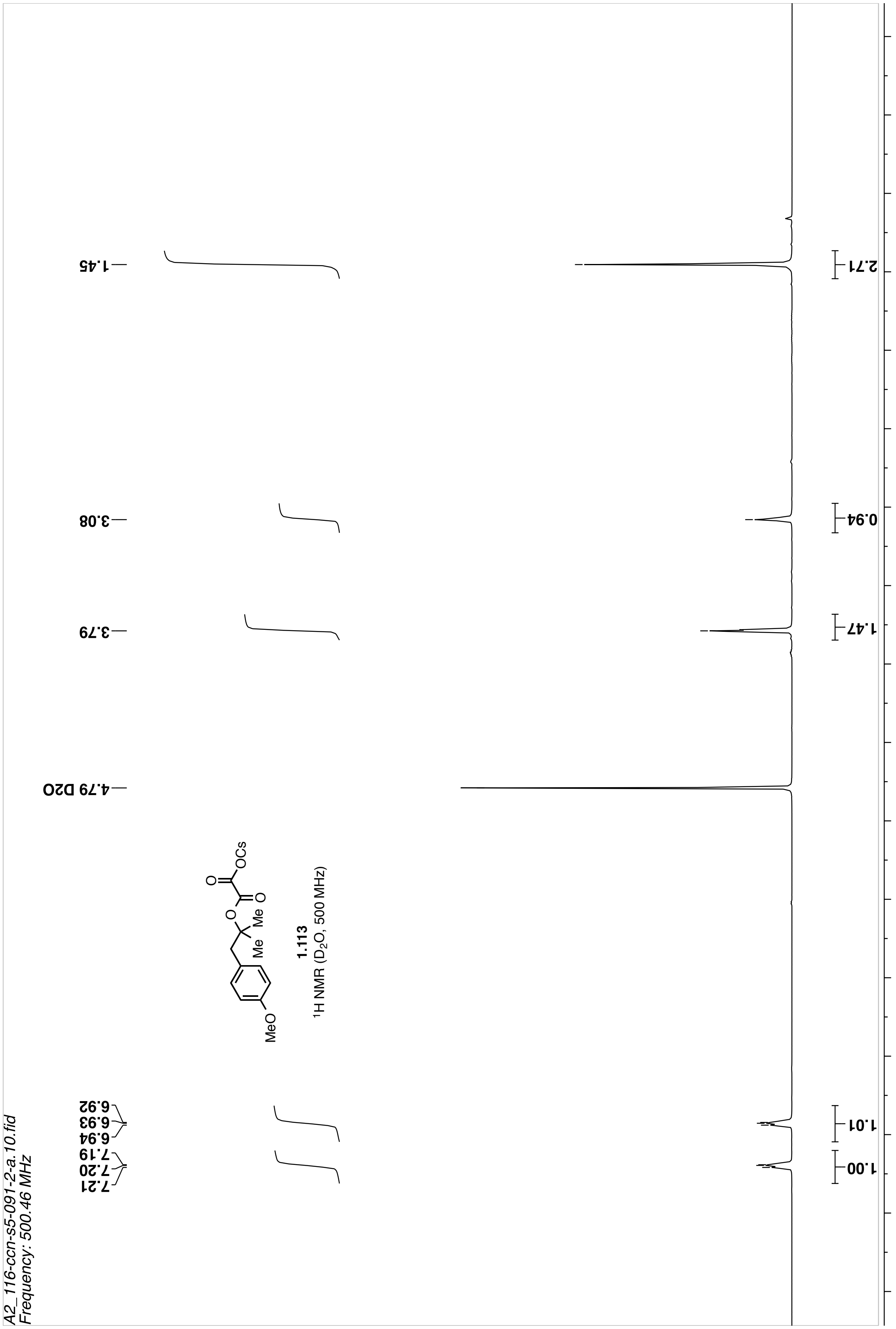
F2 - Acquisition Parameters
Date_          20150404
Time              15.23
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            DMSO
NS                  416
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

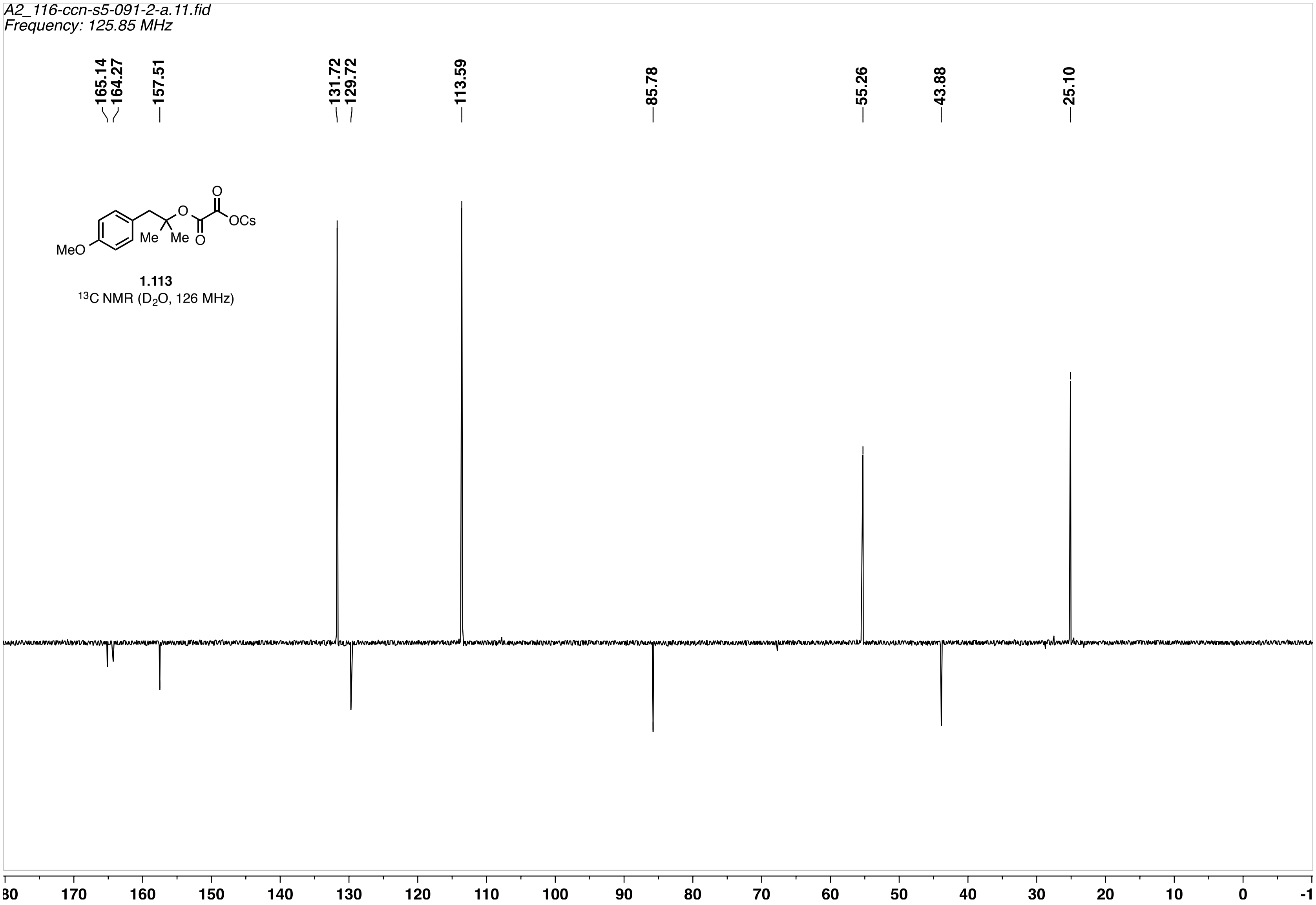
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7805417 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



1.113

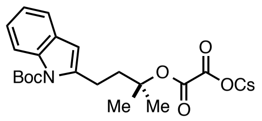
^{1}H NMR (D_2O, 500 MHz)



1.113

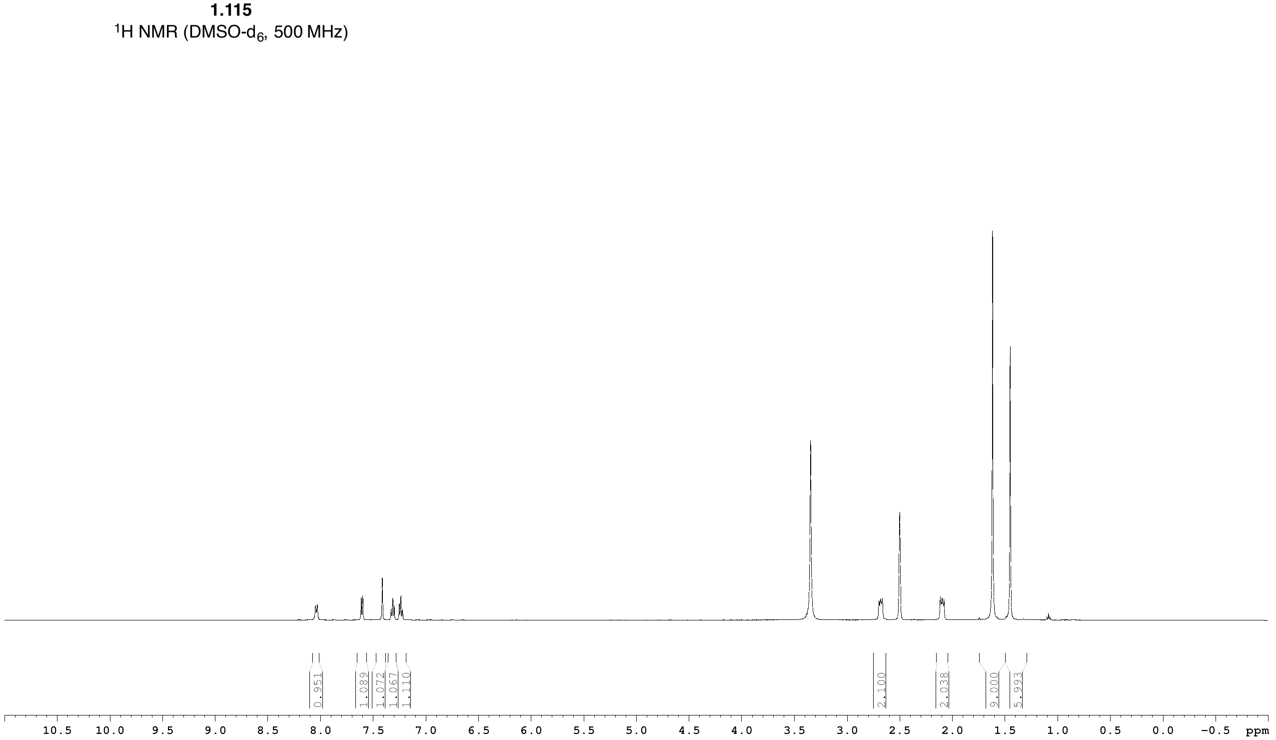
^{13}C NMR (D_2O, 126 MHz)

YS-II-251



1.115

^{1}H NMR (DMSO-d$_6$, 500 MHz)



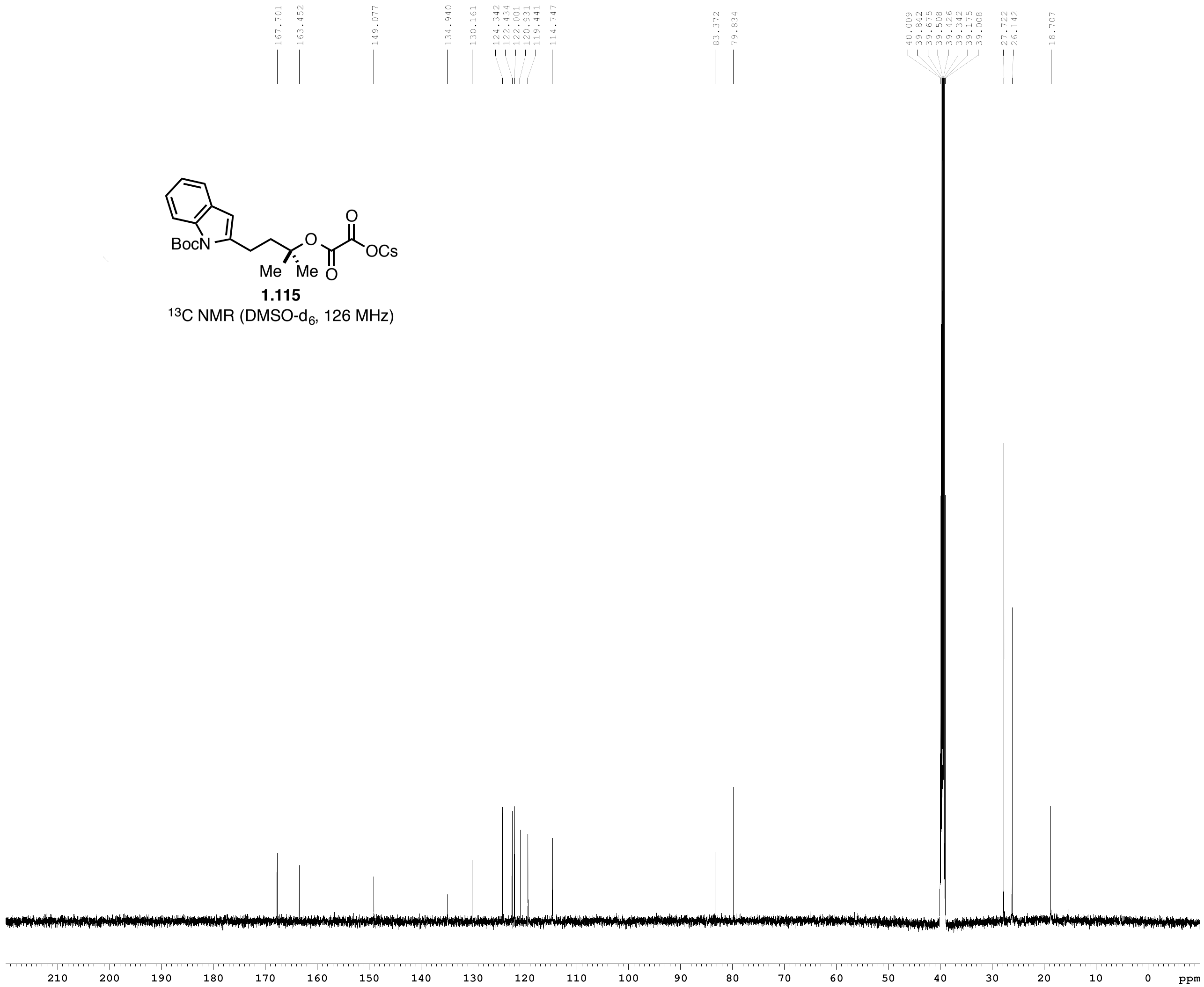
```
Current Data Parameters
NAME            YS-II-251
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150216
Time                13.38
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  32048
SOLVENT              DMSO
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.250026 Hz
AQ              1.9997952 sec
RG                    6.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200118 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-II-251



1.115

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME             YS-II-251
EXPNO                    2
PROCNO                   1

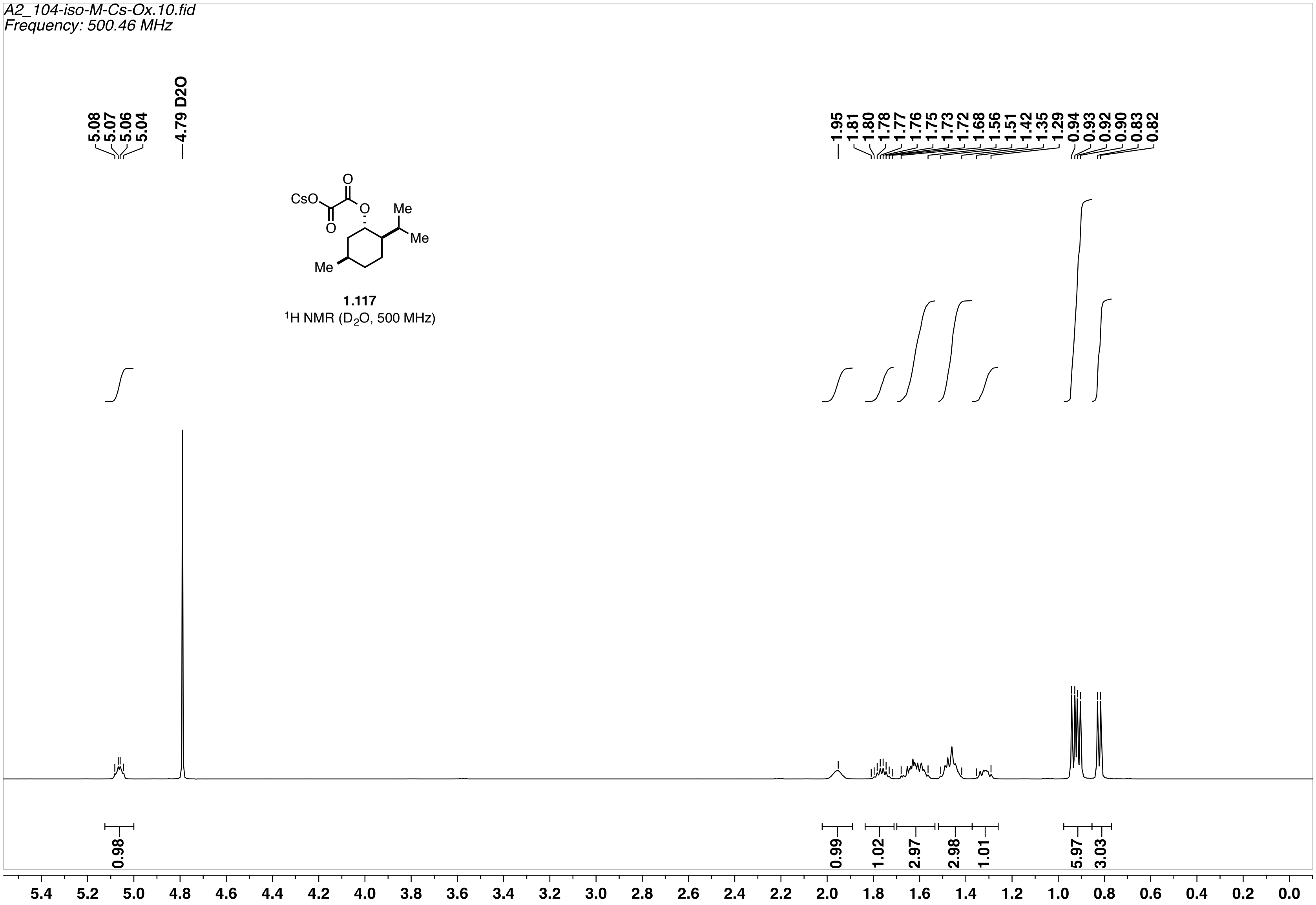
F2 - Acquisition Parameters
Date_             20150216
Time                 13.41
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT               DMSO
NS                     584
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.75000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST   0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

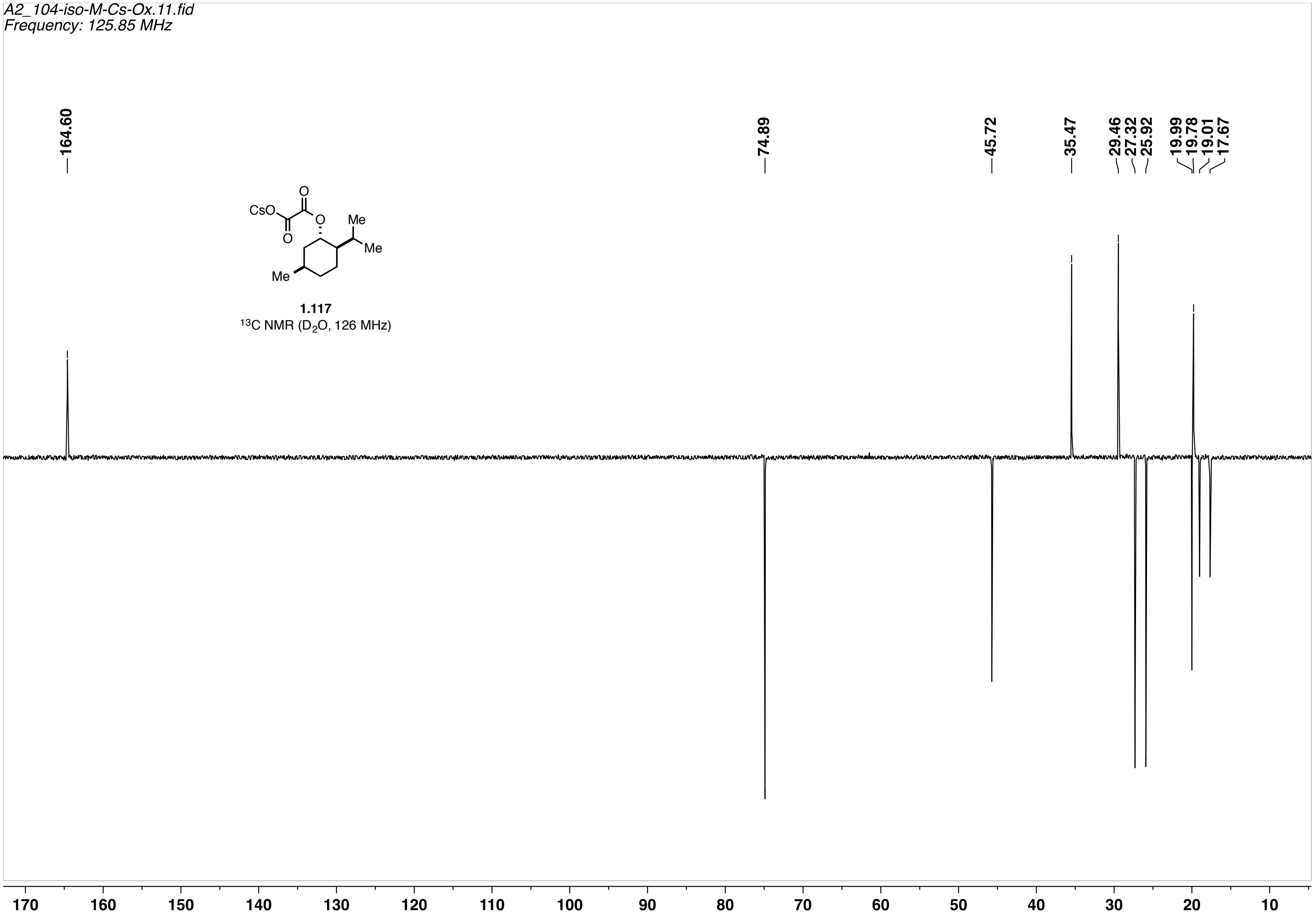
======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804792 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    2.00
```

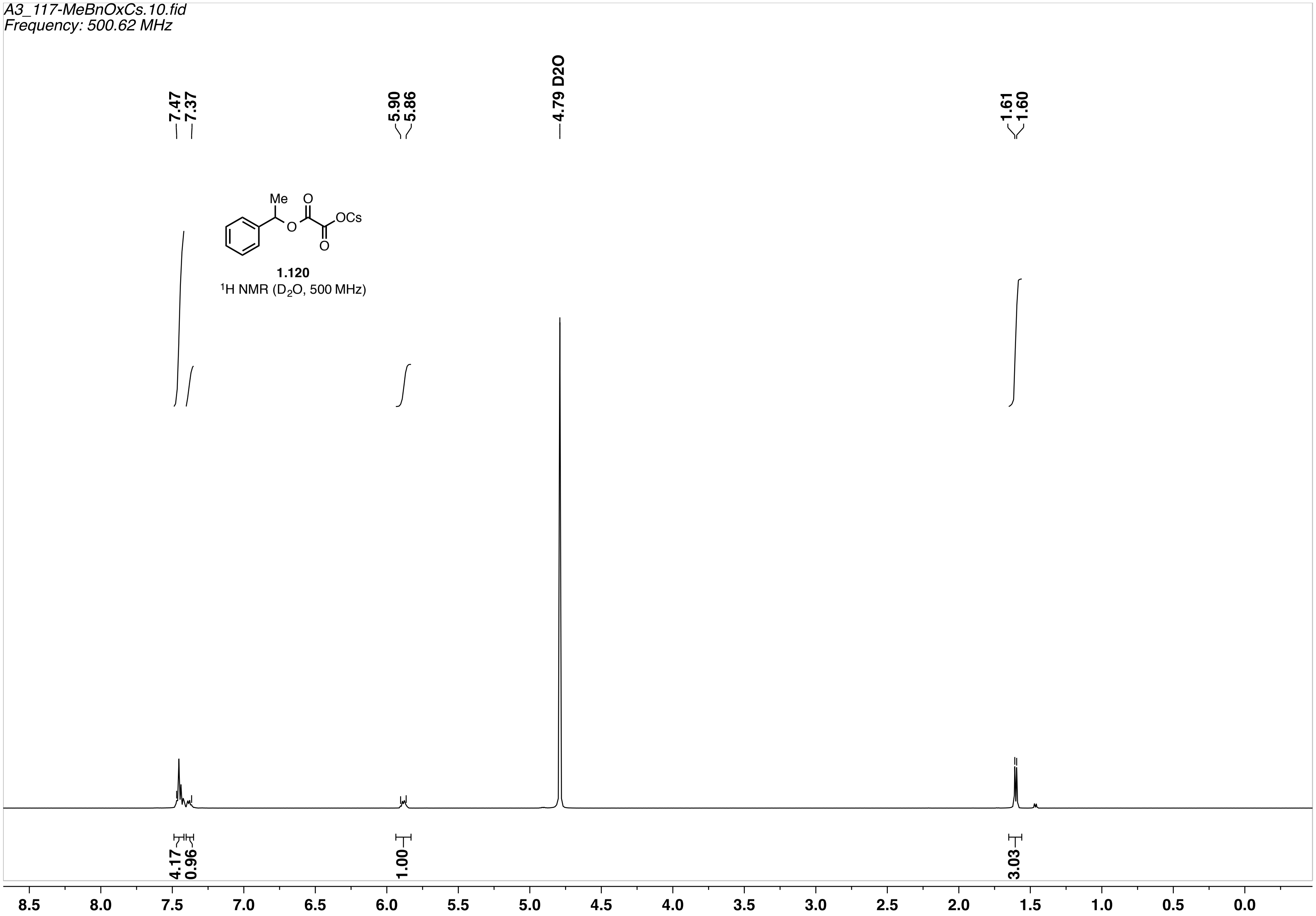


1.117
^{1}H NMR (D_2O, 500 MHz)



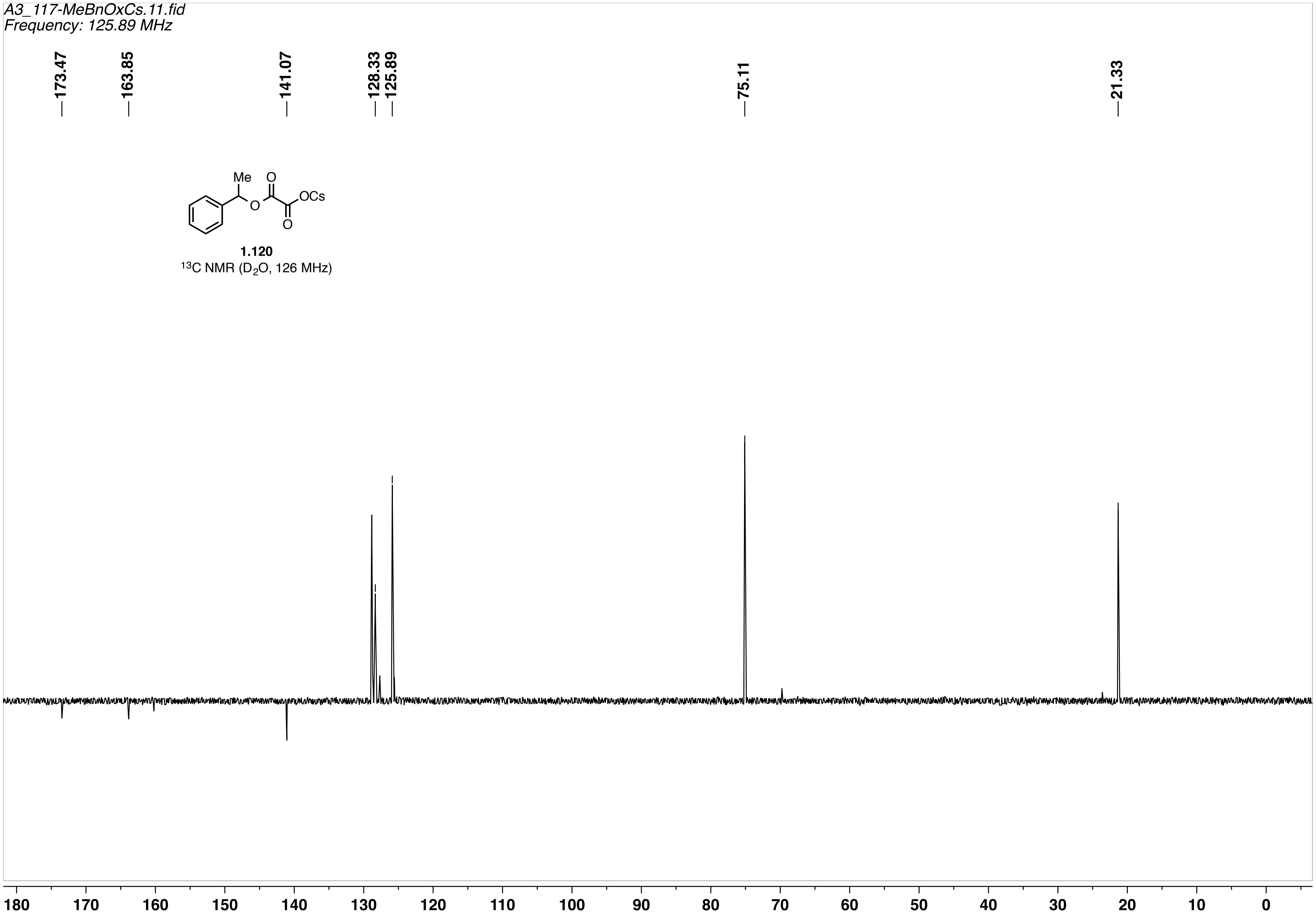
1.117

^{13}C NMR (D_2O, 126 MHz)



1.120

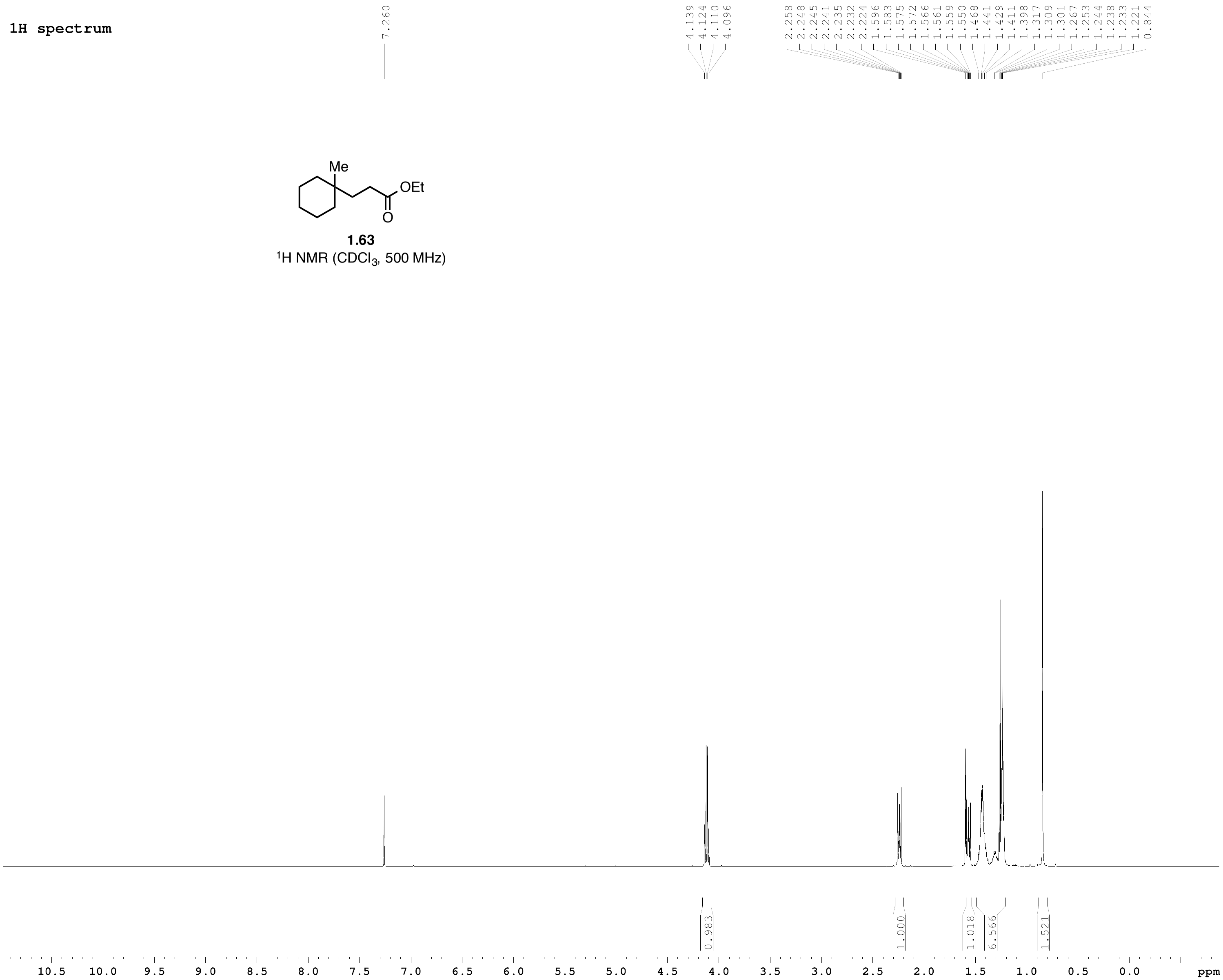
^{1}H NMR (D_2O, 500 MHz)



1.120

^{13}C NMR (D_2O, 126 MHz)

1H spectrum



1.63

^{1}H NMR (CDCl$_3$, 500 MHz)

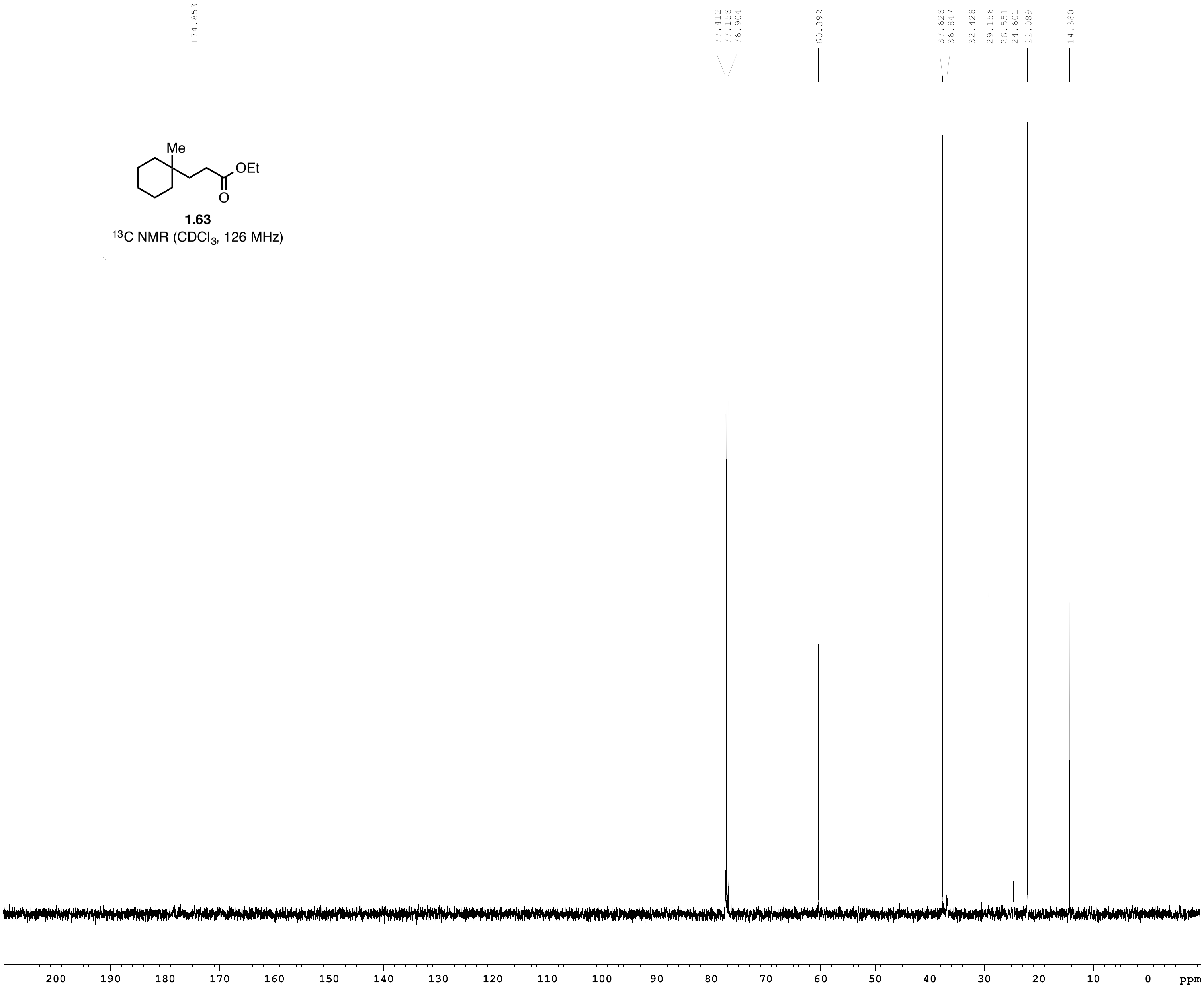
```
Current Data Parameters
NAME       CRJ1-249-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150523
Time               17.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200315 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

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



1.63

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME       CRJ1-249-pure
EXPNO                  2
PROCNO                 1

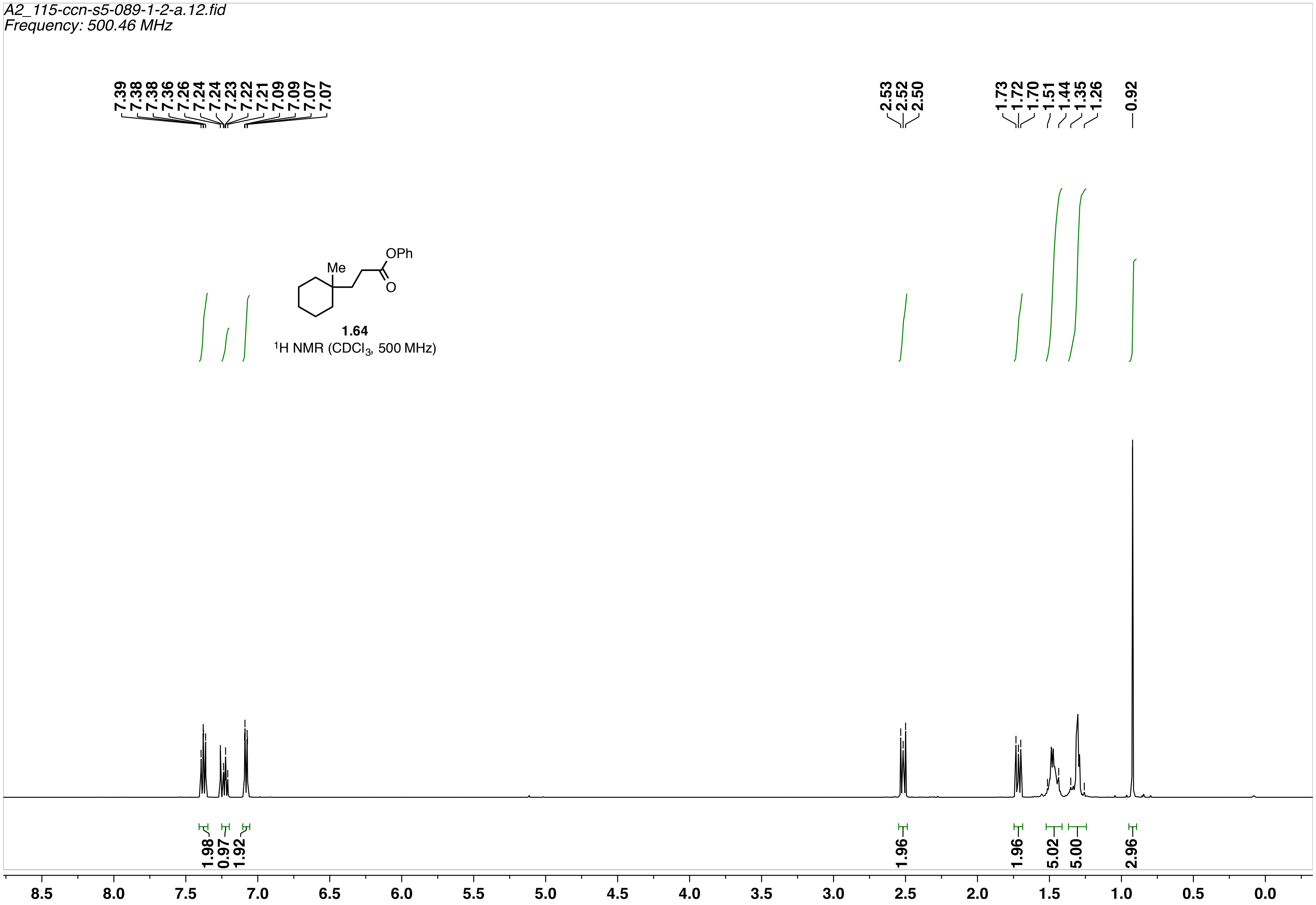
F2 - Acquisition Parameters
Date_           20150523
Time               17.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   160
DS                     8
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               11585.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

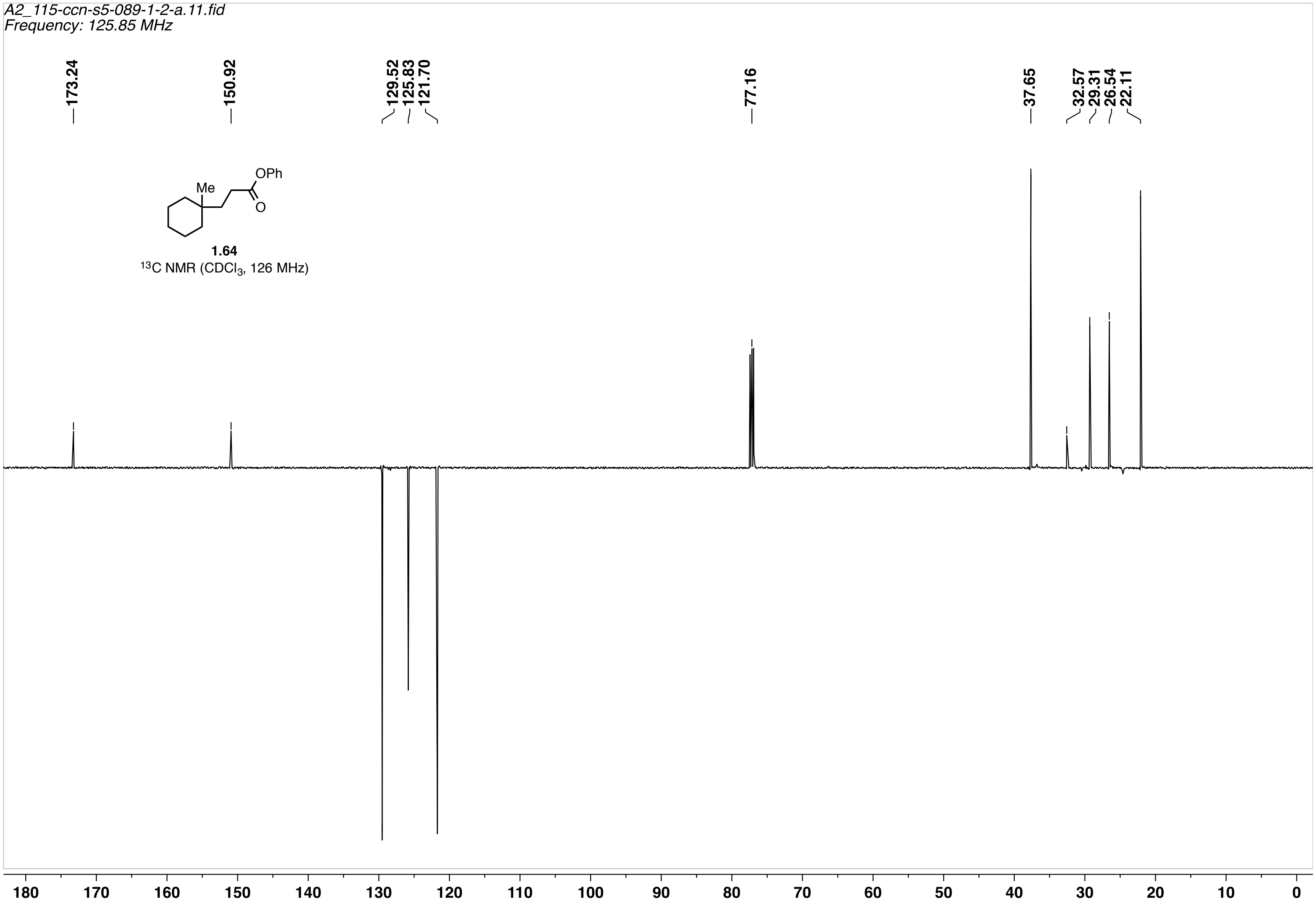
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804080 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



1.64

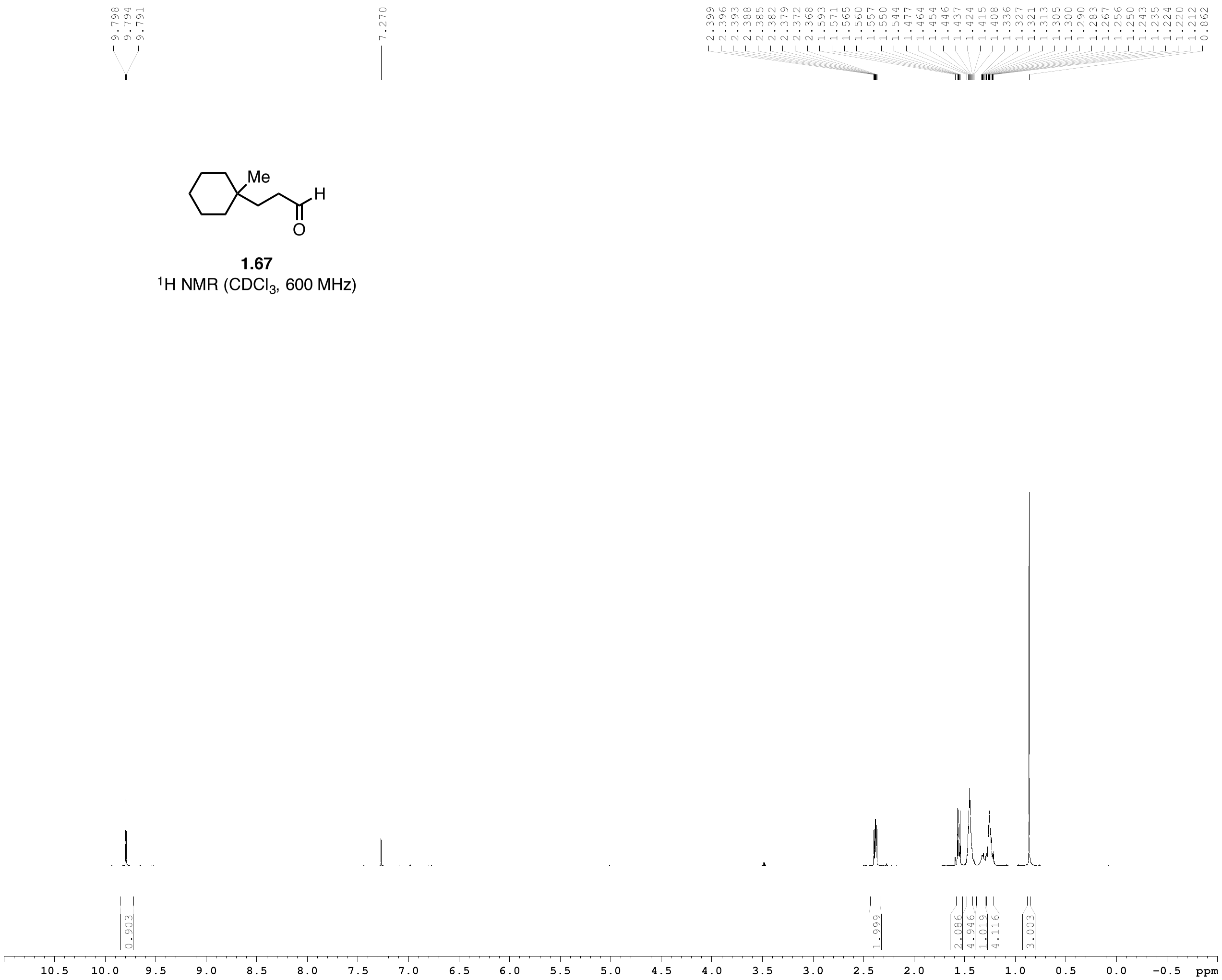
^{1}H NMR (CDCl$_3$, 500 MHz)



1.64

^{13}C NMR (CDCl$_3$, 126 MHz)

YS-III-29A



1.67

^{1}H NMR (CDCl$_3$, 600 MHz)

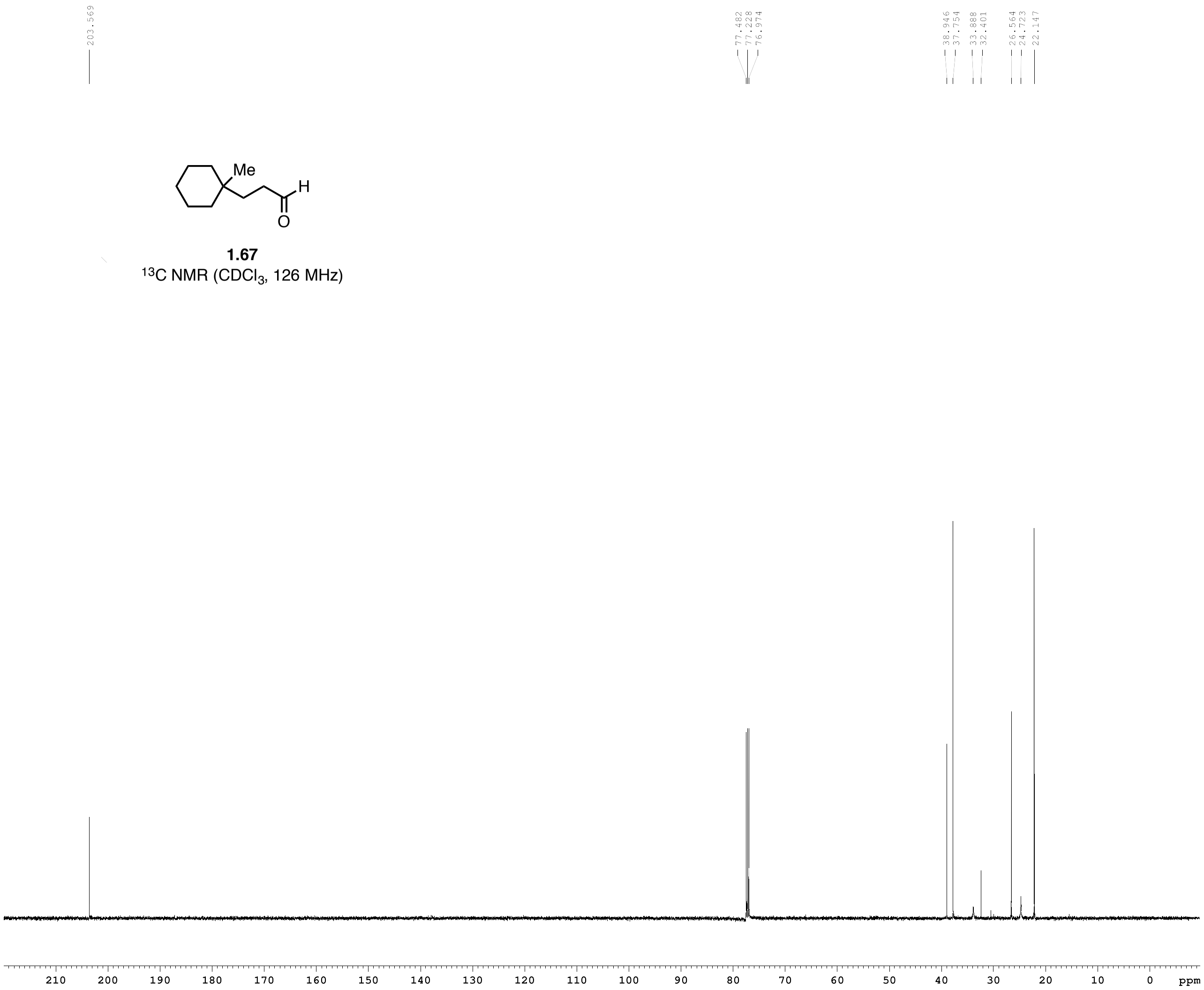
```
Current Data Parameters
NAME          YS-III-29A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150331
Time               16.08
INSTRUM            av600
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   228
DW                52.000 usec
DE                 14.33 usec
TE                 298.3 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  9.00 usec
PLW1         60.25600052 W

F2 - Processing parameters
SI                 65536
SF           600.1300281 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-III-29A



1.67

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-29A
EXPNO                  2
PROCNO                 1

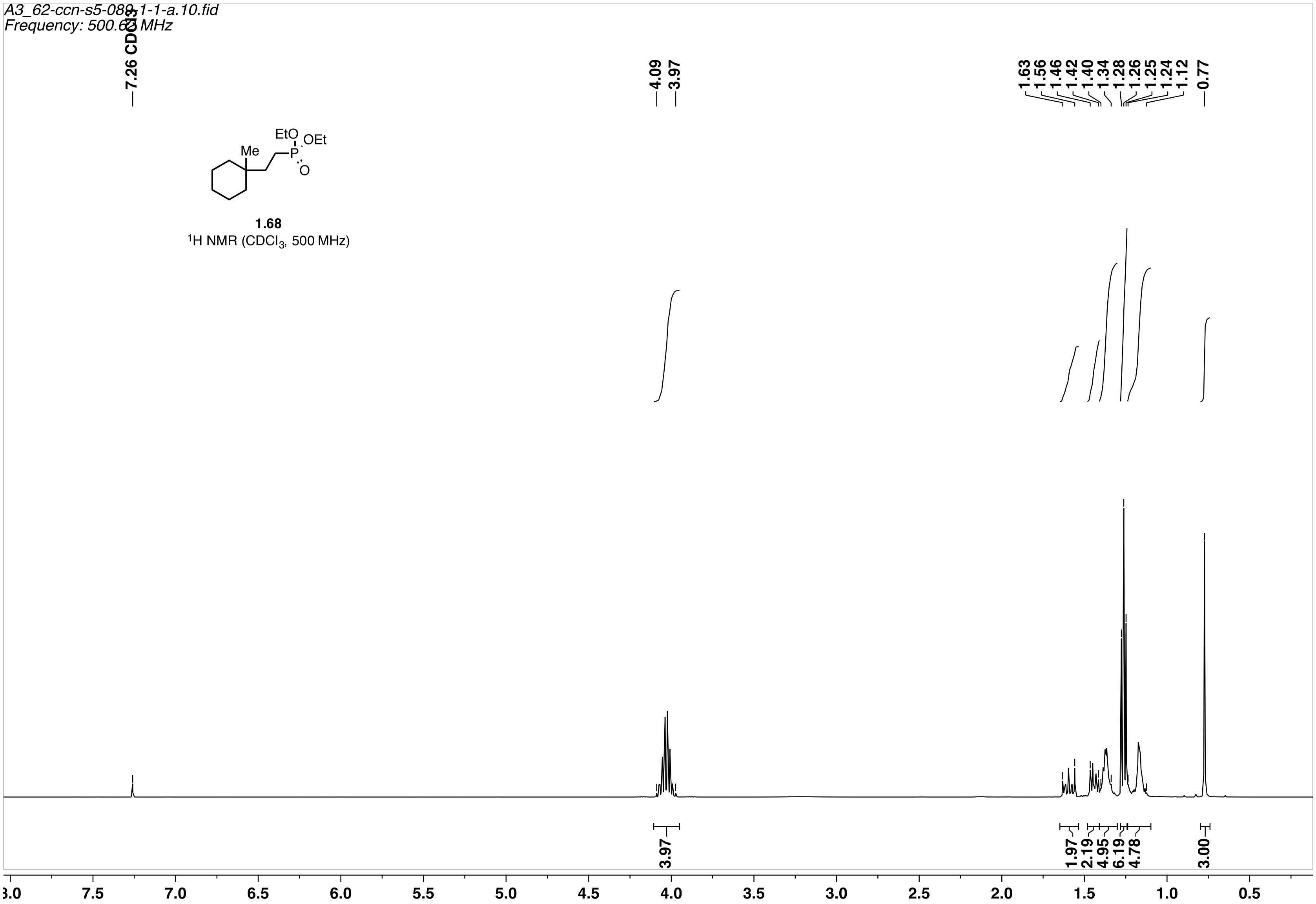
F2 - Acquisition Parameters
Date_           20150401
Time               12.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCL3
NS                   288
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

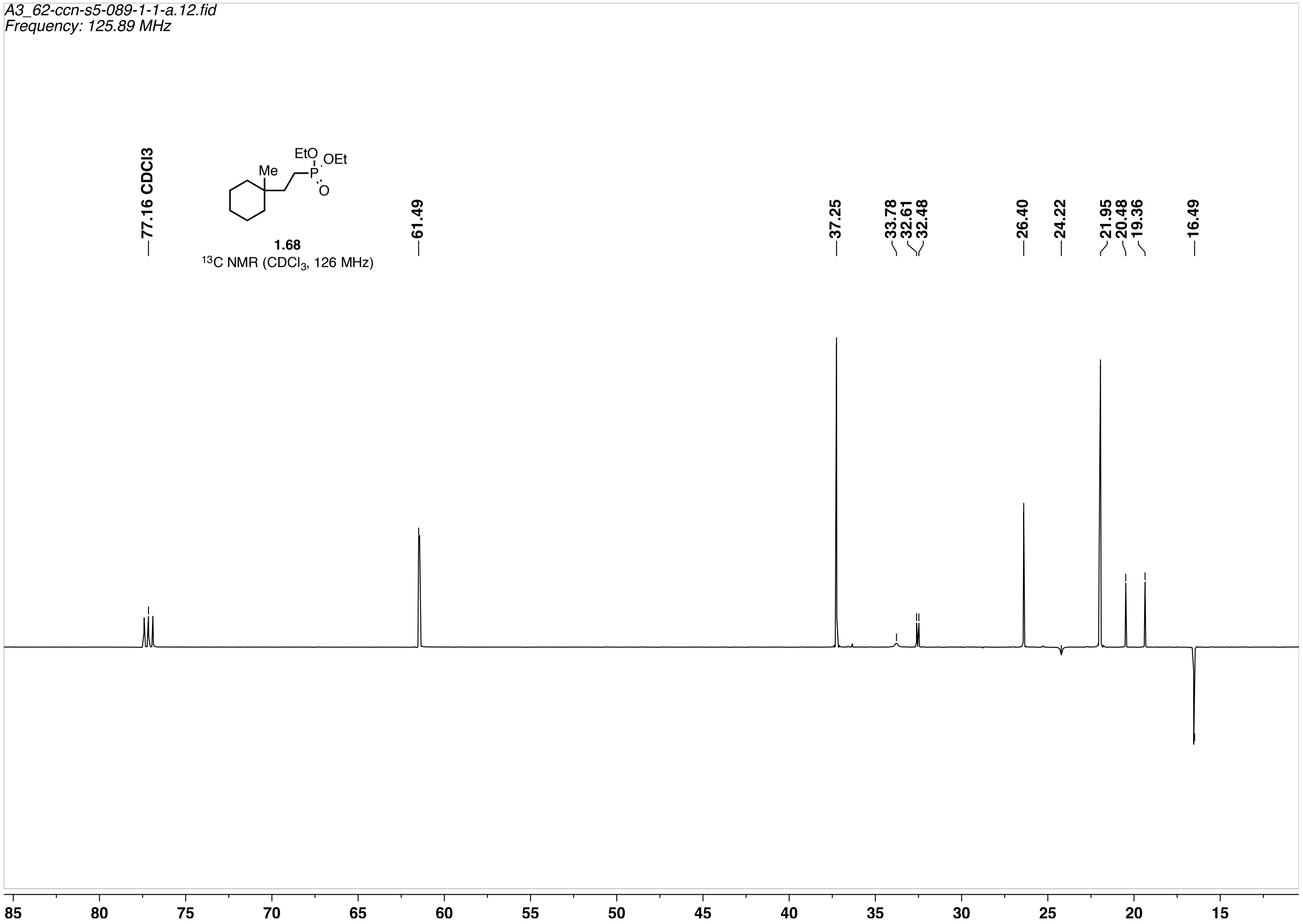
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803131 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



1.68

^{1}H NMR ($CDCl_3$, 500 MHz)



1.68

^{13}C NMR (CDCl$_3$, 126 MHz)

YS-III-24B

1.71

^{1}H NMR (CDCl$_3$, 500 MHz)

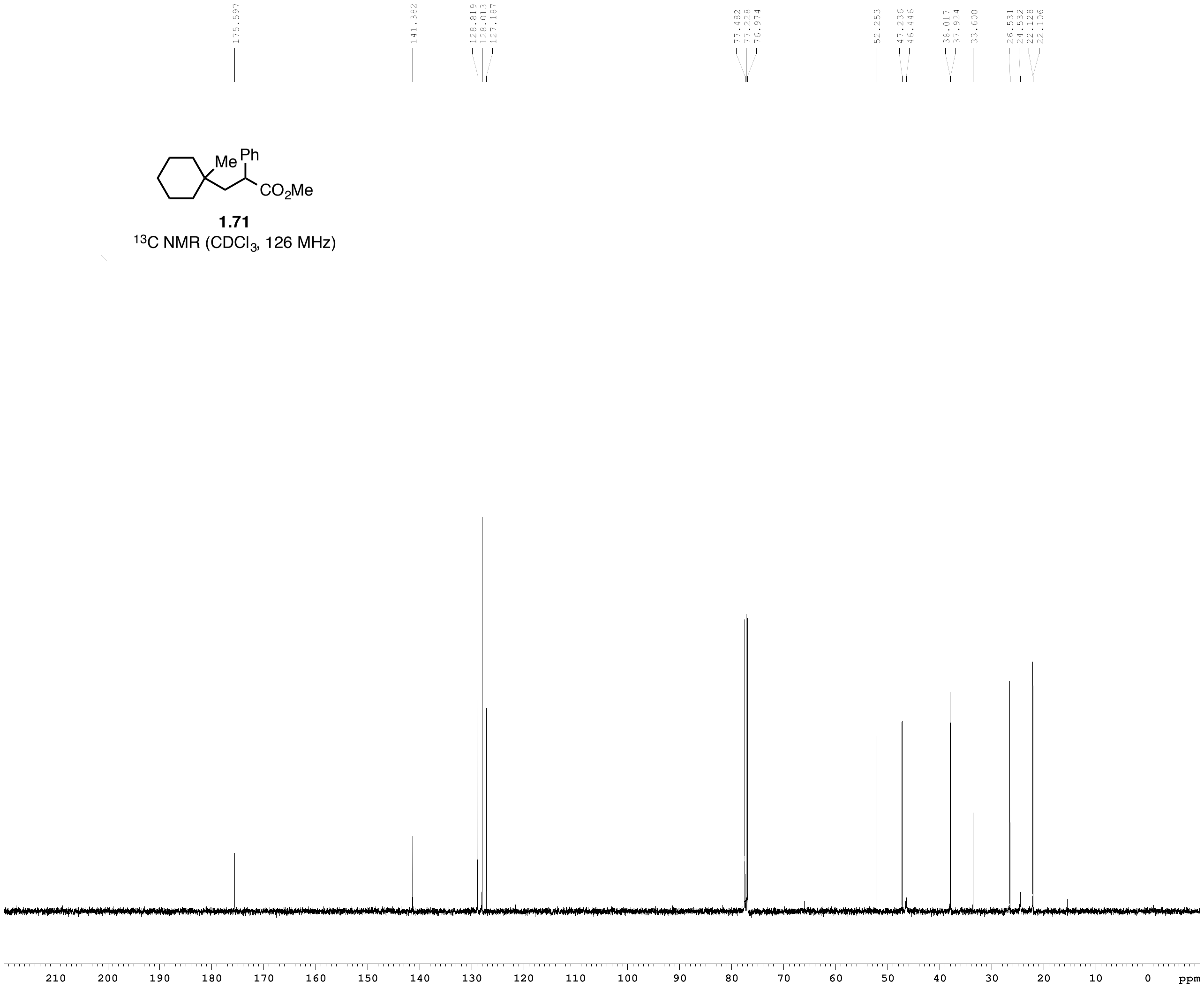
```
Current Data Parameters
NAME          YS-III-24B
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150326
Time               10.25
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200117 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

YS-III-24B



1.71

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-24B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150326
Time               10.29
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

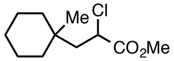
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

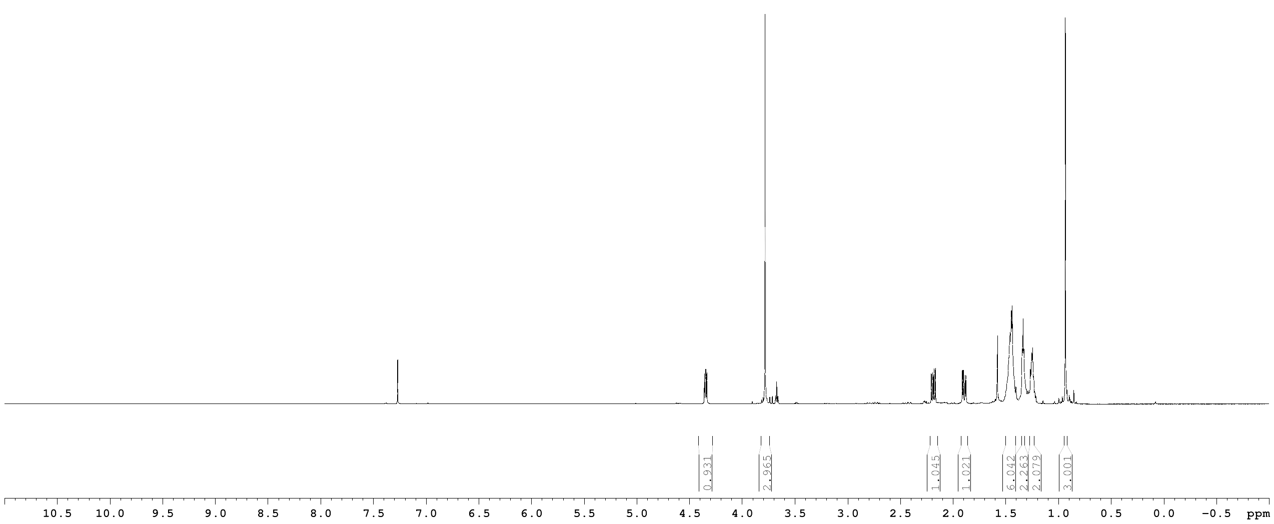
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803997 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-III-47A



1.72
^{1}H NMR (CDCl$_3$, 600 MHz)



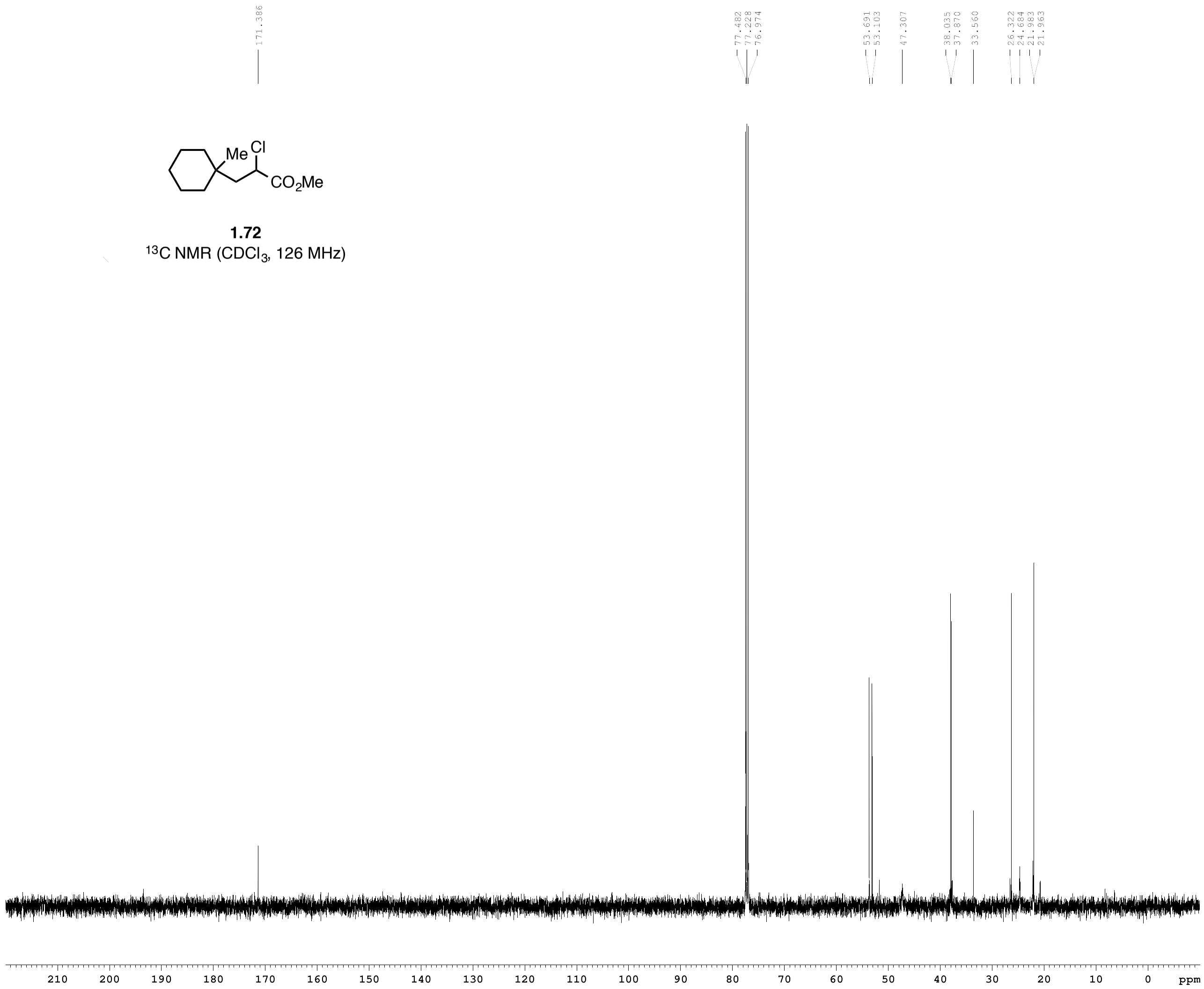
```
Current Data Parameters
NAME          YS-III-47A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150410
Time               16.32
INSTRUM            av600
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   287
DW                52.000 usec
DE                 14.33 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.00 usec
PLW1        60.25600052 W

F2 - Processing parameters
SI                 65536
SF          600.1300283 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-III-47A



1.72

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-47A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150427
Time                8.43
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

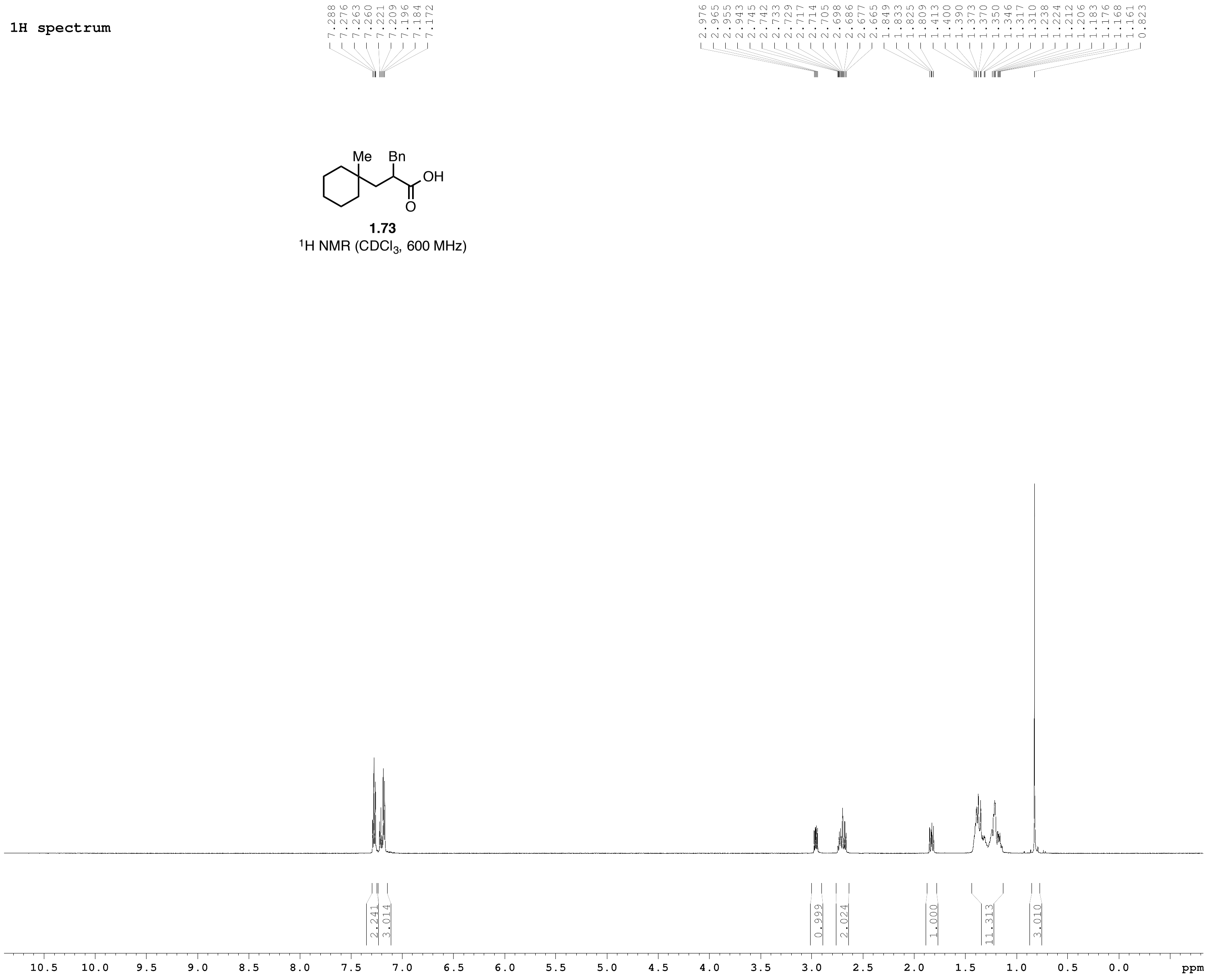
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803898 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



1.73

^{1}H NMR (CDCl$_3$, 600 MHz)

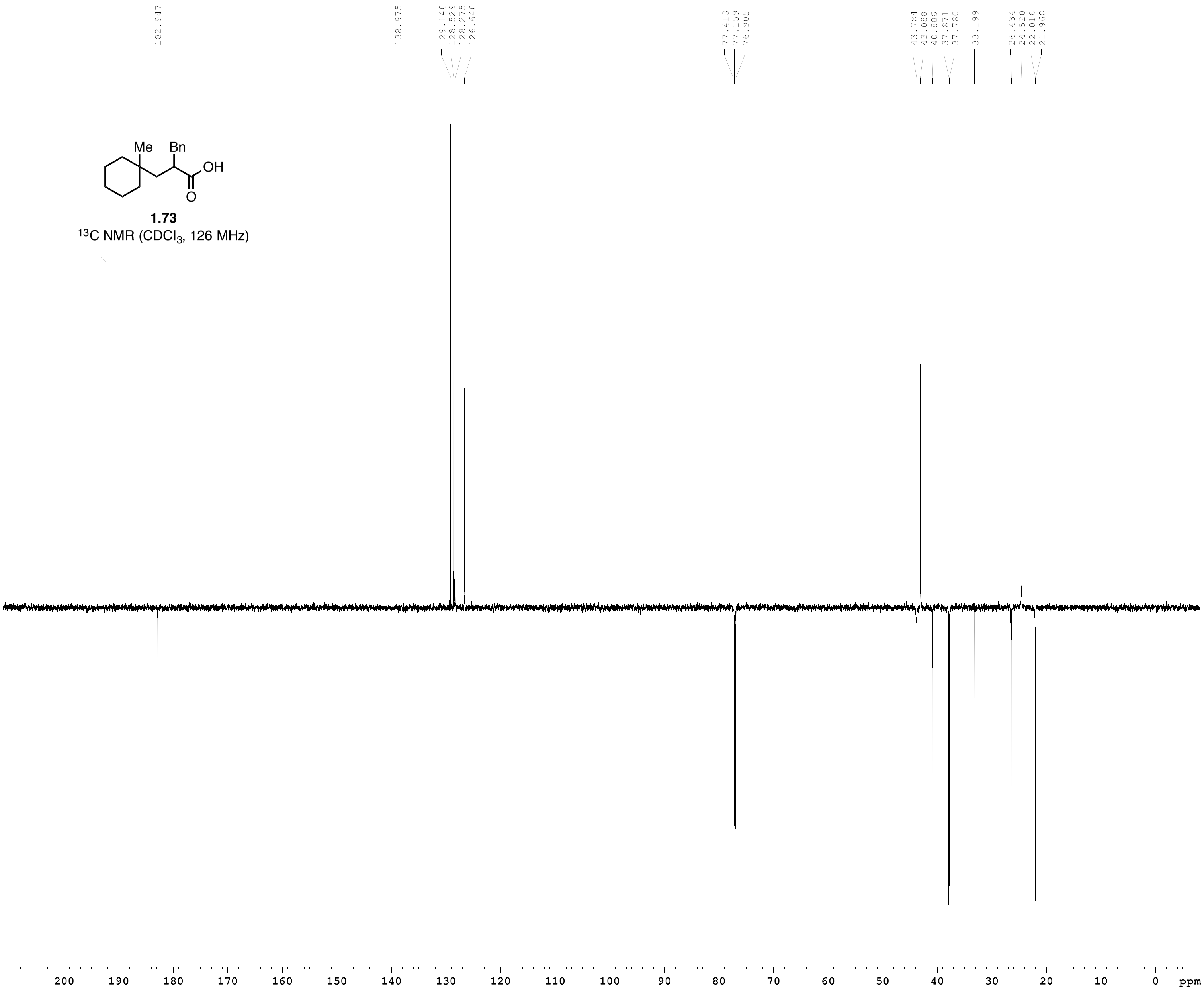
```
Current Data Parameters
NAME      CRJ1-156-pure
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20150408
Time              18.01
INSTRUM           av600
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                76922
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.125002 Hz
AQ            3.9999440 sec
RG                  256
DW               52.000 usec
DE                14.33 usec
TE                298.2 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 9.00 usec
PLW1        60.25600052 W

F2 - Processing parameters
SI                65536
SF          600.1300344 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 1.00
```

deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)



1.73

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME       CRJ1-156-pure
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150327
Time               15.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG         deptqgpsp
TD                 65536
SOLVENT            CDC13
NS                   200
DS                     8
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  2048
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
CNST2        145.0000000
CNST12         1.5000000
D1            1.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
D16           0.00020000 sec
DELTA         0.00001707 sec
DELTA1        0.00228023 sec
DELTA2        0.00226483 sec
DELTA3        0.00224828 sec
MCREST    0 sec
MCWRK         0.01500000 sec

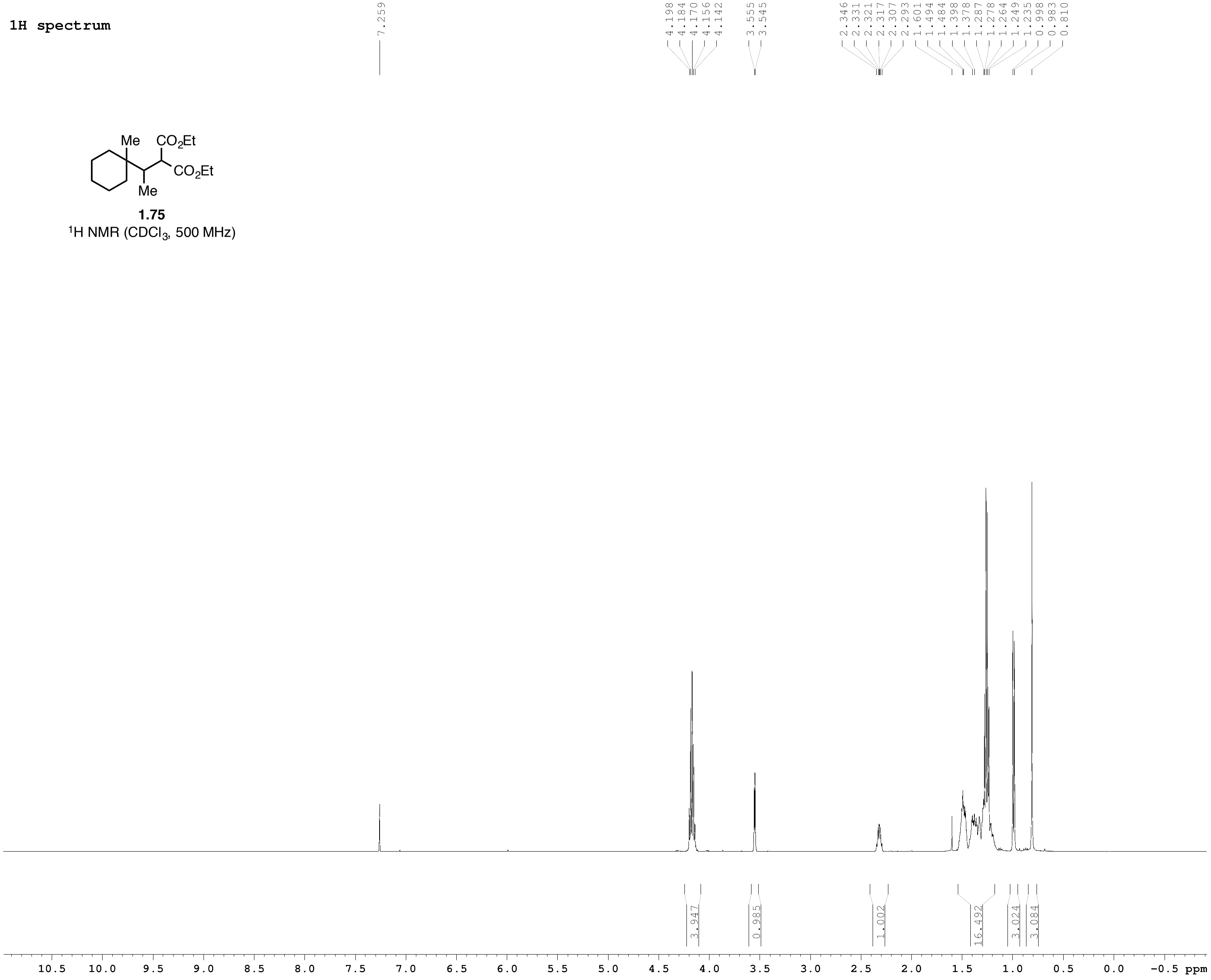
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP2                   2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                    1H
p0                   11.55 usec
P3                    7.70 usec
p4                   15.40 usec
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPNAM[3]          SINE.100
GPX1       0 %
GPX2       0 %
GPX3       0 %
GPY1       0 %
GPY2       0 %
GPY3       0 %
GPZ1                 31.00 %
GPZ2                 31.00 %
GPZ3                 31.00 %
P16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7804079 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    2.00
```

1H spectrum



1.75

^{1}H NMR ($CDCl_3$, 500 MHz)

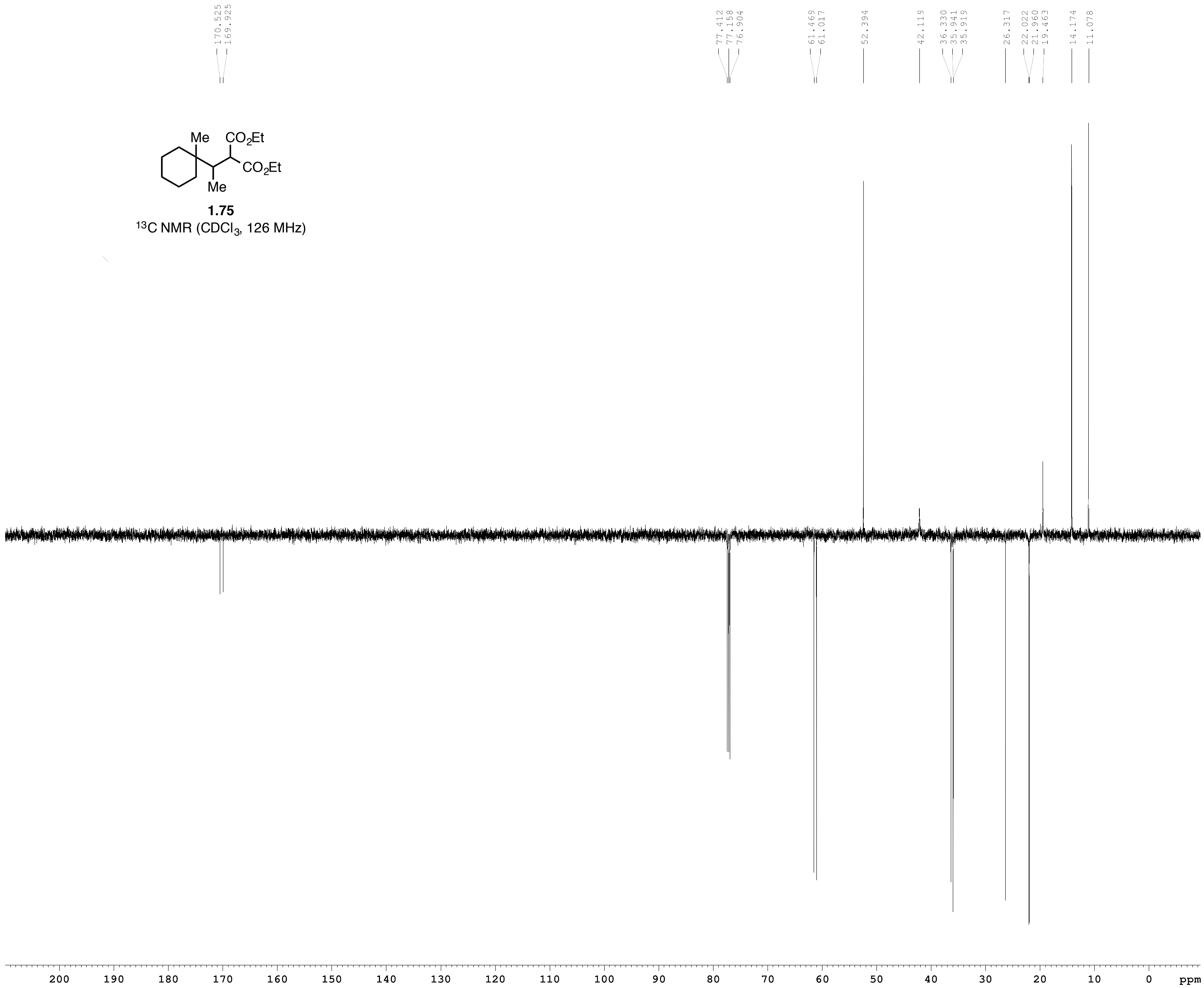
```
Current Data Parameters
NAME          CRJ1-084-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150211
Time               17.53
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200311 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)



1.75

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          CRJ1-084-1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150211
Time               17.54
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG        deptqgpsp
TD                 65536
SOLVENT            CDCl3
NS                    48
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               14596.5
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
CNST2        145.0000000
CNST12         1.5000000
D1            1.50000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
D16           0.00020000 sec
DELTA         0.00001707 sec
DELTA1        0.00228023 sec
DELTA2        0.00226483 sec
DELTA3        0.00224828 sec
MCREST   0 sec
MCWRK         0.01500000 sec

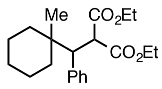
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
p0                 11.55 usec
P3                  7.70 usec
p4                 15.40 usec
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPX1     0 %
GPX2     0 %
GPX3     0 %
GPY1     0 %
GPY2     0 %
GPY3     0 %
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

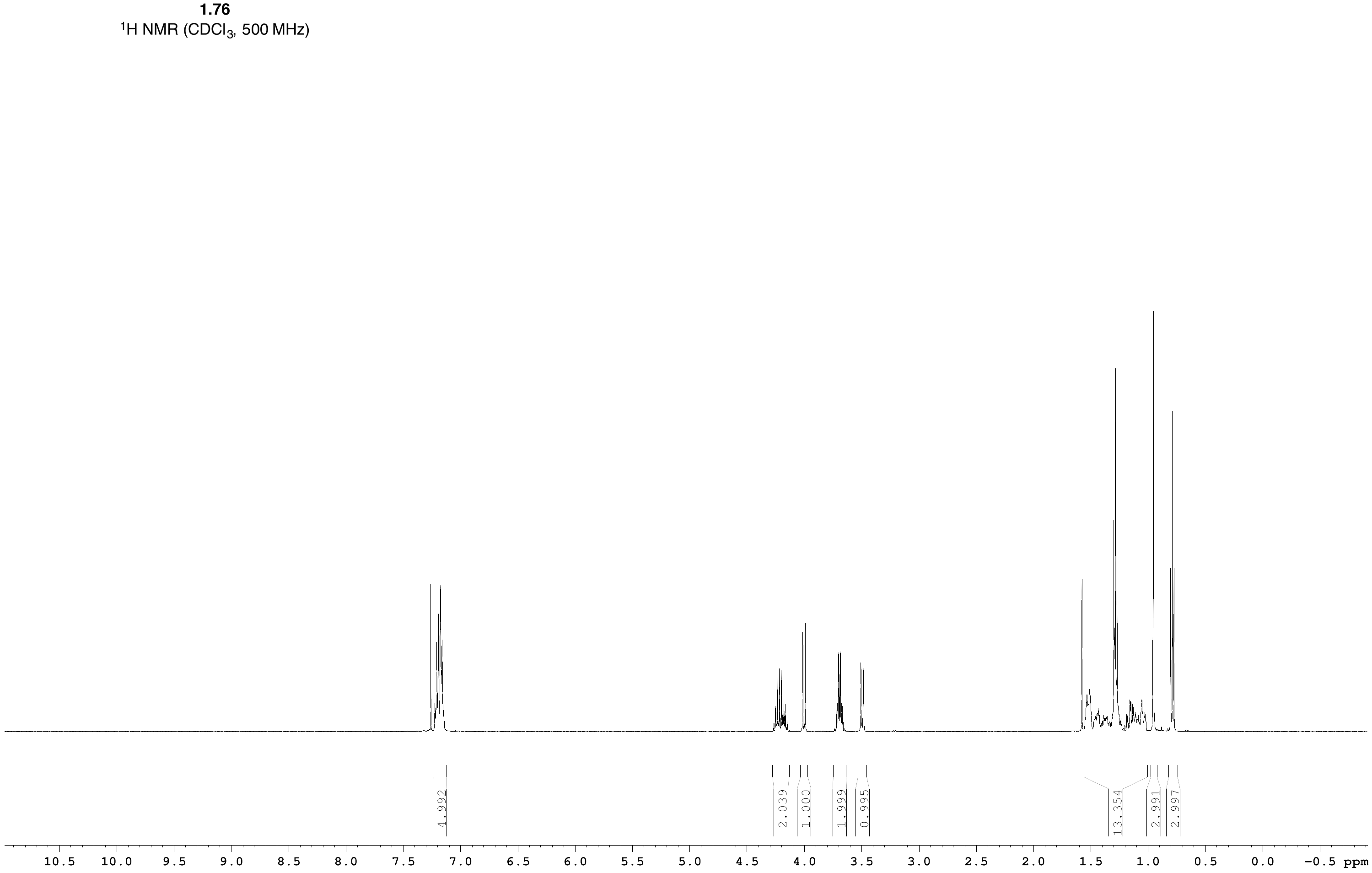
F2 - Processing parameters
SI                 65536
SF           125.7804082 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



1.76

^{1}H NMR ($CDCl_3$, 500 MHz)



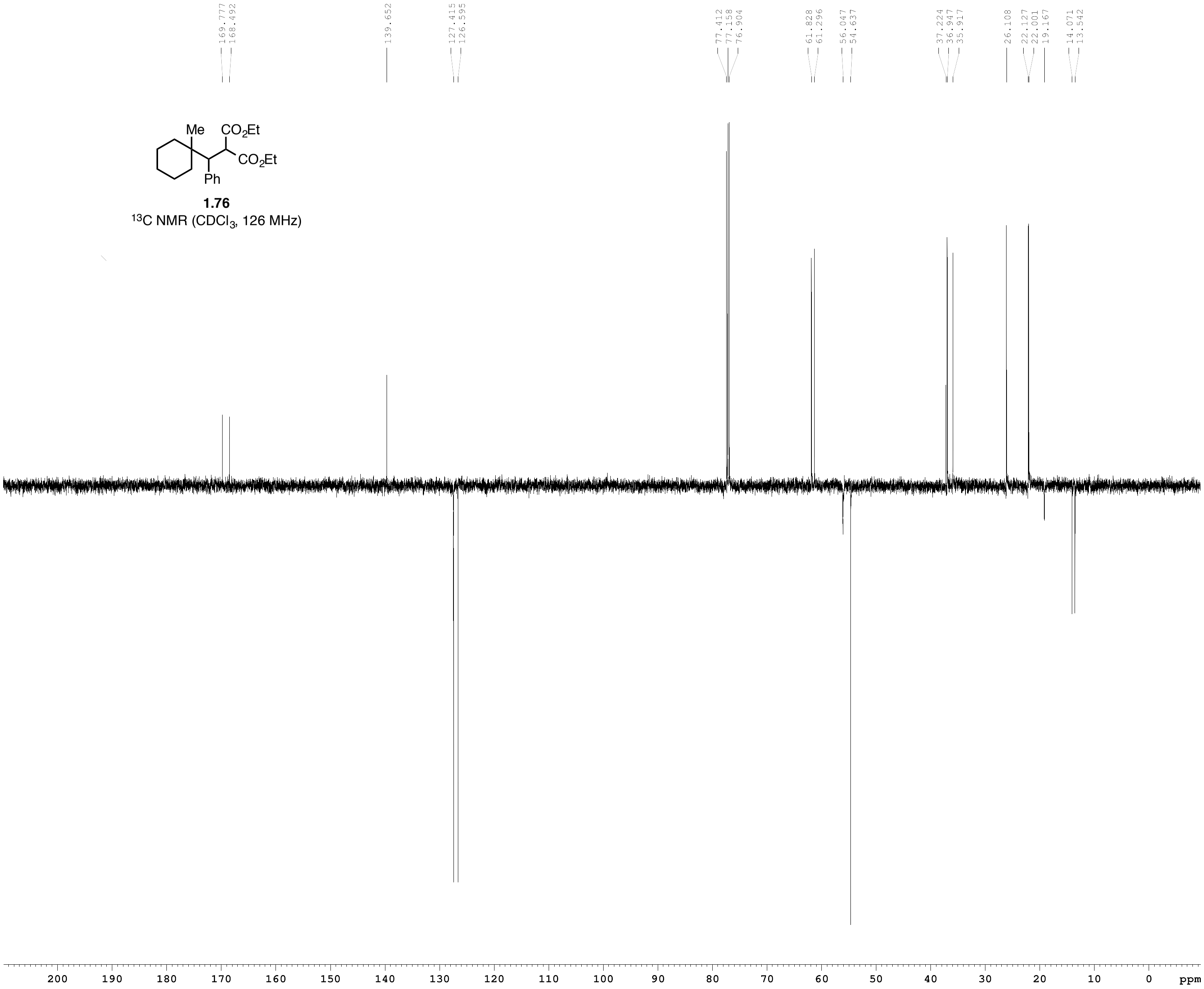
```
Current Data Parameters
NAME       CRJ1-205-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150417
Time               13.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 64100
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.125005 Hz
AQ             3.9998400 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200308 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)



1.76

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME      CRJ1-205-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150417
Time              13.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG       deptqgpsp
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    8
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
CNST2       145.0000000
CNST12        1.5000000
D1           1.00000000 sec
d2           0.00344828 sec
d12          0.00002000 sec
D16          0.00020000 sec
DELTA        0.00001707 sec
DELTA1       0.00228023 sec
DELTA2       0.00226483 sec
DELTA3       0.00224828 sec
MCREST   0 sec
MCWRK        0.01500000 sec

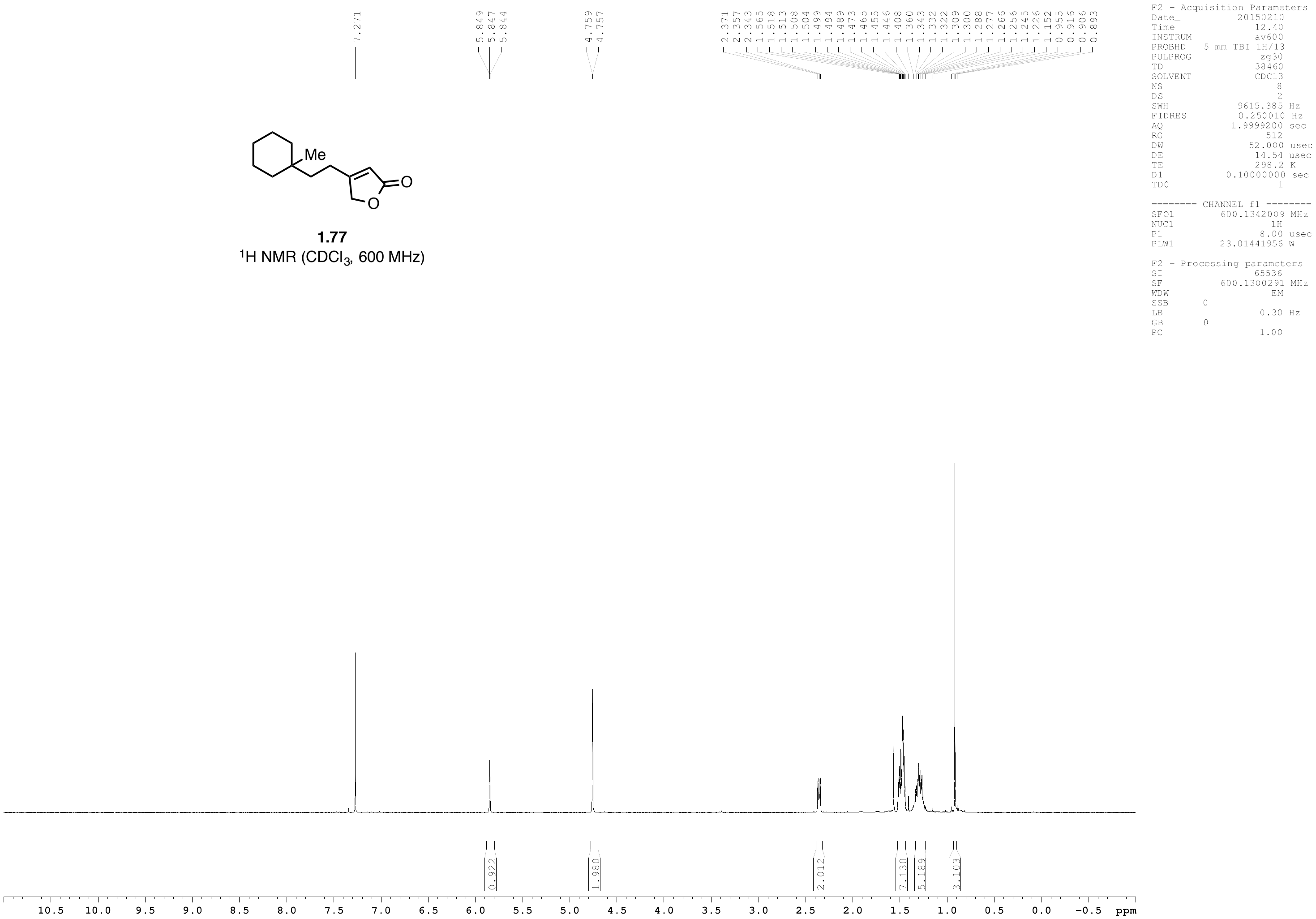
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2                2.70 dB
SPNAM[2]    Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
p0                11.55 usec
P3                 7.70 usec
p4                15.40 usec
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPNAM[3]       SINE.100
GPX1     0 %
GPX2     0 %
GPX3     0 %
GPY1     0 %
GPY2     0 %
GPY3     0 %
GPZ1              31.00 %
GPZ2              31.00 %
GPZ3              31.00 %
P16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-225B



1.77
^{1}H NMR (CDCl$_3$, 600 MHz)

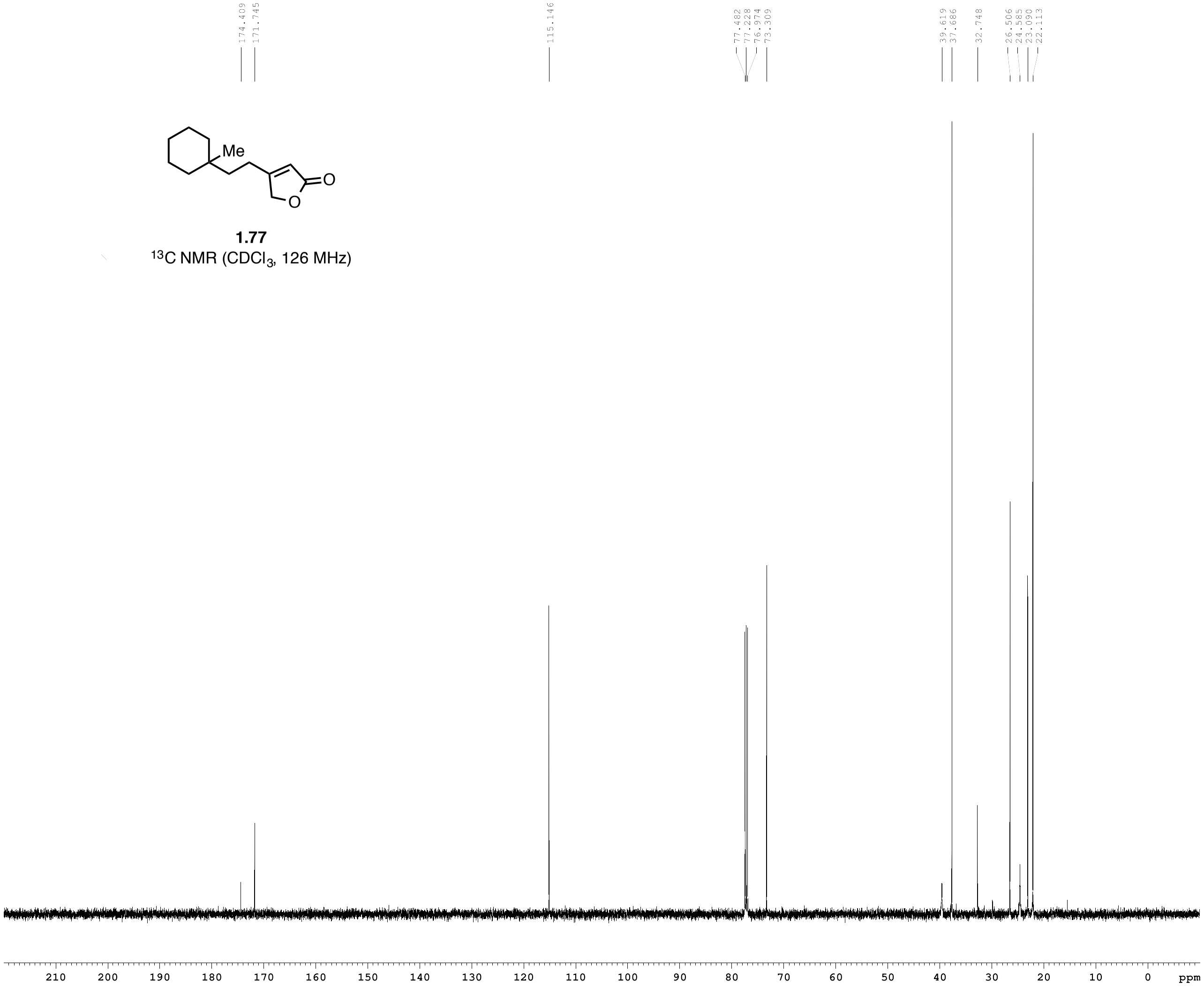
```
Current Data Parameters
NAME          YS-II-225B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150210
Time               12.40
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                   512
DW               52.000 usec
DE                14.54 usec
TE                298.2 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                 65536
SF          600.1300291 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-225B



1.77

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-225B
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150427
Time                8.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   136
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

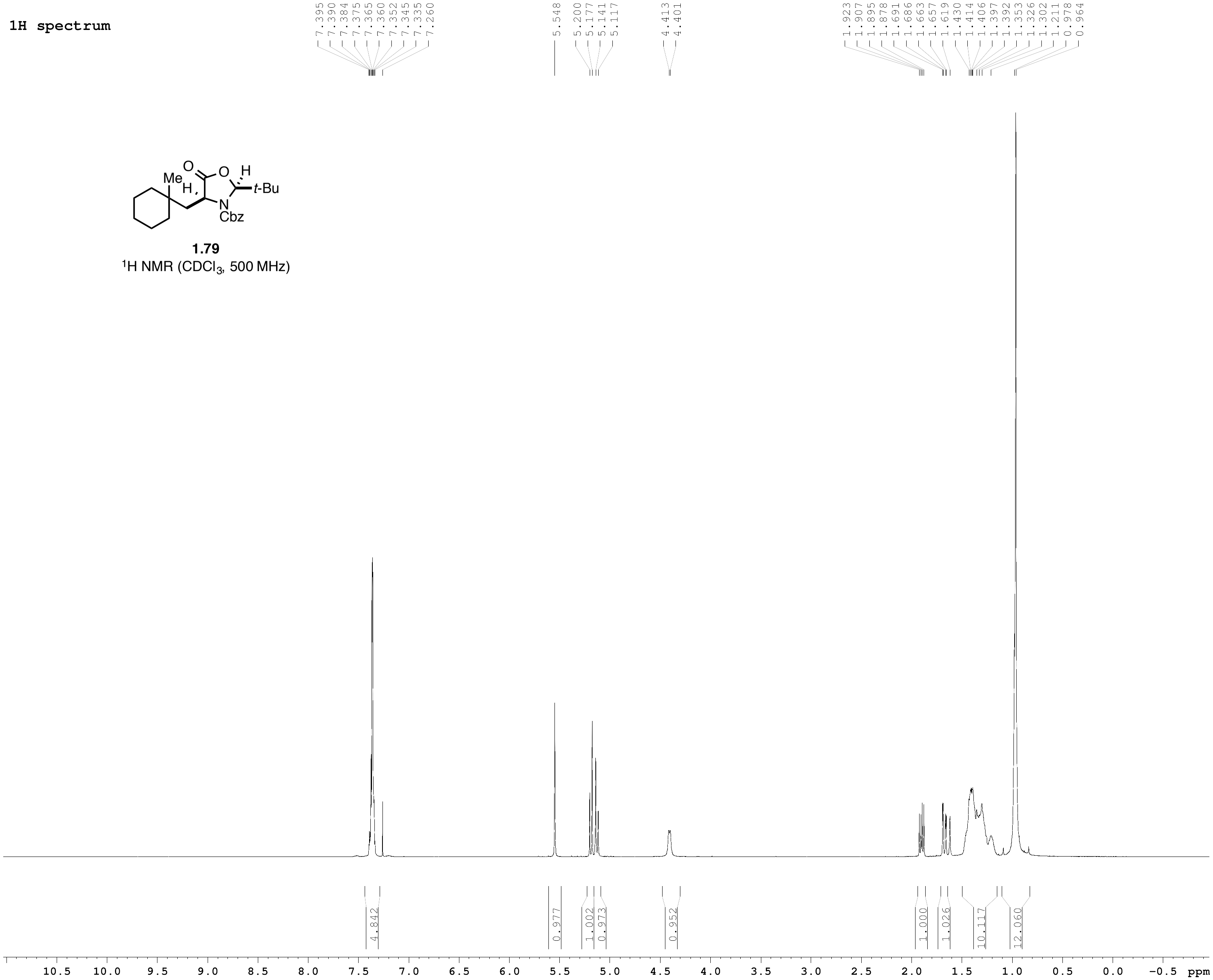
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803954 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

1.79
^{1}H NMR (CDCl$_3$, 500 MHz)



```
Current Data Parameters
NAME        CRJ1-155-NOE
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150425
Time               14.46
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   3.2
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

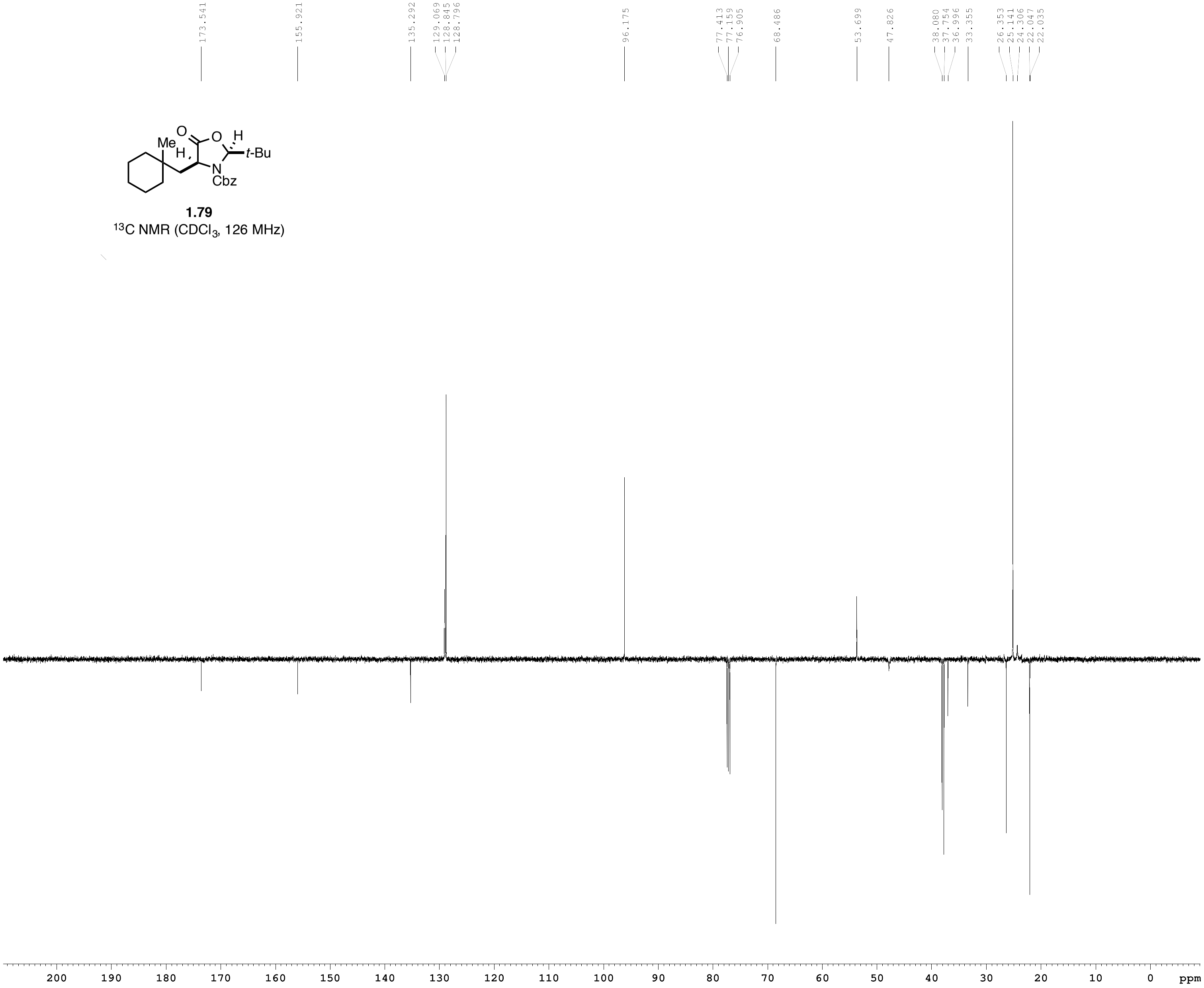
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200308 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)

1.79

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          CRJ1-082-1
EXPNO                  2
PROCNO                 1

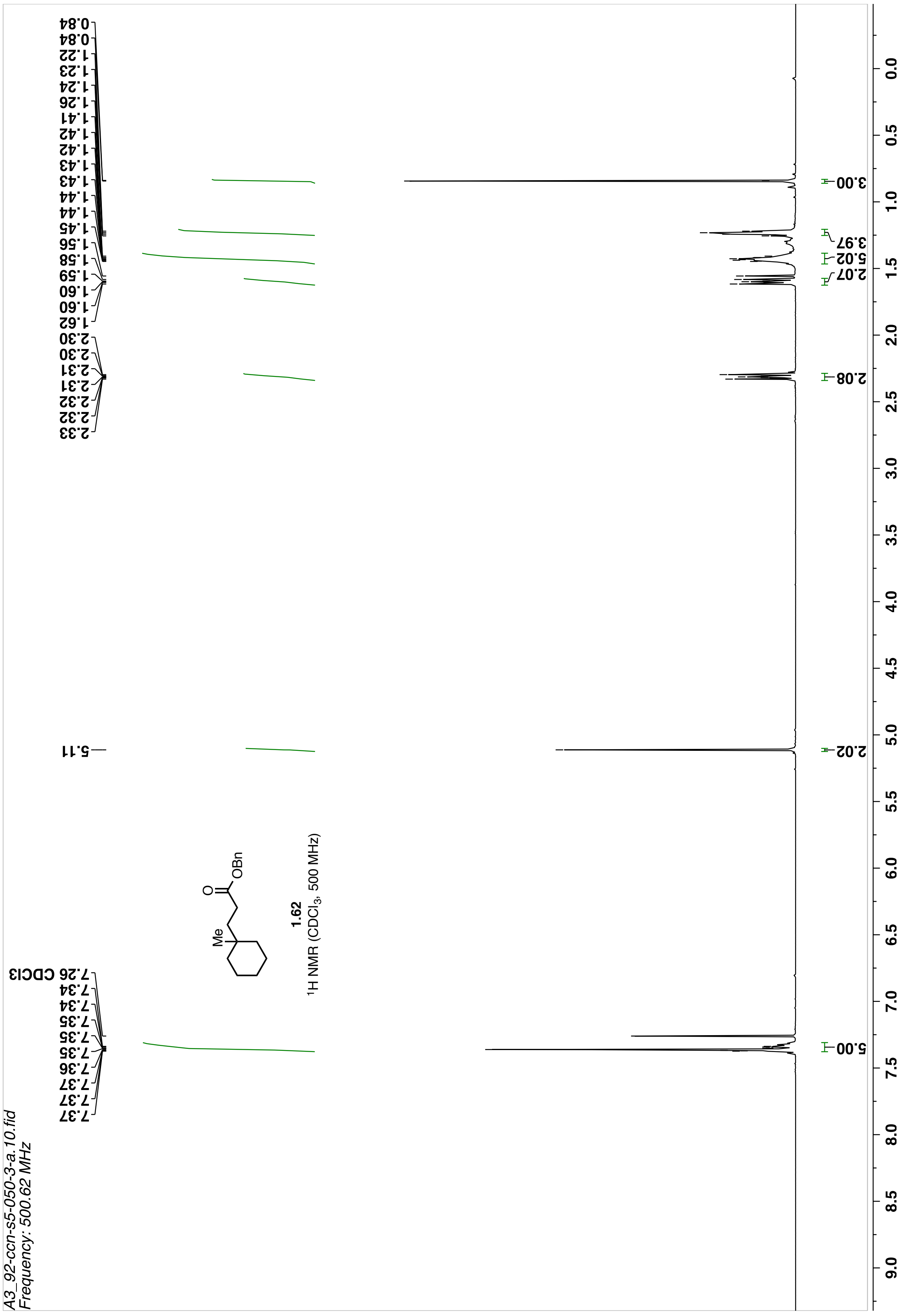
F2 - Acquisition Parameters
Date_           20150211
Time               17.46
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG        deptqgpsp
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                  2048
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
CNST2       145.0000000
CNST12        1.5000000
D1           1.50000000 sec
d2           0.00344828 sec
d12          0.00002000 sec
D16          0.00020000 sec
DELTA        0.00001707 sec
DELTA1       0.00228023 sec
DELTA2       0.00226483 sec
DELTA3       0.00224828 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                 2.70 dB
SPNAM[2]     Crp60comp.4
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
p0                 11.55 usec
P3                  7.70 usec
p4                 15.40 usec
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

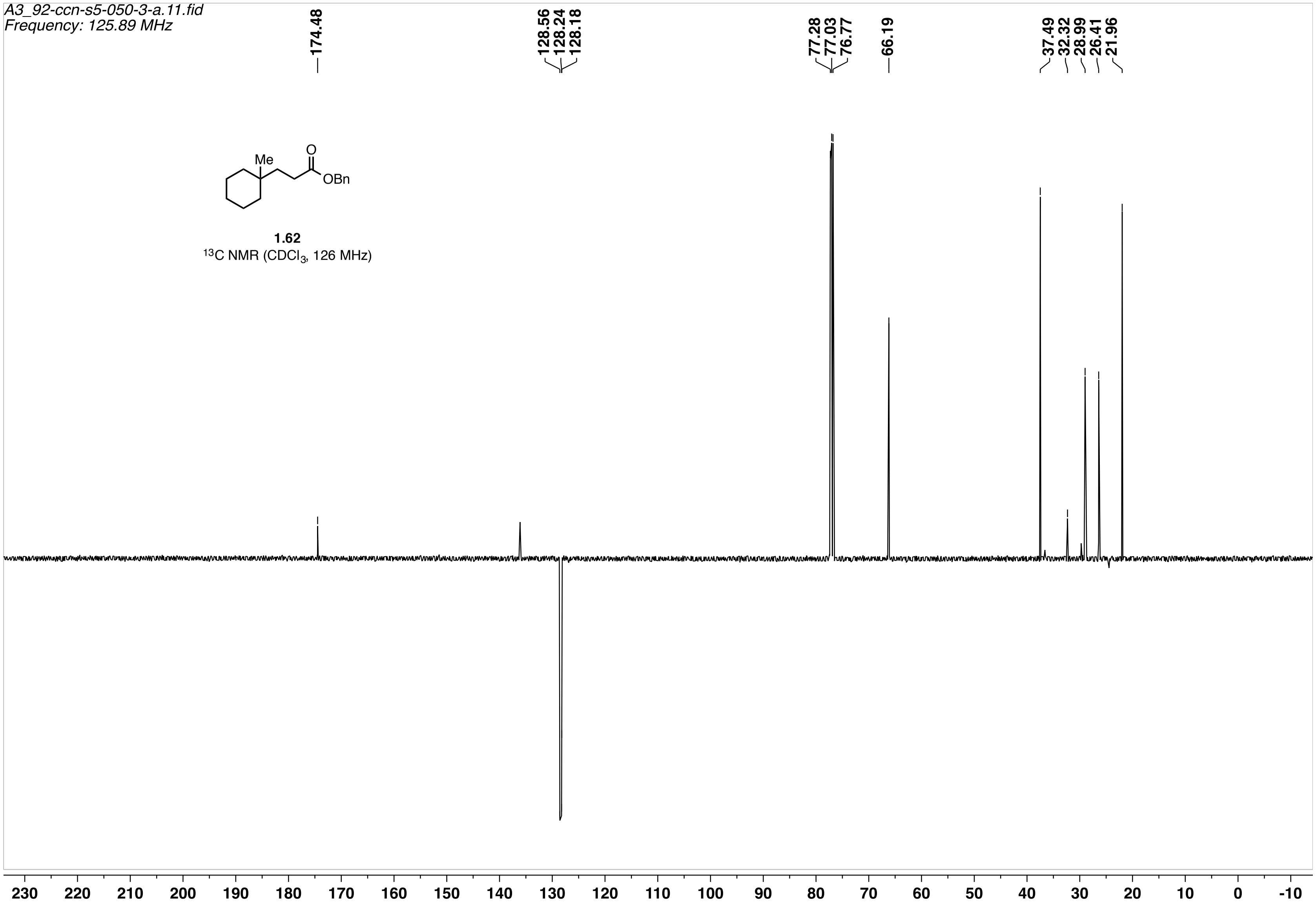
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPNAM[3]        SINE.100
GPX1      0 %
GPX2      0 %
GPX3      0 %
GPY1      0 %
GPY2      0 %
GPY3      0 %
GPZ1               31.00 %
GPZ2               31.00 %
GPZ3               31.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804094 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

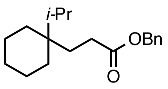


1.62

^{1}H NMR (CDCl$_3$, 500 MHz)

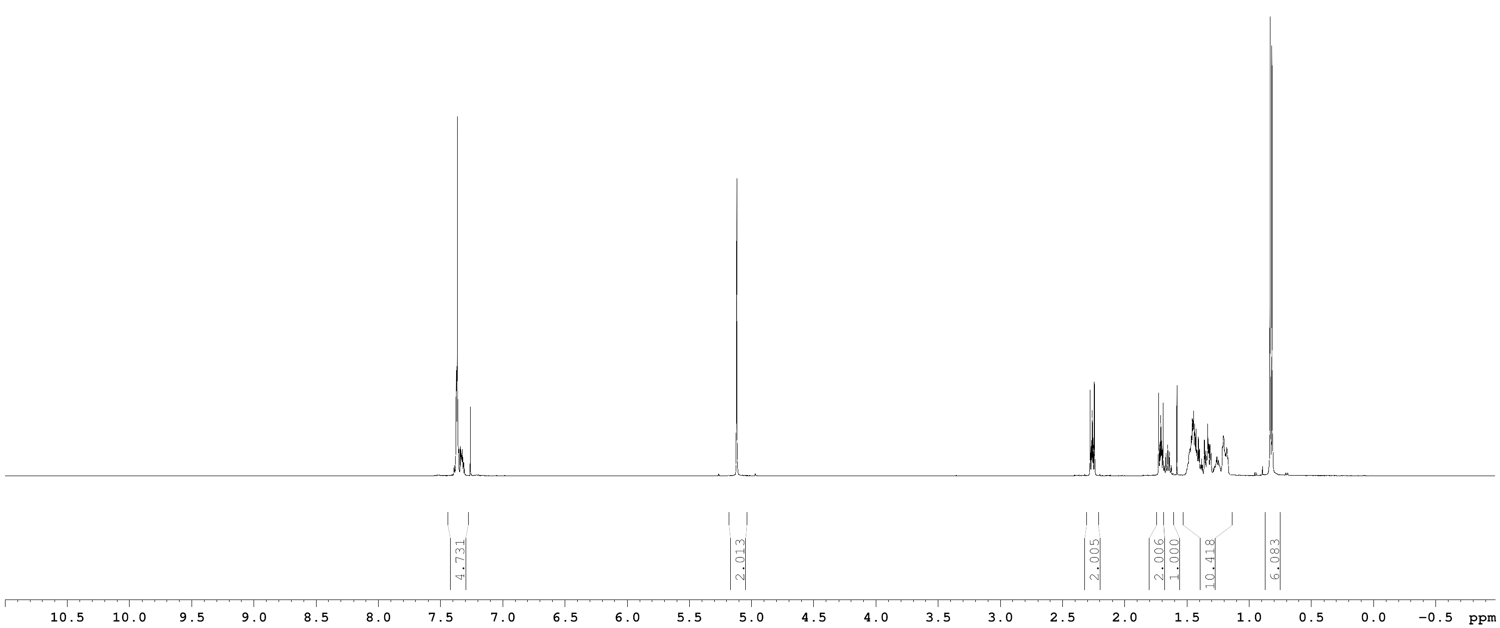

A3_92-ccn-s5-050-3-a.11.fid
Frequency: 125.89 MHz
174.48
128.56
128.24
128.18
77.28
77.03
76.77
66.19
37.49
32.32
28.99
26.41
21.96
Me
O
OBn
1.62
^{13}C NMR (CDCl$_3$, 126 MHz)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

1H spectrum



1.82

^{1}H NMR ($CDCl_3$, 500 MHz)



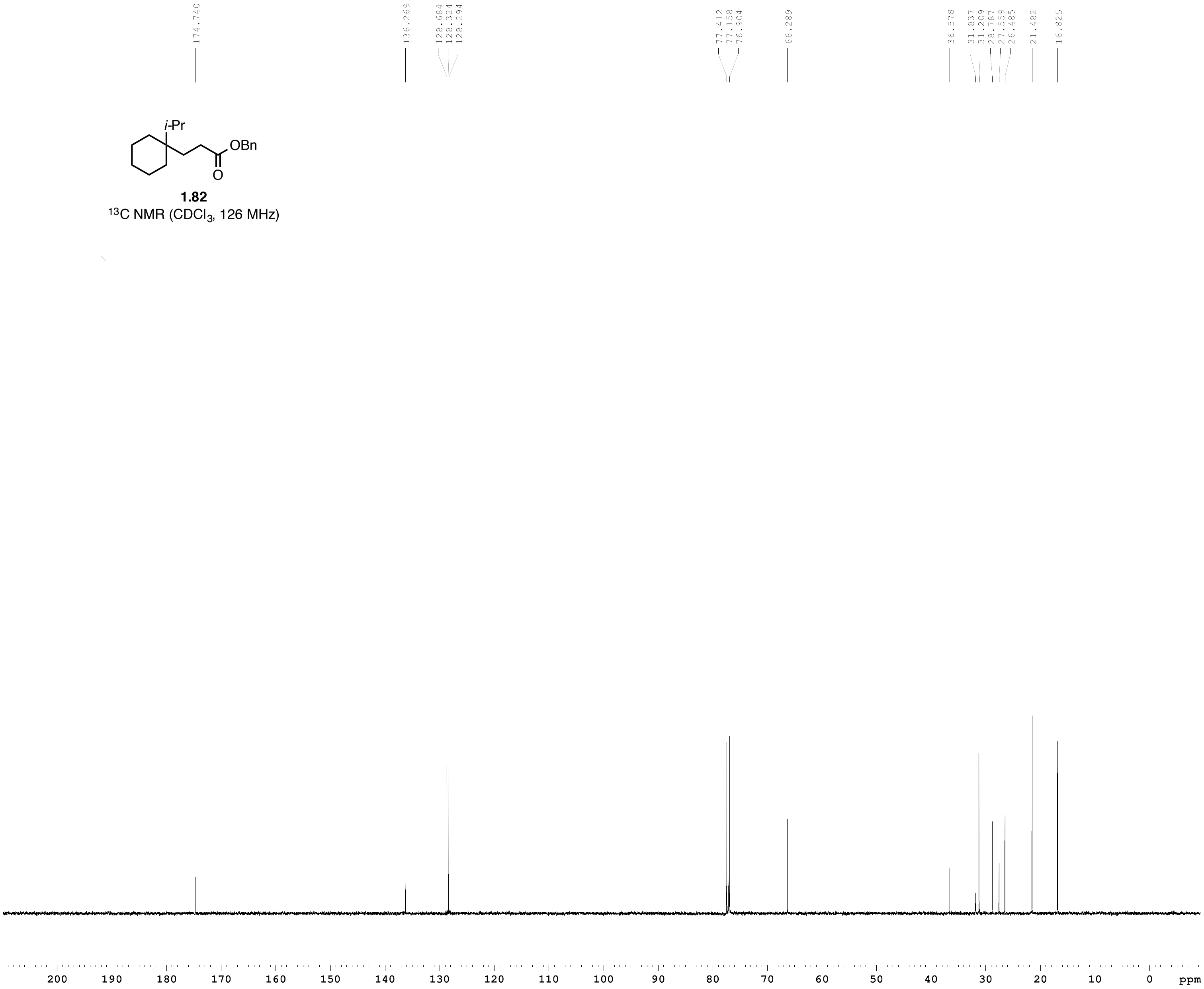
```
Current Data Parameters
NAME       CRJ1-152-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150317
Time               14.06
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                     4
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200311 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

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



1.82

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME       CRJ1-152-pure
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150317
Time               14.08
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804091 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

1.84

^{1}H NMR (CDCl$_3$, 500 MHz)

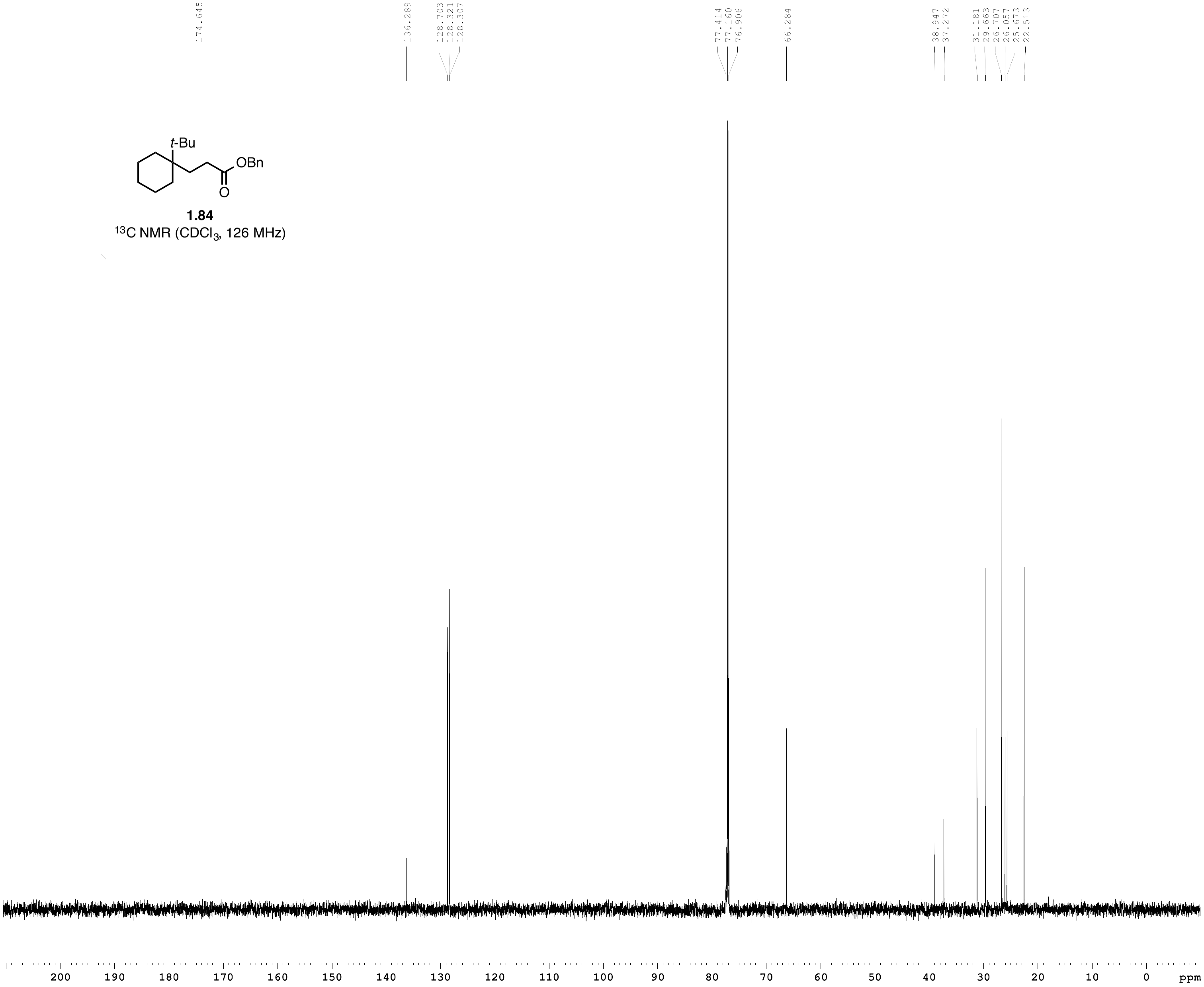
```
Current Data Parameters
NAME       CRJ1-153-pure
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150317
Time               14.14
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200309 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

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



1.84

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME      CRJ1-153-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150317
Time              14.17
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

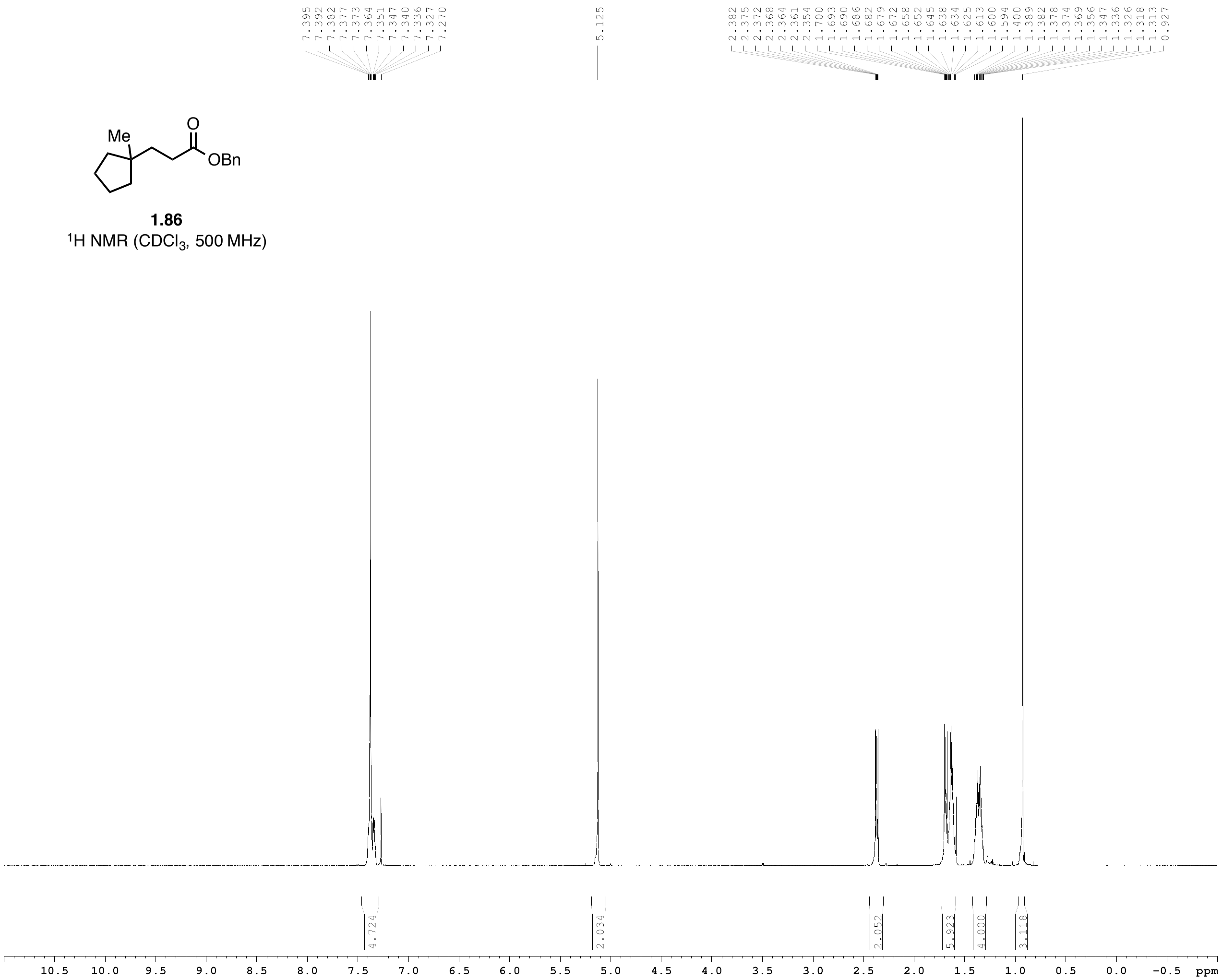
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804077 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 2.00
```

YS-II-254A

1.86

^{1}H NMR ($CDCl_3$, 500 MHz)



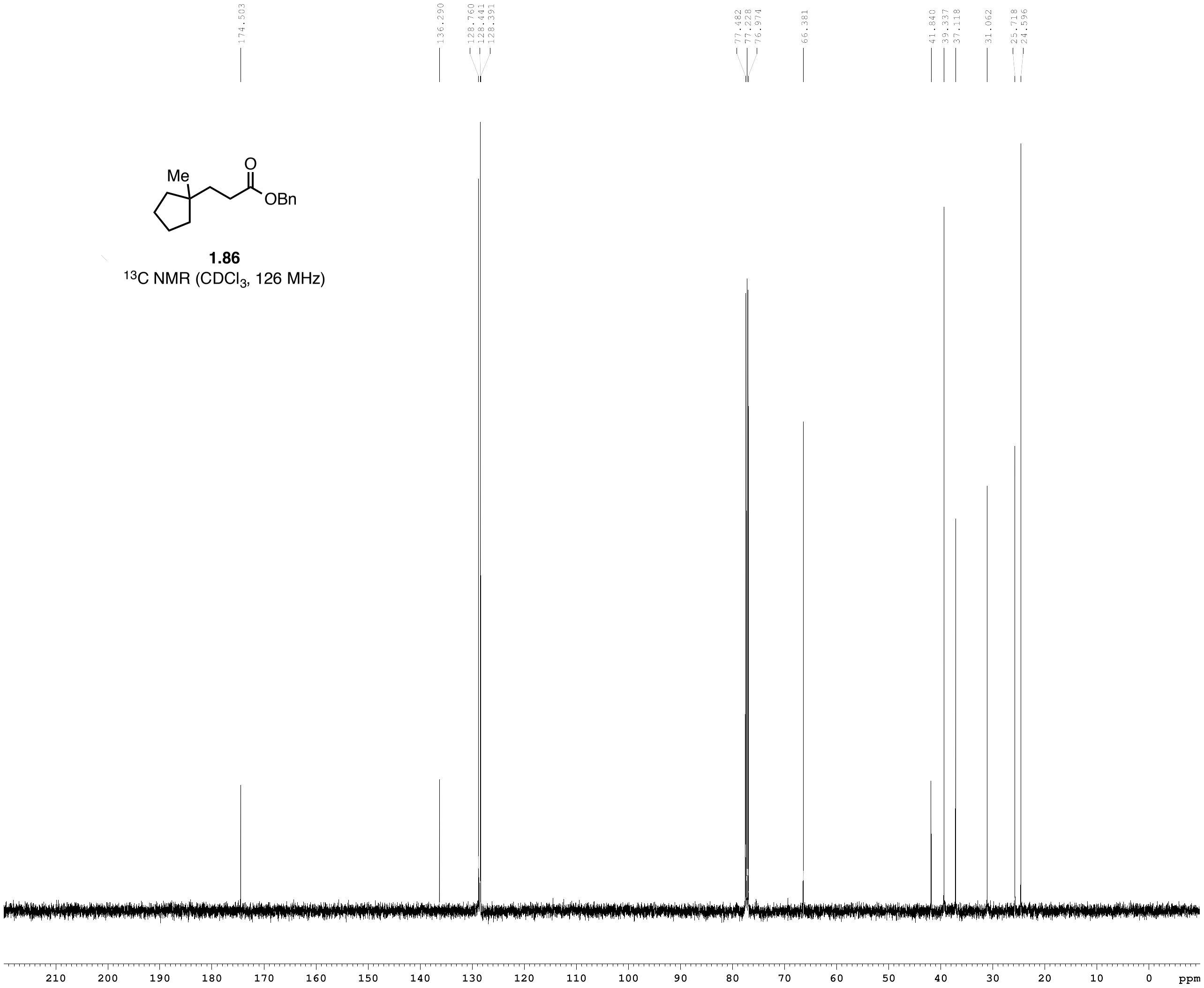
```
Current Data Parameters
NAME          YS-II-254A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150219
Time               14.59
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                   161
DW               52.000 usec
DE                14.54 usec
TE                298.1 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                   1H
P1                   8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300300 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-254A



1.86

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-254A
EXPNO                  2
PROCNO                 1

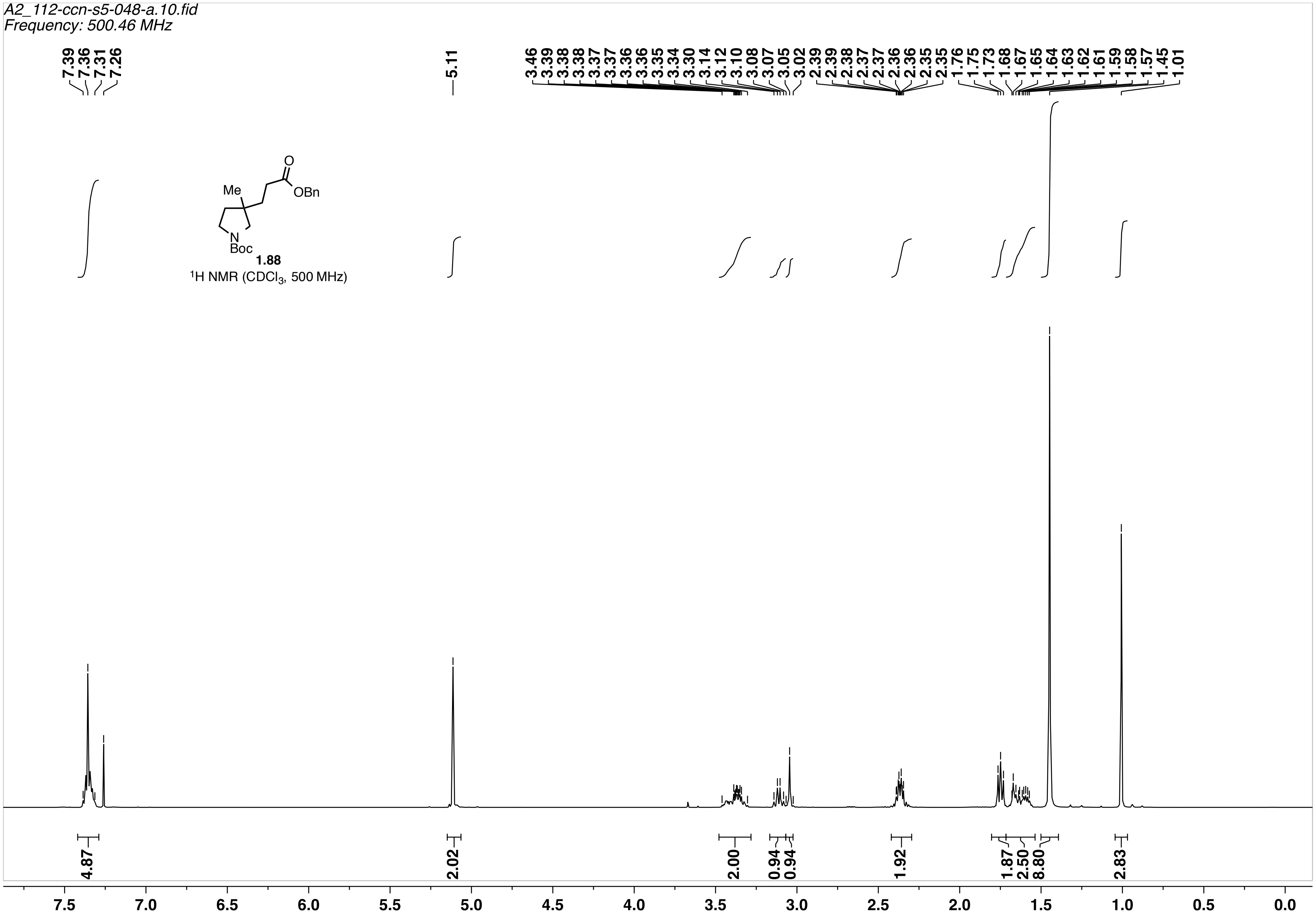
F2 - Acquisition Parameters
Date_           20150219
Time               15.29
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   184
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

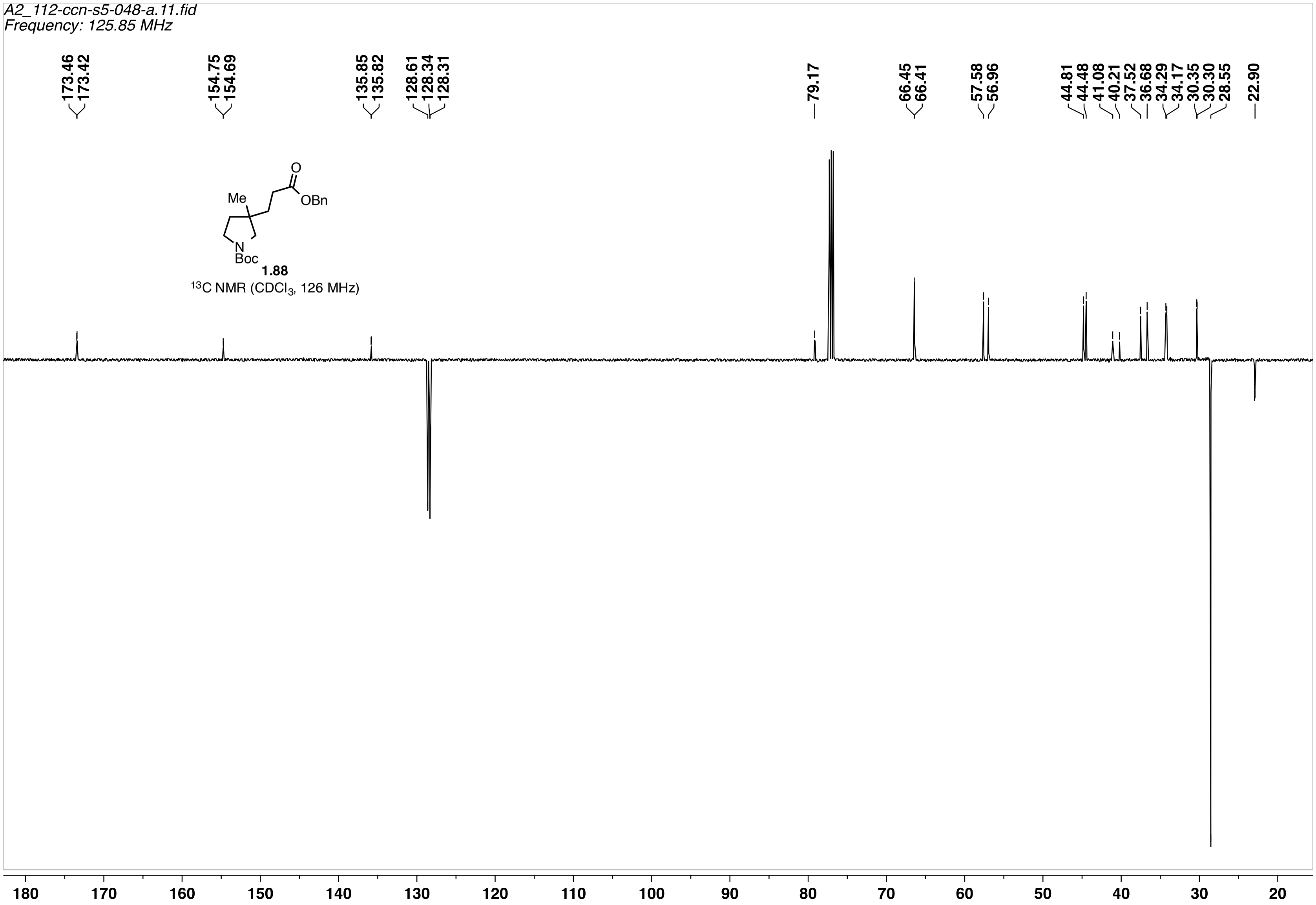
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803362 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



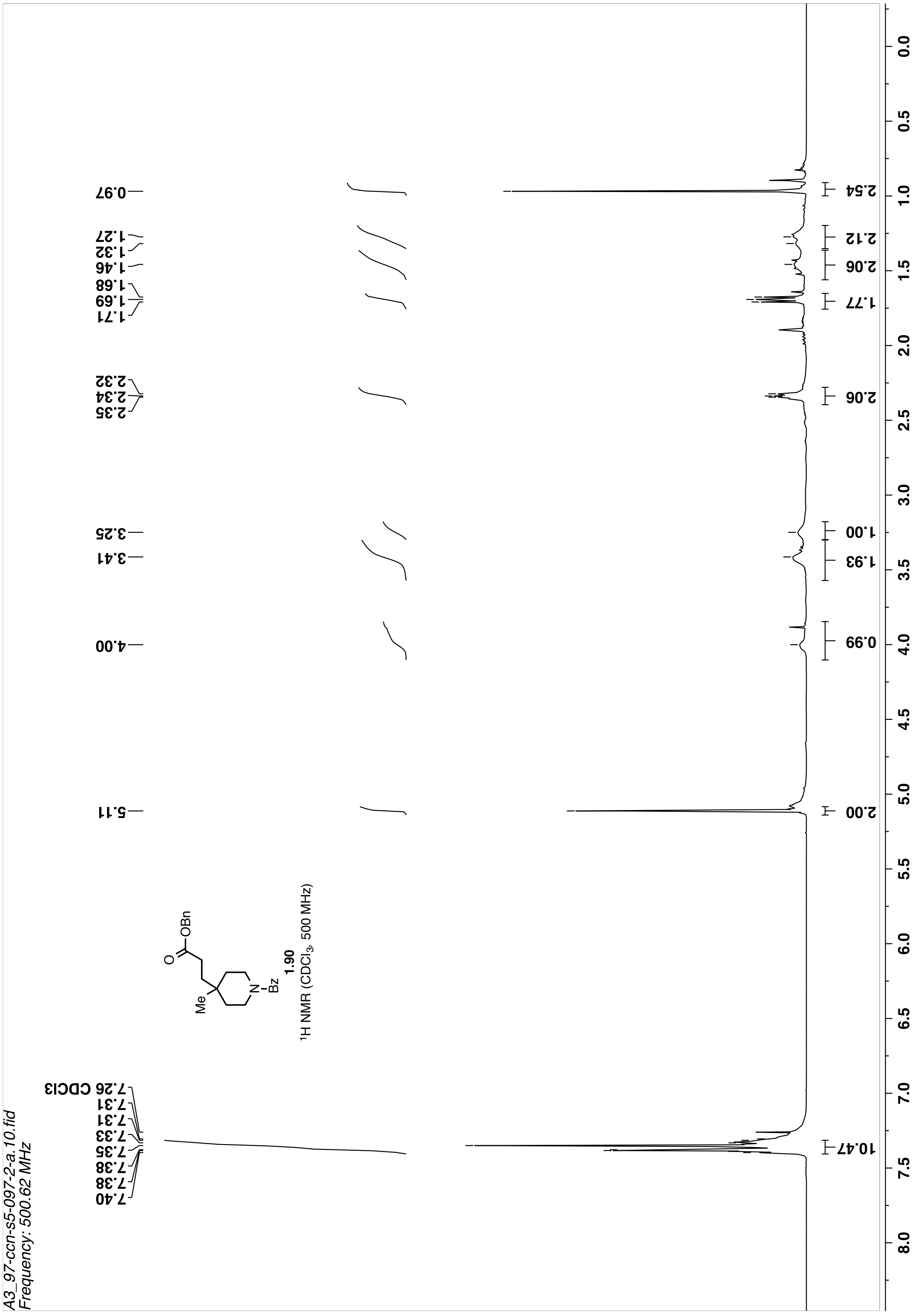
1.88

^{1}H NMR (CDCl$_3$, 500 MHz)

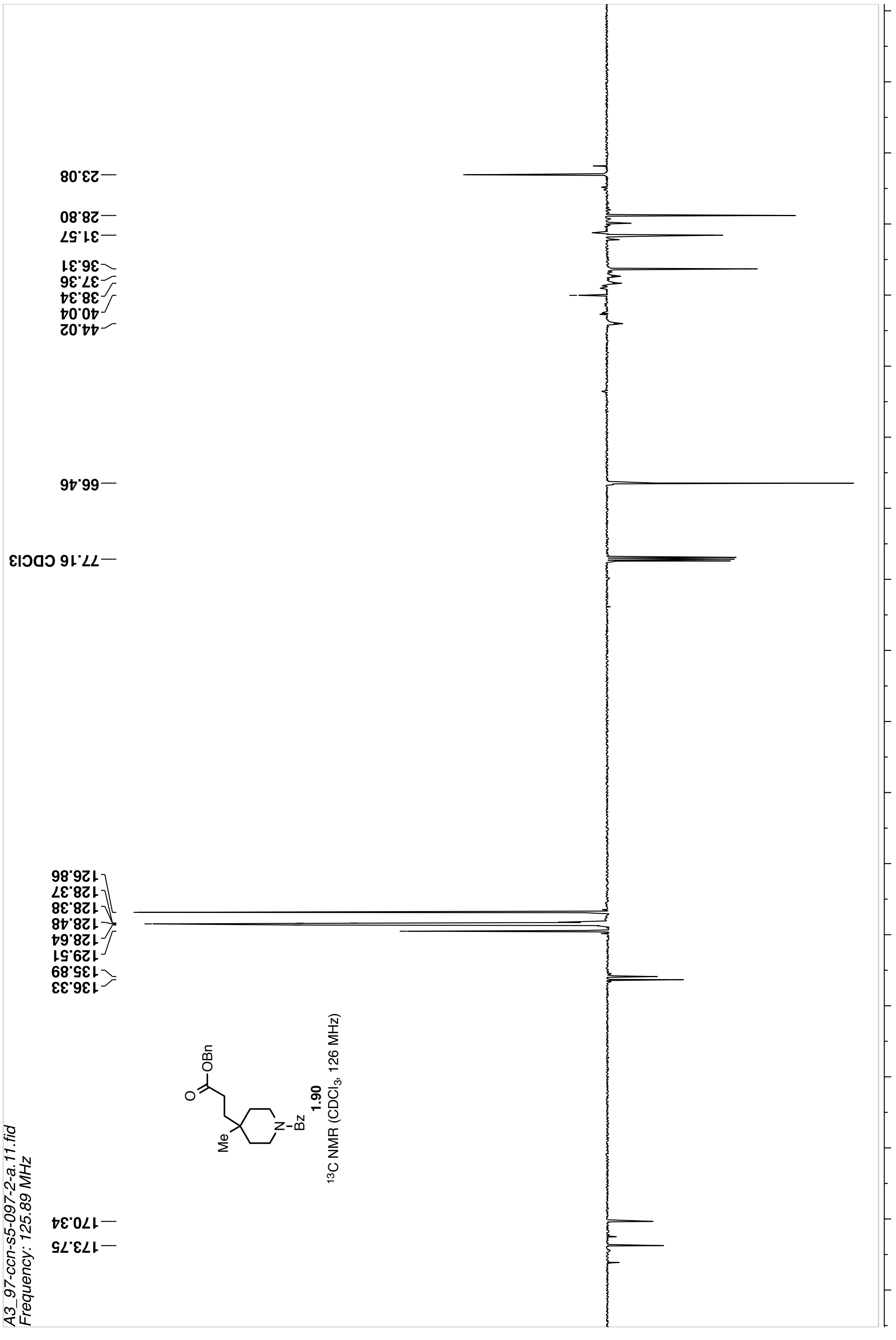


1.88

^{13}C NMR (CDCl$_3$, 126 MHz)


1.90

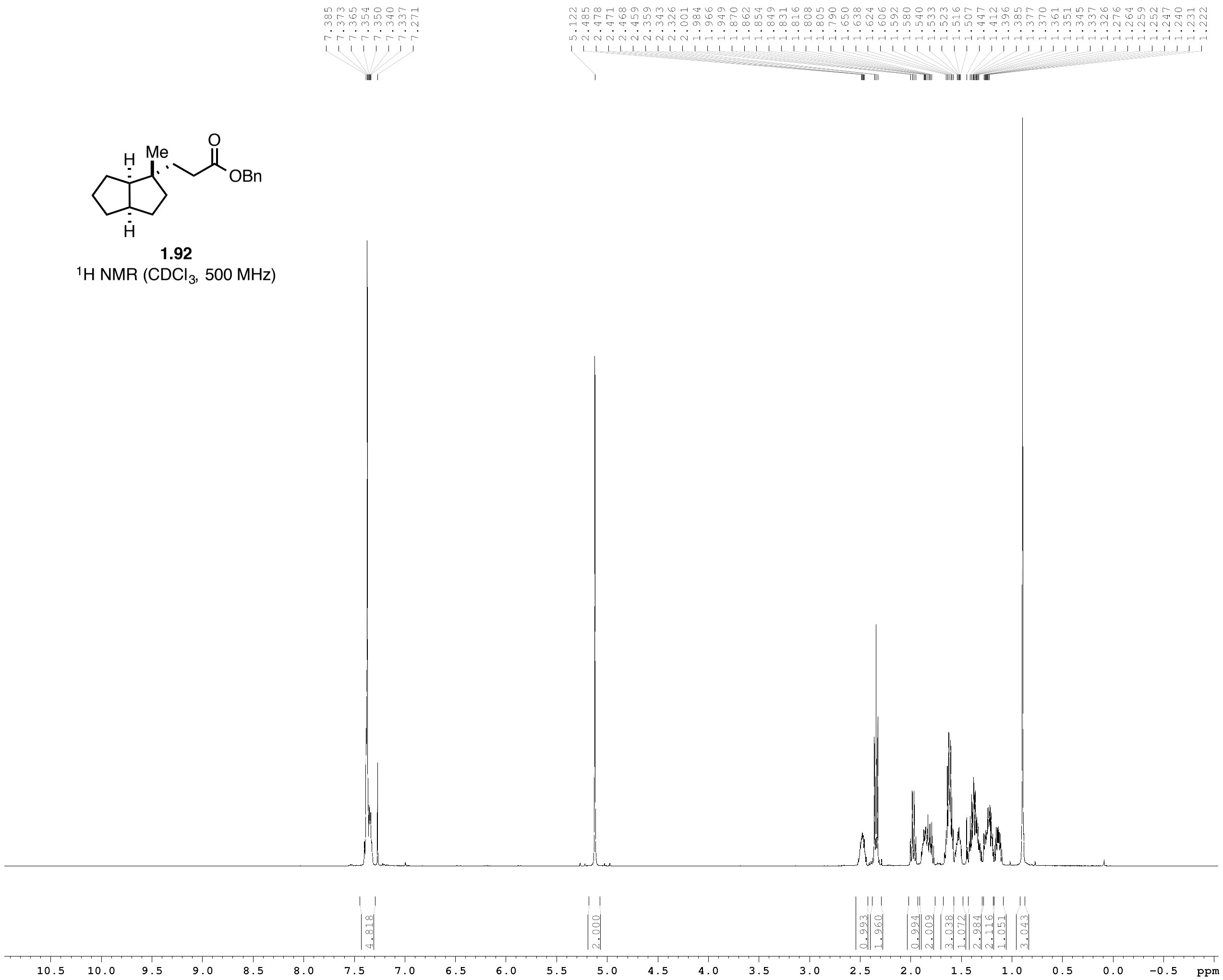
^{1}H NMR (CDCl$_3$, 500 MHz)


A3_97-ccn-s5-097-2-a.11.fid
Frequency: 125.89 MHz
1.90
^{13}C NMR (CDCl$_3$, 126 MHz)
Me
N
Bz
O
OBn
173.75
170.34
136.33
135.89
129.51
128.64
128.48
128.38
128.37
126.86
77.16 CDCl3
66.46
44.02
40.04
38.34
37.36
36.31
31.57
28.80
23.08
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

YS-II-293

1.92

^{1}H NMR (CDCl$_3$, 500 MHz)



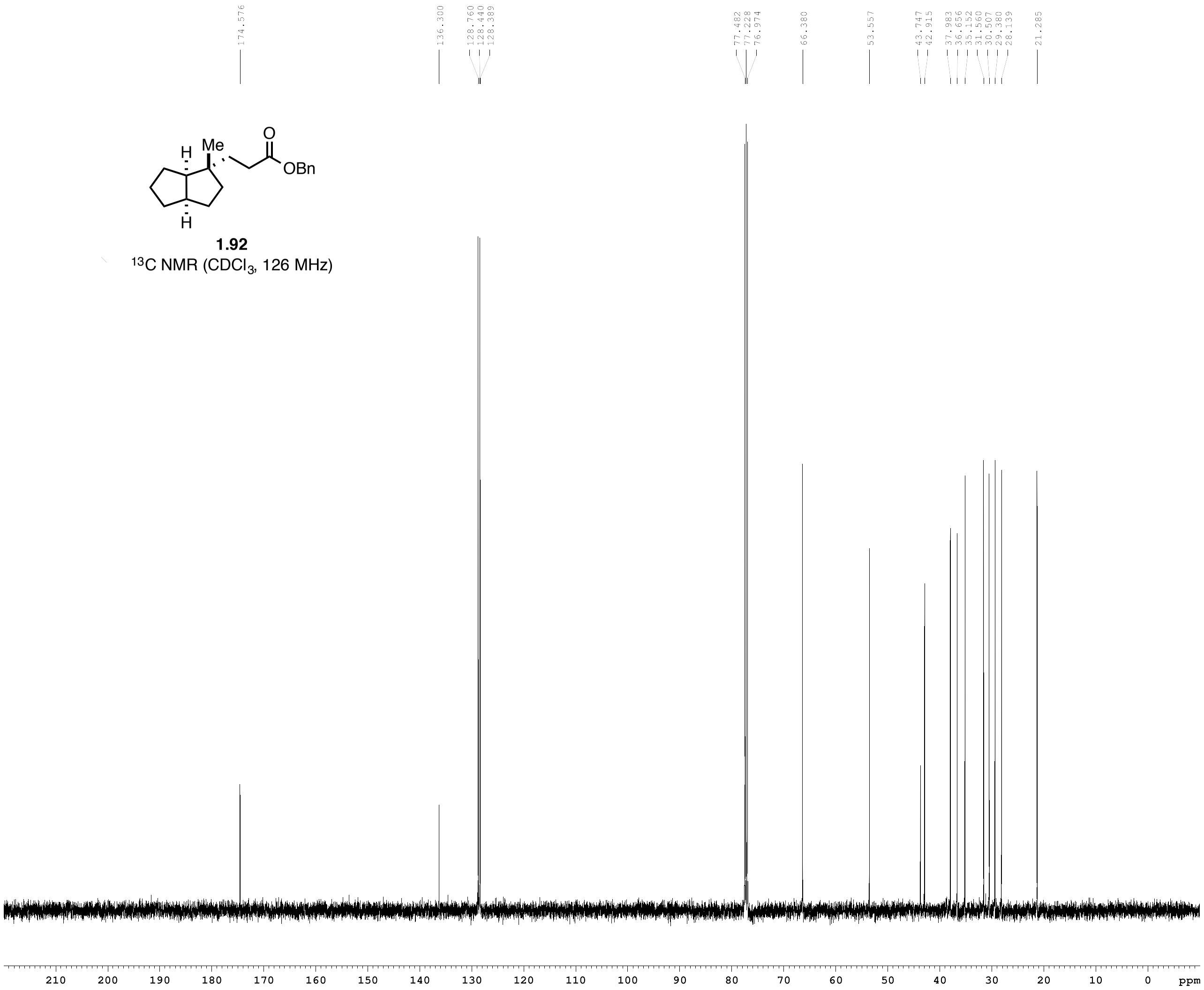
```
Current Data Parameters
NAME          YS-II-293
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150311
Time               8.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200254 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-293



1.92

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-293
EXPNO                 2
PROCNO                1

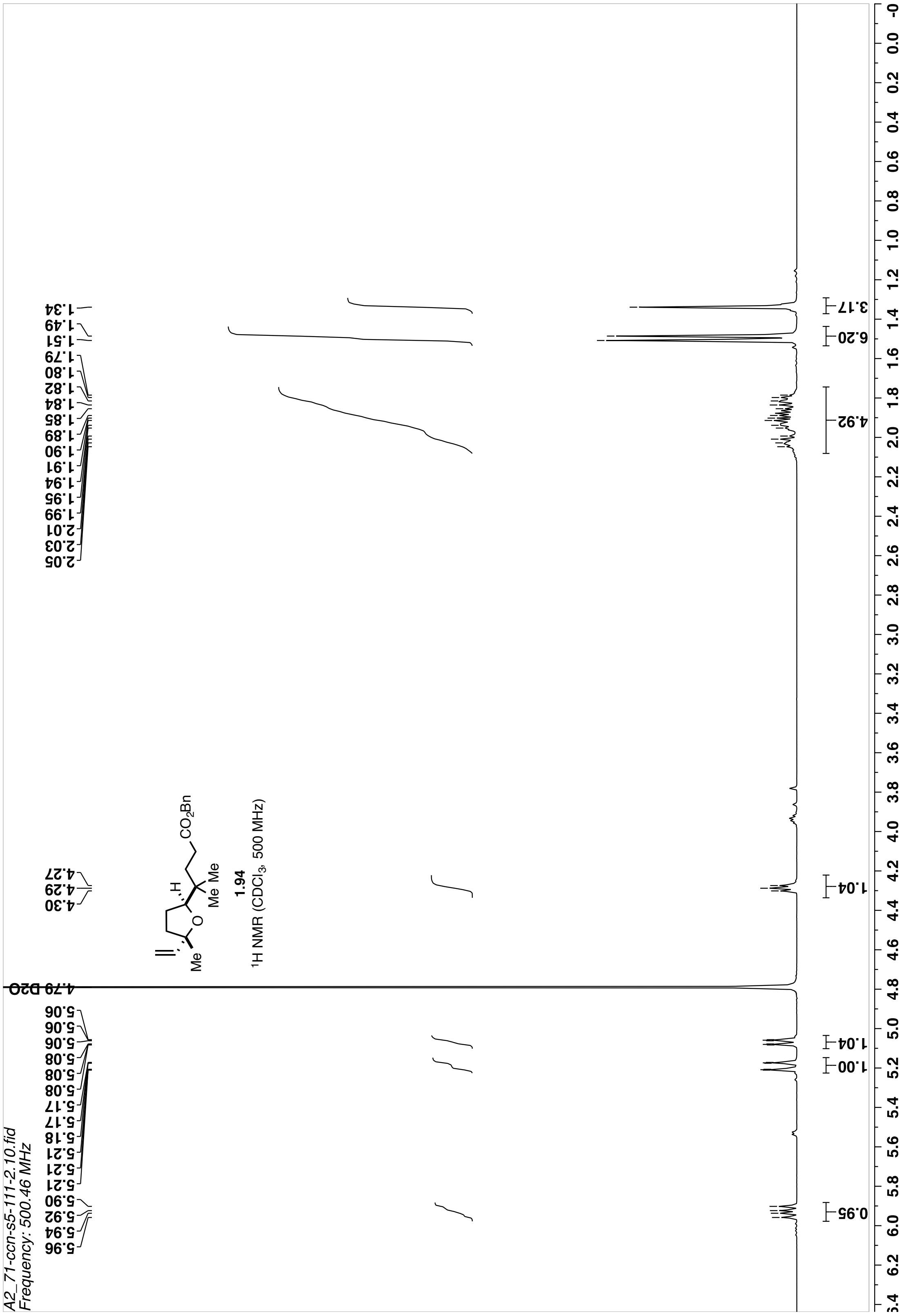
F2 - Acquisition Parameters
Date_          20150311
Time               8.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  224
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              11585.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

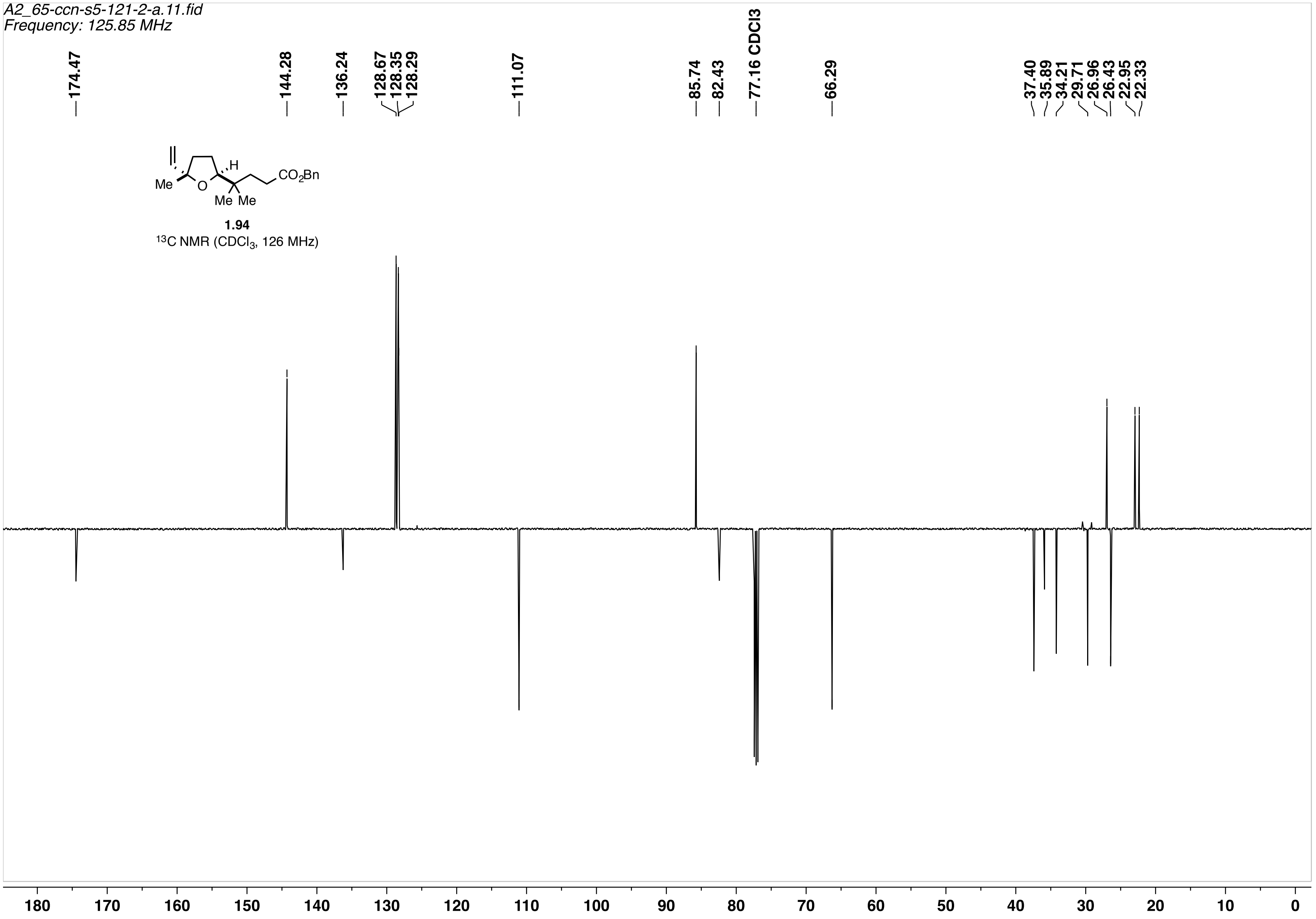
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804001 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



1.94

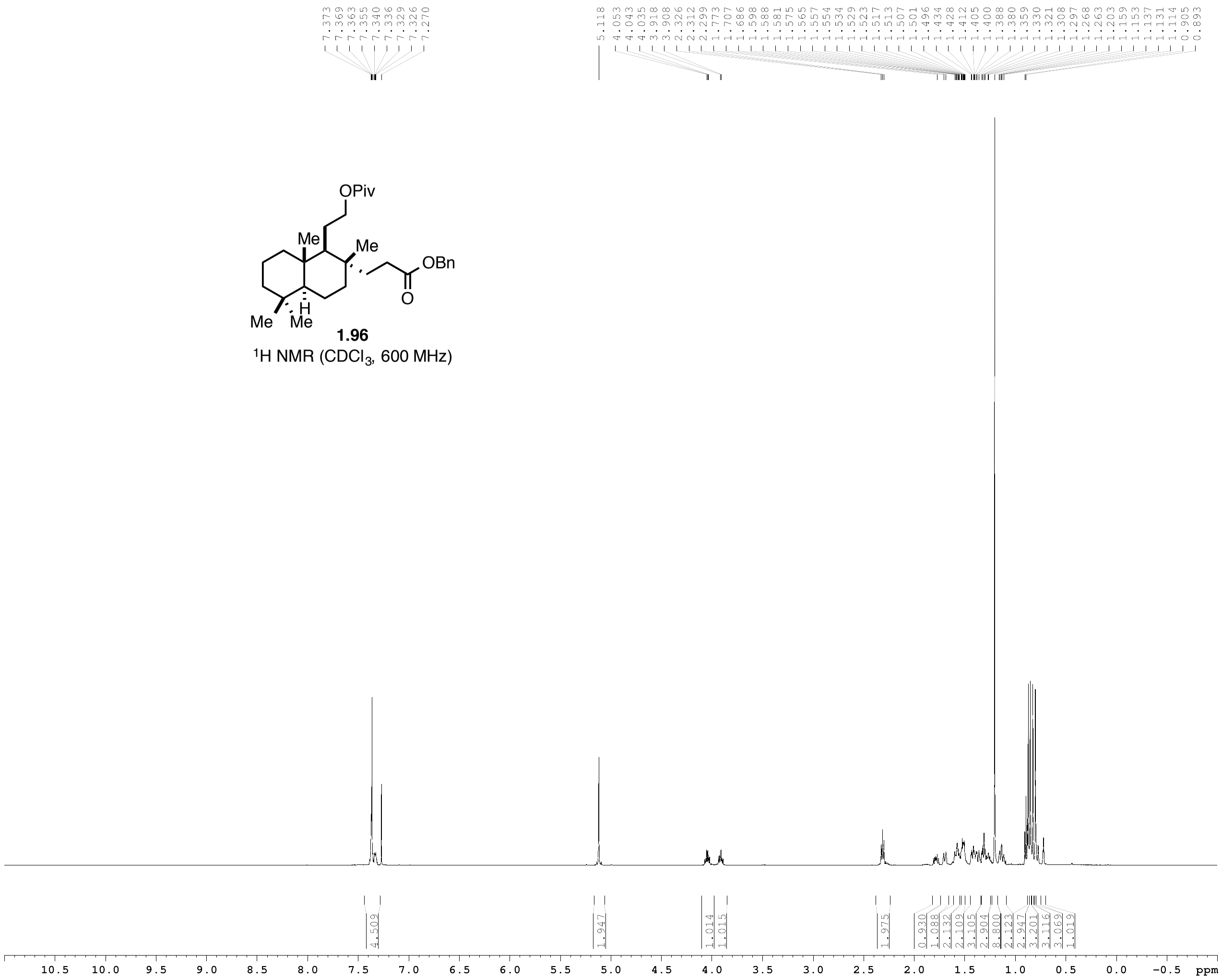
^{1}H NMR (CDCl$_3$, 500 MHz)



1.94

^{13}C NMR ($CDCl_3$, 126 MHz)

YS-II-270A



1.96

^1H NMR ($CDCl_3$, 600 MHz)

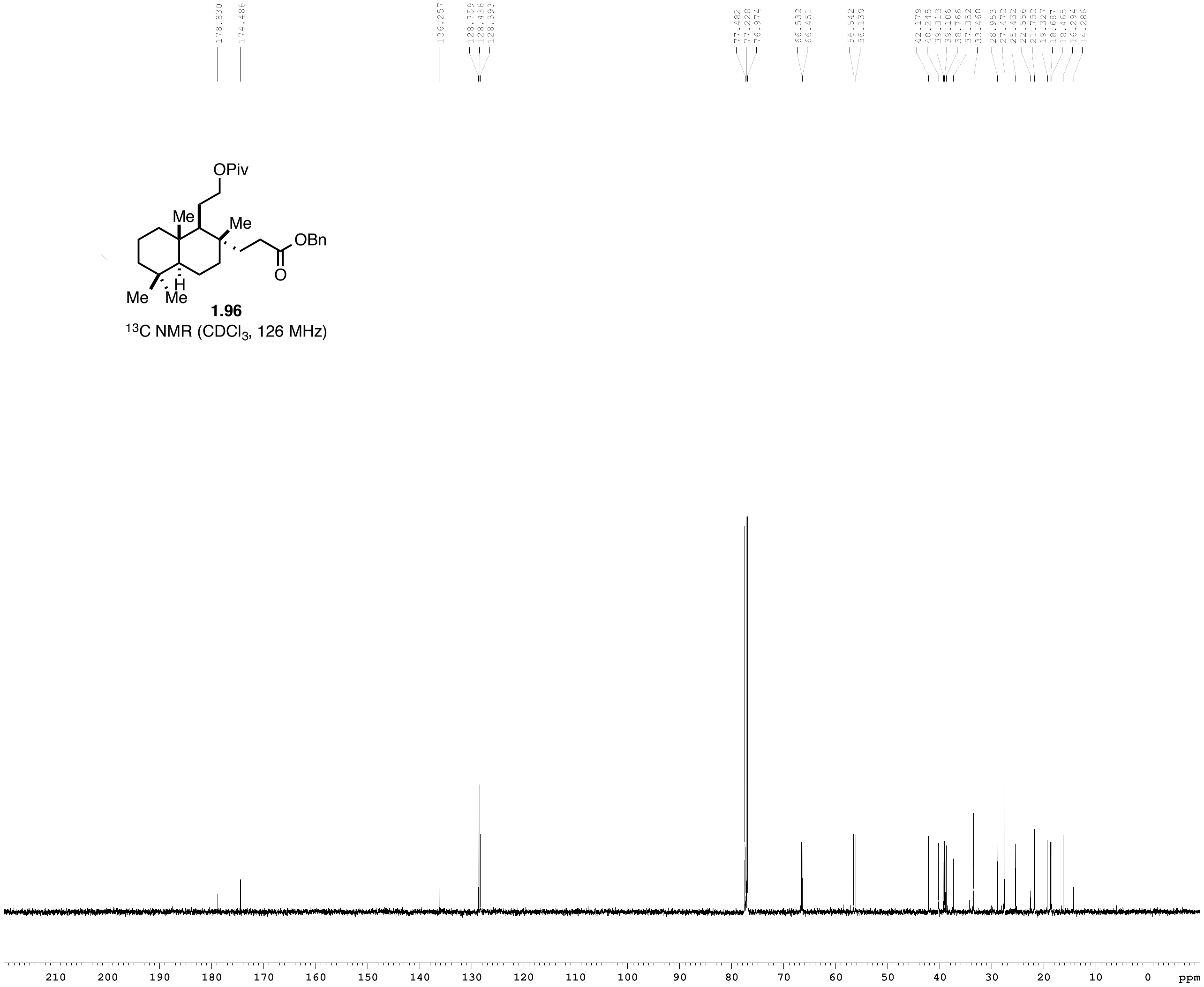
```
Current Data Parameters
NAME          YS-II-270A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150226
Time               14.06
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   256
DW                52.000 usec
DE                 14.54 usec
TE                 298.1 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300306 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-270A



1.96

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-270A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150226
Time               15.07
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   368
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

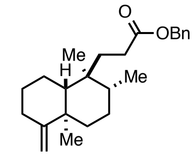
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803988 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-II-270B



1.98

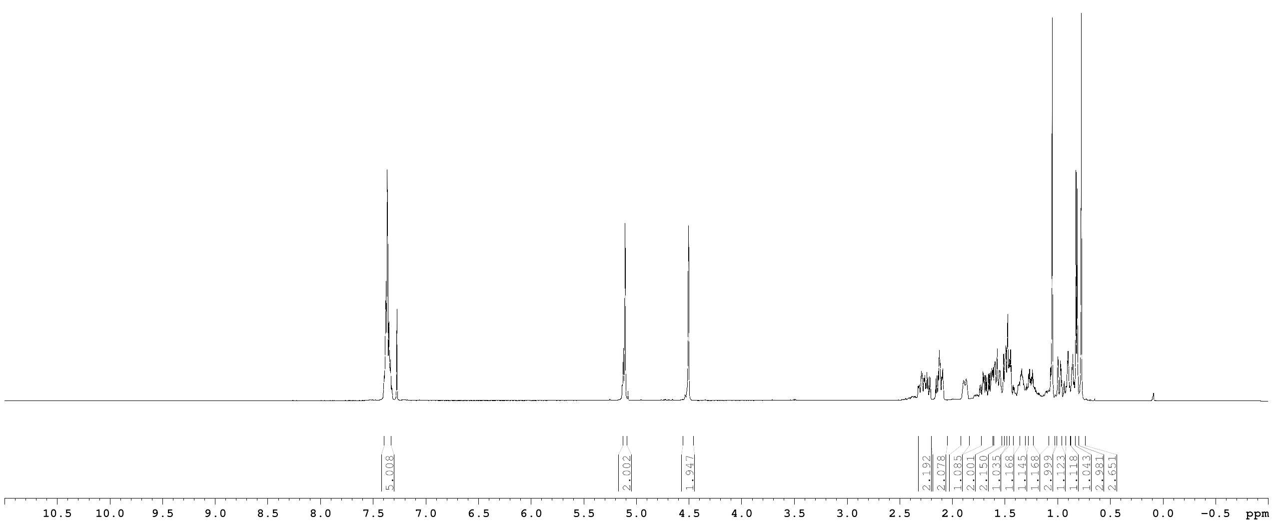
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          YS-II-270B
EXPNO                  1
PROCNO                 1

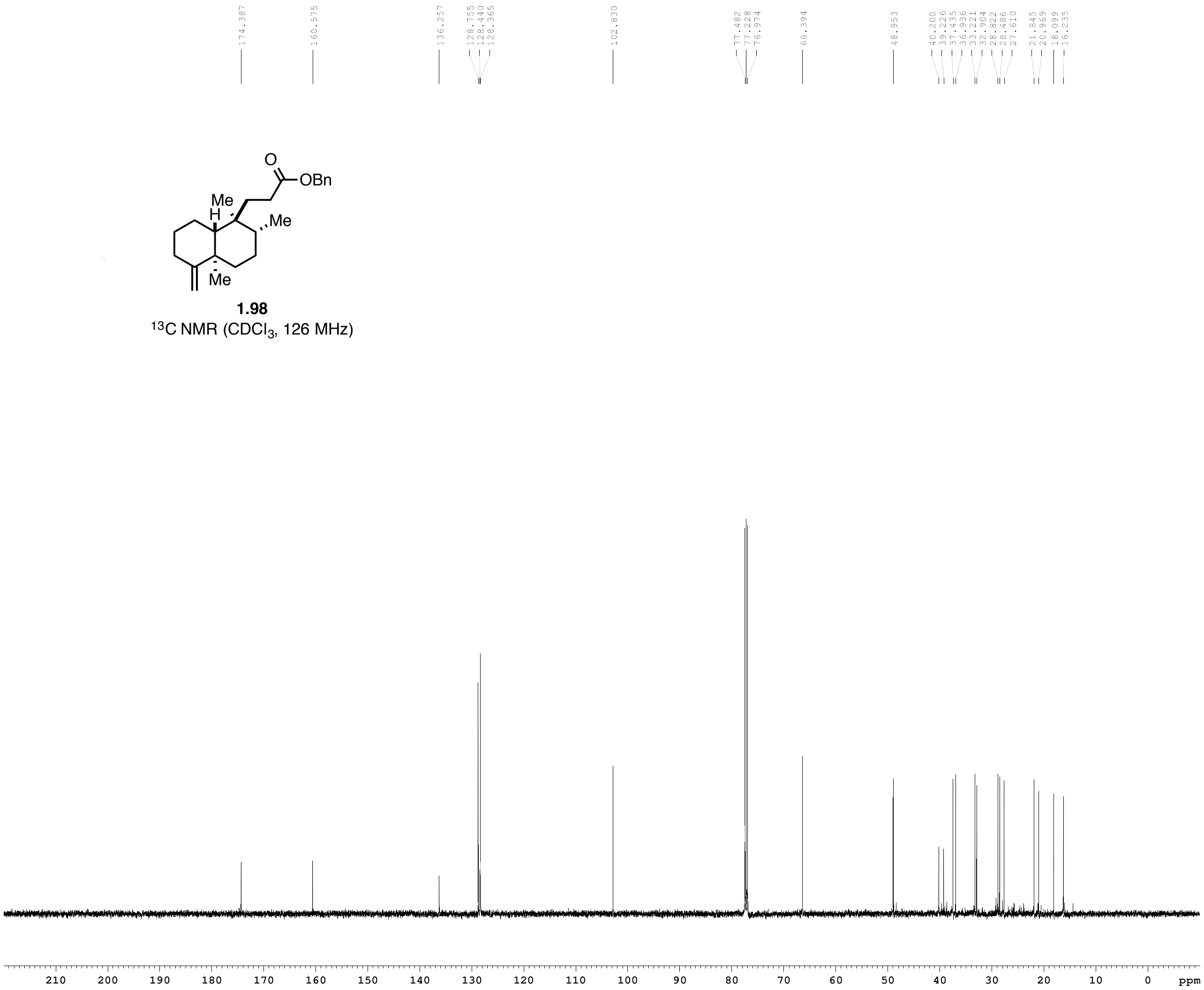
F2 - Acquisition Parameters
Date_           20150228
Time               14.41
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200243 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```



YS-II-270B



1.98

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-270B
EXPNO                  2
PROCNO                 1

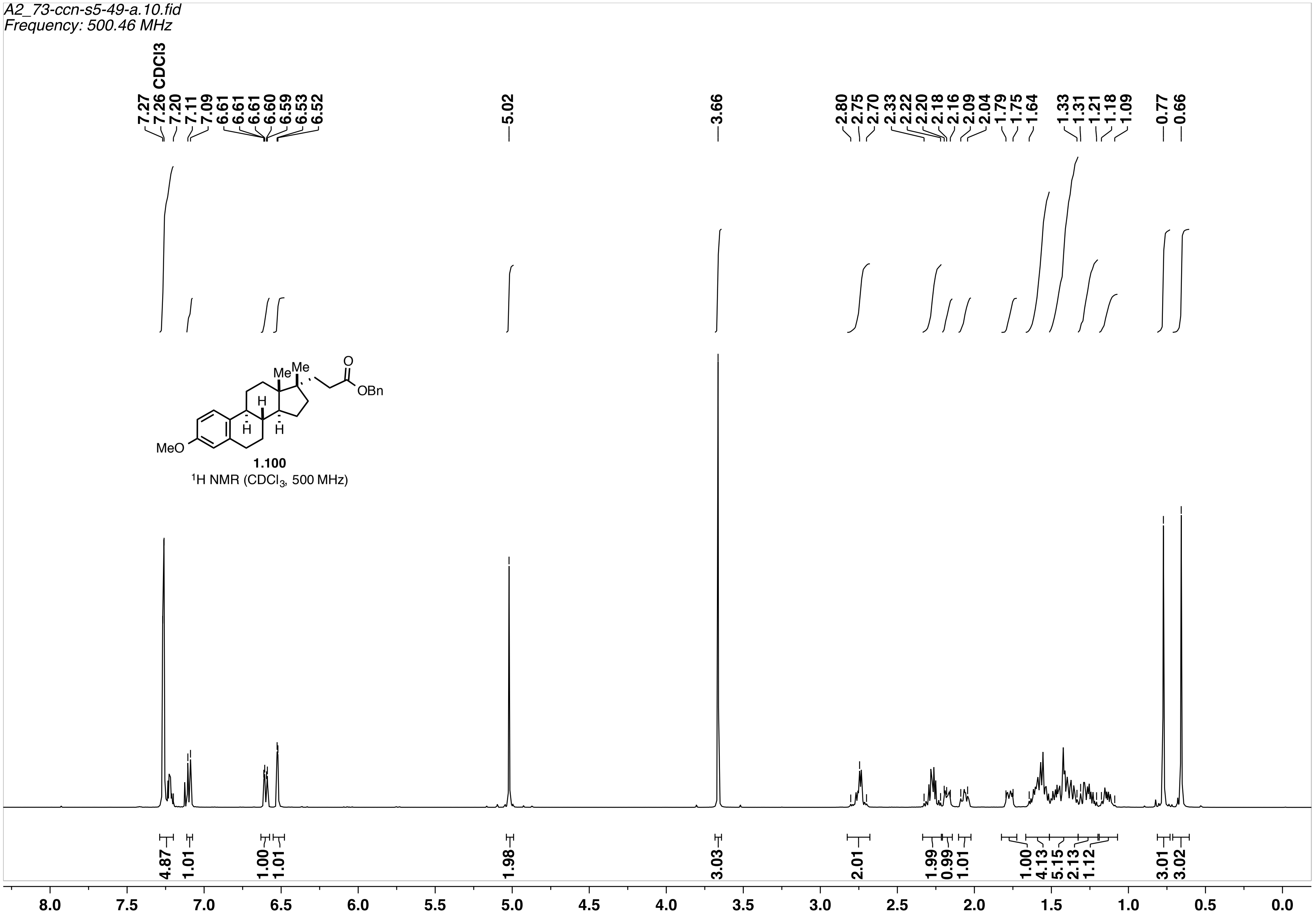
F2 - Acquisition Parameters
Date_           20150228
Time               14.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   352
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

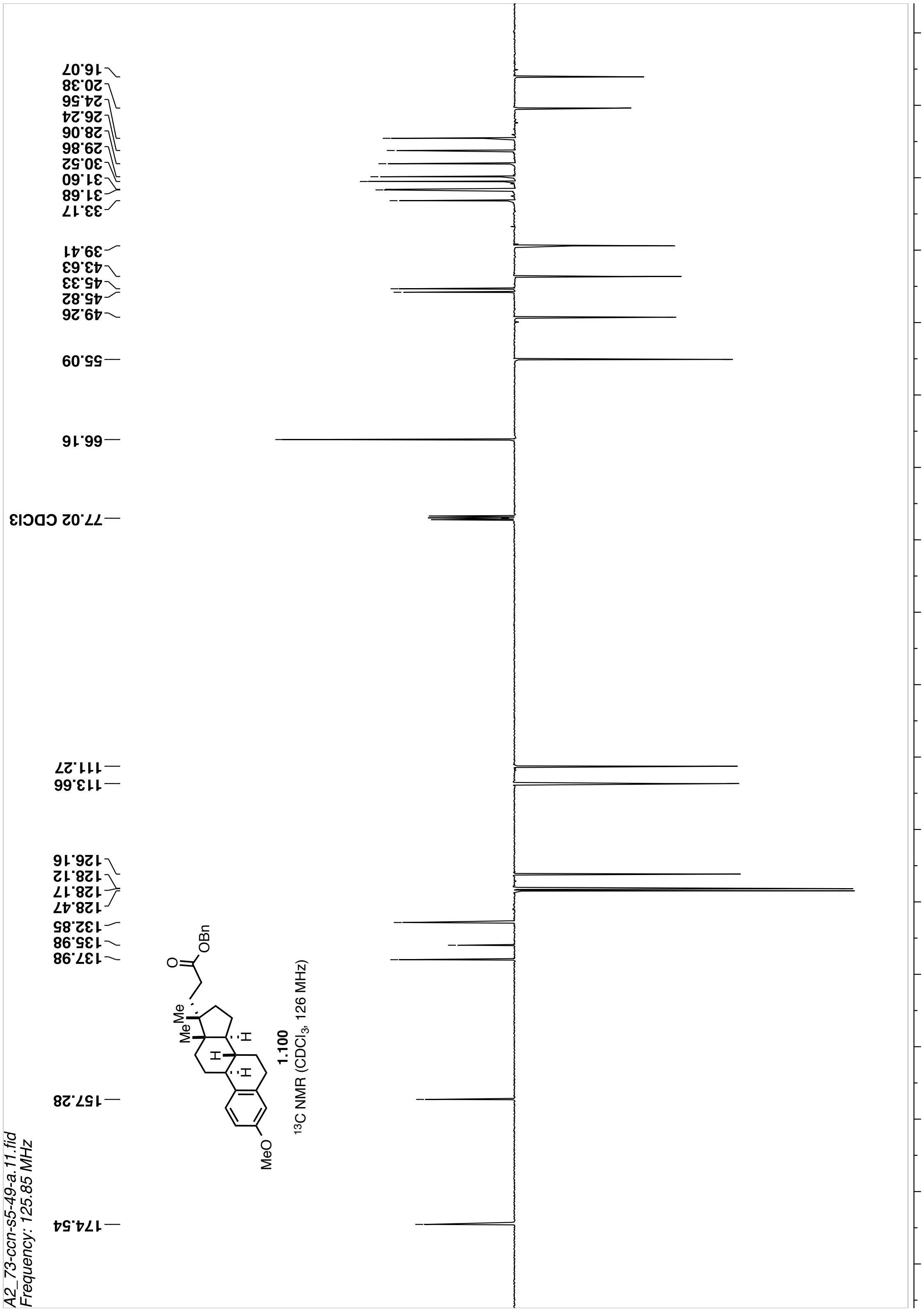
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803996 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



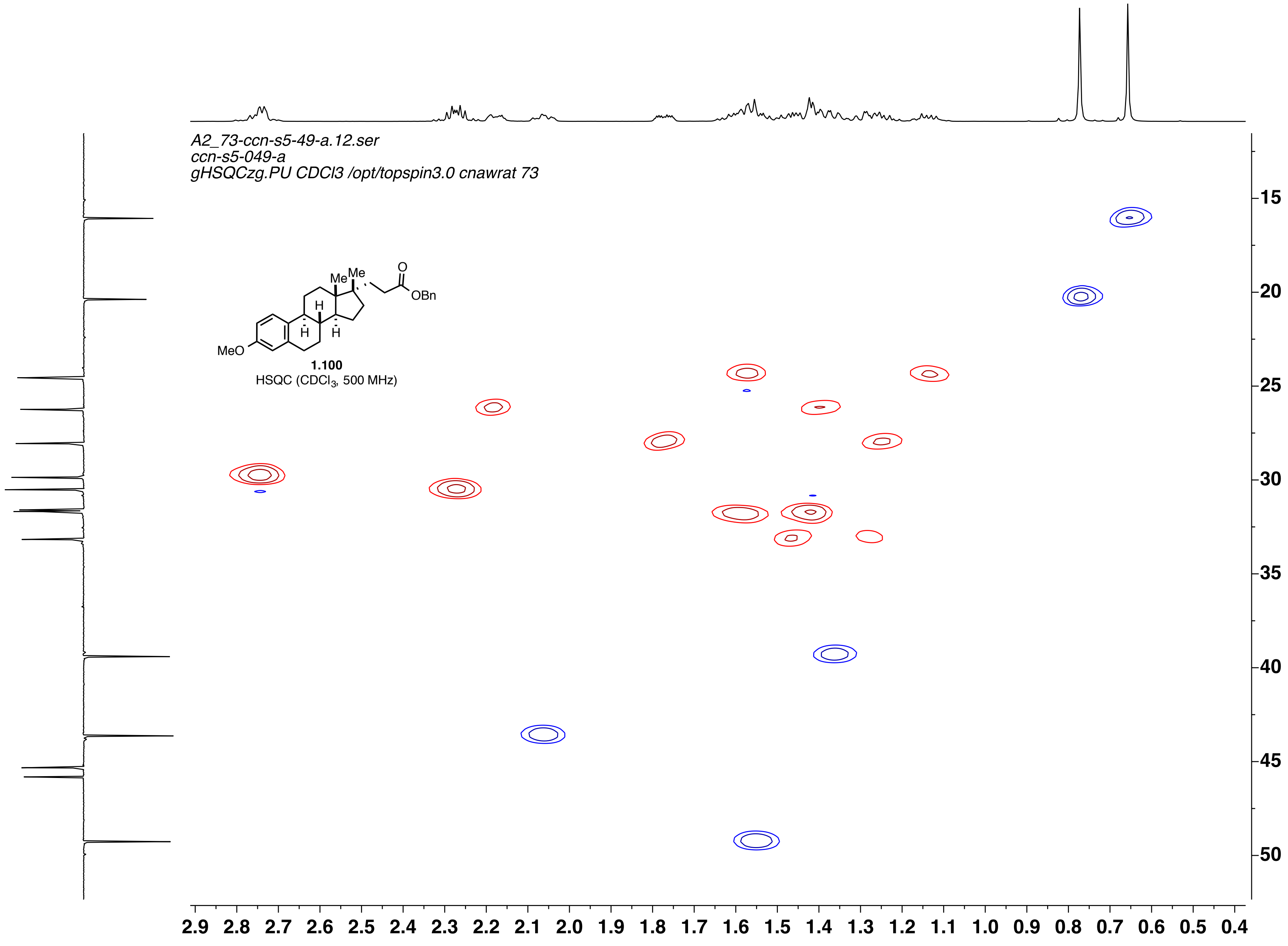
1.100

^{1}H NMR (CDCl$_3$, 500 MHz)



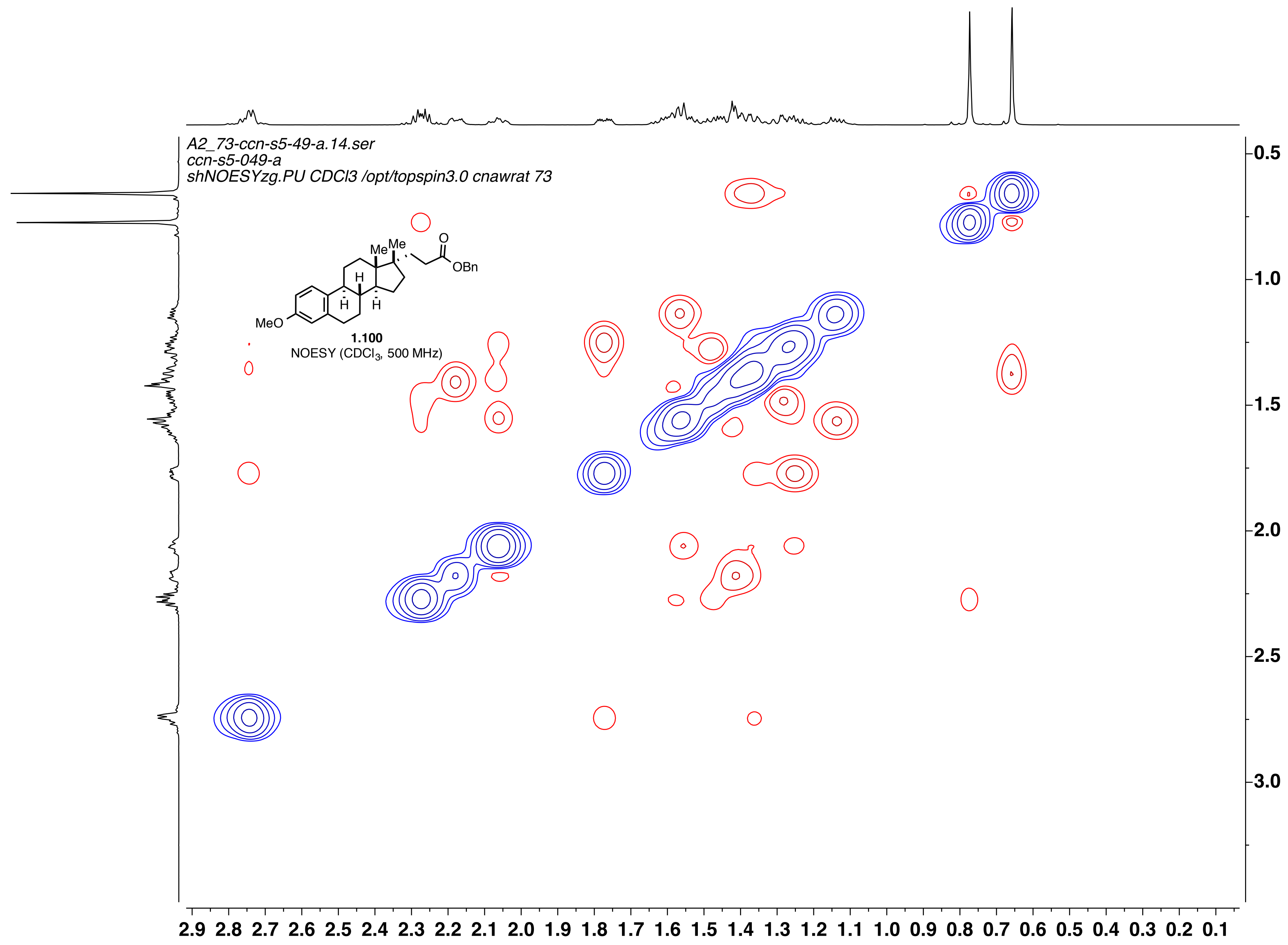
1.100

^{13}C NMR (CDCl$_3$, 126 MHz)



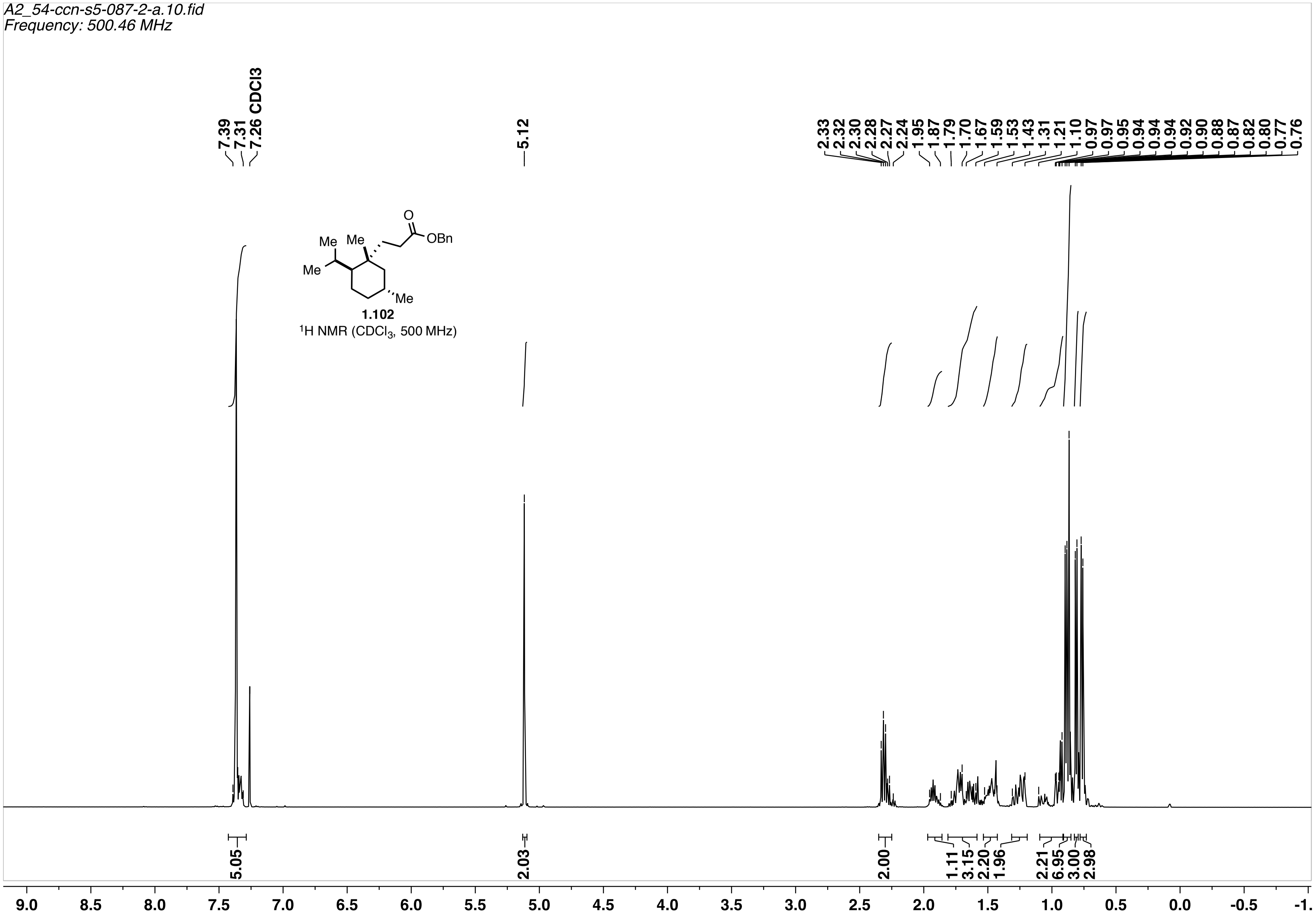
1.100

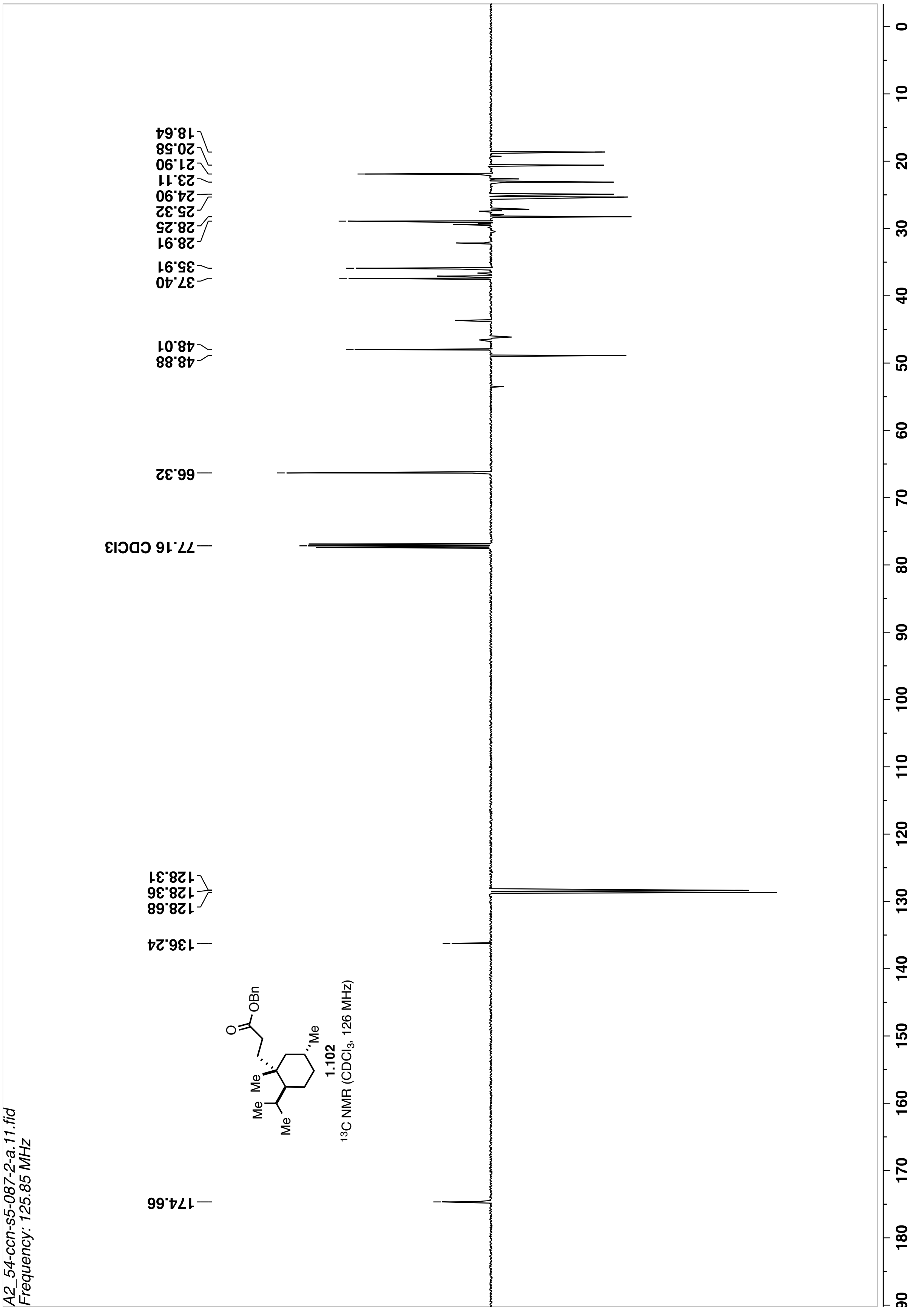
HSQC (CDCl$_3$, 500 MHz)



1.100

NOESY ($CDCl_3$, 500 MHz)

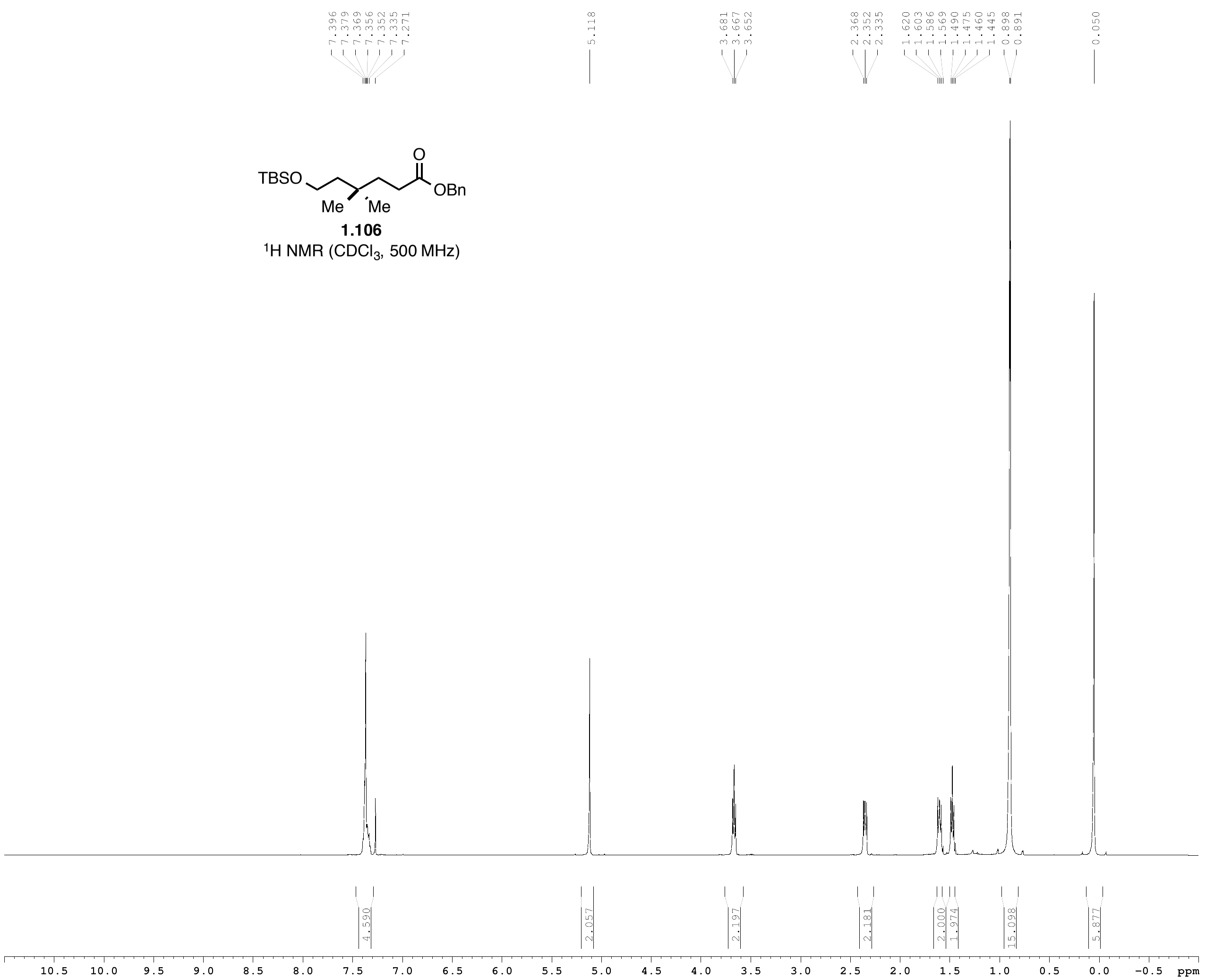

1.102
^{1}H NMR (CDCl$_3$, 500 MHz)



1.102

^{13}C NMR (CDCl$_3$, 126 MHz)

YS-II-272A



1.106

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          YS-II-272A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDC13
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

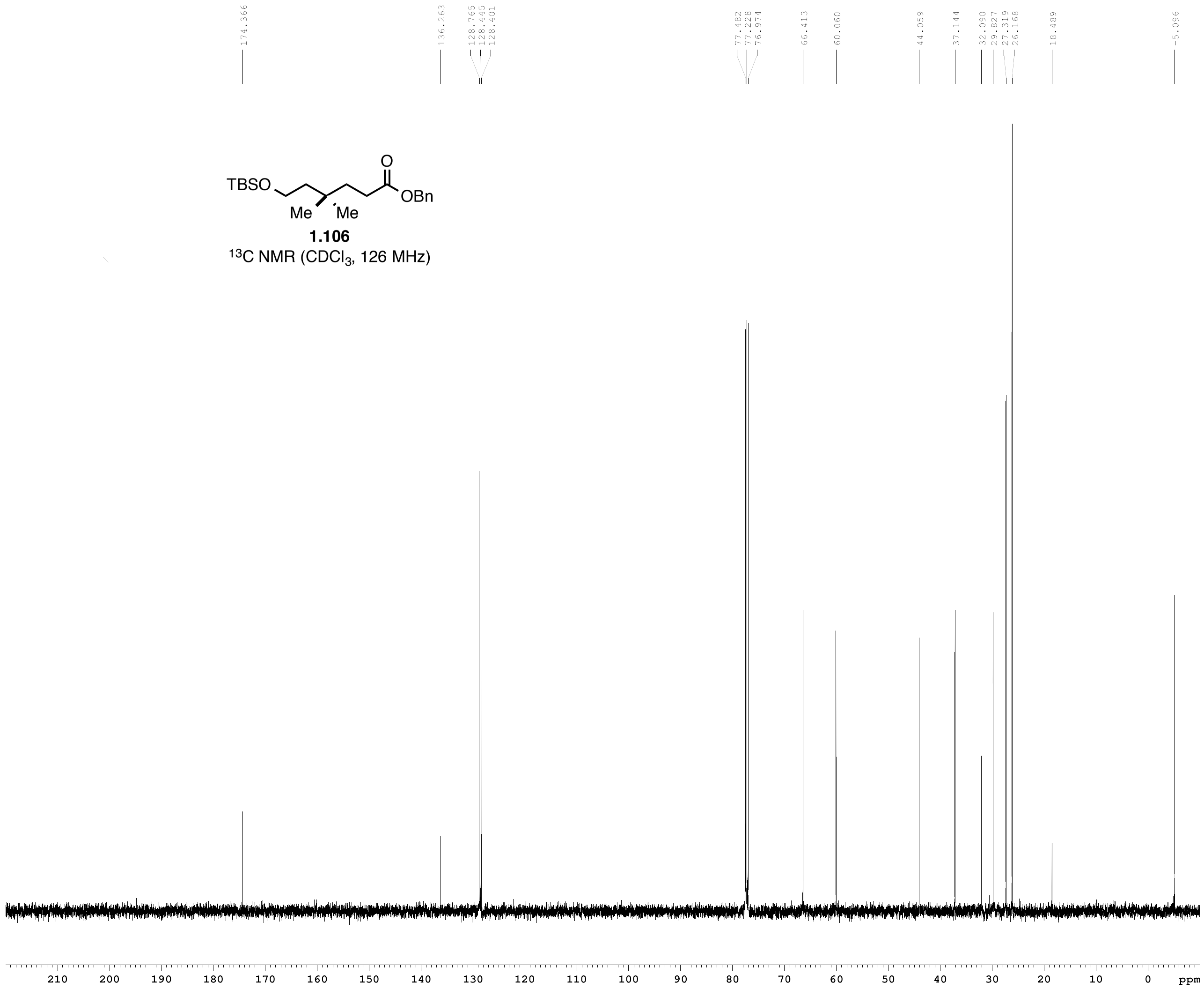
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200256 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-272A

1.106

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME         YS-II-272A
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150228
Time              14.37
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  176
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

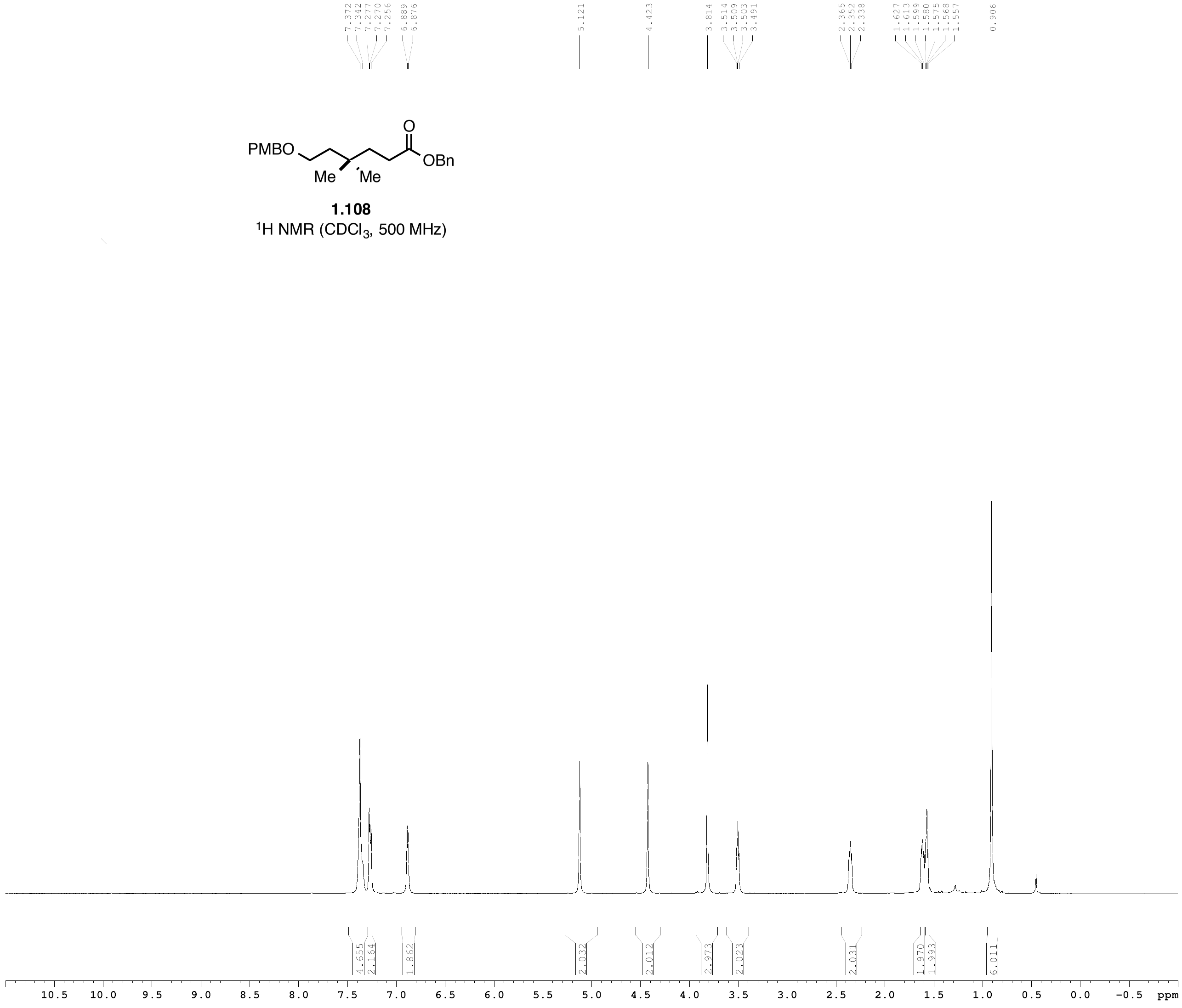
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803992 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-II-272B



1.108

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          YS-II-272B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.15
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   256
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

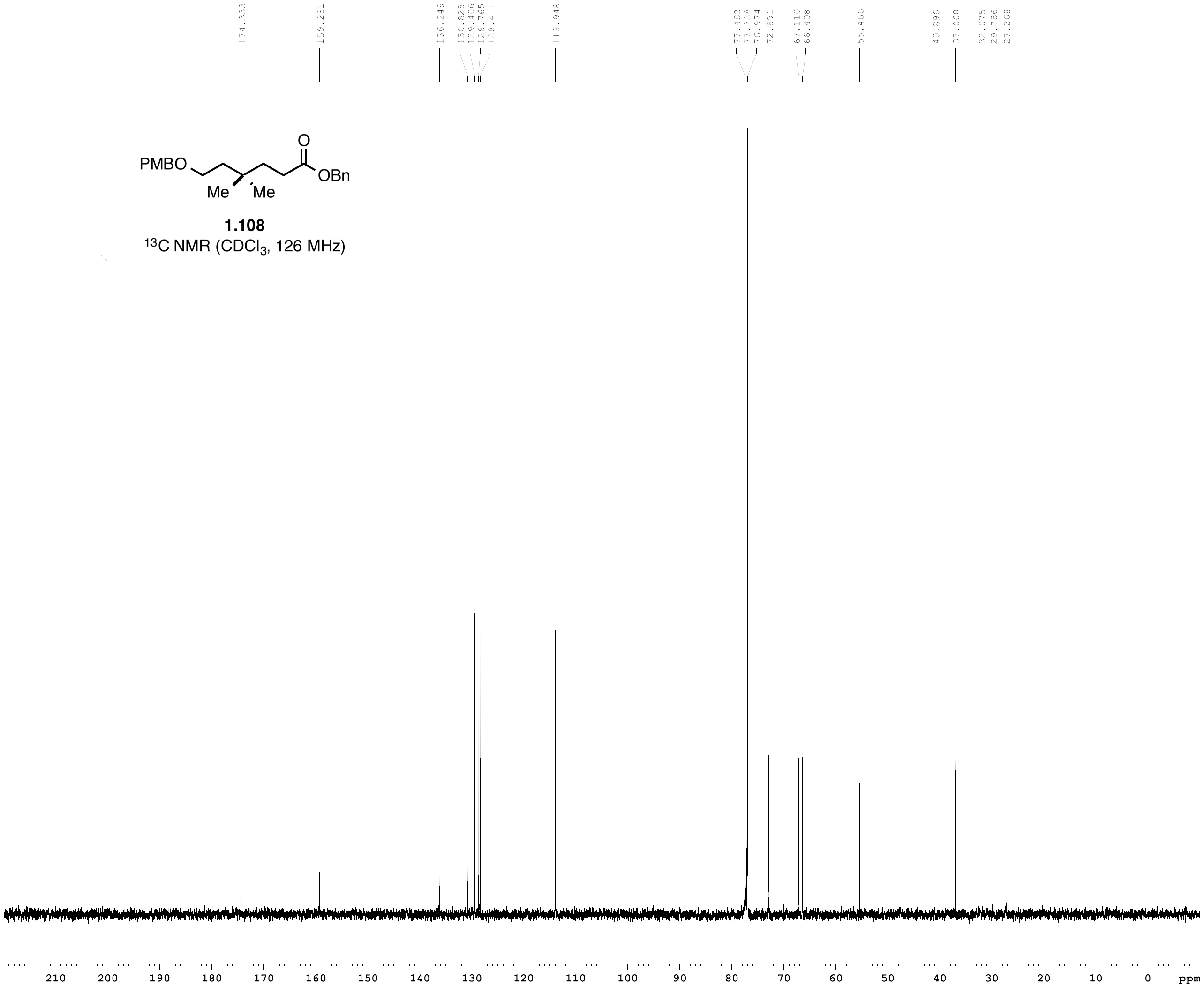
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300268 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-II-272B

1.108

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          YS-II-272B
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150228
Time               14.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   496
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

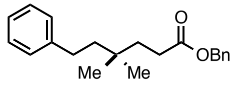
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

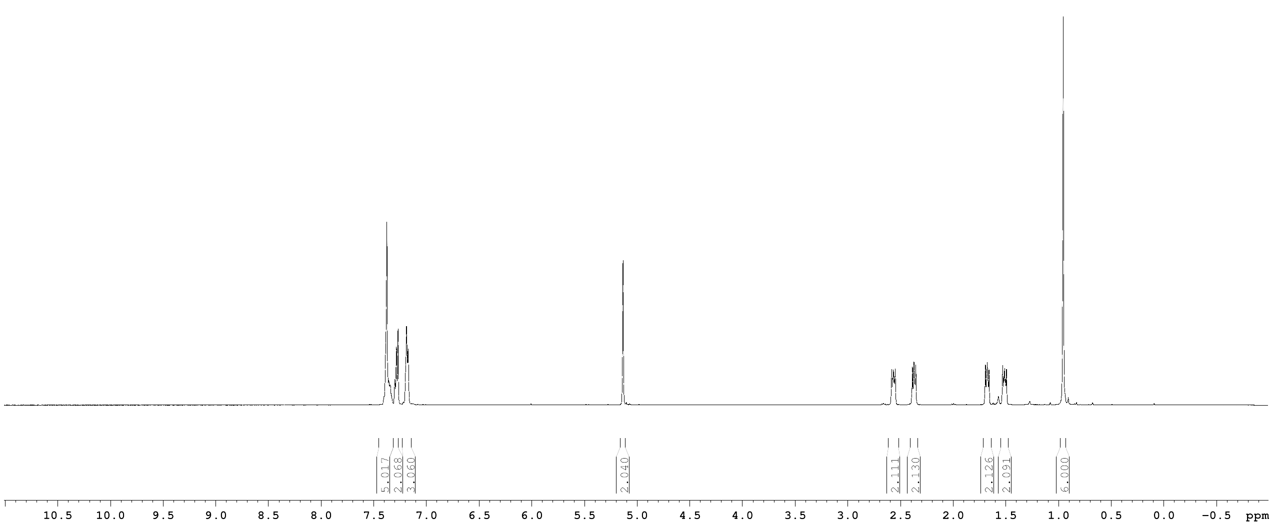
F2 - Processing parameters
SI                 65536
SF           125.7803991 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-II-141



1.110

^{1}H NMR ($CDCl_3$, 500 MHz)



```
Current Data Parameters
NAME          YS-II-141
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20141125
Time              12.54
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

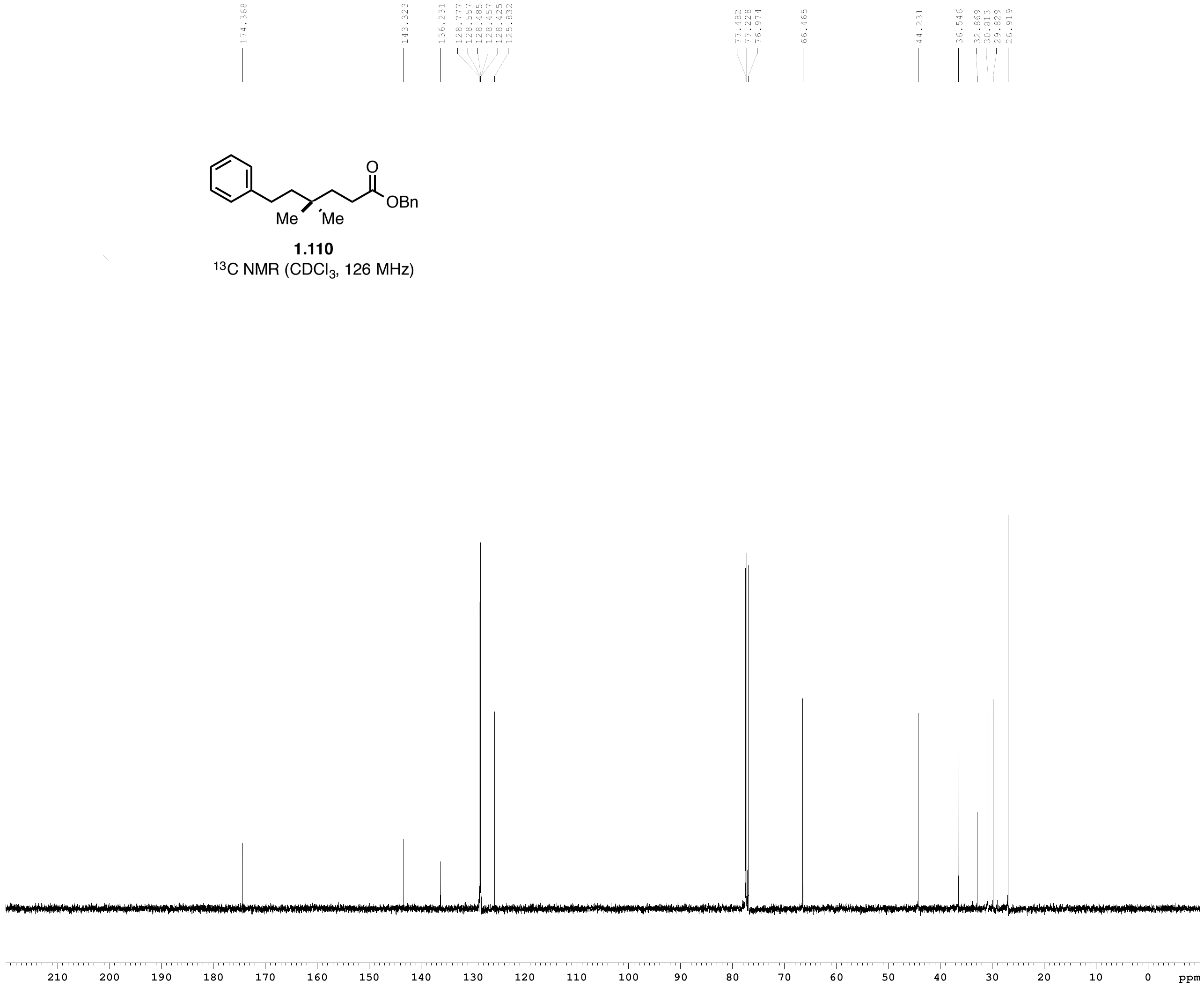
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200293 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-II-141

1.110

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME          YS-II-141
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20141125
Time              13.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  224
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.75000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

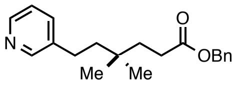
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

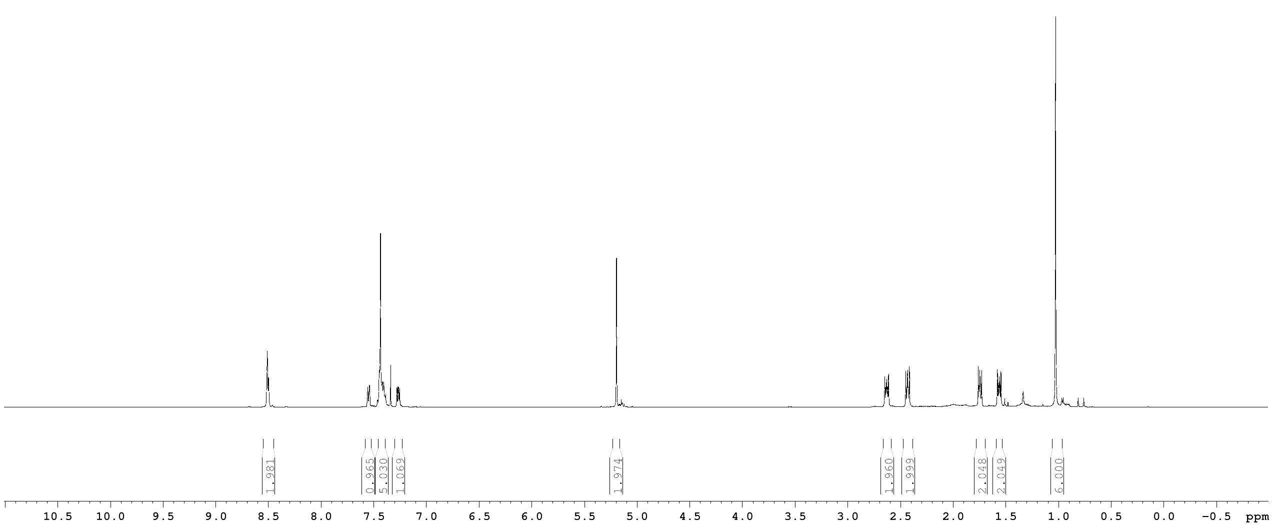
F2 - Processing parameters
SI                65536
SF          125.7804024 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-43



1.112

^{1}H NMR (CDCl$_3$, 500 MHz)



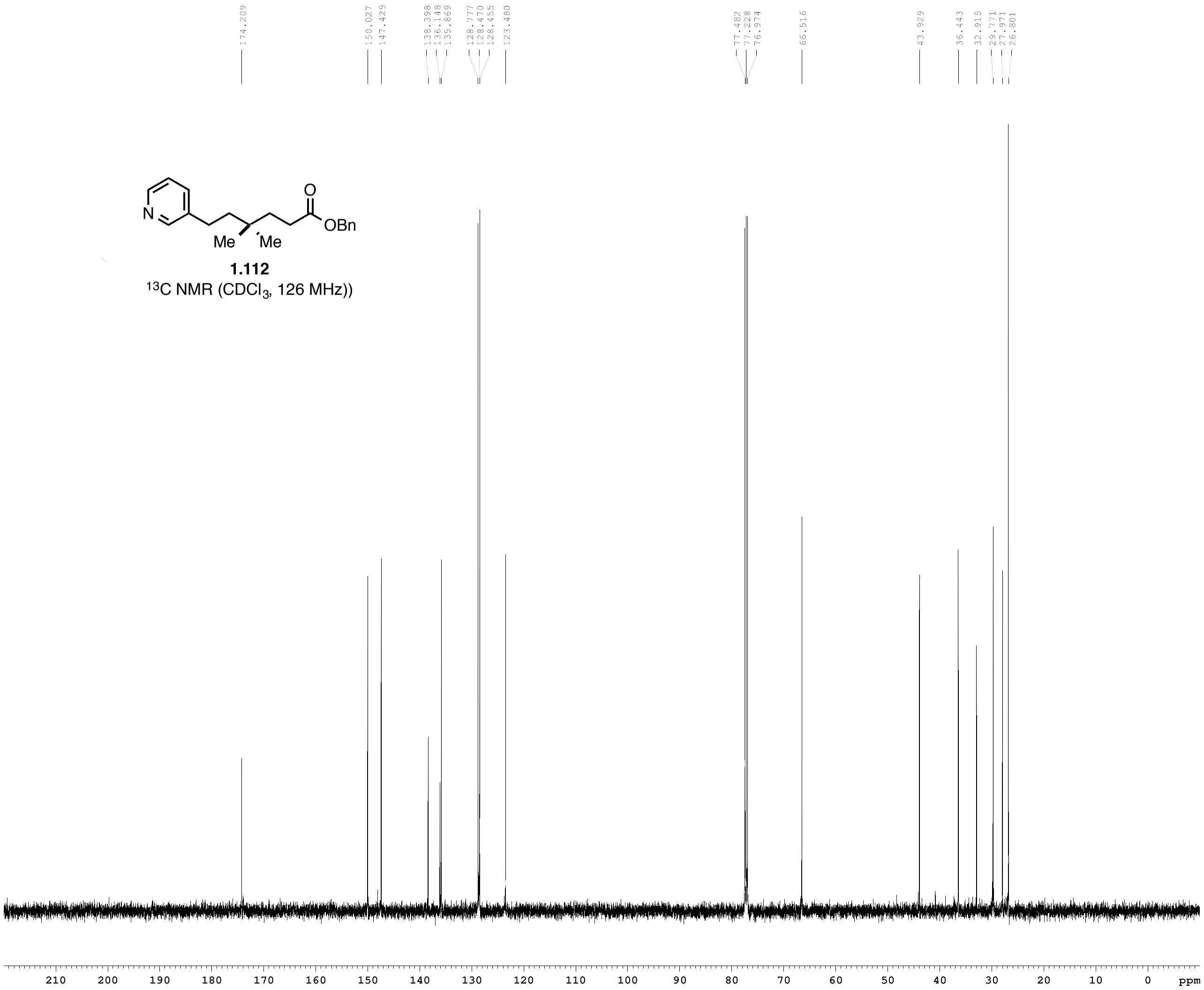
```
Current Data Parameters
NAME          YS-III-43
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150407
Time              17.51
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2199908 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-III-43



1.112

^{13}C NMR (CDCl$_3$, 126 MHz))

```
Current Data Parameters
NAME          YS-III-43
EXPNO                 2
PROCNO                1

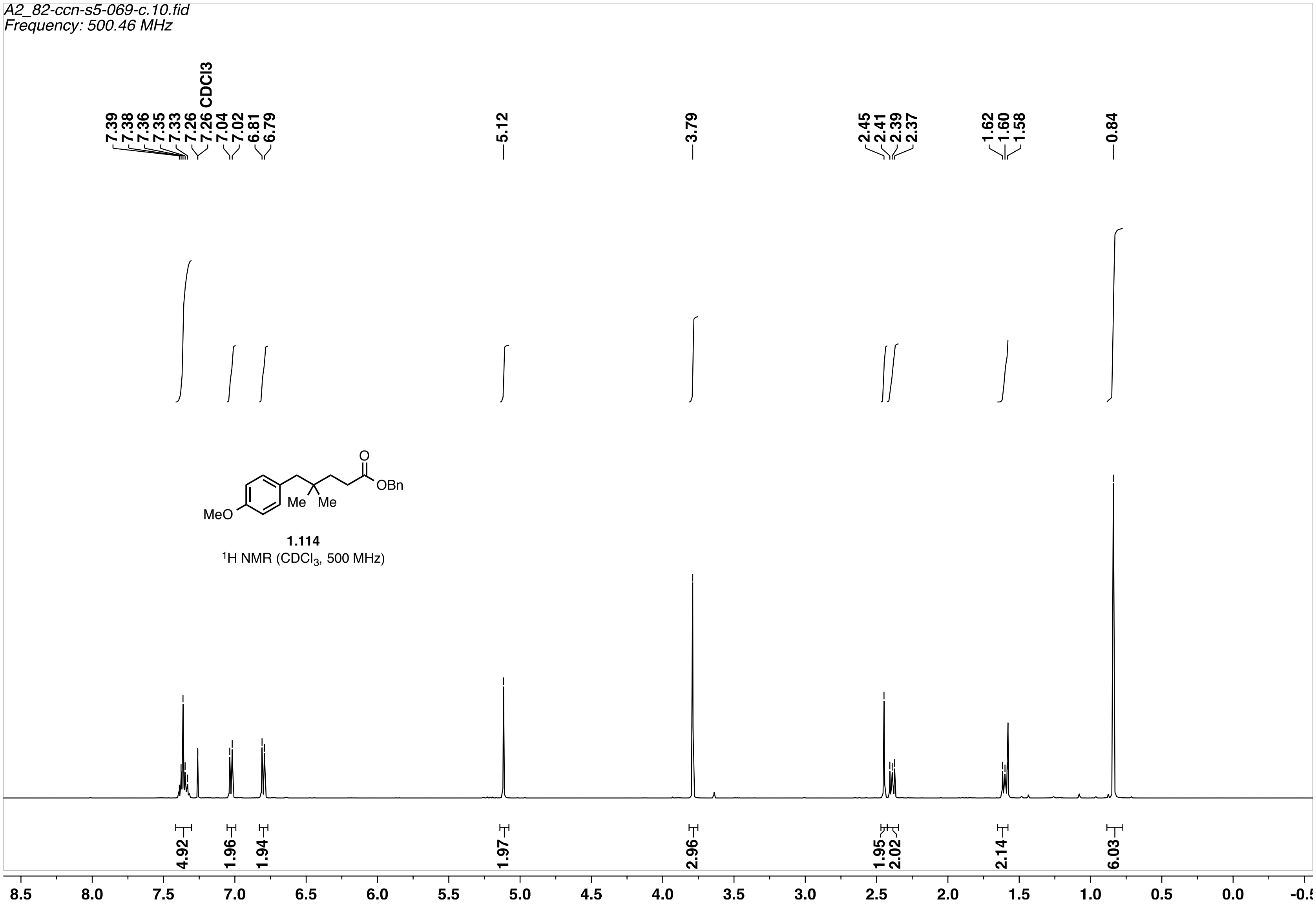
F2 - Acquisition Parameters
Date_          20150407
Time              17.54
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  208
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                13004
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

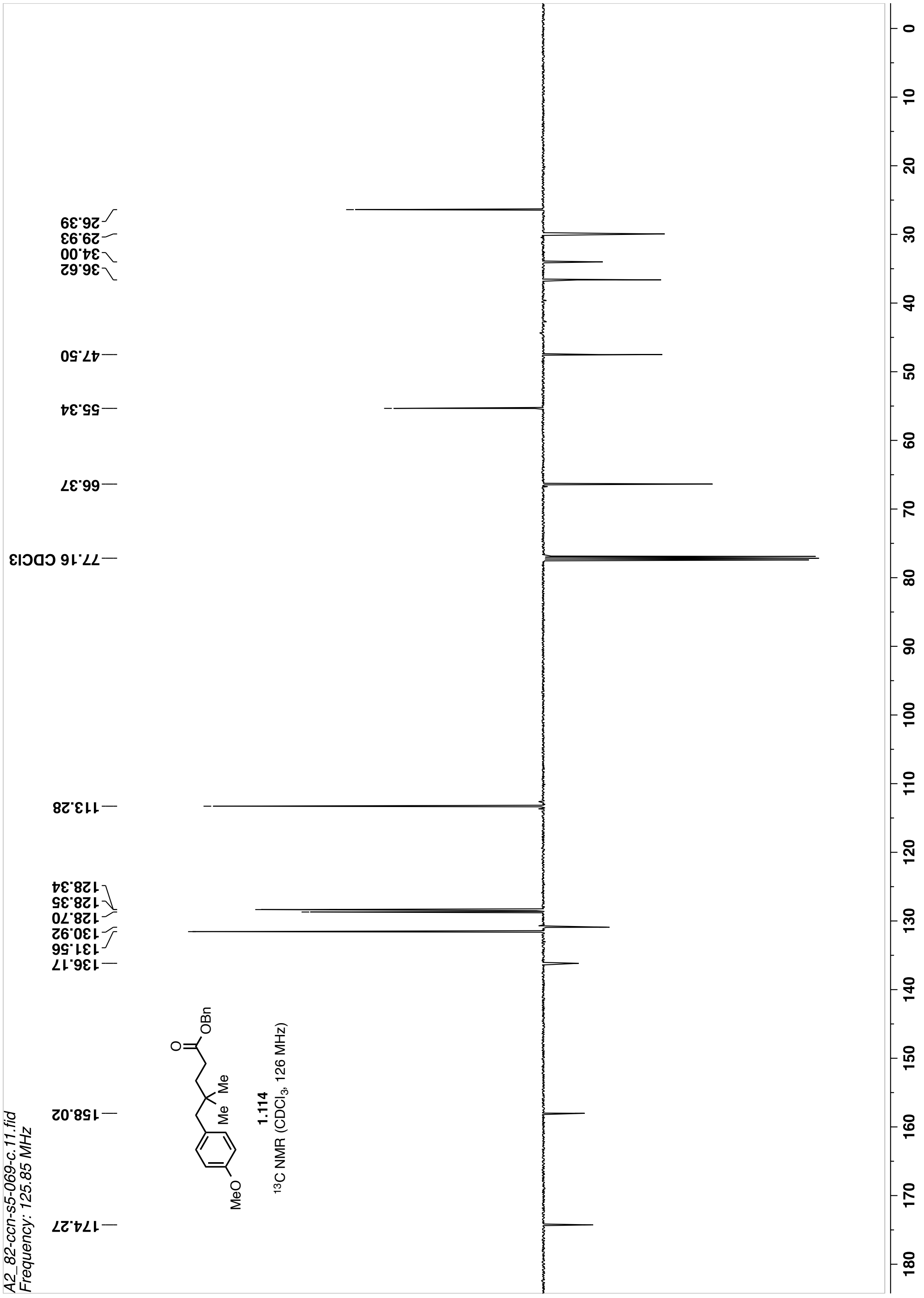
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804012 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



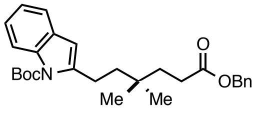
1.114
^{1}H NMR (CDCl$_3$, 500 MHz)



1.114

^{13}C NMR (CDCl$_3$, 126 MHz)

YS-II-279



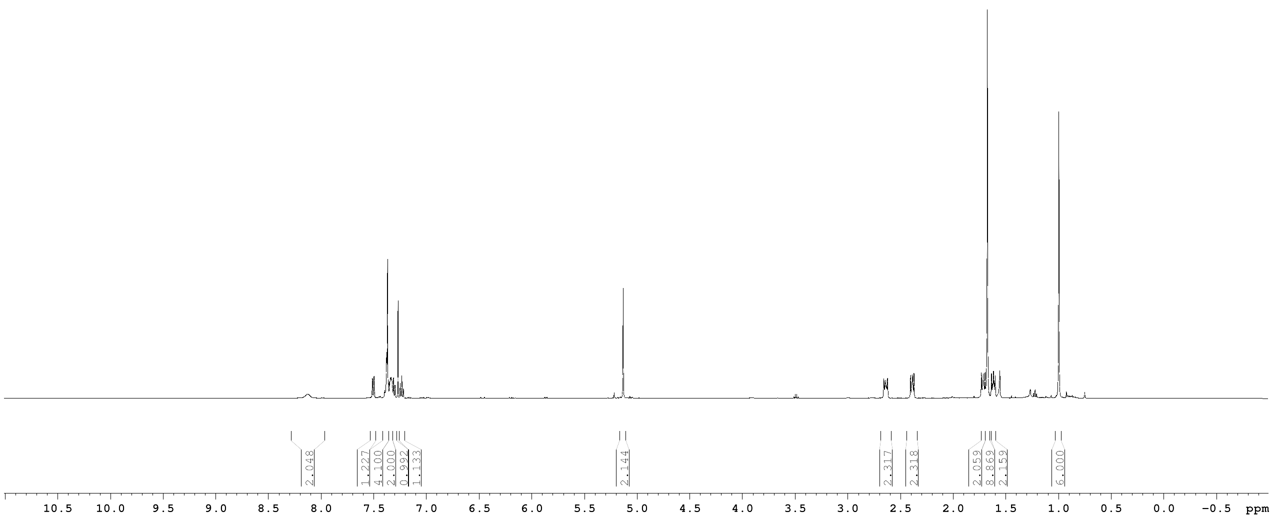
1.116
^{1}H NMR ($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME          YS-II-279
EXPNO                 2
PROCNO                1

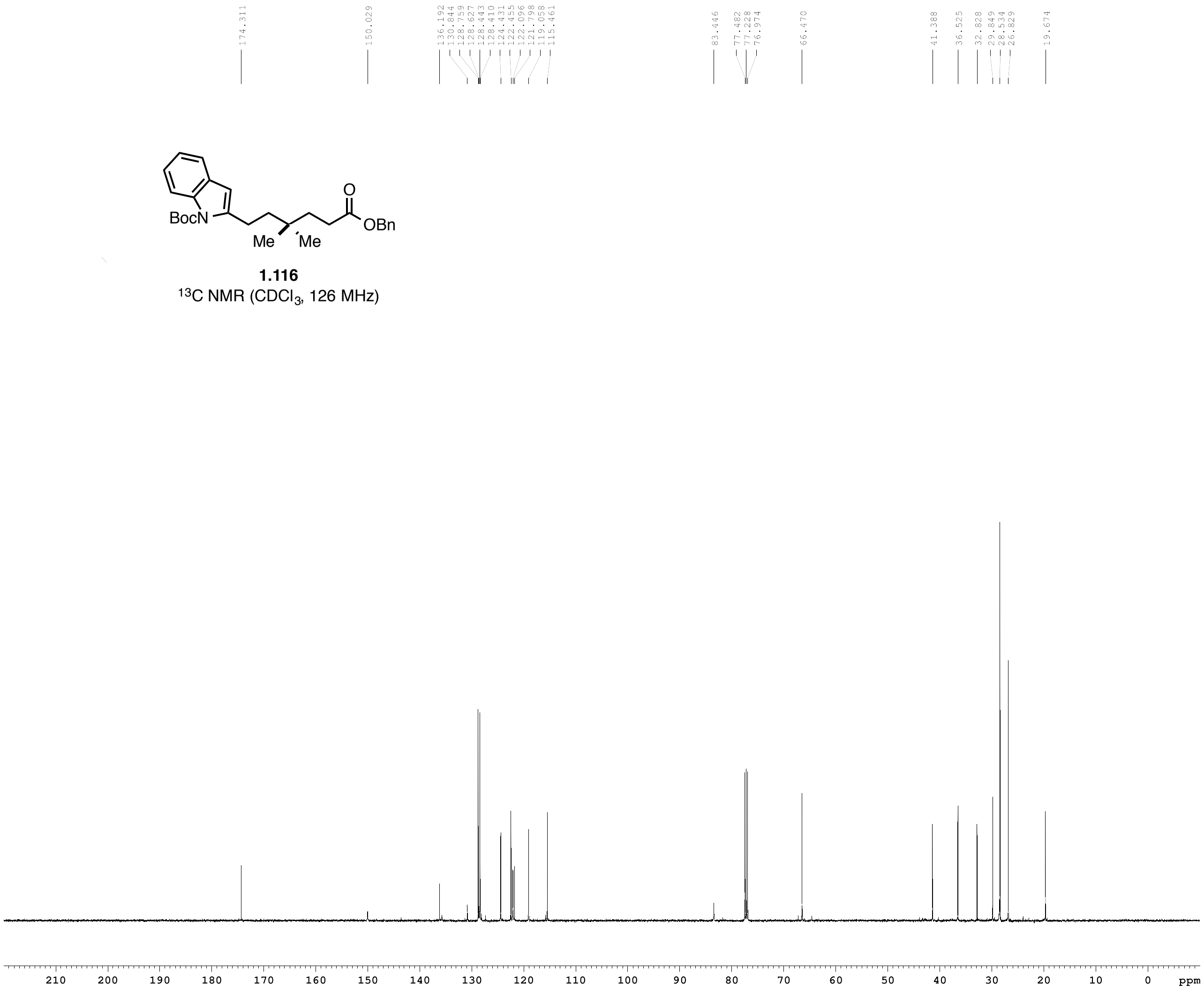
F2 - Acquisition Parameters
Date_          20150305
Time               8.57
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.250026 Hz
AQ            1.9997952 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200265 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```



YS-II-279



1.116

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-279
EXPNO                 5
PROCNO                1

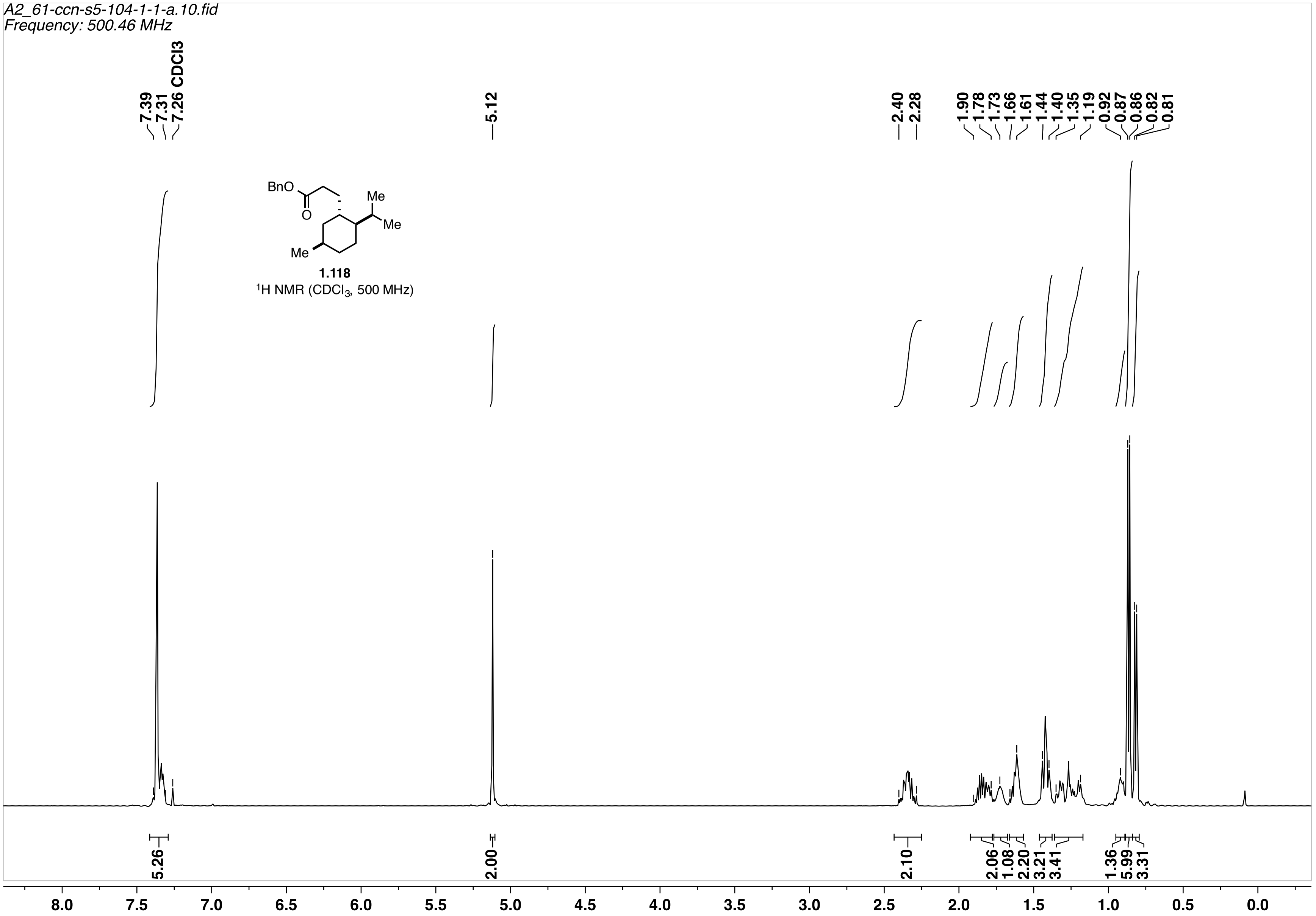
F2 - Acquisition Parameters
Date_          20150309
Time              11.05
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  464
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               3649.1
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

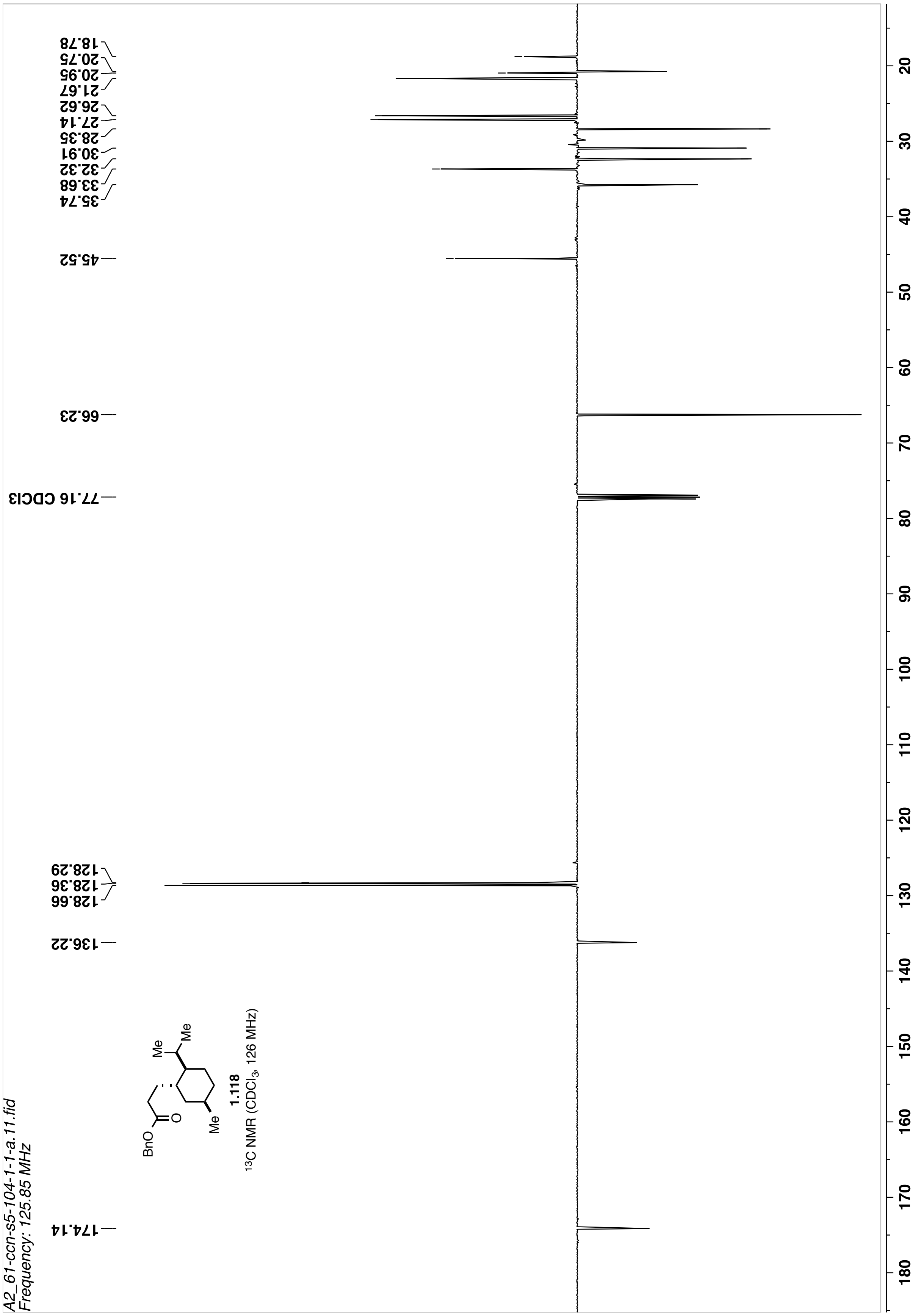
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804019 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



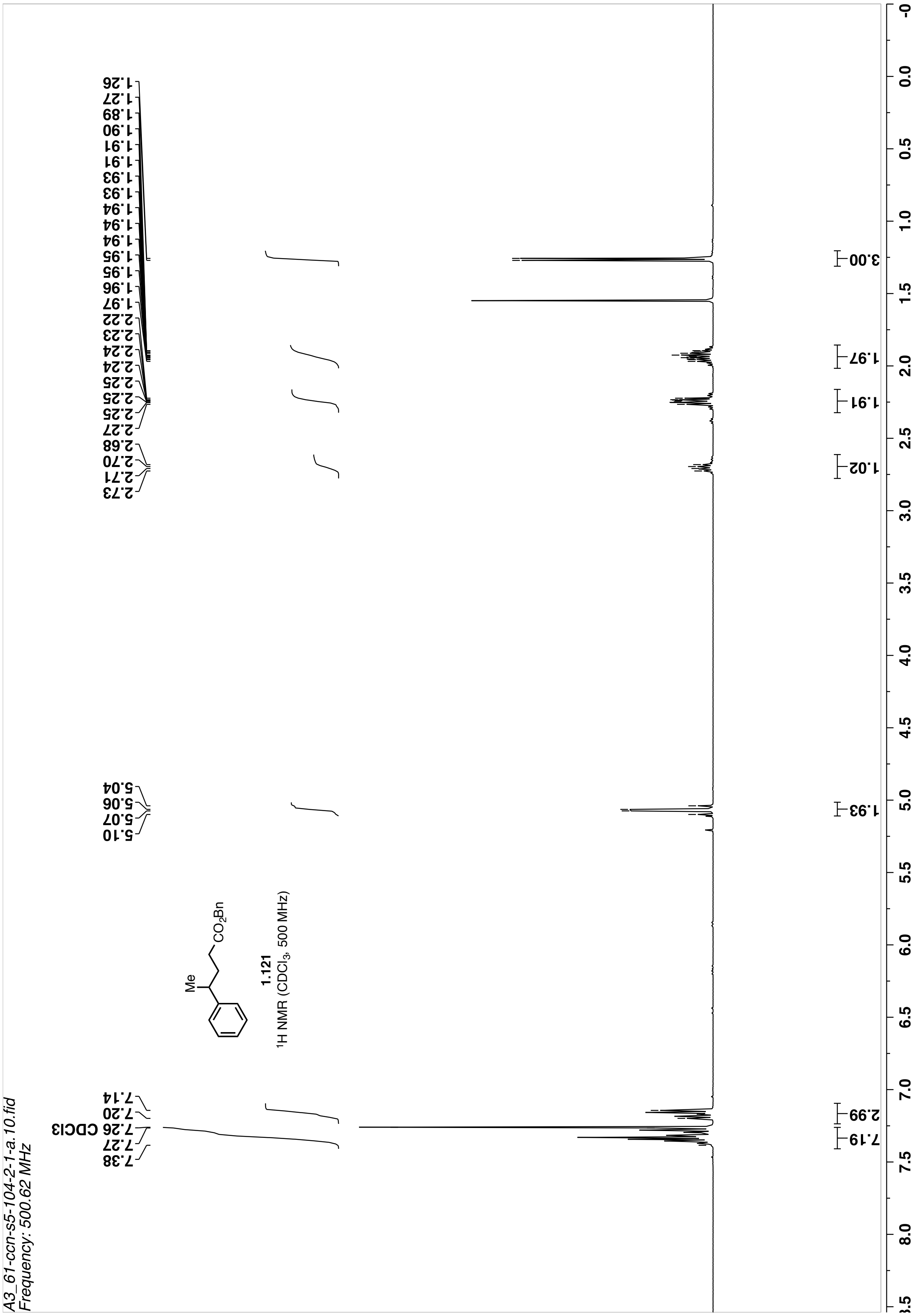
1.118

^{1}H NMR (CDCl$_3$, 500 MHz)



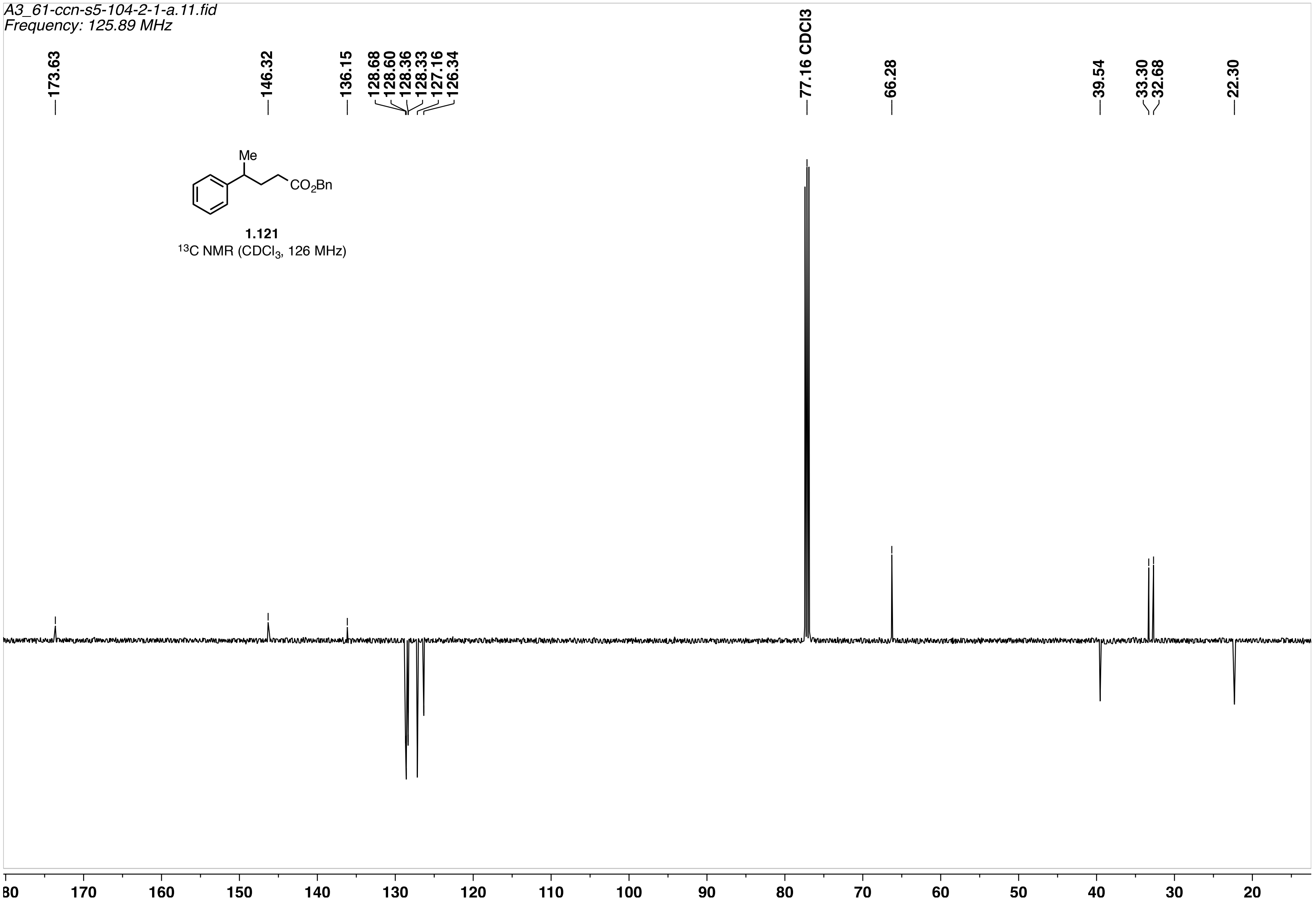
1.118

^{13}C NMR ($CDCl_3$, 126 MHz)



1.121

^{1}H NMR ($CDCl_3$, 500 MHz)

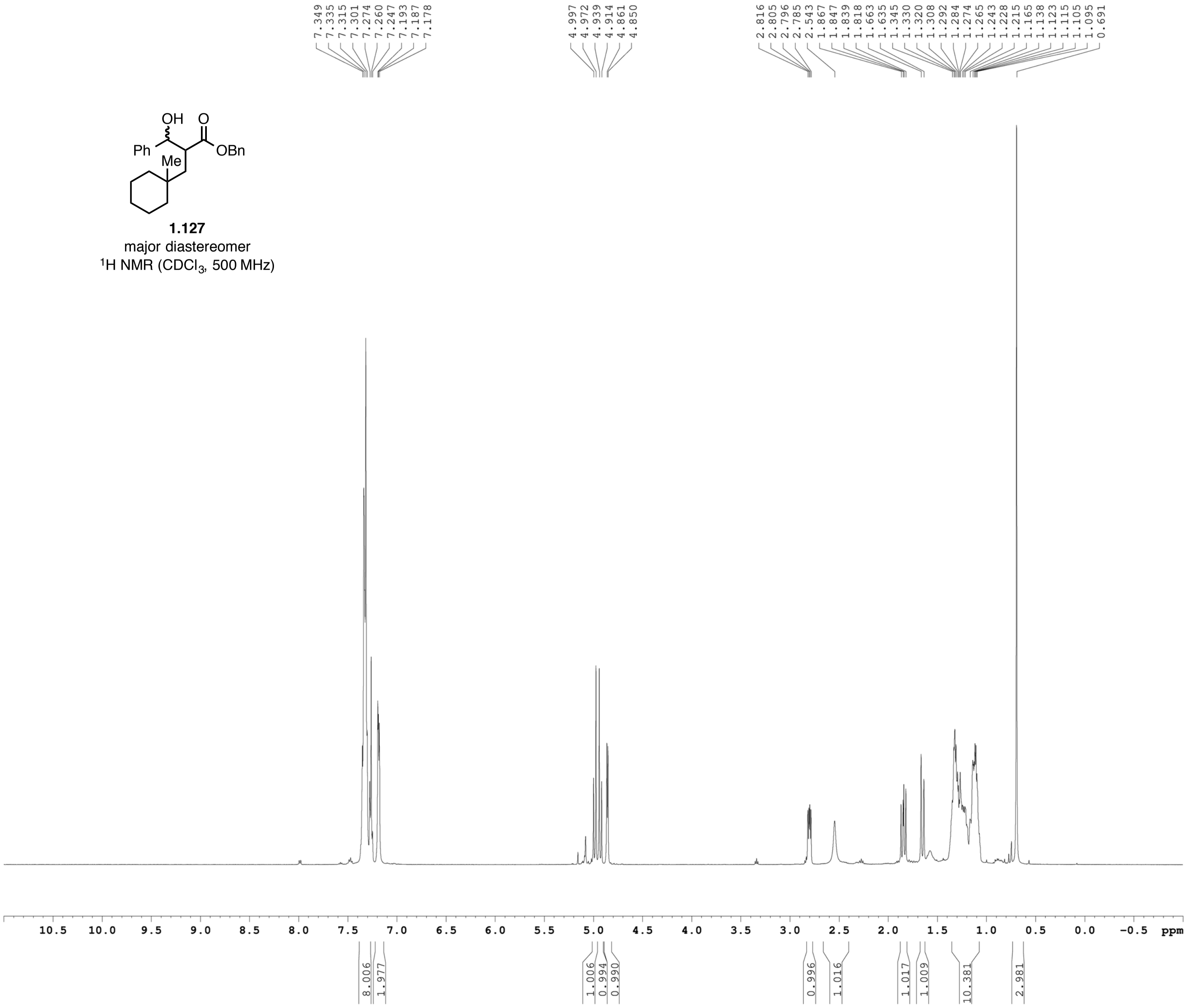


1.121

^{13}C NMR ($CDCl_3$, 126 MHz)

YS-III-56-Major

1.127
major diastereomer
^{1}H NMR (CDCl$_3$, 500 MHz)



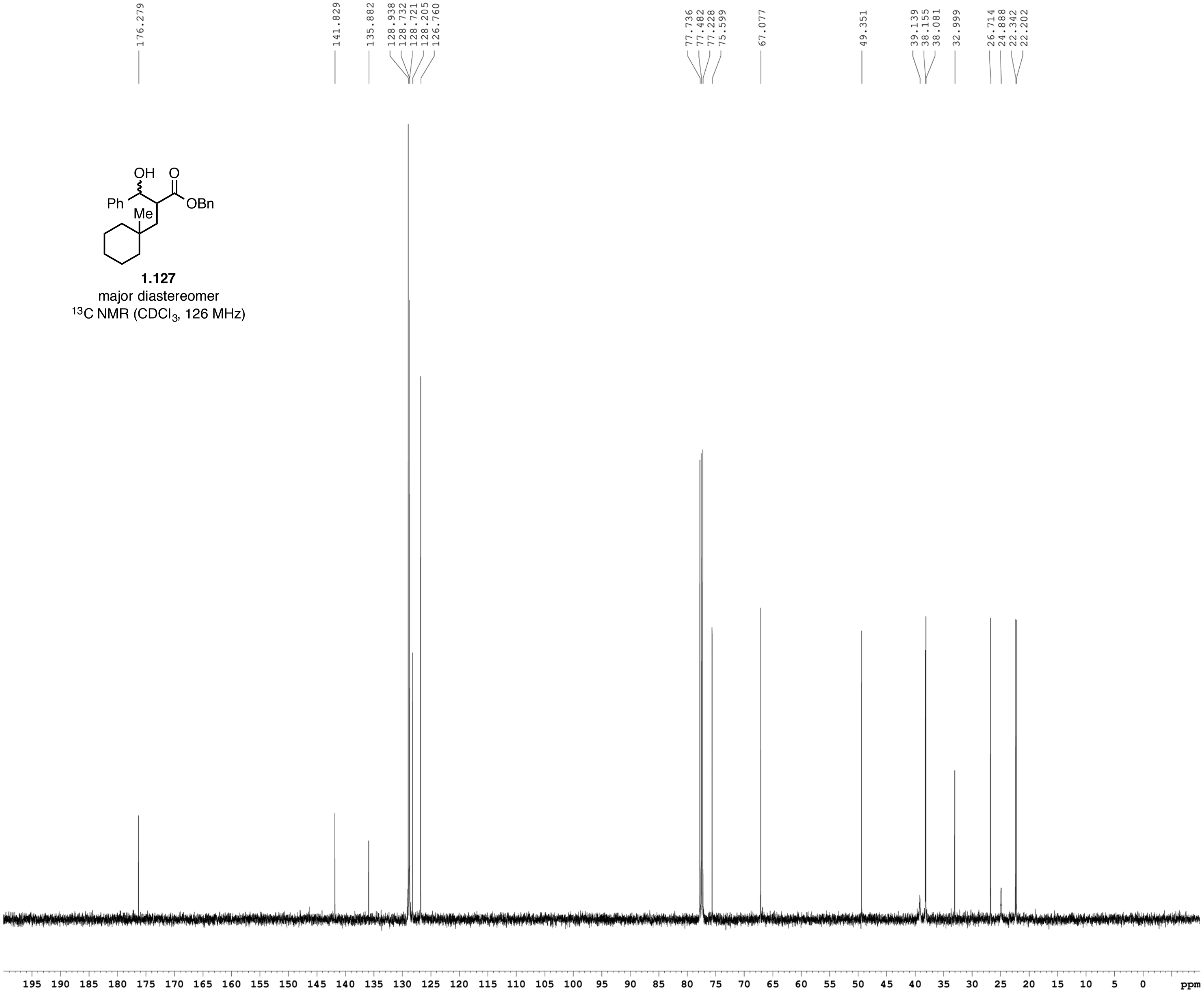
```
Current Data Parameters
NAME          YS-III-56
EXPNO                10
PROCNO                1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20180110
Time               8.04
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG                    5
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1         0.10000000 sec
MCREST   0 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 =======
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200314 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-III-56-Major



1.127
major diastereomer
^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-56
EXPNO                11
PROCNO                1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20180110
Time               8.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    1
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               9195.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

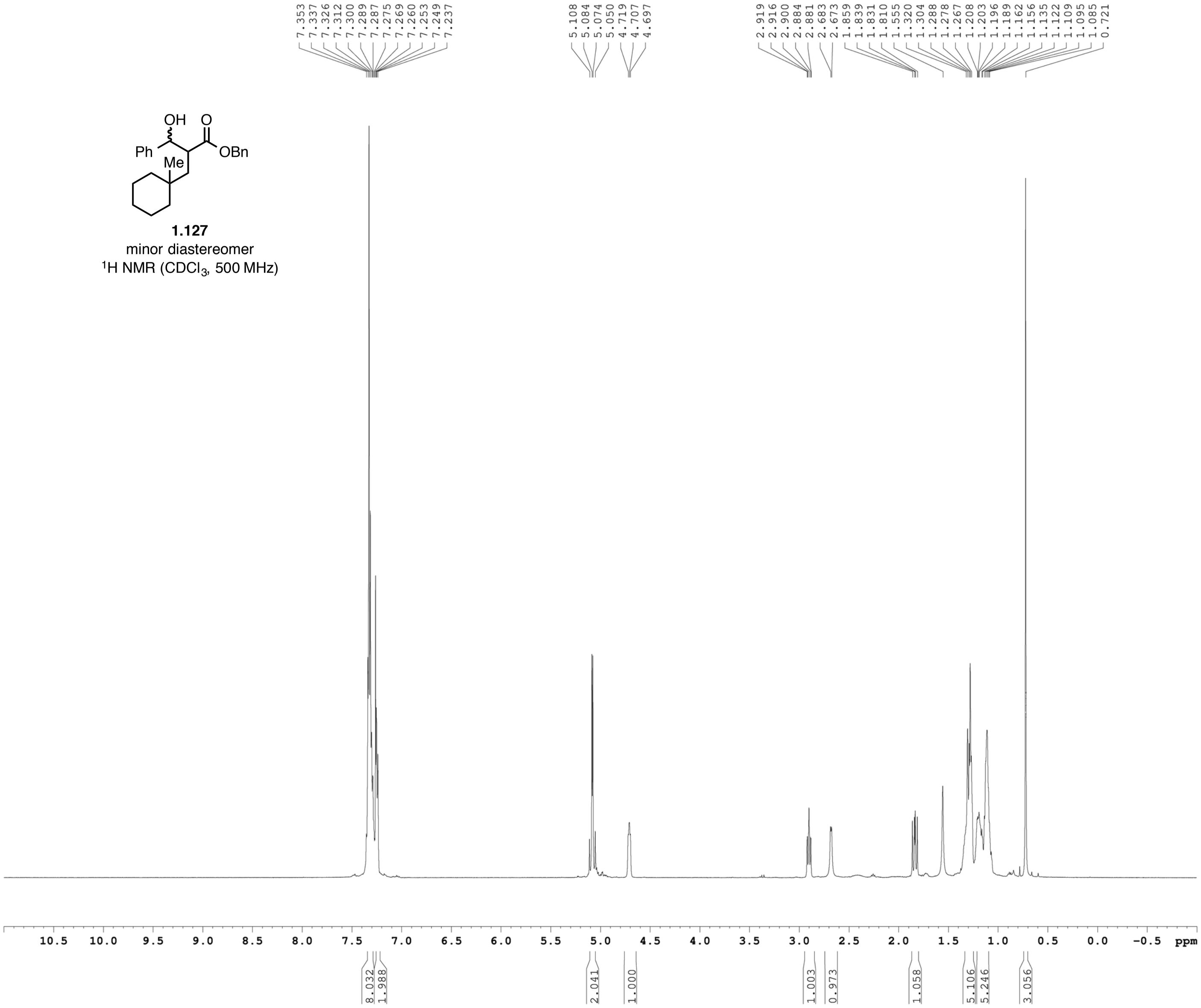
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803667 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-III-56-Minor

1.127
minor diastereomer
^{1}H NMR (CDCl$_3$, 500 MHz)



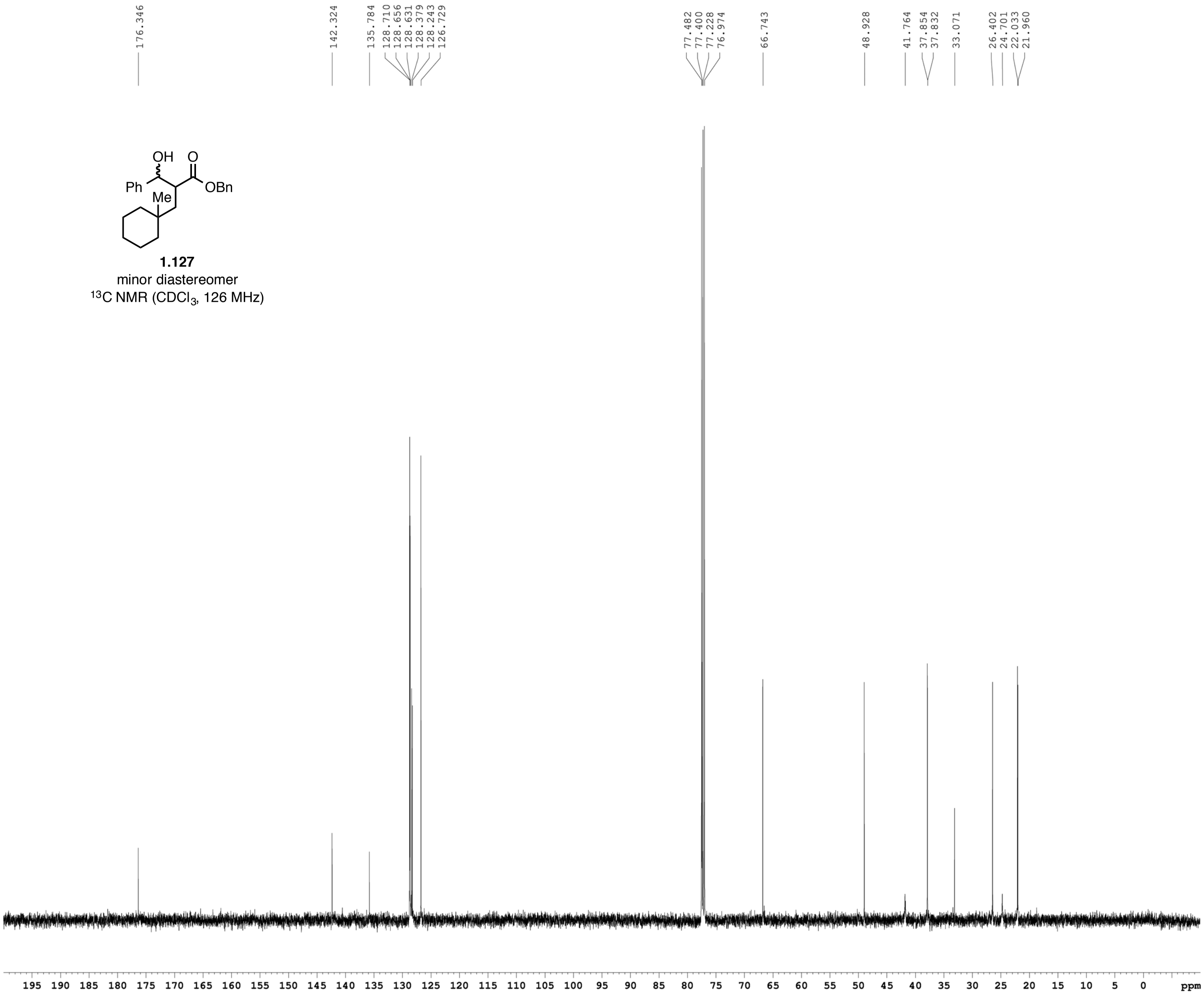
```
Current Data Parameters
NAME          YS-III-56
EXPNO                15
PROCNO                1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20180110
Time               8.40
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    1
SWH          8012.820 Hz
FIDRES       0.098043 Hz
AQ          5.0998273 sec
RG                 10.1
DW             62.400 usec
DE               6.00 usec
TE              298.0 K
D1       0.10000000 sec
MCREST   0 sec
MCWRK    0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1               7.50 usec
PL1              1.60 dB
SFO1     500.2235015 MHz

F2 - Processing parameters
SI                65536
SF       500.2200315 MHz
WDW                  EM
SSB      0
LB               0.30 Hz
GB       0
PC                 1.00
```

YS-III-56-Minor



1.127
minor diastereomer
^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-56
EXPNO                16
PROCNO                1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20180110
Time               8.43
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    1
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

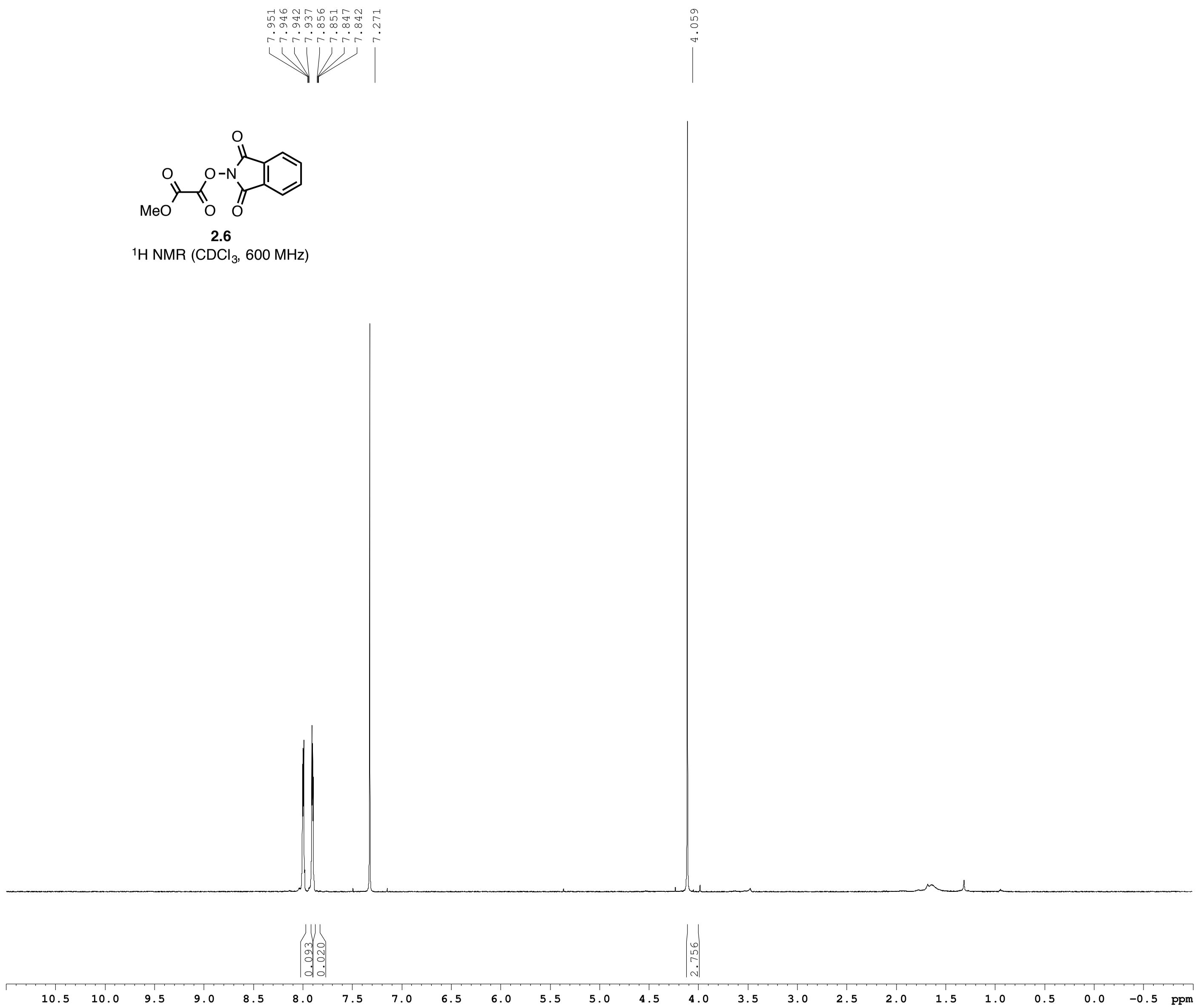
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803976 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

Appendix B: Chapter 2 NMR Spectra

YS-I-152



2.6

^{1}H NMR ($CDCl_3$, 600 MHz)

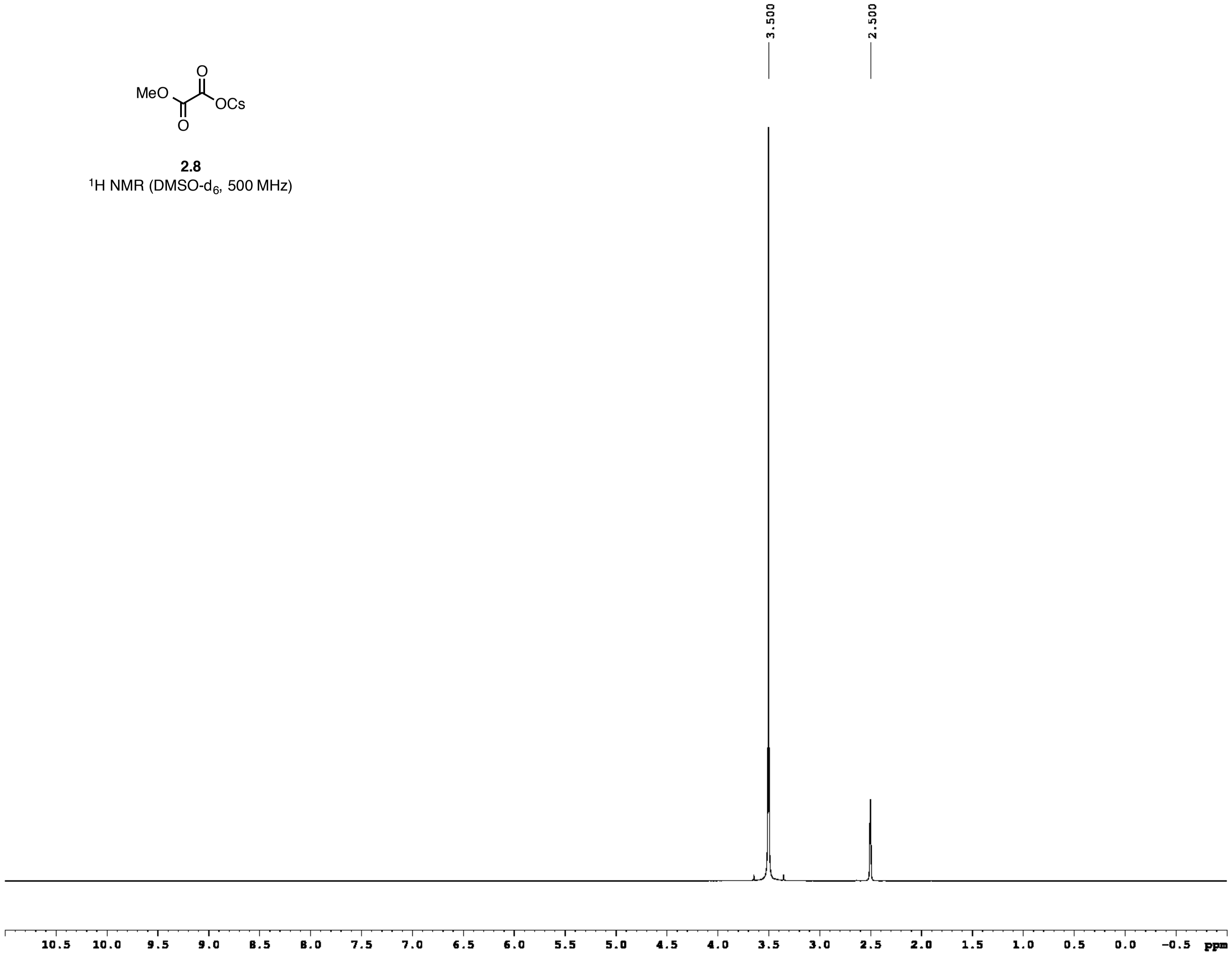
```
Current Data Parameters
NAME          YS-I-152-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140304
Time               12.57
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   812
DW                52.000 usec
DE                 14.54 usec
TE                 294.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-IV-71



2.8

^{1}H NMR (DMSO-d_6, 500 MHz)

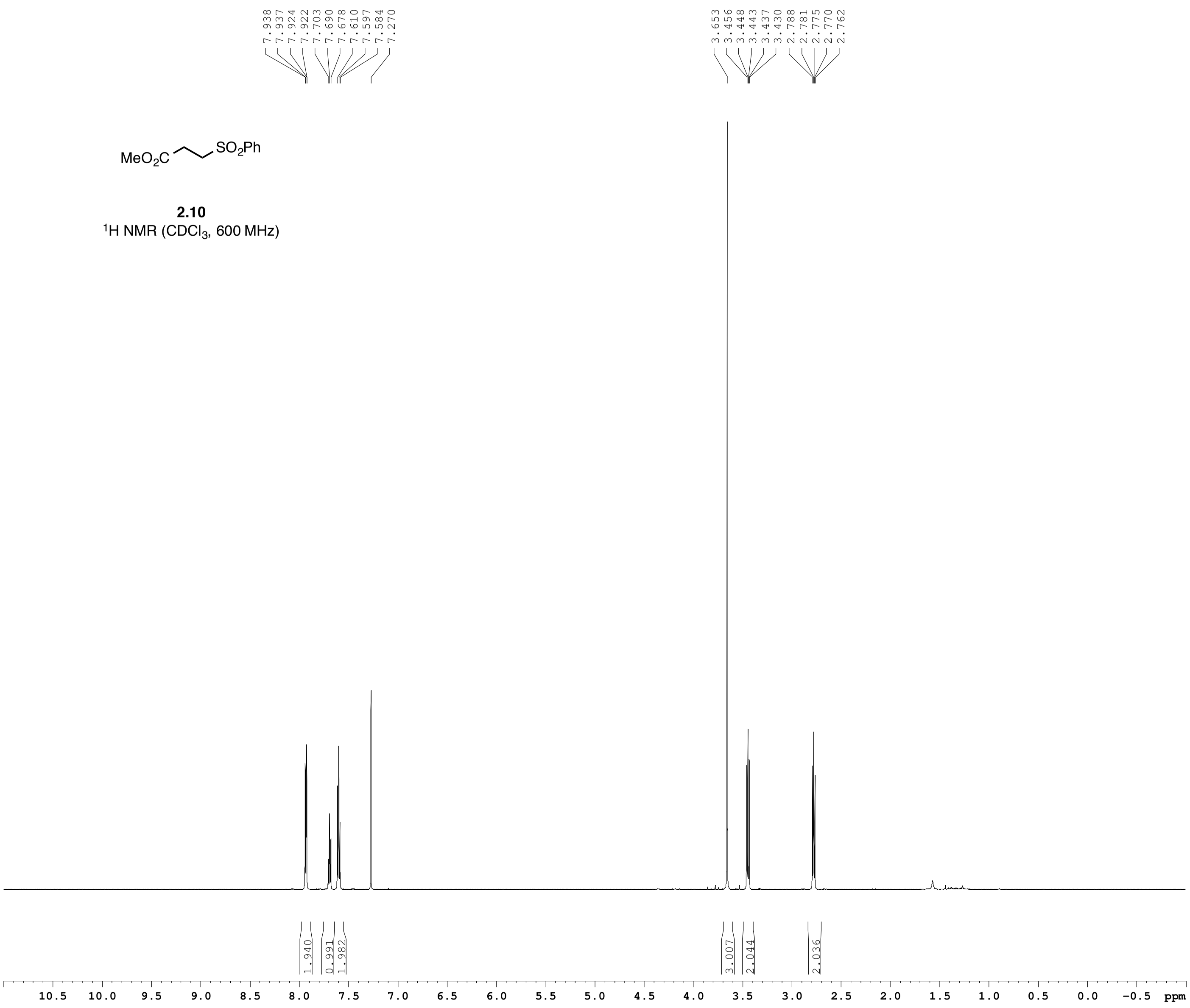
```
Current Data Parameters
NAME            YS-IV-71
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160319
Time                9.00
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT             DMSO
NS                     8
DS                     2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG                     5
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1         0.10000000 sec
MCREST   0 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1      500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF        500.2200134 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

YS-II-21



2.10
^1H NMR ($CDCl_3$, 600 MHz)

```
Current Data Parameters
NAME             YS-II-21
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140929
Time                13.40
INSTRUM             av600
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  98074
SOLVENT             CDC13
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                    406
DW                 52.000 usec
DE                  14.54 usec
TE                  297.9 K
D1             0.10000000 sec
TD0                     1

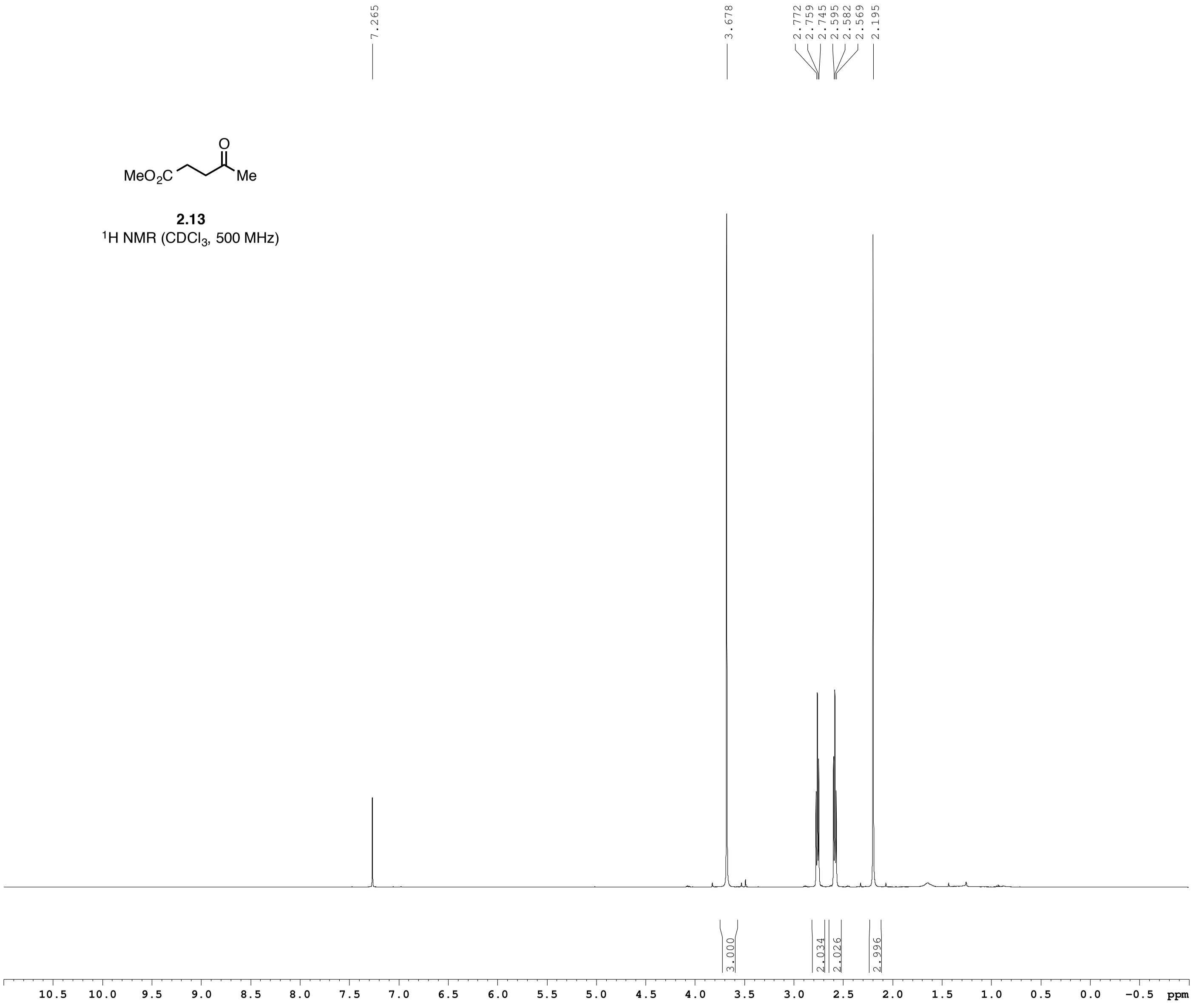
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                   8.00 usec
PLW1          23.01441956 W

F2 - Processing parameters
SI                  65536
SF           600.1300283 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

YS-II-80

2.13

^{1}H NMR ($CDCl_3$, 500 MHz)



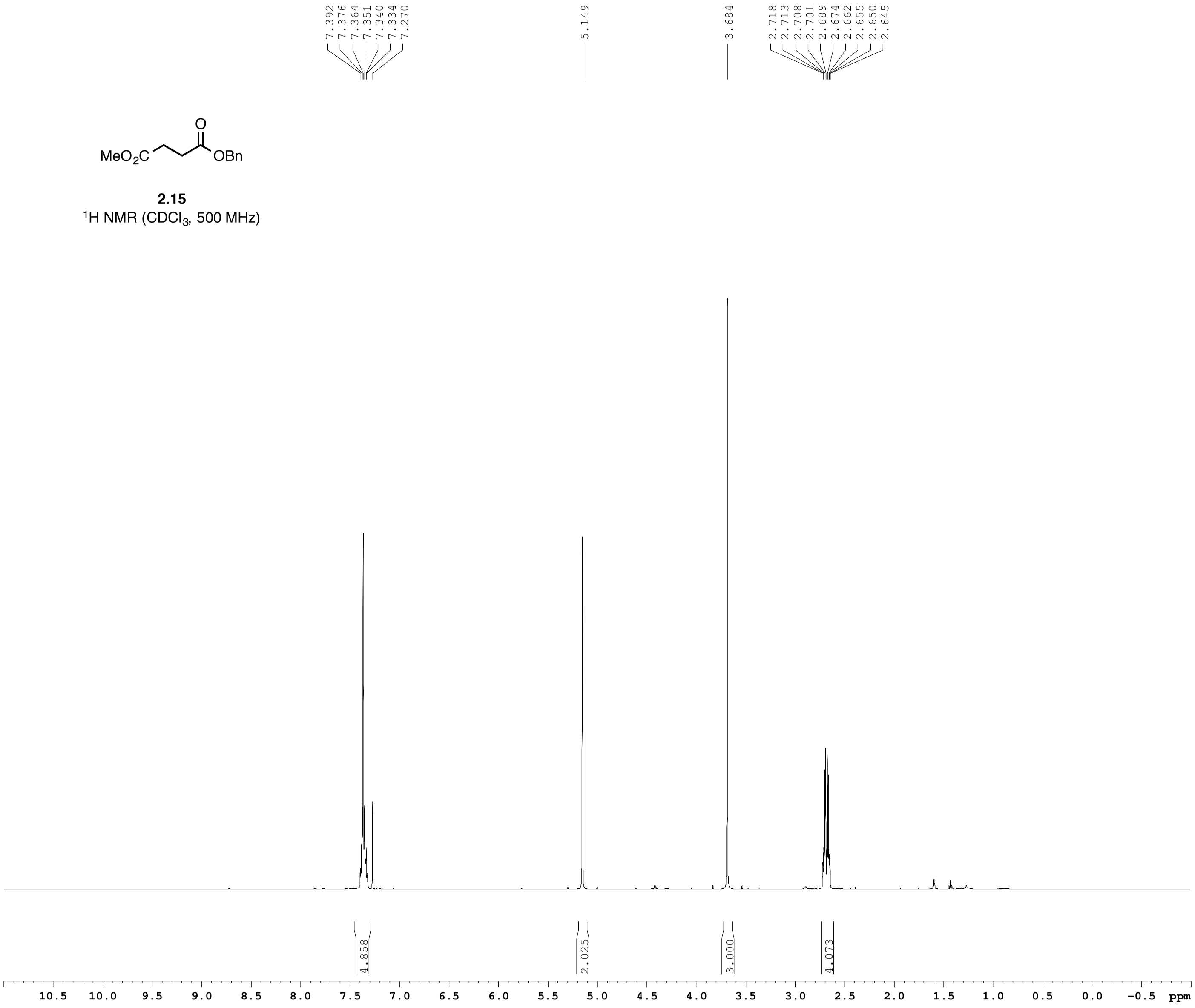
```
Current Data Parameters
NAME            YS-II-80
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141009
Time                8.56
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDC13
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200288 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

YS-II-25



2.15

^{1}H NMR ($CDCl_3$, 500 MHz)

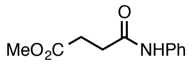
```
Current Data Parameters
NAME             YS-II-25
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140930
Time                 8.58
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDC13
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                      4
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1        500.2235015 MHz

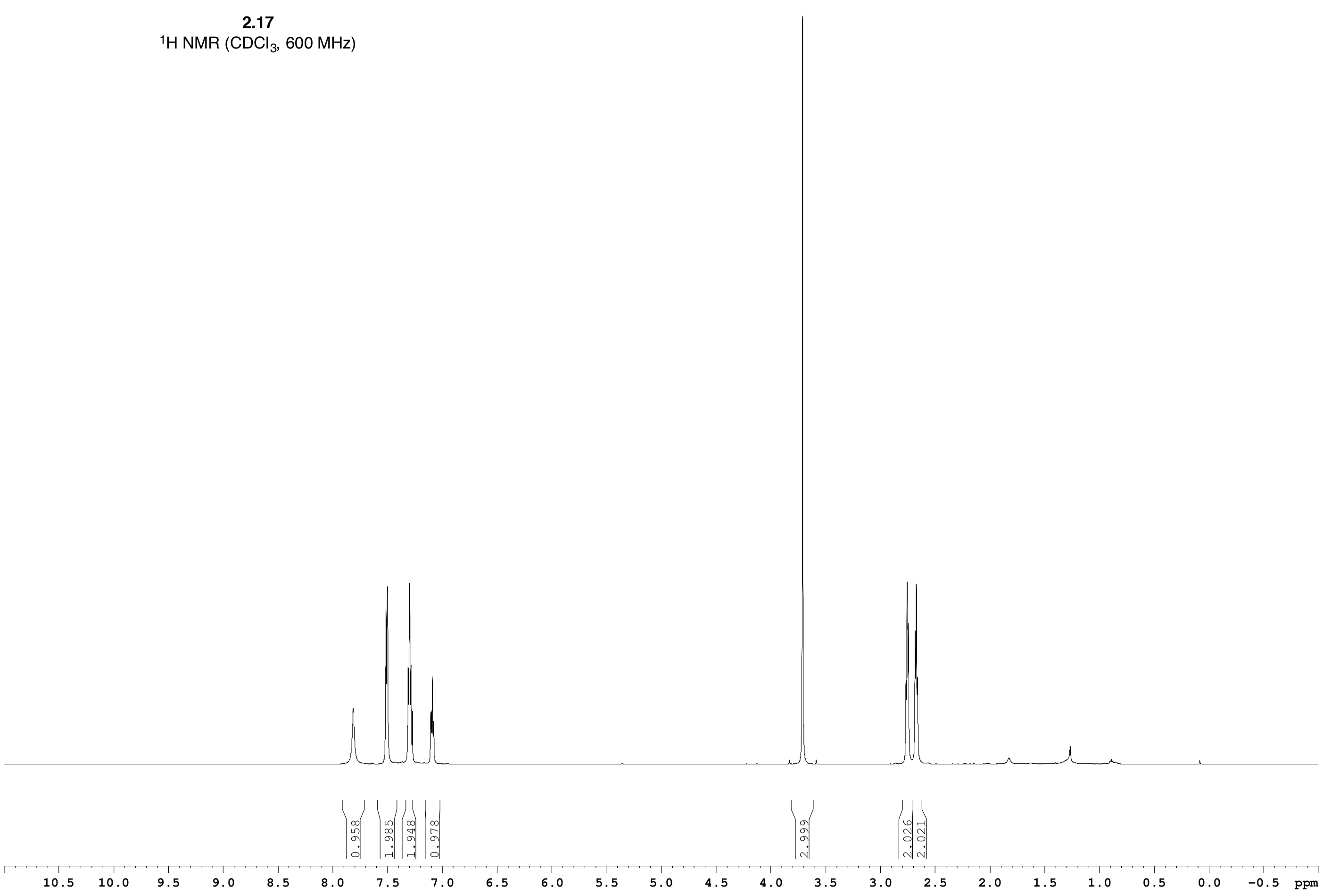
F2 - Processing parameters
SI                  65536
SF          500.2200265 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-II-32



2.17

^{1}H NMR ($CDCl_3$, 600 MHz)



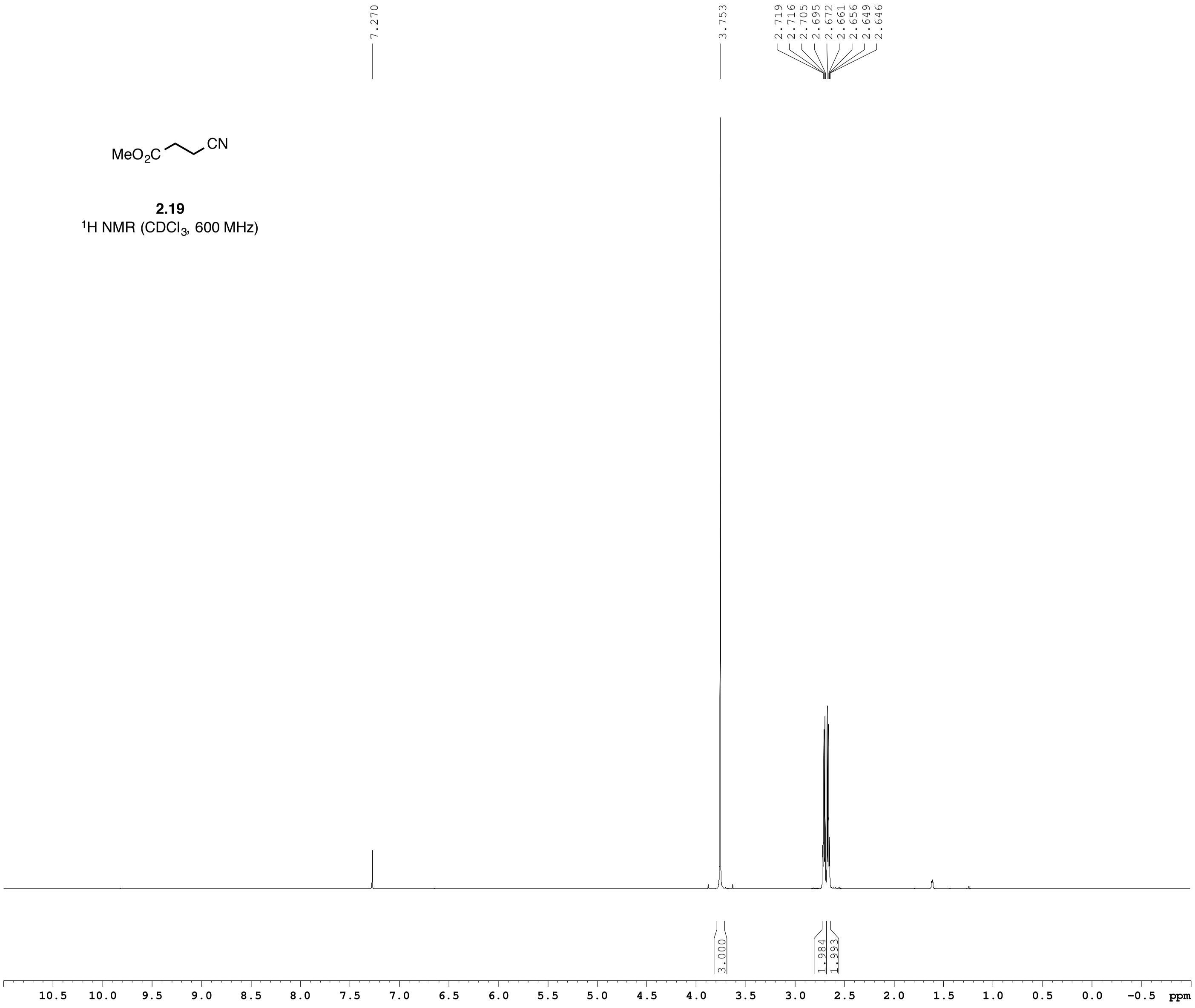
```
Current Data Parameters
NAME            YS-II-32
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141001
Time               14.09
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   322
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF          600.1300282 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-77



2.19

^{1}H NMR (CDCl$_3$, 600 MHz)

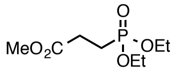
```
Current Data Parameters
NAME              YS-II-77
EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameters
Date_           20141008
Time               11.08
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   512
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1           0.10000000 sec
TD0                    1

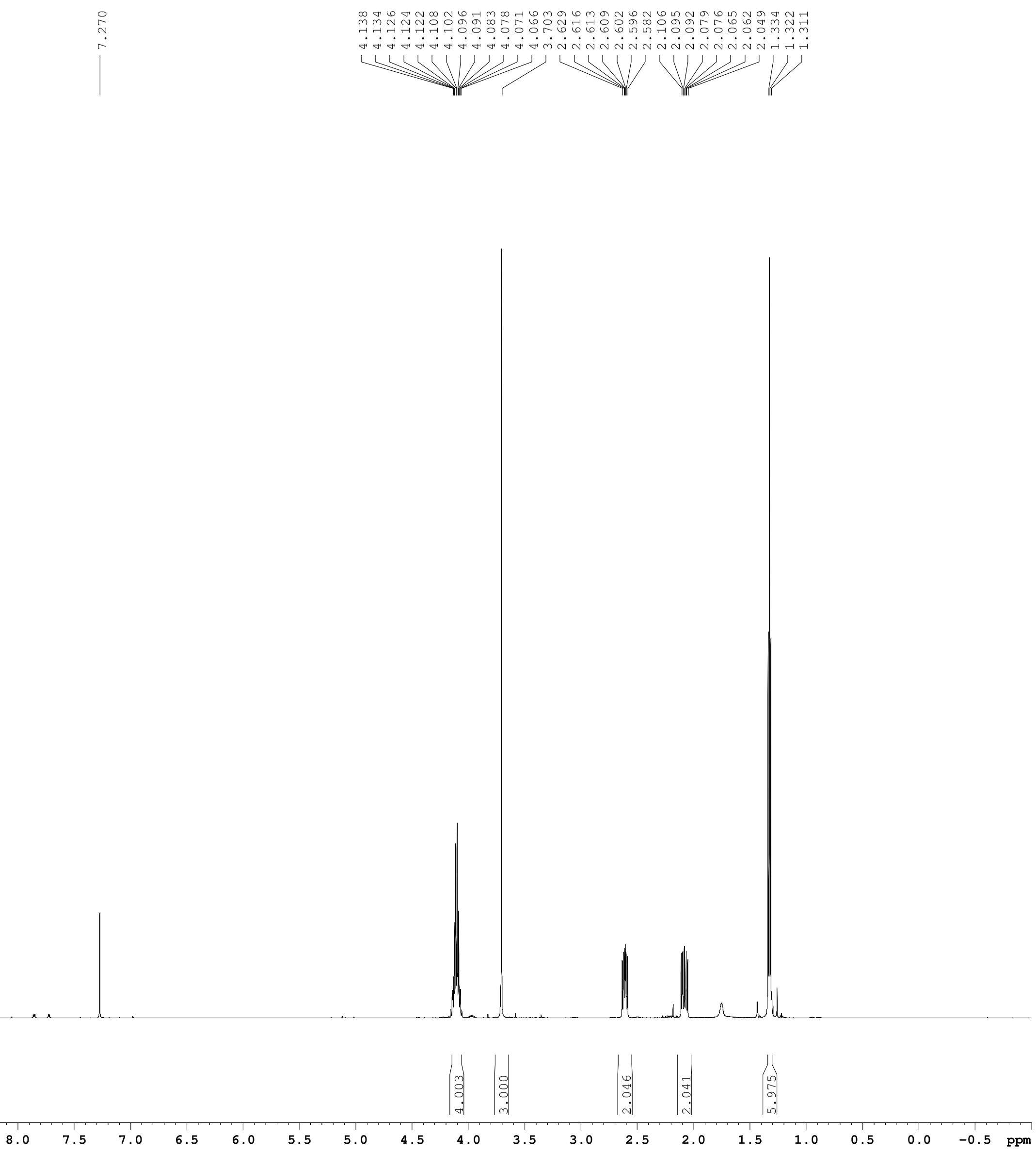
======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                 65536
SF          600.1300280 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-II-50A



2.21
^{1}H NMR ($CDCl_3$, 600 MHz)



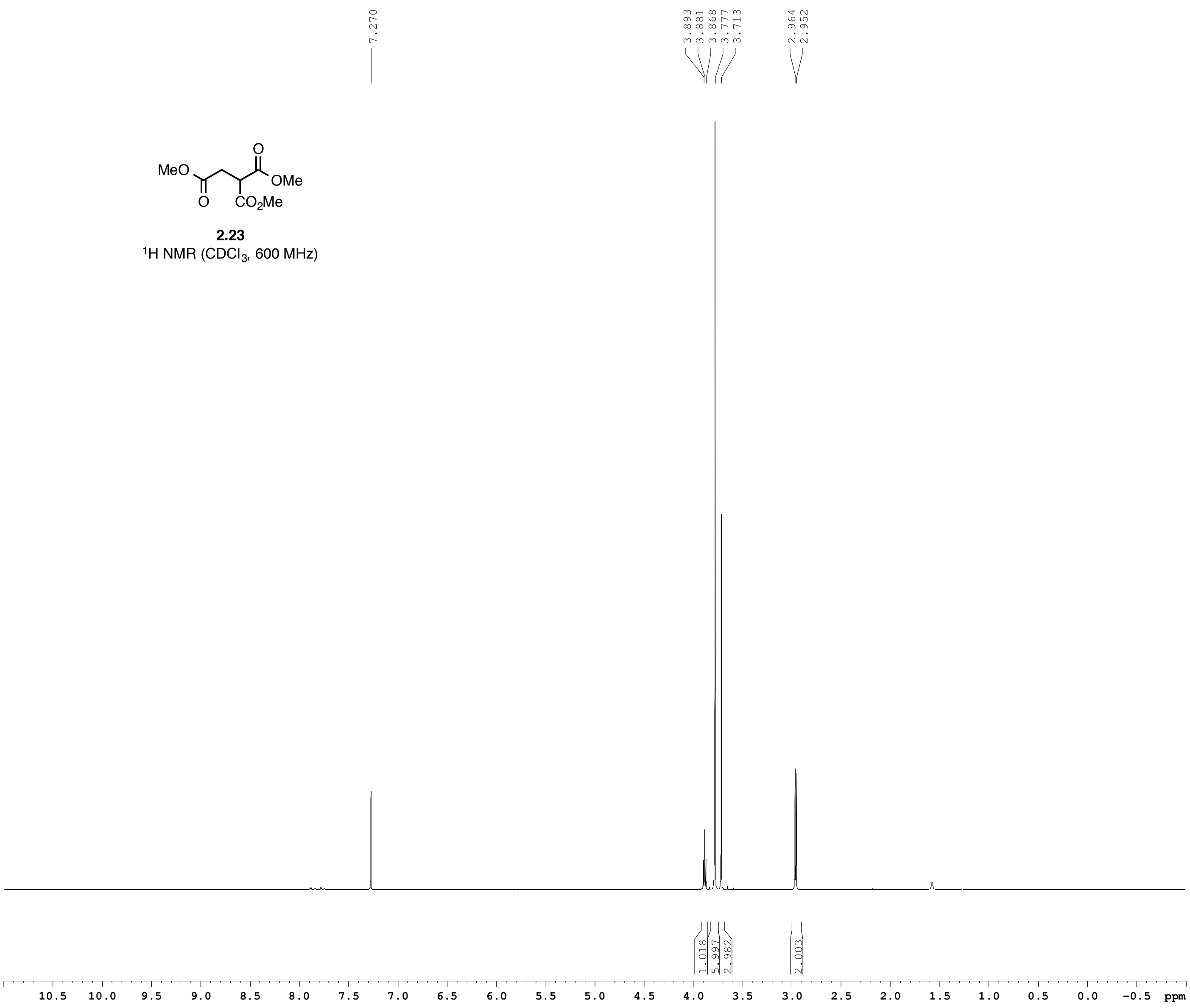
```
Current Data Parameters
NAME          YS-II-50A
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20141008
Time              12.35
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                38460
SOLVENT           CDC13
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                  575
DW               52.000 usec
DE                14.54 usec
TE                298.1 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300283 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-29A



2.23
^{1}H NMR ($CDCl_3$, 600 MHz)

```
Current Data Parameters
NAME          YS-II-29A
EXPNO                 3
PROCNO                1

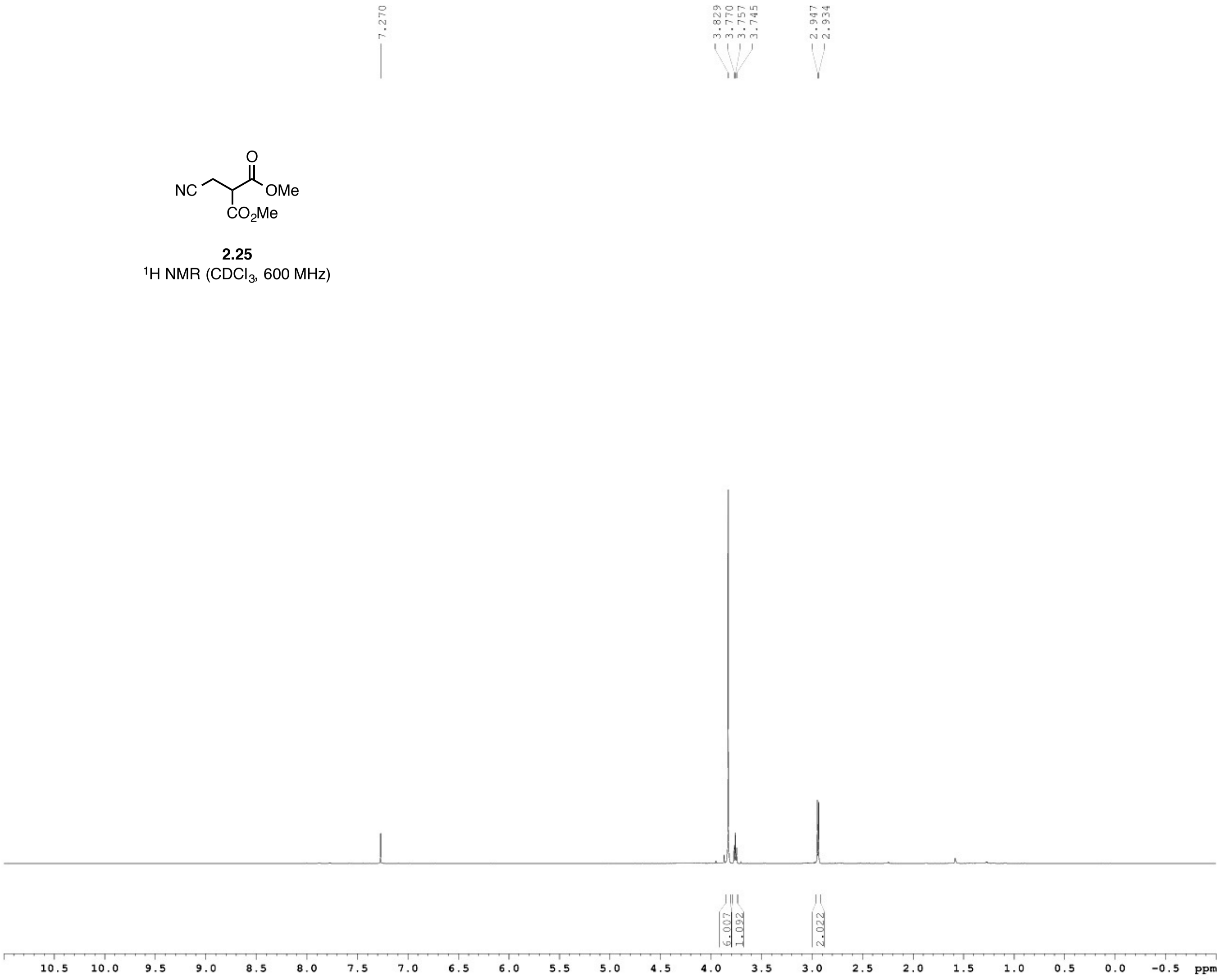
F2 - Acquisition Parameters
Date_          20140930
Time              16.40
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                98074
SOLVENT           CDC13
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                  724
DW               52.000 usec
DE                14.54 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300282 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-133

2.25
^{1}H NMR (CDCl$_3$, 600 MHz)



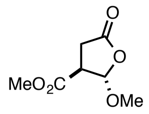
```
Current Data Parameters
NAME          YS-II-133
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20141121
Time              13.23
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           9615.385 Hz
FIDRES        0.250010 Hz
AQ           1.9999200 sec
RG                 1440
DW               52.000 usec
DE                14.54 usec
TE                298.1 K
D1          0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

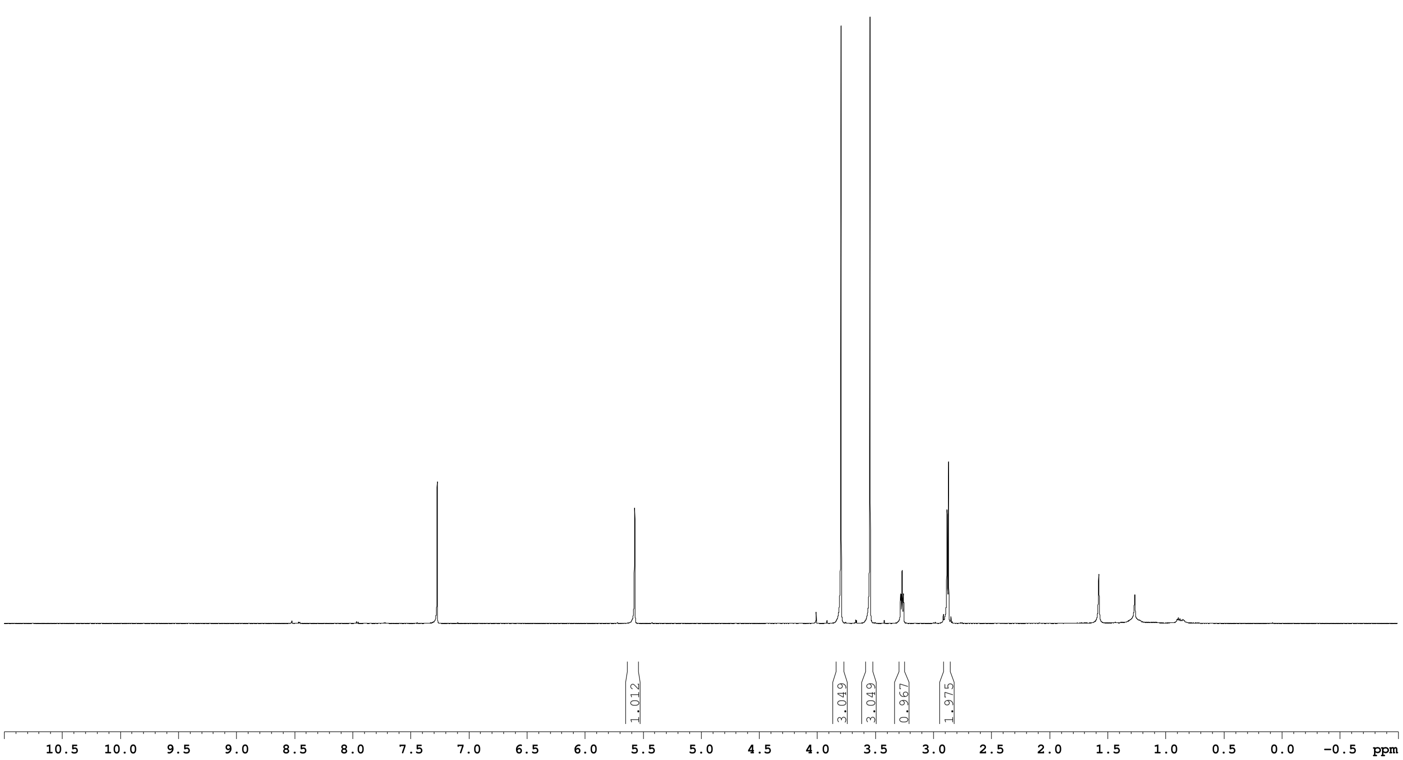
F2 - Processing parameters
SI                65536
SF          600.1300279 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-35B



2.27

^{1}H NMR (CDCl$_3$, 600 MHz)



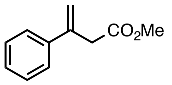
```
Current Data Parameters
NAME          YS-II-35B
EXPNO                16
PROCNO                1

F2 - Acquisition Parameters
Date_          20141015
Time              12.35
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                38460
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                 1620
DW               52.000 usec
DE                14.54 usec
TE                298.2 K
D1           0.10000000 sec
TD0                   1

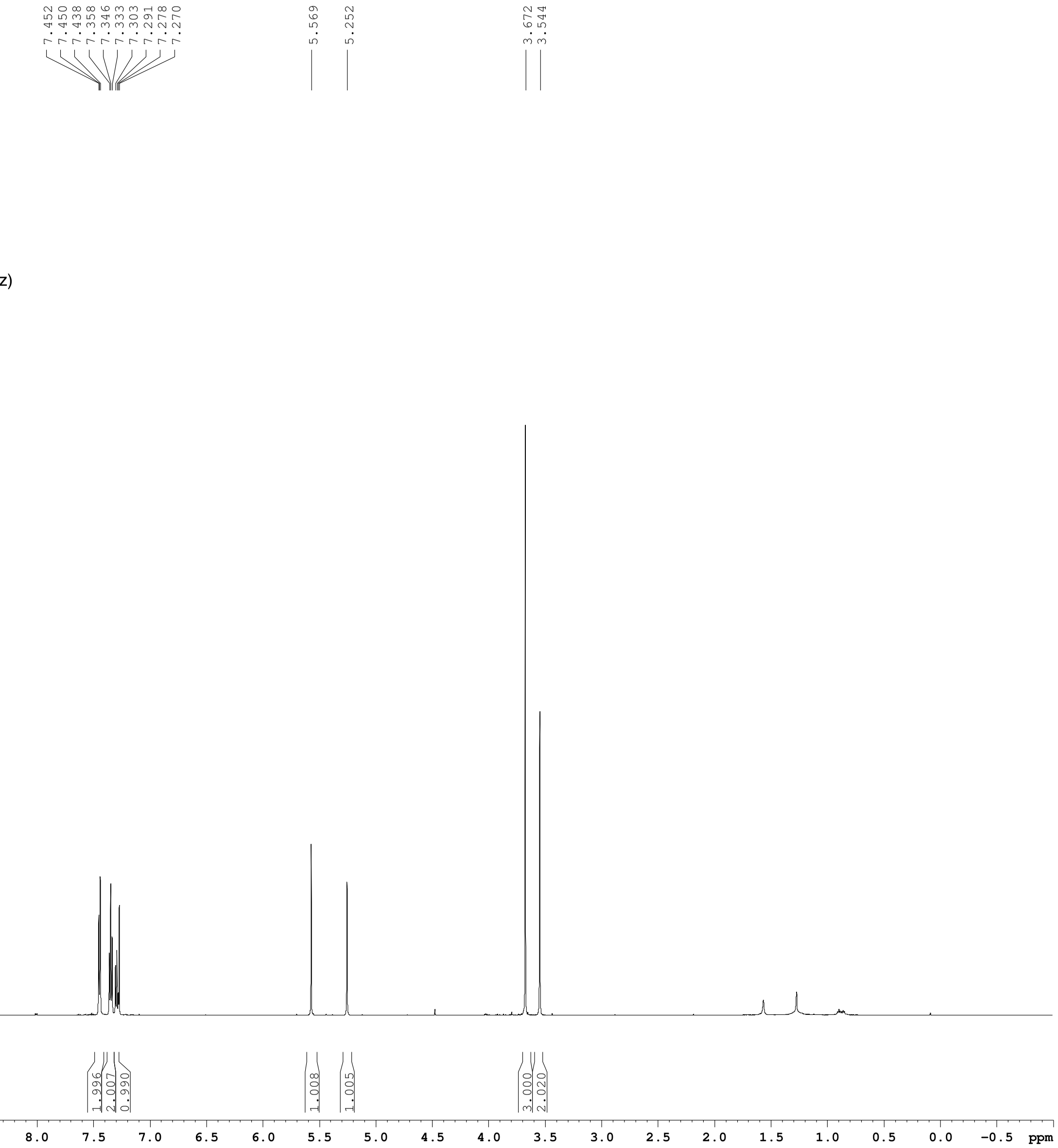
======== CHANNEL f1 ========
SFO1       600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300281 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-II-48A



2.29
^{1}H NMR (CDCl$_3$, 600 MHz)



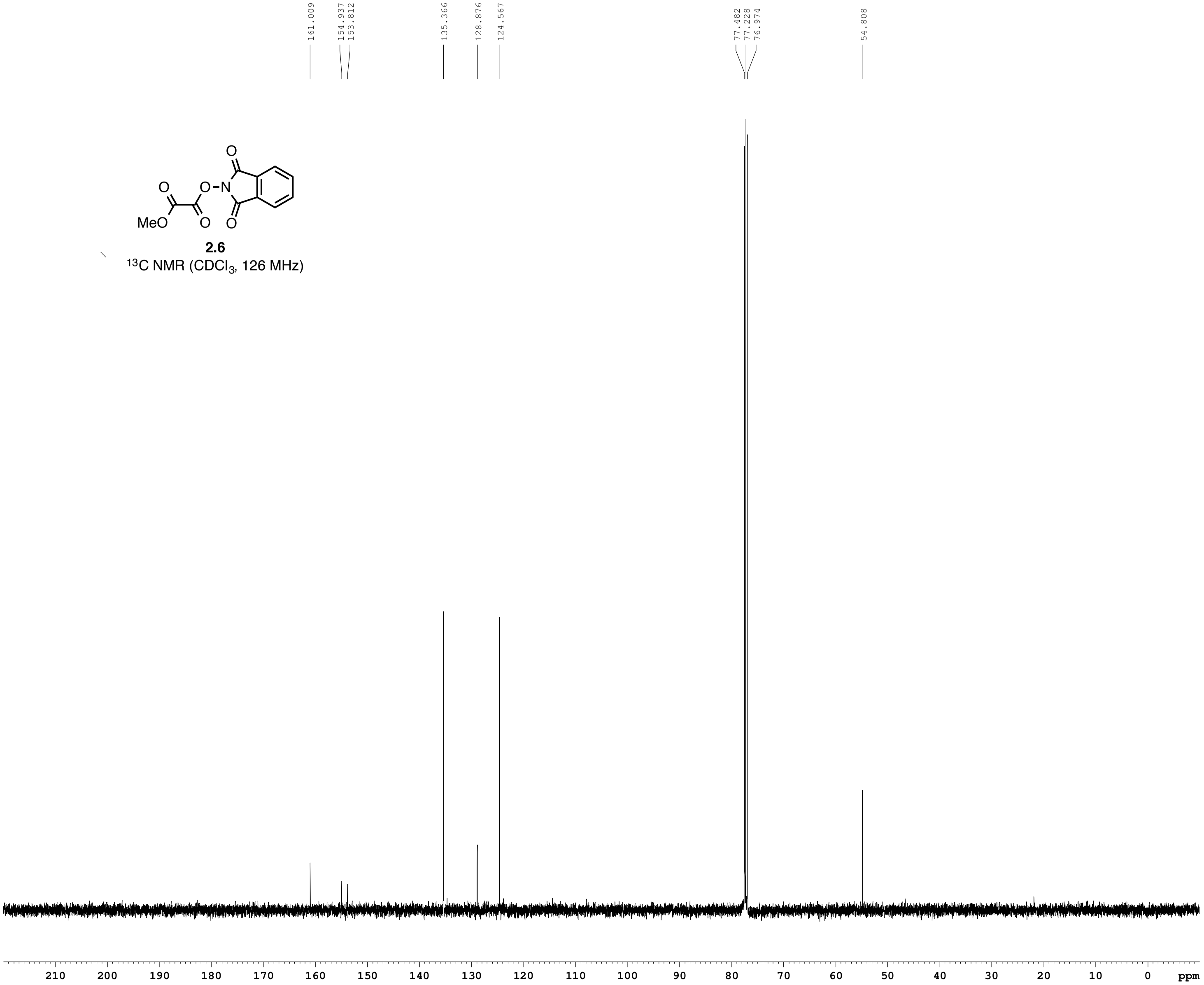
```
Current Data Parameters
NAME          YS-II-48A
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20140930
Time              16.56
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                98074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                  512
DW               52.000 usec
DE                14.54 usec
TE                297.9 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        23.01441956 W

F2 - Processing parameters
SI                65536
SF          600.1300282 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-I-100



2.6

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-100
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20141005
Time               9.01
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  472
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.75000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

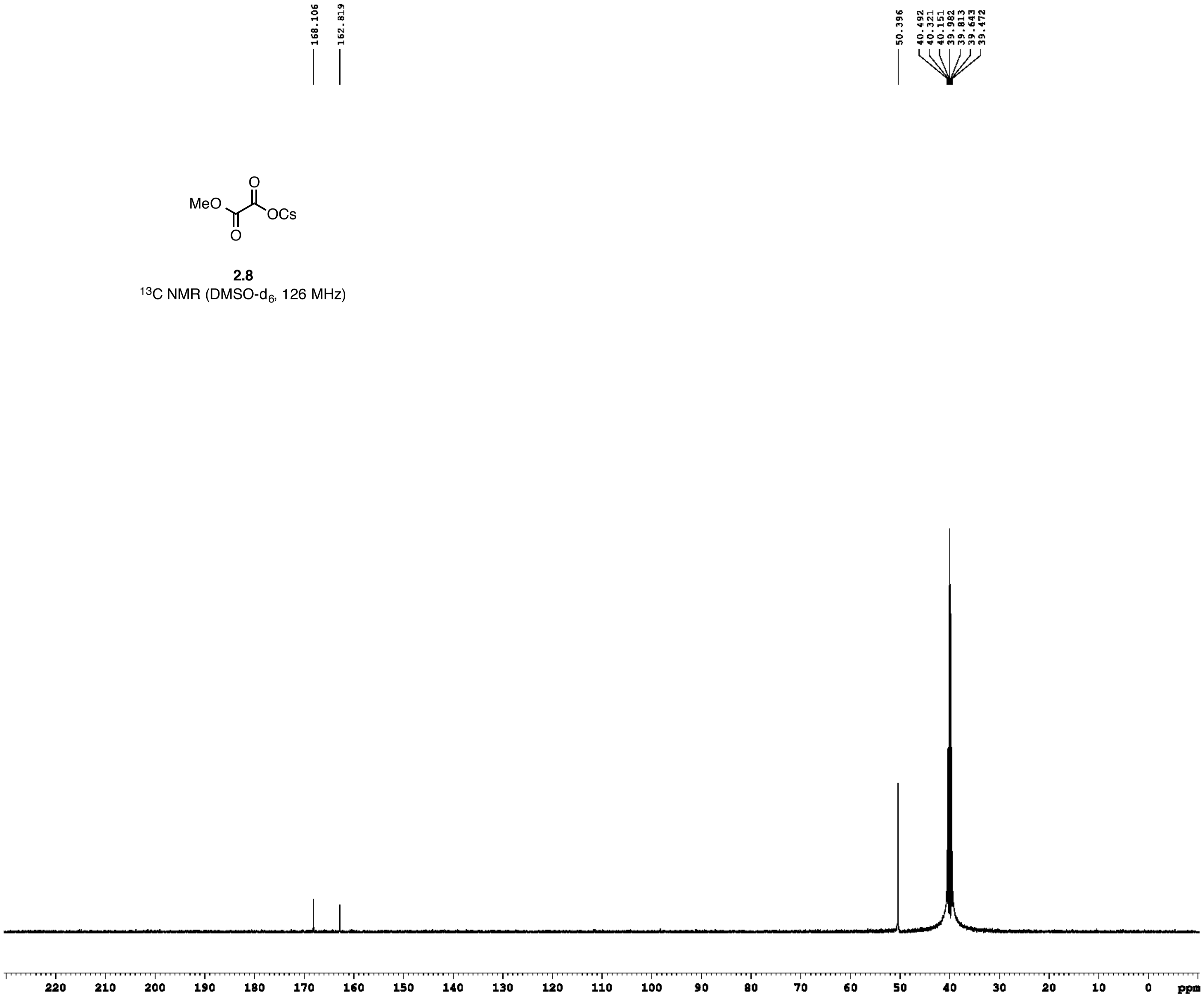
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803992 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-IV-71



2.8

^{13}C NMR (DMSO-d$_6$, 126 MHz)

```
Current Data Parameters
NAME             YS-IV-71
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160319
Time                 9.02
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

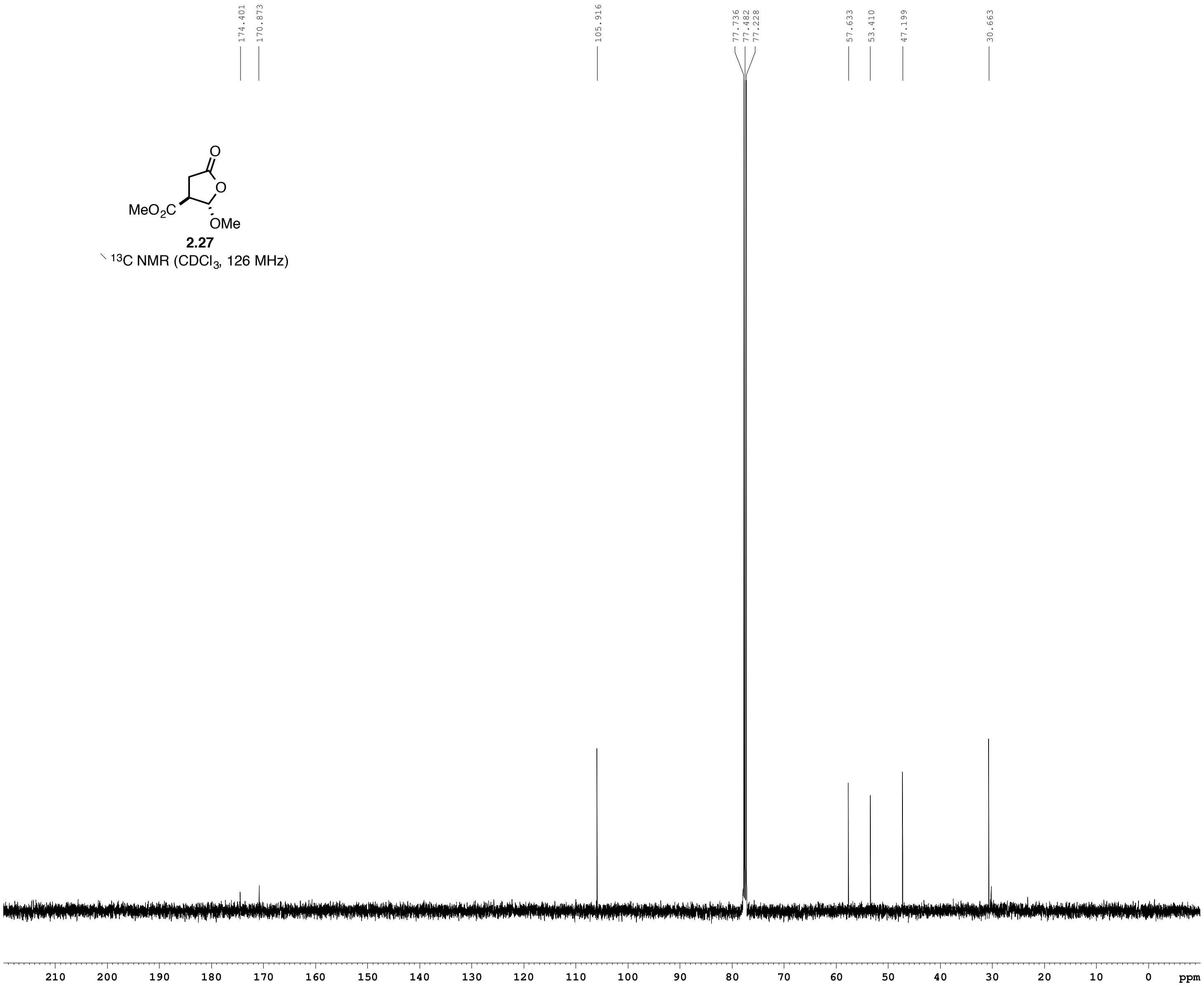
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804190 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-II-35A



2.27

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-II-35A
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20141002
Time               9.27
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  880
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

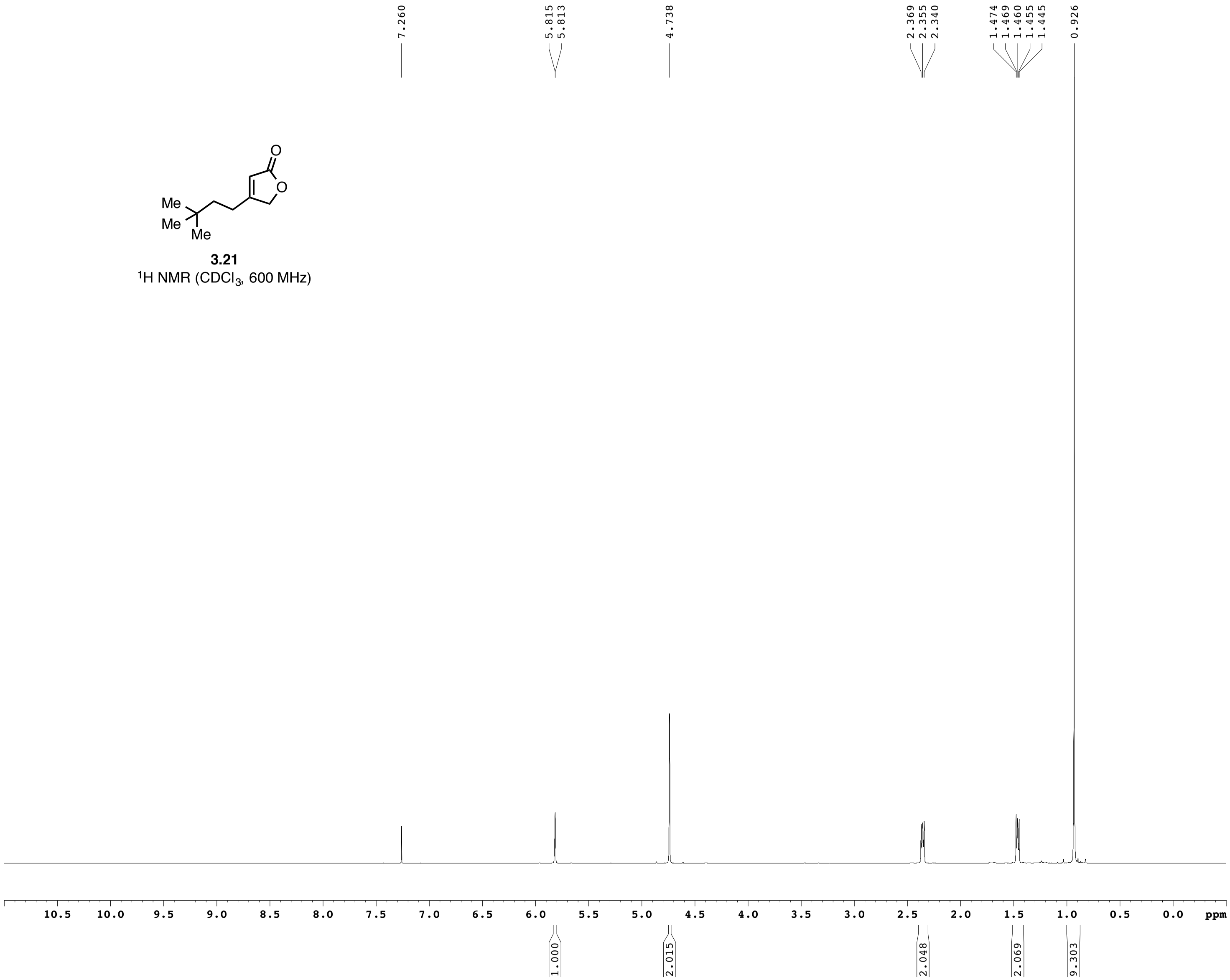
F2 - Processing parameters
SI                65536
SF          125.7803665 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

Appendix C: Chapter 3 NMR Spectra

1H spectrum

3.21

^{1}H NMR ($CDCl_3$, 600 MHz)



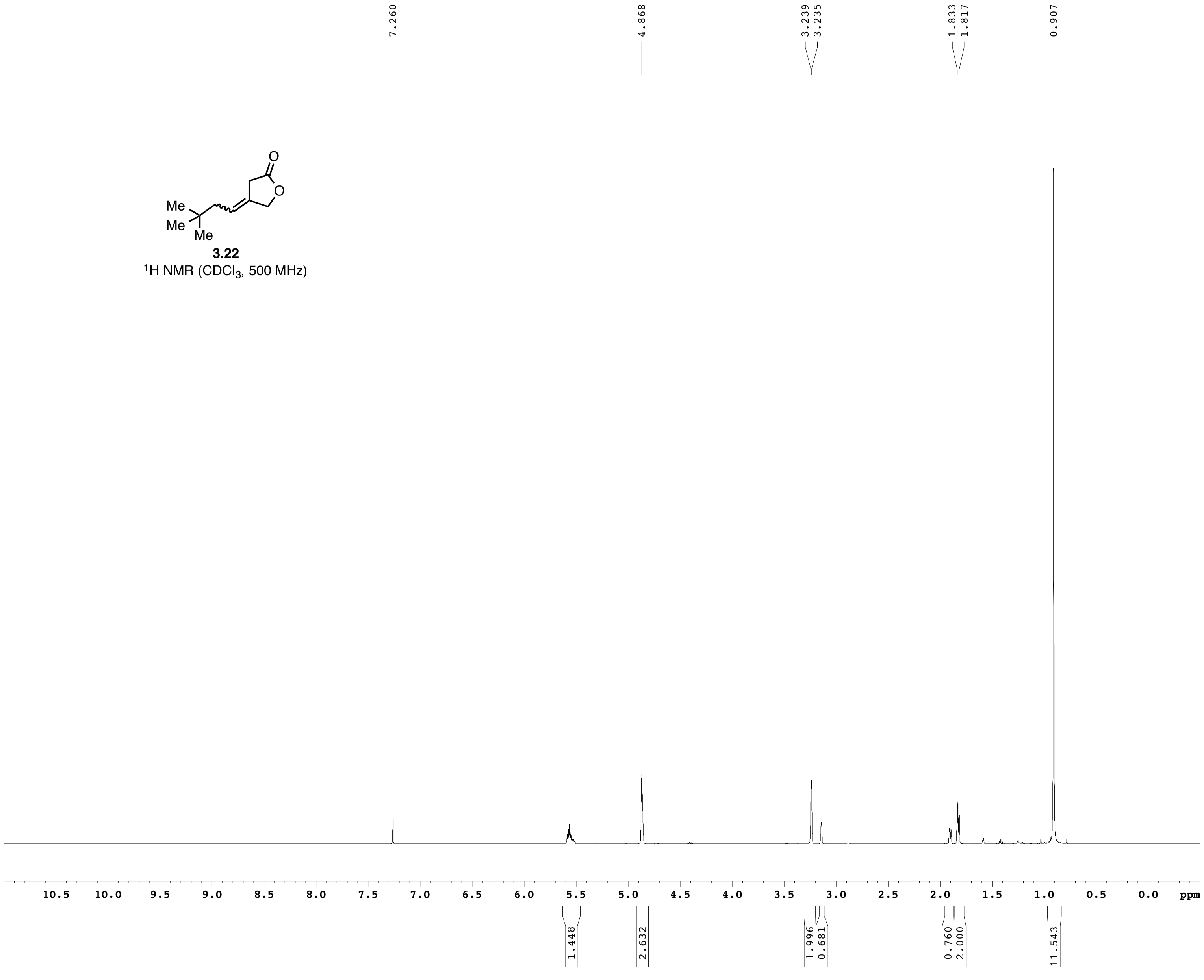
```
Current Data Parameters
NAME      GL5-247-33a33
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20151214
Time              14.28
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                98074
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                  287
DW               52.000 usec
DE                14.54 usec
TE                293.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                 8.00 usec
PLW1        24.00000000 W

F2 - Processing parameters
SI                65536
SF          600.1300356 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

1H spectrum



3.22

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME        GL5-247-33c
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20151215
Time              17.46
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT          CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                  6.3
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

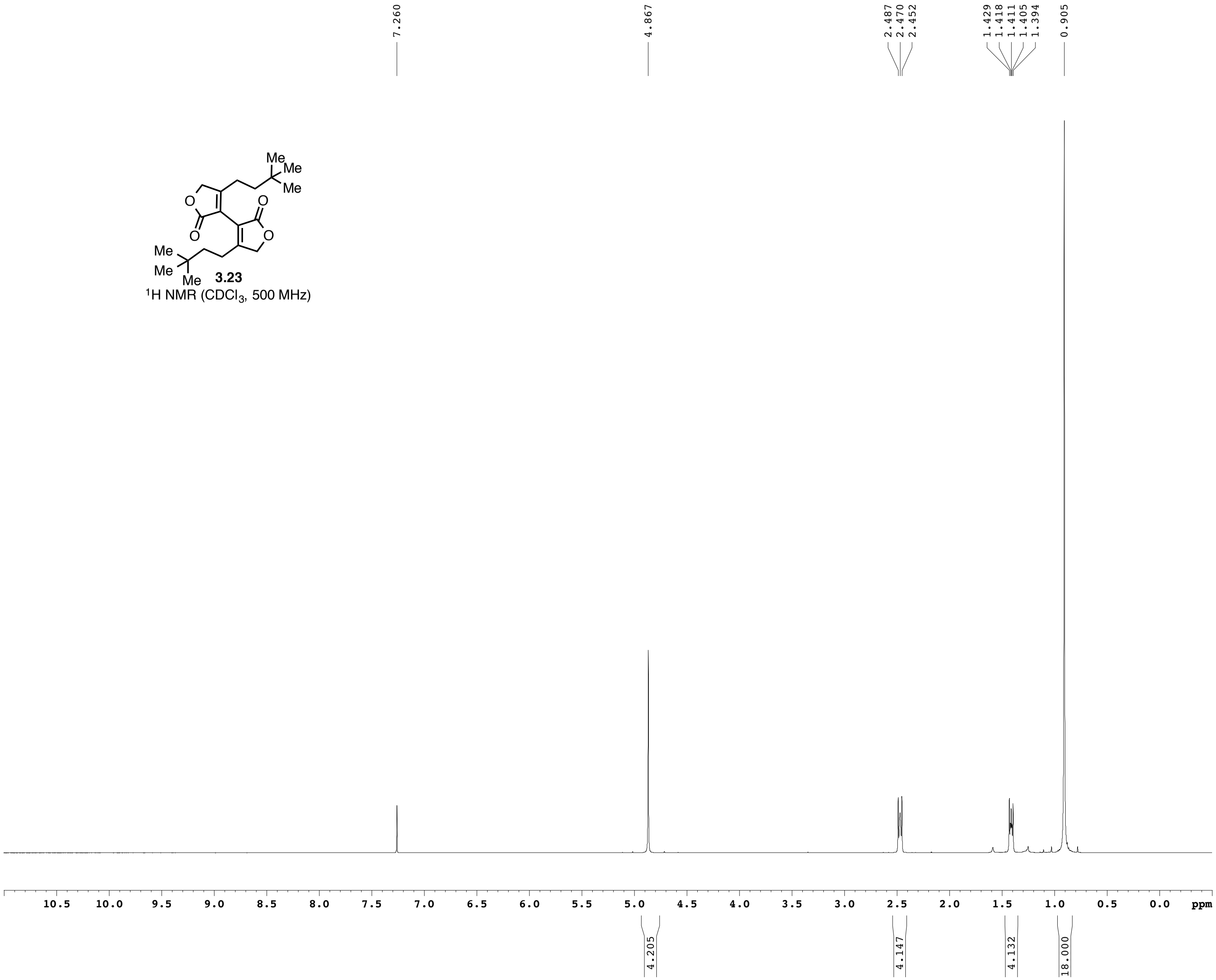
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200316 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

1H spectrum

3.23

^{1}H NMR (CDCl$_3$, 500 MHz)

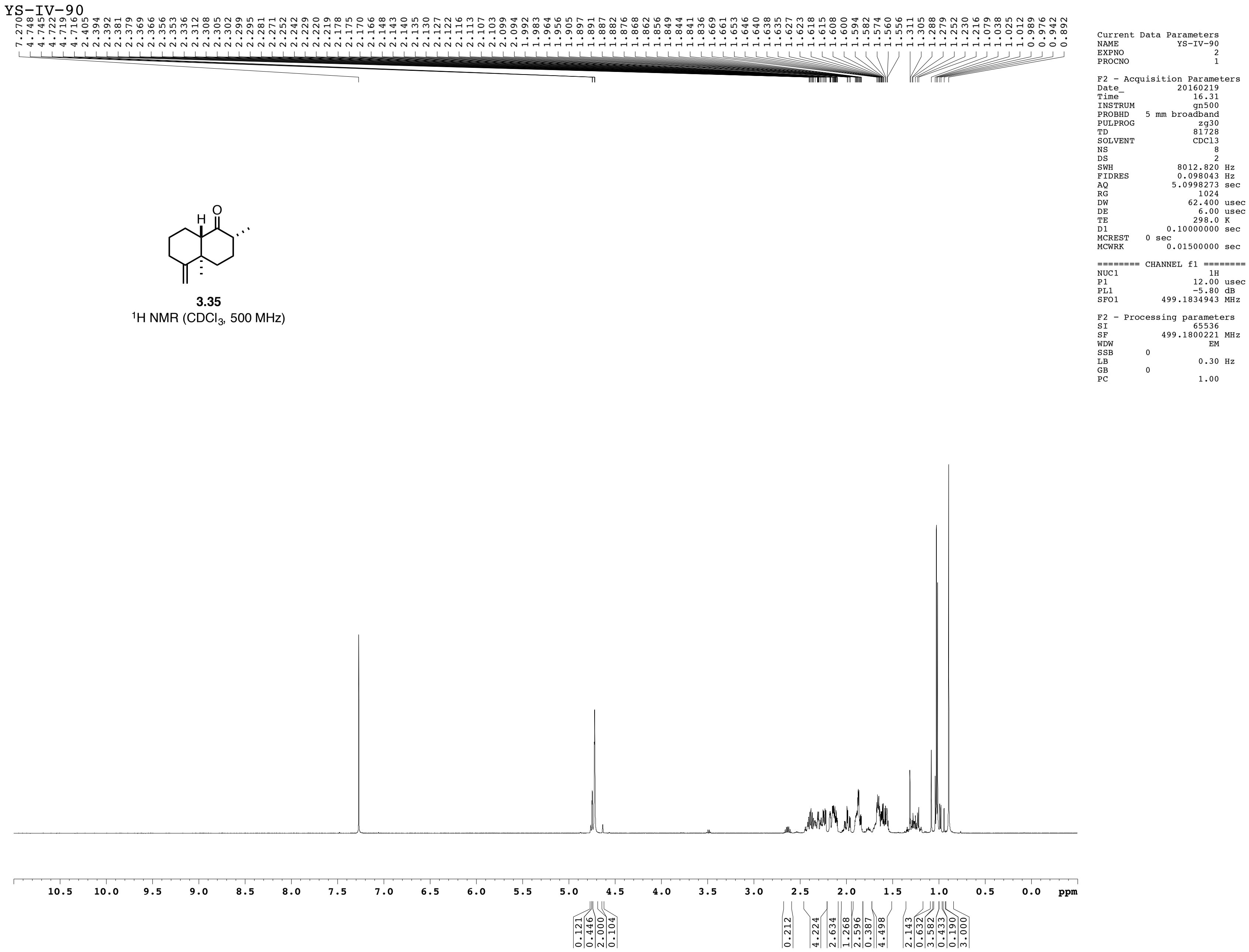


```
Current Data Parameters
NAME       GL5-247-33bhv
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time               10.44
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG                   6.3
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1         0.10000000 sec
MCREST   0 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF         500.2200315 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```



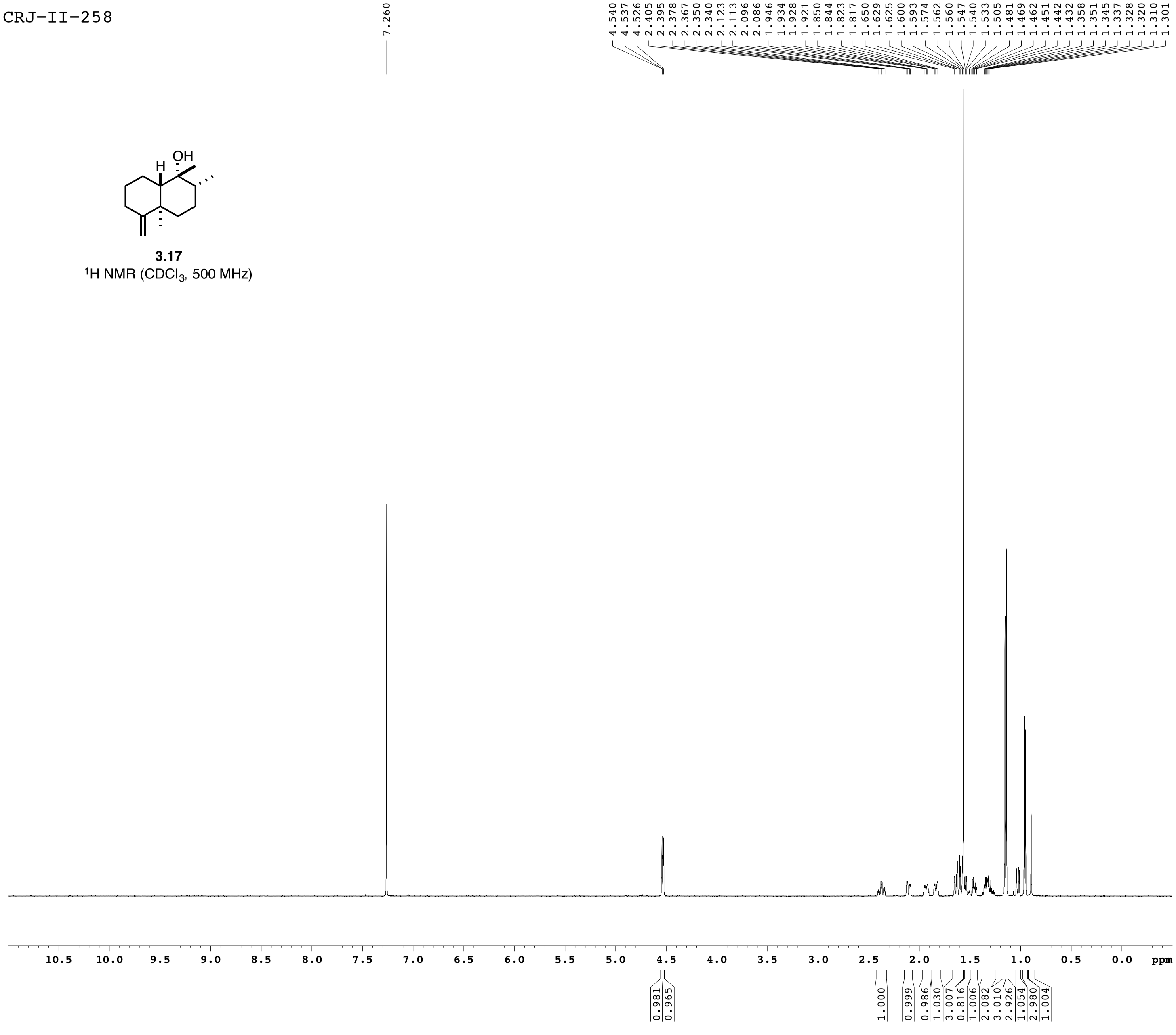
3.35

^{1}H NMR ($CDCl_3$, 500 MHz)

CRJ-II-258

3.17

^{1}H NMR ($CDCl_3$, 500 MHz)



```
Current Data Parameters
NAME          CRJ2-258-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160310
Time               17.58
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

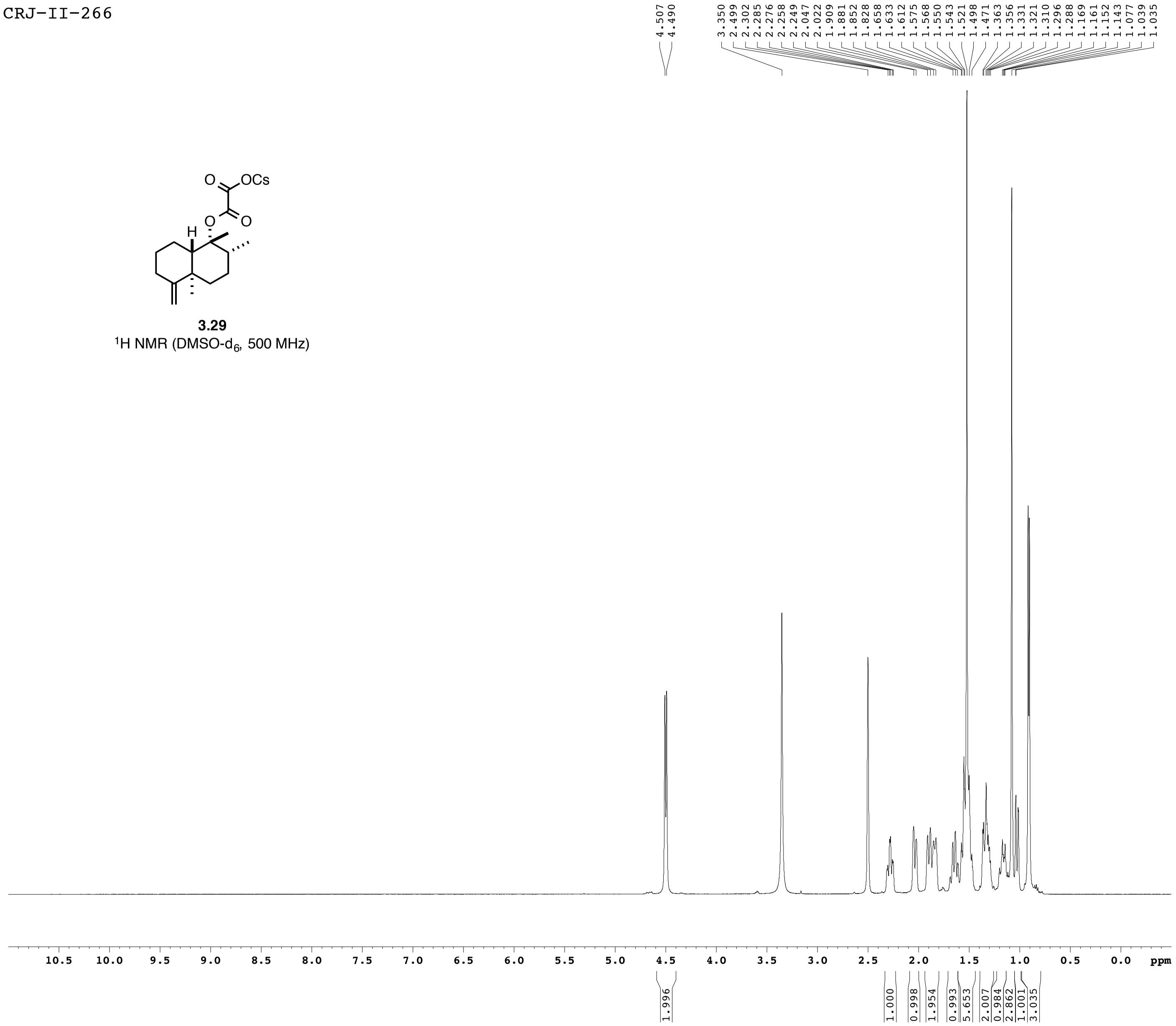
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200313 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```

CRJ-II-266

3.29

^{1}H NMR (DMSO-d_6, 500 MHz)



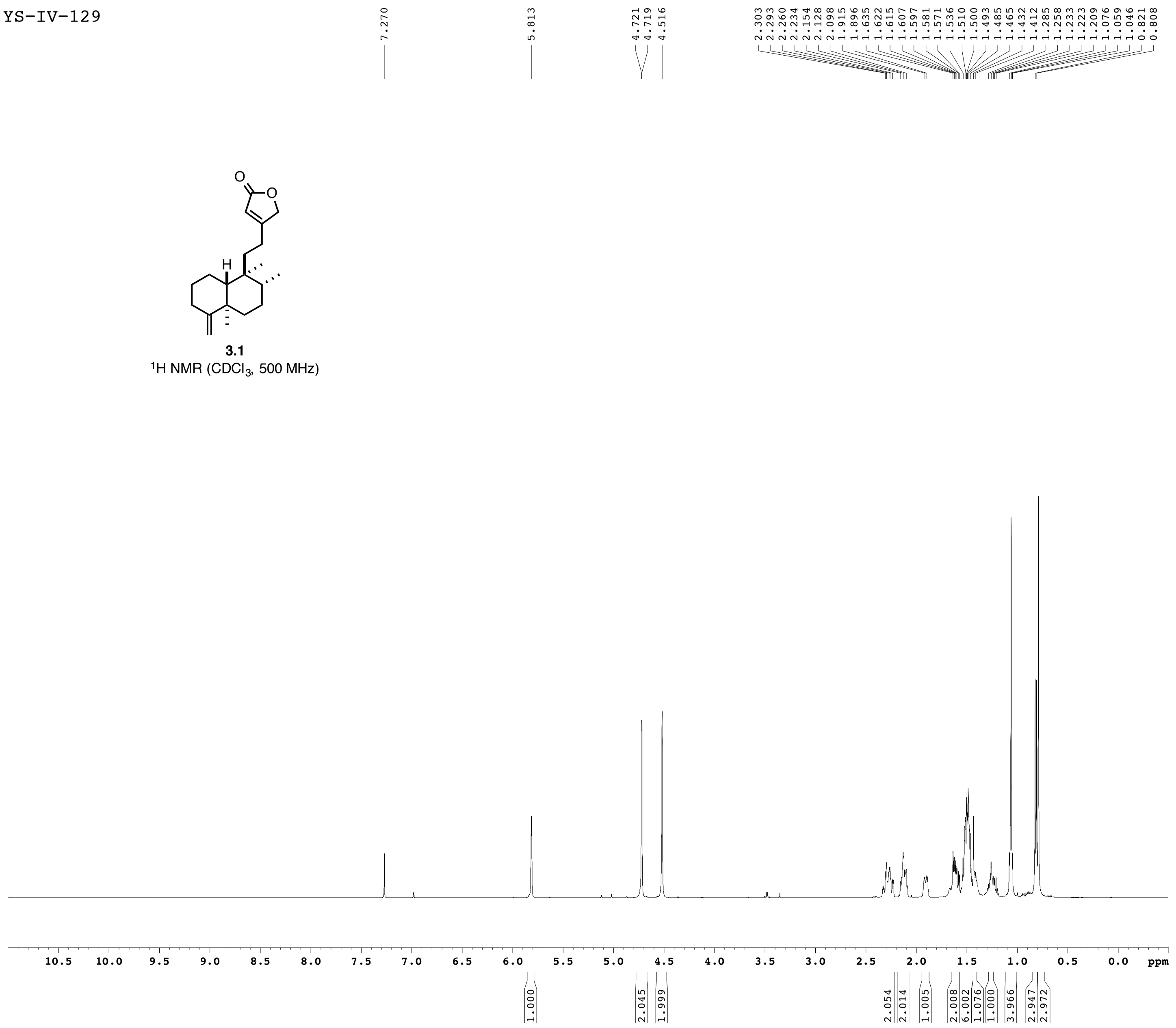
```
Current Data Parameters
NAME      CRJ2-266-pure
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160312
Time              16.33
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200136 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

YS-IV-129



3.1

^{1}H NMR ($CDCl_3$, 500 MHz)

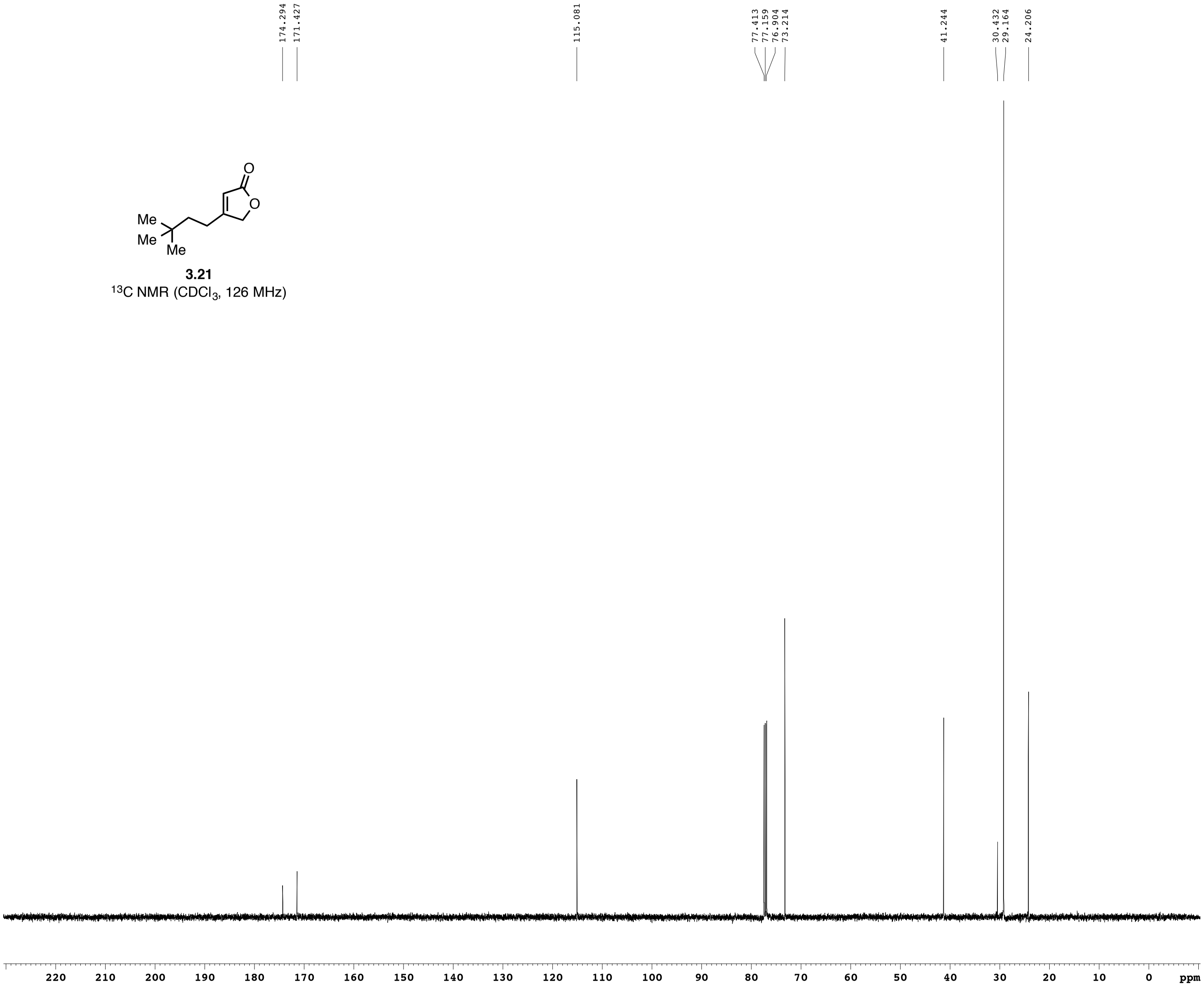
```
Current Data Parameters
NAME          YS-IV-129B
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160321
Time               14.58
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200262 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



3.21

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME       GL5-247-33a3
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameter
Date_          20151214
Time              10.53
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.pr
TD                65536
SOLVENT           CDCl3
NS                   85
DS                   16
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813440 se
RG              11585.2
DW               16.500 us
DE                 6.00 us
TE                298.0 K
D1           0.25000000 se
d11          0.03000000 se
D16          0.00020000 se
d17          0.00019600 se
MCREST   0 sec
MCWRK        0.01500000 se
P2                33.10 us

======== CHANNEL f1 ======
NUC1                13C
P1                16.55 us
P11              500.00 us
P12             2000.00 us
PL0              120.00 dE
PL1               -1.00 dE
SFO1        125.7942548 ME
SP1                2.70 dE
SP2                2.70 dE
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ======
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 us
PL2                1.60 dE
PL12              24.50 dE
SFO2        500.2225011 ME

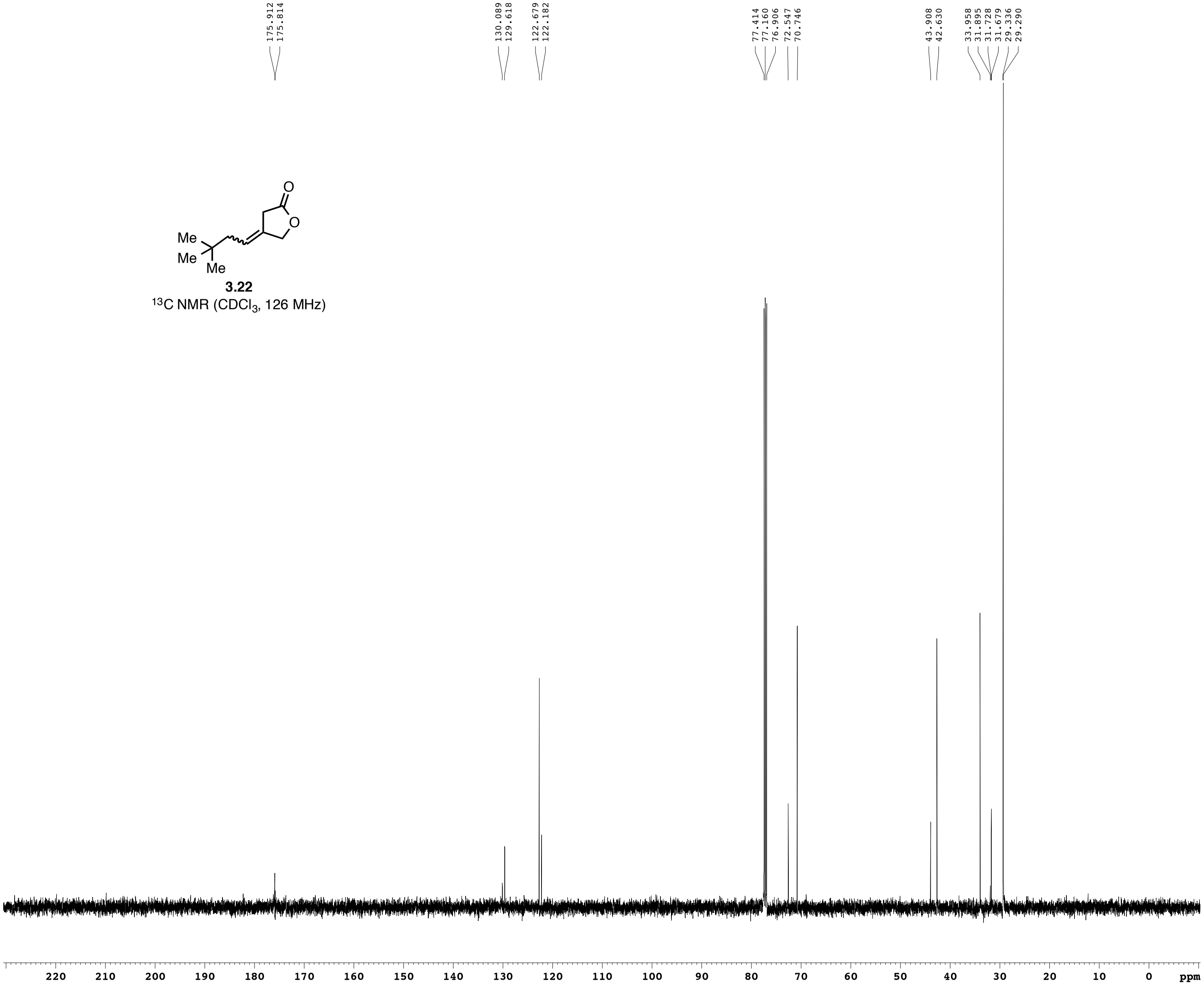
====== GRADIENT CHANNEL ==
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 us
p16             1000.00 us

F2 - Processing parameters
SI                65536
SF          125.7804117 MH
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

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

3.22

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME        GL5-247-33c
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameter
Date_          20151215
Time              17.47
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.pr
TD                65536
SOLVENT           CDCl3
NS                  109
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 se
RG               2896.3
DW               16.500 us
DE                 6.00 us
TE                298.0 K
D1           0.25000000 se
d11          0.03000000 se
D16          0.00020000 se
d17          0.00019600 se
MCREST   0 sec
MCWRK        0.01500000 se
P2                33.10 us

======== CHANNEL f1 ======
NUC1                13C
P1                16.55 us
P11              500.00 us
P12             2000.00 us
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MH
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ======
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 us
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MH

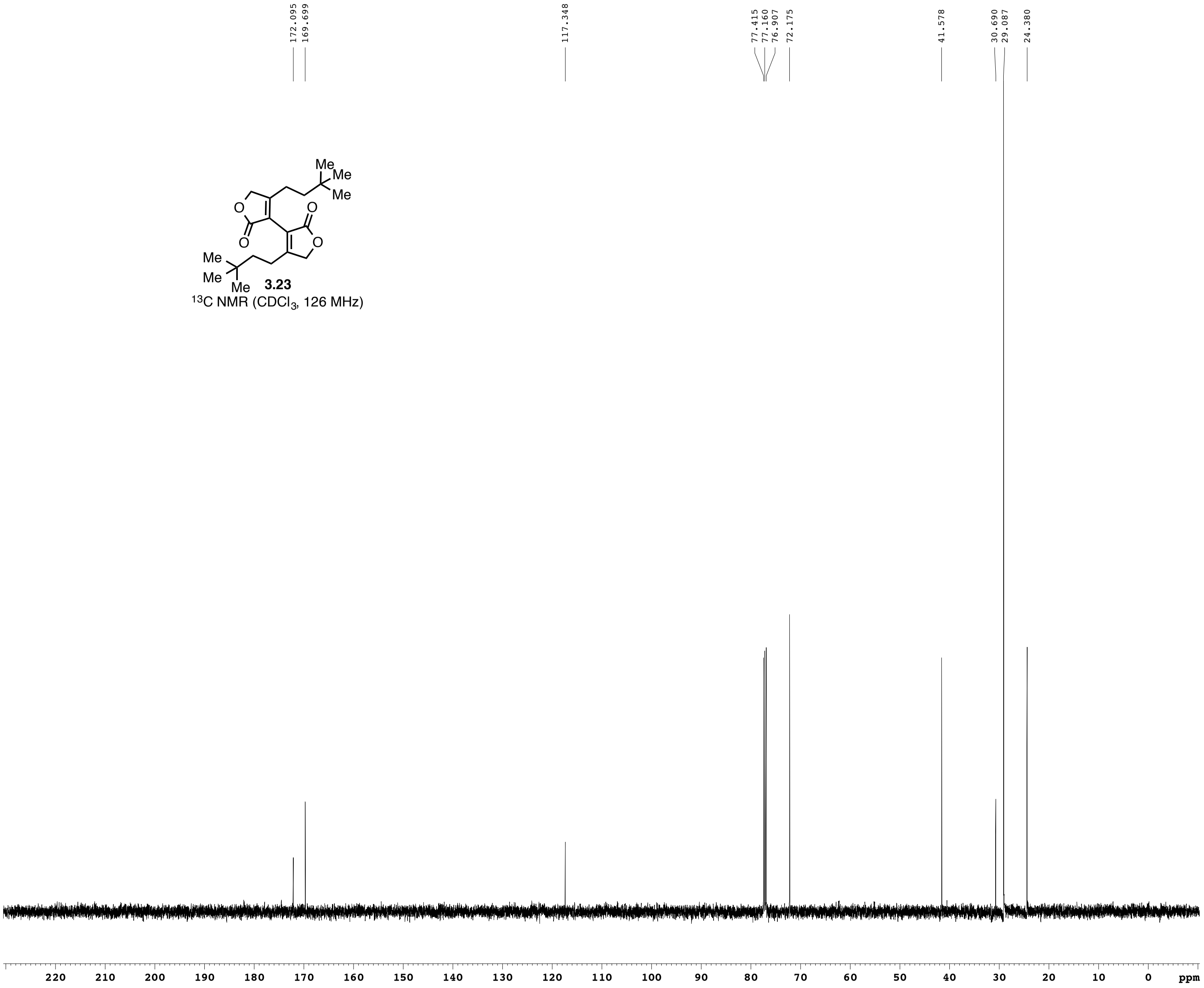
====== GRADIENT CHANNEL ==
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 us
p16             1000.00 us

F2 - Processing parameters
SI                65536
SF          125.7804086 MH
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

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

3.23

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME      GL5-247-33bhv
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameter
Date_          20151214
Time              10.45
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.pr
TD                65536
SOLVENT           CDCl3
NS                   59
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 se
RG              11585.2
DW               16.500 us
DE                 6.00 us
TE                298.0 K
D1           0.25000000 se
d11          0.03000000 se
D16          0.00020000 se
d17          0.00019600 se
MCREST   0 sec
MCWRK        0.01500000 se
P2                33.10 us

======== CHANNEL f1 ======
NUC1                13C
P1                16.55 us
P11              500.00 us
P12             2000.00 us
PL0              120.00 dE
PL1               -1.00 dE
SFO1        125.7942548 ME
SP1                2.70 dE
SP2                2.70 dE
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ======
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 us
PL2                1.60 dE
PL12              24.50 dE
SFO2        500.2225011 ME

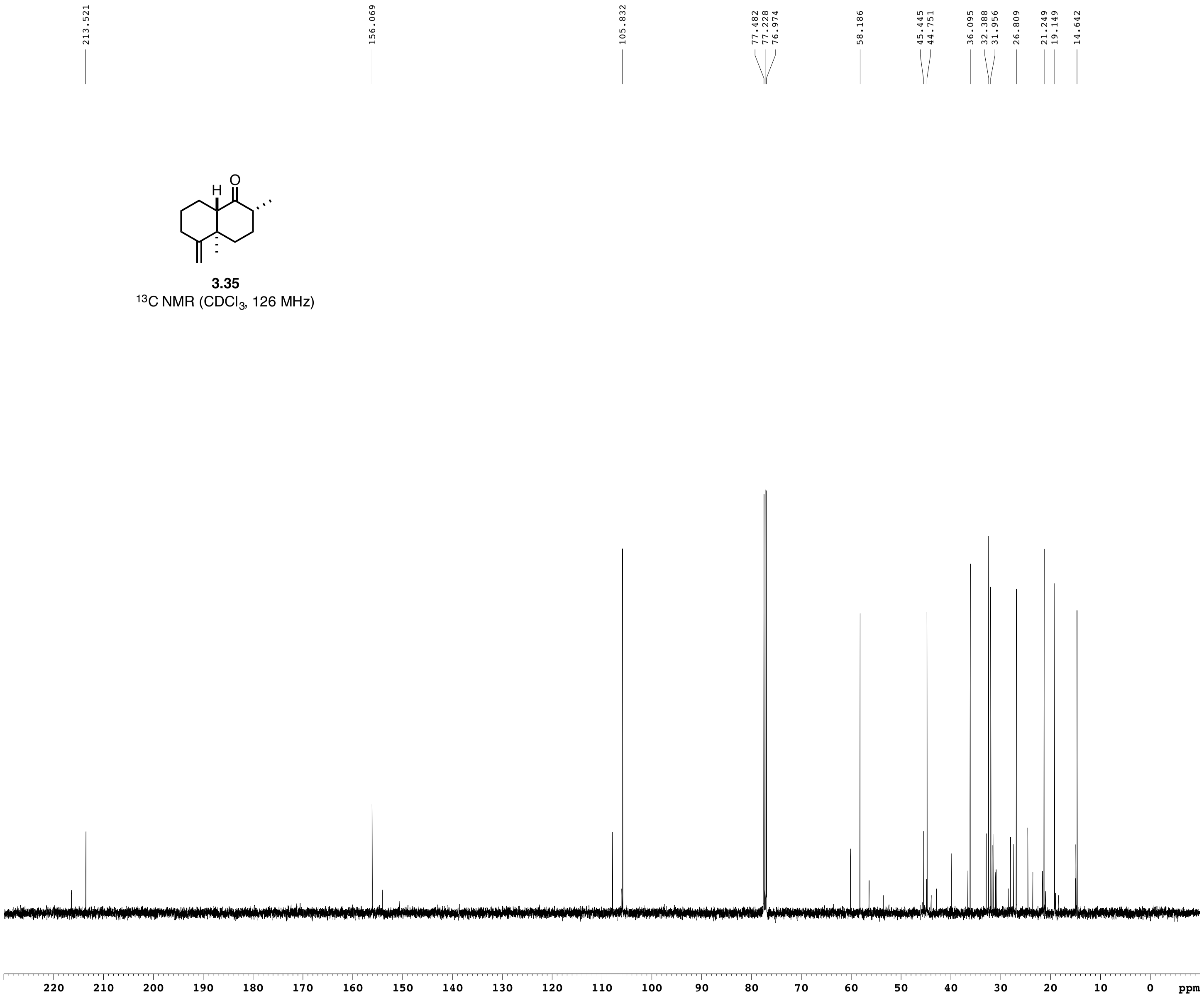
====== GRADIENT CHANNEL ==
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 us
p16             1000.00 us

F2 - Processing parameters
SI                65536
SF          125.7804090 ME
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-IV-90

3.35

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-90
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160319
Time                9.06
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

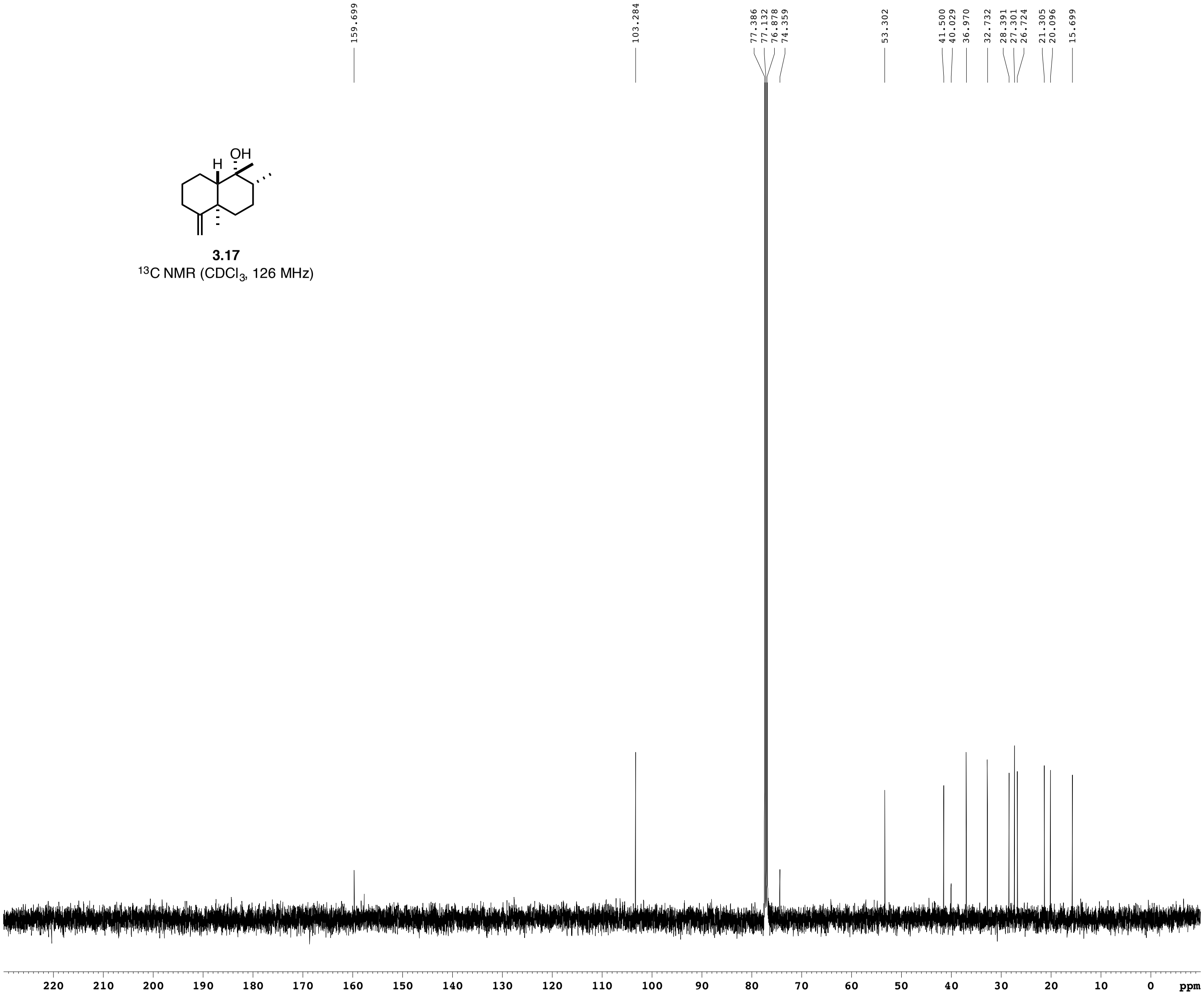
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804004 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

CRJ-II-258



3.17

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          CRJ2-258-1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160310
Time               18.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT             DMSO
NS                   512
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

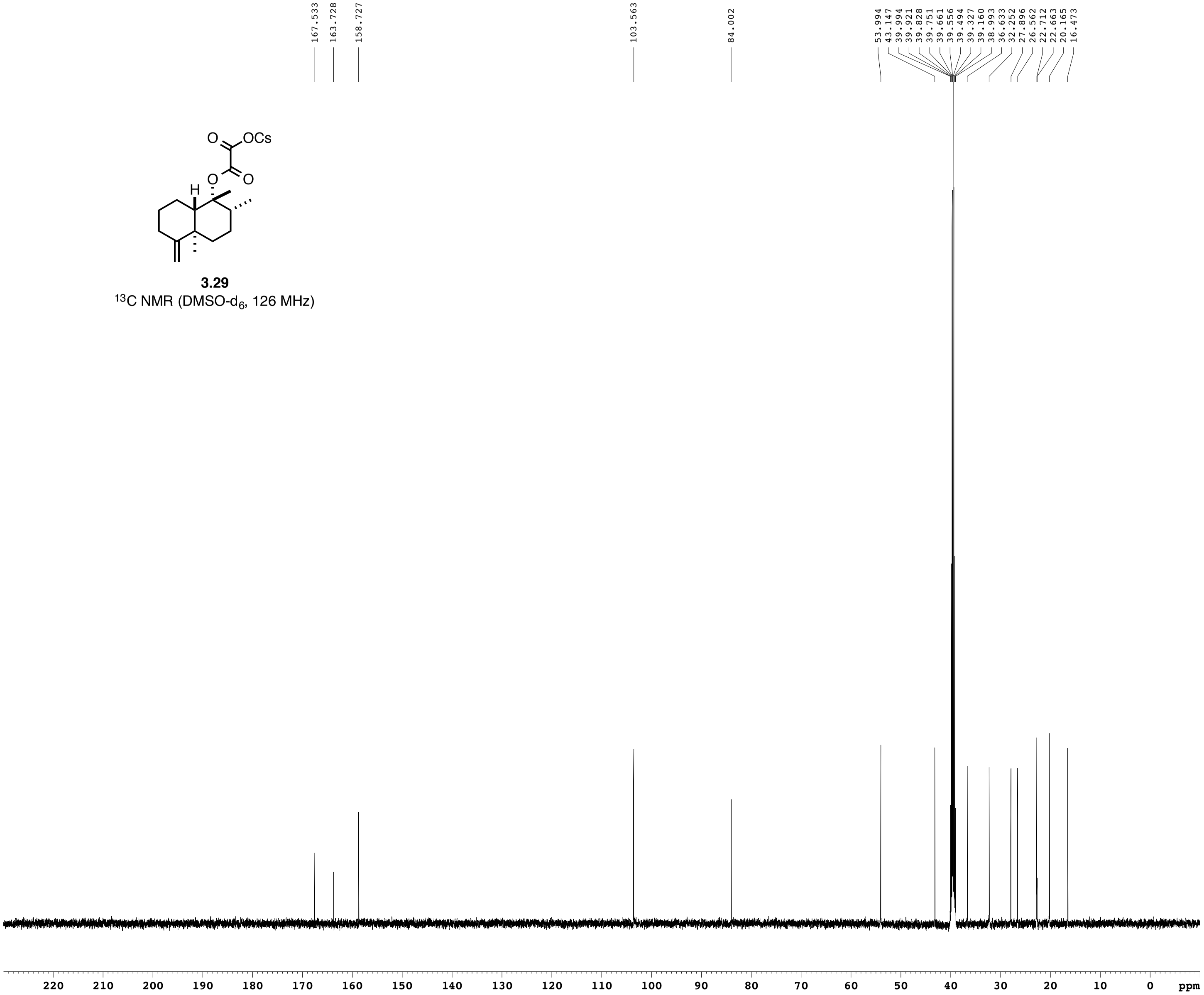
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804109 MHz
WDW                   EM
SSB        0
LB                  1.00 Hz
GB         0
PC                  2.00
```

CRJ-II-266



3.29

^{13}C NMR (DMSO-d_6, 126 MHz)

```
Current Data Parameters
NAME      CRJ2-266-pure
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20160312
Time              16.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

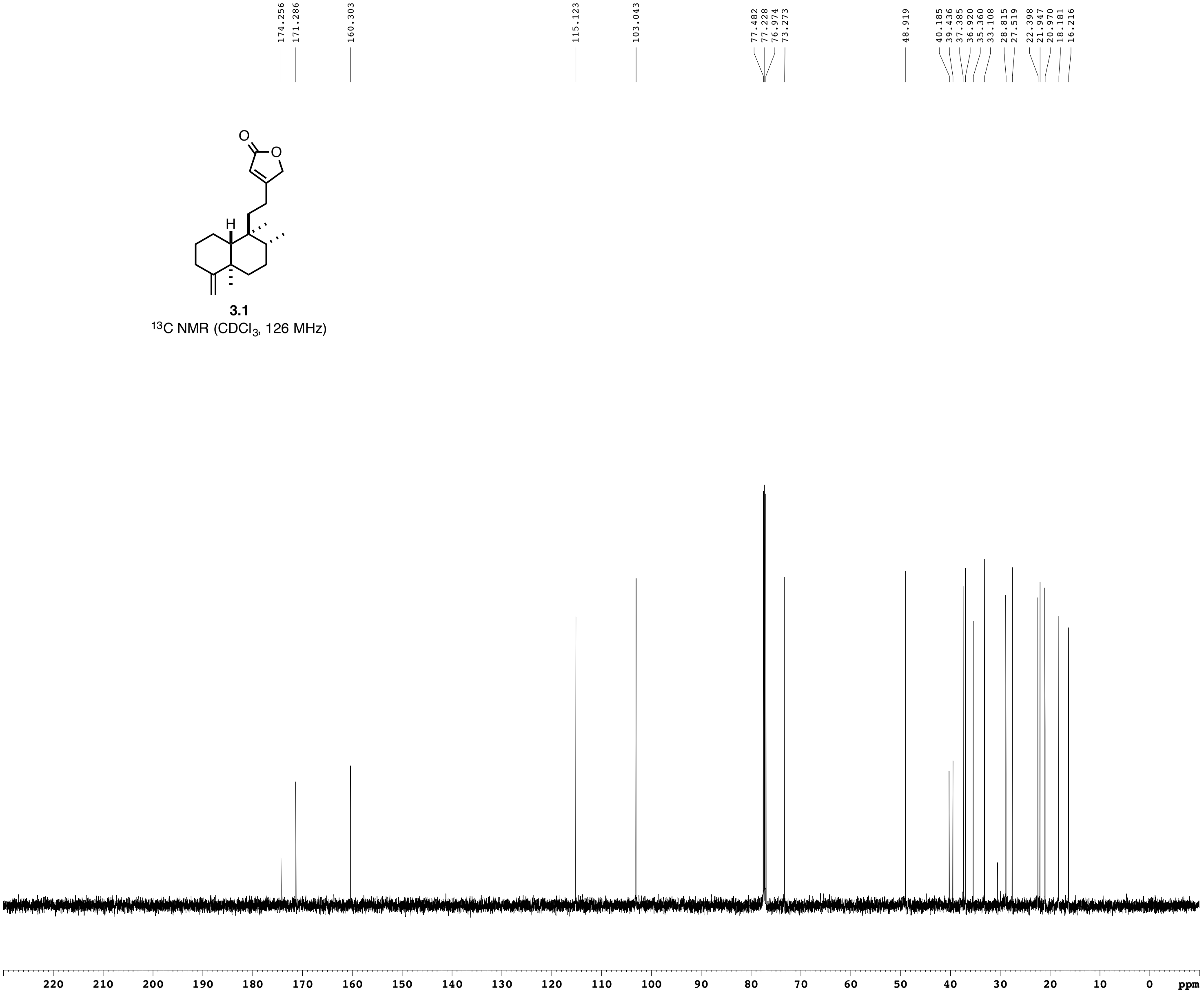
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804820 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-IV-129



3.1

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-IV-129B
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160321
Time               14.59
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    48
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1        125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

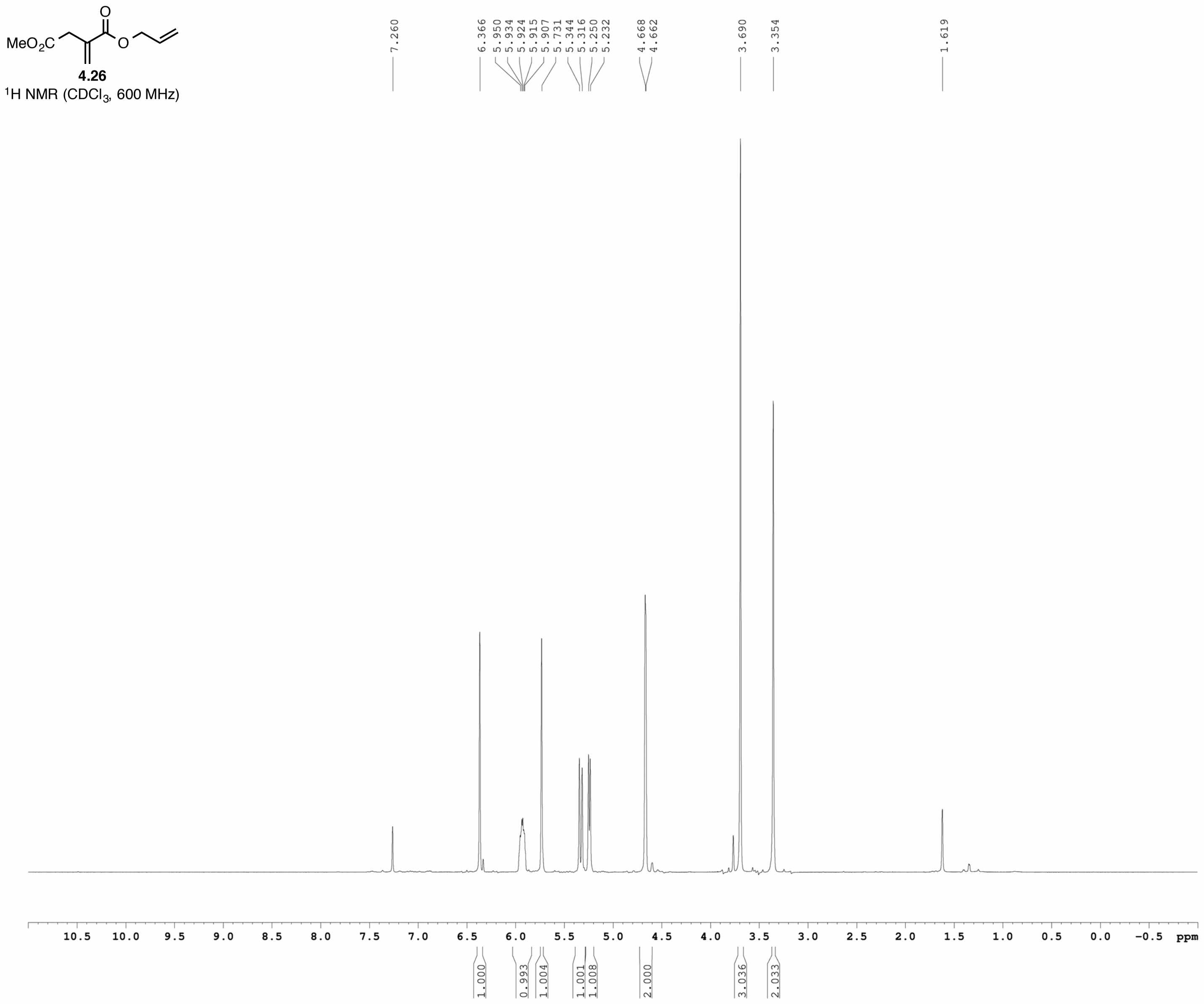
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804024 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

Appendix D: Chapter 4 NMR Spectra

YS-VI-25SM



4.26

^{1}H NMR (CDCl$_3$, 600 MHz)

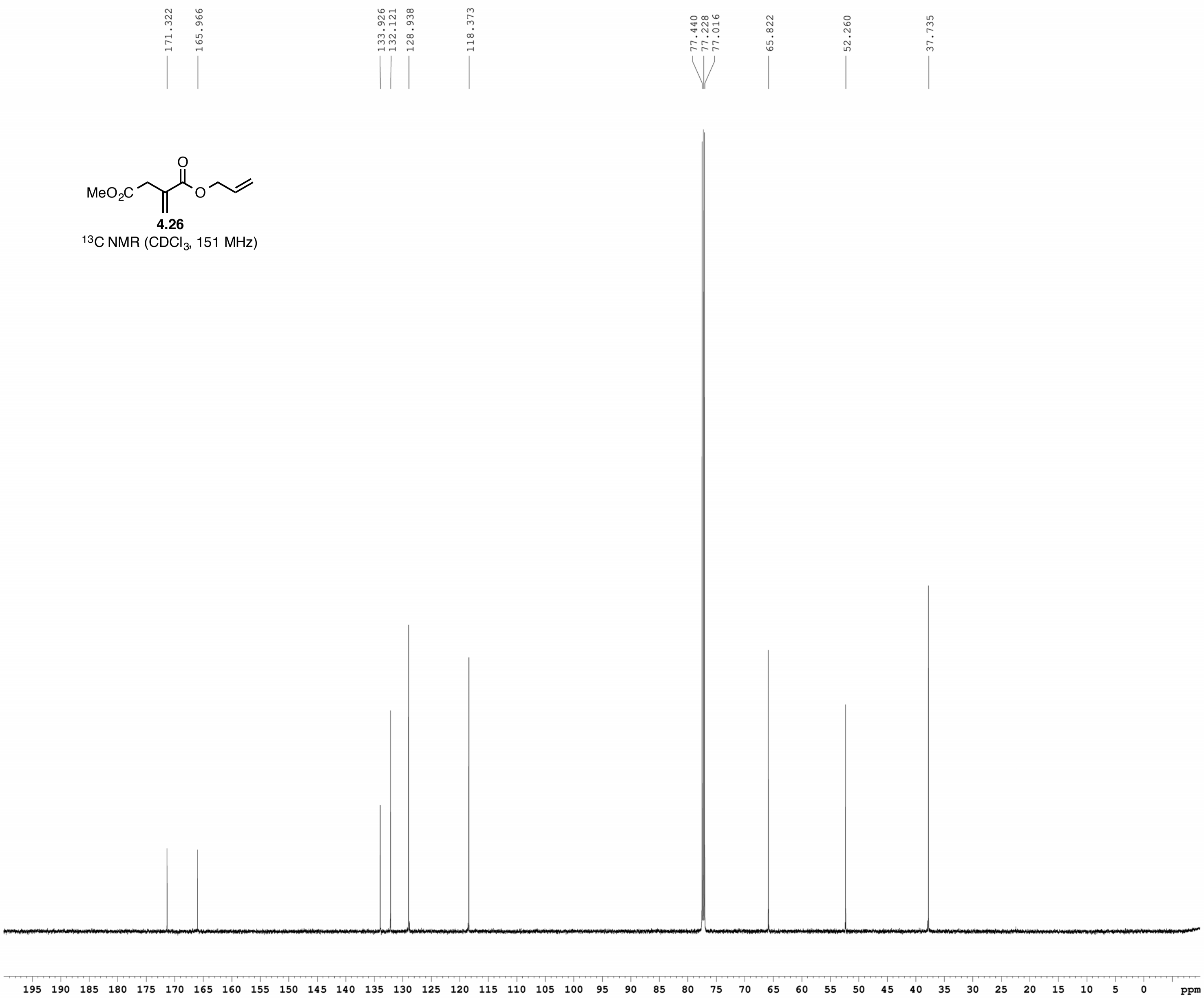
```
Current Data Parameters
NAME          YS-VI-25SM
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170816
Time               16.49
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300352 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-VI-25SM



4.26

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME          YS-VI-25SM
EXPNO                  2
PROCNO                 1

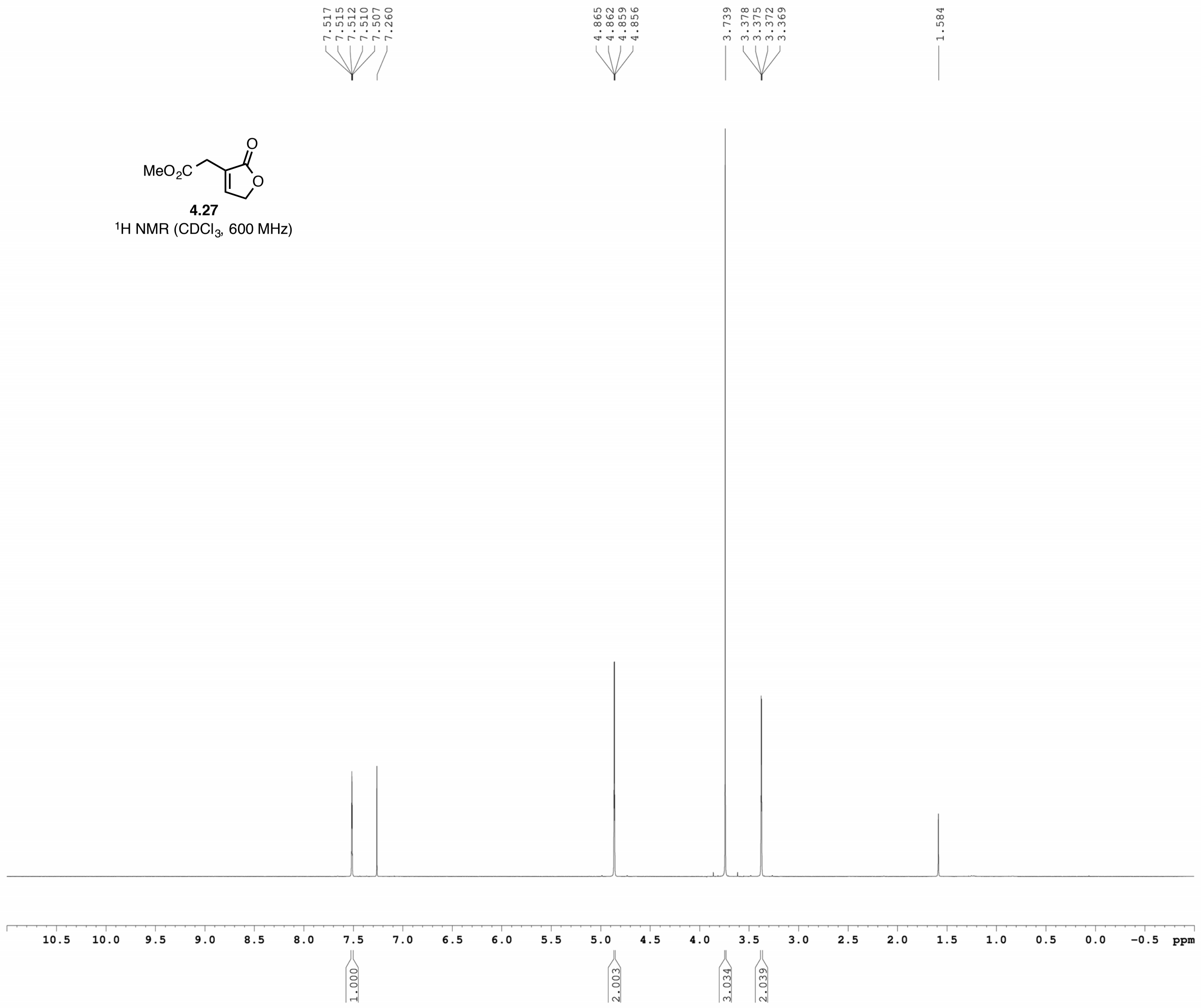
F2 - Acquisition Parameters
Date_           20170816
Time               16.51
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   160
DS                     4
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF           150.9027846 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

YS-VI-25



4.27

^{1}H NMR ($CDCl_3$, 600 MHz)

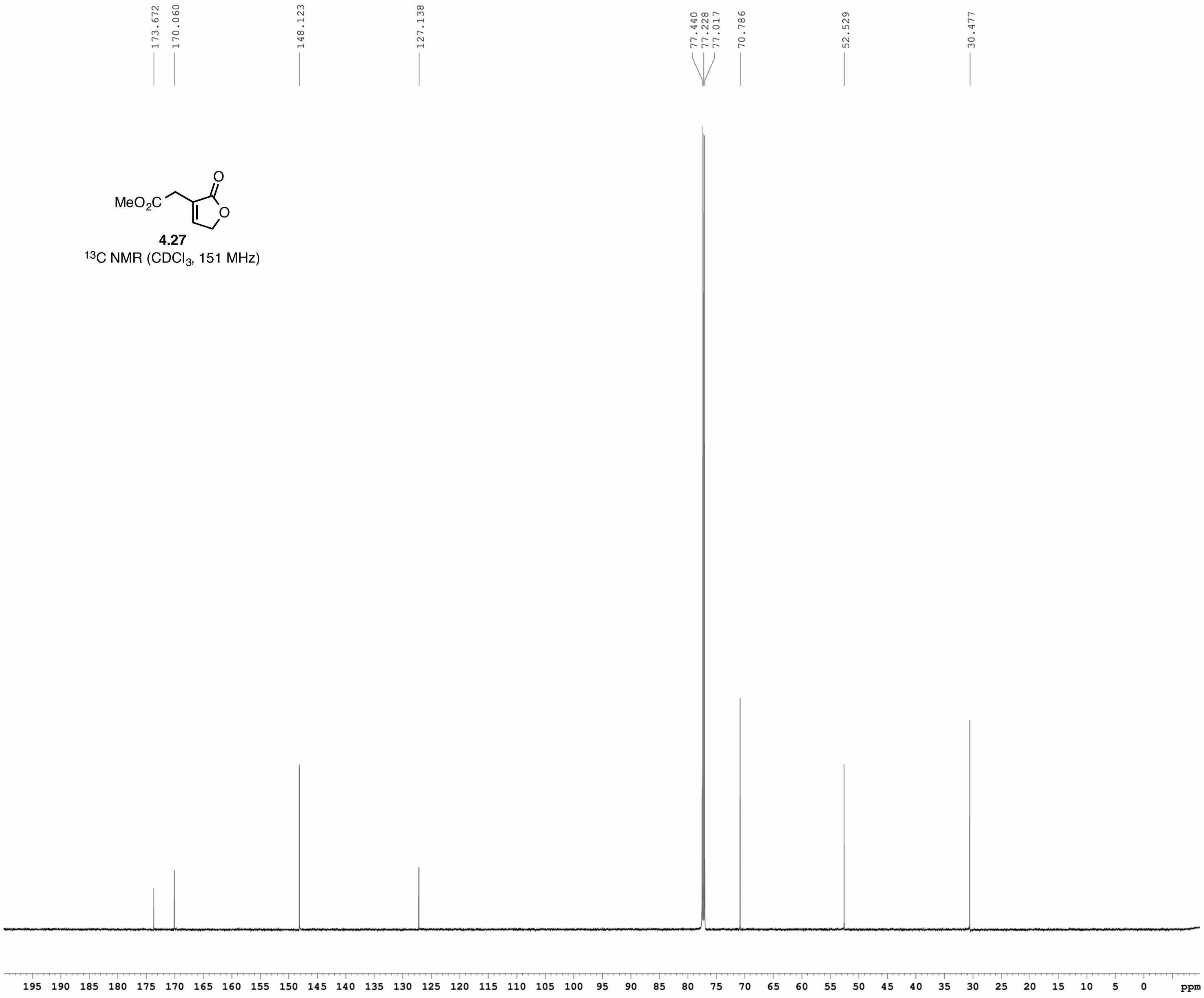
```
Current Data Parameters
NAME             YS-VI-25
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170729
Time                13.11
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      1
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                     10
DW                 52.000 usec
DE                  13.70 usec
TE                  298.0 K
D1             0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300340 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-VI-25



4.27

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME            YS-VI-25
EXPNO                  2
PROCNO                 1

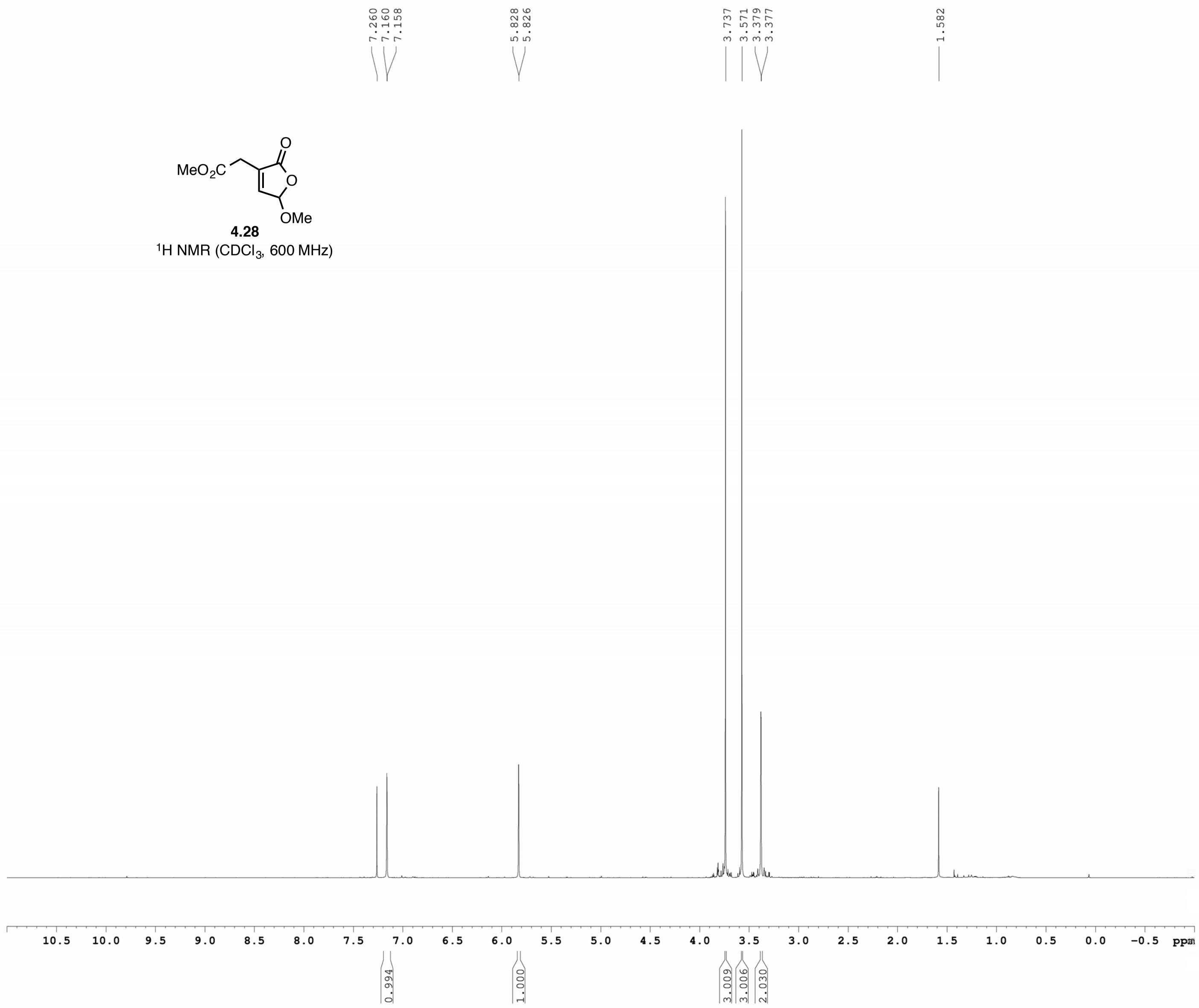
F2 - Acquisition Parameters
Date_           20170729
Time               13.13
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   400
DS                     1
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF          150.9027839 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

YS-VI-27



4.28

^{1}H NMR (CDCl$_3$, 600 MHz)

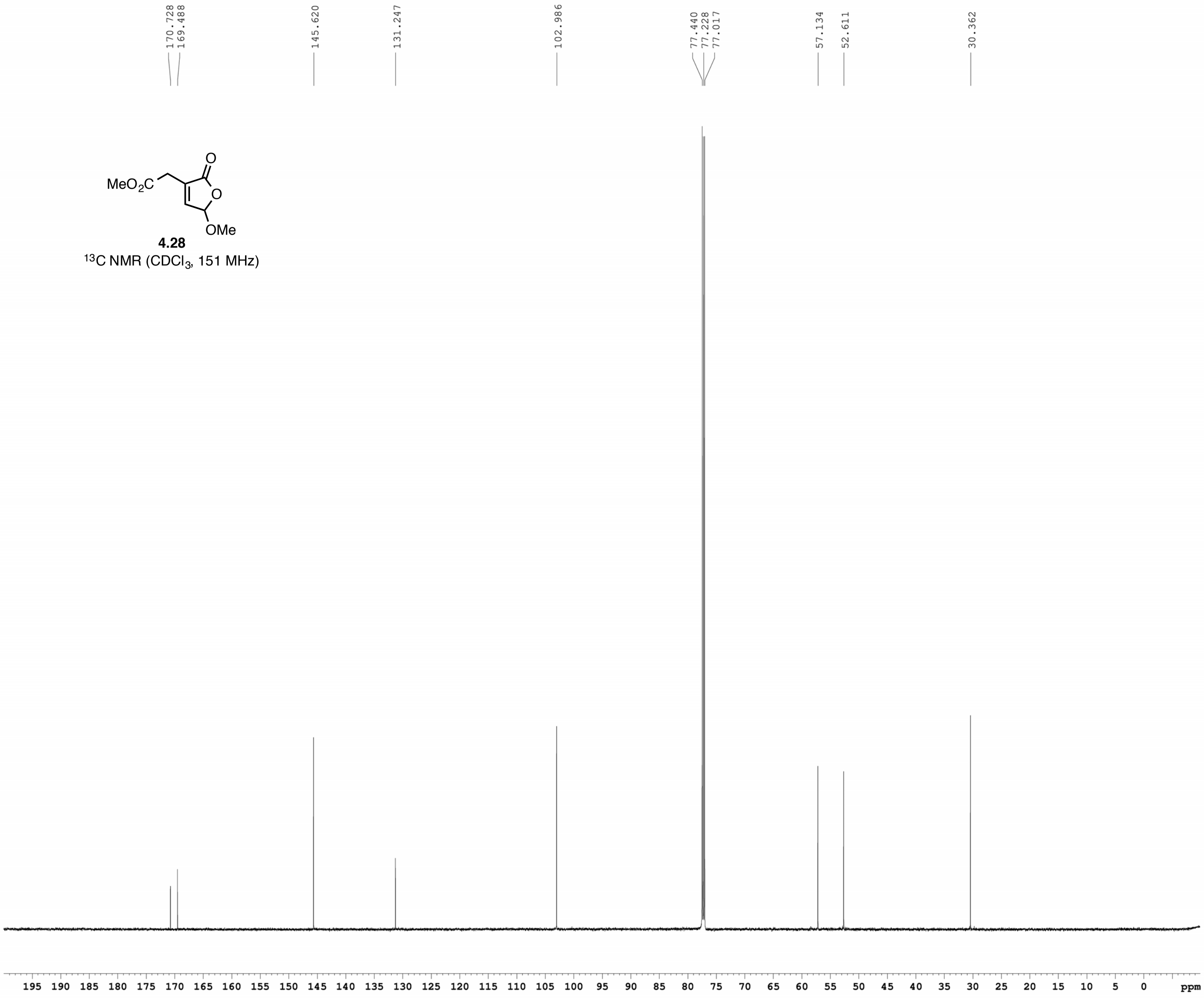
```
Current Data Parameters
NAME             YS-VI-27
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170801
Time                15.16
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG              zg30
TD                  38460
SOLVENT             CDCl3
NS                      8
DS                      1
SWH              9615.385 Hz
FIDRES           0.250010 Hz
AQ              1.9999200 sec
RG                   12.7
DW                 52.000 usec
DE                  13.70 usec
TE                  298.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                   1H
P1                  12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300356 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-VI-27



4.28

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME              YS-VI-27
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170801
Time                 15.19
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     400
DS                       1
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ           0.9043968 sec
RG                    2050
DW             13.800 usec
DE              19.65 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1                   13C
P1              10.00 usec
PLW1        64.00000000 W

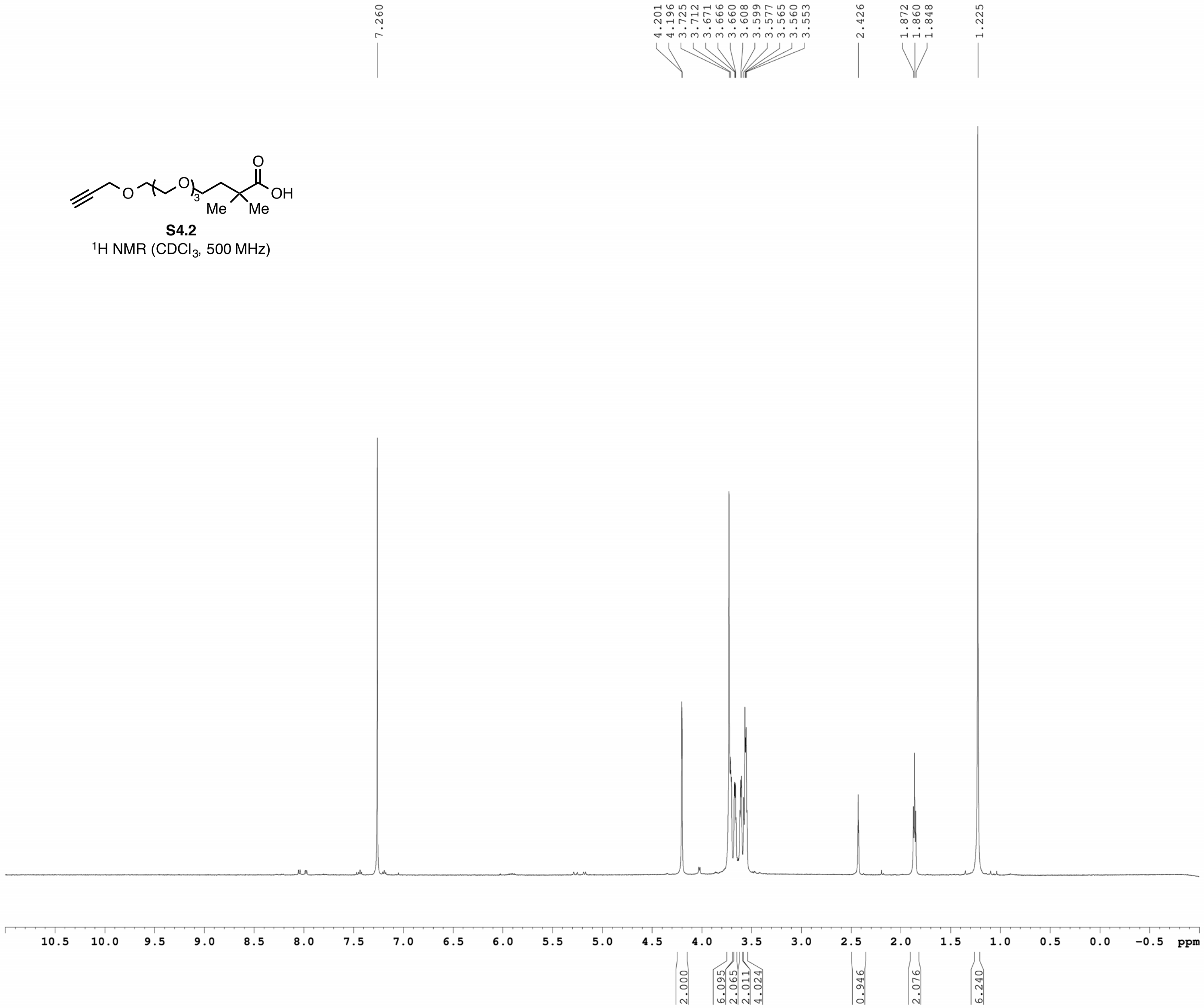
======== CHANNEL f2 ========
SFO2       600.1330010 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2           80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                   65536
SF         150.9027839 MHz
WDW                     EM
SSB      0
LB                 1.00 Hz
GB       0
PC                    1.00
```

MRG-II-217

S4.2

^{1}H NMR (CDCl$_3$, 500 MHz)



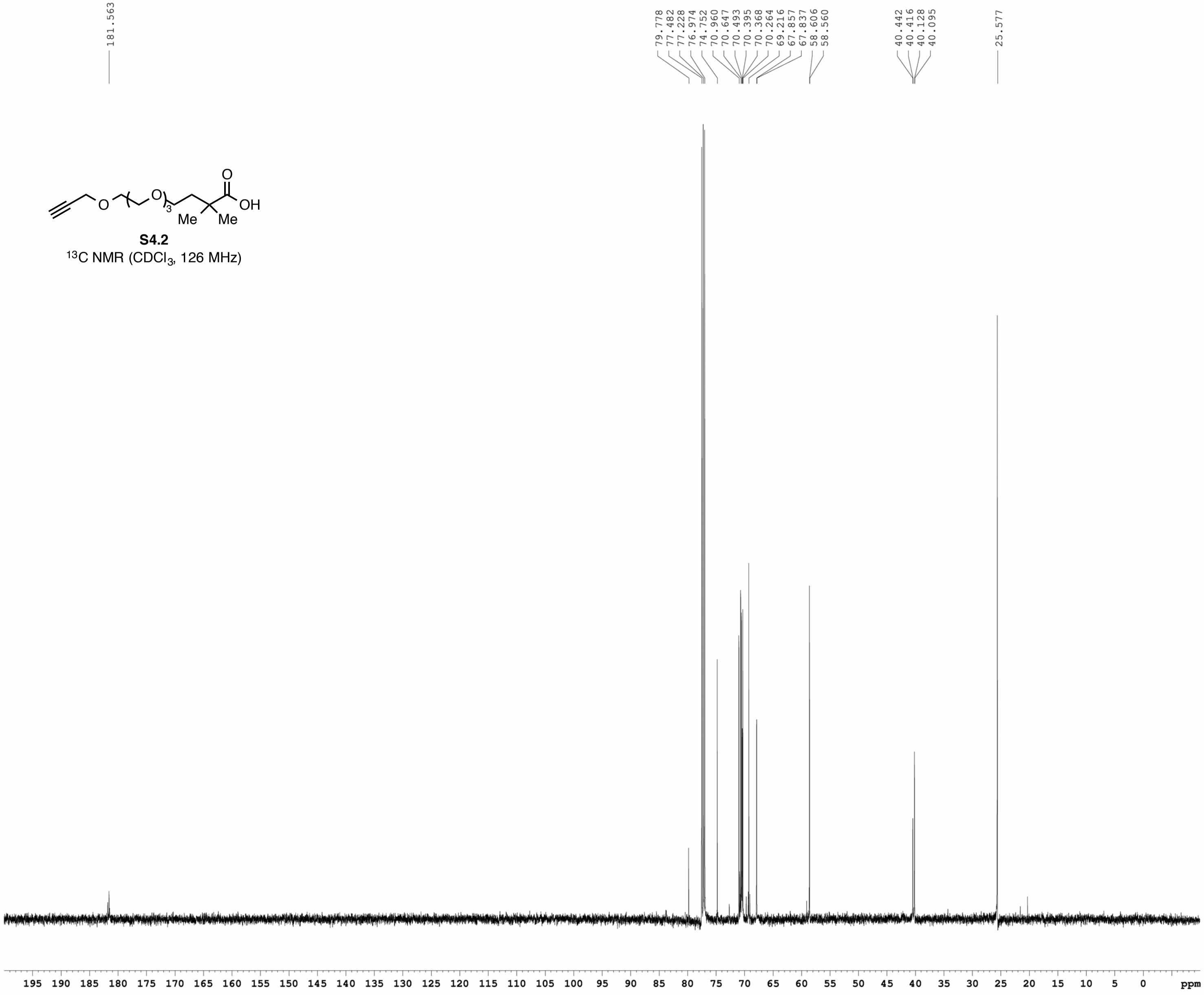
```
Current Data Parameters
NAME            S2 1HNMR
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130506
Time               18.08
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 291.3 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200327 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

MRG-II-217



S4.2

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          S2 13CNMR
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20131209
Time              13.10
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               9195.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

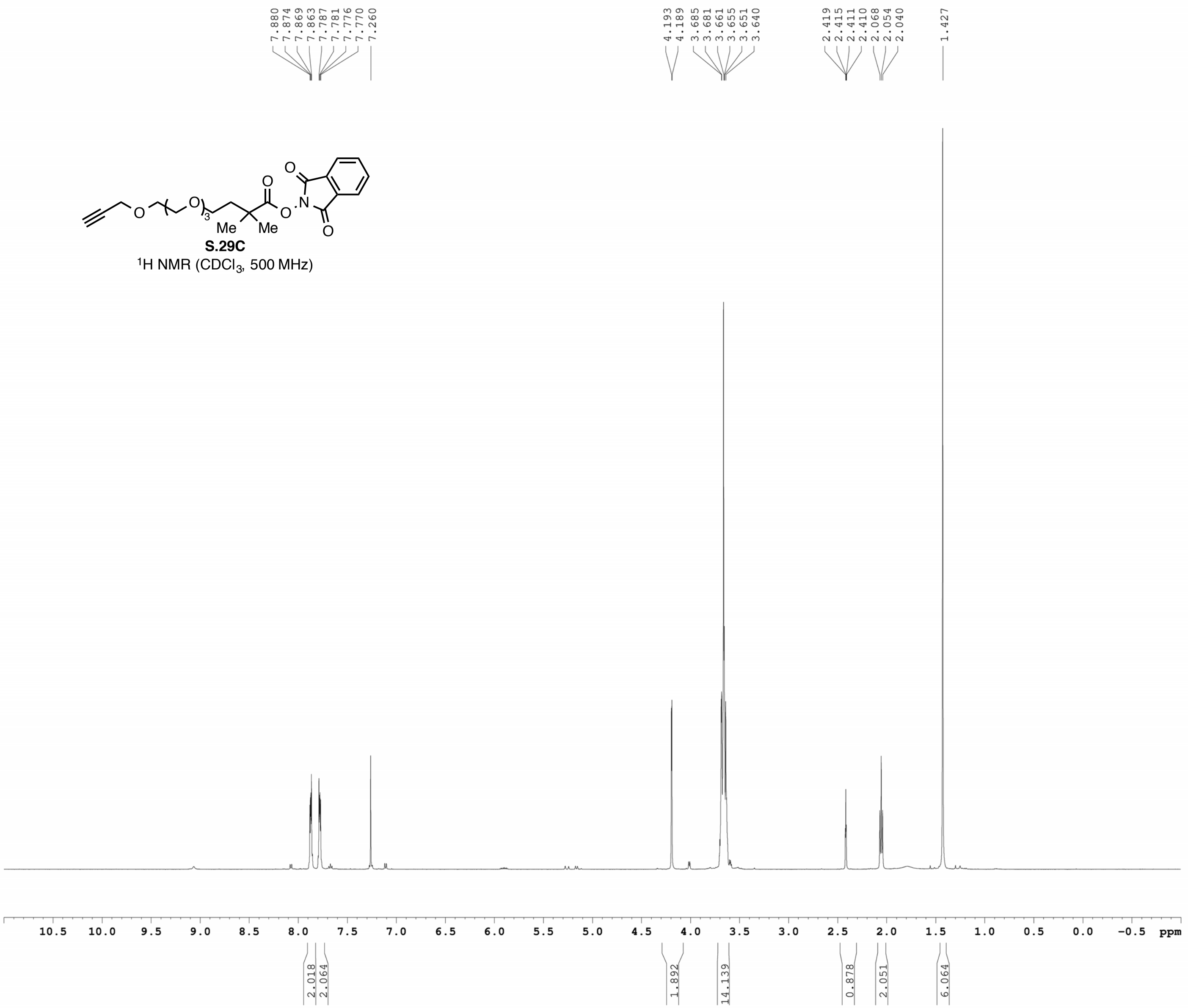
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804006 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 2.00
```

MRG-II-219B



S.29C

^{1}H NMR (CDCl$_3$, 500 MHz)

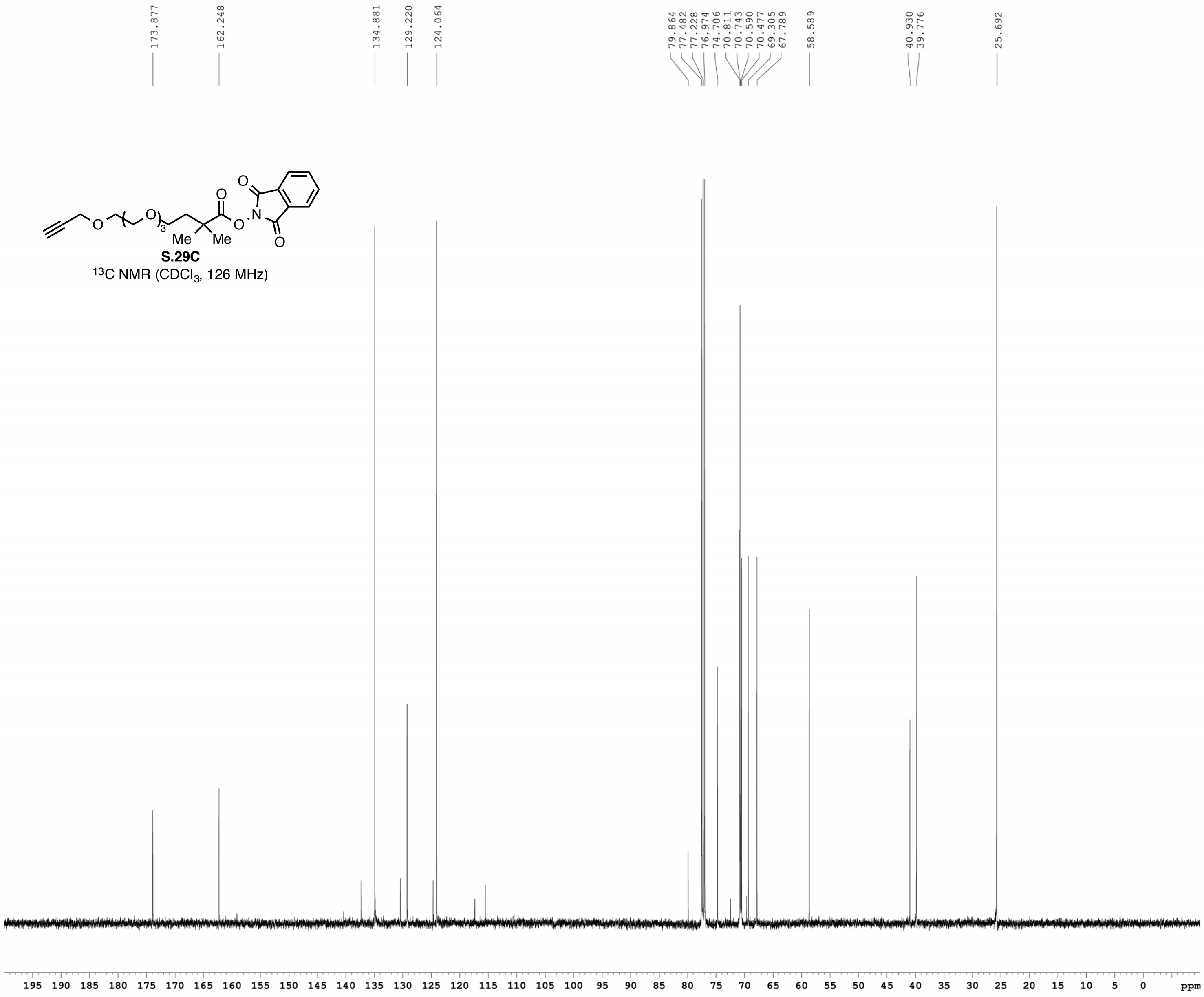
```
Current Data Parameters
NAME      29C 1Hï ¢13CNMR
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130507
Time                18.08
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  81728
SOLVENT             CDC13
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                  574.7
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.20 usec
PL1                 -5.00 dB
SFO1          499.4034958 MHz

F2 - Processing parameters
SI                  65536
SF            499.4000307 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

MRG-II-219B



S.29C

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME      29C 1Hï ¢13CNMR
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130507
Time               21.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDC13
NS                   880
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

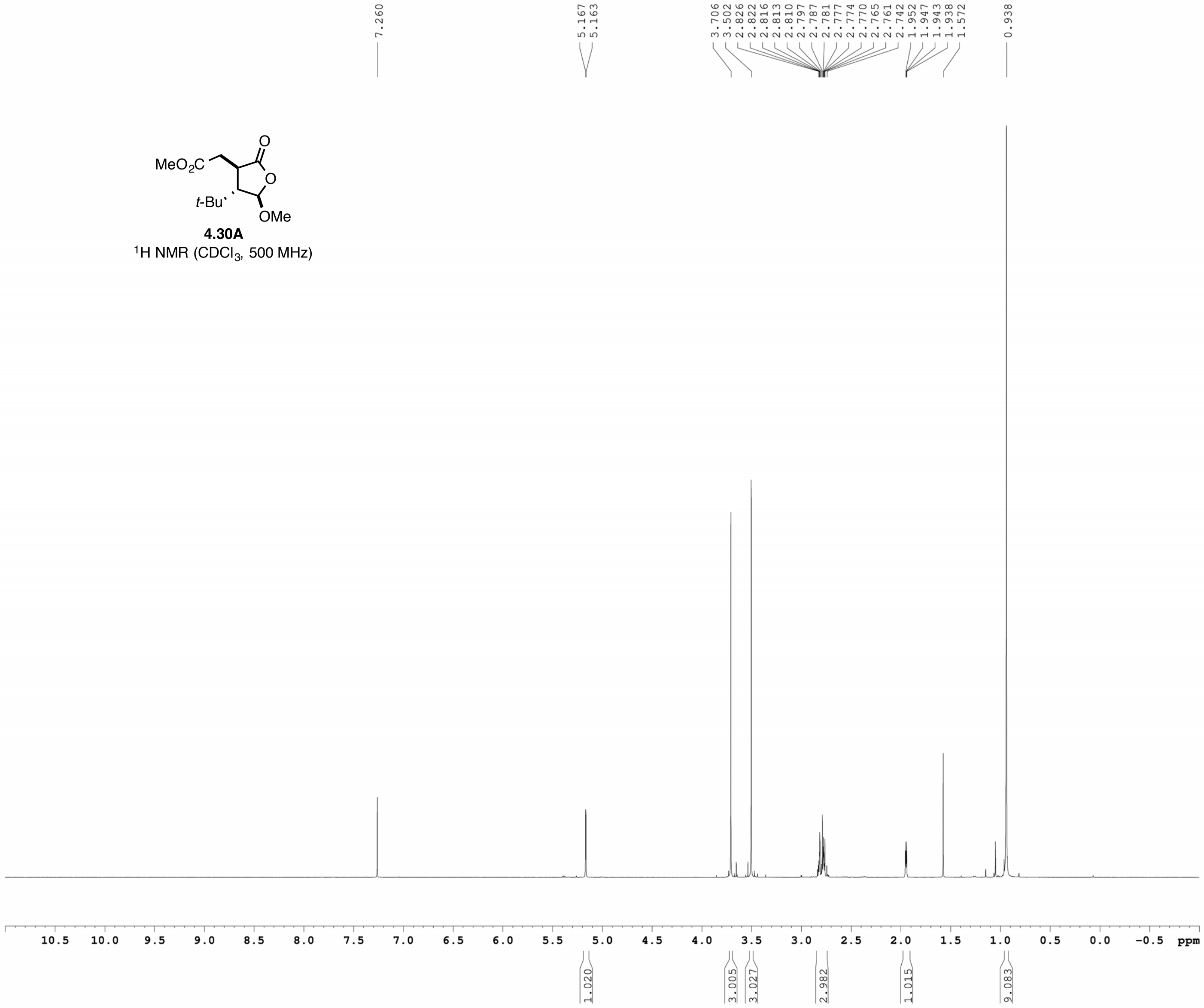
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804006 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

PZ-II-268



4.30A

^1H NMR ($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME      30A 1HÏ ¢13CNMR
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170806
Time               23.36
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

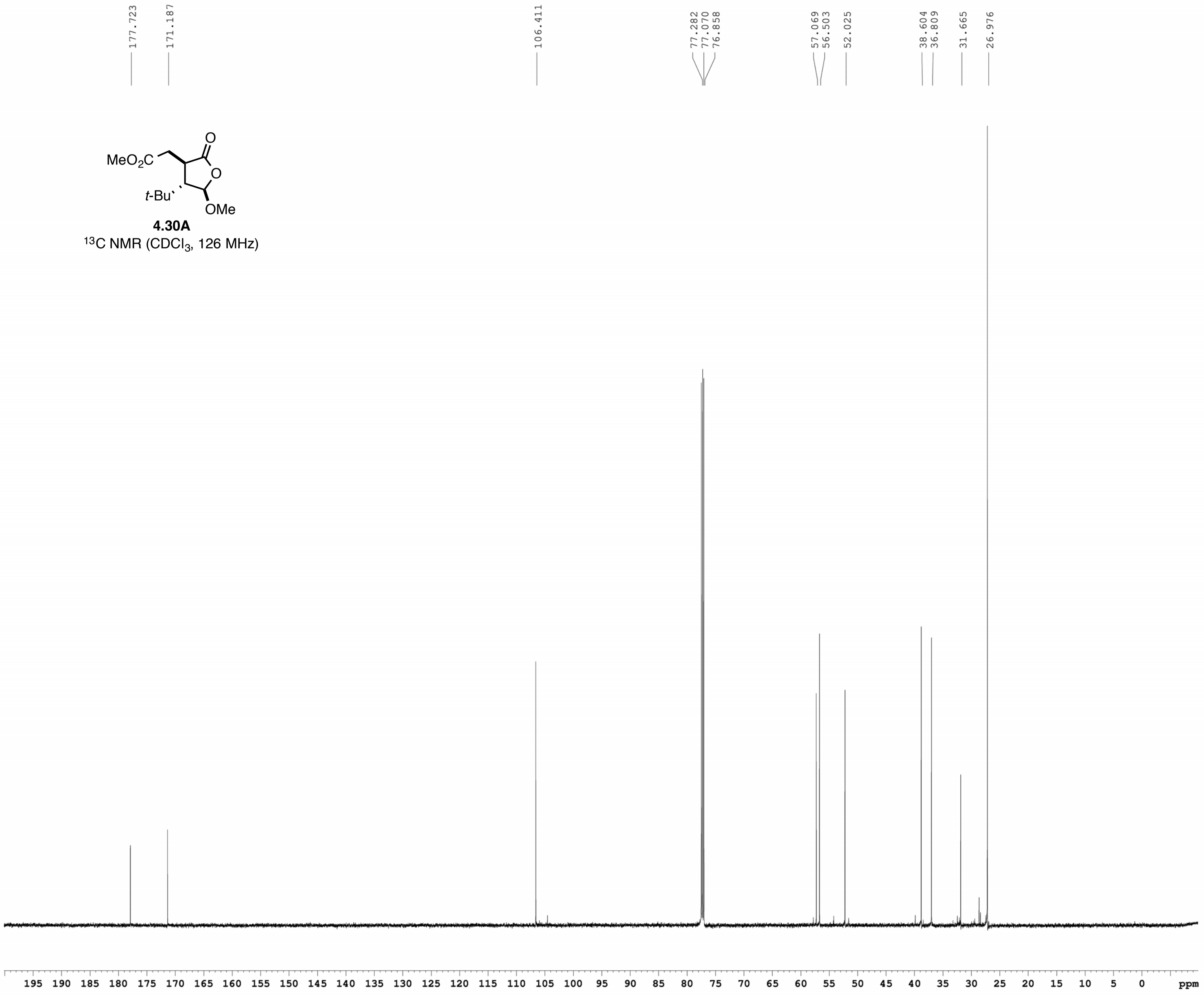
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200311 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

PZ-II-268

4.30A

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME      30A 1HÏ ¢13CNMR
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_          20170807
Time              14.20
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 121
DS                   4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9043968 sec
RG                2050
DW              13.800 usec
DE               19.65 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

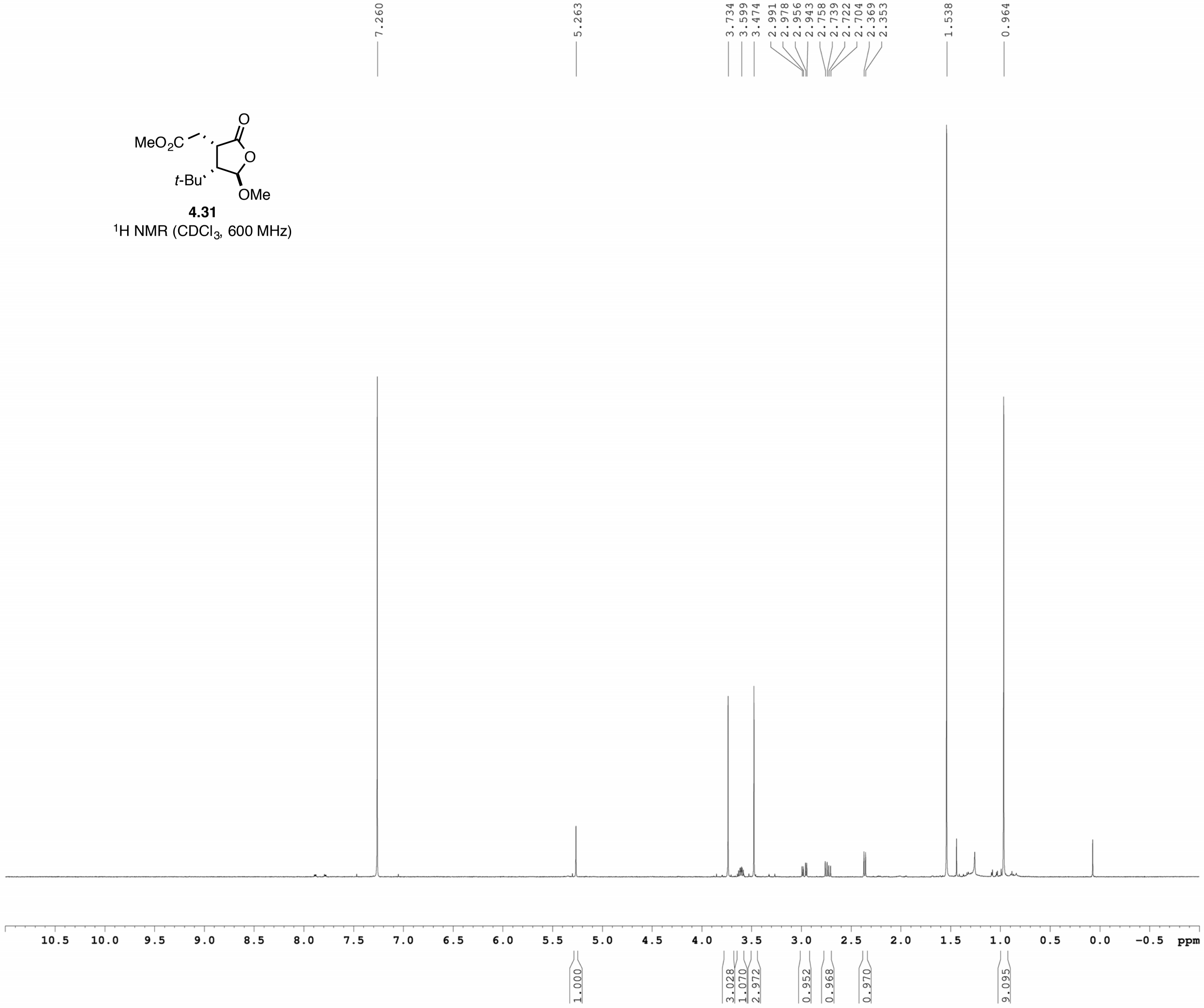
======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI               65536
SF          150.9027847 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.00
```

PZ-II-267

4.31

^{1}H NMR ($CDCl_3$, 600 MHz)



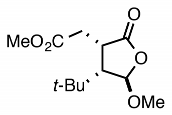
```
Current Data Parameters
NAME            31 1HNMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170806
Time               23.53
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

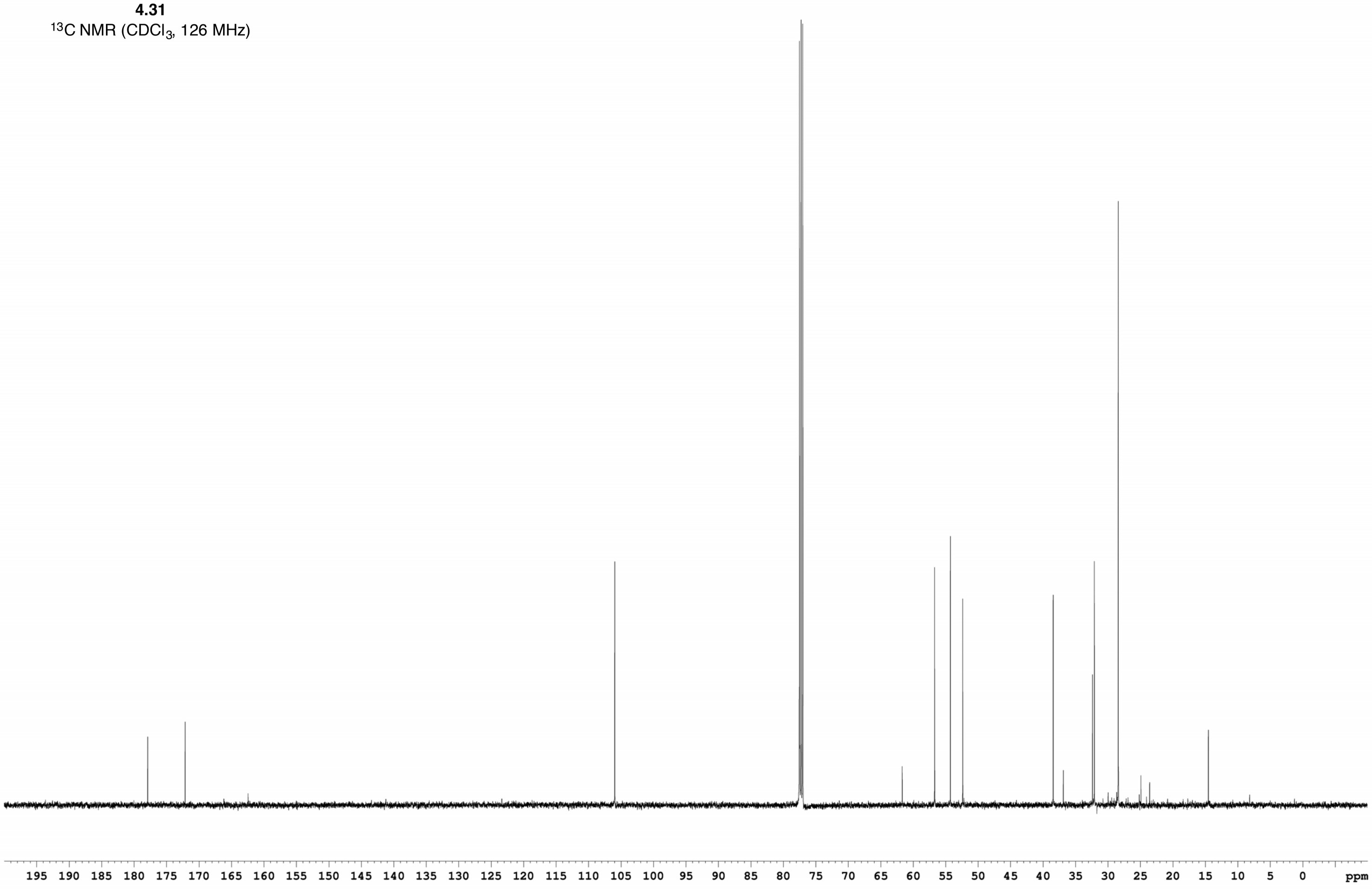
F2 - Processing parameters
SI                 65536
SF           500.2200311 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

MRG-II-71



4.31

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          31 13CNMR
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20130228
Time              15.12
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2298.8
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

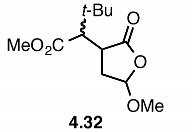
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

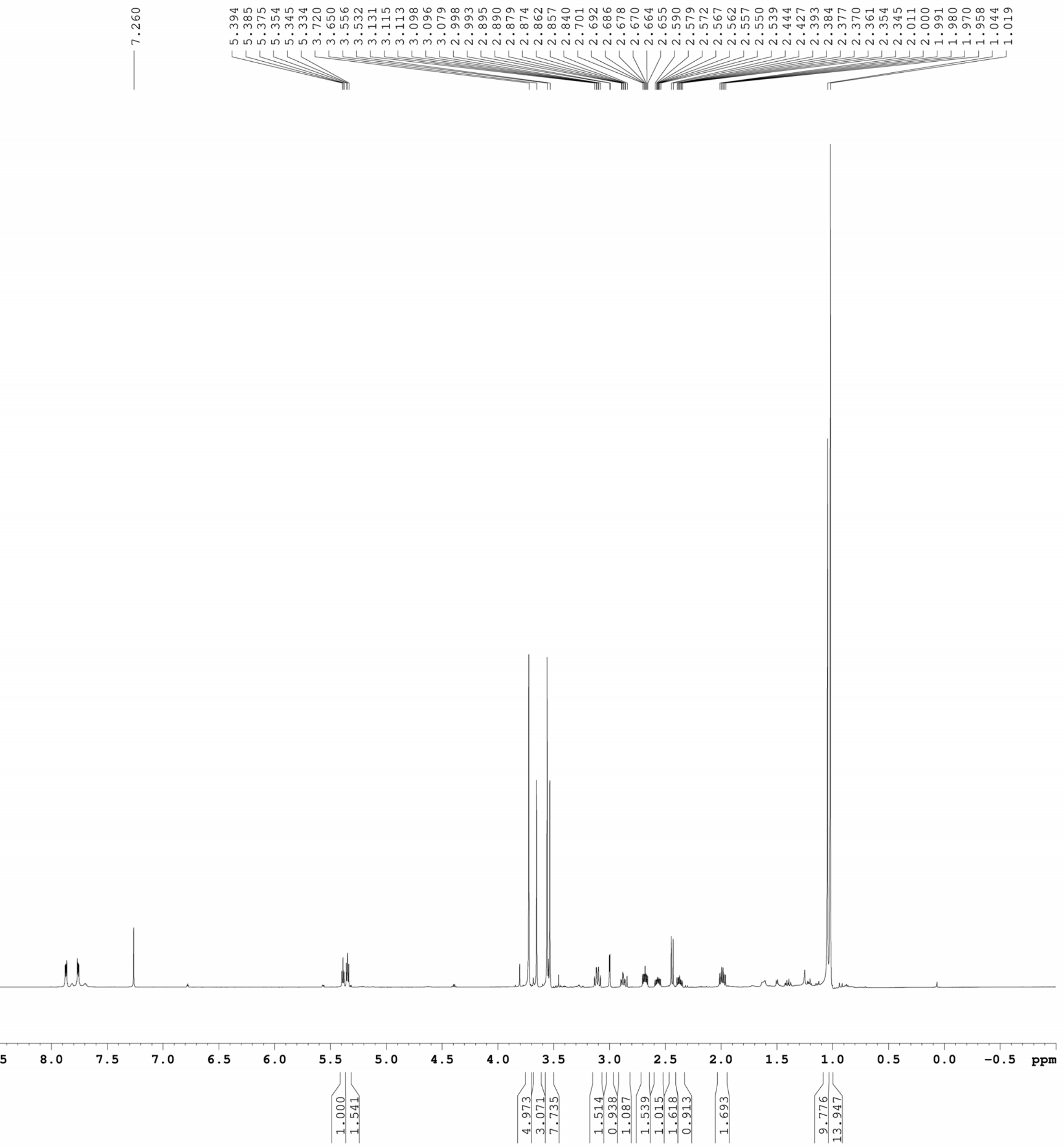
F2 - Processing parameters
SI                65536
SF          125.7803998 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-II-15



4.32

^{1}H NMR (CDCl$_3$, 500 MHz)



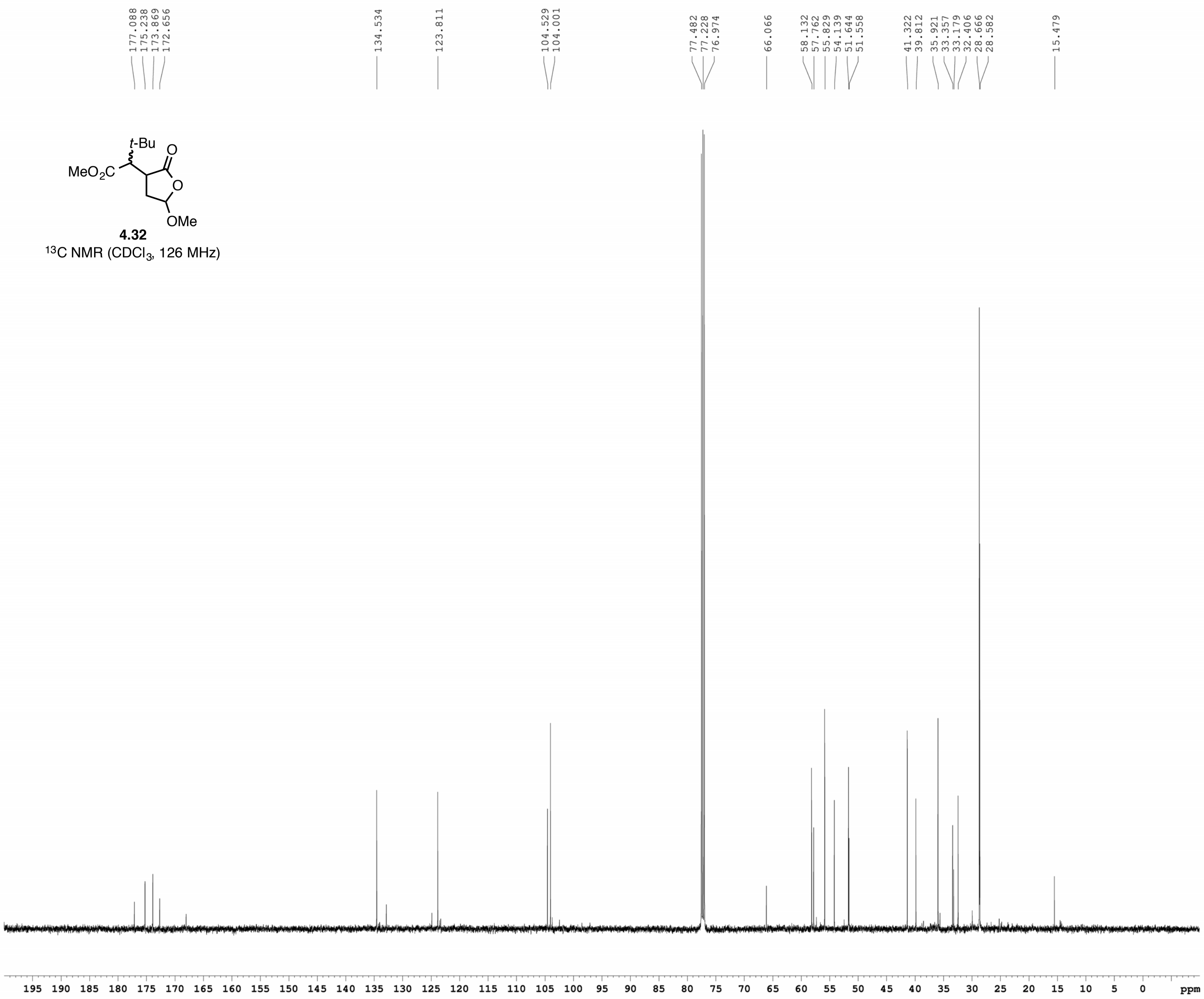
```
Current Data Parameters
NAME      32 1Hï ¢13CNMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130114
Time               15.13
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   362
DW                52.000 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W
SFO1         600.1342009 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300341 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

MRG-II-15



4.32

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME     32 1Hï ¢13CNMR
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_          20130115
Time              13.50
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  973
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

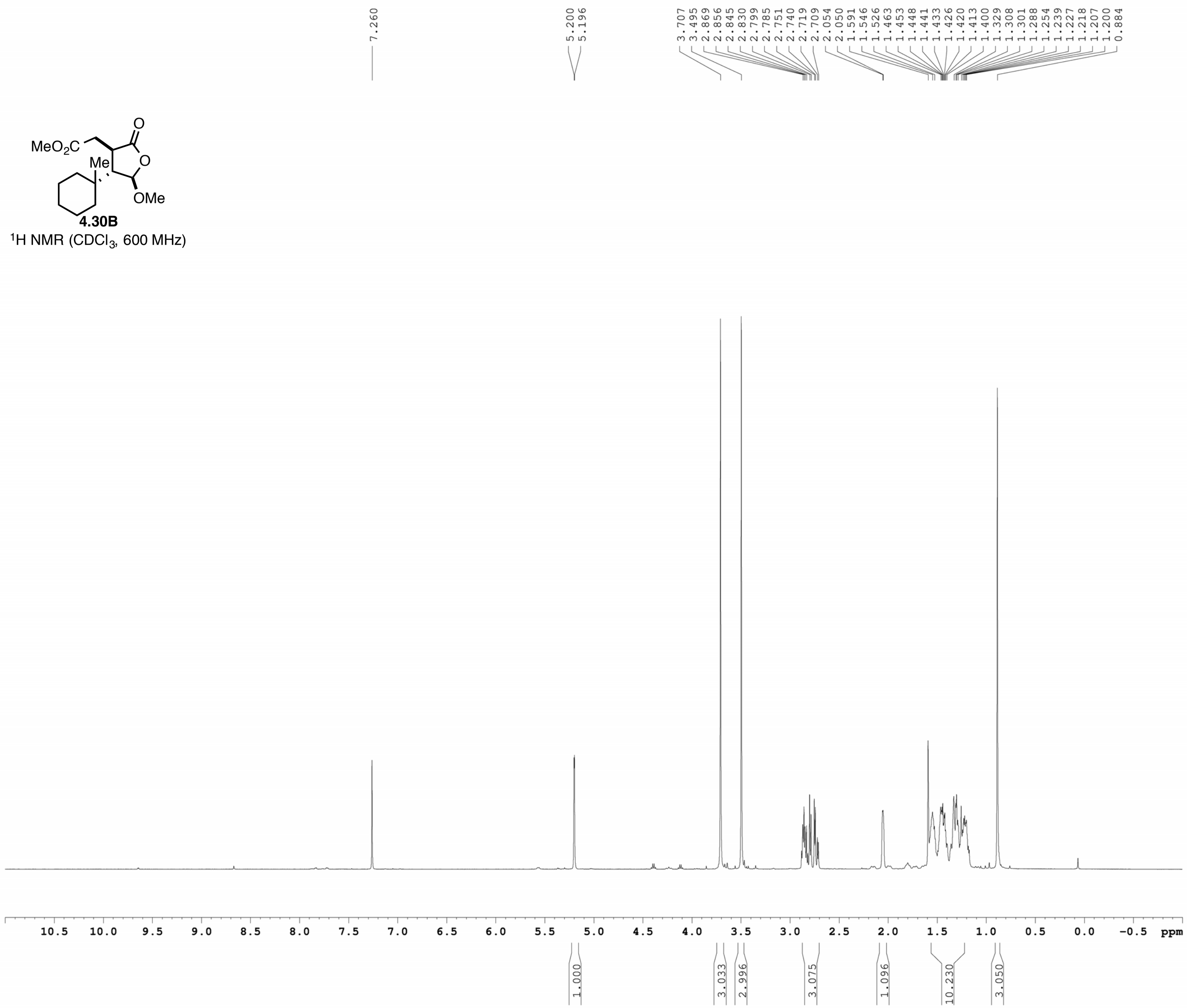
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804002 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-I-231



4.30B

^{1}H NMR (CDCl$_3$, 600 MHz)

```
Current Data Parameters
NAME     30B 1Hï ¢13CNMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121117
Time               10.14
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

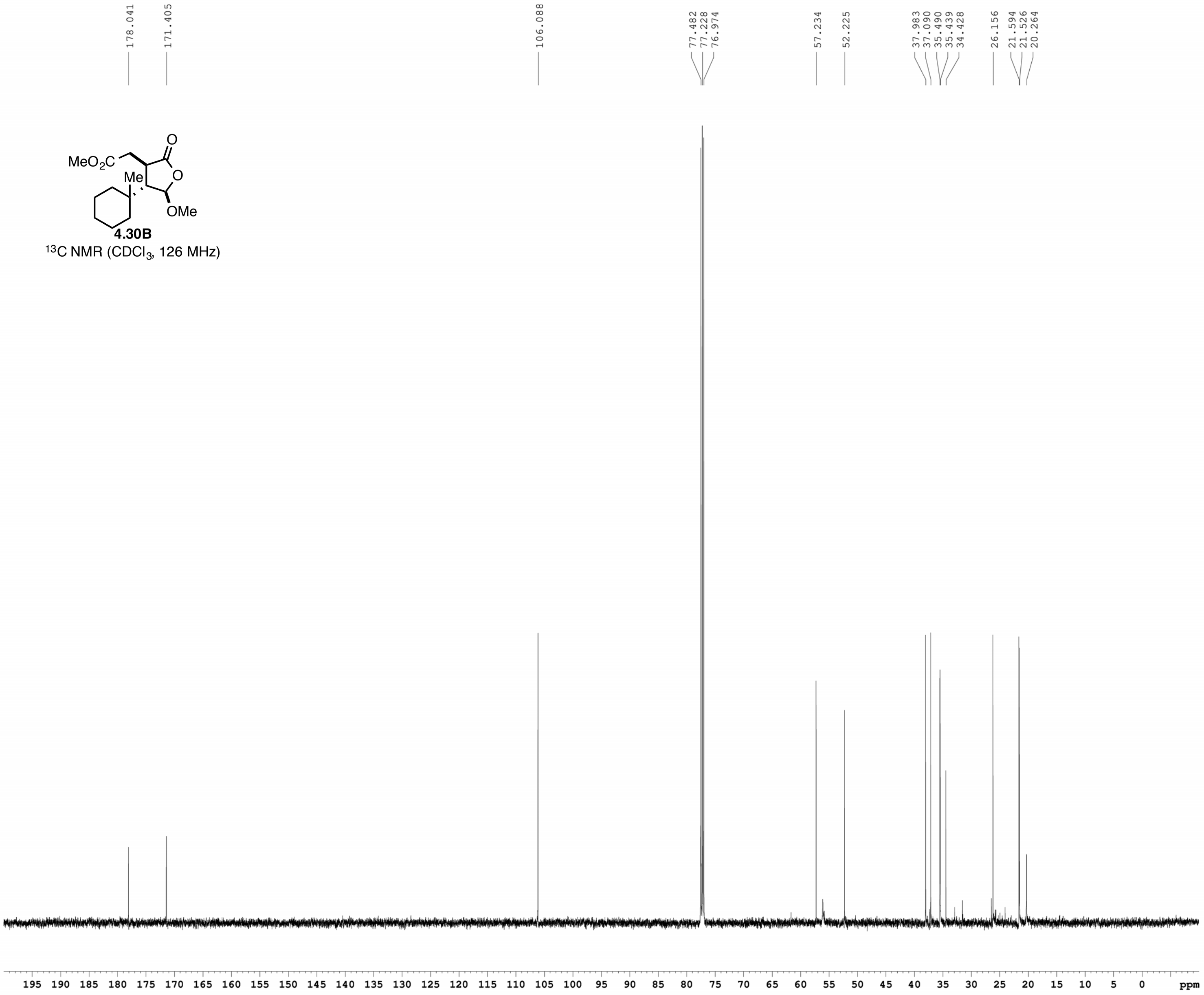
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200314 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

MRG-I-231

4.30B

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME     30B 1Hï ¢13CNMR
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20121117
Time              10.23
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  487
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

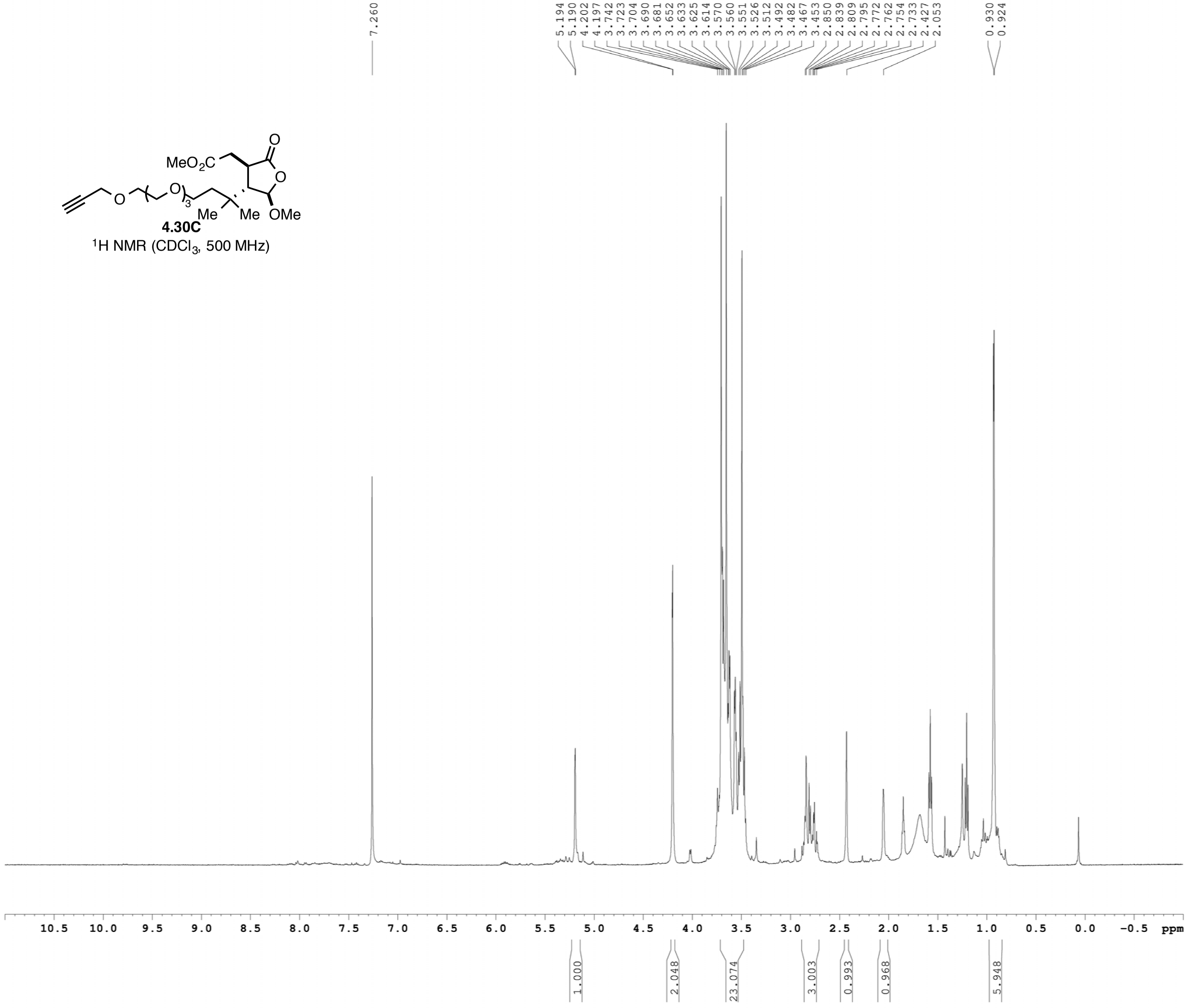
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803996 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-II-228



4.30C

^{1}H NMR (CDCl$_3$, 500 MHz)

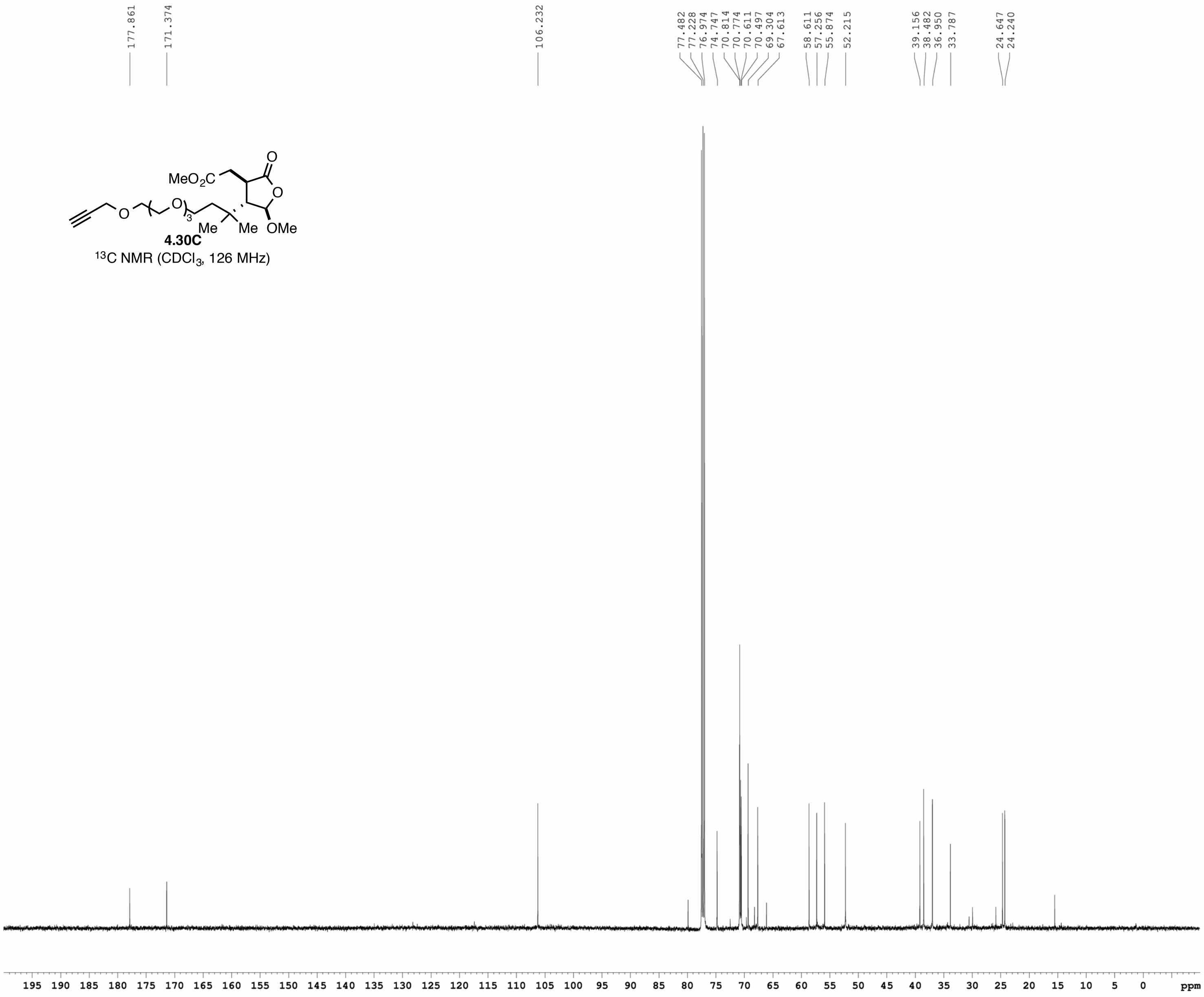
```
Current Data Parameters
NAME     30C 1Hï ¢13CNMR
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20130510
Time              18.41
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200314 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

MRG-II-228



4.30C

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME     30C 1Hï ¢13CNMR
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20130510
Time              20.21
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 3000
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

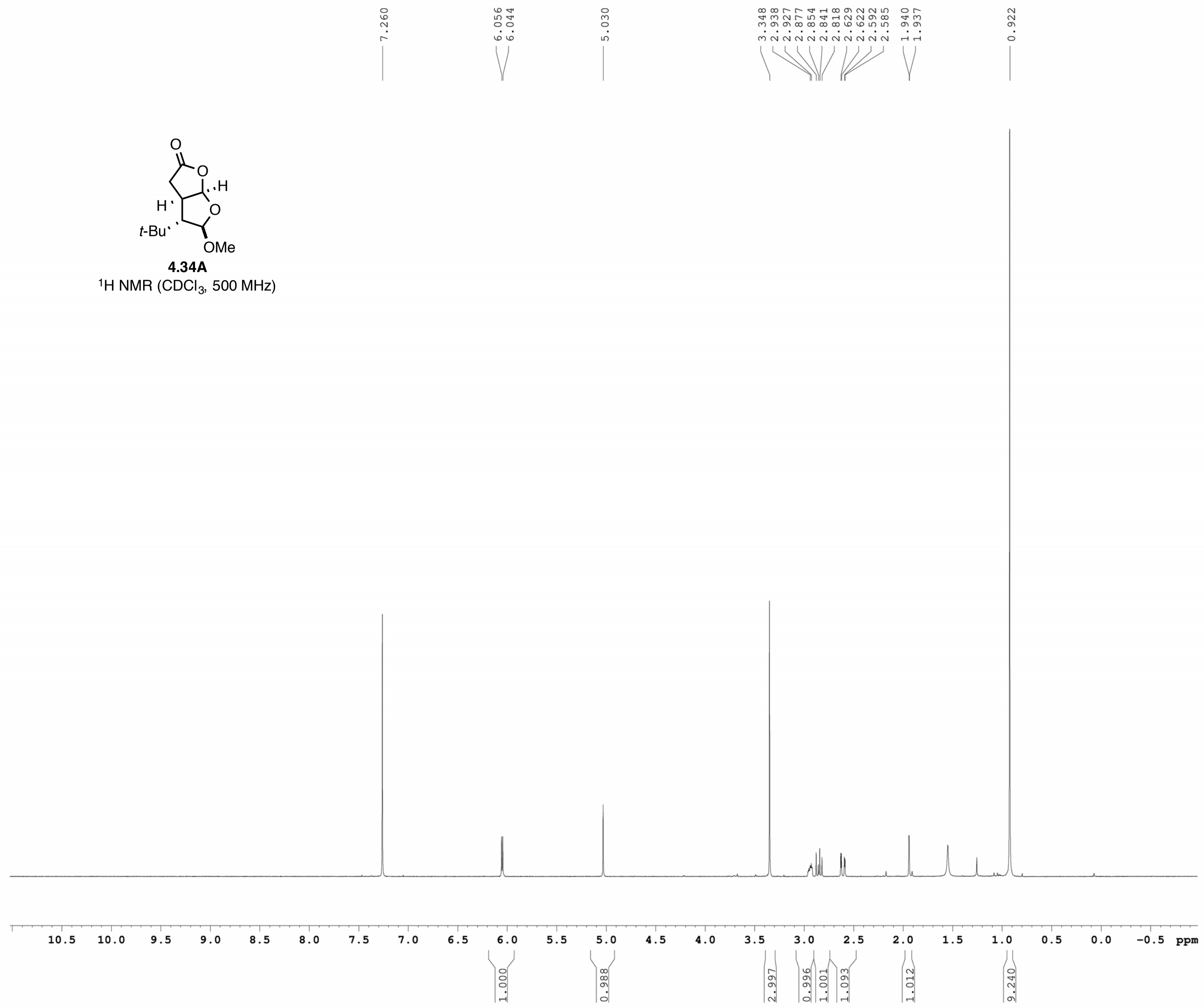
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804001 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-II-245B



4.34A

^{1}H NMR (CDCl$_3$, 500 MHz)

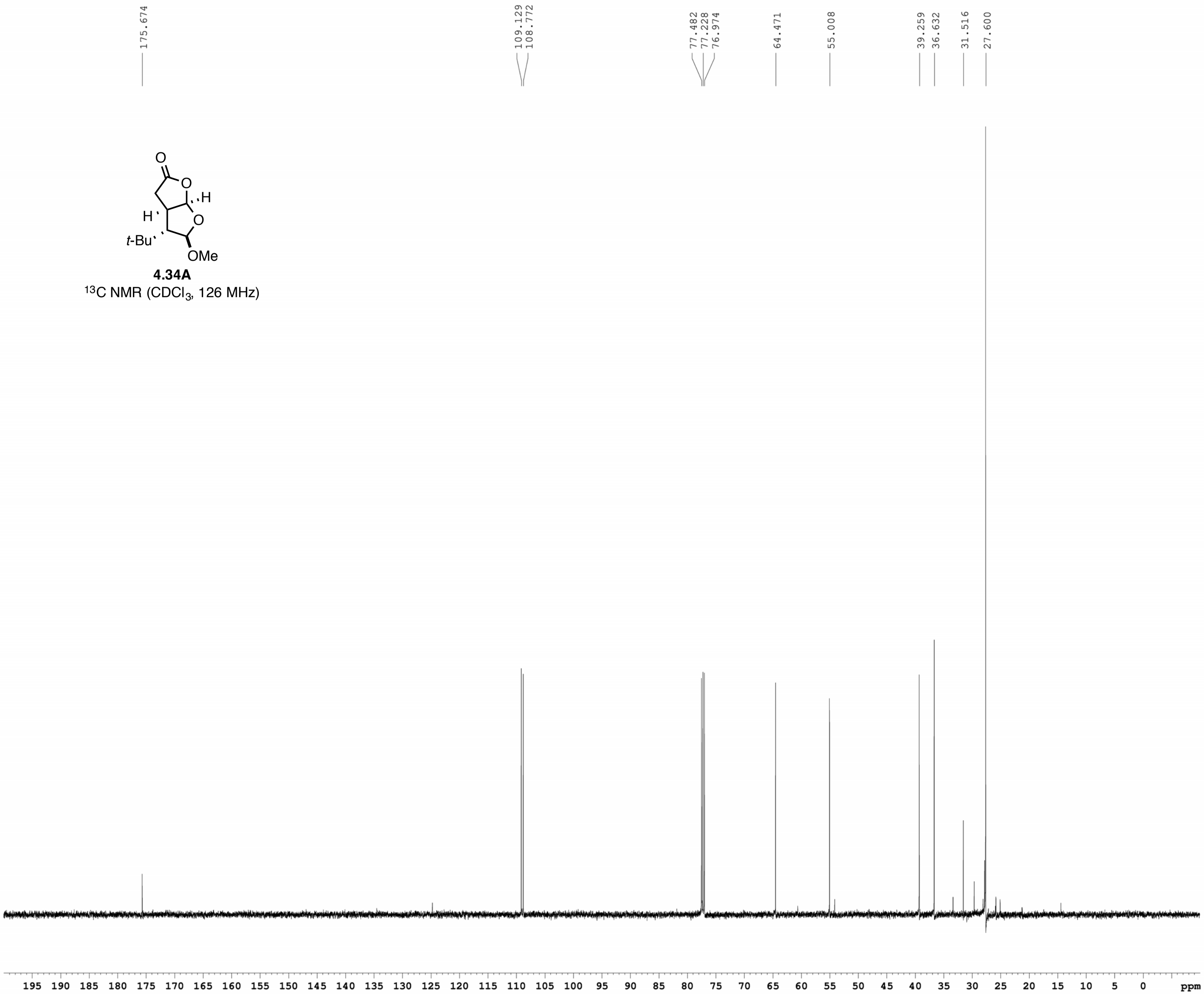
```
Current Data Parameters
NAME          34A 1HNMR
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130520
Time              14.54
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                81728
SOLVENT           CDCl3T
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG               1824.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.20 usec
PL1               -5.00 dB
SFO1        499.4034958 MHz

F2 - Processing parameters
SI                65536
SF          499.3999769 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

MRG-III-33D



4.34A

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          34A 13CNMR
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130712
Time               12.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   111
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

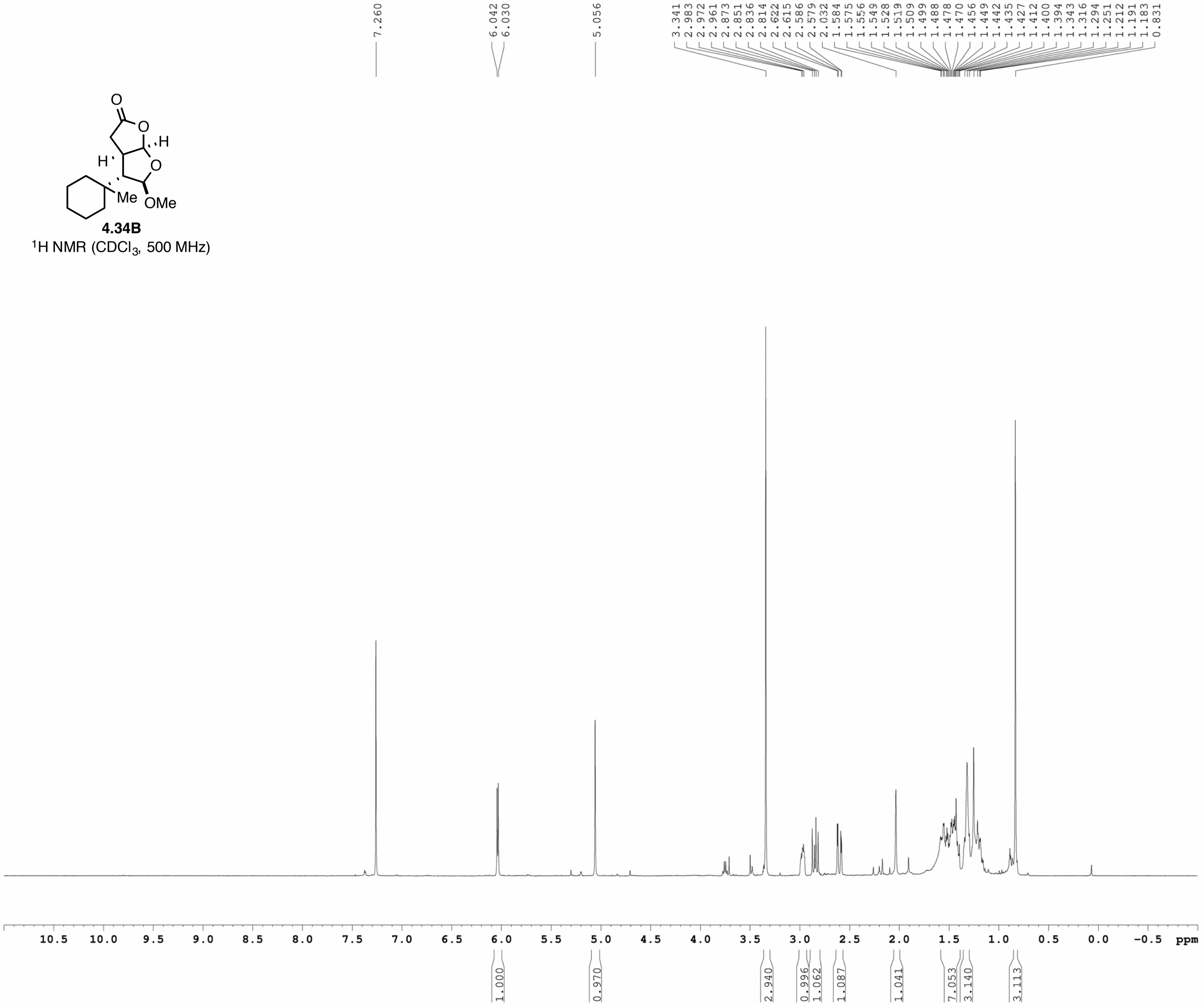
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804011 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

MRG-II-139C

4.34B

^1H NMR ($CDCl_3$, 500 MHz)



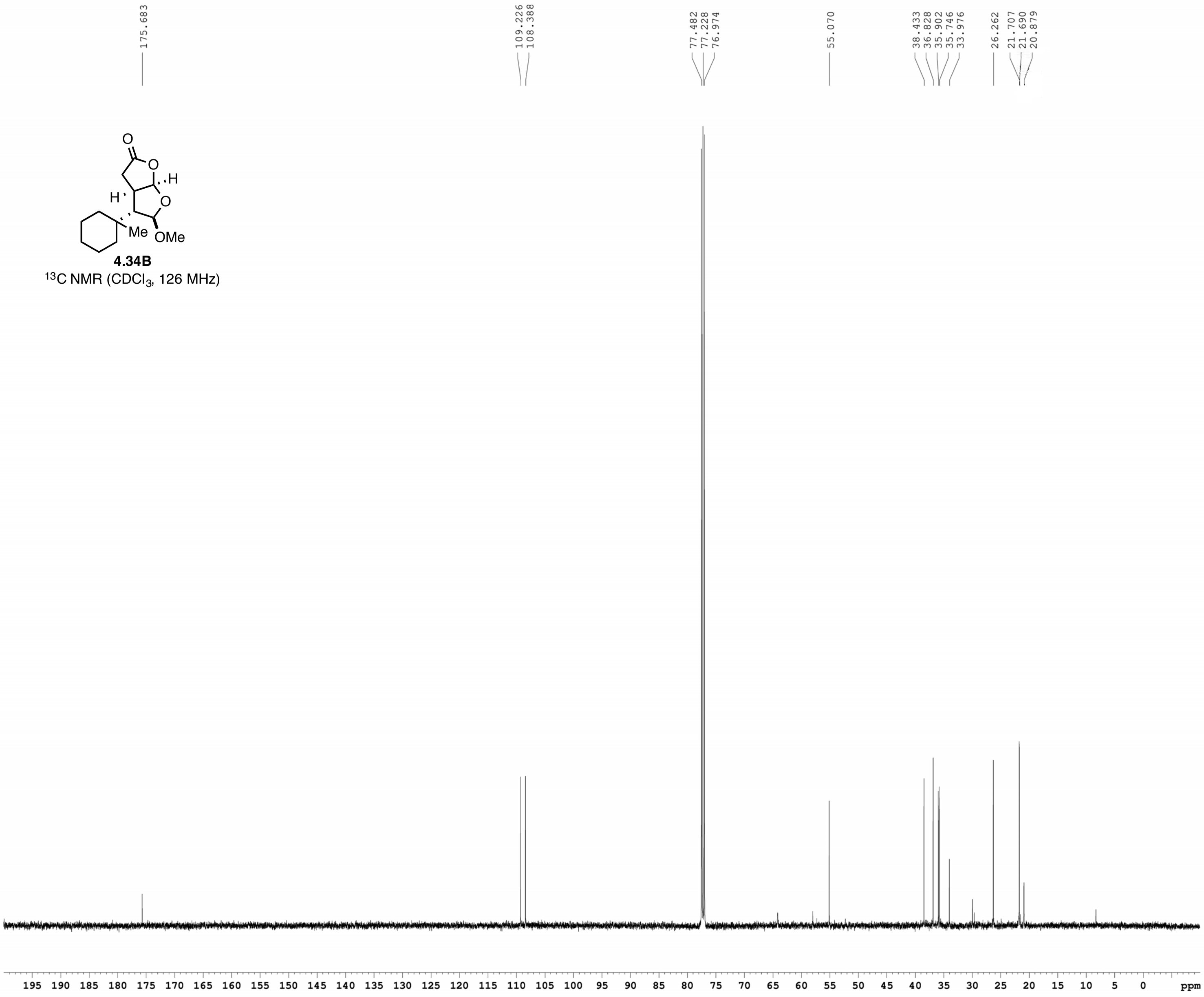
```
Current Data Parameters
NAME      34B 1Hï ¢13CNMR
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130712
Time                19.52
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                    7.1
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200322 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

MRG-II-139C



4.34B

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME     34B 1HÏ ¢13CNMR
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20130712
Time              19.57
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  914
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2580.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

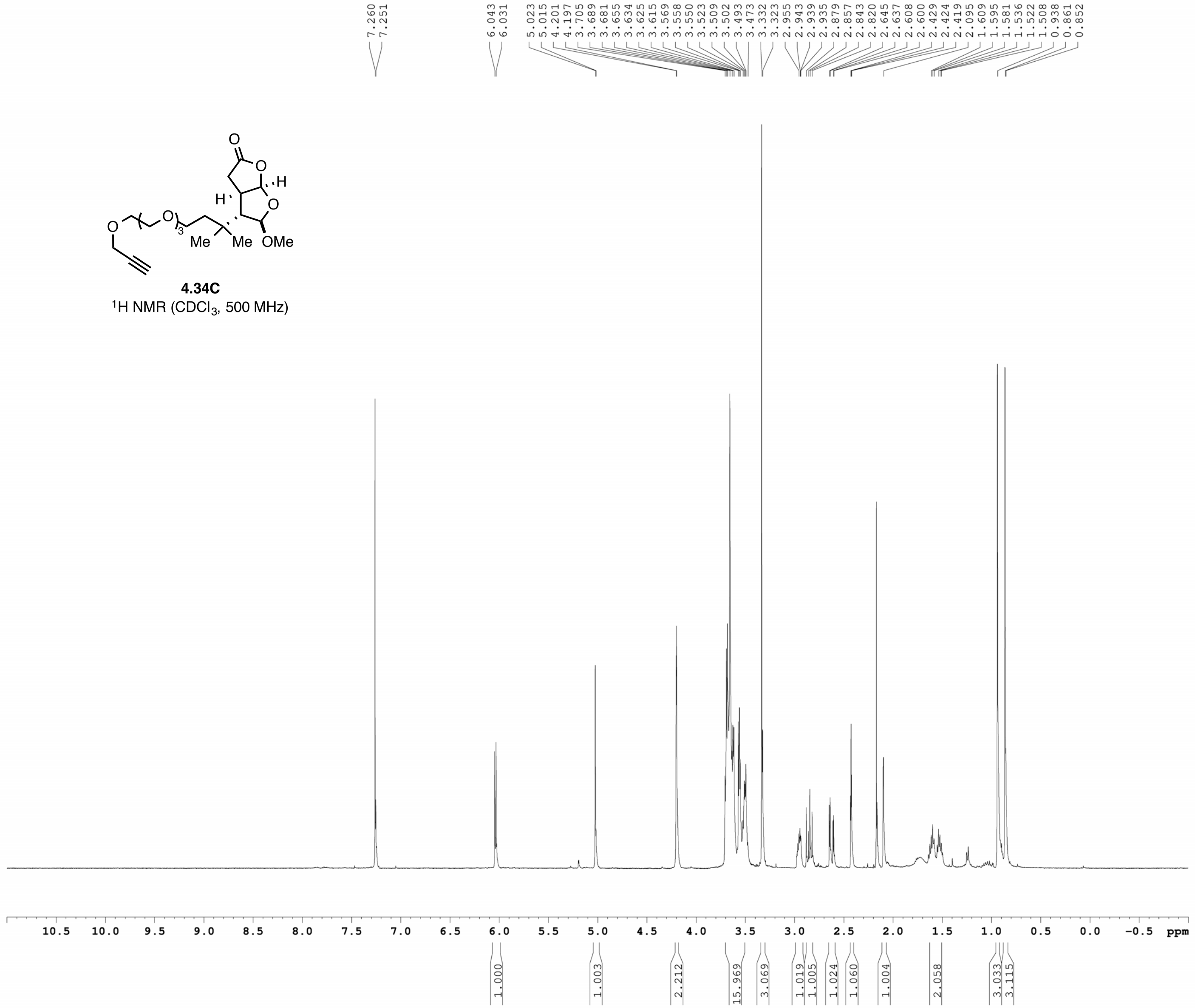
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803997 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-II-280B

4.34C

^{1}H NMR (CDCl$_3$, 500 MHz)



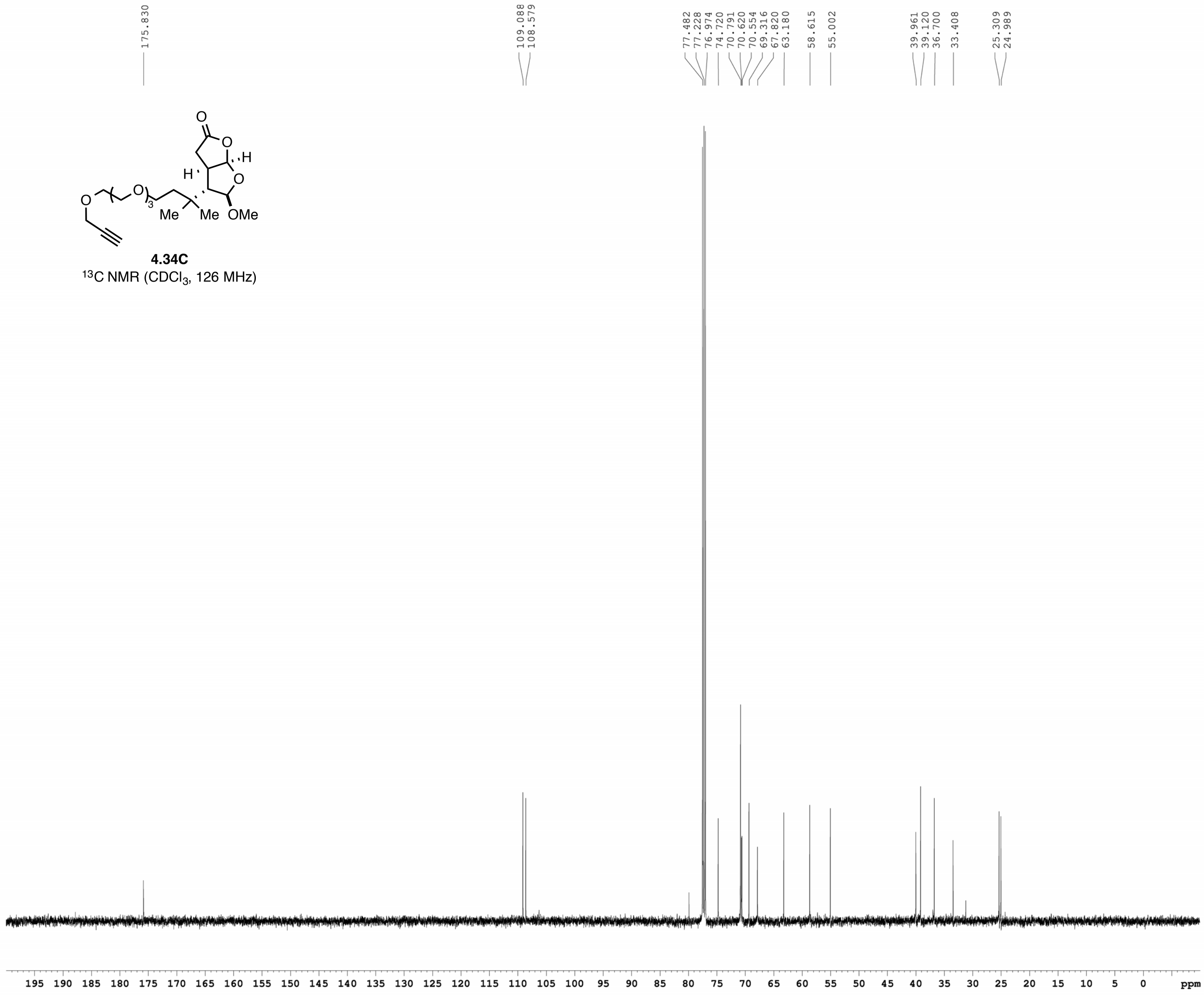
```
Current Data Parameters
NAME     34C 1Hï ¢13CNMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130607
Time               18.32
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200314 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

MRG-II-280B



4.34C

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME      34C 1Hï ¢13CNMR
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130607
Time                19.26
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  31.00 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.50 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  3.20 dB
SP2                  3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.60 dB
SFO2          500.2225011 MHz

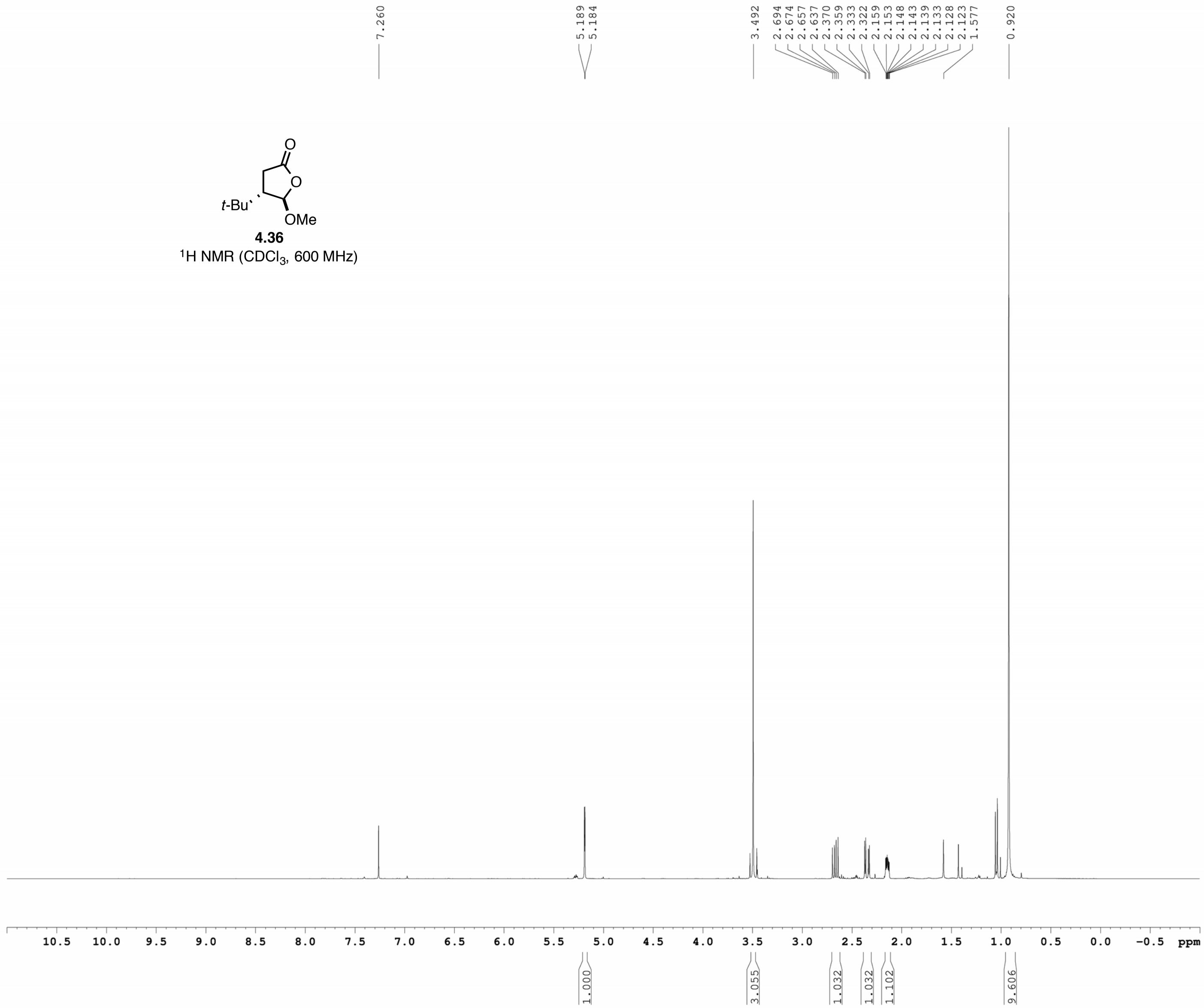
====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803993 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-VI-28

4.36

^{1}H NMR ($CDCl_3$, 600 MHz)



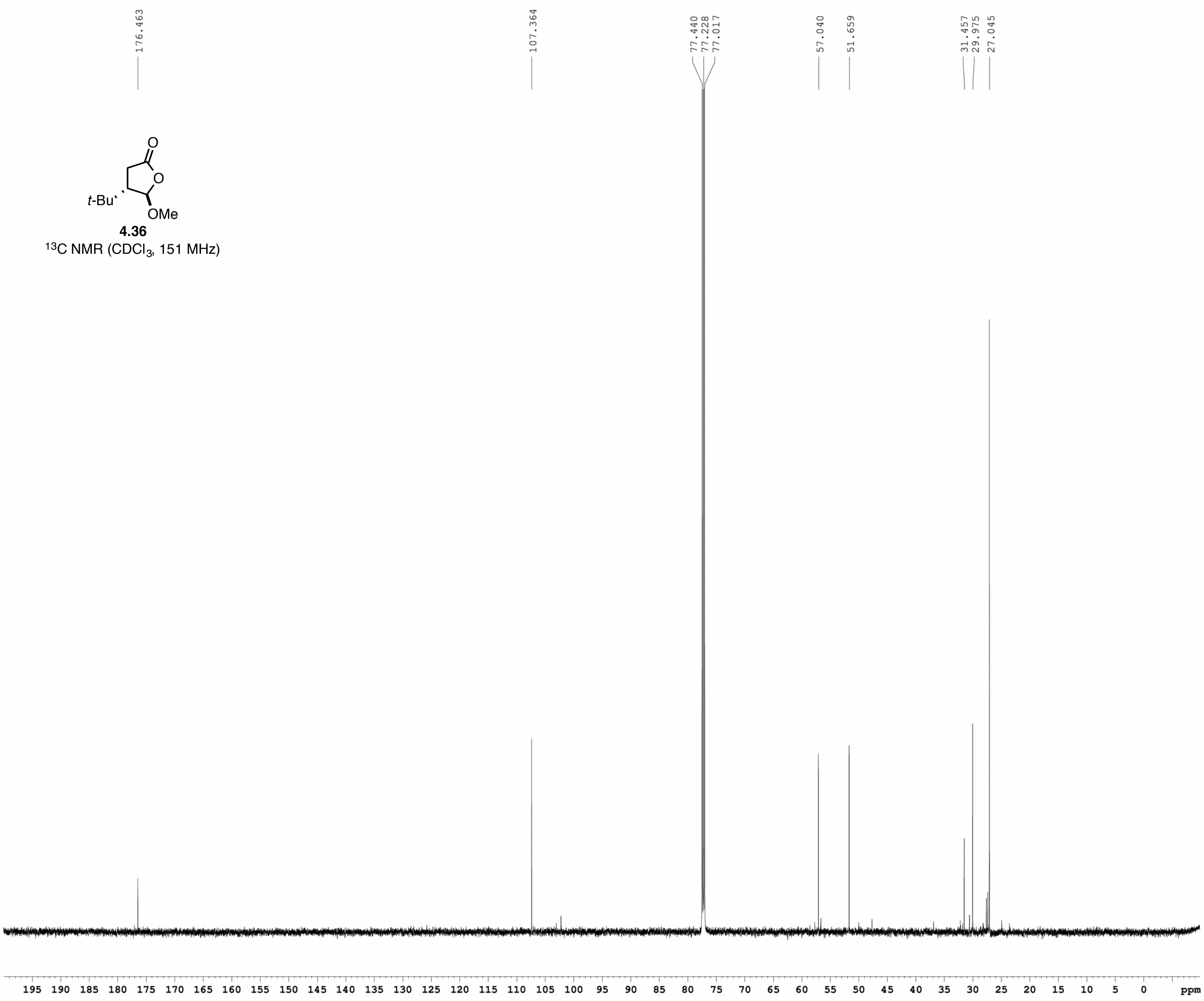
```
Current Data Parameters
NAME             YS-VI-28
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170804
Time                12.22
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  32048
SOLVENT             CDCl3
NS                      8
DS                      1
SWH              8012.820 Hz
FIDRES           0.250026 Hz
AQ              1.9997952 sec
RG                    6.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200312 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-VI-28



4.36

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME          YS-VI-28
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_         20170803
Time             16.49
INSTRUM          av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 160
DS                   1
SWH         36231.883 Hz
FIDRES       0.552855 Hz
AQ          0.9043968 sec
RG                2050
DW              13.800 usec
DE               19.65 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1               13C
P1               10.00 usec
PLW1       64.00000000 W

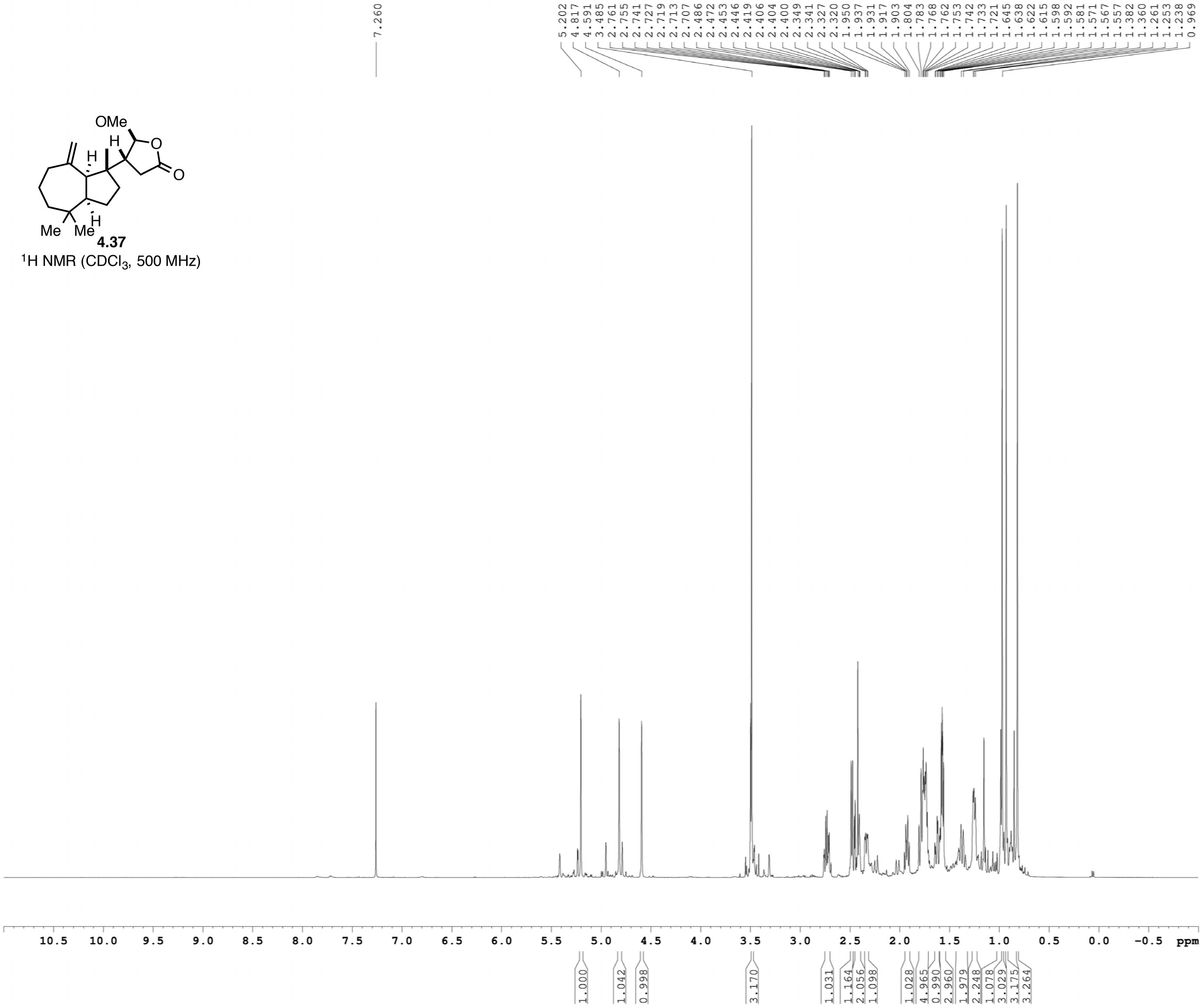
======== CHANNEL f2 ========
SFO2       600.1330010 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2            80.00 usec
PLW2       20.00000000 W
PLW12       0.36000001 W

F2 - Processing parameters
SI               65536
SF         150.9027831 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.00
```

MRG-III-177E

4.37

^{1}H NMR (CDCl$_3$, 500 MHz)



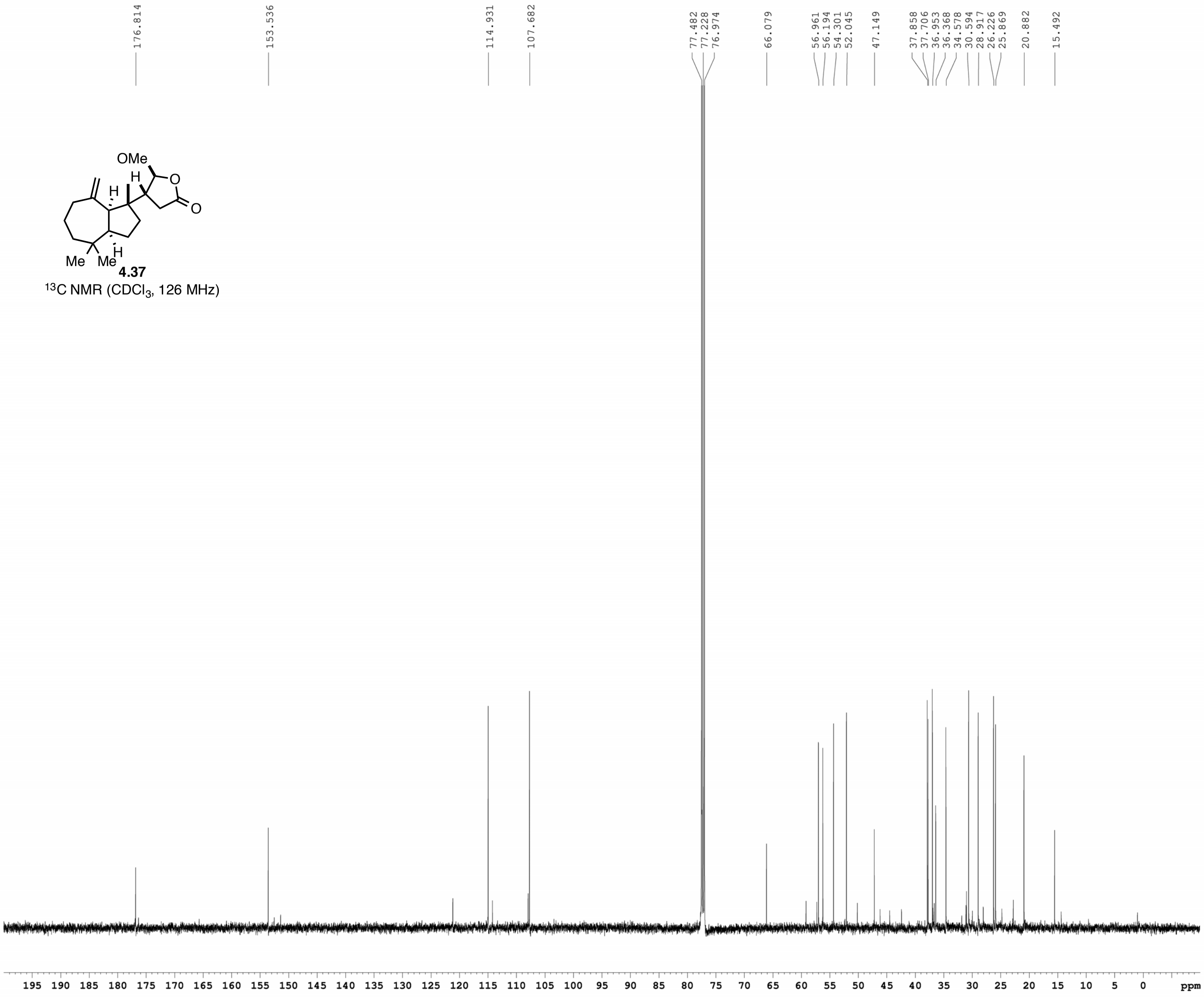
```
Current Data Parameters
NAME             37 1HNMR
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140116
Time                11.11
INSTRUM             av600
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   80.6
DW                 52.000 usec
DE                  14.54 usec
TE                  298.1 K
D1          0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                   1H
P1                   8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                  65536
SF          600.1300354 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```

MRG-III-173B



4.37

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          37 13CNMR
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20140111
Time              15.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1620
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

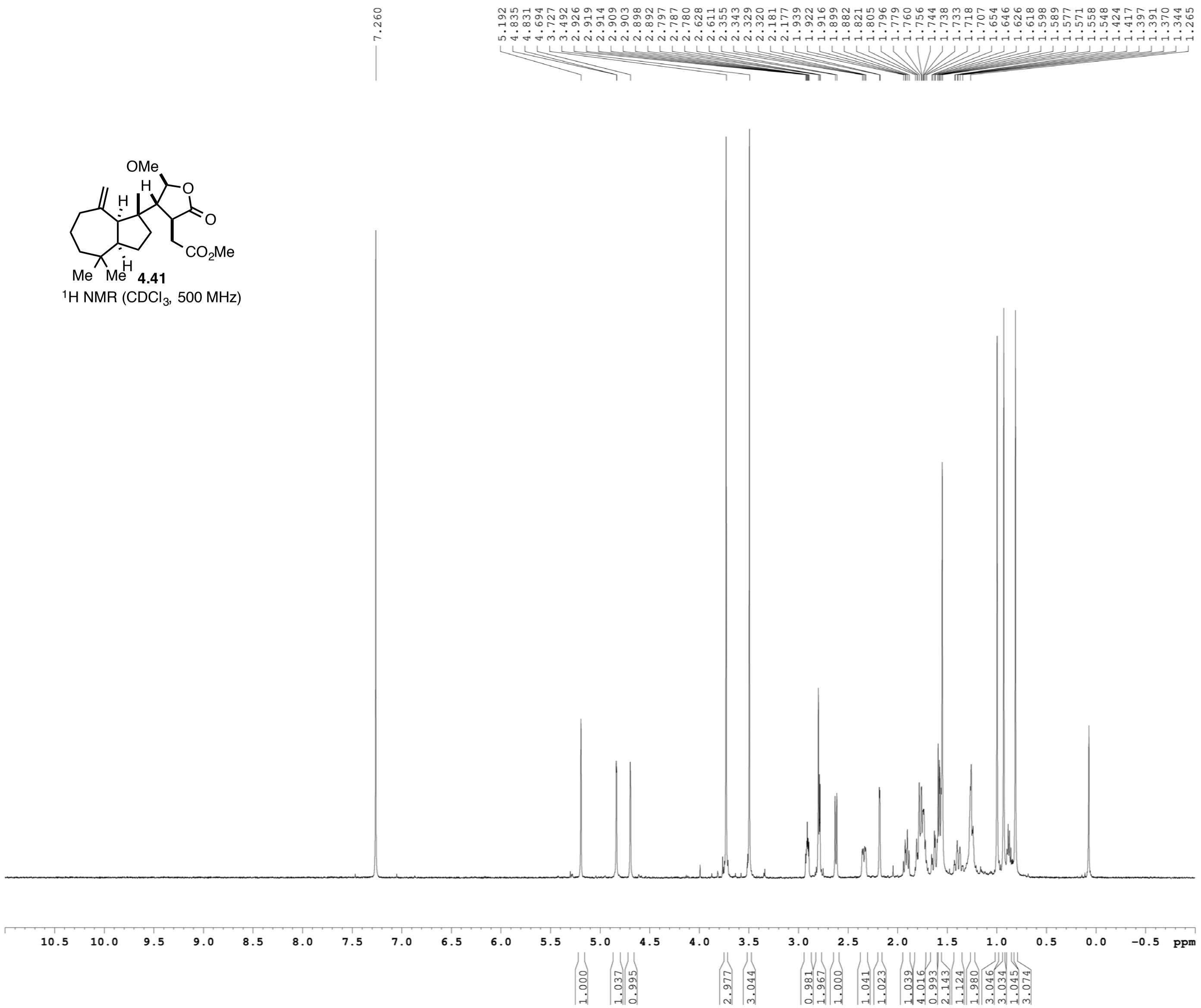
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803991 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-III-174B

4.41

^{1}H NMR (CDCl$_3$, 500 MHz)



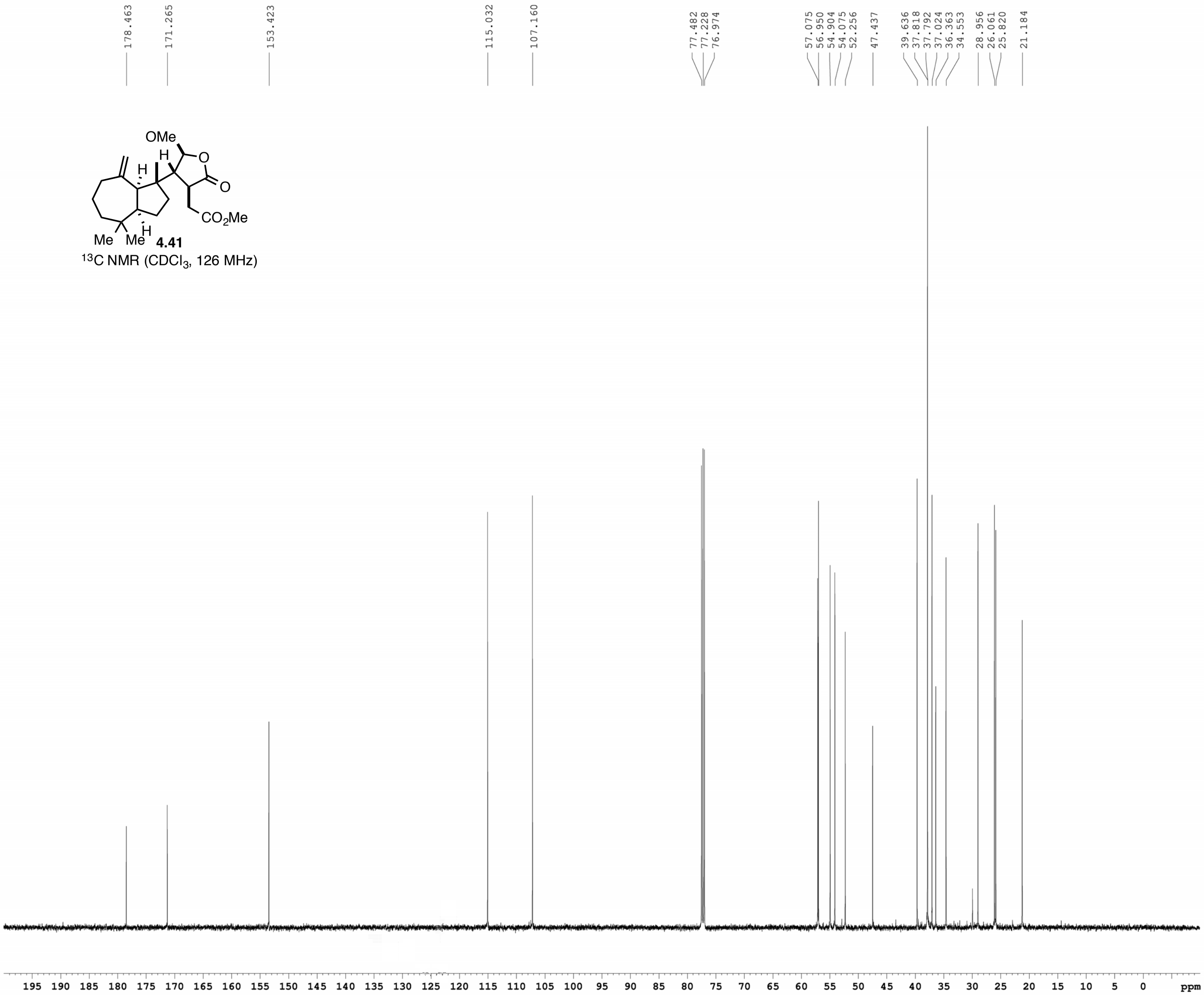
```
Current Data Parameters
NAME          41 1HNMR
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20140113
Time             15.53
INSTRUM          gn500
PROBHD   5 mm broadband
PULPROG           zg30
TD               81728
SOLVENT         CDC13T
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG              1448.2
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1         0.10000000 sec
MCREST   0 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1               12.20 usec
PL1              -5.00 dB
SFO1       499.2934950 MHz

F2 - Processing parameters
SI               65536
SF         499.2900292 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

MRG-III-180B



4.41

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          41 13CNMR
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20140118
Time              11.57
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDC13
NS                 1147
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

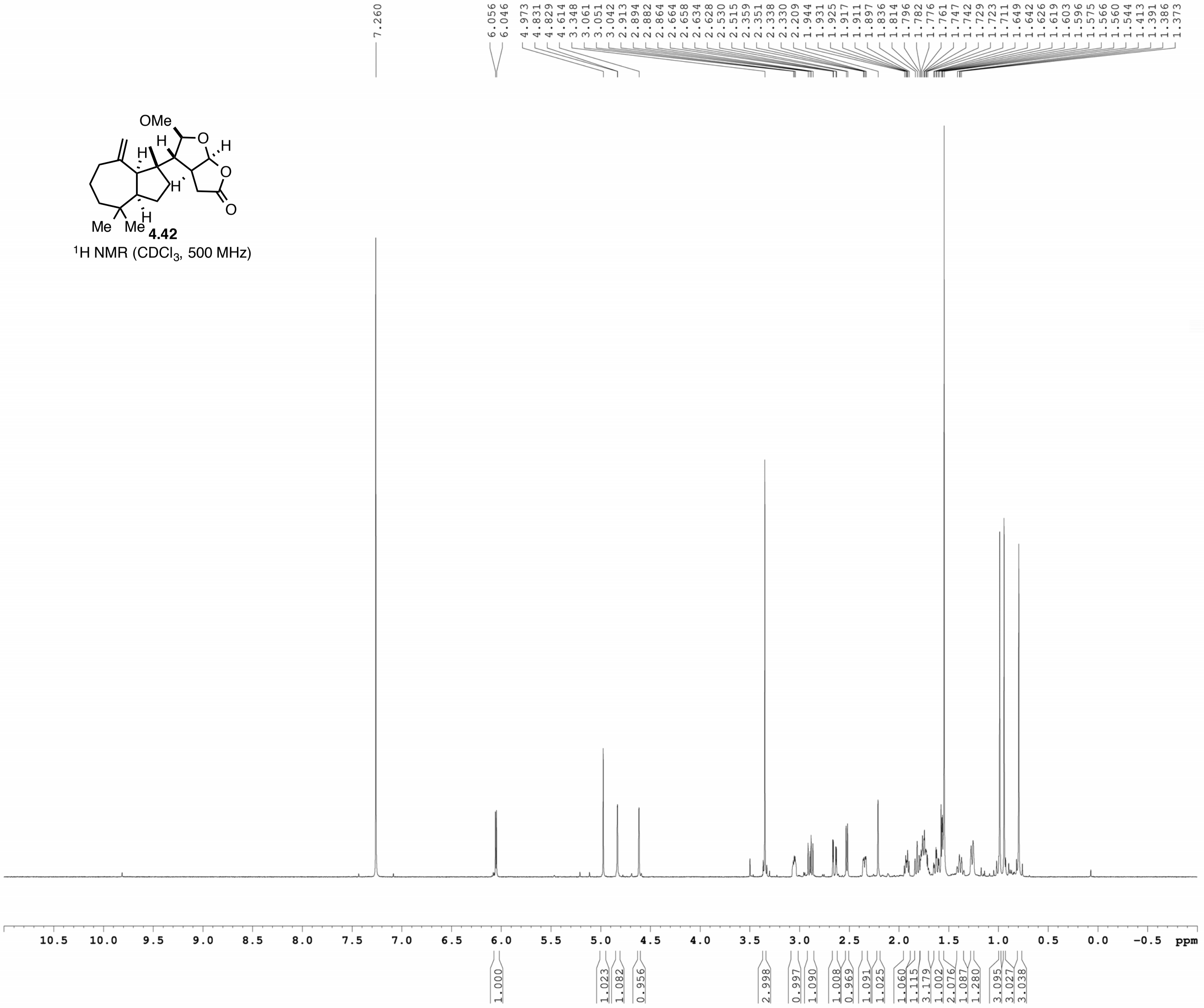
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804007 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

MRG-III-182D

4.42

^{1}H NMR (CDCl$_3$, 500 MHz)



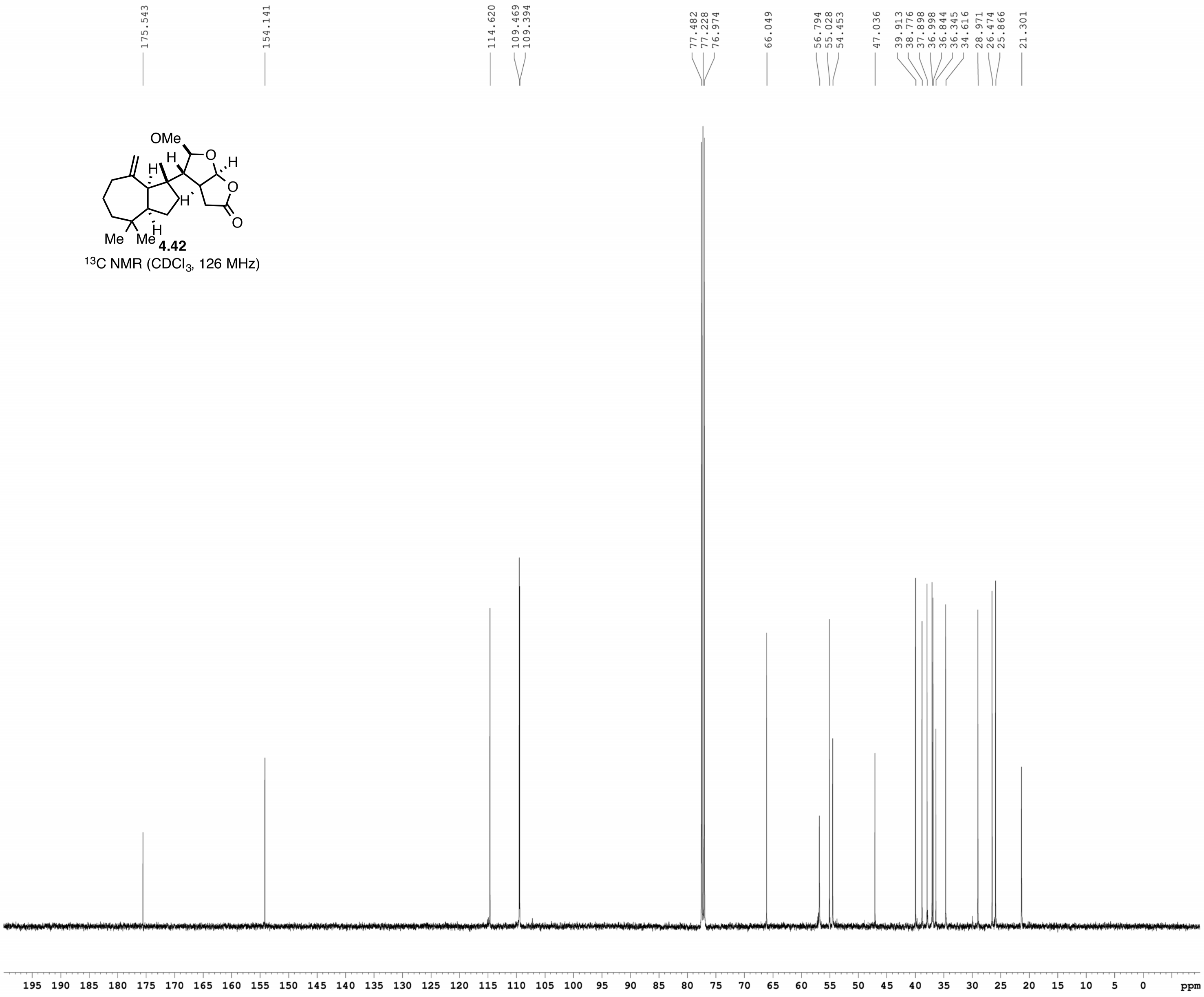
```
Current Data Parameters
NAME            42 1HNMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140121
Time               11.54
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   512
DW                52.000 usec
DE                 14.54 usec
TE                 298.1 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF           600.1300346 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

MRG-III-182D



4.42

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          42 13CNMR
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140121
Time              12.52
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1183
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 4096
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

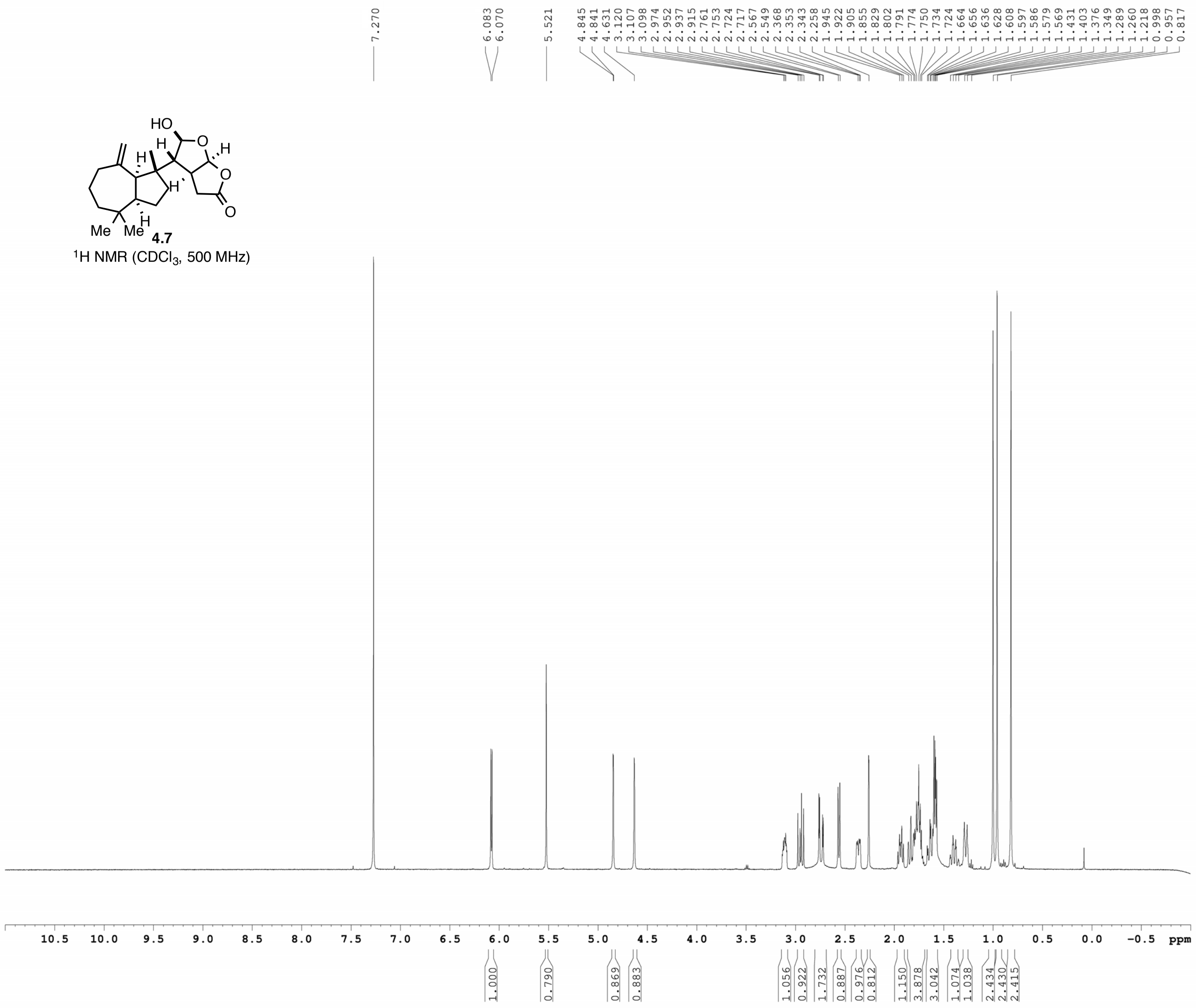
======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804000 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



4.7

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME           PZ-2131-P
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20170411
Time               22.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDC13
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

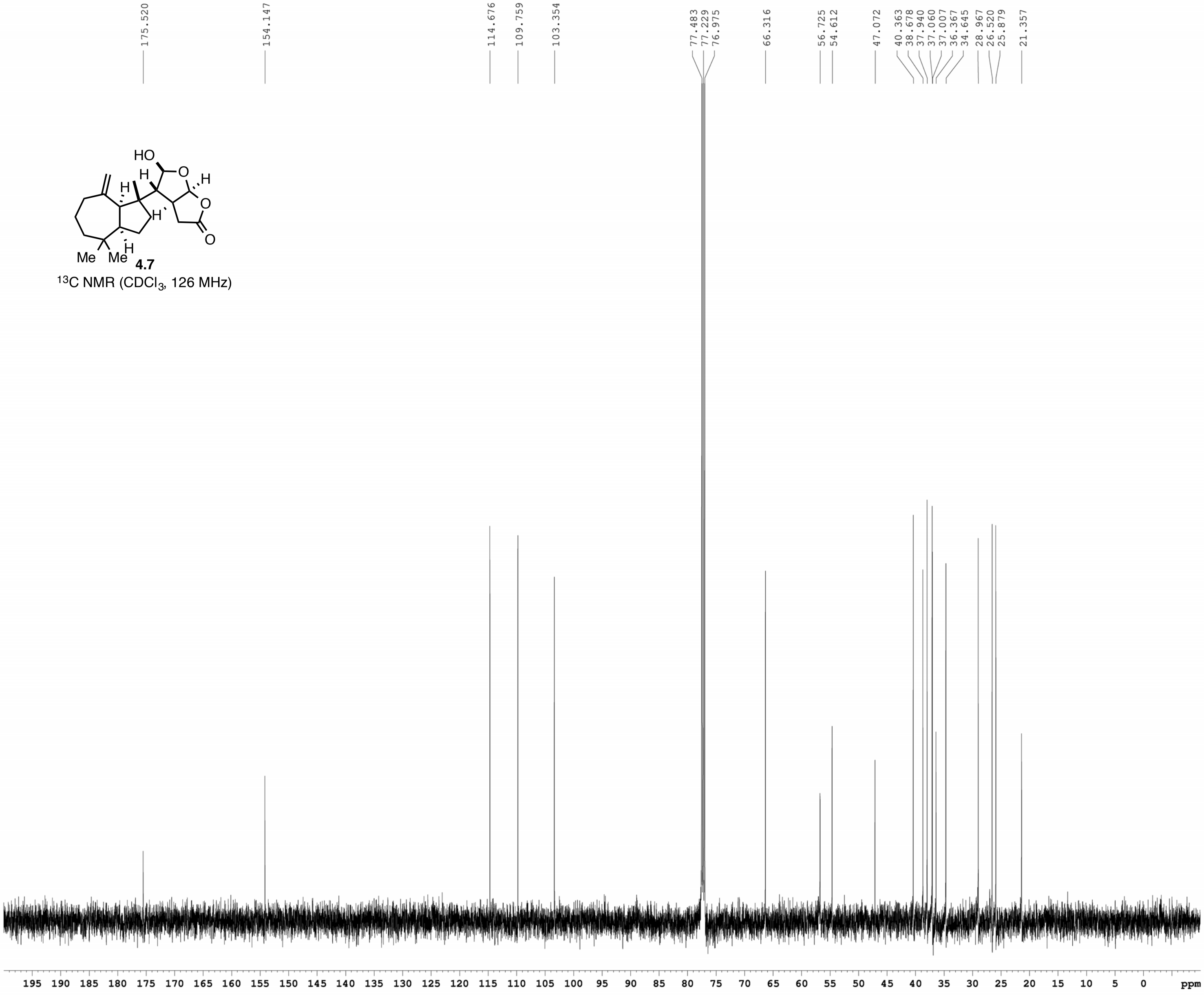
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200267 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

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

4.7

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          PZ-2131-P
EXPNO                 2
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170411
Time              22.13
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2896.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

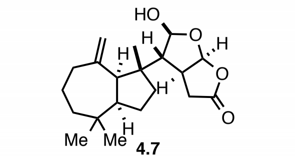
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803989 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum


4.7

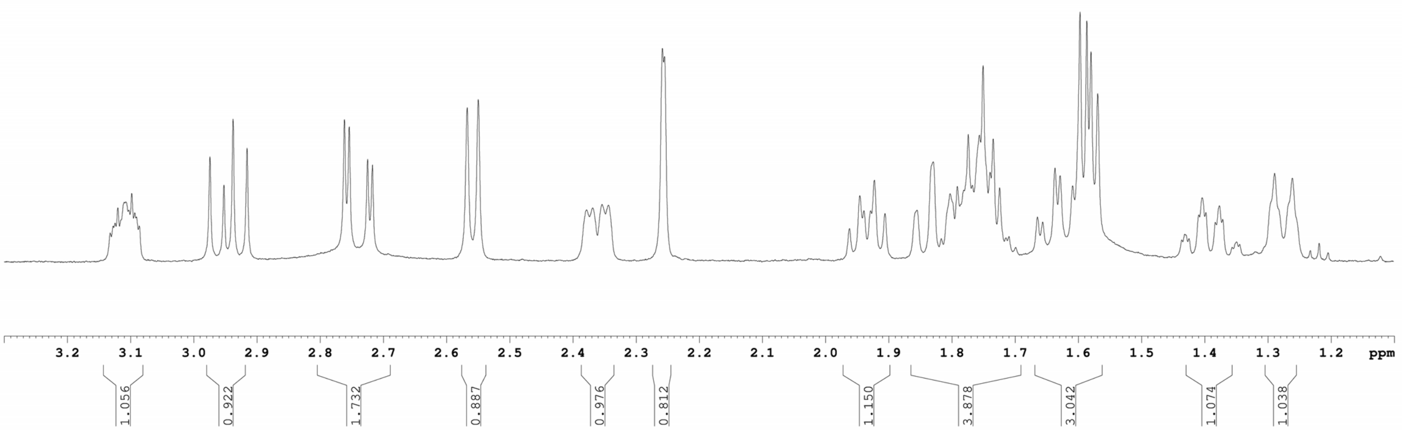
^{1}H NMR ($CDCl_3$, 500 MHz)
3.3 ppm to 1.1 ppm expanded region

```
Current Data Parameters
NAME          PZ-2131-P
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20170411
Time              22.05
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 =======
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

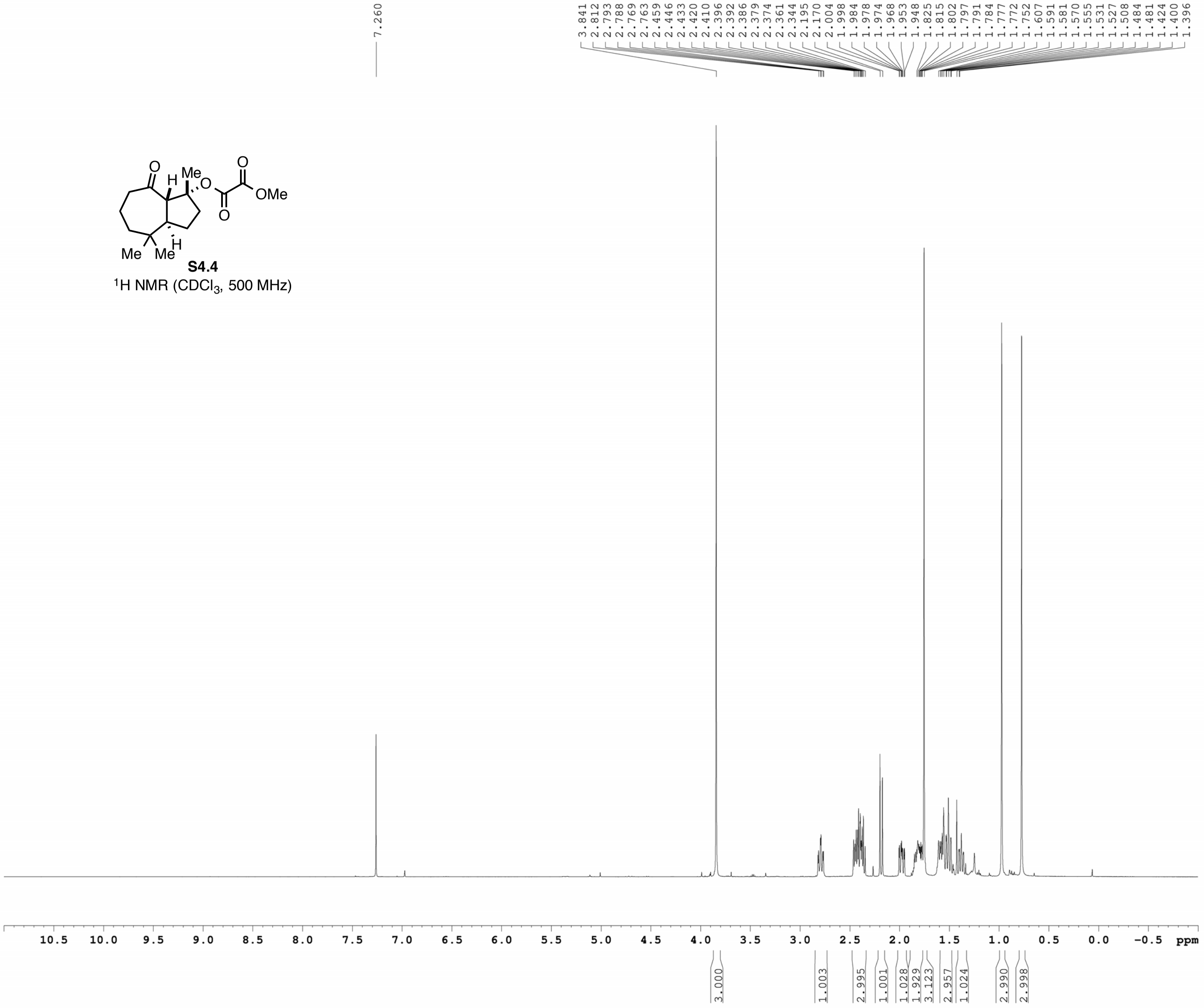
F2 - Processing parameters
SI                65536
SF          500.2200267 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



YS-V-18

S4.4

^{1}H NMR (CDCl$_3$, 500 MHz)



```
Current Data Parameters
NAME              YS-V-18
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160817
Time                17.53
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                      5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

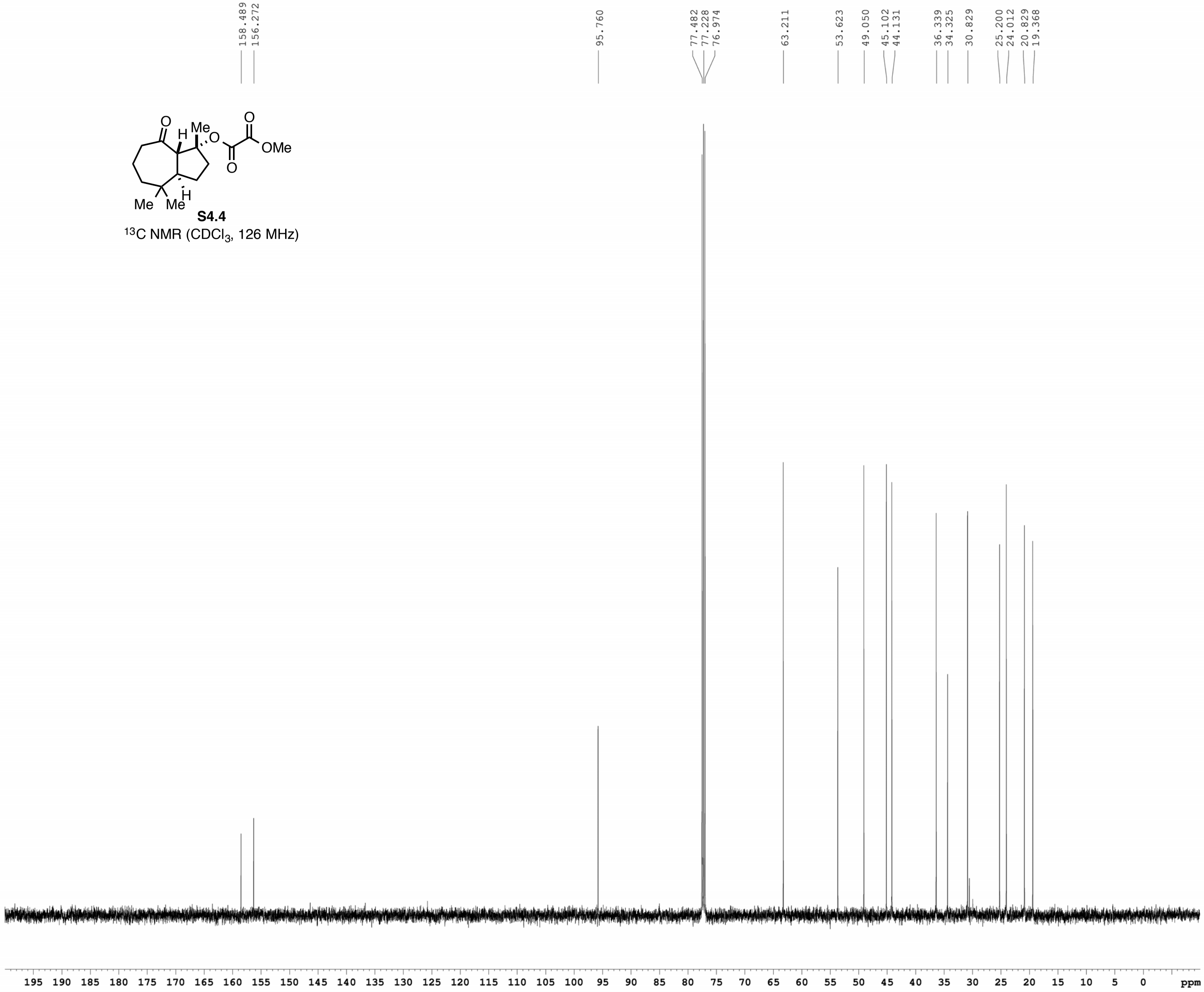
======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF          500.2200312 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-V-18

S4.4

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME             YS-V-18
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160817
Time               17.56
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                2896.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

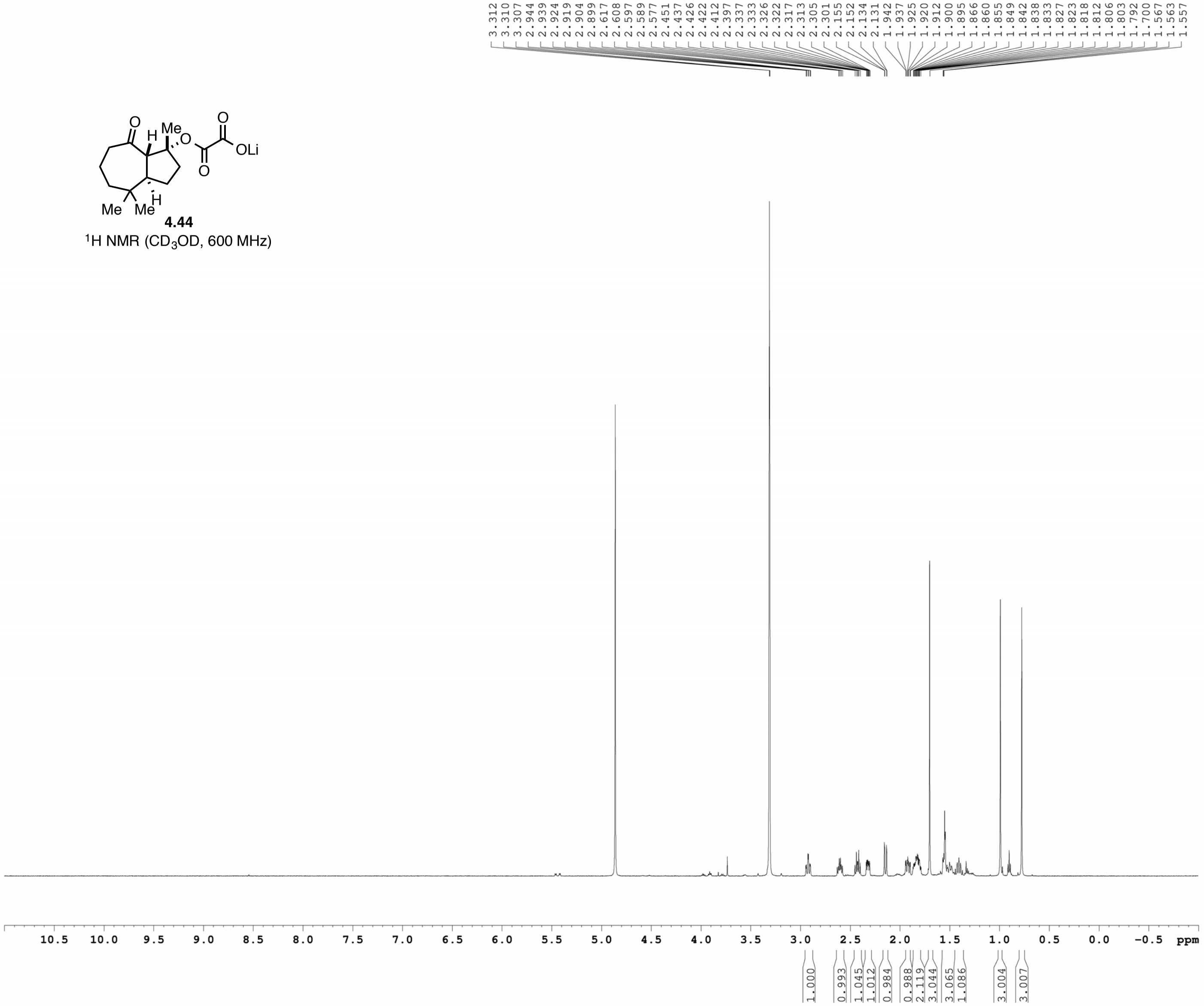
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803998 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-V-236

4.44

^{1}H NMR (CD_3OD, 600 MHz)



```
Current Data Parameters
NAME              YS-V-236
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170217
Time                  8.26
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   98074
SOLVENT              CD3OD
NS                       8
DS                       2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                      10
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1             0.10000000 sec
TD0                      1

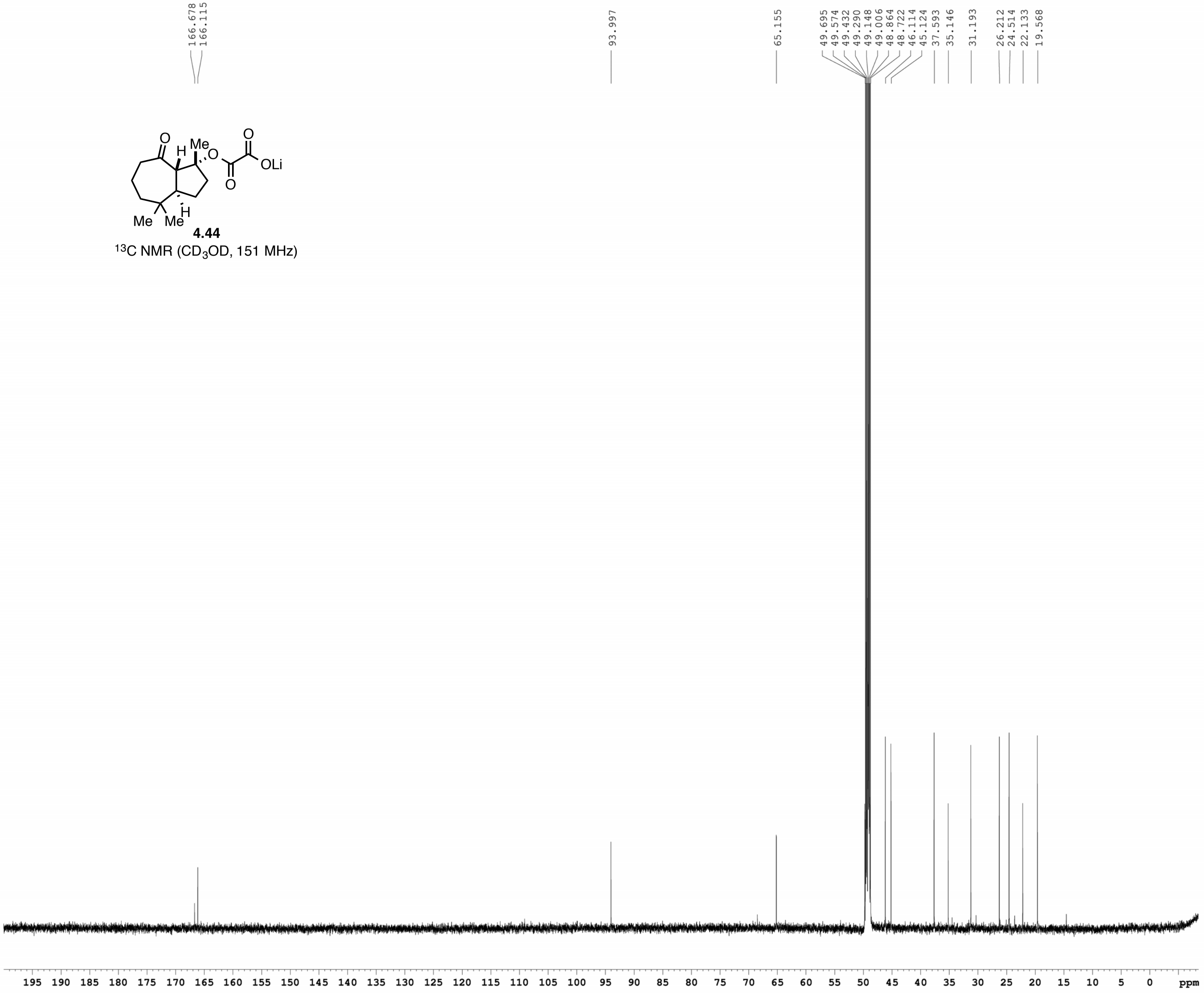
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                   65536
SF           600.1300200 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-V-236

4.44

^{13}C NMR (CD$_3$OD, 151 MHz)



```
Current Data Parameters
NAME            YS-V-236
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170217
Time                8.30
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT            CD3OD
NS                  1024
DS                     1
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

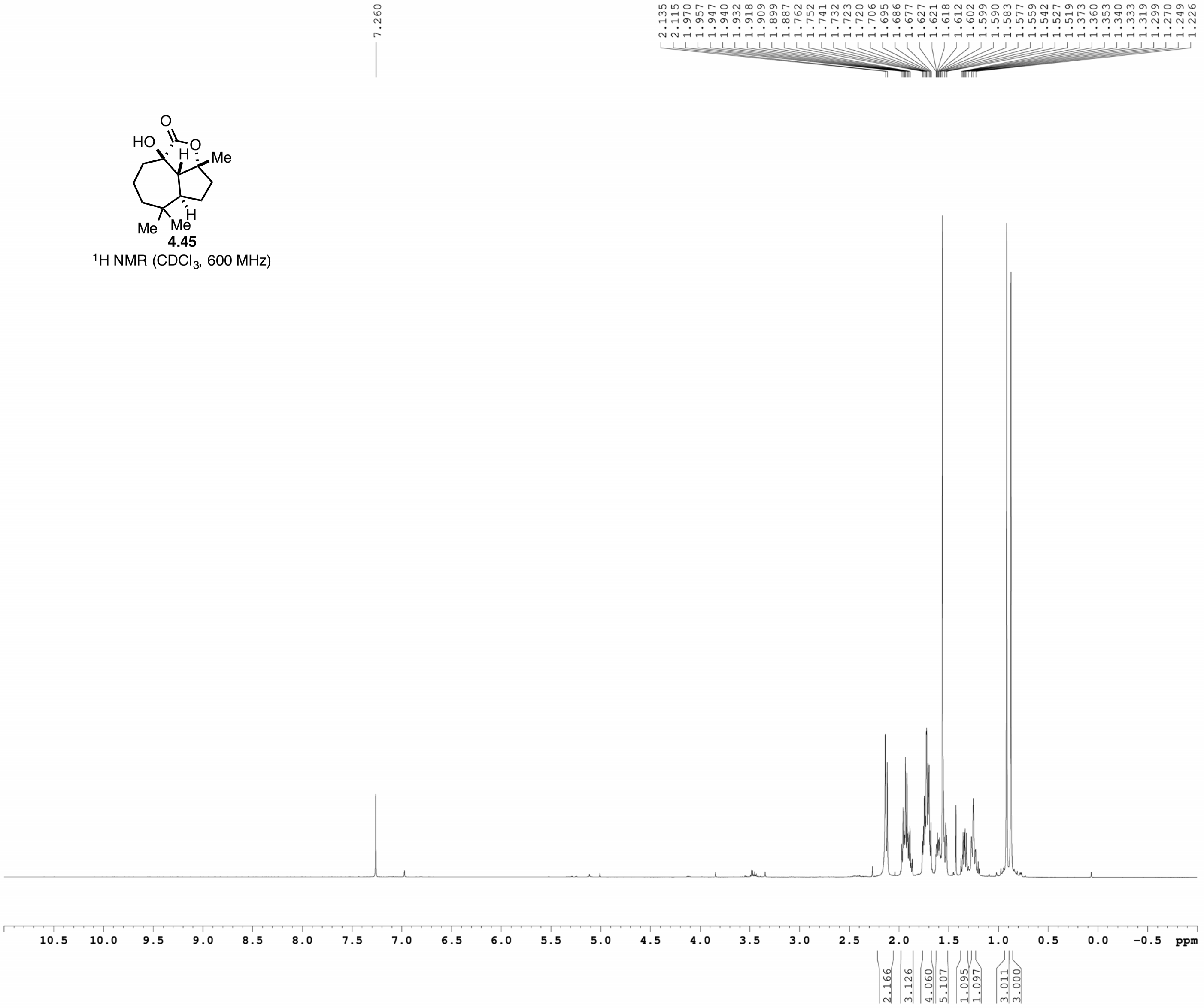
======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF           150.9025759 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

YS-V-243

4.45

^{1}H NMR (CDCl$_3$, 600 MHz)



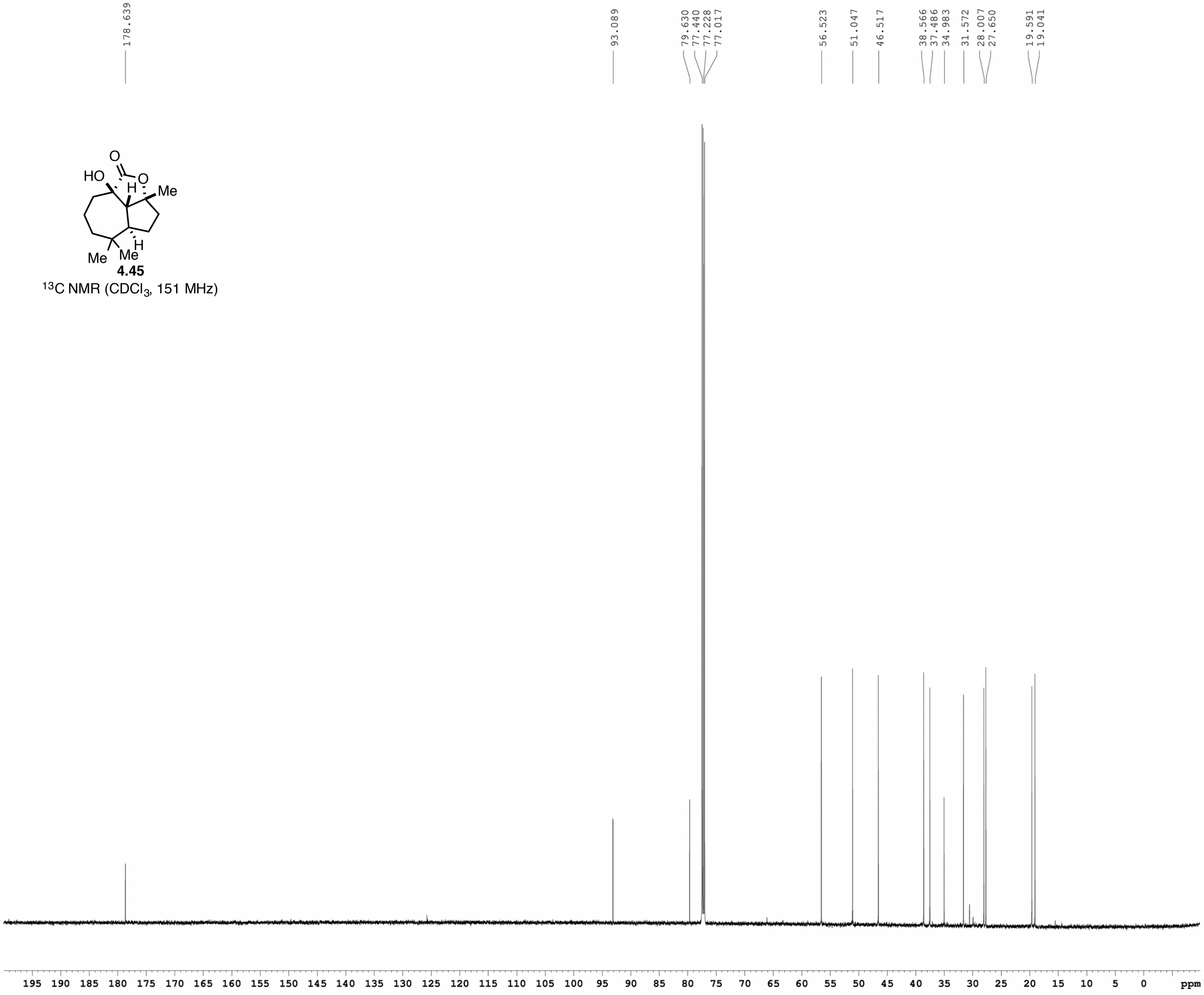
```
Current Data Parameters
NAME              YS-V-243
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170222
Time                 10.47
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   98074
SOLVENT              CDCl3
NS                       8
DS                       2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                      10
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                   65536
SF           600.1300349 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-V-243



4.45

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME              YS-V-243
EXPNO                    3
PROCNO                   1

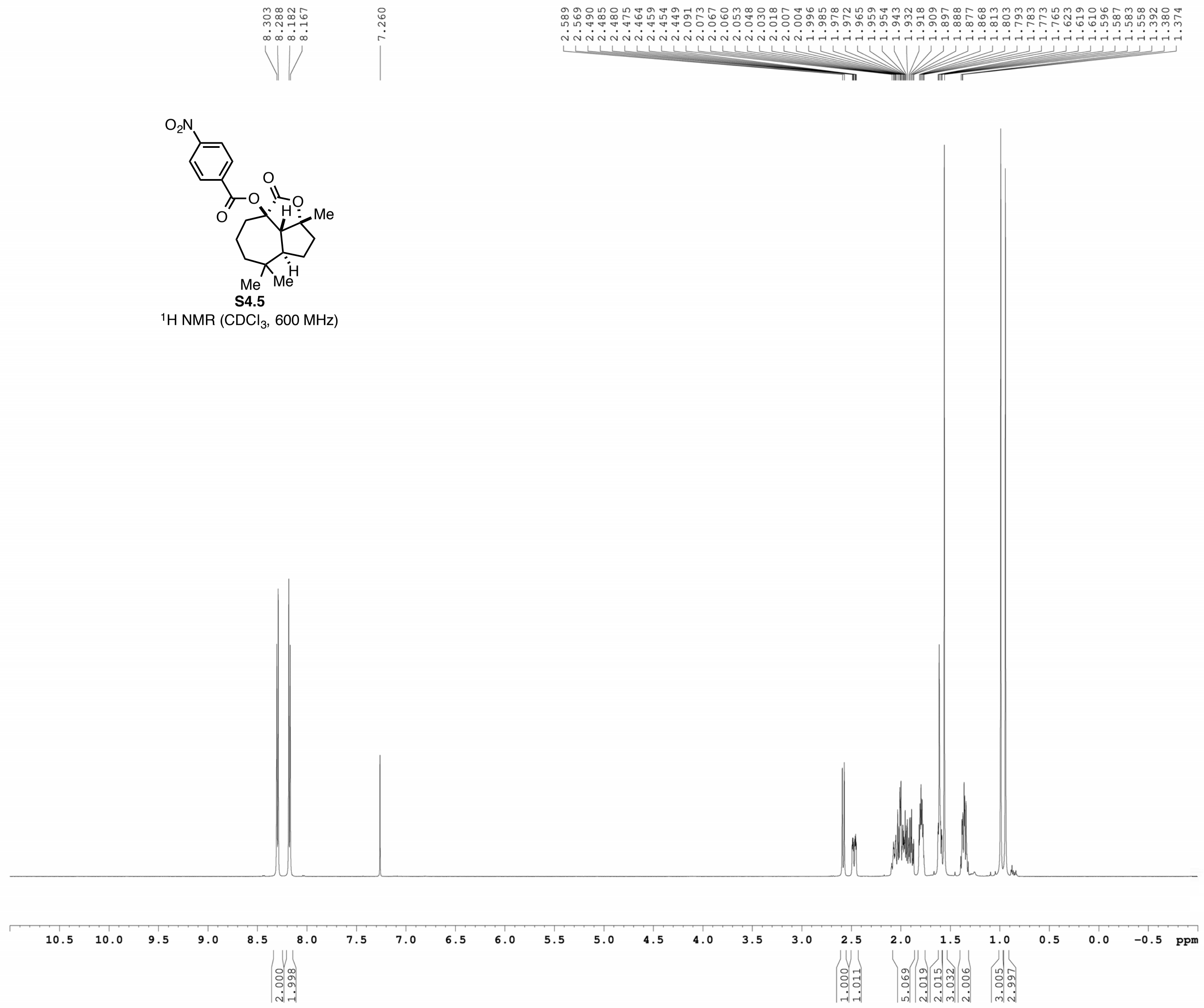
F2 - Acquisition Parameters
Date_             20170222
Time                 10.50
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     120
DS                       1
SWH              36231.883 Hz
FIDRES            0.552855 Hz
AQ               0.9043968 sec
RG                    2050
DW                  13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1              0.40000001 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           150.9194080 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           64.00000000 W

======== CHANNEL f2 ========
SFO2           600.1330010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                   65536
SF             150.9027844 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.00
```

YS-V-248



S4.5

^{1}H NMR (CDCl$_3$, 600 MHz)

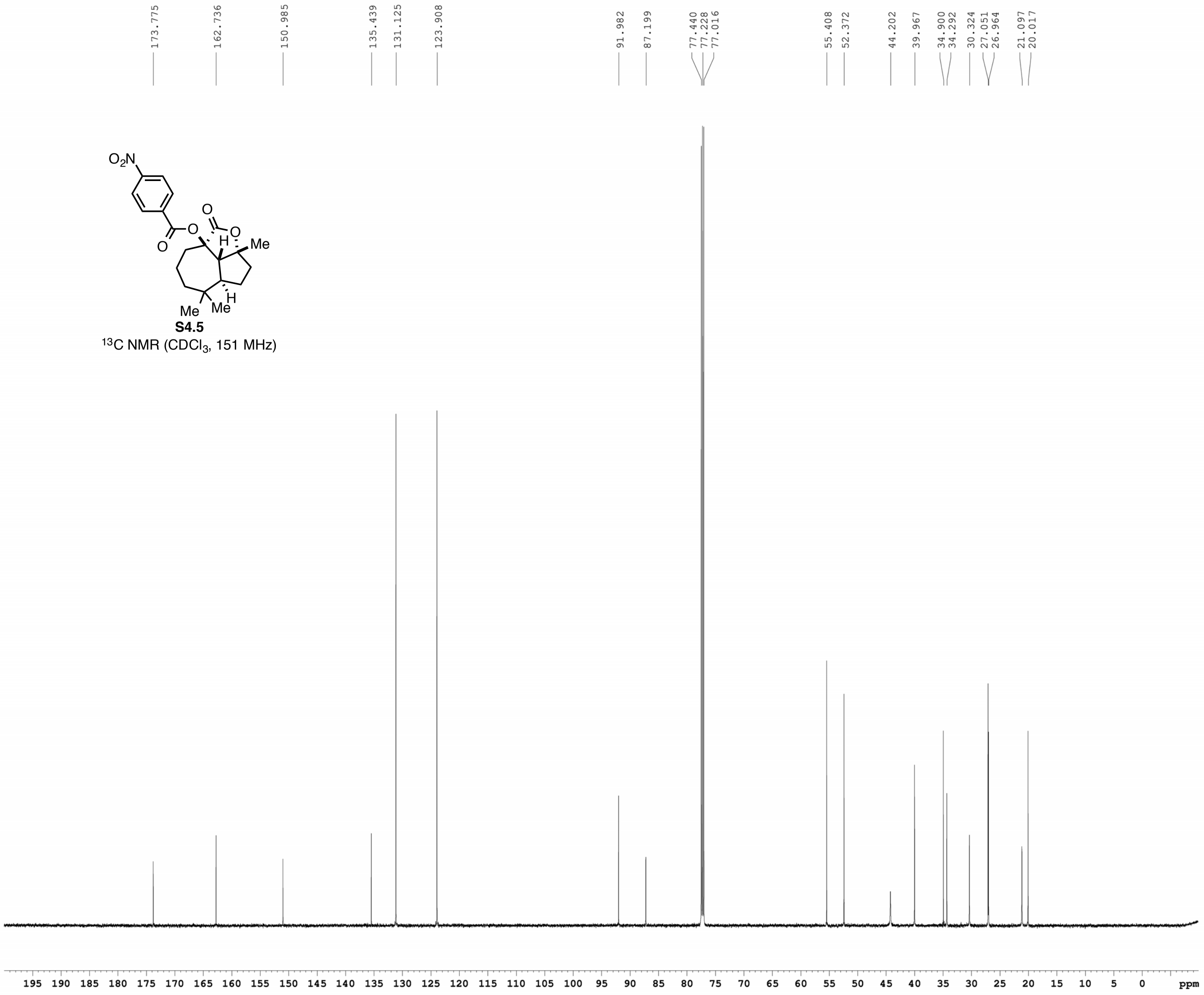
```
Current Data Parameters
NAME             YS-V-248
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170728
Time                9.01
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     1
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300349 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-248



S4.5

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME            YS-V-248
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170728
Time                9.04
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9043968 sec
RG                  2050
DW              13.800 usec
DE               19.65 usec
TE               298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1                  13C
P1                  10.00 usec
PLW1         64.00000000 W

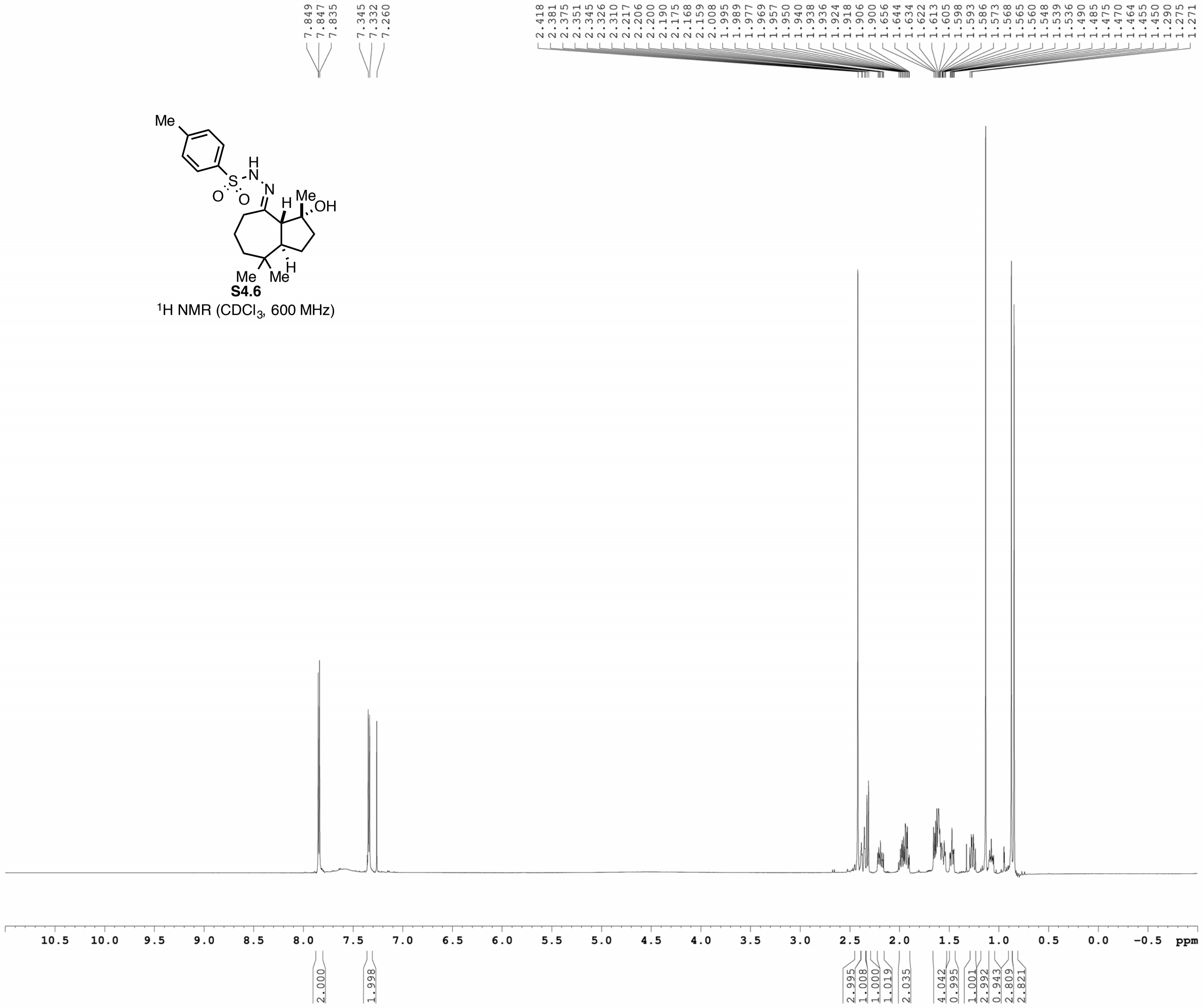
======== CHANNEL f2 ========
SFO2       600.1330010 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF          150.9027851 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

YS-VI-26

S4.6

^{1}H NMR (CDCl$_3$, 600 MHz)



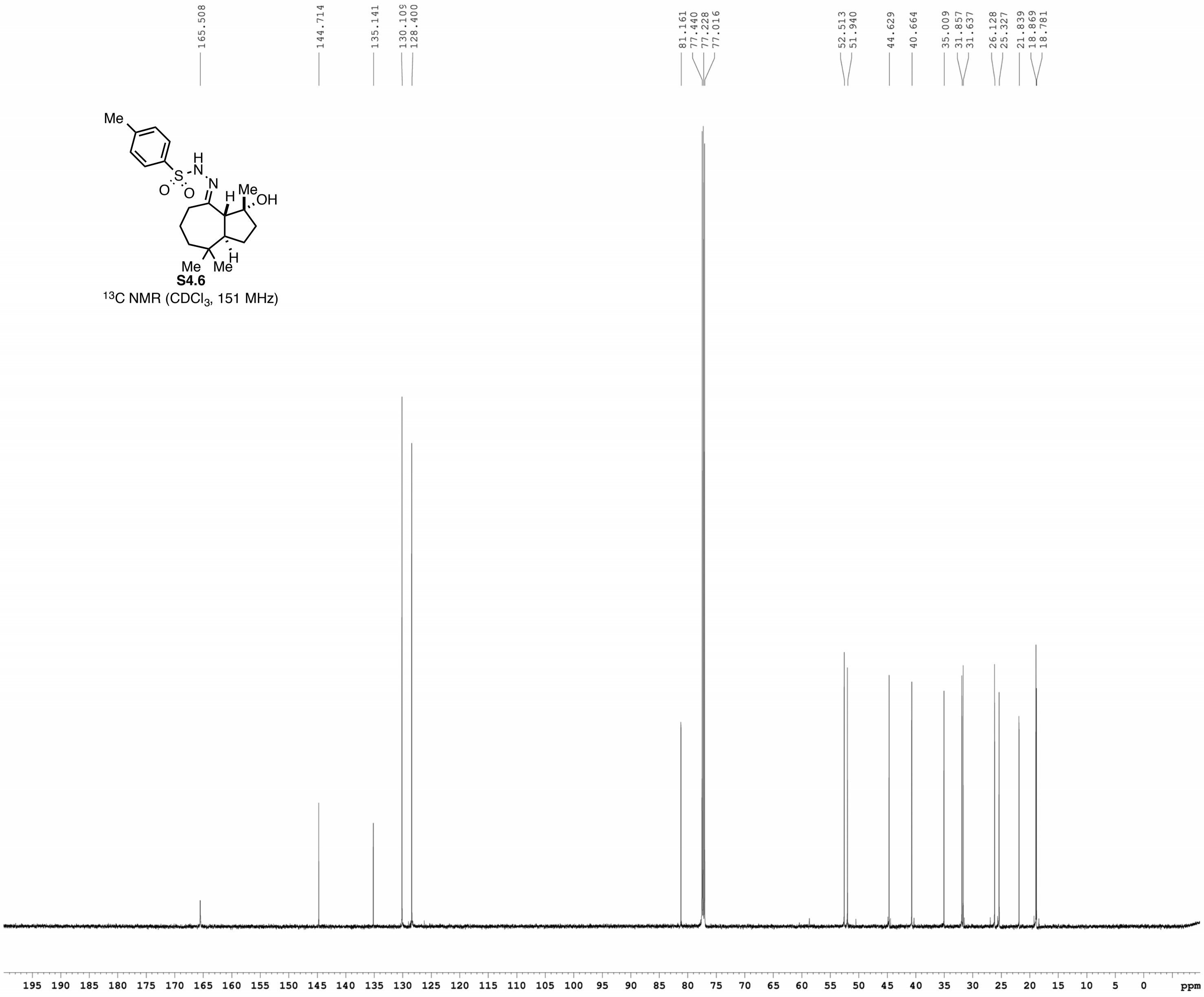
```
Current Data Parameters
NAME            YS-VI-26
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170731
Time               10.25
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     1
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300341 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-VI-26



S4.6

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME            YS-VI-26
EXPNO                  4
PROCNO                 1

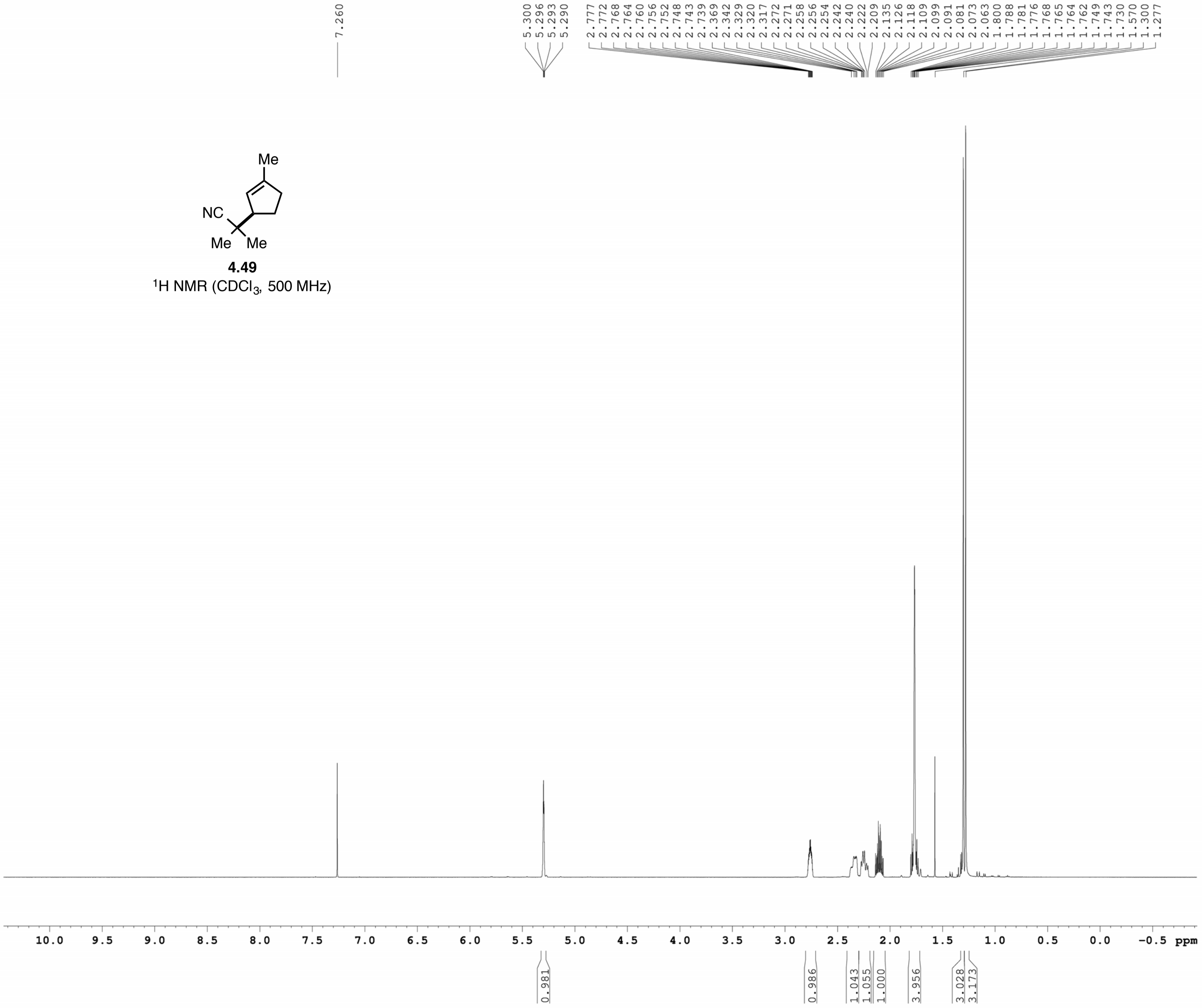
F2 - Acquisition Parameters
Date_          20170731
Time              10.31
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  360
DS                    1
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                 2050
DW               13.800 usec
DE                19.65 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9027842 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

1H spectrum



4.49

^{1}H NMR (CDCl$_3$, 500 MHz)

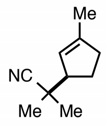
```
Current Data Parameters
NAME      CRJ3-146-pure
EXPNO                 1
PROCNO                1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_          20161201
Time              11.38
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                  7.1
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST  0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

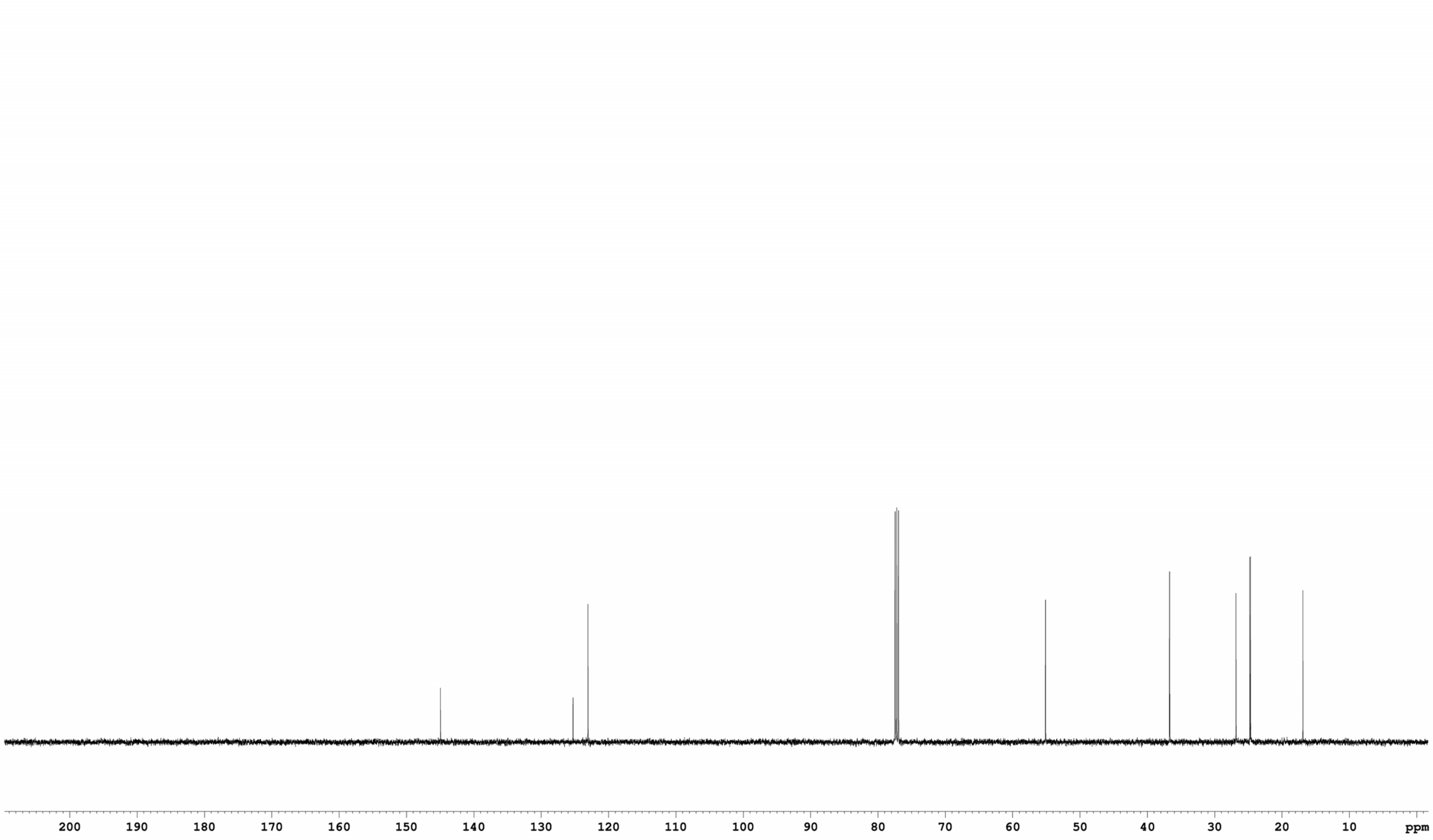
F2 - Processing parameters
SI                65536
SF          500.2200310 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

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



4.49

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME      CRJ3-146-pure
EXPNO                 2
PROCNO                1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_          20161201
Time              11.43
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               181814
SOLVENT           CDCl3
NS                   64
DS                   16
SWH           30303.031 Hz
FIDRES         0.166671 Hz
AQ            2.9999311 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

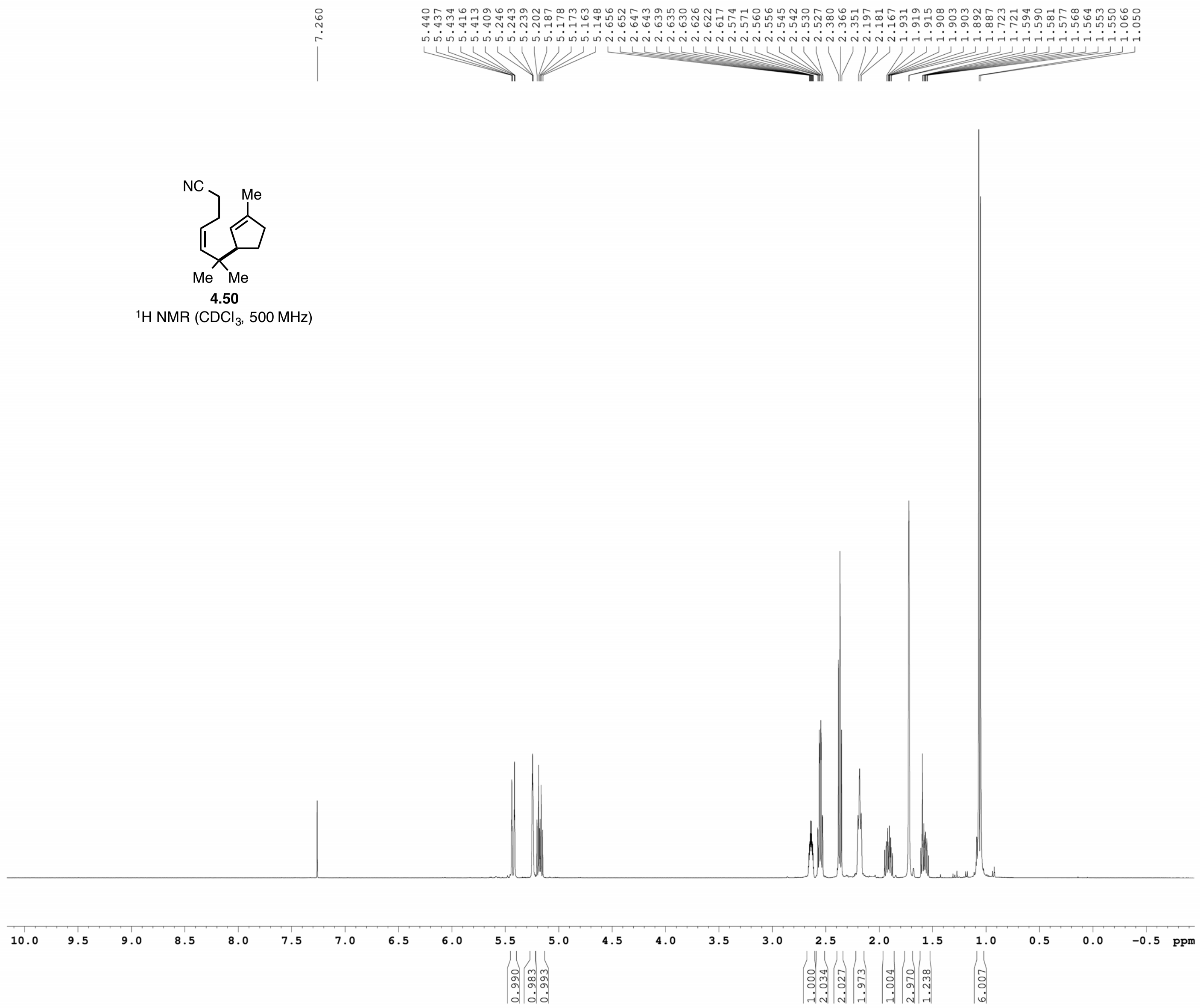
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804099 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



4.50

^{1}H NMR ($CDCl_3$, 500 MHz)

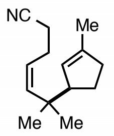
```
Current Data Parameters
NAME       CRJ3-148-pure
EXPNO                  3
PROCNO                 1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_           20161210
Time               10.21
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

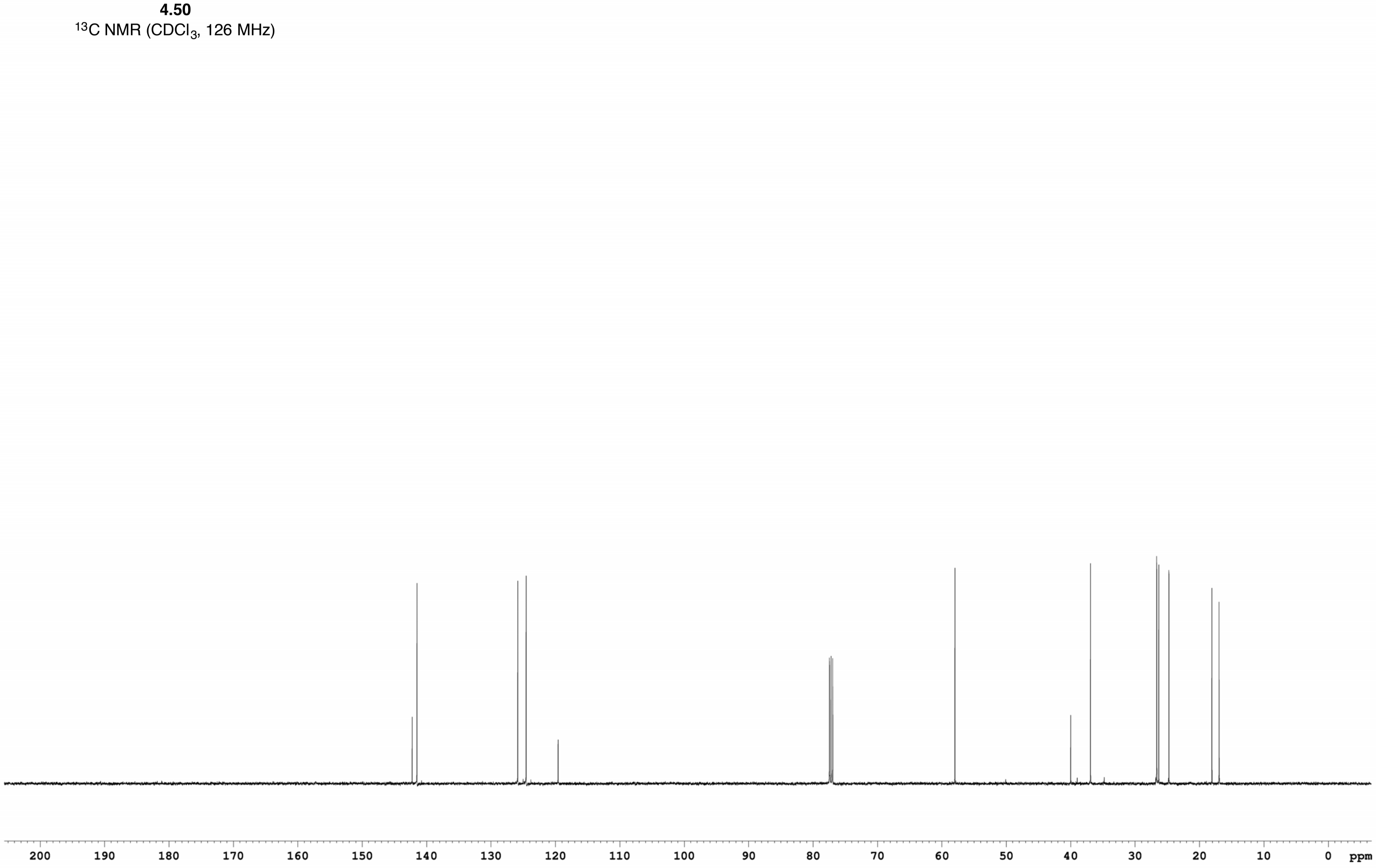
F2 - Processing parameters
SI                 65536
SF           500.2200309 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```

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



4.50

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME        CRJ3-148-pure
EXPNO                   4
PROCNO                  1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_          20161210
Time              10.26
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  168
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

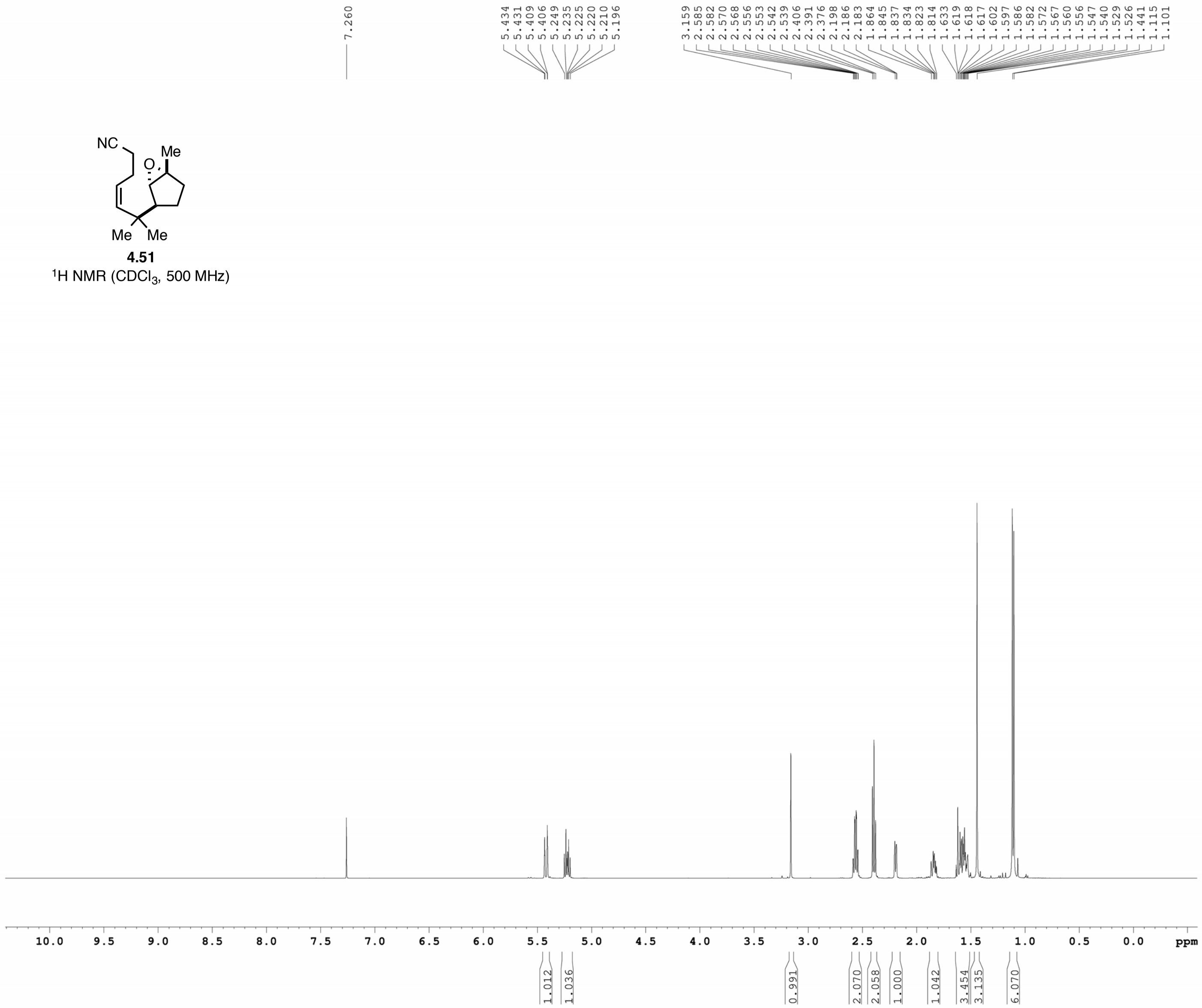
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804114 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



4.51

^{1}H NMR ($CDCl_3$, 500 MHz)

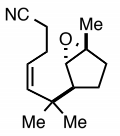
```
Current Data Parameters
NAME      CRJ3-149-major
EXPNO                  1
PROCNO                 1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_           20161209
Time               15.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.166677 Hz
AQ             2.9998176 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

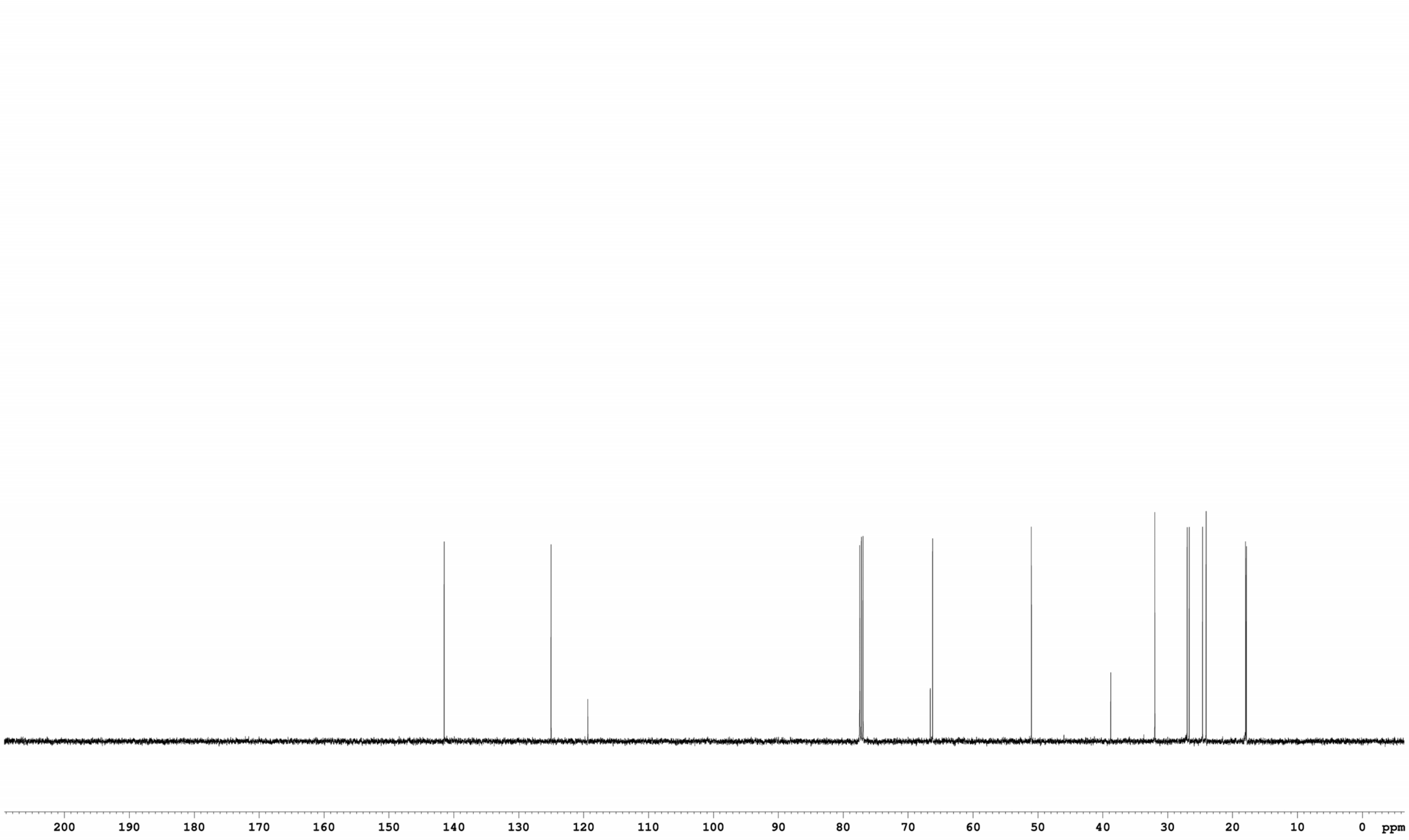
F2 - Processing parameters
SI                 65536
SF           500.2200308 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```

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



4.51

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME     CRJ3-149-major
EXPNO                 2
PROCNO                1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_          20161209
Time              15.04
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2896.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

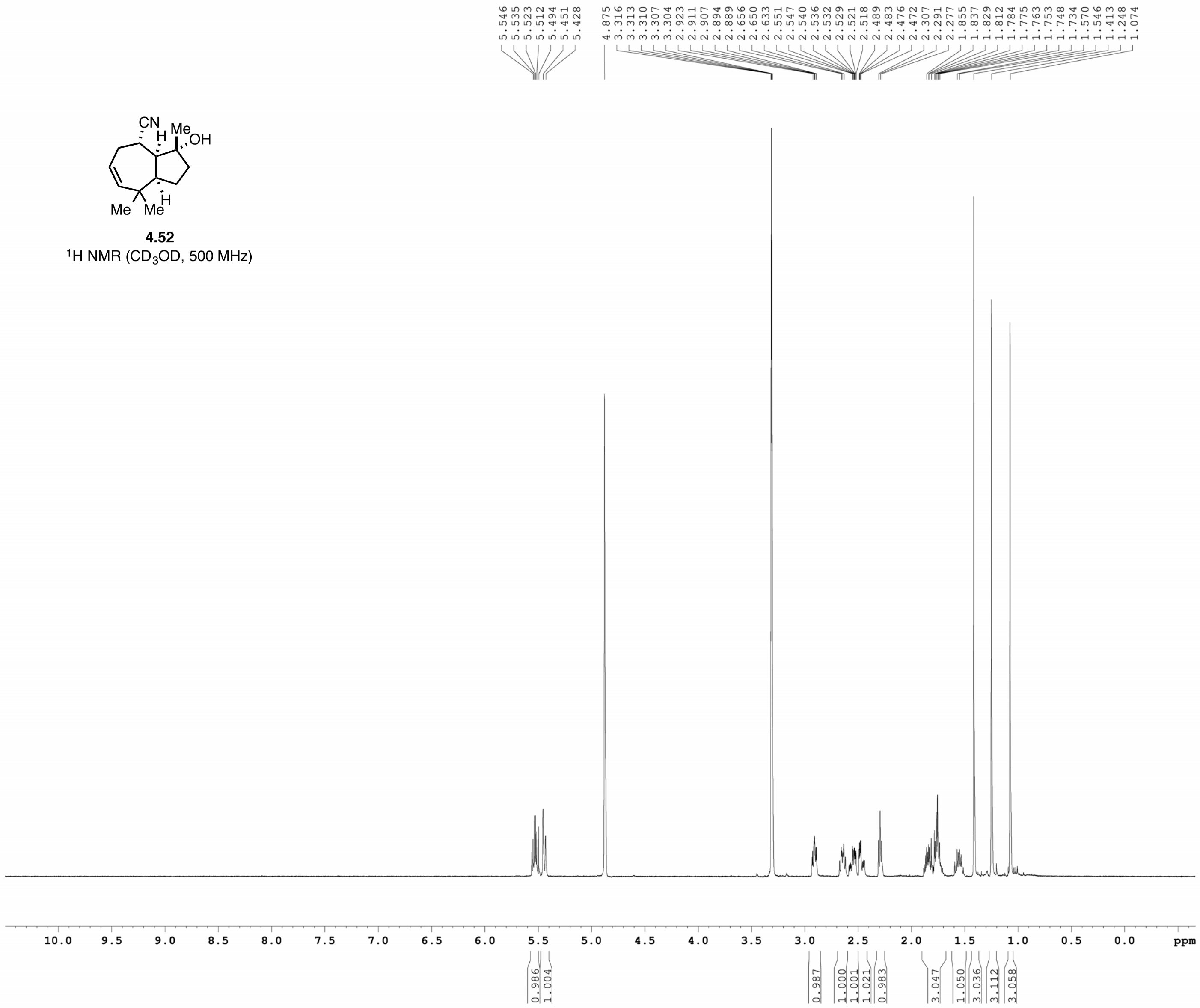
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804103 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum

4.52

^{1}H NMR (CD_3OD, 500 MHz)



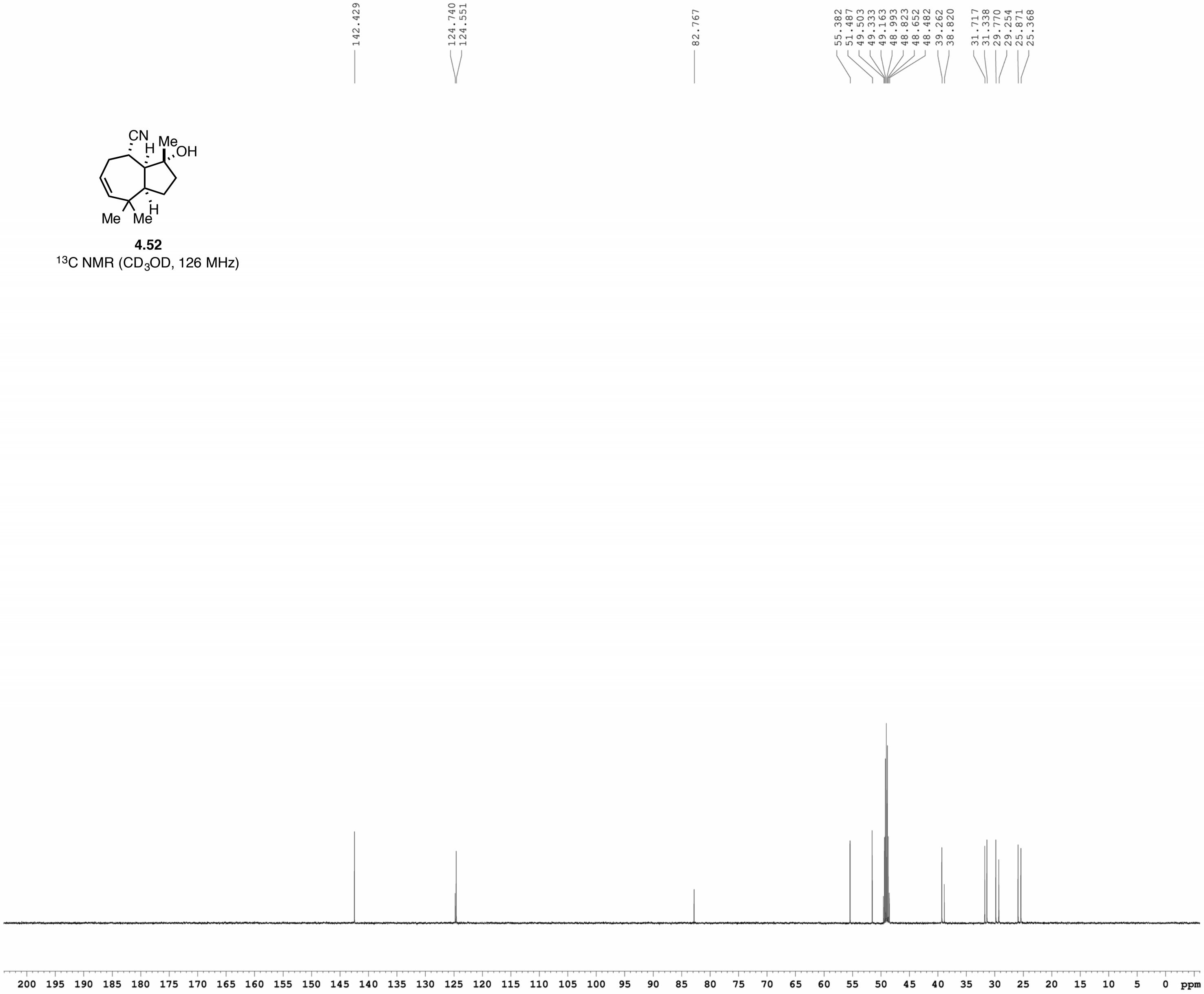
```
Current Data Parameters
NAME       CRJ3-127-MeOH
EXPNO                  1
PROCNO                 1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_          20161118
Time              13.20
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                 12.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200139 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

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



4.52

^{13}C NMR (CD$_3$OD, 126 MHz)

```
Current Data Parameters
NAME      CRJ3-127-MeOH
EXPNO              6
PROCNO             1
DATPATH  /nmr/jamiso/NMRdata

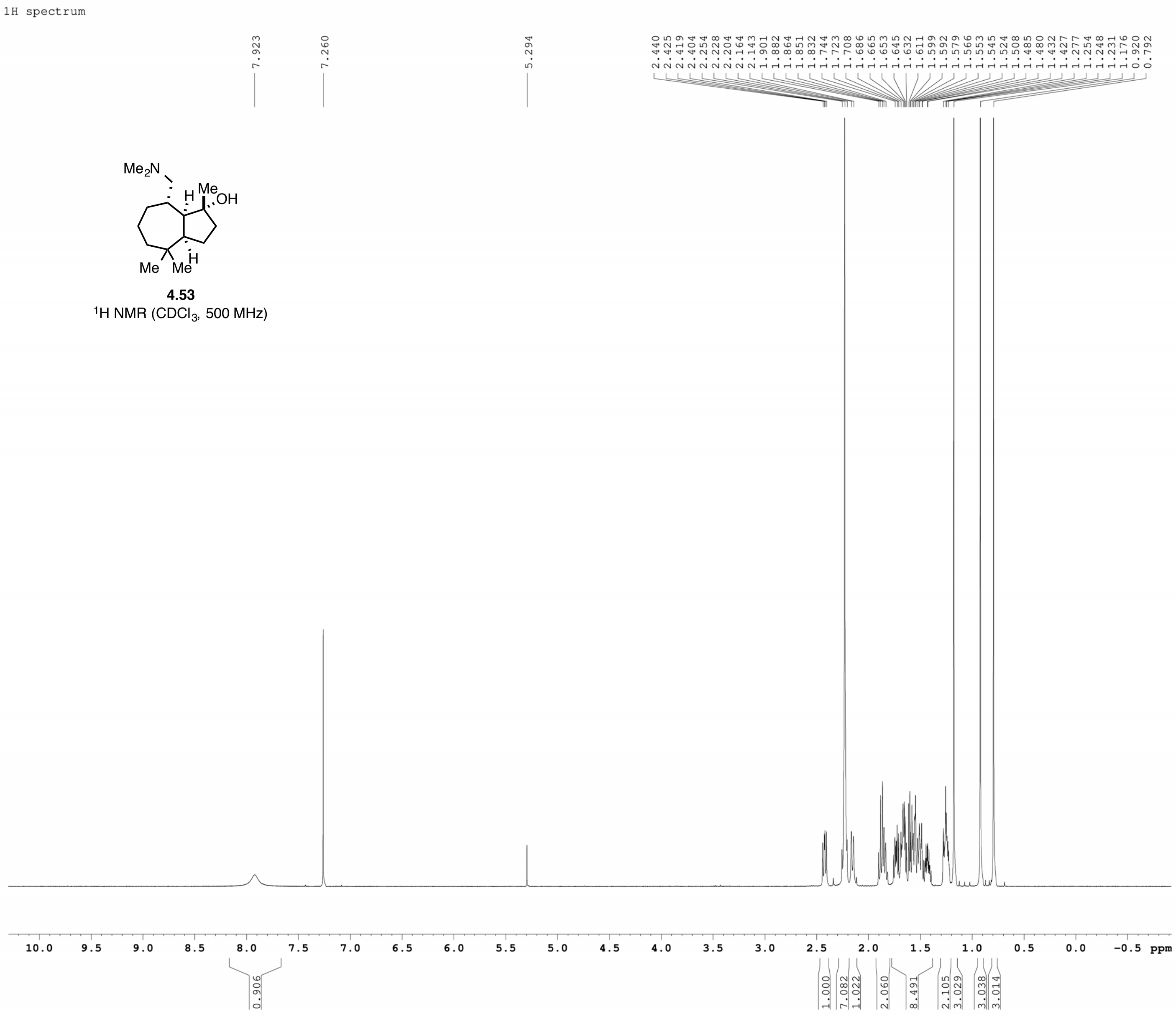
F2 - Acquisition Parameters
Date_          20161119
Time              11.19
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                   64
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               3649.1
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7802475 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



4.53

^{1}H NMR (CDCl$_3$, 500 MHz)

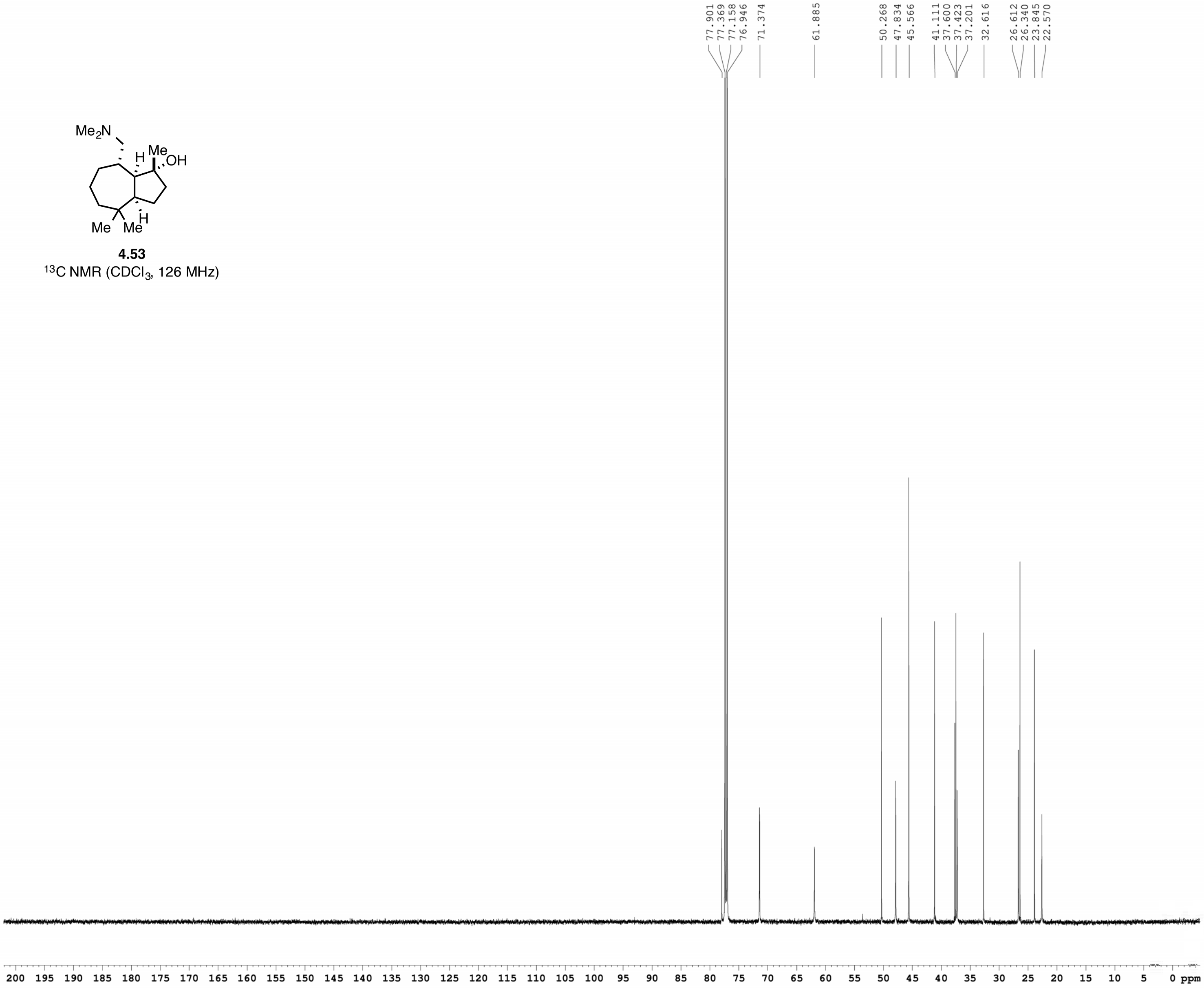
```
Current Data Parameters
NAME       CRJ3-179-pure
EXPNO                  1
PROCNO                 1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_           20170125
Time               13.56
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 96152
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.100002 Hz
AQ            4.9999042 sec
RG                     9
DW               52.000 usec
DE                13.70 usec
TE                298.0 K
D1          0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                 65536
SF          600.1300344 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```

13C spectrum with 1H decoupling



4.53

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME       CRJ3-179-pure
EXPNO                  2
PROCNO                 1
DATPATH  /nmr/jamiso/NMRdata

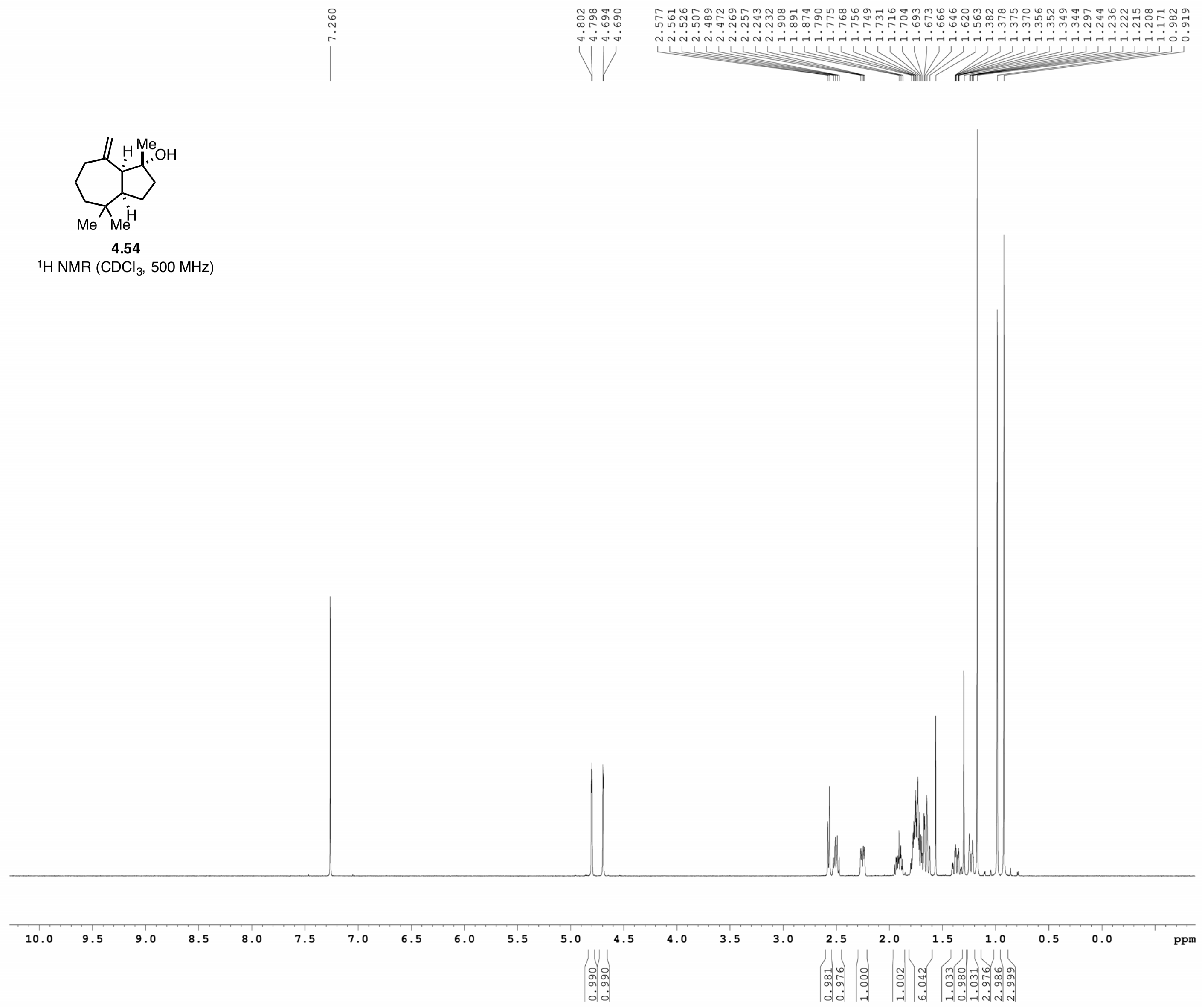
F2 - Acquisition Parameters
Date_           20170125
Time               14.02
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                 2050
DW               13.800 usec
DE                19.65 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194075 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9027937 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

1H spectrum



4.54

^{1}H NMR ($CDCl_3$, 500 MHz)

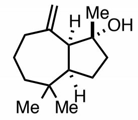
```
Current Data Parameters
NAME      CRJ3-171-pure
EXPNO                 1
PROCNO                1
DATPATH  /nmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_          20170113
Time              11.04
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                48074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.166677 Hz
AQ            2.9998176 sec
RG                    5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

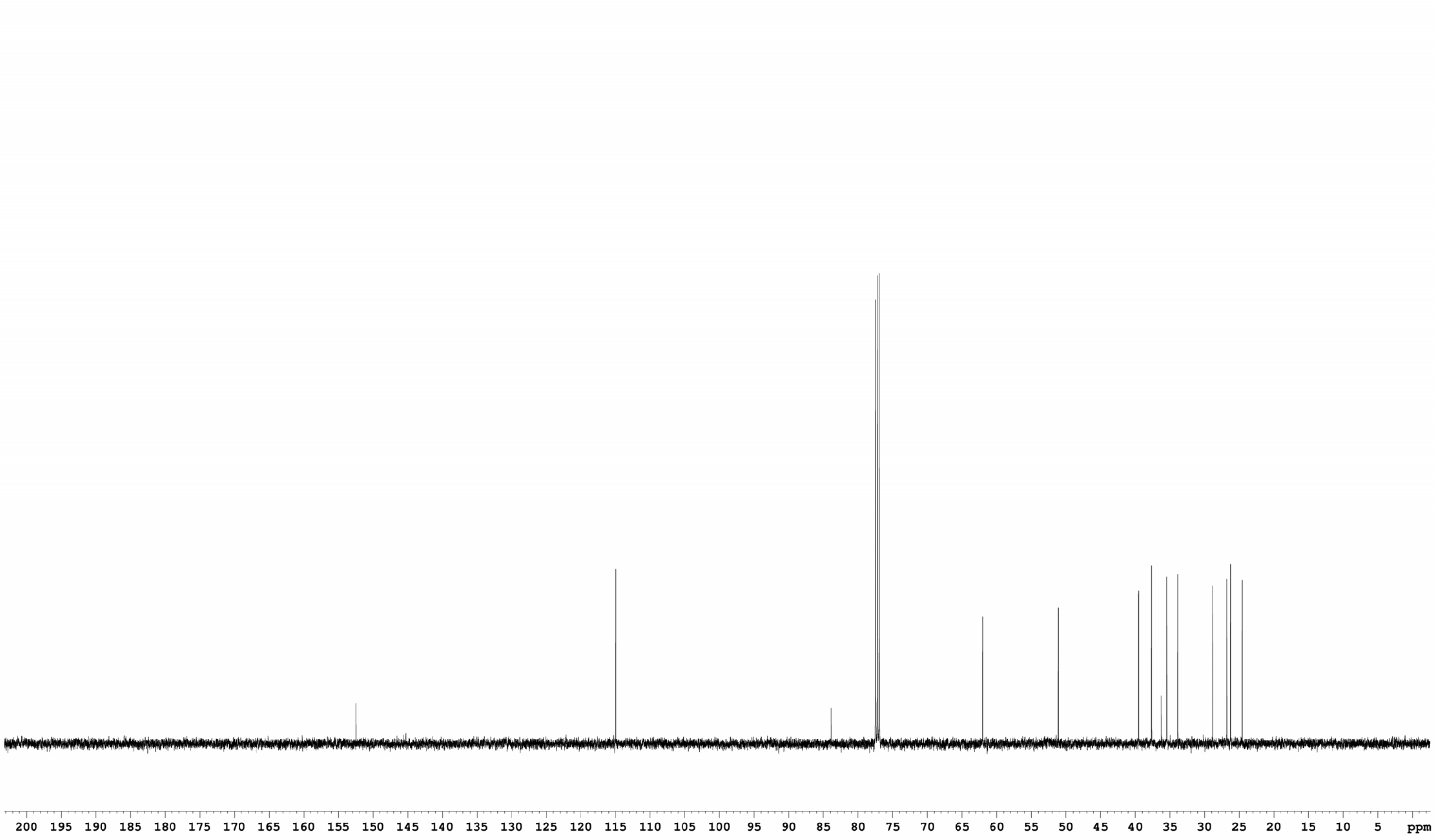
F2 - Processing parameters
SI                65536
SF          500.2200317 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 1.00
```

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



4.54

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME      CRJ3-171-pure
EXPNO                 2
PROCNO                1
DATPATH  /nmr/jamiso/NMRdata

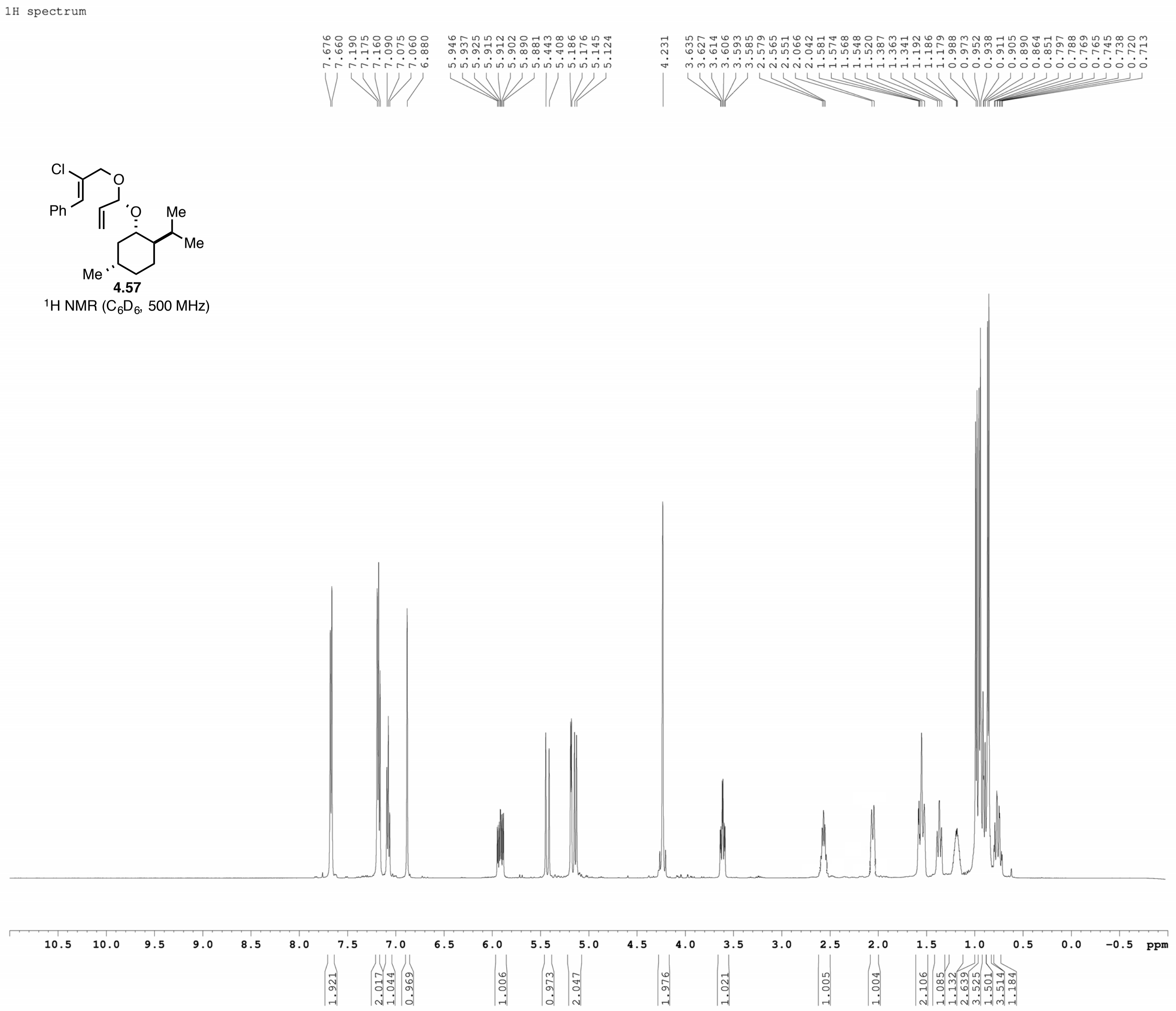
F2 - Acquisition Parameters
Date_          20170113
Time              11.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 3251
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804074 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



4.57

^{1}H NMR (C_6D_6, 500 MHz)

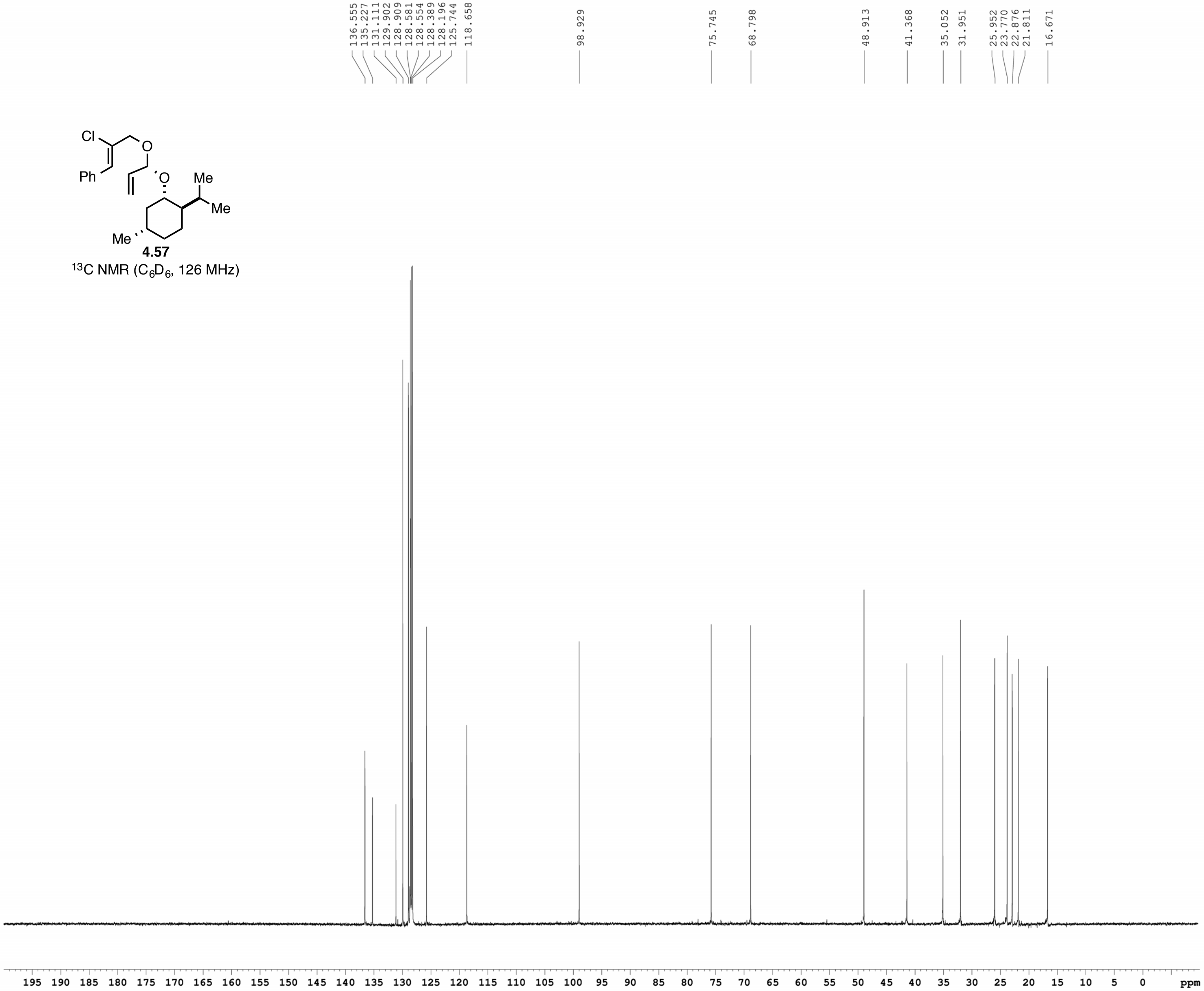
```
Current Data Parameters
NAME          PZ-2087-P
EXPNO                 1
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170223
Time              17.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT            C6D6
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                  4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2199853 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

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



4.57

^{13}C NMR (C_6D_6, 126 MHz)

```
Current Data Parameters
NAME          PZ-2087-P
EXPNO                 2
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170223
Time              17.09
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  110
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               4597.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

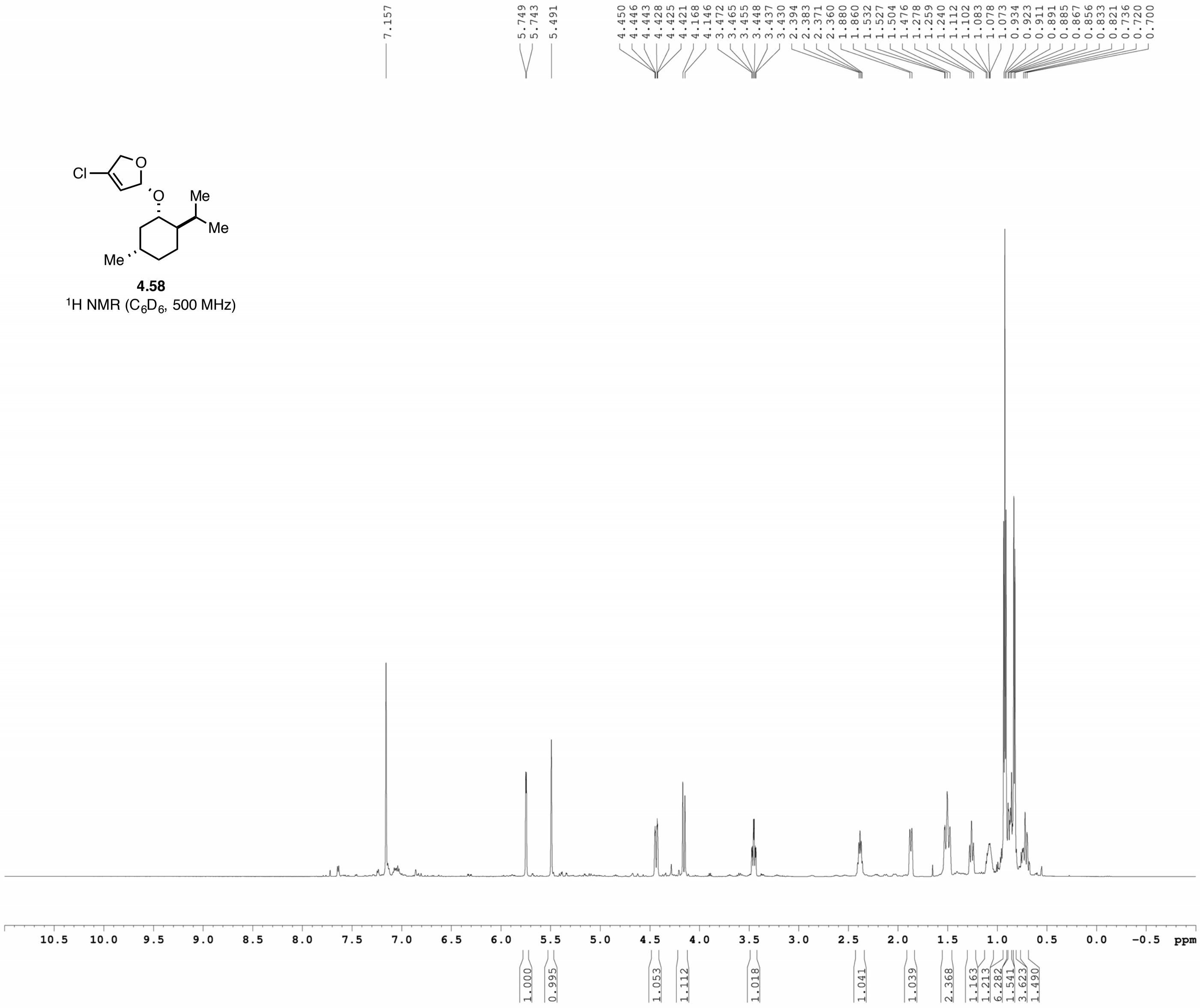
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803318 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



4.58

^{1}H NMR (C_6D_6, 500 MHz)

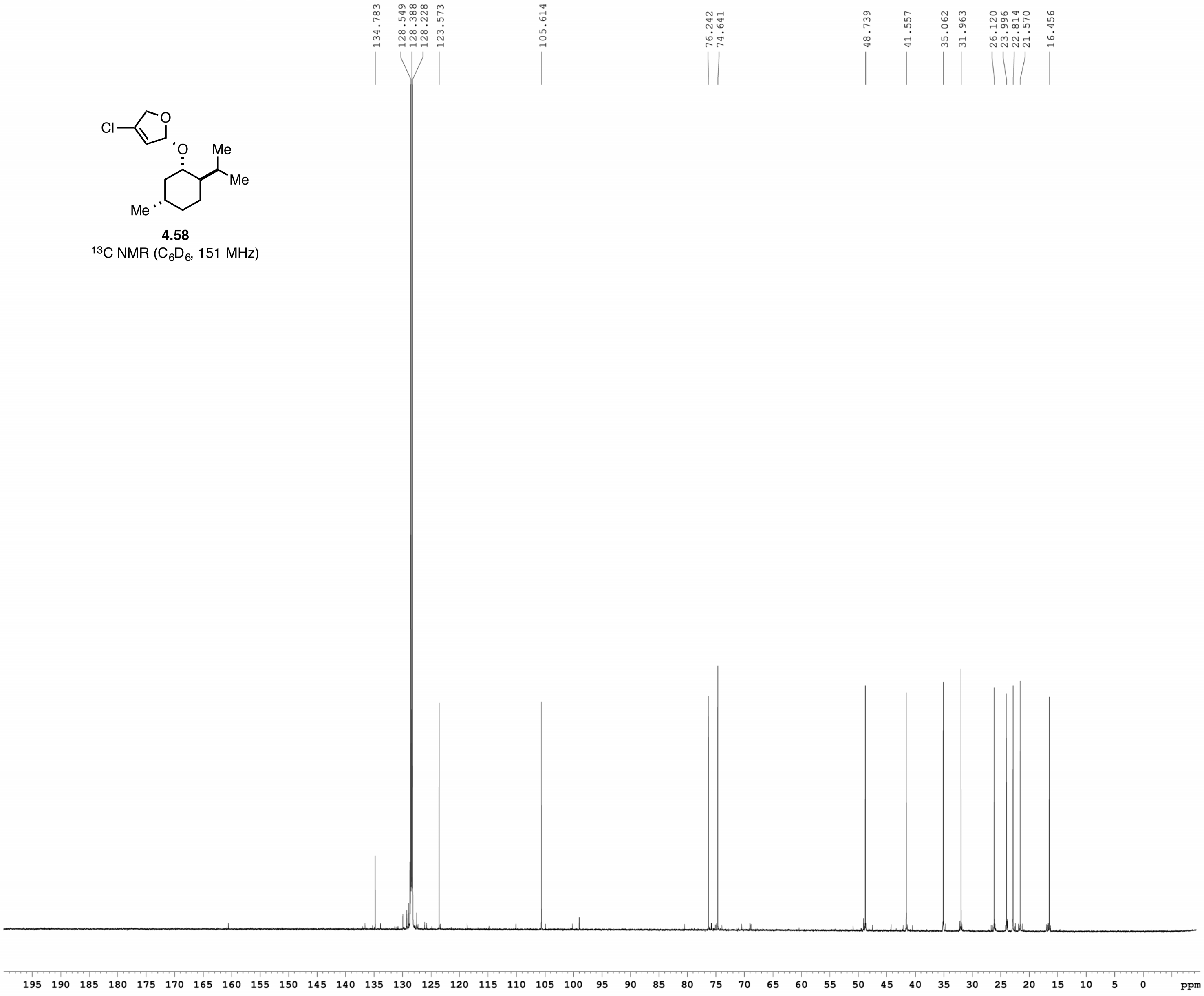
```
Current Data Parameters
NAME           PZ-2093-P
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20170225
Time               18.02
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT             C6D6
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

13C spectrum with 1H decoupling



4.58

^{13}C NMR (C_6D_6, 151 MHz)

```
Current Data Parameters
NAME           PZ-2093-P
EXPNO                  2
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170225
Time              18.07
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT            C6D6
NS                   91
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                 2050
DW               13.800 usec
DE                19.65 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

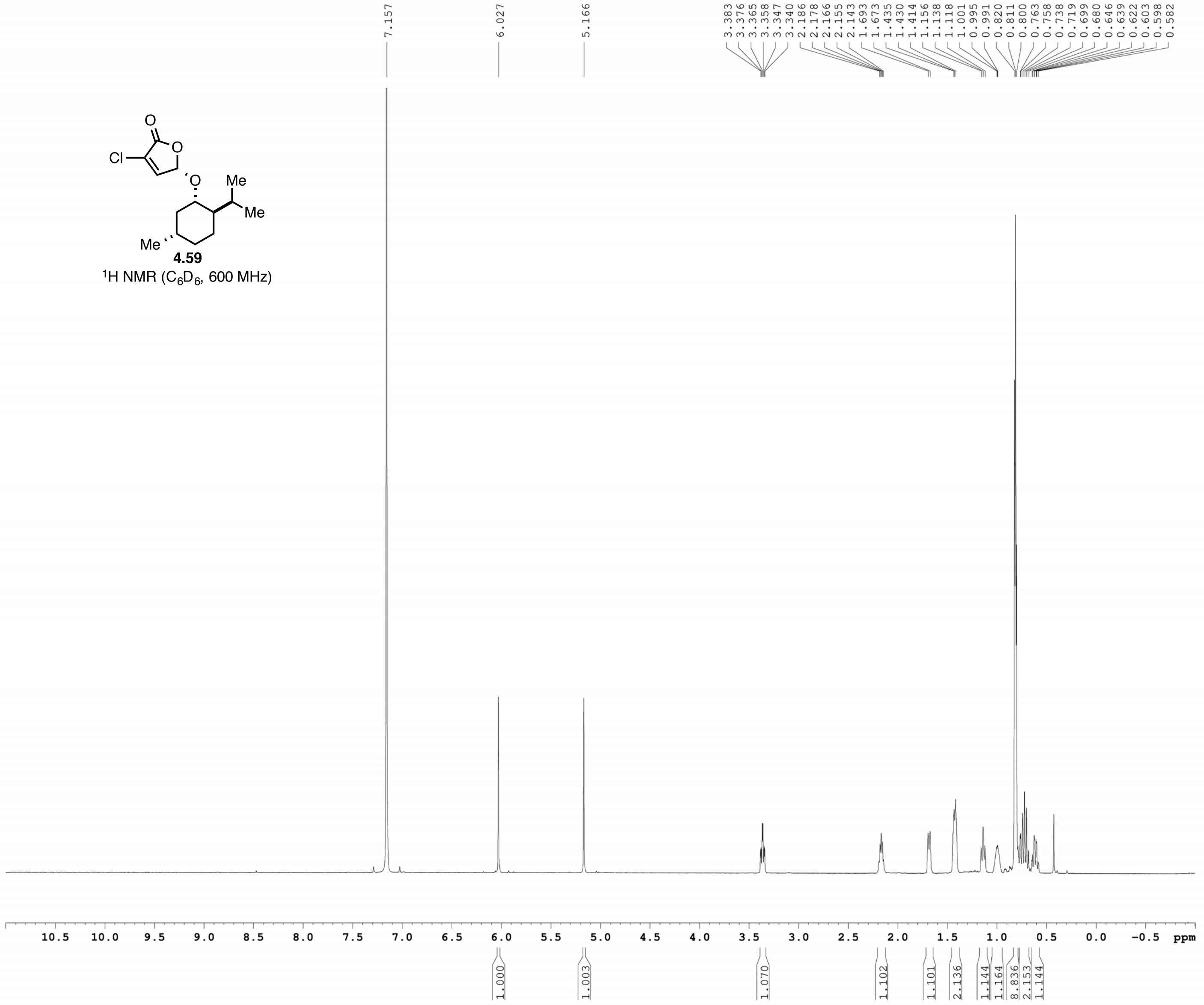
======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9027024 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

1H spectrum

4.59

^{1}H NMR (C_6D_6, 600 MHz)



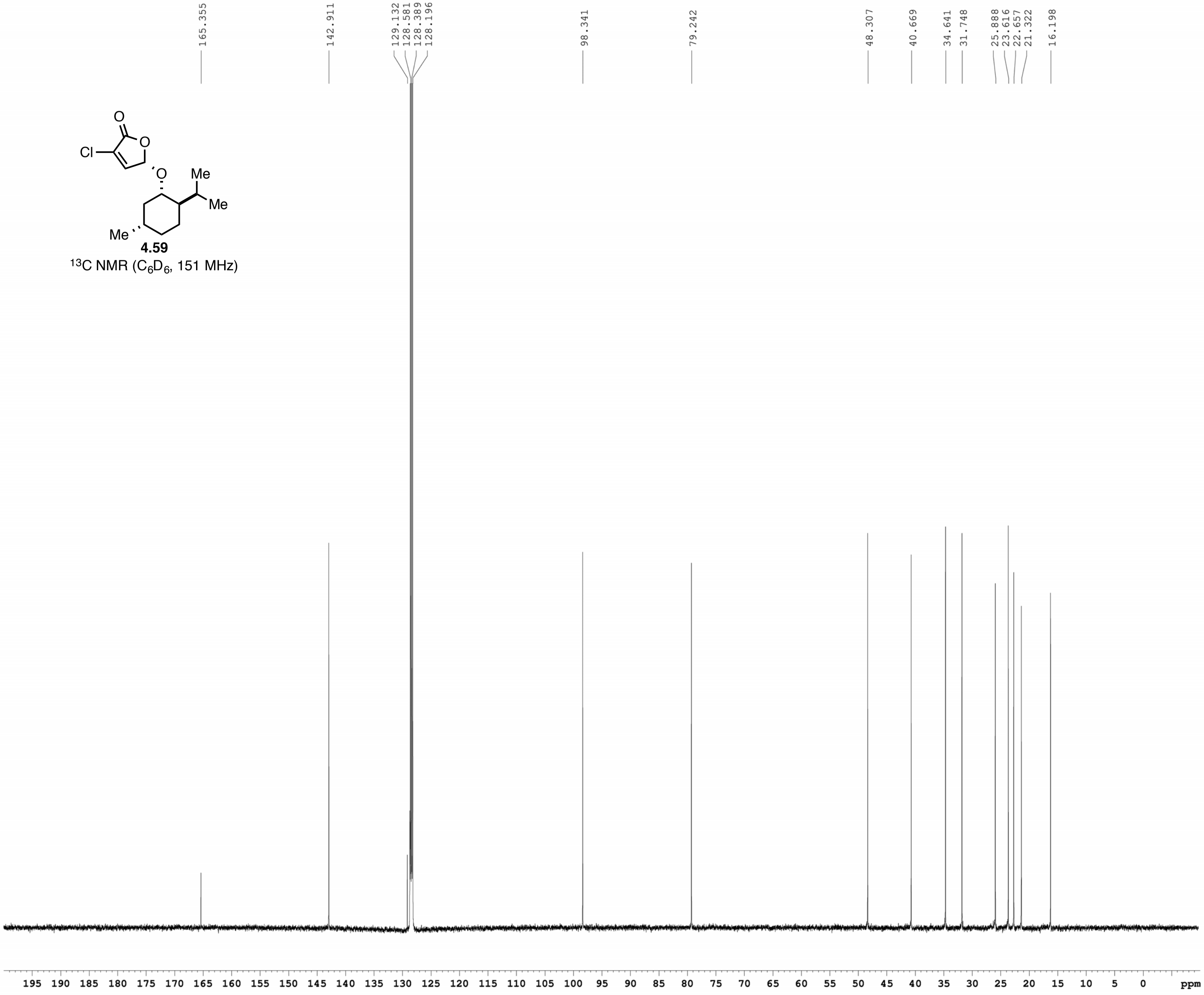
```
Current Data Parameters
NAME          PZ-2094-P
EXPNO                 1
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170227
Time              11.14
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT            C6D6
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                 40.3
DW               52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 =======
SFO1        600.1342009 MHz
NUC1                 1H
P1                12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                65536
SF          600.1300000 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

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



4.59

^{13}C NMR (C_6D_6, 151 MHz)

```
Current Data Parameters
NAME          PZ-2094-P
EXPNO                 4
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170412
Time              10.50
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT            C6D6
NS                  196
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 4096
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

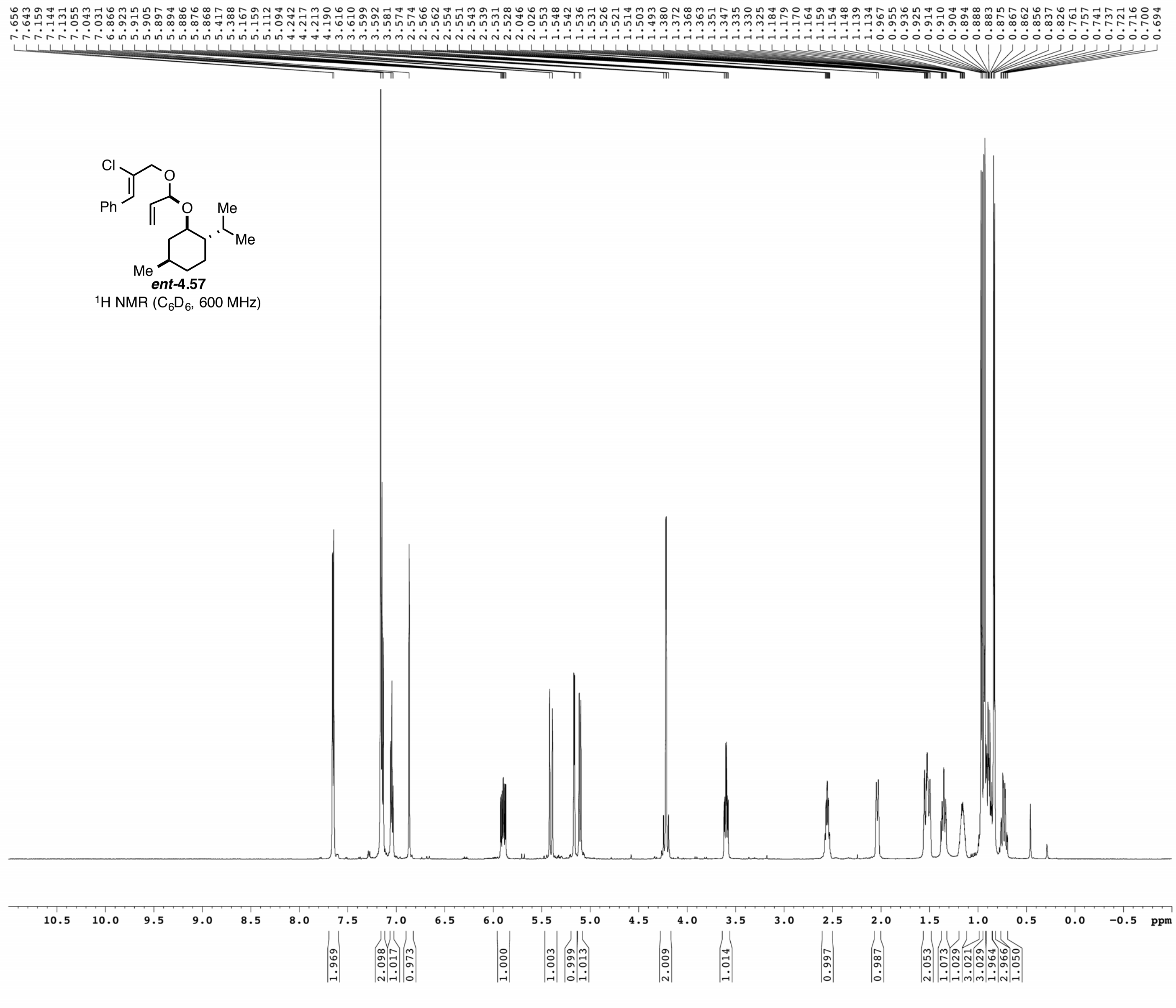
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803329 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-V-184



***ent*-4.57**
^{1}H NMR (C_6D_6, 600 MHz)

```
Current Data Parameters
NAME              YS-V-184
EXPNO                    2
PROCNO                   1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_             20170216
Time                  8.29
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   98074
SOLVENT               C6D6
NS                       8
DS                       2
SWH               9615.385 Hz
FIDRES            0.098042 Hz
AQ               5.0998478 sec
RG                      10
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1              0.10000000 sec
TD0                      1

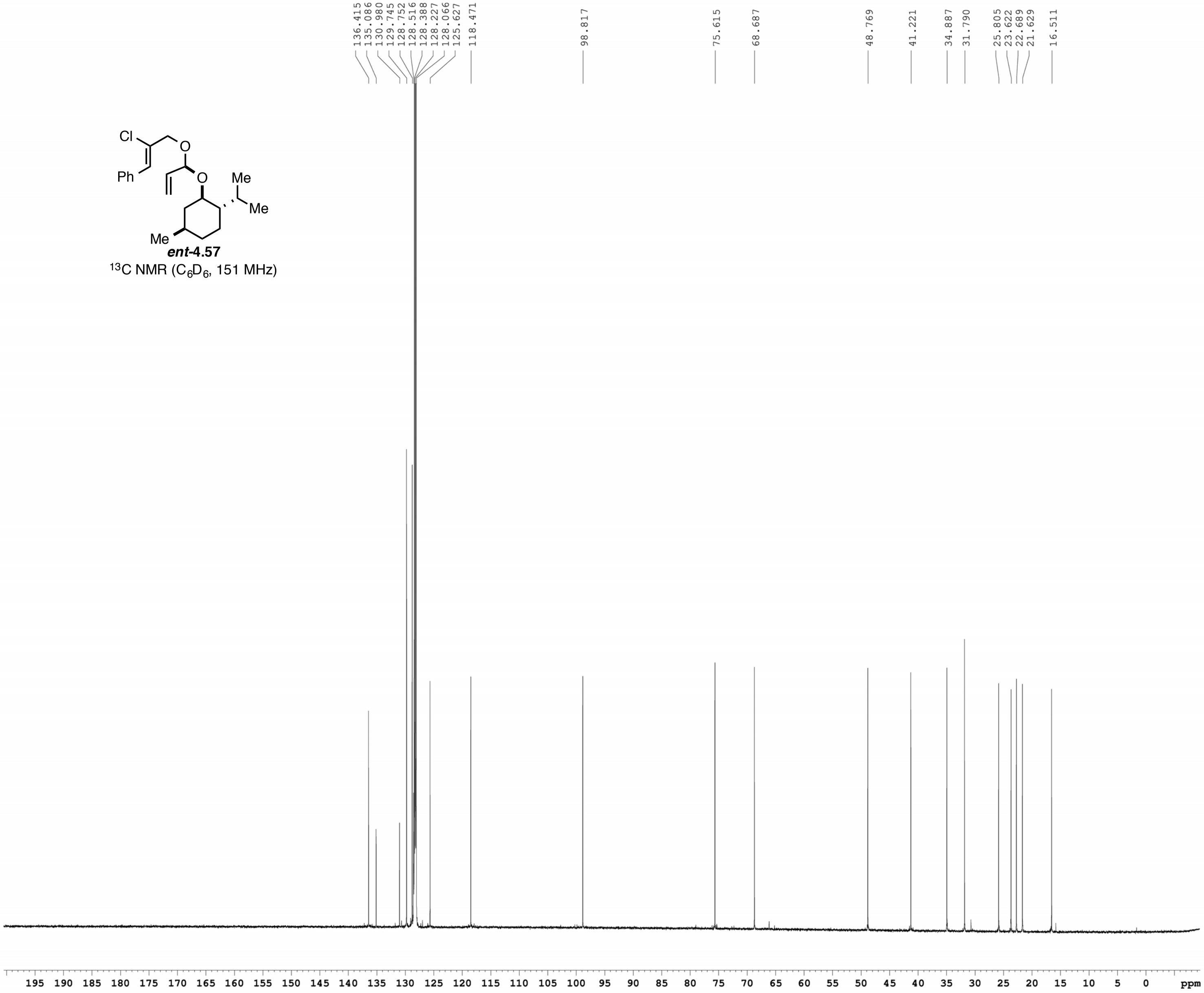
======== CHANNEL f1 ========
SFO1           600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           20.00000000 W

F2 - Processing parameters
SI                   65536
SF             600.1299982 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-V-184

***ent*-4.57**

^{13}C NMR (C_6D_6, 151 MHz)



```
Current Data Parameters
NAME             YS-V-184
EXPNO                   4
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

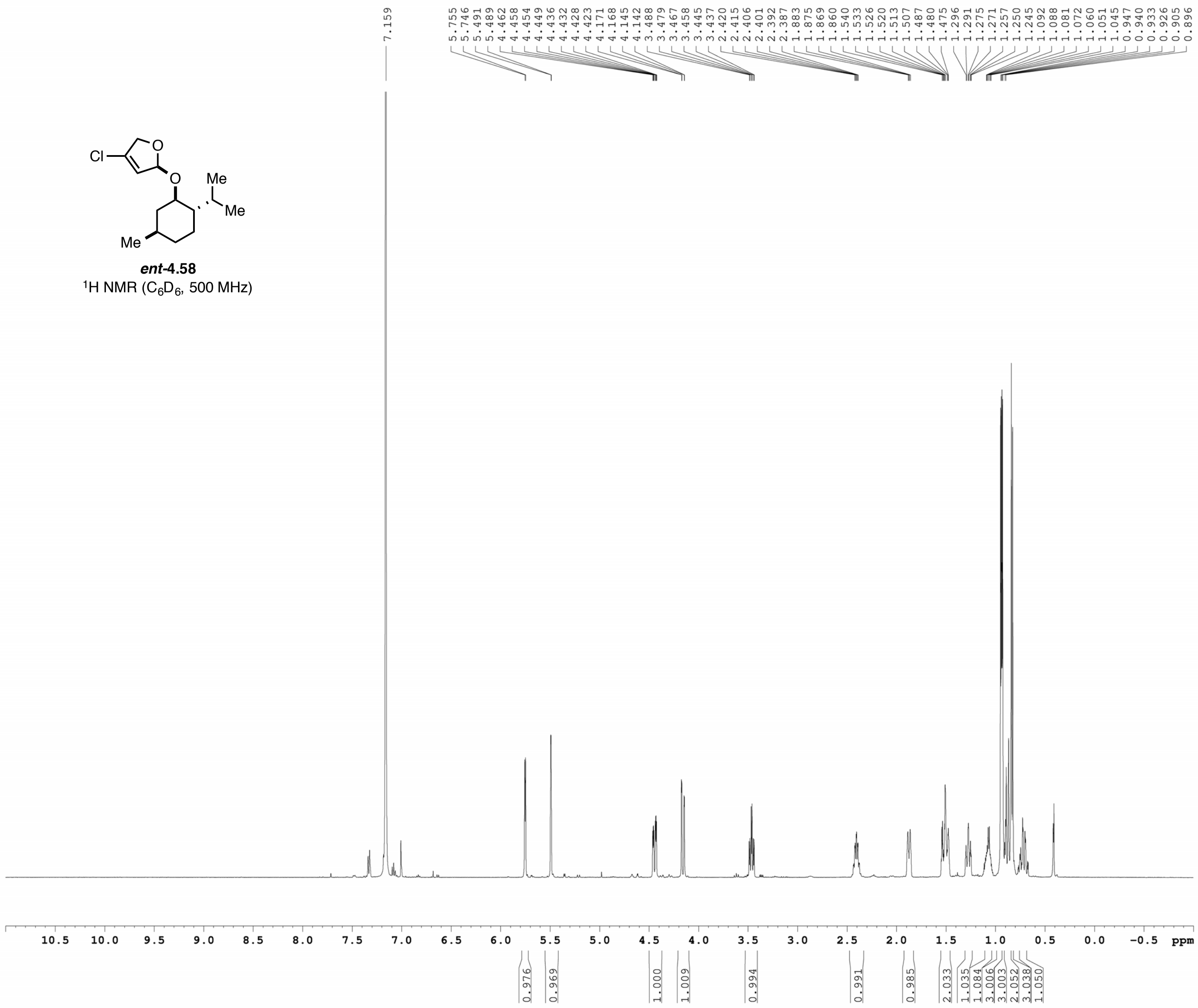
F2 - Acquisition Parameters
Date_            20170215
Time                17.47
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT             C6D6
NS                   196
DS                     1
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF           150.9027280 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

YS-V-185



***ent*-4.58**

^{1}H NMR (C_6D_6, 500 MHz)

```
Current Data Parameters
NAME            YS-V-185
EXPNO                 10
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20170118
Time               14.41
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH          8012.820 Hz
FIDRES       0.098043 Hz
AQ          5.0998273 sec
RG                   7.1
DW            62.400 usec
DE              6.00 usec
TE               298.0 K
D1        0.10000000 sec
MCREST   0 sec
MCWRK     0.01500000 sec

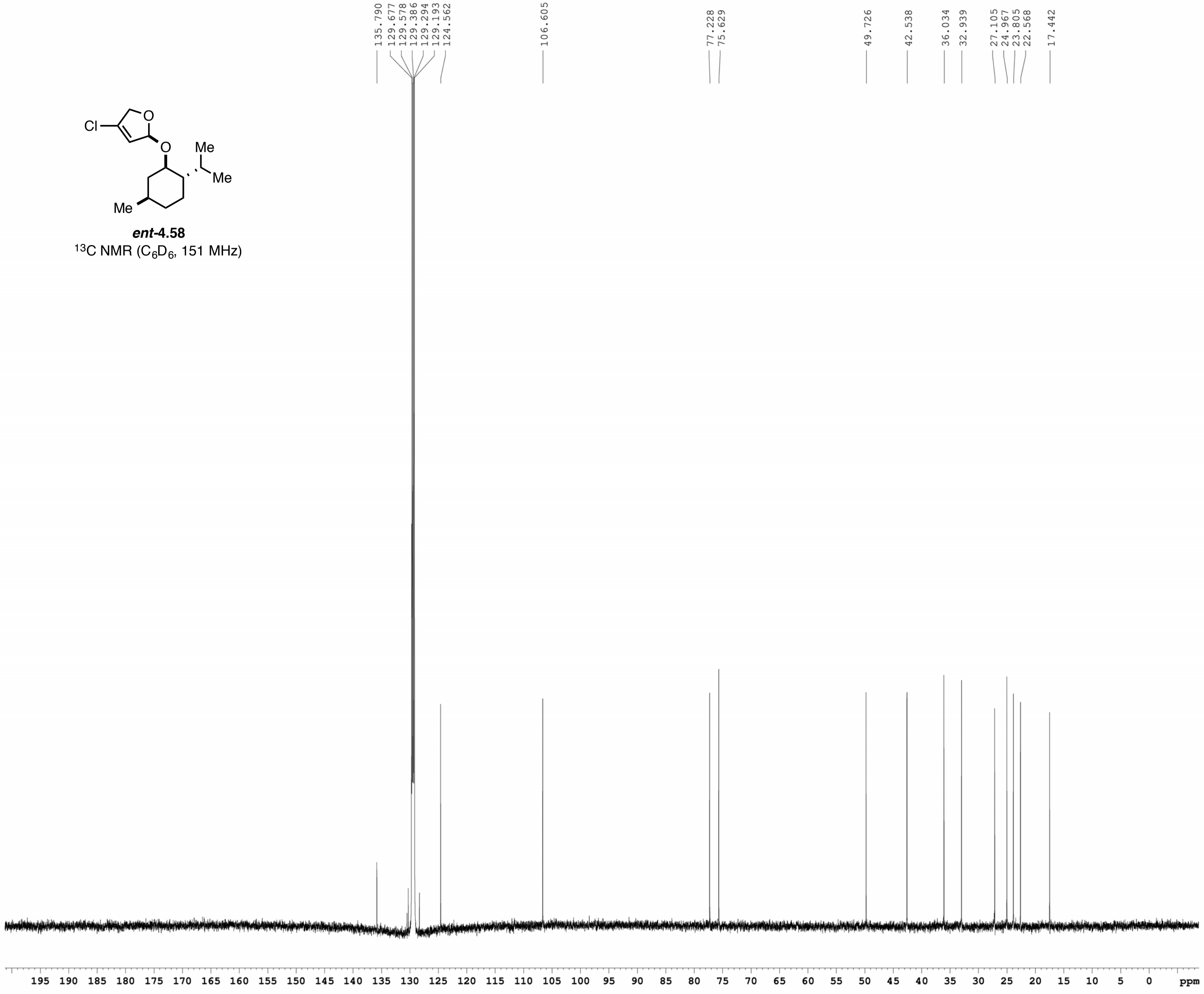
======== CHANNEL f1 ========
NUC1                  1H
P1              7.50 usec
PL1              1.60 dB
SFO1      500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF        500.2200008 MHz
WDW                   EM
SSB      0
LB               0.30 Hz
GB       0
PC                  1.00
```

YS-V-185

***ent*-4.58**

^{13}C NMR (C_6D_6, 151 MHz)



```
Current Data Parameters
NAME          YS-V-185
EXPNO               11
PROCNO               1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170118
Time              14.48
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  632
DS                    1
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

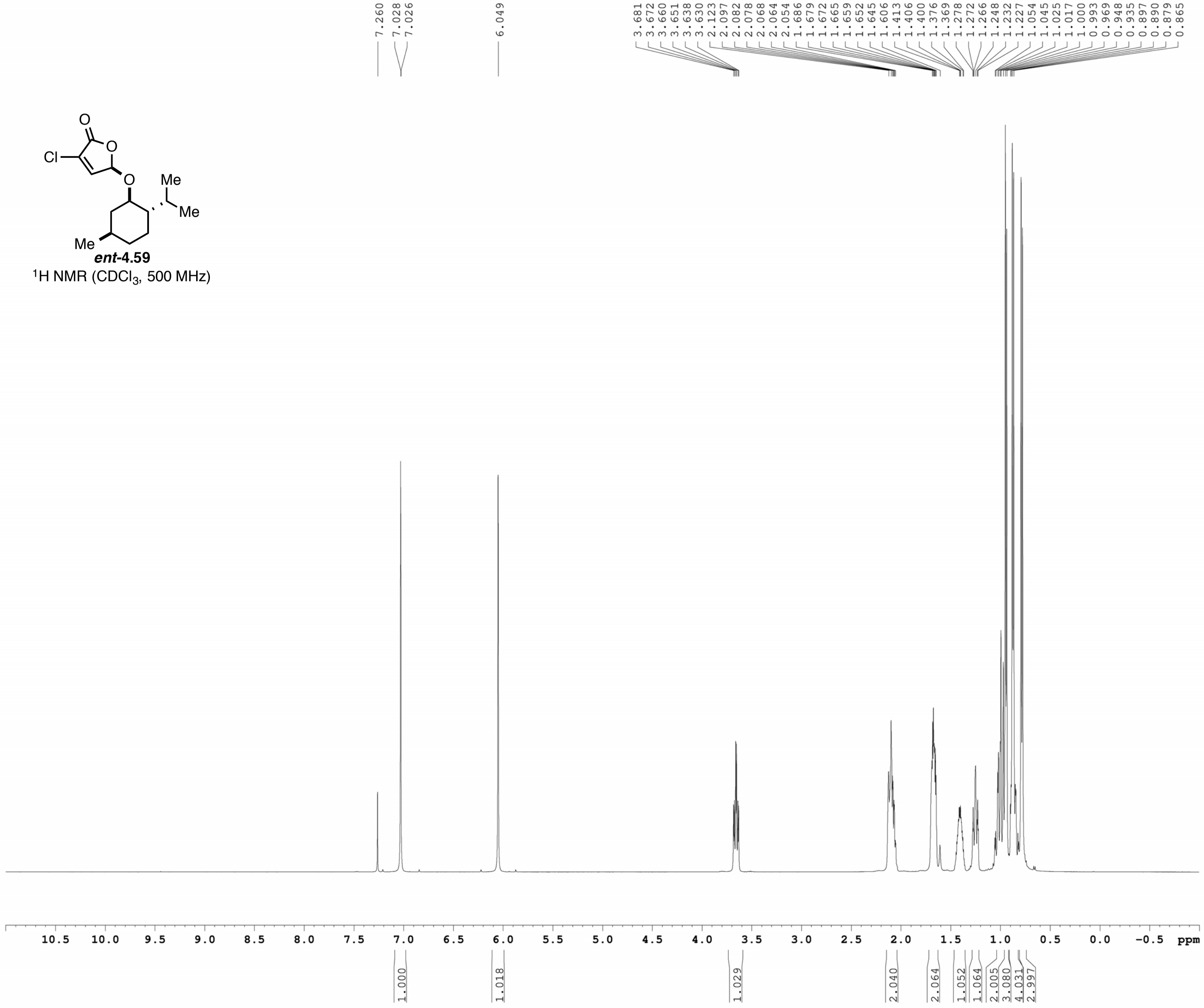
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7802077 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-V-175

***ent*-4.59**

^{1}H NMR (CDCl$_3$, 500 MHz)



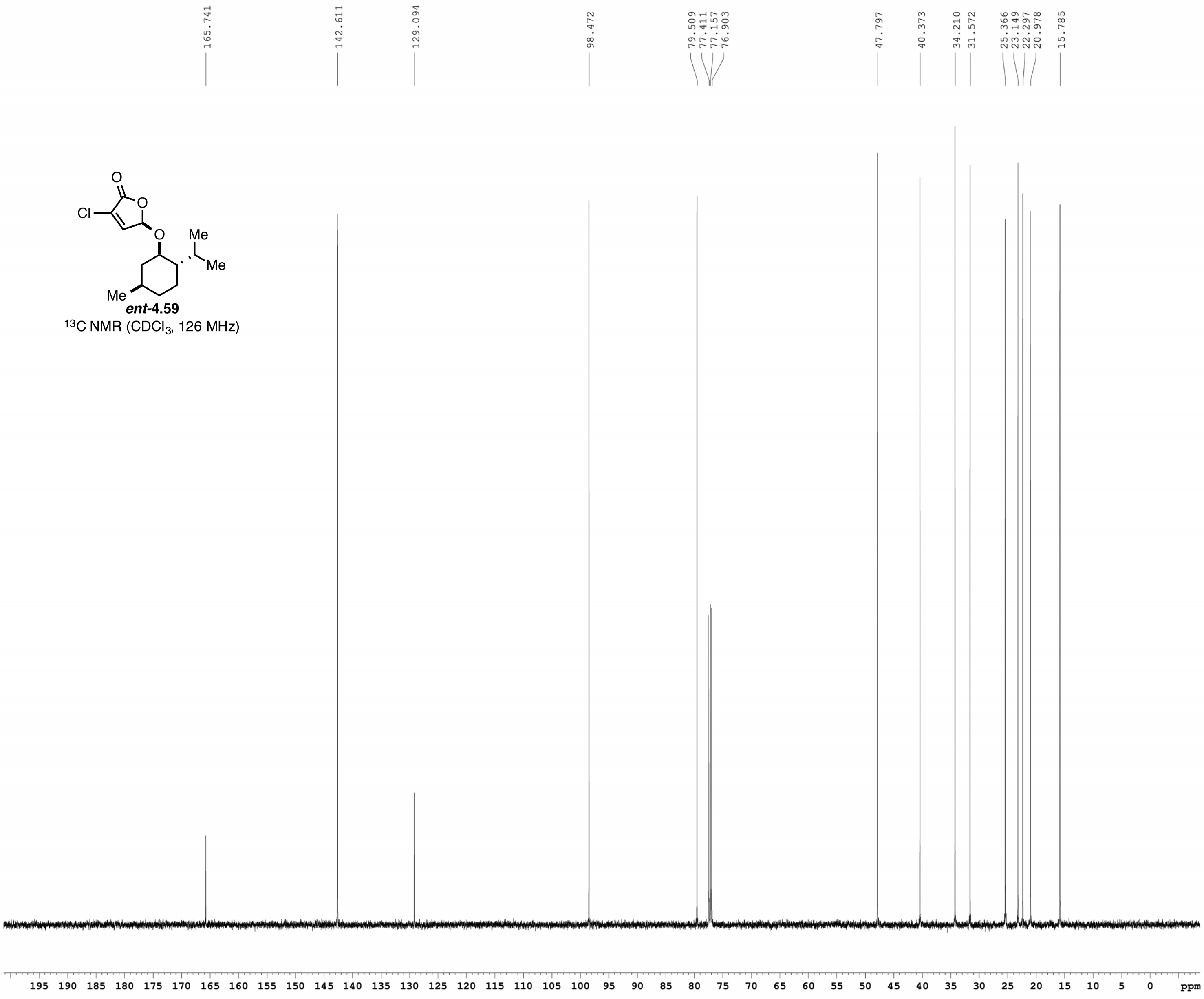
```
Current Data Parameters
NAME            YS-V-175
EXPNO                  2
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20161215
Time               15.20
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200305 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-175



***ent*-4.59**

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME             YS-V-175
EXPNO                   3
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20161215
Time                15.23
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   4096
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

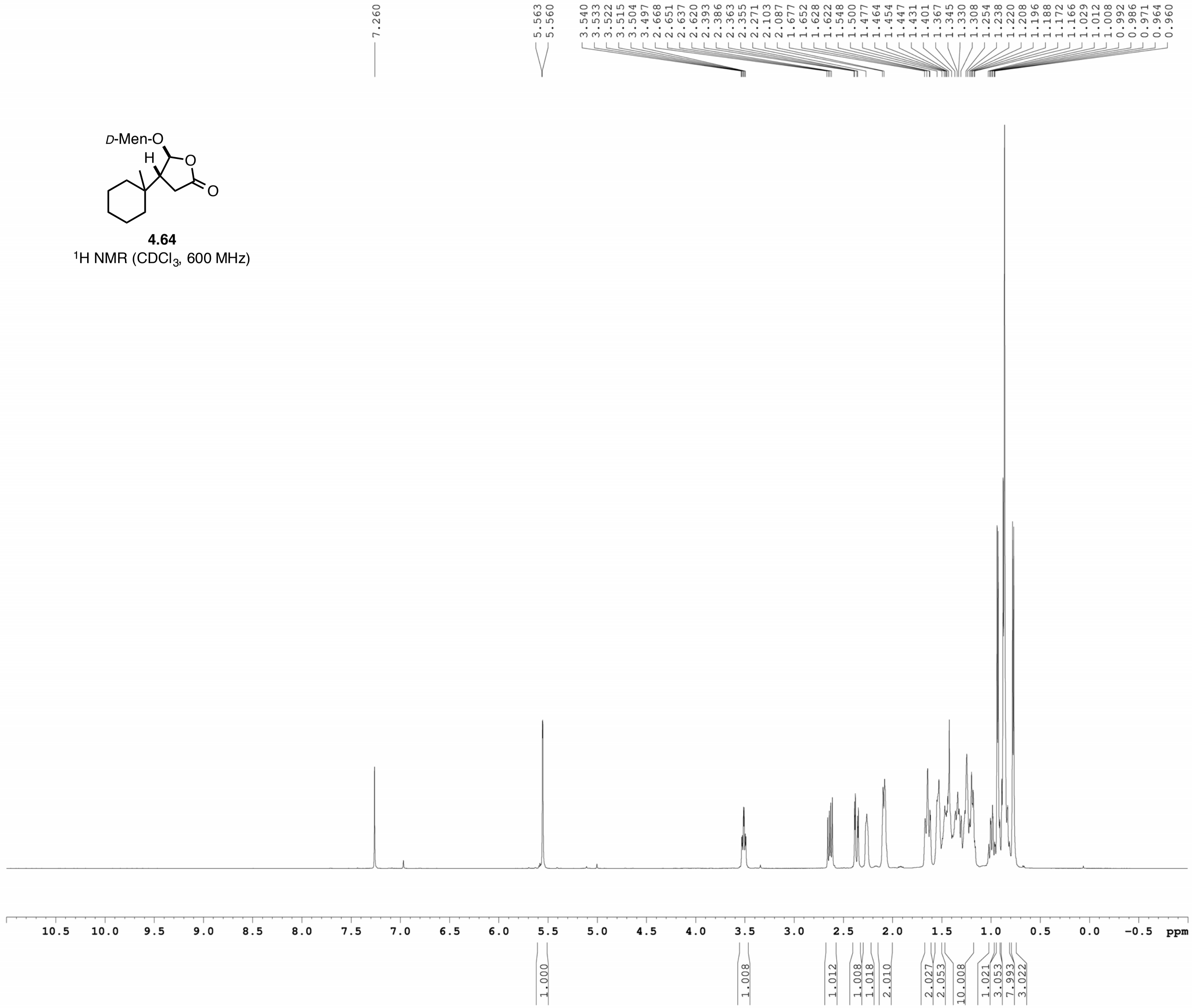
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1         125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804103 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   2.00
```

YS-V-252B



4.64

^{1}H NMR (CDCl$_3$, 600 MHz)

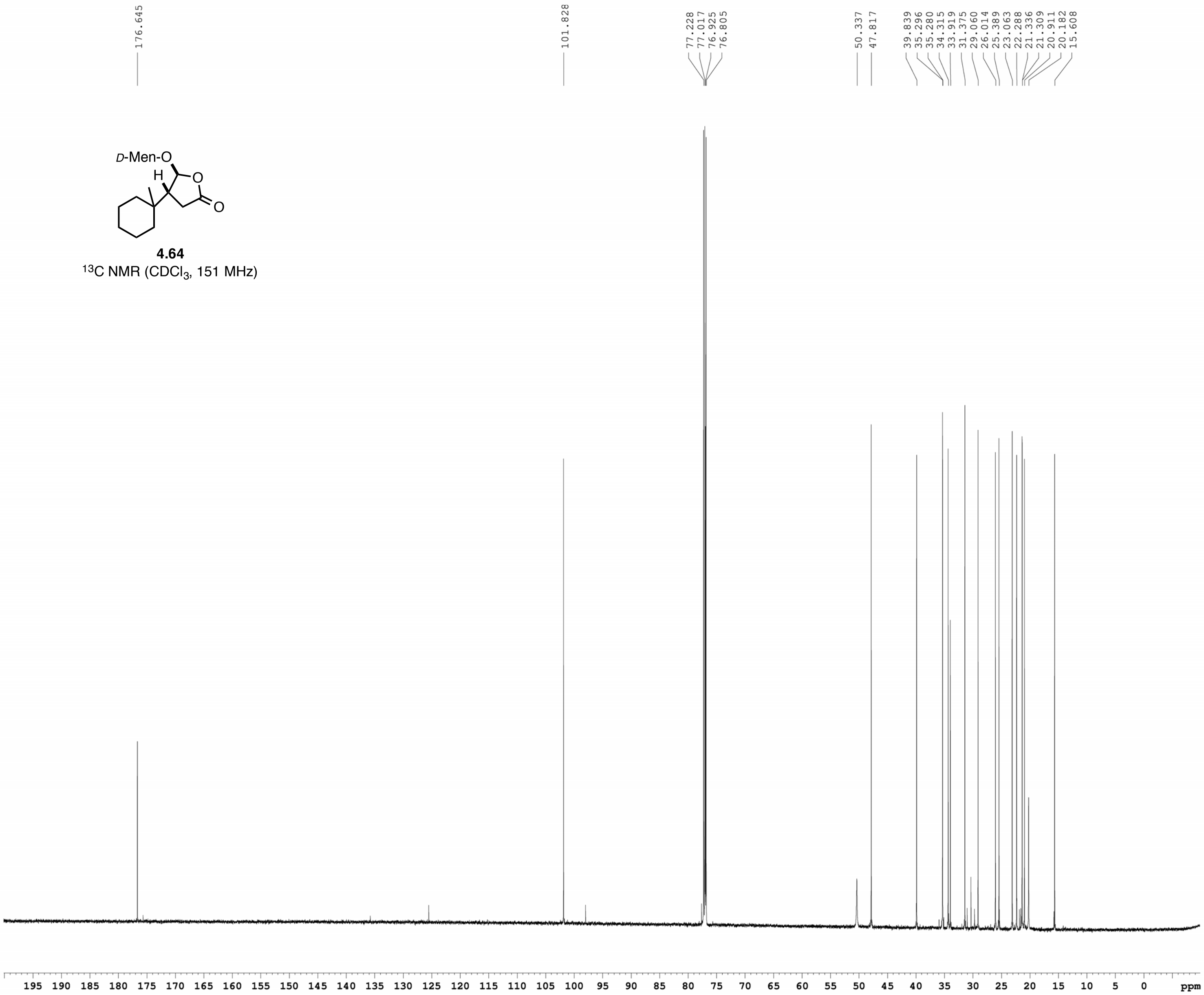
```
Current Data Parameters
NAME           YS-V-252B
EXPNO                  2
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20170310
Time                8.40
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300348 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-252B



4.64
^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME          YS-V-252B
EXPNO                 3
PROCNO                1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170310
Time               8.45
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG         zgdc30
TD                65536
SOLVENT           CDCl3
NS                  216
DS                    1
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9043968 sec
RG                 2050
DW               13.800 usec
DE                19.65 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

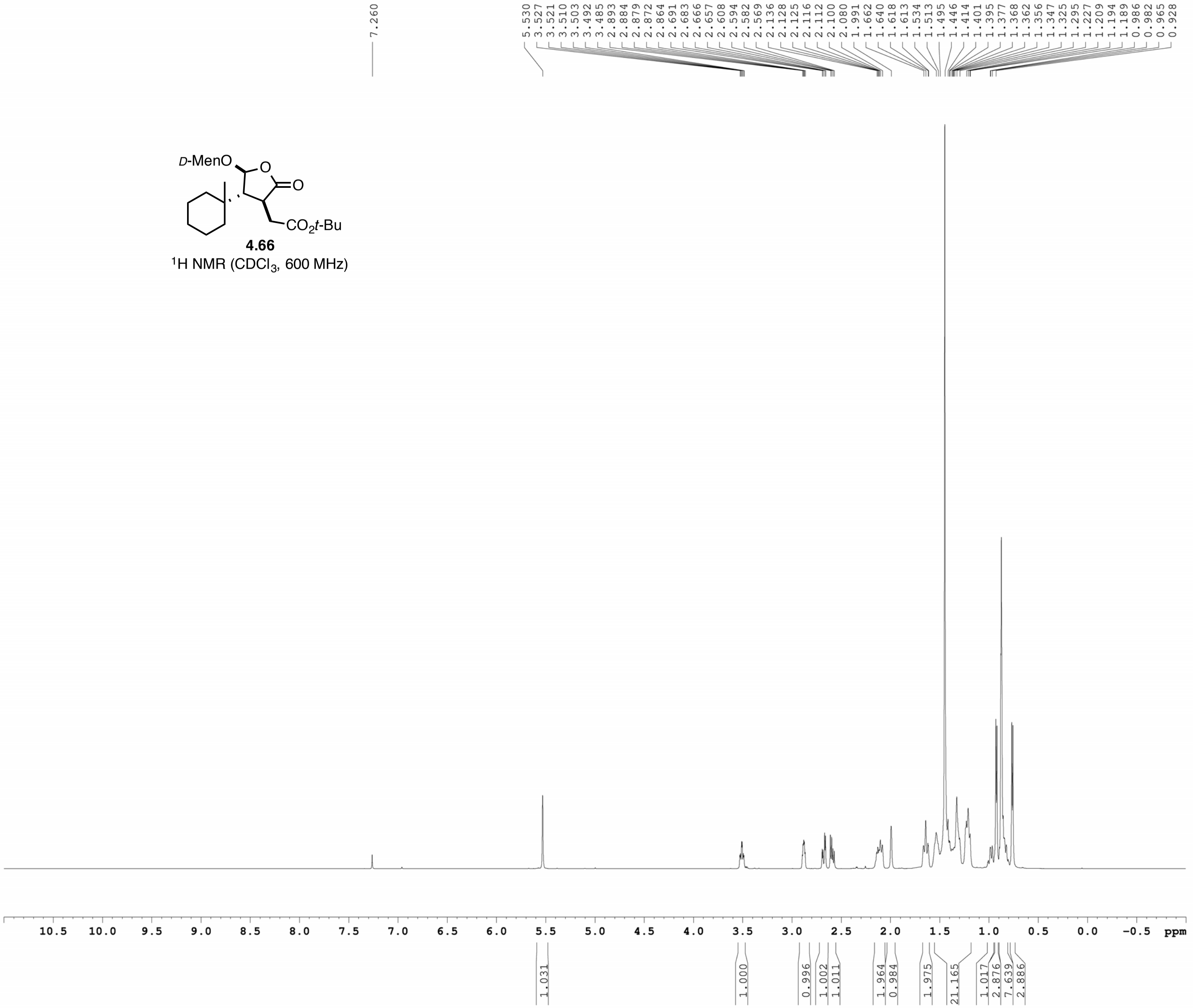
======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9028177 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

YS-V-256

4.66

^{1}H NMR ($CDCl_3$, 600 MHz)



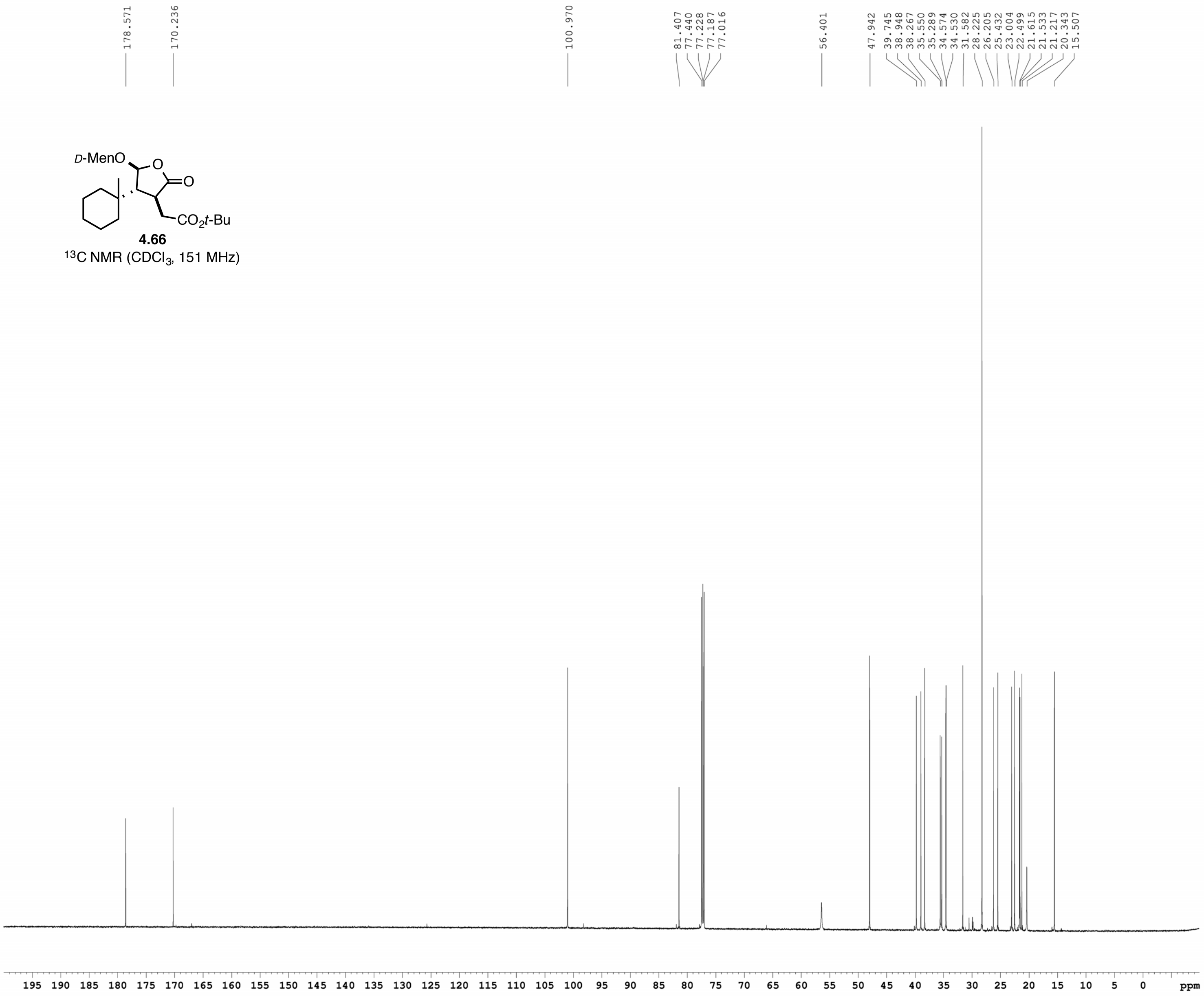
```
Current Data Parameters
NAME            YS-V-256
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170311
Time                9.07
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300346 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-256



4.66

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME              YS-V-256
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170311
Time                  9.11
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     200
DS                       1
SWH              36231.883 Hz
FIDRES            0.552855 Hz
AQ               0.9043968 sec
RG                    2050
DW                  13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1              0.40000001 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           150.9194080 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           64.00000000 W

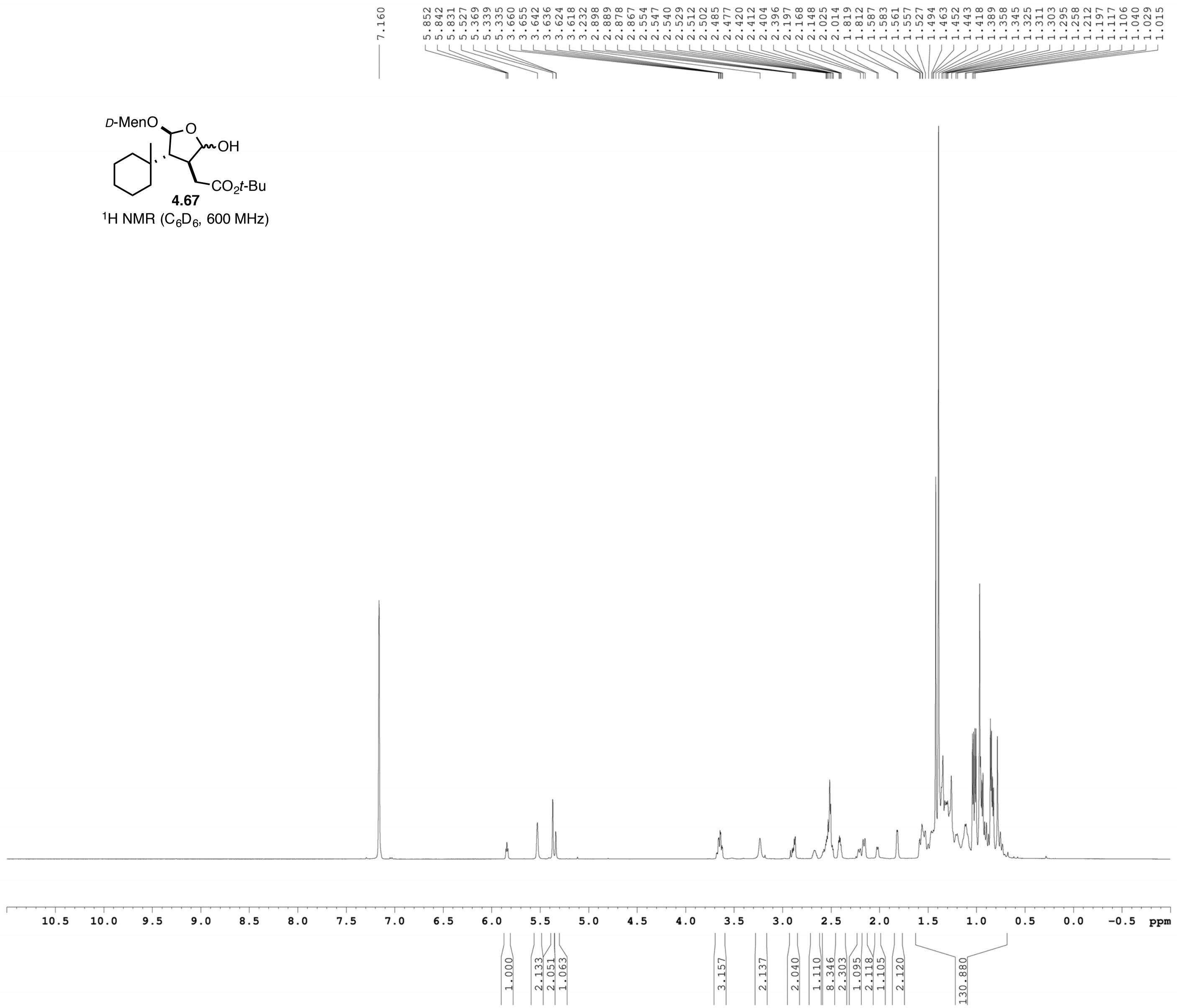
======== CHANNEL f2 ========
SFO2           600.1330010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                   65536
SF             150.9027868 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.00
```

YS-V-257

4.67

^{1}H NMR (C_6D_6, 600 MHz)



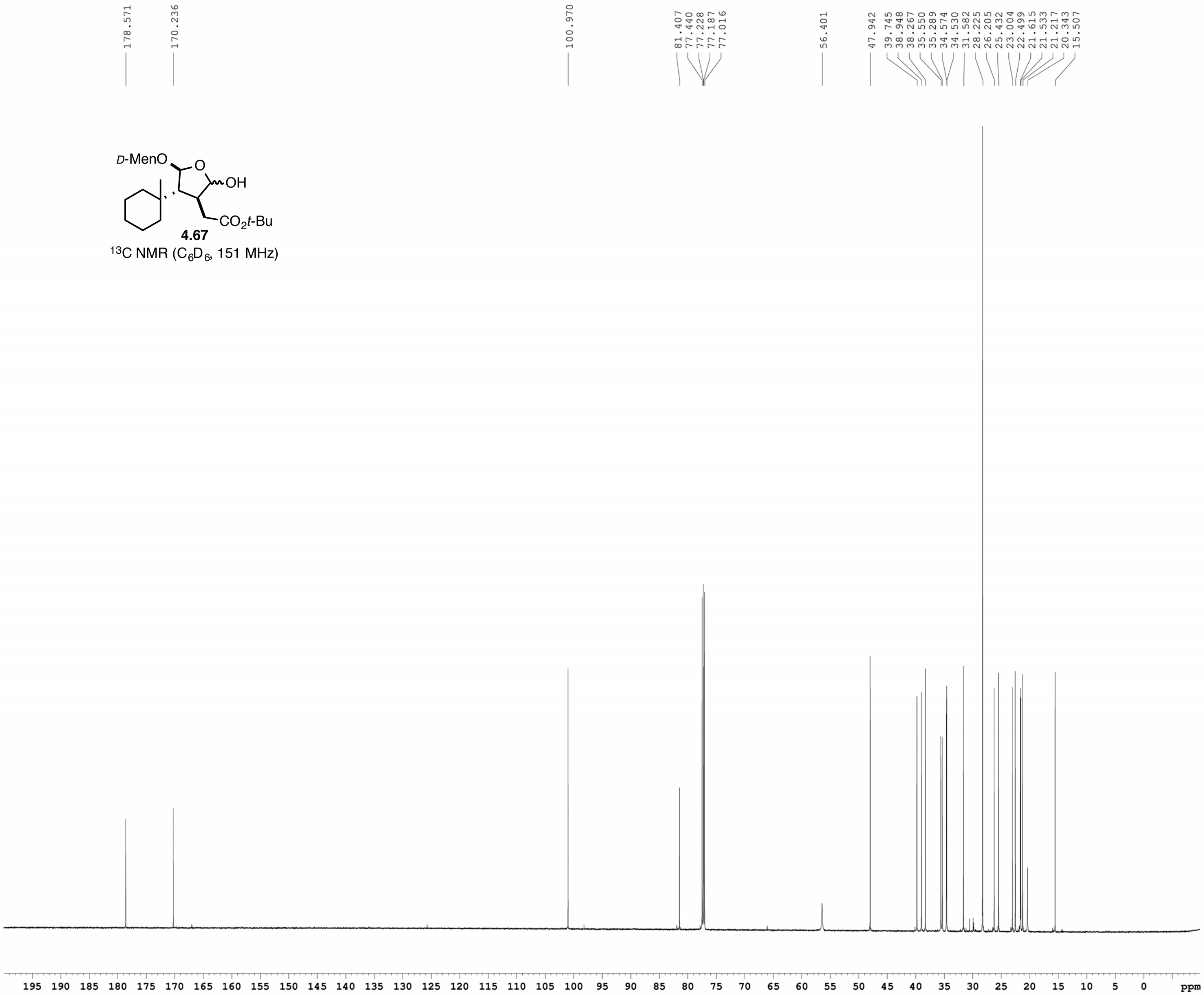
```
Current Data Parameters
NAME              YS-V-257
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170313
Time                 16.39
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   98074
SOLVENT               C6D6
NS                       8
DS                       2
SWH               9615.385 Hz
FIDRES            0.098042 Hz
AQ               5.0998478 sec
RG                      10
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           20.00000000 W

F2 - Processing parameters
SI                   65536
SF            600.1299976 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-V-256



4.67

^{13}C NMR (C_6D_6, 151 MHz)

```
Current Data Parameters
NAME             YS-V-256
EXPNO                   2
PROCNO                  1

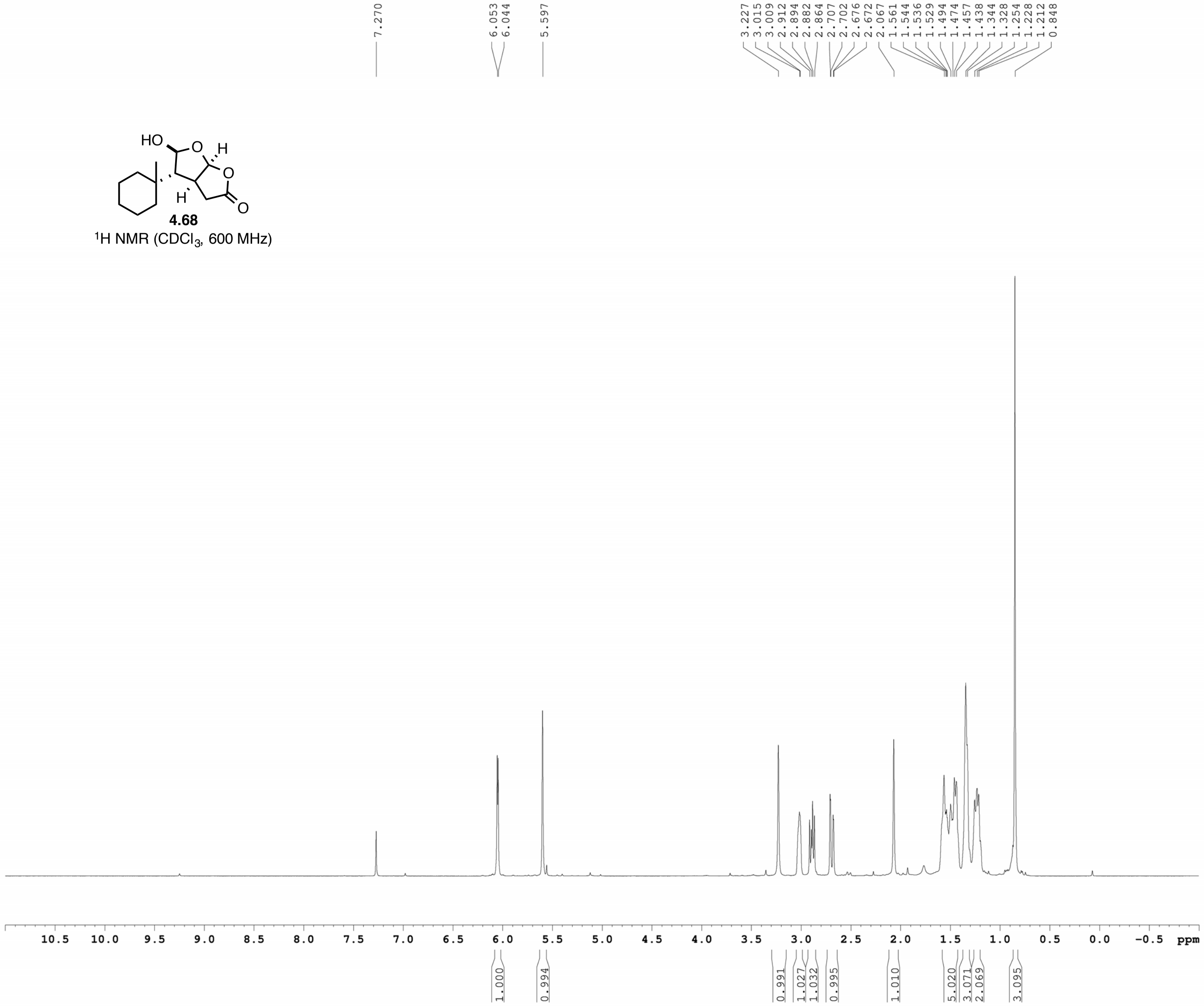
F2 - Acquisition Parameters
Date_            20170311
Time                 9.11
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    200
DS                      1
SWH             36231.883 Hz
FIDRES           0.552855 Hz
AQ              0.9043968 sec
RG                   2050
DW                 13.800 usec
DE                  19.65 usec
TE                  298.0 K
D1             0.40000001 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                  65536
SF            150.9027868 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

YS-V-268



4.68

^{1}H NMR ($CDCl_3$, 600 MHz)

```
Current Data Parameters
NAME            YS-V-268
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20170323
Time               14.57
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     1
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.1 K
D1            0.10000000 sec
TD0                    1

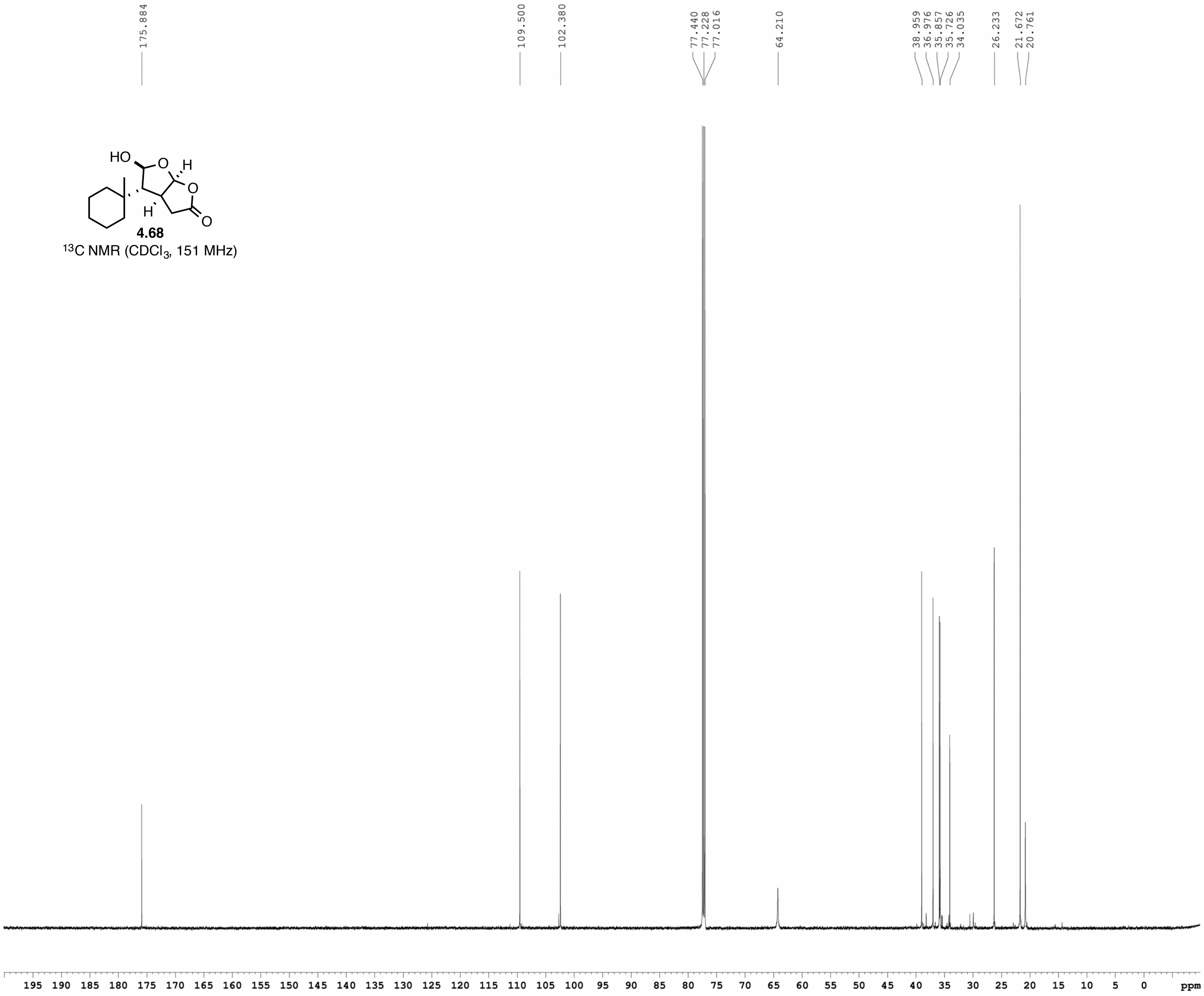
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300286 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-268

4.68

^{13}C NMR (CDCl$_3$, 151 MHz)



```
Current Data Parameters
NAME              YS-V-268
EXPNO                    2
PROCNO                   1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_             20170323
Time                 15.00
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     280
DS                       1
SWH              36231.883 Hz
FIDRES            0.552855 Hz
AQ               0.9043968 sec
RG                    2050
DW                  13.800 usec
DE                   19.65 usec
TE                   298.0 K
D1              0.40000001 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           64.00000000 W

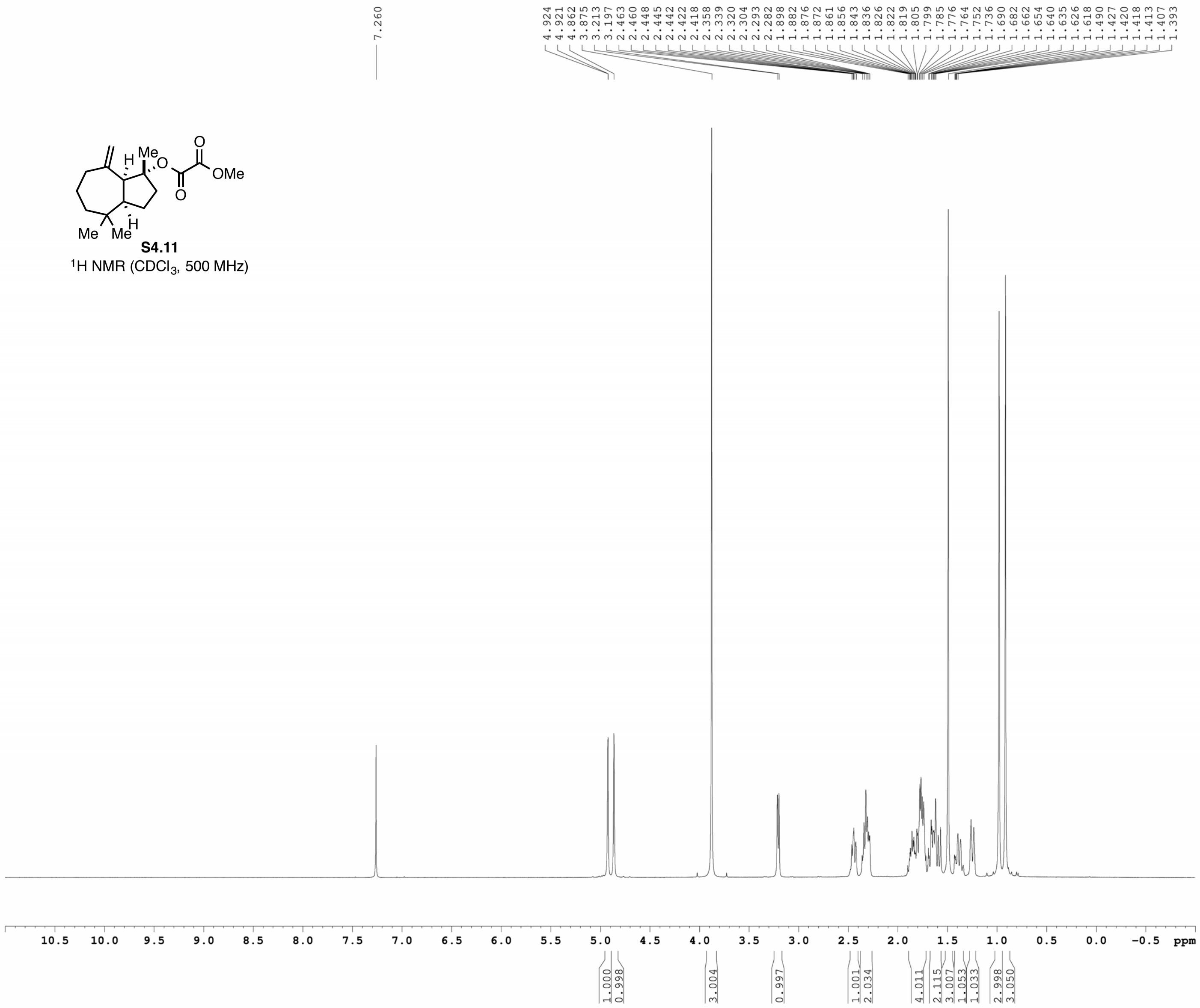
======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           20.00000000 W
PLW12           0.36000001 W

F2 - Processing parameters
SI                   65536
SF           150.9027867 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.00
```

YS-V-202

S4.11

^{1}H NMR (CDCl$_3$, 500 MHz)



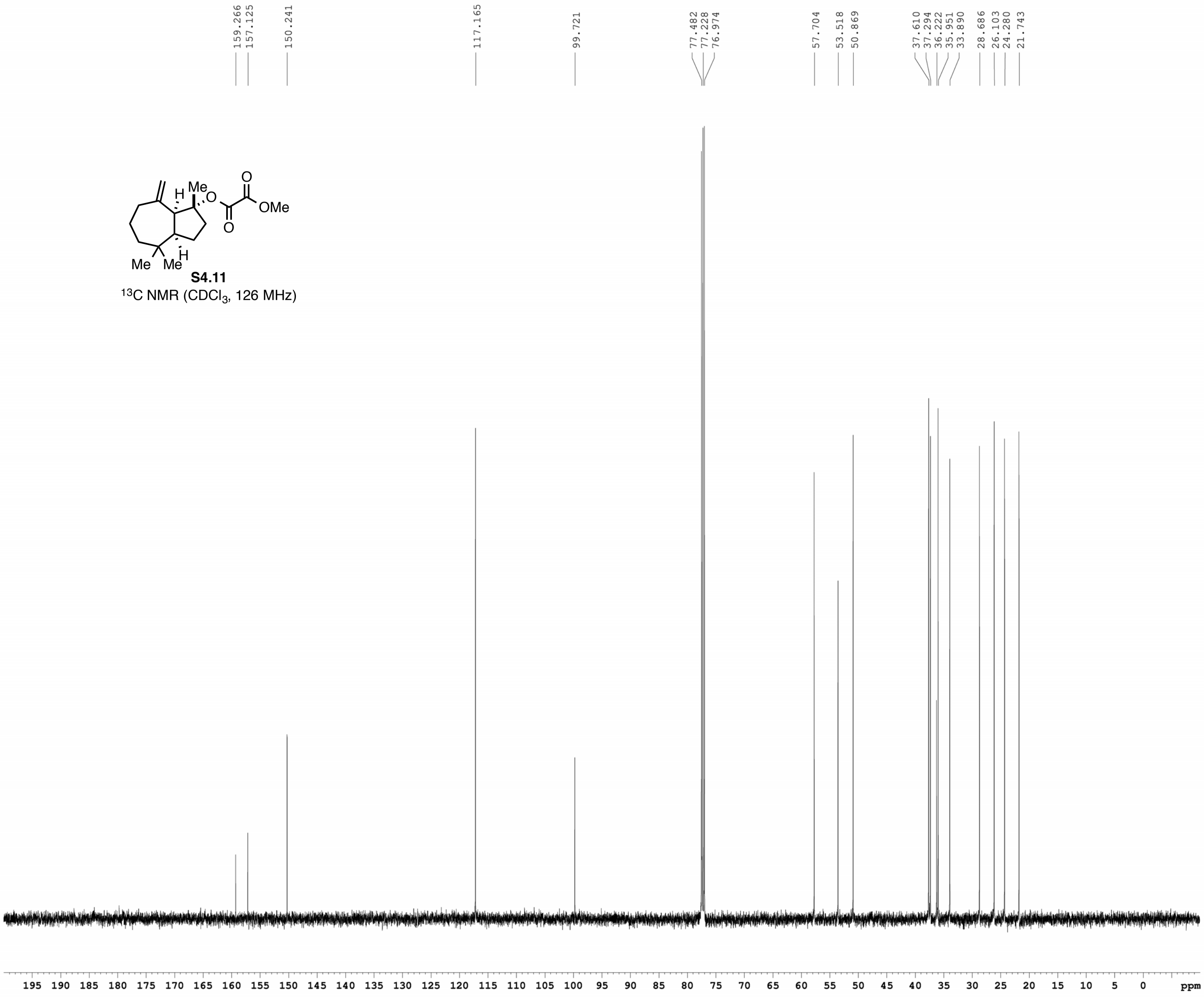
```
Current Data Parameters
NAME             YS-V-202
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170119
Time                17.07
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  80126
SOLVENT             CDCl3
NS                      8
DS                      1
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                      5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200316 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-202



S4.11

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            YS-V-202
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170119
Time               17.10
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   496
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

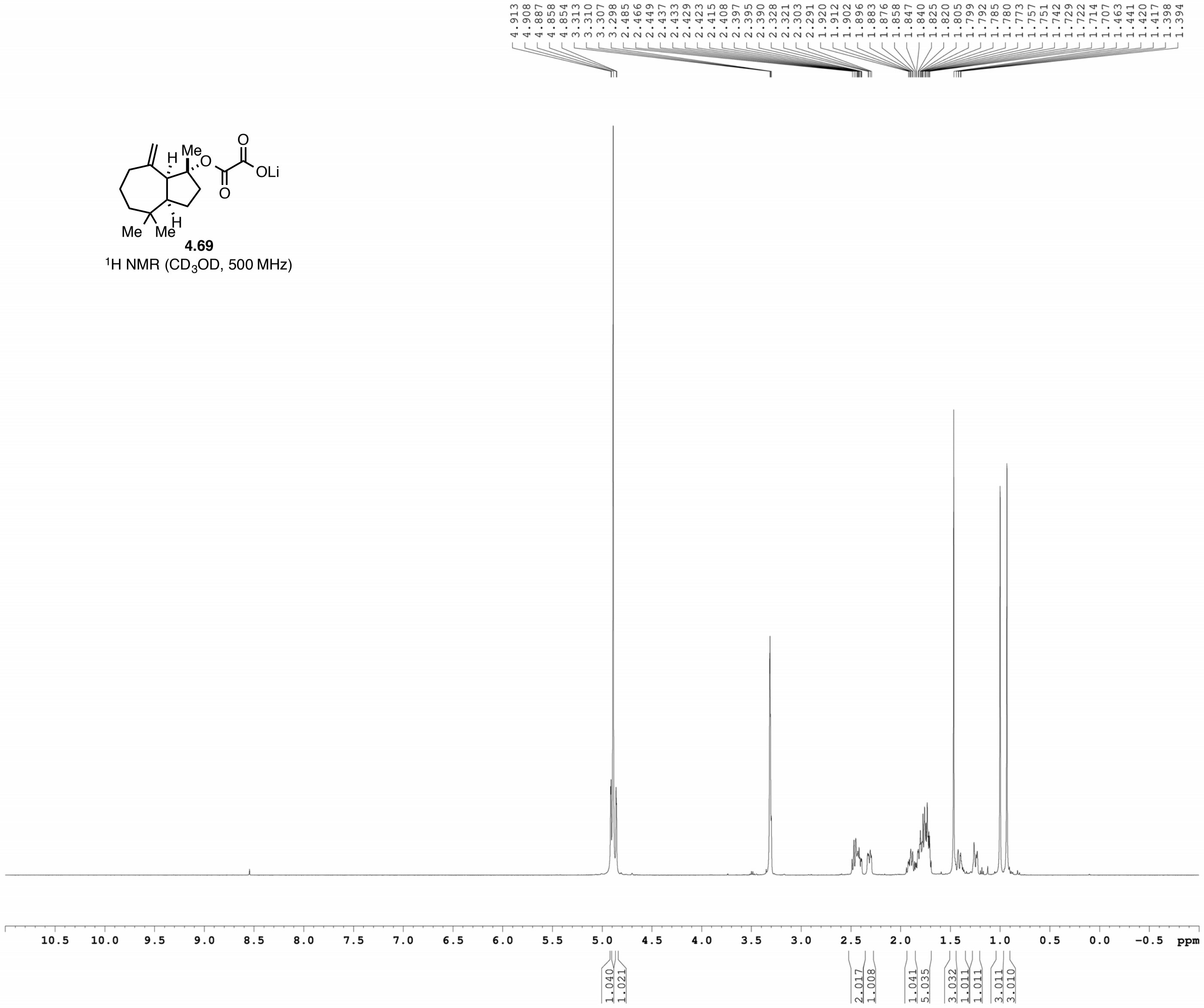
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803994 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

YS-V-203



4.69

^{1}H NMR (CD_3OD, 500 MHz)

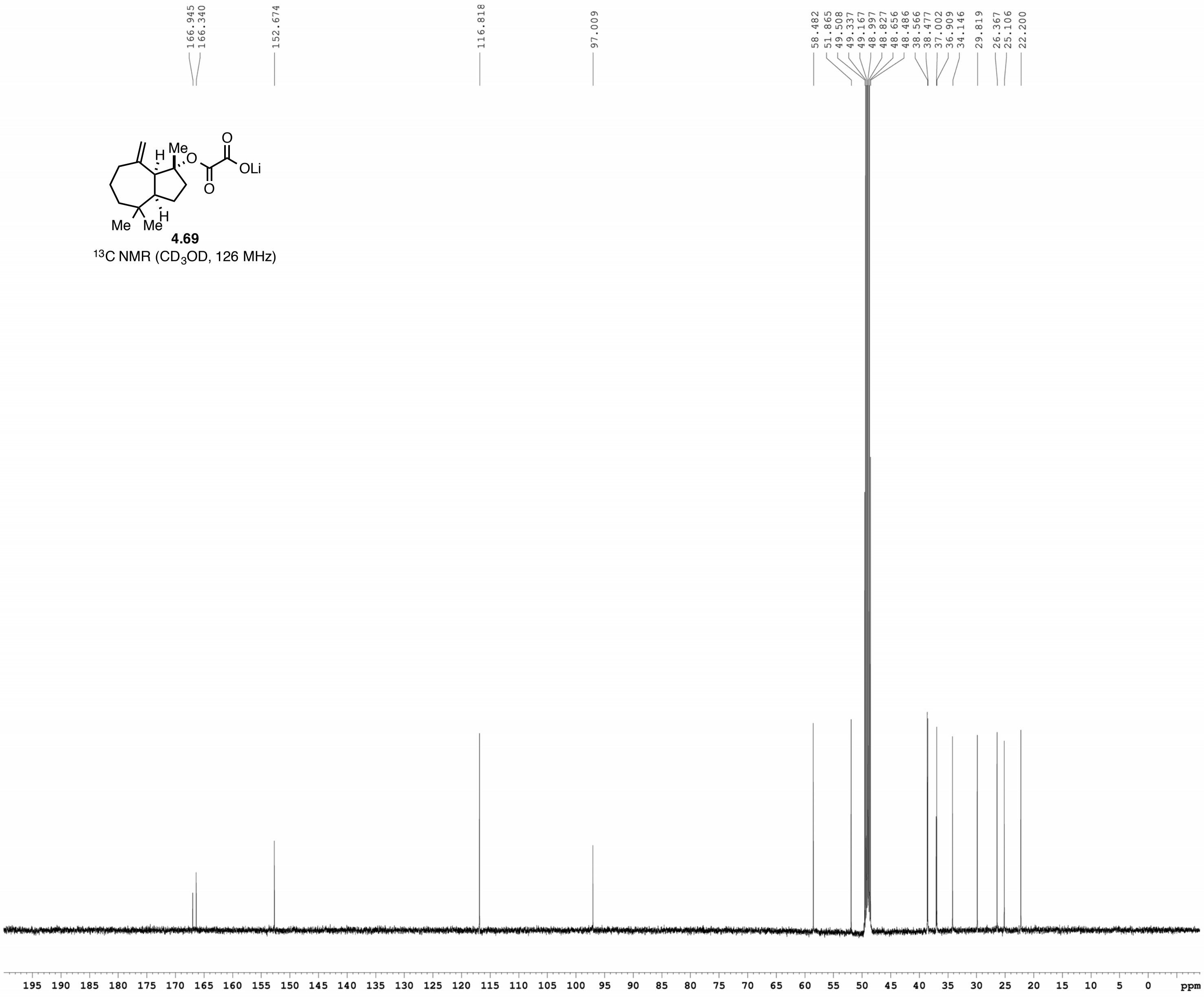
```
Current Data Parameters
NAME              YS-V-203
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170120
Time                 10.04
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT               CD3OD
NS                       8
DS                       2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                     6.3
DW              62.400 usec
DE                6.00 usec
TE                 298.0 K
D1          0.10000000 sec
MCREST   0 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF          500.2200191 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```

YS-V-203



4.69

^{13}C NMR (CD$_3$OD, 126 MHz)

```
Current Data Parameters
NAME             YS-V-203
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170120
Time                10.10
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    968
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

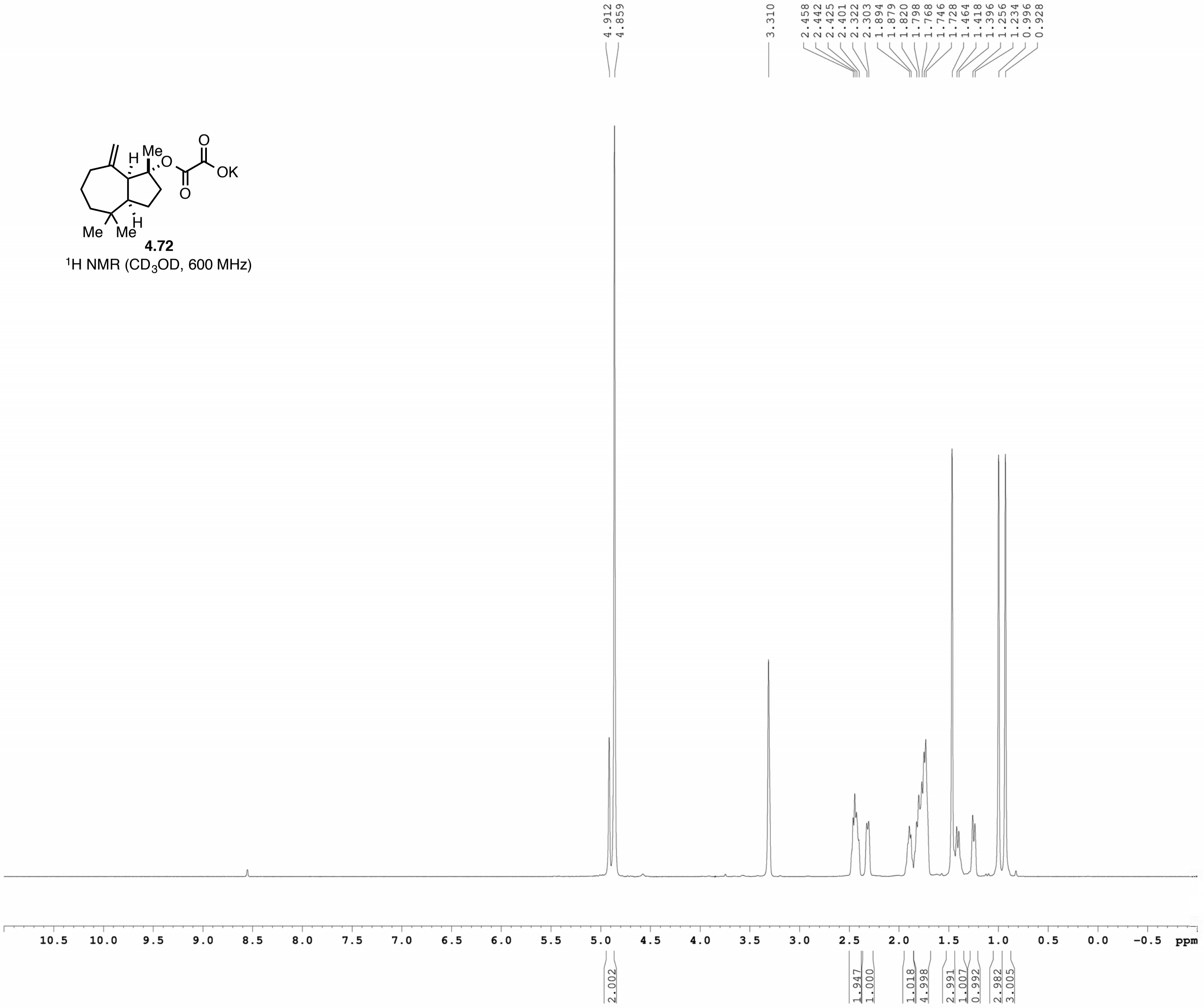
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1         125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7802454 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-VI-31



4.72

^{1}H NMR (CD_3OD, 600 MHz)

```
Current Data Parameters
NAME            YS-VI-31
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170807
Time                8.21
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 57690
SOLVENT            CD3OD
NS                     8
DS                     1
SWH            9615.385 Hz
FIDRES         0.166673 Hz
AQ            2.9998801 sec
RG                    16
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

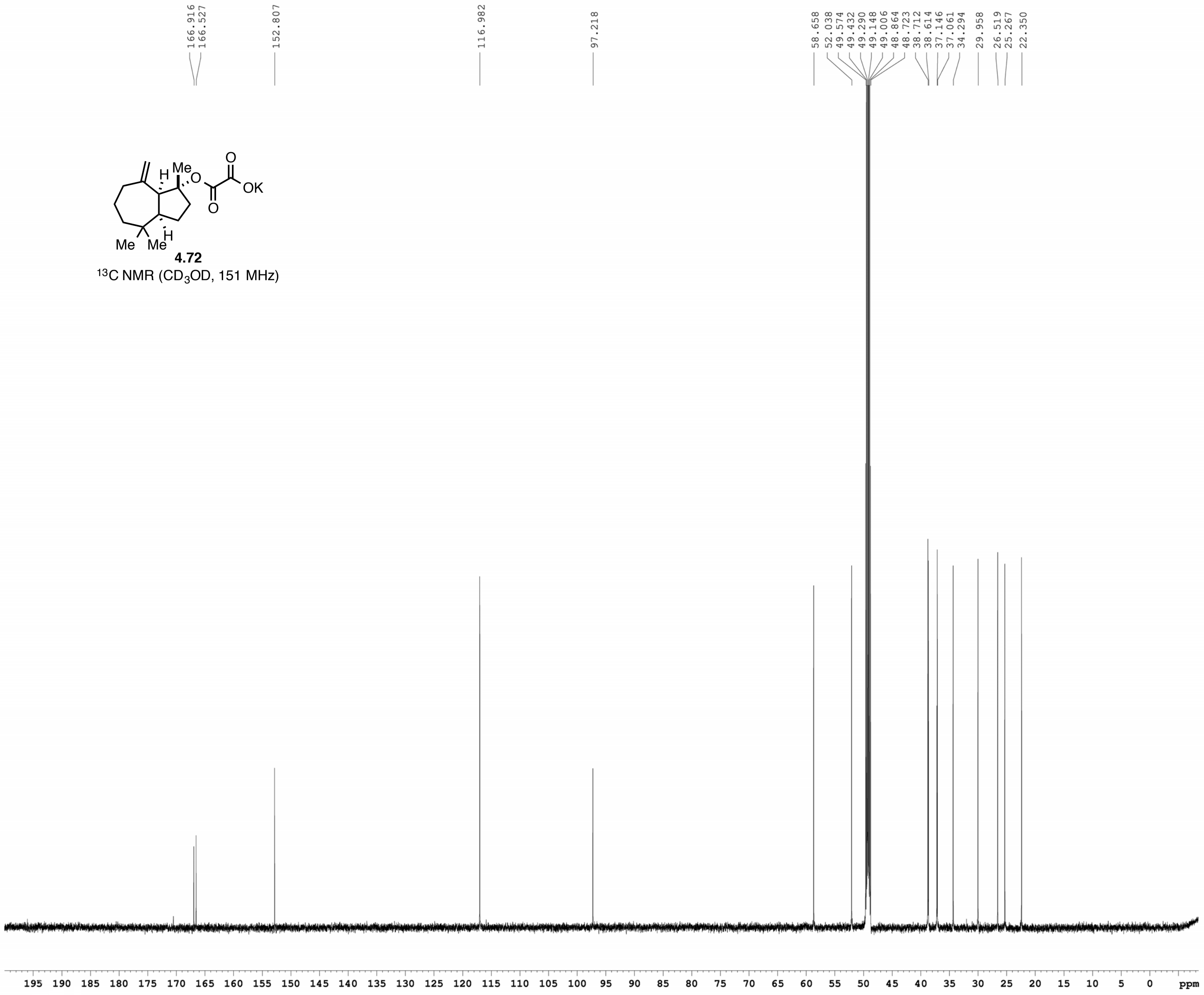
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300194 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-VI-31

4.72

^{13}C NMR (CD_3OD, 151 MHz)



```
Current Data Parameters
NAME            YS-VI-31
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170807
Time                8.25
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT             CD3OD
NS                   256
DS                     1
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

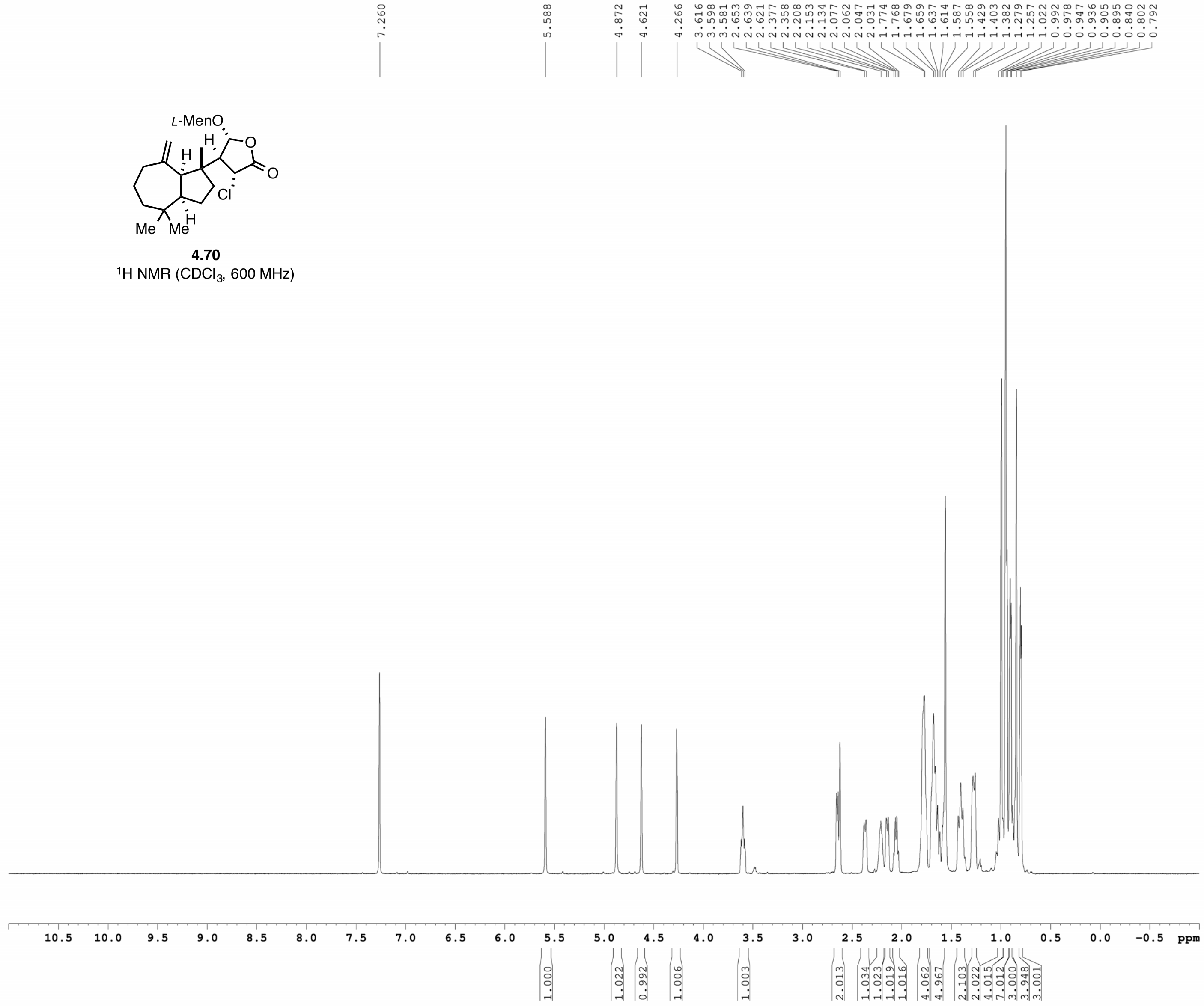
======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF           150.9025776 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

YS-V-225B

4.70

^{1}H NMR ($CDCl_3$, 600 MHz)



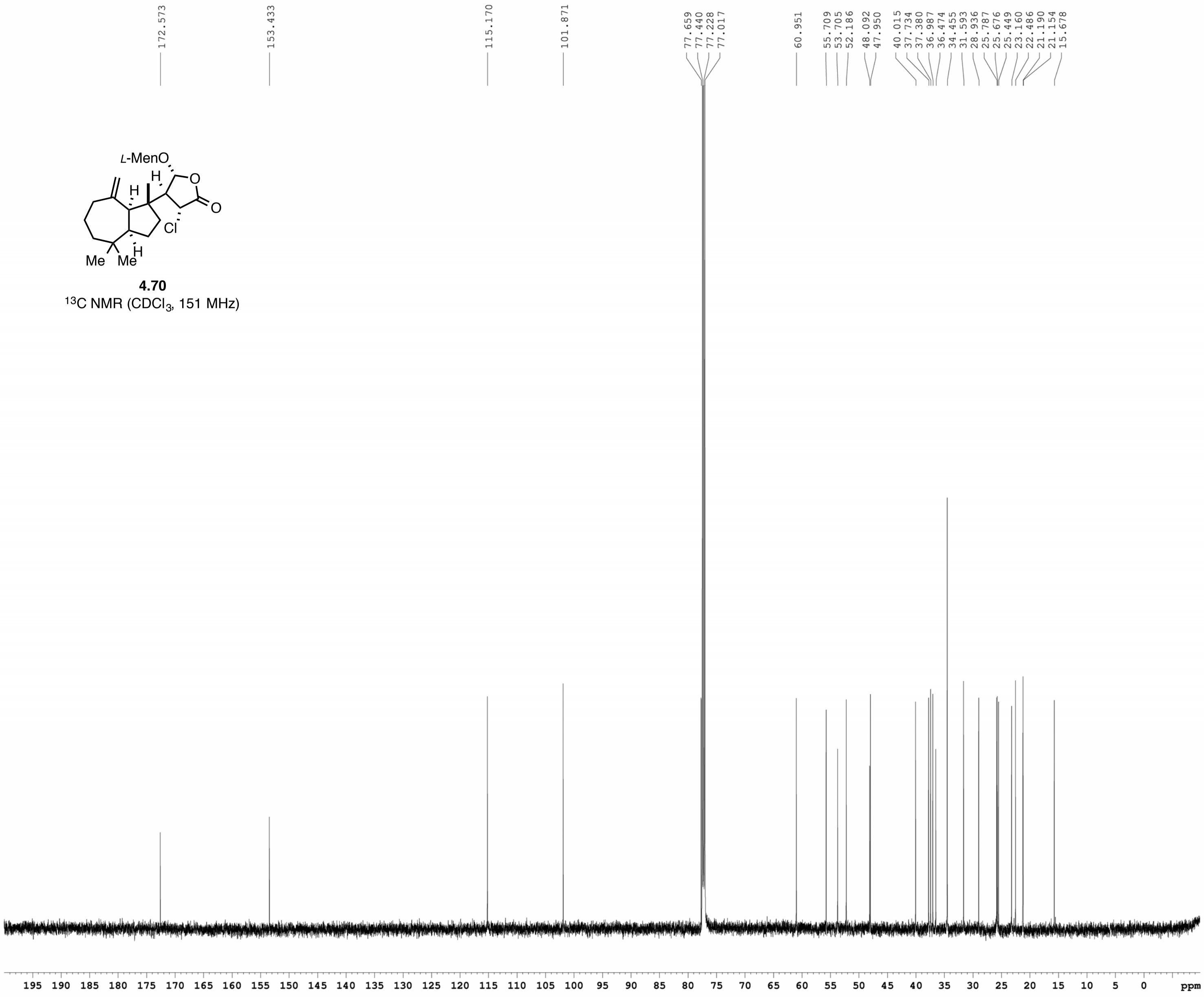
```
Current Data Parameters
NAME            YS-V-225B
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20170207
Time              12.56
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                   10
DW               52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                65536
SF          600.1300354 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-V-225B



4.70

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME          YS-V-225B
EXPNO                 2
PROCNO                1

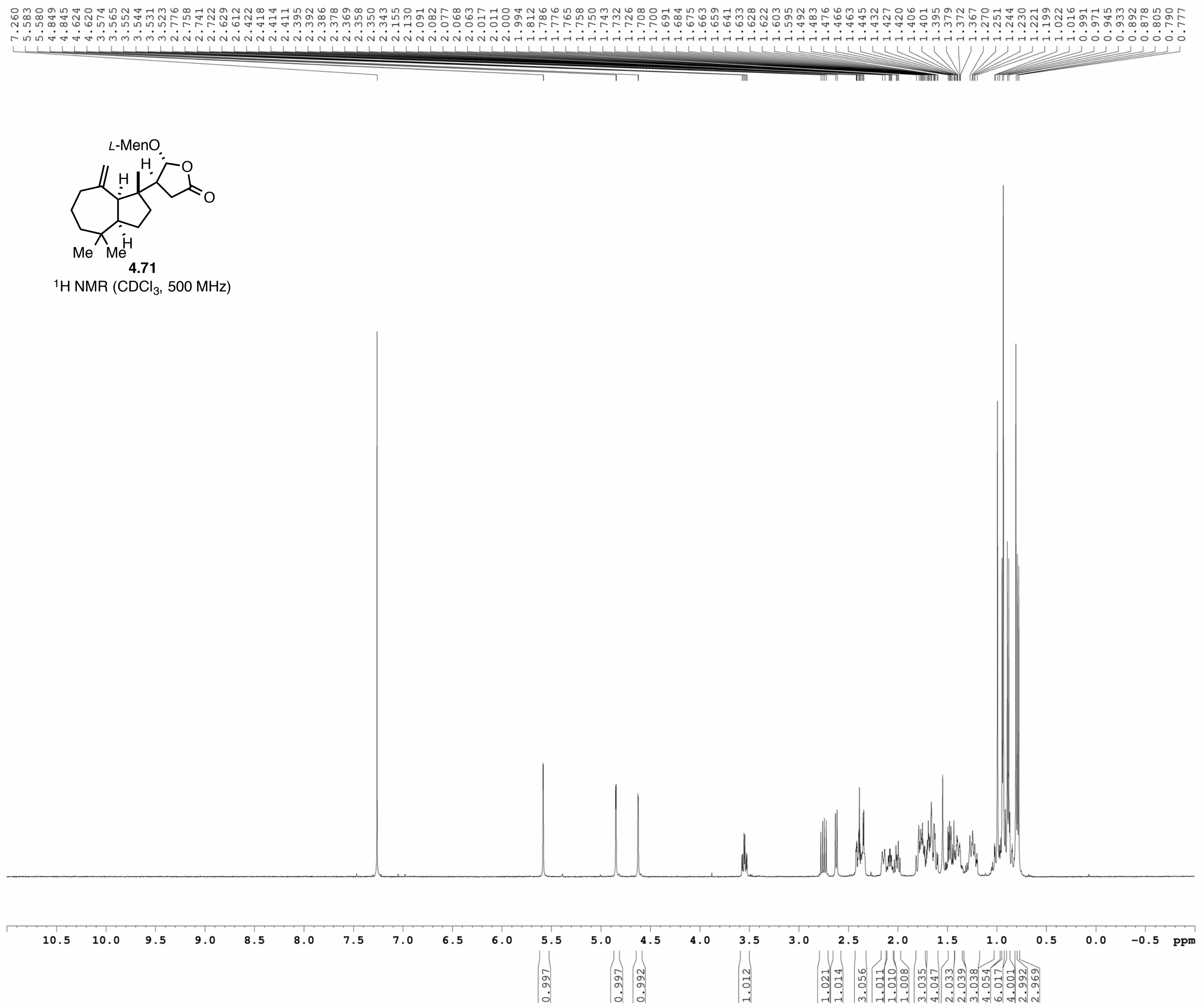
F2 - Acquisition Parameters
Date_          20170207
Time              13.00
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    1
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                 2050
DW               13.800 usec
DE                19.65 usec
TE                298.0 K
D1           0.40000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W

======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                65536
SF          150.9027830 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

YS-V-272



4.71

^{1}H NMR (CDCl$_3$, 500 MHz)

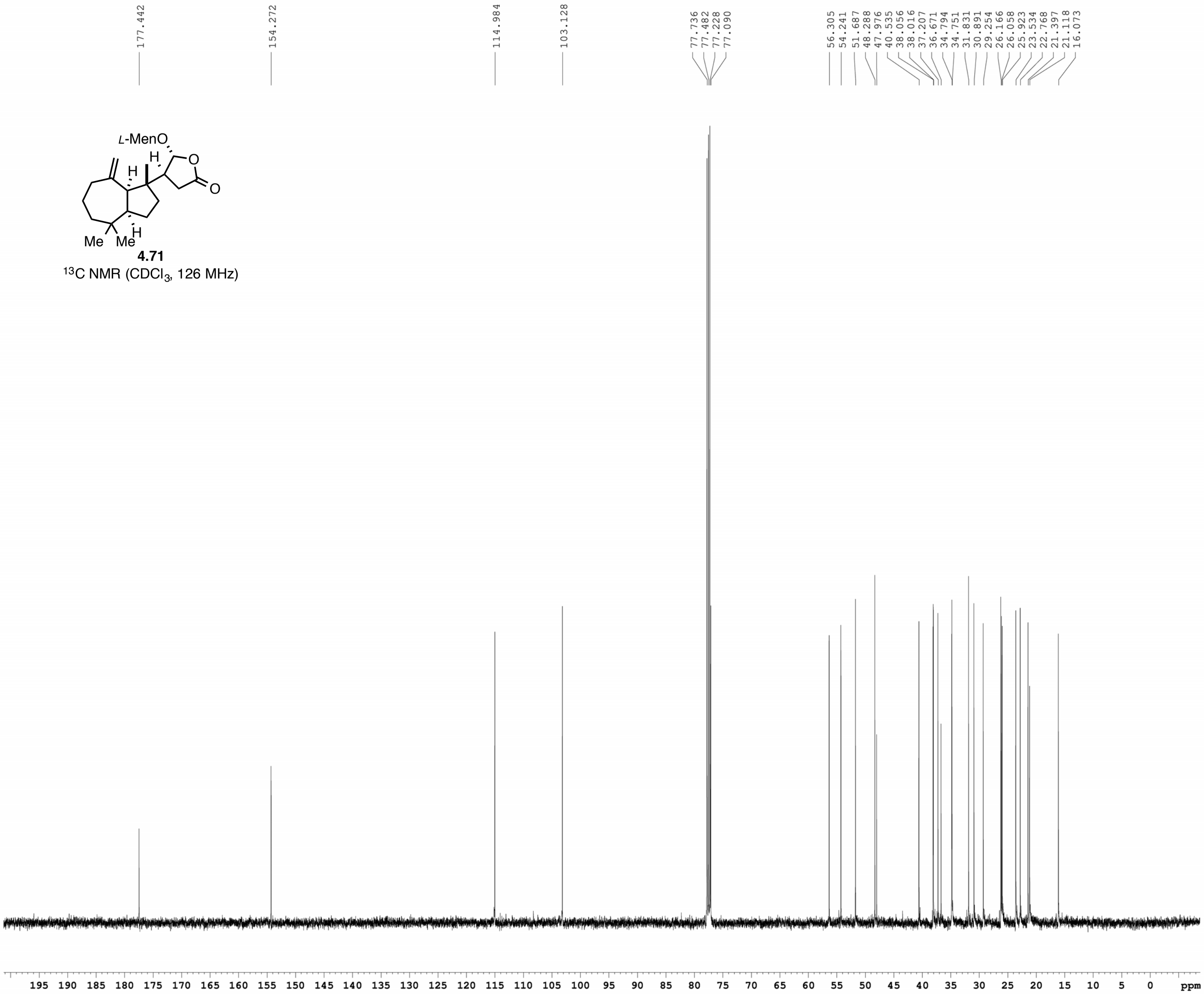
```
Current Data Parameters
NAME            YS-V-272
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170328
Time              16.30
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    1
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                 1024
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                12.00 usec
PL1               -5.80 dB
SFO1        499.0734935 MHz

F2 - Processing parameters
SI                65536
SF          499.0700316 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-V-205



4.71

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-V-205
EXPNO                3
PROCNO               1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170123
Time               8.28
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  896
DS                    1
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

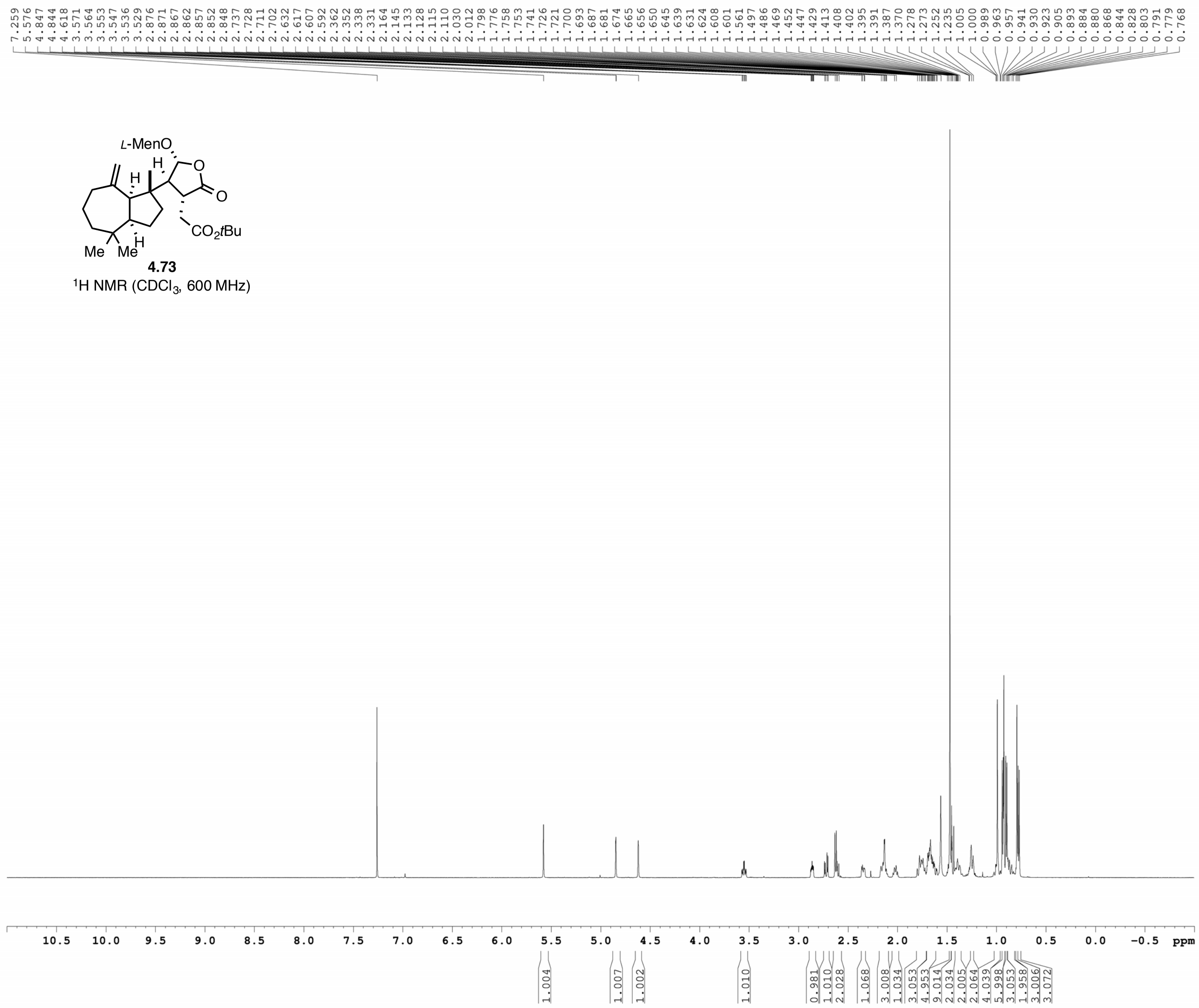
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7803674 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-V-228



4.73

^{1}H NMR ($CDCl_3$, 600 MHz)

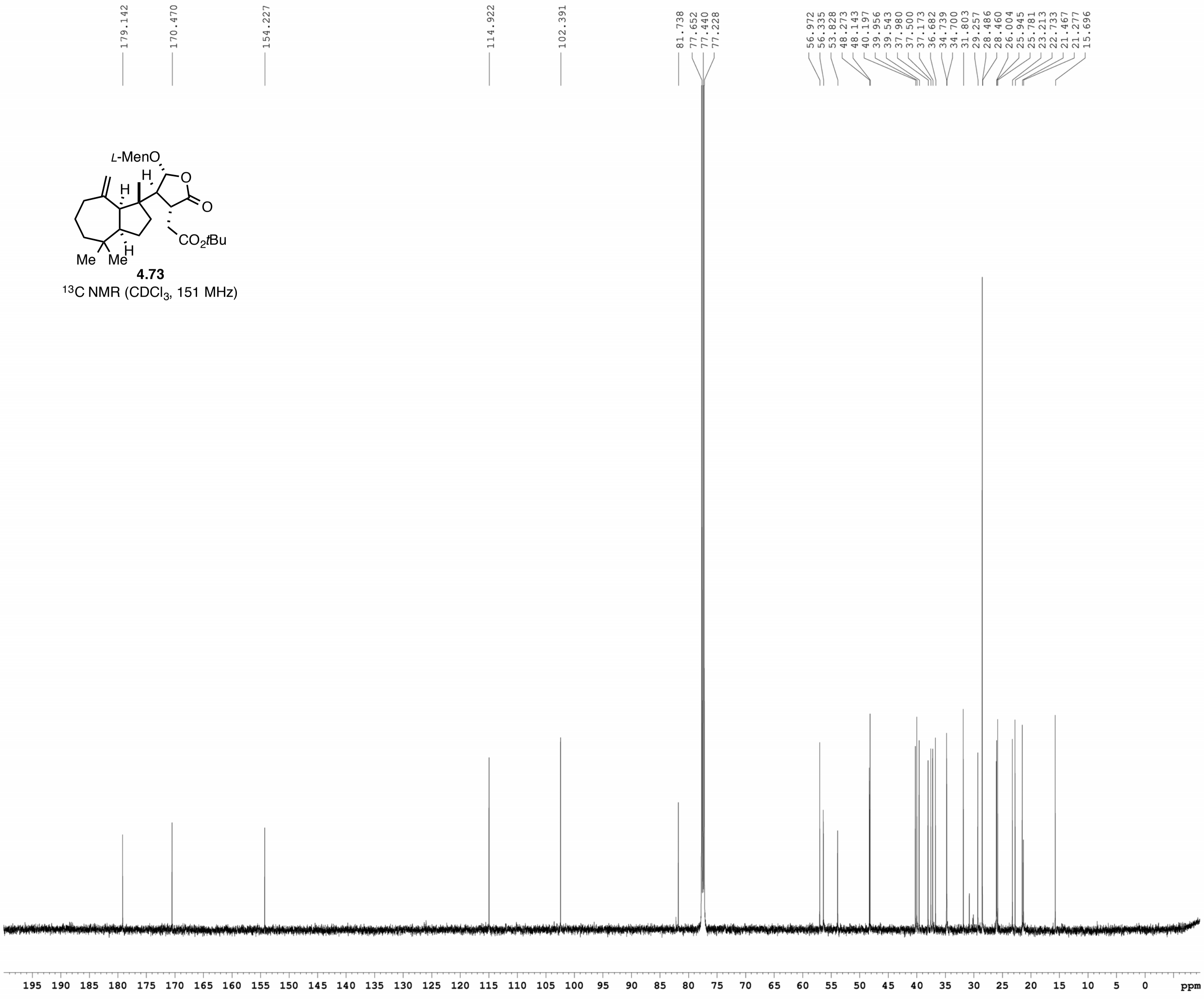
```
Current Data Parameters
NAME             YS-V-228
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170209
Time                 8.10
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                     10
DW                 52.000 usec
DE                  13.70 usec
TE                  298.0 K
D1             0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300362 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-228



4.73

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME             YS-V-228
EXPNO                   2
PROCNO                  1

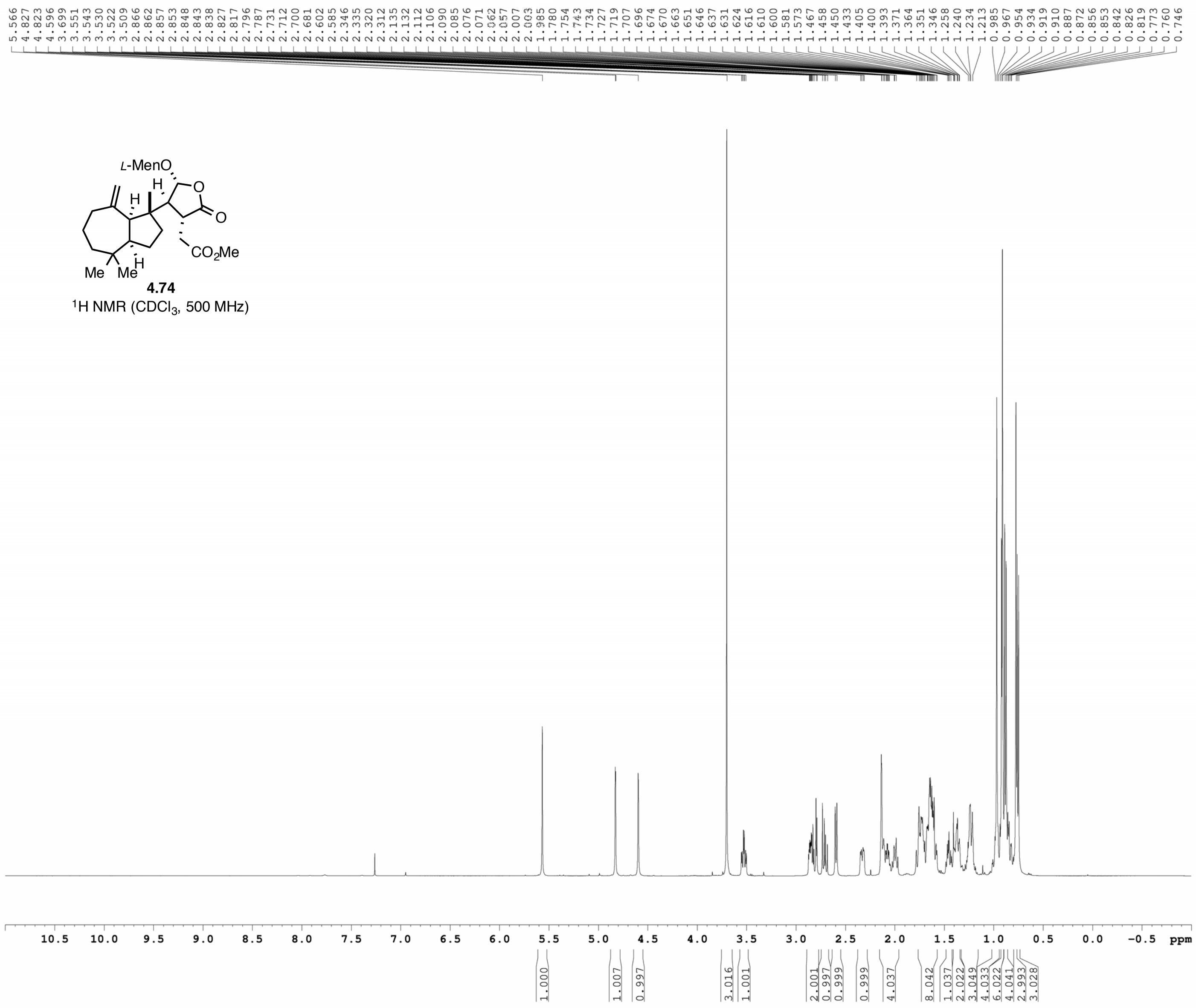
F2 - Acquisition Parameters
Date_            20170209
Time                 8.14
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      1
SWH             36231.883 Hz
FIDRES           0.552855 Hz
AQ              0.9043968 sec
RG                   2050
DW                 13.800 usec
DE                  19.65 usec
TE                  298.0 K
D1             0.40000001 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                  65536
SF            150.9027506 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

YS-V-274



4.74

^{1}H NMR ($CDCl_3$, 500 MHz)

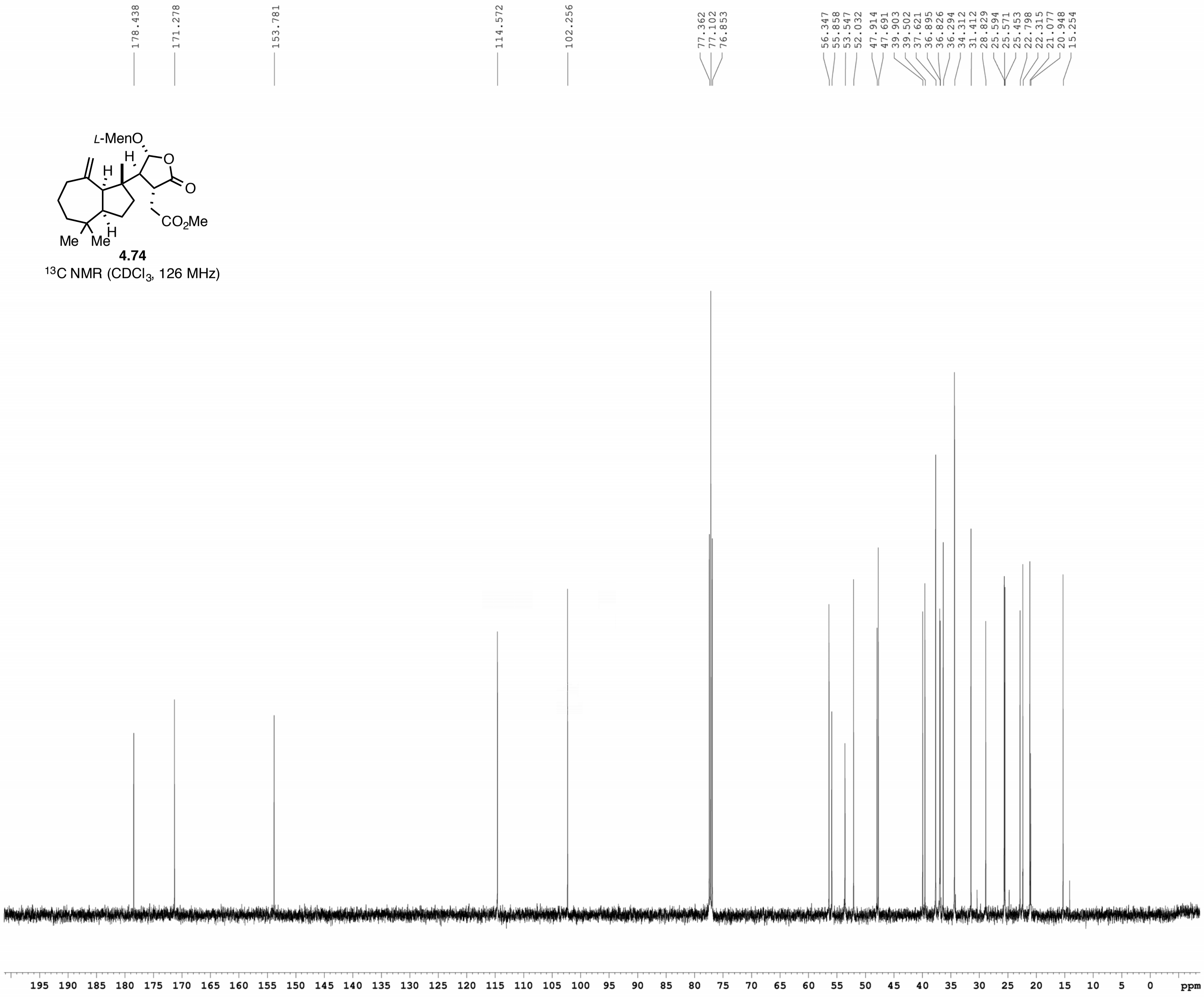
```
Current Data Parameters
NAME             YS-V-274
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20170329
Time                14.06
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                   22.6
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1          0.10000000 sec
MCREST   0 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -5.80 dB
SFO1         499.0734935 MHz

F2 - Processing parameters
SI                  65536
SF           499.0700314 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-274



4.74

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME             YS-V-274
EXPNO                   2
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

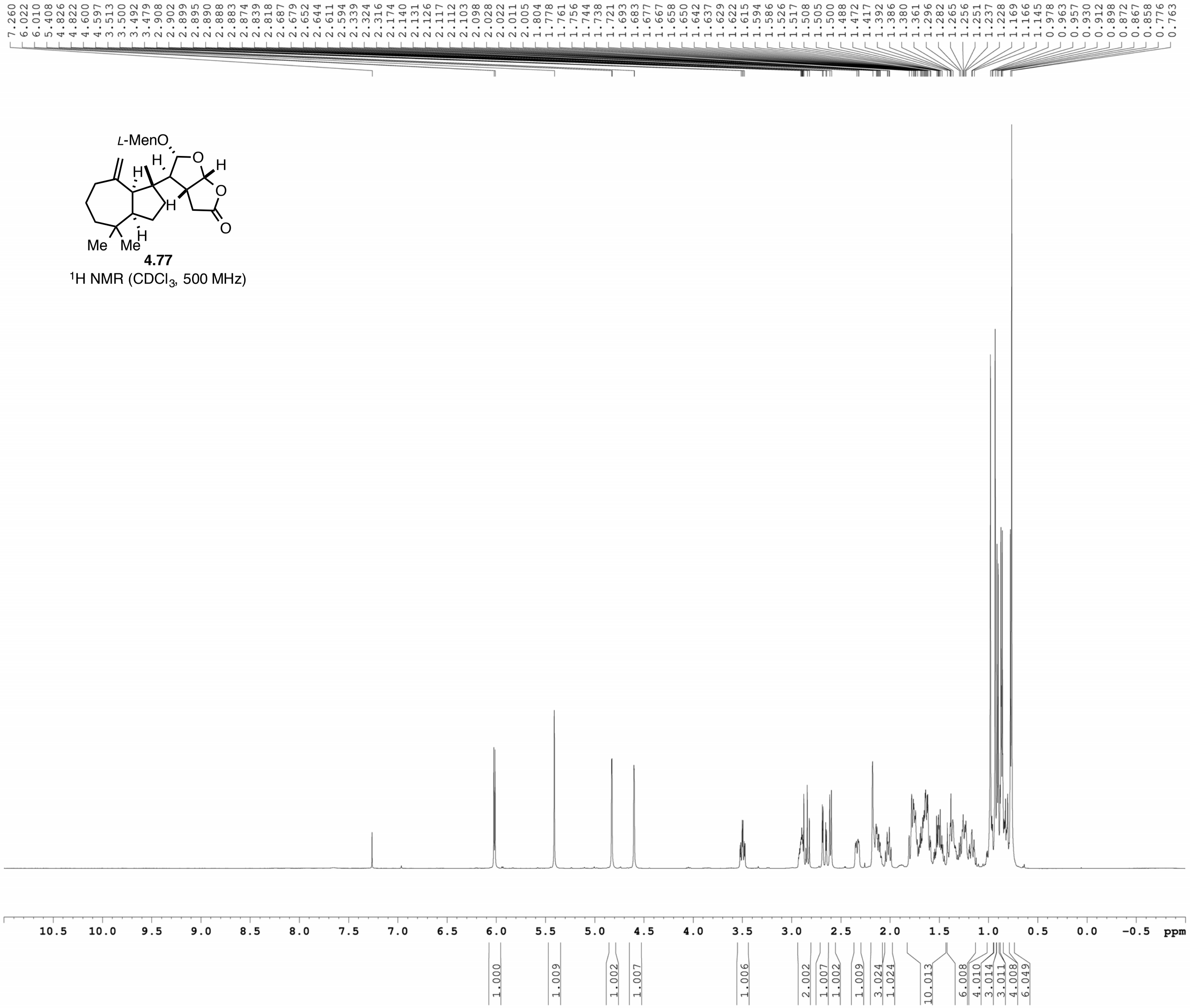
F2 - Acquisition Parameters
Date_            20170329
Time                14.07
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    100
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 1149.4
DW                 16.500 usec
DE                   4.50 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.00 usec
PL1                 -0.60 dB
SFO1          125.5050550 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                12.80 dB
SFO2          499.0724953 MHz

F2 - Processing parameters
SI                  65536
SF            125.4912510 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-V-276



4.77

^{1}H NMR ($CDCl_3$, 500 MHz)

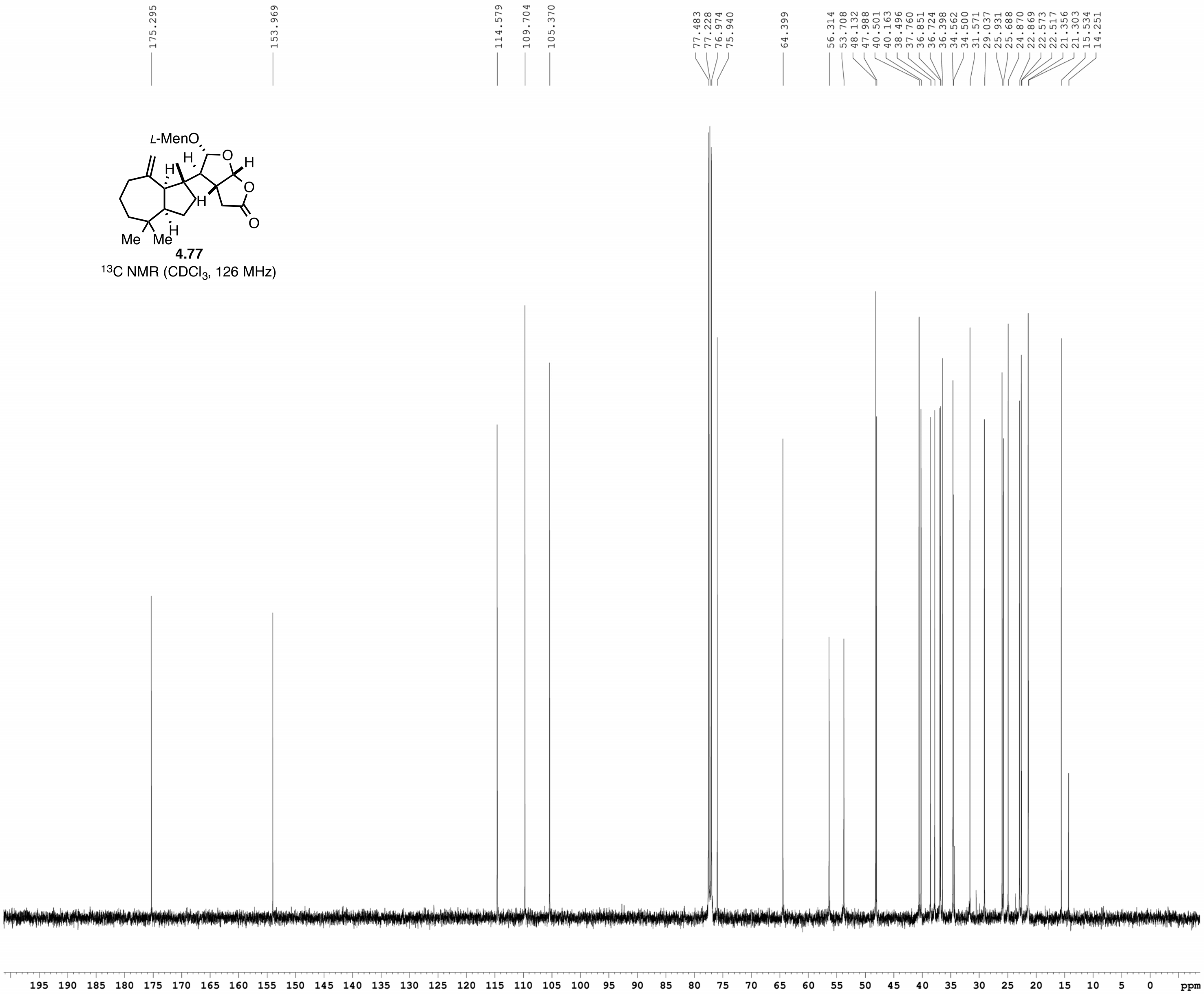
```
Current Data Parameters
NAME             YS-V-276
EXPNO                   1
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20170401
Time                13.42
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      1
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   40.3
DW                 62.400 usec
DE                   6.00 usec
TE                  295.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                 -5.80 dB
SFO1          499.0734935 MHz

F2 - Processing parameters
SI                  65536
SF            499.0700317 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-276



4.77

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-V-276
EXPNO                2
PROCNO               1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170401
Time              13.46
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG         zgdc30
TD               65536
SOLVENT           C6D6
NS                 584
DS                   1
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813440 sec
RG              4597.6
DW              16.500 usec
DE                4.50 usec
TE               295.1 K
D1          0.25000000 sec
d11         0.03000000 sec
MCREST   0 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.00 usec
PL1               -0.60 dB
SFO1        125.5050550 MHz

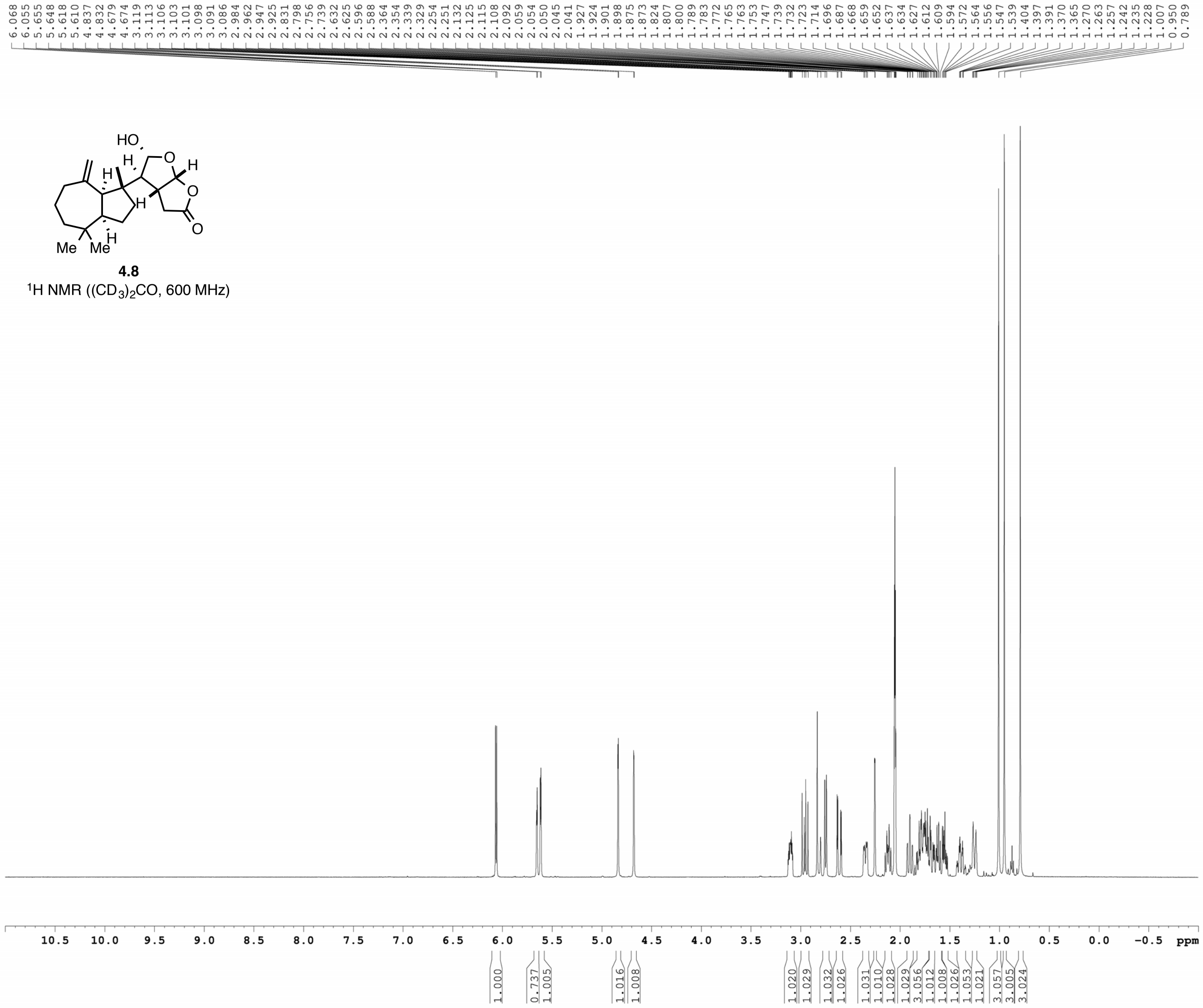
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              12.80 dB
SFO2        499.0724953 MHz

F2 - Processing parameters
SI                65536
SF          125.4912350 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-V-134

4.8

^{1}H NMR ($(CD_3)_2CO$, 600 MHz)



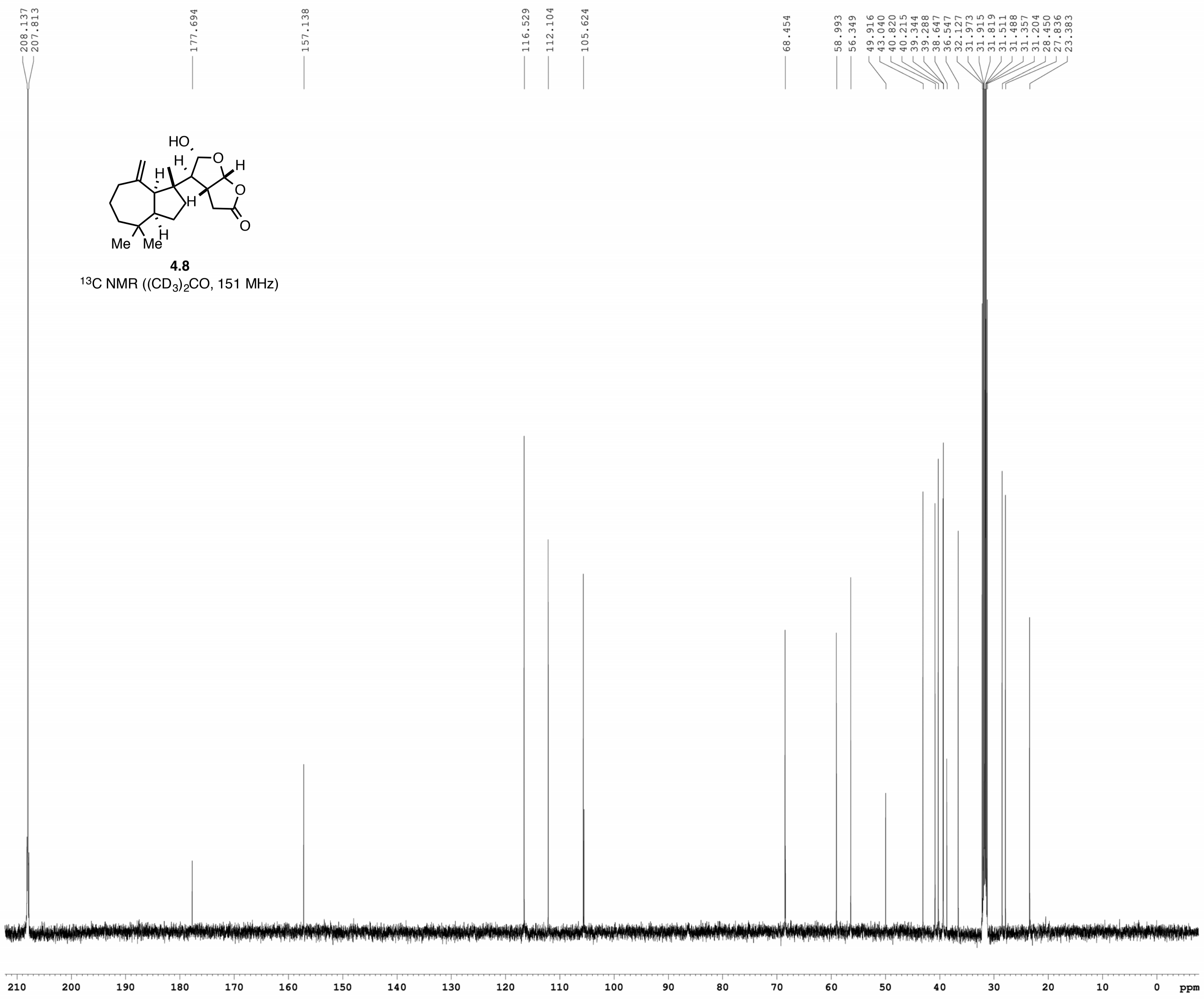
```
Current Data Parameters
NAME             YS-V-134
EXPNO                   3
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20161208
Time                 8.45
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                      8
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF          500.2200178 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-134



4.8

^{13}C NMR ((CD$_3$)$_2$CO, 151 MHz)

```
Current Data Parameters
NAME            YS-V-134
EXPNO                  4
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

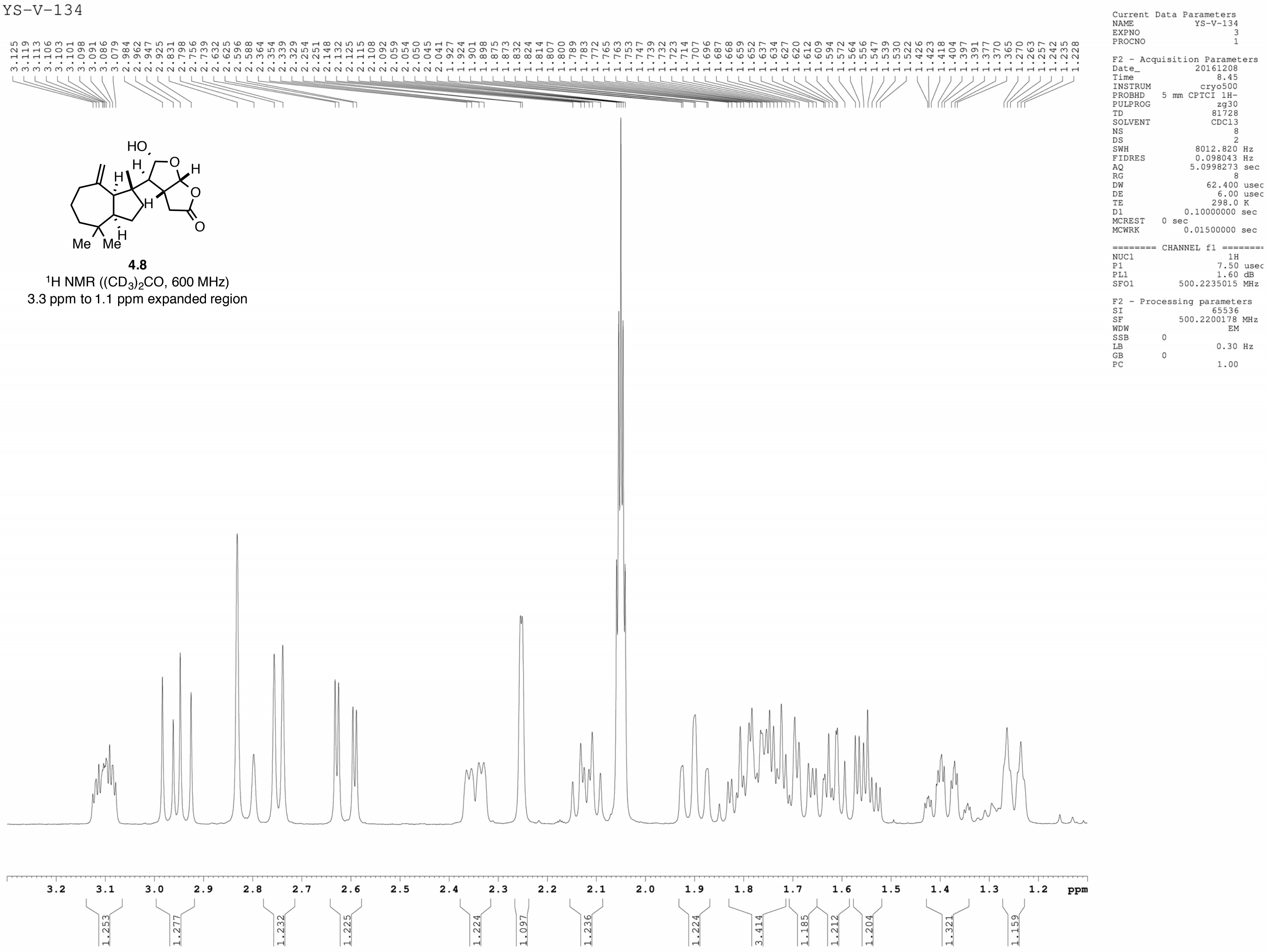
F2 - Acquisition Parameters
Date_           20161208
Time                8.47
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

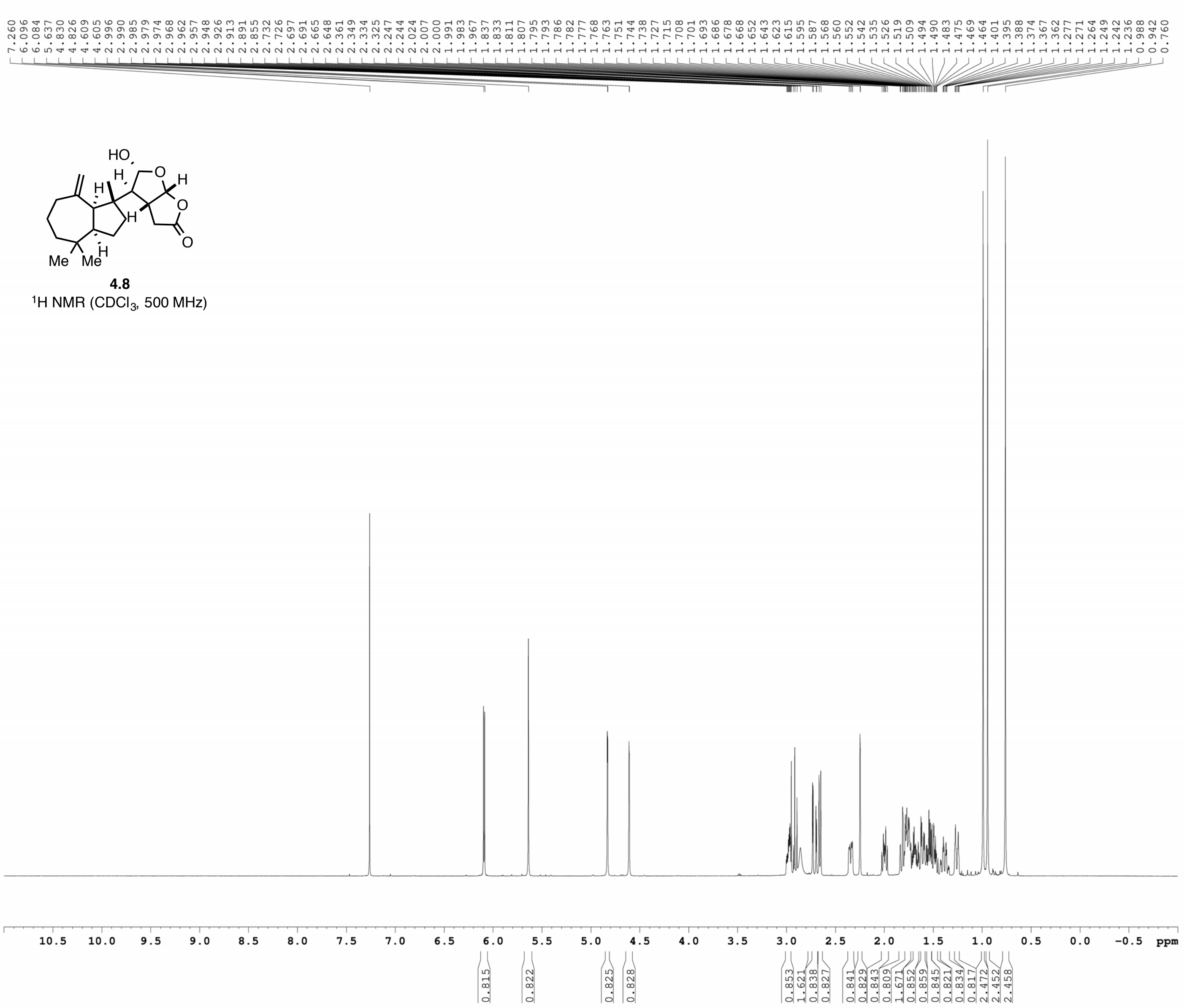
F2 - Processing parameters
SI                 65536
SF           125.7800804 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```



4.8

^{1}H NMR ($(CD_3)_2CO$, 600 MHz)
3.3 ppm to 1.1 ppm expanded region

YS-V-134



4.8

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          YS-V-134
EXPNO                1
PROCNO               1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_         20161207
Time             10.36
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG                 7.1
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST   0 sec
MCWRK       0.01500000 sec

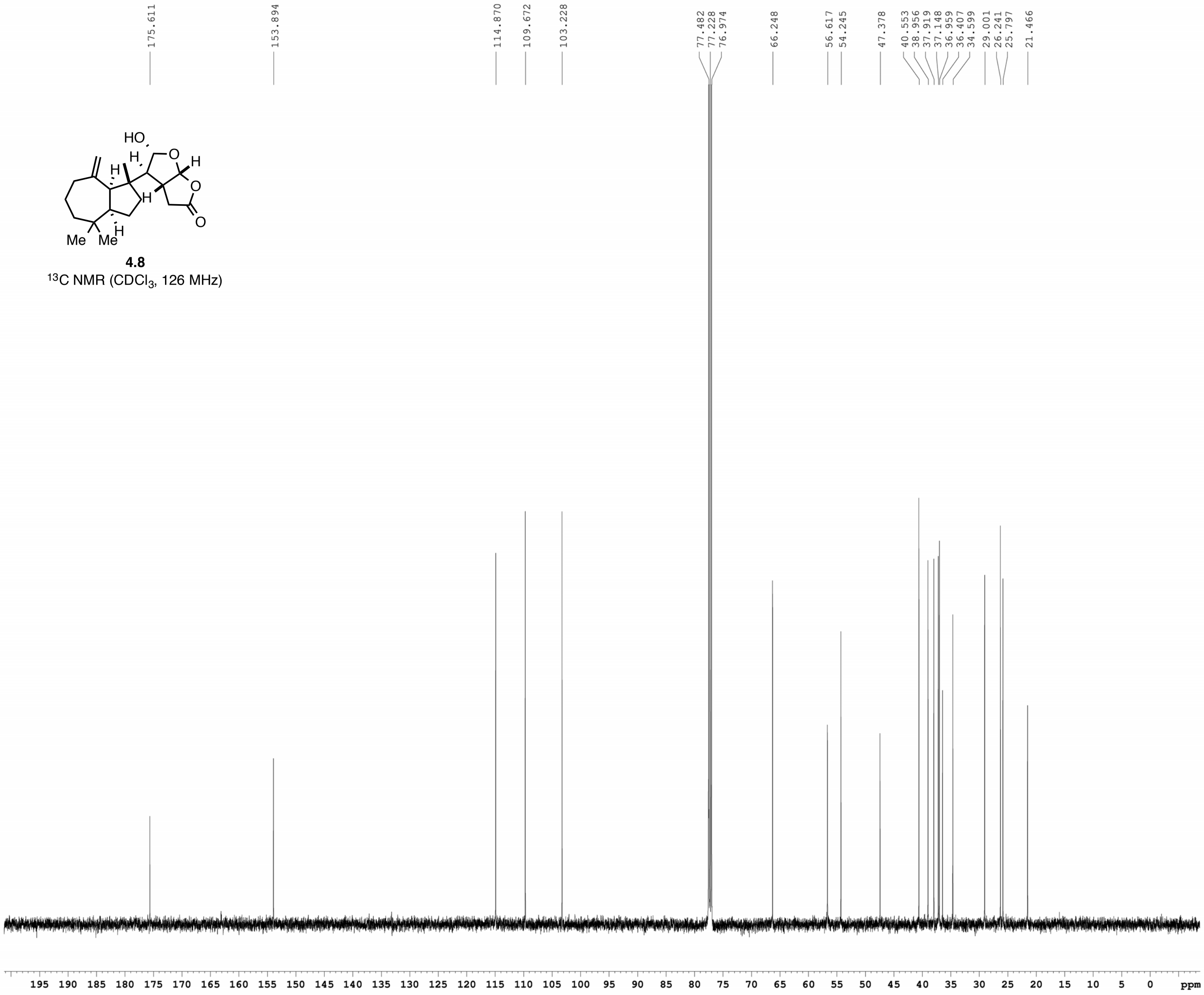
======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200308 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                4.00
```

YS-V-134

4.8

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME             YS-V-134
EXPNO                   2
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20161207
Time                10.38
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT           Acetone
NS                   1024
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   4096
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

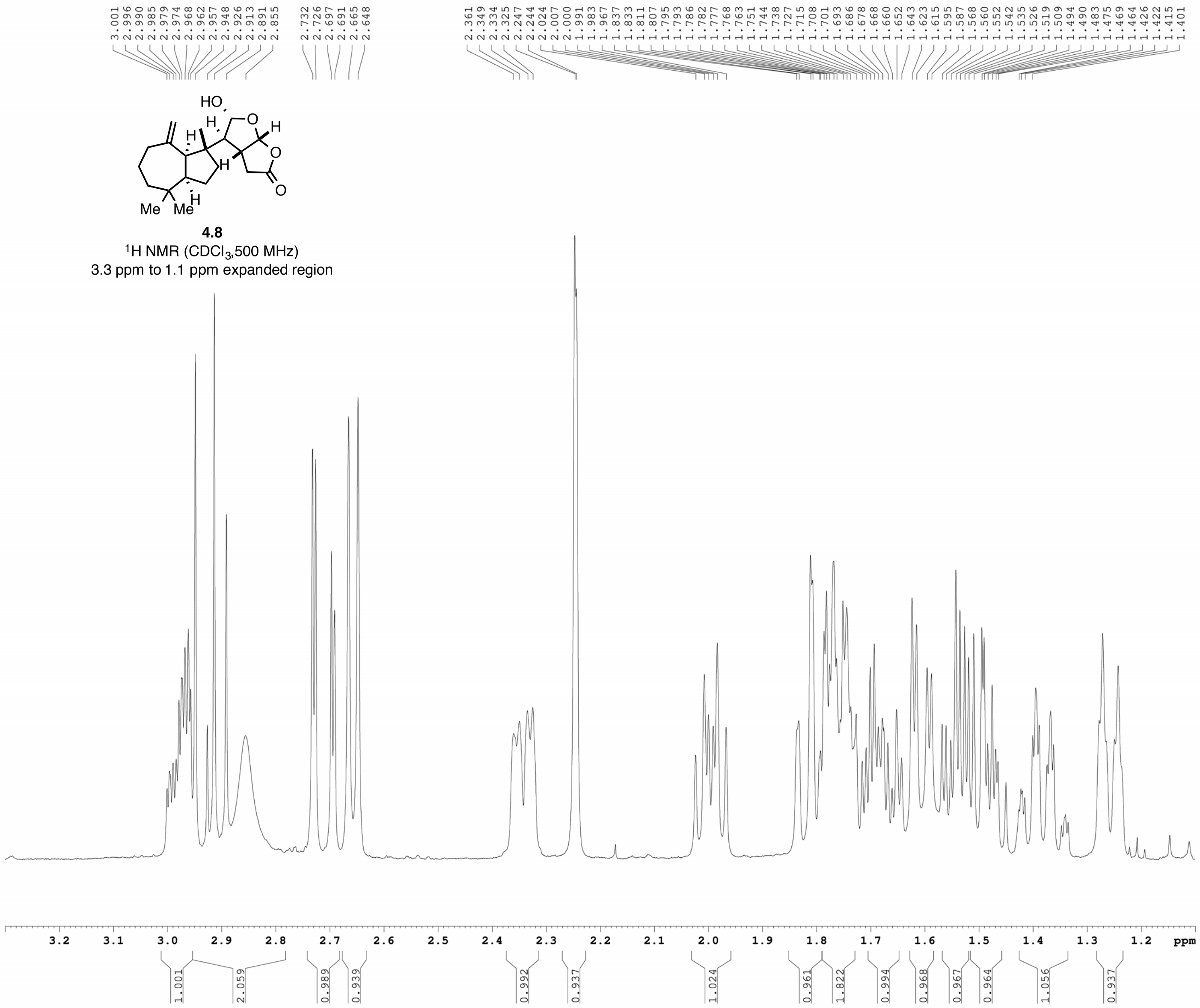
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803990 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   2.00
```

YS-V-134



4.8

^{1}H NMR ($CDCl_3$,500 MHz)
3.3 ppm to 1.1 ppm expanded region

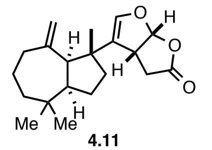
```
Current Data Parameters
NAME             YS-V-134
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20161207
Time                10.36
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                    7.1
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 =======
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

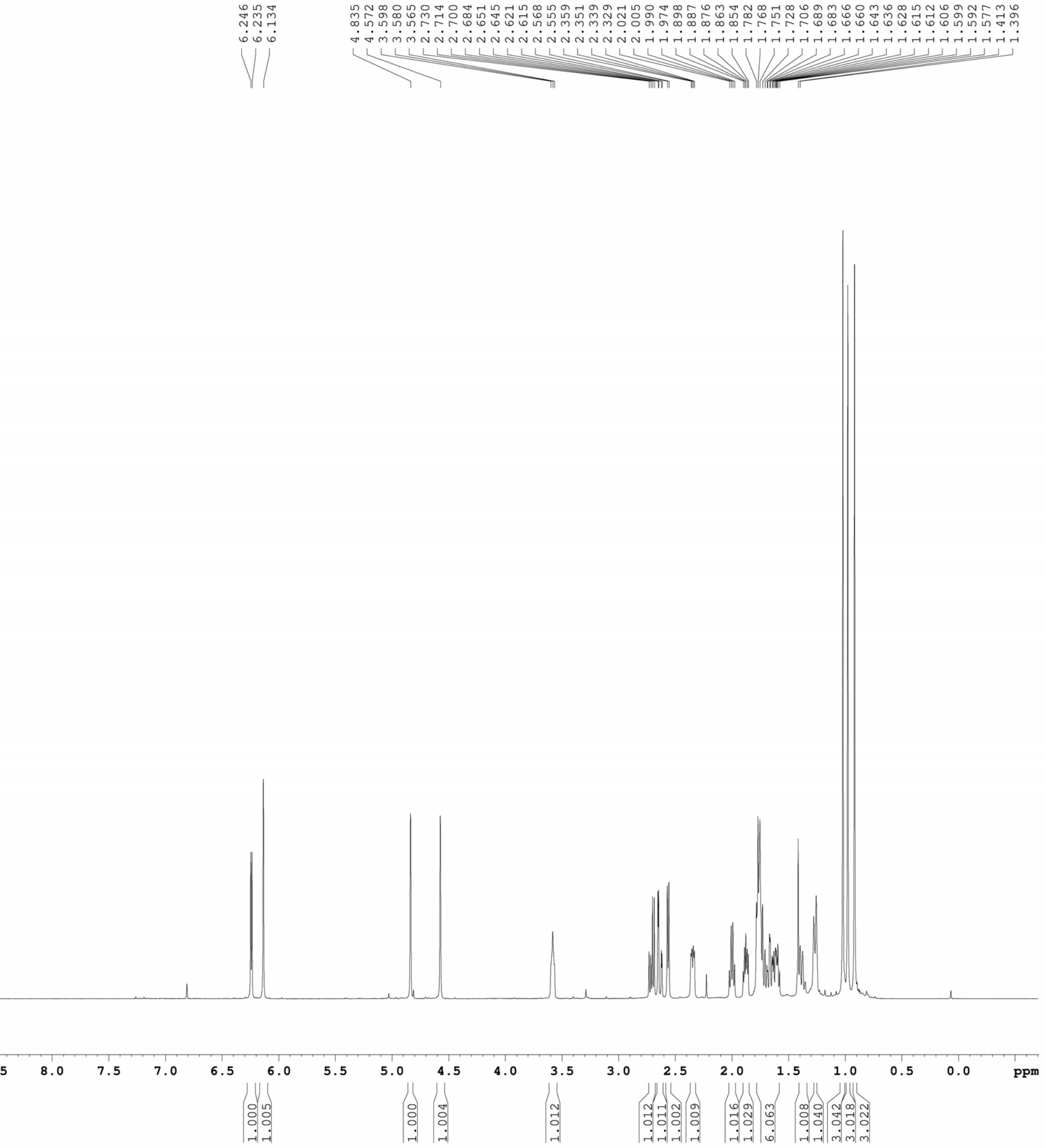
F2 - Processing parameters
SI                  65536
SF            500.2200308 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-V-237



4.11

^{1}H NMR (CCl_4, 600 MHz)



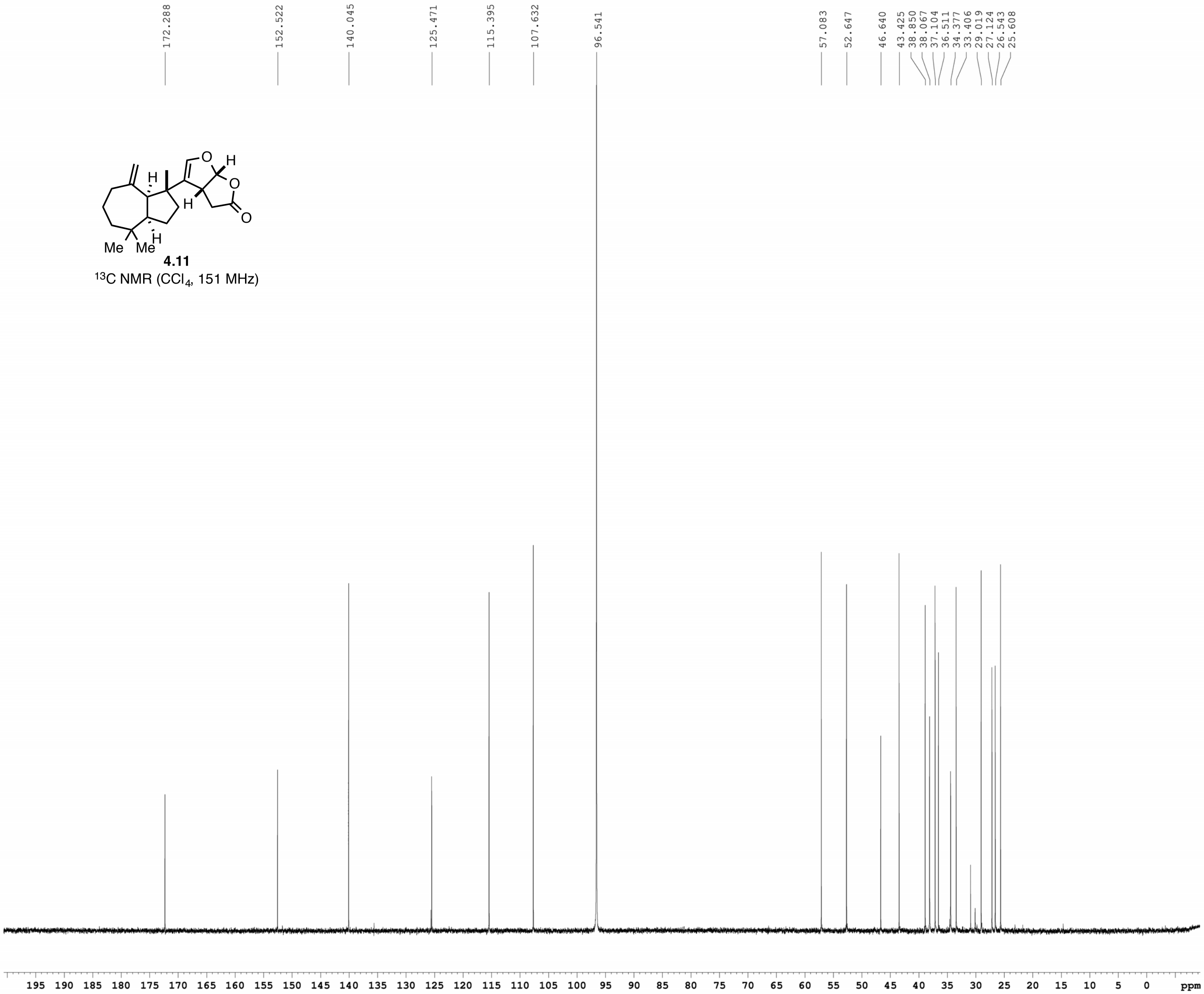
```
Current Data Parameters
NAME            YS-V-237
EXPNO                  6
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20170217
Time               10.09
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 98074
SOLVENT             DMSO
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                  12.7
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1298164 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-237



4.11

^{13}C NMR (CCl$_4$, 151 MHz)

```
Current Data Parameters
NAME            YS-V-237
EXPNO                  7
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

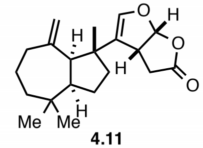
F2 - Acquisition Parameters
Date_          20170217
Time              10.10
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG          zgdc30
TD                65536
SOLVENT            DMSO
NS                  360
DS                    4
SWH          36231.883 Hz
FIDRES        0.552855 Hz
AQ           0.9043968 sec
RG                 2050
DW               13.800 usec
DE                19.65 usec
TE                298.0 K
D1          0.40000001 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       150.9194080 MHz
NUC1               13C
P1               10.00 usec
PLW1       64.00000000 W

======== CHANNEL f2 ========
SFO2       600.1330010 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       20.00000000 W
PLW12       0.36000001 W

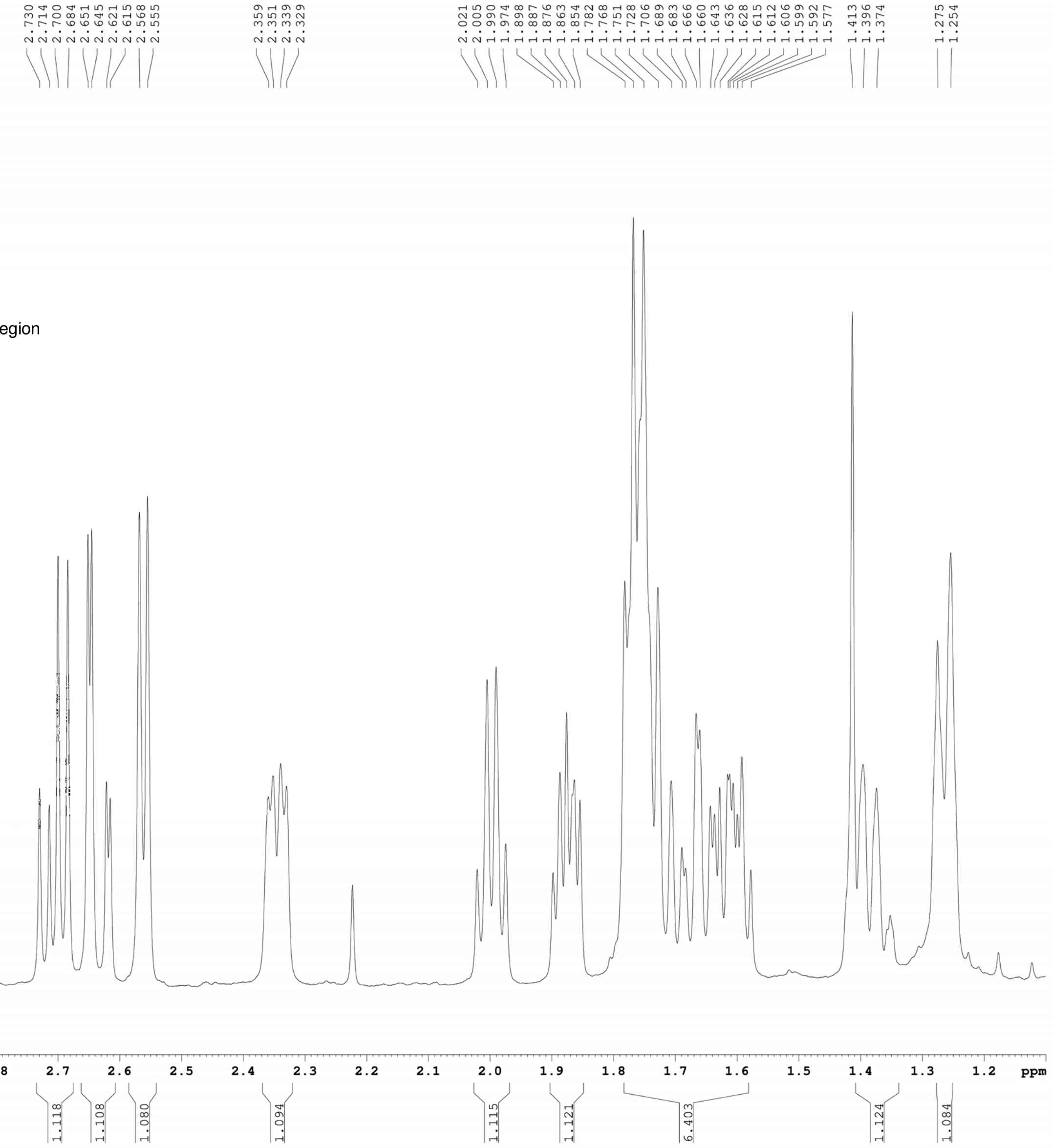
F2 - Processing parameters
SI                65536
SF         150.9027079 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

YS-V-237



4.11

^{1}H NMR (CCl_4, 600 MHz)
3.3 ppm to 1.1 ppm expanded region



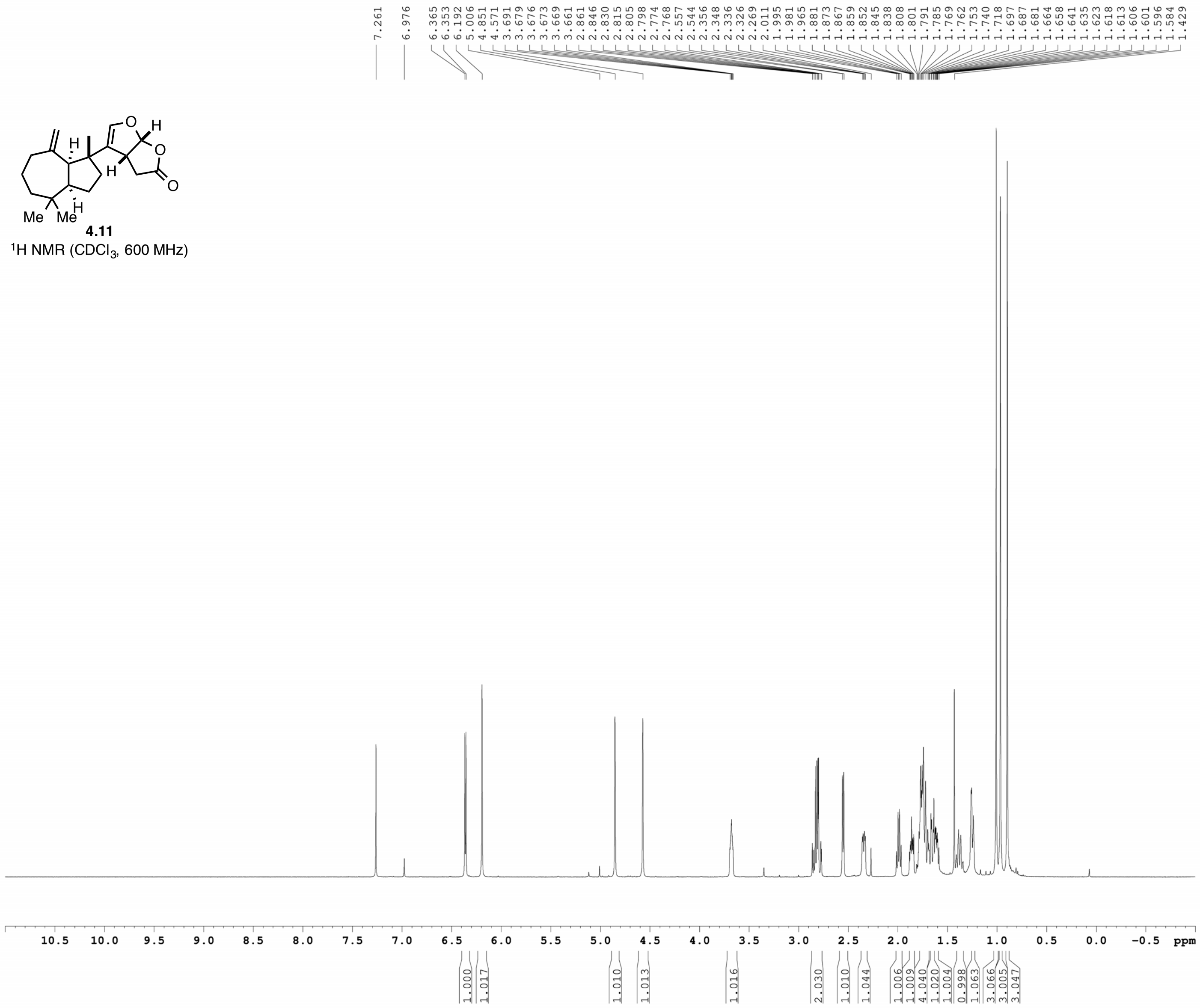
```
Current Data Parameters
NAME              YS-V-237
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170217
Time                 10.09
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   98074
SOLVENT               DMSO
NS                       8
DS                       2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    12.7
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1             0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                   65536
SF           600.1298164 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-V-237



4.11

^{1}H NMR (CDCl$_3$, 600 MHz)

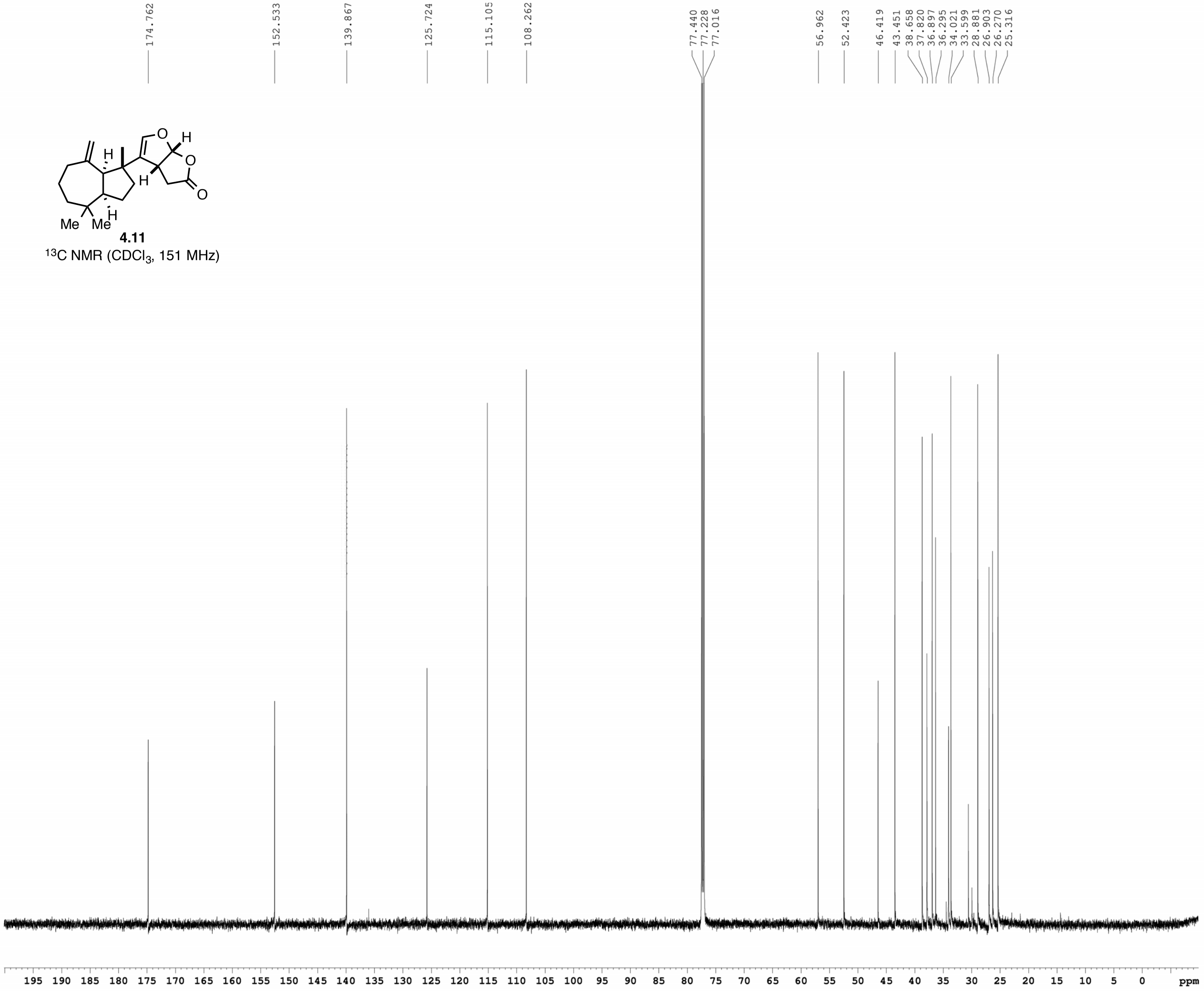
```
Current Data Parameters
NAME             YS-V-237
EXPNO                   4
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20170216
Time                14.42
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG              zg30
TD                  76922
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             9615.385 Hz
FIDRES          0.125002 Hz
AQ             3.9999440 sec
RG                   40.3
DW                 52.000 usec
DE                  13.70 usec
TE                  298.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300349 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-237



4.11

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME             YS-V-237
EXPNO                   5
PROCNO                  1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_            20170216
Time                14.48
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      1
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9043968 sec
RG                   2050
DW                 13.800 usec
DE                  19.65 usec
TE                  298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        150.9194080 MHz
NUC1                  13C
P1                  10.00 usec
PLW1        64.00000000 W

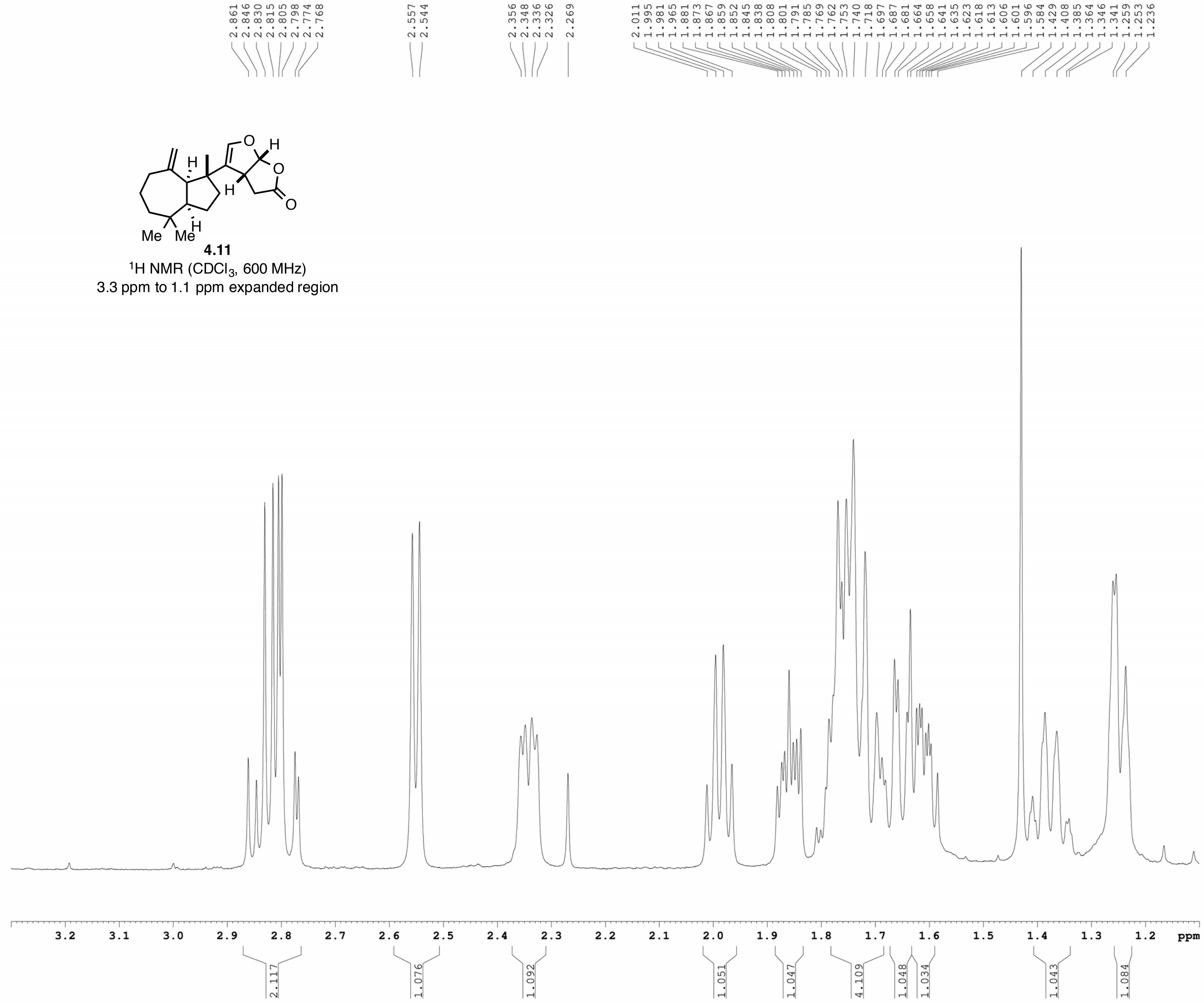
======== CHANNEL f2 ========
SFO2        600.1330010 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2        20.00000000 W
PLW12        0.36000001 W

F2 - Processing parameters
SI                  65536
SF          150.9027841 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

YS-V-237

4.11

^{1}H NMR ($CDCl_3$, 600 MHz)
3.3 ppm to 1.1 ppm expanded region



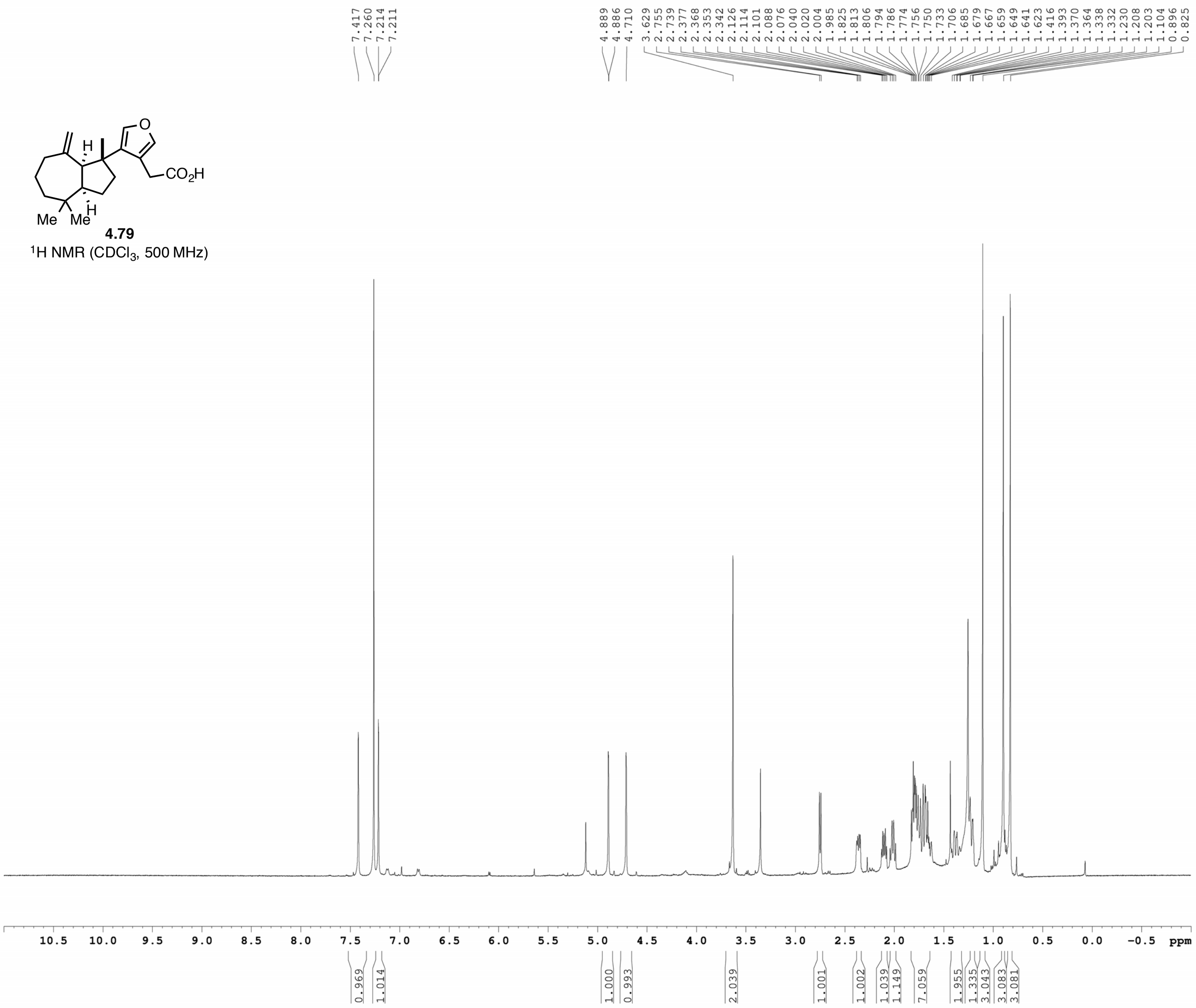
```
Current Data Parameters
NAME             YS-V-237
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170216
Time                14.42
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG              zg30
TD                  76922
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.125002 Hz
AQ              3.9999440 sec
RG                   40.3
DW                 52.000 usec
DE                  13.70 usec
TE                  298.0 K
D1            0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300349 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-V-281



4.79

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME           YS-V-281
EXPNO                 2
PROCNO                1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170405
Time              12.29
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                    8
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST  0 sec
MCWRK        0.01500000 sec

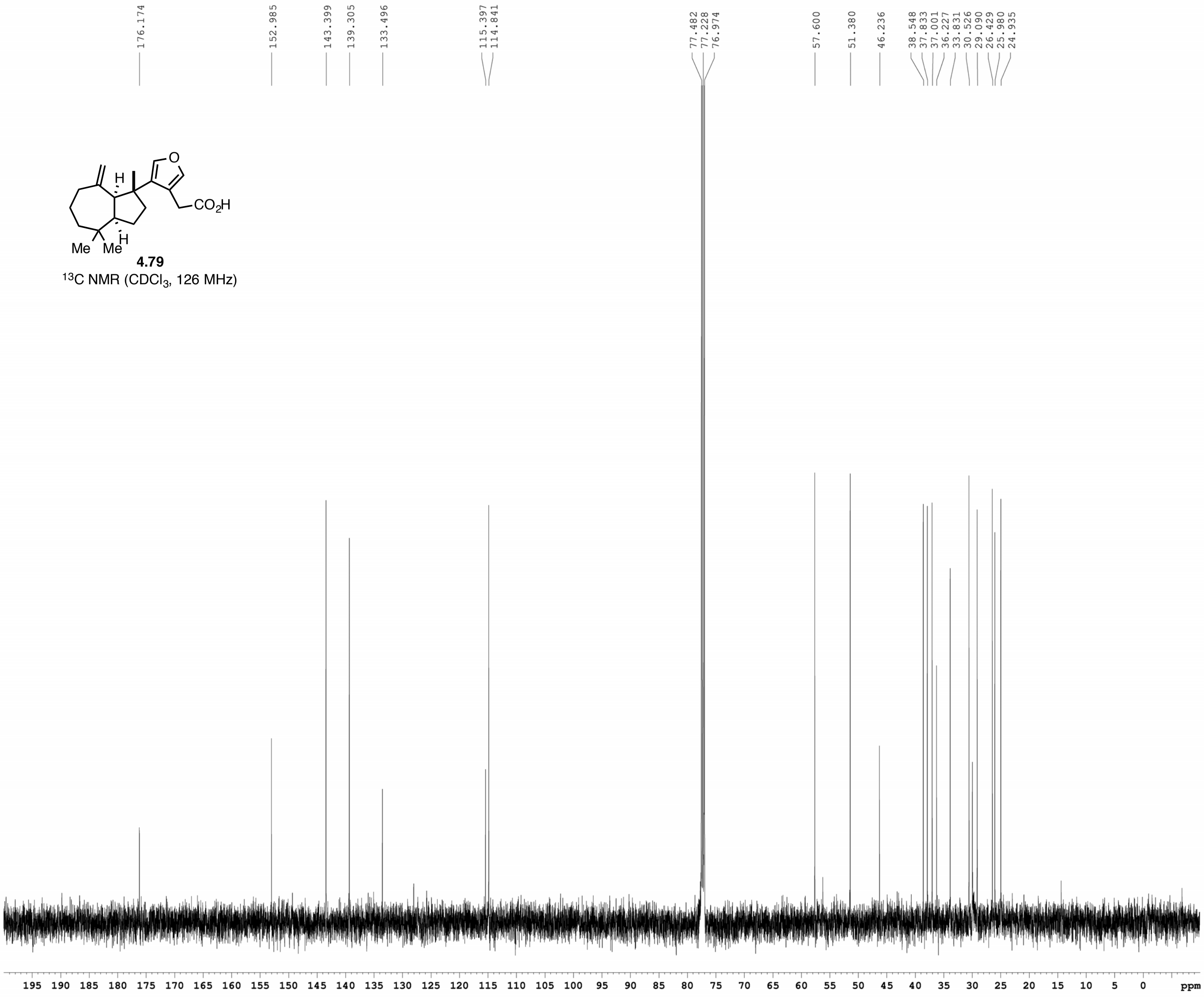
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200318 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-V-281

4.79

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-V-281
EXPNO                  3
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20170405
Time               12.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  4096
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

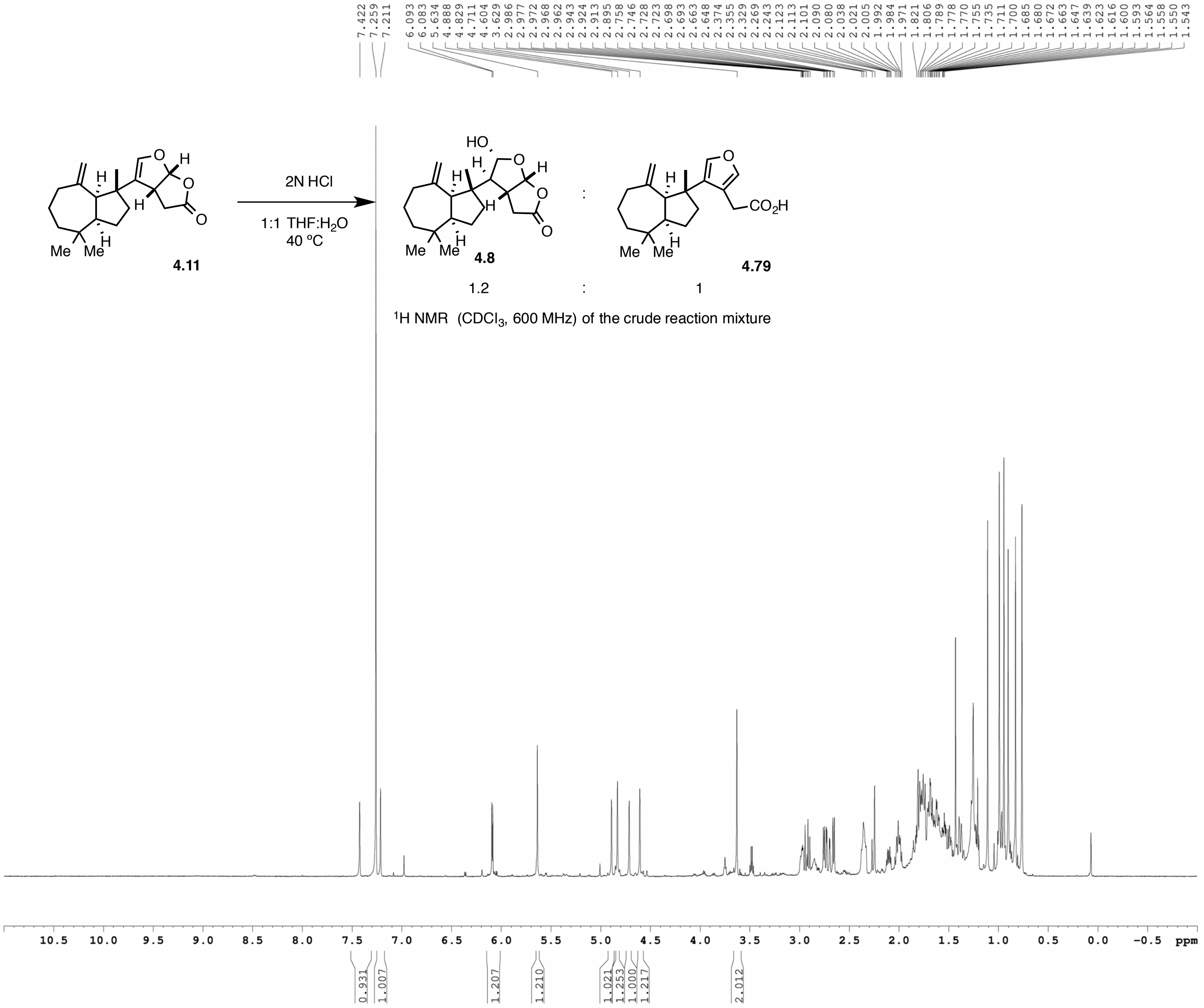
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803989 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-V-239



4.11

4.8 : **4.79**

1.2 : 1

^{1}H NMR (CDCl$_3$, 600 MHz) of the crude reaction mixture

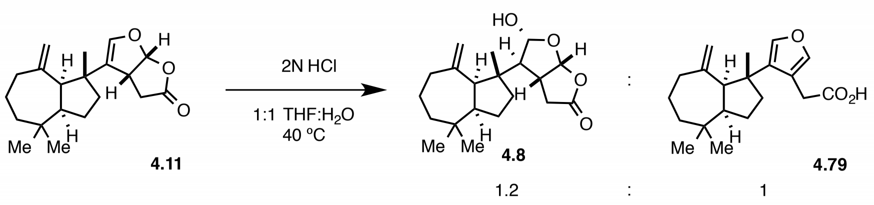
```
Current Data Parameters
NAME            YS-V-239
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_           20170218
Time                8.38
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                    32
DS                     2
SWH            9615.385 Hz
FIDRES         0.250010 Hz
AQ            1.9999200 sec
RG                    10
DW               52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                    1

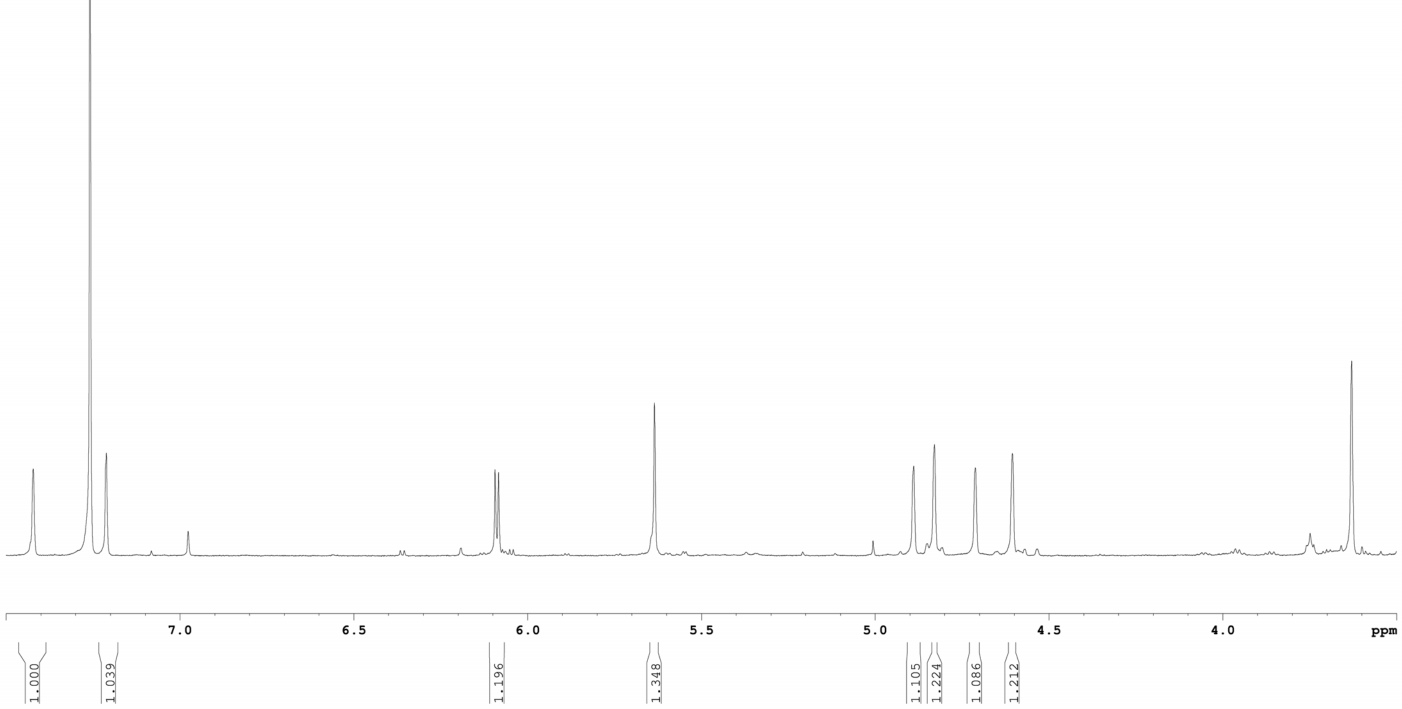
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300362 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-239



^{1}H NMR (CDCl$_3$, 600 MHz) of the crude reaction mixture



```
Current Data Parameters
NAME              YS-V-239
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20170218
Time                8.38
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                    10
DW                52.000 usec
DE                 13.70 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

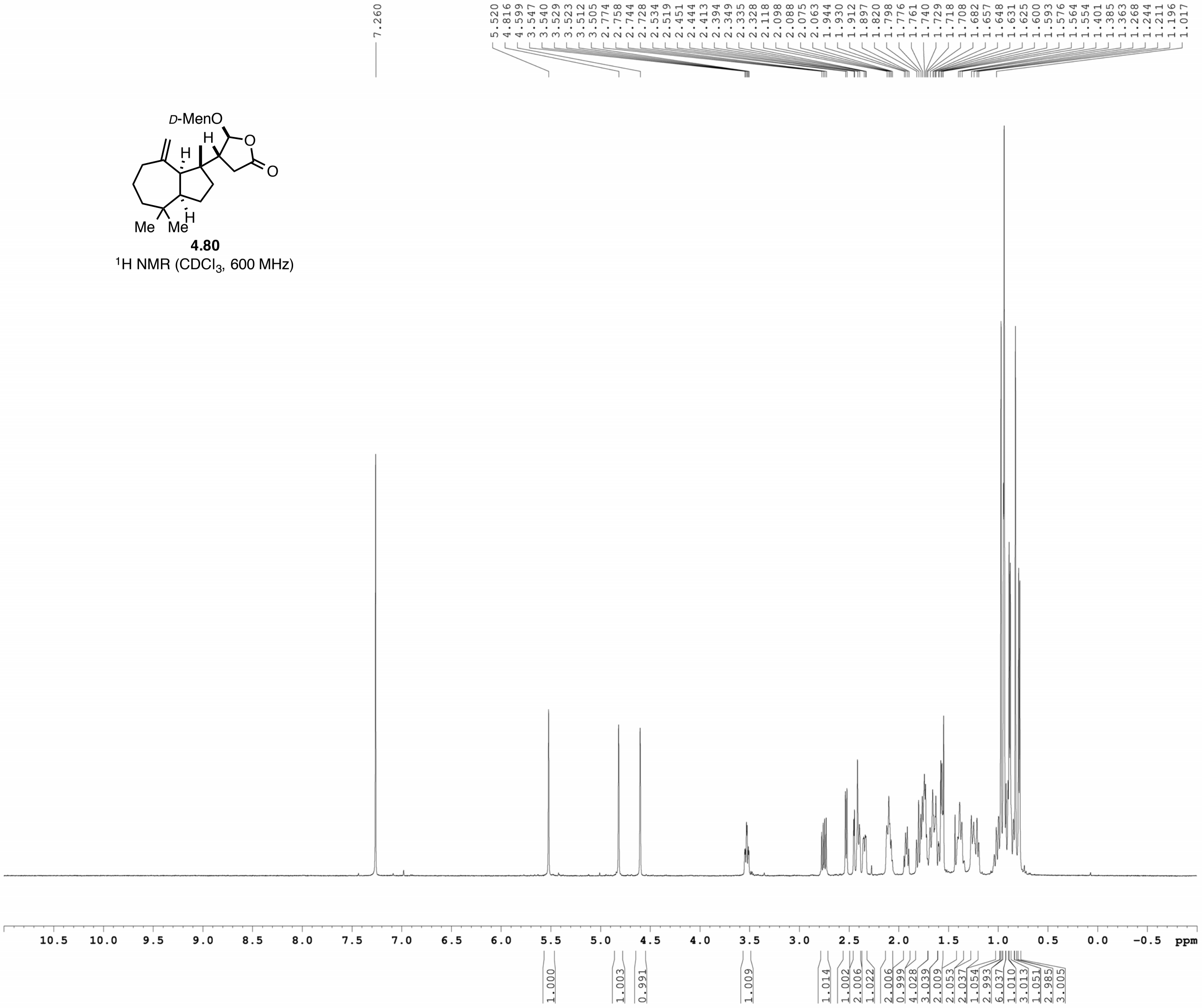
======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                   1H
P1                  12.00 usec
PLW1         20.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300362 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-V-247

4.80

^{1}H NMR (CDCl$_3$, 600 MHz)



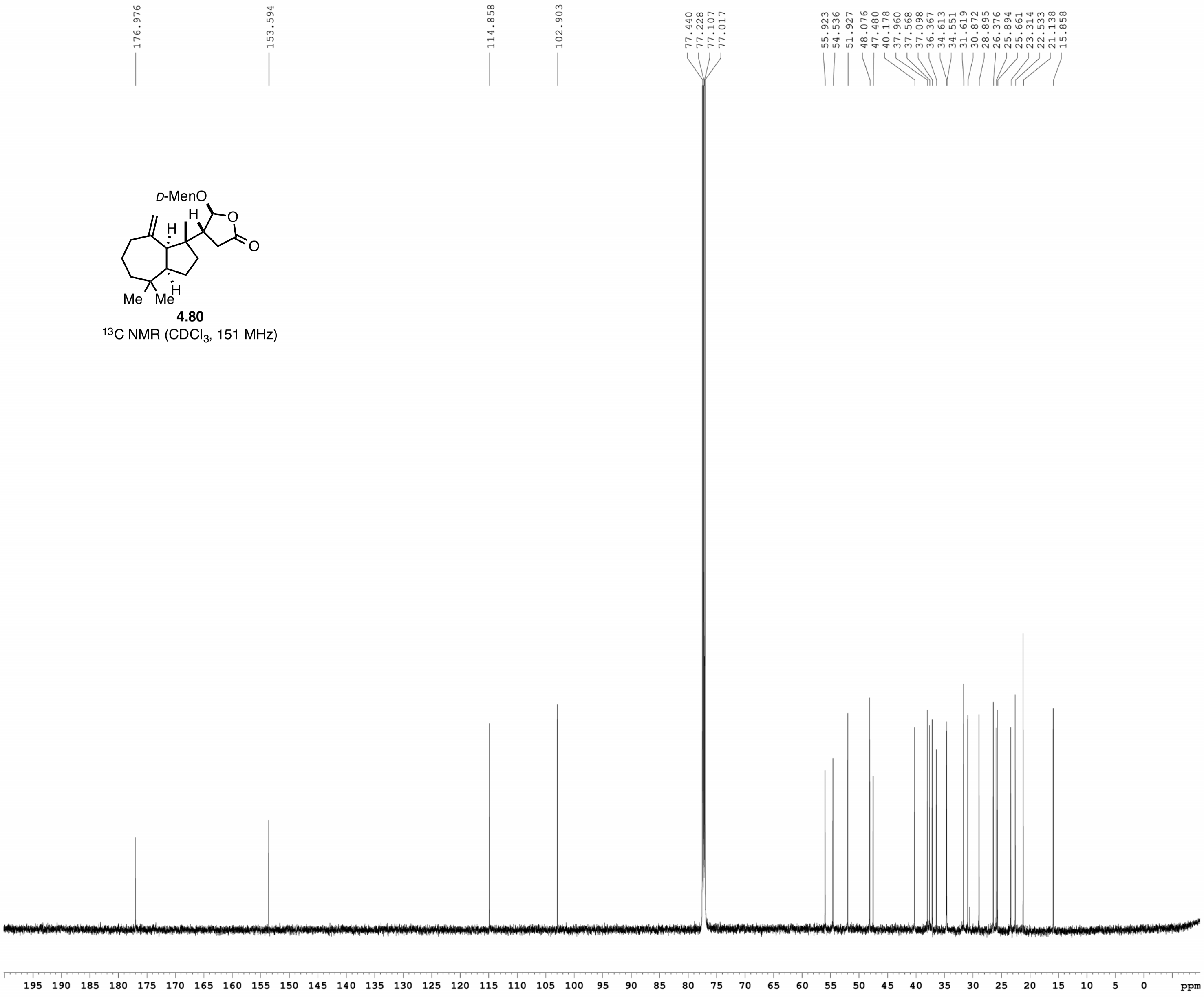
```
Current Data Parameters
NAME            YS-V-247
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

F2 - Acquisition Parameters
Date_          20170301
Time              15.14
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                   10
DW               52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                65536
SF          600.1300351 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-V-247



4.80

^{13}C NMR ($CDCl_3$, 151 MHz)

```
Current Data Parameters
NAME            YS-V-247
EXPNO                  2
PROCNO                 1
DATPATH  /v/data/yuriys/nmr

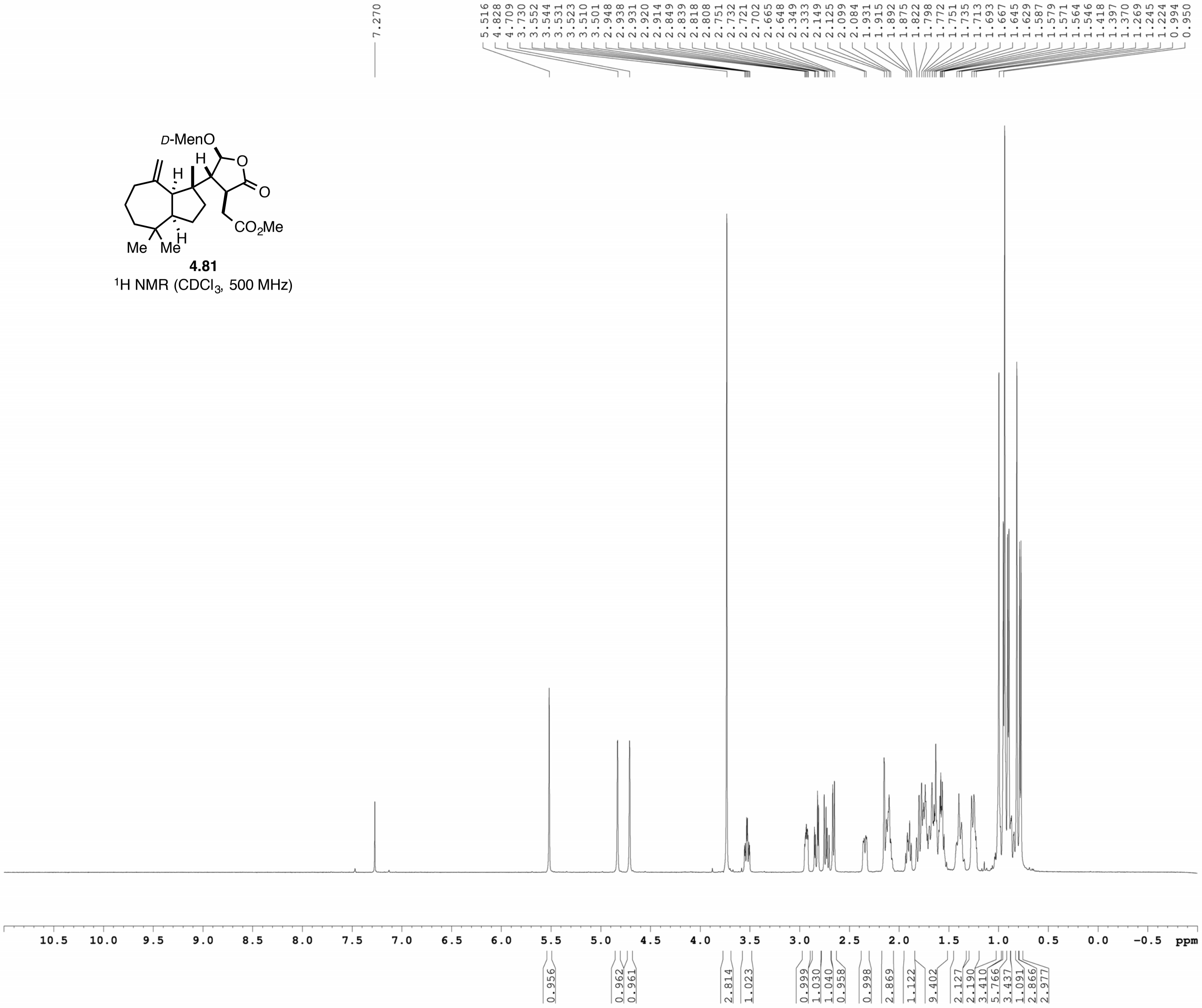
F2 - Acquisition Parameters
Date_           20170301
Time               15.17
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   600
DS                     1
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF           150.9027826 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

1H spectrum



4.81

^{1}H NMR (CDCl$_3$, 500 MHz)

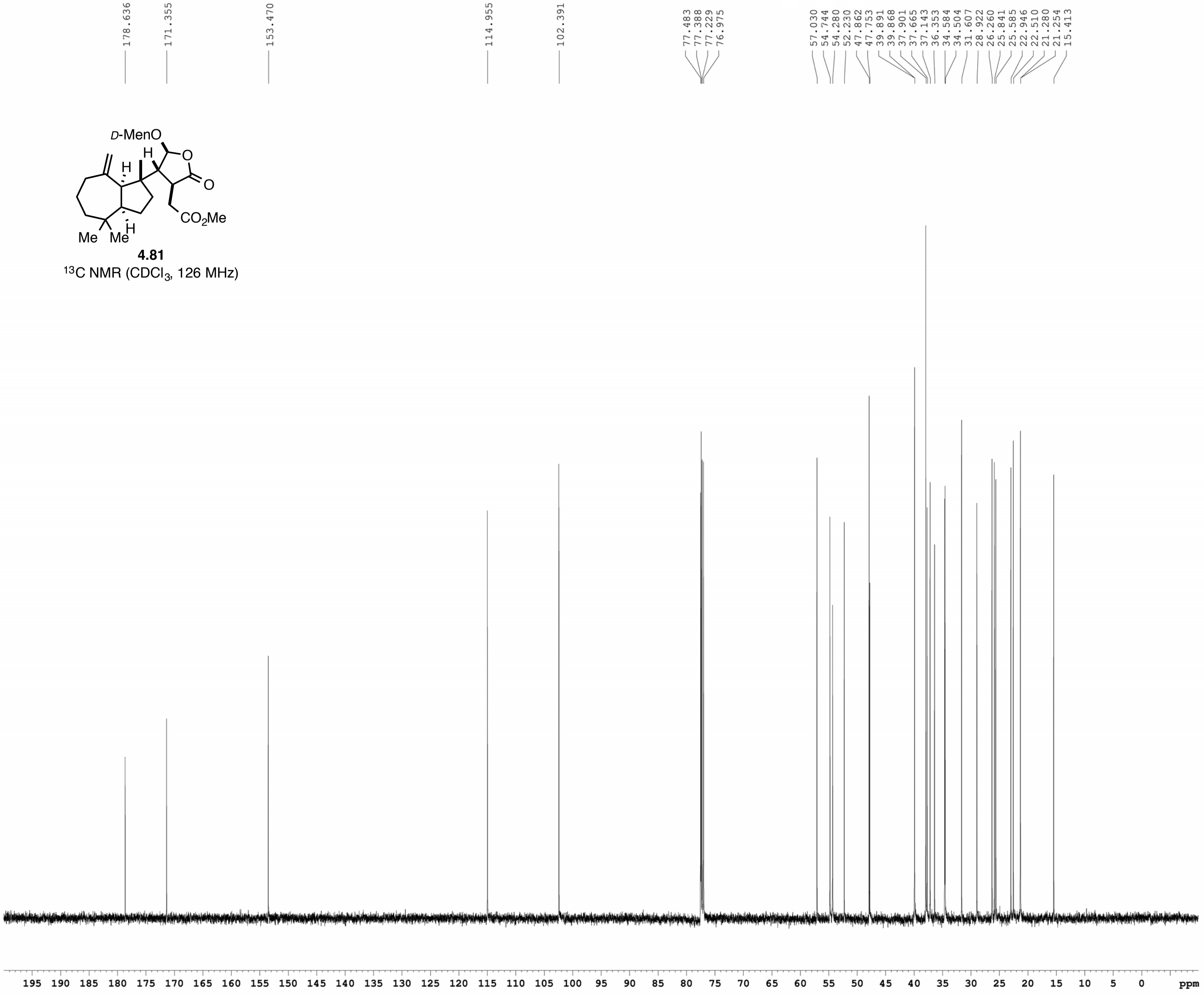
```
Current Data Parameters
NAME           PZ-2145-P
EXPNO                  1
PROCNO                 1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_           20170411
Time               11.45
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200267 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

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



4.81

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          PZ-2145-P
EXPNO                 2
PROCNO                1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_          20170411
Time              11.47
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  308
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

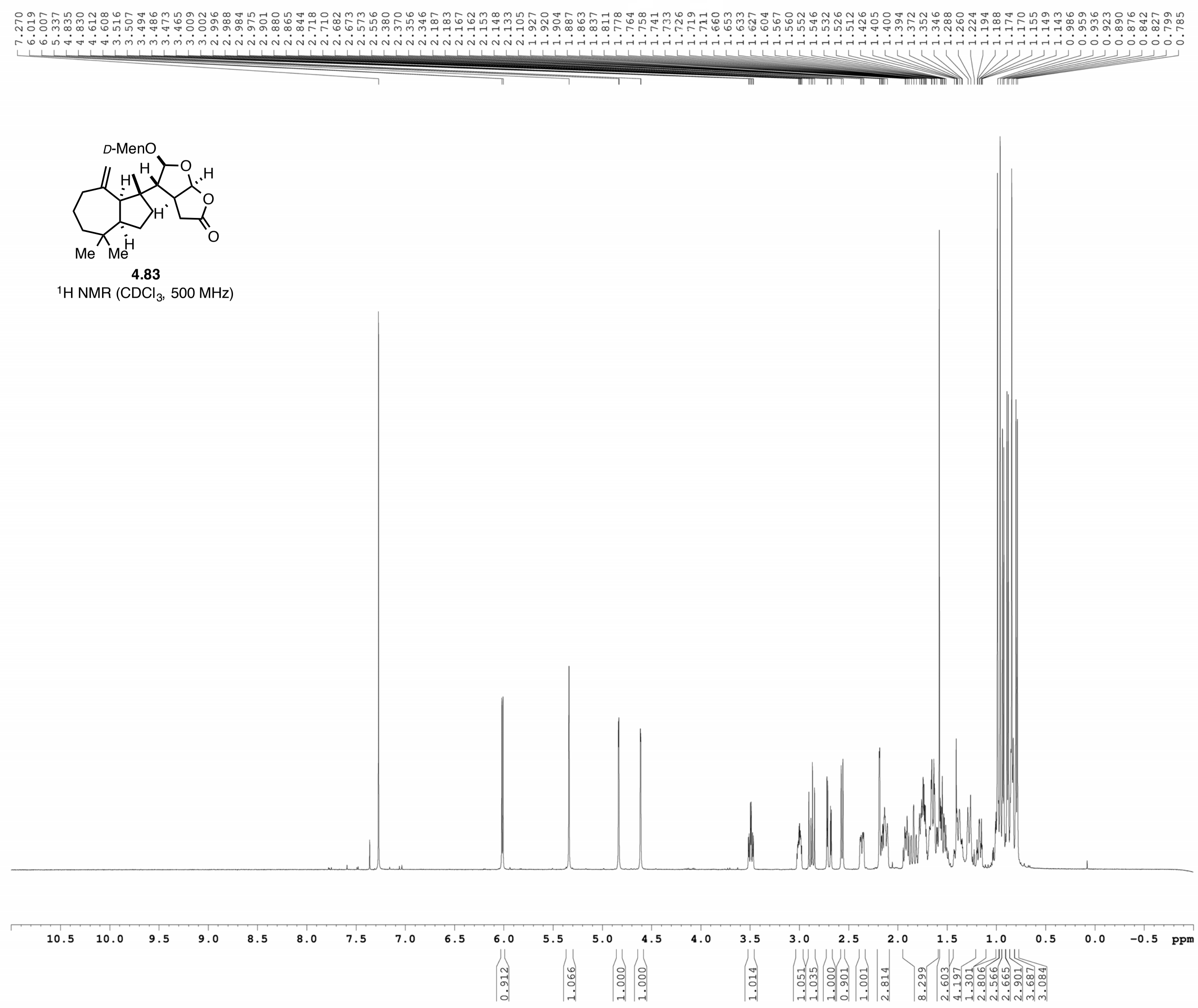
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804007 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



4.83

^{1}H NMR (CDCl$_3$, 500 MHz)

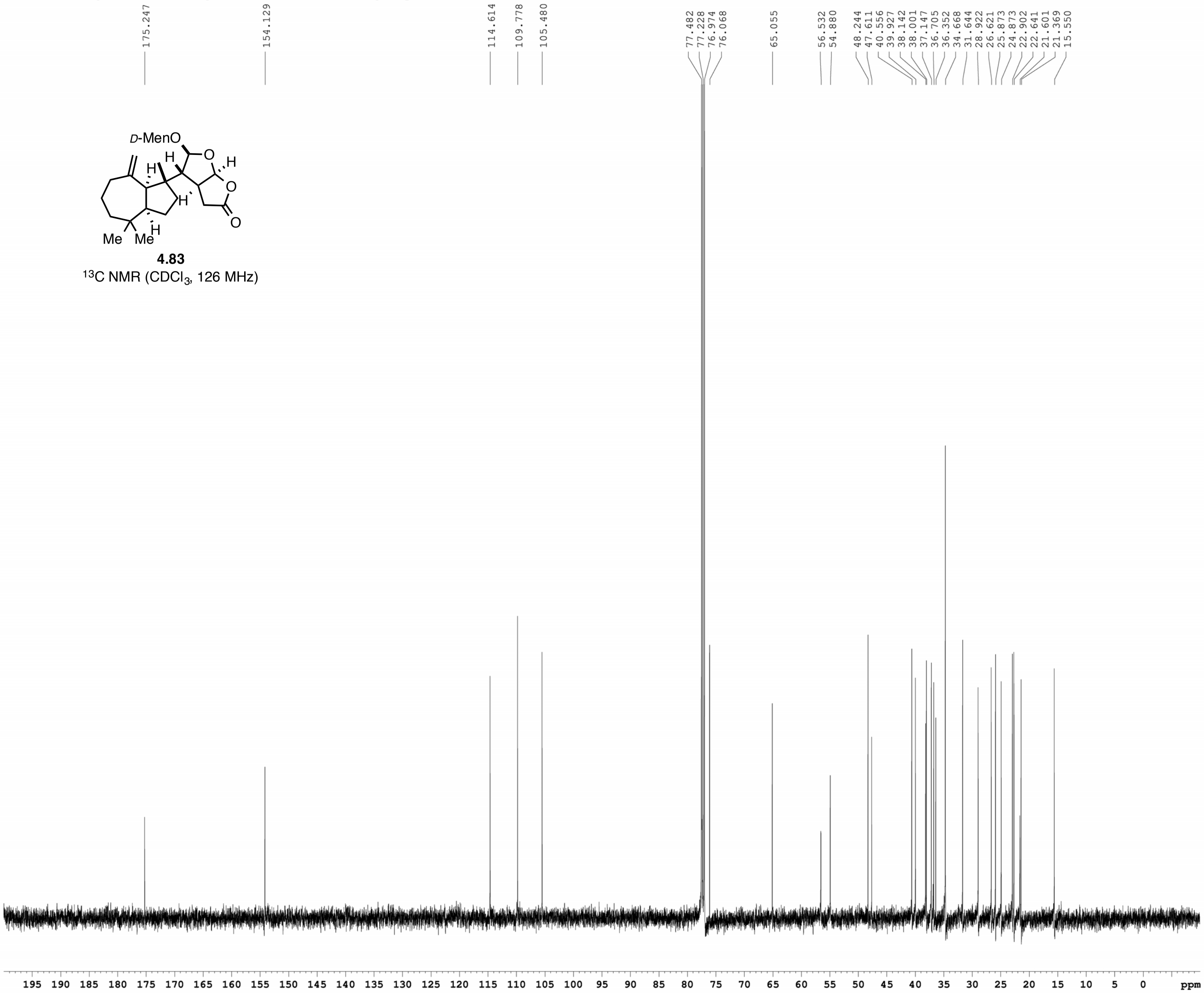
```
Current Data Parameters
NAME              PZ-2124-P
EXPNO                     1
PROCNO                    1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_              20170327
Time                  12.38
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG                zg30
TD                    81728
SOLVENT               CDCl3
NS                        8
DS                        2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                      5.7
DW                62.400 usec
DE                  6.00 usec
TE                  298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF           500.2200267 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
```

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



4.83

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            PZ-2124-P
EXPNO                   2
PROCNO                  1
DATPATH  /v/data/zhaop3/nmr

F2 - Acquisition Parameters
Date_            20170327
Time                12.40
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    328
DS                     16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                 4597.6
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

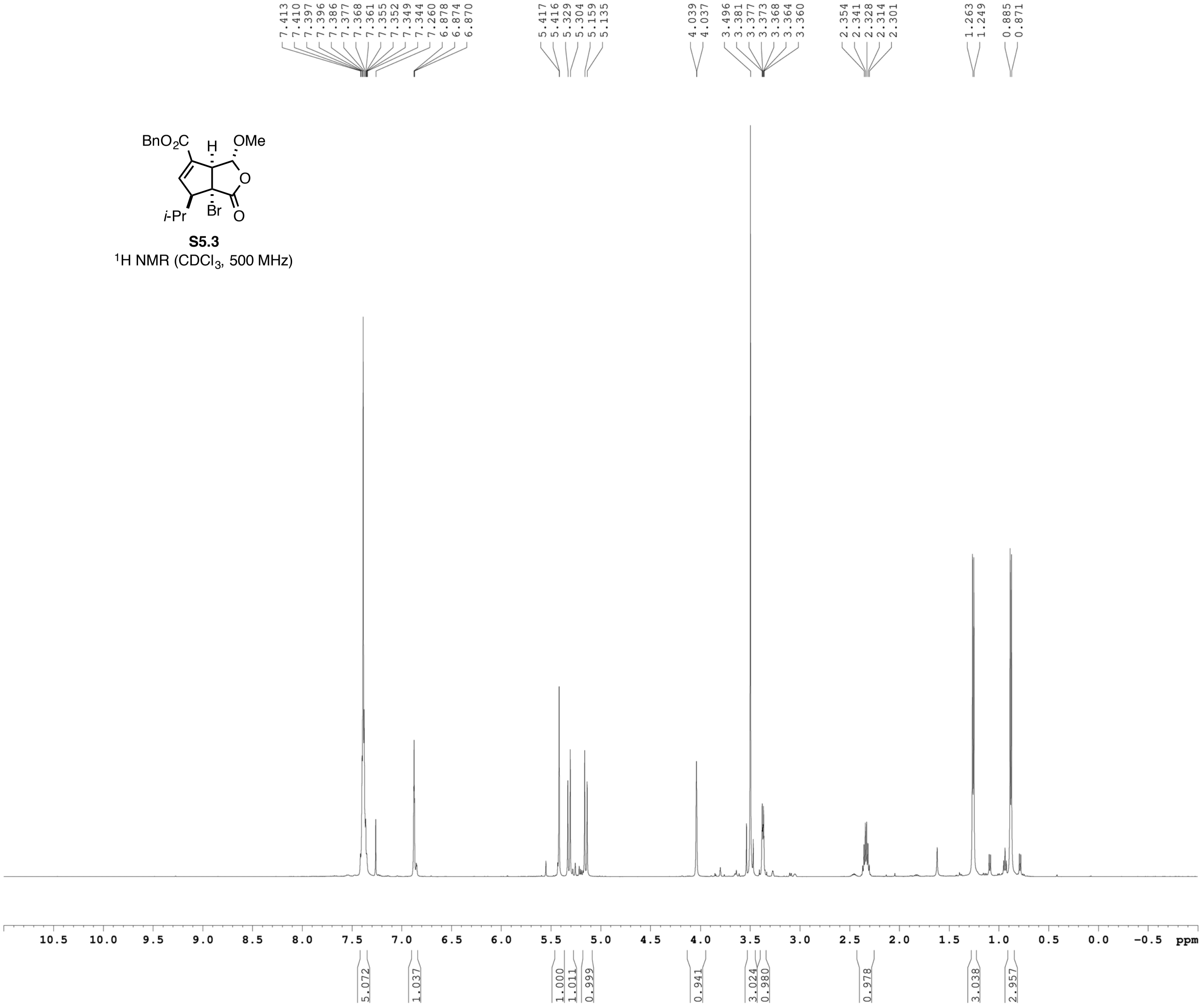
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803992 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

Appendix E: Chapter 5 NMR Spectra

PKO-I-154B



S5.3

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME        PKO-I-154B-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20101113
Time               19.21
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT           CDCl3T
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                 101.6
DW                62.400 usec
DE                  6.00 usec
TE                 675.2 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

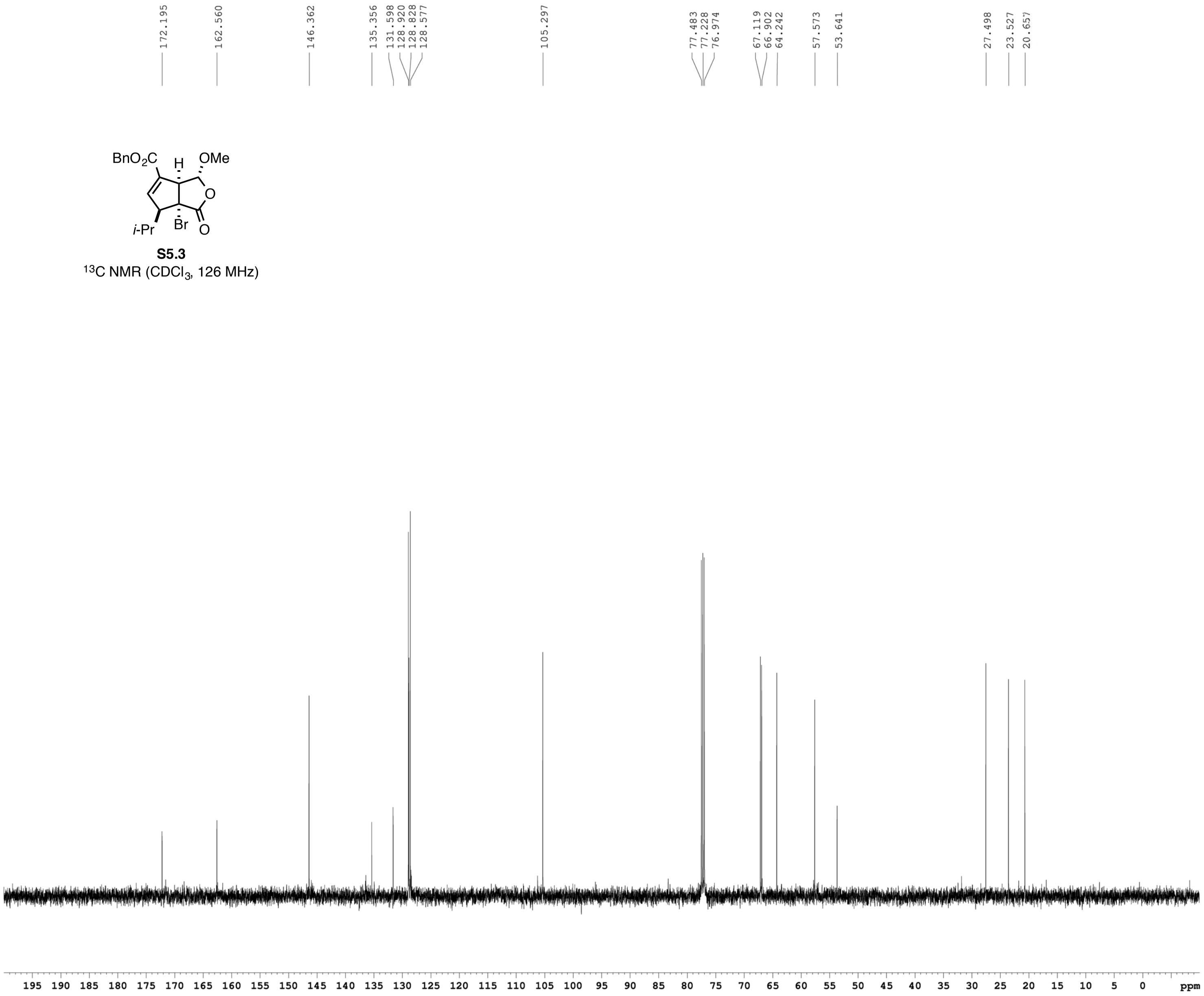
======== CHANNEL f1 ========
NUC1                  1H
P1                 13.00 usec
PL1                -4.00 dB
SFO1         499.6234973 MHz

F2 - Processing parameters
SI                 65536
SF           499.6200292 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

PKO-I-154B

S5.3

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME         PKO-I-154B-2
EXPNO                   2
PROCNO                  1

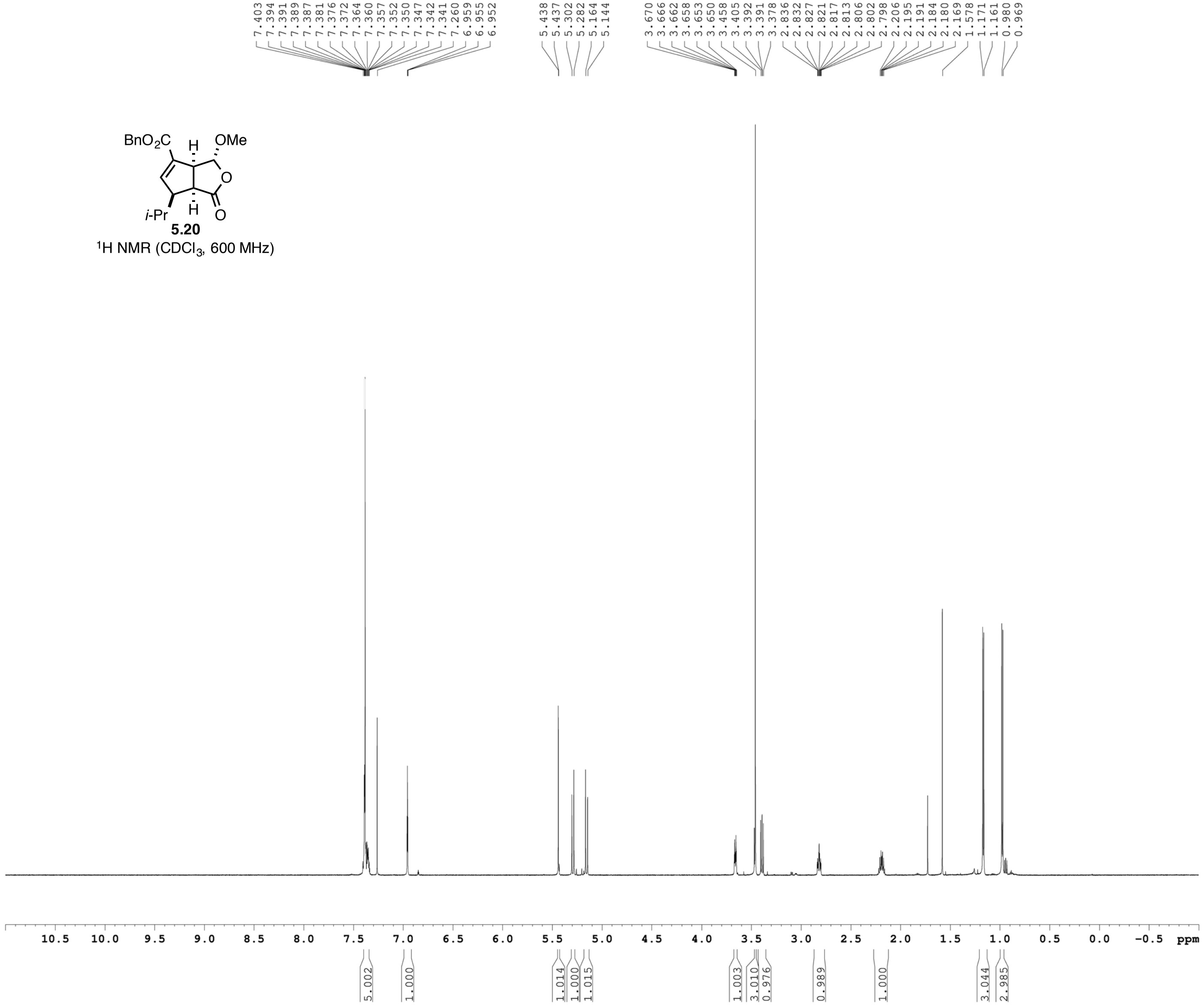
F2 - Acquisition Parameters
Date_            20101113
Time                19.24
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   218
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                 46341
DW                16.500 usec
DE                  4.50 usec
TE                 675.2 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 12.50 usec
PL1                -3.00 dB
SFO1         125.6433683 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               13.70 dB
SFO2         499.6224981 MHz

F2 - Processing parameters
SI                 65536
SF           125.6295329 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

PKO-I-162



5.20

^{1}H NMR (CDCl$_3$, 600 MHz)

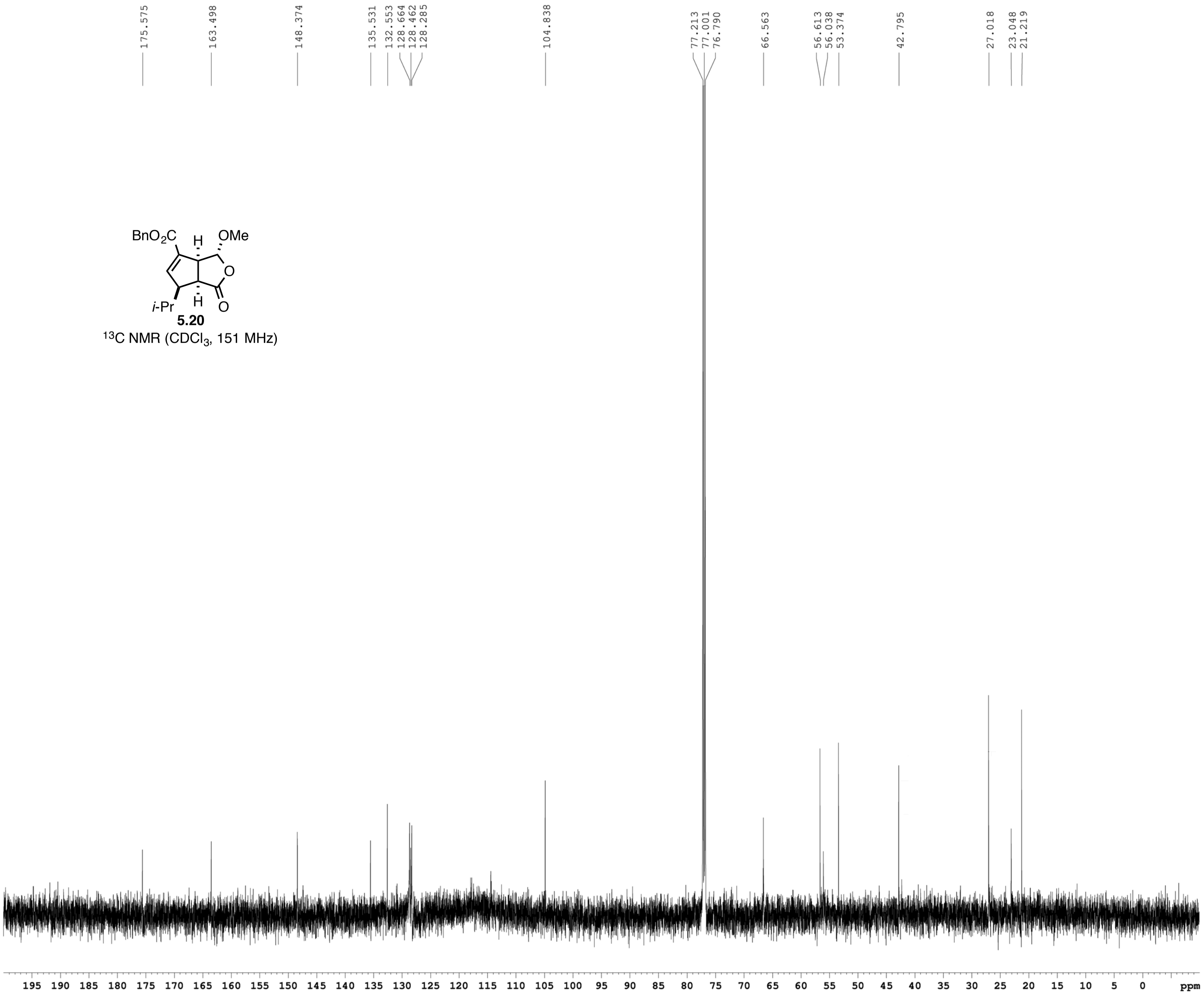
```
Current Data Parameters
NAME          PKO-I-162-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20101117
Time                16.55
INSTRUM             av600
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  98074
SOLVENT            CDCl3T
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                    912
DW                 52.000 usec
DE                   6.00 usec
TE                  298.0 K
D1           0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.00 usec
PL1                 -1.00 dB
SFO1         600.1342009 MHz

F2 - Processing parameters
SI                  65536
SF           600.1300349 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

PKO-I-162



5.20

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME        PKO-I-162-2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20101120
Time              11.02
INSTRUM           av600
PROBHD   5 mm TBI 1H/13
PULPROG         zgdc30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36231.883 Hz
FIDRES         0.552855 Hz
AQ            0.9043968 sec
RG                  114
DW               13.800 usec
DE                 6.00 usec
TE                298.0 K
D1           0.40000001 sec
d11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                15.00 usec
PL1       0 dB
SFO1        150.9194080 MHz

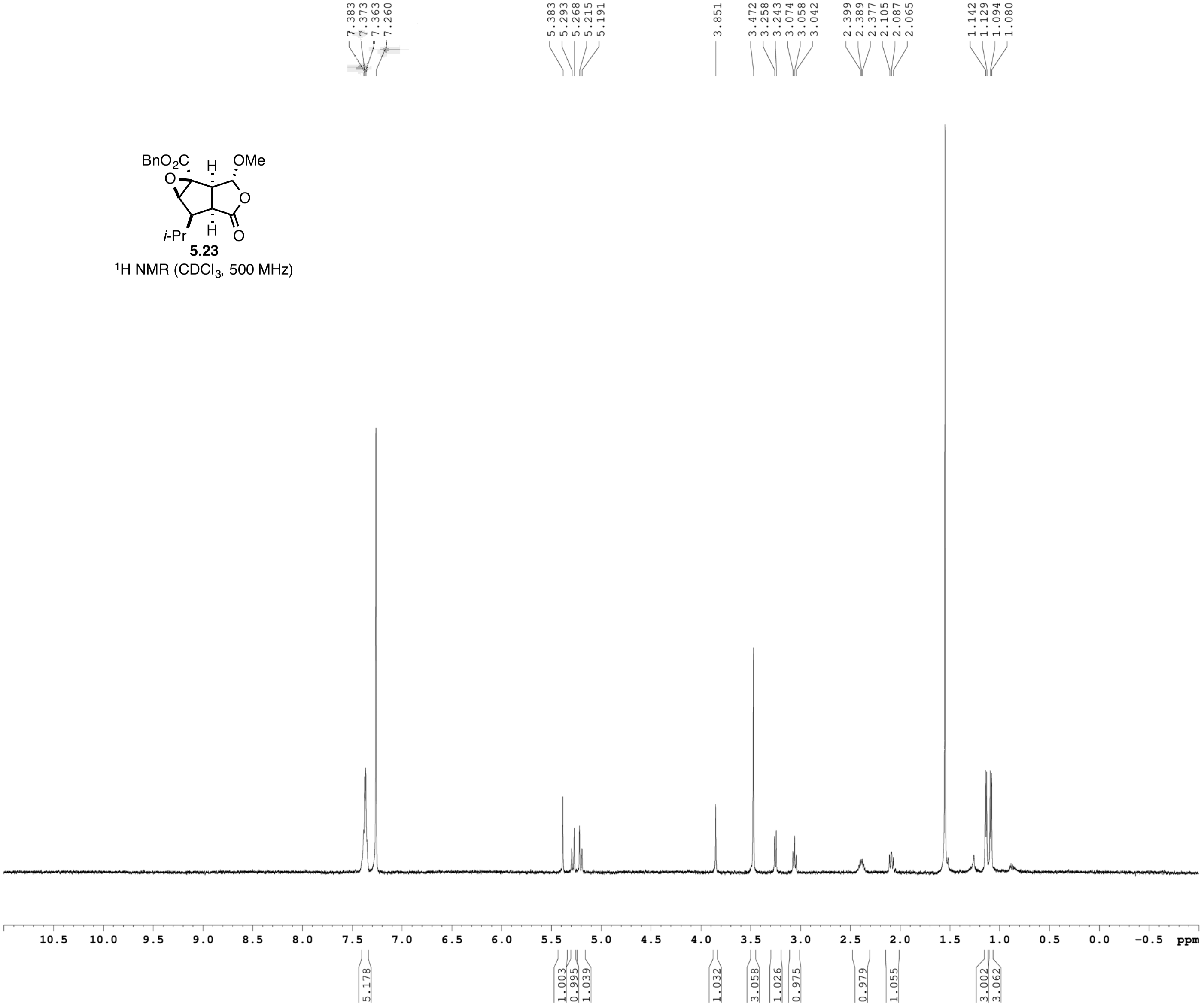
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2              120.00 dB
PL12              18.80 dB
SFO2        600.1330010 MHz

F2 - Processing parameters
SI                65536
SF          150.9028175 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```

PKO-I-290

5.23

^{1}H NMR (CDCl$_3$, 500 MHz)



```
Current Data Parameters
NAME          PKO-I-290-3
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20110322
Time                12.06
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                  46341
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

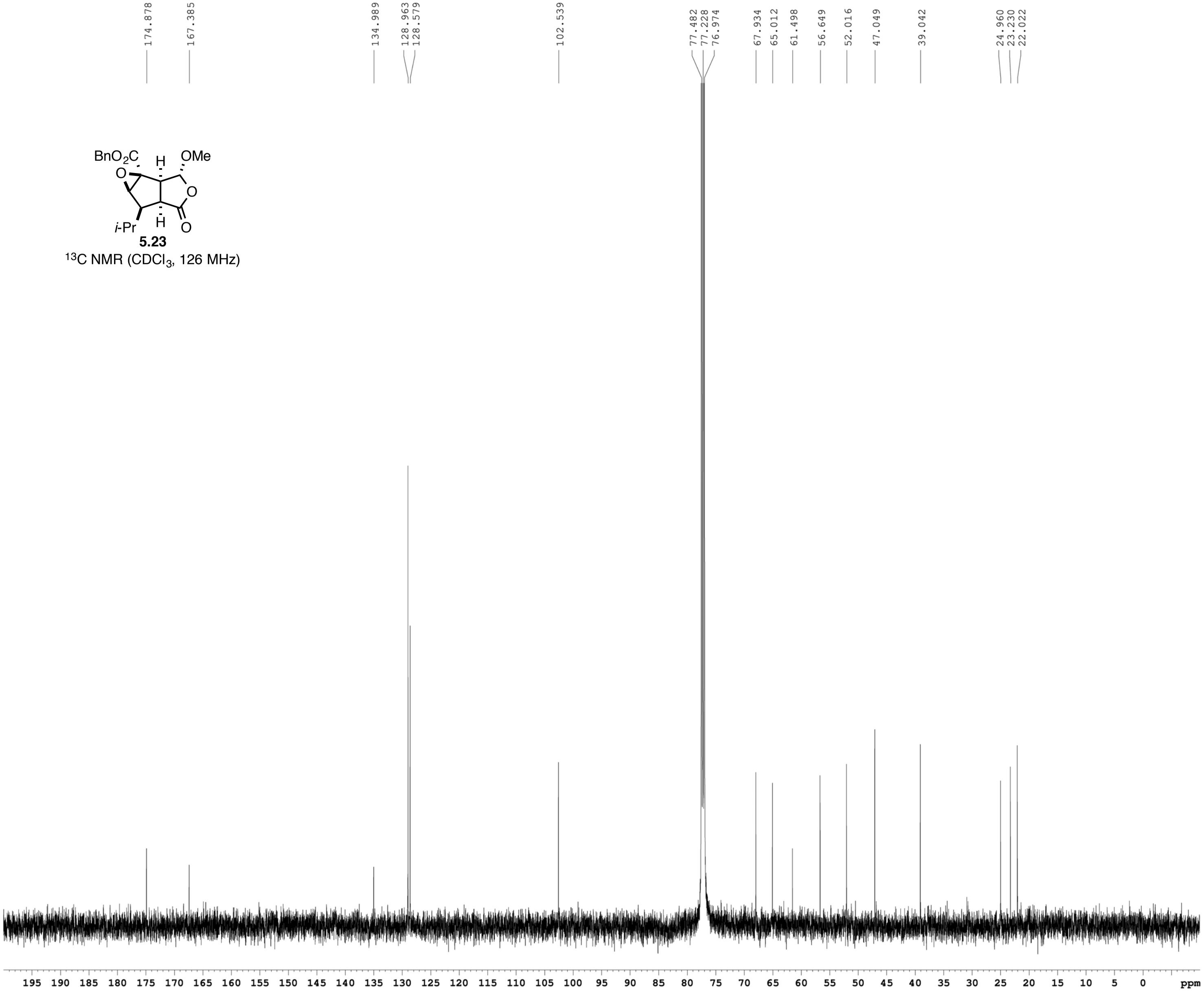
======== CHANNEL f1 ========
NUC1                   1H
P1                  12.20 usec
PL1                 -5.00 dB
SFO1          499.5134966 MHz

F2 - Processing parameters
SI                  65536
SF            499.5100268 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

PKO-I-290

5.23

^{13}C NMR (CDCl$_3$, 126 MHz)



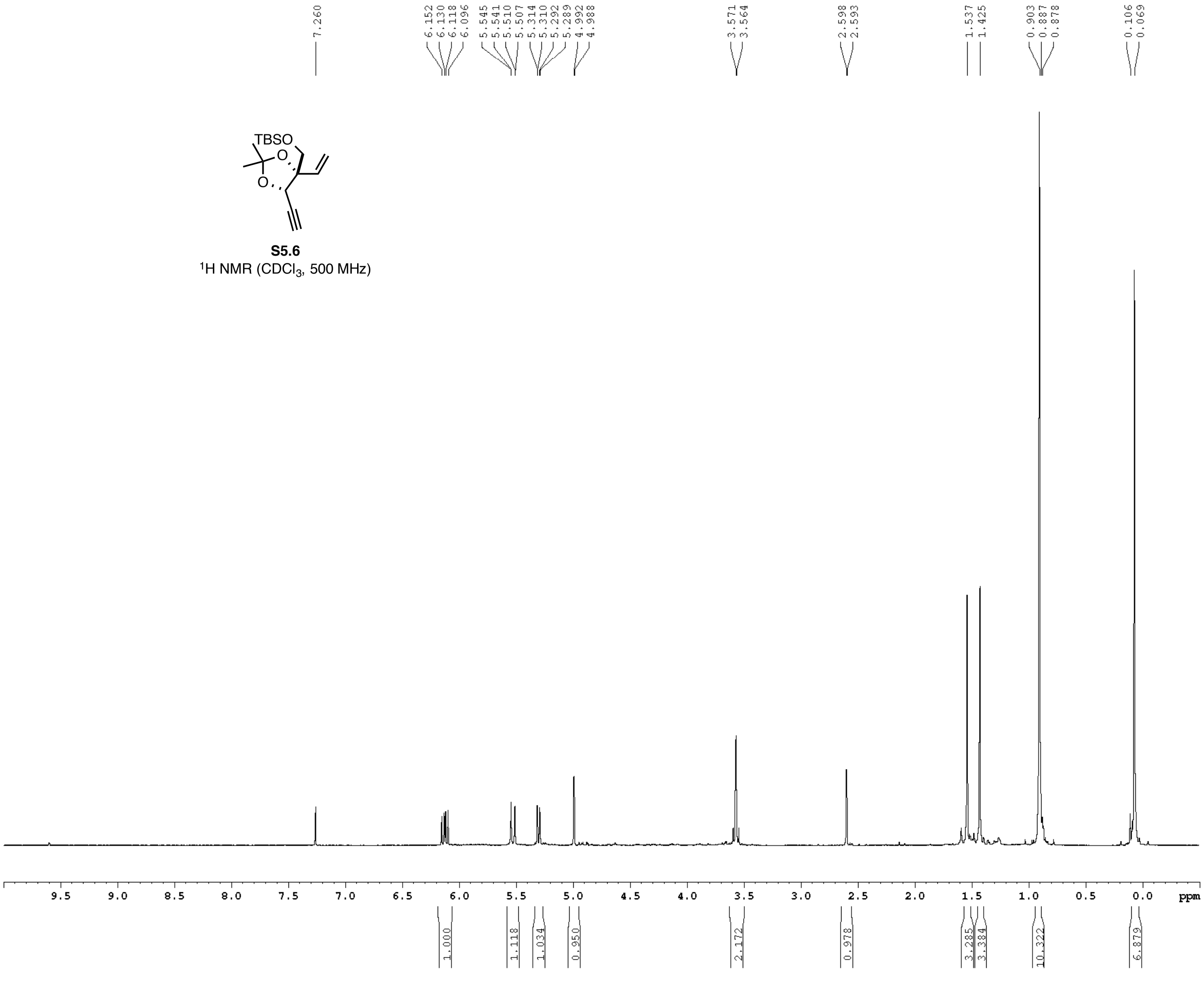
```
Current Data Parameters
NAME        PKO-I-290-3
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20110325
Time              19.04
INSTRUM           gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                 9767
DS                    4
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               4597.6
DW               16.500 usec
DE                 4.50 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
MCREST  0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 7.70 usec
PL1      0 dB
SFO1        125.6157052 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              13.20 dB
SFO2        499.5124975 MHz

F2 - Processing parameters
SI                65536
SF          125.6018665 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



S5.6

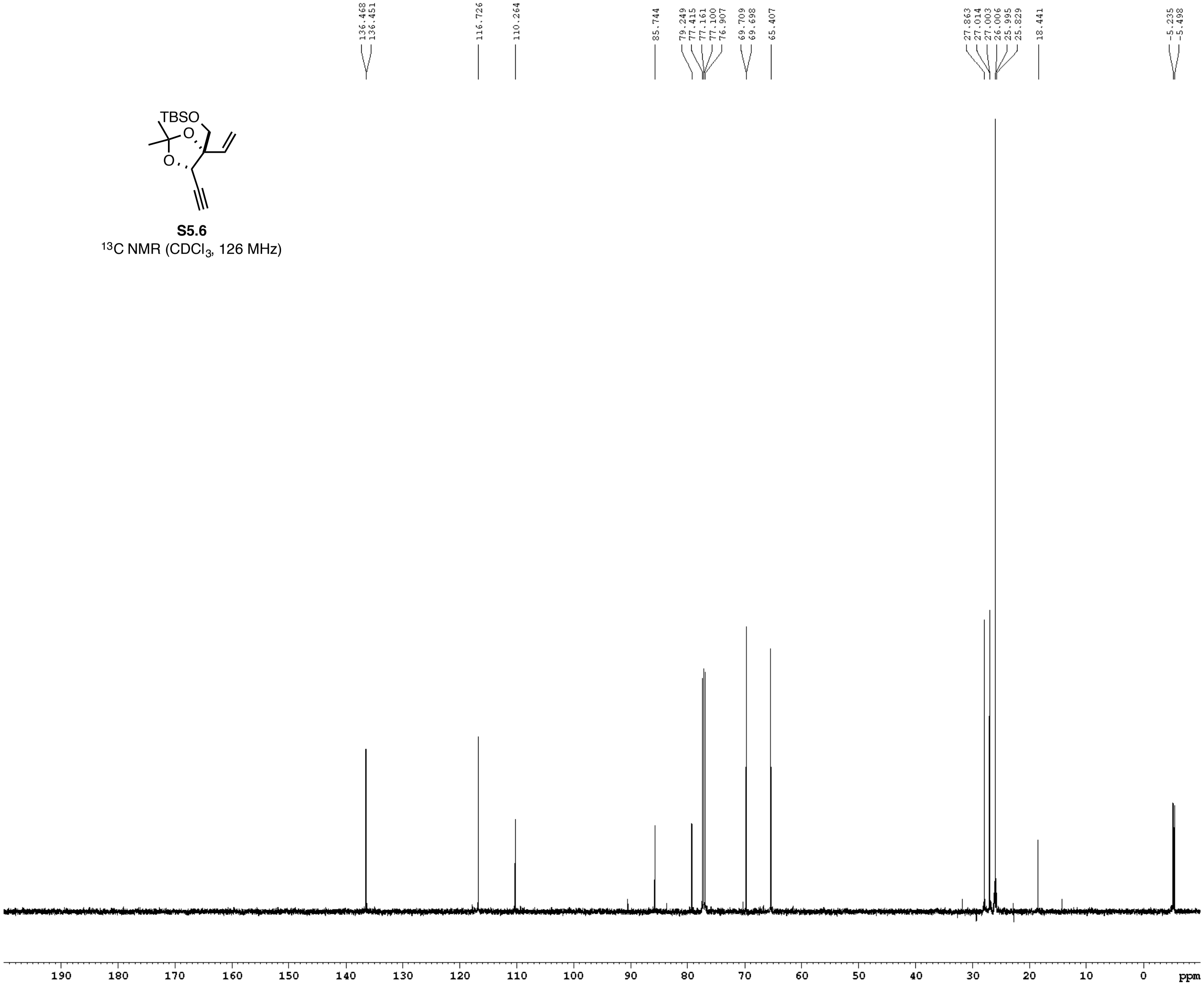
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          DJT-II-295
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131130
Time               15.24
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200308 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  4.00
```



S5.6

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-II-295
EXPNO                  4
PROCNO                 1

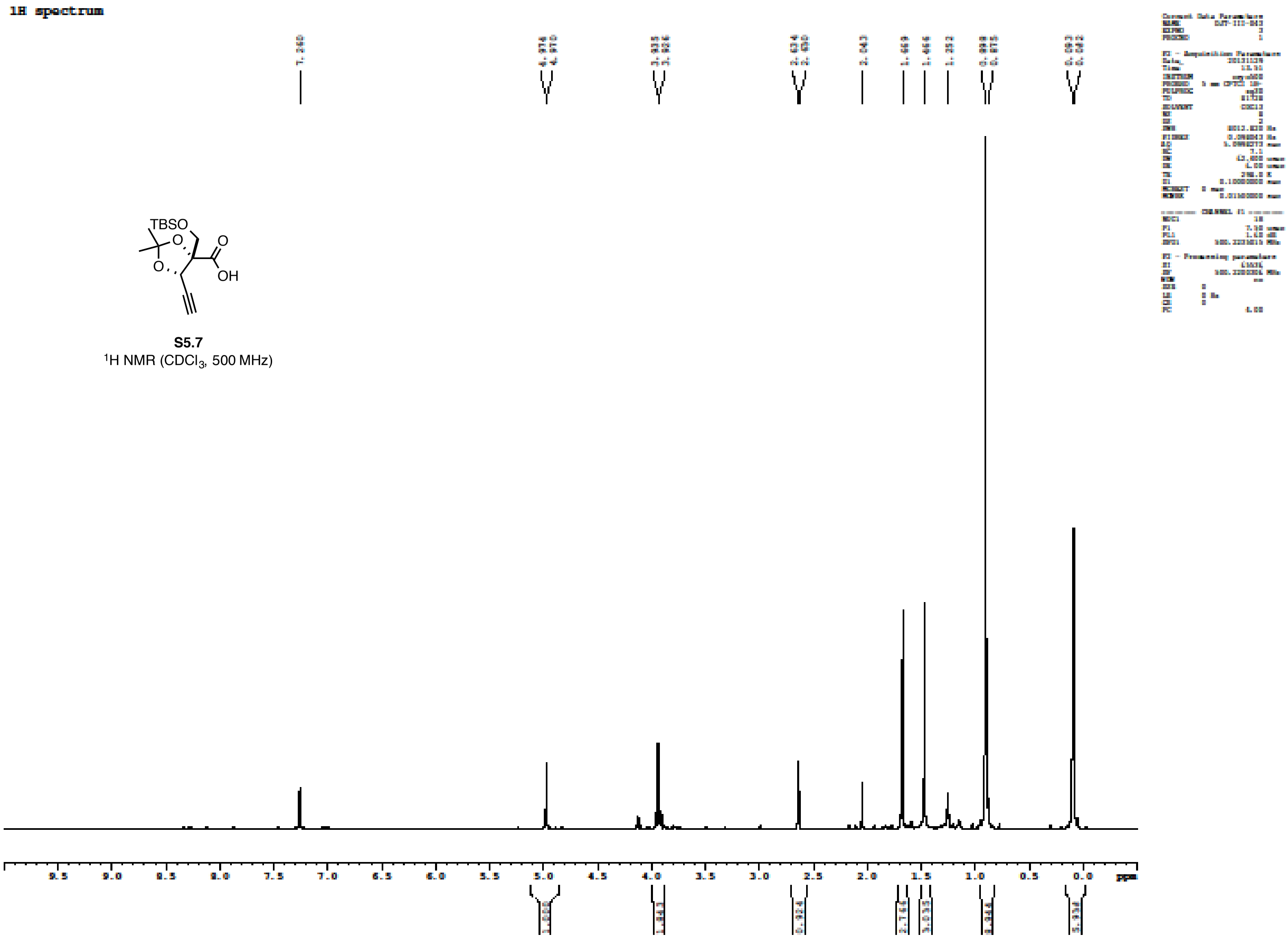
F2 - Acquisition Parameters
Date_           20131130
Time               15.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   385
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               14596.5
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST    0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

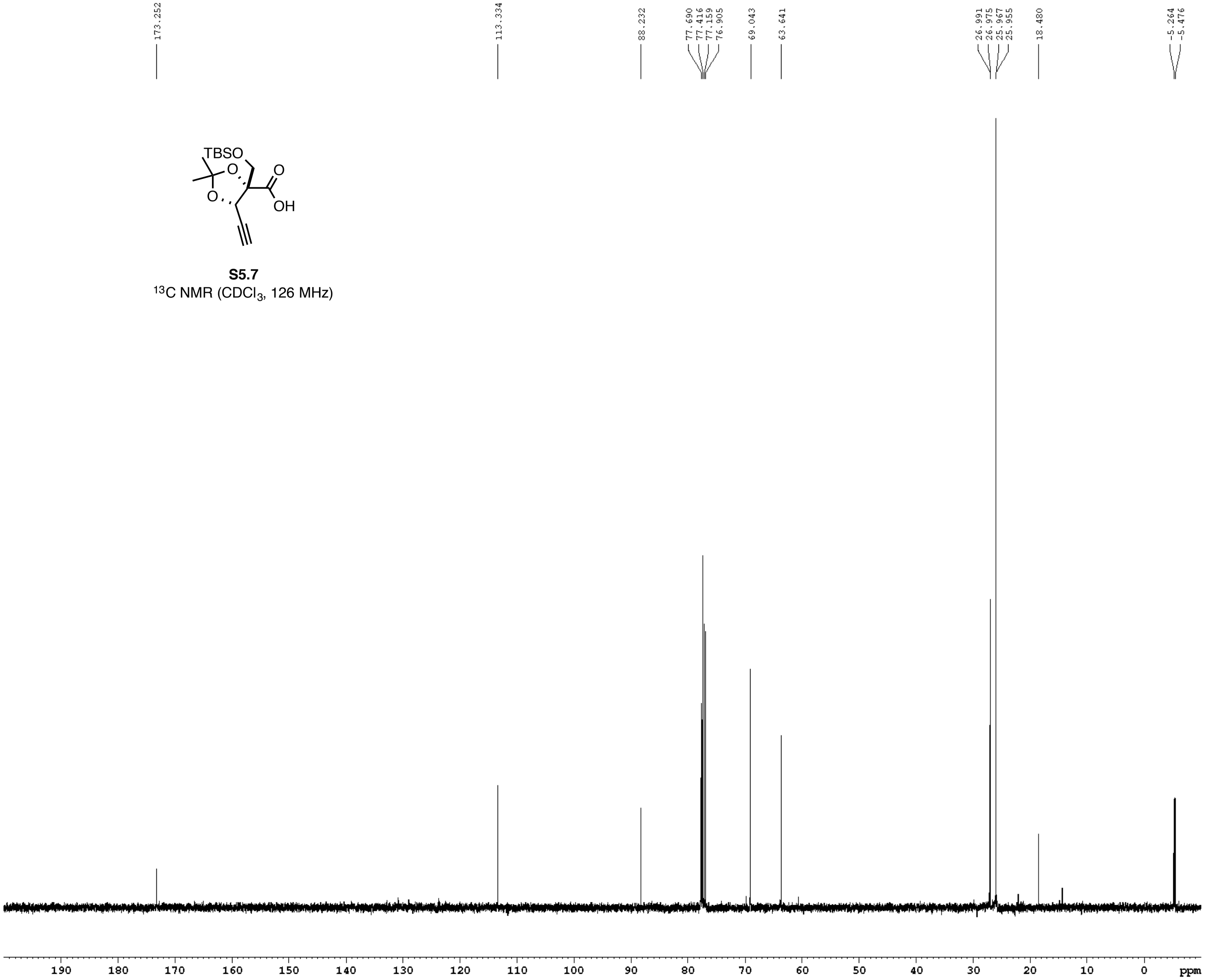
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804076 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```



S5.7

^{1}H NMR (CDCl$_3$, 500 MHz)



S5.7
^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME        DJT-III-043
EXPNO                 4
PROCNO                1

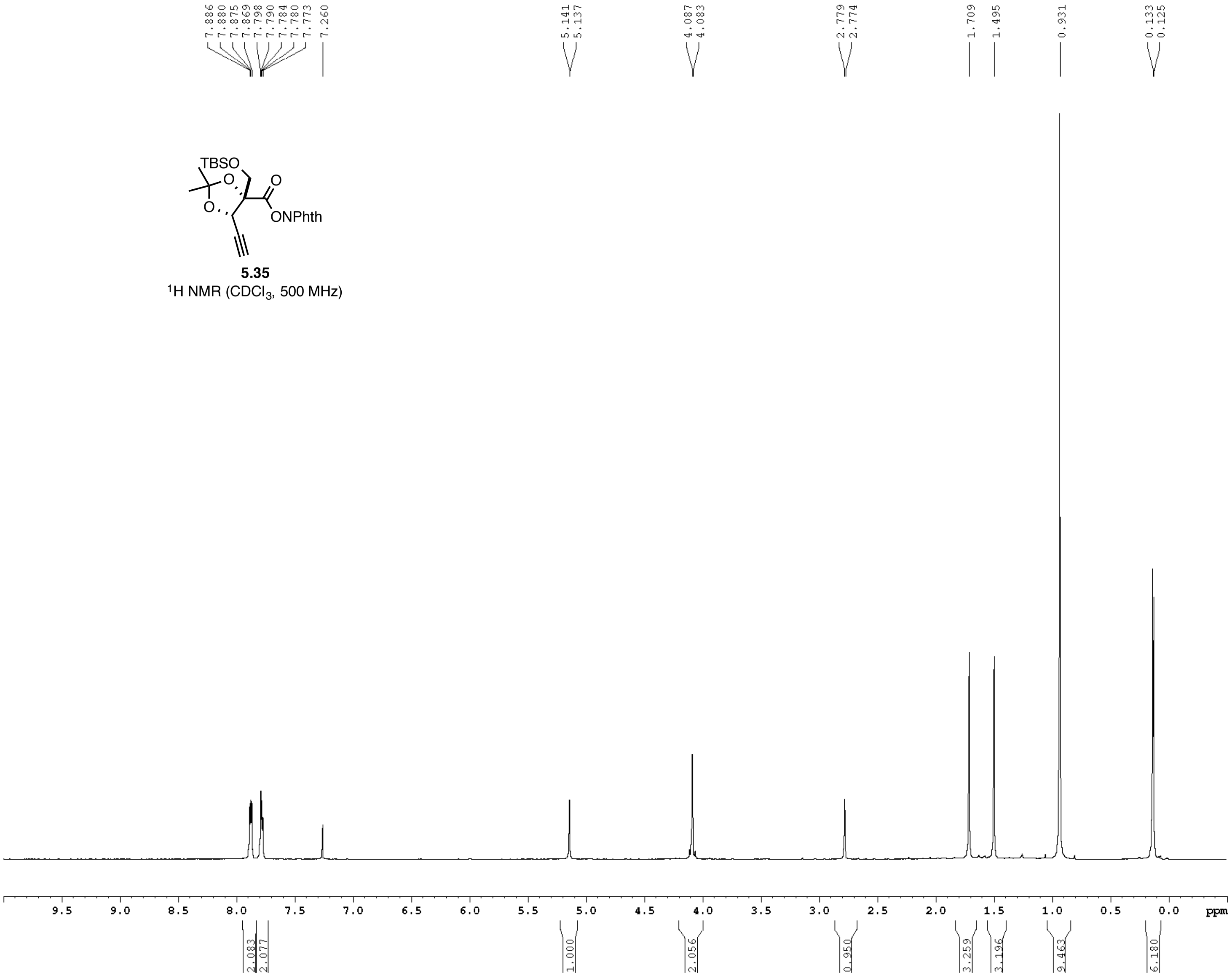
F2 - Acquisition Parameters
Date_          20131129
Time              13.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  175
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                13004
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804085 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



5.35

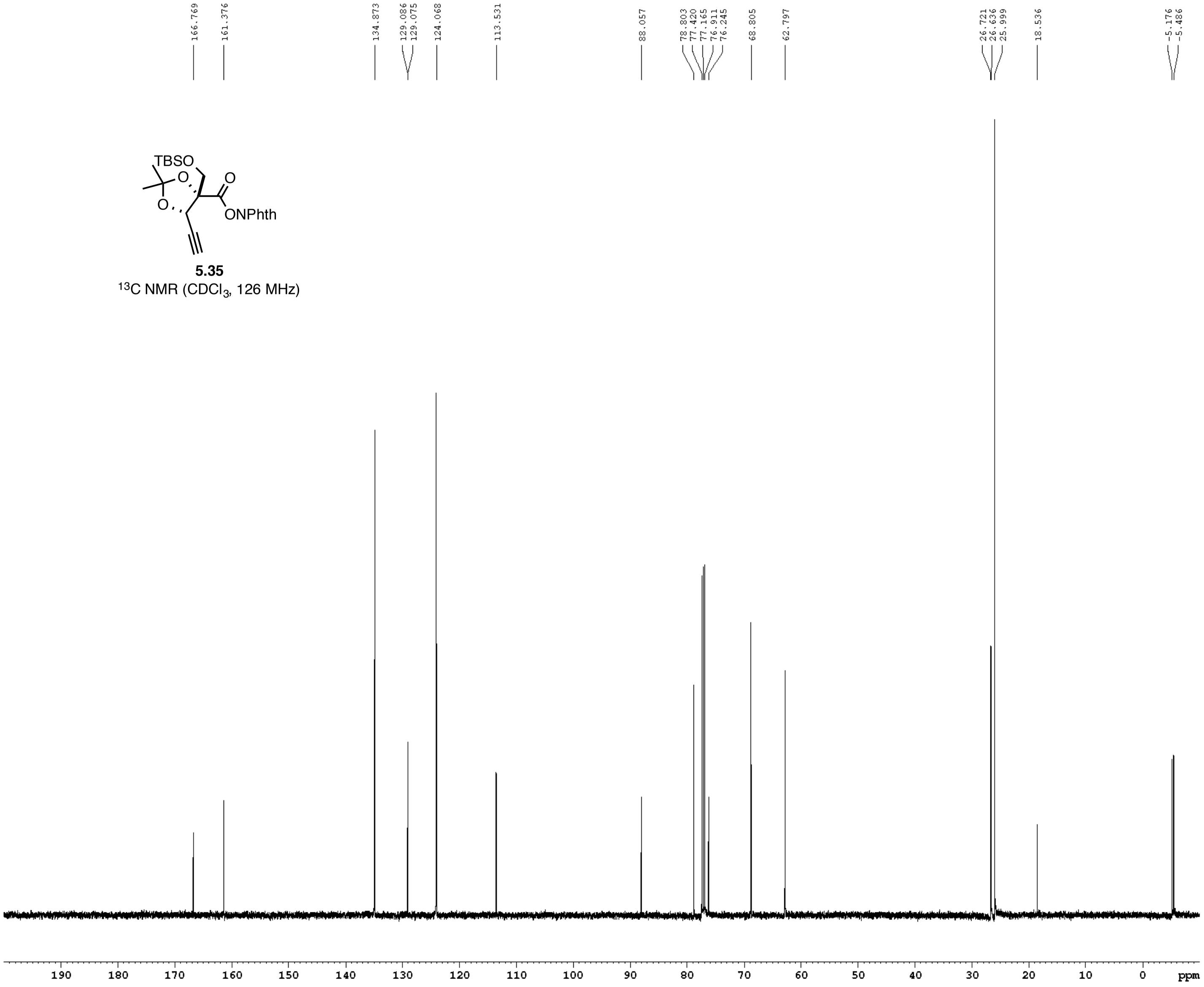
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME         DJT-III-081
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131206
Time               13.53
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   114
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.20 usec
PL1                -5.00 dB
SFO1         499.2934950 MHz

F2 - Processing parameters
SI                 65536
SF           499.2900294 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



5.35
^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME        DJT-III-081
EXPNO                 3
PROCNO                1

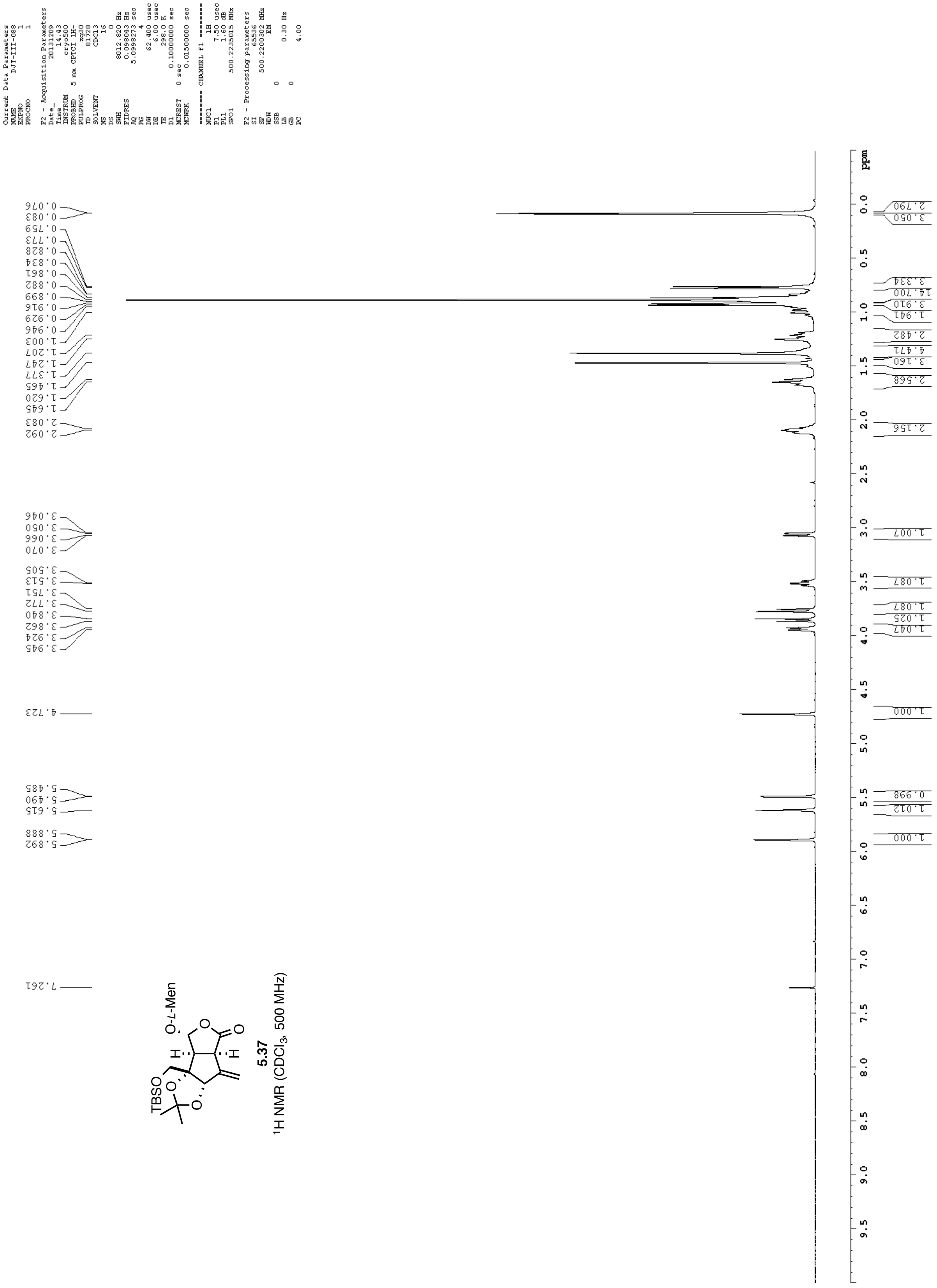
F2 - Acquisition Parameters
Date_          20131207
Time              11.22
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  338
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

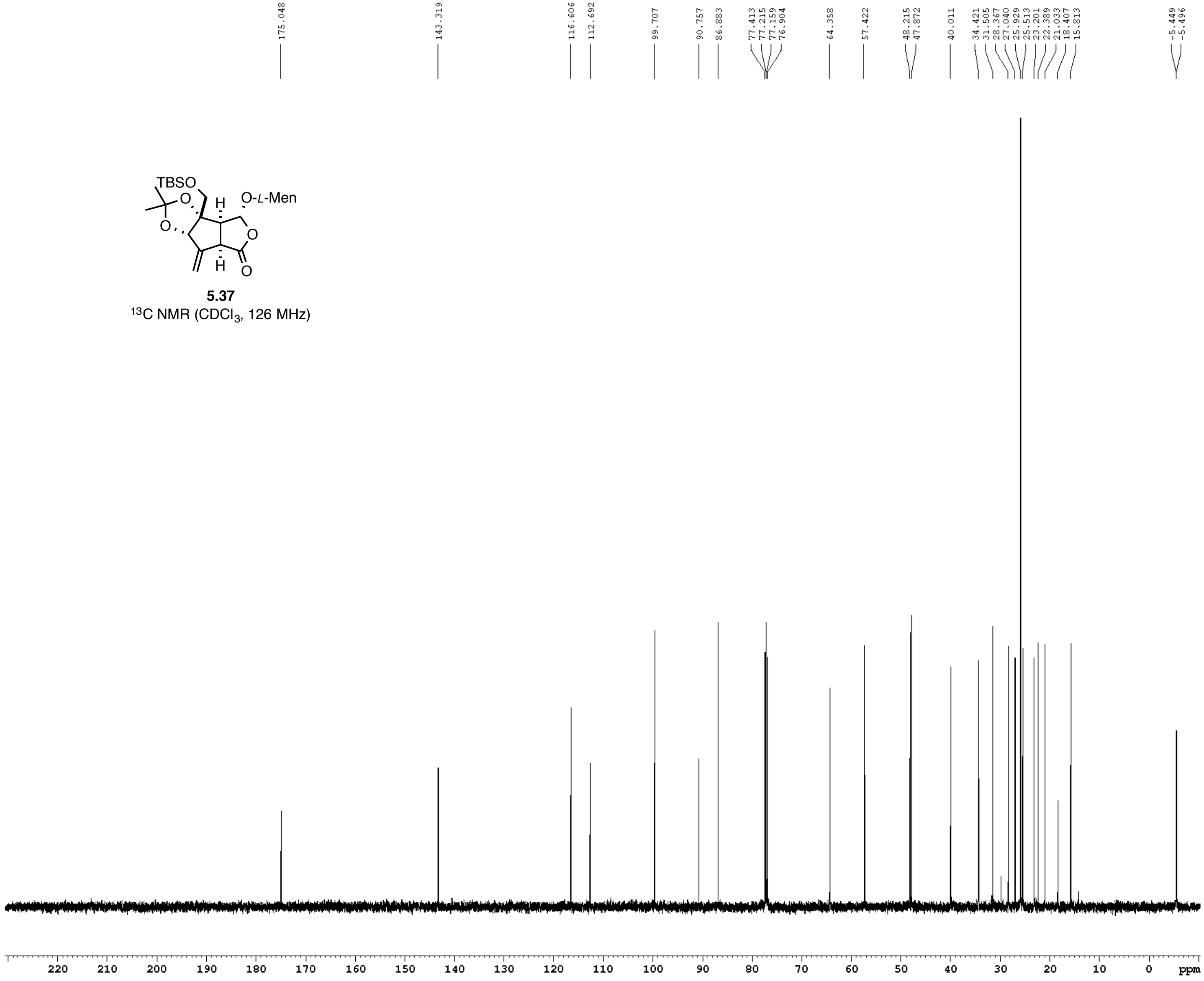


5.37

^{1}H NMR (CDCl$_3$, 500 MHz)

5.37

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          DJT-III-088
EXPNO                   2
PROCNO                  1

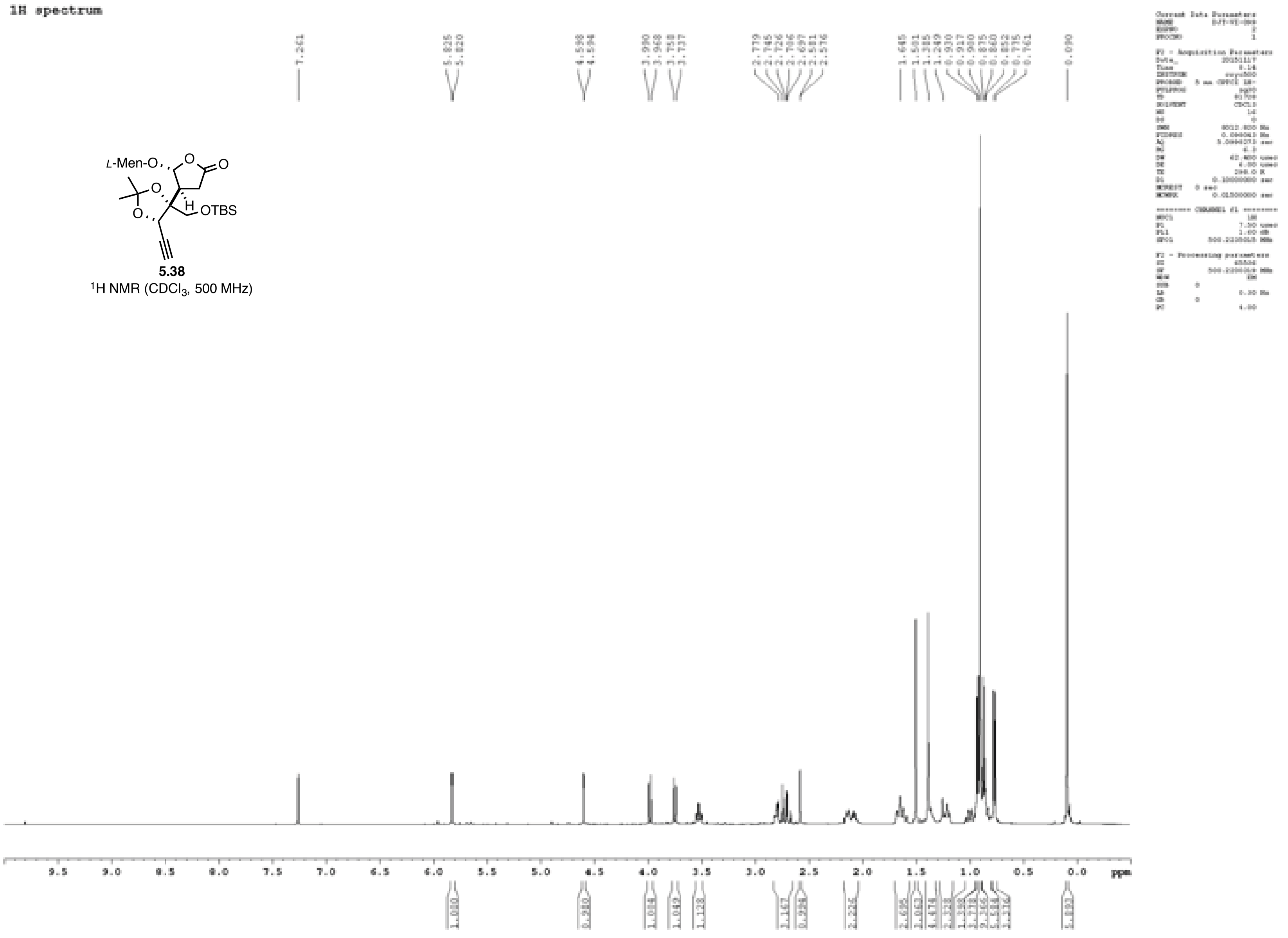
F2 - Acquisition Parameters
Date_            20131209
Time                14.48
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    143
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   8192
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  31.00 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  15.50 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  3.20 dB
SP2                  3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.60 dB
SFO2          500.2225011 MHz

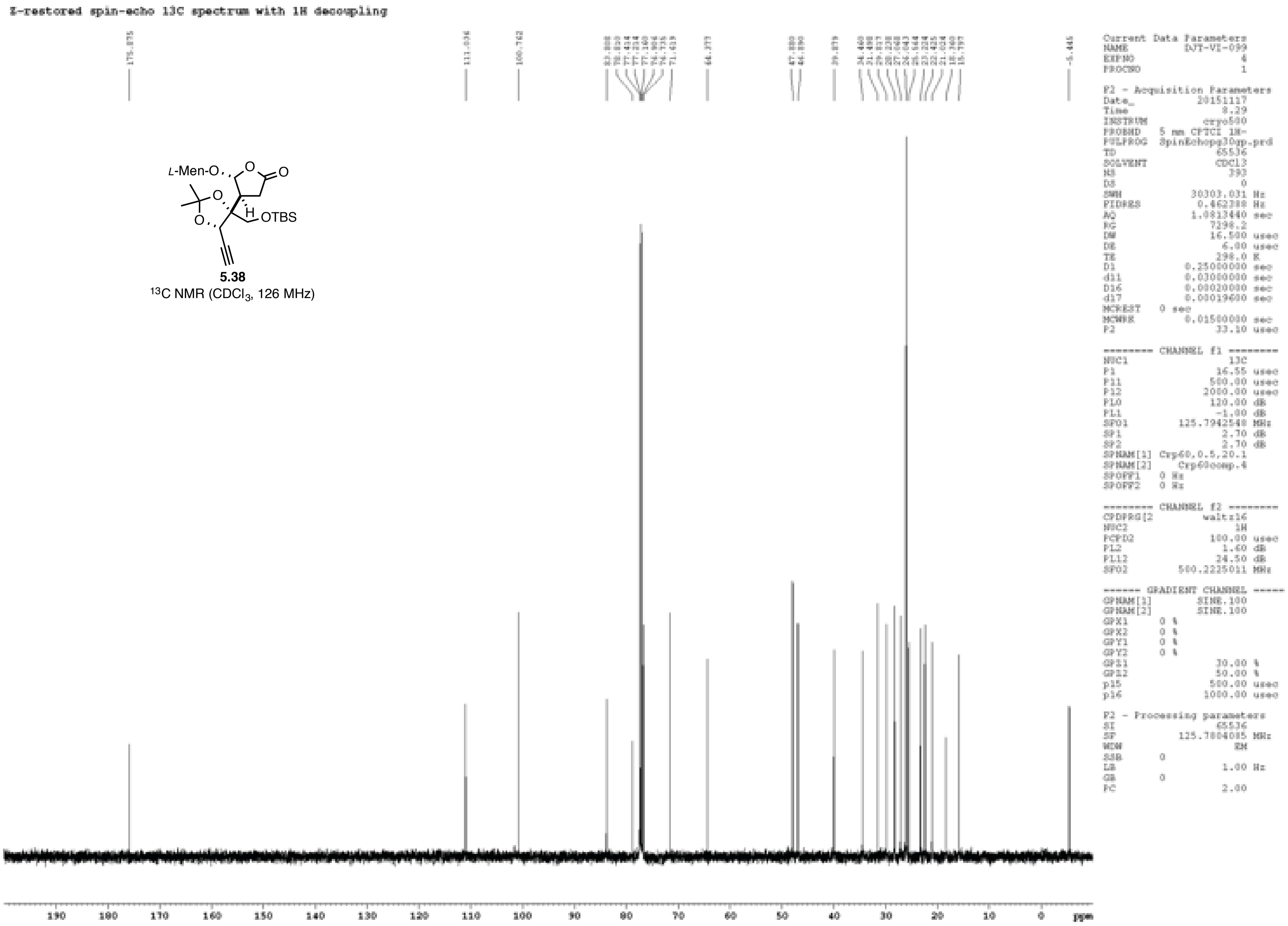
====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804090 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```



5.38

^{1}H NMR (CDCl$_3$, 500 MHz)



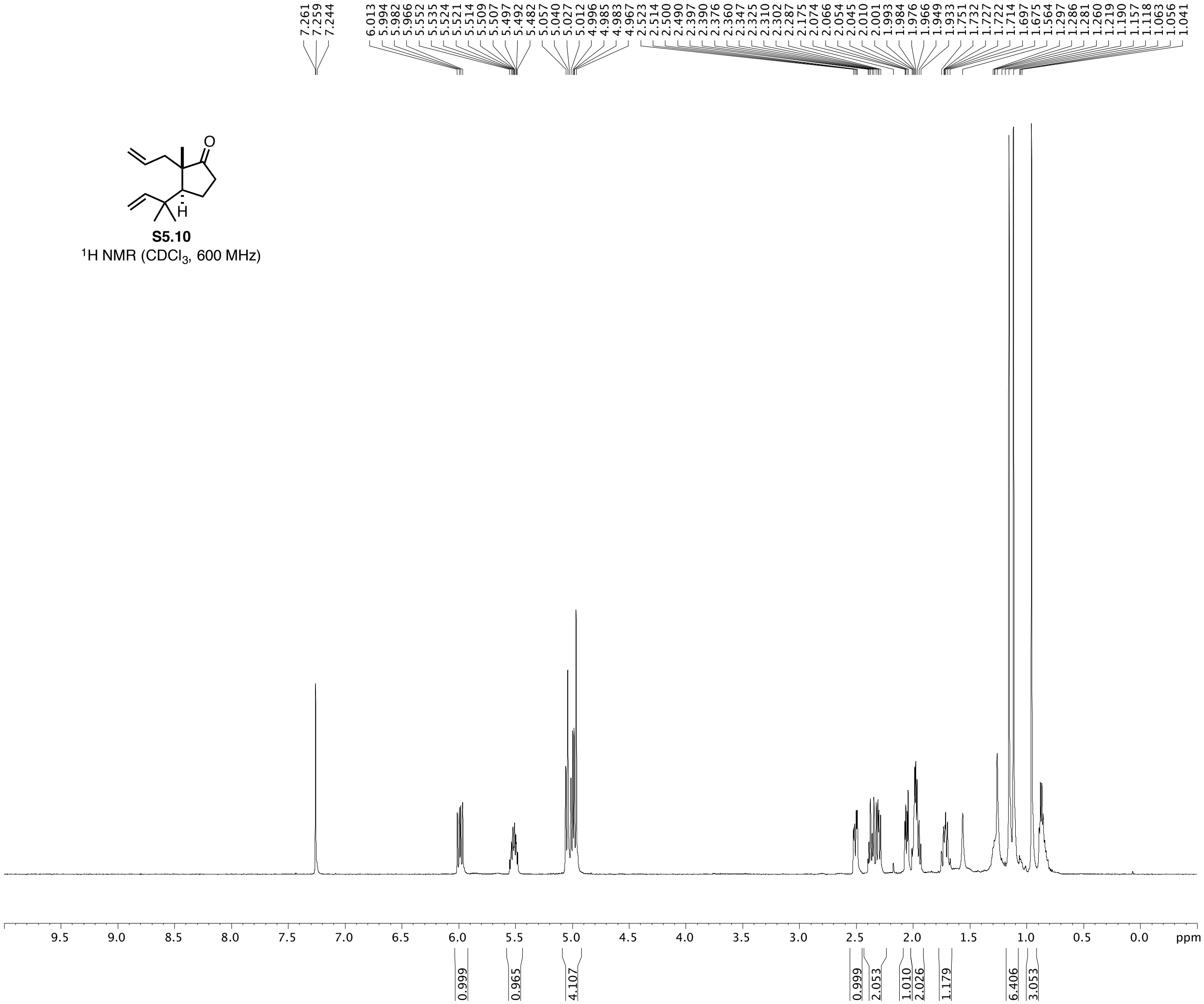
5.38

^{13}C NMR (CDCl$_3$, 126 MHz)

1H spectrum

S5.10

^{1}H NMR ($CDCl_3$, 600 MHz)



```
Current Data Parameters
NAME       DJT-III-297
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20140520
Time             15.02
INSTRUM          av600
PROBHD   5 mm TBI 1H/13
PULPROG           zg30
TD               98074
SOLVENT          CDCl3
NS                  20
DS                   0
SWH         9615.385 Hz
FIDRES      0.098042 Hz
AQ         5.0998478 sec
RG                 406
DW           52.000 usec
DE            14.54 usec
TE             298.1 K
D1       0.10000000 sec
TD0                  1

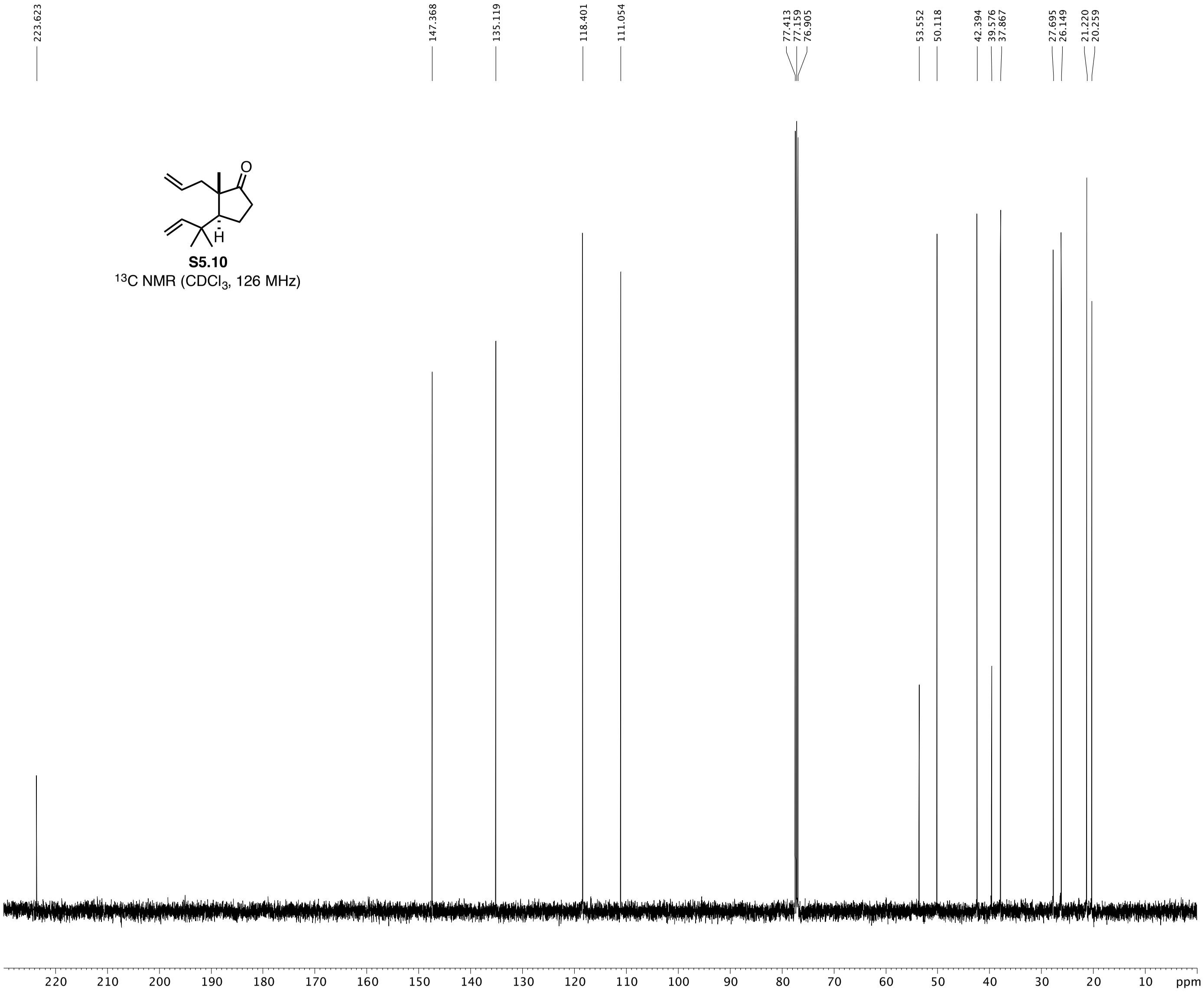
======== CHANNEL f1 =====
SFO1      600.1342009 MHz
NUC1                 1H
P1              8.00 usec
PLW1      23.01441956 W

F2 - Processing parameters
SI               65536
SF       600.1300345 MHz
WDW                 EM
SSB    0
LB             0.30 Hz
GB     0
PC                1.00
```

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

S5.10

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME         DJT-IV-293
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20150108
Time               8.02
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  142
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG              10321.3
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

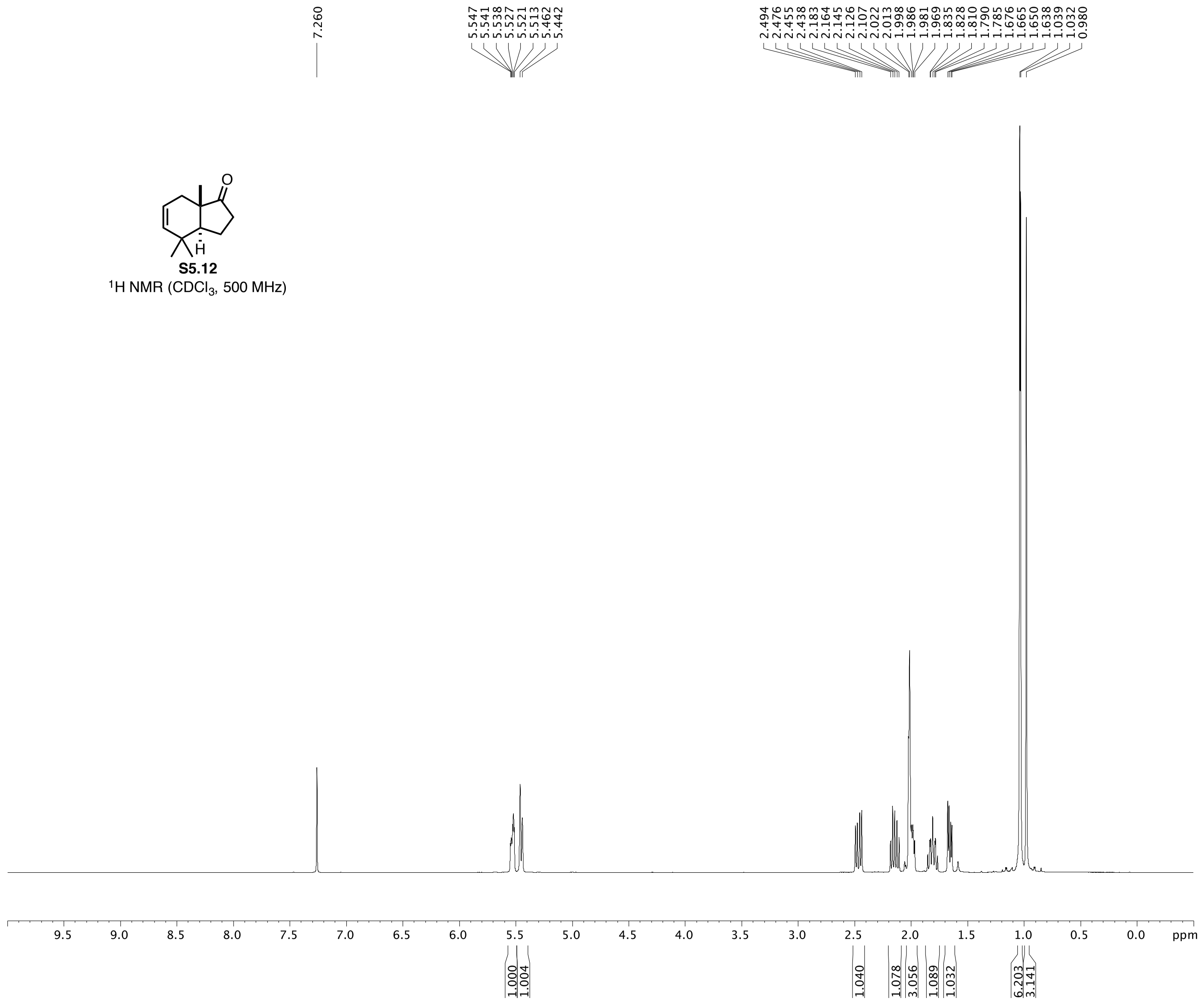
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804090 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



S5.12

^{1}H NMR (CDCl$_3$, 500 MHz)

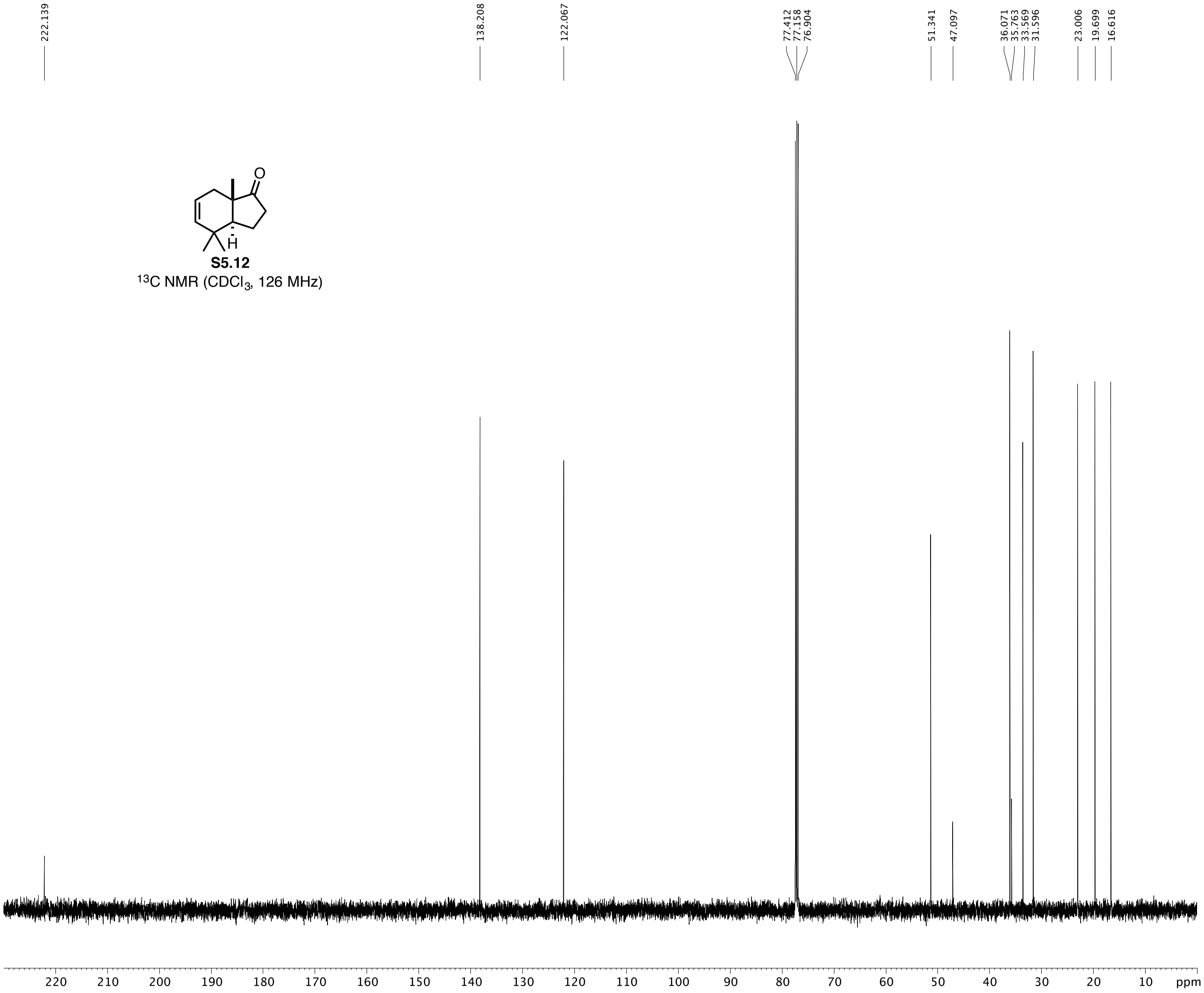
```
Current Data Parameters
NAME         DJT-IV-294
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20150108
Time              15.03
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                32048
SOLVENT           CDCl3
NS                   30
DS                    0
SWH          8012.820 Hz
FIDRES       0.250026 Hz
AQ          1.9997952 sec
RG                     8
DW            62.400 usec
DE              6.00 usec
TE               298.0 K
D1         0.10000000 sec
MCREST   0 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 =====
NUC1                 1H
P1            7.50 usec
PL1             1.60 dB
SFO1     500.2235015 MHz

F2 - Processing parameters
SI                65536
SF       500.2200317 MHz
WDW                  EM
SSB     0
LB              0.30 Hz
GB      0
PC                 4.00
```

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



S5.12

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT–IV–294
EXPNO                  4
PROCNO                 1

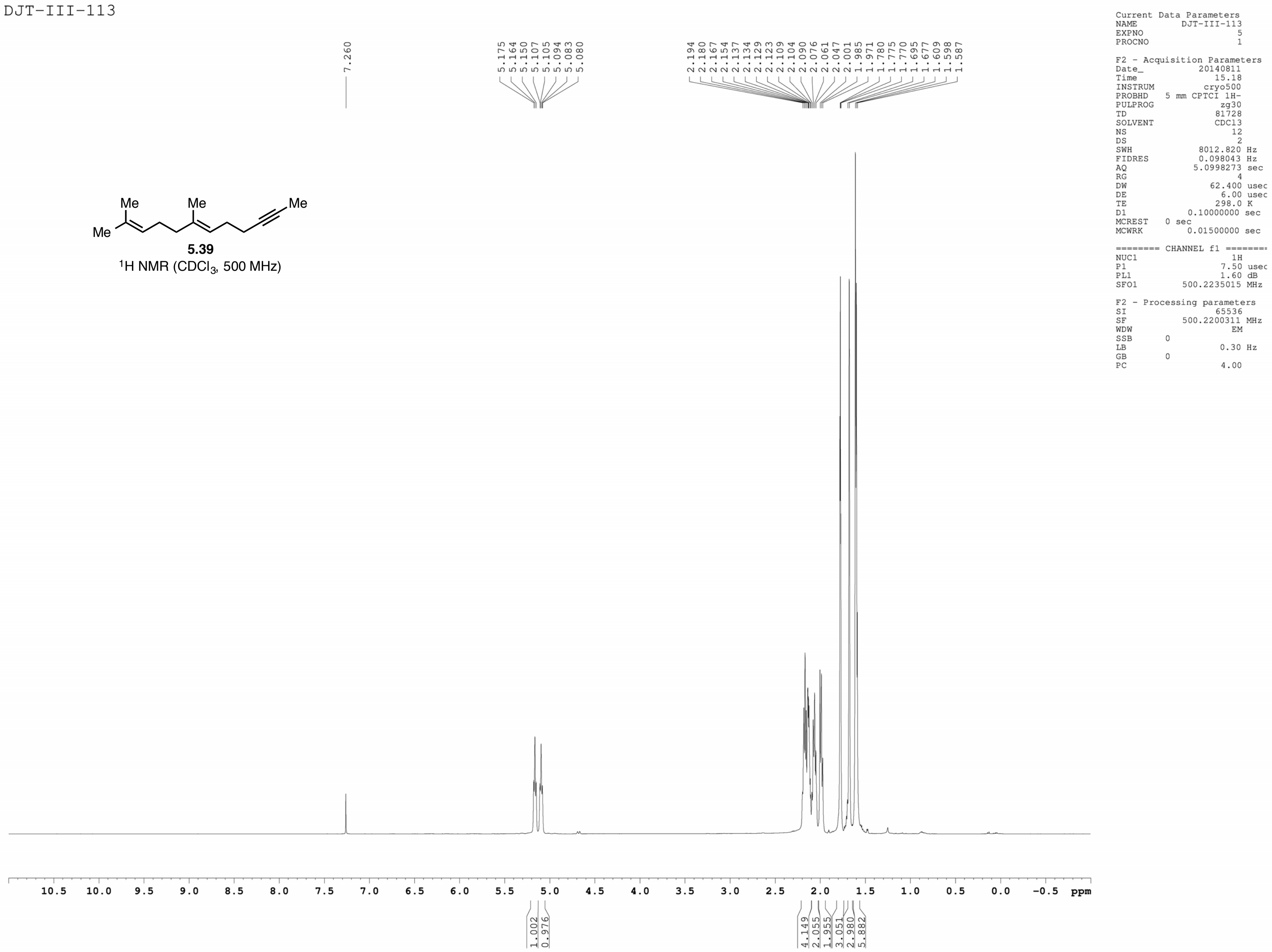
F2 – Acquisition Parameters
Date_          20150108
Time              15.07
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H–
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  309
DS                    0
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 – Processing parameters
SI                65536
SF          125.7804084 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```



5.39

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME        DJT-III-113
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20140811
Time              15.18
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                   12
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                    4
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

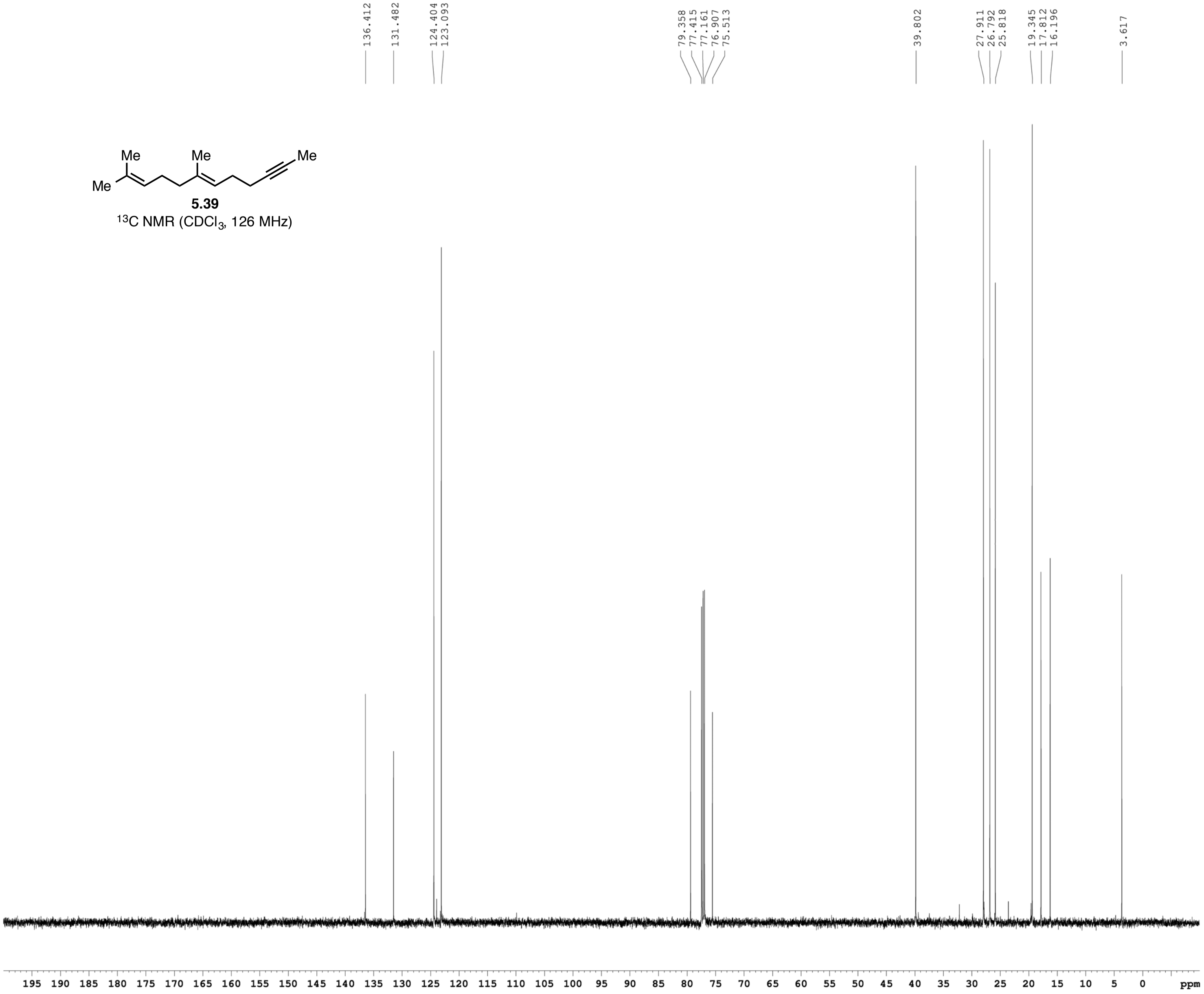
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200311 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

DJT-III-113

5.39

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME         DJT-III-113
EXPNO                  6
PROCNO                 1

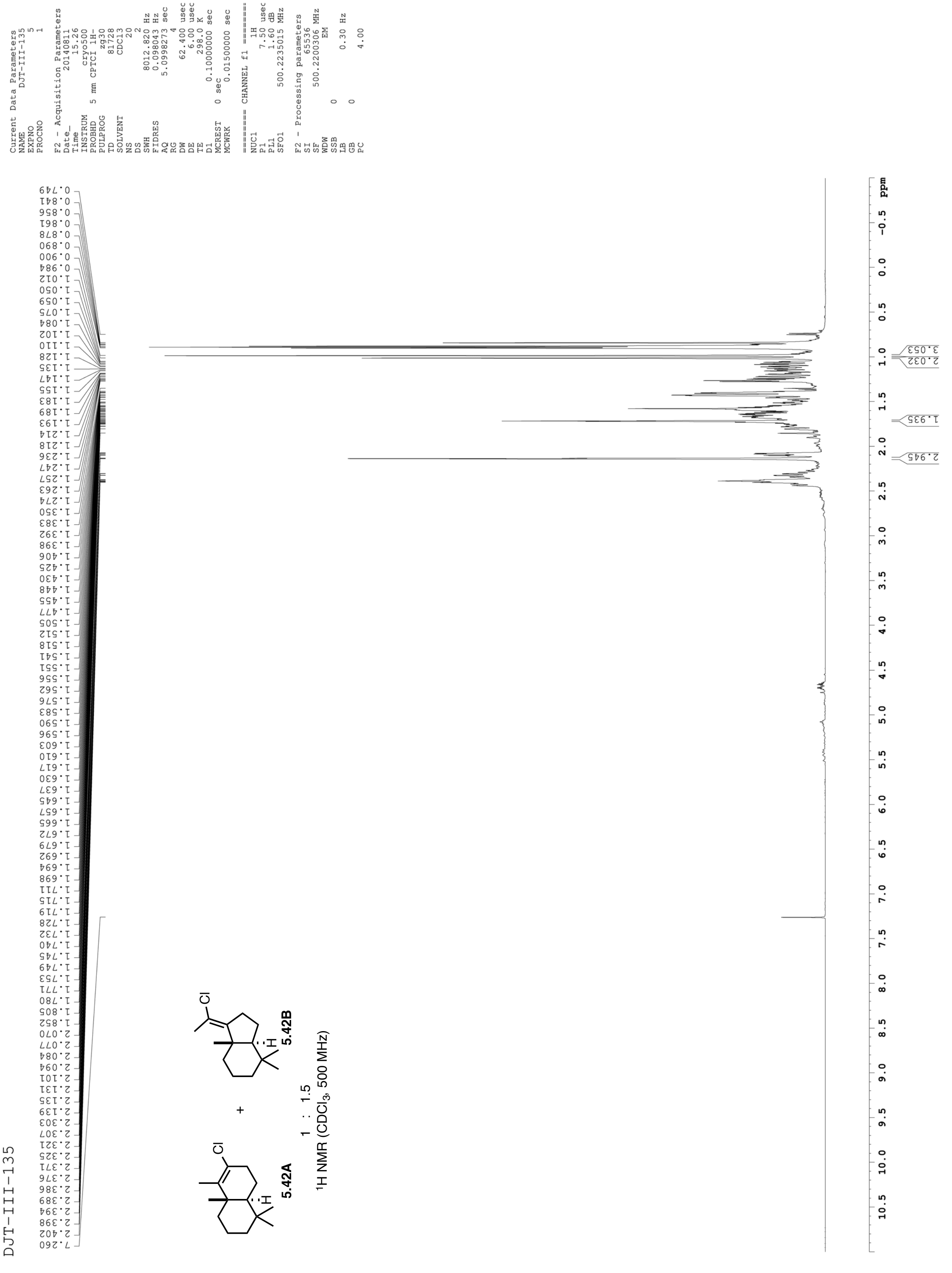
F2 - Acquisition Parameters
Date_           20140811
Time               15.22
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   143
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5160.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

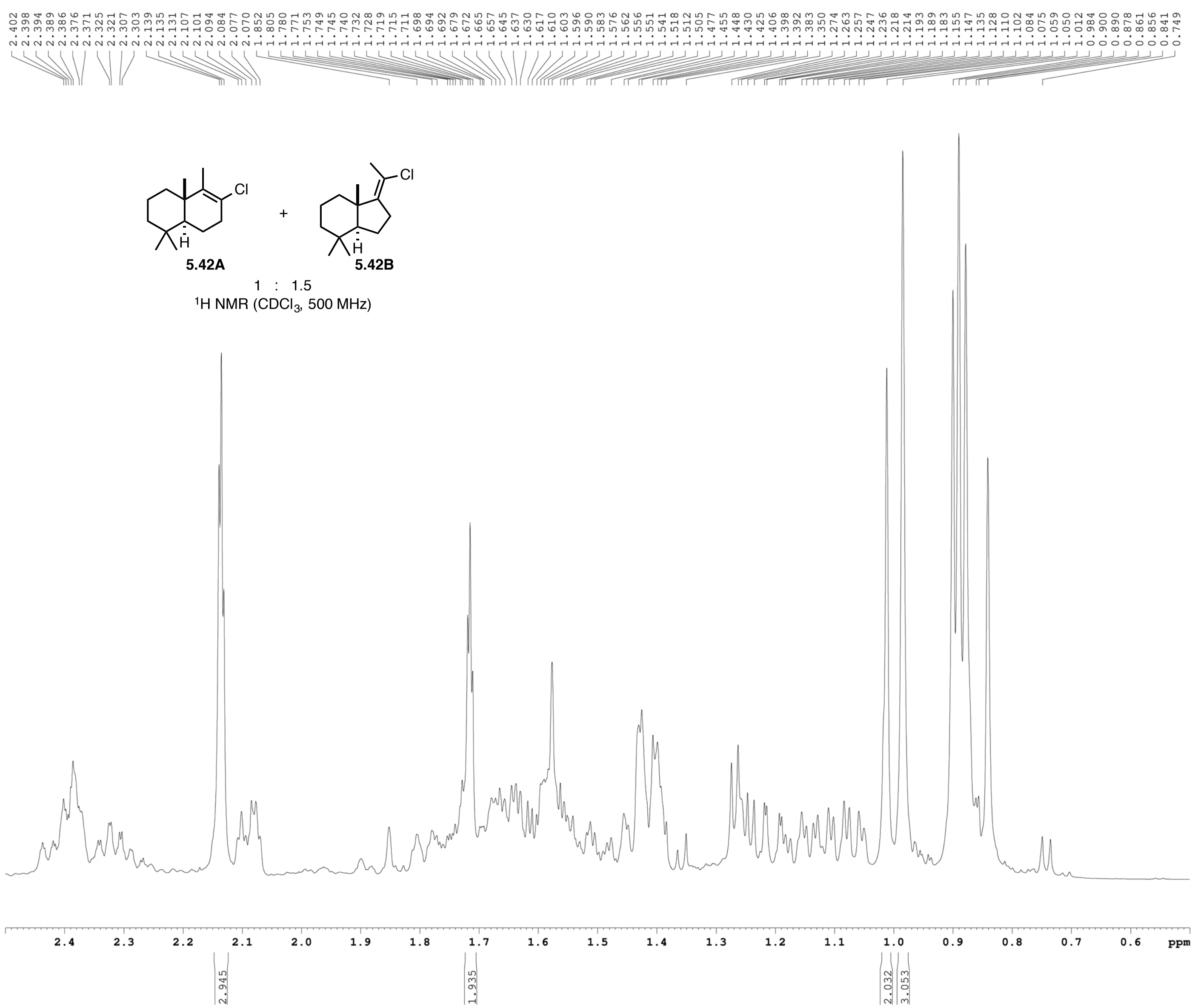
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804080 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```


DJT-III-135
5.42A
5.42B
1 : 1.5
^{1}H NMR (CDCl$_3$, 500 MHz)
Cl
Cl
H
H
+
Current Data Parameters
NAME DJT-III-135
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140811
Time 15.26
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 20
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998273 sec
RG 4
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200306 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00
0.749
0.841
0.856
0.861
0.878
0.890
0.900
0.984
1.012
1.050
1.059
1.075
1.084
1.102
1.110
1.128
1.135
1.147
1.155
1.183
1.189
1.193
1.214
1.218
1.236
1.247
1.257
1.263
1.274
1.350
1.383
1.392
1.398
1.406
1.425
1.430
1.448
1.455
1.477
1.505
1.512
1.518
1.541
1.551
1.556
1.562
1.576
1.583
1.590
1.596
1.603
1.610
1.617
1.630
1.637
1.645
1.657
1.665
1.672
1.679
1.692
1.694
1.698
1.711
1.715
1.719
1.728
1.732
1.740
1.745
1.749
1.753
1.771
1.780
1.805
1.852
2.070
2.077
2.084
2.094
2.101
2.131
2.135
2.139
2.303
2.307
2.321
2.325
2.371
2.376
2.386
2.389
2.394
2.398
2.402
7.260
3.053
2.032
1.935
2.945
ppm
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5

DJT-III-135



5.42A **5.42B**

1 : 1.5

^{1}H NMR ($CDCl_3$, 500 MHz)

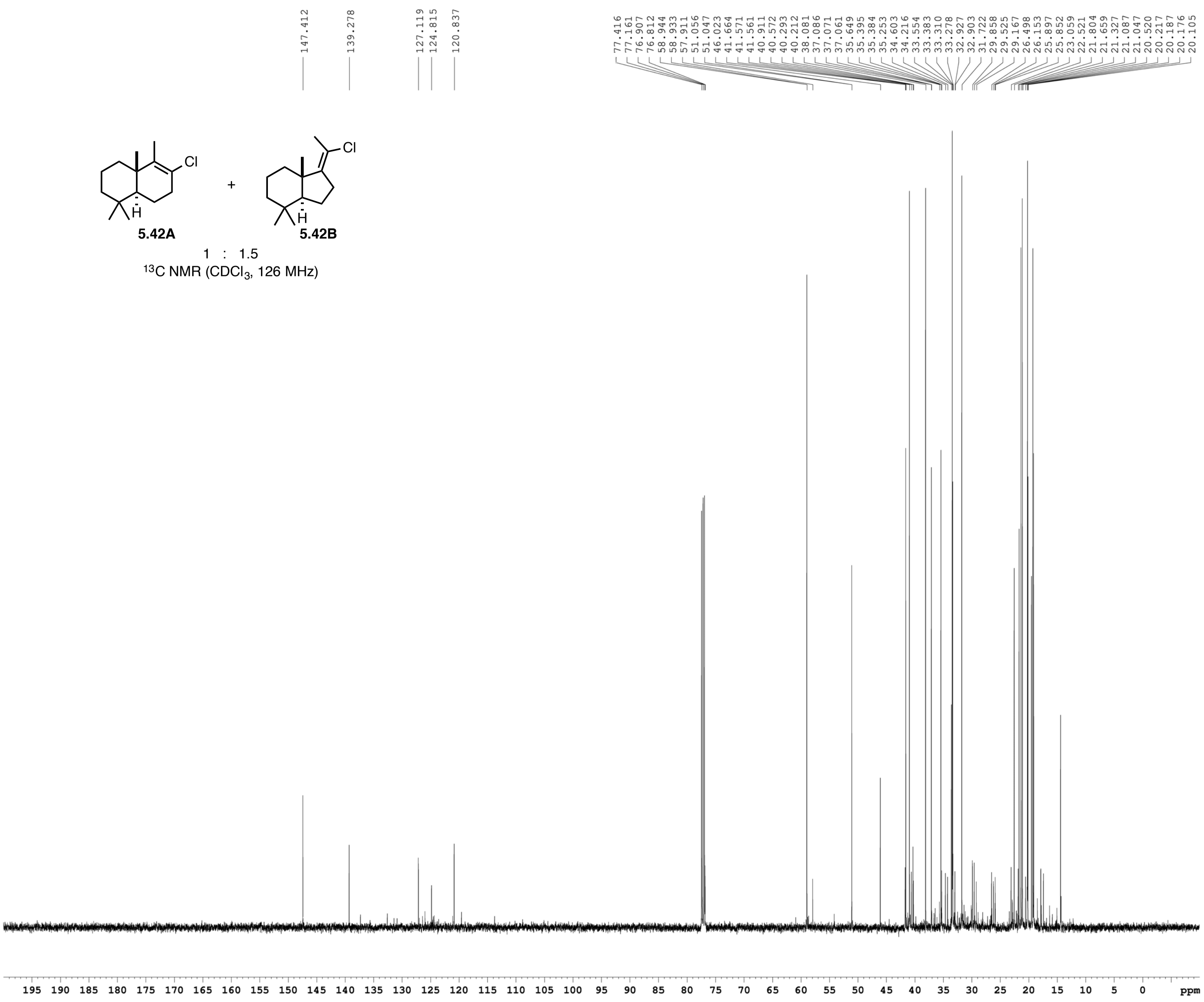
```
Current Data Parameters
NAME        DJT-III-135
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20140811
Time              15.26
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                   20
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                    4
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200306 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

DJT-III-135



5.42A **5.42B**

1 : 1.5

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME        DJT-III-135
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20140811
Time              15.33
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  317
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

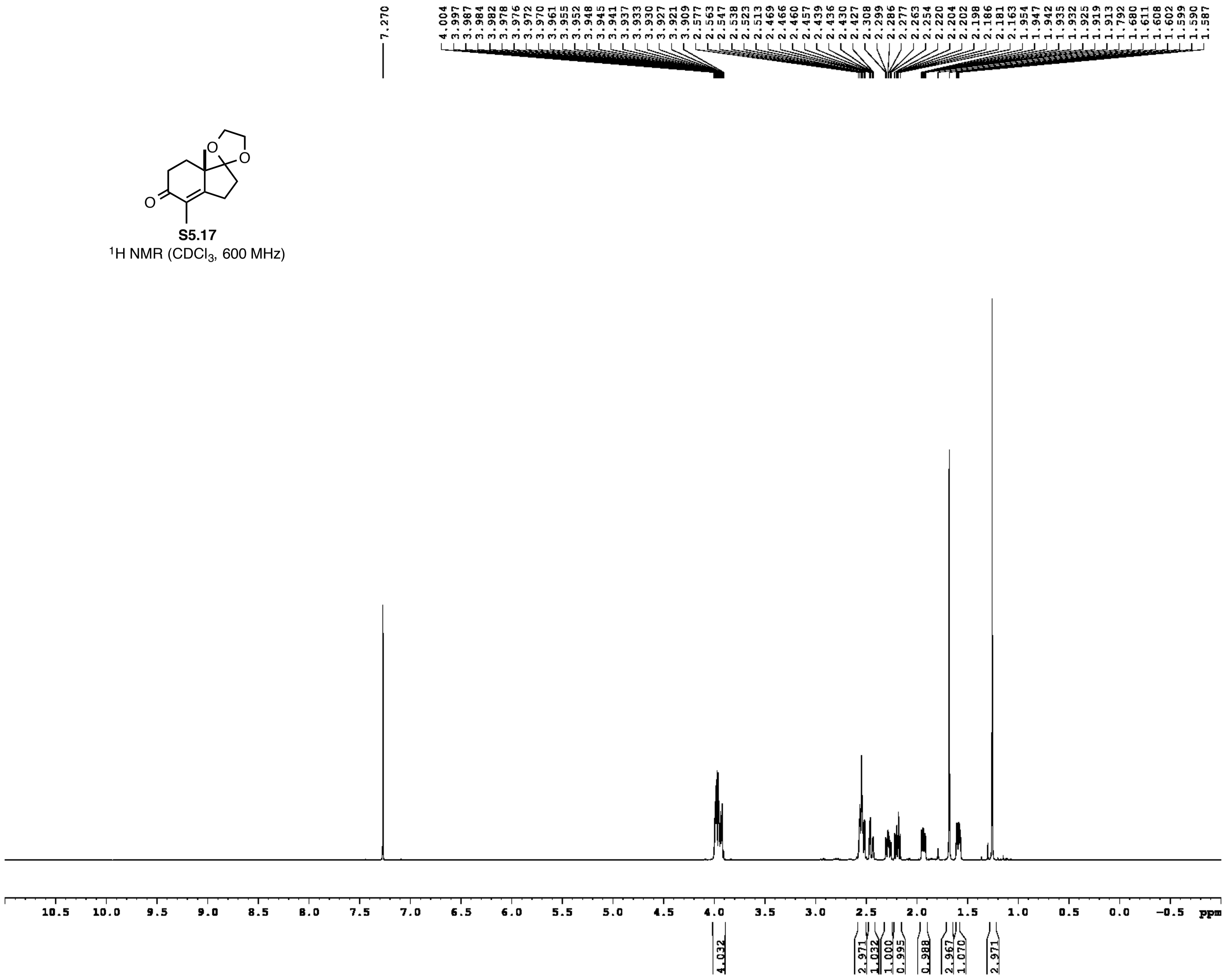
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804085 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

YS-IV-18

S5.17

^{1}H NMR (CDCl$_3$, 600 MHz)



```
Current Data Parameters
NAME            YS-IV-18
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151209
Time                8.24
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   812
DW                52.000 use
DE                 14.54 use
TE                 298.0 K
D1           0.10000000 sec
TD0                    1

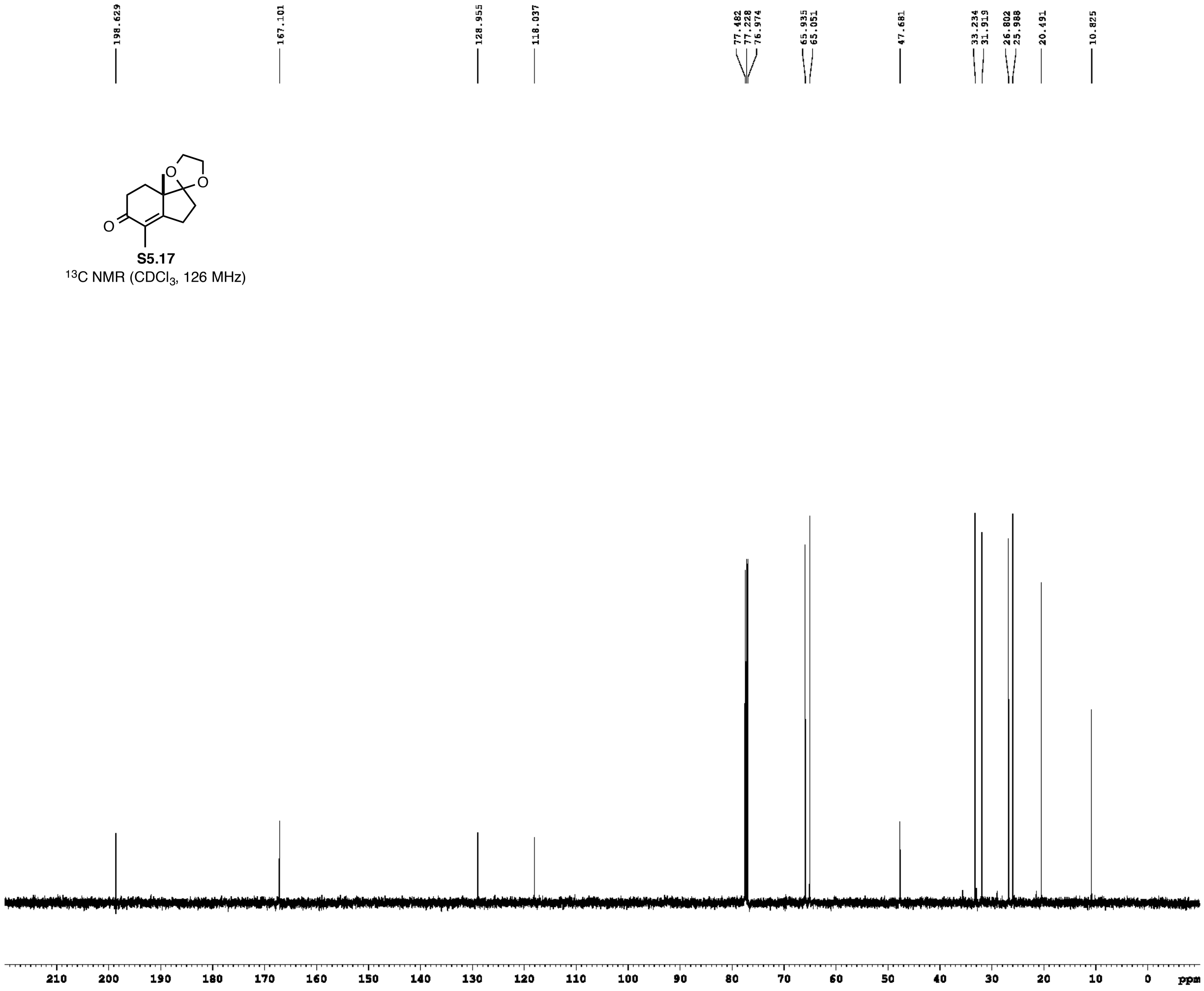
====== CHANNEL f1 ======
SFO1        600.1342009 MHz
NUC1                  1H
P1                  8.00 use
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300294 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-IV-18

S5.17

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME             YS-IV-18
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151216
Time                15.42
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    152
DS                      2
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 2896.3
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

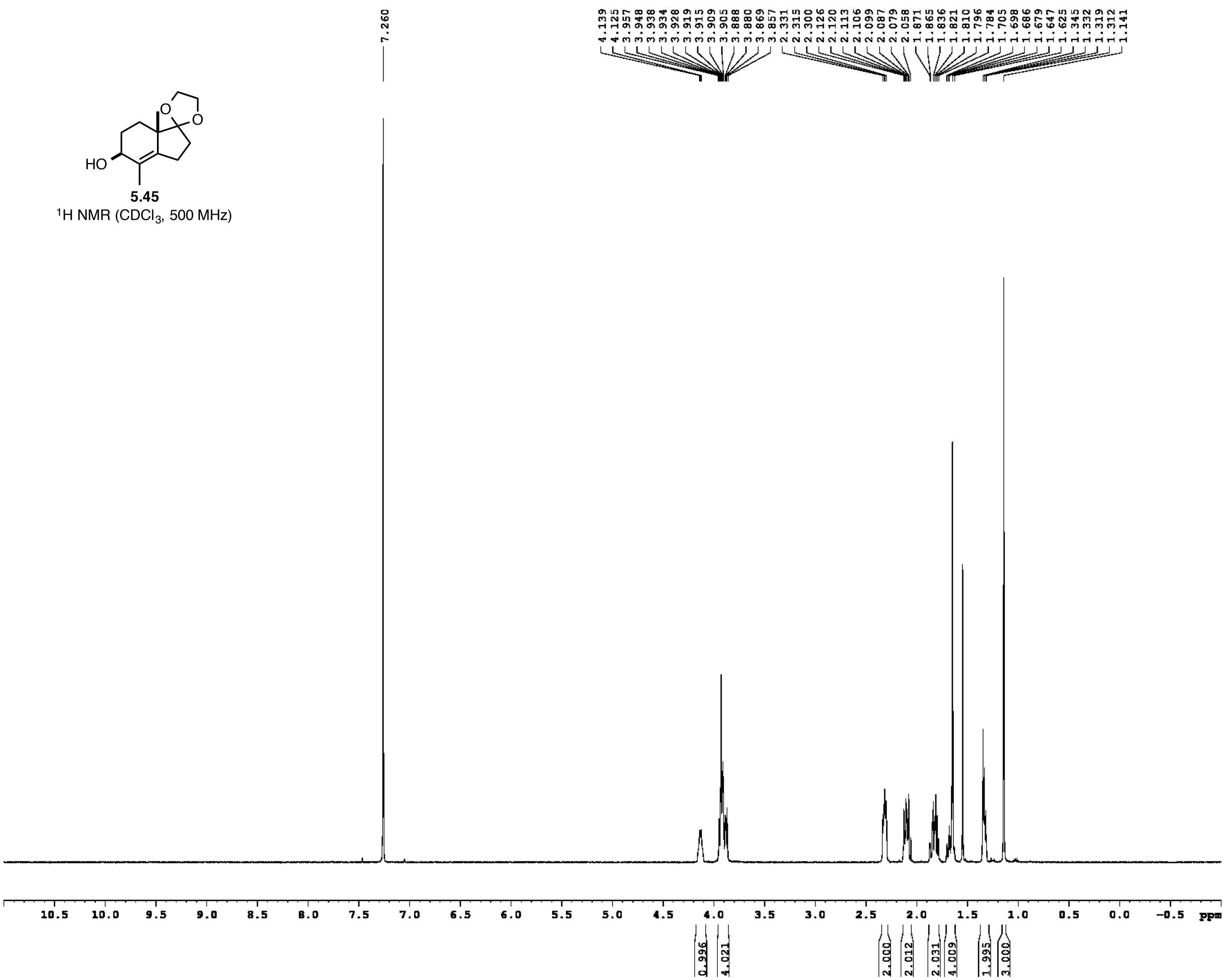
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1         125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804008 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-III-292



5.45

^{1}H NMR (CDCl$_3$, 500 MHz)

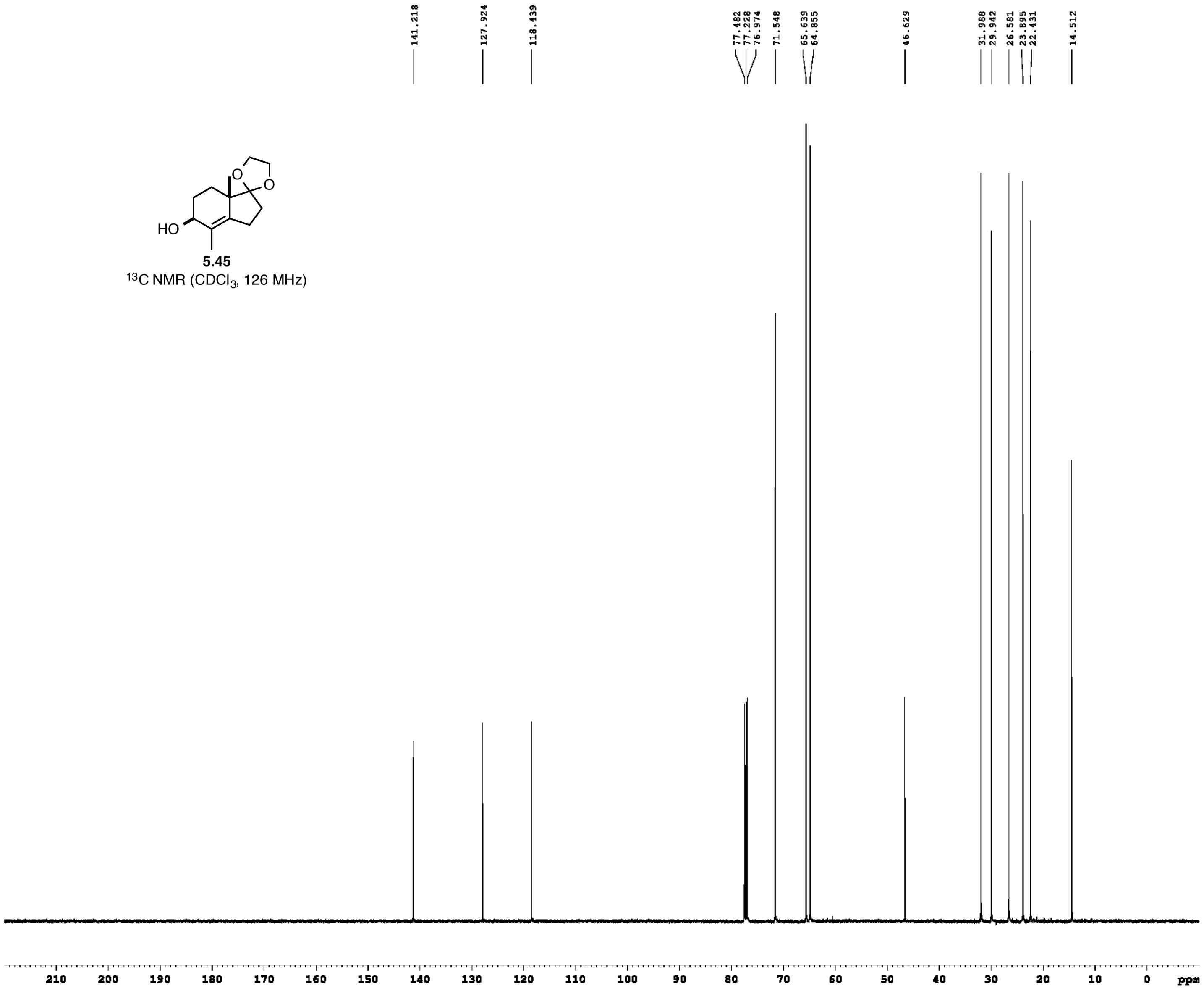
```
Current Data Parameters
NAME          YS-III-292
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151117
Time                8.52
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                   7.1
DW                62.400 use
DE                  6.00 use
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 use
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200324 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

YS-IV-20


5.45

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            YS-IV-20
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151209
Time               17.41
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   640
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

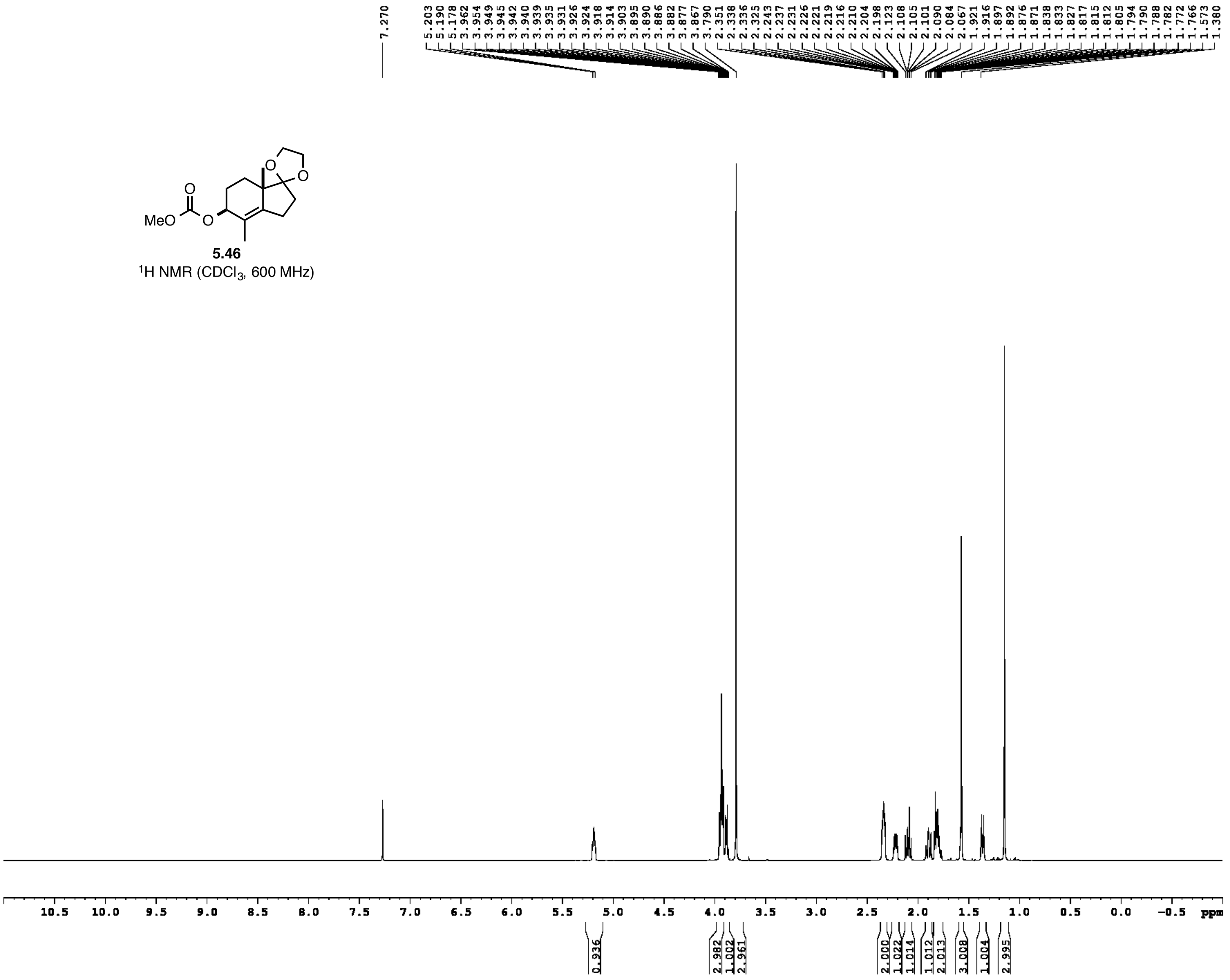
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804059 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-III-293

5.46

^{1}H NMR ($CDCl_3$, 600 MHz)



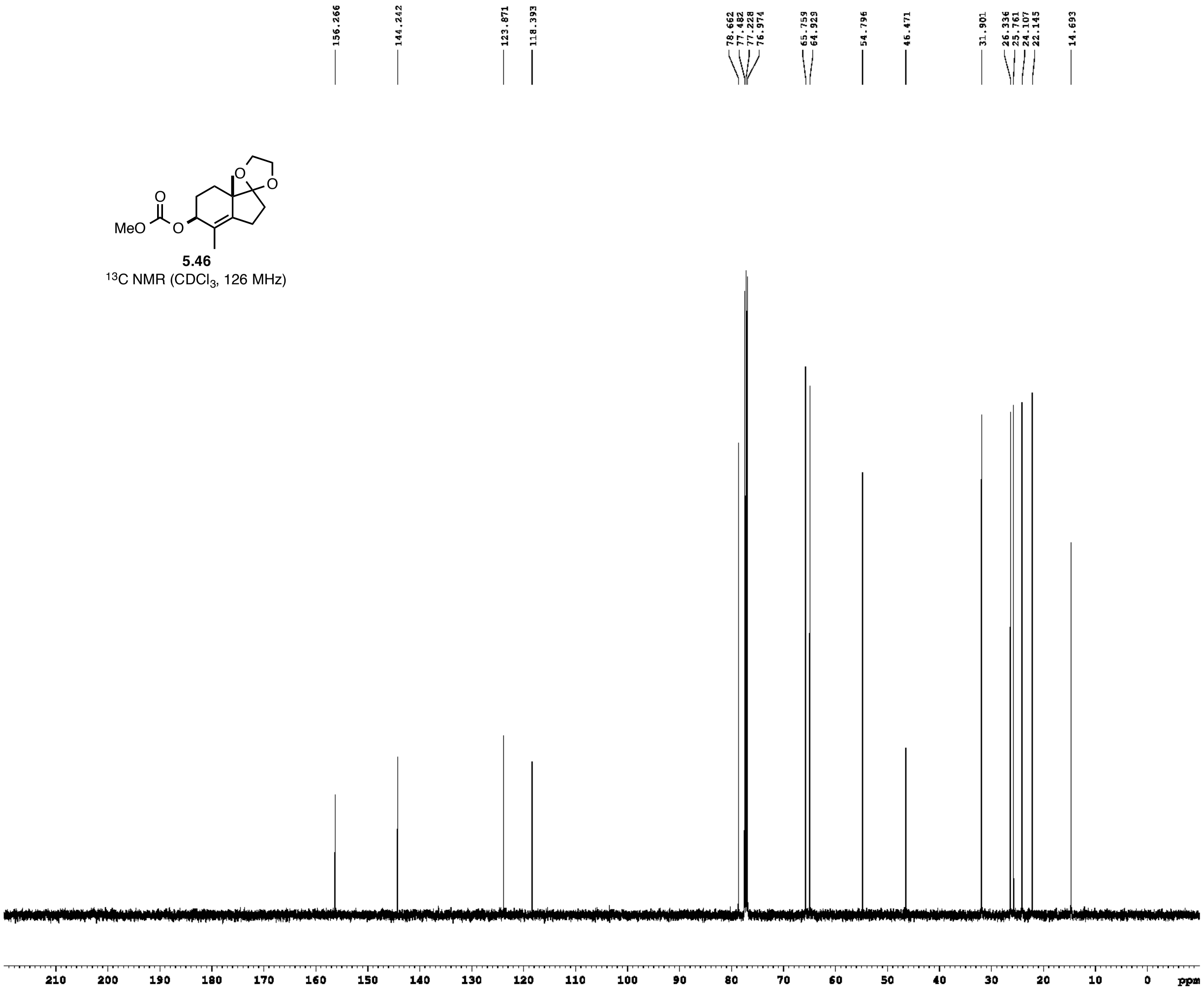
```
Current Data Parameters
NAME          YS-III-293
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151117
Time               17.10
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   161
DW                52.000 use
DE                 14.54 use
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

====== CHANNEL f1 ======
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 use
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300296 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-III-293



5.46

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-293
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151117
Time               17.20
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   424
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

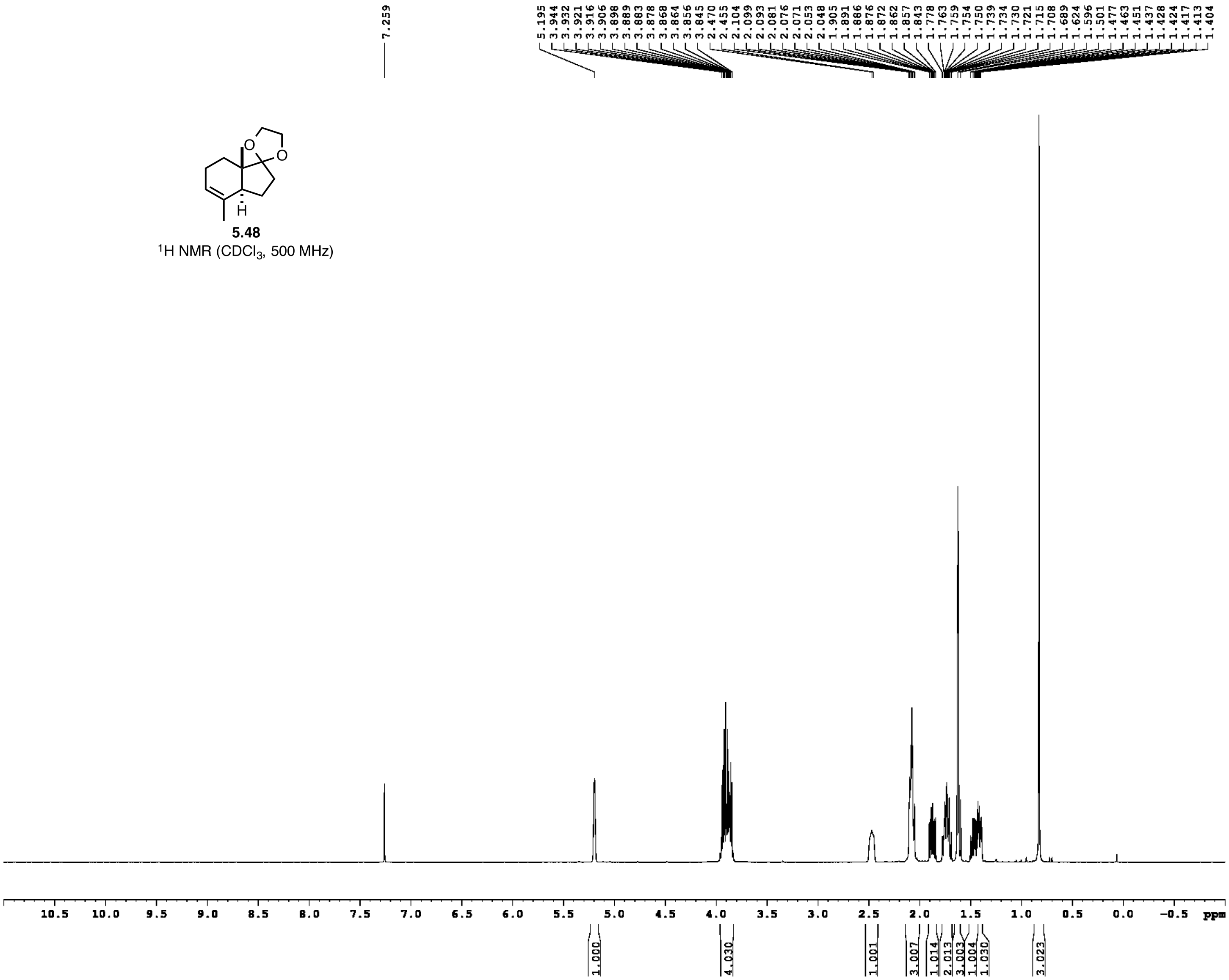
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804002 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-III-296



5.48

^{1}H NMR ($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME            YS-III-296
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151119
Time                 16.51
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                  128202
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.062502 Hz
AQ               7.9998050 sec
RG                     6.3
DW                  62.400 use
DE                    6.00 use
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

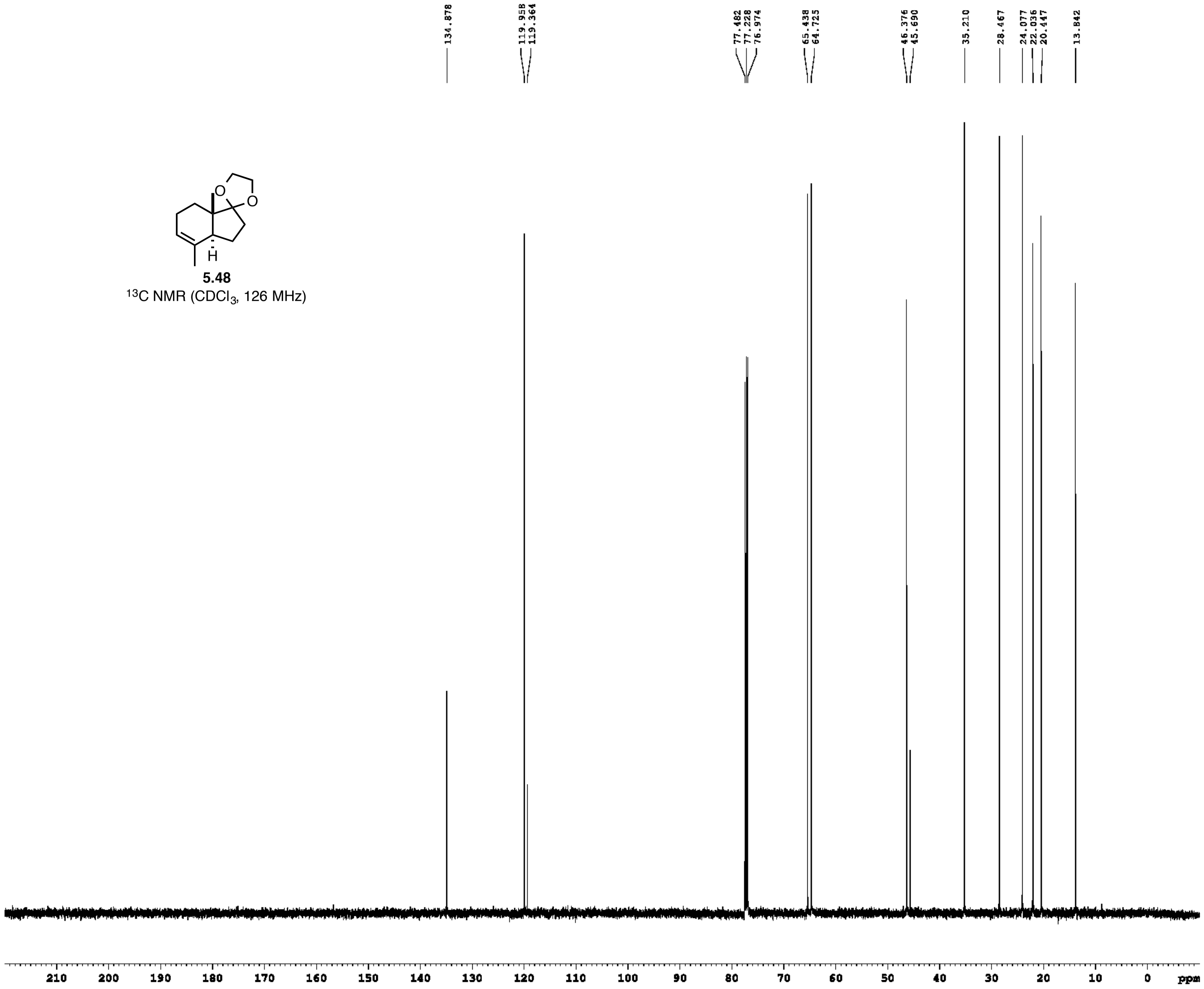
======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 use
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200323 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-III-296

5.48

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          YS-III-296
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151119
Time               16.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   504
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

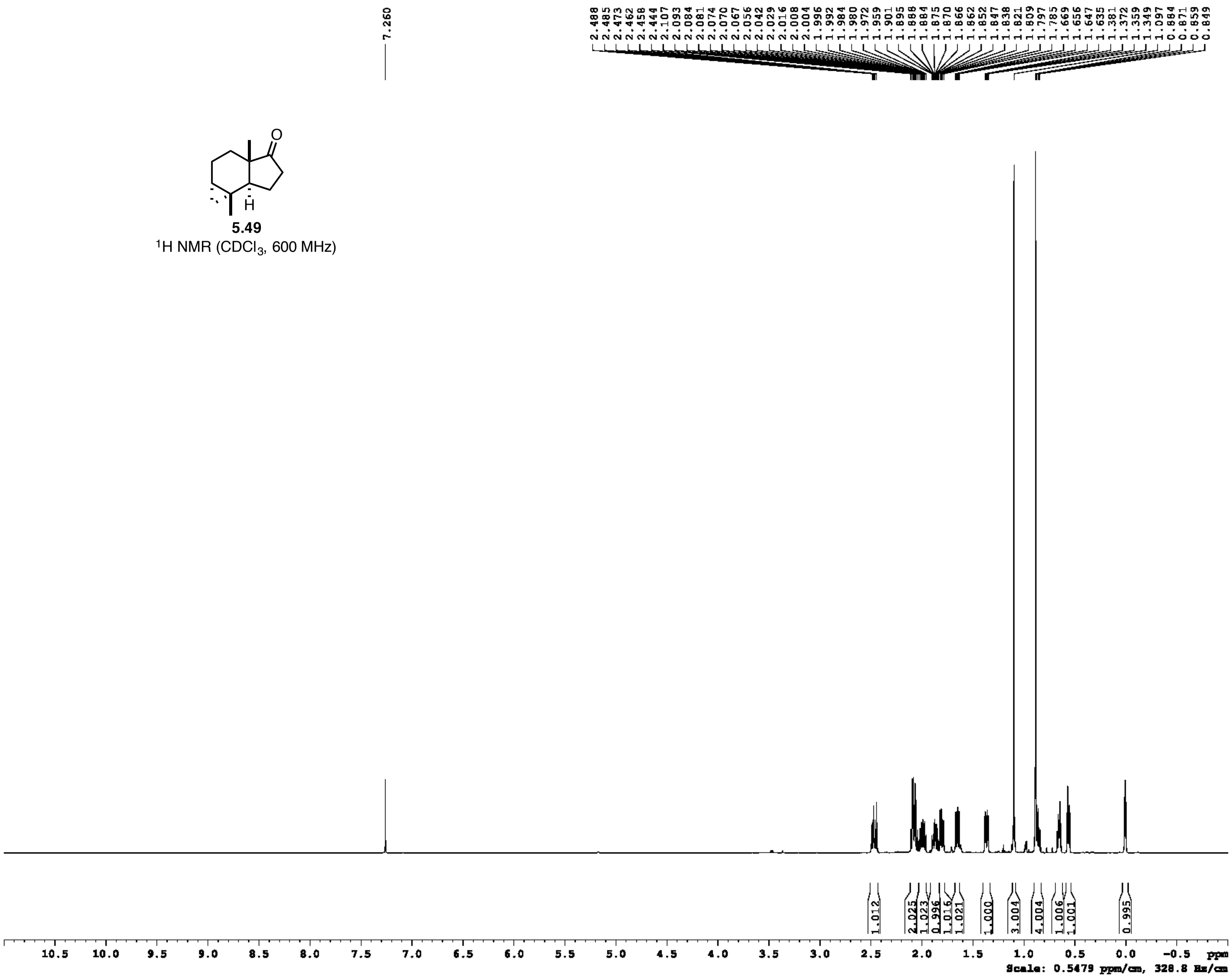
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803998 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-29



5.49

^{1}H NMR (CDCl$_3$, 600 MHz)

```
Current Data Parameters
NAME              YS-IV-29
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160107
Time                 16.39
INSTRUM              av600
PROBHD   5 mm TBI 1H/13
PULPROG               zg30
TD                   98074
SOLVENT              CDCl3
NS                       8
DS                       2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                     362
DW                 52.000 usec
DE                  14.54 usec
TE                  298.1 K
D1            0.10000000 sec
TD0                      1

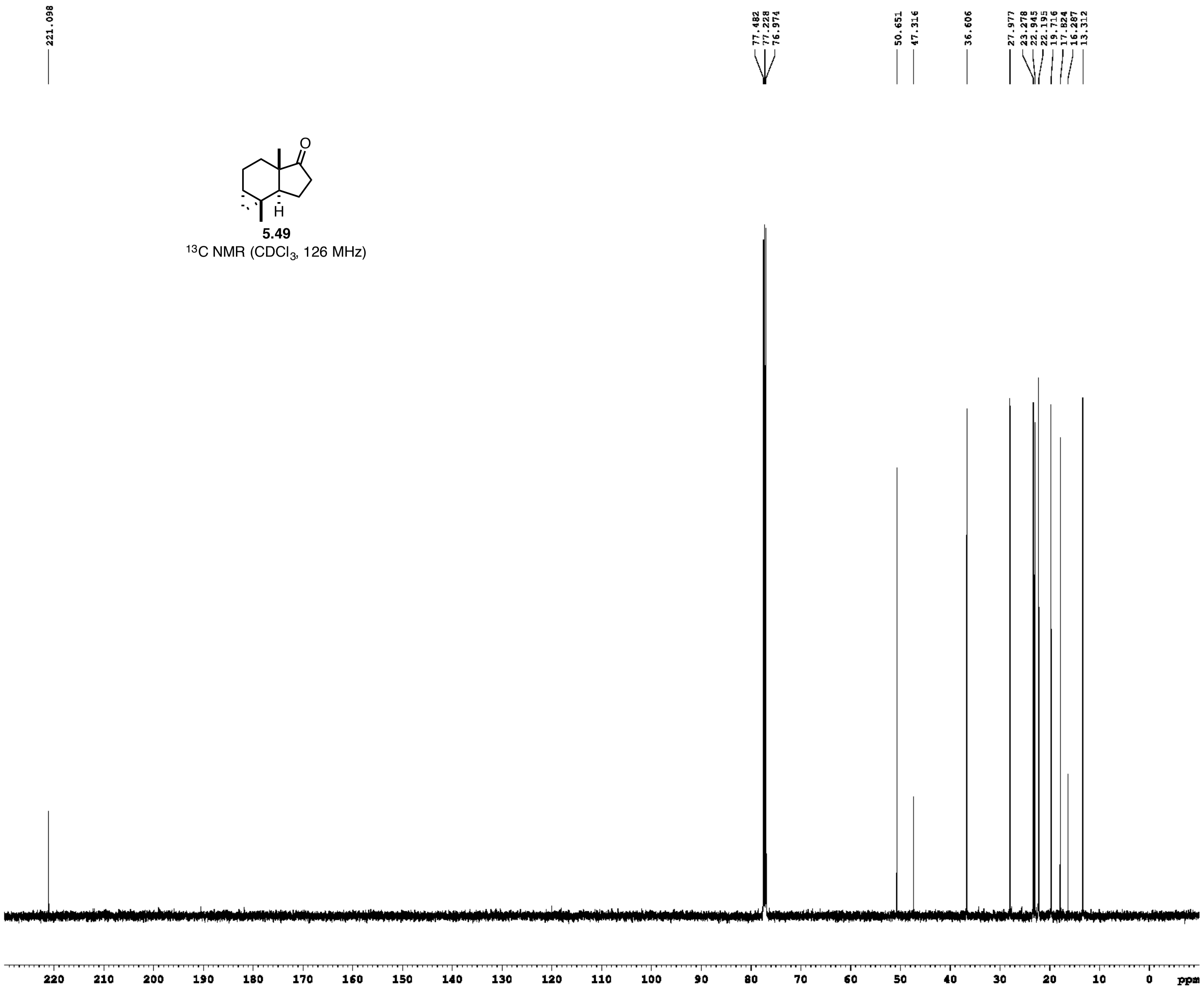
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                    1H
P1                    8.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                   65536
SF           600.1300354 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-IV-29

5.49

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME              YS-IV-29
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160107
Time                 16.47
INSTRUM            cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     832
DS                       2
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST    0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

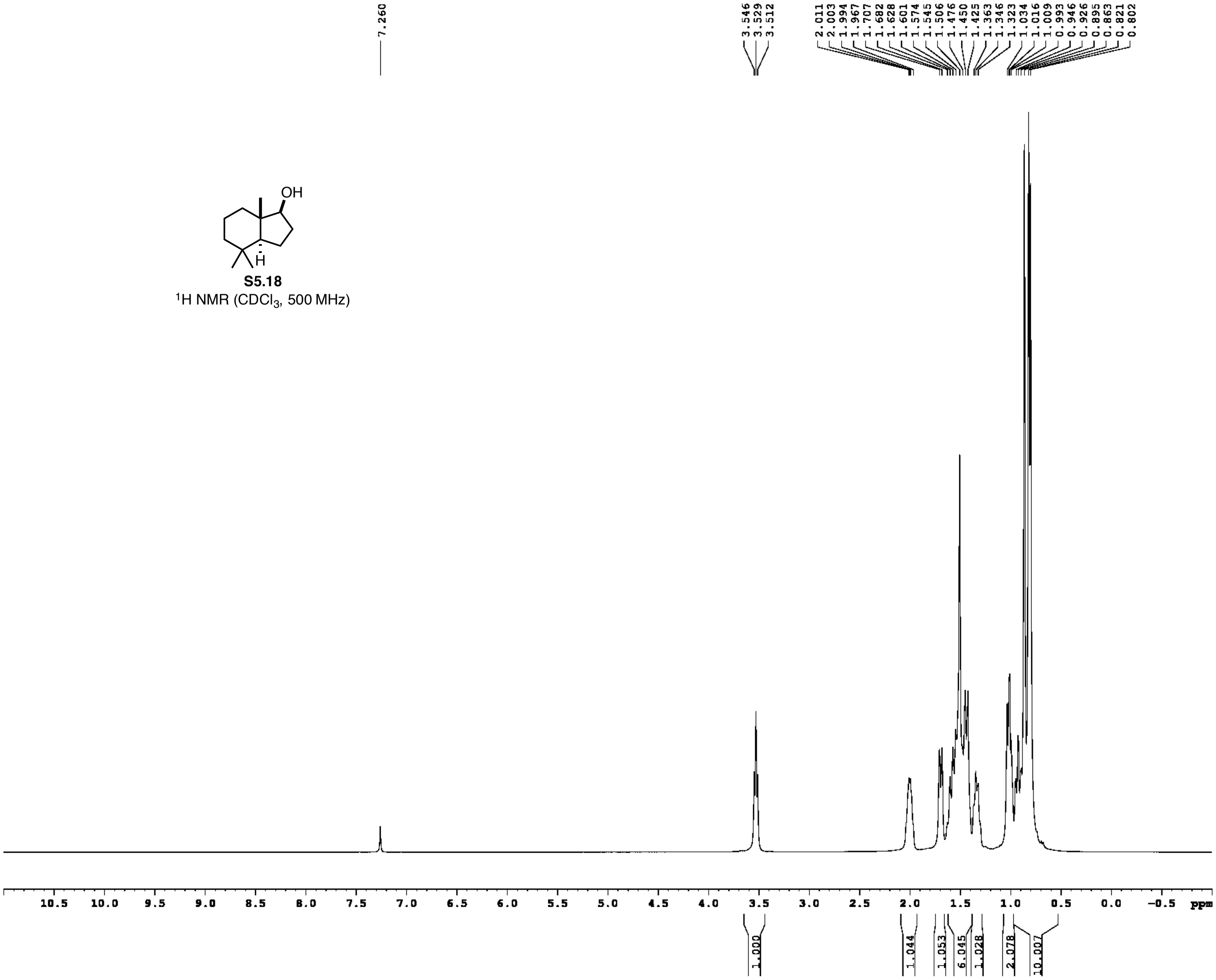
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1]  Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7803979 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    2.00
```

YS-IV-24



S5.18

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME              YS-IV-24
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151216
Time                 15.49
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                       5
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

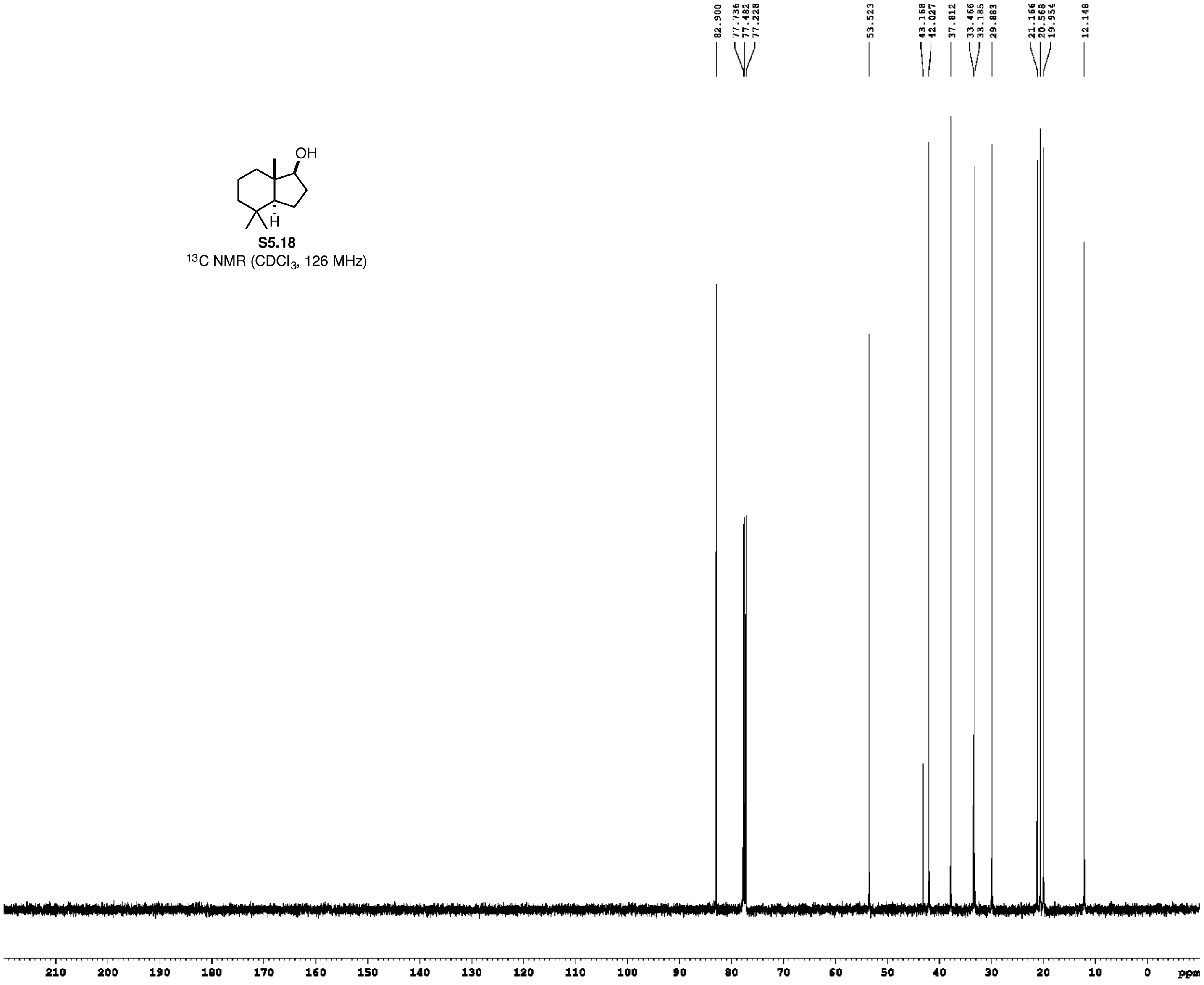
======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200314 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-IV-24

S5.18

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-24
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151216
Time               15.50
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   248
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

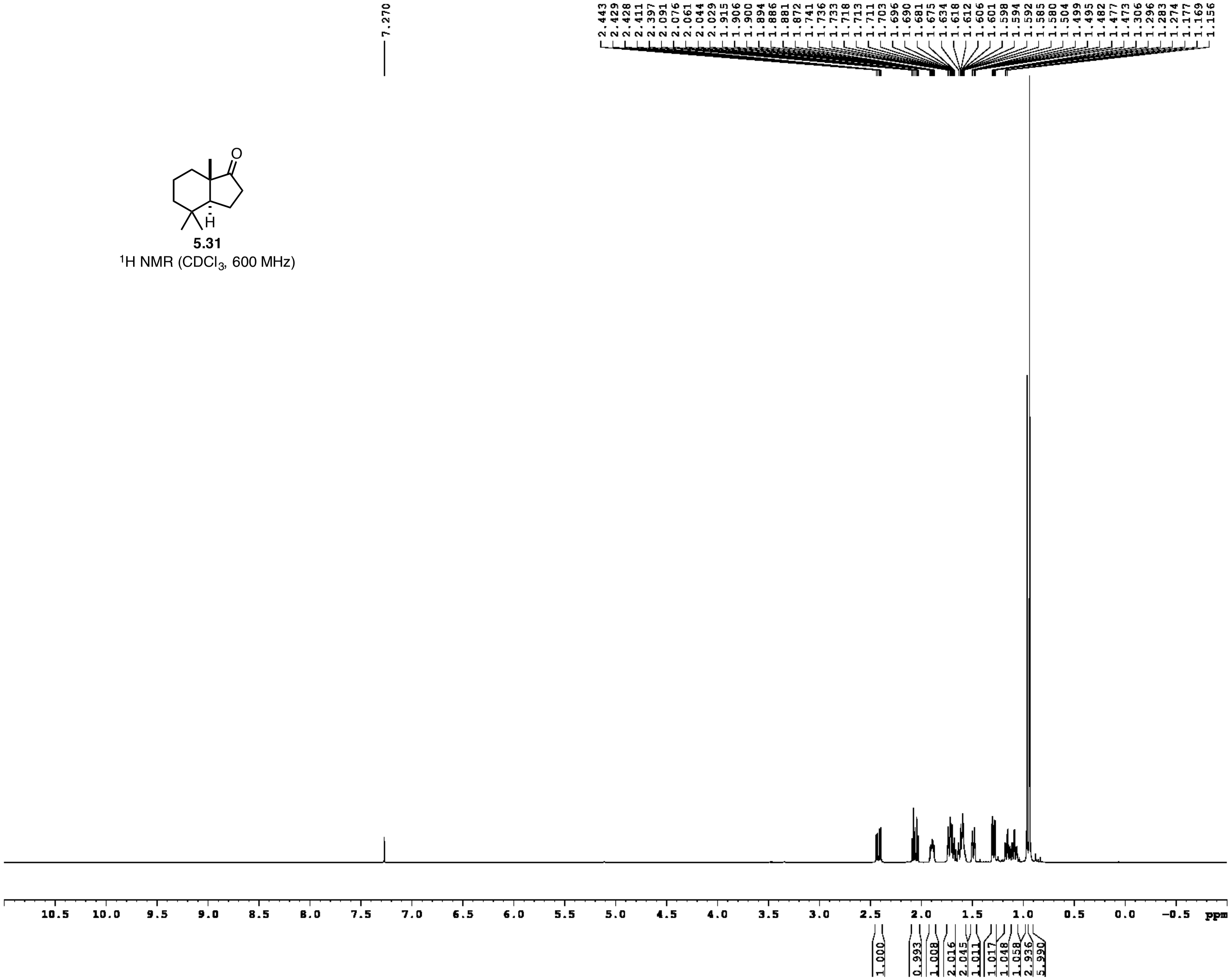
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1        0 %
GPX2        0 %
GPY1        0 %
GPY2        0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803692 MHz
WDW                   EM
SSB         0
LB                  1.00 Hz
GB          0
PC                  2.00
```

YS-IV-25



5.31

^1H NMR ($CDCl_3$, 600 MHz)

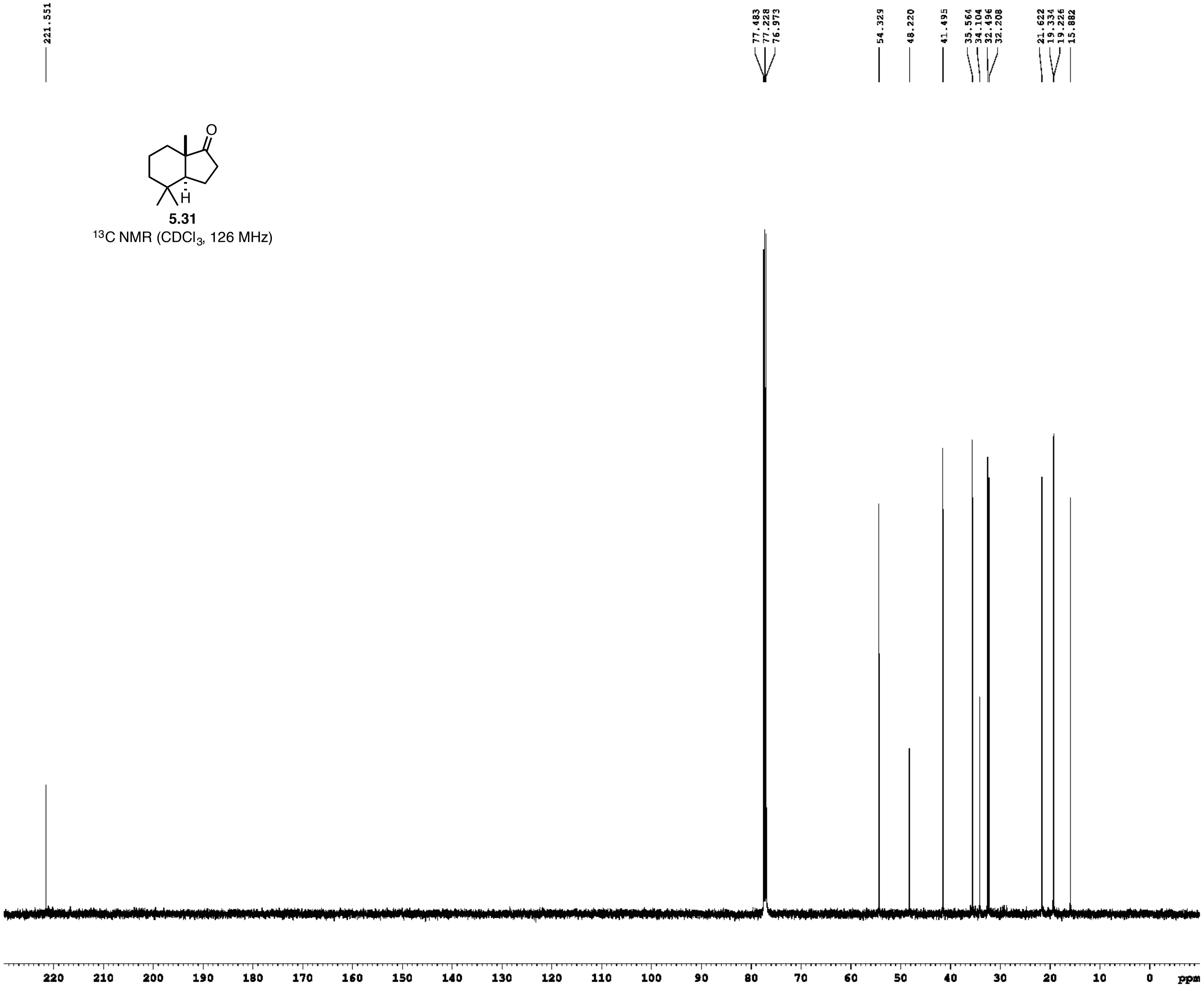
```
Current Data Parameters
NAME             YS-IV-25
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151217
Time                10.44
INSTRUM             av600
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  98074
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                    228
DW                 52.000 use
DE                  14.54 use
TE                  293.0 K
D1            0.10000000 sec
TD0                     1

====== CHANNEL f1 ======
SFO1         600.1342009 MHz
NUC1                   1H
P1                   8.00 use
PLW1         24.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1300296 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-IV-25



5.31

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            YS-IV-25
EXPNO                  2
PROCNO                 1

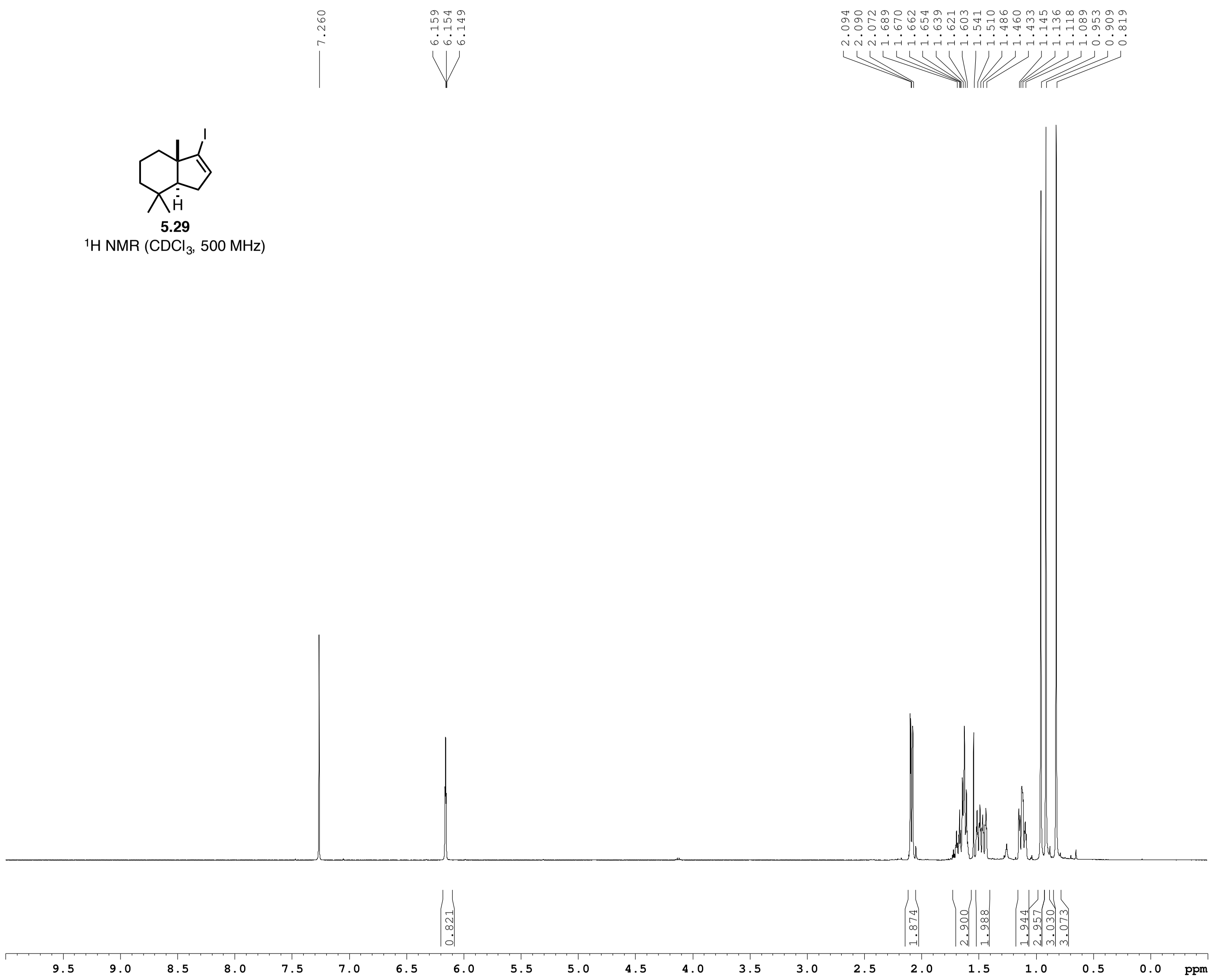
F2 - Acquisition Parameters
Date_           20151217
Time               10.53
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   800
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               18390.4
DW                16.500 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                -0.60 dB
SFO1         125.5327181 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               12.80 dB
SFO2         499.1824959 MHz

F2 - Processing parameters
SI                 65536
SF           125.5188906 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



5.29

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          DJT-V-036
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20150203
Time              18.19
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                16022
SOLVENT           CDCl3
NS                   60
DS                    0
SWH            8012.820 Hz
FIDRES         0.500114 Hz
AQ            0.9997728 sec
RG                  5.7
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

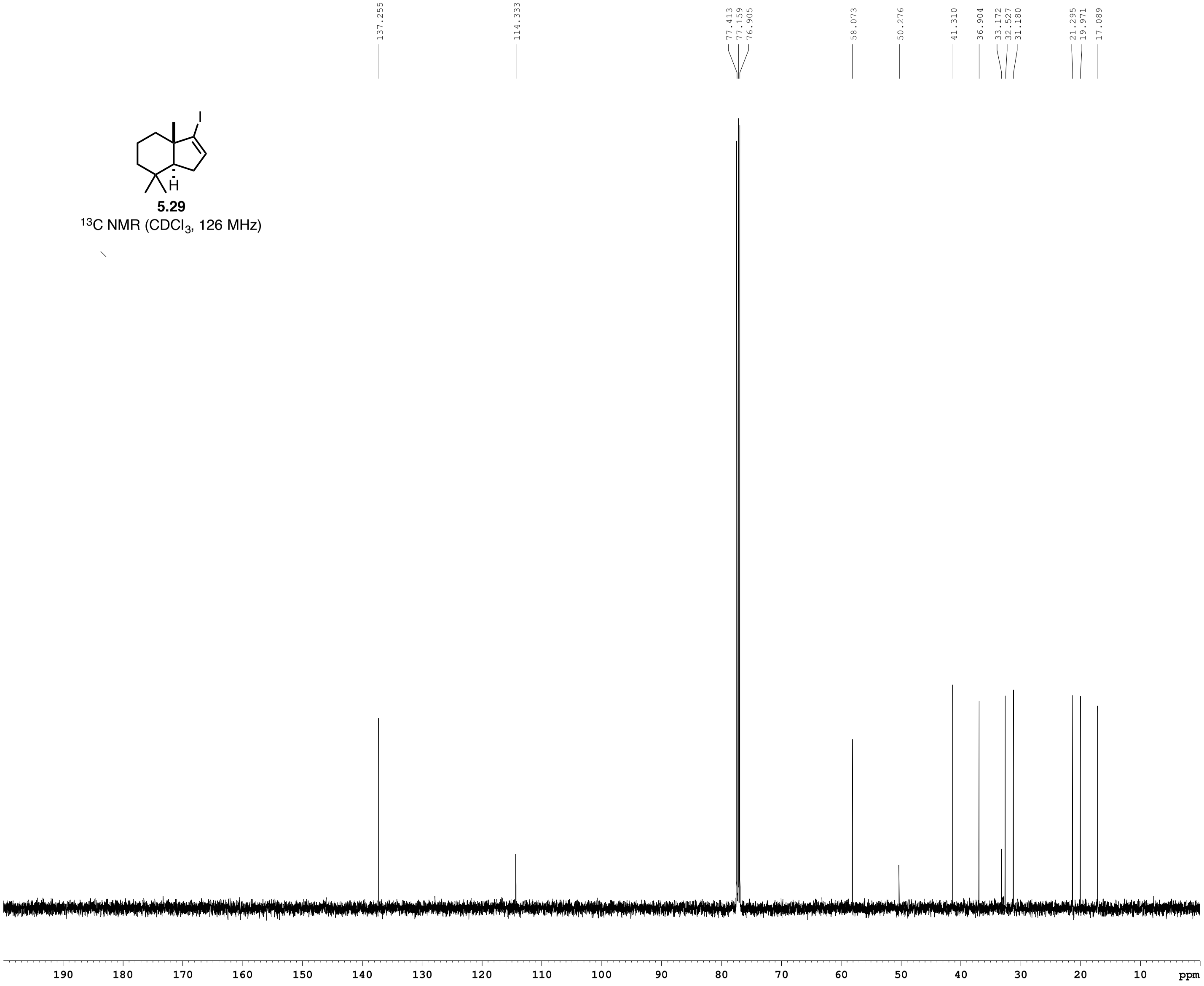
======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200311 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 4.00
```

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

5.29

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME          DJT-V-036
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150203
Time              18.24
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  391
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                13004
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

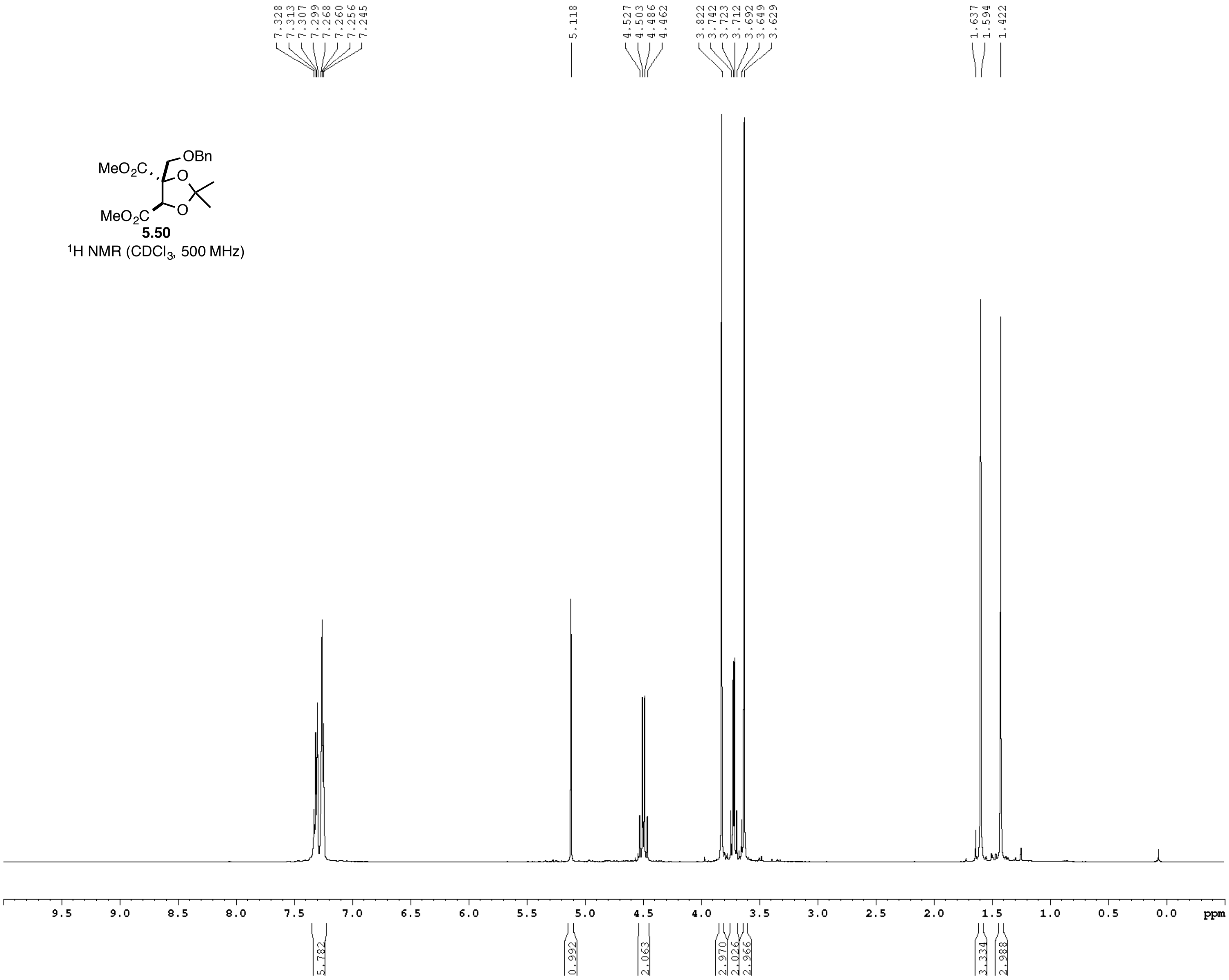
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804074 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



5.50

^{1}H NMR ($CDCl_3$, 500 MHz)

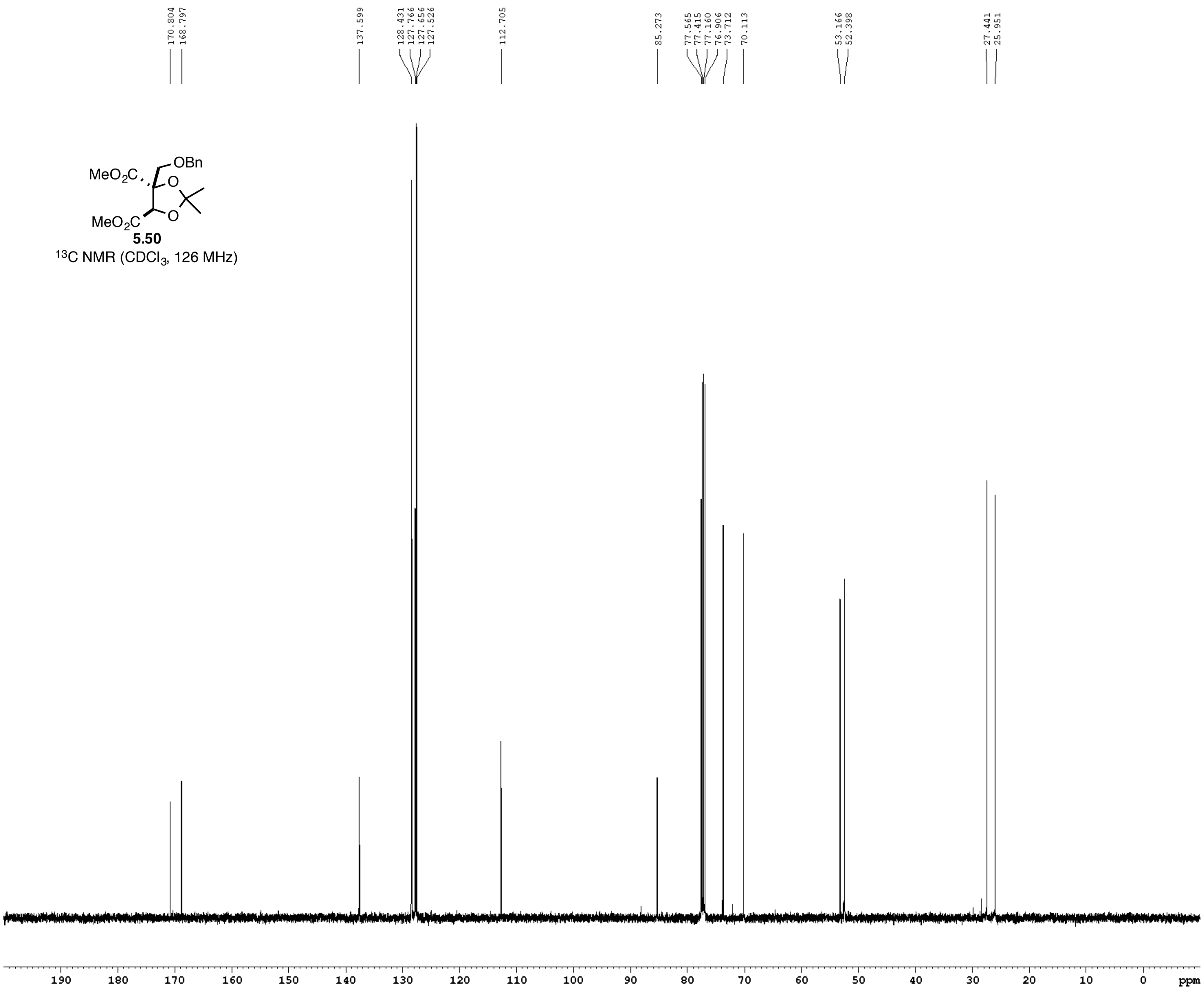
```
Current Data Parameters
NAME          DJT-VI-104
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151118
Time                7.36
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                    30
DS                     0
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200335 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.50

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-104
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151118
Time                7.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   374
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

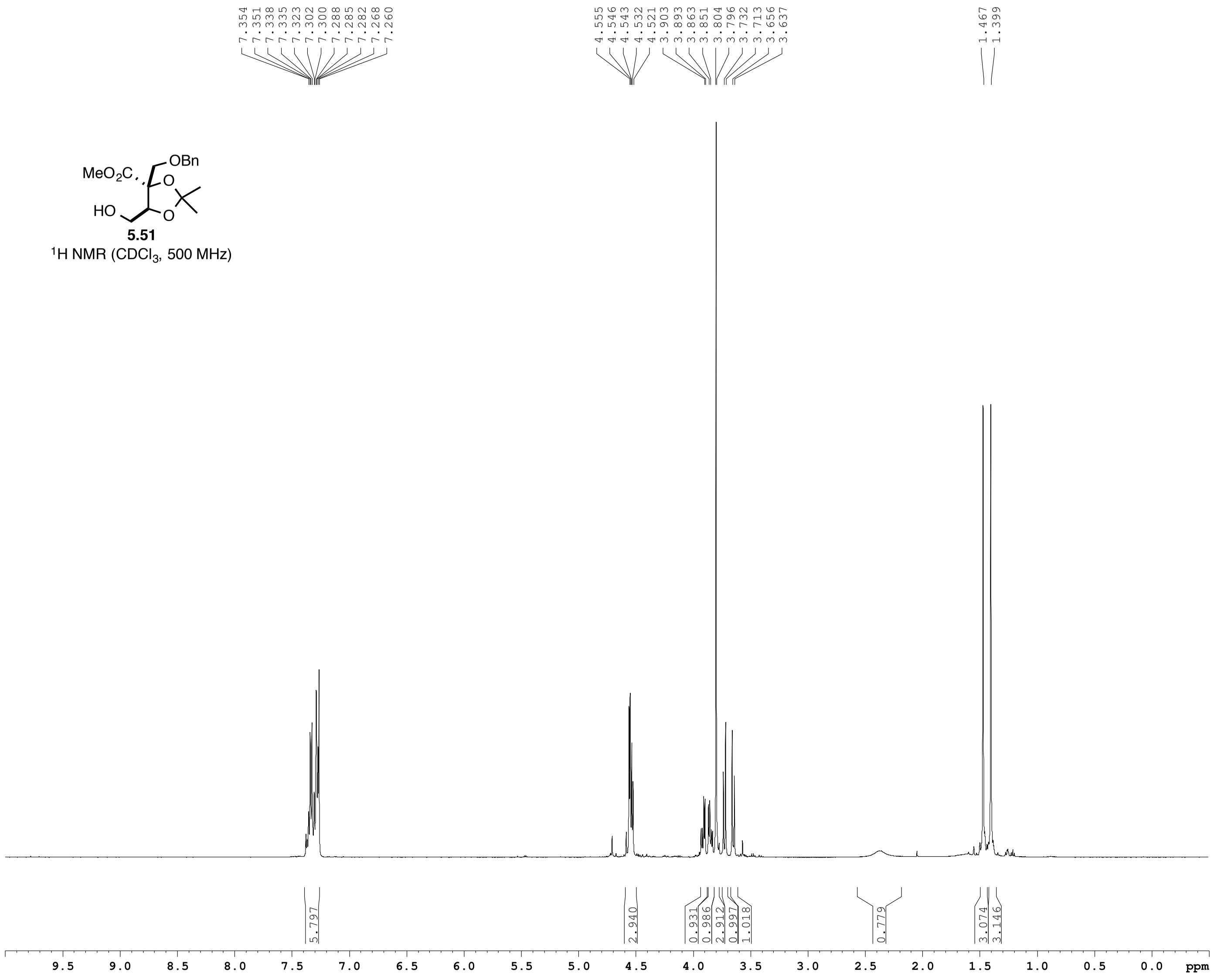
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804103 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

5.51

^{1}H NMR ($CDCl_3$, 500 MHz)

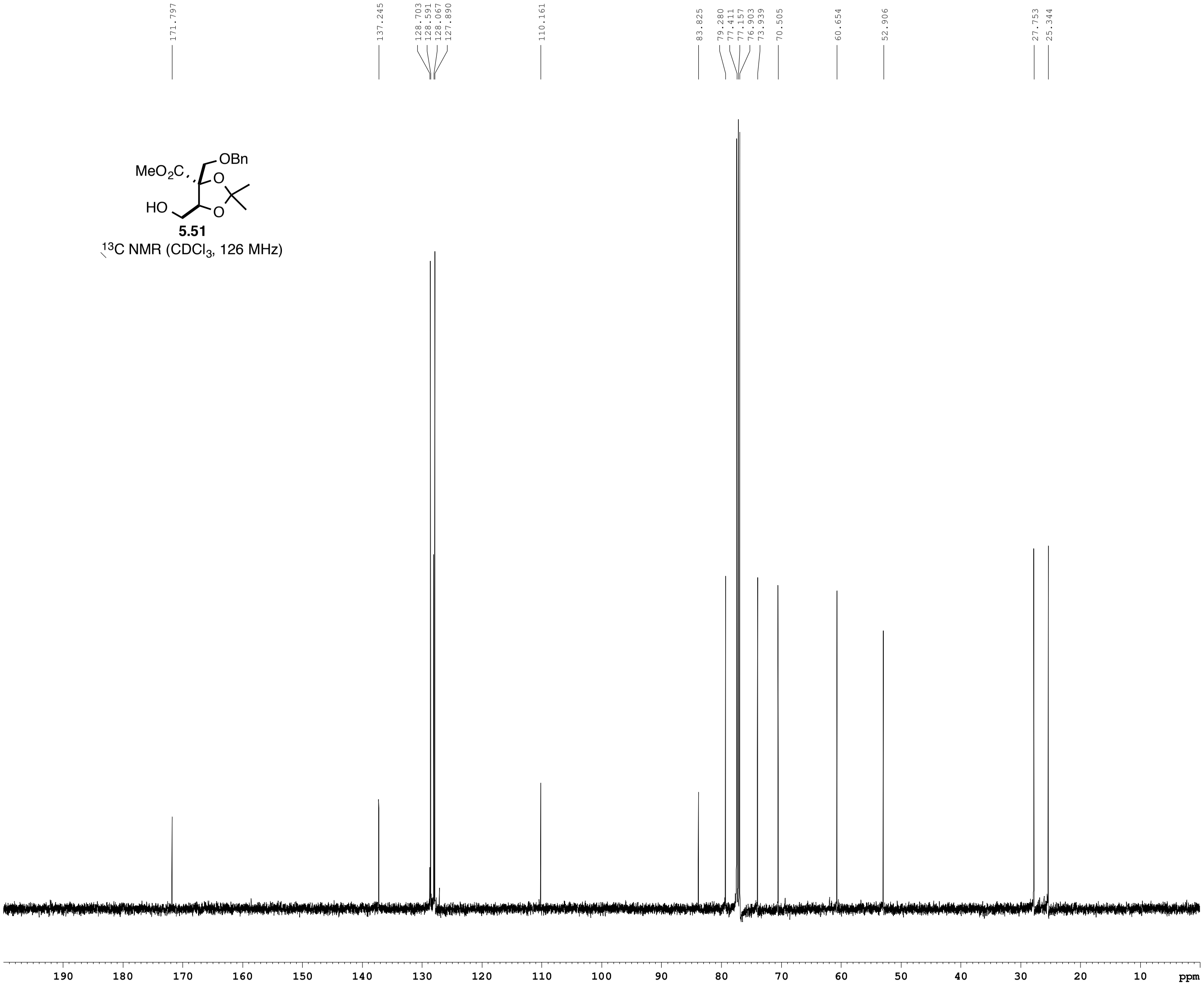


```
Current Data Parameters
NAME          DJT-IV-110
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140813
Time               14.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200307 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```



5.51

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            DJT-IV-110
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140814
Time                 11.08
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     562
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST   0 sec
MCWRK           0.01500000 sec
P2                   31.00 usec

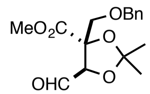
======== CHANNEL f1 ========
NUC1                   13C
P1                   15.50 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   3.20 dB
SP2                   3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.60 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

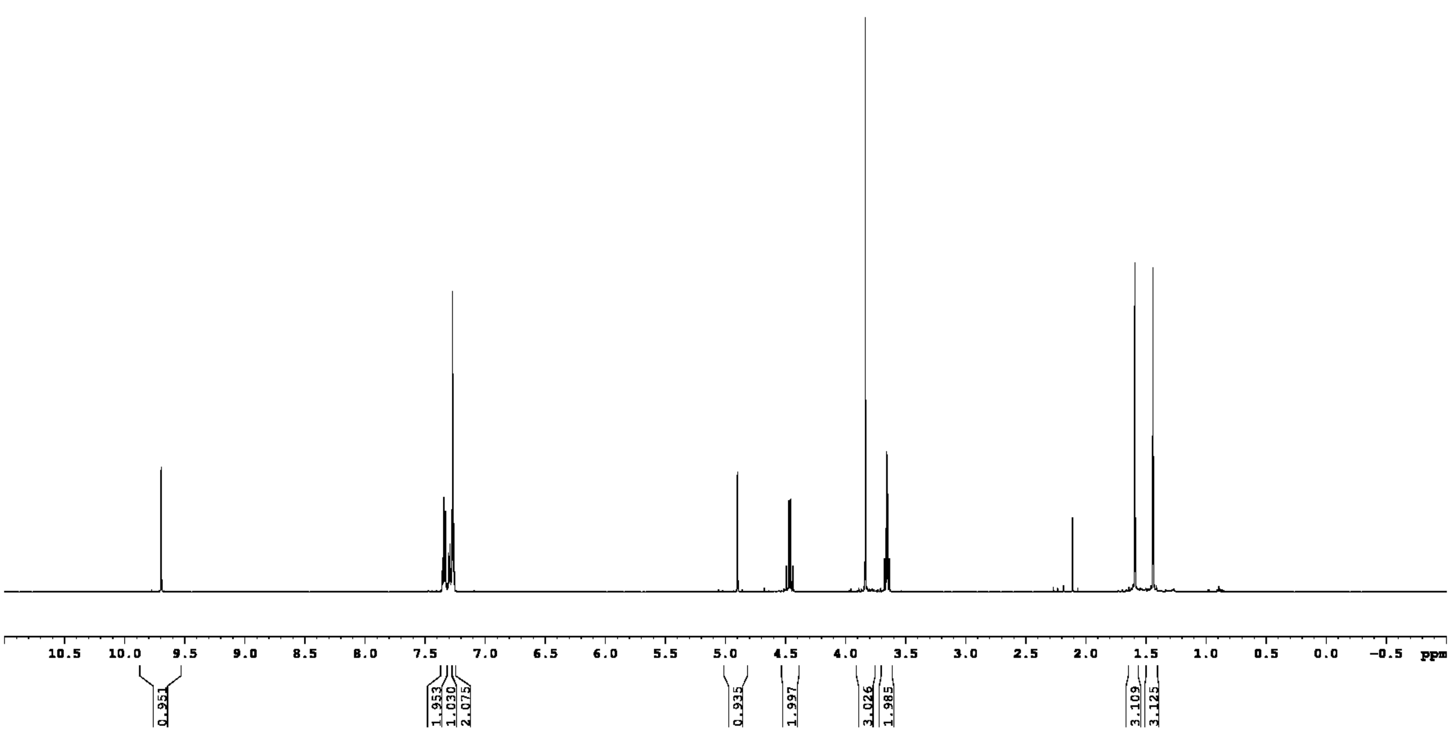
F2 - Processing parameters
SI                   65536
SF             125.7804089 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    2.00
```

YS-III-303



5.30

H NMR ($CDCl_3$, 600 MHz)



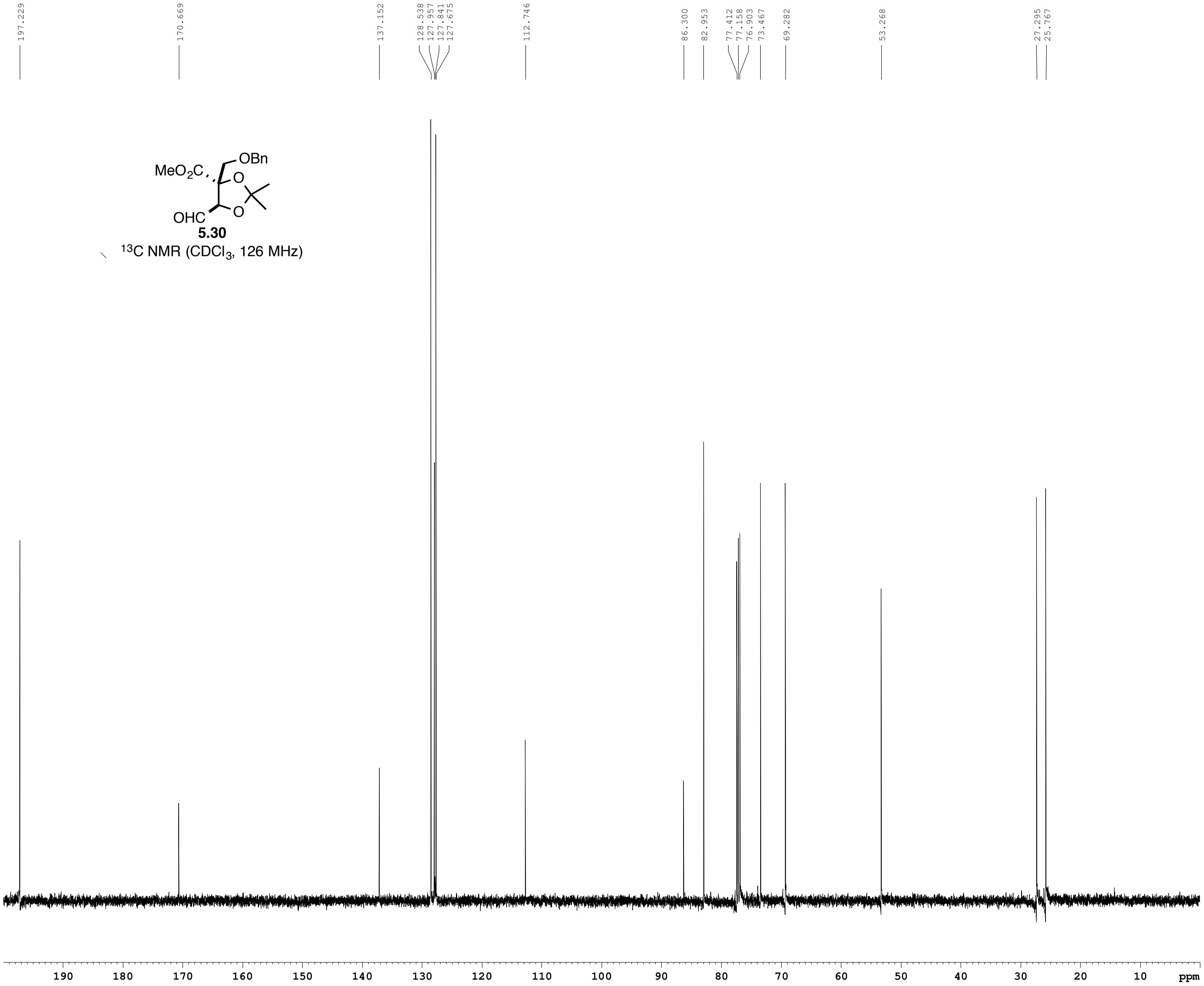
```
Current Data Parameters
NAME           YS-III-303
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151128
Time                13.45
INSTRUM             av600
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  38460
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.250010 Hz
AQ              1.9999200 sec
RG                   1620
DW                 52.000 use
DE                  14.54 use
TE                  298.0 K
D1             0.10000000 sec
TD0                     1

====== CHANNEL f1 ======
SFO1          600.1342009 MHz
NUC1                   1H
P1                   8.00 use
PLW1          24.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300297 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

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



5.30

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-IV-040
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140616
Time               16.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDC13
NS                   101
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

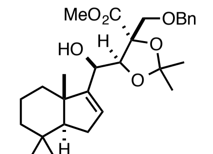
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804122 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-III-303



5.52

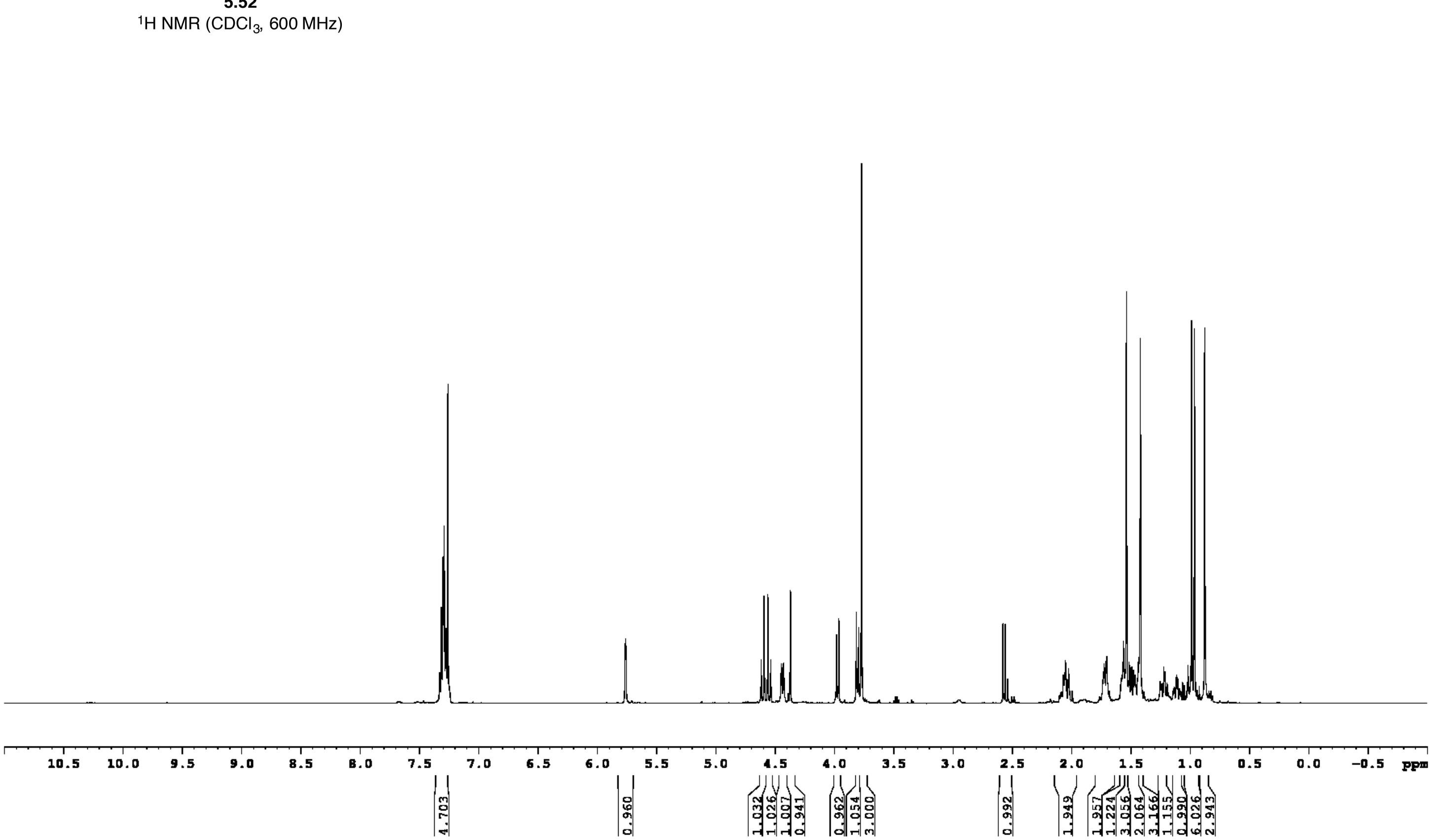
^{1}H NMR ($CDCl_3$, 600 MHz)

```
Current Data Parameters
NAME           YS-III-303
EXPNO                   5
PROCNO                  1

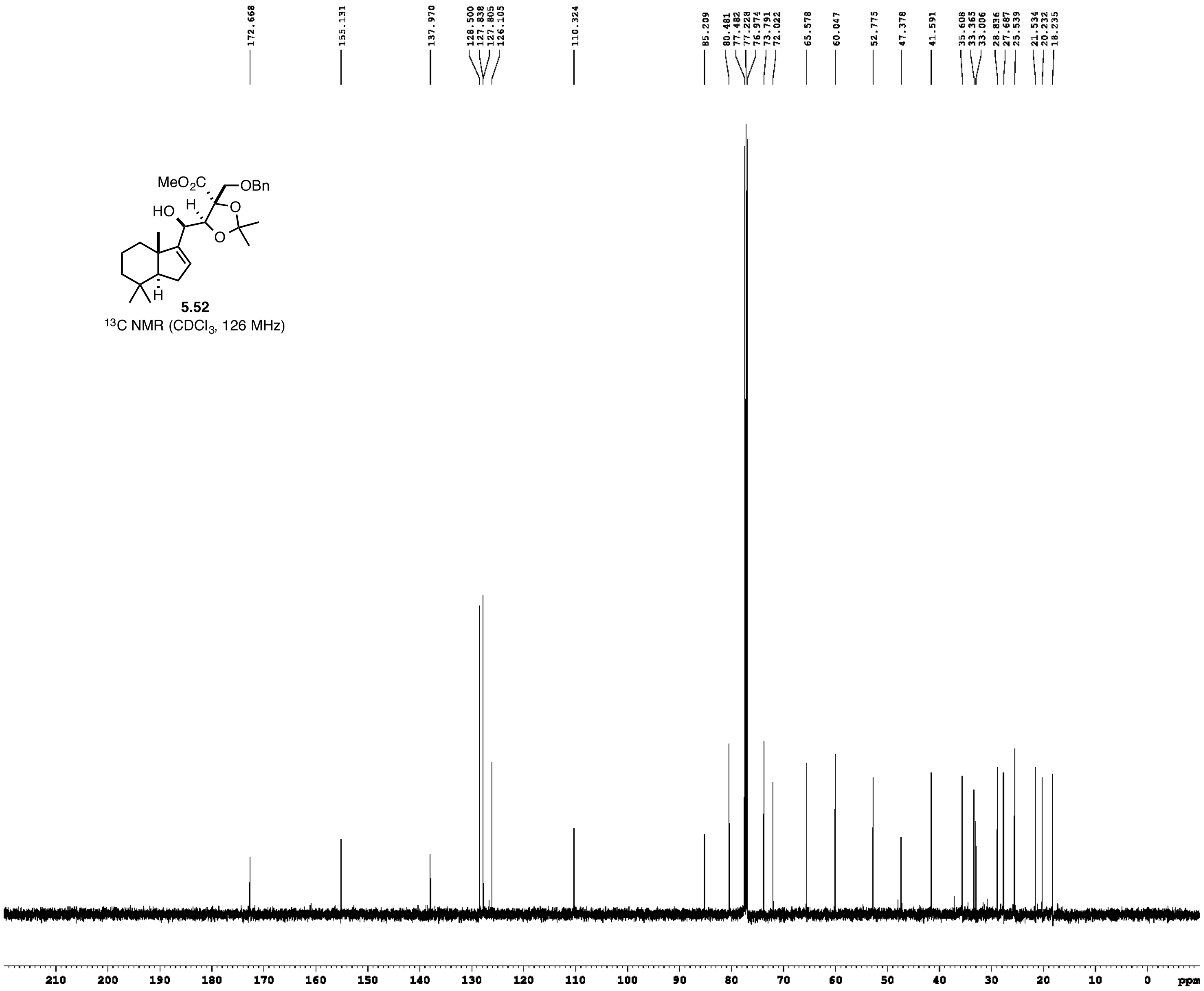
F2 - Acquisition Parameters
Date_            20151202
Time                13.46
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                      8
DW                 62.400 use
DE                   6.00 use
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 use
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200320 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```



YS-III-303



5.52

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-III-303
EXPNO                  6
PROCNO                 1

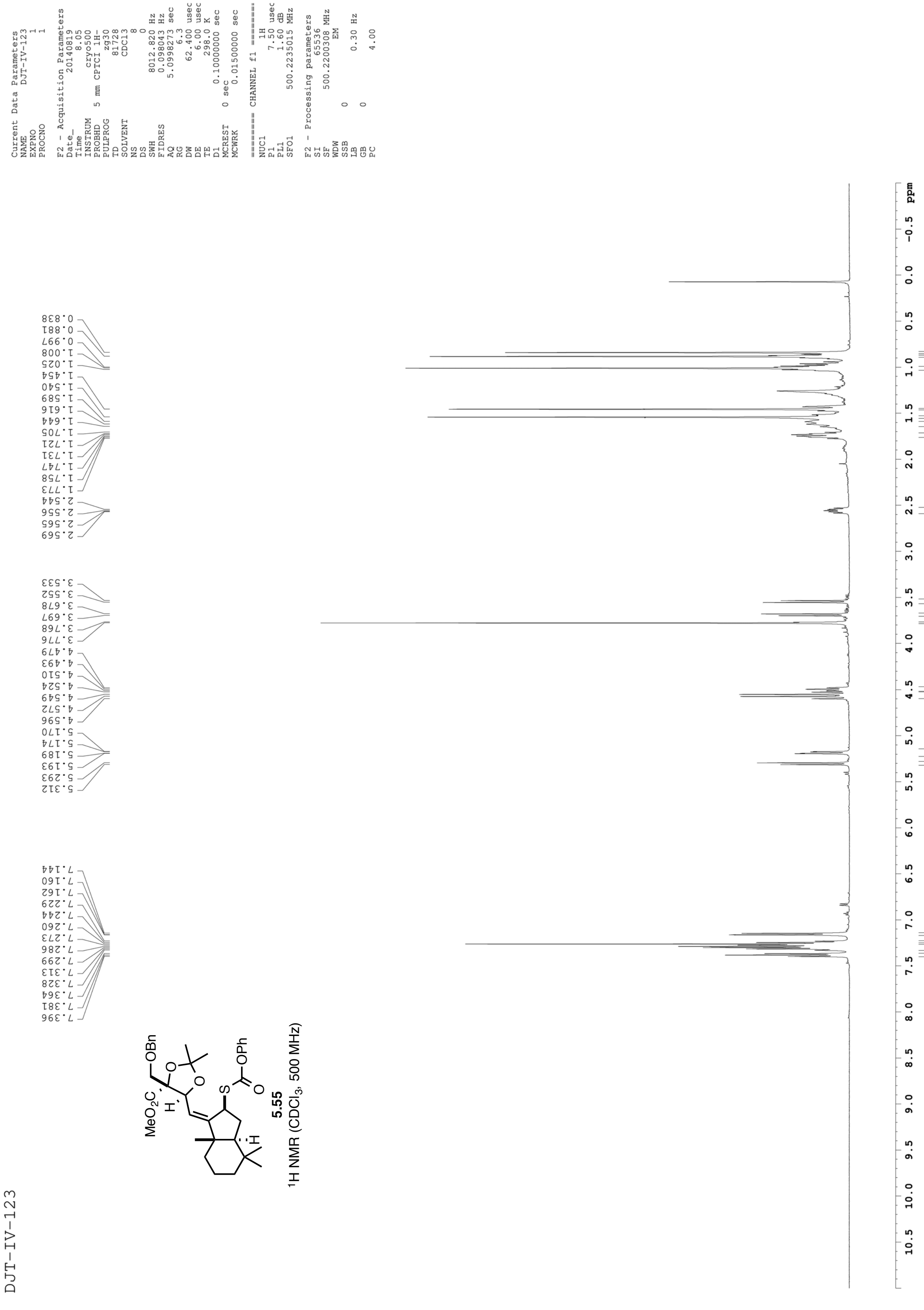
F2 - Acquisition Parameters
Date_           20151202
Time               13.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   496
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                2580.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

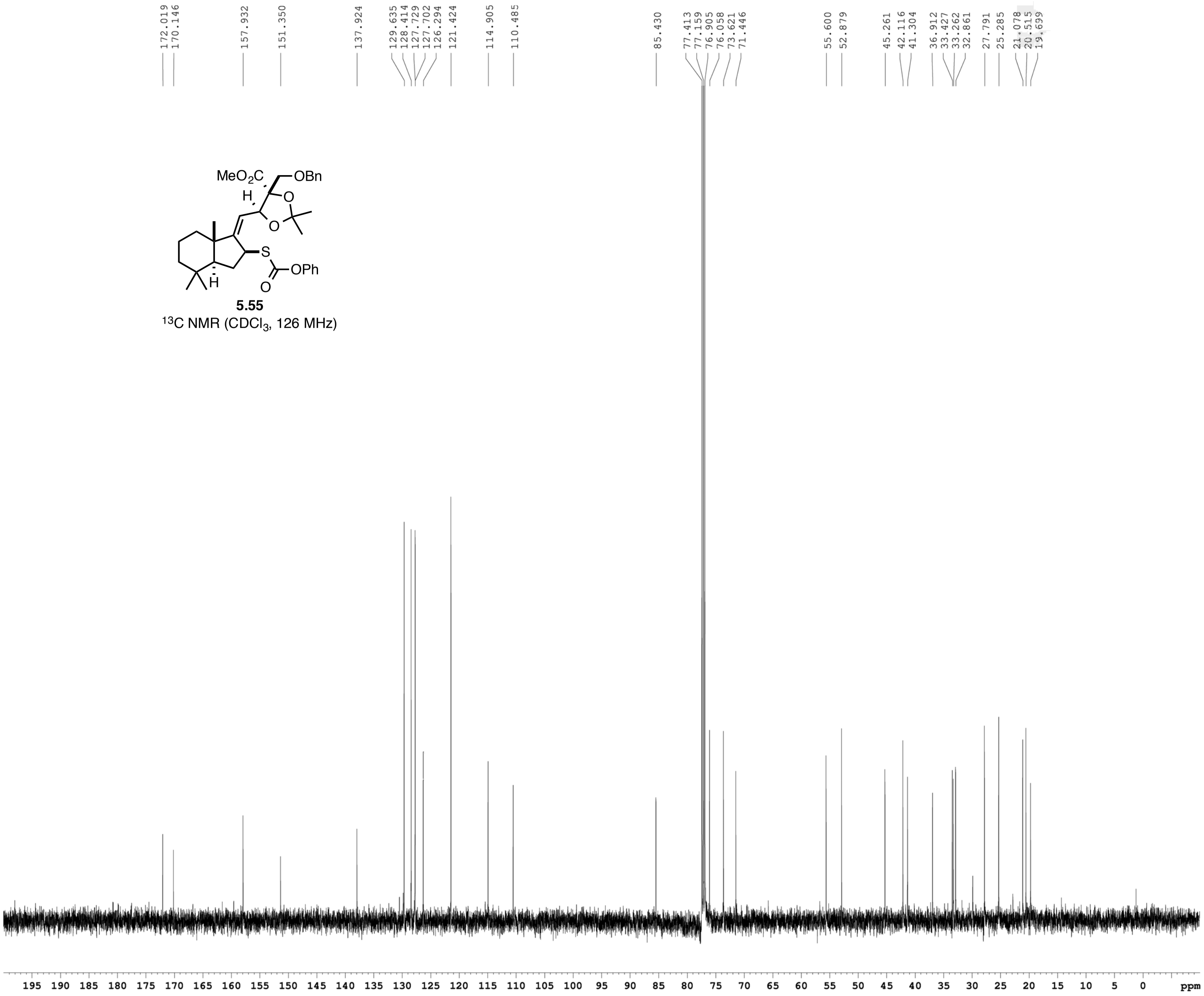
F2 - Processing parameters
SI                 65536
SF           125.7803996 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



5.55

^{1}H NMR (CDCl$_3$, 500 MHz)

DJT-IV-123



5.55

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-IV-123
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140820
Time                9.01
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   360
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

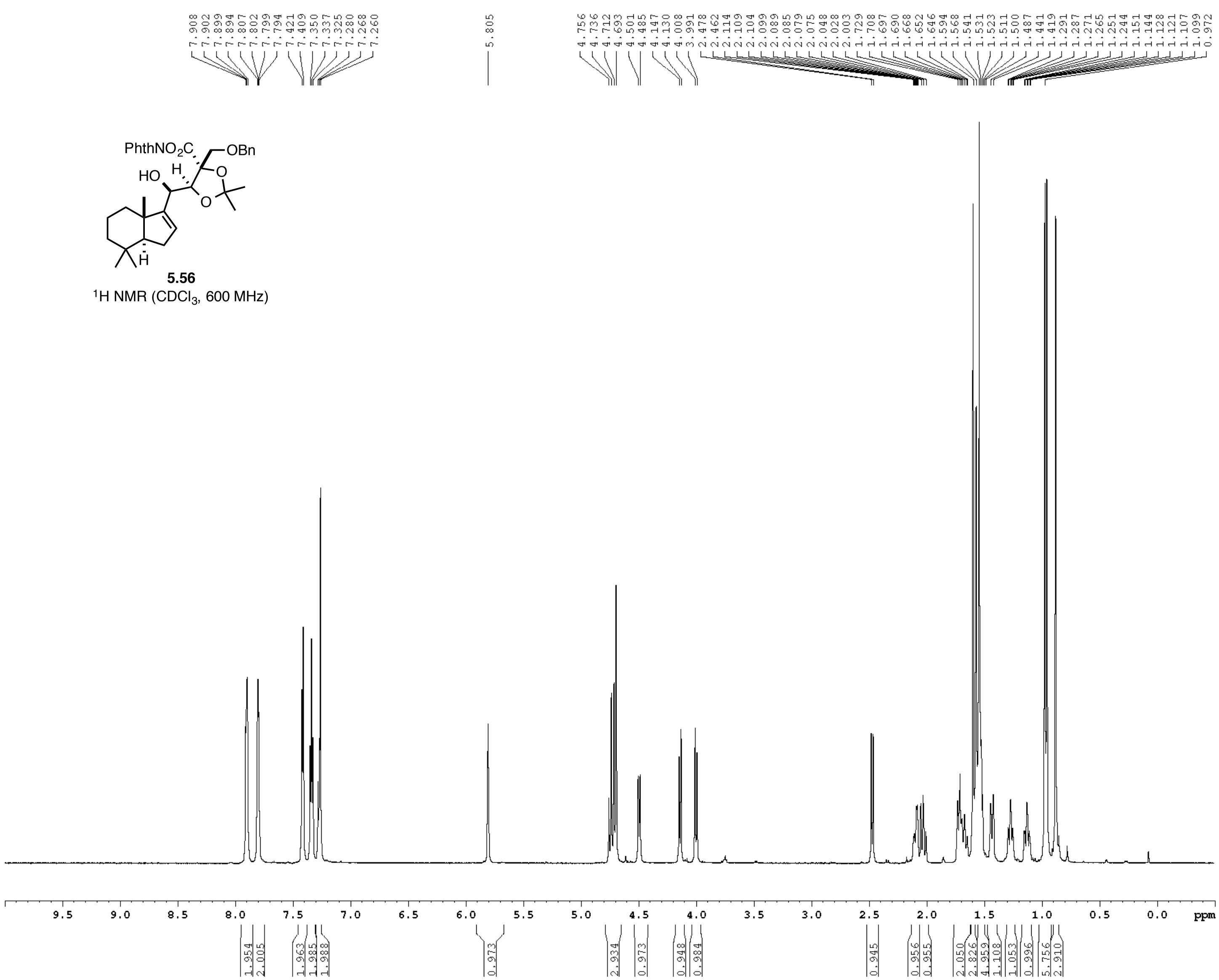
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804080 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum

5.56

^{1}H NMR ($CDCl_3$, 600 MHz)



```
Current Data Parameters
NAME          DJT-IV-203
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141013
Time               16.31
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                    12
DS                     0
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                   322
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

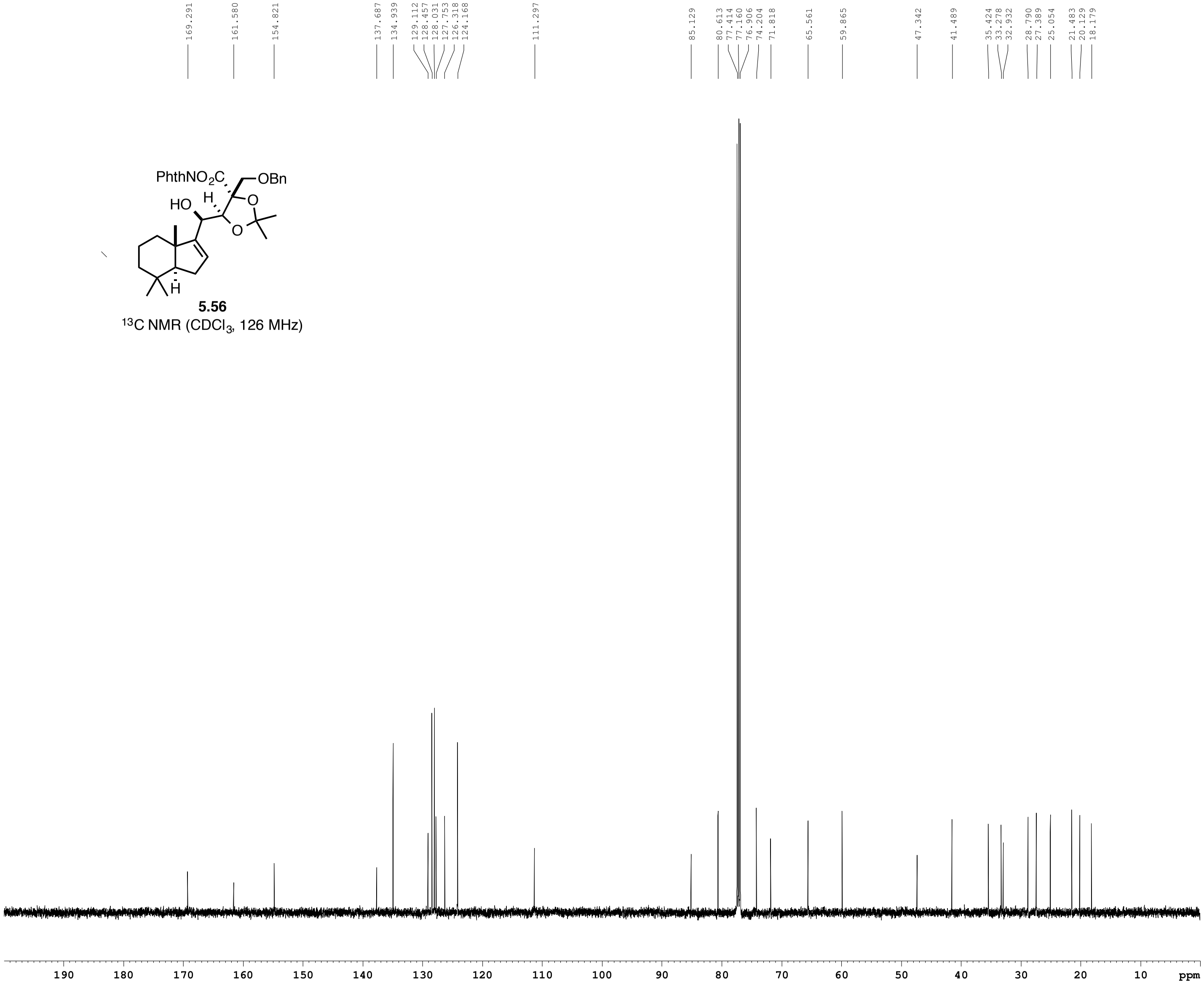
======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         23.01441956 W

F2 - Processing parameters
SI                 65536
SF          600.1300343 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

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

5.56

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME           DJT-IV-203
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150414
Time                 8.55
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    857
DS                      0
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

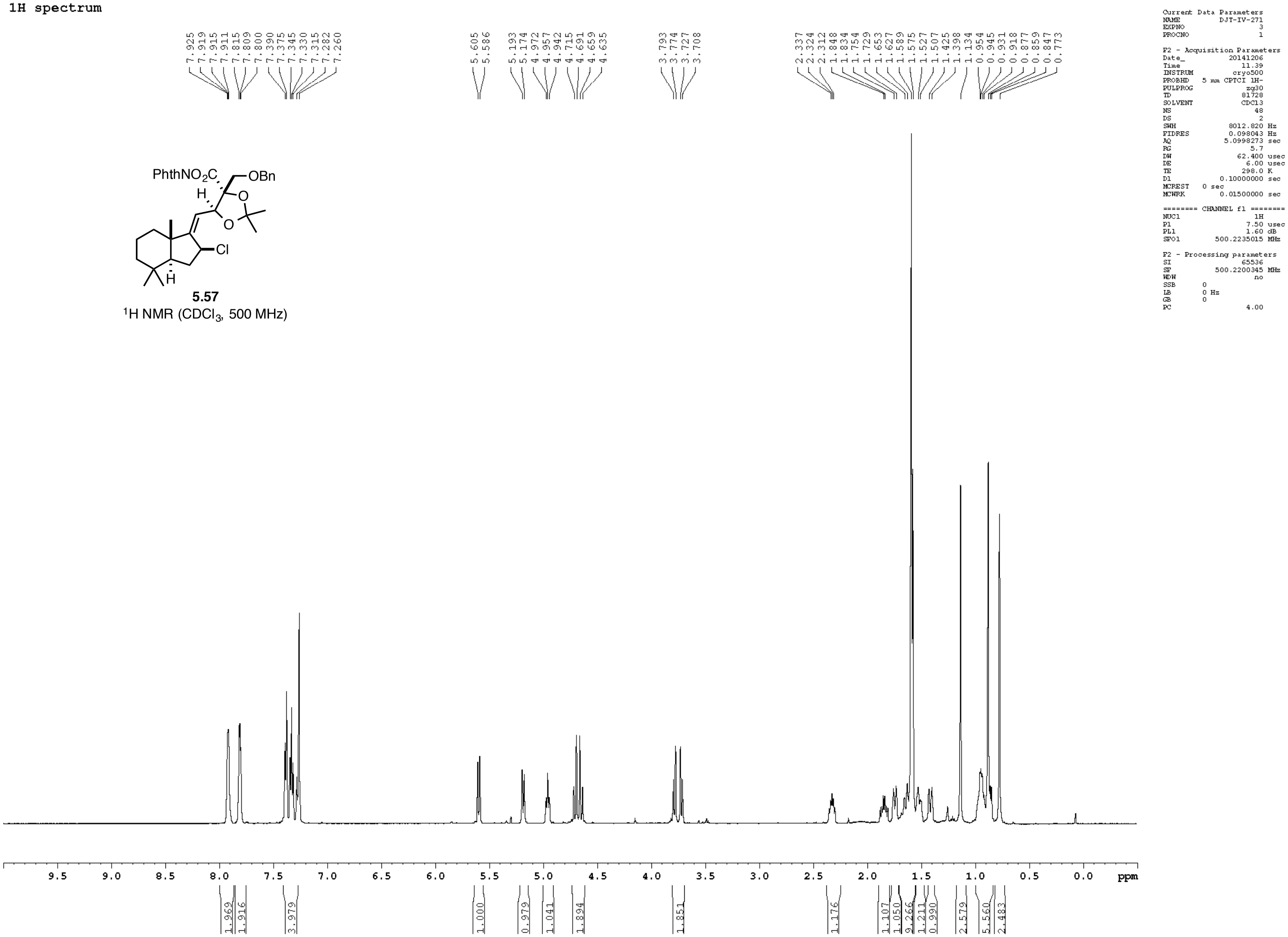
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804076 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

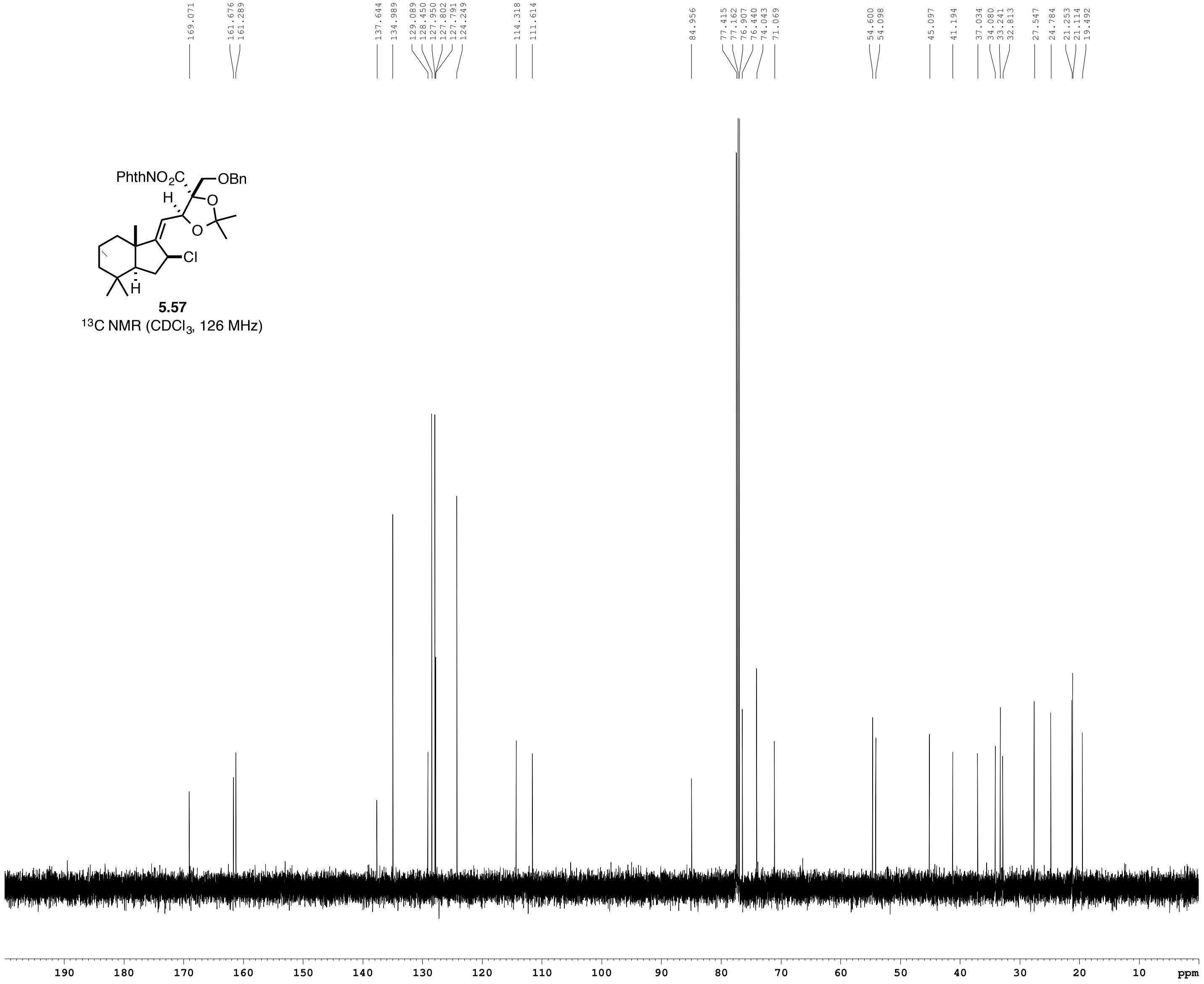
1H spectrum



5.57

^{1}H NMR (CDCl$_3$, 500 MHz)

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



5.57

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-IV-271
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141206
Time               11.49
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   269
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

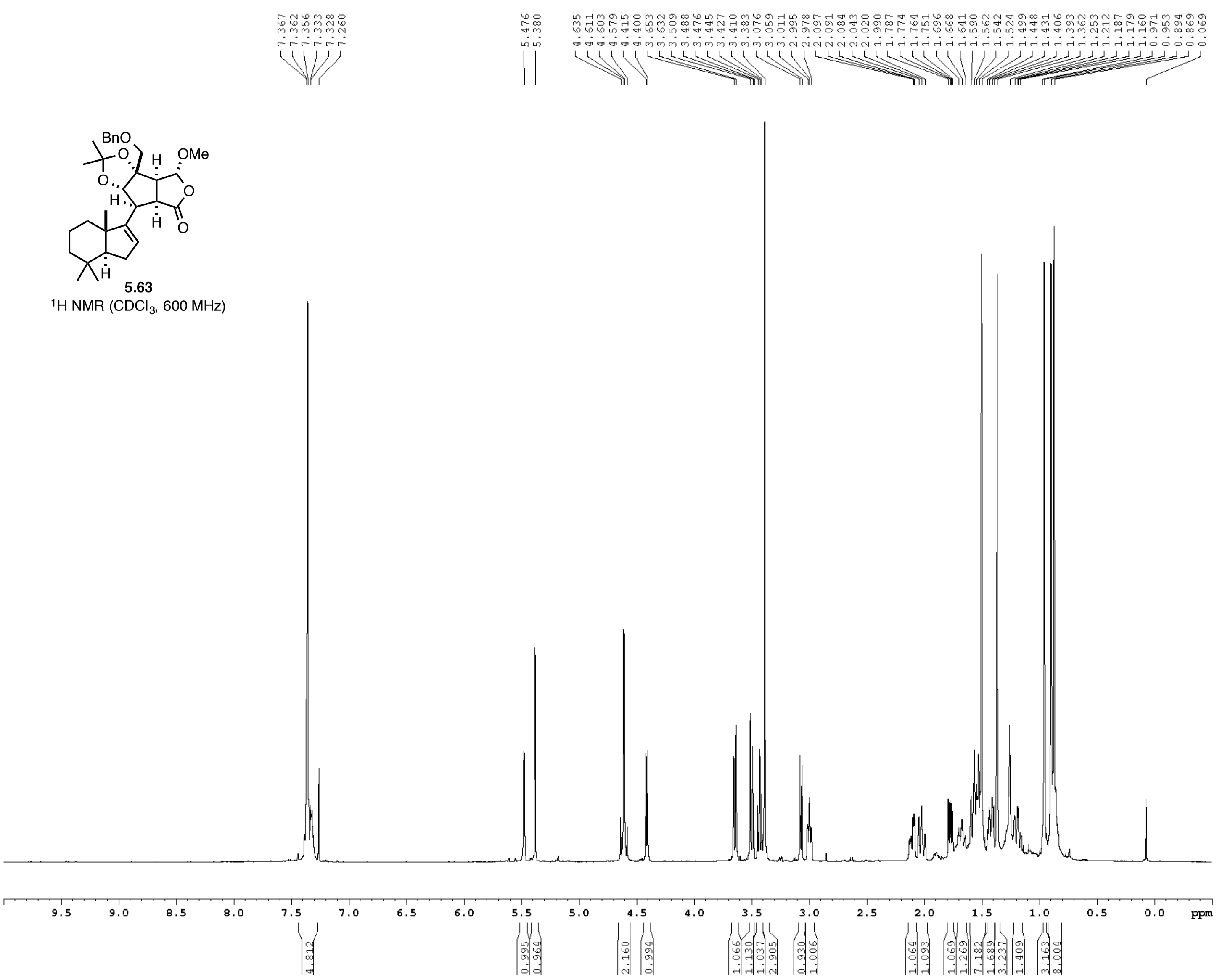
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804099 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  2.00
```

1H spectrum



5.63

^{1}H NMR (CDCl$_3$, 600 MHz)

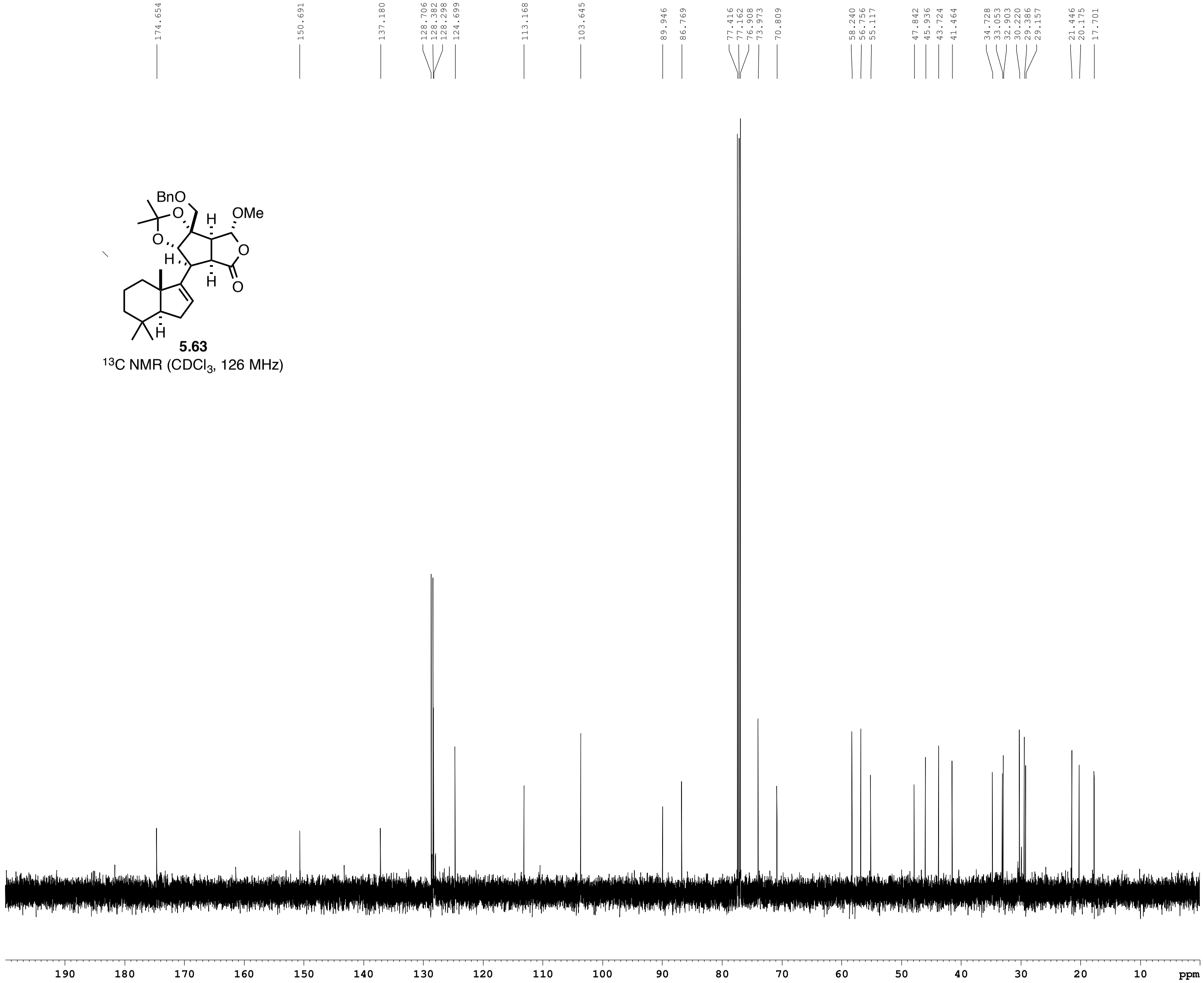
```
Current Data Parameters
NAME             DJT-V-103
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150328
Time                 14.16
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   16022
SOLVENT              CDCl3
NS                      30
DS                       0
SWH               8012.820 Hz
FIDRES            0.500114 Hz
AQ               0.9997728 sec
RG                     3.6
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200308 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

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



5.63

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-V-027
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20150128
Time               8.37
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  260
DS                   16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 6502
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

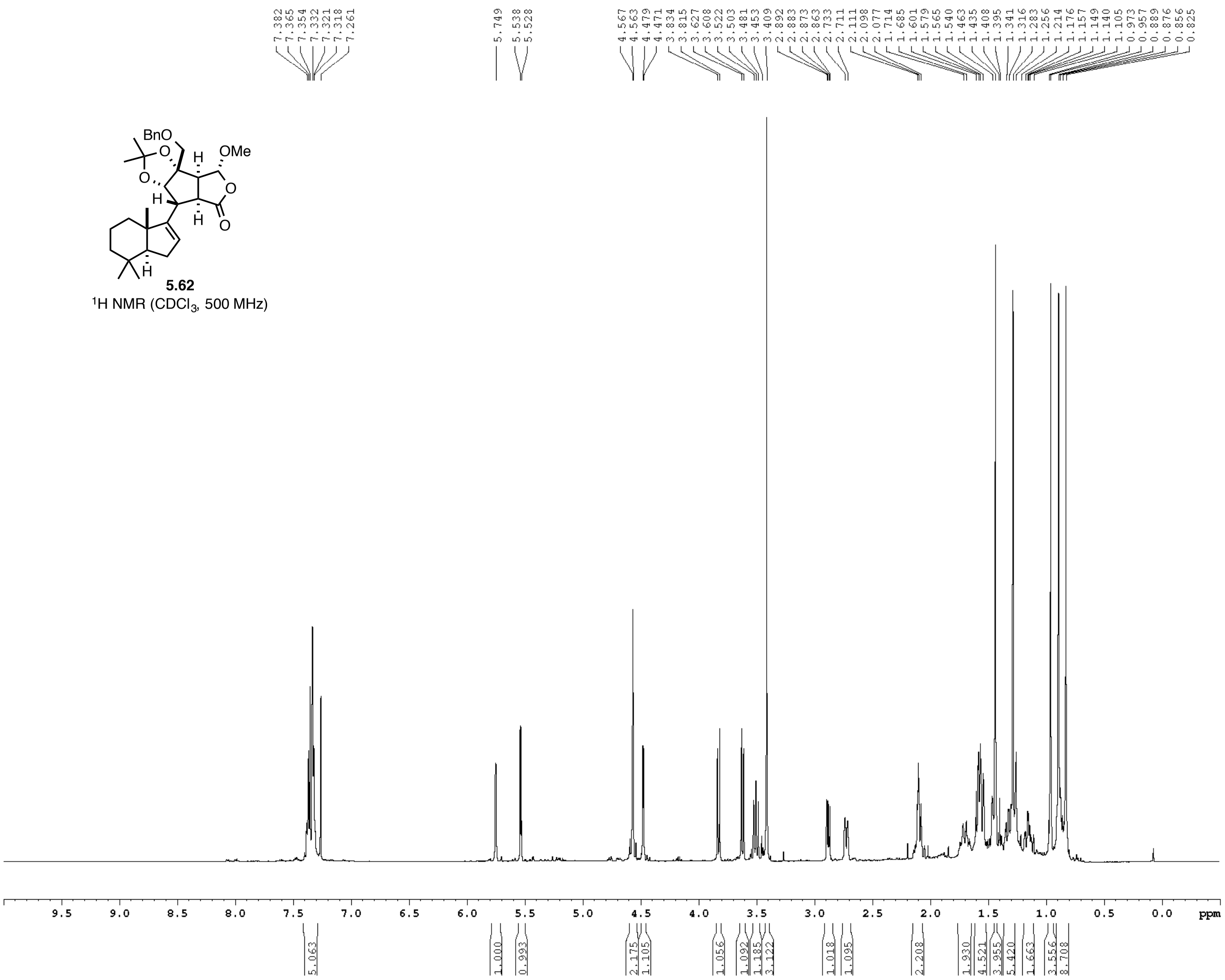
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804076 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 2.00
```

1H spectrum



5.62

^{1}H NMR ($CDCl_3$, 500 MHz)

```
Current Data Parameters
NAME           DJT-V-103
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150328
Time               14.19
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 16022
SOLVENT            CDCl3
NS                    60
DS                     0
SWH             8012.820 Hz
FIDRES          0.500114 Hz
AQ             0.9997728 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

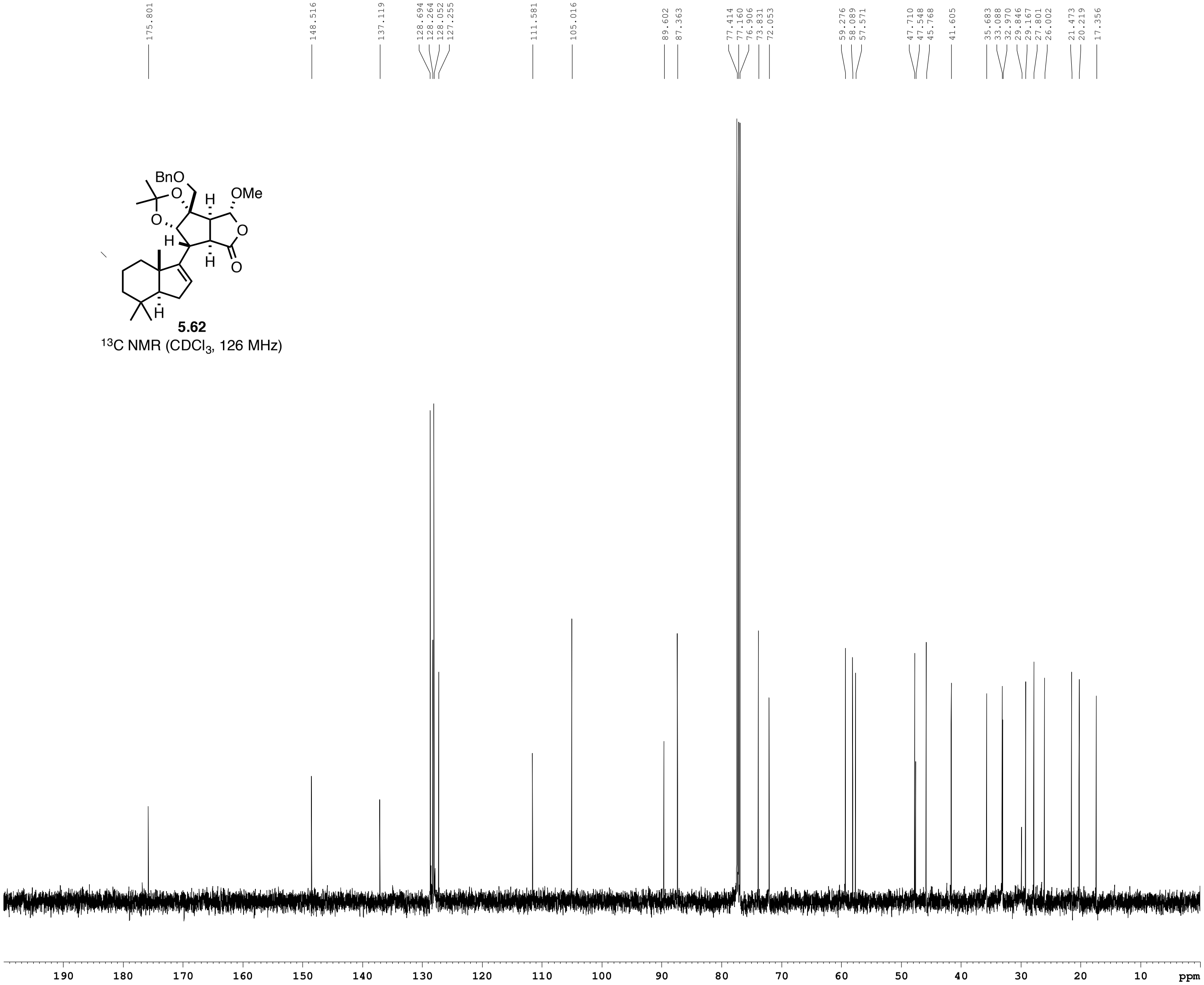
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200304 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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

5.62

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME            DJT-V-056
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150225
Time                16.33
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    135
DS                      0
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   3251
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

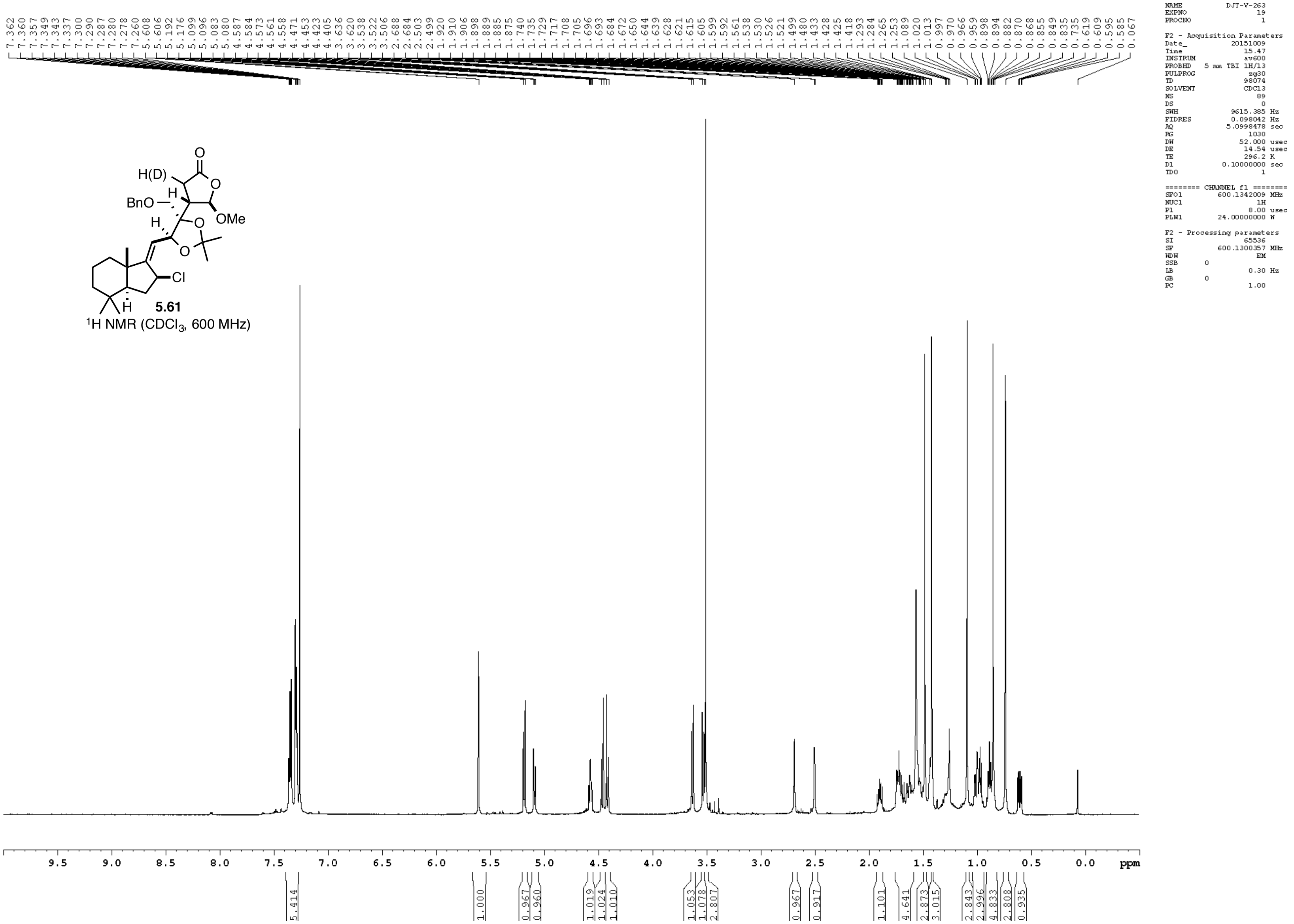
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804085 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

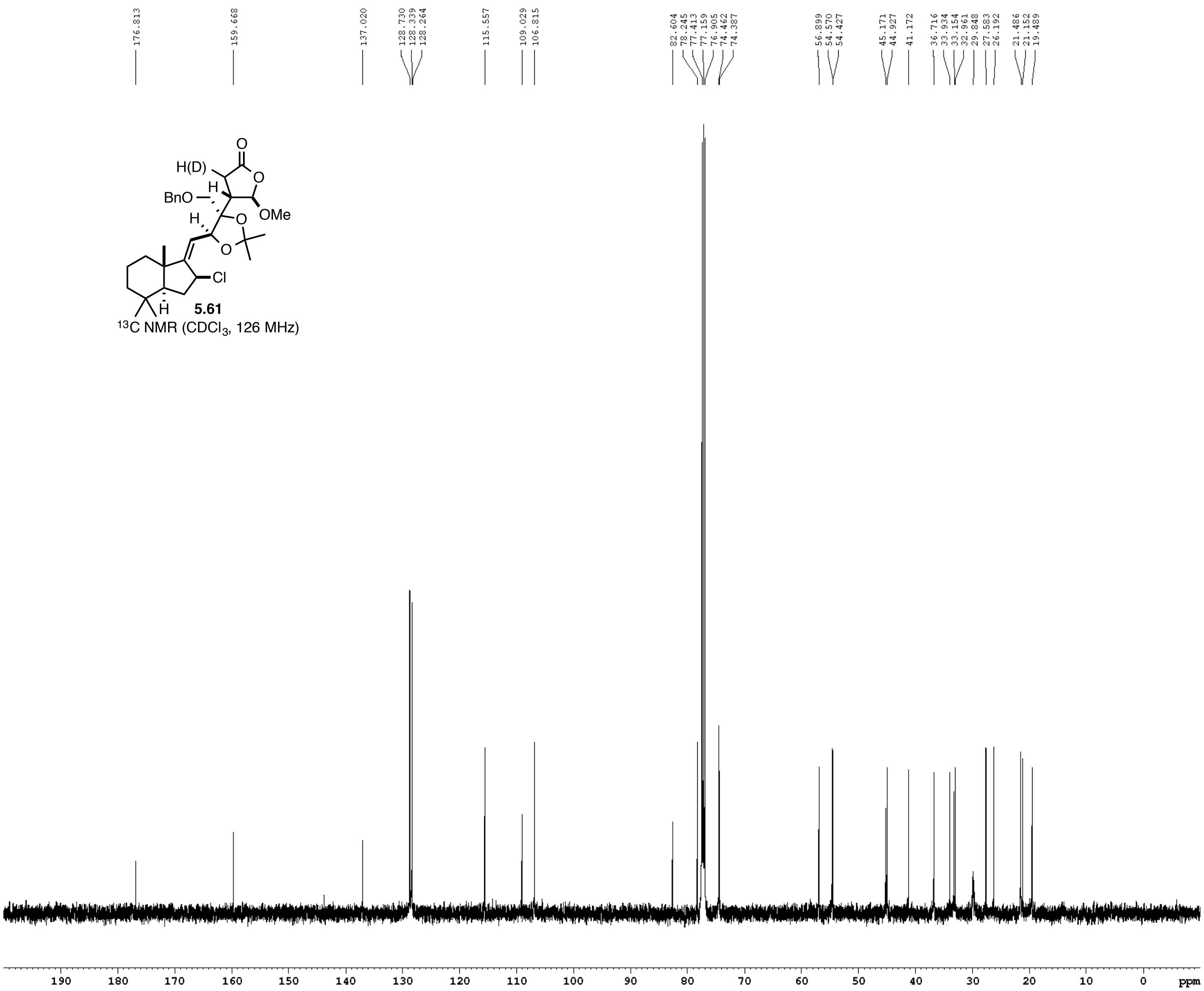
1H spectrum



5.61

^{1}H NMR (CDCl$_3$, 600 MHz)

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



5.61

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            DJT-V-263
EXPNO                  21
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151010
Time                 9.52
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDC13
NS                    842
DS                      0
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 5792.6
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

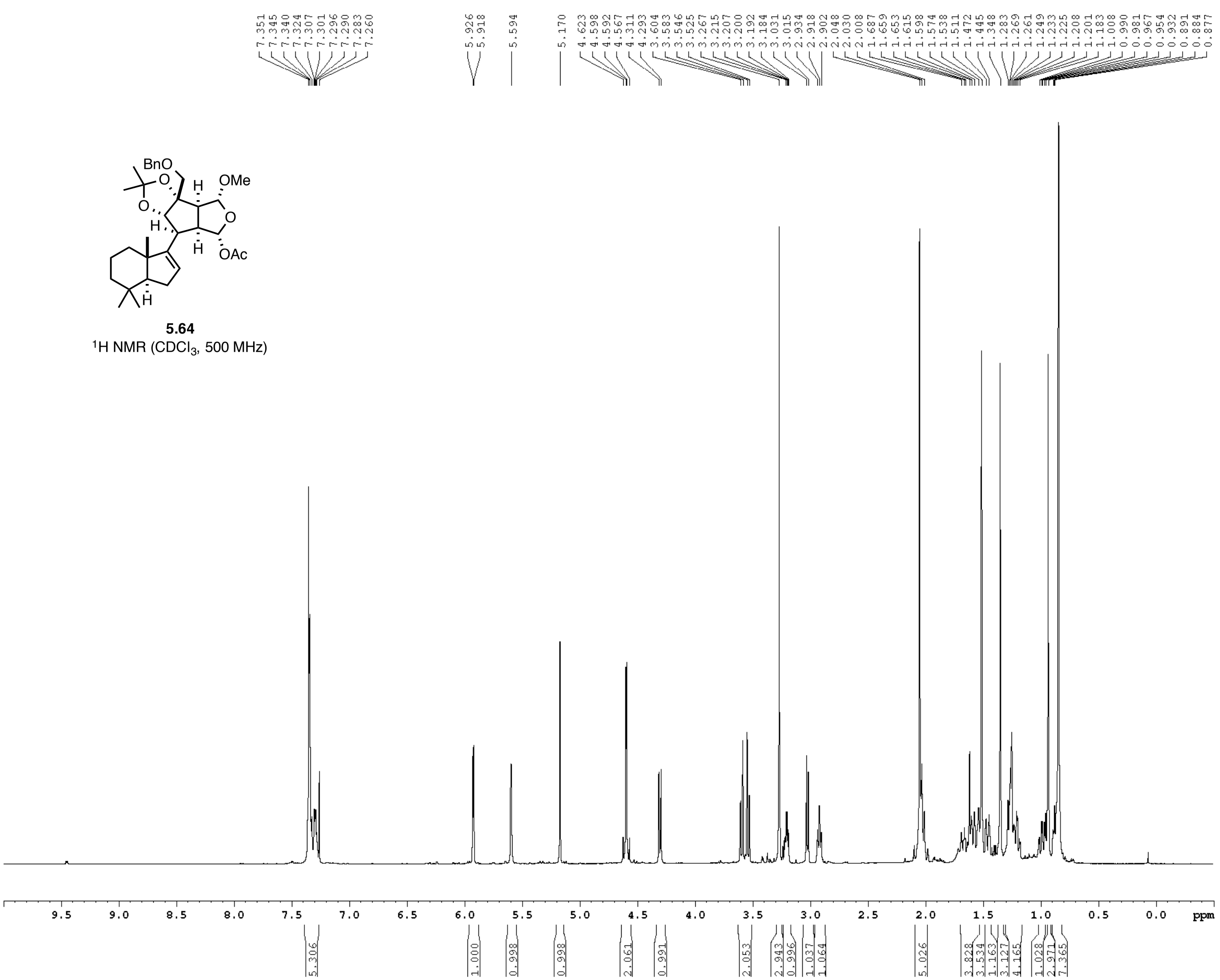
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804080 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   2.00
```

1H spectrum



5.64

^{1}H NMR (CDCl$_3$, 500 MHz)

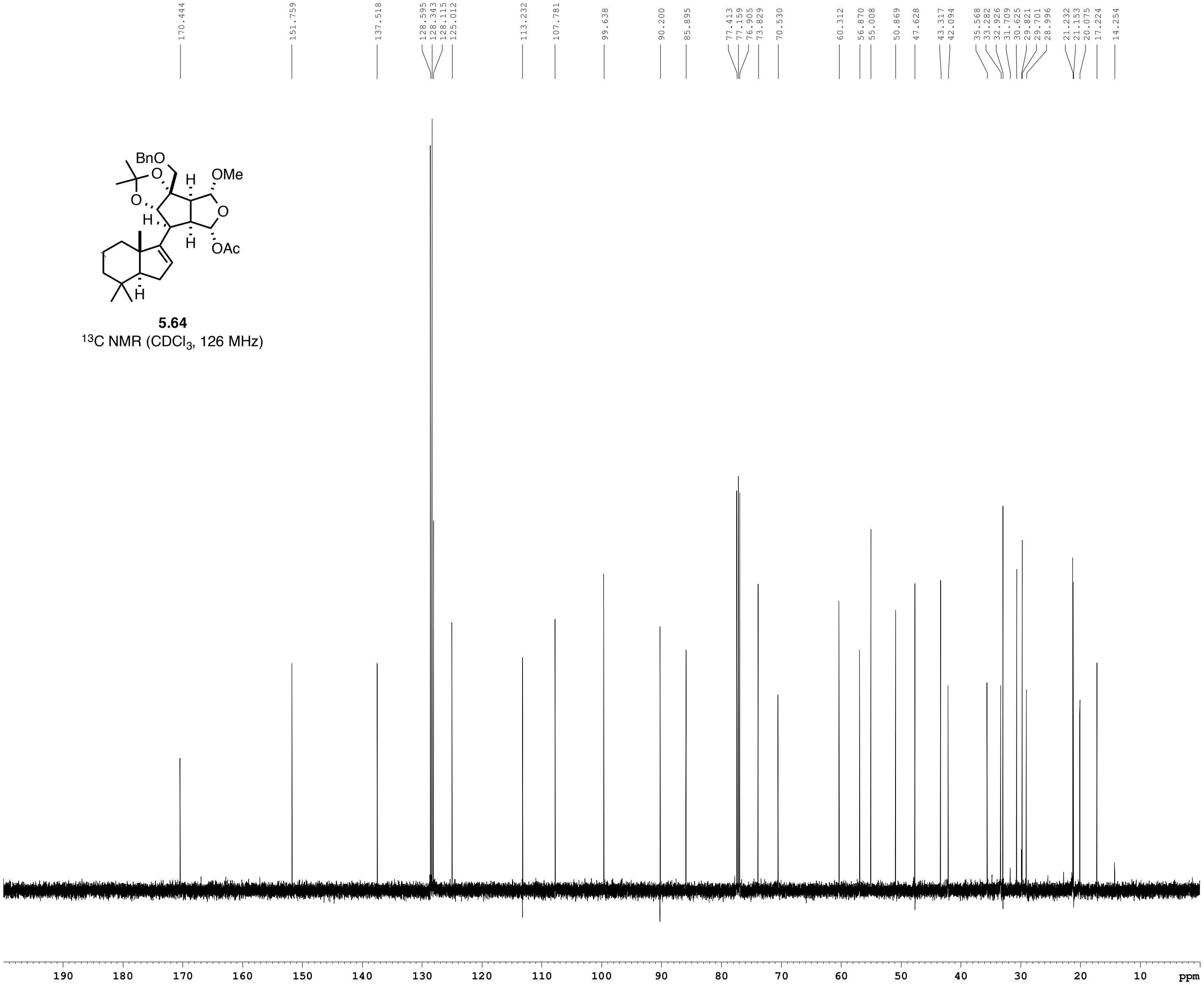
```
Current Data Parameters
NAME             DJT-V-268
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150821
Time                 11.02
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                     20
DS                      0
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                    6.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200313 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

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



5.64

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-V-268
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150821
Time              11.07
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  171
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5792.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

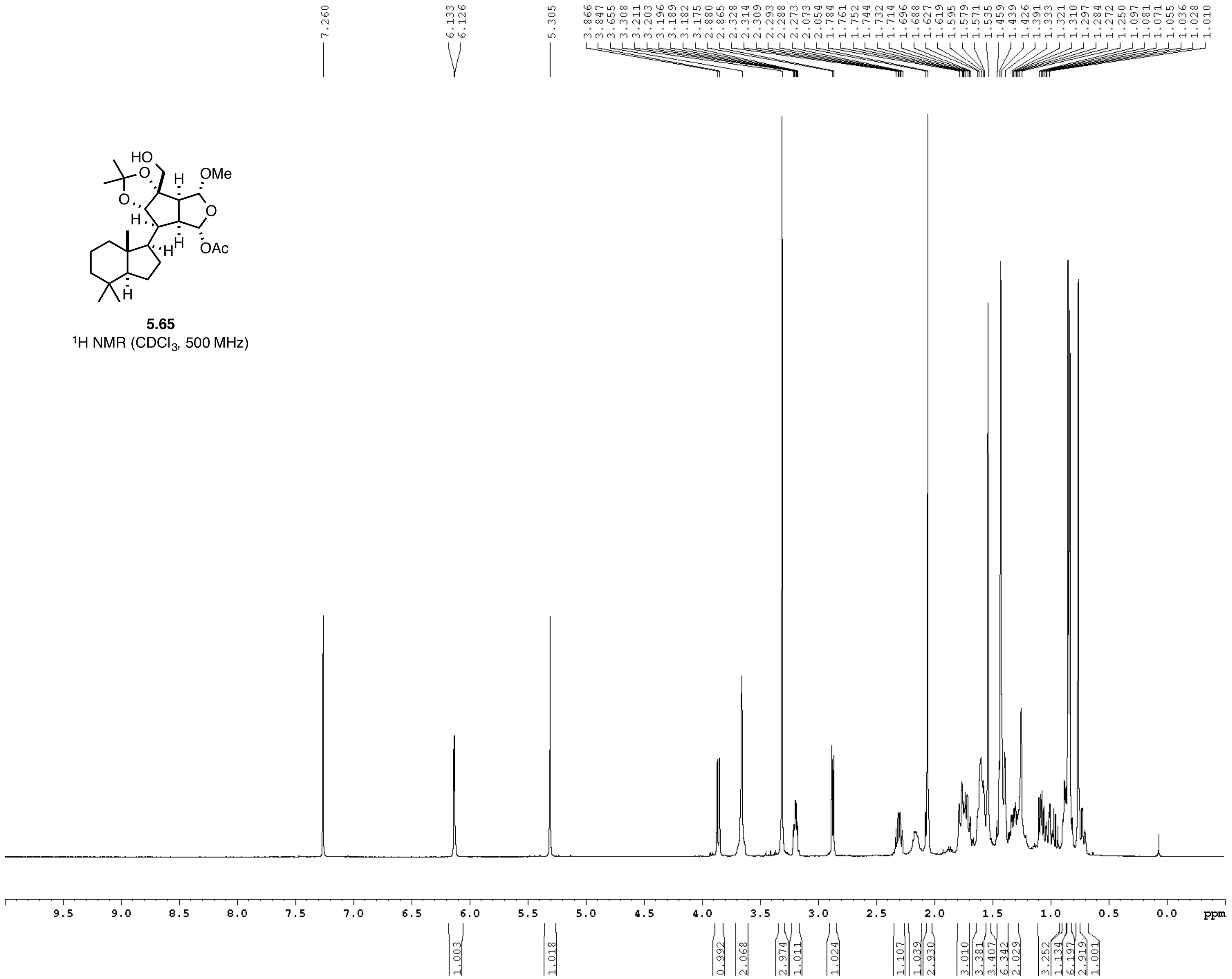
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804108 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 2.00
```

1H spectrum

5.65

^{1}H NMR ($CDCl_3$, 500 MHz)



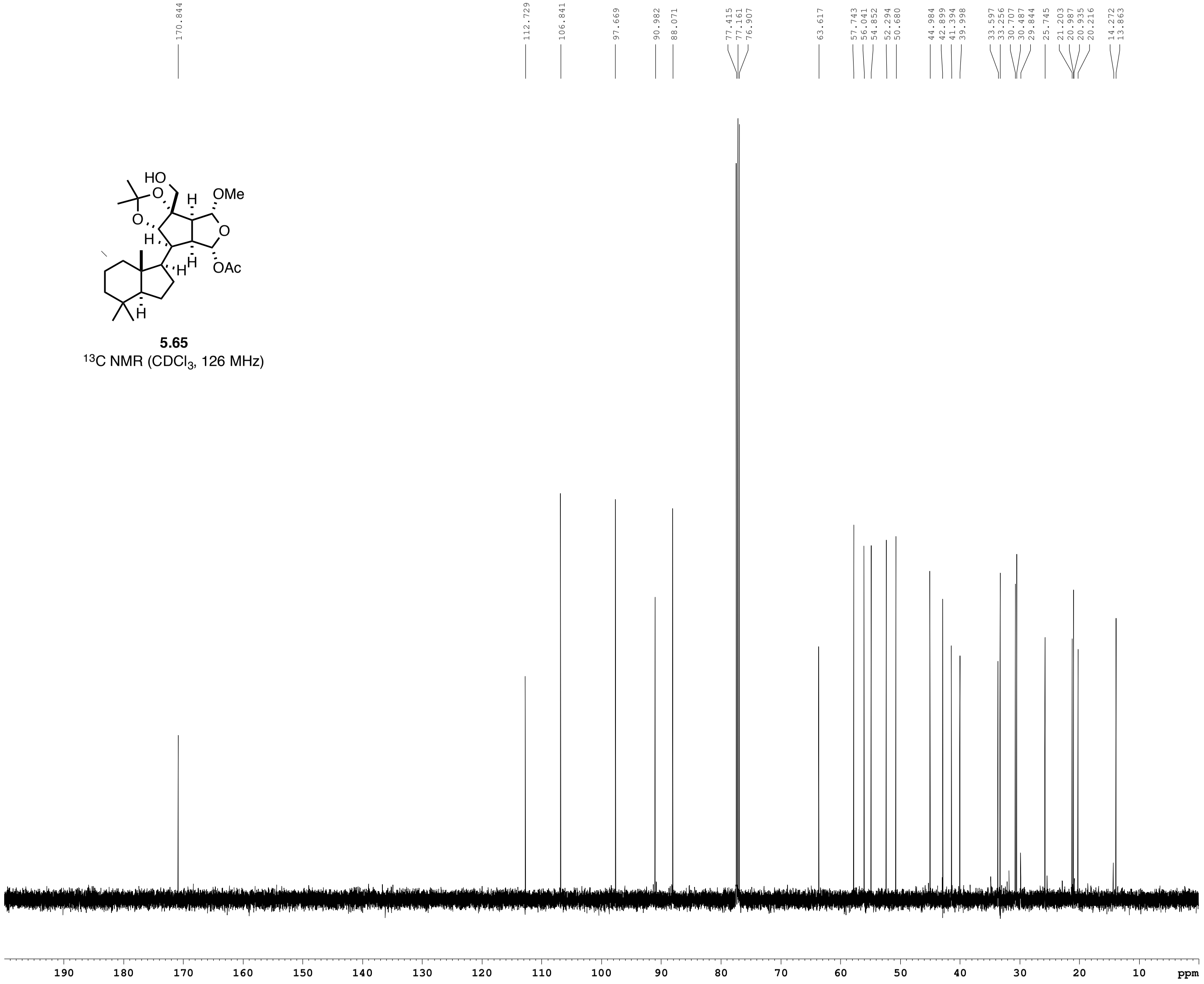
```
Current Data Parameters
NAME            DJT-V-270
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150824
Time                13.07
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200312 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.65

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-V-270
EXPNO                 6
PROCNO                1

F2 - Acquisition Parameters
Date_          20150824
Time              13.11
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  498
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG                 4096
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

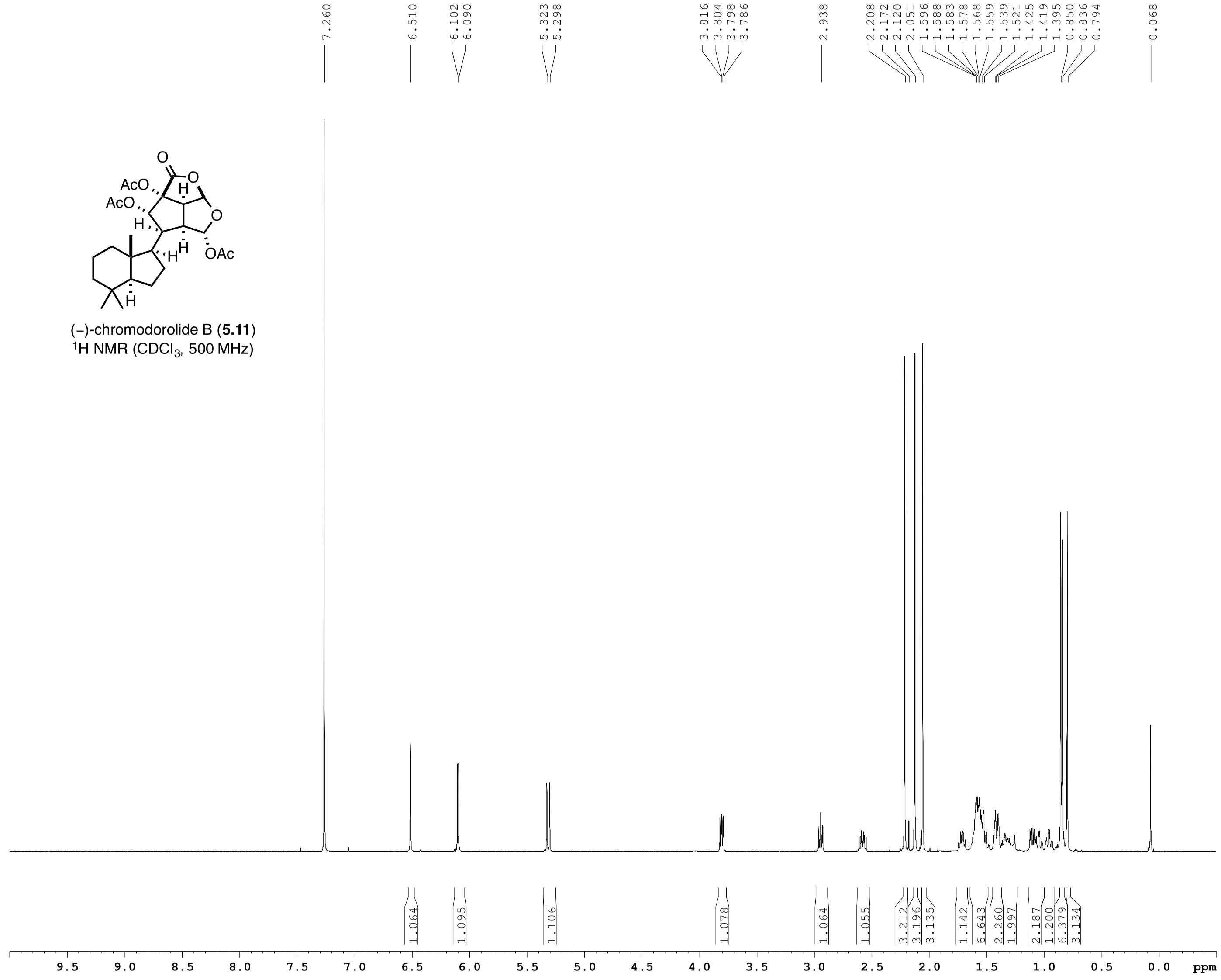
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 2.00
```

1H spectrum

(–)-chromodorolide B (**5.11**)
^{1}H NMR (CDCl$_3$, 500 MHz)



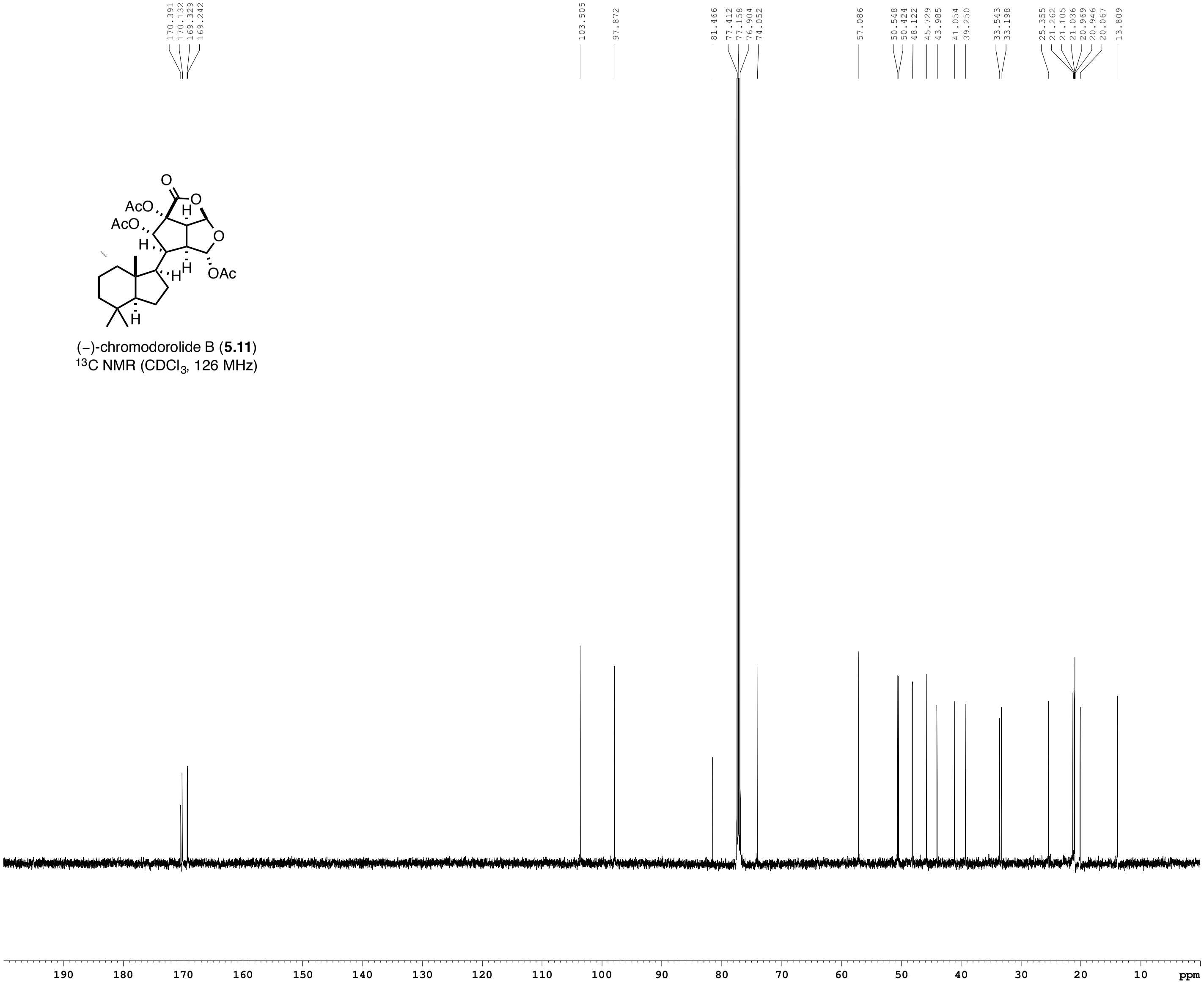
```
Current Data Parameters
NAME            DJT-V-272
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150907
Time                 9.43
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                    140
DS                      0
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                      8
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF           500.2200312 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

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



(–)-chromodorolide B (**5.11**)
^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-V-272
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20151012
Time               7.21
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                 2116
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2298.8
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

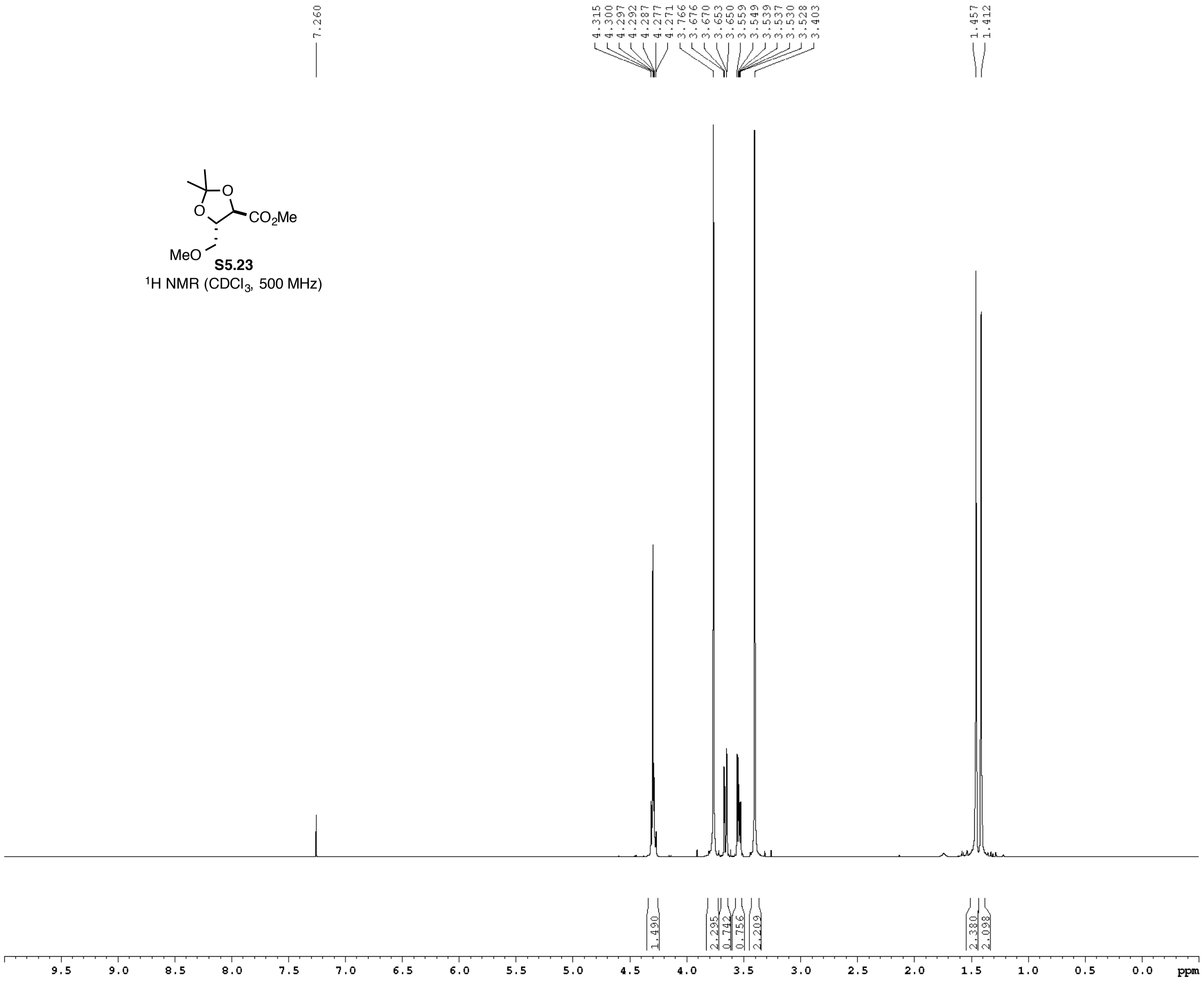
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



S5.23

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          DJT-VI-157
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160114
Time                8.30
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    28
DS                     0
SWH          8012.820 Hz
FIDRES       0.098043 Hz
AQ          5.0998273 sec
RG                     8
DW             62.400 usec
DE               6.00 usec
TE              298.0 K
D1         0.10000000 sec
MCREST   0 sec
MCWRK      0.01500000 sec

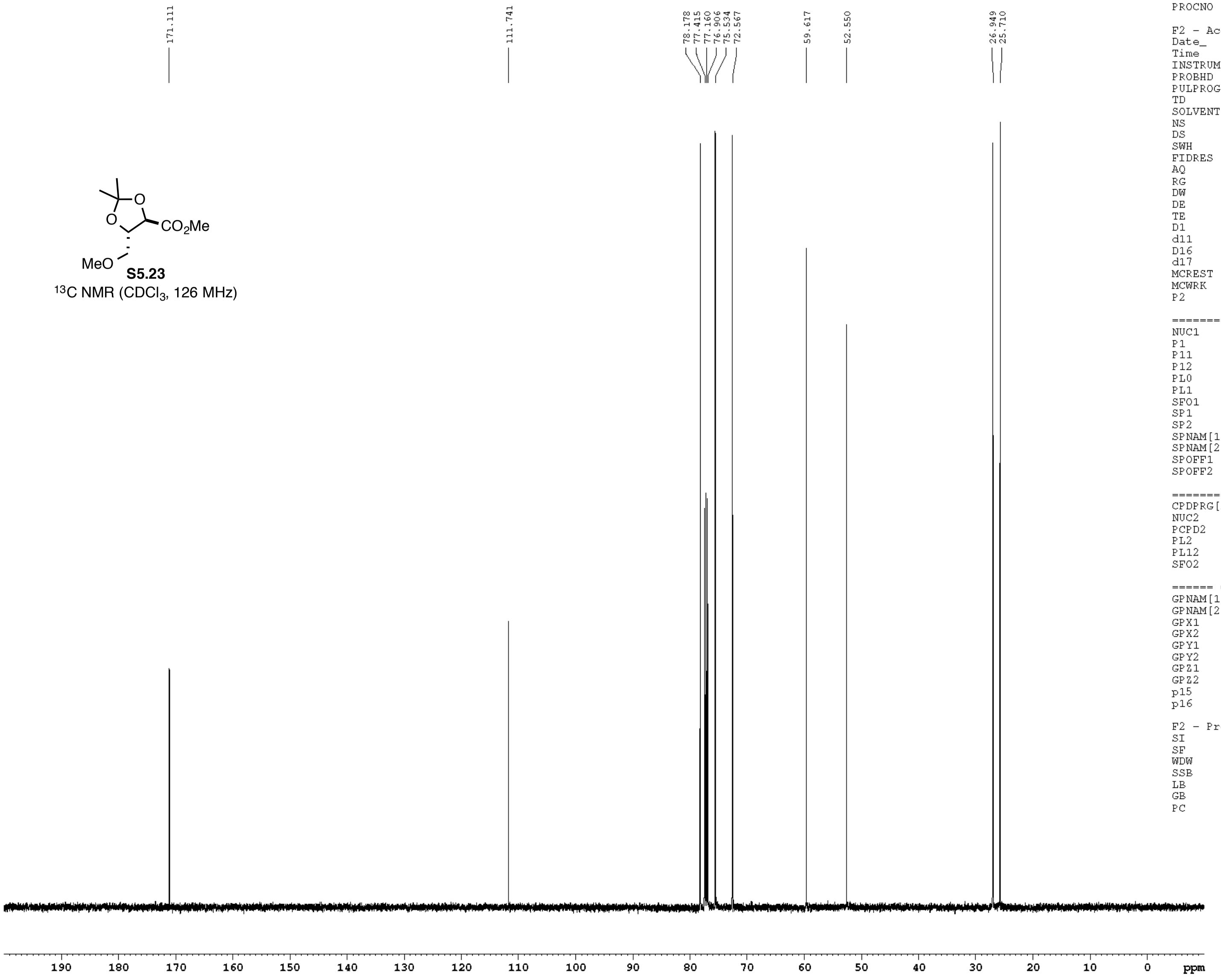
======== CHANNEL f1 =======
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200312 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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

S5.23

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME        DJT-VI-157
EXPNO                6
PROCNO               1

F2 - Acquisition Parameters
Date_         20160112
Time             15.12
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 111
DS                   0
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813440 sec
RG              5792.6
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST   0 sec
MCWRK       0.01500000 sec
P2               33.10 usec

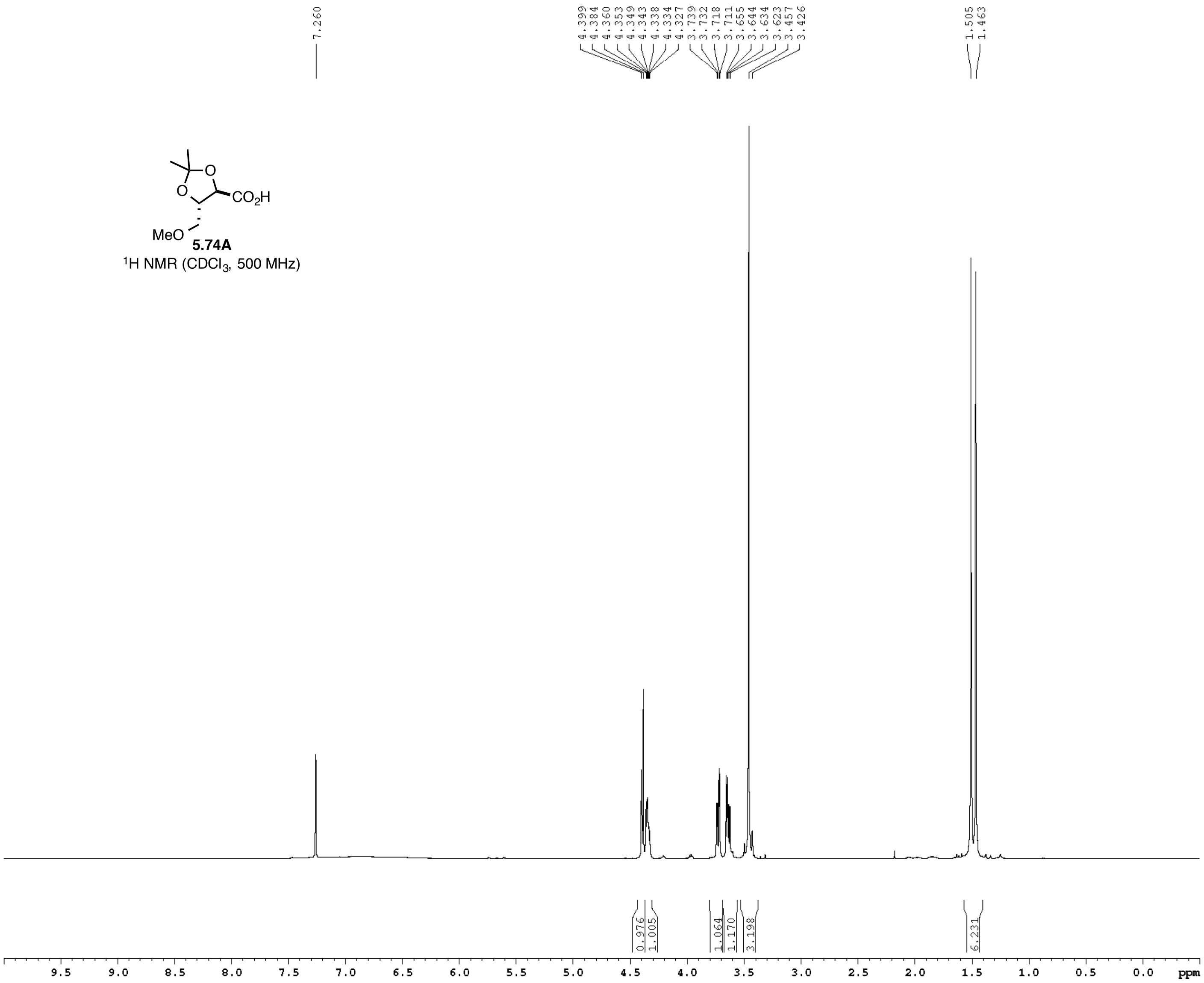
======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

F2 - Processing parameters
SI               65536
SF         125.7804140 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                2.00
```

1H spectrum



5.74A

^{1}H NMR (CDCl$_3$, 500 MHz)

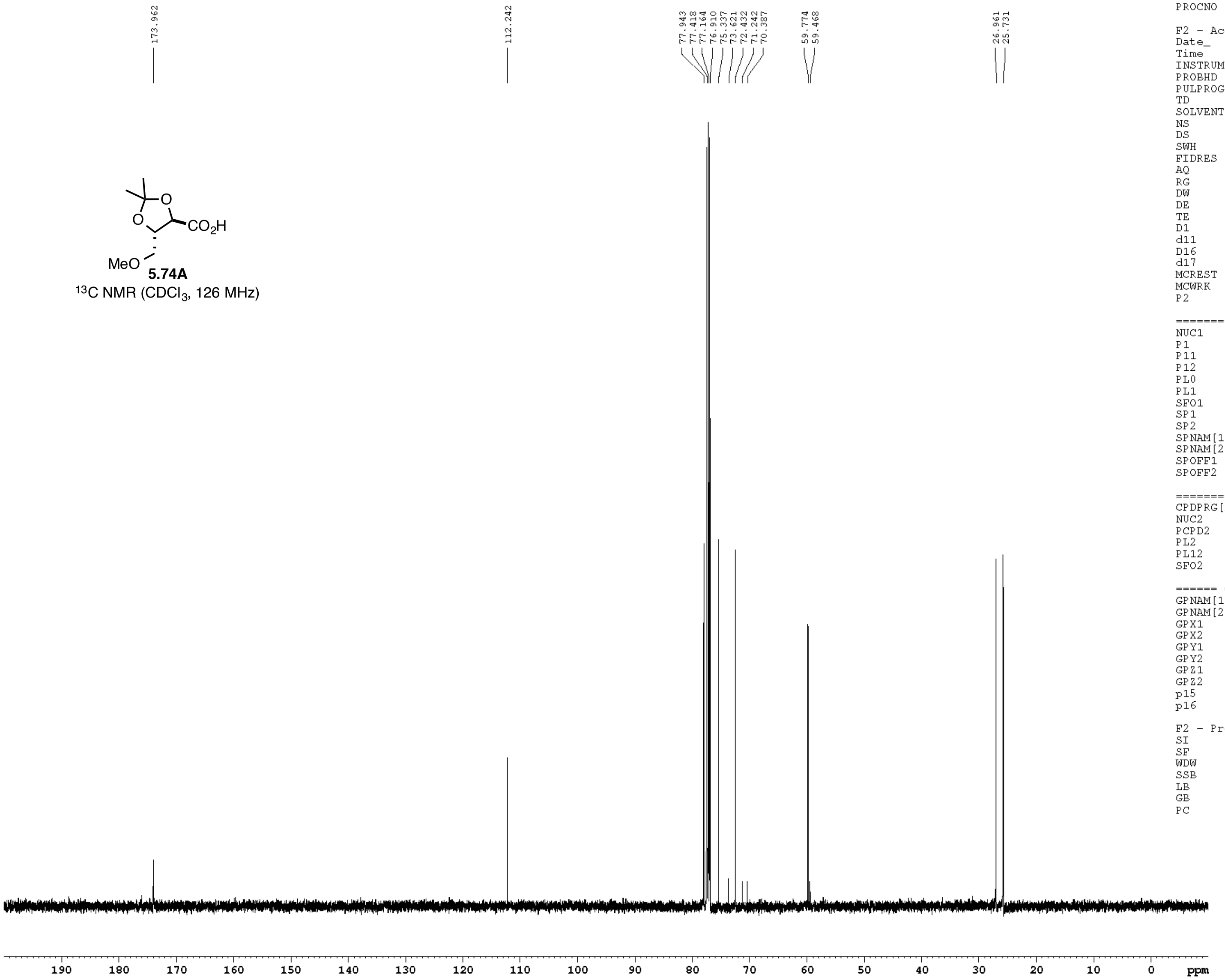
```
Current Data Parameters
NAME          DJT-VI-160
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160113
Time               11.31
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200301 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.74A

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-160
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160114
Time                8.20
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   328
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                4597.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

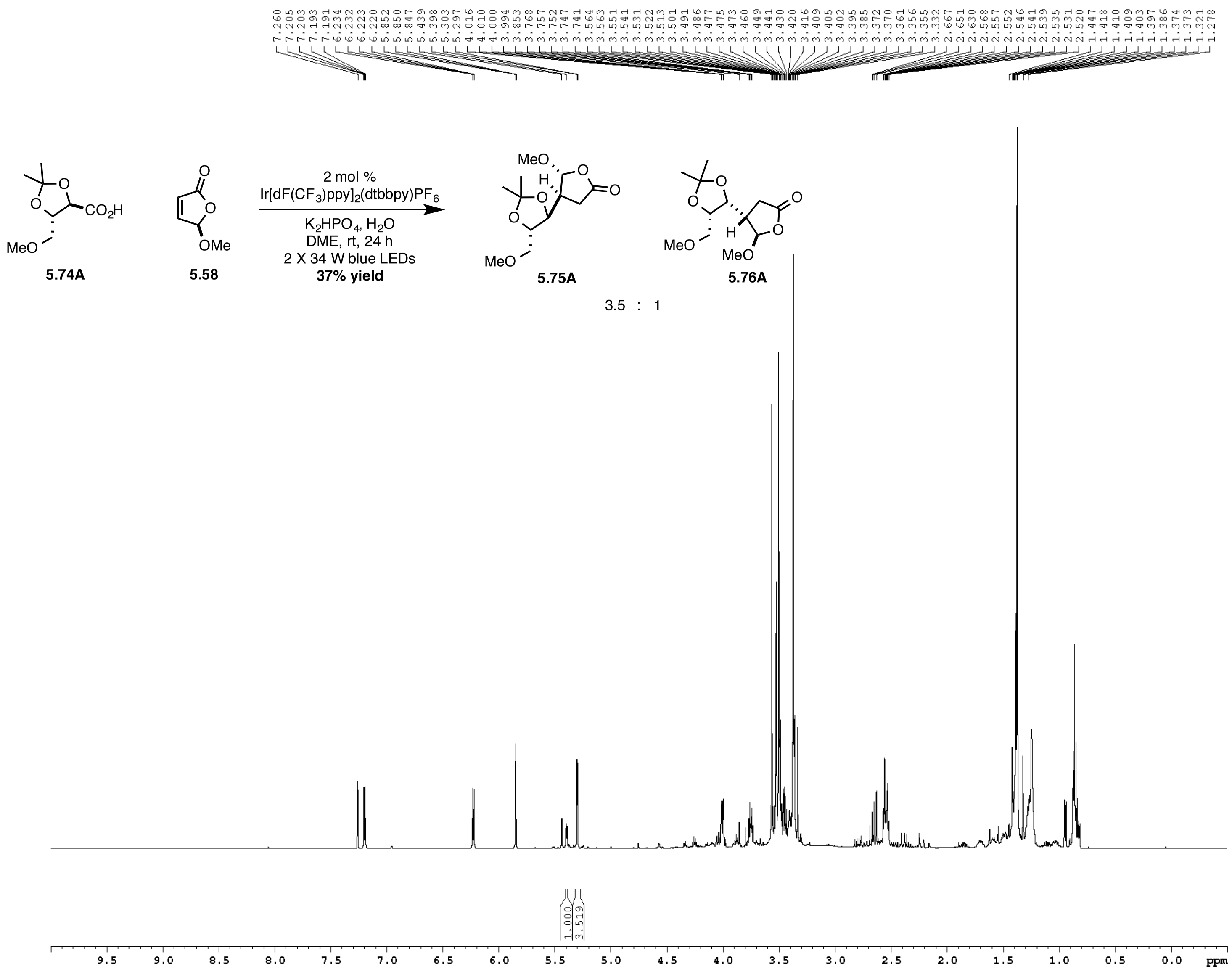
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804076 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



5.74A **5.58** **5.75A** **5.76A**

3.5 : 1

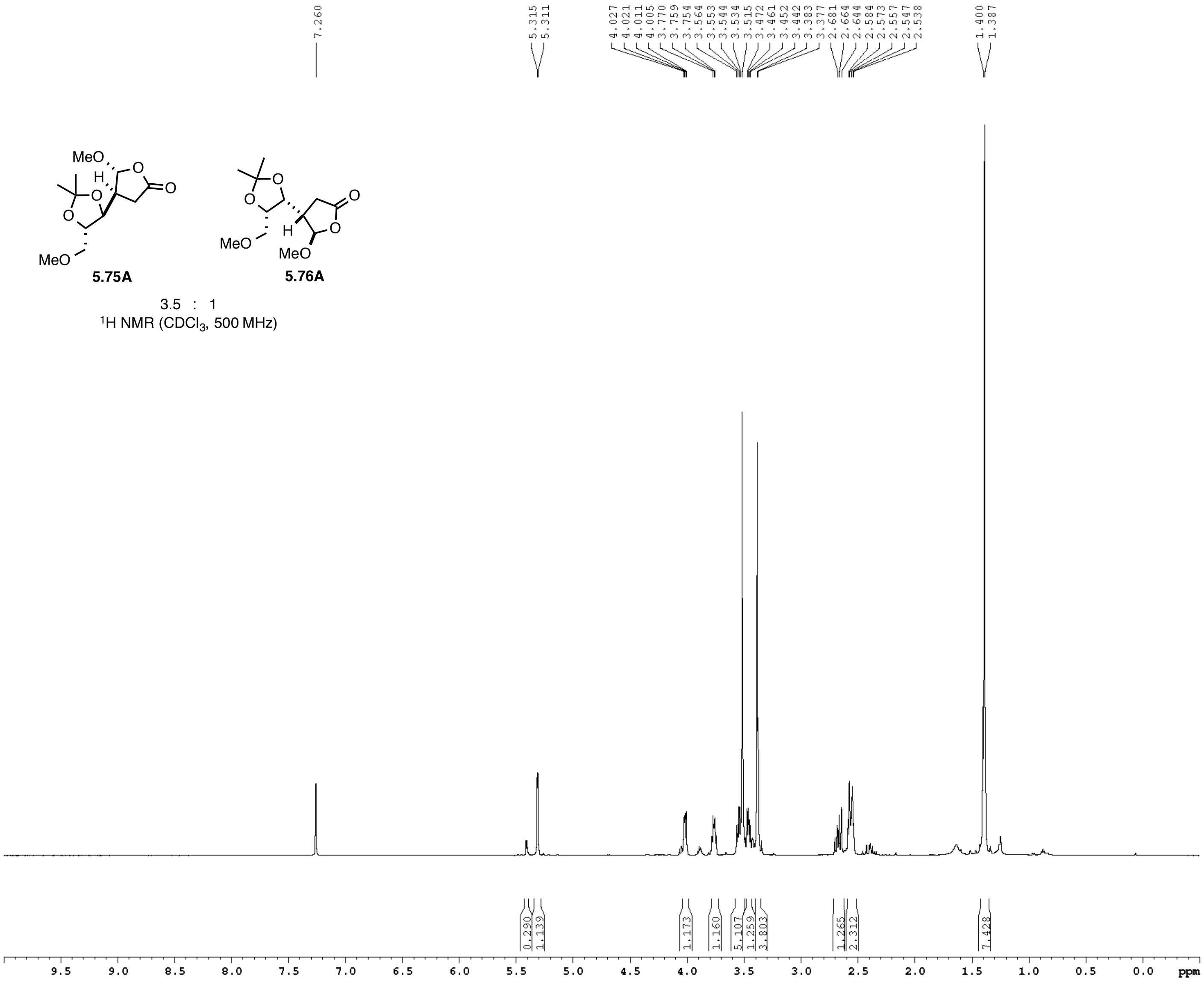
```
Current Data Parameters
NAME            DJT-VI-162
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160114
Time                  8.07
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                      20
DS                       0
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                     5.7
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200299 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

1H spectrum



5.75A **5.76A**

3.5 : 1

^{1}H NMR (CDCl$_3$, 500 MHz)

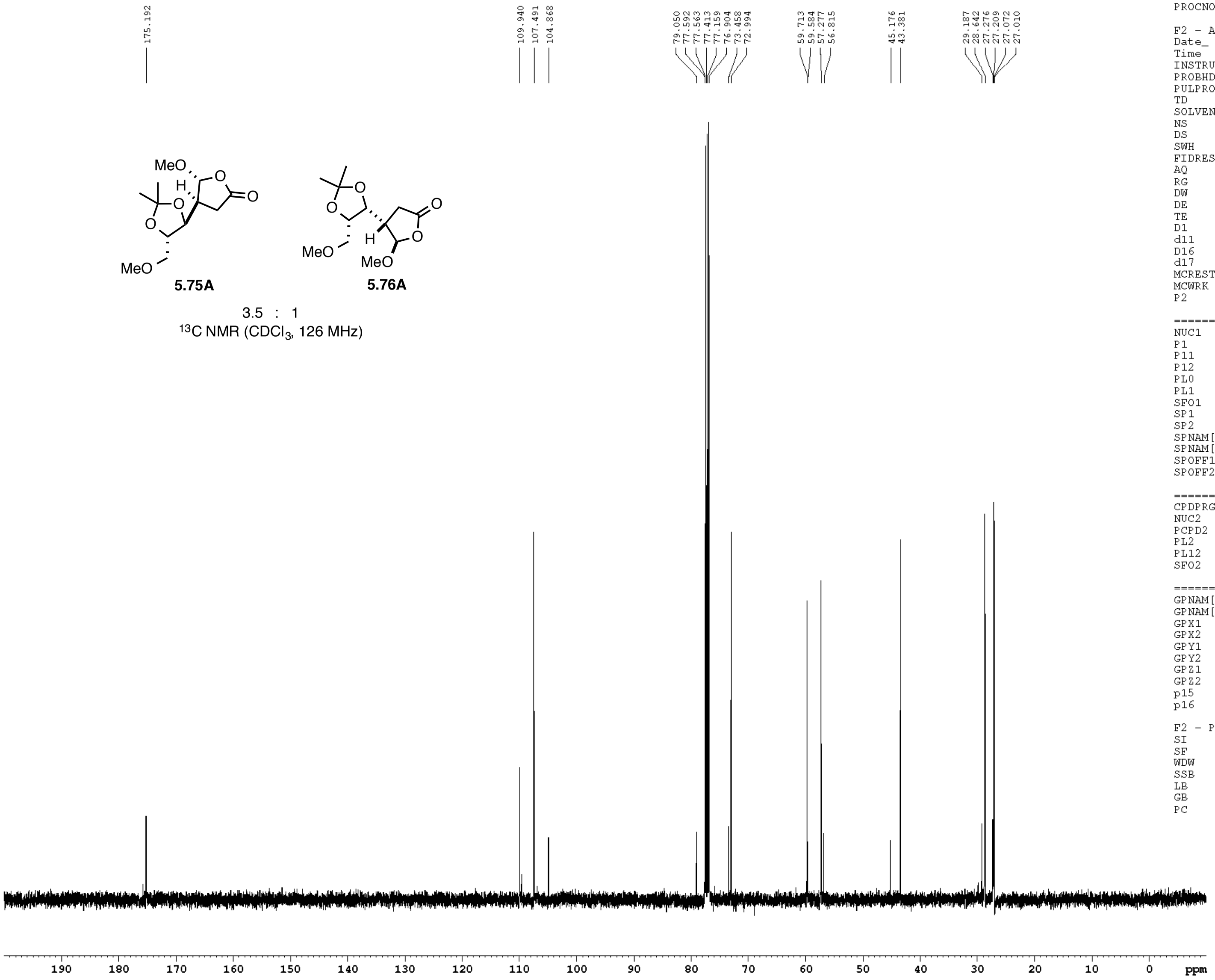
```
Current Data Parameters
NAME          DJT-VI-162
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160115
Time                9.03
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST  0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200301 MHz
WDW                   EM
SSB     0
LB                  0.30 Hz
GB      0
PC                  4.00
```

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



5.75A **5.76A**

3.5 : 1

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-162
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160115
Time                9.08
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   314
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

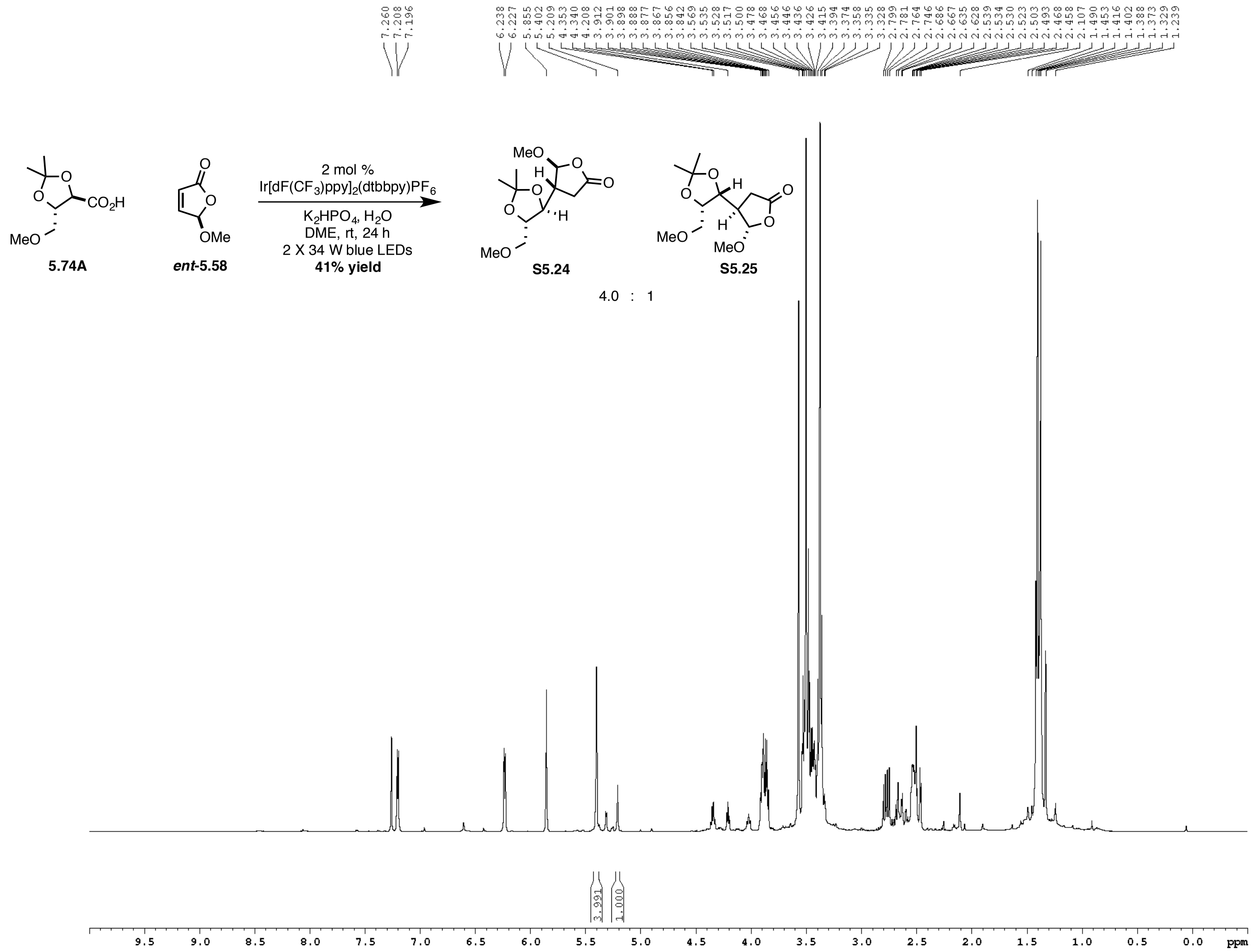
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



5.74A *ent*-**5.58**

2 mol %
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$
K$_2$HPO$_4$, H$_2$O
DME, rt, 24 h
2 X 34 W blue LEDs
41% yield

S5.24 **S5.25**

4.0 : 1

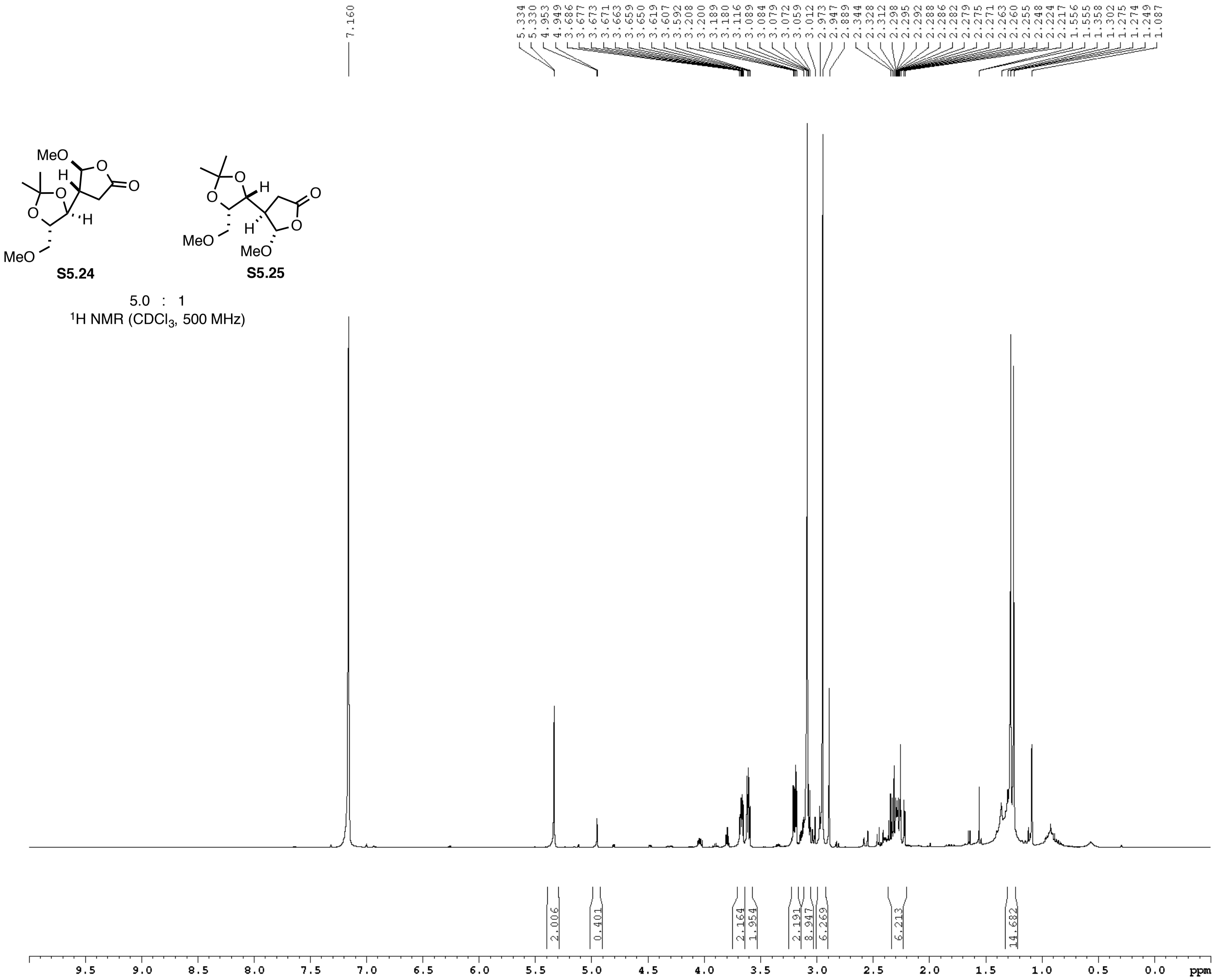
```
Current Data Parameters
NAME          DJT-VI-184
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160201
Time                8.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200322 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

1H spectrum


S5.24

S5.25

5.0 : 1
^{1}H NMR (CDCl$_3$, 500 MHz)

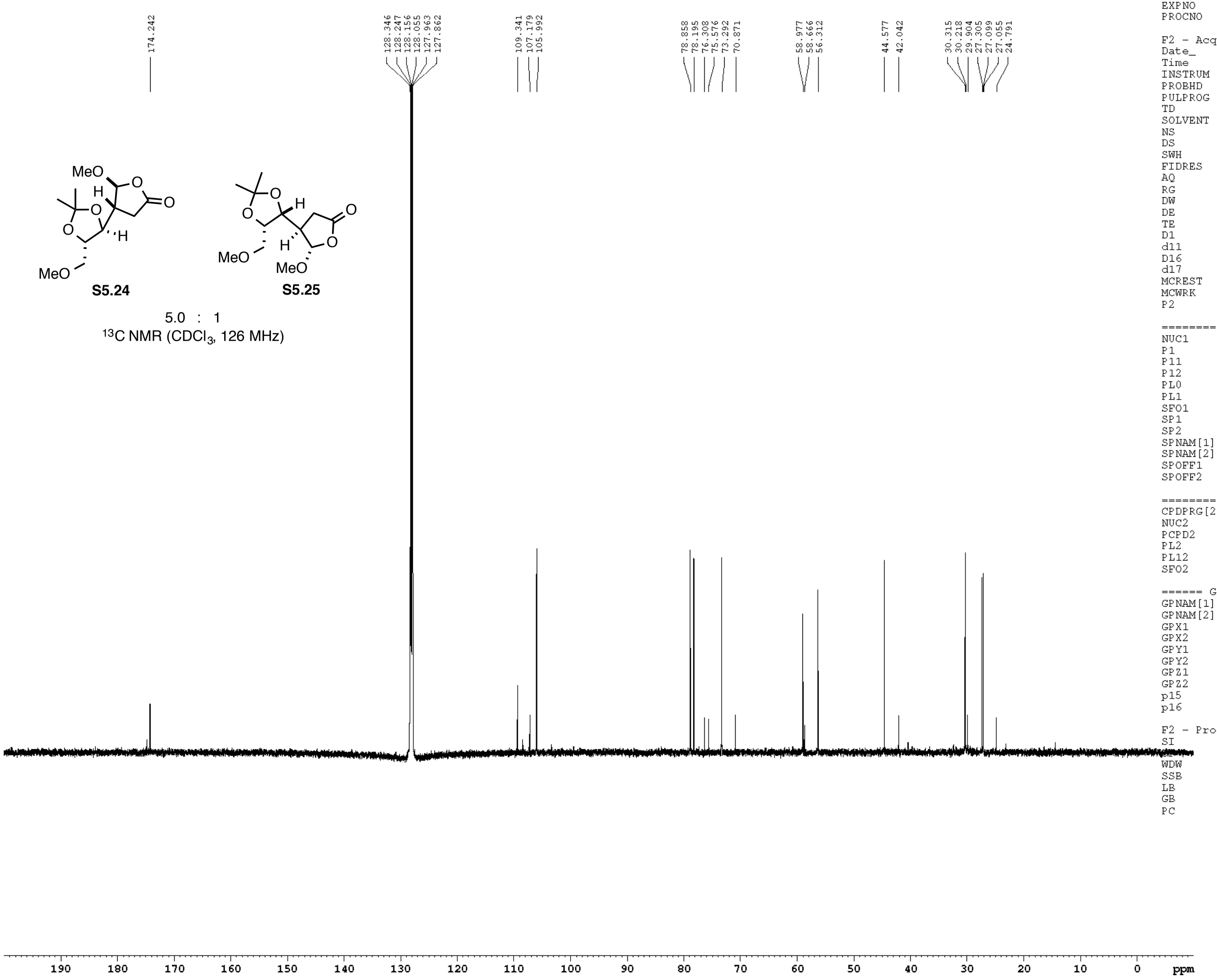
```
Current Data Parameters
NAME          DJT-VI-184
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160202
Time                9.16
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200007 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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


S5.24 S5.25

5.0 : 1

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-184
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160202
Time                9.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   401
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  4096
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

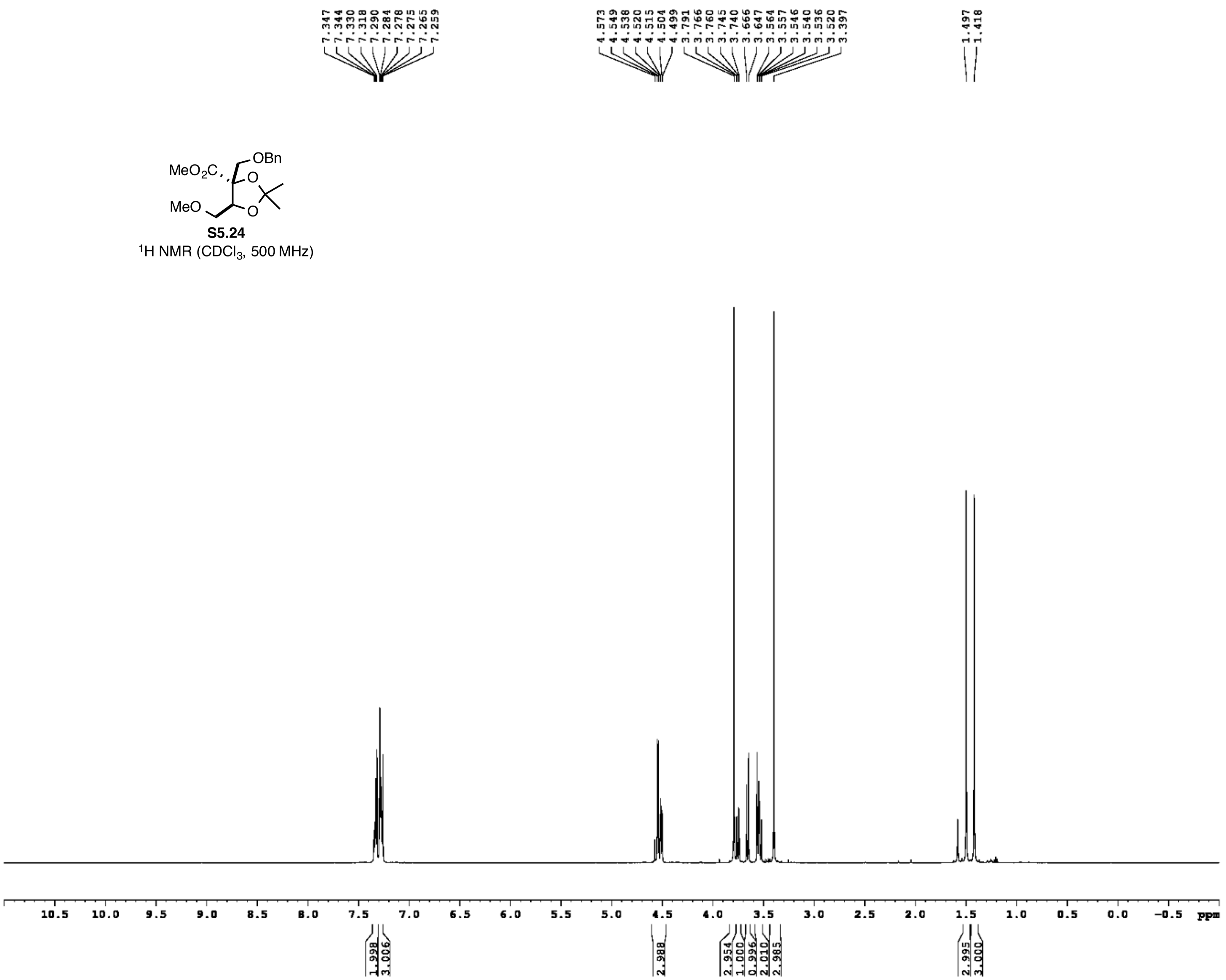
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803755 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

YS-IV-39



S5.24

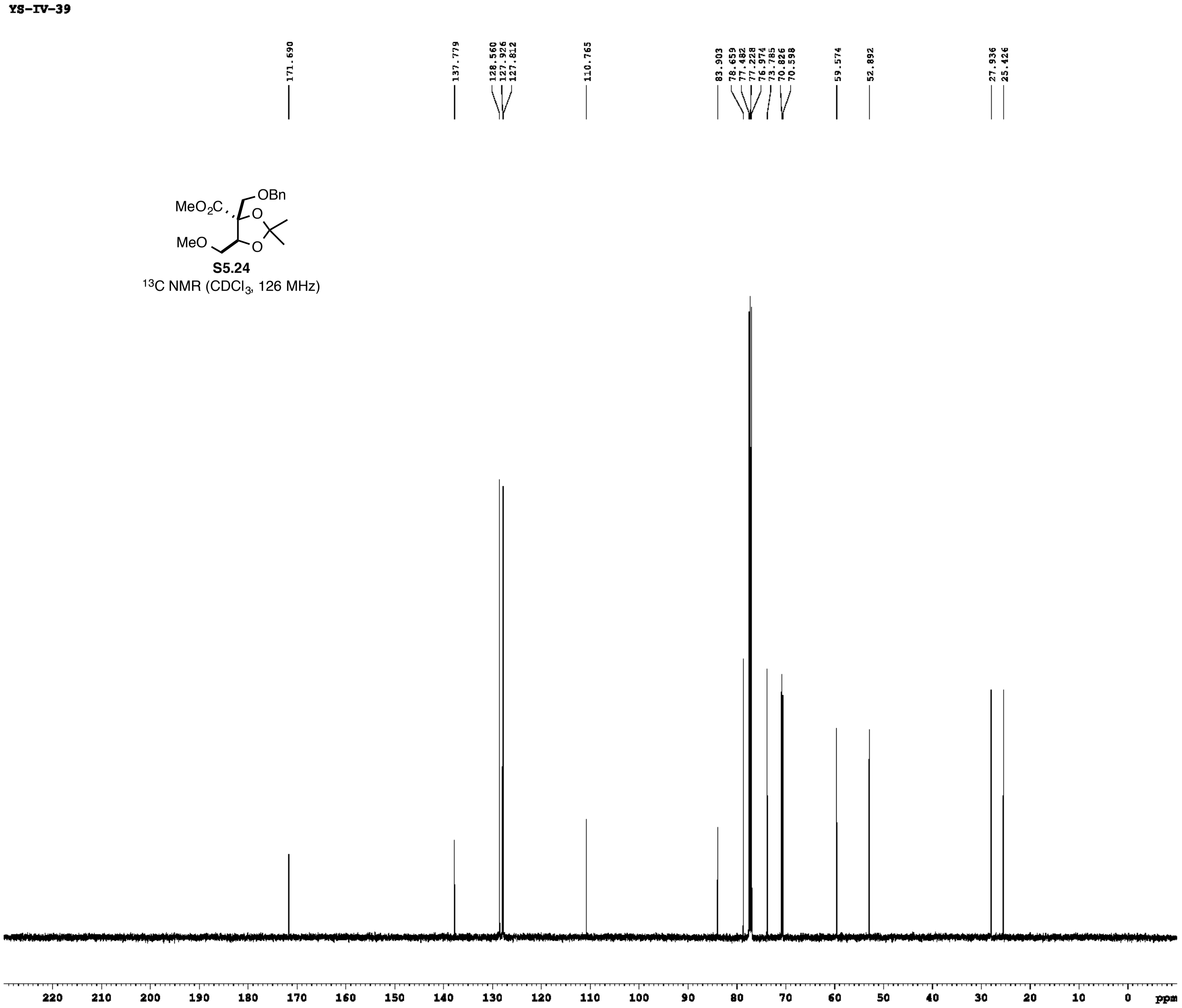
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME             YS-IV-39
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160114
Time                 9.08
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                    6.3
DW                 62.400 use
DE                   6.00 use
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 use
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200309 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```



S5.24

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME              YS-IV-39
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160114
Time                9.13
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   568
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                4597.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

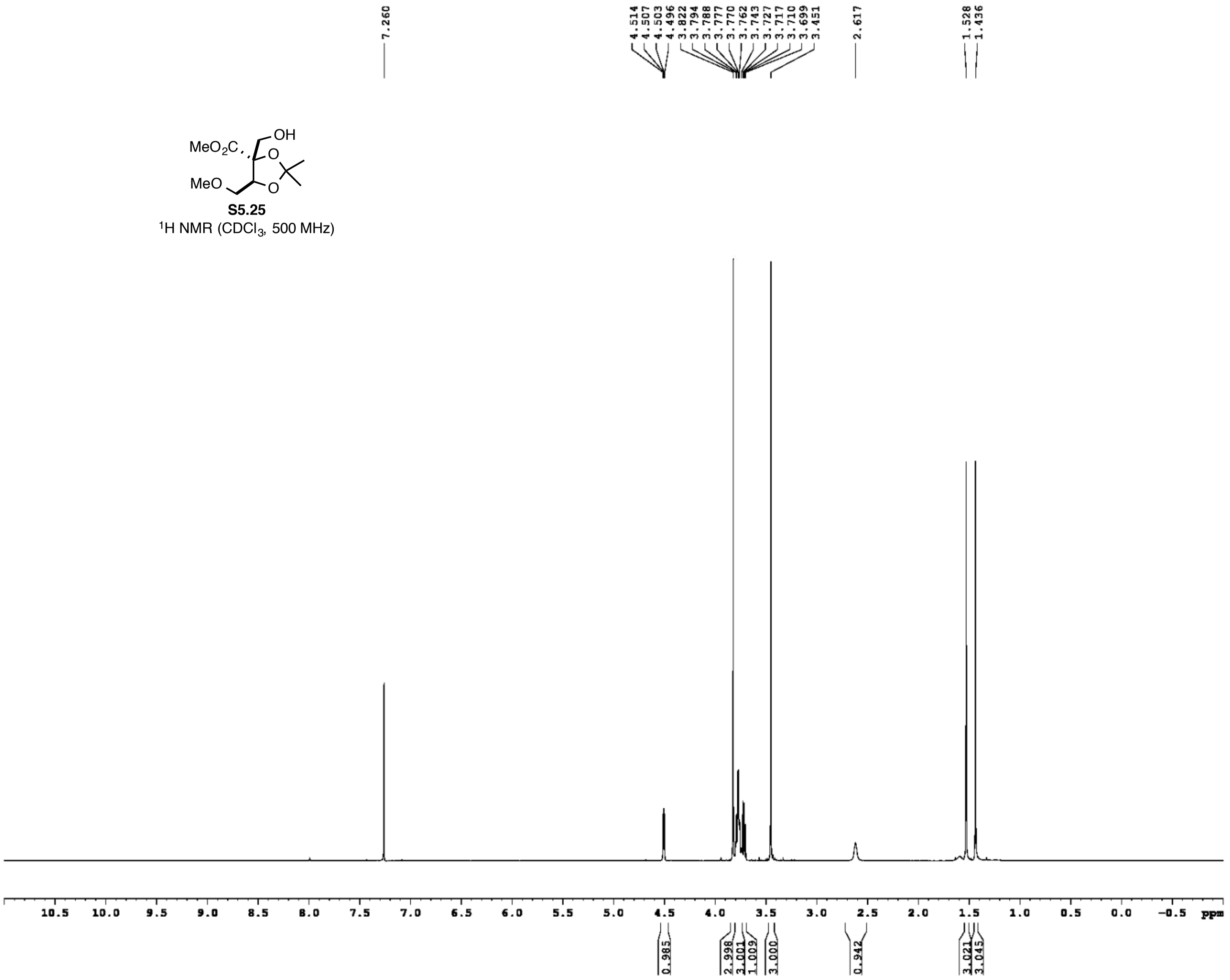
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804000 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-41



S5.25

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME            YS-IV-41
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160116
Time               10.21
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                  1440
DW                52.000 use
DE                 14.54 use
TE                 293.1 K
D1            0.10000000 sec
TD0                    1

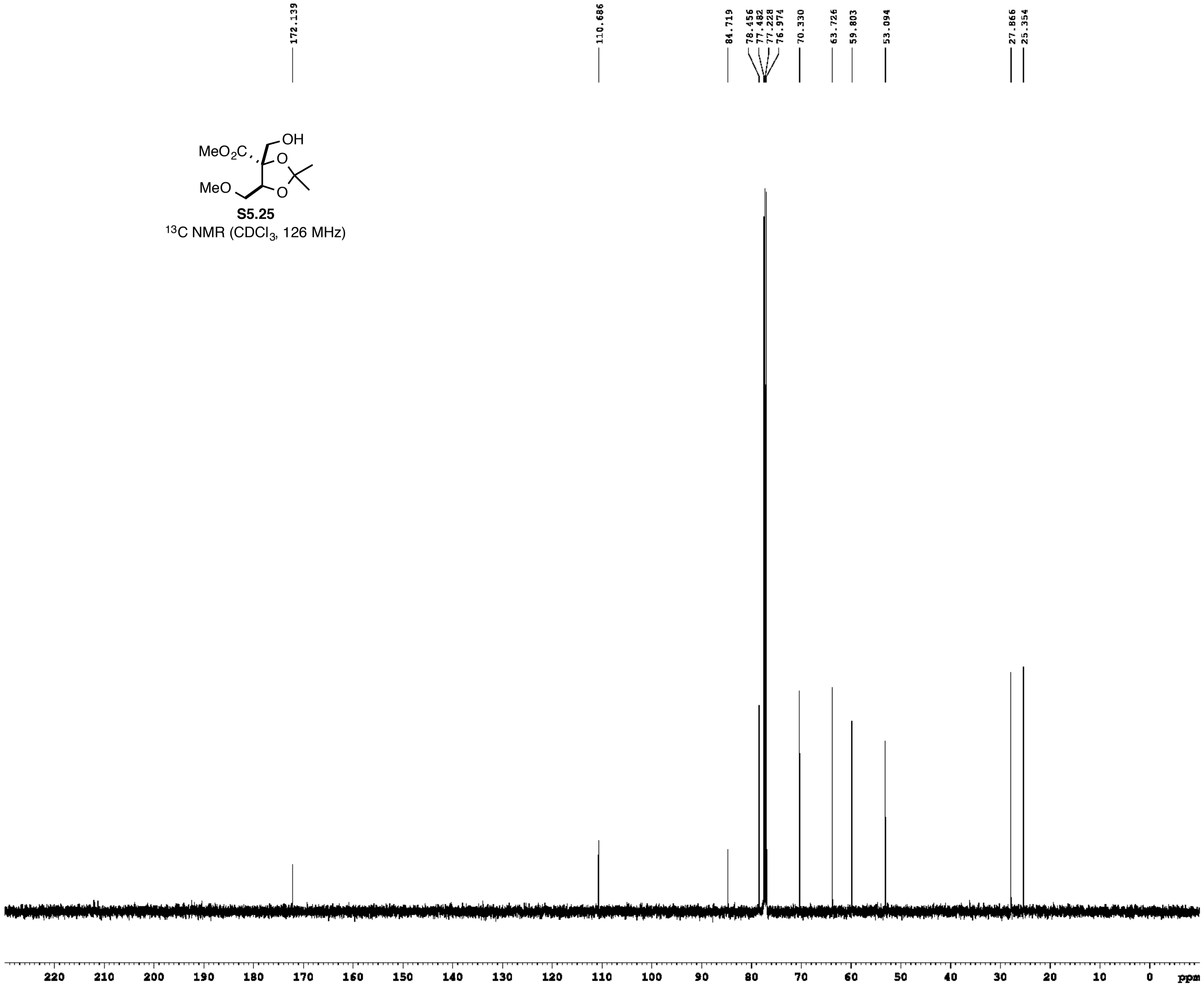
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 use
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300354 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

YS-IV-41

S5.25

^{13}C NMR ($CDCl_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-41
EXPNO                  2
PROCNO                 1

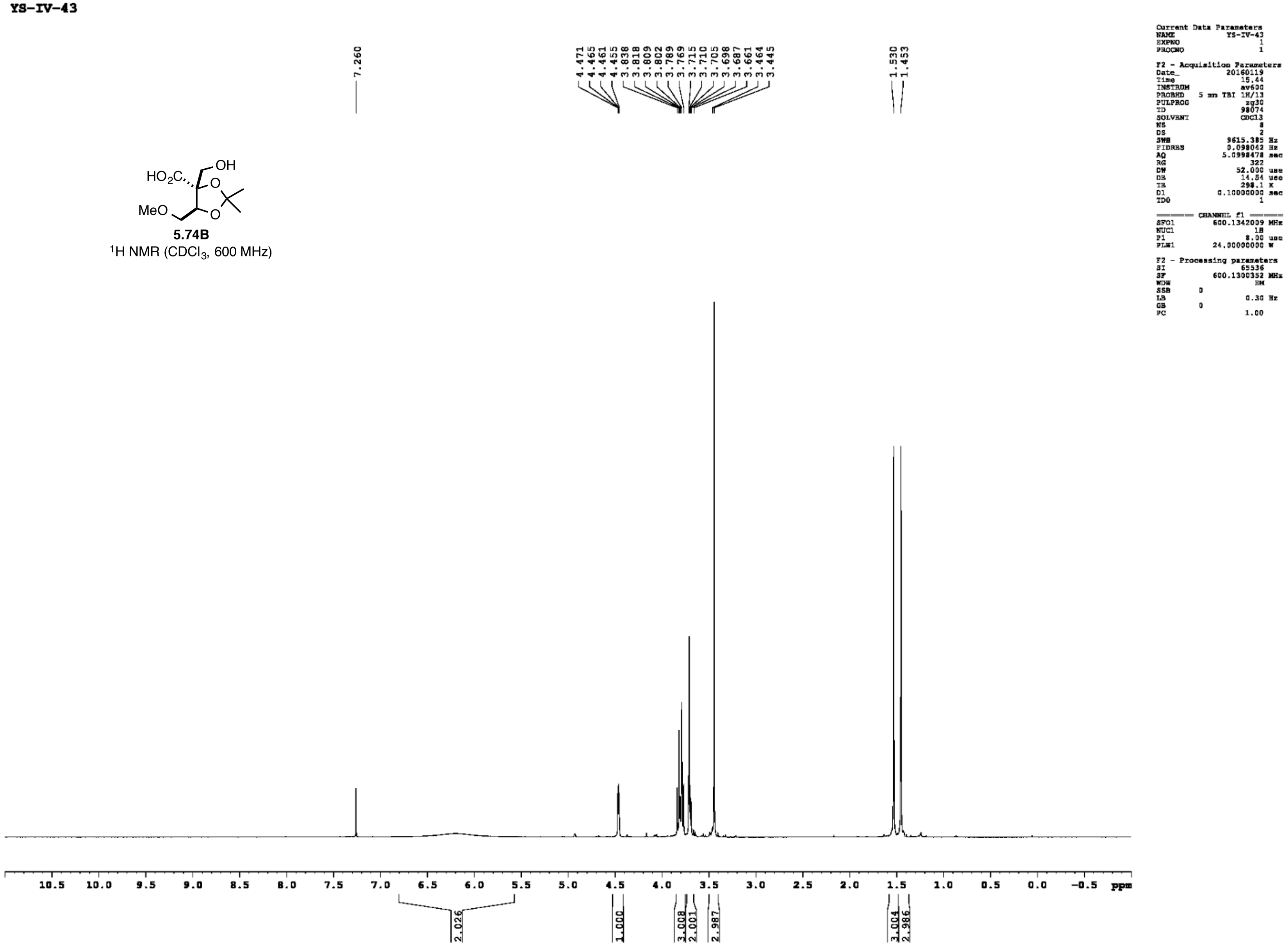
F2 - Acquisition Parameters
Date_           20160116
Time               10.28
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

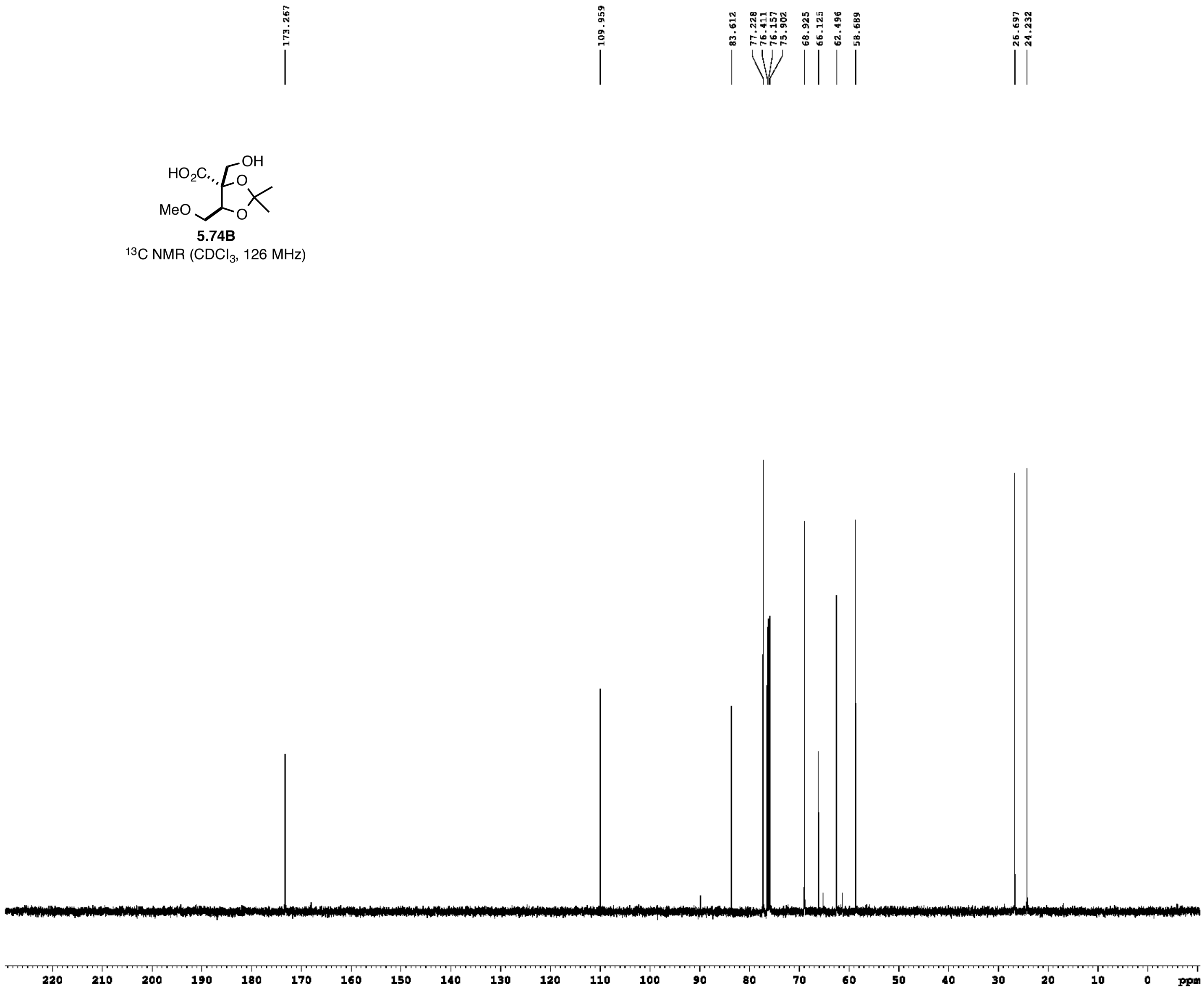
F2 - Processing parameters
SI                 65536
SF           125.7803988 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```



5.74B

^{1}H NMR (CDCl$_3$, 600 MHz)

YS-IV-43



5.74B

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME             YS-IV-43
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160119
Time                16.58
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    168
DS                      2
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   3251
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

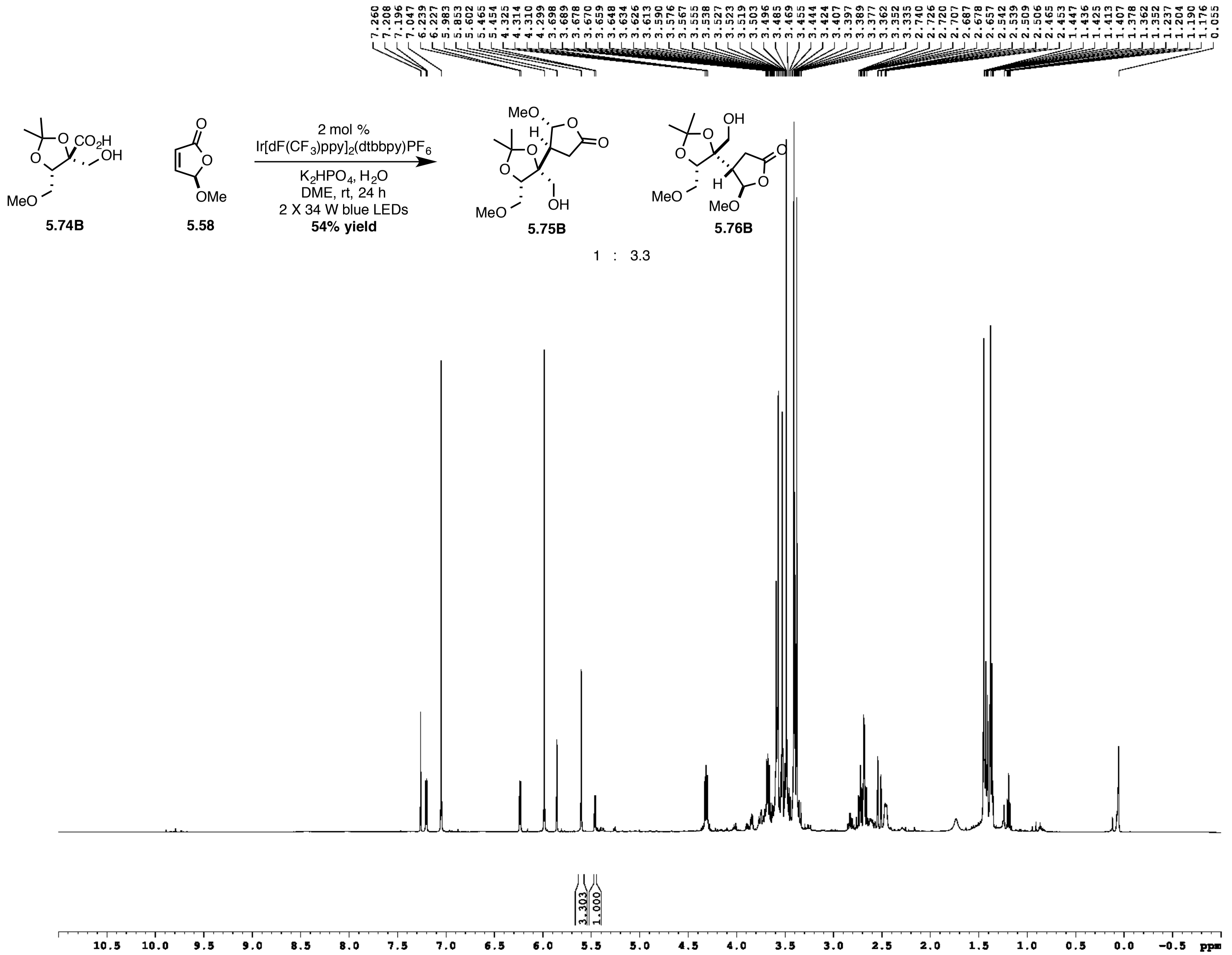
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7805370 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   2.00
```

YS-IV-51



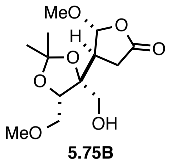
```
Current Data Parameters
NAME          YS-IV-51
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20160121
Time             10.14
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG                   8
DW              62.400 usec
DE                6.00 usec
TE               298.0 K
D1          0.10000000 sec
MCREST    0 sec
MCWRK       0.01500000 sec

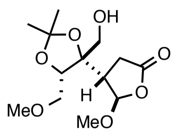
======== CHANNEL f1 ========
NUC1                1H
P1                7.50 usec
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200312 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                4.00
```

YS-IV-51



5.75B



5.76B

1 : 7

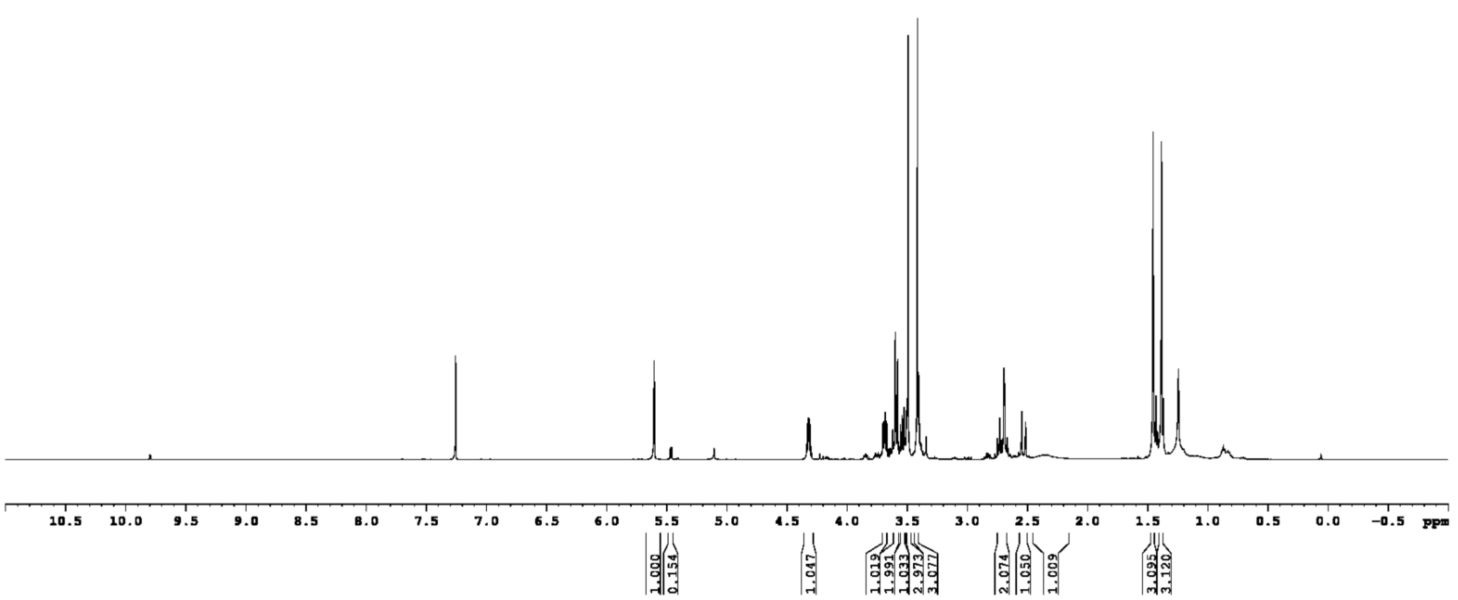
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME              YS-IV-51
EXPNO                   11
PROCNO                   1

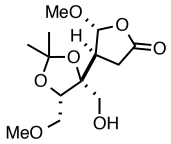
F2 - Acquisition Parameters
Date_             20160202
Time                  8.41
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                     5.7
DW                  62.400 use
DE                    6.00 use
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 use
PL1                   1.60 dB
SFO1           500.2235015 MHz

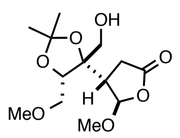
F2 - Processing parameters
SI                   65536
SF             500.2200339 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```



YS-IV-51



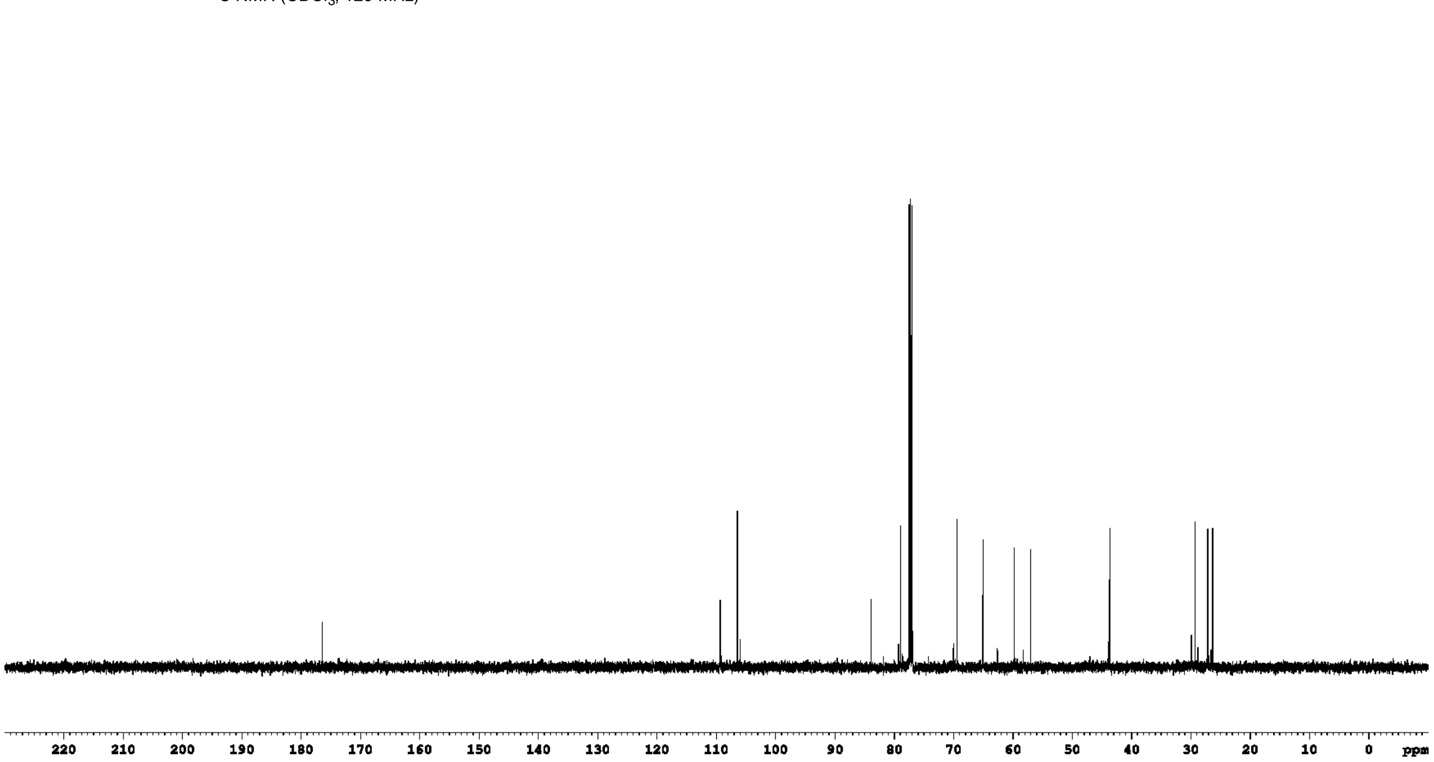
5.75B



5.76B

1 : 7

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-51
EXPNO                 12
PROCNO                 1

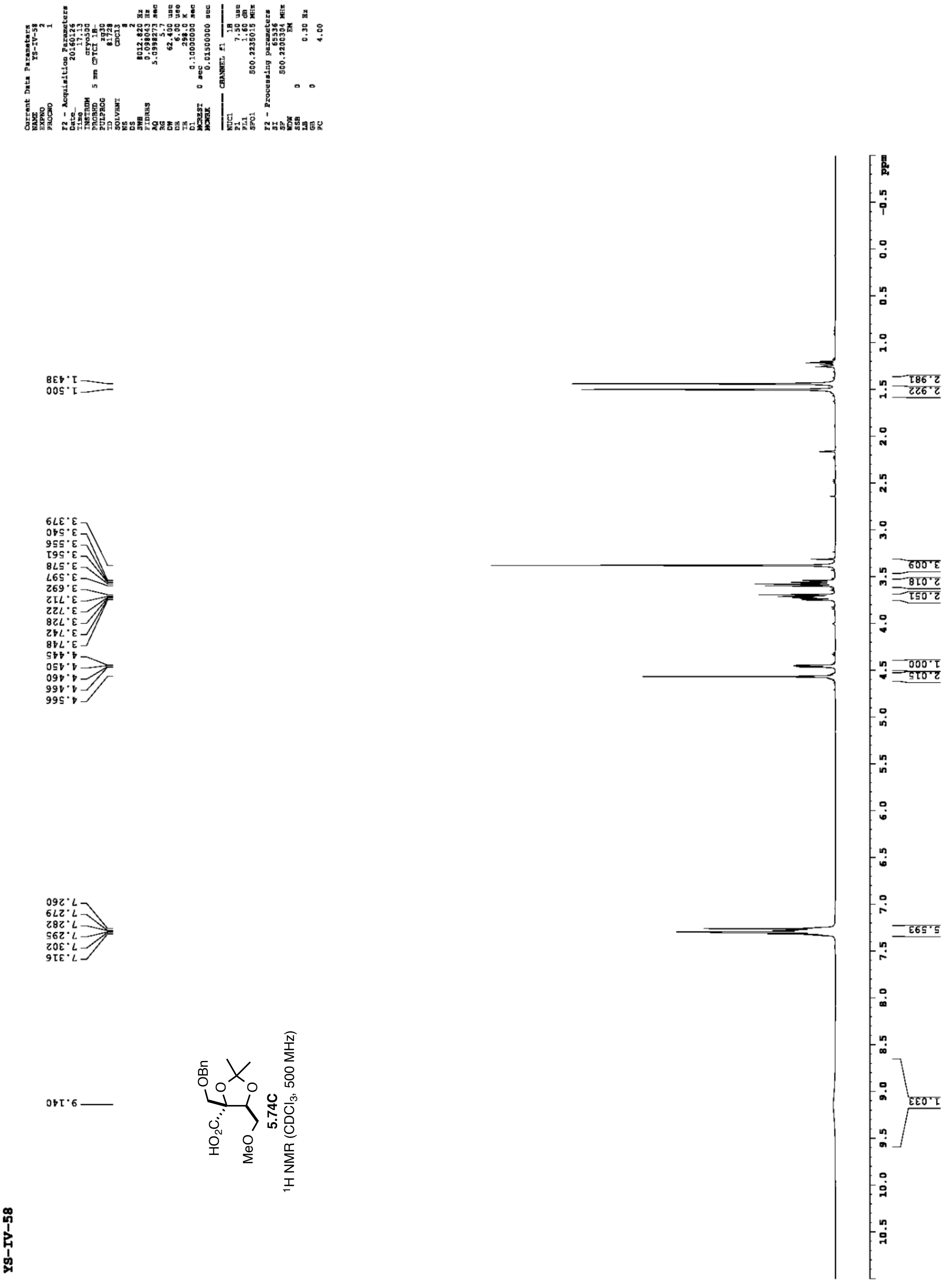
F2 - Acquisition Parameters
Date_           20160202
Time                8.44
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   112
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804004 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



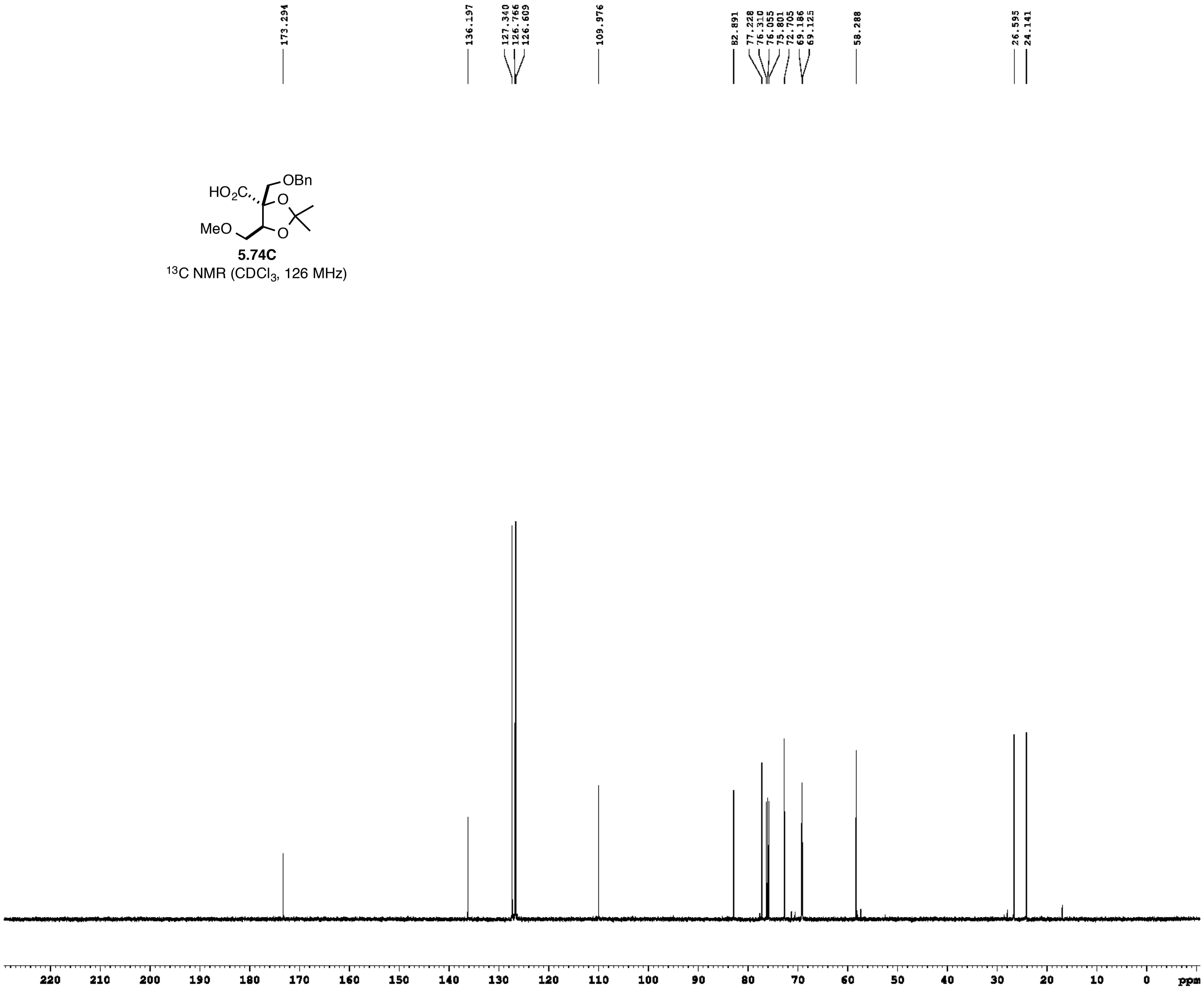
5.74C

^{1}H NMR (CDCl$_3$, 500 MHz)

YS-IV-58

5.74C

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-58
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160126
Time               17.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                2580.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.50000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

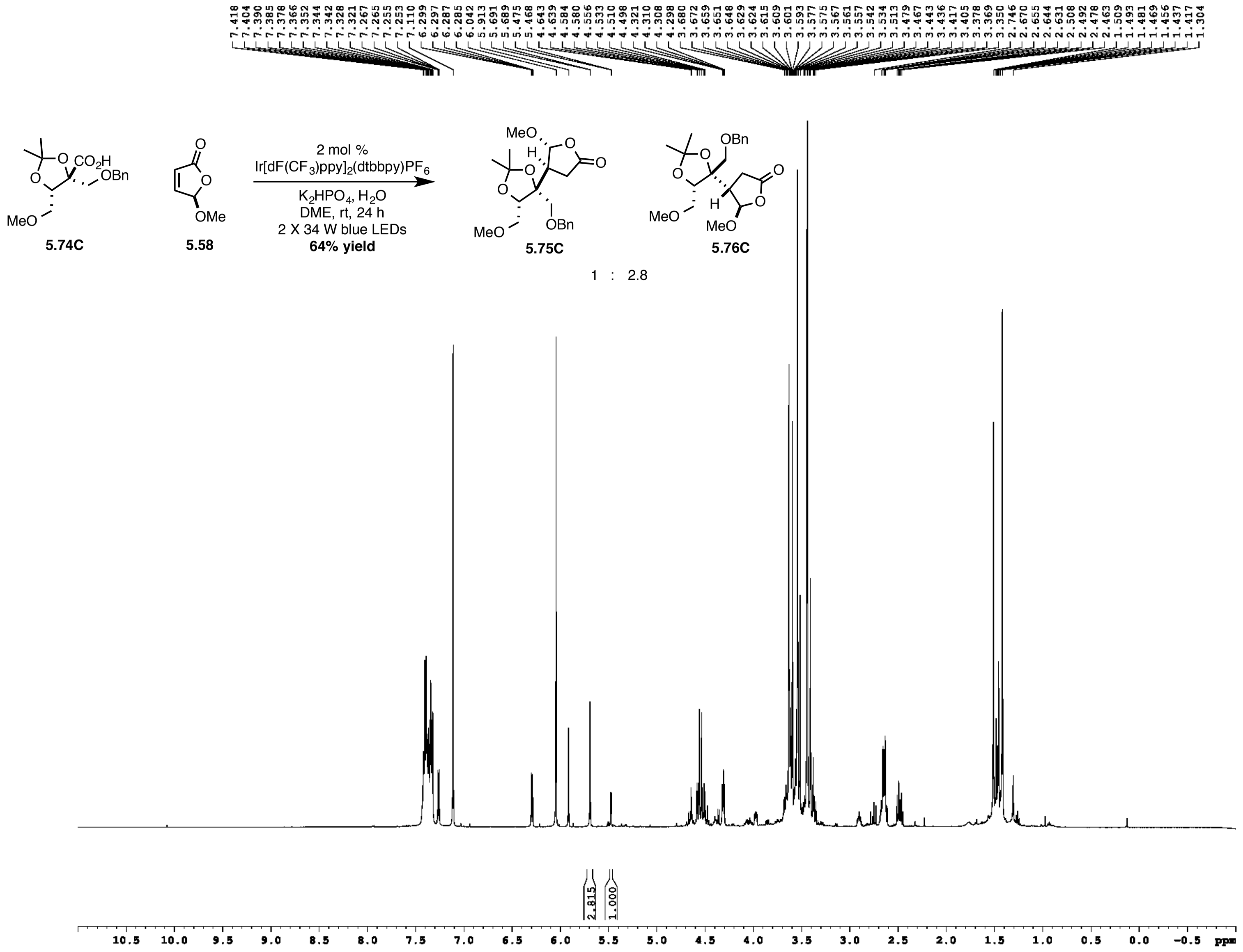
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7805602 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-61

1 : 2.8



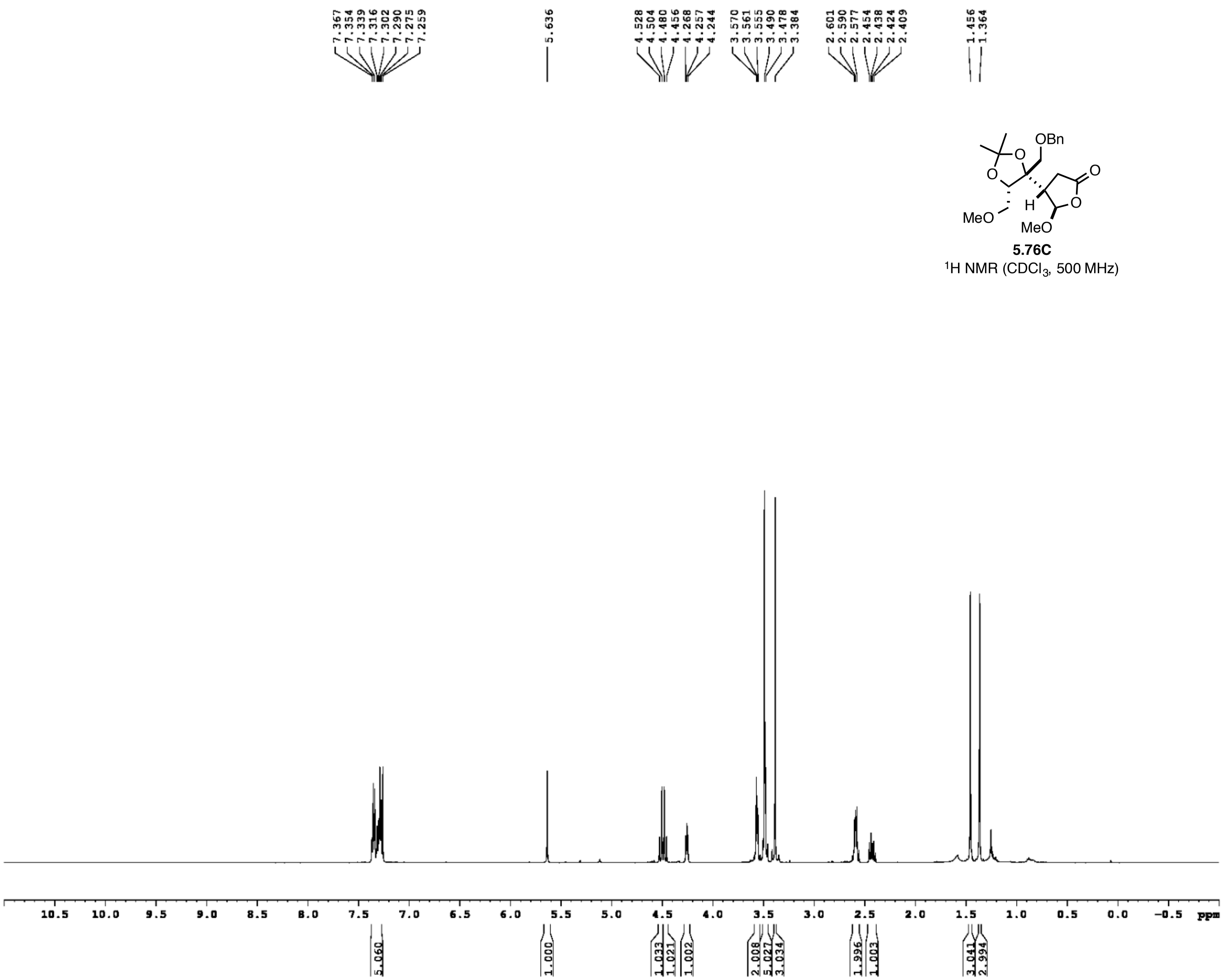
```
Current Data Parameters
NAME             YS-IV-61
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160127
Time                12.55
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                    6.3
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-IV-61



5.76C

^{1}H NMR ($CDCl_3$, 500 MHz)

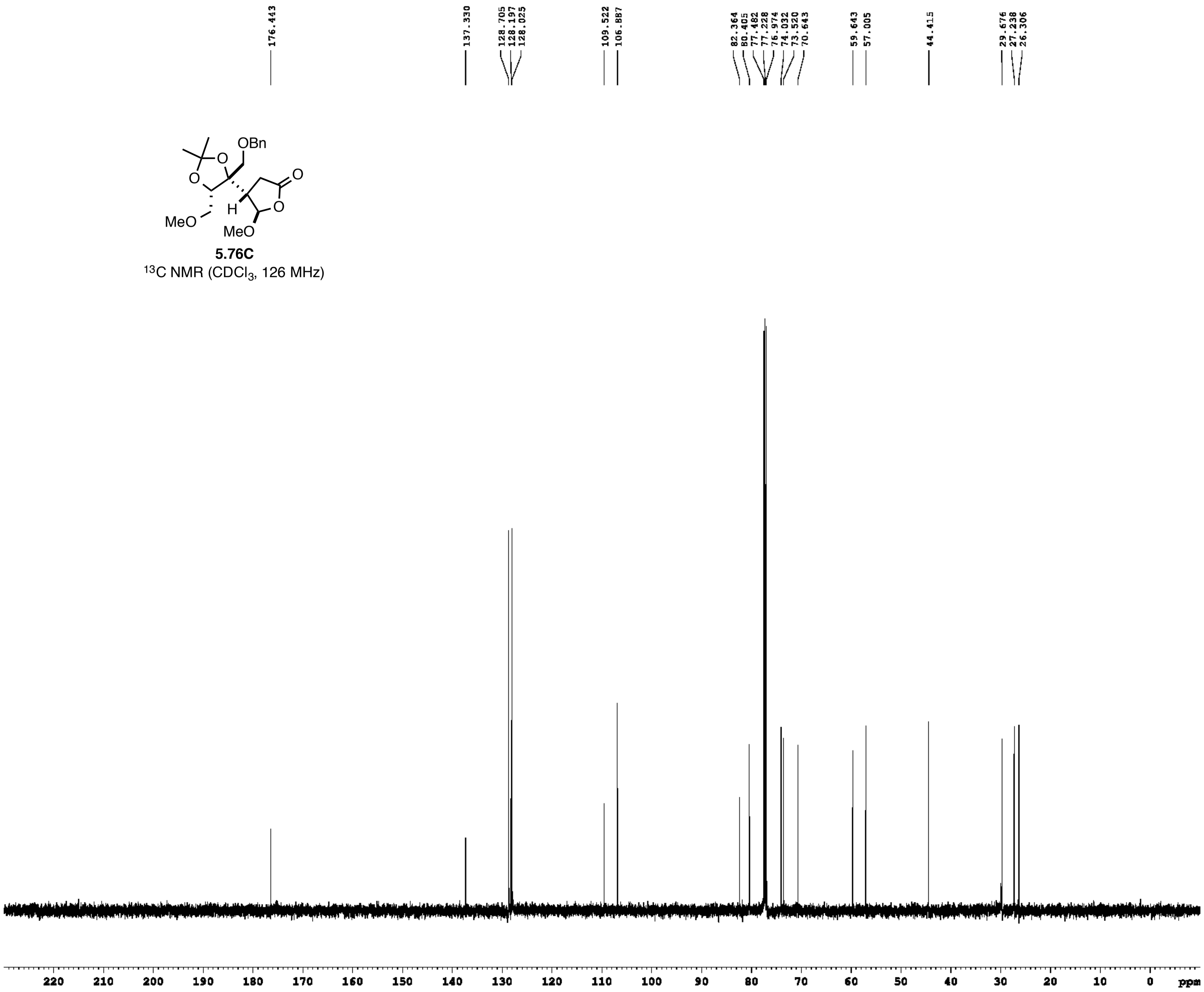
```
Current Data Parameters
NAME              YS-IV-61
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160127
Time                 17.06
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                       9
DW                  62.400 use
DE                    6.00 use
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 use
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200311 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-IV-61



5.76C

^{13}C NMR ($CDCl_3$, 126 MHz)

```
Current Data Parameters
NAME             YS-IV-61
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160127
Time                17.07
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    200
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

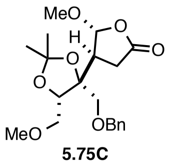
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]      Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

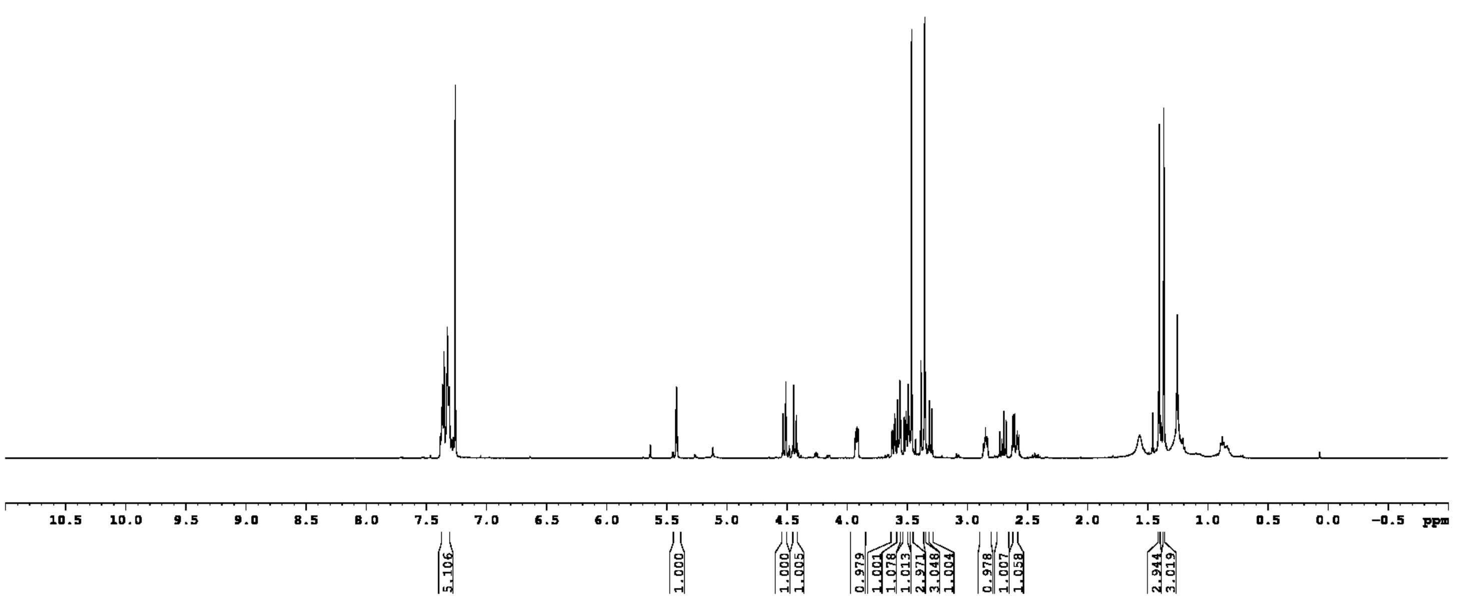
F2 - Processing parameters
SI                  65536
SF            125.7803997 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

YS-IV-61



5.75C

^{1}H NMR ($CDCl_3$, 500 MHz)



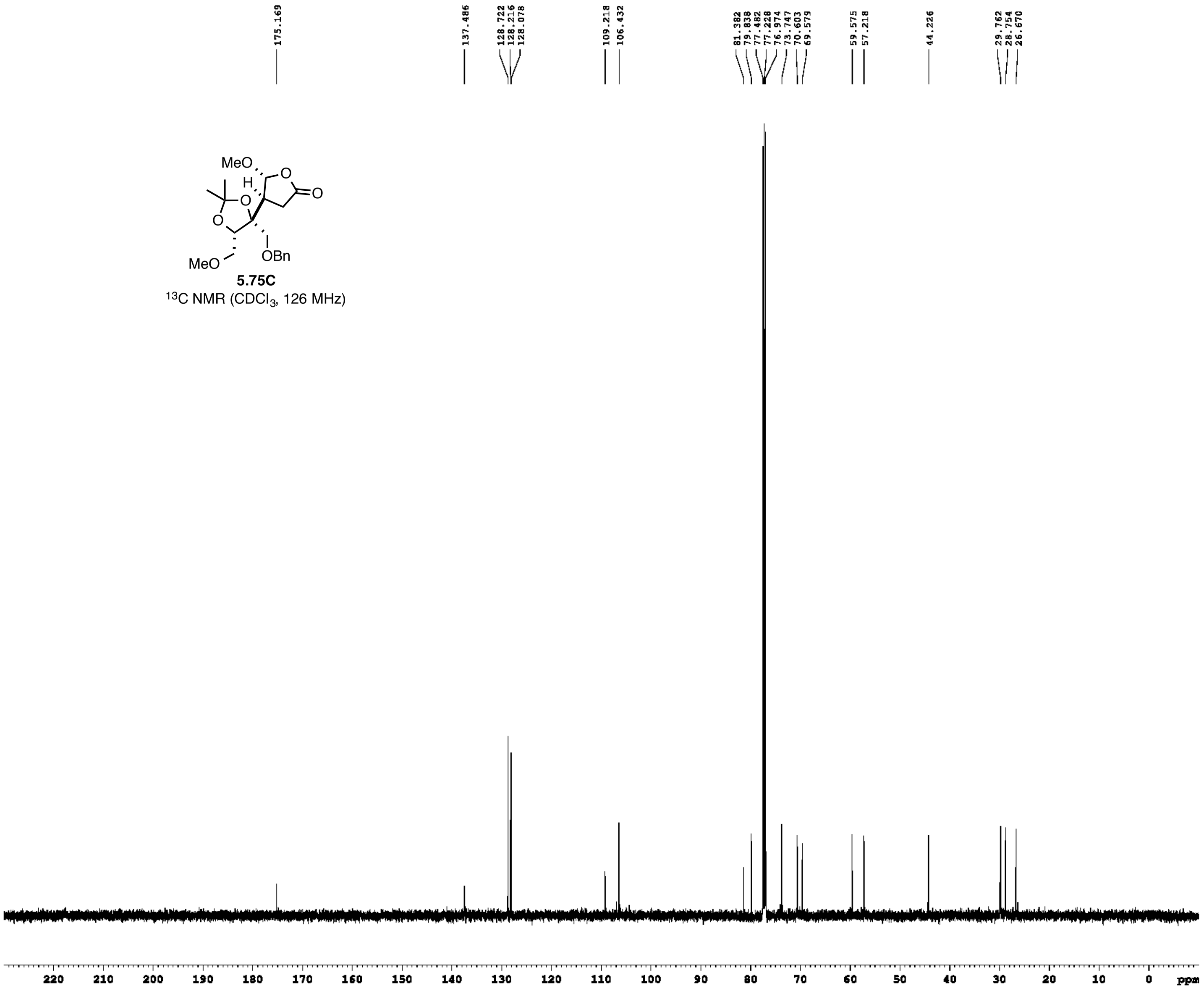
```
Current Data Parameters
NAME             YS-IV-61
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160127
Time                17.24
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                   10.1
DW                 62.400 use
DE                   6.00 use
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 use
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200311 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-IV-61



5.75C

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          YS-IV-61
EXPNO                8
PROCNO               1

F2 - Acquisition Parameters
Date_         20160127
Time             17.26
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD               65536
SOLVENT          CDCl3
NS                 584
DS                   1
SWH          30303.031 Hz
FIDRES        0.462388 Hz
AQ           1.0813440 sec
RG              5160.6
DW              16.500 usec
DE                6.00 usec
TE               298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d17         0.00019600 sec
MCREST   0 sec
MCWRK       0.01500000 sec
P2               33.10 usec

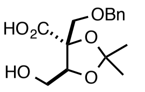
======== CHANNEL f1 ========
NUC1               13C
P1               16.55 usec
P11             500.00 usec
P12            2000.00 usec
PL0             120.00 dB
PL1              -1.00 dB
SFO1       125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2               1.60 dB
PL12             24.50 dB
SFO2       500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]      SINE.100
GPNAM[2]      SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1             30.00 %
GPZ2             50.00 %
p15             500.00 usec
p16            1000.00 usec

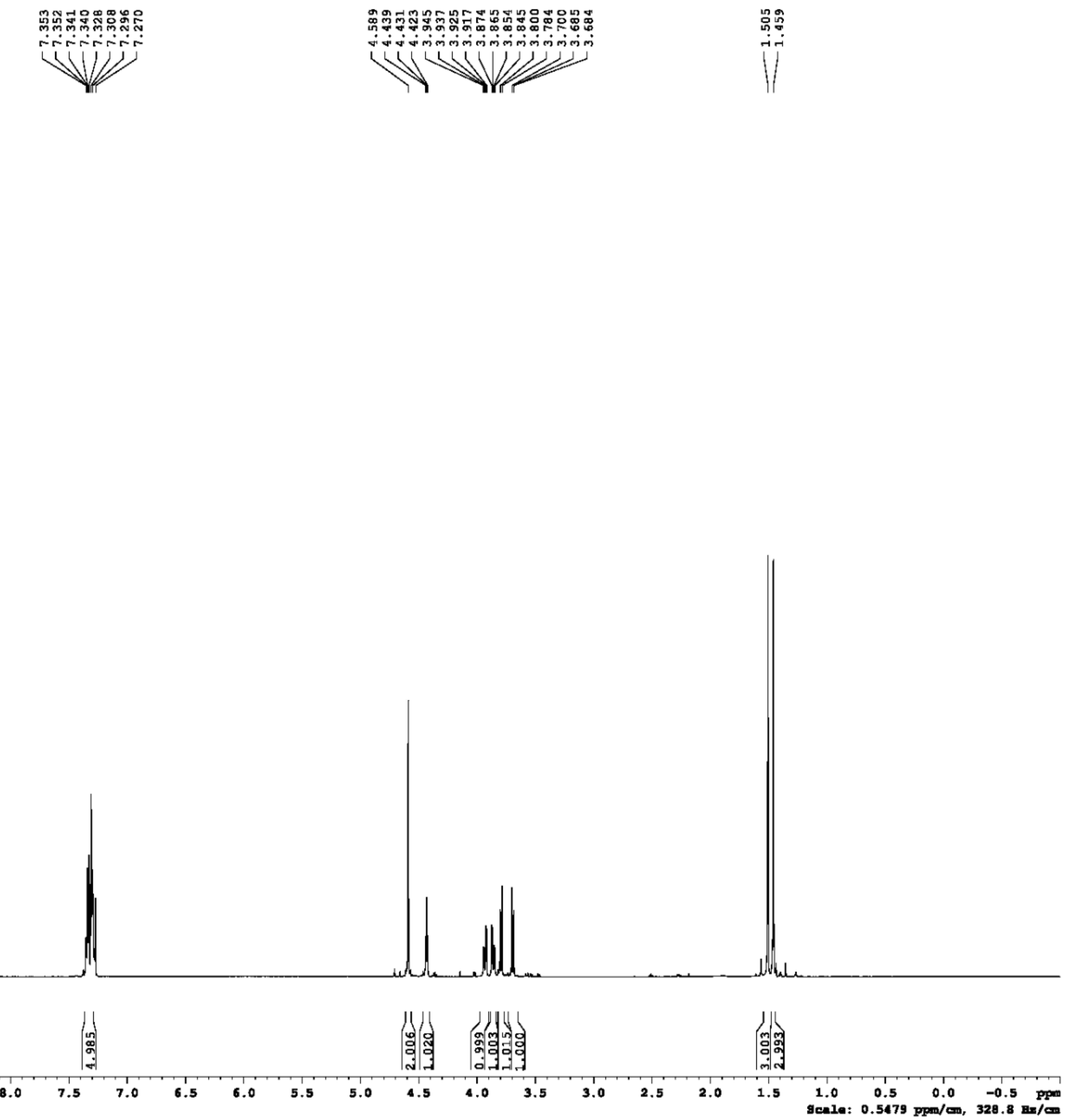
F2 - Processing parameters
SI               65536
SF         125.7803987 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                2.00
```

YS-IV-37



5.74D

^{1}H NMR ($CDCl_3$, 500 MHz)



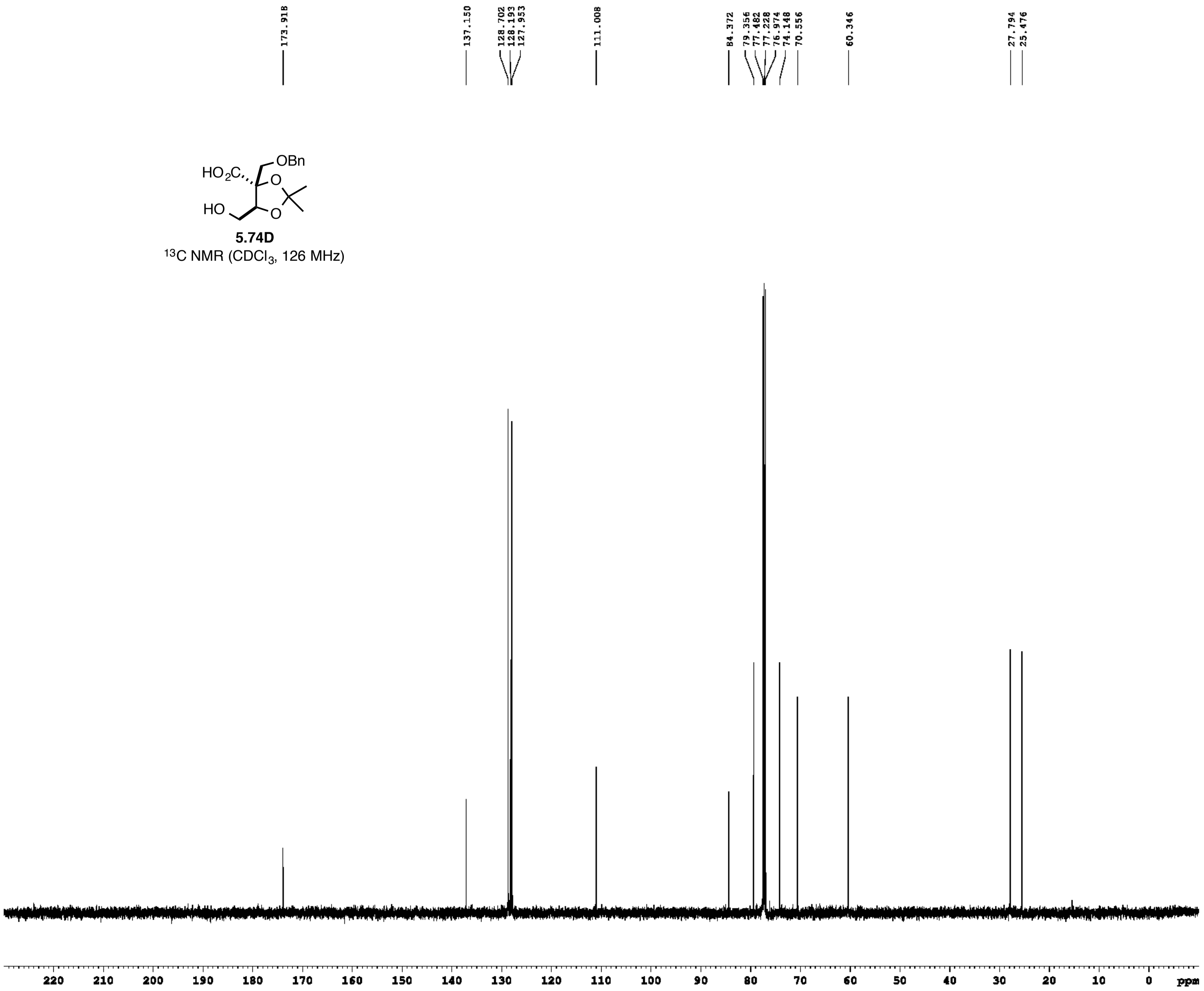
```
Current Data Parameters
NAME            YS-IV-37
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160118
Time                8.44
INSTRUM            av600
PROBHD    5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDC13
NS                     8
DS                     2
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   456
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300281 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

YS-IV-37



5.74D

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME              YS-IV-37
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160116
Time                 14.23
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     304
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST   0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

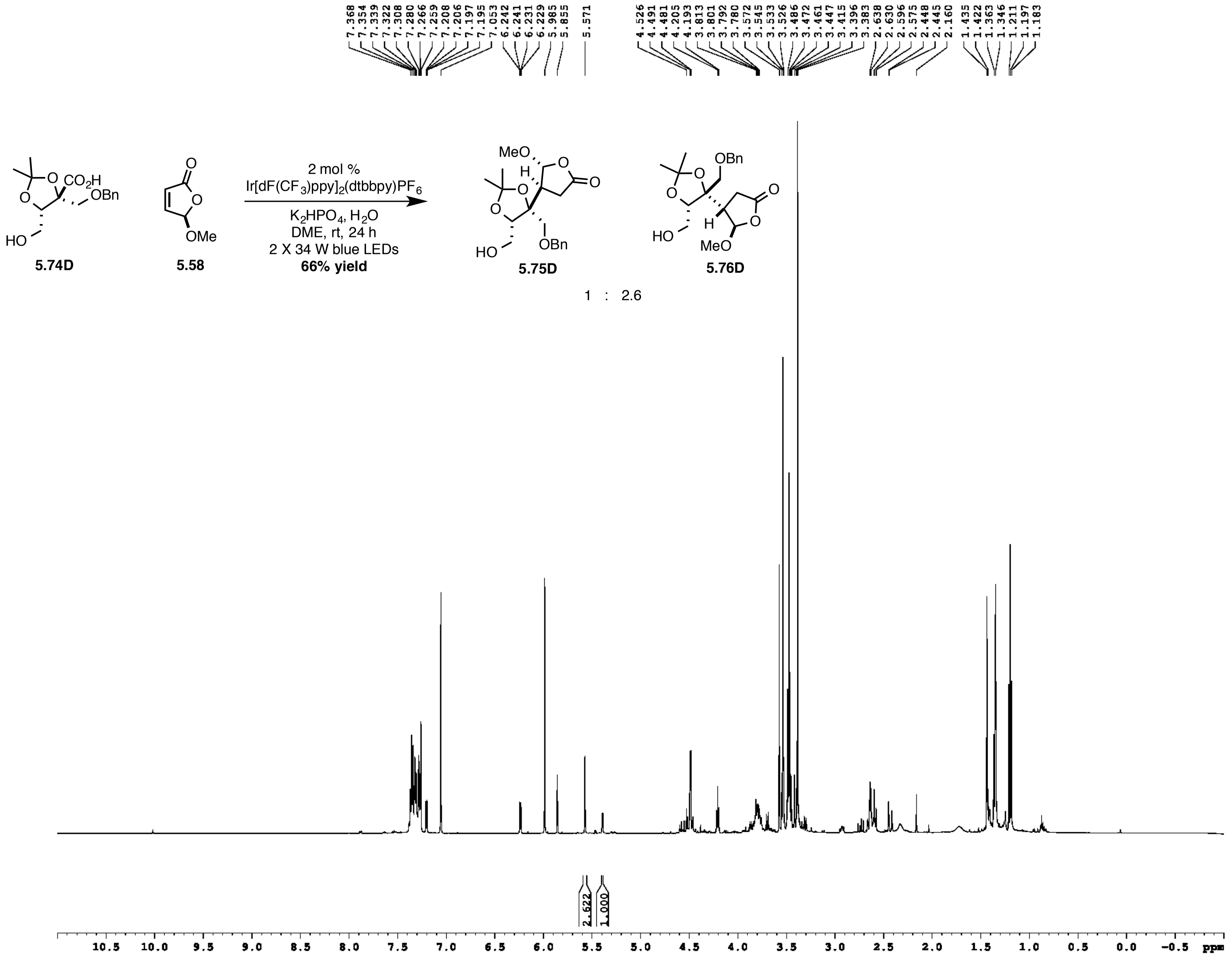
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7803997 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    2.00
```

YS-IV-45



```
Current Data Parameters
NAME            YS-IV-45
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160119
Time                9.34
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200308 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

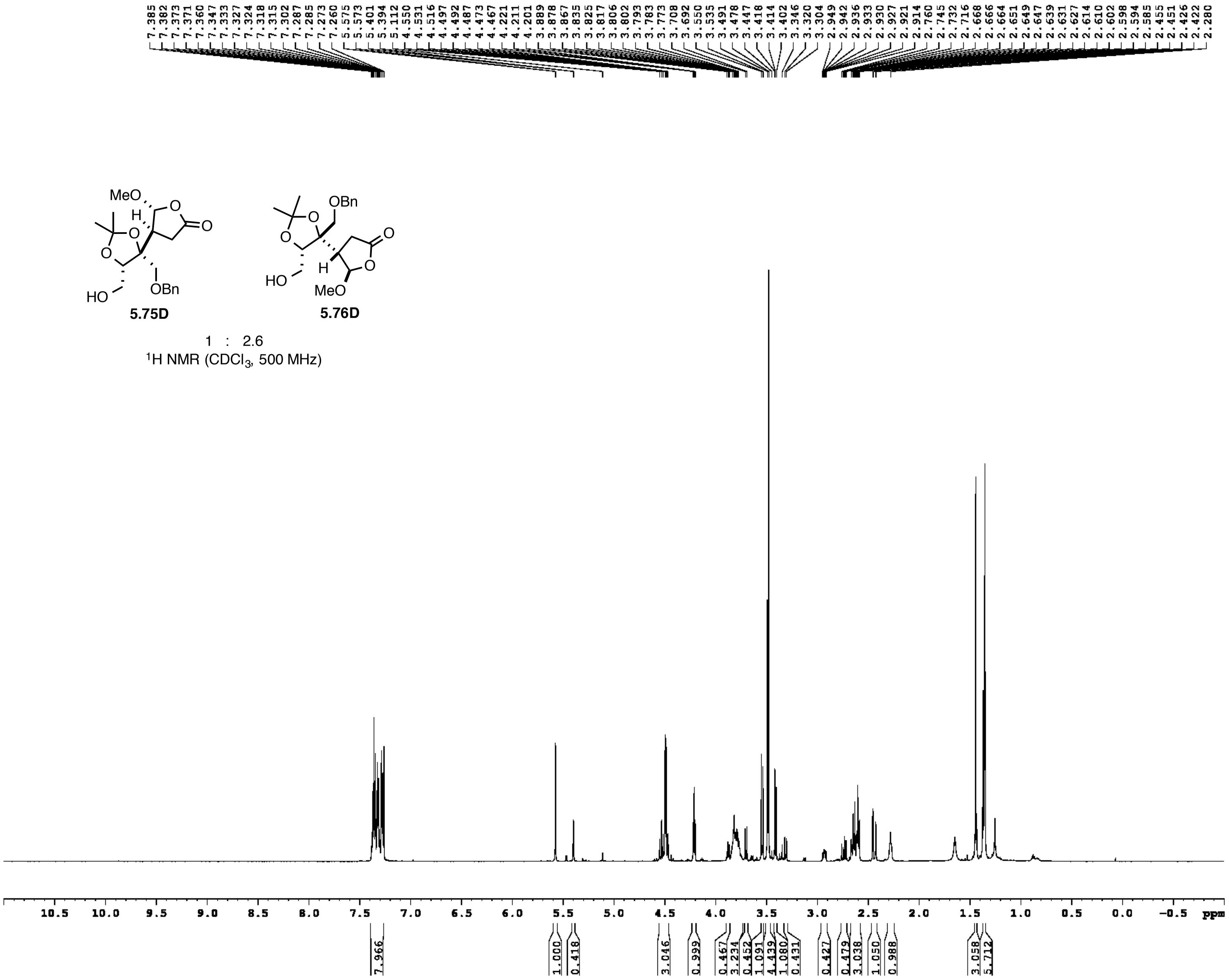
YS-IV-45

5.75D

5.76D

1 : 2.6

^{1}H NMR (CDCl$_3$, 500 MHz)



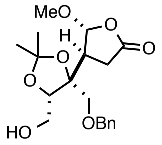
```
Current Data Parameters
NAME              YS-IV-45
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160119
Time                 15.53
INSTRUM              av600
PROBHD   5 mm TBI 1H/13
PULPROG               zg30
TD                   98074
SOLVENT              CDCl3
NS                       8
DS                       2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                     362
DW                  52.000 use
DE                   14.54 use
TE                   298.1 K
D1             0.10000000 sec
TD0                      1

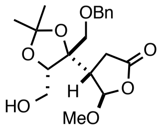
======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                    1H
P1                    8.00 use
PLW1          24.00000000 W

F2 - Processing parameters
SI                   65536
SF            600.1300352 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-IV-45



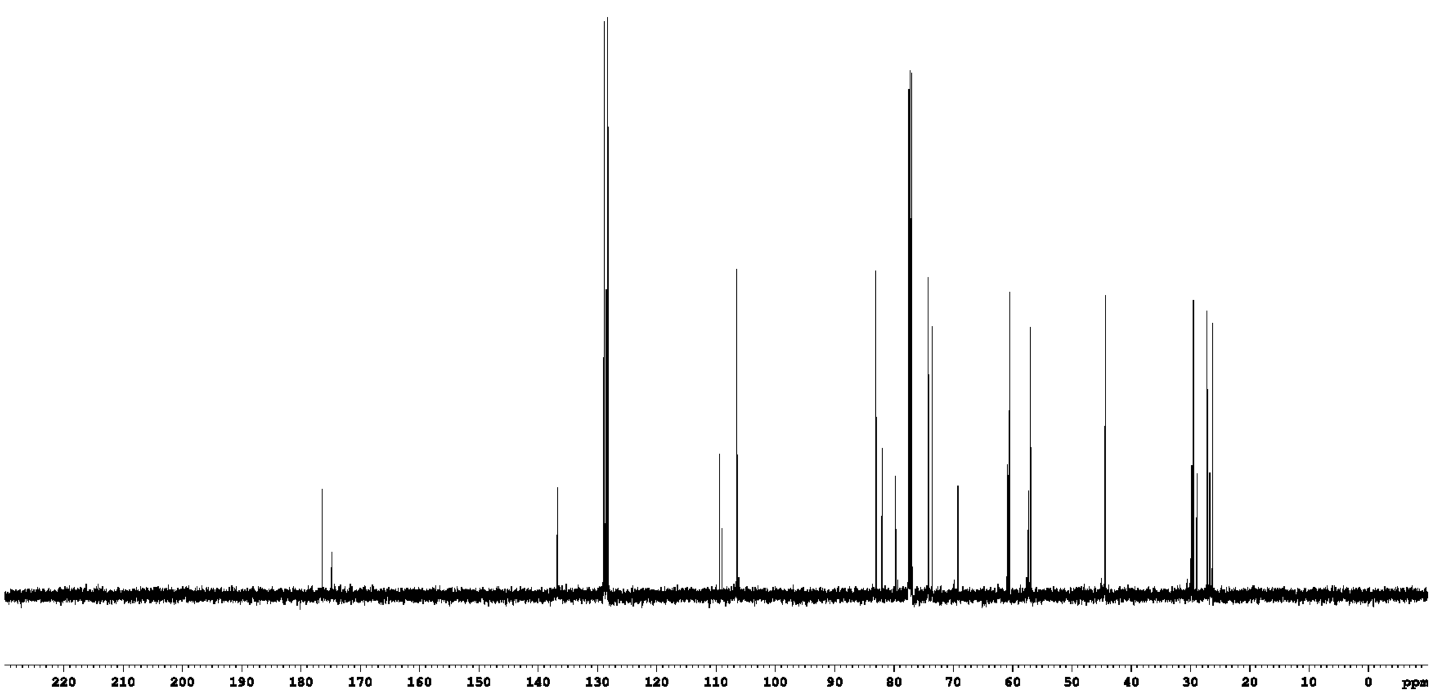
5.75D



5.76D

1 : 2.6

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-45
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160119
Time               16.42
INSTRUM          cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                9195.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST    0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

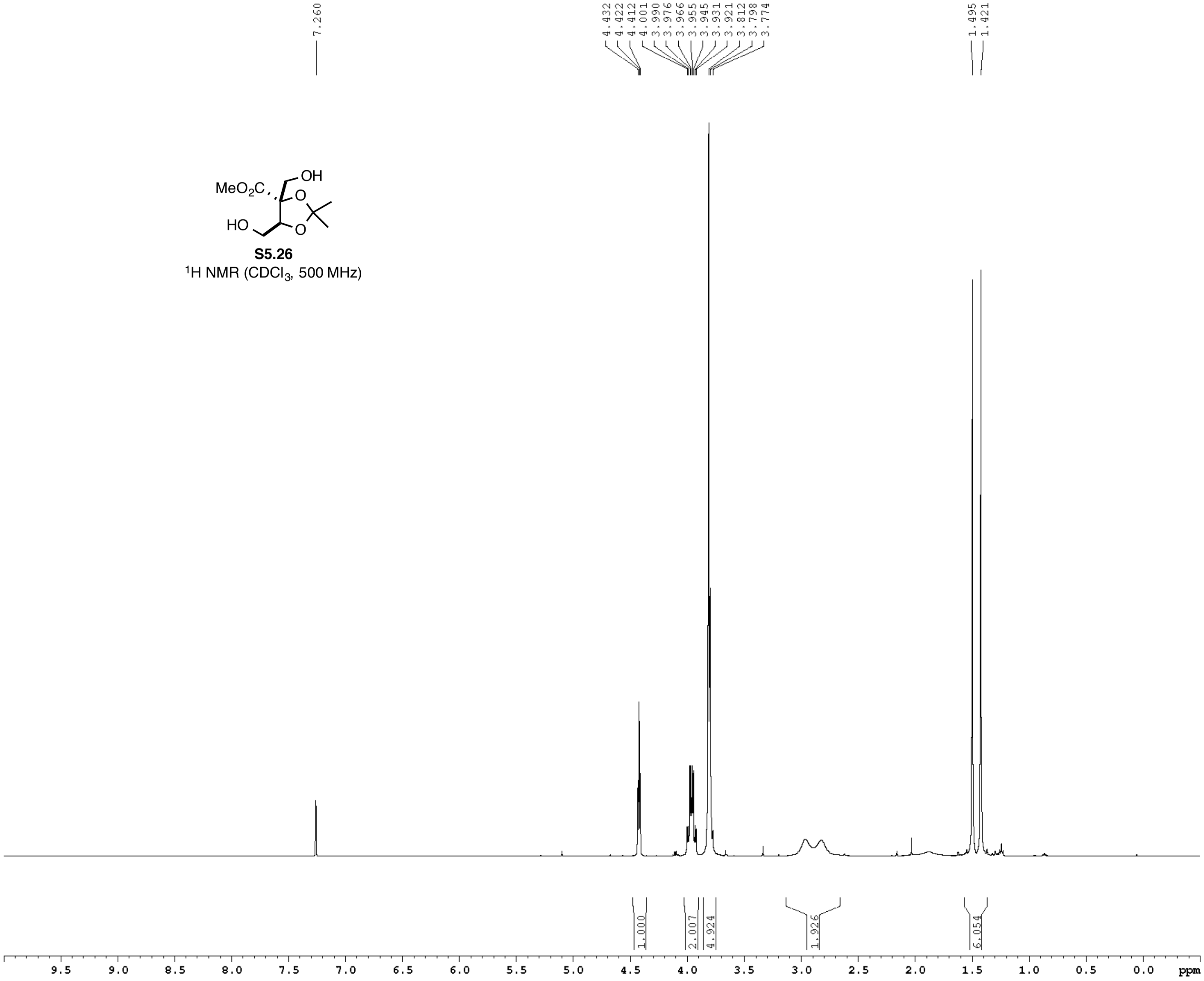
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804020 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum



S5.26

^{1}H NMR (CDCl$_3$, 500 MHz)

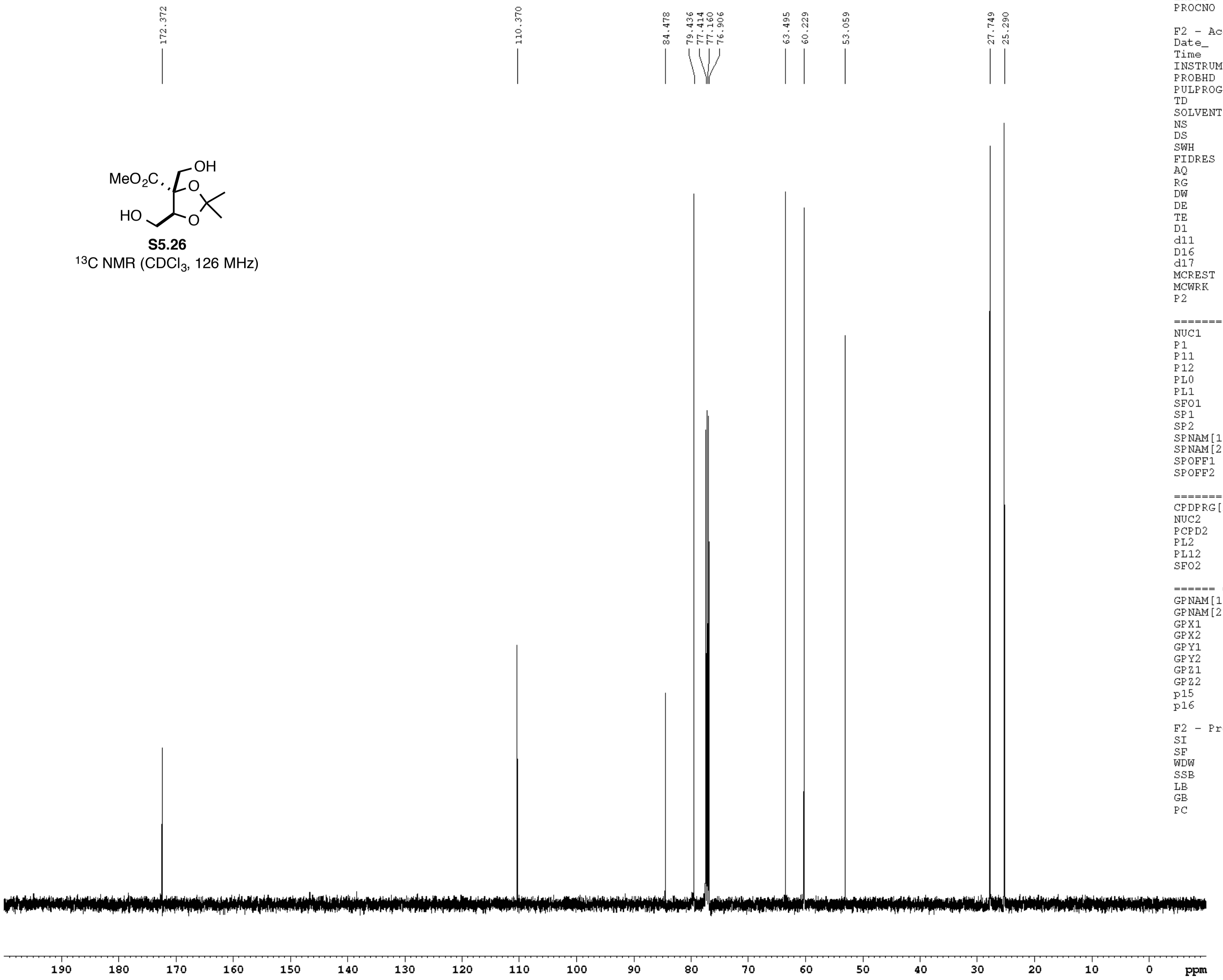
```
Current Data Parameters
NAME          DJT-VI-211
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160302
Time                9.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200313 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



S5.26

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME         DJT-VI-211
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20160302
Time               9.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  116
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               5160.6
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

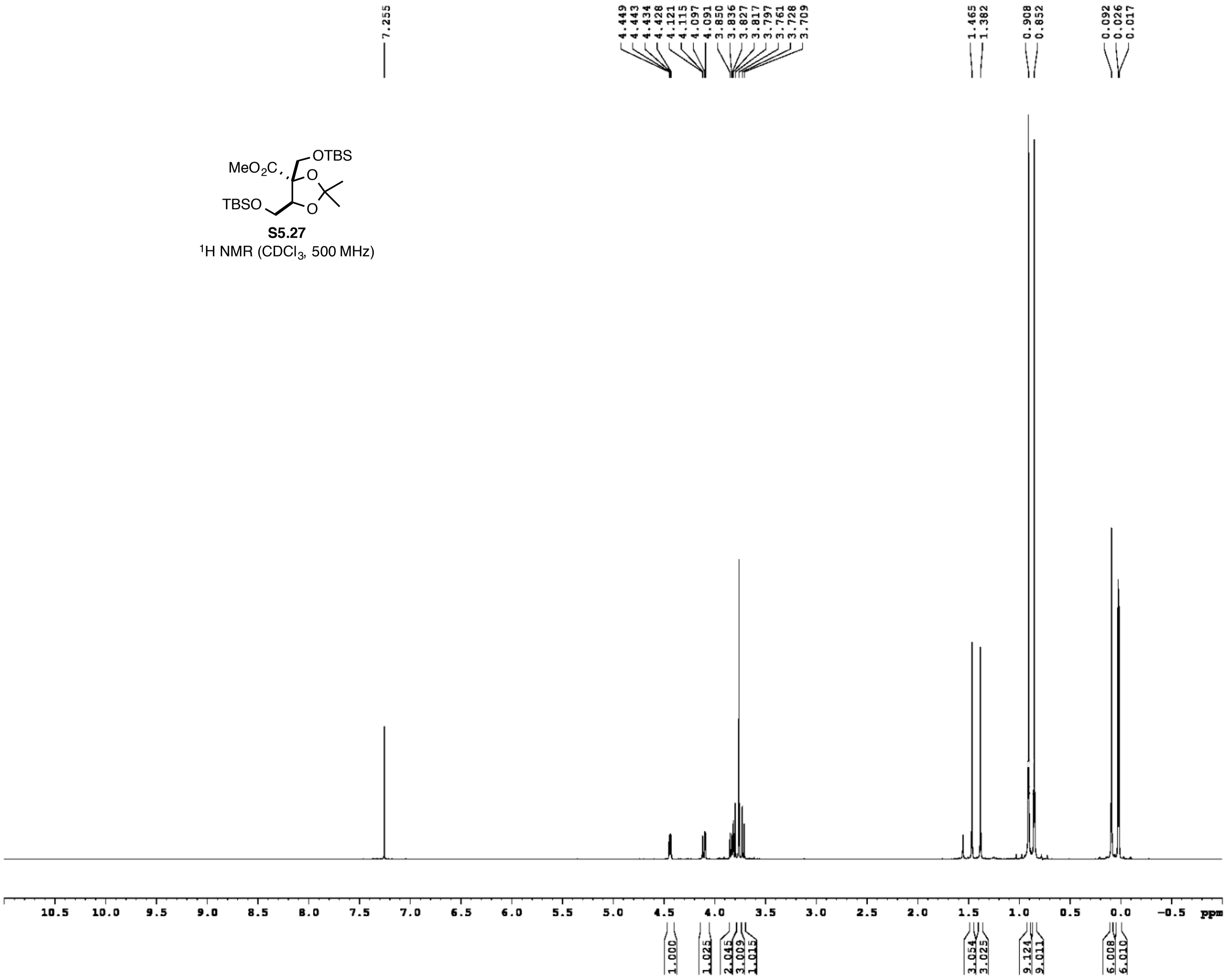
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804113 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

DJT-VI-110

S5.27

^{1}H NMR ($CDCl_3$, 500 MHz)



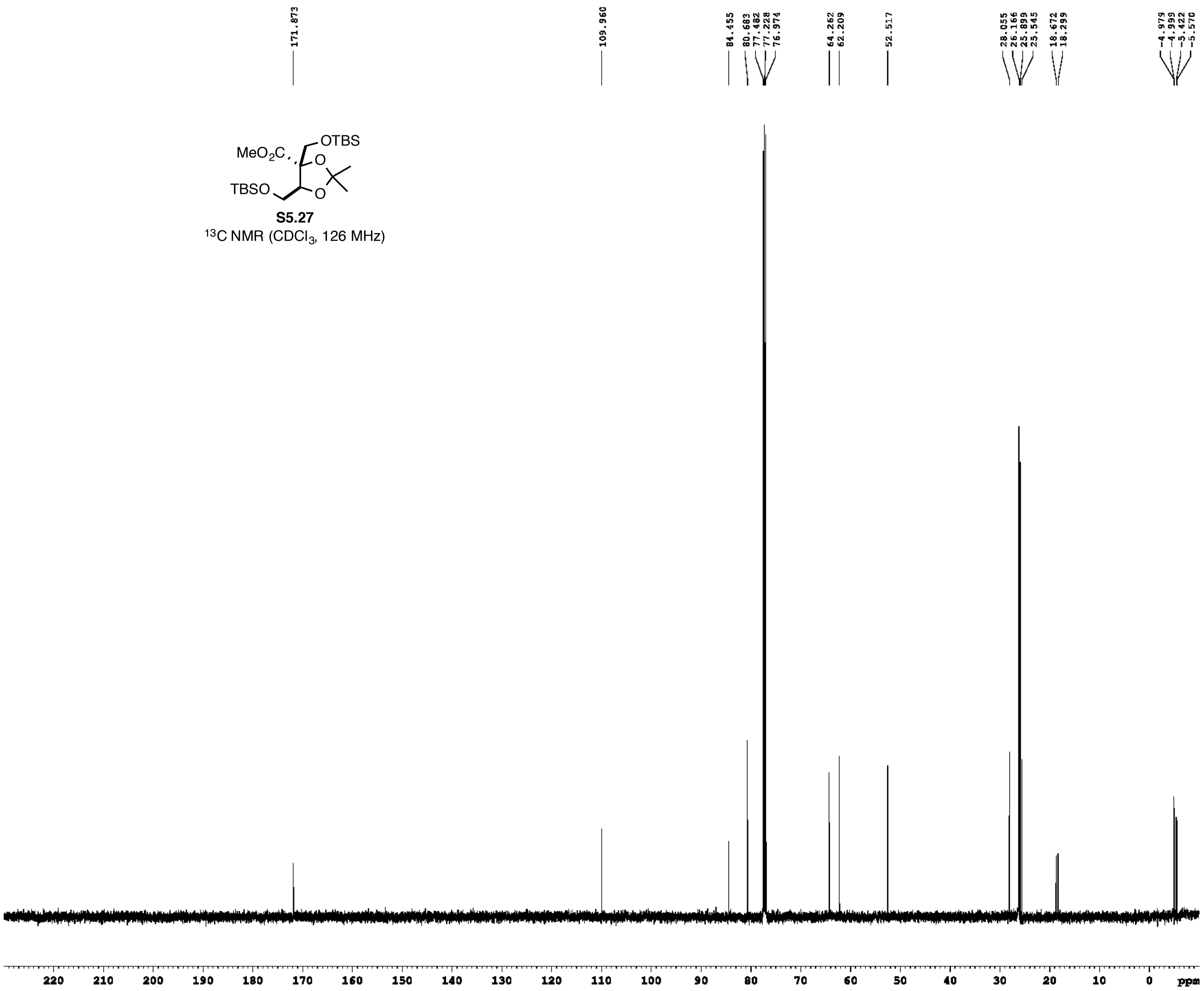
```
Current Data Parameters
NAME          DJT-VI-110
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160202
Time                8.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 use
DE                  6.00 use
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 use
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200346 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

DJT-VI-110



S5.27

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            DJT-VI-110
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160202
Time                  8.59
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     328
DS                       1
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  2298.8
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST   0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

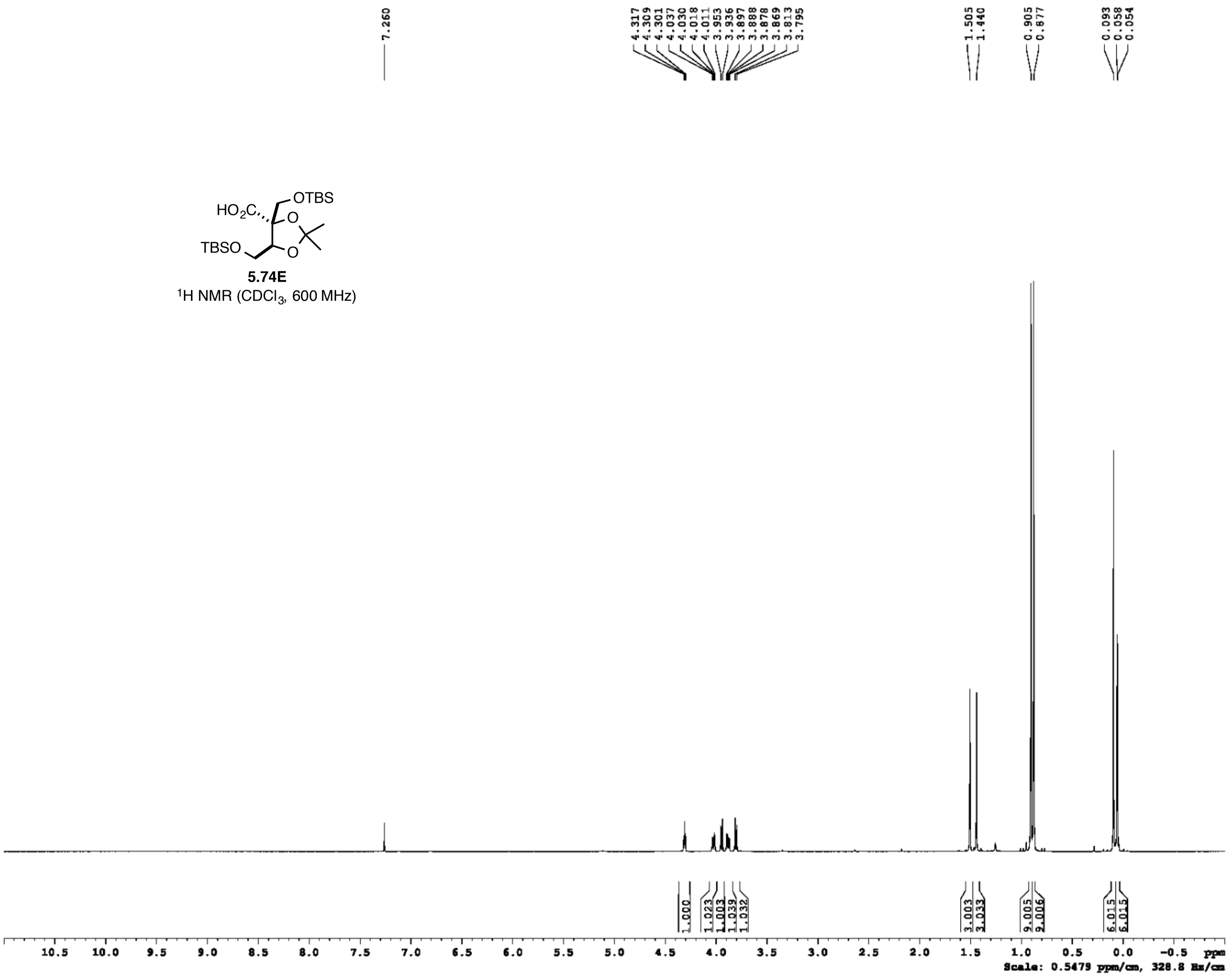
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7803989 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    2.00
```

YS-IV-38



5.74E

^{1}H NMR ($CDCl_3$, 600 MHz)

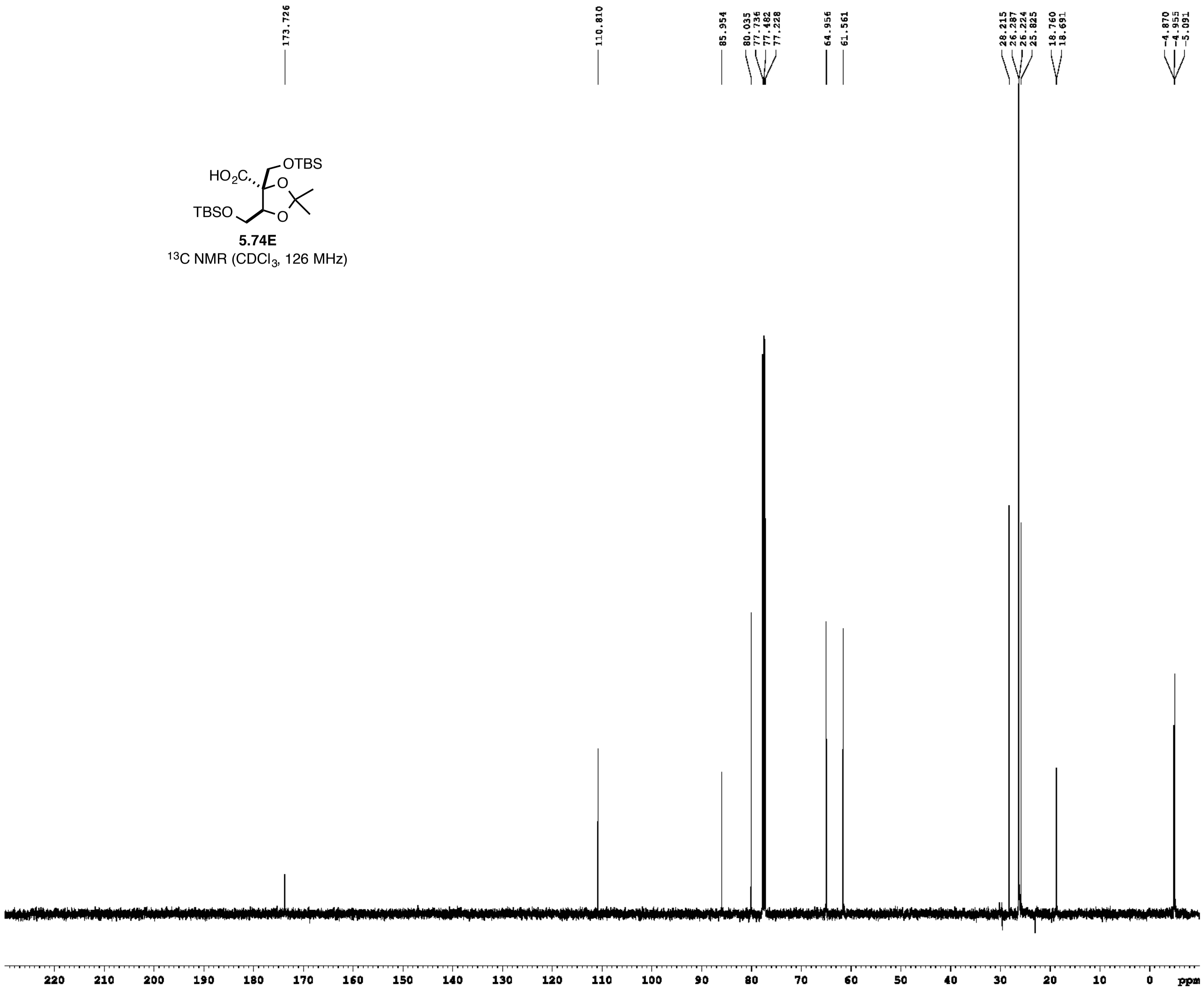
```
Current Data Parameters
NAME             YS-IV-38
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160118
Time                 8.50
INSTRUM             av600
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  98074
SOLVENT             CDC13
NS                      8
DS                      2
SWH              9615.385 Hz
FIDRES           0.098042 Hz
AQ              5.0998478 sec
RG                    322
DW                 52.000 usec
DE                  14.54 usec
TE                  298.0 K
D1             0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                   1H
P1                   8.00 usec
PLW1          24.00000000 W

F2 - Processing parameters
SI                  65536
SF            600.1300343 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

YS-IV-38



5.74E

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            YS-IV-38
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160118
Time                9.36
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   536
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

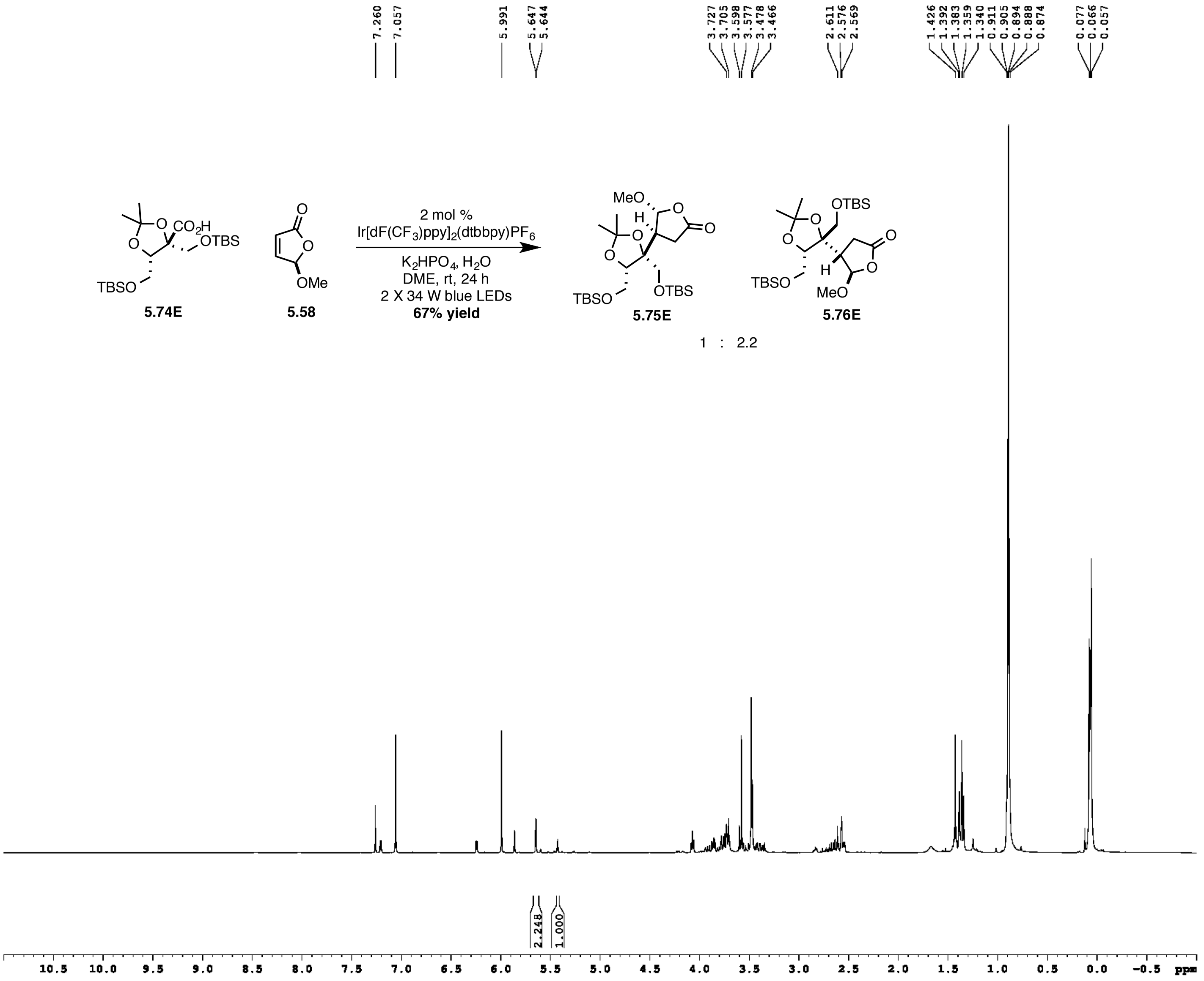
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803666 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-44



5.74E **5.58** **5.75E** **5.76E**

1 : 2.2

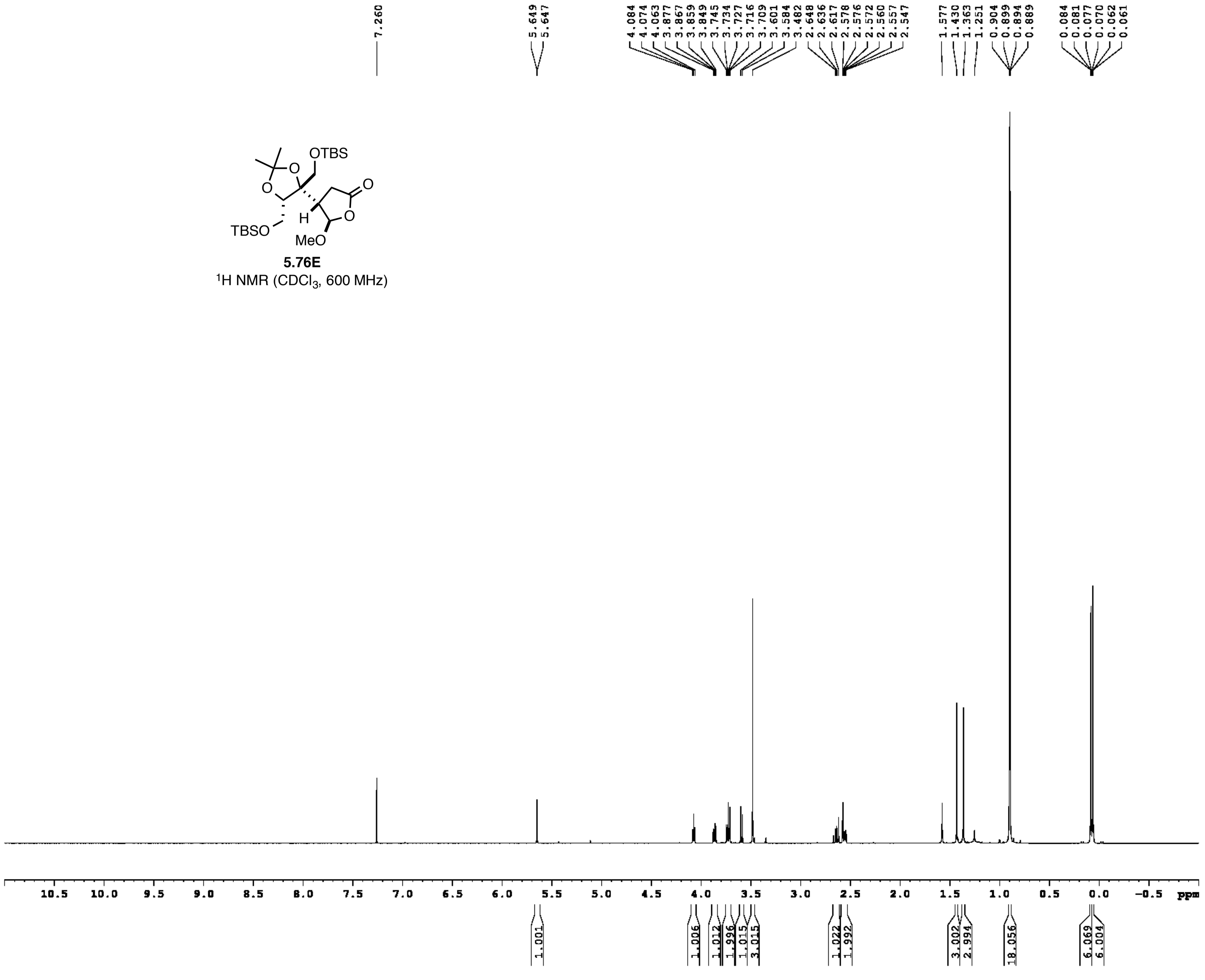
```
Current Data Parameters
NAME              YS-IV-44
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160119
Time                  9.31
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                     5.7
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200304 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-IV-44



5.76E

^{1}H NMR (CDCl$_3$, 600 MHz)

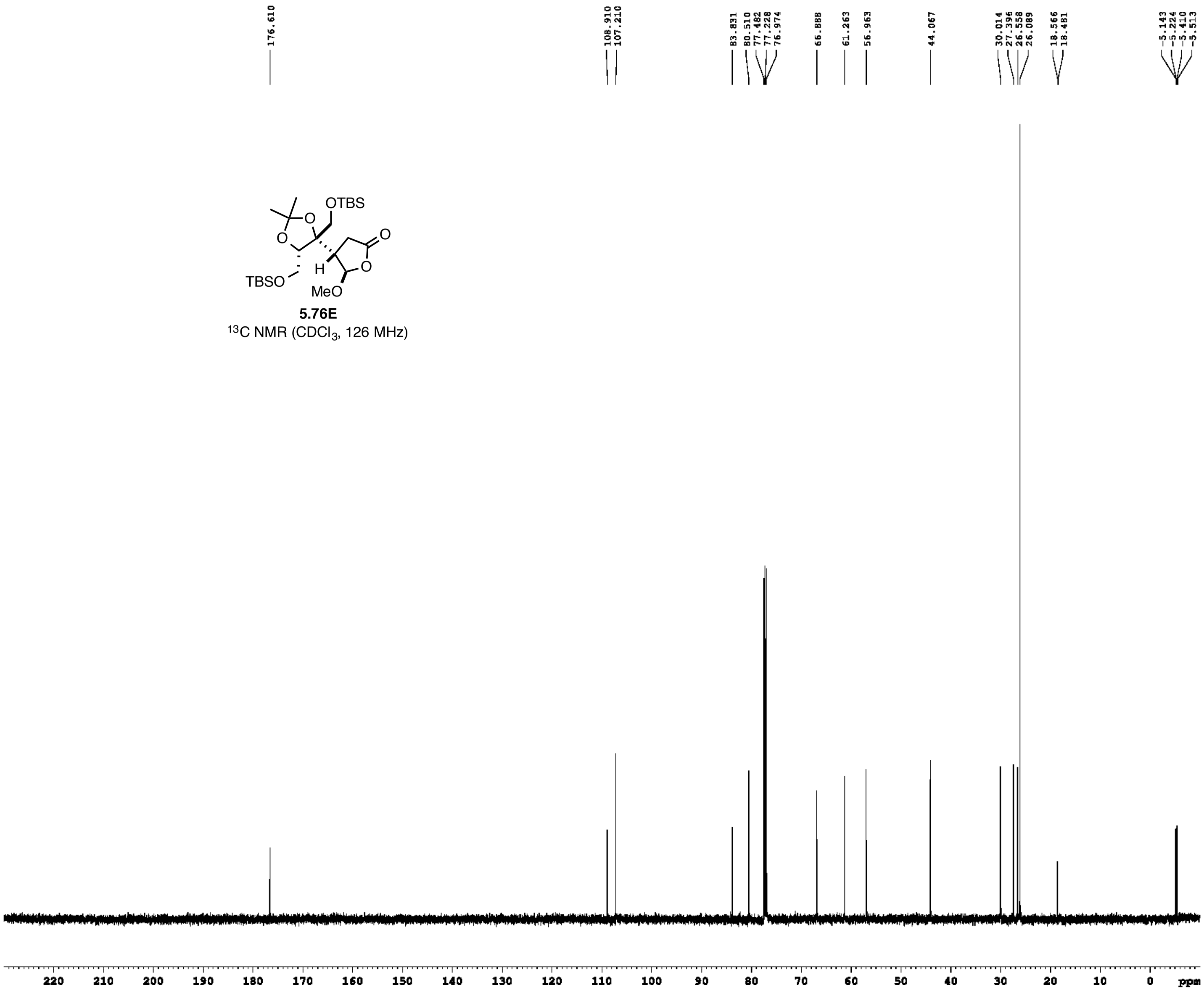
```
Current Data Parameters
NAME              YS-IV-44
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160119
Time                 15.47
INSTRUM              av600
PROBHD   5 mm TBI 1H/13
PULPROG               zg30
TD                   98074
SOLVENT              CDC13
NS                       8
DS                       2
SWH               9615.385 Hz
FIDRES            0.098042 Hz
AQ               5.0998478 sec
RG                     406
DW                  52.000 use
DE                   14.54 use
TE                   298.1 K
D1              0.10000000 sec
TD0                      1

====== CHANNEL f1 ======
SFO1           600.1342009 MHz
NUC1                    1H
P1                    8.00 use
PLW1           24.00000000 W

F2 - Processing parameters
SI                   65536
SF             600.1300357 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

YS-IV-44



5.76E

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME             YS-IV-44
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160119
Time                16.13
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    200
DS                     16
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

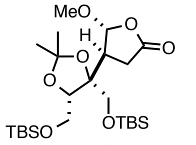
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

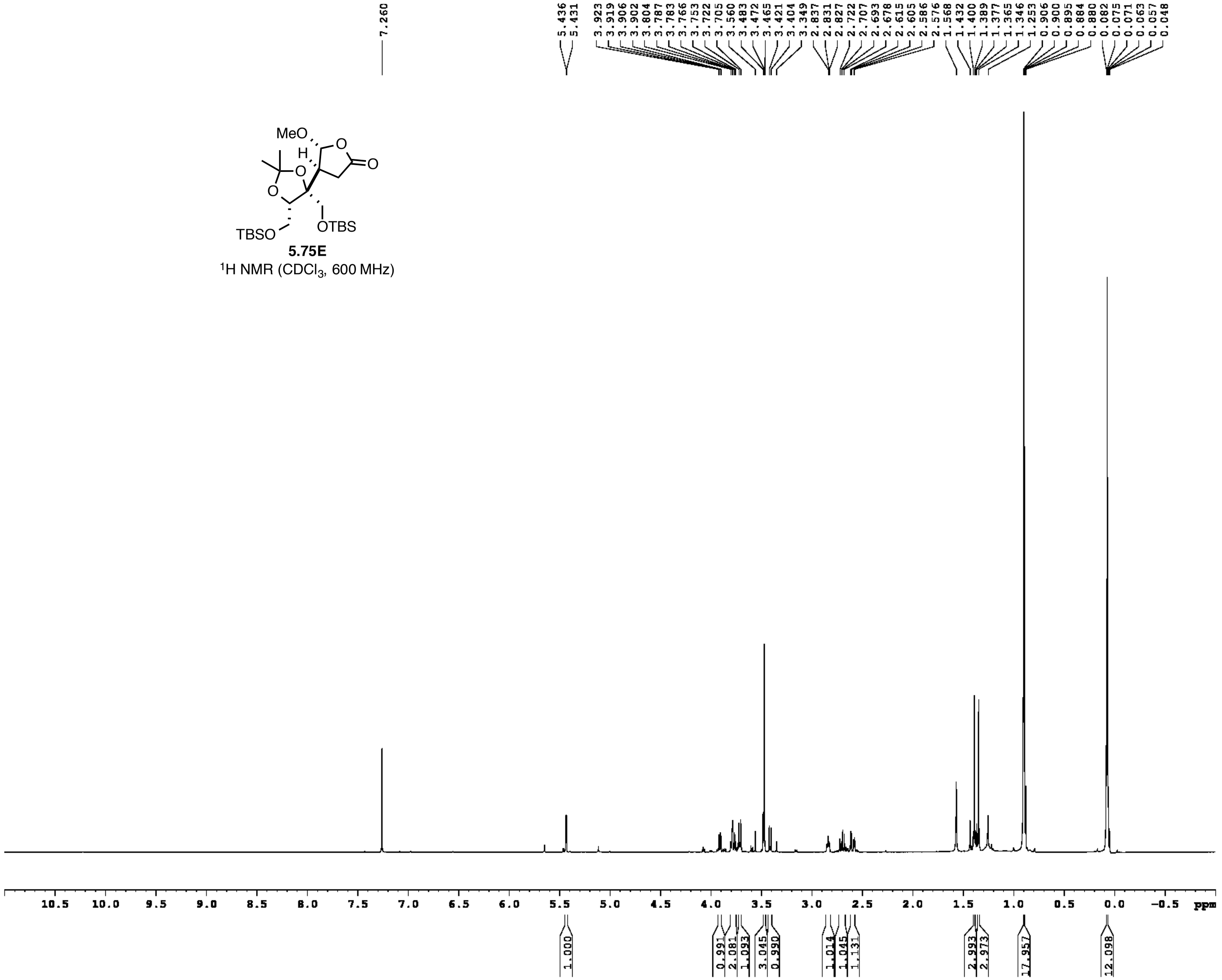
F2 - Processing parameters
SI                  65536
SF            125.7803991 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   2.00
```

YS-IV-44



5.75E

^{1}H NMR (CDCl$_3$, 600 MHz)



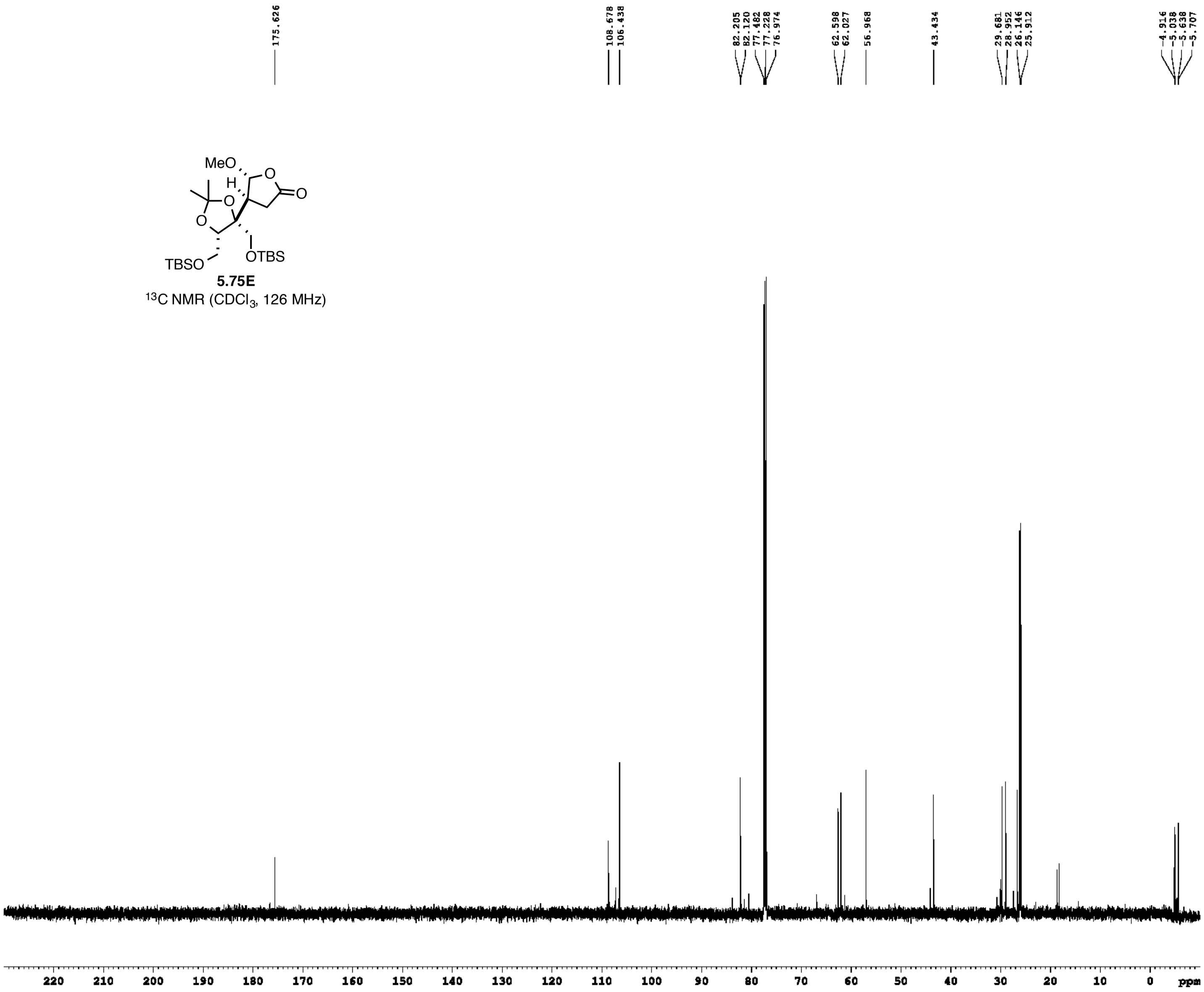
```
Current Data Parameters
NAME              YS-IV-44
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160119
Time                 15.50
INSTRUM              av600
PROBHD   5 mm TBI 1H/13
PULPROG               zg30
TD                   98074
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               9615.385 Hz
FIDRES            0.098042 Hz
AQ               5.0998478 sec
RG                     575
DW                  52.000 use
DE                   14.54 use
TE                   298.0 K
D1             0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          600.1342009 MHz
NUC1                    1H
P1                    8.00 use
PLW1          24.00000000 W

F2 - Processing parameters
SI                   65536
SF            600.1300351 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

YS-IV-44



5.75E

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME              YS-IV-44
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160119
Time                 16.31
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     320
DS                      16
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  7298.2
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST   0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

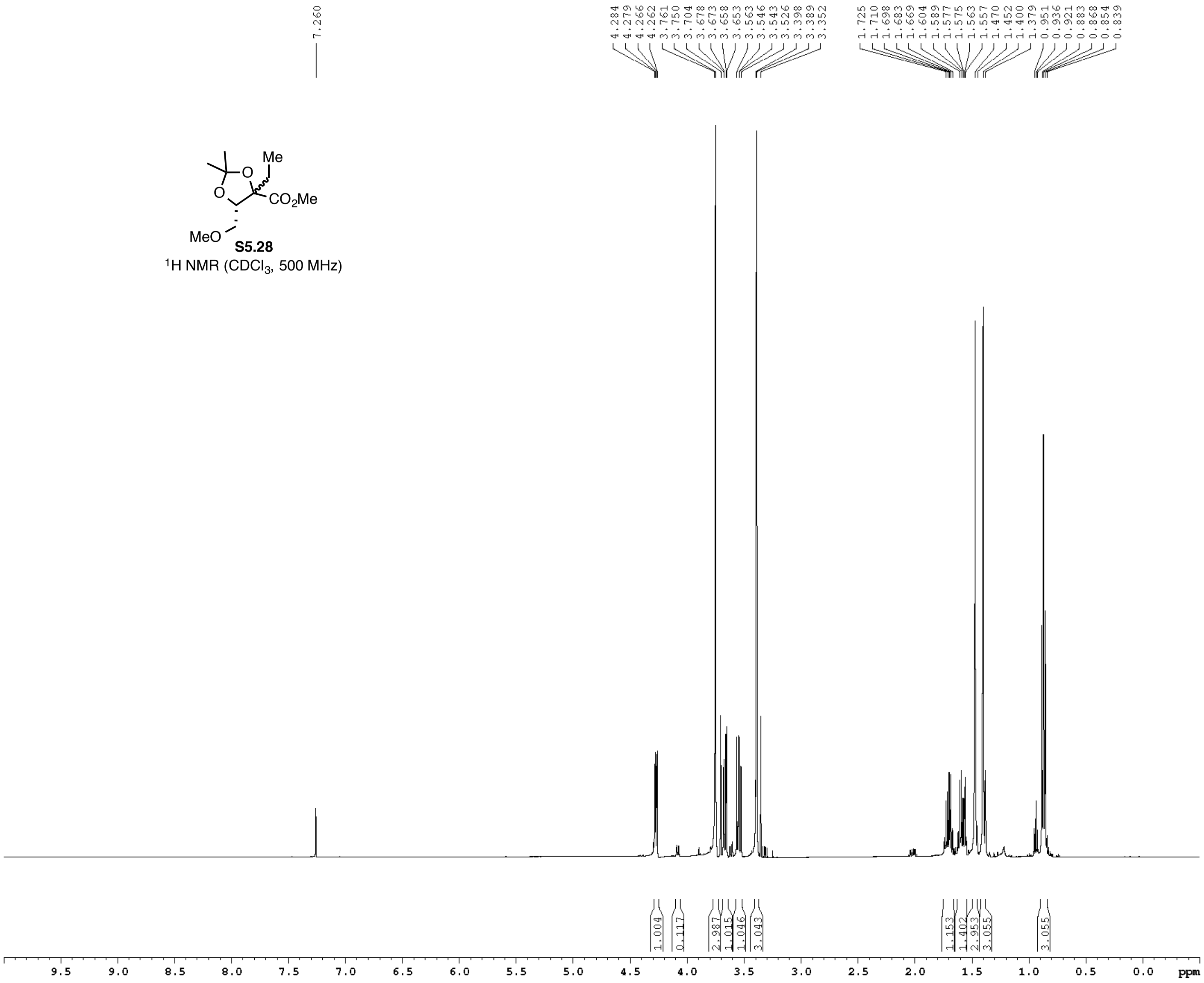
====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7803990 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    2.00
```

1H spectrum

S5.28

^{1}H NMR (CDCl$_3$, 500 MHz)



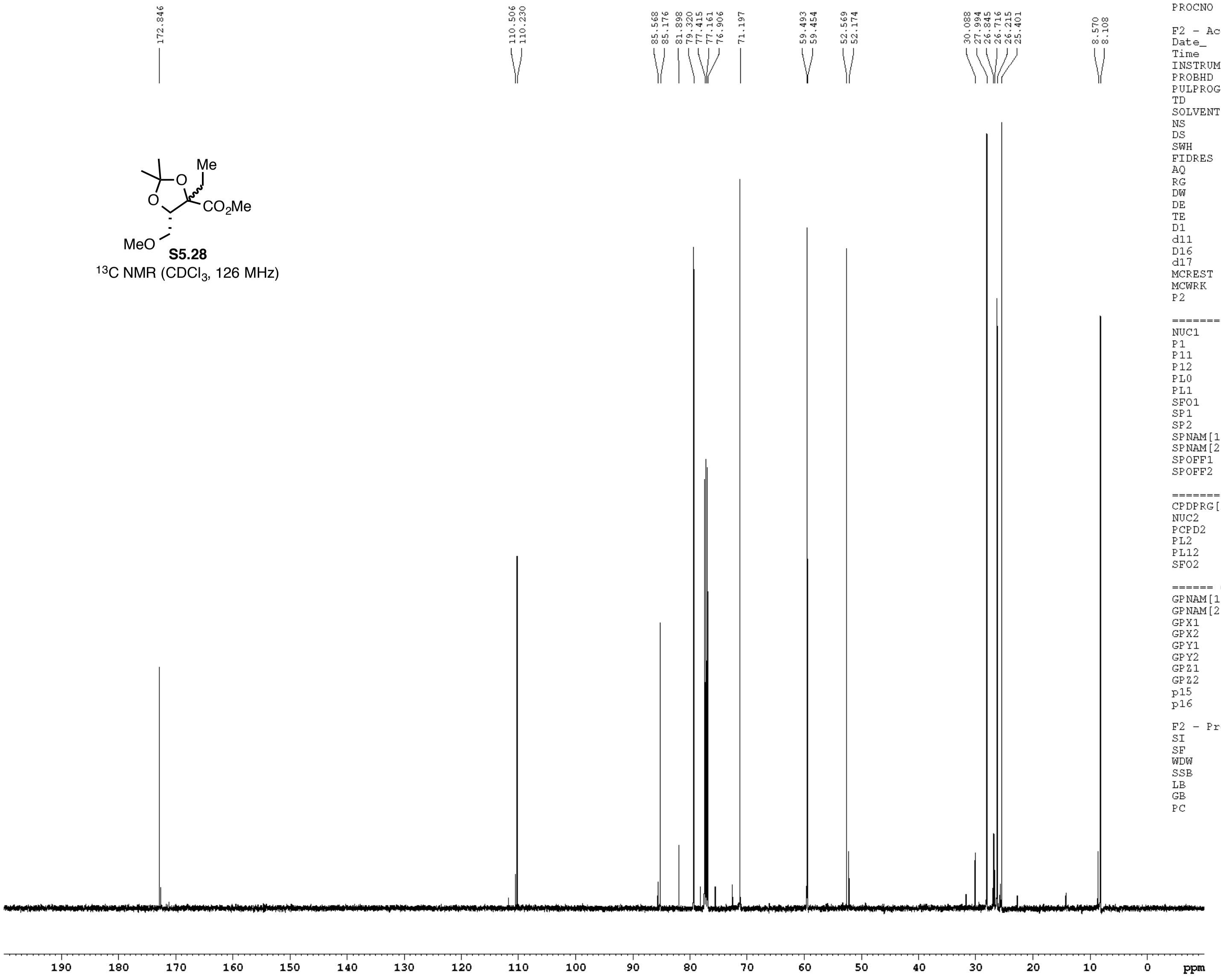
```
Current Data Parameters
NAME          DJT-VI-161
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160112
Time               15.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    10
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200302 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



S5.28

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-161
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160112
Time               15.21
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   253
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

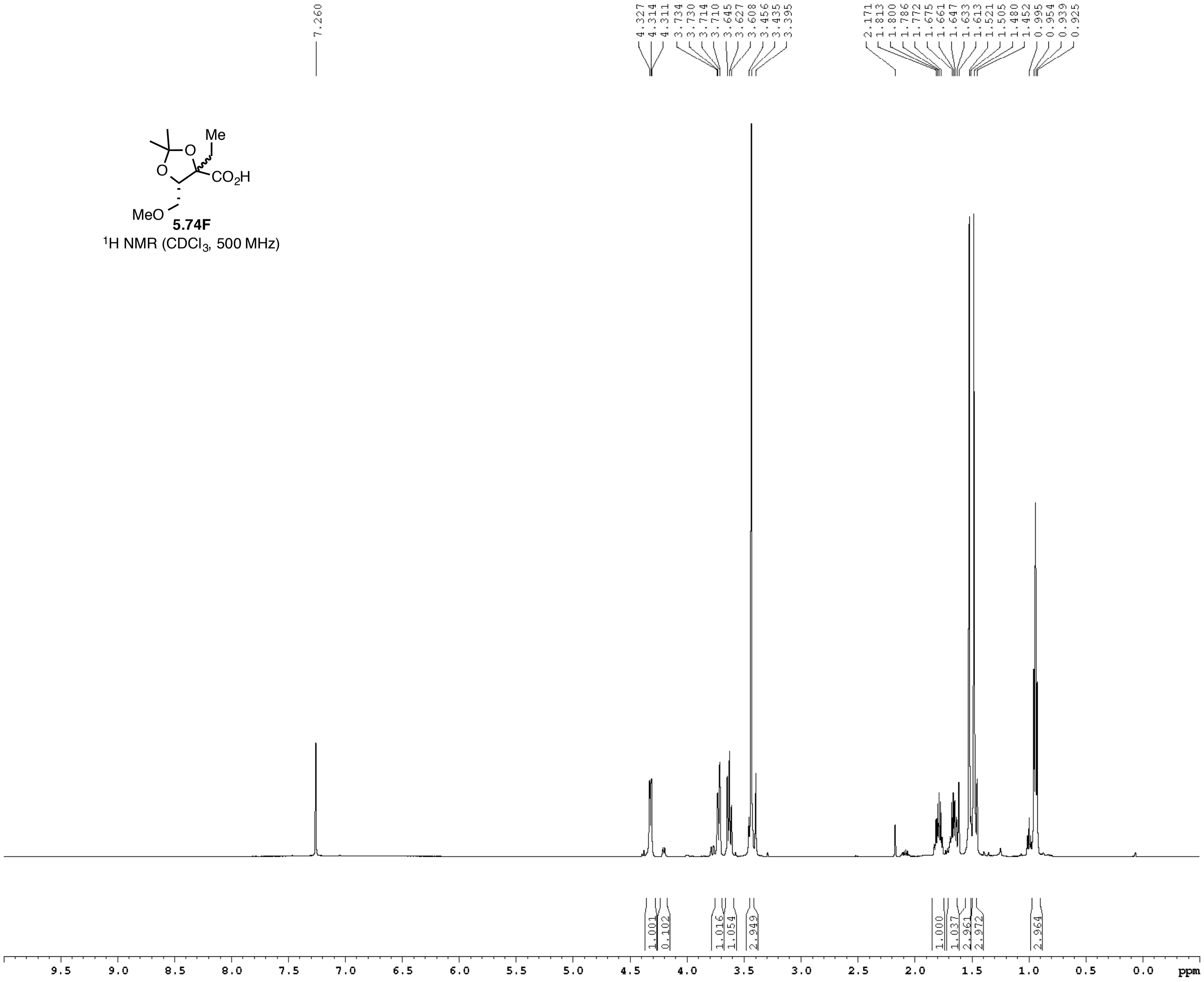
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804145 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

5.74F

^{1}H NMR (CDCl$_3$, 500 MHz)



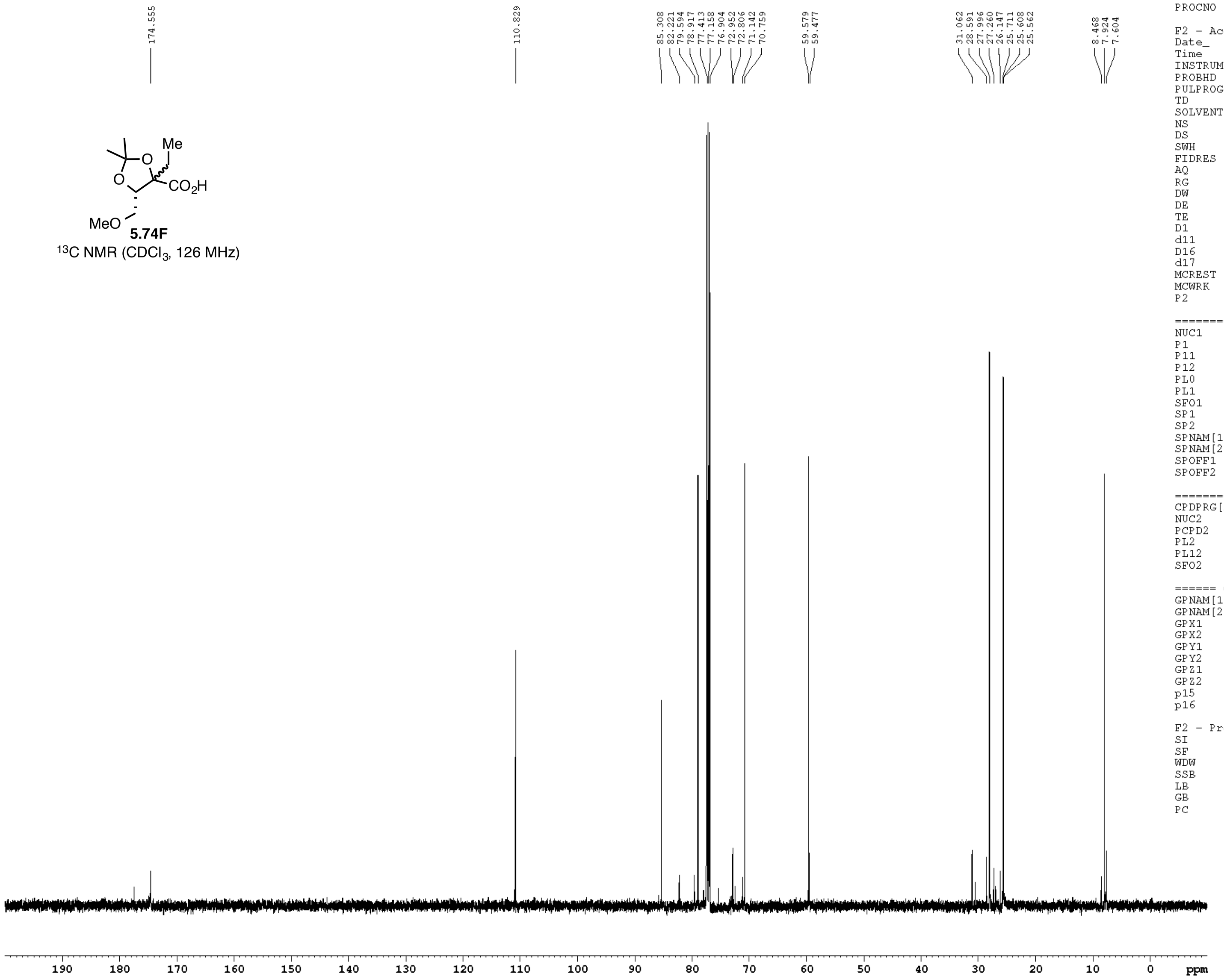
```
Current Data Parameters
NAME          DJT-VI-164
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160115
Time               10.35
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    10
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200299 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.74F

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-164
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160115
Time               14.44
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   284
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

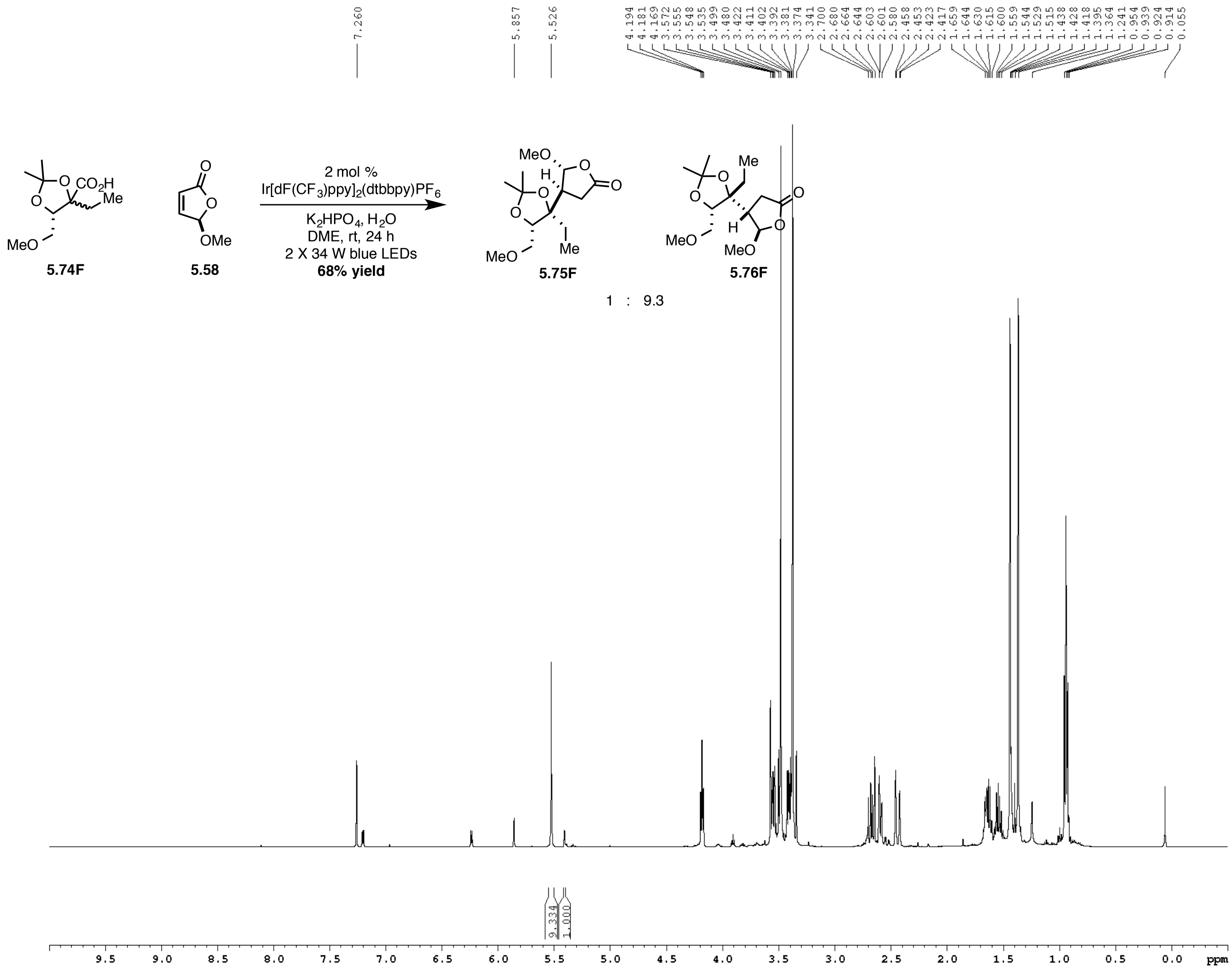
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804099 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



5.74F **5.58** **5.75F** **5.76F**

1 : 9.3

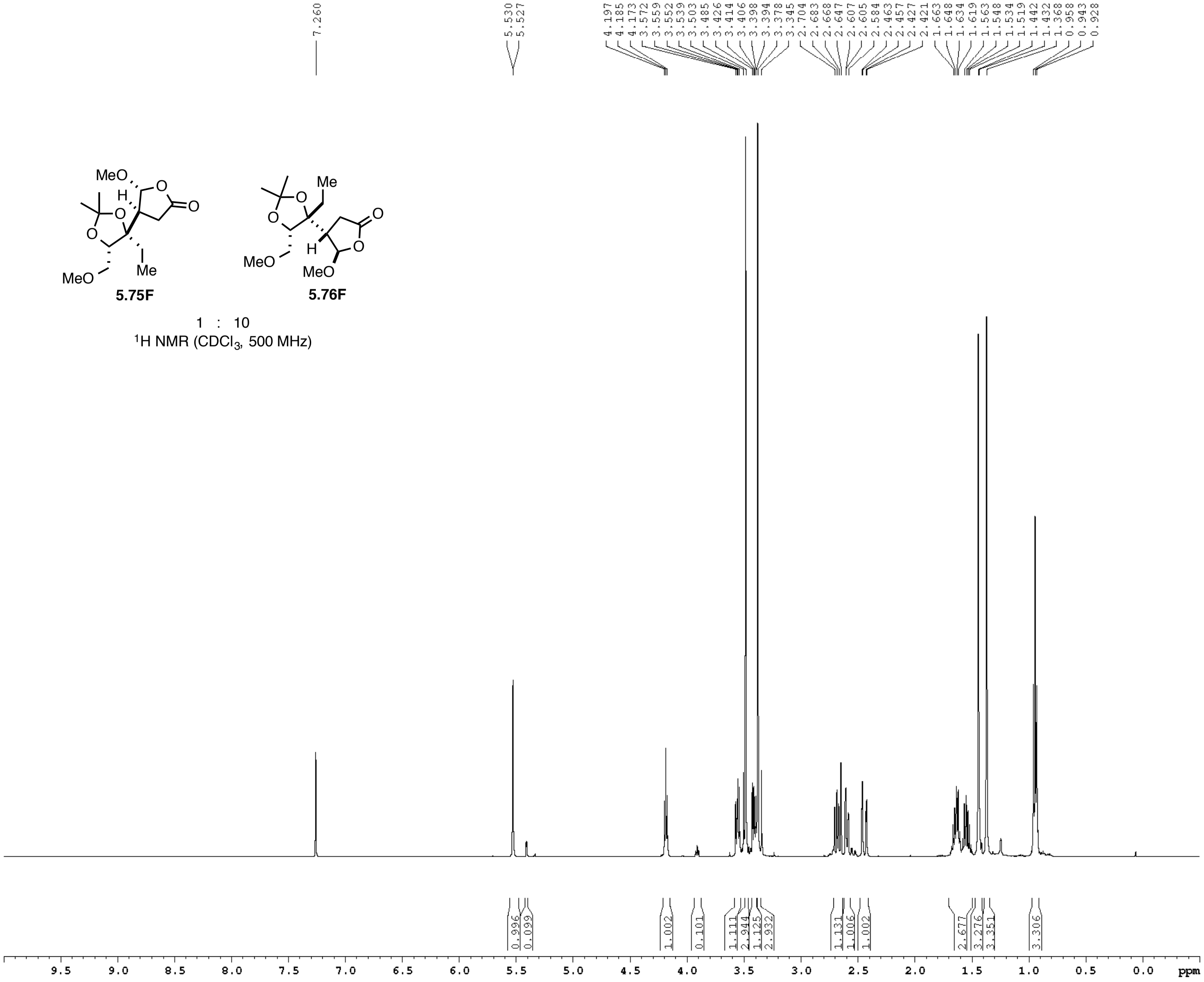
```
Current Data Parameters
NAME          DJT-VI-165
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160116
Time               16.28
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200299 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

1H spectrum



5.75F

5.76F

1 : 10

^{1}H NMR (CDCl$_3$, 500 MHz)

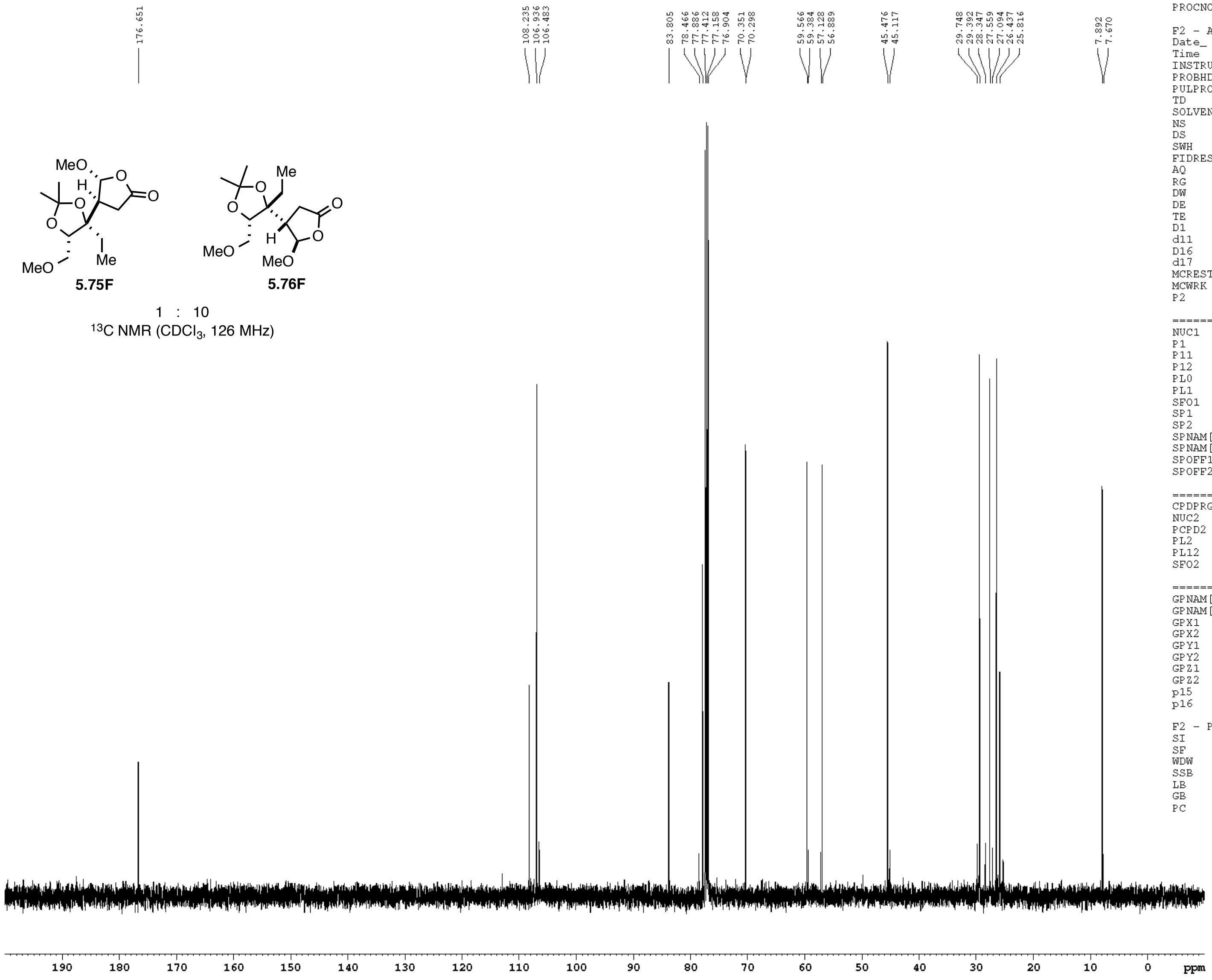
```
Current Data Parameters
NAME          DJT-VI-165
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160118
Time               10.01
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200302 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



1 : 10

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-165
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160118
Time               10.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   124
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5792.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

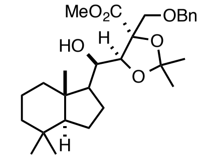
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]   Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804089 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-55



S5.21

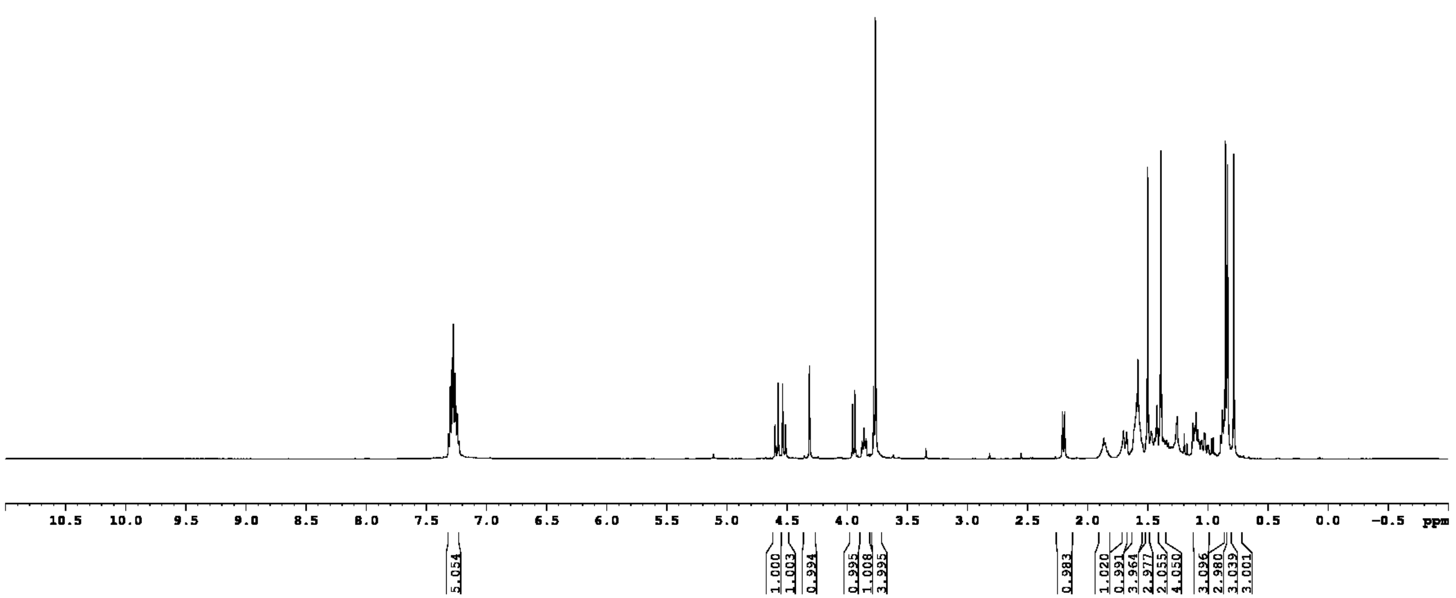
^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME              YS-IV-55
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160123
Time                 13.30
INSTRUM              gn500
PROBHD   5 mm broadband
PULPROG               zg30
TD                   81728
SOLVENT             CDCl3T
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                    40.3
DW                  62.400 use
DE                    6.00 use
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.00 use
PL1                  -5.80 dB
SFO1           499.1834943 MHz

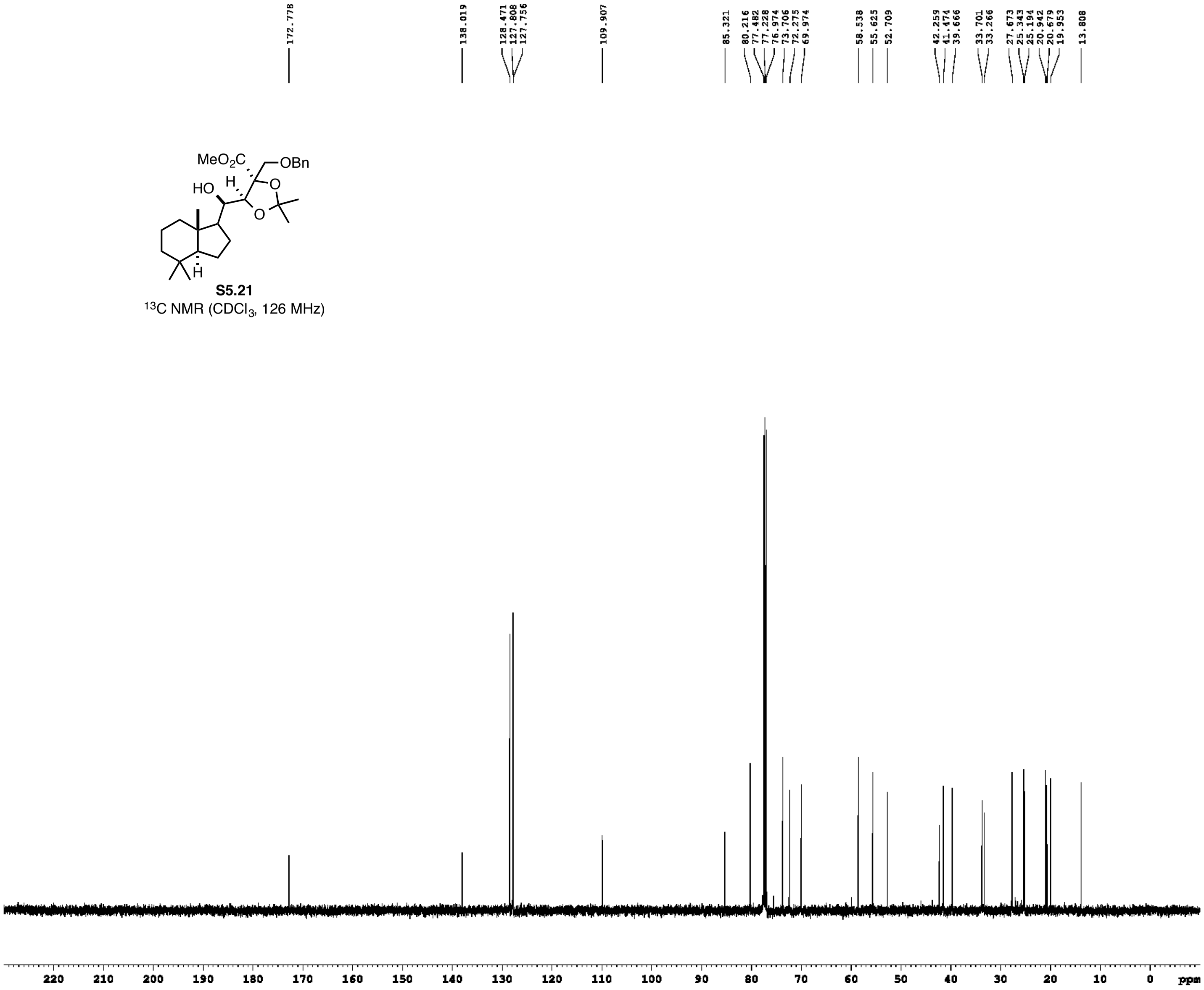
F2 - Processing parameters
SI                   65536
SF             499.1800270 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



YS-IV-55

S5.21

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME            YS-IV-55
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160125
Time               16.51
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     1
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.50000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

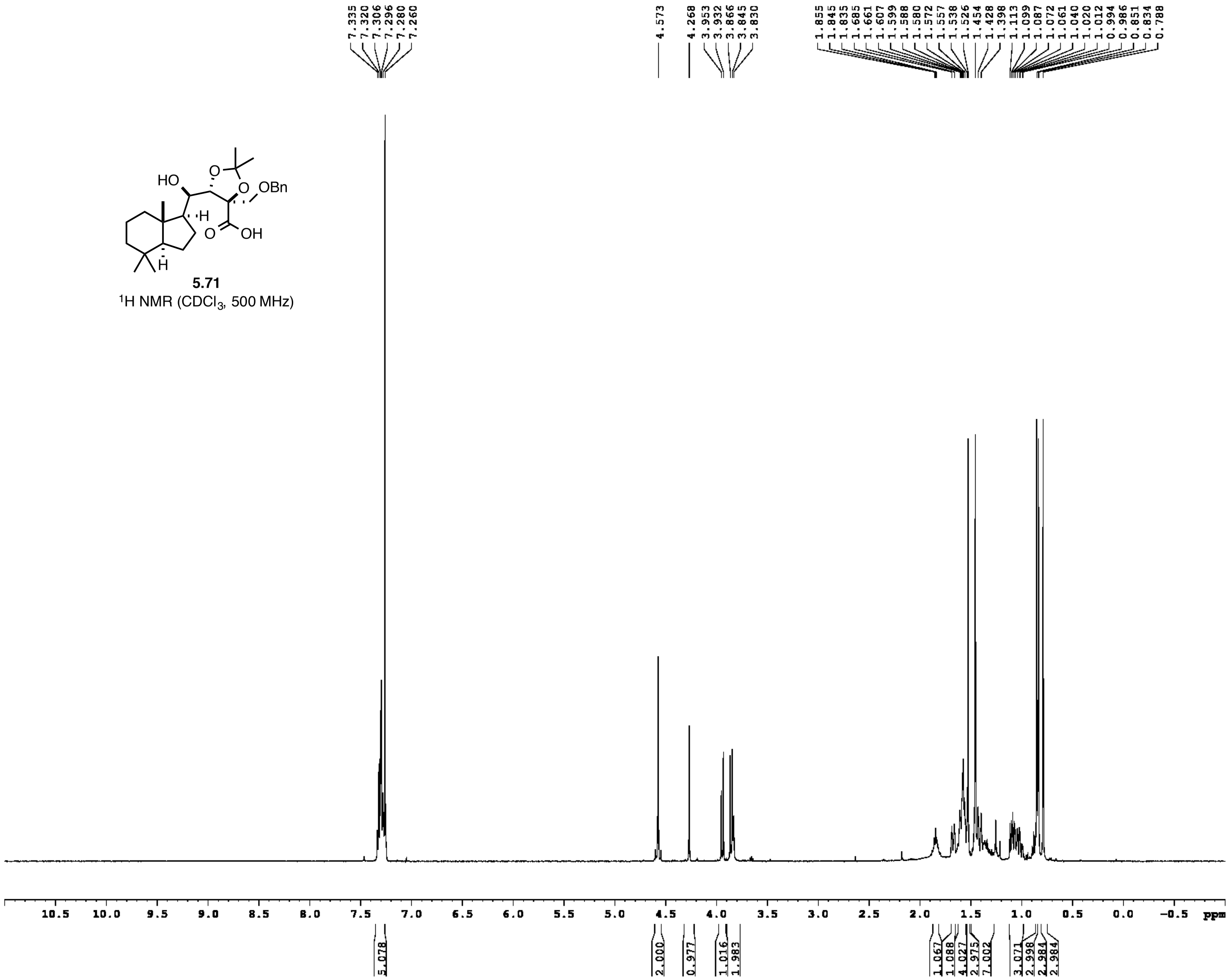
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803998 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-56



5.71

^{1}H NMR (CDCl$_3$, 500 MHz)

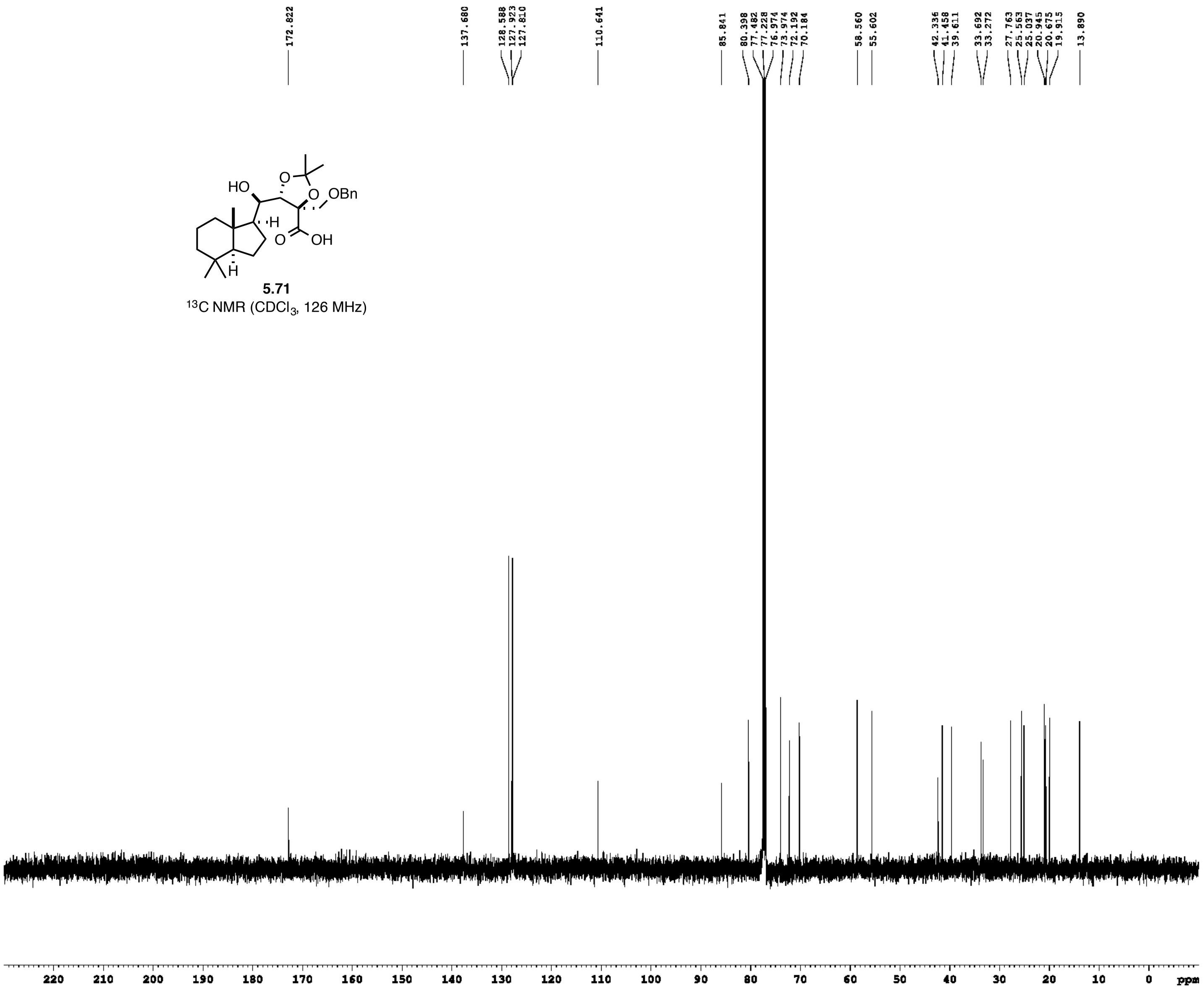
```
Current Data Parameters
NAME             YS-IV-56
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160128
Time                12.18
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                    6.3
DW                 62.400 use
DE                   6.00 use
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 use
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200325 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

YS-IV-56



5.71

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME              YS-IV-56
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160128
Time                 12.24
INSTRUM            cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     700
DS                       1
SWH              30303.031 Hz
FIDRES            0.462388 Hz
AQ               1.0813440 sec
RG                  5792.6
DW                  16.500 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST   0 sec
MCWRK           0.01500000 sec
P2                   33.10 usec

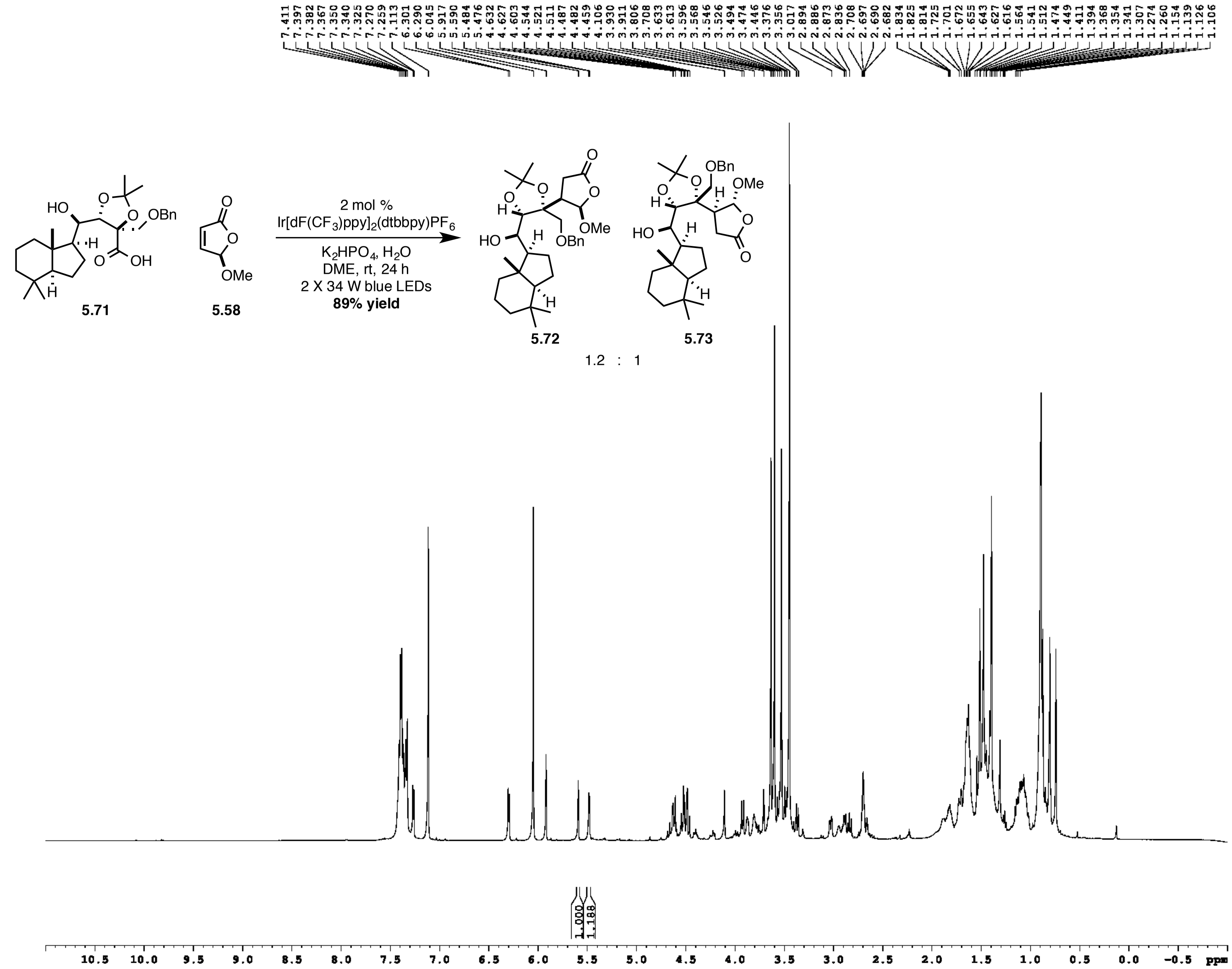
======== CHANNEL f1 ========
NUC1                   13C
P1                   16.55 usec
P11                 500.00 usec
P12                2000.00 usec
PL0                 120.00 dB
PL1                  -1.00 dB
SFO1           125.7942548 MHz
SP1                   2.70 dB
SP2                   2.70 dB
SPNAM[1]  Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                   1.60 dB
PL12                 24.50 dB
SFO2           500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1                 30.00 %
GPZ2                 50.00 %
p15                 500.00 usec
p16                1000.00 usec

F2 - Processing parameters
SI                   65536
SF             125.7803992 MHz
WDW                     EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    2.00
```

YS-IV-63



5.71 **5.58** **5.72** **5.73**

1.2 : 1

```
Current Data Parameters
NAME             YS-IV-63
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160129
Time                14.11
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ              5.0998273 sec
RG                    4.5
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2199993 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

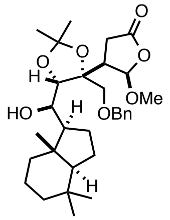
YS-IV-63

```
Current Data Parameters
NAME          YS-IV-63
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20160201
Time              8.41
INSTRUM        cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG           zg30
TD               81728
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           8012.820 Hz
FIDRES        0.098043 Hz
AQ           5.0998273 sec
RG                 5.7
DW              62.400 use
DE                6.00 use
TE               298.0 K
D1          0.10000000 sec
MCREST   0 sec
MCWRK       0.01500000 sec

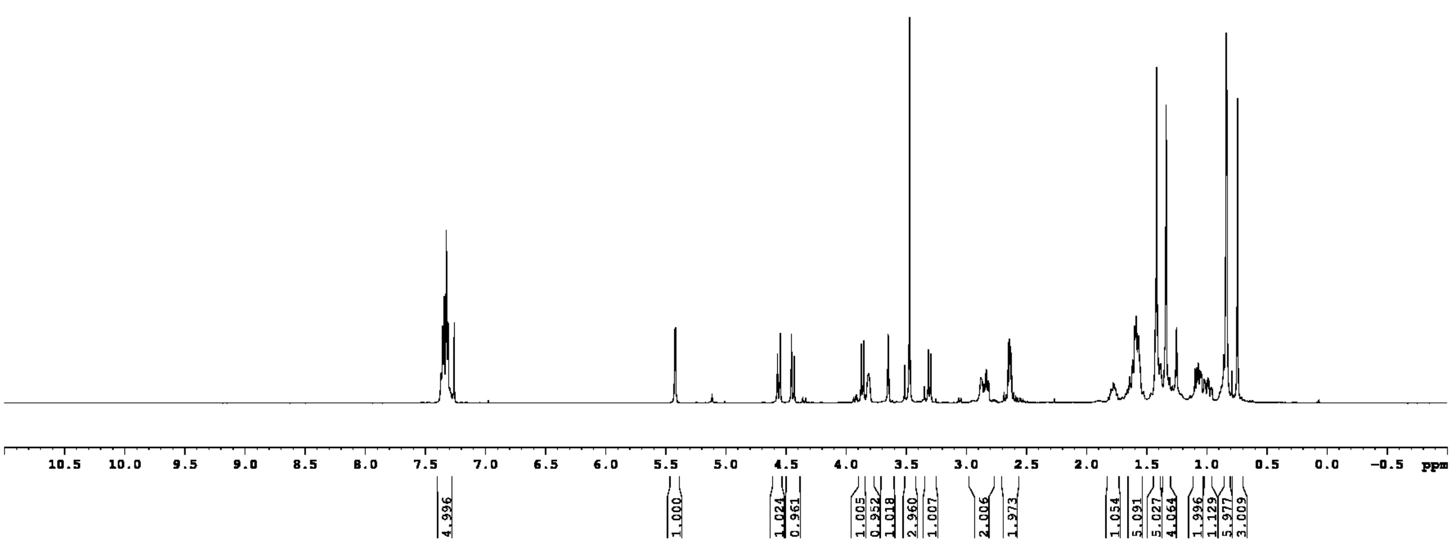
======== CHANNEL f1 ========
NUC1                1H
P1                7.50 use
PL1               1.60 dB
SFO1       500.2235015 MHz

F2 - Processing parameters
SI               65536
SF         500.2200325 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                4.00
```



5.72

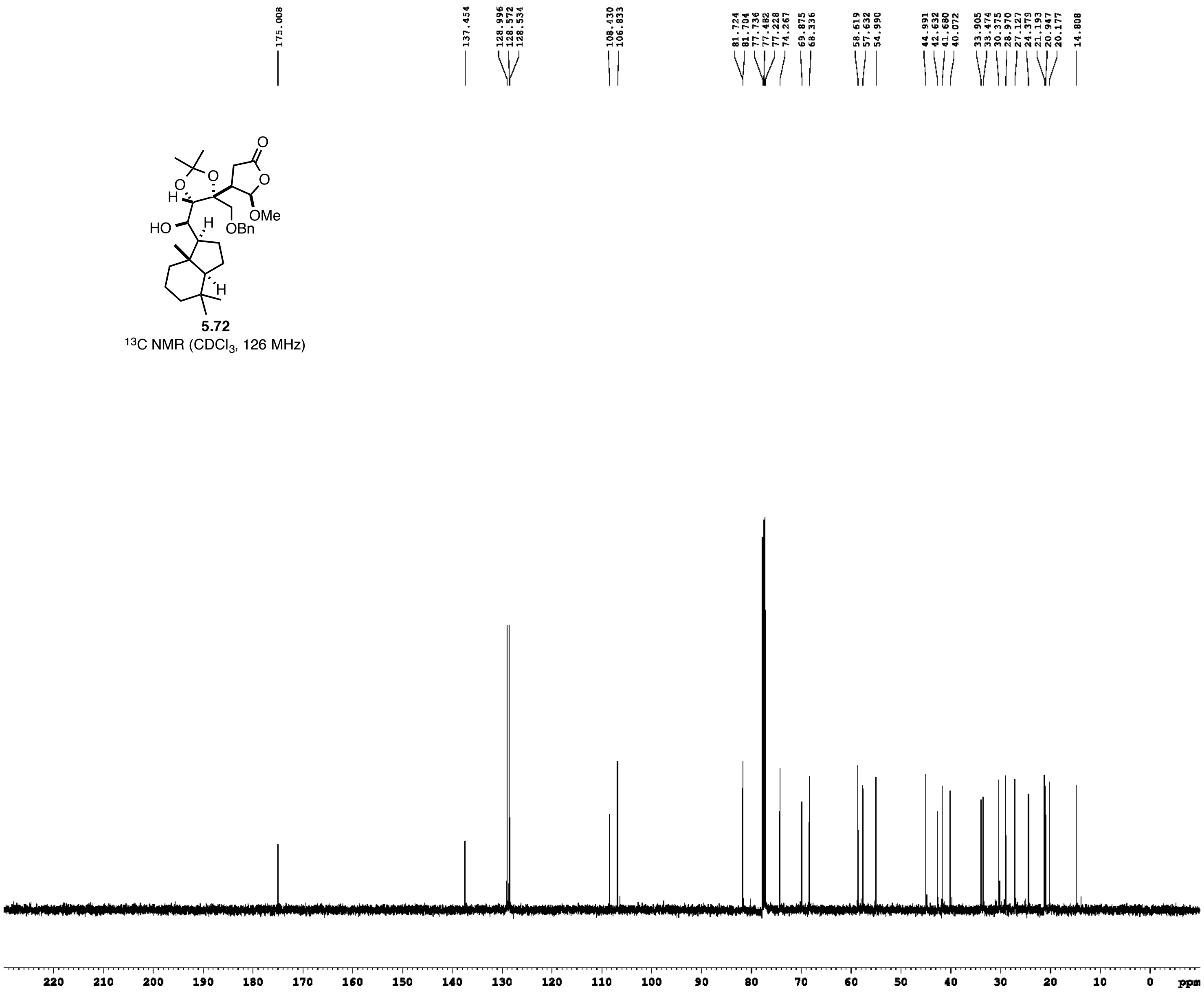
^{1}H NMR ($CDCl_3$, 500 MHz)



YS-IV-63

5.72

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME             YS-IV-63
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160201
Time                 8.44
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                     96
DS                      1
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 7298.2
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

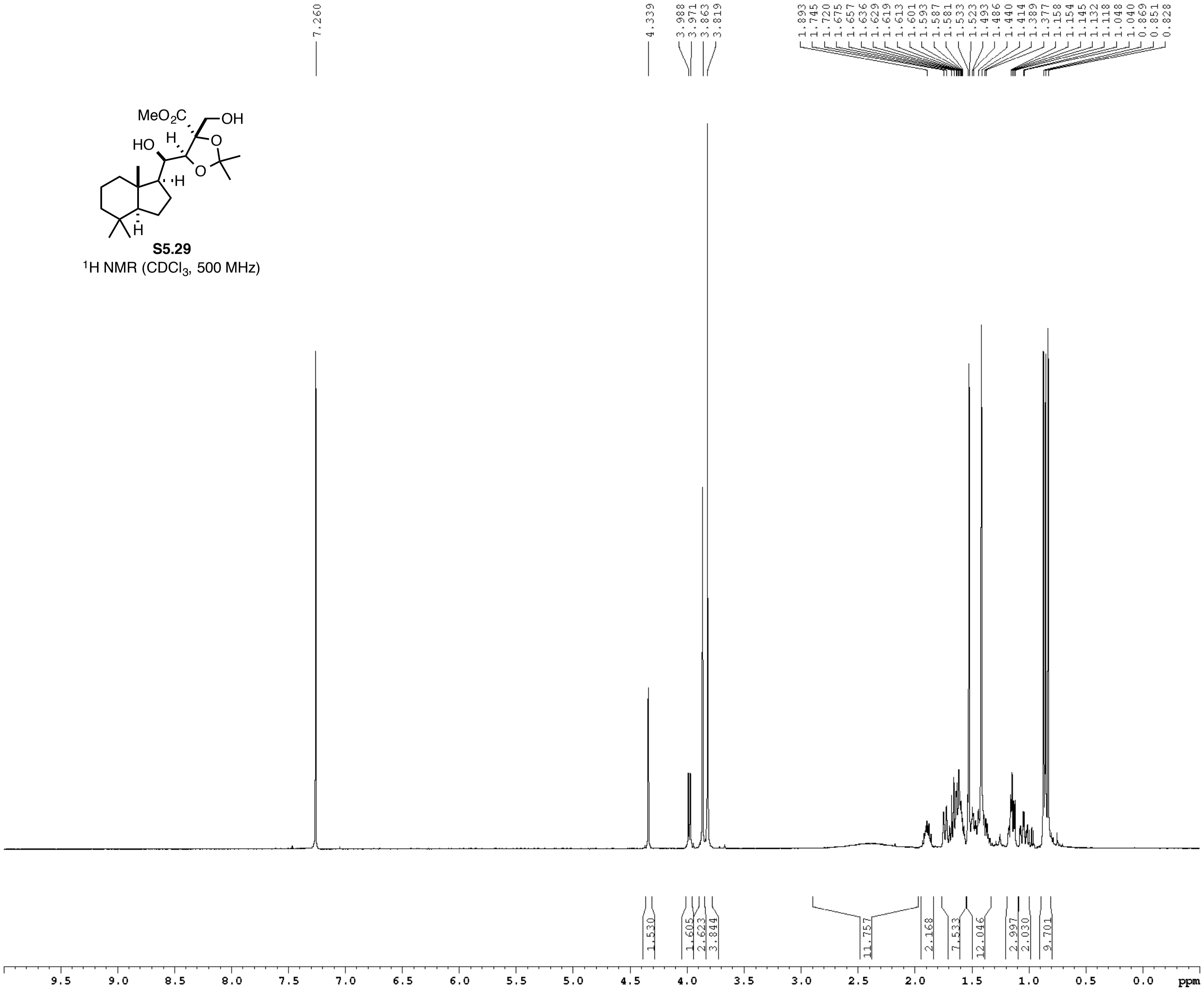
====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7803692 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

1H spectrum

S5.29

^1H NMR ($CDCl_3$, 500 MHz)



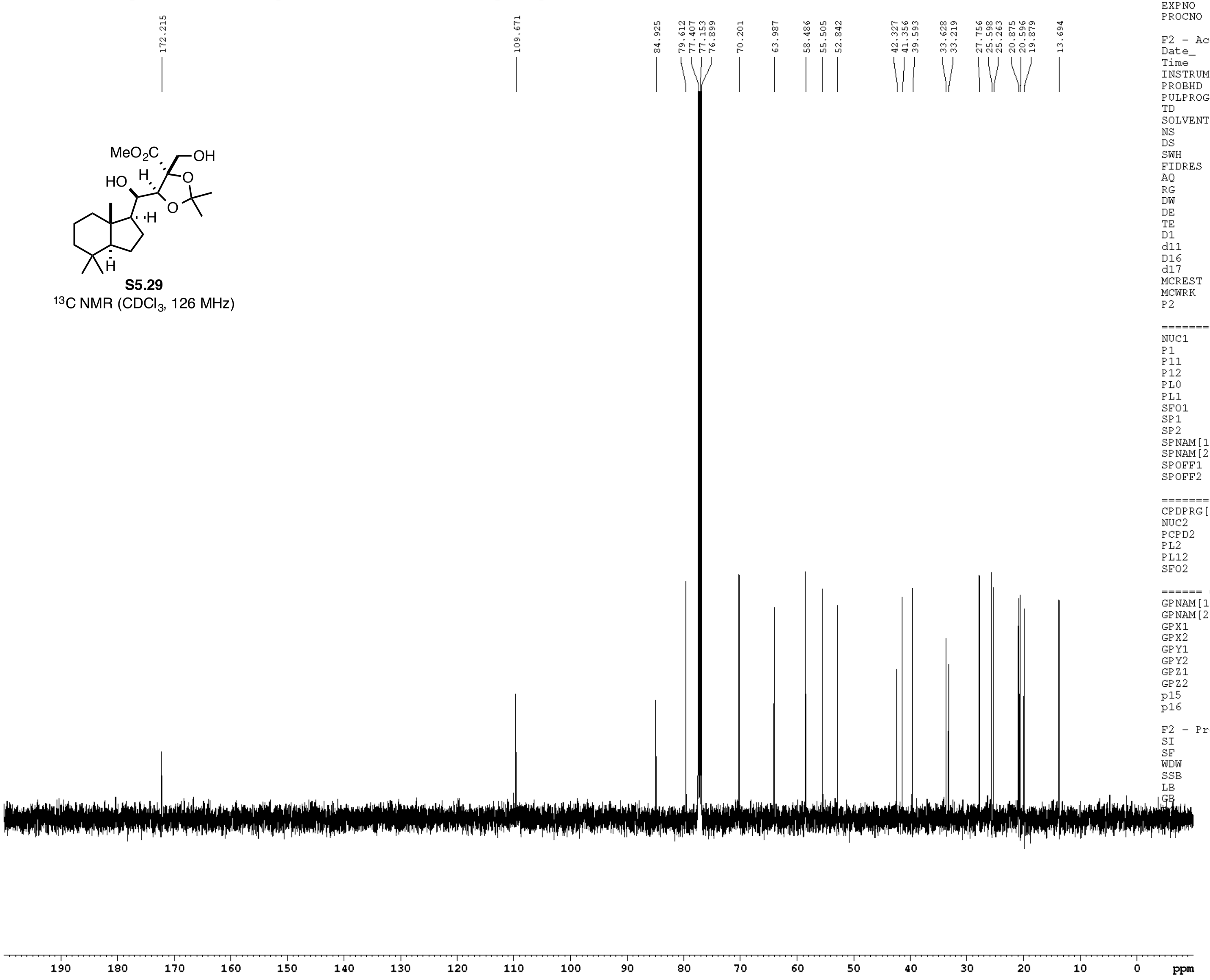
```
Current Data Parameters
NAME          DJT-VI-123
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151216
Time               12.47
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200316 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



S5.29

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-123
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151216
Time               12.53
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   922
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                2298.8
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

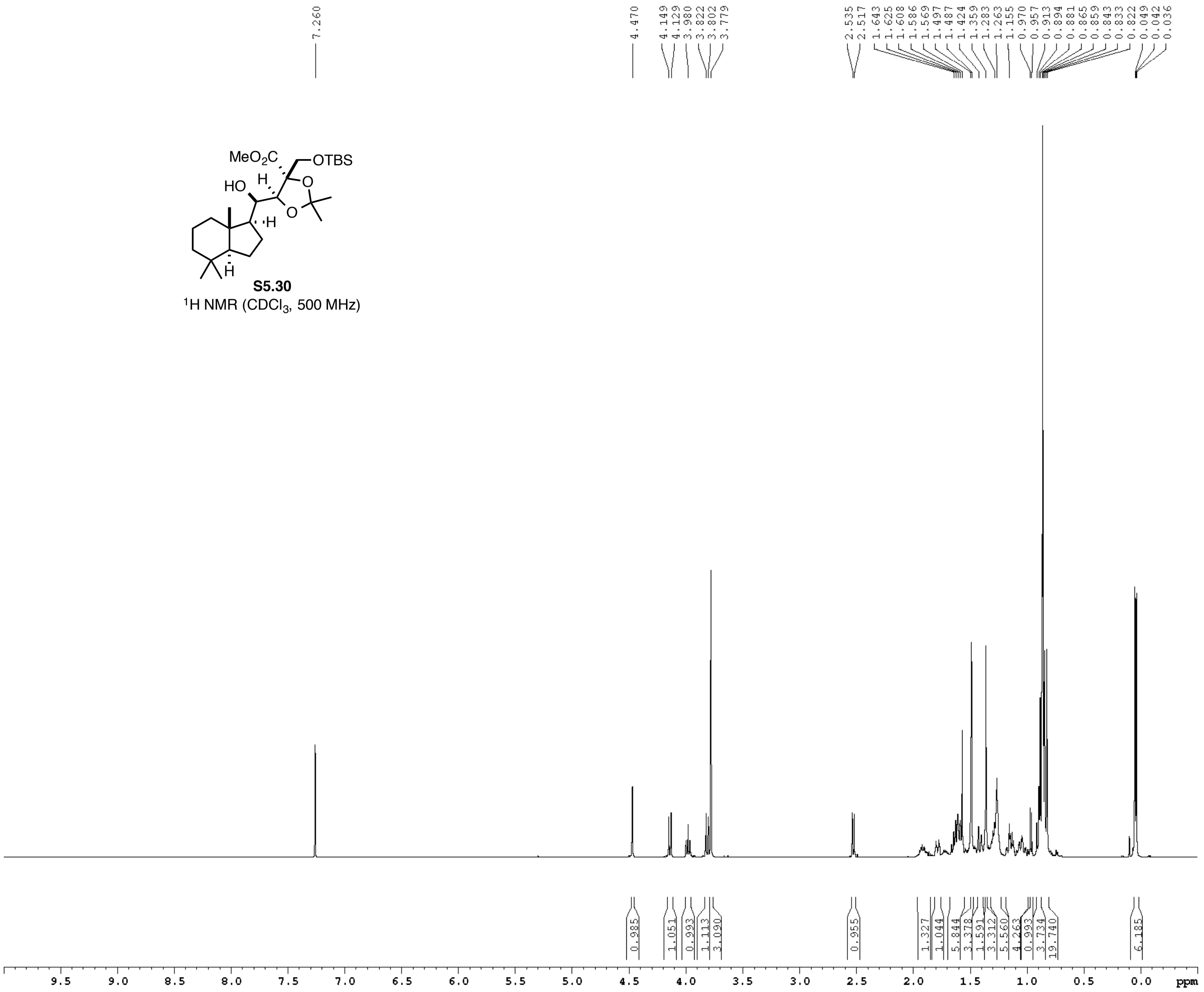
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804084 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum



S5.30

^{1}H NMR (CDCl$_3$, 500 MHz)

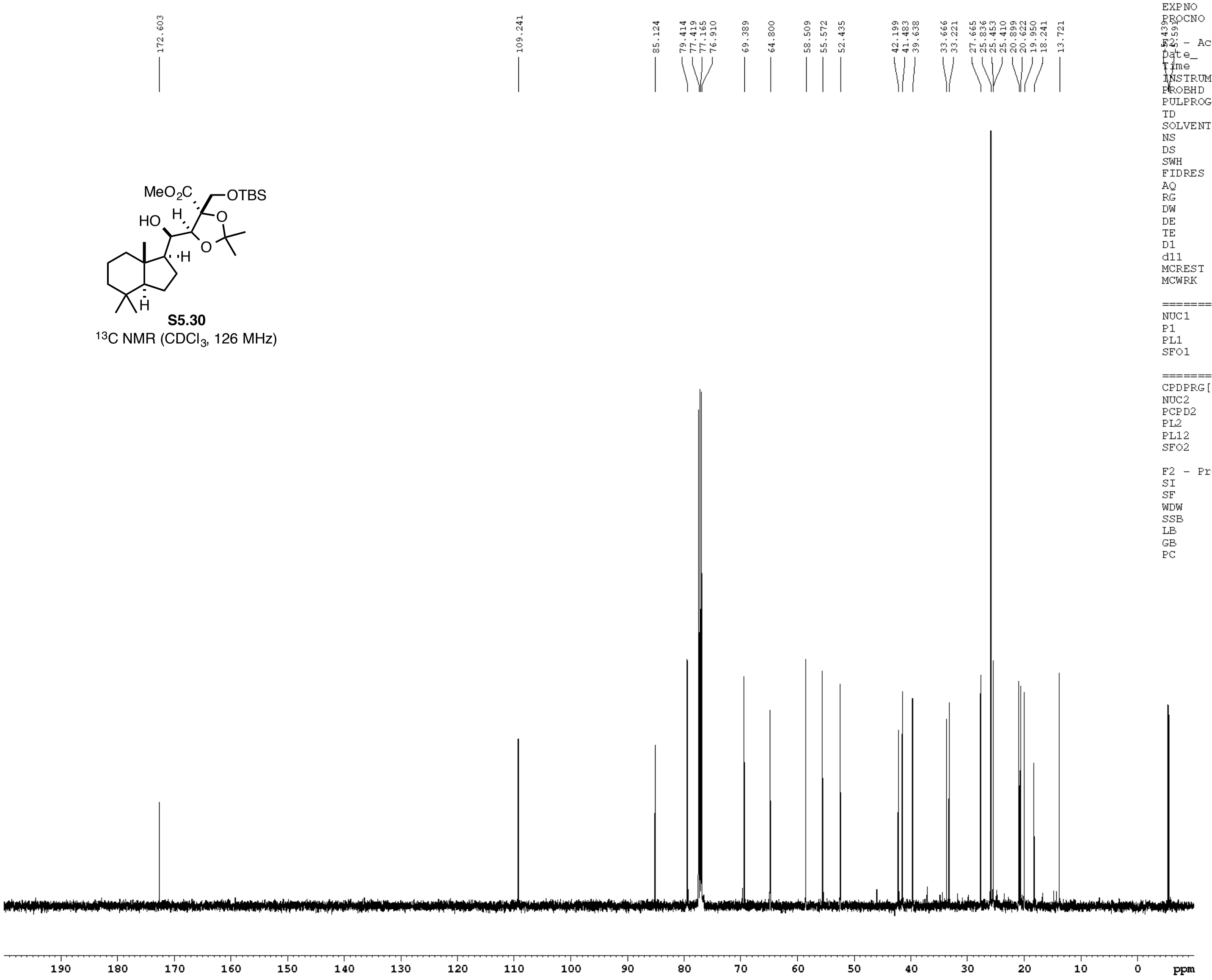
```
Current Data Parameters
NAME          DJT-VI-131
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151204
Time               18.18
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 32048
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.250026 Hz
AQ             1.9997952 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200318 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

13C spectrum with 1H decoupling



S5.30

^{13}C NMR (CDCl$_3$, 126 MHz)

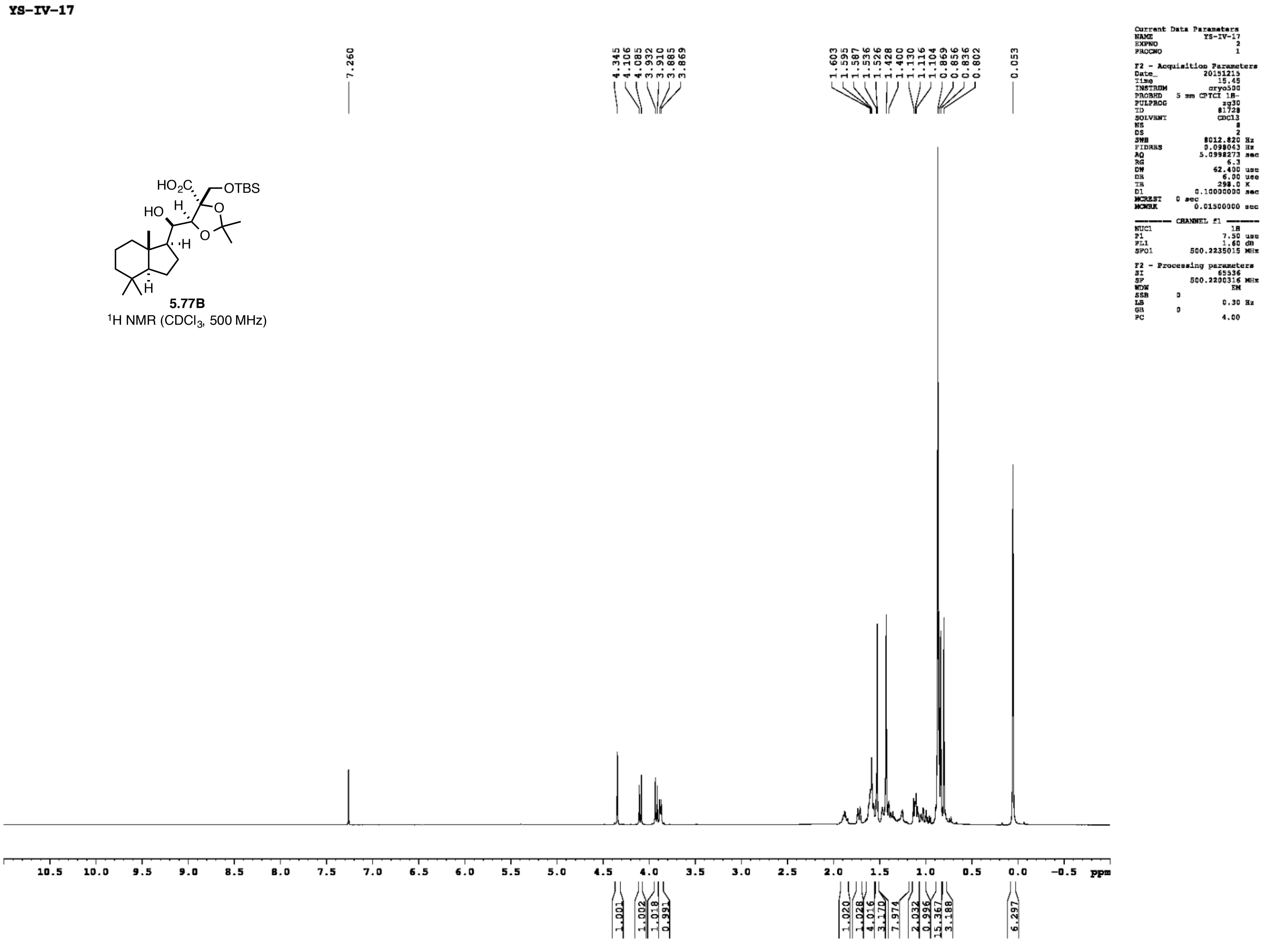
```
Current Data Parameters
NAME          DJT-VI-131
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151218
Time                8.27
INSTRUM            gn500
PROBHD   5 mm broadband
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   622
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                4597.6
DW                16.500 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.00 usec
PL1                -0.60 dB
SFO1         125.5327181 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               12.80 dB
SFO2         499.1824959 MHz

F2 - Processing parameters
SI                 65536
SF           125.5188974 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```



```
Current Data Parameters
NAME              YS-IV-17
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151215
Time                 15.45
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                     6.3
DW                  62.400 use
DE                    6.00 use
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

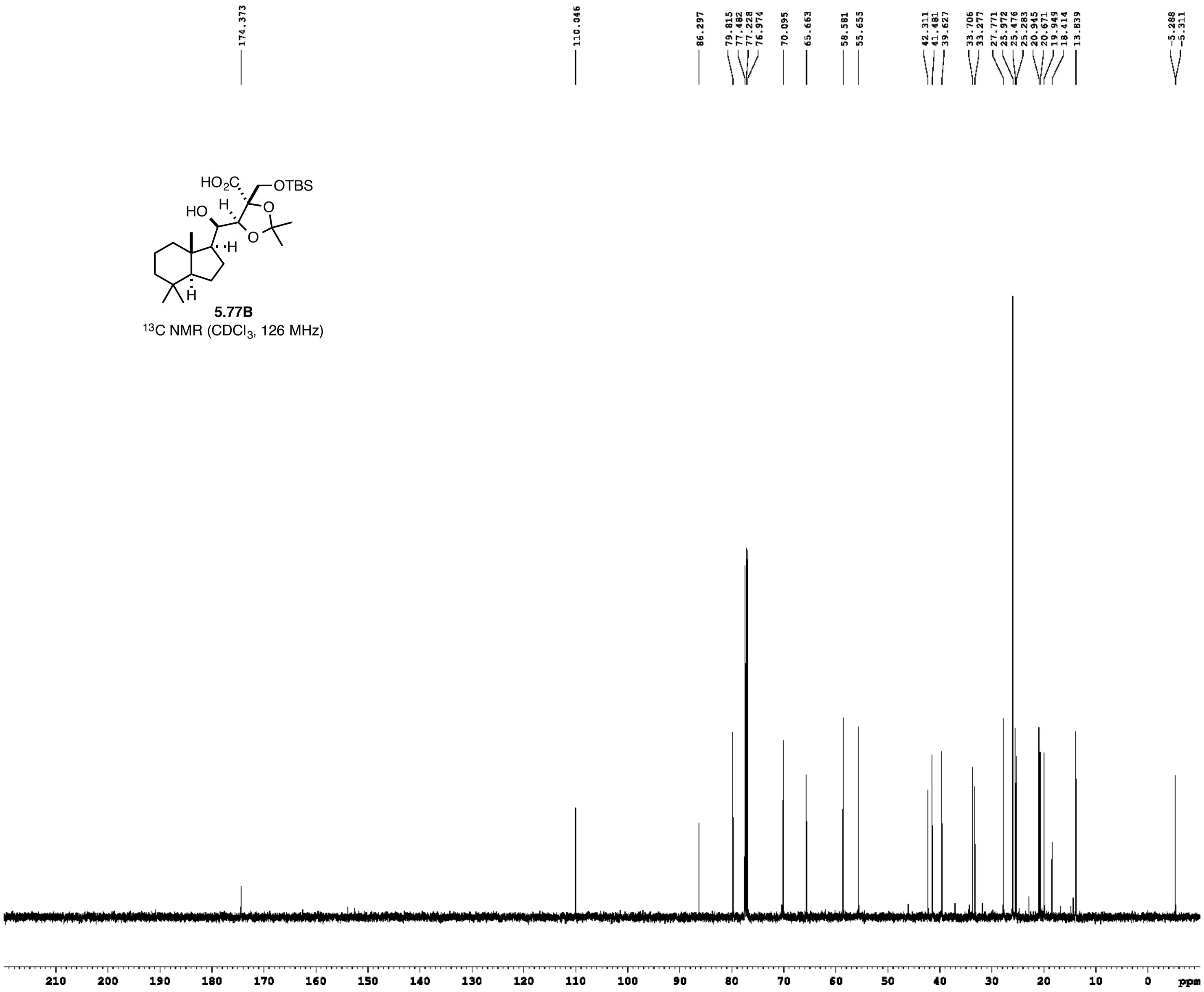
======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 use
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200316 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

5.77B

^{1}H NMR ($CDCl_3$, 500 MHz)

YS-IV-17



5.77B

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            YS-IV-17
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151215
Time               15.48
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   216
DS                     2
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

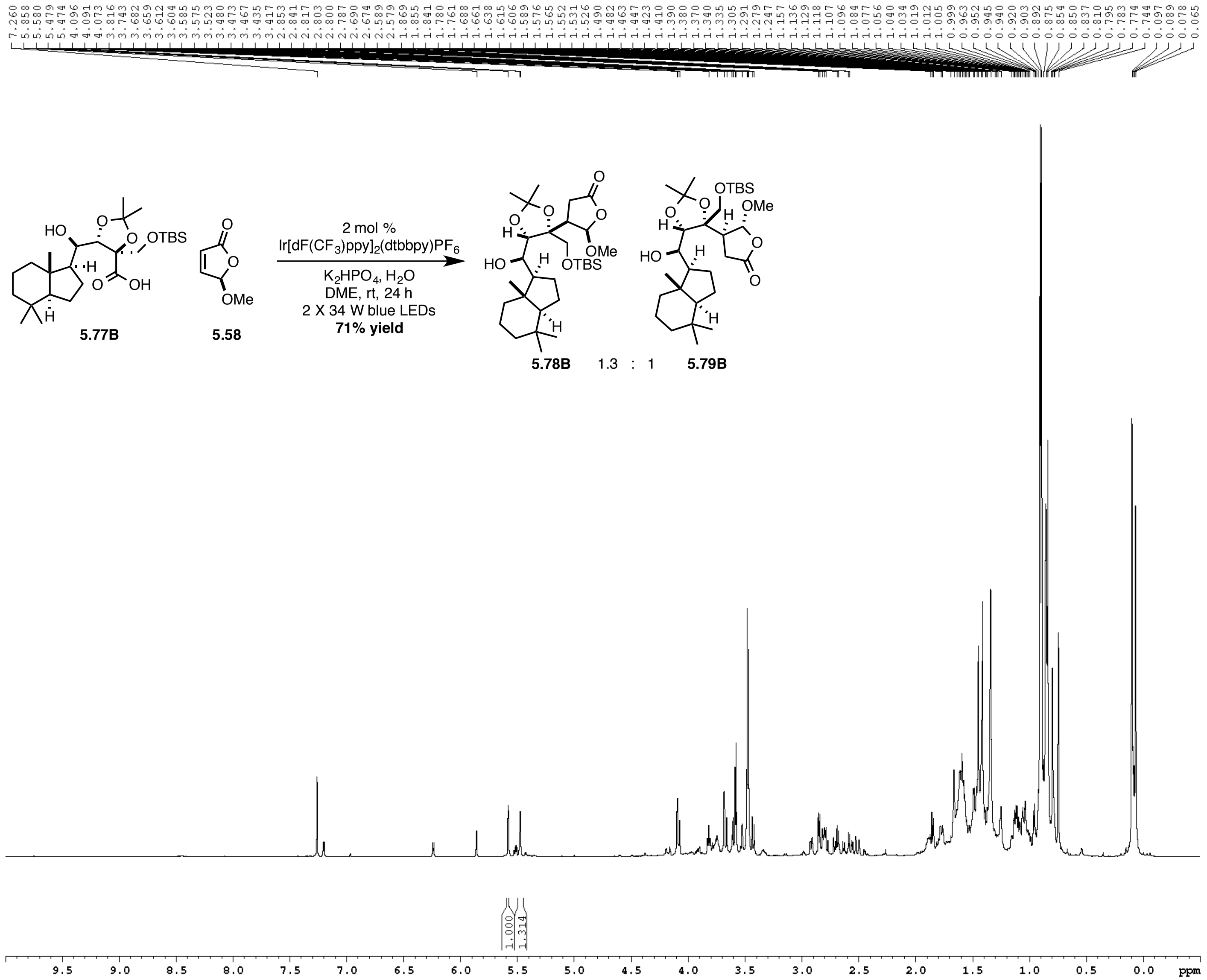
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF          125.7803994 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



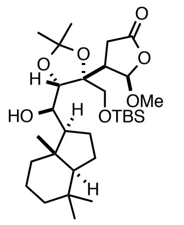
```
Current Data Parameters
NAME          DJT-VI-144
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151211
Time                8.59
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                  71.8
DW                52.000 usec
DE                 14.54 usec
TE                 298.1 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         24.00000000 W

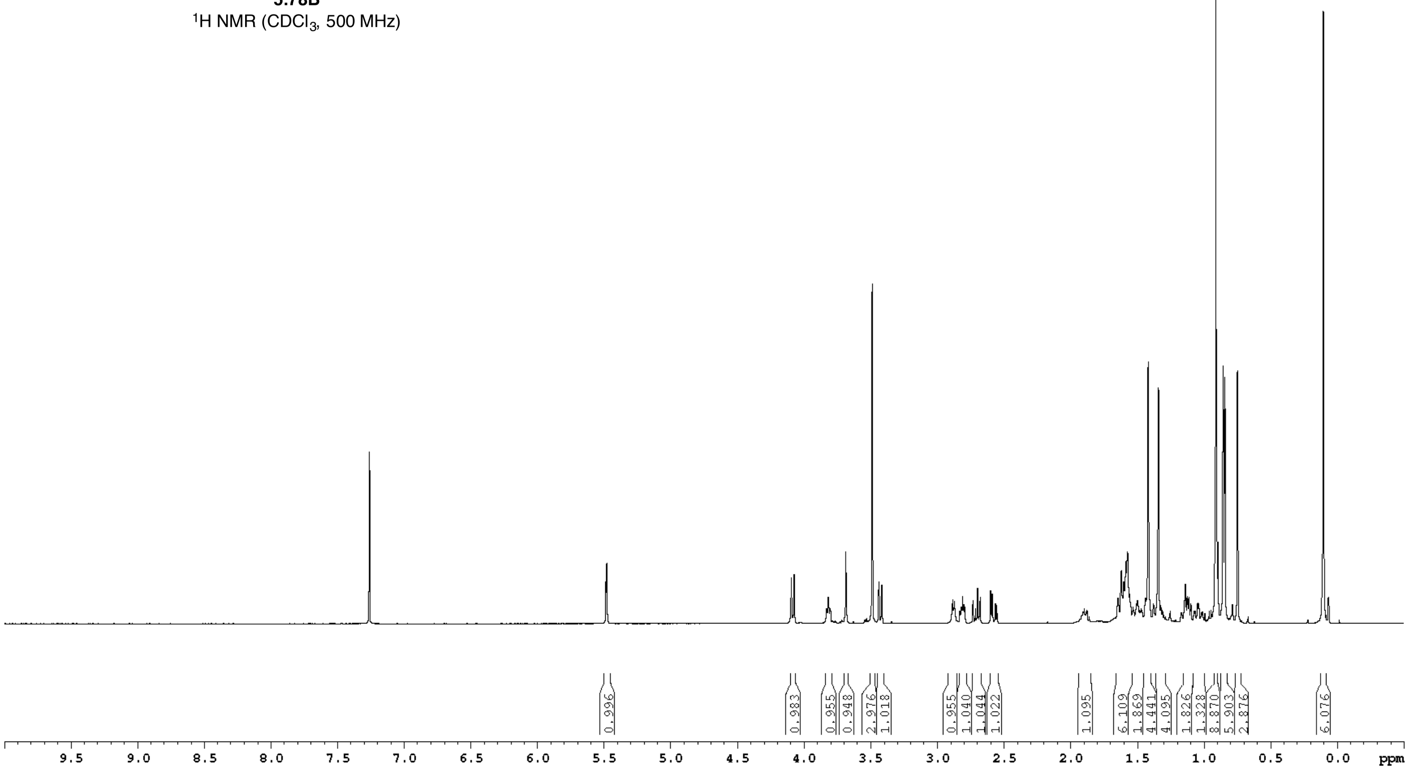
F2 - Processing parameters
SI                 65536
SF           600.1300358 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

1H spectrum



5.78B

^{1}H NMR (CDCl$_3$, 500 MHz)



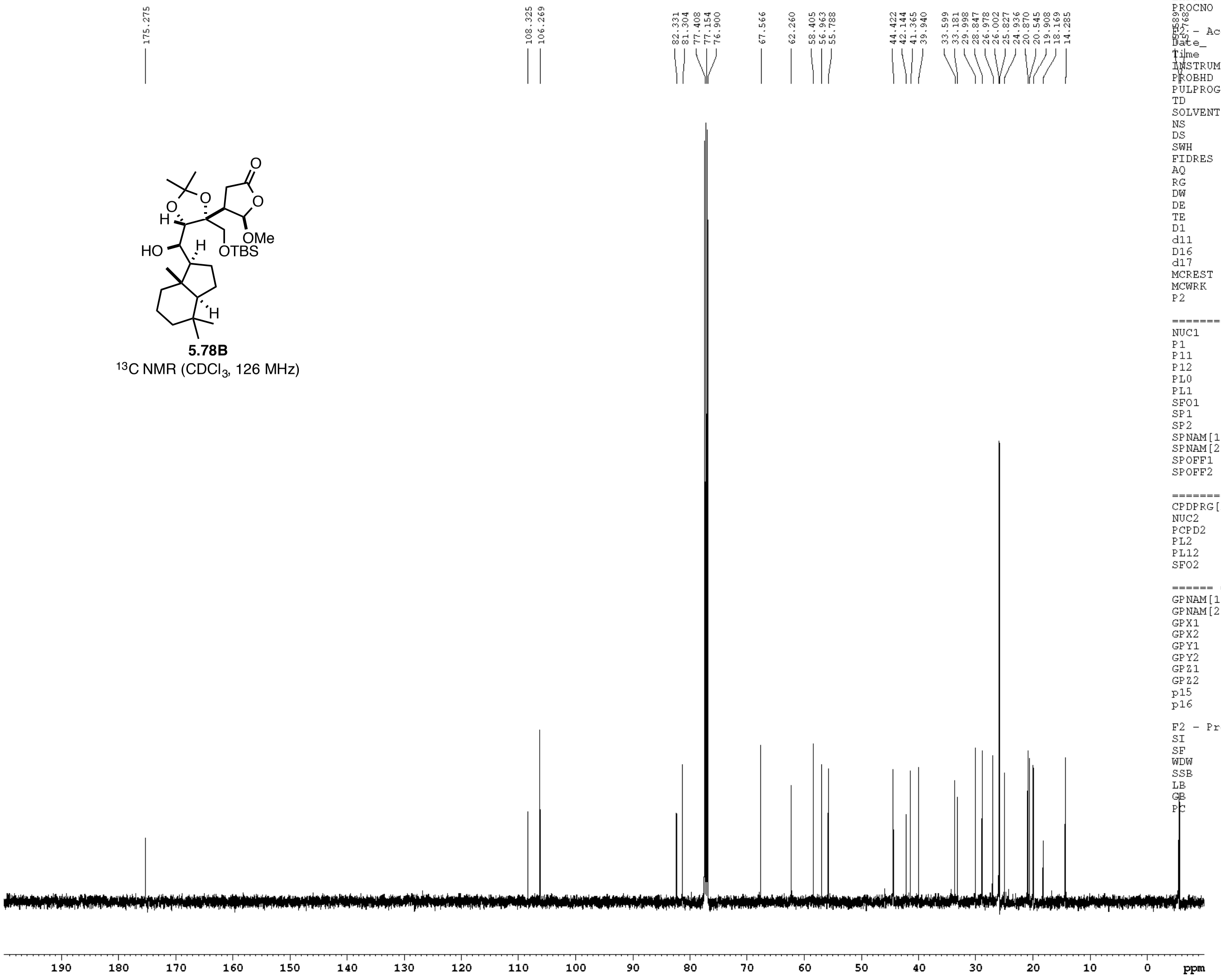
```
Current Data Parameters
NAME          DJT-VI-144
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time                8.06
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   7.1
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200316 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.78B

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-144
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time                8.13
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   518
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               10321.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

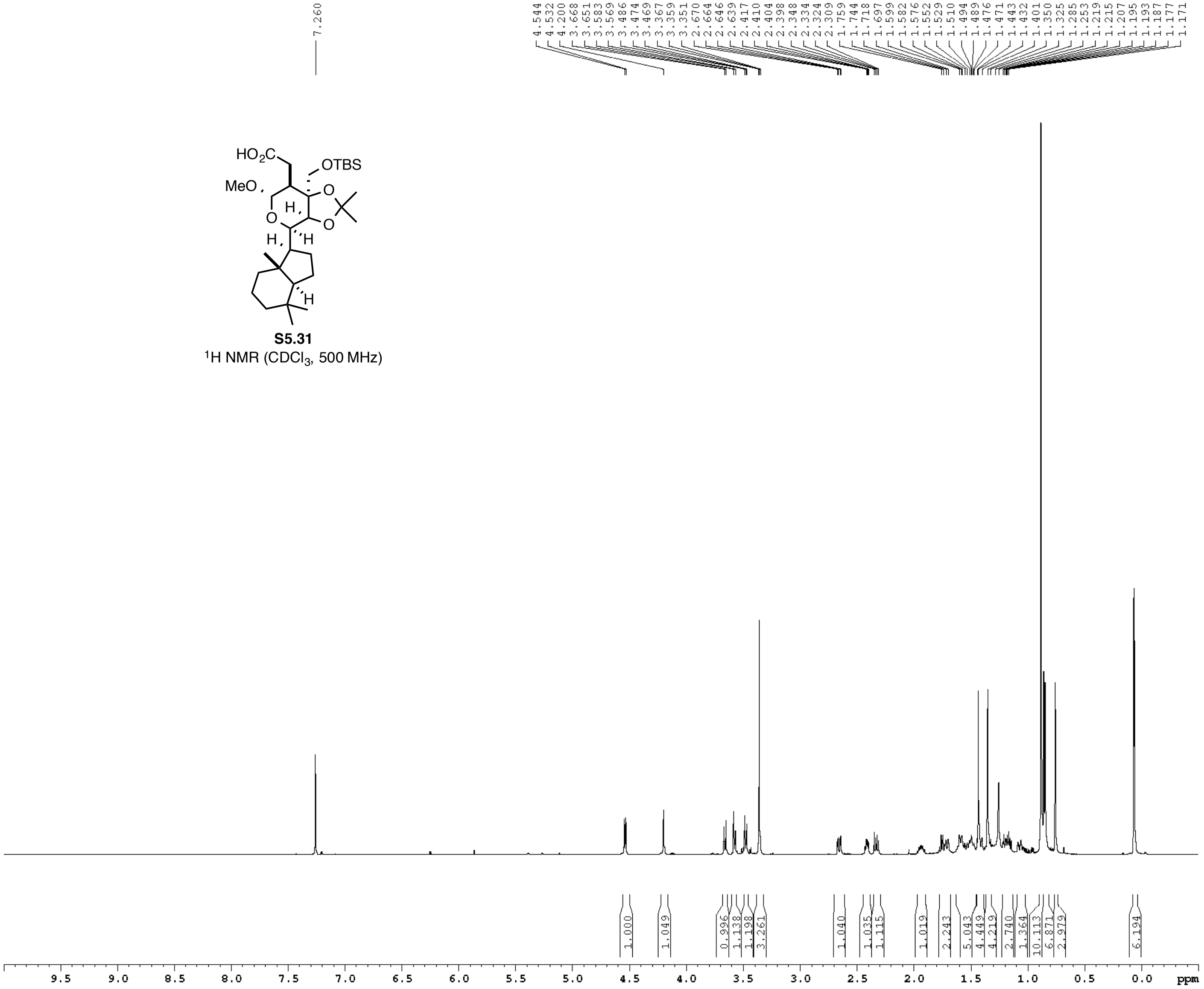
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]   Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



S5.31

^{1}H NMR ($CDCl_3$, 500 MHz)

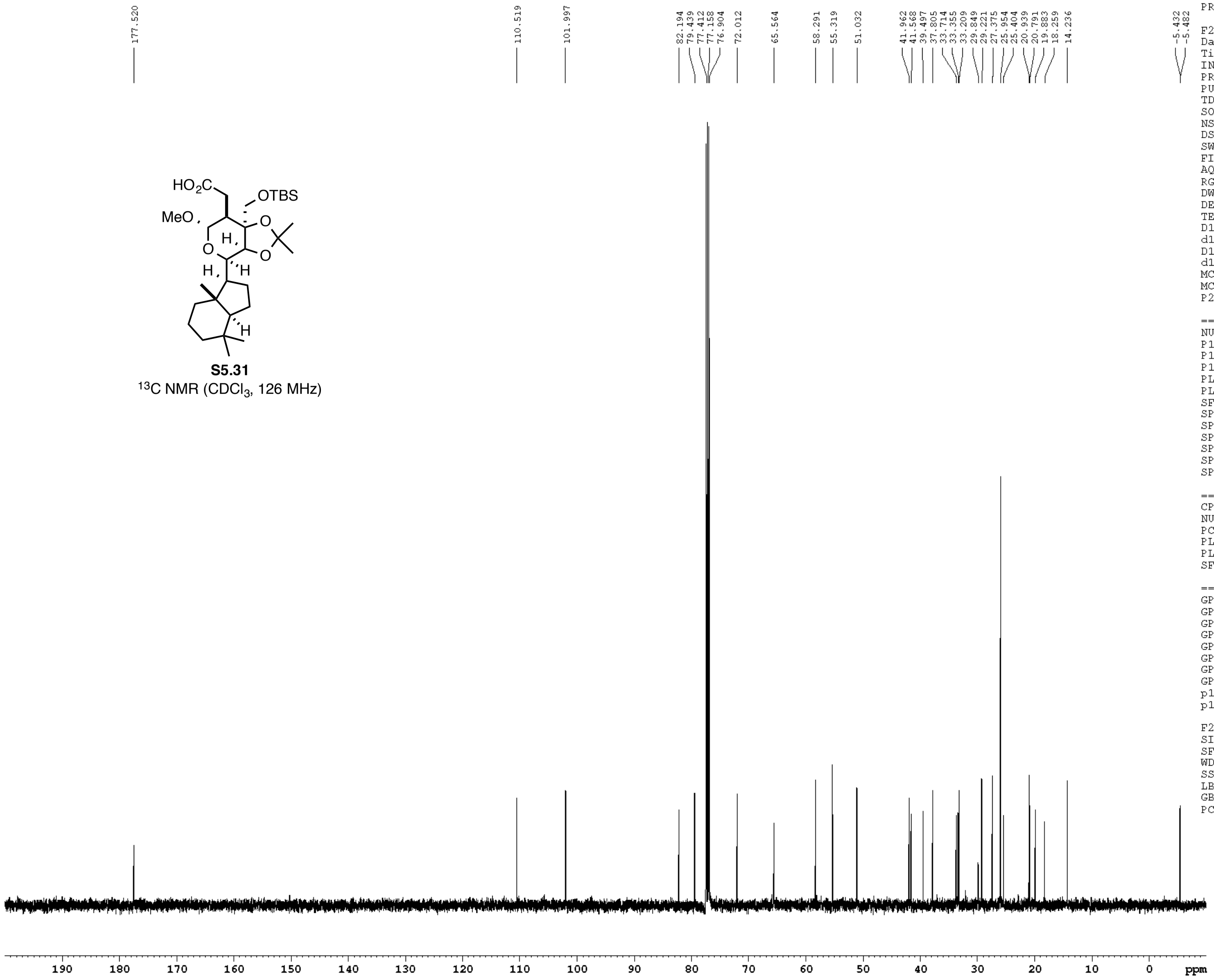
```
Current Data Parameters
NAME          DJT-VI-152
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160107
Time               12.56
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 38460
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             9615.385 Hz
FIDRES          0.250010 Hz
AQ             1.9999200 sec
RG                   456
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300357 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

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



S5.31

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME           DJT-VI-152
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160107
Time                14.14
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    253
DS                      0
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                   4096
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

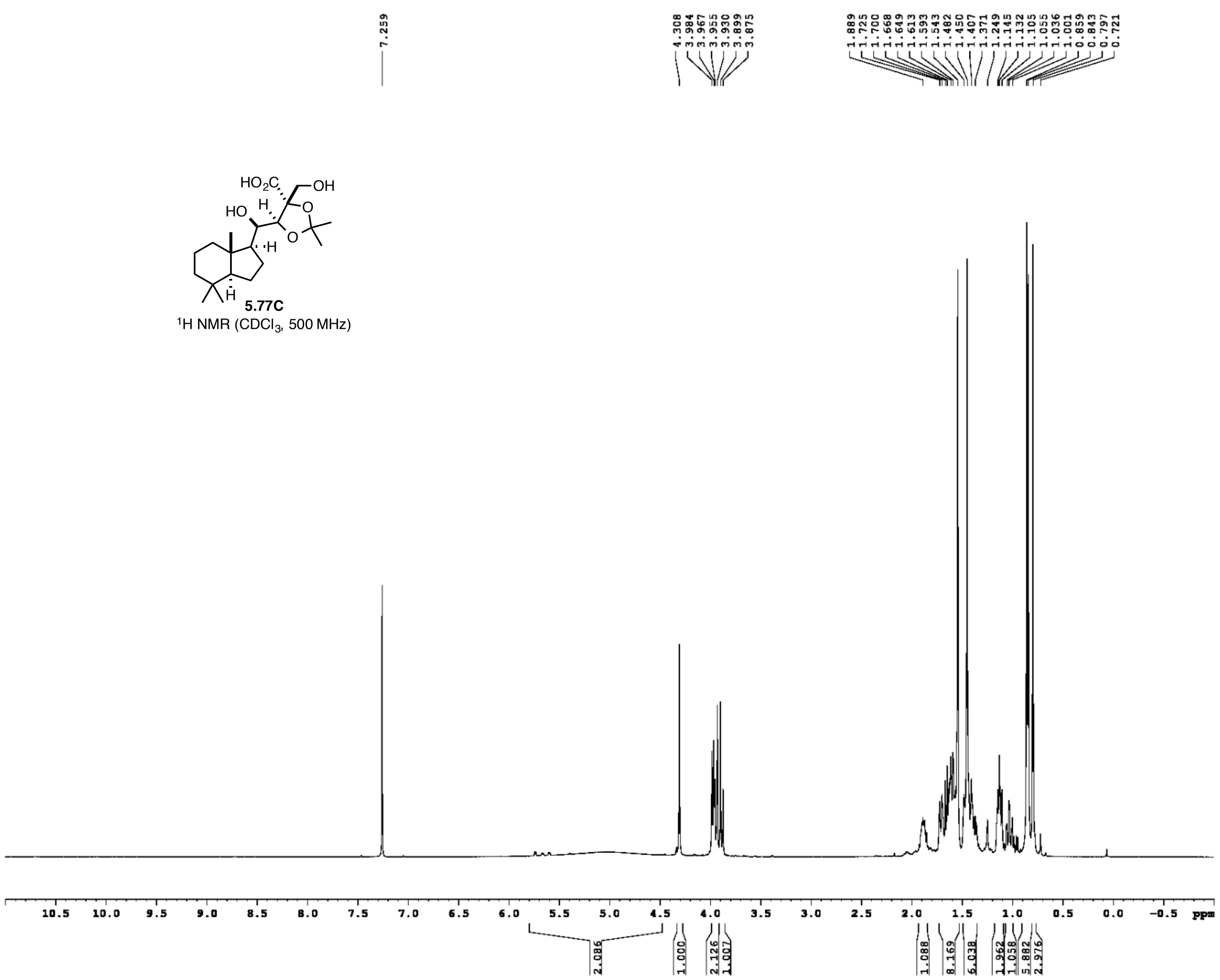
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1]  Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7804071 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   2.00
```

YS–IV–13



5.77C

^{1}H NMR (CDCl$_3$, 500 MHz)

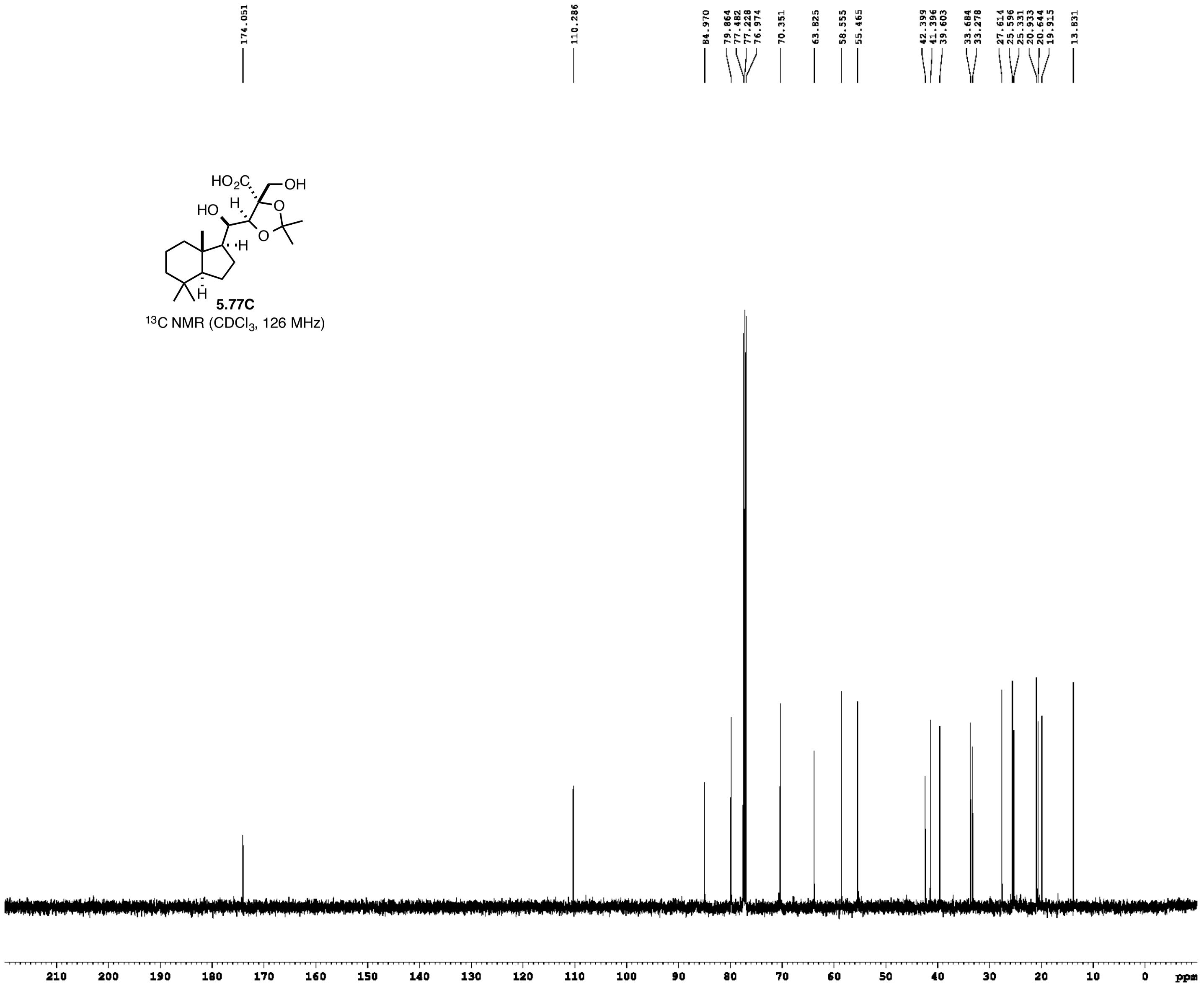
```
Current Data Parameters
NAME              YS-IV-13
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151216
Time                  8.43
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                     7.1
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200321 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-IV-13



5.77C

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME            YS-IV-13
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151216
Time                8.47
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDC13
NS                   320
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               10321.3
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

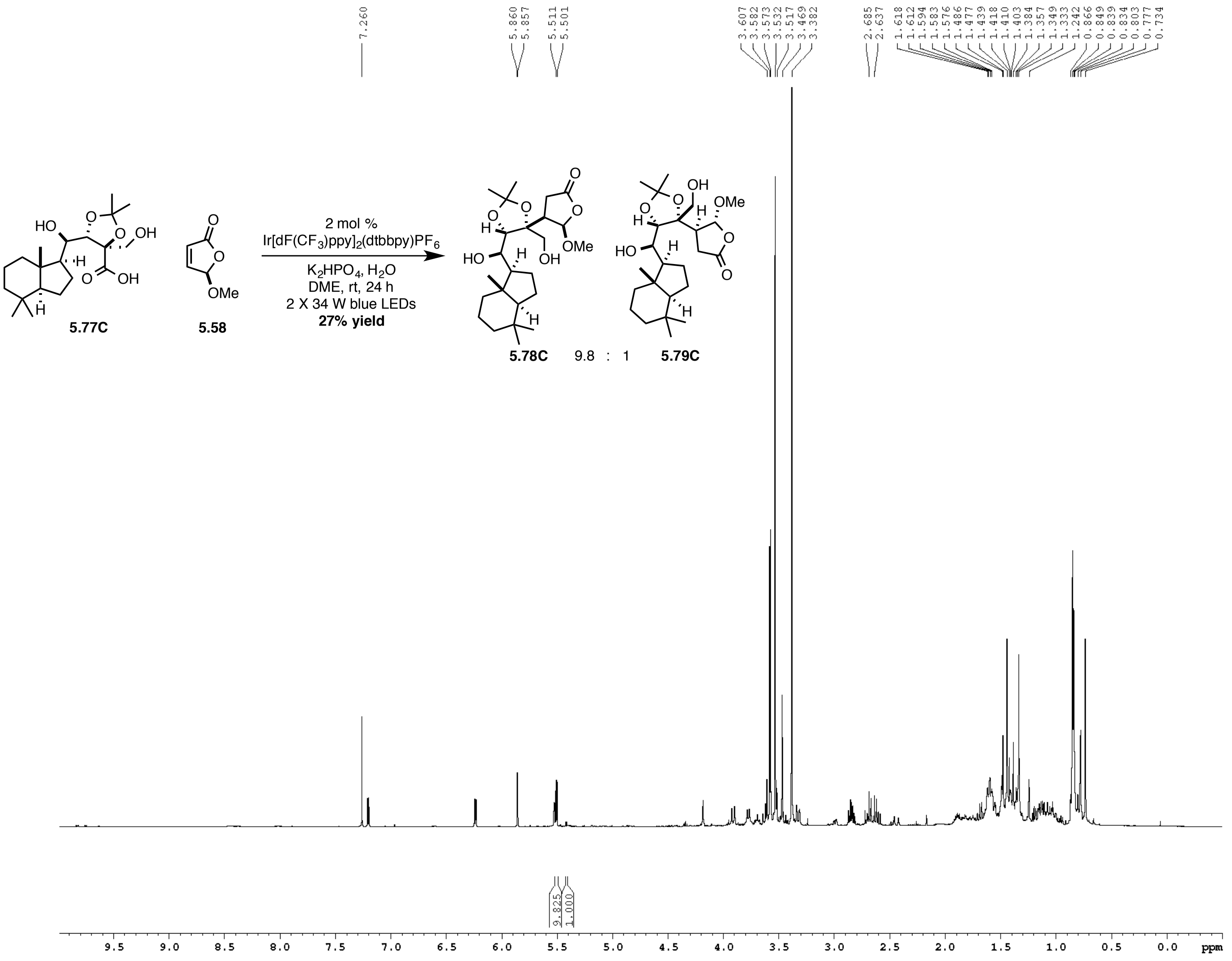
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7803996 MHz
WDW                   EM
SSB        0
LB                  1.00 Hz
GB         0
PC                  2.00
```

1H spectrum



5.77C **5.58** **5.78C** **5.79C**

```
Current Data Parameters
NAME          DJT-VI-173
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160121
Time                8.05
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   6.3
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

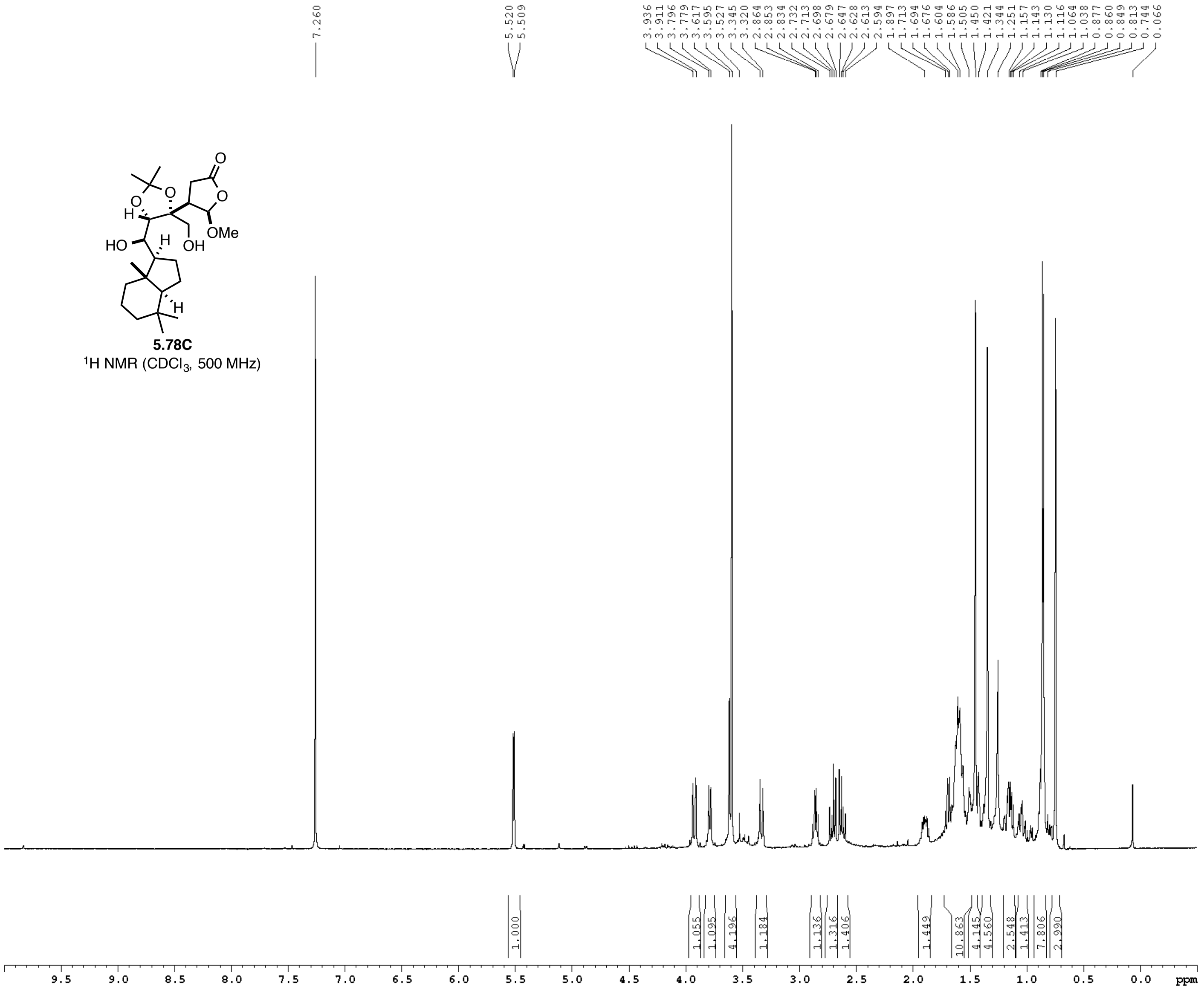
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200312 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

1H spectrum

5.78C

^{1}H NMR (CDCl$_3$, 500 MHz)



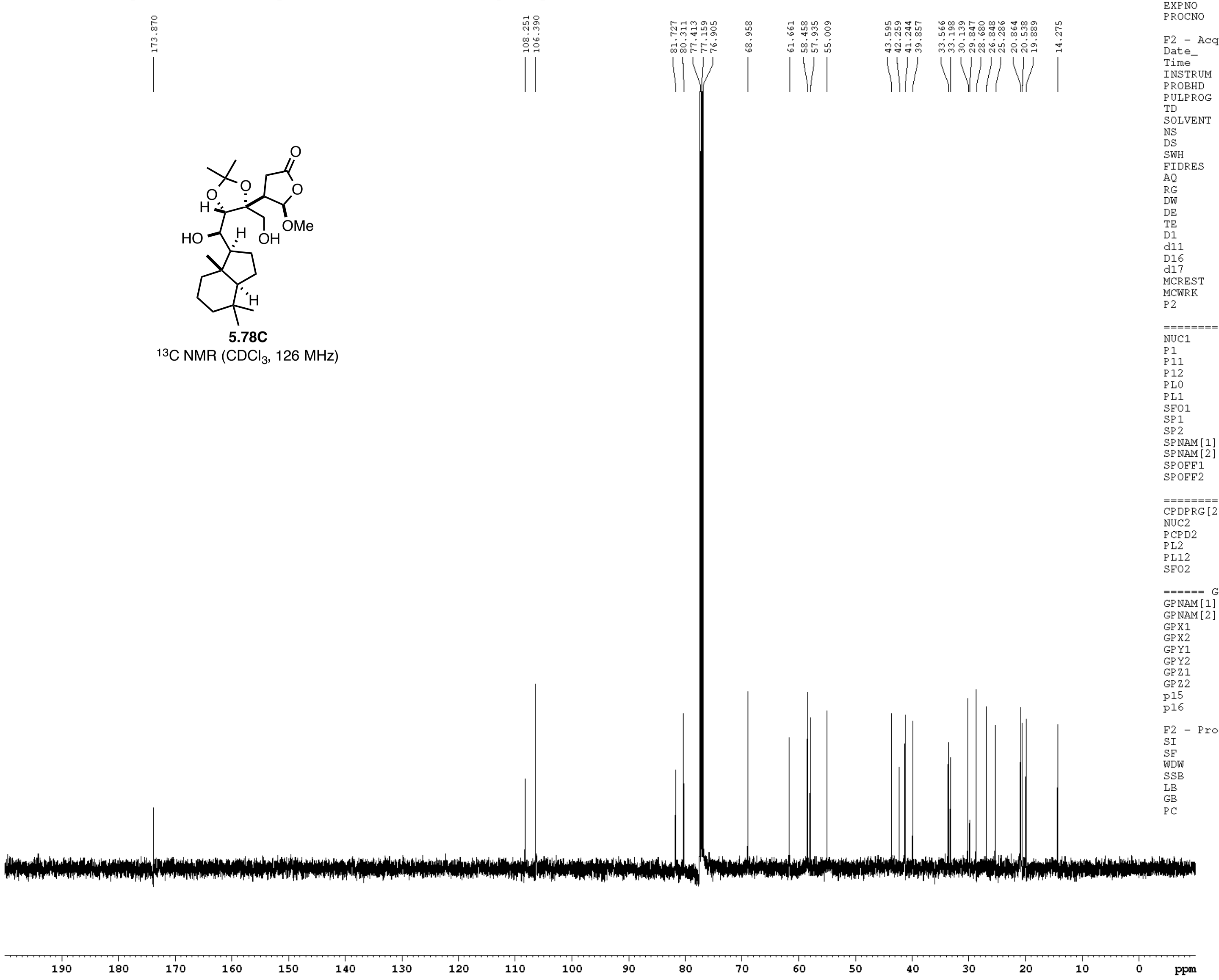
```
Current Data Parameters
NAME          DJT-VI-173
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160121
Time                9.54
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF          500.2200313 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.78C

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME         DJT-VI-173
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20160121
Time               9.59
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  632
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               2298.8
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

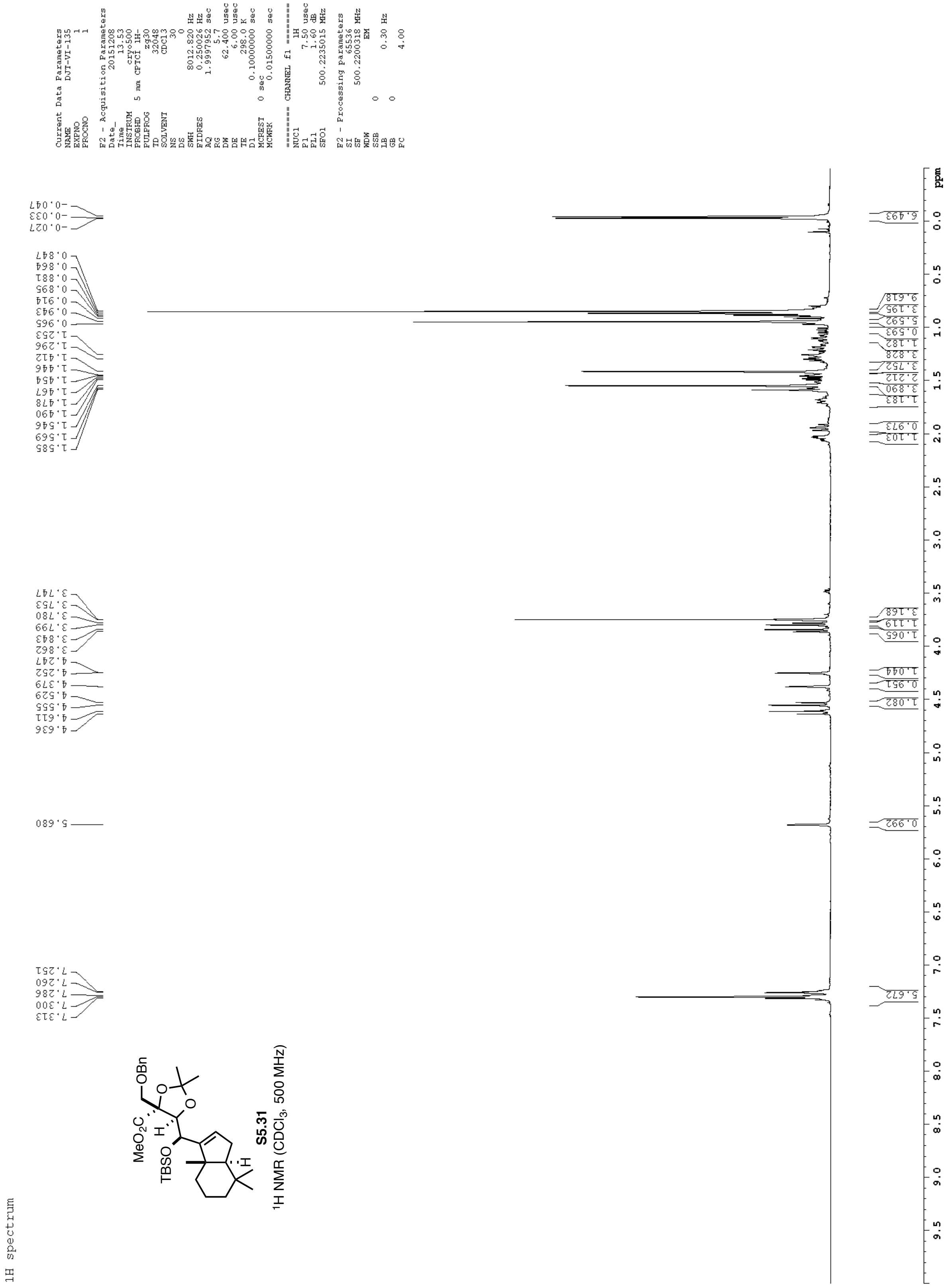
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804080 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

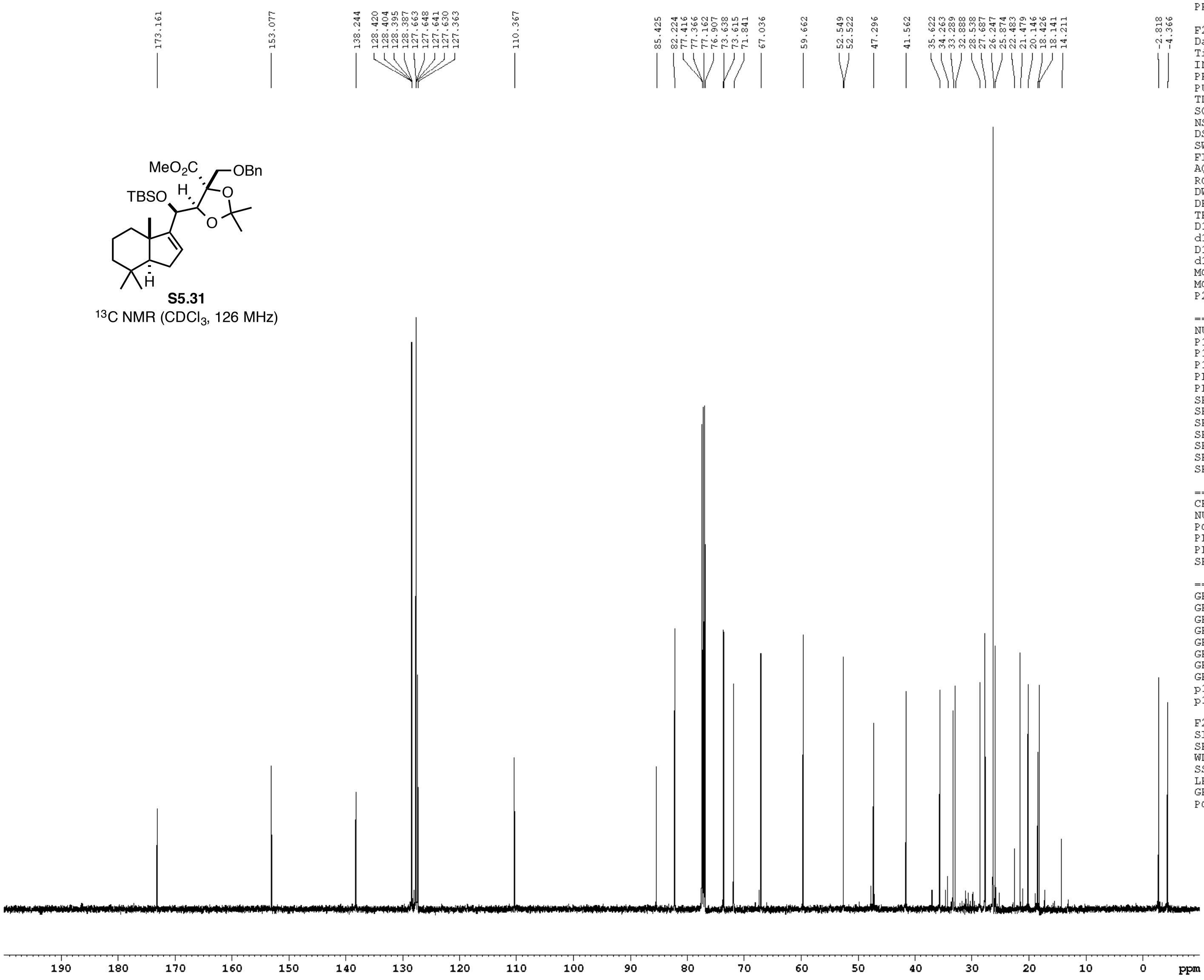
1H spectrum



S5.31

^{1}H NMR (CDCl$_3$, 500 MHz)

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



S5.31

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-135
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151208
Time               13.57
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   581
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                5160.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

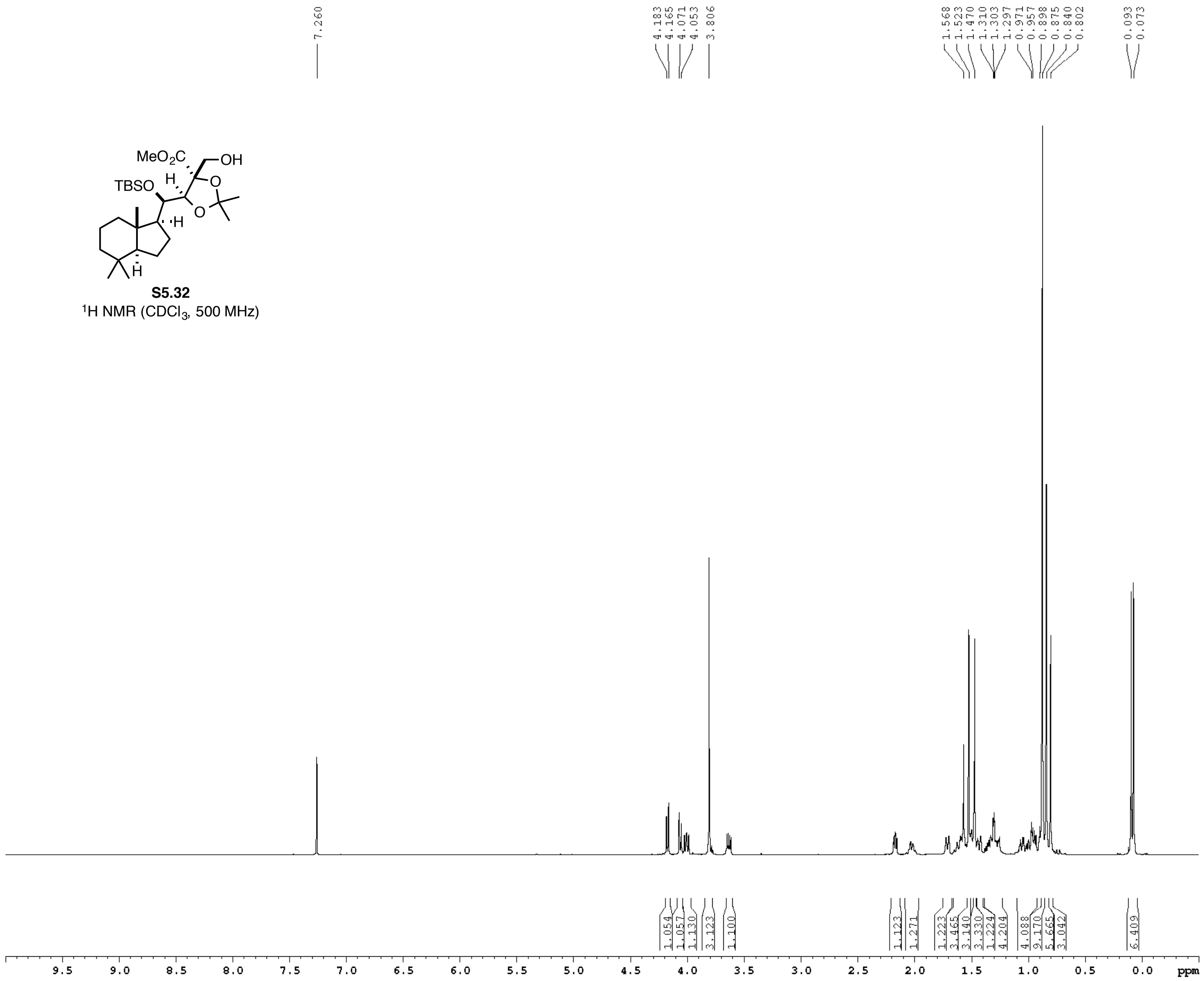
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804090 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

S5.32

^{1}H NMR ($CDCl_3$, 500 MHz)



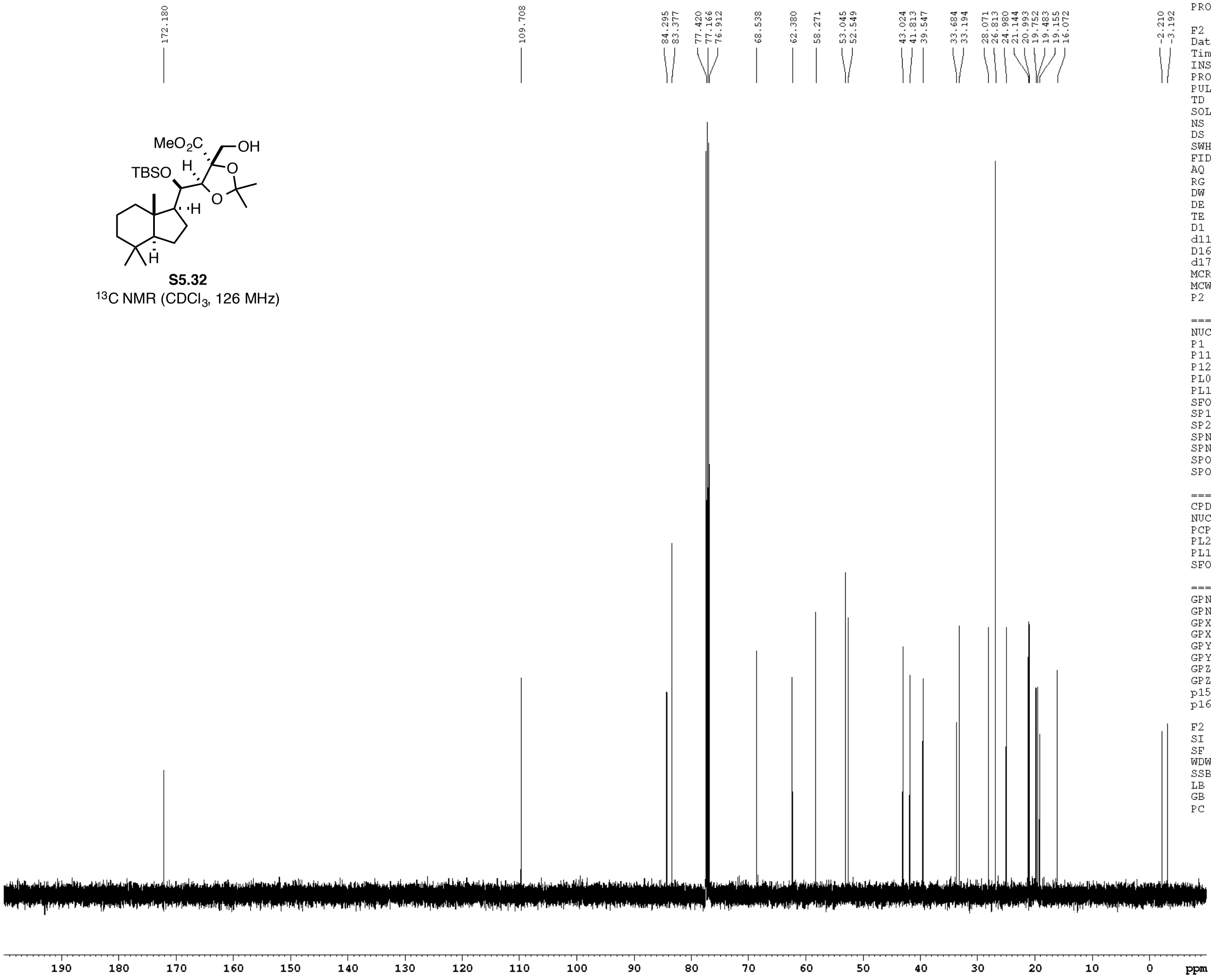
```
Current Data Parameters
NAME          DJT-VI-133
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151207
Time               13.32
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 40062
SOLVENT            CDCl3
NS                    30
DS                     0
SWH             8012.820 Hz
FIDRES          0.200010 Hz
AQ             2.4998689 sec
RG                     8
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200317 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



S5.32

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-133
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151207
Time               13.36
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   333
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                3649.1
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804071 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  2.00
```

1H spectrum

5.77D

^{1}H NMR (CDCl$_3$, 500 MHz)

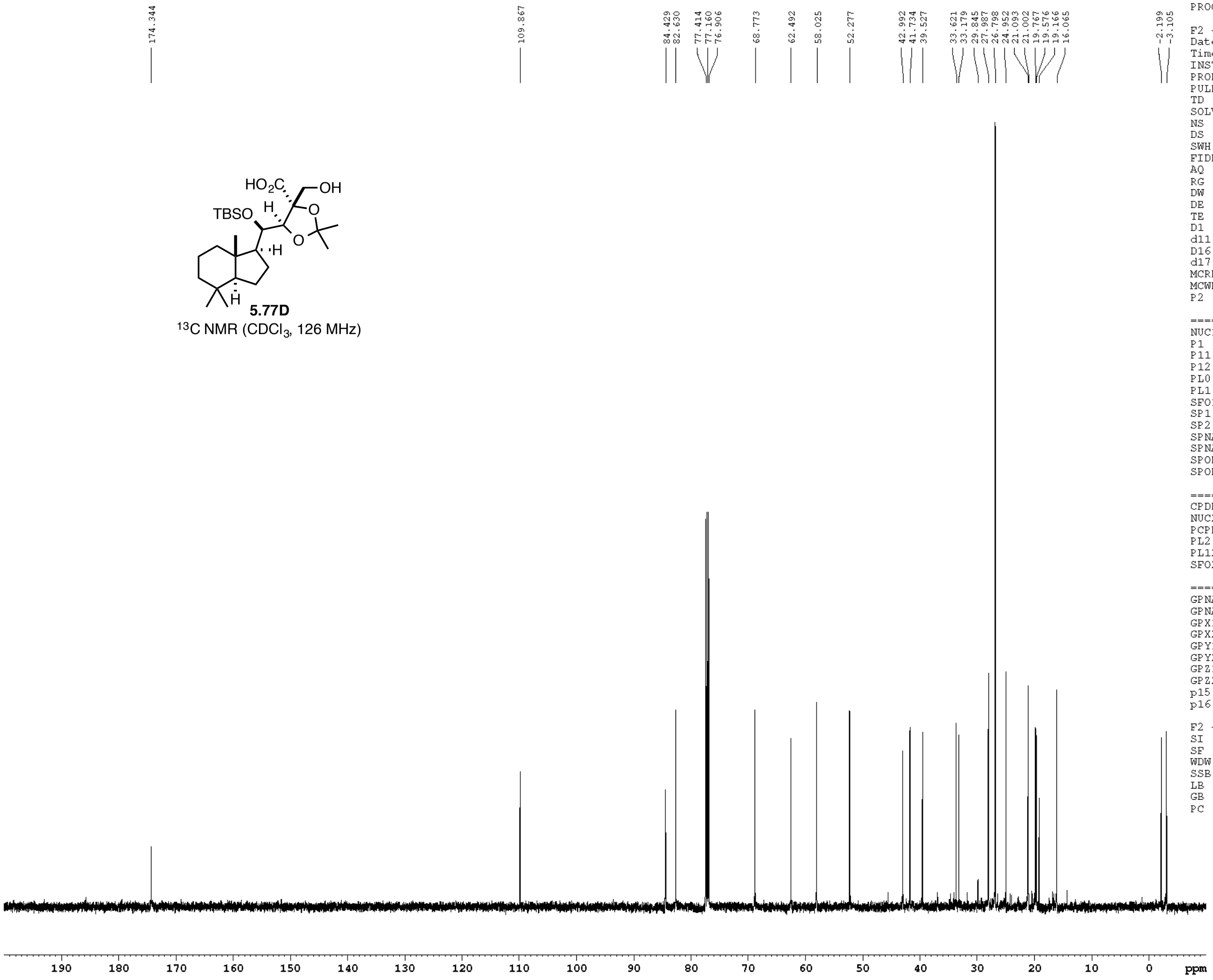
```
Current Data Parameters
NAME          DJT-VI-142
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time               13.08
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200318 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  4.00
```

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



5.77D

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-142
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time               13.11
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   239
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  6502
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

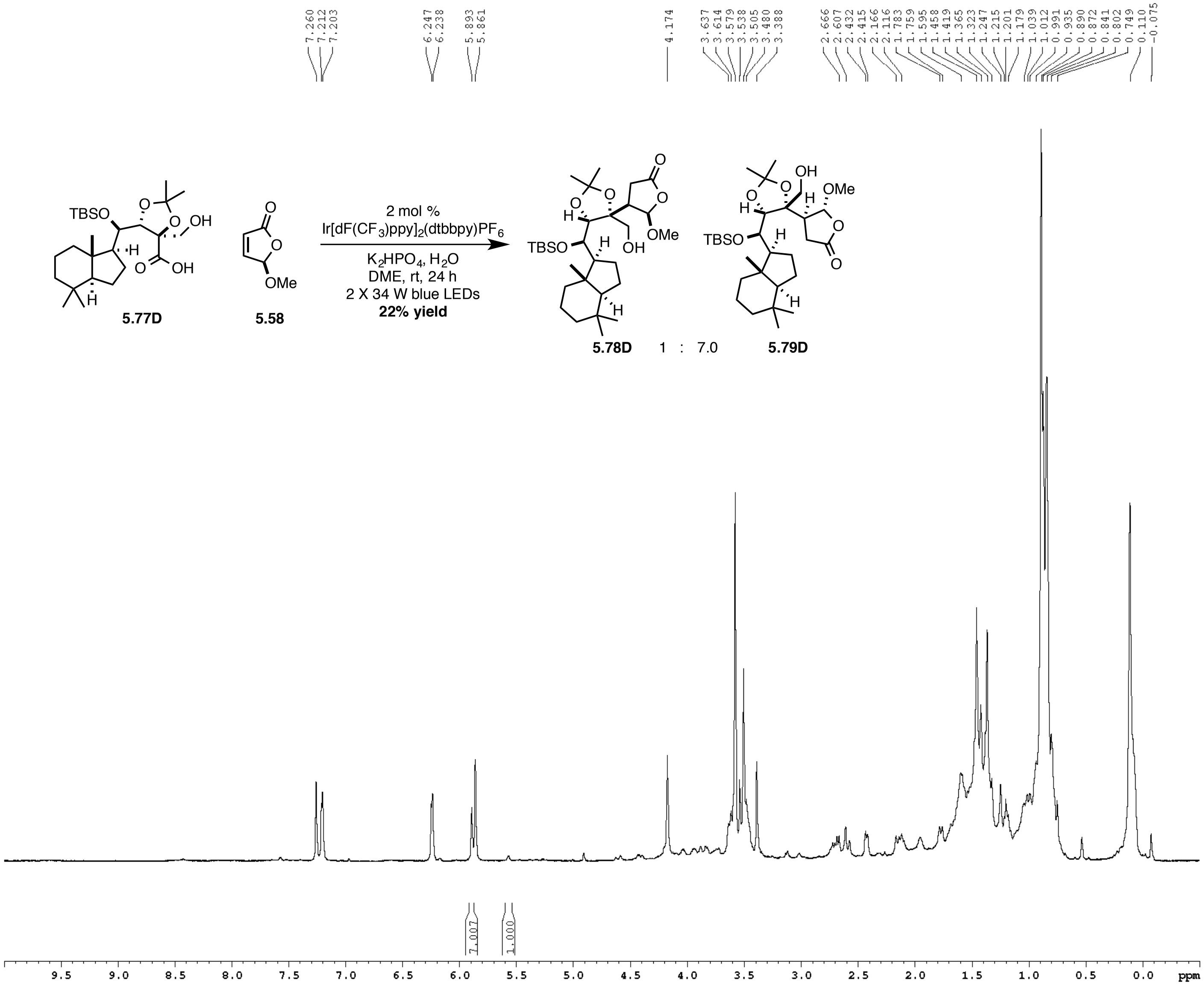
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum



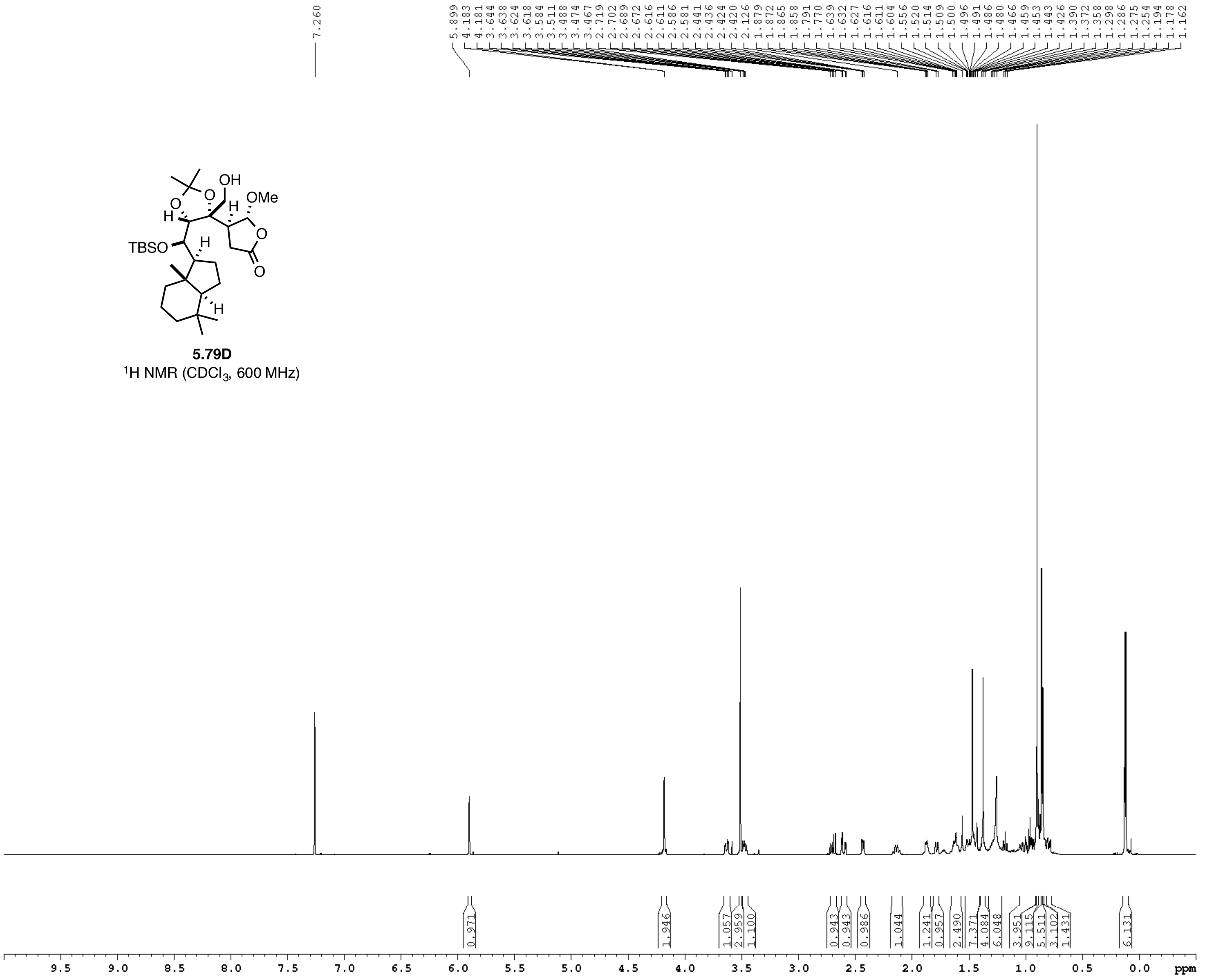
```
Current Data Parameters
NAME          DJT-VI-148
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151215
Time                9.33
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST  0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200324 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  4.00
```

1H spectrum



5.79D

^{1}H NMR (CDCl$_3$, 600 MHz)

```
Current Data Parameters
NAME          DJT-VI-148
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151215
Time               15.04
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                    20
DS                     0
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                   181
DW                52.000 usec
DE                 14.54 usec
TE                 298.0 K
D1            0.10000000 sec
TD0                    1

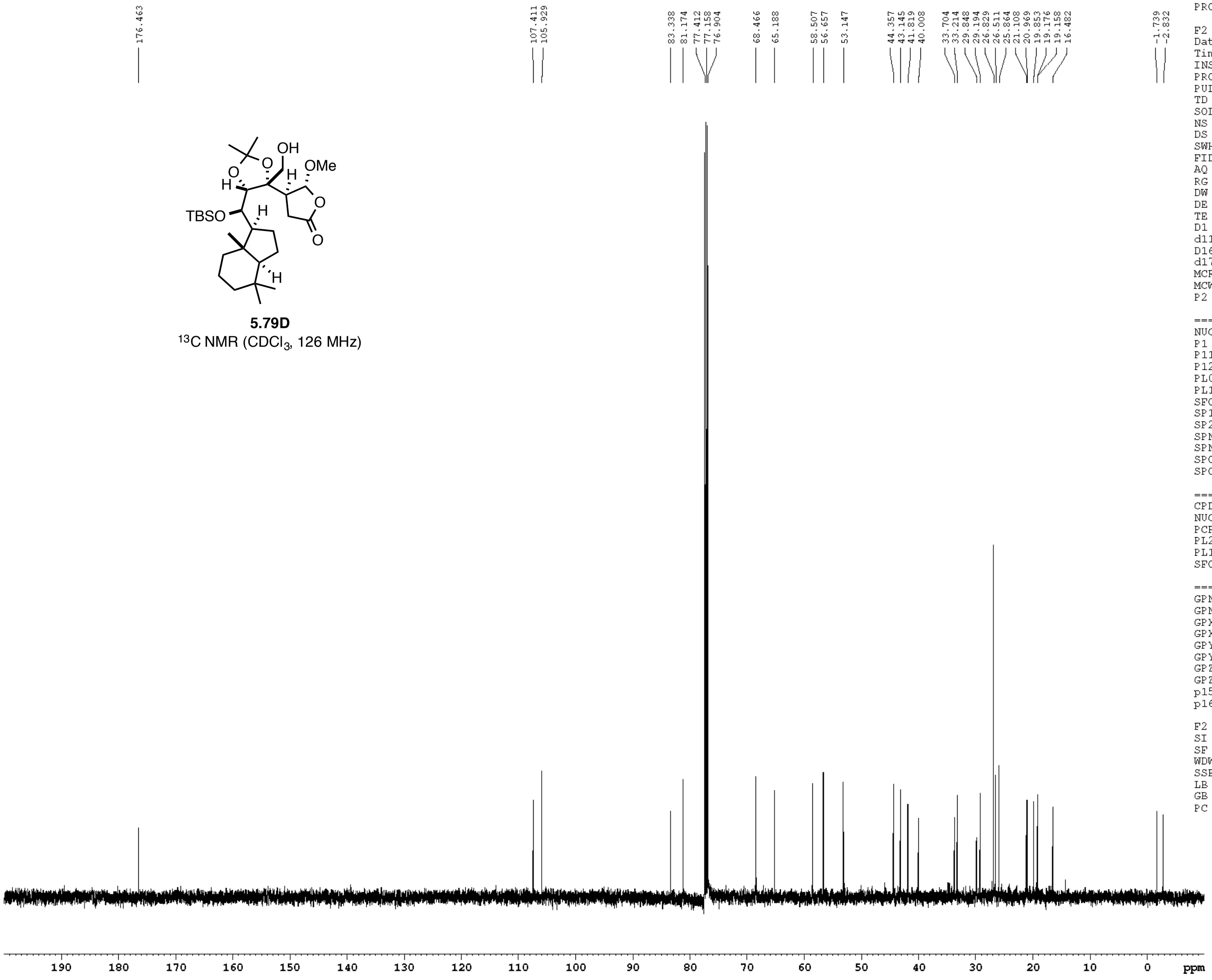
======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300357 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

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

5.79D

^{13}C NMR (CDCl$_3$, 126 MHz)



```
Current Data Parameters
NAME          DJT-VI-148
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160127
Time               13.12
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   421
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST    0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

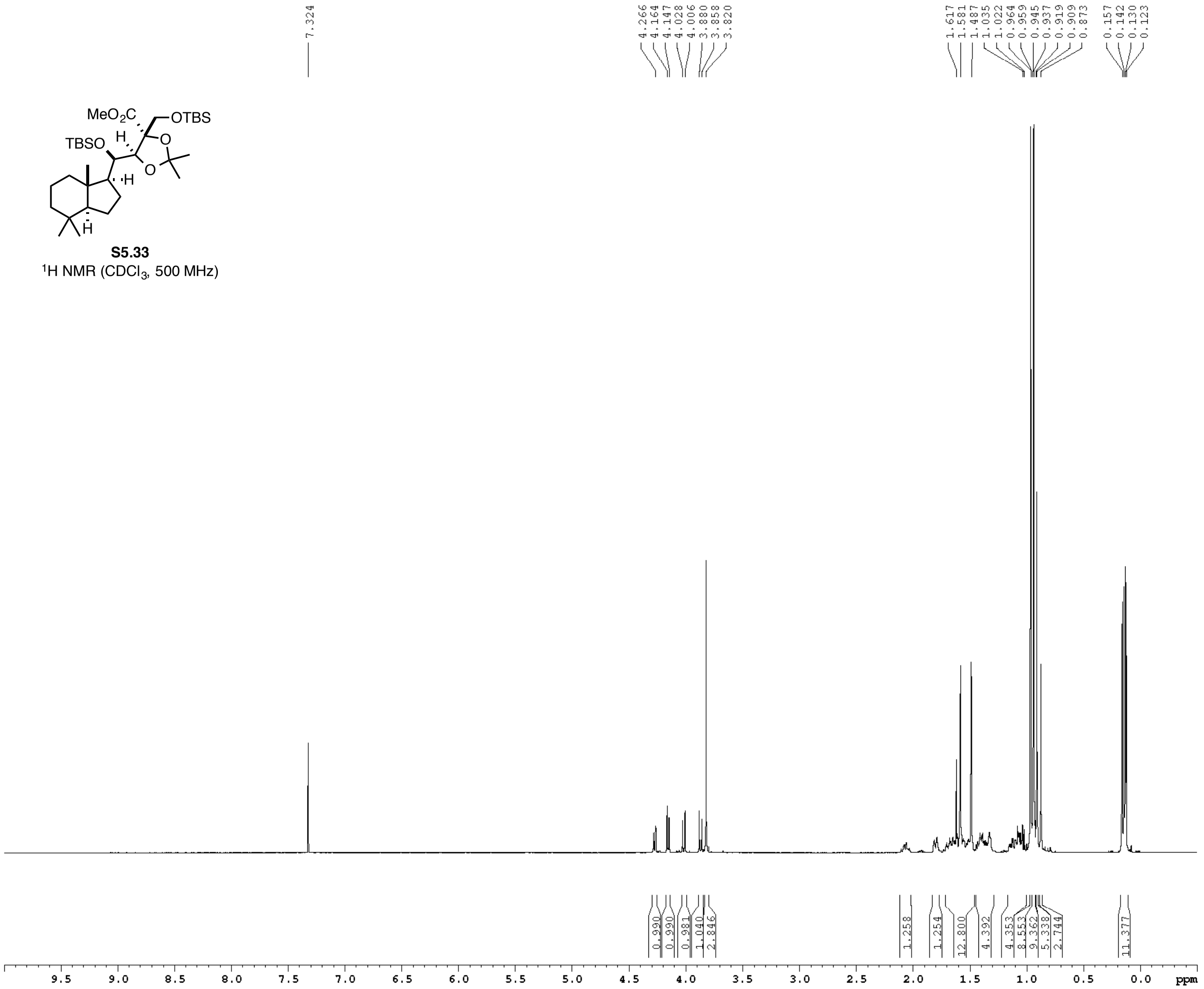
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1    0 Hz
SPOFF2    0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804076 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum



S5.33

^{1}H NMR (CDCl$_3$, 500 MHz)

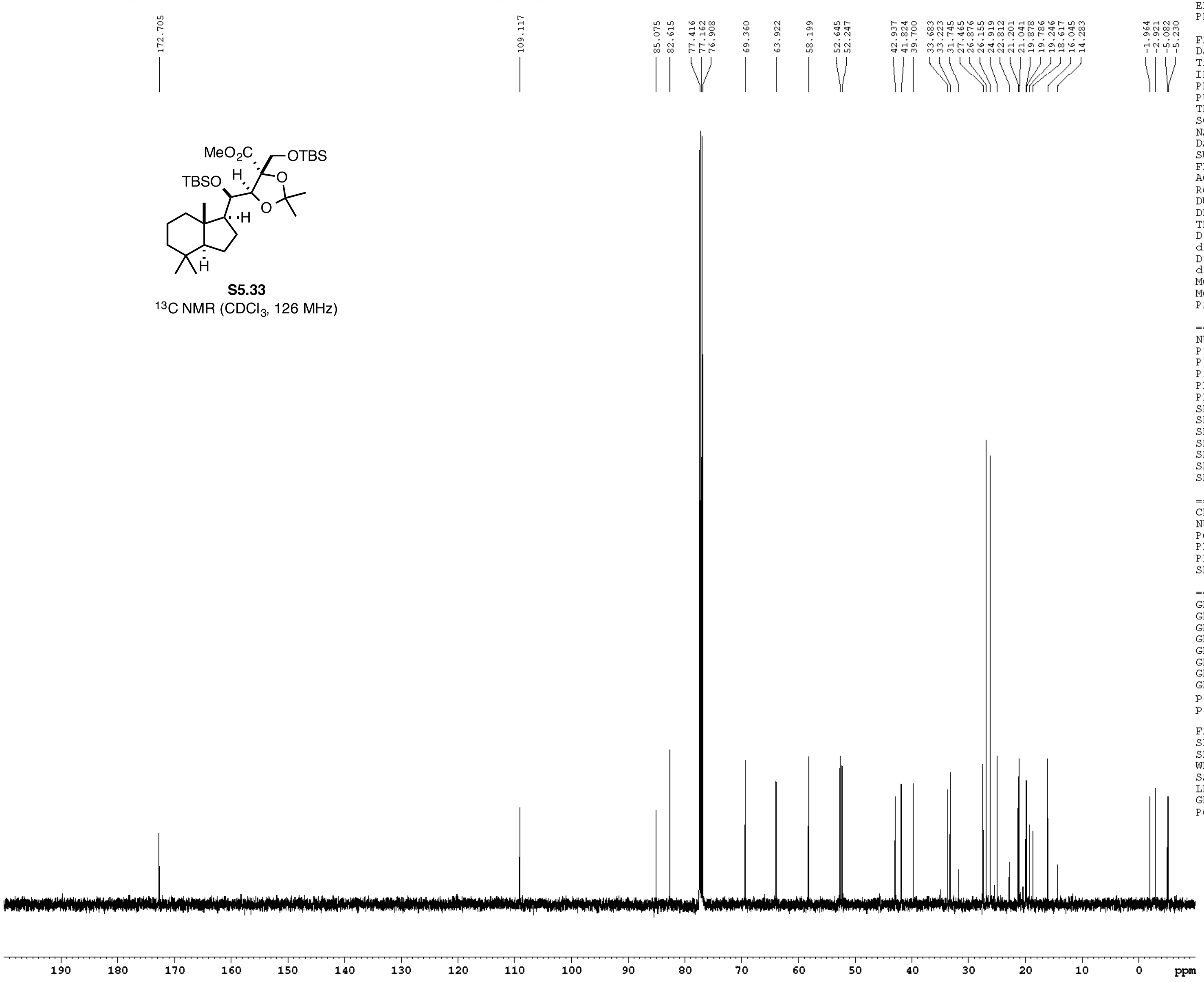
```
Current Data Parameters
NAME           DJT-VI-132
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151207
Time                13.48
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  40062
SOLVENT             CDCl3
NS                     20
DS                      0
SWH              8012.820 Hz
FIDRES           0.200010 Hz
AQ              2.4998689 sec
RG                   10.1
DW                 62.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.10000000 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.50 usec
PL1                  1.60 dB
SFO1          500.2235015 MHz

F2 - Processing parameters
SI                  65536
SF            500.2200000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   4.00
```

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



S5.33

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-132
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151207
Time               13.51
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   574
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                4597.6
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804071 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum

5.77E

^{1}H NMR (CDCl$_3$, 500 MHz)

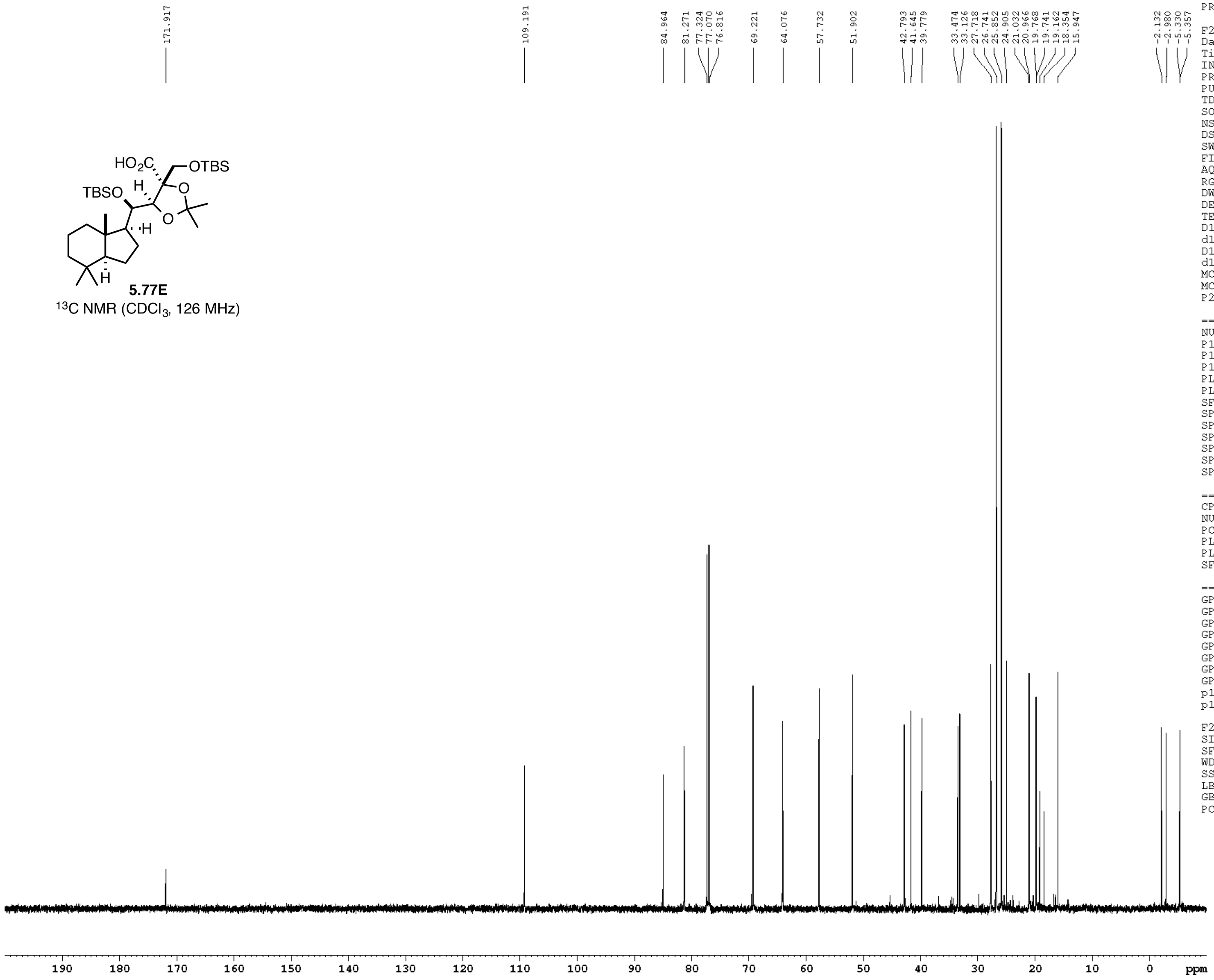
```
Current Data Parameters
NAME          DJT-VI-143
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151212
Time               10.10
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                    20
DS                     0
SWH            8012.820 Hz
FIDRES         0.100003 Hz
AQ            4.9998622 sec
RG                   4.5
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200313 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.77E

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-143
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151212
Time               10.15
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   377
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG               11585.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

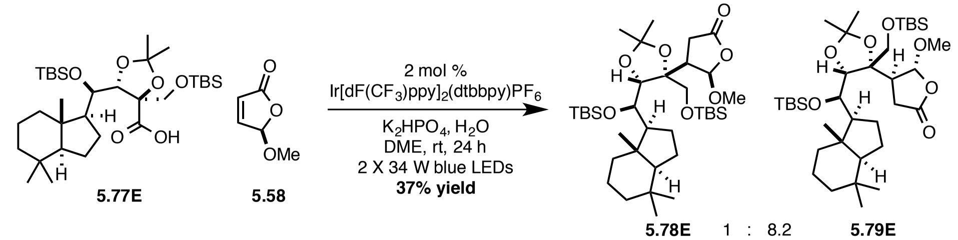
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

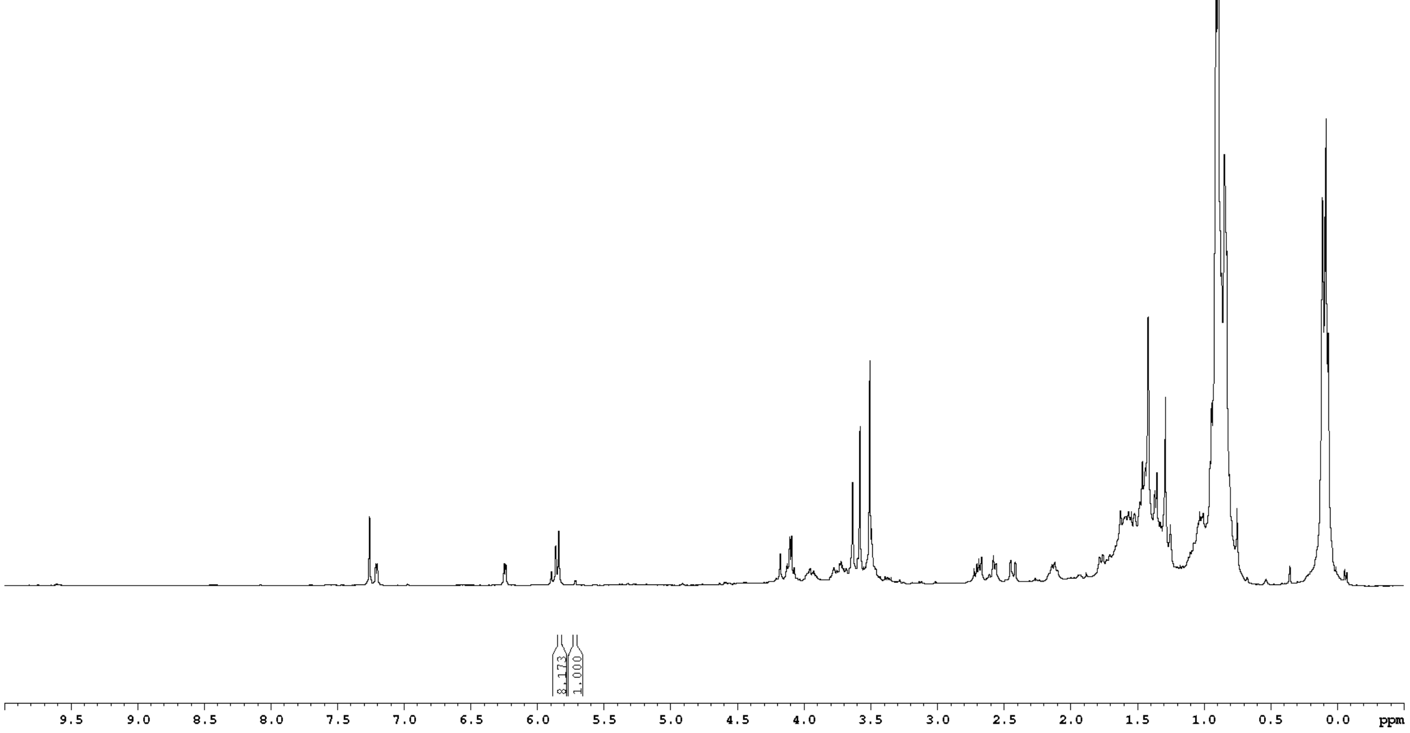
F2 - Processing parameters
SI                 65536
SF           125.7804190 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

1H spectrum


5.77E **5.58**

2 mol %
Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$
K$_2$HPO$_4$, H$_2$O
DME, rt, 24 h
2 X 34 W blue LEDs
37% yield

5.78E 1 : 8.2 **5.79E**

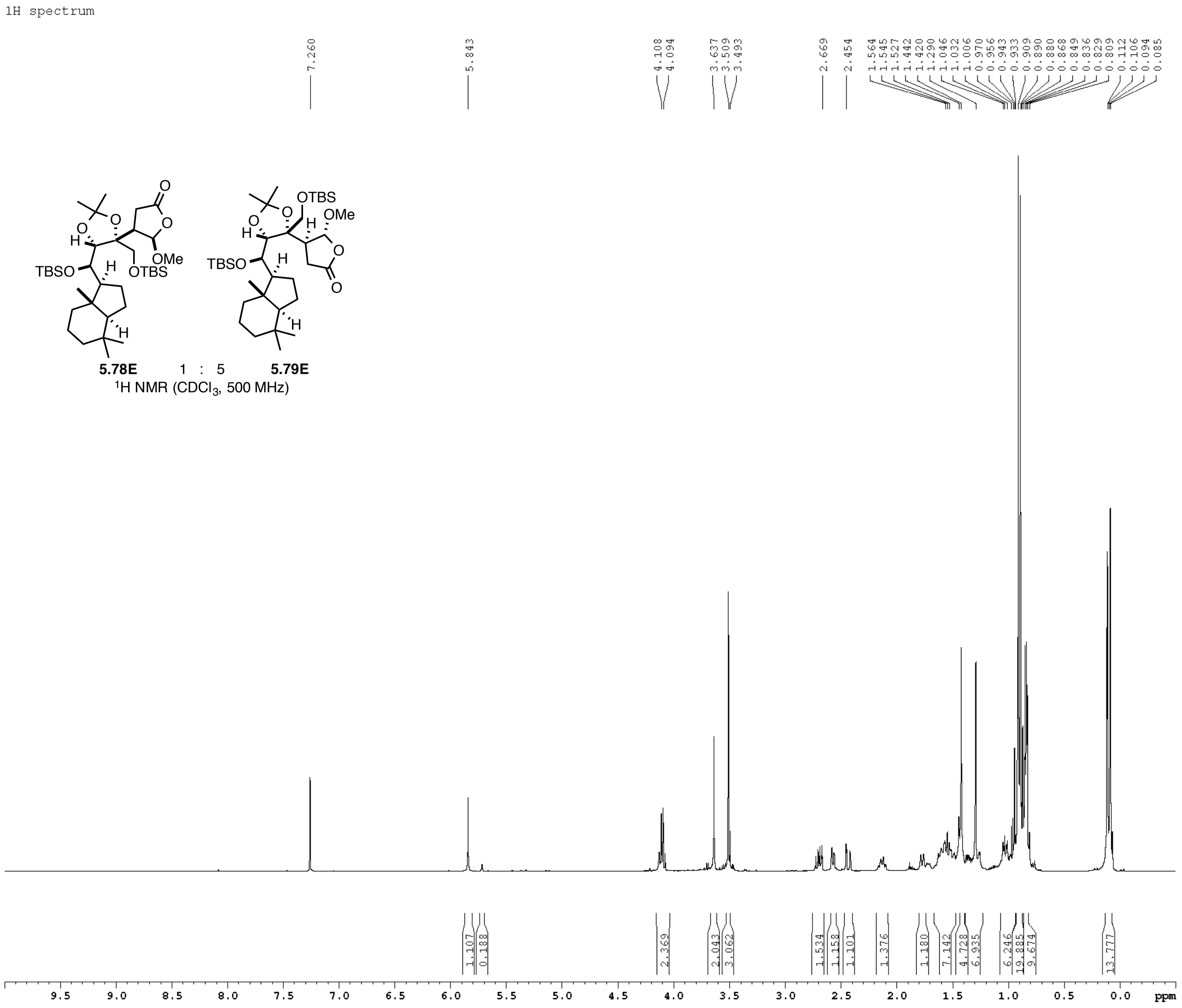


```
Current Data Parameters
NAME          DJT-VI-146
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time                7.50
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200318 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```



5.78E 1 : 5 **5.79E**

^{1}H NMR (CDCl$_3$, 500 MHz)

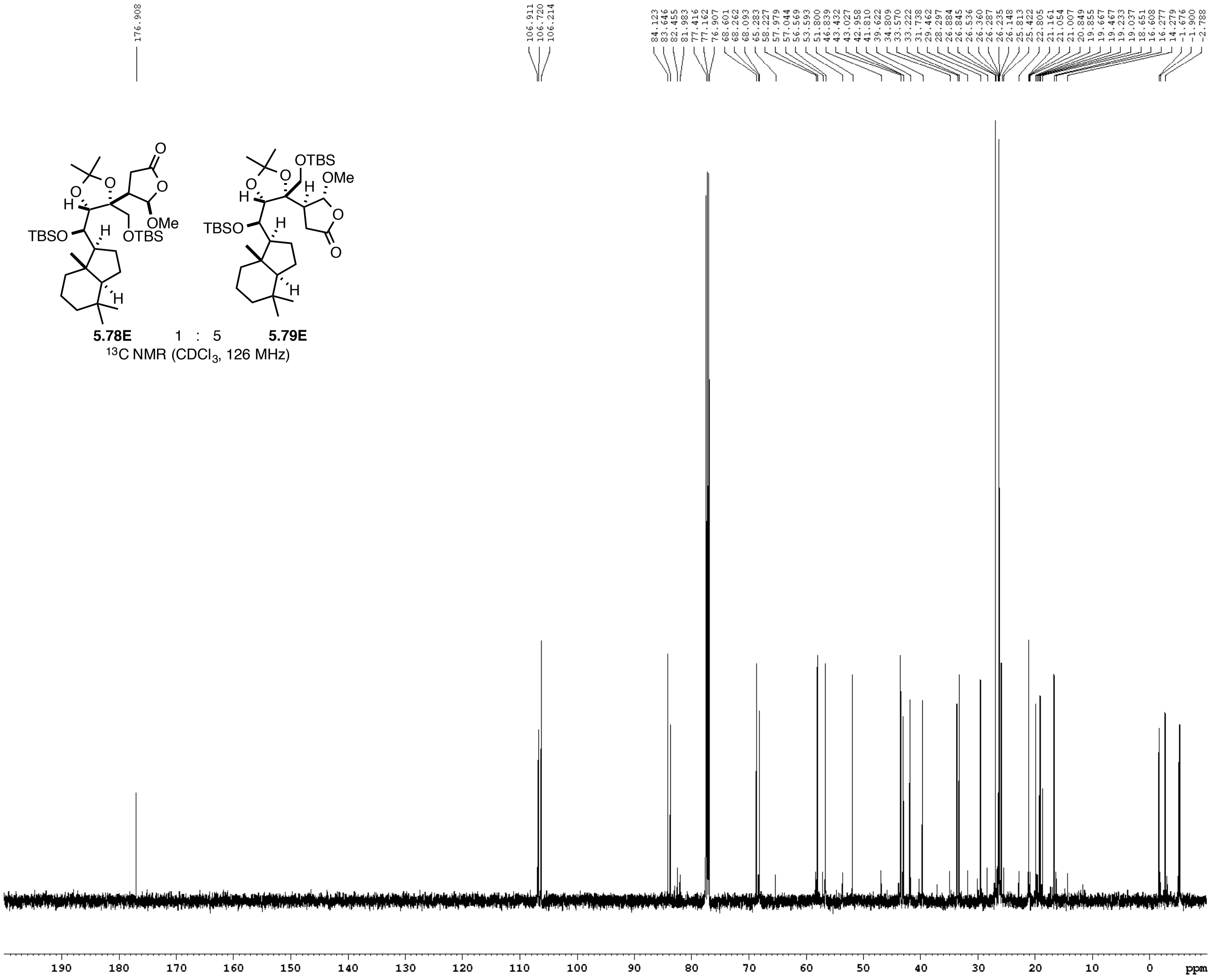
```
Current Data Parameters
NAME          DJT-VI-146
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151215
Time                7.40
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200316 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.78E 1 : 5 **5.79E**

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME         DJT-VI-146
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20151215
Time               7.46
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65536
SOLVENT           CDCl3
NS                  299
DS                    0
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813440 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST   0 sec
MCWRK        0.01500000 sec
P2                33.10 usec

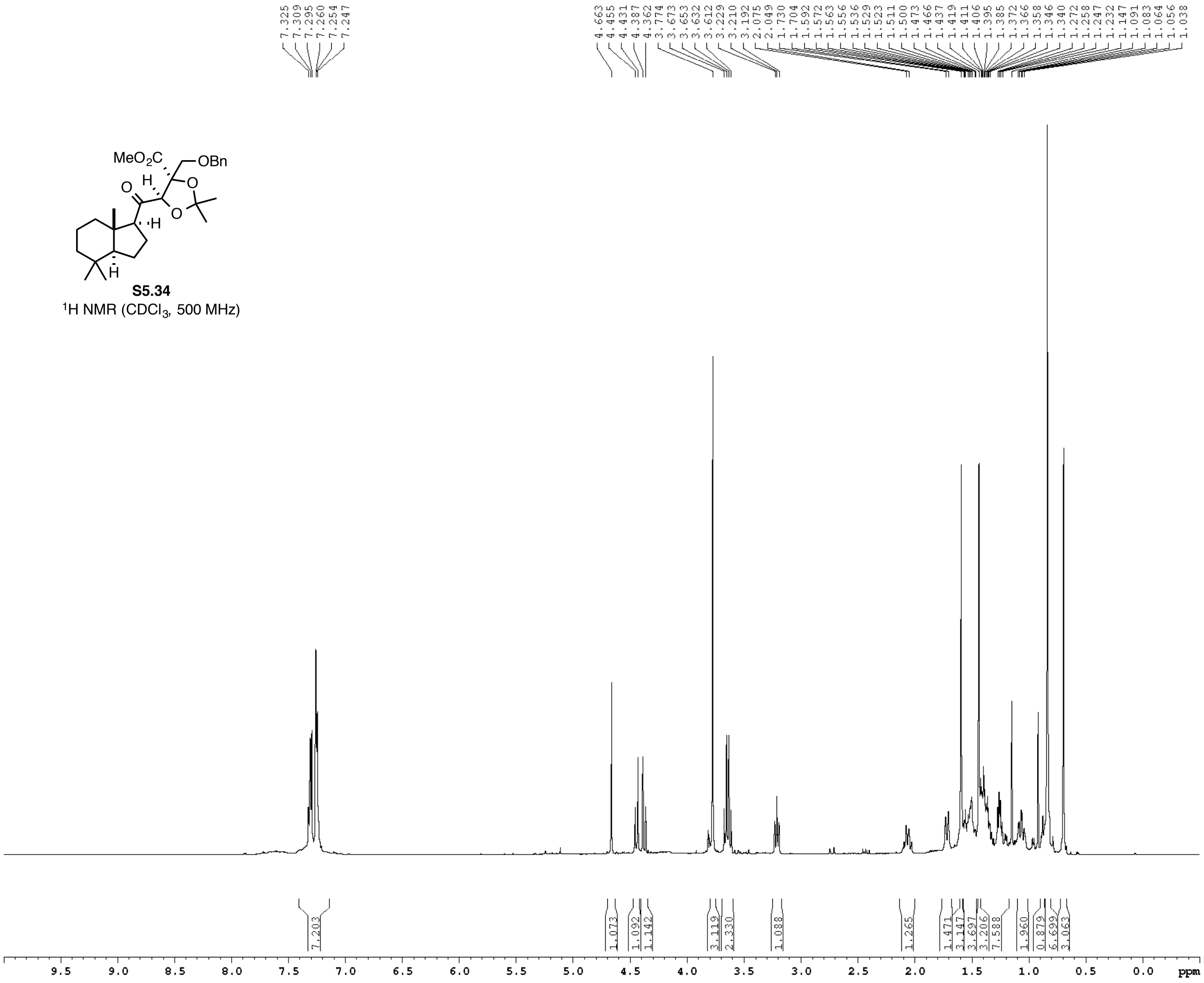
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                2.70 dB
SP2                2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7804076 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 2.00
```

1H spectrum



S5.34

^{1}H NMR (CDCl$_3$, 500 MHz)

```
Current Data Parameters
NAME          DJT-VI-177
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160127
Time               13.25
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     9
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

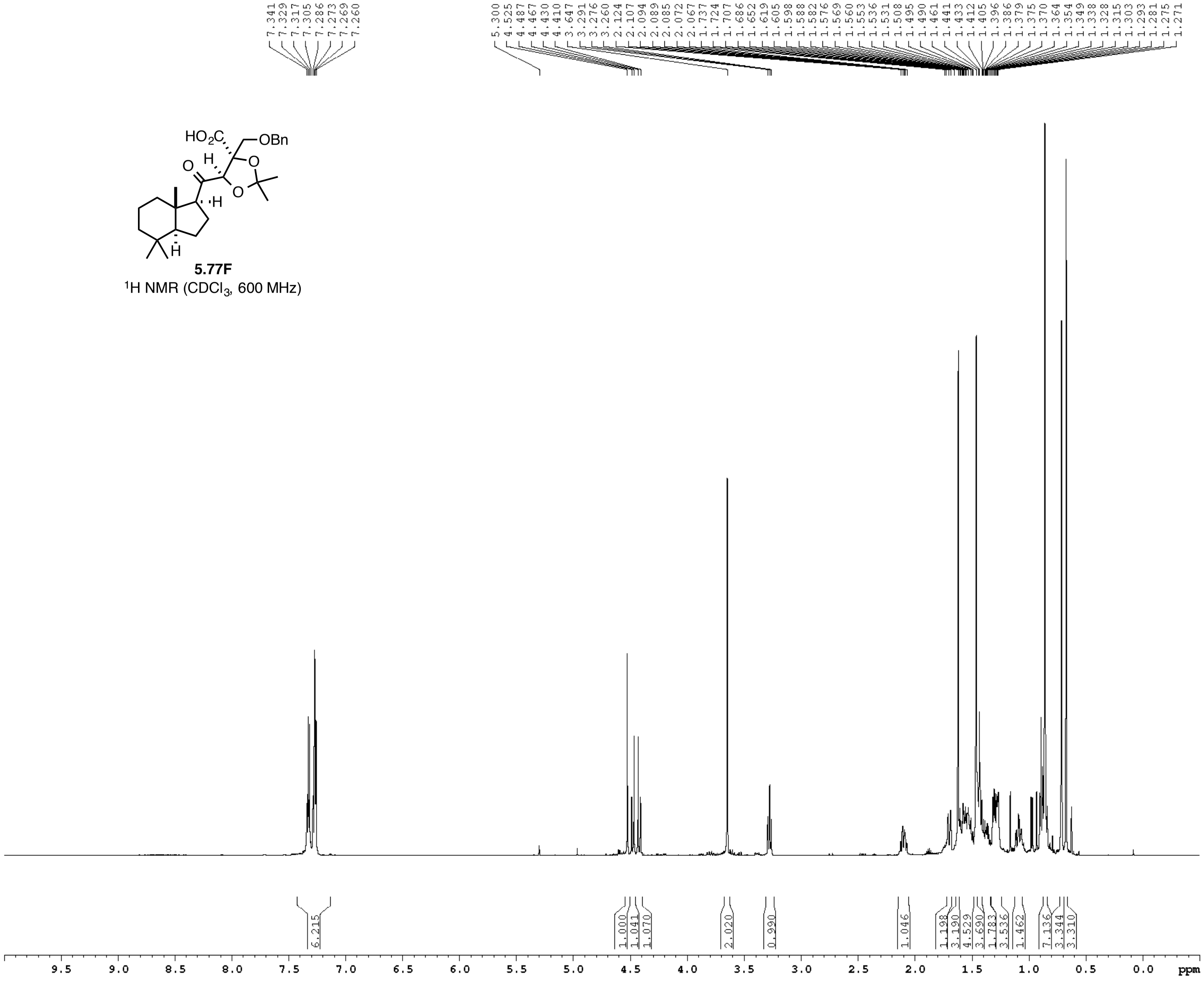
======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200340 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

1H spectrum

5.77F

^{1}H NMR (CDCl$_3$, 600 MHz)



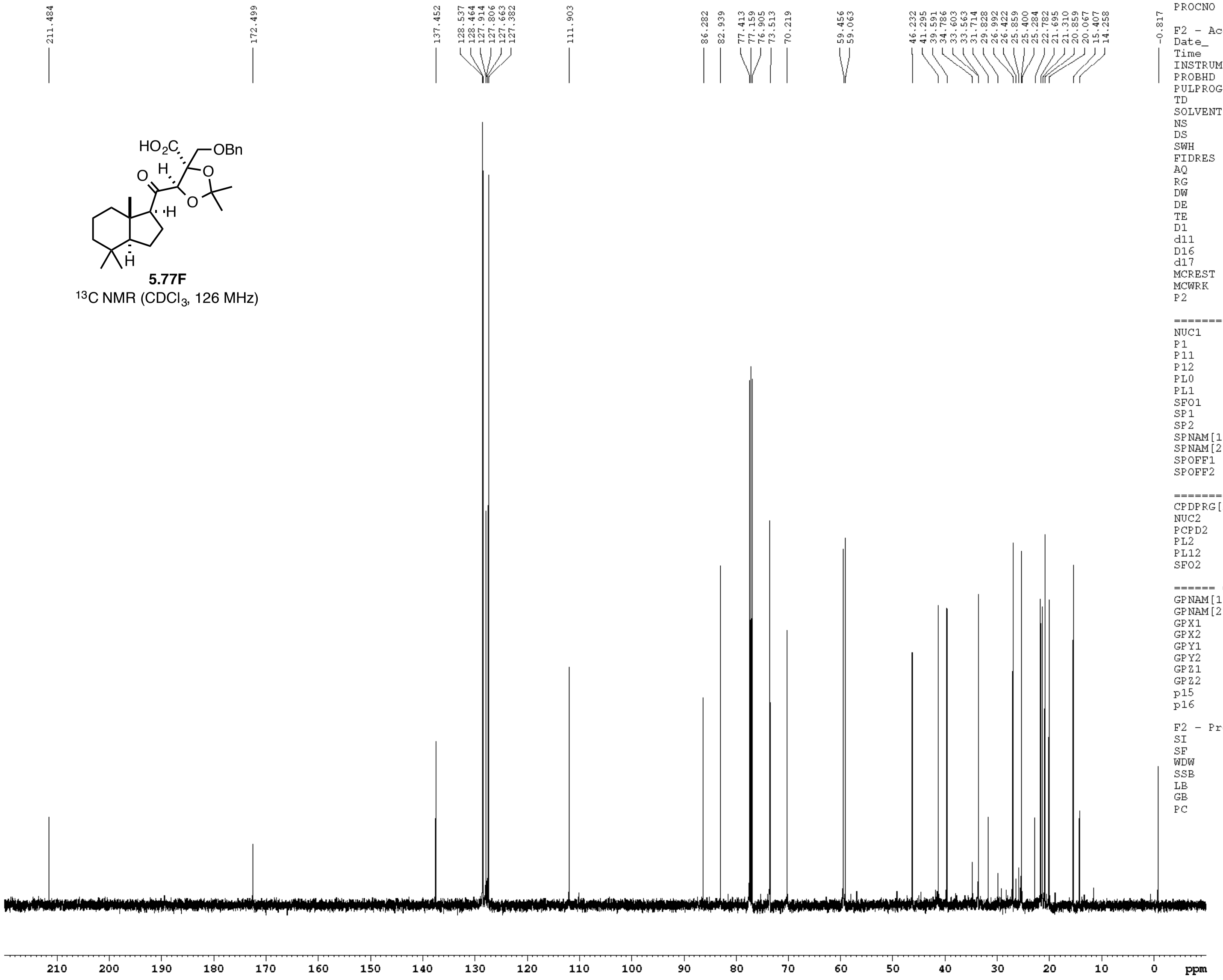
```
Current Data Parameters
NAME          DJT-VI-186
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160203
Time               15.00
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 98074
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             9615.385 Hz
FIDRES          0.098042 Hz
AQ             5.0998478 sec
RG                   228
DW                52.000 usec
DE                 14.54 usec
TE                 299.3 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1342009 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1300304 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

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



5.77F

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-186
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160204
Time                7.22
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT             C6D6
NS                   200
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                  8192
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

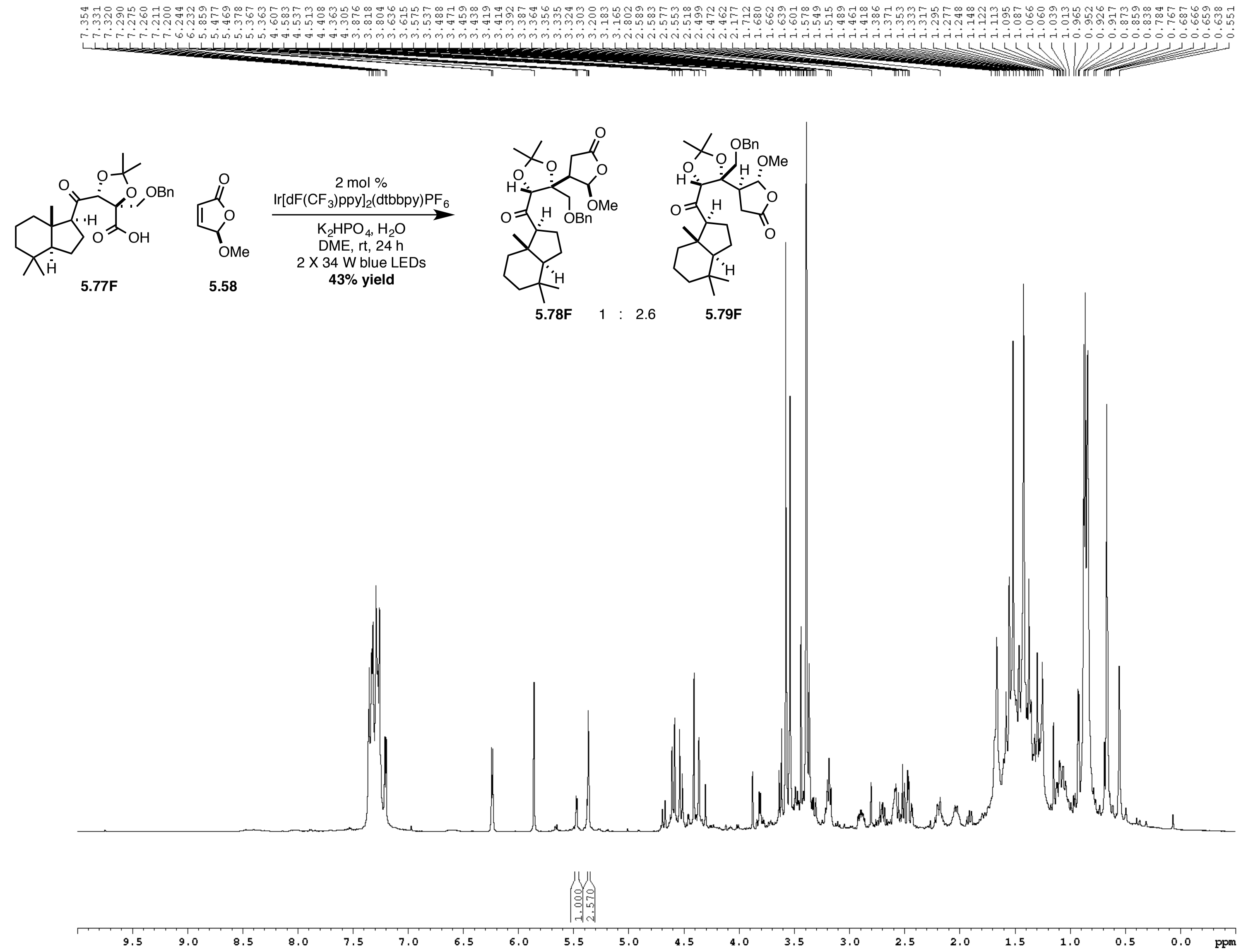
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]     Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804113 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  2.00
```

1H spectrum


5.77F

5.58

2 mol %

Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$

K$_2$HPO$_4$, H$_2$O

DME, rt, 24 h

2 X 34 W blue LEDs

43% yield

5.78F 1 : 2.6 5.79F

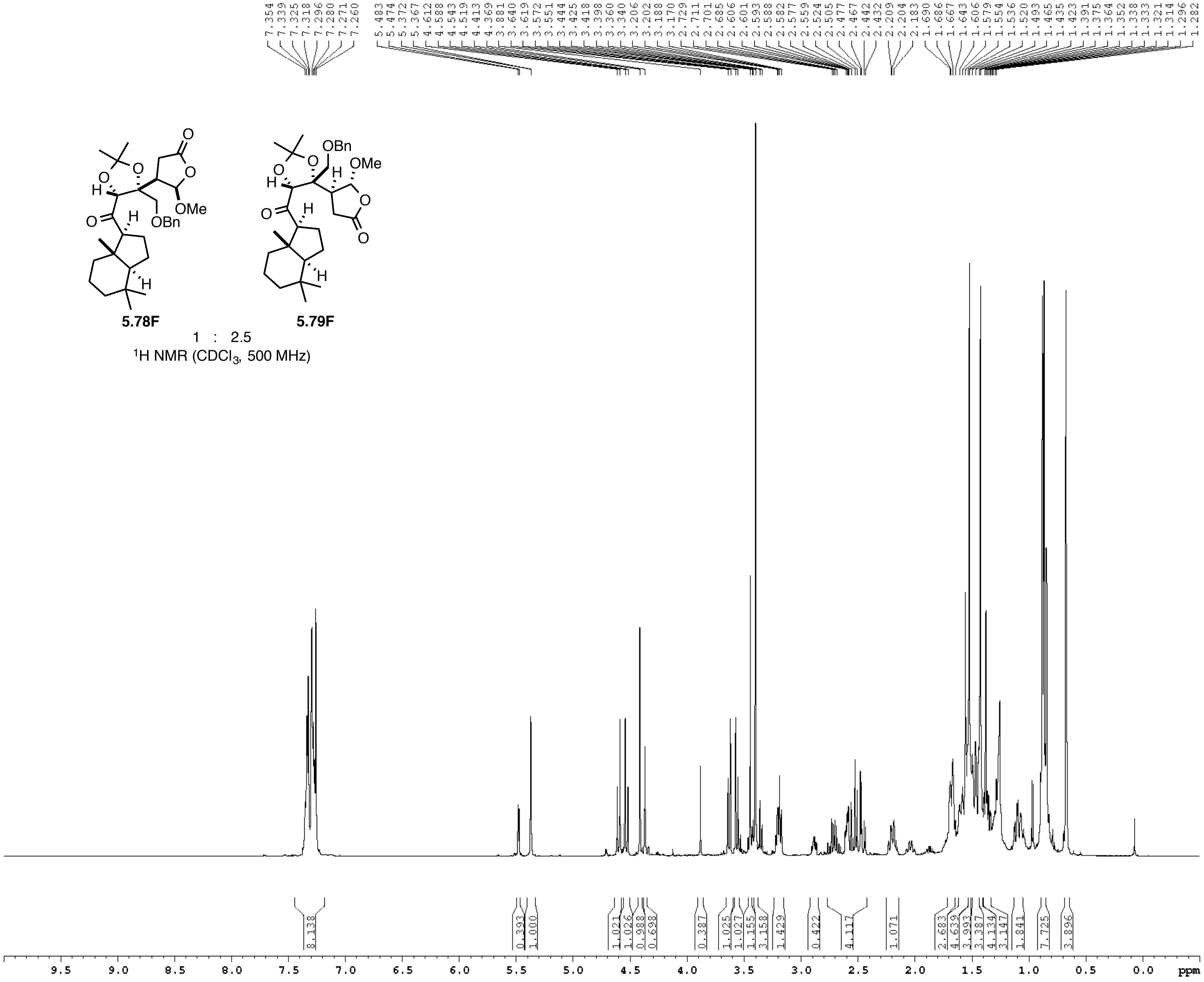
```
Current Data Parameters
NAME          DJT-VI-191
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160205
Time                7.56
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 80126
SOLVENT            CDCl3
NS                    40
DS                     0
SWH             8012.820 Hz
FIDRES          0.100003 Hz
AQ             4.9998622 sec
RG                   4.5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200323 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

1H spectrum



5.78F

5.79F

1 : 2.5

^{1}H NMR (CDCl$_3$, 500 MHz)

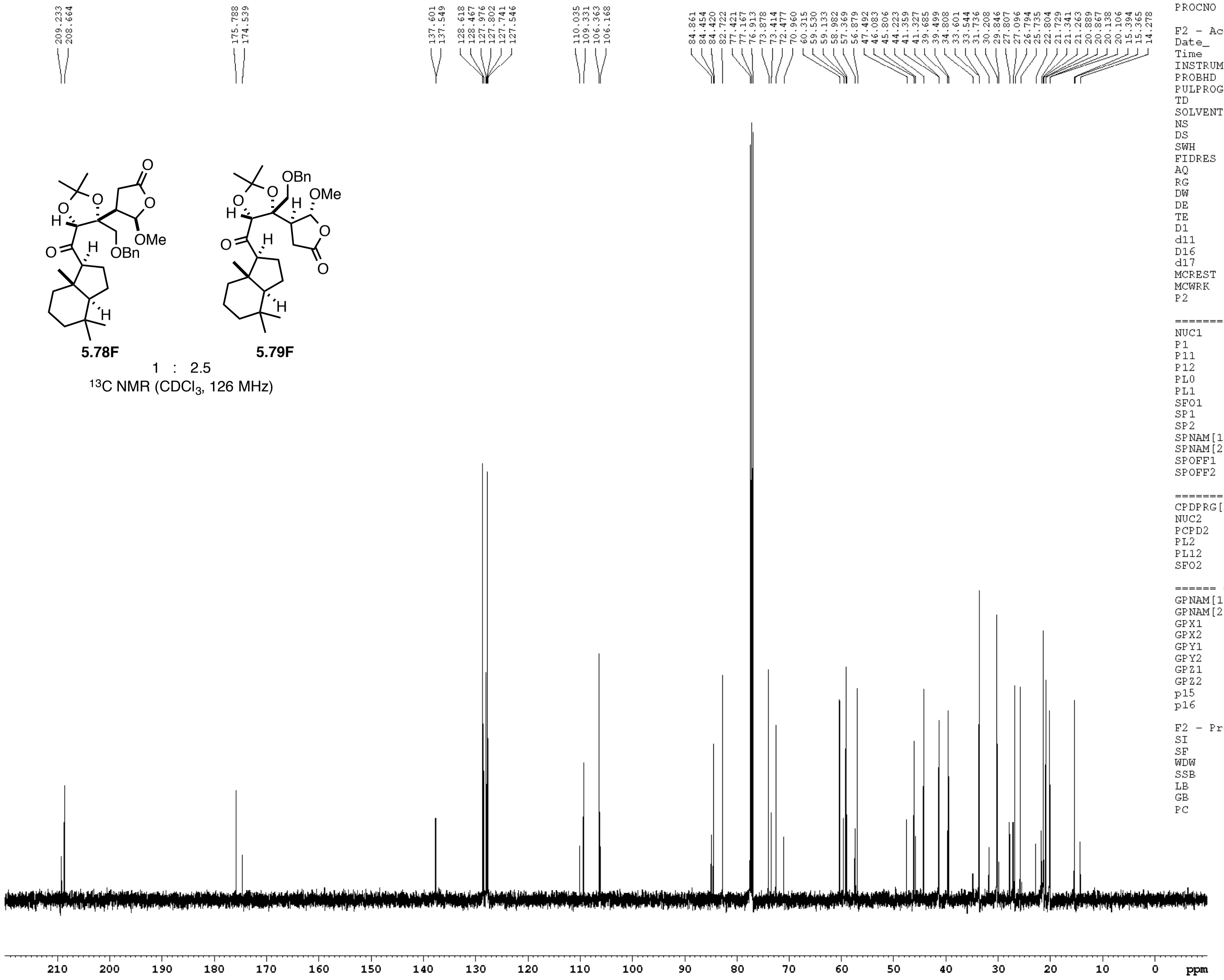
```
Current Data Parameters
NAME          DJT-VI-191
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160205
Time               13.58
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                     5
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200321 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.78F **5.79F**

1 : 2.5

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-191
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160205
Time               14.04
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   197
DS                    16
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

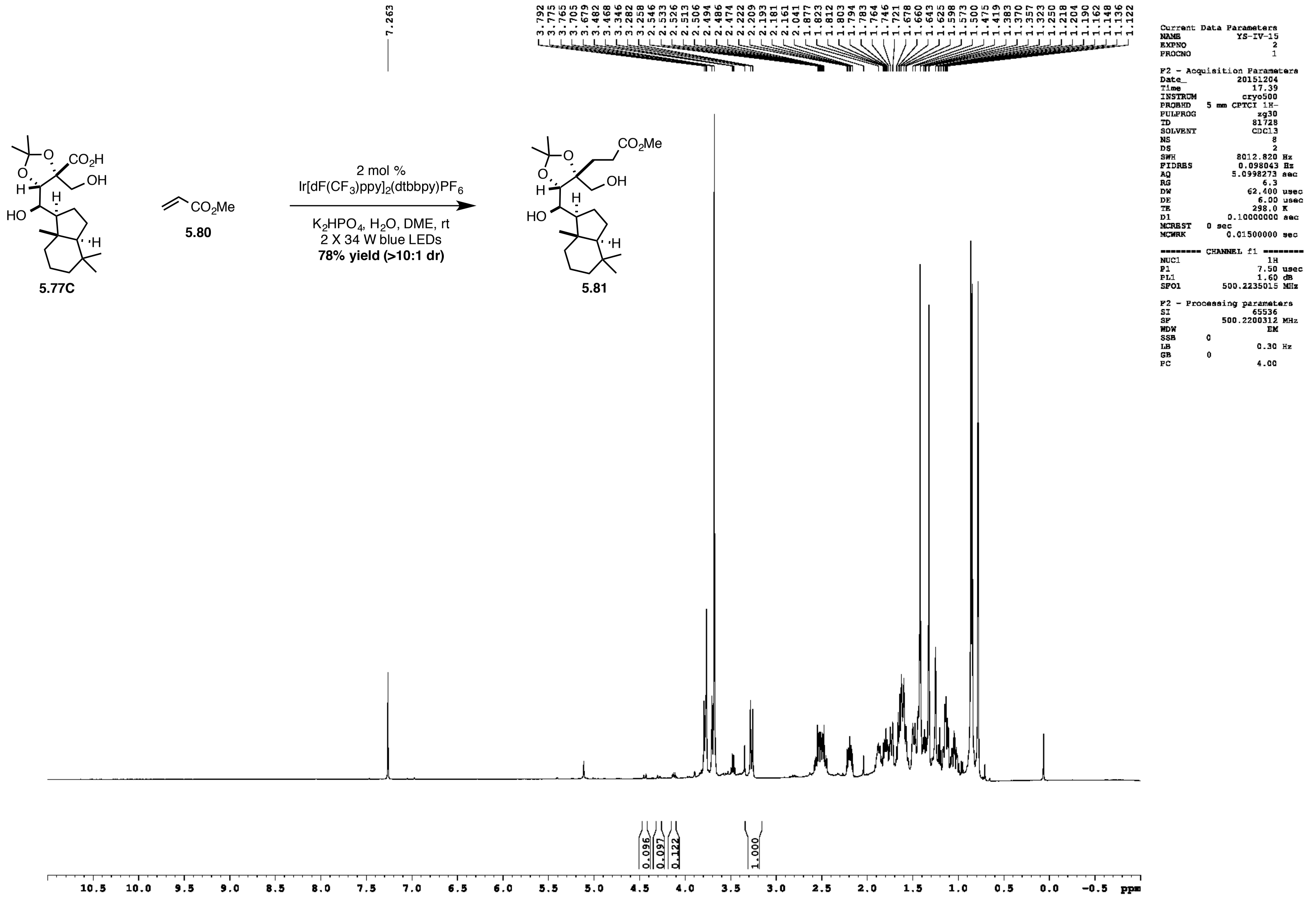
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1       0 %
GPX2       0 %
GPY1       0 %
GPY2       0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804085 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-IV-15



```
Current Data Parameters
NAME              YS-IV-15
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151204
Time                 17.39
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                     6.3
DW                  62.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

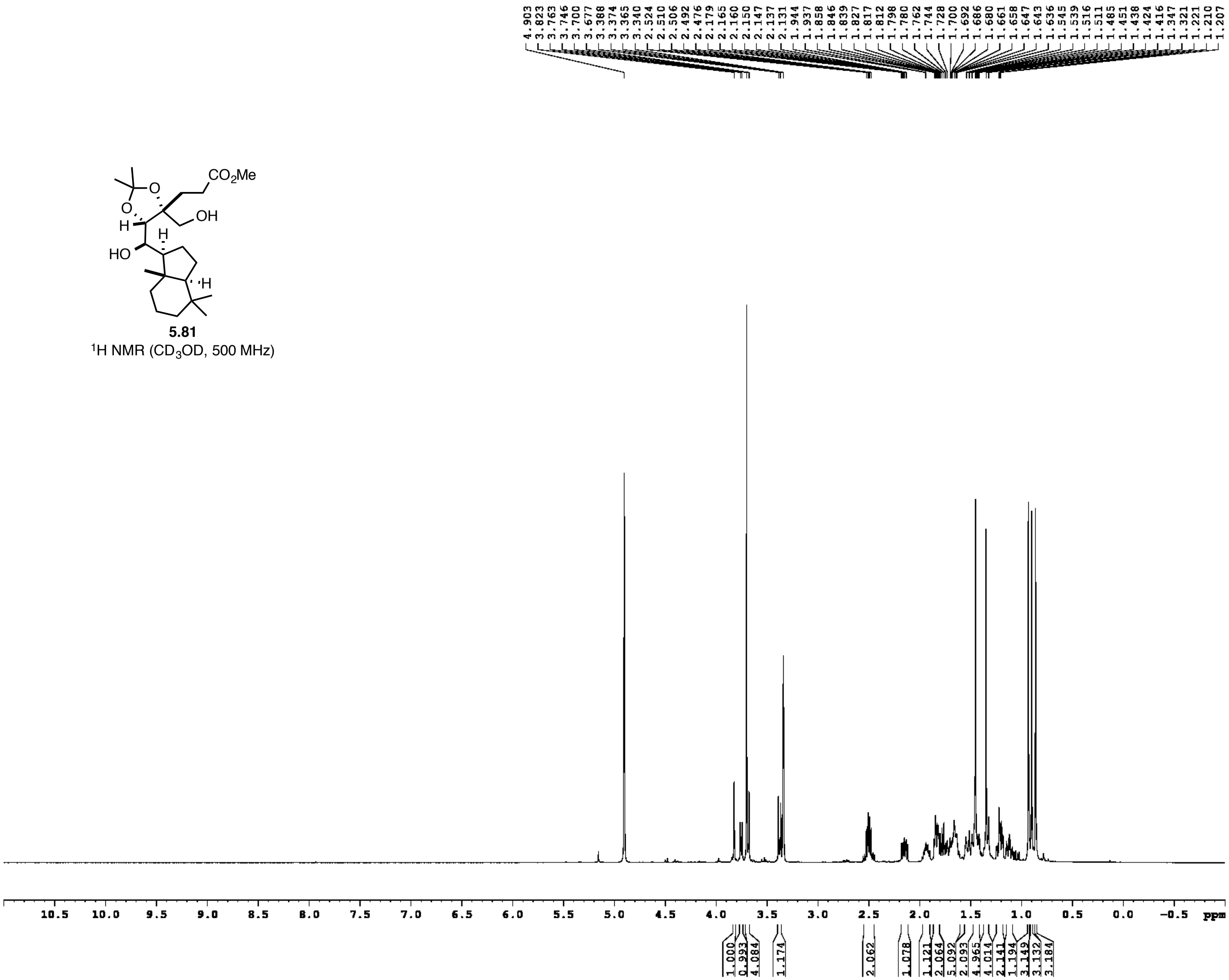
======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 usec
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200312 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-IV-15

5.81

^{1}H NMR (CD$_3$OD, 500 MHz)



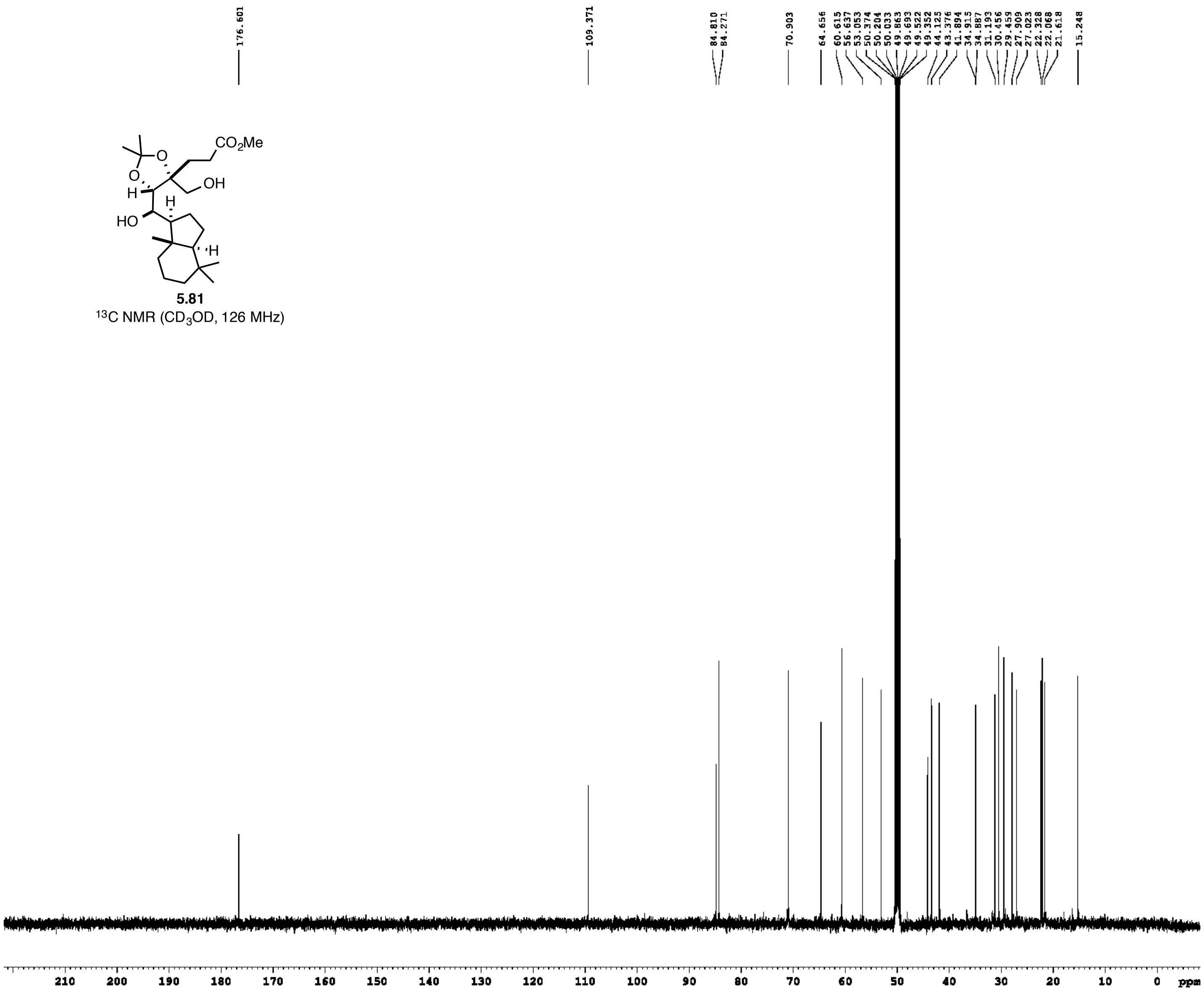
```
Current Data Parameters
NAME              YS-IV-15
EXPNO                   15
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151216
Time                  8.56
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CD3OD
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.098043 Hz
AQ               5.0998273 sec
RG                       9
DW                  62.400 use
DE                    6.00 use
TE                   298.0 K
D1              0.10000000 sec
MCREST   0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.50 use
PL1                   1.60 dB
SFO1           500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF             500.2200042 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    4.00
```

YS-IV-15



5.81

^{13}C NMR (CD_3OD, 126 MHz)

```
Current Data Parameters
NAME             YS-IV-15
EXPNO                  16
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151216
Time                 8.57
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                  65536
SOLVENT             CDCl3
NS                    320
DS                      2
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ              1.0813440 sec
RG                 4597.6
DW                 16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST   0 sec
MCWRK          0.01500000 sec
P2                  33.10 usec

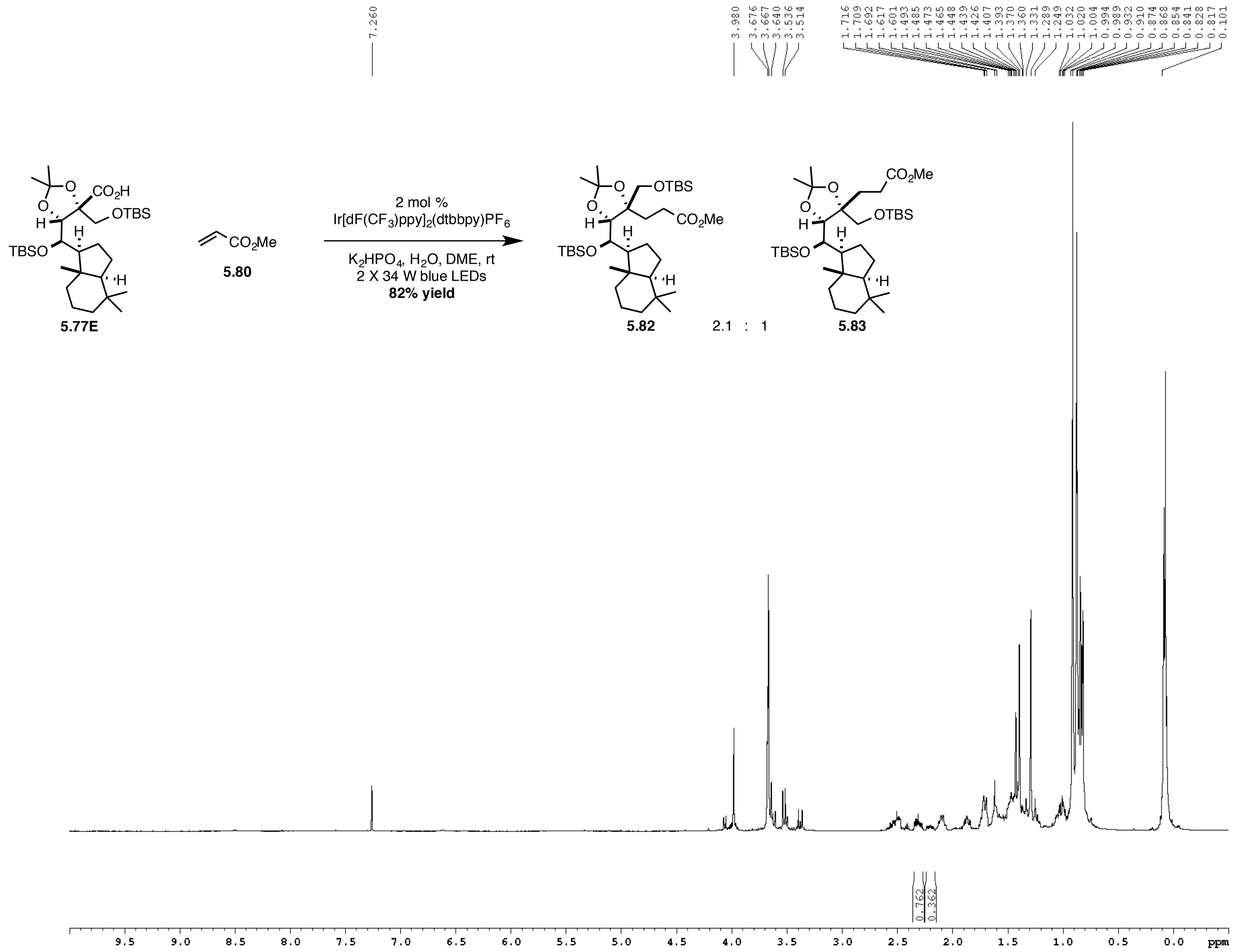
======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL ======
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPX1     0 %
GPX2     0 %
GPY1     0 %
GPY2     0 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

F2 - Processing parameters
SI                  65536
SF            125.7801371 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   2.00
```

1H spectrum



5.77E **5.80** **5.82** **5.83**

```
Current Data Parameters
NAME         DJT-VI-147
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20151214
Time               7.55
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                   20
DS                    0
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998273 sec
RG                    4
DW               62.400 usec
DE                 6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST   0 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                65536
SF          500.2200314 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 4.00
```

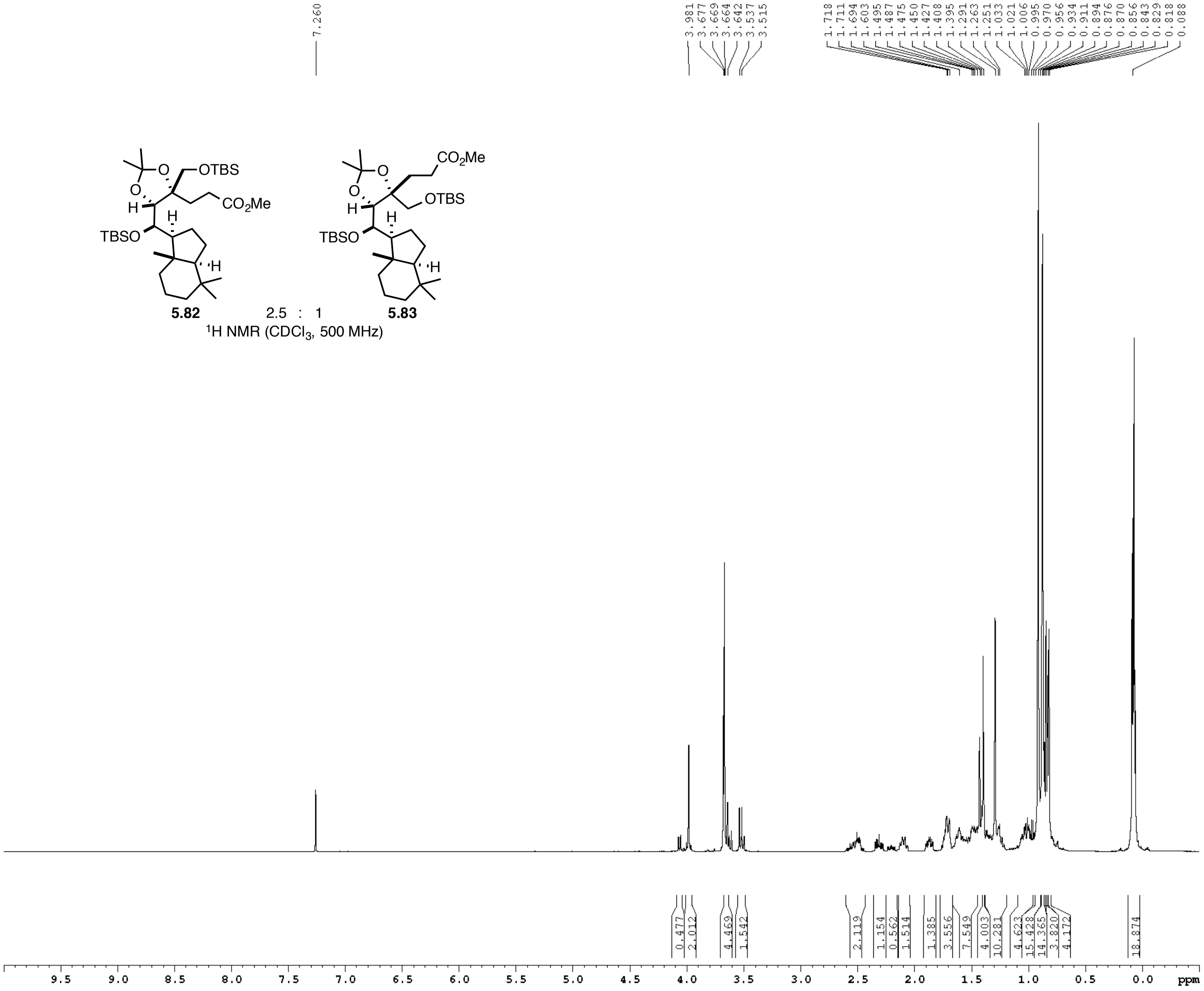
1H spectrum

5.82

5.83

2.5 : 1

^{1}H NMR (CDCl$_3$, 500 MHz)



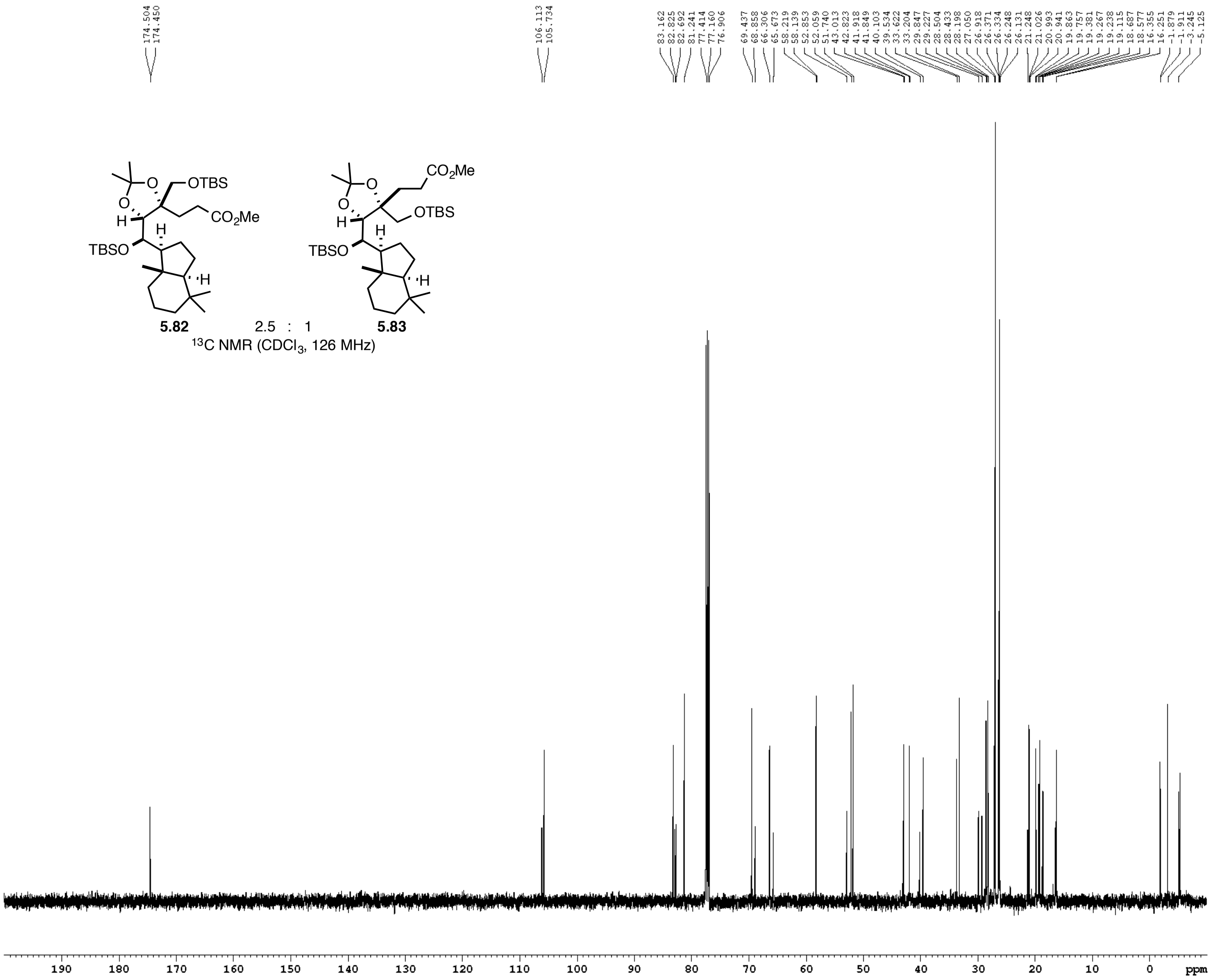
```
Current Data Parameters
NAME          DJT-VI-147
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151214
Time               13.17
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                    20
DS                     0
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998273 sec
RG                   5.7
DW                62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST   0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
SI                 65536
SF           500.2200317 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  4.00
```

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



5.82 2.5 : 1 **5.83**

^{13}C NMR (CDCl$_3$, 126 MHz)

```
Current Data Parameters
NAME          DJT-VI-147
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160127
Time               13.06
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   151
DS                     0
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ             1.0813440 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST   0 sec
MCWRK         0.01500000 sec
P2                 33.10 usec

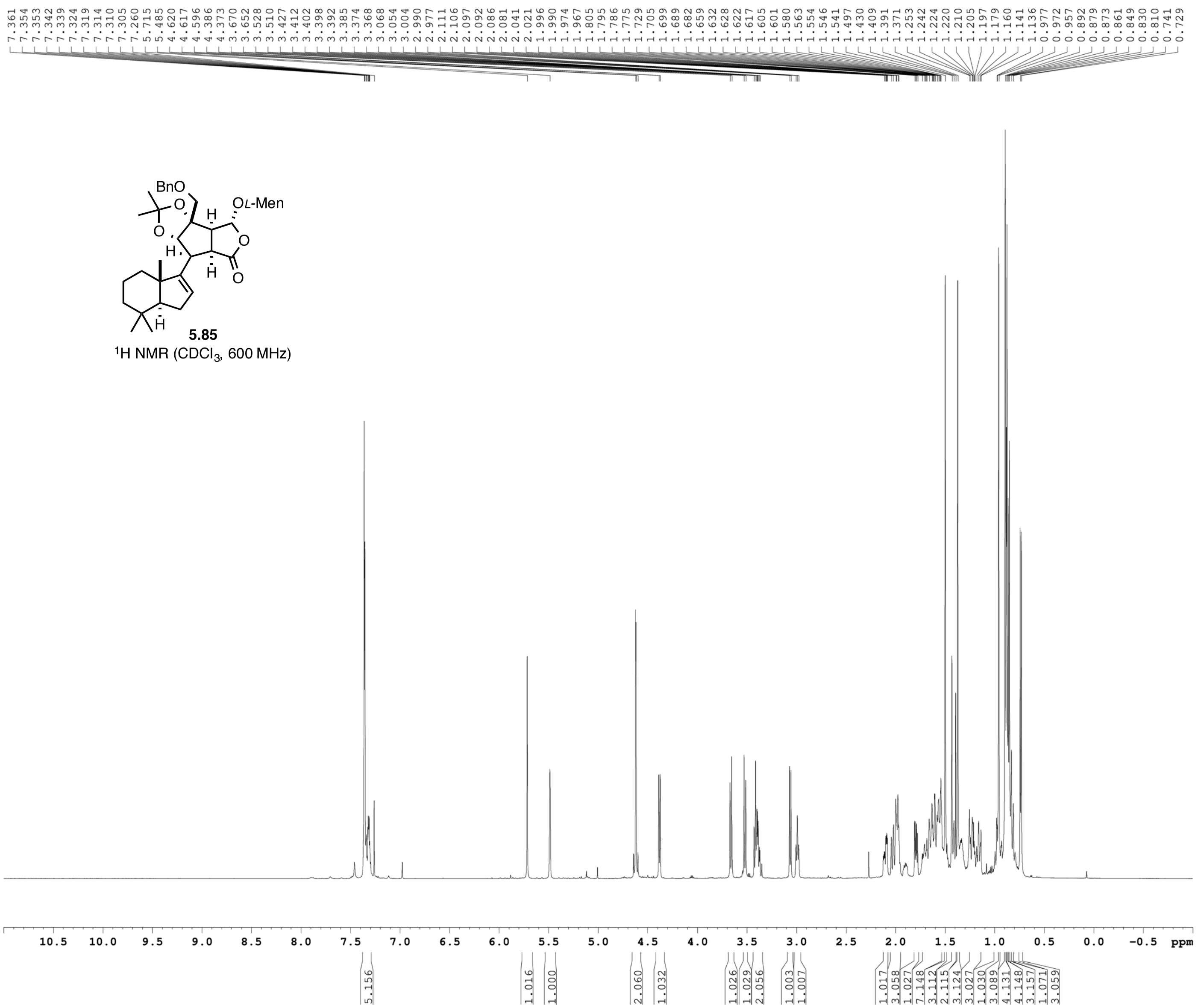
======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 2.70 dB
SP2                 2.70 dB
SPNAM[1] Crp60,0.5,20.1
SPNAM[2]    Crp60comp.4
SPOFF1   0 Hz
SPOFF2   0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804071 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  2.00
```

YS-V-312B



5.85

^{1}H NMR (CDCl$_3$, 600 MHz)

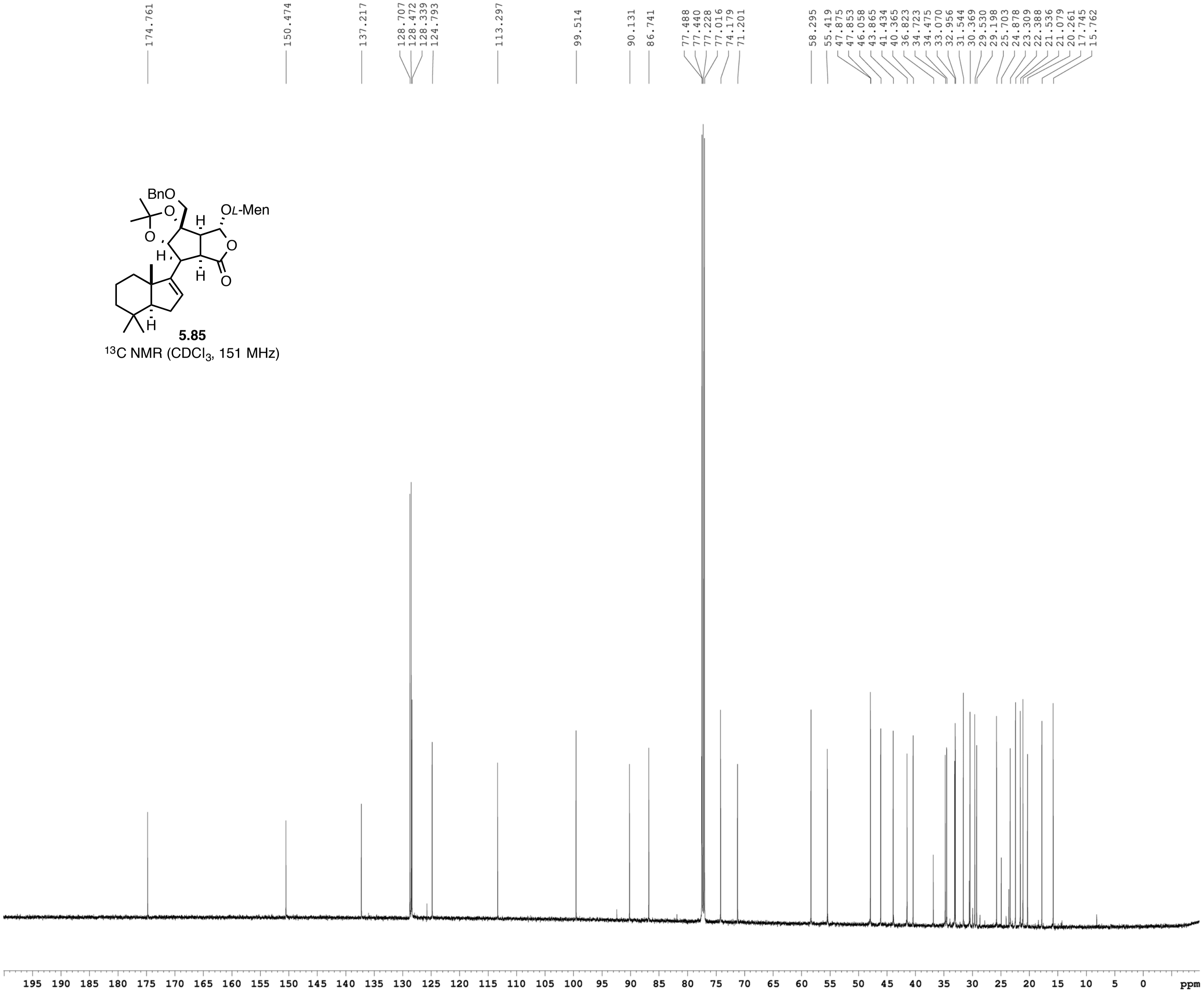
```
Current Data Parameters
NAME          YS-V-312B
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20170520
Time              13.16
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG            zg30
TD                98074
SOLVENT           CDCl3
NS                    8
DS                    1
SWH            9615.385 Hz
FIDRES         0.098042 Hz
AQ            5.0998478 sec
RG                   10
DW               52.000 usec
DE                13.70 usec
TE                298.0 K
D1           0.10000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1342009 MHz
NUC1                 1H
P1                12.00 usec
PLW1        20.00000000 W

F2 - Processing parameters
SI                65536
SF          600.1300349 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

YS-V-312B



5.85

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME            YS-V-312B
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170520
Time                13.18
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                  65536
SOLVENT             CDCl3
NS                     96
DS                      1
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9043968 sec
RG                   2050
DW                 13.800 usec
DE                  19.65 usec
TE                  298.0 K
D1             0.40000001 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          64.00000000 W

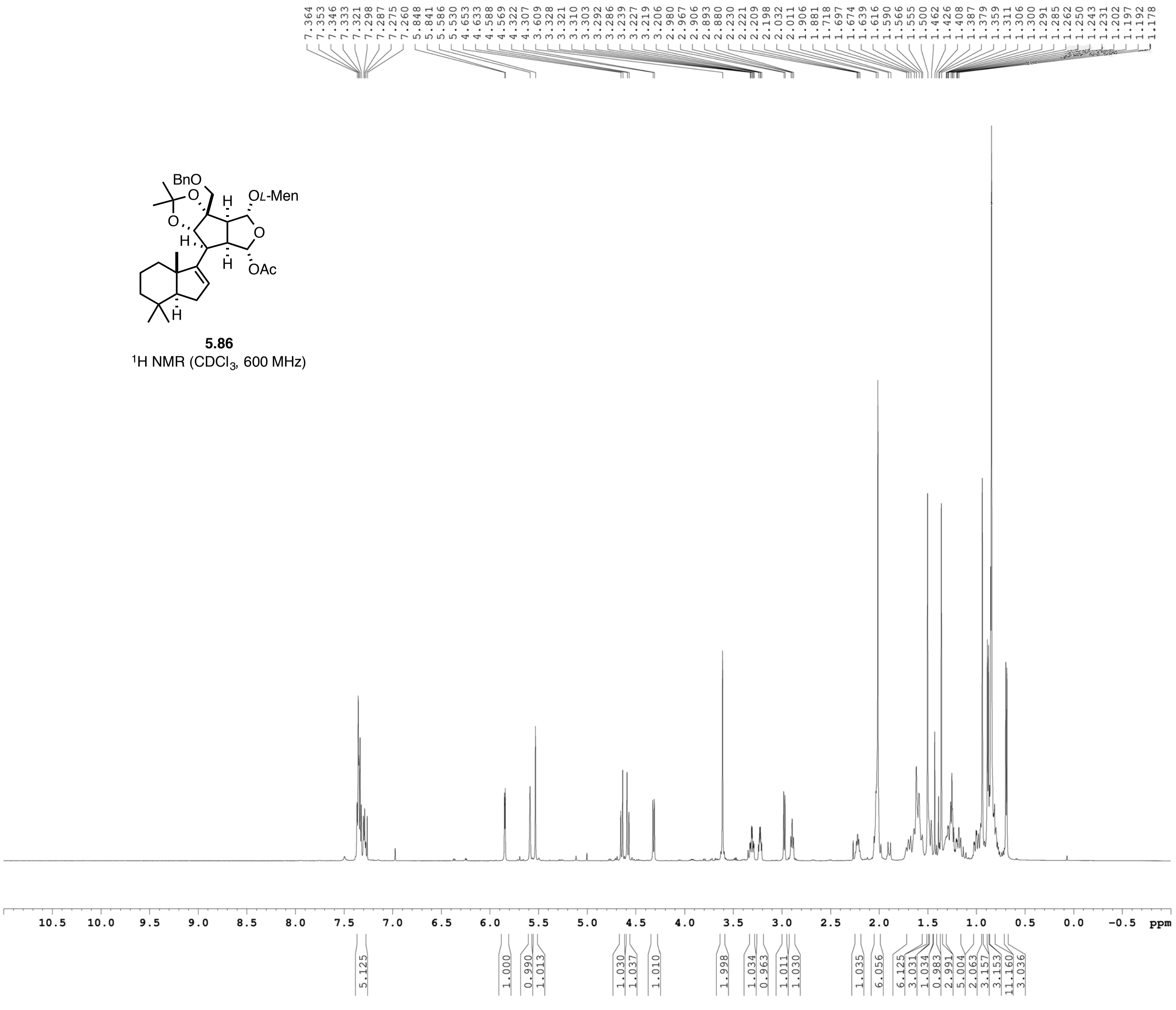
======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                  65536
SF           150.9027864 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

YS-VI-2

5.86

^{1}H NMR (CDCl$_3$, 600 MHz)



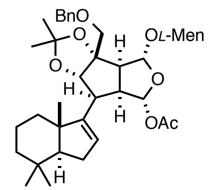
```
Current Data Parameters
NAME              YS-VI-2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170523
Time               14.15
INSTRUM            av600
PROBHD   5 mm CPBBO BB-
PULPROG             zg30
TD                 96152
SOLVENT            CDCl3
NS                     8
DS                     1
SWH          9615.385 Hz
FIDRES       0.100002 Hz
AQ          4.9999042 sec
RG                    16
DW            52.000 usec
DE             13.70 usec
TE             298.0 K
D1        0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1      600.1342009 MHz
NUC1                  1H
P1             12.00 usec
PLW1      20.00000000 W

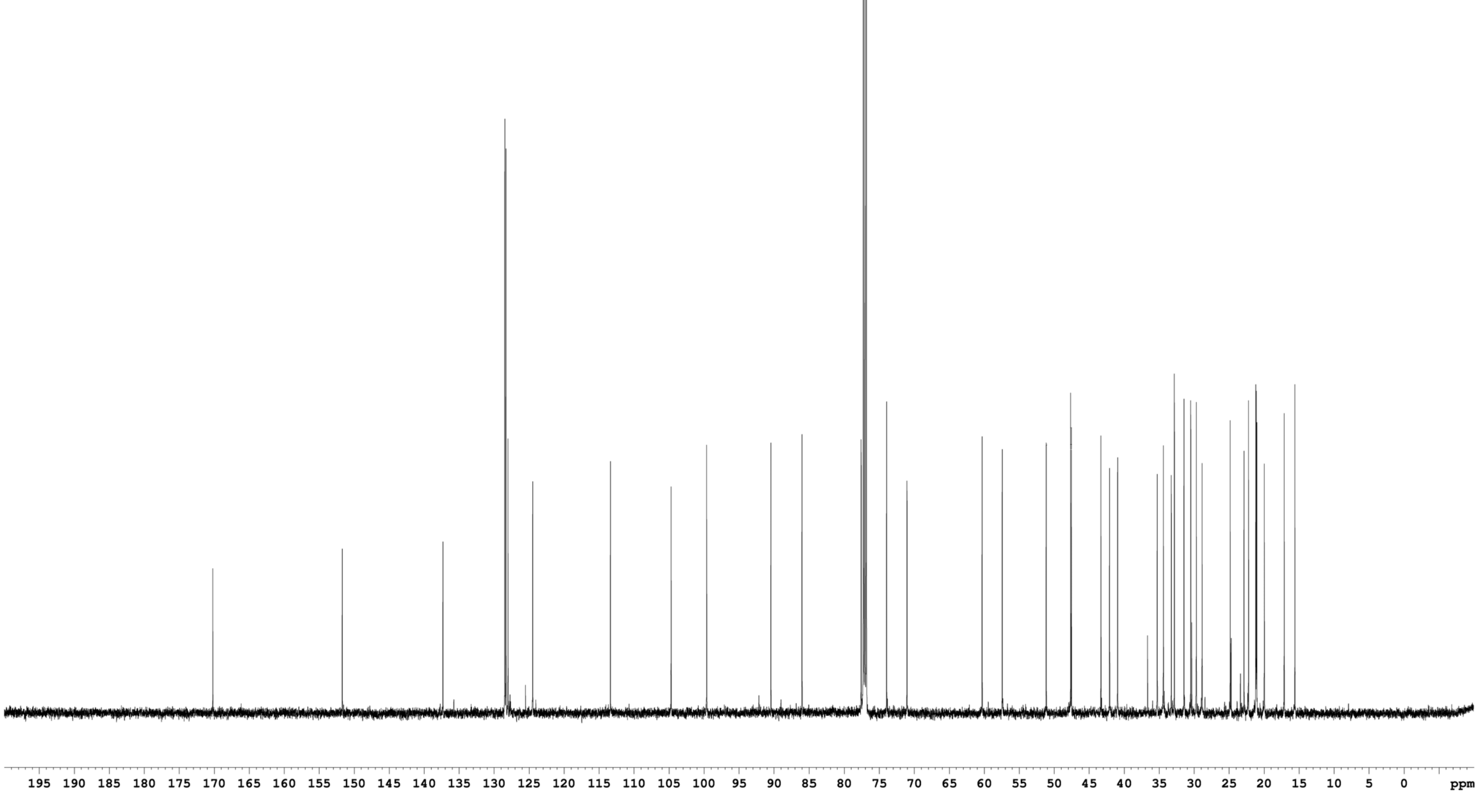
F2 - Processing parameters
SI                 65536
SF        600.1300348 MHz
WDW                   EM
SSB      0
LB                0.30 Hz
GB       0
PC                  1.00
```

YS-VI-2



5.86

^{13}C NMR (CDCl$_3$, 151 MHz)



```
Current Data Parameters
NAME              YS-VI-2
EXPNO                   3
PROCNO                  1

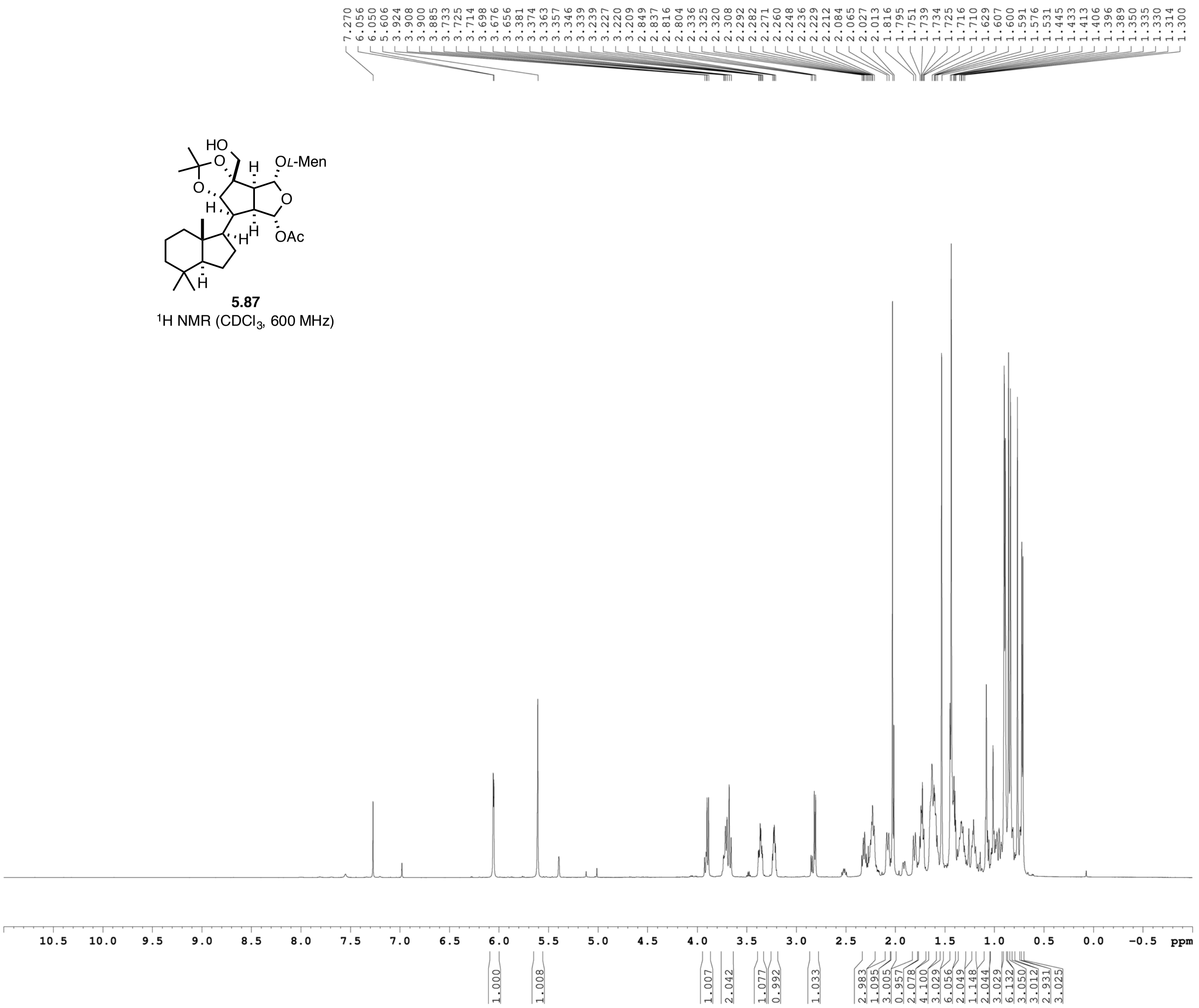
F2 - Acquisition Parameters
Date_            20170523
Time                14.04
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    320
DS                      1
SWH             36231.883 Hz
FIDRES           0.552855 Hz
AQ              0.9043968 sec
RG                   2050
DW                 13.800 usec
DE                  19.65 usec
TE                  298.0 K
D1             0.40000001 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          150.9194080 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          64.00000000 W

======== CHANNEL f2 ========
SFO2          600.1330010 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2          20.00000000 W
PLW12          0.36000001 W

F2 - Processing parameters
SI                  65536
SF            150.9028192 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

YS-VI-13



5.87

^{1}H NMR (CDCl$_3$, 600 MHz)

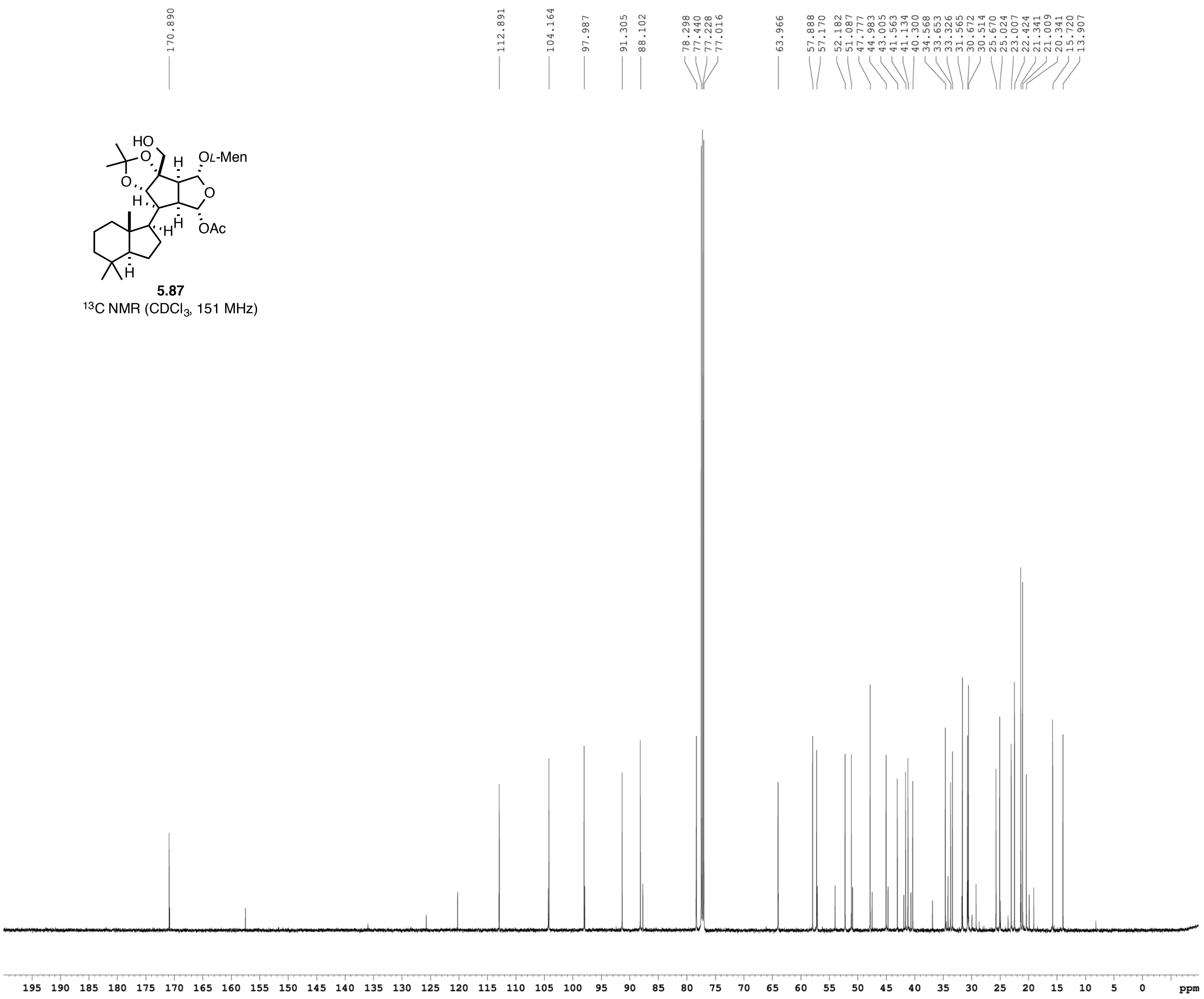
```
Current Data Parameters
NAME              YS-VI-13
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170607
Time                 10.53
INSTRUM              av600
PROBHD   5 mm CPBBO BB-
PULPROG               zg30
TD                   96152
SOLVENT              CDCl3
NS                       8
DS                       1
SWH              9615.385 Hz
FIDRES           0.100002 Hz
AQ              4.9999042 sec
RG                      10
DW                  52.000 usec
DE                   13.70 usec
TE                   298.0 K
D1             0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           600.1342009 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           20.00000000 W

F2 - Processing parameters
SI                   65536
SF             600.1300285 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

YS-VI-13



5.87

^{13}C NMR (CDCl$_3$, 151 MHz)

```
Current Data Parameters
NAME              YS-VI-13
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_            20170607
Time                10.57
INSTRUM             av600
PROBHD   5 mm CPBBO BB-
PULPROG           zgdc30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     1
SWH            36231.883 Hz
FIDRES          0.552855 Hz
AQ             0.9043968 sec
RG                  2050
DW                13.800 usec
DE                 19.65 usec
TE                 298.0 K
D1            0.40000001 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9194080 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         64.00000000 W

======== CHANNEL f2 ========
SFO2         600.1330010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         20.00000000 W
PLW12         0.36000001 W

F2 - Processing parameters
SI                 65536
SF           150.9027847 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```