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Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA,
IRVINE

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:
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Professor Scott D. Rychovsky

2018

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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)

PROFESSIONAL ACTIVITIES

June 2016 to June 2017	University of California, Irvine (Irvine, CA) <i>Student-Hosted Seminar Committee Member</i>
May 2016 to March 2018	University of California, Irvine (Irvine, CA) <i>Larry E. Overman Group Coordinator</i>

ABSTRACT OF THE DISSERTATION

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

By

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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.

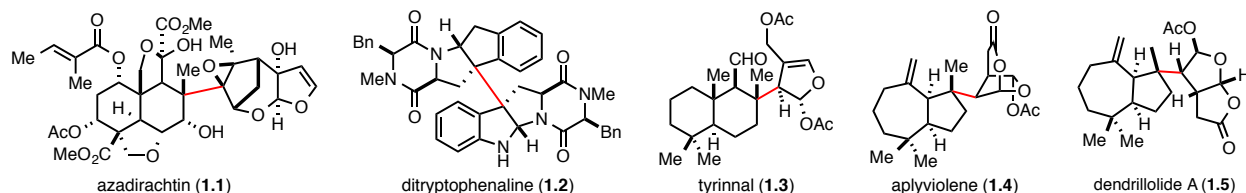
Chapter 1: Fragment Coupling and Formation of Quaternary Carbons by Visible-Light Photoredox Catalyzed Reaction of *tert*-Alkyl Hemioxalate Salts and Michael Acceptors

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-Hiyama-Kishi couplings, and olefin metathesis.¹

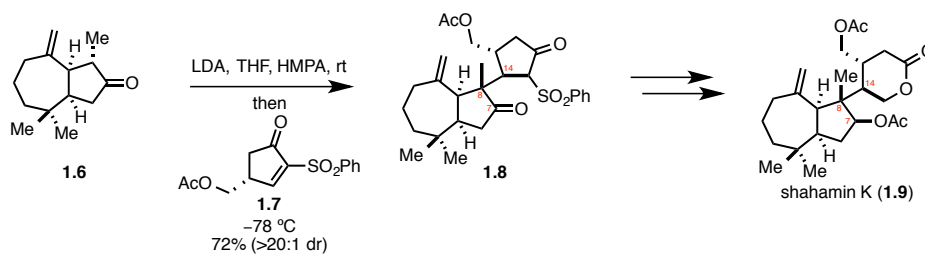
The union of complex fragments is particularly challenging when the coupling results in the formation of sp^3 - sp^3 σ bonds and two stereocenters, especially when the two stereocenters reside in different rings. The challenge is further enhanced when one of the newly formed stereocenters is quaternary.² 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 rearrangement⁸ to achieve the formation of the key bond.

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



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.

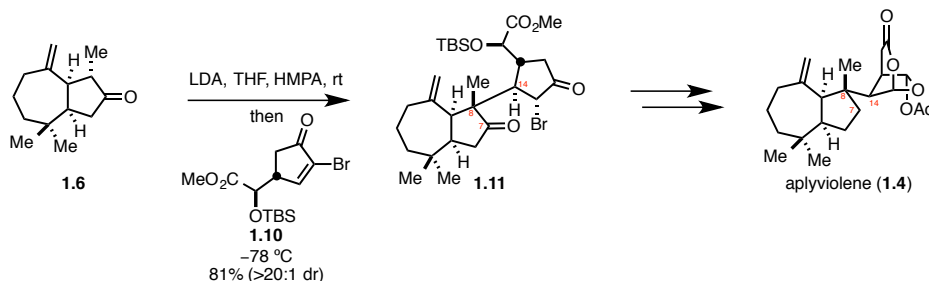
Figure 1.2. Key fragment coupling in the total synthesis of shahamin K (**1.9**).



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

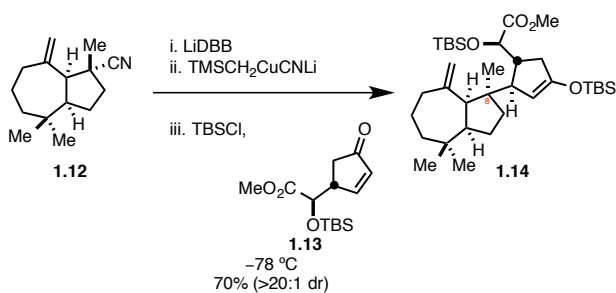
the overall efficiency of the synthetic sequence and highlighted the importance of coupling the hydroazulene unit in the correct oxidation state.

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 sp³-sp³ 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 addition¹⁵ 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.

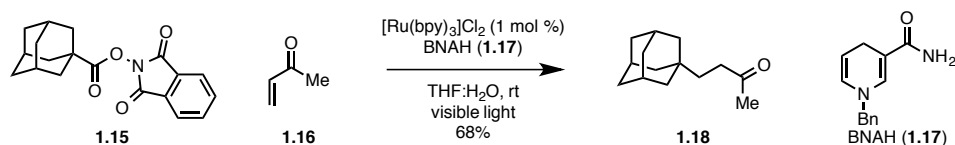
The side reactions, leading to low yields of coupled products, associated with bimolecular radical reactions of highly functionalized partners are often a consequence of the harsh reaction conditions required for radical generation (e.g., high temperatures, stoichiometric tin reagent, or high-energy 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]Cl₂, 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

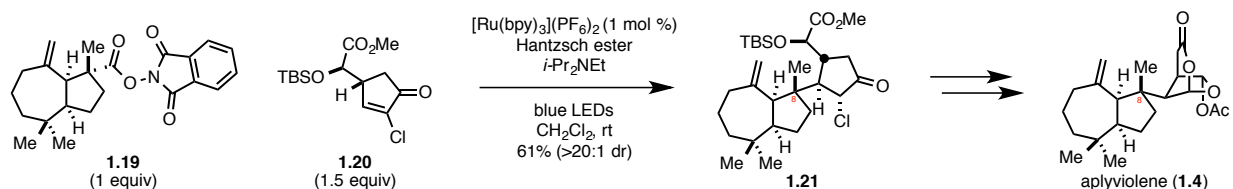
use of this methodology may be applicable for the proposed complex fragment coupling in the second-generation synthesis of aplyviolene (**1.4**).

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.

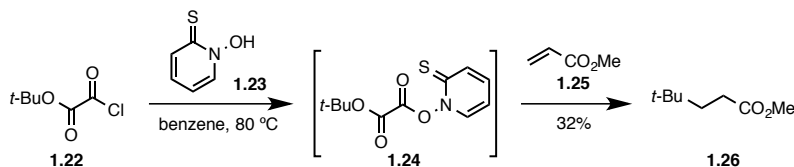


The success of the complex fragment coupling during the second-generation synthesis of aplyviolene (**1.4**), achieved via a conjugate addition of a nucleophilic tertiary radical to an electron-deficient olefin, indicated that such an approach may be useful in other total synthesis settings. Nonetheless, 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 CO₂ activates the C–O bond, allowing the generation of nucleophilic radicals from alcohols.

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

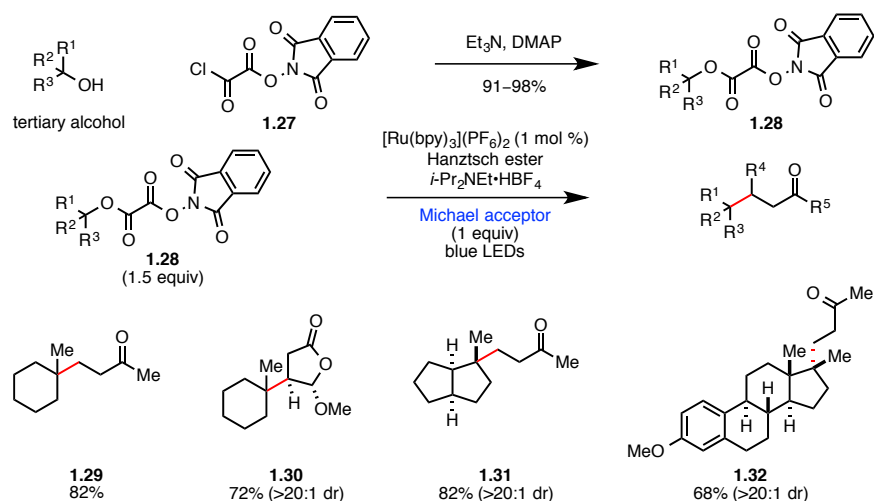


Barton described the trapping of several radicals, generated from thiohydroxamate oxalates, with electron-deficient olefins. However, the yields of the desired products such as **1.26** were low. One possible explanation for the low efficiency is the high sensitivity of these radical precursors. Barton 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-

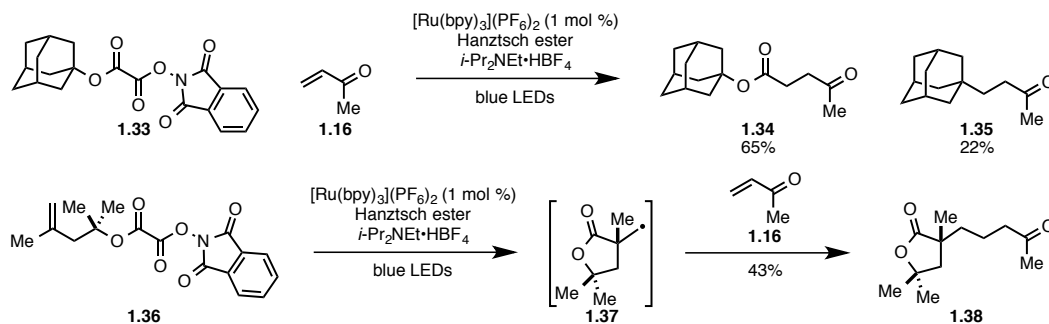
light photoredox conditions.²⁶ These radical precursors are isolable by filtration, are typically solids, and are not light-sensitive. However, they are unstable toward aqueous workup and flash chromatography on silica gel. Subjection of a slight excess *tert*-alkyl *N*-phthalimidoyl oxalates **1.28** (1.5 equiv), to photoredox reaction conditions in the presence of catalytic [Ru(bpy)₃]PF₆, 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 alkoxy-carbonyl 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.

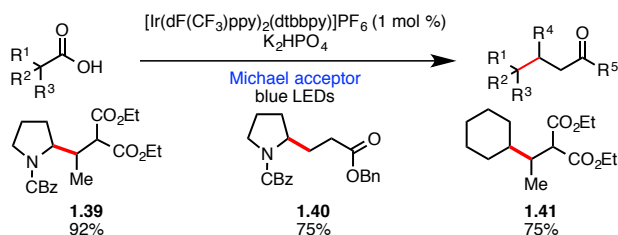
Scheme 1.1. Trapping of an intermediate alkoxy-carbonyl radicals.



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.

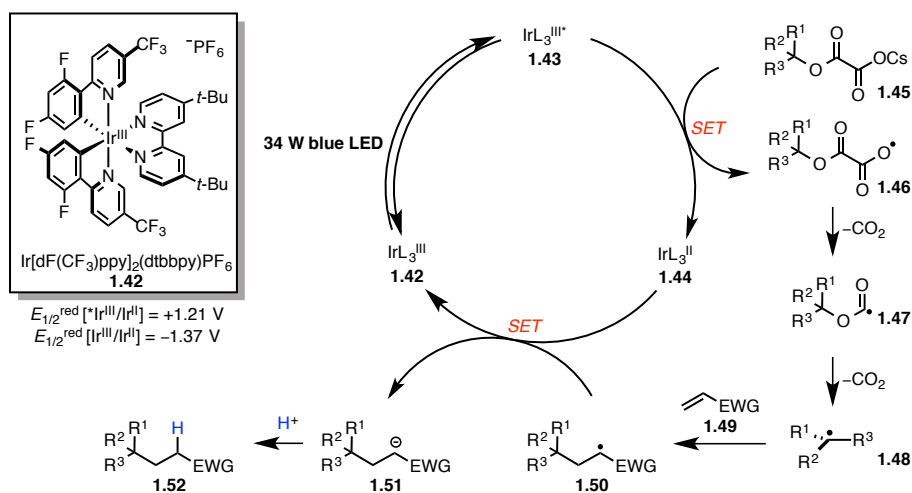


1.2 Results and Discussion

The mechanistic details of the proposed coupling reaction are outlined in Scheme 1.2. It has been shown that irradiation of heteroleptic photocatalyst $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (**1.42**) [$\text{dF}(\text{CF}_3)\text{ppy}$ = 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 ($\tau = 2.3 \mu\text{s}$) excited state $^*\text{Ir}^{\text{III}}$ **1.43**, which is a strong oxidant ($E_{1/2}^{\text{red}} [^*\text{Ir}^{\text{III}}/\text{Ir}^{\text{II}}] = +1.21 \text{ V vs. SCE in CH}_3\text{CN}$).³⁰ On this basis, we hypothesized that oxidation of the conjugate base of alkyl oxalate **1.45** ($E_{1/2}^{\text{red}} = +1.28 \text{ V vs. SCE in MeCN}$ for *t*-BuOCOCO₂Cs)³¹ by $^*\text{Ir}^{\text{III}}$ (**1.43**) via single-electron transfer should be thermodynamically feasible, generating alkyl radical **1.48** following the stepwise loss of two molecules of

CO₂.^{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 ($E_{1/2}^{\text{red}} = -0.59$ to -0.73 V vs. SCE in MeCN)³² by SET from the available Ir^{II} species **1.44 ($E_{1/2}^{\text{red}} [\text{Ir}^{\text{III}}/\text{Ir}^{\text{II}}] = -1.37$ 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.****

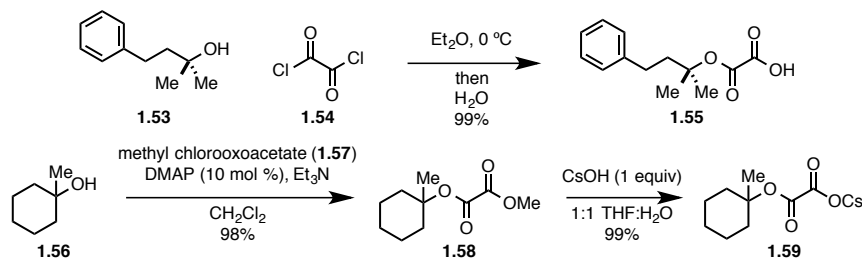
Scheme 1.2. Proposed mechanism for redox-neutral radical coupling reaction using alkyl oxalates and Michael acceptors.



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 Et₂O, 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.

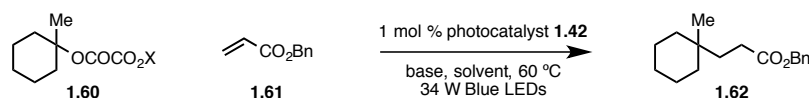


With streamlined access to the new radical precursors, we first explored the proposed decarboxylative alkylation reaction using the alkyl hydrogen oxalate derived from 1-methylcyclohexanol **1.60** in the presence of benzyl acrylate **1.61** as an archetypal Michael acceptor (Table 1.1). Using Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (**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.



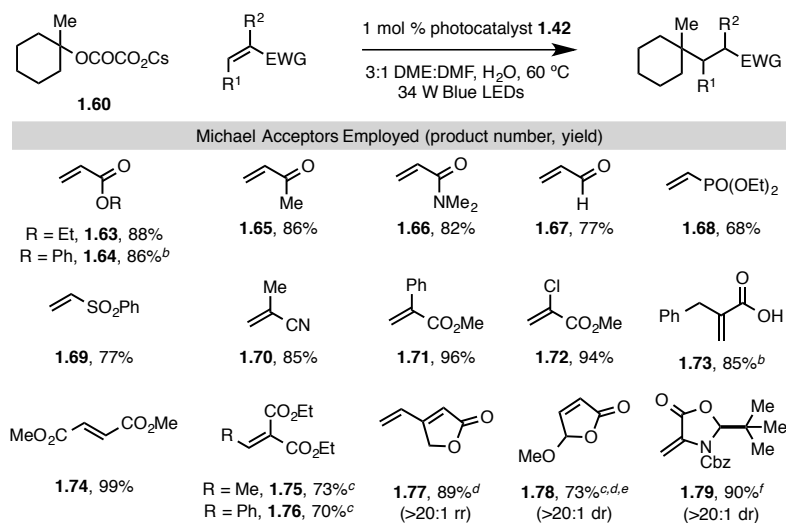
entry	X	solvent	base	yield ^a
1	H	DMF	K ₂ HPO ₄	64%
2	H	DMF	CsF	74%
3	H	DME	CsF	82%
4	H	3:1 DME:DMF	CsF	91%
5	Cs	3:1 DME:DMF	none	65%
6 ^b	Cs	3:1 DME:DMF	none	95%
7 ^b	Li	3:1 DME:DMF	none	93%
8 ^{b,c}	Cs	3:1 DME:DMF	none	66%
9 ^{b,d}	Cs	3:1 DME:DMF	none	0%
10 ^{b,e}	Cs	3:1 DME:DMF	none	0%

^aReactions on 0.2 mmol scale using 1.0 equiv acceptor and 1.1 equiv oxalate. Yields determined by ¹H NMR using mesitylene as an internal standard. ^b10 equiv water added. ^cReaction performed with 26W CFL. ^dReaction performed without photocatalyst. ^eReaction 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).

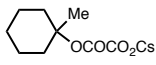
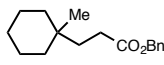
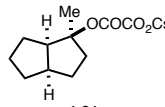
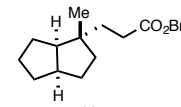
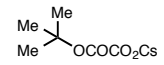
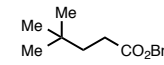
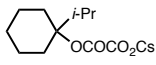
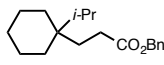
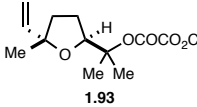
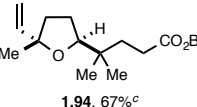
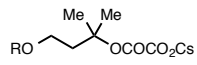
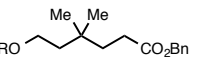
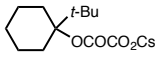
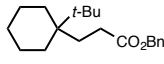
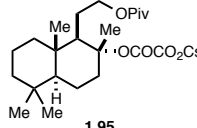
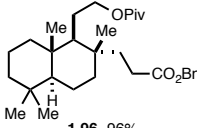
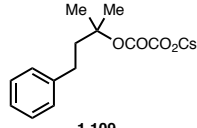
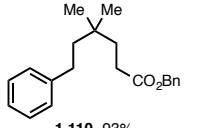
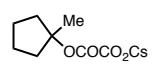
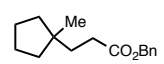
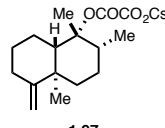
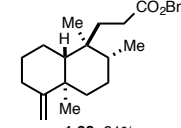
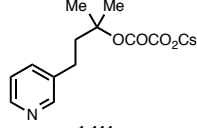
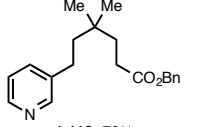
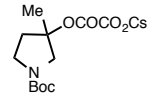
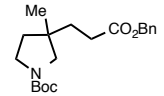
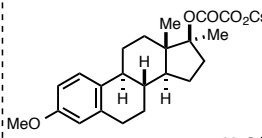
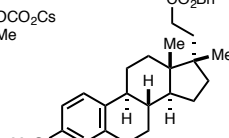
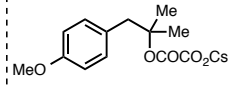
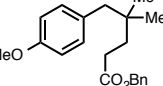
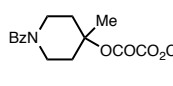
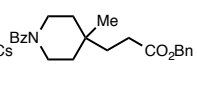
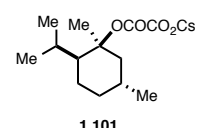
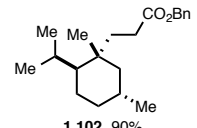
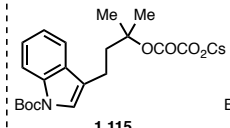
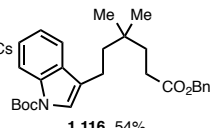
Table 1.2. Acceptor scope with alkyl cesium oxalate **1.60**.^a



^aIsolated yields using optimized conditions from Table 1.1 with 1.0 equiv acceptor and 1.1 equiv oxalate (see Experimental Information). ^bPerformed with 1.5 equiv of cesium oxalate. ^cPerformed in 100% DME. ^dRun at 22 °C. ^eProduct **1.78** isolated as *trans*-isomer. ^fProduct **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 addition¹⁴ 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

Oxalate	Product	Oxalate	Product	Oxalate	Product
	 1.80, 91%		 1.92, 85% (>20:1 dr)		 1.104, 76%
	 1.82, 93%		 1.94, 67% ^c		 1.106, 92% 1.108, 76% R = TBS 1.105 R = PMB 1.107
	 1.84, 73%		 1.96, 96% (>20:1 dr)		 1.110, 93%
	 1.86, 92%		 1.98, 91% (>20:1 dr)		 1.112, 70%
	 1.88, 72%		 1.100, 85% ^b (>20:1 dr)		 1.114, 71%
	 1.90, 77%		 1.102, 90% (>20:1 dr)		 1.116, 54%

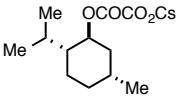
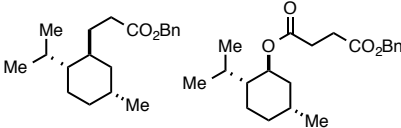
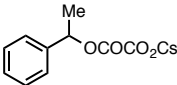
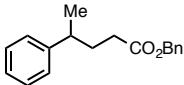
^aIsolated yields using optimized conditions from Table 1.1 with 1.0 equiv acceptor and 1.1 equiv oxalate (see Experimental Information).

^bPerformed with 1.5 equiv of oxalate. ^cUsing 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 alkoxy carbonyl 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

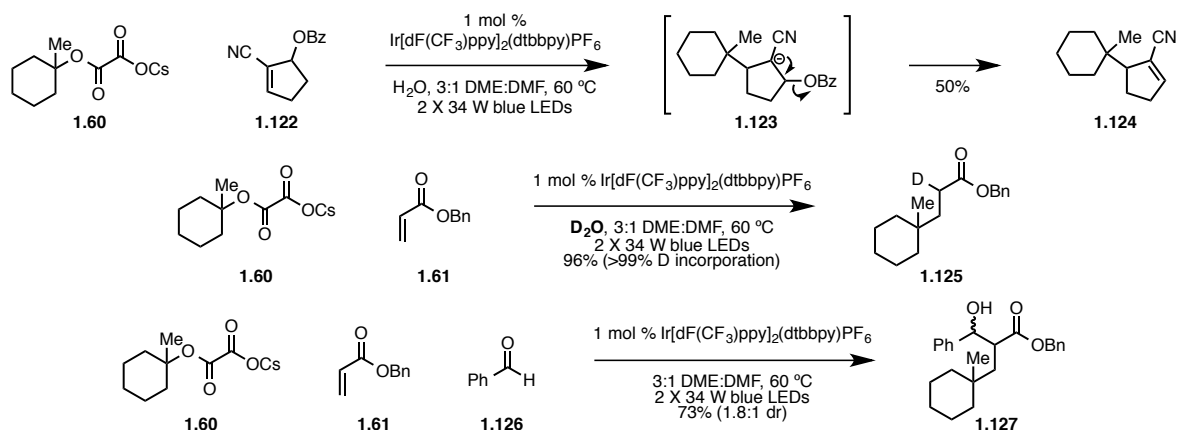
Oxalate	Product
 <p>1.117</p>	 <p>1.118, 51% 1.119, 29%</p>
 <p>1.120</p>	 <p>1.121, 57%</p>

^aIsolated 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 cyclopentenitrile 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 D₂O in place of H₂O, 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.



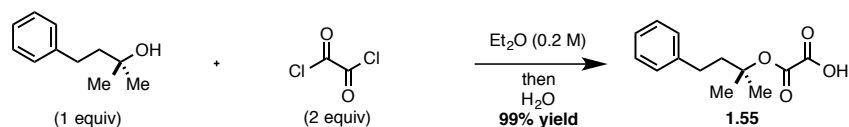
1.3 Conclusion

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

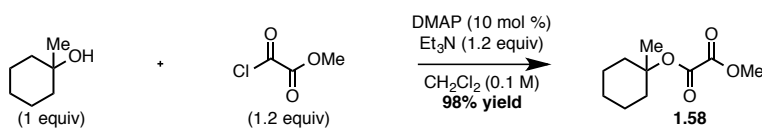
1.4 Experimental Information

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. $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6^{39}$ 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 F₂₅₄ 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. ^1H NMR spectra were recorded at 500 or 600 MHz. 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 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 ^1H 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>.

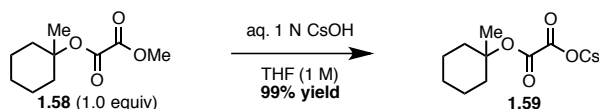


Preparation of oxalic acid 1.55: A round-bottom flask was charged with 2-methyl-4-phenylbutan-2-ol (10.4 g, 63.4 mmol 1.0 equiv) followed by the addition of Et₂O (320 mL, 0.2 M). The solution was cooled to 0 °C. Next, oxalyl chloride (11 mL, 127 mmol, 2 equiv) was added dropwise. The homogeneous reaction 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 H₂O (200 mL). The resulting mixture was transferred to a separatory funnel with Et₂O (100 mL). The resulting biphasic mixture was extracted with Et₂O (3 x 100 mL) and the organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure to yield **1.55** (14.8 g, 99% yield) as a brown solid. ¹H NMR (600 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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 C₁₃H₁₅O₄, 235.0970; found, 235.0962.

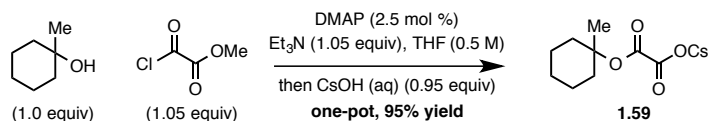


Preparation of methyl oxalate 1.58: A round-bottom flask was charged with 1-methylcyclohexan-1-ol (2.3 g, 20 mmol, 1.0 equiv) and CH₂Cl₂ (DCM) (200 mL, 0.1M). Triethylamine (3.4 mL, 24 mmol, 1.2 equiv) and DMAP (250 mg, 2 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (2.2 mL, 24 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH₄Cl (aq)

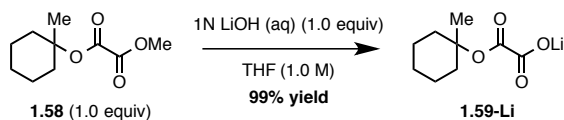
(100 mL). The aqueous phase was extracted with DCM (100 mL), and the organic extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et₂O) to give **1.58** as clear oil (3.9 g, 98% yield). R_f 0.45 (4:1 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): δ 3.88 (s, 3H), 2.23–2.21 (m, 2H), 1.60–1.49 (m, 10H), 1.32–1.28 (m, 1H); ¹³C NMR (126 MHz, CDCl₃): 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 C₁₀H₁₆O₄Na, 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-d₆): 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); ¹³C NMR (126 MHz, DMSO-d₆): 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 C₉H₁₃O₄, 185.0814; found, 185.0816.

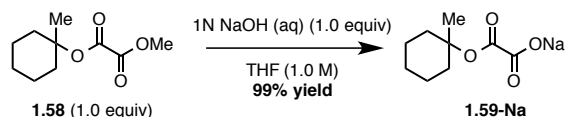


One-pot preparation of cesium oxalate 1.59: 1-methylcyclohexan-1-ol (2.28 g, 20 mmol, 1.0 equiv) was dissolved in THF (40 mL, 0.5 M). Triethylamine (2.9 mL, 21 mmol, 1.05 equiv) and DMAP (61 mg, 0.5 mmol, 0.025 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (1.9 mL, 21 mmol, 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.

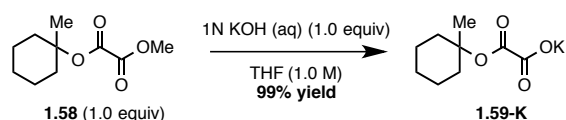


Preparation of lithium oxalate 1.59-Li: A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **1.58** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N LiOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred 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). ^1H 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 $\text{C}_9\text{H}_{13}\text{O}_4\text{Li}$ ($[\text{M-Li}]^-$) 185.0814; found 185.0816.

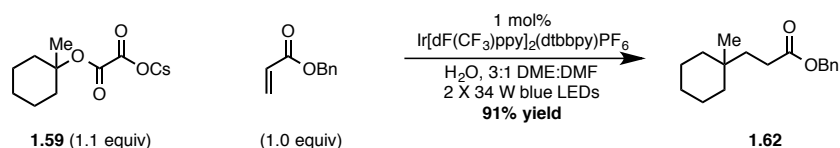


Preparation of sodium oxalate 1.59-Na: A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **1.58** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N NaOH (aq) (1.0 mL, 1.0 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.59-Na** as a colorless solid (206 mg, 99% yield). ^1H 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 $\text{C}_9\text{H}_{13}\text{O}_4\text{Na}$ ($[\text{M-Na}]^-$) 185.0814; found 185.0807.



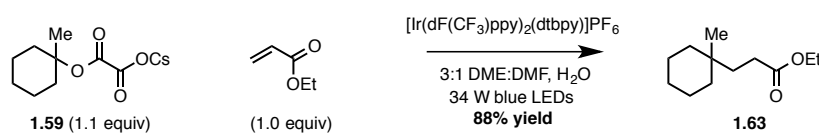
Preparation of potassium oxalate 1.59-K: A round-bottom flask was charged with 1-methylcyclohexyl methyl oxalate **1.58** (200 mg, 1.0 mmol, 1 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N KOH (aq) (1.0 mL, 1.0 mmol, 1 equiv)

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). ^1H 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 $\text{C}_9\text{H}_{13}\text{O}_4\text{K}$ ($[\text{M-K}]^-$) 185.0814; found 185.0807.

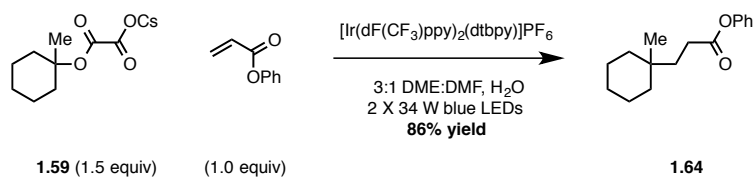


Preparation of ester 1.62: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 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 $^\circ\text{C}$ 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 . ^1H 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

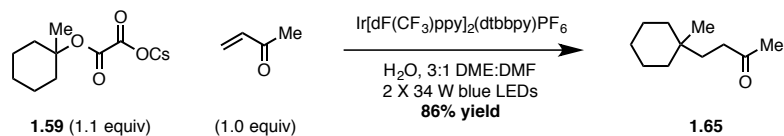
(126 MHz, CDCl₃): δ 174.6, 136.2, 128.7, 128.4, 128.3, 66.3, 37.6, 36.8, 32.4, 29.1, 26.5, 24.6, 22.1; IR (thin film): 2923, 2850, 1730, 1157, 696 cm⁻¹; HRMS-ESI (m/z) [M+Na]⁺ calculated for C₁₇H₂₄O₂Na, 283.1674; found, 283.16748.



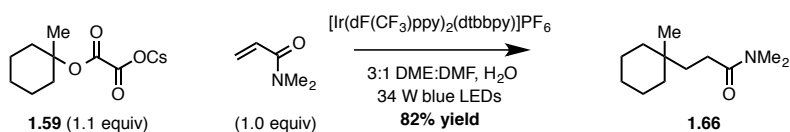
Preparation of ester 1.63: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μ L, 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) 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 C₁₂H₂₂O₂ ([M+Na]⁺) 221.1517; found 221.1523.



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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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 $\text{C}_{16}\text{H}_{23}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 247.1693; found 247.1692.

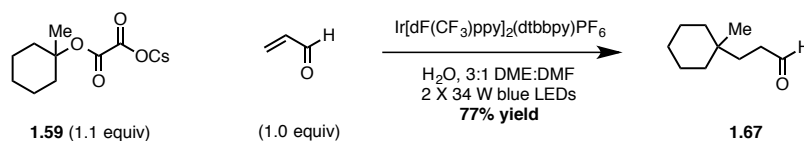


Preparation of ketone 1.65: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et₂O) to give **1.65** as a yellow oil (72 mg, 86% yield). R_f = 0.3 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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}



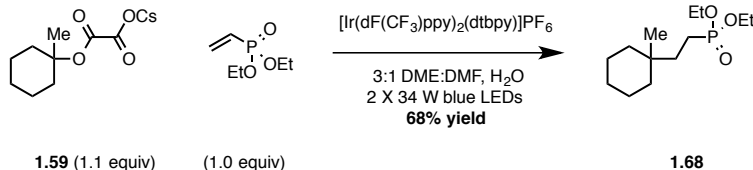
Preparation of amide 1.66: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv)

and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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}



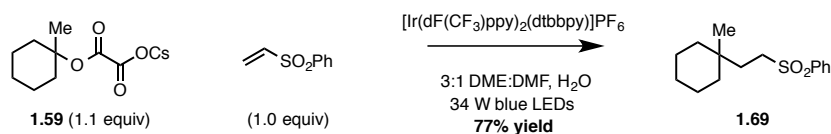
Preparation of aldehyde 1.67: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.67**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was

purified by flash column chromatography on silica gel (93:7 hexanes:Et₂O) to give **1.67** as a yellow oil (59 mg, 77% yield). *R_f* = 0.4 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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 C₁₀H₁₈ONa, 177.1255; found, 177.1257.

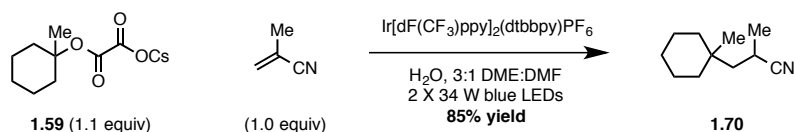


Preparation of phosphonate 1.58: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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

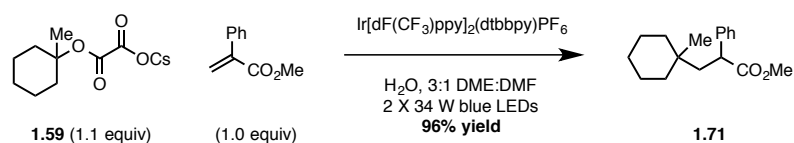
hexanes:acetone); visualized with KMnO_4 . ^1H NMR (600 MHz, CDCl_3): δ 4.14–4.04 (m, 4H), 1.71–1.63 (m, 2H), 1.56–1.39 (m, 7H), 1.33 (app t, $J = 7.0$ Hz, 7H), 1.25–1.19 (m, 4H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3): δ 61.6 (d, $J_{\text{C-P}}=6.4$), 37.4, 34.0, 26.6, 24.4, 22.1, 20.7, 19.6, 16.7 (d, $J_{\text{C-P}}=6.0$); IR (thin film): 2925, 1456, 1231, 1080, 957 cm^{-1} ; HRMS-ESI (m/z) $[\text{M} + \text{Na}]^+$ calculated for $\text{C}_{13}\text{H}_{27}\text{O}_3\text{PNa}$, 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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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}

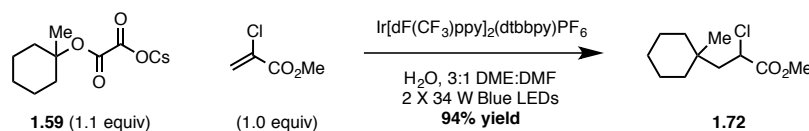


Preparation of nitrile 1.70: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 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_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 **1.70** as a yellow oil (70 mg, 85% yield). $R_f = 0.45$ (9:1 hexanes:acetone); visualized with KMnO_4 . ^1H 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



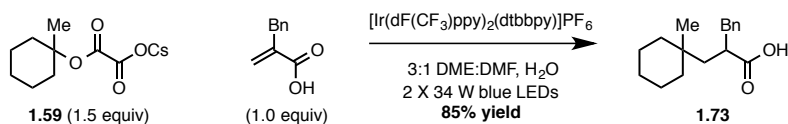
Preparation of ester 1.71: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005

mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μ L, 5.0 mmol, 10 equiv), and methyl 2-phenylacrylate⁴¹ (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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 KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [*M* + NH₄]⁺ calculated for C₁₇H₂₈NO₂, 278.2120; found, 278.2122.



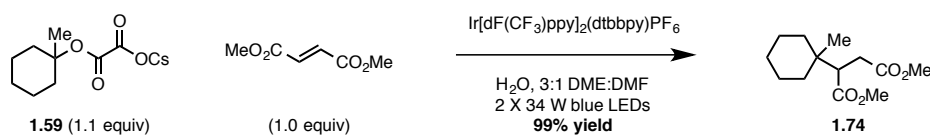
Preparation of ester 1.72: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μ L, 5.0 mmol, 10 equiv), and α -chloro methacrylate (51 μ L, 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et₂O) to give **1.72** as a yellow oil (102 mg, 94% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M + NH₄]⁺ calculated for C₁₁H₂₃ClNO₂, 236.1417; found, 236.1415.



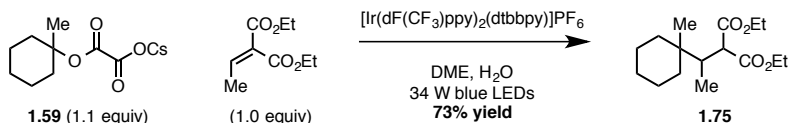
Preparation of acid 1.73: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (239 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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): R_f = 0.45 (75:25 hexanes:ethyl acetate, stained with KMnO₄). ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₇H₂₄O₂ ([M-H]⁻) 259.1698; found 259.1690.



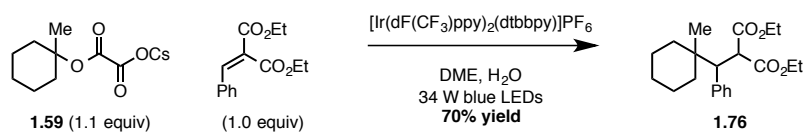
Preparation of diester 1.74: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**1.59**) (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et₂O) to give **1.74**

as a yellow oil (120 mg, 99% yield). $R_f = 0.5$ (9:1 hexanes:acetone); visualized with KMnO_4 . $^1\text{H NMR}$ (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}

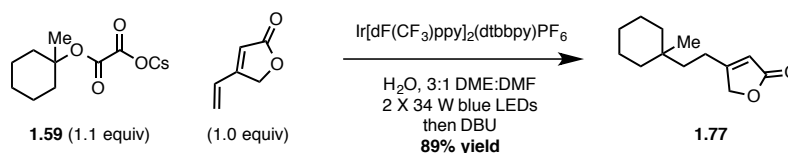


Preparation of diester 1.75: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 μL , 5.0 mmol, 10 equiv), and diethyl ethylidene malonate (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 $^\circ\text{C}$ 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 KMnO_4). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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,

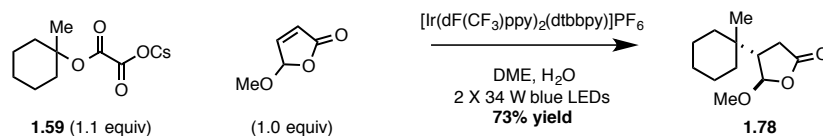
1463, 1371, 1301, 1151 cm^{-1} ; HRMS (ESI-TOF) m/z calculated for $\text{C}_{16}\text{H}_{28}\text{O}_4$ ($[\text{M}+\text{Na}]^+$) 307.1885; found 307.1894.



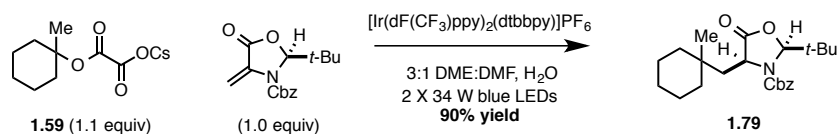
Preparation of diester 1.76: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 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 $^\circ\text{C}$ 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 KMnO_4). ^1H 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 $\text{C}_{21}\text{H}_{30}\text{O}_4$ ($[\text{M}+\text{Na}]^+$) 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(CF₃)ppy]₂(dtbbpy)PF₆ (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 butenolide⁴² (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 temperature at 23 °C. The reaction mixture was diluted with sat. LiCl (aq) (25 mL) and the aqueous phase was extracted with Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The residue was redissolved in CH₂Cl₂ (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 CH₂Cl₂ (10 mL), washed with 2 N aq. HCl (3 x 10 mL). Combined organic phases were dried over MgSO₄ 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 KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M + NH₄]⁺ calculated for C₁₃H₂₄NO₂, 226.1807; found, 226.1803.

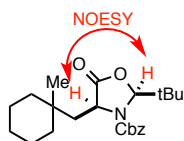


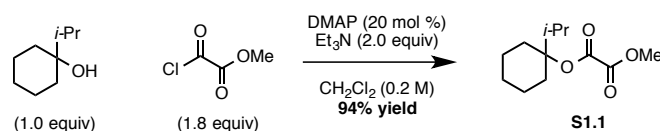
Preparation of lactone 1.78: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). DME (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and 5-methoxy butenolide⁴³ (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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}



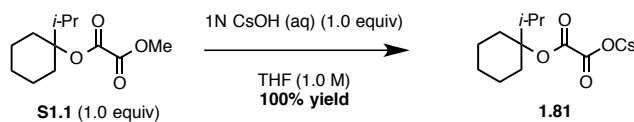
Preparation of oxooxazolidine 1.79: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.59** (175 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL, 5.0 mmol, 10 equiv), and benzyl (*S*)-2-(*tert*-butyl)-4-methylene-5-oxooxazolidine-3-carboxylate⁴⁴ (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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³₅₈₉ +36.2, [α]²³₅₇₇ +37.9, [α]²³₅₄₆ +43.3, [α]²³₄₃₅ +77.5, [α]²³₄₀₅ +98.1 (*c* = 1.0, CHCl₃). HRMS (ESI-TOF) *m/z* calculated for C₂₃H₃₃NO₄ ([M+Na]⁺) 410.2307; found 410.2315. Product stereochemistry was confirmed by a NOESY correlation:



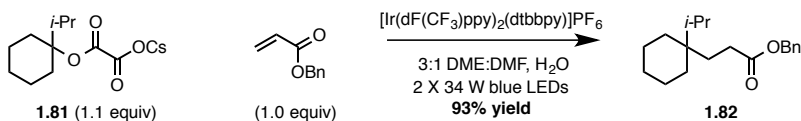


Preparation of methyl oxalate S1.1: 1-isopropylcyclohexan-1-ol (380 mg, 2.68 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (13 mL, 0.2 M). Triethylamine (750 μL , 5.4 mmol, 2.0 equiv) and DMAP (66 mg, 0.54 mmol, 0.2 equiv) were added followed by drop-wise addition of methyl chlorooxalate (440 μL , 4.83 mmol, 1.8 equiv). The reaction was stirred for 8 hours at 35 $^\circ\text{C}$, then quenched with sat. NH_4Cl (aq) (20 mL). The aqueous phase was extracted with CH_2Cl_2 (40 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 (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 KMnO_4). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 $\text{C}_{12}\text{H}_{20}\text{O}_4$ ($[\text{M}+\text{Na}]^+$) 251.1259; found 251.1251.



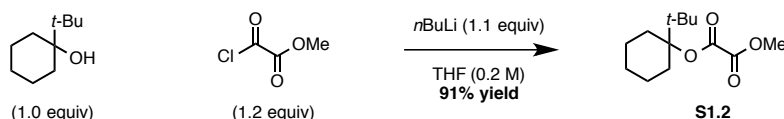
Preparation of cesium oxalate 1.81: A round-bottom flask was charged with 1-isopropylcyclohexyl methyl oxalate **S1.1** (563 mg, 2.47 mmol, 1 equiv) followed by the addition of THF (2.5 mL, 1 M). To this solution, 1 N CsOH (aq) (2.5 mL, 2.5 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature,

then concentrated under reduced pressure to give **1.81** as a colorless solid (855 mg, 100% yield). ^1H 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 $\text{C}_{11}\text{H}_{17}\text{O}_4\text{Cs}$ ($[\text{M}-\text{Cs}]^-$) 213.1127; found 213.1129.

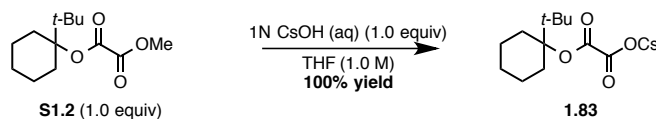


Preparation of ester 1.82: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.81** (190 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture 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 $^\circ\text{C}$ 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 **1.82** as a yellow oil (134 mg, 93% yield): $R_f = 0.35$ (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), 2.29–2.23 (m, 2H), 1.74–1.69 (m, 2H), 1.65 (hept, J

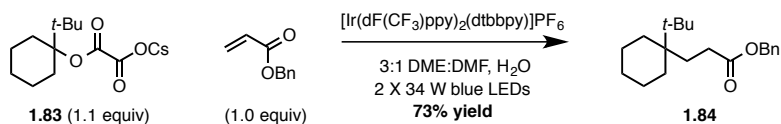
= 6.9 Hz, 1H), 1.52–1.15 (m, 10H), 0.82 (d, $J=7.0$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 174.7, 136.3, 128.7, 128.32, 128.29, 66.3, 36.6, 31.8, 31.2, 28.8, 27.6, 26.5, 21.5, 16.8. IR (KBr disk) 2933, 2866, 1729, 1456, 1388, 1216, 1163 cm^{-1} ; HRMS (ESI–TOF) m/z calculated for $\text{C}_{19}\text{H}_{28}\text{O}_2$ ($[\text{M}+\text{Na}]^+$) 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. $\text{NaHCO}_3(\text{aq})$ (20 mL). The aqueous phase was extracted with EtOAc (40 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 (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 KMnO_4). ^1H 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 $\text{C}_{13}\text{H}_{22}\text{O}_4$ ($[\text{M}+\text{Na}]^+$) 265.1416; found 265.1420.

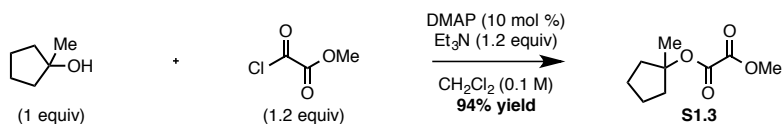


Preparation of cesium oxalate 1.83: A round-bottom flask was charged with 1-(*tert*-butyl)cyclohexyl methyl oxalate **S1.2** (311 mg, 1.29 mmol, 1 equiv) followed by the addition of THF (1.3 mL, 1 M). To this solution, 1 N CsOH (aq) (1.3 mL, 1.3 mmol, 1 equiv) was added drop-wise. The mixture was stirred vigorously for 5 min at room temperature, then concentrated under reduced pressure to give **1.83** as a colorless solid (467 mg, 100% yield). ^1H 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 $\text{C}_{12}\text{H}_{19}\text{O}_4\text{Cs}$ ($[\text{M}-\text{Cs}]^-$) 227.1283; found 227.1273.



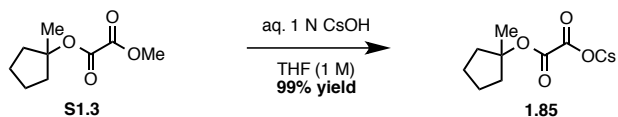
Preparation of ester 1.84: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.83** (198 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture 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 $^\circ\text{C}$ 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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): R_f = 0.40 (95:5 hexanes:ethyl acetate, stained with KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₀H₃₀O₂ ([M+Na]⁺) 325.2144; found 325.2133.

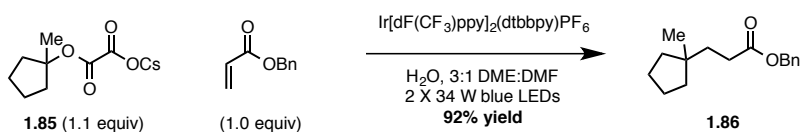


Preparation of methyl oxalate S1.3: A round-bottom flask was charged with 1-methylcyclopentanol (620 mg, 6.2 mmol, 1.0 equiv) and CH₂Cl₂ (62 mL, 0.1M). Triethylamine (1.0 mL, 7.5 mmol, 1.2 equiv) and DMAP (76 mg, 0.62 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxalate (0.7 mL, 7.5 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 °C, then quenched with sat. NH₄Cl (aq) (100 mL). The aqueous phase was extracted with CH₂Cl₂ (100 mL), and the organic extracts were dried over Na₂SO₄ 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 KMnO₄. ¹H NMR (600 MHz, CDCl₃): δ 3.87 (s, 3H), 2.22–2.20 (m, 2H), 1.78–1.75 (m, 4H), 1.69–1.64 (m, 5H); ¹³C NMR (126 MHz,

CDCl₃): 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-Cl (m/z) [M + NH₄]⁺ calculated for C₉H₁₈NO₄, 204.1236; found, 204.1233.

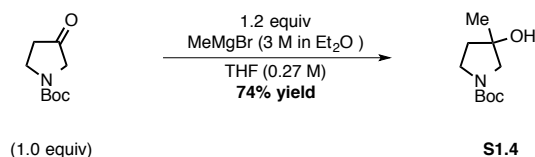


Preparation of cesium oxalate 1.85: A round-bottom flask was charged with methyl (1-methylcyclopentyl) oxalate (**S1.3**) (1.0 g, 5.4 mmol, 1.0 equiv) followed by the addition of THF (5.4 mL, 1 M). To this solution, 1 N aq. CsOH (5.4 mL, 5.4 mmol, 1.0 equiv) was added drop-wise. The mixture was stirred 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). ¹H NMR (600 MHz, DMSO-d₆): δ 1.98–1.95 (m, 2H), 1.63–1.54 (m, 6H), 1.46 (s, 3H); ¹³C NMR (126 MHz, DMSO-d₆): 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 C₈H₁₁O₄, 171.0657; found, 171.0661.



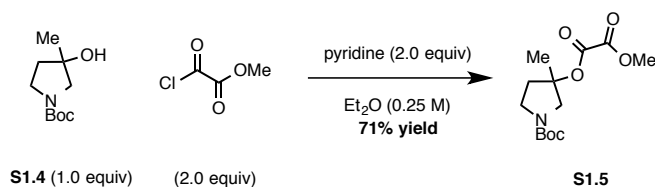
Preparation of ester 1.86: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate (**1.85**) (170 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1M) was added, followed by water (90 μ L, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μ L, 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (93:7 hexanes:Et₂O) to give **1.86** as a yellow oil (113 mg, 92% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M + NH₄]⁺ calculated for C₁₆H₂₆NO₂, 264.1964; found, 264.1967.



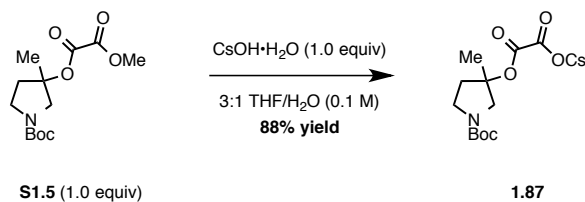
Preparation of alcohol S1.4: A solution of methyl magnesium bromide (3 M in Et₂O; 10.8 mL, 32.39 mmol, 1.2 equiv) was added dropwise to *tert*-butyl 3-oxopyrrolidine-1-carboxylate (5.0 g, 26.99 mmol, 1.0 equiv) in THF (100 mL) at 0 °C over 5 min. The resulting solution was warmed to room temperature overnight quenched with saturated aqueous NH₄Cl solution (50 mL) and diluted with Et₂O (100 mL). The layers were separated and the aqueous phase was extracted with Et₂O (3 x 50 mL). The combined ethereal extracts were washed with brine (50 mL), dried over MgSO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₀H₂₀NO₃⁺ ([M+H]⁺) 202.1438; found 202.1436.

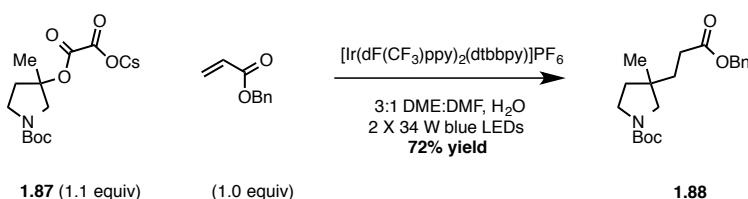


Preparation of methyl oxalate S1.5: Methyl chlorooxoacetate (920 μL, 9.94 mmol, 2.0 equiv) was added to a solution of *tert*-butyl 3-hydroxy-3-methylpyrrolidine-1-carboxylate **S1.4** (1.0 g, 4.97 mmol, 1.0 equiv) and pyridine (760 μL, 9.94 mmol, 2.0 equiv) in Et₂O (20 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 20 mL) and saturated aqueous NaHCO₃ solution (20 mL), dried over MgSO₄ 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 **S1.5** as a clear oil (1.03 g, 71% yield): *R_f* = 0.32 (2:1 hexanes:EtOAc, stained with KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 $\text{C}_{13}\text{H}_{22}\text{NO}_6^+$ ($[\text{M}+\text{H}]^+$) 288.1442, found 288.1439.

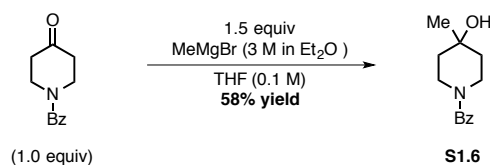


Preparation of cesium oxalate 1.87: $\text{CsOH}\cdot\text{H}_2\text{O}$ (175 mg, 1.04 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.5** (300 mg, 1.04 mmol, 1.0 equiv) in THF (10 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then 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). ^1H 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 $\text{C}_{12}\text{H}_{18}\text{NO}_6^-$ ($[\text{M}-\text{Cs}]^-$) 272.1140; found 272.1137.



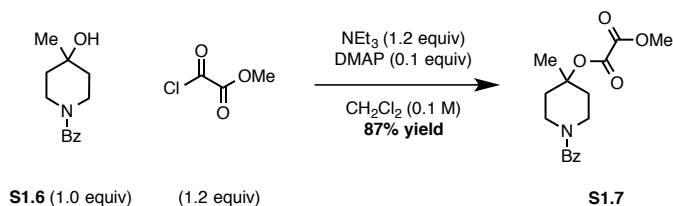
Preparation of ester 1.88: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.87** (304 mg, 0.75 mmol, 1.1 equiv)

and Ir[dF(CF₃)ppy]₂(dtbpy)PF₆ (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 Et₂O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO₄ 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₀H₂₉NaNO₄⁺ ([M+Na]⁺) 370.1989; found 370.1992.



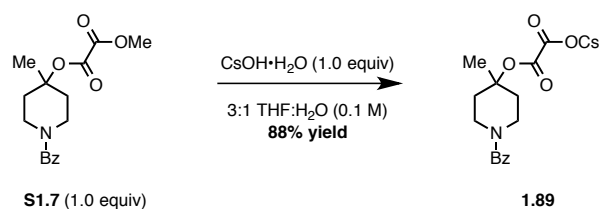
Preparation of alcohol S1.6: A solution of methyl magnesium bromide (3 M in Et₂O; 4.92 mL, 14.76 mmol, 1.5 equiv) was added dropwise to 1-benzoyl-4-piperidone (2.0 g, 9.84

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 Et₂O (4 x 50 mL) and the combined ethereal extracts were washed with brine (50 mL), dried over MgSO₄, 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₃H₁₈NO₂⁺ ([M+H]⁺) 220.1332; found 220.1331.



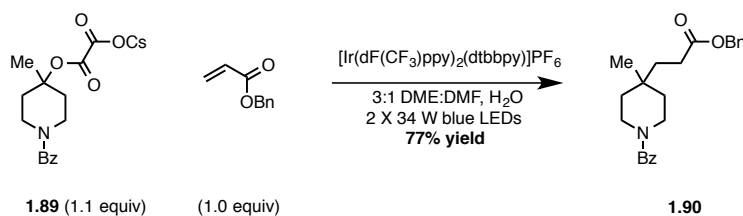
Preparation of methyl oxalate S1.7: Methyl chlorooxoacetate (373 μL, 4.05 mmol, 1.2 equiv) was added to a solution of (4-hydroxy-4-methylpiperidin-1-yl)(phenyl)methanone **S1.6** (740 mg, 3.37 mmol, 1.0 equiv), triethylamine (564 μL, 4.05 mmol, 1.2 equiv) and DMAP (42 mg, 0.34 mmol, 0.1 equiv) in CH₂Cl₂ (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 CH₂Cl₂ (2 x 50 mL). The combined organic extracts were washed with water (50 mL) and saturated aqueous NaHCO₃ solution (50 mL), dried over MgSO₄ 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). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 $\text{C}_{16}\text{H}_{20}\text{NO}_5^+$ ($[\text{M}+\text{H}]^+$) 306.1336; found 306.1335.



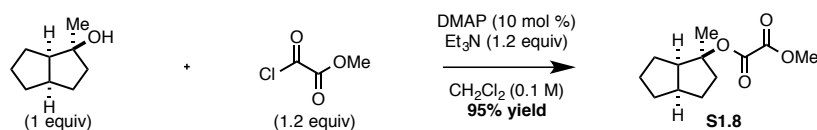
Preparation of cesium oxalate 1.89: $\text{CsOH}\cdot\text{H}_2\text{O}$ (407 mg, 2.42 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.7** (740 mg, 2.42 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then 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). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 $\text{C}_{15}\text{H}_{16}\text{NO}_5^-$ ($[\text{M}-\text{Cs}]^-$) 290.1034; found 290.1037.

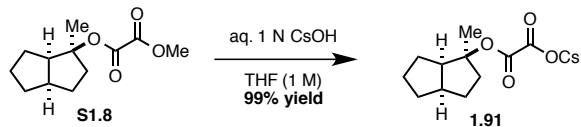


Preparation of ester 1.90: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.89** (232 mg, 0.55 mmol, 1.1 equiv) and $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture 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 $^\circ\text{C}$ 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 **1.90** as a colorless film (141 mg, 77% yield): $R_f = 0.30$ (2:1 hexanes:EtOAc, stained with KMnO_4). ^1H 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,

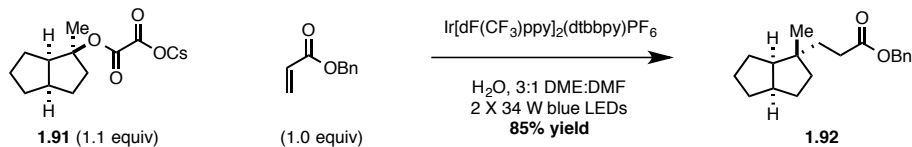
31.5, 28.8, 23.0; HRMS (ESI-TOF) m/z calculated for $C_{23}H_{28}NO_3^+$ ($[M+H]^+$) 366.2064; found 366.2066.



Preparation of methyl oxalate S1.8: A round-bottom flask was charged with (1*S*,3*R*,6*R*)-1-methyloctahydro-pentalen-1-ol⁴⁶ (280 mg, 2.0 mmol, 1.0 equiv) and CH₂Cl₂ (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. NH₄Cl (aq) (100 mL). The aqueous phase was extracted with CH₂Cl₂ (100 mL), and the organic extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et₂O) to give **S1.8** as a clear oil (430 mg, 95% yield). $R_f = 0.4$ (4:1 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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 C₁₂H₂₂NO₄, 244.1549; found, 244.1544.

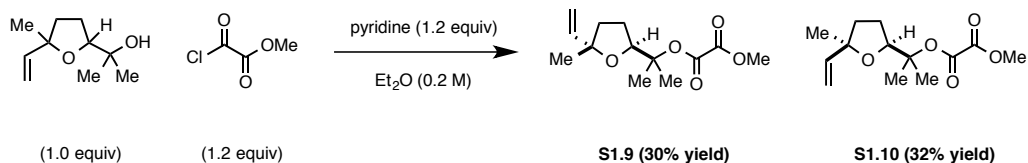


Preparation of cesium oxalate 1.91: A round-bottom flask was charged with methyl ((1*S*, 3*R*, 6*R*)-1-methyloctahydropentaien-1-yl) oxalate (**S1.8**) (390 mg, 1.7 mmol, 1.0 equiv) followed by the addition of THF (1.7 mL, 1 M). To this solution, 1 N aq. CsOH (1.7 mL, 1.7 mmol, 1.0 equiv) was added drop-wise. 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). ¹H 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); ¹³C 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 C₁₁H₁₅O₄, 211.0970; found, 211.0970.



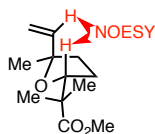
Preparation of ester 1.92: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-(((1*S*,3*R*,6*R*)-1-methyloctahydropentalen-1-yl)oxy)-2-oxoacetate (**1.91**) (190 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et₂O) to give **1.92** as a yellow oil (122 mg, 85% yield). *R*_f = 0.4 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M+NH₄]⁺ calculated for C₁₉H₃₀NO₂, 304.2277; found, 204.2266.

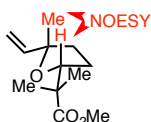


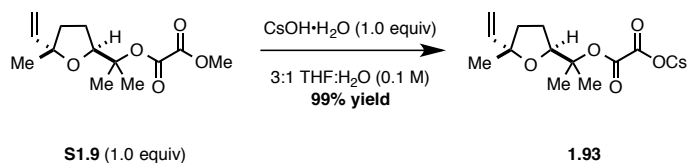
Preparation of methyl oxalate S1.9: Methyl chlorooxoacetate (1.30 mL, 14.10 mmol, 1.2 equiv) was added to a solution of linalool oxide (purchased from Aldrich as a mixture of isomers; 2.0 g, 11.75 mmol, 1.0 equiv) and pyridine (1.41 mL, 14.10 mmol, 1.2 equiv) in Et₂O (50 mL) and the resulting white suspension 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 NaHCO₃ solution (50 mL), dried over MgSO₄ 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). $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{13}\text{H}_{21}\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) 257.1384, found 257.1386 The *trans* stereochemistry was confirmed by an observed NOESY correlation between the vinyl group and the methine:

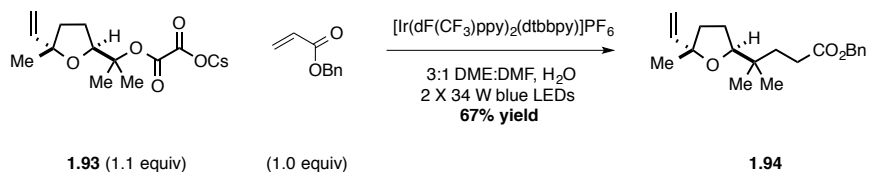


Eluted second was a fraction containing predominantly the *cis* isomer (**S1.10**) (1.04 g, 32% yield): $R_f = 0.21$ (19:1 hexanes:EtOAc, stained with KMnO_4) $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.99 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.19 (dd, $J = 17.3, 1.5$ Hz, 1H), 4.97 (dd, $J = 10.8, 1.5$ Hz, 1H), 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); $^{13}\text{C NMR}$ (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 $\text{C}_{13}\text{H}_{21}\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) 257.1384, found 257.1382. The *cis* stereochemistry was confirmed by an observed NOESY correlation between the methyl and methine groups:



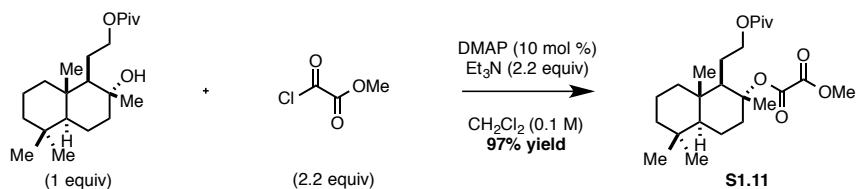


Preparation of cesium oxalate 1.93: CsOH·H₂O (328 mg, 1.95 mmol, 1.0 equiv) in water (5 mL) was added to linalool oxide-derived mixed oxalate **S1.9** (500 mg, 1.95 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for a further 5 min after addition had complete then concentrated to give the **1.93** as a colorless semi-solid that was not purified further (729 mg, 99% yield). ¹H NMR (500 MHz, D₂O) 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); ¹³C NMR (126 MHz, D₂O) 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 C₁₂H₁₇O₅⁻ ([M-Cs]⁻) 241.1082; found 241.1079.



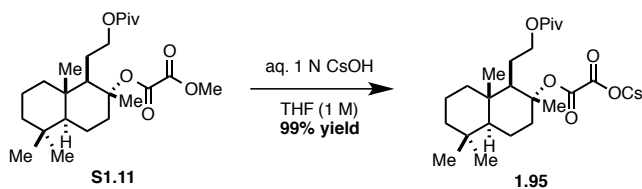
Preparation of ester 1.94: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.93** (281 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME (5 mL, 0.1 M) was added, followed by 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 Et₂O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₀H₂₉O₃⁺ ([M+H]⁺) 317.2111; found 317.2111.



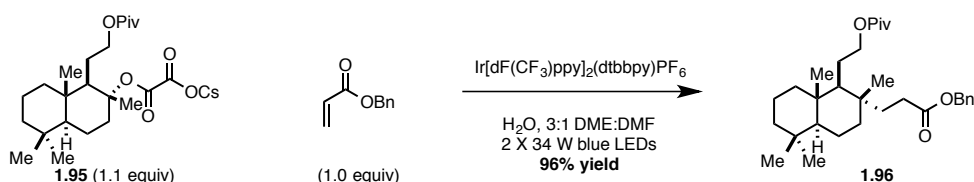
Preparation of methyl oxalate 1.11: A round-bottom flask was charged with 2-((1*R*,2*R*,4*S*,8*S*)-2-hydroxy-2,5,5,8*a*-tetramethyldecahydronaphthalen-1-yl)ethyl pivalate^{26a} (340 mg, 1.0 mmol, 1.0 equiv) and CH₂Cl₂ (10 mL, 0.1M). Triethylamine (0.17 mL, 1.2 mmol, 1.2 equiv) and DMAP (12 mg, 0.1 mmol, 0.1 equiv) were added followed by dropwise addition of methyl chlorooxalate (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:Et₂O) 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} ; $[\alpha]^{23}_{\text{D}} -2.83$, $[\alpha]^{23}_{577} -3.12$, $[\alpha]^{23}_{546} -3.78$, $[\alpha]^{23}_{435} -6.30$, $[\alpha]^{23}_{405} -7.96$ ($c = 1.00$, MeOH); HRMS-ESI (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{24}\text{H}_{40}\text{O}_6\text{Na}$, 447.2722; found, 447.2708.



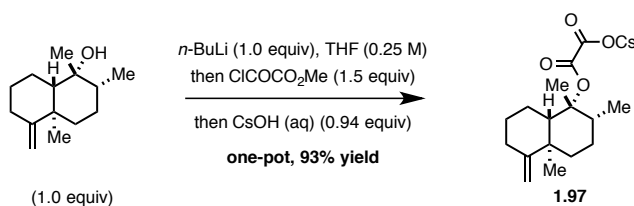
Preparation of cesium oxalate 1.95: A round-bottom flask was charged with methyl ((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy)ethyl)decahydronaphthalen-2-yl) oxalate (**S1.11**) (420 mg, 1.0 mmol, 1.0 equiv) followed by the addition of THF (1.0 mL, 1 M). To this solution, 1 N aq. CsOH (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} $[\alpha]^{23}_{\text{D}}$ -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) $[\text{M}-\text{Cs}]^-$ calculated for $\text{C}_{23}\text{H}_{37}\text{O}_6$, 409.2590; found, 409.2599.



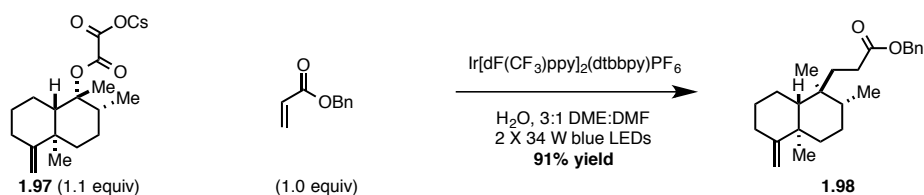
Preparation of ester 1.96: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*S*,8*S*)-2,5,5,8a-tetramethyl-1-(2-(pivaloyloxy) ethyl) decahydro-naphthalen-2-yl)oxy)acetate (**1.95**) (209 mg, 0.39 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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 **1.96** as a yellow oil (162 mg, 96%

yield). $R_f = 0.5$ (9:1 hexanes:acetone); visualized with KMnO_4 ; $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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; $[\alpha]^{23}_{\text{D}} +1.16$, $[\alpha]^{23}_{577} +1.67$, $[\alpha]^{23}_{546} +1.82$, $[\alpha]^{23}_{435} +3.45$, $[\alpha]^{23}_{405} +4.02$ ($c = 1.0$, MeOH); IR (thin film): 2921, 1734, 1720, 1252, 1166 cm^{-1} ; HRMS-Cl (m/z) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{31}\text{H}_{52}\text{NO}_4$, 502.3896; found, 502.3884.



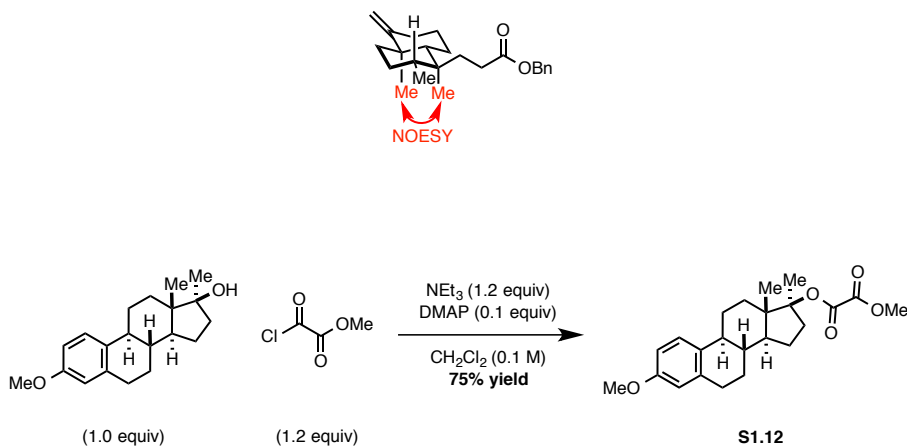
Preparation of (*rac*)-cesium oxalate 1.97: A round-bottom flask was charged with 3° alcohol⁴⁷ (233 mg, 1.12 mmol, 1.0 equiv) and THF (4.5 mL, 0.25 M) under an atmosphere of argon. The solution was stirred and cooled to -78 °C before a 2.5 M solution of *n*-BuLi in hexanes (450 μL , 1.12 mmol, 1.0 equiv) 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). ^1H 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) [$\text{M}-\text{Cs}$] $^-$ calculated for $\text{C}_{16}\text{H}_{23}\text{O}_4$, 279.1596; found, 279.1590.



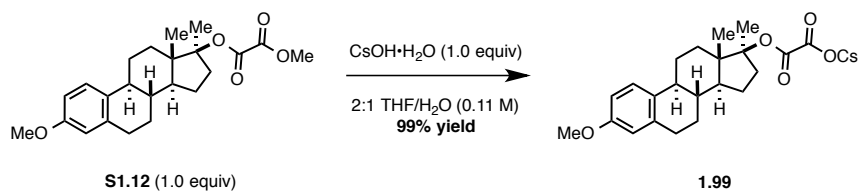
Preparation of (rac)-ester 1.98: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-oxo-2-(((1*R*,2*R*,4*R*,8*S*)-1,2,4*a*-trimethyl-5-methylenedecahydronaphthalen-1-yl)oxy)acetate (**1.97**) (137 mg, 0.39 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et₂O) to give **1.98** as a yellow oil (113 mg, 91% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M+NH₄]⁺ calculated for C₂₄H₃₈NO₂, 372.2903; found, 372.2893. Product stereochemistry was confirmed by a NOESY correlation:



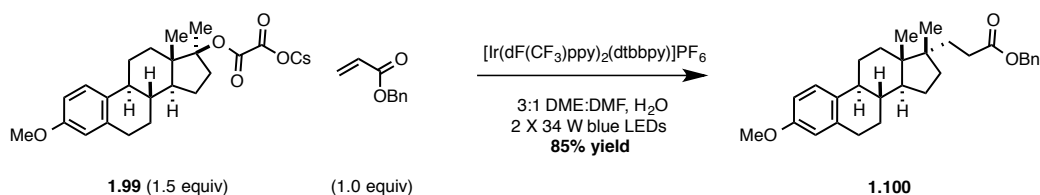
Preparation of methyl oxalate S1.12: Methyl chlorooxoacetate (514 μL, 4.19 mmol, 1.2 equiv) was added to a solution of the known sterol^{26a} (1.05 g, 3.50 mmol, 1.0 equiv), triethylamine (424 μL, 4.19 mmol, 1.2 equiv), and DMAP (43 mg, 0.35 mmol, 0.1 equiv) in CH₂Cl₂ (35 mL) and the resulting yellow solution was maintained at room temperature for

5 hours. Water (50 mL) was added and the aqueous phase was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic extracts were washed with water (50 mL) and saturated aqueous NaHCO₃ solution (50 mL), dried over MgSO₄ 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₃H₃₁O₅⁺ ([M+H]⁺) 387.2166, found 387.2164.



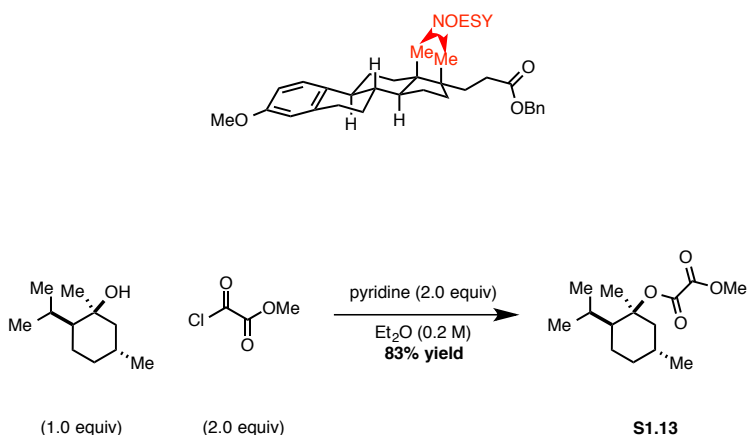
Preparation of cesium oxalate 1.99: CsOH·H₂O (367 mg, 2.24 mmol, 1.0 equiv) in water (5 mL) was added to estrone-derived mixed oxalate **S1.12** (867 mg, 2.24 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for a further 5 min after addition had completed then 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-*d*₆) δ 7.18 (d, *J* = 8.6 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.61 (d, *J* = 2.7 Hz, 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- d_6) 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 $\text{C}_{22}\text{H}_{27}\text{O}_5^-$ ($[\text{M}-\text{Cs}]^-$) 371.1864; found 371.1863.



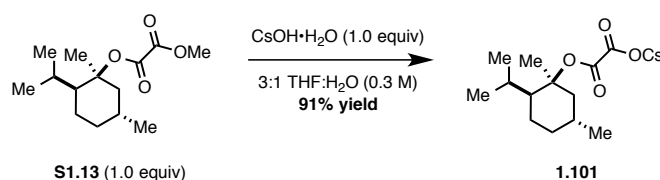
Preparation of ester 1.100: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.99** (378 mg, 0.75 mmol, 1.5 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture 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 $^\circ\text{C}$ 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 **1.100** 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 $\text{C}_{30}\text{H}_{39}\text{O}_3^+$ ($[\text{M}+\text{H}]^+$) 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

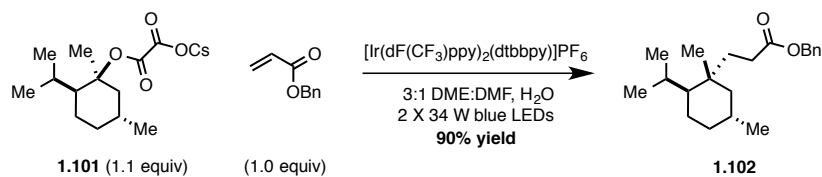


Preparation of methyl oxalate S1.13: Methyl chlorooxalate (1.08 mL, 11.74 mmol, 2 equiv) was added to a solution of the known alcohol⁴⁹ (4:1 mixture of diastereomers; major shown; 1.00 g, 5.87 mmol, 1.0 equiv) and pyridine (0.95 mL, 11.74 mmol, 2 equiv) in Et_2O (50 mL) and the resulting yellow solution 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

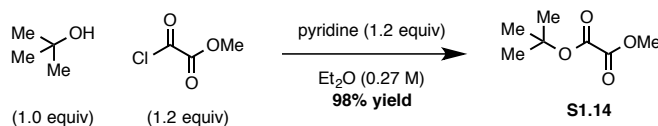
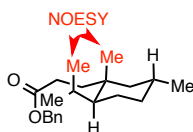
of diastereomers; 1.23 g, 83% yield): $R_f = 0.51$ (19:1 hexanes:EtOAc, stained with KMnO_4). ^1H NMR (500 MHz, CDCl_3) δ 3.88 (s, 3H), 2.76 (dt, $J = 14.4, 2.9$ Hz, 1H), 2.25–2.18 (m, 1H), 1.83–1.77 (m, 1H), 1.63 (s, 3H), 1.60–1.45 (m, 4H), 1.08 (ddd, $J = 11.7, 4.3, 1.8$ Hz, 1H), 0.96 (d, $J = 6.9$ 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 $\text{C}_{14}\text{H}_{25}\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 257.1747; found 257.1746.



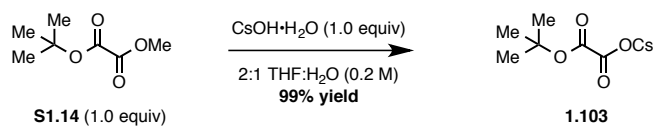
Preparation of cesium oxalate 1.101: $\text{CsOH}\cdot\text{H}_2\text{O}$ (1.05 g, 6.24 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.13** (1.60 g, 6.24 mmol, 1.0 equiv) in THF (15 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure. The resulting colorless solid was triturated with toluene (3×10 mL) and dried *in vacuo* to give **1.101** as a colorless solid that was used without further purification (1.56 g, 91% yield). ^1H NMR (500 MHz, D_2O) 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_2O) 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 $\text{C}_{13}\text{H}_{21}\text{O}_4^-$ ($[\text{M}-\text{Cs}]^-$) 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 $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (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 $^\circ\text{C}$ 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). ^1H 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 $\text{C}_{21}\text{H}_{33}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 317.2475; found 317.2475. Product stereochemistry was confirmed by a NOESY correlation:

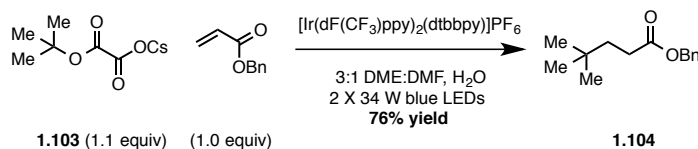


Preparation of methyl oxalate S1.14: Methyl chlorooxoacetate (2.98 mL, 32.38 mmol, 1.2 equiv) was added to a solution of *tert*-butanol (2.56 mL, 26.98 mmol, 1.0 equiv) and pyridine (3.24 mL, 32.38 mmol, 1.2 equiv) in Et₂O (100 mL) and the resulting yellow solution was maintained at room temperature for 4 hours. The organic phase was washed with water (2 x 50 mL) and saturated aqueous NaHCO₃ solution (50 mL), dried over MgSO₄ and concentrated. The crude material was purified by flash column chromatography on a short column of silica gel (1:19 – 1:9 Et₂O:hexanes) to give **S1.14** as a clear oil (4.26 g, 98% yield): R_f = 0.41 (10:1 hexanes:EtOAc, stained with KMnO₄). ¹H NMR (500 MHz, CDCl₃) δ 3.85 (s, 3H), 1.54 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) 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



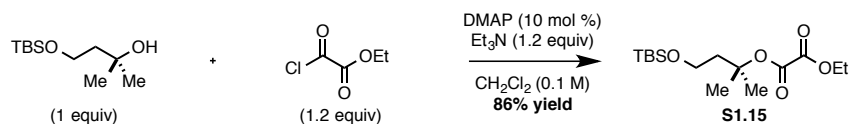
Preparation of cesium oxalate 1.103: CsOH•H₂O (1.05 g, 6.24 mmol, 1.0 equiv) in water (10 mL) was added to *tert*-butyl methyl oxalate **S1.14** (1.00 g, 6.24 mmol, 1.0 equiv) in THF (20 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition

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). ¹H NMR (500 MHz, D₂O) δ 1.50 (s, 9H); ¹³C NMR (126 MHz, D₂O) 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 C₆H₉O₄⁻ ([M-Cs]⁻) 145.0506; found 145.0506.

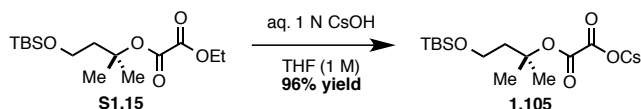


Preparation of ester 1.104: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with *tert*-butyl cesium oxalate **1.103** (153 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was 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 Et₂O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO₄ 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 $\text{C}_{14}\text{H}_{20}\text{NaO}_2^+$ ($[\text{M}+\text{Na}]^+$) 243.1356; found 243.1355. Data match those previously reported in the literature.⁵¹

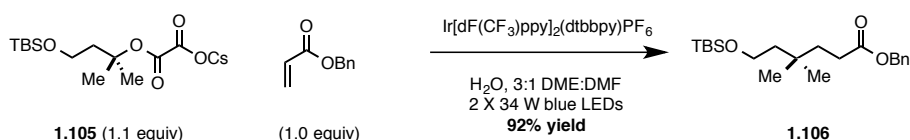


Preparation of ethyl oxalate S1.15: A round-bottom flask was charged with 4-((*tert*-butyldimethylsilyloxy)-2-methylbutan-2-yl)^{26a} (2.4 g, 11 mmol, 1.0 equiv) and CH_2Cl_2 (110 mL, 0.1M). Triethylamine (0.35 mL, 2.4 mmol, 1.2 equiv) and DMAP (25 mg, 0.62 mmol, 0.1 equiv) were added followed by drop-wise addition of ethyl chlorooxalate (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) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{31}\text{O}_5\text{Si}$, 319.1941; found, 319.1933.



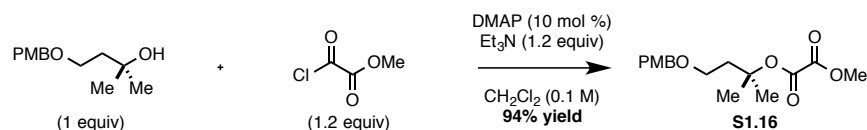
Preparation of cesium oxalate 1.105: A round-bottom flask was charged with 4-((*tert*-butyldimethylsilyloxy)-2-methylbutan-2-yl) ethyl oxalate (**S1.15**) (1.6 g, 5.0 mmol, 1.0

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). ^1H 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) [$M-\text{Cs}$] $^-$ calculated for $\text{C}_{13}\text{H}_{25}\text{O}_5\text{Si}$, 289.1471; found, 289.1464.

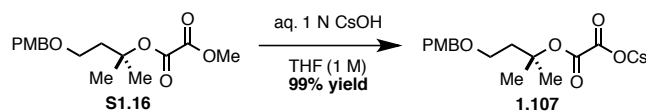


Preparation of ester 1.106: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**1.106**) (233 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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 **1.106** as a yellow oil (167 mg, 92% yield). R_f = 0.5 (9:1 hexanes:acetone); visualized with KMnO_4 . ^1H NMR (500 MHz, CDCl_3): δ 7.38–7.35 (m,

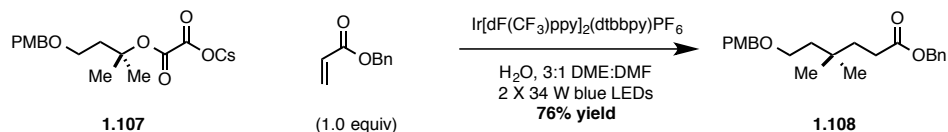
5H), 5.12 (s, 2H), 3.66 (t, $J = 7.5$ Hz, 2H), 2.35 (t, $J = 8.5$ Hz, 2H), 1.60 (t, $J = 6.0$ Hz, 2H), 1.47 (t, $J = 7.0$ Hz, 2H), 0.89 (s, 15H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3): δ 174.4, 136.3, 128.8, 128.5, 128.4, 66.4, 60.1, 44.1, 37.1, 32.1, 29.8, 27.3, 26.2, 18.5, -5.1 ; IR (thin film): 2955, 2928, 1737, 1091, 834 cm^{-1} ; HRMS-Cl (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{37}\text{O}_3\text{Si}$, 365.2512; found, 365.2515.



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 . ^1H 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) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{16}\text{H}_{22}\text{O}_6\text{Na}$, 333.1314; found, 333.1326.

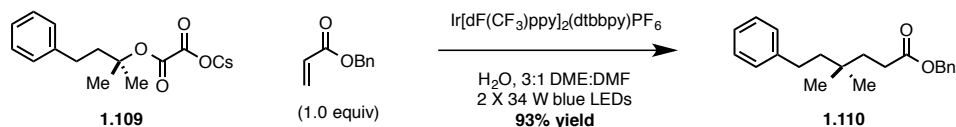


Preparation of cesium oxalate 1.107: A round-bottom flask was charged with methyl 4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl methyl oxalate (**S1.16**) (2.3 g, 7.4 mmol, 1.0 equiv) followed by the addition of THF (7.4 mL, 1 M). To this solution, 1 N aq. CsOH (7.4 mL, 7.4 mmol, 1.0 equiv) was added drop-wise. 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). ^1H 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) [$\text{M}-\text{Cs}$] $^-$ calculated for $\text{C}_{15}\text{H}_{19}\text{O}_6$, 295.1182; found, 295.1183.



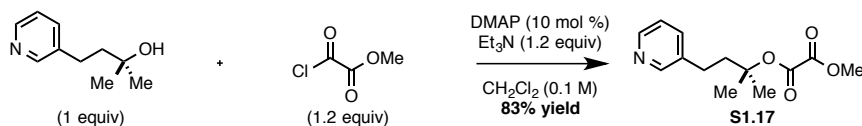
Preparation of ester 1.108: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-((4-methoxybenzyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**1.107**) (236 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir[dF(CF}_3\text{)ppy]}_2\text{(dtbbpy)PF}_6$ (5.6 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 $^\circ\text{C}$ 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (19:1 hexanes:Et₂O) to give **1.108** as a yellow oil (140 mg, 76% yield). R_f = 0.4 (9:1 hexanes:acetone); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M+NH₄]⁺ calculated for C₂₃H₃₄NO₄, 388.2488; found, 388.2482.



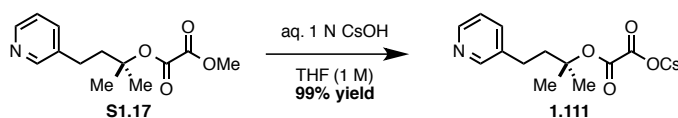
Preparation of ester 1.110: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((2-methyl-4-phenylbutan-2-yl)oxy)-2-oxoacetate (**1.109**) (167 mg, 0.55 mmol, 1.1 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture 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 Et₂O (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-Cl (m/z) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{26}\text{O}_2\text{Na}$, 333.1830; found, 333.1838.

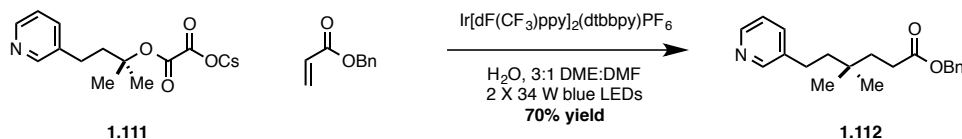


Preparation of methyl oxalate S1.17: A round-bottom flask was charged with 2-methyl-4-(pyridin-3-yl)butan-2-ol (120 mg, 0.73 mmol, 1.0 equiv) and CH_2Cl_2 (7.5 mL, 0.1M). Triethylamine (0.12 mL, 0.88 mmol, 1.2 equiv) and DMAP (9 mg, 0.073 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxoacetate (0.08 mL, 0.88 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23 $^\circ\text{C}$, 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) $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{13}\text{H}_{17}\text{NO}_4\text{Na}$, 274.1055; found, 274.1048.

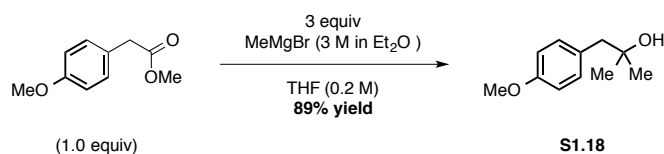


Preparation of cesium oxalate 1.111: A round-bottom flask was charged with methyl (2-methyl-4-(pyridin-3-yl)butan-2-yl) oxalate (**S1.17**) (190 mg, 0.74 mmol, 1.0 equiv) followed by the addition of THF (0.75 mL, 1 M). To this solution, 1 N aq. CsOH (0.75 mL, 0.75 mmol, 1.0 equiv) was added drop-wise. 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). ^1H 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) $[\text{M}-\text{Cs}]^-$ calculated for $\text{C}_{12}\text{H}_{14}\text{NO}_4$, 236.0923; found, 236.0922.



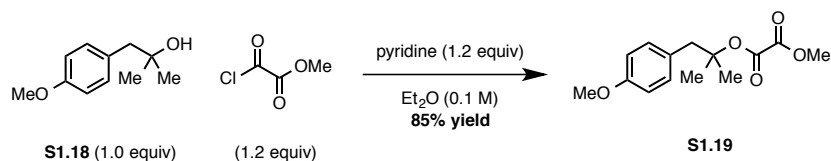
Preparation of ester 1.112: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((2-methyl-4-(pyridin-3-yl)butan-2-yl)oxy)-2-oxoacetate (**1.111**) (120 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 μ L, 5.0 mmol, 10 equiv), and benzyl acrylate (77 μ L, 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 $^{\circ}$ 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (1:1 hexanes:Et₂O) to give **1.112** as a yellow oil (76 mg, 70% yield). *R_f* = 0.4 (1:1 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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-Cl (*m/z*) [M+H]⁺ calculated for C₂₀H₂₆NO₂, 312.1964; found, 312.1953.



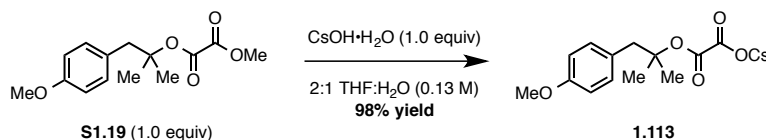
Preparation of tertiary alcohol S1.18: A solution of methyl phenylacetate (1.75 mL, 11.09 mmol, 1.0 equiv) in THF (50 mL) was added dropwise to a 0 $^{\circ}$ C solution of methyl magnesium bromide (3 M in Et₂O; 11.0 mL, 33.29 mmol, 3 equiv) over 20 min. After addition had completed, the resulting yellow 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 $\text{C}_{11}\text{H}_{17}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 181.1223; found 181.1224.

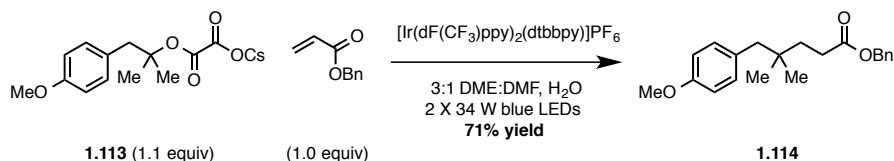


Preparation of methyl oxalate S1.19: Methyl chlorooxoacetate (1.02 mL, 11.05 mmol, 1.2 equiv) was added to a solution of 1-(4-methoxyphenyl)-2-methylpropan-2-ol **S1.18** (1.77 g, 9.21 mmol, 1.0 equiv) and pyridine (1.11 mL, 11.05 mmol, 1.2 equiv) in Et_2O (100 mL) and the resulting yellow solution was 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). $^1\text{H NMR}$ (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 $\text{C}_{11}\text{H}_{17}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 267.1227, found 267.1230.

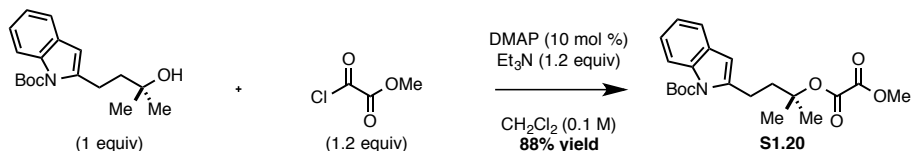


Preparation of cesium oxalate 1.113: $\text{CsOH}\cdot\text{H}_2\text{O}$ (315 mg, 1.88 mmol, 1.0 equiv) in water (5 mL) was added to mixed oxalate **S1.19** (500 mg, 1.88 mmol, 1.0 equiv) in THF (10 mL) dropwise over 5 min. The resulting solution was stirred for 5 min after addition had completed then concentrated under reduced pressure to give **1.113** as a colorless solid that was used without further purification (522 mg, 98% yield). ^1H 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 $\text{C}_{13}\text{H}_{15}\text{O}_5^-$ ($[\text{M}-\text{Cs}]^-$) 251.0925; found 251.0925.



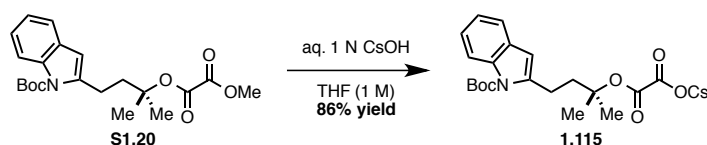
Preparation of ester 1.114: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.113** (211 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, followed by water (90 μL , 5.0 mmol, 10 equiv), and

benzyl acrylate (77 μ L, 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 $^{\circ}$ 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 Et₂O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₁H₂₇O₃⁺ ([M+H]⁺) 327.1955, found 327.1956.



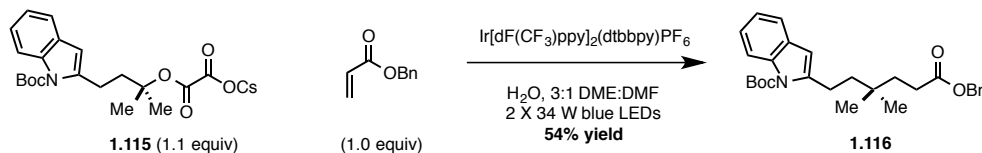
Preparation of methyl oxalate S1.20: A round-bottom flask was charged with *tert*-butyl 2-(3-hydroxy-3-methylbutyl)-1*H*-indole-1-carboxylate^{26a} (930 mg, 3.1 mmol, 1.0 equiv) and CH₂Cl₂ (31 mL, 0.1M). Triethylamine (0.51 mL, 3.7 mmol, 1.2 equiv) and DMAP (37 mg, 0.31 mmol, 0.1 equiv) were added followed by drop-wise addition of methyl chlorooxalate (0.34 mL, 3.7 mmol, 1.2 equiv). The reaction was stirred for 1 hour at 23

°C, then quenched with sat. NH₄Cl (aq) (100 mL). The aqueous phase was extracted with CH₂Cl₂ (100 mL), and the organic extracts were dried over Na₂SO₄ and concentrated. The crude material was purified by flash column chromatography on silica gel (85:15 hexanes:Et₂O) to give **S1.20** as a colorless oil (2.4 g, 95% yield). R_f = 0.3 (4:1 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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 C₂₁H₂₇NO₆Na, 412.1736; found, 412.1748.



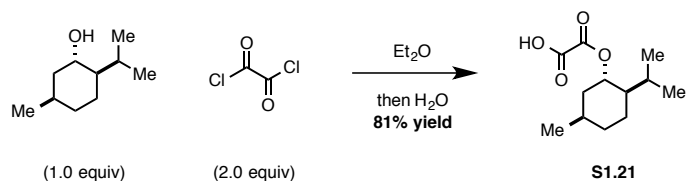
Preparation of cesium oxalate 1.115: A round-bottom flask was charged with 4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl methyl oxalate (**S1.20**) (1.0 g, 2.6 mmol, 1.0 equiv) followed by the addition of THF (2.6 mL, 1 M). To this solution, 1 N aq. CsOH (2.6 mL, 2.6 mmol, 1.0 equiv) 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); ¹³C 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) [$M-\text{Cs}$] $^-$ calculated for $\text{C}_{20}\text{H}_{24}\text{NO}_6$, 374.1604; found, 374.1608.

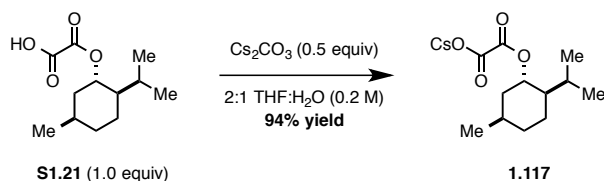


Preparation of ester 1.116: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium 2-((4-(1-(*tert*-butoxycarbonyl)-1*H*-indol-2-yl)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**1.115**) (195 mg, 0.55 mmol, 1.1 equiv) and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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 . ^1H 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

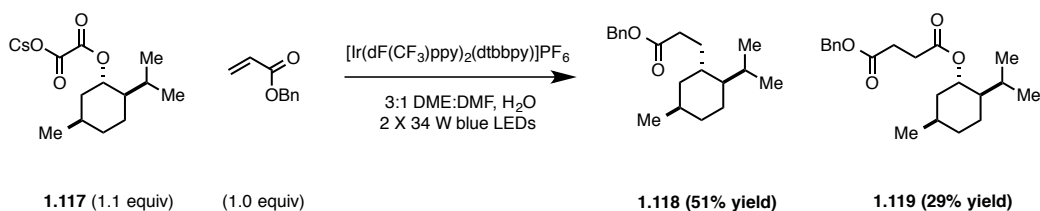
(thin film): 2955, 1727, 1452, 1368, 1153 cm^{-1} ; HRMS-Cl (m/z) $[\text{M}-\text{Boc}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{28}\text{NO}_2$, 350.2120; found, 350.2129.



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 $0\text{ }^\circ\text{C}$ solution of oxalyl chloride (2.17 mL, 25.60 mmol, 2.0 equiv) in Et_2O . The resulting pale yellow solution was stirred at $0\text{ }^\circ\text{C}$ 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). ^1H 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 $\text{C}_{12}\text{H}_{21}\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 229.1434; found 229.1435.

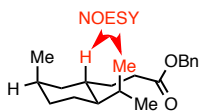


Preparation of cesium oxalate 1.117: Cs₂CO₃ (928 mg, 2.85 mmol, 0.5 equiv) in water (5 mL) was added dropwise to acid **S1.21** (1.30 g, 5.69 mmol, 1 equiv) in THF (10 mL). The resulting solution was stirred for 10 min then concentrated under reduced pressure to give **1.117** as a white powder that was washed with toluene (2 x 5 mL) and dried *in vacuo* (1.93 g, 94% yield). ¹H NMR (500 MHz, D₂O) 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); ¹³C NMR (126 MHz, D₂O) 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 C₁₂H₁₉O₄⁻ ([M-Cs]⁻) 227.1289; found 227.1291.



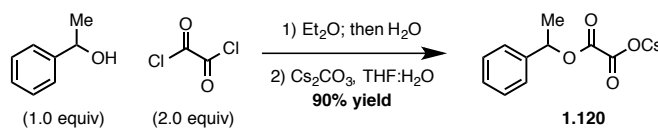
Preparation of esters 1.118 and 1.119: An 8 mL-scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with cesium oxalate **1.117** (270 mg, 0.75 mmol, 1.5 equiv) and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5.6 mg, 0.005 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (5 mL, 0.1 M) was added, 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 Et₂O (3 x 25 mL). The combined ethereal extracts were washed with water (3 x 25 mL) and brine (25 mL), dried over MgSO₄ 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₁H₃₃O₂⁺ ([M+H]⁺) 317.2475; found 317.2475. Product stereochemistry was confirmed by NOESY correlation:

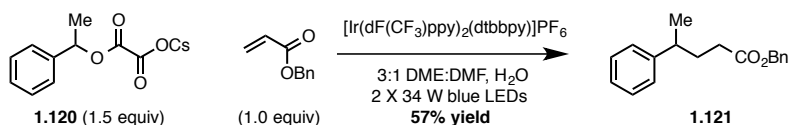


Eluted second was the isomenthol alkoxy carbonyl radical adduct (**1.119**) (50 mg, 29% yield): R_f = 0.30 (24:1 hexanes:EtOAc, stained with KMnO₄). ¹H NMR (500 MHz, CDCl₃) δ 7.39–7.34 (m, 5H), 5.15 (s, 2H), 5.09–5.06 (m, 1H), 2.72–2.69 (m, 2H), 2.68–2.65 (m, 2H), 1.91–1.85 (m, 1H), 1.78–1.71 (m, 1H), 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); ¹³C NMR (126 MHz, CDCl₃) 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,

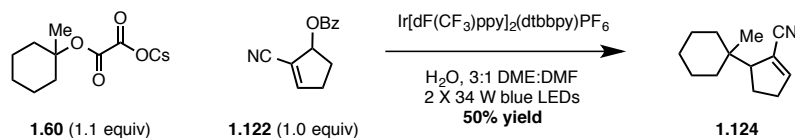
20.8, 20.6, 19.1. IR (ATR): 2955, 2927, 2871, 1730, 1212, 1154, 1140 cm^{-1} ; HRMS (ESI-TOF) m/z calculated for $\text{C}_{21}\text{H}_{31}\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 347.2217; found 347.2213.



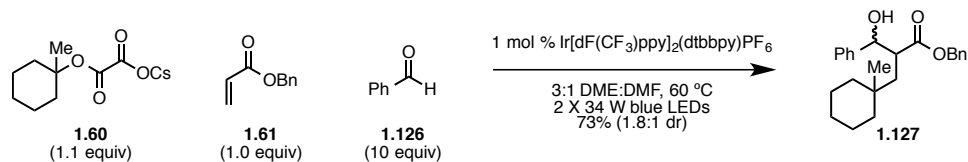
Preparation of cesium oxalate 1.120: 1-phenylethanol (7.9 mL, 65.5 mmol, 1.0 equiv) in Et_2O (100 mL) was added dropwise over 20 min to a 0°C solution of oxalyl chloride (11.08 mL, 131 mmol, 2.0 equiv) in Et_2O (300 mL). The resulting pale yellow solution was stirred at 0°C for 2 hours then concentrated 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). ^1H 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 $\text{C}_{10}\text{H}_9\text{O}_4^-$ ($[\text{M}-\text{Cs}]^-$) 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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 $^\circ\text{C}$ 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). ^1H 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 $\text{C}_{18}\text{H}_{21}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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_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 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

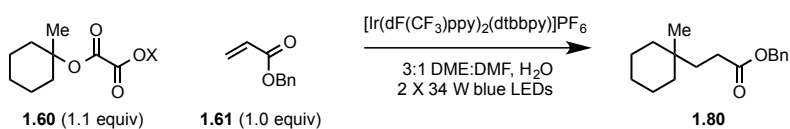
Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2.2 mg, 0.002 mmol, 0.01 equiv). A 3:1 mixture of DME:DMF (2 mL, 0.1M) was added, followed by benzyl acrylate (**1.61**) (31 μL, 0.2 mmol, 1.0 equiv) and freshly distilled benzaldehyde (**1.126**) (200 μL, 2 mmol, 10 equiv). The reaction mixture was degassed by sparging with 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 Et₂O (2 x 25 mL). The combined ethereal extracts were dried over Na₂SO₄ 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 KMnO₄) and the minor diastereomer as a clear oil (19 mg, 26% yield) (R_f = 0.09, 9:1 hexanes:EtOAc; visualized with KMnO₄).

Characterization data for the major diastereomer: ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₂₄H₃₀O₃Na⁺ ([M+Na]⁺) 389.2093; found 389.2082.

Characterization data for the minor diastereomer: ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 $\text{C}_{24}\text{H}_{30}\text{O}_3\text{Na}^+$ $[[\text{M}+\text{Na}]^+]$ 389.2093; found 389.2100.

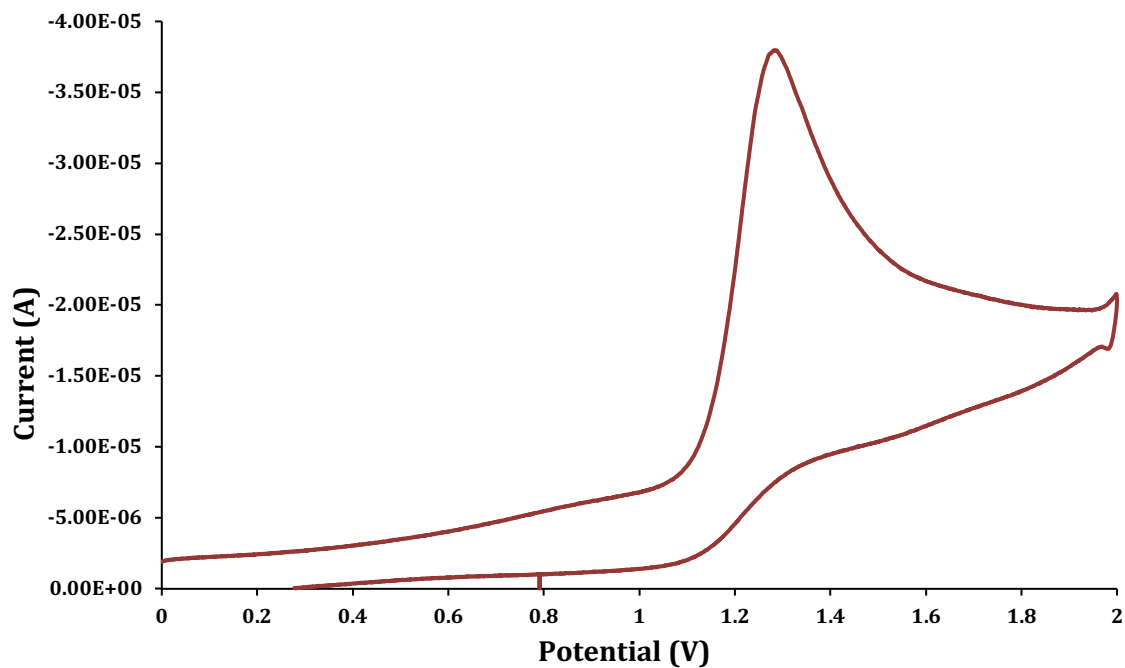
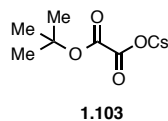
Table S1.1. Effects of counterions on the efficiency of coupling of methyl cyclohexyl oxalate salts **1.60** with benzyl acrylate (**1.61**).^a



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

^aYield based on ^1H 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**.



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

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

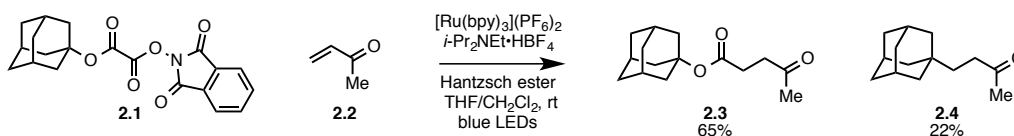
2.1 Introduction

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

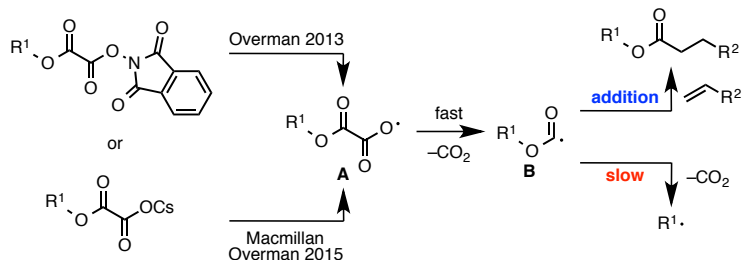
tertiary alkyl *N*-phthalimidoyl oxalate precursors, we observed that the intermediate alkoxy carbonyl radical formed from adamantanol precursor **2.1** reacted efficiently with methyl vinyl ketone (**2.2**) to give γ -ketoester **2.3** as the major product in 65% yield (Equation 2.1).^{8,9}

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 alkoxy carbonyl radicals in the context of their conjugate addition to α,β -unsaturated carbonyl compounds and related electron-deficient alkenes. Two potential precursors for producing alkoxy carbonyl radicals by visible-light photoredox catalysis would be alkyl *N*-phthalimidoyl oxalates⁸ or an alkyl hemioxalate salt (Scheme 2.1).^{10,11} For this method to be successful, β -scission of the alkoxy carbonyl radical **B** to give an alkyl radical must be slower than its reaction with the radical acceptor.¹² The rate of decarboxylation of alkoxy carbonyl radicals is known to reflect the stability of the forming alkyl radical with the rate of decarboxylation of the *tert*-butoxy carbonyl radical estimated to be \sim 500 times faster than that of a primary alkoxy carbonyl radical.¹³ As the methoxy carbonyl 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.

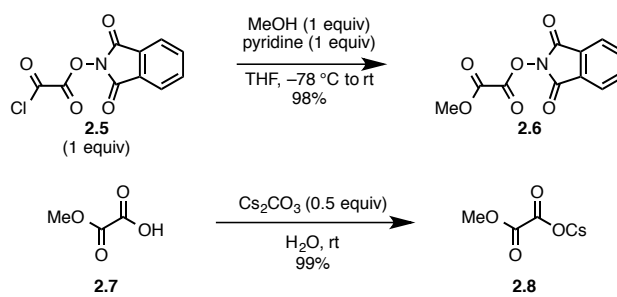
Scheme 2.1. Two potential precursors of alkoxy carbonyl radicals.



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 Et₃N 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 Cs₂CO₃ in water, followed by concentration to give **2.8** as a colorless solid.

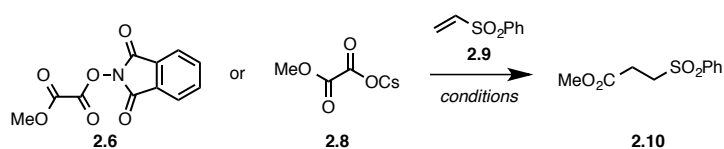
Scheme 2.2. Preparation of methyl *N*-phthalimidoyl oxalate (**2.6**) and cesium methyl oxalate (**2.8**).



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](PF₆)₂, 1.5 equiv of diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch ester, **2.11**), and 1 equiv of *i*-Pr₂NEt·HBF₄ in 1:1 THF:CH₂Cl₂ 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(CF₃)ppy]₂(dtbbpy)PF₆, 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 CH₂Cl₂ 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.



entry ^a	radical precursor (equiv)	solvent (M)	<i>t</i> (°C)	2.11 (equiv)	yield (%) ^b
1 ^c	2.6 (1.5)	1:1 CH ₂ Cl 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 ₂ Cl 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 ₂ Cl ₂ (0.1)	23	3.0	90
6 ^c	2.6 (3.0)	CH ₂ Cl ₂ (0.1)	80	3.0	50
7	2.6 (3.0)	CH ₂ Cl ₂ (0.1)	23	3.0	94 ^d
8	2.6 (2.0)	CH₂Cl₂ (0.6)	23	2.0	94^d
9 ^e	2.6 (2.0)	CH ₂ Cl ₂ (0.6)	23	2.0	0
10 ^f	2.6 (2.0)	CH ₂ Cl ₂ (0.6)	23	2.0	16
11 ^g	2.6 (2.0)	CH ₂ Cl ₂ (0.6)	23	2.0	56

^aReaction conditions for radical precursor **2.6**: 1 equiv **2.9**, 1.5 mol % [Ru(bpy)₃](PF₆)₂, low-intensity blue LEDs, 18 h; reaction conditions for radical precursor **2.8**: 1 equiv **2.9**, 2 mol % Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆, 2 X 34 W blue LEDs, 18 h. ^bYield determined by ¹H NMR analysis of the crude reaction mixture using 1,4-dimethoxybenzene as an internal standard. ^cReaction was performed in the presence of *i*-Pr₂NEt•HBF₄ (1 equiv) as an additive. ^dIsolated yield after silica gel chromatography. ^eReaction performed in the absence of visible light. ^fReaction performed in the absence of photocatalyst. ^gReaction 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

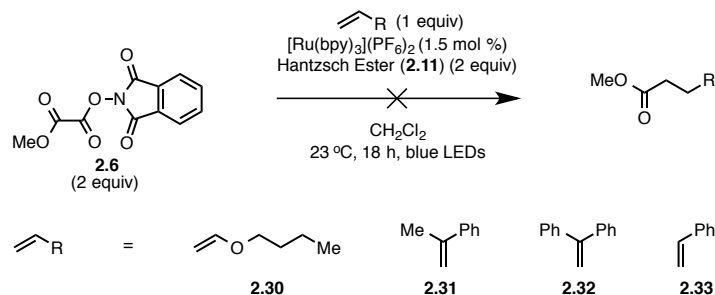
Table 2.2. Acceptor scope with *N*-phthalimidoyl oxalate **2.6**.

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

^aReaction performed using the optimized conditions (see Experimental Information). All yields are yields of pure products isolated after silica gel chromatography.

As alkoxy-carbonyl 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 ¹H 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

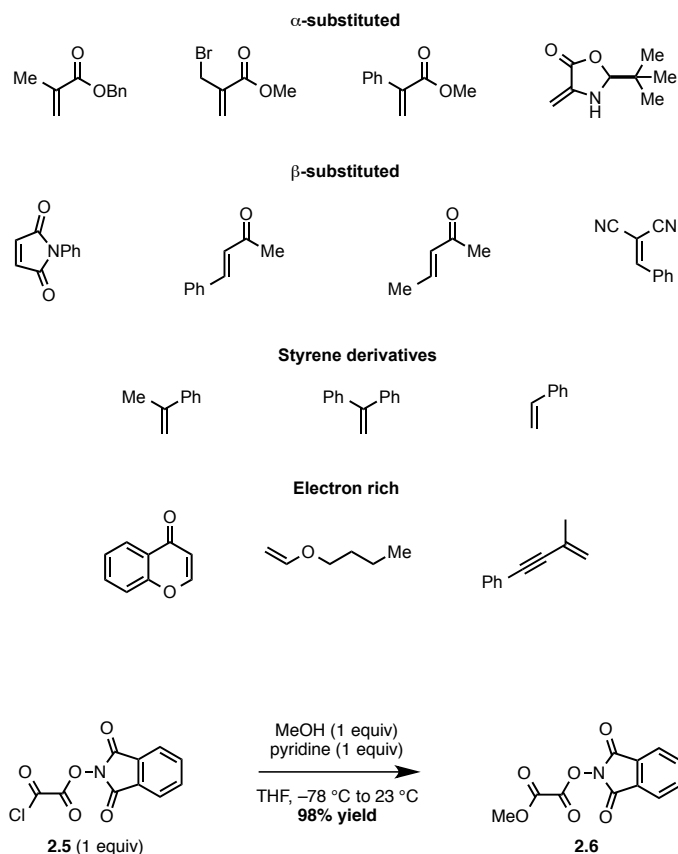
2.4 Experimental Information

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](PF₆)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*-Pr₂NEt•HBF₄,²³ 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 F₂₅₄ pre-coated plates, (0.25 mm), and visualized by exposure to UV light (254 nm) and potassium permanganate (KMnO₄) 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. ¹³C NMR spectra were recorded on a Bruker Spectrometer at 126 MHz. Data for ¹³C 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://www.creativelightings.com> (product

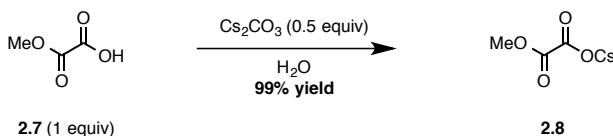
code CL-FRS5050-12WP-12V) and powered by eight AA batteries. Kessil KSH150B 34 W LED Grow Light 150, Blue was purchased from <http://www.amazon.com>.

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



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 $-78\text{ }^{\circ}\text{C}$ 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 $0\text{ }^{\circ}\text{C}$ and allowed to stir for 1 h. The reaction was then allowed to warm to $23\text{ }^{\circ}\text{C}$ 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 $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_6$ ($\text{M}+\text{NH}_4$) 267.0617, found 267.0618.



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, $\text{DMSO}-d_6$): δ 3.50 (s, 3H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ 168.1, 162.8, 50.4; IR (thin film): 3019, 2961, 2865, 1731, 1225 cm^{-1} ; HRMS (ESI) calculated for $\text{C}_3\text{H}_3\text{O}_4$ ($\text{M}-\text{Cs}$) 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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$. 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 Et₂O (2 x 10 mL). The combined ethereal extracts were dried over Na₂SO₄ and concentrated. Next, the internal standard (1,2-dibromo-4,5-methylenedioxybenzene) was added. The mixture was then diluted in CDCl₃ 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.

$\text{XO}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{OMe} + \text{SO}_2\text{Ph}-\text{CH}=\text{CH}_2$ or $\text{OBn}-\text{CH}=\text{CH}_2 \xrightarrow[\text{H}_2\text{O (10 equiv), 2 X 34 W blue LEDs}]{\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6}$ $\text{MeO}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{SO}_2\text{Ph}$ or $\text{MeO}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})\text{OBn}$

X = H, **2.7**
X = Cs, **2.8**
X = K, **2.8B**

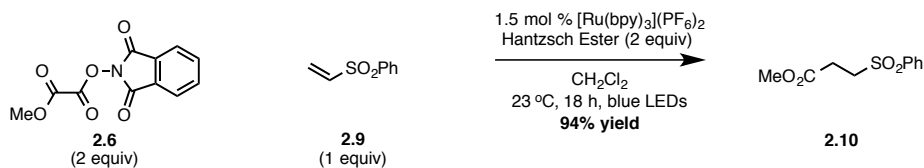
2.9 (1 equiv) **2.14** (1 equiv) **2.10** **2.15**

entry	X	base	oxalate equiv	acceptor	solvent (M)	mol % cat.	Result (¹ H NMR)
1	H	K ₂ HPO 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 ₂ O (0.1 M)	2	0% 2.15
13	K	none	1.5	2.14	10:1 CH ₃ CN:H ₂ O (0.1 M)	2	0% 2.15 19% 2.14 remaining
14	K	none	1.0	2.14	CH ₂ Cl ₂ (0.1 M)	2	0% 2.15 52% 2.14 remaining
15	K	none	1.0	2.14	CH ₃ CN (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

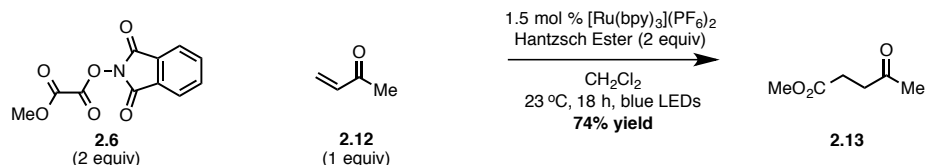
Coupling of Methyl *N*-Phthalimidoyl Oxalate with Various Acceptors

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

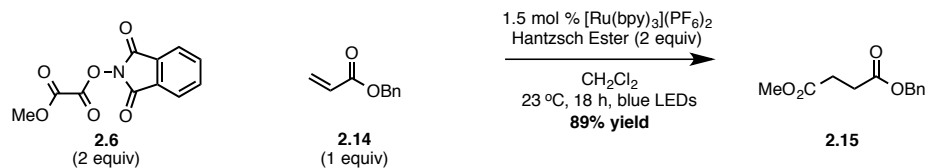
A 1-dram vial was charged with methyl *N*-phthalimidoyl oxalate (**2.6**) (130 mg, 0.53 mmol, 2.0 equiv), [Ru(bpy)₃](PF₆)₂ (4 mg, 0.004 mmol, 0.015 equiv), Hantzsch ester (**2.11**) (140 mg, 0.53 mmol, 2.0 equiv), and a magnetic stir bar. CH₂Cl₂ (0.5 mL, 0.6 M, sparged with Ar for 5 min) was added followed 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 CH₂Cl₂ (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.



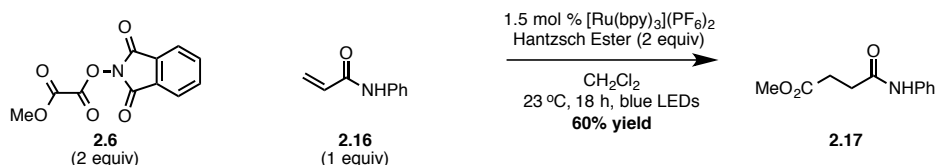
Preparation of sulfone 2.10: According to general procedure, phenyl vinyl sulfone (**2.9**) (45 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (7:3 hexanes:EtOAc) to yield sulfone **2.10** (56 mg, 0.25 mmol, 94% yield) as a colorless solid. $R_f = 0.35$ (3:2 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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



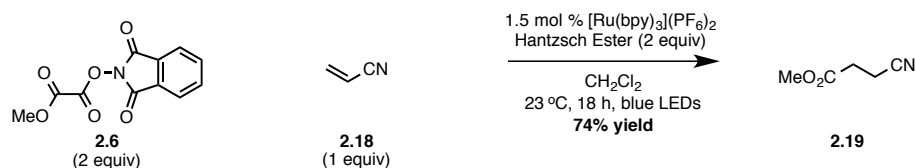
Preparation of ketone 2.13: According to general procedure, methyl vinyl ketone (**2.12**) (22 μ L, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:1 hexanes:EtOAc) to yield ketone **2.13** (29 mg, 0.20 mmol, 74% yield) as a clear oil. R_f = 0.22 (4:1 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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



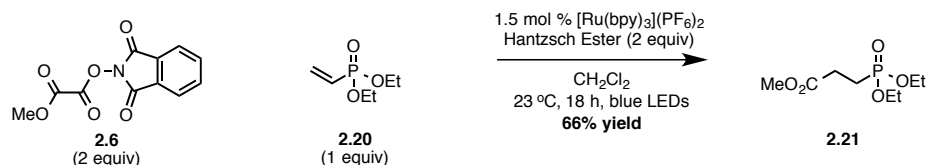
Preparation of ester 2.15: According to general procedure, benzyl acrylate (**2.14**) (40 μ L, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (9:1 hexanes:EtOAc) to yield ester **2.15** (53 mg, 0.24 mmol, 89% yield) as a clear oil. R_f = 0.55 (3:2 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (500 MHz, CDCl₃): 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



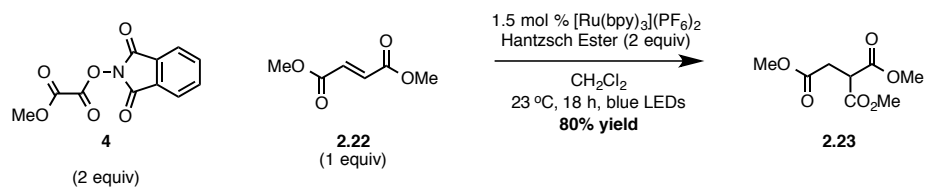
Preparation of amide 2.17: According to general procedure, *N*-phenylacrylamide (**2.16**) (40 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (65:35 hexanes:EtOAc) to yield amide **2.17** (33 mg, 0.16 mmol, 60% yield) as a colorless solid. $R_f = 0.30$ (3:2 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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



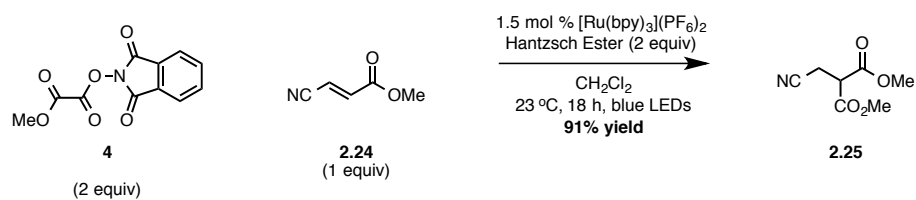
Preparation of nitrile 2.19: According to general procedure, acrylonitrile (**2.18**) (18 μ L, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:1 hexanes:EtOAc) to yield nitrile **2.19** (22 mg, 0.20 mmol, 74% yield) as a clear oil. $R_f = 0.30$ (3:2 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): δ 3.80 (s, 3H), 2.72–2.70 (m, 2H), 2.67–2.65 (m, 2H). Spectral data match those previously reported.³⁰



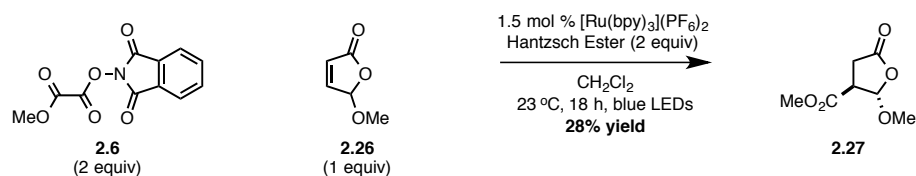
Preparation of phosphonate 2.21: According to general procedure, diethyl vinylphosphonate (**2.20**) (42 μ L, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (3:2 hexanes:acetone) to yield phosphonate **2.21** (39 mg, 0.18 mmol, 66% yield) as a clear oil. R_f = 0.22 (7:3 hexanes:acetone); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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



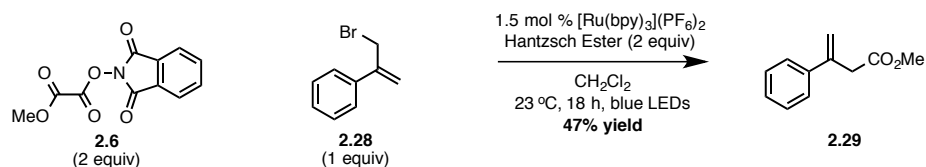
Preparation of ester 2.23: According to general procedure, dimethyl fumarate (**2.22**) (38 mg, 0.27 mmol, 1.0 equiv) was used as the acceptor. The crude residue was purified by flash chromatography (4:1 hexanes:EtOAc) to yield malonate ester **2.23** (43 mg, 0.22 mmol, 80% yield) as a colorless solid. R_f = 0.20 (4:1 hexanes:EtOAc); visualized with KMnO₄. ¹H NMR (600 MHz, CDCl₃): 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 . $^1\text{H NMR}$ (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 . $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 $\text{C}_7\text{H}_{14}\text{NO}_5$ ($\text{M}+\text{NH}_4$) 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

2.5 References and Notes:

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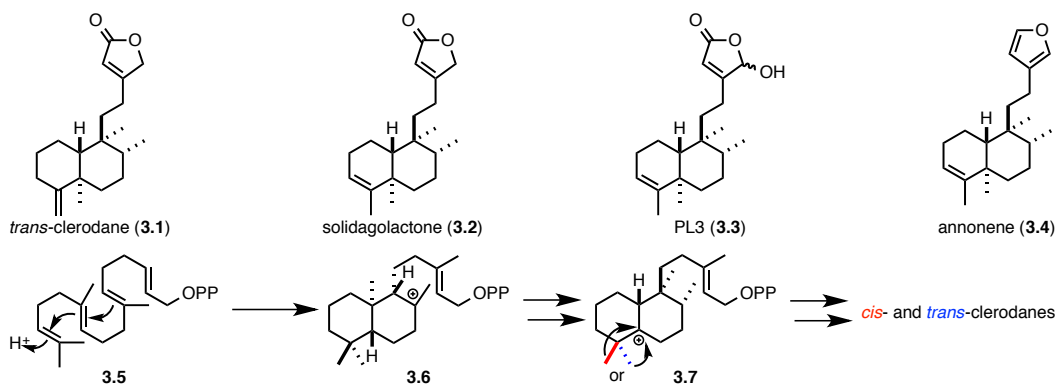
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Chapter 3: Enantioselective Total Syntheses of *trans*-Clerodane Diterpenoids via a Convergent Fragment-Coupling Strategy

3.1 Introduction

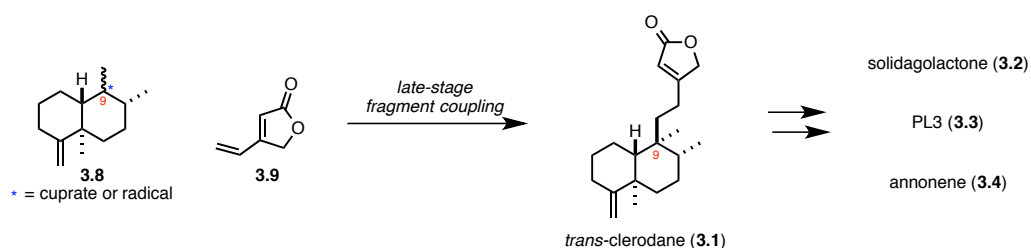
The clerodane family of diterpenoid natural products is comprised of more than 650 secondary metabolites isolated from various plant sources.¹ Many clerodane diterpenoids are known to exhibit antifeedant activity,¹ whereas the biological activity reported for certain members is much more extensive.² The *trans*-clerodane subset of this family of natural products, represented by **3.1**,³ solidagolactone (**3.2**),³ 16-hydroxycycleroda-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 nitriles⁹ and tertiary radicals from tertiary alcohols via visible-light photoredox catalyzed fragmentation of *tert*-alkyl *N*-phthalimidoyl oxalates¹⁰ or cesium hemioxalates¹¹ to achieve the desired late-stage fragment coupling.

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

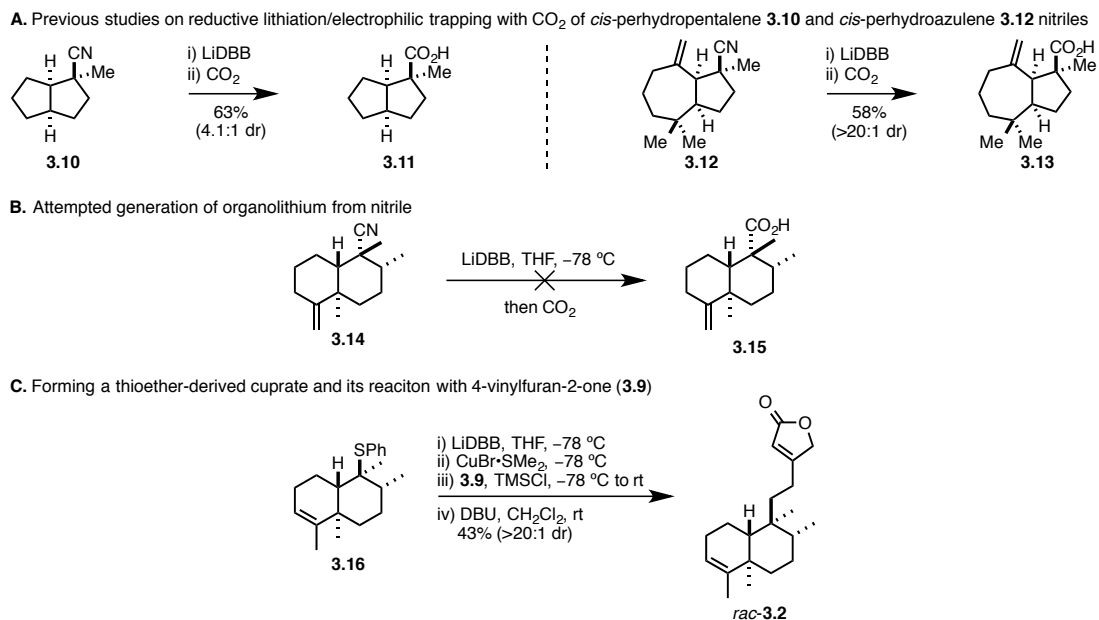


3.2 Results and Discussion

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 nitrile¹² 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 $-78\text{ }^{\circ}\text{C}$ was inefficient, as subjection of **3.14** to 2.2 equiv of lithium 4,4'-(di-*tert*-butyl)biphenylide (LiDBB) in THF at $-78\text{ }^{\circ}\text{C}$, 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 $-78\text{ }^{\circ}\text{C}$, followed successively by transmetalation with 1 equiv of $\text{CuBr}\cdot\text{SMe}_2$ 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 (\pm)-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*-octahydronaphthalene 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}

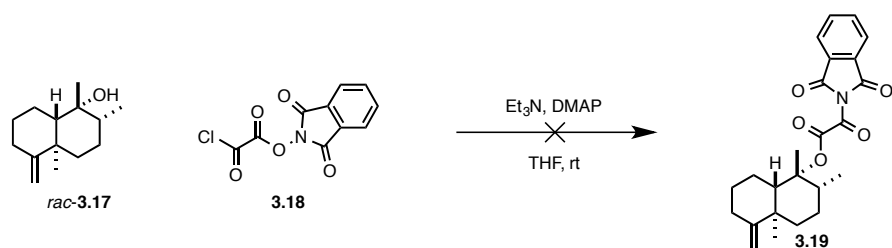
Figure 3.3. Previous studies on reductive lithiation of nitriles. Comparison of a nitrile and a phenylsulfide as precursors of a tertiary cuprate intermediate for the synthesis of *rac*-**3.2**.



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 Et₃N 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

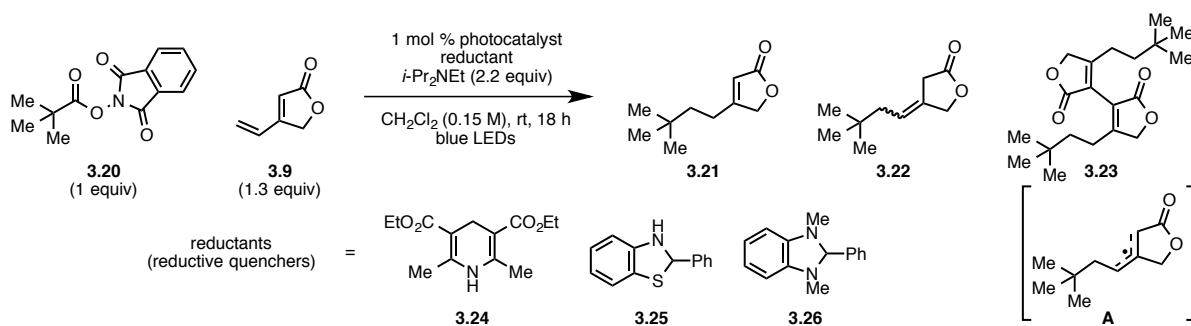
Equation 3.1



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(CF₃)ppy]₂(dtbbpy)PF₆ provided primarily radical dimer **3.23** (entries 2–4). [Ru(bpz)₃](BF₄)₂, whose +1 oxidation state is a much poorer reductant than Ru(bpy)₃¹⁺, 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](BF₄)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**).

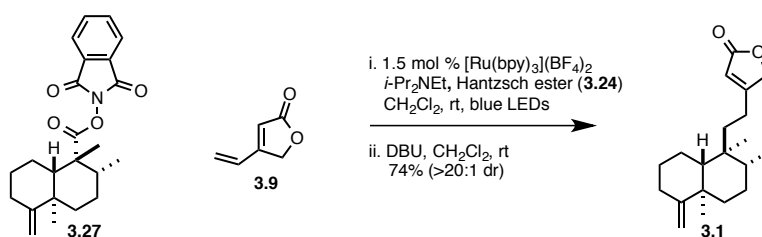


entry ^a	photocatalyst	reductant (equiv)	yield 3.21 (%) ^b	yield 3.22 (%) ^b	yield 3.23 (%) ^b
1	[Ru(bpy) ₃](BF ₄) ₂	3.24 (1.5)	36	<5	30
2 ^c	<i>fac</i> -Ir(ppy) ₃	3.24 (1.5)	0	0	0
3	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆	3.24 (1.5)	24	0	42
4 ^c	[Ir(dtbbpy)ppy ₂]PF ₆	3.24 (1.5)	25	0	33
5	[Ru(bpz) ₃](PF ₆) ₂	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](BF₄)₂	3.24 (5.0)	25	75	0

^aConditions unless otherwise noted: **3.20** (1 equiv), **3.9** (1.3 equiv), photocatalyst (0.01 equiv), *i*-Pr₂NEt (2.2 equiv), reductant (1.5 or 5 equiv), 0.15 M (with respect to **3.20**) in CH₂Cl₂, rt, 18 h, blue LEDs. ^bDetermined by ¹H NMR integration relative to an internal standard (1,4-dimethoxybenzene). ^cA compact fluorescent light was used in place of blue LEDs. ^dThe 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*-acyloxypthalimide **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 related coupling of an organocuprate intermediate (Figure 3.3C).

Equation 3.2

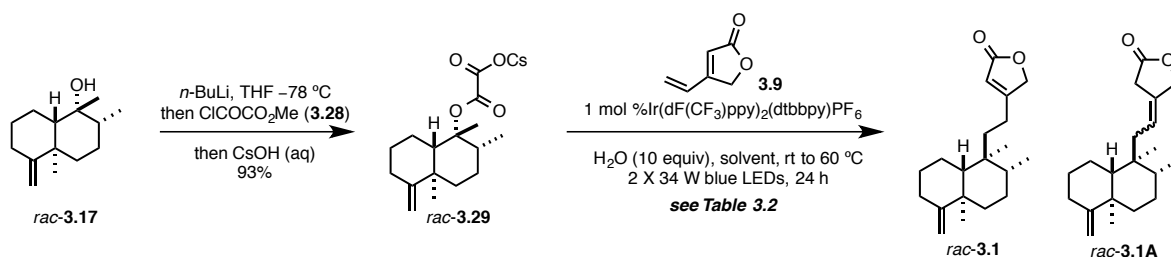


Although we successfully executed our fragment-coupling strategy utilizing *N*-acyloxypthalimide **3.27** as a radical precursor, the approach suffered from five extra steps involved in introducing the carboxyl functionality, stemming from our inability to form (*N*-phthalimidoyl)oxalate **3.19** from 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 $-78\text{ }^{\circ}\text{C}$, 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.

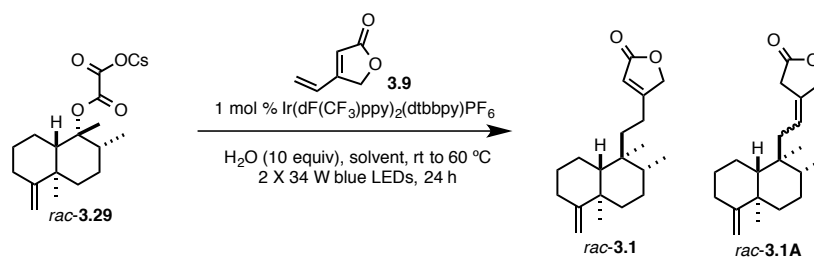
Scheme 3.1. Synthesis of cesium oxalate *rac*-**3.29** and its photoredox coupling with 4-vinylfuran-2-one (**3.9**).



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**).



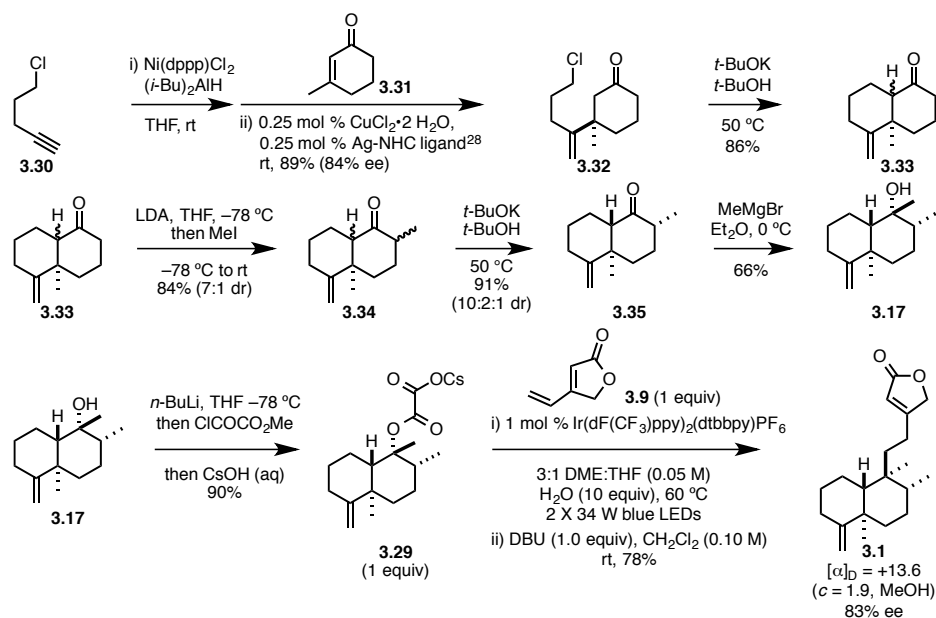
entry	solvent (M) ^a	<i>rac</i> - 3.29 (equiv)	6 (equiv)	yield <i>rac</i> - 3.1 (%) ^b	yield <i>rac</i> - 3.1A (%) ^b
1	3:1 DME:DMF (0.05 M)	1.1	1	63 (57) ^c	30
2	3:1 DME:DMF (0.05 M)	1.5	1	98 (65) ^c	0
3	3:1 DMF:CH ₃ CN (0.05 M)	1	1	48	42
4	3:1 DMF:THF (0.05 M)	1	1	52	33
5	3:1 DME:CH ₃ CN (0.05 M)	1	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

^aConcentration is reported with respect to cesium oxalate *rac*-**3.29**. ^bDetermined by ¹H NMR integration relative to an internal standard (1,2-dibromo-4,5-methylenedioxybenzene). ^cYield 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 us¹⁴ 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

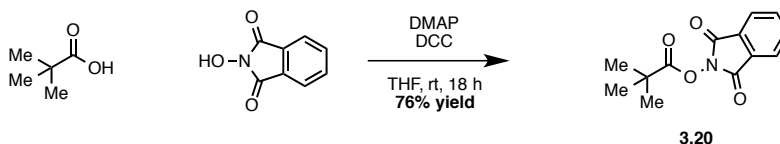
total synthesis of (+)-**3.1** was accomplished in seven steps from 3-methyl-2-cyclohexenone (**3.31**). As the *trans*-clerodane diterpenoids (-)-solidagolactone (**3.2**), (-)-PL3 (**3.3**) and (-)-annonene (**3.4**) have previously been prepared from (+)-**3.1** in 1–3 additional steps,¹⁴ the synthetic 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

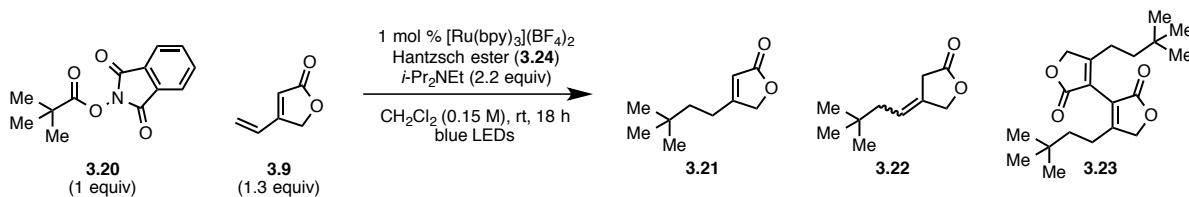
Materials and methods.

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. ¹³C NMR spectra were recorded at 126 or 151 MHz. Data for ¹³C 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:

f.



Preparation of *N*-acyloxophthalimide 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 Et₂O (200 mL) and transferred to a separatory funnel. The organic layer was washed with saturated aqueous NH₄Cl solution (3 x 150 mL) and brine (2 x 150 mL) and was dried over MgSO₄. 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*-acyloxophthalimide **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 Et₂O (0.53 M, 610 μL, 0.34 mmol, 1.3 equiv) was

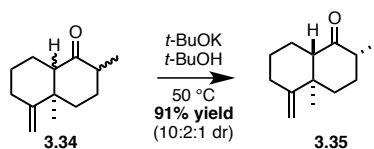
added to a 1-dram vial and the solution was concentrated under reduced pressure. The residue was immediately dissolved in CH₂Cl₂ (1.5 mL, previously sparged with Ar for 5 min) under an argon atmosphere. After sequential addition of *N*-acyloxyphthalimide **3.20** (64 mg, 0.26 mmol, 1 equiv), Hantzsch ester **3.24**³⁵ (100 mg, 0.39 mmol, 1.5 equiv), *i*-Pr₂NEt (100 μL, 0.57 mmol, 2.2 equiv) and a solution of [Ru(bpy)₃](BF₄)₂¹⁸ in CH₂Cl₂ (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 CH₂Cl₂ (1 mL) was added. The reaction mixture was stirred for 1 min and a small aliquot was removed and concentrated under reduced pressure. ¹H 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). ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₀H₁₆O₂Na, (M+Na⁺) 191.1048, found 191.1054.

***E*- and *Z*-4-(3,3-Dimethylbutylidene)dihydrofuran-2(3H)-one (3.22**, a 2.6:1 mixture of double-bond isomers): R_f = 0.3 (10:90 acetone:hexanes). ¹H NMR (500 MHz, CDCl₃, 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,

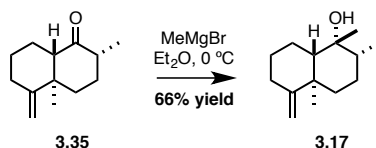
$J = 7.5$ Hz, 2H, minor isomer), 1.82 (d, $J = 7.5$ Hz, 2H, major isomer), 0.91 (s, 9H, major and minor isomers); ^{13}C NMR (126 MHz, CDCl_3 , mixture of isomers): δ 175.9, 175.8, 130.1, 129.6, 122.7, 122.2, 72.5, 70.7, 43.9, 42.6, 34.0, 31.9, 31.73, 31.68, 29.34, 29.29; IR (thin film) 2955, 1785, 1364, 1163, 1028 cm^{-1} ; HRMS (ESI-TOF) m/z calcd for $\text{C}_{10}\text{H}_{16}\text{O}_2\text{Na}$, ($\text{M}+\text{Na}^+$) 191.1048, found 191.1057.

4,4'-bis(3,3-Dimethylbutyl)-[3,3'-bifuran]-2,2'(5H,5'H)-dione (3.23): $R_f = 0.12$ (10:90 acetone:hexanes). ^1H 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 $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Na}$, ($\text{M}+\text{Na}^+$) 357.2042, found 357.2043.



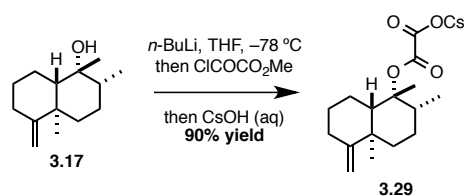
Preparation of ketone 3.35: A round-bottom flask was charged with ketone **3.34**¹⁴ (844 mg, 4.39 mmol), $t\text{-BuOH}$ (8.8 mL), and $t\text{-BuOK}$ (985 mg, 8.78 mmol). The resulting solution was maintained at $50\text{ }^\circ\text{C}$ for 2 h. The vessel was allowed to cool down to rt and the reaction 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). ^1H 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} ; $[\alpha]^{19}_{\text{D}} +63.2$, $[\alpha]^{19}_{577} +63.3$, $[\alpha]^{19}_{546} +74.1$, $[\alpha]^{19}_{435} +148$, $[\alpha]^{19}_{405} +194$ ($c = 0.6$, CH_2Cl_2); HRMS (ESI-TOF) m/z calcd for $\text{C}_{13}\text{H}_{20}\text{ONa}$ ($\text{M}+\text{Na}^+$) 215.1412, found 215.1403.



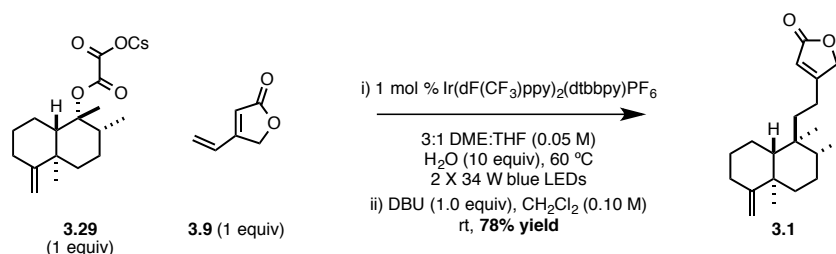
Preparation of alcohol 3.17: A round-bottom flask was charged with 13 mL of Et_2O and a solution of MeMgBr (2.5 mL, 7.5 mmol, 3.0 M solution in Et_2O) under an atmosphere of argon. The solution was stirred and cooled to 0 $^\circ\text{C}$ before a solution of ketone **3.35** (730 mg, 3.8 mmol, 10:2:1 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 $^\circ\text{C}$ 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). ^1H 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} ; $[\alpha]^{21}_{\text{D}}$ +79.3, $[\alpha]^{21}_{577}$ +82.8, $[\alpha]^{21}_{546}$ +93.6, $[\alpha]^{21}_{435}$ +156, $[\alpha]^{21}_{405}$ +187 ($c = 1.2, \text{CHCl}_3$); HRMS (GC-CI-TOF) m/z calcd for $\text{C}_{14}\text{H}_{24}\text{O}$, ($\text{M}+\text{NH}_4^+$) 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). ^1H 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} ; $[\alpha]_D^{22} +43.5$, $[\alpha]_{577}^{22} +44.7$, $[\alpha]_{546}^{22} +51.0$, $[\alpha]_{435}^{22} +85.8$, $[\alpha]_{405}^{22} +101.6$ (c = 1.0, MeOH); HRMS (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{23}\text{O}_4$, ($\text{M}-\text{Cs}^+$) 279.1596, found 279.1588.



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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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_2O (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 isomers³⁶ (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 ; $[\alpha]^{21}_{\text{D}} +12.9$, $[\alpha]^{21}_{546} +12.6$, $[\alpha]^{21}_{435} +17.9$, $[\alpha]^{21}_{405} +13.1$ ($c = 0.43$, CHCl_3); $[\alpha]^{21}_{\text{D}} +13.6$, $[\alpha]^{21}_{577} +13.9$, $[\alpha]^{21}_{546} +15.2$, $[\alpha]^{21}_{435} +21.0$ ($c = 1.9$, MeOH). Other characterization data acquired for (+)-**3.1** matched that previously reported.^{3,14}

3.5 References and Notes:

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8. The total syntheses of **3.3** and **3.4** previously described required 19–27 steps, see references 6 and 7. More efficient routes to related diterpenoids or meroterpenoids have been described that potentially could be used to prepare the *trans*-clerodane diterpenoids that are subject to this account, see, for example: (a) Ling, T.; Poupon, E.; Rueden, E. J.; Kim, S. H.; Theodorakis, E. A. *J. Am. Chem. Soc.* **2002**, 124, 12261–12267. (b) Stahl, P.; Kissau, L.; Mazitschek, R.; Huwe, A.; Furet, P.; Giannis, A.; Waldmann, H. *J. Am. Chem. Soc.* **2001**, 123, 11586–11593.

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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 CH₂Cl₂, equilibration of *rac*-**3.1A** to *rac*-**3.1** was observed (see the Experimental Information for details).
27. For a recent review of catalytic enantioselective methods to prepare quaternary carbon stereocenters, see: Quasdorf, K. W.; Overman, L. E. *Nature* **2014**, *516*, 181–194.
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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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34. This compound was prepared as previously reported and was stored as an approximately 0.5 M solution in Et₂O at –20 °C when not in use, see reference 16b.
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36. The β,γ -unsaturated lactones exist as a 1:1 mixture of *cis*- and *trans*-double bond isomers.

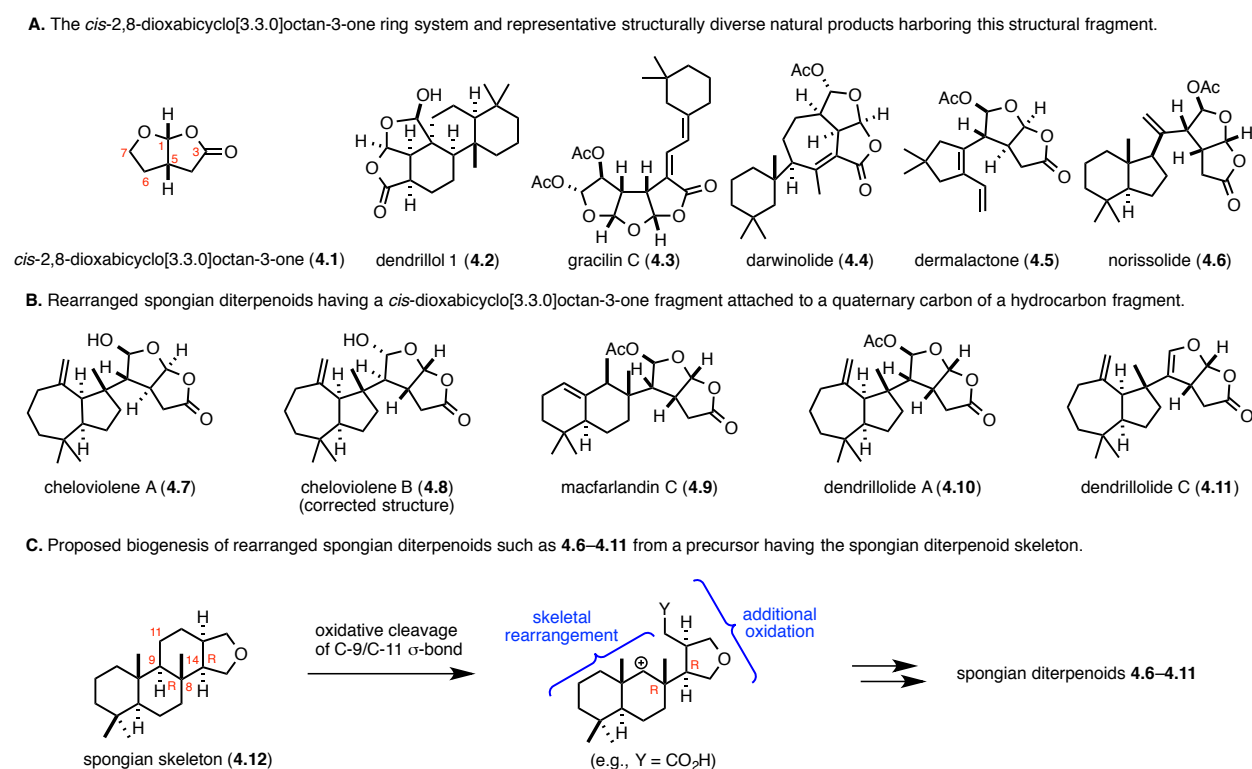
Chapter 4: Short Enantioselective Total Syntheses of Cheloviolenes A and B and Dendrillolide C via Convergent Fragment Coupling Using a Tertiary Carbon Radical

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 chelviolene 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 chelviolene 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 spongioid 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

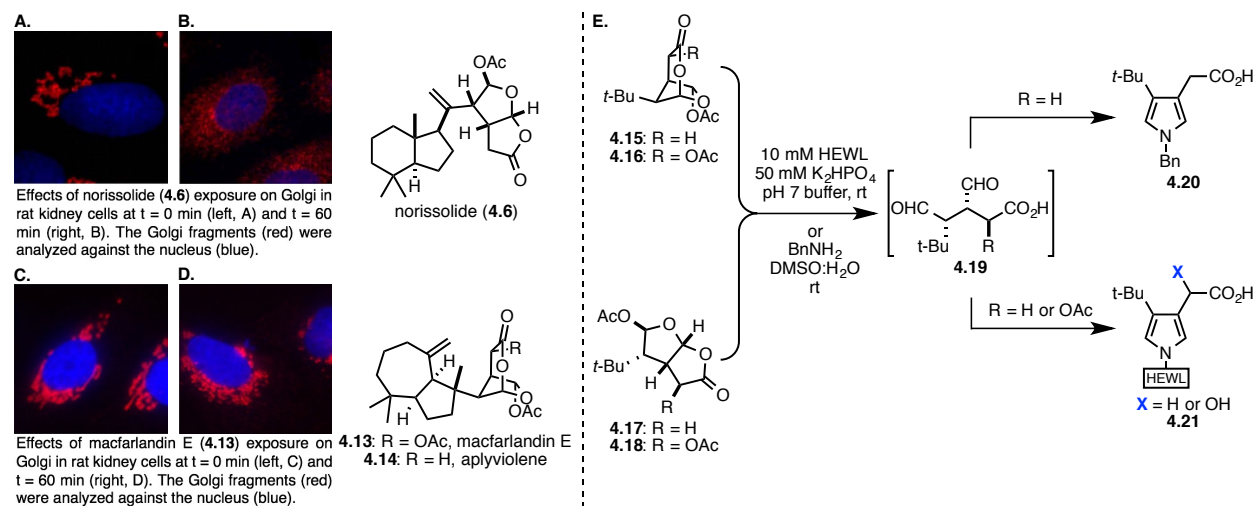
Figure 4.1. Representative natural products that harbor the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system and proposed biogenesis of rearranged spongioid diterpenoids.



The biological activity of rearranged spongioid 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 spongioid 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

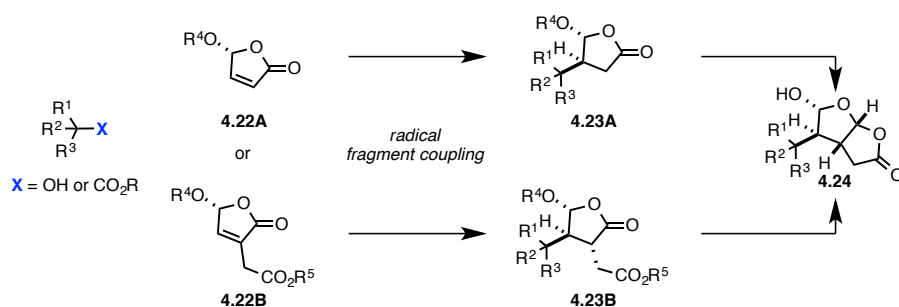
Figure 4.2. Comparison of Golgi phenotypes induced by norissolid (4.6) and macfarlandin E (4.13) and proposed origin of the bioactivity of the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one and 2,7-dioxabicyclo[3.2.1]octan-3-one fragments.



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 catalysis¹⁹ 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

methanolysis²⁷ to deliver butenolide **4.28** in five steps from commercially available itaconic acid (**4.25**).

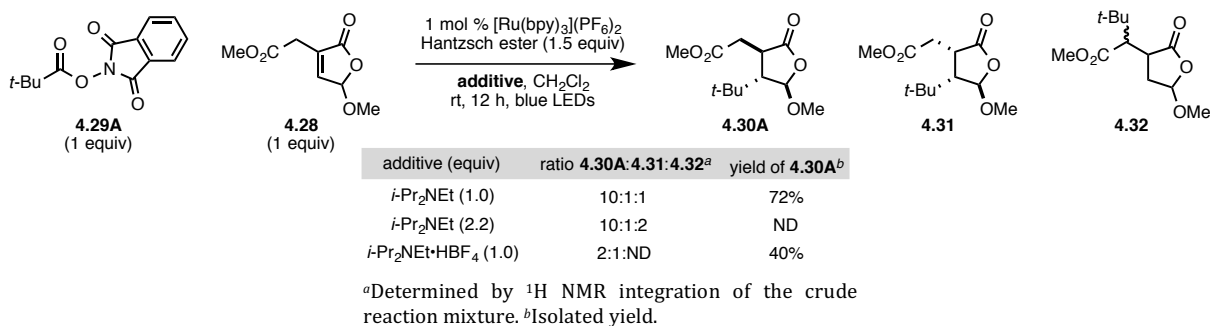
Scheme 4.2. Synthesis of butenolide **4.28**.



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 conditions²⁸ developed during our first studies in this area,²² the $\text{Ru}(\text{bpy})_3$ -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_2NEt 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 ¹H 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_2NEt enhanced the formation of byproduct **4.32**, whereas replacing *i*- Pr_2NEt with *i*- $\text{Pr}_2\text{NEt} \cdot \text{HBF}_4$ 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*- $\text{Pr}_2\text{NEt} \cdot \text{HBF}_4$. 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*-Pr₂NEt•HBF₄.³² 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*-Pr₂NEt.³⁴ In the hope of enhancing 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.

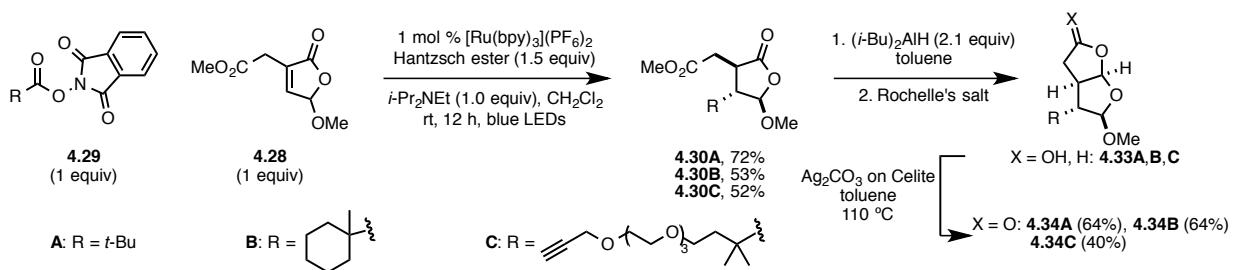
Scheme 4.3. Coupling of *N*-acyloxyphthalimide **4.29A** with butenolide **4.28**.



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*-Pr₂NEt 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)₂AlH (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 Br₂, PCC, acetone (via Oppenauer oxidation), and Ag₂CO₃ 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)₂AlH 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 Ag₂CO₃/Celite in refluxing toluene to give *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one **4.34A–C** in 40–64% yield.

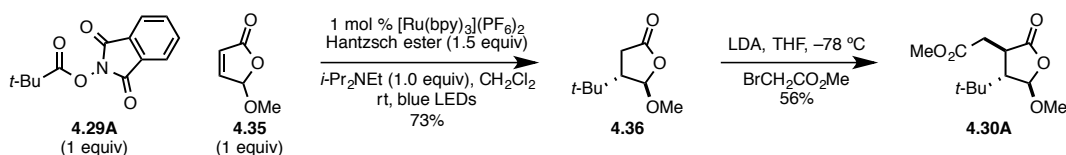
Scheme 4.4. Synthesis of analogues containing the *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one ring system via a radical fragment coupling strategy.



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*-Pr₂NEt•HBF₄ was substituted for *i*-Pr₂NEt. 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.

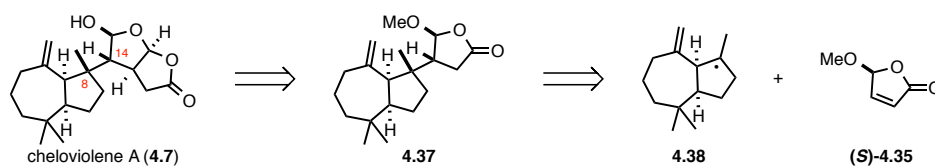
Scheme 4.5. Two-step synthesis of lactone **4.30A** via coupling of *tert*-NHP ester **4.29A** with unsubstituted butenolide **4.35**, followed by alkylation with methyl bromoacetate.



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*-

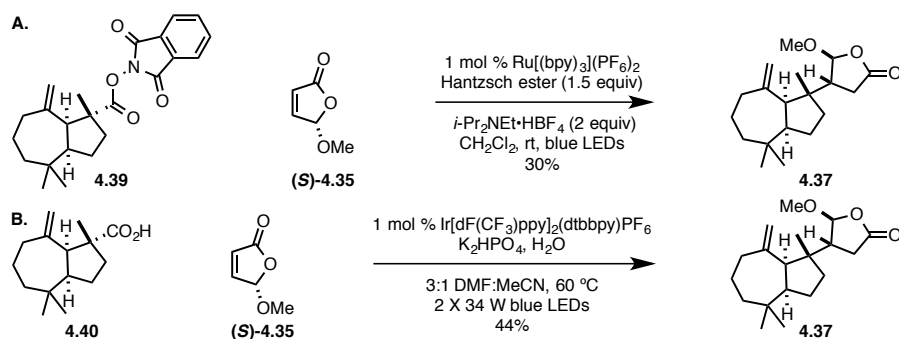
perhydroazulene radical²² and the face opposite the methoxy substituent of butenolide (**S**)-**4.35** to form coupled product **4.37**.

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



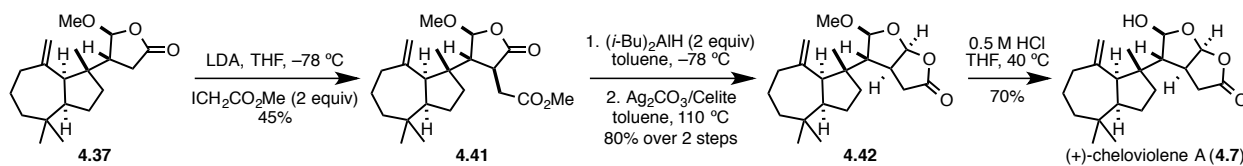
The pivotal radical coupling was examined initially using the enantiopure *cis*-perhydroazulene NHP ester **4.39**, which we had prepared earlier in 14 steps from (+)-fenchone.²² Exposure of the activated ester **4.39** and butenolide **4.35** to Ni-catalyzed Giese reaction conditions did not lead to 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*-acyloxypthalimide **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 MacMillan⁴⁰ 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, CHCl₃), literature: $[\alpha]_D +4.5$ (*c* 0.11, CHCl₃).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**).

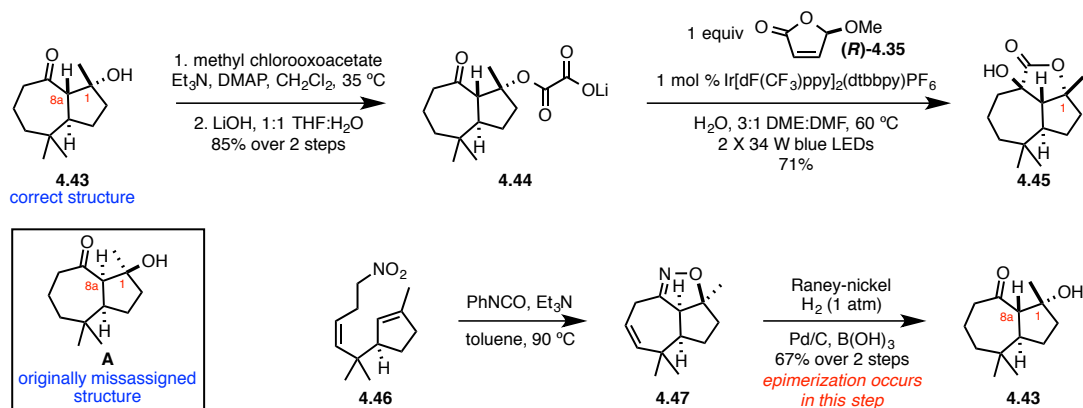


Completion of the synthesis of (+)-cheloviolene A (**4.7**) validated our strategy and identified several problems that needed to be addressed to secure a more concise approach to the family of spongioid diterpenoids containing a *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one fragment. First, the efficiency 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 alkoxyacyl radical and correct stereochemical assignment of tertiary alcohol **4.43**.



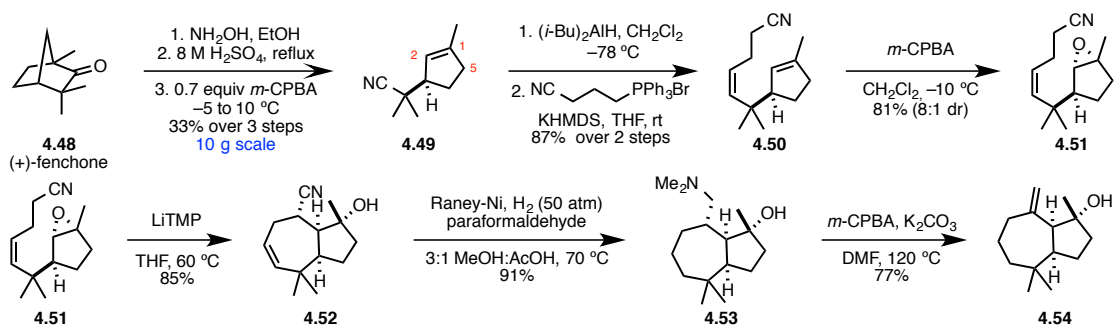
Brief comment on our original assignment of structure **A** to the perhydroazulene intermediate used to prepare *cis*-perhydroazulene carboxylic acid **4.40** is warranted. First, this structural misassignment was not detected in our earlier studies because the next step in the synthesis of **4.40**, 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 CH₂Cl₂ 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

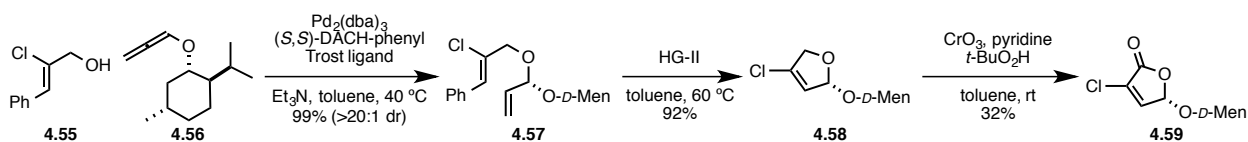
Scheme 4.9. Synthesis of *cis*-perhydroazulene tertiary alcohol **4.54**.



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 (+)-chelviolene 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 ¹H 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 CrO₃ and *tert*-butylhydroperoxide⁶¹ 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.

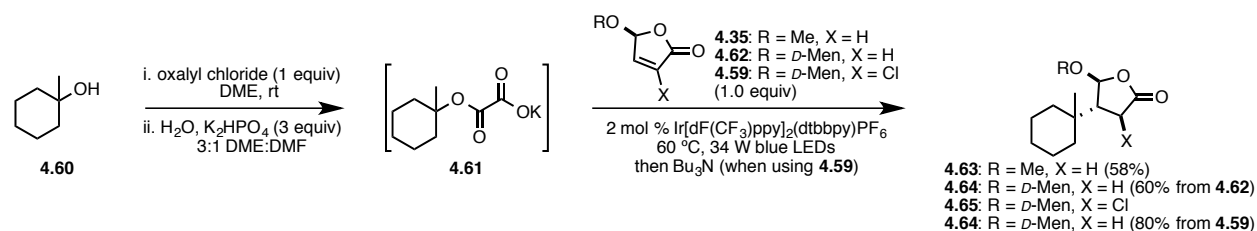
Scheme 4.10. Synthesis of chlorobutenolide **4.59**.



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 previously⁴³ provided *trans* adduct **4.63** as a single stereoisomer in 58% yield.⁶⁵ Using menthylxybutenolide **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 dechlorination⁶⁷ to proceed for 4 h gave conjugate addition product **4.64** in 80% yield in one-step from alcohol **4.60**.

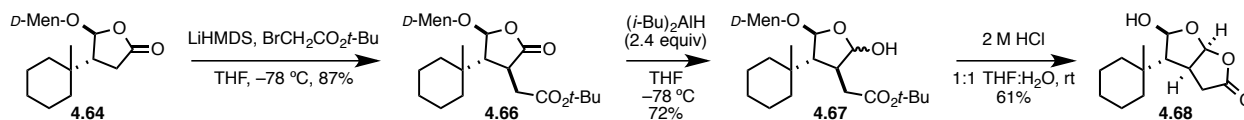
Scheme 4.11. One-step activation and coupling of 1-methylcyclohexanol with butenolides.



In our first-generation synthesis of (+)-chelviolene 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 $(i\text{-Bu})_2\text{AlH}$ in toluene at $-78\text{ }^\circ\text{C}$ 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**.

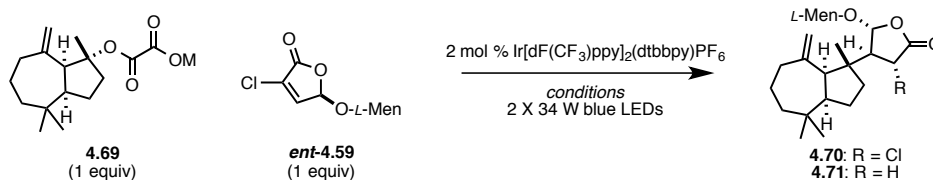
Scheme 4.12. Improved synthesis of *cis*-2,8-dioxabicyclo[3.3.0]octan-3-one **4.68** from the radical coupling product **4.64**.



Our studies aimed at second-generation total syntheses of rearranged spongioid 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 $\sim 40\%$ 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**.



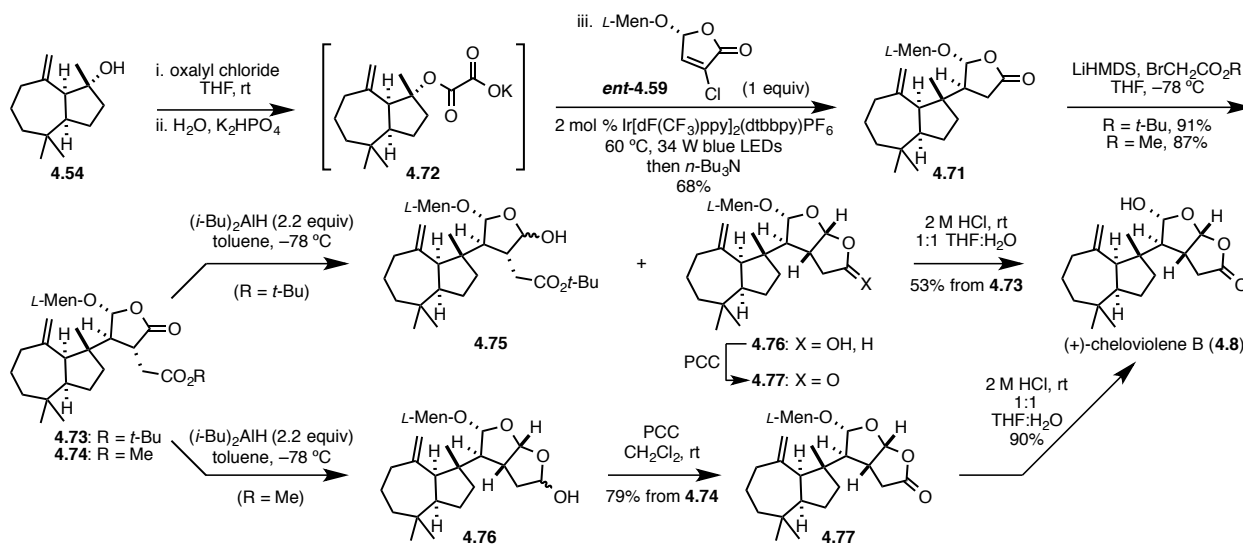
entry	M	conditions	4.70, yield (%) ^a	4.71, yield (%) ^a
1	Li	MeCN (0.05 M), H ₂ O (10 equiv)	0	0
2	Li	DMF (0.05 M), H ₂ O (10 equiv)	24	0
3	Li	DME (0.05 M), H ₂ O (10 equiv)	29	13
4	Li	THF (0.05 M), H ₂ O (10 equiv)	34	5
5	Li	THF (0.05 M), H ₂ O (100 equiv)	17	12
6 ^b	Li	THF (0.05 M), H ₂ O (10 equiv)	48	0
7	Li	THF (0.6 M), H ₂ O (5 equiv)	73 ^c	<5%
8 ^d	Li	THF (0.6 M), H₂O (5 equiv)	0	75^d
9	K	THF (0.6 M), H ₂ O (5 equiv)	72 ^c	<5%

^aDetermined by ¹H NMR integration relative to an internal standard (1,2-dibromo-4,5-methylenedioxybenzene). ^b1.5 equiv of butenolide **ent-4.59** was utilized. ^cIsolated yield. ^d*n*-Bu₃N (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*-Bu₃N 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*-Bu₃N 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 K₂HPO₄ 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*-Bu₃N 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 (+)-chelovioline B (**4.8**).

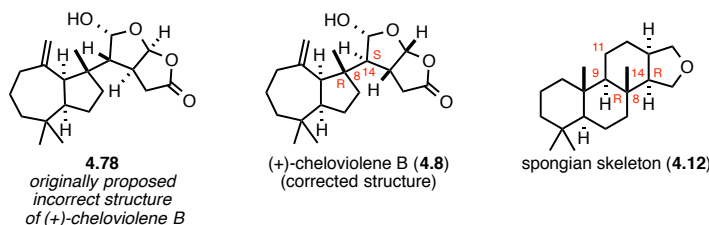


Elaboration of coupled product **4.71** to (+)-cheloviolene B (**4.8**) began with alkylation of the lactone fragment of **4.71** with *tert*-butyl bromoacetate to deliver ester **4.73** in 91% yield. In contrast to our earlier results in the model series, reduction of **4.73** with 2.2 equiv of DIBALH 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:H₂O at room temperature to give what turned out to be (+)-cheloviolene B (**4.8**), mp: 189–190 °C, [α]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:H₂O 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 (+)-cheloviolenone 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 ¹H NMR spectra of so-called chelonaplysin B was identical to that of (+)-cheloviolenone 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 (+)-cheloviolenone A (**4.7**), whose structure was confirmed by X-ray analysis, these workers isolated a related diterpenoid, (+)-cheloviolenone B, which they assigned as the lactol epimer of cheloviolenone A **4.78** (Figure 4.3).^{8b} It is this sponge isolate whose reported ¹H and ¹³C NMR spectra are indistinguishable from synthetic **4.8**. The structure of (+)-cheloviolenone B must therefore be revised to be **4.8**.

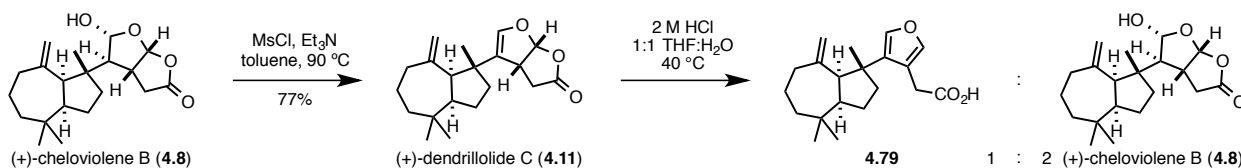
Figure 4.3. Comparison of the originally proposed structure of (+)-cheloviolenone B **4.78** and the revised structure **4.8**.



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 Et₃N in toluene at 90 °C provided (+)-dendrillolide C (**4.11**), [α]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:H₂O at 40 °C led to the formation of a 1.2:1 mixture of cheviolene 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

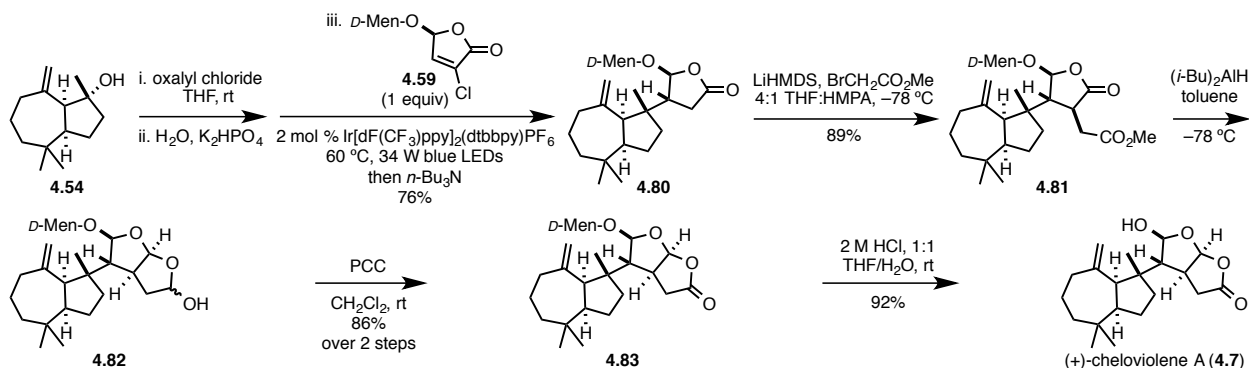
Scheme 4.14. Conversion of (+)-cheviolene B (**4.8**) to (+)-dendrillolide C (**4.11**) and stereoselective hydration of enol ether **4.11** to lactol **4.8**.



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 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

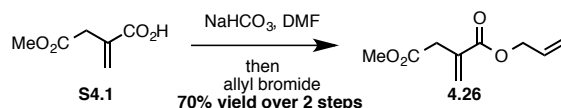
tertiary radical **4.38** from tertiary alcohol **4.54** and its *in situ* trapping with chlorobutenolides **4.59** and *ent*-**4.59**. Of critical importance, these fragment unions were accomplished using equimolar amounts of the two coupling partners. It should be noted that while this strategy has 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

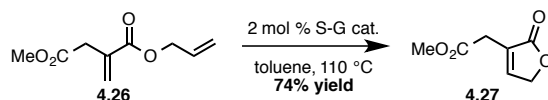
Materials and methods.

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*-Pr₂NEt), and triethylamine (Et₃N) 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 (KMnO₄). 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. ¹³C NMR spectra were recorded at 126 or 151 MHz. Data for ¹³C 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

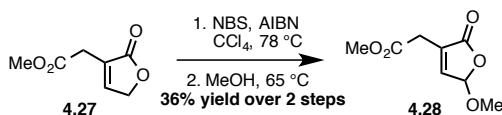
purchased from <http://www.creativelightings.com> (product code CL-FRS5050-12WP-12V) and were powered by 8 AA batteries. See JOC Standard Abbreviations and Acronyms for abbreviations (available at http://pubs.acs.org/paragonplus/submission/joceah/joceah_abbreviations.pdf).



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, H₂O (50 mL) was added to the reaction mixture and the resulting solution was transferred to a separatory funnel and extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed with H₂O (3 x 50 mL), dried over MgSO₄ 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); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₉H₁₂O₄Na 207.0633; Found 207.0637.

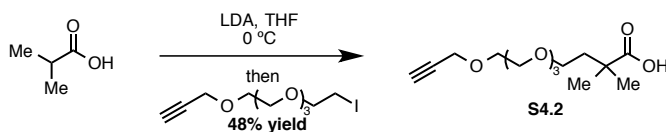


Preparation of Butenolide 4.27: A round-bottom flask was charged with diene **4.26** (800 mg, 4.3 mmol, 1.0 equiv), toluene (440 mL, 0.01 M), and a magnetic stir bar under an atmosphere of argon. Next, Stewart-Grubbs catalyst (50 mg, 0.09 mmol, 0.02 equiv)²⁶ was added to the reaction mixture and the 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 \rightarrow 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); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.52 (s, 1H), 4.87 (s, 2H), 3.75 (s, 3H), 3.38 (s, 2H); $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_7\text{H}_8\text{O}_4\text{Na}$ 179.0320; Found 179.0312.



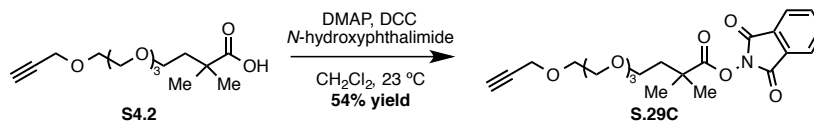
Preparation of Butenolide 4.28: A round-bottom flask was charged with butenolide **4.27** (490 mg, 3.1 mmol, 1.0 equiv), CCl_4 (21 mL, 0.15 M), *N*-bromosuccinimide (1.7 g, 9.4 mmol, 3.0 equiv), AIBN (52 mg, 0.31 mmol, 0.1 equiv), and a magnetic stir bar under an atmosphere of argon. The mixture was 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 ^1H 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 \rightarrow 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); ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_8\text{H}_{10}\text{O}_5\text{Na}$ 209.0426; Found 209.0418.



Preparation of Carboxylic Acid S4.2: A round-bottom flask was charged with *i*-Pr₂NH (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

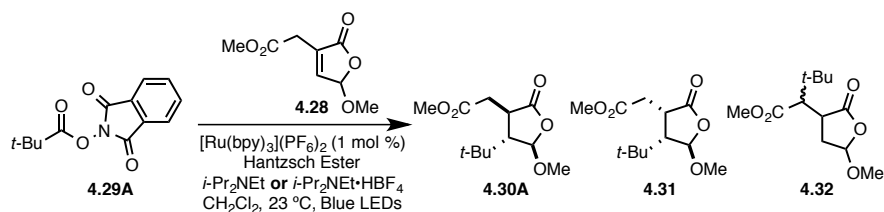
at 0 °C. The reaction was maintained at 0 °C for 20 min, followed by a dropwise addition of a solution of 1-iodo-3,6,9,12-tetraoxapentadec-14-yne (10.2 g, 28.6 mmol, 1.1 equiv)⁷⁴ in THF (60 mL, 0.43 M). The resulting heterogeneous mixture was allowed to warm to rt and stirred vigorously for 12 h. After 12 h, the reaction was quenched via addition of H₂O (50 mL). The resulting biphasic mixture was transferred to a separatory funnel and extracted with CH₂Cl₂ (2 x 200 mL). The aqueous layer was acidified with sat. NH₄Cl (aq) and extracted with CH₂Cl₂ (2 x 300 mL). The combined organic layers, resulting from extracting the acidified aqueous layer, were dried over MgSO₄ and concentrated by use of a rotary evaporator to yield **S4.2** as a clear oil (3.8 g, 13 mmol, 48% yield); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₅H₂₆O₆Na 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), CH₂Cl₂ (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. NH₄Cl (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_8\text{Na}$ 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 $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (0.01 equiv), followed by either *i*- Pr_2NEt (1.0 equiv) or *i*- $\text{Pr}_2\text{NEt}\cdot\text{HBF}_4$ (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



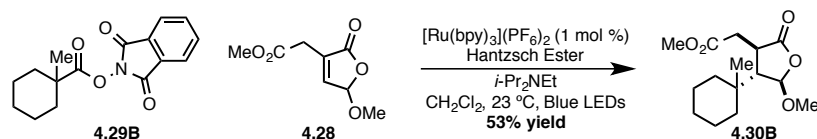
Preparation of Lactone 30a: Following the general procedure, *N*-acyloxypthalimide **4.29A** (27 mg, 0.11 mmol, 1.0 equiv) and butenolide **4.28** (20 mg, 0.11 mmol, 1.0 equiv) were coupled in the presence of $i\text{-Pr}_2\text{NEt}$ (19 μL , 0.11 mmol, 1.0 equiv), $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (1 mg, 0.001 mmol, 0.01 equiv), and Hantzsch ester (41 mg, 0.16 mmol, 1.5 equiv) in CH_2Cl_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); ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{20}\text{O}_5\text{Na}$ 267.1208; Found 267.1209.

The reaction performed in the presence of $i\text{-Pr}_2\text{NEt}\cdot\text{HBF}_4$ (53 mg, 0.24 mmol, 2.2 equiv) in place of $i\text{-Pr}_2\text{NEt}$ 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 ^1H and ^{13}C NMR analysis of crude reaction mixtures.

Lactone 4.31 was isolated in 22% yield from the above reaction when $i\text{-Pr}_2\text{NEt}\cdot\text{HBF}_4$ was used: $R_f = 0.47$ (10:90 ethyl acetate:hexanes, stained with KMnO_4); ^1H 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,

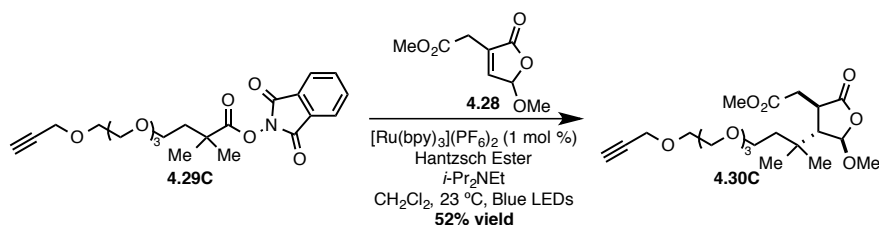
CDCl₃) δ 177.8, 172.0, 105.9, 56.6, 54.2, 52.3, 38.3, 32.3, 32.0, 28.3; IR (thin film) 2956, 2922, 1783, 1742 cm⁻¹; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₁₂H₂₀O₅Na 267.1208; Found 267.1201.

Lactone 4.32 was isolated in 1% yield as a 1.5:1 mixture of diastereomers from the above reaction when *i*-Pr₂NEt was used: R_f = 0.42 (10:90 ethyl acetate:hexanes, stained with KMnO₄); ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₂H₂₀O₅Na 267.1208; Found 267.1199.



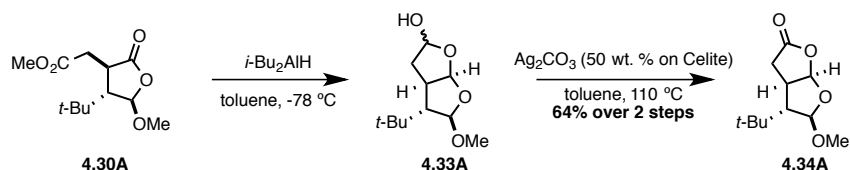
Preparation of Lactone 4.30B: Synthesized according to the general procedure from the *N*-acyloxypthalimide **4.29B** (77 mg, 0.27 mmol, 1.0 equiv),³² butenolide **4.28** (50 mg, 0.27 mmol, 1.0 equiv), *i*-Pr₂NEt (47 μ L, 0.27 mmol, 1.0 equiv), [Ru(bpy)₃](PF₆)₂ (2 mg, 0.003 mmol, 0.01 equiv) and Hantzsch ester (100 mg, 0.4 mmol, 1.5 equiv) in CH₂Cl₂ (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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_5\text{Na}$ 307.1521; Found 307.1523.



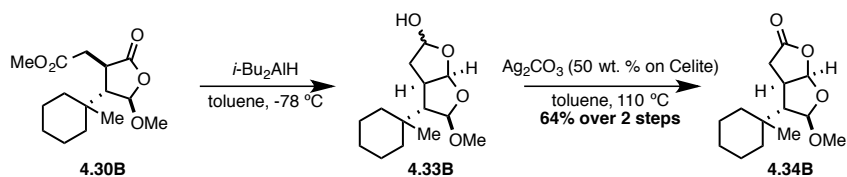
Preparation of Lactone 4.30C: Synthesized according to the general procedure from *N*-acyloxyphthalimide **4.29C** (30 mg, 0.07 mmol, 1.0 equiv), butenolide **4.28** (13 mg, 0.07 mmol, 1.0 equiv), $i\text{-Pr}_2\text{NEt}$ (12 μL , 0.07 mmol, 1.0 equiv), $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (0.6 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{36}\text{O}_9\text{Na}$ 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 $-78\text{ }^{\circ}\text{C}$, *i*-Bu₂AlH (2.1 equiv, 1 M in toluene) was added dropwise. The solution was maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction was quenched by the addition of saturated solution of Rochelle's salt (aq) (0.1 M) at $-78\text{ }^{\circ}\text{C}$. 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 CH₂Cl₂ (3 x 10 mL). The combined organic layers were dried over Na₂SO₄ 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), Ag₂CO₃ (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 $110\text{ }^{\circ}\text{C}$. 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**.



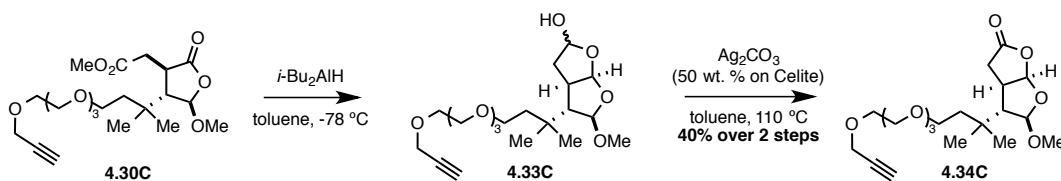
Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.34A: Synthesized according to the general procedure described above from **4.30A** (50 mg, 0.21 mmol, 1.0 equiv) and 1 M solution of *i*-Bu₂AlH in toluene (430 μL , 0.43 mmol, 2.2 equiv) in toluene (2 mL, 0.1 M).

Diagnostic data for lactol intermediate **4.33A**: ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_4\text{Na}$ 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); ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_4\text{Na}$ 237.1103; Found 237.1110.



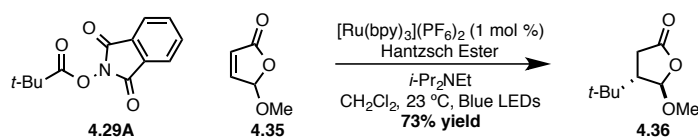
Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.34B: Synthesized according to the general procedure described above from **4.30B** (33 mg, 0.12 mmol, 1.0 equiv) and 1 M solution of $i\text{-Bu}_2\text{AlH}$ in toluene (240 μL , 0.24 mmol, 2.2 equiv) in toluene (1.2 mL, 0.1 M). Diagnostic data for lactol intermediate **4.33B**: ^1H 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); ^1H 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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{Na}$ 277.1416; Found 277.1417.

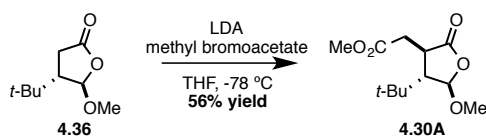


Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.34C: Synthesized according to the general procedure described above from **4.30C** (94 mg, 0.21 mmol, 1.0 equiv) and 1 M solution of $i\text{-Bu}_2\text{AlH}$ in toluene (460 μL , 0.46 mmol, 2.2 equiv) in toluene (2.1 mL, 0.1 M). Conversion of lactol **4.33C** 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); ^1H 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 $\text{C}_{21}\text{H}_{34}\text{O}_8\text{Na}$ 437.2151; Found 437.2149.

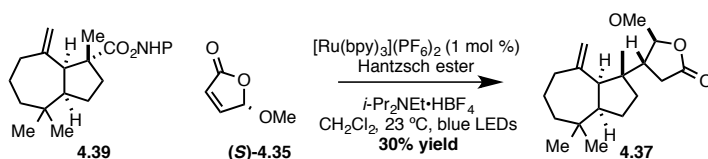


Preparation of Lactone 4.36: Synthesized according to the general fragment coupling procedure from *N*-acyloxypthalimide **4.29A** (150 mg, 0.6 mmol, 1.0 equiv), butenolide **4.35** (69 mg, 0.60 mmol, 1.0 equiv), *i*-Pr₂NEt (100 μL , 0.6 mmol, 1.0 equiv), $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (5 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 \rightarrow 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 $\text{C}_9\text{H}_{16}\text{O}_3\text{Na}$ 195.0997; Found 195.0993.



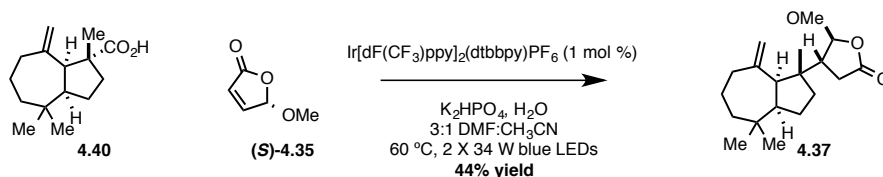
Preparation of Ester 4.30A: A round-bottom flask was charged with *i*-Pr₂NH (110 μL , 0.75 mmol, 3.8 equiv), THF (4.6 mL, 0.1 M), and a magnetic stir bar under an atmosphere of

argon. After cooling the solution to $-78\text{ }^{\circ}\text{C}$, 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 $0\text{ }^{\circ}\text{C}$ 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 $-78\text{ }^{\circ}\text{C}$. After 1 h at $-78\text{ }^{\circ}\text{C}$, 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).



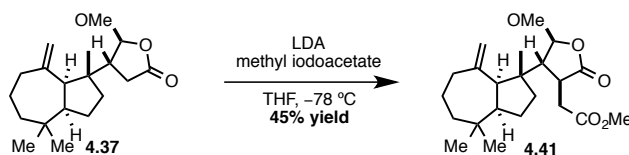
Preparation of Lactone 4.37 from 4.39: A 1-dram scintillation vial was charged with *N*-acyloxyphthalimide **4.39** (25 mg, 0.066 mmol, 1.0 equiv), butenolide (**S**)-**4.35** (8 mg, 0.07 mmol, 1.0 equiv), Hantzsch ester (25 mg, 0.11 mmol, 1.5 equiv), $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (0.6 mg, 0.0007 mmol, 0.01 equiv), $i\text{-Pr}_2\text{NEt}\cdot\text{HBF}_4$ (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

Et₂O 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; $[\alpha]^{23}_D +90.8$, $[\alpha]^{23}_{577} +93.2$, $[\alpha]^{23}_{546} +106$, $[\alpha]^{23}_{435} +181$ ($c = 1.0$, CHCl₃); HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd for C₁₉H₃₀O₃Na 329.2093; Found 329.2099.



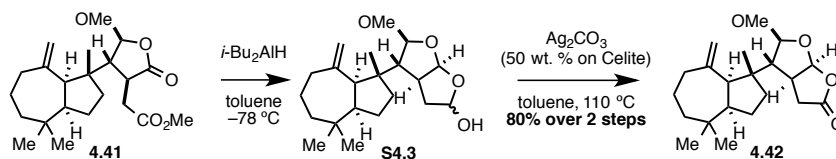
Preparation of Lactone 4.37 from 4.40: A 1-dram scintillation vial was charged with **4.40** (47 mg, 0.2 mmol, 1.0 equiv), K₂HPO₄ (38 mg, 0.22 mmol, 1.1 equiv), (Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5 mg, 0.004 mmol, 0.02 equiv), 3:1 DMF:CH₃CN (0.5 mL, 0.4 M), H₂O (36 μL, 2.0 mmol, 10 equiv), **(S)**-**4.35** (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 Et₂O (3 x 5 mL). The combined organic layers were dried over MgSO₄ 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*-Pr₂NH (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, H₂O (5 mL) was added, and the resulting biphasic mixture was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic extracts were dried over Na₂SO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]_D²³ +73.0, [α]_D²³₅₇₇ +76.4, [α]_D²³₅₄₆ +86.1, [α]_D²³₄₃₅ +146 (*c* = 1.0, CHCl₃); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd for C₂₂H₃₄O₅Na 401.2304; Found 401.2295.

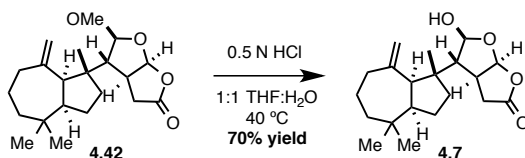


Preparation of Dioxabicyclo[3.3.0]octan-3-one 4.42: A round-bottom flask was charged with **4.41** (4 mg, 0.01 mmol, 1.0 equiv), toluene (0.1 mL, 0.1 M), and a magnetic stir bar under an atmosphere of argon. After cooling the solution to -78 °C, 1 M solution of *i*-Bu₂AlH in toluene (22 μL, 0.022 mmol, 2.2 equiv) was added dropwise. The solution was

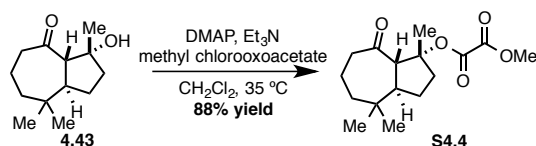
maintained at $-78\text{ }^{\circ}\text{C}$ for 30 min. The reaction was quenched by the slow addition of saturated solution of Rochelle's salt (aq) (0.1 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was allowed to warm to rt and stirred at rt for 1 h. Biphasic mixture was transferred to a separatory 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 bicyclic lactol epimers **S4.3**. Diagnostic chemical shifts of the lactol intermediate **S4.3**: ^1H 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 $110\text{ }^{\circ}\text{C}$. 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); ^1H 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} ; $[\alpha]^{23}_{\text{D}} +73.9$, $[\alpha]^{23}_{577} +77.2$,

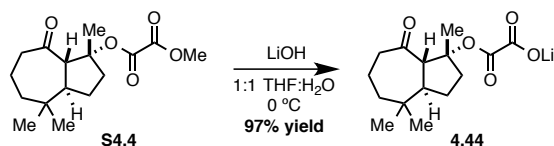
$[\alpha]^{23}_{546} +89.4$, $[\alpha]^{23}_{435} +153$ ($c = 1.0$, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{32}\text{O}_4\text{Na}$ 371.2198; Found 371.2193.



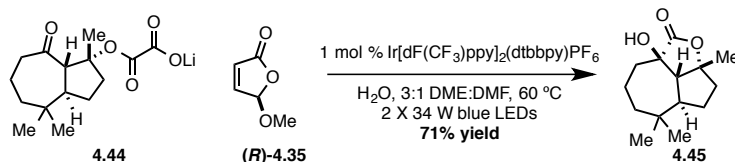
Preparation of (+)-Chelviolene A (4.7) from 4.42: A 1-dram scintillation vial was charged with lactone **4.42** (13 mg, 0.036 mmol, 1.0 equiv), 1:1 1N HCl (aq):THF (1.4 mL, 0.025 M), and a magnetic stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at 40 °C for 12 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 (+)-chelviolene 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 (+)-chelviolene 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} ; $[\alpha]^{22}_{\text{D}} +53$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Na}$ 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), CH₂Cl₂ (7 mL, 0.1 M), DMAP (170 mg, 1.4 mmol, 2.0 equiv), Et₃N (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 H₂O, transferred to a separatory funnel, and extracted with CH₂Cl₂ (3 x 10 mL). Combined organic layers were dried over MgSO₄ 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); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D –104, [α]²³₅₇₇ –113, [α]²³₅₄₆ –131, [α]²³₄₃₅ –247 (*c* = 0.4, CHCl₃); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd for C₁₆H₂₄O₅Na 319.1521; Found 319.1522.



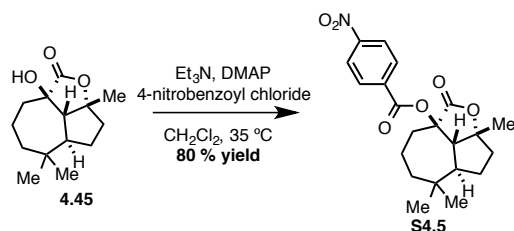
Preparation of lithium oxalate 4.44: A round-bottom flask was charged with **S4.4** (177 mg, 0.597 mmol, 1.0 equiv), 1:1 THF:H₂O (6 mL, 0.1 M), and a magnetic stir bar under ambient atmosphere. After cooling the biphasic mixture to 0 °C, 0.5 N LiOH (aq) (1.1 mL, 0.57 mmol, 0.95 equiv) was added dropwise. 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): ¹H NMR (600 MHz, CD₃OD) 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); ¹³C NMR (151 MHz, CD₃OD) 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; [α]_D²¹ -95.8, [α]_D²¹₅₇₇ -101, [α]_D²¹₅₄₆ -116, [α]_D²¹₄₃₅ -199 (*c* = 0.6, CH₃OH); HRMS (ESI-TOF) *m/z*: [M]⁻ Calcd for C₁₅H₂₁O₅ 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(CF₃)ppy]₂(dtbbpy)PF₆] (2 mg, 0.002 mmol, 0.02 equiv), 3:1

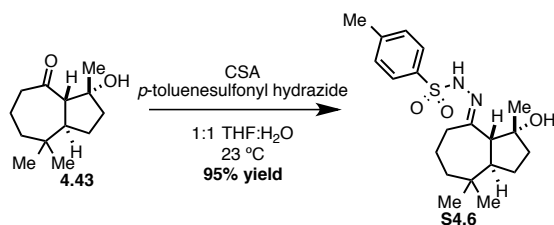
DME:DMF (2 mL, 0.05 M), H₂O (18 μ L, 1.0 mmol, 10 equiv), **(R)**-**4.35** (11 mg, 0.1 mmol, 1.0 equiv), and a magnetic stir bar. The vial was then sealed with a screw cap bearing Teflon septum. The septum of the vial was pierced with a 21 gauge x 1.5" needle that was inserted just barely through the 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 Et₂O (3 x 5 mL). The combined organic layers were dried over MgSO₄ 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 \rightarrow 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); ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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; [α]_D²¹ +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 : $[\text{M}+\text{Na}]^+$
Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3\text{Na}$ 261.1467; Found 261.1466.



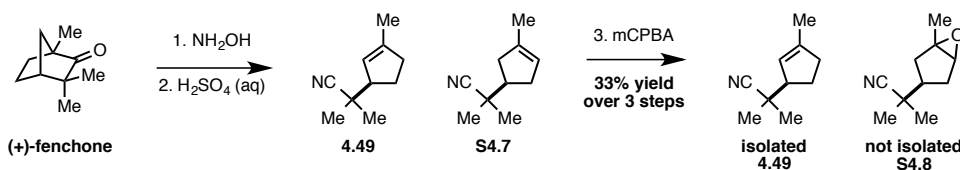
Preparation of benzoate ester S4.5: Preparation of Benzoate Ester S4.5: A 1-dram scintillation flask was charged with **4.45** (17 mg, 0.71 mmol, 1.0 equiv), CH_2Cl_2 (1.4 mL, 0.05 M), DMAP (9 mg, 0.07 mmol, 1.0 equiv), Et_3N (25 μL , 0.18 mmol, 2.5 equiv), 4-nitrobenzoyl chloride (16 mg, 0.085 mmol, 1.2 equiv), and a magnetic stir bar under an atmosphere of argon at rt. The flask was capped and heated to $35\text{ }^\circ\text{C}$ 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} ; $[\alpha]^{22}_{\text{D}} +38.7$, $[\alpha]^{22}_{577} +40.5$, $[\alpha]^{22}_{546} +45.4$, $[\alpha]^{22}_{435} +80.8$ ($c = 0.8$, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_6\text{Na}$ 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:H₂O (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 H₂O (5 mL), and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over Na₂SO₄ 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} ; $[\alpha]_D^{23}$ -79.2, $[\alpha]_{577}^{23}$ -81.1, $[\alpha]_{546}^{23}$ -105, $[\alpha]_{435}^{23}$ -183 ($c = 1.3$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 401.1875; observed 401.1868; mp: 153–156 °C (recrystallized benzene and pentanes via a vapor diffusion method).



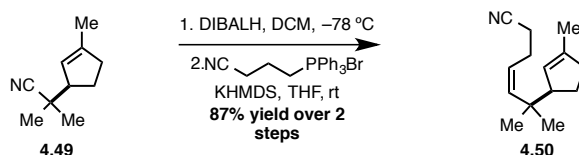
Preparation of nitrile 4.49: The original procedure reported by Kreiser has been modified to completely resolve the mixture of alkene regioisomers **4.49** and **S4.7**.⁵⁰ A round-bottom flask was charged with (+)-fenchone (30.0 g, 197 mmol, 1.0 equiv), hydroxylamine hydrochloride (23.0 g, 335 mmol, 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_2SO_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 °C 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. NaHCO₃ (aq). The organic layer was dried over Na₂SO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) δ 144.9,

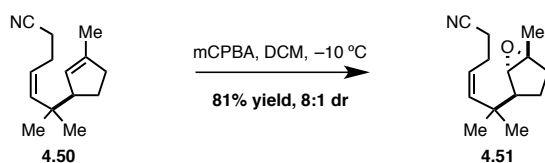
125.2, 123.0, 55.1, 36.7, 36.6, 26.8, 24.8, 24.6, 16.9; IR (thin film) 3046, 2976, 2232, 1659, 988, 826 cm^{-1} ; $[\alpha]^{22}_{\text{D}} +83.9$, $[\alpha]^{22}_{577} +87.8$, $[\alpha]^{22}_{546} +98.8$, $[\alpha]^{22}_{435} +167$, $[\alpha]^{22}_{405} +200$ ($c = 1.0$, CHCl_3); HRMS (GC-Cl/TOF) m/z calculated for $\text{C}_{10}\text{H}_{15}\text{N}$ $[\text{M} + \text{NH}_4]^+$ 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 $-78\text{ }^\circ\text{C}$, and a portion of neat (*i*-Bu)₂AlH (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).

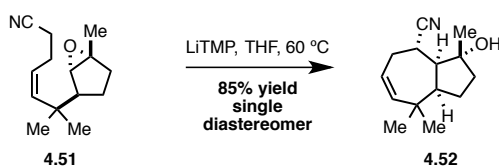
A round-bottom flask was charged with KHMDS (16.6 g, 83.0 mmol, 1.7 equiv), tetrahydrofuran (490 mL, 0.10 M), and a magnetic stir bar under an argon atmosphere. The solution was stirred and cooled to $0\text{ }^\circ\text{C}$, and (3-cyanopropyl)triphenylphosphonium bromide⁷⁷ (34 g, 83 mmol, 1.7 equiv) 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 Et₂O (2 x 200 mL). The combined organic layers were dried over MgSO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D +65.6, [α]²³₅₇₇ +68.0, [α]²³₅₄₆ +78.1, [α]²³₄₃₅ +130, [α]²³₄₀₅ +159 (*c* = 1.0, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₁₄H₂₁N [M + Na]⁺ 226.1572, observed 226.1574.



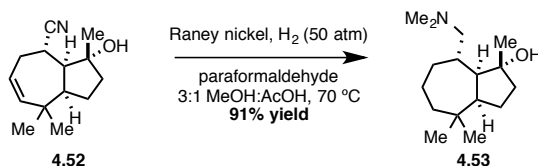
Preparation of epoxide 4.51: A round-bottom flask was charged with **4.50** (9.00 g, 44.3 mmol, 1.0 equiv), dichloromethane (150 mL, 0.3 M), and a magnetic stir bar. The solution was stirred in a large -10 °C brine/ice bath under ambient atmosphere. A portion of 70% *m*-CPBA (11.3 g, 45.6 mmol, 1.03 equiv) was added, and the mixture was stirred for 3 h at -10 °C. The reaction was quenched with sat. NaHCO₃ (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 MgSO₄ 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 KMnO₄); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D -1.6, [α]²³₅₇₇ -1.7, [α]²³₅₄₆ -1.8, [α]²³₄₃₅ -2.4, [α]²³₄₀₅ -2.6 (*c* = 0.85, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₁₄H₂₁NO [M + Na]⁺ 242.1521, observed 242.1511.



Preparation of cyclized product 4.52: A round-bottom flask was charged with 2,2,6,6-tetramethylpiperidine hydrobromide⁷⁸ (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

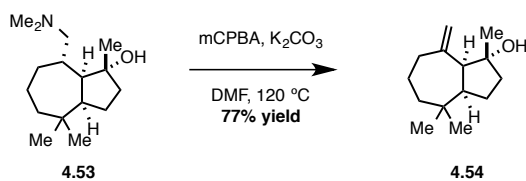
syringe. The solution was maintained at 0 °C for 10 min, then the round-bottom flask was placed into a preheated oil bath and stirred at 60 °C for 2 h. The flask was then removed from the oil bath and cooled to 0 °C with an ice bath. Portions of sat. NH₄Cl (aq) (300 mL) and hexanes (200 mL) were added and the layers were separated. The aqueous phase was extracted with hexanes (2 x 200 mL). The combined organic layers were dried over MgSO₄ 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 KMnO₄); ¹H NMR (500 MHz, CD₃OD) 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); ¹³C NMR (126 MHz, CD₃OD) 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; [α]²³_D +25.9, [α]²³₅₇₇ +27.3, [α]²³₅₄₆ +29.7, [α]²³₄₃₅ +49.0, [α]²³₄₀₅ +59.2 (*c* = 1.2, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₁₄H₂₁NO [M + Na]⁺ 242.1521, observed 242.1510.



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,

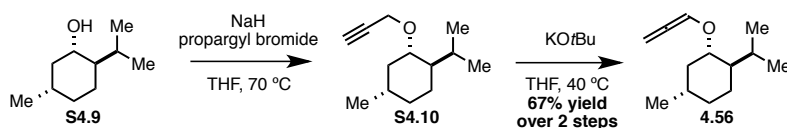
200 wt %), 3:1 methanol:acetic acid (46 mL, 0.10 M), and a magnetic stir bar under ambient atmosphere. The round-bottom flask was placed inside a Parr bomb, and the bomb was evacuated then pressurized to 50 atm with H₂. The bomb was placed on a stir plate, and the solution inside was vigorously stirred 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. K₂CO₃ (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 Na₂SO₄ 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 KMnO₄); ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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; [α]²¹_D -29.3, [α]²¹₅₇₇ -

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.



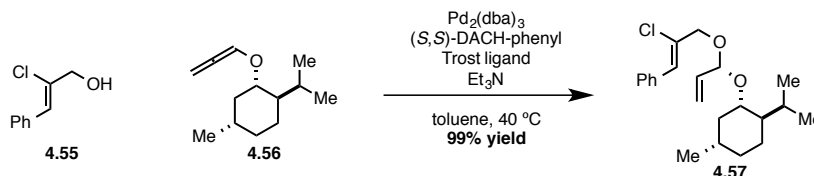
Preparation of tertiary alcohol 4.54: A round-bottom flask was charged with **4.53** (1.00 g, 3.95 mmol, 1.0 equiv), K_2CO_3 (815 mg, 5.92 mmol, 1.5 equiv), DMF (40 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. A portion of 70% *m*-CPBA (972 mg, 3.95 mmol, 1.0 equiv) was added, and the 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} ; $[\alpha]^{23}_D +70.5$, $[\alpha]^{23}_{577} +73.1$, $[\alpha]^{23}_{546} +82.6$, $[\alpha]^{23}_{435} +147$,

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



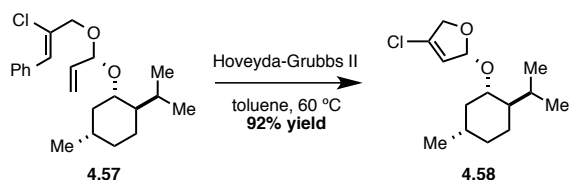
Preparation of allene 4.56: The procedure for the preparation of allene **4.56** was a slight modification of a literature procedure.⁷⁹ A round-bottom flask was charged with (*D*)-menthol (**S4.9**) (20.0 g, 128 mmol), tetrahydrofuran (210 mL, 0.6 M), and a magnetic stir bar under an atmosphere of argon. 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 SiO₂, 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



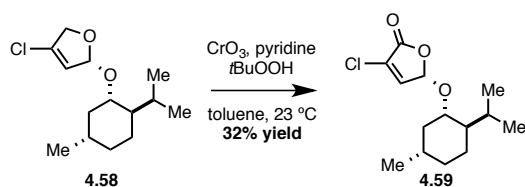
Preparation of acetal 4.57: A round-bottom flask was charged with Pd₂(dba)₃ (184 mg, 0.201 mmol, 0.015 equiv), (*S,S*)-DACH-phenyl Trost ligand (278 mg, 0.402 mmol, 0.03 equiv), toluene (27 mL, 0.5 M), Et₃N (2.8 mL, 20 mmol, 1.5 equiv), and a magnetic stir bar under an argon atmosphere. Next, allene **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 \rightarrow 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{22}_{\text{D}} +95$, $[\alpha]^{22}_{577} +100$, $[\alpha]^{22}_{546} +113$, $[\alpha]^{22}_{435} +189$ ($c = 1.0$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{22}\text{H}_{31}\text{ClO}_2$ $[\text{M} + \text{Na}]^+ 385.1910$, observed 385.1897.



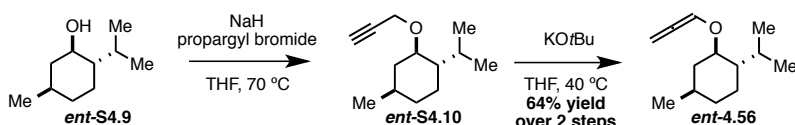
Preparation of dihydrofuran 4.58: A round-bottom flask was charged with **4.57** (4.8 g, 13.2 mmol, 1.0 equiv), toluene (66 mL, 0.2 M), and a magnetic stir bar under an argon

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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{23}_{\text{D}} +117$, $[\alpha]^{23}_{577} +120$, $[\alpha]^{23}_{546} +135$, $[\alpha]^{23}_{435} +213$ ($c = 1.0$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{14}\text{H}_{23}\text{ClO}_2$ $[\text{M} + \text{H}]^+$ 259.1465, observed 259.1472.



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 μ L, 3.2 mmol, 0.4 equiv), CrO₃ (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 equiv) 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 μ L, 3.2 mmol, 0.4 equiv), CrO₃ (160 mg, 1.61 mmol, 0.2 equiv), and a 5 M solution of *t*-BuO₂H in *n*-decane (11 mL, 56 mmol, 7.0 equiv) 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 SiO₂, 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 \rightarrow 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, C₆D₆) 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); ¹³C NMR (126 MHz, C₆D₆) δ 165.4, 142.9, 129.1, 98.3, 79.2, 47.3, 40.7,

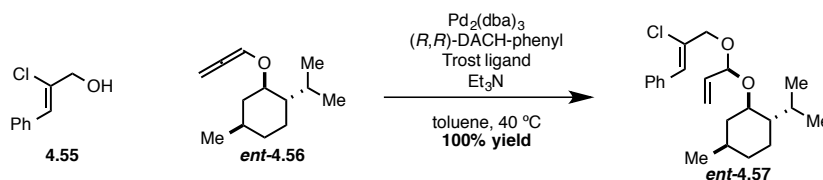
34.6, 31.8, 25.9, 23.6, 22.7, 21.3, 16.2; IR (thin film) 2957, 2922, 2864, 1770, 1343 cm^{-1} ; $[\alpha]^{23}_{\text{D}} +139$, $[\alpha]^{23}_{577} +144$, $[\alpha]^{23}_{46} +163$, $[\alpha]^{23}_{435} +267$ ($c = 1.0$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{14}\text{H}_{21}\text{ClO}_3$ $[\text{M} + \text{Na}]^+$ 295.1077 observed 295.1074; mp: 70–71 $^\circ\text{C}$ (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 $^\circ\text{C}$ 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*

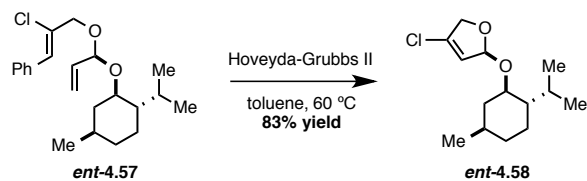
silica gel column height. This does not affect the overall yield as it is usually completely removed during the second silica gel filtration following alkyne isomerization.

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, KOtBu (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 SiO₂, 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



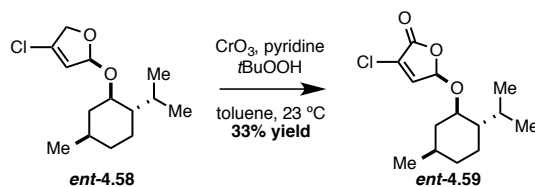
Preparation of acetal **ent-4.57:** A round-bottom flask was charged with Pd₂(dba)₃ (370 mg, 0.40 mmol, 0.015 equiv), (*R,R*)-DACH-phenyl Trost ligand (560 mg, 0.40 mmol, 0.03 equiv), toluene (54 mL, 0.5 M), Et₃N (5.7 mL, 40 mmol, 1.5 equiv), and a magnetic stir bar under an argon atmosphere. Next, allene **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 \rightarrow 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{22}_{\text{D}}$ -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 $\text{C}_{22}\text{H}_{31}\text{ClO}_2$ $[\text{M} + \text{Na}]^+$ 385.1910, observed 385.1903.



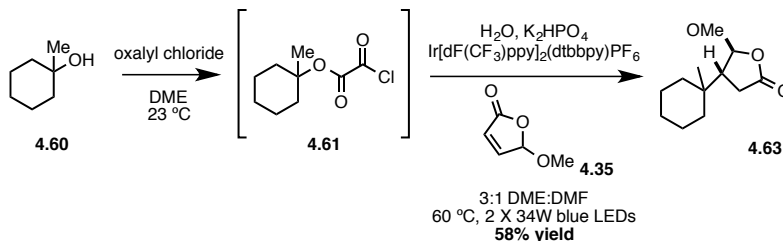
Preparation of dihydrofuran *ent-4.58*: A round-bottom flask was charged with *ent-4.57* (9.8 g, 27 mmol, 1.0 equiv), toluene (135 mL, 0.2 M), and a magnetic stir bar under an argon atmosphere. A solution of Hoveyda-Grubbs 2nd generation catalyst (840 mg, 1.3 mmol, 0.05 equiv) in toluene (135 mL, 0.2 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{22}_{\text{D}} -118$, $[\alpha]^{22}_{577} -124$, $[\alpha]^{22}_{546} -139$, $[\alpha]^{22}_{435} -217$ ($c = 1.4$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{14}\text{H}_{23}\text{ClO}_2$ $[\text{M} + \text{Na}]^+$ 281.1284, observed 281.1277.



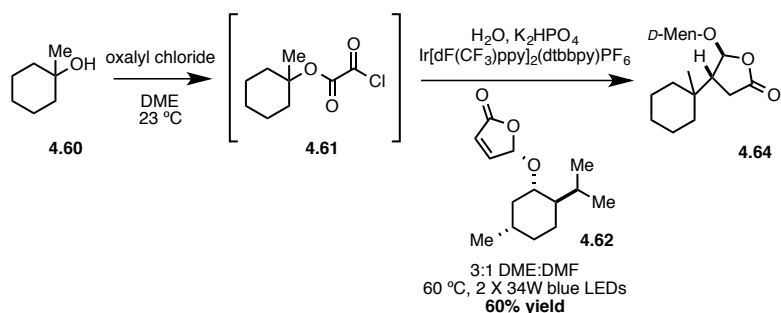
Preparation of butenolide *ent-4.59*: A round-bottom flask was charged with **ent-4.58** (5.8 g, 22.4 mmol, 1.0 equiv), benzene (225 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to $0\text{ }^\circ\text{C}$. Next, pyridine (0.7 mL, 9.0 mmol, 0.4 equiv), CrO_3 (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 equiv) 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 $0\text{ }^\circ\text{C}$ 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 equiv) 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 \rightarrow 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 $-20\text{ }^\circ\text{C}$ to yield **ent-4.59** as colorless large prisms (2.0 g, 7.3 mmol, 33% yield after 3 rounds of crystallization). ^1H 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} ; $[\alpha]_{\text{D}}^{23} -101$, $[\alpha]_{577}^{23} -108$, $[\alpha]_{546}^{23} -124$, $[\alpha]_{435}^{23} -212$ ($c = 0.5$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{14}\text{H}_{21}\text{ClO}_3$ $[\text{M} + \text{Na}]^+$ 295.1077 observed 295.1066; mp: 68–70 °C (recrystallized from hot pentanes).

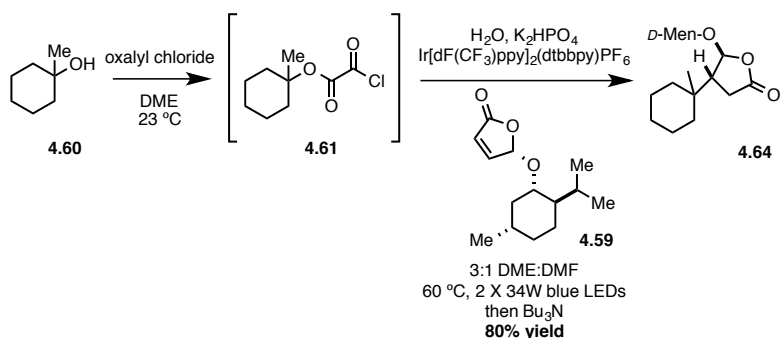


Preparation of *rac*-lactone 4.63: A 1-dram scintillation vial was charged with **4.60** (34 mg, 0.3 mmol, 1.0 equiv), DME (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C and oxalyl chloride (26 μL , 0.3 mmol, 1.0 equiv) was added dropwise. The needle 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 $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 Et₂O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ 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 KMnO₄). Spectral data match those previously reported.²⁰

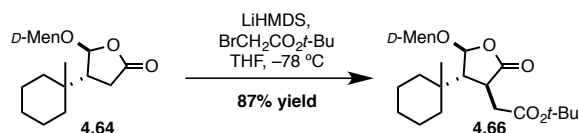


Preparation of lactone 4.64: Using an identical procedure, alcohol **4.60** (34 mg, 0.3 mmol, 1.0 equiv), and butenolide **4.62** (72 mg, 0.3 mmol, 1.0 equiv) were coupled and the product was purified by flash column chromatography on silica gel using 2:98 ethyl acetate:hexanes as eluent to yield product **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). ^1H 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} ; $[\alpha]^{22}_{\text{D}} +111$, $[\alpha]^{22}_{577} +112$, $[\alpha]^{22}_{546} +125$, $[\alpha]^{22}_{435} +199$ ($c = 0.3, \text{CHCl}_3$); HRMS (ESI/TOF) m/z calculated for $\text{C}_{21}\text{H}_{36}\text{O}_3$ $[\text{M} + \text{Na}]^+$ 359.2562, observed 359.2574.



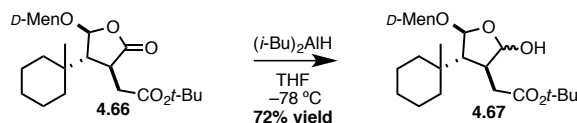
Preparation of lactone 4.64: A 1-dram scintillation vial was charged with **4.60** (34 mg, 0.3 mmol, 1.0 equiv), DME (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, oxalyl chloride (26 μL , 0.3 mmol, 1.0 equiv) was added dropwise. Needle connected 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 $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 Bu₃N (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 Et₂O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ 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).



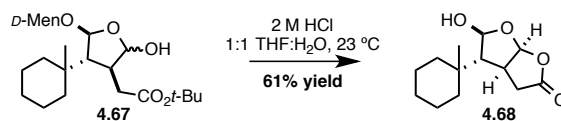
Preparation of ester 4.66: A round-bottom flask was charged with lactone **4.64** (58 mg, 0.17 mmol, 1.0 equiv), tetrahydrofuran (1.7 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to -78 °C and a 1 M solution of LiHMDS in tetrahydrofuran (210 μL, 0.21 mmol, 1.2 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. NH₄Cl (aq) (5 mL). The resulting mixture was allowed to warm to rt and transferred to a separatory funnel and extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄ 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{46}\text{O}_5\text{Na}$ 473.3243; Found 473.3250.

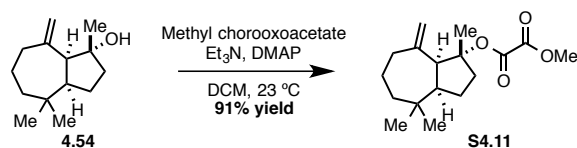


Preparation of lactol 4.67: A round-bottom flask was charged with **4.66** (64 mg, 0.14 mmol, 1.0 equiv), THF (1.2 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. After 30 min at -78 °C, TLC analysis of the reaction (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate) indicated 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

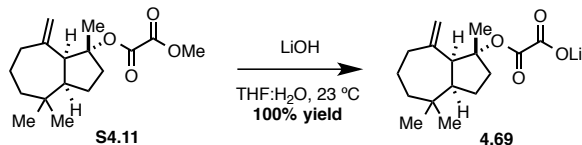
material and the reaction was quenched by addition of 100 μ L of MeOH, followed by the addition of saturated solution of Rochelle's salt (aq) (5 mL) at -78 $^{\circ}$ C. The reaction was allowed to warm to rt and stirred at rt for 30 min. Biphasic mixture was transferred to a separatory funnel and extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over Na₂SO₄ 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, C₆D₆) 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); ¹³C NMR (151 MHz, C₆D₆) 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} ; $[\alpha]^{21}_{\text{D}} +101$, $[\alpha]^{21}_{577} +101$, $[\alpha]^{21}_{546} +112$, $[\alpha]^{21}_{435} +159$ ($c = 0.15$, CHCl₃); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for C₂₇H₄₈O₅Na 475.3399; Found 475.3395.



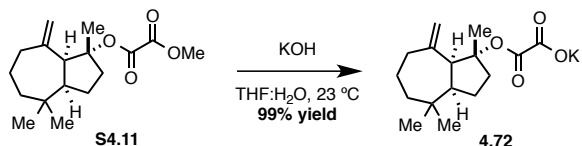
Preparation of dioxabicyclo[3.3.0]octan-3-one 4.68: A 2-dram scintillation vial was charged with lactol **4.67** (34 mg, 0.075 mmol, 1.0 equiv), 1:1 4 M HCl (aq):THF (3 mL, 0.025 M), and a magnetic stir bar under ambient atmosphere. The resulting biphasic mixture was stirred vigorously at rt for 30 min. The reaction mixture was transferred to a separatory funnel and extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over Na₂SO₄ 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, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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; [α]²²_D +27.2, [α]²²₅₇₇ +27.8, [α]²²₅₄₆ +30.2, [α]²²₄₃₅ +47.9 (*c* = 1.1, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₁₃H₂₀O₄ [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 atmosphere. Next, Et₃N (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. NH₄Cl (aq) (15 mL). The resulting biphasic mixture was transferred to a separatory funnel and extracted with CH₂Cl₂ (3 x 25 mL). Combined organic layers were dried over MgSO₄ 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D +11.5, [α]²³₅₇₇ +13.6, [α]²³₅₄₆ +14.4, [α]²³₄₃₅ +29.1 (*c* = 1.0, CHCl₃); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₆O₄Na 317.1729; Found 317.1732.

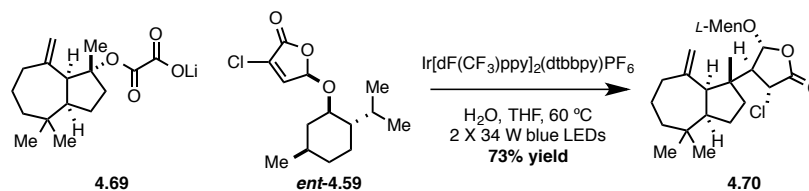


Preparation of lithium oxalate 4.69: A round-bottom flask was charged with **S4.11** (700 mg, 2.38 mmol, 1.0 equiv), 1:1 THF:H₂O (4.8 mL, 0.5 M), and a stir bar under ambient atmosphere. The resulting biphasic mixture was cooled to 0 °C. Next, 0.5N LiOH (aq) (4.8 mL, 1.0 equiv) was added dropwise. The 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); ¹H NMR (500 MHz, CD₃OD) 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); ¹³C NMR (126 MHz, CD₃OD) 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; [α]_D²³ +20.9, [α]₅₇₇²³ +22.7, [α]₅₄₆²³ +21.4, [α]₄₃₅²³ +40.4 (*c* = 0.6, MeOH); HRMS (ESI-TOF) *m/z*: [M]⁻ Calcd for C₁₆H₂₃O₄ 279.1596; Found 279.1595.



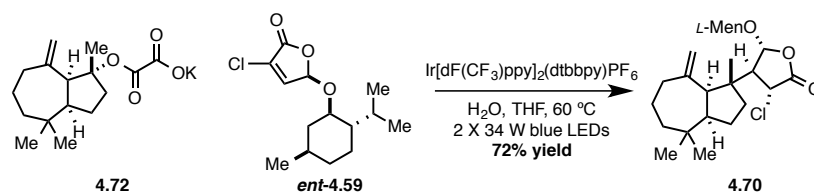
Preparation of potassium oxalate 4.72: A round-bottom flask was charged with **S4.11** (81 mg, 0.28 mmol, 1.0 equiv), 1:1 THF:H₂O (1.4 mL, 0.2 M), and a stir bar under ambient

atmosphere. The resulting biphasic mixture was cooled to 0 °C. Next, 0.85N KOH (aq) (320 μ L, 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); ^1H 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} ; $[\alpha]^{23}_{\text{D}}$ +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 : $[\text{M}]^-$ Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_4$ 279.1596; Found 279.1598.



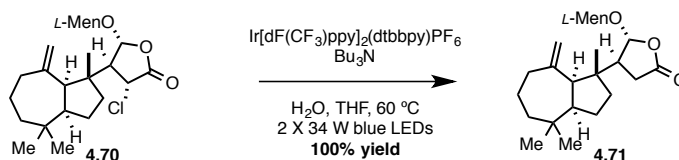
Preparation of lactone 4.70 from 4.69: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.69** (86 mg, 0.30 mmol, 1.0 equiv), **ent-4.59** (82 mg, 0.30 mmol, 1.0 equiv), $\text{Ir[dF(CF}_3\text{)ppy]}_2\text{(dtbbpy)PF}_6$ (7 mg, 0.006 mmol, 0.02 equiv), tetrahydrofuran (500 μ L, 0.6 M), H_2O (27 μ L, 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 Et₂O (1 mL) and filtered over MgSO₄. 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, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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; [α]²³_D -52.0, [α]²³₅₇₇ -54.3, [α]²³₅₄₆ -65.8, [α]²³₄₃₅ -104 (*c* = 0.6, CHCl₃); HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd for C₂₈H₄₅ClO₃Na 487.2955; Found 487.2971.



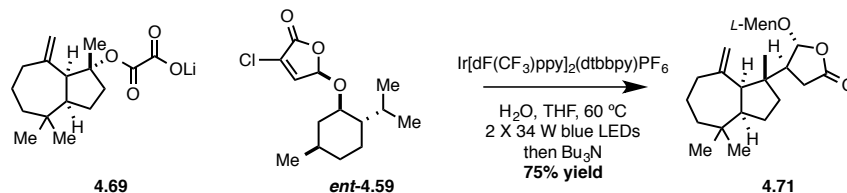
Preparation of lactone 4.70 from 4.72: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.72** (63 mg, 0.20 mmol, 1.0 equiv), *ent*-**4.59** (55 mg, 0.20 mmol, 1.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (5 mg, 0.004 mmol, 0.02 equiv), tetrahydrofuran (330 μL, 0.6 M), H₂O (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 Et₂O (1 mL) and filtered over MgSO₄. 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).



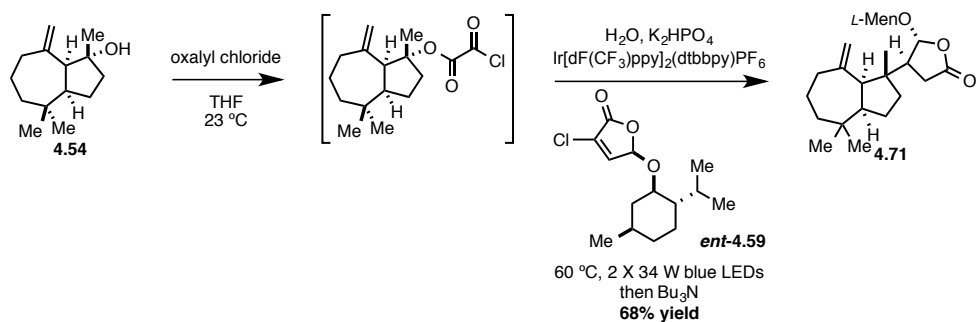
Preparation of lactone 4.71 from 4.70: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.70** (86 mg, 0.18 mmol, 1.0 equiv), Bu_3N (44 μL , 1.8 mmol, 10 equiv), $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (4 mg, 0.004 mmol, 0.02 equiv), 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 $60\text{ }^\circ\text{C}$ and the air inside the box to $40\text{--}45\text{ }^\circ\text{C}$ 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), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]_D²³ -47.5, [α]₅₇₇²³ -49.3, [α]₅₄₆²³ -56.5, [α]₄₃₅²³ -87.7 (*c* = 1.1, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₂₈H₄₆O₃ [M + Na]⁺ 453.3345, observed 453.3352.



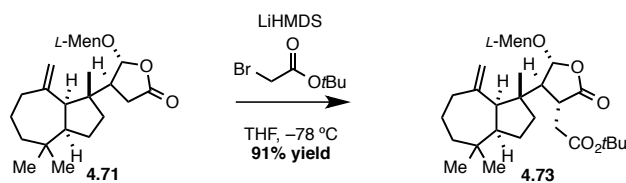
Preparation of lactone 4.71 from 4.69: On the bench under ambient atmosphere, 1-dram scintillation vial was charged with **4.69** (86 mg, 0.30 mmol, 1.0 equiv), **ent-4.59** (82 mg, 0.30 mmol, 1.0 equiv), Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (7 mg, 0.006 mmol, 0.02 equiv), tetrahydrofuran (500 μL, 0.6 M), H₂O (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 Bu₃N (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 Et₂O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ 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).



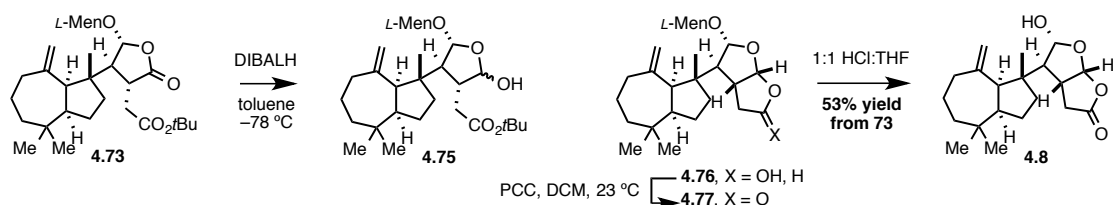
Preparation of lactone 4.71 from 4.54: A 1-dram scintillation vial was charged with **4.54** (62 mg, 0.3 mmol, 1.0 equiv), tetrahydrofuran (0.5 mL, 0.6 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C. Next, oxalyl chloride (26 μL , 0.3 mmol, 1.0 equiv) was added 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 $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (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 Bu₃N (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 Et₂O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D -47.5, [α]²³₅₇₇ -49.3, [α]²³₅₄₆ -56.5, [α]²³₄₃₅ -87.7 (*c* = 1.1, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₂₈H₄₆O₃ [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 $-78\text{ }^\circ\text{C}$. 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 $-78\text{ }^\circ\text{C}$, *tert*-butyl bromoacetate (220 μL , 1.5 mmol, 1.5 equiv) was added dropwise. After 1 h at $-78\text{ }^\circ\text{C}$, 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); ^1H 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} ; $[\alpha]^{23}_{\text{D}} -41.9$, $[\alpha]^{23}_{577} -45.2$, $[\alpha]^{23}_{546} -52.6$, $[\alpha]^{23}_{435} -83.9$ ($c = 0.9$, CHCl_3); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{56}\text{O}_5\text{Na}$ 567.4025; Found 567.4030.



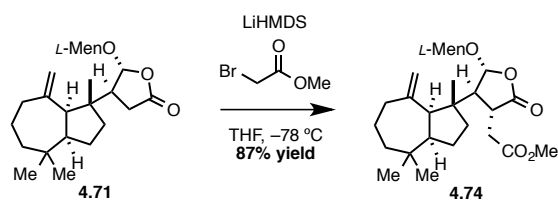
Preparation of (+)-cheloviolene B (4.8) from 4.73: A round-bottom flask was charged with **4.73** (278 mg, 0.51 mmol, 1.0 equiv), toluene (5.1 mL, 0.1 M), and a stir bar under an argon atmosphere. The solution was cooled to to $-78\text{ }^\circ\text{C}$. Next, a 1M solution of DIBALH in toluene (610 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 $-78\text{ }^\circ\text{C}$. 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 gel⁸⁰ 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 ^1H 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** as 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 ^1H 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 ^1H 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)].

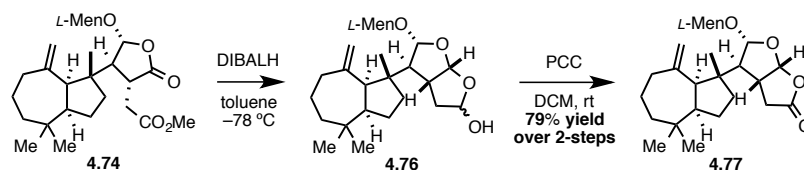
A 20 mL scintillation vial was charged with crude lactol epimers **4.75** (155 mg, 0.28 mmol, 1.0 equiv), crude bicyclic lactone **4.77** (70 mg, 0.15 mmol, 1.0 equiv), 1:1 4N HCl (aq):THF (17 mL, 0.025 M), and a stir bar under ambient atmosphere. The resulting

biphasic mixture was stirred vigorously at rt for 24 h. The reaction mixture was transferred to a separatory funnel and extracted with Et₂O (3 x 25 mL). Combined organic layers were dried over MgSO₄ 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 ¹³C NMR data in (CD₃)₂CO matched that reported for the natural product.^{8b} ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²¹_D +26.6, [α]²¹₅₇₇ +29.4, [α]²¹₅₄₆ +33.4, [α]²¹₄₃₅ +60.2, [α]²¹₄₀₅ +73.7 (*c* = 0.7, CHCl₃); HRMS (ESI/TOF) *m/z* calculated for C₂₀H₃₀O₄ [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 $-78\text{ }^\circ\text{C}$. 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 $-78\text{ }^\circ\text{C}$, methyl bromoacetate (33 μL , 3.5 mmol, 1.5 equiv) was added dropwise. After 1 h at $-78\text{ }^\circ\text{C}$, 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); ^1H 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} ;

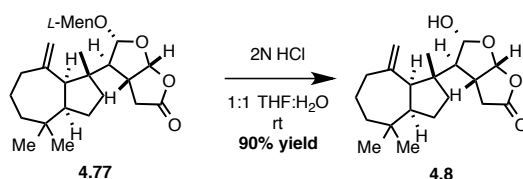
$[\alpha]^{21}_D -56.1$, $[\alpha]^{21}_{577} -60.1$, $[\alpha]^{21}_{546} -69.7$, $[\alpha]^{21}_{435} -112$ ($c = 0.18$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{31}\text{H}_{50}\text{O}_5$ $[\text{M} + \text{Na}]^+$ 525.3556, observed 525.3560.



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 bicyclic 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)].

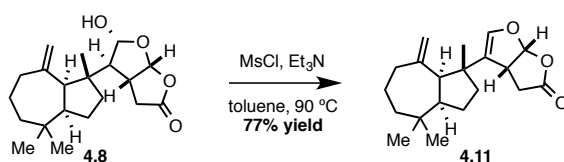
A 2-dram scintillation vial was charged with a crude mixture of bicyclic lactol epimers **4.76**, dichloromethane (1.6 mL, 0.1 M), and a magnetic stir bar under ambient

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 \rightarrow 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); $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{22}_{\text{D}} -92.7$, $[\alpha]^{22}_{577} -97.4$, $[\alpha]^{22}_{546} -110$, $[\alpha]^{22}_{435} -176$ ($c = 0.8$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{30}\text{H}_{48}\text{O}_4$ $[\text{M} + \text{Na}]^+$ 495.3450, observed 495.3457.



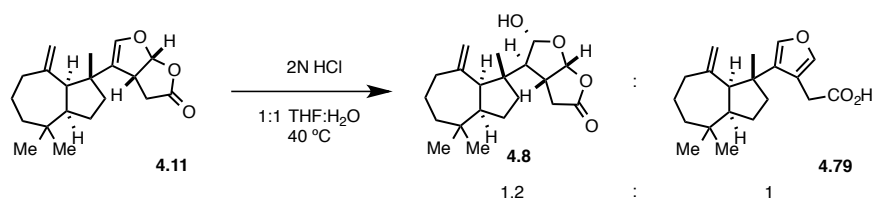
Preparation of (+)-cheloviolene B (4.8) from 4.77: A 20 mL scintillation vial was charged with lactone **4.77** (69 mg, 0.15 mmol, 1.0 equiv), 1:1 4 M HCl (aq):THF (5.8 mL,

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 Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄ 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).



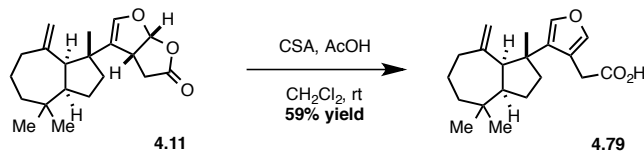
Preparation of (+)-dendrillolide C (4.11): A round-bottom flask was charged with **4.8** (40 mg, 0.12 mmol, 1.0 equiv), toluene (6 mL, 0.025 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to 0 °C, and Et₃N (83 μL, 0.60 mmol, 5.0 equiv) and MsCl (23 μL, 0.30 mmol, 2.5 equiv) 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 H₂O (5 mL). The biphasic mixture was transferred to a separatory funnel and extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄ 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 \rightarrow 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 ^1H 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; ^1H 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} ; $[\alpha]^{22}_{\text{D}} +133$ (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 $\text{C}_{20}\text{H}_{38}\text{O}_3$ $[\text{M} + \text{Na}]^+$ 339.1936, observed 339.1924.



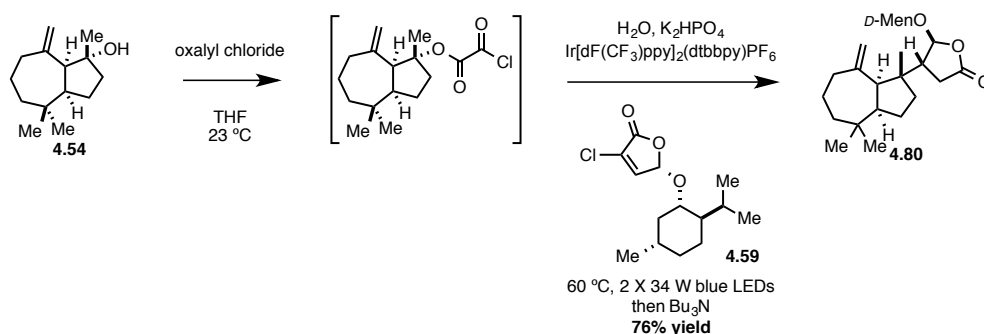
Acid-catalyzed hydration of (+)-dendrillolide C (4.11**):** A 1-dram scintillation vial was charged with **4.11** (9 mg, 0.028 mmol, 1 equiv), 1:1 4 M HCl (aq):THF (0.6 mL, 0.025 M), and a magnetic stir bar. The resulting heterogeneous mixture was stirred vigorously at 40

°C for 18 h. The reaction mixture was diluted with H₂O (1 mL) and extracted with Et₂O (3 x 2 mL). Organic layers were dried over MgSO₄ and concentrated by use of a rotary evaporator. Integration of ¹H NMR spectrum [CDCl₃, 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 μ L, 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. NaHCO₃ (aq) (1 mL), H₂O (1 mL), 4N HCl (aq) (1 mL), and brine (1 mL). Organic layer was dried over MgSO₄ and concentrated by use of a rotary evaporator. The residue was purified by flash column chromatography on silica gel using 0:100 methanol:dichloromethane \rightarrow 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, CDCl₃) 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* =

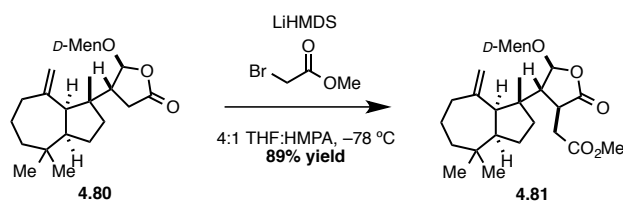
12.8, 6.0 Hz, 1H), 2.01 (q, $J = 9.5$ Hz, 1H), 1.89–1.56 (m, 7H), 1.45–1.32 (m, 2H), 1.27–1.17 (m, 1H), 1.10 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 176.2, 153.0, 143.4, 139.3, 133.5, 115.4, 114.8, 57.6, 51.4, 46.2, 38.6, 37.8, 37.0, 36.2, 33.8, 30.5, 29.1, 26.4, 26.0, 24.9; IR (thin film) 3408, 2963, 2927, 1714, 1452 cm^{-1} ; $[\alpha]^{22}_{\text{D}} +1.84$, $[\alpha]^{22}_{577} +1.98$, $[\alpha]^{22}_{546} +2.89$, $[\alpha]^{22}_{435} +6.38$ ($c = 0.5$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{20}\text{H}_{28}\text{O}_3$ $[\text{M} - \text{H}]^-$ 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 $[\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6]$ (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

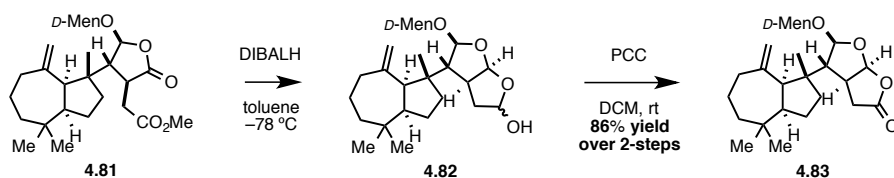
with the tip of the needle kept above the fluid level inside the vial. A separate 22 gauge x 3" needle attached to a flow of argon was also pierced through the septum, and the tip of the needle was pushed to the bottom of the vial and submersed in the fluid. The reaction mixture was degassed by sparging 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*-Bu₃N (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 Et₂O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ 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, CDCl₃) 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} ; $[\alpha]^{23}_{\text{D}} +137$, $[\alpha]^{23}_{577} +143$, $[\alpha]^{23}_{546} +162$, $[\alpha]^{23}_{435} +269$ ($c = 1.0$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{28}\text{H}_{46}\text{O}_3$ $[\text{M} + \text{Na}]^+$ 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_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 **4.81** as a clear oil (54 mg, 0.11 mmol, 89% yield): $R_f = 0.35$ (10:90 ethyl acetate:hexanes, stained with *p*-anisaldehyde); ^1H 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} ; $[\alpha]_{\text{D}}^{21} +102$, $[\alpha]_{577}^{21} +106$, $[\alpha]_{546}^{21} +120$, $[\alpha]_{435}^{21} +196$ ($c = 0.7$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{31}\text{H}_{50}\text{O}_5$ $[\text{M} + \text{Na}]^+$ 525.3556, observed 525.3568.

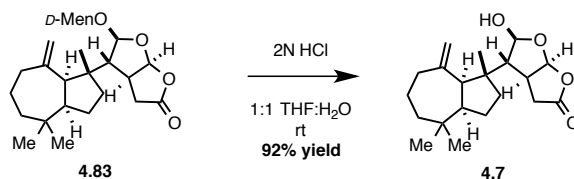


Preparation of lactone 4.83: A round-bottom flask was charged with **4.81** (54 mg, 0.11 mmol, 1.0 equiv), toluene (1.1 mL, 0.1 M), and a magnetic stir bar under an argon atmosphere. The solution was cooled to to $-78\text{ }^\circ\text{C}$ and a 1 M solution of DIBALH in toluene (240 μL , 0.24 mmol, 2.2 equiv) was added dropwise. After 1 h at $-78\text{ }^\circ\text{C}$, 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 $-78\text{ }^\circ\text{C}$. 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 bicyclic lactol epimers **4.82** [$R_f = 0.13$ (10:90 ethyl acetate:hexanes, stained with ceric ammonium molybdate)]; diagnostic ^1H NMR shifts (500 MHz, C_6D_6): major: δ 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)].

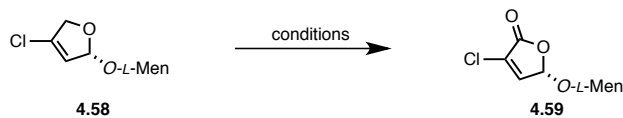
A 2-dram scintillation vial was charged with a crude mixture of bicyclic lactol epimers **4.82**, dichloromethane (1.6 mL, 0.1 M), and a magnetic stir bar under ambient atmosphere. Next, PCC (47 mg, 0.22 mmol, 2.0 equiv) was added in one portion at rt. The heterogeneous reaction mixture was stirred vigorously 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 \rightarrow 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); ^1H 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} ; $[\alpha]^{22}_{\text{D}} +140$,

$[\alpha]^{22}_{577} +146$, $[\alpha]^{22}_{546} +166$, $[\alpha]^{22}_{435} +273$ ($c = 0.9$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{30}\text{H}_{48}\text{O}_4$ $[\text{M} + \text{Na}]^+$ 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 Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄ 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**.



conditions	result ^a
Fe(acac) ₃ (10 mol %), <i>t</i> BuOOH (7.5 equiv) benzene (0.025 M), 80 °C, 18 h	0% 4.59
SeO ₂ (3 equiv), <i>t</i> BuOOH (5 equiv) CH ₂ Cl ₂ (0.2 M), 23 °C, 18 h	0% 4.59
Cr(CO) ₆ (50 mol %), <i>t</i> BuOOH (3 equiv) CH ₃ CN (0.2 M), 80 °C, 1 h	0% 4.59
<i>t</i> 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) <i>t</i> 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), <i>t</i> BuOOH (7 equiv) DBU (1.5 equiv) CH ₃ CN (0.05 M), 23 °C, 18 h	39% 4.58 12% 4.59
<i>t</i> BuOOH (5 equiv) PDC (10 mol %) toluene (0.5 M), 23 °C, 18 h	13% 4.59
CuCl (1.1 equiv), <i>t</i> 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

^aDetermined by ¹H 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.

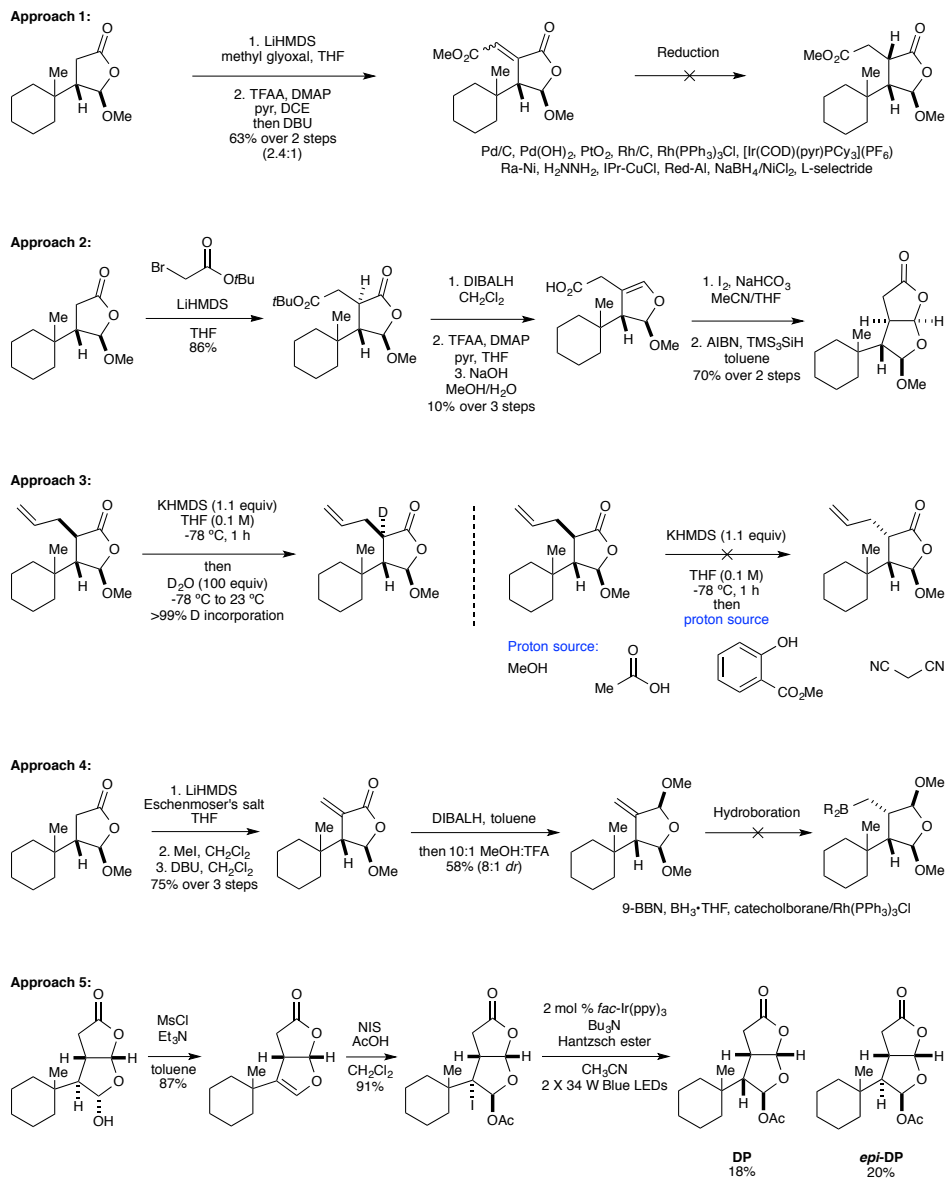
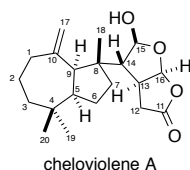
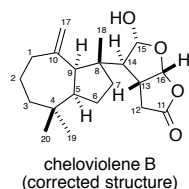


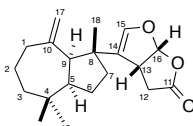
Table S4.2. Comparison table for synthetic and natural cheloviolene A.**¹H (500 MHz) and ¹³C (126 MHz) Data Solvent: CDCl₃**

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 chelviolene B.**¹H (500 MHz) and ¹³C (126 MHz) Data Solvent: (CD₃)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

¹H (600 MHz) and ¹³C (151 MHz) Data Solvent: CCl₄

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

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

5.1 Introduction

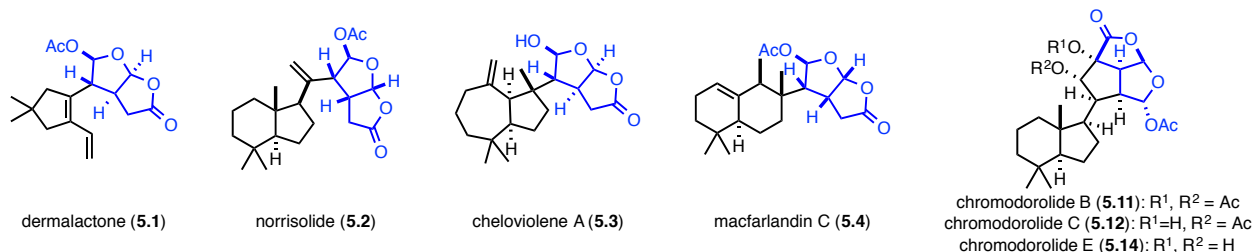
Convergent strategies where advanced fragments of a target molecule are prepared in parallel and joined together at the latest possible stage in a synthesis are nearly always more efficient than linear strategies.¹ A corollary of this fact is the importance of reactions that are capable of combining 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

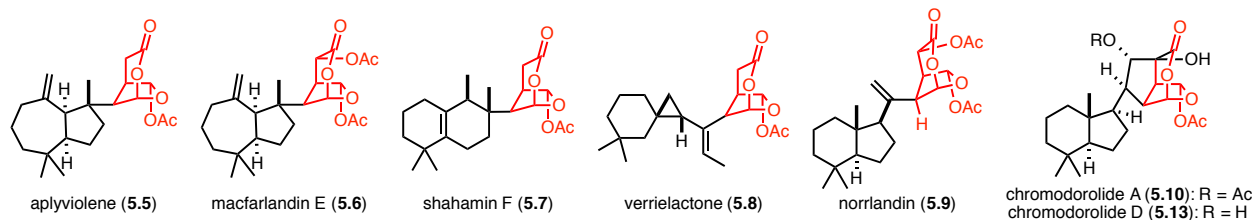
macfarladin C (**5.4**),¹¹ or a 2,7-dioxabicyclo[3.2.1]octan-3-one fragment as found in aplyviolene (**5.5**),¹² macfarlandin E (**5.6**),¹¹ shahamin F (**5.7**),¹³ verriellactone (**5.8**),¹⁴ and norrlandin (**5.9**).¹⁵ In chromodorolides A–E (**5.10–5.14**),^{16–18} these bicyclic frameworks are appended 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.



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



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 ¹H and ¹³C 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

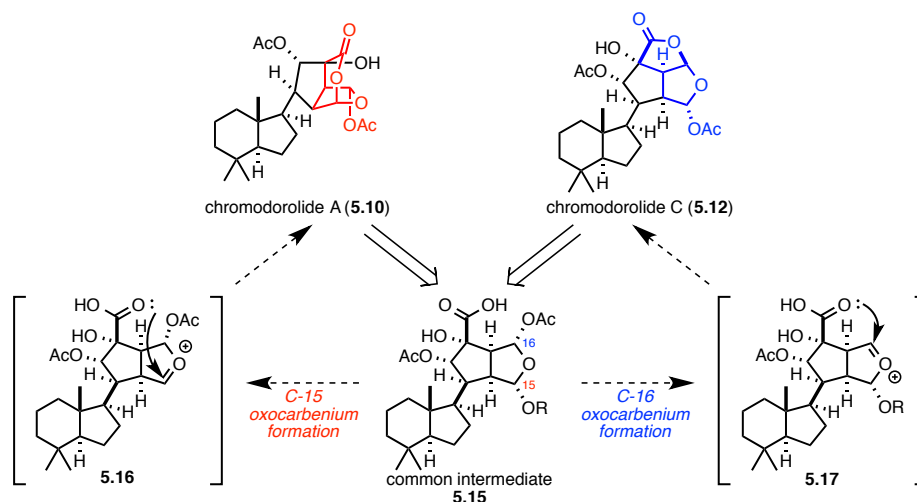
Modest *in vitro* antitumor, nematocidal and antimicrobial activities have been reported for various chromodorolides.^{16b,17,18a} Because of their structural relationship to molecules such as norrisolide (**5.2**), cheloviolene A (**5.3**) and macfarlandin E (**5.6**),^{20,21} which have pronounced 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**.

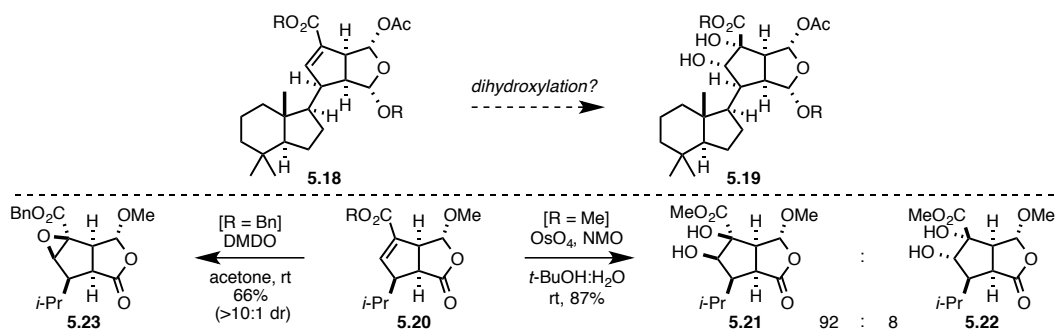
Scheme 5.1. Common tetracyclic intermediate to access both bridged and fused chromodorolides.



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 allenolate 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 dihydroxylation of *cis*-bicyclo[3.3.0]octenes, and a more general discussion of this issue has been published.²²

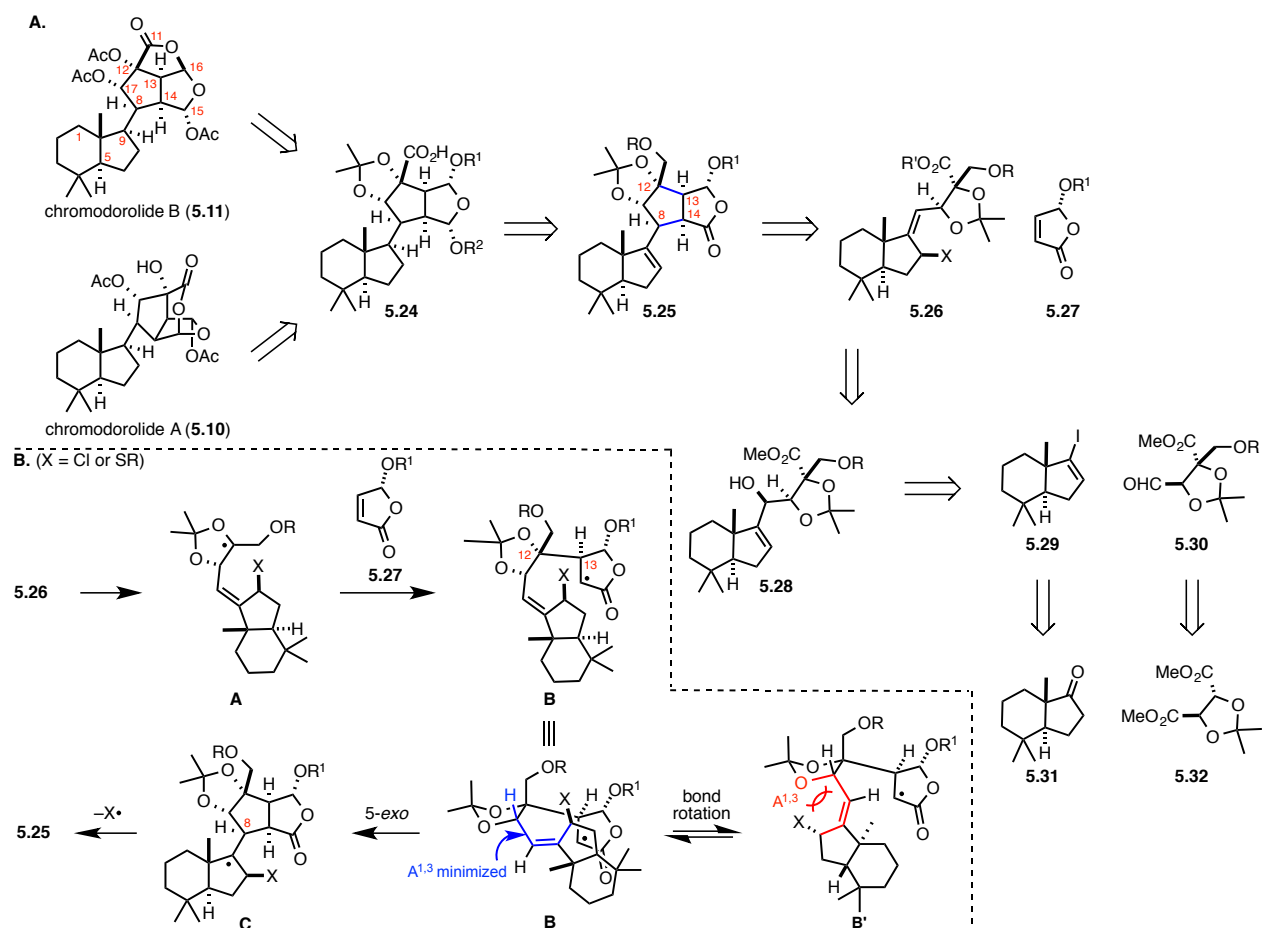
Scheme 5.2. Early attempts to introduce oxygenation via late-stage dihydroxylation or epoxidation of enoate **5.20**.



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**.

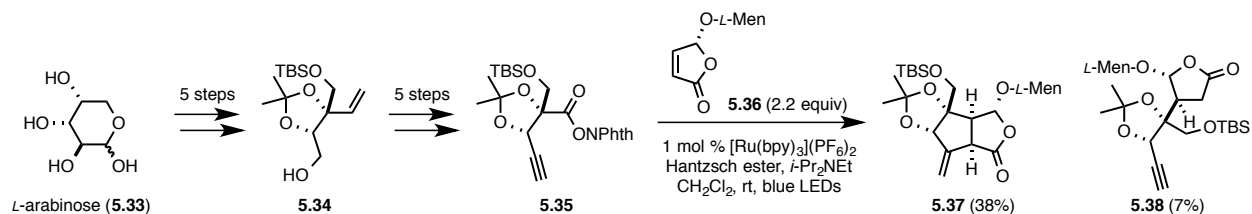


In the projected cascade sequence,⁵ chiral acetonide (2,2-dimethyl-1,3-dioxolane) radical **A**, formed from oxidative decarboxylation of precursor **5.26**, would couple with

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 modification³⁸ 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**. ¹H 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**.

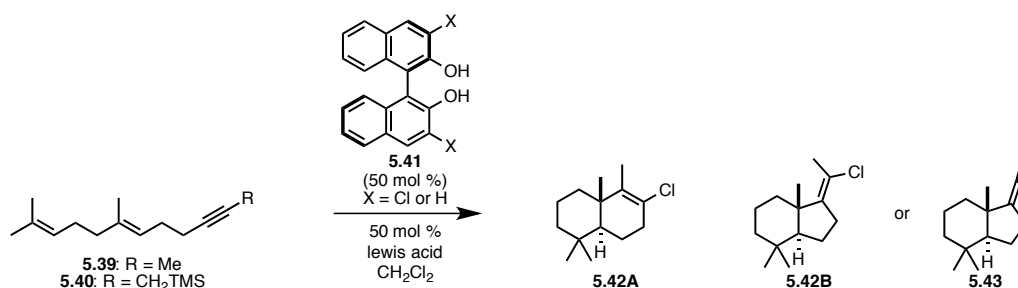


Several syntheses of enantioenriched *trans*-hydrindanone **5.31** have been reported.³⁰ We initially examined the short route reported by Granger and Snapper to prepare this ketone from 2-methylcyclopenten-2-one and prenylmagnesium bromide.^{30b} After slight modification, this approach provided initial 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 Yamamoto⁴² and Corey⁴³ 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, subjecting dienyne **5.39** to the reaction conditions reported by Corey,⁴³ using SbCl₅ 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 SnCl₄ 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**.



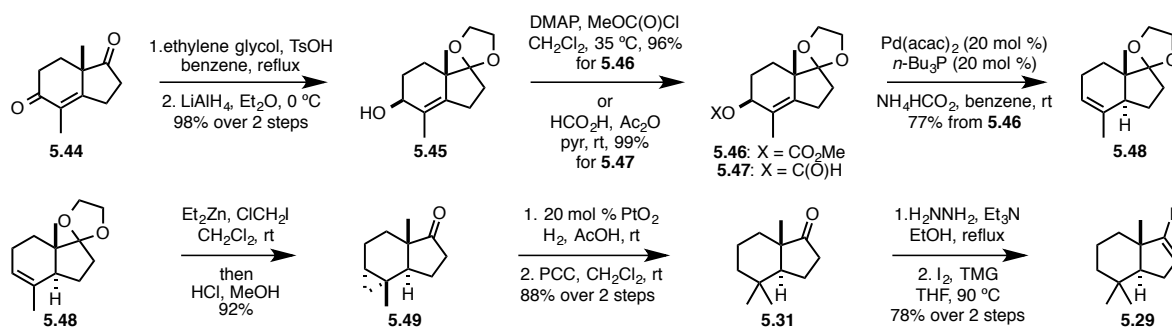
entry	Lewis acid	R	X	T (°C)	yield ^a (ratio 5.42A : 5.42B) ^b	5.31 , % <i>ee</i> ^c
1	SbCl ₅	Me	Cl	-78	35% (1.0:3.0)	0%
2	TiCl ₄	Me	Cl	-78	<5% (ND)	ND
3	SnCl ₄	Me	Cl	-78	55% (1.0:1.5)	18%
4	SnCl ₄	Me	Cl	-90	53% (1.0:1.1)	20%
5	SnCl ₄	Me	Cl	-50	12% (0:1.0)	ND
6	SnCl ₄	Me	H	-78	53% (1.1:1.0)	13%
7	SnCl ₄	CH ₂ TMS	Cl	-78	23% (0:1.0)	ND

^aIsolated combined yield of **5.42A** and **5.42B**. ^bDetermined by ¹H NMR integration of the crude reaction mixture. ^cHydrindanone **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

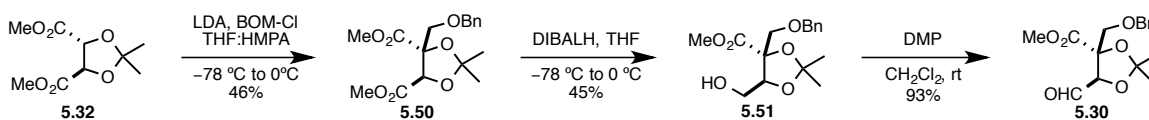
desired *trans*-hydrindene ketal **5.48**. Reaction of **5.45** with *o*-nitrobenzenesulfonylhydrazine followed by warming of the reaction to room temperature, as described by Myers,⁵¹ led to the desired *trans*-fused ketal **5.48** as a minor component of a complex mixture of product. Unable to perform 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)₃P, and finely crushed NH₄HCO₂ 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 (Cy₃P, *t*-Bu₃P, Ph₃P) 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 chloriodomethane,⁵² which after acidic workup delivered cyclopropyl ketone **5.49** in 92% yield. It was important to use chloriodomethane in this reaction, as use of diiodomethane led largely to recovery of the starting alkene. Hydrogenolysis of cyclopropane **5.49** using PtO₂ 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.



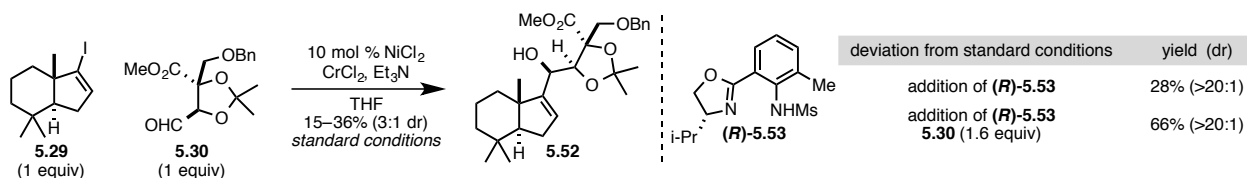
With streamlined access to vinyl iodide **5.29** in hand, we turned our attention to the synthesis of the aldehyde coupling partner **5.30** (Scheme 5.6). The sequence began with tartrate-derived acetonide **5.32**, which was desymmetrized by LDA-mediated alkylation with BOM-Cl, as reported by Crich, 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., LiAlH₄, 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 CH₂Cl₂ 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 vinyl lithium 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 iodide⁵⁹ 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

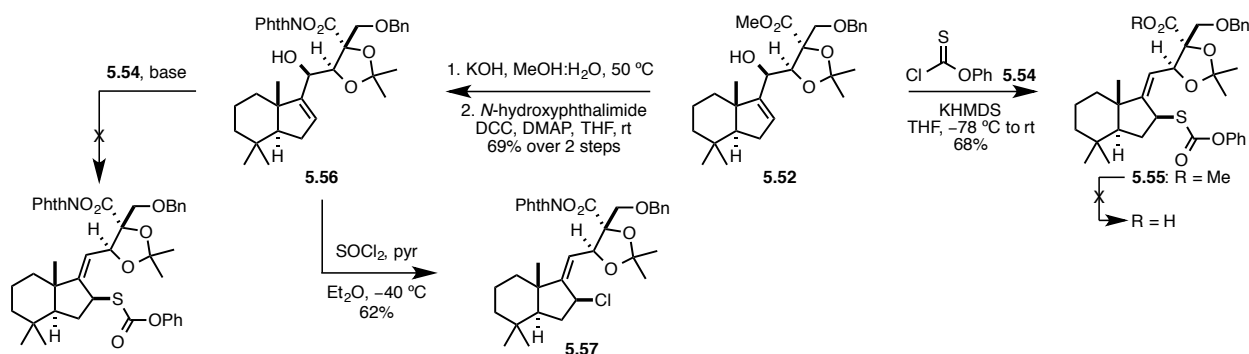
Scheme 5.7. Optimization of the NHK coupling of vinyl iodide 5.29 to aldehyde 5.30.



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 \rightarrow Cl transformations. Reaction of alcohol **5.56** with 2 equiv of $SOCl_2$ in a 10:1 mixture of Et_2O :pyridine at -40 °C⁶⁷ 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.

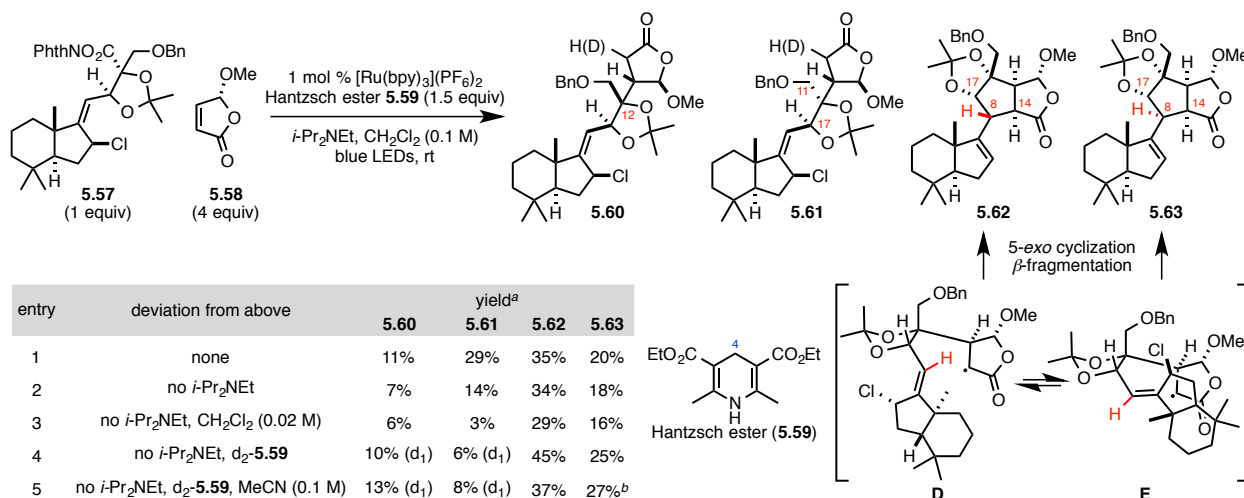
Scheme 5.8. Synthesis of radical precursor **5.57** from NHK coupling product **5.52**.



Exposure of *N*-acyloxypthalimide **5.57** to standard reductive photoredox reaction conditions³⁸ 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 ¹H 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 ¹H 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.



^aDetermined by ¹H NMR integration relative to an internal standard (1,4-dimethoxybenzene). ^bIsolated 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*-Pr₂NEt 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

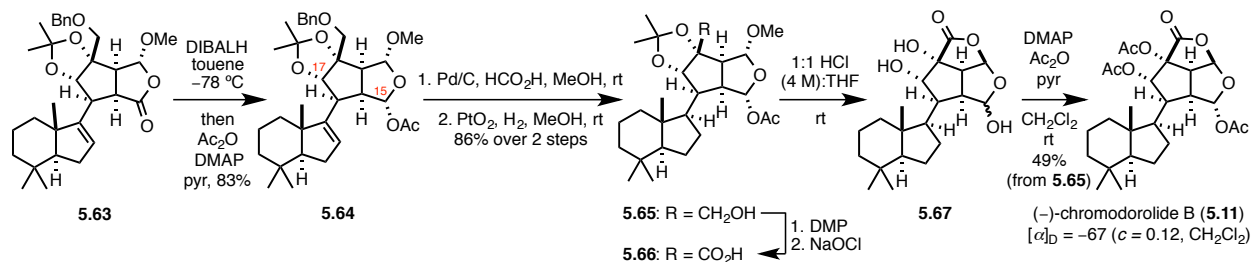
dilution, resulting in a further decrease in the yield of product **5.61** to 3% (entry 3). However, these more dilute conditions also resulted in less efficient coupling of the dioxolane radical and butenolide **5.58** leading to lower yields of pentacyclic products **5.62** and **5.63**. To attenuate 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 Ac₂O and DMAP afforded diacetal

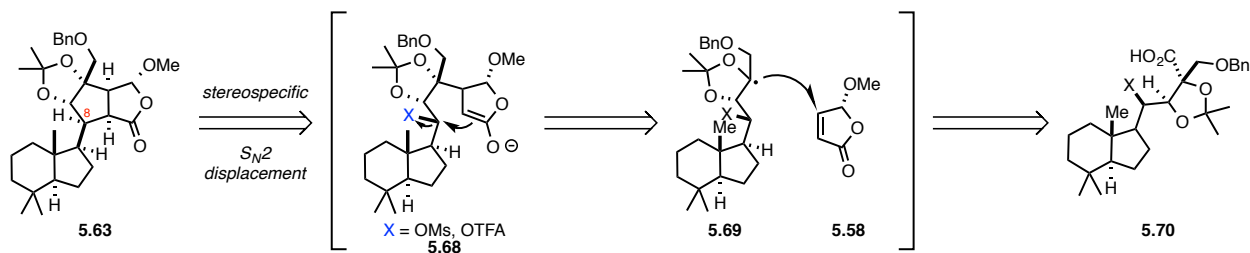
5.64 as a single epimer at C-15,⁶⁹ which was assigned the α -orientation on the basis of ¹H NOE correlations between the C-15 and C-17 methines. We speculate that stereoselection in this reduction resulted from prior coordination of DIBALH with the benzyl ether substituent. Following unsuccessful attempts 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 PtO₂-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, $[\alpha]_D = -67$ ($c = 0.12$, CH₂Cl₂), was somewhat less than that reported, $[\alpha]_D = -95$ ($c = 0.12$, CH₂Cl₂), 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**.



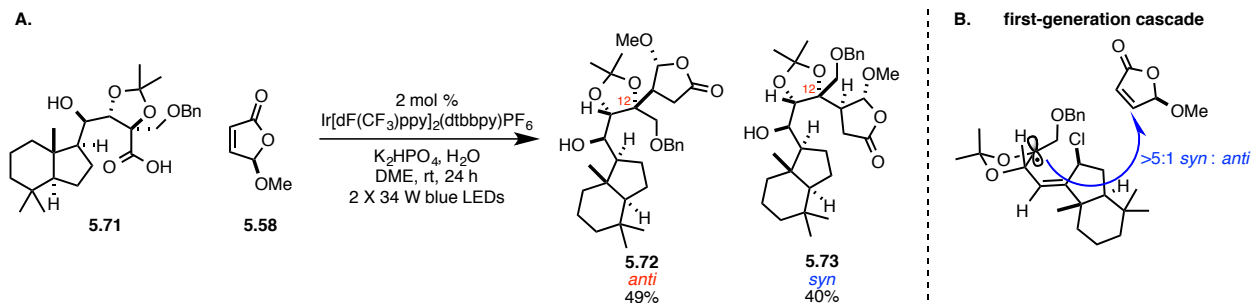
Upon completion of the synthesis of (–)-chromodorolide B (**5.11**), we shifted our focus back to optimization of the ACF cascade. As discussed earlier, we predicted that the 5-*exo* cyclization, to construct the C-8 stereocenter of diterpenoid **5.11**, would occur preferentially from a conformation 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**).



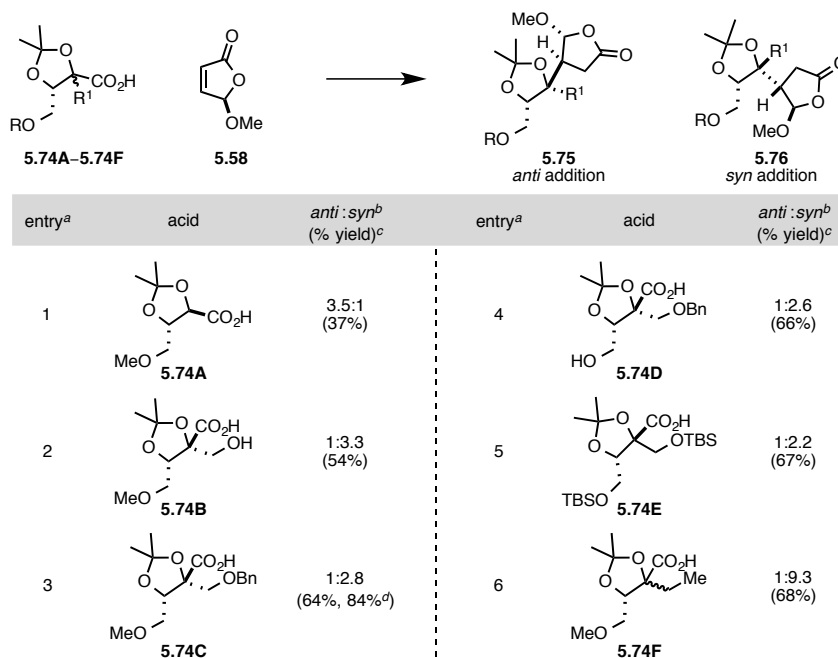
To test the feasibility of the modified cascade sequence, we prepared a simplified carboxylic acid **5.71** in two steps from the NHK product **5.52**,³⁶ bearing a secondary alcohol in place of a leaving group. To our surprise, upon subjection of the acid **5.71** to the photoredox reaction conditions 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 ^1H NOE experiments and confirmed in the case of the major product **5.76F** by single-crystal X-ray analysis.^{73, 25f}

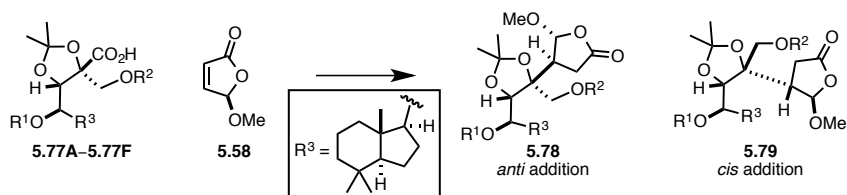
Table 5.1. Coupling of acetonide radicals generated by decarboxylation of acetonide acids **5.74A–5.74F** with (*R*)-5-methoxybutenolide (**5.58**).



^aReaction conditions: 1.0 equiv of **5.74A–5.74F**, 1.1 equiv of **5.58**, 2 mol % of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆, 1.1 equiv of K₂HPO₄, 10 equiv of H₂O in DME (0.1 M) at rt for 18 h with 2 X 34 W blue LEDs. ^bDiastereoselectivity determined by ¹H NMR analysis of the crude reaction mixture using an internal standard. ^cIsolated yield after silica gel chromatography. ^dConcentration 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	<i>anti</i> : <i>syn</i> ^b (% yield) ^c	entry ^a	acid	<i>anti</i> : <i>syn</i> ^b (% yield) ^c
1		1.2:1 (49%) ^d	4		1:7.0 (22%) ^d
2		1.3:1 (71%)	5		1:8.2 ^e (37%, 50%) ^g
3		9.8:1 ^e (45%) ^f	6		1:2.6 (43%)

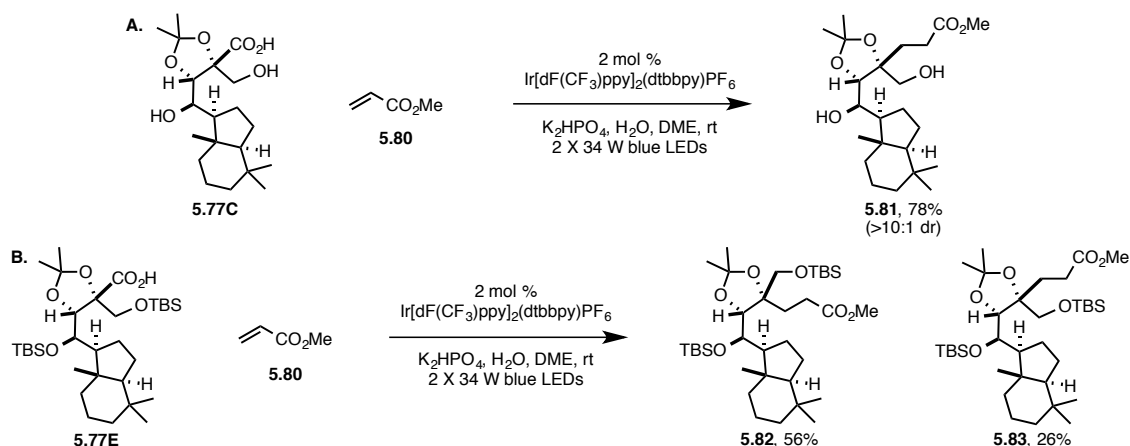
^aReaction conditions: 1.0 equiv of **5.77A–5.77F**, 1.1 equiv of **5.58**, 2 mol % of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆, 1.1 equiv of K₂HPO₄, 10 equiv of H₂O in DME (0.1 M) at rt for 18 h with 2 X 34 W blue LEDs. ^bDiastereoselectivity determined by ¹H NMR analysis of the crude reaction mixture using an internal standard. ^cIsolated yield after silica gel chromatography. ^dYield of the major product only. ^eWithin experimental uncertainty, the isomer ratio was constant over time: **5.77C** 9.4:1 at 3 h, 9.3:1 at 6 h; **5.77E** 1:8.5 at 3 h, 1:8.6 at 6 h. ^f45% combined yield by ¹H NMR analysis using an internal standard. The major diastereoisomer was isolated in 27% yield. ^gConcentration 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 R¹ and R² 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

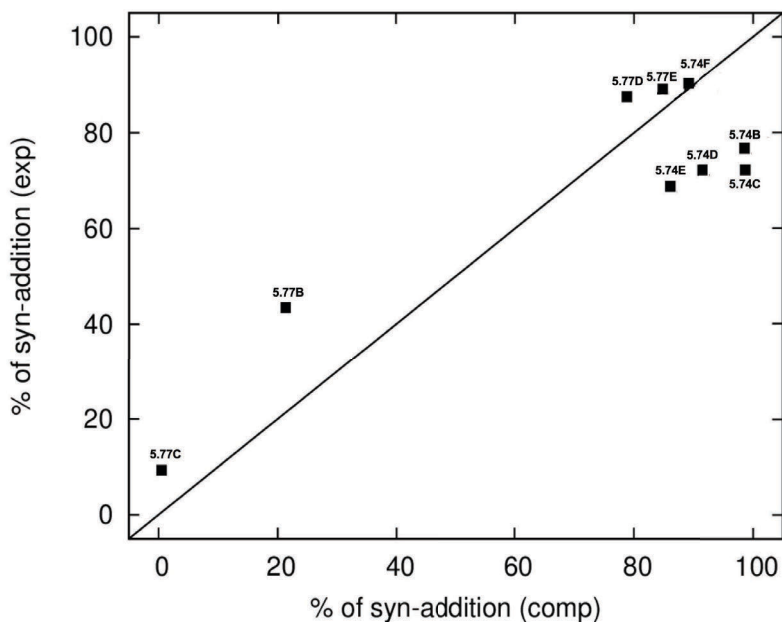
acceptor **5.58**, these acids were also coupled with methyl acrylate (**5.80**). In this case, product **5.81** was formed in high yield and >10:1 *anti* stereoselectivity from diol acid **5.77C** (Scheme 5.12A) whereas the bis-TBS precursor **5.77E** provided preferentially product **5.82** resulting 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-D3⁷⁵⁻⁷⁷ 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 acetone 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 R¹ and R² substituents were *cis* to each other, and the butenolide **5.58** was on the sterically less hindered side of the acetone 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 R¹ and R²; and (2) non-covalent interactions between

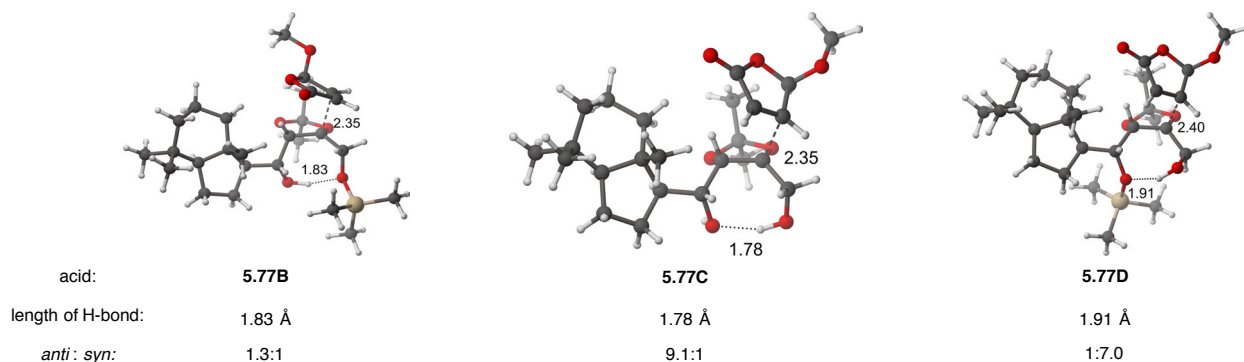
the acetonide radical and the butenolide **5.58**. The magnitude and sign of these interactions depended strongly on the size and functionalization of R¹ and R² on the acetonide radical.

For the reactions of trisubstituted acetonide radicals reported in Table 5.1, the repulsion between R¹ and R² dominated (effect 1) and *syn* stereoselectivity was observed. This conclusion was also supported by Renaud's experiments showing mostly *syn* addition when R¹ 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.

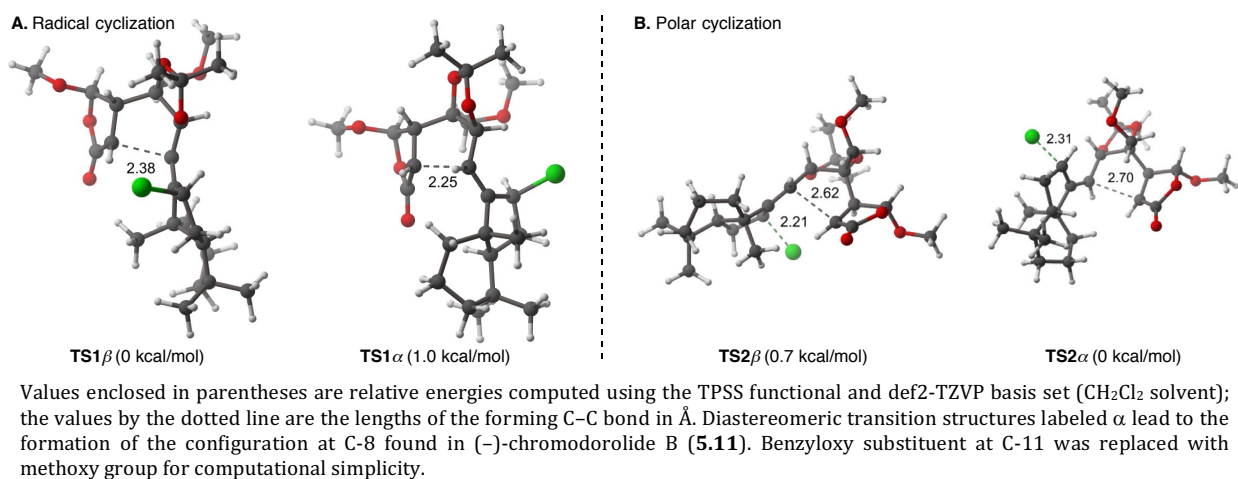


The structures were optimized using TPSS-D3/def2-TZVP. The TBS-groups were replaced TMS-groups for computational simplicity.

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 TPSS⁷² functional and def2-TZVP basis sets⁸⁰ in combination with the BJ-damped D3-dispersion correction (Figure 5.7).^{75,77} In the case of the radical pathway, transition state **TS1 β** , leading to the undesired C-8 epimer **5.62**, was found to be 1.0 kcal/mol (in CH₂Cl₂) or 0.5 kcal/mol (in MeCN) lower in energy than **TS1 α** 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 CH₂Cl₂) 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.

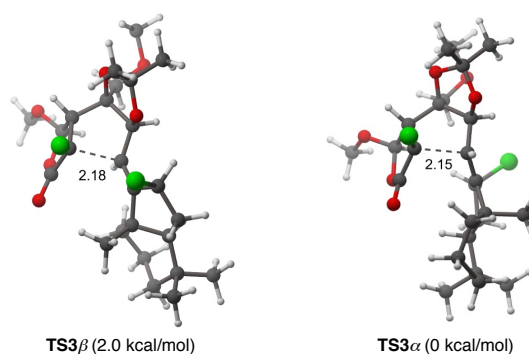


Examination of the transition structures of the two diastereomeric transition states of the radical pathway (Figure 5.7A) was instructive. The lower-energy diastereomeric transition structure, **TS1 β** , had a longer forming bond (2.38 Å vs 2.25 Å) and a somewhat helical shape. Further analysis suggested 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.

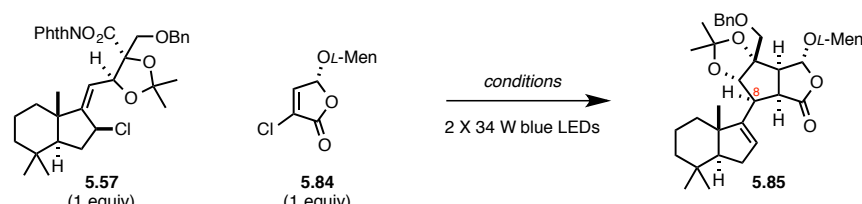


Values enclosed in parentheses are relative energies computed using the TPSS functional and def2-TZVP basis set (CH_2Cl_2 solvent); the values by the dotted line are the lengths of the forming C–C bond in Å. Benzyloxy substituent at C-11 was replaced with methoxy group for computational simplicity.

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*-Bu₃N 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*-Bu₃N and, in place of [Ru(bpy)₃](PF₆)₂, the iridium photocatalyst, Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆. 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(CF₃)ppy]₂(dtbbpy)PF₆ 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.

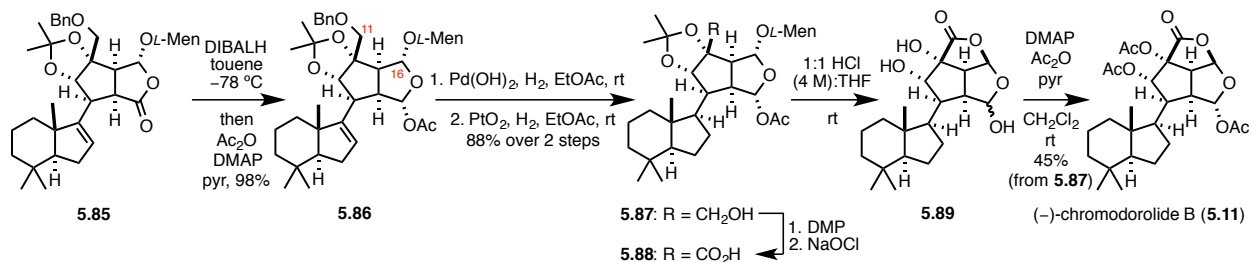
Table 5.3. Optimization of the fragment coupling between **5.57** and **5.84**.



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 , <i>n</i> -Bu ₃ N, 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 , <i>n</i> -Bu ₃ N, 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 ₃ N	56%
4	2 mol % Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆ , Hantzsch ester 5.59 , THF (0.6 M), then Bu ₃ N	57%
5	2 mol % 4CzIPN, Hantzsch ester 5.59 , THF (0.6 M), then Bu ₃ N	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 Ac₂O proceeded smoothly to deliver diacetal **5.86** in 98% yield. Deprotection of the primary alcohol proved challenging once again. Debencylation 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 H₂.⁸⁶ Without purification, the trisubstituted alkene was reduced stereoselectively with PtO₂ 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 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}

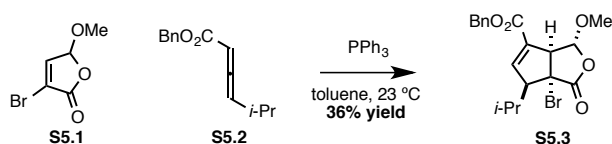
5.4 Experimental Information

Materials and methods.

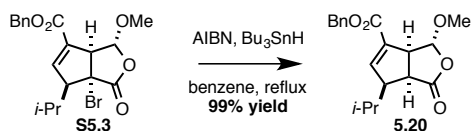
Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen or argon. Tetrahydrofuran (THF), dichloromethane, methanol (MeOH), toluene, diethyl ether, toluene, benzene, triethylamine (Et₃N), and pyridine were dried by passage through activated alumina. Acetic anhydride (Ac₂O), tributylphosphine (*n*-Bu₃P), 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 (KMnO₄). 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. ¹³C NMR spectra were recorded at 126 or 151 MHz. Data for ¹³C 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/jocean/jocean_abbreviations.pdf).

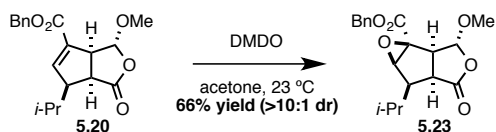
Preparation of the model system for initial dihydroxylation studies



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 $23\text{ }^\circ\text{C}$. 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 \rightarrow 10:90 ethyl acetate:hexanes as eluent to afford lactone **S5.3** (1.44 g, 3.51 mmol, 36% yield) as a clear oil. ^1H 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 $\text{C}_{19}\text{H}_{21}\text{O}_5\text{Br}$ $[\text{M}+\text{Na}]^+$ 433.0452; observed 433.0446.



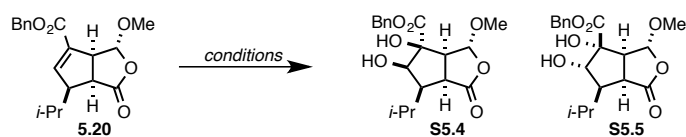
Preparation of (*rac*)-enoate 5.20: A round-bottom flask was charged with **S5.3** (1.44 g, 3.52 mmol, 1 equiv), benzene (35 mL, 0.1 M), *n*-Bu₃SnH (1.25 mL, 4.65 mmol, 1.3 equiv), AIBN (61 mg, 0.37 mmol, 0.1 equiv), and a magnetic stir bar under an atmosphere of argon. The resulting solution was heated 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. ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (151 MHz, CDCl₃) 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 C₁₉H₂₂O₅ [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 solution⁹² (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. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₉H₂₂O₆ [M+Na]⁺ 369.1314; observed 369.1311; mp: 78–79 °C (crystallized from MeOH).

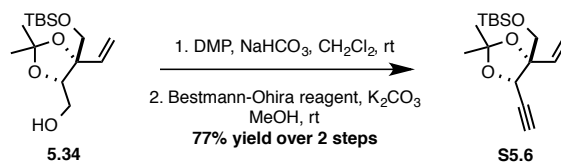
Table S5.1. Summary of reaction conditions for dihydroxylation of **5.20**.



entry	conditions	yield (S5.4 : S5.5) ^a
1	OsO ₄ (5 mol %), NMO or Me ₃ NO, various solvents	65–94% (85:15–95:5)
2	AD-mix α, K ₂ Os ₂ (OH) ₄ , (DHQ) ₂ PHAL	45% (>20:1)
3	RuCl ₃ , NaIO ₄	100% (>20:1)
4	AgOAc, I ₂ , H ₂ O, AcOH, 90 °C	0% (NR)
5	PhI(OAc) ₂ , TfOH, AcOH	0% (acetal hydrolysis)
6	KMnO ₄ , NaOAc, MeOH	50% (>20:1)

^aDetermined by ¹H NMR integration relative to an internal standard.

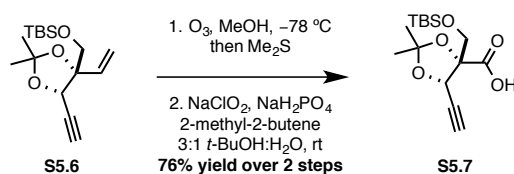
Preparation of the model system for the study of the facial selectivity of the reaction of a trisubstituted acetonide radical with butenolide 5.36



Preparation of alkyne S5.6: To a suspension of known alcohol **5.34**^{37b} (732 mg, 2.42 mmol) and solid NaHCO₃ (1.01 g, 12.1 mmol) in CH₂Cl₂ (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.

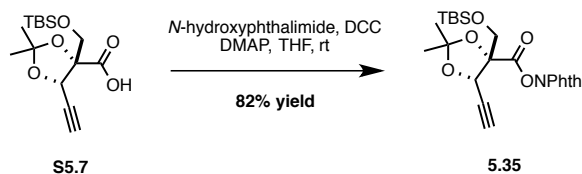
The crude aldehyde and dimethyl (1-azoacetyl)phosphonate (0.558 g, 2.90 mmol) were dissolved in MeOH (9 mL). Solid K₂CO₃ (670 mg, 4.84 mmol) was then added, and the suspension was vigorously stirred for 2 h. Celite (~5 g) was added to the reaction vessel, and the reaction was concentrated *in vacuo*. 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 KMnO₄). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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} ; $[\alpha]^{25}_{\text{D}} +0.79$ ($c = 2.5$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{29}\text{O}_3\text{Si}$ ($\text{M}+\text{H}$) 297.1887, observed 297.1890; mp 39–41 °C.

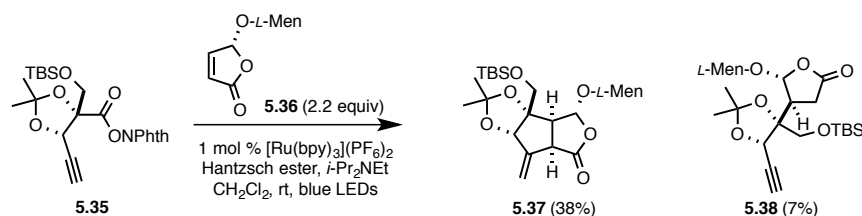


Preparation of carboxylic acid S5.7: A solution of alkyne **S5.6** (0.553 g, 1.87 mmol) in methanol (8 mL) was cooled to $-78\text{ }^\circ\text{C}$. Ozone from an ozone generator was bubbled through the solution until a pale blue color was observed (~ 5 min). The solution was then sparged with oxygen until the pale blue color disappeared. Dimethyl sulfide (0.31 mL, 4.3 mmol) was added to the solution, which was maintained at $-78\text{ }^\circ\text{C}$ for 1 h. The reaction vessel was allowed to warm to $23\text{ }^\circ\text{C}$ and concentrated *in vacuo*. The residue was then redissolved in a 3:1 solution of $t\text{-BuOH}:\text{H}_2\text{O}$ (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 $23\text{ }^\circ\text{C}$ 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} ; $[\alpha]_D^{25}$ -30.0 ($c = 2.1$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{15}\text{H}_{25}\text{O}_5\text{Si}$ (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'*-dicyclohexylcarbodiimide (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). ^1H 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} ; $[\alpha]_D^{25}$ +38.3 ($c = 2.0$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{29}\text{NO}_7\text{SiNa}$ (M+Na) 482.1611, observed 482.1612; mp 105–109 °C.



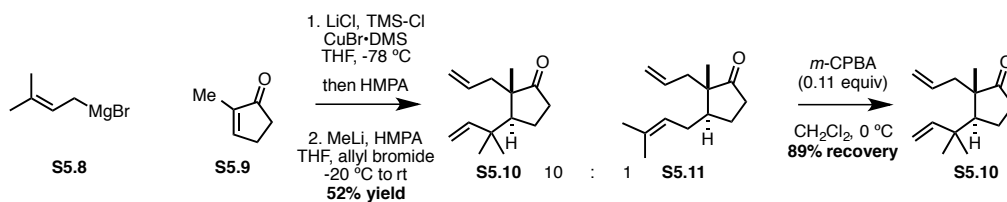
Preparation of lactones 5.37 and 5.38: To a 1-dram vial charged with *N*-acyloxyphthalimide **5.35** (100 mg, 0.218 mmol) was added CH₂Cl₂ (2 mL) that had been separately sparged with argon. Next, butenolide **5.36**²⁹ (78 mg, 0.33 mmol), Hantzsch ester (82 mg, 0.63 mmol), Ru(bpy)₃(PF₆)₂ (2 mg, 0.02 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: ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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} ; $[\alpha]^{25}_{\text{D}} -133$ ($c = 1.9$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{48}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) 531.3118, observed 531.3126; mp 136–142 $^{\circ}\text{C}$.

5.38: ^1H 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} ; $[\alpha]^{25}_{\text{D}} -93.7$ ($c = 1.2$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{48}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) 531.3118, observed 531.3131.

Modified Snapper route to hydrindanone (+)-5.31

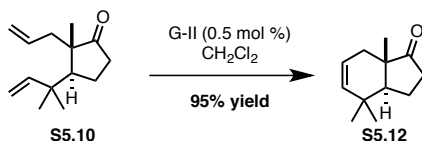


Preparation of (*rac*)-ketone S5.10: The procedure for preparation of S5.10 was a modification from the literature.^{30a} A round-bottom flask was charged with $\text{CuBr}\cdot\text{DMS}$ (14.4 g, 75.5 mmol, 1.5 equiv), anhydrous LiCl (4.26 g, 101 mmol, 2 equiv), THF (130 mL, 0.4 M), and a magnetic stir bar under an atmosphere of argon. After maintaining the solution at 23 $^{\circ}\text{C}$ for 15 min, the flask was cooled to -78 $^{\circ}\text{C}$. A solution of prenyl magnesium bromide⁹³ S5.8 (63 mmol, 290 mL, 0.22 M in THF, 1.25 equiv) was added slowly over 15 min. After

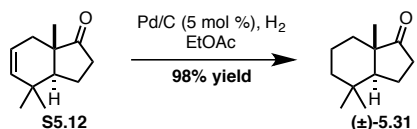
maintaining the reaction at $-78\text{ }^{\circ}\text{C}$ for 15 min, TMS-Cl (12.7 mL, 101 mmol, 2 equiv) was added dropwise, followed immediately by 2-methyl-cyclopent-2-enone **S5.9** (4.84 g, 50.3 mmol, 1 equiv) in THF (5 mL). The reaction was maintained at $-78\text{ }^{\circ}\text{C}$ for 1 h, and 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 $0\text{ }^{\circ}\text{C}$ 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 $-20\text{ }^{\circ}\text{C}$, 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 $-10\text{ }^{\circ}\text{C}$. The reaction was then allowed to warm to $23\text{ }^{\circ}\text{C}$ over 1 h. Upon cooling the reaction to $-78\text{ }^{\circ}\text{C}$, HMPA (35 mL, 201 mmol, 4 equiv) was added and the reaction was maintained at $-78\text{ }^{\circ}\text{C}$ 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 $23\text{ }^{\circ}\text{C}$ 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 \rightarrow 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).

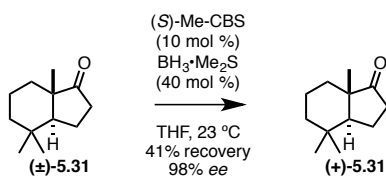
A round-bottom flask was charged with ketones **S5.10** and **S5.11** (14.9 g, 72.1 mmol, 10:1 ratio, 1 equiv), CH₂Cl₂ (150 mL, 0.5 M), and a magnetic stir bar under an atmosphere of argon. Upon cooling to 0 °C, *m*-CPBA (1.83 g, 7.93 mmol, 0.11 equiv) was added. The reaction was maintained at 0 °C for 1 h. The reaction was then 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), CH₂Cl₂ (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 Et₂O (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}

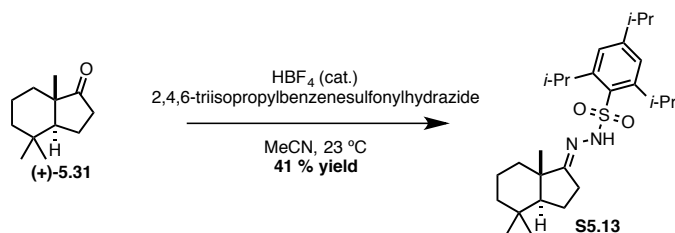


Preparation of (*rac*)-ketone 5.31: The procedure for preparation of (±)-**5.31** was a slight modification from the literature.^{30a} A round bottom-flask was charged with 10% Pd/C (1.59 g, 1.50 mmol, 0.1 equiv), ketone **S5.12** (2.68 g, 15.0 mmol, 1 equiv), EtOAc (60 mL), and a magnetic stir bar. The reaction vessel was evacuated and backfilled with H₂ (3x). The reaction was maintained at 23 °C for 20 h before purging the vessel of H₂. 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}



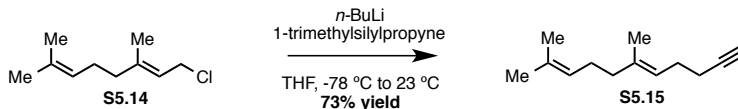
Preparation of (+)-ketone 5.31: The procedure for preparation of (+)-**5.31** was a slight modification from the literature.^{30a} A round-bottom flask was charged with (*S*)-1-methyl-3,3-diphenyl-tetrahydro-pyrrolo[1,2*c*][1,3,2]oxazaborole (0.86 mL, 0.86 mmol, 1.0 M in toluene, 0.1 equiv), THF (40 mL, 0.22 M), BH₃•Me₂S (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 portion. After 2 min, MeOH (40 mL) and aq. HCl (40 mL of 1 M soln) were added to quench the reaction, followed by Et₂O (100 mL) and H₂O (50 mL). The aqueous layer was extracted with Et₂O (3 x 30 mL), and the combined organic layers were dried over MgSO₄, filtered, and

concentrated by use of a rotary evaporator. Purification by flash chromatography on silica gel using 5:95 diethyl ether:hexanes \rightarrow 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*).

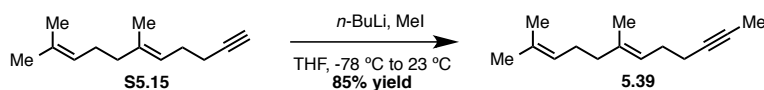


Preparation of hydrazone S5.13: The procedure for preparation of hydrazone **S5.13** was repeated from literature.^{30a} A round-bottom flask was charged with (+)-**5.31** (105 mg, 0.582 mmol, 1 equiv) 2,4,6-triisopropylbenzenesulfonylhydrazide (182 mg, 0.611 mmol, 1.05 equiv), MeCN (3 mL, 0.2 M), and a magnetic stir bar under an atmosphere of argon. The suspension was vigorously stirred for 15 min before one drop of HBF₄ was added to the suspension (which immediately became a homogeneous solution). The reaction was maintained for 14 h before addition of Et₂O (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 \rightarrow 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} HPLC 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

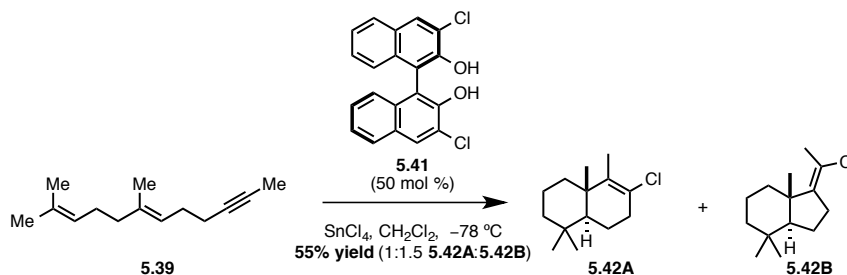


Preparation of diene **S5.15:** The procedure for preparation of **S5.15** was a modification from the literature.⁹⁴ A round-bottom flask was charged with 1-trimethylsilylpropyne (2.96 g, 26.4 mmol, 1.2 equiv), THF (100 mL, 0.22M), and a magnetic stir bar under an atmosphere of argon. Upon cooling the solution to $-78\text{ }^{\circ}\text{C}$, $n\text{-BuLi}$ (30.8 mmol, 11.8 mL, 2.5 M in hexanes, 1.4 equiv) was added slowly, and the reaction was then warmed to $0\text{ }^{\circ}\text{C}$ over 1 h. The reaction was cooled to $-78\text{ }^{\circ}\text{C}$, and geranyl chloride **S5.14** (3.8 g, 22 mmol, 1 equiv) was added. The reaction was allowed to warm to $23\text{ }^{\circ}\text{C}$ over 16 h. The reaction vessel was then cooled to $-78\text{ }^{\circ}\text{C}$, 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 $23\text{ }^{\circ}\text{C}$ 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



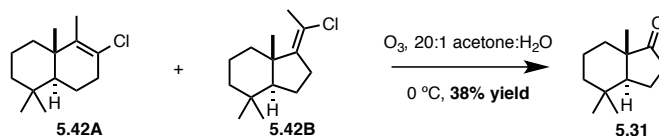
Preparation of diene **5.39:** A round-bottom flask was charged with diene **S5.15** (2.17 g, 12.3 mmol, 1 equiv), THF (120 mL, 0.1 M), and a magnetic stir bar under an atmosphere of argon. Upon cooling the solution to $-78\text{ }^{\circ}\text{C}$, $n\text{-BuLi}$ (18.5 mmol, 7.10 mL, 2.5

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. NH₄Cl (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 MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₄H₂₂ [M+NH₄]⁺ 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 CH₂Cl₂ (6.5 mL, 0.38 M) at -78 °C was added SnCl₄ (1.25 mL, 1.25 mmol, 1.0 M in CH₂Cl₂, 0.5 equiv) dropwise. After 15 min, a solution of dieneyne **5.39** (475 mg, 2.49 mmol, 1 equiv) in CH₂Cl₂ (6.5 mL, 0.38 M) cooled to -78 °C was added via cannula to the reaction. Upon full

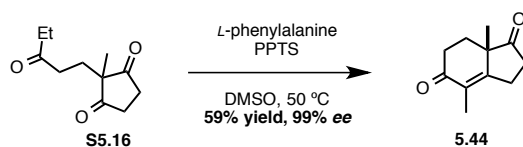
consumption of diene **5.39** (monitored by TLC), saturated aq. NH_4Cl (5 mL) was added, and the reaction was allowed to warm to 23 °C. The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated by use of a rotary evaporator. 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 ^1H NMR. Diagnostic peaks for 6-*endo* product **5.42A** in ^1H 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 ^1H 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 $\text{C}_{14}\text{H}_{23}\text{Cl}$ $[\text{M}^+]^+$ 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 \rightarrow 15:85 diethyl ether:hexanes as eluent provided ketone **5.31** as a clear oil

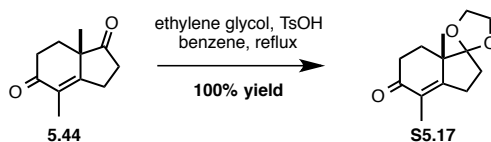
(91 mg, 0.50 mmol, 38% yield). Spectral data was consistent with reported values.^{30a} *ee* was determined to be -18% by chiral HPLC of corresponding hydrazone **S5.13**.^{30a}

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

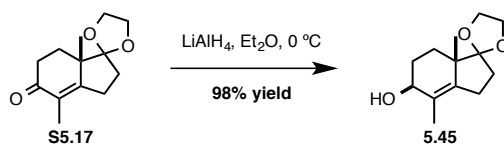


Preparation of ketone 5.44: (*S*)-enone was prepared according to a literature procedure.⁵⁰ A 100 mL round-bottom flask was charged with 2-methyl-2-(3-oxopentyl)cyclopentane-1,3-dione **S5.16** (39.6 g, 202 mmol), followed by the addition of *L*-phenylalanine (10 g, 61 mmol), PPTS (25.3 g, 101 mmol), 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 H₂O (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. NaHCO₃ (1 x 500 mL), and brine (1 x 500 mL). The organic phase was dried over MgSO₄ and concentrated *in vacuo* to yield a viscous red oil. The resulting oil was filtered through a silica gel plug (100 g SiO₂) 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 Et₂O (23 mL) at -20 °C utilizing a seed crystal (obtained via crystallization from Et₂O: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

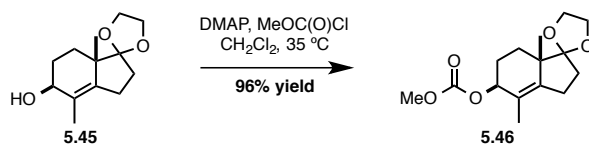
determined by chiral stationary-phase HPLC analysis (Chiracel OB-H column; flow: 2.0 mL/min, 20% isopropanol:*n*-hexane; $\lambda = 254$ nm; minor enantiomer $t_R = 5.86$ min, major enantiomer $t_R = 7.25$ min).



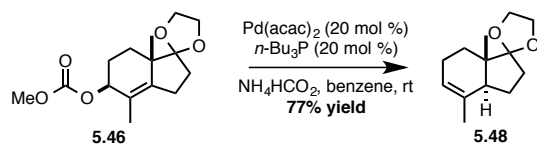
Preparation of ketal S5.17: A 2 L round-bottom flask was charged with enone (+)-**5.44** (7.7 g, 43 mmol), followed by the addition of benzene (860 mL), ethylene glycol (2.9 mL, 52 mmol), and *p*-TsOH•H₂O (1.6 g, 8.6 mmol). A Dean-Stark apparatus was fitted to the flask, and the homogeneous reaction 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. NaHCO₃ (300 mL) was added. The resulting biphasic mixture was separated and the aqueous layer was extracted with Et₂O (3 x 200 mL). The combined organic layers were washed with brine (1 x 500 mL), dried over MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; $[\alpha]^{21}_D -7.79$ ($c = 1.6, \text{CH}_2\text{Cl}_2$); HRMS (ESI) calculated for [C₁₃H₁₈O₃Na]⁺ (M+Na) 245.1154, observed 245.1163.



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 Et₂O (310 mL). The solution was cooled to -78 °C. A solution of LiAlH₄ (65 mL of 1 M in Et₂O, 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 Et₂O (3 x 150 mL). Combined organic layers were washed with brine (1 x 500 mL), dried over MgSO₄, 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). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²¹_D -32.0 (*c* = 1.8, CH₂Cl₂); HRMS (ESI) calculated for [C₁₃H₂₀O₃] (M) 224.1413, observed 224.1406; mp 86–88 °C.

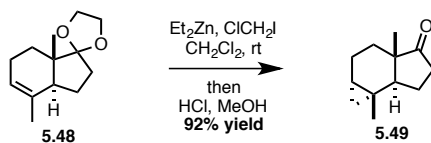


Preparation of allylic carbonate 5.46: A 1 L round-bottom flask was charged with allylic alcohol **5.45** (9.5 g, 42 mmol), followed by the addition of DMAP (15.0 g, 126 mmol), CH_2Cl_2 (420 mL), and methyl chloroformate (13 mL, 170 mmol). The resulting homogeneous solution was maintained at 35 °C until 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} ; $[\alpha]^{22}_{\text{D}}$ -41.32 ($c = 1.1$, CH_2Cl_2); HRMS (ESI) calculated for $[\text{C}_{15}\text{H}_{22}\text{O}_5\text{Na}]^+$ ($\text{M}+\text{Na}$) 305.1365, observed 305.1370; mp 56–58 °C.



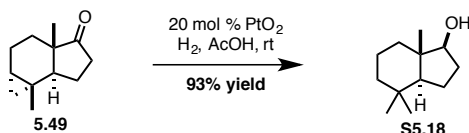
Preparation of olefin 5.48: A 200 mL round-bottom flask was charged with Pd(acac)₂ (490 mg, 1.6 mmol), followed by the addition of benzene (21 mL), PBU₃ (0.4 mL, 1.6 mmol). The homogeneous mixture was maintained at room temperature for 5 min. Ammonium formate (4.2 g, 67 mmol) was finely crushed with 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 SiO₂, 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. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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

1; $[\alpha]_D^{21}$ -62.3 ($c = 1.0$, CH_2Cl_2); HRMS (ESI) calculated for $[\text{C}_{13}\text{H}_{20}\text{O}_2]$ (M) 208.1463, observed 208.1460.

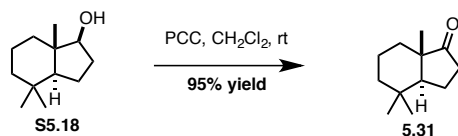


Preparation of cyclopropane 5.49: A 500 mL round-bottom was charged with ketal **5.48** (6.2 g, 30 mmol), followed by the addition of CH_2Cl_2 (150 mL). The solution was cooled to 0°C , and a solution of Et_2Zn (60 mL of 1 M in hexanes, 60 mmol) was added dropwise. After 10 min at 0°C , chloriodomethane (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). ^1H 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

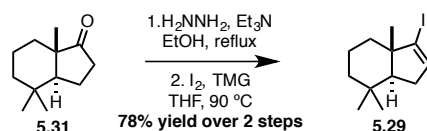
= 9.5, 4.3 Hz, 1H), 0.01 (app t, $J = 5.3$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 221.2, 50.7, 47.3, 36.6, 28.0, 23.3, 23.0, 22.2, 19.7, 17.8, 16.3, 13.3; IR (thin film) 3051, 2945, 2864, 1737, 1445, 1024 cm^{-1} ; $[\alpha]^{22}_{\text{D}} +118$ ($c = 1.0$, CH_2Cl_2); HRMS (ESI) calculated for $[\text{C}_{12}\text{H}_{18}\text{O}]$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



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), $\text{PtO}_2 \cdot \text{H}_2\text{O}$ (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

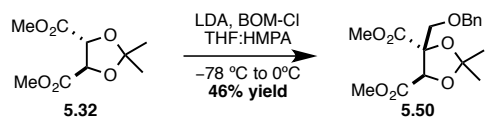


Preparation of ketone 5.31: A 100 mL round-bottom flask was charged with alcohol **S5.18** (0.80 g, 4.4 mmol), followed by the addition of PCC (2.0 g, 9.4 mmol), Celite (2.0 g), and CH₂Cl₂ (22 mL). The resulting heterogeneous solution was stirred vigorously at room temperature, until TLC analysis (10% 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; $\lambda = 254$ 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**.

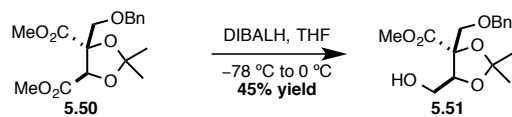


Preparation of vinyl iodide 5.29: Hydrazine hydrate (20 mL) and NEt_3 (16.3 mL, 118 mmol) were added to a solution of ketone **5.31** (1.06 g, 5.88 mmol) in EtOH (45 mL). The reaction was heated to reflux for 20 h; upon cooling to 23 °C, CH_2Cl_2 (100 mL) and H_2O (150 mL) were added. The aqueous layer 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.

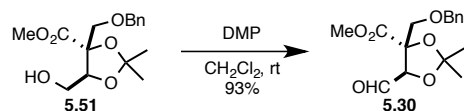
A solution of 1,1,3,3-tetramethylguanidine (5.15 mL, 41.2 mmol) in THF (30 mL) was added dropwise over 10 min to a solution of I_2 (3.28 g, 12.9 mmol) in THF (30 mL). The hydrazone (5.88 mmol) in THF (6 mL) was then added dropwise over 10 min, and the reaction was maintained for 30 min. The dark red 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}



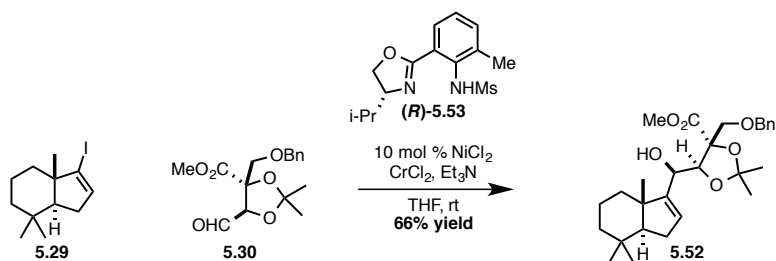
Preparation of diester 5.50: The procedure for the preparation of diester **5.50** was a slight modification from the literature procedure.³¹ Dimethyl 2,3,-*O*-isopropylidene-*L*-tartrate (3.83 g, 17.6 mmol) was dissolved in THF (67 mL) and cooled to $-78\text{ }^{\circ}\text{C}$. HMPA (13 mL) was added, 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 $-78\text{ }^{\circ}\text{C}$, before warming to $0\text{ }^{\circ}\text{C}$. 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 ($120\text{ }^{\circ}\text{C}$, 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 ($\sim 5\times$) with similar yields (41–43% yield). $R_f = 0.80$ (40% EtOAc in hexanes; visualized with ceric ammonium molybdate). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{25}_{\text{D}} -33.8$ ($c = 1.7$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{17}\text{H}_{22}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 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 $-78\text{ }^\circ\text{C}$. DIBALH (14 mL, 79 mmol) was added dropwise to the reaction. After 5 min, the reaction was warmed to $0\text{ }^\circ\text{C}$. 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 $23\text{ }^\circ\text{C}$, 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). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{25}_{\text{D}} -2.17$ ($c = 1.2$); HRMS (ESI) calculated for $\text{C}_{16}\text{H}_{22}\text{O}_6\text{NH}_4$ ($\text{M}+\text{NH}_4$) 328.1760, observed 328.1754.

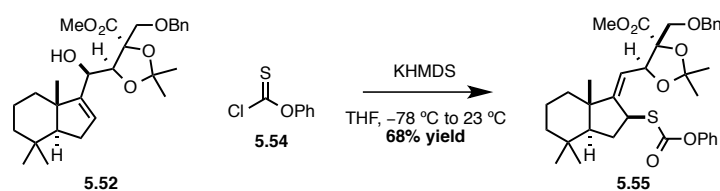


Preparation of aldehyde 5.30: To a stirring suspension of alcohol **5.51** (4.80 g, 15.5 mmol) and NaHCO₃ (6.50 g, 77.4 mmol) in CH₂Cl₂ (40 mL) was added Dess-Martin periodinane (7.87 g, 18.6 mmol) in two portions over 5 min. After 2 h, the reaction mixture was diluted with Et₂O (40 mL) and filtered through a cotton plug to remove solid NaHCO₃. 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]_D²⁵ -2.37 (c = 2.5, CH₂Cl₂); HRMS (ESI) calculated for [C₁₆H₂₀O₆NH₄]⁺ (M+NH₄) 326.1604, observed 326.1612.



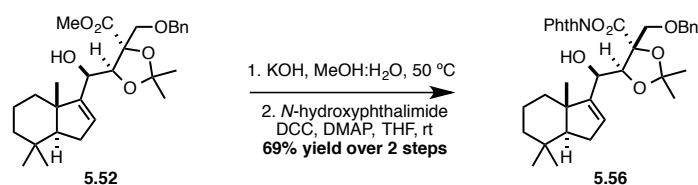
Preparation of allylic alcohol 5.52: *L*-Oxazoline **5.53**⁶⁰ (2.86 g, 9.65 mmol) and CrCl_2 (1.19 g, 9.65 mmol) were dissolved in THF (20 mL) in the glove box, and NEt_3 (1.34 mL, 9.65 mmol) was then added. The suspension was vigorously stirred for 6 h, and then NiCl_2 (36 mg, 0.28 mmol) was added, 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_2O (40 mL) and Et_2O (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_2O :hexanes for reuse. $R_f = 0.50$ for **5.52** (20% EtOAc in hexanes; visualized with ceric ammonium molybdate). $^1\text{H NMR}$ (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} ; $[\alpha]^{25}_{\text{D}} -4.85$ ($c = 1.5$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{40}\text{O}_6\text{NH}_4$ ($\text{M}+\text{NH}_4$) 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 $-78\text{ }^\circ\text{C}$, 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 $-78\text{ }^\circ\text{C}$, **5.54** (70 μL , 0.51 mmol, 4 equiv) was added dropwise. The solution was maintained at $-78\text{ }^\circ\text{C}$ for 30 min and then allowed to warm to $23\text{ }^\circ\text{C}$ 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); ^1H 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,

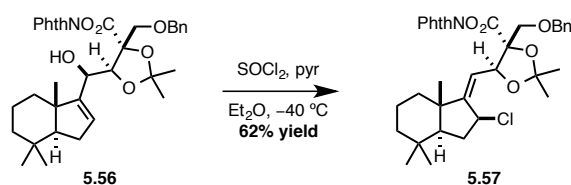
1H), 1.74 (dt, $J = 13.1, 3.9$ Hz, 2H), 1.62 (dd, $J = 15.6, 12.1$ Hz, 2H), 1.54 (s, 4H), 1.45 (s, 3H), 1.02–0.99 (m, 5H), 0.90–0.86 (m, 4H), 0.84 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.0, 170.1, 157.9, 151.4, 129.6, 128.4, 127.73, 127.70, 126.3, 121.4, 114.9, 110.5, 85.4, 76.1, 73.6, 71.4, 55.6, 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} ; $[\alpha]^{21}_{\text{D}}$ 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 $\text{C}_{35}\text{H}_{44}\text{O}_7\text{S}$ $[\text{M}+\text{Na}]^+$ 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 $^\circ\text{C}$. After 3 h, TLC analysis confirmed starting material was consumed; and the reaction was cooled to 23 $^\circ\text{C}$. 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.

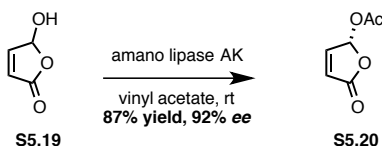
The crude acid was dissolved in THF (20 mL) to which *N*-hydroxyphthalimide (0.881 g, 5.40 mmol), DCC (0.483 g, 2.34 mmol), and DMAP (11 mg, 0.090 mmol) were added. The reaction was maintained for 3 h at 23 $^\circ\text{C}$, at which point Celite (~2 g) was added. The reaction mixture was concentrated *in vacuo*, and the resulting residue was

purified by flash column chromatography using pH 7 silica gel⁹⁷ (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). ¹H NMR (600 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; $[\alpha]_D^{25} -7.60$ ($c = 1.6$, CH₂Cl₂); HRMS (ESI) calculated for C₃₅H₄₁NO₈Na (M+Na) 626.2730, observed 626.2712; mp 139–141 °C.

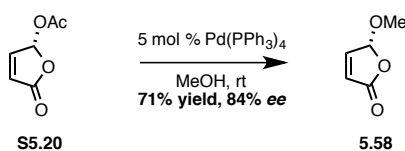


Preparation of allylic chloride 5.57: *N*-acyloxyphthalimide **5.56** (0.223 g, 0.369 mmol) was dissolved in a 10:1 mixture of Et₂O:pyridine (3.5 mL) and cooled to –45 °C. A solution of SOCl₂ (54 μL, 0.74 mmol) in a 10:1 mixture of Et₂O:pyridine (0.5 mL) was then added dropwise to the reaction over 5 min. The reaction was maintained at –45 °C until full

conversion of starting material was observed by TLC analysis (~45 min). Saturated aq. NaHCO₃ solution (2 mL) was added, and the reaction was allowed to warm to 23 °C. The mixture was then diluted with H₂O (2 mL) and washed with EtOAc (3 x 3 mL). The combined organic layers were washed with brine (1 x 2 mL), dried over MgSO₄, filtered, and concentrated *in vacuo* onto Celite (~1 g). Purification by flash column chromatography using pH 7 silica gel⁹⁷ (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, CDCl₃) 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 Hz, 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]_D²⁵ +83.2 (*c* = 1.8, CH₂Cl₂); HRMS (ESI) calculated for C₃₅H₄₀ClNO₇Na (M+Na) 644.2391, observed 644.2383; mp 154–158 °C.

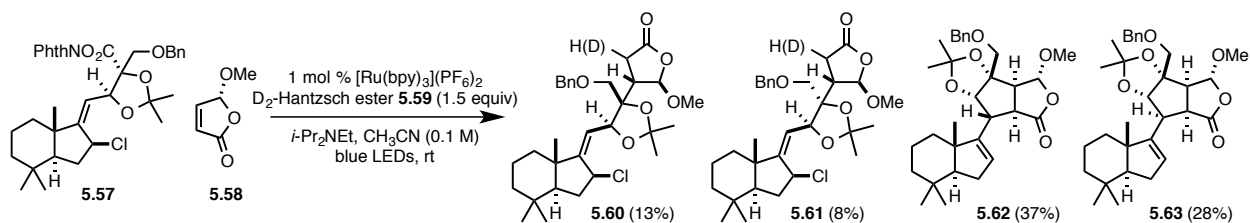


Preparation of butenolide S5.20: The procedure for preparation of acetoxy butenolide **S5.20** was a slight modification from the literature procedure.⁹⁸ 5-Hydroxyfuran-2(5H)-one^{29a} (2.90 g, 28.9 mmol) was dissolved in vinyl acetate (30 mL). Amano lipase AK (2.00 g) was then added, and the suspension 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-acetoxypentenolide **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 $\text{Pd(PPh}_3)_4$ (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 HPLC analysis was used to determine the enantiomeric ratio to be 92:8 (Chiracel AS column; flow: 2.0 mL/min, 10% isopropanol:*n*-hexane; $\lambda = 210$ 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 $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (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 H₂O (2 x 2 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated *in vacuo*. ¹H 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).

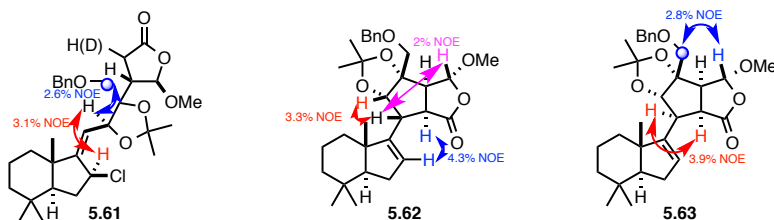
Desired ACF product **5.63** for ^1H NMR (500 MHz, CDCl_3) δ 7.38–7.28 (m, 5H), 5.48 (app s, 1H), 5.38 (app s, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.59 (d, J = 12.1 Hz, 1H), 4.41 (d, J = 7.5 Hz, 1H), 3.64 (d, J = 10.5 Hz, 1H), 3.50 (d, J = 10.3 Hz, 1H), 3.43 (app t, J = 8.7 Hz, 1H), 3.38 (s, 3H), 3.07 (app 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; $[\alpha]^{25}_{\text{D}}$ -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 $\text{C}_{31}\text{H}_{42}\text{O}_6\text{NH}_4$ ($\text{M}+\text{NH}_4$) 528.3325, observed 528.3331.

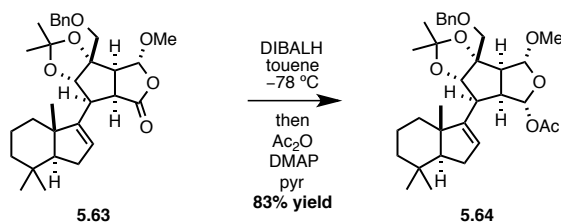
Epimer **5.62**: ^1H NMR (500 MHz, CDCl_3) δ 7.39–7.29 (m, 5H), 5.75 (app s, 1H), 5.53 (d, J = 4.8 Hz, 1H), 4.57 (d, J = 12.3 Hz, 1H), 4.55 (d, J = 12.3 Hz, 1H), 4.47 (d, J = 3.7 Hz, 1H), 3.82 (d, J = 9.6 Hz, 1H), 3.61 (d, J = 9.7 Hz, 1H), 3.50 (app t, J = 10.8 Hz, 1H), 3.41 (s, 3H), 2.88 (dd, J = 9.7, 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 $\text{C}_{31}\text{H}_{42}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 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 $\text{C}_{31}\text{H}_{42}\text{DClO}_6\text{Na}$ ($\text{M}+\text{Na}$) 570.2709, observed 570.2702.

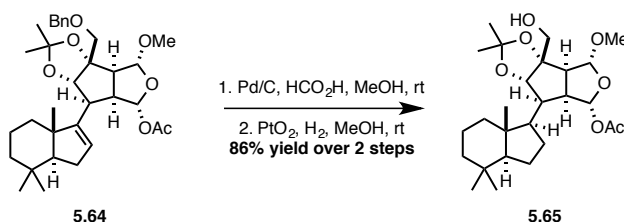
Diagnostic peaks of addition product **5.60**: ^1H NMR (500 MHz, CDCl_3) δ 5.43 (d, $J = 2.9$ Hz, 1H), 5.21 (d, $J = 9.6$, 1.7 Hz, 1H), 4.75 (d, $J = 9.6$ Hz, 1H), 4.59 (app t, $J = 7.0$ Hz, 1H).





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 $-78\text{ }^\circ\text{C}$. 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 $-78\text{ }^\circ\text{C}$. 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_2Cl_2 (0.2 mL) was added, followed by Ac_2O (44 μL , 0.47 mmol). The reaction was maintained at $-78\text{ }^\circ\text{C}$ for 12 h, at which point it was allowed to warm to $23\text{ }^\circ\text{C}$. 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). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.38–7.27 (m, 5H), 5.92 (d, $J = 4.1\text{ Hz}$, 1H), 5.60 (app s, 1H), 5.17 (s, 1H), 4.61 (d, $J = 12.3\text{ Hz}$, 1H), 4.58 (d, $J = 12.3\text{ Hz}$, 1H), 4.30 (d, $J = 8.8\text{ Hz}$, 1H), 3.60 (d, $J = 10.4\text{ Hz}$, 1H), 3.54 (d, $J = 10.5\text{ Hz}$, 1H), 3.27 (s, 3H), 3.20 (app td, $J = 7.8, 4.0\text{ Hz}$, 1H), 3.03 (d, $J = 8.0\text{ Hz}$, 1H), 2.92 (app t, $J = 8.1\text{ Hz}$, 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, $J = 13.6\text{ Hz}$, 1H), 1.35 (s, 3H), 1.28–1.24 (m, 1H), 1.20 (td, $J = 12.7, 3.9\text{ Hz}$, 1H), 0.98 (td, $J =$

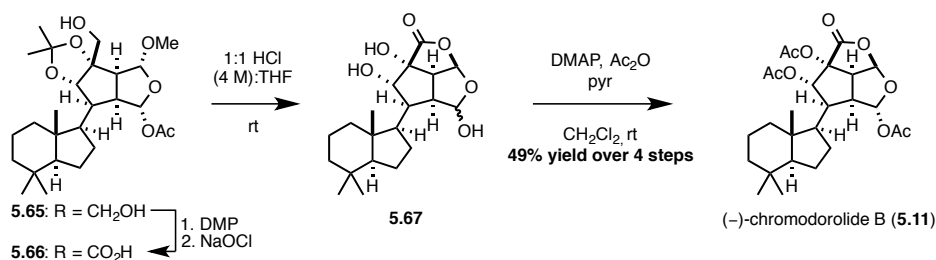
13.7, 4.4 Hz, 1H), 0.93 (s, 3H), 0.90–0.85 (m, 1H), 0.84 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.5, 151.8, 137.5, 128.6, 128.4, 128.1, 125.0, 113.3, 107.8, 99.7, 90.2, 85.9, 73.8, 70.5, 50.9, 47.6, 43.3, 42.1, 36.8, 35.6, 33.3, 33.0, 31.7, 30.6, 29.7, 29.0, 24.8, 22.8, 21.3, 21.2, 20.1, 17.2, 14.3; $[\alpha]^{25}_{\text{D}} -46.3$ ($c = 2.1$, CH_2Cl_2); IR (thin film) 2991, 2930, 2861, 1748, 1455, 1367 cm^{-1} ; HRMS (ESI) calculated for $\text{C}_{33}\text{H}_{46}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 577.3141, observed 577.3127.



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 $^\circ\text{C}$, 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). ^1H 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; $[\alpha]^{25}_{\text{D}} -17.6$ ($c = 1.7$, CH_2Cl_2); IR (thin film) 3490, 2951, 2931, 2873, 1745, 1459, 1368 cm^{-1} ; HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{42}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 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_2Cl_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.

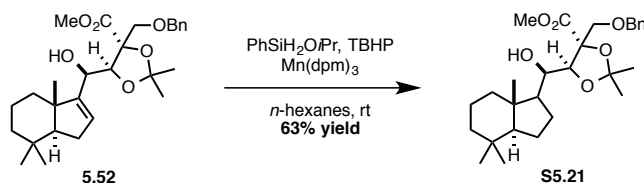
To a solution of aldehyde in THF (0.1 mL) was added *t*-BuOH (0.1 mL), H_2O (0.1 mL), 2-methyl-2-butene (50 μL), NaH_2PO_4 (25 mg, 0.21 mmol), and NaClO_2 (14 mg, 0.15 mmol). The reaction was maintained at 23 °C for 12 h and then diluted with H_2O (1 mL). The

solution was washed with EtOAc (3 x 1 mL); and the combined organic layers were dried over Na₂SO₄, 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 H₂O (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 Na₂SO₄, filtered, and concentrated *in vacuo* to afford crude lactol **5.67**.

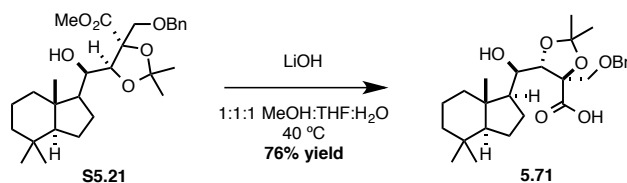
Crude lactol **5.67** was then dissolved in CH₂Cl₂ (0.3 mL). Next, DMAP (2 mg, 0.019 mmol) and pyridine (31 μL, 0.38 mmol) were added, followed by Ac₂O (28 μL, 0.29 mmol). The reaction was maintained at 23 °C for 24 h, at which point it was diluted with H₂O (2 mL), and the heterogeneous solution was washed with EtOAc (3 x 2 mL). The combined organic layers were washed with brine (1 x 3 mL), dried over Na₂SO₄, 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} [α]²⁵_D -66.8 (*c* = 0.12, CH₂Cl₂) compared to isolation sample [α]²⁵_D -95 (*c* = 0.10, CH₂Cl₂)^{16b}; IR (thin film) 2948, 2876, 1813, 1752, 1370, 1214, 1093, 1000, 964 cm⁻¹; HRMS (ESI) calculated for C₂₆H₃₆O₉Na (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

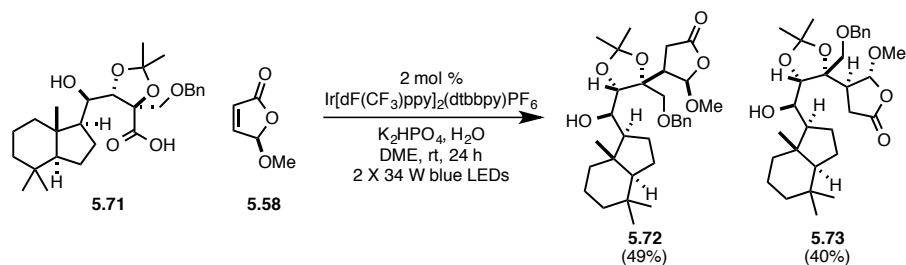


Preparation of alcohol S5.21: A 4 mL scintillation vial was charged with **5.52** (130 mg, 0.275 mmol), followed by the addition of *n*-hexanes (0.55 mL, 0.5 M). To this stirring solution, $\text{PhSiH}_2\text{OiPr}$ (69 mg, 0.41 mmol), and a solution of TBHP in hexanes (75 μL mL of 5.5 M soln, 0.41 mmol) were added and the resulting mixture was degassed by sparging with argon for 10 min. Next, $\text{Mn}(\text{dpm})_3$ (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} ; $[\alpha]^{23}_{\text{D}} +19.1$ ($c = 0.4$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{42}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 497.2879, observed 497.2855.

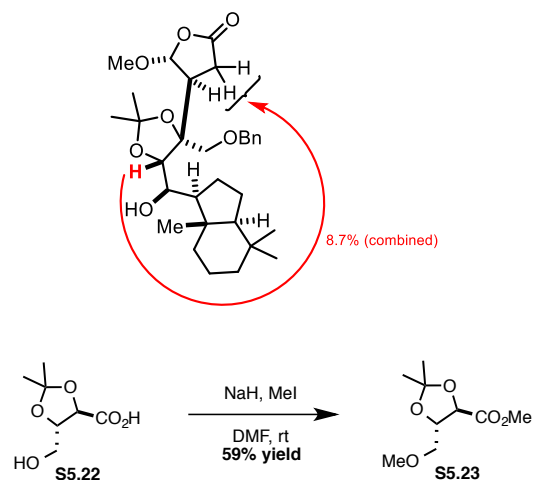


Preparation of carboxylic acid 5.71: A 20 mL scintillation vial was charged with ester **S5.21** (76 mg, 0.16 mmol), followed by the addition of 1:1:1 MeOH:THF:H₂O (4.9 mL, 0.033 M). Next, LiOH•H₂O (42 mg, 1.0 mmol) was added. The resulting heterogeneous mixture was stirred vigorously at 40 °C for 72 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 MgSO₄, and evaporated under reduced pressure to yield acid **5.71** as a clear oil (55 mg, 0.12 mmol, 76% yield). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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} ; $[\alpha]^{23}_{\text{D}} +27.8$ ($c = 2.7$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{40}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 483.2722, observed 483.2706.



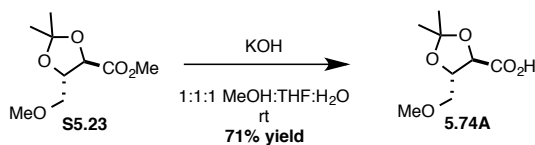
Preparation of lactones 5.72 and 5.73: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.71** (32 mg, 0.070 mmol), K₂HPO₄ (13 mg, 0.77 mmol), and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed 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 MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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} ; $[\alpha]_{\text{D}}^{23} +12.17$ ($c = 1.2$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{31}\text{H}_{46}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 553.3141, observed 553.3146.

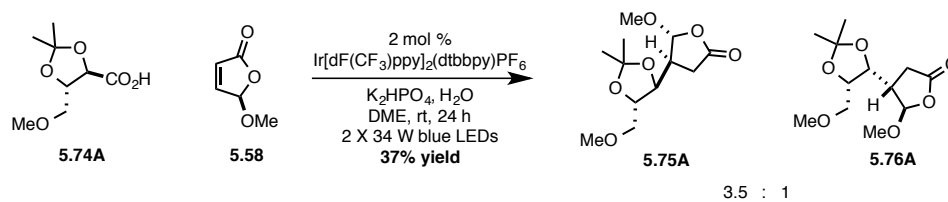


Preparation of methyl ester S5.23: A solution of **S5.22**¹⁰⁰ (1.06 g, 5.57 mmol) in DMF (40 mL) was cooled to 0 °C, and methyl iodide (1.7 mL, 28 mmol) was added. NaH (60% dispersion in mineral oil, 0.234 g, 5.85 mmol) was then added at 0 °C, and the reaction vessel was allowed to slowly warm to 23 °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} ; $[\alpha]^{25}_{\text{D}} -15.5$ ($c = 2.5$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_9\text{H}_{16}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) 227.0895, observed 227.0900.



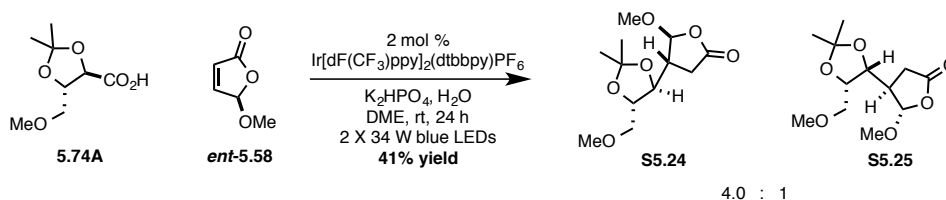
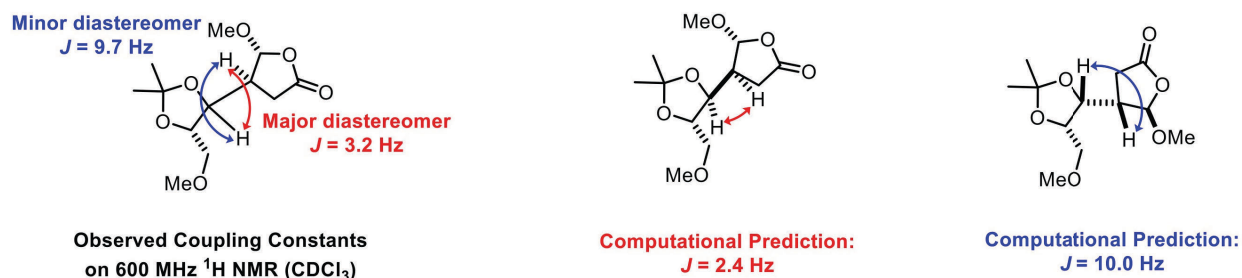
Preparation of carboxylic acid 5.74A: Ester **S5.23** (0.104 g, 0.509 mmol) was dissolved in 1:1:1 THF:H₂O:MeOH (1.5 mL), and KOH pellets (43 mg, 0.76 mmol) were added. The resulting homogeneous solution was maintained at 23 °C for 3 h before Et₂O (2 mL) and H₂O (2 mL) were added. The resulting organic 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 Na₂SO₄. Concentration *in vacuo* afforded acid **5.74A** (69 mg, 0.36 mmol, 71% yield) as a clear oil. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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} ; $[\alpha]^{25}_{\text{D}} -1.2$ ($c = 4.2$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_8\text{H}_{14}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) 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 μ L, 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 $^{\circ}$ C. The reaction mixture was filtered through $MgSO_4$, and evaporated under reduced pressure. 1H 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). 1H 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.

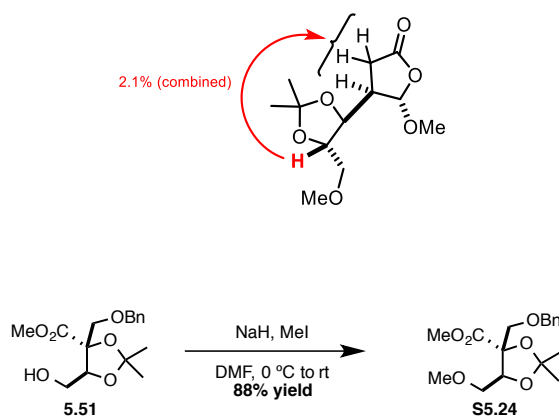
1H NMR NOE studies were unsuccessful to assign diastereomers **5.75A** and **5.76A**. The distinctive vicinal coupling constant of the methine hydrogens noted below was 3.2 Hz

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.).



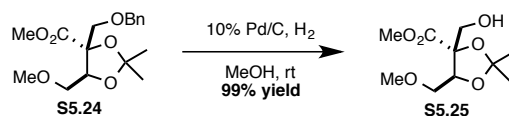
Preparation of lactones S5.24 and S5.25: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74A** (18 mg, 0.094 mmol), K_2HPO_4 (18 mg, 0.10 mmol), and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (2 mg, 0.002 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 $^\circ\text{C}$. The reaction mixture was filtered through MgSO_4 , and evaporated under reduced pressure. ^1H 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). ^1H 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} ; $[\alpha]^{25}_{\text{D}} +51.0$ ($c = 1.0$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{20}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 283.1158, observed 283.1150.



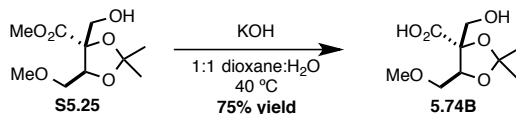
Preparation of methyl ether S5.24: A 25 mL round-bottom flask was charged with **5.51** (500 mg, 1.61 mmol), followed by the addition of DMF (11 mL, 0.15 M). The resulting mixture was cooled down to 0 °C. Next, the solution was treated with NaH (60% dispersion in mineral oil, 77 mg, 1.9 mmol). After 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 Et₂O (3 x 30 mL). The combined organic layers were washed with brine (1 x 100 mL), dried over MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]_D²³ -3.65 (*c* = 6.7, CH₂Cl₂); HRMS (ESI) calculated for C₁₇H₂₄O₆Na (M+Na) 347.1471, observed 347.1464.

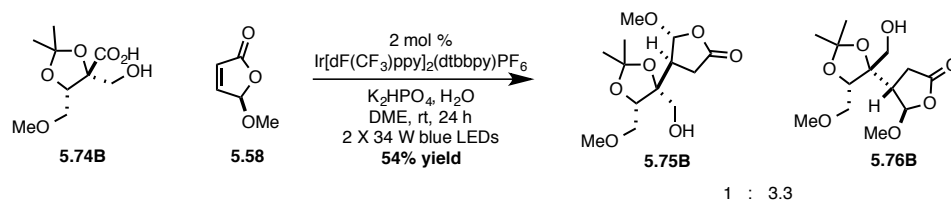


Preparation of alcohol S5.25: A 4 mL scintillation vial was charged with ester **S5.24** (200 mg, 0.616 mmol), followed by the addition of MeOH (1.8 mL, 0.14 M). Next, 10% Pd/C (200 mg) was added. The reaction vessel was then evacuated and refilled with Ar (3x). The heterogeneous mixture was then treated 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, CDCl₃) 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); ¹³C NMR

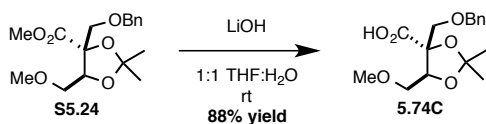
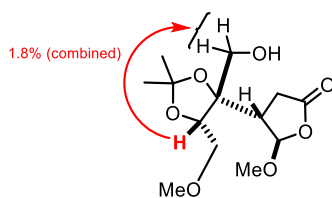
(126 MHz, CDCl₃) δ 172.1, 110.7, 84.7, 78.5, 70.3, 63.7, 59.8, 53.1, 27.9, 25.4; IR (thin film) 3472, 2938, 1741, 1383, 1098 cm⁻¹; [α]²¹_D -4.44 (*c* = 3.4, CH₂Cl₂); HRMS (ESI) calculated for C₁₀H₁₈O₆Na (M+Na) 257.1001, observed 257.0997.



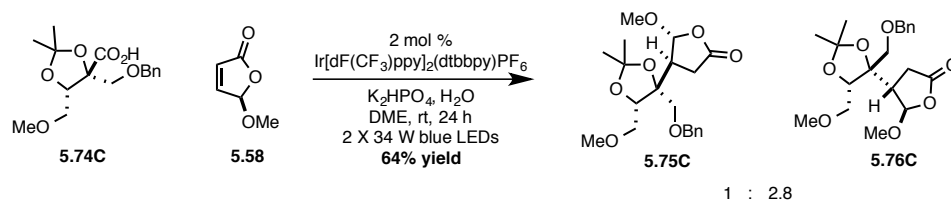
Preparation of carboxylic acid 5.74B: A 4 mL scintillation vial was charged with ester **S5.25** (80 mg, 0.34 mmol), followed by the addition of 1:1 dioxane:H₂O (2 mL, 0.17 M). Next, KOH (76 mg, 1.4 mmol) was added. The resulting biphasic mixture was stirred vigorously at 40 °C for 18 h. Upon allowing 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 MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²¹_D +3.69 (*c* = 1.9, CH₂Cl₂); HRMS (ESI) calculated for C₉H₁₆O₆Na (M+Na) 243.0845, observed 243.0845.



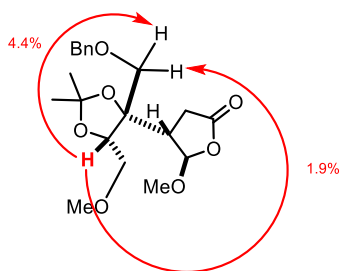
Preparation of lactones 5.75B and 5.76B: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with acid **5.74B** (16 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 μ L, 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 1:3.3 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). 1H 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_2Cl_2); HRMS (ESI) calculated for $C_{13}H_{22}O_7Na$ ($M+Na$) 313.1263, observed 313.1262.



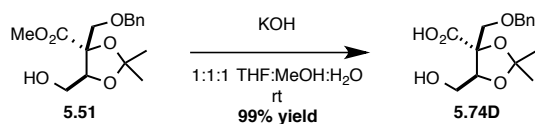
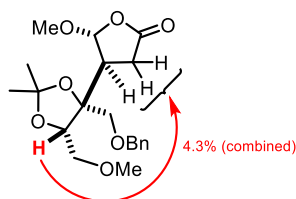
Preparation of carboxylic acid 5.74C: A 4 mL scintillation vial was charged with ester **S5.24** (100 mg, 0.308 mmol), followed by the addition of 1:1 THF:H₂O (1.8 mL, 0.17 M). Next, LiOH•H₂O (26 mg, 0.62 mmol) was added. The resulting biphasic mixture was stirred vigorously at 23 °C for 18 h. The reaction 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 MgSO₄, and evaporated under reduced pressure to yield acid **5.74C** (84 mg, 0.27 mmol, 88% yield) as a clear oil. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D +10.4 (*c* = 3.0, CH₂Cl₂); HRMS (ESI) calculated for C₁₆H₂₂O₆Na (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 μ L, 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 $^{\circ}C$. 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 1:2.8 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). 1H 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} ; $[\alpha]_D^{23}$ -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.

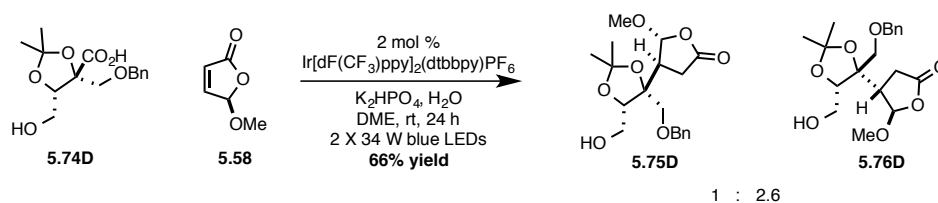


^1H NMR for minor diastereomer **5.75C** (500 MHz, CDCl_3) δ 7.38–7.28 (m, 5H), 5.41 (d, J = 2.5 Hz, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 3.92 (dd J = 7.5, 3.5 Hz, 1 H), 3.61 (dd, J = 10.5, 3.5 Hz, 1H), 3.58–3.55 (m, 1H), 3.52–3.50 (m, 1H), 3.46 (s, 3H), 3.35 (s, 3H), 3.30 (d, J = 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} ; $[\alpha]^{23}_{\text{D}}$ -19.4 (c = 0.4, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{28}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 403.1733, observed 403.1740.



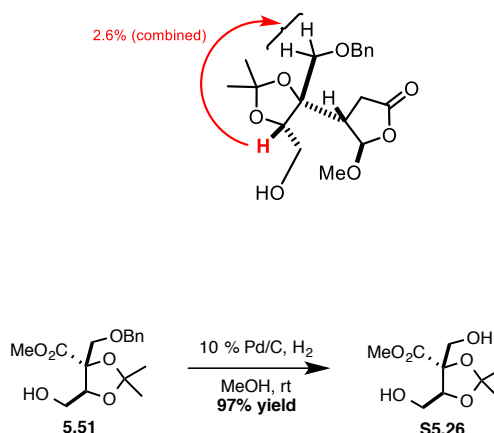
Preparation of carboxylic acid 5.74D: A 4 mL scintillation vial was charged **5.51** (200 mg, 0.644 mmol), followed by the addition of 1:1:1 THF:MeOH:H₂O (2.0 mL, 0.32 M). Next, KOH (72 mg, 1.3 mmol) was added. The resulting biphasic mixture was stirred vigorously

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 MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²²_D +9.53 (*c* = 4.3, CH₂Cl₂); HRMS (ESI) calculated for C₁₅H₂₀O₆Na (M+Na) 319.1158, observed 319.1157.



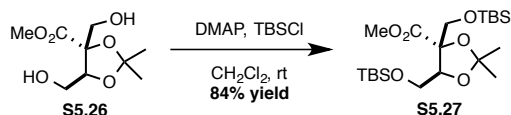
Preparation of lactones 5.75D and 5.76D: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74D** (21 mg, 0.070 mmol), K₂HPO₄ (13 mg, 0.77 mmol), and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, 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 MgSO₄, 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). ^1H 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} ; $[\alpha]^{22}_{\text{D}} -21.7$ ($c = 1.7$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{26}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 389.1576, observed 389.1576.

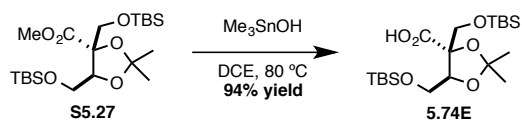


Preparation of diol S5.26: A reaction vessel was charged with methyl **5.51** (0.250 g, 0.806 mmol) and 10% Pd/C (0.200 g). The vessel was then evacuated and refilled with Ar (3X) before MeOH (4 mL) was added followed by formic acid (0.2 mL). The suspension was then vigorously stirred for 4 h at 23 °C 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). ^1H 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, $J = 12.3, 5.1$

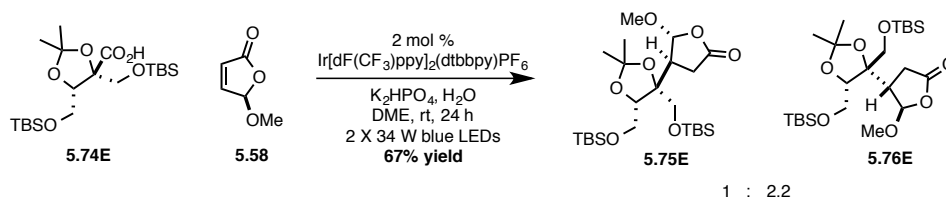
Hz, 1H), 3.84–3.77 (m, 2H), 3.81 (s, 3H), 2.97 (bs, 1H), 2.82 (bs, 1H), 1.50 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.4, 110.4, 84.5, 79.4, 63.5, 60.2, 53.1, 27.8, 25.3; IR (thin film) 3426, 2990, 2954, 2886, 1742, 1457, 1438, 1384 cm^{-1} ; $[\alpha]^{25}_{\text{D}}$ +6.1 ($c = 2.6$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_9\text{H}_{16}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 243.0845, 243.0842.



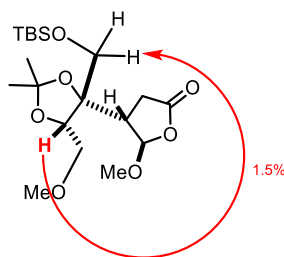
Preparation of ester S5.27: To a solution of ester **S5.26** (0.108 g, 0.490 mmol) in CH_2Cl_2 (2.5 mL) at 23 °C was added imidazole (0.167 g, 2.45 mmol) followed by DMAP (3 mg, 0.03 mmol) and then TBSCl (0.222 g, 1.47 mmol). The reaction was maintained for 2 h before quenching with H_2O (2 mL), and 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). ^1H 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} ; $[\alpha]^{22}_{\text{D}}$ -7.84 ($c = 4.0$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{44}\text{O}_6\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) 471.2574, observed 471.2574.



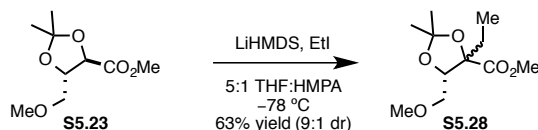
Preparation of carboxylic acid 5.74E: The procedure for the preparation of **5.74E** was a slight modification from the literature procedure.^{65b} A 4 mL scintillation vial was charged with ester **S5.27** (80 mg, 0.18 mmol), followed by the addition of DCE (1.1 mL, 0.16 M). Next, Me_3SnOH (225 mg, 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). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{22}_{\text{D}} +2.70$ ($c = 1.3, \text{CH}_2\text{Cl}_2$); HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{42}\text{O}_6\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) 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 μ L, 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.

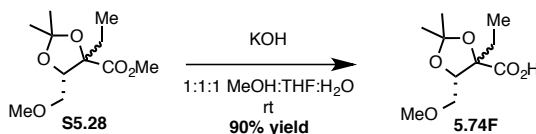


^1H NMR for minor diastereomer **5.75E** (600 MHz, CDCl_3) δ 5.43 (d, $J = 3.0$ Hz, 1H), 3.92 (d, $J = 2.4$ Hz, 1H), 3.80–3.75 (m, 2H), 3.73 (d, $J = 10.2$ Hz, 1H), 3.46 (s, 3H), 3.41 (d, $J = 10.2$, 1H), 2.83 (t, $J = 2.0$ Hz, 1H), 2.69 (dd, $J = 17.4, 9.0$ Hz, 1H), 2.58 (dd, $J = 17.4, 6.0$ Hz, 1H), 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} ; $[\alpha]^{23}_{\text{D}} -19.7$ ($c = 0.7$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{48}\text{O}_7\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) 527.2836, observed 527.2825.



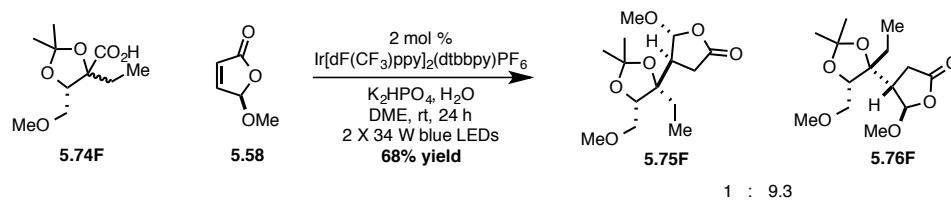
Preparation of ester S5.28: Ester **S5.23** (0.151 g, 0.739 mmol) was dissolved in a mixture of THF (3 mL) and HMPA (0.6 mL). The solution was then cooled to -78°C , and ethyl iodide (0.24 mL, 3.0 mmol) was added followed by LiHMDS (0.8 mL of 1.0 M soln in THF, 0.8 mmol). The reaction was maintained 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). ^1H 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} ; $[\alpha]^{25}_{\text{D}} +10.1$ ($c = 1.7$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{20}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) 255.1208, observed 255.1218.



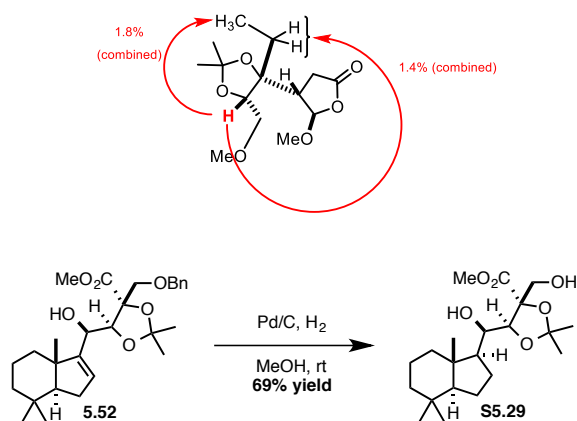
Preparation of acid 5.74F: Ester **S5.28** (59 mg, 0.25 mmol) was dissolved in 1:1:1 MeOH:THF:H₂O (0.9 mL), and KOH pellets (29 mg, 0.51 mmol) were added to the solution. The reaction was maintained at 23 °C for 14 h, at which point the reaction was diluted with H₂O (1 mL) and Et₂O (1 mL). The aqueous layer was washed with Et₂O (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 MgSO₄, 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). ^1H 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, CDCl₃) 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; $[\alpha]^{25}_D +37.8$ ($c = 1.1$, CH₂Cl₂); HRMS (ESI) calculated for C₁₀H₁₈O₅Na (M+Na) 241.1052, observed 241.1054.



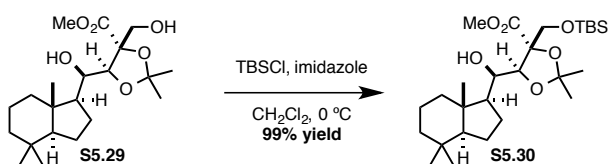
Preparation of lactones 5.75F and 5.76F: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.74F** (20 mg, 0.092 mmol), K₂HPO₄ (18 mg, 0.10 mmol), and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2 mg, 0.002 mmol). Next, DME (0.9 mL, 0.1 M) was added, followed by water (17 μ L, 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 MgSO₄, 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, CDCl₃) 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} ; $[\alpha]_D^{25}$ -17.7 ($c = 1.0$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{14}\text{H}_{24}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 311.1471, observed 311.1474; mp 105–113 $^\circ\text{C}$.

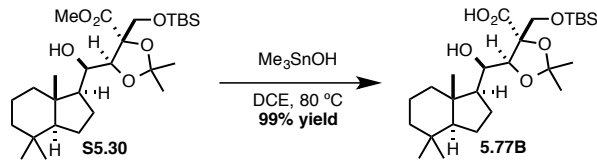


Preparation of diol **5.5.29:** To a suspension of 10% Pd/C (0.207 g, 0.195 mmol) in MeOH (4 mL) was added **5.52** (0.230 g, 0.487 mmol) in a solution of MeOH (0.5 mL). The reaction vessel was then evacuated and refilled with H_2 (3X). The reaction was then vigorously stirred at 23 $^\circ\text{C}$ 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 **5.5.29** 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). ^1H 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,

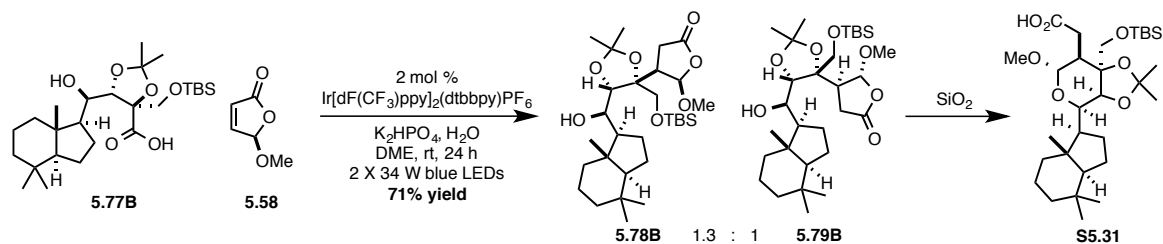
42.3, 41.4, 39.6, 33.6, 33.2, 27.8, 25.6, 25.3, 20.9, 20.6, 19.9, 13.7; IR (thin film) 3415, 2985, 2963, 2875, 1739, 1457 cm^{-1} ; $[\alpha]^{25}_{\text{D}} +40.1$ ($c = 1.3$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{21}\text{H}_{36}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 407.2410, observed 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 $0\text{ }^\circ\text{C}$ was added imidazole (85 mg, 1.3 mmol), followed by TBSCl (94 mg, 0.62 mmol). The reaction was stirred at $0\text{ }^\circ\text{C}$ 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} ; $[\alpha]^{25}_{\text{D}} +23.0$ ($c = 2.9$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{50}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) 521.3275, observed 521.3280.



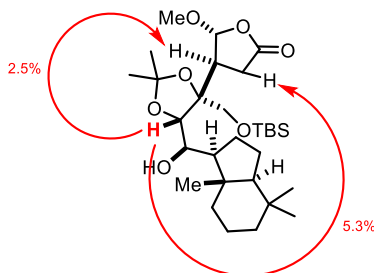
Preparation of carboxylic acid 5.77B: The procedure for the preparation of **5.77B** was a slight modification from the literature procedure.^{65b} A 4 mL scintillation vial was charged with ester **S5.30** (94 mg, 0.19 mmol), followed by the addition of DCE (1.2 mL, 0.16 M). Next, Me₃SnOH (170 mg, 0.94 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 CH₂Cl₂ (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 MgSO₄, 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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D +24.4 (c = 2.0, CH₂Cl₂); HRMS (ESI) calculated for C₂₆H₄₈O₆SiNa (M+Na) 507.3118, observed 507.3131.



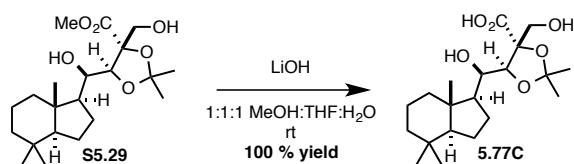
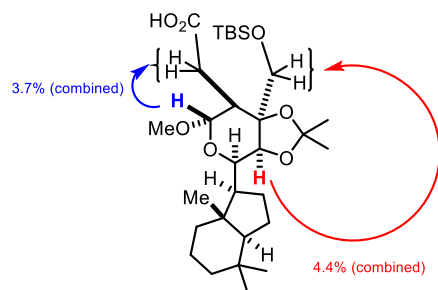
Preparation of lactone 5.78B and acid S5.31: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77B** (32 mg, 0.067 mmol), K₂HPO₄ (13 mg, 0.77 mmol), and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, 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 MgSO₄, and evaporated under reduced pressure. ¹H 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 SiO₂-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).

¹H NMR for major diastereomer **5.78B** (500 MHz, CDCl₃) 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

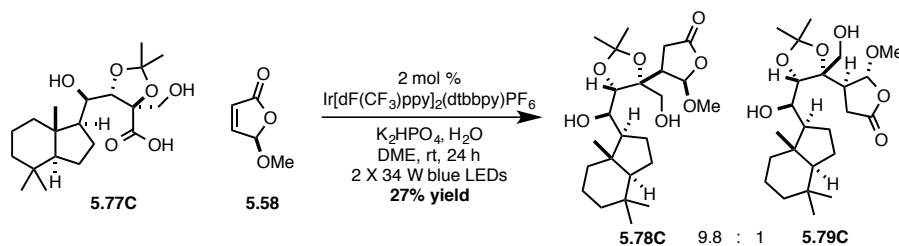
(s, 9H), 0.85 (s, 3H), 0.84 (s, 3H), 0.75 (s, 3H), 0.10 (s, 6H); ^{13}C NMR for major diastereomer **5.78B** (126 MHz, CDCl_3) δ 175.3, 108.3, 106.3, 82.3, 81.3, 67.6, 62.3, 58.4, 57.0, 55.8, 44.4, 42.1, 41.4, 40.0, 33.6, 33.2, 30.0, 28.9, 27.0, 25.8, 24.9, 20.9, 20.6, 19.9, 18.2, 14.3, -5.6, -5.8; IR (thin film) 3568, 2953, 2929, 2858, 1794, 1463, 1382 cm^{-1} ; $[\alpha]^{25}_{\text{D}}$ -1.7 ($c = 2.5$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{54}\text{O}_7\text{SiNa}$ ($\text{M}+\text{Na}$) 577.3536, observed 577.3520.



^1H 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} ; $[\alpha]^{25}_{\text{D}}$ +45.1 ($c = 1.2$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{54}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 577.3536, observed 577.3536.

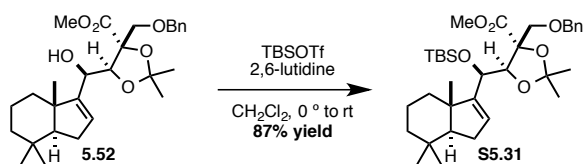
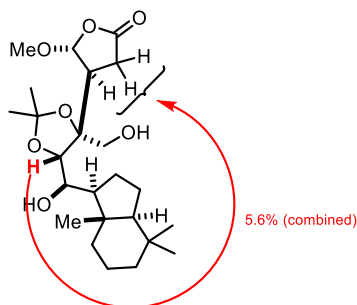


Preparation of carboxylic acid 5.77C: A 20mL scintillation vial was charged with ester **S5.29** (82 mg, 0.21 mmol), followed by the addition of 1:1:1 MeOH:THF:H₂O (3.6 mL, 0.06 M). Next, LiOH•H₂O (18 mg, 0.42 mmol) was added. The resulting heterogeneous mixture was stirred vigorously at 23 °C for 18 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 MgSO₄, and evaporated under reduced pressure to yield acid **5.77C** as a clear oil (77 mg, 0.21 mmol, 100% yield). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; [α]²³_D +22.6 (c = 1.7, CH₂Cl₂); HRMS (ESI) calculated for C₂₀H₃₄O₆Na (M+Na) 393.2253, observed 393.2256.



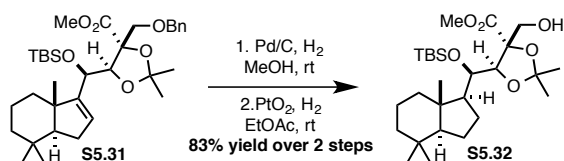
Preparation of lactones 5.78C and 5.79C: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77C** (25 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $\text{Ir[dF(CF}_3\text{)ppy]}_2\text{(dtbbpy)PF}_6$ (1.6 mg, 0.0014 mmol). Next, DME (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 $^\circ\text{C}$. The reaction mixture was filtered through MgSO_4 , and evaporated under reduced pressure. ^1H 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 gel⁹⁷ (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). ^1H 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} ; $[\alpha]^{25}_{\text{D}} +37.0$ ($c = 0.7$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{24}\text{H}_{40}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 463.2672, observed 463.2667.



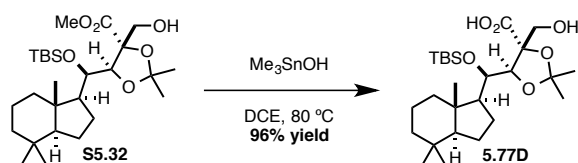
Preparation of ester S5.31: To a solution at 0°C of **5.52** (0.132 g, 0.279 mmol), in CH_2Cl_2 (2 mL), and 2,6-lutidine (0.10 mL, 1.1 mmol) was added TBSOTf (160 μL , 0.56 mmol). The reaction was maintained at 0°C for 15 min before allowing to warm to 23°C for 6 h, at which point H_2O (1 mL) was added 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} ; $[\alpha]^{25}_{\text{D}}$ -27.9 ($c = 2.2$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{34}\text{H}_{54}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) 609.3588, observed 609.3602.



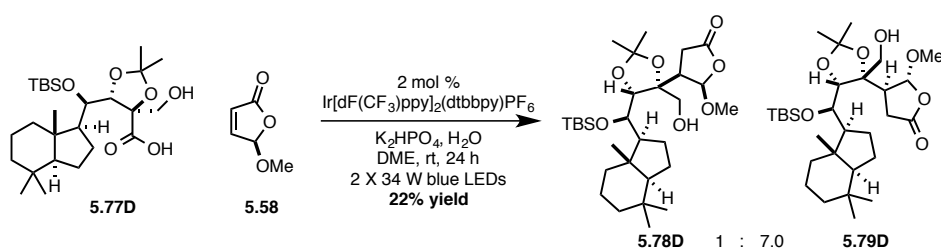
Preparation of alcohol S5.32: Ester **S5.31** (32 mg, 0.055 mmol) and 10% Pd/C (12 mg, 0.011 mmol) were charged into a flask with MeOH (1.0 mL). The reaction vessel was then evacuated and refilled with H_2 (3x). The reaction was then vigorously stirred at 23 °C for 12 h, at which point the reaction vessel 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). ^1H 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} ; $[\alpha]^{25}_{\text{D}} +23.7$ ($c = 1.4$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{50}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) 521.3275, observed 521.3281.



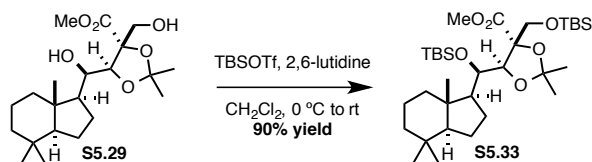
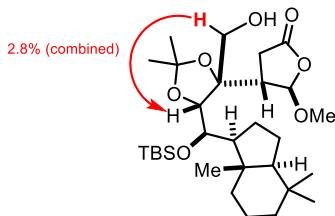
Preparation of carboxylic acid 5.77D: The procedure for the preparation of **5.77D** was a slight modification from the literature procedure.^{65b} To a solution of ester **5.32** (61 mg, 0.12 mmol) in DCE (0.5 mL) was added Me_3SnOH (0.110 g, 0.608 mmol). The heterogeneous mixture was then heated to 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_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 **5.77D** was obtained (57 mg, 0.12 mmol, 96% yield) as a colorless solid. ^1H 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} ; $[\alpha]^{25}_{\text{D}} +32.7$ ($c = 1.0$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{48}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) 507.3118, observed 507.3113.



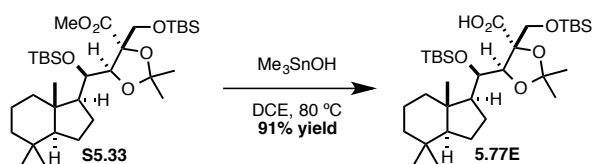
Preparation of lactones 5.78D and 5.79D: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77D** (32 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (1.6 mg, 0.0014 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 $^\circ\text{C}$. The reaction mixture was filtered through MgSO_4 , and evaporated under reduced pressure. ^1H 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). ^1H 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} ; $[\alpha]_{\text{D}}^{25} +11.7$ ($c = 0.7, \text{CH}_2\text{Cl}_2$); HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{54}\text{O}_7\text{SiNa}$ ($\text{M}+\text{Na}$) 577.3536, observed 577.3541.



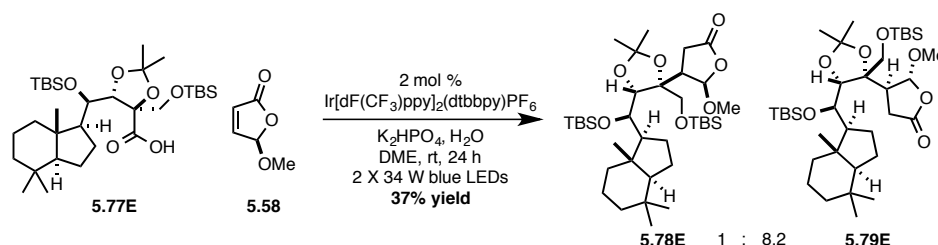
Preparation of ester S5.33: To a solution of **S5.29** (0.117 g, 0.304 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added 2,6-lutidine (170 μL , 1.8 mmol) followed by TBSOTf (260 μL , 0.91 mmol). The reaction was then allowed to warm to 23 °C over 12 h before H_2O (2 mL) was added. Celite (3 g) was then added 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). ^1H 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} ; $[\alpha]_{\text{D}}^{25} +24.4$ ($c = 1.2$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{33}\text{H}_{64}\text{O}_6\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) 635.4139, observed 635.4146.



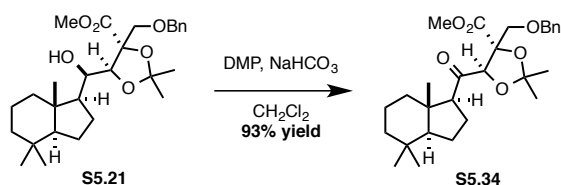
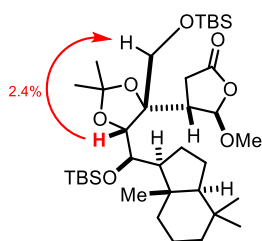
Preparation of carboxylic acid 5.77E: The procedure for the preparation of **5.77E** was a slight modification from the literature procedure.^{65b} To a solution of ester **5.33** (0.122 g, 0.199 mmol) in DCE (1.2 mL) was added Me_3SnOH (0.252 g, 1.39 mmol). The heterogeneous mixture was then heated 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_2Cl_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_2SO_4 . Upon concentration *in vacuo*, acid **5.77E** was obtained (0.109 g, 0.182 mmol, 91% yield) as a colorless foam. ^1H 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} ; $[\alpha]_D^{25} +31.6$ ($c = 2.5$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{32}\text{H}_{62}\text{O}_6\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) 621.3983, observed 621.3972.



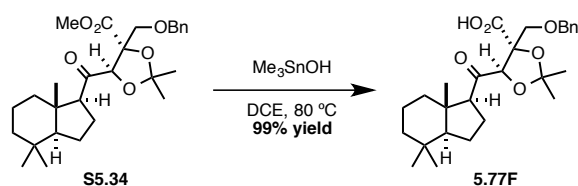
Preparation of lactones 5.78E and 5.79E: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77E** (40 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (1.6 mg, 0.0014 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 $^\circ\text{C}$. The reaction mixture was filtered through MgSO_4 , and evaporated under reduced pressure. ^1H 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). ^1H 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} ; $[\alpha]^{25}_{\text{D}} +10.2$ ($c = 1.6, \text{CH}_2\text{Cl}_2$); HRMS (ESI) calculated for $\text{C}_{36}\text{H}_{68}\text{O}_7\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) 691.4401, observed 691.4407.



Preparation of ketone S5.34: To a stirring suspension of alcohol **S5.21** (10 mg, 0.02 mmol) and NaHCO₃ (7 mg, 0.08 mmol) in CH₂Cl₂ (0.4 mL) was added Dess-Martin periodinane (12 mg, 0.03 mmol). After 2 h, the reaction mixture was diluted with Et₂O (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). ^1H 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} ; $[\alpha]^{25}_{\text{D}} +63.8$ ($c = 0.8$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{28}\text{H}_{40}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 495.2722, observed 495.2704.



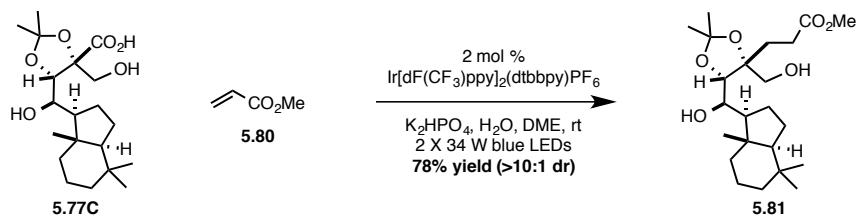
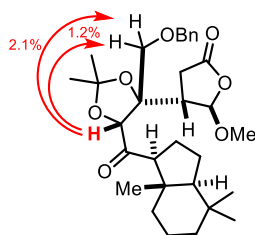
Preparation of carboxylic acid 5.77F: The procedure for the preparation of **5.77F** was a slight modification from the literature procedure.^{65b} To a solution of ester **5.34** (32 mg, 0.068 mmol) in DCE (0.7 mL) was added Me_3SnOH (61 mg, 0.34 mmol). The heterogeneous mixture was then heated to 80 °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. ^1H 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,

CDCl₃) 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; [α]²⁵_D +63.3 (*c* = 0.8, CH₂Cl₂); HRMS (ESI) calculated for C₂₇H₃₈O₆Na (M+Na) 481.2566, observed 481.2562.



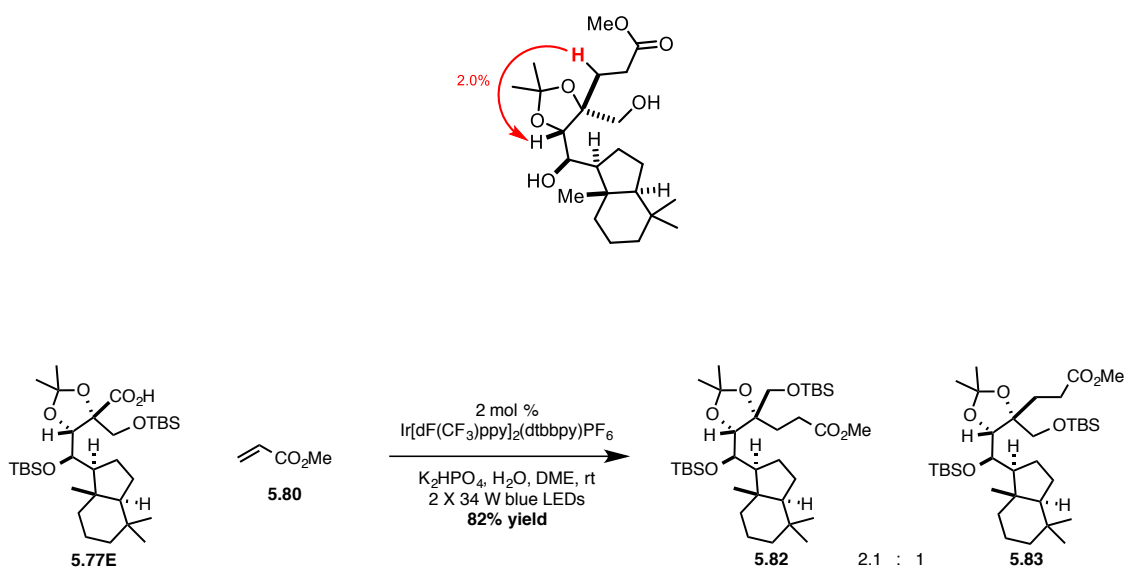
Preparation of lactones 5.78F and 5.79F: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77F** (31 mg, 0.067 mmol), K₂HPO₄ (13 mg, 0.77 mmol), and Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (1.6 mg, 0.0014 mmol). Next, DME (0.7 mL, 0.1 M) was added, followed by water (13 μ L, 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 MgSO₄, 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, CDCl₃) 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} ; $[\alpha]^{25}_{\text{D}}$ +54.9 ($c = 1.4$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{31}\text{H}_{44}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) 551.2985, observed 551.2964.



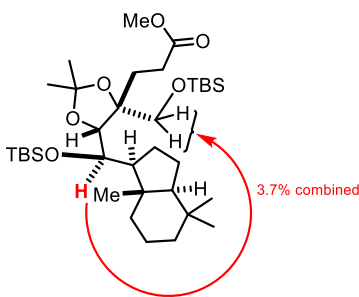
Preparation of ester 5.81: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77C** (26 mg, 0.070 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (1.6 mg, 0.0014 mmol). Next, 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 $^\circ\text{C}$. 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). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]_D^{23} +20.5$ ($c = 1.6$, CH_2Cl_2); HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{40}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) 435.2722, observed 435.2729.

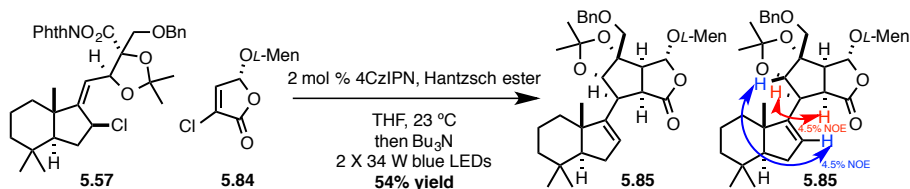


Preparation of esters 5.82 and 5.83: A 4 mL scintillation vial equipped with a Teflon septum and magnetic stir bar was charged with carboxylic acid **5.77E** (40 mg, 0.067 mmol), K_2HPO_4 (13 mg, 0.77 mmol), and $\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy})\text{PF}_6$ (1.6 mg, 0.0014 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 MgSO₄, 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, CDCl₃) 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); ¹³C NMR for major diastereomer **5.82** (126 MHz, CDCl₃) 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; [α]²⁵_D +30.8 (*c* = 2.5, CH₂Cl₂); HRMS (ESI) calculated for C₃₅H₆₈O₆Si₂Na (M+Na) 663.4452, observed 663.4431.

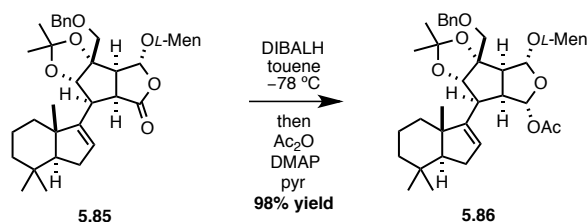


Experimental procedures for the second-generation synthesis of (-)-chromodorolide B



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), 4CzIPN⁸³ (2.4 mg, 0.003 mmol, 0.02 equiv), tetrahydrofuran (250 μ L, 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 Bu₃N (350 μ L, 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 Et₂O (15 mL). The solution was then sequentially washed with 1N HCl (aq) (10 mL), H₂O (10 mL), and brine (10 mL). The organic layer was dried over MgSO₄ and concentrated by use of a rotary evaporator. The

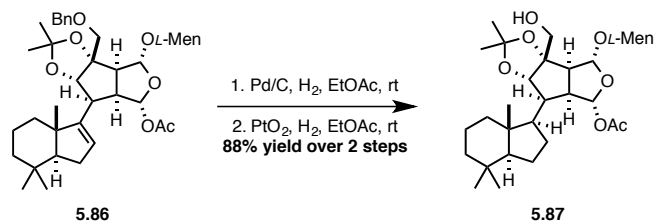
crude product was purified by flash column chromatography on silica gel using 0:100 ethyl acetate:hexanes \rightarrow 4:96 ethyl acetate:hexanes as eluent to yield the desired product **5.85** as a thick colorless foam (51 mg, 0.08 mmol, 54% yield): $R_f = 0.13$ (5:95 ethyl acetate:hexanes, stained with ceric ammonium molybdate). $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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} ; $[\alpha]^{21}_{\text{D}} -116$, $[\alpha]^{21}_{577} -119$, $[\alpha]^{21}_{546} -134$, $[\alpha]^{21}_{435} -225$ ($c = 0.15$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{40}\text{H}_{58}\text{O}_6$ $[\text{M}+\text{Na}]^+$ 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 $-78\text{ }^{\circ}\text{C}$. 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 $-78\text{ }^{\circ}\text{C}$. 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 $-78\text{ }^{\circ}\text{C}$ for 8 h, at which point it was allowed to warm to $23\text{ }^{\circ}\text{C}$. 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 \rightarrow 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). ^1H 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} ;

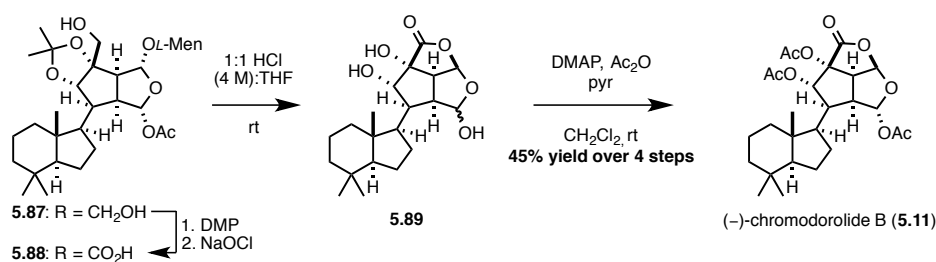
$[\alpha]^{21}_{\text{D}} -43.2$, $[\alpha]^{21}_{577} -47.3$, $[\alpha]^{21}_{546} -56.0$, $[\alpha]^{21}_{435} -92.3$ ($c = 0.2$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{42}\text{H}_{62}\text{O}_7$ $[\text{M}+\text{Na}]^+$ 701.4393; observed 701.4374.



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 H₂ (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), PtO₂ (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 H₂ (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, CDCl₃) 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} ; $[\alpha]^{22}_{\text{D}} -56.2$, $[\alpha]^{22}_{577} -57.2$, $[\alpha]^{22}_{546} -60.0$, $[\alpha]^{22}_{435} -105$ ($c = 0.1$, CHCl_3); HRMS (ESI/TOF) m/z calculated for $\text{C}_{35}\text{H}_{58}\text{O}_7$ $[\text{M}+\text{Na}]^+$ 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 H₂O (1 mL). The solution was washed with EtOAc (3 x 1 mL). The combined organic layers were dried over Na₂SO₄, 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 H₂O (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 Na₂SO₄, 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**, CH₂Cl₂ (0.4 mL, 0.06 M), DMAP (3 mg, 0.024 mmol, 1 equiv), pyridine (38 μL, 0.47 mmol, 20 equiv), Ac₂O (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 H₂O (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 Na₂SO₄, 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 TPSS⁷⁶ functional with def2-SVP or def2-TZVP basis sets⁸⁰ 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 sets¹⁰⁸ 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-D3¹¹¹ 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 PBE¹¹⁴ 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 ($G = E(0) + \text{c.p.}$), 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 accurately¹⁰⁷ and from first principles. In our preliminary study for radical **5.74D**, we also employed MP2/def2-QZVP to study the selectivity. The wavefunctions 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-pVXZ¹¹⁷ 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.

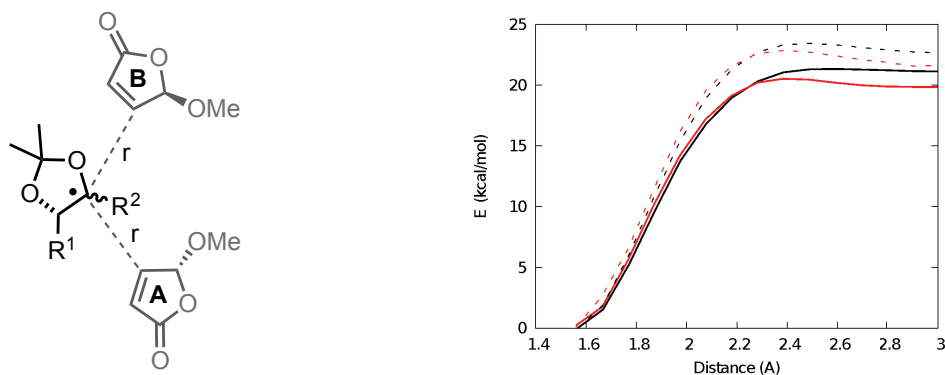
Basis set	$\Delta\Delta E(\mathbf{5.74A-anti} - \mathbf{5.74A-syn})$	$\Delta\Delta E(\mathbf{5.74C-anti} - \mathbf{5.74C-syn})$
def2-TZVP	0.12	3.26
cc-pVTZ	-0.08	3.01
cc-pVQZ	0.13	3.24
CBS(3,4)	0.13	3.30

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 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 C¹ and C², 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 sp³ carbon radicals. The Cartesian coordinates of C¹ and C² 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 C¹ and C² 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 were 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.

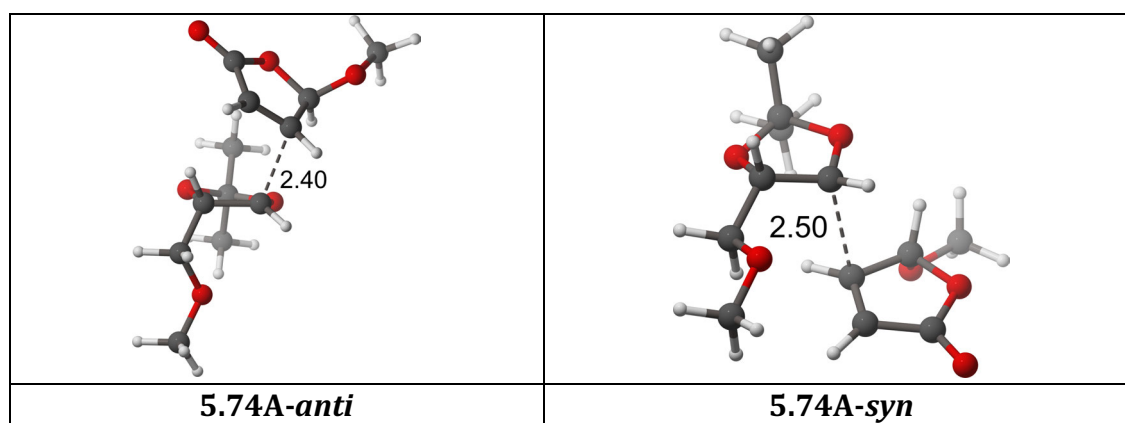
The effect of entropy on the selectivity can be assessed by comparing approaches (i) and (iii) (Table S5.3 and Table S5.5). In most cases, the correlation is still qualitative but

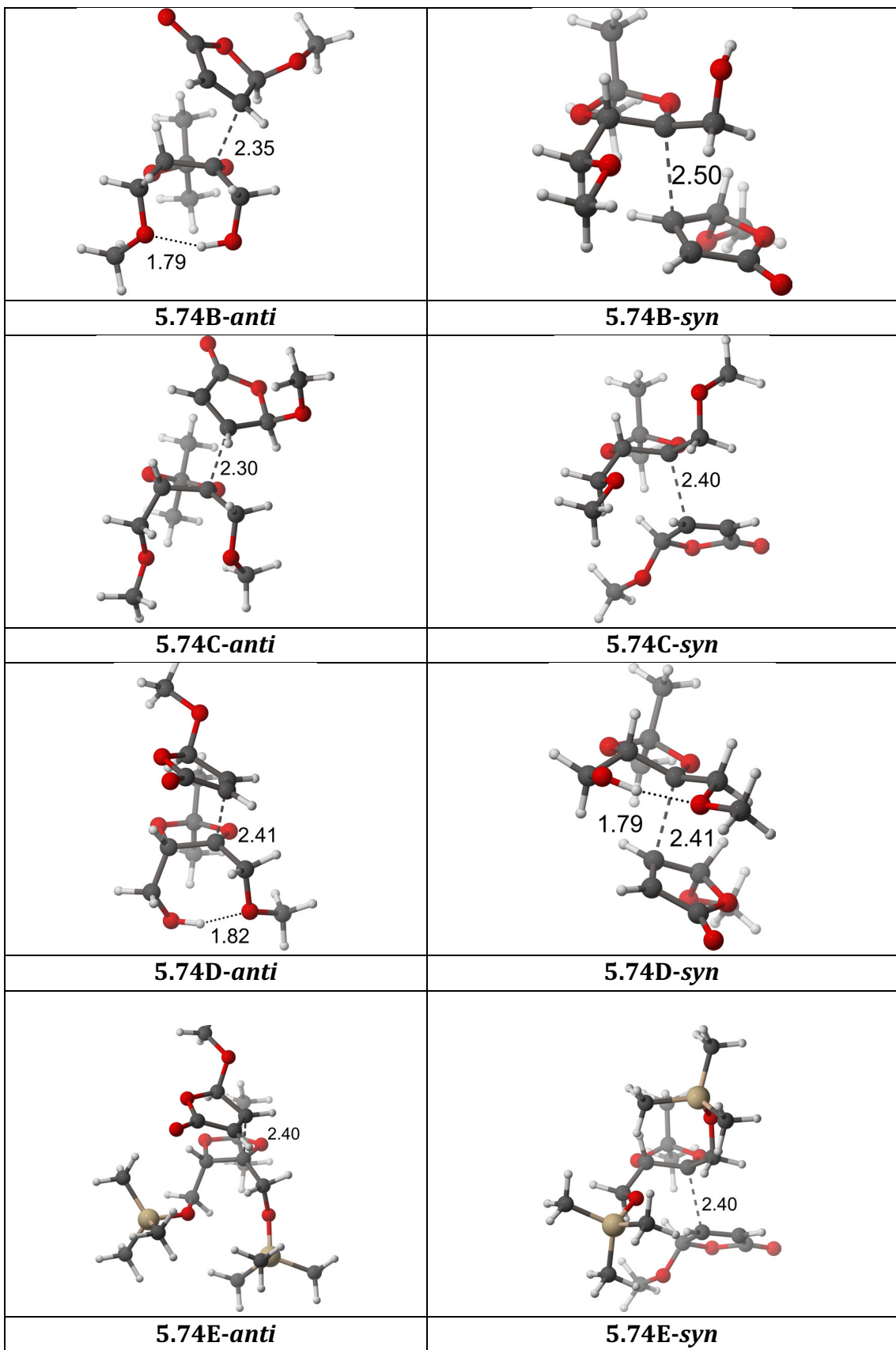
not quantitative for approach (i). Thus, the effect of entropy on these results is significant. The standard RRHO-approximation predicts too high entropies especially for larger complexes (5.77) with more low-lying frequencies whereas the smaller complexes (5.74) are not affected much.

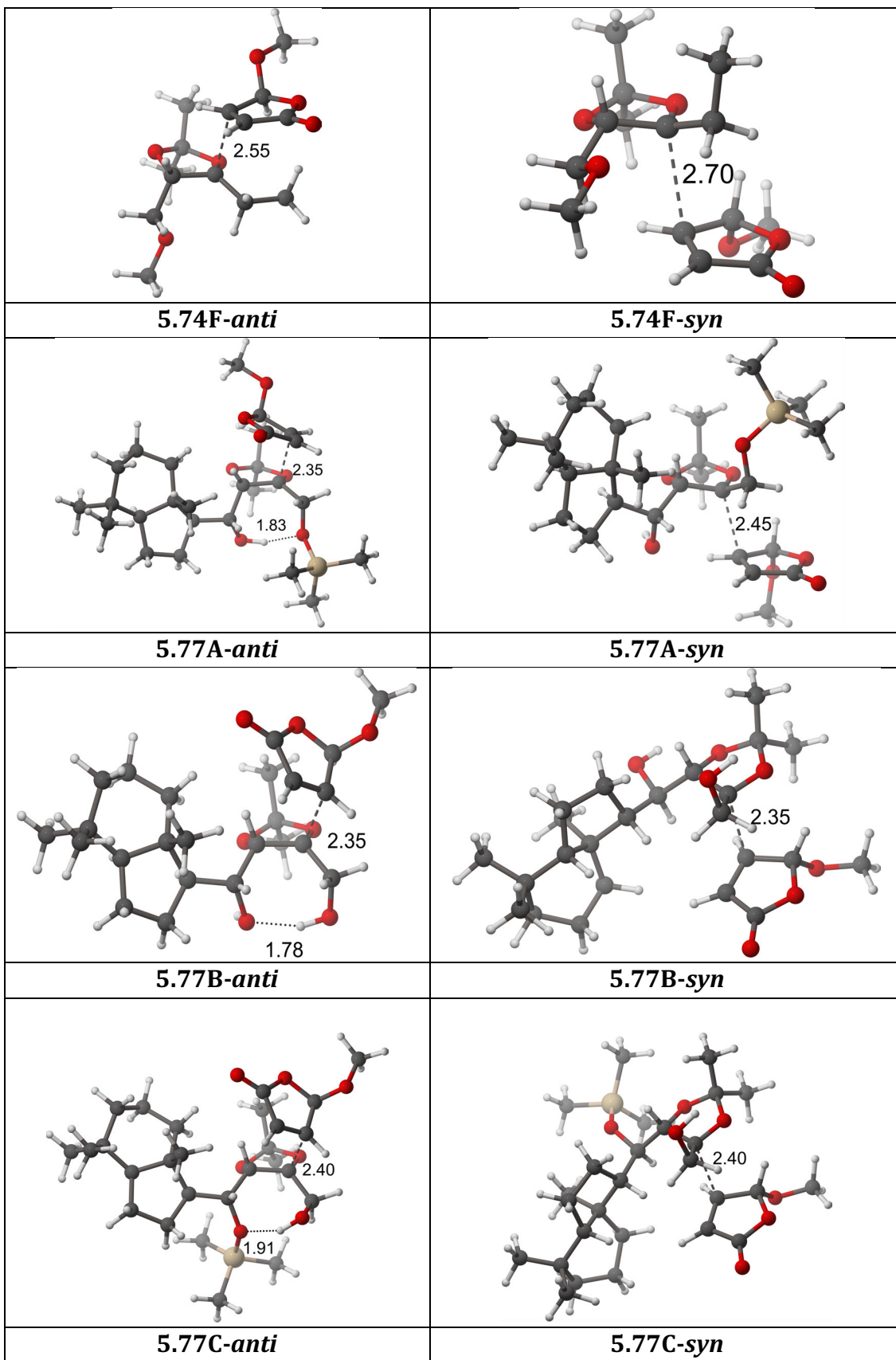
In summary, the selectivity of the radical addition can be computed with high accuracy if the following aspects are carefully taken into account: For large molecules, the conformational freedom causes much larger deviation to the energy than is needed to induce the selectivity. In addition, the computational 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.







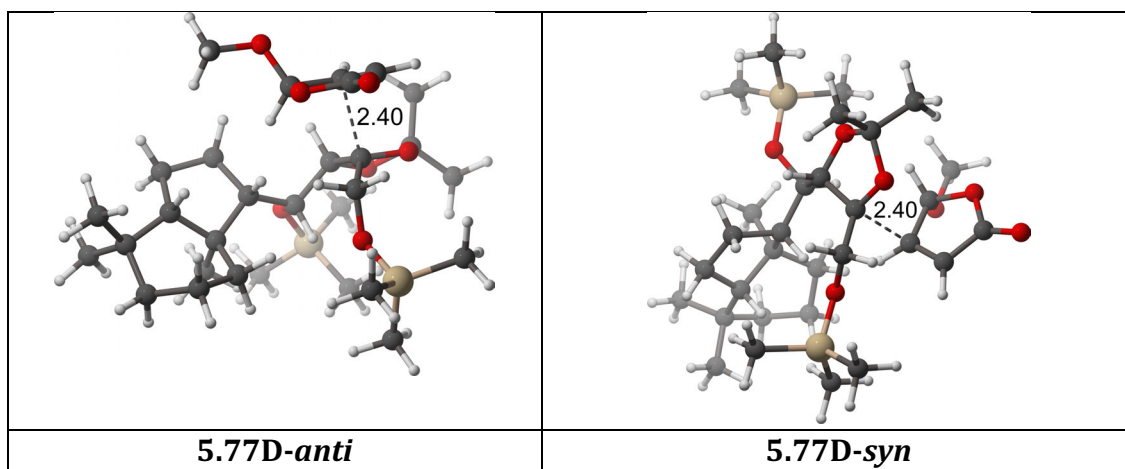
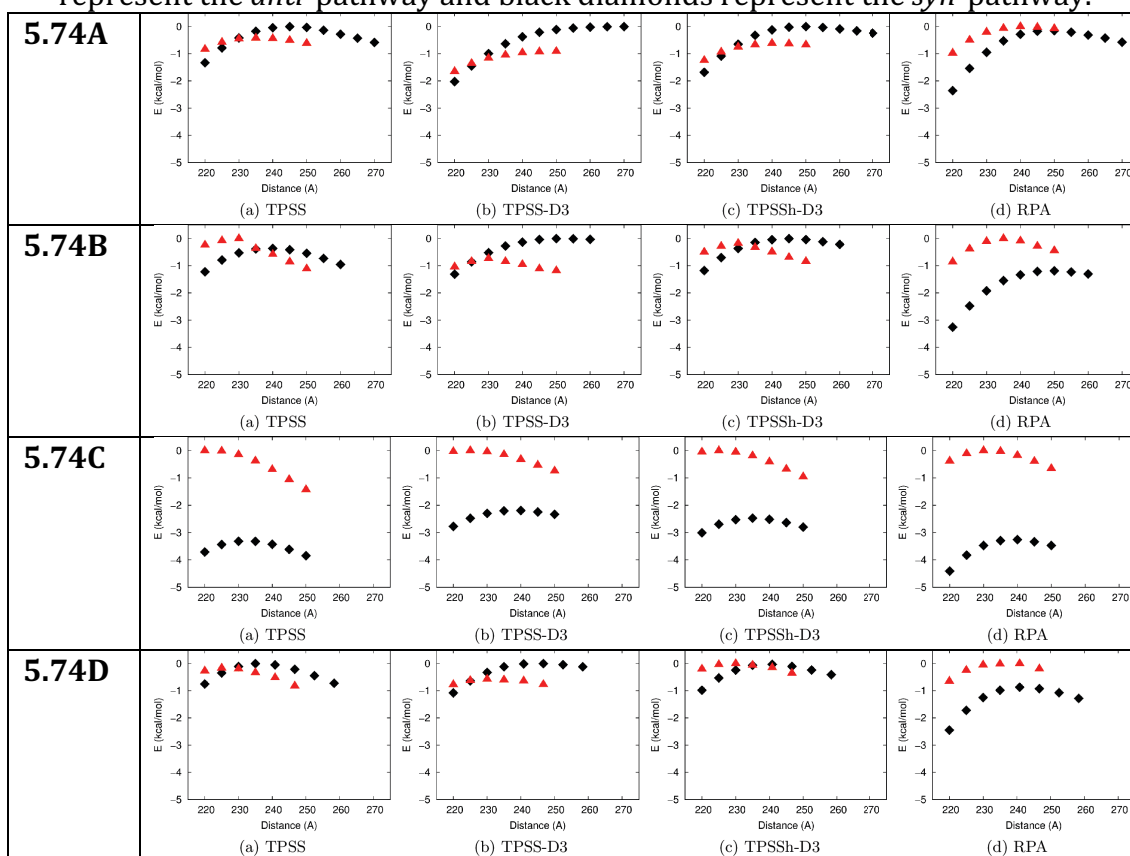


Figure S5.4. The PES's for the studied radicals computed using different methods. The geometries were relaxed at TPSS-D3/def2-TZVP/COSMO level and different methods were used for single-point energies with def2-TZVP basis set and COSMO. The red-triangles represent the *anti*-pathway and black diamonds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



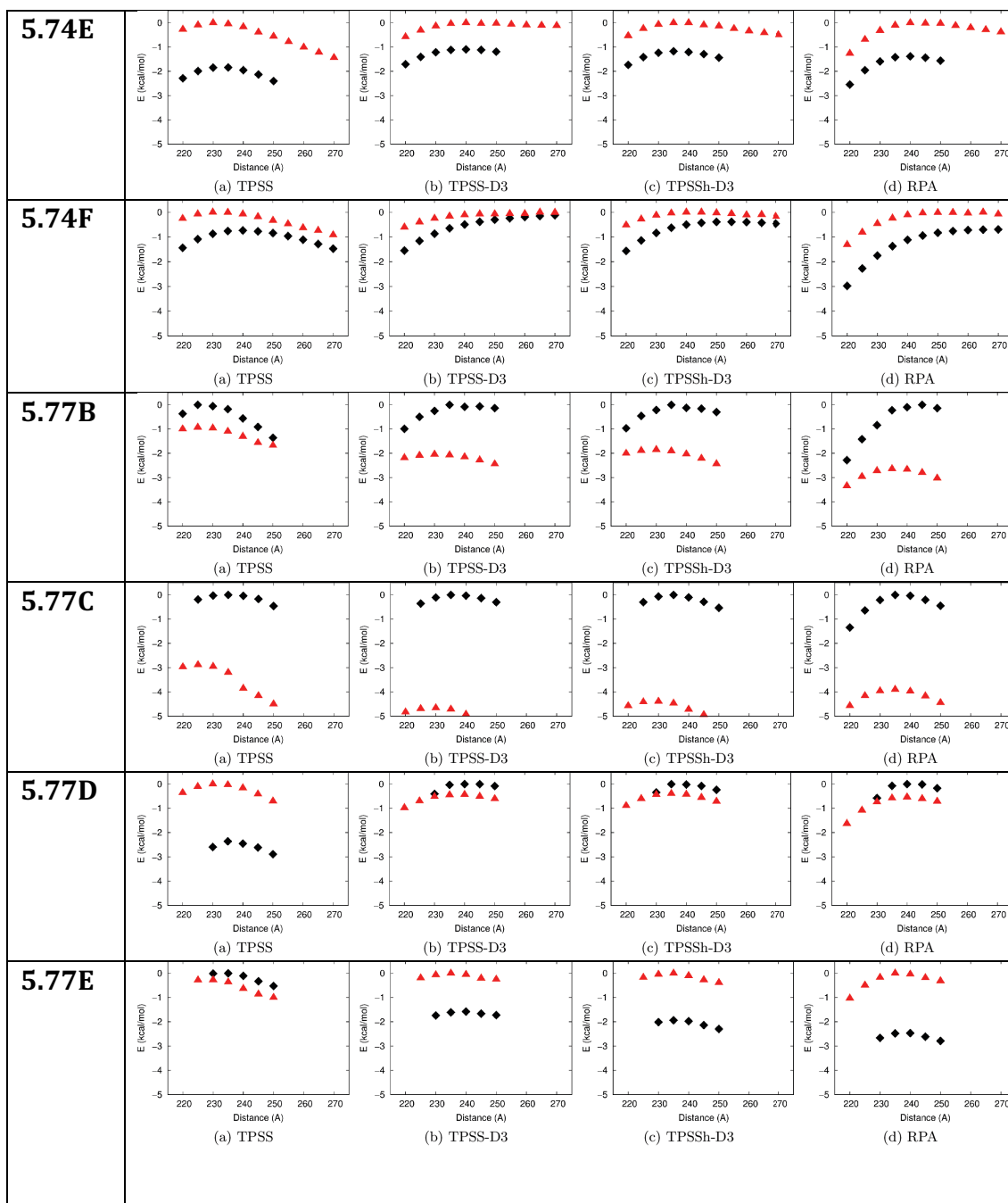


Table S5.3. The energy difference (ΔE) between TS-*anti* and TS-*syn* computed with several methods in kcal/mol. The %-values represent the computed amount of *syn*-product which is calculated from the ΔE values using the Boltzmann distribution at 298 K.

Radical	TPSS		TPSS-D3		TPSSh-D3		RPA		Exp
	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.

Radical	TPSS		TPSS-D3		TPSSh-D3		RPA		Exp
	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.

Radical	TPSS		TPSS-D3		TPSSh-D3		RPA		Exp
	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-<i>anti</i>	-920.475563	-920.525971	-920.418546	-919.972228
5.74A-<i>syn</i>	-920.474888	-920.524515	-920.41756	-919.97242
5.74B-<i>anti</i>	-1035.07049	-1035.13179	-1035.01093	-1034.51537
5.74B-<i>syn</i>	-1035.07107	-1035.13062	-1035.01065	-1034.51726
5.74C-<i>anti</i>	-1074.3841	-1074.45138	-1074.32649	-1073.81699
5.74C-<i>syn</i>	-1074.38939	-1074.45488	-1074.33043	-1073.82218
5.74D-<i>anti</i>	-1035.07171	-1035.13381	-1035.01282	-1034.51728
5.74D-<i>syn</i>	-1035.07145	-1035.1329	-1035.01287	-1034.51866
5.74E-<i>anti</i>	-1813.36302	-1813.46534	-1813.31944	-1811.93735
5.74E-<i>syn</i>	-1813.36596	-1813.46708	-1813.32131	-1811.93955
5.74F-<i>anti</i>	-999.147161	-999.210532	-999.096534	-998.624269
5.74F-<i>syn</i>	-999.14832	-999.210717	-999.097153	-998.625353
5.77B-<i>anti</i>	-1874.12141	-1874.2673	-1874.09605	-1872.97609
5.77B-<i>syn</i>	-1874.11993	-1874.26405	-1874.0931	-1872.97188
5.77C-<i>anti</i>	-1465.3137	-1465.43771	-1465.28123	-1464.61189
5.77C-<i>syn</i>	-1465.3091	-1465.43028	-1465.27423	-1464.60567
5.77D-<i>anti</i>	-1874.10962	-1874.26208	-1874.09122	-1872.97076
5.77D-<i>syn</i>	-1874.11339	-1874.26139	-1874.09059	-1872.96991
5.77E-<i>anti</i>	-2282.91775	-2283.09017	-2282.90445	-2281.33148
5.77E-<i>syn</i>	-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 TPSS⁷⁶ functional and def2-TZVP basis sets⁸⁰ in combination with the BJ-damped D3-dispersion correction, denoted with -D3.⁷⁵ Solvation effects were accounted for using the COSMO¹⁰⁹ model for dichloromethane ($\epsilon = 8.9$) unless otherwise noted, and for acetonitrile, dielectric constant of 37.5 was used. Chemical potentials (c.p.) and the Gibbs free energies ($G = E(0) + \text{c.p.}$) 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-D3¹¹¹ 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 package¹¹⁸ 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***

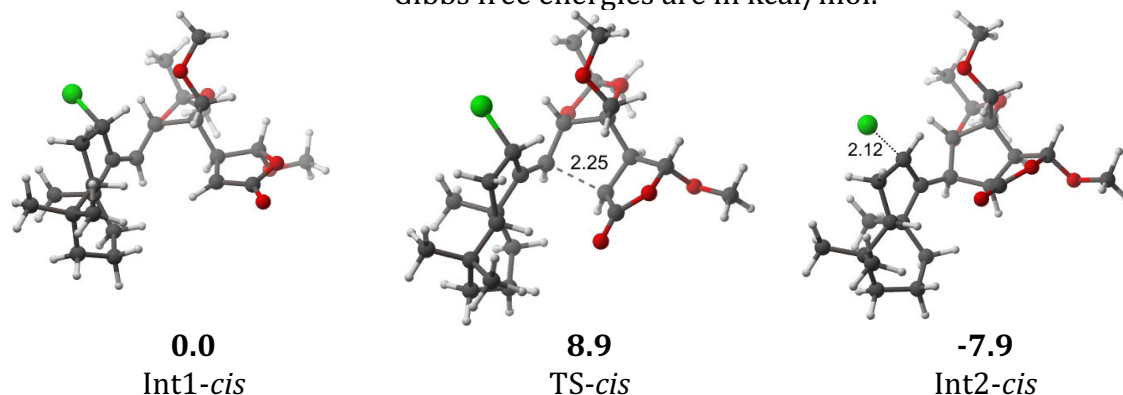
and **TS-trans**, while they are 2.70 and 2.62 Å in the enolate pathway. The kinetic barriers are 8.1 and 8.6 kcal/mol for the enolate **TS-cis** and **TS-trans**, respectively.

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	
	$\Delta G(\text{cis-trans})$	<i>cis:trans</i>	<i>cis:trans</i>	$\Delta G(\text{cis-trans})$	<i>cis:trans</i>
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.



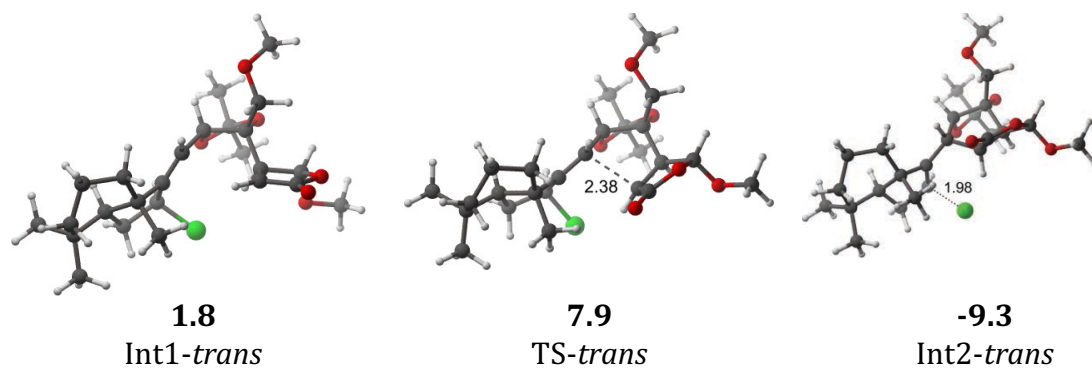
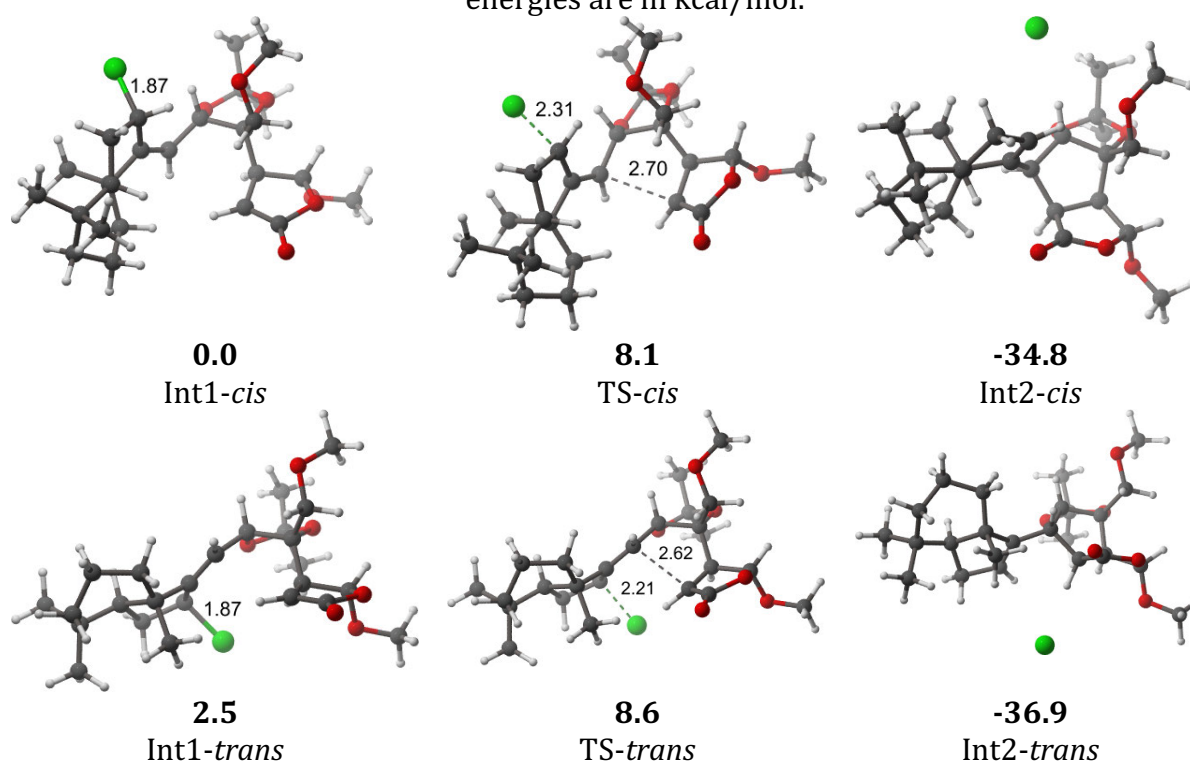


Figure S5.6. *Cis* and *trans* 5-*exo* cyclizations from the enolate intermediate. The Gibbs free energies are in kcal/mol.

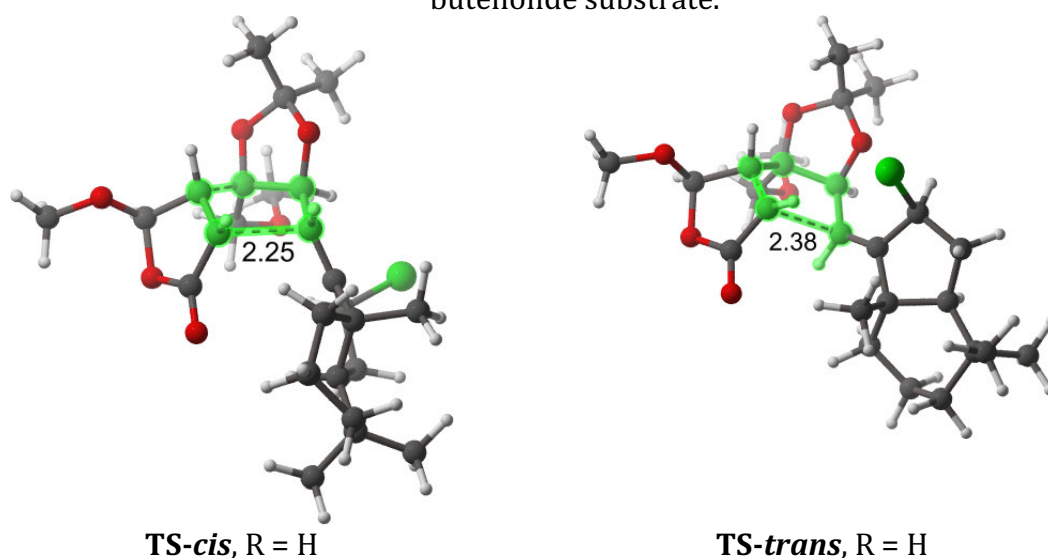


Predicted Substrate Modifications

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.



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.

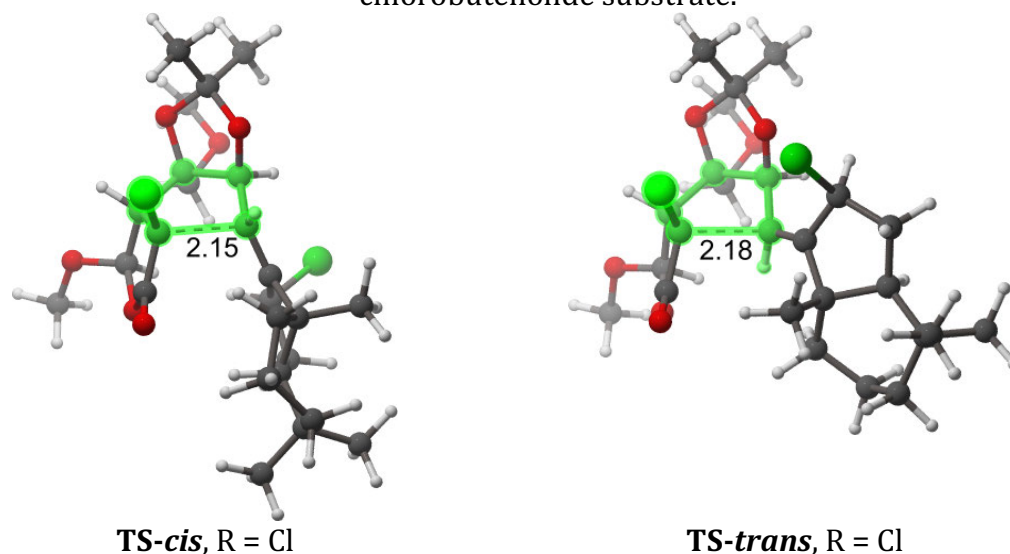
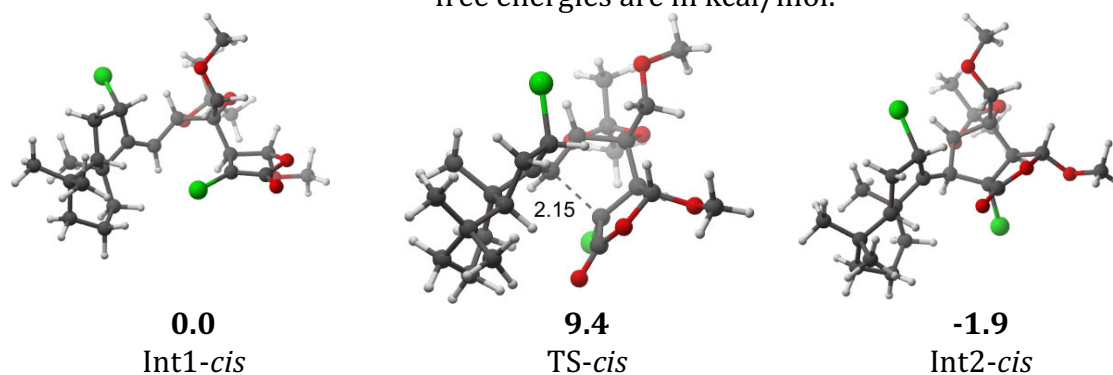


Table S5.9. The relative Gibbs free energies and populations of **TS-*cis*** and **TS-*trans*** for α -H, α -Cl and α -Br butenolide substrates.

Functional	R = H		R = Cl		R = Br	
	$\Delta G(\text{cis-trans})$	<i>cis:trans</i>	$\Delta G(\text{cis-trans})$	<i>cis:trans</i>	$\Delta G(\text{cis-trans})$	<i>cis:trans</i>
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.



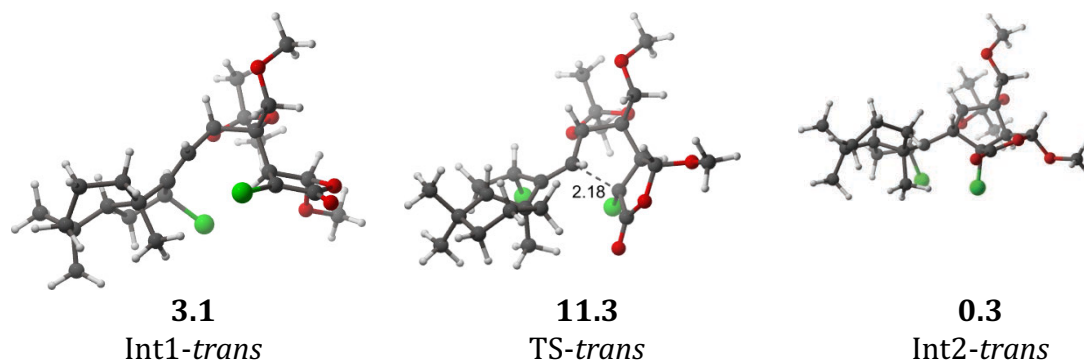
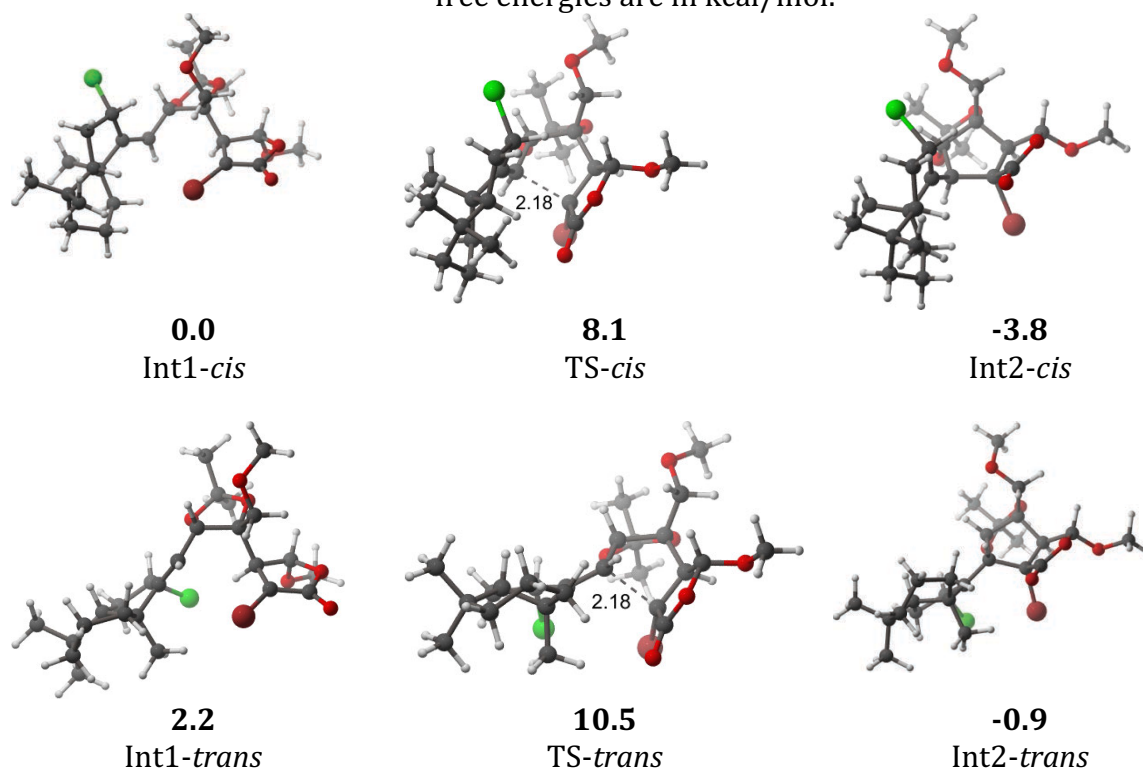


Figure S5.10. *Cis* and *trans* 5-*exo* cyclizations for the bromobutenolide analogue. The Gibbs free energies are in kcal/mol.



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	-0.53209884080804	-1.42984893977026
O	-0.45290043289258	-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	0.50493338787975	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	0.195135035977022
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	0.21564324255102	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	-1.54551540200761	-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	-0.22508796390408	-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	O	3.72672436319102	2.70329847078340	-1.83577386664466
C	3.27147673936485	-0.27535046214933	2.43636950435068	C	-2.02903745312687	-2.54293974154925	0.44309341481985
O	4.42317801055238	0.56664509663424	2.27611638424404	C	0.39101090745951	-3.36289448638026	0.43360774261546
C	5.68483249616626	-0.12459522870473	2.41555430995674	C	0.33907700982560	0.74853207026088	2.47323476076916
C	2.65027778631291	-3.02860948119086	-1.17988516773233	O	0.16131036386623	2.12228375492635	2.14231049349458
C	4.86842125444183	-1.82318576054943	-1.55601217897065	C	0.82780472839243	2.98223718596570	3.07318200090321
H	1.88433846609971	-1.52251845217450	1.43486564042361	H	-1.50815531793510	0.21435911067608	1.52763986230706
H	1.73265655738489	-3.01775644173199	-0.58947614904231	H	-2.64815416258962	-1.64820299445847	0.54705711546994
H	3.19228428828479	-3.95623746774013	-0.97463018374778	H	-2.28697537325364	-3.25174523024280	1.23518152263814
H	2.39140119472817	-3.00069021471284	-2.24169645323876	H	-2.23454236772412	-3.00566031055132	0.52626963519727
H	5.41411974274583	-0.91228065847055	-1.29758403572463	H	1.42736085881464	-3.01692473837077	0.45612768049455
H	4.70265390218295	-1.85683700142445	-2.63591116587479	H	0.20806803445569	-3.90097922525968	-0.50036331680630
H	5.45861148019198	-2.69606793274849	-1.26201844924602	H	0.22190685460840	-4.04641717514609	1.27035279608159
H	2.47641778618052	0.35683834206272	2.84491860928155	H	-0.05841942676701	0.53634262167932	3.47693183611145
H	3.49152328384977	-1.06695204761166	3.16169804141361	H	1.40328805339548	0.47767638125413	2.45934383372913
H	0.63965976646763	-1.08522227767703	-1.83735244743197	H	1.72663075257526	-0.94013451658739	-1.84099918459814
H	-2.17162156968936	-0.36633234721043	3.80076096250207	H	4.37096364568298	-3.16340624478909	-2.38913511255723
H	-1.83038496802022	-1.97639405022236	3.09422024781170	H	4.04126665426923	-1.71793710296294	-3.39446708235093
H	-0.49658756691851	-1.00506396716642	3.80069434286400	H	2.68354876217081	-2.74191382721484	-2.82391308047628
H	0.10083480704167	1.08245911229980	-0.12776699360366	H	2.32004869336851	-0.62658666480755	0.85658008679006
H	1.94640784146831	1.89667264200092	0.87364676599856	H	0.21393088490496	2.05840445170204	-0.43204028419630
H	2.01985930081111	1.90335925709540	-0.90521132229935	H	0.27416909701934	0.99270928613043	-1.86289637661287
H	-0.47700588414818	-0.28196436585774	2.11251359318027	H	3.04467653785946	1.97380968990054	0.81782722621892
H	5.82188603501427	-0.85419720588404	1.61323356133603	H	-1.99645808301058	0.74372784837795	1.62496106317350
H	6.45592109462176	0.64586842108595	2.36709466779230	H	0.42542754355267	2.84446445622238	4.08625934211861
H	5.72216698448832	-0.62761878277827	3.38894672522055	H	1.90895123210955	2.78176559245682	3.08496515492589
H	4.24749586271120	1.57722751111806	0.81247937888561	H	0.64672034410421	4.00518444128972	2.73852556945352

5.74C-anti				5.74C-syn			
C	0.03046738854703	0.00076715362467	-0.00697832546452	C	0.01913454061731	0.00141504545321	0.00997496576968
C	2.33045190234167	-0.00410059245984	-0.00009646367982	C	2.41909285787648	0.01008789866705	-0.00119166204335
C	2.42675522986880	1.49909027706750	-0.00036432659528	C	2.62532549432449	1.50396126020661	-0.00352600347178
O	3.75102400512618	2.02469999542314	0.15679908170975	O	2.98569491425585	1.82791992008380	1.37217943307105
C	4.58438000396951	1.88122175887608	-1.00291476519436	C	3.12677850170913	0.64527631713774	2.09270889538573
C	-0.25006786792159	0.25031298008937	-1.47633069252632	C	2.81426236810829	-0.46842724002892	1.21223354075686
O	-0.83596003675582	-1.00059864145569	1.94654793294218	C	-0.47989271291224	0.67690353822733	-1.25111813806824
C	-1.01436190579120	-1.86482414565455	0.86810559192997	O	-0.66080489473013	2.04063962778650	0.82259719393531
C	-0.49706577787634	-1.22389199445635	0.32311569106415	C	-1.03235554005375	1.99149341511196	0.55511556831551
C	2.63487296833881	-0.89839648896044	1.17874911682107	O	-0.31808449931253	0.79824875559902	1.06740195234031
O	2.86373704678538	-2.17921570354125	0.55941087202112	C	-0.09888539101635	-1.47457611366941	0.23579115488020
C	3.12346410639735	-2.02107842627384	-0.84029538033922	O	-1.48202780481391	-1.87550741922256	.35649691413379
O	2.73765754398686	0.62207704366287	-1.13543747941288	C	-1.95093209676690	-1.86478963547155	1.71502124896386
C	3.77848018670959	-0.45760700663542	2.09370882804929	C	0.43391127656434	0.69436529725522	-2.47227715606774
O	5.00803663907894	-0.41299515693501	1.38673498880680	O	0.70988773438643	-0.65926693117622	-2.82261768800410
C	6.02230431562782	0.27124309318782	2.12571956218878	C	1.52258810563891	-0.73751123992439	-4.00296497973781
C	2.23522727148308	-2.96162893947065	-1.63101279821115	C	-2.52527796257632	1.74576704367664	0.72885874879050
C	4.59815432945122	-2.17192059523368	-1.17897119868085	C	-0.52186397921404	3.22413335011244	1.26792977765763
O	-1.09689561996077	1.33608742996643	1.75329682050147	O	3.65693889848907	1.83324858445983	-0.89249327520317
C	-2.35365506885606	1.33355479023550	-1.03892962378948	C	3.78895818669428	3.25869247726062	-1.09172836236976
O	-1.54787032183362	-2.95228491452796	1.03146370141008	O	3.46917558795515	0.67113215146003	3.26347477988650
H	1.19245686895129	-2.84027087743705	-1.34027686864689	H	-2.82910586096009	0.83040233987631	0.21411466224825
H	2.53970420938054	-3.99274507889669	-1.42919982683560	H	-3.08030027812798	2.59141307639366	0.31232726924137
H	2.34317018497819	-2.76754518055396	-2.70186471618706	H	-2.76765496239640	1.65090902385627	1.79044693721341
H	5.19266704465350	-1.48903040297193	-0.57242890428136	H	0.56207786070386	3.30684497006943	1.16453190249988
H	4.75565394871918	-1.97006307391664	-2.24271015629442	H	-0.77585903873862	3.16857480837842	2.32937517086952
H	4.90335754914491	-3.20185841369370	-0.97106168121303	H	-0.99610112030981	4.11102529926260	0.83938989109080
H	1.75453115146203	-1.00576432935775	1.82380774670550	H	1.73261128506889	2.09921021298361	-0.22340667481962
H	3.84644019832891	-1.16377834433755	2.93602238233511	H	2.89121069389310	-1.49856415609265	1.53155605898739
H	3.52544072052789	0.53549355449012	2.49660667034703	H	-1.44505085173705	0.22939552119227	1.54279329254185
H	6.92722395244917	0.24425495094150	1.51517705537947	H	1.36546713581789	1.23508456511705	-2.25738143456244
H	6.21232857931231	-0.22718337717436	3.08693857965456	H	-0.07880464929563	1.21077987066209	3.29661265815650
H	5.72782121938329	1.31379236937216	2.30760316608716	H	1.69189807632613	-1.79769813194016	-4.19577618459397
H	1.87048999159769	1.89081562456282	0.85441056207257	H	2.48352993526673	-0.22887809298119	-3.84652882233561
H	1.98024794881259	1.88972300092864	-0.92589478264681	H	1.00615055244725	-0.2792720180775	-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	2.0484287513585	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 2.1644593306810	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 2.8258296893240	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	2.7884323614793	-0.74057656622176	O	3.07340703780911	-2.307430329576790	1.689122735501479
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	2.09252268369321	-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	2.7884323614793	-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	3.70500738132222
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	0.3436331432045
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	-2.057612439880673	H	4.47961855516139	-3.06876841099927	-2.3956230268000
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	0.62348488312029	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	3.181675886372021	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	1.24081222560543	C	-0.19234974256006	0.37493509707979	0.37493509707979
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	-1.62681222560543	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	-1.43006068489912	H	1.50193851969813	0.74073257438263	-2.925311709029745
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	-3.38904723883859	-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	-2.06816154060374
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	O	-0.17841713809499	0.01506834244861	1.52179950806630
O	-1.32298648551677	0.96082223738816	-1.71053936838876	C	-1.06566427698936	-0.927265947933376	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	-0.793075570791688	O	1.17598371241831	-1.92097012603884	-2.17630695070039
C	2.07044551874223	2.79927379469432	-1.78814158566684	C	4.962171109227484	-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	4.38085520355586	-0.66048513485016	-3.96223981660306
C	4.12979838562606	-3.41861042860448	-4.65598384216661	C	4.64562003130686	-1.25046235333761	-5.37531993054127
C	5.35053289828281	-3.96639399201715	-3.90302975573743	C	3.25744384500373	-1.32638157329692	-6.02165850431499
C	5.55484877643794	-2.96775483654060	-2.733615568807000	C	2.32158435425970	-1.71295458849381	-4.84849817376382
C	3.42516018107907	-4.32791866165712	-5.69923974706408	C	5.81451494395602	-0.62656308664355	-6.18411089255579
C	1.96987333194958	-3.81704254259067	-5.89591945533687	C	6.91060453402423	-0.16144522894792	-5.18433285103041
C	1.86613083756276	-2.30496444952281	-5.67504871943099	C	6.93531859577794	-1.03645875210552	-3.92735302255477
C	2.13461382704813	-1.92346940844015	-4.20237308501166	C	5.65157907531188	-0.85939832923711	-3.08621726431052
C	2.58426529203820	-3.87743583457869	-2.64581408738169	C	3.98588488993607	0.82894403162735	-3.99212626911813
C	3.40443883267828	-5.81659432263848	-5.31557539896548	C	5.39224295674164	0.54971172859090	-7.07966603418285
C	4.18479749115157	-4.18977567373828	-7.03378605542360	C	6.40114243285122	-1.72666645304791	-7.08985727586858
H	1.04394316655897	2.45332462554634	-1.64935282787857	H	5.34861751599802	-0.83691580265850	0.60415048544569
H	2.22785398171595	3.03948062450045	-2.84317582697865	H	5.51844689163205	-2.57495337032965	0.96300014259442
H	2.22418326286726	3.70410377204777	-1.19451436848156	H	5.10478926340553	-1.43176982343201	2.26298181537180
H	5.16884904917560	1.37843368878677	-1.11928230220974	H	1.77207310521618	-3.05554908348114	1.46199984302760
H	4.63487446111083	3.03626943136419	-0.69356919114064	H	2.94456519277050	-2.78925592934354	2.78109716068963
H	4.75260129348338	2.54738937497301	-2.39902507236645	H	3.31962687147185	-3.94192947433884	1.48173533290244
H	-0.46969847387792	-1.51006960231036	1.51769111123672	H	0.21116098415616	-0.99883308746059	-0.48914625861864
H	2.01746164285009	-1.69048533261984	1.22461511013188	H	0.73749504982632	-0.09307241899122	2.10259545098859
H	1.99032504778464	-0.12997547658613	2.08699302225135	H	-0.58496897342182	1.30855183447504	-1.58715113382068
H	4.92124028179949	-0.79095423563051	0.16076250592398	H	4.03630487582907	-0.36868861065540	-1.34418379088505
H	3.69121626091178	-2.41430508311440	-0.73725575111789	H	2.00256627632851	1.87359551312921	-0.87371121060072
H	4.56892564111342	-1.12831265504251	-3.34924917099938	H	2.10102339955997	1.90404389969032	1.90404389969032
H	5.60980131007260	-3.49274027902644	-1.77327046324693	H	-2.23027055178451	-1.40646397798656	0.38188709764553
H	6.48138543642311	-2.39751428970578	-2.83287227870791	H	-2.85117757185502	-0.05546852980042	1.38445132544544
H	6.23288189306509	-4.04318060629504	-4.54633507266523	H	-2.92590309542798	-1.73214718042060	1.99875859563591
H	5.14735546606281	-4.96942757963801	-3.51448359101548	H	1.55199031150893	-2.68911982974455	-1.70810184283270
H	2.42093237157029	-0.86771083002038	-4.15204512484006	H	1.82481485837104	-0.06764686617765	-2.67821600662835
H	1.20037690108476	-2.02506582284048	-3.63667862576277	H	3.55329596457552	-2.51296578598479	-3.24151505132493
H	2.58737061991302	-1.79656387821750	-6.32865802116890	H	1.43342438079615	-1.07262435824325	-4.82321250236058
H	0.87485747423279	-1.94142139607275	-5.96980150679661	H	1.96440801145939	-2.741833299454208	-5.173320977677473
H	1.63296884942630	-0.8504897788815	-6.90522516235930	H	3.21879924037820	-2.04806305218657	-6.84375535578340
H	1.29504658903178	-4.32936103843277	-5.19771974872694	H	2.97101554409857	-0.35300698101421	-6.43195641151337
H	4.48314206219864	-2.54068581196040	-5.21953994820402	H	5.52732974405876	-1.73249984244454	-2.43415225321585
H	2.94173301484719	-5.98393410216796	-4.33849346885012	H	5.78076365773292	0.01153689773247	-2.42988869342471
H	4.41625672198394	-6.23621373670275	-5.28952163453792	H	7.04233125245731	-2.08800541921289	-4.22426780144023
H	2.82872347412921	-6.37895821164744	-6.06083055471596	H	7.80948329119912	-0.79894333466402	-3.31041827996130
H	4.13453086035440	-3.15936215608109	-7.40644065136363	H	7.88511431743471	-0.18159607048864	-5.68883116999252
H	3.75206704614538	-4.85092992899331	-7.79435985873197	H	6.73420267621382	0.88242028954071	-4.89290401320197
H	5.24165960356493	-4.45360843093816	-6.91160025036629	H	4.94621470266362	-2.29105799410667	-5.17333485804338
H	3.32800839718981	-4.53069882893515	-2.17620801477657	H	4.89972026560097	1.34506105353843	-6.51365841798145
H	1.89071512260400	-4.50271576658982	-3.21192101935864	H	4.70767837207094	0.22159598839313	-7.86993471402593
H	2.00046401752084	-3.40806210979247	-1.84584801981010	H	6.27928486823885	0.97835984897977	-7.56166592063872
H	0.54676420957726	0.24707813424579	-2.15727532531625	H	6.82123719764629	-2.54387717339964	-6.49125255051073

5.77C-anti			5.77C-syn				
C	0.08655832090475	0.16432393240688	-0.03976950649872	C	0.01132808860699	-0.07136371085792	0.06648197455398
C	2.43364146551782	0.04794389548523	-0.02727375974309	C	2.35944000523041	0.00923014356128	0.01774917010823
C	2.56762525958800	1.54883940986764	-0.05039504113069	C	2.53799588001467	1.49631425794795	0.01607007113588
O	3.93471476175773	1.97383292209102	-0.12676915947286	O	3.93231903930979	1.86604202429577	-0.04898353736379
C	-0.39920609198524	-0.31740920045976	1.14698719553343	C	-0.54337564071354	0.98825015940138	-0.60161250567582
C	-0.84876047250500	-1.68631999362505	0.96557037848668	C	-0.95267691951244	2.00482282811950	0.35189589198543
O	-0.67689836600962	-2.02701688966442	-0.37529800796891	O	-0.69391651757676	1.53297152488295	1.63399700868863
O	-0.22502566181707	-0.84631660583892	-1.11218293453432	C	-0.18059308514702	0.16580336740931	1.54539338716710
C	2.78895153486730	-0.86324078005514	1.13903385811532	C	2.85315148886988	-0.92232056249448	-1.06625077750032
O	3.74970405050217	-1.77164604013397	0.55501367524500	O	2.74380436694440	-2.20473581751374	-0.39893362226101
C	3.49041294512522	-1.86283148324624	-0.84197234392719	C	3.07234757266005	-1.99307178385102	0.96974697575024
O	2.83904909532128	-0.57056348761279	-1.16991531500012	O	2.68302037846827	-0.57996577570900	1.20947889142460
C	2.54425705502078	3.00983560169898	-1.16140971516848	C	2.15799991839085	-1.06980610035674	-2.42565995183215
C	4.80512007505804	-1.91024313297539	-1.59216868017667	O	2.82699027713446	-2.14536237900072	-3.10915861157382
C	3.45197308428178	-0.24801086534433	2.37606241836578	C	4.56792760863261	-2.09617772337991	1.22853486095936
O	4.67710687491471	0.42891126983827	1.99036105822531	C	2.21963684342922	-2.89474173076497	1.83609786552051
O	-1.30904545634229	-2.49401127993183	1.75610281970156	O	-1.10682987571949	-0.75675695103606	2.04597757734815
O	-1.24092239909342	-0.35087187415933	-1.93823052275325	C	-1.20386362469474	-0.72732308447327	3.48798893774576
C	-1.47583648600553	-1.18464035324996	-3.09519100623265	O	-1.44495323494399	3.10893695947360	0.18295852246196

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C 2.58225674545955	-2.06662780950949	4.09571852177428	C 1.51717729355451	0.25116842057015	-4.63813515855432
C 3.30919256518945	-2.64741196558762	5.33937844379159	C 2.01550079166535	1.65166467410026	-5.09073326863546
C 4.09292415549291	-1.45912319644257	5.91502942174192	C 3.52860105791729	1.61624767290623	-4.81742910996409
C 4.50647191382290	-0.63366292344948	4.66750252742626	C 3.66817834513106	0.72381540518962	-3.55054662871046
C 2.44991849530635	-3.51346375772504	6.30055307212879	C 1.50343820557265	2.16574305155518	-6.46174093282810
C 1.36358946147186	-4.24703686855527	5.46356432315476	C 0.06537155894125	1.61111096190084	-6.68313642708235
C 1.84254301377137	-4.53684352209272	4.03750175372696	C -0.67572111011703	1.38224976194920	-5.35978265533260
C 2.03737784402024	-3.23514851677197	3.22804959156920	C -0.03052876220184	0.23883685867891	-4.54781504938944
C 1.44717174306963	-1.09387192140289	4.46340046576571	C 1.98458696415369	-0.87384473474832	-5.58015301711675
C 1.77771698765262	-2.71239742594685	7.42786024969965	C 2.39810921508787	1.78177892881881	-7.65204340040059
C 3.37597748258325	-4.56137027162011	6.94657958985478	C 1.43975463035275	3.70352390350867	-6.39145426615677
H 1.63879834315529	-2.95343711260256	-0.55352692613152	H 5.12206241731966	-1.43158788564189	0.56084401378471
H 3.05214858040363	-3.95474003805262	-0.94841106385979	H 4.89318093175041	-3.12638390490697	-1.05771202112272
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H 5.40096715205676	-1.02623579670868	-1.35141121809998	H 1.16017874213894	-2.73493911428600	1.61954231678783
H 4.62106812736723	-1.94435702487499	-2.66906691592058	H 2.41180548574742	-2.68910442991169	2.89279187801880
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H 1.89443028729951	-1.41439696751318	1.46204013824962	H 0.14080312381601	-1.07726932060708	-0.31074728683233
H 4.95691307820381	-1.78042184187084	6.50497236282931	H 0.73345764220366	0.15062942791743	2.14619049431806
H 3.45783711066361	-0.85922139766160	6.57364379745003	H -0.68570316348543	1.10799924253102	1.66583352135196
H 2.71765200956694	-3.43111476097702	2.39076622868703	H 3.91561966907204	-0.70021369557334	-1.26195339796032
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H 1.12597984697465	-5.18253861138245	3.51710856308099	H -1.85810014378259	-1.55498832657948	3.76343636384548
H 1.08928728995997	-5.17848096644699	5.97515297746738	H 3.94256910875734	2.61708745026021	-4.66347781835822
H 0.45245070755979	-3.67201504752069	5.41873717572069	H 4.066488949052806	1.16931047984053	-5.65862442179256
H 4.05816750134357	-3.33305399783131	4.91213176529193	H -0.35386181226275	0.30551535215050	3.50274000419760
H 1.16295239966884	-1.89398101898857	7.04346677651170	H -0.40523751401187	-0.72152539987428	4.92195720543139
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H 2.82414820922471	-5.16740336647059	7.67555432737216	H 0.11443001045995	0.66220835089548	-7.23253193864889
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H 4.43092279671439	-2.03059790527469	3.00384360872585	H 3.07276512827352	-0.89759840006658	-5.69480826844238
H 5.24591704220756	-0.25550931288316	1.59124188383634	H 1.53829584062586	-0.74772449547484	-6.56995537756143
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H 0.62952750605304	-1.17061074383470	-1.71411594351654	H 1.10534252573891	-1.34178302555833	-2.26313264654200
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H -2.19127212299052	-0.64448675973465	-3.71613792588798	H 2.83324282587963	-2.90103573132121	-2.49609000576781
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5.77D-anti			5.77D-syn		
C 0.01027690297860	0.00183471381443	-0.00338502853882	C 0.03810162125915	0.01494946030597	0.01351002488465
C 2.41024121274122	0.00329969352530	-0.01639693692345	C 2.43794053494121	0.00275587008276	-0.01148403477624
C 2.63254812779756	1.49221246976387	0.01490500945603	O 2.74494652085390	1.33525771785110	-0.01402416458572
O 3.04117106201614	1.76660938542429	1.39375298939103	C 3.25976760374501	1.72576288149422	1.32375473164298
C 3.25689418171119	0.55634398079369	2.05182349654522	O 2.97531176396098	0.60021265762425	2.13463956139064
C 2.88498456822070	-0.52228527854135	1.15027925023677	C 2.98184272565526	-0.56654042263792	1.28592337575706
O -0.44632345633433	1.25754315601504	0.28852750274318	C -0.17416863308922	1.376223117234789	-0.60199114710400
C -1.19206824365135	1.78190512242551	0.89409218062029	O -0.66295009147755	1.09605201805218	-1.95298673162559
O -1.45465877056842	0.61626405489007	1.65981222763298	C -0.87867844070876	-0.26945943325682	-2.08278471814049
C -0.33455496717885	-0.27414234088974	1.44978270548653	C -0.47367489888756	-0.91703709911925	-0.84517342686953
C -0.13312165928826	-0.92719824912741	1.18813532923080	C 2.59847467269524	-0.63529764359009	-1.35896252286318
O 0.34135739318192	-2.24710815702638	-0.95264544818672	O 3.99159132380320	-0.83101015578731	-1.68856037637395
O 3.68419467849185	0.54056204770420	3.19423551643119	O -1.33783591168231	-0.73354939183637	-3.11384447913826
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C 3.80041014227694	3.26045536142020	-1.04662528813490	C -1.25167863366077	3.46168671600347	-0.26259951996163
C -0.68718472461409	-1.68961792790409	1.89316975915687	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	0.23391666186556	-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	-0.60527871118896
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	-2.72096890004538	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	-0.23506354565990
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	1.94708051060920	-1.79854936169022	5.00314716129853	H	1.81464402429732	-7.76137472105611	0.65858771328881
H	1.69192773466294	-1.61758214304116	3.28033810512936	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				
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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	0.589074265204691	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	-0.7903505309284	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	-3.90263798685228	-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	-4.60123585072030	-4.60123585072030
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	-2.925283648296835	0.925283648296835	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	-1.3440006142183
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	3.0777735042859	-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- <i>cis</i> enolate pathway (R=H)				Int1- <i>trans</i> 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	1.7674905	2.8184174	2.6553182
C	1.9182815	1.5017393	0.1900956	C	1.2737265	1.8666447	1.7948866
C	-0.9555573	0.7271795	-1.4335315	C	-1.5052509	0.8973870	0.1674022
O	-0.8836407	0.9737169	-2.8568437	O	-1.5622141	1.1483355	-1.2408286
C	-1.2730499	2.3455659	-3.0400027	C	-2.0305886	2.4961516	-1.4056517
O	-1.0024432	3.0019145	-1.7807946	O	-1.7320560	3.1740043	-0.1689198
C	-0.9056236	2.3375635	0.5559495	C	-1.6128954	2.4999555	2.1574087
O	-2.3126635	2.1295439	0.7368742	O	-3.0358516	2.3457546	2.2549916
C	-3.1050859	3.3036555	0.5239954	C	-3.7504489	3.5814960	2.1344532
C	-0.2019329	-0.5154037	-1.1108704	C	-0.6552088	-0.2743236	0.5198579
C	-0.5982699	-1.4211982	-0.2106508	C	0.0886627	-1.0802798	-0.2481879
C	0.1747512	-2.6479514	0.2499211	C	0.8210019	-2.3229720	0.2567557
C	-0.1519131	-2.5927228	1.7713284	C	0.5322293	-3.2905862	-0.9255468
C	-1.6567481	-2.2838538	1.8146969	C	0.7516803	-2.4267734	-2.1760430
C	-1.8372720	-1.2955541	0.6491106	C	0.2461845	-1.0334110	-1.7491181
C	0.3965125	-3.7563222	2.6375286	C	1.2140946	-4.6833325	-0.8563971
C	1.7449047	-4.2227996	2.0155695	C	1.3372278	-5.0879360	0.6413342
C	2.4741278	-3.0811108	1.2970731	C	0.2137492	-4.4885112	1.4948214
C	1.7085514	-2.6087371	0.0408499	C	0.2860561	-2.9443588	1.5687437
C	-2.7708670	2.4466877	-3.3199606	C	-3.5442840	2.5151598	-1.6086784
C	-0.4140043	2.9425271	-4.1452256	C	-1.2572255	3.1276962	-2.5538042
O	2.5800463	3.8300628	-1.8710123	O	1.7721356	4.3300383	-0.1412294
C	3.0188752	5.1916417	-1.9153366	C	2.0952902	5.7234259	-0.1070435
O	3.1699410	2.4287319	2.0672716	O	2.4371345	2.8214842	3.7159324
C	-0.4241354	-3.8807004	-0.4717405	C	2.3183990	-1.9611684	0.4130199
Cl	-3.3876161	-1.6830782	-0.3166364	Cl	1.4735929	0.2646445	-2.2963571
C	-0.5663633	-4.9490841	2.7495373	C	2.6001154	-4.7272420	-1.5196805
C	0.6577977	-3.2095466	4.0538570	C	0.3020063	-5.6944660	-1.5771495
H	-3.3335938	1.9392237	-2.5313566	H	-4.0357639	2.0082138	-0.7734703
H	-3.0053503	1.9833279	-4.2834181	H	-3.8057506	2.0102463	-2.5440776
H	-3.0765068	3.4971420	-3.3494966	H	-3.9036402	3.5479827	-1.6528296
H	0.6386834	2.9033511	-3.8558398	H	-0.1900788	3.1147202	-2.3238196
H	-0.6986904	3.9857057	-4.3127927	H	-1.5859991	4.1614870	-2.6971535
H	-0.5607573	2.3854154	-5.0760660	H	-1.4350052	2.5695845	-3.4784295
H	0.8333750	4.3499935	-0.9207743	H	-0.0401889	4.6531962	0.7719674
H	1.9150744	0.4458094	0.4195714	H	1.4550194	0.8078697	1.9106759
H	-0.3919473	1.6462378	1.2291895	H	-1.1606391	1.7583589	2.8211830
H	-0.6314784	3.3598246	0.8483058	H	-1.3142018	3.4944120	2.5132557
H	3.5558075	5.4632058	-0.9987716	H	2.5859150	5.9927067	0.8358616
H	2.1615338	5.8692370	-2.0456304	H	1.1873488	6.3339356	-0.2278605
H	3.6876930	5.2793371	-2.7745299	H	2.7741627	5.9101426	-0.9423615
H	-3.0203329	3.6601388	-0.5071555	H	-3.5880783	4.0395751	1.1537991
H	-4.1386319	3.0206611	0.7376862	H	-4.8089007	3.3410324	2.2629619
H	-2.7946584	4.1039048	1.2115979	H	-3.4374457	4.2830267	2.9215827
H	-2.0315799	-0.2752096	0.9735695	H	-0.6591753	-0.7118027	-2.2531649
H	-1.9882116	-1.8493627	2.7611712	H	0.2157260	-2.7910651	-3.0569065
H	-2.2440559	-3.1874340	1.6358360	H	1.8126901	-2.3766660	-2.4294543
H	2.0337004	-1.5957115	-0.2160408	H	-0.7148719	-2.5571217	1.7880361
H	1.9718911	-3.2488877	-0.8094111	H	0.9314076	-2.6436446	2.4023488
H	2.5990543	-2.2401078	1.9915053	H	-0.7525967	-4.7892052	1.0688032
H	3.4839367	-3.3953850	1.0104068	H	0.2451840	-4.9038956	2.5084812
H	2.3747523	-4.6413069	2.8107664	H	1.3282223	-6.1831784	0.7135062
H	1.5621827	-5.0370014	1.3022956	H	2.3064767	-4.7592482	1.0363707
H	0.3637836	-1.6862643	2.1220323	H	-0.5497952	-3.4802746	-0.8576998
H	-0.8509432	-5.3411731	1.7690763	H	3.2768210	-3.9742128	-1.1064046
H	-1.4810776	-4.6736523	3.2866486	H	2.5300167	-4.5675759	-2.6015546
H	-0.0818089	-5.7586121	3.3088304	H	3.0519032	-5.7133657	-1.3564863
H	1.4216569	-2.4233687	4.0335106	H	-0.6660642	-5.7780627	-1.0687875
H	1.0062742	-4.0102159	4.7171197	H	0.7665950	-6.6876559	-1.5960497
H	-0.2554842	-2.7822289	4.4843875	H	0.1147586	-5.3851671	-2.6122709
H	-1.5010341	-3.9761300	-0.3041733	H	2.7469253	-1.5794094	-0.5178423
H	0.0627443	-4.8052387	-0.1500561	H	2.9071281	-2.8212220	0.7429745
H	-0.2612694	-3.7690084	-1.5490645	H	2.4150100	-1.1749897	1.1686237
H	0.7418540	-0.6472068	-1.6359133	H	-0.6976085	-0.4958268	1.5855052
H	-2.0044150	0.6420125	-1.1281714	H	-2.5223064	0.7058708	0.5487769
H	1.4234894	1.7834069	-1.9325361	H	0.7834666	2.1764390	-0.3194250

TS- <i>cis</i> enolate pathway (R=H, DCM)				TS- <i>trans</i> 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	0.2259225	-1.2694037	-1.5470299
H	1.3912163	-1.4062116	1.2486360
H	-1.8520929	-3.0787411	0.0418832

H	-0.2967133	-3.5138416	2.0517413
H	-1.2283443	-2.3759014	1.0712286
H	-0.0439742	-0.8728090	-1.3482349
H	0.8683445	1.2082814	-2.0759484

Int2- <i>cis</i> enolate pathway (R=H)				Int2- <i>trans</i> 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- <i>cis</i> enolate pathway (R=H, MeCN)				TS- <i>trans</i> 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	-1.8136660
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	0.3122289
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- <i>cis</i> radical pathway (R=H)				Int1- <i>trans</i> 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- <i>cis</i> radical pathway (R=H, DCM)				TS- <i>trans</i> radical 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- <i>cis</i> radical pathway (R=H)				Int2- <i>trans</i> 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- <i>cis</i> radical pathway (R=H, MeCN)				TS- <i>trans</i> radical 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- <i>cis</i> radical pathway (R=Cl)				Int1- <i>trans</i> 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- <i>cis</i> radical pathway (R=Cl, DCM)	TS- <i>trans</i> radical 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- <i>cis</i> radical pathway (R=Cl)			Int2- <i>trans</i> 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	-0.9347333	2.5099674	-0.8052054
C	0.8500352	2.7662574	-1.3432585	C	0.0426611	1.6362447	-0.0056167
C	1.1309413	2.9243030	0.1591032	O	-0.9254185	3.7607411	-0.1109849
C	0.7089010	1.5646511	0.7411002	C	-0.3409548	3.5442849	1.2136141
C	0.3998775	-1.7139938	0.6780449	O	-0.1754440	2.1240846	1.3214319
C	-0.7320276	-2.0475930	1.6713644	C	-2.4789908	-0.4340337	-1.5965356
C	-2.0373301	-1.7729957	0.8555112	O	-3.1026702	0.4423541	-2.4260146
O	0.5875525	-2.9745242	0.0105285	C	-3.2878841	1.7576108	-1.7751342
C	0.4043685	-3.9950823	1.0007111	C	0.1923410	-0.8284258	0.7344070
O	-0.5953637	-3.4521201	1.9141587	C	0.5570917	-2.2449674	0.3196042
C	-2.3326049	0.5689595	0.3053018	C	1.9111178	-2.4021361	1.0765122
O	-3.1128696	0.2965654	1.3796653	C	1.6570619	-1.7425966	2.4347019
C	-3.2294845	-1.1672952	1.5965966	C	0.7621954	-0.5457684	2.0757880
C	1.4621409	3.7829705	-2.3399167	C	2.5588967	-3.8119402	1.0407770
C	1.4653231	3.1190731	-3.7486184	C	2.2106543	-4.4651185	-0.3274371
C	0.3291881	2.1013771	-3.9133787	C	2.0281583	-3.4171177	-1.4313423
C	0.4897643	0.8753264	-2.9816079	C	0.8076021	-2.4957342	-1.1887761
C	-0.6268931	-1.2986229	3.0046717	C	-0.5663360	-3.1852628	0.8350910
O	0.6061919	-1.5696465	3.6589022	Cl	-0.5277859	-0.3357438	3.4642746
C	0.4851309	-2.5299417	4.7197569	C	2.1102893	-4.7285281	2.1902162
O	-4.4060914	-1.6397930	1.0422985	C	4.0857487	-3.6290489	1.1369953
C	-5.5909943	-1.2094249	1.7514967	C	-0.5325263	2.7279780	-2.2639045
O	-2.2092017	1.6853183	-0.1400210	O	0.8191770	3.1617975	-2.3903480
C	1.6950695	-4.2556133	1.7699779	C	0.9519747	4.5840922	-2.5499884
C	-0.1599401	-5.2268775	0.3184896	C	1.0021967	4.2636306	1.2684526
C	2.6500595	0.8930010	-1.6462253	C	-1.3150199	3.9882910	2.2888862
Cl	2.1246700	0.9628445	1.9565363	O	-4.5802339	1.8719570	-1.2867982
C	2.8832292	4.2379743	-1.9723889	C	-5.5802011	1.9822516	-2.3254269
C	0.5478466	5.0226501	-2.3689463	O	-2.3367561	-1.5989550	-1.8821673
H	2.0472846	-3.3328451	2.2374936	H	-2.7909844	2.2313838	0.2532582
H	2.4618770	-4.6355980	1.0882516	H	1.6687492	3.8810471	0.4908676
H	1.5178219	-4.9990661	2.5524821	H	1.4649022	4.1103738	2.2478328
H	-1.0754360	-4.9672261	-0.2189681	H	0.8574019	5.3361707	1.1094613
H	-0.3841166	-5.9928959	1.0657697	H	-2.2534153	3.4368056	2.1941854
H	0.5715039	-5.6304562	-0.3876055	H	-1.5122550	5.0594674	2.1921945
H	-3.2277270	-1.2757472	2.6840616	H	-0.8876893	3.7956635	3.2770476
Cl	-2.5041769	-1.0565910	-1.7896468	H	-3.1002201	2.4806746	-2.5738484
H	-0.6755783	-0.2173878	2.8241082	Cl	-2.9308799	-0.3808245	1.0327460
H	-1.4650693	-1.5715919	3.6563302	H	-0.6174289	1.7768366	-2.8051049
H	-5.7340184	-0.1308138	1.6377137	H	-1.2092406	3.4500314	-2.7371244
H	-5.5050730	-1.4674404	2.8138721	H	-5.6551941	1.0457190	-2.8860783
H	-6.4224394	-1.7488282	1.2985795	H	-5.3263271	2.8063471	-3.0031773
H	0.1188860	-3.4905932	4.3434999	H	-6.5201069	2.1906766	-1.8148286
H	1.4873676	-2.6515708	5.1355735	H	0.5512982	5.1173265	-1.6824125
H	-0.1927097	-2.1555104	5.4992298	H	2.0213938	4.7807324	-2.6477412
H	-0.1060003	1.6011789	1.4600791	H	0.4320931	4.9154073	-3.4591984
H	0.5726201	3.7415409	0.6225707	H	1.2528719	0.4236376	2.1379765
H	2.1928367	3.0942073	0.3491078	H	2.5667245	-1.4217304	2.9487510
H	-0.4966259	0.4310311	-2.8156604	H	1.1167840	-2.4205808	3.0990944
H	1.1039756	0.1127204	-3.4745427	H	0.9908562	-1.5494934	-1.7117217
H	-0.6265209	2.5974490	-3.7015515	H	-0.0903970	-2.9300030	-1.6365529
H	0.2750802	1.7596975	-4.9529441	H	2.9400410	-2.8091503	-1.4934753
H	1.3826237	3.9047060	-4.5100022	H	1.9190499	-3.9074984	-2.4050331
H	2.4266913	2.6200489	-3.9224492	H	3.0102502	-5.1656815	-0.5990605
H	-0.2385419	2.8433008	-1.4601542	H	1.2949545	-5.0616886	-0.2356377
H	3.5705029	3.3945096	-1.8634076	H	2.5995318	-1.7412156	0.5283255
H	2.8894355	4.8079963	-1.0364804	H	1.0234693	-4.8417949	2.2267768
H	3.2740762	4.8910074	-2.7620593	H	2.4473638	-4.3449601	3.1597665
H	-0.4543084	4.7600112	-2.7281031	H	2.5491015	-5.7244986	2.0550985
H	0.9610418	5.7896915	-3.0345264	H	4.4672311	-3.0691592	0.2747224
H	0.4449279	5.4585451	-1.3683165	H	4.5883904	-4.6030659	1.1632561
H	3.1646543	1.2457185	-0.7482235	H	4.3590021	-3.0794911	2.0454246
H	3.1496311	1.3036809	-2.5275037	H	-0.7245391	-3.0727131	1.9116294
H	2.7465991	-0.1979690	-1.6853087	H	-0.3359854	-4.2313860	0.6186570
H	0.0884732	-1.1633208	-1.3470282	H	-1.4986406	-2.9291340	0.3251825
H	1.3143202	-1.3897717	1.1786838	H	-0.0705796	-0.0792069	-1.1921630
H	-2.3400267	-2.7166751	0.4057203	H	1.0839985	1.7753554	-0.3162047

Int1- <i>cis</i> radical pathway (R=Br)				Int1- <i>trans</i> 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- <i>cis</i> radical pathway (R=Br, DCM)				TS- <i>trans</i> radical 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

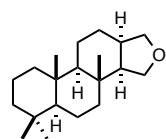
Int2- <i>cis</i> radical pathway (R=Br)				Int2- <i>trans</i> radical pathway (R=Br)			
C	-1.6815991	-0.7229282	-0.1899599	C	-1.9921770	0.3000540	-0.3552687
C	-0.1169754	-0.7002500	-0.3830937	C	-0.4283295	0.1802492	-0.1657822
C	0.5304329	0.6493916	-0.3928203	C	-2.3087391	1.7784905	-0.6113921
C	1.1479315	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	0.9542509	-1.5553251	-1.7072157
H	-0.6021444	2.5815929	-3.7205105	H	-0.1136551	-2.9445762	-1.6181536
H	0.3172470	1.7466780	-4.9608715	H	2.9168653	-2.7964024	-1.5069543
H	1.4097932	3.8981511	-4.5112268	H	1.8959807	-3.9039357	-2.4074408
H	2.4532474	2.6201545	-3.9079434	H	3.0183625	-5.1514263	-0.6128251
H	-0.2416926	2.8372159	-1.4768218	H	1.3060853	-5.0637668	-0.2315577
H	3.5682156	3.4066924	-1.8336026	H	2.5880657	-1.7303305	0.5154135
H	2.8700130	4.8221563	-1.0247159	H	1.0577018	-4.8429722	2.2342071
H	3.2768112	4.8961385	-2.7456379	H	2.4863182	-4.3311027	3.1515993
H	-0.4524905	4.7484303	-2.7534806	H	2.5896488	-5.7116984	2.0483481
H	0.9609793	5.7847495	-3.0460635	H	4.4648838	-3.0421247	0.2440591
H	0.4269918	5.4553867	-1.3851330	H	4.6088774	-4.5736511	1.1332845
H	3.1572908	1.2498474	-0.7133555	H	4.3751397	-3.0509641	2.0158193
H	3.1688081	1.3179924	-2.4923213	H	-0.7149189	-3.0894818	1.9328678
H	2.7602060	-0.1903866	-1.6649668	H	-0.3188733	-4.2476302	0.6414530
H	0.0828549	-1.1597884	-1.3534257	H	-1.4988498	-2.9603772	0.3507347
H	1.3148662	-1.3898648	1.1618173	H	-0.0801829	-0.0895834	-1.1748990
H	-2.3461102	-2.7163891	0.4258429	H	1.0753967	1.7584250	-0.2901885

5.5 References and Notes:

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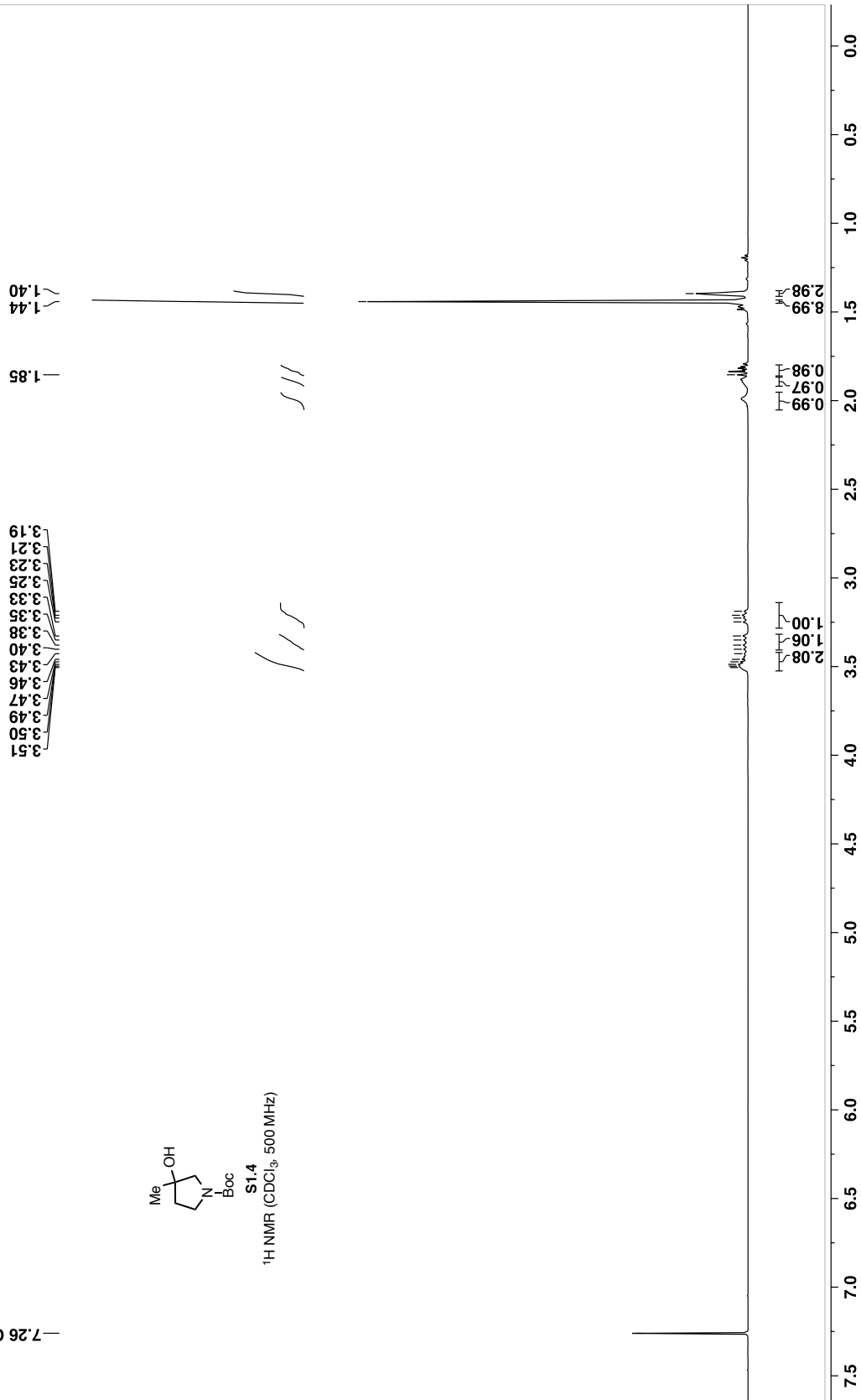
Appendix A: Chapter 1 NMR Spectra

A3_91-con-s5-002.10.fid
Frequency: 500.62 MHz

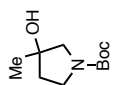
- 7.26 CDCl₃



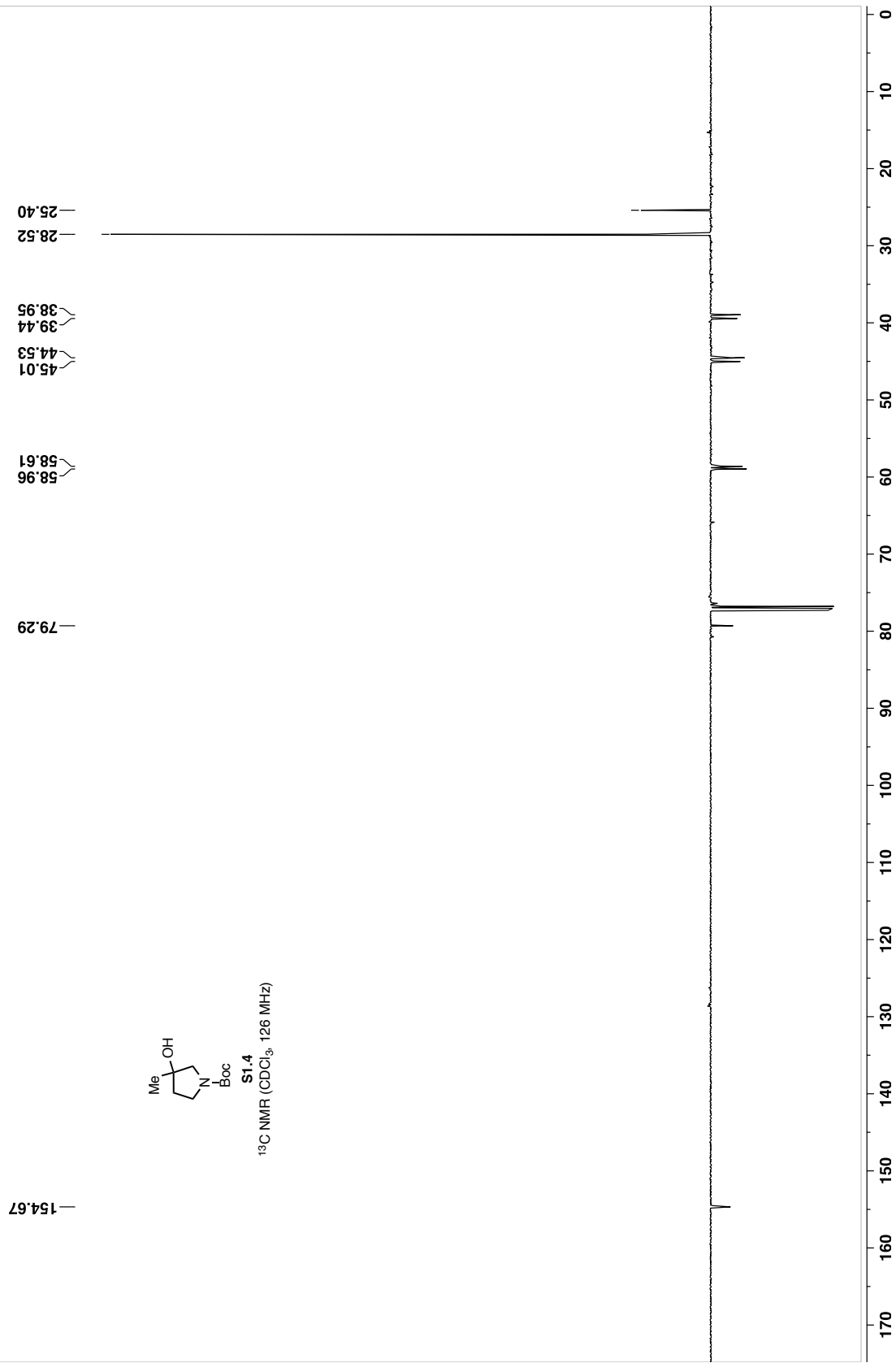
S1.4
¹H NMR (CDCl₃, 500 MHz)



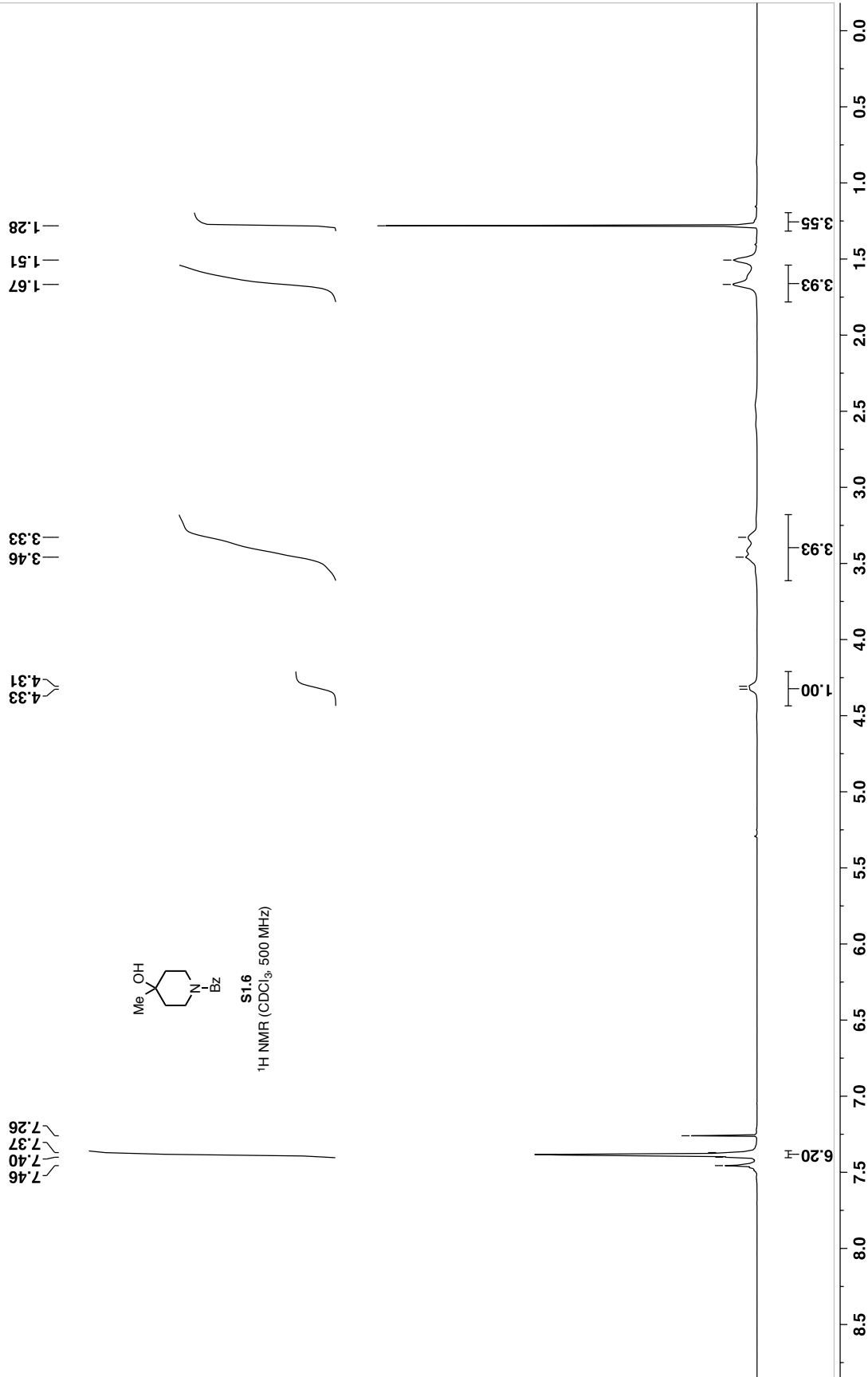
A3_91-can-s5-002.11.fid
Frequency: 125.89 MHz



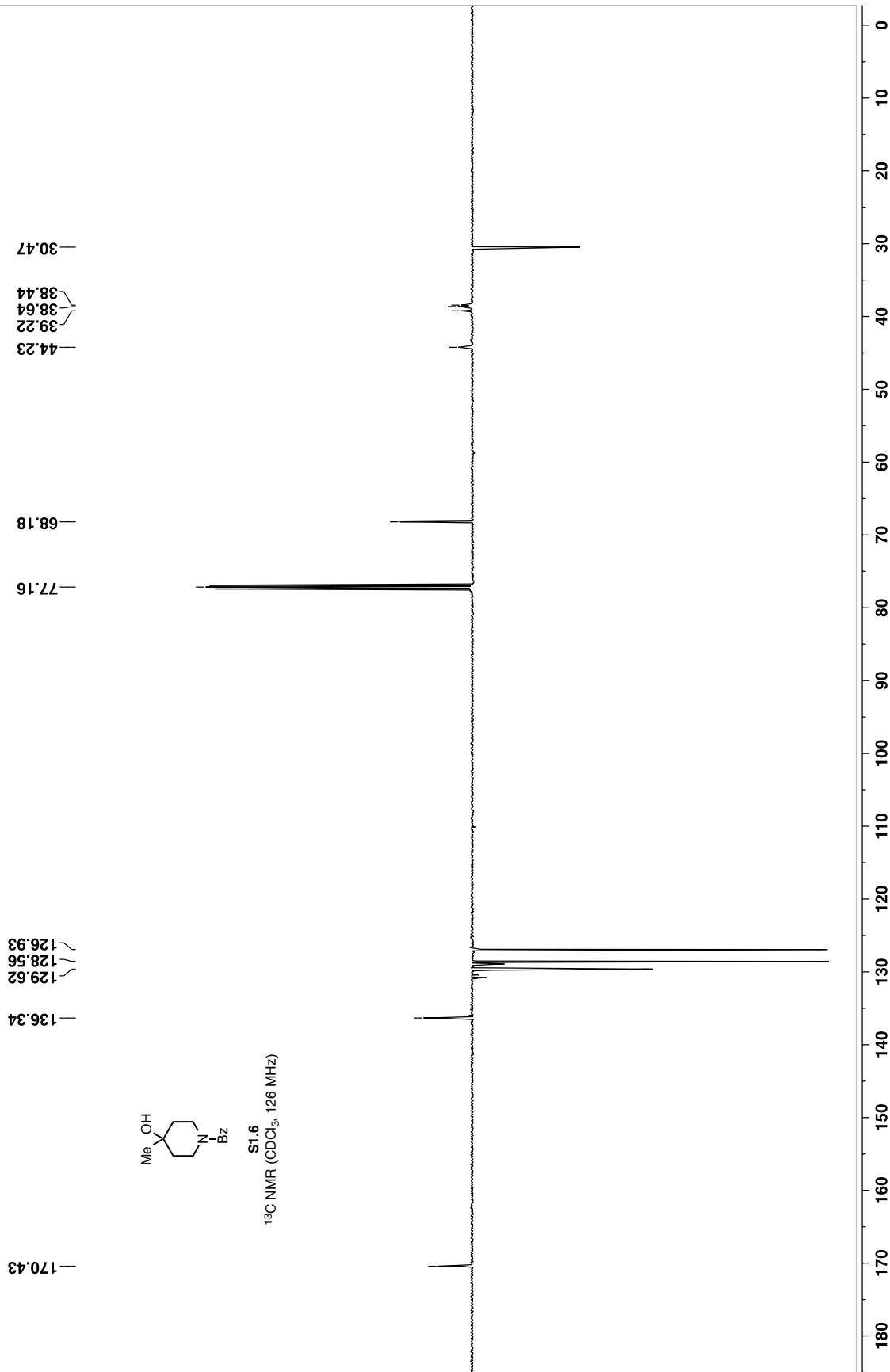
S1.4
¹³C NMR (CDCl₃, 126 MHz)



A2_81-ccn-s4-123-a.10.fid
Frequency: 500.46 MHz

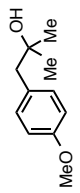


A2_81-ccn-s4-123-a.11.fid
Frequency: 125.85 MHz

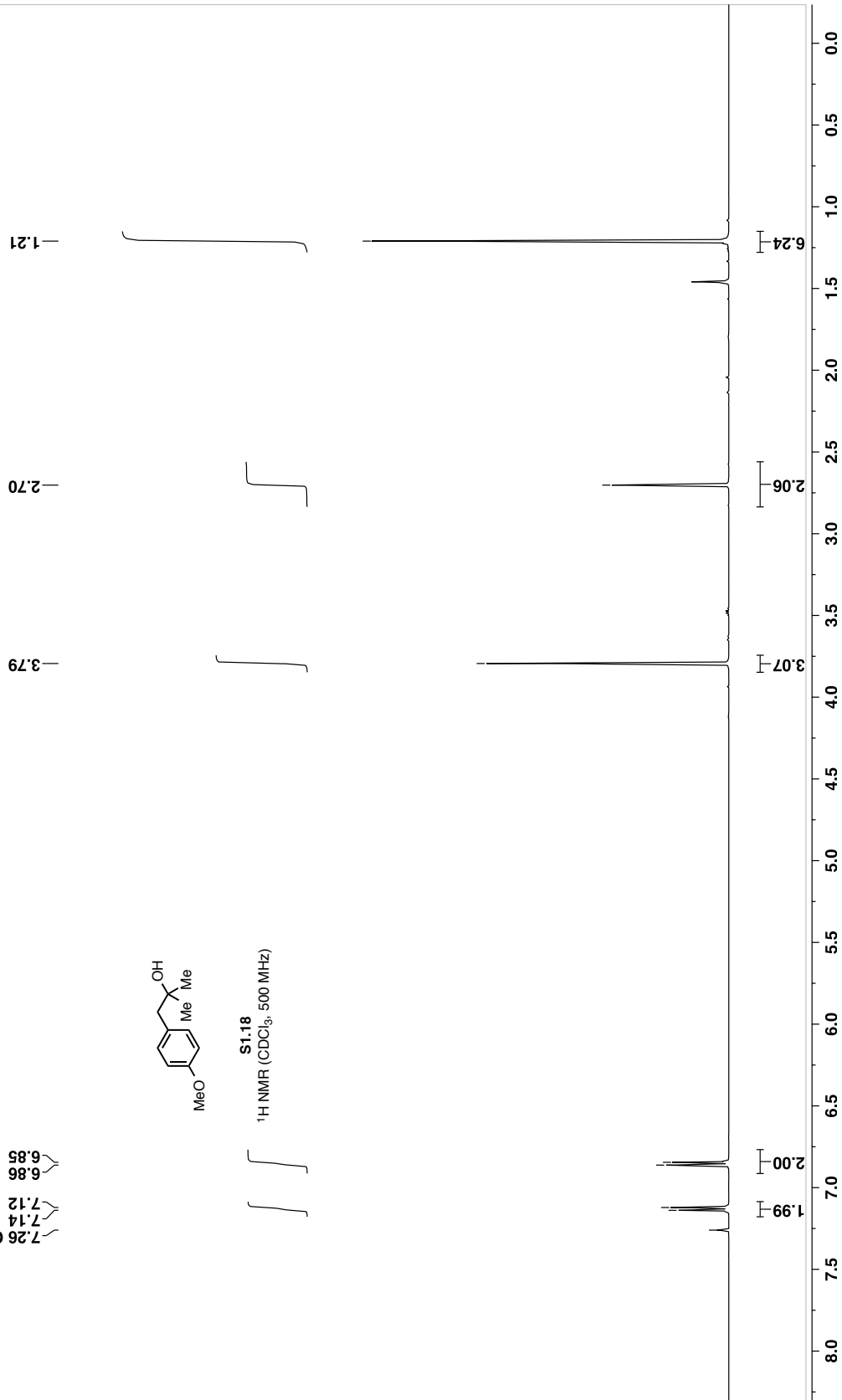


A2_108-ccn-s5-076-a.10.fid
Frequency: 500.46 MHz

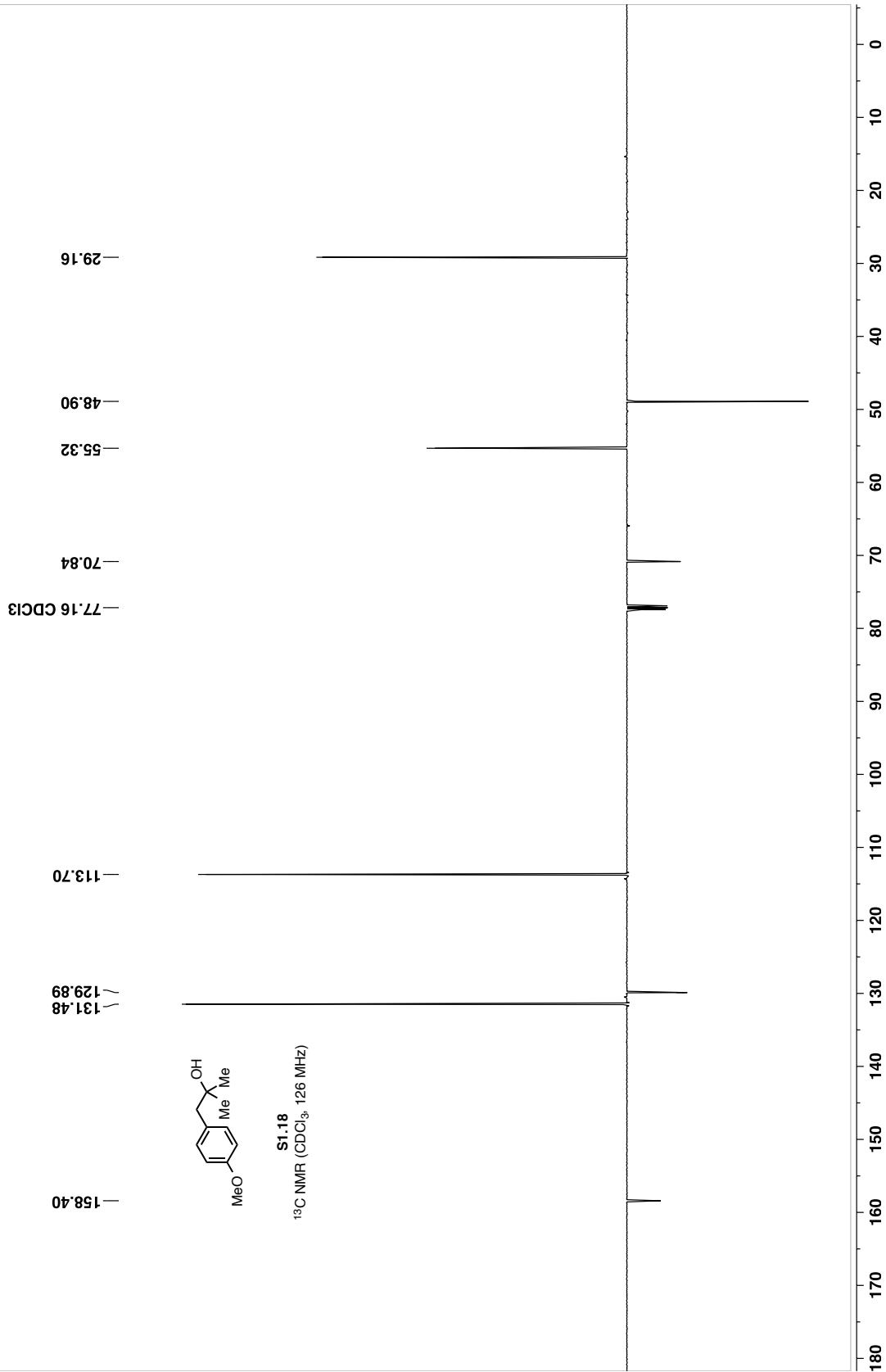
7.26 CDCl3
7.14
7.12
6.86
6.85



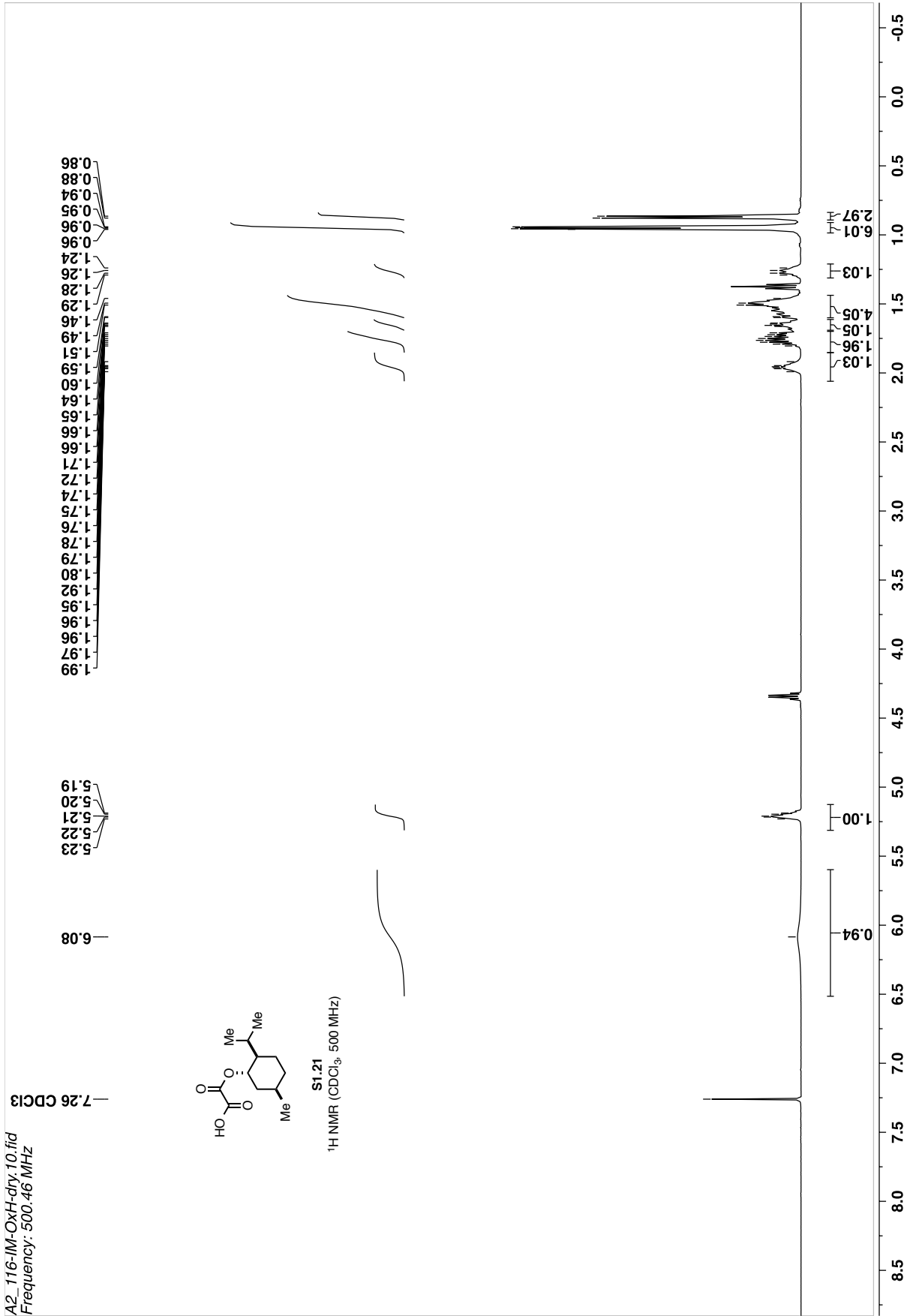
S1.18
1H NMR (CDCl3, 500 MHz)



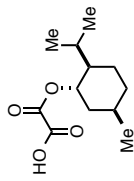
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Frequency: 125.85 MHz



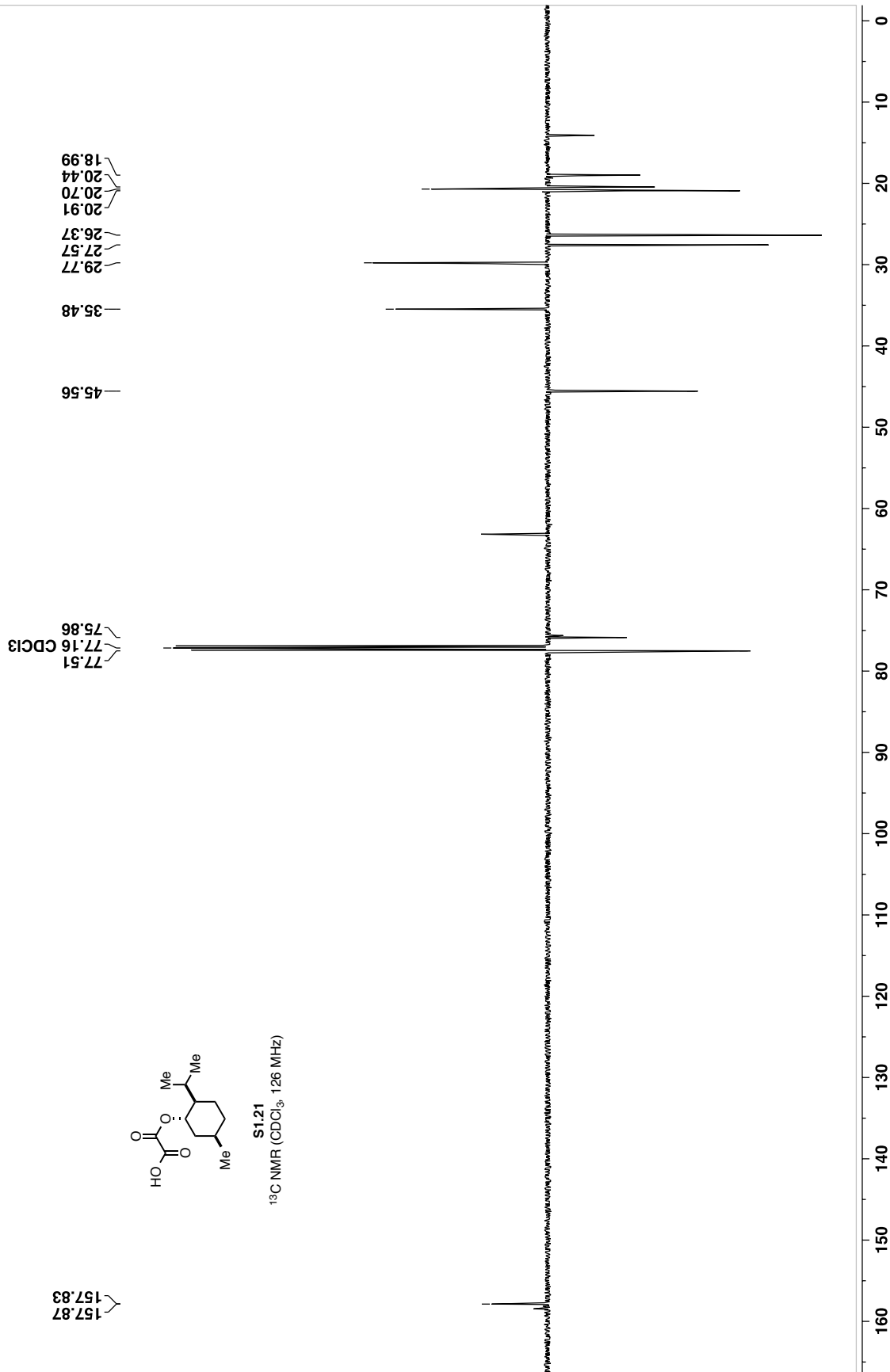
A2_116-IM-OxH-drv.10.fid
Frequency: 500.46 MHz



A2_T16-1M-OxH-dry.11.fid
Frequency: 125.85 MHz



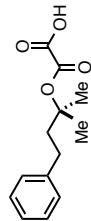
S1.21
¹³C NMR (CDCl₃, 126 MHz)



YS-II-149

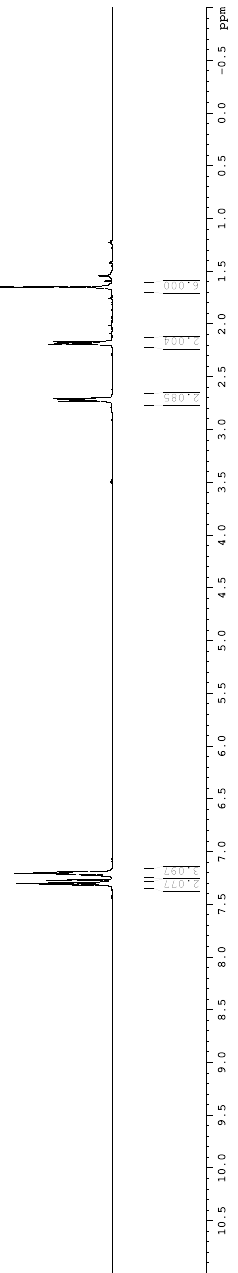
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NAME          YS-II-149
PROCNO       4
PROCDS       2
===== Acquisition Parameters =====
Date_       20141212
Time        8:59
INSTRUM     spect
PROBHD      5 mm TD1 1H/13
PULPROG     zgpg30
PCPRG2      cozpr2
SOLVENT     CDCl3
NS          8
DS          2
ES          0.915, 0.85 Hz
AQ          0.500072 Hz
RG          0.9998560 sec
TX          50.000 usec
P1          14.50 usec
PL          0.00 dB
TD          6.10000000 usec
===== CHANNEL f1 =====
SFO1        601.1342019 MHz
NUC1        13
PROB1       8.00 usec
P1A1        23.0141556 N sec
===== F2 - Processing Parameters =====
SI          45.536
SF          601.1303279 MHz
WDW         EM
SSB         0
LB          0.30 Hz
GB          0
PC          1.00
```

7.518
7.506
7.293
7.287
7.281
7.274
7.268
7.208
7.195



1.55
¹H NMR (CDCl₃, 600 MHz)

7.21
7.202
7.195
7.188
7.181
7.174
7.167
7.160
7.153
7.146
7.139
7.132
7.125
7.118
7.111
7.104
7.097
7.090
7.083
7.076
7.069
7.062
7.055
7.048
7.041
7.034
7.027
7.020
7.013
7.006
7.000



Current Data Parameters
 YS-II-152
 EXNO
 FRCQCN I

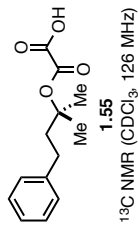
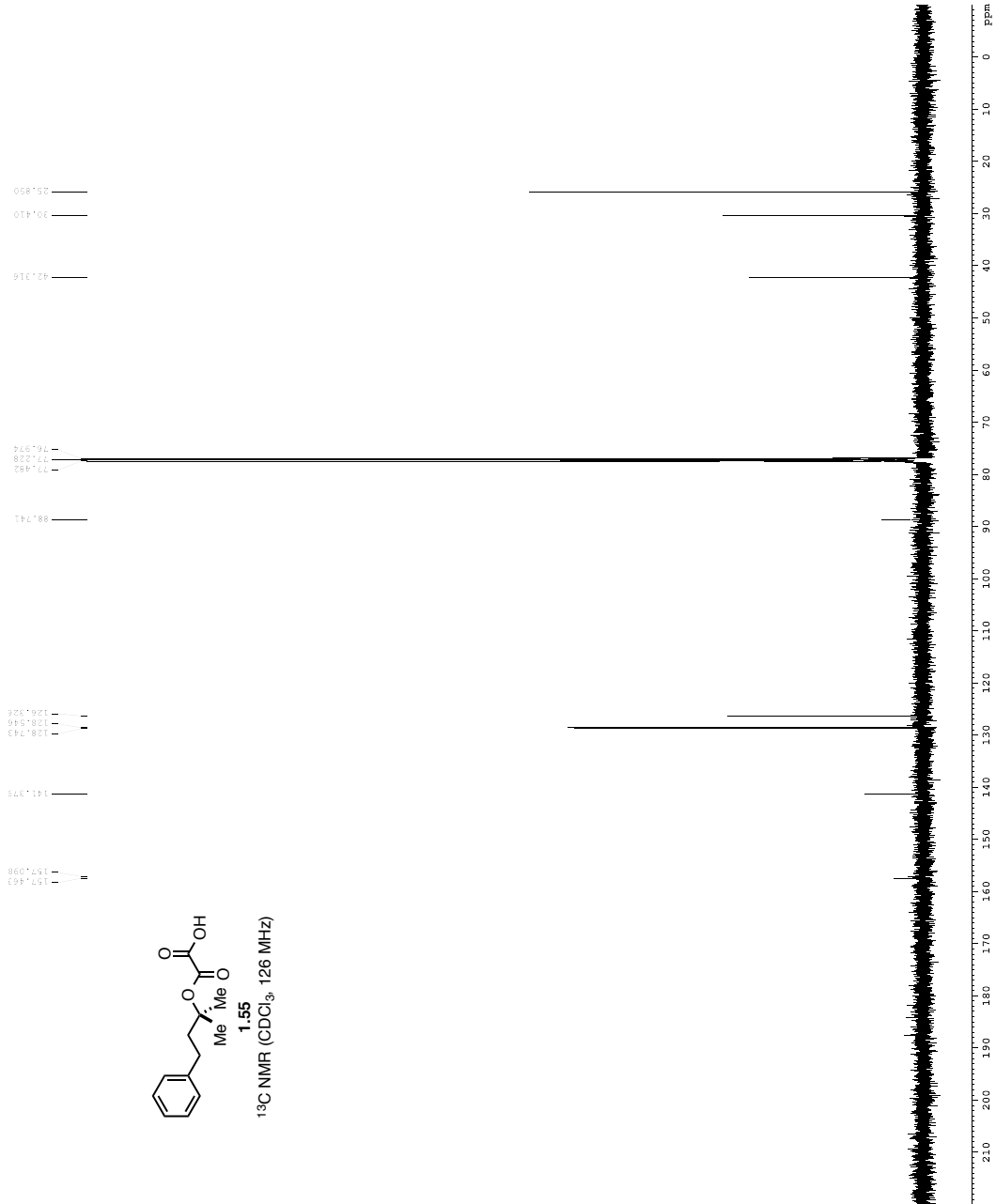
File Acquisition Parameters
 Time_ 2014.14.14
 INSTRUM cty500
 PROBED 5 mm CP1CI IH-
 ZDUPROG gpinactopsp.prd
 62535
 SOLVENT CDCl3
 NS 52
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0913440 sec
 RG 128.000
 DM 128.000 USBC
 DE 6.00 USBC
 FE 289.0 K
 O1 0.7500000 sec
 O11 0.7500000 sec
 O16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MARK 0.0150000 sec
 F2 33.10 USBC

===== CHANNEL f1 =====
 NU1 16.25 USBC
 FL1 500.00 USBC
 F12 2000.00 USBC
 F10 120.00 dB
 F11 0.00 dB
 SF01 125.7842548 MHz
 SF1 2.70 dB
 SFOFF1 Cpq60.0.5.20.0
 SFOFF2 Cpq60.comp.4
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 wallz16
 NUC2 1H
 FL2 100.00 usec
 F12 120.00 dB
 F11 24.50 dB
 SF02 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GPMAX(1) SINE.100
 GPMAX(2) SINE.100
 GPC1 0 %
 GPC2 0 %
 GPC3 0 %
 GPC4 0 %
 GPC5 30.00 %
 GPC6 500.00 USBC
 p15 1000.00 usec
 p16

F2 - Processing Parameters
 SI 62535
 SF 125.784002 MHz
 WDW EM
 GB 0 1.00 Hz
 GE 0 2.00



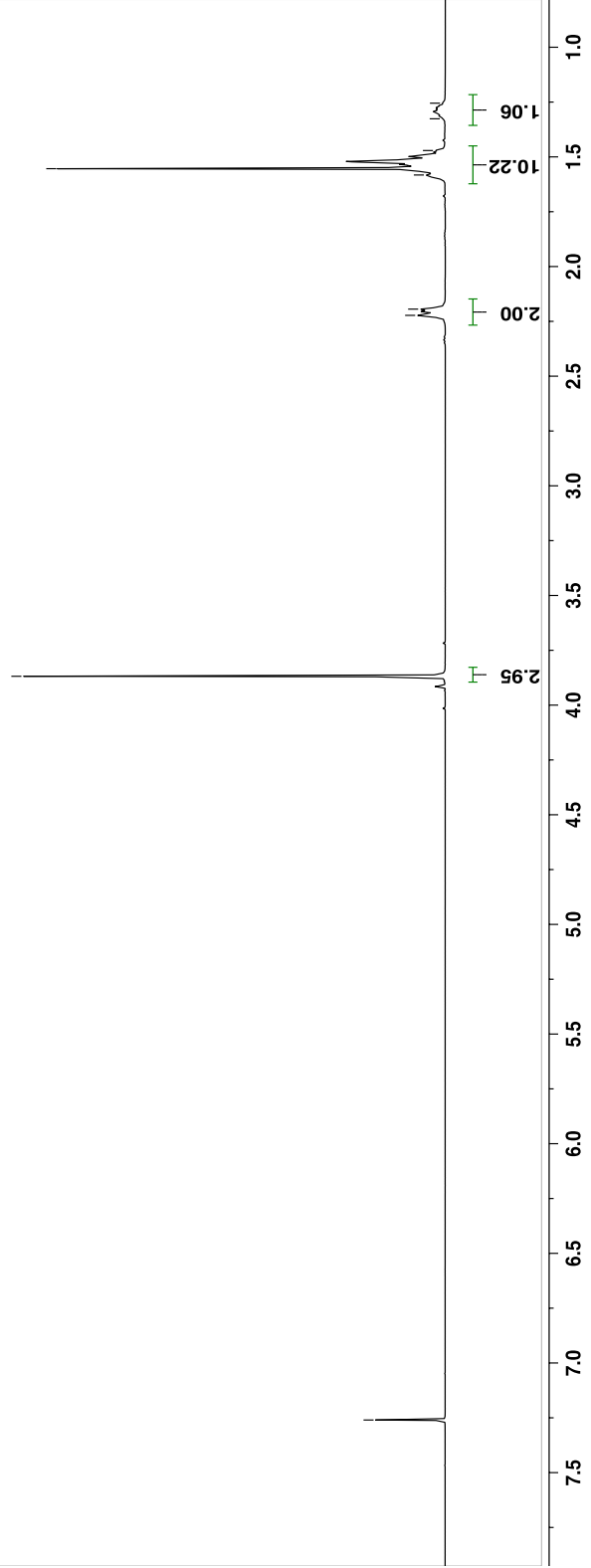
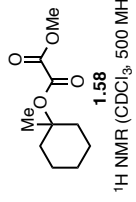
A2_71-ccn-s5-040-crude.10.fid
Frequency: 500.46 MHz

7.26 CDCl₃

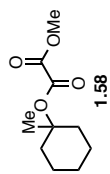
1.58
1.55
1.47
1.33
1.26

2.22
2.19

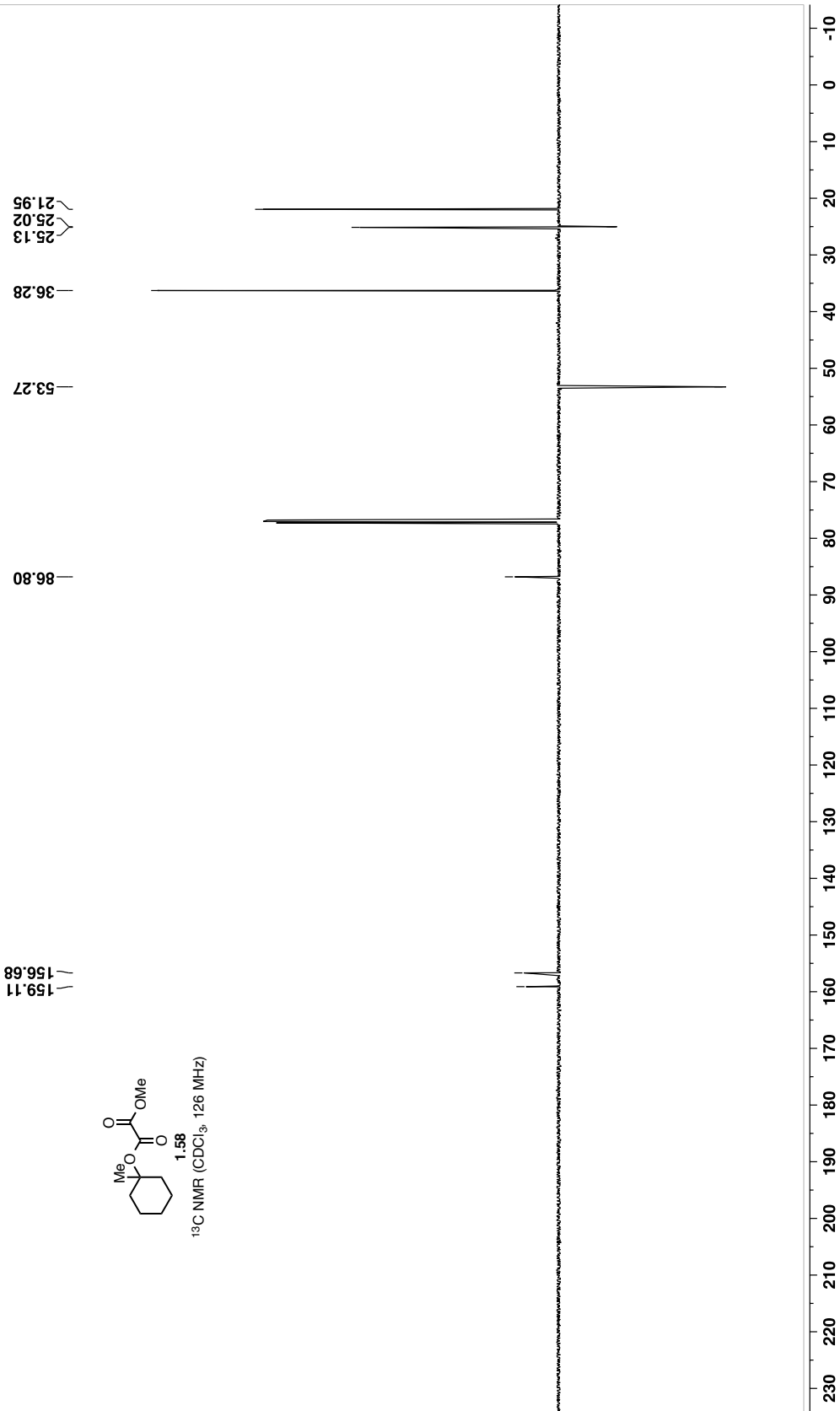
3.87



A2_71-con-s5-040-crude.11.fid
Frequency: 125.85 MHz



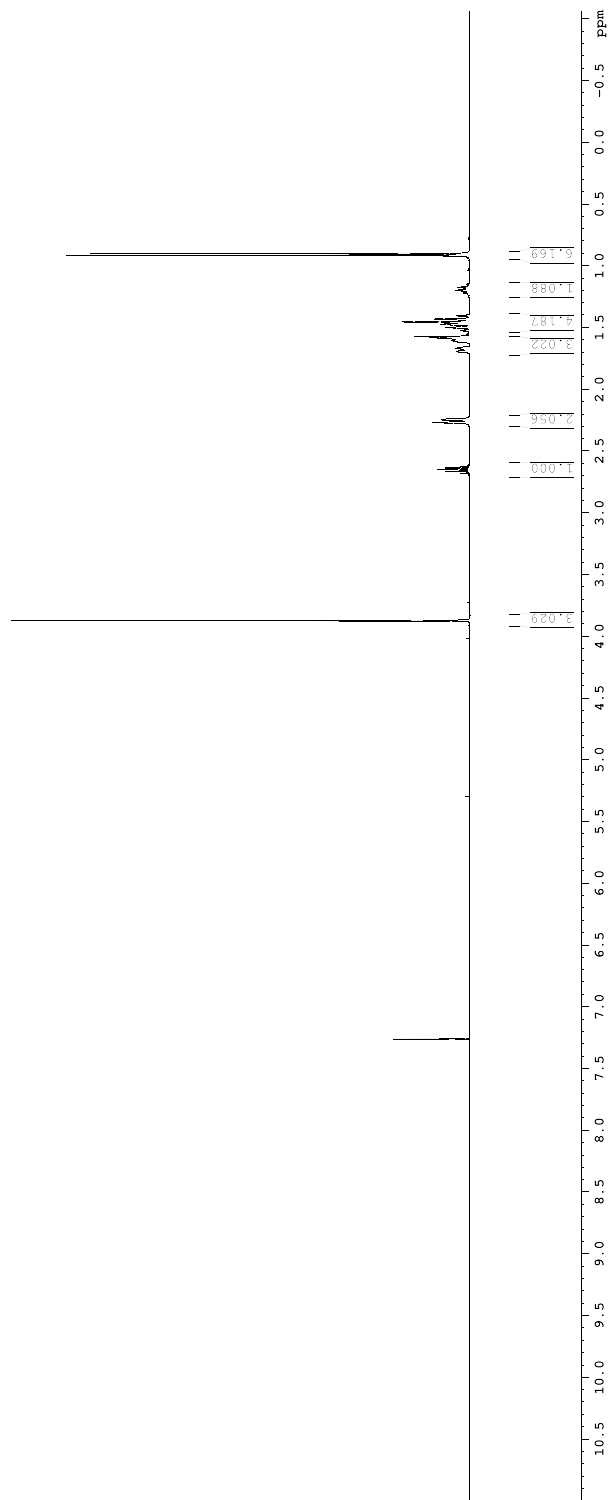
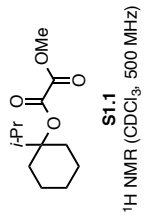
¹³C NMR (CDCl₃, 126 MHz)



¹H spectrum

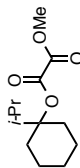


Current Data Parameters
 NAME CAJ1-093-pure
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20150223
 Time 8:02
 Instrument spect
 PROBR1 5 mm CPY1 1H
 PULPROG zg30
 TD 48074
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.166677 Hz
 AQ 2.3998176 sec
 RG 5.7
 DE 62.400 usec
 DB 6.00 usec
 TE 298.0 K
 D1 0.10000000 sec
 MCREST 0 sec
 RCMRK 0.01000000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 PL0 0.00 usec
 SFO1 500.2235013 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.2200319 MHz
 DSF 0
 SSB 0
 LB 0 Hz
 GB 0
 FC 4.00



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

159.373
156.783



S1.1

¹³C NMR (CDCl₃, 126 MHz)

93.354
77.413
77.159
76.900
53.337
33.280
30.025
23.979
21.592
17.171

```

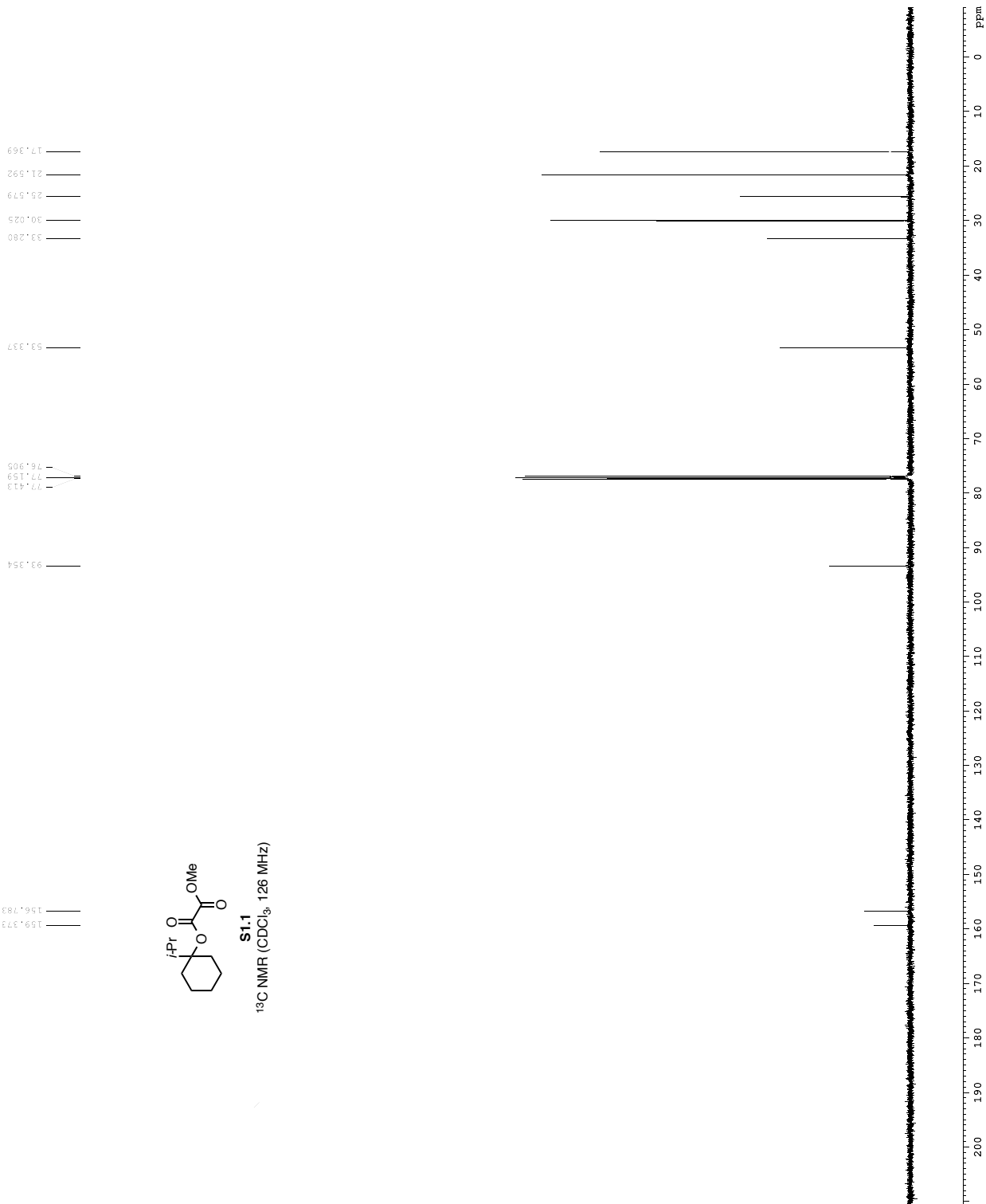
Current Data Parameters
NAME      CR01-093-bure
EXPNO     2
PROCNO    1
F2 - Acquisition Parameters
Date_     20150223
Time      8.05
INSTRUM   cryo500
PROBHD    5 mm CPFI 1H-
PULPROG   SpinEchozg30gp-prd
TD         65536
SOLVENT   DMSO
NS         32
DS         4
SWH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813440 sec
RG         5792.6
DW         16.500 usec
DE         6.00 usec
TE         298.10 K
D1         1.0000000 sec
d11        0.0000000 sec
d12        0.0000000 sec
d16        0.0002000 sec
d17        0.00019600 sec
MCREST     0 sec
MCWRK     0.01500000 sec
P2         33.10 usec
    
```

```

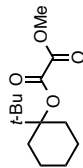
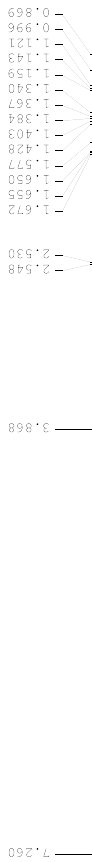
===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        0.00 dB
PCPD2      200.00 usec
P2         120.00 dB
PL2        -1.00 dB
SFO1       125.7942548 MHz
SP1        2.70 dB
SP2        2.70 dB
SPNAM[1]   Crp60.0.5.20.1
SPNAM[2]   Crp60comp.4
SFOFF1     0 Hz
SFOFF2     0 Hz
    
```

```

===== CHANNEL f2 =====
CPDPRGf2   waltz16
NUC2        1H
P2         100.00 usec
PL2         1.60 dB
P12        24.50 dB
SFO2       500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNM[1]    SINE.100
GPNM[2]    SINE.100
GFX1       0 %
GFX2       0 %
GFX3       0 %
GFX4       0 %
GFX5       0 %
GFX6       0 %
GFX7       0 %
GFX8       0 %
GFX9       0 %
GFX10      0 %
GFX11      0 %
GFX12      0 %
GFX13      0 %
GFX14      0 %
GFX15      0 %
GFX16      0 %
GFX17      0 %
GFX18      0 %
GFX19      0 %
GFX20      0 %
F2 - Processing parameters
SI         65536
SF         125.7804082 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
    
```



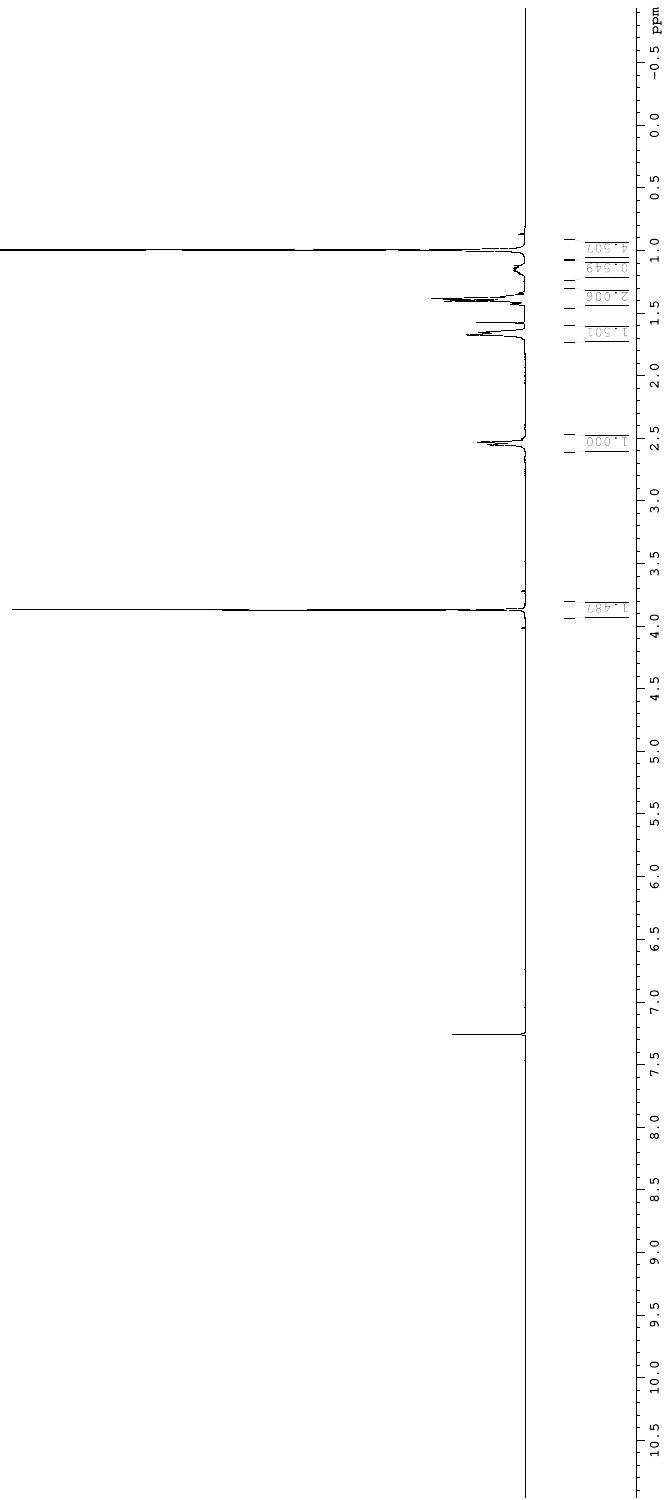
¹H spectrum



S1.2
¹H NMR (CDCl₃, 500 MHz)

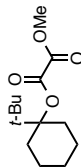
```

Current Data Parameters
Date_ 20150310
Time_ 11:56:56
INSTRUM crys500
PROBHD 5 mm QNP1H-
PULPROG zgpg30
TD 48074
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.999917 sec
RG 517
DE 62.400 usec
TE 298.2 K
ACQRES 0.10000000 sec
SFO1 500.225015 MHz
CHANNEL F1
NUC1 1H
P1 1.50 usec
PL1 1.50 dB
SFO2 500.225015 MHz
F2 - Processing parameters
SI 6551
SF 500.220011 MHz
WDW 0
SSB 0
LB 0 Hz
GB 0
PC 4.00
  
```

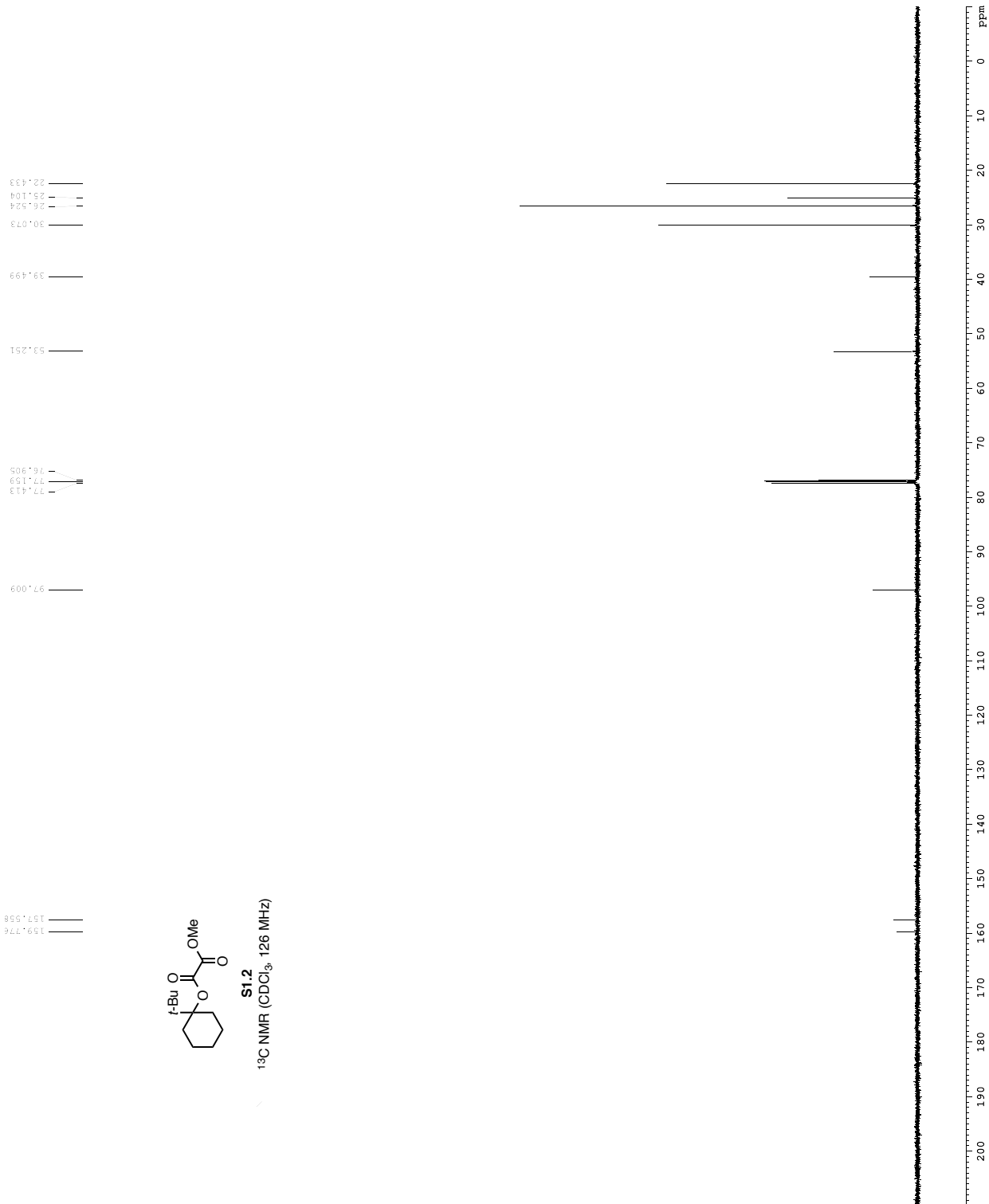


Z-restored spin-echo 13C spectrum with 1H decoupling

157.536
159.776



S1.2
13C NMR (CDCl₃, 126 MHz)



Current Data Parameters
 NAME CRJ1-137-pure
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20150310
 Time 13:34
 INSTRUM cryo130
 PROBHD 5 mm CPY131-4
 PULPROG Spinechop3Bp.prd
 TD 65536
 SOLVENT CDCl3
 NS 72
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.462398 Hz
 AQ 1.081340 sec
 RG 369.0
 DM 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 ACQRES 0 sec
 ACQRESK 0.0150000 sec
 F2 33.10 usec

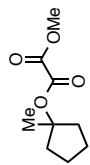
===== CHANNEL f1 =====
 NUC1 13C
 P1 16.55 usec
 PL1 500.00 usec
 PL2 2000.00 usec
 F10 120.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF10 120.00 MHz
 SE2 2.70 dB
 SPNAM11 Ccp60_0_5_26_1
 SPNAM21 Ccp60comp_4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 1H
 P2 100.00 usec
 PL2 1.60 dB
 F12 24.50 dB
 SFO2 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GPM1[1] SINE.100
 GPM1[2] SINE.100
 GPC1 0 %
 GPC2 0 %
 GPC3 0 %
 GPC4 0 %
 GPC5 30.00 %
 GPC6 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

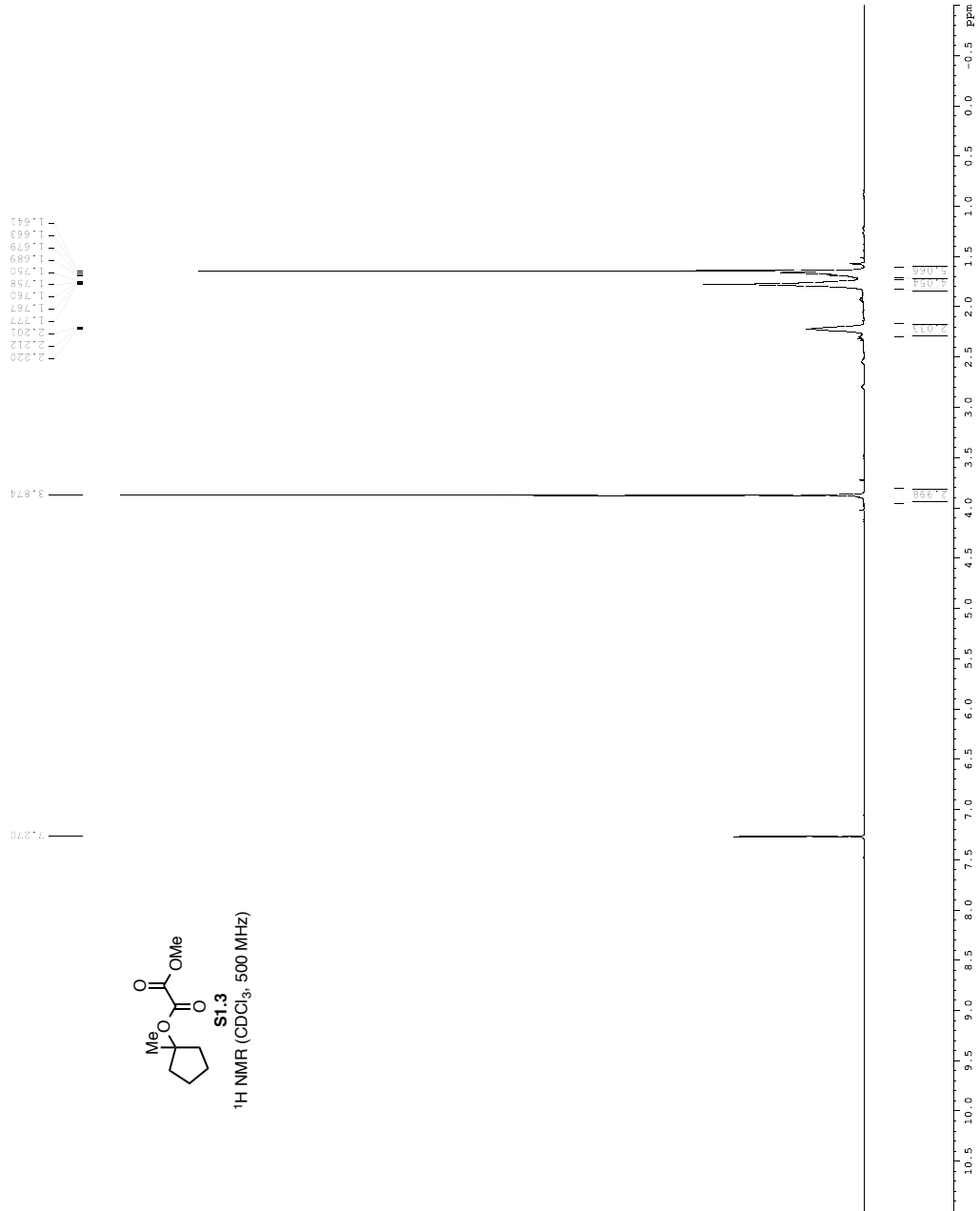
F2 - Processing parameters
 SI 65536
 SF 125.7804081 MHz
 GAM 0
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 2.00

YS-II-240



S1.3
¹H NMR (CDCl₃, 500 MHz)

Current Data Parameters
NAME: YS-II-240
PROCNO: 4
F2 - Acquisition Parameters
Date_ Time: 01/05/21 10:09
INSTRUM: spect
PROBHD: 5 mm CPY1 1H
PULPROG: zg30
SOLVENT: CDCl3
NS: 8
DS: 4
AQ: 0.250026 Hz
RG: 1.9997952 sec
EX: 60.400 usec
DE: 6.00 usec
DI: 0.10000000 sec
MCHEST: 0 sec
SCANS: 0.01500000 sec
===== CHANNEL f1 =====
NUC1: 1H
PUL1: 7.50 usec
FL1: 1.60 dB
SFO1: 500.2235015 MHz
F2 - Processing parameters
SI: 65536
SF: 500.2235015 MHz
WDW: EM
SSB: 0
GB: 0
CB: 0
PC: 4.00



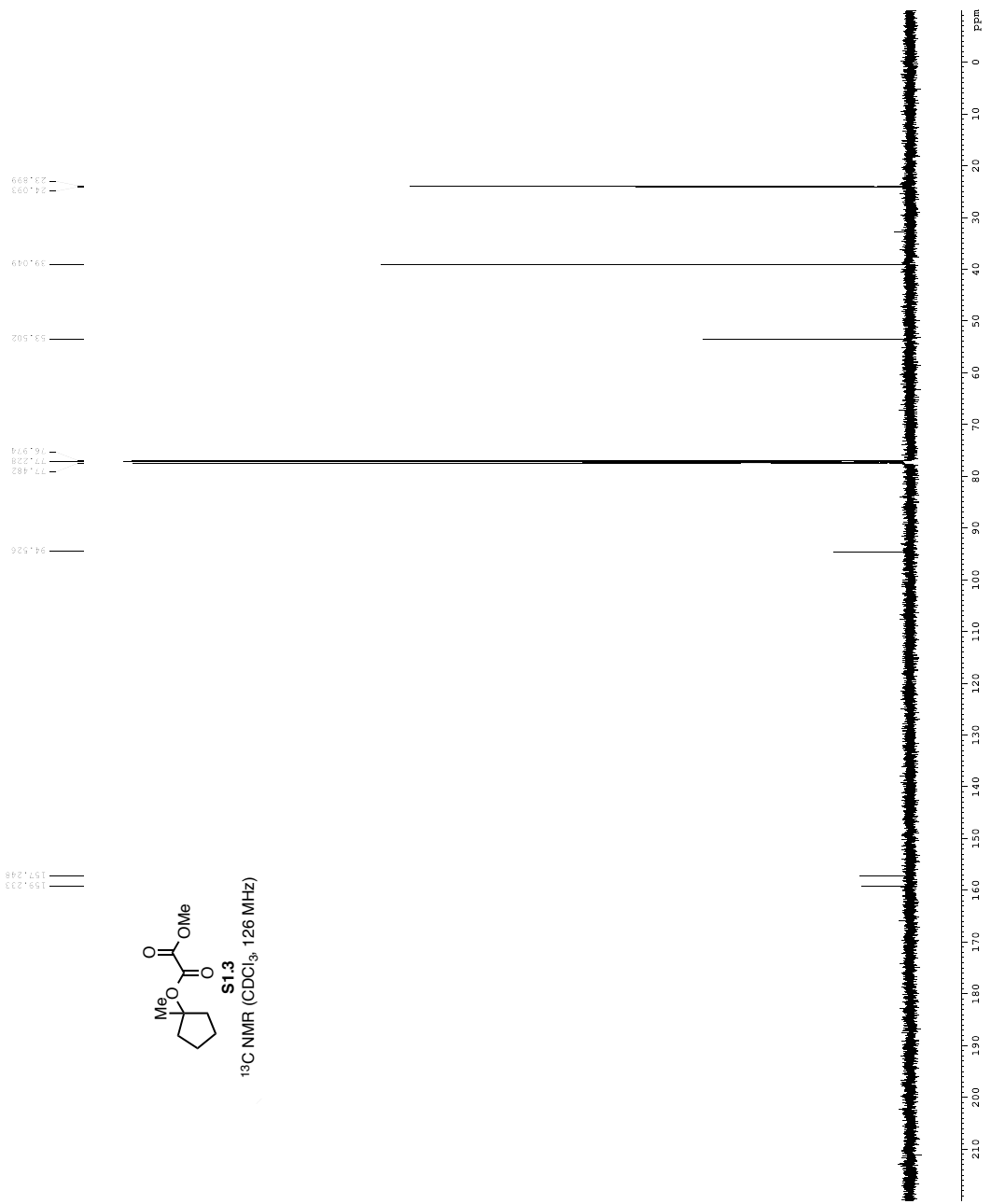
```

Current Data Parameters
NAME      YS-II-240
EXPNO     3
PROCNO    1

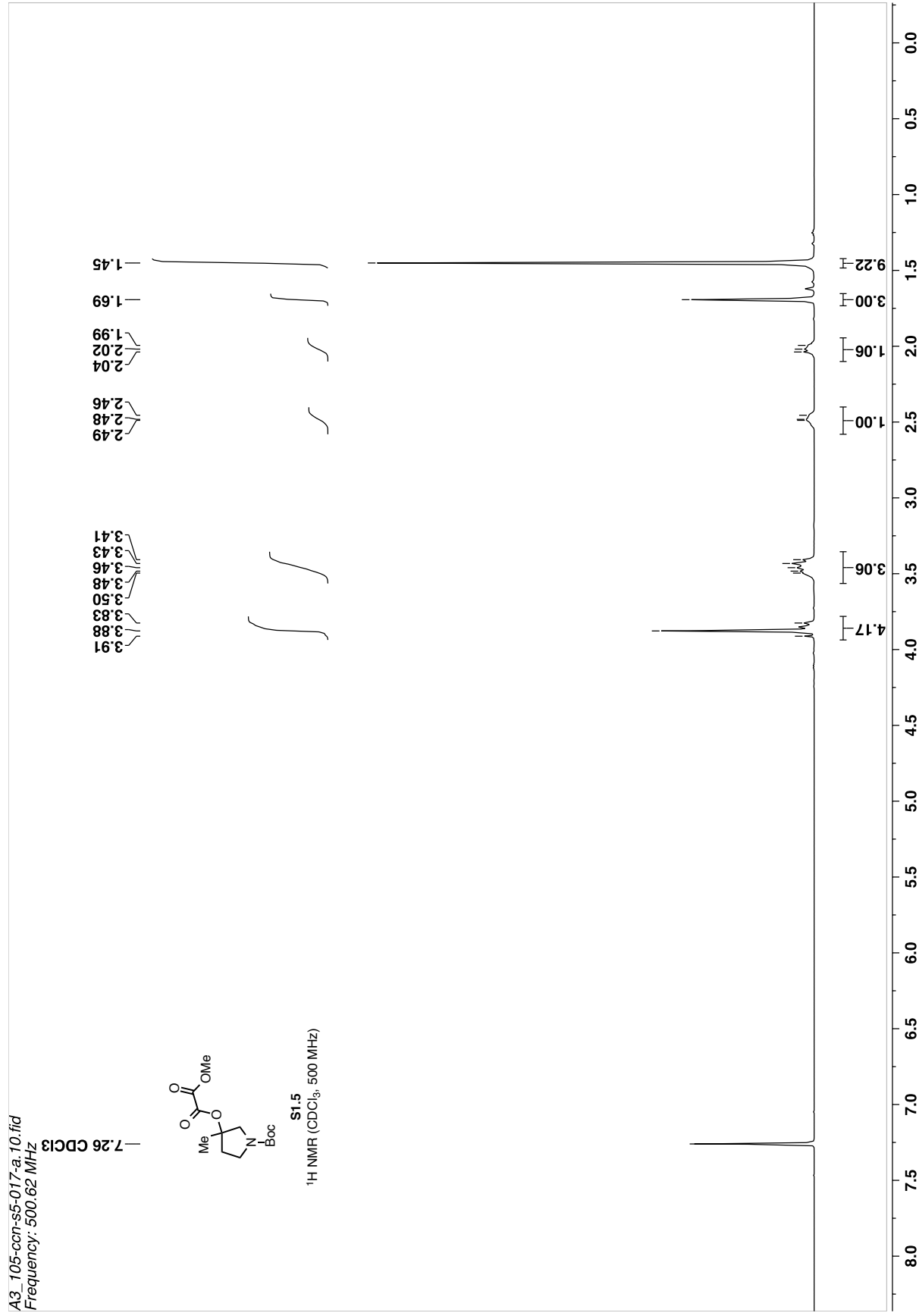
F2 - Acquisition Parameters
Date_     20160223
Time      10:13
INSTRUM   crys500
PROBHD    5 mm CRY500-H
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         312
DS         4
SWH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813440 sec
RG         327.5
DE         16.500 usec
TE         298.0 K
D1         0.3000000 sec
d11        0.0020000 sec
D16        0.0020000 sec
d17        0.0019600 sec
MCREST    0 sec
F2PWR     0.01500000 sec
F2PRR     33.10 usec

===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        500.00 usec
P2         2000.00 usec
PL2        19.00 dB
PL3        19.00 dB
PL4        19.00 dB
SFO1       125.7945348 MHz
SF1        2.70 dB
SFO2       500.1364200 MHz
SFO3       500.1364200 MHz
SFO4       500.1364200 MHz
SFO5       500.1364200 MHz
SFO6       500.1364200 MHz
SFO7       500.1364200 MHz
SFO8       500.1364200 MHz
SFO9       500.1364200 MHz
SFO10      500.1364200 MHz
SFO11      500.1364200 MHz
SFO12      500.1364200 MHz
SFO13      500.1364200 MHz
SFO14      500.1364200 MHz
SFO15      500.1364200 MHz
SFO16      500.1364200 MHz
SFO17      500.1364200 MHz
SFO18      500.1364200 MHz
SFO19      500.1364200 MHz
SFO20      500.1364200 MHz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
P2         100.00 usec
PL2        19.00 dB
PL3        19.00 dB
PL4        19.00 dB
SFO1       500.2250111 MHz
===== GRADIENT CHANNEL =====
GENDM[1]   SINE.100
GENDM[2]   SINE.100
GEX1       0 %
GEX2       0 %
GXY1       0 %
GXY2       0 %
GYZ1       0 %
GYZ2       0 %
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
    
```

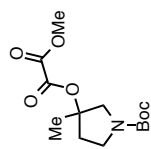


A3_105-con-s5-017-a.10.tif
Frequency: 500.62 MHz

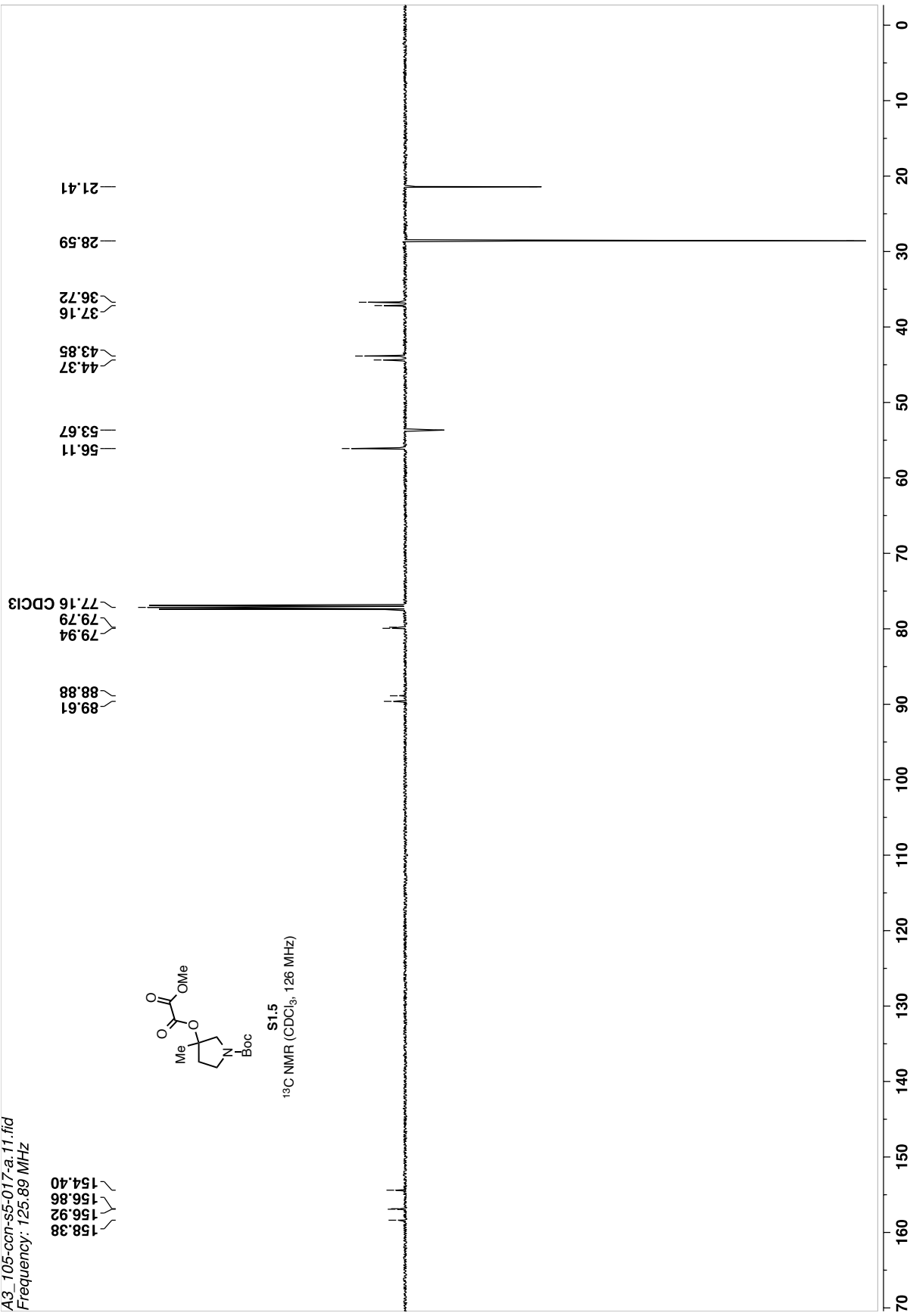


A3_105-con-s5-017-a.11.fid
Frequency: 125.89 MHz

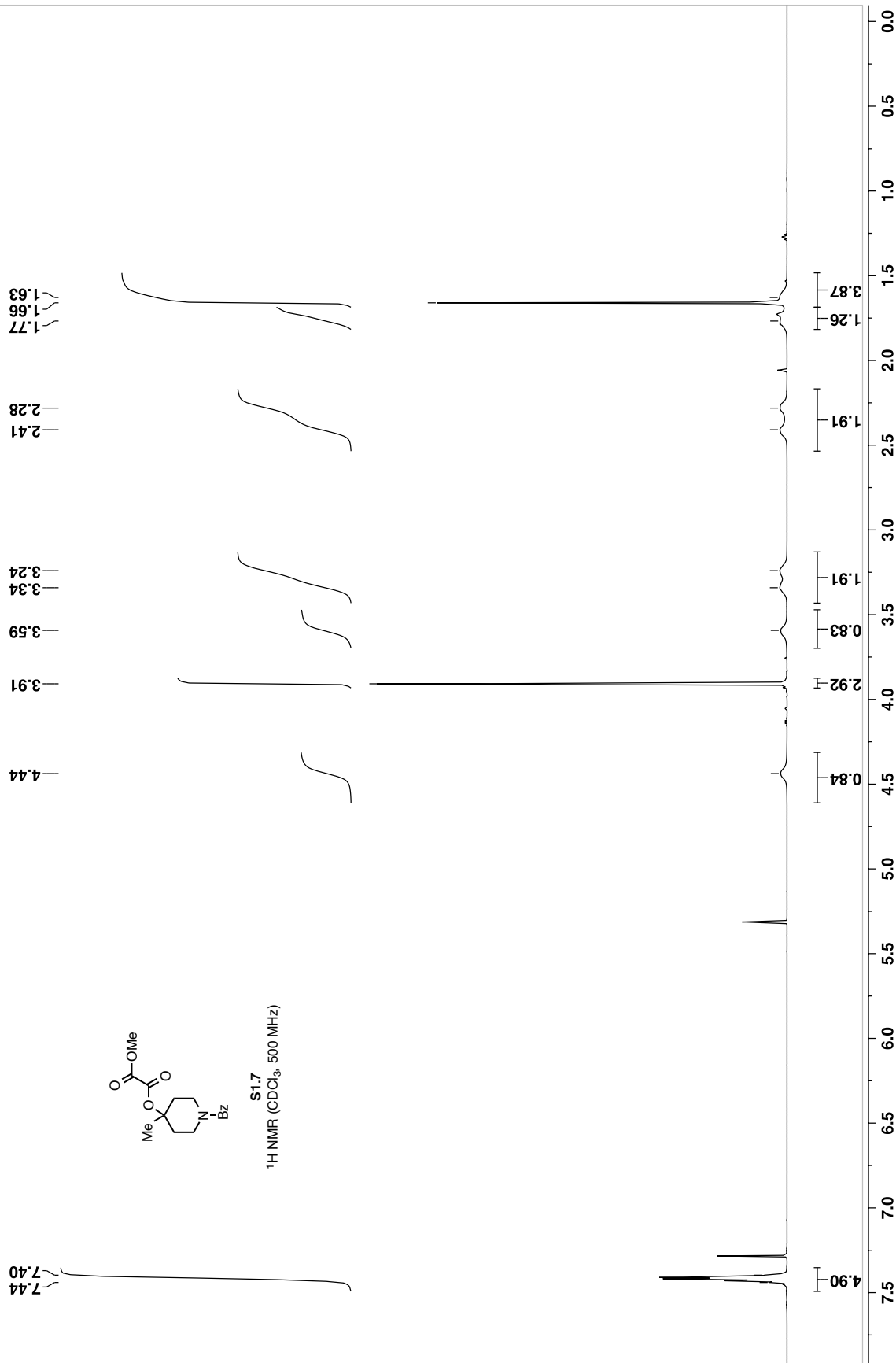
158.38
156.92
156.86
154.40



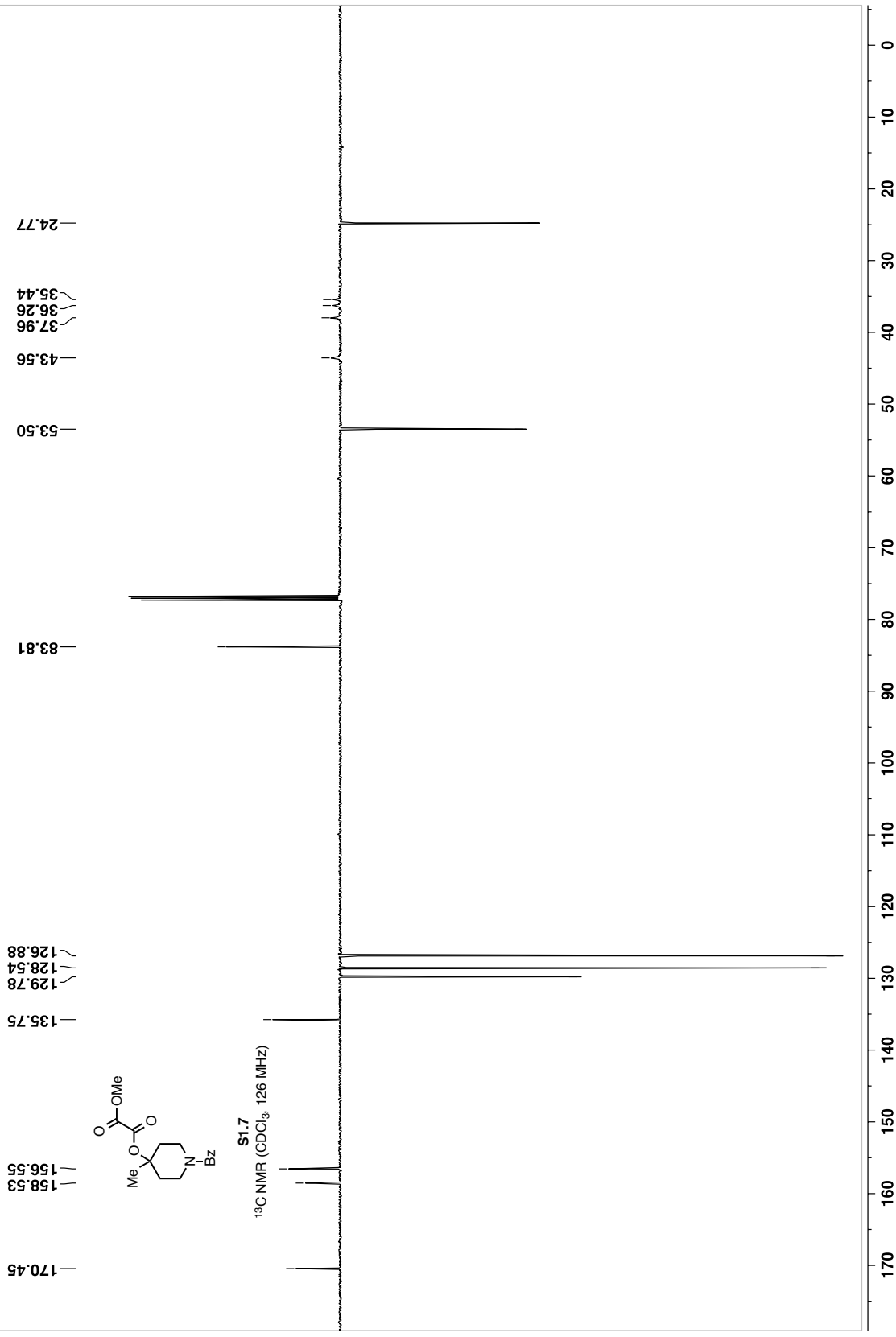
S1.5
¹³C NMR (CDCl₃, 126 MHz)



A3_5-ccn-s5-093-2-a.10.fid
Frequency: 500.62 MHz



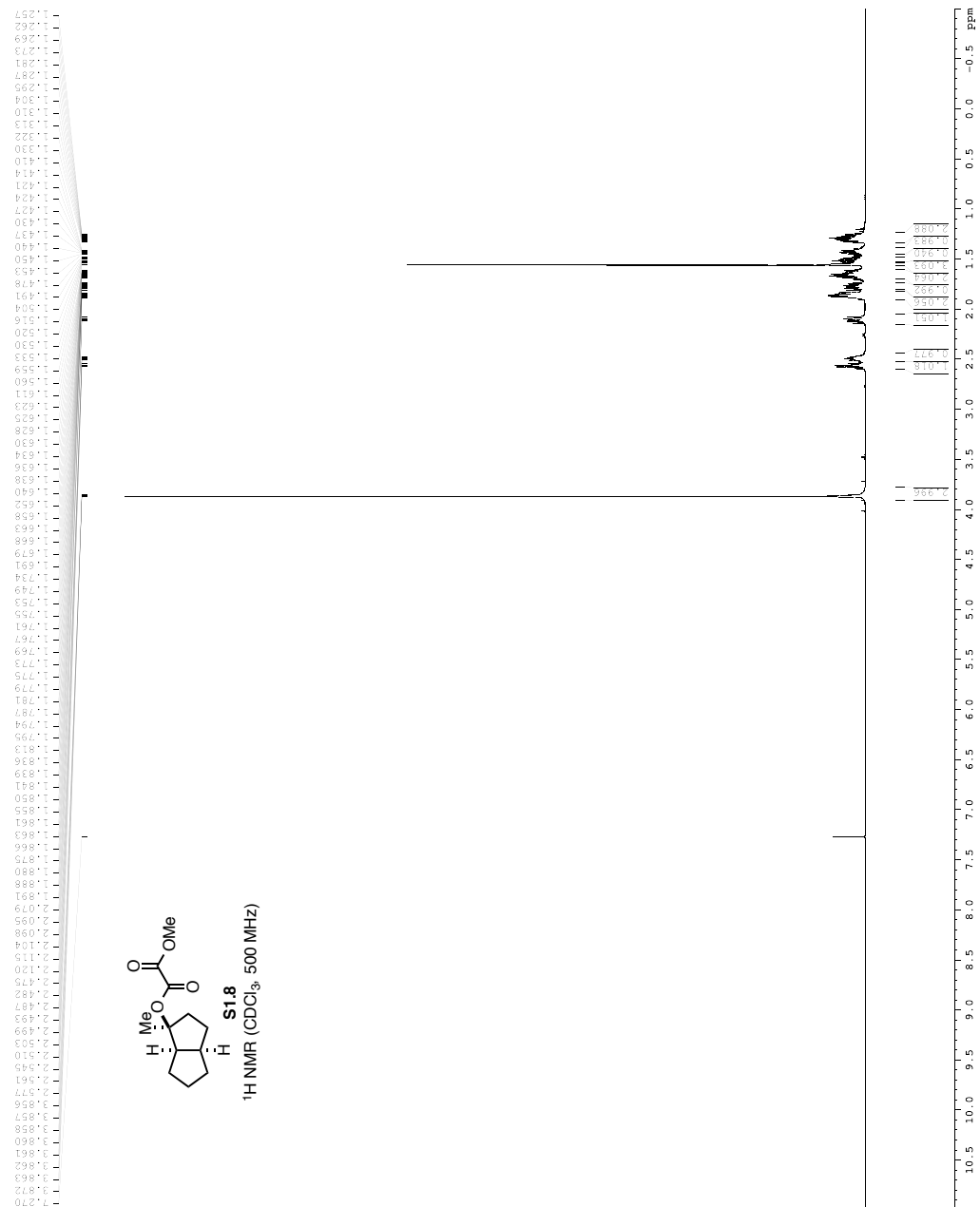
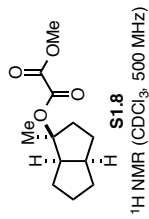
A3_5-ccn-s5-093-2-a.11.tif
Frequency: 125.89 MHz



XS-II-286

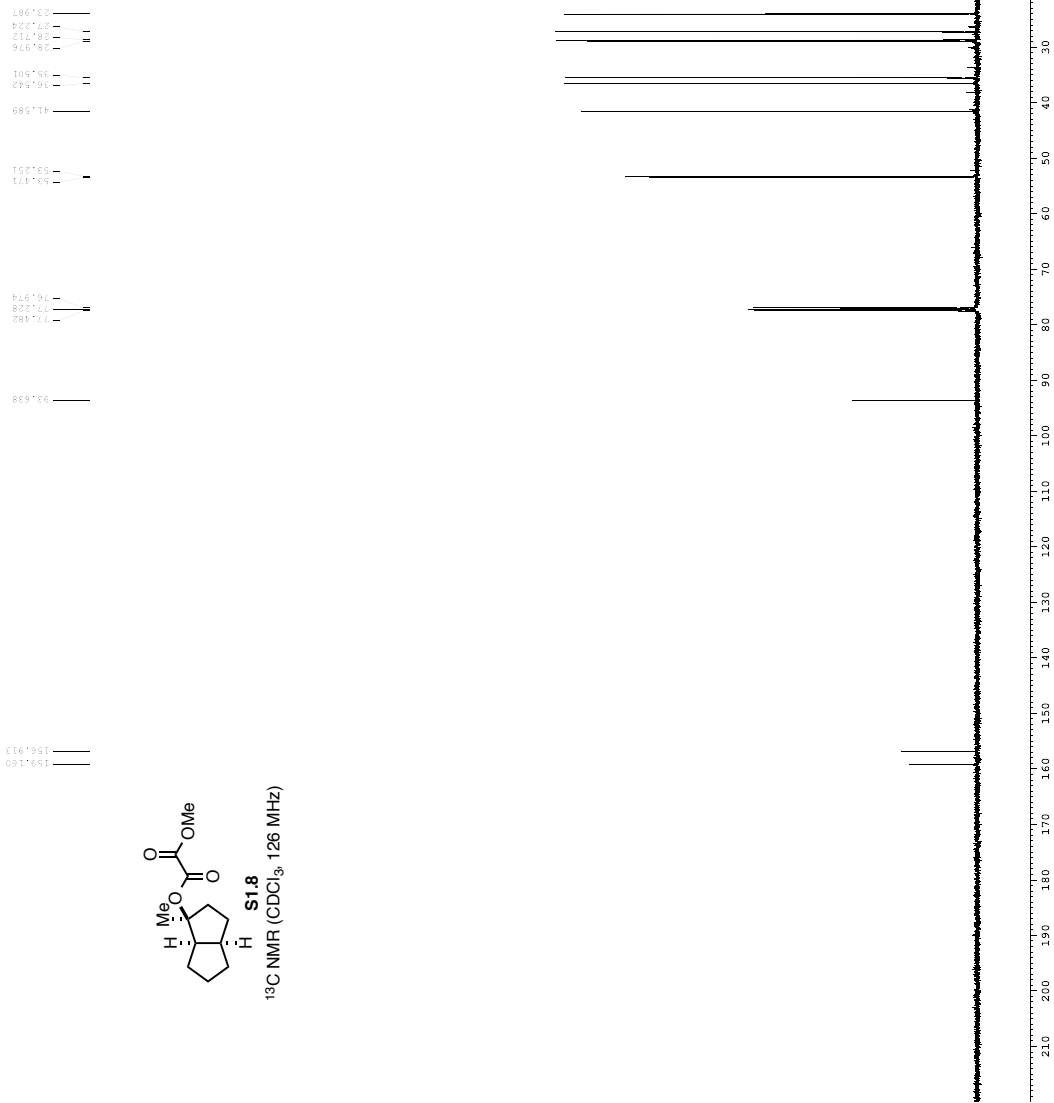
Current Data Parameters
NAME XS-II-286
PROCNO 1
SOLVENT CDCl3

F2 - Acquisition Parameters
Date_ Time 01/09/96 17:55
INSTRUM spect
PULPROG zgpg30
SOLVENT CDCl3
NUC1 13
NUC2 13
P1 8.00 usec
PC 0.1500000 sec
===== CHANNEL F1 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F2 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F3 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F4 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F5 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F6 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F7 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F8 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F9 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F10 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F11 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F12 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F13 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F14 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F15 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F16 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F17 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F18 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F19 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F20 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F21 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F22 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F23 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F24 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F25 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F26 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F27 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F28 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F29 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec
===== CHANNEL F30 =====
NUC1 13
P1 12.00 usec
PC 0.1500000 sec



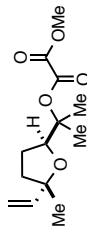
YS-II-286

```
Current Data Parameters
Date_ Time_
EXPNO 1
PROCNO 1
===== CHANNEL f1 =====
F2 - Acquisition Parameters
Date_ Time_
INSTRUM cryo500
PROBHD 5 mm CPICL 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 144
DS 4
SWH 30300.070 Hz
FIDRES 0.462388 Hz
AQ 1.0813450 sec
RG 327.500
DW 18.500 usec
DE 6.00 usec
TE 300.200 K
C11 0.300000 sec
d11 0.0100000 sec
D16 0.0002000 sec
d17 0.00019600 sec
MKREST 0 sec
NAMER 0.0150000 sec
PR 33.10 usec
===== CHANNEL f2 =====
NUC1 16F15
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
P13 2.00 usec
P14 1.40 usec
P15 24.50 usec
P16 500.2225011 MHz
SFO1 125.7942548 MHz
SFO2 500.2225011 MHz
SP1 2.70 usec
SP2 0.0100000 sec
SPHM[1] GPR60.5.70.0 GB
SPHM[2] CRR6COMP.4 GB
SFOFF1 0 Hz
SFOFF2 0 Hz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 13C
P2 100.00 usec
P21 1.40 usec
P22 1.40 usec
P23 1.40 usec
P24 24.50 usec
P25 500.2225011 MHz
SFO3 100.6281550 MHz
===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GCX2 0 %
GCY2 0 %
GZ1 50.00 %
GZ2 50.00 %
GZ3 50.00 %
P16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 125.7803334 MHz
WDW EM
SSB 0
LB 0
GB 0
FC 2.00
```



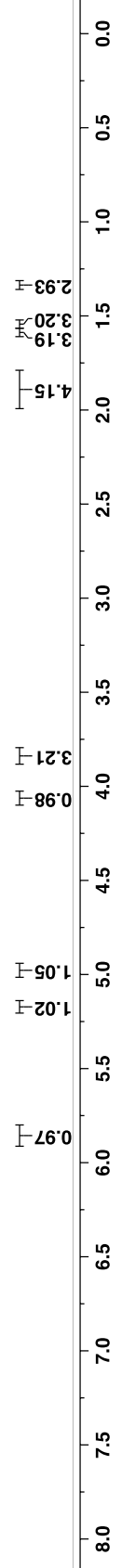
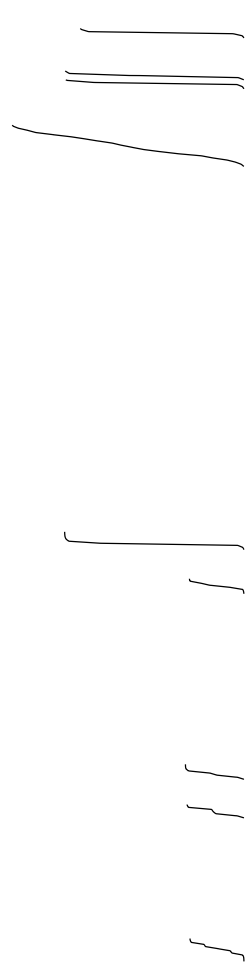
A3_106-ccn-s5-109-2_10.tif
Frequency: 500.62 MHz

-7.26 CDCl₃

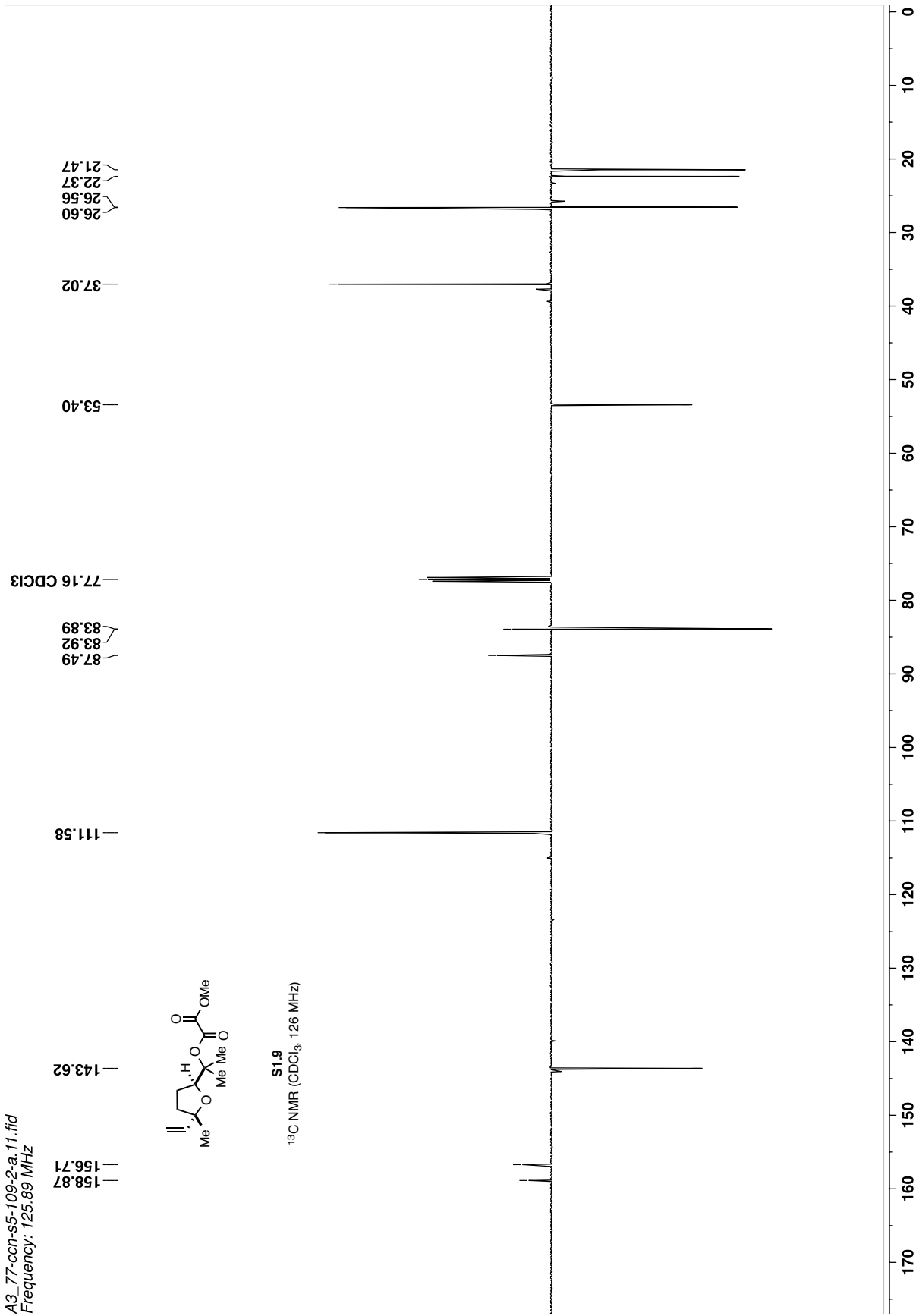


S1.9
¹H NMR (CDCl₃, 500 MHz)

5.88
5.86
5.84
5.82
5.19
5.16
5.16
5.00
5.00
4.98
4.98
4.07
4.06
4.06
4.05
3.85
1.98
1.97
1.96
1.96
1.95
1.95
1.94
1.94
1.94
1.93
1.93
1.93
1.93
1.92
1.92
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.86
1.85
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1.84
1.83
1.82
1.81
1.80
1.79
1.58
1.55
1.33

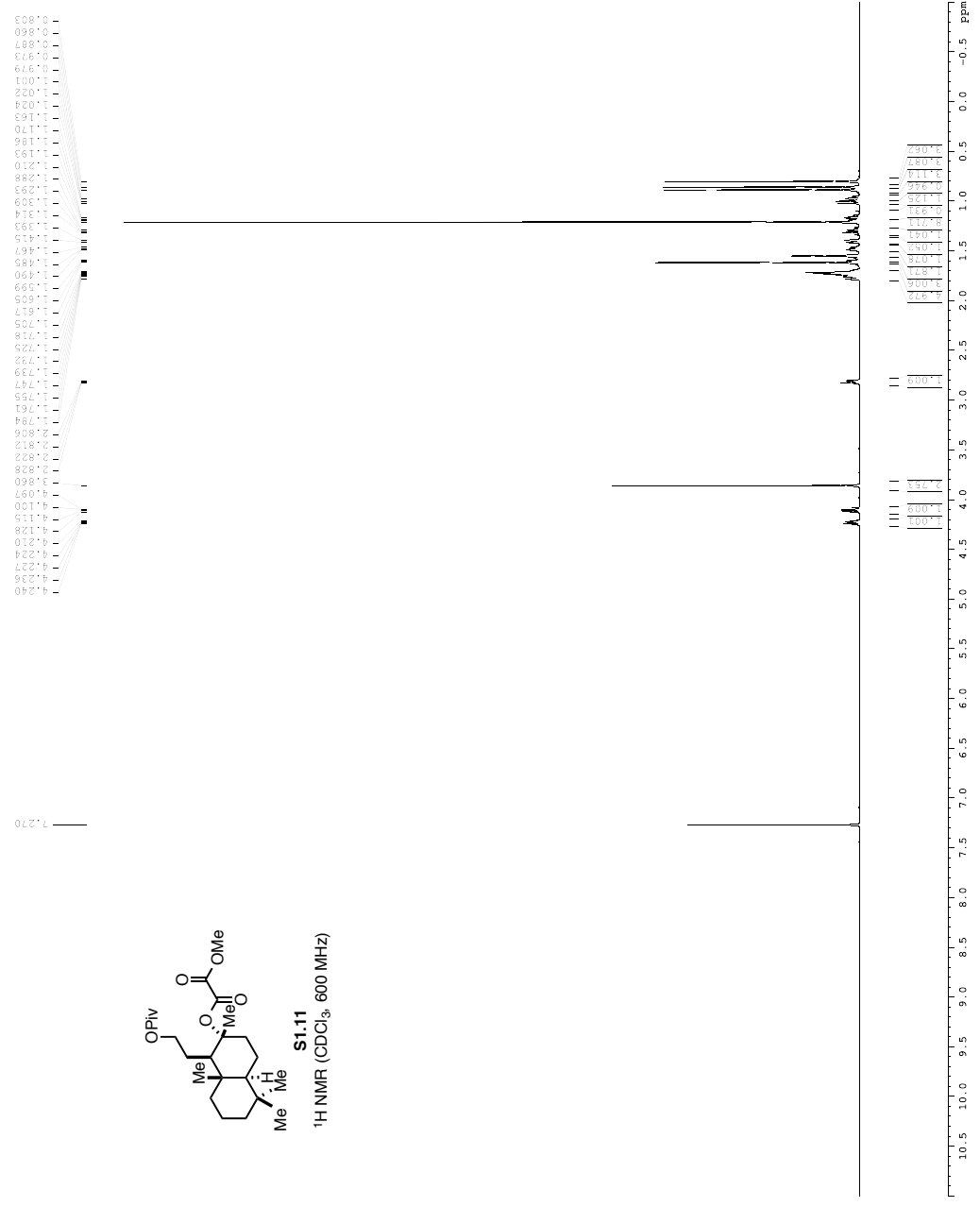


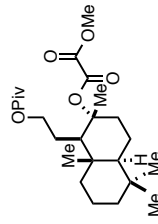
A3_77-ccn-s5-109-2-a.11.fid
Frequency: 125.89 MHz



YS-II-169

Current Data Parameters
 NAME YS-II-169
 PROCNO 1
 ===== Acquisition Parameters
 Date_ Time 01/20/10
 02:04:47
 INSTRUM 5 mm TBI 1H/13
 PULPROG zgpg30
 SOLVENT CDCl3
 NS 8
 DS 2
 SW 8615.962 Hz
 FIDRES 0.100072 Hz
 AQ 0.999950 sec
 LG 52.000 usec
 DE 14.54 usec
 DI 0.1000000 sec
 TD0 1
 ===== CHANNEL f1 =====
 SFO1 600.1342000 MHz
 NU1 8
 P1 8.00 usec
 PL1 23.0141356 dB
 ===== Processing Parameters
 SI 65536
 SF 600.1300297 MHz
 EQ 1
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00





```

Current Data Parameters
Date_      15-II-169
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     2011-09-06
Time     9:06
INSTRUM   cryo500
PROBHD    5 mm CPCC1H1
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        1024
DS        4
SWH        30300.031 Hz
FIDRES    0.462388 Hz
AQ         1.081345 sec
RG         18.500 usec
DE         6.00 usec
TE         300.2 K
CPDPRG2   0
AQ         0.000000 sec
AQ         0.000000 sec
D16       0.0002000 sec
d17       0.0019600 sec
MKRESST   0 sec
MWDATA    0.150000 sec
F2        33.10 usec

===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        500.00 usec
PL2        2000.00 usec
PL3        0.00 usec
PL4        1.00 usec
PL5        1.00 usec
SFO1       125.7942548 MHz
SF1        2.70 usec
SFO2       0.00 usec
SF2        0.00 usec
SFO3       0.00 usec
SF3        0.00 usec
SFO4       0.00 usec
SF4        0.00 usec
SFO5       0.00 usec
SF5        0.00 usec
SFO6       0.00 usec
SF6        0.00 usec
SFO7       0.00 usec
SF7        0.00 usec
SFO8       0.00 usec
SF8        0.00 usec
SFO9       0.00 usec
SF9        0.00 usec
SFO10      0.00 usec
SF10       0.00 usec
SFO11      0.00 usec
SF11       0.00 usec
SFO12      0.00 usec
SF12       0.00 usec
SFO13      0.00 usec
SF13       0.00 usec
SFO14      0.00 usec
SF14       0.00 usec
SFO15      0.00 usec
SF15       0.00 usec
SFO16      0.00 usec
SF16       0.00 usec
SFO17      0.00 usec
SF17       0.00 usec
SFO18      0.00 usec
SF18       0.00 usec
SFO19      0.00 usec
SF19       0.00 usec
SFO20      0.00 usec
SF20       0.00 usec
SFO21      0.00 usec
SF21       0.00 usec
SFO22      0.00 usec
SF22       0.00 usec
SFO23      0.00 usec
SF23       0.00 usec
SFO24      0.00 usec
SF24       0.00 usec
SFO25      0.00 usec
SF25       0.00 usec
SFO26      0.00 usec
SF26       0.00 usec
SFO27      0.00 usec
SF27       0.00 usec
SFO28      0.00 usec
SF28       0.00 usec
SFO29      0.00 usec
SF29       0.00 usec
SFO30      0.00 usec
SF30       0.00 usec
SFO31      0.00 usec
SF31       0.00 usec
SFO32      0.00 usec
SF32       0.00 usec
SFO33      0.00 usec
SF33       0.00 usec
SFO34      0.00 usec
SF34       0.00 usec
SFO35      0.00 usec
SF35       0.00 usec
SFO36      0.00 usec
SF36       0.00 usec
SFO37      0.00 usec
SF37       0.00 usec
SFO38      0.00 usec
SF38       0.00 usec
SFO39      0.00 usec
SF39       0.00 usec
SFO40      0.00 usec
SF40       0.00 usec
SFO41      0.00 usec
SF41       0.00 usec
SFO42      0.00 usec
SF42       0.00 usec
SFO43      0.00 usec
SF43       0.00 usec
SFO44      0.00 usec
SF44       0.00 usec
SFO45      0.00 usec
SF45       0.00 usec
SFO46      0.00 usec
SF46       0.00 usec
SFO47      0.00 usec
SF47       0.00 usec
SFO48      0.00 usec
SF48       0.00 usec
SFO49      0.00 usec
SF49       0.00 usec
SFO50      0.00 usec
SF50       0.00 usec
SFO51      0.00 usec
SF51       0.00 usec
SFO52      0.00 usec
SF52       0.00 usec
SFO53      0.00 usec
SF53       0.00 usec
SFO54      0.00 usec
SF54       0.00 usec
SFO55      0.00 usec
SF55       0.00 usec
SFO56      0.00 usec
SF56       0.00 usec
SFO57      0.00 usec
SF57       0.00 usec
SFO58      0.00 usec
SF58       0.00 usec
SFO59      0.00 usec
SF59       0.00 usec
SFO60      0.00 usec
SF60       0.00 usec
SFO61      0.00 usec
SF61       0.00 usec
SFO62      0.00 usec
SF62       0.00 usec
SFO63      0.00 usec
SF63       0.00 usec
SFO64      0.00 usec
SF64       0.00 usec
SFO65      0.00 usec
SF65       0.00 usec
SFO66      0.00 usec
SF66       0.00 usec
SFO67      0.00 usec
SF67       0.00 usec
SFO68      0.00 usec
SF68       0.00 usec
SFO69      0.00 usec
SF69       0.00 usec
SFO70      0.00 usec
SF70       0.00 usec
SFO71      0.00 usec
SF71       0.00 usec
SFO72      0.00 usec
SF72       0.00 usec
SFO73      0.00 usec
SF73       0.00 usec
SFO74      0.00 usec
SF74       0.00 usec
SFO75      0.00 usec
SF75       0.00 usec
SFO76      0.00 usec
SF76       0.00 usec
SFO77      0.00 usec
SF77       0.00 usec
SFO78      0.00 usec
SF78       0.00 usec
SFO79      0.00 usec
SF79       0.00 usec
SFO80      0.00 usec
SF80       0.00 usec
SFO81      0.00 usec
SF81       0.00 usec
SFO82      0.00 usec
SF82       0.00 usec
SFO83      0.00 usec
SF83       0.00 usec
SFO84      0.00 usec
SF84       0.00 usec
SFO85      0.00 usec
SF85       0.00 usec
SFO86      0.00 usec
SF86       0.00 usec
SFO87      0.00 usec
SF87       0.00 usec
SFO88      0.00 usec
SF88       0.00 usec
SFO89      0.00 usec
SF89       0.00 usec
SFO90      0.00 usec
SF90       0.00 usec
SFO91      0.00 usec
SF91       0.00 usec
SFO92      0.00 usec
SF92       0.00 usec
SFO93      0.00 usec
SF93       0.00 usec
SFO94      0.00 usec
SF94       0.00 usec
SFO95      0.00 usec
SF95       0.00 usec
SFO96      0.00 usec
SF96       0.00 usec
SFO97      0.00 usec
SF97       0.00 usec
SFO98      0.00 usec
SF98       0.00 usec
SFO99      0.00 usec
SF99       0.00 usec
SFO100     0.00 usec
SF100      0.00 usec
===== CHANNEL f2 =====
CPDPRG2    waitz16
NUC2       13C
P2         100.00 usec
PL2        1.00 usec
PL3        1.00 usec
PL4        1.00 usec
PL5        1.00 usec
PL6        1.00 usec
SFO1       500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GAMMA[1]   0 %
GAMMA[2]   0 %
GXY1       0 %
GXY2       0 %
GYZ1       0 %
GYZ2       0 %
GZ1        50.00 %
GZ2        50.00 %
P15        500.00 usec
P16        1000.00 usec

F2 - Processing parameters
SI         65536
SF         125.7803825 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         1.00 Hz
FC         2.00
    
```

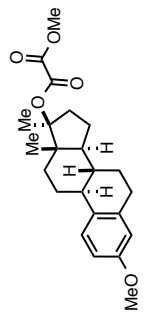
A2_94-ccn-s4-084-1-a.10.fid
Frequency: 500.46 MHz

7.26 CDCl3

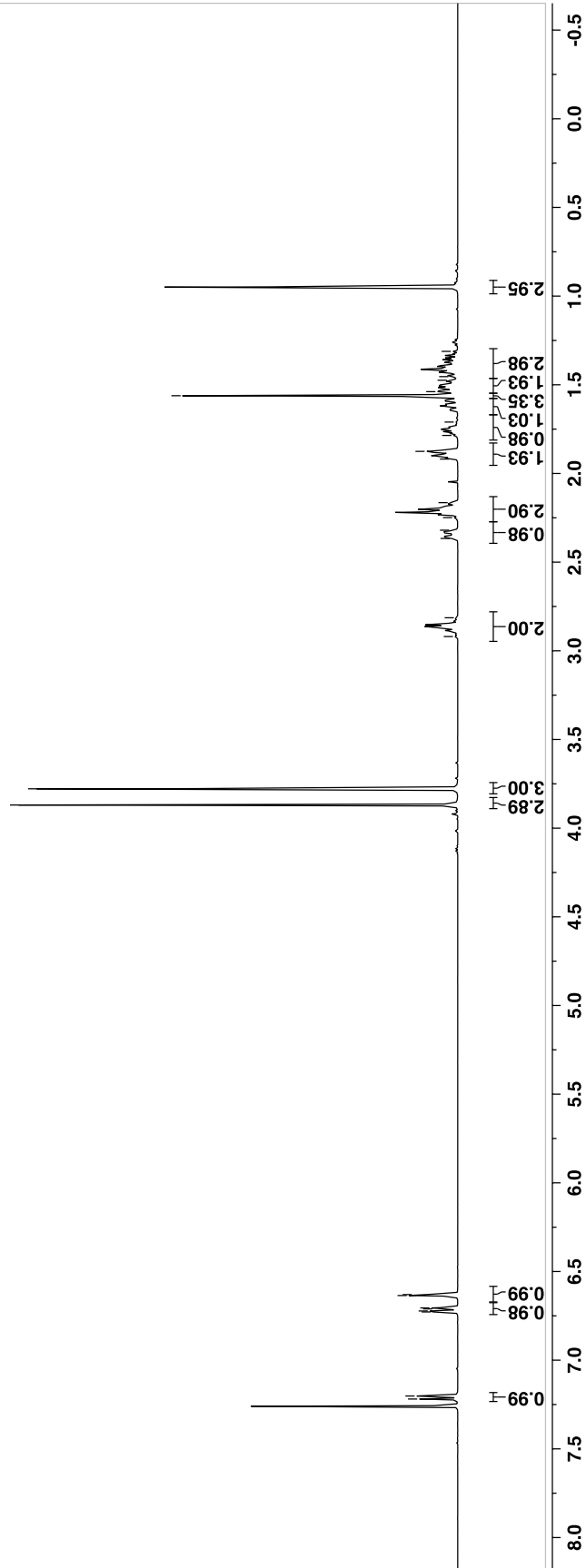
7.22
7.20
6.73
6.72
6.71
6.71
6.64
6.63

3.87
3.78

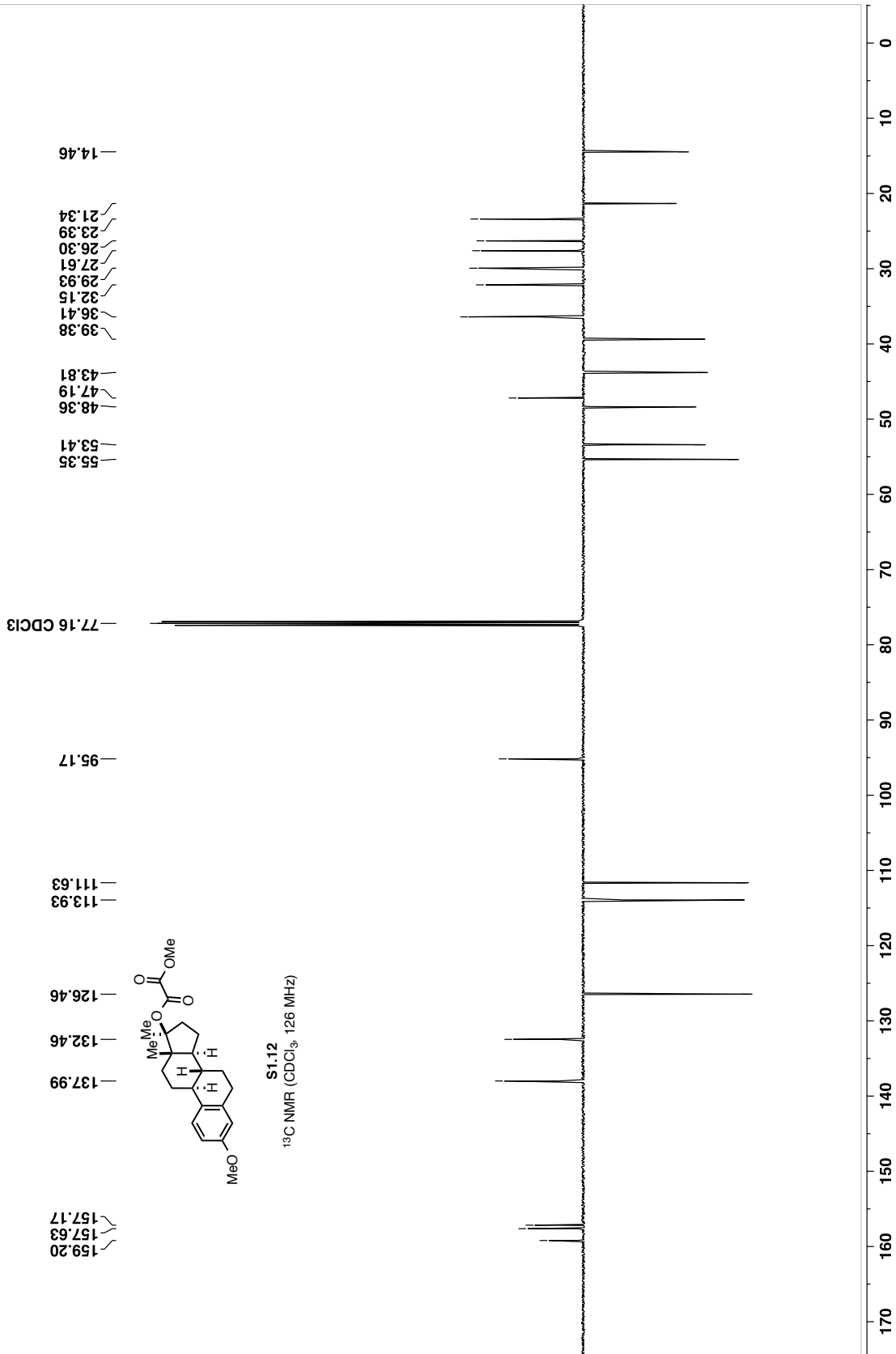
2.37
2.32
2.25
2.16
1.92
1.88
1.79
1.71
1.56
1.54
1.47
1.45
1.31



S1.12
¹H NMR (CDCl₃, 500 MHz)



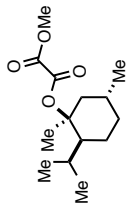
A2_94-can-s4-084-1-a.11.fid
Frequency: 125.85 MHz



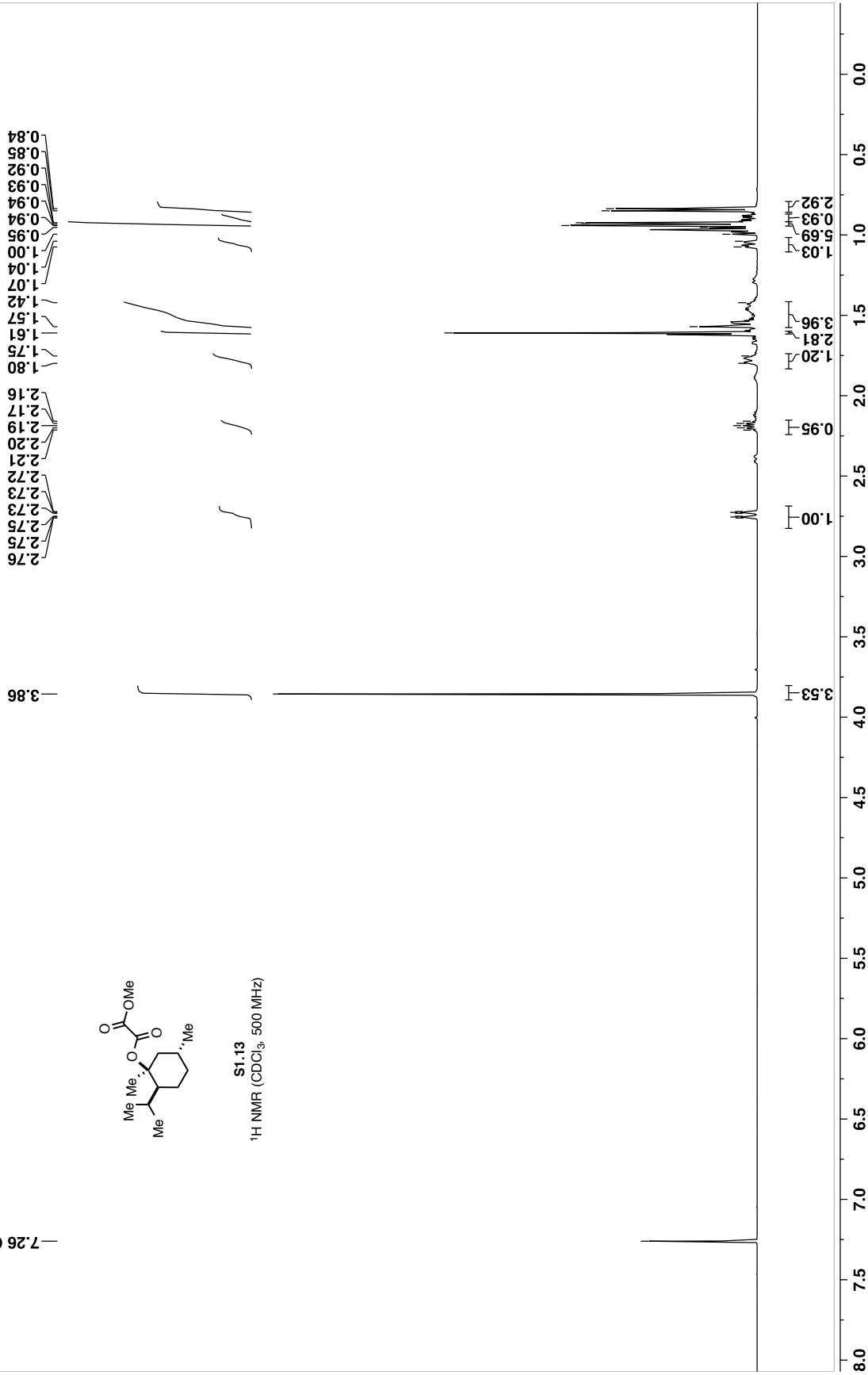
A2_61-ccn-s5-070-a.10.fid
Frequency: 500.46 MHz

7.26 CDCl₃

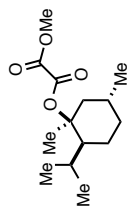
2.76
2.75
2.75
2.73
2.73
2.72
2.21
2.20
2.19
2.17
2.16
1.80
1.75
1.61
1.57
1.42
1.07
1.04
1.00
0.95
0.94
0.94
0.93
0.92
0.85
0.84



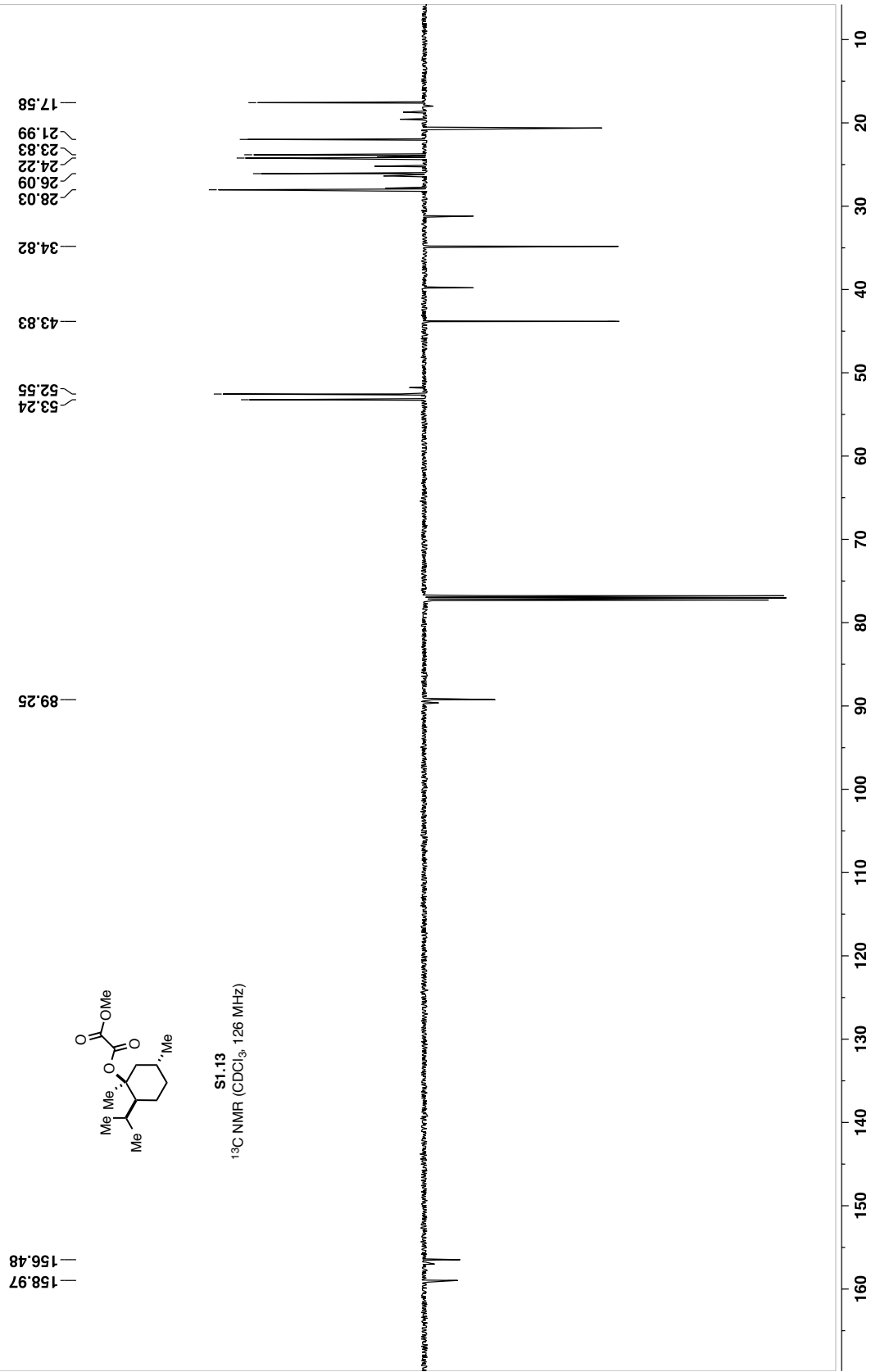
S1.13
¹H NMR (CDCl₃, 500 MHz)



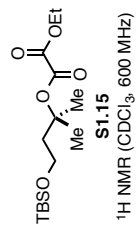
A2_61-can-s5-070-a.11.fid
Frequency: 125.85 MHz



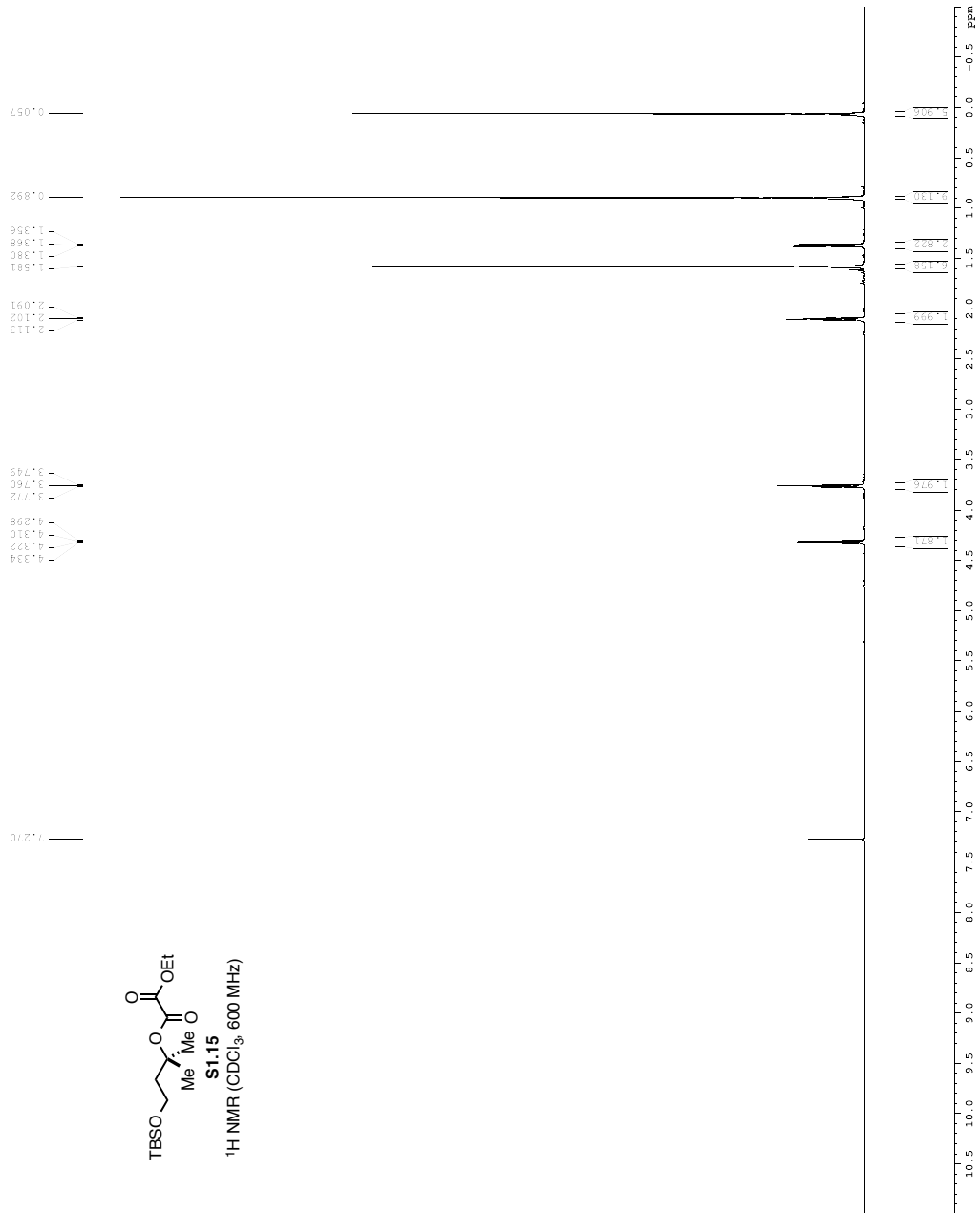
S1.13
¹³C NMR (CDCl₃, 126 MHz)



YS-II-199

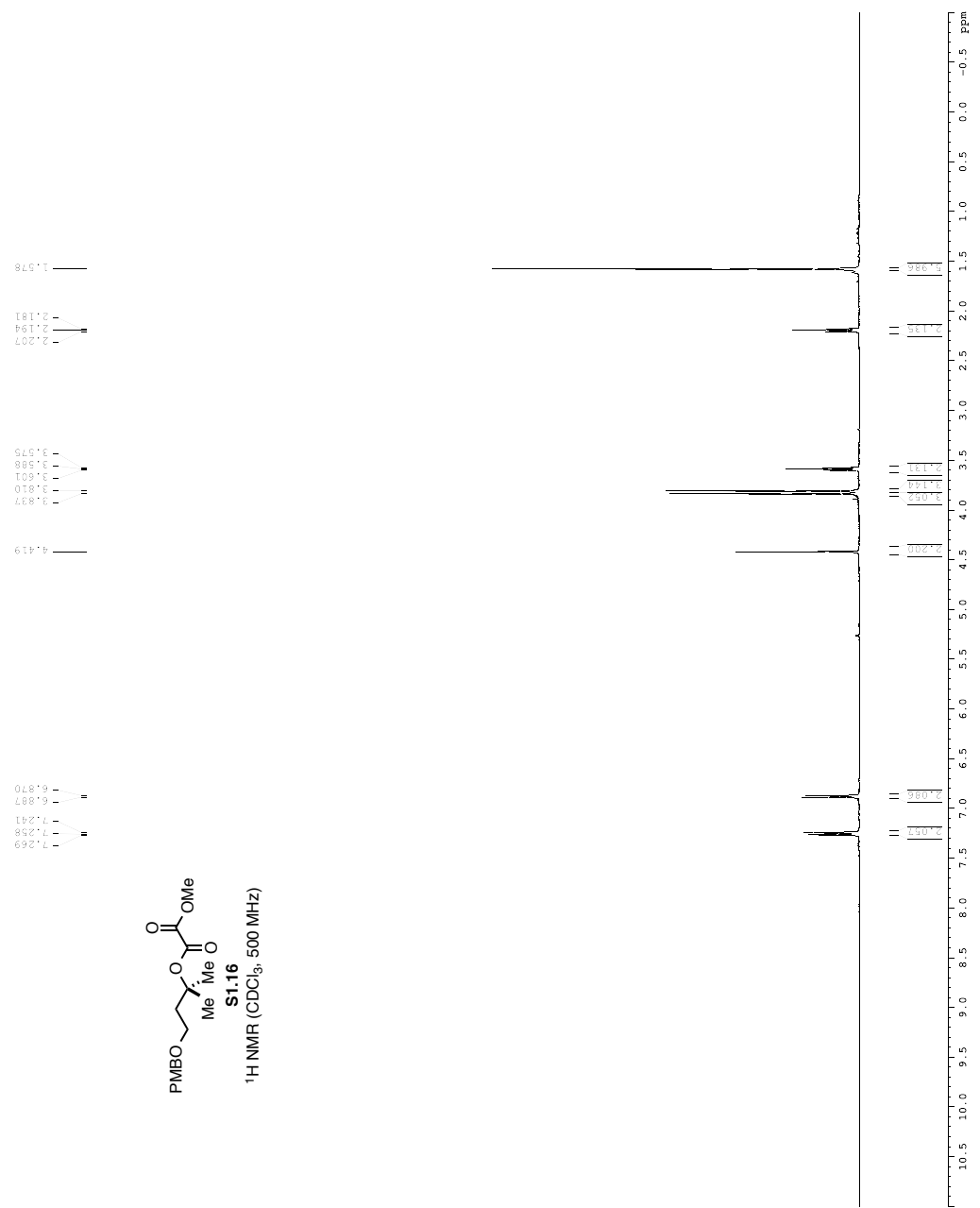
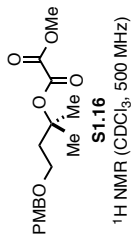


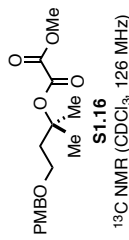
Current Data Parameters
NAME YS-II-199
PROCNO 1
===== Acquisition Parameters =====
Date_ Time 01/30/23 17:08
Time 17.08
INSTRUM spect
PROBHD 5 mm TBI 13712
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 2
SS 8615.362 Hz
AQ 0.100072 Hz
RG 0.999956 sec
DQ 50.000 usec
DE 14.5% usec
DI 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.134200 MHz
NUC1 13C
P1 8.00 usec
PL1 23.0141556 V
===== CHANNEL f2 =====
SFO2 600.130029 MHz
NUC2 1H
P2 0.00 usec
PL2 0.00 V
===== Processing Parameters =====
SI 65536
SF 600.130029 MHz
RG 4096
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



XS-II-259

Current Data Parameters
NAME XS-II-259
PROCNO 1
===== Acquisition Parameters =====
Date_ Acq 01/05/20
Time 8:52
INSTRUM spect
PROBHD 5 mm CPCLP1H
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 2
SS 6012.820 Hz
AQ 0.250026 Hz
RG 1.939792 sec
LW 62.400 usec
DE 6.00 usec
DI 0.1000000 sec
MCNMR1 0 sec
MCNMR2 0.01500000 sec
===== CHANNEL F1 =====
NUC1 13C
PULP1 zgpg30
FL1 7.50 usec
PL1 1.60 dB
SFO1 500.2235012 MHz
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
RG 64
GB 0
WB 0
DB 0
PC 4.00





```

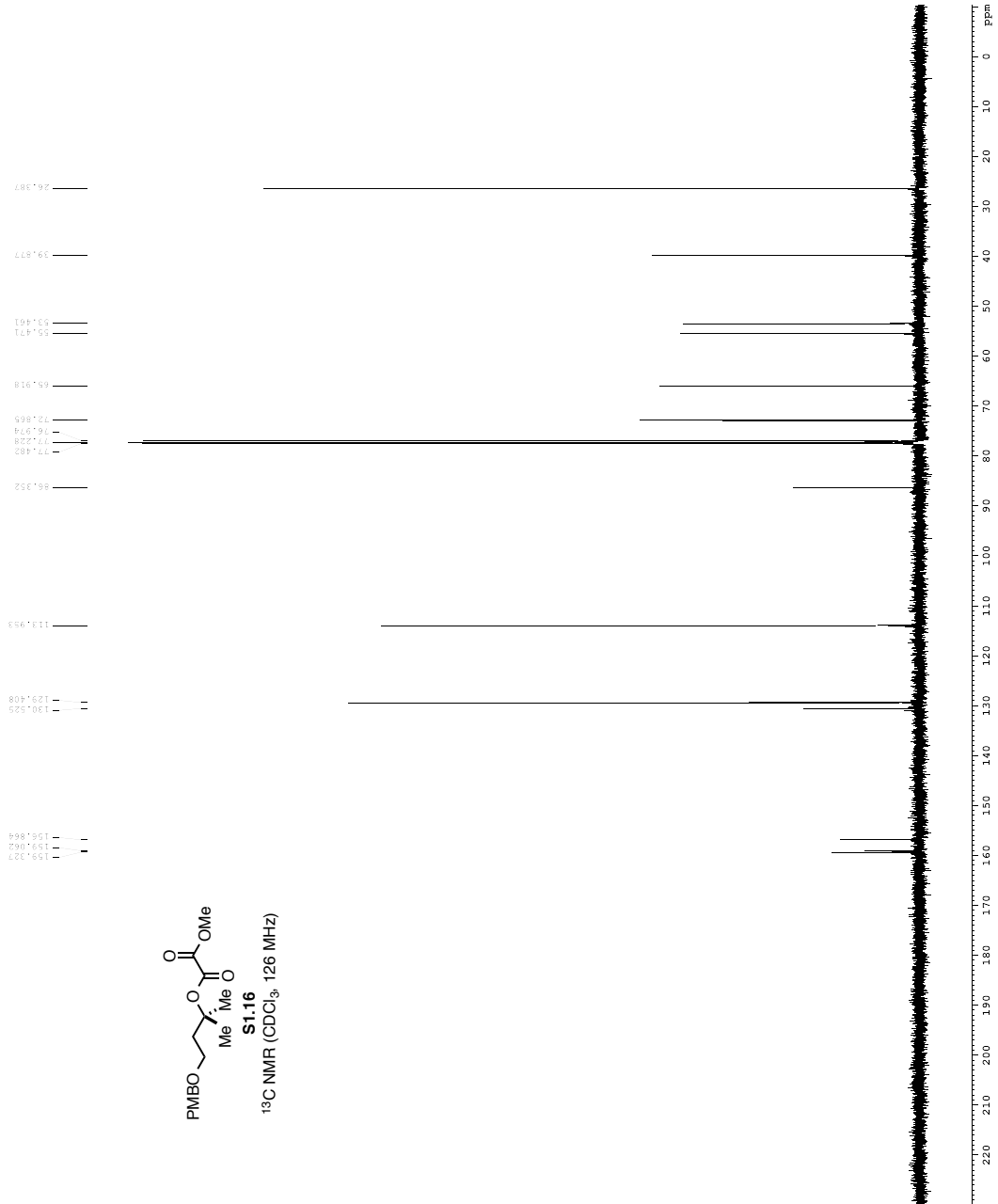
Current Data Parameters
NAME      YS-II-259
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     20110727
Time      8.55
INSTRUM   cryo500
PROBHD    5 mm CPYX 1H-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         256
DS         4
SWH        30300.071 Hz
FIDRES     0.462388 Hz
AQ         1.081345 sec
RG         182.500
DW         12.500 usec
DE         6.00 usec
TE         300.2 K
T1         0.36296 sec
T1RHO     0.130000 sec
d11        0.000000 sec
d16        0.0002000 sec
d17        0.00019600 sec
MKREST    0 sec
NAMEPR    0.0150000 sec
F2        33.10 usec

===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        0 dB
PC1        500.00 usec
PL2        2000.00 usec
PC2        0 dB
PL3        12.00 dB
PC3        12.00 dB
SFO1       125.7942548 MHz
SF1        2.70 GHz
SFO2       0 Hz
PCPD1      0 Hz
SFO3       0 Hz
PCPD2      0 Hz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P2         100.00 usec
PL2        0 dB
PC2        1.60 dB
PL12       24.50 dB
PC12       0 dB
SFO2       500.2225011 MHz

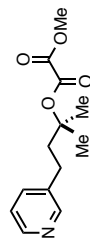
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GXY1       0 %
GXY2       0 %
GYZ1       0 %
GYZ2       0 %
GZ1        50.00 %
GZ2        50.00 %
PL5        500.00 usec
PC5        0 dB
PL6        1000.00 usec
PC6        0 dB

F2 - Processing parameters
SI         65536
SF         125.7804006 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
    
```

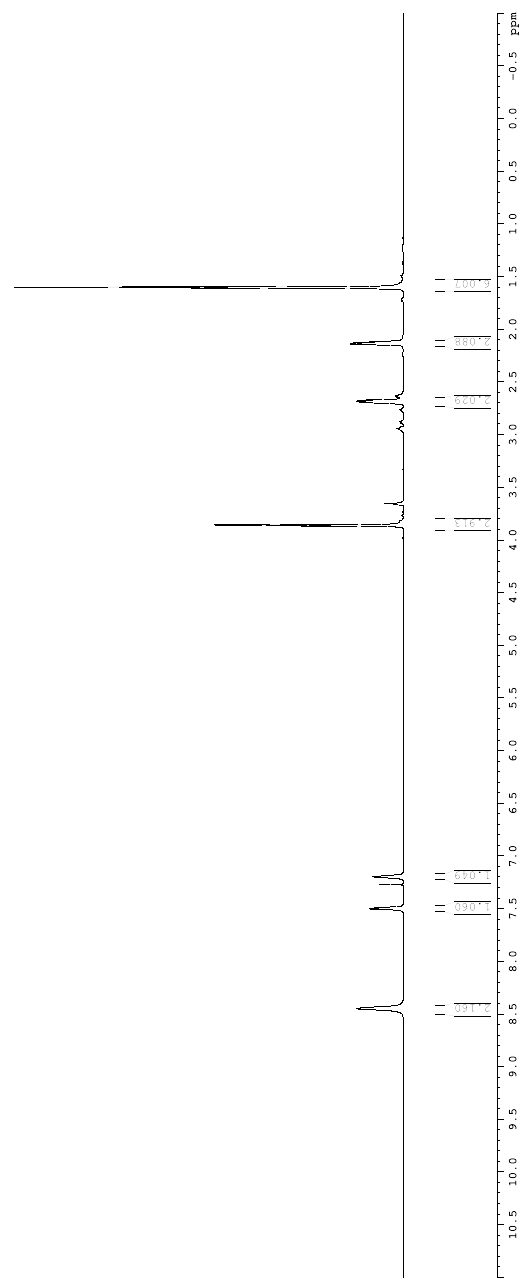


YS-III-54

Current Data Parameters
NAME YS-III-54
PROCNO 1
EXPNO 1
F2 - Acquisition Parameters
Date_ 20150228
Time 8.29
INSTRUM spect
PROBHD 5 mm BBO 5mm-1H
PULPROG zgpg30
SFO 2930
AQ 0.0333
RG 6613
NS 8
DS 2
SWH 8615.952 Hz
FIDRES 0.150010 Hz
AQ 1.9399500 sec
RG 6613
WDW 52.000 usec
SSB 0
LB 14.32 usec
GB 0
DT 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342008 MHz
NUC1 13C
P1 8
PL1 0
PLA1 60.25600052 W
SFO2 - Processing Parameters
SF 600.1300273 MHz
WDW 0
SSB 0
LB 0.30 Hz
GB 0
DT 1.00



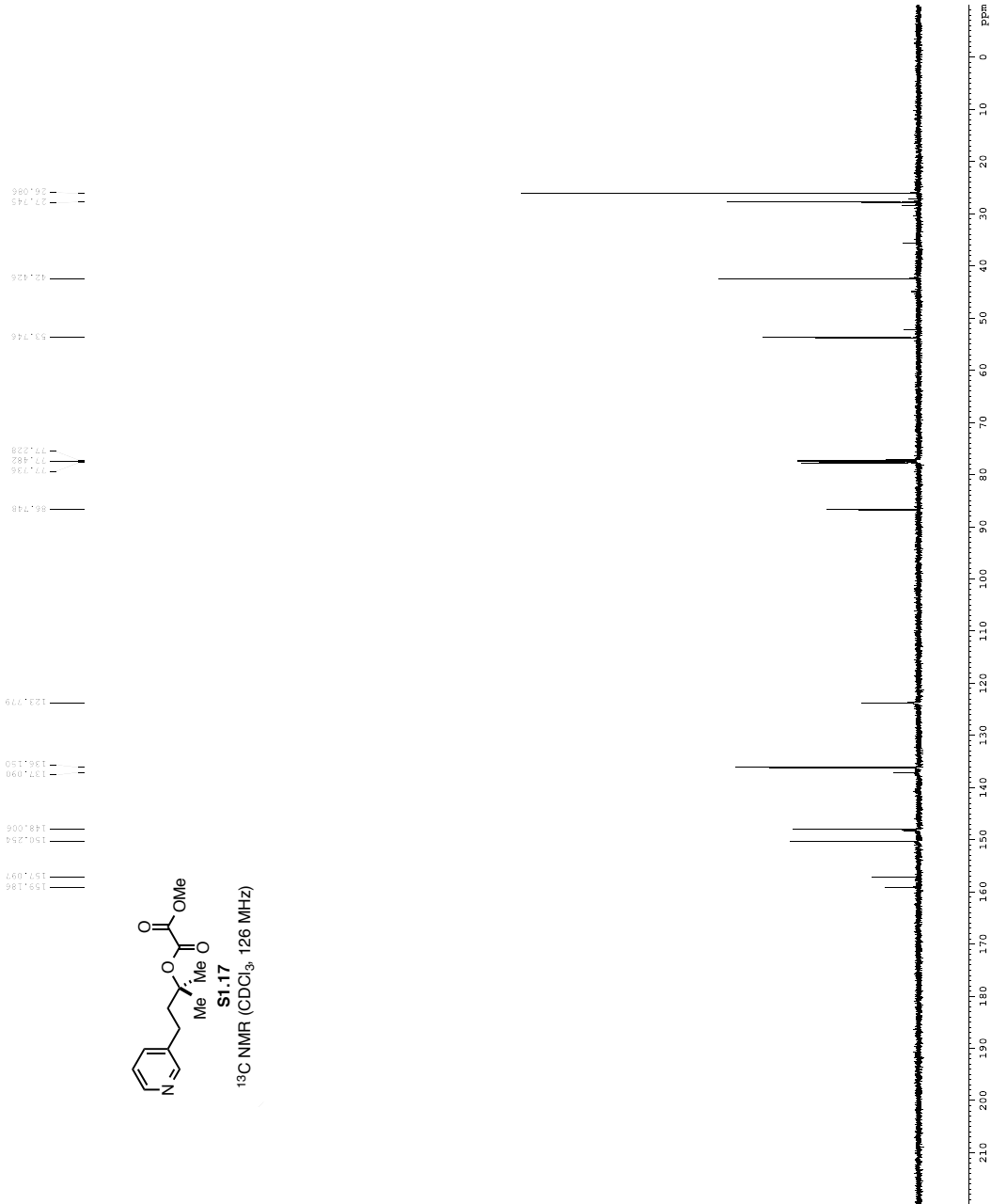
S1.17
¹H NMR (CDCl₃, 600 MHz)



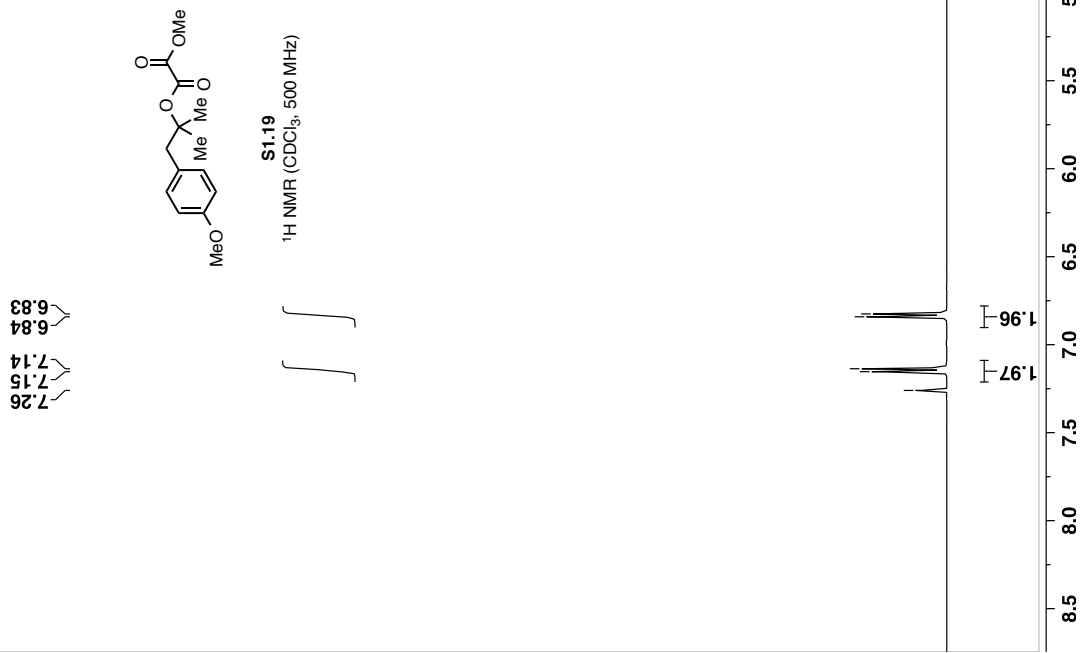
```

Current Data Parameters
=====
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
Date_      20110822
Time       8:22
INSTRUM    cryo500
PROBHD     5 mm CPYX1.4H
PULPROG    zgpg30
TD          65536
SOLVENT    CDCl3
NS          56
DS          4
SWH         30300.071 Hz
FIDRES     0.462388 Hz
AQ          1.0813440 sec
RG          655
DM          16.500 usec
DE          6.000 usec
TE          300.2 K
C11        0.06296.0 K
C12        0.06296.0 K
C13        0.0300000 sec
C14        0.0300000 sec
C15        0.00020000 sec
C16        0.00020000 sec
C17        0.00019600 sec
MKSFT      0 sec
MKSCA      0.01500000 sec
MKWD       33.10 usec
F2
===== CHANNEL f1 =====
NUC1        13C
P1          16.55 usec
PL1         0.00 dB
P12         500.00 usec
PL12        0.00 dB
P13         1.00 usec
PL13        0.00 dB
P14         1.00 usec
PL14        0.00 dB
SFO1        125.7942548 MHz
SF1         2.70 GHz
SFO2        500.2225011 MHz
SFX1        CPDPRG2, 0.5, 70.0, GB
SFX2        SFO1, 0.5, 70.0, GB
SFX3        SFO2, 0.5, 70.0, GB
SFX4        SFO1, 0.5, 70.0, GB
SFOFF1     0 Hz
SFOFF2     0 Hz
===== CHANNEL f2 =====
CPDPRG2     waltz16
NUC2        1H
P2          100.00 usec
PL2         0.00 dB
P12         1.00 usec
PL12        0.00 dB
P13         1.00 usec
PL13        0.00 dB
SFO1        500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]    SINE.100
GPNAM[2]    SINE.100
GPA1        0 %
GPA2        0 %
GPA3        0 %
GPA4        0 %
GPA5        0 %
GPA6        0 %
GPA7        0 %
GPA8        0 %
GPA9        0 %
GPA10       0 %
GPA11       0 %
GPA12       0 %
GPA13       0 %
GPA14       0 %
GPA15       0 %
GPA16       0 %
F2 - Processing parameters
SI          65536
SF          125.7883737 MHz
WDW         EM
SSB         0
LB          0
GB          0
PC          1.00 Hz
FC          2.00

```

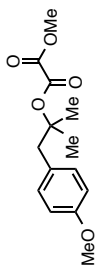


A2_65-con-s5-091-1-a.10.fid
Frequency: 500.46 MHz

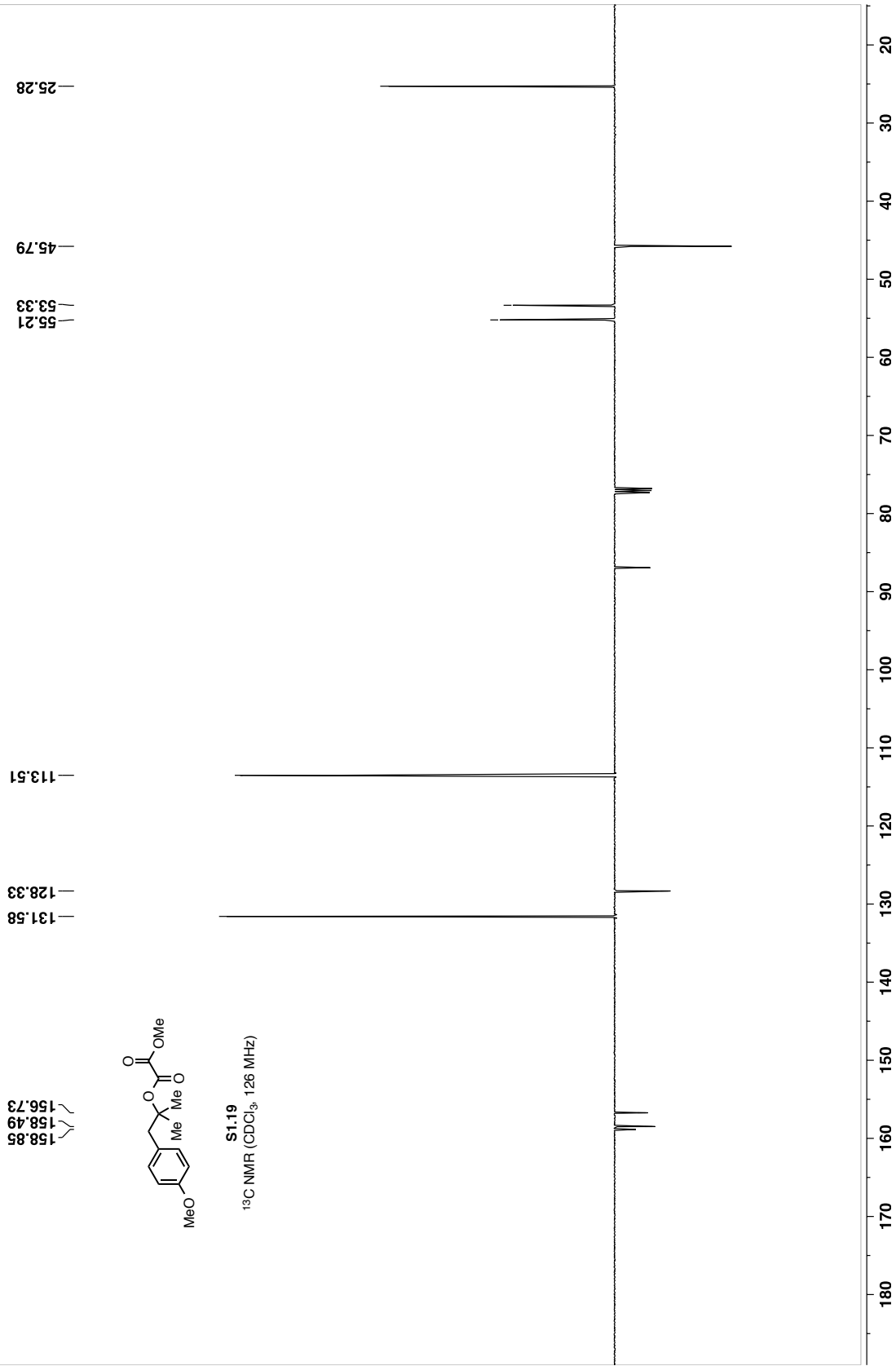


A2_65-con-s5-091-1-a.12.fid
Frequency: 125.85 MHz

158.85
158.49
156.73



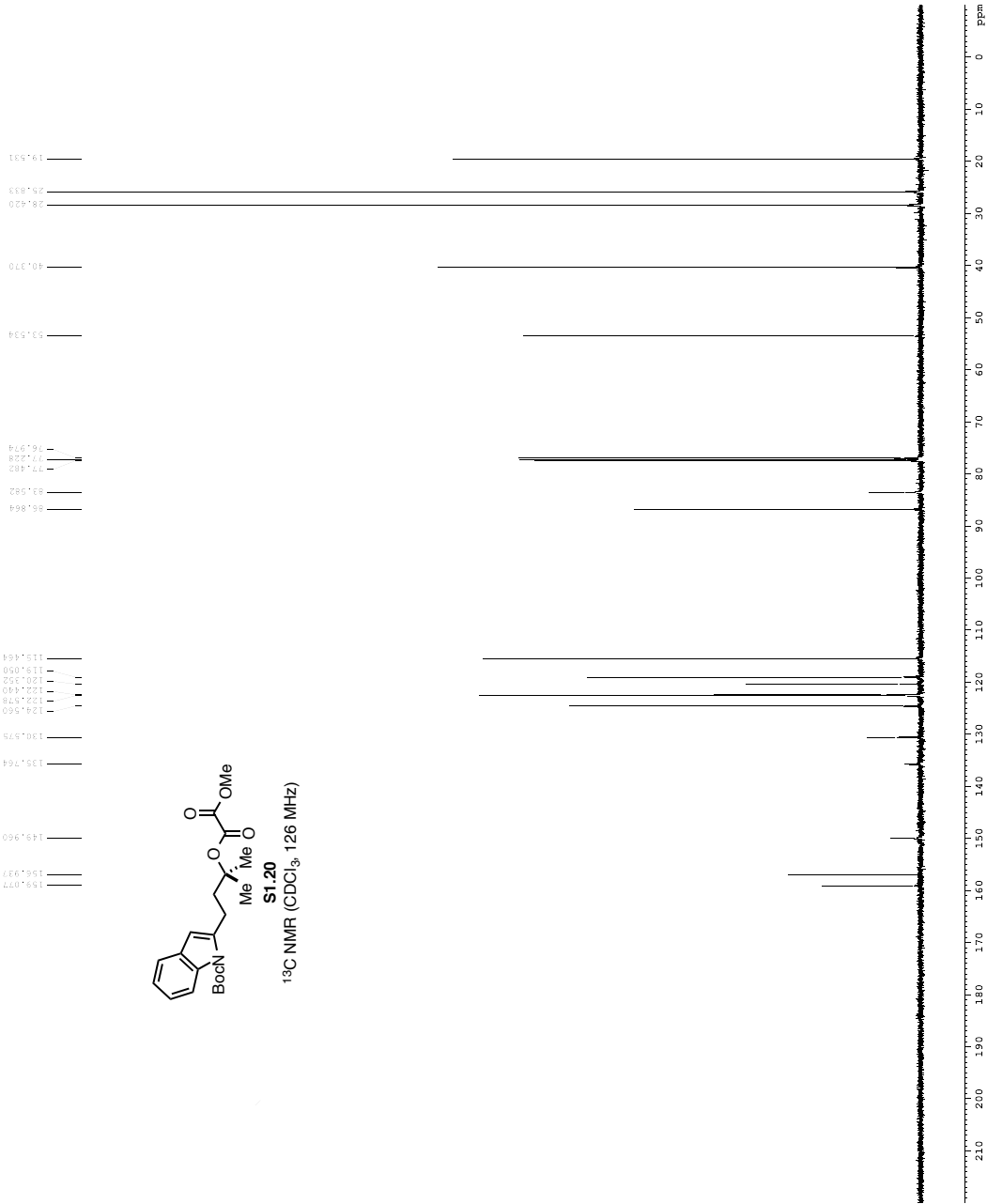
S1.19
¹³C NMR (CDCl₃, 126 MHz)



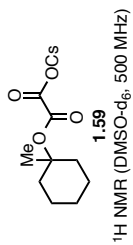

```

Current Data Parameters
Date_ 15-11-24
EXPNO 1
PROCNO 1
=====
F2 - Acquisition Parameters
Date_ 20151324
Time_ 13:24
INSTRUM cryo500
PROBHD 5 mm CPYX 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 584
DS 4
SWH 30300.075 Hz
FIDRES 0.462388 Hz
AQ 1.0813440 sec
RG 16.500 usec
DE 6.00 usec
TE 298.0 K
C11 0.000000 sec
C12 0.000000 sec
C13 0.000000 sec
C14 0.000000 sec
C15 0.000000 sec
C16 0.000000 sec
C17 0.000000 sec
MKREST 0 sec
MKRG 0.0150000 sec
MKWD 33.10 usec
=====
CHANNEL f1
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
P13 1.00 usec
P14 1.00 usec
P15 1.00 usec
P16 1.00 usec
SFO1 125.7942548 MHz
SFO2 500.1364200 MHz
SFO3 500.1364200 MHz
SFO4 500.1364200 MHz
SFO5 500.1364200 MHz
SFO6 500.1364200 MHz
SFO7 500.1364200 MHz
SFO8 500.1364200 MHz
SFO9 500.1364200 MHz
SFO10 500.1364200 MHz
SFO11 500.1364200 MHz
SFO12 500.1364200 MHz
SFO13 500.1364200 MHz
SFO14 500.1364200 MHz
SFO15 500.1364200 MHz
SFO16 500.1364200 MHz
SFO17 500.1364200 MHz
SFO18 500.1364200 MHz
SFO19 500.1364200 MHz
SFO20 500.1364200 MHz
SFO21 500.1364200 MHz
SFO22 500.1364200 MHz
SFO23 500.1364200 MHz
SFO24 500.1364200 MHz
SFO25 500.1364200 MHz
SFO26 500.1364200 MHz
SFO27 500.1364200 MHz
SFO28 500.1364200 MHz
SFO29 500.1364200 MHz
SFO30 500.1364200 MHz
SFO31 500.1364200 MHz
SFO32 500.1364200 MHz
SFO33 500.1364200 MHz
SFO34 500.1364200 MHz
SFO35 500.1364200 MHz
SFO36 500.1364200 MHz
SFO37 500.1364200 MHz
SFO38 500.1364200 MHz
SFO39 500.1364200 MHz
SFO40 500.1364200 MHz
SFO41 500.1364200 MHz
SFO42 500.1364200 MHz
SFO43 500.1364200 MHz
SFO44 500.1364200 MHz
SFO45 500.1364200 MHz
SFO46 500.1364200 MHz
SFO47 500.1364200 MHz
SFO48 500.1364200 MHz
SFO49 500.1364200 MHz
SFO50 500.1364200 MHz
SFO51 500.1364200 MHz
SFO52 500.1364200 MHz
SFO53 500.1364200 MHz
SFO54 500.1364200 MHz
SFO55 500.1364200 MHz
SFO56 500.1364200 MHz
SFO57 500.1364200 MHz
SFO58 500.1364200 MHz
SFO59 500.1364200 MHz
SFO60 500.1364200 MHz
SFO61 500.1364200 MHz
SFO62 500.1364200 MHz
SFO63 500.1364200 MHz
SFO64 500.1364200 MHz
SFO65 500.1364200 MHz
SFO66 500.1364200 MHz
SFO67 500.1364200 MHz
SFO68 500.1364200 MHz
SFO69 500.1364200 MHz
SFO70 500.1364200 MHz
SFO71 500.1364200 MHz
SFO72 500.1364200 MHz
SFO73 500.1364200 MHz
SFO74 500.1364200 MHz
SFO75 500.1364200 MHz
SFO76 500.1364200 MHz
SFO77 500.1364200 MHz
SFO78 500.1364200 MHz
SFO79 500.1364200 MHz
SFO80 500.1364200 MHz
SFO81 500.1364200 MHz
SFO82 500.1364200 MHz
SFO83 500.1364200 MHz
SFO84 500.1364200 MHz
SFO85 500.1364200 MHz
SFO86 500.1364200 MHz
SFO87 500.1364200 MHz
SFO88 500.1364200 MHz
SFO89 500.1364200 MHz
SFO90 500.1364200 MHz
SFO91 500.1364200 MHz
SFO92 500.1364200 MHz
SFO93 500.1364200 MHz
SFO94 500.1364200 MHz
SFO95 500.1364200 MHz
SFO96 500.1364200 MHz
SFO97 500.1364200 MHz
SFO98 500.1364200 MHz
SFO99 500.1364200 MHz
SFO100 500.1364200 MHz
=====
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
P2 100.00 usec
P21 1.00 usec
P22 1.00 usec
P23 1.00 usec
P24 1.00 usec
P25 1.00 usec
P26 1.00 usec
P27 1.00 usec
P28 1.00 usec
P29 1.00 usec
P30 1.00 usec
P31 1.00 usec
P32 1.00 usec
P33 1.00 usec
P34 1.00 usec
P35 1.00 usec
P36 1.00 usec
P37 1.00 usec
P38 1.00 usec
P39 1.00 usec
P40 1.00 usec
P41 1.00 usec
P42 1.00 usec
P43 1.00 usec
P44 1.00 usec
P45 1.00 usec
P46 1.00 usec
P47 1.00 usec
P48 1.00 usec
P49 1.00 usec
P50 1.00 usec
P51 1.00 usec
P52 1.00 usec
P53 1.00 usec
P54 1.00 usec
P55 1.00 usec
P56 1.00 usec
P57 1.00 usec
P58 1.00 usec
P59 1.00 usec
P60 1.00 usec
P61 1.00 usec
P62 1.00 usec
P63 1.00 usec
P64 1.00 usec
P65 1.00 usec
P66 1.00 usec
P67 1.00 usec
P68 1.00 usec
P69 1.00 usec
P70 1.00 usec
P71 1.00 usec
P72 1.00 usec
P73 1.00 usec
P74 1.00 usec
P75 1.00 usec
P76 1.00 usec
P77 1.00 usec
P78 1.00 usec
P79 1.00 usec
P80 1.00 usec
P81 1.00 usec
P82 1.00 usec
P83 1.00 usec
P84 1.00 usec
P85 1.00 usec
P86 1.00 usec
P87 1.00 usec
P88 1.00 usec
P89 1.00 usec
P90 1.00 usec
P91 1.00 usec
P92 1.00 usec
P93 1.00 usec
P94 1.00 usec
P95 1.00 usec
P96 1.00 usec
P97 1.00 usec
P98 1.00 usec
P99 1.00 usec
P100 1.00 usec
=====
===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GPA[1] 0 %
GPA[2] 0 %
GPA[3] 0 %
GPA[4] 0 %
GPA[5] 0 %
GPA[6] 0 %
GPA[7] 0 %
GPA[8] 0 %
GPA[9] 0 %
GPA[10] 0 %
GPA[11] 0 %
GPA[12] 0 %
GPA[13] 0 %
GPA[14] 0 %
GPA[15] 0 %
GPA[16] 0 %
GPA[17] 0 %
GPA[18] 0 %
GPA[19] 0 %
GPA[20] 0 %
GPA[21] 0 %
GPA[22] 0 %
GPA[23] 0 %
GPA[24] 0 %
GPA[25] 0 %
GPA[26] 0 %
GPA[27] 0 %
GPA[28] 0 %
GPA[29] 0 %
GPA[30] 0 %
GPA[31] 0 %
GPA[32] 0 %
GPA[33] 0 %
GPA[34] 0 %
GPA[35] 0 %
GPA[36] 0 %
GPA[37] 0 %
GPA[38] 0 %
GPA[39] 0 %
GPA[40] 0 %
GPA[41] 0 %
GPA[42] 0 %
GPA[43] 0 %
GPA[44] 0 %
GPA[45] 0 %
GPA[46] 0 %
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GPA[48] 0 %
GPA[49] 0 %
GPA[50] 0 %
GPA[51] 0 %
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GPA[55] 0 %
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GPA[76] 0 %
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GPA[78] 0 %
GPA[79] 0 %
GPA[80] 0 %
GPA[81] 0 %
GPA[82] 0 %
GPA[83] 0 %
GPA[84] 0 %
GPA[85] 0 %
GPA[86] 0 %
GPA[87] 0 %
GPA[88] 0 %
GPA[89] 0 %
GPA[90] 0 %
GPA[91] 0 %
GPA[92] 0 %
GPA[93] 0 %
GPA[94] 0 %
GPA[95] 0 %
GPA[96] 0 %
GPA[97] 0 %
GPA[98] 0 %
GPA[99] 0 %
GPA[100] 0 %
=====
F2 - Processing parameters
SI 65536
SF 125.7804026 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00
=====

```



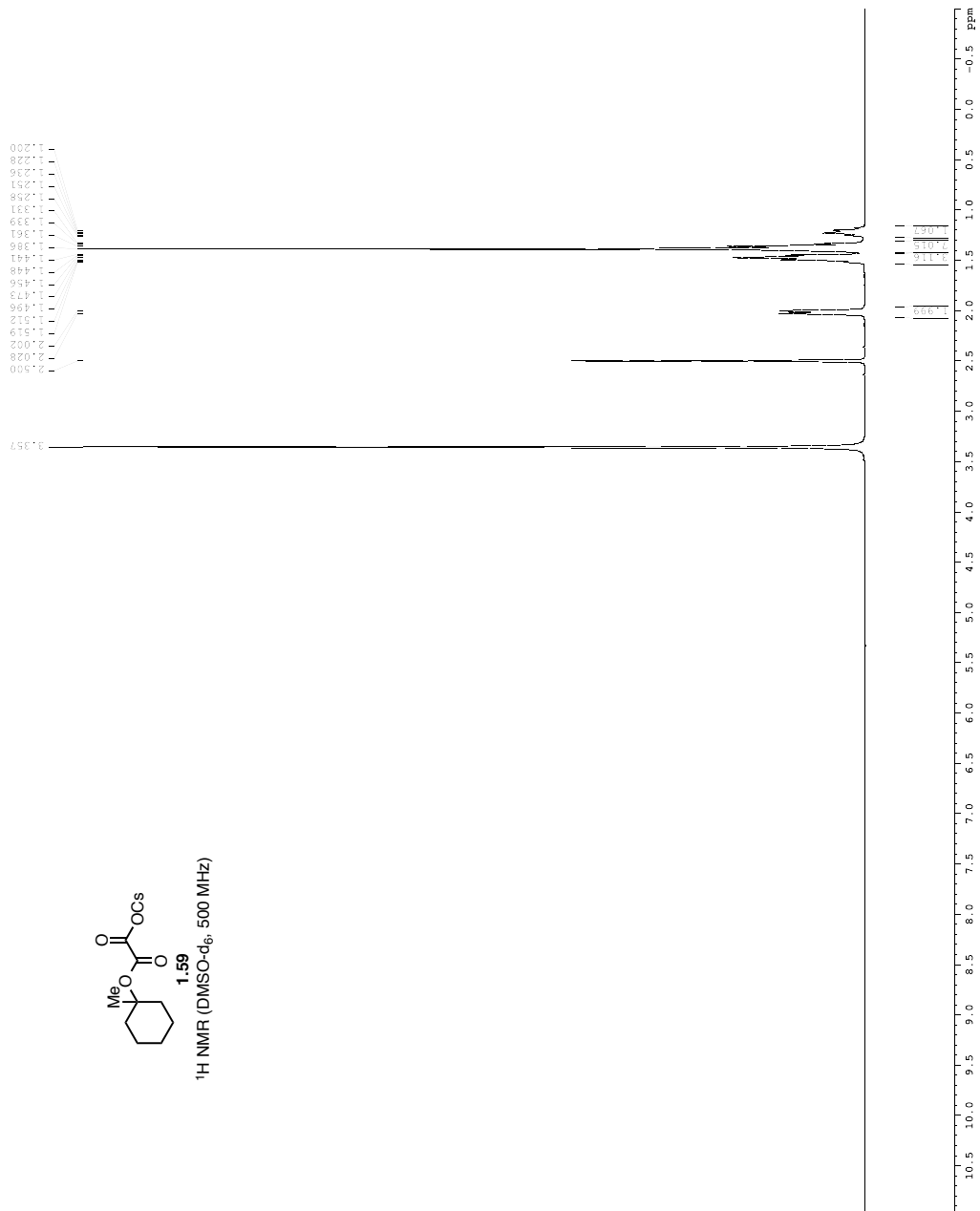
YS-II-192

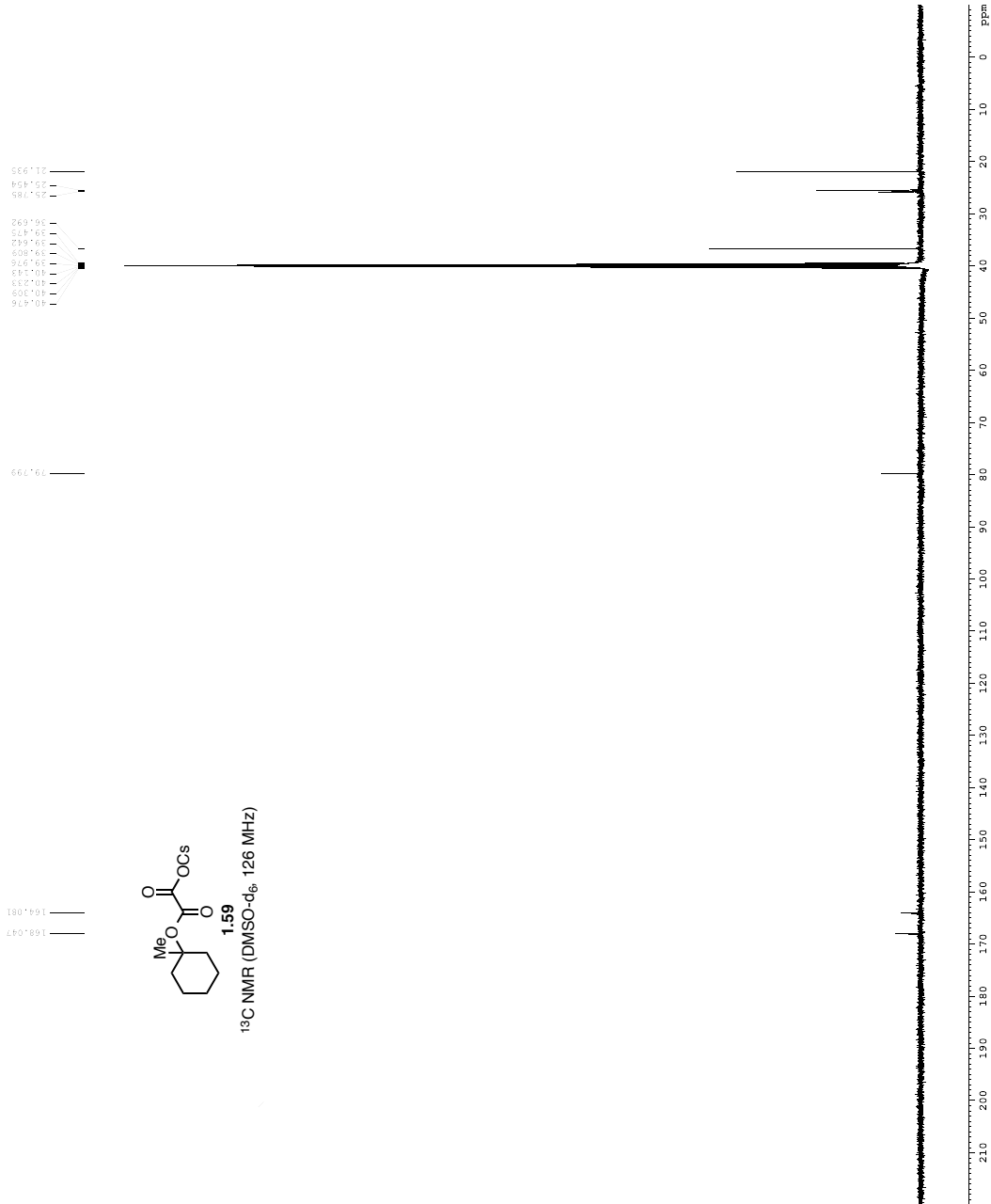


Current Data Parameters
NAME YS-II-192
PROCNO 1

F2 - Acquisition Parameters
Date_ Acq 01/30/20
Time 14:17
INSTRUM spect
PROBHD 5 mm CPCLP1H4
PULPROG zgpg30
SOLVENT DMSO
NS 8
DS 7
SS 8012.820 Hz
FIDRES 0.500114 Hz
AQ 0.999772 sec
RG 62.400 usec
DE 6.00 usec
D1 0.10000000 sec
MCRES21 0 sec
MCNMR 0.01500000 sec
----- CHANNEL F1 -----
NUC1 13C
P1 1.50 usec
PL1 1.60 dB
SFO1 500.2235012 MHz

F2 - Processing parameters
SI 65536
SF 500.2235012 MHz
RG 62.400 usec
DE 6.00 usec
D1 0.10000000 sec
PC 4.00





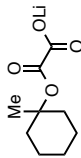
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Current Data Parameters
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110727
Time 14:19
INSTRUM cryo500
PROBHD 5 mm CPYX 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 232
DS 4
SWH 30300.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813450 sec
RG 16.500 usec
DE 6.00 usec
TE 300.2 K
C11 0.000000 sec
C12 0.000000 sec
C13 0.000000 sec
C14 0.000000 sec
C15 0.000000 sec
C16 0.000000 sec
C17 0.000000 sec
MKSST 0 sec
MKSR 0.0150000 sec
PC 33.10 usec

===== CHANNEL f1 =====
NUC1 13C
P1 16.55 usec
PL1 500.00 usec
PL2 2000.00 usec
PL3 1.00 usec
PL4 1.00 usec
PL5 1.00 usec
PL6 1.00 usec
SFO1 125.7942548 MHz
SF1 2.70 usec
SFO2 500.2225011 MHz
SFX1 0 Hz
SFX2 0 Hz
SFOFF1 0 Hz
SFOFF2 0 Hz

===== CHANNEL f2 =====
CPDPRG2 waitz16
NUC2 1H
P2 100.00 usec
PL2 1.60 usec
PL3 1.60 usec
PL4 24.50 usec
PL5 24.50 usec
PL6 500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GPA1 0 %
GPA2 0 %
GPA3 0 %
GPA4 0 %
GPA5 0 %
GPA6 0 %
GPA7 0 %
GPA8 0 %
GPA9 0 %
GPA10 0 %
GPA11 0 %
GPA12 0 %
GPA13 0 %
GPA14 0 %
GPA15 0 %
GPA16 0 %
GPA17 0 %
GPA18 0 %
GPA19 0 %
GPA20 0 %
GPA21 0 %
GPA22 0 %
GPA23 0 %
GPA24 0 %
GPA25 0 %
GPA26 0 %
GPA27 0 %
GPA28 0 %
GPA29 0 %
GPA30 0 %
===== Processing parameters =====
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00
    
```

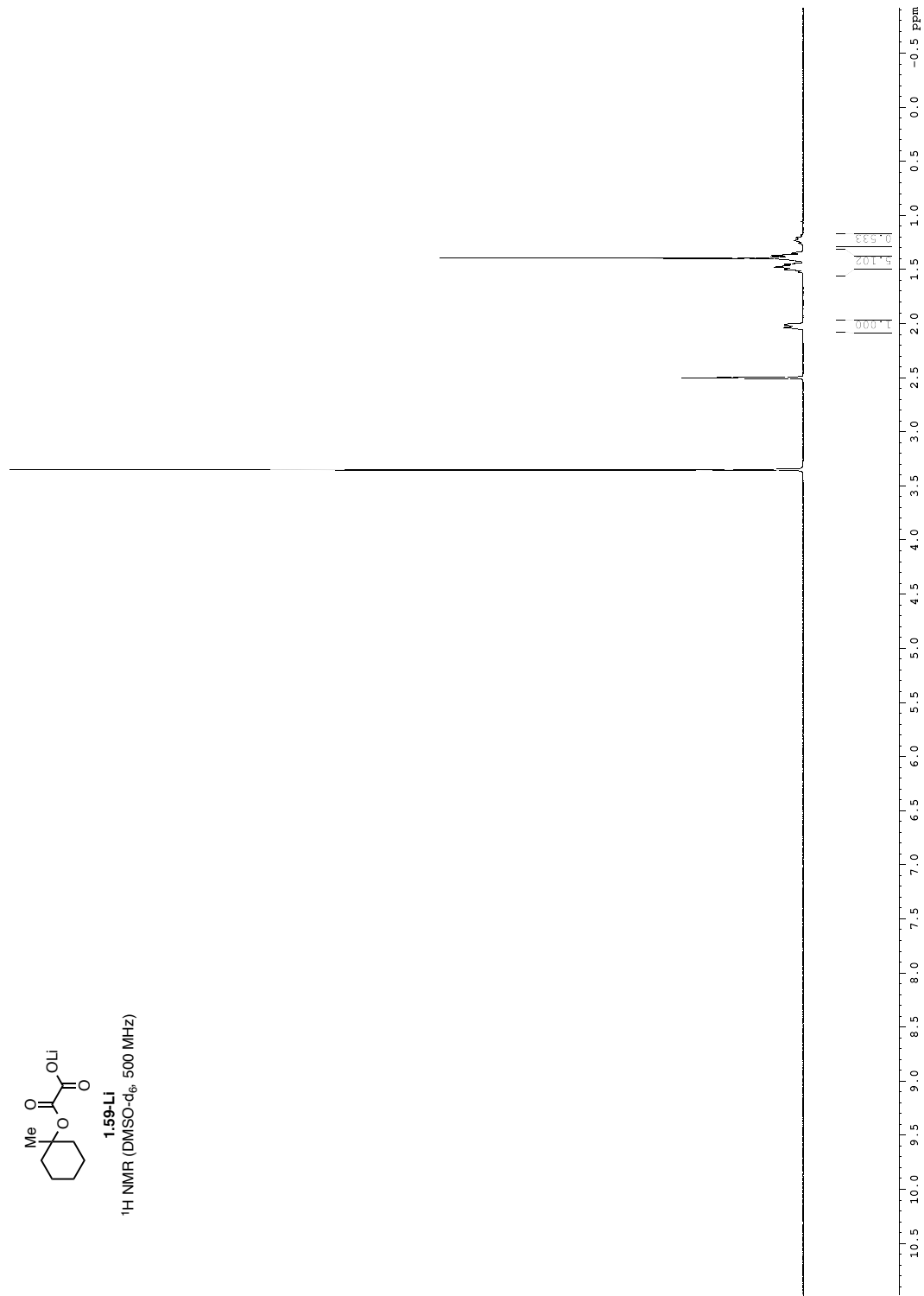

¹H spectrum



¹H NMR (DMSO-d₆, 500 MHz)

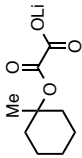
3.350
2.507
2.504
2.500
2.496
2.493
2.036
2.010
1.500
1.476
1.469
1.459
1.452
1.444
1.395
1.370
1.349
1.344
1.327
1.324
1.321
1.318
1.315
1.312
1.309
1.306
1.303
1.300
1.297
1.294
1.291
1.288
1.285
1.282
1.279
1.276
1.273
1.270
1.267
1.264
1.261
1.258
1.255
1.252
1.249
1.246
1.243
1.240
1.237
1.234
1.231
1.228
1.225
1.222
1.219
1.216
1.213
1.210
1.207
1.204
1.201
1.198
1.195
1.192
1.189
1.186
1.183
1.180
1.177
1.174
1.171
1.168
1.165
1.162
1.159
1.156
1.153
1.150
1.147
1.144
1.141
1.138
1.135
1.132
1.129
1.126
1.123
1.120
1.117
1.114
1.111
1.108
1.105
1.102
1.100

Current Data Parameters
NAME CRJ1-177-L1
EXNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150401
Time 14.03
INSTRUM cryo500
PROBHD 5 mm QNP1HHR
PULPROG zgpg30
TD 48074
SOLVENT CDCl3
NS 8
DSH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.9998176 sec
RG 14.3
DW 62.100 usec
DE 288.0 K
D1 0.10000000 sec
MCREST 0 sec
RCWRK 0.01500000 sec
***** CHANNEL f1 *****
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2239019 MHz
F2 - Processing parameters
SI 6536
SF 500.2200122 MHz
WDW no
SSB 0 Hz
LB 0 Hz
GB 0
PC 4.00



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

167.342
163.449



1.59-LI
13C NMR (DMSO-d₆, 126 MHz)



```

Current Data Parameters
NAME          CR31-177-L1
EXPNO         2
PROCNO        1

F2 - Acquisition Parameters
Date_         20150401
Time          14.06
INSTRUM       cryo500
PROBHD        5 mm CPYX500
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            64
DS            16
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813440 sec
RG            2580.3
CW            16.500 usec
DE            298.0 K
TE            298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0 sec
MCWALT        0.01500000 sec
F2            33.10 usec

===== CHANNEL f1 =====
NUC1          13C
P1            16.55 usec
PL1           500.00 usec
P12           2000.00 usec
PL2           120.00 dB
PL11          -1.00 dB
SFO1          125.7942548 MHz
SFO2          2.70 MHz
SFO3          2.70 MHz
SFO4          2.70 MHz
SFO5          2.70 MHz
SFO6          2.70 MHz
SFO7          2.70 MHz
SFO8          2.70 MHz
SFO9          2.70 MHz
SFO10         2.70 MHz
SFO11         2.70 MHz
SFO12         2.70 MHz
SFO13         2.70 MHz
SFO14         2.70 MHz
SFO15         2.70 MHz
SFO16         2.70 MHz
SFO17         2.70 MHz
SFO18         2.70 MHz
SFO19         2.70 MHz
SFO20         2.70 MHz
SFO21         2.70 MHz
SFO22         2.70 MHz
SFO23         2.70 MHz
SFO24         2.70 MHz
SFO25         2.70 MHz
SFO26         2.70 MHz
SFO27         2.70 MHz
SFO28         2.70 MHz
SFO29         2.70 MHz
SFO30         2.70 MHz
SFO31         2.70 MHz
SFO32         2.70 MHz
SFO33         2.70 MHz
SFO34         2.70 MHz
SFO35         2.70 MHz
SFO36         2.70 MHz
SFO37         2.70 MHz
SFO38         2.70 MHz
SFO39         2.70 MHz
SFO40         2.70 MHz
SFO41         2.70 MHz
SFO42         2.70 MHz
SFO43         2.70 MHz
SFO44         2.70 MHz
SFO45         2.70 MHz
SFO46         2.70 MHz
SFO47         2.70 MHz
SFO48         2.70 MHz
SFO49         2.70 MHz
SFO50         2.70 MHz
SFO51         2.70 MHz
SFO52         2.70 MHz
SFO53         2.70 MHz
SFO54         2.70 MHz
SFO55         2.70 MHz
SFO56         2.70 MHz
SFO57         2.70 MHz
SFO58         2.70 MHz
SFO59         2.70 MHz
SFO60         2.70 MHz
SFO61         2.70 MHz
SFO62         2.70 MHz
SFO63         2.70 MHz
SFO64         2.70 MHz
SFO65         2.70 MHz
SFO66         2.70 MHz
SFO67         2.70 MHz
SFO68         2.70 MHz
SFO69         2.70 MHz
SFO70         2.70 MHz
SFO71         2.70 MHz
SFO72         2.70 MHz
SFO73         2.70 MHz
SFO74         2.70 MHz
SFO75         2.70 MHz
SFO76         2.70 MHz
SFO77         2.70 MHz
SFO78         2.70 MHz
SFO79         2.70 MHz
SFO80         2.70 MHz
SFO81         2.70 MHz
SFO82         2.70 MHz
SFO83         2.70 MHz
SFO84         2.70 MHz
SFO85         2.70 MHz
SFO86         2.70 MHz
SFO87         2.70 MHz
SFO88         2.70 MHz
SFO89         2.70 MHz
SFO90         2.70 MHz
SFO91         2.70 MHz
SFO92         2.70 MHz
SFO93         2.70 MHz
SFO94         2.70 MHz
SFO95         2.70 MHz
SFO96         2.70 MHz
SFO97         2.70 MHz
SFO98         2.70 MHz
SFO99         2.70 MHz
SFO100        2.70 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2        100.00 usec
PL2          1.50 dB
SFO2         500.225011 MHz

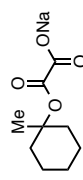
===== GRADIENT CHANNEL =====
GPNAM[1]      SINE.100
GPNAM[2]      SINE.100
GPK1          0 %
GPK2          0 %
GPT1          0 %
GPT2          0 %
GPA2          30.00 %
GPA1          50.00 %
P15           500.00 usec
P16           1000.00 usec

F2 - Processing parameters
SI            65536
SF            125.7804773 MHz
RG            no
WDW           no
SSB           0 Hz
GB            0
PC            2.00
    
```

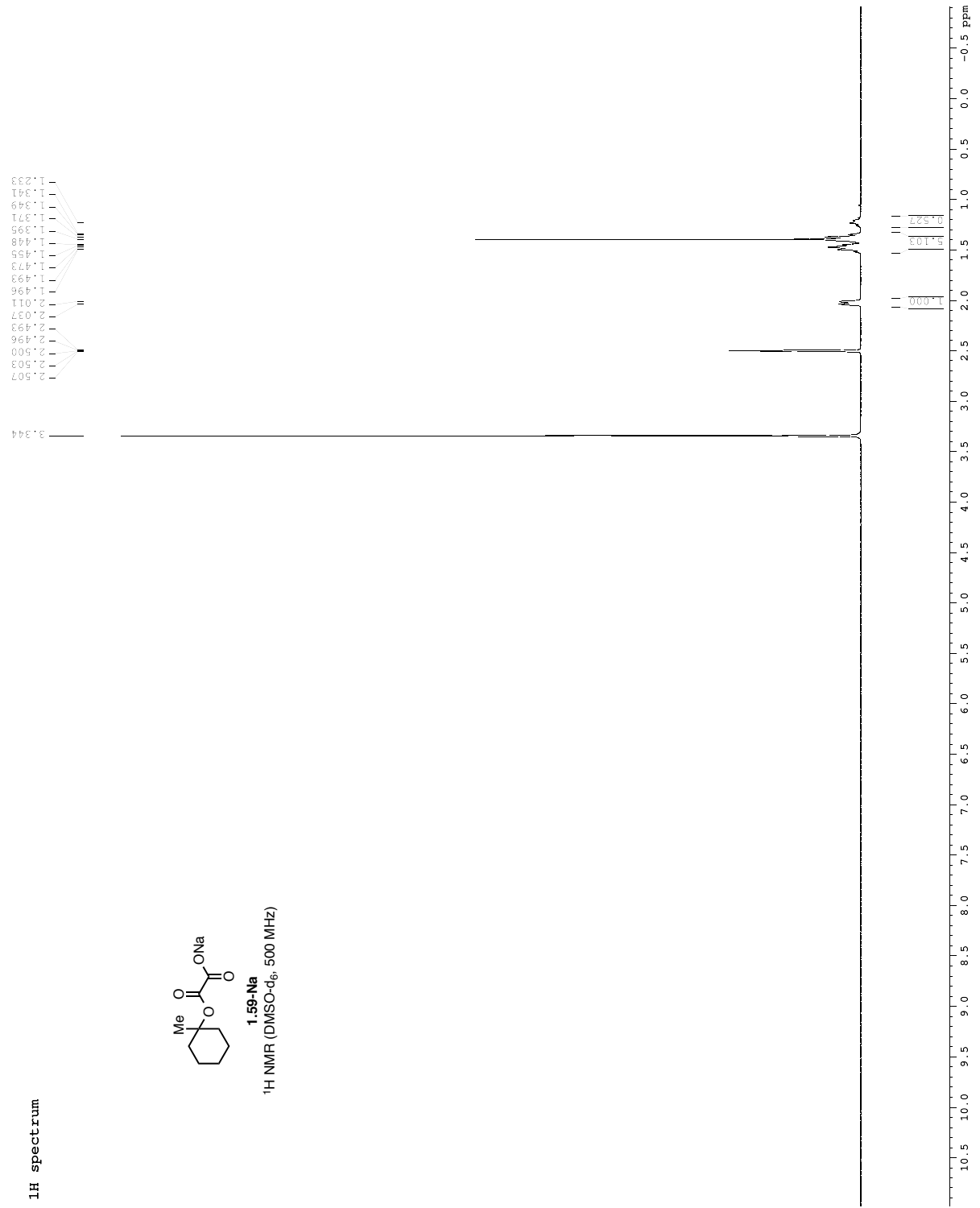
¹H spectrum

3.244
 1.282
 1.241
 1.349
 1.371
 1.396
 1.448
 1.459
 1.473
 1.493
 1.496
 1.011
 1.037
 1.493
 1.496
 1.500
 1.503
 1.507

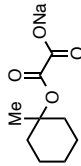
Current Data Parameters
 NAME GRJ1-177-Na
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20150401
 Time 14.11
 INSTRUM cryo100
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.250026 Hz
 AQ 1.9997952 sec
 RG 62.418
 DW 62.400 usec
 DE 238.0 usec
 TE 298.0 K
 D1 0.10000000 sec
 MCREST 0 sec
 MCWRR 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 ¹H
 P1 7.50 usec
 PL1 1.60 dB
 SFO1 500.223013 MHz
 F2 - Processing Parameters
 SI 65536
 SF 500.2200122 MHz
 SD 32768
 SSB 0 Hz
 LB 0 Hz
 GB 0
 PC 4.00



1.59-Na
¹H NMR (DMSO-d₆, 500 MHz)



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



1.59-Na
¹³C NMR (DMSO-d₆, 126 MHz)

```

Current Data Parameters
NAME           CR01-177-Na
EXPNO         2
PROCNO        1

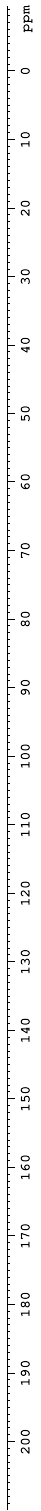
F2 - Acquisition Parameters
Date_         20150401
Time          14.12
INSTRUM       cryo500
PROBHD        5 mm CPXI 1H-
PULPROG       Spinechop2
TD            65536
SOLVENT       CDCl3
NS            64
DS            2
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813440 sec
RG            8192
DW            16.500 usec
DE            298.00 K
TE            298.00 K
D1            1.00000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0 sec
MCWREX        0.01500000 sec
P2            33.10 usec

===== CHANNEL f1 =====
NUC1          13C
P1            16.15 usec
P11           500.00 usec
P12           2000.00 usec
P10           120.00 dB
P11           -1.00 dB
SFO1          125.7942548 MHz
SFO2          2.70 dB
SFO3          2.70 dB
SFO4          2.70 dB
SFO5          2.70 dB
SFO6          2.70 dB
SFO7          2.70 dB
SFO8          2.70 dB
SFO9          2.70 dB
SFO10         2.70 dB
SFO11         2.70 dB
SFO12         2.70 dB
SFO13         2.70 dB
SFO14         2.70 dB
SFO15         2.70 dB
SFO16         2.70 dB
SFO17         2.70 dB
SFO18         2.70 dB
SFO19         2.70 dB
SFO20         2.70 dB
SFO21         2.70 dB
SFO22         2.70 dB
SFO23         2.70 dB
SFO24         2.70 dB
SFO25         2.70 dB
SFO26         2.70 dB
SFO27         2.70 dB
SFO28         2.70 dB
SFO29         2.70 dB
SFO30         2.70 dB
SFO31         2.70 dB
SFO32         2.70 dB
SFO33         2.70 dB
SFO34         2.70 dB
SFO35         2.70 dB
SFO36         2.70 dB
SFO37         2.70 dB
SFO38         2.70 dB
SFO39         2.70 dB
SFO40         2.70 dB
SFO41         2.70 dB
SFO42         2.70 dB
SFO43         2.70 dB
SFO44         2.70 dB
SFO45         2.70 dB
SFO46         2.70 dB
SFO47         2.70 dB
SFO48         2.70 dB
SFO49         2.70 dB
SFO50         2.70 dB
SFO51         2.70 dB
SFO52         2.70 dB
SFO53         2.70 dB
SFO54         2.70 dB
SFO55         2.70 dB
SFO56         2.70 dB
SFO57         2.70 dB
SFO58         2.70 dB
SFO59         2.70 dB
SFO60         2.70 dB
SFO61         2.70 dB
SFO62         2.70 dB
SFO63         2.70 dB
SFO64         2.70 dB
SFO65         2.70 dB
SFO66         2.70 dB
SFO67         2.70 dB
SFO68         2.70 dB
SFO69         2.70 dB
SFO70         2.70 dB
SFO71         2.70 dB
SFO72         2.70 dB
SFO73         2.70 dB
SFO74         2.70 dB
SFO75         2.70 dB
SFO76         2.70 dB
SFO77         2.70 dB
SFO78         2.70 dB
SFO79         2.70 dB
SFO80         2.70 dB
SFO81         2.70 dB
SFO82         2.70 dB
SFO83         2.70 dB
SFO84         2.70 dB
SFO85         2.70 dB
SFO86         2.70 dB
SFO87         2.70 dB
SFO88         2.70 dB
SFO89         2.70 dB
SFO90         2.70 dB
SFO91         2.70 dB
SFO92         2.70 dB
SFO93         2.70 dB
SFO94         2.70 dB
SFO95         2.70 dB
SFO96         2.70 dB
SFO97         2.70 dB
SFO98         2.70 dB
SFO99         2.70 dB
SFO100        2.70 dB

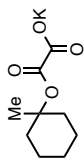
===== CHANNEL f2 =====
CPDPRG12      waltz16
NUC2          1H
P2D2          100.00 usec
P2F2          4.00 dB
P2F1          2.00 dB
SFO2          500.2223011 MHz

===== GRADIENT CHANNEL =====
GENDAM[1]     SINE.100
GENDAM[2]     SINE.100
GFX1          0 %
GFX2          0 %
GFX3          0 %
GFX4          0 %
GFX5          0 %
GFX6          0 %
GFX7          0 %
GFX8          0 %
GFX9          0 %
GFX10         0 %
GFX11         0 %
GFX12         0 %
GFX13         0 %
GFX14         0 %
GFX15         0 %
GFX16         0 %
GFX17         0 %
GFX18         0 %
GFX19         0 %
GFX20         0 %
GFX21         0 %
GFX22         0 %
GFX23         0 %
GFX24         0 %
GFX25         0 %
GFX26         0 %
GFX27         0 %
GFX28         0 %
GFX29         0 %
GFX30         0 %
GFX31         0 %
GFX32         0 %
GFX33         0 %
GFX34         0 %
GFX35         0 %
GFX36         0 %
GFX37         0 %
GFX38         0 %
GFX39         0 %
GFX40         0 %
GFX41         0 %
GFX42         0 %
GFX43         0 %
GFX44         0 %
GFX45         0 %
GFX46         0 %
GFX47         0 %
GFX48         0 %
GFX49         0 %
GFX50         0 %
GFX51         0 %
GFX52         0 %
GFX53         0 %
GFX54         0 %
GFX55         0 %
GFX56         0 %
GFX57         0 %
GFX58         0 %
GFX59         0 %
GFX60         0 %
GFX61         0 %
GFX62         0 %
GFX63         0 %
GFX64         0 %
GFX65         0 %
GFX66         0 %
GFX67         0 %
GFX68         0 %
GFX69         0 %
GFX70         0 %
GFX71         0 %
GFX72         0 %
GFX73         0 %
GFX74         0 %
GFX75         0 %
GFX76         0 %
GFX77         0 %
GFX78         0 %
GFX79         0 %
GFX80         0 %
GFX81         0 %
GFX82         0 %
GFX83         0 %
GFX84         0 %
GFX85         0 %
GFX86         0 %
GFX87         0 %
GFX88         0 %
GFX89         0 %
GFX90         0 %
GFX91         0 %
GFX92         0 %
GFX93         0 %
GFX94         0 %
GFX95         0 %
GFX96         0 %
GFX97         0 %
GFX98         0 %
GFX99         0 %
GFX100        0 %

F2 - Processing parameters
SI            65536
SF            125.7804777 MHz
WDW           no
SSB           0 Hz
GB            0
PC            2.00
    
```

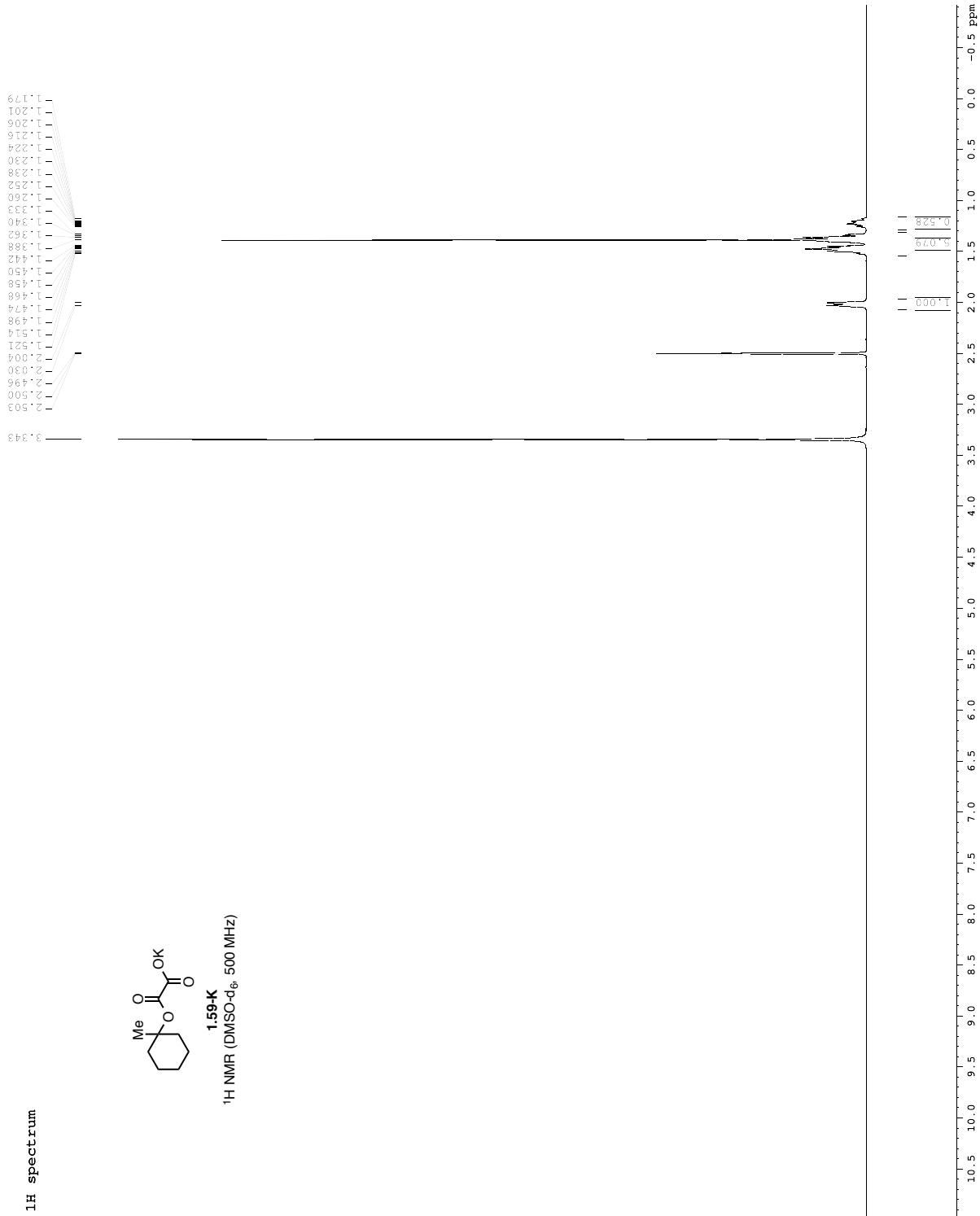


1H spectrum

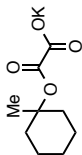


1.59-K
1H NMR (DMSO-d₆, 500 MHz)

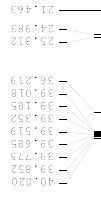
Current Data Parameters
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150401
Time 14.44
INSTRUM cryo500
PROBHD 5 mm CP1H1H-
PULPROG zgpg30
TD 32048
SOLVENT DMSO
NS 2
DS 2
SWH 8012.620 Hz
FIDRES 0.250026 Hz
AQ 1.997202 sec
RG 202
DVI 62.400 usec
DE 6.00 usec
TE 298.2 K
AQC 0.10000000 sec
MCRET 0 sec
MCKRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 32768
SF 500.2200121 MHz
WDW 0
SSB 0 Hz
LB 0 Hz
GB 0
PC 4.00



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



1.59-K
13C NMR (DMSO-d₆, 126 MHz)



Current Data Parameters
 NAME CR01-177-K
 EXPNO 2
 PROCNO 1

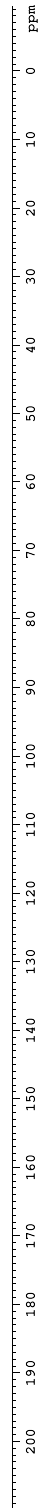
F2 - Acquisition Parameters
 Date_ 20150401
 Time 14:18
 NUC1 13C
 PULPROG zgpg30
 PRGHD 5 mm CPZTC131
 F1F2PROG Spinechop3dpp.prd
 TD 65536
 SOLVENT DMSO
 NS 80
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.462398 Hz
 AQ 1.081340 sec
 RG 169.00
 DM 16.00 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 ACQRES 0 sec
 PCWREK 0.0150000 sec
 F2 33.10 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 F10 120.00 dB
 F11 -1.00 dB
 SFO1 125.7942548 MHz
 SF1 2.00 dB
 SF2 2.70 dB
 SPNAM[1] Crp60_0_5_26_1
 SPNAM[2] Crp60comp_4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 F12 24.50 dB
 SFO2 500.2225011 MHz

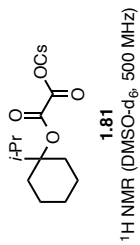
===== GRADIENT CHANNEL =====
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GPZ1 30.00 %
 GPZ2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

F2 - Processing Parameters
 SI 65536
 SF 125.7804779 MHz
 DS 2
 SSB 0 Hz
 GB 0
 FC 2.00

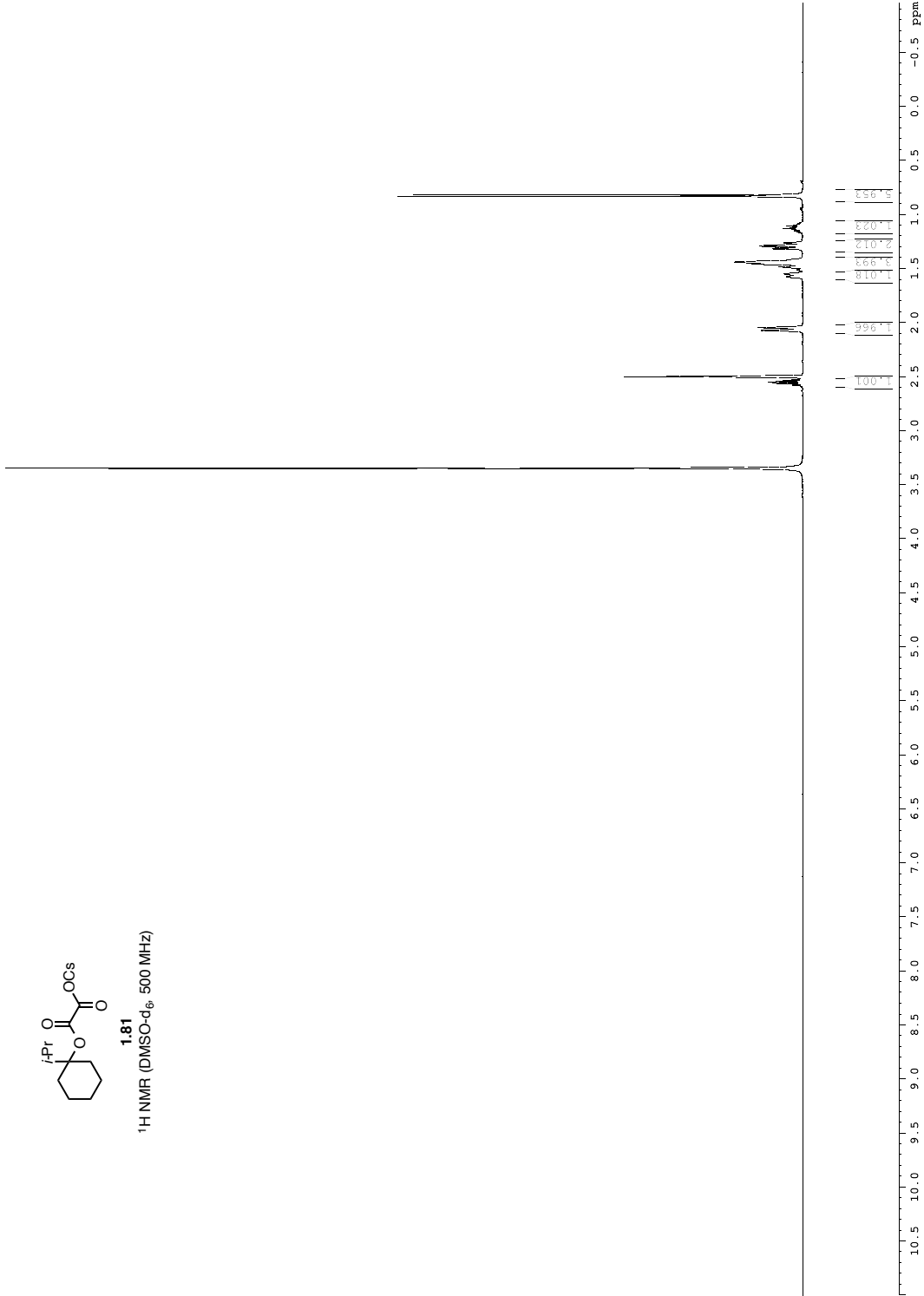


¹H spectrum

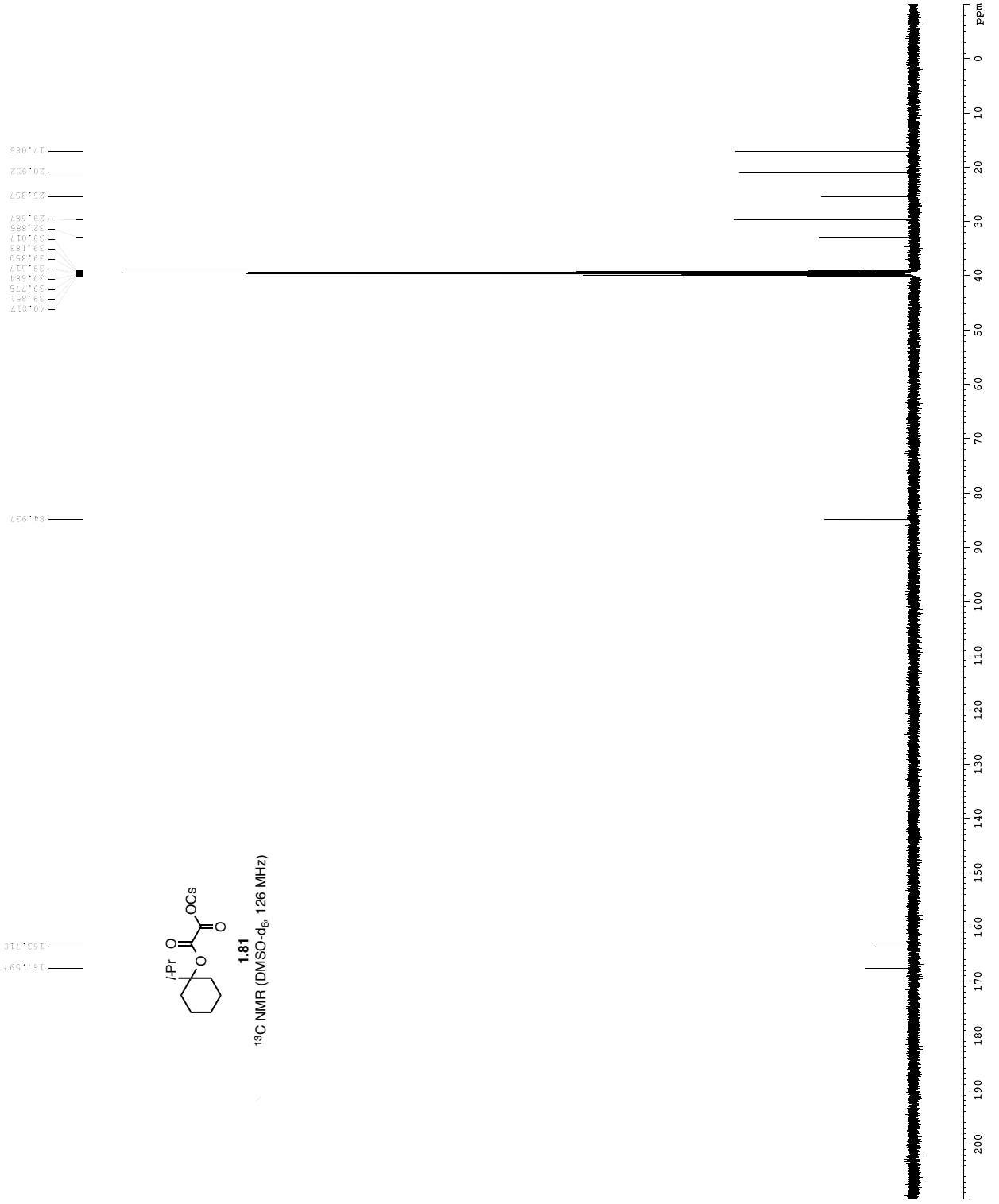
3.348
3.298
3.248
3.198
3.148
3.098
3.048
3.000
2.950
2.900
2.850
2.800
2.750
2.700
2.650
2.600
2.550
2.500
2.450
2.400
2.350
2.300
2.250
2.200
2.150
2.100
2.050
2.000
1.950
1.900
1.850
1.800
1.750
1.700
1.650
1.600
1.550
1.500
1.450
1.400
1.350
1.300
1.250
1.200
1.150
1.100
1.050
1.000
0.950
0.900
0.850
0.800
0.750
0.700
0.650
0.600
0.550
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000



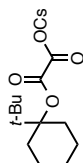
Current Data Parameters
NAME CSJ1-094-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150223
Time 13.17
INSTRUM cryo500
PROBHD 5 mm QNP1H
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
NS 8
DSH 8012.870 Hz
FIDRES 0.0986043 Hz
AQ 5.0998273 sec
RG 10.11
DW 62.100 usec
DE 2.00 usec
TE 298.0 K
D1 3.00000000 sec
MCRETST 0 sec
MCORR 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 0
SSB 0 Hz
LB 0
GB 0
PC 4.00



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



¹H spectrum



1.83
¹H NMR (DMSO-d₆, 500 MHz)

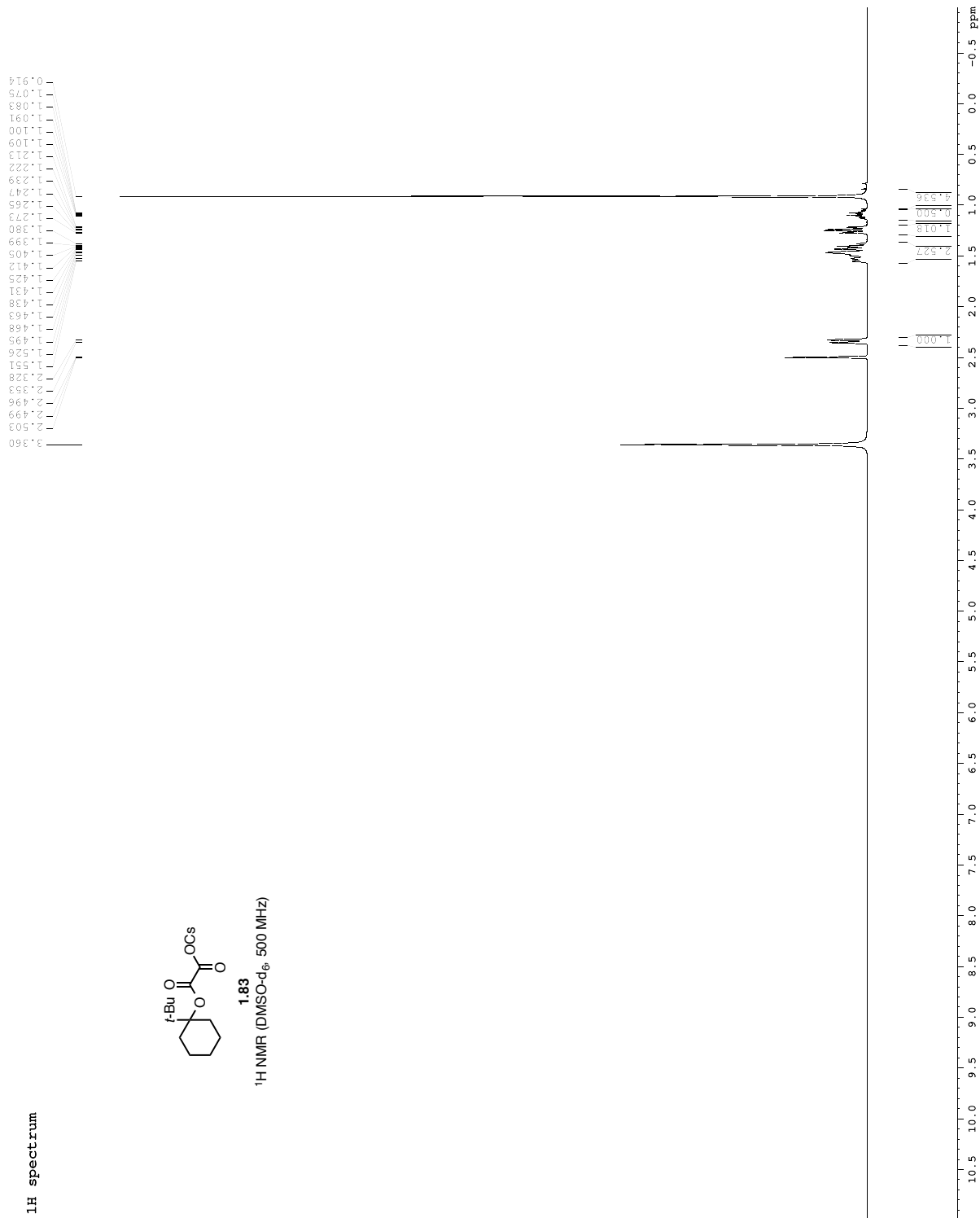
```

Current Data Parameters
NAME      C001-127-1.pars
EXPNO     1
PROCNO    1

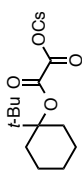
F2 - Acquisition Parameters
Date_     20180116
Time      11.16
INSTRUM   cryo500
PROBHD    5 mm CFTCI 1H-
PULPROG   zgpg
RG         2930
AQ         0.0354
SOLVENT   DMSO
NS         8
DS         2
SWH        8012.820 Hz
FIDRES     0.16577 Hz
AQRES      2.3999376 sec
RG         5.7
DW         62.400 usec
DE         6.00 usec
TE         298.0 K
D1         0.10000000 sec
MCORBST   0 sec
MCONRK     0.01500000 sec

===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL1        1.60 dB
SFO1       500.2235015 MHz

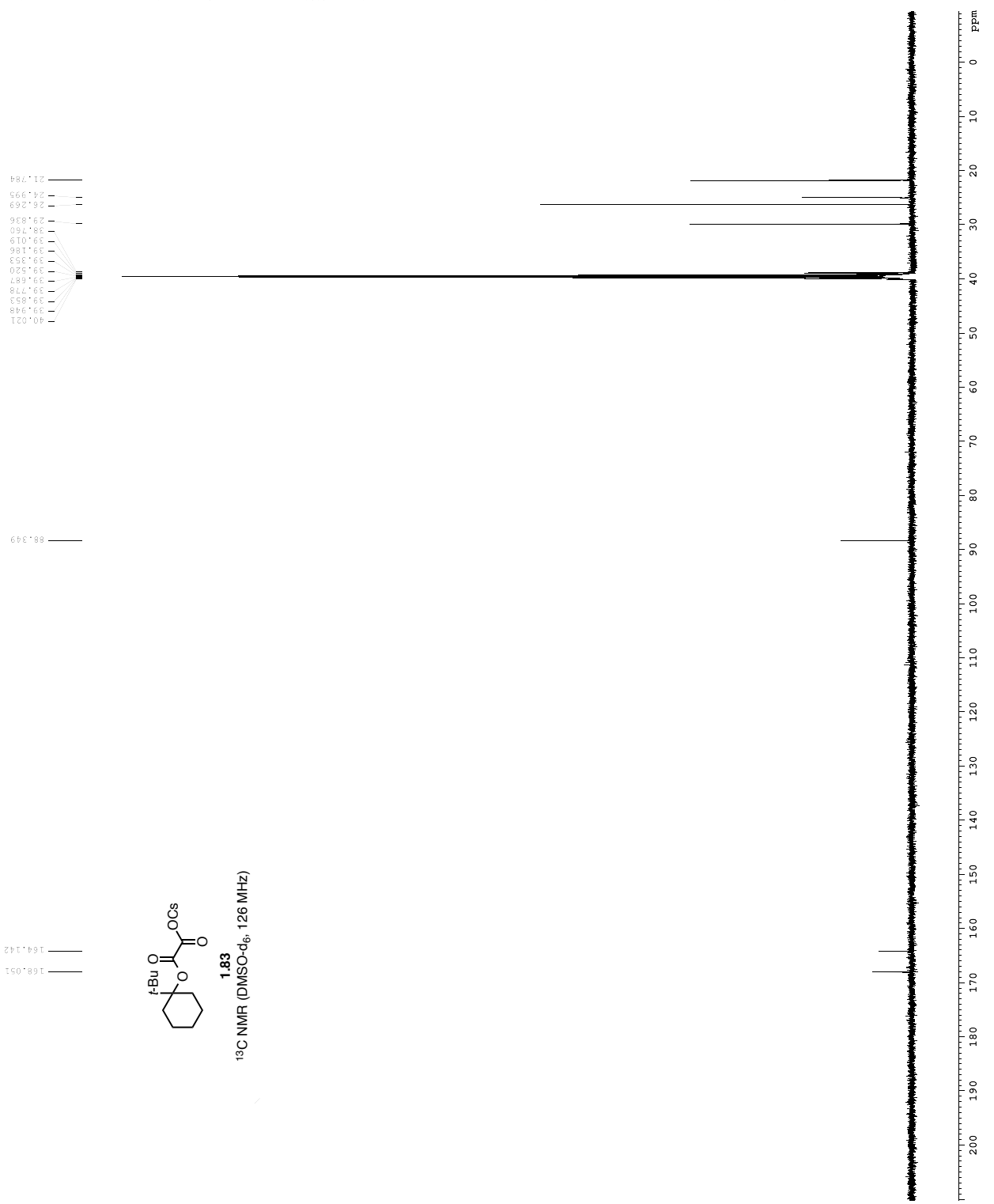
F2 - Processing parameters
SI         500.2200127 MHz
SF         65536
WDW        0
SSB        0 Hz
LB         0
GB         0
PC         4.00
    
```



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



13C NMR (DMSO-d₆, 126 MHz)



Current Data Parameters
 NAME CRJ-127-pure
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20150311
 Time 11:18
 NUC1 13C
 PULPROG zgpg30
 PRGHD 5 mm CPDPR1
 FUPROG Spinechop3dpp.prd
 TD 65536
 SOLVENT DMSO
 NS 64
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.462398 Hz
 AQ 1.081340 sec
 RG 320
 DM 16.00 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.0000000 sec
 d11 0.0300000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 ACQRES 0 sec
 PCWREK 0.0150000 sec
 F2 33.10 usec

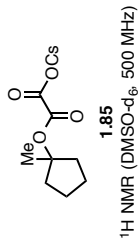
===== CHANNEL f1 =====
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 F10 120.00 dB
 F11 -1.00 dB
 SFO1 125.7942548 MHz
 SF1 2.70 dB
 SF2 2.70 dB
 SPNAM[1] Crp60_0_5_26_1
 SPNAM[2] Crp60comp_4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 1H
 P2 100.00 usec
 P21 1.00 dB
 F12 24.50 dB
 SFO2 500.2225011 MHz

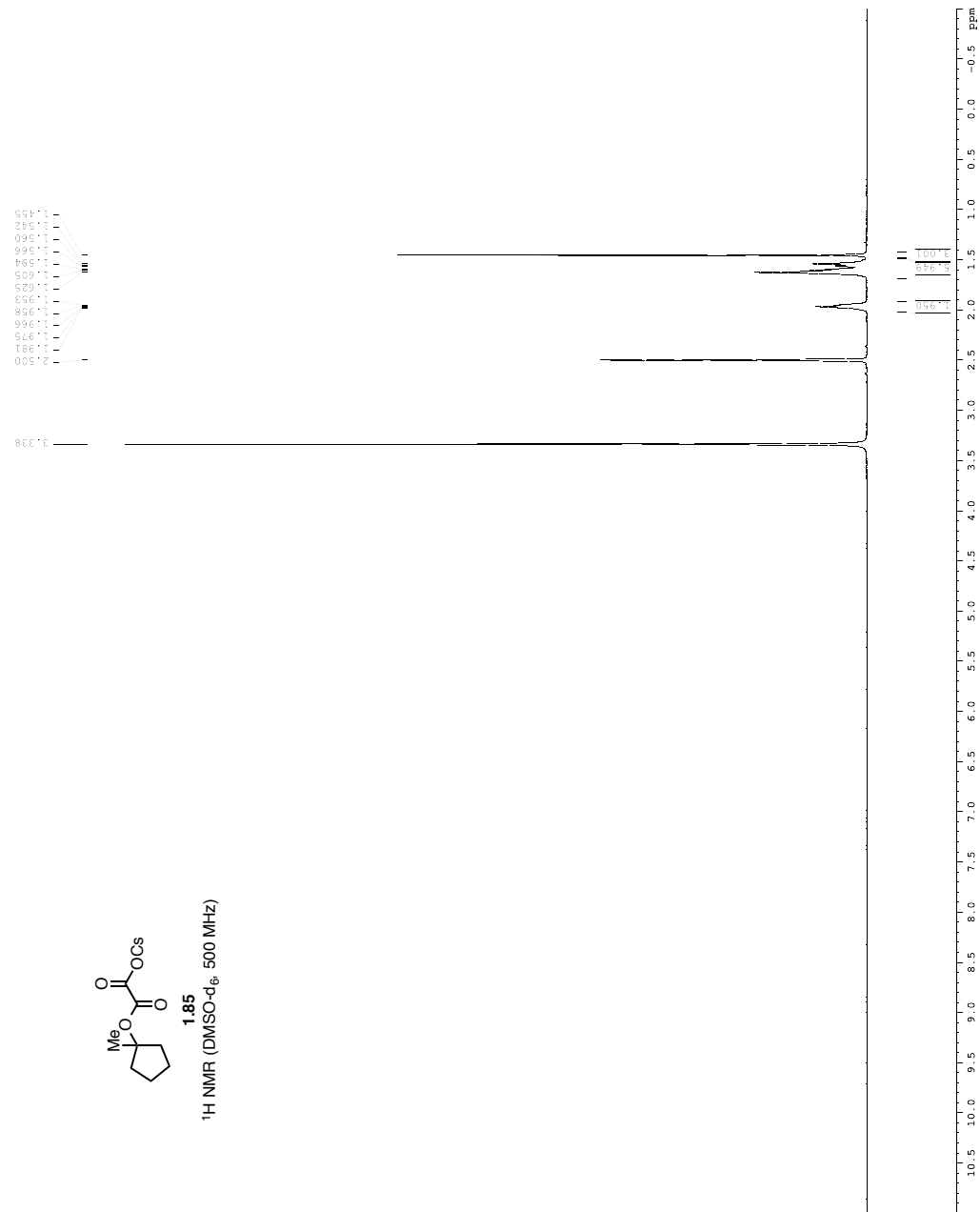
===== GRADIENT CHANNEL =====
 GPMAM[1] SINE.100
 GPMAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GPZ1 30.00 %
 GPZ2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

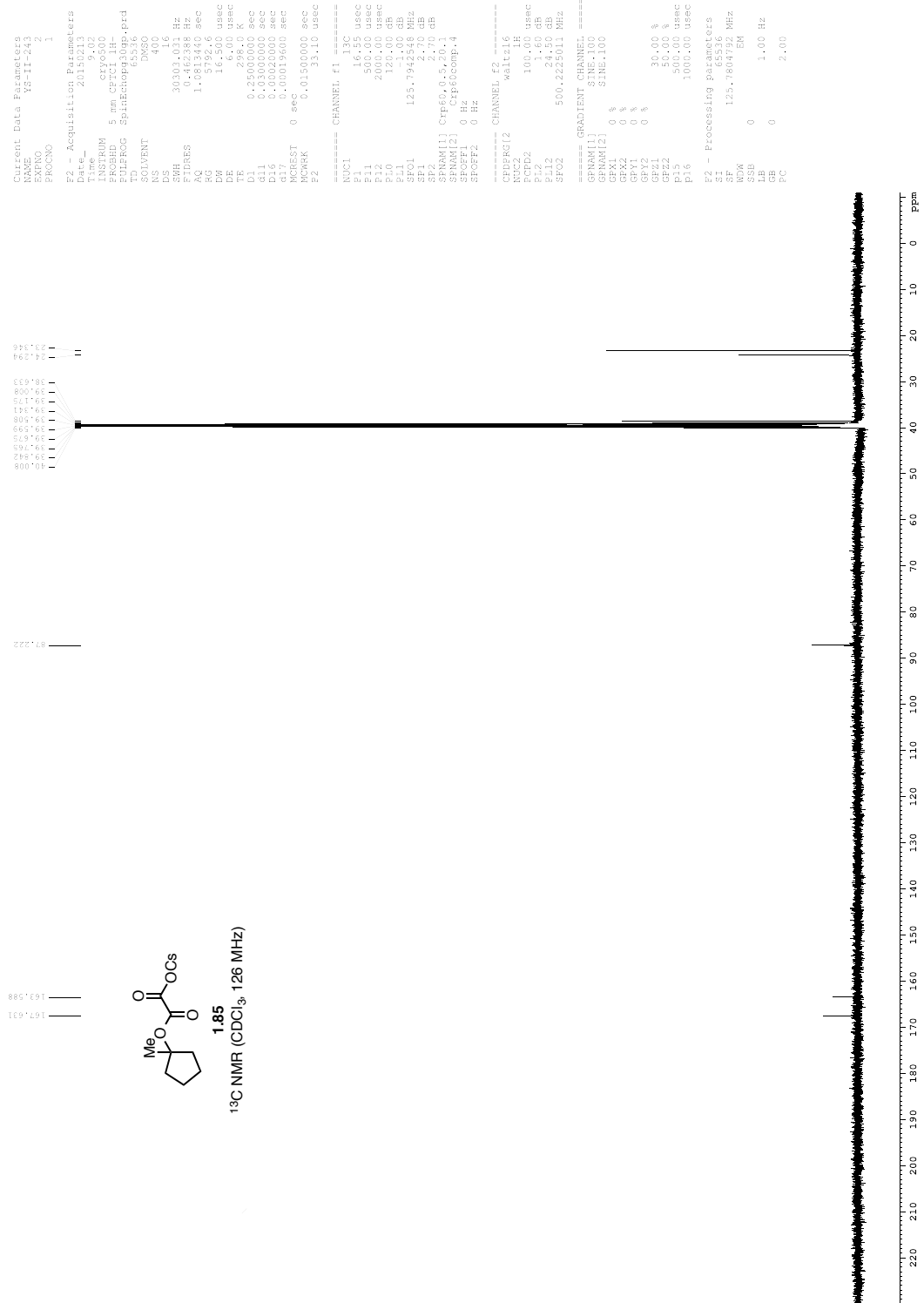
F2 - Processing Parameters
 SI 65536
 SF 125.7804769 MHz
 EQ
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 2.00

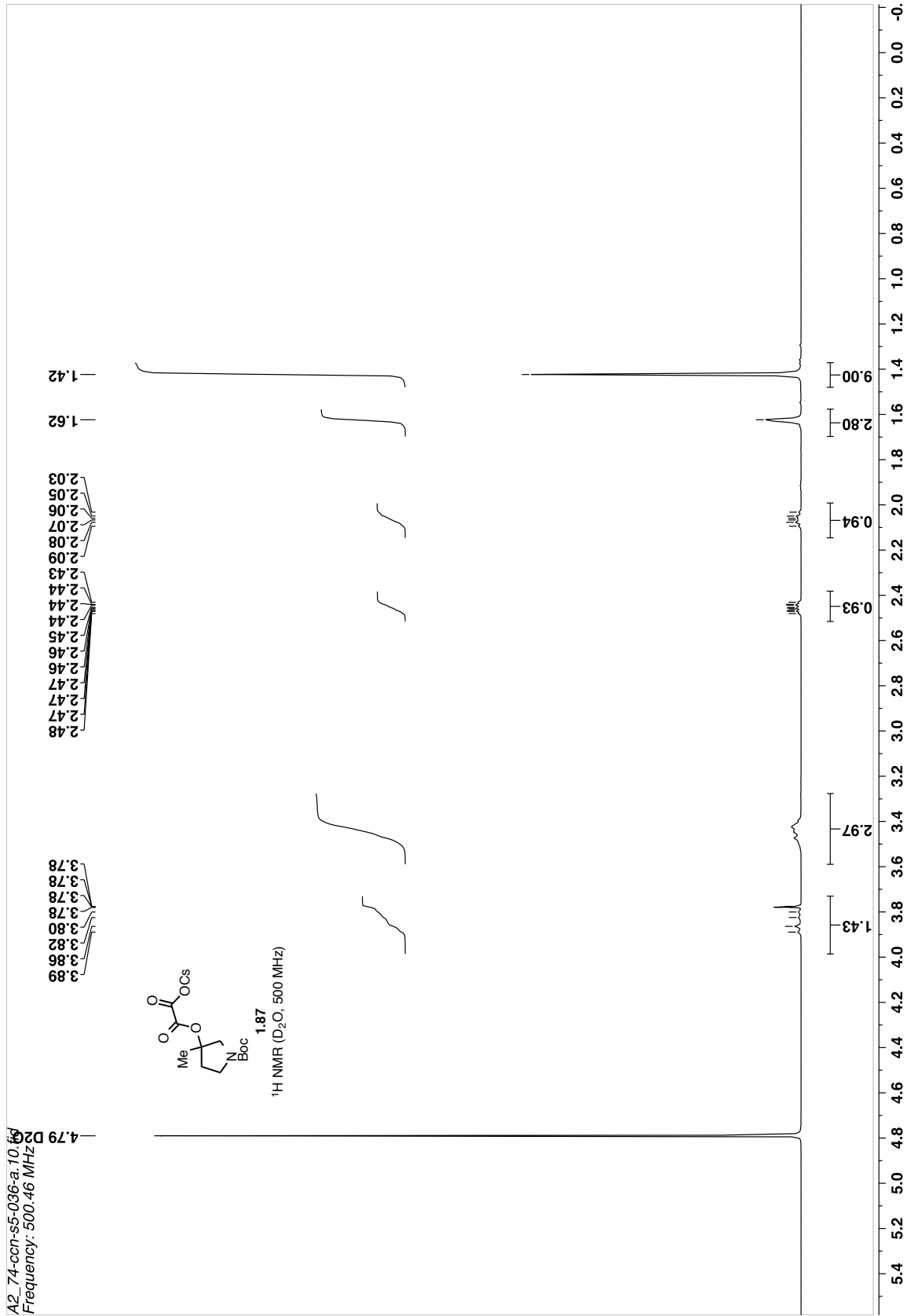
YS-II-243



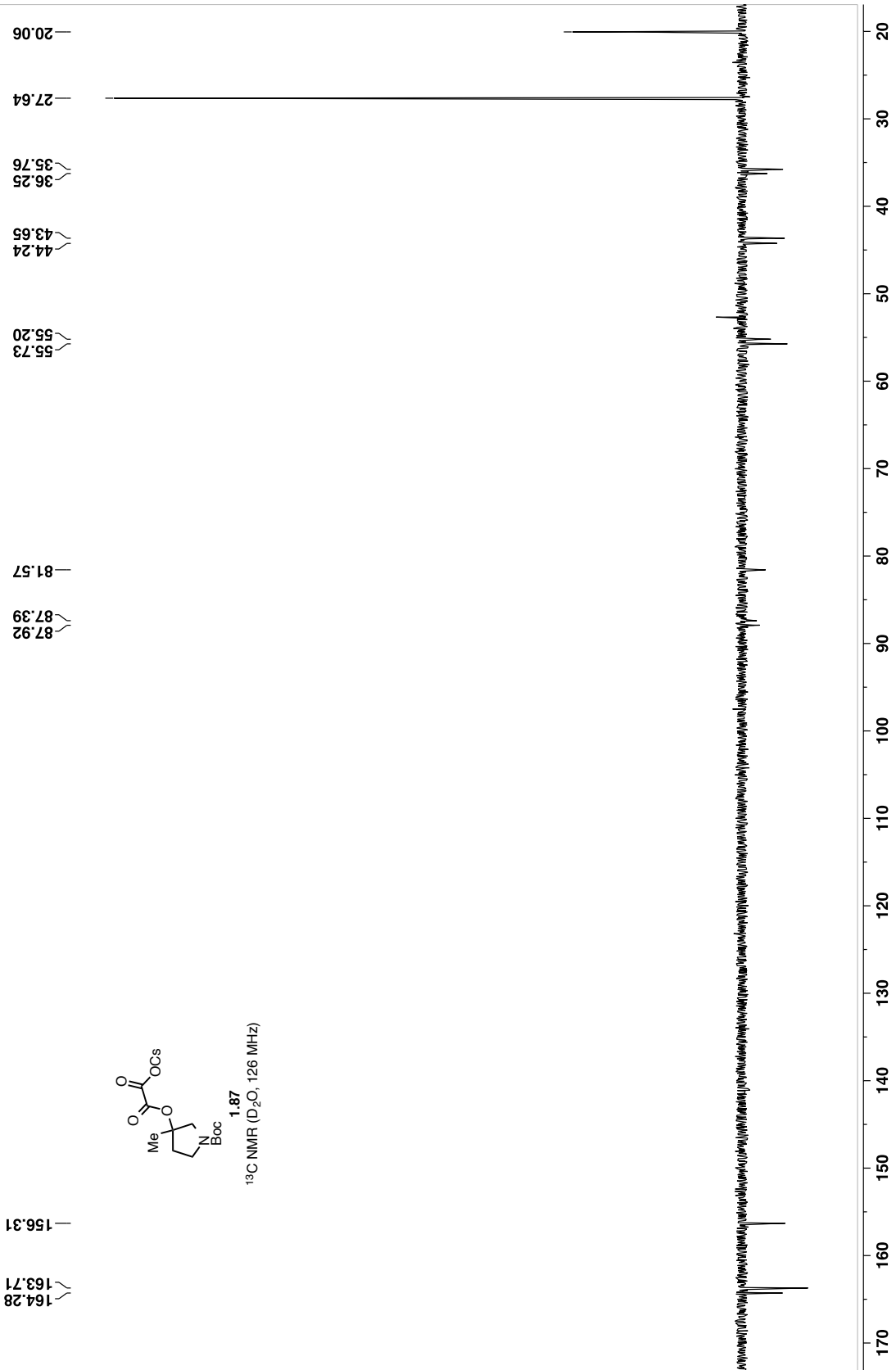
Current Data Parameters
NAME YS-II-243
PROCNO 1
===== Acquisition Parameters =====
Date_ 01/02/15
Time 8:59
INSTRUM spect
PROBHD 5 mm CPY 13H
PULPROG zgpg30
AQ 2.930
RG 320
SFO1 500.135012 MHz
NUC1 13C
P1 1.50
PL1 0.00
PL2 0.00
PL3 1.60
PL4 0.00
PL5 0.00
PL6 0.00
PL7 0.00
PL8 0.00
PL9 0.00
PL10 0.00
PL11 0.00
PL12 0.00
PL13 0.00
PL14 0.00
PL15 0.00
PL16 0.00
PL17 0.00
PL18 0.00
PL19 0.00
PL20 0.00
===== CHANNEL F1 =====
NUC1 13C
P1 1.50
PL1 0.00
PL2 0.00
PL3 1.60
PL4 0.00
PL5 0.00
PL6 0.00
PL7 0.00
PL8 0.00
PL9 0.00
PL10 0.00
PL11 0.00
PL12 0.00
PL13 0.00
PL14 0.00
PL15 0.00
PL16 0.00
PL17 0.00
PL18 0.00
PL19 0.00
PL20 0.00
===== CHANNEL F2 =====
SFO2 500.135012 MHz
NUC2 1H
P2 1.50
PL2 0.00
PL3 0.00
PL4 0.00
PL5 0.00
PL6 0.00
PL7 0.00
PL8 0.00
PL9 0.00
PL10 0.00
PL11 0.00
PL12 0.00
PL13 0.00
PL14 0.00
PL15 0.00
PL16 0.00
PL17 0.00
PL18 0.00
PL19 0.00
PL20 0.00
===== Processing parameters =====
SI 65536
SF 500.135012 MHz
RG 320
WDW EM
SSB 0
GB 0
PC 4.00

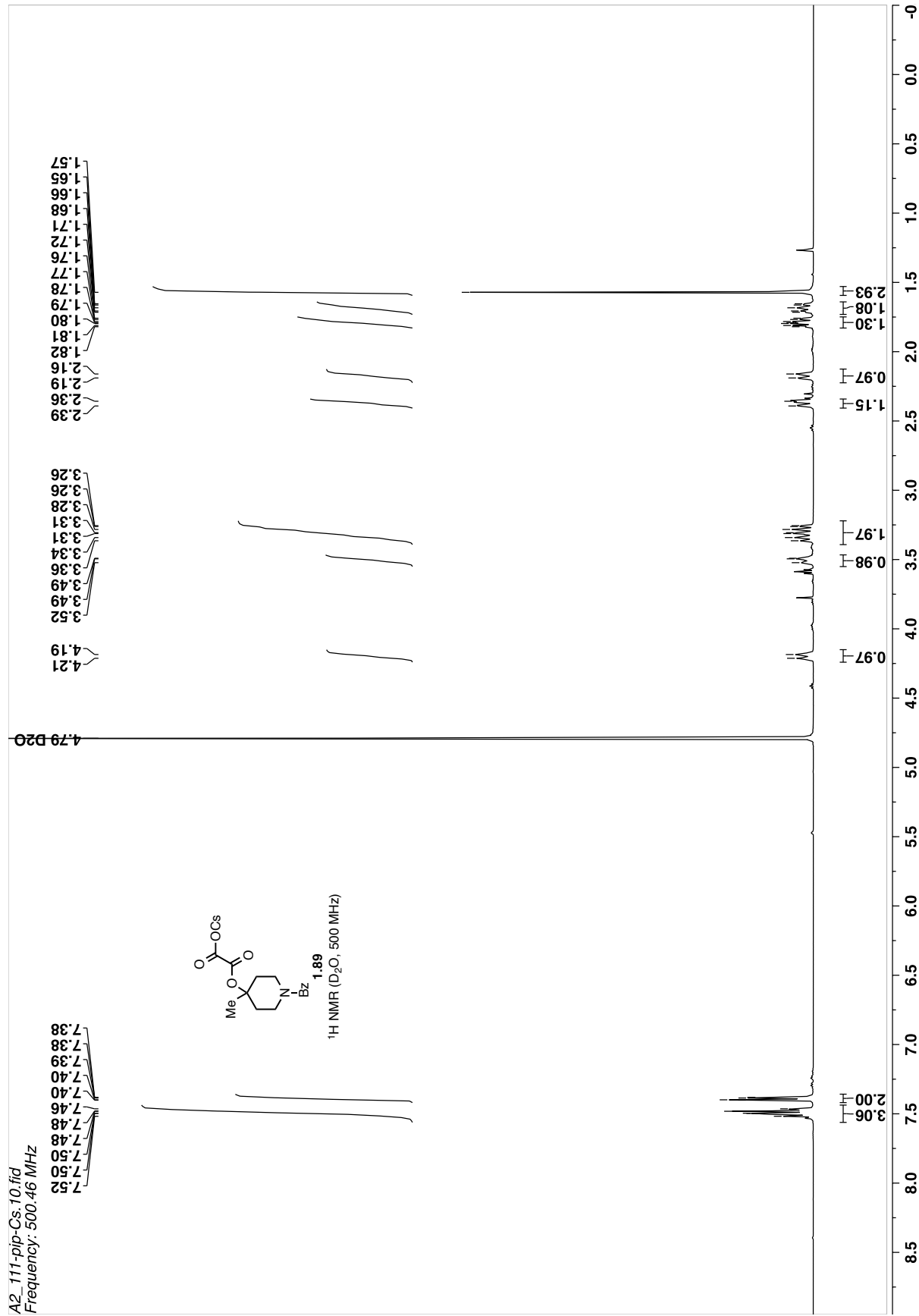




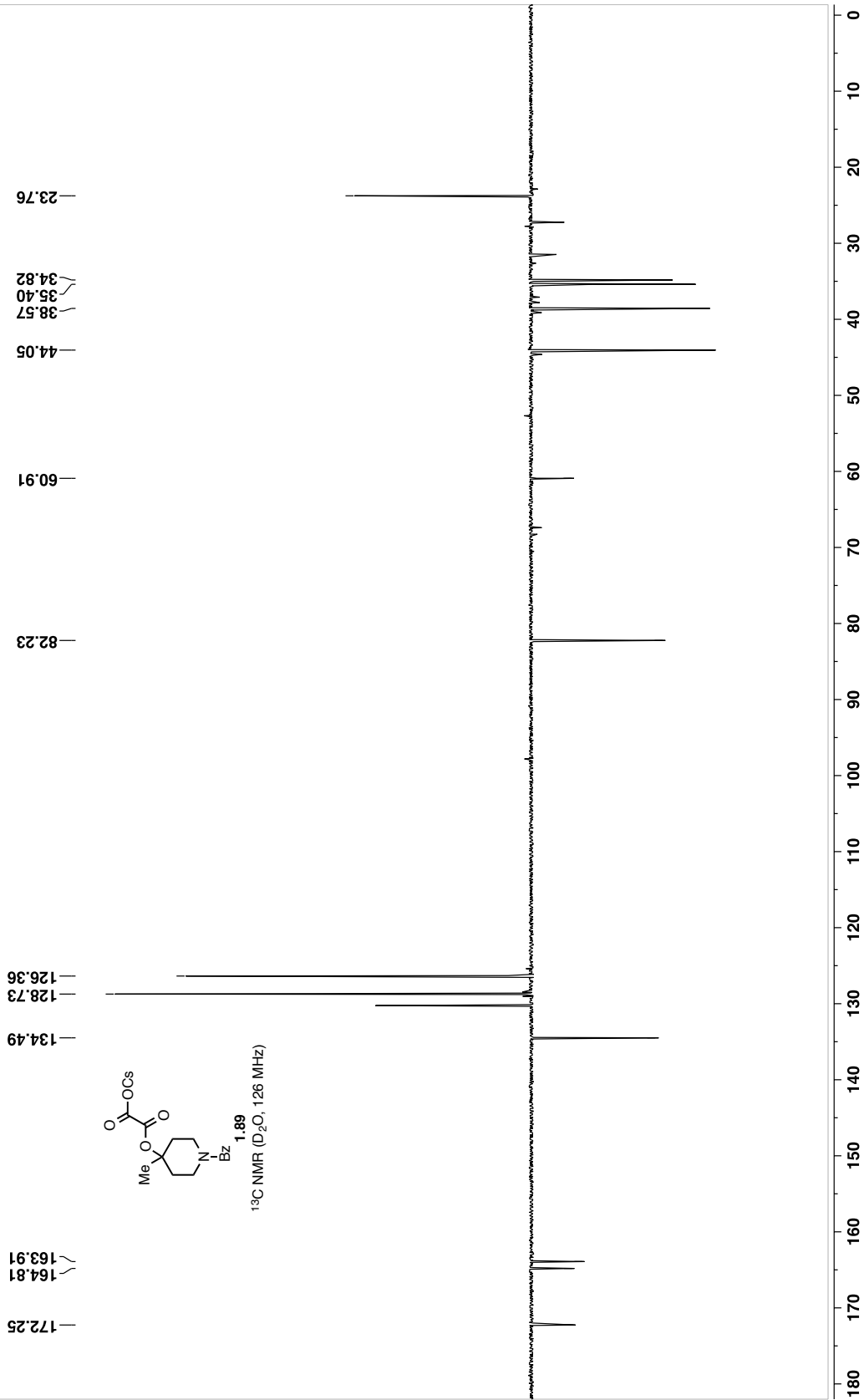


A2_74-can-s5-036-a.11.fid
Frequency: 125.85 MHz



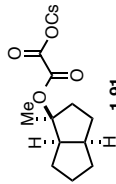


A2_111-pip-Cs.11.fid
Frequency: 125.85 MHz

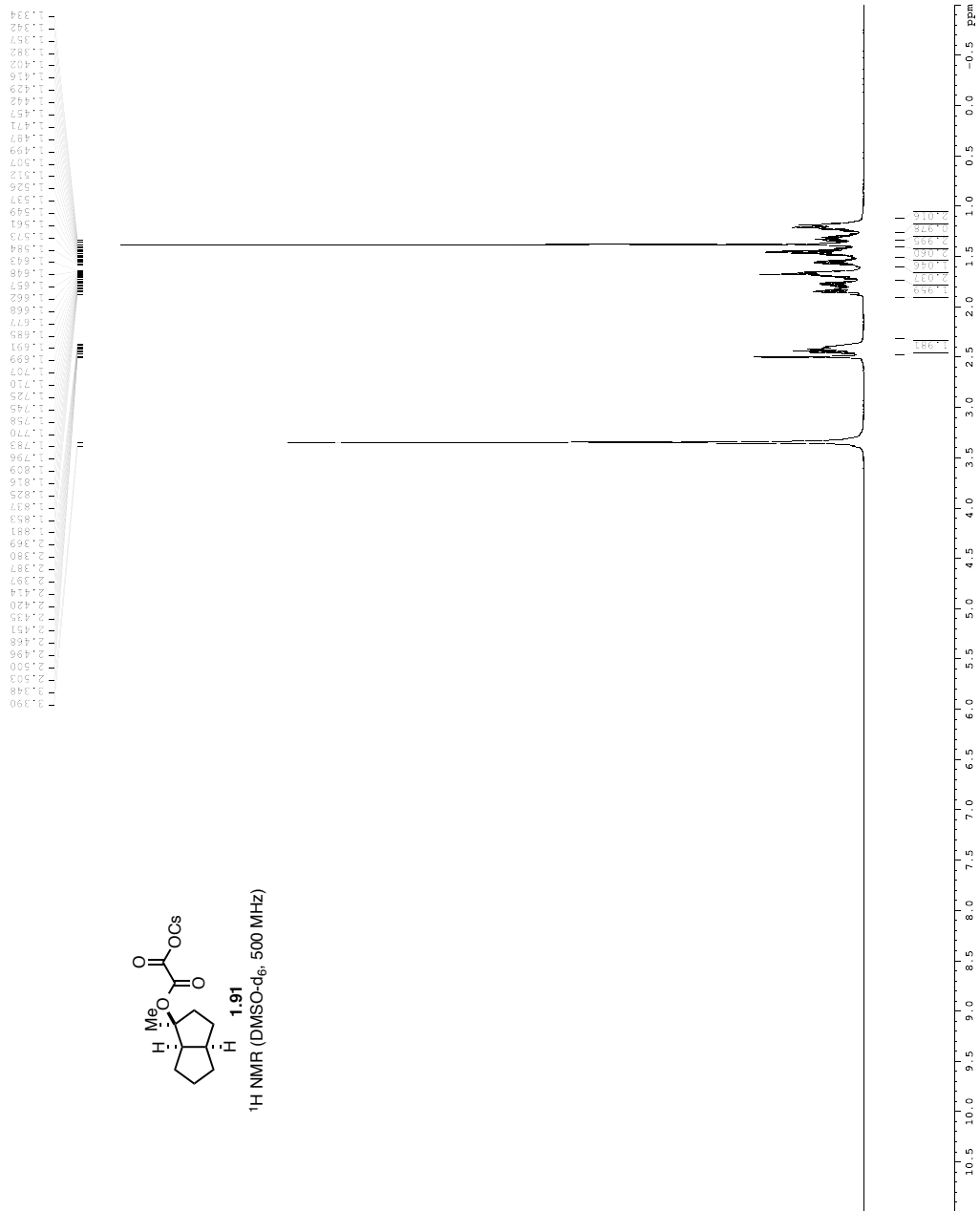


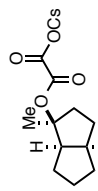
YS-II-288

Current Data Parameters
NAME YS-II-288
PROCNO 1
=====
F2 - Acquisition Parameters
Date_ 01/30/06
Time 18:00
INSTRUM spect
PROBHD 5 mm broadband
PULPROG zgpg30
SOLVENT DMSO
NS 8
DS 2
SS 8012.820 Hz
FIDRES 0.1500026 Hz
AQ 1.9397952 sec
RG 62.400 usec
DE 6.00 usec
TE 300.2 K
MRESPT 0 sec
MORPH 0.01500000 sec
===== CHANNEL F1 =====
NUC1 13C
PULP 8
PUL 12.00 usec
PL1 -5.80 dB
SFO1 499.183491 MHz
===== CHANNEL F2 =====
SI 05536
SF 499.183491 MHz
RG 62.400 usec
DE 6.00 usec
TE 300.2 K
MRESPT 0 sec
MORPH 0.01500000 sec



¹H NMR (DMSO-d₆, 500 MHz)



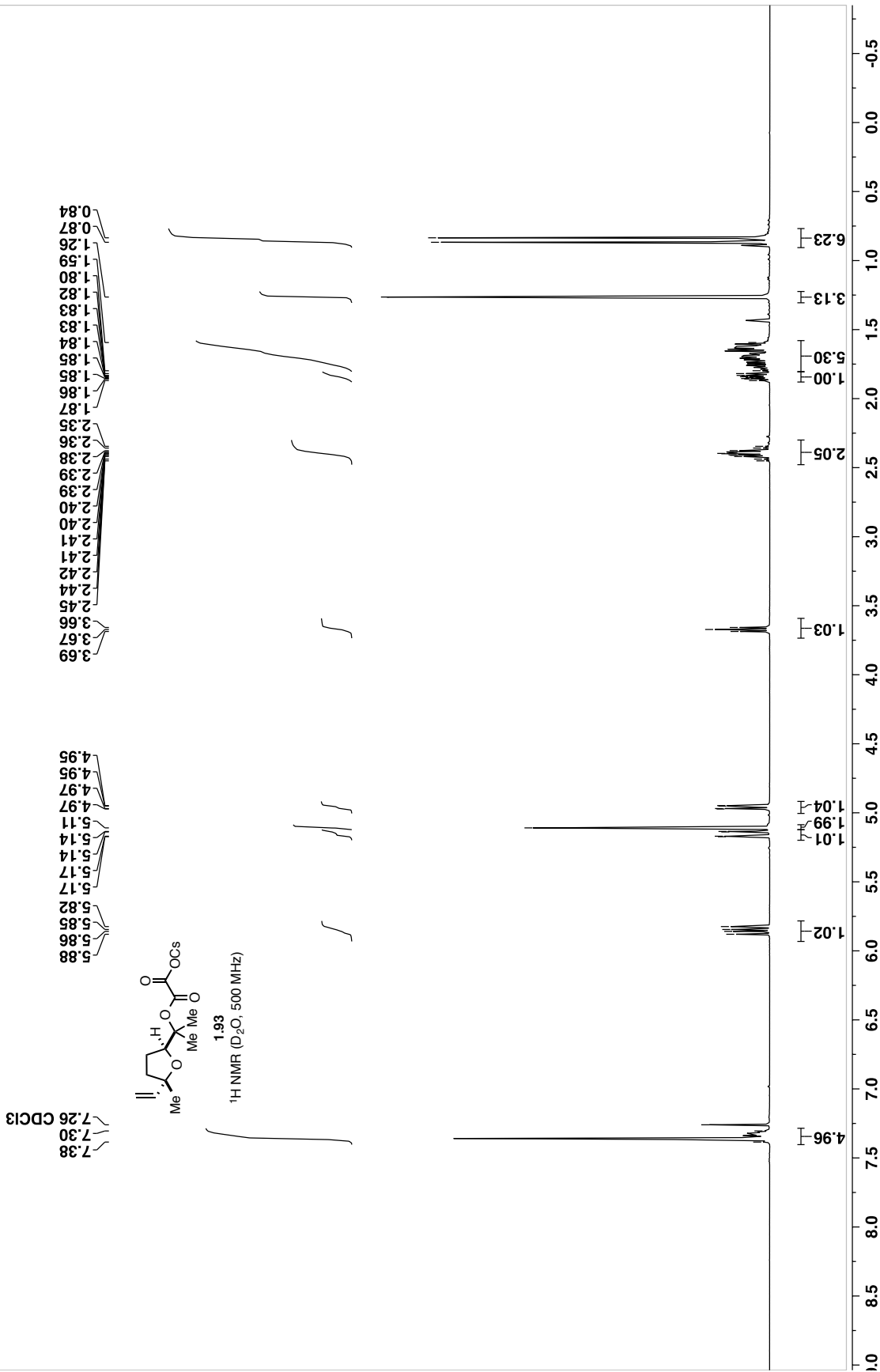


1.91
¹³C NMR (DMSO-d₆, 126 MHz)

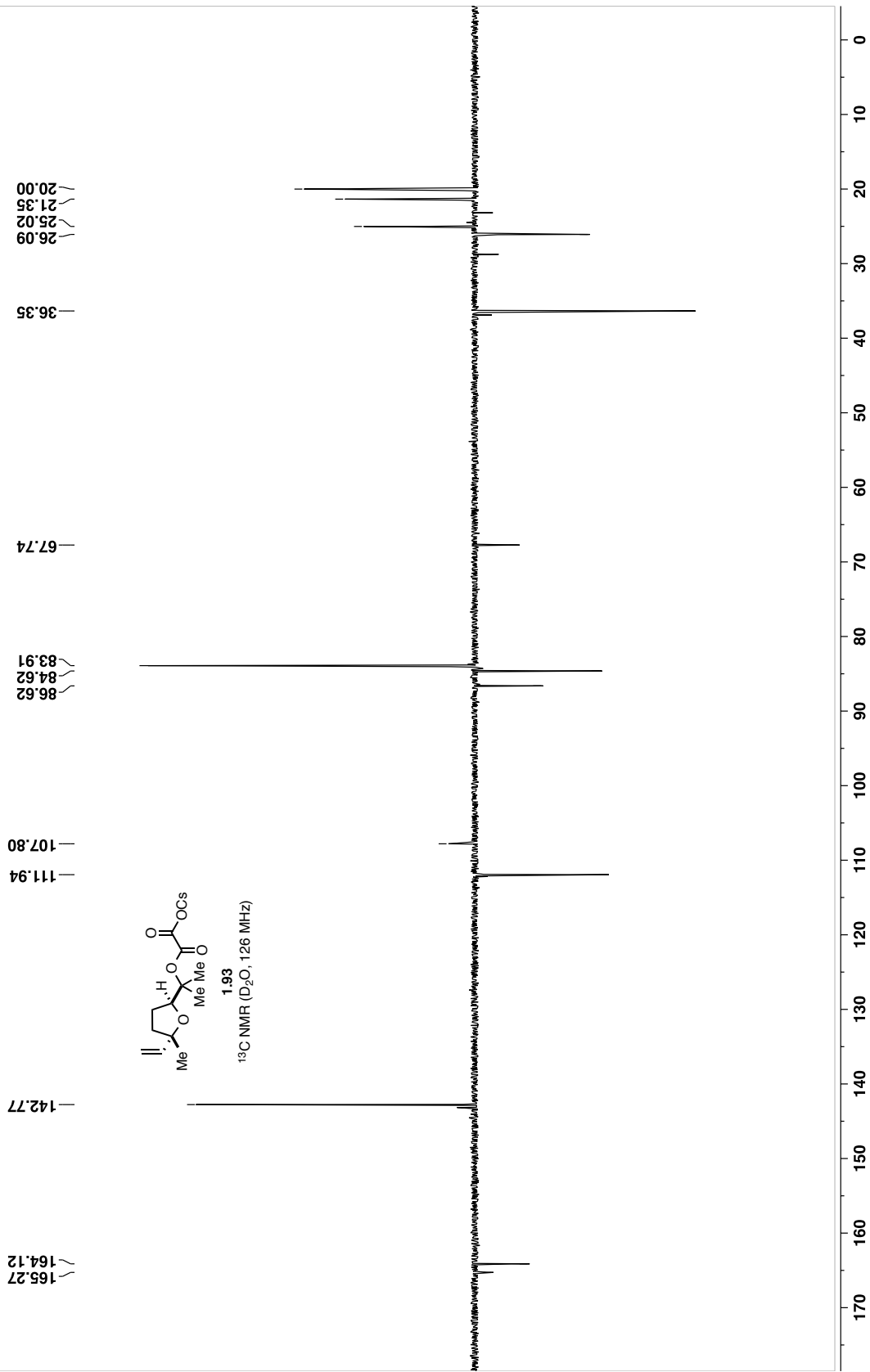
```

Current Data Parameters
=====
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
=====
Date_      20110905
Time       10:56
INSTRUM    cryo500
PROBHD     5 mm CPCC1H1
PULPROG    zgpg30
TD          65536
SOLVENT    DMSO
NS          248
DS          4
SWH         30300.071 Hz
FIDRES     0.462388 Hz
AQ          1.081345 sec
RG          182.500 ussec
DE          6.00 ussec
TE          298.2 K
AQ          0.000000 sec
SFO1       125.7942548 MHz
SF          500.1362996 MHz
SFO2        500.1362996 MHz
SFO3        500.1362996 MHz
SFO4        500.1362996 MHz
SFO5        500.1362996 MHz
SFO6        500.1362996 MHz
SFO7        500.1362996 MHz
SFO8        500.1362996 MHz
SFO9        500.1362996 MHz
SFO10       500.1362996 MHz
SFO11       500.1362996 MHz
SFO12       500.1362996 MHz
SFO13       500.1362996 MHz
SFO14       500.1362996 MHz
SFO15       500.1362996 MHz
SFO16       500.1362996 MHz
SFO17       500.1362996 MHz
SFO18       500.1362996 MHz
SFO19       500.1362996 MHz
SFO20       500.1362996 MHz
SFO21       500.1362996 MHz
SFO22       500.1362996 MHz
SFO23       500.1362996 MHz
SFO24       500.1362996 MHz
SFO25       500.1362996 MHz
SFO26       500.1362996 MHz
SFO27       500.1362996 MHz
SFO28       500.1362996 MHz
SFO29       500.1362996 MHz
SFO30       500.1362996 MHz
SFO31       500.1362996 MHz
SFO32       500.1362996 MHz
SFO33       500.1362996 MHz
SFO34       500.1362996 MHz
SFO35       500.1362996 MHz
SFO36       500.1362996 MHz
SFO37       500.1362996 MHz
SFO38       500.1362996 MHz
SFO39       500.1362996 MHz
SFO40       500.1362996 MHz
SFO41       500.1362996 MHz
SFO42       500.1362996 MHz
SFO43       500.1362996 MHz
SFO44       500.1362996 MHz
SFO45       500.1362996 MHz
SFO46       500.1362996 MHz
SFO47       500.1362996 MHz
SFO48       500.1362996 MHz
SFO49       500.1362996 MHz
SFO50       500.1362996 MHz
=====
Channel f1 126 MHz
=====
NUC1       13C
P1         16.55 ussec
PL1        0.00 dB
PL2        0.00 dB
PL3        0.00 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
PL7        0.00 dB
PL8        0.00 dB
PL9        0.00 dB
PL10       0.00 dB
PL11       0.00 dB
PL12       0.00 dB
PL13       0.00 dB
PL14       0.00 dB
PL15       0.00 dB
PL16       0.00 dB
PL17       0.00 dB
PL18       0.00 dB
PL19       0.00 dB
PL20       0.00 dB
PL21       0.00 dB
PL22       0.00 dB
PL23       0.00 dB
PL24       0.00 dB
PL25       0.00 dB
PL26       0.00 dB
PL27       0.00 dB
PL28       0.00 dB
PL29       0.00 dB
PL30       0.00 dB
PL31       0.00 dB
PL32       0.00 dB
PL33       0.00 dB
PL34       0.00 dB
PL35       0.00 dB
PL36       0.00 dB
PL37       0.00 dB
PL38       0.00 dB
PL39       0.00 dB
PL40       0.00 dB
PL41       0.00 dB
PL42       0.00 dB
PL43       0.00 dB
PL44       0.00 dB
PL45       0.00 dB
PL46       0.00 dB
PL47       0.00 dB
PL48       0.00 dB
PL49       0.00 dB
PL50       0.00 dB
=====
Channel f2 500 MHz
=====
CPDPRG2    waltz16
NUC2       1H
P2         100.00 ussec
PL2        0.00 dB
PL3        0.00 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
PL7        0.00 dB
PL8        0.00 dB
PL9        0.00 dB
PL10       0.00 dB
PL11       0.00 dB
PL12       0.00 dB
PL13       0.00 dB
PL14       0.00 dB
PL15       0.00 dB
PL16       0.00 dB
PL17       0.00 dB
PL18       0.00 dB
PL19       0.00 dB
PL20       0.00 dB
PL21       0.00 dB
PL22       0.00 dB
PL23       0.00 dB
PL24       0.00 dB
PL25       0.00 dB
PL26       0.00 dB
PL27       0.00 dB
PL28       0.00 dB
PL29       0.00 dB
PL30       0.00 dB
PL31       0.00 dB
PL32       0.00 dB
PL33       0.00 dB
PL34       0.00 dB
PL35       0.00 dB
PL36       0.00 dB
PL37       0.00 dB
PL38       0.00 dB
PL39       0.00 dB
PL40       0.00 dB
PL41       0.00 dB
PL42       0.00 dB
PL43       0.00 dB
PL44       0.00 dB
PL45       0.00 dB
PL46       0.00 dB
PL47       0.00 dB
PL48       0.00 dB
PL49       0.00 dB
PL50       0.00 dB
=====
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GPA1       0.00 %
GPA2       0.00 %
GPA3       0.00 %
GPA4       0.00 %
GPA5       0.00 %
GPA6       0.00 %
GPA7       0.00 %
GPA8       0.00 %
GPA9       0.00 %
GPA10      0.00 %
GPA11      0.00 %
GPA12      0.00 %
GPA13      0.00 %
GPA14      0.00 %
GPA15      0.00 %
GPA16      0.00 %
GPA17      0.00 %
GPA18      0.00 %
GPA19      0.00 %
GPA20      0.00 %
GPA21      0.00 %
GPA22      0.00 %
GPA23      0.00 %
GPA24      0.00 %
GPA25      0.00 %
GPA26      0.00 %
GPA27      0.00 %
GPA28      0.00 %
GPA29      0.00 %
GPA30      0.00 %
GPA31      0.00 %
GPA32      0.00 %
GPA33      0.00 %
GPA34      0.00 %
GPA35      0.00 %
GPA36      0.00 %
GPA37      0.00 %
GPA38      0.00 %
GPA39      0.00 %
GPA40      0.00 %
GPA41      0.00 %
GPA42      0.00 %
GPA43      0.00 %
GPA44      0.00 %
GPA45      0.00 %
GPA46      0.00 %
GPA47      0.00 %
GPA48      0.00 %
GPA49      0.00 %
GPA50      0.00 %
=====
===== Processing parameters =====
SI          32768
SF          500.1362996 MHz
WDW         EM
SSB         0
LB          0
GB          0
PC          2.00
    
```

A2_65-ccn-s5-121-2-a.10.fid
Frequency: 500.46 MHz

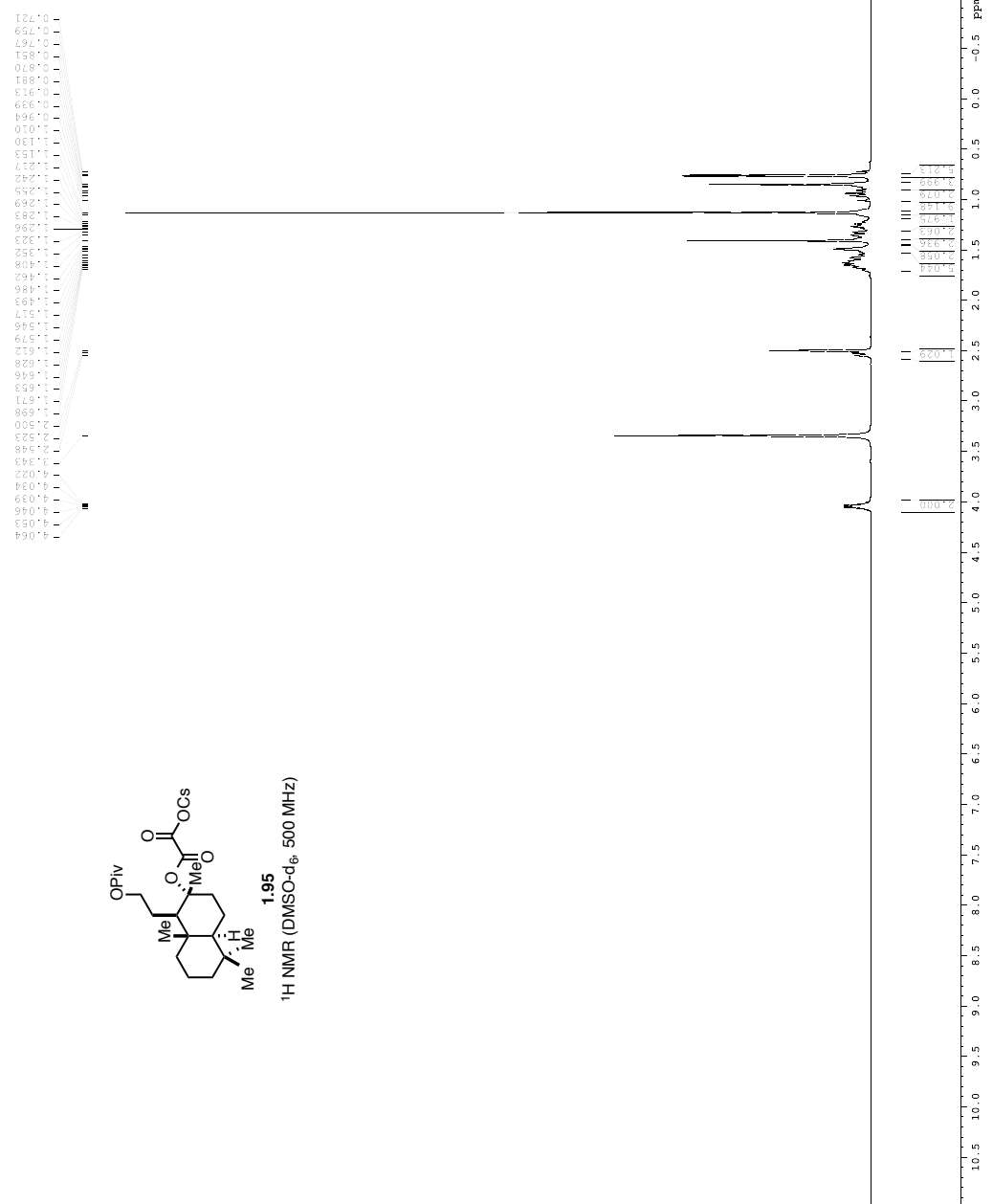


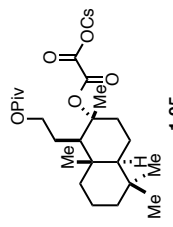
A2_71-con-s5-111-2_11.fid
Frequency: 125.85 MHz



XS-II-268

Current Data Parameters
NAME XS-II-268
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160225
Time 5.44
INSTRUM spect
PROBHD 5 mm CUI31 1H-
PULPROG zgpg30
SOLVENT DMSO
NS 8
DS 8
AQ 0.250026 Hz
FIDRES 1.997792 sec
SFO1 500.225015 MHz
DQ 62.400 usac
DE 6.00 usac
DI 0.1000000 sec
MORST 0 sec
RCORR 0.0150000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.10 usac
PL1 1.60 dBc
SFO1 500.225015 MHz
F2 - Processing parameters
SI 65536
SF 500.225015 MHz
WDW EM
SSB 0
CB 0
GB 0
PC 4.00



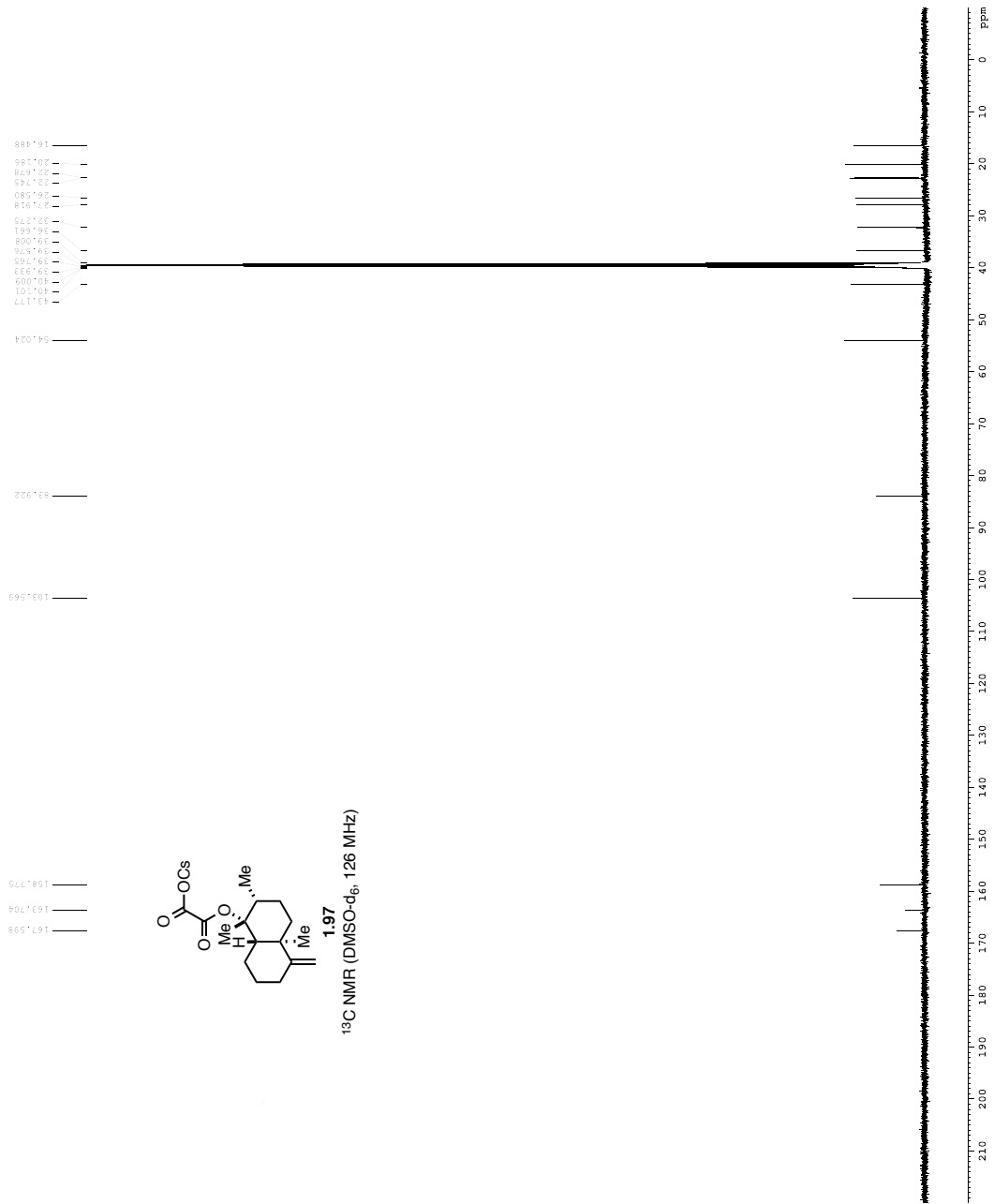


1.95
¹³C NMR (DMSO-d₆, 126 MHz)

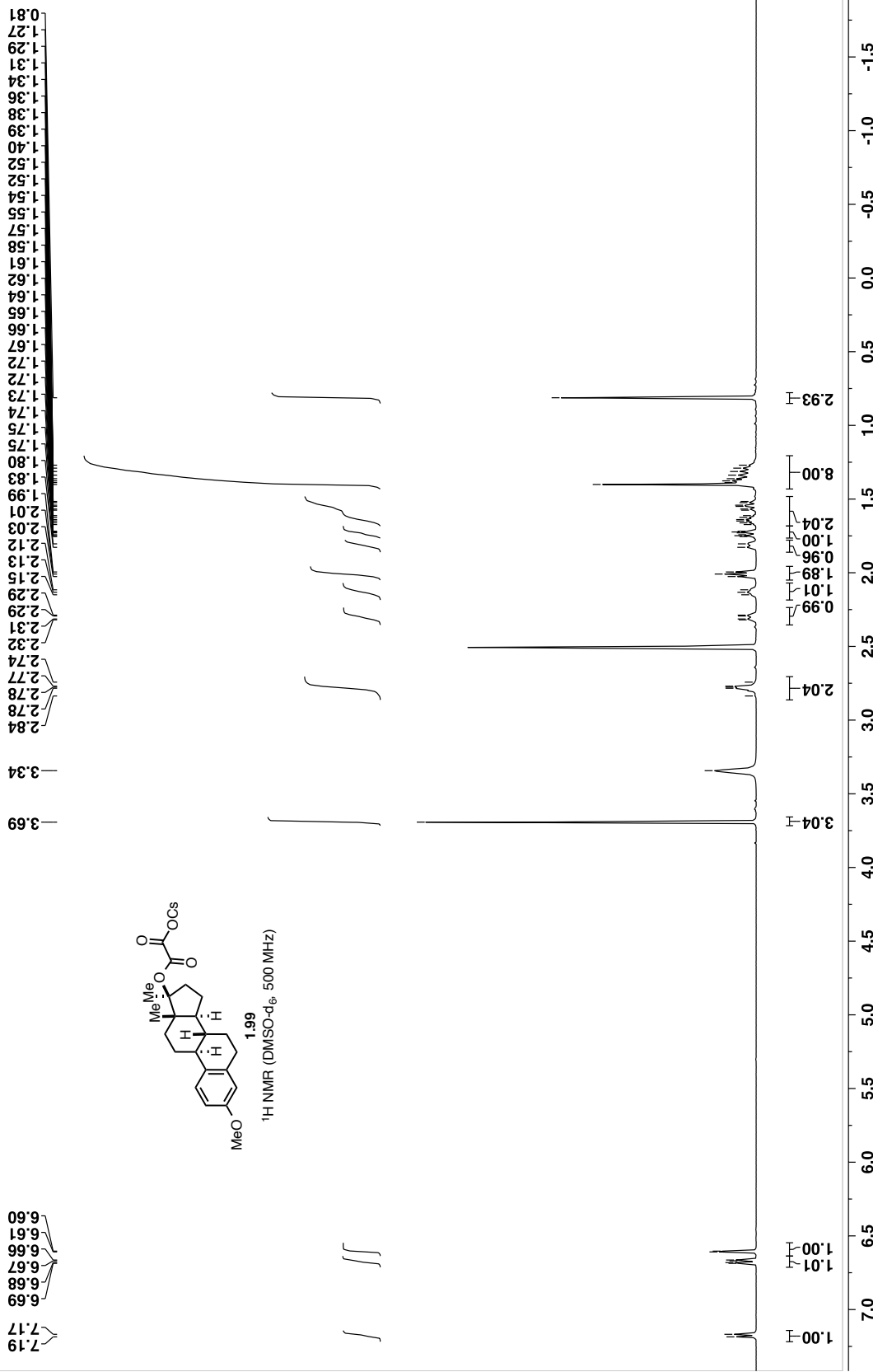
```

Current Data Parameters
=====
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
=====
Date_      20110727
Time       9.46
INSTRUM    cryo500
PROBHD     5 mm CPYX 1H-
PULPROG    zgpg30
TD          65536
SOLVENT    DMSO
NS          312
DS          4
SWH         30300.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813450 sec
RG          16.500
WDW         EM
SSB         0
GB          0.000000 sec
DE         6.00 usec
TE         300.2 K
AQ         0.0629600 sec
SI          32768
SF          500.1362600 MHz
D16        0.0002000 sec
d17        0.0002000 sec
d18        0.0002000 sec
d19        0.0002000 sec
d20        0.0002000 sec
d21        0.0002000 sec
d22        0.0002000 sec
d23        0.0002000 sec
d24        0.0002000 sec
d25        0.0002000 sec
d26        0.0002000 sec
d27        0.0002000 sec
d28        0.0002000 sec
d29        0.0002000 sec
d30        0.0002000 sec
d31        0.0002000 sec
d32        0.0002000 sec
d33        0.0002000 sec
d34        0.0002000 sec
d35        0.0002000 sec
d36        0.0002000 sec
d37        0.0002000 sec
d38        0.0002000 sec
d39        0.0002000 sec
d40        0.0002000 sec
d41        0.0002000 sec
d42        0.0002000 sec
d43        0.0002000 sec
d44        0.0002000 sec
d45        0.0002000 sec
d46        0.0002000 sec
d47        0.0002000 sec
d48        0.0002000 sec
d49        0.0002000 sec
d50        0.0002000 sec
d51        0.0002000 sec
d52        0.0002000 sec
d53        0.0002000 sec
d54        0.0002000 sec
d55        0.0002000 sec
d56        0.0002000 sec
d57        0.0002000 sec
d58        0.0002000 sec
d59        0.0002000 sec
d60        0.0002000 sec
d61        0.0002000 sec
d62        0.0002000 sec
d63        0.0002000 sec
d64        0.0002000 sec
d65        0.0002000 sec
d66        0.0002000 sec
d67        0.0002000 sec
d68        0.0002000 sec
d69        0.0002000 sec
d70        0.0002000 sec
d71        0.0002000 sec
d72        0.0002000 sec
d73        0.0002000 sec
d74        0.0002000 sec
d75        0.0002000 sec
d76        0.0002000 sec
d77        0.0002000 sec
d78        0.0002000 sec
d79        0.0002000 sec
d80        0.0002000 sec
d81        0.0002000 sec
d82        0.0002000 sec
d83        0.0002000 sec
d84        0.0002000 sec
d85        0.0002000 sec
d86        0.0002000 sec
d87        0.0002000 sec
d88        0.0002000 sec
d89        0.0002000 sec
d90        0.0002000 sec
d91        0.0002000 sec
d92        0.0002000 sec
d93        0.0002000 sec
d94        0.0002000 sec
d95        0.0002000 sec
d96        0.0002000 sec
d97        0.0002000 sec
d98        0.0002000 sec
d99        0.0002000 sec
d100       0.0002000 sec
=====
CHANNEL f1
NUC1       13C
P1         16.55 usec
PL1        0.00 dB
PL2        0.00 dB
PL3        0.00 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
PL7        0.00 dB
PL8        0.00 dB
PL9        0.00 dB
PL10       0.00 dB
PL11       0.00 dB
PL12       0.00 dB
PL13       0.00 dB
PL14       0.00 dB
PL15       0.00 dB
PL16       0.00 dB
PL17       0.00 dB
PL18       0.00 dB
PL19       0.00 dB
PL20       0.00 dB
PL21       0.00 dB
PL22       0.00 dB
PL23       0.00 dB
PL24       0.00 dB
PL25       0.00 dB
PL26       0.00 dB
PL27       0.00 dB
PL28       0.00 dB
PL29       0.00 dB
PL30       0.00 dB
PL31       0.00 dB
PL32       0.00 dB
PL33       0.00 dB
PL34       0.00 dB
PL35       0.00 dB
PL36       0.00 dB
PL37       0.00 dB
PL38       0.00 dB
PL39       0.00 dB
PL40       0.00 dB
PL41       0.00 dB
PL42       0.00 dB
PL43       0.00 dB
PL44       0.00 dB
PL45       0.00 dB
PL46       0.00 dB
PL47       0.00 dB
PL48       0.00 dB
PL49       0.00 dB
PL50       0.00 dB
PL51       0.00 dB
PL52       0.00 dB
PL53       0.00 dB
PL54       0.00 dB
PL55       0.00 dB
PL56       0.00 dB
PL57       0.00 dB
PL58       0.00 dB
PL59       0.00 dB
PL60       0.00 dB
PL61       0.00 dB
PL62       0.00 dB
PL63       0.00 dB
PL64       0.00 dB
PL65       0.00 dB
PL66       0.00 dB
PL67       0.00 dB
PL68       0.00 dB
PL69       0.00 dB
PL70       0.00 dB
PL71       0.00 dB
PL72       0.00 dB
PL73       0.00 dB
PL74       0.00 dB
PL75       0.00 dB
PL76       0.00 dB
PL77       0.00 dB
PL78       0.00 dB
PL79       0.00 dB
PL80       0.00 dB
PL81       0.00 dB
PL82       0.00 dB
PL83       0.00 dB
PL84       0.00 dB
PL85       0.00 dB
PL86       0.00 dB
PL87       0.00 dB
PL88       0.00 dB
PL89       0.00 dB
PL90       0.00 dB
PL91       0.00 dB
PL92       0.00 dB
PL93       0.00 dB
PL94       0.00 dB
PL95       0.00 dB
PL96       0.00 dB
PL97       0.00 dB
PL98       0.00 dB
PL99       0.00 dB
PL100      0.00 dB
=====
CHANNEL f2
CPDPRG2    waltz16
NUC2       1H
P2         100.00 usec
PL2        0.00 dB
PL3        0.00 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
PL7        0.00 dB
PL8        0.00 dB
PL9        0.00 dB
PL10       0.00 dB
PL11       0.00 dB
PL12       0.00 dB
PL13       0.00 dB
PL14       0.00 dB
PL15       0.00 dB
PL16       0.00 dB
PL17       0.00 dB
PL18       0.00 dB
PL19       0.00 dB
PL20       0.00 dB
PL21       0.00 dB
PL22       0.00 dB
PL23       0.00 dB
PL24       0.00 dB
PL25       0.00 dB
PL26       0.00 dB
PL27       0.00 dB
PL28       0.00 dB
PL29       0.00 dB
PL30       0.00 dB
PL31       0.00 dB
PL32       0.00 dB
PL33       0.00 dB
PL34       0.00 dB
PL35       0.00 dB
PL36       0.00 dB
PL37       0.00 dB
PL38       0.00 dB
PL39       0.00 dB
PL40       0.00 dB
PL41       0.00 dB
PL42       0.00 dB
PL43       0.00 dB
PL44       0.00 dB
PL45       0.00 dB
PL46       0.00 dB
PL47       0.00 dB
PL48       0.00 dB
PL49       0.00 dB
PL50       0.00 dB
PL51       0.00 dB
PL52       0.00 dB
PL53       0.00 dB
PL54       0.00 dB
PL55       0.00 dB
PL56       0.00 dB
PL57       0.00 dB
PL58       0.00 dB
PL59       0.00 dB
PL60       0.00 dB
PL61       0.00 dB
PL62       0.00 dB
PL63       0.00 dB
PL64       0.00 dB
PL65       0.00 dB
PL66       0.00 dB
PL67       0.00 dB
PL68       0.00 dB
PL69       0.00 dB
PL70       0.00 dB
PL71       0.00 dB
PL72       0.00 dB
PL73       0.00 dB
PL74       0.00 dB
PL75       0.00 dB
PL76       0.00 dB
PL77       0.00 dB
PL78       0.00 dB
PL79       0.00 dB
PL80       0.00 dB
PL81       0.00 dB
PL82       0.00 dB
PL83       0.00 dB
PL84       0.00 dB
PL85       0.00 dB
PL86       0.00 dB
PL87       0.00 dB
PL88       0.00 dB
PL89       0.00 dB
PL90       0.00 dB
PL91       0.00 dB
PL92       0.00 dB
PL93       0.00 dB
PL94       0.00 dB
PL95       0.00 dB
PL96       0.00 dB
PL97       0.00 dB
PL98       0.00 dB
PL99       0.00 dB
PL100      0.00 dB
=====
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GPA[1]     0 %
GPA[2]     0 %
GPA[3]     0 %
GPA[4]     0 %
GPA[5]     0 %
GPA[6]     0 %
GPA[7]     0 %
GPA[8]     0 %
GPA[9]     0 %
GPA[10]    0 %
GPA[11]    0 %
GPA[12]    0 %
GPA[13]    0 %
GPA[14]    0 %
GPA[15]    0 %
GPA[16]    0 %
GPA[17]    0 %
GPA[18]    0 %
GPA[19]    0 %
GPA[20]    0 %
GPA[21]    0 %
GPA[22]    0 %
GPA[23]    0 %
GPA[24]    0 %
GPA[25]    0 %
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GPA[91]    0 %
GPA[92]    0 %
GPA[93]    0 %
GPA[94]    0 %
GPA[95]    0 %
GPA[96]    0 %
GPA[97]    0 %
GPA[98]    0 %
GPA[99]    0 %
GPA[100]   0 %
=====
F2 - Processing parameters
SI          32768
SF          500.1362600 MHz
WDW         EM
SSB         0
GB          0
PC          2.00
=====

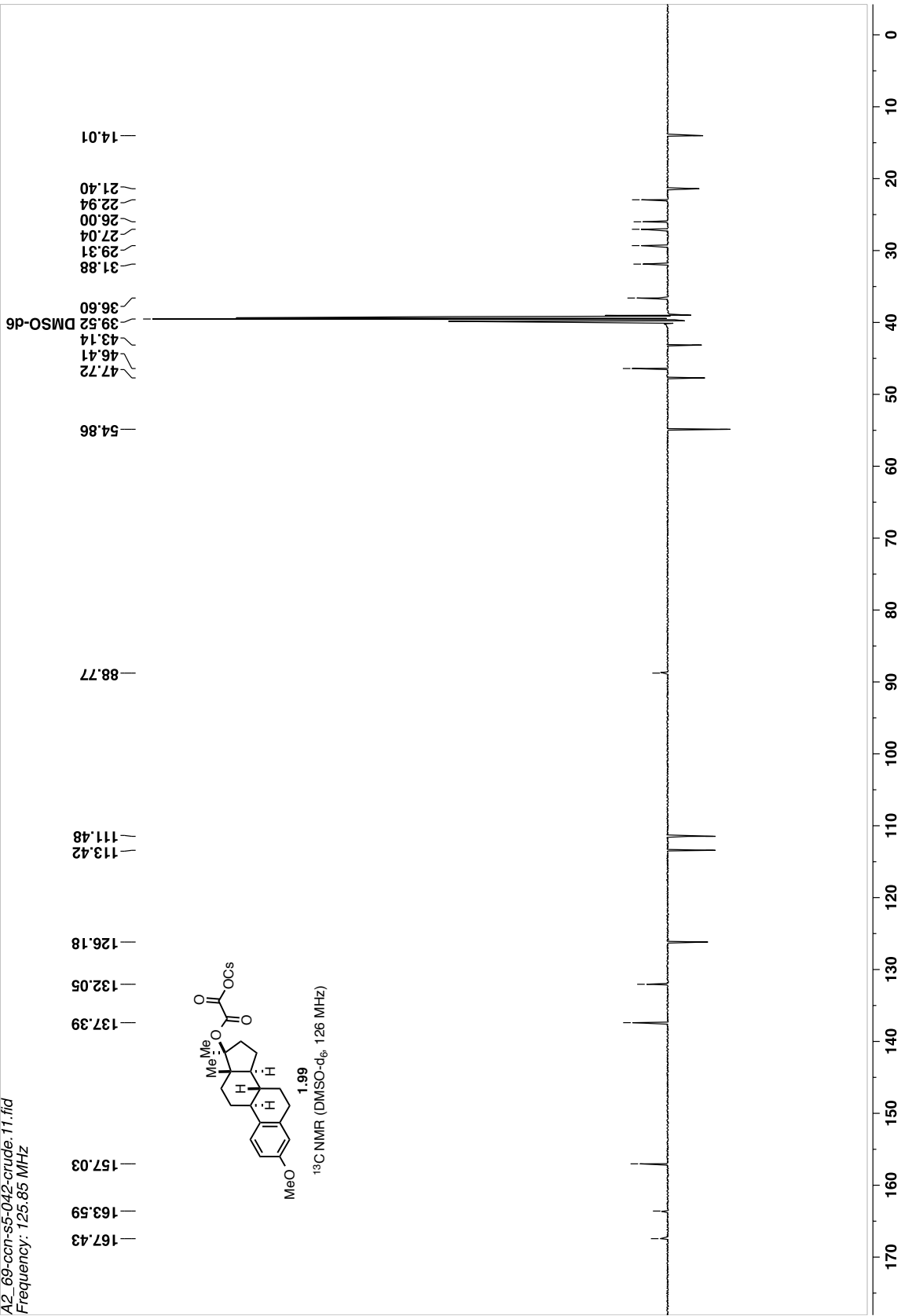
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A2_69-con-s5-042-crude.10.fid
Frequency: 500.46 MHz



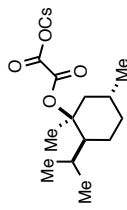
A2_69-con-s5-042-crude.11.fid
Frequency: 125.85 MHz



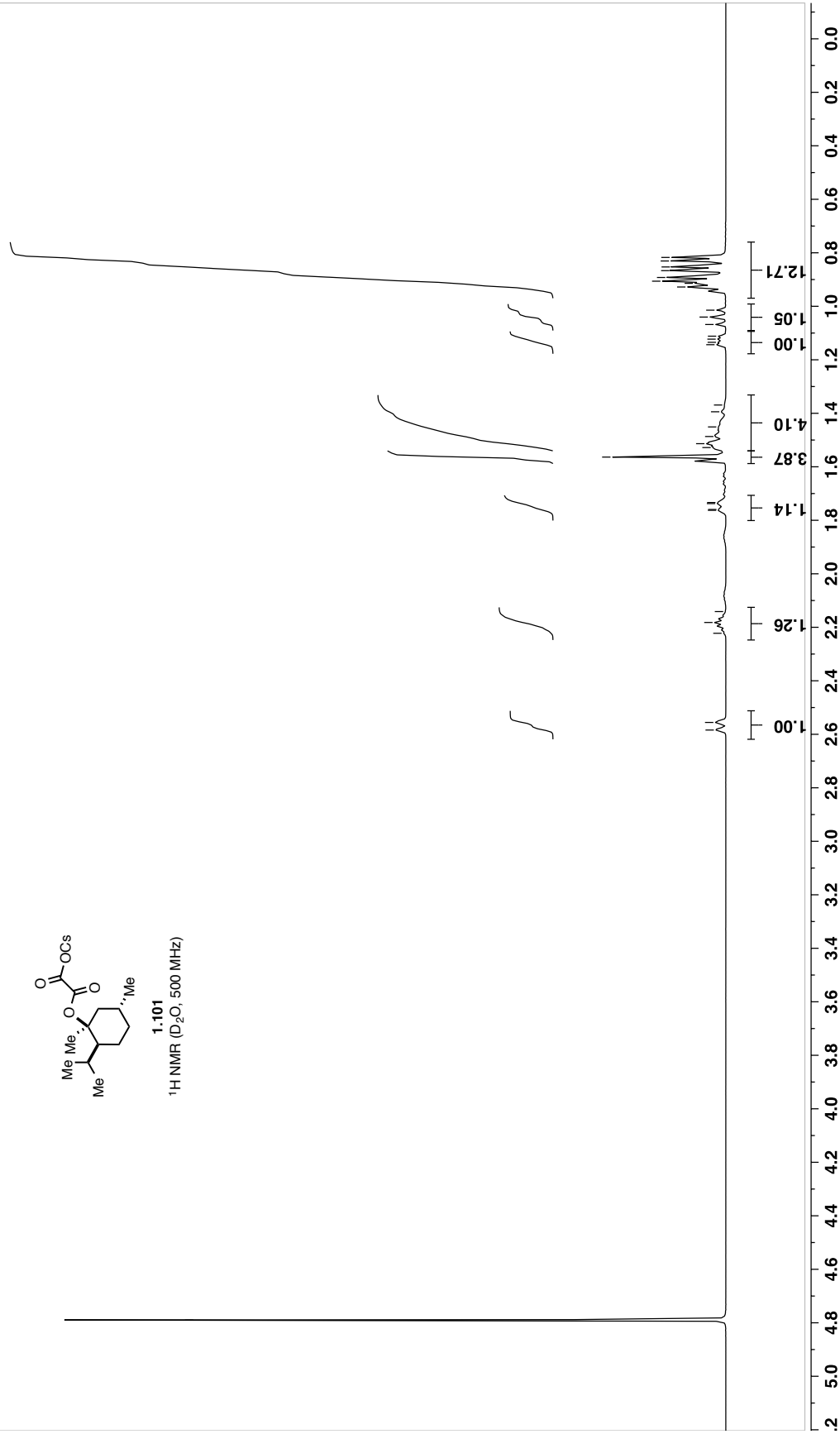
A2_74-ccn-s5-073-2-a.10.fid
Frequency: 500.46 MHz

4.79 D2O

2.58
2.22
2.18
2.14
1.76
1.76
1.74
1.73
1.56
1.53
1.51
1.49
1.45
1.39
1.37
1.14
1.13
1.12
1.11
1.07
1.04
1.01
0.93
0.91
0.89
0.87
0.85
0.83
0.82



1:101
¹H NMR (D₂O, 500 MHz)

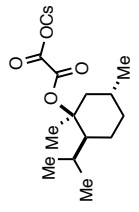


A2_74-ccn-s5-073-2-a.11.fid
Frequency: 125.85 MHz

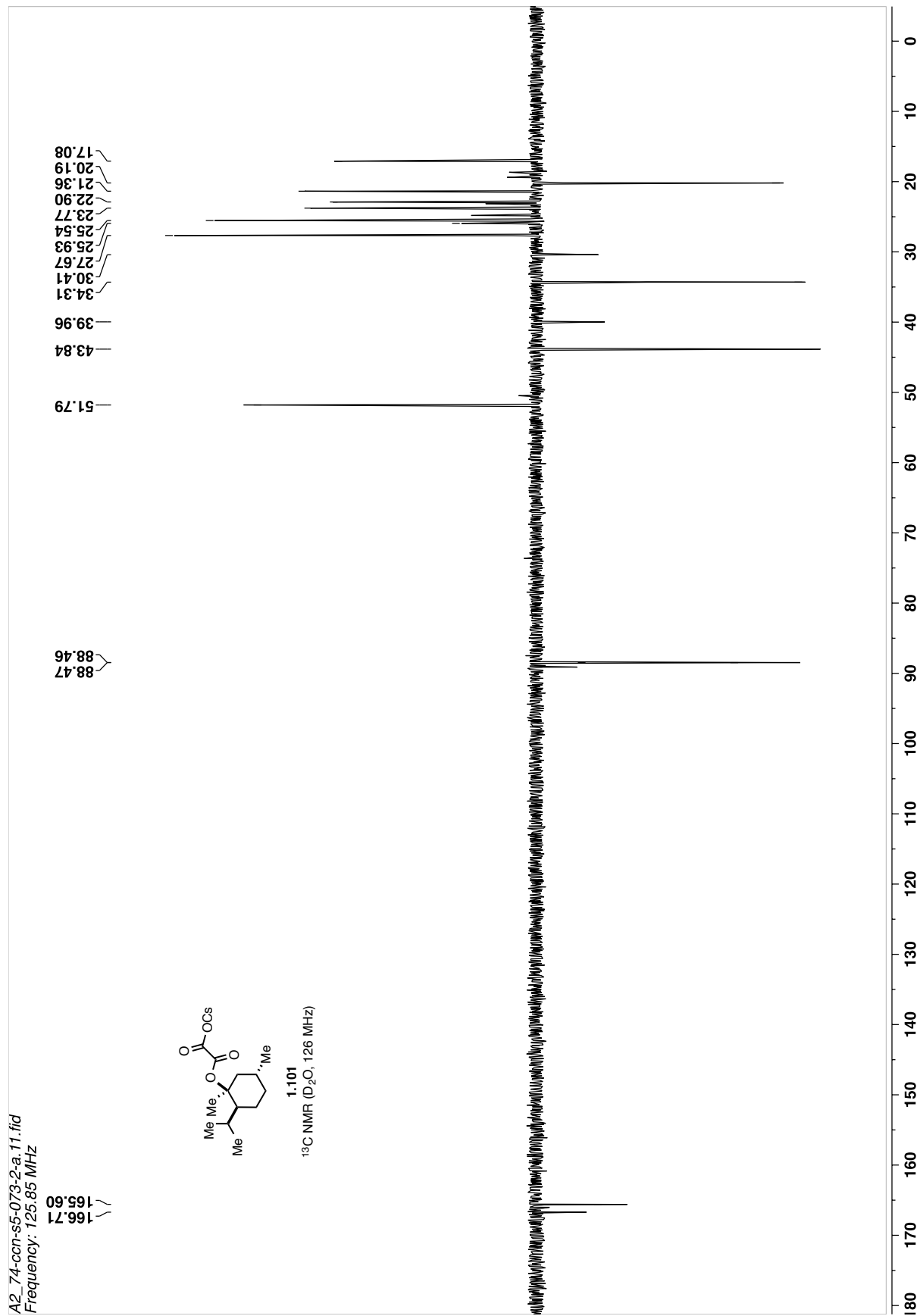
166.71
165.60

88.47
88.46

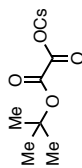
51.79
43.84
39.96
34.31
30.41
27.67
25.93
25.54
23.77
22.90
21.36
20.19
17.08



1:101
¹³C NMR (D₂O, 126 MHz)



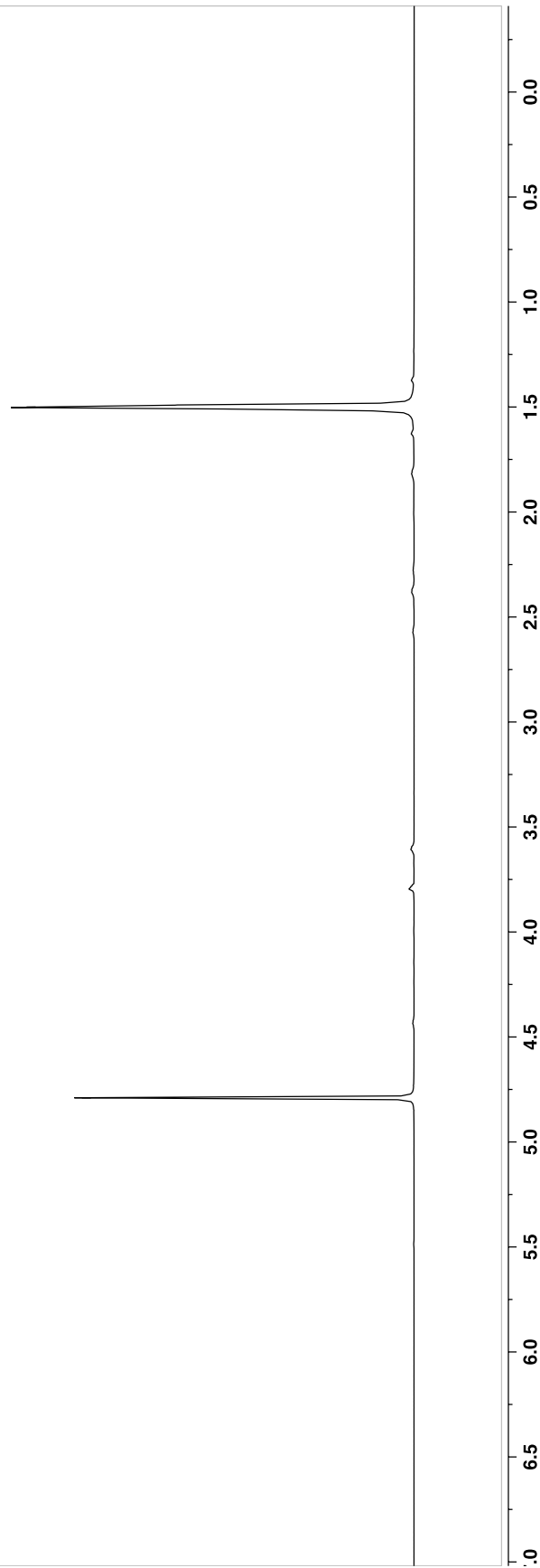
A2_104-t-Bu-Cs-Ox_10.tif
Frequency: 500.46 MHz



1:103
¹H NMR (D₂O, 500 MHz)

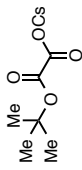
4.79 D2O

1.50



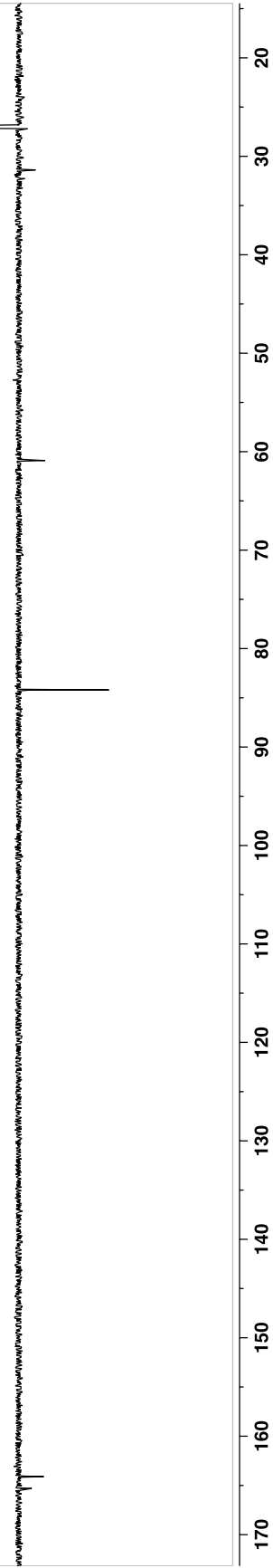
A2_104-t-Bu-Cs-Ox_11.fid
Frequency: 125.85 MHz

165.31
164.10

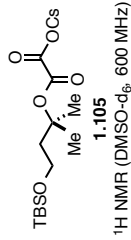


1.103
¹³C NMR (D₂O, 126 MHz)

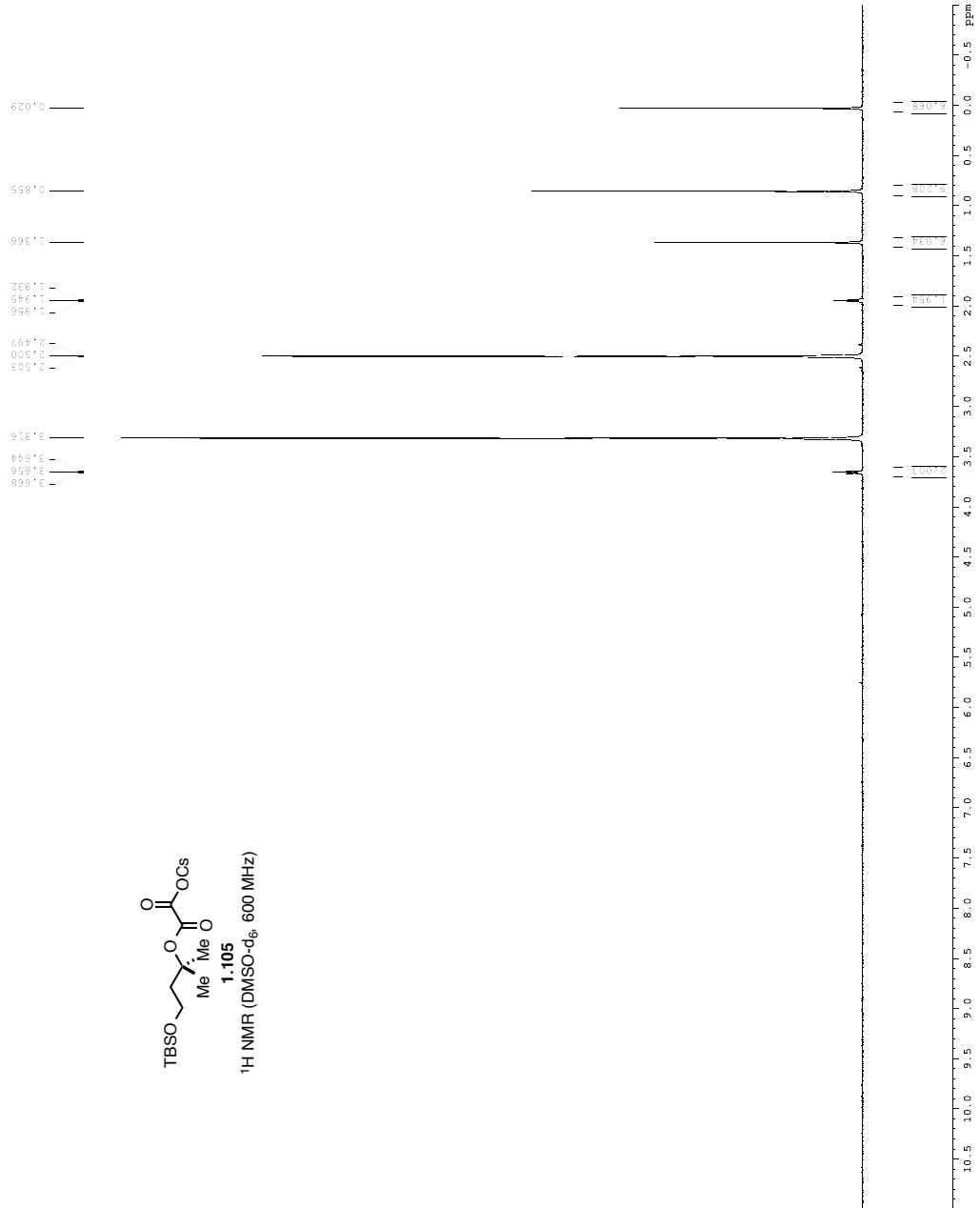
84.21
27.07



YS-II-202



Current Data Parameters
NAME YS-II-202
PROCNO 1
===== CHANNEL f1 =====
Date_ Acquisition Parameters
Time 01:50:28
Time 8.49
Date_ 200808
PULPROG zgpg30
PROBHD 5 mm TBI 13112
PULPROG 2930
SOLVENT DMSO
SOLVENT 8
NUC1 13C
NUC2 13C
F1RES 0.098042 Hz
AQ 5.099475 sec
RG 327.5
WDW EM
SSB 0
LB 14.5 Hz
GB 0
PC 1.00
===== CHANNEL f2 =====
SFO1 600.134200 MHz
NUC1 1H
P1 8.00 usec
PLA1 23.014156 dB
===== Processing Parameters =====
SI 65336
SF 600.130013 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

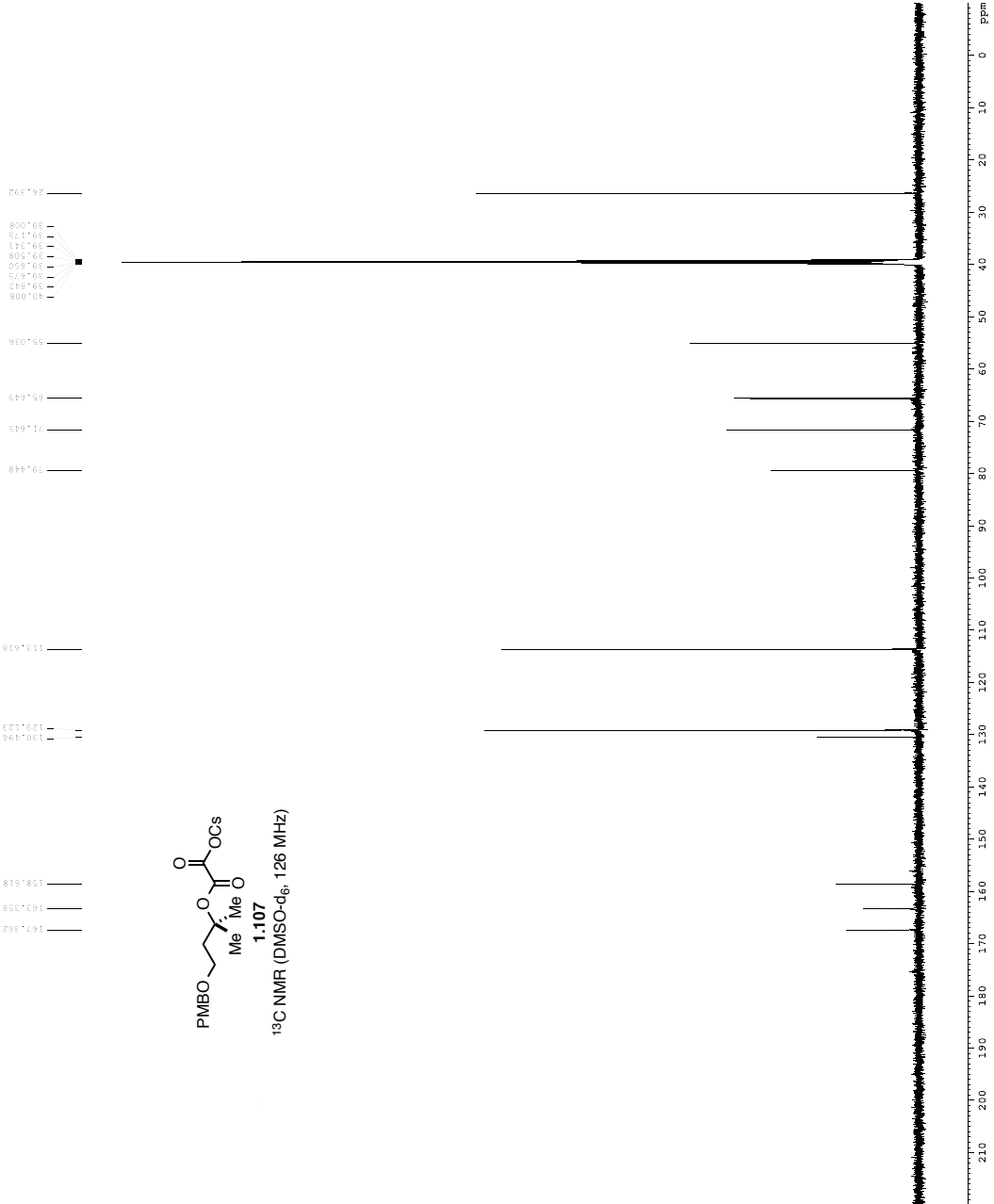



```

Current Data Parameters
Date_ 15-11-260
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 2013.12.29
Time_ 13.29
INSTRUM cryo500
PROBHD 5 mm CPFGC 1H-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 128
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813450 sec
RG 327.500
DW 18.500 usec
DE 6.00 usec
TE 300.298 K
T8 0.26298 sec
C11 0.0300000 sec
D16 0.0002000 sec
d17 0.00019600 sec
MKREST 0 sec
NAMEA 1
NAMEB 0.1500000 sec
F2 33.10 usec

===== CHANNEL f1 =====
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
P13 1.40 usec
P14 1.40 usec
P15 1.40 usec
SFO1 125.7942548 MHz
SF1 2.70 usec
SFO2 500.2225011 MHz
SFXM1(1) Cpfg0.5.70.0 GB
SFXM1(2) Cpfgcomp.4
SFOFF1 0 Hz
SFOFF2 0 Hz

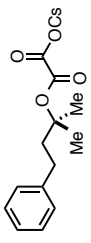
===== CHANNEL f2 =====
CPDPRG2 waitz16
NUC2 1H
P2 100.00 usec
P21 1.40 usec
P22 1.40 usec
P23 1.40 usec
P24 1.40 usec
SFO2 500.2225011 MHz
===== GRADIENT CHANNEL =====
GPMAX(1) SINE.100
GPMAX(2) SINE.100
GPA1 0 %
GPA2 0 %
GPA3 0 %
GPA4 0 %
GPA5 0 %
GPA6 0 %
GPA7 0 %
GPA8 0 %
GPA9 0 %
GPA10 0 %
GPA11 0 %
GPA12 0 %
GPA13 0 %
GPA14 0 %
GPA15 0 %
GPA16 0 %
===== Processing parameters =====
SI 65536
SF 125.7804781 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00
    
```



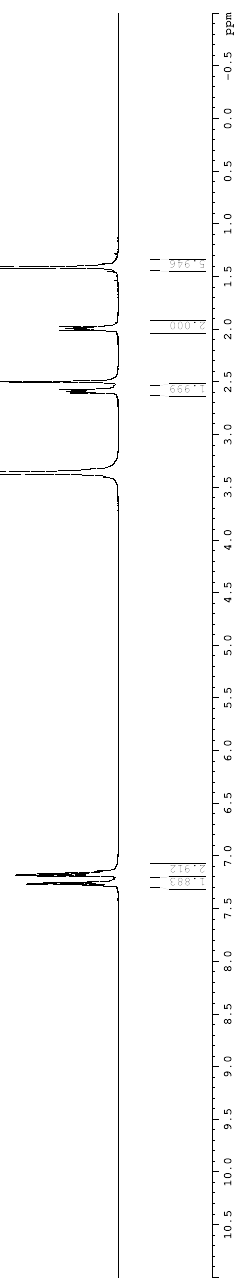
YS-II-195

Current Data Parameters
NAME YS-II-195
PROCNO 1
===== Acquisition Parameters =====
Date_ Time 01/05/02 14:16
Time 14.16
Date_ Time 01/05/02 14:16
PROCNO 1
PROCWD 5 mm broadband
PULPROG zgpg30
TD 65536
SFO 499.130950 MHz
AQ 0.10000000 sec
RG 655.36
WDW EM
SSB 0
GB 0
PC 1.00
===== CHANNEL F1 =====
NUC1 13C
PULPROG zgpg30
PC 12.00 usec
PL1 0.00 dB
PL2 0.00 dB
PL3 0.00 dB
SFO1 499.130950 MHz
===== CHANNEL F2 =====
SFO2 499.130950 MHz
===== Processing parameters =====
SI 65536
SF 499.130950 MHz
WDW EM
SSB 0
GB 0
PC 1.00

7.281
7.266
7.251
7.236
7.221
7.206
7.191
7.176
7.161
7.146
7.131
7.116
7.101
7.086
7.071
7.056
7.041
7.026
7.011
7.000
2.000
1.985
1.970
1.955
1.940
1.925
1.910
1.895
1.880
1.865
1.850
1.835
1.820
1.805
1.790
1.775
1.760
1.745
1.730
1.715
1.700
1.685
1.670
1.655
1.640
1.625
1.610
1.595
1.580
1.565
1.550
1.535
1.520
1.505
1.490
1.475
1.460
1.445
1.430
1.415
1.400
1.385
1.370
1.355
1.340
1.325
1.310
1.295
1.280
1.265
1.250
1.235
1.220
1.205
1.190
1.175
1.160
1.145
1.130
1.115
1.100
0.985
0.970
0.955
0.940
0.925
0.910
0.895
0.880
0.865
0.850
0.835
0.820
0.805
0.790
0.775
0.760
0.745
0.730
0.715
0.700
0.685
0.670
0.655
0.640
0.625
0.610
0.595
0.580
0.565
0.550
0.535
0.520
0.505
0.490
0.475
0.460
0.445
0.430
0.415
0.400
0.385
0.370
0.355
0.340
0.325
0.310
0.295
0.280
0.265
0.250
0.235
0.220
0.205
0.190
0.175
0.160
0.145
0.130
0.115
0.100
0.085
0.070
0.055
0.040
0.025
0.010
-0.005
-0.020
-0.035
-0.050

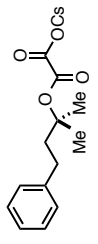
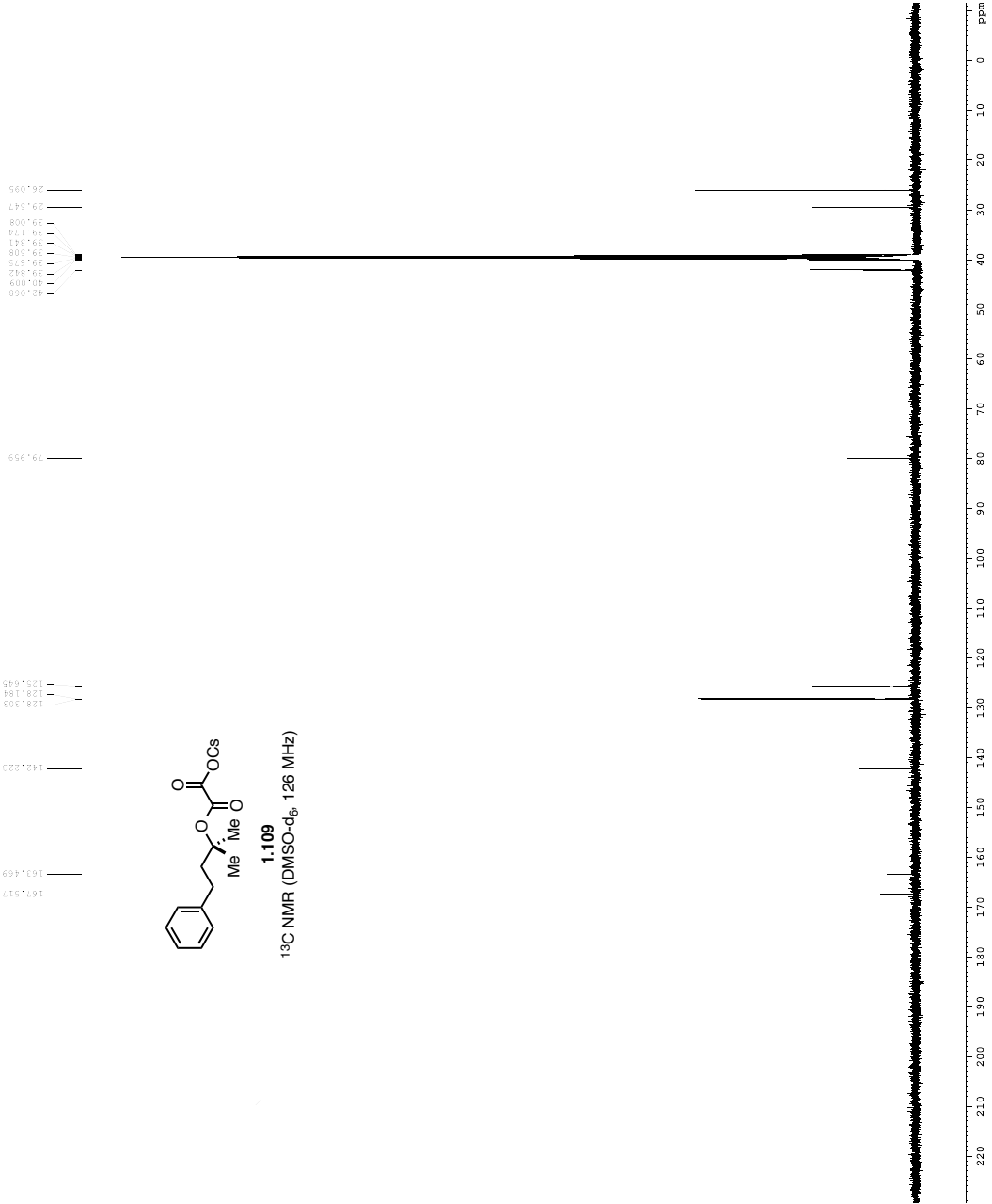


1.109
1H NMR (DMSO-d6, 500 MHz)



```

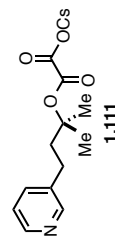
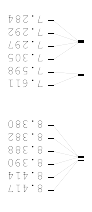
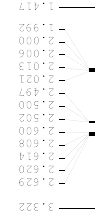
Current Data Parameters
NAME      YS-II-195
EXPNO     1
PROCNO    1
----- Acquisition Parameters -----
Date_     20110726
Time      9:26
INSTRUM   cryo500
PROBHD    5 mm CPCC1H1
PULPROG   zgpg30
TD         65536
SOLVENT   DMSO
NS         160
DS         4
SWH        30300.075 Hz
FIDRES     0.462388 Hz
AQ         1.0813450 sec
RG         16.500 usec
DE         6.000 usec
TE         300.2 K
D1         0.0629600 sec
d11        0.0300000 sec
d12        0.0300000 sec
d13        0.0300000 sec
d14        0.0300000 sec
d15        0.0300000 sec
d16        0.0002000 sec
d17        0.00019600 sec
MKREST    0 sec
NAMEPR    0.0150000 sec
F2         33.10 usec
----- CHANNEL f1 -----
NUC1       13C
P1         16.55 usec
PL1        0.00 dB
PL2        0.00 dB
PL3        0.00 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
SFO1       125.7642548 MHz
SF         500.1362500 MHz
SPINPROG   cpdpr0
SPNAM[1]   CPDPR0.5.70.0 GB
SPNAM[2]   CPDPR0.5.70.0 GB
SFOFF1     0 Hz
SFOFF2     0 Hz
----- CHANNEL f2 -----
CPDPR[2]   waltz16
NUC2       1H
P2         100.00 usec
PL2        0.00 dB
PL3        1.60 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
SFO2       500.2225011 MHz
----- GRADIENT CHANNEL -----
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GFA1       0 %
GFA2       0 %
GFA3       0 %
GFA4       0 %
GFA5       0 %
GFA6       0 %
GFA7       0 %
GFA8       0 %
GFA9       0 %
GFA10      0 %
GFA11      0 %
GFA12      0 %
GFA13      0 %
GFA14      0 %
GFA15      0 %
GFA16      0 %
GFA17      0 %
GFA18      0 %
GFA19      0 %
GFA20      0 %
GFA21      0 %
GFA22      0 %
GFA23      0 %
GFA24      0 %
GFA25      0 %
GFA26      0 %
GFA27      0 %
GFA28      0 %
GFA29      0 %
GFA30      0 %
GFA31      0 %
GFA32      0 %
GFA33      0 %
GFA34      0 %
GFA35      0 %
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GFA93      0 %
GFA94      0 %
GFA95      0 %
GFA96      0 %
GFA97      0 %
GFA98      0 %
GFA99      0 %
GFA100     0 %
----- Processing parameters -----
SI         65536
SF         125.7680494 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         1.00 Hz
FC         2.00
  
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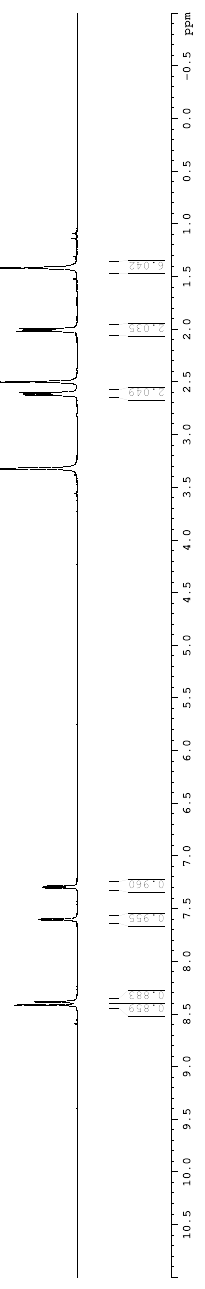
1.109
¹³C NMR (DMSO-d₆, 126 MHz)

YS-III-41

```
Current Data Parameters
NAME      YS-III-41
PROCNO    1
=====
F2 - Acquisition Parameters
Data File  0150494
Time       14.53
Date_     14.11.04
PULPROG   zgpg30
PCPDPR05  5 mm BBO BP1H
PULPROG3  zgpg30
PROCNO3    1
SOLVENT   DMSO
NS         8
DS         2
SS         8615.95 Hz
AQ         0.150010 Hz
RG         1.9399500 sec
AQ         1.9399500 sec
RG         1.9399500 sec
FREQ       52.000 MHz
DS         14.17 usec
DS         14.17 usec
AQ         1.9399500 sec
RG         1.9399500 sec
RG         1.9399500 sec
===== CHANNEL f1 =====
SFO1      600.1342000 MHz
NUC1      13
PULPROG   zgpg30
PCPDPR05  5 mm BBO BP1H
PULPROG3  zgpg30
PCPDPR05  5 mm BBO BP1H
SFO2      600.256000000 MHz
SFO3      600.1300112 MHz
SI         55336
SF         600.1300112 MHz
RG         8.00
SS         0
DS         0
LP         0
RG         0
RG         1.00
PC         0
```



¹H NMR (DMSO-d₆, 600 MHz)

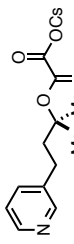
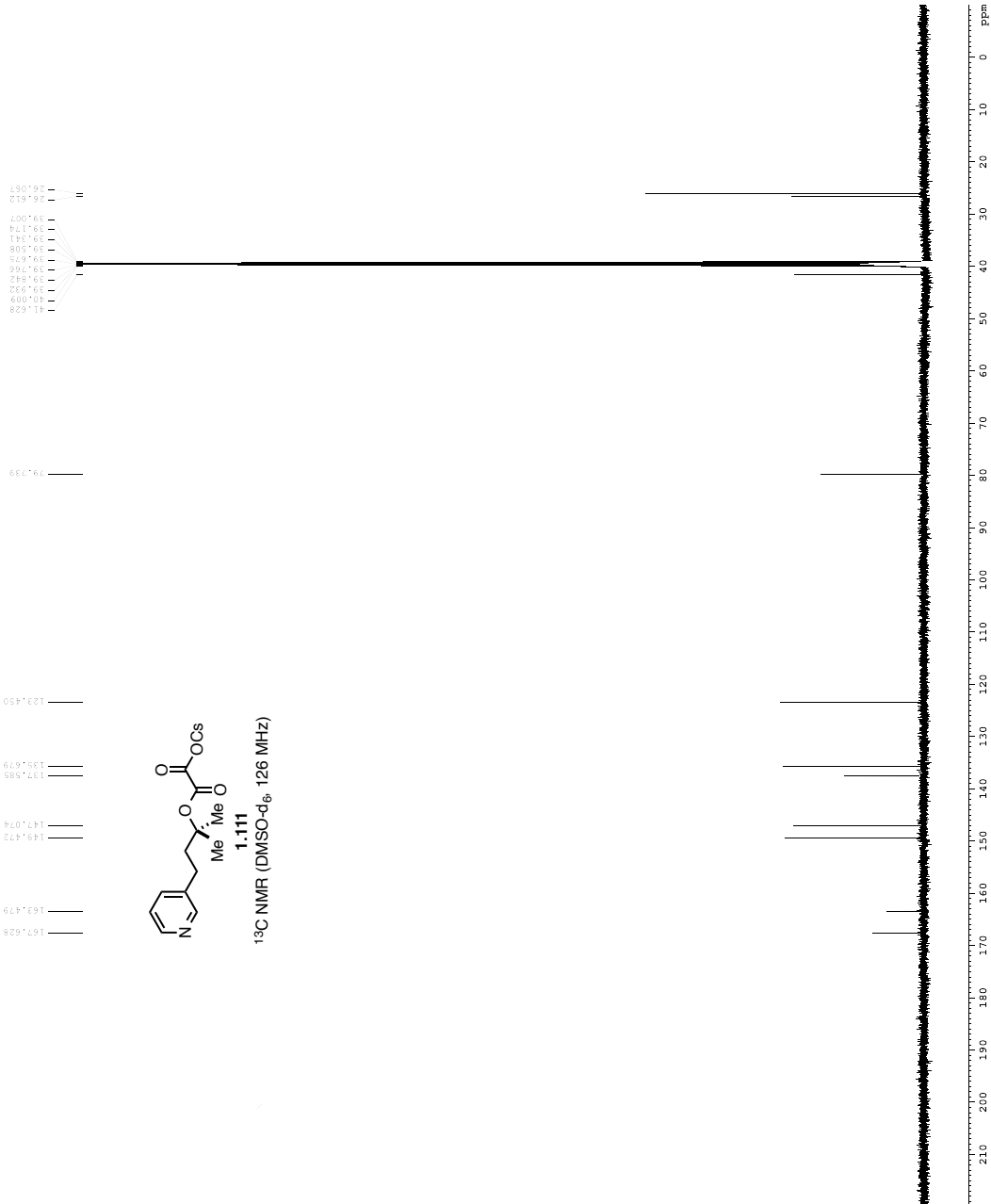



```

Current Data Parameters
NAME      YS-III-41
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     20110420
Time      15:23
INSTRUM   cryo500
PROBHD    5 mm CPYX 1H-
PULPROG   zgpg30
SOLVENT   DMSO
NS         416
DS         4
SWH        30300.075 Hz
FIDRES    0.462388 Hz
AQ         1.0813450 sec
RG         16.500
DE         6.000 usec
TE         300.2 K
D1         0.0629600 sec
d11        0.0300000 sec
d12        0.0300000 sec
d13        0.0300000 sec
d14        0.0300000 sec
d15        0.0300000 sec
d16        0.0002000 sec
d17        0.00019600 sec
MKREST    0 sec
NAMEPR    0.0150000 sec
F2        33.10 usec

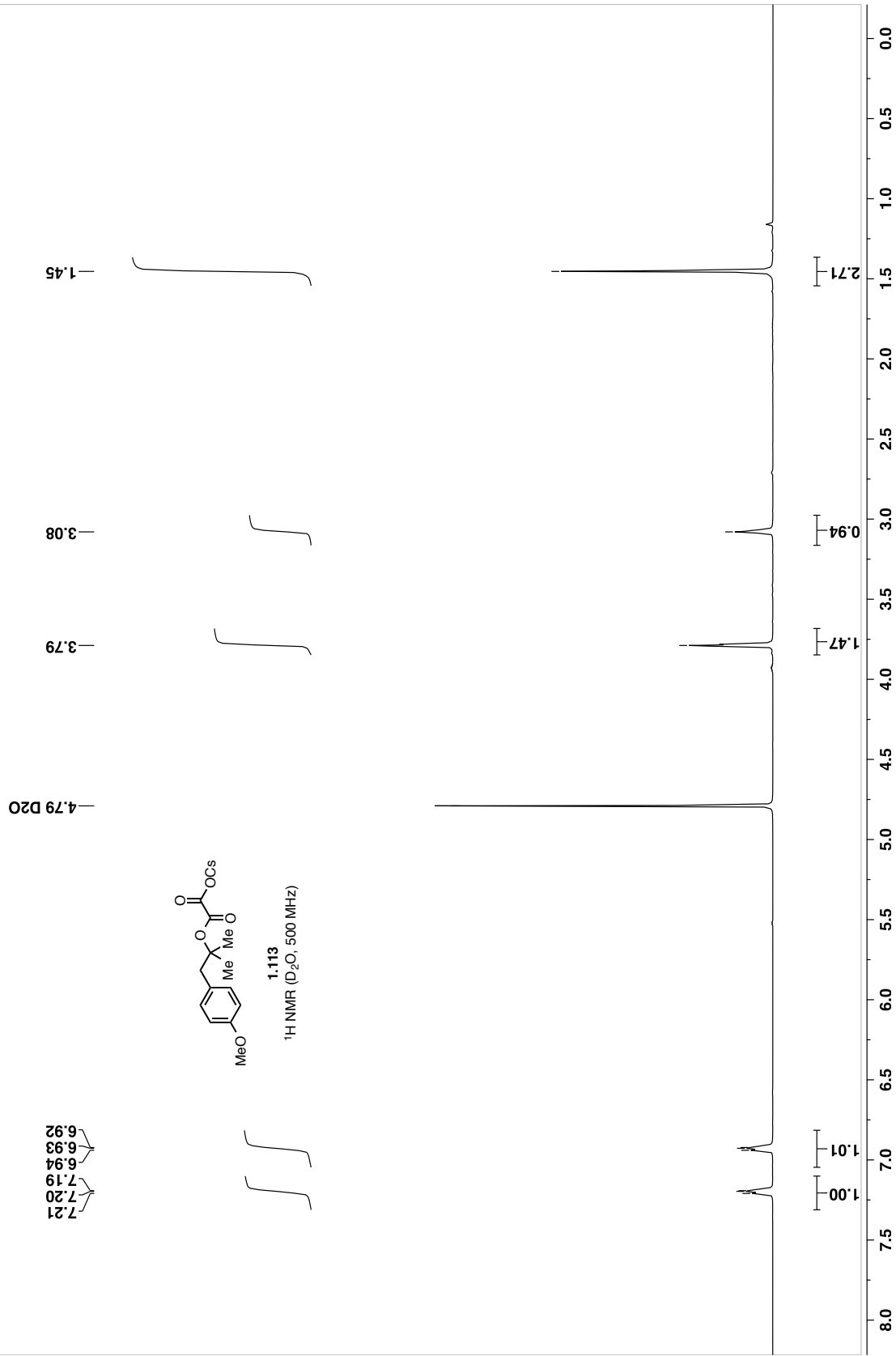
===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        500.00 usec
PL2        2000.00 usec
PL3        1.00 usec
PL4        1.00 usec
PL5        1.00 usec
PL6        1.00 usec
SFO1       125.7942548 MHz
SF1        2.70 usec
SFO2       500.2225011 MHz
SFXM1[1]   CpP60,0.5,70.0 GB
SFXM1[2]   CpP60,0.5,70.0 GB
SFXM2[1]   CpP60,0.5,70.0 GB
SFXM2[2]   CpP60,0.5,70.0 GB
SFOFF1     0 Hz
SFOFF2     0 Hz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P2         100.00 usec
PL2        1.00 usec
PL3        1.00 usec
PL4        1.00 usec
PL5        1.00 usec
PL6        1.00 usec
SFO1       500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GXY1       0 %
GXY2       0 %
GXY3       0 %
GXY4       0 %
GXY5       0 %
GXY6       0 %
GXY7       0 %
GXY8       0 %
GXY9       0 %
GXY10      0 %
GXY11      0 %
GXY12      0 %
GXY13      0 %
GXY14      0 %
GXY15      0 %
GXY16      0 %
GXY17      0 %
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GXY46      0 %
GXY47      0 %
GXY48      0 %
GXY49      0 %
GXY50      0 %
GXY51      0 %
GXY52      0 %
GXY53      0 %
GXY54      0 %
GXY55      0 %
GXY56      0 %
GXY57      0 %
GXY58      0 %
GXY59      0 %
GXY60      0 %
GXY61      0 %
GXY62      0 %
GXY63      0 %
GXY64      0 %
GXY65      0 %
GXY66      0 %
GXY67      0 %
GXY68      0 %
GXY69      0 %
GXY70      0 %
GXY71      0 %
GXY72      0 %
GXY73      0 %
GXY74      0 %
GXY75      0 %
GXY76      0 %
GXY77      0 %
GXY78      0 %
GXY79      0 %
GXY80      0 %
GXY81      0 %
GXY82      0 %
GXY83      0 %
GXY84      0 %
GXY85      0 %
GXY86      0 %
GXY87      0 %
GXY88      0 %
GXY89      0 %
GXY90      0 %
GXY91      0 %
GXY92      0 %
GXY93      0 %
GXY94      0 %
GXY95      0 %
GXY96      0 %
GXY97      0 %
GXY98      0 %
GXY99      0 %
GXY100     0 %
===== Processing parameters =====
SI         65536
SF         125.7805417 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         2.00
  
```

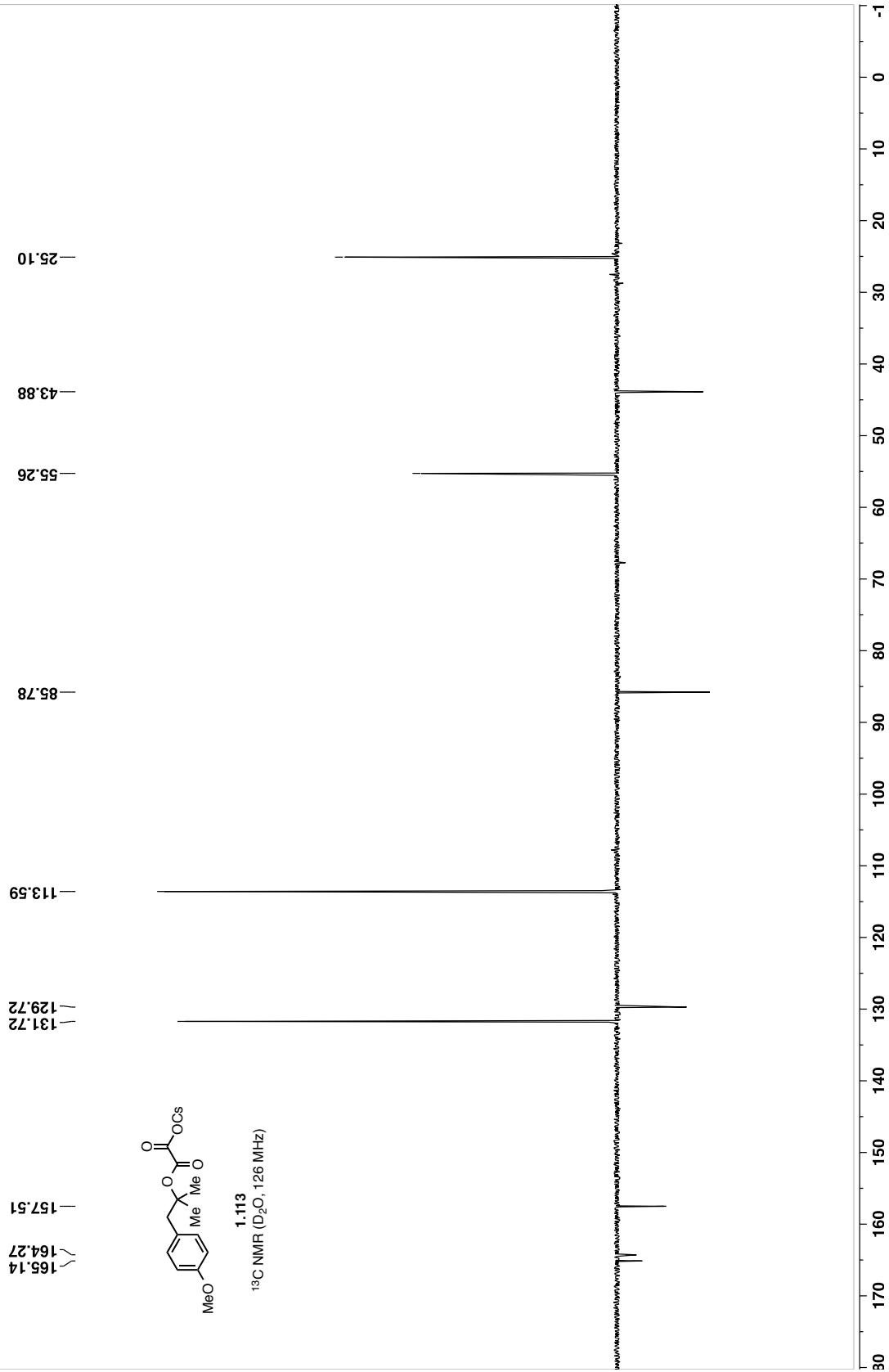


1.111
¹³C NMR (DMSO-d₆, 126 MHz)

A2_116-ccn-s5-091-2-a.10.fid
Frequency: 500.46 MHz

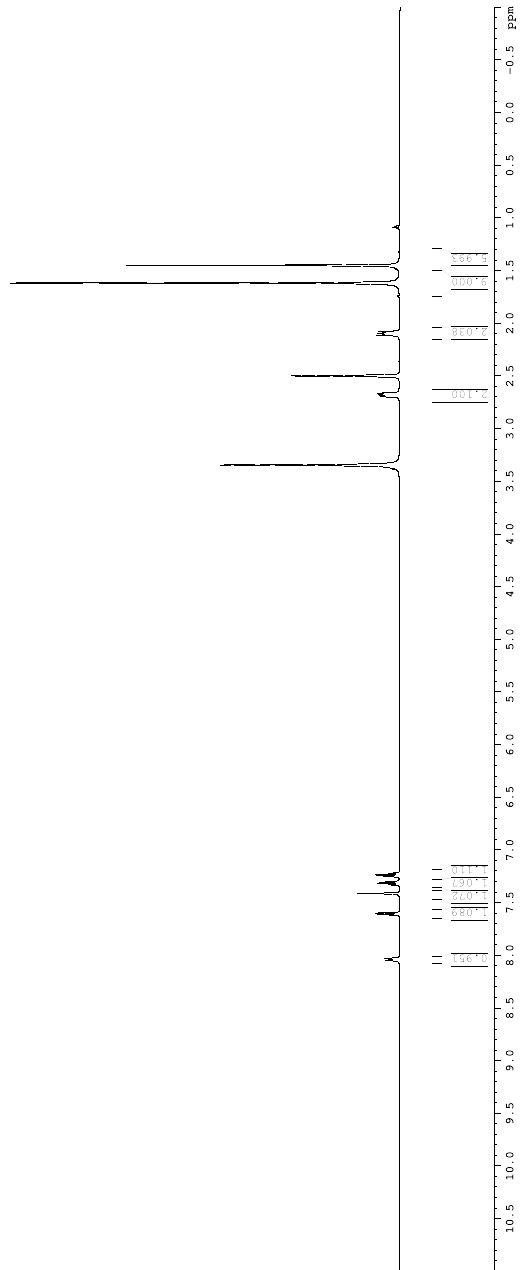
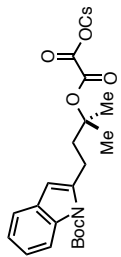


A2_116-ccn-s5-091-2-a.11.fid
Frequency: 125.85 MHz



YS-II-251

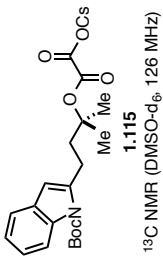
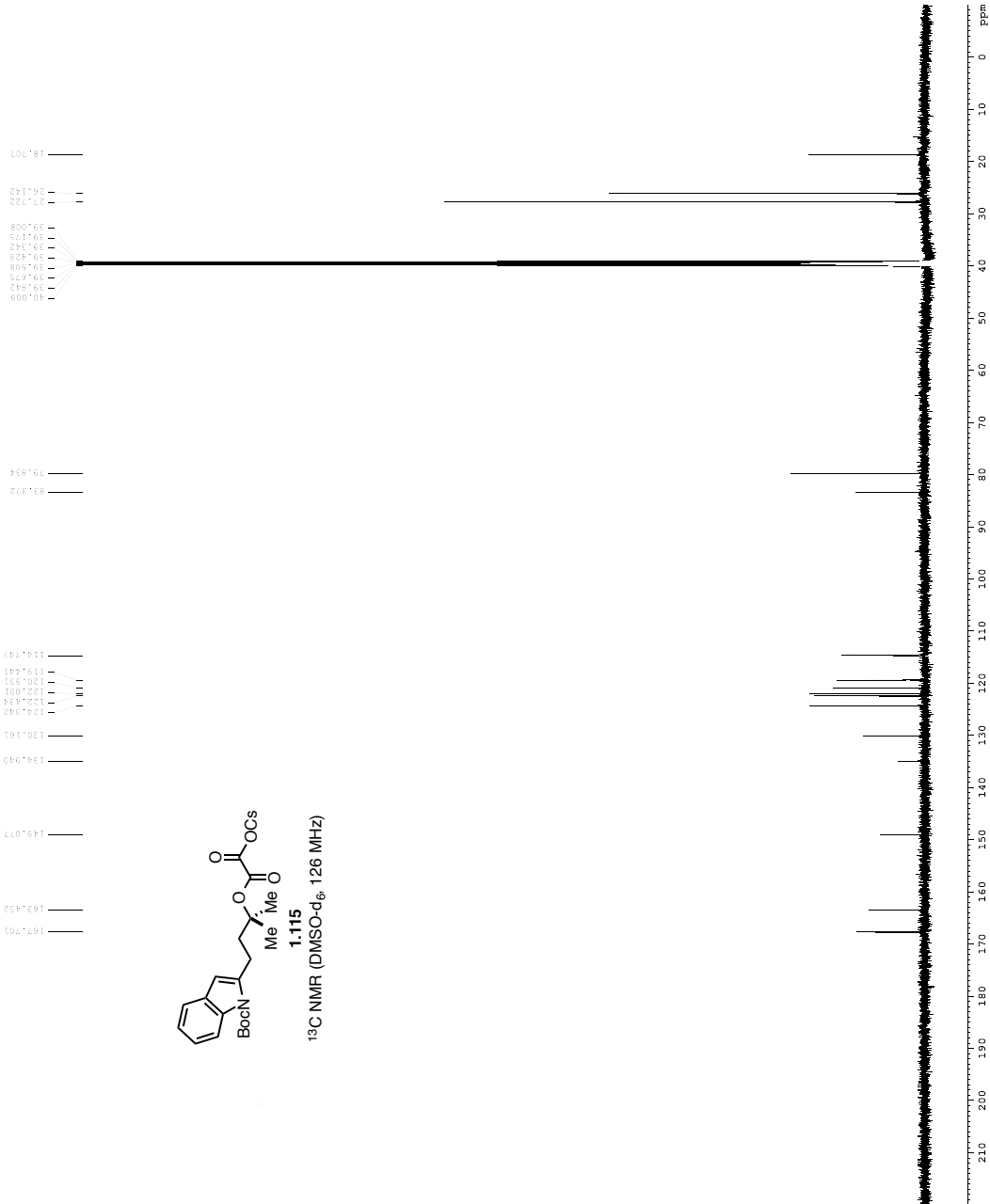
Current Data Parameters
NAME YS-II-251
PROCNO 1
===== Acquisition Parameters
Date_ 01/02/16
Time 13:38
INSTRUM spect
PROBHD 5 mm CPCLP1H4
PULPROG zgpg30
SOLVENT DMSO
NS 8
DS 8
SS 2
AQ 6012.820 Hz
FIDRES 0.250024 Hz
AQ 1.939792 sec
RG 62.400 usec
RG 62.400 usec
DE 6.00 usec
DI 0.1000000 sec
MCN31 0 sec
MCN32 0.0150000 sec
===== CHANNEL F1 =====
NUC1 13C
P1 1.50 usec
PL1 1.60 dB
SFO1 500.2235012 MHz
===== CHANNEL F2 =====
F2 - Processing parameters
SI 65516
SF 500.2235012 MHz
RG 62.400 usec
DE 6.00 usec
DI 0.1000000 sec
PC 0.30 Hz
GB 0
FC 4.00



```

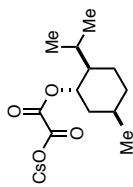
Current Data Parameters
Date_ 18-11-25
EXPNO 1
PROCNO 1
=====
F2 - Acquisition Parameters
Date_ 20130513
Time 13:41
INSTRUM cryo500
PROBHD 5 mm CPYX 4H
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 584
DS 4
SWH 30300.075 Hz
FIDRES 0.462388 Hz
AQ 1.0813450 sec
RG 327.500
AQ 16.500 usec
DE 6.00 usec
TE 300.2 K
NUC1 13C
NUC2 13C
D1 0.300000 sec
D11 0.000000 sec
D16 0.0002000 sec
d17 0.00019600 sec
MKREST 0 sec
NAME 1.115
=====
CHANNEL f1
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
P13 1.00 usec
P14 1.00 usec
P15 1.00 usec
SFO1 125.7942548 MHz
SF1 2.70 GHz
SFO2 500.1362500 MHz
SF2 125.7600000 MHz
SFO3 500.1362500 MHz
SF3 125.7600000 MHz
SFO4 500.1362500 MHz
SF4 125.7600000 MHz
SFO5 500.1362500 MHz
SF5 125.7600000 MHz
SFO6 500.1362500 MHz
SF6 125.7600000 MHz
SFO7 500.1362500 MHz
SF7 125.7600000 MHz
SFO8 500.1362500 MHz
SF8 125.7600000 MHz
SFO9 500.1362500 MHz
SF9 125.7600000 MHz
SFO10 500.1362500 MHz
SF10 125.7600000 MHz
SFO11 500.1362500 MHz
SF11 125.7600000 MHz
SFO12 500.1362500 MHz
SF12 125.7600000 MHz
SFO13 500.1362500 MHz
SF13 125.7600000 MHz
SFO14 500.1362500 MHz
SF14 125.7600000 MHz
SFO15 500.1362500 MHz
SF15 125.7600000 MHz
SFO16 500.1362500 MHz
SF16 125.7600000 MHz
SFO17 500.1362500 MHz
SF17 125.7600000 MHz
SFO18 500.1362500 MHz
SF18 125.7600000 MHz
SFO19 500.1362500 MHz
SF19 125.7600000 MHz
SFO20 500.1362500 MHz
SF20 125.7600000 MHz
SFO21 500.1362500 MHz
SF21 125.7600000 MHz
SFO22 500.1362500 MHz
SF22 125.7600000 MHz
SFO23 500.1362500 MHz
SF23 125.7600000 MHz
SFO24 500.1362500 MHz
SF24 125.7600000 MHz
SFO25 500.1362500 MHz
SF25 125.7600000 MHz
SFO26 500.1362500 MHz
SF26 125.7600000 MHz
SFO27 500.1362500 MHz
SF27 125.7600000 MHz
SFO28 500.1362500 MHz
SF28 125.7600000 MHz
SFO29 500.1362500 MHz
SF29 125.7600000 MHz
SFO30 500.1362500 MHz
SF30 125.7600000 MHz
SFO31 500.1362500 MHz
SF31 125.7600000 MHz
SFO32 500.1362500 MHz
SF32 125.7600000 MHz
SFO33 500.1362500 MHz
SF33 125.7600000 MHz
SFO34 500.1362500 MHz
SF34 125.7600000 MHz
SFO35 500.1362500 MHz
SF35 125.7600000 MHz
SFO36 500.1362500 MHz
SF36 125.7600000 MHz
SFO37 500.1362500 MHz
SF37 125.7600000 MHz
SFO38 500.1362500 MHz
SF38 125.7600000 MHz
SFO39 500.1362500 MHz
SF39 125.7600000 MHz
SFO40 500.1362500 MHz
SF40 125.7600000 MHz
SFO41 500.1362500 MHz
SF41 125.7600000 MHz
SFO42 500.1362500 MHz
SF42 125.7600000 MHz
SFO43 500.1362500 MHz
SF43 125.7600000 MHz
SFO44 500.1362500 MHz
SF44 125.7600000 MHz
SFO45 500.1362500 MHz
SF45 125.7600000 MHz
SFO46 500.1362500 MHz
SF46 125.7600000 MHz
SFO47 500.1362500 MHz
SF47 125.7600000 MHz
SFO48 500.1362500 MHz
SF48 125.7600000 MHz
SFO49 500.1362500 MHz
SF49 125.7600000 MHz
SFO50 500.1362500 MHz
SF50 125.7600000 MHz
=====
CHANNEL f2
CPDPRG2 waltz16
NUC1 13C
NUC2 13C
P1 100.00 usec
P11 100.00 usec
P12 1.00 usec
P13 1.00 usec
P14 1.00 usec
P15 1.00 usec
SFO1 125.7942548 MHz
SF1 2.70 GHz
SFO2 500.1362500 MHz
SF2 125.7600000 MHz
SFO3 500.1362500 MHz
SF3 125.7600000 MHz
SFO4 500.1362500 MHz
SF4 125.7600000 MHz
SFO5 500.1362500 MHz
SF5 125.7600000 MHz
SFO6 500.1362500 MHz
SF6 125.7600000 MHz
SFO7 500.1362500 MHz
SF7 125.7600000 MHz
SFO8 500.1362500 MHz
SF8 125.7600000 MHz
SFO9 500.1362500 MHz
SF9 125.7600000 MHz
SFO10 500.1362500 MHz
SF10 125.7600000 MHz
SFO11 500.1362500 MHz
SF11 125.7600000 MHz
SFO12 500.1362500 MHz
SF12 125.7600000 MHz
SFO13 500.1362500 MHz
SF13 125.7600000 MHz
SFO14 500.1362500 MHz
SF14 125.7600000 MHz
SFO15 500.1362500 MHz
SF15 125.7600000 MHz
SFO16 500.1362500 MHz
SF16 125.7600000 MHz
SFO17 500.1362500 MHz
SF17 125.7600000 MHz
SFO18 500.1362500 MHz
SF18 125.7600000 MHz
SFO19 500.1362500 MHz
SF19 125.7600000 MHz
SFO20 500.1362500 MHz
SF20 125.7600000 MHz
SFO21 500.1362500 MHz
SF21 125.7600000 MHz
SFO22 500.1362500 MHz
SF22 125.7600000 MHz
SFO23 500.1362500 MHz
SF23 125.7600000 MHz
SFO24 500.1362500 MHz
SF24 125.7600000 MHz
SFO25 500.1362500 MHz
SF25 125.7600000 MHz
SFO26 500.1362500 MHz
SF26 125.7600000 MHz
SFO27 500.1362500 MHz
SF27 125.7600000 MHz
SFO28 500.1362500 MHz
SF28 125.7600000 MHz
SFO29 500.1362500 MHz
SF29 125.7600000 MHz
SFO30 500.1362500 MHz
SF30 125.7600000 MHz
SFO31 500.1362500 MHz
SF31 125.7600000 MHz
SFO32 500.1362500 MHz
SF32 125.7600000 MHz
SFO33 500.1362500 MHz
SF33 125.7600000 MHz
SFO34 500.1362500 MHz
SF34 125.7600000 MHz
SFO35 500.1362500 MHz
SF35 125.7600000 MHz
SFO36 500.1362500 MHz
SF36 125.7600000 MHz
SFO37 500.1362500 MHz
SF37 125.7600000 MHz
SFO38 500.1362500 MHz
SF38 125.7600000 MHz
SFO39 500.1362500 MHz
SF39 125.7600000 MHz
SFO40 500.1362500 MHz
SF40 125.7600000 MHz
SFO41 500.1362500 MHz
SF41 125.7600000 MHz
SFO42 500.1362500 MHz
SF42 125.7600000 MHz
SFO43 500.1362500 MHz
SF43 125.7600000 MHz
SFO44 500.1362500 MHz
SF44 125.7600000 MHz
SFO45 500.1362500 MHz
SF45 125.7600000 MHz
SFO46 500.1362500 MHz
SF46 125.7600000 MHz
SFO47 500.1362500 MHz
SF47 125.7600000 MHz
SFO48 500.1362500 MHz
SF48 125.7600000 MHz
SFO49 500.1362500 MHz
SF49 125.7600000 MHz
SFO50 500.1362500 MHz
SF50 125.7600000 MHz
=====
F2 - Processing parameters
SI 65536
SF 125.7604792 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00

```



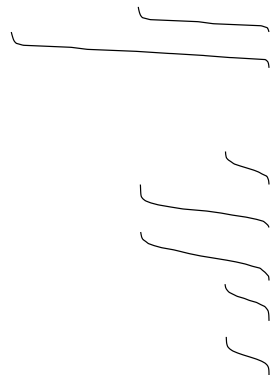
A2_104-iso-M-Cs-Ox.10.tif
Frequency: 500.46 MHz

5.08
5.07
5.06
5.04
4.79 D2O

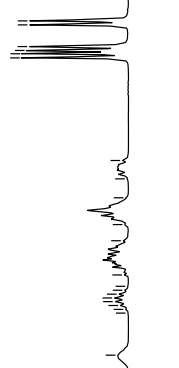


1.117
¹H NMR (D₂O, 500 MHz)

1.95
1.81
1.80
1.78
1.77
1.76
1.75
1.73
1.72
1.68
1.56
1.51
1.42
1.35
1.29
0.94
0.93
0.92
0.90
0.83
0.82



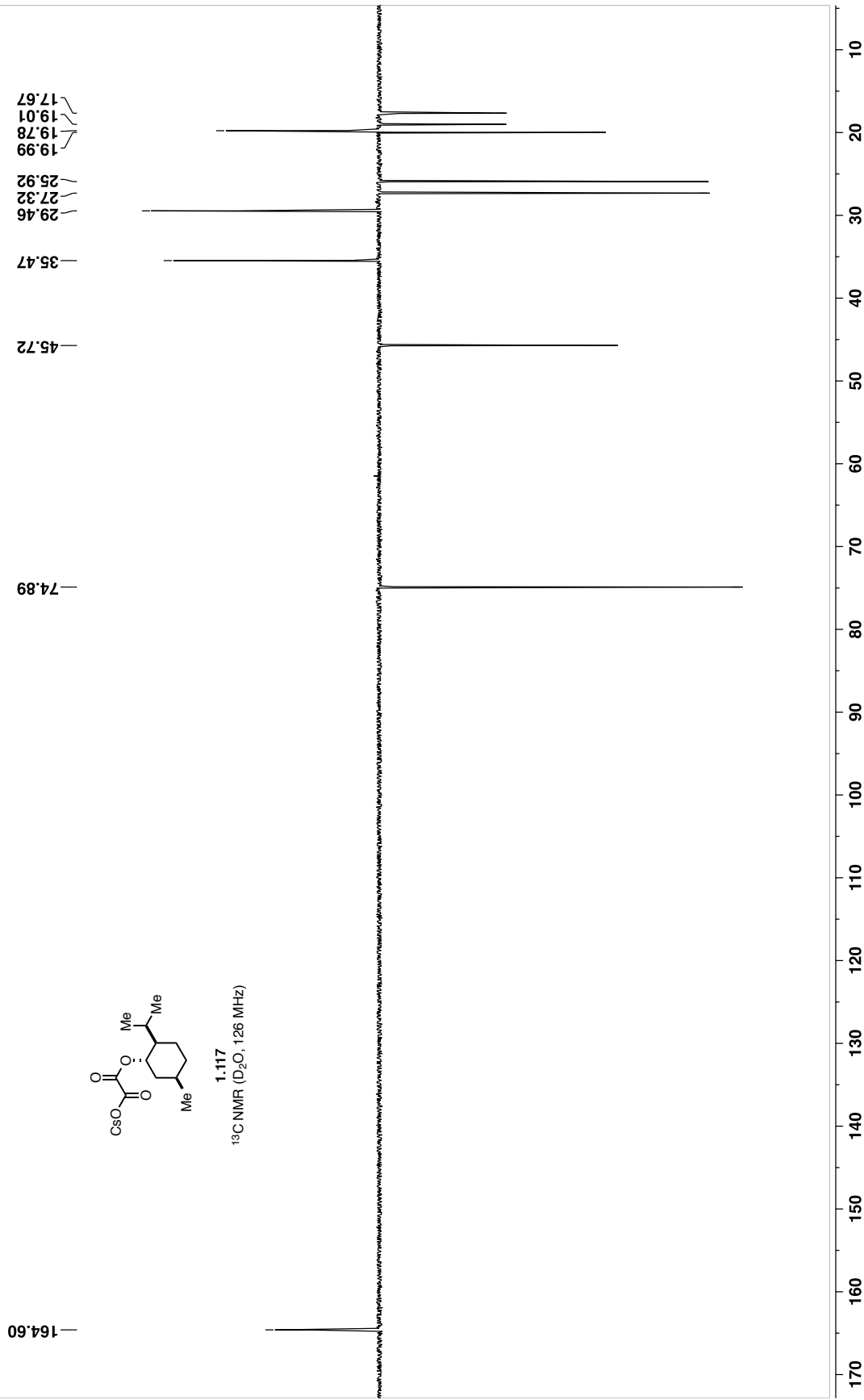
0.98



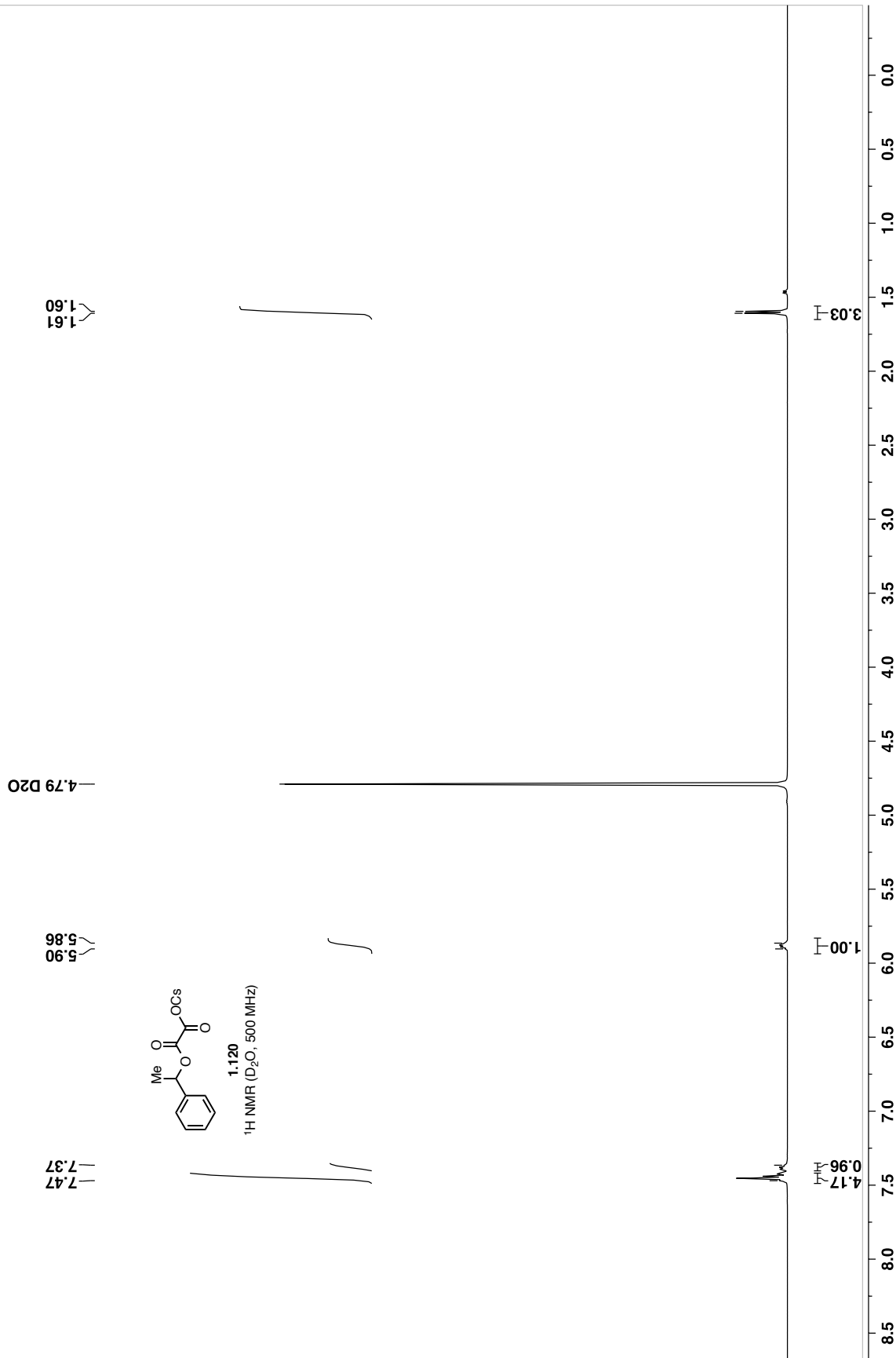
0.99
1.02
2.97
2.98
1.01
5.97
3.03

5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0

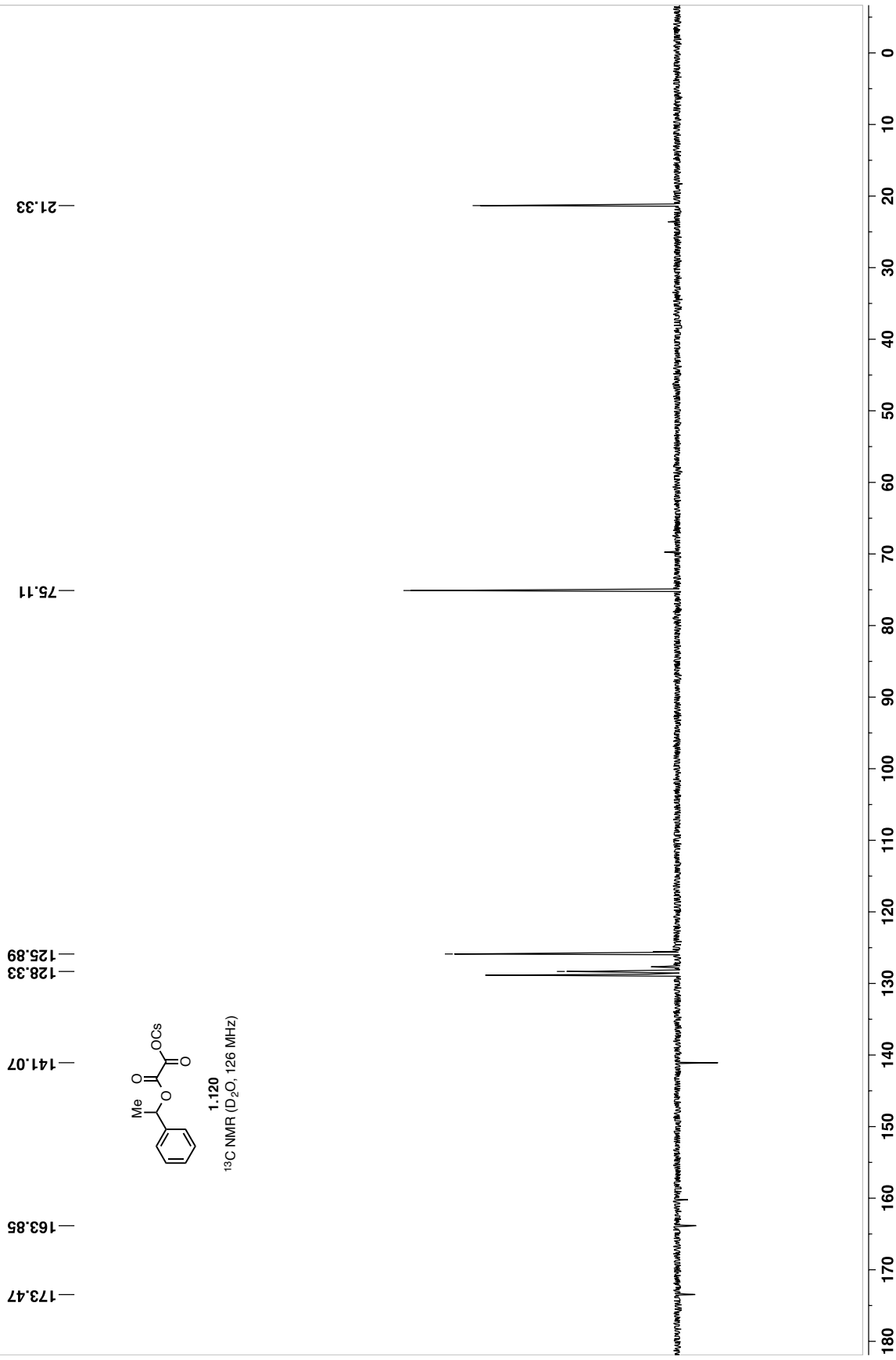
A2_104-iso-M-Cs-Ox.11.fid
Frequency: 125.85 MHz



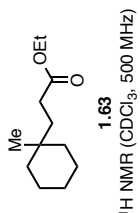
A3_117-MeBrnOxCs.10.tif
Frequency: 500.62 MHz



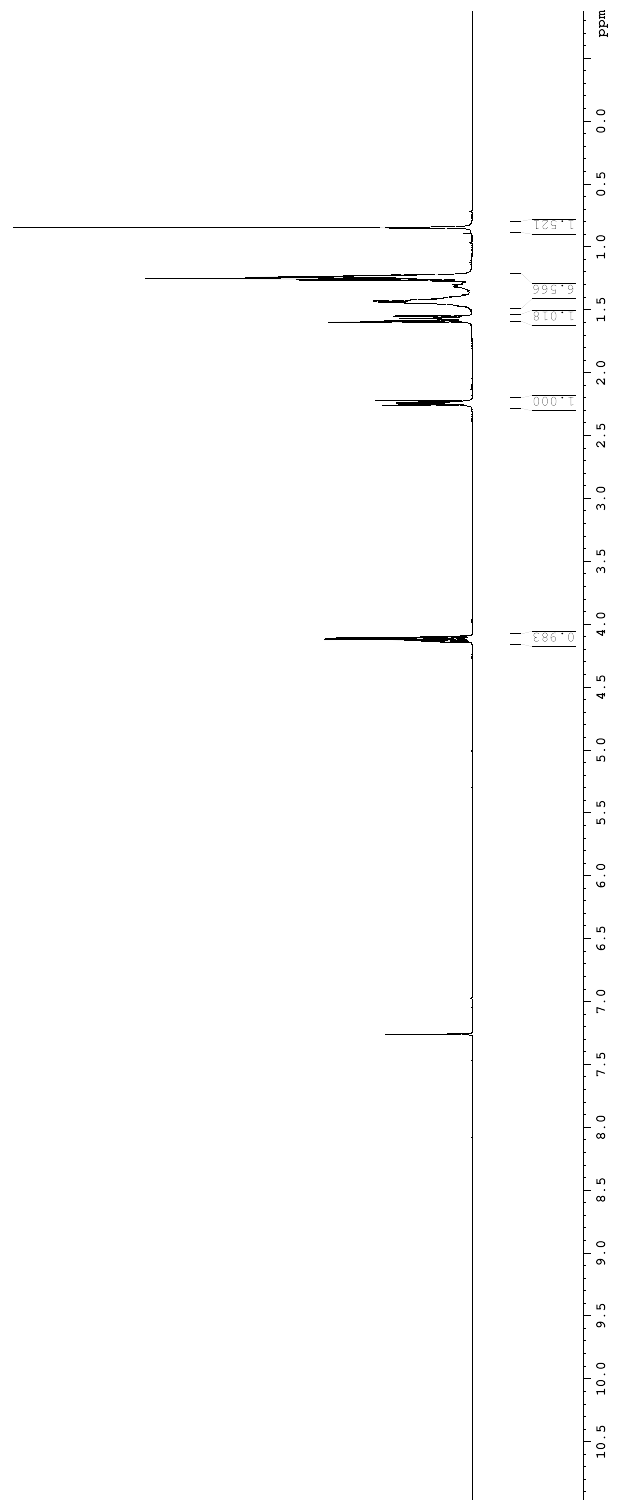
A3_117-MeBrnOxCs.11.fid
Frequency: 125.89 MHz



¹H spectrum



Current Data Parameters
 NAME CAJL-249-pure
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20150523
 Time 17.33
 INSTRUM cty900
 PULPROG zgpg30
 TD 80126
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.100003 Hz
 AQ 4.89398622 sec
 RG 62.405
 DE 6.00 usec
 TE 298.0 K
 D1 0.10000000 sec
 MCREST 0 sec
 KWRRK 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 PL1 1.60 dB
 SFO1 500.2239015 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.2200315 MHz
 GB 0
 SB 0
 IB 0 Hz
 GB 0
 FC 4.00



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

```

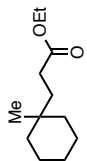
Current Data Parameters
NAME      CHJ1-249-pure
EXPNO    2
PROCNO   1
F2 - Acquisition Parameters
Date_    20150523
Time     17.40
INSTRUM  cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  Spinecho30gp.prd
TD        65536
SOLVENT  CDCl3
NS        160
DS        4
AQ        30393.038 Hz
FIDRES    0.462388 Hz
RG        1.0813446 sec
AQ        11585.2
DM        16.500 usec
DE        6.00 usec
TE        298.0 K
D1        1.00000000 sec
d11       0.03000000 sec
d15       0.00200000 sec
d16       0.00019600 sec
MC68BT    0 sec
MC68BK    0.01500000 sec
F2        33.10 usec

===== CHANNEL f1 =====
NUC1      13C
P1        16.55 usec
PL1       500.00 usec
P12       2000.00 usec
PL12      121.00 dB
PL0        121.00 dB
SFO1      125.7842548 MHz
SFO2      2.70 dB
SFO3      2.70 dB
SPNAM[1]  Crp60,0.5,20.1
SPNAM[2]  Crp60comp.4
SFOFF1    0 Hz
SFOFF2    0 Hz

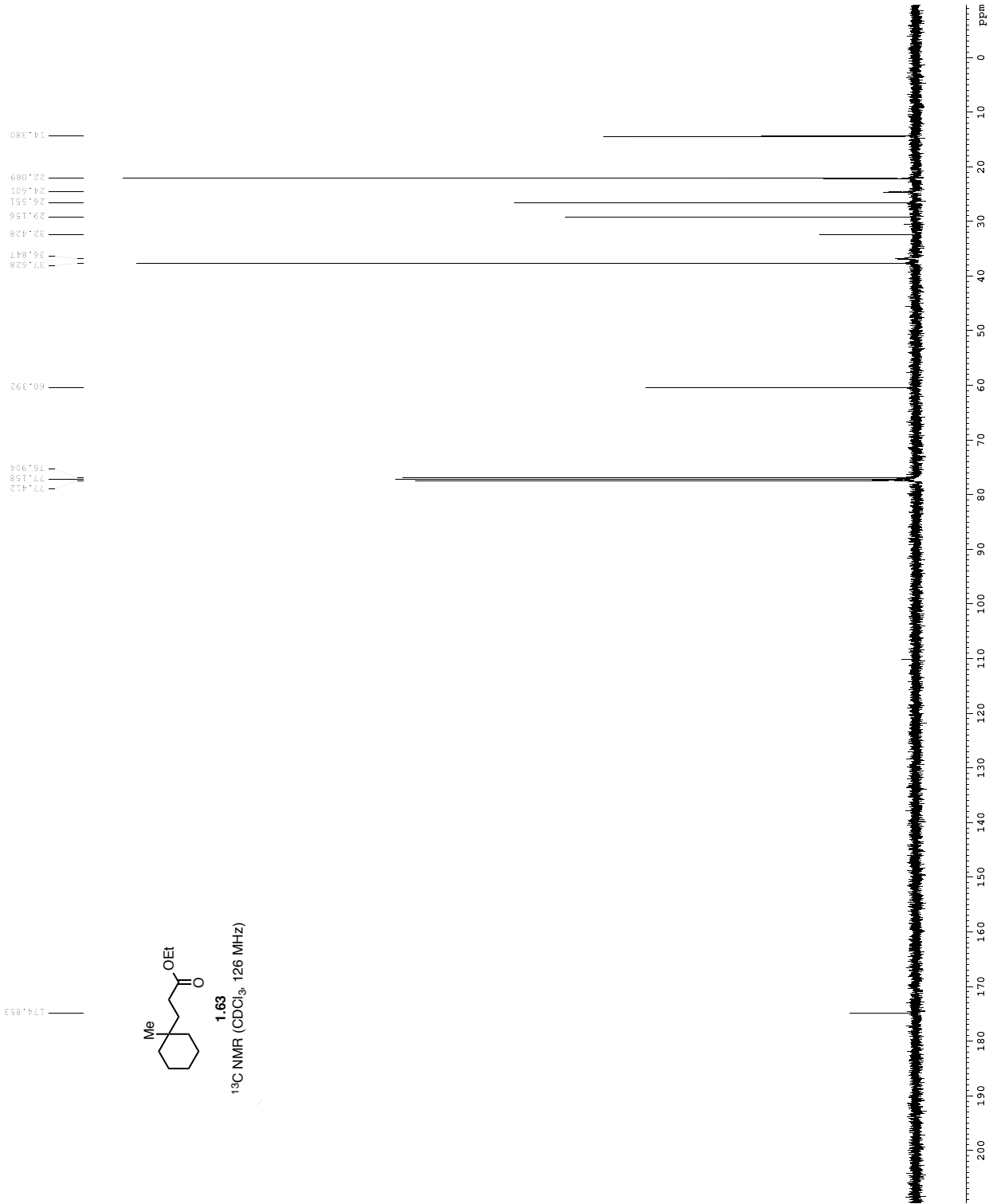
===== CHANNEL f2 =====
CPRPRG[2] waitz16
NUC2      1H
P2        100.00 usec
PL2       1.60 dB
PL12      24.50 dB
SFO2      500.2225011 MHz

===== GRADIENT CHANNEL =====
GPMAX[1]  SINE.100
GPMAX[2]  SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPR21     30.00 %
GPR22     50.00 %
P15       500.00 usec
P16       1000.00 usec

F2 - Processing Parameters
SI         CS13c
SF         125.7804080 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
  
```



1.63
¹³C NMR (CDCl₃, 126 MHz)

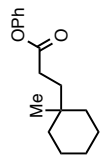


A2_115-ccn-s5-089-1-2-a_12.fid
Frequency: 500.46 MHz

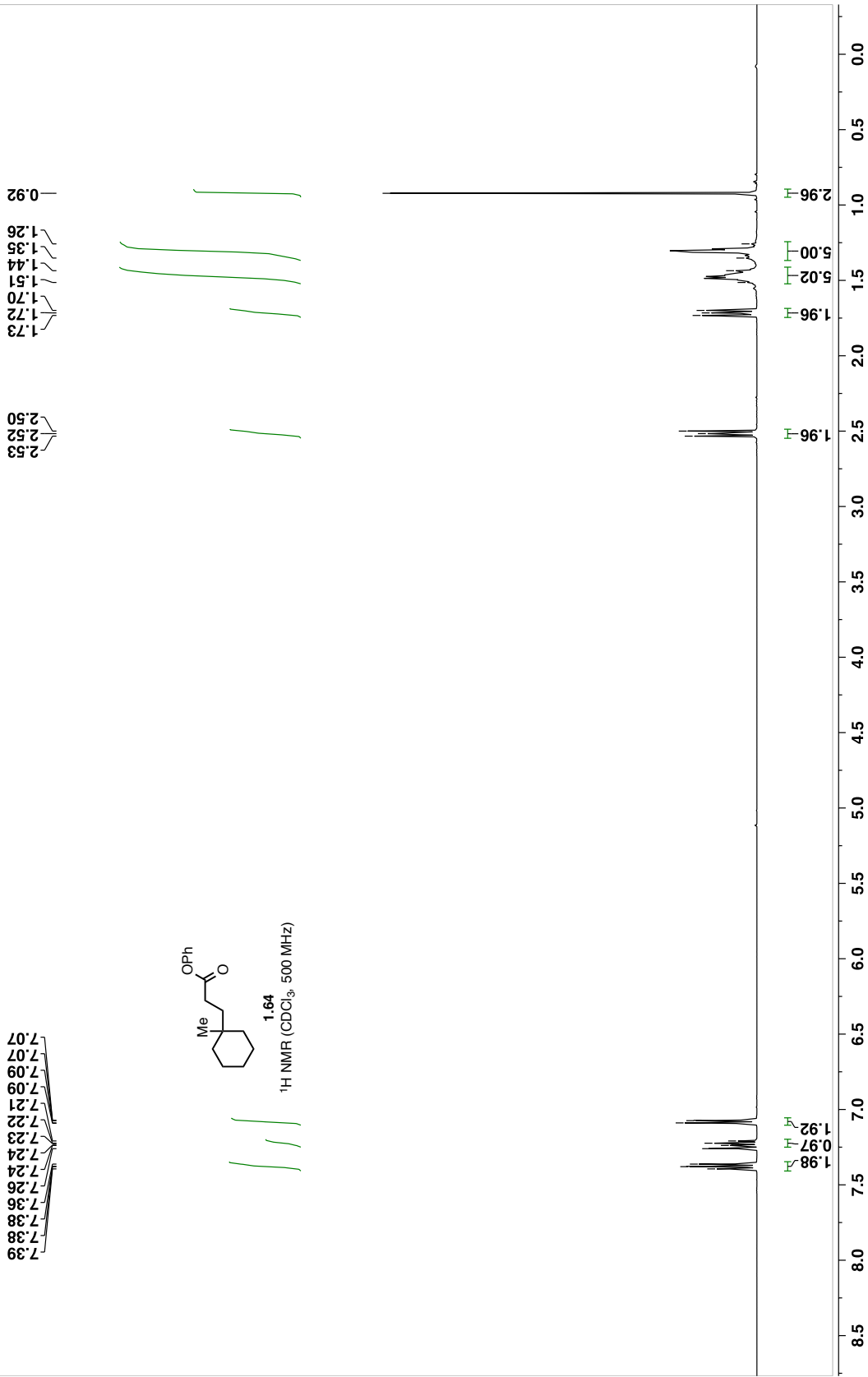
7.39
7.38
7.38
7.36
7.26
7.24
7.24
7.23
7.22
7.21
7.09
7.09
7.07
7.07

2.53
2.52
2.50

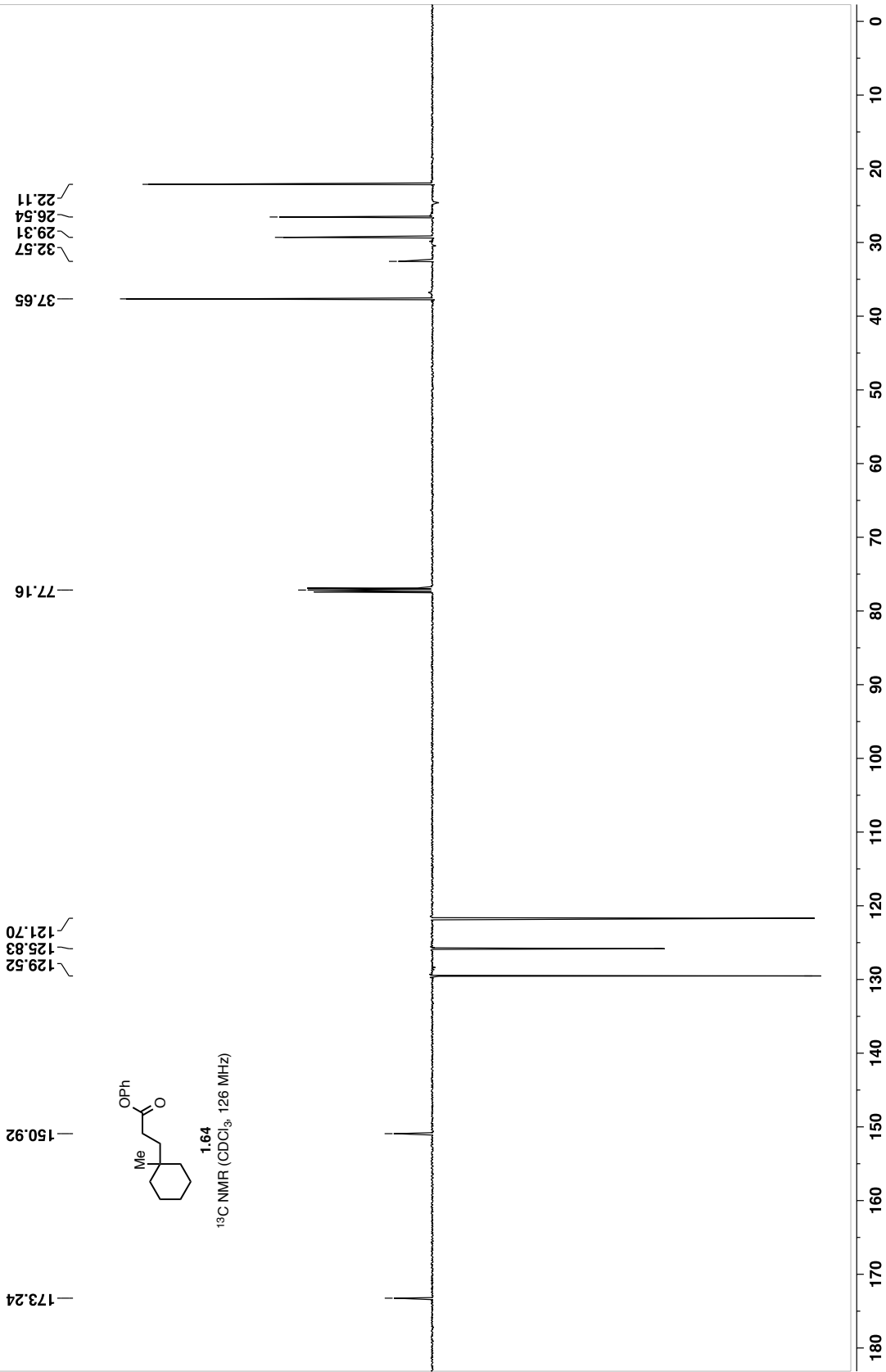
1.73
1.72
1.70
1.51
1.44
1.35
1.26



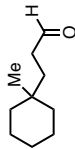
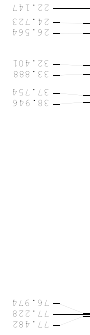
1.64
¹H NMR (CDCl₃, 500 MHz)



A2_115-ccn-s5-089-1-2-a.11.fid
Frequency: 125.85 MHz



YS-III-29A



1.67
¹³C NMR (CDCl₃, 126 MHz)

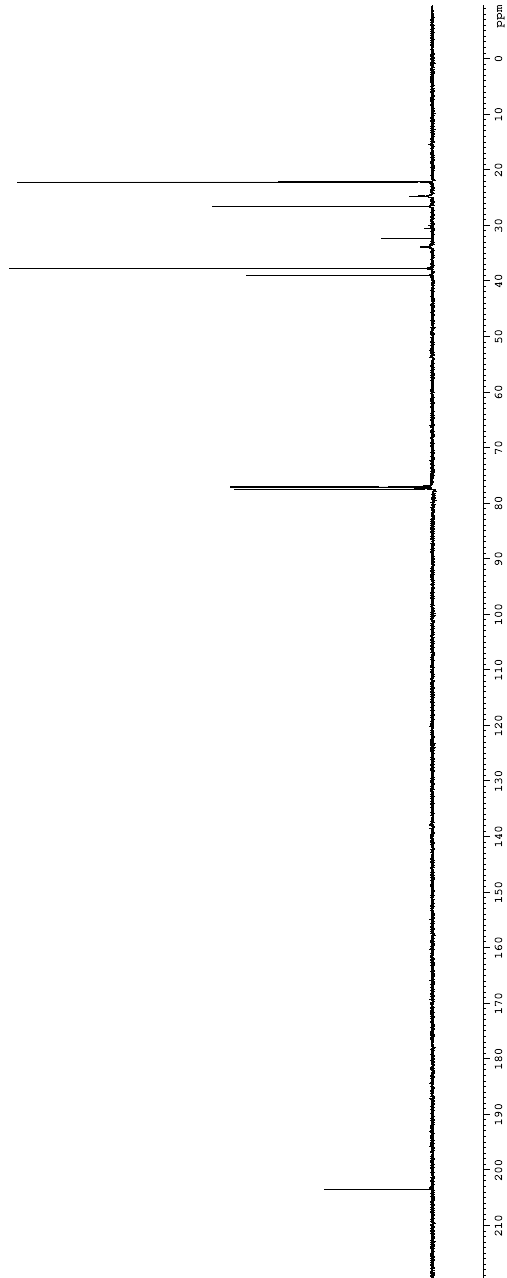
```

Current Data Parameters
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110402
Time 12.42
INSTRUM cryo500
PROBHD 5 mm CPCLP1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 288
DS 4
SWH 30300.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813450 sec
RG 16.500 usec
DE 6.00 usec
TE 300.2 K
C11 0.0300000 sec
D16 0.0002000 sec
d17 0.00019600 sec
MKEST 0 sec
NAME 0.0150000 sec
P2 33.10 usec

===== CHANNEL f1 =====
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
P13 1.00 usec
P14 1.00 usec
P15 1.00 usec
SFO1 125.7942548 MHz
SF1 2.70 usec
SFO2 500.1362500 MHz
SFX1 0 Hz
SFX2 0 Hz
SFOFF1 0 Hz
SFOFF2 0 Hz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 100.00 usec
P21 1.60 usec
P22 1.60 usec
P23 1.60 usec
P24 1.60 usec
P25 1.60 usec
SFO3 500.2225011 MHz

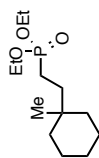
===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GXY1 0 %
GXY2 0 %
GXY3 0 %
GXY4 0 %
GXY5 0 %
GXY6 0 %
GXY7 0 %
GXY8 0 %
GXY9 0 %
GXY10 0 %
GXY11 0 %
GXY12 0 %
GXY13 0 %
GXY14 0 %
GXY15 0 %
GXY16 0 %
GXY17 0 %
GXY18 0 %
GXY19 0 %
GXY20 0 %
GXY21 0 %
GXY22 0 %
GXY23 0 %
GXY24 0 %
GXY25 0 %
GXY26 0 %
GXY27 0 %
GXY28 0 %
GXY29 0 %
GXY30 0 %
GXY31 0 %
GXY32 0 %
GXY33 0 %
GXY34 0 %
GXY35 0 %
GXY36 0 %
GXY37 0 %
GXY38 0 %
GXY39 0 %
GXY40 0 %
GXY41 0 %
GXY42 0 %
GXY43 0 %
GXY44 0 %
GXY45 0 %
GXY46 0 %
GXY47 0 %
GXY48 0 %
GXY49 0 %
GXY50 0 %
GXY51 0 %
GXY52 0 %
GXY53 0 %
GXY54 0 %
GXY55 0 %
GXY56 0 %
GXY57 0 %
GXY58 0 %
GXY59 0 %
GXY60 0 %
GXY61 0 %
GXY62 0 %
GXY63 0 %
GXY64 0 %
GXY65 0 %
GXY66 0 %
GXY67 0 %
GXY68 0 %
GXY69 0 %
GXY70 0 %
GXY71 0 %
GXY72 0 %
GXY73 0 %
GXY74 0 %
GXY75 0 %
GXY76 0 %
GXY77 0 %
GXY78 0 %
GXY79 0 %
GXY80 0 %
GXY81 0 %
GXY82 0 %
GXY83 0 %
GXY84 0 %
GXY85 0 %
GXY86 0 %
GXY87 0 %
GXY88 0 %
GXY89 0 %
GXY90 0 %
GXY91 0 %
GXY92 0 %
GXY93 0 %
GXY94 0 %
GXY95 0 %
GXY96 0 %
GXY97 0 %
GXY98 0 %
GXY99 0 %
GXY100 0 %
===== GRADIENT PARAMETERS =====
SI 65536
SF 125.7883131 MHz
EM
LB 0
GB 0
PC 2.00
  
```



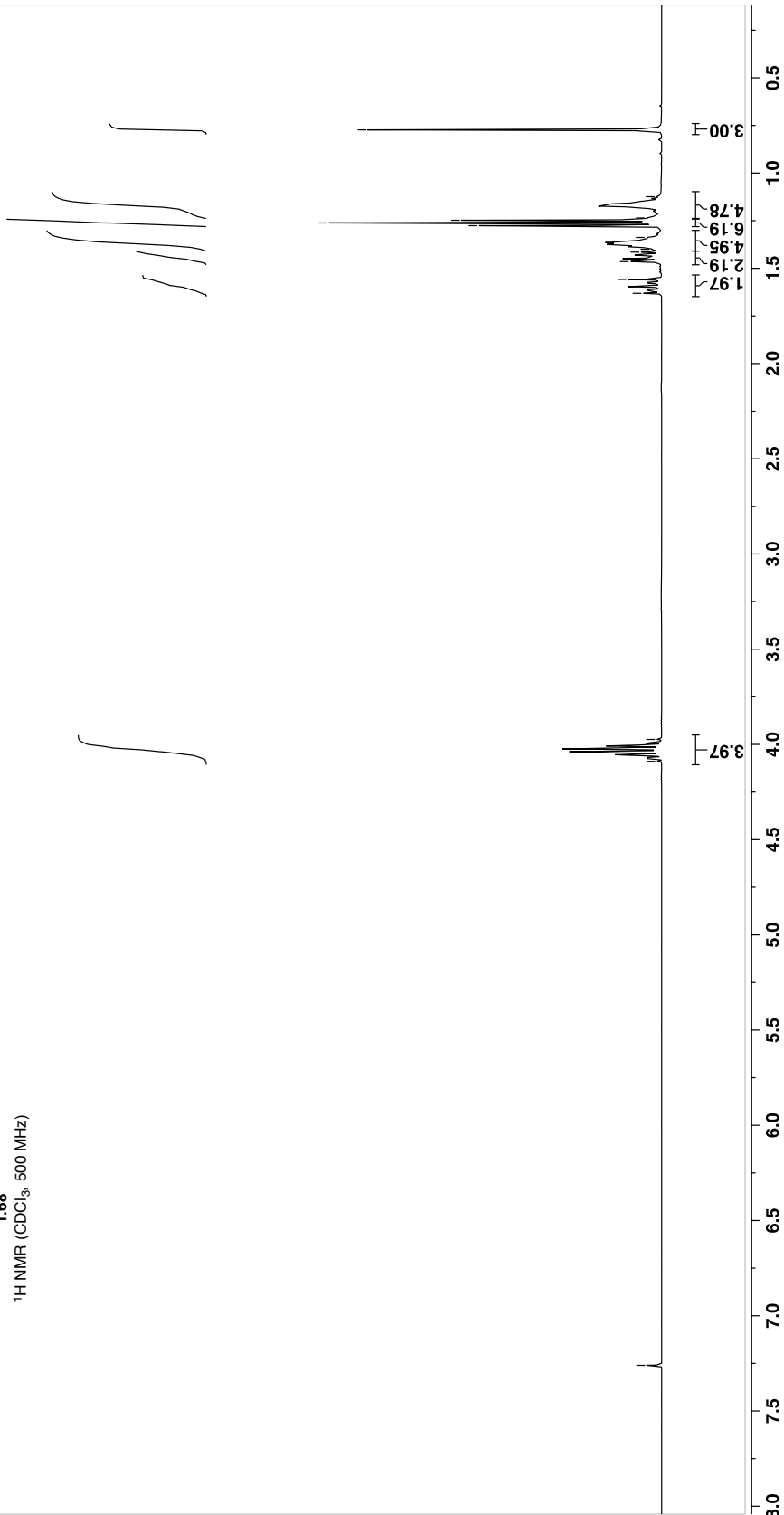
A3_62-con-s5-086_1-1-a_10.fid
Frequency: 500.63 MHz

0.77
1.12
1.24
1.25
1.26
1.28
1.34
1.40
1.42
1.46
1.56
1.63

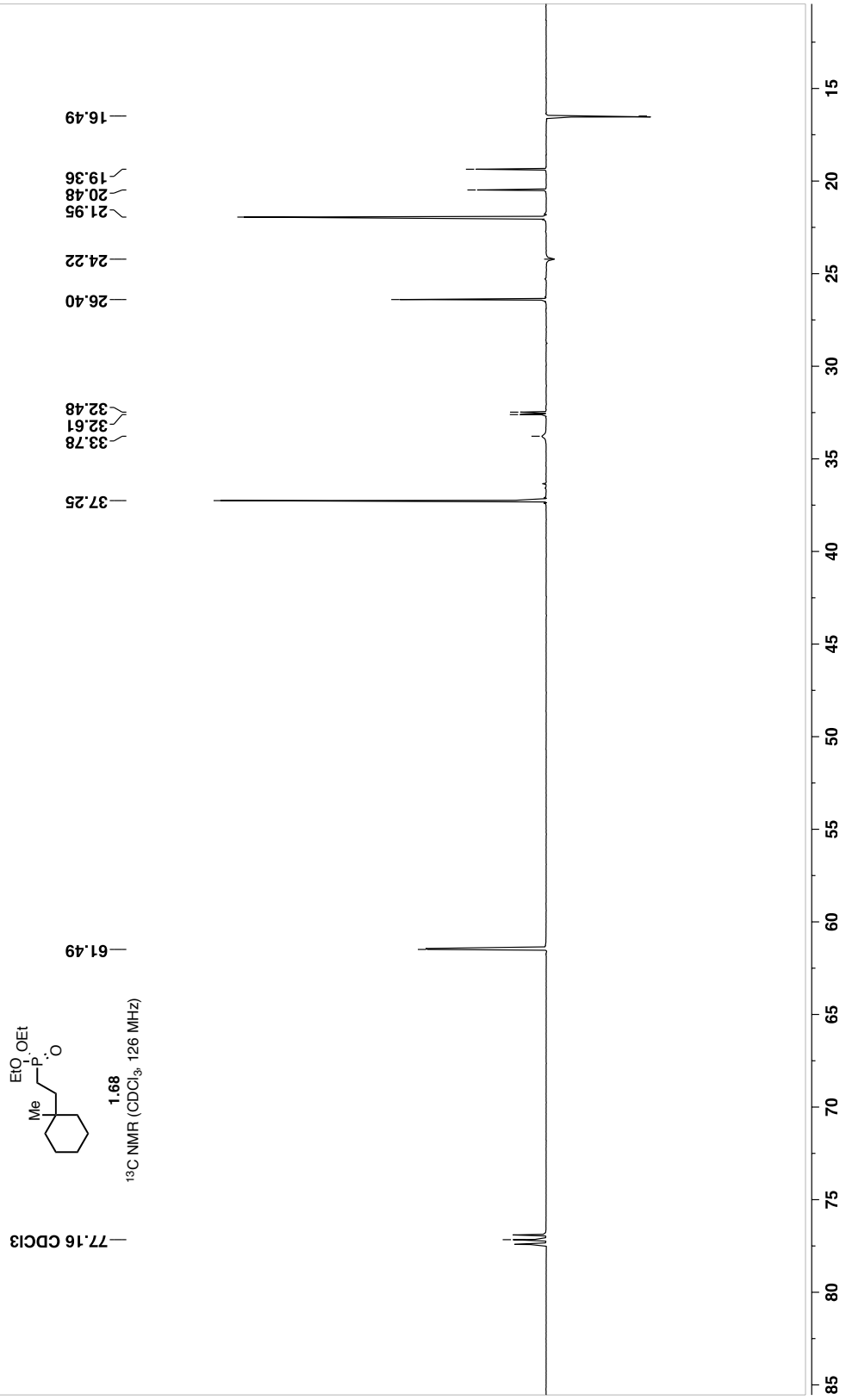
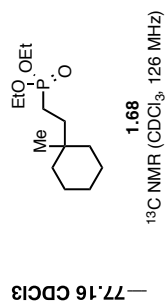
3.97
4.09



1.68
¹H NMR (CDCl₃, 500 MHz)

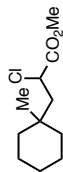


A3_62-ccn-s5-089-1-1-a.12.fid
Frequency: 125.89 MHz



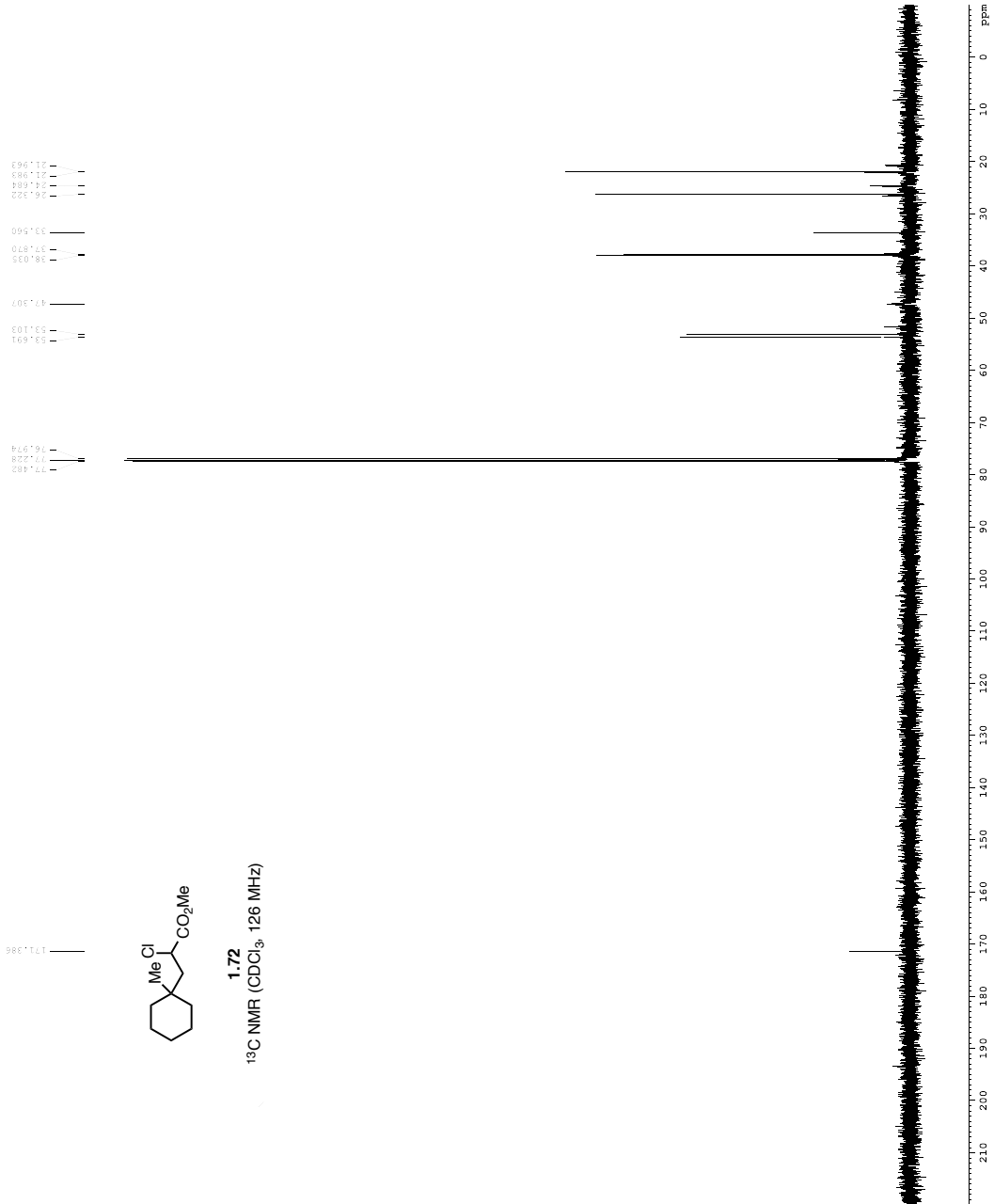
YS-III-47A

173.711

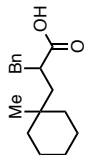


1.72
13C NMR (CDCl₃, 126 MHz)

```
Current Data Parameters
=====
EXPNO          1
PROCNO         1
F2 - Acquisition Parameters
=====
Date_          20110427
Time           8.43
INSTRUM        cryo500
PROBHD         5 mm CPCC1H1
PULPROG        zgpg30
TD             65536
SOLVENT        CDCl3
NS             136
DS             4
SWH            30300.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813450 sec
RG            16.500 usec
DE            6.00 usec
TE            0.06296.0 K
C11           0.0300000 sec
D16           0.0002000 sec
d17           0.0019600 sec
MKREST        0 sec
NAME          YS-III-47A
F2           0.1500000 sec
===== CHANNEL f1 =====
NUC1          13C
P1            16.55 usec
PL1          500.00 usec
PL2          2000.00 usec
PL3          1.00 usec
PL4          1.00 usec
PL5          1.00 usec
PL6          1.00 usec
SFO1         125.7942548 MHz
SF1          2.70 usec
SFO2         500.2225011 MHz
SFX1          0 Hz
SFX2          0 Hz
SFX3          0 Hz
SFX4          0 Hz
SFX5          0 Hz
SFX6          0 Hz
SFX7          0 Hz
SFX8          0 Hz
SFX9          0 Hz
SFX10         0 Hz
SFX11         0 Hz
SFX12         0 Hz
SFX13         0 Hz
SFX14         0 Hz
SFX15         0 Hz
SFX16         0 Hz
SFX17         0 Hz
SFX18         0 Hz
SFX19         0 Hz
SFX20         0 Hz
SFX21         0 Hz
SFX22         0 Hz
SFX23         0 Hz
SFX24         0 Hz
SFX25         0 Hz
SFX26         0 Hz
SFX27         0 Hz
SFX28         0 Hz
SFX29         0 Hz
SFX30         0 Hz
SFX31         0 Hz
SFX32         0 Hz
SFX33         0 Hz
SFX34         0 Hz
SFX35         0 Hz
SFX36         0 Hz
SFX37         0 Hz
SFX38         0 Hz
SFX39         0 Hz
SFX40         0 Hz
SFX41         0 Hz
SFX42         0 Hz
SFX43         0 Hz
SFX44         0 Hz
SFX45         0 Hz
SFX46         0 Hz
SFX47         0 Hz
SFX48         0 Hz
SFX49         0 Hz
SFX50         0 Hz
SFX51         0 Hz
SFX52         0 Hz
SFX53         0 Hz
SFX54         0 Hz
SFX55         0 Hz
SFX56         0 Hz
SFX57         0 Hz
SFX58         0 Hz
SFX59         0 Hz
SFX60         0 Hz
SFX61         0 Hz
SFX62         0 Hz
SFX63         0 Hz
SFX64         0 Hz
SFX65         0 Hz
SFX66         0 Hz
SFX67         0 Hz
SFX68         0 Hz
SFX69         0 Hz
SFX70         0 Hz
SFX71         0 Hz
SFX72         0 Hz
SFX73         0 Hz
SFX74         0 Hz
SFX75         0 Hz
SFX76         0 Hz
SFX77         0 Hz
SFX78         0 Hz
SFX79         0 Hz
SFX80         0 Hz
SFX81         0 Hz
SFX82         0 Hz
SFX83         0 Hz
SFX84         0 Hz
SFX85         0 Hz
SFX86         0 Hz
SFX87         0 Hz
SFX88         0 Hz
SFX89         0 Hz
SFX90         0 Hz
SFX91         0 Hz
SFX92         0 Hz
SFX93         0 Hz
SFX94         0 Hz
SFX95         0 Hz
SFX96         0 Hz
SFX97         0 Hz
SFX98         0 Hz
SFX99         0 Hz
SFX100        0 Hz
===== CHANNEL f2 =====
CPDPRG2        waltz16
NUC2          1H
P2            100.00 usec
PL2          1.60 usec
PL3          1.60 usec
PL4          1.60 usec
PL5          1.60 usec
PL6          1.60 usec
SFO1         500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GAMMA[1]       0 %
GAMMA[2]       0 %
GXY1           0 %
GXY2           0 %
GYZ1           0 %
GYZ2           0 %
GZ1            50.00 %
GZ2            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
```



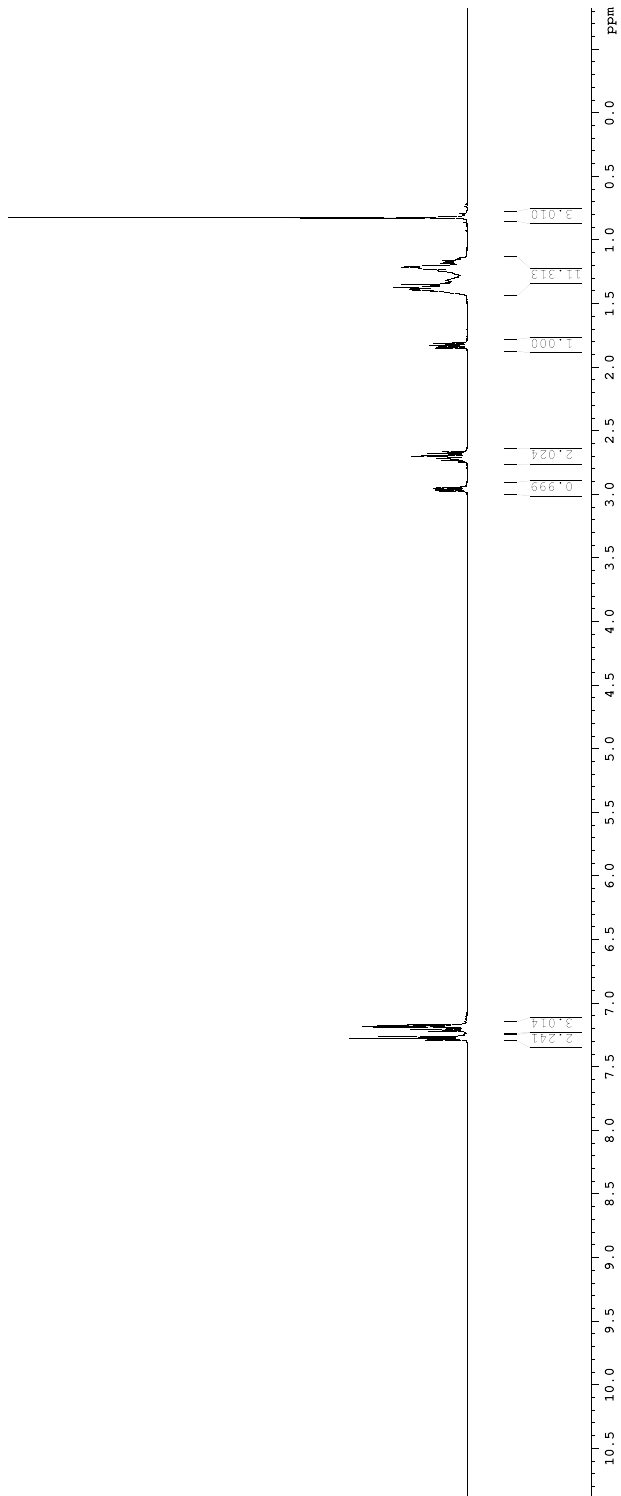
¹H spectrum



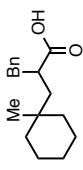
1.73
¹H NMR (CDCl₃, 600 MHz)

```

Current Data Parameters
=====
EXPNO      1
PROCNO     1
Date_      20150408
Time       14.04
INSTRUM    av600
PROBHD     5 mm BBO BB-1H
PULPROG    zgpg30
TD         65536
SOLVENT    CDCl3
NS         2
DS         2
SWH        9615.385 Hz
FIDRES     0.125002 Hz
AQ         3.5999436 sec
RG         256
DM         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         9.40 usec
PL1        0.00
=====
F2 - Processing parameters
SI         65536
SF         600.1300344 MHz
WDW        EM
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)



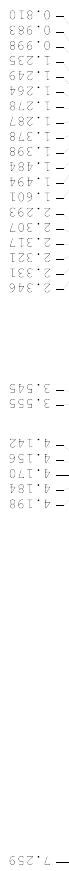
1.73
13C NMR (CDCl₃, 126 MHz)

```

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 IH-
PULPROG  deptqgbpp
TD        65536
SOLVENT  CDCl3
NS        208
DS        4
SWH       30303.031 Hz
FIDRES    0.462388 Hz
AQ         1.0813440 sec
RG         2048
EW         16.500 usec
DE         6.000 usec
TE         298.0 K
CONST2   145.000000
CONST12  1.500000
D1        0.000000 sec
d2        0.0034828 sec
d12       0.0002000 sec
D16       0.0002000 sec
DELTA     0.0001707 sec
DELTA1    0.00228023 sec
DELTA2    0.00226483 sec
DELTA3    0.00224828 sec
ACQRES1   0 sec
PCPRK     0.01500000 sec
===== CHANNEL f1 =====
NUC1      13C
P1        16.55 usec
P2        2000.00 usec
P20       120.00 dB
P1-1      -1.00 dB
SFO1      125.7642548 MHz
SFO2      2.70 dB
SFO3      0 Hz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
P2        11.55 usec
P3         7.70 usec
P4         15.40 usec
P40        100.00 usec
P1-2       24.50 dB
SFO2      500.225911 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]  SINE.100
GPNAM[2]  SINE.100
GPNAM[3]  SINE.100
GPR1      0 %
GPR2      0 %
GPR3      0 %
GPR4      0 %
GPR5      0 %
GPR6      0 %
GPR7      0 %
GPR8      0 %
GPR9      0 %
GPR10     0 %
GPR11     0 %
GPR12     0 %
GPR13     0 %
GPR14     0 %
GPR15     0 %
GPR16     0 %
GPR17     0 %
GPR18     0 %
GPR19     0 %
GPR20     0 %
===== Processing parameters =====
SI         0.000000 MHz
SF         125.7604076 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         2.00

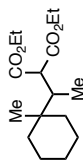
```


¹H spectrum

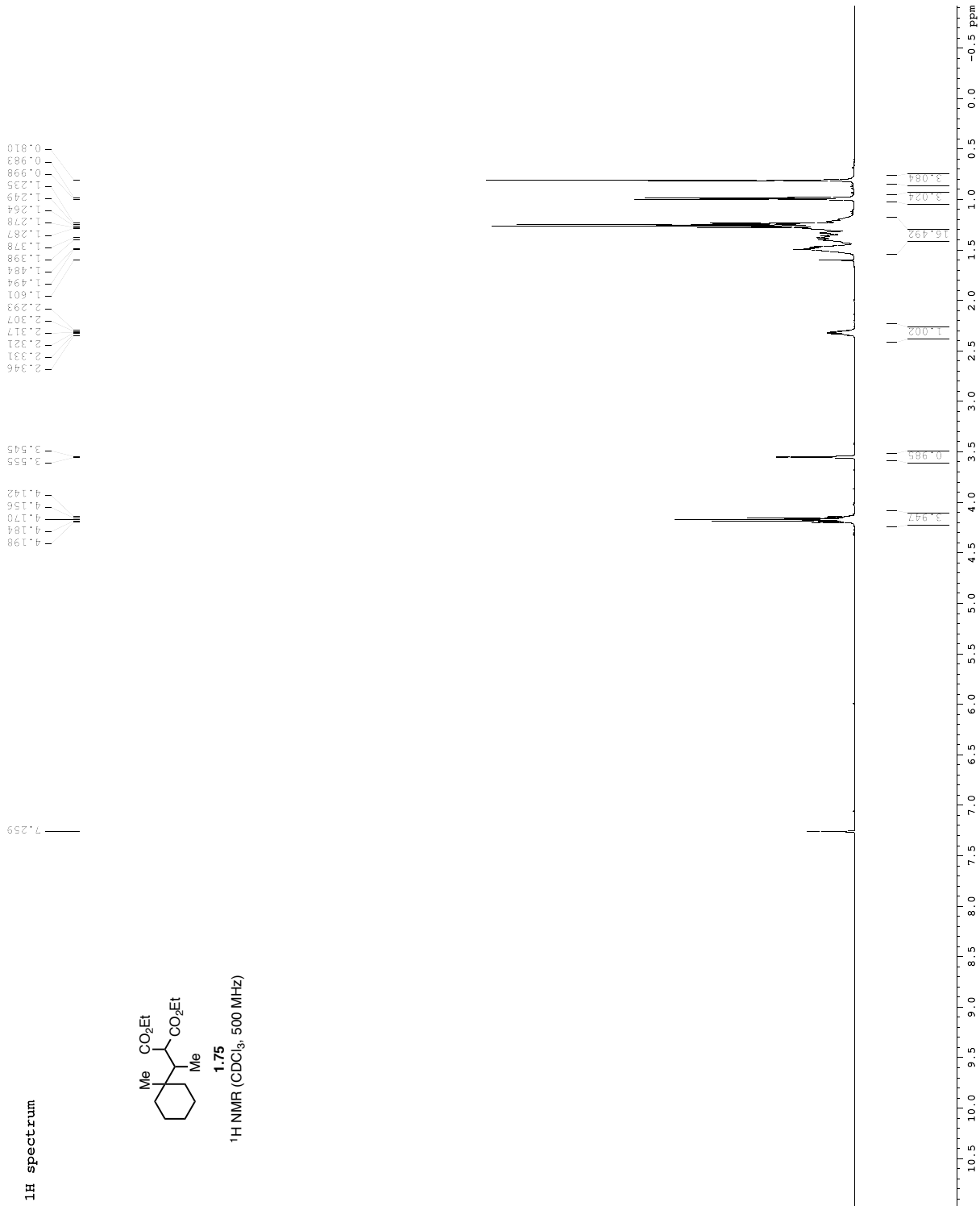


Current Data Parameters
 NAME: CSJ1-041-1
 EXPNO: 2
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20150211
 Time: 17.53
 INSTRUM: cryo500
 PULPROG: zgpg30
 FIDRES: 5 mm QNP1H1
 TD: 65536
 SOLVENT: CDCl3
 NS: 8
 DS: 8
 SWH: 8012.870 Hz
 F2: 500.136277 MHz
 AQ: 2.9998176 sec
 RG: 5
 LB: 62.400 usec
 GB: 0.000000 sec
 PC: 2880.0 KHz
 D1: 0.10000000 sec
 MCREST: 0 sec
 MCWRR: 0.01000000 sec
 ===== CHANNEL f1 =====
 NUC1: 1H
 P1: 7.50 usec
 PL1: 1.60 dB
 SFO1: 500.2230015 MHz
 F2 - Processing parameters
 SI: 65536
 SF: 500.2200311 MHz
 WDW: no
 GB: 0 Hz
 CB: 0
 PC: 4.00

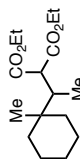


1.75
¹H NMR (CDCl₃, 500 MHz)

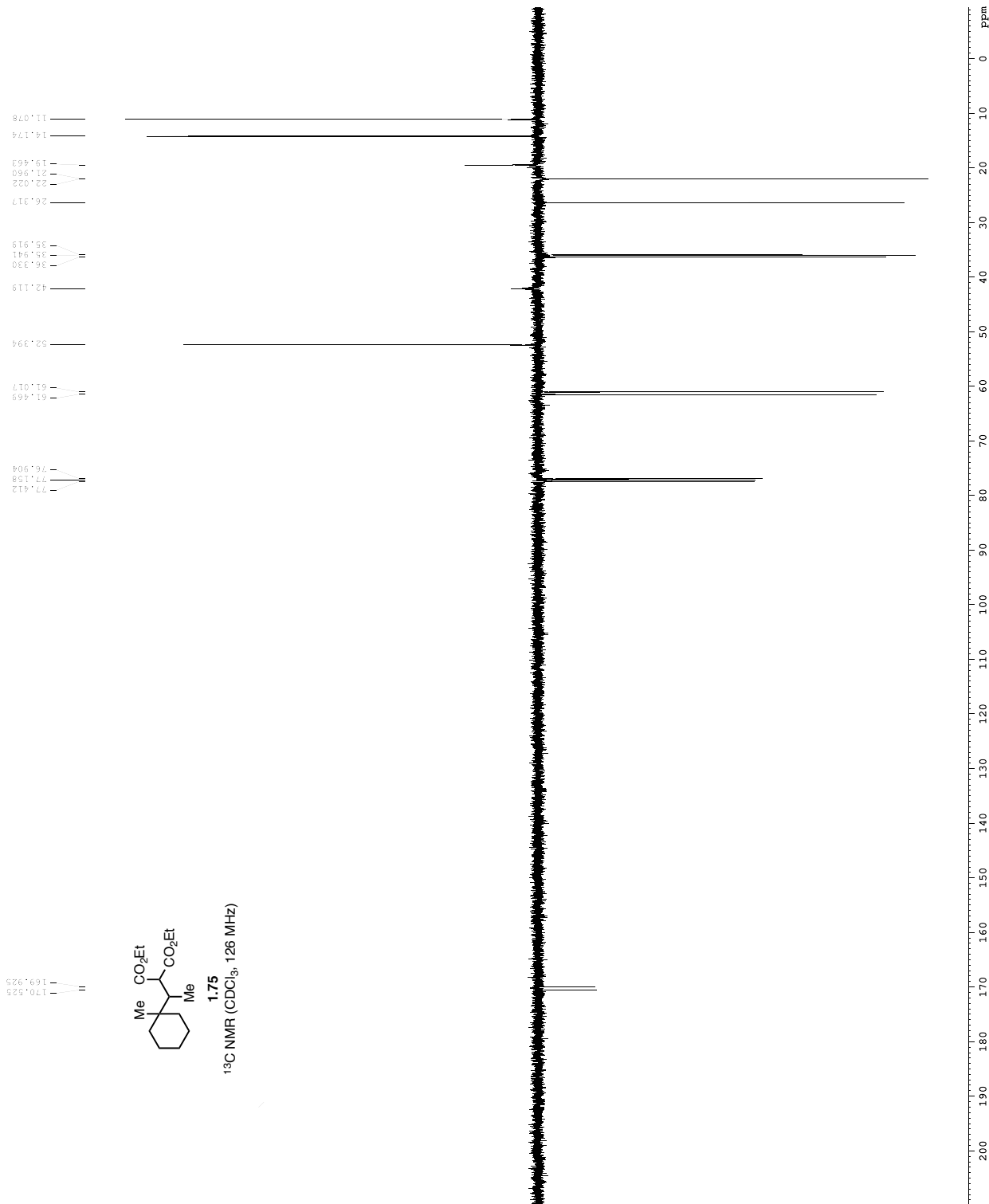


deptq 13c spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)

170.152
169.925



1.75
13C NMR (CDCl₃, 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 CP131 H-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           46
DS           2
SWH          30303.031 Hz
FIDRES       0.462398 Hz
AQ           1.0813440 sec
RG           14396.5
DW           16.500 usec
DE           298.0 usec
TE           298.0 K
CNSRT2       145.0000000
CNSRT12      1.5000000
D1           1.5000000 sec
d2           0.00344828 sec
d12          0.0002000 sec
D16          0.0002000 sec
DELTA        0.0001707 sec
DELTA1       0.0028023 sec
DELTA2       0.0028023 sec
DELTA3       0.00224828 sec
XCHREST      0 sec
MCRRK        0.01500000 sec

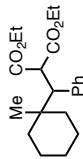
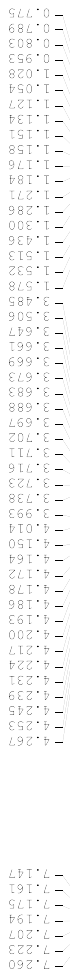
===== CHANNEL f1 =====
NUC1          13C
P1            16.55 usec
PL1           2000.00 usec
PL2           120.00 dB
PL3           120.00 dB
SFO1          125.7942548 MHz
SE2           2.70 dB
SFRAM12       Cpf60comp.4
SFOFE2        0 Hz

===== CHANNEL f2 =====
CHPDRG[2]    waitz16
NUC2          1H
P2            11.75 usec
PL2           15.40 usec
PL3           15.40 usec
PCPD2         100.00 usec
PL12          1.60 dB
PL13          24.50 dB
SFO2          500.2225011 MHz

===== GRADIENT CHANNEL =====
GPRAM11       SINE.100
GPRAM12       SINE.100
GPRAM13       SINE.100
GPA1          0 %
GPA2          0 %
GPA3          0 %
GPA4          0 %
GPA5          0 %
GPA6          0 %
GPA7          0 %
GPA8          0 %
GPA9          0 %
GPA10         0 %
GPA11         0 %
GPA12         0 %
GPA13         0 %
GPA14         0 %
GPA15         0 %
GPA16         0 %
GPA17         0 %
GPA18         0 %
GPA19         0 %
GPA20         0 %

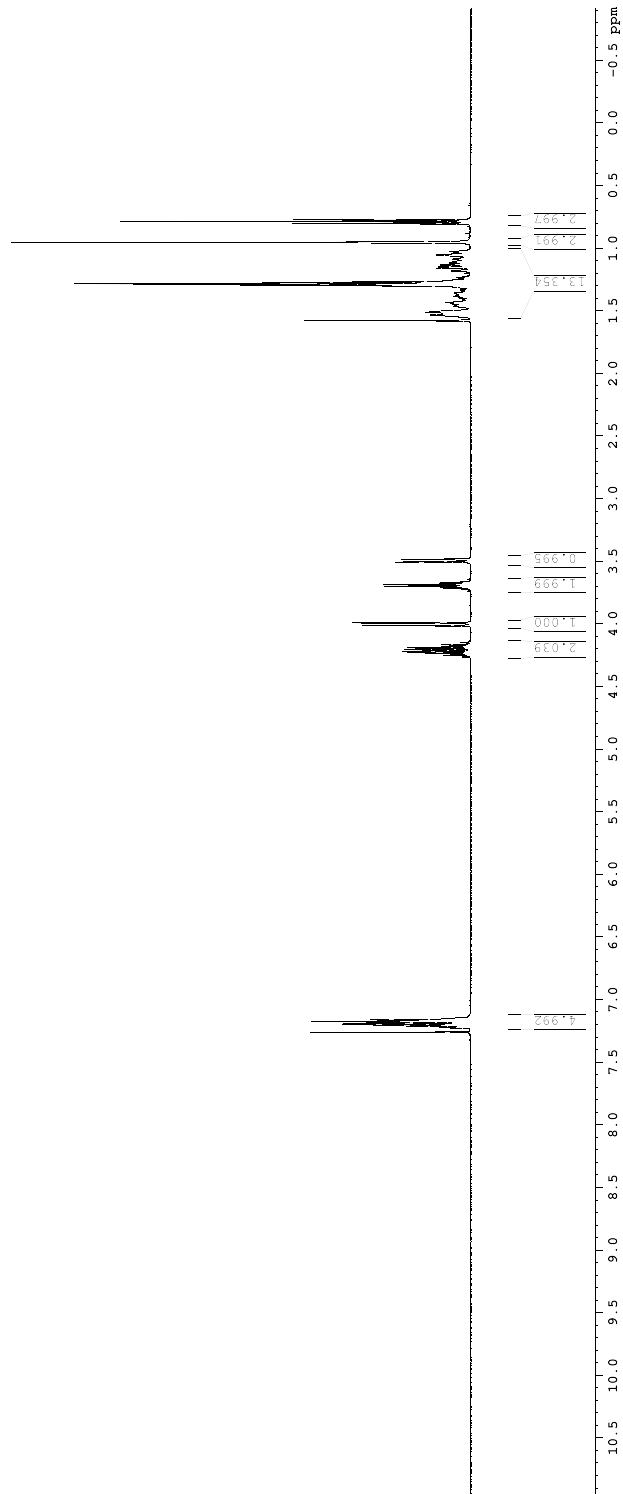
F2 - Processing parameters
SI            65536
SF            125.7804082 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            2.00
  
```

1H spectrum

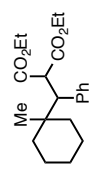


1.76
1H NMR (CDCl₃, 500 MHz)

Current Data Parameters
NAME CKJ1-205-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150417
Time 13.05
INSTRUM cryo500
PROBHD 5 mm CFX500
PULPROG zgpg30
TD 64100
SOLVENT CDCl3
NS 9
DS 2
SWH 8012.820 Hz
FIDRES 0.1125005 Hz
AQ 3.9998100 sec
RG 4.5
SR 62.400 usec
TE 298.0 K sec
D1 0.10000000 sec
MRRST 0 sec
RGWRK 0.01500000 sec
***** CHANNEL f1 *****
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.225915 MHz
F2 - Processing parameters
SI 65536
SF 500.2200305 MHz
WDW no
SSB 0 Hz
LB 0 Hz
GB 0
PC 4.00



depcq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)



1.76
¹³C NMR (CDCl₃, 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 cP1H-1H
PULPROG   deptgppsp
TD         65536
SOLVENT   CDCl3
NS         128
DS         4
AQ         3030.938 Hz
RG         0.462388 Hz
RG         1.0813440 sec
RG         5160.6
DE         16.500 usec
DE         6.00 usec
TE         298.0 K
CNS12     145.000000
CNS112    1.5000000
D1         0.0000000 sec
D2         0.0000000 sec
D3         0.0000000 sec
D4         0.0002000 sec
D5         0.0002000 sec
D6         0.0002000 sec
DELTA     0.0001707 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
PL1        2000.00 usec
PL2        120.00 dB
PL3        -1.00 dB
SFO1       125.7942598 MHz
SF02       500.2223011 MHz
SFOFF2     0 Hz

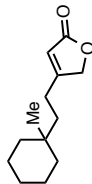
===== CHANNEL f2 =====
CPDPRG12  wait16
NUC2       1H
P2         11.55 usec
PL2        7.70 usec
PL3        15.40 usec
PCPD2     100.00 usec
PL2        1.60 dB
PL3        24.50 dB
SFO2       500.2223011 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]  SINE.100
GPNAM[2]  SINE.100
GPNAM[3]  SINE.100
GPX1      0 %
GPX2      0 %
GPX3      0 %
GPA1      0 %
GPA2      0 %
GPA3      0 %
GZ1       31.00 %
GZ2       31.00 %
GZ3       31.00 %
P16       1000.00 usec

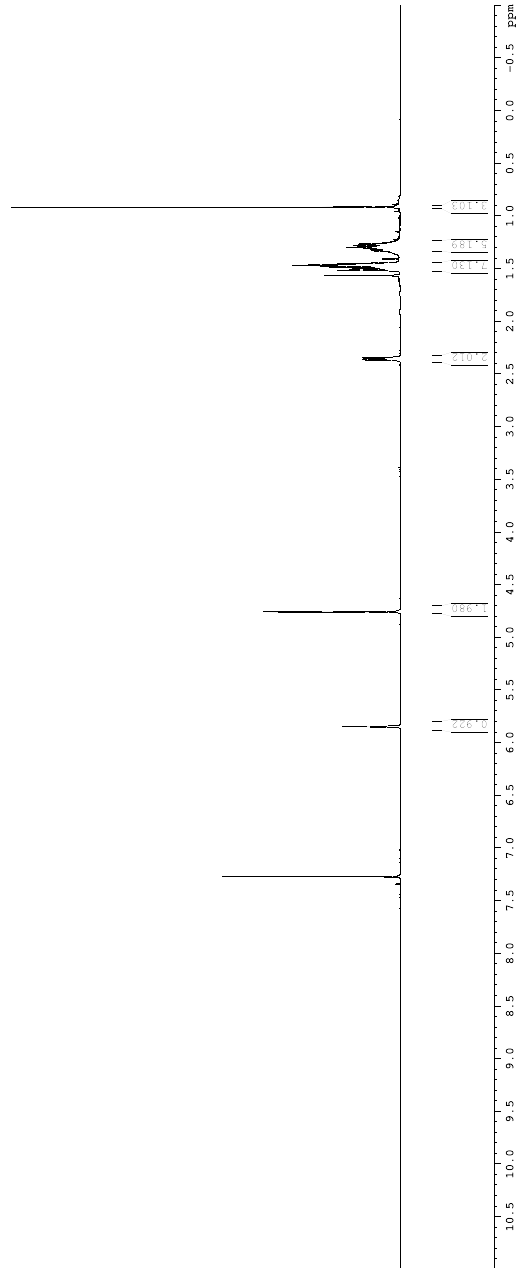
F2 - Processing parameters
SI         65536
SF         125.7804080 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
  
```

YS-II-225B

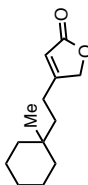
Current Data Parameters
NAME YS-II-225B
PROCNO 1
===== Acquisition Parameters =====
Date_ 01/02/10
Time 12:40
INSTRUM spect
PULPROG zgpg30
PROBHD 5 mm TBI 13113
PULPROG 2930
SOLVENT CDCl3
NS 8
DS 2
SS 8615.962 Hz
AQ 0.150010 Hz
RG 1.9399500 sec
DQ 52.000 usec
DE 14.5% usec
DI 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342000 MHz
NUC1 13C
P1 8.00 usec
PL1 23.0141356 dB
SFO2 - Processing Parameters
SF 600.1300291 MHz
NUC 13C
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



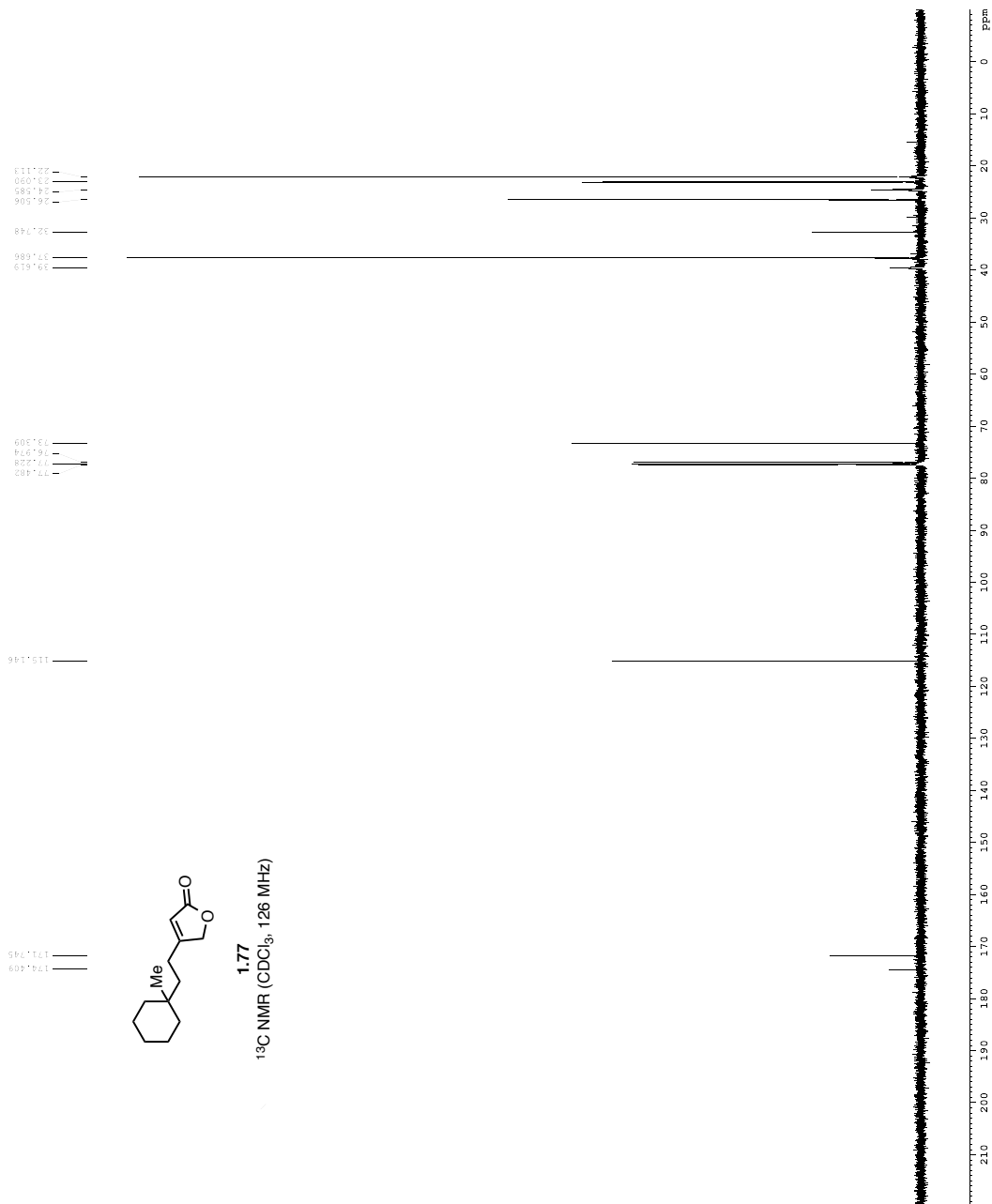
1.77
¹H NMR (CDCl₃, 600 MHz)



594.741
594.741



1.77
¹³C NMR (CDCl₃, 126 MHz)



```

Current Data Parameters
=====
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
=====
Date_      20110822
Time       8.32
INSTRUM    cryo500
PROBHD     5 mm CPY1H1
PULPROG    zgpg30
TD         65536
SOLVENT    CDCl3
NS         136
DS         4
SWH        30300.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813450 sec
RG         18.500
WDW        EM
SSB        0
DE         6.00 usec
TE         300.2 K
C11        0.06296.0 K
C12        0.0300000 sec
D16        0.0002000 sec
d17        0.0019600 sec
MKREST     0 sec
NAME       1.77
=====
===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        0.00 dB
PL2        0.00 dB
PL3        0.00 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
SFO1       125.7942548 MHz
SF1        2.70 GHz
SFO2        0.00 MHz
SFM1[1]    CpP60.0.5.70.0 GB
SFM1[2]    CpP60.0.5.70.0 GB
SFOFF1     0 Hz
SFOFF2     0 Hz
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P2         100.00 usec
PL2        0.00 dB
PL3        1.60 dB
PL4        0.00 dB
PL5        0.00 dB
PL6        0.00 dB
SFO2       500.2225011 MHz
===== GRADIENT CHANNEL =====
GPM1[1]    SINE.100
GPM1[2]    SINE.100
GAX1       0 %
GAX2       0 %
GPY1       0 %
GPY2       0 %
GZ1        0 %
GZ2        0 %
P16        1000.00 usec
F2 - Processing parameters
=====
SI         65536
SF         125.7803954 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         1.00 Hz
FC         2.00
    
```

¹H spectrum

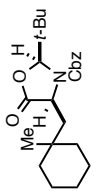
```

Current Data Parameters
NAME          GAD1-135-NB2
EXPNO         1
PROCNO        1

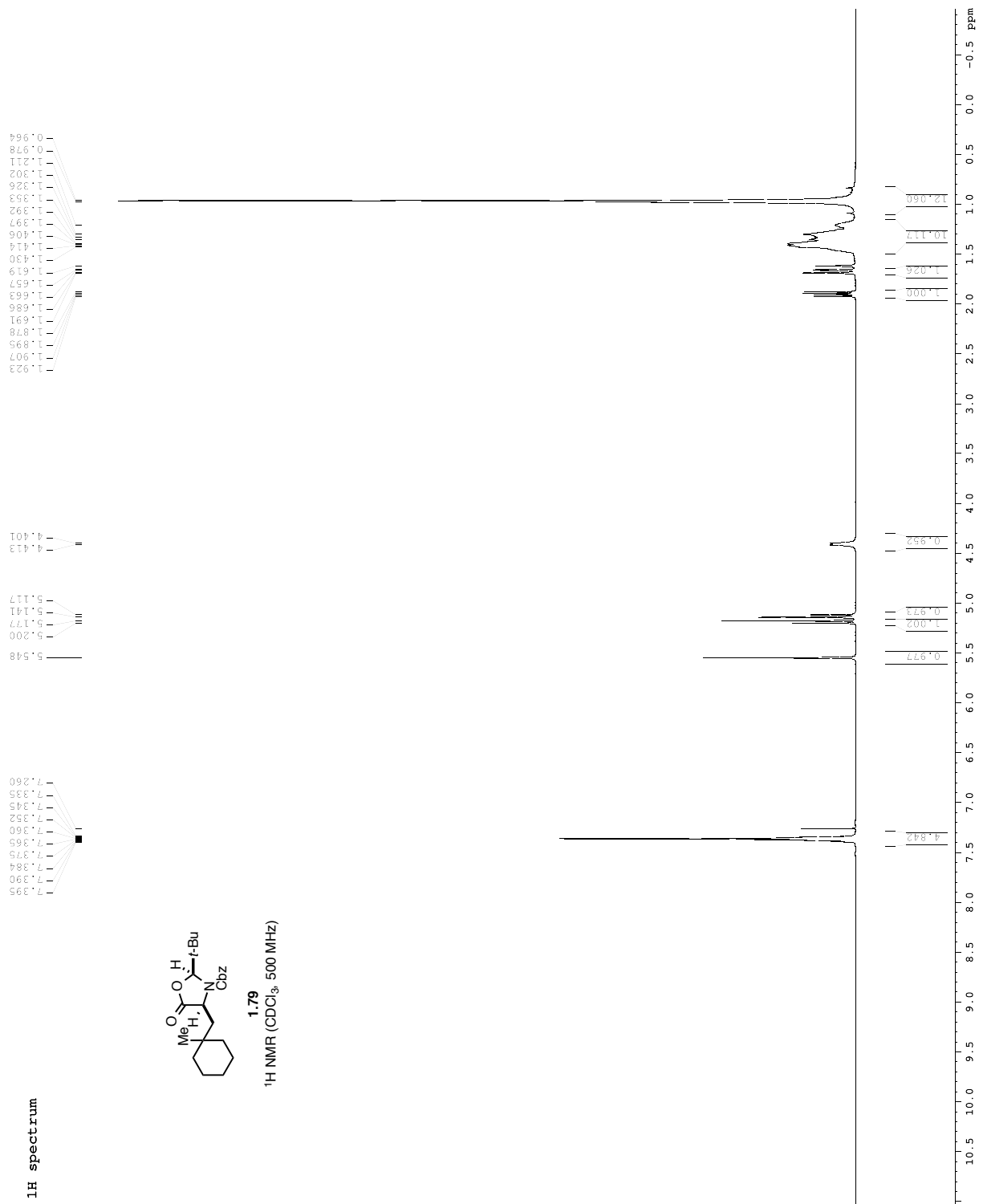
F2 - Acquisition Parameters
Date_         20150924
Time          14.46
INSTRUM       cryo500
PROBHD        5 mm CPTCI 1H-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            2
SWH           8012.820 Hz
AQ            0.686373 sec
RG            512
RG2           3.2
DW            62.400 usec
DE            6.00 usec
TE            298.0 K
D1            0.10000000 sec
MCBREST       0 sec
MCRRK         0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            7.50 usec
PL1          1.60 dB
SFO1         500.2235015 MHz

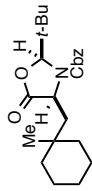
F2 - Processing parameters
SI            500.2200308 MHz
SF           65536
WDW           0
SSB           0 Hz
LB            0
GB            0
PC            4.00
  
```



1.79
¹H NMR (CDCl₃, 500 MHz)



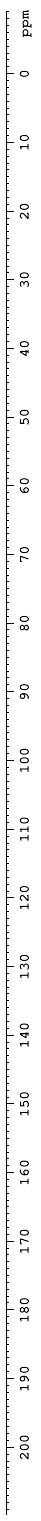
deptq 13C spectrum with 1H decoupling (CH & CH3 one way up; C, CH2 and solvent the other)

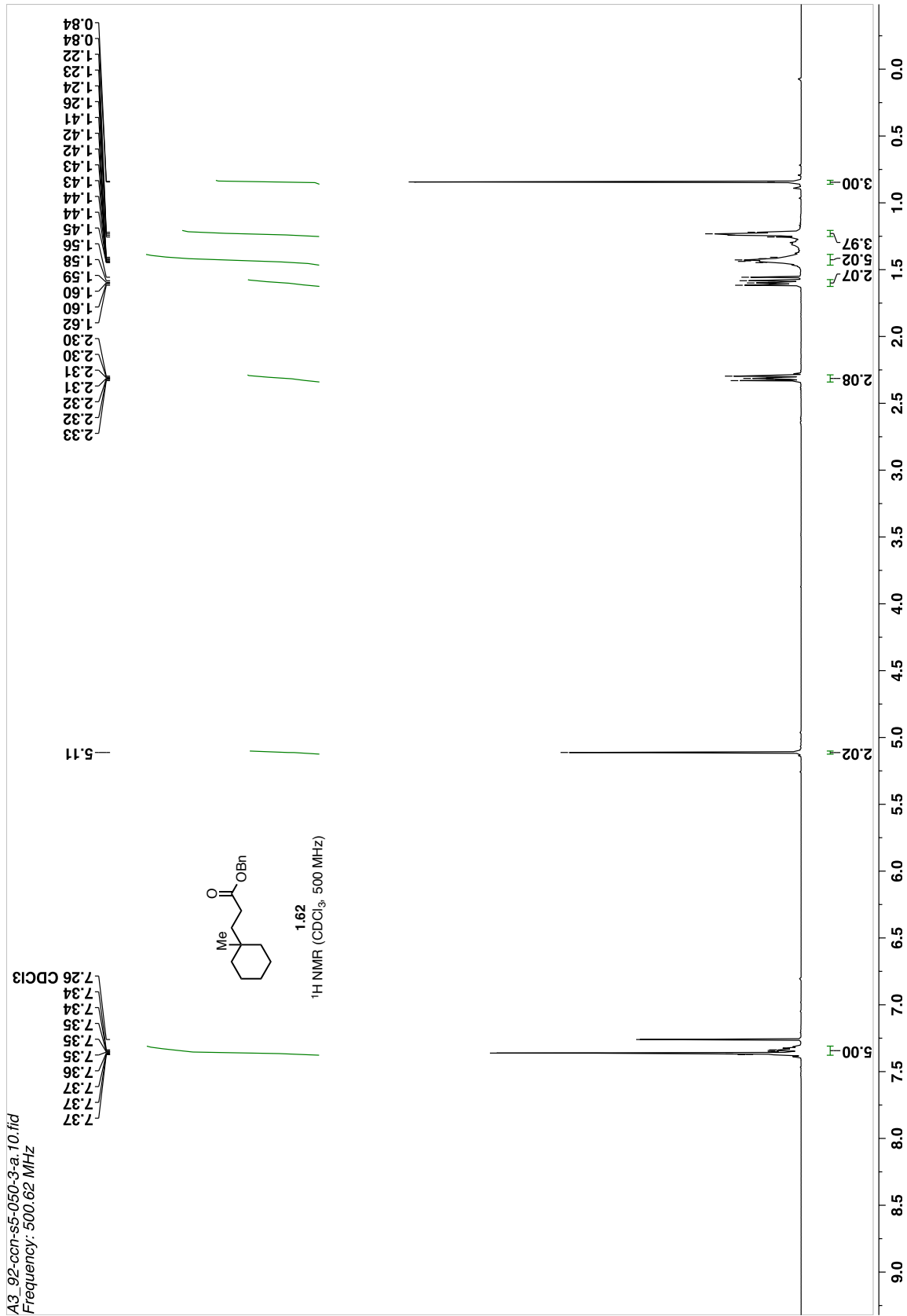


1.79
13C NMR (CDCl₃, 126 MHz)

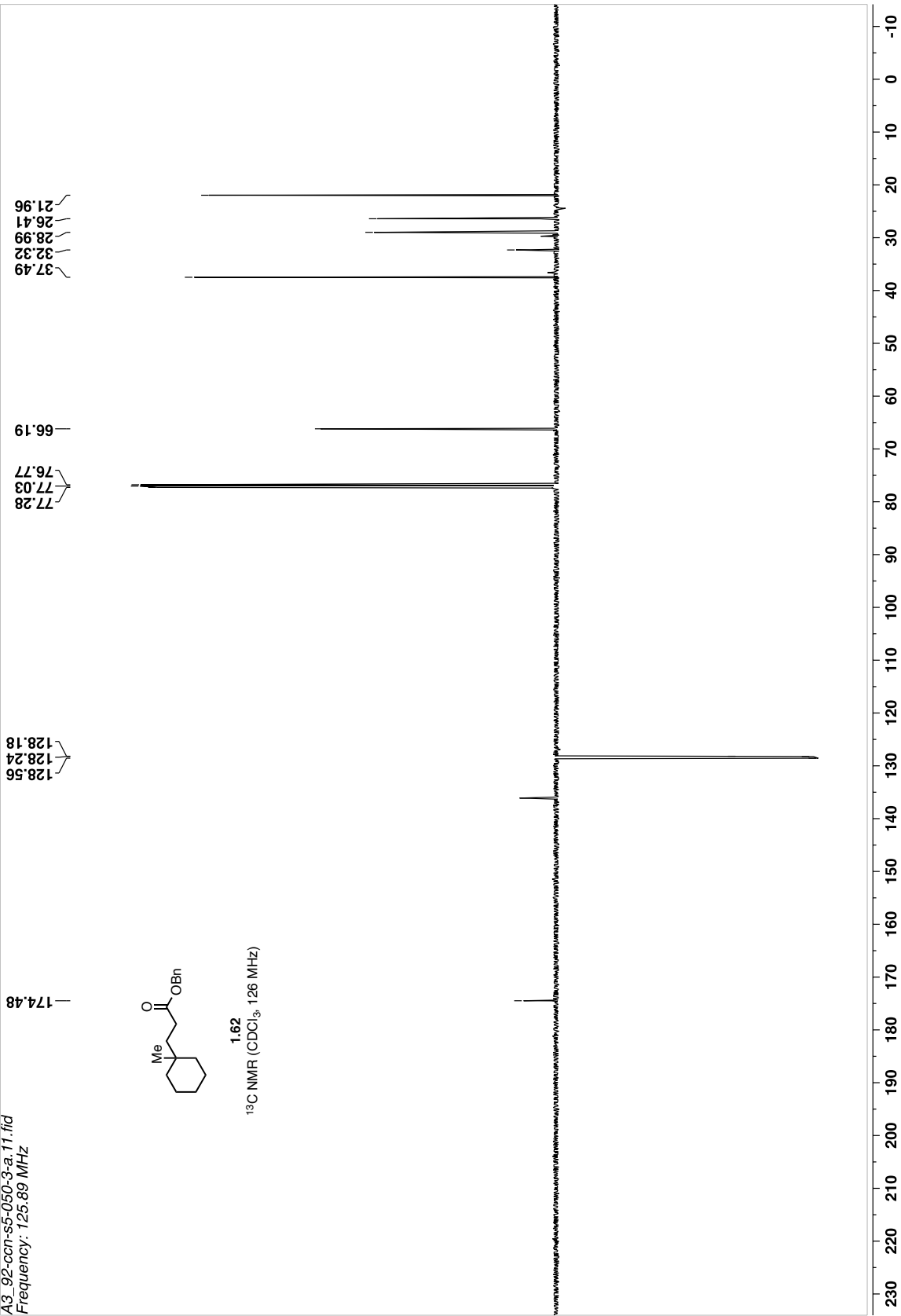
```

Current Data Parameters
NAME          CRJ1-082-1
EXPNO         2
PROCNO        1
F2 - Acquisition Parameters
Date_         20150211
Time          17.46
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PROBHD        5 mm CPTCI 1H-
PULPROG       deptqgssp
TD            65536
SOLVENT       CDCl3
NS            64
DS            4
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
CNS1Z         145.0000000
CNS1Z2        11.5000000
AQ2           0.0034828 sec
AQ3           0.0034828 sec
AQ4           0.0002000 sec
D12           0.0002000 sec
D16           0.0002000 sec
DELTA         0.0001707 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
PL1           2000.00 dB
PL0           120.00 dB
PL2           -1.00 dB
PL3           -1.00 dB
SFO1          125.7942548 MHz
SFO2          2.70 dB
SFO3          500.2228011 MHz
SFO4          500.2228011 MHz
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
P2            11.55 usec
PL2           15.40 dB
PL3           100.00 dB
PCPD2         1.60 dB
PL4           1.60 dB
PL5           1.60 dB
SFO2          500.2228011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]     SINE.100
GPNAM[2]     SINE.100
GPNAM[3]     SINE.100
GEX1         0 %
GEX2         0 %
GEX3         0 %
GEX4         0 %
GEX5         0 %
GEX6         0 %
GEX7         0 %
GEX8         0 %
GEX9         0 %
GEX10        0 %
GEX11        0 %
GEX12        0 %
GEX13        0 %
GEX14        0 %
GEX15        0 %
GEX16        0 %
F2 - Processing Parameters
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SF            125.7604024 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            2.00
  
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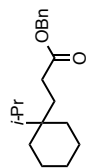




A3_92-con-s5-050-3-a.T1.fid
Frequency: 125.89 MHz

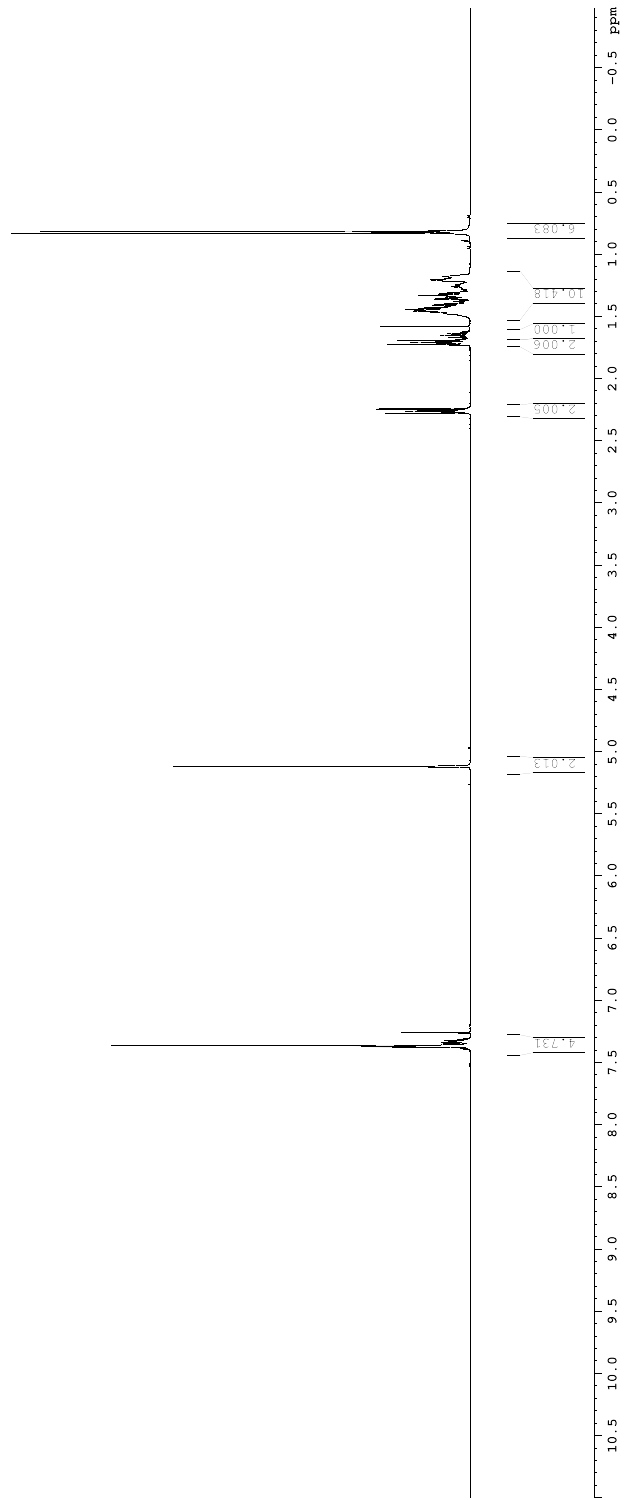


¹H spectrum

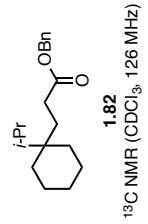


1.82
¹H NMR (CDCl₃, 500 MHz)

Current Data Parameters
 NAME: G01132-Exp1
 EXPNO: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_ : 20130414
 Time : 14.406
 INSTRUM: cryo500
 PROBED: 5 mm CPXI 1H-
 PULPROG: zgpg30
 ACQPRG: 400014
 SOLVENT: CDCl3
 NS: 8
 DS: 2
 SWH: 8012.620 Hz
 FIDRES: 0.600000 Hz
 AQRES: 2.9398176 sec
 SFO1: 500.2235015 MHz
 DW: 62.400 usec
 DE: 6.00 usec
 TE: 296.0 K
 D1: 0.10000000 sec
 MCRST: 0 sec
 MCRK: 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: 500.2200111 MHz
 MDW: 0 Hz
 SSB: 0 Hz
 GB: 0 Hz
 PC: 4.00



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



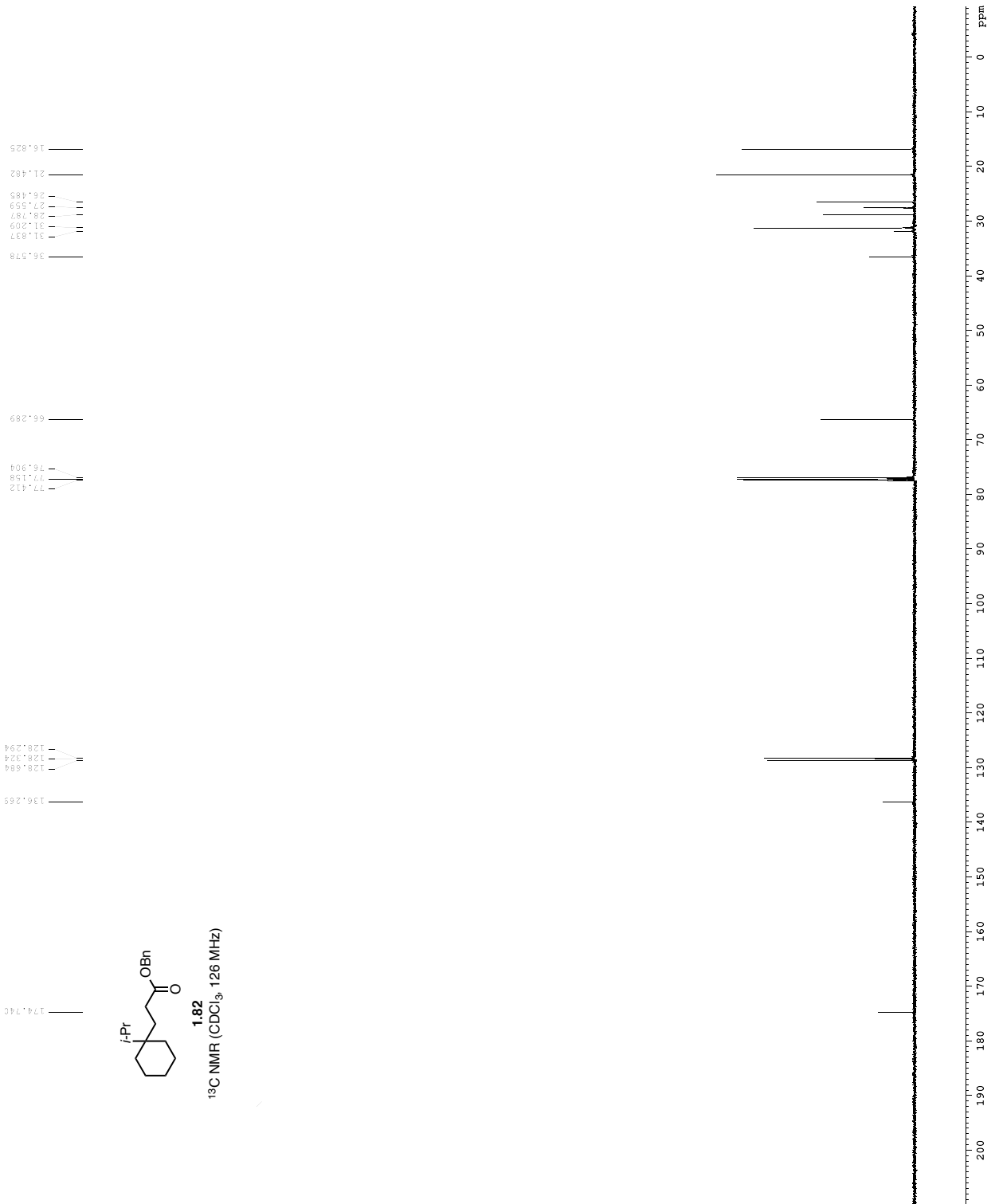
Current Data Parameters
 NAME CRJ1-152-pure
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20150317
 Time 14.08
 INSTRUM cryo500
 PROBHD 5 mm CPTCI IH-
 PULPROG Spinechop3-rgp-prd
 ID 65536
 SOLVENT CDCl3
 NS 64
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 7298.2
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 1.000000 sec
 d11 0.000000 sec
 D12 0.000000 sec
 D13 0.000000 sec
 D14 0.000000 sec
 D15 0.000000 sec
 D16 0.000000 sec
 D17 0.000000 sec
 ACREST 0 sec
 ACQMEK 0.0150000 sec
 F2 33.10 usec

==== CHANNEL f1 =====
 NUC1 ¹³C
 F1 13C
 F1 16.55 usec
 P1 40.00 usec
 P2 2000.00 usec
 F10 120.00 dB
 P11 -1.00 dB
 SF01 125.7942548 MHz
 SF1 2.70 dB
 SF2 2.70 dB
 SFOFF1 Cyp60, 0.5, 20.1
 SFOFF2 C-p60comp, 4
 SFOFF2 0 Hz

==== CHANNEL f2 =====
 CPDPRG12 waltz16
 NUC2 ¹H
 F1 100.00 usec
 F2 1.60 dB
 F12 24.50 dB
 SFO2 500.2225011 MHz

==== GRADIENT CHANNEL =====
 GPNAM11 SINE, 100
 GPNAM12 SINE, 100
 GPC1 0 %
 GPC2 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
 XWDW 0 EM
 LB 1.00 Hz
 GB 0
 FC 2.00

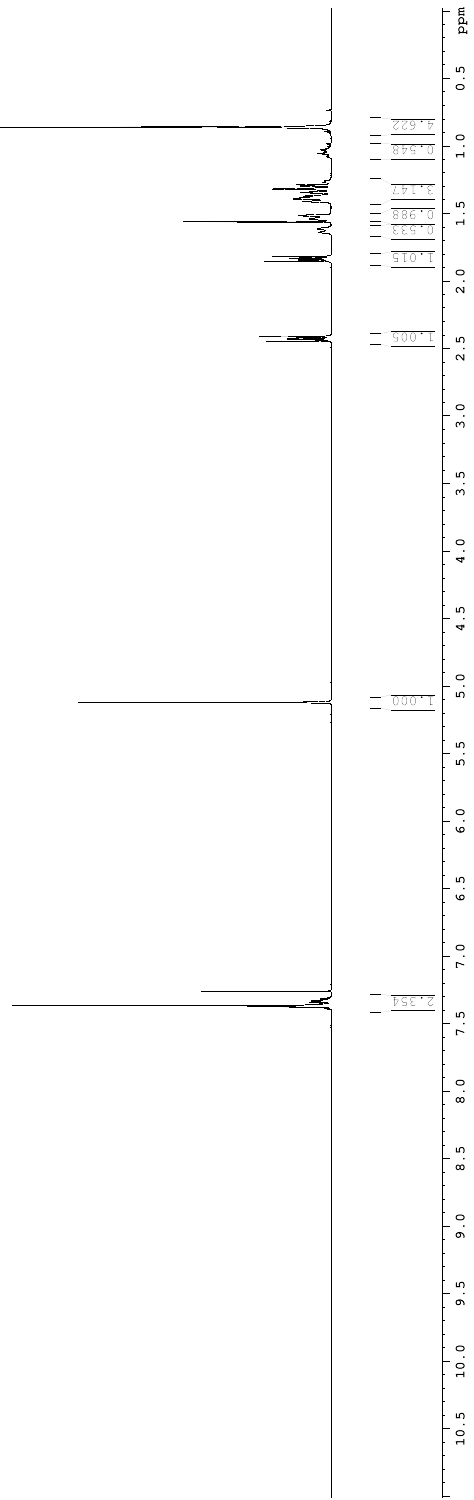
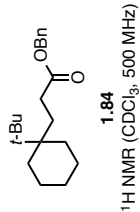


¹H spectrum

7.379
7.375
7.373
7.372
7.364
7.358
7.351
7.342
7.337
7.334
7.328
7.260

5.120
4.444
4.438
4.432
4.426
4.420
4.414
4.408
4.402
4.396
4.390
4.384
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4.372
4.366
4.360
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Current Data Parameters
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 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
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 Time 14.14
 INSTRUM spect
 PROBHD 5 mm CPY131H
 PULPROG zgpg30
 TD 48074
 SOLVENT CDCl3
 NS 2
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.166677 Hz
 AQ 2.3998176 sec
 RG 5
 DD 62.400 usec
 DE 5.400 usec
 TE 298.0 K
 D1 0.10000000 sec
 MCREST 0 sec
 HGRNK 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 PL 0.00 dB
 SFO1 500.225015 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.2200303 MHz
 WF 4096
 SSF 0
 LB 0 Hz
 GB 0
 PC 4.00



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

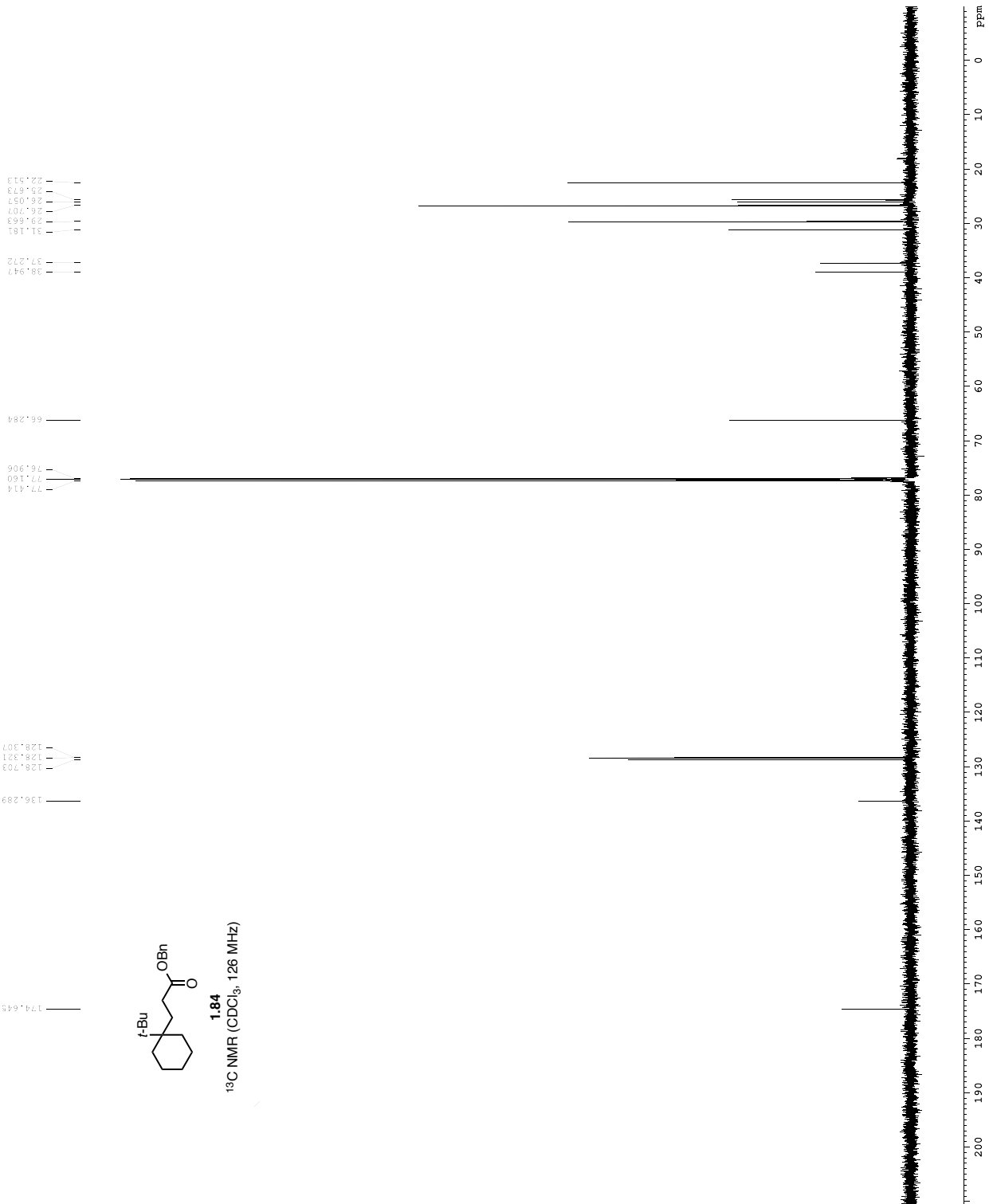


¹³C NMR (CDCl₃, 126 MHz)

```

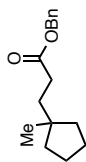
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EXPNO    2
PROCNO   1
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Date_    20150317
Time     14.17
INSTRUM  cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  Spinechop3Sgp-prd
TD        65536
SOLVENT  CDCl3
NS        64
DS        4
SWH       30303.031 Hz
FIDRES   0.462388 Hz
AQ        1.0813440 sec
RG        7298.2
EW        16.500 usec
DE        6.00 usec
TE        298.0 K
D1        1.000000 sec
d11       0.000000 sec
D16       0.0002000 sec
d17       0.00019600 sec
RGREST    0 sec
RGXPRK    0.01500000 sec
RGYPRK    33.10 usec
F2
===== CHANNEL f1 =====
NUC1      13C
P1        16.55 usec
PL1       0.000000 usec
PR1       2000.00 dB
F10       120.00 MHz
PL10      -1.00 dB
SFO1      125.7942548 MHz
SF1        2.70 dB
SP2        2.70 dB
SFO2       0 Hz
SFR1       0 Hz
SFR2       0 Hz
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
P2        100.00 usec
PL2       0.000000 usec
PR2       1.60 dB
F20       24.50 MHz
SFO2      500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM1[1] SINE_100
GPNAM1[2] SINE_100
GPM1      0 %
GPM2      0 %
GPM3      0 %
GPM4      0 %
GPM5      0 %
GPM6      0 %
GPM7      0 %
GPM8      0 %
GPM9      0 %
GPM10     0 %
GPM11     0 %
GPM12     0 %
GPM13     0 %
GPM14     0 %
GPM15     0 %
GPM16     0 %
F2 - Processing parameters
SI        65536
SF        125.7804077 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        2.00

```

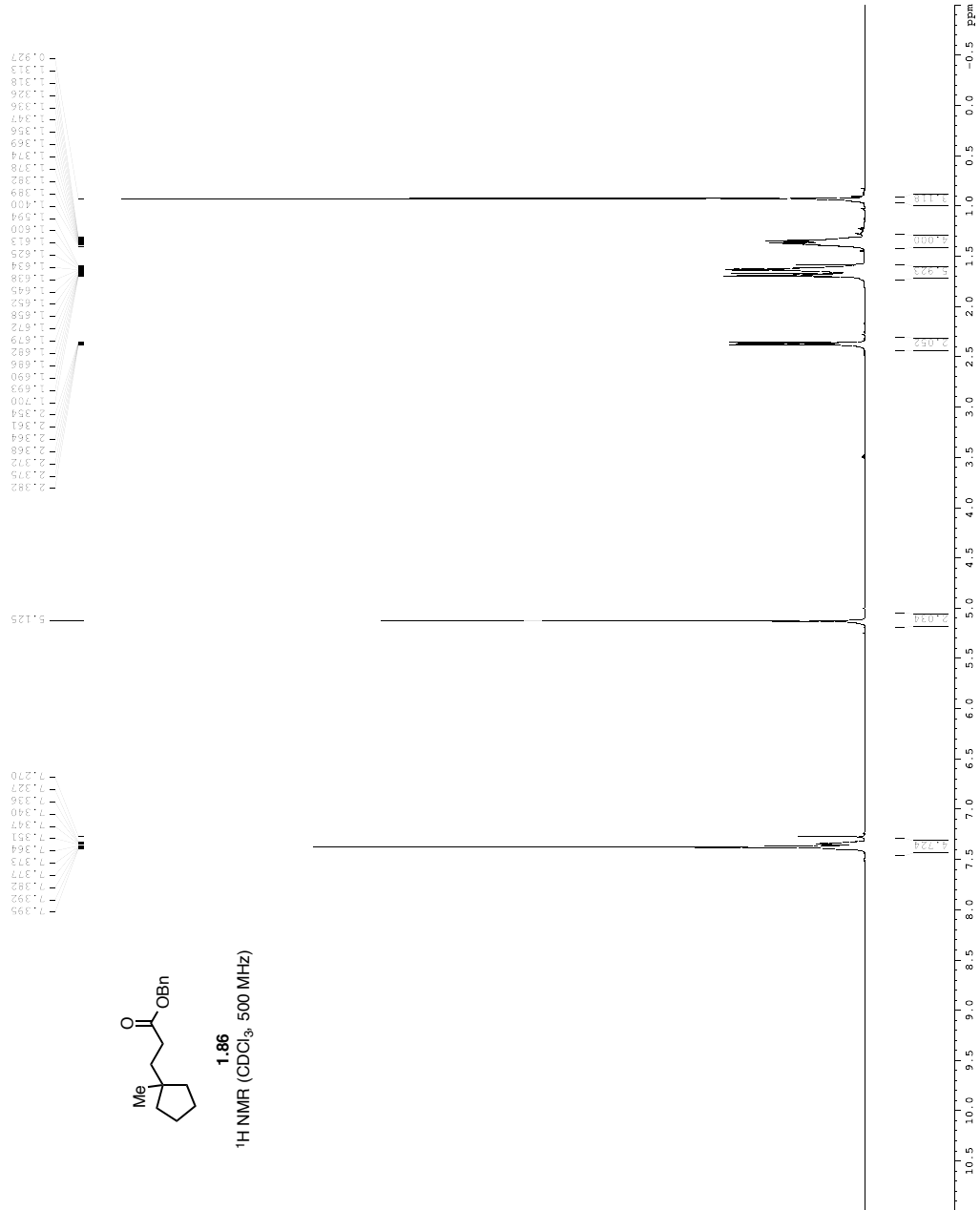


YS-II-254A

Current Data Parameters
NAME YS-II-254A
PROCNO 1
===== Acquisition Parameters =====
Date_ Time 01/02/15 14:55
Time 14:55
INSTRUM spect
PULPROG zgpg30
PROCNO 5 300 TBA 13013
PULPROG 2930
SOLVENT CDCl3
NS 8
DS 2
SS 8615.362 Hz
AQ 0.150010 Hz
RG 1.9399500 sec
DQ 52.000 usec
DE 14.5% usec
DI 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342000 MHz
NUC1 13
P1 8.00 usec
PL1 23.0141356 dB
===== Processing Parameters =====
SI 65336
SF 600.1300300 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



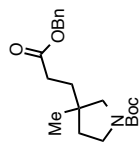
1.86
1H NMR (CDCl₃, 500 MHz)



A2_112-ccn-s5-048-a.10.tif
Frequency: 500.46 MHz

7.39
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7.31
7.26

3.46
3.39
3.38
3.38
3.37
3.37
3.36
3.36
3.35
3.34
3.30
3.30
3.14
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3.10
3.08
3.07
3.05
3.02
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2.38
2.37
2.37
2.36
2.36
2.35
2.35
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1.75
1.73
1.68
1.67
1.65
1.64
1.63
1.62
1.61
1.59
1.58
1.57
1.45
1.01



¹H NMR (CDCl₃, 500 MHz)

Integration values: 1.88, 2.00, 1.92, 2.83

4.87

2.02

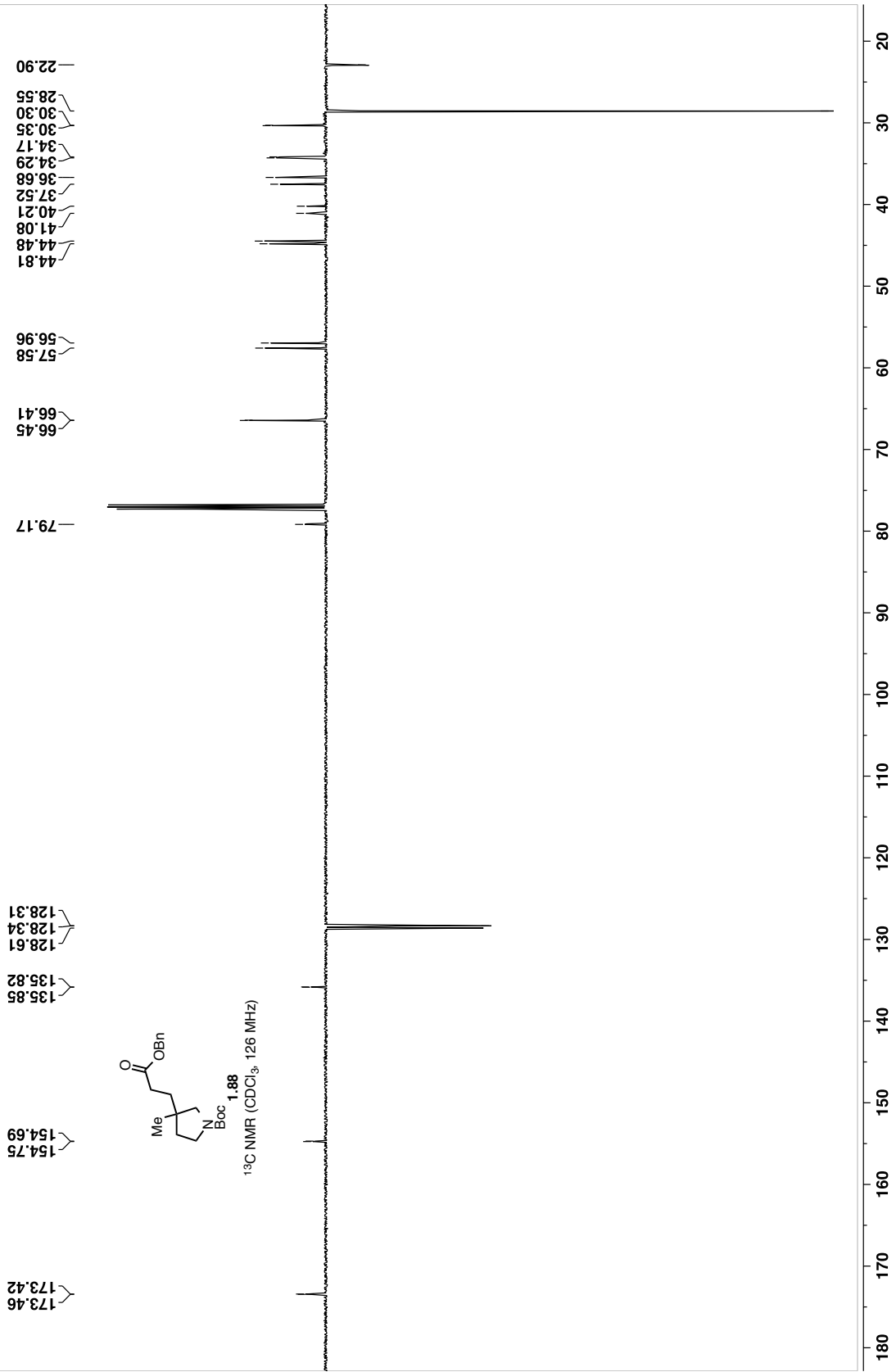
0.94
0.94

1.92

1.87
2.50
8.80
2.83

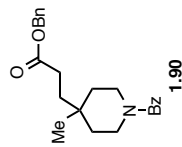
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

A2_112-ccn-s5-048-a.11.fid
Frequency: 125.85 MHz

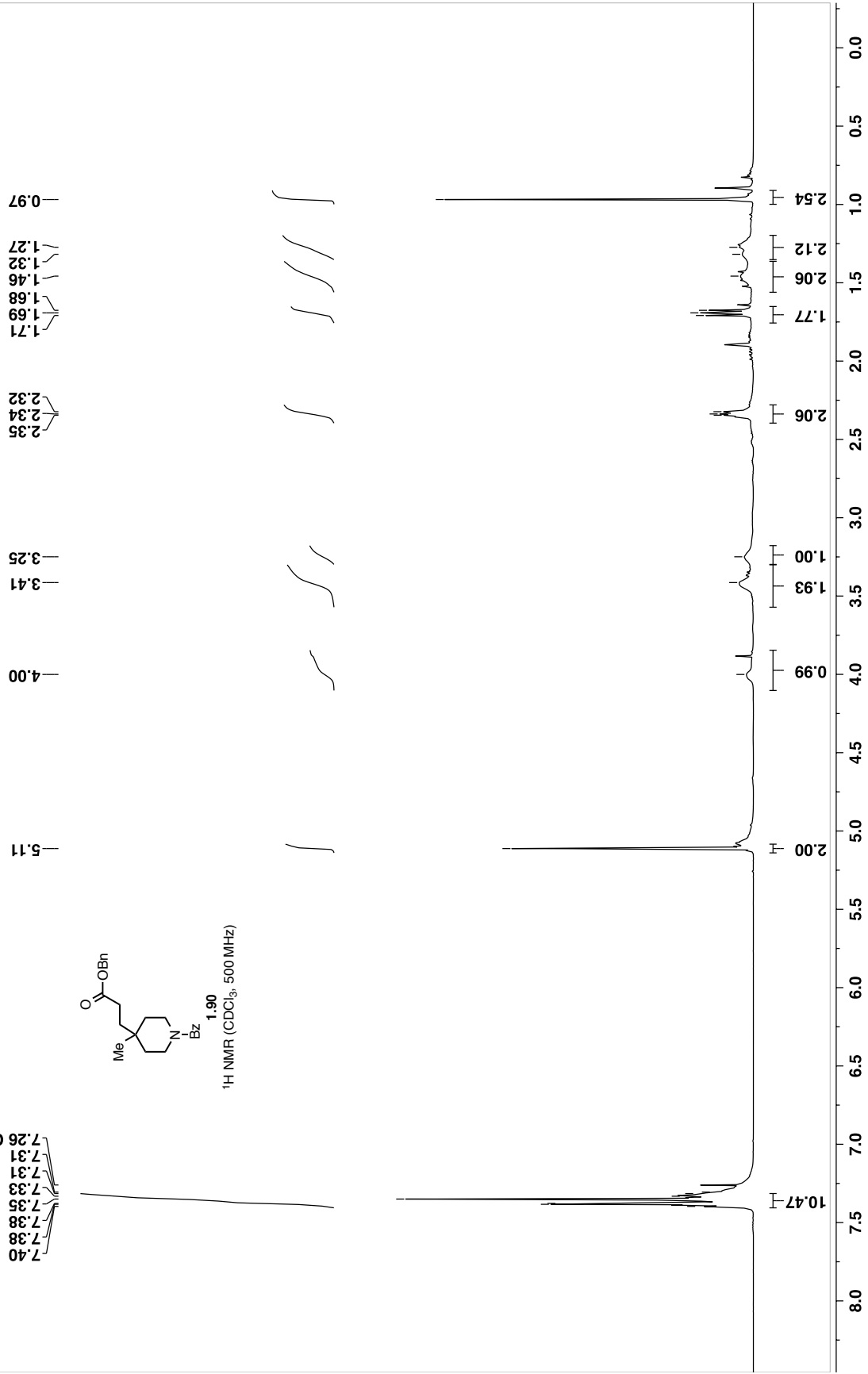


A3_97-ccn-s5-097-2-a.10.fid
Frequency: 500.62 MHz

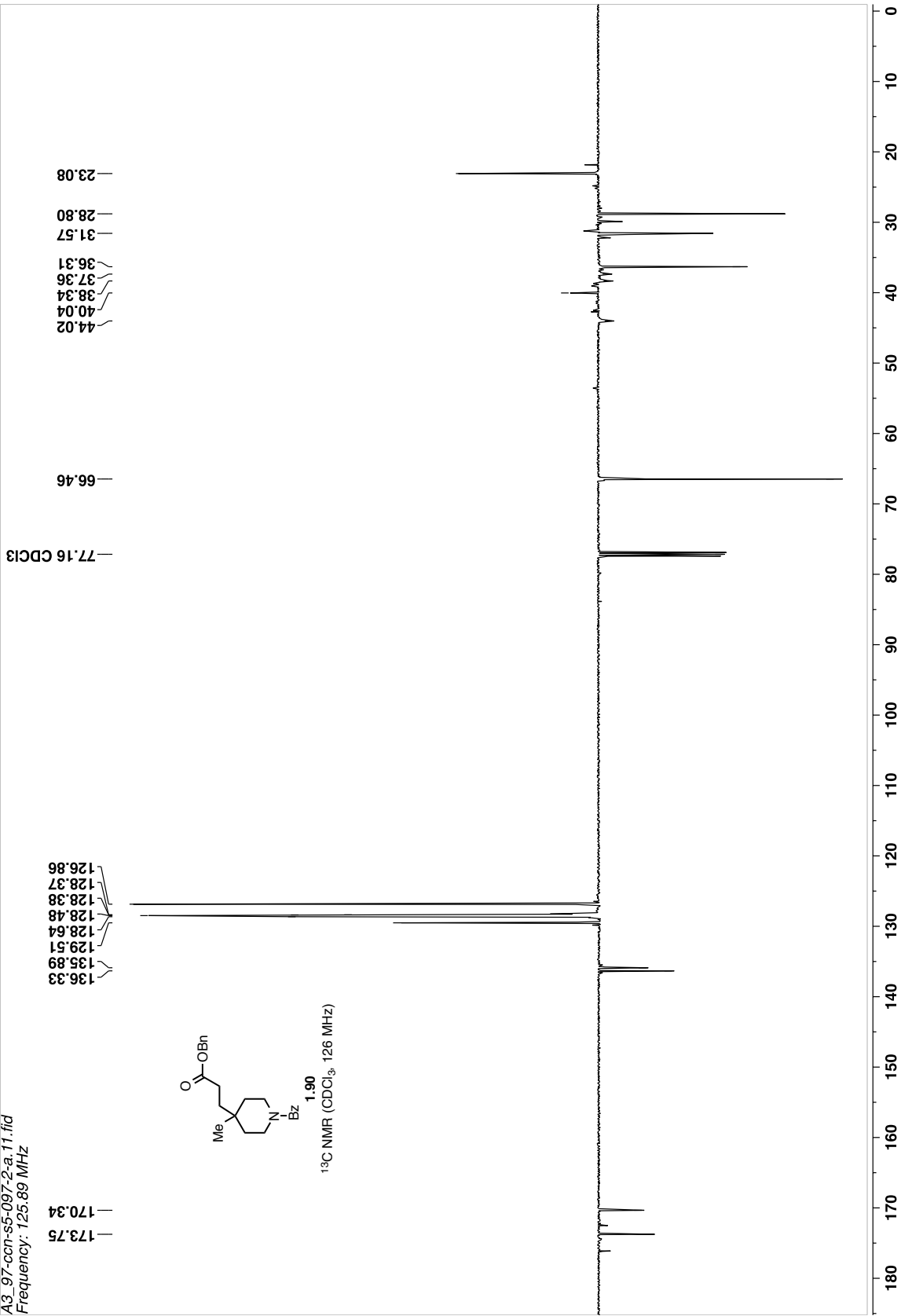
7.40
7.38
7.38
7.35
7.33
7.31
7.26 CDCl₃



¹H NMR (CDCl₃, 500 MHz)



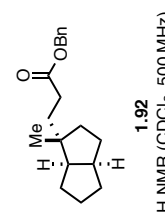
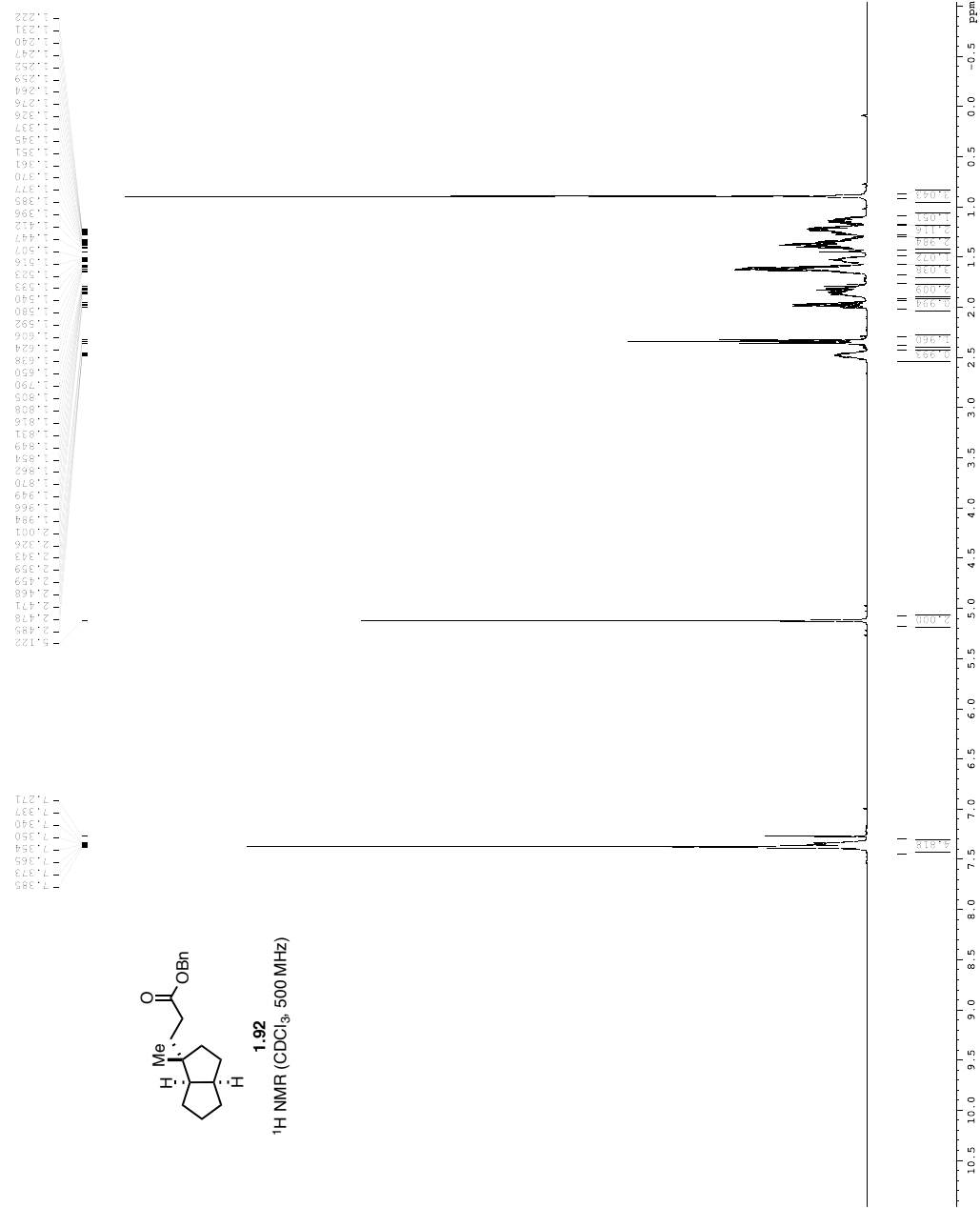
A3_97-con-s5-097-2-a.11.fid
Frequency: 125.89 MHz

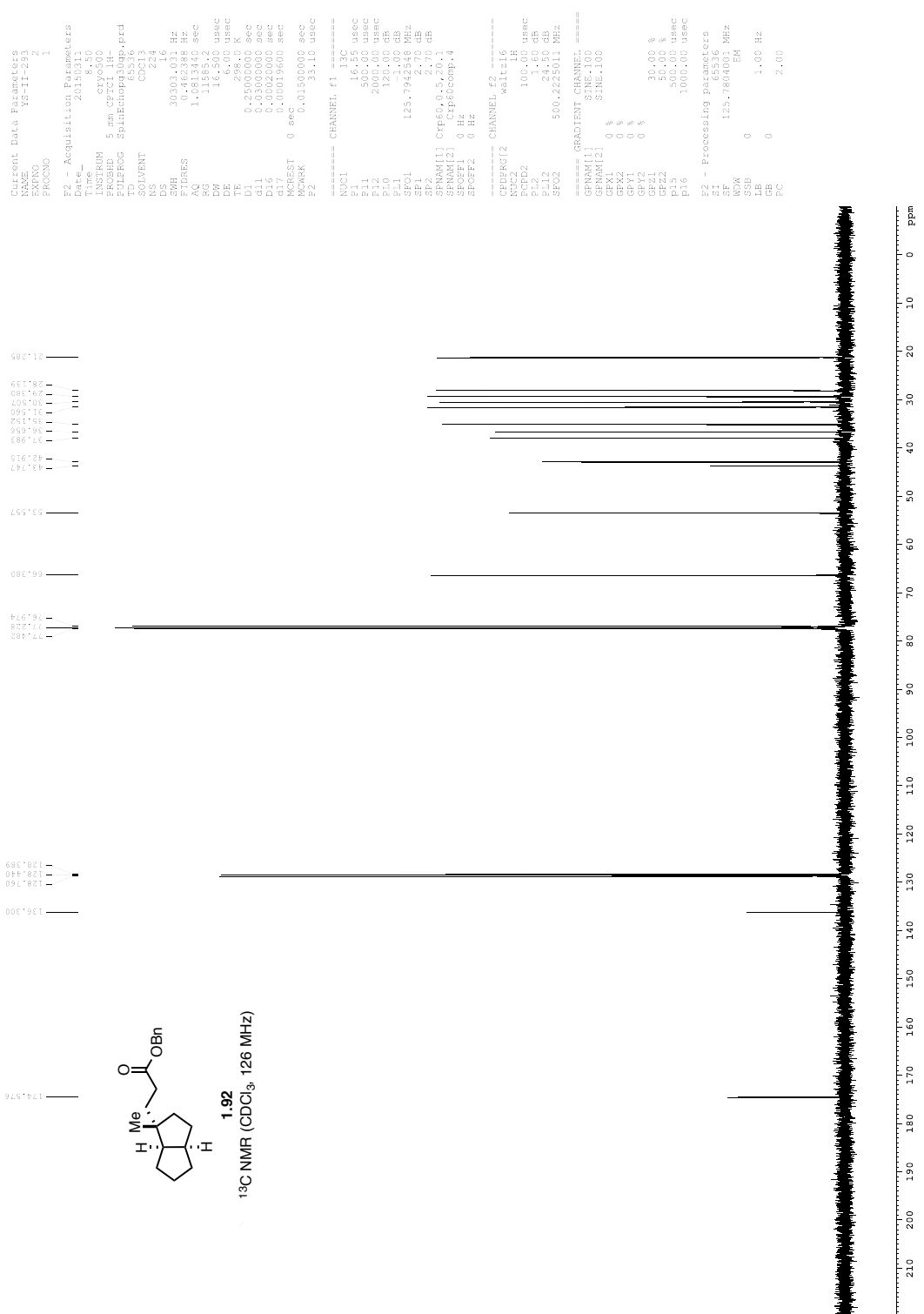


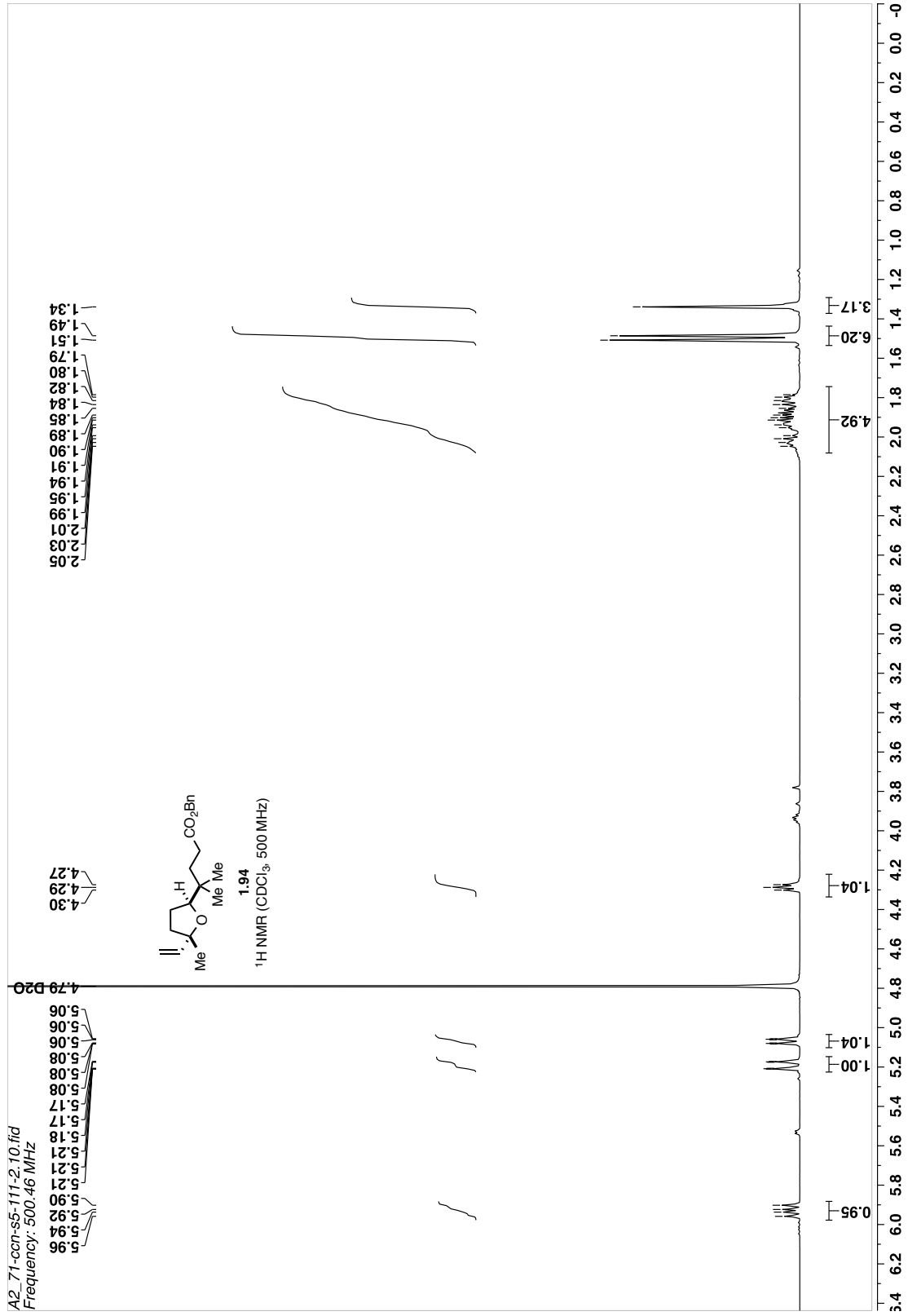
YS-II-293

```

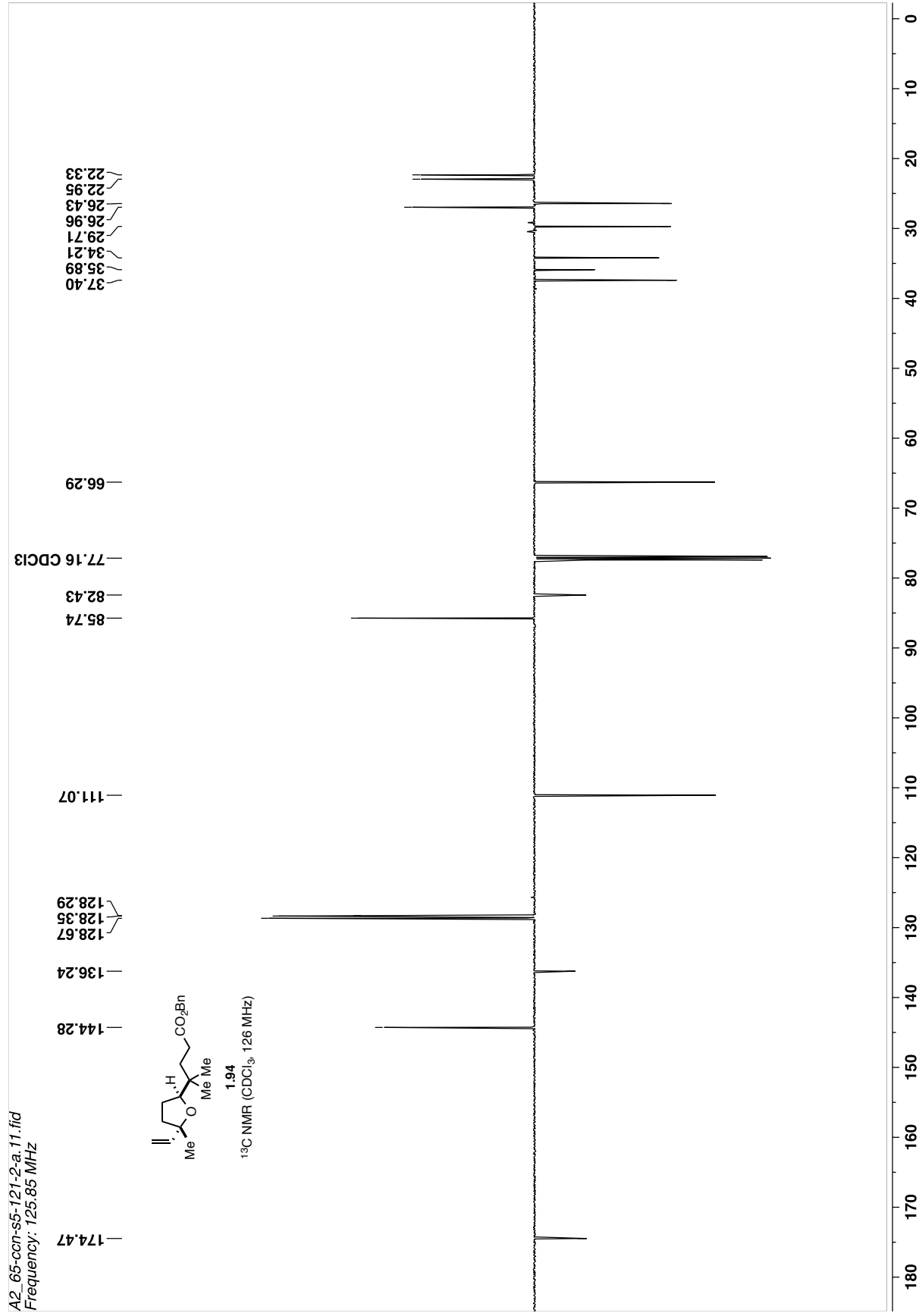
Current Data Parameters
NAME      YS-II-293
PROCNO    1
=====
F2 - Acquisition Parameters
Date_     01/09/11
Time      8:48
INSTRUM   spect
PULPROG   zgpg30
PROCPRG   5 nm CPTCL34
F2 - Processing parameters
SOLVENT   CDCl3
NS         8
DS         2
SS         8012.870 Hz
AQ         0.250026 Hz
RG         1.9397952 sec
OR         62.400 usec
DE         6.00 usec
TE         300.2 K
=====
MCNMR31  0 sec  0.10000000 sec
MCNMR4   0.01500000 sec
===== CHANNEL F1 =====
NUC1      13C
P1         8
PL1        0
SFO1      500.225012 MHz
RG1        0
=====
F2 - Processing parameters
SI         65536
SF         500.225012 MHz
RG         0
GB         0
PC         4.00
  
```







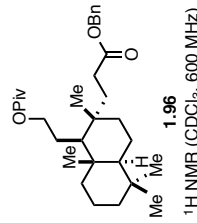
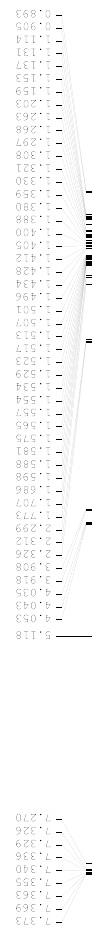
A2_65-ccn-s5-121-2-a.11.fid
Frequency: 125.85 MHz



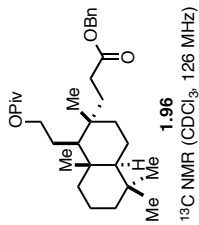
YS-II-270A

```

Current Data Parameters
NAME      YS-II-270A
PROCNO    1
=====
F2 - Acquisition Parameters
Date_     01/05/24
Time      14:06
INSTRUM   spect
PROBHD    5 mm TBI 1H/13
PULPROG   zgpg30
SOLVENT   CDCl3
NS        8
DS        2
SS        8615.945 Hz
AQ        0.150010 Hz
RG        1.9399500 sec
FIDRES    0.1454400 Hz
AQ        52.000 usec
DE        14.544 usec
DI        0.1000000 sec
TD0       1
=====
CHANNEL f1
SFO1      600.1342000 MHz
NUC1      13C
P1         8.00 usec
PLA1      23.0141356 dB
=====
F2 - Processing Parameters
SF        600.1300300 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```



YS-II-270A



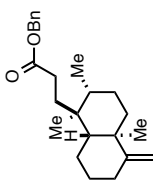
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Current Data Parameters
Date_ 18-11-2022
Time_ 15:07
PROCNO 1
=====
F2 - Acquisition Parameters
Date_ 2011-11-07
Time_ 15:07
INSTRUM cryo500
PROBHD 5 mm CPYX 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 368
DS 4
SWH 30300.075 Hz
FIDRES 0.462388 Hz
AQ 1.081340 sec
RG 327.500
DE 16.500 usec
TE 300.2 K
C1 0.06296 sec
C2 0.030000 sec
C3 0.030000 sec
C4 0.030000 sec
C5 0.030000 sec
C6 0.030000 sec
C7 0.030000 sec
C8 0.030000 sec
C9 0.030000 sec
C10 0.030000 sec
C11 0.030000 sec
C12 0.030000 sec
C13 0.030000 sec
C14 0.030000 sec
C15 0.030000 sec
C16 0.030000 sec
C17 0.030000 sec
C18 0.030000 sec
C19 0.030000 sec
C20 0.030000 sec
C21 0.030000 sec
C22 0.030000 sec
C23 0.030000 sec
C24 0.030000 sec
C25 0.030000 sec
C26 0.030000 sec
C27 0.030000 sec
C28 0.030000 sec
C29 0.030000 sec
C30 0.030000 sec
C31 0.030000 sec
C32 0.030000 sec
C33 0.030000 sec
C34 0.030000 sec
C35 0.030000 sec
C36 0.030000 sec
C37 0.030000 sec
C38 0.030000 sec
C39 0.030000 sec
C40 0.030000 sec
C41 0.030000 sec
C42 0.030000 sec
C43 0.030000 sec
C44 0.030000 sec
C45 0.030000 sec
C46 0.030000 sec
C47 0.030000 sec
C48 0.030000 sec
C49 0.030000 sec
C50 0.030000 sec
C51 0.030000 sec
C52 0.030000 sec
=====
CHANNEL f1
NUC1 13C
P1 16.55 usec
PL1 0.00 dB
PL2 0.00 dB
PL3 0.00 dB
PL4 0.00 dB
PL5 0.00 dB
PL6 0.00 dB
PL7 0.00 dB
PL8 0.00 dB
PL9 0.00 dB
PL10 0.00 dB
PL11 0.00 dB
PL12 0.00 dB
PL13 0.00 dB
PL14 0.00 dB
PL15 0.00 dB
PL16 0.00 dB
PL17 0.00 dB
PL18 0.00 dB
PL19 0.00 dB
PL20 0.00 dB
PL21 0.00 dB
PL22 0.00 dB
PL23 0.00 dB
PL24 0.00 dB
PL25 0.00 dB
PL26 0.00 dB
PL27 0.00 dB
PL28 0.00 dB
PL29 0.00 dB
PL30 0.00 dB
PL31 0.00 dB
PL32 0.00 dB
PL33 0.00 dB
PL34 0.00 dB
PL35 0.00 dB
PL36 0.00 dB
PL37 0.00 dB
PL38 0.00 dB
PL39 0.00 dB
PL40 0.00 dB
PL41 0.00 dB
PL42 0.00 dB
PL43 0.00 dB
PL44 0.00 dB
PL45 0.00 dB
PL46 0.00 dB
PL47 0.00 dB
PL48 0.00 dB
PL49 0.00 dB
PL50 0.00 dB
PL51 0.00 dB
PL52 0.00 dB
PL53 0.00 dB
PL54 0.00 dB
PL55 0.00 dB
PL56 0.00 dB
PL57 0.00 dB
PL58 0.00 dB
PL59 0.00 dB
PL60 0.00 dB
PL61 0.00 dB
PL62 0.00 dB
PL63 0.00 dB
PL64 0.00 dB
PL65 0.00 dB
PL66 0.00 dB
PL67 0.00 dB
PL68 0.00 dB
PL69 0.00 dB
PL70 0.00 dB
PL71 0.00 dB
PL72 0.00 dB
PL73 0.00 dB
PL74 0.00 dB
PL75 0.00 dB
PL76 0.00 dB
PL77 0.00 dB
PL78 0.00 dB
PL79 0.00 dB
PL80 0.00 dB
PL81 0.00 dB
PL82 0.00 dB
PL83 0.00 dB
PL84 0.00 dB
PL85 0.00 dB
PL86 0.00 dB
PL87 0.00 dB
PL88 0.00 dB
PL89 0.00 dB
PL90 0.00 dB
PL91 0.00 dB
PL92 0.00 dB
PL93 0.00 dB
PL94 0.00 dB
PL95 0.00 dB
PL96 0.00 dB
PL97 0.00 dB
PL98 0.00 dB
PL99 0.00 dB
PL100 0.00 dB
=====
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
P2 100.00 usec
PL2 0.00 dB
PL3 1.60 dB
PL4 1.60 dB
PL5 1.60 dB
PL6 1.60 dB
PL7 1.60 dB
PL8 1.60 dB
PL9 1.60 dB
PL10 1.60 dB
PL11 1.60 dB
PL12 1.60 dB
PL13 1.60 dB
PL14 1.60 dB
PL15 1.60 dB
PL16 1.60 dB
PL17 1.60 dB
PL18 1.60 dB
PL19 1.60 dB
PL20 1.60 dB
PL21 1.60 dB
PL22 1.60 dB
PL23 1.60 dB
PL24 1.60 dB
PL25 1.60 dB
PL26 1.60 dB
PL27 1.60 dB
PL28 1.60 dB
PL29 1.60 dB
PL30 1.60 dB
PL31 1.60 dB
PL32 1.60 dB
PL33 1.60 dB
PL34 1.60 dB
PL35 1.60 dB
PL36 1.60 dB
PL37 1.60 dB
PL38 1.60 dB
PL39 1.60 dB
PL40 1.60 dB
PL41 1.60 dB
PL42 1.60 dB
PL43 1.60 dB
PL44 1.60 dB
PL45 1.60 dB
PL46 1.60 dB
PL47 1.60 dB
PL48 1.60 dB
PL49 1.60 dB
PL50 1.60 dB
PL51 1.60 dB
PL52 1.60 dB
PL53 1.60 dB
PL54 1.60 dB
PL55 1.60 dB
PL56 1.60 dB
PL57 1.60 dB
PL58 1.60 dB
PL59 1.60 dB
PL60 1.60 dB
PL61 1.60 dB
PL62 1.60 dB
PL63 1.60 dB
PL64 1.60 dB
PL65 1.60 dB
PL66 1.60 dB
PL67 1.60 dB
PL68 1.60 dB
PL69 1.60 dB
PL70 1.60 dB
PL71 1.60 dB
PL72 1.60 dB
PL73 1.60 dB
PL74 1.60 dB
PL75 1.60 dB
PL76 1.60 dB
PL77 1.60 dB
PL78 1.60 dB
PL79 1.60 dB
PL80 1.60 dB
PL81 1.60 dB
PL82 1.60 dB
PL83 1.60 dB
PL84 1.60 dB
PL85 1.60 dB
PL86 1.60 dB
PL87 1.60 dB
PL88 1.60 dB
PL89 1.60 dB
PL90 1.60 dB
PL91 1.60 dB
PL92 1.60 dB
PL93 1.60 dB
PL94 1.60 dB
PL95 1.60 dB
PL96 1.60 dB
PL97 1.60 dB
PL98 1.60 dB
PL99 1.60 dB
PL100 1.60 dB
=====
GRADIENT CHANNEL
GPMAM[1] SINE.100
GPMAM[2] SINE.100
GPR2 0 %
GPR3 0 %
GPR4 0 %
GPR5 0 %
GPR6 0 %
GPR7 0 %
GPR8 0 %
GPR9 0 %
GPR10 0 %
GPR11 0 %
GPR12 0 %
GPR13 0 %
GPR14 0 %
GPR15 0 %
GPR16 0 %
GPR17 0 %
GPR18 0 %
GPR19 0 %
GPR20 0 %
GPR21 0 %
GPR22 0 %
GPR23 0 %
GPR24 0 %
GPR25 0 %
GPR26 0 %
GPR27 0 %
GPR28 0 %
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GPR30 0 %
GPR31 0 %
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GPR33 0 %
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GPR35 0 %
GPR36 0 %
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GPR85 0 %
GPR86 0 %
GPR87 0 %
GPR88 0 %
GPR89 0 %
GPR90 0 %
GPR91 0 %
GPR92 0 %
GPR93 0 %
GPR94 0 %
GPR95 0 %
GPR96 0 %
GPR97 0 %
GPR98 0 %
GPR99 0 %
GPR100 0 %
=====
Processing parameters
SI 65536
SF 125.7603988 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00

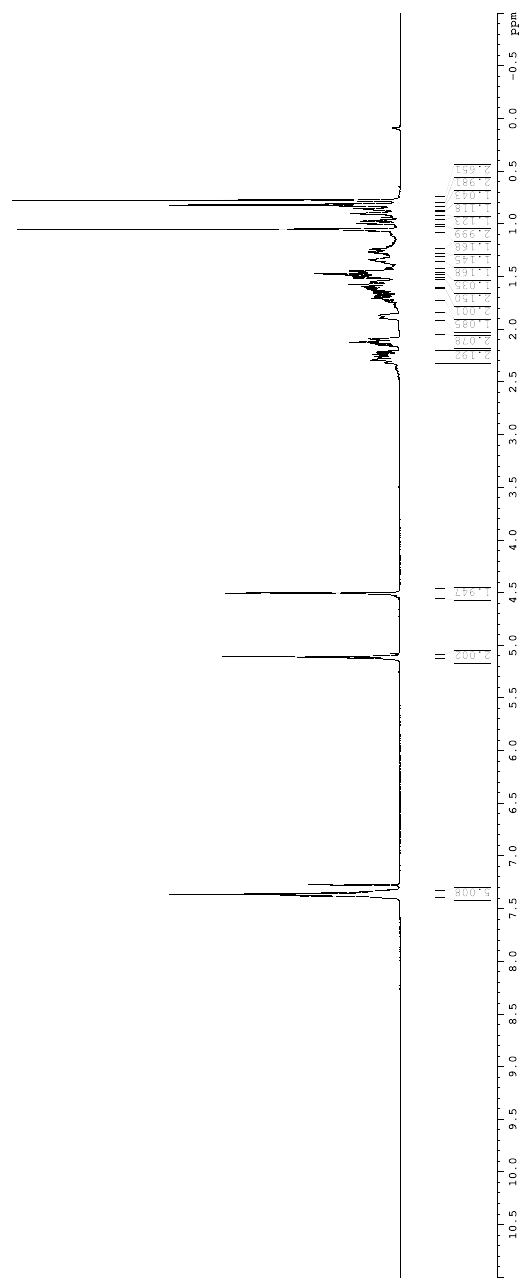
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YS-II-270B

Current Data Parameters
NAME YS-II-270B
PROCNO 1
EXPNO 1
F2 - Acquisition Parameters
Date_UTC 20150228
Time 14:41
PROBHD 5 mm QNP1 1H
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 8
SS 8012.870 Hz
FIDRES 0.100003 Hz
AQ 4.939862 sec
RG 62.403 usec
DE 6.00 usec
D1 0.1000000 sec
MCHEBT 0 sec
MCHBR 0.01500000 sec
***** CHANNEL F1 *****
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235012 MHz
F2 - Processing parameters
SI 65536
SF 500.2235012 MHz
RG 62.403
WDW EM
SSB 0
GB 0
PC 4.00



1.98
1H NMR (CDCl₃, 500 MHz)

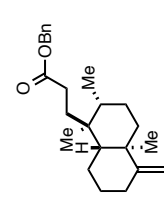
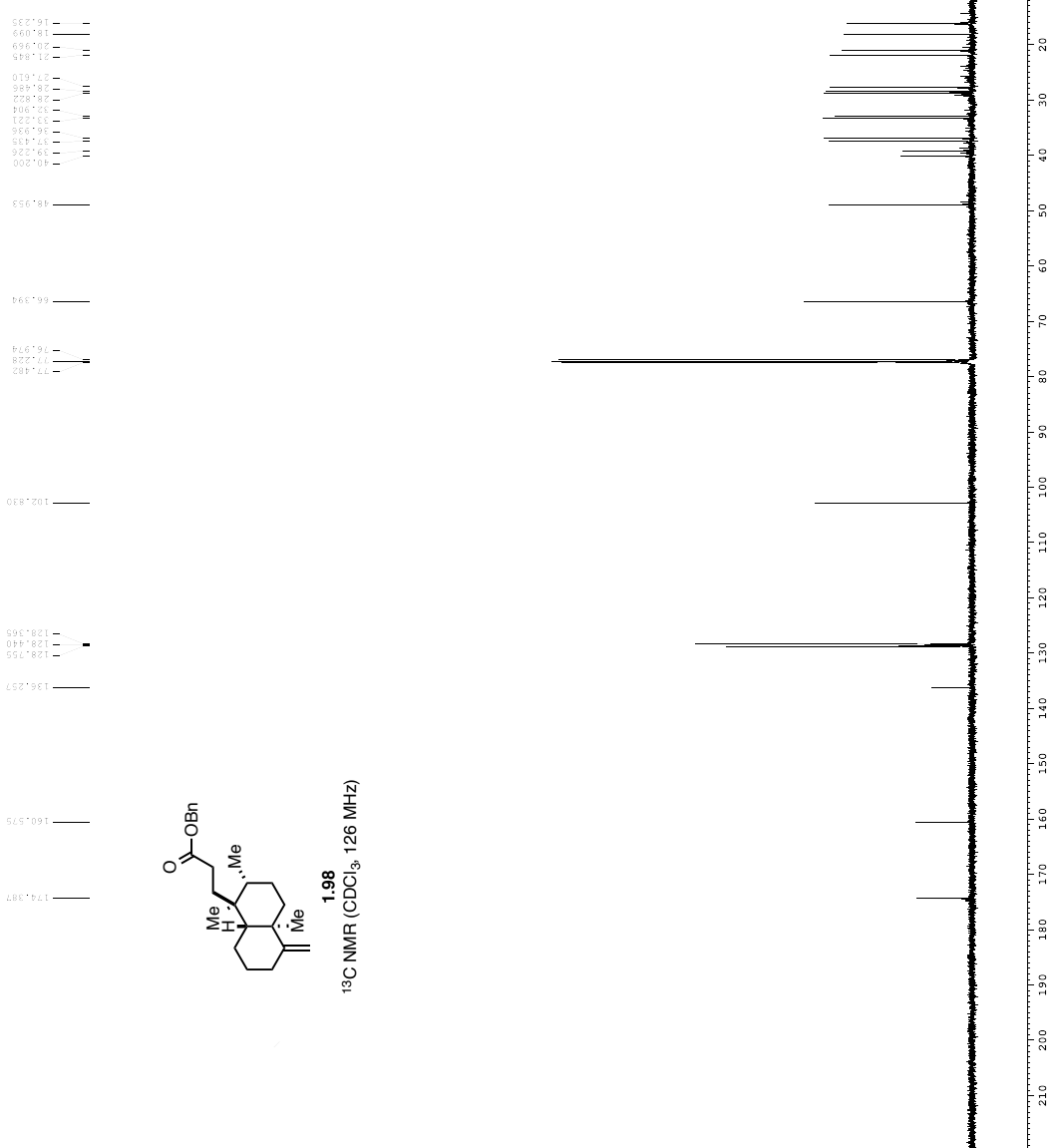


YS-II-270B

```

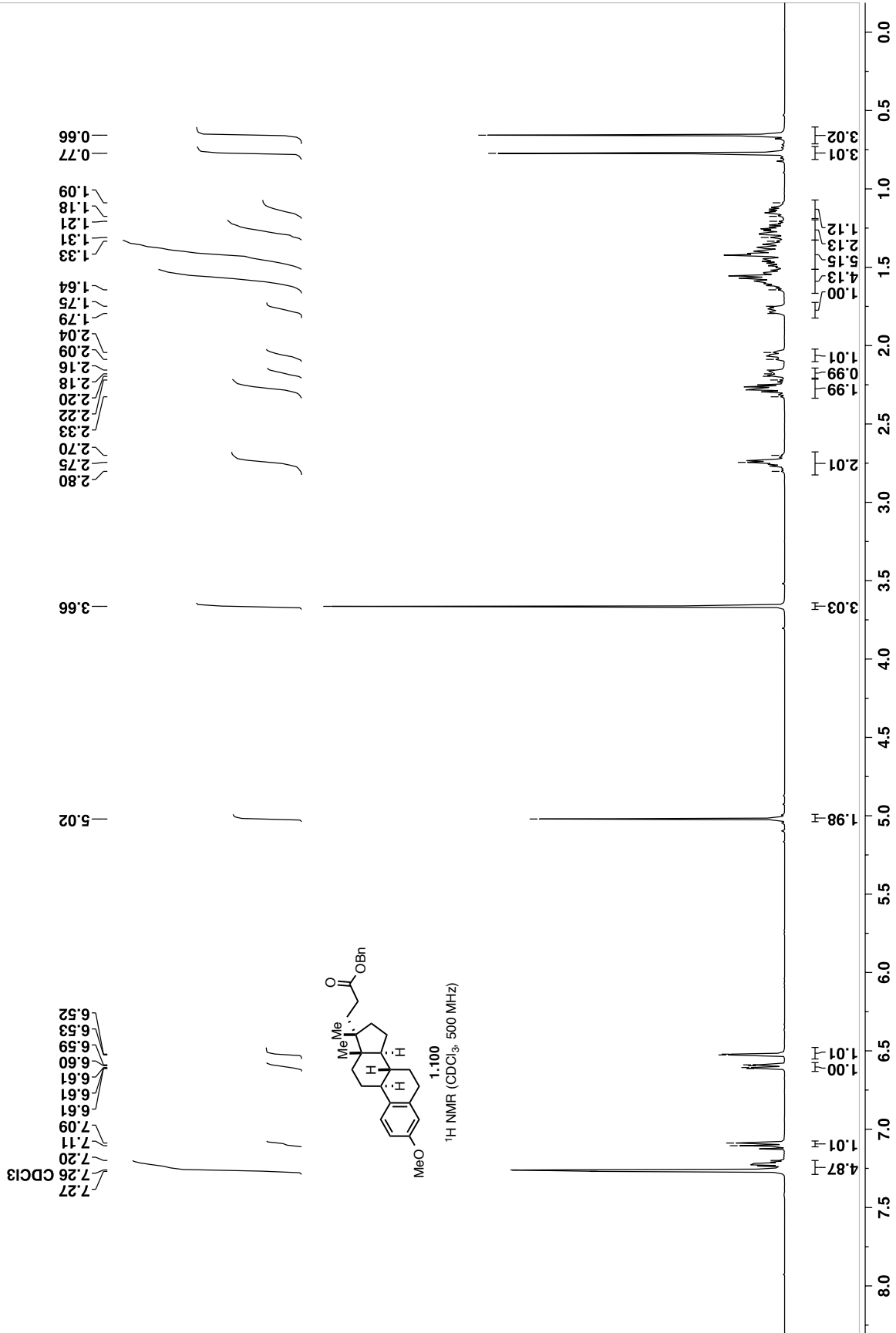
Current Data Parameters
Date_ 18-11-2018
EXPNO 1
PROCNO 1
=====
F2 - Acquisition Parameters
Date_ 20181127
Time_ 14.42
INSTRUM cryo500
PROBHD 5 mm CPCC1H1R
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 4
SWH 30300.031 Hz
FIDRES 0.462388 Hz
AQ 1.081345 sec
RG 327.500
AQ 16.500 usec
DE 6.00 usec
TE 300.298 K
C11 0.300000 sec
C12 0.300000 sec
C13 0.300000 sec
C14 0.300000 sec
C15 0.300000 sec
C16 0.300000 sec
C17 0.300000 sec
C18 0.300000 sec
C19 0.300000 sec
C20 0.300000 sec
C21 0.300000 sec
C22 0.300000 sec
C23 0.300000 sec
C24 0.300000 sec
C25 0.300000 sec
C26 0.300000 sec
C27 0.300000 sec
C28 0.300000 sec
C29 0.300000 sec
C30 0.300000 sec
C31 0.300000 sec
C32 0.300000 sec
=====
===== CHANNEL f1 =====
NUC1 13C
P1 16.55 usec
PL1 0.00 dB
PC1 100.00 usec
PL2 2000.00 usec
PL3 0.00 dB
PL4 0.00 dB
PL5 0.00 dB
PL6 0.00 dB
SFO1 125.7942548 MHz
SF1 2.70 GHz
SFO2 500.1362996 MHz
SF2 125.7942548 MHz
SFO3 500.1362996 MHz
SFO4 500.1362996 MHz
SFO5 500.1362996 MHz
SFO6 500.1362996 MHz
SFO7 500.1362996 MHz
SFO8 500.1362996 MHz
SFO9 500.1362996 MHz
SFO10 500.1362996 MHz
SFO11 500.1362996 MHz
SFO12 500.1362996 MHz
SFO13 500.1362996 MHz
SFO14 500.1362996 MHz
SFO15 500.1362996 MHz
SFO16 500.1362996 MHz
SFO17 500.1362996 MHz
SFO18 500.1362996 MHz
SFO19 500.1362996 MHz
SFO20 500.1362996 MHz
SFO21 500.1362996 MHz
SFO22 500.1362996 MHz
SFO23 500.1362996 MHz
SFO24 500.1362996 MHz
SFO25 500.1362996 MHz
SFO26 500.1362996 MHz
SFO27 500.1362996 MHz
SFO28 500.1362996 MHz
SFO29 500.1362996 MHz
SFO30 500.1362996 MHz
SFO31 500.1362996 MHz
SFO32 500.1362996 MHz
SFO33 500.1362996 MHz
SFO34 500.1362996 MHz
SFO35 500.1362996 MHz
SFO36 500.1362996 MHz
SFO37 500.1362996 MHz
SFO38 500.1362996 MHz
SFO39 500.1362996 MHz
SFO40 500.1362996 MHz
SFO41 500.1362996 MHz
SFO42 500.1362996 MHz
SFO43 500.1362996 MHz
SFO44 500.1362996 MHz
SFO45 500.1362996 MHz
SFO46 500.1362996 MHz
SFO47 500.1362996 MHz
SFO48 500.1362996 MHz
SFO49 500.1362996 MHz
SFO50 500.1362996 MHz
SFO51 500.1362996 MHz
SFO52 500.1362996 MHz
SFO53 500.1362996 MHz
SFO54 500.1362996 MHz
SFO55 500.1362996 MHz
SFO56 500.1362996 MHz
SFO57 500.1362996 MHz
SFO58 500.1362996 MHz
SFO59 500.1362996 MHz
SFO60 500.1362996 MHz
SFO61 500.1362996 MHz
SFO62 500.1362996 MHz
SFO63 500.1362996 MHz
SFO64 500.1362996 MHz
SFO65 500.1362996 MHz
SFO66 500.1362996 MHz
SFO67 500.1362996 MHz
SFO68 500.1362996 MHz
SFO69 500.1362996 MHz
SFO70 500.1362996 MHz
SFO71 500.1362996 MHz
SFO72 500.1362996 MHz
SFO73 500.1362996 MHz
SFO74 500.1362996 MHz
SFO75 500.1362996 MHz
SFO76 500.1362996 MHz
SFO77 500.1362996 MHz
SFO78 500.1362996 MHz
SFO79 500.1362996 MHz
SFO80 500.1362996 MHz
SFO81 500.1362996 MHz
SFO82 500.1362996 MHz
SFO83 500.1362996 MHz
SFO84 500.1362996 MHz
SFO85 500.1362996 MHz
SFO86 500.1362996 MHz
SFO87 500.1362996 MHz
SFO88 500.1362996 MHz
SFO89 500.1362996 MHz
SFO90 500.1362996 MHz
SFO91 500.1362996 MHz
SFO92 500.1362996 MHz
SFO93 500.1362996 MHz
SFO94 500.1362996 MHz
SFO95 500.1362996 MHz
SFO96 500.1362996 MHz
SFO97 500.1362996 MHz
SFO98 500.1362996 MHz
SFO99 500.1362996 MHz
SFO100 500.1362996 MHz
=====
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 100.00 usec
PL2 0.00 dB
PL3 1.60 dB
PL4 24.50 dB
PL5 24.50 dB
PL6 24.50 dB
SFO1 500.2225011 MHz
=====
===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GPA1 0 %
GPA2 0 %
GPA3 0 %
GPA4 0 %
GPA5 0 %
GPA6 0 %
GPA7 0 %
GPA8 0 %
GPA9 0 %
GPA10 0 %
GPA11 0 %
GPA12 0 %
GPA13 0 %
GPA14 0 %
GPA15 0 %
GPA16 0 %
GPA17 0 %
GPA18 0 %
GPA19 0 %
GPA20 0 %
GPA21 0 %
GPA22 0 %
GPA23 0 %
GPA24 0 %
GPA25 0 %
GPA26 0 %
GPA27 0 %
GPA28 0 %
GPA29 0 %
GPA30 0 %
GPA31 0 %
GPA32 0 %
GPA33 0 %
GPA34 0 %
GPA35 0 %
GPA36 0 %
GPA37 0 %
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GPA41 0 %
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GPA84 0 %
GPA85 0 %
GPA86 0 %
GPA87 0 %
GPA88 0 %
GPA89 0 %
GPA90 0 %
GPA91 0 %
GPA92 0 %
GPA93 0 %
GPA94 0 %
GPA95 0 %
GPA96 0 %
GPA97 0 %
GPA98 0 %
GPA99 0 %
GPA100 0 %
=====
F2 - Processing parameters
SI 65536
SF 125.7883996 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00
=====

```

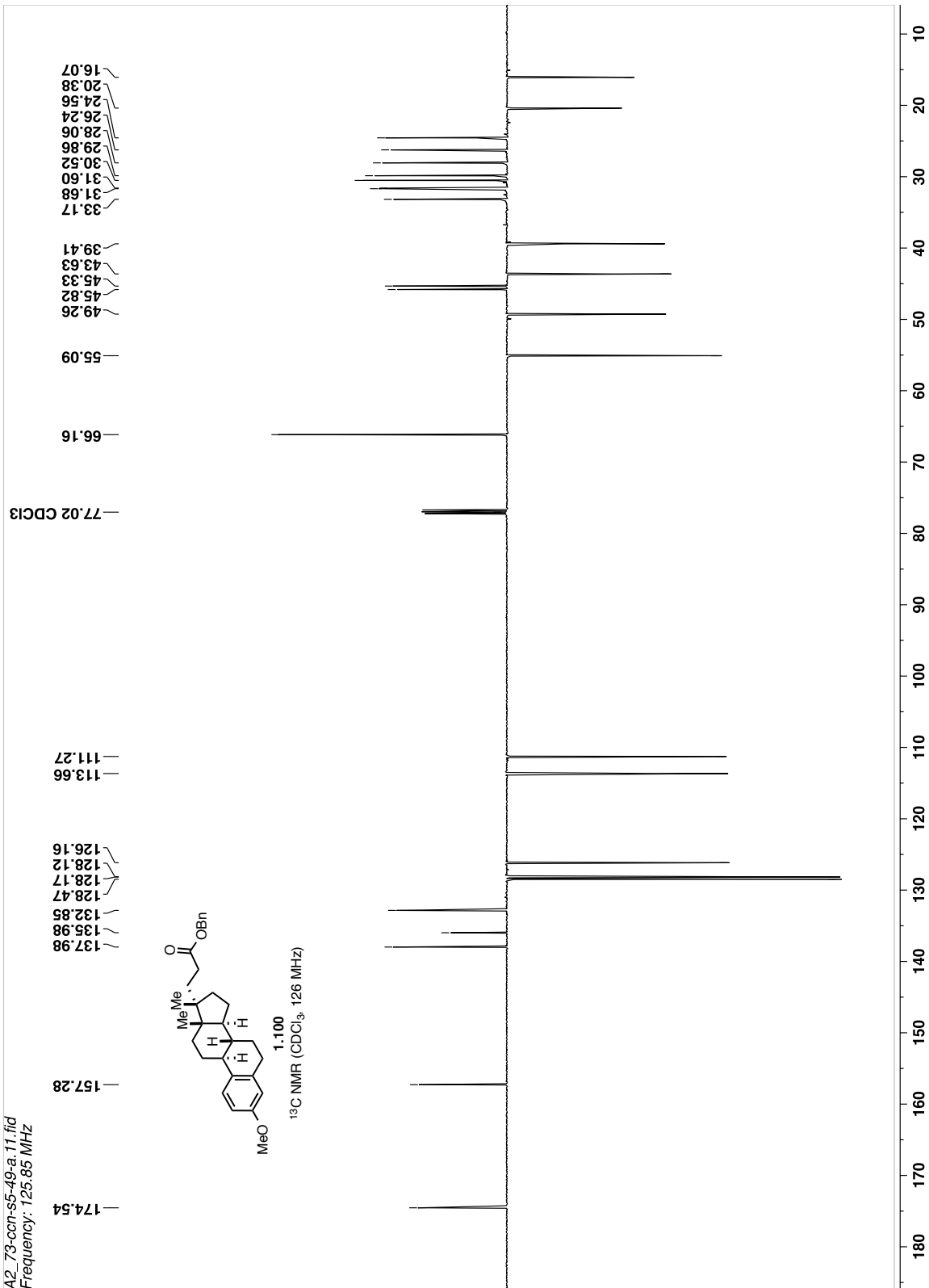


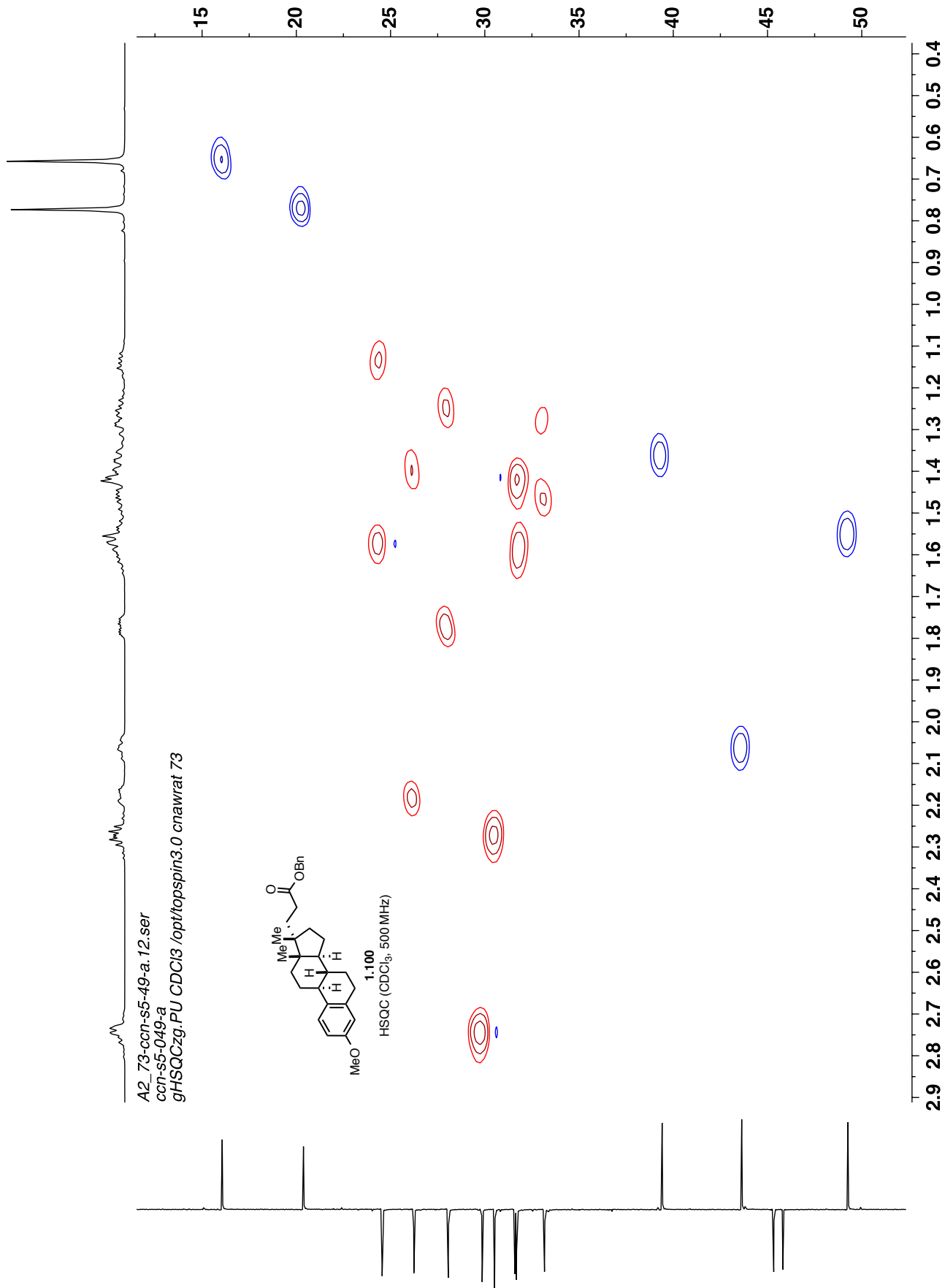
1.98
¹³C NMR (CDCl₃, 126 MHz)

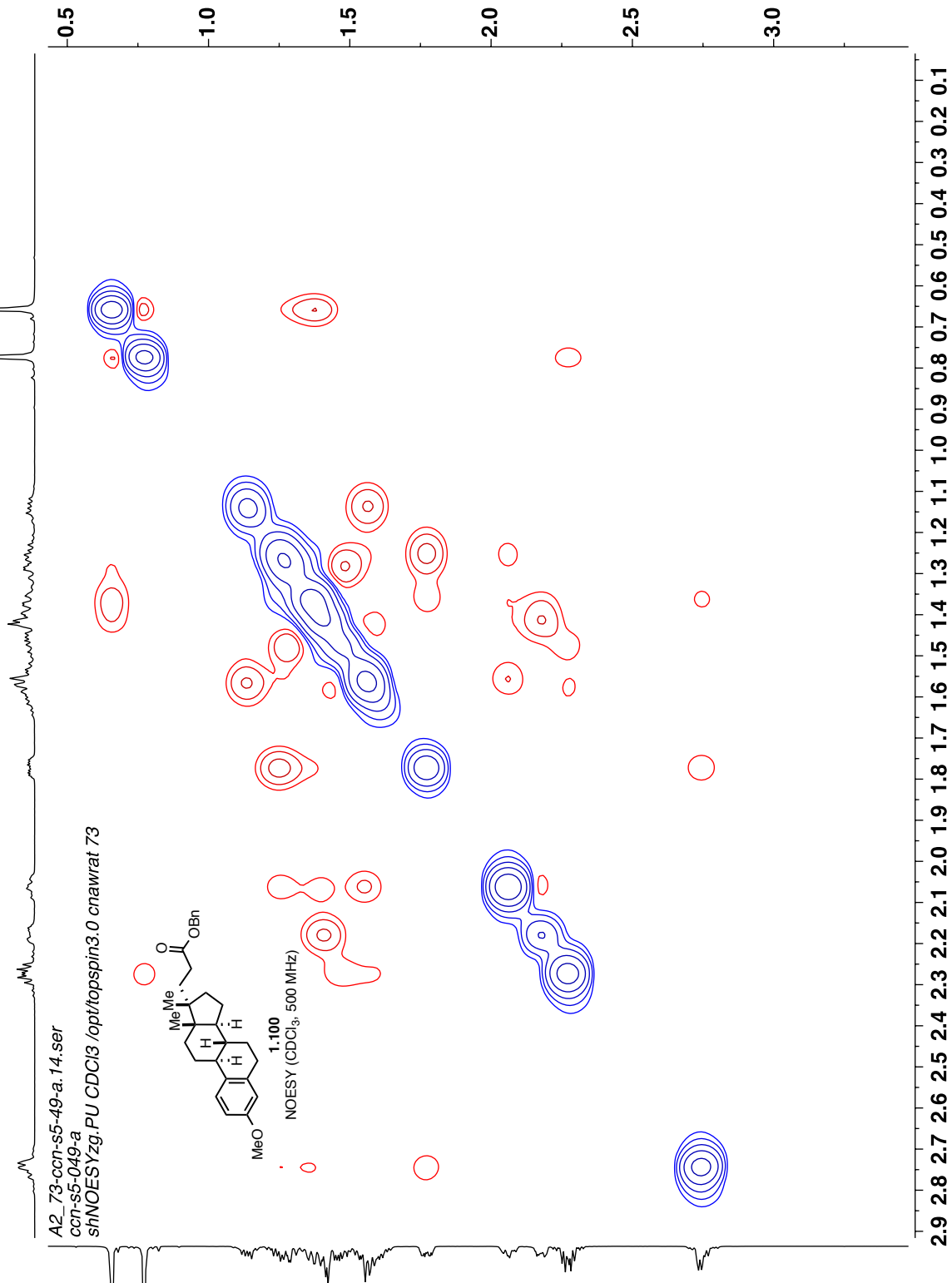
A2_73-ccn-s5-49-a.10.fid
Frequency: 500.46 MHz



A2_79-ccn-s5-49-a.11.fid
Frequency: 125.85 MHz





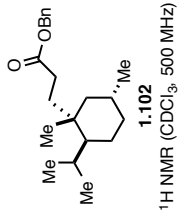


A2_54-ccn-s5-087-2-a.10.fid
Frequency: 500.46 MHz

7.39
7.31
7.26 CDCl₃

5.12

2.33
2.32
2.30
2.28
2.27
2.24
1.95
1.87
1.79
1.70
1.67
1.59
1.53
1.43
1.31
1.21
1.10
0.97
0.94
0.94
0.92
0.90
0.88
0.87
0.82
0.80
0.77



5.05

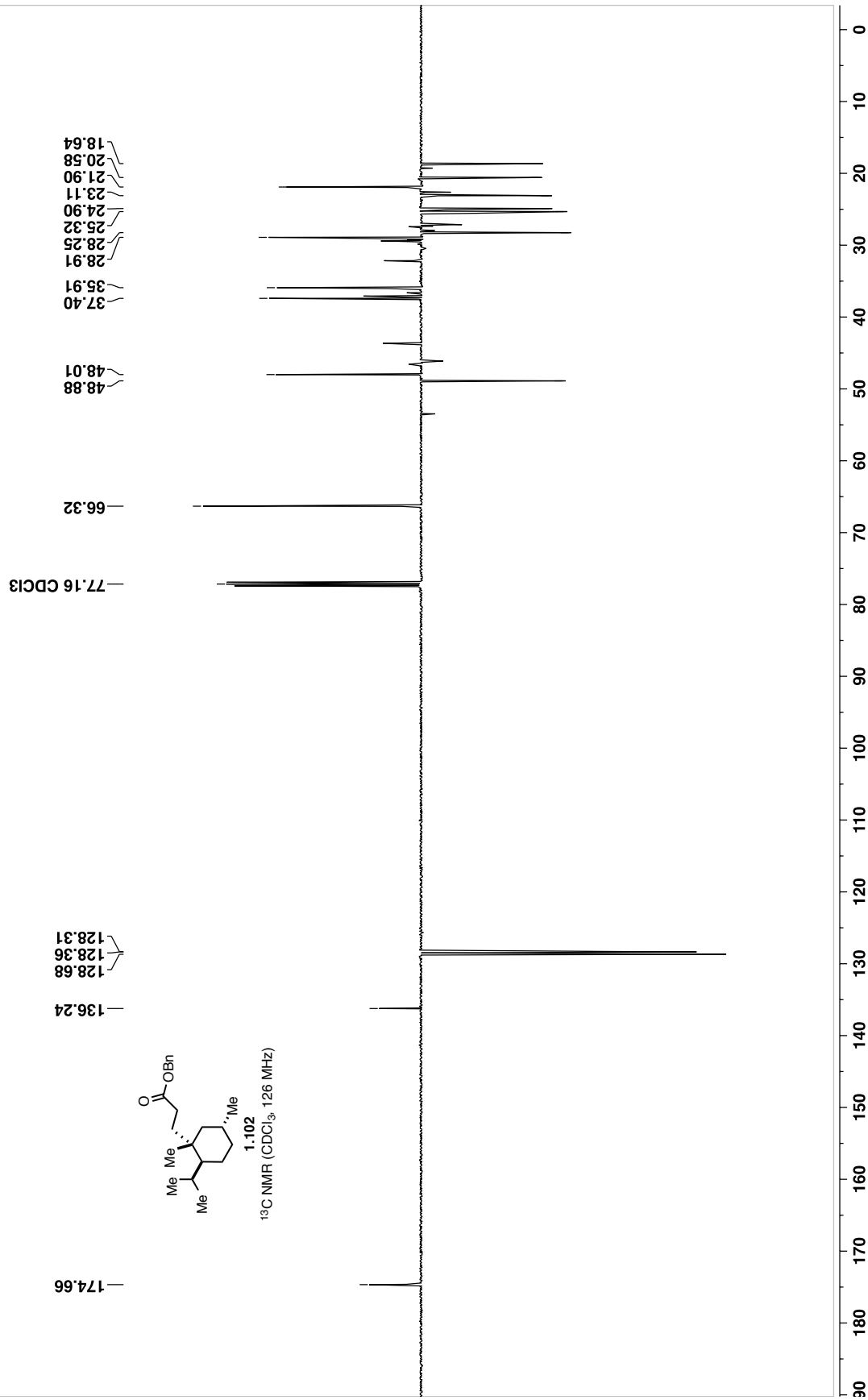
2.03

2.00

1.11
3.15
2.20
1.96
2.21
6.95
3.00
2.98

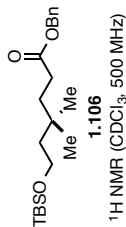
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

A2_54-ccn-s5-087-2-a.11.fid
Frequency: 125.85 MHz

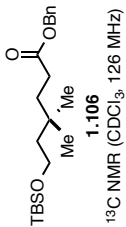
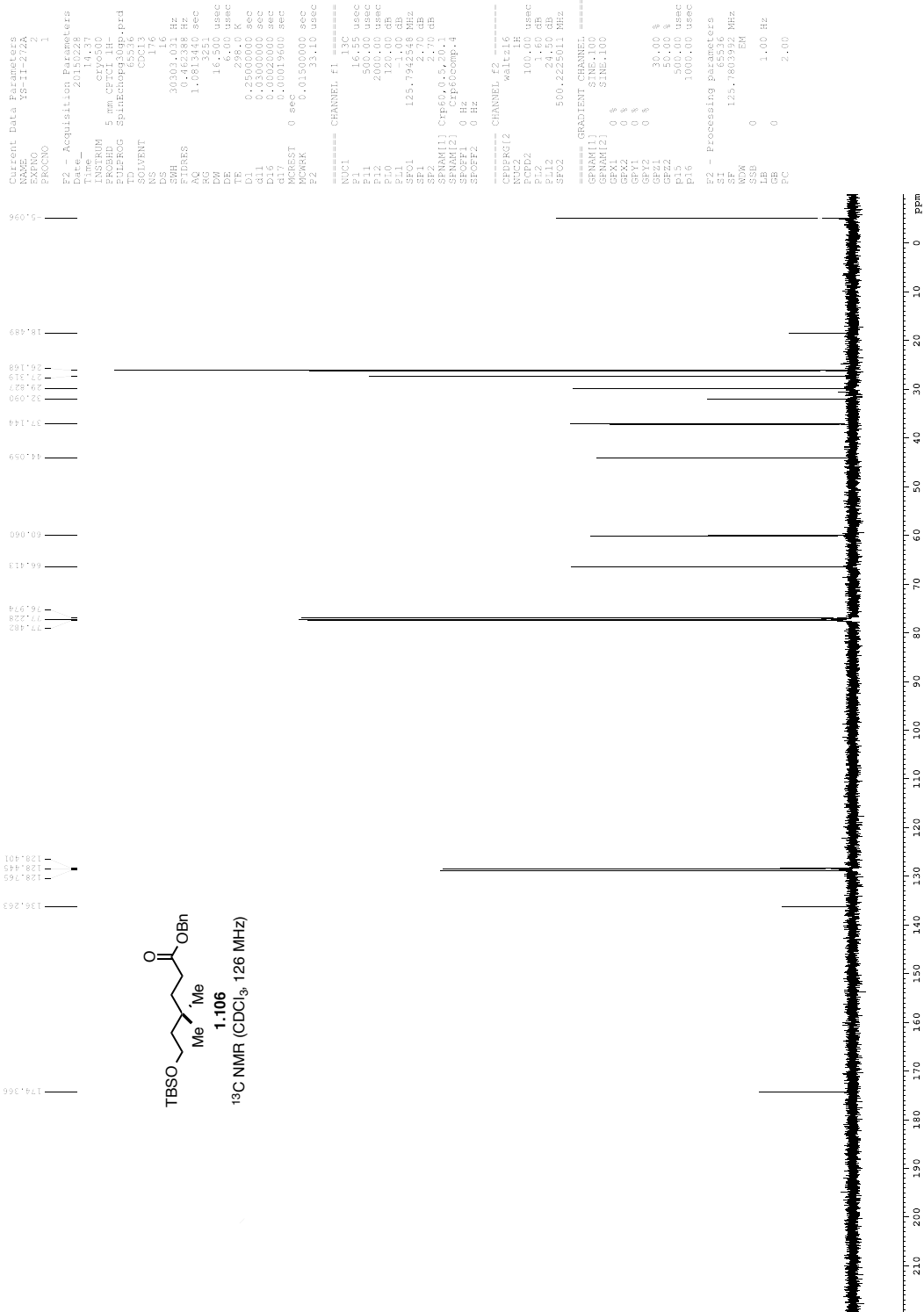


YS-II-272A

```
Current Data Parameters
NAME      YS-II-272A
PROCNO    1
=====
F2 - Acquisition Parameters
Date_     01/05/28
Time      14.33
INSTRUM   spect
PROBHD    5 mm QNP1 1H
PULPROG   zgpg30
SOLVENT   CDCl3
NS        8
DS        2
SS        6012.820 Hz
FIDRES    0.250024 Hz
AQ         1.9397952 sec
RG         62.400 usec
DW         6.00 usec
DE         6.00 usec
DI         0.10000000 sec
MCNEST    0 sec
SCNMR      0.01500000 sec
===== CHANNEL F1 =====
NUC1       1H
P1         7.50 usec
PL1        1.60 dB
SFO1       500.2235012 MHz
=====
F2 - Processing parameters
SI         65536
SF         500.2200000 MHz
RG         655
RGHM       EN
SSB        0
GB         0
PC         1.00
```

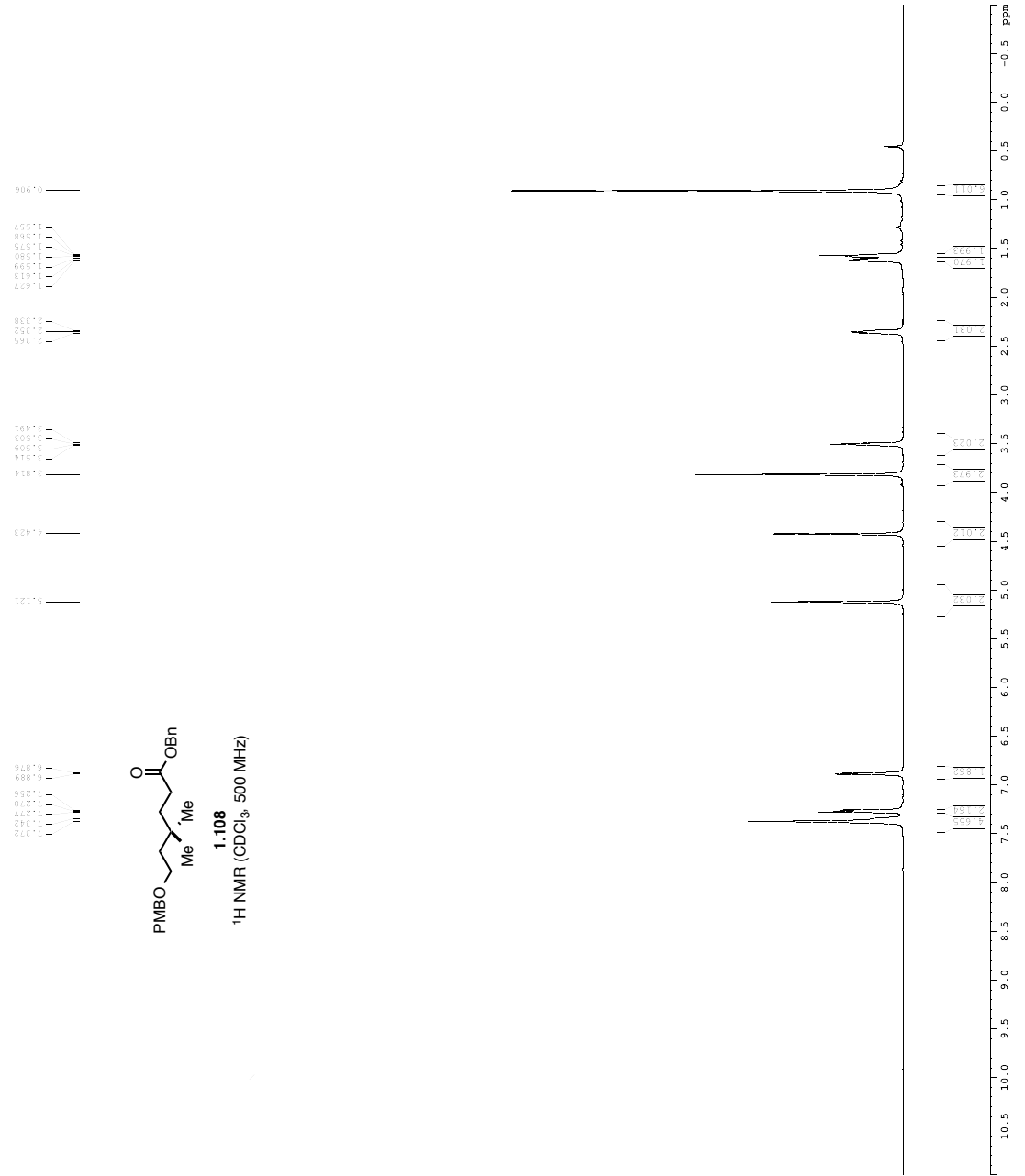


YS-II-272A



```

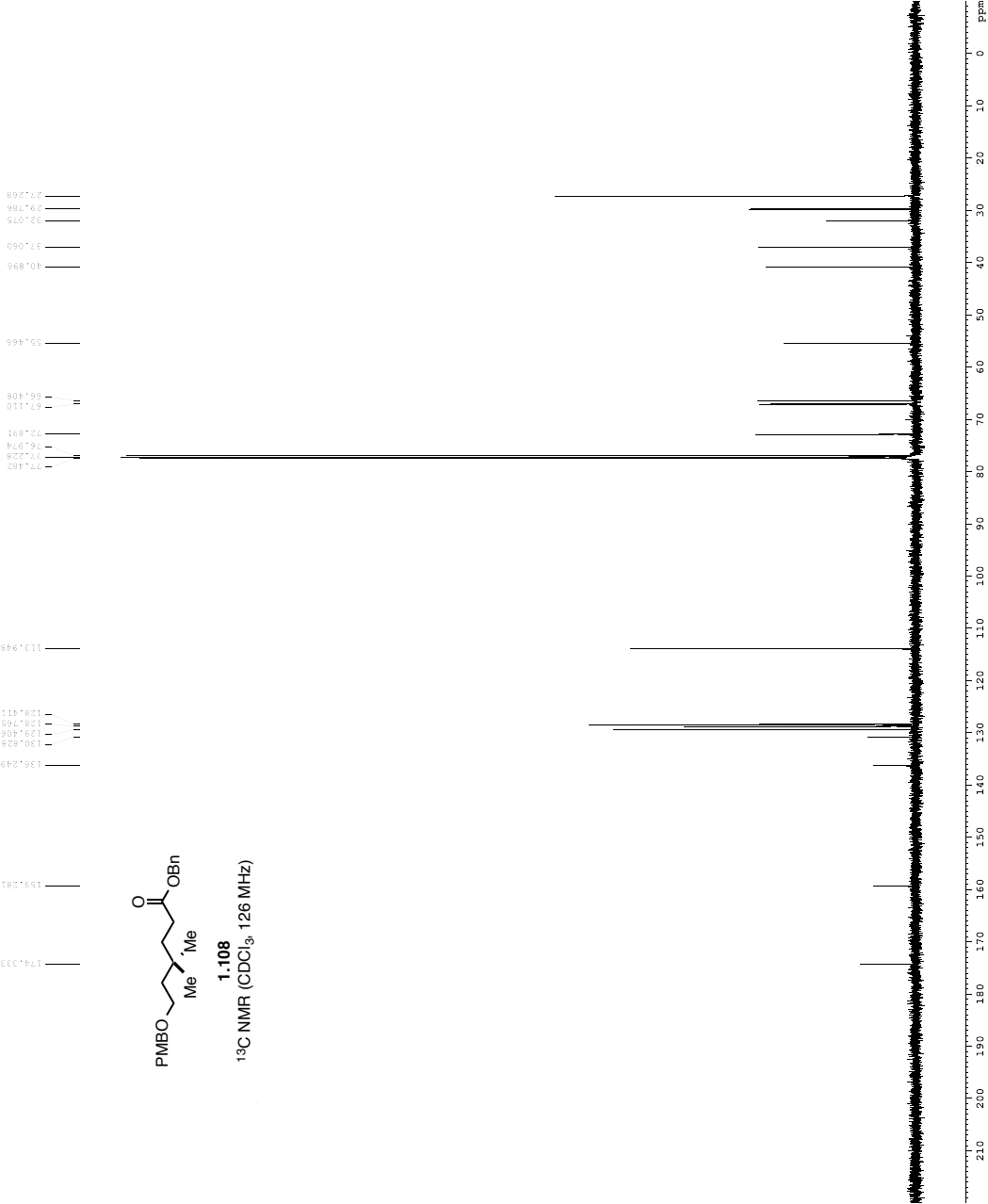
Current Data Parameters
NAME      1S-II-272B
EXPNO     1
PROCNO    1
----- Acquisition Parameters
Date_     20110728
Time      14.15
INSTRUM   AV600
PROBHD    5 mm TBI LE/13
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         8
DS         4
SWH        9615.385 Hz
FIDRES     0.240010 Hz
AQ         1.9999200 sec
RG         655.36
DQ         52.000 usec
DE         14.54 usec
TE         296.0 K
D0         0.10000000 Sec
----- CHANNEL f1 -----
SFO1      600.1362000 MHz
NUC1       13C
P1         8.00 usec
PLA1       23.01441956 W
----- Processing parameters
SI - Processing parameters
SF         600.1360268 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         2.00
    
```



```

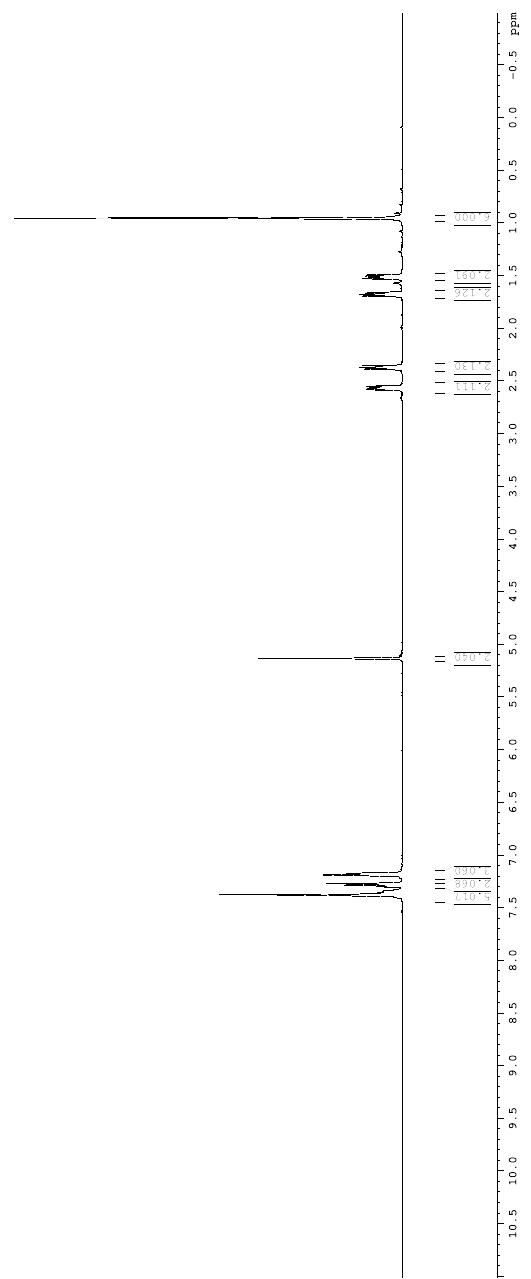
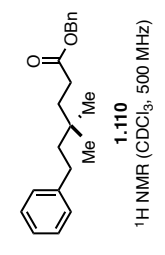
Current Data Parameters
=====
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
Date_      20110726
Time       14:57
INSTRUM    cryo500
PROBHD     5 mm CPXCCH-1H
PULPROG    zgpg30
TD          65536
SOLVENT    CDCl3
NS          496
DS          4
SWH         30300.075 Hz
FIDRES     0.462388 Hz
AQ          1.0813450 sec
RG          16.500 usec
DE          6.000 usec
TE          300.2 K
AQ          0.0629600 sec
G1         0.3000000 sec
G2         0.0000000 sec
G3         0.0000000 sec
G4         0.0000000 sec
G5         0.0000000 sec
G6         0.0000000 sec
G7         0.0000000 sec
G8         0.0000000 sec
G9         0.0000000 sec
G10        0.0000000 sec
G11        0.0000000 sec
G12        0.0000000 sec
G13        0.0000000 sec
G14        0.0000000 sec
G15        0.0000000 sec
G16        0.0000000 sec
G17        0.0000000 sec
MKREST     0 sec
MORPH      0
MORPH2     0
MORPH3     0
MORPH4     0
MORPH5     0
MORPH6     0
MORPH7     0
MORPH8     0
MORPH9     0
MORPH10    0
MORPH11    0
MORPH12    0
MORPH13    0
MORPH14    0
MORPH15    0
MORPH16    0
MORPH17    0
MORPH18    0
MORPH19    0
MORPH20    0
MORPH21    0
MORPH22    0
MORPH23    0
MORPH24    0
MORPH25    0
MORPH26    0
MORPH27    0
MORPH28    0
MORPH29    0
MORPH30    0
MORPH31    0
MORPH32    0
MORPH33    0
MORPH34    0
MORPH35    0
MORPH36    0
MORPH37    0
MORPH38    0
MORPH39    0
MORPH40    0
MORPH41    0
MORPH42    0
MORPH43    0
MORPH44    0
MORPH45    0
MORPH46    0
MORPH47    0
MORPH48    0
MORPH49    0
MORPH50    0
MORPH51    0
MORPH52    0
MORPH53    0
MORPH54    0
MORPH55    0
MORPH56    0
MORPH57    0
MORPH58    0
MORPH59    0
MORPH60    0
MORPH61    0
MORPH62    0
MORPH63    0
MORPH64    0
MORPH65    0
MORPH66    0
MORPH67    0
MORPH68    0
MORPH69    0
MORPH70    0
MORPH71    0
MORPH72    0
MORPH73    0
MORPH74    0
MORPH75    0
MORPH76    0
MORPH77    0
MORPH78    0
MORPH79    0
MORPH80    0
MORPH81    0
MORPH82    0
MORPH83    0
MORPH84    0
MORPH85    0
MORPH86    0
MORPH87    0
MORPH88    0
MORPH89    0
MORPH90    0
MORPH91    0
MORPH92    0
MORPH93    0
MORPH94    0
MORPH95    0
MORPH96    0
MORPH97    0
MORPH98    0
MORPH99    0
MORPH100   0
=====
CHANNEL f1
NUC1        13C
P1          16.55 usec
PL1         0.00 dB
P2          500.00 usec
PL2         0.00 dB
P3          2000.00 usec
PL3         0.00 dB
P4          12.00 usec
PL4         0.00 dB
P5          12.00 usec
PL5         0.00 dB
P6          125.7942548 MHz
PL6         0.00 dB
SFO1        125.7942548 MHz
SFO2        500.2225011 MHz
SFO3        500.2225011 MHz
SFO4        500.2225011 MHz
SFO5        500.2225011 MHz
SFO6        500.2225011 MHz
SFO7        500.2225011 MHz
SFO8        500.2225011 MHz
SFO9        500.2225011 MHz
SFO10       500.2225011 MHz
SFO11       500.2225011 MHz
SFO12       500.2225011 MHz
SFO13       500.2225011 MHz
SFO14       500.2225011 MHz
SFO15       500.2225011 MHz
SFO16       500.2225011 MHz
SFO17       500.2225011 MHz
SFO18       500.2225011 MHz
SFO19       500.2225011 MHz
SFO20       500.2225011 MHz
SFO21       500.2225011 MHz
SFO22       500.2225011 MHz
SFO23       500.2225011 MHz
SFO24       500.2225011 MHz
SFO25       500.2225011 MHz
SFO26       500.2225011 MHz
SFO27       500.2225011 MHz
SFO28       500.2225011 MHz
SFO29       500.2225011 MHz
SFO30       500.2225011 MHz
SFO31       500.2225011 MHz
SFO32       500.2225011 MHz
SFO33       500.2225011 MHz
SFO34       500.2225011 MHz
SFO35       500.2225011 MHz
SFO36       500.2225011 MHz
SFO37       500.2225011 MHz
SFO38       500.2225011 MHz
SFO39       500.2225011 MHz
SFO40       500.2225011 MHz
SFO41       500.2225011 MHz
SFO42       500.2225011 MHz
SFO43       500.2225011 MHz
SFO44       500.2225011 MHz
SFO45       500.2225011 MHz
SFO46       500.2225011 MHz
SFO47       500.2225011 MHz
SFO48       500.2225011 MHz
SFO49       500.2225011 MHz
SFO50       500.2225011 MHz
SFO51       500.2225011 MHz
SFO52       500.2225011 MHz
SFO53       500.2225011 MHz
SFO54       500.2225011 MHz
SFO55       500.2225011 MHz
SFO56       500.2225011 MHz
SFO57       500.2225011 MHz
SFO58       500.2225011 MHz
SFO59       500.2225011 MHz
SFO60       500.2225011 MHz
SFO61       500.2225011 MHz
SFO62       500.2225011 MHz
SFO63       500.2225011 MHz
SFO64       500.2225011 MHz
SFO65       500.2225011 MHz
SFO66       500.2225011 MHz
SFO67       500.2225011 MHz
SFO68       500.2225011 MHz
SFO69       500.2225011 MHz
SFO70       500.2225011 MHz
SFO71       500.2225011 MHz
SFO72       500.2225011 MHz
SFO73       500.2225011 MHz
SFO74       500.2225011 MHz
SFO75       500.2225011 MHz
SFO76       500.2225011 MHz
SFO77       500.2225011 MHz
SFO78       500.2225011 MHz
SFO79       500.2225011 MHz
SFO80       500.2225011 MHz
SFO81       500.2225011 MHz
SFO82       500.2225011 MHz
SFO83       500.2225011 MHz
SFO84       500.2225011 MHz
SFO85       500.2225011 MHz
SFO86       500.2225011 MHz
SFO87       500.2225011 MHz
SFO88       500.2225011 MHz
SFO89       500.2225011 MHz
SFO90       500.2225011 MHz
SFO91       500.2225011 MHz
SFO92       500.2225011 MHz
SFO93       500.2225011 MHz
SFO94       500.2225011 MHz
SFO95       500.2225011 MHz
SFO96       500.2225011 MHz
SFO97       500.2225011 MHz
SFO98       500.2225011 MHz
SFO99       500.2225011 MHz
SFO100      500.2225011 MHz
=====
CHANNEL f2
CPDPRG2     waltz16
NUC2        1H
P2          100.00 usec
PL2         0.00 dB
P3          1.60 usec
PL3         0.00 dB
P4          24.50 usec
PL4         0.00 dB
P5          500.2225011 MHz
PL5         0.00 dB
=====
GRADIENT CHANNEL
GPNAM[1]    SINE.100
GPNAM[2]    SINE.100
GPA1        0 %
GPA2        0 %
GPA3        0 %
GPA4        0 %
GPA5        0 %
GPA6        0 %
GPA7        0 %
GPA8        0 %
GPA9        0 %
GPA10       0 %
GPA11       0 %
GPA12       0 %
GPA13       0 %
GPA14       0 %
GPA15       0 %
GPA16       0 %
GPA17       0 %
GPA18       0 %
GPA19       0 %
GPA20       0 %
GPA21       0 %
GPA22       0 %
GPA23       0 %
GPA24       0 %
GPA25       0 %
GPA26       0 %
GPA27       0 %
GPA28       0 %
GPA29       0 %
GPA30       0 %
GPA31       0 %
GPA32       0 %
GPA33       0 %
GPA34       0 %
GPA35       0 %
GPA36       0 %
GPA37       0 %
GPA38       0 %
GPA39       0 %
GPA40       0 %
GPA41       0 %
GPA42       0 %
GPA43       0 %
GPA44       0 %
GPA45       0 %
GPA46       0 %
GPA47       0 %
GPA48       0 %
GPA49       0 %
GPA50       0 %
GPA51       0 %
GPA52       0 %
GPA53       0 %
GPA54       0 %
GPA55       0 %
GPA56       0 %
GPA57       0 %
GPA58       0 %
GPA59       0 %
GPA60       0 %
GPA61       0 %
GPA62       0 %
GPA63       0 %
GPA64       0 %
GPA65       0 %
GPA66       0 %
GPA67       0 %
GPA68       0 %
GPA69       0 %
GPA70       0 %
GPA71       0 %
GPA72       0 %
GPA73       0 %
GPA74       0 %
GPA75       0 %
GPA76       0 %
GPA77       0 %
GPA78       0 %
GPA79       0 %
GPA80       0 %
GPA81       0 %
GPA82       0 %
GPA83       0 %
GPA84       0 %
GPA85       0 %
GPA86       0 %
GPA87       0 %
GPA88       0 %
GPA89       0 %
GPA90       0 %
GPA91       0 %
GPA92       0 %
GPA93       0 %
GPA94       0 %
GPA95       0 %
GPA96       0 %
GPA97       0 %
GPA98       0 %
GPA99       0 %
GPA100      0 %
=====
F2 - Processing parameters
SI          65536
SF          125.7803991 MHz
WDW         EM
SSB         0
LB          0
GB          0
PC          1.00 Hz
FC          2.00

```



YS-II-141

Current Data Parameters
NAME YS-II-141
PROCNO 1
===== Acquisition Parameters
Date_ Time 01/21/2005 12:54
INSTRUM spect
PROBHD 5 mm CQCP1 3H
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 2
SS 6012.820 Hz
AQ 0.2500026 Hz
RG 1.9397932 sec
DQ 62.400 usec
DE 6.00 usec
DI 0.10000000 sec
MCNRS1 0 sec
MCNRS2 0.01500000 sec
===== CHANNEL F1 =====
NUC1 13C
PULP 8
PL1 7.50 usec
PL2 1.60 dB
SFO1 500.2235012 MHz
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
RG 64
GB 0
DB 0
EB 0
EC 4.00

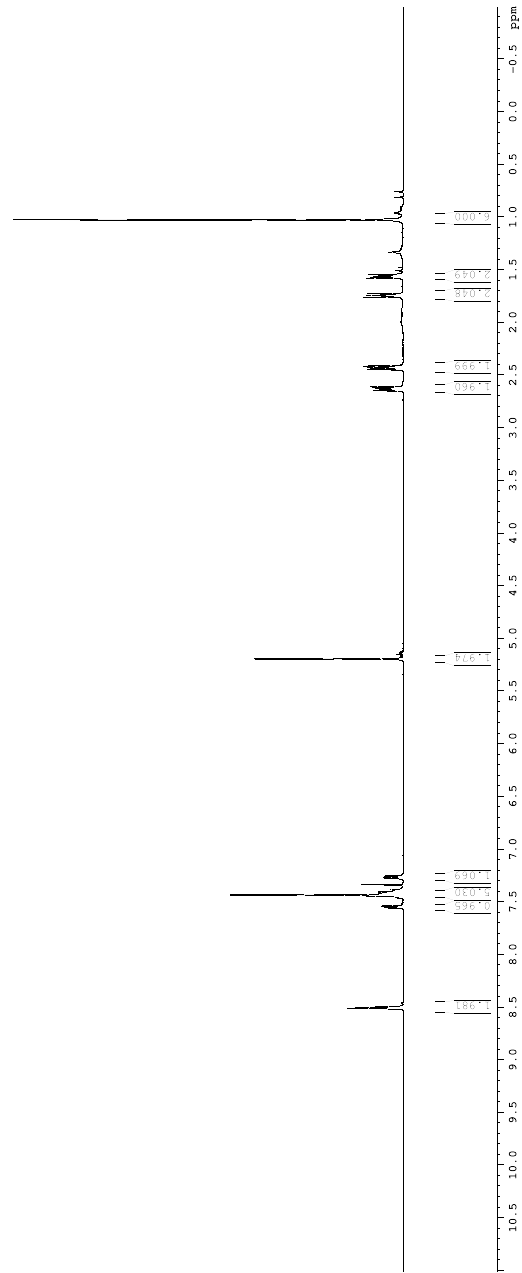


YS-III-43

Current Data Parameters
NAME YS-III-43
PROCNO 1
EXPNO 1
PROCNO 1
Data Acquisition Parameters
Date_ Time 01/20/09
Time 17.51
Time 17.51
PROBHD 5 mm QNP1 1H
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 8
SW 8012.820 Hz
AQ 0.250026 Hz
RG 1.939792 sec
AQ 1.939792 sec
RG 1.939792 sec
LW 62.400 usec
DE 6.00 usec
TE 300.2 K
D1 0.10000000 sec
MCNTR1 0 sec
MCNTR2 0.01500000 sec
===== CHANNEL F1 =====
NUC1 1H
P1 13.00 usec
PL1 0.00 dB
PL2 1.60 dB
SFO1 500.2235012 MHz
F2 - Processing parameters
SI 65536
SF 500.217956 MHz
RG 655
SXB 0
GB 0
DB 0
PC 4.00



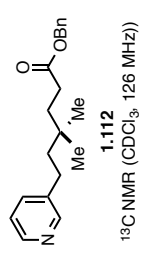
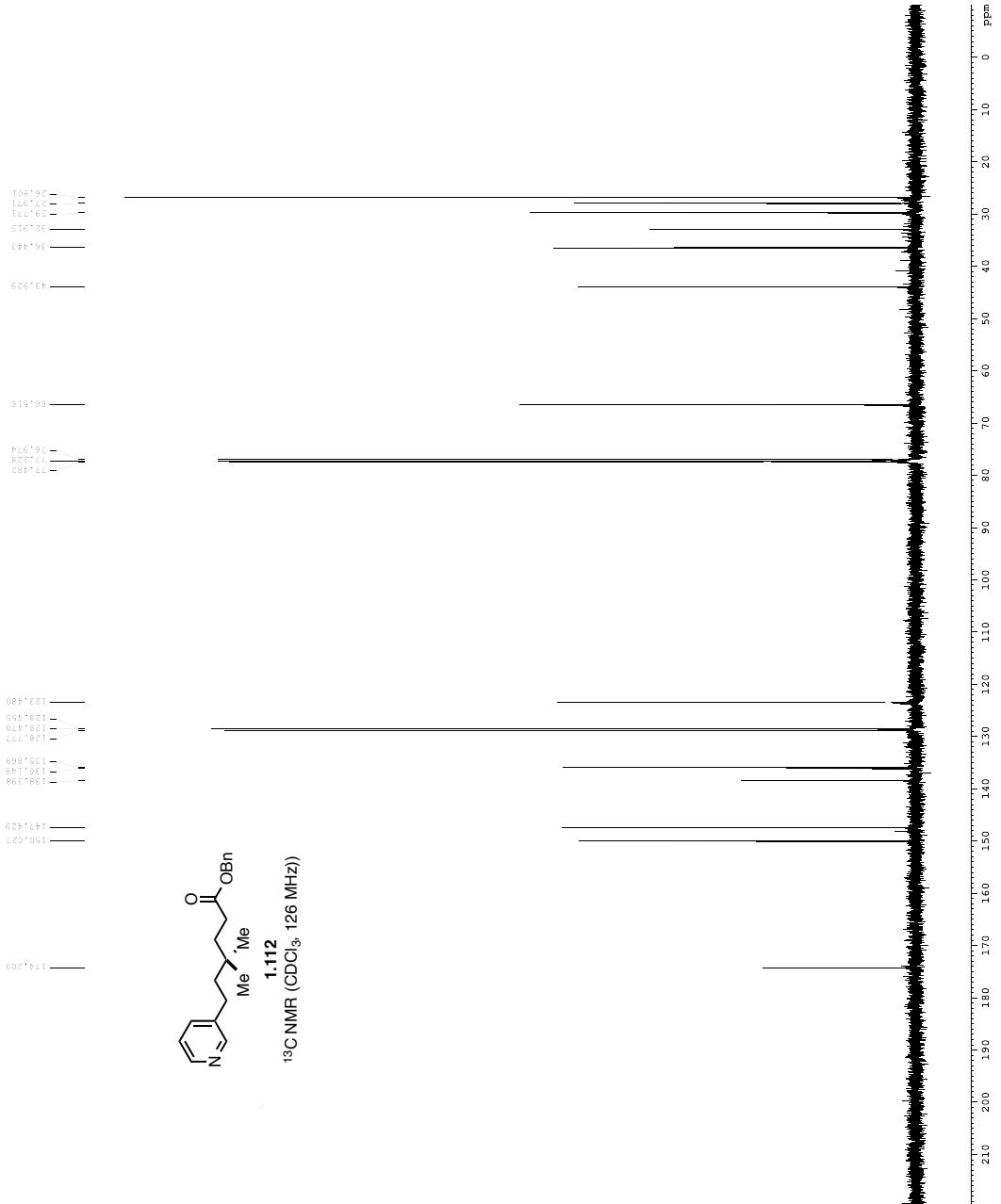
1.112
1H NMR (CDCl₃, 500 MHz)



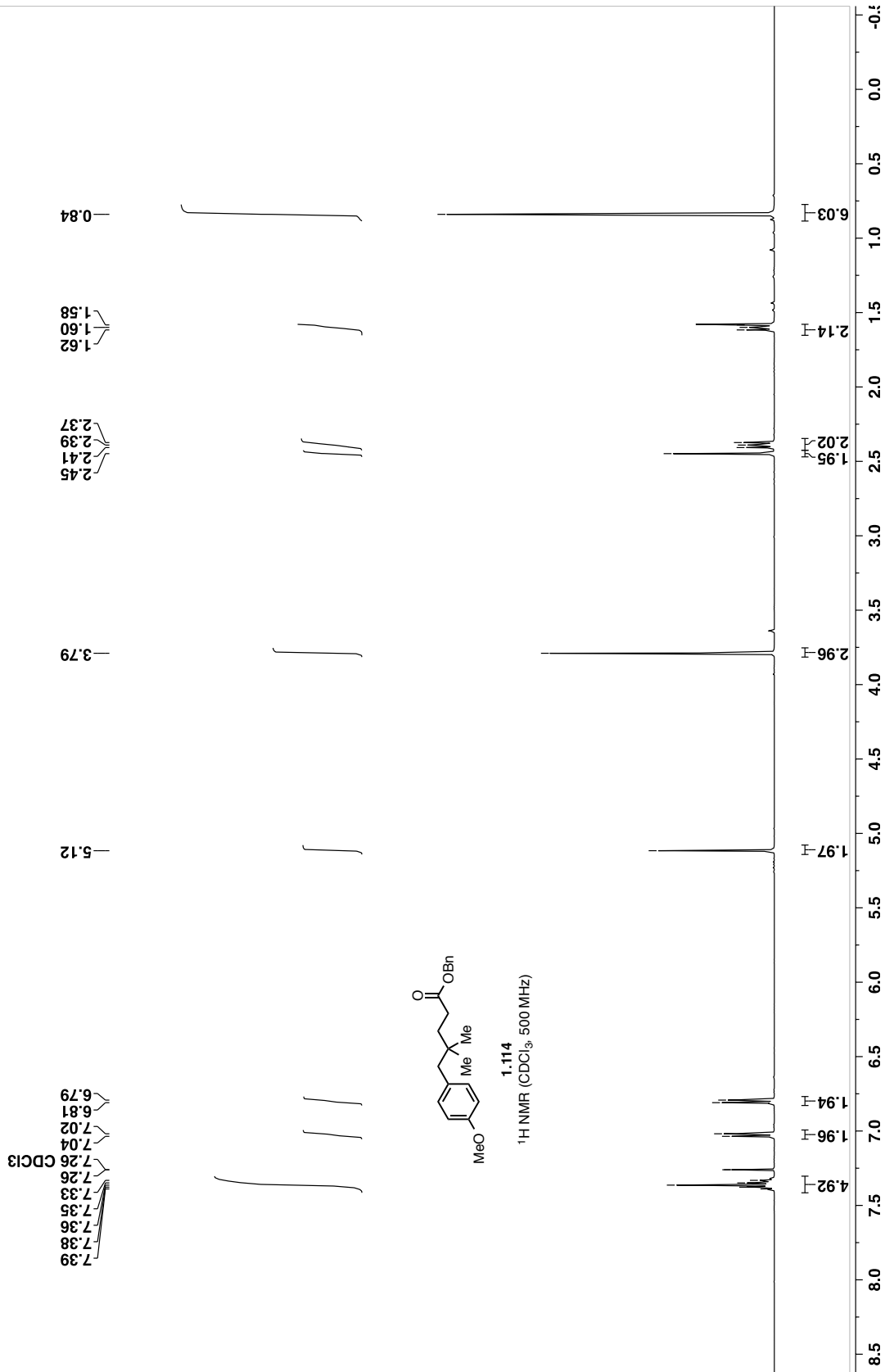
```

Current Data Parameters
NAME      YS-III-43
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     20110401
Time      17.54
INSTRUM   cryo500
PROBHD    5 mm CPYX 1H-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         208
DS         4
SWH        30300.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813440 sec
RG         16.500 usec
DE         6.000 usec
TE         300.2 K
C11        0.06296.0 K
C12        0.06296.0 K
C13        0.06296.0 K
C14        0.06296.0 K
C15        0.06296.0 K
C16        0.06296.0 K
C17        0.06296.0 K
C18        0.06296.0 K
C19        0.06296.0 K
C20        0.06296.0 K
C21        0.06296.0 K
C22        0.06296.0 K
C23        0.06296.0 K
C24        0.06296.0 K
C25        0.06296.0 K
C26        0.06296.0 K
C27        0.06296.0 K
C28        0.06296.0 K
C29        0.06296.0 K
C30        0.06296.0 K
C31        0.06296.0 K
C32        0.06296.0 K
C33        0.06296.0 K
C34        0.06296.0 K
C35        0.06296.0 K
C36        0.06296.0 K
C37        0.06296.0 K
C38        0.06296.0 K
C39        0.06296.0 K
C40        0.06296.0 K
C41        0.06296.0 K
C42        0.06296.0 K
C43        0.06296.0 K
C44        0.06296.0 K
C45        0.06296.0 K
C46        0.06296.0 K
C47        0.06296.0 K
C48        0.06296.0 K
C49        0.06296.0 K
C50        0.06296.0 K
C51        0.06296.0 K
C52        0.06296.0 K
C53        0.06296.0 K
C54        0.06296.0 K
C55        0.06296.0 K
C56        0.06296.0 K
C57        0.06296.0 K
C58        0.06296.0 K
C59        0.06296.0 K
C60        0.06296.0 K
C61        0.06296.0 K
C62        0.06296.0 K
C63        0.06296.0 K
C64        0.06296.0 K
C65        0.06296.0 K
C66        0.06296.0 K
C67        0.06296.0 K
C68        0.06296.0 K
C69        0.06296.0 K
C70        0.06296.0 K
C71        0.06296.0 K
C72        0.06296.0 K
C73        0.06296.0 K
C74        0.06296.0 K
C75        0.06296.0 K
C76        0.06296.0 K
C77        0.06296.0 K
C78        0.06296.0 K
C79        0.06296.0 K
C80        0.06296.0 K
C81        0.06296.0 K
C82        0.06296.0 K
C83        0.06296.0 K
C84        0.06296.0 K
C85        0.06296.0 K
C86        0.06296.0 K
C87        0.06296.0 K
C88        0.06296.0 K
C89        0.06296.0 K
C90        0.06296.0 K
C91        0.06296.0 K
C92        0.06296.0 K
C93        0.06296.0 K
C94        0.06296.0 K
C95        0.06296.0 K
C96        0.06296.0 K
C97        0.06296.0 K
C98        0.06296.0 K
C99        0.06296.0 K
C100       0.06296.0 K
===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        0.00 dB
P2         500.00 usec
PL2        19.00 dB
P3         0.00 usec
PL3        0.00 dB
P4         1.00 usec
PL4        0.00 dB
P5         1.00 usec
PL5        0.00 dB
P6         1.00 usec
PL6        0.00 dB
SFO1       125.7642548 MHz
SF         125.760 MHz
SFO2       500.1360994 MHz
SFO3       500.1360994 MHz
SFO4       500.1360994 MHz
SFO5       500.1360994 MHz
SFO6       500.1360994 MHz
SFO7       500.1360994 MHz
SFO8       500.1360994 MHz
SFO9       500.1360994 MHz
SFO10      500.1360994 MHz
SFO11      500.1360994 MHz
SFO12      500.1360994 MHz
SFO13      500.1360994 MHz
SFO14      500.1360994 MHz
SFO15      500.1360994 MHz
SFO16      500.1360994 MHz
SFO17      500.1360994 MHz
SFO18      500.1360994 MHz
SFO19      500.1360994 MHz
SFO20      500.1360994 MHz
SFO21      500.1360994 MHz
SFO22      500.1360994 MHz
SFO23      500.1360994 MHz
SFO24      500.1360994 MHz
SFO25      500.1360994 MHz
SFO26      500.1360994 MHz
SFO27      500.1360994 MHz
SFO28      500.1360994 MHz
SFO29      500.1360994 MHz
SFO30      500.1360994 MHz
SFO31      500.1360994 MHz
SFO32      500.1360994 MHz
SFO33      500.1360994 MHz
SFO34      500.1360994 MHz
SFO35      500.1360994 MHz
SFO36      500.1360994 MHz
SFO37      500.1360994 MHz
SFO38      500.1360994 MHz
SFO39      500.1360994 MHz
SFO40      500.1360994 MHz
SFO41      500.1360994 MHz
SFO42      500.1360994 MHz
SFO43      500.1360994 MHz
SFO44      500.1360994 MHz
SFO45      500.1360994 MHz
SFO46      500.1360994 MHz
SFO47      500.1360994 MHz
SFO48      500.1360994 MHz
SFO49      500.1360994 MHz
SFO50      500.1360994 MHz
SFO51      500.1360994 MHz
SFO52      500.1360994 MHz
SFO53      500.1360994 MHz
SFO54      500.1360994 MHz
SFO55      500.1360994 MHz
SFO56      500.1360994 MHz
SFO57      500.1360994 MHz
SFO58      500.1360994 MHz
SFO59      500.1360994 MHz
SFO60      500.1360994 MHz
SFO61      500.1360994 MHz
SFO62      500.1360994 MHz
SFO63      500.1360994 MHz
SFO64      500.1360994 MHz
SFO65      500.1360994 MHz
SFO66      500.1360994 MHz
SFO67      500.1360994 MHz
SFO68      500.1360994 MHz
SFO69      500.1360994 MHz
SFO70      500.1360994 MHz
SFO71      500.1360994 MHz
SFO72      500.1360994 MHz
SFO73      500.1360994 MHz
SFO74      500.1360994 MHz
SFO75      500.1360994 MHz
SFO76      500.1360994 MHz
SFO77      500.1360994 MHz
SFO78      500.1360994 MHz
SFO79      500.1360994 MHz
SFO80      500.1360994 MHz
SFO81      500.1360994 MHz
SFO82      500.1360994 MHz
SFO83      500.1360994 MHz
SFO84      500.1360994 MHz
SFO85      500.1360994 MHz
SFO86      500.1360994 MHz
SFO87      500.1360994 MHz
SFO88      500.1360994 MHz
SFO89      500.1360994 MHz
SFO90      500.1360994 MHz
SFO91      500.1360994 MHz
SFO92      500.1360994 MHz
SFO93      500.1360994 MHz
SFO94      500.1360994 MHz
SFO95      500.1360994 MHz
SFO96      500.1360994 MHz
SFO97      500.1360994 MHz
SFO98      500.1360994 MHz
SFO99      500.1360994 MHz
SFO100     500.1360994 MHz
===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P2         100.00 usec
PL2        0.00 dB
P3         1.00 usec
PL3        0.00 dB
P4         1.00 usec
PL4        0.00 dB
P5         1.00 usec
PL5        0.00 dB
P6         1.00 usec
PL6        0.00 dB
SFO1       125.7642548 MHz
SFO2       500.1360994 MHz
SFO3       500.1360994 MHz
SFO4       500.1360994 MHz
SFO5       500.1360994 MHz
SFO6       500.1360994 MHz
SFO7       500.1360994 MHz
SFO8       500.1360994 MHz
SFO9       500.1360994 MHz
SFO10      500.1360994 MHz
SFO11      500.1360994 MHz
SFO12      500.1360994 MHz
SFO13      500.1360994 MHz
SFO14      500.1360994 MHz
SFO15      500.1360994 MHz
SFO16      500.1360994 MHz
SFO17      500.1360994 MHz
SFO18      500.1360994 MHz
SFO19      500.1360994 MHz
SFO20      500.1360994 MHz
SFO21      500.1360994 MHz
SFO22      500.1360994 MHz
SFO23      500.1360994 MHz
SFO24      500.1360994 MHz
SFO25      500.1360994 MHz
SFO26      500.1360994 MHz
SFO27      500.1360994 MHz
SFO28      500.1360994 MHz
SFO29      500.1360994 MHz
SFO30      500.1360994 MHz
SFO31      500.1360994 MHz
SFO32      500.1360994 MHz
SFO33      500.1360994 MHz
SFO34      500.1360994 MHz
SFO35      500.1360994 MHz
SFO36      500.1360994 MHz
SFO37      500.1360994 MHz
SFO38      500.1360994 MHz
SFO39      500.1360994 MHz
SFO40      500.1360994 MHz
SFO41      500.1360994 MHz
SFO42      500.1360994 MHz
SFO43      500.1360994 MHz
SFO44      500.1360994 MHz
SFO45      500.1360994 MHz
SFO46      500.1360994 MHz
SFO47      500.1360994 MHz
SFO48      500.1360994 MHz
SFO49      500.1360994 MHz
SFO50      500.1360994 MHz
SFO51      500.1360994 MHz
SFO52      500.1360994 MHz
SFO53      500.1360994 MHz
SFO54      500.1360994 MHz
SFO55      500.1360994 MHz
SFO56      500.1360994 MHz
SFO57      500.1360994 MHz
SFO58      500.1360994 MHz
SFO59      500.1360994 MHz
SFO60      500.1360994 MHz
SFO61      500.1360994 MHz
SFO62      500.1360994 MHz
SFO63      500.1360994 MHz
SFO64      500.1360994 MHz
SFO65      500.1360994 MHz
SFO66      500.1360994 MHz
SFO67      500.1360994 MHz
SFO68      500.1360994 MHz
SFO69      500.1360994 MHz
SFO70      500.1360994 MHz
SFO71      500.1360994 MHz
SFO72      500.1360994 MHz
SFO73      500.1360994 MHz
SFO74      500.1360994 MHz
SFO75      500.1360994 MHz
SFO76      500.1360994 MHz
SFO77      500.1360994 MHz
SFO78      500.1360994 MHz
SFO79      500.1360994 MHz
SFO80      500.1360994 MHz
SFO81      500.1360994 MHz
SFO82      500.1360994 MHz
SFO83      500.1360994 MHz
SFO84      500.1360994 MHz
SFO85      500.1360994 MHz
SFO86      500.1360994 MHz
SFO87      500.1360994 MHz
SFO88      500.1360994 MHz
SFO89      500.1360994 MHz
SFO90      500.1360994 MHz
SFO91      500.1360994 MHz
SFO92      500.1360994 MHz
SFO93      500.1360994 MHz
SFO94      500.1360994 MHz
SFO95      500.1360994 MHz
SFO96      500.1360994 MHz
SFO97      500.1360994 MHz
SFO98      500.1360994 MHz
SFO99      500.1360994 MHz
SFO100     500.1360994 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPMAG[1]   0.00000000
GPHZ[1]    0.00000000
GPHZ[2]    0.00000000
GPHZ[3]    0.00000000
GPHZ[4]    0.00000000
GPHZ[5]    0.00000000
GPHZ[6]    0.00000000
GPHZ[7]    0.00000000
GPHZ[8]    0.00000000
GPHZ[9]    0.00000000
GPHZ[10]   0.00000000
GPHZ[11]   0.00000000
GPHZ[12]   0.00000000
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GPHZ[14]   0.00000000
GPHZ[15]   0.00000000
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GPHZ[17]   0.00000000
GPHZ[18]   0.00000000
GPHZ[19]   0.00000000
GPHZ[20]   0.00000000
GPHZ[21]   0.00000000
GPHZ[22]   0.00000000
GPHZ[23]   0.00000000
GPHZ[24]   0.00000000
GPHZ[25]   0.00000000
GPHZ[26]   0.00000000
GPHZ[27]   0.00000000
GPHZ[28]   0.00000000
GPHZ[29]   0.00000000
GPHZ[30]   0.00000000
GPHZ[31]   0.00000000
GPHZ[32]   0.00000000
GPHZ[33]   0.00000000
GPHZ[34]   0.00000000
GPHZ[35]   0.00000000
GPHZ[36]   0.00000000
GPHZ[37]   0.00000000
GPHZ[38]   0.00000000
GPHZ[39]   0.00000000
GPHZ[40]   0.00000000
GPHZ[41]   0.00000000
GPHZ[42]   0.00000000
GPHZ[43]   0.00000000
GPHZ[44]   0.00000000
GPHZ[45]   0.00000000
GPHZ[46]   0.00000000
GPHZ[47]   0.00000000
GPHZ[48]   0.00000000
GPHZ[49]   0.00000000
GPHZ[50]   0.00000000
GPHZ[51]   0.00000000
GPHZ[52]   0.00000000
GPHZ[53]   0.00000000
GPHZ[54]   0.00000000
GPHZ[55]   0.00000000
GPHZ[56]   0.00000000
GPHZ[57]   0.00000000
GPHZ[58]   0.00000000
GPHZ[59]   0.00000000
GPHZ[60]   0.00000000
GPHZ[61]   0.00000000
GPHZ[62]   0.00000000
GPHZ[63]   0.00000000
GPHZ[64]   0.00000000
GPHZ[65]   0.00000000
GPHZ[66]   0.00000000
GPHZ[67]   0.00000000
GPHZ[68]   0.00000000
GPHZ[69]   0.00000000
GPHZ[70]   0.00000000
GPHZ[71]   0.00000000
GPHZ[72]   0.00000000
GPHZ[73]   0.00000000
GPHZ[74]   0.00000000
GPHZ[75]   0.00000000
GPHZ[76]   0.00000000
GPHZ[77]   0.00000000
GPHZ[78]   0.00000000
GPHZ[79]   0.00000000
GPHZ[80]   0.00000000
GPHZ[81]   0.00000000
GPHZ[82]   0.00000000
GPHZ[83]   0.00000000
GPHZ[84]   0.00000000
GPHZ[85]   0.00000000
GPHZ[86]   0.00000000
GPHZ[87]   0.00000000
GPHZ[88]   0.00000000
GPHZ[89]   0.00000000
GPHZ[90]   0.00000000
GPHZ[91]   0.00000000
GPHZ[92]   0.00000000
GPHZ[93]   0.00000000
GPHZ[94]   0.00000000
GPHZ[95]   0.00000000
GPHZ[96]   0.00000000
GPHZ[97]   0.00000000
GPHZ[98]   0.00000000
GPHZ[99]   0.00000000
GPHZ[100]  0.00000000
===== Processing parameters =====
SI         32768
SF         125.764012 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         2.00

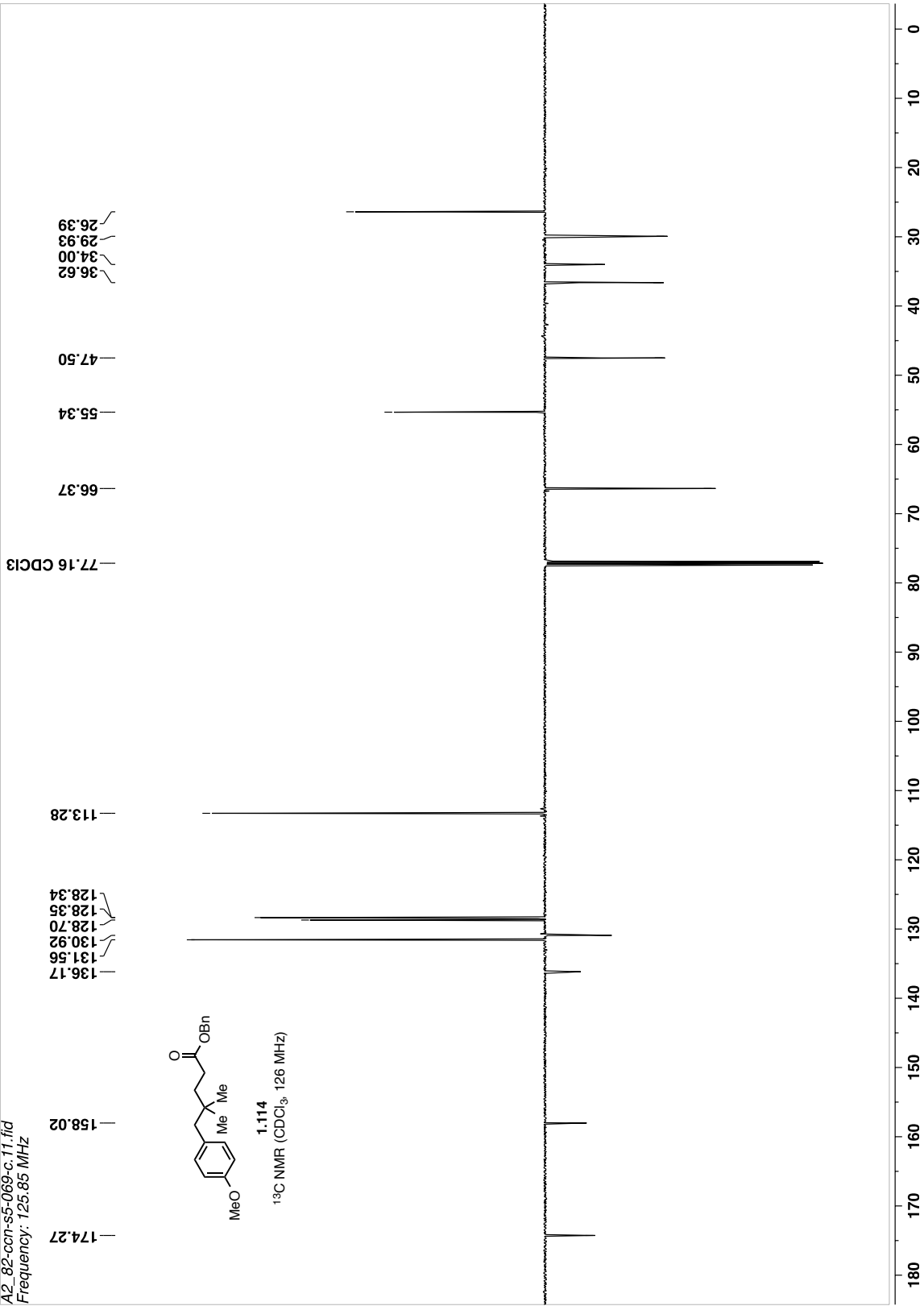
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A2_82-con-s5-069-c.10.fid
Frequency: 500.46 MHz

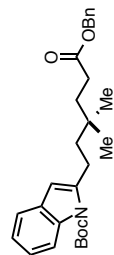


A2_82-ccn-s5-069-c.11.fid
Frequency: 125.85 MHz

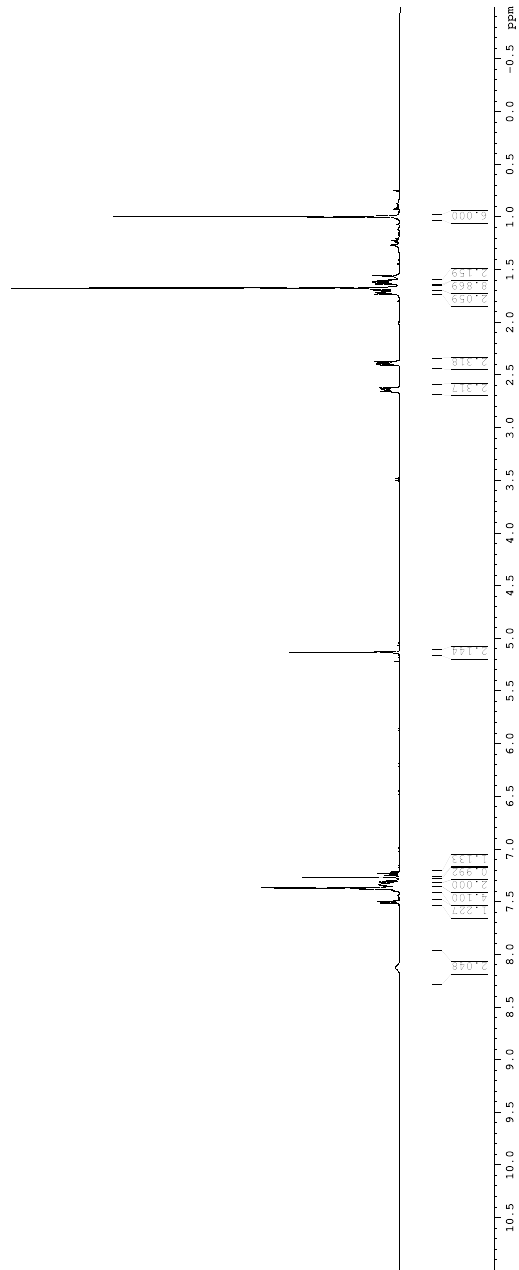


YS-II-279

Current Data Parameters
NAME YS-II-279
PROCNO 1
EXPNO 1
F2 - Acquisition Parameters
Date_ Acq 01/09/05
Time 8:57
INSTRUM spect
PROBHD 5 mm CQCI 1H
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 2
SS 6012.820 Hz
AQ 0.2500024 Hz
RG 1.9397932 sec
DQ 62.400 usec
DE 6.00 usec
DI 0.10000000 sec
MCN3T 0 sec
MCN3R 0.01500000 sec
***** CHANNEL F1 *****
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235012 MHz
F2 - Processing parameters
SI 65536
SF 500.2235012 MHz
RG 655
SFO 500.2235012 MHz
DS 8
SS 6012.820 Hz
DE 6.00 usec
DI 0.10000000 sec



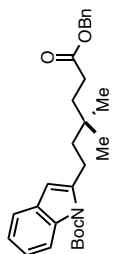
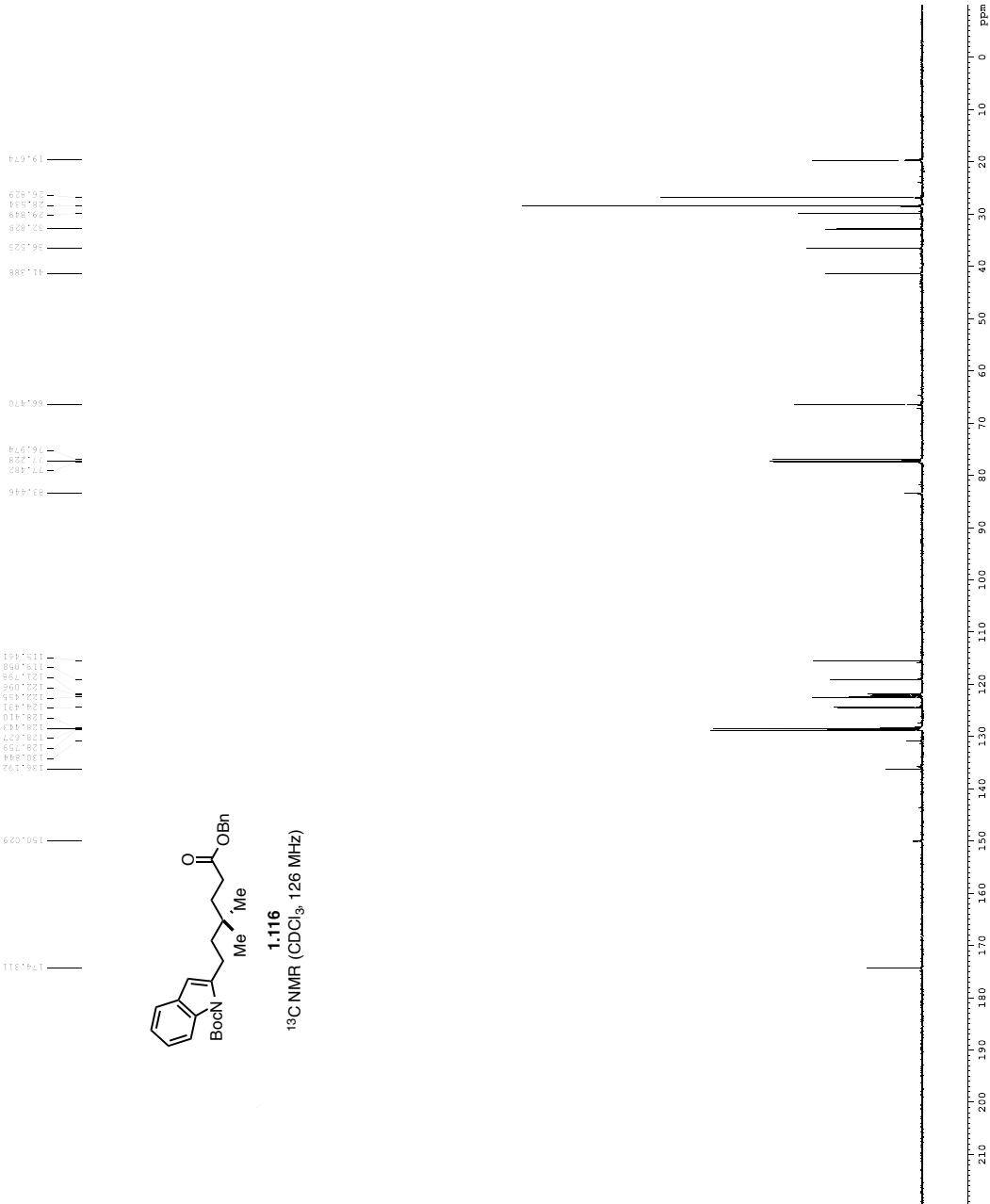
1.116
1H NMR (CDCl₃, 500 MHz)



```

Current Data Parameters
=====
EXPNO      1
PROCNO     1
F2 - Acquisition Parameters
=====
Date_      20110305
Time       11.05
INSTRUM    cryo500
PROBHD     5 mm CPCC 1H-
PULPROG    zgpg30
TD          65536
SOLVENT    CDCl3
NS          464
DS          4
SWH         30300.075 Hz
FIDRES     0.462388 Hz
AQ          1.0813440 sec
RG          16.500 usec
DE          6.00 usec
TE          1.00296.0 K
T1         0.000000 sec
d11        0.000000 sec
D16        0.00020000 sec
d17        0.00019600 sec
MKREST     0 sec
NAME       1.116
INSTRUM    cryo500
=====
CHANNEL f1 126 MHz
=====
NUC1        13C
P1          16.55 usec
PL1         500.00 usec
PL2         2000.00 usec
PL3         1.00 usec
PL4         1.00 usec
PL5         1.00 usec
PL6         1.00 usec
SFO1        125.7942548 MHz
SF1         2.70 usec
SFO2        500.2225011 MHz
SFX1        SFO1
SFX2        SFO2
SFX3        SFO1
SFX4        SFO2
SFX5        SFO1
SFX6        SFO2
SFX7        SFO1
SFX8        SFO2
SFX9        SFO1
SFX10       SFO2
SFX11       SFO1
SFX12       SFO2
SFX13       SFO1
SFX14       SFO2
SFX15       SFO1
SFX16       SFO2
SFX17       SFO1
SFX18       SFO2
SFX19       SFO1
SFX20       SFO2
SFX21       SFO1
SFX22       SFO2
SFX23       SFO1
SFX24       SFO2
SFX25       SFO1
SFX26       SFO2
SFX27       SFO1
SFX28       SFO2
SFX29       SFO1
SFX30       SFO2
SFX31       SFO1
SFX32       SFO2
SFX33       SFO1
SFX34       SFO2
SFX35       SFO1
SFX36       SFO2
SFX37       SFO1
SFX38       SFO2
SFX39       SFO1
SFX40       SFO2
SFX41       SFO1
SFX42       SFO2
SFX43       SFO1
SFX44       SFO2
SFX45       SFO1
SFX46       SFO2
SFX47       SFO1
SFX48       SFO2
SFX49       SFO1
SFX50       SFO2
SFX51       SFO1
SFX52       SFO2
SFX53       SFO1
SFX54       SFO2
SFX55       SFO1
SFX56       SFO2
SFX57       SFO1
SFX58       SFO2
SFX59       SFO1
SFX60       SFO2
SFX61       SFO1
SFX62       SFO2
SFX63       SFO1
SFX64       SFO2
SFX65       SFO1
SFX66       SFO2
SFX67       SFO1
SFX68       SFO2
SFX69       SFO1
SFX70       SFO2
SFX71       SFO1
SFX72       SFO2
SFX73       SFO1
SFX74       SFO2
SFX75       SFO1
SFX76       SFO2
SFX77       SFO1
SFX78       SFO2
SFX79       SFO1
SFX80       SFO2
SFX81       SFO1
SFX82       SFO2
SFX83       SFO1
SFX84       SFO2
SFX85       SFO1
SFX86       SFO2
SFX87       SFO1
SFX88       SFO2
SFX89       SFO1
SFX90       SFO2
SFX91       SFO1
SFX92       SFO2
SFX93       SFO1
SFX94       SFO2
SFX95       SFO1
SFX96       SFO2
SFX97       SFO1
SFX98       SFO2
SFX99       SFO1
SFX100      SFO2
=====
CHANNEL f2 126 MHz
=====
CPDPRG2    waltz16
NUC2        13C
P2          16.55 usec
PL2         500.00 usec
PL3         2000.00 usec
PL4         1.00 usec
PL5         1.00 usec
PL6         1.00 usec
SFO1        125.7942548 MHz
SFO2        500.2225011 MHz
SFX1        SFO1
SFX2        SFO2
SFX3        SFO1
SFX4        SFO2
SFX5        SFO1
SFX6        SFO2
SFX7        SFO1
SFX8        SFO2
SFX9        SFO1
SFX10       SFO2
SFX11       SFO1
SFX12       SFO2
SFX13       SFO1
SFX14       SFO2
SFX15       SFO1
SFX16       SFO2
SFX17       SFO1
SFX18       SFO2
SFX19       SFO1
SFX20       SFO2
SFX21       SFO1
SFX22       SFO2
SFX23       SFO1
SFX24       SFO2
SFX25       SFO1
SFX26       SFO2
SFX27       SFO1
SFX28       SFO2
SFX29       SFO1
SFX30       SFO2
SFX31       SFO1
SFX32       SFO2
SFX33       SFO1
SFX34       SFO2
SFX35       SFO1
SFX36       SFO2
SFX37       SFO1
SFX38       SFO2
SFX39       SFO1
SFX40       SFO2
SFX41       SFO1
SFX42       SFO2
SFX43       SFO1
SFX44       SFO2
SFX45       SFO1
SFX46       SFO2
SFX47       SFO1
SFX48       SFO2
SFX49       SFO1
SFX50       SFO2
SFX51       SFO1
SFX52       SFO2
SFX53       SFO1
SFX54       SFO2
SFX55       SFO1
SFX56       SFO2
SFX57       SFO1
SFX58       SFO2
SFX59       SFO1
SFX60       SFO2
SFX61       SFO1
SFX62       SFO2
SFX63       SFO1
SFX64       SFO2
SFX65       SFO1
SFX66       SFO2
SFX67       SFO1
SFX68       SFO2
SFX69       SFO1
SFX70       SFO2
SFX71       SFO1
SFX72       SFO2
SFX73       SFO1
SFX74       SFO2
SFX75       SFO1
SFX76       SFO2
SFX77       SFO1
SFX78       SFO2
SFX79       SFO1
SFX80       SFO2
SFX81       SFO1
SFX82       SFO2
SFX83       SFO1
SFX84       SFO2
SFX85       SFO1
SFX86       SFO2
SFX87       SFO1
SFX88       SFO2
SFX89       SFO1
SFX90       SFO2
SFX91       SFO1
SFX92       SFO2
SFX93       SFO1
SFX94       SFO2
SFX95       SFO1
SFX96       SFO2
SFX97       SFO1
SFX98       SFO2
SFX99       SFO1
SFX100      SFO2
=====
===== GRADIENT CHANNEL =====
GPNAM[1]    SINE.100
GPNAM[2]    SINE.100
GPA1        0 %
GPA2        0 %
GPA3        0 %
GPA4        0 %
GPA5        0 %
GPA6        0 %
GPA7        0 %
GPA8        0 %
GPA9        0 %
GPA10       0 %
GPA11       0 %
GPA12       0 %
GPA13       0 %
GPA14       0 %
GPA15       0 %
GPA16       0 %
=====
F2 - Processing parameters
=====
SI          65536
SF          125.7880019 MHz
WDW         EM
SSB         0
LB          0
GB          0
PC          2.00

```



1.116
¹³C NMR (CDCl₃, 126 MHz)

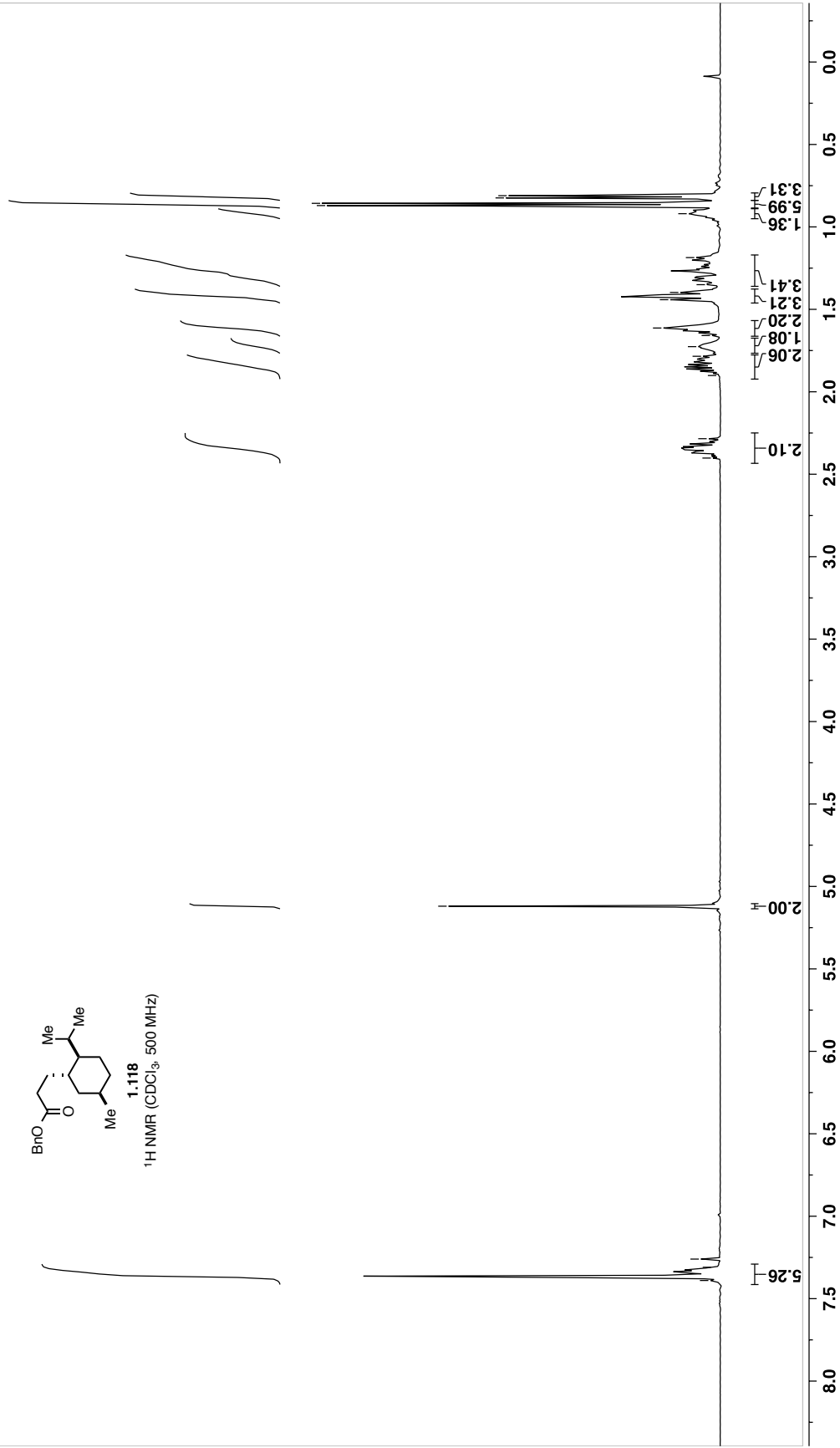
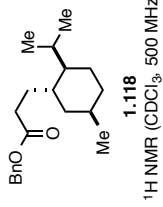
A2_61-ccn-s5-104-1-1-a.10.fid
Frequency: 500.46 MHz

7.39
7.31
7.26 CDCl₃

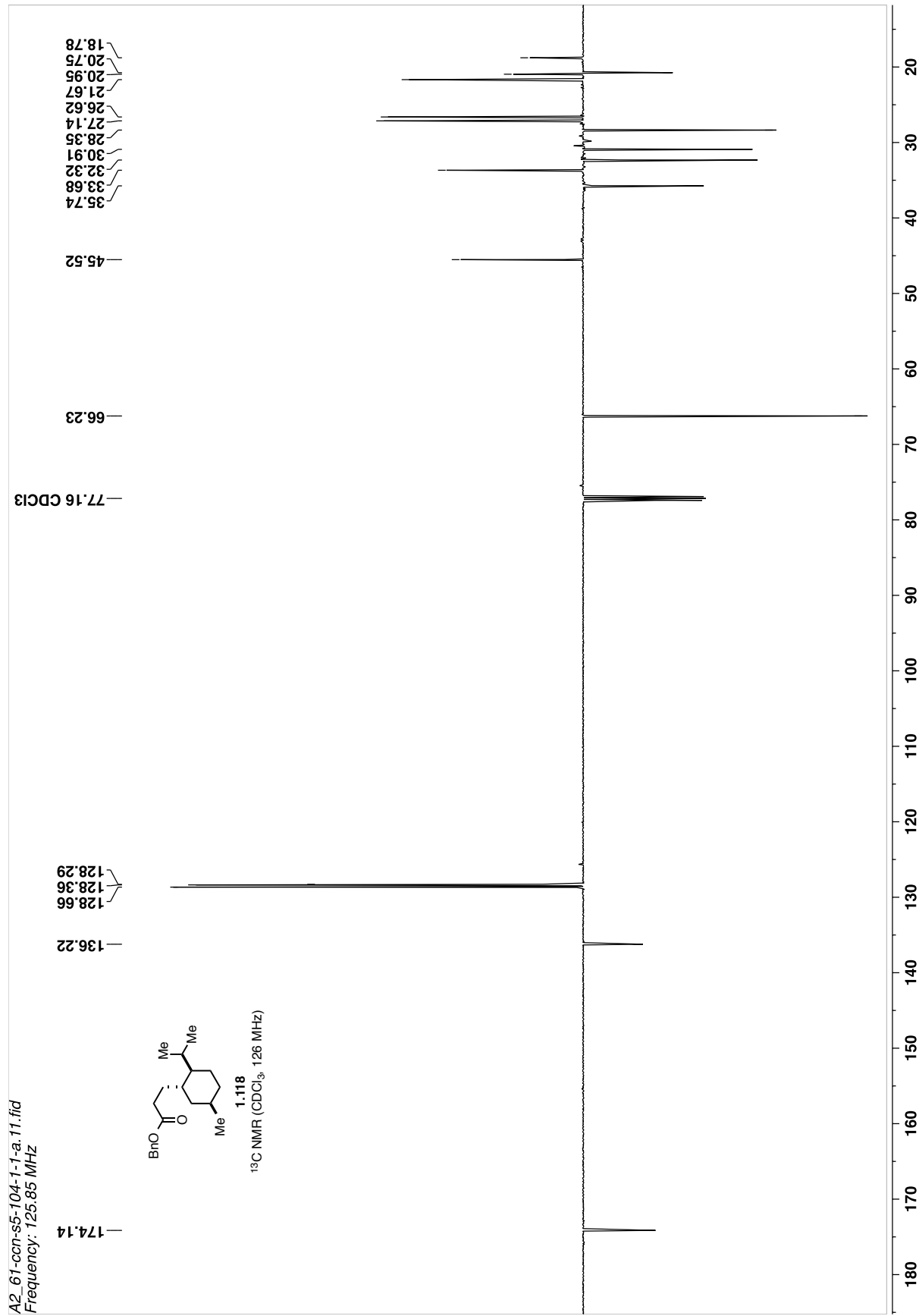
1.90
1.78
1.73
1.66
1.61
1.44
1.40
1.35
1.19
0.92
0.87
0.86
0.82
0.81

2.40
2.28

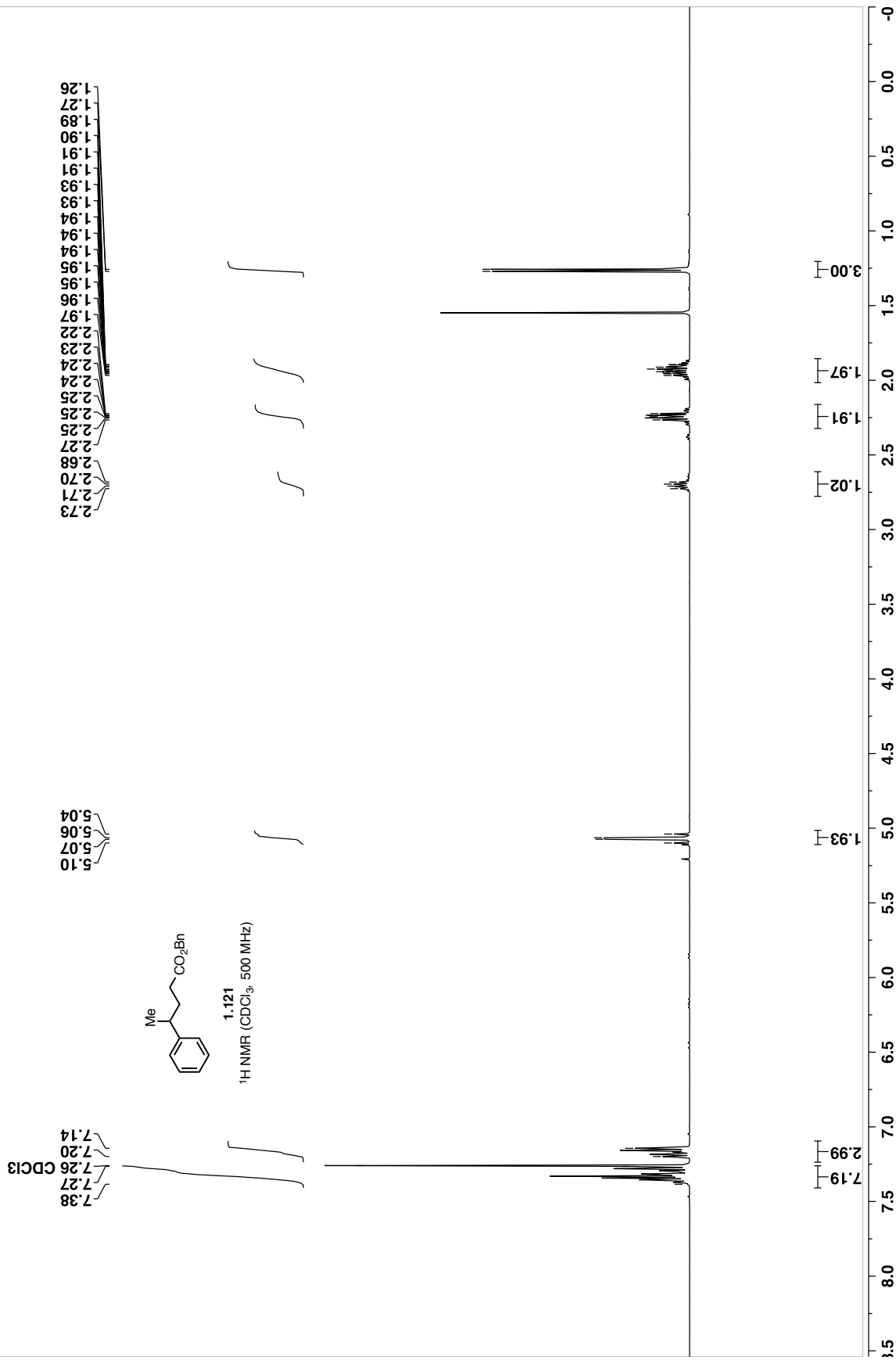
5.12



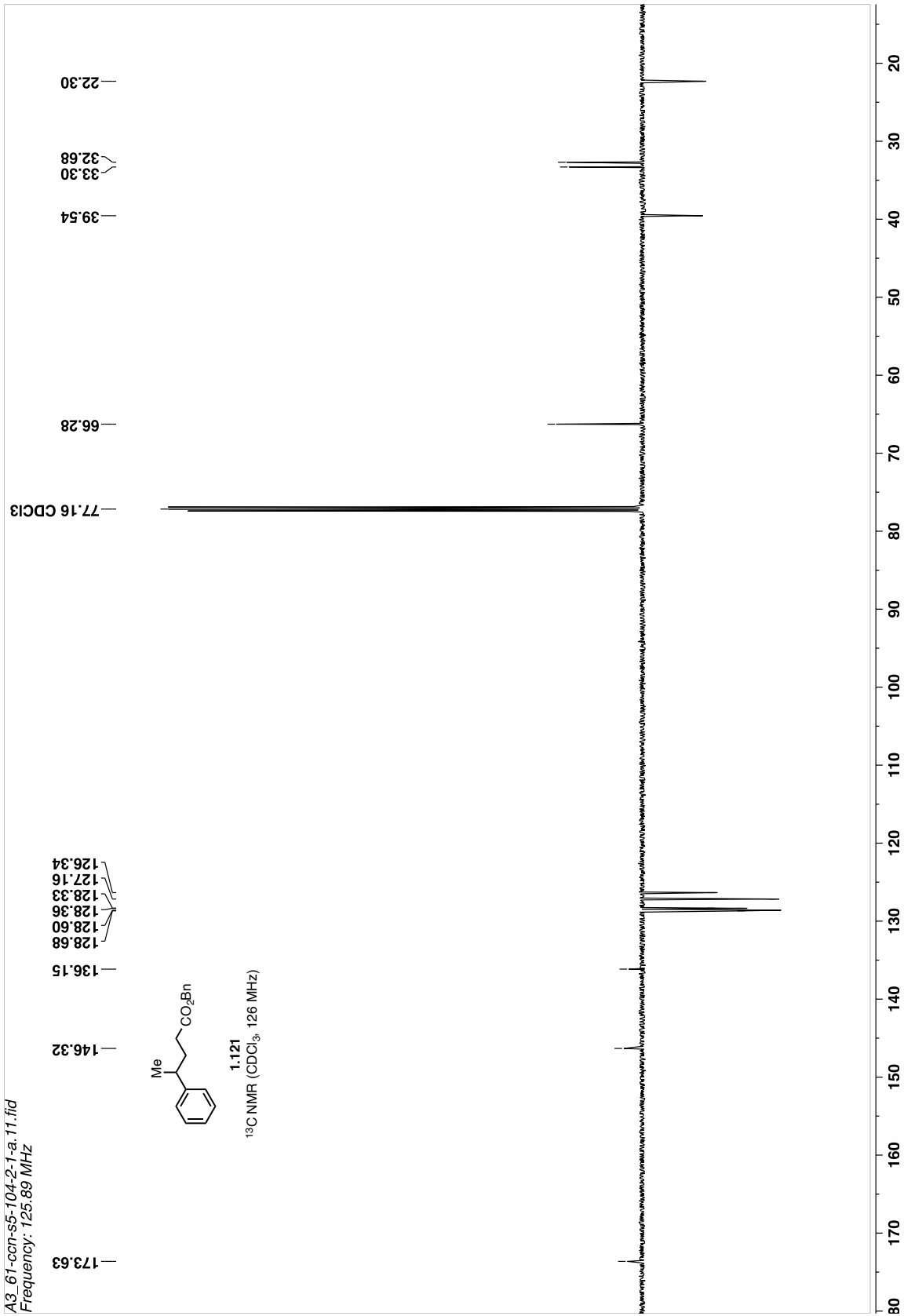
A2_61-ccn-s5-104-1-1-a.11.fid
Frequency: 125.85 MHz



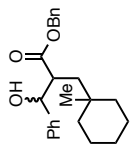
A3_61-ccn-s5-104-2-1-a.10.fid
Frequency: 500.62 MHz



A3_61-con-s5-104-2-1-a.11.fid
Frequency: 125.89 MHz



YS-III-56-Major



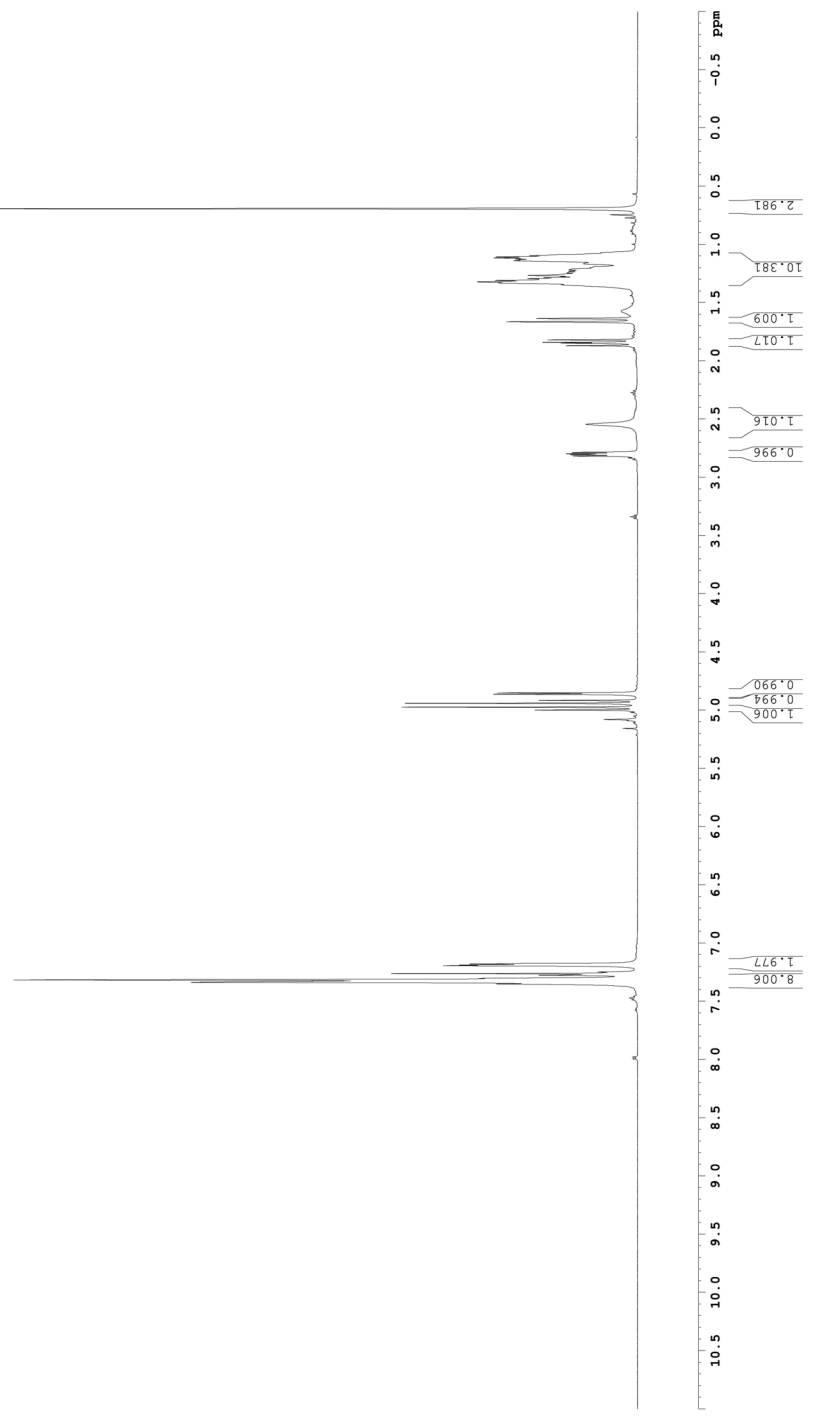
1.127
major diastereomer
1H NMR (CDCl₃, 500 MHz)

Current Data Parameters
EXPNO 1
PROCNO 1
DATAFILE /v/data/yurly/nmr
Date_ 20180110
F2 - Acquisition Parameters
INSTRUM cryo500
PROBHD 5 mm CPYCI 1H-
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.096043 Hz
AQ 5.0999273 sec
RG 327.14
DM 62.400 usec
DE 6.00 usec
TE 298.0 K
PROC 0.1000000 sec
MCWRRK 0.0150000 sec
***** CHANNEL f1 *****
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 500.2235015 MHz
S2 - Processing parameters
WDW EM
SSB 0
GB 0
EC 1.00

7.349
7.335
7.315
7.301
7.274
7.260
7.247
7.193
7.187
7.178
2.816
2.805
2.796
2.785
2.543
1.867
1.847
1.839
1.818
1.663
1.635
1.345
1.330
1.320
1.308
1.292
1.284
1.274
1.265
1.243
1.228
1.215
1.165
1.138
1.123
1.115
1.105
1.095
0.691

4.997
4.972
4.939
4.914
4.861
4.850

8.006
1.977

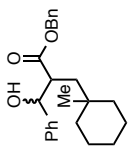


8.006
1.977
1.006
0.994
0.990
0.996
1.016
1.017
1.009
10.381
2.981

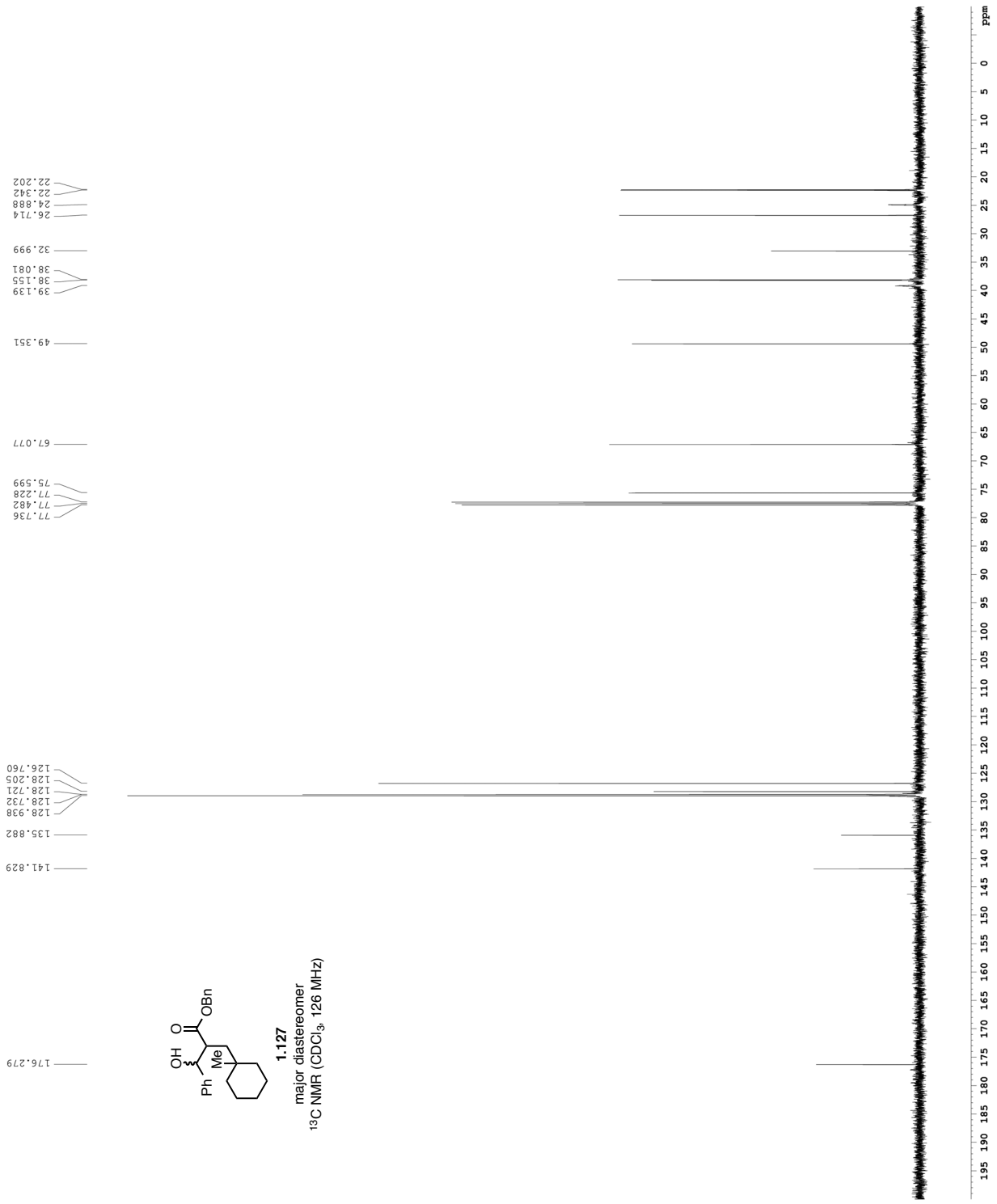
YS-III-56-Major

```

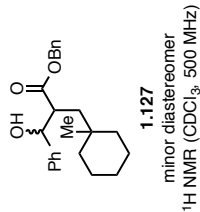
Current Data Parameters
NAME: YS-III-56
PROCNO: 11
DATE: 20180801
TIME: 16:00
INSTRUM: crys500
PROBHD: 5 mm cryoProbe
PULPROG: zgpg30
TD: 65536
SFO2: 125.760311 MHz
NUC1: 13C
NUC2: 1H
AQ: 0.01500000 sec
RG: 327.50000000
FIDRES: 0.462388 Hz
AQ: 1.081340 sec
RG: 327.50000000
DE: 6.00000000 usec
TE: 298.20000000 K
D1: 0.25000000 sec
d11: 0.00000000 sec
d12: 0.00000000 sec
d17: 0.00018600 sec
MCMSK: 0
PCPD2: 100.00 usec
P12: 2000.00 usec
P11: 500.00 usec
P14: 1.00000000 usec
P15: 50.00 usec
P16: 1000.00 usec
SFO1: 125.7942518 MHz
SFO2: 500.2225011 MHz
SF01: 125.7942518 MHz
SF02: 500.2225011 MHz
NAME1: Cryo0.5.20.1
NAME2: Cryo0.5.20.1
SFOFF1: 0 Hz
SFOFF2: 0 Hz
===== CHANNEL f1 =====
NUC1: 13C
P1: 16.13C
P2: 500.00 usec
P3: 2000.00 usec
P4: 1.00000000 usec
P5: 50.00 usec
P6: 1000.00 usec
SFO1: 125.7942518 MHz
SFO2: 500.2225011 MHz
===== CHANNEL f2 =====
NUC1: 1H
P1: 16.1H
P2: 100.00 usec
P3: 2000.00 usec
P4: 1.00000000 usec
P5: 50.00 usec
P6: 1000.00 usec
SFO1: 500.2225011 MHz
SFO2: 125.7603111 MHz
===== GRADIENT CHANNEL =====
GENAM1: SINE.100
GENAM2: SINE.100
GENP1: 0 Hz
GENP2: 0 Hz
GENP3: 0 Hz
GENP4: 0 Hz
GENP5: 0 Hz
GENP6: 0 Hz
===== Processing Parameters =====
WDW: EM
SSB: 0
LB: 0
GB: 0
PC: 2.00
  
```



1.127
major diastereomer
¹³C NMR (CDCl₃, 126 MHz)

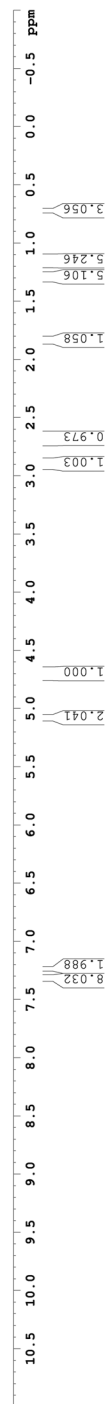


YS-III-56-Minor



Current Data Parameters
NAME YS-III-56
EXPNO 15
DATE_ 20110110
DATAPATH /v/data/yuriys/nmr
F2 - Acquisition Parameters
Date_ 20110110
Time 8:40
INSTRUM cryo-500
PROBHD 5 mm CPICZ-300
PULPROG zg30
ID 81728
SOLVENT CDCl3
DS 1
SWH 8012.820 Hz
FIDRES 0.0998273 sec
AQ 5.0998273 sec
RG 10.1
DM 62.400 usec
DE 298.0 K sec
TE 298.0 K sec
D1 0.10000000 sec
KICKOFF 0 sec
KORRECT 0.01500000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2255015 MHz
F2 - Processing parameters
SI 65536
SF 500.2255015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

7.353
7.337
7.326
7.312
7.300
7.289
7.287
7.275
7.269
7.260
7.253
7.249
7.237
5.108
5.084
5.074
5.050
4.719
4.707
4.697
2.919
2.916
2.900
2.884
2.881
2.683
2.673
1.859
1.839
1.831
1.810
1.555
1.320
1.304
1.288
1.278
1.267
1.208
1.203
1.196
1.182
1.162
1.156
1.135
1.122
1.109
1.095
1.085
0.721

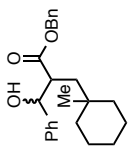
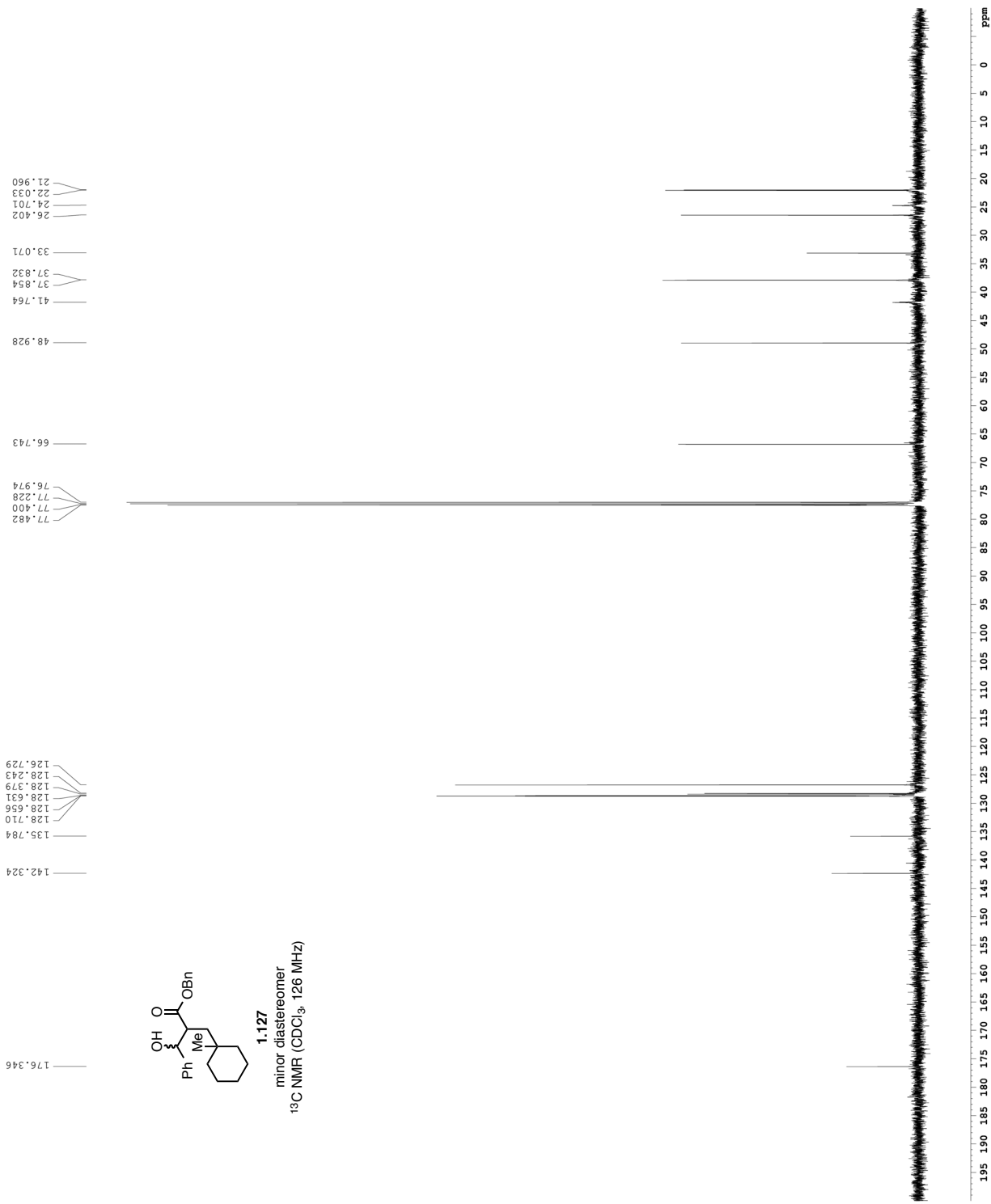


YS-III-56-Minor

```

Comment: Data Parameters
NAME YS-III-56
EXPERO 16
GAINPATH /v/data/yur/yur/mr
F2 - Acquisition Parameters
Date_ 2018010
Time 8.43
PROBHD 5 mm CPTCI 1H-
PULPROG Spinecho90p-prd
SOLVENT CDCl3
NS 511
DS 4
SWH 30300.031 Hz
AQ 1.0813440 sec
RG 7298.2
GB 15.000 usec
DE 6.00 usec
TE 298.0 K
D1 0.03000000 sec
d11 0.00000000 sec
d16 0.00190000 sec
MCREST 0 sec
PCYORK 0.01500000 sec
PC 2.00 usec

===== CHANNEL f1 =====
NUC1 13C
P1 16.55 usec
PCPD2 2000.00 usec
PL1 120.00 dB
PL2 120.00 dB
PL0 120.00 dB
SF01 125.7625148 MHz
SF1 2.70 dB
SFO1 125.7625148 MHz
SFO2 500.225011 MHz
SFO3 500.225011 MHz
===== CHANNEL f2 =====
CPDPRG2 waitz16
PCPD2 100.00 usec
PL2 1.60 dB
PL0 1.60 dB
PL1 1.60 dB
SF02 500.225011 MHz
===== GRADIENT CHANNEL =====
GPNM1(1) SINE.100
GPNM1(2) 0 $
GPNM2(1) 0 $
GPNM2(2) 0 $
GPC1 0 $
GPC2 0 $
GPD1 0 $
GPD2 0 $
GPI6 30.00 $
===== Processing parameters =====
SI 65536
WDW 125.760356 MHz
SSB 0
GB 1.00 Hz
PC 2.00
  
```



1.127
minor diastereomer
¹³C NMR (CDCl₃, 126 MHz)

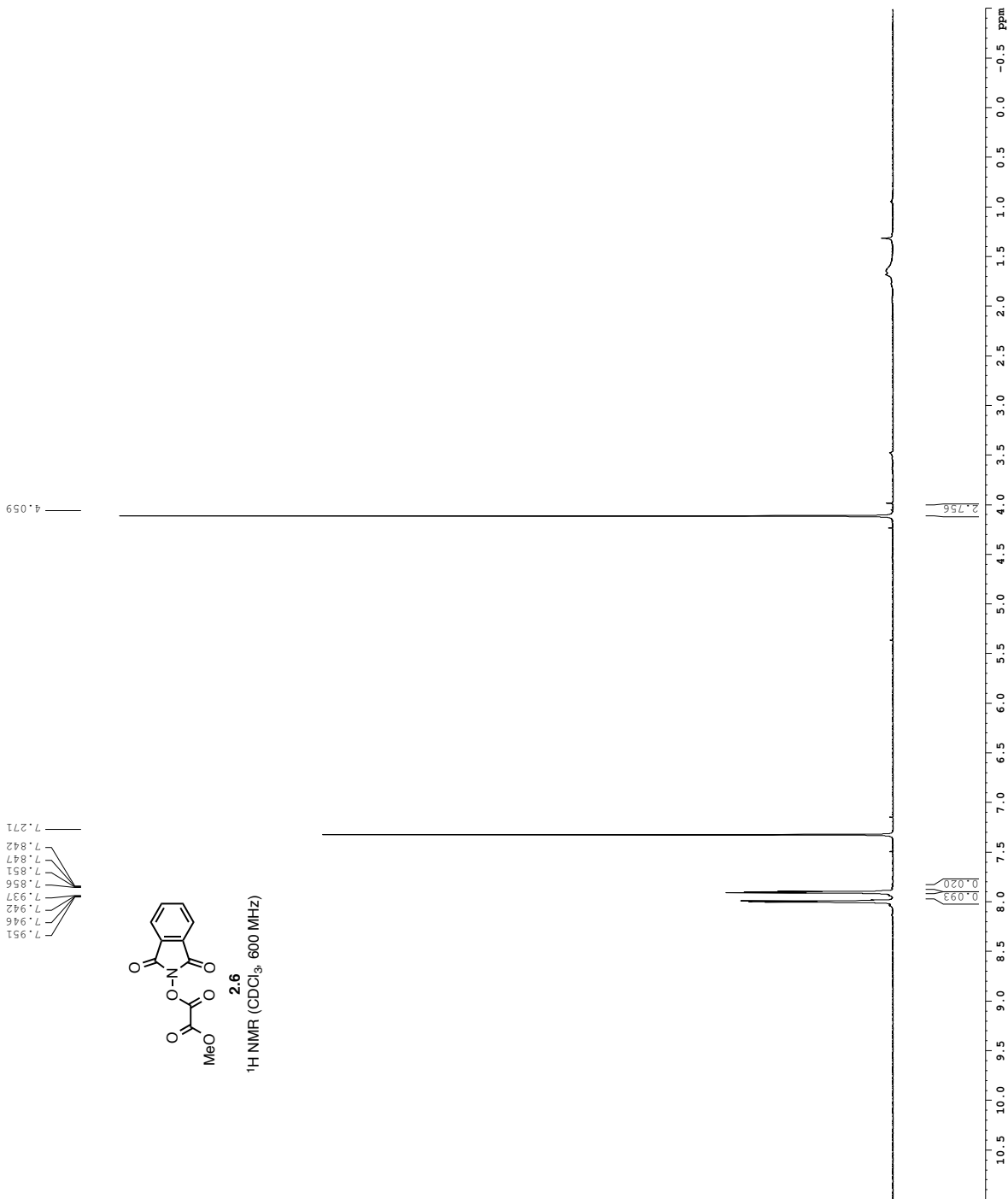
Appendix B: Chapter 2 NMR Spectra

YS-I-152

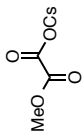
Current Data Parameters
NAME YS-I-152-1
EXNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140304
Time_ 12.57
PROCNO 1
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.962 Hz
FIDRES 0.09005 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



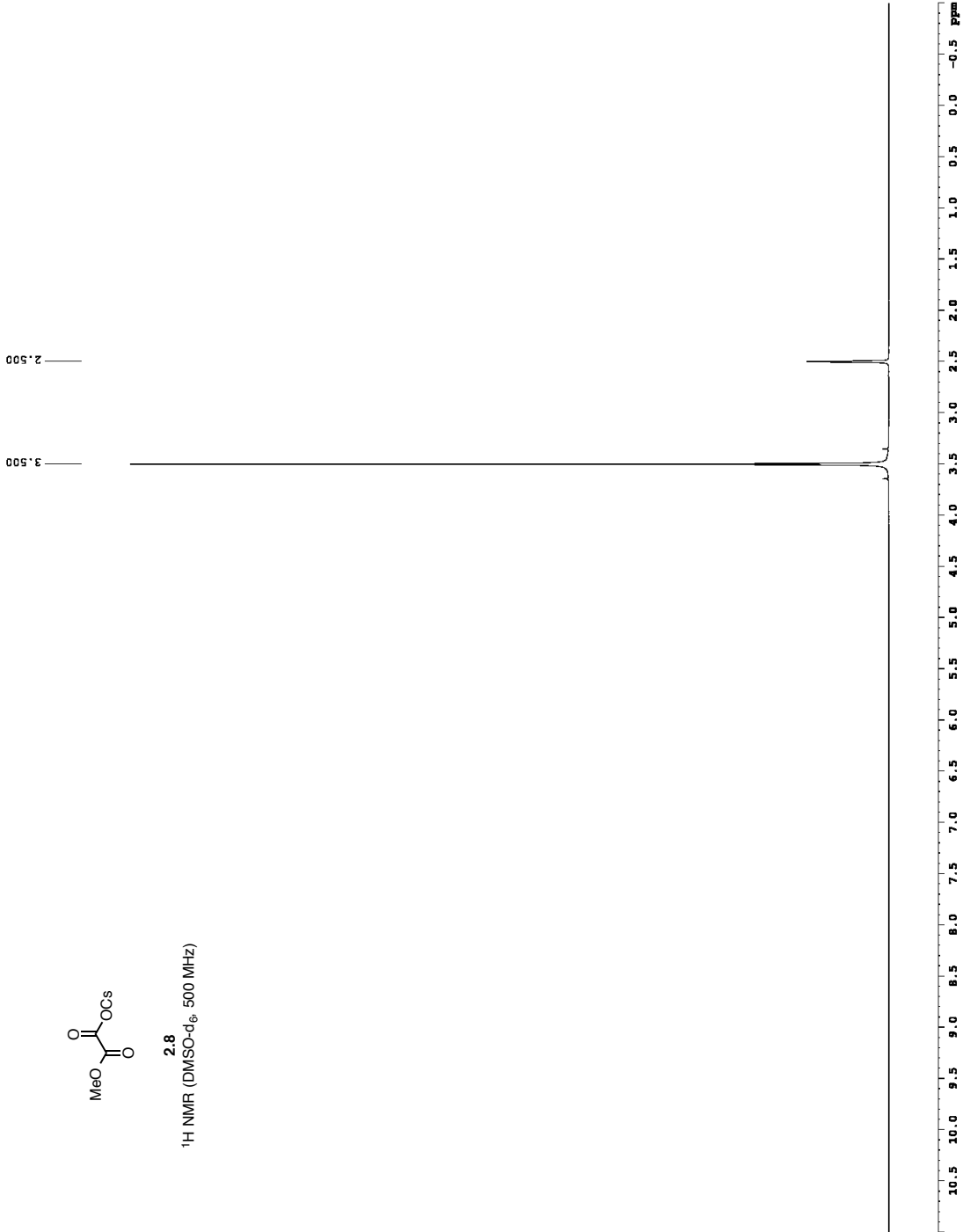
YS-IV-71



2.8

¹H NMR (DMSO-d₆, 500 MHz)

Current Data Parameters
NAME YS-IV-71
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160319
Time 11:00:00
INSTRUM cryo500
PROBHD 5 mm CP1CI 1H-
P1 8.43
TD 65536
SOLVENT DMSO
NS 8
DS 8
SHE 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998273 sec
RG 327.5
DN 62.400 usec
DE 6.00 usec
TE 300.2 K
D1 0.1000000 sec
MCREST 0 sec
MCWRK 0.0150000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL 0
SFO1 500.2234015 MHz
F2 - Processing parameters
SF 500.2200134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

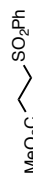


YS-II-21

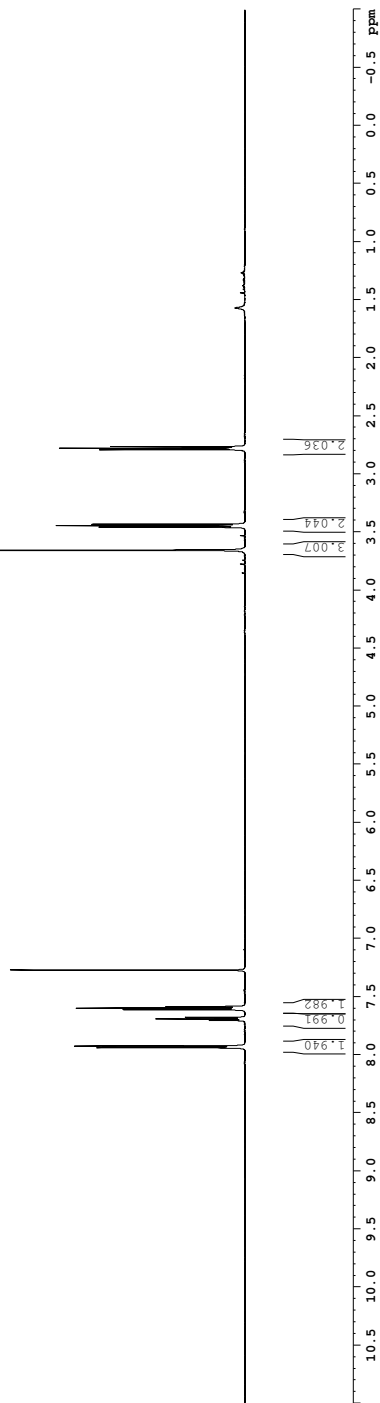
Current Data Parameters
Date_ 15-11-11
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140929
Time 13.40
INSTRUM av600
PROBHD 5 mm TBI 1H/3
PULPROG zgpg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 0.0599448 sec
RG 406
DW 52.000 usec
DE 14.54 usec
TE 297.9 K
D1 0.10000000 sec
TD0 1
===== CHANNEL F1 =====
SFO1 600.1342009 MHz
NUC1 1H
P1 8.00 usec
PLW1 23.01441956 W
F2 - Processing parameters
SI 32768
SF 600.1300283 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

7.938
7.937
7.924
7.922
7.920
7.918
7.678
7.610
7.597
7.584
7.270

3.653
3.456
3.448
3.443
3.437
3.430
2.788
2.781
2.775
2.770
2.762



2.10
¹H NMR (CDCl₃, 600 MHz)

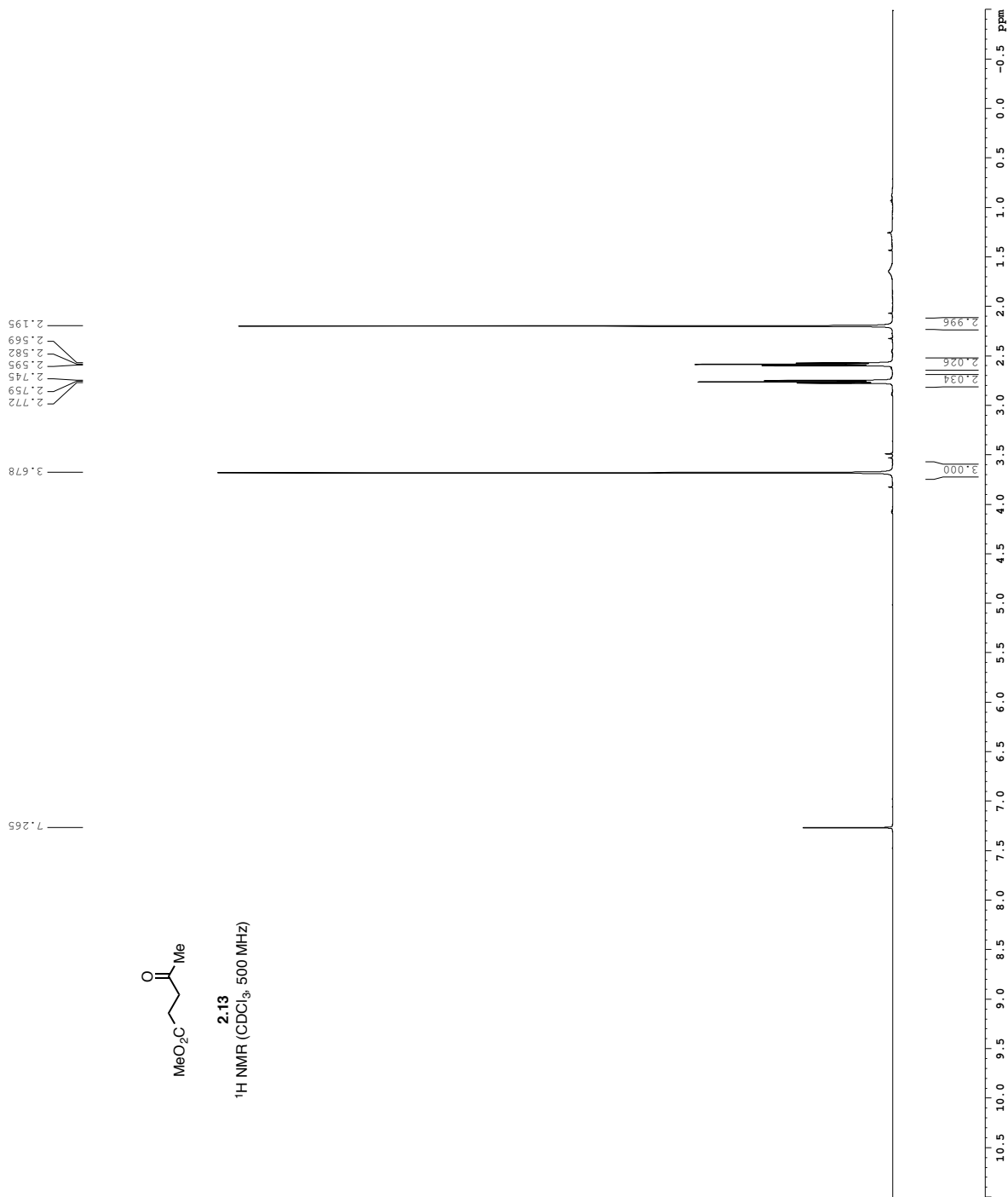


YS-II-80



2.13
¹H NMR (CDCl₃, 500 MHz)

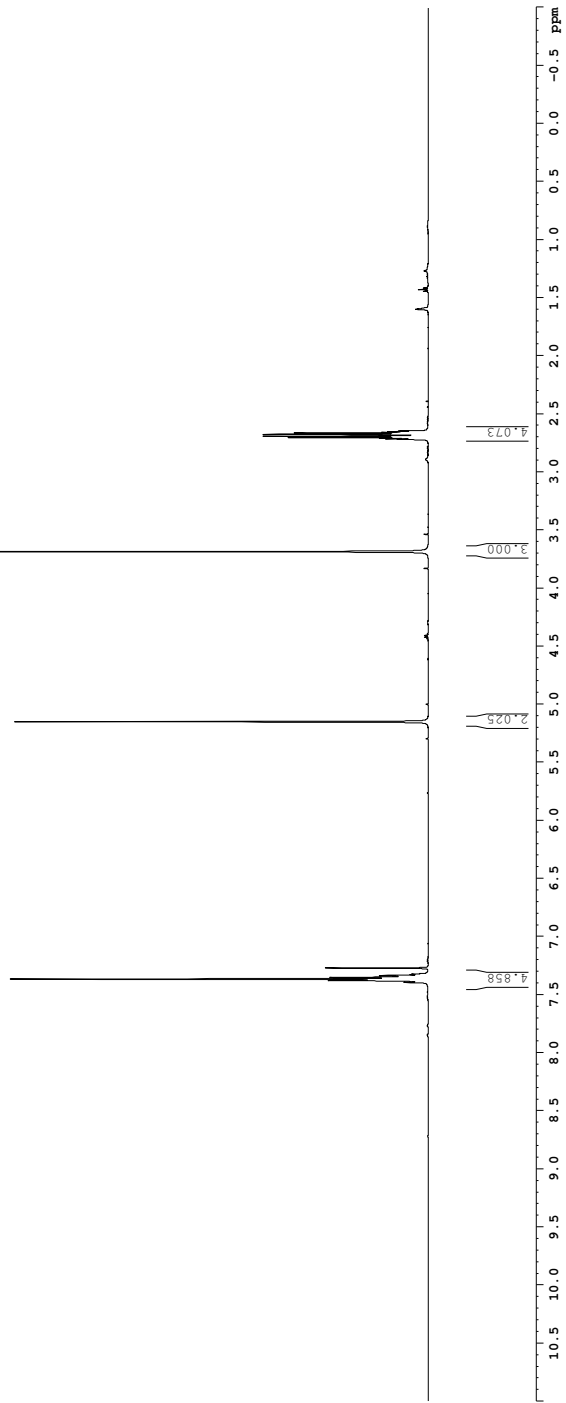
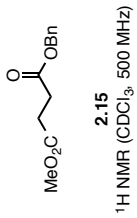
Current Data Parameters
Date_ 15-11-09
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20141009
Time 8.56
INSTRUM cryo500
PROBHD 5 mm CP131-130
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
RG 5.0998279 sec
DE 62.400 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0 sec
PCWRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 ¹H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing Parameters
SI 500.2200288 MHz
SF 500.2200288 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00



YS-II-25

Current Data Parameters
Date_ 15-11-25
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140930
Time 8.58
INSTRUM cryo500
PROBHD 5 mm CP131-130
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
RG 5.0998274 sec
DE 62.400 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0 sec
PCWRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing Parameters
SI 500.2200265 MHz
SF 500.2200265 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

7.392
7.376
7.364
7.351
7.340
7.334
7.270
2.718
2.713
2.708
2.702
2.699
2.674
2.674
2.662
2.655
2.650
2.645
3.684
5.149



YS-II-32

Current Data Parameters
Date_ 20141001
Time 14.09
INSTRUM av600
PROBHD 5 mm TBI H/3
PULPROG zgpg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.250010 Hz
AQ 1.3999722 sec
RG 322
DW 52.000 usec
DE 14.54 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1

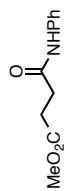
=====
CHANNEL F1
SFO1 600.1342009 MHz
NUC1 1H
P1 8.00 usec
PLW1 23.01441956 W

F2 - Processing parameters
SI 32768
SF 600.1300282 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

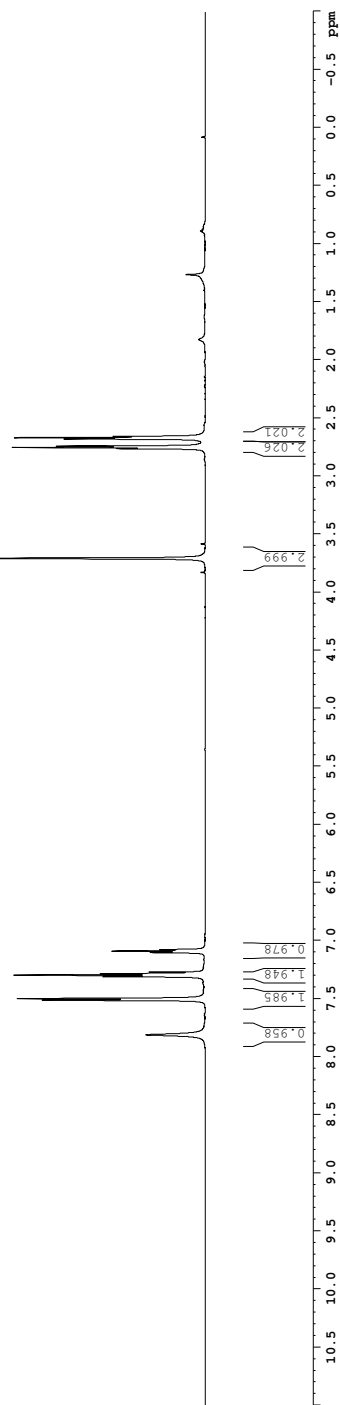
7.810
7.511
7.498
7.309
7.296
7.283
7.270
7.101
7.089
7.077

2.762
2.752
2.741
2.679
2.668
2.658

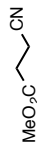
3.708



2.17
¹H NMR (CDCl₃, 600 MHz)

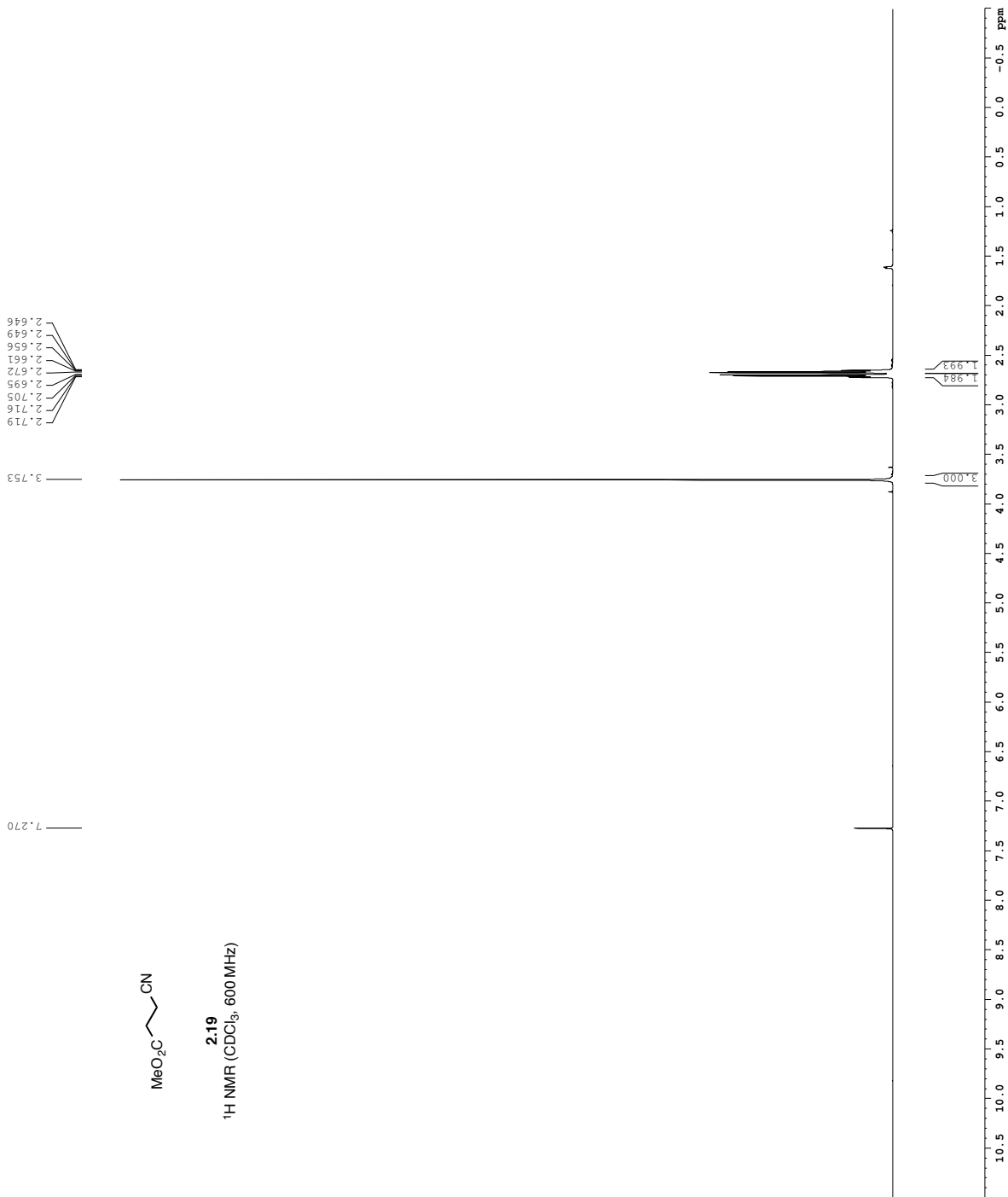


YS-II-77

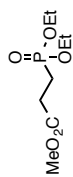


2.19
¹H NMR (CDCl₃, 600 MHz)

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 H/0
PULPROG zgpg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.65910 Hz
AQ 1.93920 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 650
SF 600.1300280 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



YS-II-50A

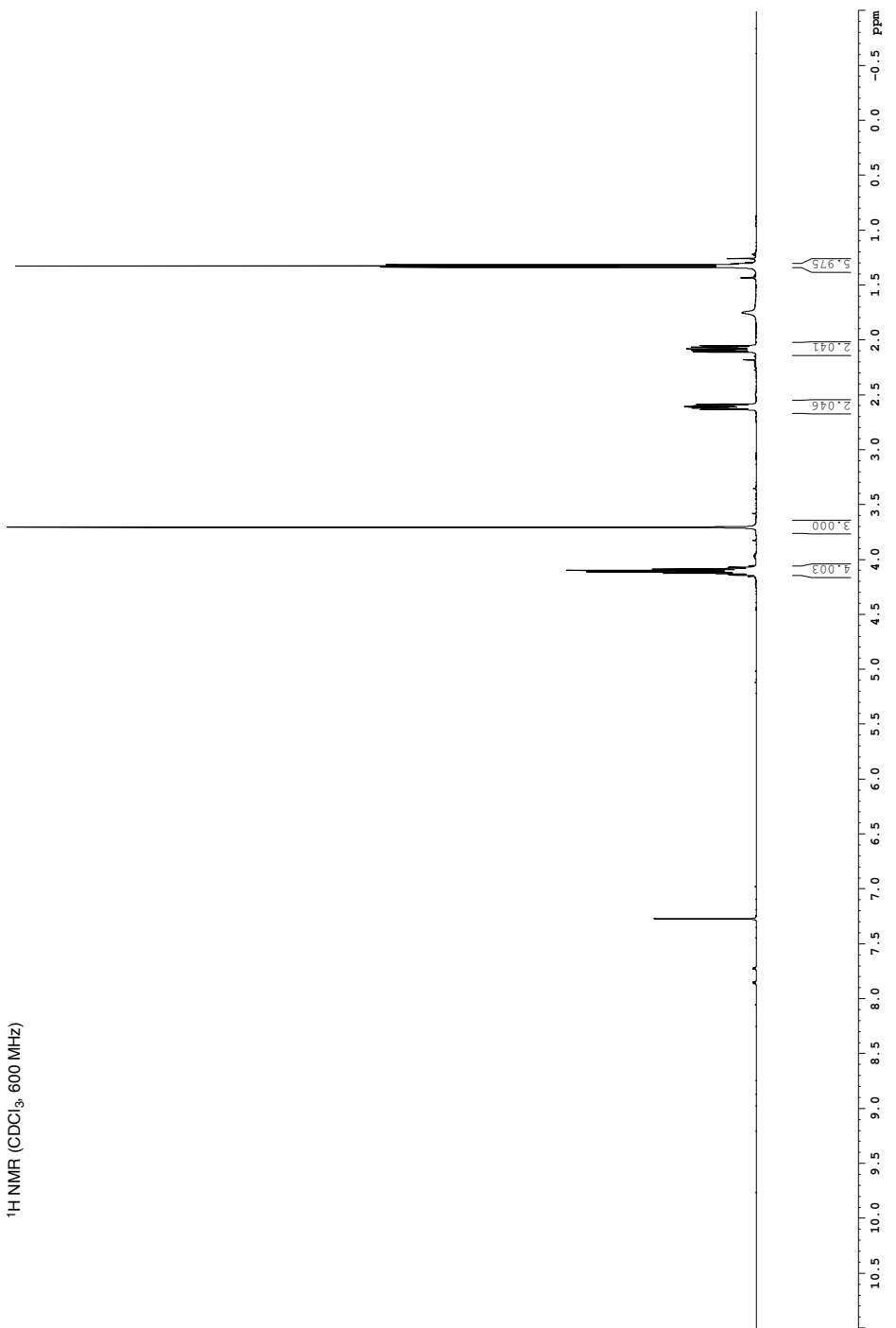


2.21
¹H NMR (CDCl₃, 600 MHz)

Current Data Parameters
Name YS-II-50A
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20141008
Time 12.35
INSTRUM av600
PROBHD 5 mm TBI 1H/3
PULPROG zgpg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.250010 Hz
AQ 1.3999700 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 32768
SF 600.1300283 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

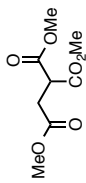
4.138
4.134
4.126
4.124
4.122
4.108
4.102
4.096
4.091
4.083
4.078
4.071
4.066
3.703
2.629
2.616
2.613
2.609
2.602
2.596
2.582
2.106
2.095
2.092
2.079
2.076
2.065
2.062
2.049
1.334
1.322
1.311

7.270

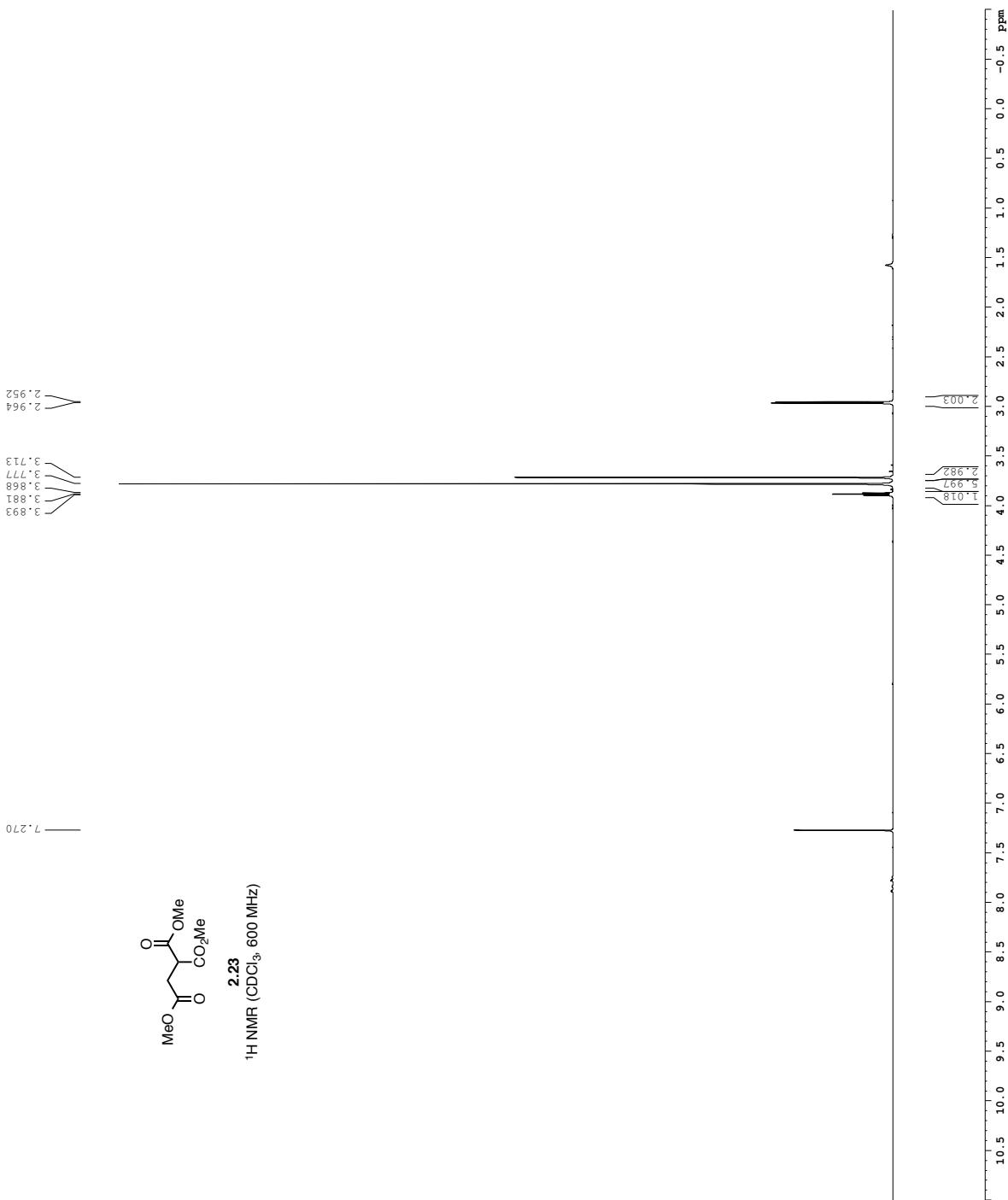


YS-II-29A

Current Data Parameters
Name YS-II-29A
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140930
Time 16.40
INSTRUM av600
PROBHD 5 mm TBI 1H/3
PULPROG zgpg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 5.099972 sec
RG 724
DW 52.000 usec
DE 14.54 usec
TE 298.0 K
D1 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 1H
P1 8.00 usec
PLW1 23.01441956 W
F2 - Processing parameters
SI 32768
SF 600.1300282 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

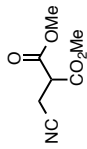


2.23
¹H NMR (CDCl₃, 600 MHz)

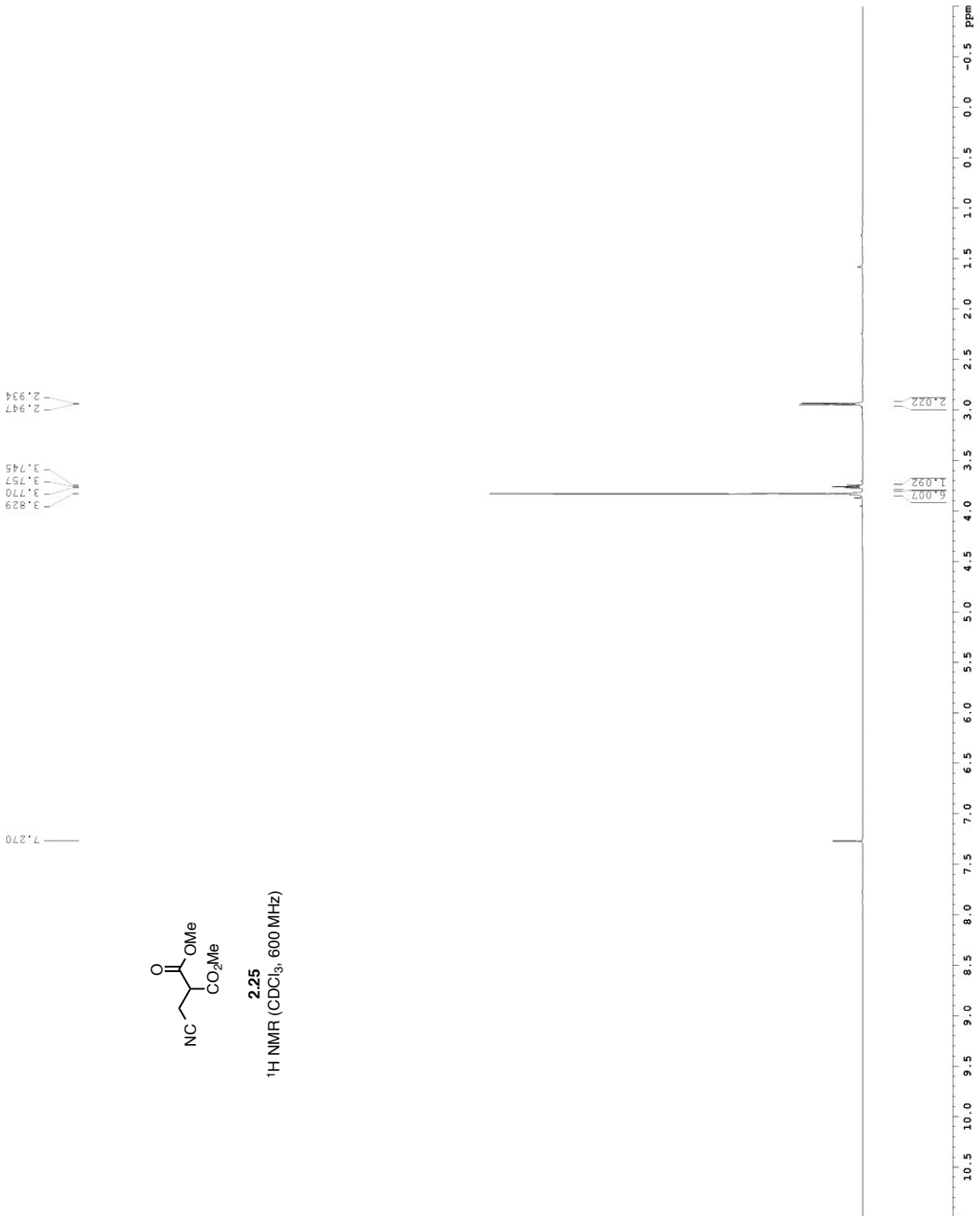


YS-II-133

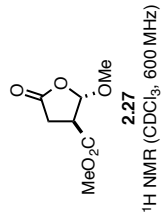
Current Data Parameters
NAME YS-II-133
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 2014122
Time 11:23
INSTRUM av600
PROBHD 5 mm TBI av600
PULPROG zgpg30
TD 38466
SOLVENT CDCl3
DS 2
SWH 9615.385 Hz
FIDRES 0.090000 Hz
AQ 0.049000 sec
RG 1440
DM 32.000 usec
DE 288.1 usec
TE 298.1 K
D1 0.10000000 sec
TD0 1
----- CHANNEL f1 -----
SFO1 600.1342009 MHz
NUC1 13C
P1M1 23.01441356 H
S2 - Processing parameters
SF 600.1300279 MHz
RG 0
LB 0.30 Hz
GB 0
FC 1.00



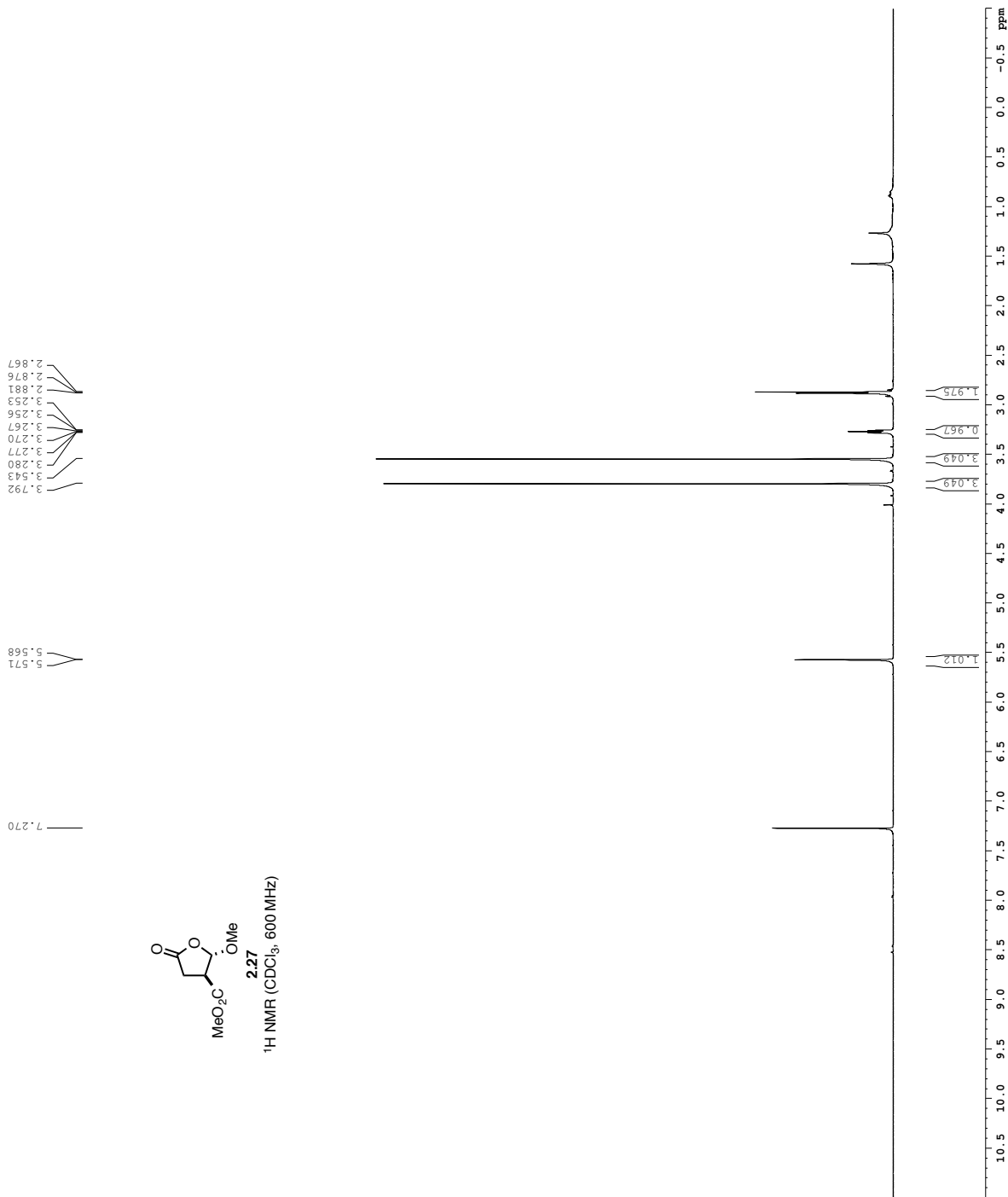
2.25
1H NMR (CDCl₃, 600 MHz)



YS-II-35B

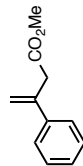


Current Data Parameters
NAME YS-II-35B
EXPNO 16
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110115
Time 12.35
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zg30
TD 38400
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.250010 Hz
AQ 1.9999200 sec
RG 1620
DH 51.00 usec
DM 4.00 usec
TE 298.2 K
D1 0.10000000 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

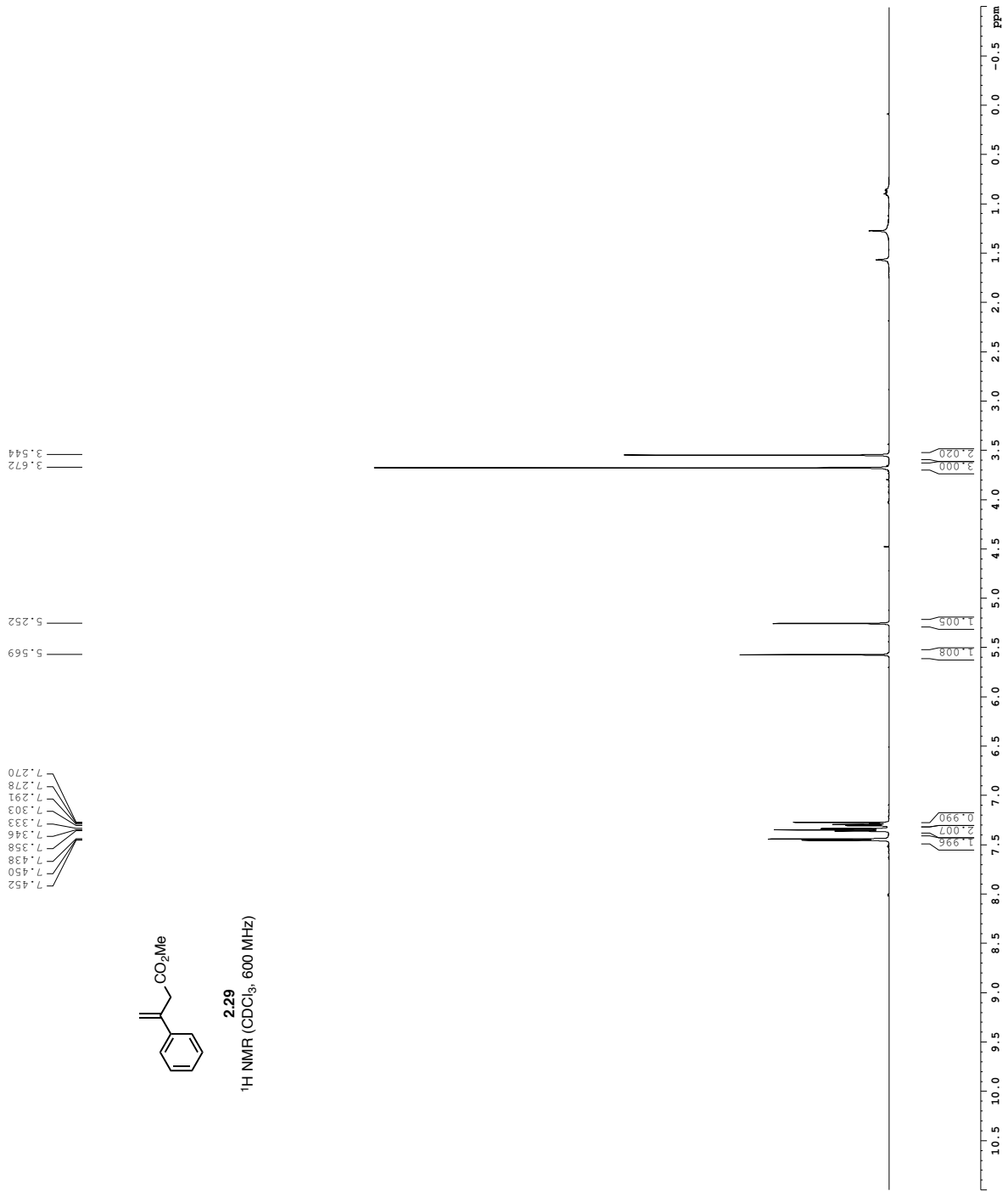


YS-II-48A

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 H/BO
PULPROG zgpg30
TD 98074
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.988072 Hz
AQ 5.099942 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 32768
SF 600.1300282 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



2.29
¹H NMR (CDCl₃, 600 MHz)



Current Data Parameters
 Name_ 15-II-100
 EXNO 2
 PROCNO 1

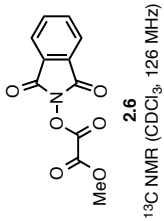
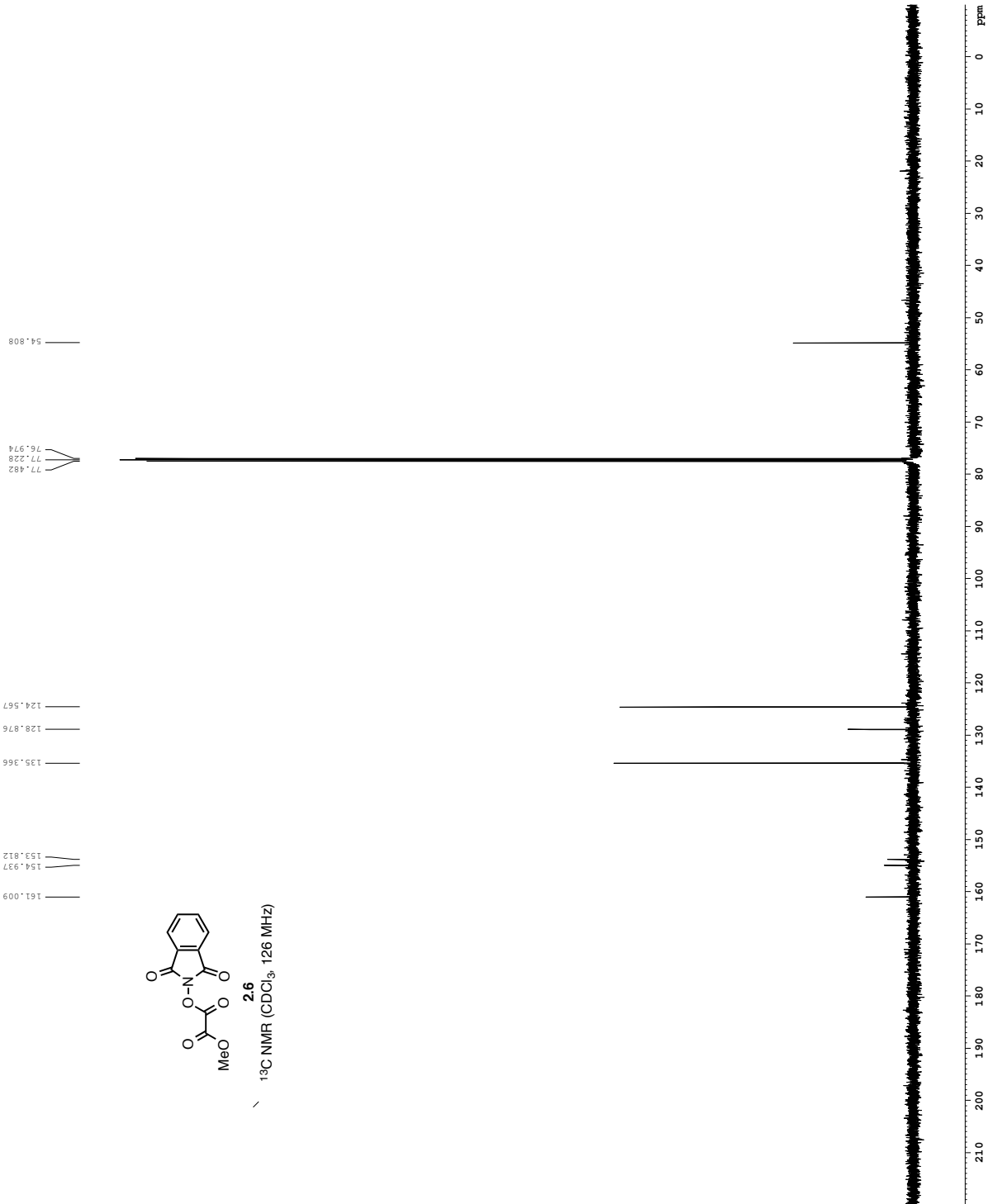
F2 - Acquisition Parameters
 Date_ 20141005
 Time 9.01
 INSTRUM cryo500
 PROBHD 5 mm CPY500
 PULPROG SpineEcho30pp.prd
 TD 65536
 SOLVENT CDCl3
 NS 472
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.25288 Hz
 AQ 1.0782480 sec
 RG 72987.2
 DW 16.500 usec
 DE 6.00 usec
 TE 288.0 K
 D1 0.75000000 sec
 d11 0.03000000 sec
 d12 0.03000000 sec
 d17 0.00196000 sec
 MCREST 0 sec
 MCWRK 0.01500000 sec
 F2 31.00 usec

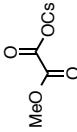
===== CHANNEL f1 =====
 NUC1 13C
 P1 15.00 usec
 PL1 500.00 usec
 P12 2000.00 usec
 PL2 2000.00 usec
 PL0 120.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF1 3.20 dB
 SENAM[1] Crp60_0_5_20_1
 SENAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 PCPD2 1.60 dB
 PL12 24.60 dB
 SFO2 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GRAM[1] SINE.100
 GRAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GFZ1 30.00 %
 GFZ2 50.00 %
 P15 500.00 usec
 P16 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7803992 MHz
 WDW EM
 SSB 0
 GB 0
 PC 2.00



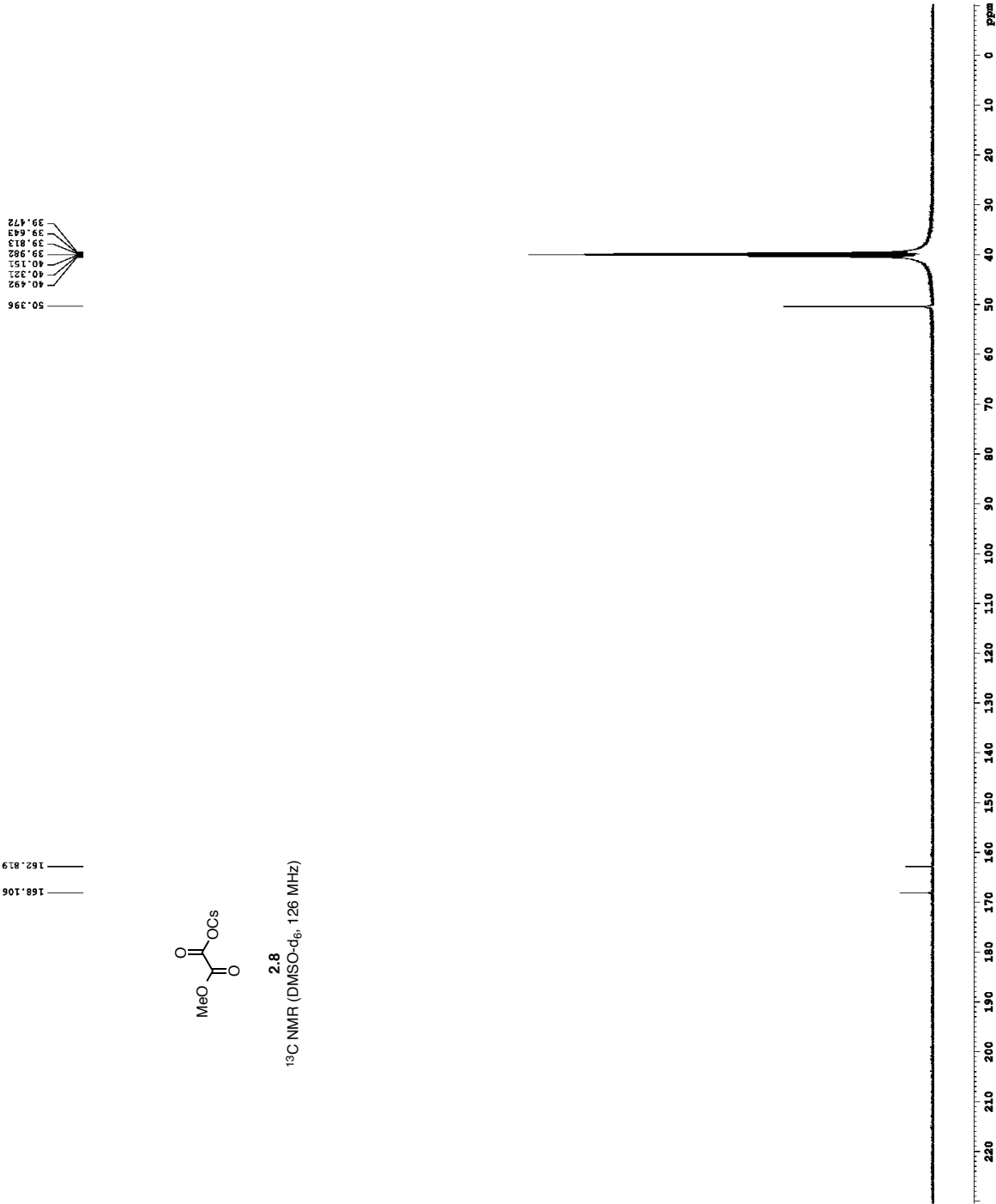


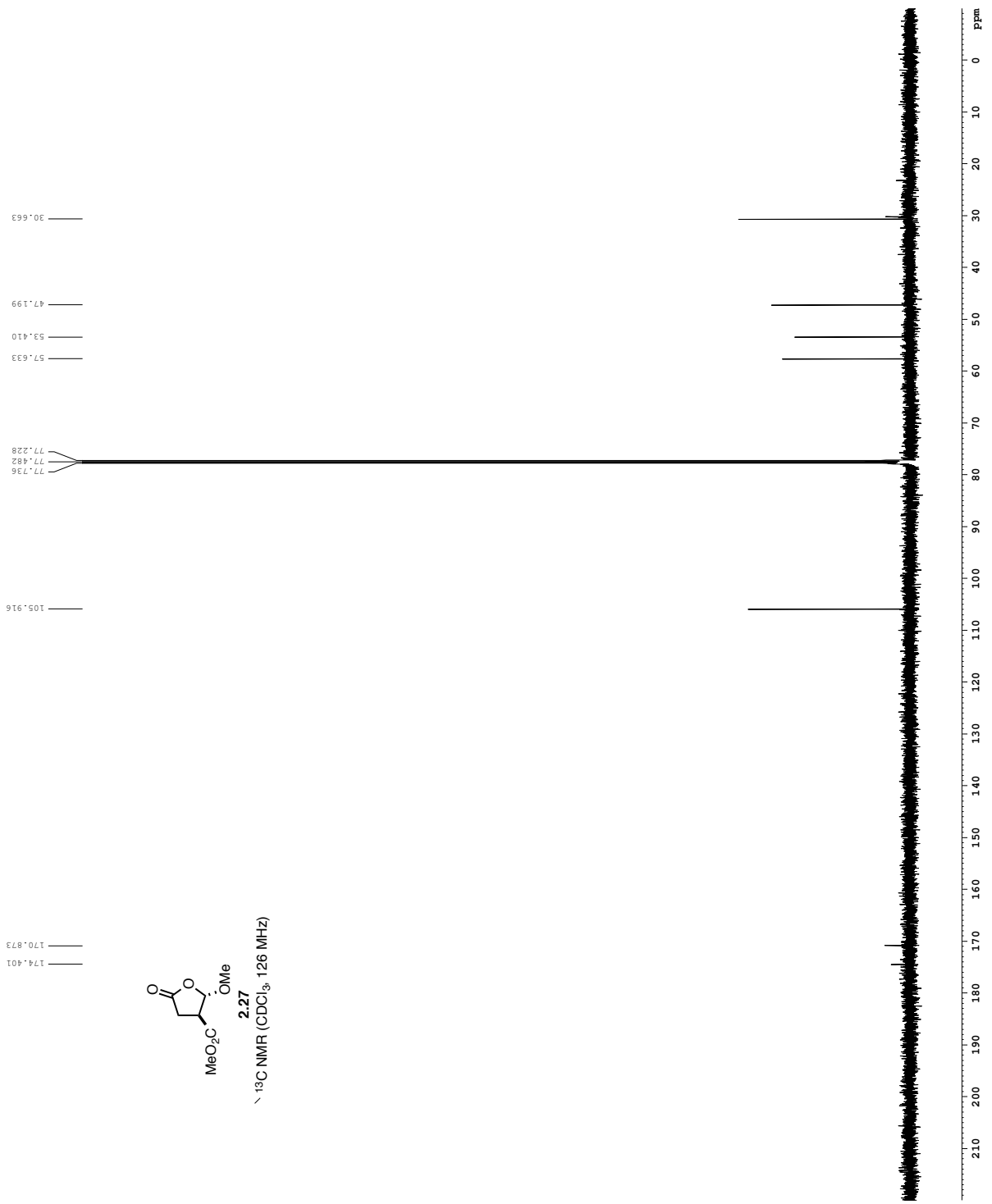
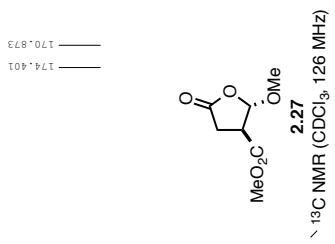
2.8
¹³C NMR (DMSO-d₆, 126 MHz)

168.106
 162.919

50.196
 40.432
 40.151
 39.982
 39.643
 39.472

```
Current Data Parameters
=====
EXPNO        2
PROCNO       1
Date_        20160319
Time         9.02
Operator     ch
PULPROG     zgpg30
PROBHD      5 mm CPXI 1H-
PULPROG2    Spinech99
SOLVENT     CDCl3
NS          128
DS          4
SWH         30363.031 Hz
FIDRES     0.462388 Hz
AQ         1.0013440 sec
RG          655
DM         16.500 usec
DE         6.00 usec
D1         0.25000000 sec
d11        0.03000000 sec
d12        7.00000000 sec
d13        0.00250000 sec
d14        0.00250000 sec
d15        0.00250000 sec
d16        0.00250000 sec
d17        0.00250000 sec
d18        0.01500000 sec
d19        30.00000000 sec
PC          0.01500000 sec
=====
CHANNEL f1
NUC1        13C
P1         16.25 usec
P2         500.00 usec
P3         200.00 usec
P4         200.00 usec
P5         200.00 usec
P6         200.00 usec
P7         1.00 dB
P8         1.00 dB
P9         1.00 dB
P10        125.7942548 MHz
P11        2.70 dB
P12        2.70 dB
P13        2.70 dB
P14        2.70 dB
SRBIN[1]   Cyp60.05, 20.1
SRBIN[2]   Cyp60.05, 20.1
SGPRG1     0 Hz
SGPRG2     0 Hz
=====
CHANNEL f2
CPDPRG2    waltz16
NUC2        1H
P2         100.00 usec
P3         100.00 usec
P4         1.60 dB
P5         24.50 dB
P6         500.2249911 MHz
P7         500.2249911 MHz
=====
GRADIENT CHANNEL
=====
GPRGM[2]   gpmzi
GPRGM[1]   gpmzi
GPRM[2]    0 Hz
GPRM[1]    0 Hz
GPRM[2]    0 Hz
GPRM[1]    0 Hz
P1         30.00 usec
P2         500.00 usec
P3         1000.00 usec
P4         30.00 usec
P5         500.00 usec
P6         1000.00 usec
P7         30.00 usec
P8         500.00 usec
P9         1000.00 usec
P10        30.00 usec
P11        500.00 usec
P12        1000.00 usec
P13        30.00 usec
P14        500.00 usec
P15        1000.00 usec
P16        30.00 usec
P17        500.00 usec
P18        1000.00 usec
P19        30.00 usec
P20        500.00 usec
P21        1000.00 usec
P22        30.00 usec
P23        500.00 usec
P24        1000.00 usec
P25        30.00 usec
P26        500.00 usec
P27        1000.00 usec
P28        30.00 usec
P29        500.00 usec
P30        1000.00 usec
```





Current Data Parameters
 NAME YS-II-35A
 PROCNO 1
 PRGNO 1
 F2 - Acquisition Parameters
 Date_ 20141002
 Time 9.27
 INSTRUM cryo500
 PROBHD 5 mm CP1H1H
 PULPROG Spinechop30.Prd
 TD 65532
 SOLVENT CDCl3
 NS 880
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.001860 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
 MCREST 0 sec
 MCWREK 0.01500000 sec
 P2 31.00 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 15.00 usec
 PL1 50.00 dB
 PL2 2000.00 usec
 PLO 120.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF1 3.20 dB
 SF2 3.20 dB
 SFNAM[1] Crp60.0.5.20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

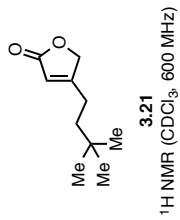
===== CHANNEL f2 =====
 CDEPRG[2] waltz16
 NUC2 1H
 P1 100.00 usec
 PL2 1.60 dB
 PL1 24.60 dB
 SFO2 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GENAM[1] SINE.100
 GENAM[2] SINE.100
 GF1 0 %
 GF2 0 %
 GFY1 0 %
 GFY2 0 %
 GFZ1 30.00 %
 GFZ2 50.00 %
 P15 500.00 usec
 P16 1000.00 usec

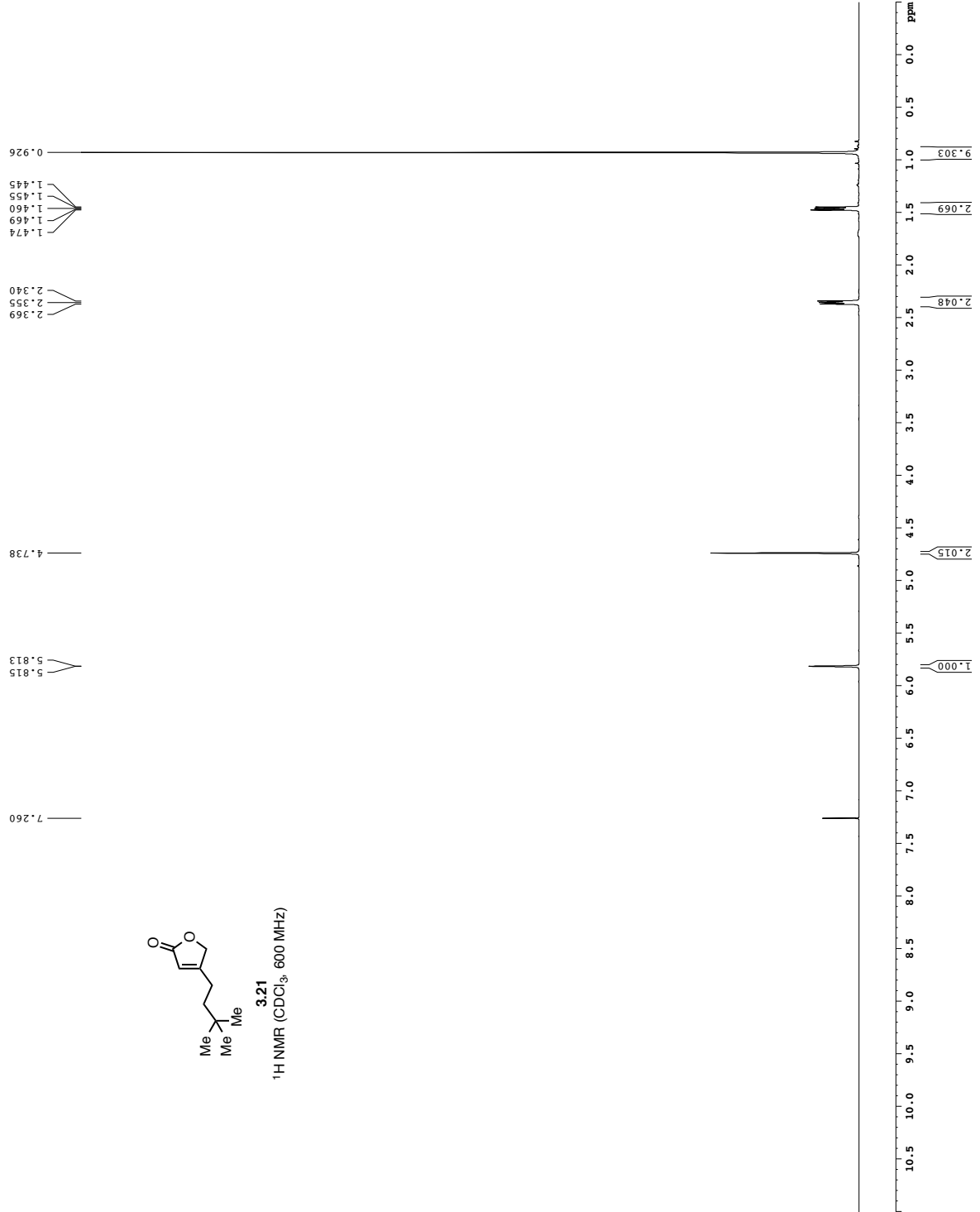
F2 - Processing parameters
 SI 65536
 SF 125.7803665 MHz
 NDUW 0 EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

Appendix C: Chapter 3 NMR Spectra

¹H spectrum



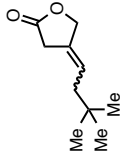
Current Data Parameters
EXPNO 025-47-2382 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110707
Time 14.28
INSTRUM spect
PULPROG zgpg30
PROBHD 5 mm TBI WALT
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.0019188 Hz
AQ 5.0958478 sec
RG 327
AQ 14.24 usec
RG 14.24 usec
AQ 0.1000000 sec
TD 1
===== CHANNEL f1 =====
NUC1 600.1362009 MHz
P1 8.00 usec
PL1 24.0000000 dB
F2 - Processing parameters
SI 0
SF 600.1360356 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00



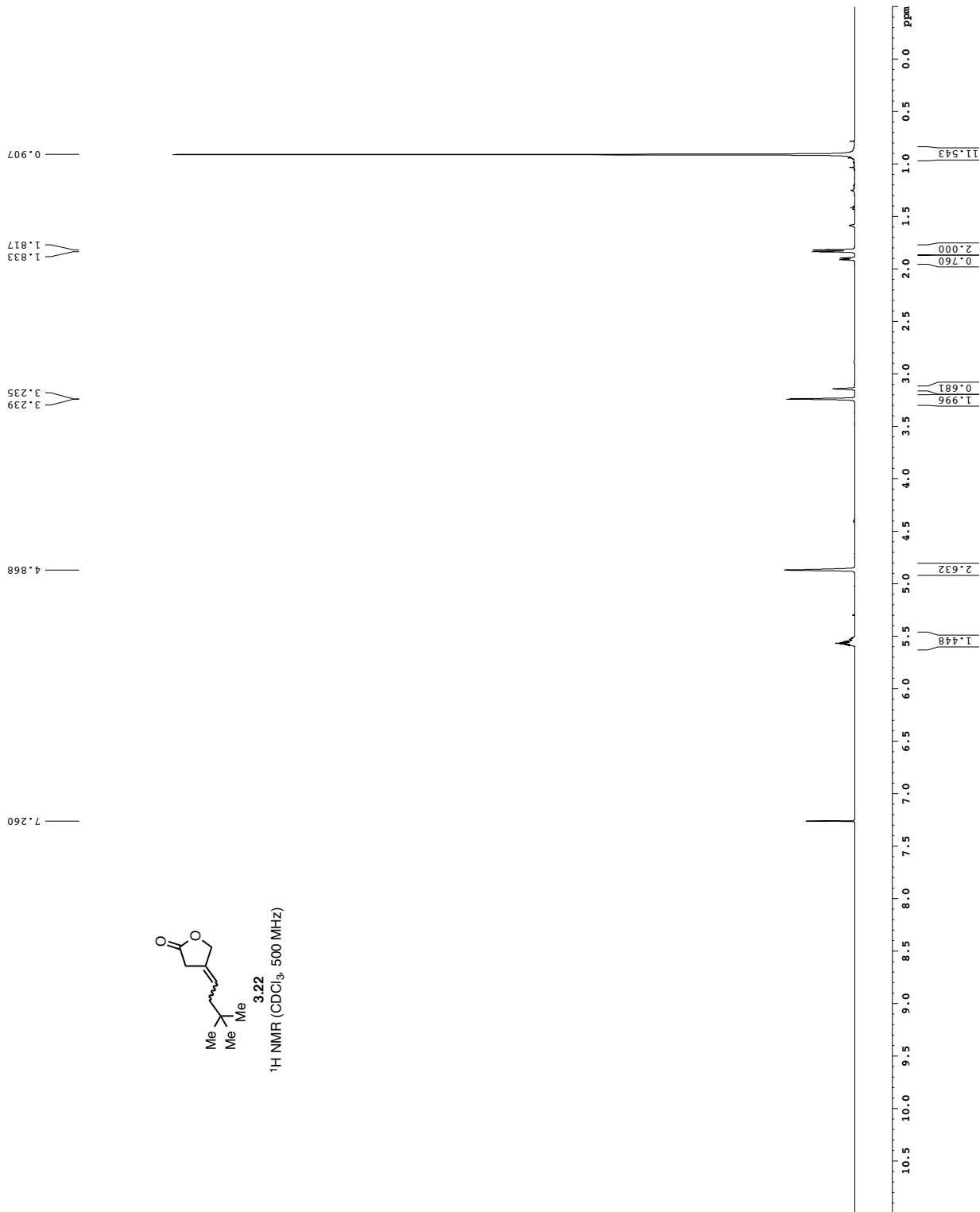
1H spectrum

```

Current Data Parameters
NAME      GSA-247-331
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Time      2.0000000
Date_     17.46
INSTRUM   spect
PROBHD    5 mm CPYAC-500
PULPROG   zgpg30
SOLVENT   CDCl3
NS         8
DS         4
SWH        8012.820 Hz
FIDRES     0.098043 Hz
AQ         5.039686 sec
RG         6.3
DQ         62.400 usec
DE         6.000 usec
TE         298.0 K
MCREG1    0 sec
MCREG2    0.1000000 sec
MCREG3    0.1500000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         13.00 usec
PL1        0.00 dB
SFO1       500.235015 MHz
F2 - Processing parameters
SI         32768
SF         500.220316 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         4.00
  
```

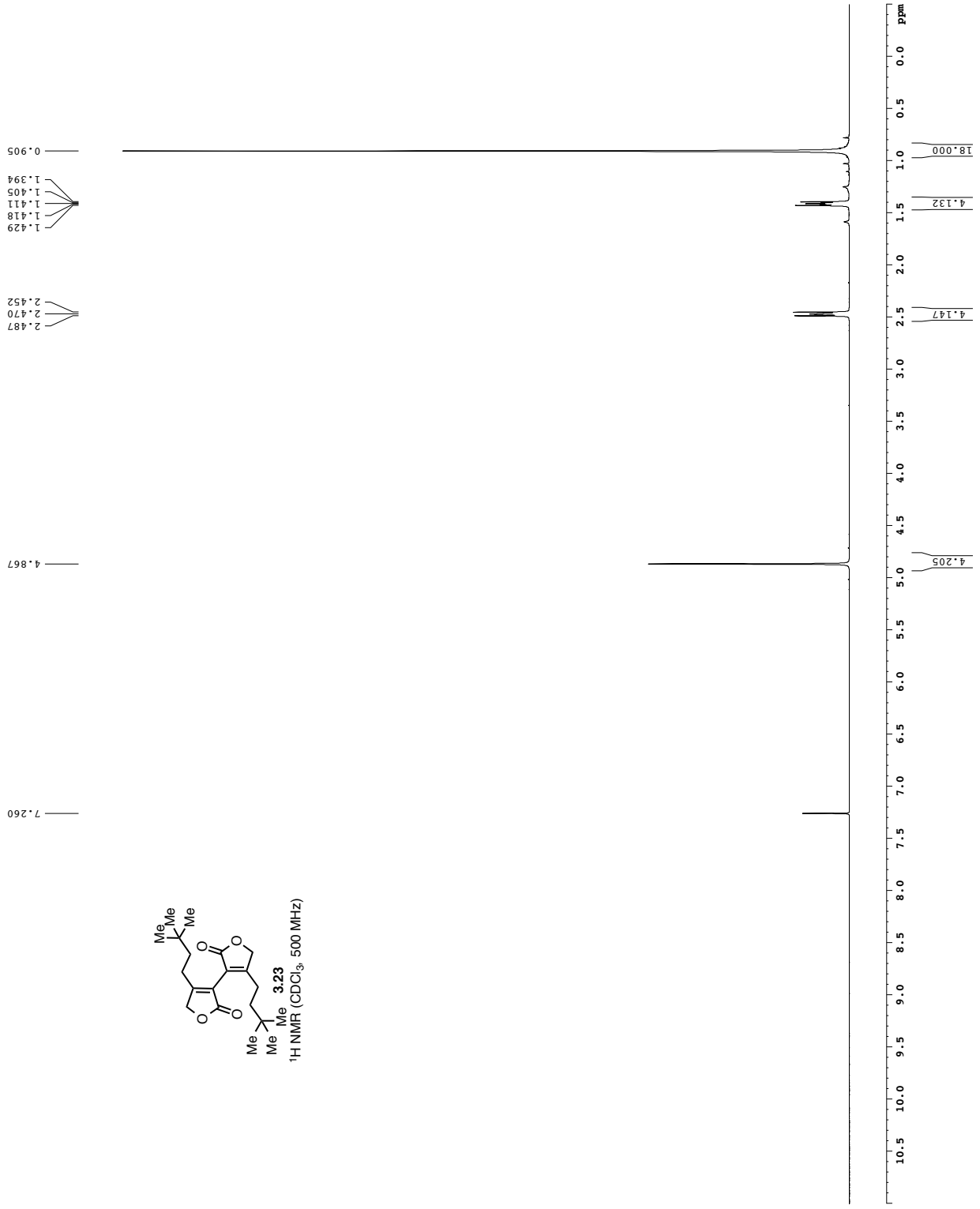


3.22
 1H NMR (CDCl₃, 500 MHz)

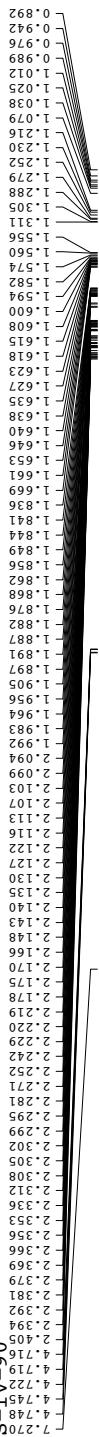


¹H spectrum

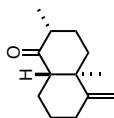
Current Data Parameters
 NAME GLS-247-33hiv
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151214
 TIME 11:00:00
 INSTRUM spect
 PROBRD 5 mm CPXI 1H-
 PULPROG zgpg30
 ZD 8128
 SOLVENT CDCl3
 DS 2
 SWH 811.500 MHz
 FWHZ 8.098633 Hz
 AQ 5.098273 sec
 SFO1 500.2225015 MHz
 DQ 62.400 usec
 DE 6.00 usec
 DI 0.10000000 sec
 MCHRG 0 sec
 PCPRG 0.1500000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 SFO1 500.2225015 MHz
 F2 - Processing parameters
 SI 85536
 SF 500.2200333 MHz
 DS 4
 SSB 0
 GB 0
 CB 0
 PC 4.00



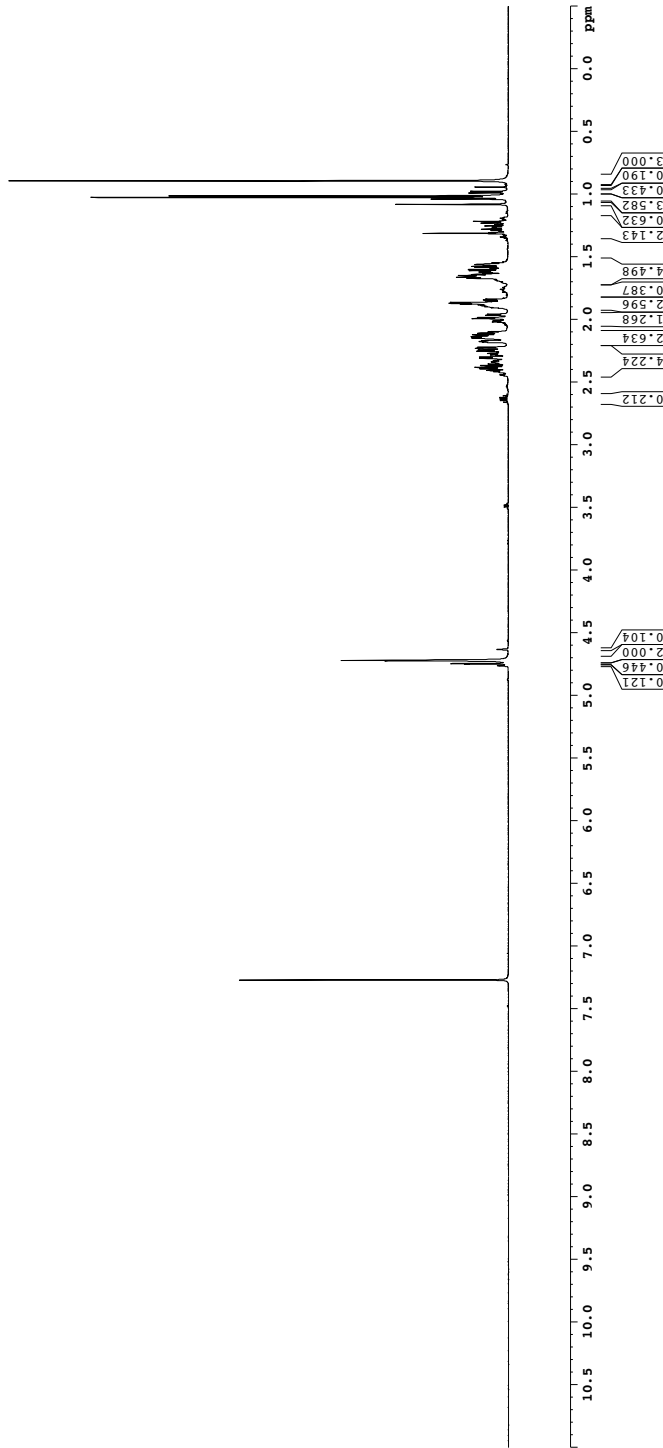
YS-IV-90



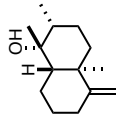
Current Data Parameters
NAME YS-IV-90
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160219
Time 16:31
PULPROG zg30
PROBHD 5 mm broadband
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8015.820 Hz
FIDRES 0.0998273 sec
AQ 0.0998273 sec
RG 1024
DW 62.400 usec
DE 296.0 Hz
TE 296.0 K
D1 0.1000000 sec
MCRRBT 0 sec
MCRRR 0.1500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.1834943 MHz
F2 - Processing parameters
SI 65536
SF 499.1800221 MHz
RGW 0
LFB 0
GB 0
PC 1.00



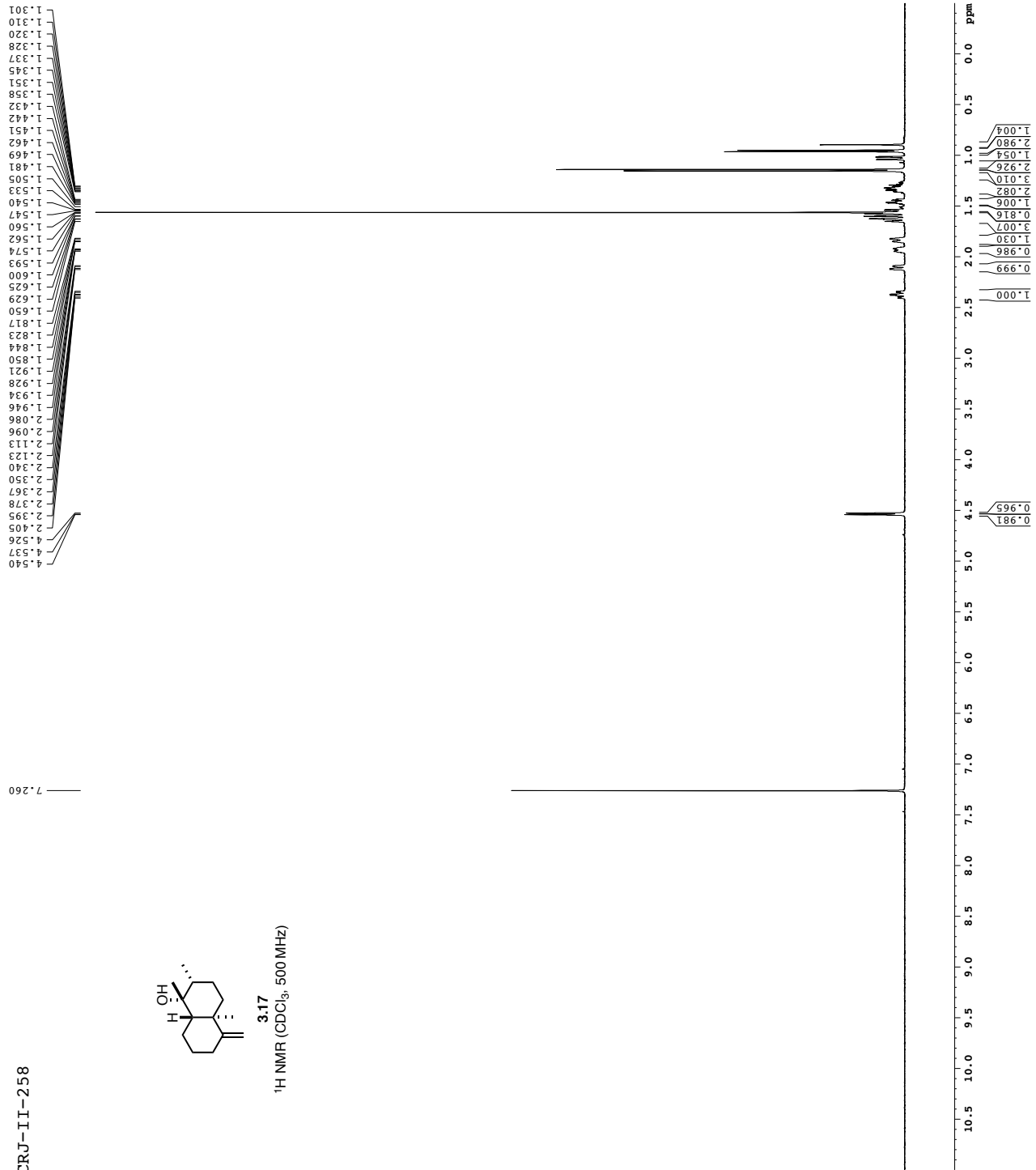
3.35
¹H NMR (CDCl₃, 500 MHz)



CRJ-II-258



3.17
¹H NMR (CDCl₃, 500 MHz)



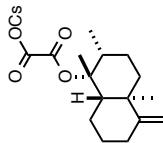
Current Data Parameters
NAME CRJ2-258-1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20111108
Time 17:58
INSTRUM cryo500
PROBHD 5 mm CPYCI 1H-
PULPROG zgpg30
TD 48874
SOLVENT CDCl3
NS 8
DS 2
SFRH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.9998176 sec
RG 62.400 usec
DE 6.00 usec
TE 298.0 K
MCREST 0 sec
MCYCLE 0.01500000 sec

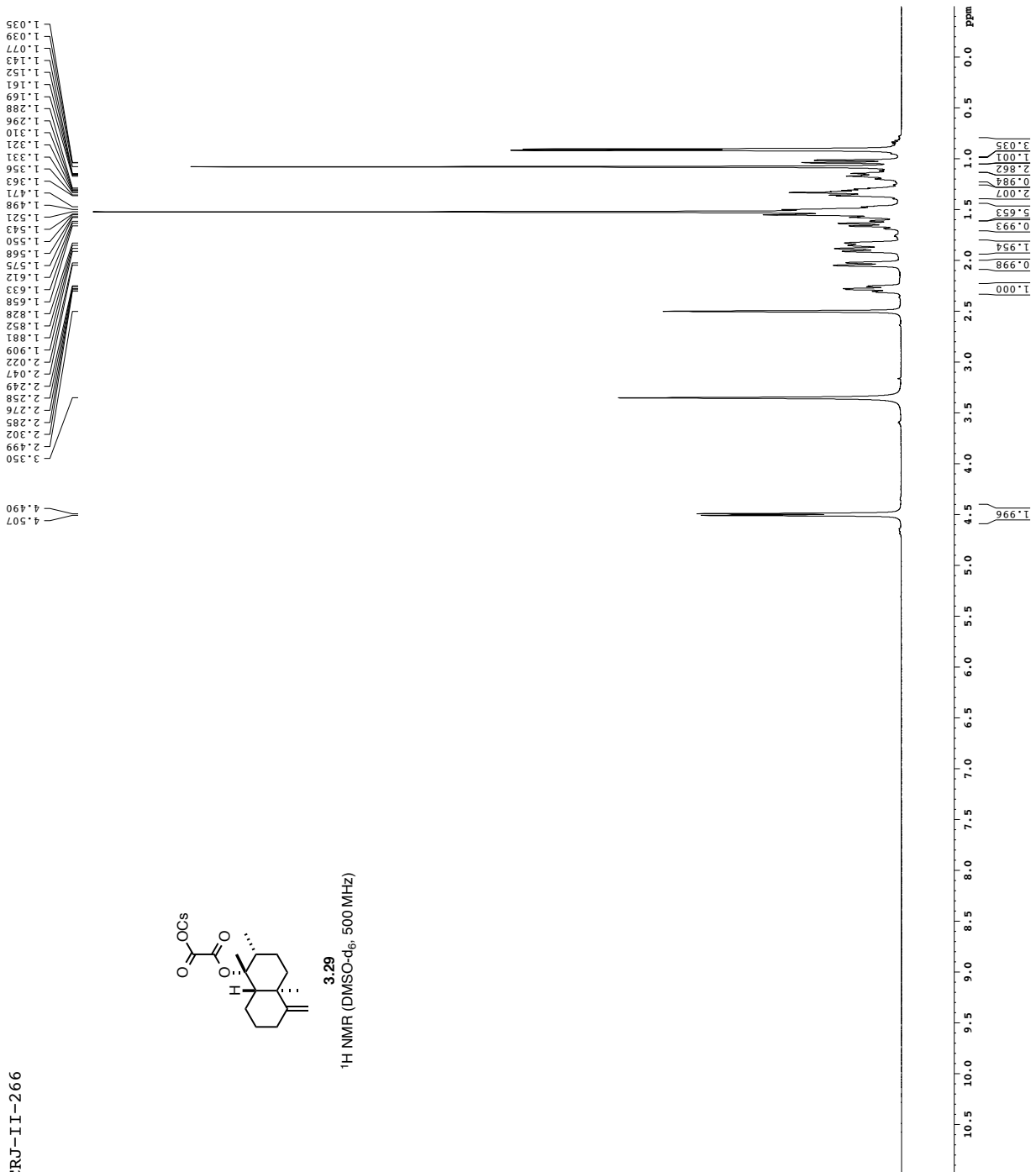
***** CHANNEL f1 *****
NUC1 1H
P1 7.50 usec
PL 0.00 dB
SFO1 500.225015 MHz

F2 - Processing parameters
SI 65536
SF 500.225015 MHz
WDW NO
SSB 0 Hz
CB 0
PC 4.00

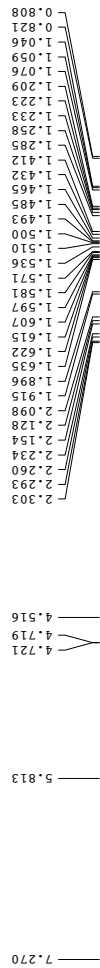
CRJ-II-266



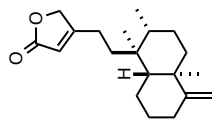
3.29
1H NMR (DMSO-d₆, 500 MHz)



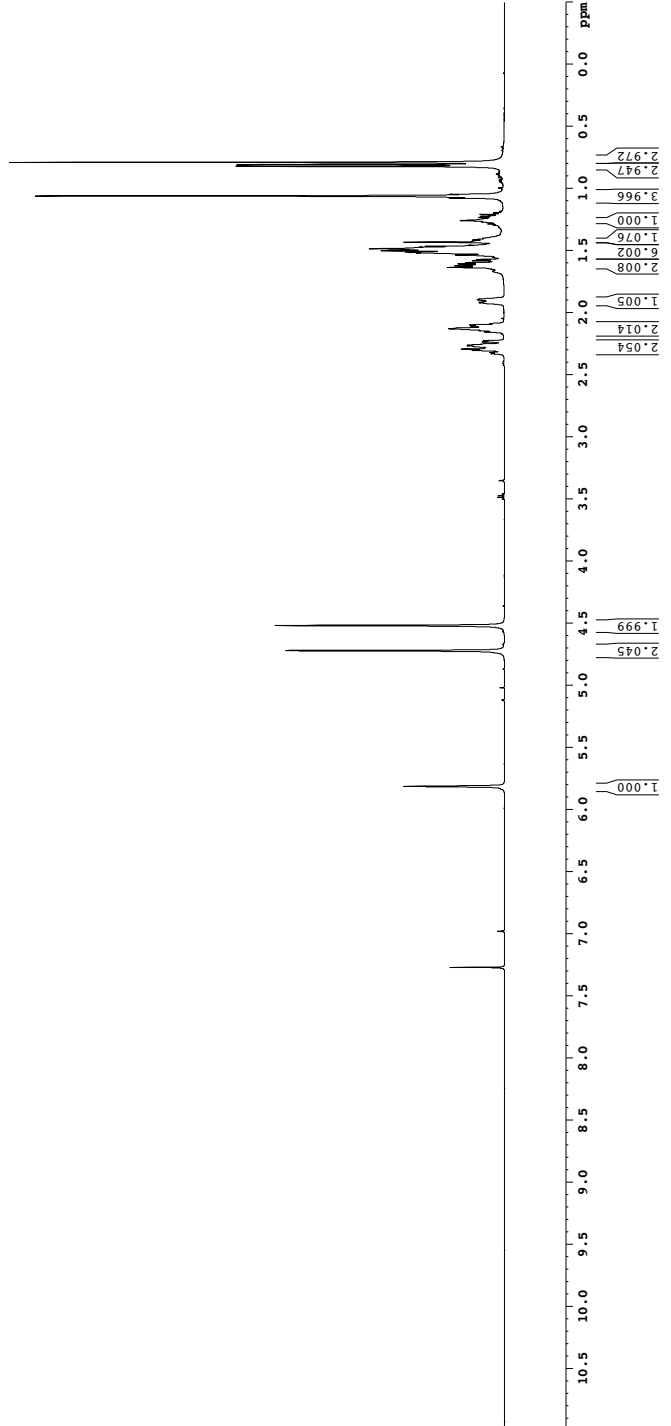
YS-IV-129



Current Data Parameters
NAME YS-IV-129
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160303
Time 14.58
INSTRUM cryo500
PROBHD 5 mm CPTCI 430
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0999773 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 300.2 K
D1 0.10000000 sec
MCREST 0 sec
MCWRT 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 500.2335015 MHz
F2 - Processing parameters
SI 32768
SF 500.220262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

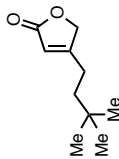


¹H NMR (CDCl₃, 500 MHz)

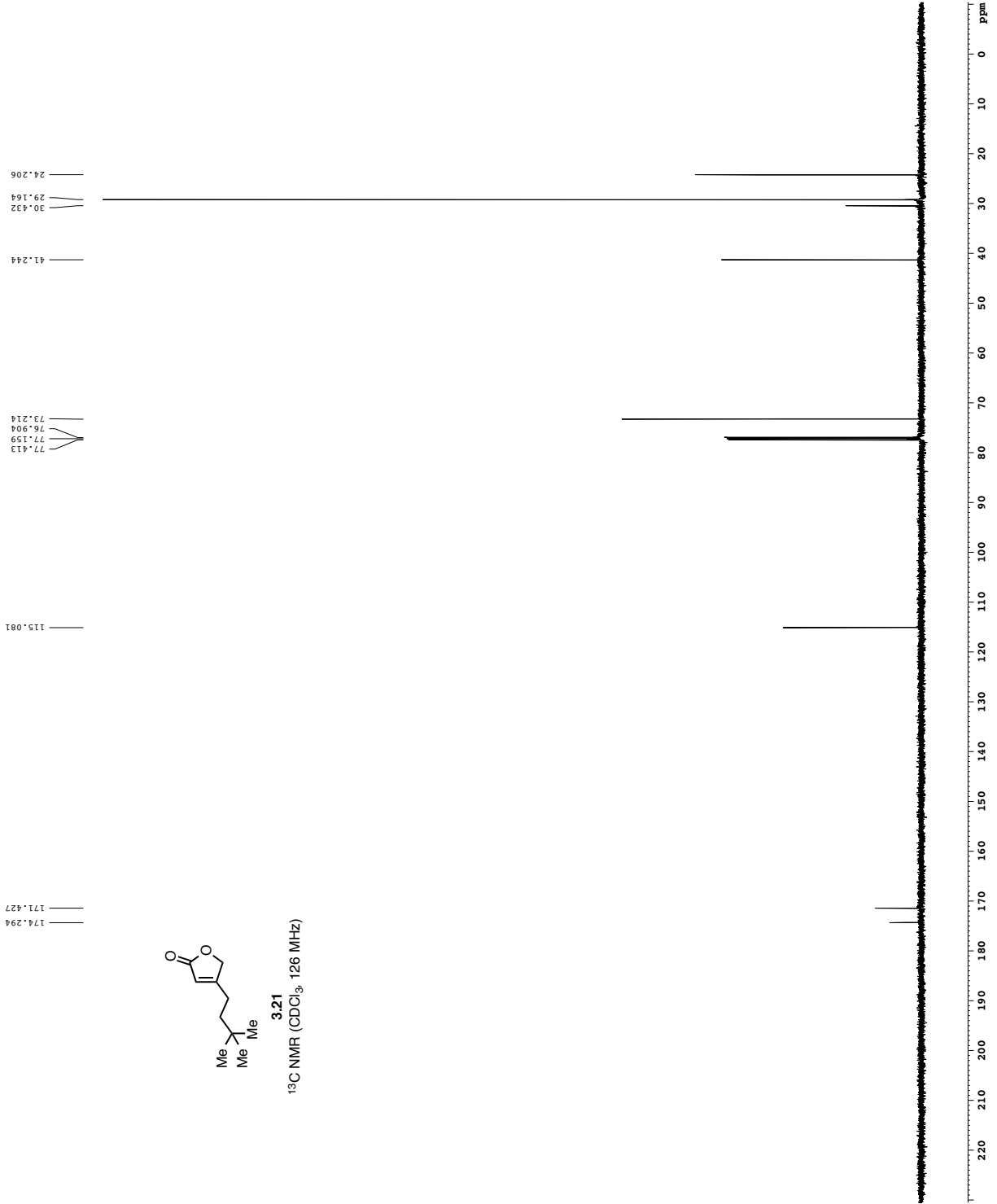


Z-restored spin-echo 13C spectrum with 1H decoupling

174.294
171.427



3.21
13C NMR (CDCl₃, 126 MHz)



Current Data Parameters
 NAME GL5-247-33a3
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameter
 Date_ 20151214
 Time 15:55
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG Spinechoyg30pp.pi
 TD 65536
 SOLVENT CDCl3
 NS 85
 DS 16
 SWH 30303.0316 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 11585.2
 DW 16.500 us
 DE 6.00 us
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.05000000 sec
 d12 0.05000000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRK 0.01500000 sec
 P2 33.10 us

==== CHANNEL f1 =====
 NUC1 13C
 P1 16.35 us
 P2 500.00 us
 PL0 2000.00 us
 PL1 120.00 dE
 PL2 -1.00 dE
 SF01 125.7942548 MHz
 SE1 2.70 dE
 SE2AM[1] Crp60.0.5.20.1
 SE2AM[2] Crp600comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 us
 PL0 24.50 dE
 PL1 24.50 dE
 SF02 500.2225011 MHz

==== GRADIENT CHANNEL ==
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GEX1 0 %
 GEX2 0 %
 GEX3 0 %
 GPZ1 0 %
 GPZ2 0 %
 P15 30.00 %
 P15 50.00 %
 P16 500.00 us
 P16 1000.00 us

F2 - Processing parameters
 SI 6317
 SF 125.7804117 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

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

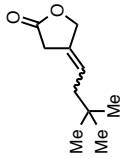
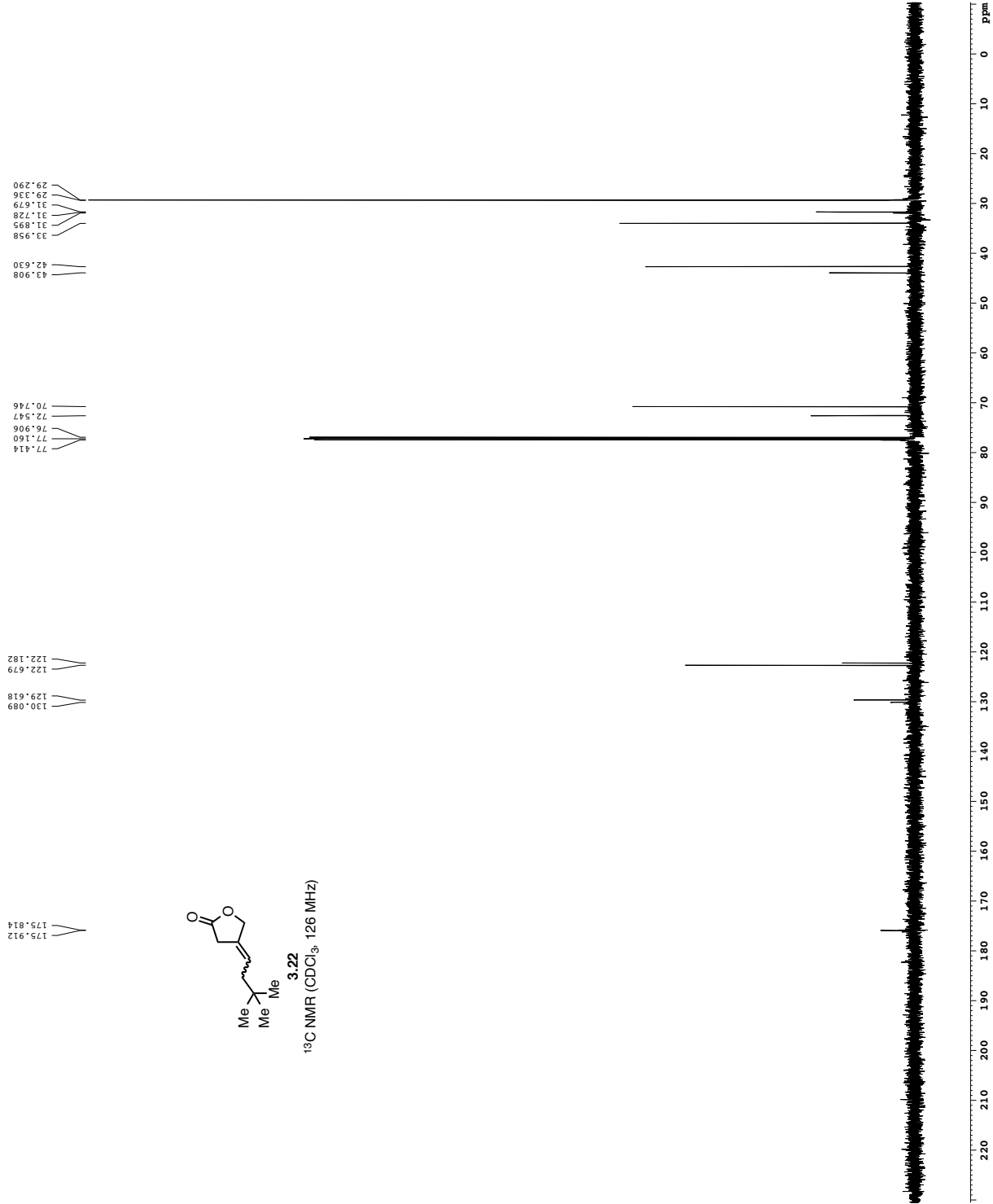
Current Data Parameters
 NAME GL5-247-33c
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameter
 Date_ 20151215
 Time 17.47
 INSTRUM cryo500
 PROBHD 5 mm CPXI IH-
 PULPROG spinechop3sgppr
 CPDPRG2 zgpg30
 SOLVENT CDCl3
 NS 109
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 2896.3
 DW 16.500 usec
 DE 1.000 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
 F2 35.10 usec

==== CHANNEL f1 =====
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 120.00 dB
 SFO1 125.7942548 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SPNAM[1] Crp60,0.5,20.1
 SPNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

==== CHANNEL f2 =====
 CPDPRG[2] waitz16
 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 %
 GZ1 30.00 %
 GZ2 50.00 %
 P1 100.00 usec
 P16 1000.00 usec

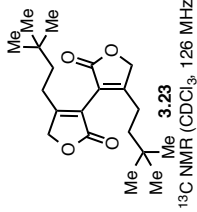
F2 - Processing parameters
 SI 65536
 SF 125.7804086 MHz
 WDW 0
 SSB 0
 B 0
 GB 0
 PC 2.00



¹³C NMR (CDCl₃, 126 MHz)

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

172.095
169.699



117.348

77.415
76.907
72.175

41.578

29.690
24.380

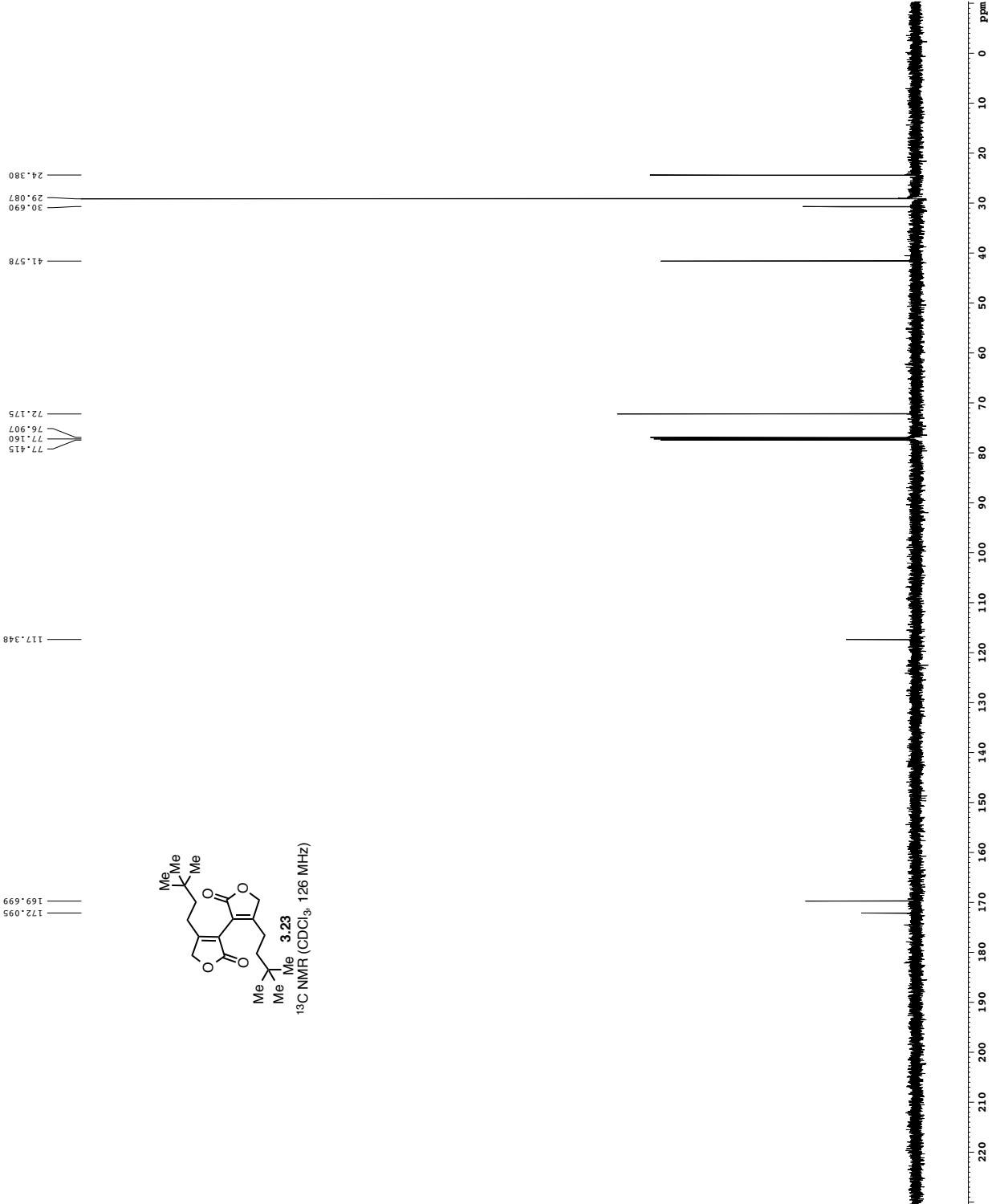
Current Data Parameters
NAME GL5-247-33bhv
EXPNO 2
PROCNO 1
F2 - Acquisition Parameter
Date_ 20151214
Time 10.45
INSTRUM cryos00
PROBHD 5 mm CPACX 1H-
PULPROG Spinechop30
TD 65536
SOLVENT CDCl3
NS 59
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.081340 sec
RG 1185.2
DW 16.50 us
DE 6.00 us
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0 sec
MCWRRK 0.01500000 sec
F2 33.10 us

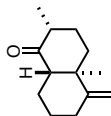
==== CHANNEL f1 =====
NUC1 13C
P1 16.55 us
P11 500.00 us
P12 2000.00 us
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SFO2 27.0 MHz
SFNAM[1] Crp60_0_5_20_1
SFNAM[2] Crp60comp_4
SFOFF1 0 Hz
SFOFF2 0 Hz

==== CHANNEL f2 =====
CPDPRG[2] waitz16
NUC2 1H
PCPD2 100.00 us
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

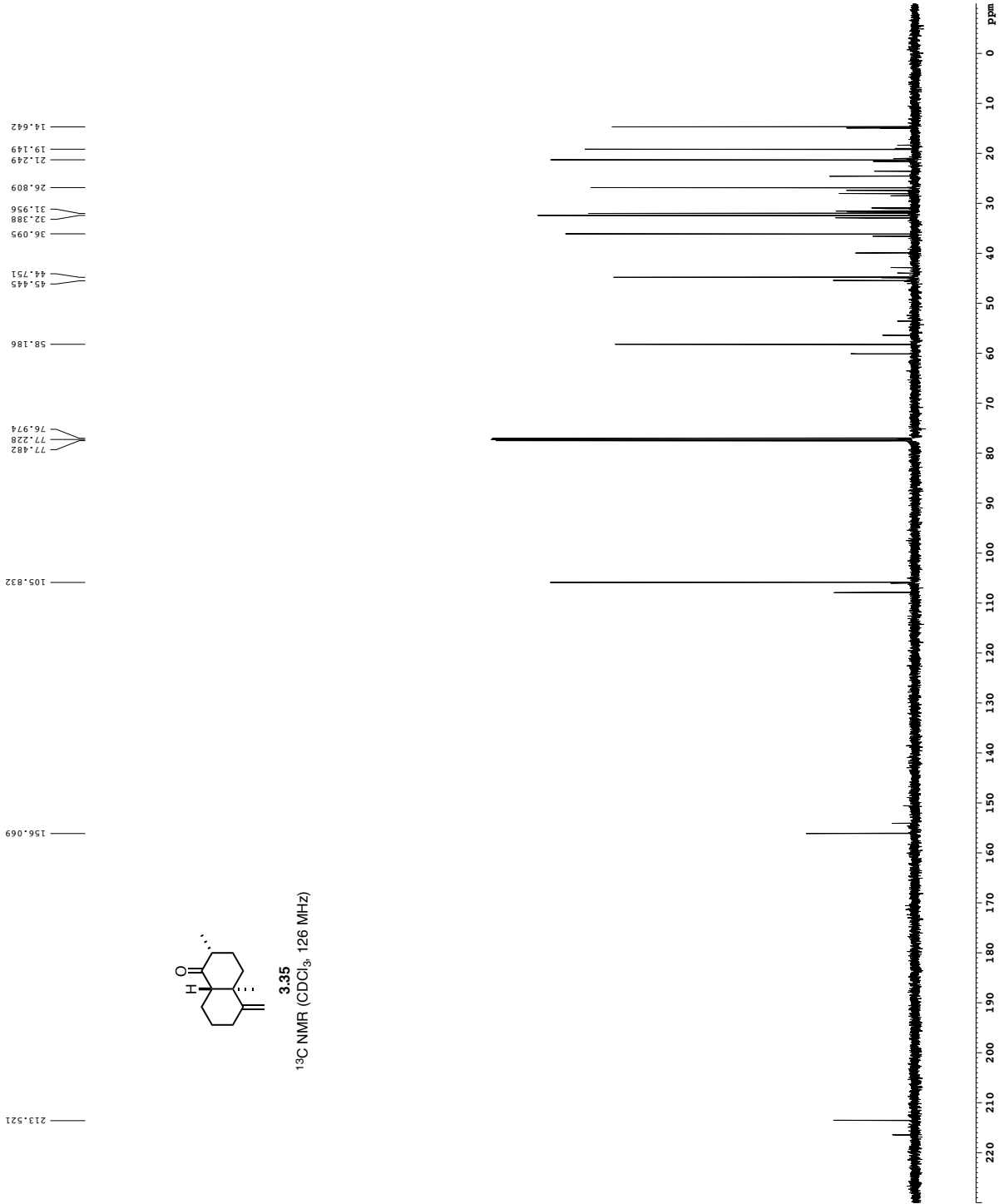
==== GRADIENT CHANNEL ==
GFNAM[1] SINE.100
GFNAM[2] SINE.100
GFX1 0 %
GFX2 0 %
GFY1 0 %
GFY2 0 %
GPF1 30.00 %
GPF2 50.00 %
p15 500.00 us
p16 1000.00 us

F2 - Processing parameters
SI 65536
SF 125.7804090 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00





3.35
¹³C NMR (CDCl₃, 126 MHz)



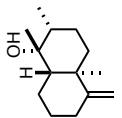
```

Current Data Parameters
NAME      YS-IV-90
PROCNO    1
F2 - Acquisition Parameters
Time      2019_09_06
INSTRUM   cryo500
PULPROG   zgpg30
TD         65536
SOLVENT    CDCl3
DS         1
SWH        30303.031 Hz
FIDRES     0.0013480 sec
RG         7298.2
DM         16.500 usec
DE         2.000 usec
TE         298.0 K
D1         0.25000000 sec
d11        0.00000000 sec
d12        0.00000000 sec
d17        0.00019600 sec
MKREST    0 sec
MARK      0.01500000 sec
P2         33.10 usec

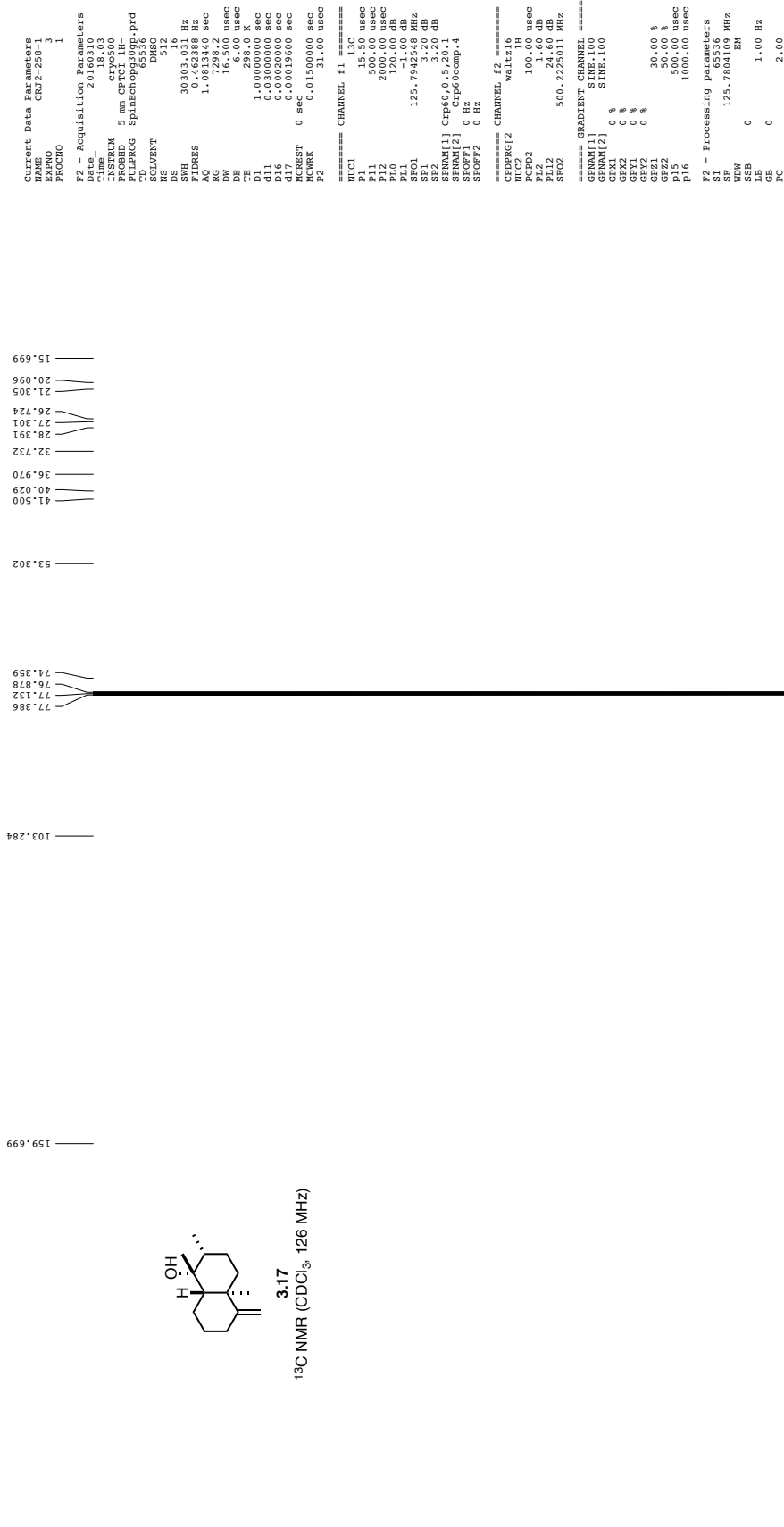
===== CHANNEL f1 =====
NUC1       13C
P1         16.55 usec
PL1        500.00 usec
PL2        200.00 usec
PL0        120.00 dB
PL1        -1.00 dB
SFO1       125.7942548 MHz
SF2        2.70 dB
SP2        2.70 dB
SFOFF1     0 Hz
SFOFF2     0 Hz

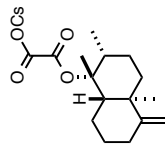
===== CHANNEL f2 =====
CPDPRG2    walz16
NUC2       1H
P2         100.00 usec
PL2        1.80 dB
PL12       24.50 dB
SFO2       500.2225011 MHz

===== GRADIENT CHANNEL =====
GPMAM[1]   SINE.100
GPMAM[2]   SINE.100
GPX0        0 %
GPX2        0 %
GPX1        0 %
GPZ0        0 %
GPZ1        0 %
GPZ2        30.00 %
P15         50.00 usec
P16         100.00 usec
P18         1000.00 usec
F2 - Processing parameters
SI          65536
SF          125.7804004 MHz
WDW         EM
SSB         0
GB          0
PC          2.00
    
```

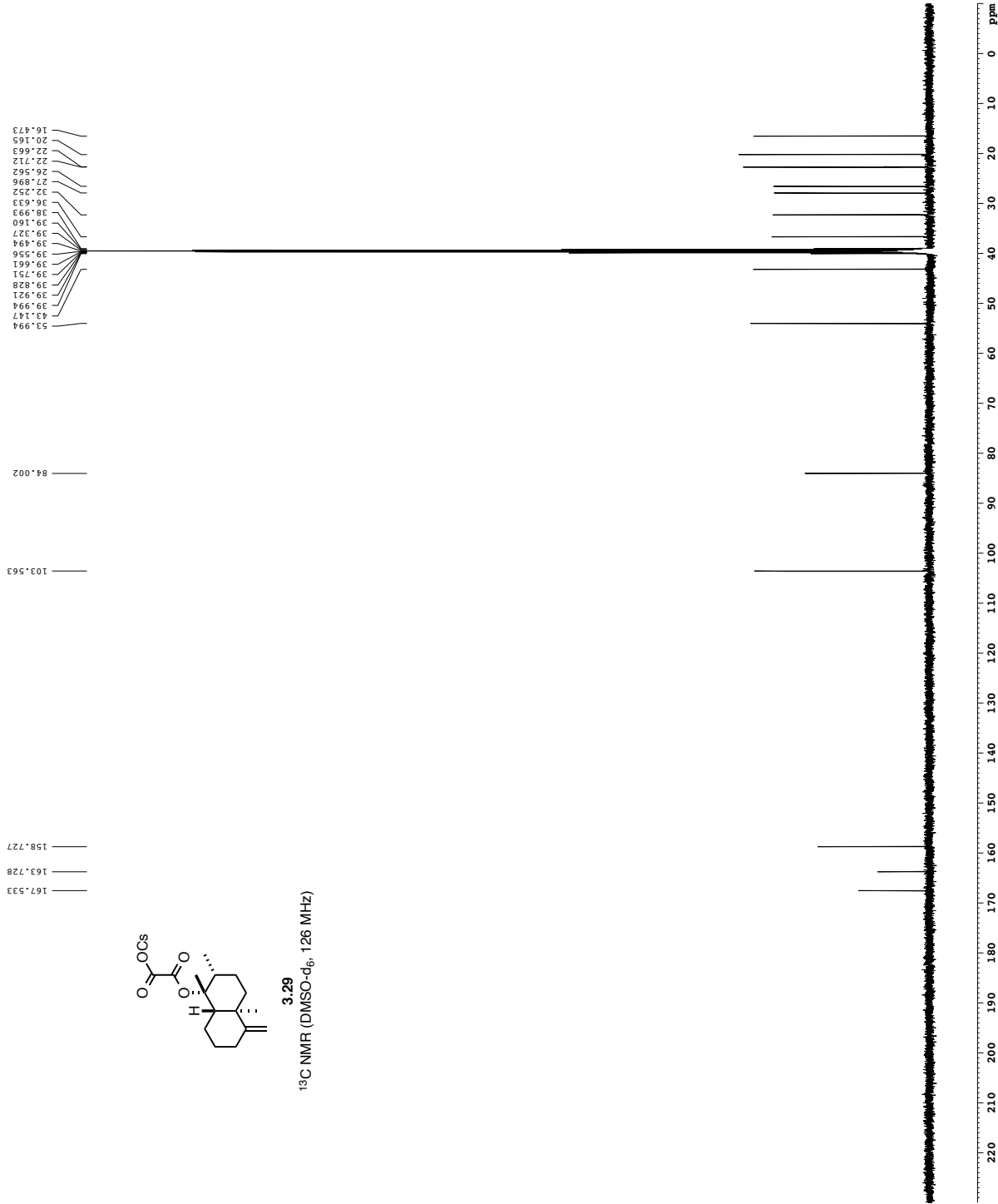


¹³C NMR (CDCl₃, 126 MHz)



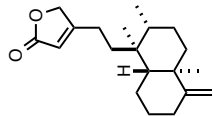


3.29
¹³C NMR (DMSO-d₆, 126 MHz)



```

Current Data Parameters
NAME      CRJ2-266-4
EXNO      2
PROCNO    1
F2 - Acquisition Parameters
Date_     20160312
Time      16:50
INSTRUM   cryo500
PROBHD    5 mm CPCL1 H-
PULPROG   SpInch99sp9p-prd
SOLVENT   DMSO
NS        128
DS        4
AQ        30303.016 Hz
FIDRES    0.462388 Hz
AQ         1.0813440 sec
RG         655.500
DM         16.500 usec
DE         6.00 usec
TE        298.0 K
D1         0.25000000 sec
d11        0.03000000 sec
D16        0.00200000 sec
DELTA     0.00196000 sec
MCHRGST   0 sec
MCHRGK    0.01500000 sec
F2         33.10 usec
===== CHANNEL f1 =====
NUC1       13C
P1         16.50 usec
PL1        0.00 usec
P12        2000.00 usec
PL2        120.00 dB
SFO1       125.7942548 MHz
SPL        2.70 dB
SFO2       125.7942548 MHz
SPNAM[1]   C1p60.0.5.20.0
SPNAM[2]   C1p60comp.4
SFOFF1     0 Hz
SFOFF2     0 Hz
===== CHANNEL f2 =====
P2         16.50 usec
waltz16
PCPD2      100.00 usec
PL2        1.60 dB
SFO1       125.7942548 MHz
SFO2       500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]
GPX1       0 %
GPY1       0 %
GPZ1       0 %
GPA1       0 %
GPA2       0 %
GPA3       0 %
GPA4       0 %
GPA5       0 %
GPA6       0 %
GPA7       0 %
GPA8       0 %
GPA9       0 %
GPA10      0 %
F2 - Processing Parameters
SI         65536
SF         125.7804820 MHz
EN
LB         0
GB         0
PC         2.00
    
```

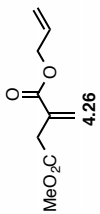


3.1
¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
NAME YS-IV-129B
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160221
Time 09:27
INSTRUM cty5000
PROBHD 5 mm CPYCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 48
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0913440 sec
RG 655
DM 16.500 usec
DE 6.00 usec
TE 300.2 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d16 0.00019600 sec
MCREST 0 sec
MCWRR 0.01500000 sec
F2
===== CHANNEL f1 =====
NUC1 13C
P1 16.35 usec
PL1 0.00 dB
PL2 2000.00 usec
PL0 120.00 dB
SFO1 125.7942548 MHz
SF1 2.70 dB
SFO2 500.1362500 MHz
SF2 2.70 dB
SFOFF1 0 Hz
SFOFF2 0 Hz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL0 24.50 dB
SFO2 500.2225011 MHz
===== GRADIENT CHANNEL =====
GPM1(1) SINE.100
GPM1(2) SINE.100
GPM2 0 %
GPM3 0 %
GPM4 0 %
GPM5 0 %
GPM6 0 %
GPM7 0 %
GPM8 0 %
GPM9 0 %
GPM10 0 %
GPM11 0 %
GPM12 0 %
GPM13 0 %
GPM14 0 %
GPM15 0 %
GPM16 0 %
GPM17 0 %
GPM18 0 %
GPM19 0 %
GPM20 0 %
F2 - Processing parameters
Z 2
SF 125.7804024 MHz
WDW EM
SSB 0
GB 0
PC 2.00

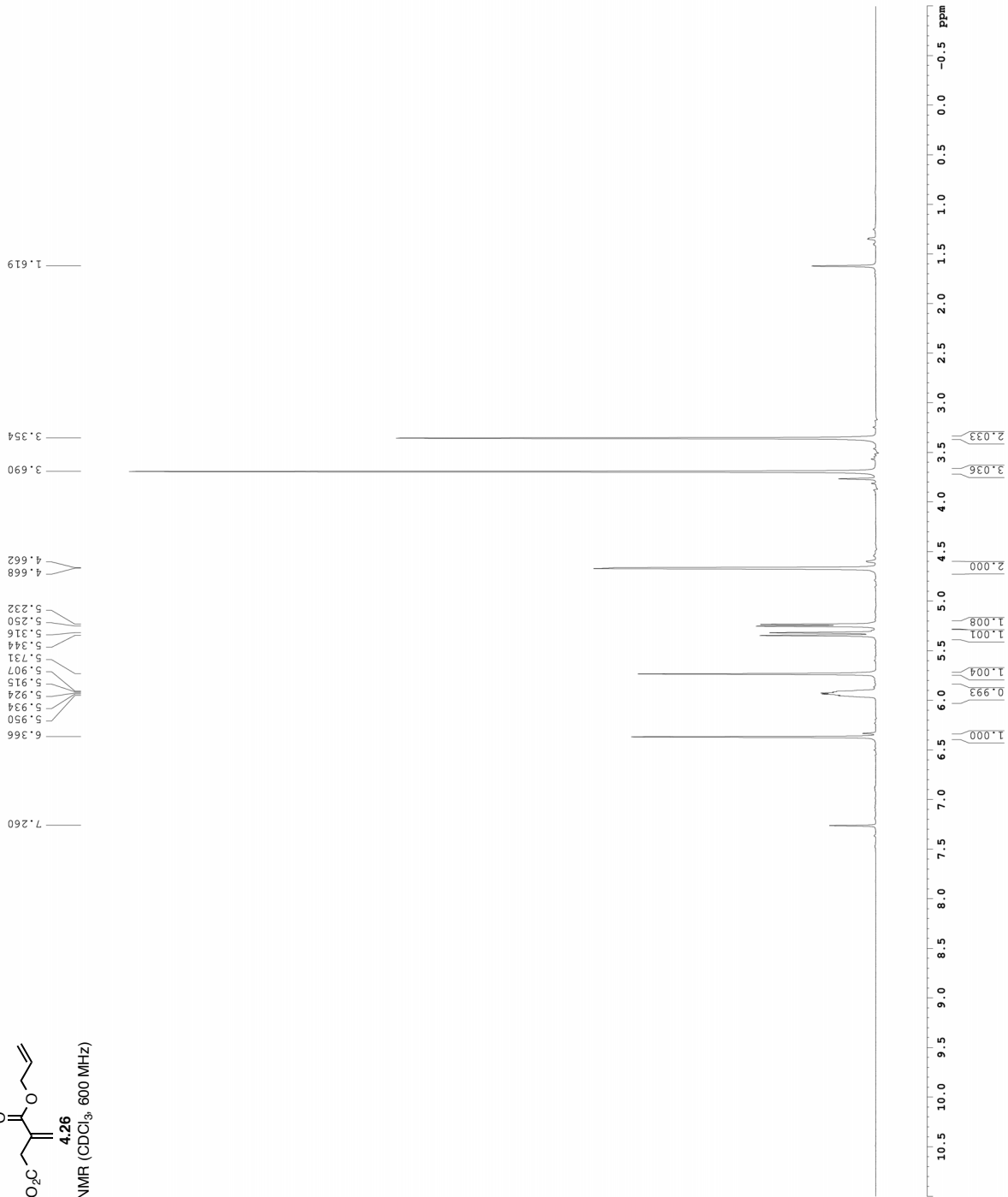
Appendix D: Chapter 4 NMR Spectra

YS-VI-25SM



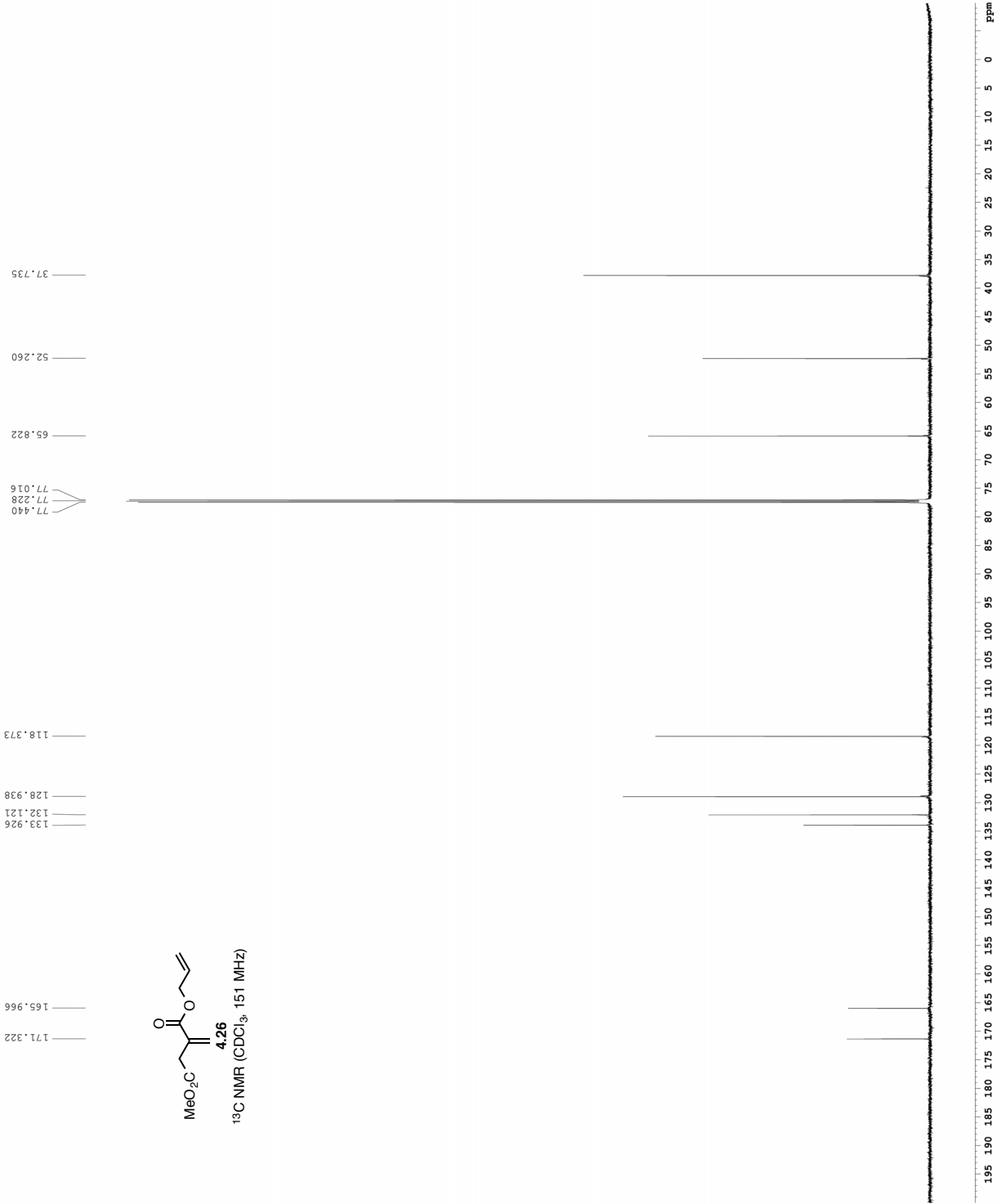
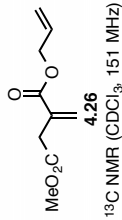
¹H NMR (CDCl₃, 600 MHz)

Current Data Parameters
NAME YS-VI-25SM
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170816
Time 16:47
INSTRUM 5 mm CPBBO BB-
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 8
SWH 9615.382 Hz
FIDRES 0.096042 Hz
AQ 5.0996478 sec
RG 655
SFO 600.1342009 MHz
DE 13.70 usec
TE 298.0 K
TD 1
F2 - Processing parameters
SI 32768
SF 600.1342009 MHz
WDW EM
SSB 0
GB 0
PC 1.00



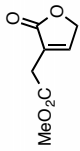
YS-VI-25SM

Current Data Parameters
NAME YS-VI-25SM
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070816
Time 16:51
INSTRUM spect
PROBHD 5 mm CPBBO-BB
PULPROG zgpg30
PCPDPRG2 zgpg30
SOLVENT CDCl3
NS 160
DS 4
SWH 36231.883 Hz
FIDRES 0.552855 Hz
RG 0.3047850 sec
RG 2050
AQ 0.02000000 sec
SFO2 600.1330010 MHz
WDW EM
SSB 0
GB 0
PC 1.00
===== CHANNEL f1 =====
SFO1 150.9194080 MHz
NUC1 13C
P1 10.00 usec
PL1 64.00000000 W
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 13C
P2 10.00 usec
PL2 64.00000000 W
===== Processing parameters =====
SI 65536
SF 150.9028000 MHz
WDW EM
SSB 0
GB 0
PC 1.00

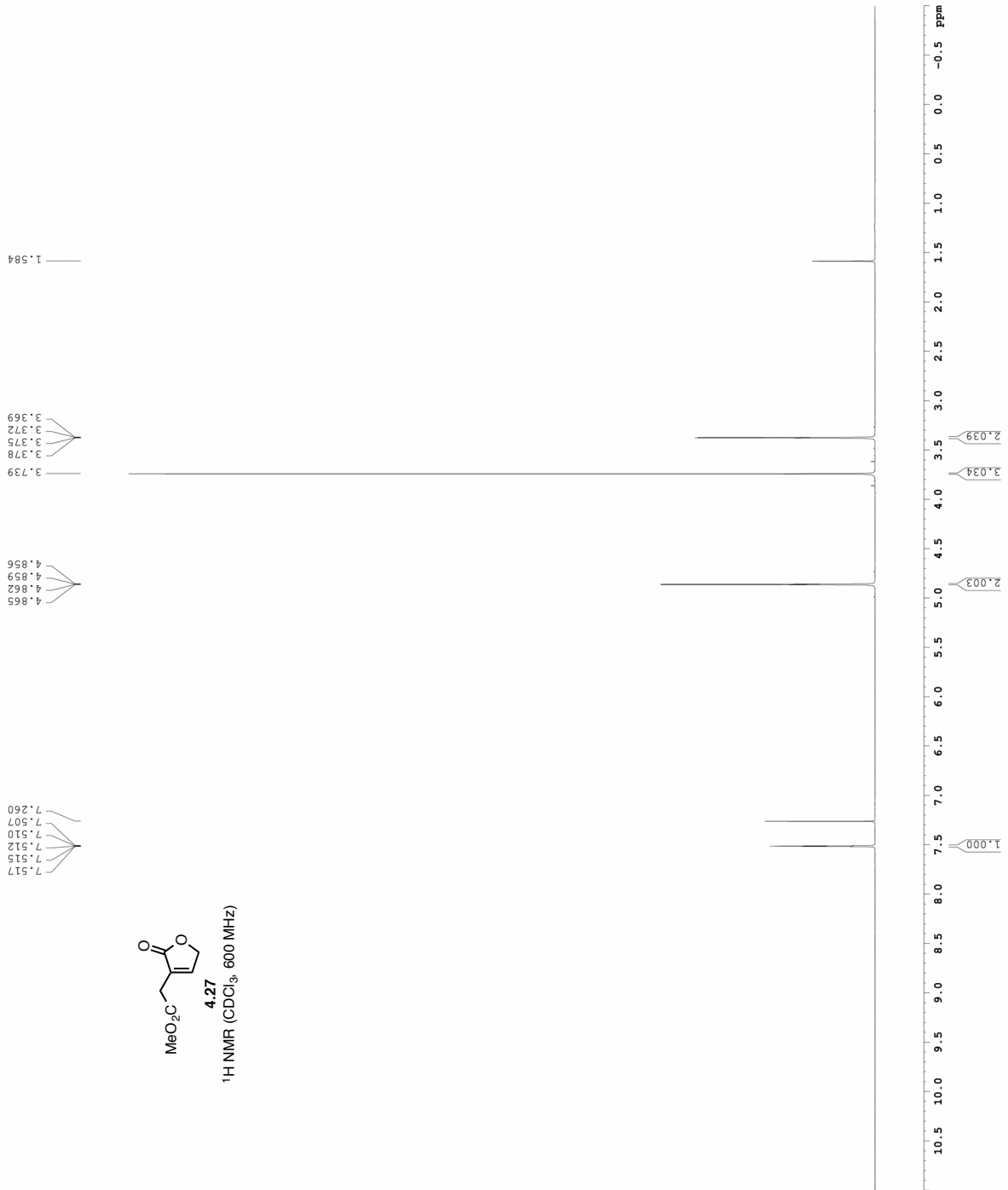


YS-VI-25

Current Data Parameters
NAME YS-VI-25
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111111
Time 13:11
INSTRUM AV600
PROBHD 5 mm CPBBO ZG30
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 0
DS 1
SWH 9615.385 Hz
FIDRES 0.098042 Hz
RG 3.1337410 sec
AQ 1.0000000 sec
DM 52.000 usec
DE 298.2 K sec
TE 298.2 K sec
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.1342009 MHz
NUC1 13C
P1C1 12.00 usec
PLM1 20.00000000 M
F2 - Processing Parameters
SI 65536
SF 600.1300340 MHz
RGW EM
L8 0
L9 0
GB 0
PC 1.00

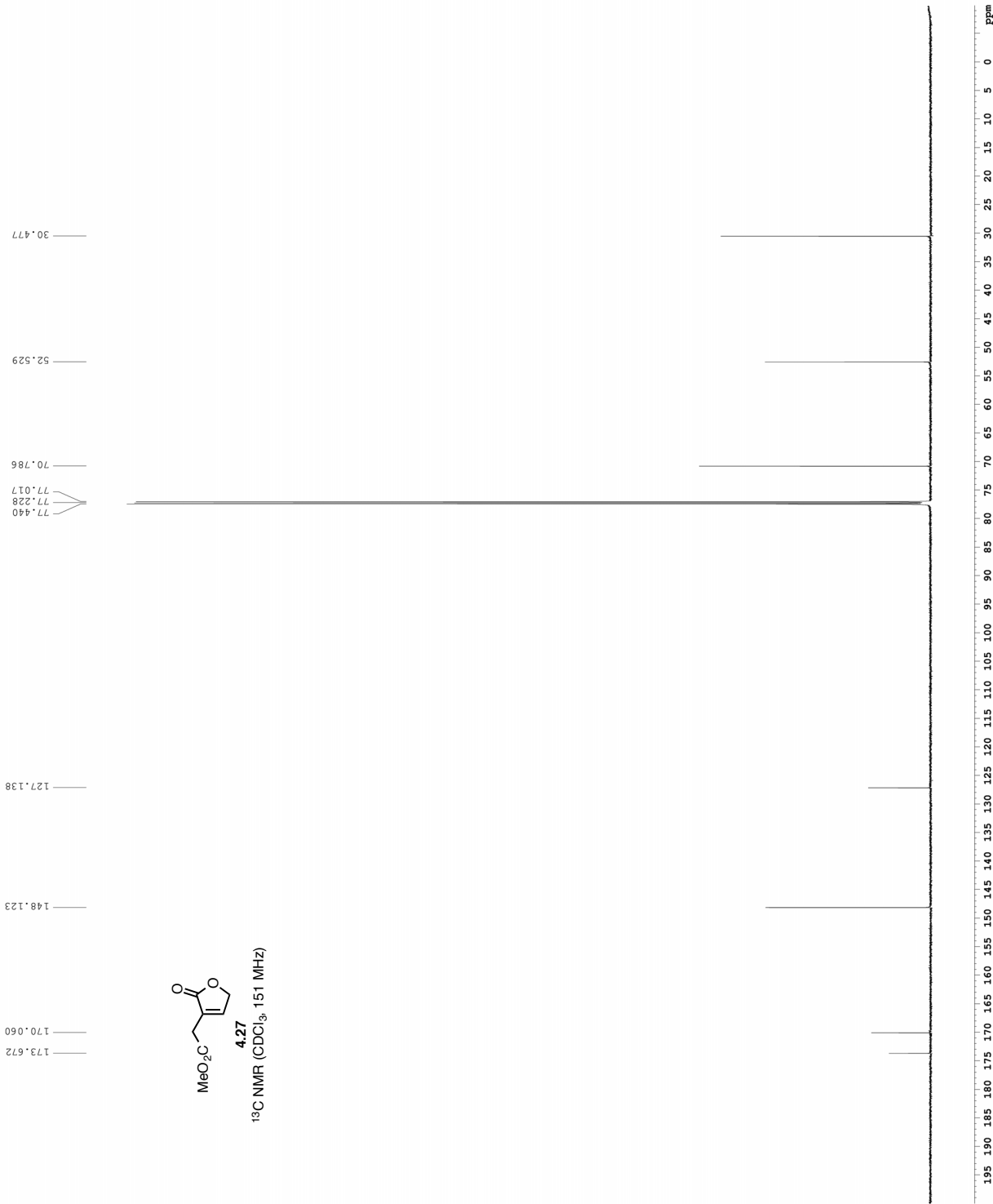
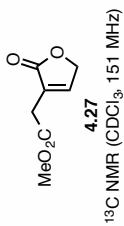


4.27
¹H NMR (CDCl₃, 600 MHz)



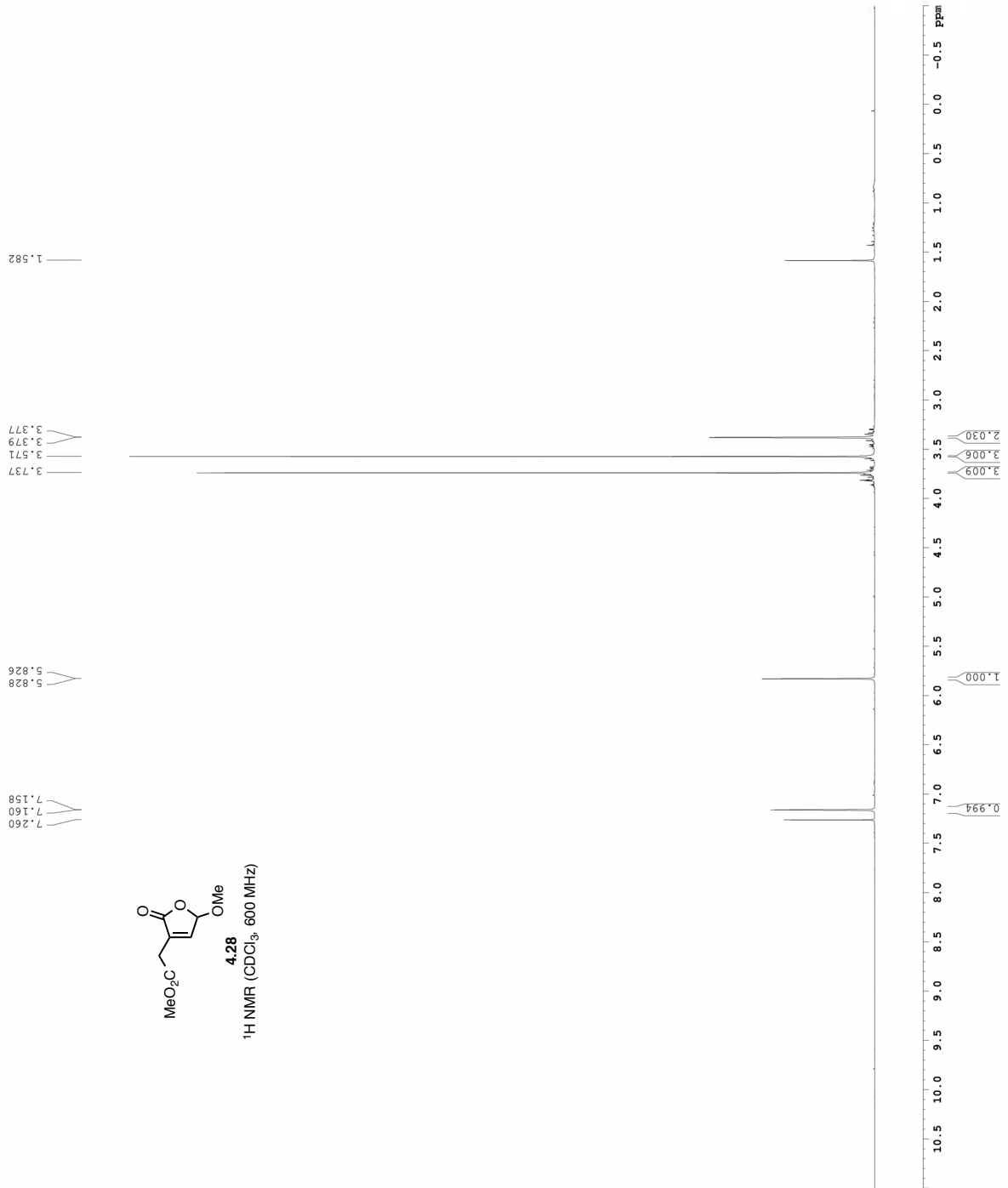
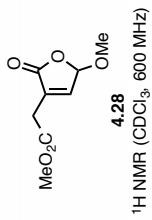
YS-VI-25

Current Data Parameters
NAME YS-VI-25
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110713
Time 13:13
INSTRUM av600
PROBHD 5 mm CPBPR600
PULPROG zgpg30
PCPDPR cpmpr30
SOLVENT CDCl3
NS 400
DS 4
SWH 36231.883 Hz
FIDRES 0.522855 Hz
AQ 0.390477 sec
RG 2050
DM 13.800 usec
DE 1.000 usec
TE 298.0 K
D1 0.6000001 sec
D11 0.1500001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.9194080 MHz
NUC1 13C
P1 1.00 usec
PL1 64.00000000 W
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 1H
PCPDPR2 waitzg16
PCPDZ 80.00 usec
PL12 20.00000000 W
PL122 0.36000001 W
F2 - Processing parameters
SI 65536
SF 150.9078200 MHz
WDW 0
SSB 0
GB 0
PC 1.00



YS-VI-27

Current Data Parameters
NAME YS-VI-27
PROC 4
PROB 1
F2 - Acquisition Parameters
Date_ 20130515
Time_ 15:16
INSTRUM 5 mm CPBBO BB
PROBHD 5 mm CPBBO BB
TD 38460
SOLVENT CDCl3
S 8
SRH 9615.385 Hz
FIDRES 0.250010 Hz
AQ 1.939944 sec
RG 12.7
DW 52.000 usec
DE 298.0 usec
TE 300.2 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.1342009 MHz
NUC1 1H
PULP1 20.00000000 M
===== CHANNEL f2 =====
SF02 600.1300556 MHz
NUC2 1H
PULP2 20.00000000 M
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

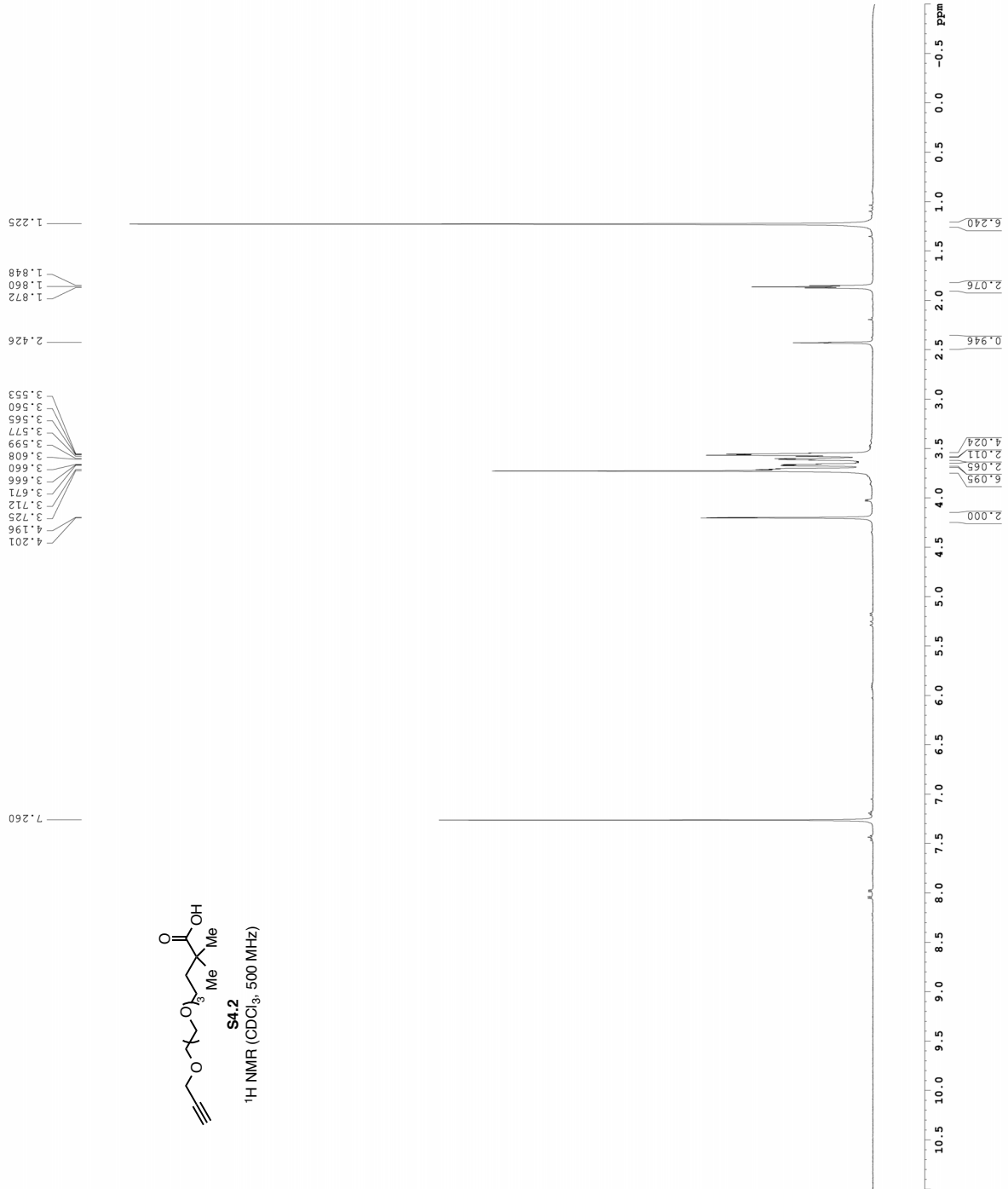


MRC-II-217

Current Data Parameters
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130506
Time 18:08
PROBHD 5 mm CFCF2 1H
PULPROG zg30
SOLVENT CDCl3
NS 8
DS 2
AQ 8013.600 Hz
FIDRES 0.098843 Hz
AQ 5.0998273 sec
RG 62.400 5
DE 6.00 usec
TE 291.3 K
MCREG 0 sec
MCMRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL 0.00 dB
SFO1 500.223515 MHz
F2 - Processing parameters
SI 32768
SF 500.220027 MHz
WDW EM
SSB 0
GB 0
PC 4.00



S4.2
1H NMR (CDCl₃, 500 MHz)



MRG-II-219B

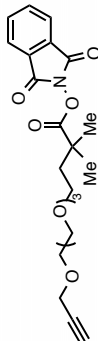
Current Data Parameters
NAME 23C 1H1 613CMR
PROCNO 1
F2 - Acquisition Parameters
Date_ 2017
Time 18:08
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
DS 2
SFO1 801.2820 Hz
SMH 801.2820 Hz
FIDRES 0.098043 Hz
RG 327.7 sec
RG 574.7 sec
DM 62.400 usec
DE 288.0 usec
D1 0.10000000 sec
MCREST 0 sec
PC 0.01500000 sec
===== CHANNEL f1 =====
NUC1 12.0156 usec
P1 12.0156 usec
PL1 -5.00 dB
SFO1 499.4034958 MHz
F2 - Processing parameters
SI 65536
SF 499.4000307 MHz
SFO 499.4000307 MHz
SFB 0
SGB 0
LB 0.30 Hz
PC 1.00

7.880
7.874
7.869
7.863
7.877
7.881
7.776
7.770
7.260

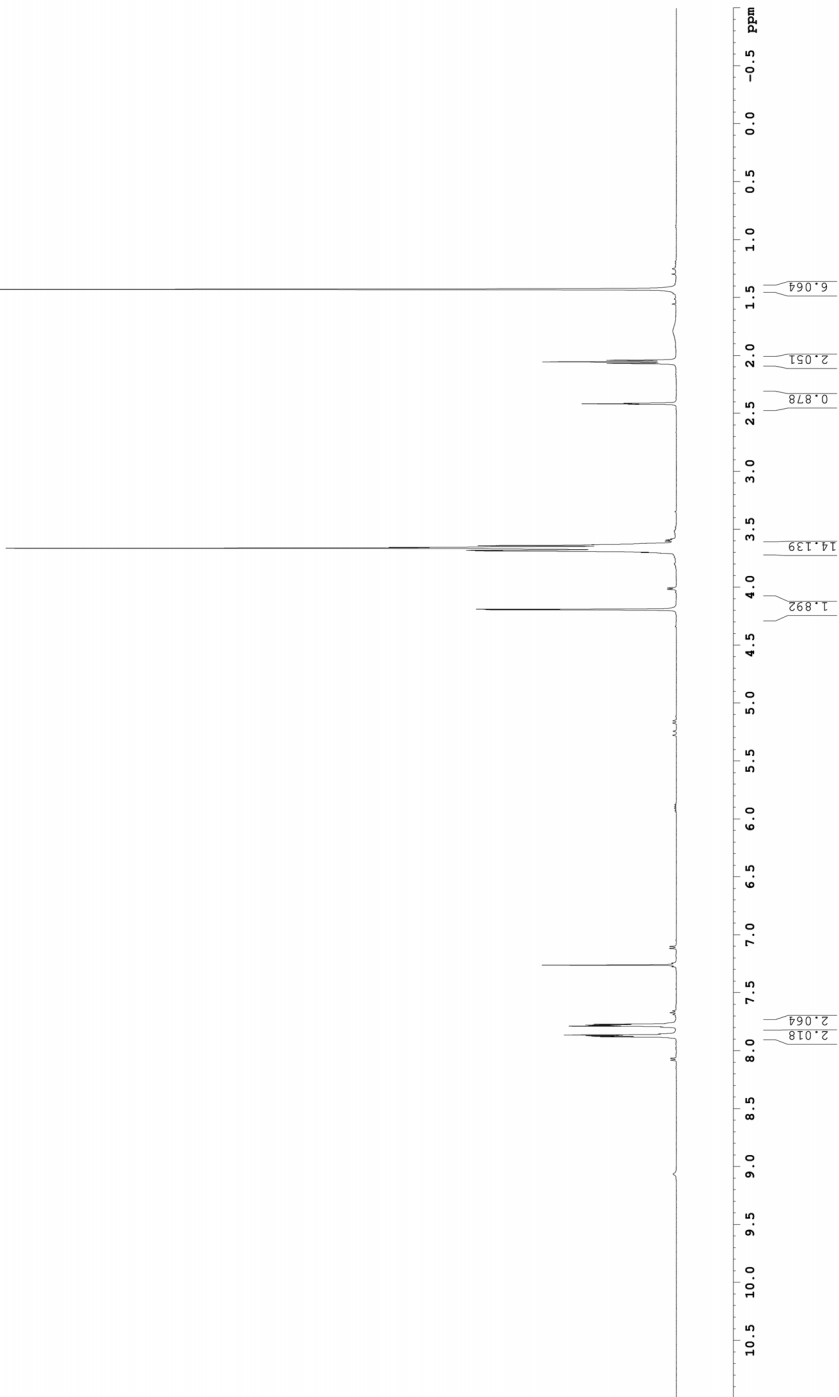
4.193
4.189
3.685
3.681
3.661
3.655
3.651
3.640

2.419
2.415
2.411
2.410
2.068
2.054
2.040

1.427



¹H NMR (CDCl₃, 500 MHz)




```

Current Data Parameters
NAME      30A 1H 13C NMR
PROCNO    2
PROBHD    5 mm CFCT 1H
PULPROG   zgpg30
SOLVENT   CDCl3
NS         2
DS         2
SWH        8012.820 Hz
FIDRES     0.098043 Hz
AQ         3.0399613 sec
RG         6.3
DW         62.400 usec
DE         6.00 usec
TE         298.2 K
D1         0.10000000 sec
MCRESST    0 sec
PCPRK      0.01500000 sec

===== CHANNEL f1 =====
NUC1       13C
P1         7.18 usec
PL1        1.60 dB
SFO1       500.2235015 MHz

===== CHANNEL f2 =====
NUC2       1H
P2         7.18 usec
PL2        1.60 dB
SFO2       500.2235015 MHz

===== CHANNEL f3 =====
NUC3       13C
P3         7.18 usec
PL3        1.60 dB
SFO3       500.2235015 MHz

===== CHANNEL f4 =====
NUC4       1H
P4         7.18 usec
PL4        1.60 dB
SFO4       500.2235015 MHz

===== CHANNEL f5 =====
NUC5       13C
P5         7.18 usec
PL5        1.60 dB
SFO5       500.2235015 MHz

===== CHANNEL f6 =====
NUC6       1H
P6         7.18 usec
PL6        1.60 dB
SFO6       500.2235015 MHz

===== CHANNEL f7 =====
NUC7       13C
P7         7.18 usec
PL7        1.60 dB
SFO7       500.2235015 MHz

===== CHANNEL f8 =====
NUC8       1H
P8         7.18 usec
PL8        1.60 dB
SFO8       500.2235015 MHz

===== CHANNEL f9 =====
NUC9       13C
P9         7.18 usec
PL9        1.60 dB
SFO9       500.2235015 MHz

===== CHANNEL f10 =====
NUC10      1H
P10        7.18 usec
PL10       1.60 dB
SFO10      500.2235015 MHz

===== CHANNEL f11 =====
NUC11      13C
P11        7.18 usec
PL11       1.60 dB
SFO11      500.2235015 MHz

===== CHANNEL f12 =====
NUC12      1H
P12        7.18 usec
PL12       1.60 dB
SFO12      500.2235015 MHz

===== CHANNEL f13 =====
NUC13      13C
P13        7.18 usec
PL13       1.60 dB
SFO13      500.2235015 MHz

===== CHANNEL f14 =====
NUC14      1H
P14        7.18 usec
PL14       1.60 dB
SFO14      500.2235015 MHz

===== CHANNEL f15 =====
NUC15      13C
P15        7.18 usec
PL15       1.60 dB
SFO15      500.2235015 MHz

===== CHANNEL f16 =====
NUC16      1H
P16        7.18 usec
PL16       1.60 dB
SFO16      500.2235015 MHz

===== CHANNEL f17 =====
NUC17      13C
P17        7.18 usec
PL17       1.60 dB
SFO17      500.2235015 MHz

===== CHANNEL f18 =====
NUC18      1H
P18        7.18 usec
PL18       1.60 dB
SFO18      500.2235015 MHz

===== CHANNEL f19 =====
NUC19      13C
P19        7.18 usec
PL19       1.60 dB
SFO19      500.2235015 MHz

===== CHANNEL f20 =====
NUC20      1H
P20        7.18 usec
PL20       1.60 dB
SFO20      500.2235015 MHz

===== CHANNEL f21 =====
NUC21      13C
P21        7.18 usec
PL21       1.60 dB
SFO21      500.2235015 MHz

===== CHANNEL f22 =====
NUC22      1H
P22        7.18 usec
PL22       1.60 dB
SFO22      500.2235015 MHz

===== CHANNEL f23 =====
NUC23      13C
P23        7.18 usec
PL23       1.60 dB
SFO23      500.2235015 MHz

===== CHANNEL f24 =====
NUC24      1H
P24        7.18 usec
PL24       1.60 dB
SFO24      500.2235015 MHz

===== CHANNEL f25 =====
NUC25      13C
P25        7.18 usec
PL25       1.60 dB
SFO25      500.2235015 MHz

===== CHANNEL f26 =====
NUC26      1H
P26        7.18 usec
PL26       1.60 dB
SFO26      500.2235015 MHz

===== CHANNEL f27 =====
NUC27      13C
P27        7.18 usec
PL27       1.60 dB
SFO27      500.2235015 MHz

===== CHANNEL f28 =====
NUC28      1H
P28        7.18 usec
PL28       1.60 dB
SFO28      500.2235015 MHz

===== CHANNEL f29 =====
NUC29      13C
P29        7.18 usec
PL29       1.60 dB
SFO29      500.2235015 MHz

===== CHANNEL f30 =====
NUC30      1H
P30        7.18 usec
PL30       1.60 dB
SFO30      500.2235015 MHz

===== CHANNEL f31 =====
NUC31      13C
P31        7.18 usec
PL31       1.60 dB
SFO31      500.2235015 MHz

===== CHANNEL f32 =====
NUC32      1H
P32        7.18 usec
PL32       1.60 dB
SFO32      500.2235015 MHz

===== CHANNEL f33 =====
NUC33      13C
P33        7.18 usec
PL33       1.60 dB
SFO33      500.2235015 MHz

===== CHANNEL f34 =====
NUC34      1H
P34        7.18 usec
PL34       1.60 dB
SFO34      500.2235015 MHz

===== CHANNEL f35 =====
NUC35      13C
P35        7.18 usec
PL35       1.60 dB
SFO35      500.2235015 MHz

===== CHANNEL f36 =====
NUC36      1H
P36        7.18 usec
PL36       1.60 dB
SFO36      500.2235015 MHz

===== CHANNEL f37 =====
NUC37      13C
P37        7.18 usec
PL37       1.60 dB
SFO37      500.2235015 MHz

===== CHANNEL f38 =====
NUC38      1H
P38        7.18 usec
PL38       1.60 dB
SFO38      500.2235015 MHz

===== CHANNEL f39 =====
NUC39      13C
P39        7.18 usec
PL39       1.60 dB
SFO39      500.2235015 MHz

===== CHANNEL f40 =====
NUC40      1H
P40        7.18 usec
PL40       1.60 dB
SFO40      500.2235015 MHz

===== CHANNEL f41 =====
NUC41      13C
P41        7.18 usec
PL41       1.60 dB
SFO41      500.2235015 MHz

===== CHANNEL f42 =====
NUC42      1H
P42        7.18 usec
PL42       1.60 dB
SFO42      500.2235015 MHz

===== CHANNEL f43 =====
NUC43      13C
P43        7.18 usec
PL43       1.60 dB
SFO43      500.2235015 MHz

===== CHANNEL f44 =====
NUC44      1H
P44        7.18 usec
PL44       1.60 dB
SFO44      500.2235015 MHz

===== CHANNEL f45 =====
NUC45      13C
P45        7.18 usec
PL45       1.60 dB
SFO45      500.2235015 MHz

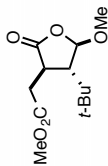
===== CHANNEL f46 =====
NUC46      1H
P46        7.18 usec
PL46       1.60 dB
SFO46      500.2235015 MHz

===== CHANNEL f47 =====
NUC47      13C
P47        7.18 usec
PL47       1.60 dB
SFO47      500.2235015 MHz

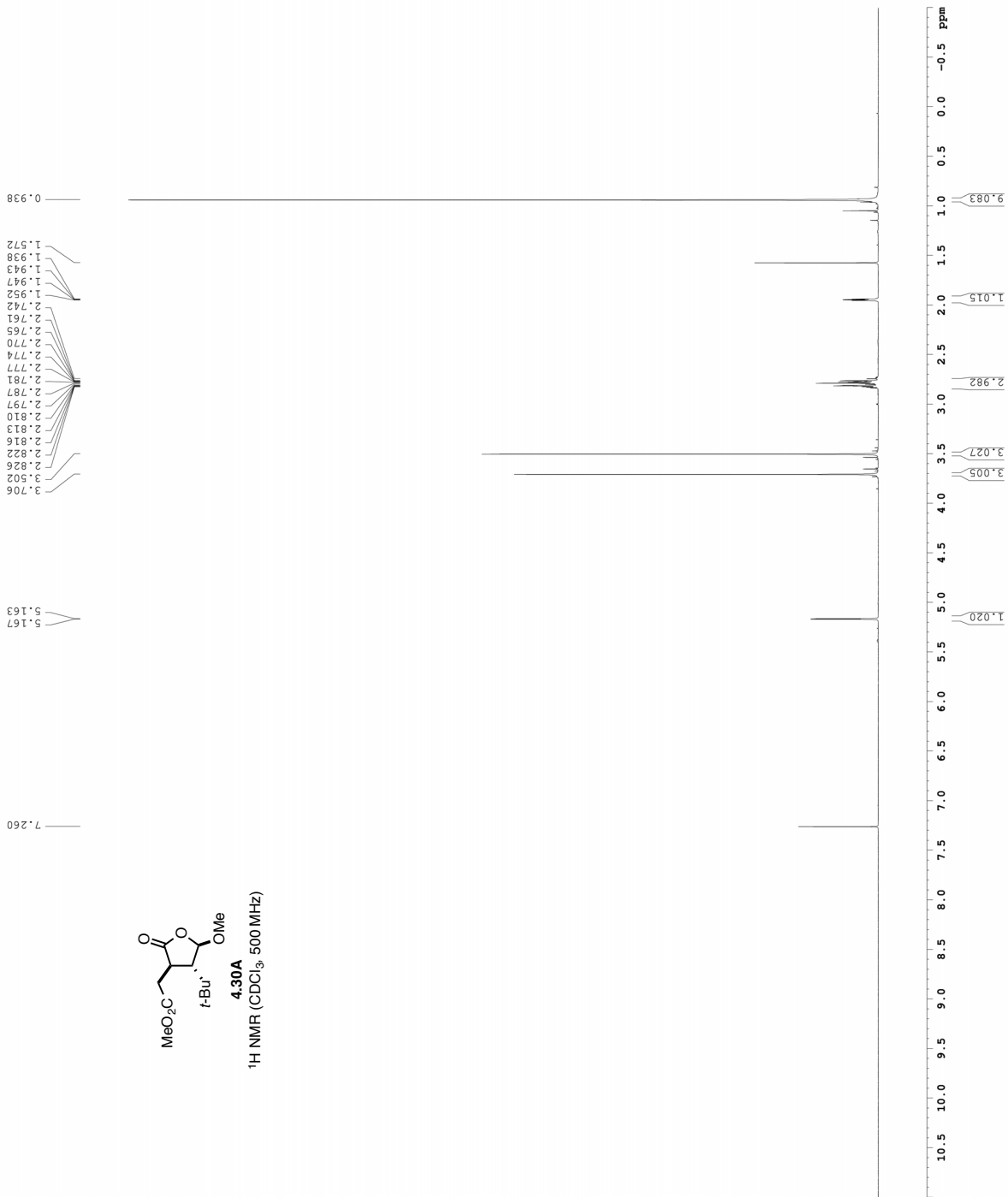
===== CHANNEL f48 =====
NUC48      1H
P48        7.18 usec
PL48       1.60 dB
SFO48      500.2235015 MHz

===== CHANNEL f49 =====
NUC49      13C
P49        7.18 usec
PL49       1.60 dB
SFO49      500.2235015 MHz

===== CHANNEL f50 =====
NUC50      1H
P50        7.18 usec
PL50       1.60 dB
SFO50      500.2235015 MHz
    
```

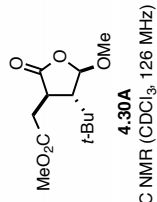
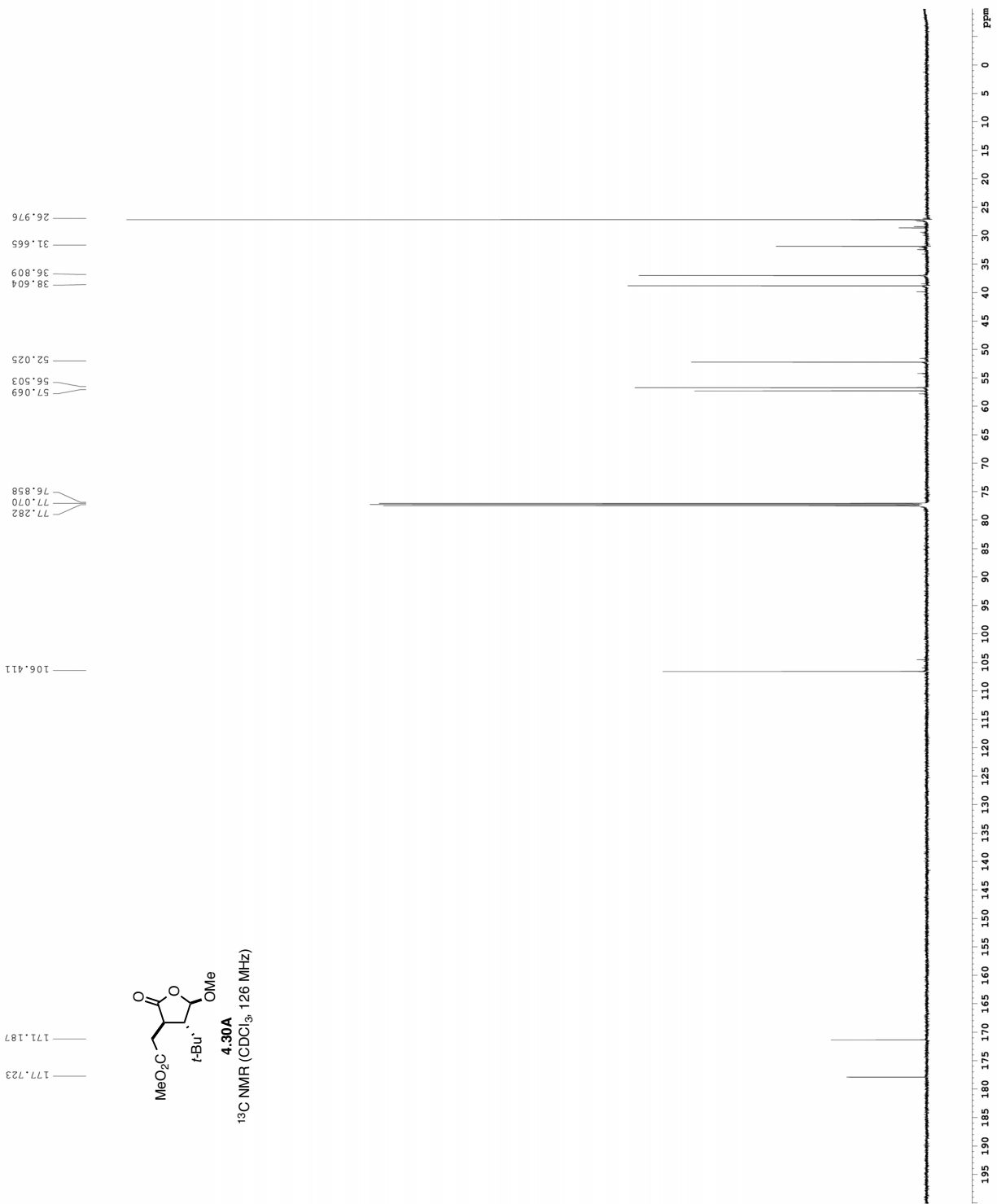


4.30A
1H NMR (CDCl₃, 500 MHz)

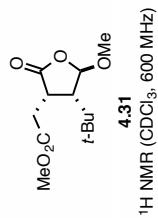


PZ-II-268

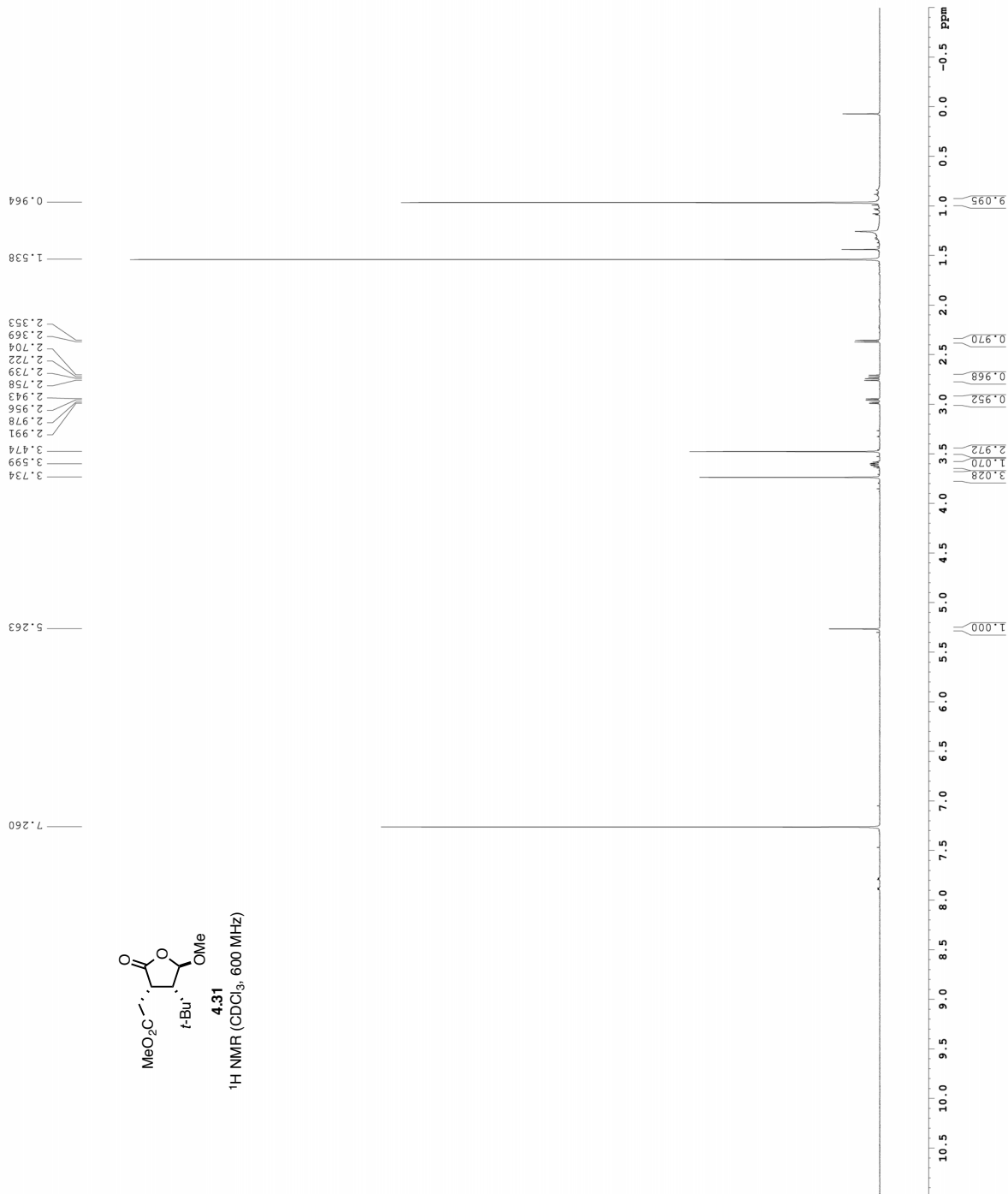
Current Data Parameters
NAME 30A 1H1 C13CNSR
PROCNO 4
F2 - Acquisition Parameters
Date_ 2010
Time 14.20
INSTRUM spect
PROBHD 5 mm CPBPR
PULPROG zgpg30
PCPRG2 waltz16
SOLVENT CDCl3
NS 121
DS 2
SWH 36231.883 Hz
FIDRES 0.522855 Hz
AQ 0.3947779 sec
RG 2050
DM 13.800 usec
DE 2.000 usec
TE 298.0 K
D1 0.4000001 sec
D11 0.1300001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 100.626125 MHz
P1 12.00 usec
PL1 0.00 dB
PLM1 64.00000000 M
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
P2 12.00 usec
PL2 0.00 dB
PCPRG12 waltz16
PCPDZ 20.00000000 M
PLM2 0.36000001 M
===== CHANNEL f3 =====
SFO3 150.9027826 MHz
P3 12.00 usec
PL3 0.00 dB
PCPDZ 20.00000000 M
PLM3 0.36000001 M



PZ-II-267

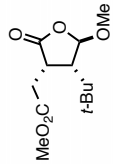


Current Data Parameters
NAME 31 LHNR
PROC 1
PROB0
F2 - Acquisition Parameters
Time 20180627 23:53
INSTRUM 5 mm CFCL JPC
PROBHD 5 mm CFCL JPC
TD 8128
SOLVENT CDCl3
NS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 3.0398711 sec
RG 7.1
DW 62.400 usec
DE 9.60 usec
DI 0.10000000 sec
MCRESST 0 sec
PCPRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
PULP 7.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200311 MHz
SM 2M
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



MRG-II-71

172.110
177.868



4.31

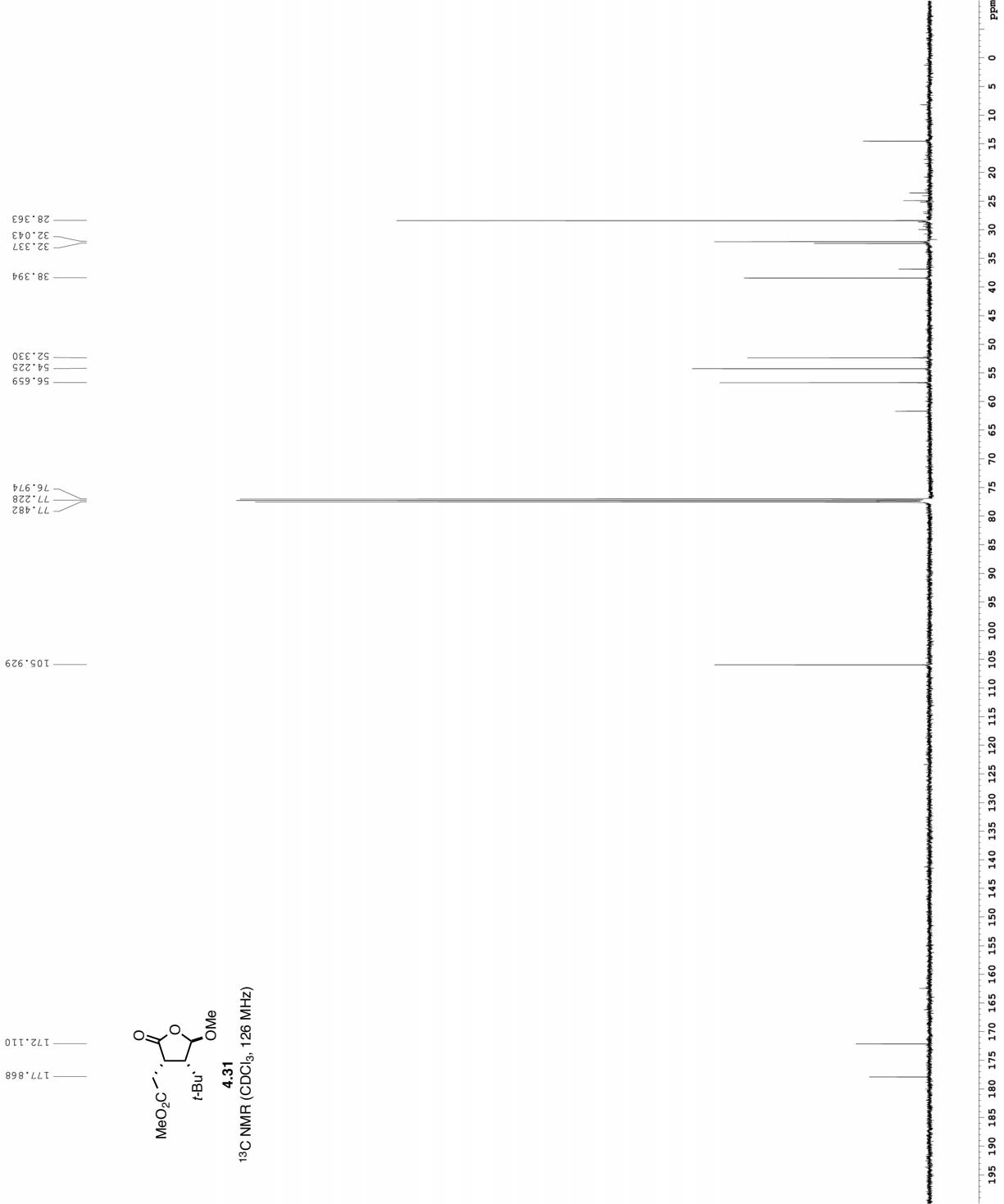
¹³C NMR (CDCl₃, 126 MHz)

105.929

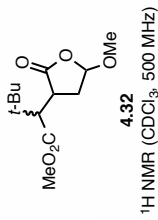
77.482
77.228
76.974

38.394
32.337
32.043
28.363

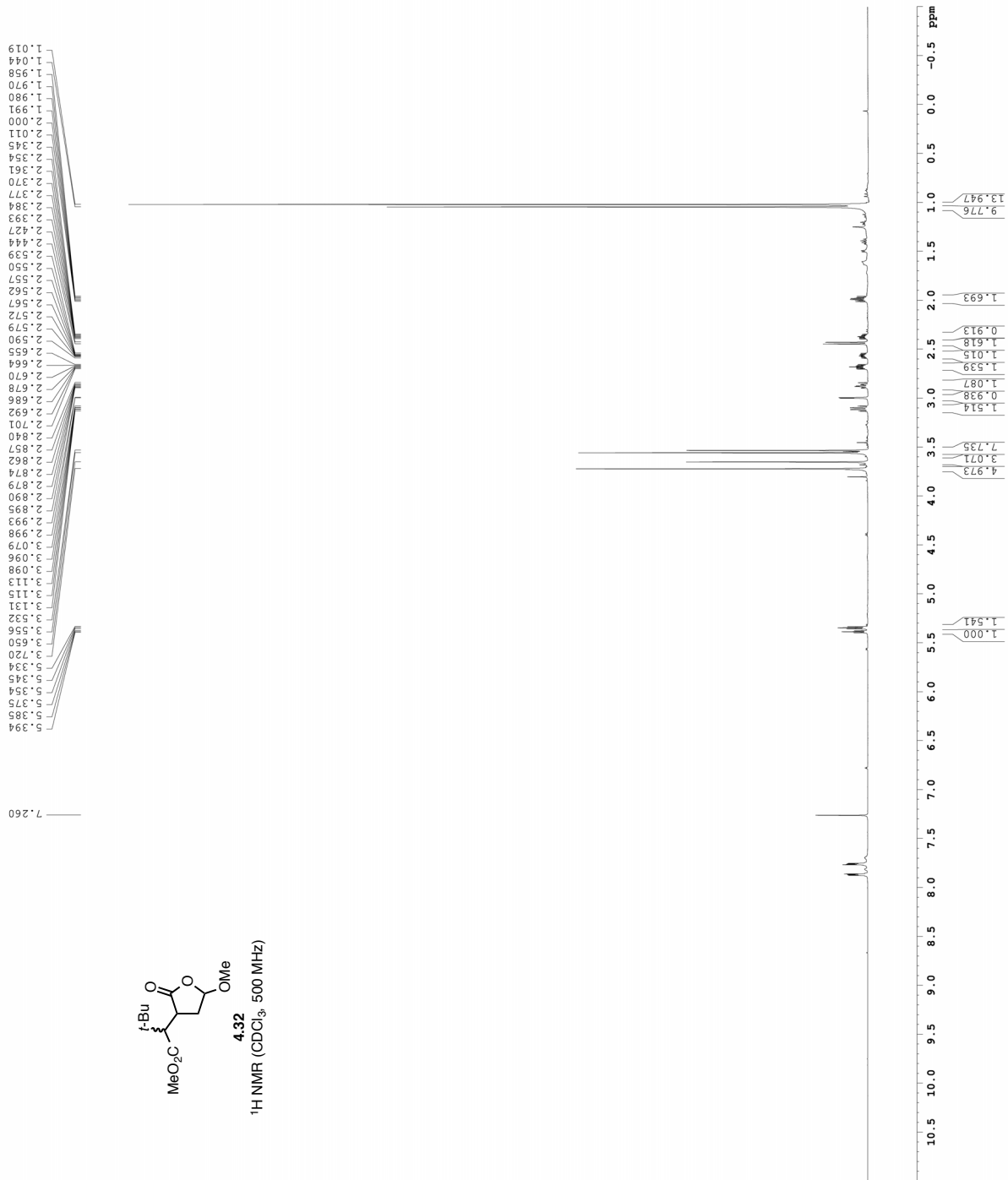
Current Data Parameters
NAME 31.13CMR
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110512
Time 15.12
INSTRUM spect
PROBHD 5 mm CPY-130
PULPROG Spinalcchop31ppf.prd
AQ 0.0200000 sec
SFO 125.760311 MHz
GPROG zgpg30
SOLVENT CDCl3
NS 1024
DS 4
SWH 30303.011 Hz
FIDRES 0.462288 Hz
AQ 1.22988 sec
RG 2298.8
DW 16.500 usec
DE 2.000 usec
TE 298.0 K
D1 0.2500000 sec
D11 0.0000000 sec
D15 0.0002000 sec
MCREST 0 sec
MCWRR 0.01500000 sec
F2 31.00 usec
===== CHANNEL f1 =====
NUC1 13C
P1 15.50 usec
PL1 0.00 dB
PL2 0.00 dB
PL3 0.00 dB
PL4 120.00 dB
PL5 0.00 dB
PL6 0.00 dB
PL7 0.00 dB
PL8 0.00 dB
PL9 0.00 dB
PL10 0.00 dB
PL11 0.00 dB
PL12 0.00 dB
PL13 0.00 dB
PL14 0.00 dB
PL15 0.00 dB
PL16 0.00 dB
PL17 0.00 dB
PL18 0.00 dB
PL19 0.00 dB
PL20 0.00 dB
PL21 0.00 dB
PL22 0.00 dB
PL23 0.00 dB
PL24 0.00 dB
PL25 0.00 dB
PL26 0.00 dB
PL27 0.00 dB
PL28 0.00 dB
PL29 0.00 dB
PL30 0.00 dB
PL31 0.00 dB
PL32 0.00 dB
PL33 0.00 dB
PL34 0.00 dB
PL35 0.00 dB
PL36 0.00 dB
PL37 0.00 dB
PL38 0.00 dB
PL39 0.00 dB
PL40 0.00 dB
PL41 0.00 dB
PL42 0.00 dB
PL43 0.00 dB
PL44 0.00 dB
PL45 0.00 dB
PL46 0.00 dB
PL47 0.00 dB
PL48 0.00 dB
PL49 0.00 dB
PL50 0.00 dB
PL51 0.00 dB
PL52 0.00 dB
PL53 0.00 dB
PL54 0.00 dB
PL55 0.00 dB
PL56 0.00 dB
PL57 0.00 dB
PL58 0.00 dB
PL59 0.00 dB
PL60 0.00 dB
PL61 0.00 dB
PL62 0.00 dB
PL63 0.00 dB
PL64 0.00 dB
PL65 0.00 dB
PL66 0.00 dB
PL67 0.00 dB
PL68 0.00 dB
PL69 0.00 dB
PL70 0.00 dB
PL71 0.00 dB
PL72 0.00 dB
PL73 0.00 dB
PL74 0.00 dB
PL75 0.00 dB
PL76 0.00 dB
PL77 0.00 dB
PL78 0.00 dB
PL79 0.00 dB
PL80 0.00 dB
PL81 0.00 dB
PL82 0.00 dB
PL83 0.00 dB
PL84 0.00 dB
PL85 0.00 dB
PL86 0.00 dB
PL87 0.00 dB
PL88 0.00 dB
PL89 0.00 dB
PL90 0.00 dB
PL91 0.00 dB
PL92 0.00 dB
PL93 0.00 dB
PL94 0.00 dB
PL95 0.00 dB
PL96 0.00 dB
PL97 0.00 dB
PL98 0.00 dB
PL99 0.00 dB
PL100 0.00 dB
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 13C
P1 100.00 usec
PL1 0.00 dB
PL2 0.00 dB
PL3 0.00 dB
PL4 0.00 dB
PL5 0.00 dB
PL6 0.00 dB
PL7 0.00 dB
PL8 0.00 dB
PL9 0.00 dB
PL10 0.00 dB
PL11 0.00 dB
PL12 0.00 dB
PL13 0.00 dB
PL14 0.00 dB
PL15 0.00 dB
PL16 0.00 dB
PL17 0.00 dB
PL18 0.00 dB
PL19 0.00 dB
PL20 0.00 dB
PL21 0.00 dB
PL22 0.00 dB
PL23 0.00 dB
PL24 0.00 dB
PL25 0.00 dB
PL26 0.00 dB
PL27 0.00 dB
PL28 0.00 dB
PL29 0.00 dB
PL30 0.00 dB
PL31 0.00 dB
PL32 0.00 dB
PL33 0.00 dB
PL34 0.00 dB
PL35 0.00 dB
PL36 0.00 dB
PL37 0.00 dB
PL38 0.00 dB
PL39 0.00 dB
PL40 0.00 dB
PL41 0.00 dB
PL42 0.00 dB
PL43 0.00 dB
PL44 0.00 dB
PL45 0.00 dB
PL46 0.00 dB
PL47 0.00 dB
PL48 0.00 dB
PL49 0.00 dB
PL50 0.00 dB
PL51 0.00 dB
PL52 0.00 dB
PL53 0.00 dB
PL54 0.00 dB
PL55 0.00 dB
PL56 0.00 dB
PL57 0.00 dB
PL58 0.00 dB
PL59 0.00 dB
PL60 0.00 dB
PL61 0.00 dB
PL62 0.00 dB
PL63 0.00 dB
PL64 0.00 dB
PL65 0.00 dB
PL66 0.00 dB
PL67 0.00 dB
PL68 0.00 dB
PL69 0.00 dB
PL70 0.00 dB
PL71 0.00 dB
PL72 0.00 dB
PL73 0.00 dB
PL74 0.00 dB
PL75 0.00 dB
PL76 0.00 dB
PL77 0.00 dB
PL78 0.00 dB
PL79 0.00 dB
PL80 0.00 dB
PL81 0.00 dB
PL82 0.00 dB
PL83 0.00 dB
PL84 0.00 dB
PL85 0.00 dB
PL86 0.00 dB
PL87 0.00 dB
PL88 0.00 dB
PL89 0.00 dB
PL90 0.00 dB
PL91 0.00 dB
PL92 0.00 dB
PL93 0.00 dB
PL94 0.00 dB
PL95 0.00 dB
PL96 0.00 dB
PL97 0.00 dB
PL98 0.00 dB
PL99 0.00 dB
PL100 0.00 dB
===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GXX 0 %
GXX1 0 %
GXX2 0 %
GXX3 0 %
GXX4 0 %
GXX5 0 %
GXX6 0 %
GXX7 0 %
GXX8 0 %
GXX9 0 %
GXX10 0 %
GXX11 0 %
GXX12 0 %
GXX13 0 %
GXX14 0 %
GXX15 0 %
GXX16 0 %
GXX17 0 %
GXX18 0 %
GXX19 0 %
GXX20 0 %
GXX21 0 %
GXX22 0 %
GXX23 0 %
GXX24 0 %
GXX25 0 %
GXX26 0 %
GXX27 0 %
GXX28 0 %
GXX29 0 %
GXX30 0 %
GXX31 0 %
GXX32 0 %
GXX33 0 %
GXX34 0 %
GXX35 0 %
GXX36 0 %
GXX37 0 %
GXX38 0 %
GXX39 0 %
GXX40 0 %
GXX41 0 %
GXX42 0 %
GXX43 0 %
GXX44 0 %
GXX45 0 %
GXX46 0 %
GXX47 0 %
GXX48 0 %
GXX49 0 %
GXX50 0 %
GXX51 0 %
GXX52 0 %
GXX53 0 %
GXX54 0 %
GXX55 0 %
GXX56 0 %
GXX57 0 %
GXX58 0 %
GXX59 0 %
GXX60 0 %
GXX61 0 %
GXX62 0 %
GXX63 0 %
GXX64 0 %
GXX65 0 %
GXX66 0 %
GXX67 0 %
GXX68 0 %
GXX69 0 %
GXX70 0 %
GXX71 0 %
GXX72 0 %
GXX73 0 %
GXX74 0 %
GXX75 0 %
GXX76 0 %
GXX77 0 %
GXX78 0 %
GXX79 0 %
GXX80 0 %
GXX81 0 %
GXX82 0 %
GXX83 0 %
GXX84 0 %
GXX85 0 %
GXX86 0 %
GXX87 0 %
GXX88 0 %
GXX89 0 %
GXX90 0 %
GXX91 0 %
GXX92 0 %
GXX93 0 %
GXX94 0 %
GXX95 0 %
GXX96 0 %
GXX97 0 %
GXX98 0 %
GXX99 0 %
GXX100 0 %
F2 - Processing parameters
SI 655536
SF 125.760311 MHz
WDW EM
SSB 0
GB 0
PC 2.00



MRG-II-15



Current Data Parameters
NAME 32 1H 613CNR
PROCNO 1
PROCNO 1
F2 - Acquisition Parameters
Time 20.71
Time 15.13
INSTRUM av600
PROBHD 5 mm TBI 1H/13
PULPROG zgpg30
TD 98074
SOLVENT CDCl3
DS 2
SFR 9615.385 Hz
SMH 0.098042 Hz
FIDRES 5.039394 Hz
RG 362 sec
DM 52.000 usec
DE 288.00 usec
TE 298.15 K
D1 0.10000000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL1 23.01441956 W
SFO1 600.134205 MHz
F2 - Processing parameters
SI 32768
SF 600.1300341 MHz
WDW EM
SSB 0
GB 0
PC 1.00



MRG-II-15

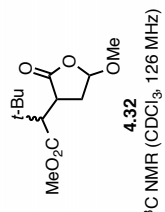
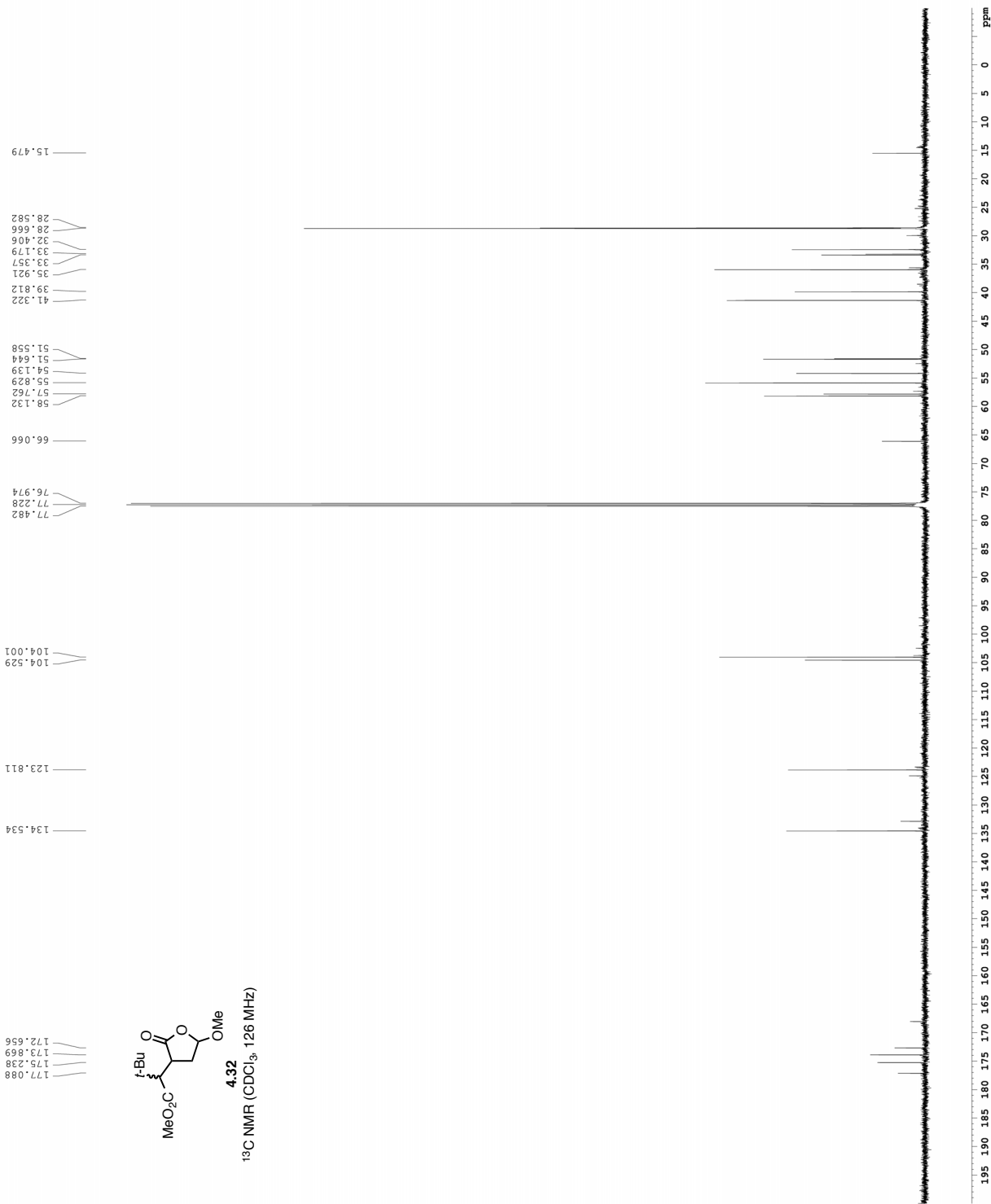
Current Data Parameters
NAME 32 1H1.C13CMR5
PROCNO 6

F2 - Acquisition Parameters
Date_ 2013.00
Time 20:13:40
INSTRUM spect
PULPROG zgpg30
SOLVENT CDCl3
NS 973
DS 2
SWH 30300.031 Hz
FIDRES 0.462888 Hz
AQ 1.729872 sec
RG 7298.72
DM 16.500 usec
DE 2.000 usec
TE 298.2 K
D1 0.2500000 sec
D11 0.0002000 sec
D16 0.0002000 sec
MCREST 0 sec
MCWRRK 0.01500000 sec
F2 31.00 usec

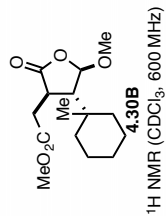
===== CHANNEL f1 =====
NUC1 13C
P1 15.50 usec
PL1 500.00 usec
PL12 1.60 dB
PL13 120.00 dB
PL14 120.00 dB
PL15 120.00 dB
PL16 120.00 dB
PL17 120.00 dB
PL18 120.00 dB
PL19 120.00 dB
PL20 120.00 dB
PL21 120.00 dB
PL22 120.00 dB
PL23 120.00 dB
PL24 120.00 dB
PL25 120.00 dB
PL26 120.00 dB
PL27 120.00 dB
PL28 120.00 dB
PL29 120.00 dB
PL30 120.00 dB
PL31 120.00 dB
PL32 120.00 dB
PL33 120.00 dB
PL34 120.00 dB
PL35 120.00 dB
PL36 120.00 dB
PL37 120.00 dB
PL38 120.00 dB
PL39 120.00 dB
PL40 120.00 dB
PL41 120.00 dB
PL42 120.00 dB
PL43 120.00 dB
PL44 120.00 dB
PL45 120.00 dB
PL46 120.00 dB
PL47 120.00 dB
PL48 120.00 dB
PL49 120.00 dB
PL50 120.00 dB
PL51 120.00 dB
PL52 120.00 dB
PL53 120.00 dB
PL54 120.00 dB
PL55 120.00 dB
PL56 120.00 dB
PL57 120.00 dB
PL58 120.00 dB
PL59 120.00 dB
PL60 120.00 dB
PL61 120.00 dB
PL62 120.00 dB
PL63 120.00 dB
PL64 120.00 dB
PL65 120.00 dB
PL66 120.00 dB
PL67 120.00 dB
PL68 120.00 dB
PL69 120.00 dB
PL70 120.00 dB
PL71 120.00 dB
PL72 120.00 dB
PL73 120.00 dB
PL74 120.00 dB
PL75 120.00 dB
PL76 120.00 dB
PL77 120.00 dB
PL78 120.00 dB
PL79 120.00 dB
PL80 120.00 dB
PL81 120.00 dB
PL82 120.00 dB
PL83 120.00 dB
PL84 120.00 dB
PL85 120.00 dB
PL86 120.00 dB
PL87 120.00 dB
PL88 120.00 dB
PL89 120.00 dB
PL90 120.00 dB
PL91 120.00 dB
PL92 120.00 dB
PL93 120.00 dB
PL94 120.00 dB
PL95 120.00 dB
PL96 120.00 dB
PL97 120.00 dB
PL98 120.00 dB
PL99 120.00 dB
PL100 120.00 dB

===== CHANNEL f2 =====
NUC2 1H
P2 100.00 usec
PL2 1.60 dB
PL3 1.60 dB
PL4 1.60 dB
PL5 1.60 dB
PL6 1.60 dB
PL7 1.60 dB
PL8 1.60 dB
PL9 1.60 dB
PL10 1.60 dB
PL11 1.60 dB
PL12 1.60 dB
PL13 1.60 dB
PL14 1.60 dB
PL15 1.60 dB
PL16 1.60 dB
PL17 1.60 dB
PL18 1.60 dB
PL19 1.60 dB
PL20 1.60 dB
PL21 1.60 dB
PL22 1.60 dB
PL23 1.60 dB
PL24 1.60 dB
PL25 1.60 dB
PL26 1.60 dB
PL27 1.60 dB
PL28 1.60 dB
PL29 1.60 dB
PL30 1.60 dB
PL31 1.60 dB
PL32 1.60 dB
PL33 1.60 dB
PL34 1.60 dB
PL35 1.60 dB
PL36 1.60 dB
PL37 1.60 dB
PL38 1.60 dB
PL39 1.60 dB
PL40 1.60 dB
PL41 1.60 dB
PL42 1.60 dB
PL43 1.60 dB
PL44 1.60 dB
PL45 1.60 dB
PL46 1.60 dB
PL47 1.60 dB
PL48 1.60 dB
PL49 1.60 dB
PL50 1.60 dB
PL51 1.60 dB
PL52 1.60 dB
PL53 1.60 dB
PL54 1.60 dB
PL55 1.60 dB
PL56 1.60 dB
PL57 1.60 dB
PL58 1.60 dB
PL59 1.60 dB
PL60 1.60 dB
PL61 1.60 dB
PL62 1.60 dB
PL63 1.60 dB
PL64 1.60 dB
PL65 1.60 dB
PL66 1.60 dB
PL67 1.60 dB
PL68 1.60 dB
PL69 1.60 dB
PL70 1.60 dB
PL71 1.60 dB
PL72 1.60 dB
PL73 1.60 dB
PL74 1.60 dB
PL75 1.60 dB
PL76 1.60 dB
PL77 1.60 dB
PL78 1.60 dB
PL79 1.60 dB
PL80 1.60 dB
PL81 1.60 dB
PL82 1.60 dB
PL83 1.60 dB
PL84 1.60 dB
PL85 1.60 dB
PL86 1.60 dB
PL87 1.60 dB
PL88 1.60 dB
PL89 1.60 dB
PL90 1.60 dB
PL91 1.60 dB
PL92 1.60 dB
PL93 1.60 dB
PL94 1.60 dB
PL95 1.60 dB
PL96 1.60 dB
PL97 1.60 dB
PL98 1.60 dB
PL99 1.60 dB
PL100 1.60 dB

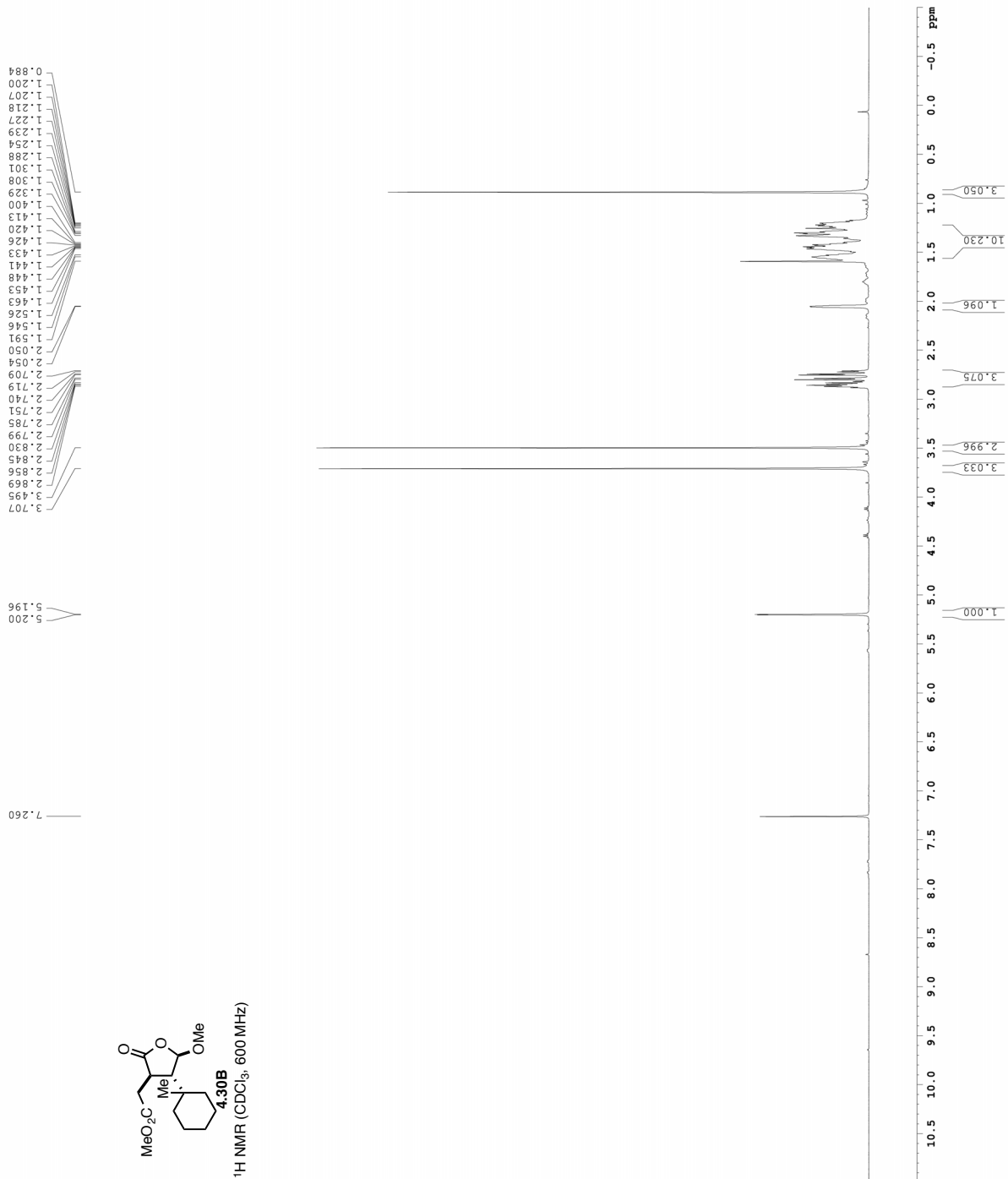
F2 - Processing parameters
SI 65536
SF 125.7604000 MHz
WDW EM
SSB 0
GB 0
PC 2.00



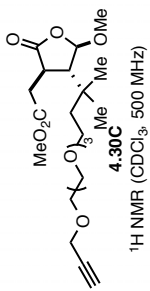
MRG-I-231



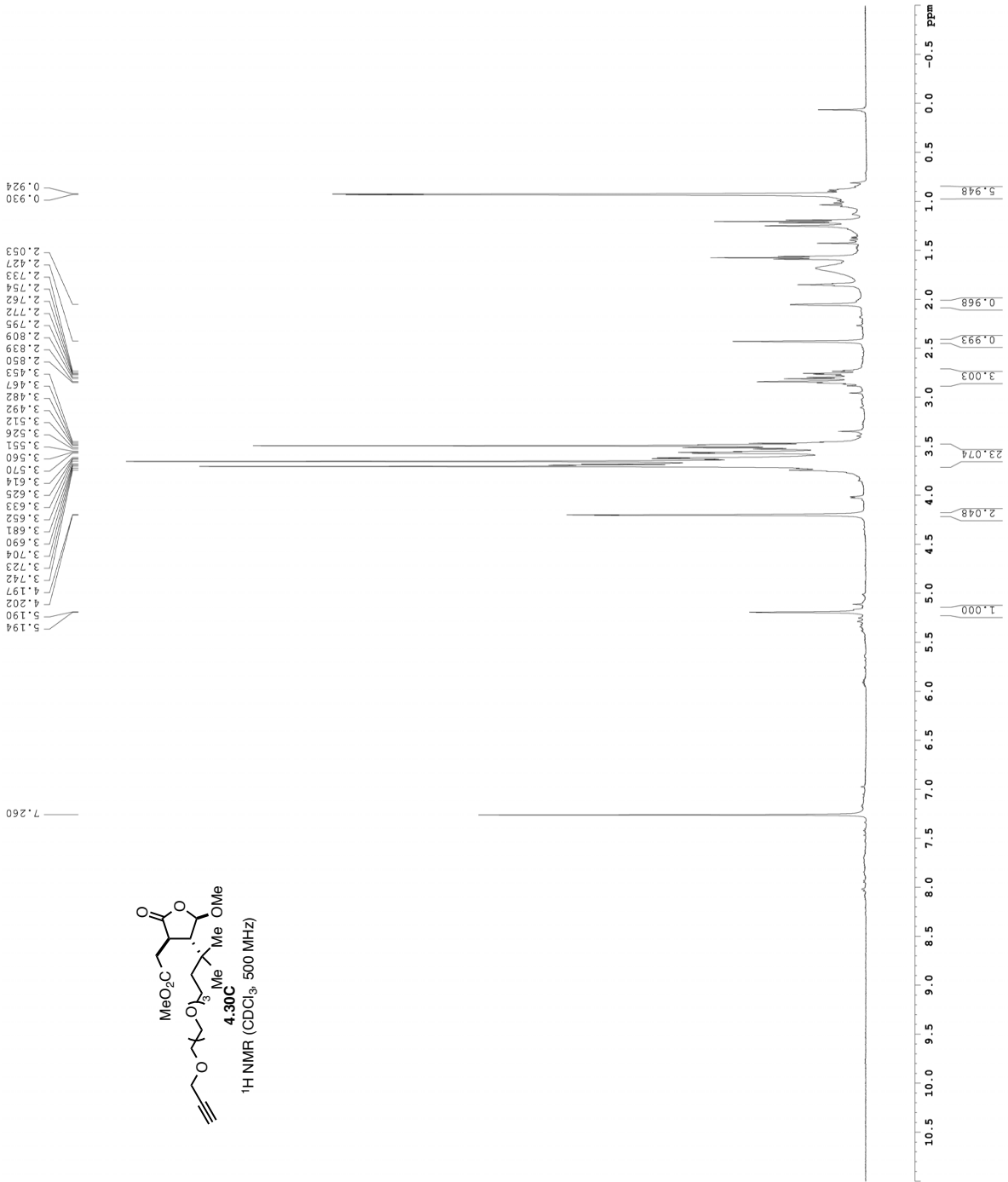
Current Data Parameters
NAME 30B 1H 13C NMR
PROC 1
PROBHD 5 mm CETCI 1H
PULPROG zgpg30
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 3.0399617 sec
RG 51.7
DW 62.400 usec
DE 9.60 usec
TE 298.2 K
D1 0.10000000 sec
MCRESST 0 sec
PCPRG2 0.01500000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 1.00 usec
PL1 1.60 dB
SFO1 500.225015 MHz
===== CHANNEL f2 =====
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

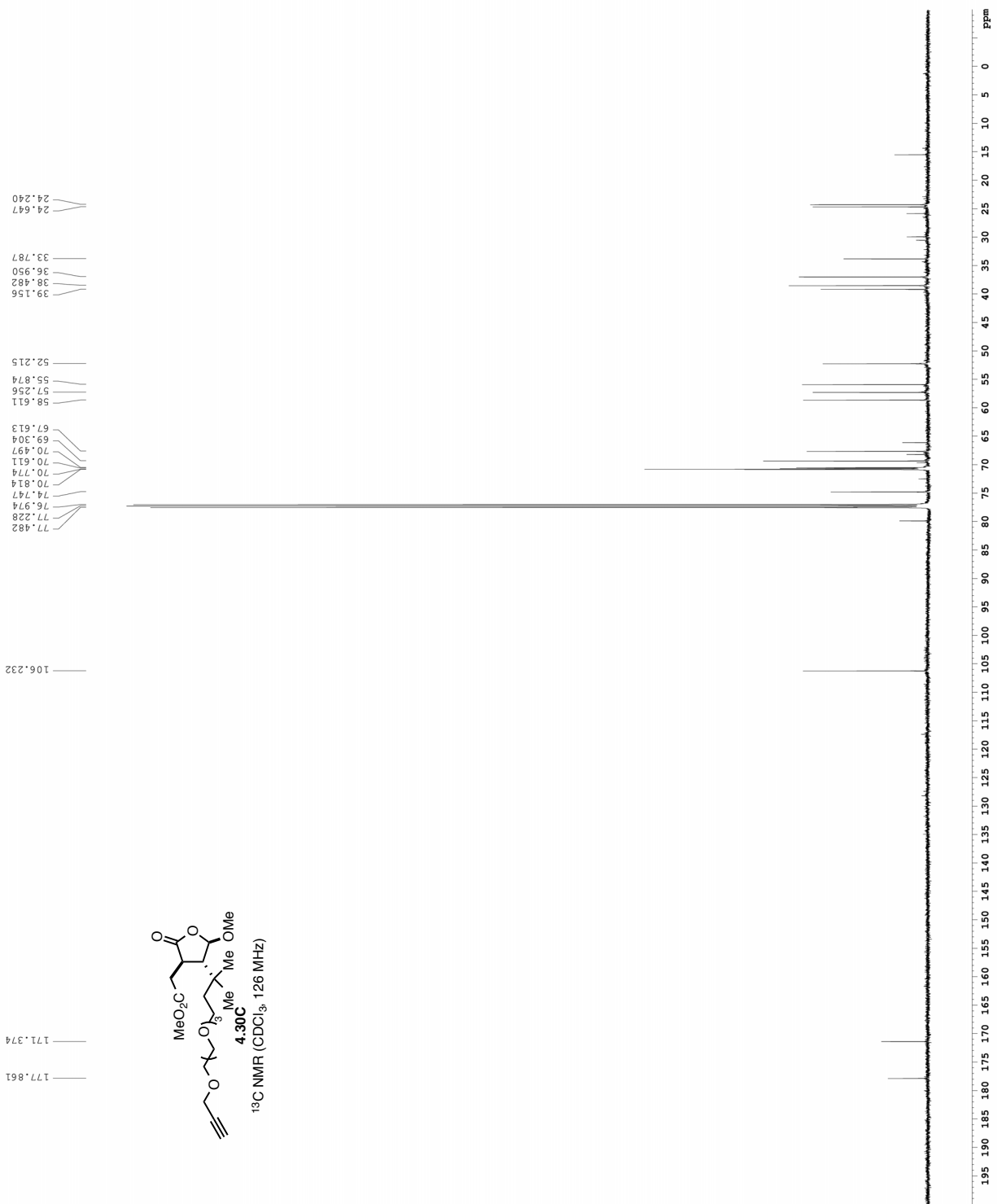


Current Data Parameters
NAME 30C 1H1 613CMR
PROCNO 1
F2 - Acquisition Parameters
Time 20.18.41
INSTRUM cryo500
PROBHD 5 mm CPTCI 420
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
DS 2
SWH 8012.820 Hz
FIDRES 0.0998273 Hz
AQ 5.0998273 sec
RG 4.5
DM 62.400 usec
DE 1.0000000 usec
TE 298.0 K
D1 0.10000000 sec
MCNST 0 sec
MCHRG 0.01500000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PL1 1.60 dB
SFO1 500.225015 MHz
F2 - Processing parameters
SI 65536
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00



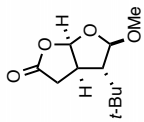
MRG-II-228

Current Date Parameters
NAME 30C IH1 E1SCHNR
EXPNO 6
PROCNO 6
F2 - Acquisition Parameters
Time 20.21
PULPROG 5 mm cpzg3000
FILLPROG Spinechop300p-prd
SOLVENT CDCl3
NS 3000
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
RG 1.000000 sec
RG 728.2
AQ 16.500 usec
SFO 125.761000 MHz
TE 298.0 K
D1 0.25000000 sec
D11 0.00200000 sec
D16 0.00200000 sec
D17 0.00200000 sec
MCORST 0 sec
MCORST 0.00190000 sec
MCORST 0.01500000 sec
F2 Processing Parameters
SI 65536
SF 125.7604001 MHz
WDW 8N
SSB 0
GB 0
PC 2.00

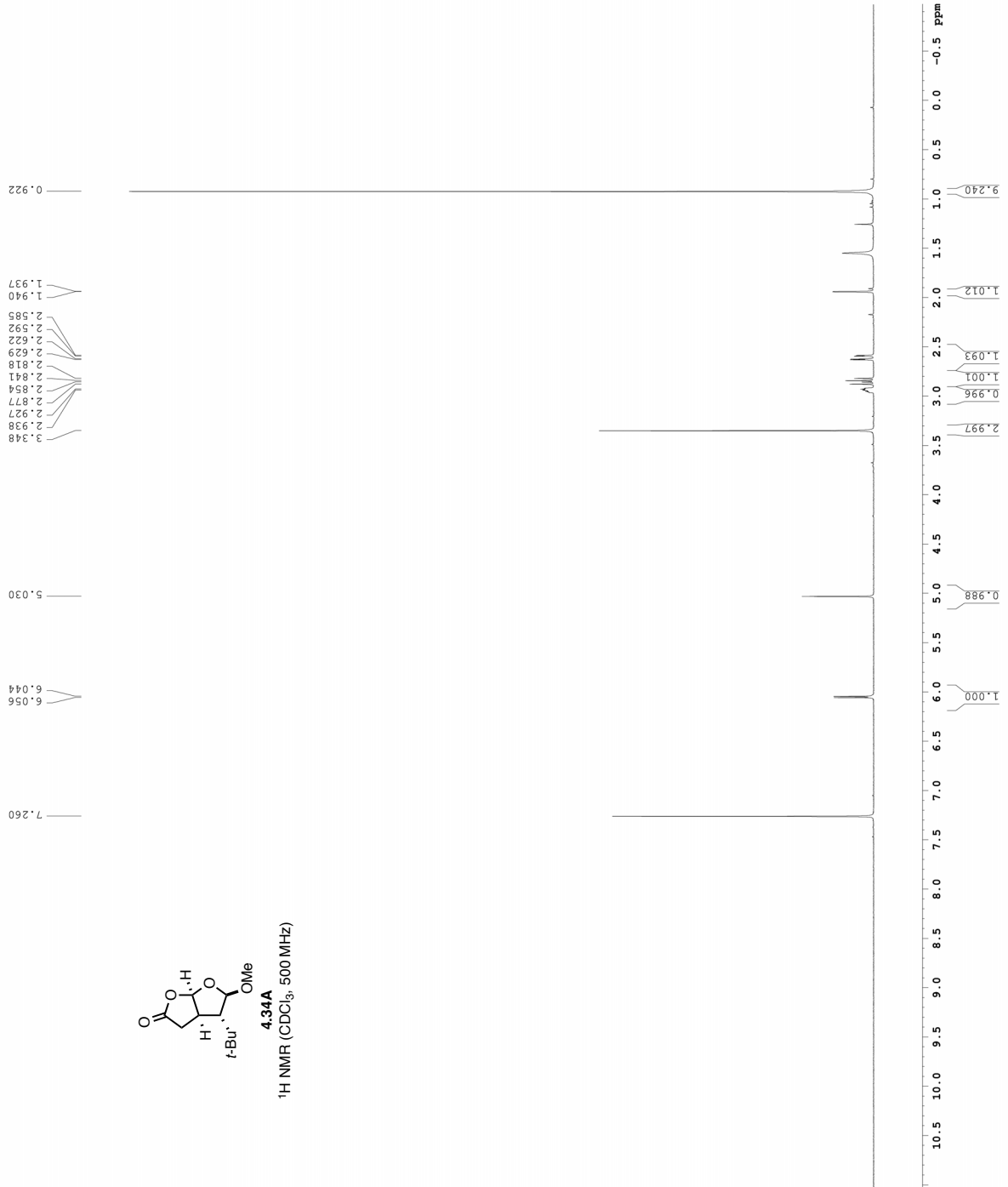


MRG-II-245B

Current Data Parameters
NAME 34A_1HNMR
PROC 1
PRONO 1
F2 - Acquisition Parameters
Time 2011-04-29 14:59
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
NS 2
DS 8
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 0.0200000 sec
RG 1824.6
DM 62.400 usec
DE 296.00 usec
TE 298.2 K
D1 0.10000000 sec
MCREST 0 sec
PCPRG2 0.15000000 sec
===== CHANNEL f1 =====
NUC1 1H
PULPROG zgpg30
PL1 12.70 usec
PL2 5.00 usec
PL3 5.00 dB
SFO1 499.4034956 MHz
F2 - Processing parameters
SI 65536
SF 499.3999765 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



4.34A
1H NMR (CDCl₃, 500 MHz)



MRG-III-33D

Current: Data Parameters
 NAME 34a.13CMB9
 PROCNO 1

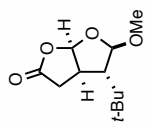
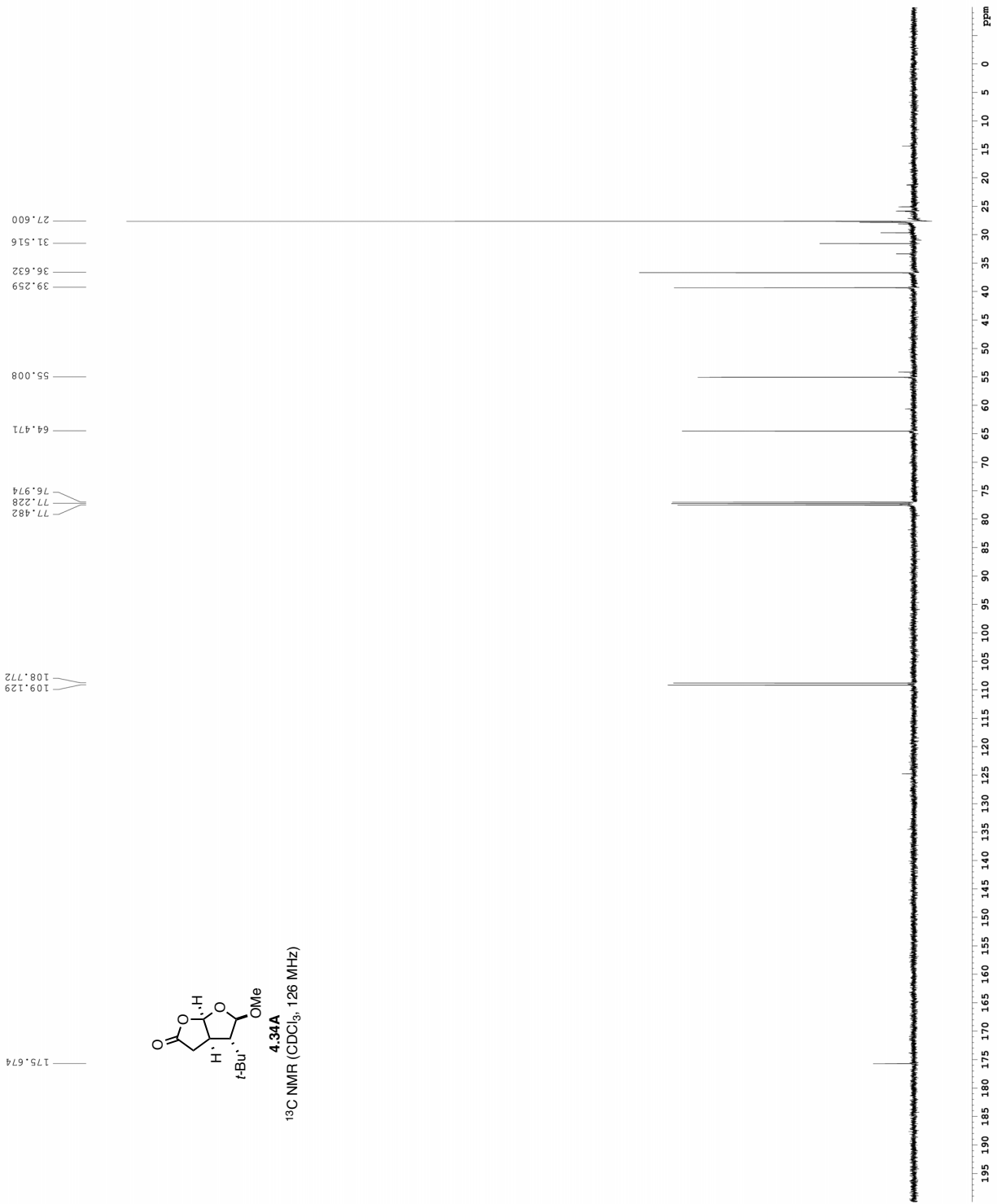
F2 - Acquisition Parameters
 Date_ 20130712
 Time_ 10:05:00
 INSTRUM spect
 PROBHD 5 mm CPYCI 1H-
 TD 65536
 DLPFG0 SpinEcho
 SOLVENT CDCl3
 NS 16
 DS 4
 SWH 30300.000 Hz
 FIDRES 0.338 Hz
 AQRRES 1.0813440 sec
 RG 655.000
 BK 15.500 usec
 DE 6.00 usec
 DI 0.25000000 sec
 d11 0.43000000 sec
 d12 0.00019600 sec
 d17 0.00019600 sec
 MCREST 0 sec
 SFRK 0.01510000 sec
 F2 31.00 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 100.00 usec
 PL1 50.00 usec
 P12 2000.00 usec
 PL12 12.00 dB
 PL0 12.00 dB
 SF01 125.794248 MHz
 SF2 3.200 MHz
 SPNM(f1) Cp60,0.5,20.1
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 NUC2 13C
 P1 100.00 usec
 PL1 50.00 usec
 P12 2000.00 usec
 PL12 12.00 dB
 PL0 12.00 dB
 SF01 125.794248 MHz
 SF2 3.200 MHz
 SPNM(f2) Cp60,0.5,20.1
 SFOFF1 0 Hz
 SFOFF2 0 Hz

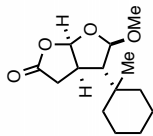
===== GRADIENT CHANNEL =====
 GPMN(f1) SINE-100
 GPMN(f2) SINE-100
 GPX1 0 %
 GPX2 0 %
 GPX3 0 %
 GPX4 0 %
 GPX5 50.00 %
 GPX6 500.00 usec
 p15 1000.00 usec
 p16 1000.00 usec

F2 - Processing parameters
 SI 32768
 SF 125.760411 MHz
 WDW EM
 LB 0
 GB 0
 PC 2.00



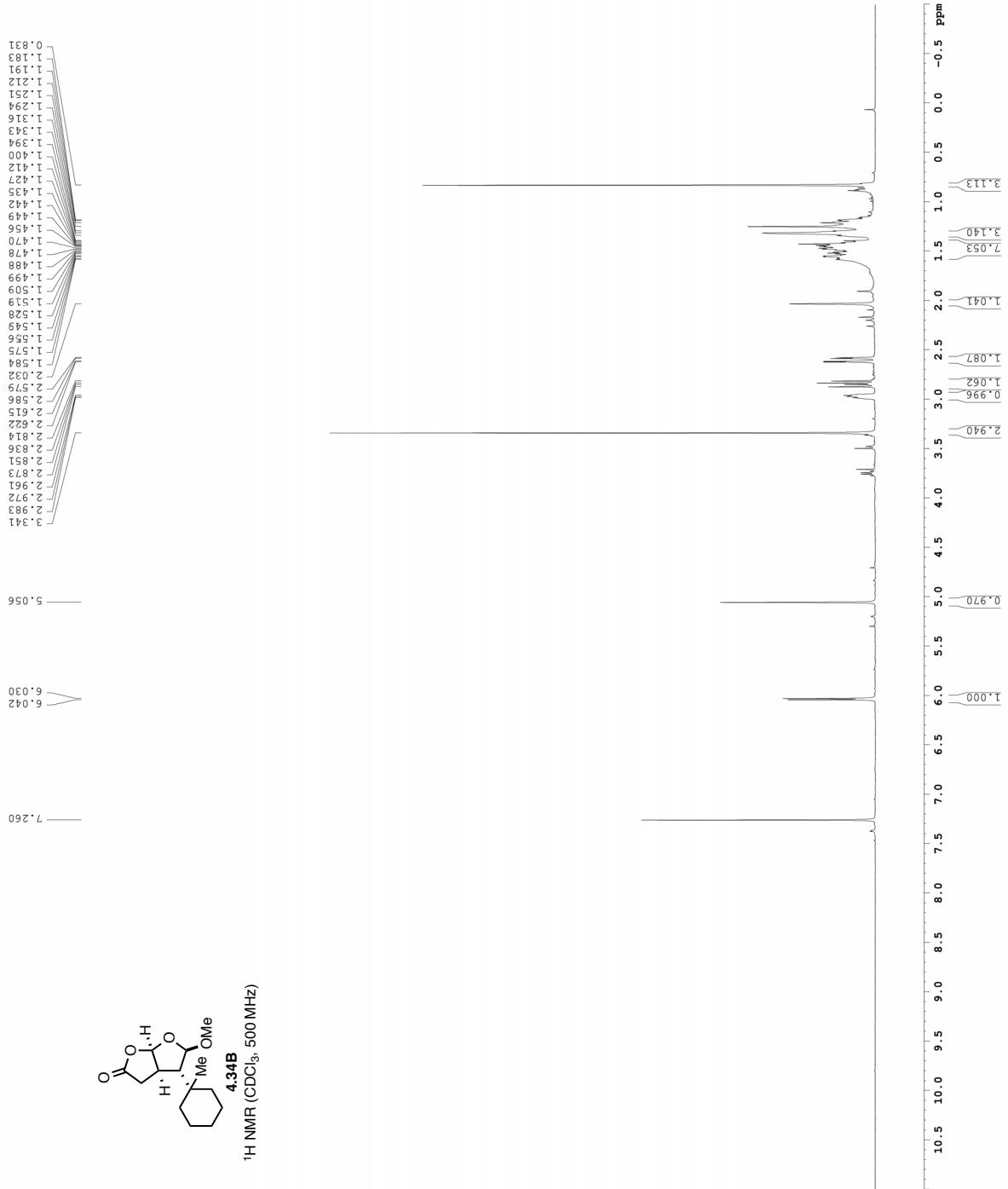
¹³C NMR (CDCl₃, 126 MHz)

MRG-II-139C



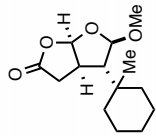
4.34B
¹H NMR (CDCl₃, 500 MHz)

Current Data Parameters
NAME 34B 1H 613CNMR
PROCNO 1
P2 - Acquisition Parameters
Time 2019.152
INSTRUM cryo-500
PROBHD 5 mm CPXI 1H
TD 65536
SOLVENT CDCl3
NS 2
SWH 8012.820 Hz
FIDRES 0.096043 Hz
RG 3.093971 sec
AQ 7.1 sec
DM 62.400 usec
DE 296.00 usec
TE 298.2 K
D1 0.10000000 sec
MCREST 0 sec
PCPRG 0.15000000 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

175.63



4.34B
¹³C NMR (CDCl₃, 126 MHz)

109.226
108.388

77.482
77.228
76.974

55.070

38.433
36.828
35.902
35.746
33.976

26.262
21.707
21.690
20.879

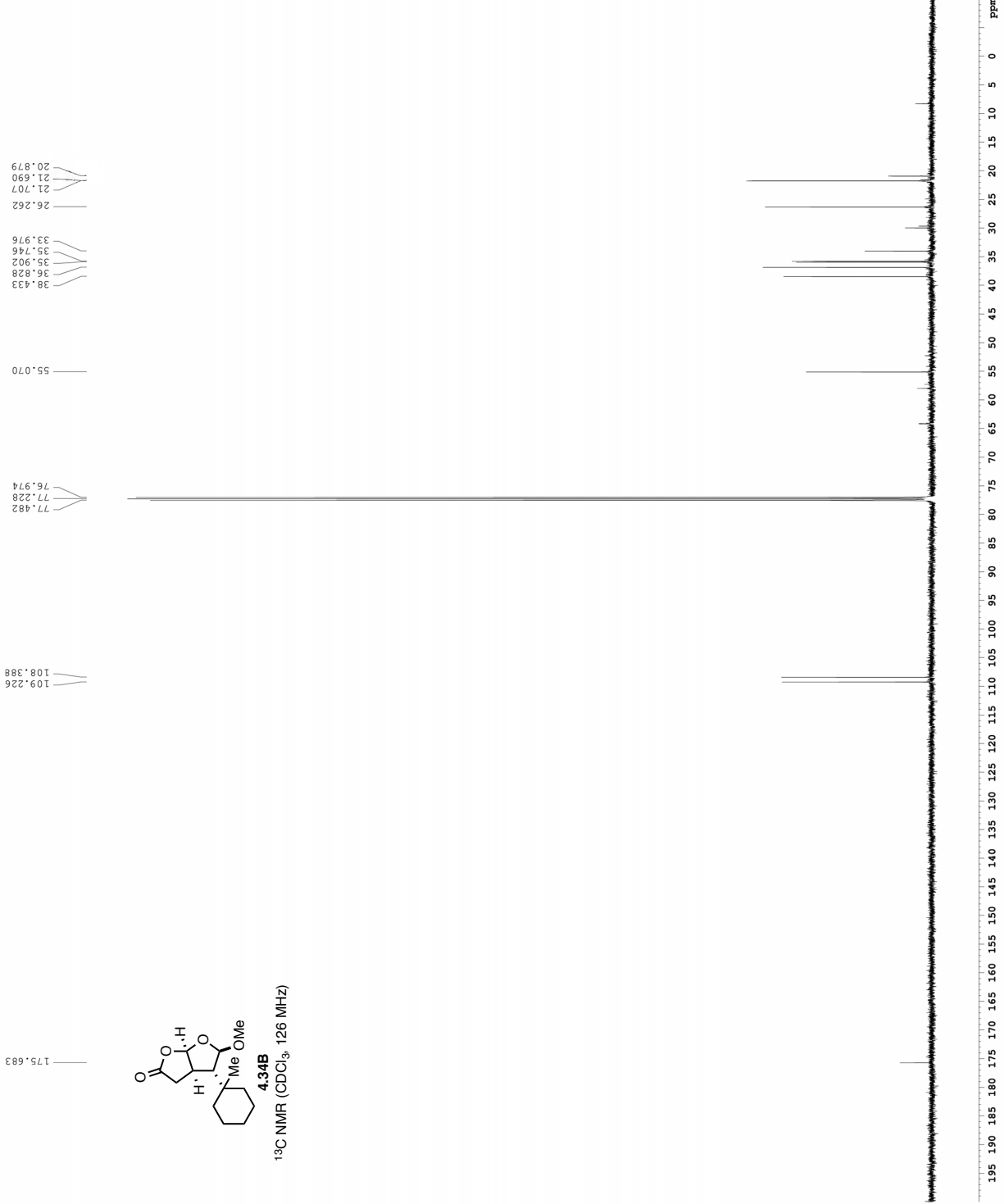
```

Current Data Parameters
NAME      MRG-II-139C
EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Time     2019-07-19 19:47
INSTRUM  spect
PULPROG  zgpg30
SOLVENT  CDCl3
NS       64
DS       4
SWH      30300.031 Hz
FIDRES   0.462288 Hz
AQ       1.228603 sec
RG        256
DM       16.500 usec
TE        298.0 K
D1       0.2500000 sec
D11      0.0002000 sec
D16      0.0002000 sec
MCWREST  0
MCWRRK   0.0150000 sec
F2

===== CHANNEL f1 =====
NUC1      13C
P1        15.50 usec
PL1       0.00 dB
PL12      120.00 dB
PL13      120.00 dB
PL14      120.00 dB
PL15      120.00 dB
PL16      120.00 dB
PL17      120.00 dB
PL18      120.00 dB
PL19      120.00 dB
PL20      120.00 dB
PL21      120.00 dB
PL22      120.00 dB
PL23      120.00 dB
PL24      120.00 dB
PL25      120.00 dB
PL26      120.00 dB
PL27      120.00 dB
PL28      120.00 dB
PL29      120.00 dB
PL30      120.00 dB
PL31      120.00 dB
PL32      120.00 dB
PL33      120.00 dB
PL34      120.00 dB
PL35      120.00 dB
PL36      120.00 dB
PL37      120.00 dB
PL38      120.00 dB
PL39      120.00 dB
PL40      120.00 dB
PL41      120.00 dB
PL42      120.00 dB
PL43      120.00 dB
PL44      120.00 dB
PL45      120.00 dB
PL46      120.00 dB
PL47      120.00 dB
PL48      120.00 dB
PL49      120.00 dB
PL50      120.00 dB
PL51      120.00 dB
PL52      120.00 dB
PL53      120.00 dB
PL54      120.00 dB
PL55      120.00 dB
PL56      120.00 dB
PL57      120.00 dB
PL58      120.00 dB
PL59      120.00 dB
PL60      120.00 dB
PL61      120.00 dB
PL62      120.00 dB
PL63      120.00 dB
PL64      120.00 dB
PL65      120.00 dB
PL66      120.00 dB
PL67      120.00 dB
PL68      120.00 dB
PL69      120.00 dB
PL70      120.00 dB
PL71      120.00 dB
PL72      120.00 dB
PL73      120.00 dB
PL74      120.00 dB
PL75      120.00 dB
PL76      120.00 dB
PL77      120.00 dB
PL78      120.00 dB
PL79      120.00 dB
PL80      120.00 dB
PL81      120.00 dB
PL82      120.00 dB
PL83      120.00 dB
PL84      120.00 dB
PL85      120.00 dB
PL86      120.00 dB
PL87      120.00 dB
PL88      120.00 dB
PL89      120.00 dB
PL90      120.00 dB
PL91      120.00 dB
PL92      120.00 dB
PL93      120.00 dB
PL94      120.00 dB
PL95      120.00 dB
PL96      120.00 dB
PL97      120.00 dB
PL98      120.00 dB
PL99      120.00 dB
PL100     120.00 dB
===== CHANNEL f2 =====
NAME      MRG-II-139C
EXPNO    3
PROCNO   1

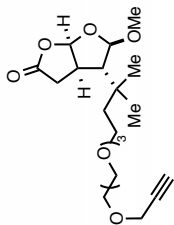
F2 - Processing Parameters
SI        65536
SF        125.7603937 MHz
WDW       EM
SSB       0
GB        0
PC        2.00
  
```



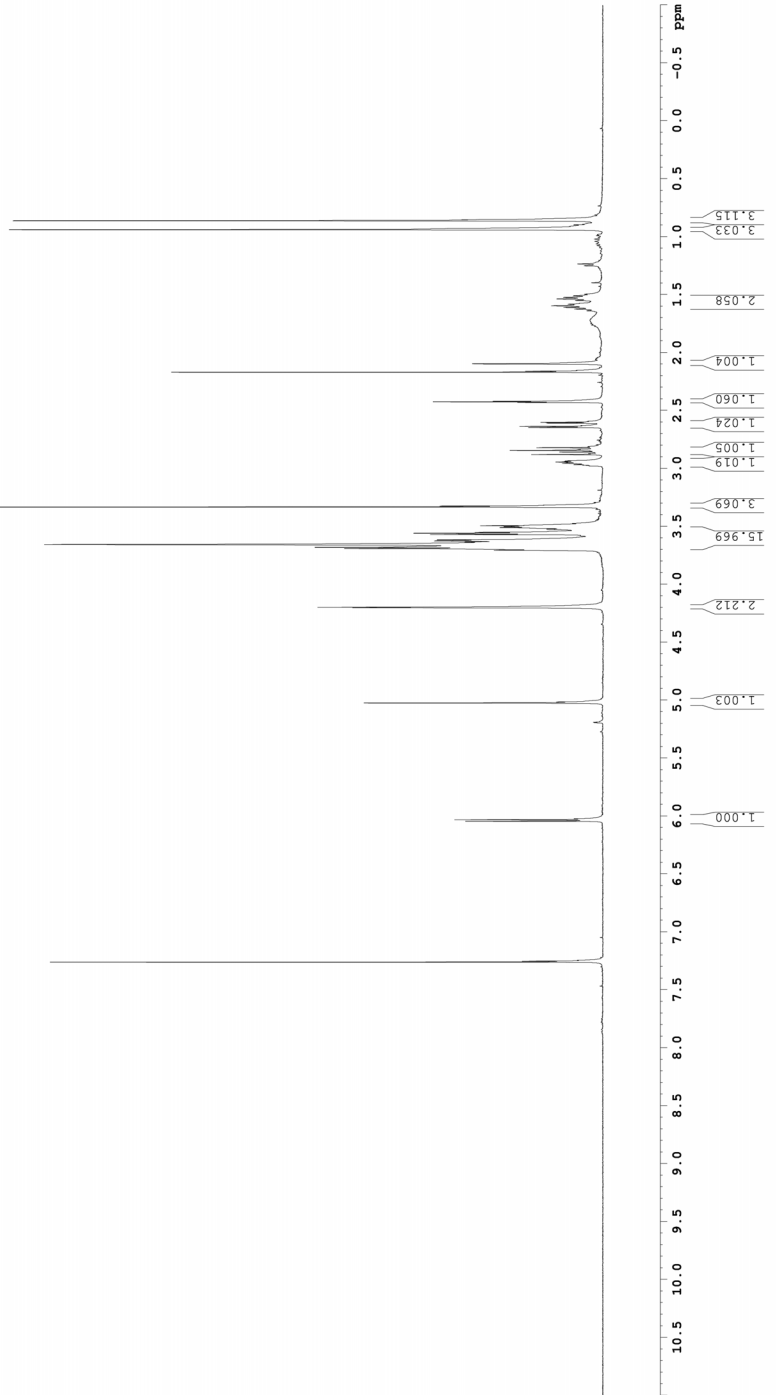
MRG-II-280B

Current Data Parameters
NAME 34C 1H1 c13CNMR
PROCNO 1
P2 - Acquisition Parameters
Time 2018.32
INSTRUM cryo-500
PROBHD 5 mm CPFI1 1H
TD 65536
SOLVENT CDCl3
NS 8
SWH 8012.820 Hz
FIDRES 0.096043 Hz
AQ 3.0939617 sec
RG 5.7
DM 62.400 usec
DE 296.00 usec
D1 0.10000000 sec
MCREST 0 sec
PCPRG 0.01500000 sec
CHANNEL f1
NUC1 13C
PULPROG zgpg30
FL1 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

7.260
7.251
6.043
6.031
5.023
5.015
4.201
4.197
3.705
3.689
3.681
3.655
3.634
3.625
3.615
3.569
3.558
3.550
3.523
3.509
3.493
3.473
3.323
3.322
2.955
2.943
2.939
2.935
2.919
2.879
2.857
2.843
2.820
2.645
2.637
2.608
2.600
2.429
2.424
2.413
2.200
1.995
1.609
1.595
1.581
1.536
1.522
1.508
0.938
0.861
0.852

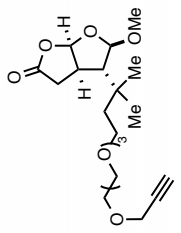
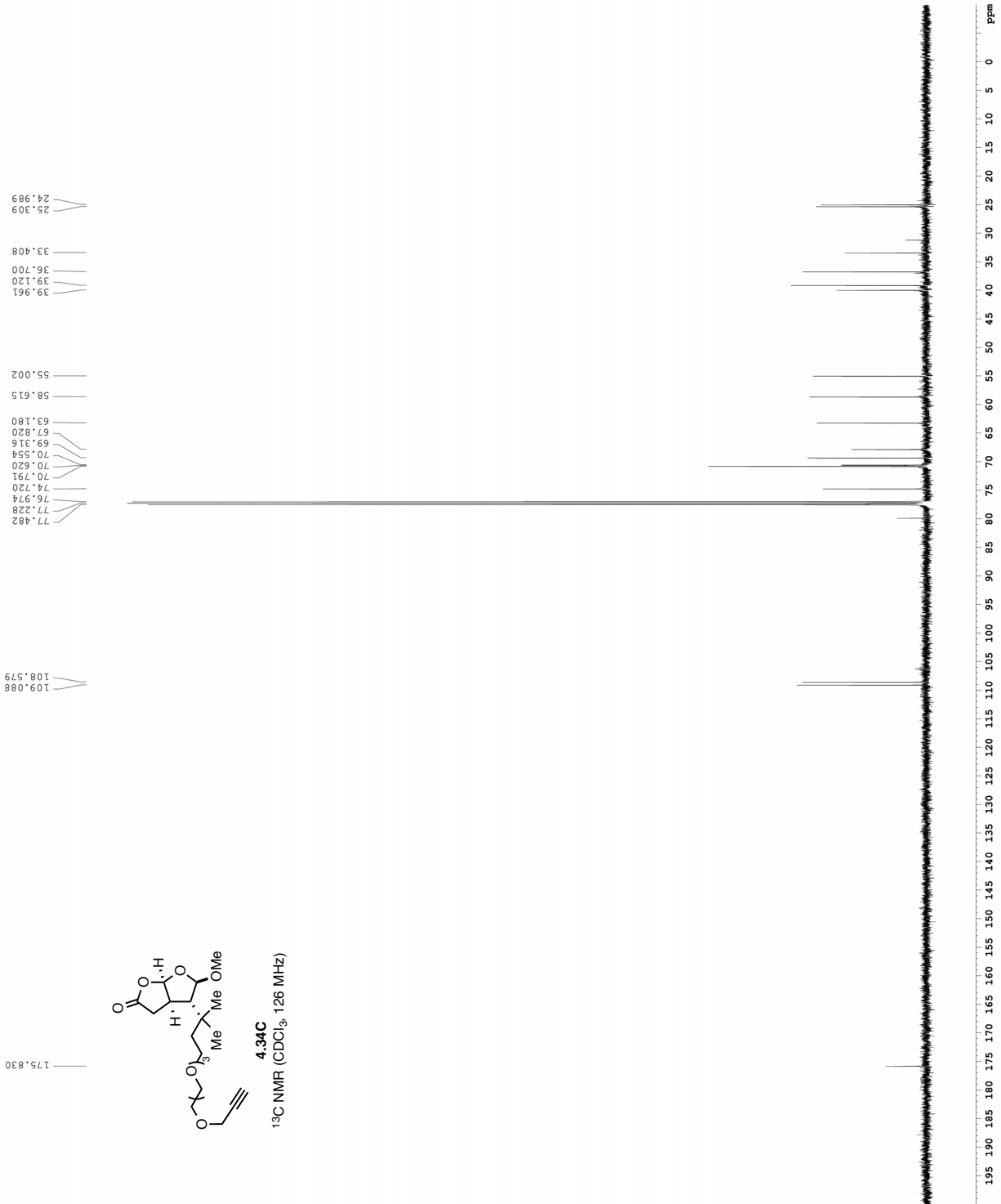


4.34C
1H NMR (CDCl₃, 500 MHz)



MRG-II-280B

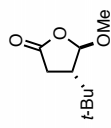
Current Date Parameters
NAME 34C IH1 E1SCHRR
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110926
Time 19:26
INSTRUM 5 mm CPY130QD
PULPROG Spinchop30p-prd
SOLVENT CDCl3
NS 1024
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
RG 1.000000 sec
AQ 7298.2
SFO4 500.225011 MHz
WDW 16.500 usec
SSB 298.0 KHz
TE 300.2 K
D1 0.25000000 sec
D16 0.00020000 sec
D17 0.00020000 sec
D18 0.00020000 sec
D19 0.00020000 sec
D20 0.00020000 sec
MCORST 0 sec
MCORST 0.01500000 sec
F2 Processing Parameters
SI 65536
SF 125.7603933 MHz
WDW 64
SSB 0
GB 0
PC 2.00



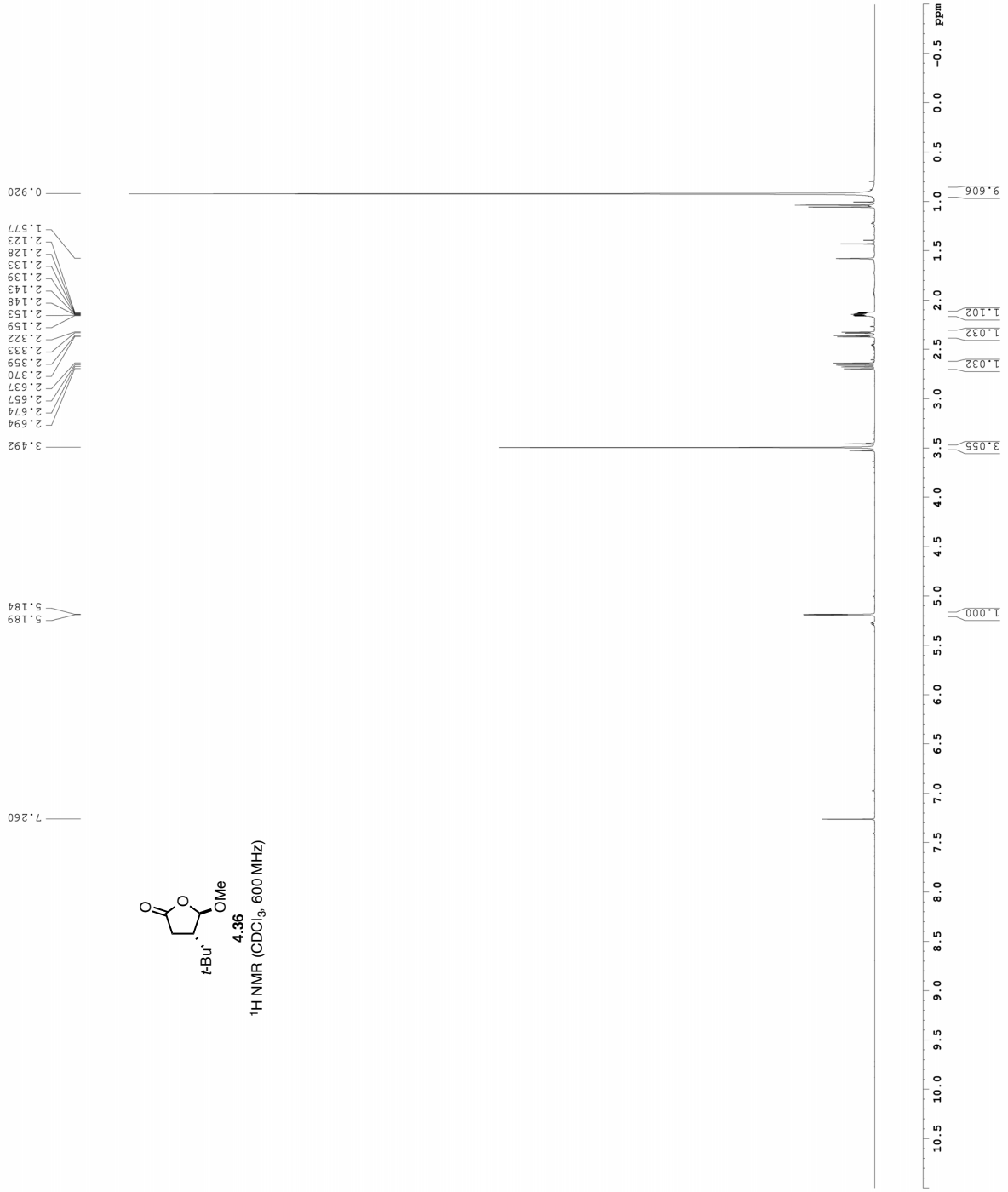
4.34C
13C NMR (CDCl3, 126 MHz)

YS-VI-28

Current Data Parameters
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170804
Time 12.22
PROBHD 5 mm CPYHC-1H
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 2
AQ 0.250026 Hz
FIDRES 1.9997952 sec
RG 62
DE 6.00 usec
TE 298.0 K
MCREST 0 sec
MCWRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL 0.00 dB
SFO1 500.2253515 MHz
F2 - Processing parameters
SF 500.220312 MHz
WDW EM
SSB 0
GB 0
PC 1.00

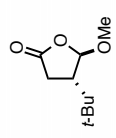
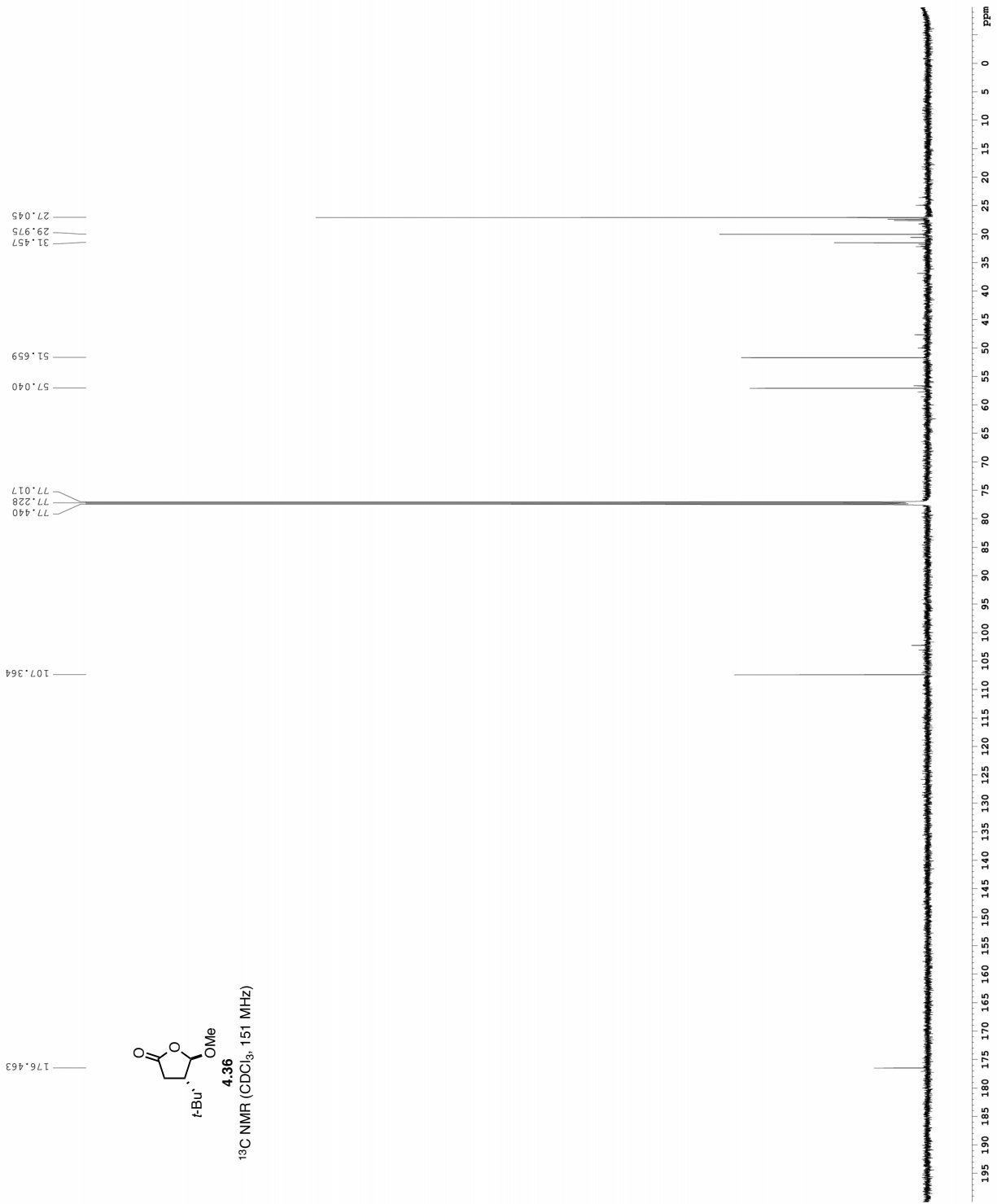


¹H NMR (CDCl₃, 600 MHz)



YS-VI-28

Current Data Parameters
NAME YS-VI-28
PROCNO 1
F2 - Acquisition Parameters
Time 2016.49
INSTRUM av600
PULPROG zgpg30
SOLVENT CDCl3
NS 1691
SRH 36231.883 Hz
FIDRES 0.52852 Hz
AQ 0.22878 sec
RG 272.00
DM 13.800 usec
TE 298.20 K
D1 0.4000001 sec
D11 0.15500001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.919480 MHz
NUC1 13C
P1 10.00 usec
PL1 64.00000000 N
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
CPDPRG2 waltz16
PCPD2 80.00 usec
PL2 20.00000000 W
PLM12 0.36000001 W
F2 - Processing parameters
SI 65536
SF 150.902782 MHz
WDW 0
SSB 0
GB 0
PC 1.00



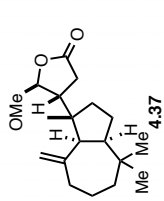
4.36
13C NMR (CDCl₃, 151 MHz)

MRG-III-177E

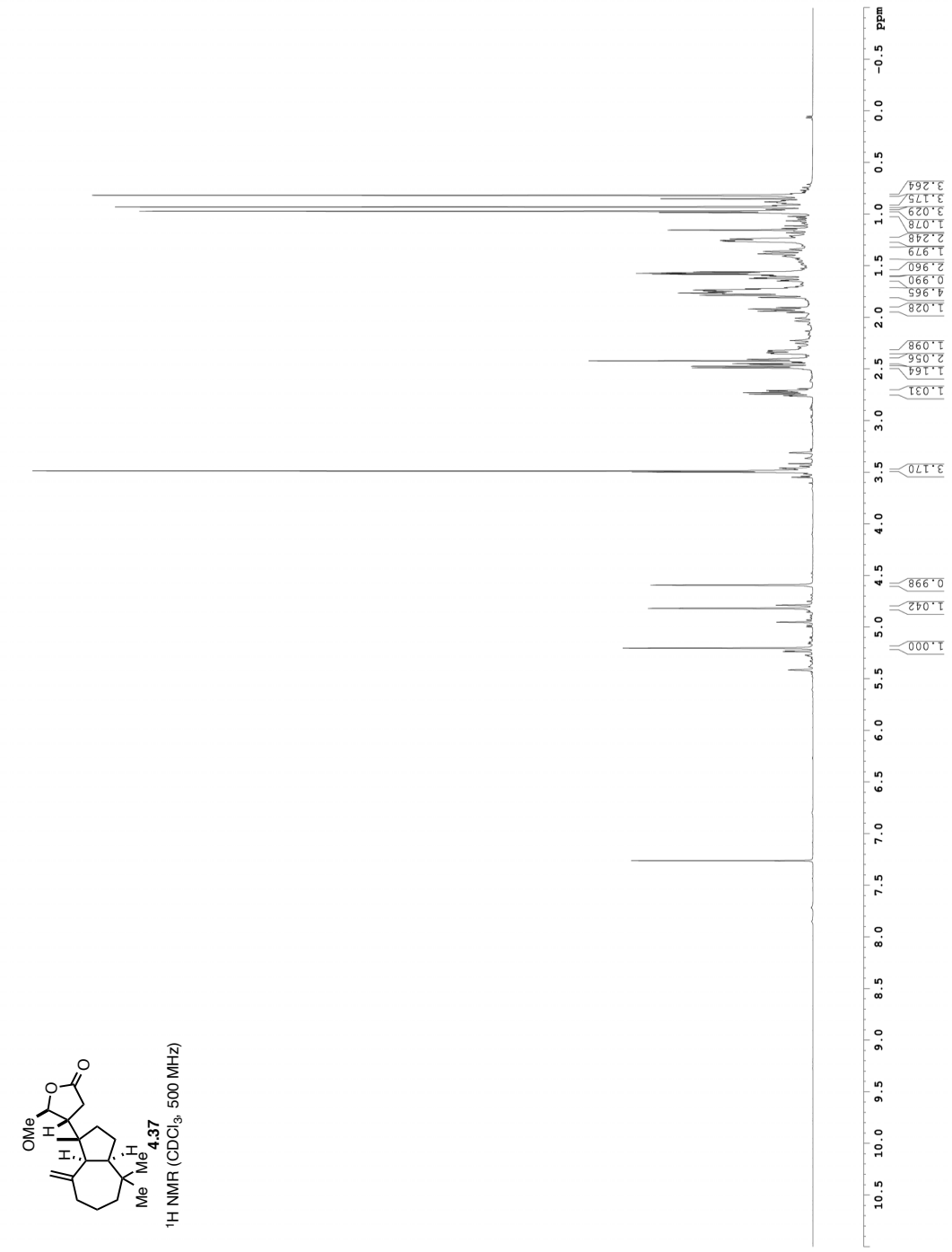
Current Data Parameters
NAME: 37_AHNS2
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20140116
Time: 11:01
INSTRUM: spect
PROBHD: 5 mm TBI IH/13
PULPROG: zg30
AQ: 0.098478 sec
SOLVENT: CDCl3
NS: 8
DS: 9615.382 Hz
FIDRES: 0.098478 Hz
AQ: 0.098478 sec
RG: 327.500 usec
DE: 14.54 usec
TE: 296.1 K
TD0: 0.10000001
===== CHANNEL f1 =====
SFO1: 600.132003 MHz
NUC1: 1H
P1: 8.00 usec
PL1: 23.0141556 W
===== F2 - Processing parameters =====
SI: 327.500 usec
SF: 600.1300354 MHz
WDW: EM
SSB: 0
GB: 0
PC: 1.00

0.969
1.238
1.253
1.261
1.360
1.382
1.557
1.567
1.581
1.592
1.598
1.615
1.622
1.638
1.645
1.721
1.733
1.742
1.753
1.753
1.762
1.768
1.783
1.804
1.903
1.917
1.931
1.937
1.950
2.320
2.327
2.341
2.349
2.400
2.404
2.406
2.419
2.446
2.453
2.472
2.486
2.707
2.713
2.719
2.727
2.741
2.755
2.761
3.485
4.591
4.817
5.202

7.260



¹H NMR (CDCl₃, 500 MHz)



MRG-III-173B

Current Data Parameters
 NAME 37 13CNR5
 EXRNO 5
 PROCNO 1

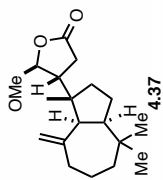
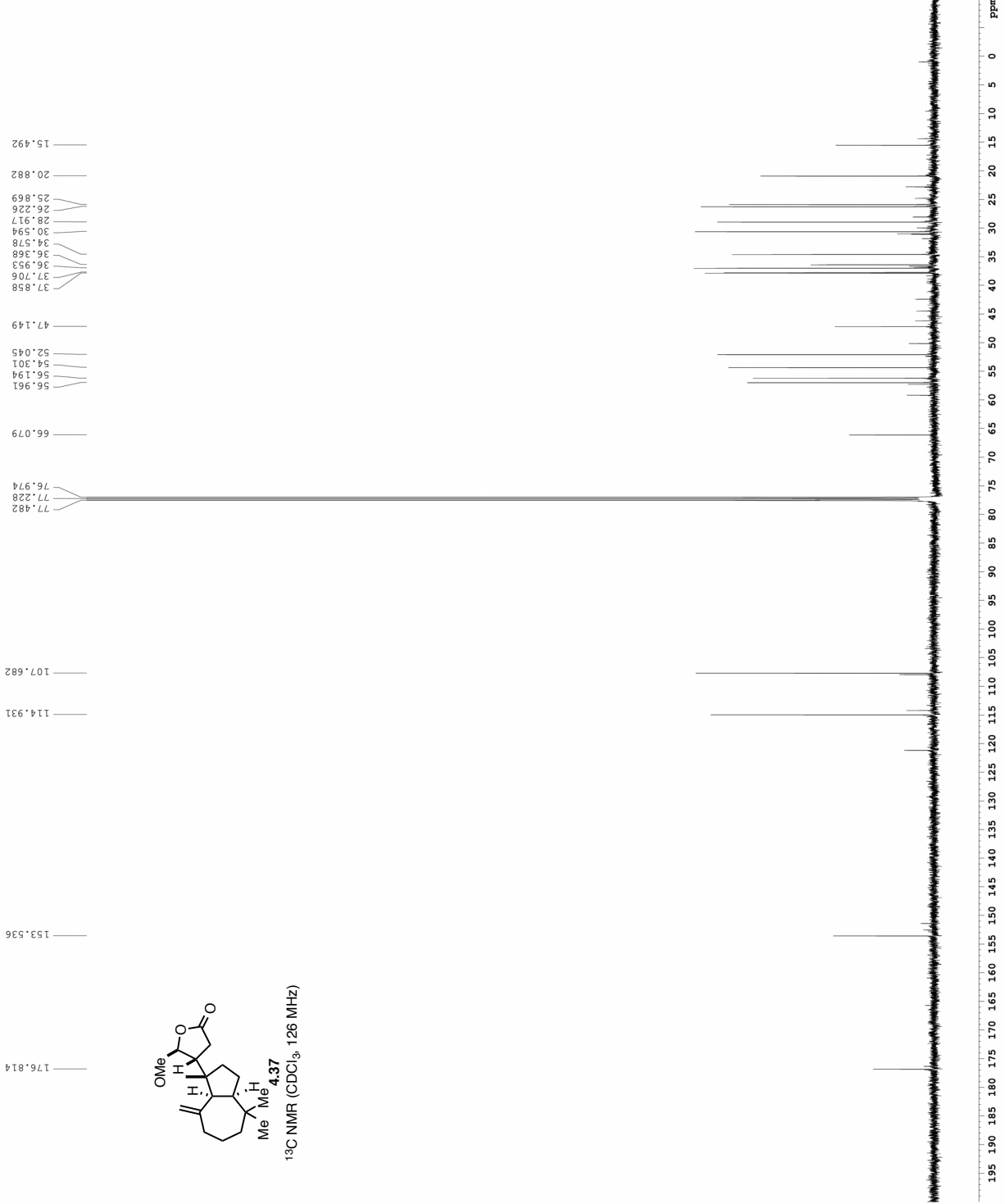
F2 - Acquisition Parameters
 Time 20.155
 INSTRON cryo-50
 PULPROG SpinEcho30pp-prd
 SOLVENT CDCl3
 NS 1620
 SRH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 7298.2 sec
 DM 16.500 usec
 TE 298.0 K
 D11 0.2500000 sec
 D16 0.0002000 sec
 MCOREST 0 sec
 MCORRK 0.01500000 sec
 F2 31.00 usec

===== CHANNEL f1 =====
 P1C1 15.50 usec
 P11 500.00 usec
 P12 120.00 usec
 PLO 120.00 dB
 FLD1 125.792500 dB
 SP1 3.20 dB
 SFOF1 0 Hz
 SFOF2 0 Hz

===== CHANNEL f2 =====
 CFPFG12 waltz16
 NUC2 100.1H
 P12 100.1H usec
 P12 1.60 dB
 SFO2 500.225311 MHz

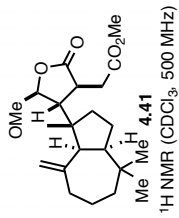
===== GRADIENT CHANNEL =====
 GPNM1(1) SINE.100
 GPNM2(2) SINE.100
 GPXZ 0 %
 GPFY1 0 %
 GPFY2 0 %
 GPFZ1 0 %
 GPFZ2 0 %
 P16 30.00 %
 P16 50.00 %
 P16 1000.00 usec

F2 - Processing Parameters
 SF 125.760393 MHz
 SSB 0
 GB 0
 PC 2.00

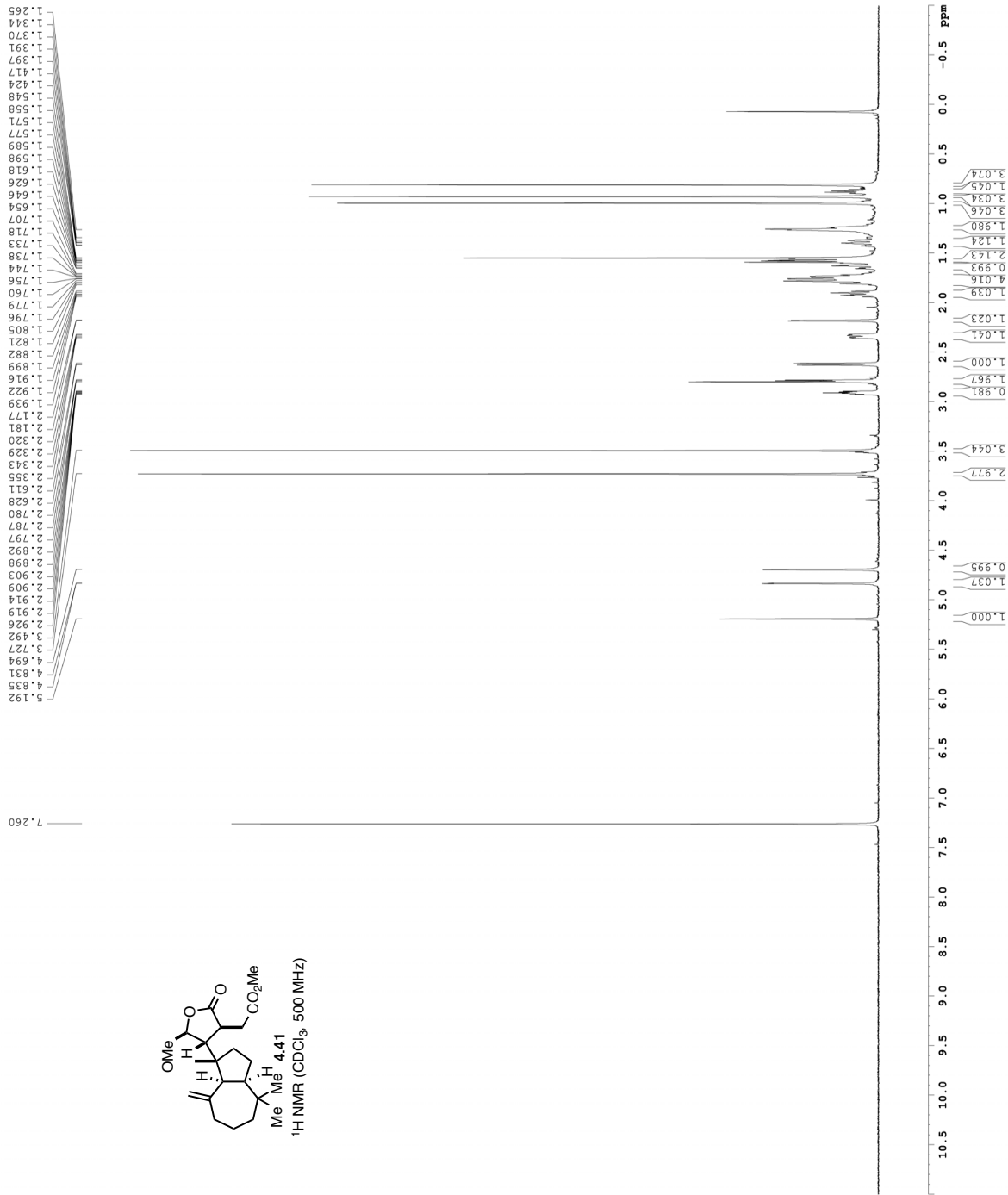


¹³C NMR (CDCl₃, 126 MHz)

MRG-III-174B



Current Data Parameters
NAME 41_1HNMR
PROCNO 1
F2 - Acquisition Parameters
Time 2.00
Time 15.33
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgpg30
ID 81728
SOLVENT CDCl3
DS 2
SWH 8012.820 Hz
FIDRES 0.0998273 Hz
AQ 5.0098273 sec
RG 1.44812 sec
DM 62.4100 usec
DE 1.9000 usec
TE 298.0 K
D1 0.10000000 sec
MKREST 0 sec
MKRES 0.01500000 sec
===== CHANNEL f1 =====
NUC1 12.00 usec
P1 12.00 usec
PL1 -5.00 dB
SFO1 499.2934950 MHz
F2 - Processing parameters
SI 65536
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



MRG-III-180B

Current Data Parameters
 NAME 41 13CNR5
 EXPRNO 5
 PROCNO 1

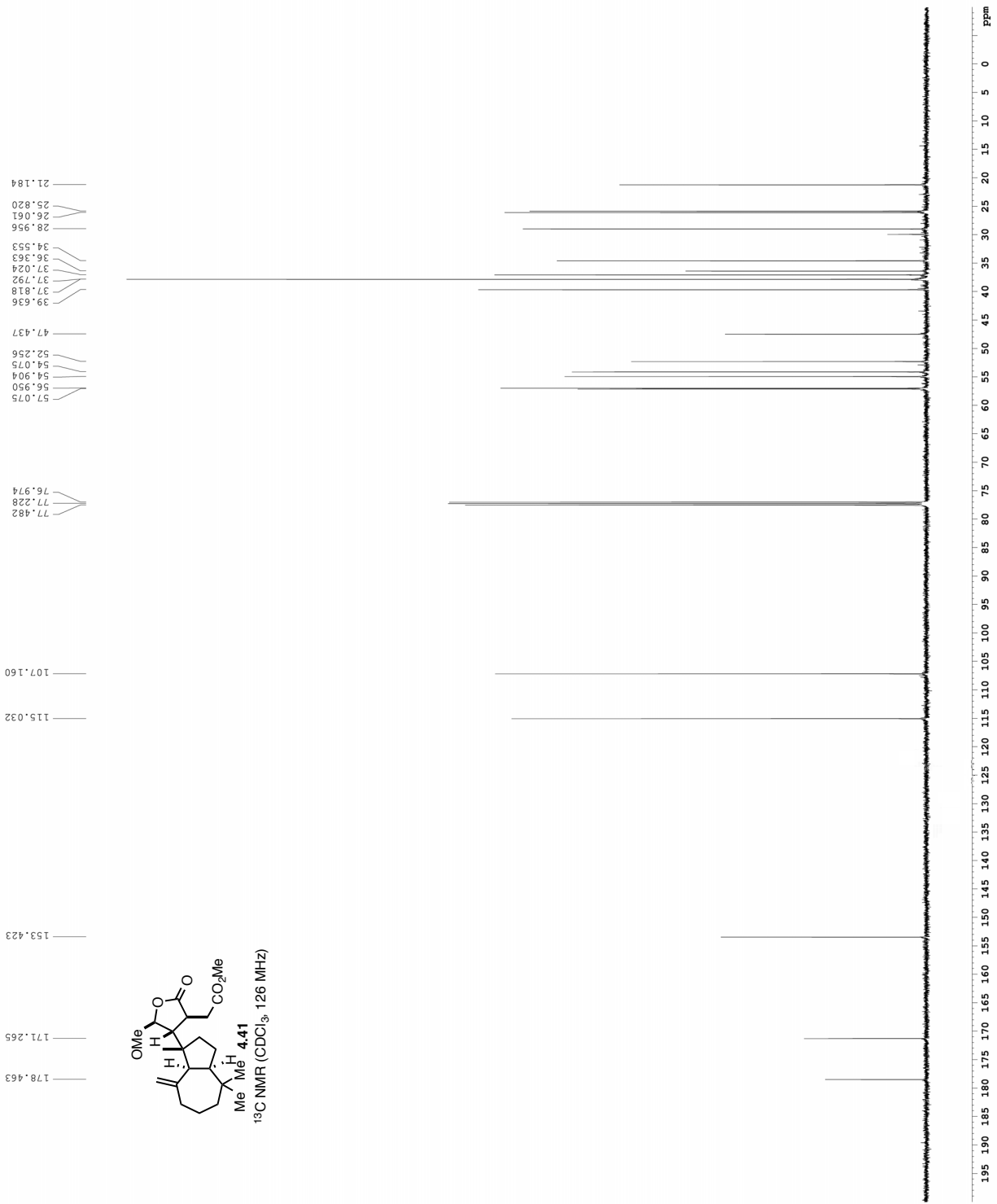
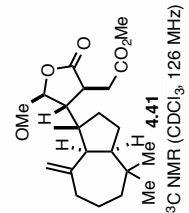
F2 - Acquisition Parameters
 Time 20110711 11:57
 INSTRON cryo-500
 PULPROG zgpg30
 SOLVENT CDCl3
 NS 1147
 SRH 30300.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.729842 sec
 RG 729842
 DM 16.500 usec
 TE 298.0 K
 D11 0.2500000 sec
 D16 0.0002000 sec
 MCOREST 0
 MCORRK 0.0150000 sec
 F2 31.00 usec

===== CHANNEL f1 =====
 P1C1 15.50 usec
 P1L1 500.00 usec
 P1F1 120.00 dB
 P1D1 120.00 usec
 P1E1 120.00 dB
 P1S1 125.791500 dBz
 SP1 3.20 dBz
 SPNAM(1) Cry60.0.5.20.3
 SPNAM(2) Cry60comp-4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

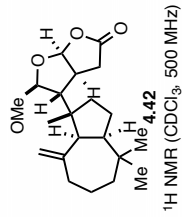
===== CHANNEL f2 =====
 CFPFG12 wait+16
 NUC2 100.1H
 P1L2 100.1H usec
 P1F2 1.60 dB
 P1D2 120.00 usec
 P1E2 120.00 dB
 P1S2 500.225501 dBz
 SP2 3.20 dBz

===== GRADIENT CHANNEL =====
 GPNAM(1) SINE.100
 GPNAM(2) SINE.100
 GPX1 0 %
 GPX2 0 %
 GPF1 0 %
 GPF2 0 %
 GPT1 30.00 %
 GPT2 50.00 %
 P16 1000.00 usec
 P17 1000.00 usec

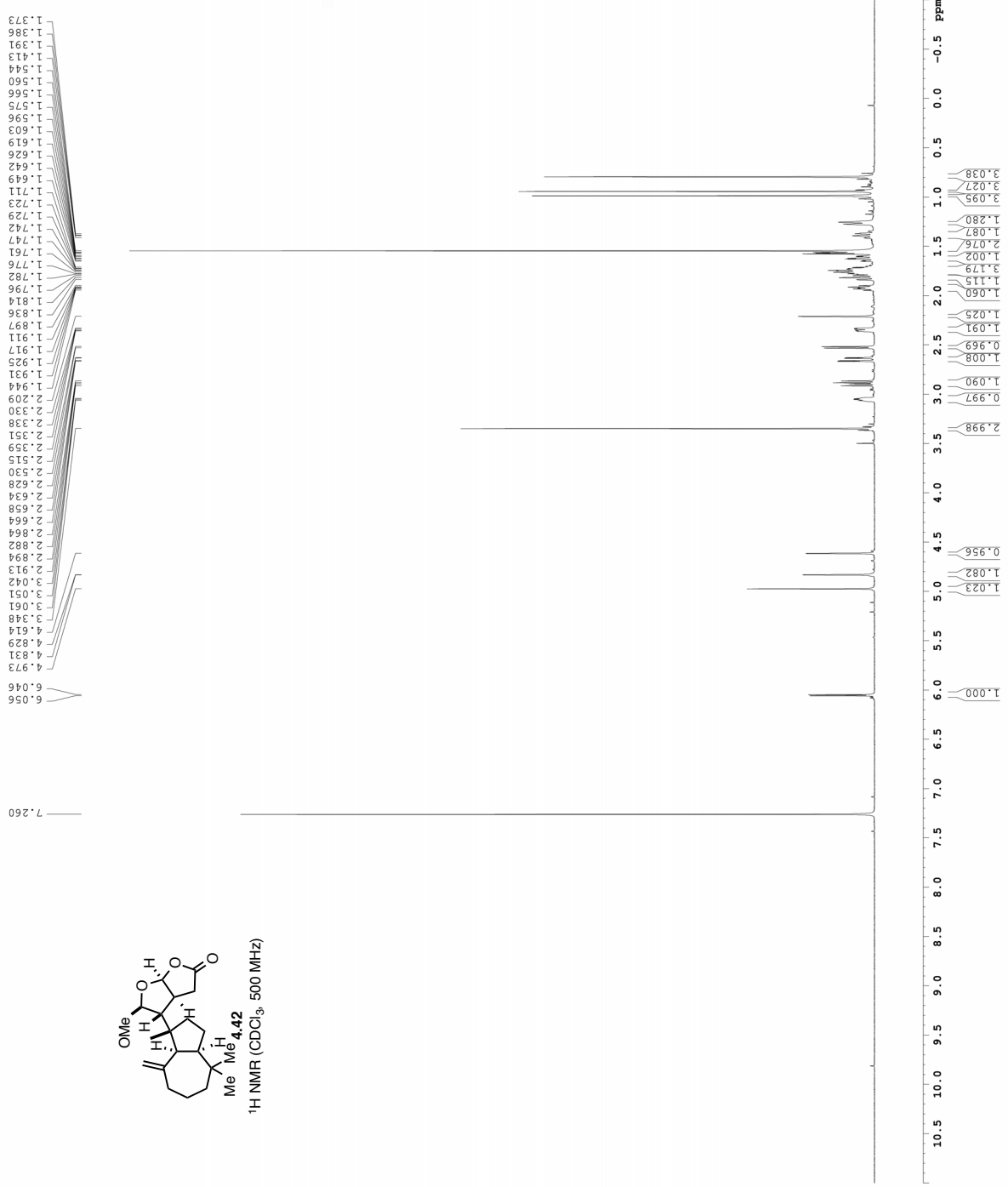
F2 - Processing Parameters
 S1 45336
 SF 125.7604007 MHz
 SSB 0
 GB 1.00 Hz
 PC 2.00



MRG-III-182D



Current Data Parameters
NAME 42 1HNMR
PROCNO 1
F2 - Acquisition Parameters
Time 20111154
INSTRUM AV600
PROBHD 5 mm TBI IH/13
TDPRG 98874
SOLVENT CDCl3
RS 2
SMH 9615.385 Hz
FIDRES 0.096042 Hz
RG 3.0929812 sec
RG 512
DM 52.000 usec
DE 298.15 K usec
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.1342003 MHz
NUC1 13C
FLM1 23.01441956 W
F2 - Processing parameters
SI 65534
SF 600.1300346 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



MRG-III-182D

Current Data Parameters
 NAME 42 13CNR5
 EXPRNO 3
 PROCNO 1

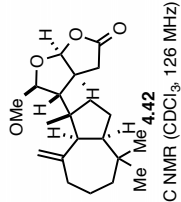
F2 - Acquisition Parameters
 Date_ 20120712
 Time 12:52
 INSTRON cryo-500
 PULPROG zgpg30
 SOLVENT CDCl3
 NS 1183
 SRH 30300.031 Hz
 FIDRES 0.462388 Hz
 RG 4096
 DW 16.500 usec
 TE 298.0 K
 D1 0.2500000 sec
 D11 0.0002000 sec
 D16 0.0002000 sec
 MCOREST 0 sec
 MCWRRK 0.0150000 sec
 F2 31.00 usec

===== CHANNEL f1 =====
 P1C1 15.50 usec
 P11 500.00 usec
 P12 1.60 dB
 PLO 120.00 dB
 P13 125.791500 dB
 SP1 3.20 dB
 SP1AM(1) Crp50.0.5.20.0
 SP1AM(2) Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

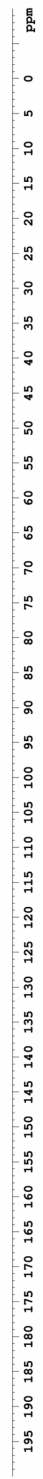
===== CHANNEL f2 =====
 CFPFRG12 wait.216
 NUC2 100.1H
 P12 1.60 dB
 P13 24.60 dB
 SFO2 500.225511 MHz

===== GRADIENT CHANNEL =====
 GPNAM(1) SINE.100
 GPCX 0 %
 GPF1 0 %
 GPF2 0 %
 GPF3 0 %
 GPF4 0 %
 GPF5 0 %
 GPF6 0 %
 GPF7 0 %
 GPF8 0 %
 GPF9 0 %
 GPF10 0 %
 GPF11 0 %
 GPF12 0 %
 GPF13 0 %
 GPF14 0 %
 GPF15 0 %
 GPF16 0 %
 S1 30.00 %
 S2 50.00 %
 S3 1000.00 usec
 S4 1000.00 usec
 S5 1000.00 usec

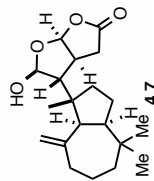
F2 - Processing Parameters
 SF 125.7604000 MHz
 DSF 500.1310000 MHz
 SSB 0
 GB 0
 PC 2.00



¹³C NMR (CDCl₃, 126 MHz)



1H spectrum

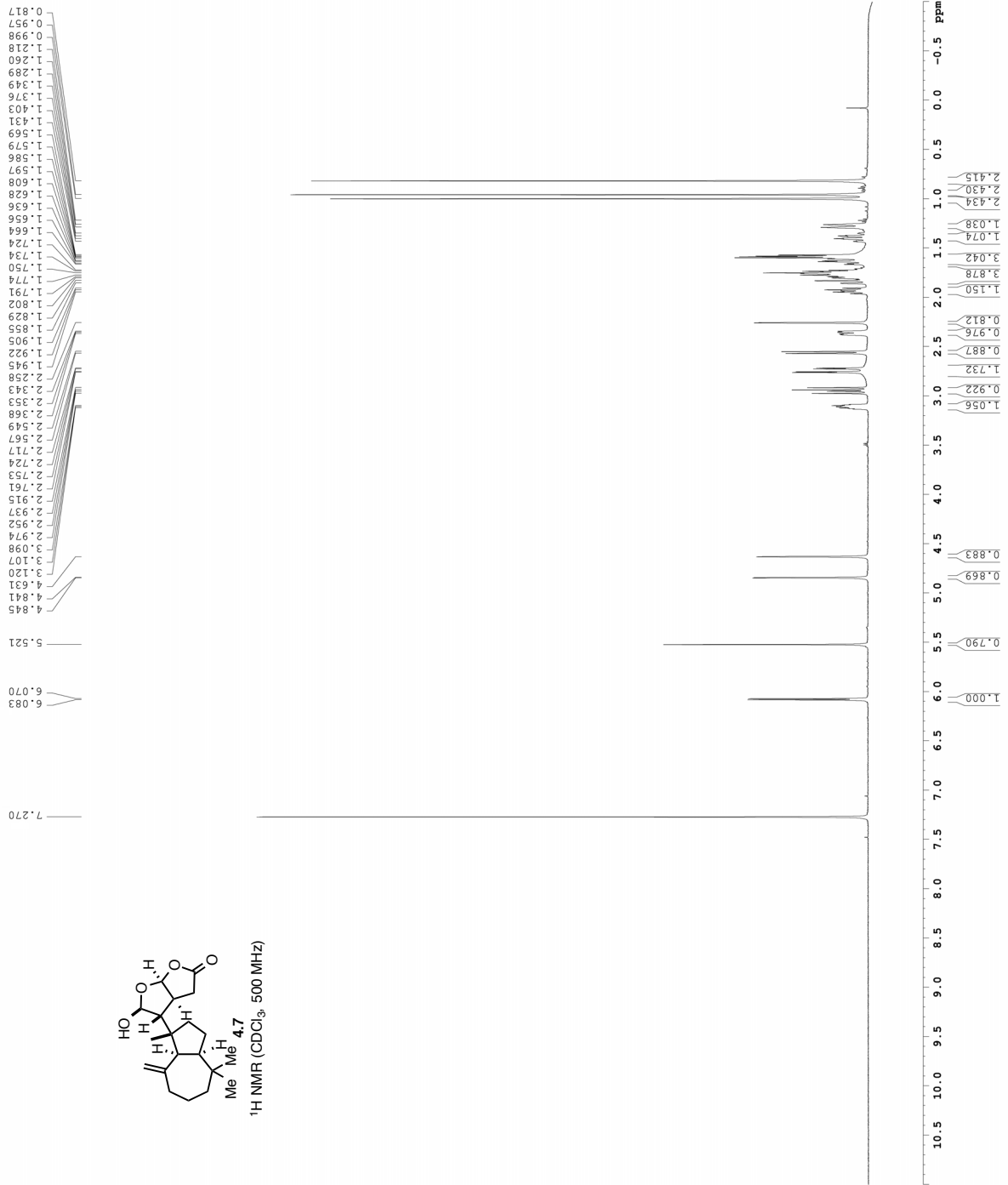


¹H NMR (CDCl₃, 500 MHz)

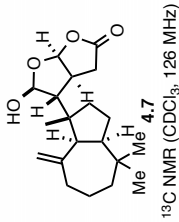
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Current Data Parameters
NAME      F2-2131-P
EXPNO    1
PROCNO   1
DATAF3   /v/data/zhaop3/nmr
Date_    20170411
Time     22.05
PULPROG  zgpg30
PROBHD   5 mm CFX500
PULPROG  zgpg30
TD        81728
SFO1     500.136261 MHz
RG        62.400
AQ        7.11 usec
RG        62.400
TE        298.0 K
D1        0.10000000 sec
DELTA    0.10000000 sec
MCWRSK   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        500.220261 MHz
WDW       EM
SSB       0
GB        0
PC        1.00
```



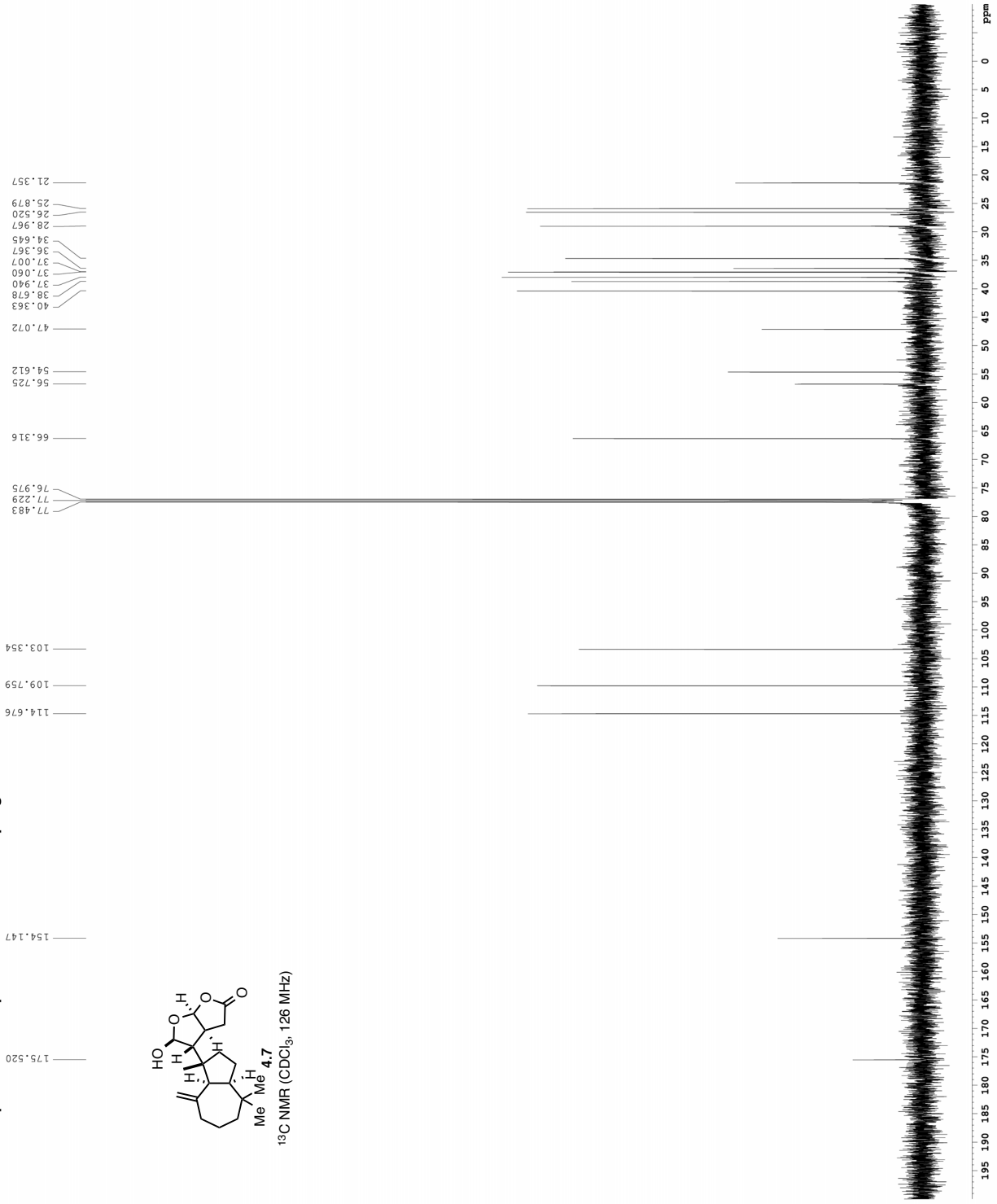
Z-restored spin-echo ¹³C spectrum with 1H decoupling



¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME          F2-211-P
EXPNO        2
DATAPATH     /v/data/zhoop3/mf
F2 - Acquisition Parameters
Date_        20170411
Time        22:05:00
INSTRUM      spect
PROBHD       5 mm CPTCL1H-
TD          65536
AQ          0.00018600 sec
SOLVENT      CDCl3
DS          16
SWH          30303.071 Hz
FIDRES      0.25788000 Hz
RG          2896.3
DE          6.00 usec
TE          300.2 K
d11         0.03000000 sec
d12         0.00000000 sec
d13         0.00018600 sec
d14         0.00000000 sec
d15         0.00018600 sec
d16         0.00000000 sec
d17         0.00018600 sec
d18         0.00000000 sec
d19         0.00018600 sec
d20         0.00000000 sec
d21         0.00018600 sec
d22         0.00000000 sec
d23         0.00018600 sec
d24         0.00000000 sec
d25         0.00018600 sec
d26         0.00000000 sec
d27         0.00018600 sec
d28         0.00000000 sec
d29         0.00018600 sec
d30         0.00000000 sec
d31         0.00018600 sec
d32         0.00000000 sec
d33         0.00018600 sec
d34         0.00000000 sec
d35         0.00018600 sec
d36         0.00000000 sec
d37         0.00018600 sec
d38         0.00000000 sec
d39         0.00018600 sec
d40         0.00000000 sec
d41         0.00018600 sec
d42         0.00000000 sec
d43         0.00018600 sec
d44         0.00000000 sec
d45         0.00018600 sec
d46         0.00000000 sec
d47         0.00018600 sec
d48         0.00000000 sec
d49         0.00018600 sec
d50         0.00000000 sec
d51         0.00018600 sec
d52         0.00000000 sec
d53         0.00018600 sec
d54         0.00000000 sec
d55         0.00018600 sec
d56         0.00000000 sec
d57         0.00018600 sec
d58         0.00000000 sec
d59         0.00018600 sec
d60         0.00000000 sec
d61         0.00018600 sec
d62         0.00000000 sec
d63         0.00018600 sec
d64         0.00000000 sec
d65         0.00018600 sec
d66         0.00000000 sec
d67         0.00018600 sec
d68         0.00000000 sec
d69         0.00018600 sec
d70         0.00000000 sec
d71         0.00018600 sec
d72         0.00000000 sec
d73         0.00018600 sec
d74         0.00000000 sec
d75         0.00018600 sec
d76         0.00000000 sec
d77         0.00018600 sec
d78         0.00000000 sec
d79         0.00018600 sec
d80         0.00000000 sec
d81         0.00018600 sec
d82         0.00000000 sec
d83         0.00018600 sec
d84         0.00000000 sec
d85         0.00018600 sec
d86         0.00000000 sec
d87         0.00018600 sec
d88         0.00000000 sec
d89         0.00018600 sec
d90         0.00000000 sec
d91         0.00018600 sec
d92         0.00000000 sec
d93         0.00018600 sec
d94         0.00000000 sec
d95         0.00018600 sec
d96         0.00000000 sec
d97         0.00018600 sec
d98         0.00000000 sec
d99         0.00018600 sec
d100        0.00000000 sec
===== CHANNEL f1 13C =====
NUC1         13C
P1          16.55 usec
PCPD1       100.00 usec
PL1         2.00 dB
PL2         120.00 dB
PL3         120.00 dB
PL4         120.00 dB
PL5         120.00 dB
PL6         120.00 dB
PL7         120.00 dB
PL8         120.00 dB
PL9         120.00 dB
PL10        120.00 dB
PL11        120.00 dB
PL12        120.00 dB
PL13        120.00 dB
PL14        120.00 dB
PL15        120.00 dB
PL16        120.00 dB
PL17        120.00 dB
PL18        120.00 dB
PL19        120.00 dB
PL20        120.00 dB
PL21        120.00 dB
PL22        120.00 dB
PL23        120.00 dB
PL24        120.00 dB
PL25        120.00 dB
PL26        120.00 dB
PL27        120.00 dB
PL28        120.00 dB
PL29        120.00 dB
PL30        120.00 dB
PL31        120.00 dB
PL32        120.00 dB
PL33        120.00 dB
PL34        120.00 dB
PL35        120.00 dB
PL36        120.00 dB
PL37        120.00 dB
PL38        120.00 dB
PL39        120.00 dB
PL40        120.00 dB
PL41        120.00 dB
PL42        120.00 dB
PL43        120.00 dB
PL44        120.00 dB
PL45        120.00 dB
PL46        120.00 dB
PL47        120.00 dB
PL48        120.00 dB
PL49        120.00 dB
PL50        120.00 dB
PL51        120.00 dB
PL52        120.00 dB
PL53        120.00 dB
PL54        120.00 dB
PL55        120.00 dB
PL56        120.00 dB
PL57        120.00 dB
PL58        120.00 dB
PL59        120.00 dB
PL60        120.00 dB
PL61        120.00 dB
PL62        120.00 dB
PL63        120.00 dB
PL64        120.00 dB
PL65        120.00 dB
PL66        120.00 dB
PL67        120.00 dB
PL68        120.00 dB
PL69        120.00 dB
PL70        120.00 dB
PL71        120.00 dB
PL72        120.00 dB
PL73        120.00 dB
PL74        120.00 dB
PL75        120.00 dB
PL76        120.00 dB
PL77        120.00 dB
PL78        120.00 dB
PL79        120.00 dB
PL80        120.00 dB
PL81        120.00 dB
PL82        120.00 dB
PL83        120.00 dB
PL84        120.00 dB
PL85        120.00 dB
PL86        120.00 dB
PL87        120.00 dB
PL88        120.00 dB
PL89        120.00 dB
PL90        120.00 dB
PL91        120.00 dB
PL92        120.00 dB
PL93        120.00 dB
PL94        120.00 dB
PL95        120.00 dB
PL96        120.00 dB
PL97        120.00 dB
PL98        120.00 dB
PL99        120.00 dB
PL100       120.00 dB
===== CHANNEL f2 =====
CPDPRG2     walz16
NUC2         13C
P2          16.55 usec
PCPD2       100.00 usec
PL2         2.00 dB
PL3         120.00 dB
PL4         120.00 dB
PL5         120.00 dB
PL6         120.00 dB
PL7         120.00 dB
PL8         120.00 dB
PL9         120.00 dB
PL10        120.00 dB
PL11        120.00 dB
PL12        120.00 dB
PL13        120.00 dB
PL14        120.00 dB
PL15        120.00 dB
PL16        120.00 dB
PL17        120.00 dB
PL18        120.00 dB
PL19        120.00 dB
PL20        120.00 dB
PL21        120.00 dB
PL22        120.00 dB
PL23        120.00 dB
PL24        120.00 dB
PL25        120.00 dB
PL26        120.00 dB
PL27        120.00 dB
PL28        120.00 dB
PL29        120.00 dB
PL30        120.00 dB
PL31        120.00 dB
PL32        120.00 dB
PL33        120.00 dB
PL34        120.00 dB
PL35        120.00 dB
PL36        120.00 dB
PL37        120.00 dB
PL38        120.00 dB
PL39        120.00 dB
PL40        120.00 dB
PL41        120.00 dB
PL42        120.00 dB
PL43        120.00 dB
PL44        120.00 dB
PL45        120.00 dB
PL46        120.00 dB
PL47        120.00 dB
PL48        120.00 dB
PL49        120.00 dB
PL50        120.00 dB
PL51        120.00 dB
PL52        120.00 dB
PL53        120.00 dB
PL54        120.00 dB
PL55        120.00 dB
PL56        120.00 dB
PL57        120.00 dB
PL58        120.00 dB
PL59        120.00 dB
PL60        120.00 dB
PL61        120.00 dB
PL62        120.00 dB
PL63        120.00 dB
PL64        120.00 dB
PL65        120.00 dB
PL66        120.00 dB
PL67        120.00 dB
PL68        120.00 dB
PL69        120.00 dB
PL70        120.00 dB
PL71        120.00 dB
PL72        120.00 dB
PL73        120.00 dB
PL74        120.00 dB
PL75        120.00 dB
PL76        120.00 dB
PL77        120.00 dB
PL78        120.00 dB
PL79        120.00 dB
PL80        120.00 dB
PL81        120.00 dB
PL82        120.00 dB
PL83        120.00 dB
PL84        120.00 dB
PL85        120.00 dB
PL86        120.00 dB
PL87        120.00 dB
PL88        120.00 dB
PL89        120.00 dB
PL90        120.00 dB
PL91        120.00 dB
PL92        120.00 dB
PL93        120.00 dB
PL94        120.00 dB
PL95        120.00 dB
PL96        120.00 dB
PL97        120.00 dB
PL98        120.00 dB
PL99        120.00 dB
PL100       120.00 dB
===== GRADIENT CHANNEL =====
GENDM[1]    SINE.100
GENDM[2]    0
GEX[1]      0
GEX[2]      0
GEX[3]      0
GEX[4]      0
GEX[5]      0
GEX[6]      0
GEX[7]      0
GEX[8]      0
GEX[9]      0
GEX[10]     0
GEX[11]     0
GEX[12]     0
GEX[13]     0
GEX[14]     0
GEX[15]     0
GEX[16]     0
GEX[17]     0
GEX[18]     0
GEX[19]     0
GEX[20]     0
GEX[21]     0
GEX[22]     0
GEX[23]     0
GEX[24]     0
GEX[25]     0
GEX[26]     0
GEX[27]     0
GEX[28]     0
GEX[29]     0
GEX[30]     0
GEX[31]     0
GEX[32]     0
GEX[33]     0
GEX[34]     0
GEX[35]     0
GEX[36]     0
GEX[37]     0
GEX[38]     0
GEX[39]     0
GEX[40]     0
GEX[41]     0
GEX[42]     0
GEX[43]     0
GEX[44]     0
GEX[45]     0
GEX[46]     0
GEX[47]     0
GEX[48]     0
GEX[49]     0
GEX[50]     0
GEX[51]     0
GEX[52]     0
GEX[53]     0
GEX[54]     0
GEX[55]     0
GEX[56]     0
GEX[57]     0
GEX[58]     0
GEX[59]     0
GEX[60]     0
GEX[61]     0
GEX[62]     0
GEX[63]     0
GEX[64]     0
GEX[65]     0
GEX[66]     0
GEX[67]     0
GEX[68]     0
GEX[69]     0
GEX[70]     0
GEX[71]     0
GEX[72]     0
GEX[73]     0
GEX[74]     0
GEX[75]     0
GEX[76]     0
GEX[77]     0
GEX[78]     0
GEX[79]     0
GEX[80]     0
GEX[81]     0
GEX[82]     0
GEX[83]     0
GEX[84]     0
GEX[85]     0
GEX[86]     0
GEX[87]     0
GEX[88]     0
GEX[89]     0
GEX[90]     0
GEX[91]     0
GEX[92]     0
GEX[93]     0
GEX[94]     0
GEX[95]     0
GEX[96]     0
GEX[97]     0
GEX[98]     0
GEX[99]     0
GEX[100]    0
===== F2 - Processing Parameters =====
SI          32768
SF          125.769536 MHz
WDW         EM
SSB         0
GB          0
PC          2.00
  
```



1H spectrum

1.431
 1.403
 1.376
 1.349
 1.322
 1.295
 1.268
 1.241
 1.214
 1.187
 1.160
 1.133
 1.106
 1.079
 1.052
 1.025
 0.998
 0.971
 0.944
 0.917
 0.890
 0.863
 0.836
 0.809
 0.782
 0.755
 0.728
 0.701
 0.674
 0.647
 0.620
 0.593
 0.566
 0.539
 0.512
 0.485
 0.458
 0.431
 0.404
 0.377
 0.350
 0.323
 0.296
 0.269
 0.242
 0.215
 0.188
 0.161
 0.134
 0.107
 0.080
 0.053
 0.026
 0.000

1.569
 1.579
 1.579
 1.586
 1.597
 1.608
 1.628
 1.636
 1.656
 1.664
 1.724
 1.734
 1.750
 1.774
 1.791
 1.802
 1.829
 1.855
 1.905
 1.922
 1.945

2.258

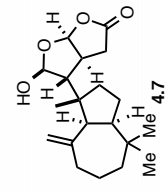
2.343
2.353
2.368

2.549
2.567

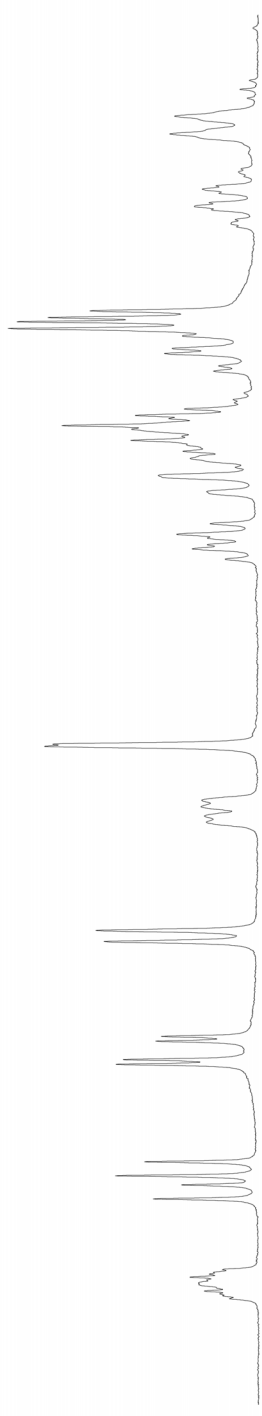
2.717
2.724
2.753
2.761

2.915
2.937
2.952
2.974

3.098
3.107
3.120



Me Me 4.7
¹H NMR (CDCl₃, 500 MHz)
 3.3 ppm to 1.1 ppm expanded region

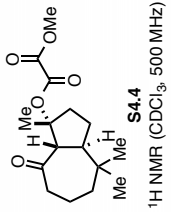
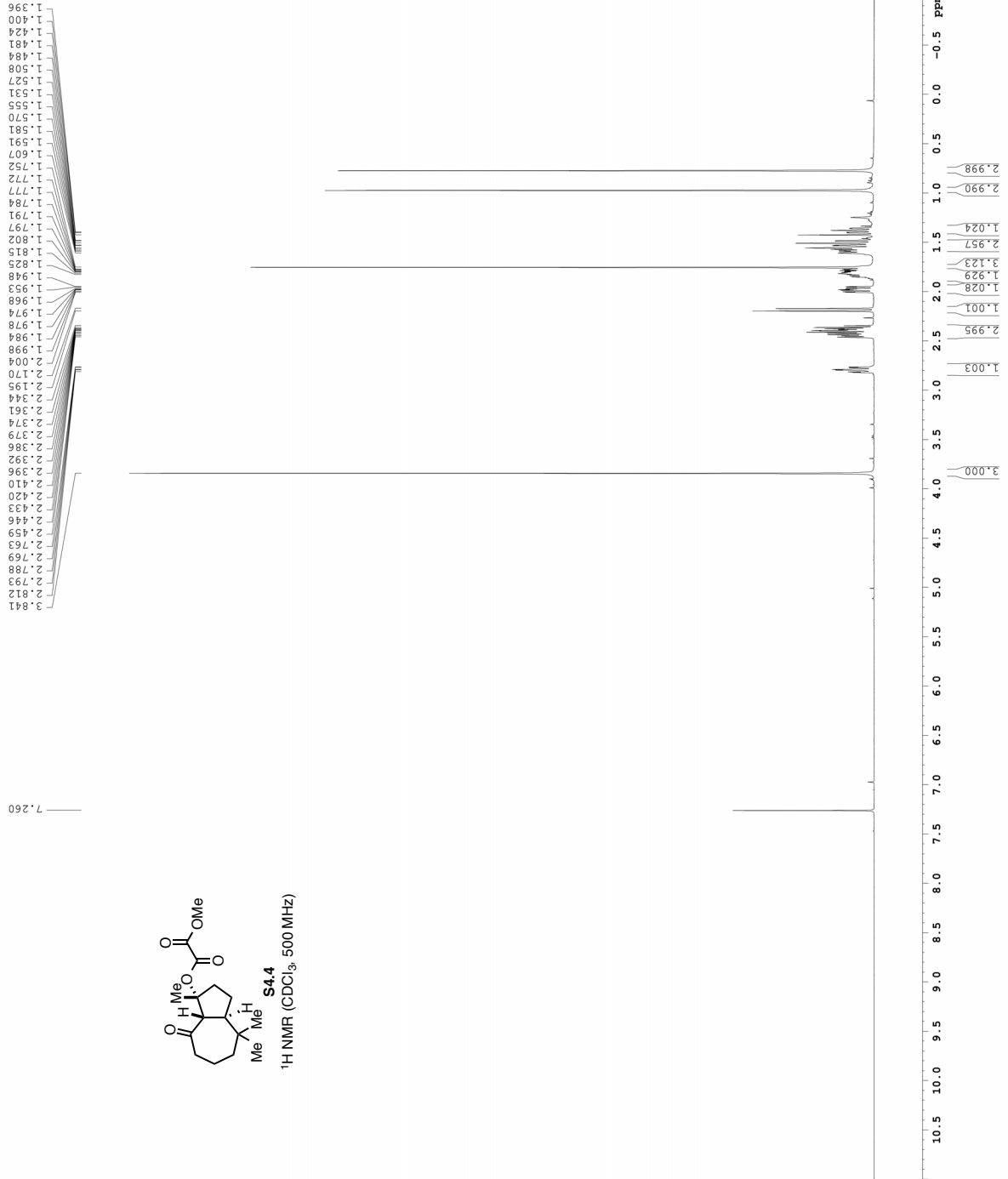


3.2
 3.1
 3.0
 2.9
 2.8
 2.7
 2.6
 2.5
 2.4
 2.3
 2.2
 2.1
 2.0
 1.9
 1.8
 1.7
 1.6
 1.5
 1.4
 1.3
 1.2
 1.1

1.056
 0.922
 1.732
 0.887
 0.976
 0.812
 3.878
 3.042
 1.074
 1.038
 1.150

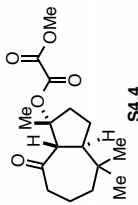
YS-V-18

Current Data Parameters
NAME YS-V-18
PROCNO 1
F2 - Acquisition Parameters
Time 2017-11-17 17:53
INSTRUM cryo500
PROBHD 5 mm CP131-HP
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
RG 3.0398275 sec
DM 62.400 usec
DE 298.00 Ksec
D1 0.10000000 sec
MCREST 0 sec
ACQBRK 0.15000000 sec
===== CHANNEL f1 =====
NUC1 13C
PULP 7.50 usec
PL1 1.60 dB
SF01 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

156.272
158.489

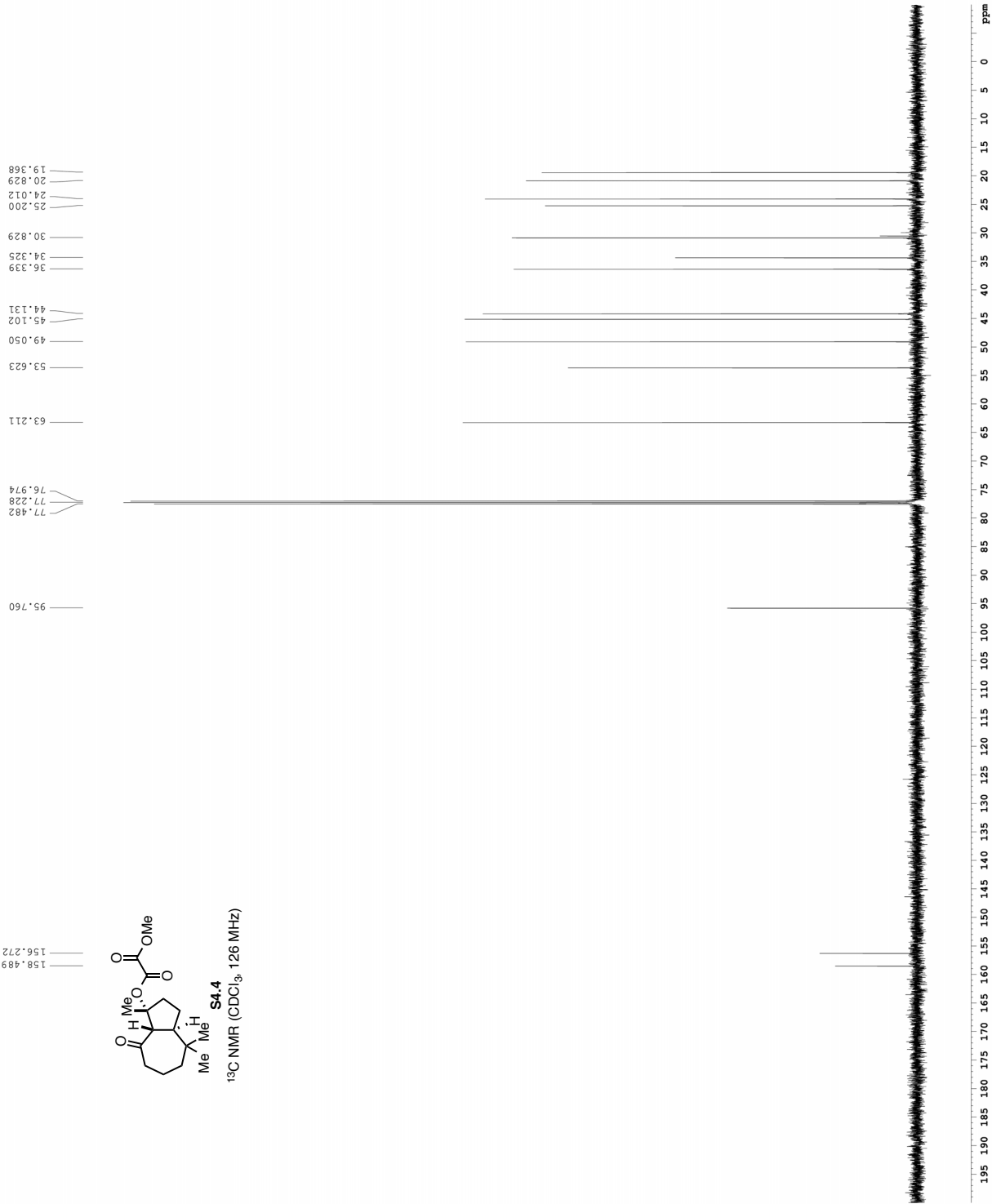


¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME      YS-V-18
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Time      201.8756
INSTRUM   spect
PROBHD    5 mm cryo-50
PULPROG   zgpg30
SOLVENT   spincchop30ppr.prd
NS        6583
DS        4
AQ        2.00
RG        30303.031 Hz
FIDRES    0.462888 Hz
AQ        1.128963 sec
RG        2896.3
DM        16.500 usec
TE        298.0 K
D1        0.2500000 sec
D11       0.0002000 sec
D16       0.0002000 sec
d16REST   0.00019600 sec
MCPRK1    0.03150000 sec
MCPRK2    33.10 usec
===== CHANNEL f1 =====
NUC1       13C
P1         16.25 usec
PL1        0.00 dB
PL12       500.00 usec
PL13       120.00 dB
PL14       120.00 dB
PL15       120.00 dB
PL16       120.00 dB
SS1        125.792100 dB
SS12       2.70 dB
SS13       2.70 dB
SS14       2.70 dB
SS15       2.70 dB
SS16       2.70 dB
SPRAME1[1] Cpf60.0.5.270
SPRAME2[1] Cpf60comp.4
SFOFF1     0 Hz
SFOFF2     0 Hz
===== CHANNEL f2 =====
CPRPRG12  waltz16
NUC2       13C
PCPR2      100.00 usec
PL2        0.00 dB
PL12       1.60 dB
PL13       24.50 dB
PL14       24.50 dB
SFO2       500.2225011 MHz
===== CHANNEL GRADIENT =====
GPRAM[1]   SINE.100
GPRAM[2]   0 %
GPRAM[3]   0 %
GPRAM[4]   0 %
GPRAM[5]   0 %
GPRAM[6]   0 %
GPRAM[7]   0 %
GPRAM[8]   0 %
GPRAM[9]   0 %
GPRAM[10]  0 %
GPRAM[11]  0 %
GPRAM[12]  0 %
GPRAM[13]  0 %
GPRAM[14]  0 %
GPRAM[15]  0 %
GPRAM[16]  0 %
GPRAM[17]  0 %
GPRAM[18]  0 %
GPRAM[19]  0 %
GPRAM[20]  0 %
===== CHANNEL =====
F2 - Processing parameters
SI         65536
SF         125.7603598 MHz
WDW        EM
SSB        0
GB         0
PC         2.00

```

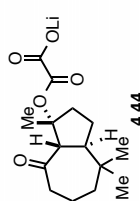


YS-V-236

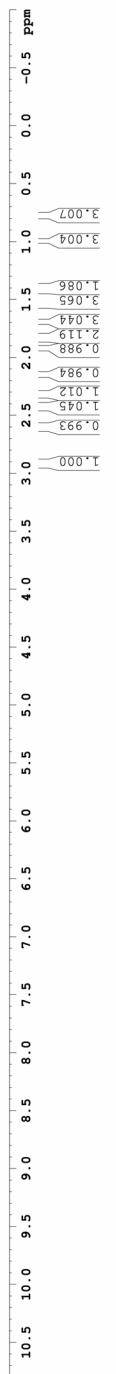
Current Data Parameters
EXNO 1
PROCNO 1
Date - Acquisition Parameters
Time 8.26
Date_ 20170217
PROBHD 5 mm CPBBO 5B-0
PULPROG zg30
TD 98074
NS 8
SOLVENT CD308
DS 2
SI 6515.862
SF 600.1342018 MHz
F2 - Processing parameters
AQ 5.0998478 sec
RG 1.0
DE 13.70 usec
TE 298.0 K
D1 0.10000000 sec
190

===== CHANNEL f1 =====
NUC1 13C
P1 12.00 usec
PL1 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

3.312
3.310
3.307
2.944
2.939
2.924
2.919
2.904
2.899
2.617
2.608
2.597
2.589
2.577
2.451
2.437
2.426
2.412
2.397
2.337
2.333
2.326
2.322
2.317
2.313
2.305
2.301
2.155
2.152
2.134
2.131
1.942
1.937
1.925
1.920
1.912
1.900
1.895
1.866
1.860
1.855
1.849
1.842
1.838
1.833
1.827
1.823
1.818
1.806
1.803
1.792
1.700
1.567
1.563
1.557

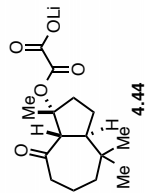


¹H NMR (CD₃OD, 600 MHz)



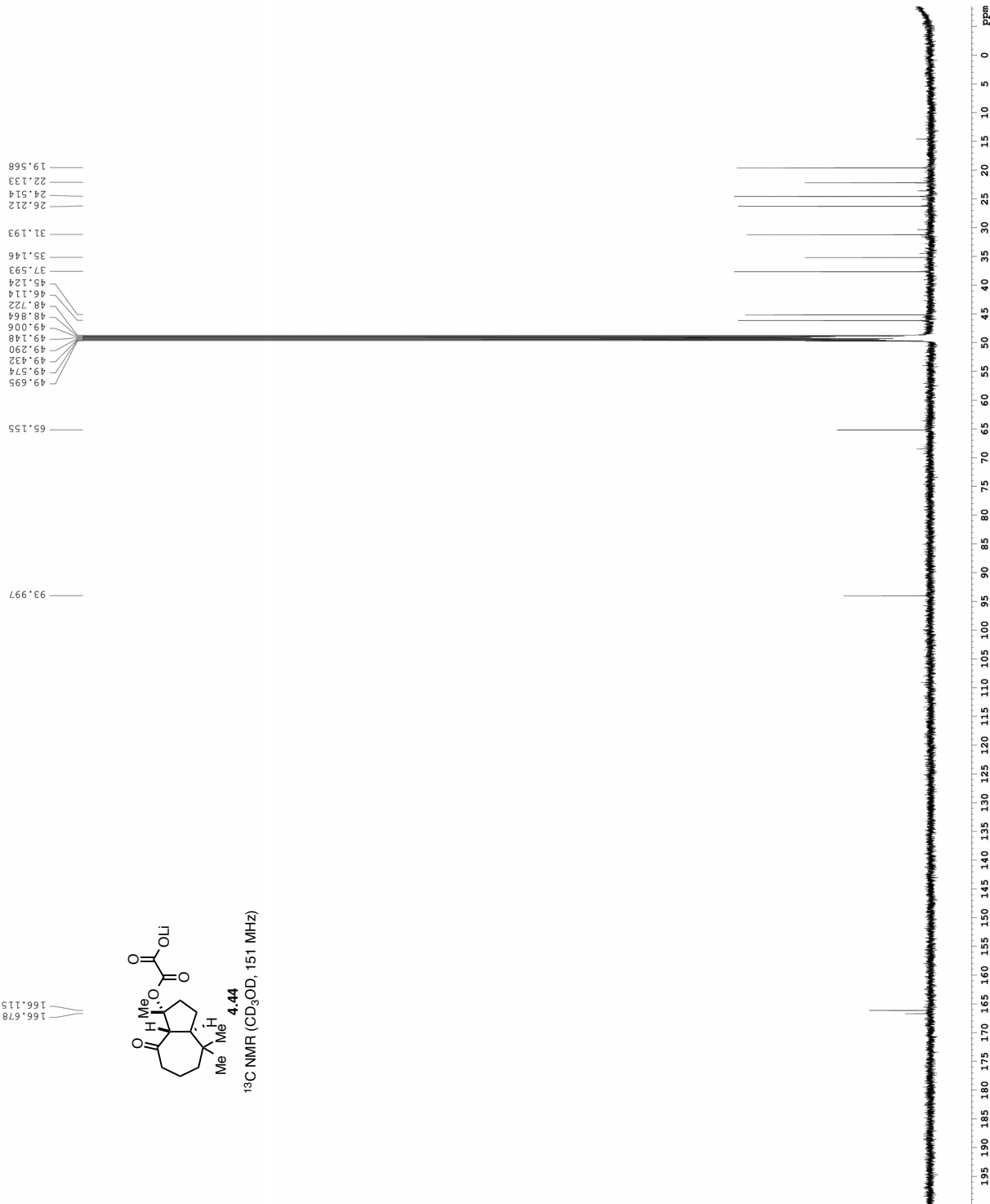
YS-V-236

166.115
166.678

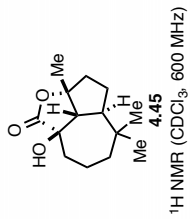


¹³C NMR (CD₃OD, 151 MHz)

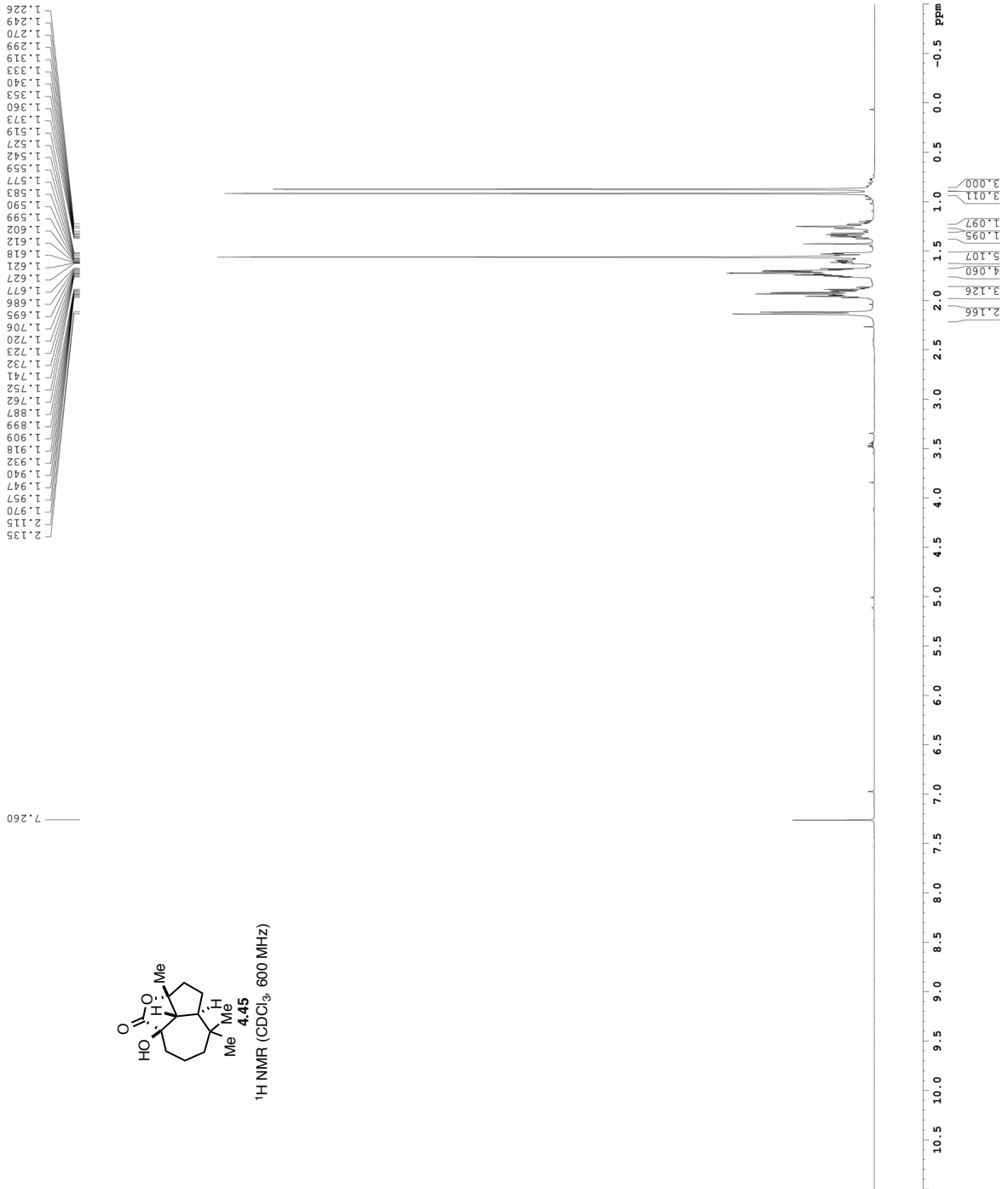
===== Solvent Data Parameters =====
NAME: YS-V-236
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Date_ 20080808
Time 8:30
INSTRUM: av600
PROBHD: 5 mm CPB
PULPROG: zgpg30
TD: 65536
SFO1: 125.761 MHz
NS: 1024
DSB: 36231.883 Hz
FIDRES: 0.552835 Hz
AQ: 0.5042058 sec
RG: 27056
DM: 13.800 usec
DE: 228.0 usec
TE: 298.2 K
D1: 0.40000001 sec
D11: 0.05000000 sec
D12: 0.05000000 sec
D13: 0.05000000 sec
===== CHANNEL f1 =====
SFO1: 125.761 MHz
NUC1: 13C
P1M1: 64.00000000 Wsec
===== CHANNEL f2 =====
SFO2: 600.1330010 MHz
NUC2: 1H
P1M2: 64.00000000 Wsec
PCPD2: 20.000 usec
PCPD1: 0.36000000 W
P1M12: 0.36000000 W
===== F2 - Processing Parameters =====
SI: 65536
SF: 125.761 MHz
RG: 27056
SFO: 125.761 MHz
WDW: EM
SSB: 0
GB: 0
PC: 1.00



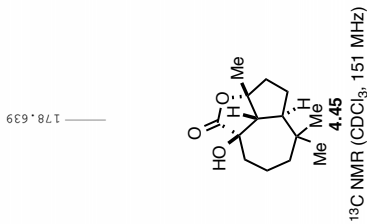
YS-V-243



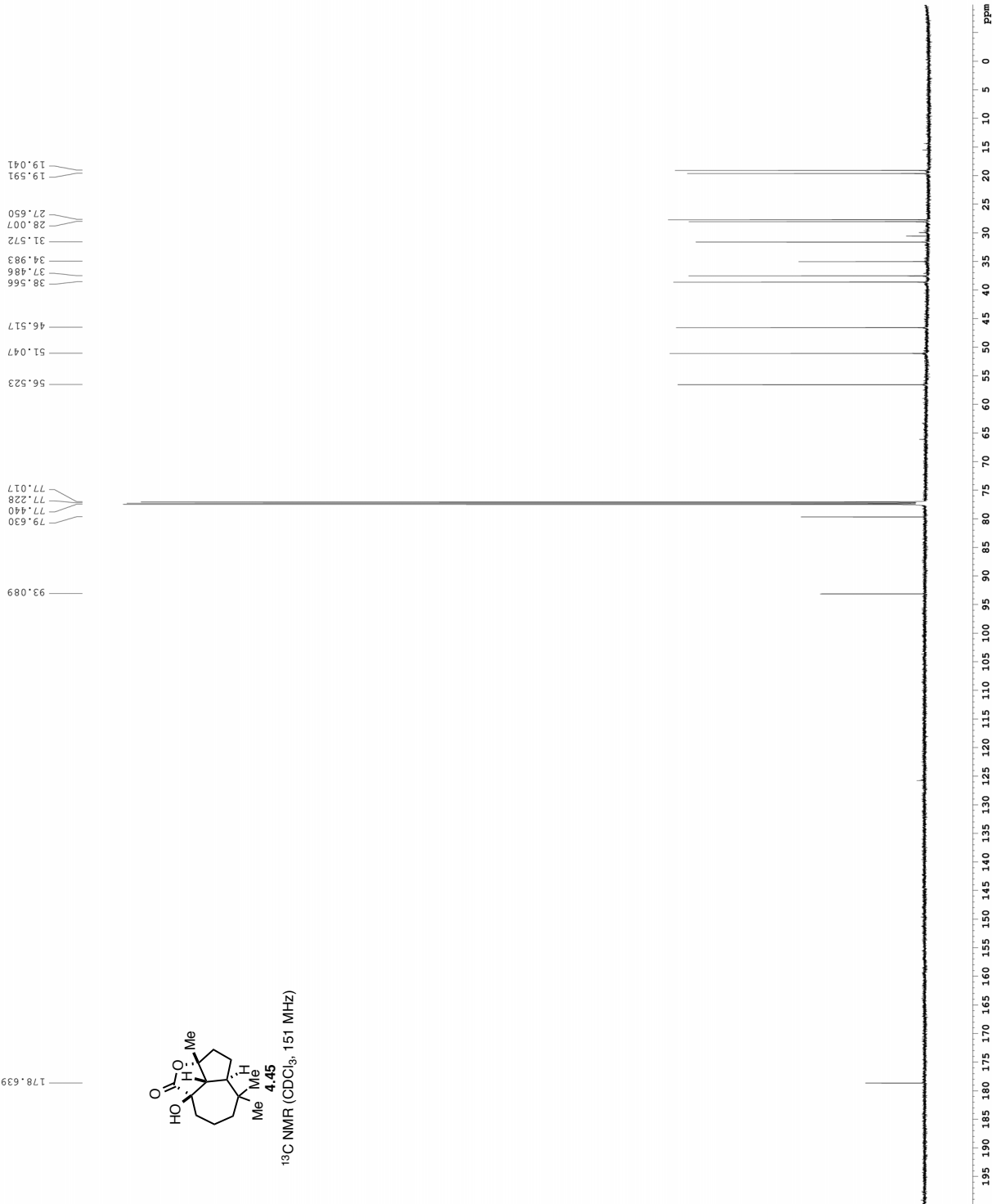
Current Data Parameters
NAME YS-V-243
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 2011.10.17
Time 10.47
INSTRUM 5 mm CPBBO BB
PROBHD 5 mm CPBBO BB
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.096042 Hz
AQ 3.0936416 sec
RG 10
DM 52.000 usec
DE 236.0 usec
TE 300.2 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.1342003 MHz
NUC1 13C
PULPROG zgpg30
FLM1 2D.00000000 M
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



Current Data Parameters
NAME YS-V-243
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080610
Time 10:50
INSTRUM spect
PROBHD 5 mm CPBBOV600
PULPROG zgpg30
PCPDPR 120
SOLVENT CDCl3
NS 120
DS 4
SWH 36231.883 Hz
FIDRES 0.552895 Hz
RG 2050 sec
RG 2050 sec
AQ 13.800 usec
SFO1 150.9194080 MHz
TE 298.0 K
D1 0.40000001 sec
D11 0.15000000 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
P2 10.00 usec
PLW2 600.1330010 MHz
PCPDPR2 waltz16
F2P2 20.00000000 usec
F2P22 0.36000000 W
F2P23 0.36000000 W
F2 - Processing parameters
SI 6536
SF 150.9027800 MHz
WDW EM
SSB 0
GB 0
PC 1.00



YS-V-248

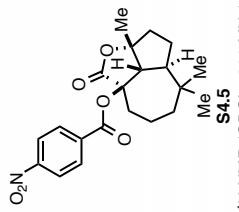
Current Data Parameters
NAME YS-V-248
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110101
Time 9.01
INSTRUM av600
PROBHD 5 mm CPBBO Z30
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
DS 0
SWH 9615.385 Hz
FIDRES 0.098042 Hz
RG 3.0339616 sec
DM 52.000 usec
DE 298.0 K usec
TE 298.0 K usec
D1 0.10000000 sec
TD0 1

===== CHANNEL f1 =====
SF01 600.1342009 MHz
NUC1 13C
P1 12.00 usec
PL1 20.00000000 M

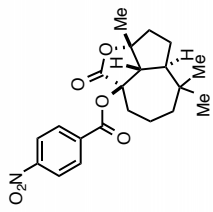
F2 - Processing Parameters
SI 65536
SF 600.1300349 MHz
RGW 0
LS 0
GB 0
PC 1.00

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8.288
8.303
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2.569
2.490
2.485
2.480
2.475
2.464
2.454
2.449
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2.434
2.429
2.424
2.419
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1.376
1.374



YS-V-248

Current Data Parameters
NAME XS-V-248
PROCNO 5
F2 - Acquisition Parameters
Time 20.04
Date_ 9.04
INSTRUM spect
PROBHD 5 mm CPBBO600
PULPROG zgpg30
PCPDPRG2 3DZ
SOLVENT CDCl3
NS 256
DS 4
SWH 36231.883 Hz
FIDRES 0.552895 Hz
RG 329.500 sec
RG 2050
AQ 13.800 usec
RG 13.800 usec
TE 298.0 K
D1 0.40000001 sec
D11 0.40000001 sec
D12 0.40000001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.9194080 MHz
NUC1 13C
PUL1 10.00 usec
PLW1 64.00000000 W
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 1H
PUL2 waltz16
PCPDPRG2
F2P2 20.000 usec
RG 20.000 usec
PLW2 0.36000001 W
F2 - Processing parameters
SI 6536
SF 600.1330010 MHz
WDW EM
SSB 0
GB 0
PC 1.00

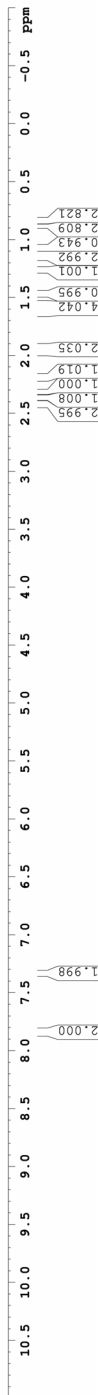
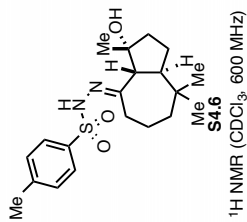


¹³C NMR (CDCl₃, 151 MHz)

Current Data Parameters
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170731
Time 10.25
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zg30
SOLVENT CDCl3
NS 8
DS 8
AQ 0.096022 Hz
FIDRES 5.0998478 sec
RG 52.00 usec
DE 13.70 usec
TE 298.0 K
TD 0.1000000 sec
===== CHANNEL f1 =====
NUC1 600.130052 MHz
P1 12.00 usec
PL1 20.0000000 W
F2 - Processing parameters
SI 65536
WDW EM
SSB 0
LB 0
GB 0
PC 1.00

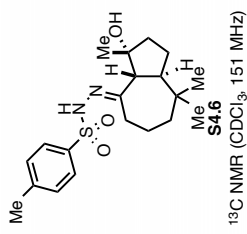
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2.159
2.008
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1.985
1.977
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1.918
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1.622
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1.560
1.548
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1.536
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1.470
1.464
1.455
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1.275
1.271

7.849
7.847
7.835
7.345
7.332
7.260



YS-VI-26

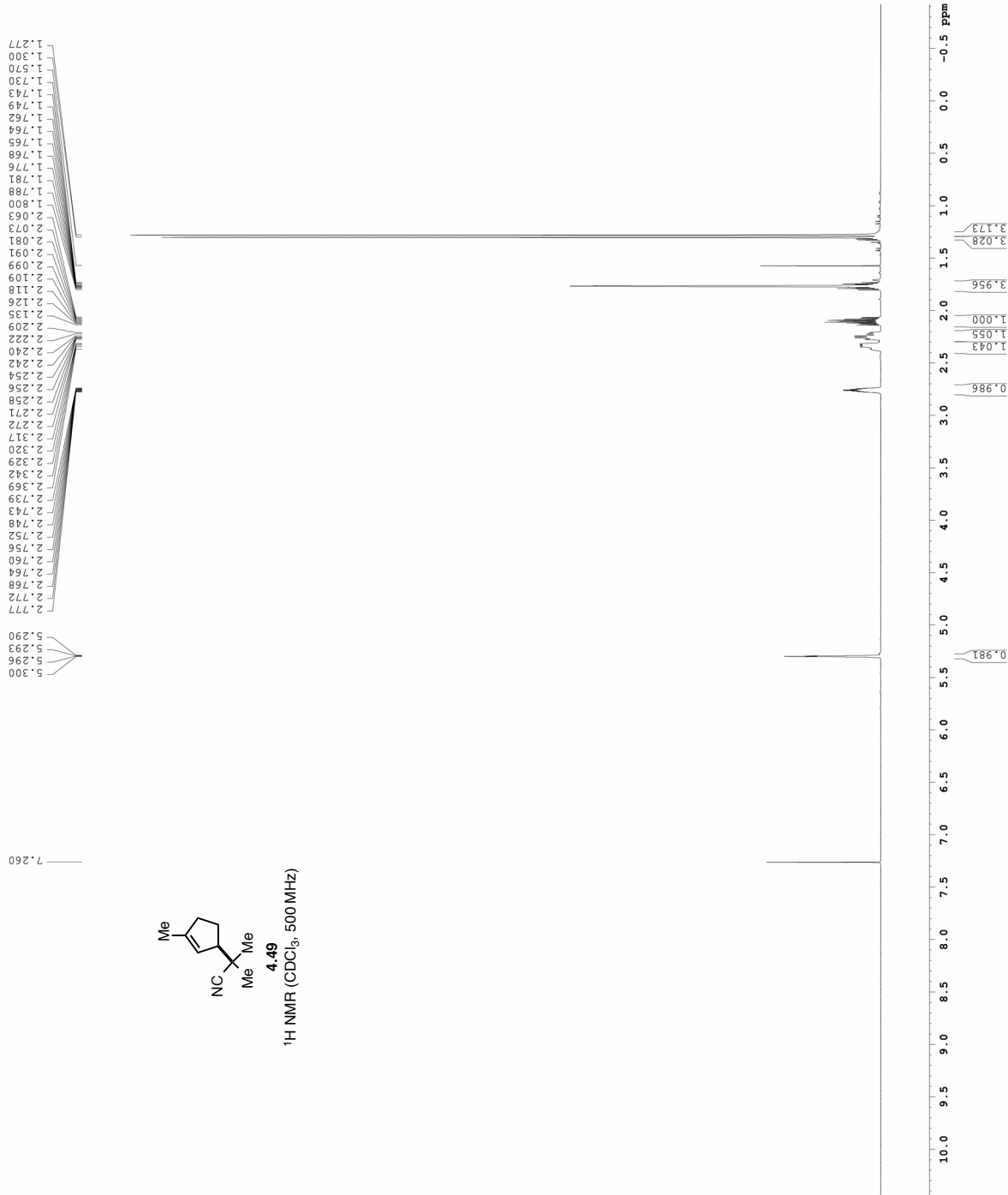
Current Data Parameters
NAME YS-VI-26
PROCNO 1
F2 - Acquisition Parameters
Time 201.31
INSTRUM 5 mm CPBAC600
PULPROG zgpg30
SOLVENT CDCl3
NS 360
SRH 36231.883 Hz
FIDRES 0.522852 Hz
AQ 0.22280 sec
RG 228.000
DM 13.600 usec
TE 298.2 K
D1 0.4000001 sec
D11 0.15500001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.9194880 MHz
NUC1 13C
PL1 10.00 usec
PLLM1 64.000000000 M
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
CPDPRG2 waltz16
PCPD2 80.000 usec
PLM12 20.000000000 W
PLM12 0.360000001 W
F2 - Processing parameters
SI 65536
SF 600.1330010 MHz
WDW 0
SSB 0
GB 0
PC 1.00



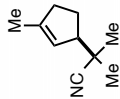
¹H spectrum

```

Current Data Parameters
NAME      CRJ3-146-pure
EXPNO    1
PROCNO   1
DATAPATH /nmr/jamiso/NMRdata
F2 - Acquisition Parameters
Time     20161201
Date_    11.38
INSTRUM  cryo500
PROBHD   5 mm CPYC500
PULPROG  zg30
ID       48074
NS       48074
DS       2
SWH      8012.620 Hz
FIDRES   0.345000 Hz
AQ        2.4999176 sec
RG        7.1
BW        62.400 usec
TE        298.0 K sec
D1        0.10000000 sec
DELTA    0.00000000 sec
MCWNRZ   0.01500000 sec
===== CHANNEL f1 =====
NUC1     13C
P1       7.50 usec
PL1     -1.60 dB
SFO1    500.225015 MHz
F2 - Processing parameters
SI       65536
SF       500.225015 MHz
WDW      EM
SSB      0
GB       0
PC       4.00
  
```



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



4.49
¹³C NMR (CDCl₃, 126 MHz)

```

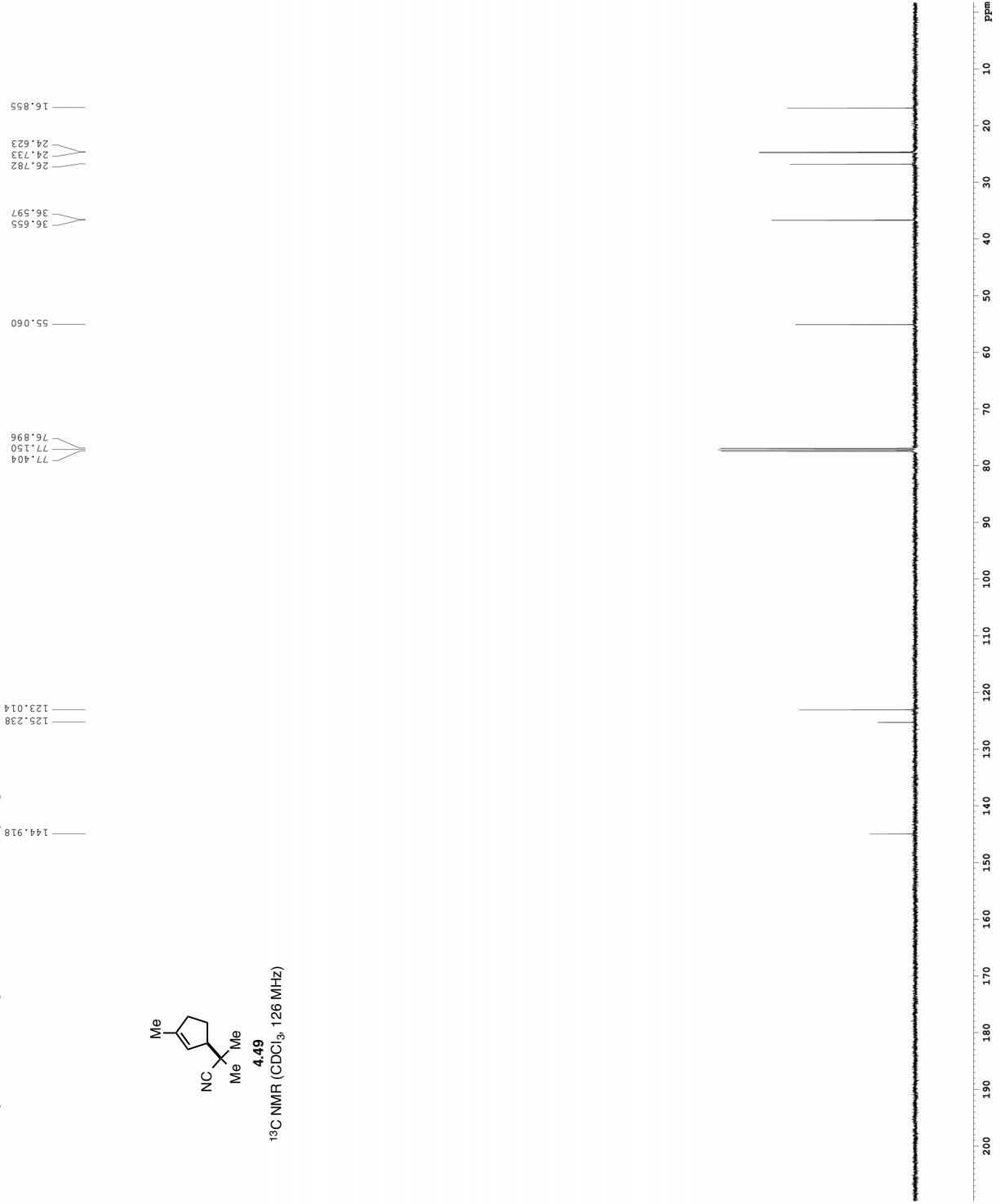
Current Date: Parameters
NAME: GRN3-146-porc 2
EXPNO: 2
PROCNO: 1
DATE_ATH: /nmr/jamiso/NMRdata
F2 - Acquisition Parameters
Date_ Acq: 20161201
Time: 11.43
PROBHD: 5 mm CPTCI 1H-
PULPROG: zgpg30
SOLVENT: CDCl3
NS: 64
DS: 4
SWH: 30303.031 Hz
FIDRES: 0.3400000 Hz
AQ: 2.9989311 sec
RG: 7298.2
DE: 6.000 usec
TE: 0.2500000 K
d11: 0.03000000 sec
d16: 0.00000000 sec
d17: 0.00000000 sec
MCREST: 0 sec
SFOFF2: 0.01500000 sec
F2: 0.01500000 sec

===== CHANNEL f1 =====
NUC1: 13C
P1: 16.55 usec
PL1: 0.00 dB
P12: 2000.00 usec
PL12: 120.00 dB
SFO1: 125.7942548 MHz
SF02: 2.0000000 MHz
SFO2: 2.0000000 MHz
SP1: 2.70 dB
SP2: 2.70 dB
SPRAME: C-CPDcomp-4
SFOFF1: 0 Hz
SFOFF2: 0 Hz

===== CHANNEL f2 =====
CPDPRG2: waltz16
P2: 16.55 usec
PL2: 0.00 dB
P22: 100.00 usec
PL22: 1.60 dB
SFO2: 500.225011 MHz
SF02: 500.225011 MHz

===== GRADIENT CHANNEL =====
GPNAM(1): SINE.100
GPNAM(2): SINE.100
GPA1: 0 %
GPA2: 0 %
GPA3: 0 %
GPA4: 0 %
GPF1: 30.00 %
GPF2: 30.00 %
GPF3: 30.00 %
GPF4: 30.00 %
PL3: 500.00 usec
PL4: 1000.00 usec

F2 - Processing parameters
SI: 65536
SF: 125.769458 MHz
WDW: 0
SSB: 0
GB: 1.00 Hz
PC: 2.00
    
```

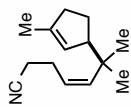


1H spectrum

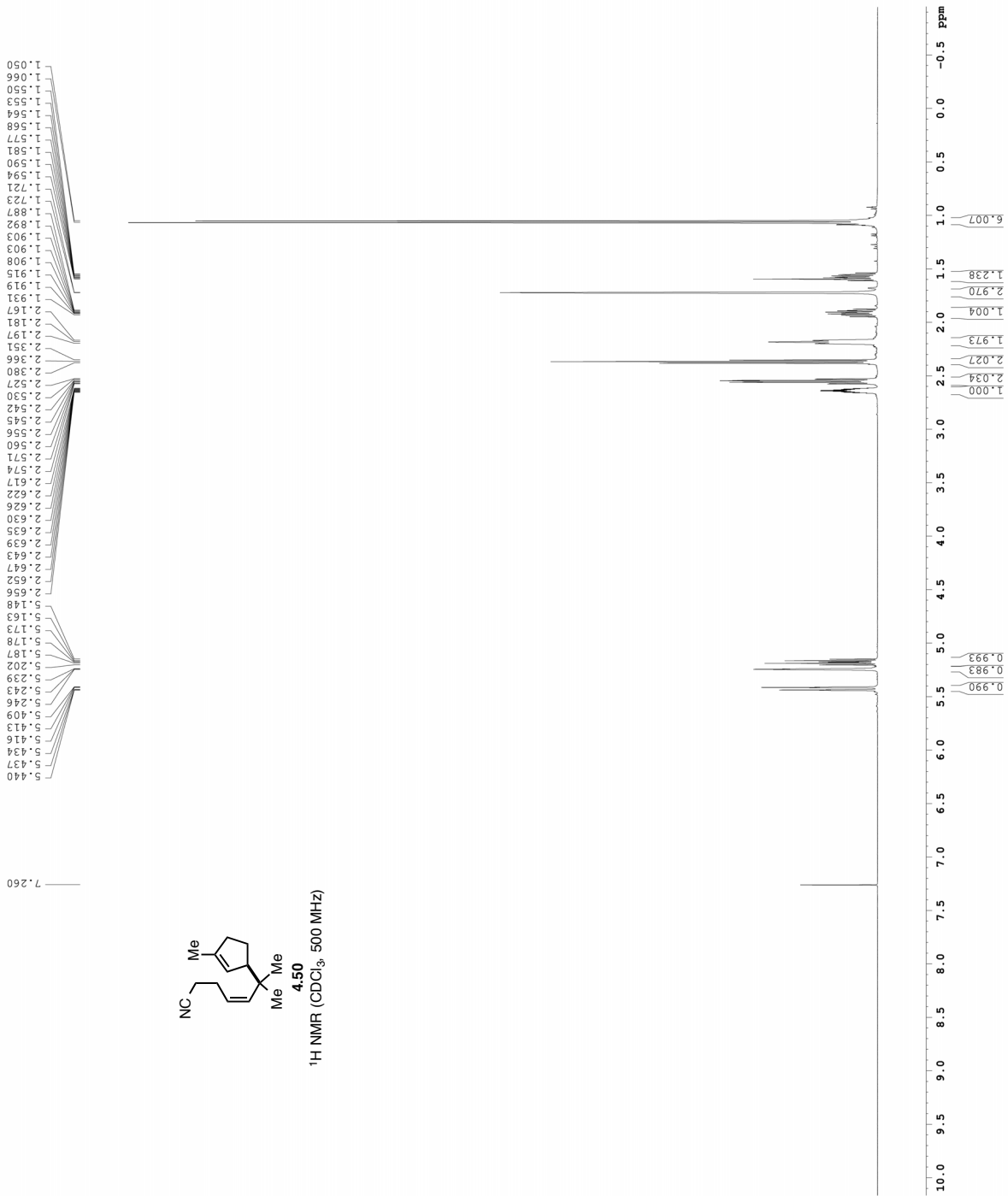
```

Current Data Parameters
NAME      CRJ3-148-Pure
PROCNO    1
DATAPATH /nmr/jan140/NMRdata
F2 - Acquisition Parameters
Date_     20161210
Time      10.21
INSTRUM   5 mm CPY131 QNP1H
PULPROG   zgpg30
ID         48074
NS         2
DS         2
SWHRES    8012.850 Hz
FIDRES    2.9998176 sec
AQ         2.9998176 sec
RG         51.7
DE         62.500 usec
TE         298.0 K
D1         0.10000000 sec
d11        0.00000000 sec
KICKST    0.01500000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL1        1.60 dB
SFO1       500.225015 MHz
F2 - Processing parameters
SI         65536
WDW         EM
SSB         0 Hz
GB          0
PC         1.00
    
```

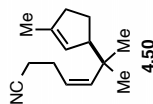
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5.178
5.173
5.168
5.148
5.148
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2.652
2.647
2.643
2.639
2.635
2.630
2.626
2.622
2.617
2.617
2.574
2.571
2.560
2.556
2.545
2.542
2.530
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1.590
1.581
1.577
1.568
1.564
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1.066
1.050



4.50
¹H NMR (CDCl₃, 500 MHz)



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



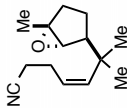
¹³C NMR (CDCl₃, 126 MHz)

```

Current: Data Parameters
NAME          CEA3-148p04r  4
EXCNO
NAME          /nmr/jamiso/nmrdata
DATA PATH
===== Acquisition Parameters
Date_         20161210
Time_        10.26
PROBHD       5 mm CPTCI 1H-
PULPROG      SpinEchoq1pp-prd
SOLVENT      CDCl3
DS           16.4
SWH          30300.031 Hz
AQ          1.0813440 sec
RG          72988.2
AQ          16.200000 usec
DE          6.00 usec
TE          298.0 K
D1          0.25000000 sec
d11         0.03000000 sec
D16         0.00020000 sec
d16         0.00134989 sec
MCRET1      0 sec
MCRET2      0.01300000 sec
PC          43.140 usec
===== CHANNEL f1 13C =====
NUC1         13C
P1           16.55 usec
PL1          0.00 dB
P2           2000.00 usec
PL2          120.00 dB
P3           120.00 usec
PL3          120.00 dB
SF01         125.7942548 MHz
SP1          2.70 dB
SFOFF1       0 Hz
SFOFF2       0 Hz
SFOFF3       0 Hz
===== CHANNEL f2 =====
CPDPRG2      waltz16
PCPD2        100.00 usec
PL2          1.60 dB
PL3          1.60 dB
SF02         500.2225011 MHz
===== GRADIENT CHANNEL =====
GPMAX(1)     SINE.100
GPMAX(2)     SINE.100
GPMIN(1)     0
GPMIN(2)     0
GPX2         0
GPY2         0
GPZ2         0
GF21        30.00 %
GF22        30.00 %
GF23        30.00 %
PL2         500.00 usec
PL3         500.00 usec
PL6         1000.00 usec
F2 - Processing parameters
SI           65136
SF           125.7604158 MHz
WDW          0
SSB          0
GB          1.00 Hz
PC          2.00
    
```

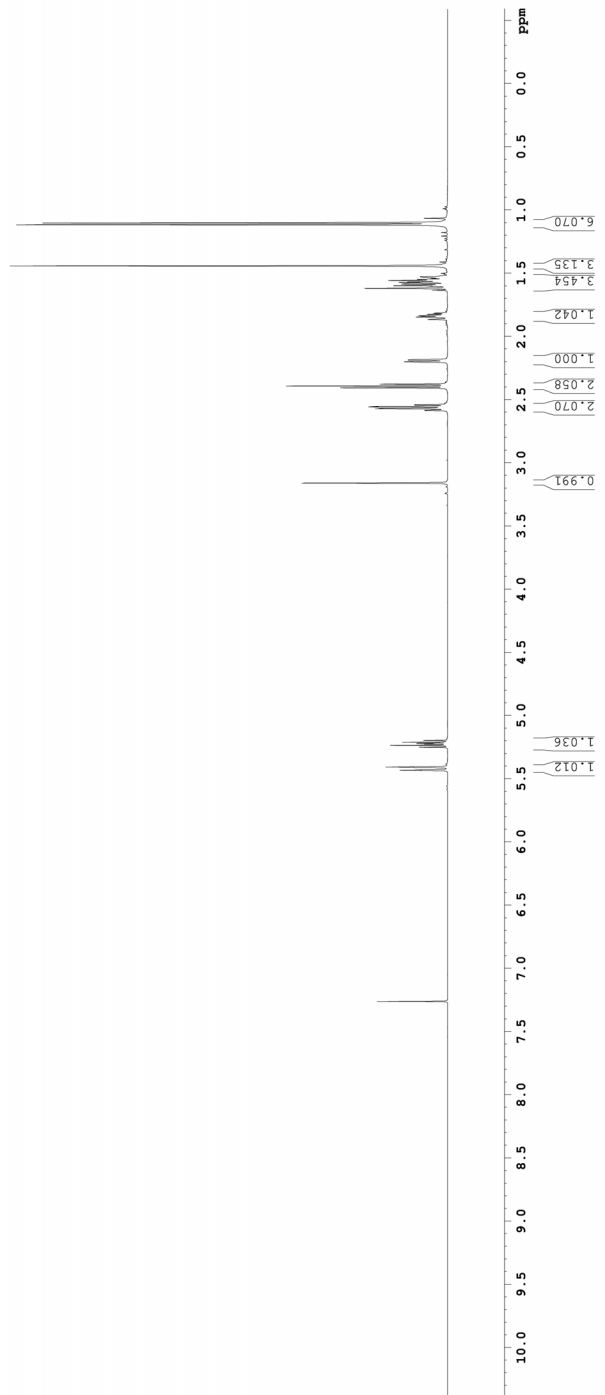
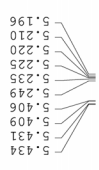
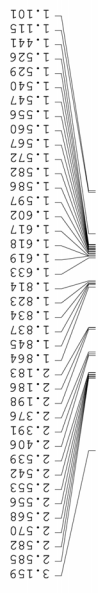


1H spectrum

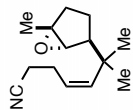


4.51
1H NMR (CDCl₃, 500 MHz)

Current Data Parameters
NAME CRJ3-149-maJor
PROC 1
F2 - Acquisition Parameters
Date_ 2011.01.20
Time_ 15.20
INSTRUM czt500
PULPROG zg30
TD 48074
FIDRES 0.0150000
SOLVENT CDCl₃
DS 2
SWH 8012.820 Hz
AQ 2.9398176 sec
RG 6.3
WDW EM
SSB 0 Hz
TE 298.0 K
D1 0.10000000 sec
DELTA 0.01500000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2253015 MHz
F2 - Processing parameters
SI 65536
WDW EM
SSB 0 Hz
GB 0
PC 1.00



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



4.51
¹³C NMR (CDCl₃, 126 MHz)

```

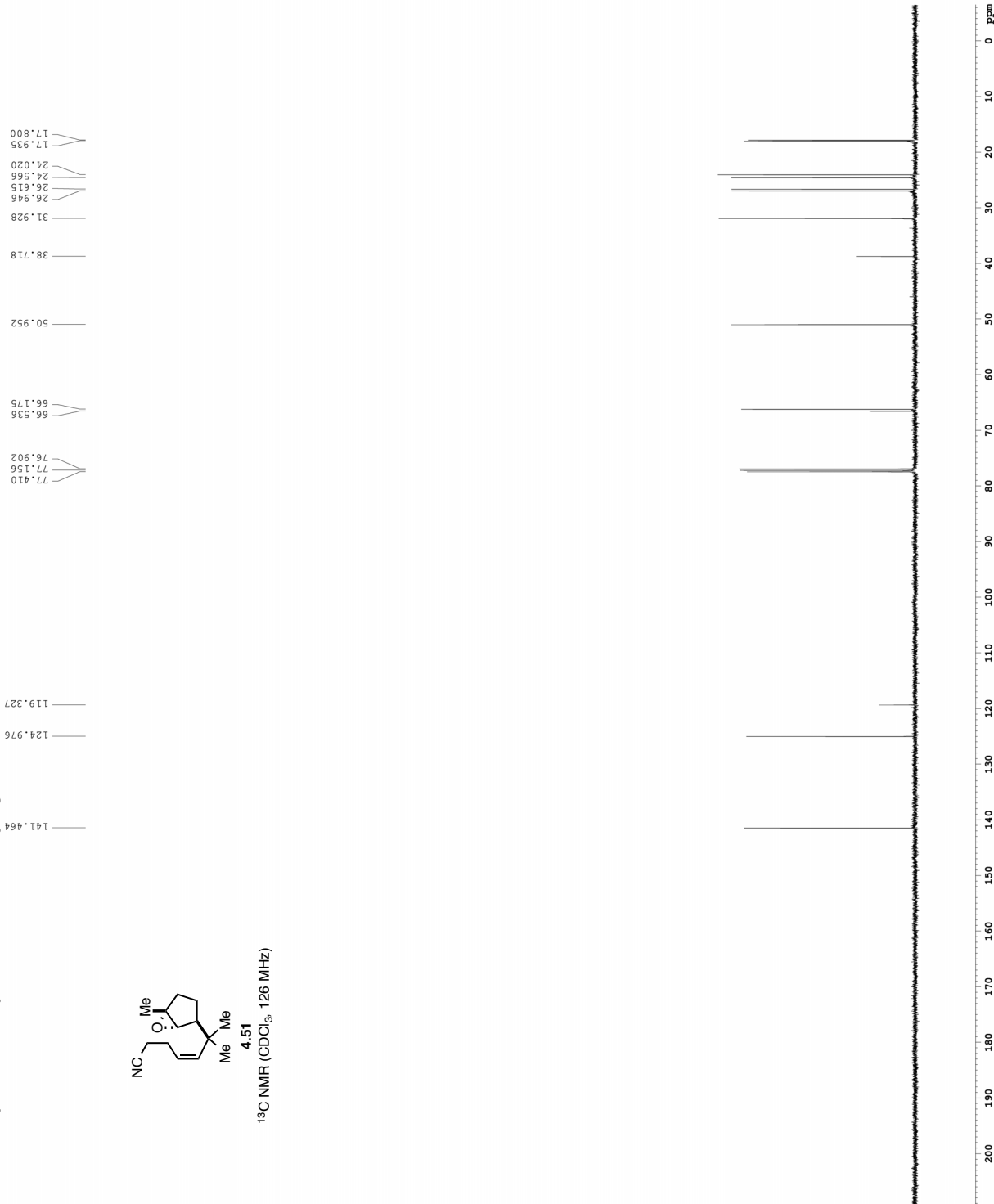
Current: Exp. Parameters
NAME: C03-19-madp 2
EXNO: 2
DATE_ TIME: /mm/yyyy/HH:MM:SS
DATA_PATH: /mmr/jamiso/NMRdata

F2 - Acquisition Parameters
Date_ Time: 20161209 15:04
PROBHD: 5 mm CPTCI 1H-
PULPROG: Spinecho30p-prd
SOLVENT: CDCl3
NS: 124
DS: 4
SWH: 30300.031 Hz
FIDRES: 0.482888 Hz
AQ: 1.0813480 sec
RG: 2896.3
AQ: 16.700000 usec
DE: 6.00 usec
TE: 0.29810 K
D1: 0.03000000 sec
d11: 0.00000000 sec
D16: 0.00000000 sec
MCREST: 0 sec
MCRPRG: 0
MCRW: 0.01300000 sec
F2: 126.140 usec

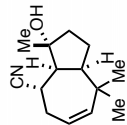
===== CHANNEL f1 13C =====
NUC1: 13C
P1: 16.55 usec
PL1: 0.00 dB
P12: 2000.00 usec
PL12: 120.00 dB
SF01: 125.7942548 MHz
SF02: 500.2225911 MHz
SFO1: 2.70 dB
SFO2: 2.70 dB
SPRAME[1]: Crp60.0.5.20.1 GB
SPRAME[2]: Crp60comp.4 GB
SFOFF1: 0 Hz
SFOFF2: 0 Hz

===== CHANNEL f2 =====
CPDPRG[2]: waltz16
PCPD2: 100.00 usec
PL2: 1.60 dB
PL2: 1.60 dB
SF02: 500.2225911 MHz
===== GRADIENT CHANNEL =====
GPMAX[1]: 0 %
GPMAX[2]: 0 %
SINE: 100
GPMIN[1]: 0 %
GPMIN[2]: 0 %
GF21: 30.00 %
GF22: 0 %
GF23: 0 %
GF24: 0 %
P15: 500.00 usec
P16: 1000.00 usec

F2 - Processing parameters
SI: 65536
SF: 125.7691438 MHz
WDW: 0
SSB: 0
GB: 1.00 Hz
PC: 2.00
    
```

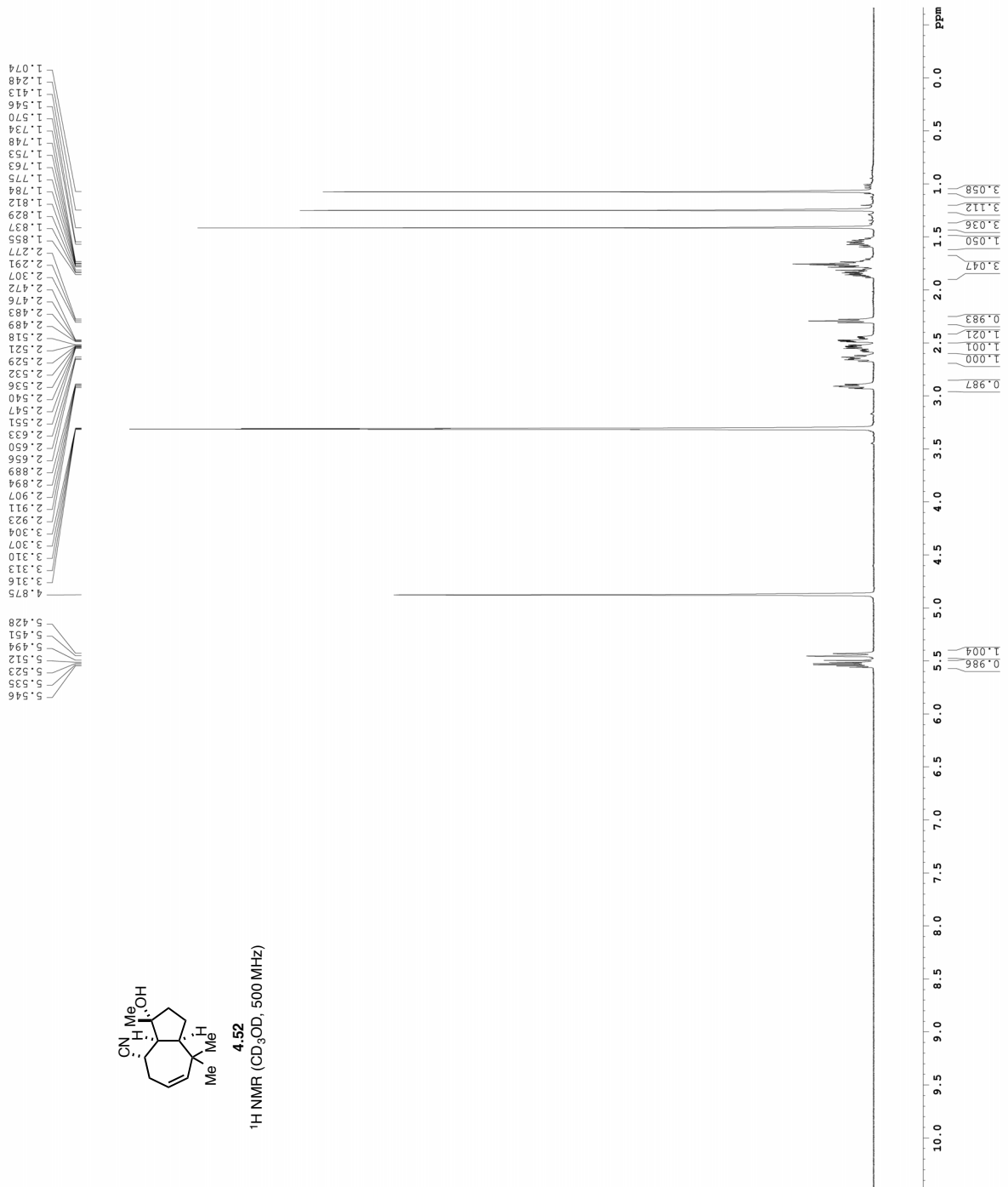


1H spectrum

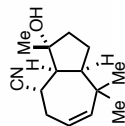


4.52
1H NMR (CD₃OD, 500 MHz)

Current Data Parameters
NAME CRJ3-127-MeOH
PROCNO 1
DATE_ /mm/dd/yyyy
DATAPATH /nmr/jamiso/nmrdata
D2 - Acquisition Parameters
Time_ 20161116
Time 13.20
INSTRUM czi-500
PROBHD 5 mm CPY-500
PULPROG zg30
TD 48074
NS 2
DS 2
SWH 8012.820 Hz
AQ 2.9398176 sec
RG 12.7
WDW EM
SSB 0
TE 298.0 K
D1 0.10000000 sec
D11 0.00000000 sec
MCNRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2253015 MHz
F2 - Processing parameters
SI 65536
SF 500.2253015 MHz
WDW EM
SSB 0
GB 0
PC 4.00



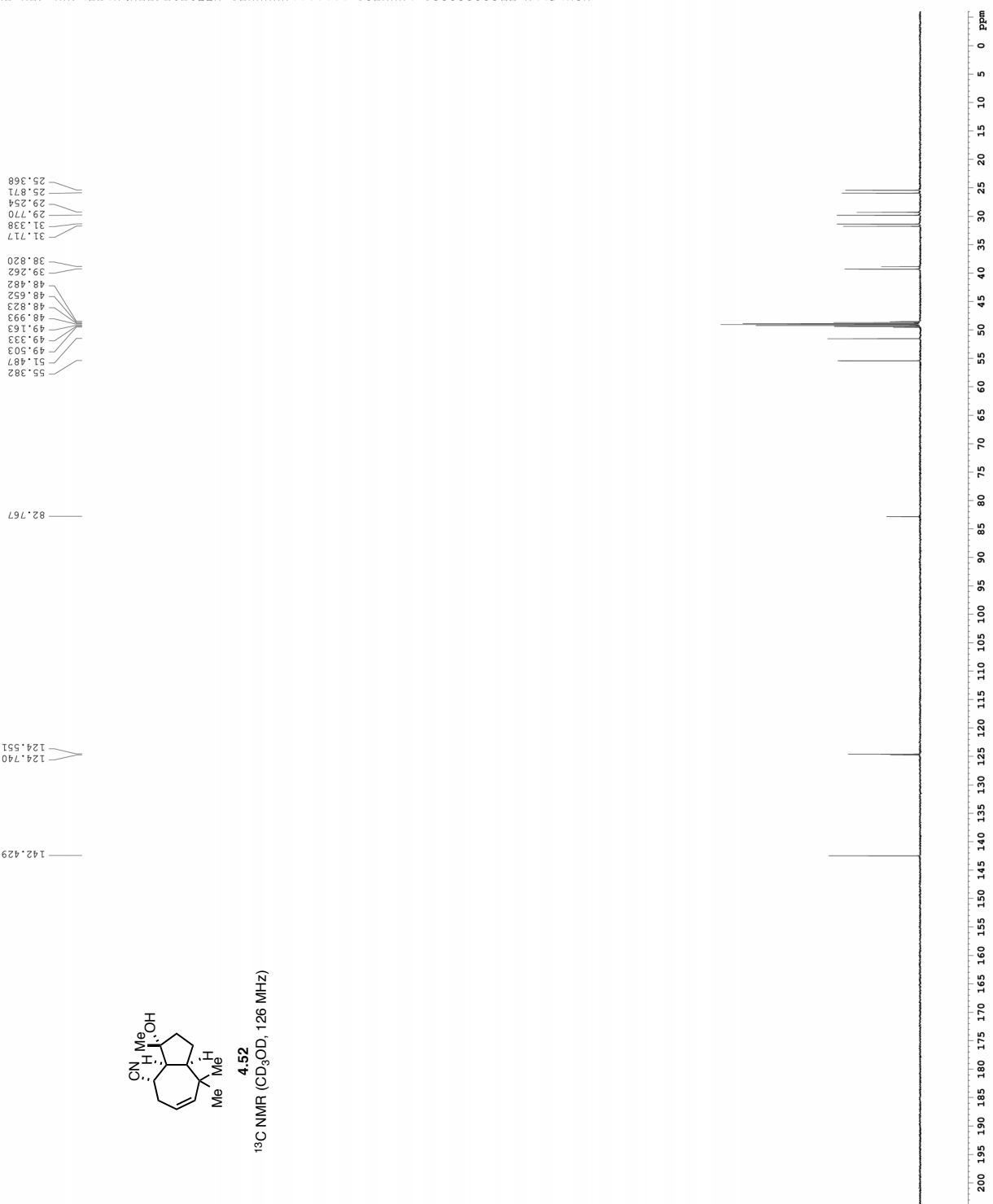
Z-restored spin-echo ¹³C spectrum with ¹H decoupling



4.52
¹³C NMR (CD₃OD, 126 MHz)

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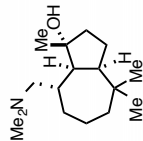
Current Data Parameters
NAME          CN3-127-660H
EXPNO        6
PROCNO       1
DATAF1       /mr/jmlsc/NMRdata
Date_        20161119
Time        11:00
PROBHD       5 mm CPCL1H-
PULPROG      spinvchegp-prd
SOLVENT      CDCl3
DS           16
SRH          30303.031 Hz
AQ           1.0813440 sec
RG           3649.1 usec
DE           16.00 usec
TE           0.257888 K
d11          0.03800000 sec
d17          0.00019600 sec
d19          0.00019600 sec
d21          0.00019600 sec
d23          0.00019600 sec
d25          0.00019600 sec
d27          0.00019600 sec
d29          0.00019600 sec
d31          0.00019600 sec
d33          0.00019600 sec
d35          0.00019600 sec
d37          0.00019600 sec
d39          0.00019600 sec
d41          0.00019600 sec
d43          0.00019600 sec
d45          0.00019600 sec
d47          0.00019600 sec
d49          0.00019600 sec
d51          0.00019600 sec
d53          0.00019600 sec
d55          0.00019600 sec
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d59          0.00019600 sec
d61          0.00019600 sec
d63          0.00019600 sec
d65          0.00019600 sec
d67          0.00019600 sec
d69          0.00019600 sec
d71          0.00019600 sec
d73          0.00019600 sec
d75          0.00019600 sec
d77          0.00019600 sec
d79          0.00019600 sec
d81          0.00019600 sec
d83          0.00019600 sec
d85          0.00019600 sec
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d107         0.00019600 sec
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d985         0.00019600 sec
d987         0.00019600 sec
d989         0.00019600 sec
d991         0.00019600 sec
d993         0.00019600 sec
d995         0.00019600 sec
d997         0.00019600 sec
d999         0.00019600 sec
===== CHANNEL f1 13C =====
NUC1          13C
P1           16.55 usec
PCPD2        100.00 usec
P12          120.00 dB
SFO1         125.7942548 MHz
SFO2         500.2223011 MHz
SF          500.2223011 MHz
===== CHANNEL f2 =====
CPDPRG2      waitz16
PCPD2        100.00 usec
P12          120.00 dB
SFO1         125.7942548 MHz
SFO2         500.2223011 MHz
SF          500.2223011 MHz
===== GRADIENT CHANNEL =====
GENDM[1]     SINE.100
GENDM[2]     SINE.100
GEXZ1        0 %
GEXZ2        0 %
GEXZ3        0 %
GEXZ4        0 %
GEXZ5        0 %
GEXZ6        0 %
GEXZ7        0 %
GEXZ8        0 %
GEXZ9        0 %
GEXZ10       0 %
GEXZ11       0 %
GEXZ12       0 %
GEXZ13       0 %
GEXZ14       0 %
GEXZ15       0 %
GEXZ16       0 %
GEXZ17       0 %
GEXZ18       0 %
GEXZ19       0 %
GEXZ20       0 %
GEXZ21       0 %
GEXZ22       0 %
GEXZ23       0 %
GEXZ24       0 %
GEXZ25       0 %
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GEXZ95       0 %
GEXZ96       0 %
GEXZ97       0 %
GEXZ98       0 %
GEXZ99       0 %
GEXZ100      0 %
===== Processing Parameters =====
SI           65536
SF           125.7694254 MHz
WDW          EM
SSB          0
GB           0
PC           2.00
  
```



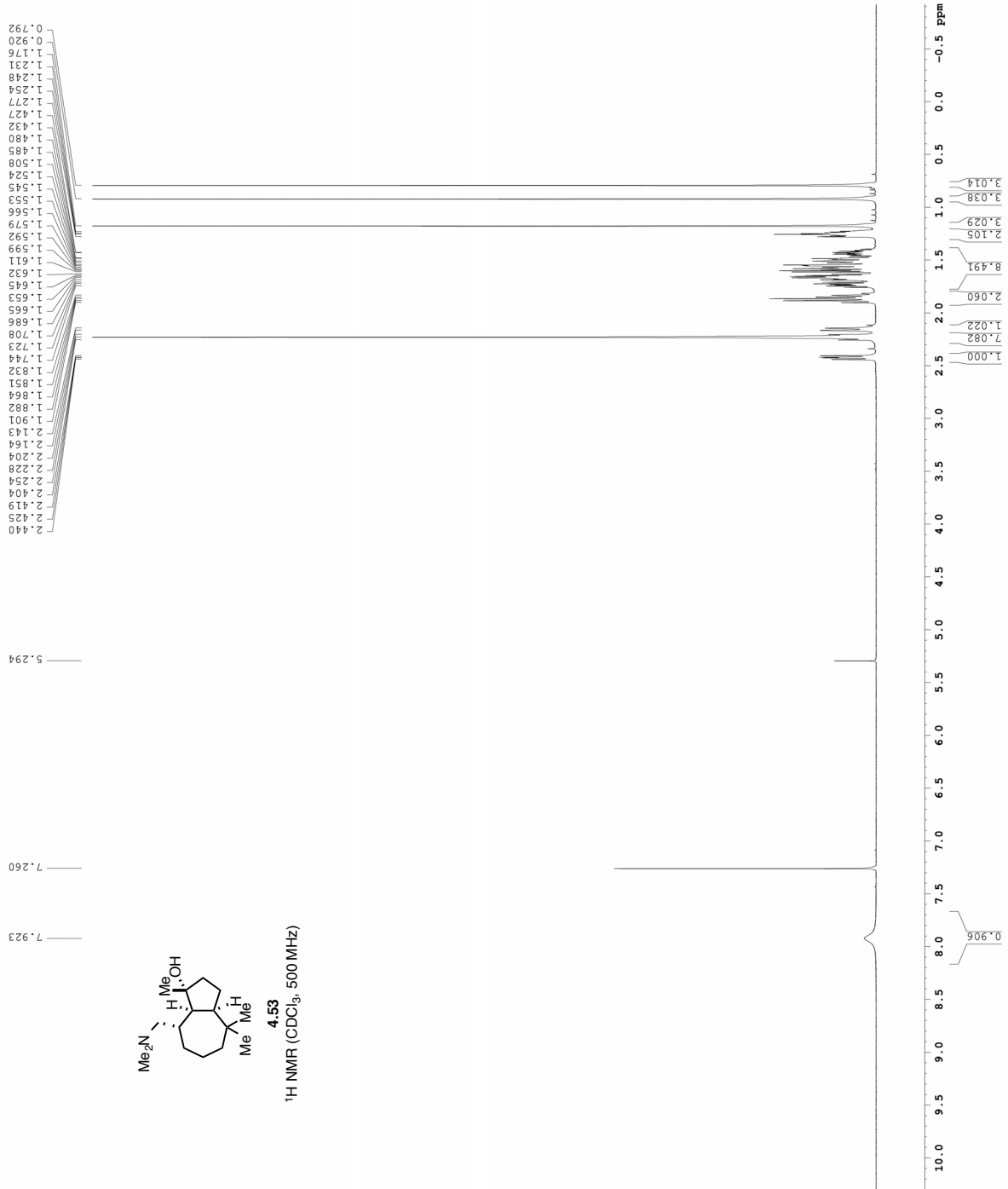
1H spectrum

Current Data Parameters
NAME CRJ3-173-pure
EXPNO 1
PROCNO 1
DATE_ /nmr/jamiso/NMRdata
DATA_PATH /nmr/jamiso/NMRdata
F2 - Acquisition Parameters
Time 20170126
Time 13.56
INSTRUM av600
PROBHD 5 mm CPBPR
PULPROG zg30
TD 96152
FIDRES 0.1352
SOLVENT CDCl3
NS 2
DS 2
SWH 9615.395 Hz
AQ 0.00000000 sec
RG 4.9399042 sec
RG 59.000 usec
DE 3.070 usec
TE 298.0 K
D1 0.10000000 sec
D0 1

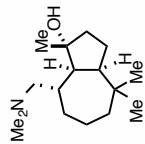
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 13C
P1 12.00 usec
PL1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 600.1300344 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



4.53
1H NMR (CDCl₃, 500 MHz)



¹³C spectrum with ¹H decoupling



4.53
¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME          CRJ3-175-pure
EXPNO        2
PROCNO       1
PROCNAME     /nmr/jamiso/NMRdata
Date_        20170225
Time         14:00
INSTRUM      spect
PROBHD       5 mm CPBBO BB-
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
DS           3
SWH           36231.883 Hz
AQ           0.9043566 sec
RG           11.2650 usec
DE           19.65 usec
TE           298.0 K
D1           0.40000000 sec
D11          0.03000000 sec
TD0          1

===== CHANNEL f1 =====
NUC1          13C
P1           10.00 usec
PL1          64.00000000 W

===== CHANNEL f2 =====
NUC2          13C
P2           10.00 usec
PL2          64.00000000 W

===== CHANNEL f3 =====
NUC3          1H
P3           19.65 usec
PL3          0.36000001 W

===== CHANNEL f4 =====
NUC4          1H
P4           19.65 usec
PL4          0.36000001 W

===== CHANNEL f5 =====
NUC5          13C
P5           10.00 usec
PL5          64.00000000 W

===== CHANNEL f6 =====
NUC6          13C
P6           10.00 usec
PL6          64.00000000 W

===== CHANNEL f7 =====
NUC7          13C
P7           10.00 usec
PL7          64.00000000 W

===== CHANNEL f8 =====
NUC8          13C
P8           10.00 usec
PL8          64.00000000 W

===== CHANNEL f9 =====
NUC9          13C
P9           10.00 usec
PL9          64.00000000 W

===== CHANNEL f10 =====
NUC10         13C
P10          10.00 usec
PL10         64.00000000 W

===== CHANNEL f11 =====
NUC11         13C
P11          10.00 usec
PL11         64.00000000 W

===== CHANNEL f12 =====
NUC12         13C
P12          10.00 usec
PL12         64.00000000 W

===== CHANNEL f13 =====
NUC13         13C
P13          10.00 usec
PL13         64.00000000 W

===== CHANNEL f14 =====
NUC14         13C
P14          10.00 usec
PL14         64.00000000 W

===== CHANNEL f15 =====
NUC15         13C
P15          10.00 usec
PL15         64.00000000 W

===== CHANNEL f16 =====
NUC16         13C
P16          10.00 usec
PL16         64.00000000 W

===== CHANNEL f17 =====
NUC17         13C
P17          10.00 usec
PL17         64.00000000 W

===== CHANNEL f18 =====
NUC18         13C
P18          10.00 usec
PL18         64.00000000 W

===== CHANNEL f19 =====
NUC19         13C
P19          10.00 usec
PL19         64.00000000 W

===== CHANNEL f20 =====
NUC20         13C
P20          10.00 usec
PL20         64.00000000 W

===== CHANNEL f21 =====
NUC21         13C
P21          10.00 usec
PL21         64.00000000 W

===== CHANNEL f22 =====
NUC22         13C
P22          10.00 usec
PL22         64.00000000 W

===== CHANNEL f23 =====
NUC23         13C
P23          10.00 usec
PL23         64.00000000 W

===== CHANNEL f24 =====
NUC24         13C
P24          10.00 usec
PL24         64.00000000 W

===== CHANNEL f25 =====
NUC25         13C
P25          10.00 usec
PL25         64.00000000 W

===== CHANNEL f26 =====
NUC26         13C
P26          10.00 usec
PL26         64.00000000 W

===== CHANNEL f27 =====
NUC27         13C
P27          10.00 usec
PL27         64.00000000 W

===== CHANNEL f28 =====
NUC28         13C
P28          10.00 usec
PL28         64.00000000 W

===== CHANNEL f29 =====
NUC29         13C
P29          10.00 usec
PL29         64.00000000 W

===== CHANNEL f30 =====
NUC30         13C
P30          10.00 usec
PL30         64.00000000 W

===== CHANNEL f31 =====
NUC31         13C
P31          10.00 usec
PL31         64.00000000 W

===== CHANNEL f32 =====
NUC32         13C
P32          10.00 usec
PL32         64.00000000 W

===== CHANNEL f33 =====
NUC33         13C
P33          10.00 usec
PL33         64.00000000 W

===== CHANNEL f34 =====
NUC34         13C
P34          10.00 usec
PL34         64.00000000 W

===== CHANNEL f35 =====
NUC35         13C
P35          10.00 usec
PL35         64.00000000 W

===== CHANNEL f36 =====
NUC36         13C
P36          10.00 usec
PL36         64.00000000 W

===== CHANNEL f37 =====
NUC37         13C
P37          10.00 usec
PL37         64.00000000 W

===== CHANNEL f38 =====
NUC38         13C
P38          10.00 usec
PL38         64.00000000 W

===== CHANNEL f39 =====
NUC39         13C
P39          10.00 usec
PL39         64.00000000 W

===== CHANNEL f40 =====
NUC40         13C
P40          10.00 usec
PL40         64.00000000 W

===== CHANNEL f41 =====
NUC41         13C
P41          10.00 usec
PL41         64.00000000 W

===== CHANNEL f42 =====
NUC42         13C
P42          10.00 usec
PL42         64.00000000 W

===== CHANNEL f43 =====
NUC43         13C
P43          10.00 usec
PL43         64.00000000 W

===== CHANNEL f44 =====
NUC44         13C
P44          10.00 usec
PL44         64.00000000 W

===== CHANNEL f45 =====
NUC45         13C
P45          10.00 usec
PL45         64.00000000 W

===== CHANNEL f46 =====
NUC46         13C
P46          10.00 usec
PL46         64.00000000 W

===== CHANNEL f47 =====
NUC47         13C
P47          10.00 usec
PL47         64.00000000 W

===== CHANNEL f48 =====
NUC48         13C
P48          10.00 usec
PL48         64.00000000 W

===== CHANNEL f49 =====
NUC49         13C
P49          10.00 usec
PL49         64.00000000 W

===== CHANNEL f50 =====
NUC50         13C
P50          10.00 usec
PL50         64.00000000 W

===== CHANNEL f51 =====
NUC51         13C
P51          10.00 usec
PL51         64.00000000 W

===== CHANNEL f52 =====
NUC52         13C
P52          10.00 usec
PL52         64.00000000 W

===== CHANNEL f53 =====
NUC53         13C
P53          10.00 usec
PL53         64.00000000 W

===== CHANNEL f54 =====
NUC54         13C
P54          10.00 usec
PL54         64.00000000 W

===== CHANNEL f55 =====
NUC55         13C
P55          10.00 usec
PL55         64.00000000 W

===== CHANNEL f56 =====
NUC56         13C
P56          10.00 usec
PL56         64.00000000 W

===== CHANNEL f57 =====
NUC57         13C
P57          10.00 usec
PL57         64.00000000 W

===== CHANNEL f58 =====
NUC58         13C
P58          10.00 usec
PL58         64.00000000 W

===== CHANNEL f59 =====
NUC59         13C
P59          10.00 usec
PL59         64.00000000 W

===== CHANNEL f60 =====
NUC60         13C
P60          10.00 usec
PL60         64.00000000 W

===== CHANNEL f61 =====
NUC61         13C
P61          10.00 usec
PL61         64.00000000 W

===== CHANNEL f62 =====
NUC62         13C
P62          10.00 usec
PL62         64.00000000 W

===== CHANNEL f63 =====
NUC63         13C
P63          10.00 usec
PL63         64.00000000 W

===== CHANNEL f64 =====
NUC64         13C
P64          10.00 usec
PL64         64.00000000 W

===== CHANNEL f65 =====
NUC65         13C
P65          10.00 usec
PL65         64.00000000 W

===== CHANNEL f66 =====
NUC66         13C
P66          10.00 usec
PL66         64.00000000 W

===== CHANNEL f67 =====
NUC67         13C
P67          10.00 usec
PL67         64.00000000 W

===== CHANNEL f68 =====
NUC68         13C
P68          10.00 usec
PL68         64.00000000 W

===== CHANNEL f69 =====
NUC69         13C
P69          10.00 usec
PL69         64.00000000 W

===== CHANNEL f70 =====
NUC70         13C
P70          10.00 usec
PL70         64.00000000 W

===== CHANNEL f71 =====
NUC71         13C
P71          10.00 usec
PL71         64.00000000 W

===== CHANNEL f72 =====
NUC72         13C
P72          10.00 usec
PL72         64.00000000 W

===== CHANNEL f73 =====
NUC73         13C
P73          10.00 usec
PL73         64.00000000 W

===== CHANNEL f74 =====
NUC74         13C
P74          10.00 usec
PL74         64.00000000 W

===== CHANNEL f75 =====
NUC75         13C
P75          10.00 usec
PL75         64.00000000 W

===== CHANNEL f76 =====
NUC76         13C
P76          10.00 usec
PL76         64.00000000 W

===== CHANNEL f77 =====
NUC77         13C
P77          10.00 usec
PL77         64.00000000 W

===== CHANNEL f78 =====
NUC78         13C
P78          10.00 usec
PL78         64.00000000 W

===== CHANNEL f79 =====
NUC79         13C
P79          10.00 usec
PL79         64.00000000 W

===== CHANNEL f80 =====
NUC80         13C
P80          10.00 usec
PL80         64.00000000 W

===== CHANNEL f81 =====
NUC81         13C
P81          10.00 usec
PL81         64.00000000 W

===== CHANNEL f82 =====
NUC82         13C
P82          10.00 usec
PL82         64.00000000 W

===== CHANNEL f83 =====
NUC83         13C
P83          10.00 usec
PL83         64.00000000 W

===== CHANNEL f84 =====
NUC84         13C
P84          10.00 usec
PL84         64.00000000 W

===== CHANNEL f85 =====
NUC85         13C
P85          10.00 usec
PL85         64.00000000 W

===== CHANNEL f86 =====
NUC86         13C
P86          10.00 usec
PL86         64.00000000 W

===== CHANNEL f87 =====
NUC87         13C
P87          10.00 usec
PL87         64.00000000 W

===== CHANNEL f88 =====
NUC88         13C
P88          10.00 usec
PL88         64.00000000 W

===== CHANNEL f89 =====
NUC89         13C
P89          10.00 usec
PL89         64.00000000 W

===== CHANNEL f90 =====
NUC90         13C
P90          10.00 usec
PL90         64.00000000 W

===== CHANNEL f91 =====
NUC91         13C
P91          10.00 usec
PL91         64.00000000 W

===== CHANNEL f92 =====
NUC92         13C
P92          10.00 usec
PL92         64.00000000 W

===== CHANNEL f93 =====
NUC93         13C
P93          10.00 usec
PL93         64.00000000 W

===== CHANNEL f94 =====
NUC94         13C
P94          10.00 usec
PL94         64.00000000 W

===== CHANNEL f95 =====
NUC95         13C
P95          10.00 usec
PL95         64.00000000 W

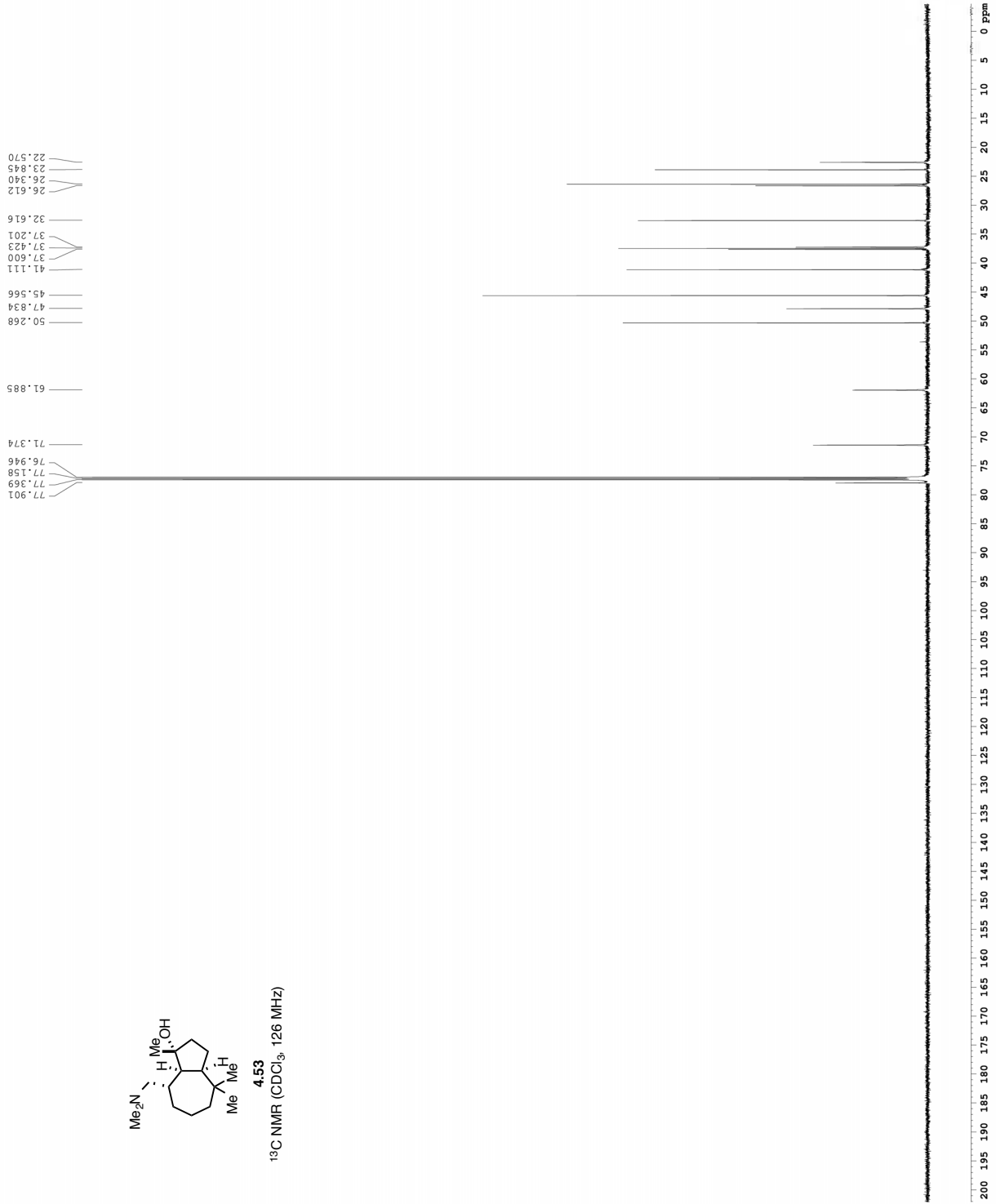
===== CHANNEL f96 =====
NUC96         13C
P96          10.00 usec
PL96         64.00000000 W

===== CHANNEL f97 =====
NUC97         13C
P97          10.00 usec
PL97         64.00000000 W

===== CHANNEL f98 =====
NUC98         13C
P98          10.00 usec
PL98         64.00000000 W

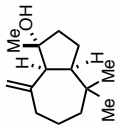
===== CHANNEL f99 =====
NUC99         13C
P99          10.00 usec
PL99         64.00000000 W

===== CHANNEL f100 =====
NUC100        13C
P100         10.00 usec
PL100        64.00000000 W
    
```

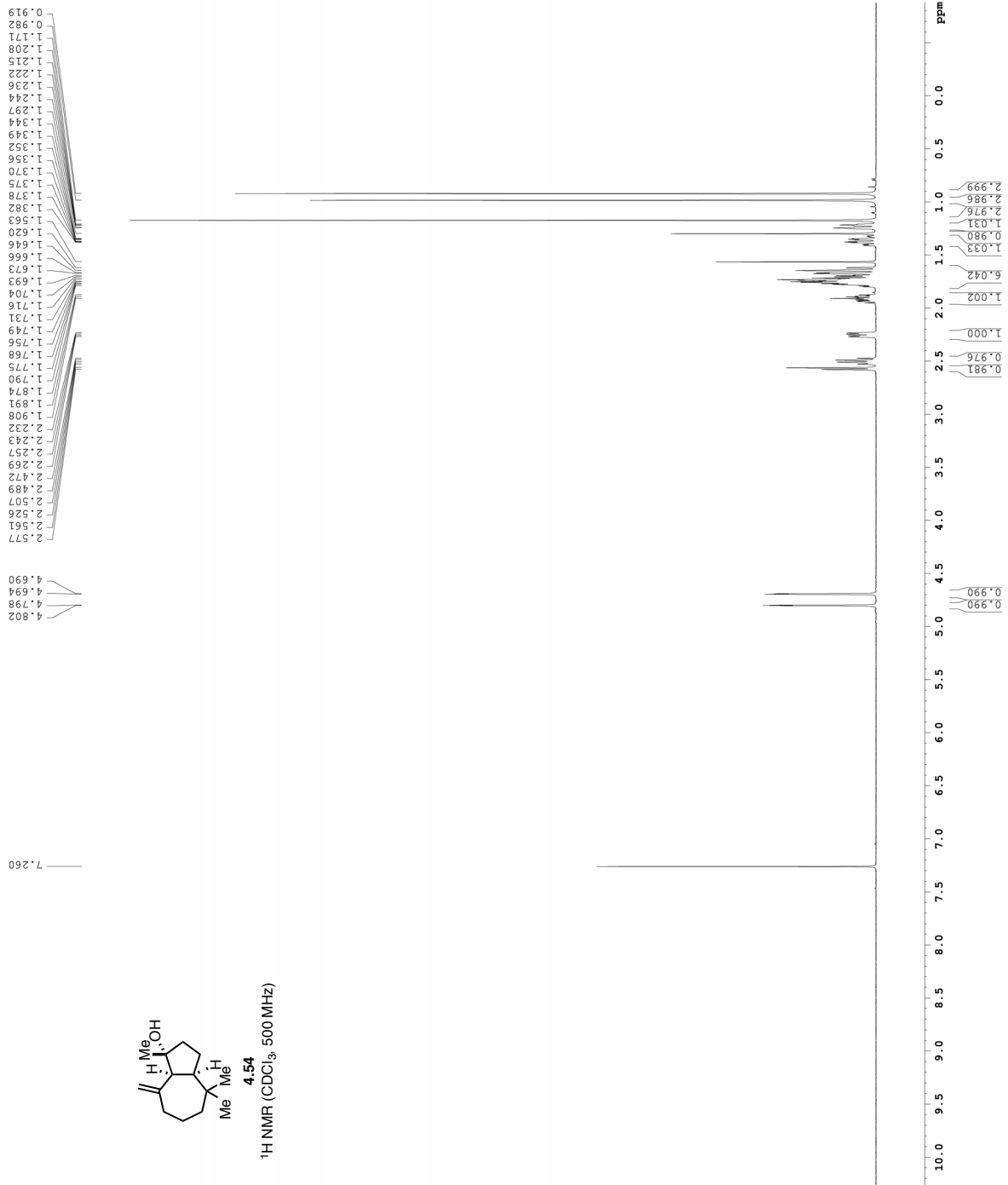


¹H spectrum

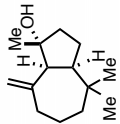
Current Data Parameters
NAME CRJ3-171-pure
EXPNO 1
DATE_ 20170113
DATAPATH /nmr/jamiso/NMRdata
F2 - Acquisition Parameters
Time 11.04
INSTRUM cryo-500
PULPROG zg30
ID 48074
NS 2
DS 2
SWH 8012.620 Hz
AQ 0.01500000 sec
RG 62.415
DE 2.980 usec
TE 298.0 K sec
D1 0.10000000 sec
MCNRSZ 0 sec, 0.01500000 sec
===== CHANNEL f1 =====
NUC1
P1 7.50 usec
PL1 1.60 dB
SFO1 500.225015 MHz
F2 - Processing Parameters
SI 65534
WDW 500.225015 MHz
SSB 0 Hz
GB 0
PC 1.00



4.54
¹H NMR (CDCl₃, 500 MHz)



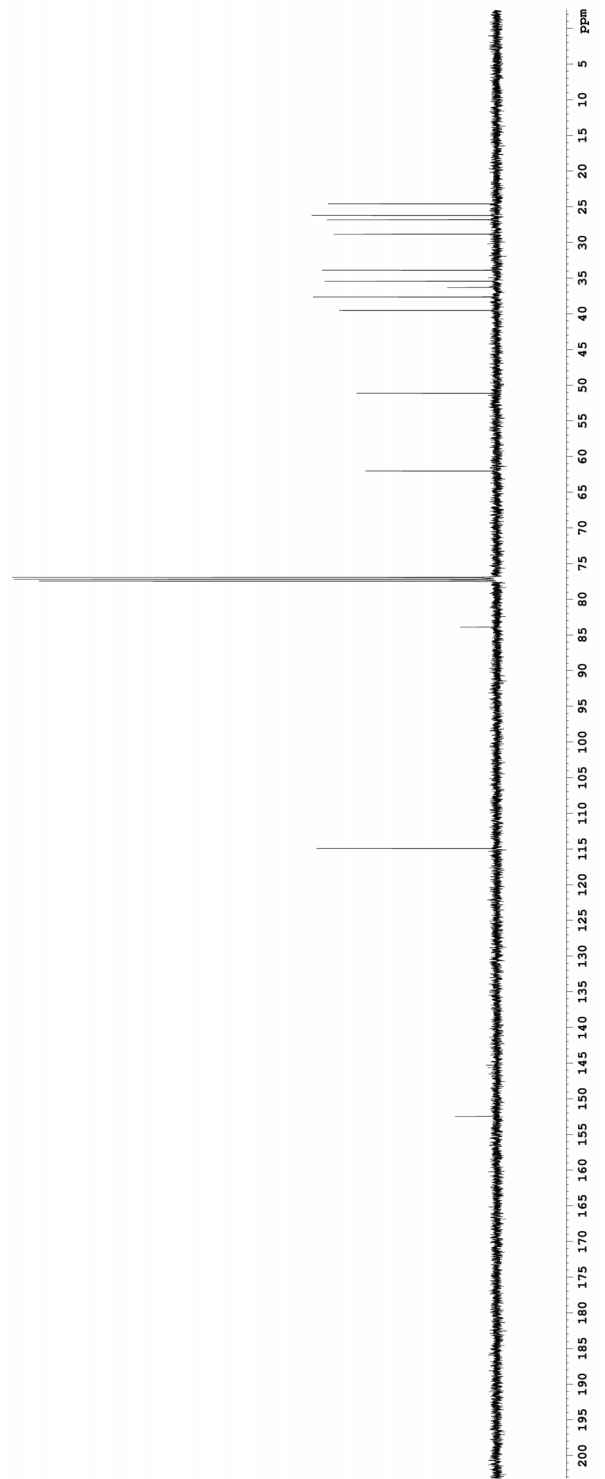
Z-restored spin-echo 13C spectrum with 1H decoupling



4.54

13C NMR (CDCl₃, 126 MHz)

```
Current Data Parameters
NAME      CRJ3-171-pure
PROCNO    1
DATAPATH /nmr/jmiso/nmrdata
F2 - Acquisition Parameters
  CPDPRG2  waltz16
  Time     201.18
  INSTRUM  spect
  PULPROG  zgpg30
  TD        65536
  NS       2256
  DS        4
  SWH      30303.01 Hz
  FIDRES   0.462288 Hz
  AQ       1.081993 sec
  RG        32
  DM       16.500 usec
  DE        2.000 usec
  TE       298.0 K
  D1       0.2500000 sec
  d11      0.0002000 sec
  d12      0.0002000 sec
  d13      0.00019600 sec
  ACQTIME  0.50019600 sec
  MCHNK1   0.431500000 sec
  F2       33.10 usec
  ===== CHANNEL f1 =====
  NU1      13C
  P1       16.25 usec
  PL1      0.00 dB
  PC1      500.00 usec
  ===== CHANNEL f2 =====
  NU2      1H
  P2       10.00 usec
  PL2      19.00 dB
  PL12     24.50 dB
  SF02     500.2225011 MHz
  ===== GRADIENT CHANNEL =====
  GPMAX[1] 0 %
  GPHY[1]  0 %
  GPMAX[2] 0 %
  GPHY[2]  0 %
  GPMAX[3] 30.00 %
  GPHY[3]  50.00 %
  GPMAX[4] 50.00 %
  GPHY[4]  1000.00 usec
  P15      1000.00 usec
  ===== Processing parameters =====
  SF       125.7604074 MHz
  ASK      0
  ASB      0
  LB       0
  PC       2.00
```



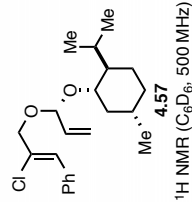
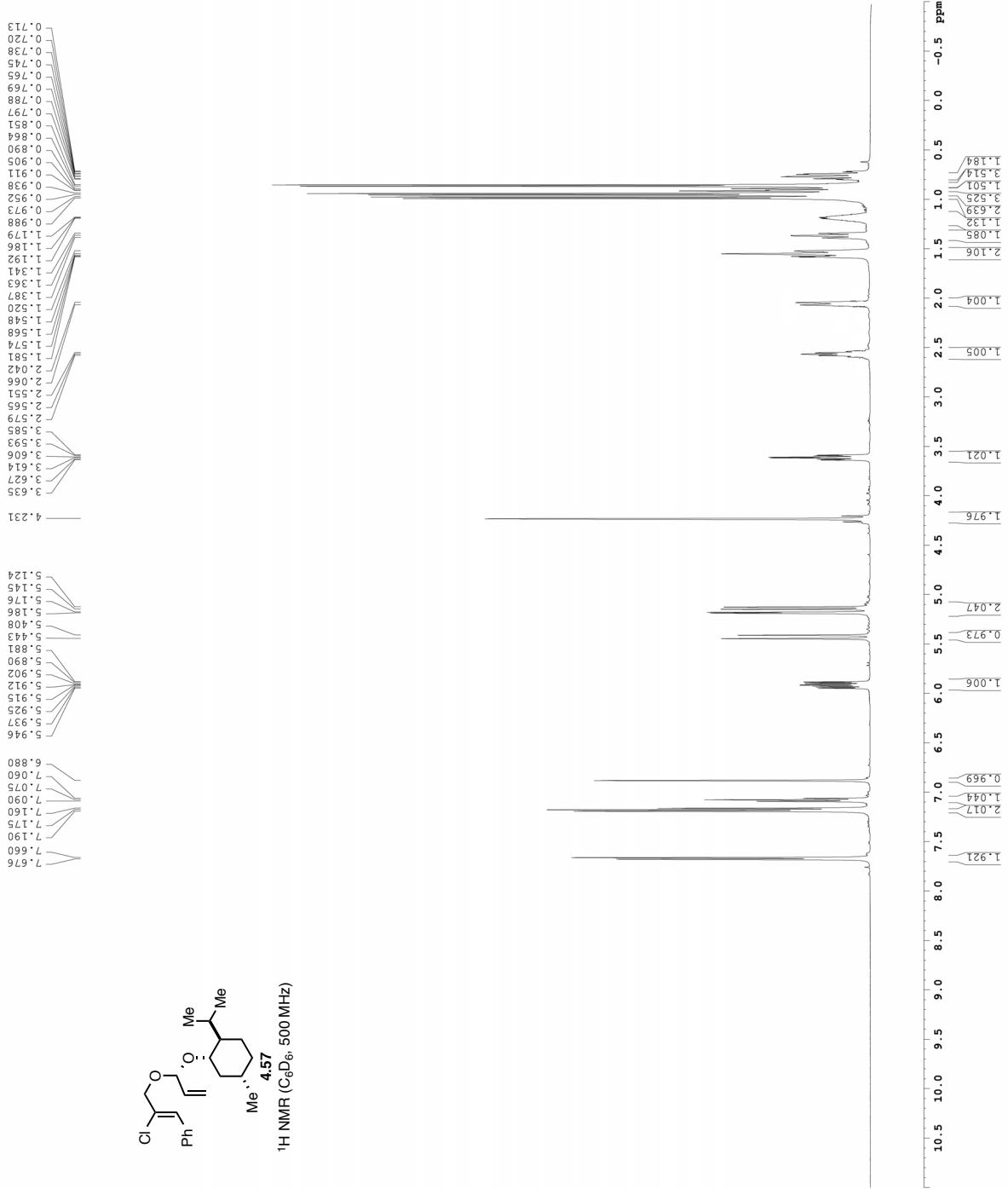
¹H spectrum

```

Current Data Parameters
NAME          PG-2087P
EXPNO         1
PROCNO        1
DATAF1        /v/data/zhaops/nmr
F2 - Acquisition Parameters
Date_         20170223
Time         11:05:00
PROBHD        5 mm CPTCI 1H-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            8
DS            4
SRH           8012.820 Hz
FIDRES        0.098043 Hz
AQ            5.0982775 sec
RG            327.5
RW            62.400 usec
DE            6.00 usec
TE            300.2
D1            0.10000000 sec
MCREST        0 sec
MCWRK         0.01500000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            12.00 usec
PL1          -1.50 dB
SFO1         500.2235015 MHz

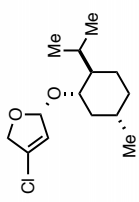
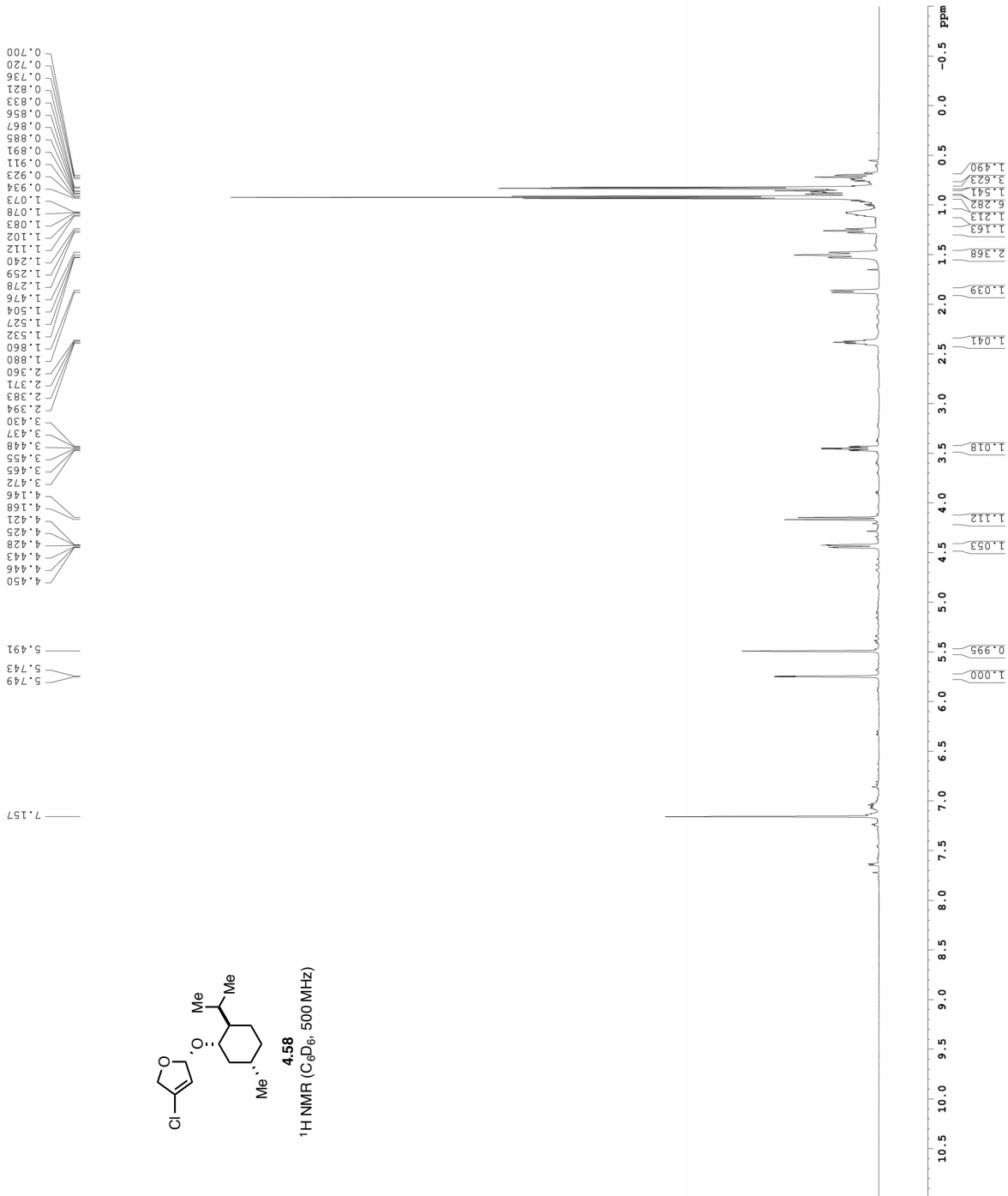
F2 - Processing parameters
SI            65536
SF           500.2198953 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```



1H spectrum

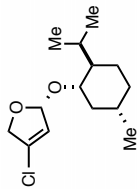
```

Current Data Parameters
NAME      F2-2093-P
EXPNO    1
PROCNO   1
DATAF1   /v/data/zhaop3/mr
DATAF2   /v/data/zhaop3/mr
F2 - Acquisition Parameters
Date_    20170225
Time     18:02
INSTRUM  av600
PROBHD   5 mm CPBBO 430
PULPROG  zgpg30
TD        98074
SOLVENT  CDCl3
DS        2
SWH       9615.385 Hz
FIDRES    0.0998478 Hz
AQ         5.0998478 sec
RG         512.000 usec
DW         52.000 usec
DE         238.0 K
TE         300.2 K
D1         0.10000000 sec
TD0        1
===== CHANNEL f1 =====
SFO1      600.1342009 MHz
NUC1       13C
P1         12.00 usec
PL1        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
  
```



4.58
¹H NMR (C₆D₆, 500 MHz)

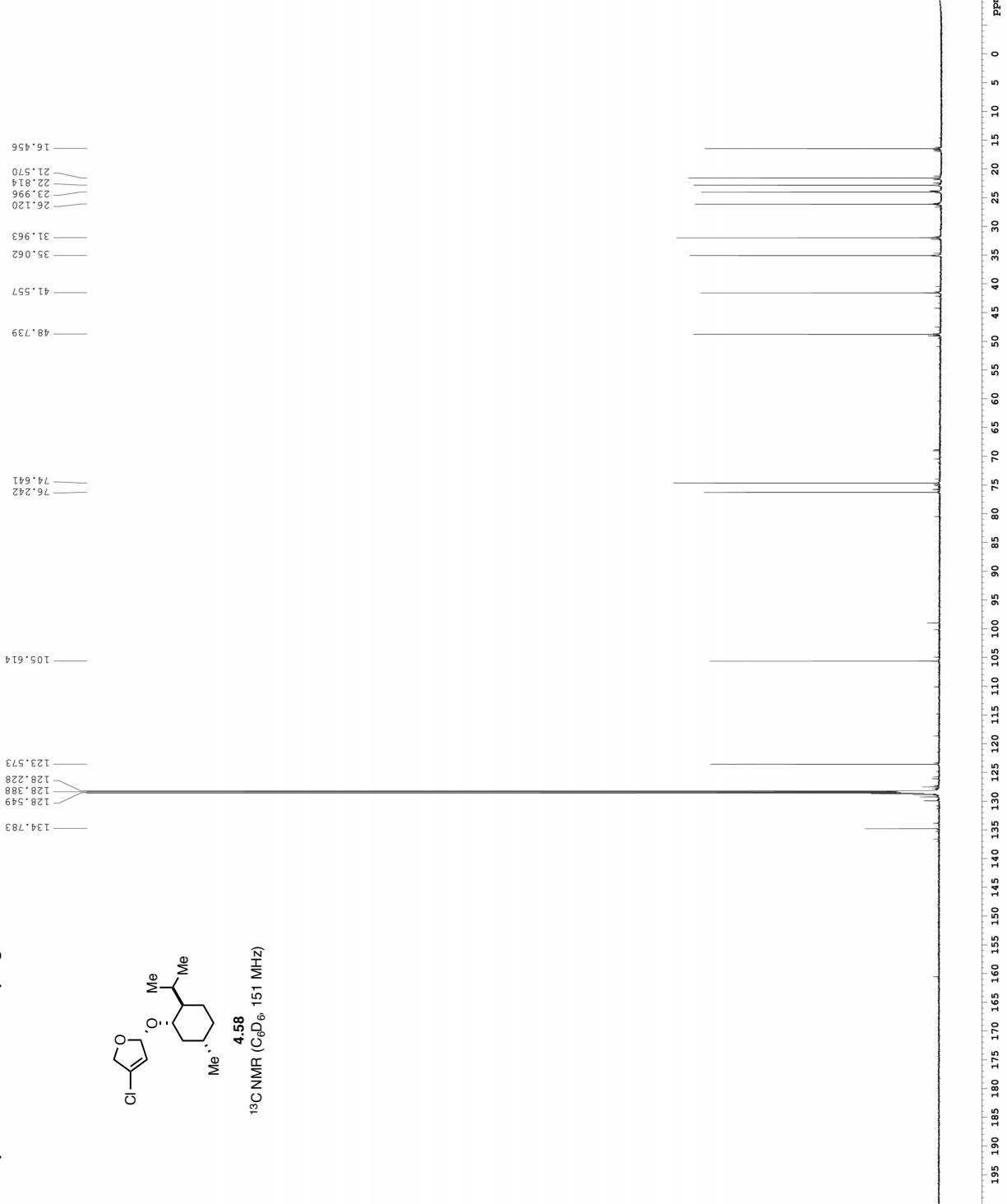
¹³C spectrum with ¹H decoupling



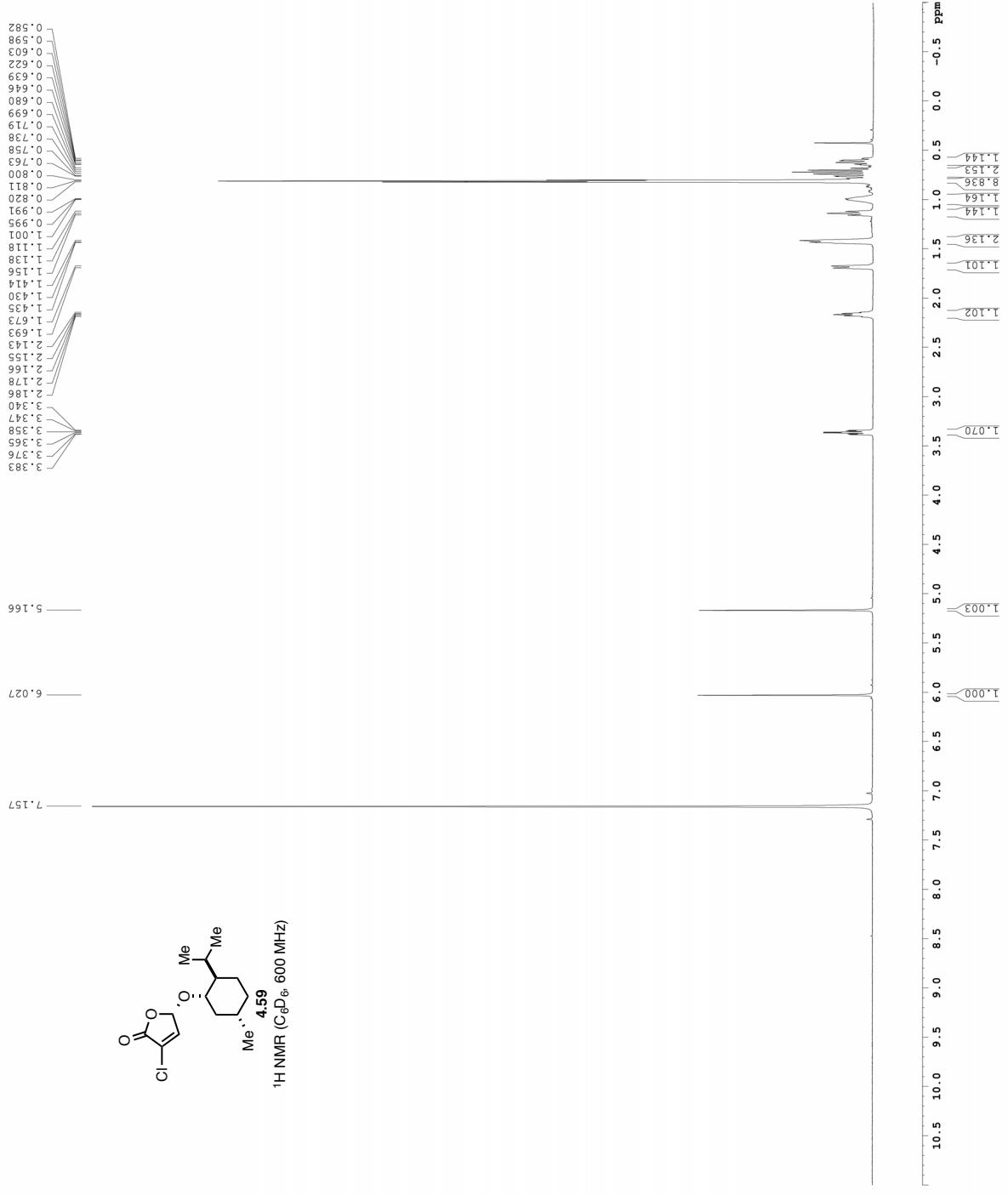
4.58
¹³C NMR (C₆D₆, 151 MHz)

```

Current Data Parameters
NAME      F2-2093-P
EXPNO    2
PROCNO   1
DATAFATH /v/data/zhuop3/mr
F2 - Acquisition Parameters
Date_    20170225
Time     18.00
INSTRUM  spect
PROBHD   5 mm CPBBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
DS        4
SWH      36231.883 Hz
FREQ     125.762 MHz
AQ       0.5902968 sec
RG       13.2050
DE       19.65 usec
TE       300.2 K
D1       0.402880 sec
D11      0.03000000 sec
TD0      1
===== CHANNEL f1 =====
NUC1     13C
MPC1    150.31936 MHz
P1      10.00 usec
PL1     64.00000000 W
===== CHANNEL f2 =====
NUC2     13C
MPC2    605.1336010 MHz
P2      1.00 usec
PL2     0.36000000 W
===== CHANNEL f3 =====
CPDPRG2  waltz16
NUC3     1H
MPC3    500.1360000 MHz
P3      20.00000000 usec
PL3     0.36000000 W
===== CHANNEL f4 =====
PL4     0.36000000 W
F2 - Processing parameters
SI      32768
SF      150.9820284 MHz
WDW     EM
SSB     0
LB      0
GB      0
PC      1.00
  
```



1H spectrum



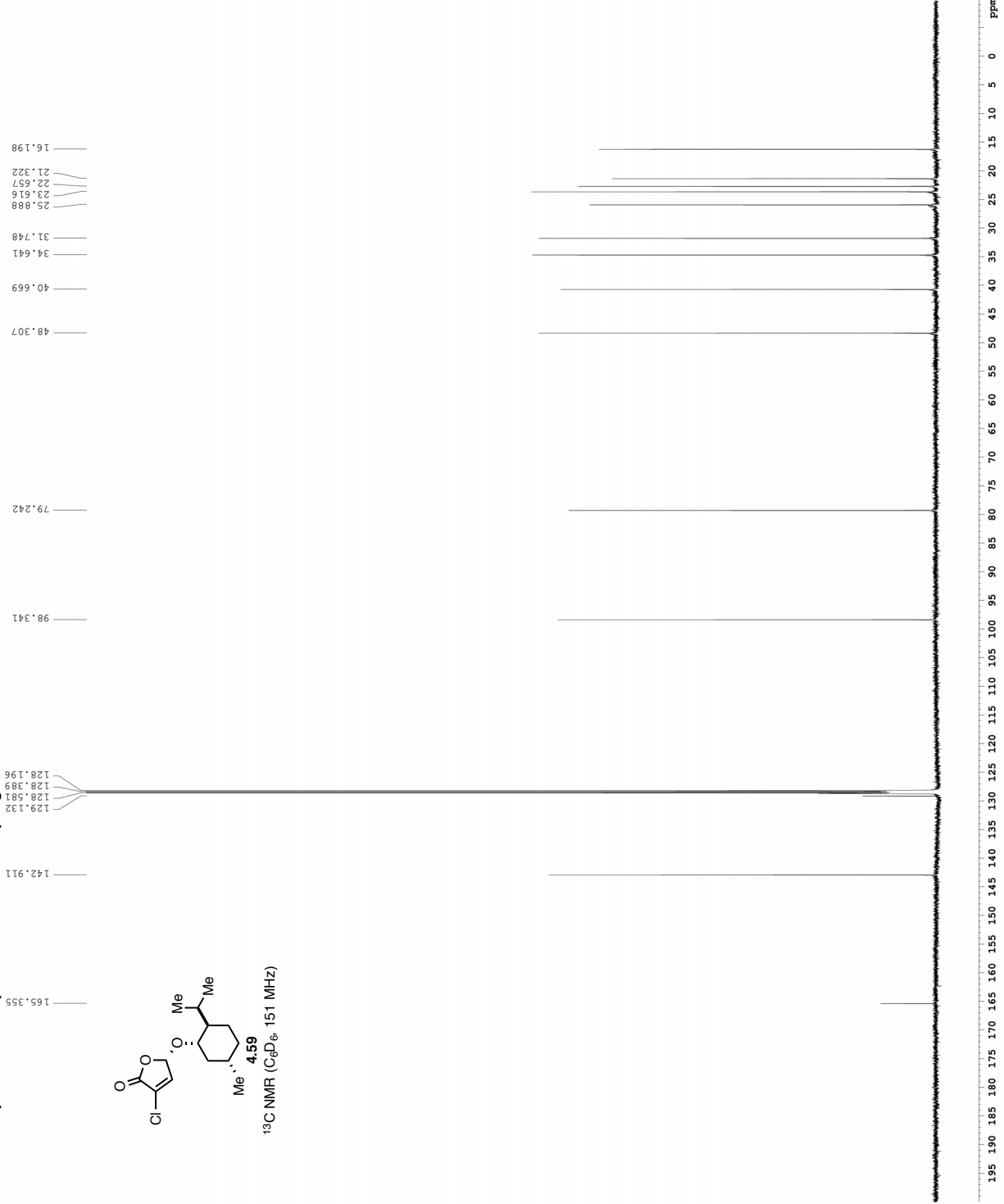
Current Data Parameters
 NAME F2-2094-P
 PROCNO 1
 DATE_ /n/data/zhaop3/nmr
 Date 20170227
 Time 11:14
 F2 - Acquisition Parameters
 NSRROM av600
 PULPROG 5 mm CPBPG 2930
 TD 98074
 NS 8
 DS 2
 SWH 9615.385 Hz
 FREQ 600.1342009 MHz
 AQ 5.0998478 sec
 RG 40.3
 DW 215.00 usec
 DE 236.0 K
 TE 0.10000000 sec
 D1 1

===== CHANNEL f1 =====
 NFO1 600.1342009 MHz
 P1 12.00 usec
 PL1 20.0000000 W
 F2 - Processing parameters
 SI 65536
 SF 600.1300000 MHz
 SSF 0
 LB 0
 GB 0
 PC 1.00

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

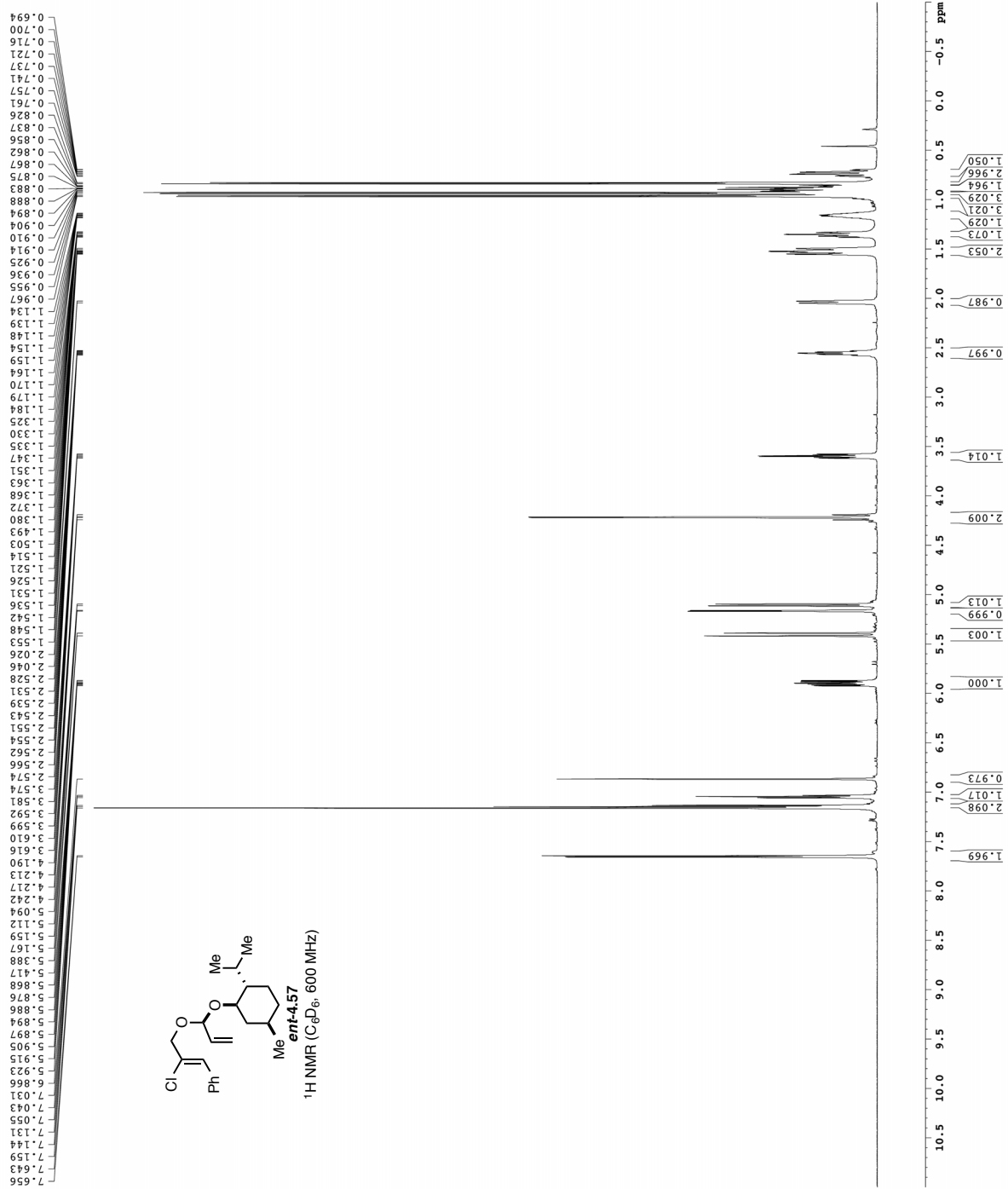
```

Current Data Parameters
NAME          FZ-2094-F
EXPNO        4
DATAPATH    /v/data/zhaep3/mr
F2 - Acquisition Parameters
Date_       20170412
Time       10:50
NAME       cp1300
PROBHD     5 mm CPTCI 1H-
PULPROG    zgpg30
SOLVENT    CDCl3
DS         4
SWH        30303.031 Hz
AQRES     1.0983440 sec
RG         4096
DE         6.000 usec
TE         298.0 K
d11       0.03000000 sec
d12       0.03000000 sec
d13       0.03000000 sec
d14       0.03000000 sec
d15       0.03000000 sec
d16       0.03000000 sec
d17       0.03000000 sec
d18       0.03000000 sec
d19       0.03000000 sec
d20       0.03000000 sec
d21       0.03000000 sec
d22       0.03000000 sec
d23       0.03000000 sec
d24       0.03000000 sec
d25       0.03000000 sec
d26       0.03000000 sec
d27       0.03000000 sec
d28       0.03000000 sec
d29       0.03000000 sec
d30       0.03000000 sec
d31       0.03000000 sec
d32       0.03000000 sec
d33       0.03000000 sec
d34       0.03000000 sec
d35       0.03000000 sec
d36       0.03000000 sec
d37       0.03000000 sec
d38       0.03000000 sec
d39       0.03000000 sec
d40       0.03000000 sec
d41       0.03000000 sec
d42       0.03000000 sec
d43       0.03000000 sec
d44       0.03000000 sec
d45       0.03000000 sec
d46       0.03000000 sec
d47       0.03000000 sec
d48       0.03000000 sec
d49       0.03000000 sec
d50       0.03000000 sec
d51       0.03000000 sec
d52       0.03000000 sec
d53       0.03000000 sec
d54       0.03000000 sec
d55       0.03000000 sec
d56       0.03000000 sec
d57       0.03000000 sec
d58       0.03000000 sec
d59       0.03000000 sec
d60       0.03000000 sec
d61       0.03000000 sec
d62       0.03000000 sec
d63       0.03000000 sec
d64       0.03000000 sec
d65       0.03000000 sec
d66       0.03000000 sec
d67       0.03000000 sec
d68       0.03000000 sec
d69       0.03000000 sec
d70       0.03000000 sec
d71       0.03000000 sec
d72       0.03000000 sec
d73       0.03000000 sec
d74       0.03000000 sec
d75       0.03000000 sec
d76       0.03000000 sec
d77       0.03000000 sec
d78       0.03000000 sec
d79       0.03000000 sec
d80       0.03000000 sec
d81       0.03000000 sec
d82       0.03000000 sec
d83       0.03000000 sec
d84       0.03000000 sec
d85       0.03000000 sec
d86       0.03000000 sec
d87       0.03000000 sec
d88       0.03000000 sec
d89       0.03000000 sec
d90       0.03000000 sec
d91       0.03000000 sec
d92       0.03000000 sec
d93       0.03000000 sec
d94       0.03000000 sec
d95       0.03000000 sec
d96       0.03000000 sec
d97       0.03000000 sec
d98       0.03000000 sec
d99       0.03000000 sec
d100      0.03000000 sec
PC
  
```



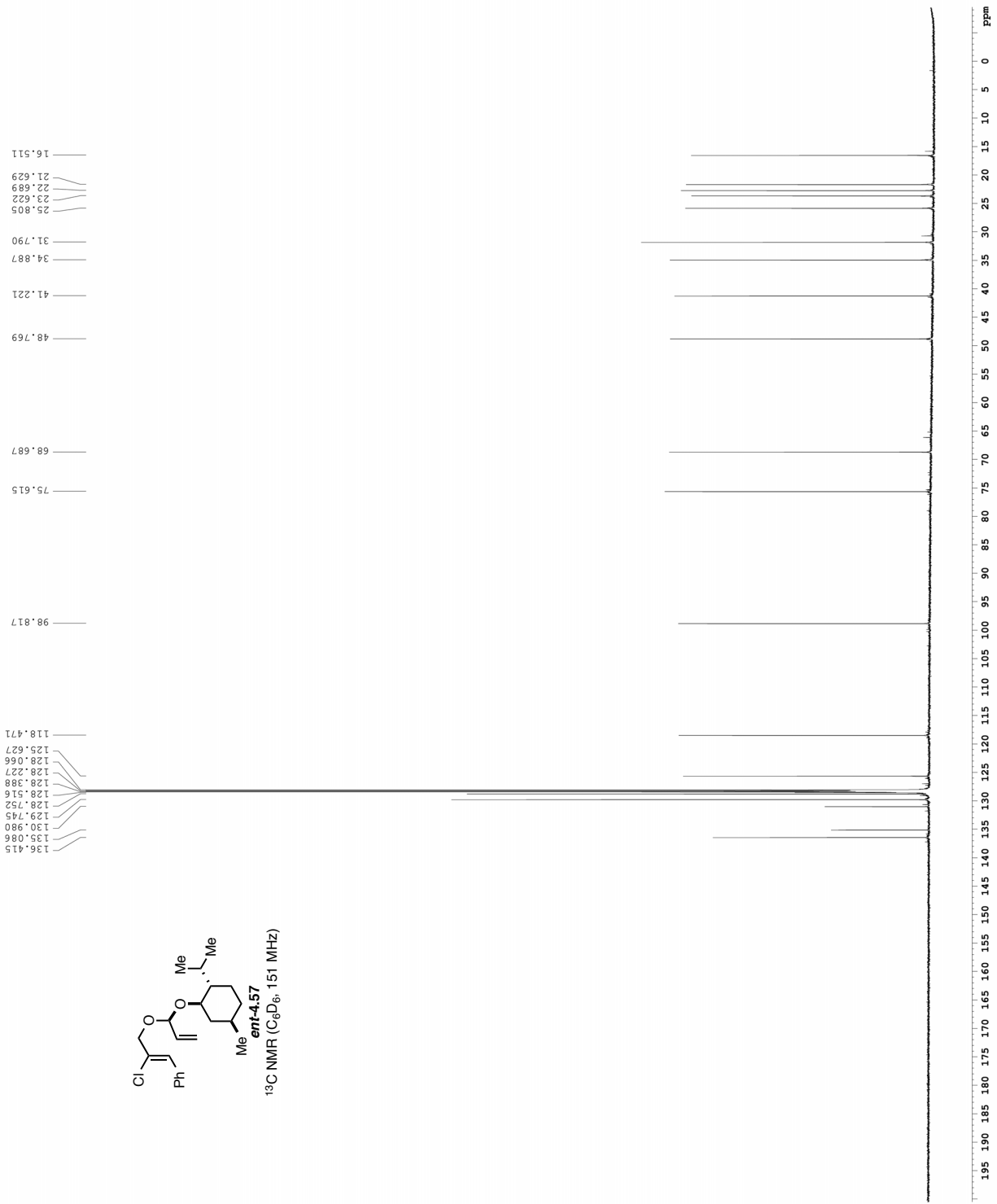
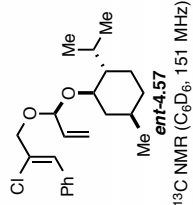
YS-V-184

Current Data Parameters
IS-V-184
EXPNO 1
PROCNO 1
DATE_ /v\data/yur/ys/nmr
F2 - Acquisition Parameters
Date_ 2017016
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
SOLVENT C6D6
NS 8
DS 4
SWH 9615.385 Hz
FIDRES 0.09642 Hz
AQ 5.0998778 sec
RG 327.0
DE 52.000 usec
TE 13.70 usec
D1 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 13
P1M1 20.00000000 usec
===== CHANNEL f2 =====
SFO2 600.1299882 MHz
NUC2 1H
P2M2 20.00000000 usec
===== CHANNEL f3 =====
SFO3 600.1299882 MHz
NUC3 1H
P3M3 20.00000000 usec
===== CHANNEL f4 =====
SFO4 600.1299882 MHz
NUC4 1H
P4M4 20.00000000 usec

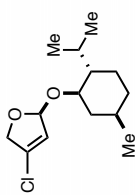


YS-V-184

Current Data Parameters
EXPERNO YS-V-184 4
DATE_ 20170215
TIME 17:40:00
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
SOLVENT CDCl3
DS 1
SWH 36231.883 Hz
FIDRES 0.9043566 sec
RG 1.2050 usec
DE 19.65 usec
TE 298.0 K
D11 0.40000000 sec
TD0 0.03000000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 64.0000000 W
===== CHANNEL f2 =====
NUC2 13C
P2 10.00 usec
PL2 64.0000000 W
===== CHANNEL f3 =====
NUC3 1H
P3 19.00 usec
PL3 0.0000000 W
===== CHANNEL f4 =====
NUC4 1H
P4 19.00 usec
PL4 0.0000000 W
===== CHANNEL f5 =====
NUC5 13C
P5 10.00 usec
PL5 64.0000000 W
===== CHANNEL f6 =====
NUC6 13C
P6 10.00 usec
PL6 64.0000000 W
===== CHANNEL f7 =====
NUC7 13C
P7 10.00 usec
PL7 64.0000000 W
===== CHANNEL f8 =====
NUC8 13C
P8 10.00 usec
PL8 64.0000000 W
===== CHANNEL f9 =====
NUC9 13C
P9 10.00 usec
PL9 64.0000000 W
===== CHANNEL f10 =====
NUC10 13C
P10 10.00 usec
PL10 64.0000000 W
===== CHANNEL f11 =====
NUC11 13C
P11 10.00 usec
PL11 64.0000000 W
===== CHANNEL f12 =====
NUC12 13C
P12 10.00 usec
PL12 64.0000000 W
===== CHANNEL f13 =====
NUC13 13C
P13 10.00 usec
PL13 64.0000000 W
===== CHANNEL f14 =====
NUC14 13C
P14 10.00 usec
PL14 64.0000000 W
===== CHANNEL f15 =====
NUC15 13C
P15 10.00 usec
PL15 64.0000000 W
===== CHANNEL f16 =====
NUC16 13C
P16 10.00 usec
PL16 64.0000000 W
===== CHANNEL f17 =====
NUC17 13C
P17 10.00 usec
PL17 64.0000000 W
===== CHANNEL f18 =====
NUC18 13C
P18 10.00 usec
PL18 64.0000000 W
===== CHANNEL f19 =====
NUC19 13C
P19 10.00 usec
PL19 64.0000000 W
===== CHANNEL f20 =====
NUC20 13C
P20 10.00 usec
PL20 64.0000000 W
===== CHANNEL f21 =====
NUC21 13C
P21 10.00 usec
PL21 64.0000000 W
===== CHANNEL f22 =====
NUC22 13C
P22 10.00 usec
PL22 64.0000000 W
===== CHANNEL f23 =====
NUC23 13C
P23 10.00 usec
PL23 64.0000000 W
===== CHANNEL f24 =====
NUC24 13C
P24 10.00 usec
PL24 64.0000000 W
===== CHANNEL f25 =====
NUC25 13C
P25 10.00 usec
PL25 64.0000000 W
===== CHANNEL f26 =====
NUC26 13C
P26 10.00 usec
PL26 64.0000000 W
===== CHANNEL f27 =====
NUC27 13C
P27 10.00 usec
PL27 64.0000000 W
===== CHANNEL f28 =====
NUC28 13C
P28 10.00 usec
PL28 64.0000000 W
===== CHANNEL f29 =====
NUC29 13C
P29 10.00 usec
PL29 64.0000000 W
===== CHANNEL f30 =====
NUC30 13C
P30 10.00 usec
PL30 64.0000000 W
===== CHANNEL f31 =====
NUC31 13C
P31 10.00 usec
PL31 64.0000000 W
===== CHANNEL f32 =====
NUC32 13C
P32 10.00 usec
PL32 64.0000000 W
===== CHANNEL f33 =====
NUC33 13C
P33 10.00 usec
PL33 64.0000000 W
===== CHANNEL f34 =====
NUC34 13C
P34 10.00 usec
PL34 64.0000000 W
===== CHANNEL f35 =====
NUC35 13C
P35 10.00 usec
PL35 64.0000000 W
===== CHANNEL f36 =====
NUC36 13C
P36 10.00 usec
PL36 64.0000000 W
===== CHANNEL f37 =====
NUC37 13C
P37 10.00 usec
PL37 64.0000000 W
===== CHANNEL f38 =====
NUC38 13C
P38 10.00 usec
PL38 64.0000000 W
===== CHANNEL f39 =====
NUC39 13C
P39 10.00 usec
PL39 64.0000000 W
===== CHANNEL f40 =====
NUC40 13C
P40 10.00 usec
PL40 64.0000000 W
===== CHANNEL f41 =====
NUC41 13C
P41 10.00 usec
PL41 64.0000000 W
===== CHANNEL f42 =====
NUC42 13C
P42 10.00 usec
PL42 64.0000000 W
===== CHANNEL f43 =====
NUC43 13C
P43 10.00 usec
PL43 64.0000000 W
===== CHANNEL f44 =====
NUC44 13C
P44 10.00 usec
PL44 64.0000000 W
===== CHANNEL f45 =====
NUC45 13C
P45 10.00 usec
PL45 64.0000000 W
===== CHANNEL f46 =====
NUC46 13C
P46 10.00 usec
PL46 64.0000000 W
===== CHANNEL f47 =====
NUC47 13C
P47 10.00 usec
PL47 64.0000000 W
===== CHANNEL f48 =====
NUC48 13C
P48 10.00 usec
PL48 64.0000000 W
===== CHANNEL f49 =====
NUC49 13C
P49 10.00 usec
PL49 64.0000000 W
===== CHANNEL f50 =====
NUC50 13C
P50 10.00 usec
PL50 64.0000000 W
===== CHANNEL f51 =====
NUC51 13C
P51 10.00 usec
PL51 64.0000000 W
===== CHANNEL f52 =====
NUC52 13C
P52 10.00 usec
PL52 64.0000000 W
===== CHANNEL f53 =====
NUC53 13C
P53 10.00 usec
PL53 64.0000000 W
===== CHANNEL f54 =====
NUC54 13C
P54 10.00 usec
PL54 64.0000000 W
===== CHANNEL f55 =====
NUC55 13C
P55 10.00 usec
PL55 64.0000000 W
===== CHANNEL f56 =====
NUC56 13C
P56 10.00 usec
PL56 64.0000000 W
===== CHANNEL f57 =====
NUC57 13C
P57 10.00 usec
PL57 64.0000000 W
===== CHANNEL f58 =====
NUC58 13C
P58 10.00 usec
PL58 64.0000000 W
===== CHANNEL f59 =====
NUC59 13C
P59 10.00 usec
PL59 64.0000000 W
===== CHANNEL f60 =====
NUC60 13C
P60 10.00 usec
PL60 64.0000000 W
===== CHANNEL f61 =====
NUC61 13C
P61 10.00 usec
PL61 64.0000000 W
===== CHANNEL f62 =====
NUC62 13C
P62 10.00 usec
PL62 64.0000000 W
===== CHANNEL f63 =====
NUC63 13C
P63 10.00 usec
PL63 64.0000000 W
===== CHANNEL f64 =====
NUC64 13C
P64 10.00 usec
PL64 64.0000000 W
===== CHANNEL f65 =====
NUC65 13C
P65 10.00 usec
PL65 64.0000000 W
===== CHANNEL f66 =====
NUC66 13C
P66 10.00 usec
PL66 64.0000000 W
===== CHANNEL f67 =====
NUC67 13C
P67 10.00 usec
PL67 64.0000000 W
===== CHANNEL f68 =====
NUC68 13C
P68 10.00 usec
PL68 64.0000000 W
===== CHANNEL f69 =====
NUC69 13C
P69 10.00 usec
PL69 64.0000000 W
===== CHANNEL f70 =====
NUC70 13C
P70 10.00 usec
PL70 64.0000000 W
===== CHANNEL f71 =====
NUC71 13C
P71 10.00 usec
PL71 64.0000000 W
===== CHANNEL f72 =====
NUC72 13C
P72 10.00 usec
PL72 64.0000000 W
===== CHANNEL f73 =====
NUC73 13C
P73 10.00 usec
PL73 64.0000000 W
===== CHANNEL f74 =====
NUC74 13C
P74 10.00 usec
PL74 64.0000000 W
===== CHANNEL f75 =====
NUC75 13C
P75 10.00 usec
PL75 64.0000000 W
===== CHANNEL f76 =====
NUC76 13C
P76 10.00 usec
PL76 64.0000000 W
===== CHANNEL f77 =====
NUC77 13C
P77 10.00 usec
PL77 64.0000000 W
===== CHANNEL f78 =====
NUC78 13C
P78 10.00 usec
PL78 64.0000000 W
===== CHANNEL f79 =====
NUC79 13C
P79 10.00 usec
PL79 64.0000000 W
===== CHANNEL f80 =====
NUC80 13C
P80 10.00 usec
PL80 64.0000000 W
===== CHANNEL f81 =====
NUC81 13C
P81 10.00 usec
PL81 64.0000000 W
===== CHANNEL f82 =====
NUC82 13C
P82 10.00 usec
PL82 64.0000000 W
===== CHANNEL f83 =====
NUC83 13C
P83 10.00 usec
PL83 64.0000000 W
===== CHANNEL f84 =====
NUC84 13C
P84 10.00 usec
PL84 64.0000000 W
===== CHANNEL f85 =====
NUC85 13C
P85 10.00 usec
PL85 64.0000000 W
===== CHANNEL f86 =====
NUC86 13C
P86 10.00 usec
PL86 64.0000000 W
===== CHANNEL f87 =====
NUC87 13C
P87 10.00 usec
PL87 64.0000000 W
===== CHANNEL f88 =====
NUC88 13C
P88 10.00 usec
PL88 64.0000000 W
===== CHANNEL f89 =====
NUC89 13C
P89 10.00 usec
PL89 64.0000000 W
===== CHANNEL f90 =====
NUC90 13C
P90 10.00 usec
PL90 64.0000000 W
===== CHANNEL f91 =====
NUC91 13C
P91 10.00 usec
PL91 64.0000000 W
===== CHANNEL f92 =====
NUC92 13C
P92 10.00 usec
PL92 64.0000000 W
===== CHANNEL f93 =====
NUC93 13C
P93 10.00 usec
PL93 64.0000000 W
===== CHANNEL f94 =====
NUC94 13C
P94 10.00 usec
PL94 64.0000000 W
===== CHANNEL f95 =====
NUC95 13C
P95 10.00 usec
PL95 64.0000000 W
===== CHANNEL f96 =====
NUC96 13C
P96 10.00 usec
PL96 64.0000000 W
===== CHANNEL f97 =====
NUC97 13C
P97 10.00 usec
PL97 64.0000000 W
===== CHANNEL f98 =====
NUC98 13C
P98 10.00 usec
PL98 64.0000000 W
===== CHANNEL f99 =====
NUC99 13C
P99 10.00 usec
PL99 64.0000000 W
===== CHANNEL f100 =====
NUC100 13C
P100 10.00 usec
PL100 64.0000000 W

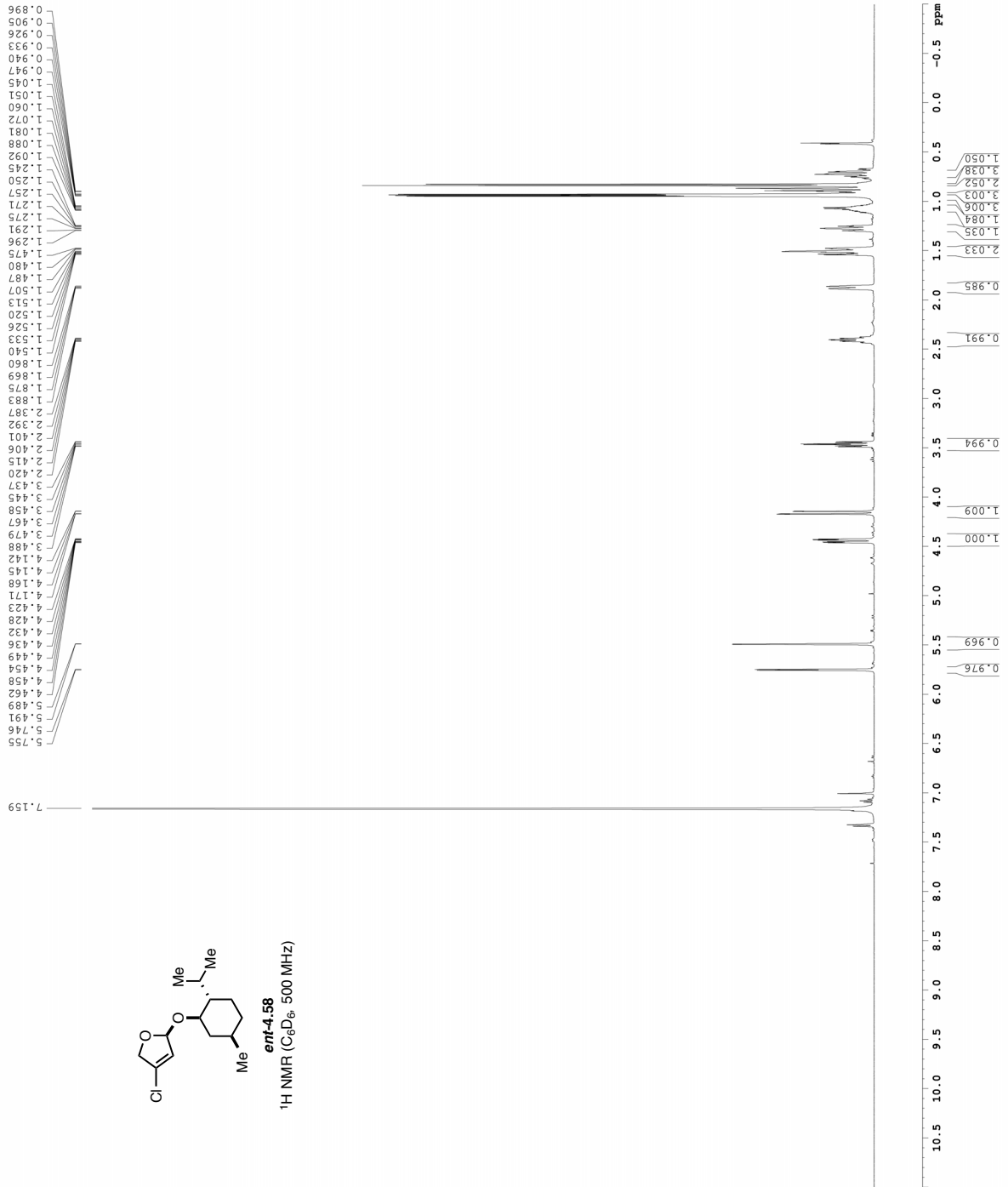


YS-V-185

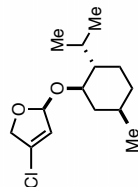


ent-4.58
¹H NMR (C₆D₆, 500 MHz)

Current Data Parameters
NAME YS-V-185
EXPNO 10
PROCNO 1
DATE_ /v/data/yuriy/nmr
DATE_ 20170118
Time 14.41
Date_ Acquisition Parameters
INSTRUM cryo500
PULPROG zg30
ID 8128
SOLVENT CDCl3
DS 2
SWH 8015.820 Hz
AQ 5.098273 sec
RG 7.1
DE 2.00 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.01500000 sec
D12 0.01500000 sec
D13 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.225015 MHz
F2 - Processing parameters
SI 65536
WDW EM
SSB 0
GB 0
PC 1.00

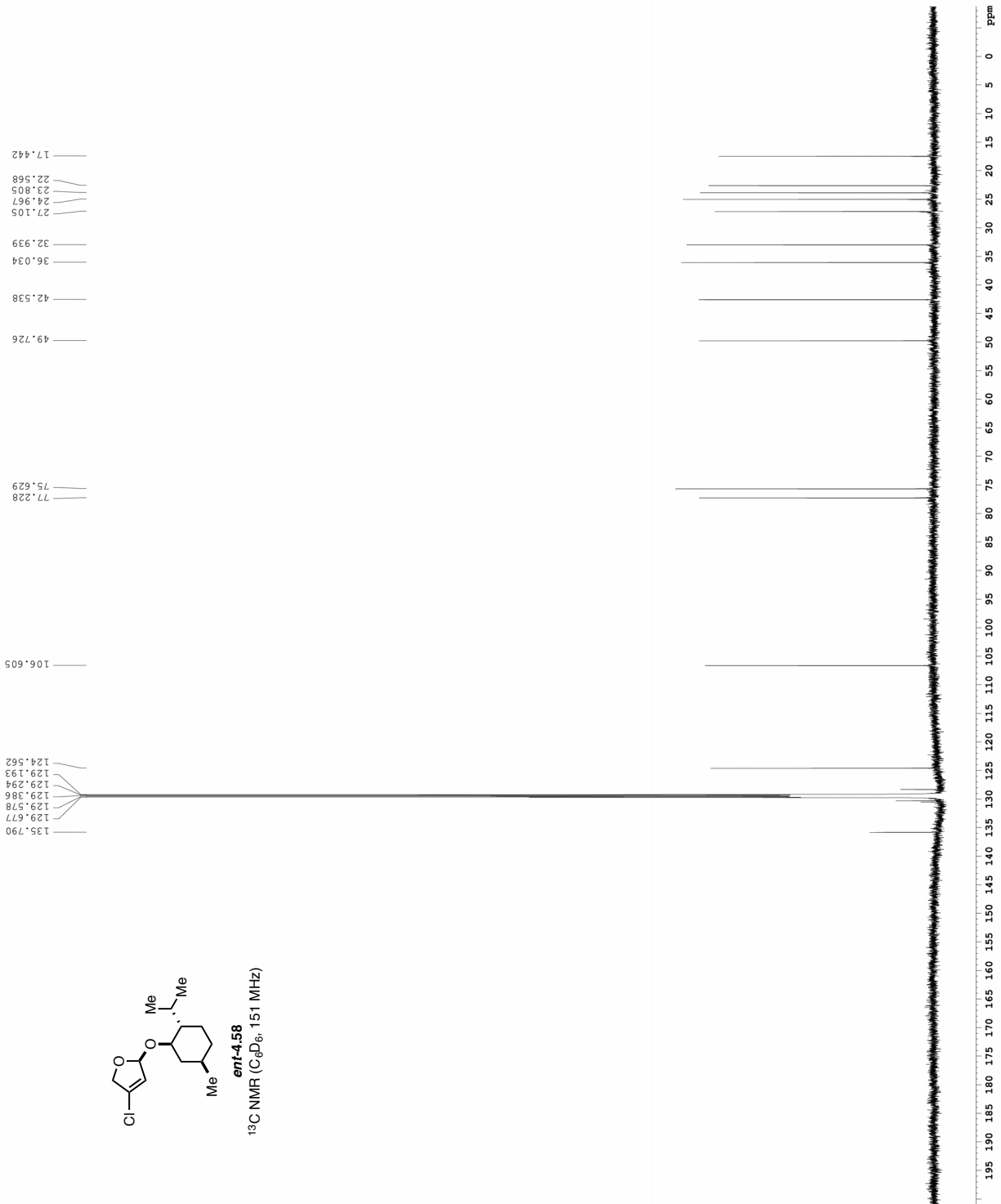


YS-V-185

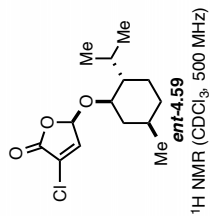


ent-4.58
¹³C NMR (C₆D₆, 151 MHz)

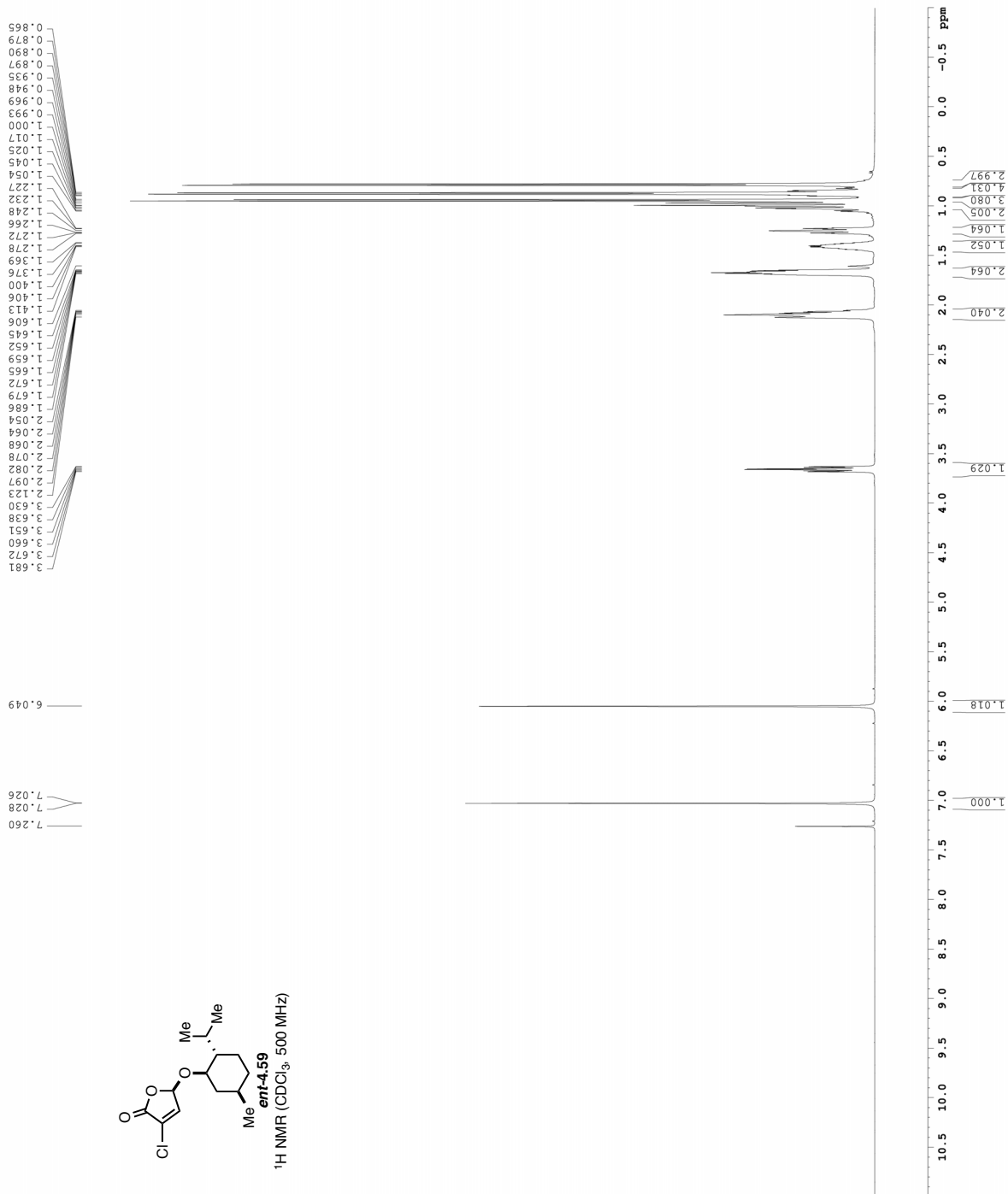
```
Current Data Parameters
=====
EXPNO 0
NAME YS-V-185
PROCNO 11
DATAF1 /v/data/yuriyf/nmr
F2 - Acquisition Parameters
Date_ 20170118
Time 14:40
PROBHD 5 mm cpcci 1H-
PULPROG spinchegp2-prd
SOLVENT CDCl3
DS 631
SRH 30303.031 Hz
AQ 1.0813440 sec
RG 5160.6
DE 6.000 usec
TE 300.2
D1 0.2512880 sec
d11 0.033000000 sec
d12 0.033000000 sec
d17 0.000190000 sec
d18 0.000190000 sec
d19 0.000190000 sec
d20 0.000190000 sec
d21 0.000190000 sec
d22 0.000190000 sec
d23 0.000190000 sec
d24 0.000190000 sec
d25 0.000190000 sec
d26 0.000190000 sec
d27 0.000190000 sec
d28 0.000190000 sec
d29 0.000190000 sec
d30 0.000190000 sec
d31 0.000190000 sec
d32 0.000190000 sec
d33 0.000190000 sec
d34 0.000190000 sec
d35 0.000190000 sec
d36 0.000190000 sec
d37 0.000190000 sec
d38 0.000190000 sec
d39 0.000190000 sec
d40 0.000190000 sec
d41 0.000190000 sec
d42 0.000190000 sec
d43 0.000190000 sec
d44 0.000190000 sec
d45 0.000190000 sec
d46 0.000190000 sec
d47 0.000190000 sec
d48 0.000190000 sec
d49 0.000190000 sec
d50 0.000190000 sec
d51 0.000190000 sec
d52 0.000190000 sec
d53 0.000190000 sec
d54 0.000190000 sec
d55 0.000190000 sec
d56 0.000190000 sec
d57 0.000190000 sec
d58 0.000190000 sec
d59 0.000190000 sec
d60 0.000190000 sec
d61 0.000190000 sec
d62 0.000190000 sec
d63 0.000190000 sec
d64 0.000190000 sec
d65 0.000190000 sec
d66 0.000190000 sec
d67 0.000190000 sec
d68 0.000190000 sec
d69 0.000190000 sec
d70 0.000190000 sec
d71 0.000190000 sec
d72 0.000190000 sec
d73 0.000190000 sec
d74 0.000190000 sec
d75 0.000190000 sec
d76 0.000190000 sec
d77 0.000190000 sec
d78 0.000190000 sec
d79 0.000190000 sec
d80 0.000190000 sec
d81 0.000190000 sec
d82 0.000190000 sec
d83 0.000190000 sec
d84 0.000190000 sec
d85 0.000190000 sec
d86 0.000190000 sec
d87 0.000190000 sec
d88 0.000190000 sec
d89 0.000190000 sec
d90 0.000190000 sec
d91 0.000190000 sec
d92 0.000190000 sec
d93 0.000190000 sec
d94 0.000190000 sec
d95 0.000190000 sec
d96 0.000190000 sec
d97 0.000190000 sec
d98 0.000190000 sec
d99 0.000190000 sec
d100 0.000190000 sec
===== CHANNEL f1 13C =====
NUC1 13C
P1 16.55 usec
PCPD1 100.00 usec
P12 2800.00 usec
P13 120.00 dB
P14 120.00 dB
SFO1 125.7642548 MHz
SFO2 500.2223011 MHz
SFO3 500.2223011 MHz
SFO4 500.2223011 MHz
SFO5 500.2223011 MHz
SFO6 500.2223011 MHz
SFO7 500.2223011 MHz
SFO8 500.2223011 MHz
SFO9 500.2223011 MHz
SFO10 500.2223011 MHz
SFO11 500.2223011 MHz
SFO12 500.2223011 MHz
SFO13 500.2223011 MHz
SFO14 500.2223011 MHz
SFO15 500.2223011 MHz
SFO16 500.2223011 MHz
SFO17 500.2223011 MHz
SFO18 500.2223011 MHz
SFO19 500.2223011 MHz
SFO20 500.2223011 MHz
SFO21 500.2223011 MHz
SFO22 500.2223011 MHz
SFO23 500.2223011 MHz
SFO24 500.2223011 MHz
SFO25 500.2223011 MHz
SFO26 500.2223011 MHz
SFO27 500.2223011 MHz
SFO28 500.2223011 MHz
SFO29 500.2223011 MHz
SFO30 500.2223011 MHz
SFO31 500.2223011 MHz
SFO32 500.2223011 MHz
SFO33 500.2223011 MHz
SFO34 500.2223011 MHz
SFO35 500.2223011 MHz
SFO36 500.2223011 MHz
SFO37 500.2223011 MHz
SFO38 500.2223011 MHz
SFO39 500.2223011 MHz
SFO40 500.2223011 MHz
SFO41 500.2223011 MHz
SFO42 500.2223011 MHz
SFO43 500.2223011 MHz
SFO44 500.2223011 MHz
SFO45 500.2223011 MHz
SFO46 500.2223011 MHz
SFO47 500.2223011 MHz
SFO48 500.2223011 MHz
SFO49 500.2223011 MHz
SFO50 500.2223011 MHz
SFO51 500.2223011 MHz
SFO52 500.2223011 MHz
SFO53 500.2223011 MHz
SFO54 500.2223011 MHz
SFO55 500.2223011 MHz
SFO56 500.2223011 MHz
SFO57 500.2223011 MHz
SFO58 500.2223011 MHz
SFO59 500.2223011 MHz
SFO60 500.2223011 MHz
SFO61 500.2223011 MHz
SFO62 500.2223011 MHz
SFO63 500.2223011 MHz
SFO64 500.2223011 MHz
SFO65 500.2223011 MHz
SFO66 500.2223011 MHz
SFO67 500.2223011 MHz
SFO68 500.2223011 MHz
SFO69 500.2223011 MHz
SFO70 500.2223011 MHz
SFO71 500.2223011 MHz
SFO72 500.2223011 MHz
SFO73 500.2223011 MHz
SFO74 500.2223011 MHz
SFO75 500.2223011 MHz
SFO76 500.2223011 MHz
SFO77 500.2223011 MHz
SFO78 500.2223011 MHz
SFO79 500.2223011 MHz
SFO80 500.2223011 MHz
SFO81 500.2223011 MHz
SFO82 500.2223011 MHz
SFO83 500.2223011 MHz
SFO84 500.2223011 MHz
SFO85 500.2223011 MHz
SFO86 500.2223011 MHz
SFO87 500.2223011 MHz
SFO88 500.2223011 MHz
SFO89 500.2223011 MHz
SFO90 500.2223011 MHz
SFO91 500.2223011 MHz
SFO92 500.2223011 MHz
SFO93 500.2223011 MHz
SFO94 500.2223011 MHz
SFO95 500.2223011 MHz
SFO96 500.2223011 MHz
SFO97 500.2223011 MHz
SFO98 500.2223011 MHz
SFO99 500.2223011 MHz
SFO100 500.2223011 MHz
===== CHANNEL f2 =====
CPDPRG2 waitz16
PCPD2 100.00 usec
P12 2800.00 usec
P13 120.00 dB
P14 120.00 dB
SFO1 125.7642548 MHz
SFO2 500.2223011 MHz
SFO3 500.2223011 MHz
SFO4 500.2223011 MHz
SFO5 500.2223011 MHz
SFO6 500.2223011 MHz
SFO7 500.2223011 MHz
SFO8 500.2223011 MHz
SFO9 500.2223011 MHz
SFO10 500.2223011 MHz
SFO11 500.2223011 MHz
SFO12 500.2223011 MHz
SFO13 500.2223011 MHz
SFO14 500.2223011 MHz
SFO15 500.2223011 MHz
SFO16 500.2223011 MHz
SFO17 500.2223011 MHz
SFO18 500.2223011 MHz
SFO19 500.2223011 MHz
SFO20 500.2223011 MHz
SFO21 500.2223011 MHz
SFO22 500.2223011 MHz
SFO23 500.2223011 MHz
SFO24 500.2223011 MHz
SFO25 500.2223011 MHz
SFO26 500.2223011 MHz
SFO27 500.2223011 MHz
SFO28 500.2223011 MHz
SFO29 500.2223011 MHz
SFO30 500.2223011 MHz
SFO31 500.2223011 MHz
SFO32 500.2223011 MHz
SFO33 500.2223011 MHz
SFO34 500.2223011 MHz
SFO35 500.2223011 MHz
SFO36 500.2223011 MHz
SFO37 500.2223011 MHz
SFO38 500.2223011 MHz
SFO39 500.2223011 MHz
SFO40 500.2223011 MHz
SFO41 500.2223011 MHz
SFO42 500.2223011 MHz
SFO43 500.2223011 MHz
SFO44 500.2223011 MHz
SFO45 500.2223011 MHz
SFO46 500.2223011 MHz
SFO47 500.2223011 MHz
SFO48 500.2223011 MHz
SFO49 500.2223011 MHz
SFO50 500.2223011 MHz
SFO51 500.2223011 MHz
SFO52 500.2223011 MHz
SFO53 500.2223011 MHz
SFO54 500.2223011 MHz
SFO55 500.2223011 MHz
SFO56 500.2223011 MHz
SFO57 500.2223011 MHz
SFO58 500.2223011 MHz
SFO59 500.2223011 MHz
SFO60 500.2223011 MHz
SFO61 500.2223011 MHz
SFO62 500.2223011 MHz
SFO63 500.2223011 MHz
SFO64 500.2223011 MHz
SFO65 500.2223011 MHz
SFO66 500.2223011 MHz
SFO67 500.2223011 MHz
SFO68 500.2223011 MHz
SFO69 500.2223011 MHz
SFO70 500.2223011 MHz
SFO71 500.2223011 MHz
SFO72 500.2223011 MHz
SFO73 500.2223011 MHz
SFO74 500.2223011 MHz
SFO75 500.2223011 MHz
SFO76 500.2223011 MHz
SFO77 500.2223011 MHz
SFO78 500.2223011 MHz
SFO79 500.2223011 MHz
SFO80 500.2223011 MHz
SFO81 500.2223011 MHz
SFO82 500.2223011 MHz
SFO83 500.2223011 MHz
SFO84 500.2223011 MHz
SFO85 500.2223011 MHz
SFO86 500.2223011 MHz
SFO87 500.2223011 MHz
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SFO89 500.2223011 MHz
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SFO91 500.2223011 MHz
SFO92 500.2223011 MHz
SFO93 500.2223011 MHz
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SFO95 500.2223011 MHz
SFO96 500.2223011 MHz
SFO97 500.2223011 MHz
SFO98 500.2223011 MHz
SFO99 500.2223011 MHz
SFO100 500.2223011 MHz
===== GRADIENT CHANNEL =====
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GENAM1[2] SINE.100
GENAM2[1] SINE.100
GENAM2[2] SINE.100
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GENZ2 0 %
GENZ3 0 %
GENZ4 0 %
GENZ5 0 %
GENZ6 0 %
GENZ7 0 %
GENZ8 0 %
GENZ9 0 %
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GENZ92 0 %
GENZ93 0 %
GENZ94 0 %
GENZ95 0 %
GENZ96 0 %
GENZ97 0 %
GENZ98 0 %
GENZ99 0 %
GENZ100 0 %
===== Processing Parameters =====
SI 65536
SF 125.7642548 MHz
WDW EM
SSB 0
GB 0
PC 2.00
```



YS-V-175



```
Current Data Parameters
NAME       YS-V-175
PROCNO    1
DATE_     /v/data/yuris/nmr
Date_     20161215
Time      15.20
PROBHD    5 mm CPY130
PULPROG   zgpg30
TD         81728
SOLVENT   CDCl3
NS         2
DS         8013.820 Hz
SFR        5.0998273 sec
AQ         6.3
RG         625.00 usec
DE         298.0 K
TE         0.1000000 sec
DQ        0.0150000 sec
MCMRST    CHANNEL f1
=====
NUC1       1H
P1         7.50 usec
PL1        1.60 dB
SFO1      500.2235015 MHz
=====
F2 - Processing Parameters
SI         65536
SF         500.2235015 MHz
WDW        EM
SSB        0
GB         0
PC         1.00
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YS-V-175

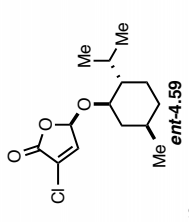
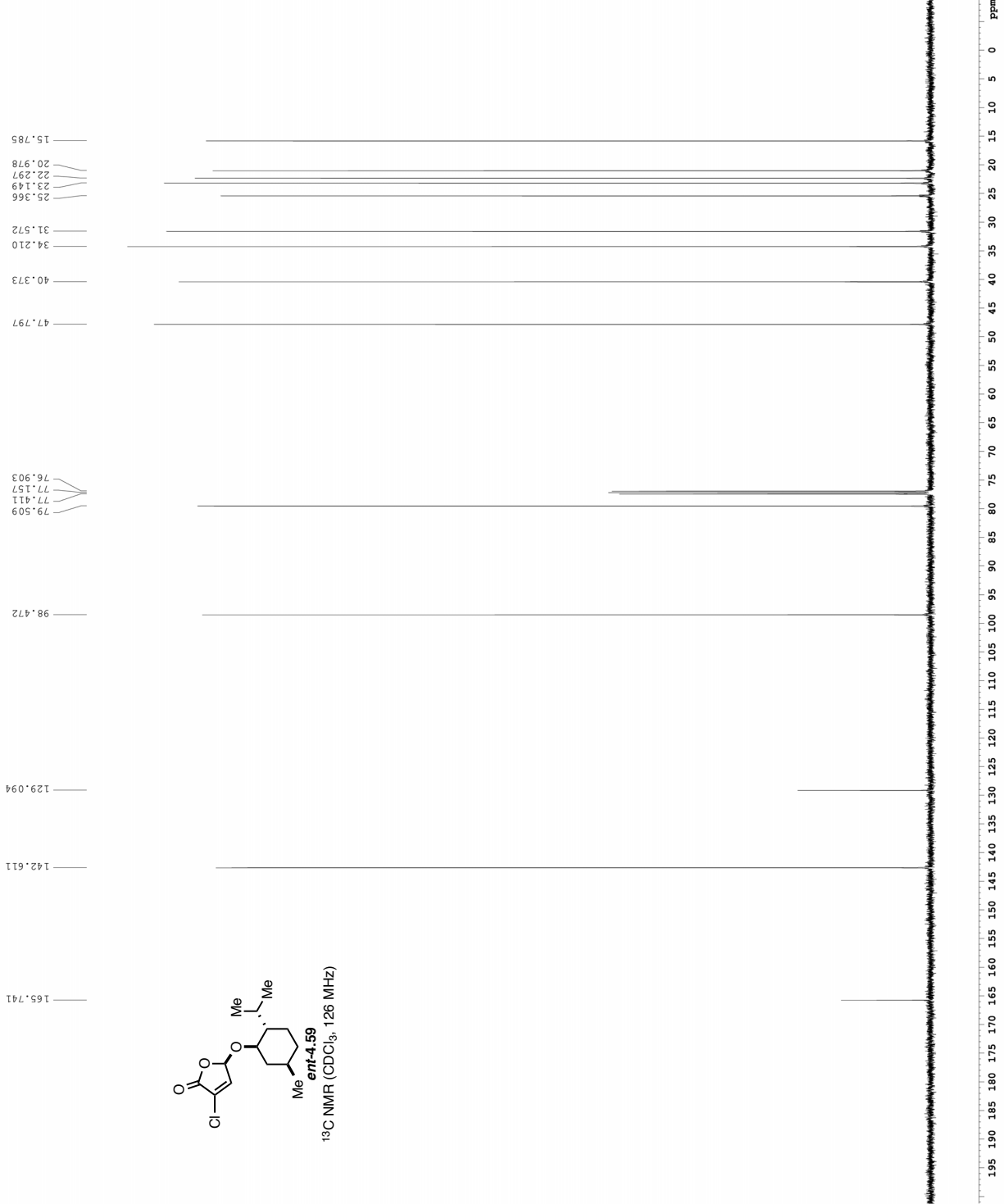
Current Data Parameters
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DATEPATH /v/data/yuriys/mr
F2 - Acquisition Parameters
Date_ 20161215
Time 15:00
INSTRUM spect
PROBHD 5 mm CPYCI 1H-
PULPROG Spinechopg30
TD 65536
SOLVENT CDCl3
DS 2
ZG 1

SWH 3030.031 Hz
FIDRES 0.482880 Hz
AQ 0.083440 sec
RG 4096
DE 18.4096 usec
TE 298.0 K
NUC1 13C
P1 16.55 usec
PL1 0.00 dB
P12 2000.00 usec
PL2 120.00 dB
P10 120.00 dB
SF01 125.7942548 MHz
SF02 125.7942548 MHz
SP2 2.70 GB
SFO1 125.7942548 MHz
SFO2 125.7942548 MHz
SFO3 125.7942548 MHz
SFO4 125.7942548 MHz
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SFO95 125.7942548 MHz
SFO96 125.7942548 MHz
SFO97 125.7942548 MHz
SFO98 125.7942548 MHz
SFO99 125.7942548 MHz
SFO100 125.7942548 MHz

NUC1 13C
P1 16.55 usec
PL1 0.00 dB
P12 2000.00 usec
PL2 120.00 dB
P10 120.00 dB
SF01 125.7942548 MHz
SF02 125.7942548 MHz
SP2 2.70 GB
SFO1 125.7942548 MHz
SFO2 125.7942548 MHz
SFO3 125.7942548 MHz
SFO4 125.7942548 MHz
SFO5 125.7942548 MHz
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SFO90 125.7942548 MHz
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SFO92 125.7942548 MHz
SFO93 125.7942548 MHz
SFO94 125.7942548 MHz
SFO95 125.7942548 MHz
SFO96 125.7942548 MHz
SFO97 125.7942548 MHz
SFO98 125.7942548 MHz
SFO99 125.7942548 MHz
SFO100 125.7942548 MHz

CPDPRG2 waltz16
PCPD2 100.00 usec
PL2 1.60 dB
PL12 120.00 dB
SF02 500.2225011 MHz
***** GRADIENT CHANNEL *****
GPMN(1) SINE.100
GPMN(2) SINE.100
GPMN(3) SINE.100
GPMN(4) SINE.100
GPMN(5) SINE.100
GPMN(6) SINE.100
GPMN(7) SINE.100
GPMN(8) SINE.100
GPMN(9) SINE.100
GPMN(10) SINE.100
GPMN(11) SINE.100
GPMN(12) SINE.100
GPMN(13) SINE.100
GPMN(14) SINE.100
GPMN(15) SINE.100
GPMN(16) SINE.100
GPMN(17) SINE.100
GPMN(18) SINE.100
GPMN(19) SINE.100
GPMN(20) SINE.100
GPMN(21) SINE.100
GPMN(22) SINE.100
GPMN(23) SINE.100
GPMN(24) SINE.100
GPMN(25) SINE.100
GPMN(26) SINE.100
GPMN(27) SINE.100
GPMN(28) SINE.100
GPMN(29) SINE.100
GPMN(30) SINE.100
GPMN(31) SINE.100
GPMN(32) SINE.100
GPMN(33) SINE.100
GPMN(34) SINE.100
GPMN(35) SINE.100
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GPMN(79) SINE.100
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GPMN(82) SINE.100
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GPMN(84) SINE.100
GPMN(85) SINE.100
GPMN(86) SINE.100
GPMN(87) SINE.100
GPMN(88) SINE.100
GPMN(89) SINE.100
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GPMN(92) SINE.100
GPMN(93) SINE.100
GPMN(94) SINE.100
GPMN(95) SINE.100
GPMN(96) SINE.100
GPMN(97) SINE.100
GPMN(98) SINE.100
GPMN(99) SINE.100
GPMN(100) SINE.100

F2 - Processing Parameters
SI 65536
SF 125.7894254 MHz
WDW EM
SSB 0
GB 1.00 Hz
PC 2.00



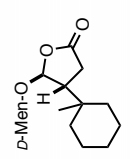
¹³C NMR (CDCl₃, 126 MHz)

YS-V-252B

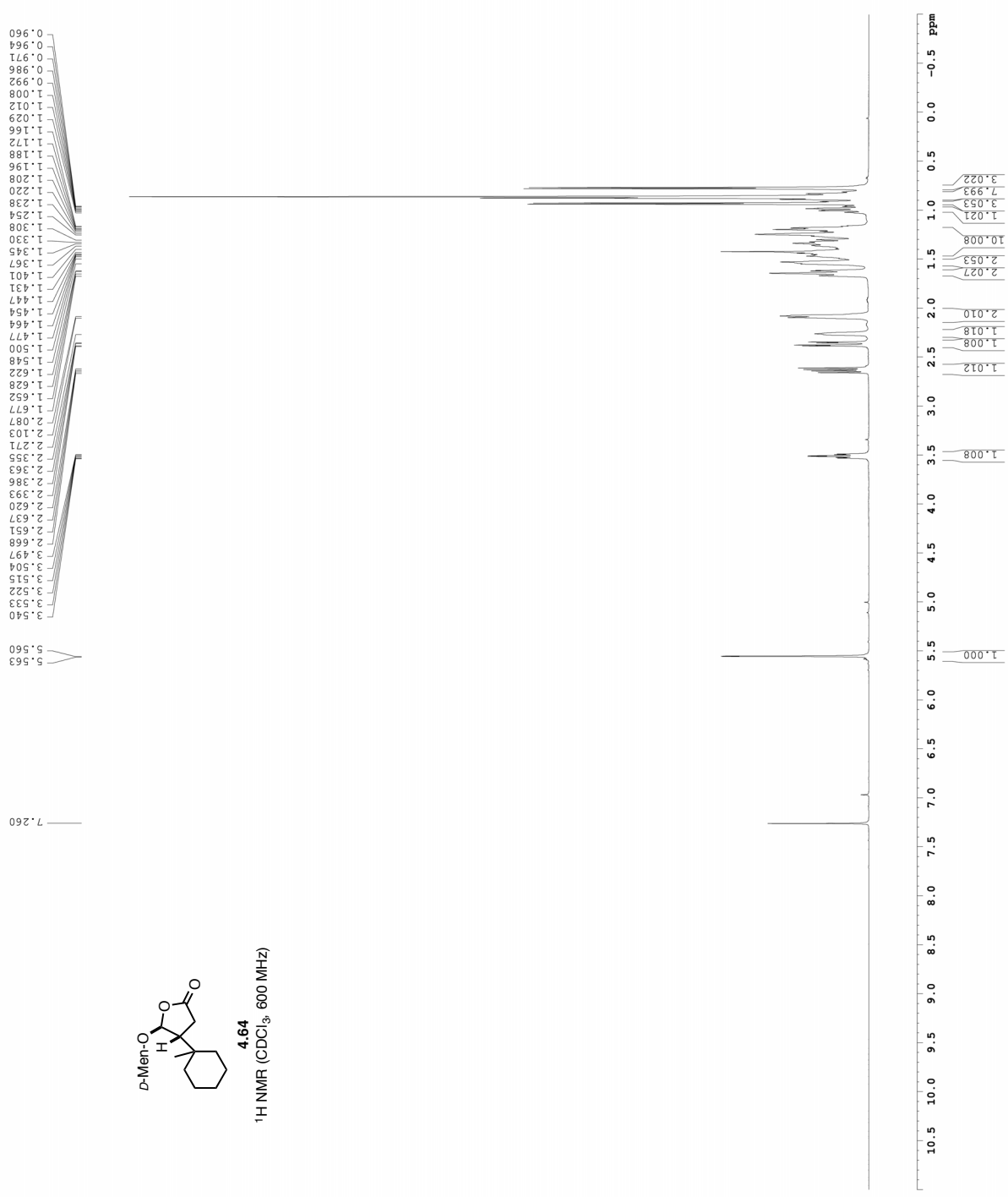
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EXPNO 2
PROCNO 1
DATAPATH /v/data/yuris/mr
F2 - Acquisition Parameters
Date_ 20170310
Time 8:40
INSTRUM av600
PROBHD 5 mm CPBPG 4330
PULPROG zgpg30
TD 98074
FIDRES 0.3000000
SFO1 600.1300348 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 1.00

===== CHANNEL f1 =====
SFO1 600.1300348 MHz
NUC1 13C
P1 12.00 usec
PL1 20.0000000 W
SI - Processing parameters
SF 600.1300348 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 1.00

0.960
0.964
0.971
0.986
0.992
1.008
1.010
1.012
1.015
1.029
1.066
1.172
1.188
1.196
1.208
1.220
1.238
1.254
1.308
1.330
1.343
1.367
1.401
1.431
1.447
1.454
1.464
1.477
1.500
1.548
1.622
1.628
1.652
1.677
1.677
2.087
2.103
2.271
2.355
2.363
2.386
2.393
2.620
2.637
2.651
2.668
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3.504
3.515
3.522
3.533
5.540
5.560
5.563



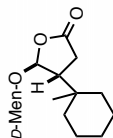
¹H NMR (CDCl₃, 600 MHz)



YS-V-252B

Current Data Parameters
NAME YS-V-252B
PROCNO 1
DATPATH /v/cac/yur/ys/mr
F2 - Acquisition Parameters
Time 8.45
INSTRUM av600
PULPROG zgpg30
TD 65536
NS 216
DSH 36231.883 Hz
FIDRES 0.552853 Hz
RG 0.90000000 sec
DM 13.800 usec
DE 298.0 K
D1 0.40000001 sec
D11 0.05000000 sec
D10 1
SF01 CHANNEL f1 150.9194980 MHz
NUC1 13C 10.13C usec
PLM1 64.00000000 W
SF02 CHANNEL f2 600.1330010 MHz
CPDPRG2 waltz16
PCPD2 20.00000000 usec
PLM2 0.36000001 W
F2 - Processing Parameters
SI 65536
SF 150.9028177 MHz
SSB 0
GB 0
PC 1.00 Hz

176.645
77.228
77.017
76.805
101.828
39.839
35.296
35.280
34.315
33.919
31.375
29.650
26.014
25.389
23.063
22.288
21.336
20.911
20.182
15.608

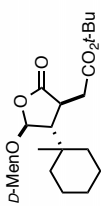


4.64
¹³C NMR (CDCl₃, 151 MHz)

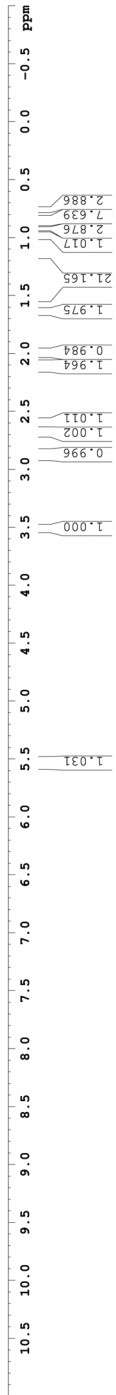


YS-V-256

Current Data Parameters
NAME YS-V-256
PROCNO 1
F2 - Acquisition Parameters
Time 20.79, 9.07
INSTRUM av600
PROBHD 5 mm CPBBO BB
PULPROG zgpg30
TD 98074
SOLVENT CDCl3
DS 2
SMH 9645.385 Hz
FIDRES 0.098042 Hz
RG 5.0398410 sec
DM 52.000 usec
TE 298.70 Ksec
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 13C
P1 12.00 usec
PLM1 20.00000000 N
F2 - Processing parameters
SI 600.1300346 MHz
RG 6.5536
ADM EM
LB 0 0.30 Hz
GB 0
PC 1.00



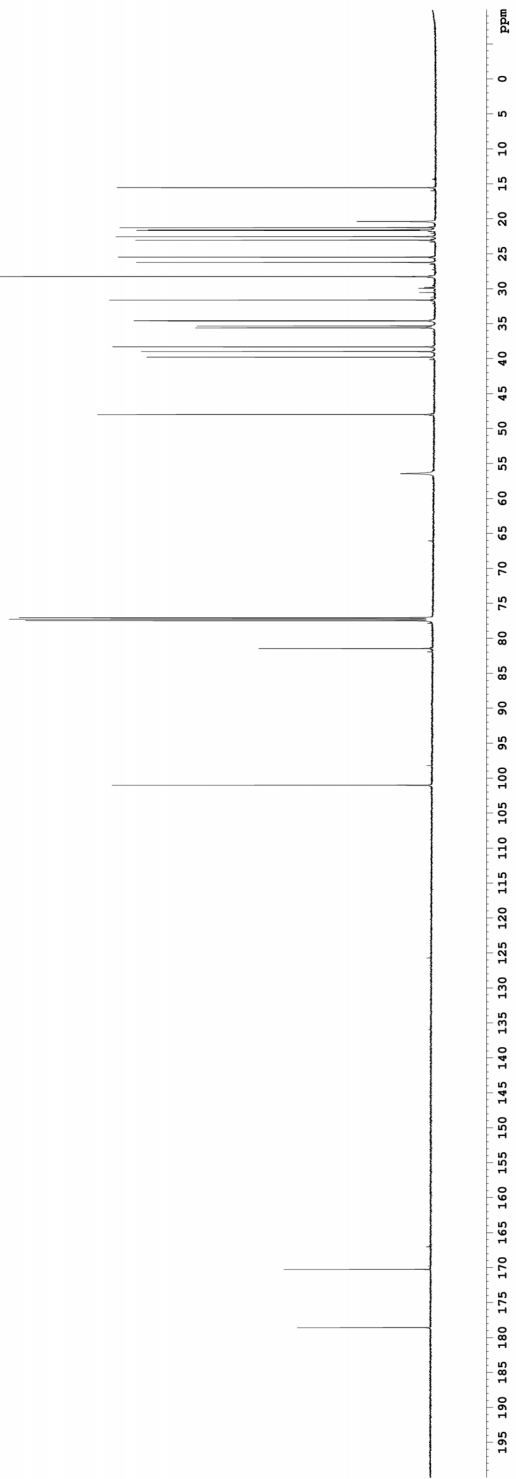
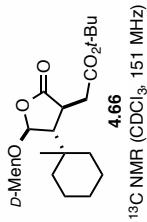
¹H NMR (CDCl₃, 600 MHz)



YS-V-256

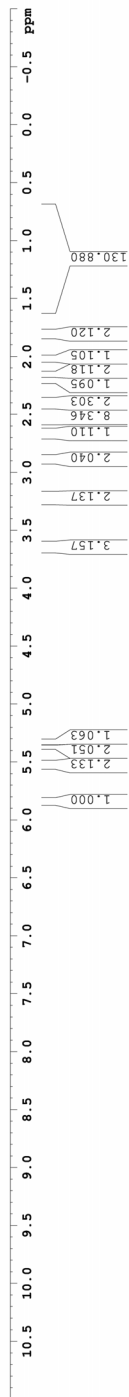
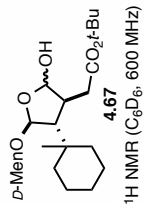
Current Data Parameters
NAME YS-V-256
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170911
Time 9:11
INSTRUM 5 mm CPBPR00
PULPROG zgpg30
SOLVENT CDCl3
NS 200
DSH 36231.863 Hz
FIDRES 0.532653 Hz
AQ 0.59000000 sec
RG 200.000000
DM 13.800 usec
DE 238.0 K
TE 300.2 K
D1 0.40000001 sec
D11 0.05000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.919480 MHz
NUC1 13C
P1 10.00 usec
PL1 64.00000000 W
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 1H
P2 19.00 usec
PL2 0.36000001 W
PCPD2 wait:15
===== Processing parameters =====
SI 65536
SF 150.9027568 MHz
WDW 0
SSB 0
GB 0
PC 1.00

15.507
20.343
21.217
21.533
21.615
22.499
23.004
23.432
25.432
26.202
28.225
31.582
34.530
34.574
35.289
35.550
38.267
38.948
39.745
47.942
56.401
77.016
77.187
77.228
77.440
81.407
100.970



YS-V-257

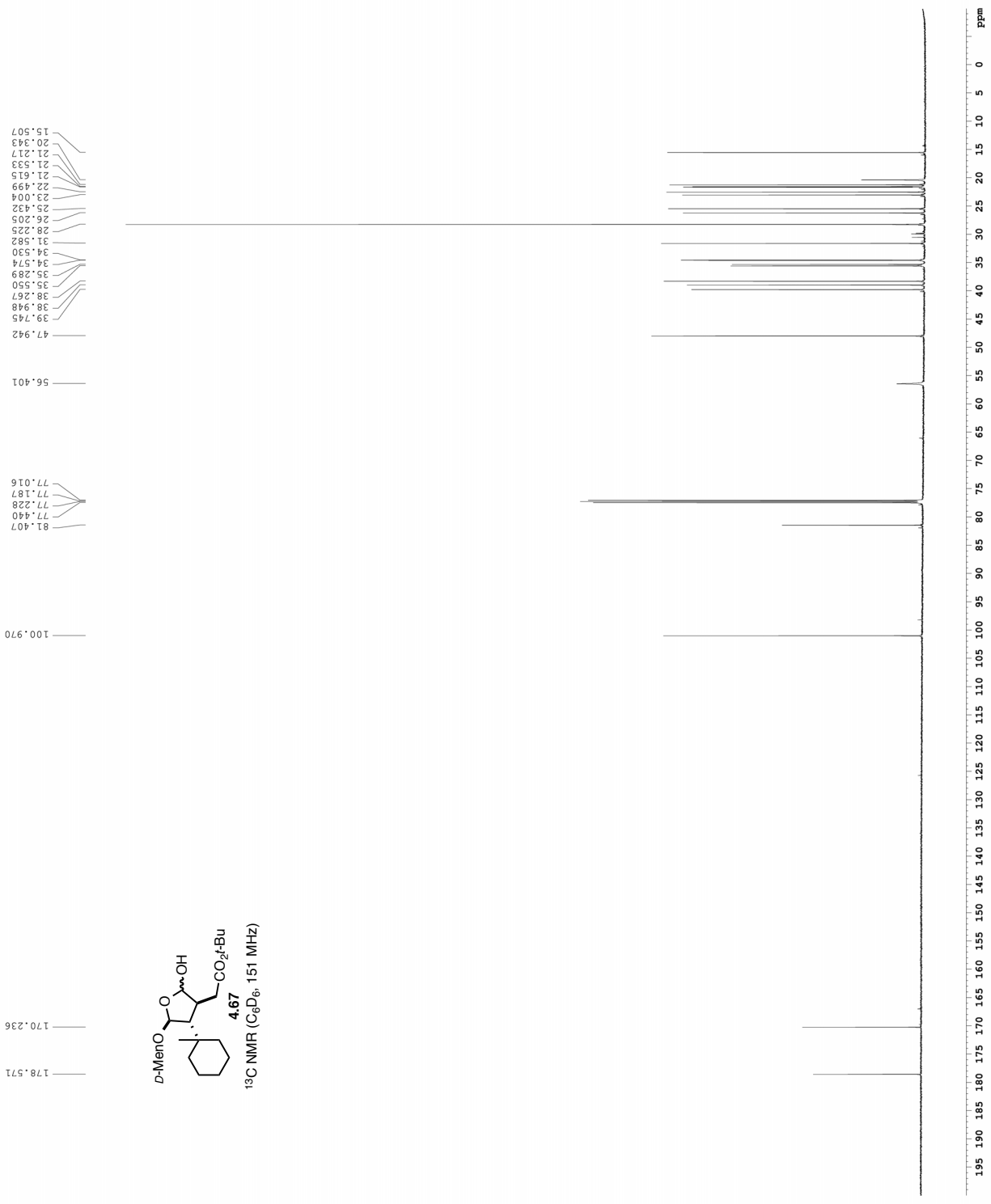
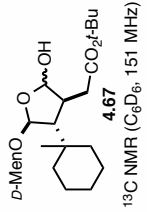
Current Data Parameters
NAME YS-V-257
PROCNO 1
F2 - Acquisition Parameters
Time 2016.39
INSTRUM av600
PULPROG 5 mm CPBPG2 Z30
TD 98674
SOLVENT C6D6
NS 2
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
RG 3.039394 Hz
AQ 1.0 sec
DM 52.000 usec
DE 298.0 K
TE 298.0 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.1342009 MHz
NUC1 13C
P1 12.00 usec
PL1 20.00000000 M
===== Processing Parameters =====
SI 65536
SF 600.129976 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



YS-V-256

Current Data Parameters
NAME YS-V-256
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Time 9.11
INSTRUM av600
PULPROG zgpg30
SOLVENT CDCl3
NS 200
DSH 36231.883 Hz
FIDRES 0.522855 Hz
RG 0.39000000 sec
RG 2050 sec
DM 13.800 usec
TE 298.0 K
D1 0.40000001 sec
D11 0.13300001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.914080 MHz
NUC1 13C
P1 12.00 usec
PL1 64.00000000 M
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 1H
P2 12.00 usec
PL2 64.00000000 M
===== CHANNEL f3 =====
SFO3 600.1330010 MHz
P3 12.00 usec
PL3 64.00000000 M
===== CHANNEL f4 =====
SFO4 600.1330010 MHz
P4 12.00 usec
PL4 64.00000000 M
===== CHANNEL f5 =====
SFO5 600.1330010 MHz
P5 12.00 usec
PL5 64.00000000 M
===== CHANNEL f6 =====
SFO6 600.1330010 MHz
P6 12.00 usec
PL6 64.00000000 M
===== CHANNEL f7 =====
SFO7 600.1330010 MHz
P7 12.00 usec
PL7 64.00000000 M
===== CHANNEL f8 =====
SFO8 600.1330010 MHz
P8 12.00 usec
PL8 64.00000000 M
===== CHANNEL f9 =====
SFO9 600.1330010 MHz
P9 12.00 usec
PL9 64.00000000 M
===== CHANNEL f10 =====
SFO10 600.1330010 MHz
P10 12.00 usec
PL10 64.00000000 M
===== CHANNEL f11 =====
SFO11 600.1330010 MHz
P11 12.00 usec
PL11 64.00000000 M
===== CHANNEL f12 =====
SFO12 600.1330010 MHz
P12 12.00 usec
PL12 64.00000000 M
===== CHANNEL f13 =====
SFO13 600.1330010 MHz
P13 12.00 usec
PL13 64.00000000 M
===== CHANNEL f14 =====
SFO14 600.1330010 MHz
P14 12.00 usec
PL14 64.00000000 M
===== CHANNEL f15 =====
SFO15 600.1330010 MHz
P15 12.00 usec
PL15 64.00000000 M
===== CHANNEL f16 =====
SFO16 600.1330010 MHz
P16 12.00 usec
PL16 64.00000000 M
===== CHANNEL f17 =====
SFO17 600.1330010 MHz
P17 12.00 usec
PL17 64.00000000 M
===== CHANNEL f18 =====
SFO18 600.1330010 MHz
P18 12.00 usec
PL18 64.00000000 M
===== CHANNEL f19 =====
SFO19 600.1330010 MHz
P19 12.00 usec
PL19 64.00000000 M
===== CHANNEL f20 =====
SFO20 600.1330010 MHz
P20 12.00 usec
PL20 64.00000000 M
===== CHANNEL f21 =====
SFO21 600.1330010 MHz
P21 12.00 usec
PL21 64.00000000 M
===== CHANNEL f22 =====
SFO22 600.1330010 MHz
P22 12.00 usec
PL22 64.00000000 M
===== CHANNEL f23 =====
SFO23 600.1330010 MHz
P23 12.00 usec
PL23 64.00000000 M
===== CHANNEL f24 =====
SFO24 600.1330010 MHz
P24 12.00 usec
PL24 64.00000000 M
===== CHANNEL f25 =====
SFO25 600.1330010 MHz
P25 12.00 usec
PL25 64.00000000 M
===== CHANNEL f26 =====
SFO26 600.1330010 MHz
P26 12.00 usec
PL26 64.00000000 M
===== CHANNEL f27 =====
SFO27 600.1330010 MHz
P27 12.00 usec
PL27 64.00000000 M
===== CHANNEL f28 =====
SFO28 600.1330010 MHz
P28 12.00 usec
PL28 64.00000000 M
===== CHANNEL f29 =====
SFO29 600.1330010 MHz
P29 12.00 usec
PL29 64.00000000 M
===== CHANNEL f30 =====
SFO30 600.1330010 MHz
P30 12.00 usec
PL30 64.00000000 M
===== CHANNEL f31 =====
SFO31 600.1330010 MHz
P31 12.00 usec
PL31 64.00000000 M
===== CHANNEL f32 =====
SFO32 600.1330010 MHz
P32 12.00 usec
PL32 64.00000000 M
===== CHANNEL f33 =====
SFO33 600.1330010 MHz
P33 12.00 usec
PL33 64.00000000 M
===== CHANNEL f34 =====
SFO34 600.1330010 MHz
P34 12.00 usec
PL34 64.00000000 M
===== CHANNEL f35 =====
SFO35 600.1330010 MHz
P35 12.00 usec
PL35 64.00000000 M
===== CHANNEL f36 =====
SFO36 600.1330010 MHz
P36 12.00 usec
PL36 64.00000000 M
===== CHANNEL f37 =====
SFO37 600.1330010 MHz
P37 12.00 usec
PL37 64.00000000 M
===== CHANNEL f38 =====
SFO38 600.1330010 MHz
P38 12.00 usec
PL38 64.00000000 M
===== CHANNEL f39 =====
SFO39 600.1330010 MHz
P39 12.00 usec
PL39 64.00000000 M
===== CHANNEL f40 =====
SFO40 600.1330010 MHz
P40 12.00 usec
PL40 64.00000000 M
===== CHANNEL f41 =====
SFO41 600.1330010 MHz
P41 12.00 usec
PL41 64.00000000 M
===== CHANNEL f42 =====
SFO42 600.1330010 MHz
P42 12.00 usec
PL42 64.00000000 M
===== CHANNEL f43 =====
SFO43 600.1330010 MHz
P43 12.00 usec
PL43 64.00000000 M
===== CHANNEL f44 =====
SFO44 600.1330010 MHz
P44 12.00 usec
PL44 64.00000000 M
===== CHANNEL f45 =====
SFO45 600.1330010 MHz
P45 12.00 usec
PL45 64.00000000 M
===== CHANNEL f46 =====
SFO46 600.1330010 MHz
P46 12.00 usec
PL46 64.00000000 M
===== CHANNEL f47 =====
SFO47 600.1330010 MHz
P47 12.00 usec
PL47 64.00000000 M
===== CHANNEL f48 =====
SFO48 600.1330010 MHz
P48 12.00 usec
PL48 64.00000000 M
===== CHANNEL f49 =====
SFO49 600.1330010 MHz
P49 12.00 usec
PL49 64.00000000 M
===== CHANNEL f50 =====
SFO50 600.1330010 MHz
P50 12.00 usec
PL50 64.00000000 M
===== CHANNEL f51 =====
SFO51 600.1330010 MHz
P51 12.00 usec
PL51 64.00000000 M
===== CHANNEL f52 =====
SFO52 600.1330010 MHz
P52 12.00 usec
PL52 64.00000000 M
===== CHANNEL f53 =====
SFO53 600.1330010 MHz
P53 12.00 usec
PL53 64.00000000 M
===== CHANNEL f54 =====
SFO54 600.1330010 MHz
P54 12.00 usec
PL54 64.00000000 M
===== CHANNEL f55 =====
SFO55 600.1330010 MHz
P55 12.00 usec
PL55 64.00000000 M
===== CHANNEL f56 =====
SFO56 600.1330010 MHz
P56 12.00 usec
PL56 64.00000000 M
===== CHANNEL f57 =====
SFO57 600.1330010 MHz
P57 12.00 usec
PL57 64.00000000 M
===== CHANNEL f58 =====
SFO58 600.1330010 MHz
P58 12.00 usec
PL58 64.00000000 M
===== CHANNEL f59 =====
SFO59 600.1330010 MHz
P59 12.00 usec
PL59 64.00000000 M
===== CHANNEL f60 =====
SFO60 600.1330010 MHz
P60 12.00 usec
PL60 64.00000000 M
===== CHANNEL f61 =====
SFO61 600.1330010 MHz
P61 12.00 usec
PL61 64.00000000 M
===== CHANNEL f62 =====
SFO62 600.1330010 MHz
P62 12.00 usec
PL62 64.00000000 M
===== CHANNEL f63 =====
SFO63 600.1330010 MHz
P63 12.00 usec
PL63 64.00000000 M
===== CHANNEL f64 =====
SFO64 600.1330010 MHz
P64 12.00 usec
PL64 64.00000000 M
===== CHANNEL f65 =====
SFO65 600.1330010 MHz
P65 12.00 usec
PL65 64.00000000 M
===== CHANNEL f66 =====
SFO66 600.1330010 MHz
P66 12.00 usec
PL66 64.00000000 M
===== CHANNEL f67 =====
SFO67 600.1330010 MHz
P67 12.00 usec
PL67 64.00000000 M
===== CHANNEL f68 =====
SFO68 600.1330010 MHz
P68 12.00 usec
PL68 64.00000000 M
===== CHANNEL f69 =====
SFO69 600.1330010 MHz
P69 12.00 usec
PL69 64.00000000 M
===== CHANNEL f70 =====
SFO70 600.1330010 MHz
P70 12.00 usec
PL70 64.00000000 M
===== CHANNEL f71 =====
SFO71 600.1330010 MHz
P71 12.00 usec
PL71 64.00000000 M
===== CHANNEL f72 =====
SFO72 600.1330010 MHz
P72 12.00 usec
PL72 64.00000000 M
===== CHANNEL f73 =====
SFO73 600.1330010 MHz
P73 12.00 usec
PL73 64.00000000 M
===== CHANNEL f74 =====
SFO74 600.1330010 MHz
P74 12.00 usec
PL74 64.00000000 M
===== CHANNEL f75 =====
SFO75 600.1330010 MHz
P75 12.00 usec
PL75 64.00000000 M
===== CHANNEL f76 =====
SFO76 600.1330010 MHz
P76 12.00 usec
PL76 64.00000000 M
===== CHANNEL f77 =====
SFO77 600.1330010 MHz
P77 12.00 usec
PL77 64.00000000 M
===== CHANNEL f78 =====
SFO78 600.1330010 MHz
P78 12.00 usec
PL78 64.00000000 M
===== CHANNEL f79 =====
SFO79 600.1330010 MHz
P79 12.00 usec
PL79 64.00000000 M
===== CHANNEL f80 =====
SFO80 600.1330010 MHz
P80 12.00 usec
PL80 64.00000000 M
===== CHANNEL f81 =====
SFO81 600.1330010 MHz
P81 12.00 usec
PL81 64.00000000 M
===== CHANNEL f82 =====
SFO82 600.1330010 MHz
P82 12.00 usec
PL82 64.00000000 M
===== CHANNEL f83 =====
SFO83 600.1330010 MHz
P83 12.00 usec
PL83 64.00000000 M
===== CHANNEL f84 =====
SFO84 600.1330010 MHz
P84 12.00 usec
PL84 64.00000000 M
===== CHANNEL f85 =====
SFO85 600.1330010 MHz
P85 12.00 usec
PL85 64.00000000 M
===== CHANNEL f86 =====
SFO86 600.1330010 MHz
P86 12.00 usec
PL86 64.00000000 M
===== CHANNEL f87 =====
SFO87 600.1330010 MHz
P87 12.00 usec
PL87 64.00000000 M
===== CHANNEL f88 =====
SFO88 600.1330010 MHz
P88 12.00 usec
PL88 64.00000000 M
===== CHANNEL f89 =====
SFO89 600.1330010 MHz
P89 12.00 usec
PL89 64.00000000 M
===== CHANNEL f90 =====
SFO90 600.1330010 MHz
P90 12.00 usec
PL90 64.00000000 M
===== CHANNEL f91 =====
SFO91 600.1330010 MHz
P91 12.00 usec
PL91 64.00000000 M
===== CHANNEL f92 =====
SFO92 600.1330010 MHz
P92 12.00 usec
PL92 64.00000000 M
===== CHANNEL f93 =====
SFO93 600.1330010 MHz
P93 12.00 usec
PL93 64.00000000 M
===== CHANNEL f94 =====
SFO94 600.1330010 MHz
P94 12.00 usec
PL94 64.00000000 M
===== CHANNEL f95 =====
SFO95 600.1330010 MHz
P95 12.00 usec
PL95 64.00000000 M
===== CHANNEL f96 =====
SFO96 600.1330010 MHz
P96 12.00 usec
PL96 64.00000000 M
===== CHANNEL f97 =====
SFO97 600.1330010 MHz
P97 12.00 usec
PL97 64.00000000 M
===== CHANNEL f98 =====
SFO98 600.1330010 MHz
P98 12.00 usec
PL98 64.00000000 M
===== CHANNEL f99 =====
SFO99 600.1330010 MHz
P99 12.00 usec
PL99 64.00000000 M
===== CHANNEL f100 =====
SFO100 600.1330010 MHz
P100 12.00 usec
PL100 64.00000000 M

15.507
15.343
20.343
21.217
21.533
21.615
22.499
23.004
23.432
25.209
26.225
28.582
31.582
34.530
34.574
35.289
35.550
38.267
38.948
39.745
47.942
56.401
77.016
77.187
77.228
77.480
81.407
100.970



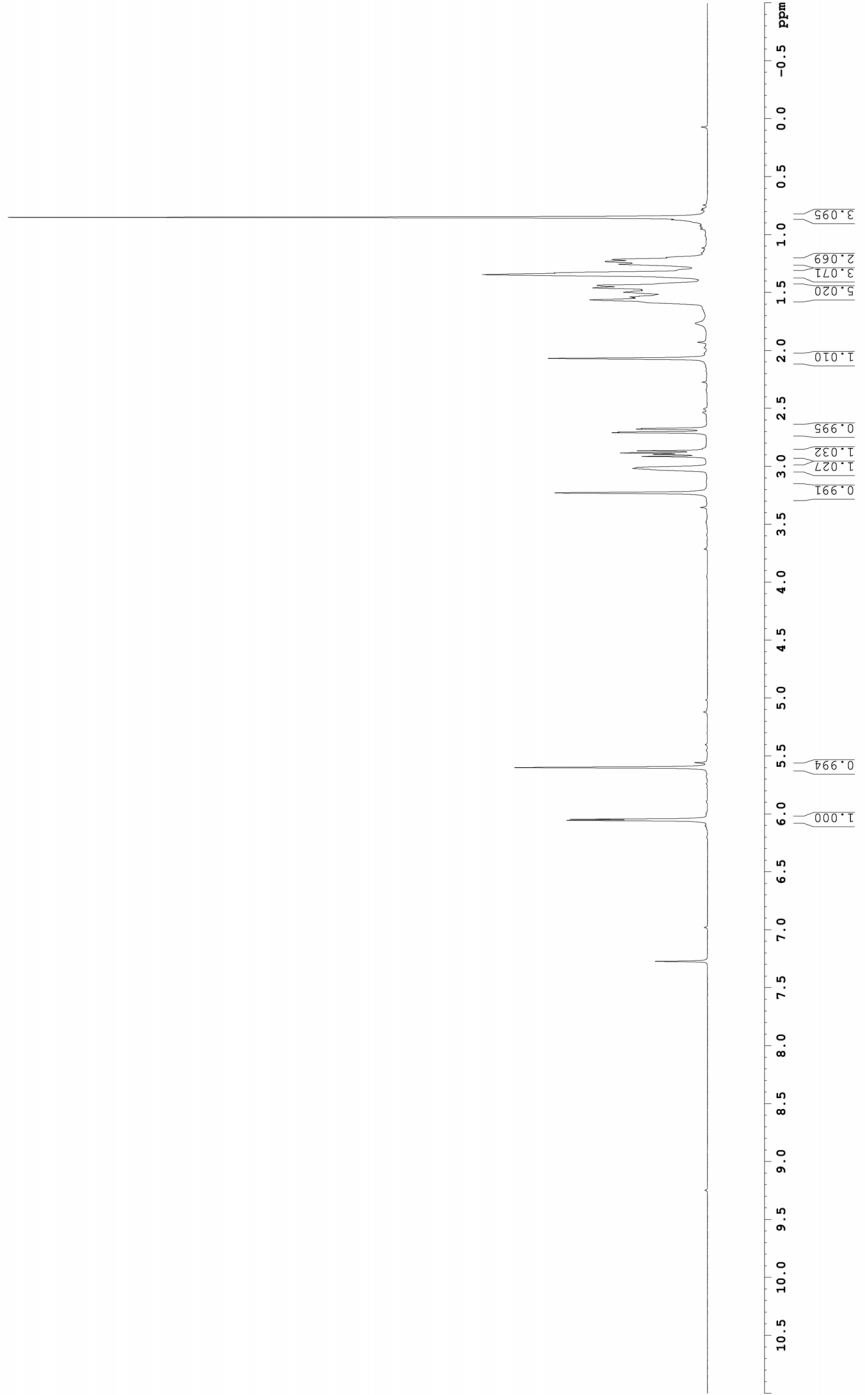
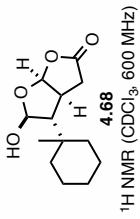
YS-V-268

Current Data Parameters
NAME YS-V-268
PROC 1
DATE /v/date/yuri/y/nmr
Date - Acquisition Parameters
Time 20170323
INSTRUM av600
PULPROG zg30
TD 88074
SOLVENT CDCl3
DS 1
SWH 0615.395 Hz
AQ 5.0398478 sec
RG 10
WDW 50
SS 3.00 usec
TE 298.1 K
D1 0.10000000 sec
D0 1

===== CHANNEL f1 =====
SFO1 600.1342009 MHz
P1 12.00 usec
PL1 20.00000000 M
F2 - Processing parameters
SI 65536
SF 600.1300286 MHz
SM 32768
SSB 0
LB 0
GB 0
PC 1.00

0.848
1.212
1.228
1.254
1.328
1.348
1.438
1.457
1.474
1.494
1.529
1.536
1.544
1.561
1.567
1.572
2.676
2.702
2.707
2.864
2.882
2.894
2.912
3.009
3.015
3.227

5.997
6.044
6.053
7.270

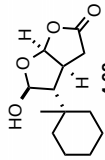


YS-V-268

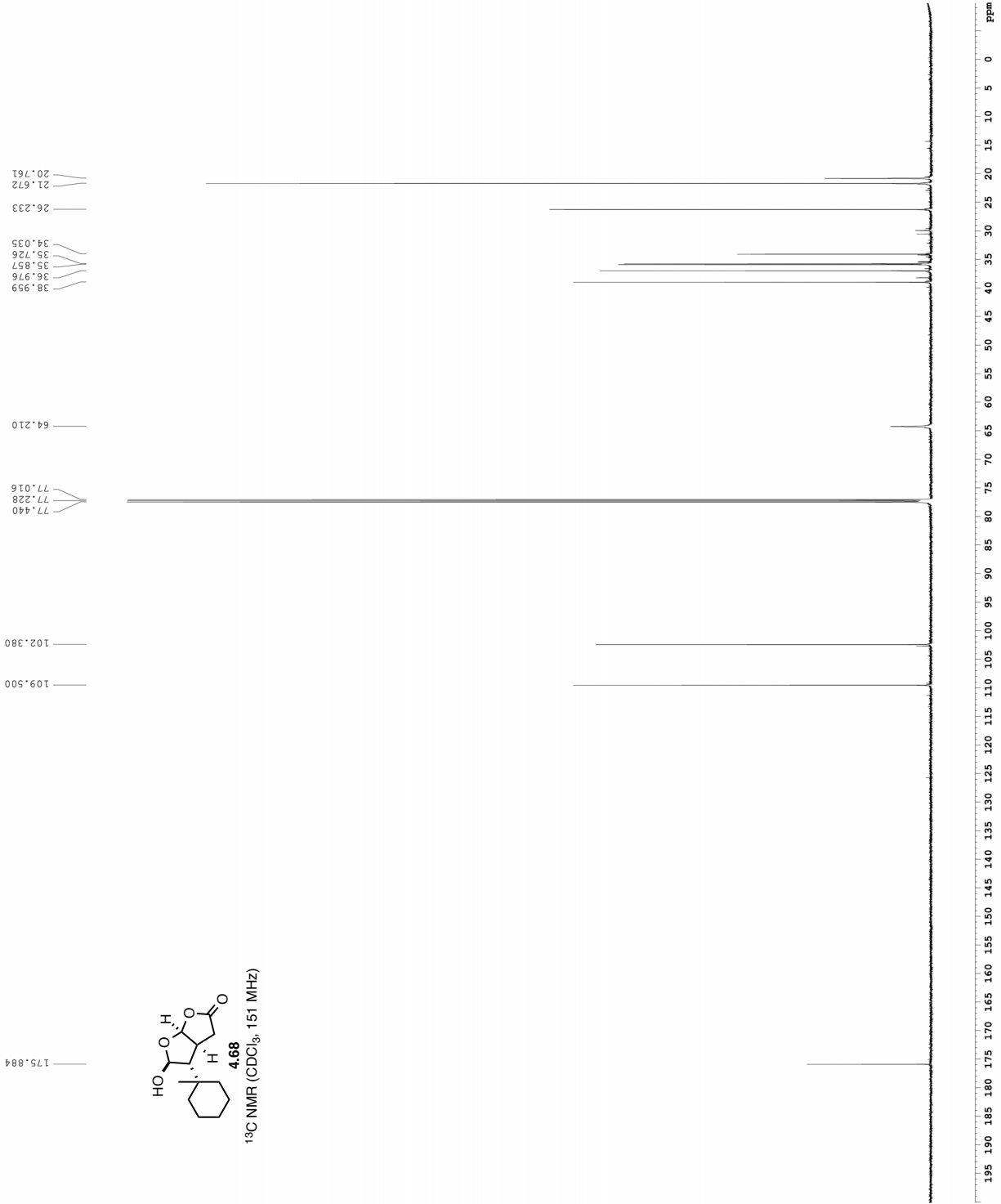
Current Data Parameters
NAME YS-V-268 2
EXPERO
DATEPATH /v/data/yv/yv15/mr
F2 - Acquisition Parameters
Date_ 20170323
Time 15:00
INSTRUM spect
PROBHD 5 mm CPBBO BB-
ZPP00
PULPROG zgpg30
SOLVENT CDCl3
DS 2
ZG 1
SWH 36231.883 Hz
FIDRES 0.90435868 sec
RG 11
AQ 11.2050 usec
DE 19.65 usec
TE 298.0 K
D1 0.40000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 64.00000000 W
===== CHANNEL f2 =====
NUC2 13C
P2 10.00 usec
PL2 64.00000000 W
===== CHANNEL f3 =====
NUC3 1H
P3 10.00 usec
PL3 0.00000000 W
===== CHANNEL f4 =====
CPDPRG2 waltz16
NUC4 13C
P4 10.00 usec
PL4 64.00000000 W
===== CHANNEL f5 =====
CPDPRG2 waltz16
NUC5 1H
P5 10.00 usec
PL5 0.00000000 W

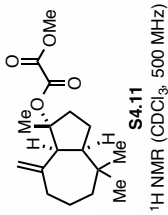
F2 - Processing parameters
SI 32768
SF 150.902767 MHz
WDW EM
SSB 0
GB 0
PC 1.00



¹³C NMR (CDCl₃, 151 MHz)

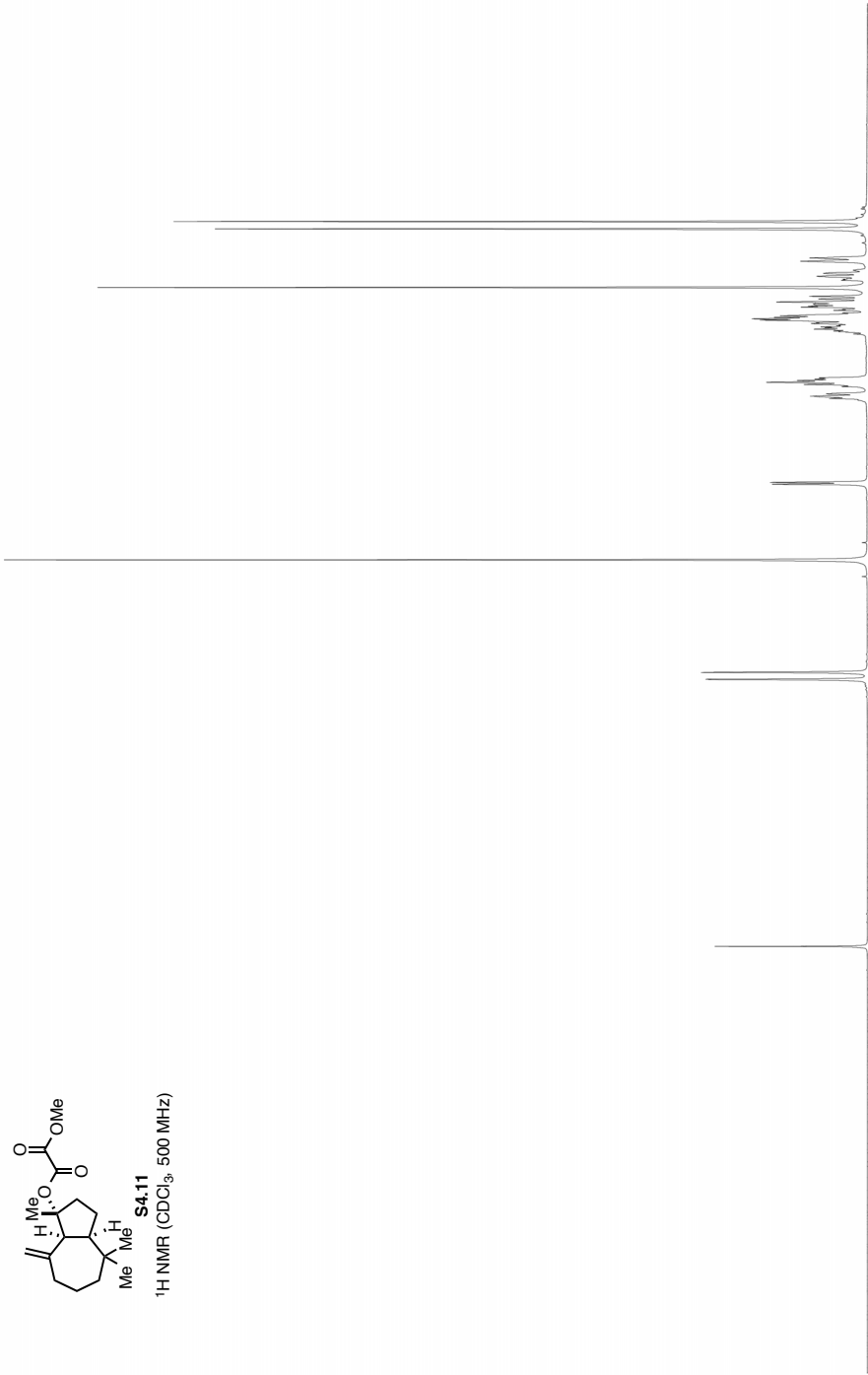


YS-V-202



Current Data Parameters
NAME YS-V-202
PROC 1
PROB0
F2 - Acquisition Parameters
Time 20110717
Time 17.07
INSTRUM cryo500
PROBHD 5 mm CFCT 1H
TD 65536
SOLVENT CDCl3
S CDCl3
NS 9
SWH 8012.820 Hz
FIDRES 0.100003 Hz
AQ 4.3398625 sec
RG 62.400 usec
DW 62.400 usec
DE 99.0 usec
TE 298.2 K
D1 0.10000000 sec
MCRESST 0 sec
PCPRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
PULP 7.18 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200316 MHz
SM 2M
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

4.924
4.862
3.875
3.213
3.197
2.463
2.448
2.442
2.422
2.418
2.358
2.339
2.320
2.304
2.282
1.898
1.882
1.876
1.872
1.861
1.856
1.843
1.836
1.826
1.822
1.819
1.805
1.799
1.785
1.776
1.764
1.752
1.736
1.682
1.662
1.654
1.640
1.635
1.626
1.618
1.610
1.490
1.470
1.420
1.418
1.413
1.407
1.393



YS-V-202

Current Data Parameters
NAME YS-V-202
PROCNO 2

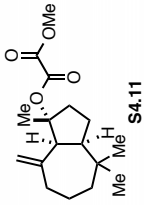
F2 - Acquisition Parameters
Time 2017.10
INSTRUM cryo-500
PULPROG zgpg30
SOLVENT CDCl3

NS 496
SRH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 6.502 sec
RG 653
DM 16.500 usec
TE 298.0 K
D11 0.2500000 sec
D16 0.0004000 sec
MCOREST 0 sec
MCORRK 0.0150000 sec
F2 33.10 usec

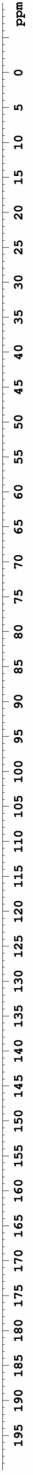
===== CHANNEL f1 =====
P1C1 16.25 usec
P11 500.00 usec
P12 120.00 dB
P10 120.00 dB
P14 125.797100 dB
SP1 2.70 dBz
SPNAM[1] Cp50.0.5.20.1
SPNAM[2] Cp60.comp.4
SFOFF1 0 Hz
SFOFF2 0 Hz

===== CHANNEL f2 =====
CFFPRG[2] wait+16
NUC2 100.1H
P12 1.60 usec
P14 24.50 dB
SP2 500.225311 MHz

===== GRADIENT CHANNEL =====
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GPXX 0 %
GPY1 0 %
GPZ1 0 %
GP22 30.00 %
G16 50.00 %
P16 1000.00 usec
F2 - Processing Parameters
SI 45536
SF 125.7603934 MHz
SFO 64
SSB 0
GB 1.00 Hz
PC 2.00



¹³C NMR (CDCl₃, 126 MHz)

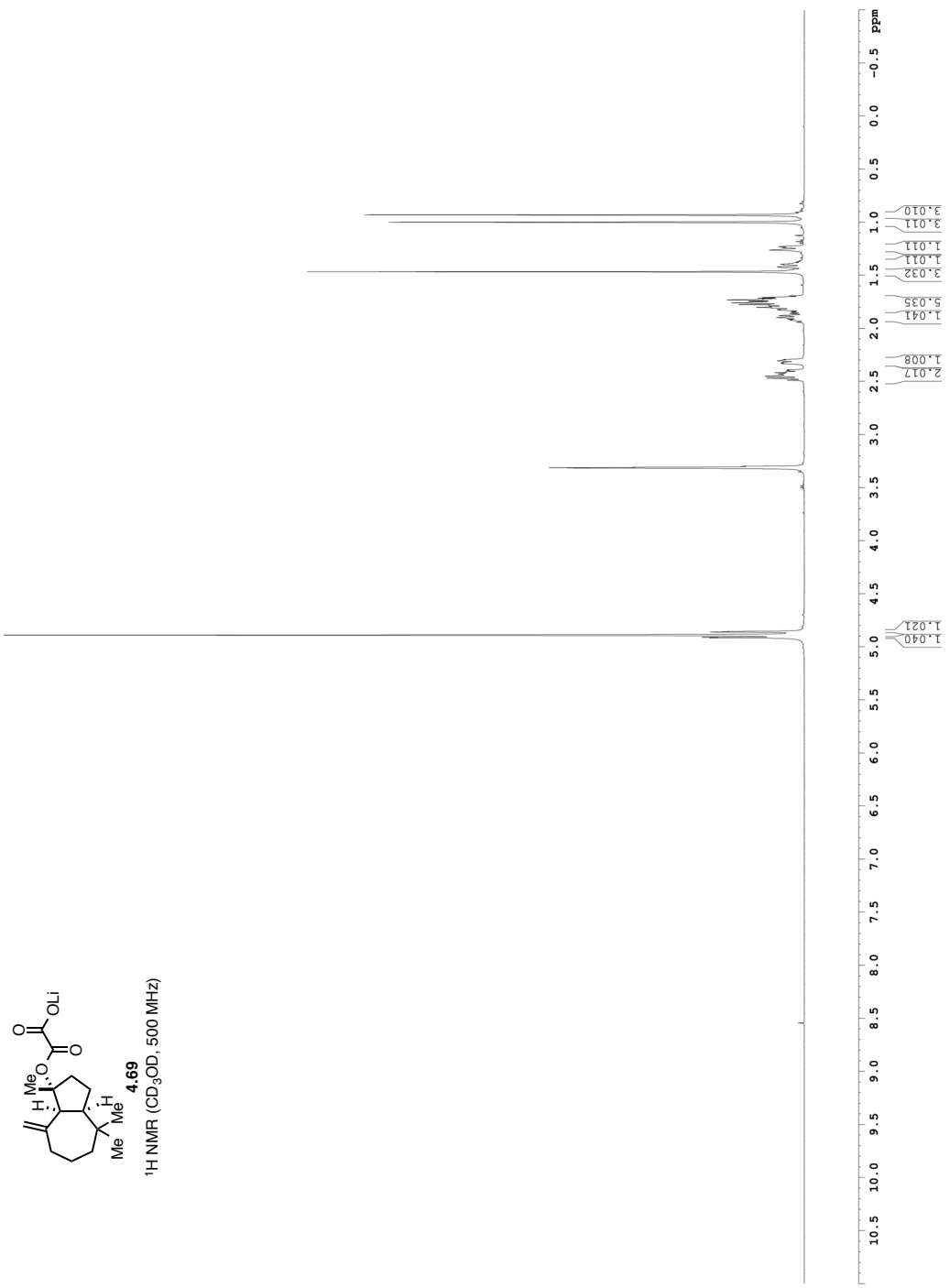
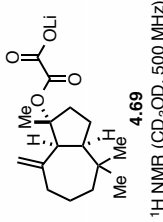


YS-V-203

Current Data Parameters
NAME YS-V-203
PROCNO 1
F2 - Acquisition Parameters

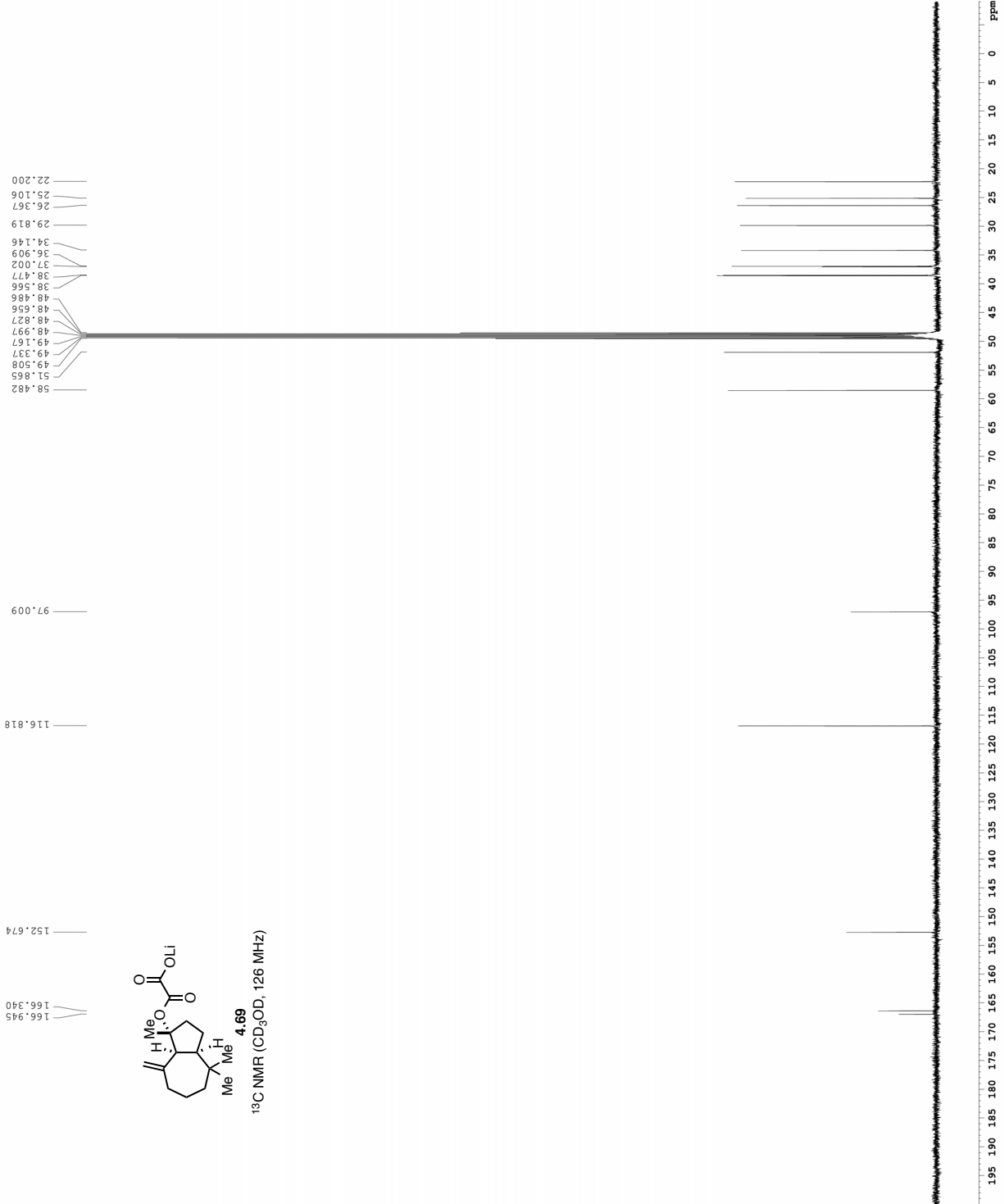
Time 20110104
INSTRUM cryo-500
PROBHD 5 mm CPIC1 1H
TD 81728
SOLVENT CD3OD
P1 8
SWH 8012.820 Hz
FIDRES 0.098643 Hz
RG 6.3
AQ 62.400 usec
SFO1 500.2235015 MHz
D1 0.10000000 sec
MCREST 0 sec
PC 1.00

4.913
4.908
4.887
4.858
4.854
3.313
3.310
3.307
3.298
2.485
2.466
2.453
2.437
2.429
2.423
2.415
2.408
2.397
2.395
2.390
2.328
2.321
2.303
2.291
1.920
1.912
1.902
1.896
1.883
1.876
1.858
1.847
1.840
1.825
1.820
1.805
1.799
1.792
1.785
1.780
1.773
1.757
1.751
1.742
1.729
1.722
1.714
1.707
1.463
1.420
1.417
1.398
1.394

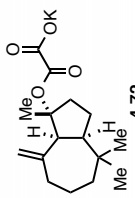


YS-V-203

Current Data Parameters
NAME XS-V-203
PROCNO 2
F2 - Acquisition Parameters
Time 40.10
INSTRUM 5 mm CPY3000
PULPROG zgpg30p-prd
SOLVENT CDCl3
NS 968
SI 30303.031 Hz
FIDRES 0.462388 Hz
RG 328.2
DR 16.500 usec
TE 298.0 K
D1 0.2500000 sec
D16 0.0002000 sec
MCORST 0 sec/0001900 sec
MCORST 0.0150000 sec
F2 Processing Parameters
SI 65536
SFO 125.760454 MHz
GB 0 1.00 Hz
PC 2.00

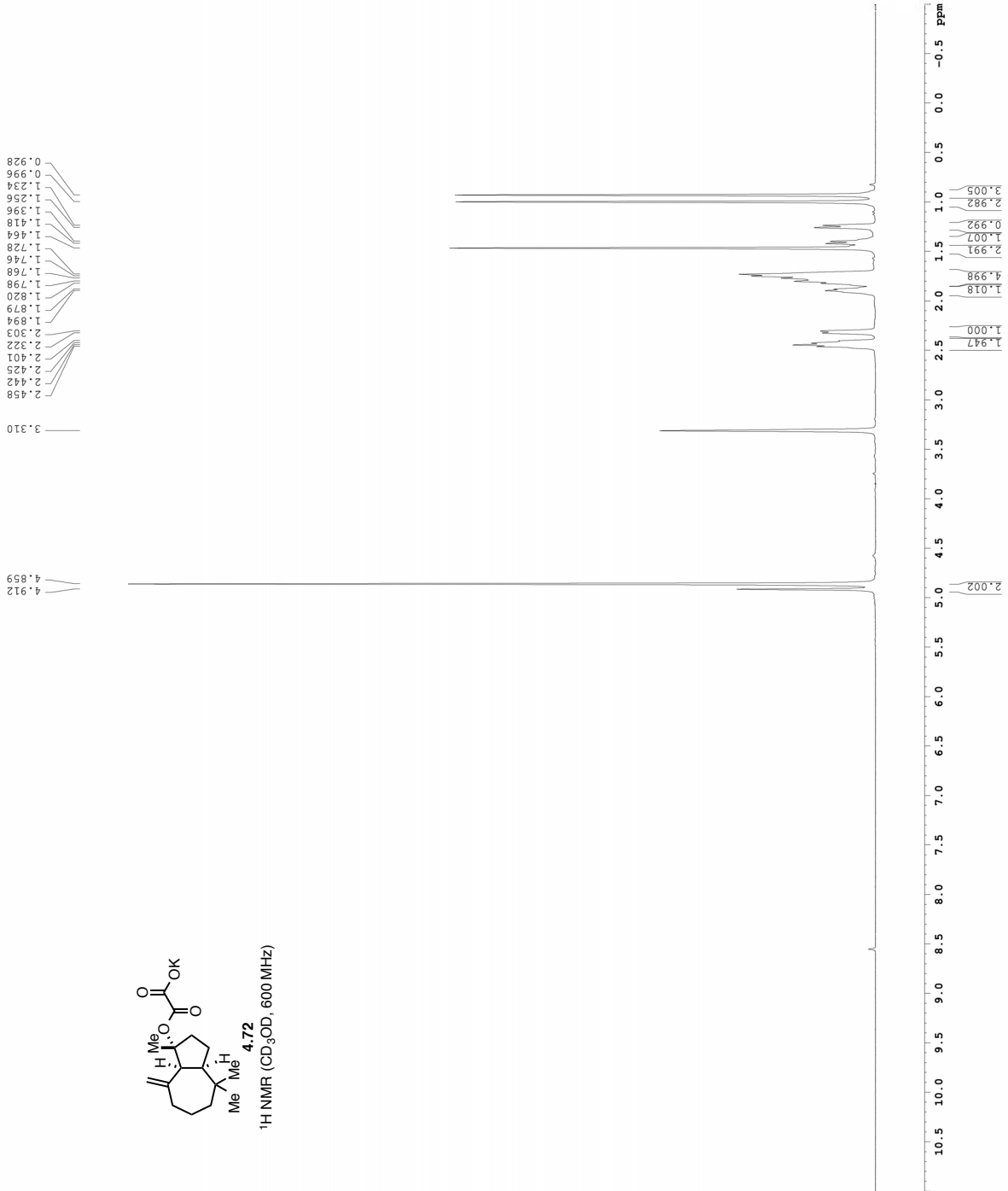


YS-VI-31



¹H NMR (CD₃OD, 600 MHz)

Current Data Parameters
NAME YS-VI-31
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180727
Time 8:21
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.166673 Hz
AQ 0.0200000 sec
RG 327.16
RG2 16
DM 52.000 usec
DE 238.0 usec
TE 300.2 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.1342003 MHz
NUC1 12.01 usec
P1 12.01 usec
PL1 20.00000000 M
===== CHANNEL f2 =====
SF02 600.1300194 MHz
NUC2 12.01 usec
P2 12.01 usec
PL2 20.00000000 M
===== Processing parameters =====
SI 65536
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



YS-VI-31

Current Data Parameters
EXPNO 2
NAME YS-VI-31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080808
Time 8.25
INSTRUM spect
PROBHD 5 mm CPBPR600
PULPROG zgpg30
SOLVENT CDCl3
NS 256
DS 4
SWH 36221.883 Hz
FIDRES 0.552825 Hz
RG 0.592650 sec
DW 13.800 usec
TE 298.0 K
D1 0.40000001 sec
D11 0.10000001 sec
TD 65536

===== CHANNEL f1 =====
SFO1 150.9194080 MHz
NUC1 13C
P1 10.00 usec
PL1 64.00000000 W

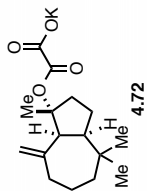
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 1H
PCPD2 waltz16
P2 20.00 usec
PL2 0.36000001 W

F2 - Processing Parameters
SI 65536
SF 150.9025250 MHz
WDW EM
SSB 0
GB 0
PC 1.00

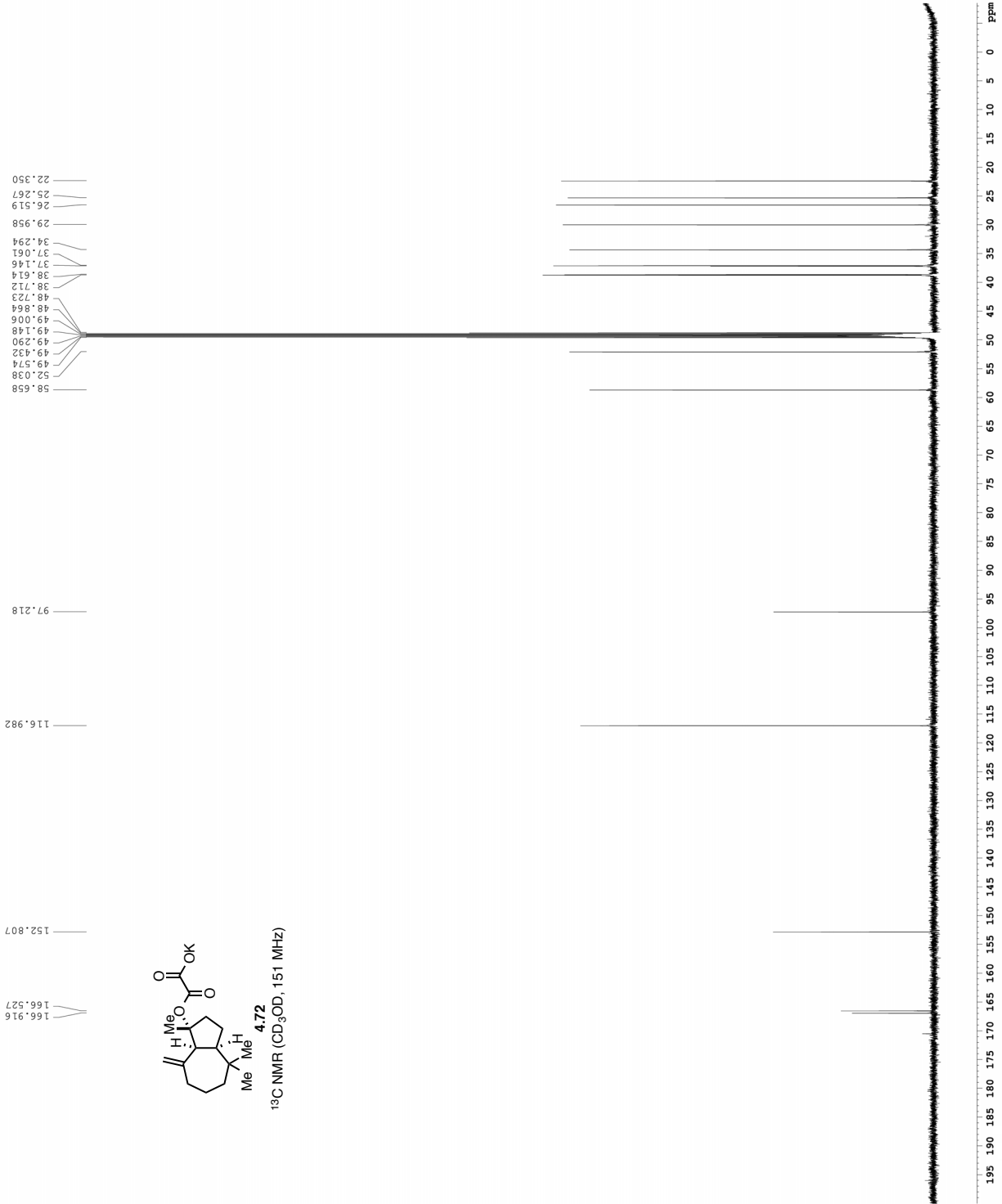
22.350
25.267
26.519
29.958
34.294
37.061
37.146
38.614
38.712
48.723
48.864
49.006
49.148
49.290
49.432
49.574
52.038
58.658

97.218
116.982

152.807
166.527
166.916

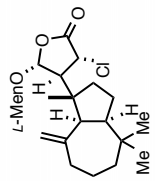


¹³C NMR (CD₃OD, 151 MHz)

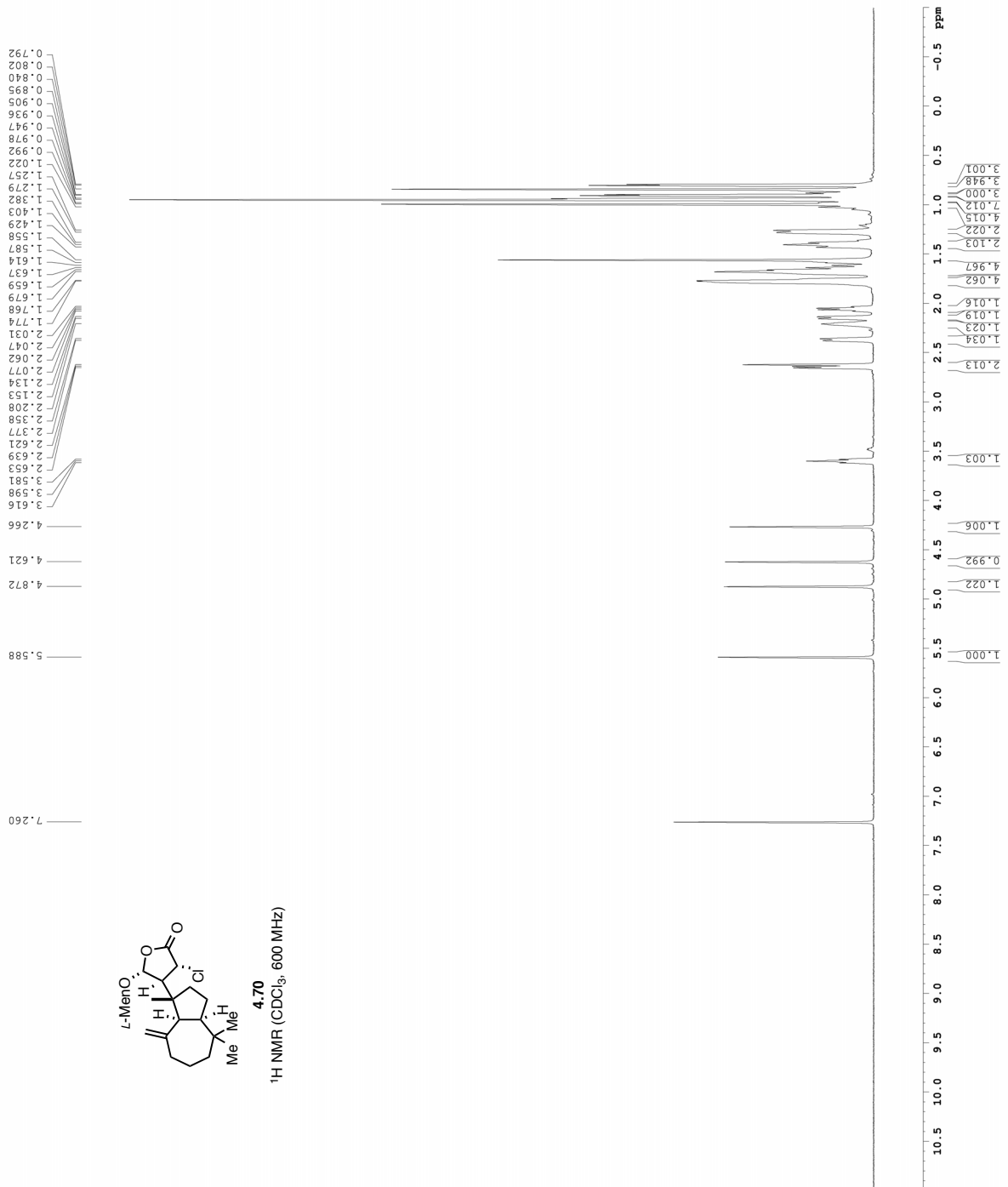


YS-V-225B

Current Data Parameters
NAME YS-V-225B
PROC 1
PROB 1
P2 - Acquisition Parameters
Time 2012.56
INSTRUM 5 mm CPBBO BB
PROBHD 8874
TD 8874
SOLVENT CDCl3
NS 2
SRH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 3.0398170 sec
RG 10 sec
DW 52.000 usec
DE 298.0 K usec
TE 298.0 K usec
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 1H
PULP1 20.00000000 M
PL1 12.00 usec
P2 - Processing parameters
SI 65536
SF 600.1300354 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

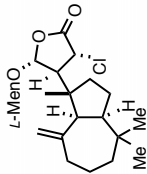


4.70
¹H NMR (CDCl₃, 600 MHz)

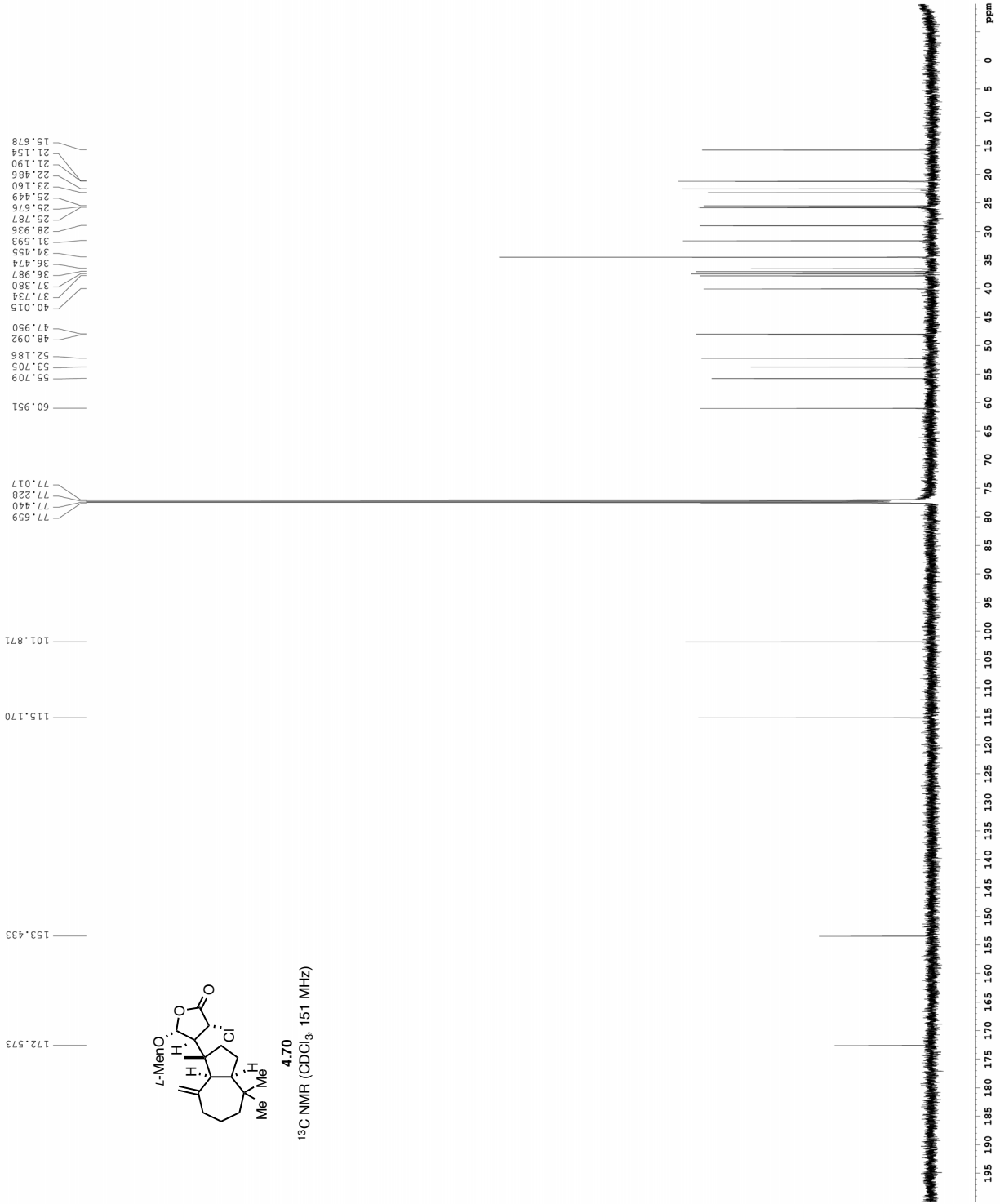


YS-V-225B

Current Data Parameters
NAME YS-V-225B
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110101
Time 13:00
INSTRUM av600
PROBHD 5 mm CPBPR00
PULPROG zgpg30
SOLVENT CDCl3
NS 200
DS 4
SWH 36231.883 Hz
FIDRES 0.522855 Hz
AQ 0.390478 sec
RG 2050
DM 13.800 usec
DE 2.000 usec
TE 298.0 K
D1 0.4000001 sec
D11 0.1500001 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.914080 MHz
NUC1 13C
P1 12.00 usec
PL1 0.00000000 M
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
NUC2 1H
P2 12.00 usec
PL2 0.00000000 M
===== CHANNEL f3 =====
SFO3 600.1330010 MHz
P3 12.00 usec
PL3 0.00000000 M
===== CHANNEL f4 =====
SFO4 600.1330010 MHz
P4 12.00 usec
PL4 0.00000000 M
===== CHANNEL f5 =====
SFO5 600.1330010 MHz
P5 12.00 usec
PL5 0.00000000 M
===== CHANNEL f6 =====
SFO6 600.1330010 MHz
P6 12.00 usec
PL6 0.00000000 M
===== CHANNEL f7 =====
SFO7 600.1330010 MHz
P7 12.00 usec
PL7 0.00000000 M
===== CHANNEL f8 =====
SFO8 600.1330010 MHz
P8 12.00 usec
PL8 0.00000000 M
===== CHANNEL f9 =====
SFO9 600.1330010 MHz
P9 12.00 usec
PL9 0.00000000 M
===== CHANNEL f10 =====
SFO10 600.1330010 MHz
P10 12.00 usec
PL10 0.00000000 M
===== CHANNEL f11 =====
SFO11 600.1330010 MHz
P11 12.00 usec
PL11 0.00000000 M
===== CHANNEL f12 =====
SFO12 600.1330010 MHz
P12 12.00 usec
PL12 0.36000001 M
===== CHANNEL f13 =====
SFO13 600.1330010 MHz
P13 12.00 usec
PL13 0.36000001 M
===== CHANNEL f14 =====
SFO14 600.1330010 MHz
P14 12.00 usec
PL14 0.36000001 M
===== CHANNEL f15 =====
SFO15 600.1330010 MHz
P15 12.00 usec
PL15 0.36000001 M
===== CHANNEL f16 =====
SFO16 600.1330010 MHz
P16 12.00 usec
PL16 0.36000001 M
===== CHANNEL f17 =====
SFO17 600.1330010 MHz
P17 12.00 usec
PL17 0.36000001 M
===== CHANNEL f18 =====
SFO18 600.1330010 MHz
P18 12.00 usec
PL18 0.36000001 M
===== CHANNEL f19 =====
SFO19 600.1330010 MHz
P19 12.00 usec
PL19 0.36000001 M
===== CHANNEL f20 =====
SFO20 600.1330010 MHz
P20 12.00 usec
PL20 0.36000001 M
===== CHANNEL f21 =====
SFO21 600.1330010 MHz
P21 12.00 usec
PL21 0.36000001 M
===== CHANNEL f22 =====
SFO22 600.1330010 MHz
P22 12.00 usec
PL22 0.36000001 M
===== CHANNEL f23 =====
SFO23 600.1330010 MHz
P23 12.00 usec
PL23 0.36000001 M
===== CHANNEL f24 =====
SFO24 600.1330010 MHz
P24 12.00 usec
PL24 0.36000001 M
===== CHANNEL f25 =====
SFO25 600.1330010 MHz
P25 12.00 usec
PL25 0.36000001 M
===== CHANNEL f26 =====
SFO26 600.1330010 MHz
P26 12.00 usec
PL26 0.36000001 M
===== CHANNEL f27 =====
SFO27 600.1330010 MHz
P27 12.00 usec
PL27 0.36000001 M
===== CHANNEL f28 =====
SFO28 600.1330010 MHz
P28 12.00 usec
PL28 0.36000001 M
===== CHANNEL f29 =====
SFO29 600.1330010 MHz
P29 12.00 usec
PL29 0.36000001 M
===== CHANNEL f30 =====
SFO30 600.1330010 MHz
P30 12.00 usec
PL30 0.36000001 M
===== CHANNEL f31 =====
SFO31 600.1330010 MHz
P31 12.00 usec
PL31 0.36000001 M
===== CHANNEL f32 =====
SFO32 600.1330010 MHz
P32 12.00 usec
PL32 0.36000001 M
===== CHANNEL f33 =====
SFO33 600.1330010 MHz
P33 12.00 usec
PL33 0.36000001 M
===== CHANNEL f34 =====
SFO34 600.1330010 MHz
P34 12.00 usec
PL34 0.36000001 M
===== CHANNEL f35 =====
SFO35 600.1330010 MHz
P35 12.00 usec
PL35 0.36000001 M
===== CHANNEL f36 =====
SFO36 600.1330010 MHz
P36 12.00 usec
PL36 0.36000001 M
===== CHANNEL f37 =====
SFO37 600.1330010 MHz
P37 12.00 usec
PL37 0.36000001 M
===== CHANNEL f38 =====
SFO38 600.1330010 MHz
P38 12.00 usec
PL38 0.36000001 M
===== CHANNEL f39 =====
SFO39 600.1330010 MHz
P39 12.00 usec
PL39 0.36000001 M
===== CHANNEL f40 =====
SFO40 600.1330010 MHz
P40 12.00 usec
PL40 0.36000001 M
===== CHANNEL f41 =====
SFO41 600.1330010 MHz
P41 12.00 usec
PL41 0.36000001 M
===== CHANNEL f42 =====
SFO42 600.1330010 MHz
P42 12.00 usec
PL42 0.36000001 M
===== CHANNEL f43 =====
SFO43 600.1330010 MHz
P43 12.00 usec
PL43 0.36000001 M
===== CHANNEL f44 =====
SFO44 600.1330010 MHz
P44 12.00 usec
PL44 0.36000001 M
===== CHANNEL f45 =====
SFO45 600.1330010 MHz
P45 12.00 usec
PL45 0.36000001 M
===== CHANNEL f46 =====
SFO46 600.1330010 MHz
P46 12.00 usec
PL46 0.36000001 M
===== CHANNEL f47 =====
SFO47 600.1330010 MHz
P47 12.00 usec
PL47 0.36000001 M
===== CHANNEL f48 =====
SFO48 600.1330010 MHz
P48 12.00 usec
PL48 0.36000001 M
===== CHANNEL f49 =====
SFO49 600.1330010 MHz
P49 12.00 usec
PL49 0.36000001 M
===== CHANNEL f50 =====
SFO50 600.1330010 MHz
P50 12.00 usec
PL50 0.36000001 M
===== CHANNEL f51 =====
SFO51 600.1330010 MHz
P51 12.00 usec
PL51 0.36000001 M
===== CHANNEL f52 =====
SFO52 600.1330010 MHz
P52 12.00 usec
PL52 0.36000001 M
===== CHANNEL f53 =====
SFO53 600.1330010 MHz
P53 12.00 usec
PL53 0.36000001 M
===== CHANNEL f54 =====
SFO54 600.1330010 MHz
P54 12.00 usec
PL54 0.36000001 M
===== CHANNEL f55 =====
SFO55 600.1330010 MHz
P55 12.00 usec
PL55 0.36000001 M
===== CHANNEL f56 =====
SFO56 600.1330010 MHz
P56 12.00 usec
PL56 0.36000001 M
===== CHANNEL f57 =====
SFO57 600.1330010 MHz
P57 12.00 usec
PL57 0.36000001 M
===== CHANNEL f58 =====
SFO58 600.1330010 MHz
P58 12.00 usec
PL58 0.36000001 M
===== CHANNEL f59 =====
SFO59 600.1330010 MHz
P59 12.00 usec
PL59 0.36000001 M
===== CHANNEL f60 =====
SFO60 600.1330010 MHz
P60 12.00 usec
PL60 0.36000001 M
===== CHANNEL f61 =====
SFO61 600.1330010 MHz
P61 12.00 usec
PL61 0.36000001 M
===== CHANNEL f62 =====
SFO62 600.1330010 MHz
P62 12.00 usec
PL62 0.36000001 M
===== CHANNEL f63 =====
SFO63 600.1330010 MHz
P63 12.00 usec
PL63 0.36000001 M
===== CHANNEL f64 =====
SFO64 600.1330010 MHz
P64 12.00 usec
PL64 0.36000001 M
===== CHANNEL f65 =====
SFO65 600.1330010 MHz
P65 12.00 usec
PL65 0.36000001 M
===== CHANNEL f66 =====
SFO66 600.1330010 MHz
P66 12.00 usec
PL66 0.36000001 M
===== CHANNEL f67 =====
SFO67 600.1330010 MHz
P67 12.00 usec
PL67 0.36000001 M
===== CHANNEL f68 =====
SFO68 600.1330010 MHz
P68 12.00 usec
PL68 0.36000001 M
===== CHANNEL f69 =====
SFO69 600.1330010 MHz
P69 12.00 usec
PL69 0.36000001 M
===== CHANNEL f70 =====
SFO70 600.1330010 MHz
P70 12.00 usec
PL70 0.36000001 M
===== CHANNEL f71 =====
SFO71 600.1330010 MHz
P71 12.00 usec
PL71 0.36000001 M
===== CHANNEL f72 =====
SFO72 600.1330010 MHz
P72 12.00 usec
PL72 0.36000001 M
===== CHANNEL f73 =====
SFO73 600.1330010 MHz
P73 12.00 usec
PL73 0.36000001 M
===== CHANNEL f74 =====
SFO74 600.1330010 MHz
P74 12.00 usec
PL74 0.36000001 M
===== CHANNEL f75 =====
SFO75 600.1330010 MHz
P75 12.00 usec
PL75 0.36000001 M
===== CHANNEL f76 =====
SFO76 600.1330010 MHz
P76 12.00 usec
PL76 0.36000001 M
===== CHANNEL f77 =====
SFO77 600.1330010 MHz
P77 12.00 usec
PL77 0.36000001 M
===== CHANNEL f78 =====
SFO78 600.1330010 MHz
P78 12.00 usec
PL78 0.36000001 M
===== CHANNEL f79 =====
SFO79 600.1330010 MHz
P79 12.00 usec
PL79 0.36000001 M
===== CHANNEL f80 =====
SFO80 600.1330010 MHz
P80 12.00 usec
PL80 0.36000001 M
===== CHANNEL f81 =====
SFO81 600.1330010 MHz
P81 12.00 usec
PL81 0.36000001 M
===== CHANNEL f82 =====
SFO82 600.1330010 MHz
P82 12.00 usec
PL82 0.36000001 M
===== CHANNEL f83 =====
SFO83 600.1330010 MHz
P83 12.00 usec
PL83 0.36000001 M
===== CHANNEL f84 =====
SFO84 600.1330010 MHz
P84 12.00 usec
PL84 0.36000001 M
===== CHANNEL f85 =====
SFO85 600.1330010 MHz
P85 12.00 usec
PL85 0.36000001 M
===== CHANNEL f86 =====
SFO86 600.1330010 MHz
P86 12.00 usec
PL86 0.36000001 M
===== CHANNEL f87 =====
SFO87 600.1330010 MHz
P87 12.00 usec
PL87 0.36000001 M
===== CHANNEL f88 =====
SFO88 600.1330010 MHz
P88 12.00 usec
PL88 0.36000001 M
===== CHANNEL f89 =====
SFO89 600.1330010 MHz
P89 12.00 usec
PL89 0.36000001 M
===== CHANNEL f90 =====
SFO90 600.1330010 MHz
P90 12.00 usec
PL90 0.36000001 M
===== CHANNEL f91 =====
SFO91 600.1330010 MHz
P91 12.00 usec
PL91 0.36000001 M
===== CHANNEL f92 =====
SFO92 600.1330010 MHz
P92 12.00 usec
PL92 0.36000001 M
===== CHANNEL f93 =====
SFO93 600.1330010 MHz
P93 12.00 usec
PL93 0.36000001 M
===== CHANNEL f94 =====
SFO94 600.1330010 MHz
P94 12.00 usec
PL94 0.36000001 M
===== CHANNEL f95 =====
SFO95 600.1330010 MHz
P95 12.00 usec
PL95 0.36000001 M
===== CHANNEL f96 =====
SFO96 600.1330010 MHz
P96 12.00 usec
PL96 0.36000001 M
===== CHANNEL f97 =====
SFO97 600.1330010 MHz
P97 12.00 usec
PL97 0.36000001 M
===== CHANNEL f98 =====
SFO98 600.1330010 MHz
P98 12.00 usec
PL98 0.36000001 M
===== CHANNEL f99 =====
SFO99 600.1330010 MHz
P99 12.00 usec
PL99 0.36000001 M
===== CHANNEL f100 =====
SFO100 600.1330010 MHz
P100 12.00 usec
PL100 0.36000001 M

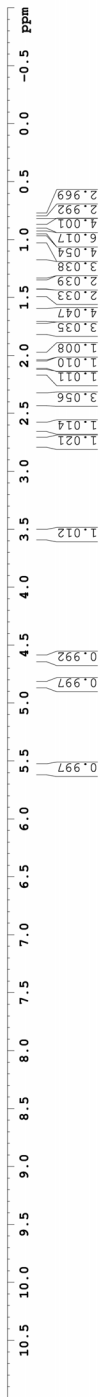
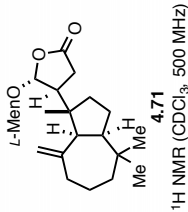
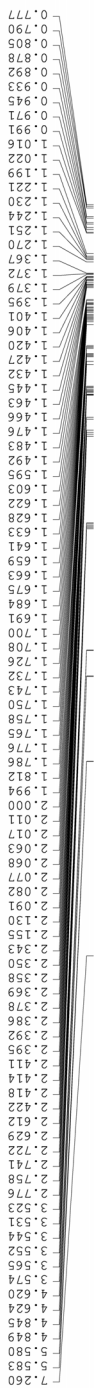


4.70
¹³C-NMR (CDCl₃, 151 MHz)



YS-V-272

```
Current Data Parameters
NAME      YS-V-272
PROBHD   5mm QNP1H
PROGNO    1
DATAFATH /v/data/yuris/mr
F2 - Acquisition Parameters
Date      20170328
Time      16.30
INSTRUM   spect
PULPROG   zgpg30
TD         65536
FIDRES    0.15000000
AQ         5.0998273 sec
RG         62.1024
DE         62.100 usec
TE         298.0 K
D1         0.10000000 sec
d11        0.01500000 sec
KCMASK    ***** CHANNEL f1 *****
NUC1      1H
P1         12.00 usec
PL1        -5.80 dB
SFO1      499.0734935 MHz
F2 - Processing parameters
SI         65536
SF         499.0700350 MHz
WDW        EM
SSB        0
GB         0
PC         1.00
```



YS-V-205

```

Current Data Parameters
EXPNO 1
PROCNO 1
DATAF1H /v/data/furys/mr
F2 - Acquisition Parameters
Time 201.828
INSTRUM 5 mm cryo-50
PULPROG zgpg30
TD 65536
SOLVENT NS
NS 896
DSH 30303.031 Hz
FIDRES 0.462288 Hz
AQ 1.72862 sec
DM 16.500 usec
TE 298.0 K
D1 0.2500000 sec
d11 0.5000000 sec
d16 0.5000000 sec
dLYST 0.00019600 sec
MCPRST 0.03150000 sec
F2 CHANNEL F1
=====
P1C1 16.25 usec
P11 500.00 usec
PL1 120.00 dB
PL2 120.00 dB
PL3 120.00 dB
PL4 120.00 dB
PL5 120.00 dB
PL6 120.00 dB
PL7 120.00 dB
PL8 120.00 dB
PL9 120.00 dB
PL10 120.00 dB
PL11 120.00 dB
PL12 120.00 dB
PL13 120.00 dB
PL14 120.00 dB
PL15 120.00 dB
PL16 120.00 dB
PL17 120.00 dB
PL18 120.00 dB
PL19 120.00 dB
PL20 120.00 dB
PL21 120.00 dB
PL22 120.00 dB
PL23 120.00 dB
PL24 120.00 dB
PL25 120.00 dB
PL26 120.00 dB
PL27 120.00 dB
PL28 120.00 dB
PL29 120.00 dB
PL30 120.00 dB
PL31 120.00 dB
PL32 120.00 dB
PL33 120.00 dB
PL34 120.00 dB
PL35 120.00 dB
PL36 120.00 dB
PL37 120.00 dB
PL38 120.00 dB
PL39 120.00 dB
PL40 120.00 dB
PL41 120.00 dB
PL42 120.00 dB
PL43 120.00 dB
PL44 120.00 dB
PL45 120.00 dB
PL46 120.00 dB
PL47 120.00 dB
PL48 120.00 dB
PL49 120.00 dB
PL50 120.00 dB
PL51 120.00 dB
PL52 120.00 dB
PL53 120.00 dB
PL54 120.00 dB
PL55 120.00 dB
PL56 120.00 dB
PL57 120.00 dB
PL58 120.00 dB
PL59 120.00 dB
PL60 120.00 dB
PL61 120.00 dB
PL62 120.00 dB
PL63 120.00 dB
PL64 120.00 dB
PL65 120.00 dB
PL66 120.00 dB
PL67 120.00 dB
PL68 120.00 dB
PL69 120.00 dB
PL70 120.00 dB
PL71 120.00 dB
PL72 120.00 dB
PL73 120.00 dB
PL74 120.00 dB
PL75 120.00 dB
PL76 120.00 dB
PL77 120.00 dB
PL78 120.00 dB
PL79 120.00 dB
PL80 120.00 dB
PL81 120.00 dB
PL82 120.00 dB
PL83 120.00 dB
PL84 120.00 dB
PL85 120.00 dB
PL86 120.00 dB
PL87 120.00 dB
PL88 120.00 dB
PL89 120.00 dB
PL90 120.00 dB
PL91 120.00 dB
PL92 120.00 dB
PL93 120.00 dB
PL94 120.00 dB
PL95 120.00 dB
PL96 120.00 dB
PL97 120.00 dB
PL98 120.00 dB
PL99 120.00 dB
PL100 120.00 dB
=====
===== GRADIENT CHANNEL =====
GPNAM1 C
GPNAM2
GPNAM3
GPNAM4
GPNAM5
GPNAM6
GPNAM7
GPNAM8
GPNAM9
GPNAM10
GPNAM11
GPNAM12
GPNAM13
GPNAM14
GPNAM15
GPNAM16
GPNAM17
GPNAM18
GPNAM19
GPNAM20
GPNAM21
GPNAM22
GPNAM23
GPNAM24
GPNAM25
GPNAM26
GPNAM27
GPNAM28
GPNAM29
GPNAM30
GPNAM31
GPNAM32
GPNAM33
GPNAM34
GPNAM35
GPNAM36
GPNAM37
GPNAM38
GPNAM39
GPNAM40
GPNAM41
GPNAM42
GPNAM43
GPNAM44
GPNAM45
GPNAM46
GPNAM47
GPNAM48
GPNAM49
GPNAM50
=====
===== CHANNEL F2 =====
NUC2 13C
P1C2 16.25 usec
P12 500.00 usec
PL2 120.00 dB
PL3 120.00 dB
PL4 120.00 dB
PL5 120.00 dB
PL6 120.00 dB
PL7 120.00 dB
PL8 120.00 dB
PL9 120.00 dB
PL10 120.00 dB
PL11 120.00 dB
PL12 120.00 dB
PL13 120.00 dB
PL14 120.00 dB
PL15 120.00 dB
PL16 120.00 dB
PL17 120.00 dB
PL18 120.00 dB
PL19 120.00 dB
PL20 120.00 dB
PL21 120.00 dB
PL22 120.00 dB
PL23 120.00 dB
PL24 120.00 dB
PL25 120.00 dB
PL26 120.00 dB
PL27 120.00 dB
PL28 120.00 dB
PL29 120.00 dB
PL30 120.00 dB
PL31 120.00 dB
PL32 120.00 dB
PL33 120.00 dB
PL34 120.00 dB
PL35 120.00 dB
PL36 120.00 dB
PL37 120.00 dB
PL38 120.00 dB
PL39 120.00 dB
PL40 120.00 dB
PL41 120.00 dB
PL42 120.00 dB
PL43 120.00 dB
PL44 120.00 dB
PL45 120.00 dB
PL46 120.00 dB
PL47 120.00 dB
PL48 120.00 dB
PL49 120.00 dB
PL50 120.00 dB
PL51 120.00 dB
PL52 120.00 dB
PL53 120.00 dB
PL54 120.00 dB
PL55 120.00 dB
PL56 120.00 dB
PL57 120.00 dB
PL58 120.00 dB
PL59 120.00 dB
PL60 120.00 dB
PL61 120.00 dB
PL62 120.00 dB
PL63 120.00 dB
PL64 120.00 dB
PL65 120.00 dB
PL66 120.00 dB
PL67 120.00 dB
PL68 120.00 dB
PL69 120.00 dB
PL70 120.00 dB
PL71 120.00 dB
PL72 120.00 dB
PL73 120.00 dB
PL74 120.00 dB
PL75 120.00 dB
PL76 120.00 dB
PL77 120.00 dB
PL78 120.00 dB
PL79 120.00 dB
PL80 120.00 dB
PL81 120.00 dB
PL82 120.00 dB
PL83 120.00 dB
PL84 120.00 dB
PL85 120.00 dB
PL86 120.00 dB
PL87 120.00 dB
PL88 120.00 dB
PL89 120.00 dB
PL90 120.00 dB
PL91 120.00 dB
PL92 120.00 dB
PL93 120.00 dB
PL94 120.00 dB
PL95 120.00 dB
PL96 120.00 dB
PL97 120.00 dB
PL98 120.00 dB
PL99 120.00 dB
PL100 120.00 dB
=====
===== Processing Parameters =====
SI 65536
SF 125.7603674 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

```

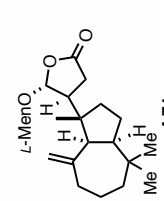
16.073
 21.113
 21.397
 22.768
 23.534
 25.923
 26.058
 26.166
 26.254
 29.69
 30.891
 31.831
 34.751
 34.794
 36.671
 37.207
 38.016
 38.056
 40.535
 47.976
 48.288
 51.687
 54.241
 56.205

77.090
 77.228
 77.482
 77.736

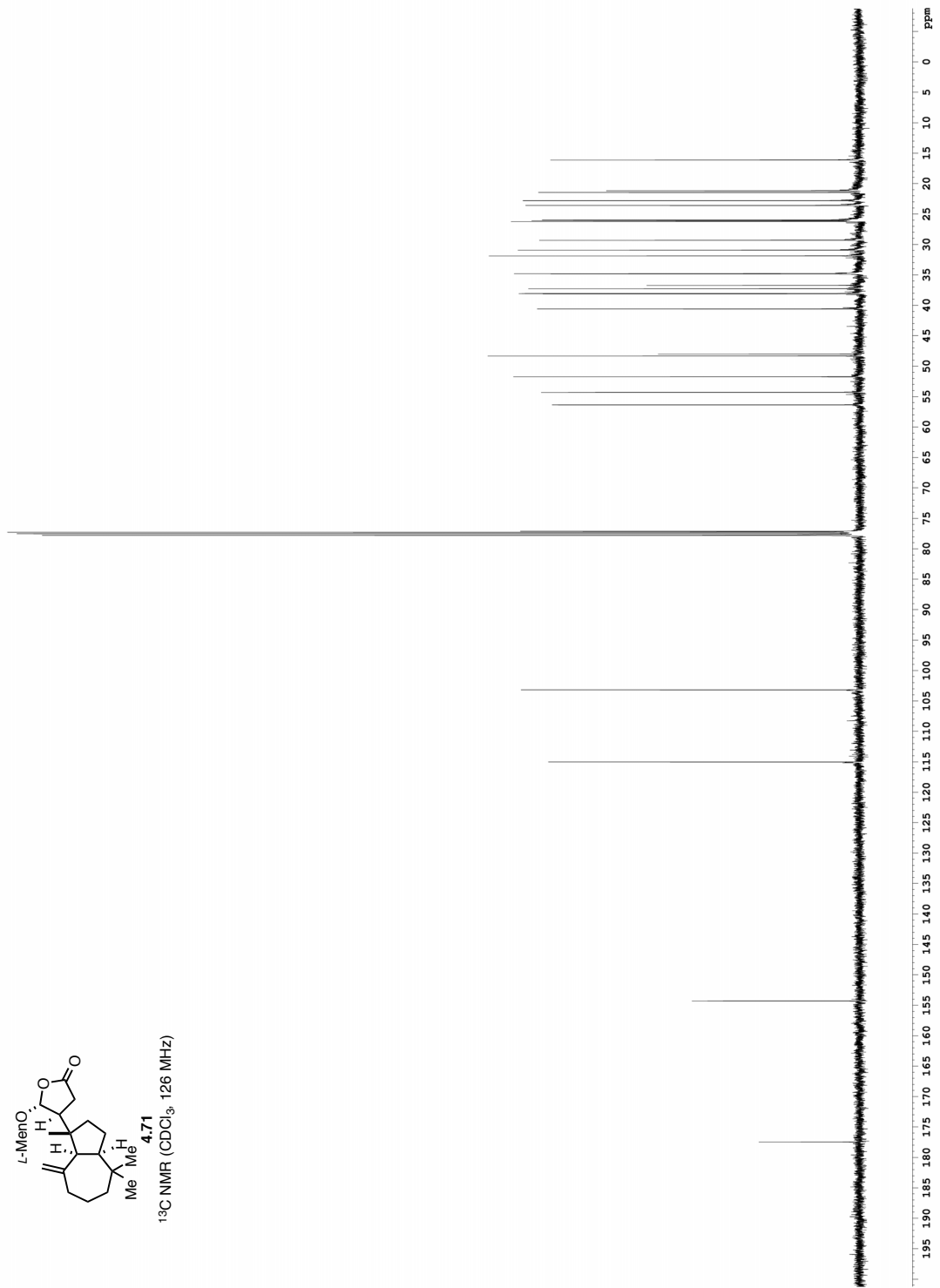
103.128
 114.984

154.272

177.442

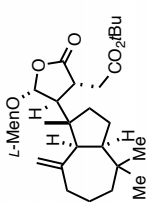
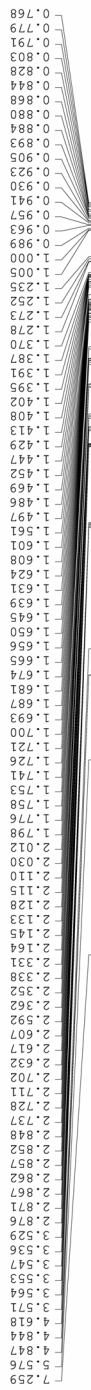


¹³C NMR (CDCl₃, 126 MHz)

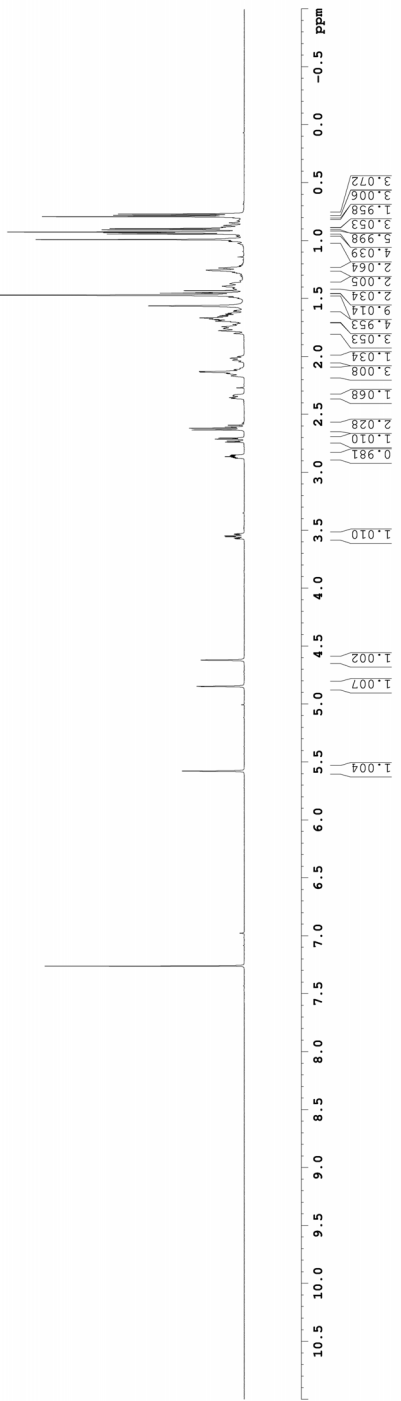


YS-V-228

Current Data Parameters
NAME YS-V-228
PROCNO 1
F2 - Acquisition Parameters
Time 201.0 8.10
INSTRUM 5 mm CPBBO BP
PROBHD 5 mm CPBBO BP
TD 98874
SOLVENT CDCl3
NS 2
SRH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 3.0398160 sec
RG 10
DW 52.000 usec
DE 298.0 usec
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 13C
PULM1 2D.00000000 M
===== CHANNEL f2 =====
SFO2 600.1300562 MHz
NUC2 1H
PULM2 2D.00000000 M
===== Processing parameters =====
SI 655536
WDW EM
SSB 0
GB 0
PC 1.00



¹H NMR (CDCl₃, 600 MHz)



YS-V-228

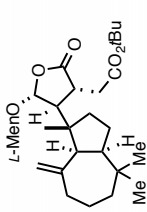
Current Data Parameters
NAME YS-V-228
PROCNO 2
F2 - Acquisition Parameters
Time 201.814
INSTRUM av600
PULPROG zgpg30
SOLVENT CDCl3
NS 512
DS 4
SWH 36231.863 Hz
FIDRES 0.52855 Hz
AQ 0.900000 sec
RG 2020
DM 13.000 usec
DE 2.000 usec
TE 298.2 K
D1 0.6000000 sec
D11 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 150.919480 MHz
P1 12.00 usec
PL1 0.00 dB
PLM1 64.00000000 W
===== CHANNEL f2 =====
SFO2 600.1330010 MHz
P2 12.00 usec
PL2 0.00 dB
PLM2 64.00000000 W
===== Processing parameters =====
SI 65536
SF 150.907250 MHz
WDW 0
SSB 0 1.00 Hz
GB 0
PC 1.00

15.696
21.277
21.467
22.733
23.213
25.781
25.945
26.004
28.460
28.485
29.252
31.803
34.700
34.739
36.682
37.173
37.500
37.980
39.543
39.956
40.197
48.143
48.279
53.528
56.335
56.972

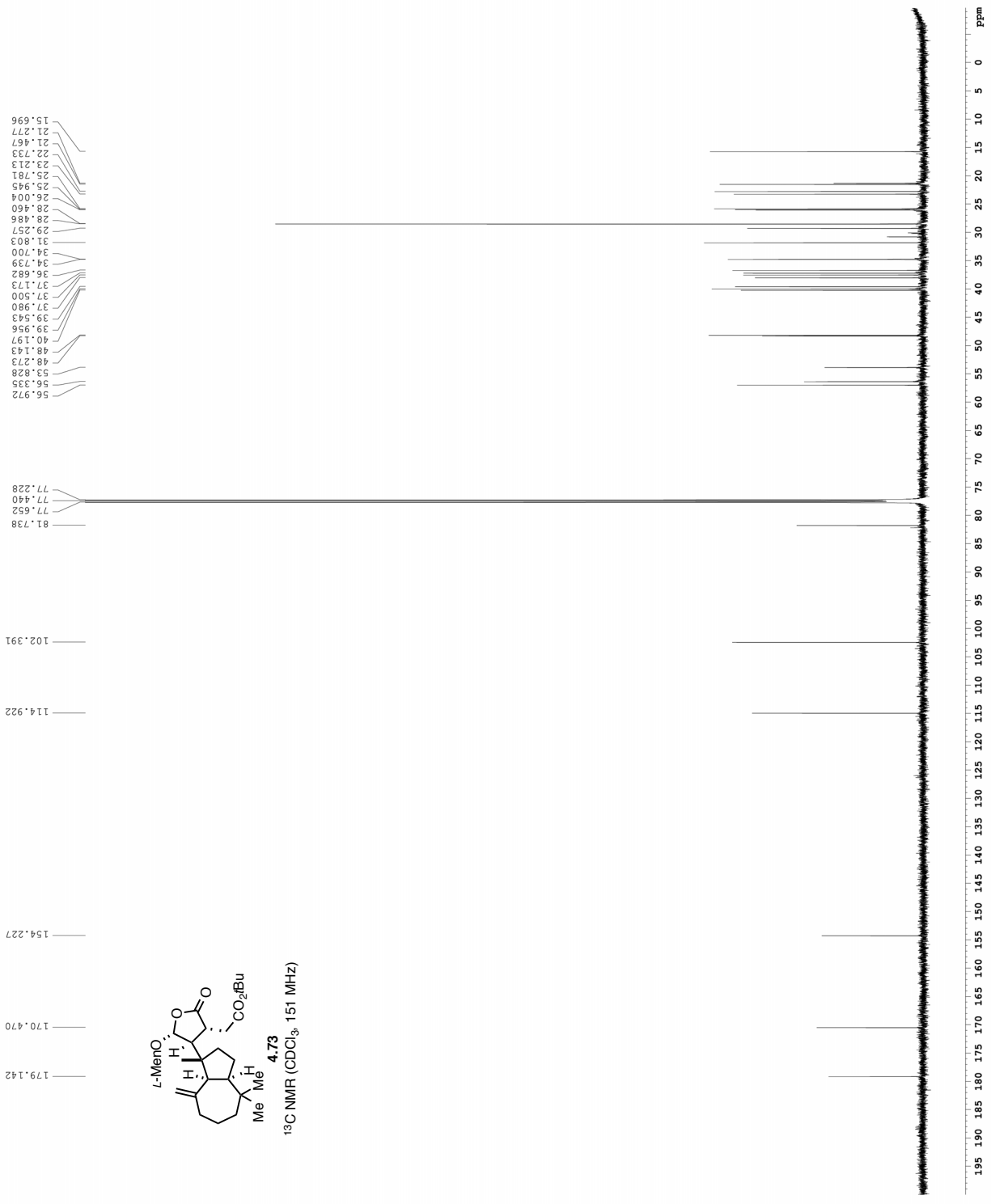
77.228
77.440
77.652
81.738

154.227

170.470
179.142

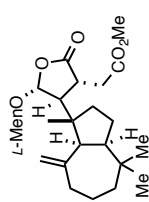
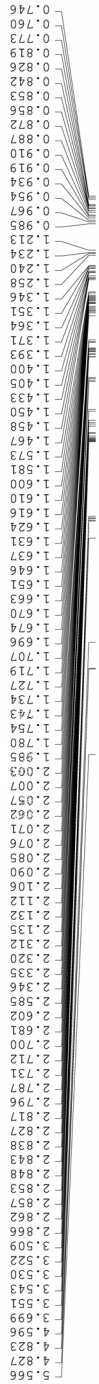


¹³C NMR (CDCl₃, 151 MHz)

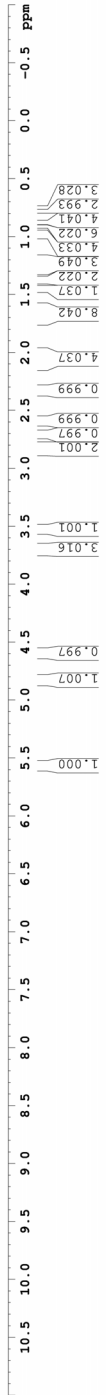


YS-V-274

Current Data Parameters
NAME YS-V-274
PROCNO 1
DATE_ /v/data/yuriy/nmr
Date_ Acquisition Parameters
Time 20170326 14.06
INSTRUM qn500
PULPROG zg30
TD 8128
SOLVENT CDCl3
DS 2
SWH 8013.820 Hz
AQ 5.0398273 sec
RG 22.6
DE 6.00 usec
TE 298.0 K
D1 0.1000000 sec
MCNRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 12.00 usec
P1 12.00 usec
F1 499.0734955 MHz
SF01 499.0734955 MHz
F2 - Processing Parameters
SI 65536
WDW EM
SSB 0
GB 0
PC 1.00



¹H NMR (CDCl₃, 500 MHz)



YS-V-274

Current Data Parameters
NAME YS-V-274
EXNO 2
DATE_ 20170329
Date_ 20170329
Time_ 14:00
INSTRUM spect
PROBHD 5 mm broadband
PULPROG zgpg30
SOLVENT CDCl3
DS 10
SWH 3030.031 Hz
AQ 0.05880000 sec
RG 1249.4
DE 4.50 usec
TE 298.0 K
D11 0.03000000 sec
WARRST 0 sec
NUC1 CHANNEL F1 13C
P1 9.00 usec
SFO1 125.5005050 MHz
CPRPRG2 wait216
NUC2 13C
P2 12.00 usec
PL2 2 -3.00 dB
SFO2 499.0724953 MHz
SI - Processing parameters
SF 125.4912510 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 2.00

15.254
20.948
21.077
22.315
22.798
25.453
25.571
25.594
28.829
31.412
34.212
36.294
36.826
36.895
36.821
37.621
39.502
39.903
47.651
47.914
52.032
53.547
55.858
56.347

76.853
77.102
77.362

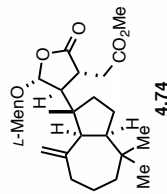
102.256

114.572

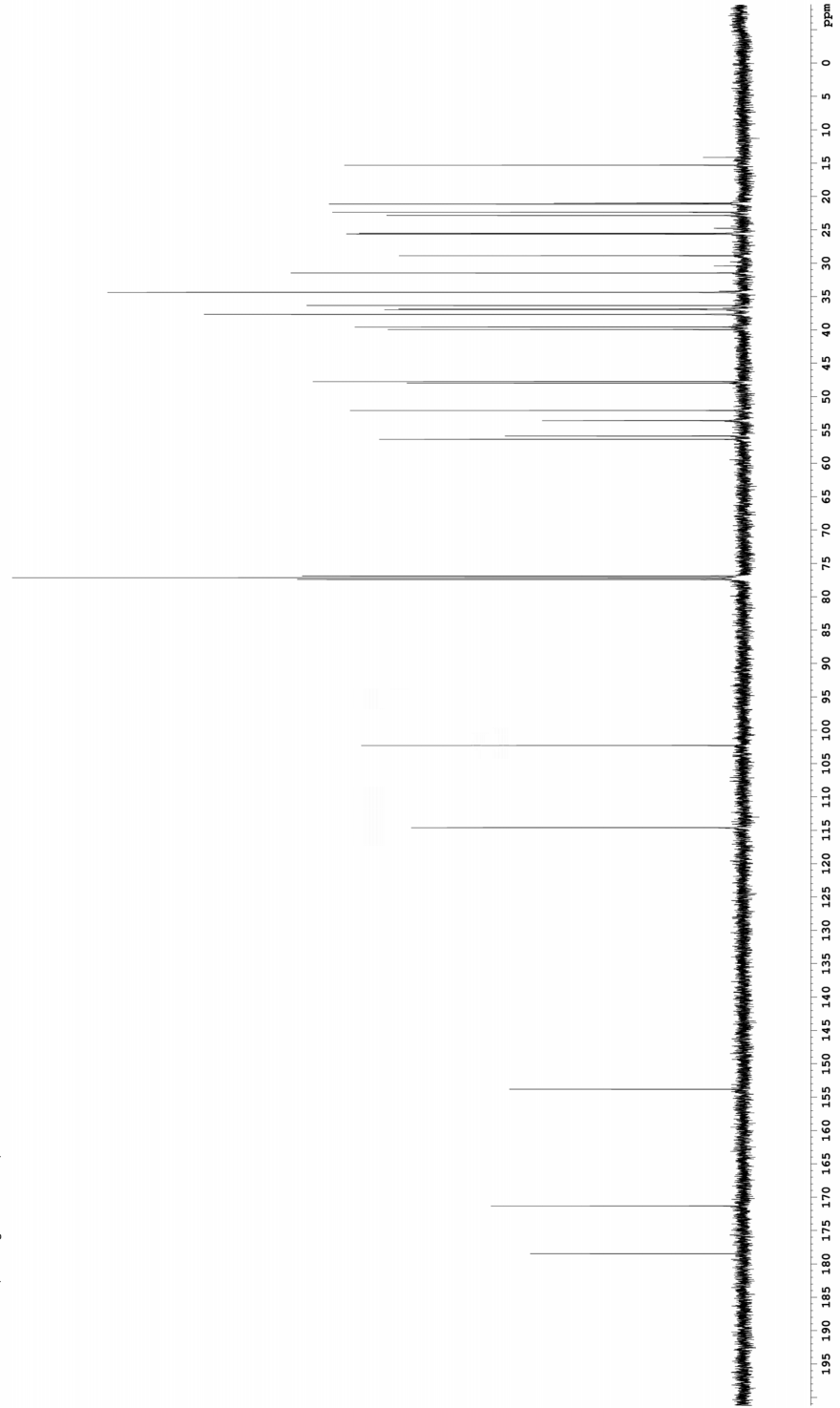
153.781

171.278

178.438

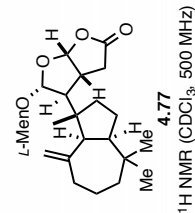
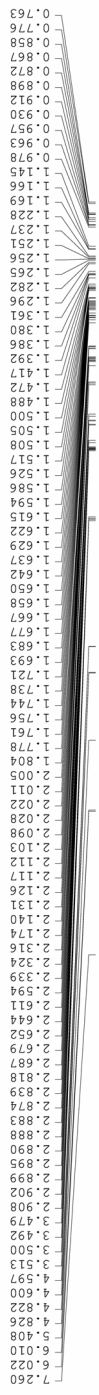


¹³C NMR (CDCl₃, 126 MHz)

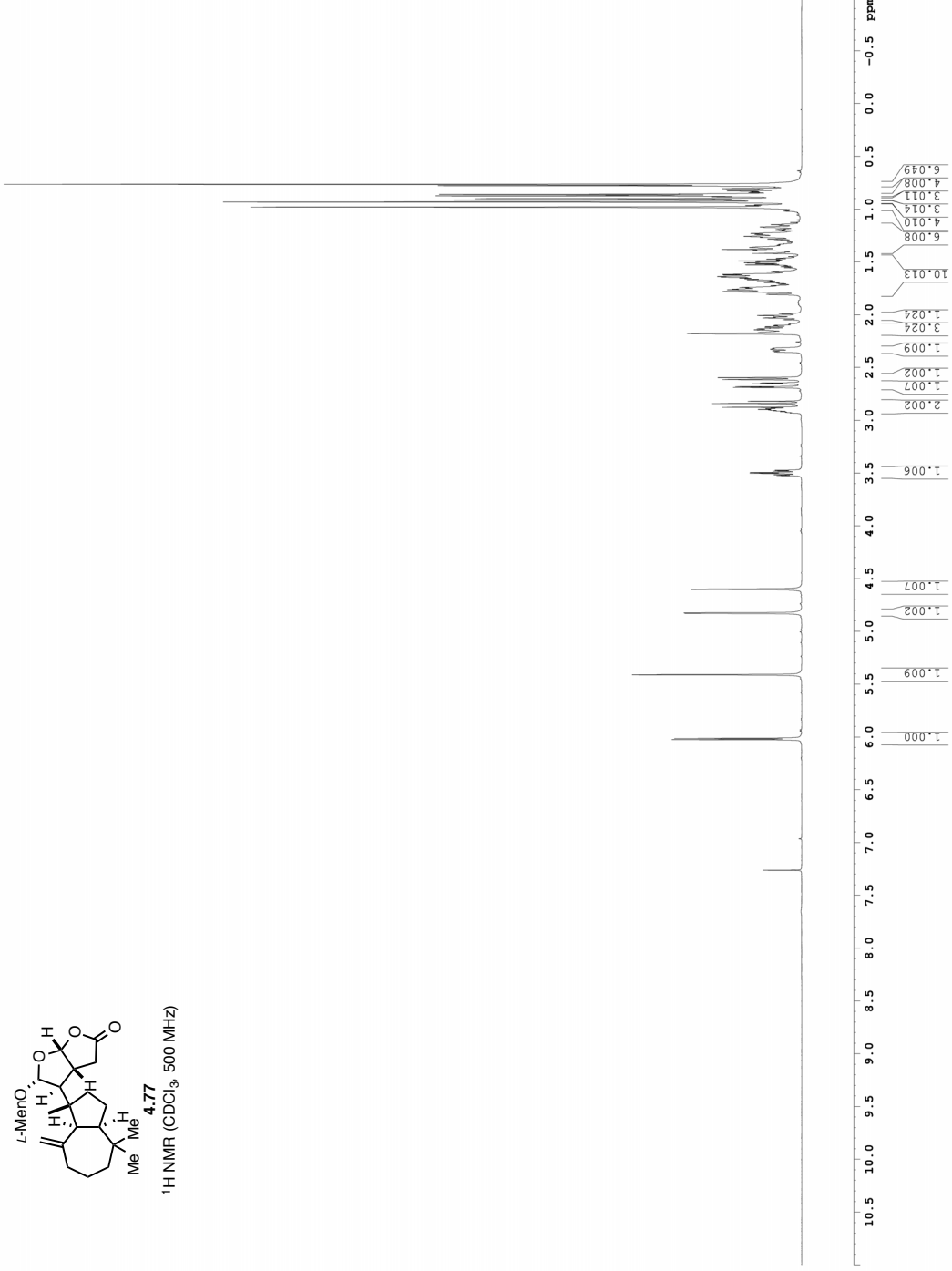


YS-V-276

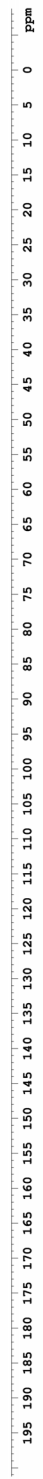
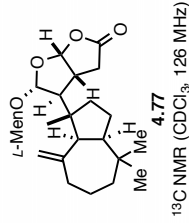
Current Data Parameters
NAME YS-V-276
PROCNO 1
DATE_ /v/data/yuriy/nmr
DATPATH /v/data/yuriy/nmr
Date_Acquisition Parameters
Time 20170403
Time 13.42
INSTRUM qn500
PULPROG zg30
TD 81728
NS 1
SOLVENT CDCl3
DS 1
SWH 8015.820 Hz
AQ 5.0398273 sec
RG 40.3
WDW EM
SSB 0
TE 295.0 K
D1 0.10000000 sec
DELTA 0.01500000 sec
MCKR 0.01500000 sec
===== CHANNEL f1 =====
NUC1 12.00 usec
P1 12.00 usec
PL1 -5.80 dB
SFO1 499.0734955 MHz
F2 - Processing parameters
SF 65536 MHz
WDW EM
SSB 0
GB 0
PC 1.00



¹H NMR (CDCl₃, 500 MHz)

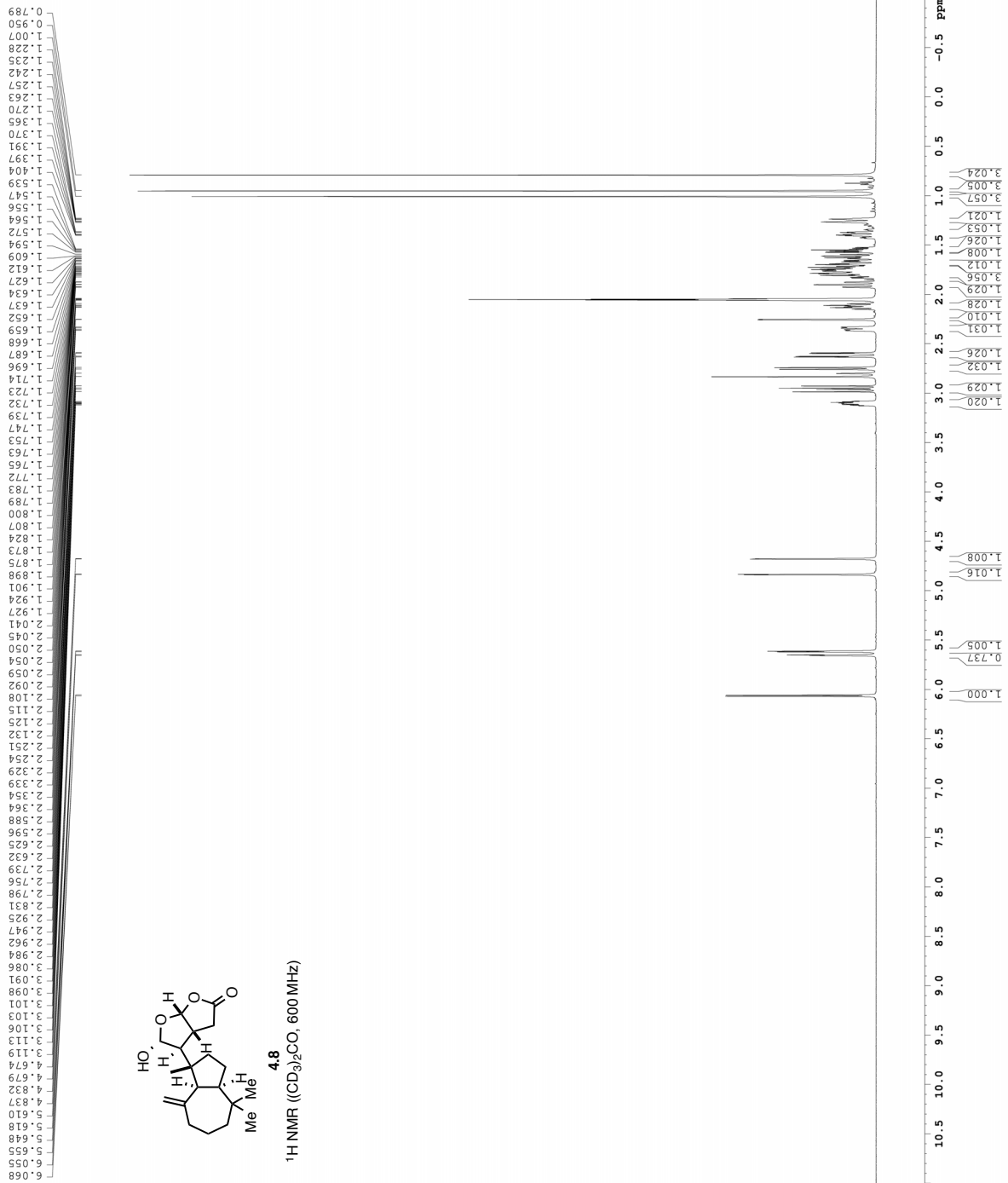


Current Data Parameters
NAME YS-V-276
EXPNO 2
DATE_ /v/data/purys/mr
Date_ 20170601
Time 13:06
INSTRUM spect
PROBHD 5 mm broadband
PULPROG zgpg30
SOLVENT CDCl3
DS 5
SWH 3030.031 Hz
F2 125.500250 MHz
AQ 1.0983440 sec
RG 459.16 usec
DE 1.80 usec
BE 4.50 usec
TE 298.15 K
D1 0.25000000 sec
d11 0.03000000 sec
DECOR 0
NS 0.01500000 sec
NUC1 CHANNEL F1 13C
P1 9.00 usec
SFO1 125.500250 MHz
CDDPRG12 CHANNEL F2 waitz16
NUC2 13C
P2 80.00 usec
SFO2 499.0724953 MHz
SI - Processing Parameters
SF 125.491250 MHz
RG 4096
SSB 0
LB 1.00 Hz
PC 2.00



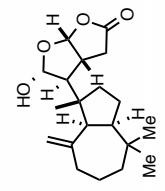
YS-V-134

Current Data Parameters
EXPNO 3
PROCNO 1
DATAF1H /v/data/yurys/mr
Date_ 20161208
F2 - Acquisition Parameters
PROBHD 5 mm CFC1 IH-
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 4
SRH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0598273 sec
RG 62.400 usec
DE 6.00 usec
TE 300.2 K
D1 0.10000000 sec
MCREST 0 sec
MCWRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 500.2225015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200178 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 1.00

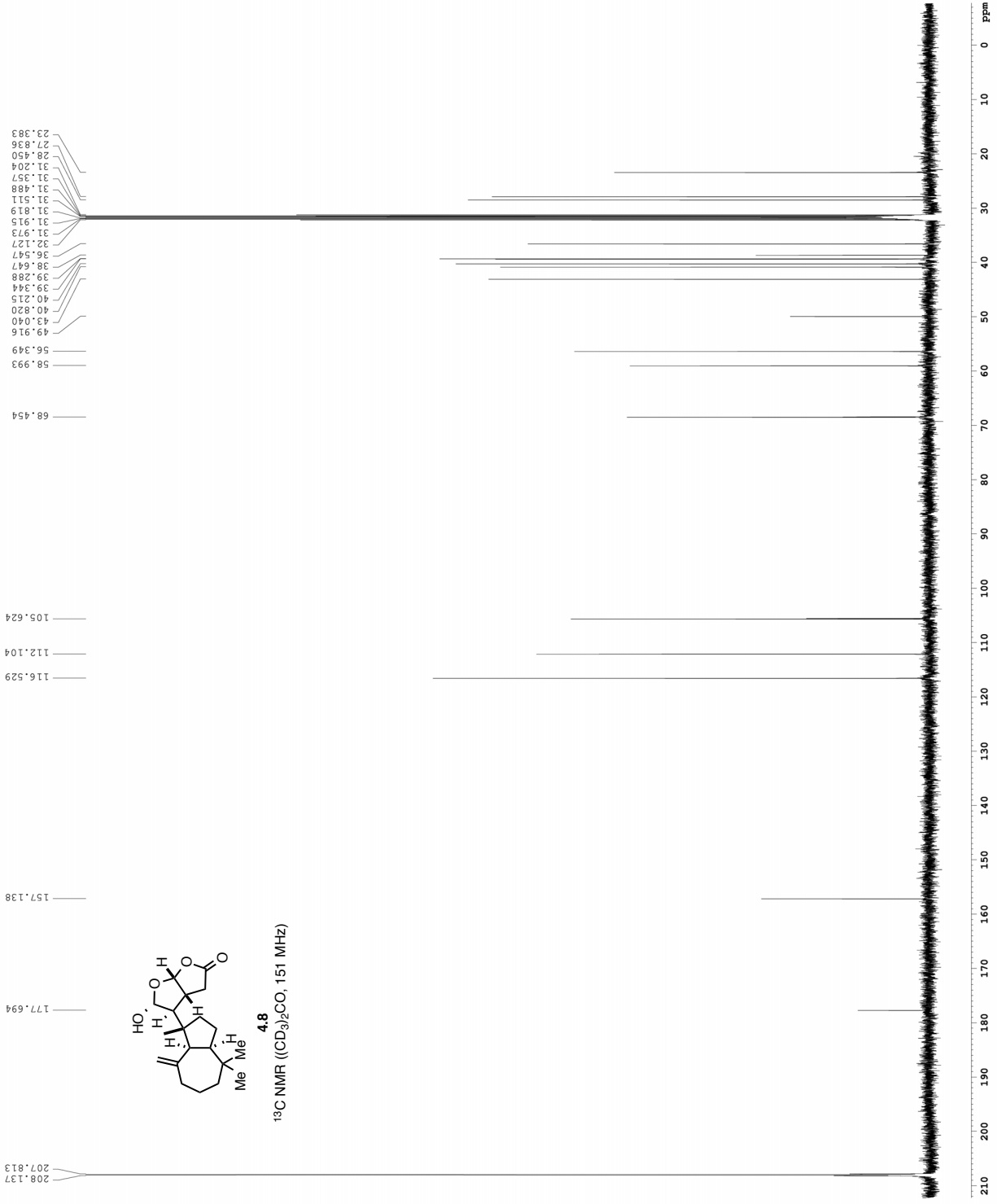


YS-V-134

Current Data Parameters
EXPNO 4
NAME YS-V-134
DATE_ /v/data/yuyiy/rmr
Date_ 2016208
Time 8:50
PROBHD 5 mm cpcci.hi-
PULPROG spinchegp3-prd
SOLVENT CDCl3
DS 1024
SRH 30303.031 Hz
RG 1.0813440 sec
DE 156.00 usec
TE 300.2 K
d11 0.0300000 sec
d12 0.0300000 sec
d17 0.0001500 sec
PC 33.10 usec

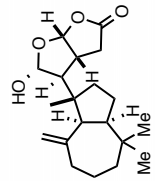
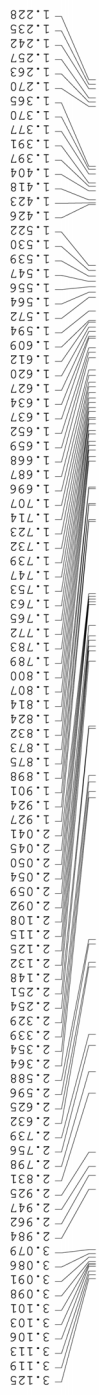


4.8
¹³C NMR (CD₂Cl₂, 151 MHz)

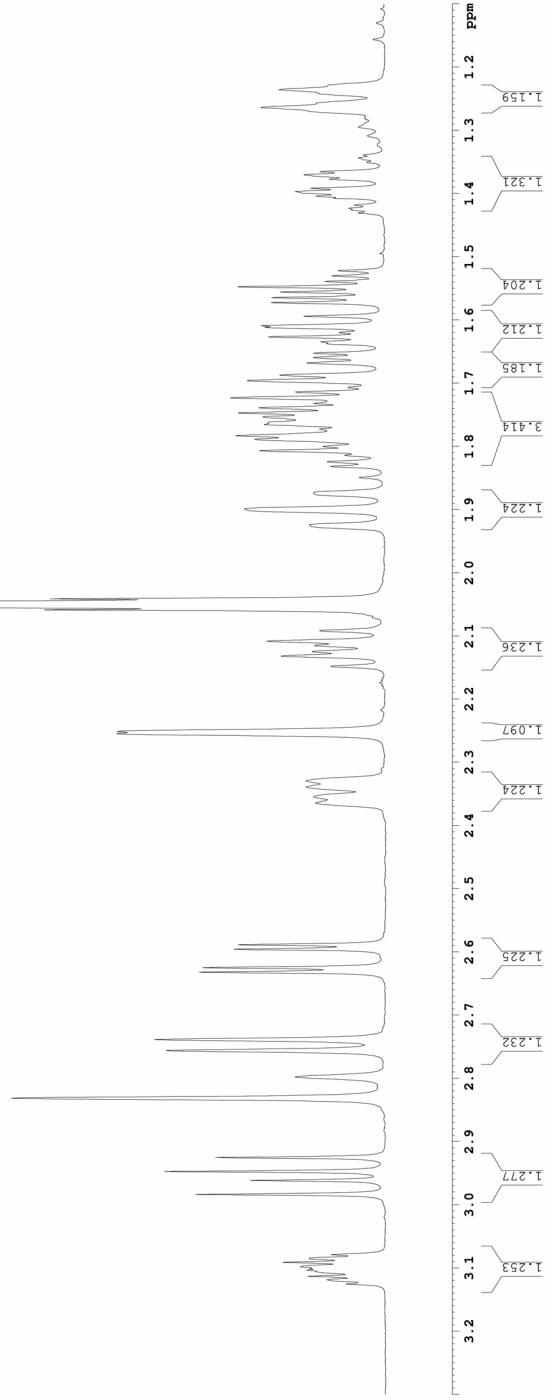


YS-V-134

Current Data Parameters
NAME YS-V-134
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Time 2011-08-15 8:45
INSTRUM cryo500
PROBHD 5 mm CPXI 1H
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 8012.820 Hz
FIDRES 0.098643 Hz
AQ 3.0398278 sec
RG 327.5
DM 62.400 usec
DE 296.00 usec
D1 0.10000000 sec
MRESST 0 sec
PCPRG 0.01500000 sec
CHANNEL f1
NUC1 1H
PULPROG zgpg30
FLL 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.220178 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

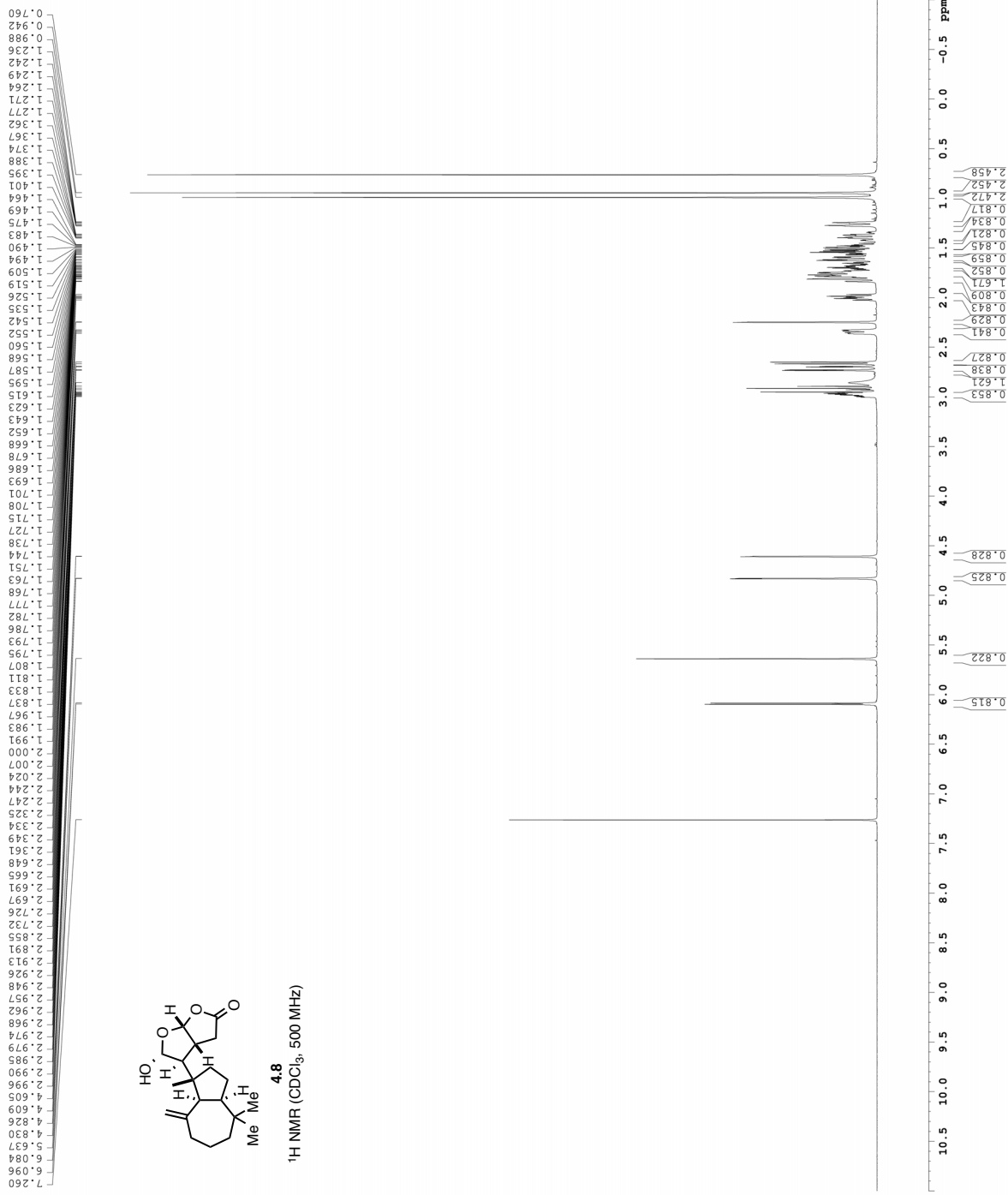


4.8
¹H NMR (CD₃CO, 600 MHz)
3.3 ppm to 1.1 ppm expanded region



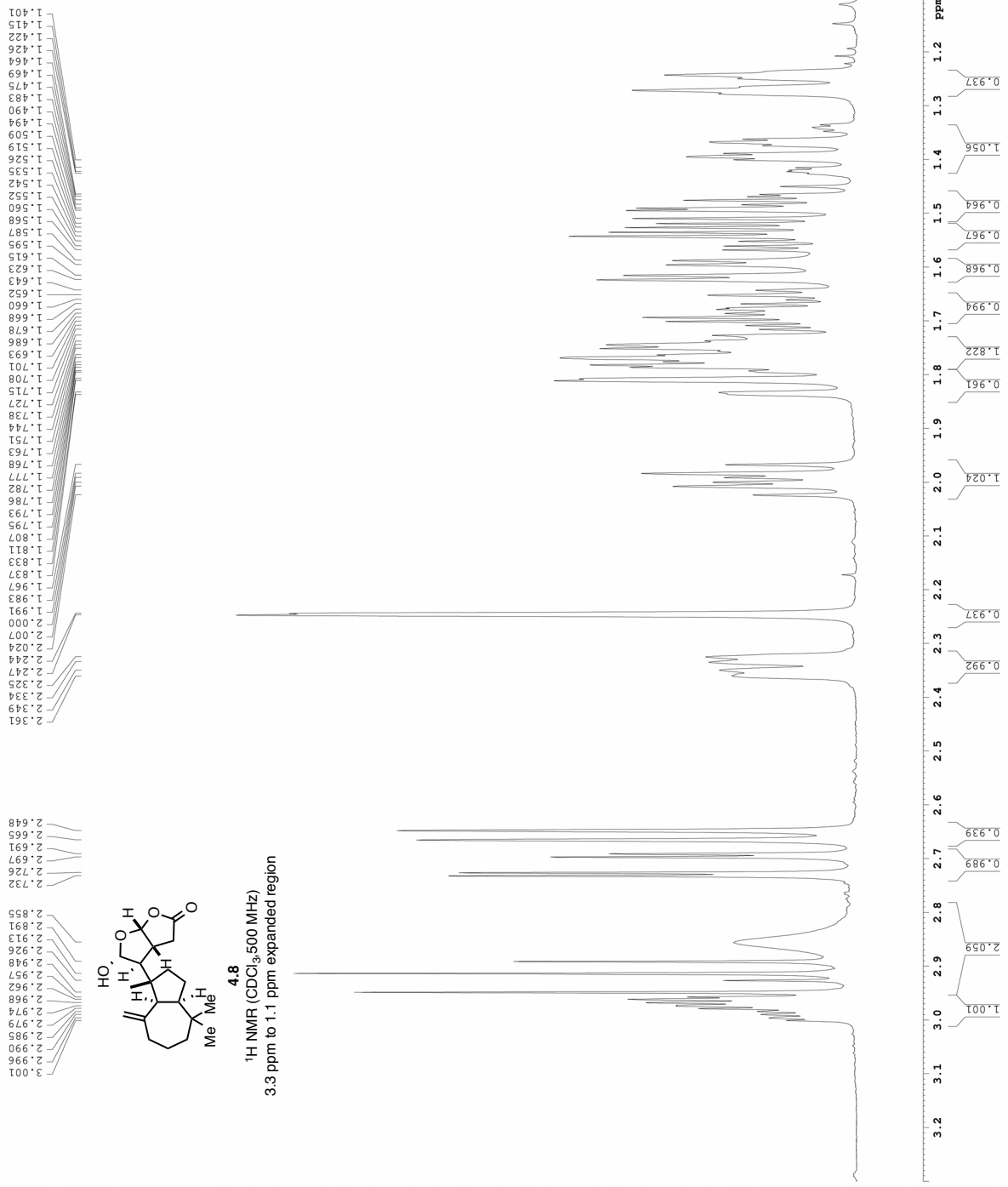
YS-V-134

Current Data Parameters
NAME YS-V-134
PROCNO 1
DATE_ /v/data/yuriy/nmr
Date_ 20161207
Time_ 10:36
INSTRUM cryo-500
PULPROG zg30
TD 8128
NS 2
DS 2
SWH 8015.820 Hz
AQ 5.0998273 sec
RG 7.1
DE 2.00 usec
TE 298.0 K
D1 0.10000000 sec
MCNMRZ 0 sec 0.01500000 sec
===== CHANNEL f1 =====
NUC1 ¹H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.225015 MHz
F2 - Processing parameters
SI 65536
WDW EM
SSB 0
GB 0
PC 4.00

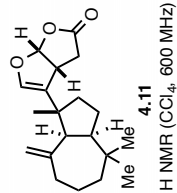


YS-V-134

Current Data Parameters
NAME YS-V-134
PROCNO 1
PROBHD 5 mm CFCF 1H
PULPROG zgpg30
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 3.0398771 sec
RG 327.500
DW 62.400 usec
DE 9.00 usec
TE 298.2 K
D1 0.10000000 sec
MCREST 0 sec
PCPRGK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
===== CHANNEL f2 =====
F2 - Processing parameters
SF 500.2200308 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00



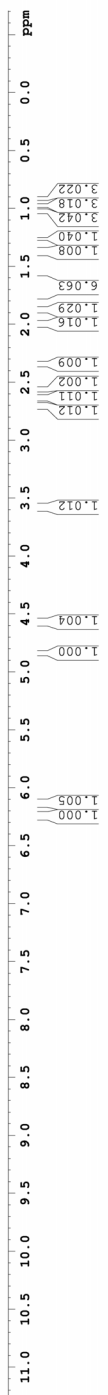
YS-V-237



Current Data Parameters
NAME YS-V-237
EXPNO 6
PROCNO 1
DATE_ /v/data/yariys/nmr
Date_ 20170217
Time_ 10.09
F2 - Acquisition Parameters
INSTRUM av600
PROBHD 5 mm CPBBO
PULPROG zg30
ID 98074
NS 8
DS 2
SWH 9615.282 Hz
FIDRES 0.090478 Hz
AQ 0.098478 sec
RG 12.7
BW 51.070 usec
TE 296.0 K usec
D1 0.10000000 sec
TD0 1

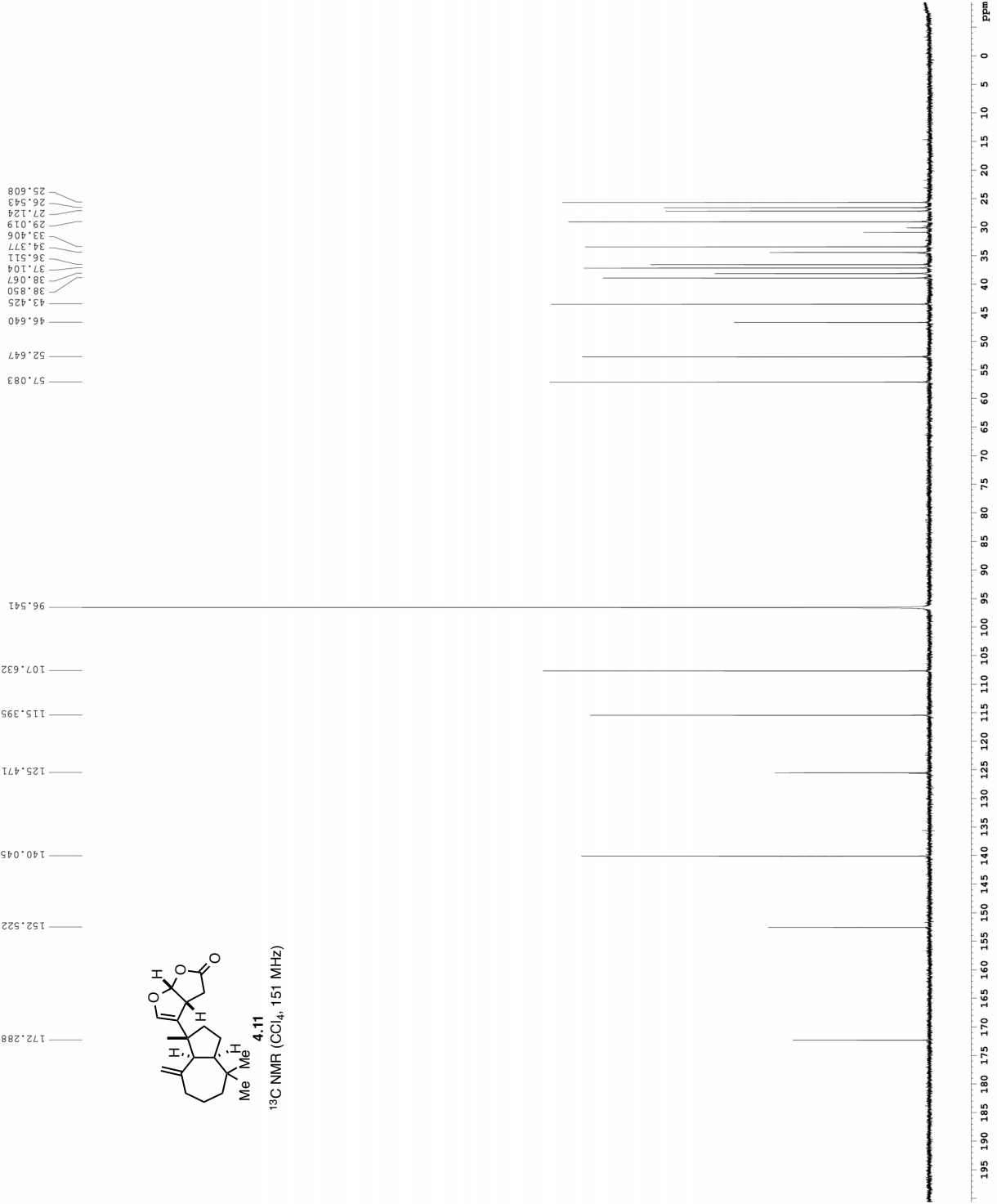
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
P1 12.00 usec
PL1 0.00 dB
FIR1 20.00000000 M
=====

F2 - Processing parameters
SI 65536
SF 600.1298164 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



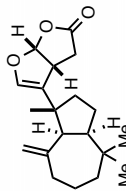
YS-V-237

Current Data Parameters
NAME YS-V-237
EXPNO 7
DATAPATH /v/data/yr15/mr
F2 - Acquisition Parameters
Date_ 20170217
Time 10:40
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
DS 3
SI 4
SWH 36231.883 Hz
FIDRES 0.30439268 sec
RG 132050
RG 132050 ussec
DE 19.65 ussec
DE 19.65 ussec
DT 0.60000000 sec
D11 0.03000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 10.00 ussec
PL1 64.00000000 W
===== CHANNEL f2 =====
NUC2 13C
P2 10.00 ussec
PL2 64.00000000 W
===== CHANNEL f3 =====
CPDPRG12 waitzlg
PL3 20.00000000 W
PL4 20.00000000 W
PL5 20.00000000 W
PL6 20.00000000 W
===== Processing parameters =====
WDW EM
SS 0
SF 150.907779 MHz
GB 0
PC 1.00



YS-V-237

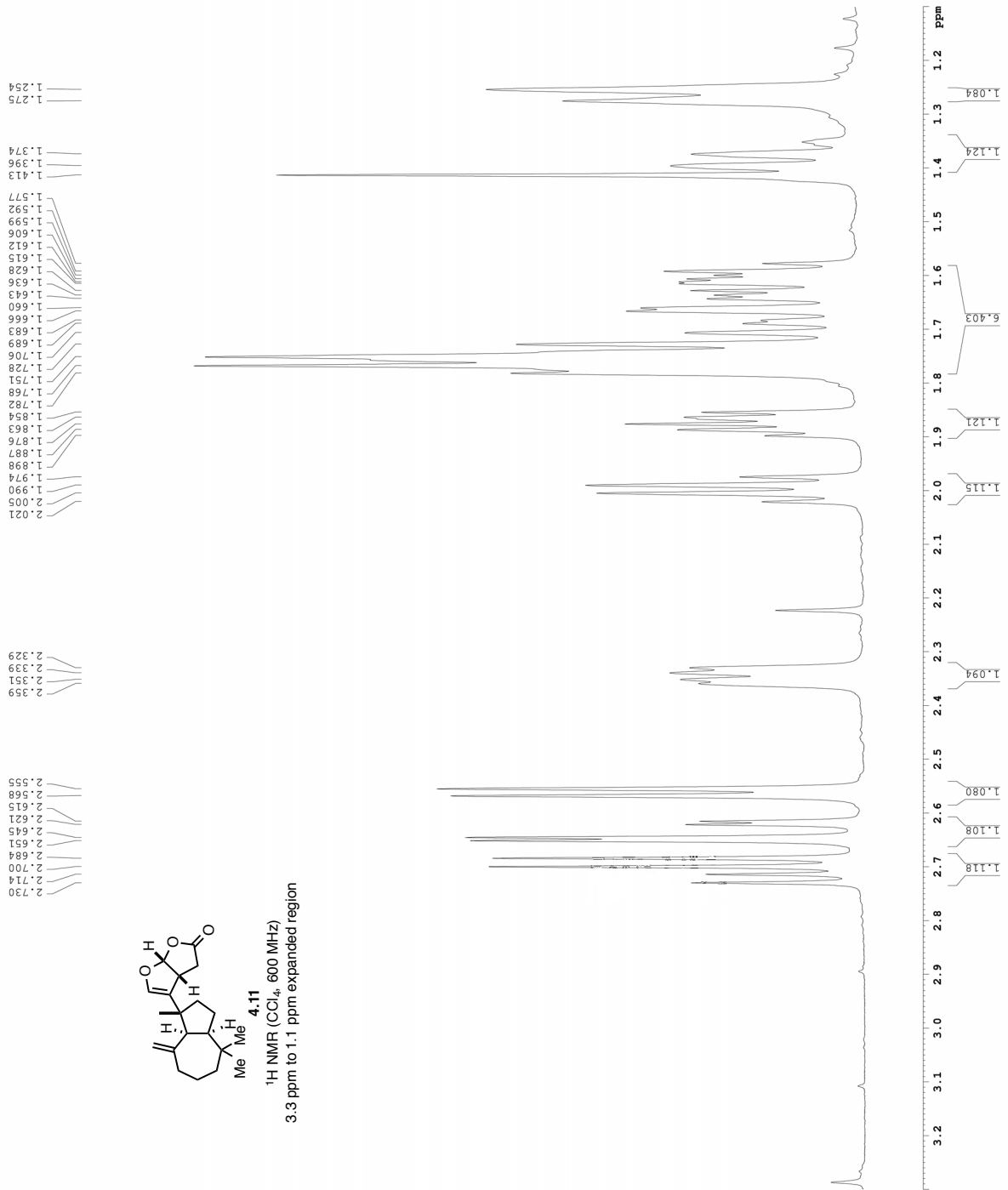
Current Data Parameters
NAME YS-V-237
PROCNO 6
F2 - Acquisition Parameters
Time 20.10.09
INSTRUM av600
PROBHD 5 mm CPBBO BBI
TD 98074
SOLVENT DMSO
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
RG 5.09317 sec
RC 12.7 sec
DM 52.000 usec
DE 236.0 usec
TE 300.2 K
D1 0.1000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 1H
PUL1 12.0 usec
PLM1 20.0000000 M
F2 - Processing Parameters
SI 68536
SF 600.1298164 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



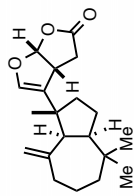
Me Me 4.11

¹H NMR (CCl₄, 600 MHz)

3.3 ppm to 1.1 ppm expanded region



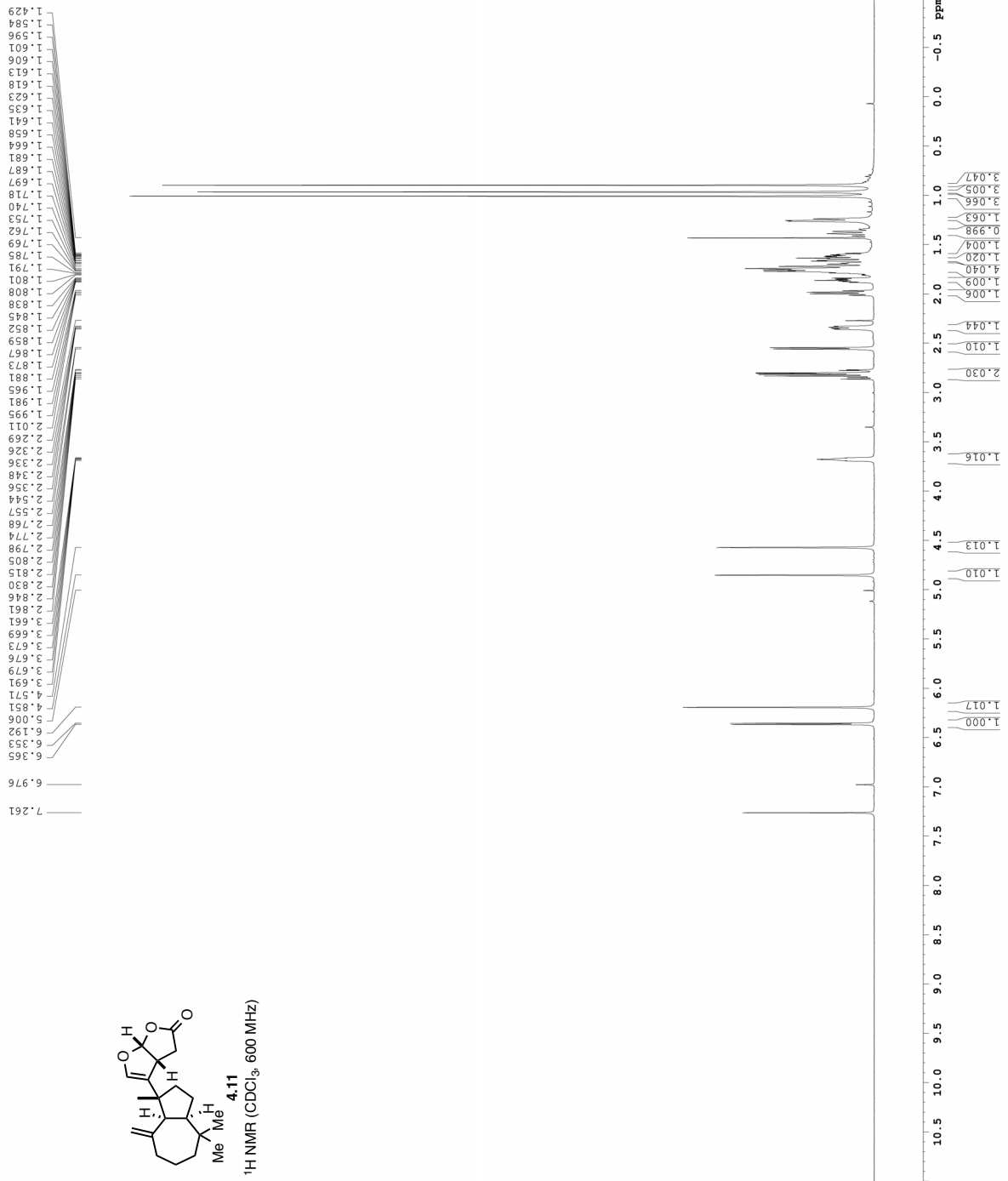
YS-V-237



¹H NMR (CDCl₃, 600 MHz)

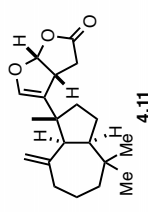
Current Data Parameters
NAME YS-V-237
PROCNO 4
DATE_ /v/data/yuriy7/nmr
DATA07
Date_ Acquisition Parameters
Time 20170216
14.42
INSTRUM av600
PROBHD 5 mm CEBB0
PULPROG zg30
TD 76822
NS 2
DS 2
SWH 9615.385 Hz
AQ 3.9399440 sec
RG 40.3
DE 51.070 usec
TE 298.0 K
D1 0.10000000 sec
D0 1

===== CHANNEL f1 =====
SF01 600.1342009 MHz
PC1 12.00 usec
PL1 20.00000000 W
F2 - Processing parameters
SI 65536
SF 600.1300349 MHz
SM 2M
SSB 0
LB 0 0.30 Hz
GB 0
PC 1.00

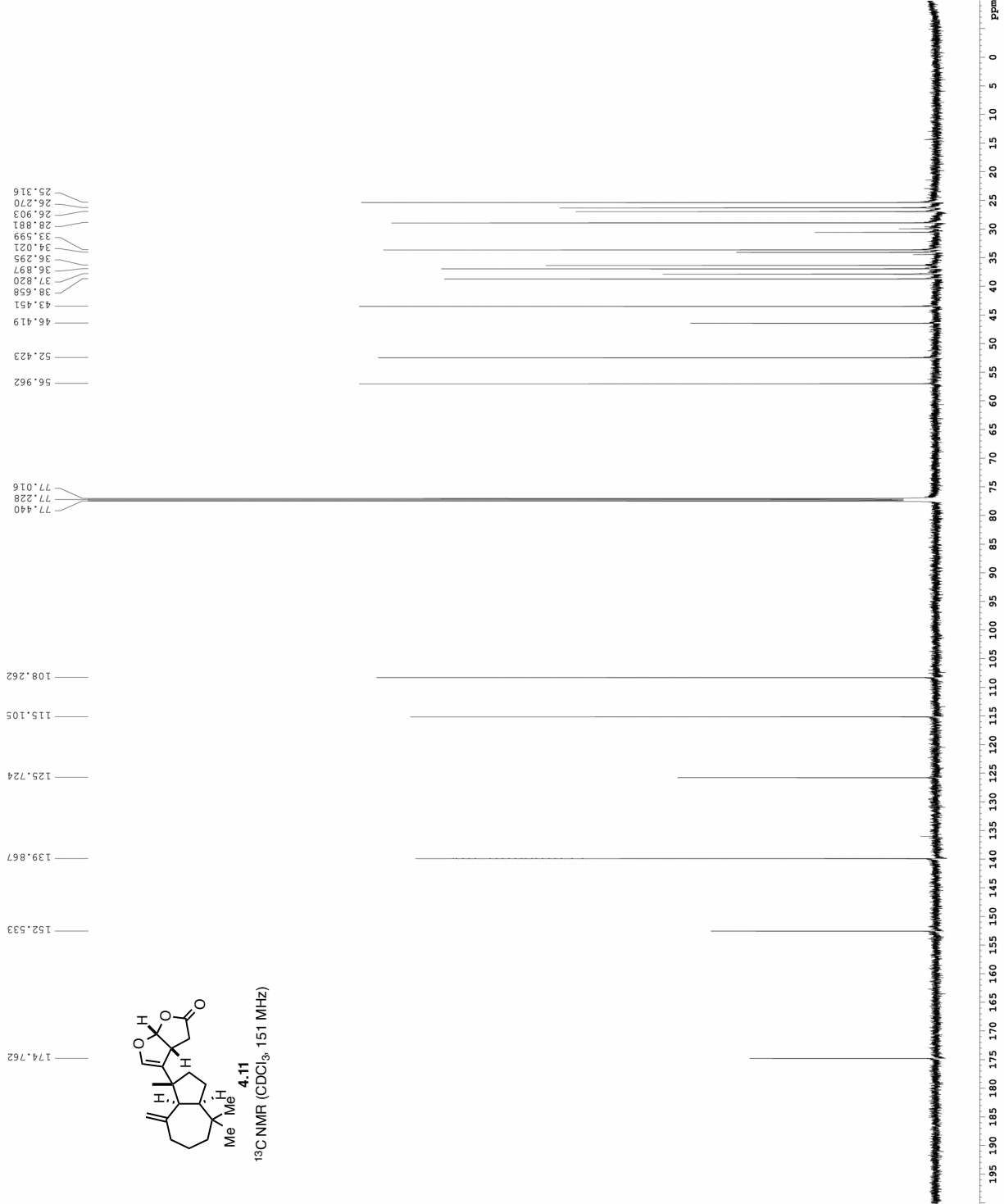


YS-V-237

Current Data Parameters
NAME YS-V-237
PROCNO 1
DATE_ /data/yr15/ys/mr
F2 - Acquisition Parameters
Date_ 20170216
Time_ 11:00:00
INSTRUM spect
PROBHD 5 mm CPBPR030
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 226
DS 2
AQ 36231.80 Hz
FIDRES 0.552855 Hz
AQ 0.9043268 sec
RG 13.800 usec
DW 13.800 usec
DE 2.96 usec
TE 298.65 usec
D1 0.40000001 sec
D11 0.40000001 sec
D12 0.40000001 sec
D13 0.40000001 sec
D14 0.40000001 sec
D15 0.40000001 sec
SFO1 CHANNEL f1 125.762 MHz
NUC1 13C
PL1 1.3C
PLA1 64.00000000 M
SFO2 CHANNEL f2 600.1330010 MHz
NUC2 1H
PL2 wait: 1H
PCPD2 20.00000000 usec
PLM2 0.50000001 M
SFO2 CHANNEL f3 600.1330010 MHz
NUC3 1H
PL3 wait: 1H
PCPD3 20.00000000 usec
PLM3 0.50000001 M
SI - Processing parameters
SF 150.9027841 MHz
WDW EM
SSB 0
GB 0
PC 1.00



¹³C NMR (CDCl₃, 151 MHz)



YS-V-237

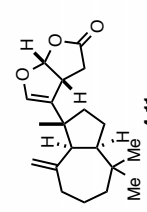
Current Data Parameters
NAME YS-V-237
PROC 1
PROB 4
P2 - Acquisition Parameters
Time 2011.14.42
INSTRUM AV600
PROBHD 5 mm CPBBO BB
TD 76322
SOLVENT CDCl3
NS 9
SRH 9615.385 Hz
FIDRES 0.155002 Hz
AQ 3.9399443 sec
RG 40.3
DW 52.000 usec
DE 298.0 usec
DI 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 13C
PULP1 20.00000000 M
PLM1 12.00 usec
P2 - Processing parameters
SI 65536
SF 600.1300349 MHz
WDW EM
SSB 0
GB 0
PC 1.00

2.011
1.995
1.981
1.965
1.881
1.873
1.867
1.859
1.852
1.845
1.838
1.808
1.801
1.791
1.785
1.769
1.762
1.753
1.740
1.718
1.697
1.687
1.681
1.664
1.658
1.641
1.635
1.623
1.613
1.606
1.601
1.596
1.584
1.429
1.408
1.385
1.364
1.344
1.326
1.259
1.253
1.236

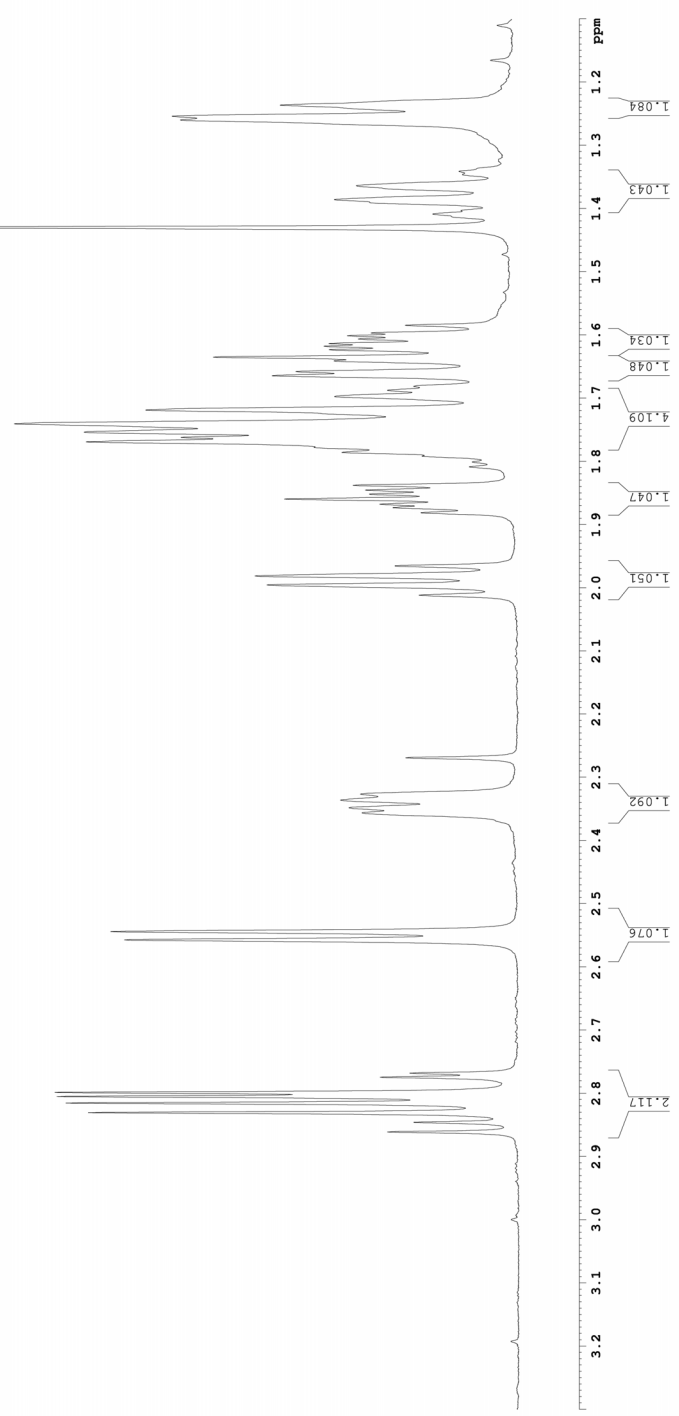
2.768
2.774
2.778
2.805
2.815
2.830
2.846
2.861

2.356
2.348
2.336
2.326
2.269

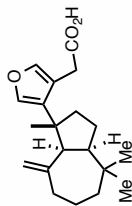
2.544
2.557



¹H NMR (CDCl₃, 600 MHz)
3.3 ppm to 1.1 ppm expanded region

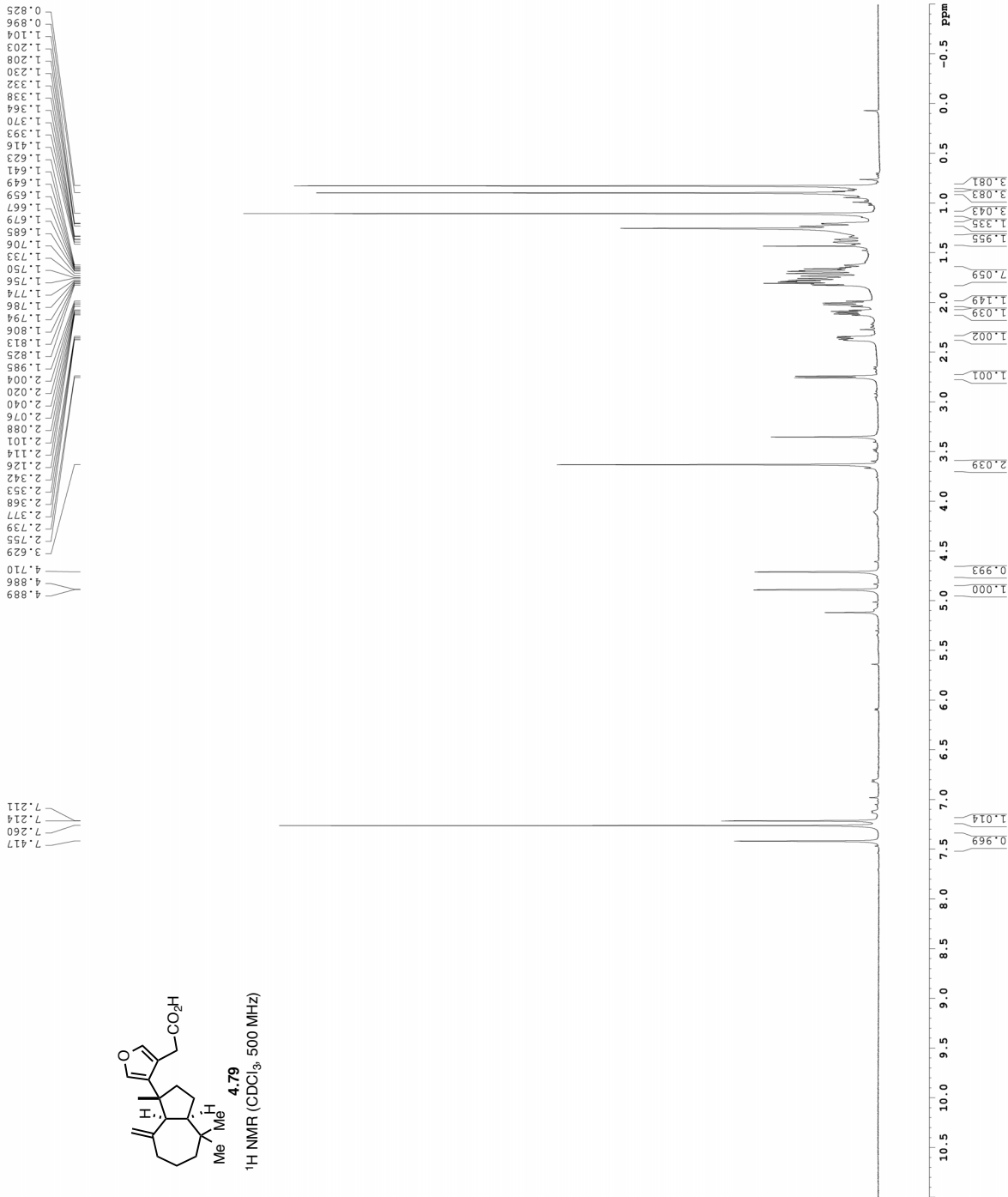


YS-V-281



4.79
¹H NMR (CDCl₃, 500 MHz)

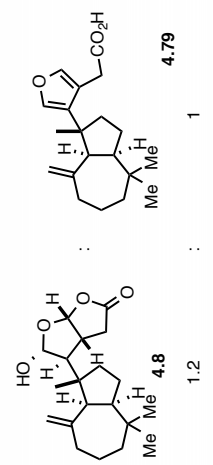
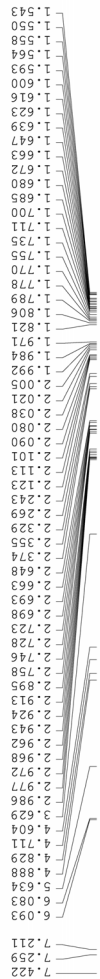
Current Data Parameters
NAME YS-V-281
EXPNO 1
PROCNO 2
DATE_ /v/data/yuriy/nmr
DATE_ 20170405
Time 12.29
F2 - Acquisition Parameters
INSTRUM cryo500
PULPROG zg30
ID 8128
NS 2
DS 2
SWH 8015.820 Hz
FIDRES 5.0998273 sec
AQ 0.01500000 sec
RG 62.400 usec
DE 298.0 K sec
TE 0.10000000 sec
D1 0.10000000 sec
MCNRSZ 0 sec
MCNRS 0.01500000 sec
===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PL1 0.00 dB
SFO1 500.225015 MHz
F2 - Processing parameters
SI 65536 MHz
WDW EM
SSB 0
GB 0
PC 1.00



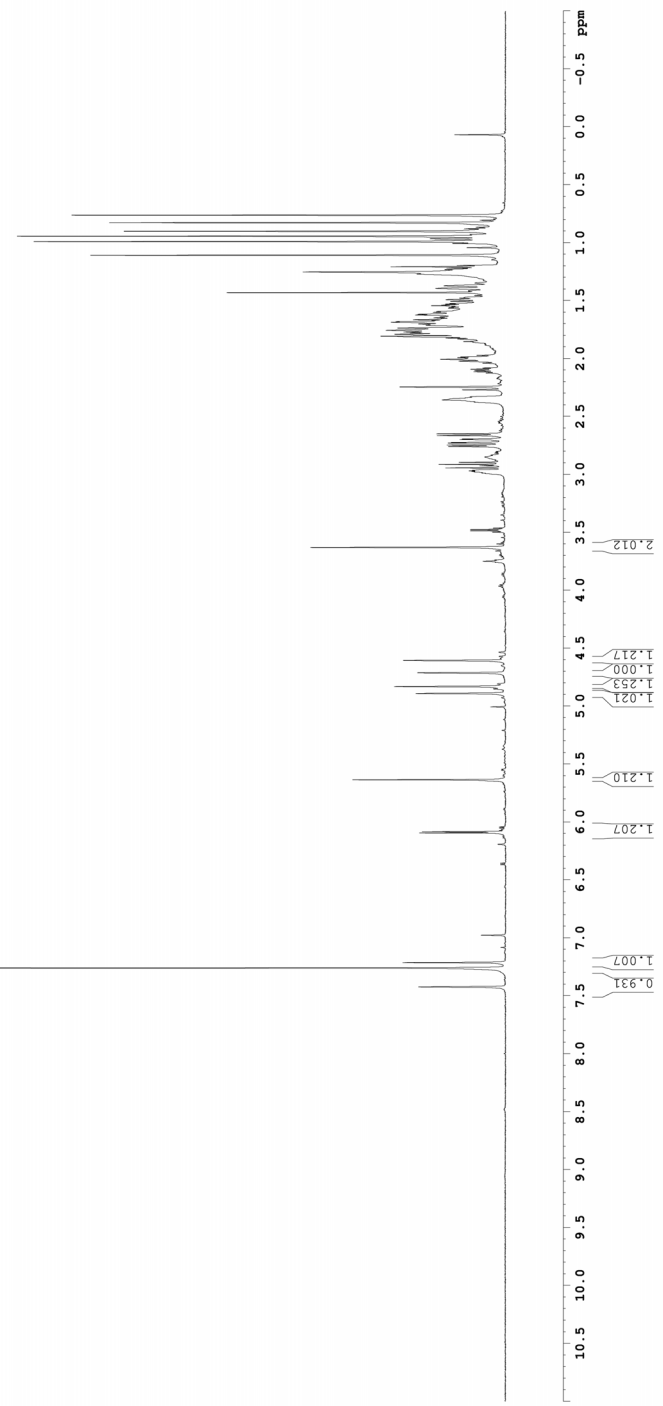
YS-V-239

Current Data Parameters

NAME YS-V-239
 EXPNO 1
 PROCNO 1
 DATAPATH /v/data/yuris/nmr
 F2 - Acquisition Parameters
 Date_ 20170218
 Time 8:38
 INSTRUM av600
 PULPROG zg30
 ID 38460
 NS 2
 DS 2
 SWH 9615.262 Hz
 FIDRES 0.0999999 Hz
 AQRES 1.9999999 sec
 RG 10
 DW 59.10 usec
 DE 13.00 usec
 TE 296.0 K
 D1 0.10000000 sec
 TD0 1
 CHANNEL f1
 SF01 600.1342009 MHz
 P1 12.00 usec
 F1M1 20.00000000 M
 F2 - Processing parameters
 SI 65536
 SF 600.1300362 MHz
 EQ 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



¹H NMR (CDCl₃, 600 MHz) of the crude reaction mixture

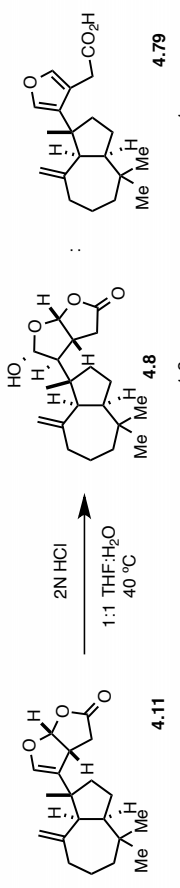


YS-V-239

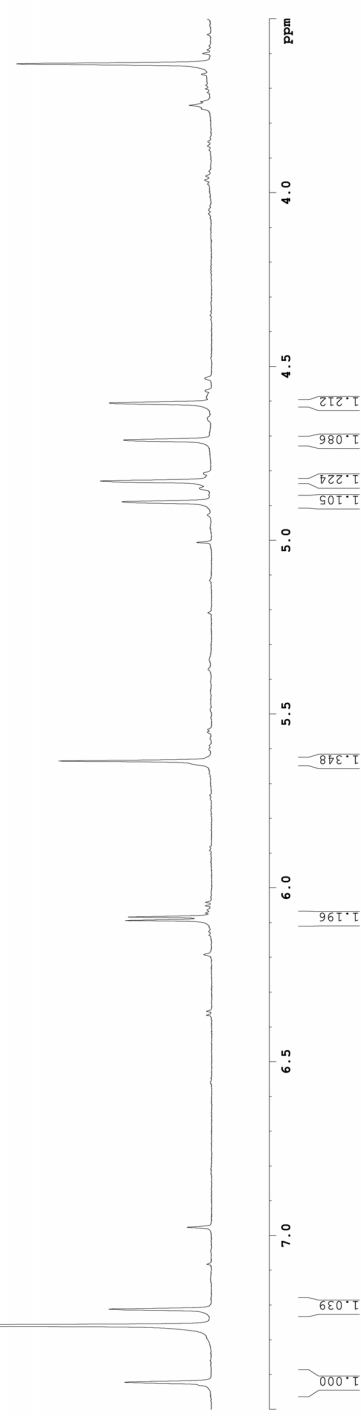
Current Data Parameters
NAME YS-V-239
PROCNO 1
PROBHD 5 mm CPBBO BB
PULPROG zgpg30
SOLVENT CDCl3
NS 32
DS 2
SWH 9615.385 Hz
FIDRES 0.250010 Hz
AQ 1.9399410 sec
RG 10
DW 52.000 usec
DE 2.000 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 13C
PULP1 20.00000000 usec
PLM1 20.00000000 M

===== Processing parameters =====
SI 65536
SF 600.1300362 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

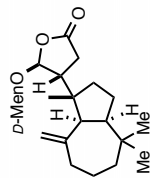
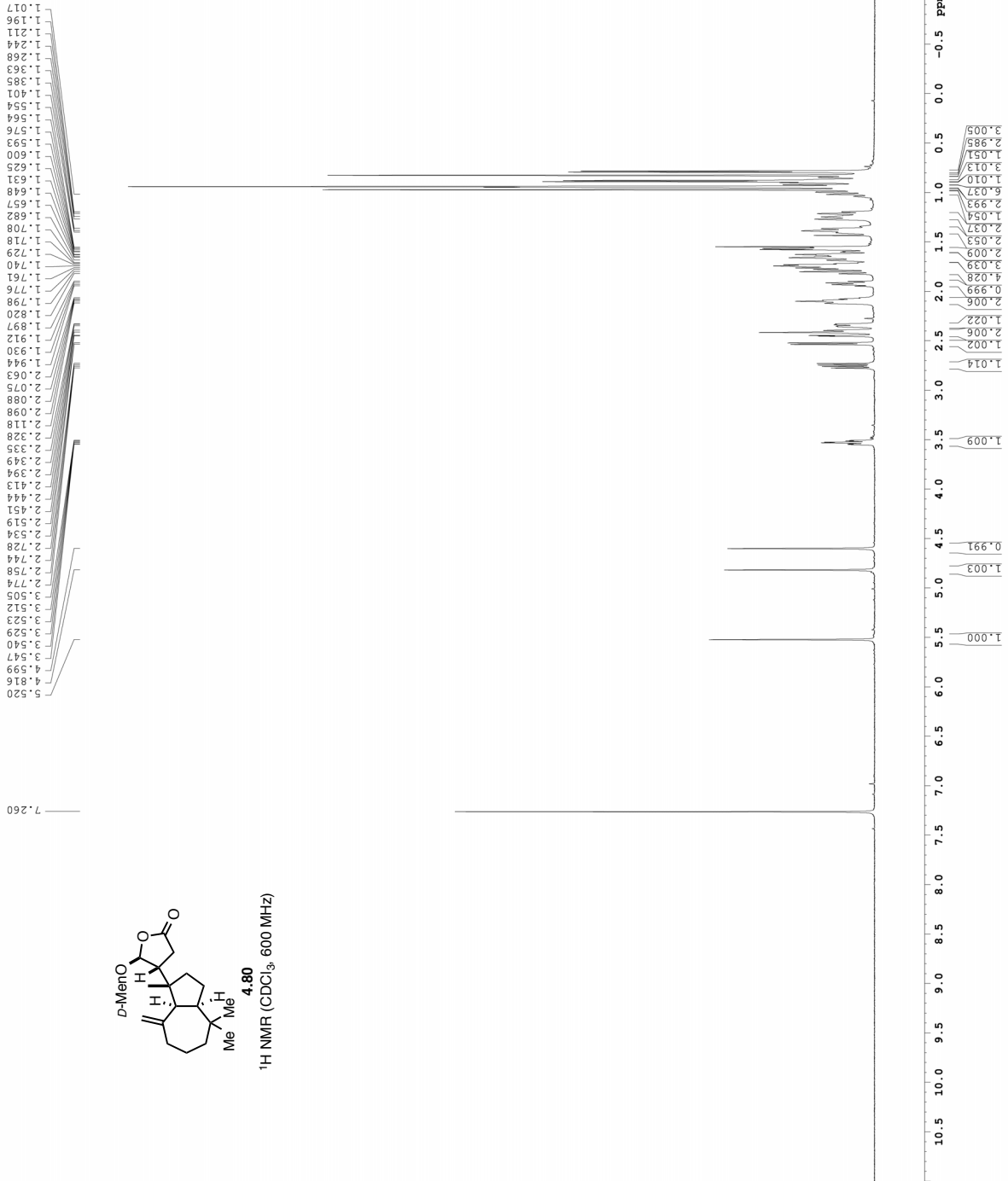


¹H NMR (CDCl₃, 600 MHz) of the crude reaction mixture



YS-V-247

Current Data Parameters
NAME YS-V-247
EXPNO 1
PROCNO 1
DATE_ /v/data/yuriy/nmr
Date_ 20170301
Time_ 15.14
INSTRUM 5 mm CPBBO
PULPROG zgpg30
SOLVENT CDCl3
DS 2
SWH 9615.282 Hz
AQ 5.098478 sec
RG 50.10 usec
DE 1.00 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 600.134209 MHz
PC1 12.00 usec
PL1 20.00000000 M
===== F2 - Processing parameters =====
SI 65536
SF 600.1300351 MHz
RG 0
LB 0.30 Hz
GB 0
PC 1.00



4.80
¹H NMR (CDCl₃, 600 MHz)

YS-V-247

Current Data Parameters
NAME YS-V-247
EXPERNO 2
DATE_ 20170101
TIME 15:40
F2 - Acquisition Parameters
Date_ 20170101
Time 15:40
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
DS 4
SWH 36231.883 Hz
FIDRES 0.9043566 sec
RG 20600
AQ 11.2650 usec
DE 19.45 usec
TE 298.0 K
D11 0.40000000 sec
D12 0.03000000 sec
D13 1
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 64.00000000 W
===== CHANNEL f2 =====
NUC2 13C
P2 10.00 usec
PL2 64.00000000 W
===== CHANNEL f3 =====
CPDPRG12 waltz16
PL12 20.00000000 W
PL122 0.36000001 W
===== F2 - Processing parameters =====
SI 150.9027246 MHz
SF 150.9027246 MHz
WDW EM
SSB 0
GB 0
PC 1.00

15.958
21.138
22.533
23.314
25.661
25.894
26.376
28.895
30.872
31.619
34.551
34.613
36.367
37.098
37.568
37.960
40.178
47.480
48.076
51.927
54.536
55.923

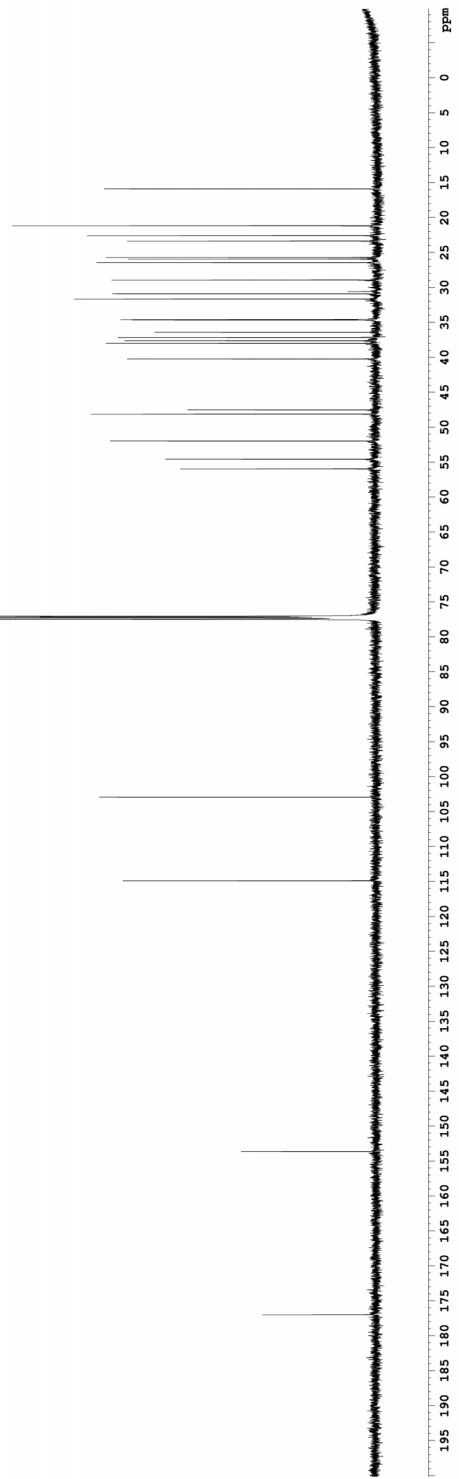
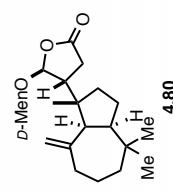
77.017
77.107
77.228
77.440

102.903

114.858

153.594

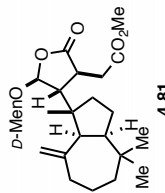
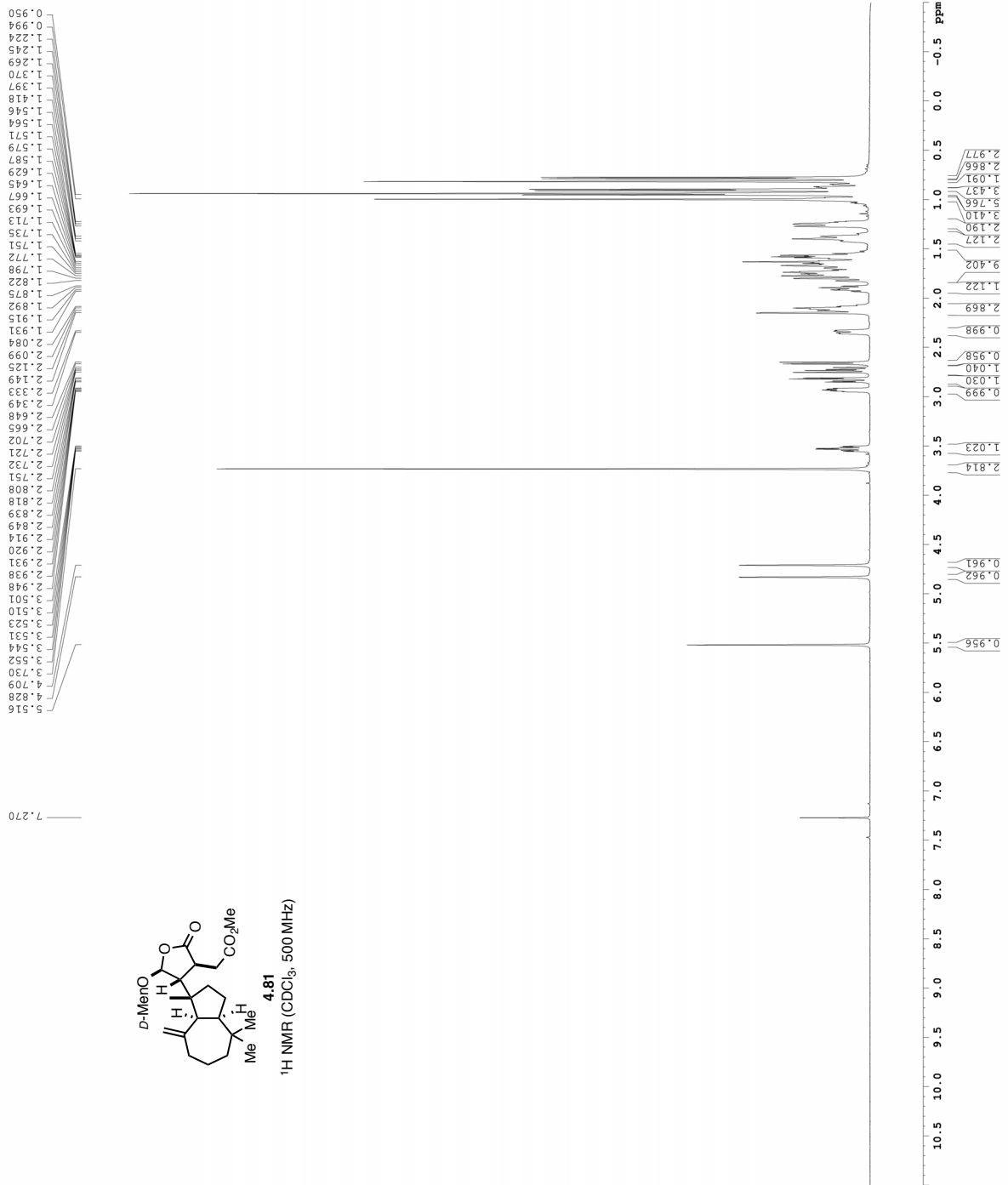
176.976



¹H spectrum

```

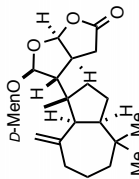
Current Data Parameters
NAME      F2-2145-P
EXPNO    1
PROCNO   1
DATE_    /v/data/zhaop2/nmr
Date_    20170111
Time     11:45
F2 - Acquisition Parameters
INSTRUM  cryo500
PULPROG  zg30
ID        81728
NS        2
DS        2
SWH       8015.820 Hz
AQ        5.0998273 sec
RG        5.7
BW        62.400 usec
TE        298.0 K sec
D1        0.10000000 sec
d11secr  0 sec
d11srr   0.01500000 sec
MCNRSZ   0
===== CHANNEL f1 =====
NUC1      1H
P1        7.50 usec
PL1       0.00 dB
SFO1      500.225015 MHz
F2 - Processing parameters
SI        65534
SF        500.225015 MHz
WDW       EM
SSB       0
GB        0
PC        1.00
  
```



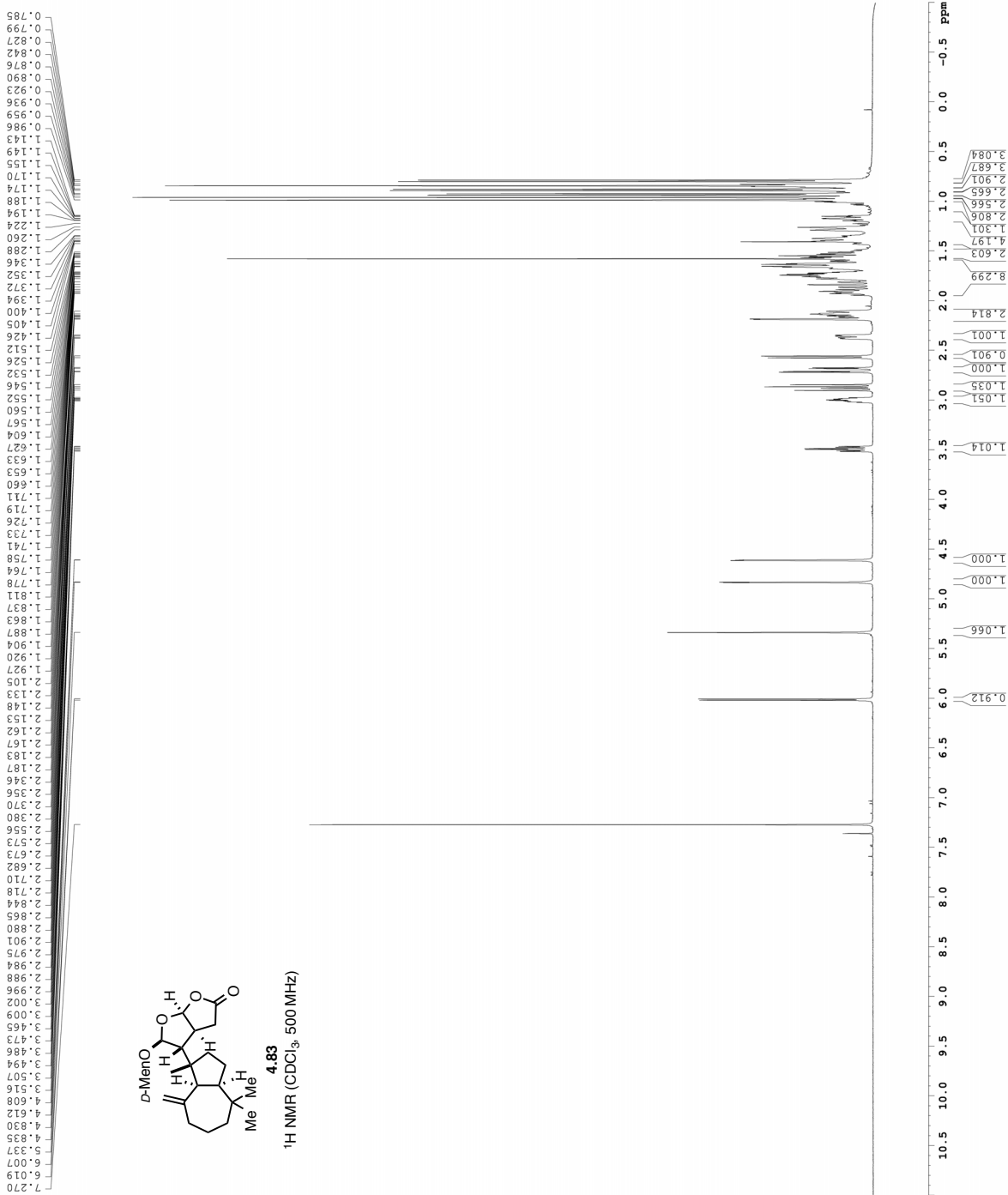
¹H NMR (CDCl₃, 500 MHz)

1H spectrum

Current Data Parameters
NAME Pr-2124-P
PROCNO 1
DATE_ /v/data/zhaop3/nmr
Date_ Acquisition Parameters
Time 20170321
INSTRUM czt500
PULPROG zg30
TD 8128
SOLVENT CDCl3
DS 2
SWH 8013.820 Hz
AQ 5.0398273 sec
RG 5.7
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
SFO1 500.2253015 MHz
PC 1.00



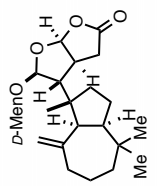
4.83
1H NMR (CDCl₃, 500 MHz)



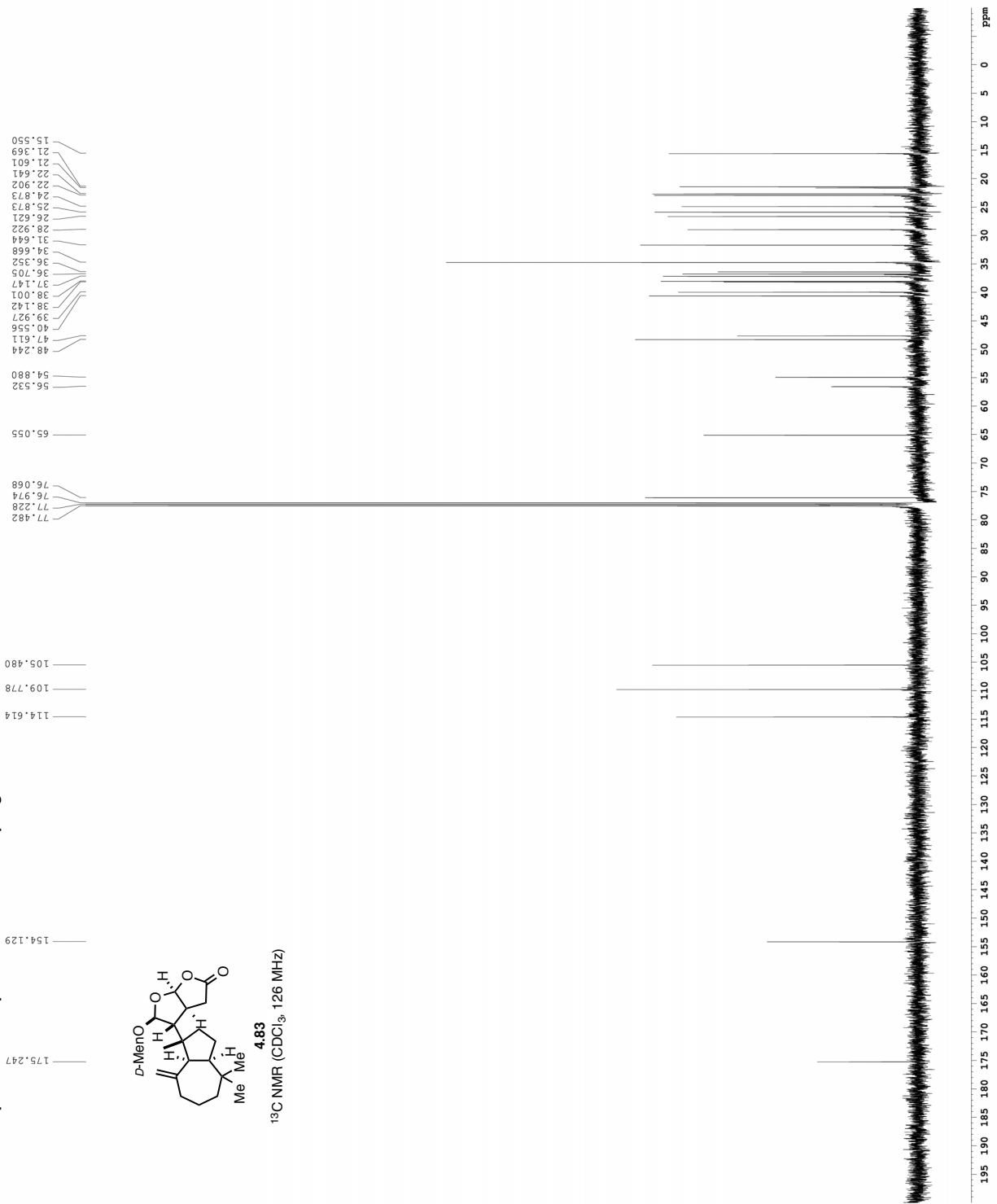
Z-restored spin-echo 13C spectrum with 1H decoupling

```

Current Data Parameters
NAME          Fz-2124-F
EXPNO        2
DATAPATH    /v/darc/zhao3/mr
F2 - Acquisition Parameters
Date_        20170327
Time         12:00
INSTRUM      cp130
PROBHD       5 mm CP131 H-
PULPROG      zgpg30
SOLVENT      CDCl3
DS           3
SWH          30300.031 Hz
AQ           1.0813480 sec
RG           4597.6
DE           1.6000000 usec
TE           298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
d15          0.00030000 sec
d19          0.00030000 sec
MCREST       0 sec
SFOFF1       0.01566005 Hz
SFOFF2       0.01566005 Hz
F2           33.10 usec
  
```



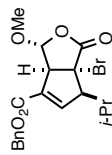
¹³C NMR (CDCl₃, 126 MHz)



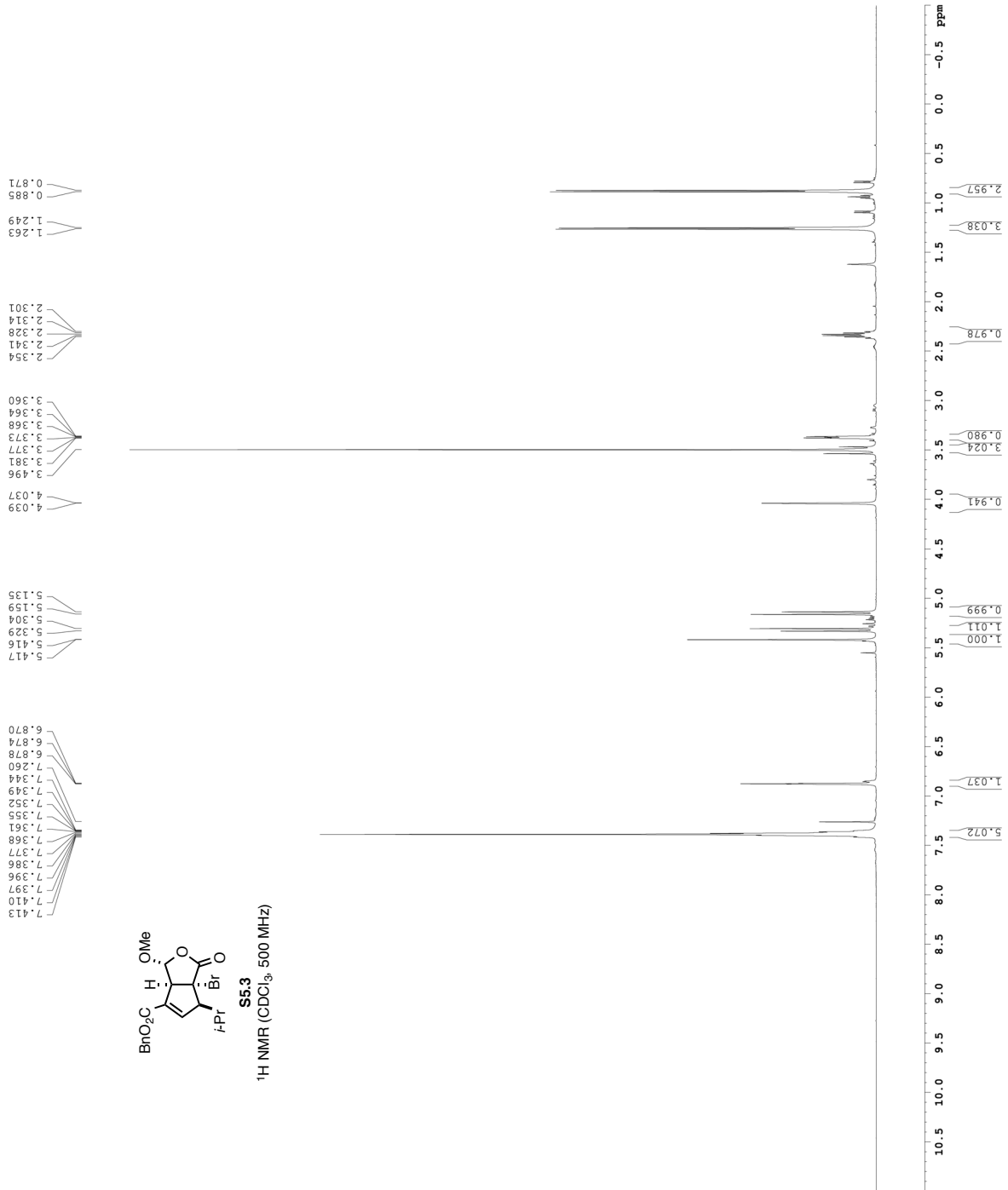
Appendix E: Chapter 5 NMR Spectra

PKO-I-154B

Current Data Parameters
 NAME PKO-I-154B-2
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Time 201113
 19.21
 INSTRUM gn500
 PROBHD 5 mm broadband
 PULPROG zgpg30
 TD 81728
 SOLVENT CDCl3T
 NS 9
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.098893 Hz
 AQ 0.020000 sec
 RG 101.6
 DR 62.400 usec
 DE 675.00 usec
 DI 0.10000000 sec
 MCREST 0 sec
 ACQBRK 0.15000000 sec
 CHANNEL f1
 NUC1 13
 P1 13.00 usec
 PL1 -4.00 dB
 SF01 499.6234973 MHz
 F2 - Processing parameters
 SI 65536
 SF 499.6200292 MHz
 EQ 2Hz
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



S53
¹H NMR (CDCl₃, 500 MHz)

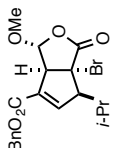


PKO-I-154B

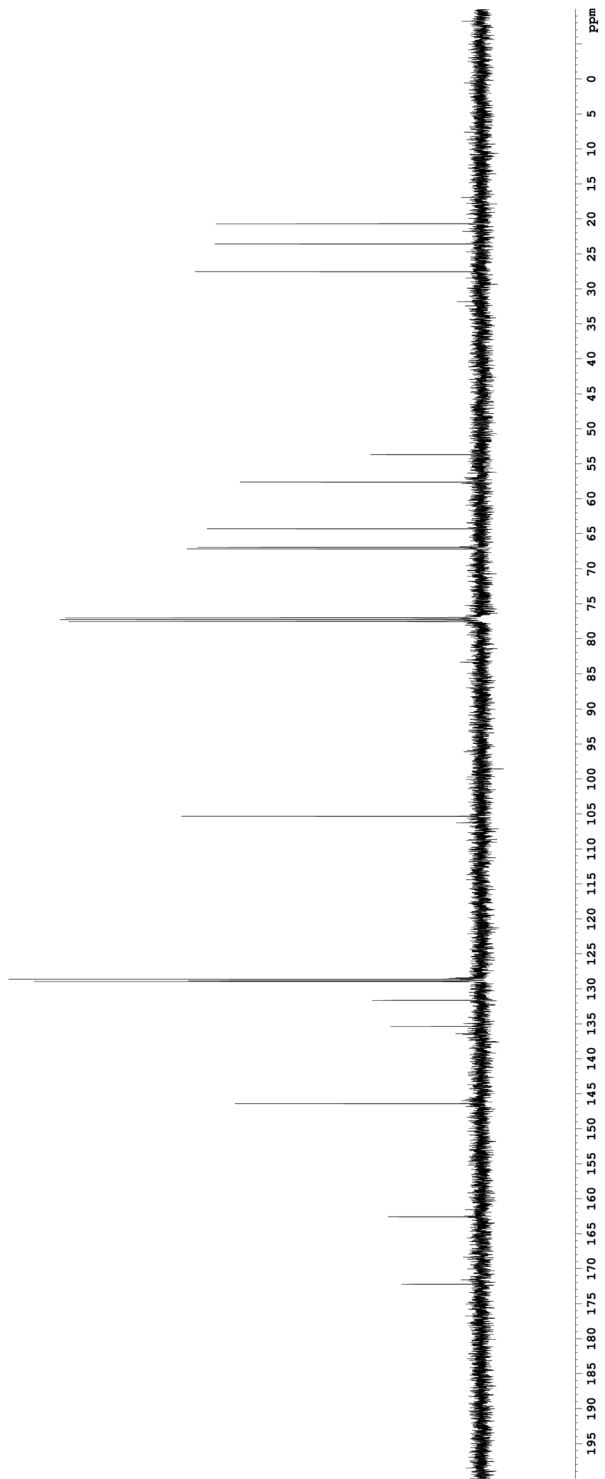
```

Current Data Parameters
NAME      PKO-I-154B-2
PROCNO    1
F2 - Acquisition Parameters
Time      2019-07-19 19:24
INSTRUM   spect
PULPROG   zgpg30
SOLVENT   CDCl3
NS         218
SRH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.095341 sec
RG         46341
DM         16.500 usec
DE         9.000 usec
TE         675.2 K
D1         0.25000000 sec
d11        0.05000000 sec
MCWRRK    0 sec
MCWRRK    0.01500000 sec
===== CHANNEL F1 =====
NUC1       13C
P1         12.50 usec
PL1        -3.00 dB
SFO1       125.6131883 MHz
===== CHANNEL F2 =====
PROBHD1    5 mm
PULPROG2   zgpg30
NUC2       13C
PCPD2      80.00 usec
PL2         1.00 dB
PL12        13.70 dB
SFO2       499.6224981 MHz
F2 - Processing parameters
SI         32768
SF         125.6285325 MHz
WDW        EM
SSB        0
ZFB        0
GB         0
PC         2.00
  
```

172.195
 162.560
 146.362
 135.356
 131.598
 128.920
 128.828
 128.577
 105.297
 77.483
 77.228
 76.974
 67.119
 66.902
 64.242
 57.573
 53.641
 27.498
 23.527
 20.657



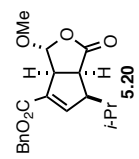
S5.3
¹³C NMR (CDCl₃, 126 MHz)



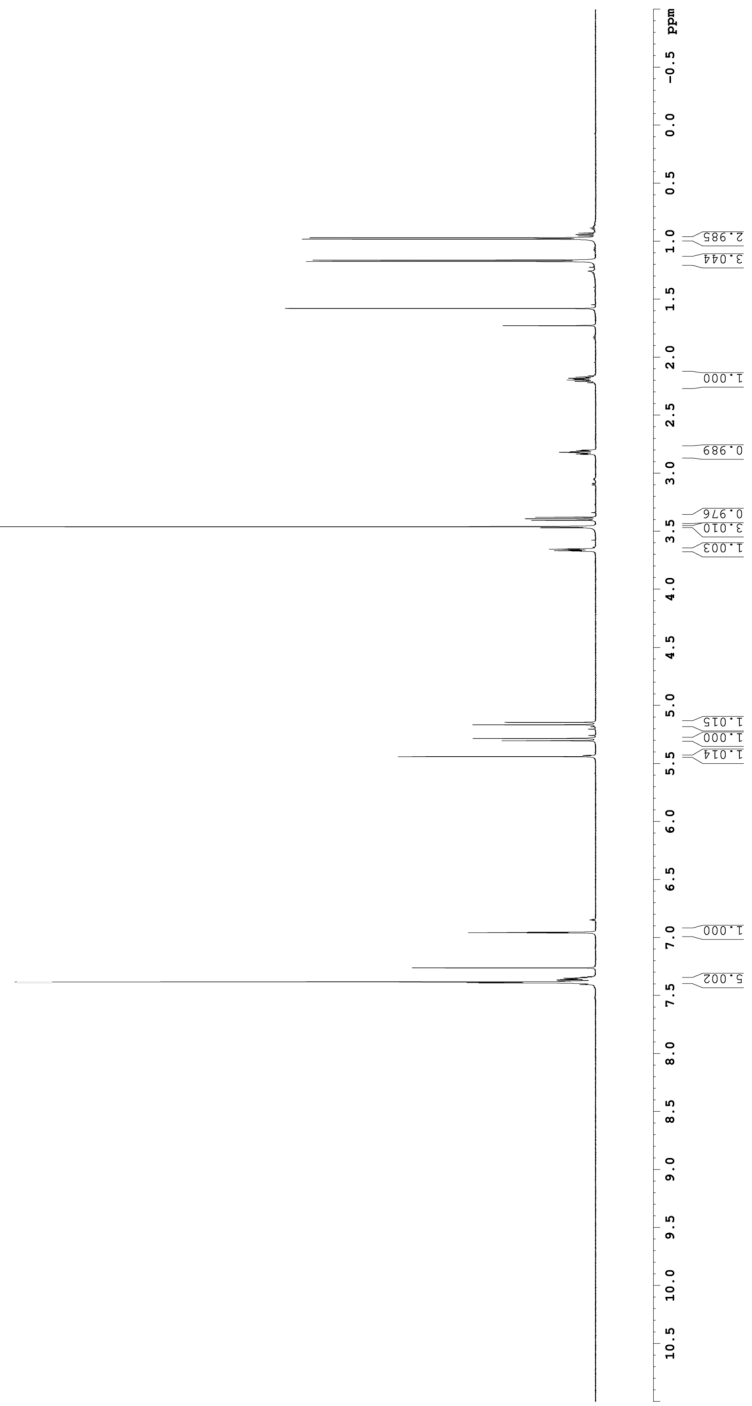
PKO-I-162

Current Data Parameters
NAME PKO-I-162-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110615
Time 16:55
INSTRUM AV600
PROBHD 5 mm TBI IH/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3I
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 0.0200000 sec
RG 312
DR 52.000 usec
DE 9.00 usec
TE 300.2 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 1H
P1 8.00 usec
PL 0.00 dB
SFO1 600.1342003 MHz
SF01 600.1342003 MHz
F2 - Processing parameters
SI 65536
SF 600.1300349 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

7.403
7.394
7.391
7.387
7.389
7.376
7.372
7.360
7.352
7.350
7.347
7.342
7.341
7.260
6.955
6.952
5.438
5.437
5.302
5.282
5.144
3.670
3.666
3.658
3.653
3.650
3.458
3.405
3.392
3.378
3.336
2.832
2.827
2.821
2.817
2.813
2.806
2.802
2.798
2.700
2.195
2.191
2.184
2.180
2.169
1.578
1.171
1.161
0.980
0.969



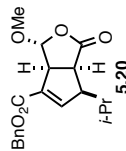
¹H NMR (CDCl₃, 600 MHz)



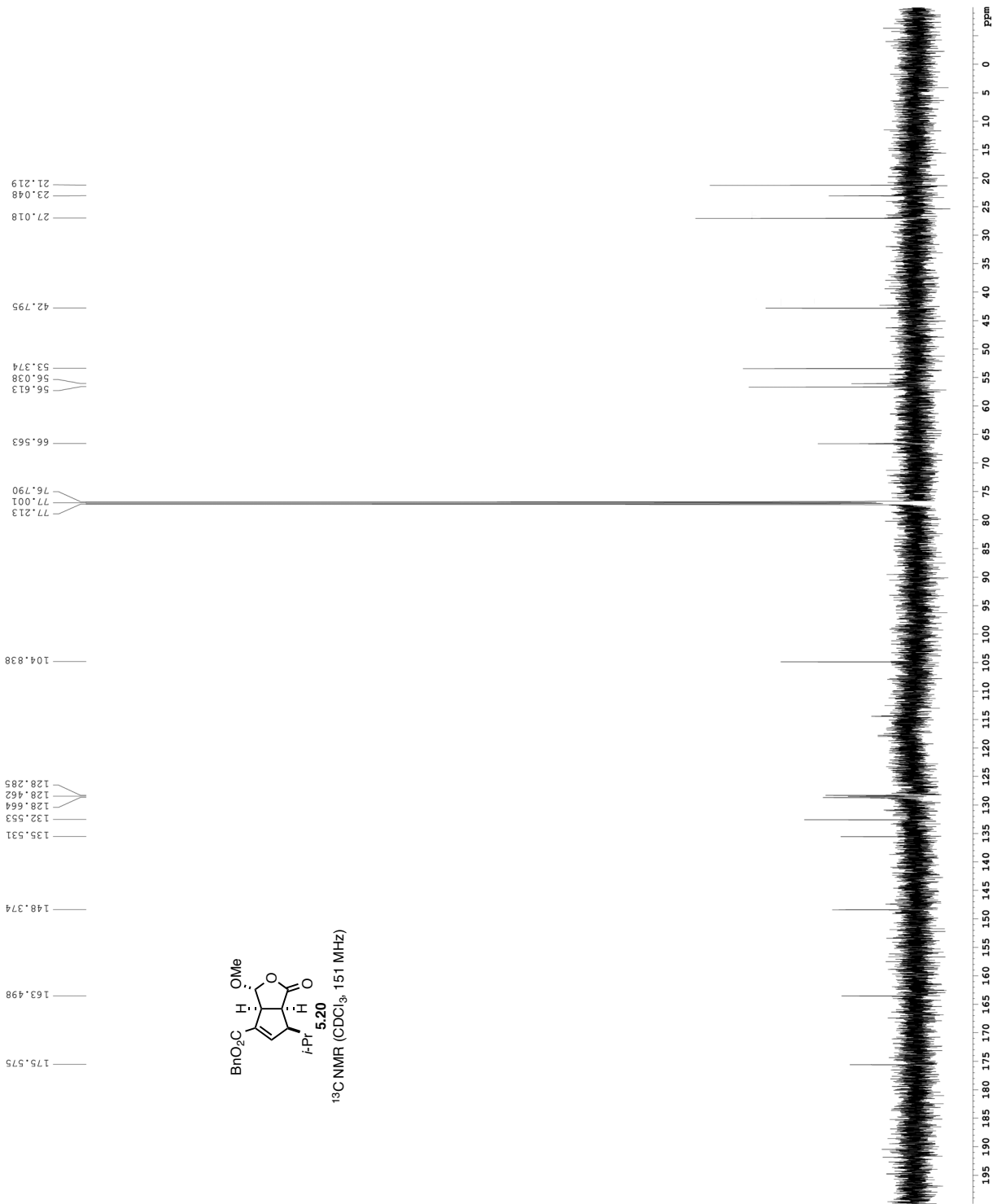
PKO-I-162

```

Current Data Parameters
NAME          PKO-I-162-2
PROCNO       1
F2 - Acquisition Parameters
Time         20.16
INSTRUM      5 mm TBI AVX00
PULPROG      zgpg30
SOLVENT      CDCl3
NS           1024
DS           4
SRH          36231.883 Hz
FIDRES       0.522855 Hz
AQ           0.9004374 sec
RG           314.4
DM           13.600 usec
DE           1.000 usec
TE           298.2 K
D1           0.6000001 sec
D11          0.13500001 sec
TD0          1
===== CHANNEL f1 =====
NUC1          13C
P1           15.00 usec
PL1          0 dB
SFO1         150.919480 MHz
===== CHANNEL f2 =====
CPRPG12      waltz16
PCPD2        80.00 usec
PL2          120.00 dB
SFO2         600.1330010 MHz
F2 - Processing Parameters
SI           65536
SF           150.9028256 MHz
WDW          EM
SSB          0
GB           0
PC           1.00
  
```

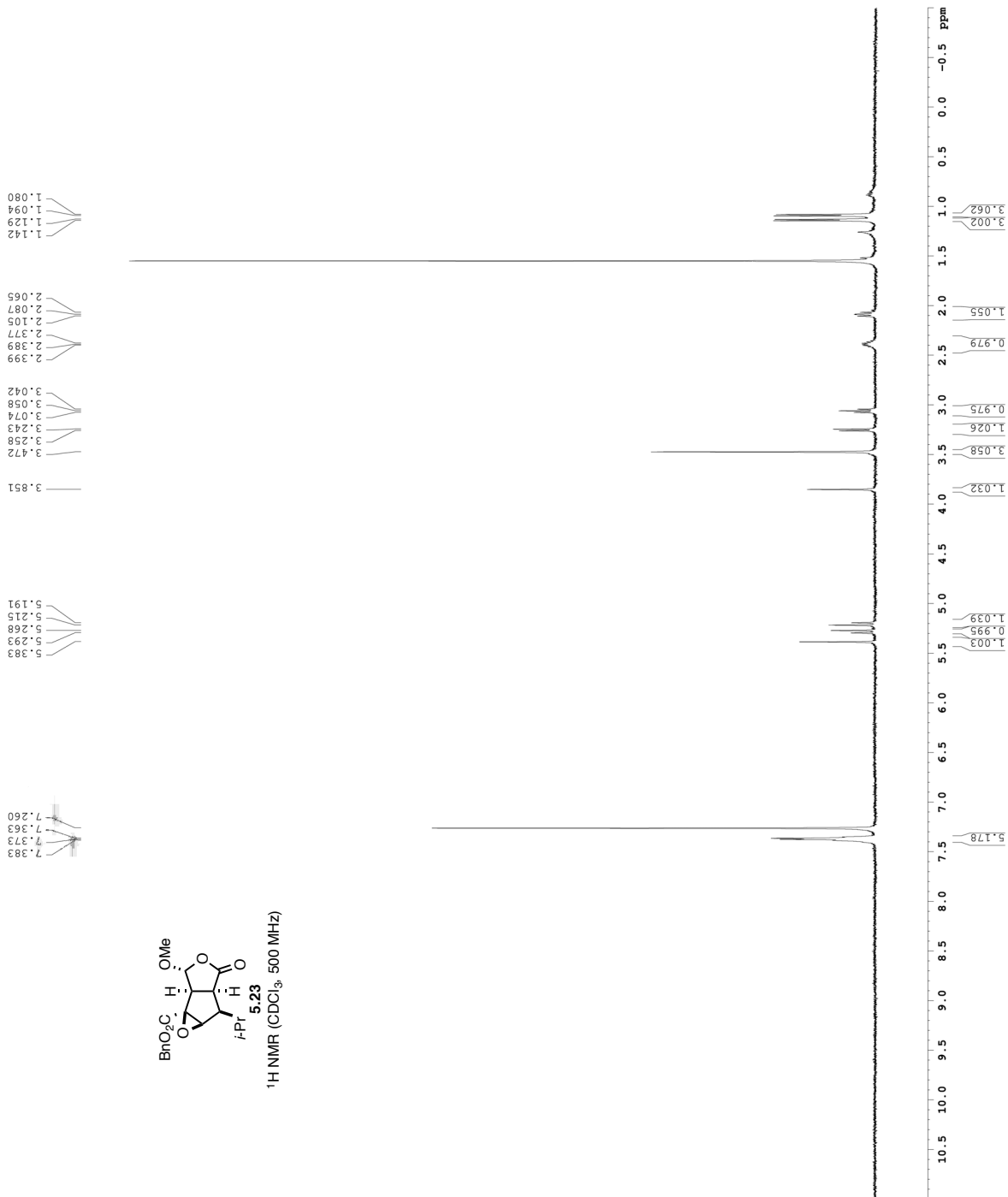
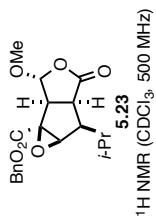


¹³C NMR (CDCl₃, 151 MHz)

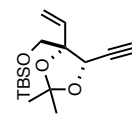


PKO-I-290

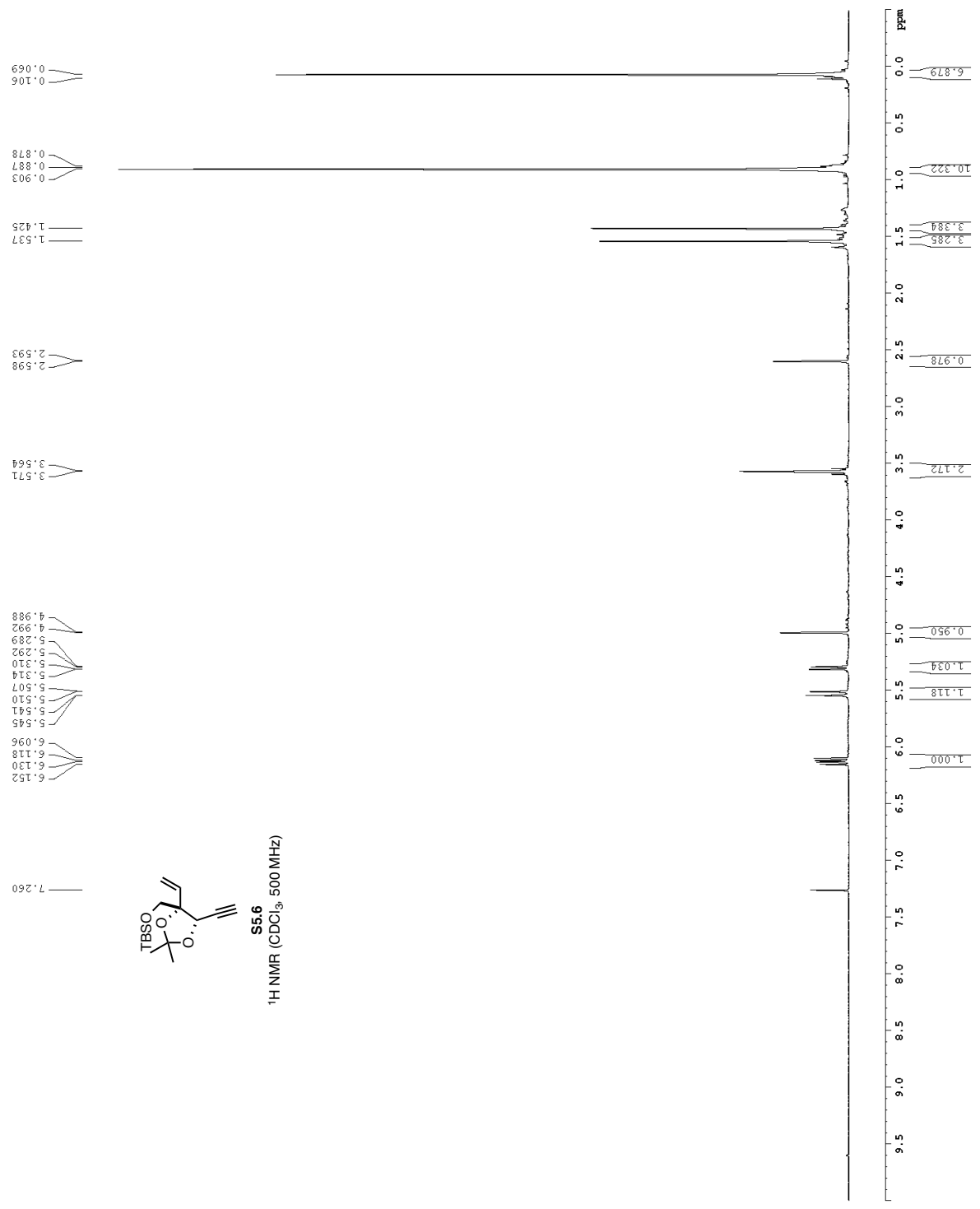
Current Data Parameters
NAME PKO-I-290-3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 201202
Time_ 12:02
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 0.0200000 sec
RG 46341 sec
DR 62.400 usec
DE 9.00 usec
D1 0.10000000 sec
MCREST 0 sec
MCWRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -2.00 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



Current Data Parameters
 NAME: S56
 PROCNO: 1
 DTORIG: 2
 F2 - Acquisition Parameters
 INSTRUM: spect
 PULPROG: zgpg30
 SOLVENT: CDCl3
 NS: 8
 DS: 4
 SWH: 8032.820 Hz
 FIDRES: 0.098271 Hz
 AQ: 5.098271 Hz
 PC: 62.468 sec
 RE: 4.000000 sec
 PI: 0.1000000 sec
 MRST: 0 sec
 RMWA: 0.0500000 sec
 ===== CHANNEL f1 =====
 P1: 7.50 usec
 PL1: 0.00 dB
 SFO1: 500.2320013 MHz
 F2 - Processing parameters
 SI: 65536
 SF: 500.2320013 MHz
 DSF: 0 Hz
 OSF: 0 Hz
 PC: 4.00



S56
¹H NMR (CDCl₃, 500 MHz)



Current Data Parameters
 NAME DVT-II-255
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20131130
 Time 15.34
 INSTRUM cryo500
 PROBHD 5 mm CP1CIH-1H
 PULPROG SpinEchoPrd
 TD 65536
 SOLVENT CDCl3
 NS 385

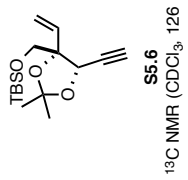
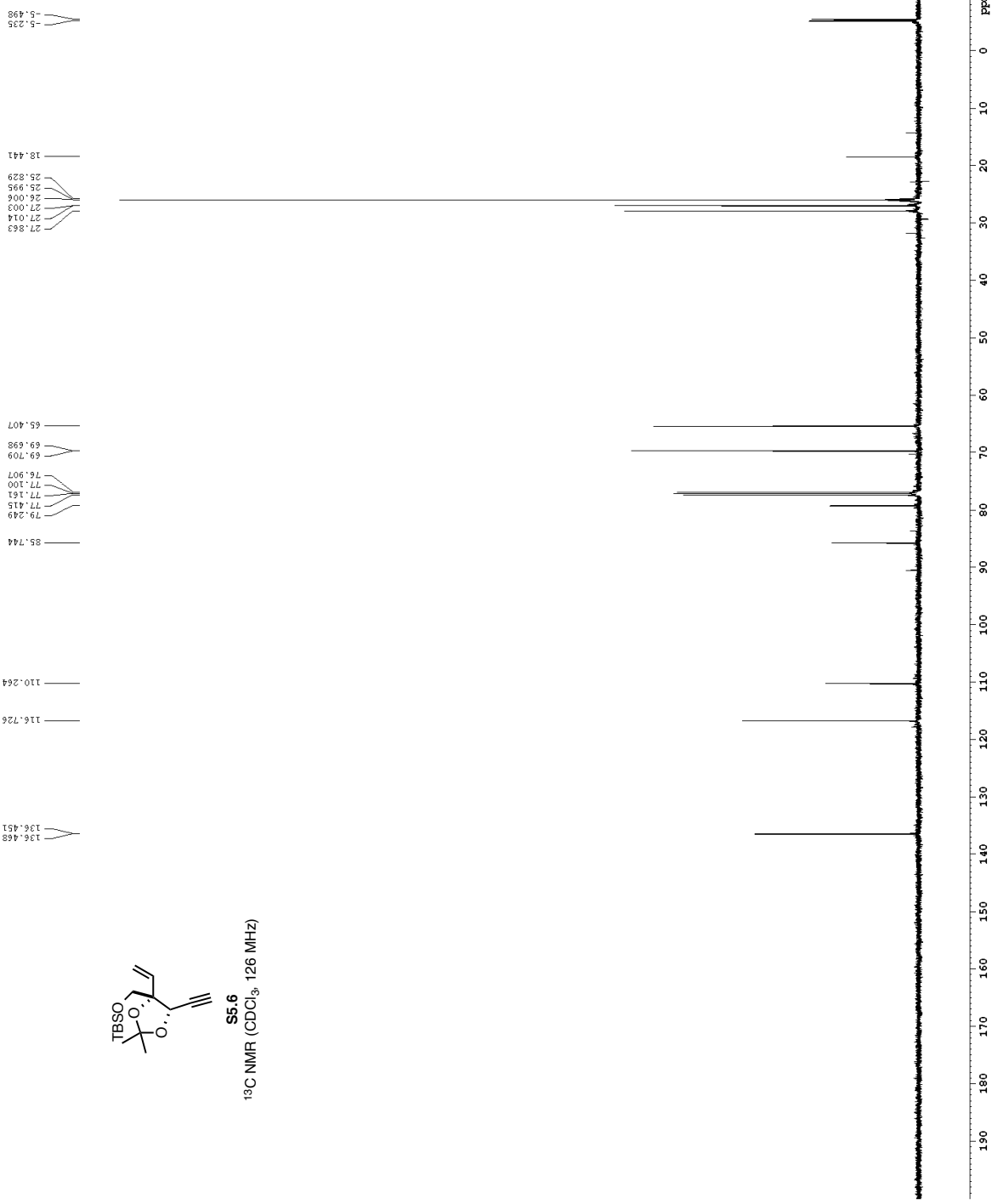
DS 16
 SWH 30303.031 Hz
 FIDRES 0.773480 Hz
 AQ 1.0813440 sec
 RG 144596.5
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 D11 0.2000000 sec
 D12 0.2000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCNREK 0.01500000 sec
 F2 31.00 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 15.50 usec
 F11 500.00 usec
 F12 2000.00 usec
 F10 120.00 dB
 SF01 125.7942568 MHz
 SF1 3.20 dB
 SF2 3.20 dB
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 FCFD2 100.00 usec
 F11 1.60 dB
 F12 2.60 dB
 SF02 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GP1 0 %
 GP2 0 %
 GP3 0 %
 GP4 0 %
 GP5 0 %
 GP6 0 %
 GP7 0 %
 GP8 0 %
 GP9 0 %
 GP10 0 %
 GP11 30.00 %
 GP12 50.00 %
 GP13 500.00 usec
 GP14 1000.00 usec
 GP15
 GP16

F2 - Processing parameters
 SI 65536
 SF 125.7804076 MHz
 WDW EM
 SSB 0
 GB 0
 FC 2.00




```

Current Data Parameters
NAME      DUT-III-043
EXPNO     4
PROCNO    1
F2 - Acquisition Parameters
Date_     20131129
Time      13.55
INSTRUM   cryo500
PROBHD    5 mm CPXI 1H-
PULPROG   Spinecho99sgpprpd
PCPDPRG2  gdd
SOLVENT   CDCl3
NS         175
DS         16
SWH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813440 sec
RG         384
DM         16.500 usec
DE         6.00 usec
TE         298.0 K
D1         0.25000000 sec
d11        0.03000000 sec
d12        0.06000000 sec
d13        0.06000000 sec
d14        0.00019600 sec
d15        0.00019600 sec
d16        0.00019600 sec
d17        0.00019600 sec
d18        0.00019600 sec
d19        0.00019600 sec
d20        0.00019600 sec
d21        0.00019600 sec
d22        0.00019600 sec
d23        0.00019600 sec
d24        0.00019600 sec
d25        0.00019600 sec
d26        0.00019600 sec
d27        0.00019600 sec
d28        0.00019600 sec
d29        0.00019600 sec
d30        0.00019600 sec
d31        0.00019600 sec
d32        0.00019600 sec
d33        0.00019600 sec
d34        0.00019600 sec
d35        0.00019600 sec
d36        0.00019600 sec
d37        0.00019600 sec
d38        0.00019600 sec
d39        0.00019600 sec
d40        0.00019600 sec
d41        0.00019600 sec
d42        0.00019600 sec
d43        0.00019600 sec
d44        0.00019600 sec
d45        0.00019600 sec
d46        0.00019600 sec
d47        0.00019600 sec
d48        0.00019600 sec
d49        0.00019600 sec
d50        0.00019600 sec
d51        0.00019600 sec
d52        0.00019600 sec
d53        0.00019600 sec
d54        0.00019600 sec
d55        0.00019600 sec
d56        0.00019600 sec
d57        0.00019600 sec
d58        0.00019600 sec
d59        0.00019600 sec
d60        0.00019600 sec
d61        0.00019600 sec
d62        0.00019600 sec
d63        0.00019600 sec
d64        0.00019600 sec
d65        0.00019600 sec
d66        0.00019600 sec
d67        0.00019600 sec
d68        0.00019600 sec
d69        0.00019600 sec
d70        0.00019600 sec
d71        0.00019600 sec
d72        0.00019600 sec
d73        0.00019600 sec
d74        0.00019600 sec
d75        0.00019600 sec
d76        0.00019600 sec
d77        0.00019600 sec
d78        0.00019600 sec
d79        0.00019600 sec
d80        0.00019600 sec
d81        0.00019600 sec
d82        0.00019600 sec
d83        0.00019600 sec
d84        0.00019600 sec
d85        0.00019600 sec
d86        0.00019600 sec
d87        0.00019600 sec
d88        0.00019600 sec
d89        0.00019600 sec
d90        0.00019600 sec
d91        0.00019600 sec
d92        0.00019600 sec
d93        0.00019600 sec
d94        0.00019600 sec
d95        0.00019600 sec
d96        0.00019600 sec
d97        0.00019600 sec
d98        0.00019600 sec
d99        0.00019600 sec
d100       0.00019600 sec

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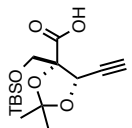
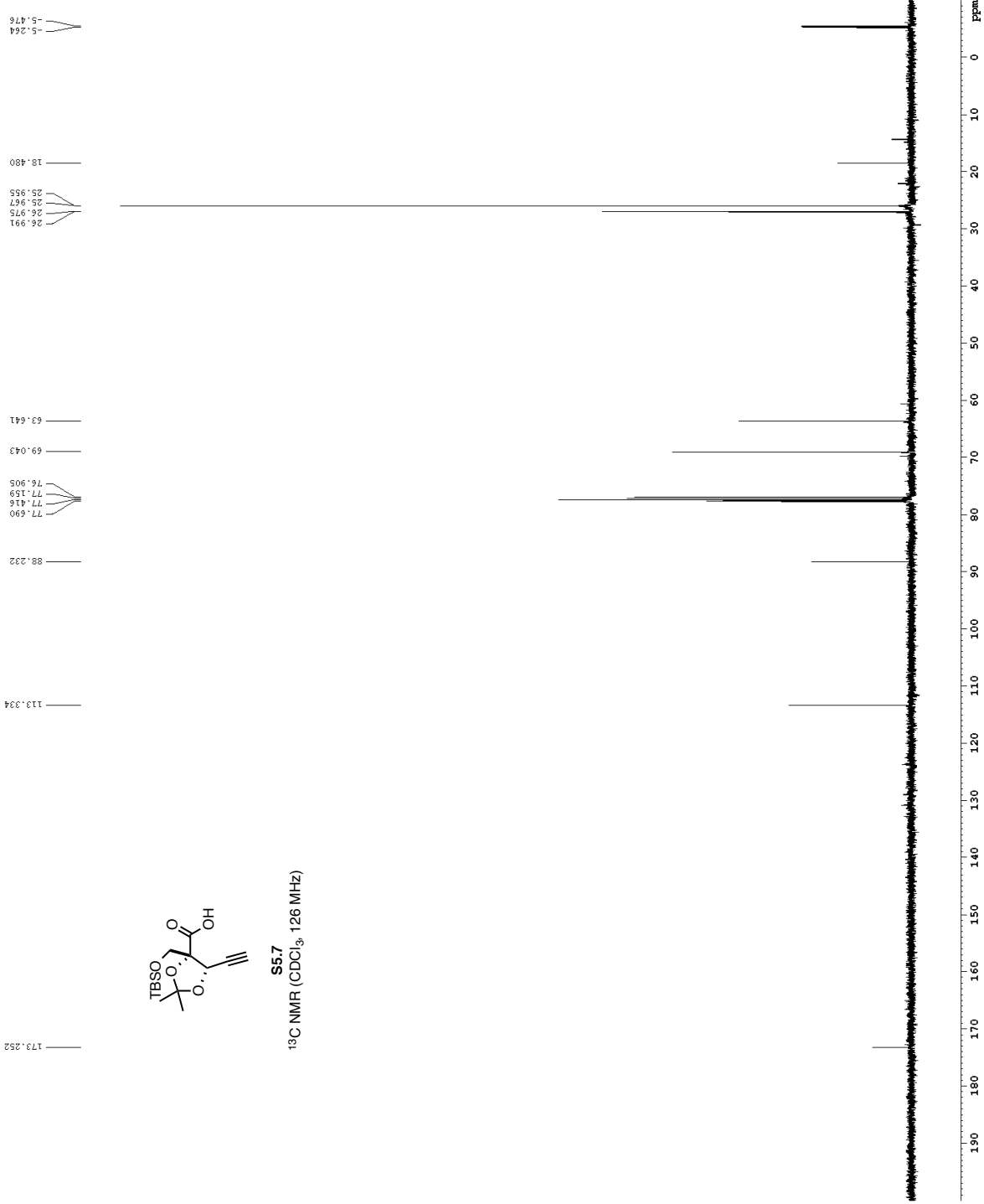
===== CHANNEL f1 =====
NUC1      13C
PCPDPRG1  zgpg30
P1         15.50 usec
P11        500.00 usec
P12        2000.00 usec
P10        120.00 dB
P11        1.00 dB
P12        1.00 dB
SF01       125.7942598 MHz
SF02       125.7600000 MHz
SF03       3.20 dB
SF04       3.20 dB
SFOFF1     0 Hz
SFOFF2     0 Hz
SFOFF3     0 Hz
SFOFF4     0 Hz
SFOFF5     0 Hz
SFOFF6     0 Hz
SFOFF7     0 Hz
SFOFF8     0 Hz
SFOFF9     0 Hz
SFOFF10    0 Hz
===== CHANNEL f2 =====
PCPDPRG2  waltz16
NUC2      1H
PCPDPRG1  zgpg30
P1         15.50 usec
P11        500.00 usec
P12        2000.00 usec
P10        120.00 dB
P11        1.00 dB
P12        1.00 dB
SF01       125.7942598 MHz
SF02       125.7600000 MHz
SF03       3.20 dB
SF04       3.20 dB
SFOFF1     0 Hz
SFOFF2     0 Hz
SFOFF3     0 Hz
SFOFF4     0 Hz
SFOFF5     0 Hz
SFOFF6     0 Hz
SFOFF7     0 Hz
SFOFF8     0 Hz
SFOFF9     0 Hz
SFOFF10    0 Hz
===== GRADIENT CHANNEL =====
GPNAM[1]  SINE.100
GPNAM[2]  SINE.100
GPA1      0 %
GPA2      0 %
GPA3      0 %
GPA4      0 %
GPA5      0 %
GPA6      0 %
GPA7      0 %
GPA8      0 %
GPA9      0 %
GPA10     0 %
GPA11     0 %
GPA12     0 %
GPA13     0 %
GPA14     0 %
GPA15     0 %
GPA16     0 %
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GPA53     0 %
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GPA55     0 %
GPA56     0 %
GPA57     0 %
GPA58     0 %
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GPA71     0 %
GPA72     0 %
GPA73     0 %
GPA74     0 %
GPA75     0 %
GPA76     0 %
GPA77     0 %
GPA78     0 %
GPA79     0 %
GPA80     0 %
GPA81     0 %
GPA82     0 %
GPA83     0 %
GPA84     0 %
GPA85     0 %
GPA86     0 %
GPA87     0 %
GPA88     0 %
GPA89     0 %
GPA90     0 %
GPA91     0 %
GPA92     0 %
GPA93     0 %
GPA94     0 %
GPA95     0 %
GPA96     0 %
GPA97     0 %
GPA98     0 %
GPA99     0 %
GPA100    0 %

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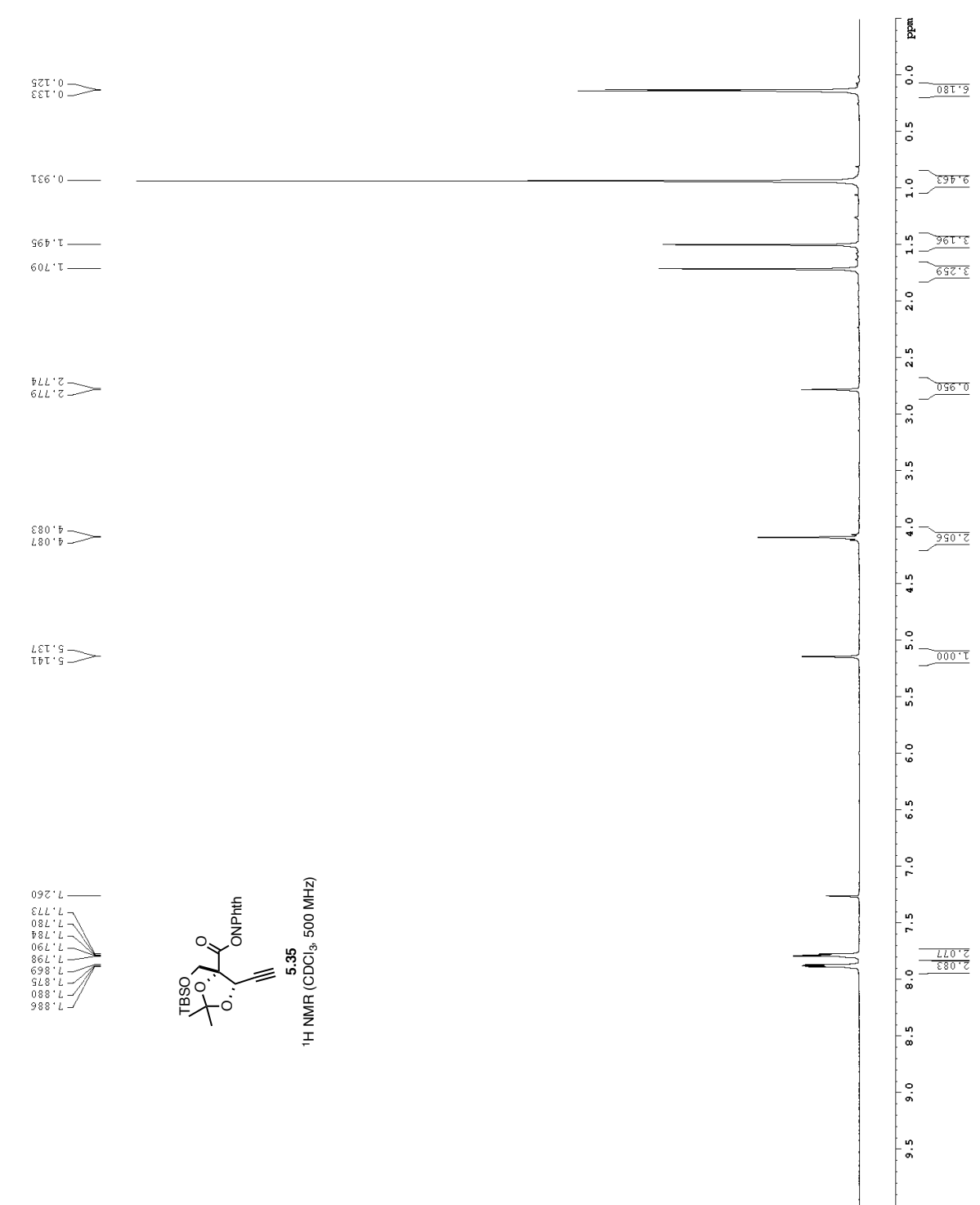
F2 - Processing parameters
SI         32768
SF         125.7804085 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         2.00

```



S5.7
¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME: D:\7-11-01
 PROCNO: 1
 FT - Acquisition Parameters
 Date_ Time: 20111108
 12:53
 INSTRUM: spect
 PPROBHD: 5 mm broadband
 T1: 3.00 sec
 T2: 0.125 sec
 T2*PFG: 0.125
 SOLVENT: CDCl3
 NS: 0
 DS: 0
 FIDRES: 0.01450 Hz
 AQ: 0.00400 Hz
 RG: 5.09960 Hz
 IN: 62.400 usec
 DE: 2.000 usec
 TE: 298.2 K usec
 TILT: 0.000000 sec
 METER: 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1: 12.78 Hz
 P1: 1.20 usec
 PL1: -3.00 dB
 SFO1: 499.294500 MHz
 F2 - Processing parameters
 SF: 499.294500 MHz
 G: 0.000000 Hz
 AS: 0
 SB: 0
 SC: 0
 SD: 0.30 Hz
 SE: 1.00



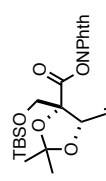
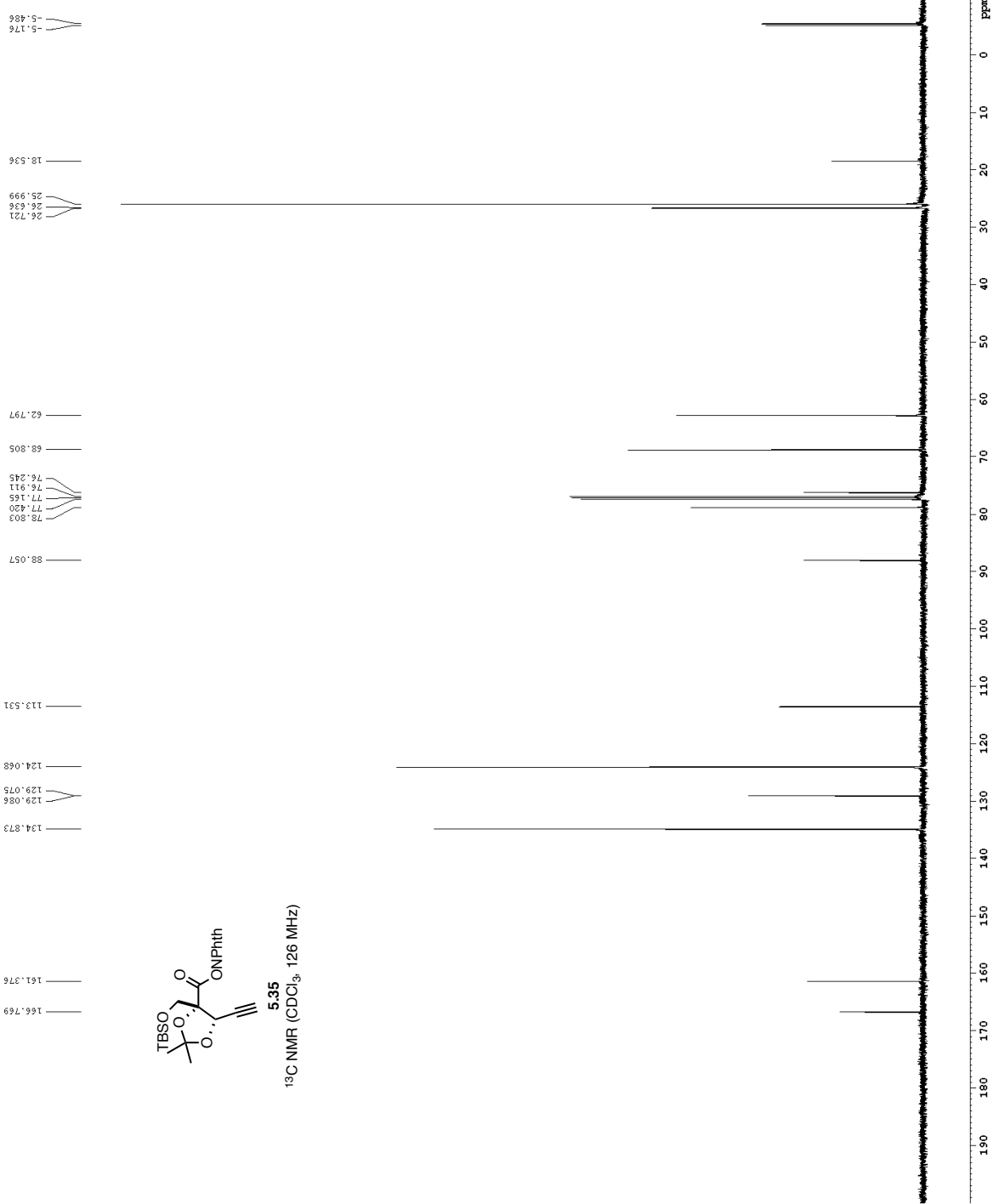
Current Data Parameters
 NAME DJT-III-081
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20131207
 Time_ 11.22
 INSTRUM cryo-500
 PROBDH 5 mm CPTCI 1H
 TD 65536
 TD1PROC SpinEchoProc
 SOLVENT CDCl3
 NS 338
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.72840 sec
 RG 1298.2
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCMRK 0.01500000 sec
 F2 31.00 usec

----- CHANNEL f1 -----
 NUC1 13C
 P1 15.50 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 0.00 dB
 SF01 125.7942568 MHz
 SF2 3.20 dB
 SF2 3.20 dB
 SFOFF1 Crp60, 0.5, 20.1
 SFOFF2 0 Hz

----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 2.00 dB
 PL2 0.00 dB
 SF02 500.2228011 MHz

----- GRADIENT CHANNEL -----
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 0 %
 GPY2 0 %
 GPZ2 0 %
 P15 50.00 %
 P16 1000.00 usec

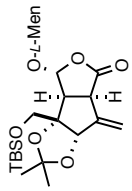
F2 - Processing parameters
 SI 65536
 SF 125.780480 MHz
 WDW EM
 SSB 0
 GB 0
 FC 2.00



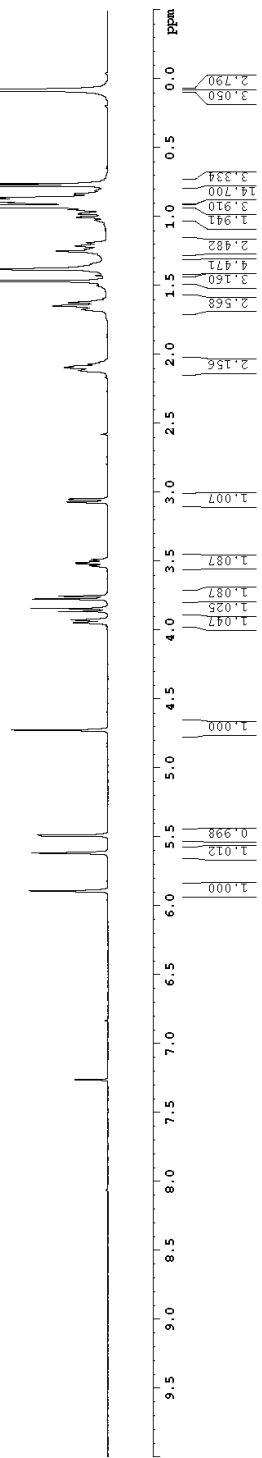
5.35
¹³C NMR (CDCl₃, 126 MHz)

Output Data Parameters
 NAME DFT-III-069
 PROCNO 1
 P2 - Acquisition Parameters
 Date_ 201109
 INSTRUM crys500
 PULPROG zgpg30
 TD 65536
 NS 4096
 DS 4
 SWH 8012.860 Hz
 FIDRES 0.098043 Hz
 AQ 5.0985774 sec
 RG 67.4
 IN 67.400 usec
 DE 1.000 usec
 TE 300.2 K
 REFEST 0 sec
 AVER 0.0150000 sec
 ===== CHANNEL f1 =====
 NU1 1
 PR1 1 7.10 usec
 PL1 0
 SFO1 500.2232000 MHz
 P2 - Processing parameters
 SI 65536
 SF 500.2232000 MHz
 DS 4
 SSB 0 0.30 Hz
 GB 0
 PC 4.00

7.261
 5.892
 5.888
 5.615
 5.490
 5.485
 4.723
 3.945
 3.924
 3.862
 3.840
 3.772
 3.751
 3.513
 3.505
 3.070
 3.066
 3.050
 3.046
 2.092
 2.083
 1.645
 1.630
 1.465
 1.377
 1.247
 1.207
 1.003
 0.946
 0.929
 0.916
 0.899
 0.861
 0.834
 0.828
 0.773
 0.759
 0.083
 0.076



5.37
¹H NMR (CDCl₃, 500 MHz)



Current Data Parameters
 NAME DDT-III-088
 EXPNO 2
 PROCNO 1

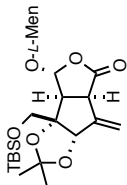
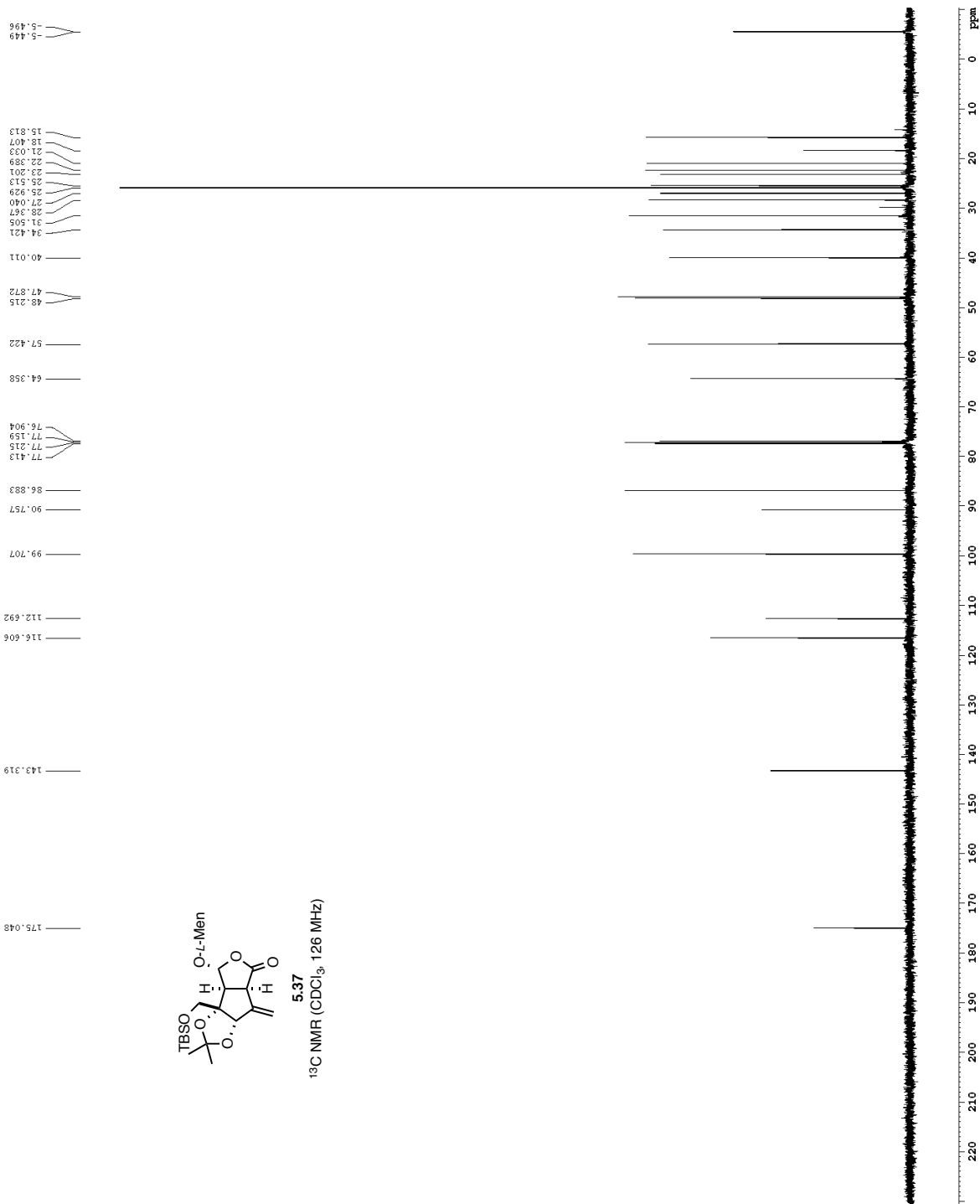
F2 - Acquisition Parameters
 Date_ 20181220
 Time 13:48
 INSTRUM cryo500
 PROBHD 5 mm CPYCI 1H-
 PULPROG SpinEcho930gp.prd
 TD 65536
 SOLVENT CDCl3
 NS 48
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 8192
 HW 16.500 usec
 EQ 60.000 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 ACQRES 0 sec
 WPRR 0.01500000 sec
 F2 31.00 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 15.50 usec
 PL1 0.00 dB
 P12 2000.00 usec
 PL2 120.00 dB
 P13 120.00 dB
 PL3 -1.00 dB
 SF01 125.7942548 MHz
 SFO2 500.1325011 MHz
 SP1 3.20 dB
 SP2 3.20 dB
 SFOFF[1] Cyp60.0.5.2.20 dB
 SFOFF[2] Cyp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 NUC2 1H
 P2 15.50 usec
 PL2 0.00 dB
 P22 100.00 usec
 PL2 1.60 dB
 P23 24.60 dB
 PL2 24.60 dB
 SF02 500.2225011 MHz
 SFOFF[1] SINE.100
 SFOFF[2] SINE.100

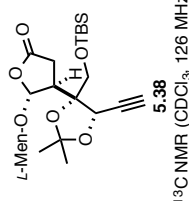
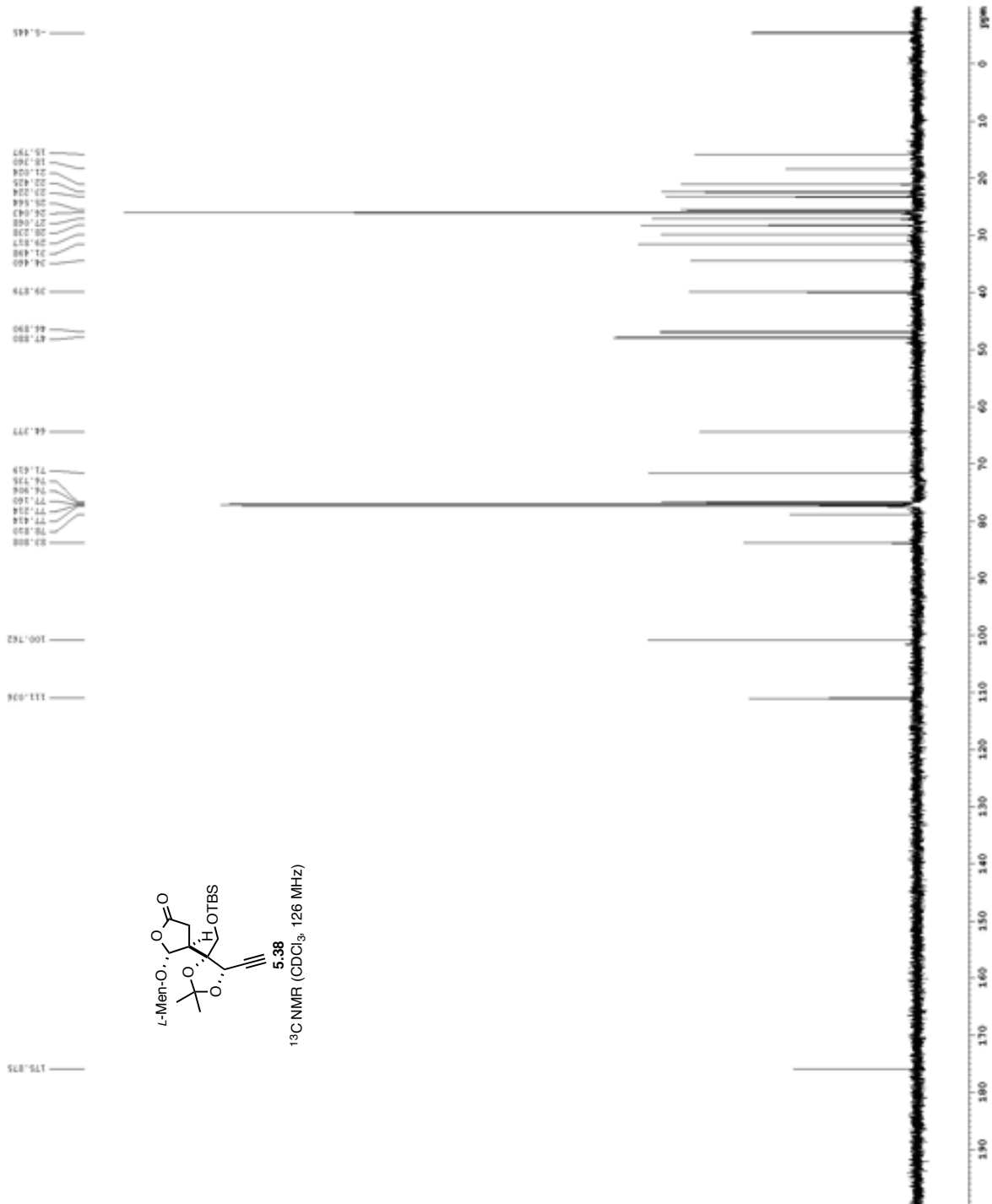
===== GRADIENT CHANNEL =====
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GZ1 30.00 %
 GZ2 50.00 %
 GZ3 50.00 %
 Y15 500.00 usec
 Y16 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 500.1325011 MHz
 WDM 125.7942548 MHz
 EM
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 2.00



5.37
¹³C NMR (CDCl₃, 126 MHz)

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



Current Data Parameters
 NAME INT-VI-059
 EXPNO 4
 F2PROC0 1

Acquisition Parameters
 Date_ 20151117
 Time 8:29
 INSTRUM cryo500
 PULPROG 5 mm CPTCI 18-
 TD 65536
 SFO 500.1362500 MHz
 SOLVENT CDCl₃
 NS 256
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.4622388 Hz
 AQ 1.0513440 sec
 RG 1239.2
 IQ 1.4000000 usec
 DE 4.0000000 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00200000 sec
 WALTZ16 0 usec
 WALTZ17 0 usec
 WALTZ18 0 usec
 WALTZ19 0 usec
 WALTZ20 0 usec
 WALTZ21 0 usec
 WALTZ22 0 usec
 WALTZ23 0 usec
 WALTZ24 0 usec
 WALTZ25 0 usec
 WALTZ26 0 usec
 WALTZ27 0 usec
 WALTZ28 0 usec
 WALTZ29 0 usec
 WALTZ30 0 usec
 WALTZ31 0 usec
 WALTZ32 0 usec
 WALTZ33 0 usec
 WALTZ34 0 usec
 WALTZ35 0 usec
 WALTZ36 0 usec
 WALTZ37 0 usec
 WALTZ38 0 usec
 WALTZ39 0 usec
 WALTZ40 0 usec
 WALTZ41 0 usec
 WALTZ42 0 usec
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 WALTZ87 0 usec
 WALTZ88 0 usec
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 WALTZ91 0 usec
 WALTZ92 0 usec
 WALTZ93 0 usec
 WALTZ94 0 usec
 WALTZ95 0 usec
 WALTZ96 0 usec
 WALTZ97 0 usec
 WALTZ98 0 usec
 WALTZ99 0 usec
 WALTZ100 0 usec

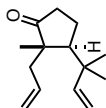
CHANNEL F1
 NUCL1 ¹³C
 P1 16.00 usec
 F1 500.1362500 MHz
 F12 500.1362500 MHz
 F13 2000.00 usec
 F14 120.00 dB
 F15 -1.00 dB
 SFO1 125.7942548 MHz
 SFO2 500.1362500 MHz
 SFO3 500.1362500 MHz
 SFO4 500.1362500 MHz
 SFO5 500.1362500 MHz
 SFO6 500.1362500 MHz
 SFO7 500.1362500 MHz
 SFO8 500.1362500 MHz
 SFO9 500.1362500 MHz
 SFO10 500.1362500 MHz
 SFO11 500.1362500 MHz
 SFO12 500.1362500 MHz
 SFO13 500.1362500 MHz
 SFO14 500.1362500 MHz
 SFO15 500.1362500 MHz
 SFO16 500.1362500 MHz
 SFO17 500.1362500 MHz
 SFO18 500.1362500 MHz
 SFO19 500.1362500 MHz
 SFO20 500.1362500 MHz
 SFO21 500.1362500 MHz
 SFO22 500.1362500 MHz
 SFO23 500.1362500 MHz
 SFO24 500.1362500 MHz
 SFO25 500.1362500 MHz
 SFO26 500.1362500 MHz
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 SFO30 500.1362500 MHz
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 SFO85 500.1362500 MHz
 SFO86 500.1362500 MHz
 SFO87 500.1362500 MHz
 SFO88 500.1362500 MHz
 SFO89 500.1362500 MHz
 SFO90 500.1362500 MHz
 SFO91 500.1362500 MHz
 SFO92 500.1362500 MHz
 SFO93 500.1362500 MHz
 SFO94 500.1362500 MHz
 SFO95 500.1362500 MHz
 SFO96 500.1362500 MHz
 SFO97 500.1362500 MHz
 SFO98 500.1362500 MHz
 SFO99 500.1362500 MHz
 SFO100 500.1362500 MHz

CHANNEL F2
 NUCL2 ¹H
 P2 16.00 usec
 F2 500.1362500 MHz
 F22 500.1362500 MHz
 F23 2000.00 usec
 F24 120.00 dB
 F25 -1.00 dB
 SFO1 125.7942548 MHz
 SFO2 500.1362500 MHz
 SFO3 500.1362500 MHz
 SFO4 500.1362500 MHz
 SFO5 500.1362500 MHz
 SFO6 500.1362500 MHz
 SFO7 500.1362500 MHz
 SFO8 500.1362500 MHz
 SFO9 500.1362500 MHz
 SFO10 500.1362500 MHz
 SFO11 500.1362500 MHz
 SFO12 500.1362500 MHz
 SFO13 500.1362500 MHz
 SFO14 500.1362500 MHz
 SFO15 500.1362500 MHz
 SFO16 500.1362500 MHz
 SFO17 500.1362500 MHz
 SFO18 500.1362500 MHz
 SFO19 500.1362500 MHz
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 SFO29 500.1362500 MHz
 SFO30 500.1362500 MHz
 SFO31 500.1362500 MHz
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 SFO33 500.1362500 MHz
 SFO34 500.1362500 MHz
 SFO35 500.1362500 MHz
 SFO36 500.1362500 MHz
 SFO37 500.1362500 MHz
 SFO38 500.1362500 MHz
 SFO39 500.1362500 MHz
 SFO40 500.1362500 MHz
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 SFO78 500.1362500 MHz
 SFO79 500.1362500 MHz
 SFO80 500.1362500 MHz
 SFO81 500.1362500 MHz
 SFO82 500.1362500 MHz
 SFO83 500.1362500 MHz
 SFO84 500.1362500 MHz
 SFO85 500.1362500 MHz
 SFO86 500.1362500 MHz
 SFO87 500.1362500 MHz
 SFO88 500.1362500 MHz
 SFO89 500.1362500 MHz
 SFO90 500.1362500 MHz
 SFO91 500.1362500 MHz
 SFO92 500.1362500 MHz
 SFO93 500.1362500 MHz
 SFO94 500.1362500 MHz
 SFO95 500.1362500 MHz
 SFO96 500.1362500 MHz
 SFO97 500.1362500 MHz
 SFO98 500.1362500 MHz
 SFO99 500.1362500 MHz
 SFO100 500.1362500 MHz

GRABBER CHANNEL
 GRAB1 0 Hz
 GRAB2 0 Hz
 GRAB3 0 Hz
 GRAB4 0 Hz
 GRAB5 0 Hz
 GRAB6 0 Hz
 GRAB7 0 Hz
 GRAB8 0 Hz
 GRAB9 0 Hz
 GRAB10 0 Hz
 GRAB11 0 Hz
 GRAB12 0 Hz
 GRAB13 0 Hz
 GRAB14 0 Hz
 GRAB15 0 Hz
 GRAB16 0 Hz
 GRAB17 0 Hz
 GRAB18 0 Hz
 GRAB19 0 Hz
 GRAB20 0 Hz
 GRAB21 0 Hz
 GRAB22 0 Hz
 GRAB23 0 Hz
 GRAB24 0 Hz
 GRAB25 0 Hz
 GRAB26 0 Hz
 GRAB27 0 Hz
 GRAB28 0 Hz
 GRAB29 0 Hz
 GRAB30 0 Hz
 GRAB31 0 Hz
 GRAB32 0 Hz
 GRAB33 0 Hz
 GRAB34 0 Hz
 GRAB35 0 Hz
 GRAB36 0 Hz
 GRAB37 0 Hz
 GRAB38 0 Hz
 GRAB39 0 Hz
 GRAB40 0 Hz
 GRAB41 0 Hz
 GRAB42 0 Hz
 GRAB43 0 Hz
 GRAB44 0 Hz
 GRAB45 0 Hz
 GRAB46 0 Hz
 GRAB47 0 Hz
 GRAB48 0 Hz
 GRAB49 0 Hz
 GRAB50 0 Hz
 GRAB51 0 Hz
 GRAB52 0 Hz
 GRAB53 0 Hz
 GRAB54 0 Hz
 GRAB55 0 Hz
 GRAB56 0 Hz
 GRAB57 0 Hz
 GRAB58 0 Hz
 GRAB59 0 Hz
 GRAB60 0 Hz
 GRAB61 0 Hz
 GRAB62 0 Hz
 GRAB63 0 Hz
 GRAB64 0 Hz
 GRAB65 0 Hz
 GRAB66 0 Hz
 GRAB67 0 Hz
 GRAB68 0 Hz
 GRAB69 0 Hz
 GRAB70 0 Hz
 GRAB71 0 Hz
 GRAB72 0 Hz
 GRAB73 0 Hz
 GRAB74 0 Hz
 GRAB75 0 Hz
 GRAB76 0 Hz
 GRAB77 0 Hz
 GRAB78 0 Hz
 GRAB79 0 Hz
 GRAB80 0 Hz
 GRAB81 0 Hz
 GRAB82 0 Hz
 GRAB83 0 Hz
 GRAB84 0 Hz
 GRAB85 0 Hz
 GRAB86 0 Hz
 GRAB87 0 Hz
 GRAB88 0 Hz
 GRAB89 0 Hz
 GRAB90 0 Hz
 GRAB91 0 Hz
 GRAB92 0 Hz
 GRAB93 0 Hz
 GRAB94 0 Hz
 GRAB95 0 Hz
 GRAB96 0 Hz
 GRAB97 0 Hz
 GRAB98 0 Hz
 GRAB99 0 Hz
 GRAB100 0 Hz

Processing parameters
 SI 32768
 SF 500.1362500 MHz
 WCN 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

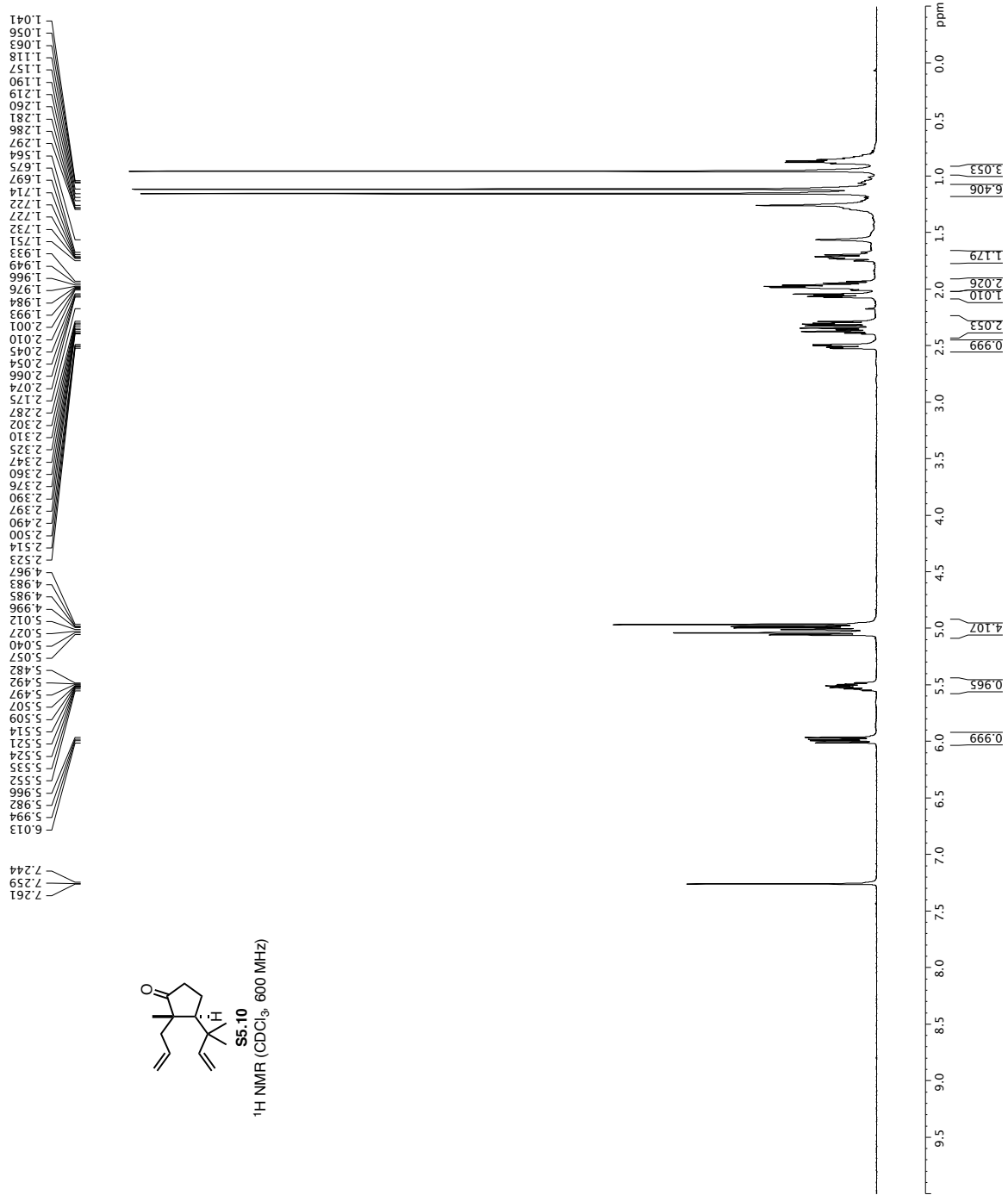
1H spectrum



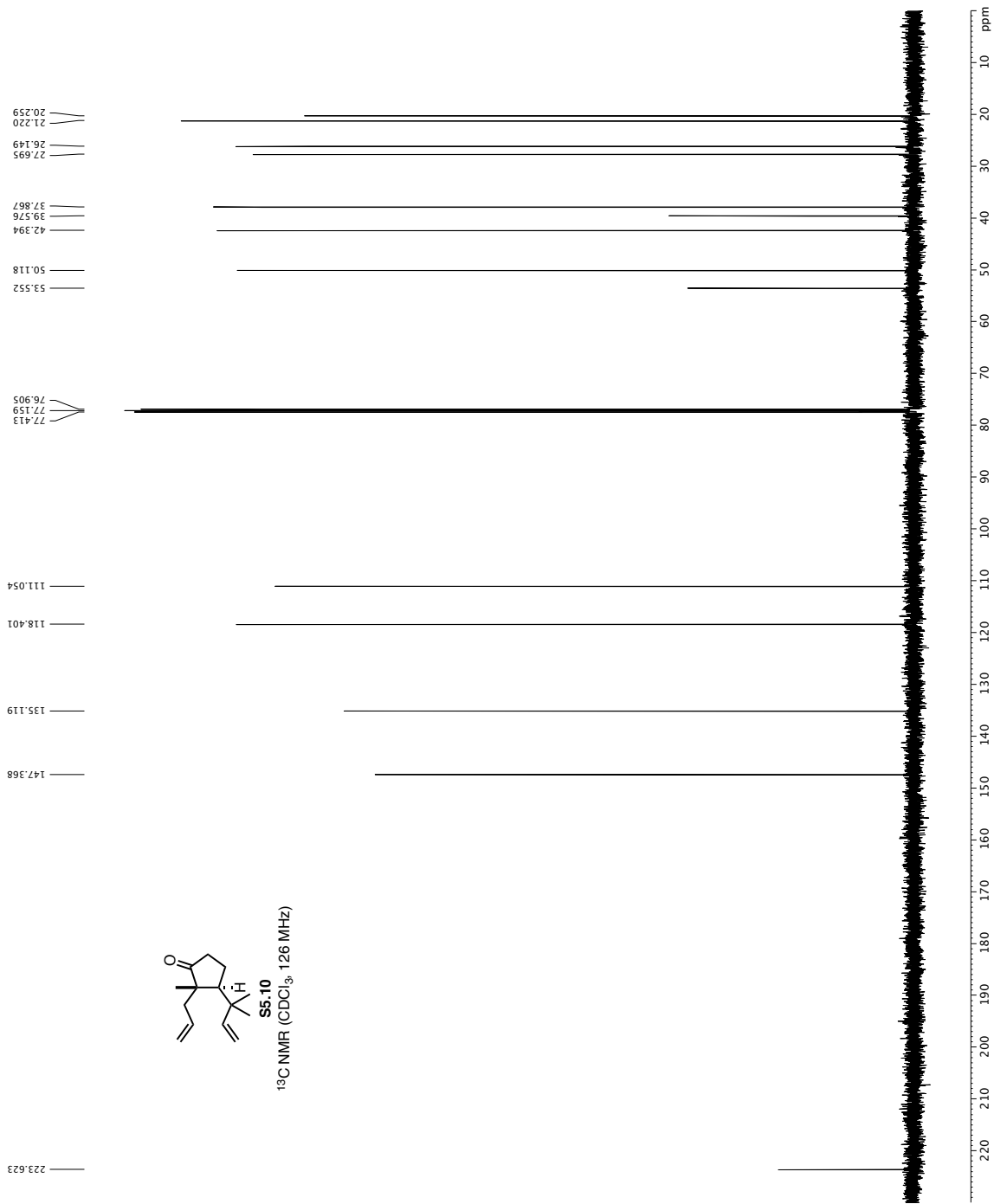
S5.10
¹H NMR (CDCl₃, 600 MHz)

```

Current Data Parameters
NAME      DJI-II-297
PROCNO    1
=====
F2 - Acquisition Parameters
Date_     25.02.20
Time      15.02
INSTRUM   av600
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
DS         0
SWH        9613.385 Hz
AQ         0.0377488 sec
RG         406
RC         12.000 usec
DE         298.1 K
TE         0.10000000 sec
TD0        1
=====
CHANNEL F1
NUC1       600.132009 MHz
P1         8.00 usec
PLW1       23.01441956 W
=====
F2 - Processing parameters
SI         65536
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```



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

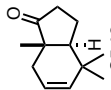


```
Current Data Parameters
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150108
INSTRUM spect
PROBHD 5 mm CPTCL1H-
TD 65536
SOLVENT CDCl3
NS 142
DS 4
SWH 30303.031 Hz
FIDRES 0.462288 Hz
RG 10321.3
AQ 0.0200000 sec
RG 10321.3
TE 298.0 K
D1 0.25000000 sec
d11 0.00000000 sec
d16 0.00020000 sec
d17 0.00019600 sec
MCWST 0.0001500000 sec
MCWRK 33.10 usec
===== CHANNEL f1 =====
NUC1 13C
P1 16.55 usec
PL1 2000.00 usec
PL2 2000.00 usec
PL0 120.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SPNAM11 Crp60.0.52.0.1
SPNAM2 Crp60.comp.4
SFO2 0.00000000 Hz
SFOFF2 0.00000000 Hz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 24.50 dB
SFO2 500.2225011 MHz
===== GRADIENT CHANNEL =====
GPNAM11 SINE100
GPNAM2 SINE100
GPA1 0.00000000 %
GPA2 0.00000000 %
GPA3 0.00000000 %
GPA4 0.00000000 %
GPA5 0.00000000 %
GPA6 0.00000000 %
GPA7 0.00000000 %
GPA8 0.00000000 %
GPA9 0.00000000 %
GPA10 0.00000000 %
GPA11 0.00000000 %
GPA12 0.00000000 %
GPA13 0.00000000 %
GPA14 0.00000000 %
GPA15 0.00000000 %
GPA16 0.00000000 %
F2 - Processing parameters
SI 65536
SF 125.7804090 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
```

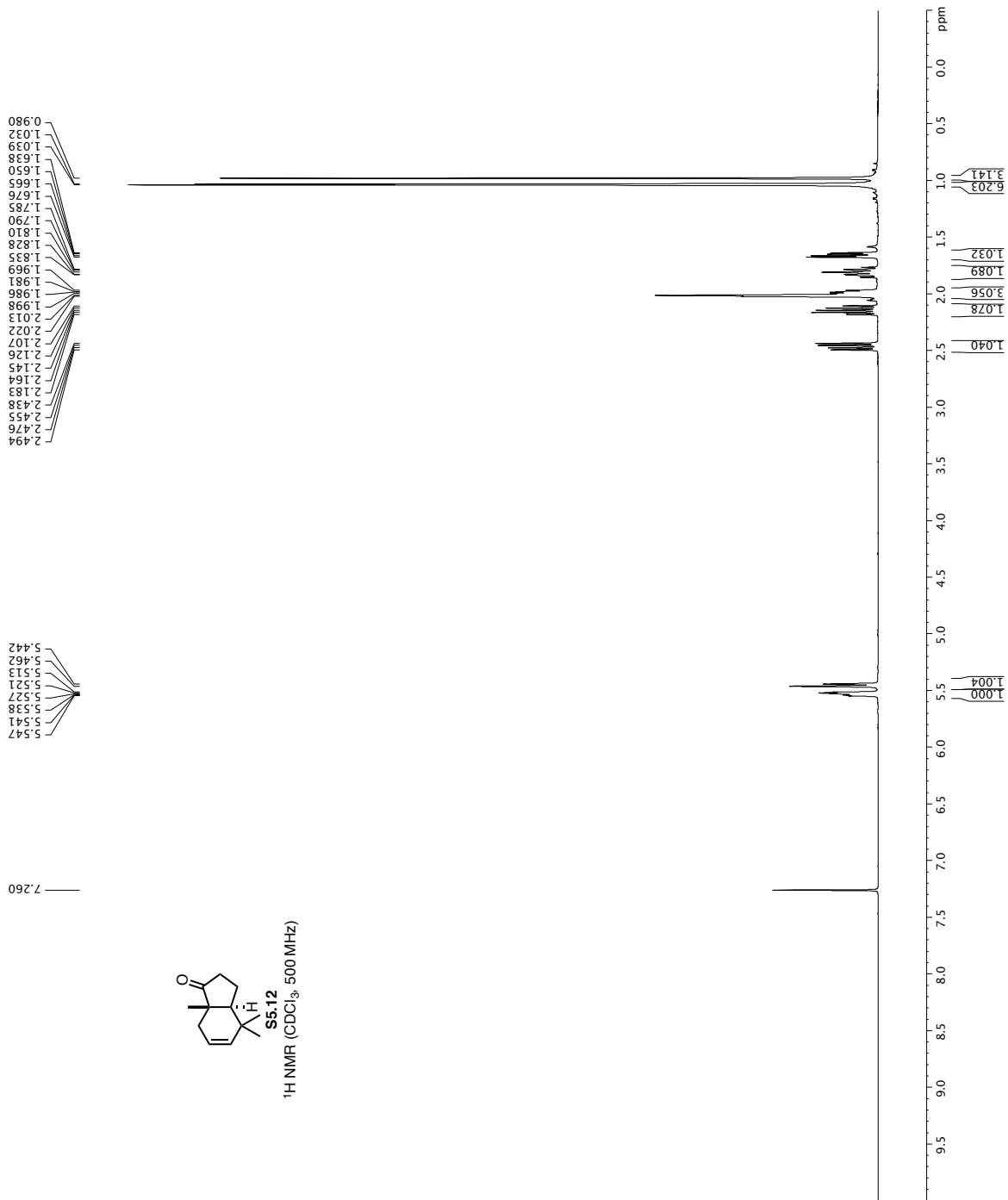
¹H spectrum

```

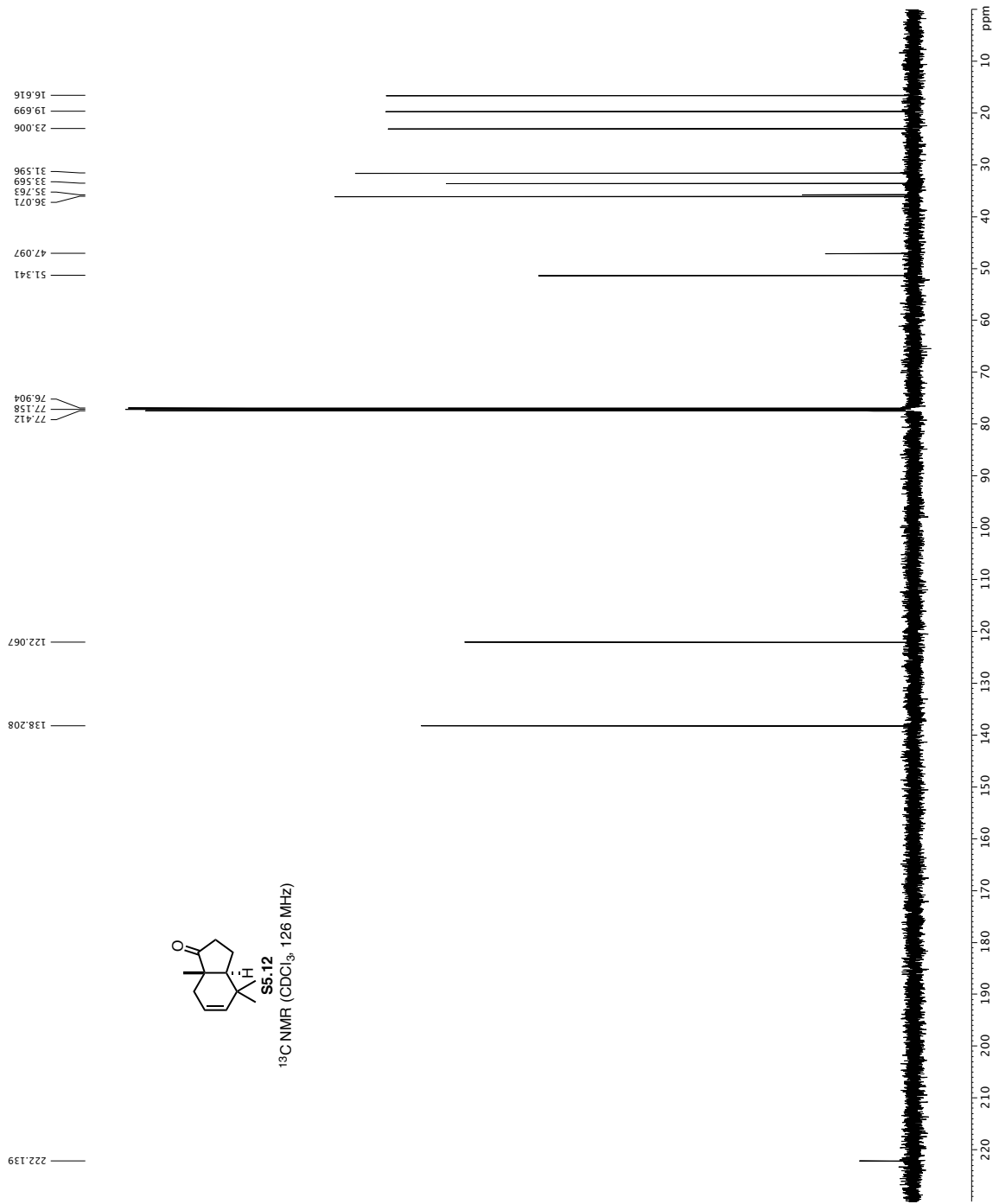
Current Data Parameters
NAME      DJT-IV-294
EXPNO    1
PROCNO   5
F2 - Acquisition Parameters
Date_    20110108
Time     11.11
INSTRUM  spect
PROBHD   5 mm CP1CI 1H-
PULPROG  zgpg30
SOLVENT  CDCl3
NS       30
DS       4
SWH      8012.820 Hz
FIDRES   0.250026 Hz
AQ       1.9997952 sec
RG       655.36
DE       62.400 usec
TE       300.2
D1       0.10000000 sec
MCREST   0 sec
MCWRK    0.01500000 sec
===== CHANNEL f1 =====
NUC1      1H
P1       12.00 usec
PL1      0.00 dB
SFO1     500.2233015 MHz
F2 - Processing parameters
SI       655.36
SF       500.2200317 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       4.00
    
```



¹H NMR (CDCl₃, 500 MHz)



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



```
Current Data Parameters
NAME DJT-IV-294
PROCNO 4
F2 - Acquisition Parameters
Date_ 21.03.08
Time 15:02
INSTRUM spect
PROBHD 5mm cryo500
PULPROG zgpg30
SFO1 125.764548 MHz
TD 65536
FIDRES 0.04633883 Hz
AQ 1.0813440 sec
RG 798.70
DE 6.00 usec
TE 298.0 K
D11 0.03000000 sec
D16 0.00020000 sec
DELTA 0.00196000 sec
MCKREST 0 sec
MCWRK 0.01500000 sec
PZ 33.10 usec

===== CHANNEL F1 =====
NUC1 13C
P1 16.15 usec
PL1 500.00 usec
P12 2000.00 usec
PL2 -1.00 dB
PL1 -1.00 dB
SFO1 125.764548 MHz
SPNAM1 Cp600.520.1
SPNAM2 Cp600comp.4
SFOF1 0 Hz
SFOF2 0 Hz

===== CHANNEL F2 =====
CPDPRG2 waltz16
NUC2 13C
PCPD2 100.00 usec
PL2 1.60 dB
PL1 2.50 dB
SFO2 500.225011 MHz

===== GRADIENT CHANNEL =====
GPMAX1 0 %
GPMAX2 0 %
SINE 100
GPI1 0 %
GPI2 0 %
GPI3 0 %
GPI4 0 %
GPI5 0 %
GPI6 0 %
GPI7 0 %
GPI8 0 %
GPI9 0 %
GPI10 0 %
GPI11 0 %
GPI12 0 %
GPI13 0 %
GPI14 0 %
GPI15 0 %
GPI16 0 %
GPI17 0 %
GPI18 0 %
GPI19 0 %
GPI20 0 %
GPI21 0 %
GPI22 0 %
GPI23 0 %
GPI24 0 %
GPI25 0 %
GPI26 0 %
GPI27 0 %
GPI28 0 %
GPI29 0 %
GPI30 0 %
GPI31 0 %
GPI32 0 %
GPI33 0 %
GPI34 0 %
GPI35 0 %
GPI36 0 %
GPI37 0 %
GPI38 0 %
GPI39 0 %
GPI40 0 %
GPI41 0 %
GPI42 0 %
GPI43 0 %
GPI44 0 %
GPI45 0 %
GPI46 0 %
GPI47 0 %
GPI48 0 %
GPI49 0 %
GPI50 0 %
GPI51 0 %
GPI52 0 %
GPI53 0 %
GPI54 0 %
GPI55 0 %
GPI56 0 %
GPI57 0 %
GPI58 0 %
GPI59 0 %
GPI60 0 %
GPI61 0 %
GPI62 0 %
GPI63 0 %
GPI64 0 %
GPI65 0 %
GPI66 0 %
GPI67 0 %
GPI68 0 %
GPI69 0 %
GPI70 0 %
GPI71 0 %
GPI72 0 %
GPI73 0 %
GPI74 0 %
GPI75 0 %
GPI76 0 %
GPI77 0 %
GPI78 0 %
GPI79 0 %
GPI80 0 %
GPI81 0 %
GPI82 0 %
GPI83 0 %
GPI84 0 %
GPI85 0 %
GPI86 0 %
GPI87 0 %
GPI88 0 %
GPI89 0 %
GPI90 0 %
GPI91 0 %
GPI92 0 %
GPI93 0 %
GPI94 0 %
GPI95 0 %
GPI96 0 %
GPI97 0 %
GPI98 0 %
GPI99 0 %
GPI100 0 %
F2 - Processing parameters
SI 65536
SF 125.764548 MHz
WDW EM
SSB 0
GB 0
PC 2.00
```

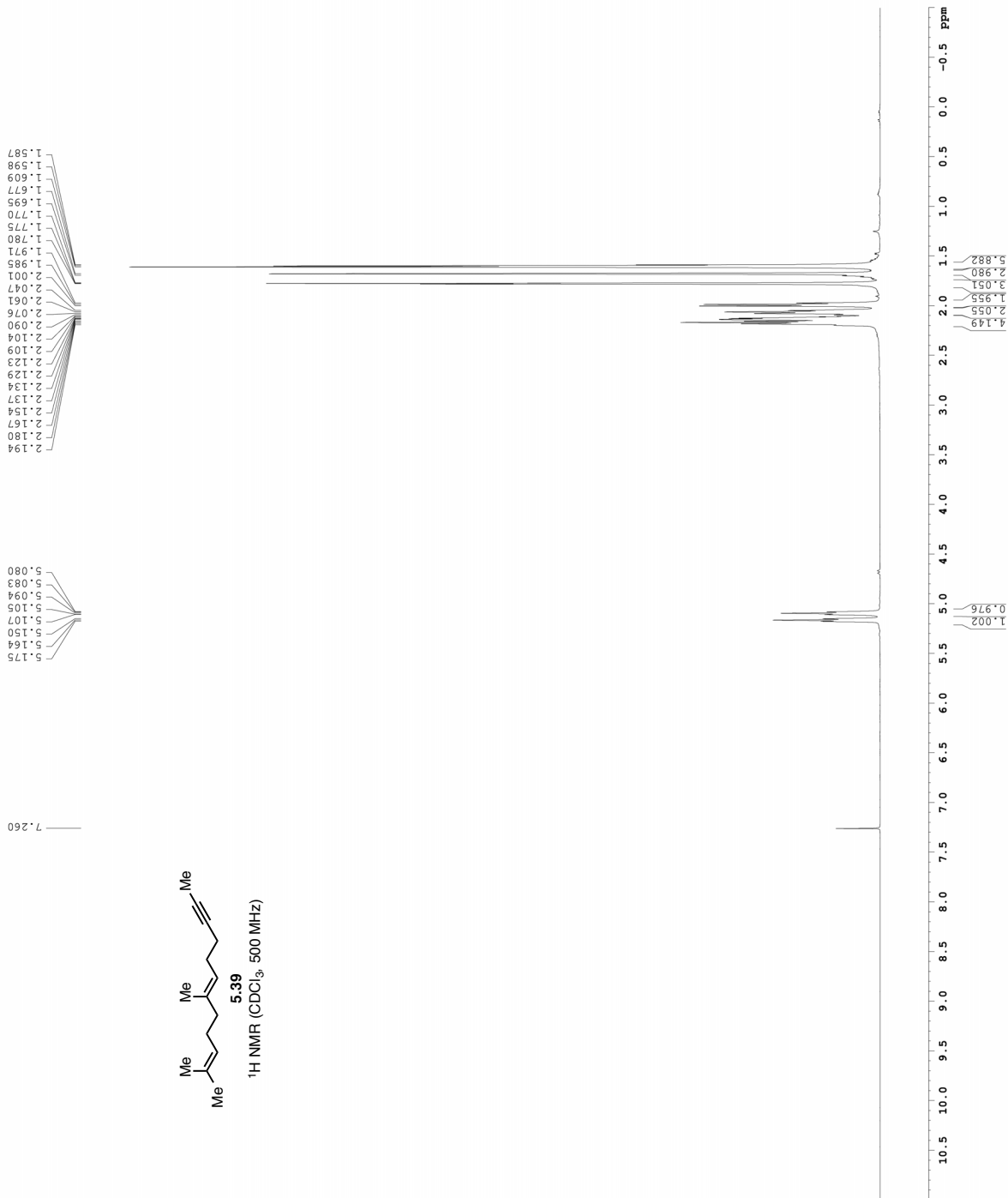
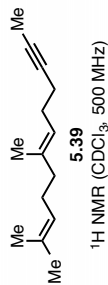

DJT-III-113

Current Data Parameters
NAME DJT-III-113
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110518
Time 15:18
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
TDPRG 8128
SOLVENT CDCl3
NS 12
DS 1
SWH 8012.820 Hz
FIDRES 0.096643 Hz
AQ 0.0800000 sec
RG 3.0996273 sec
DM 62.400 usec
DE 9.00 usec
D1 0.10000000 sec
MCREST 0 sec
MCRRK 0.01500000 sec
***** CHANNEL f1 *****
NUC1 1H
P1 7.00 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

2.194
2.180
2.167
2.154
2.137
2.134
2.129
2.123
2.109
2.104
2.090
2.076
2.061
2.047
1.985
1.971
1.780
1.770
1.770
1.695
1.677
1.609
1.598
1.587

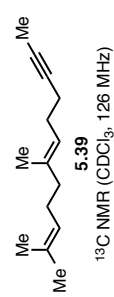
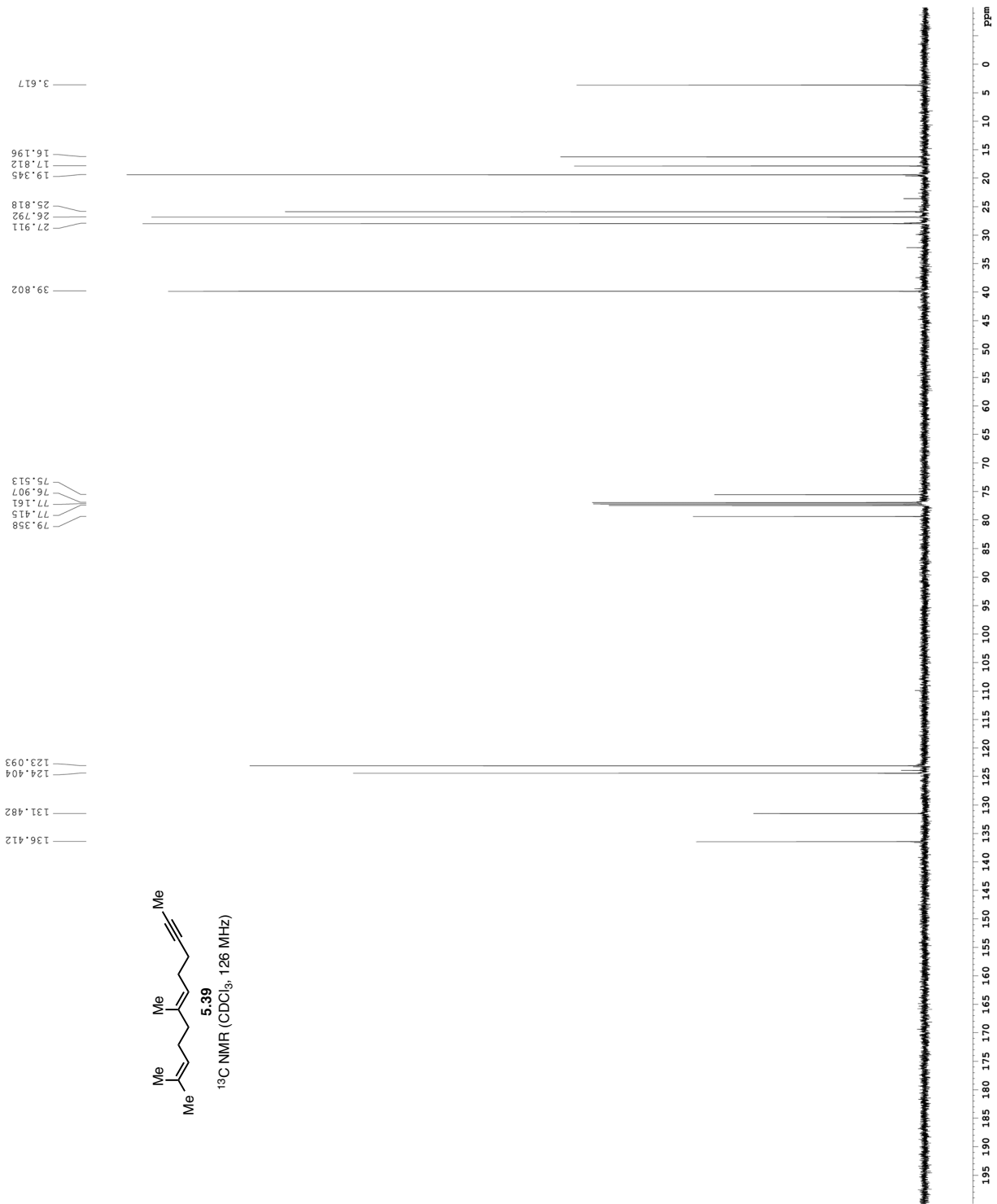
5.175
5.164
5.150
5.107
5.094
5.083
5.080

7.260



DJT-III-113

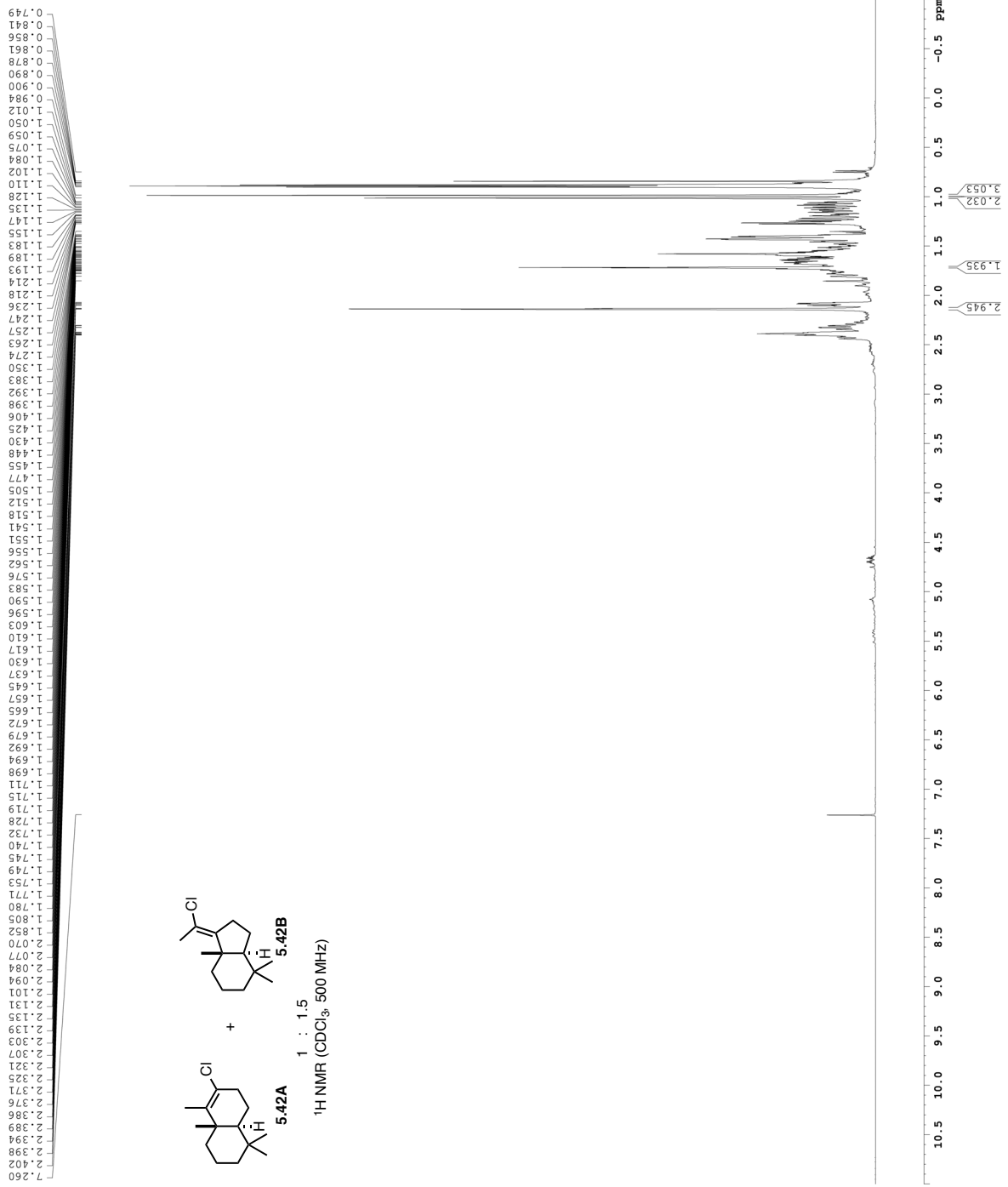
Current Data Parameters
NAME DJT-III-113
PROCNO 6
F2 - Acquisition Parameters
Time 2015.22
INSTRUM spect
PULPROG zgpg30
SOLVENT CDCl3
NS 143
SRH 30300.031 Hz
FIDRES 0.462288 Hz
AQ 1.16049 sec
RG 16.500 usec
DM 16.500 usec
TE 298.0 K
D1 0.25000000 sec
D11 0.00000000 sec
D16 0.00000000 sec
MCOREST 0 sec
MCORRK 0.01500000 sec
F2 31.00 usec
===== CHANNEL f1 =====
P1C1 15.50 usec
P11 500.00 usec
PL1 120.00 dB
PL2 120.00 dB
PL3 120.00 dB
PL4 120.00 dB
PL5 120.00 dB
PL6 120.00 dB
PL7 120.00 dB
PL8 120.00 dB
PL9 120.00 dB
PL10 120.00 dB
PL11 120.00 dB
PL12 120.00 dB
PL13 120.00 dB
PL14 120.00 dB
PL15 120.00 dB
PL16 120.00 dB
PL17 120.00 dB
PL18 120.00 dB
PL19 120.00 dB
PL20 120.00 dB
PL21 120.00 dB
PL22 120.00 dB
PL23 120.00 dB
PL24 120.00 dB
PL25 120.00 dB
PL26 120.00 dB
PL27 120.00 dB
PL28 120.00 dB
PL29 120.00 dB
PL30 120.00 dB
PL31 120.00 dB
PL32 120.00 dB
PL33 120.00 dB
PL34 120.00 dB
PL35 120.00 dB
PL36 120.00 dB
PL37 120.00 dB
PL38 120.00 dB
PL39 120.00 dB
PL40 120.00 dB
PL41 120.00 dB
PL42 120.00 dB
PL43 120.00 dB
PL44 120.00 dB
PL45 120.00 dB
PL46 120.00 dB
PL47 120.00 dB
PL48 120.00 dB
PL49 120.00 dB
PL50 120.00 dB
PL51 120.00 dB
PL52 120.00 dB
PL53 120.00 dB
PL54 120.00 dB
PL55 120.00 dB
PL56 120.00 dB
PL57 120.00 dB
PL58 120.00 dB
PL59 120.00 dB
PL60 120.00 dB
PL61 120.00 dB
PL62 120.00 dB
PL63 120.00 dB
PL64 120.00 dB
PL65 120.00 dB
PL66 120.00 dB
PL67 120.00 dB
PL68 120.00 dB
PL69 120.00 dB
PL70 120.00 dB
PL71 120.00 dB
PL72 120.00 dB
PL73 120.00 dB
PL74 120.00 dB
PL75 120.00 dB
PL76 120.00 dB
PL77 120.00 dB
PL78 120.00 dB
PL79 120.00 dB
PL80 120.00 dB
PL81 120.00 dB
PL82 120.00 dB
PL83 120.00 dB
PL84 120.00 dB
PL85 120.00 dB
PL86 120.00 dB
PL87 120.00 dB
PL88 120.00 dB
PL89 120.00 dB
PL90 120.00 dB
PL91 120.00 dB
PL92 120.00 dB
PL93 120.00 dB
PL94 120.00 dB
PL95 120.00 dB
PL96 120.00 dB
PL97 120.00 dB
PL98 120.00 dB
PL99 120.00 dB
PL100 120.00 dB
===== CHANNEL f2 =====
NUC2 13C
P2C2 100.00 usec
P21 500.00 usec
PL2 120.00 dB
PL3 120.00 dB
PL4 120.00 dB
PL5 120.00 dB
PL6 120.00 dB
PL7 120.00 dB
PL8 120.00 dB
PL9 120.00 dB
PL10 120.00 dB
PL11 120.00 dB
PL12 120.00 dB
PL13 120.00 dB
PL14 120.00 dB
PL15 120.00 dB
PL16 120.00 dB
PL17 120.00 dB
PL18 120.00 dB
PL19 120.00 dB
PL20 120.00 dB
PL21 120.00 dB
PL22 120.00 dB
PL23 120.00 dB
PL24 120.00 dB
PL25 120.00 dB
PL26 120.00 dB
PL27 120.00 dB
PL28 120.00 dB
PL29 120.00 dB
PL30 120.00 dB
PL31 120.00 dB
PL32 120.00 dB
PL33 120.00 dB
PL34 120.00 dB
PL35 120.00 dB
PL36 120.00 dB
PL37 120.00 dB
PL38 120.00 dB
PL39 120.00 dB
PL40 120.00 dB
PL41 120.00 dB
PL42 120.00 dB
PL43 120.00 dB
PL44 120.00 dB
PL45 120.00 dB
PL46 120.00 dB
PL47 120.00 dB
PL48 120.00 dB
PL49 120.00 dB
PL50 120.00 dB
PL51 120.00 dB
PL52 120.00 dB
PL53 120.00 dB
PL54 120.00 dB
PL55 120.00 dB
PL56 120.00 dB
PL57 120.00 dB
PL58 120.00 dB
PL59 120.00 dB
PL60 120.00 dB
PL61 120.00 dB
PL62 120.00 dB
PL63 120.00 dB
PL64 120.00 dB
PL65 120.00 dB
PL66 120.00 dB
PL67 120.00 dB
PL68 120.00 dB
PL69 120.00 dB
PL70 120.00 dB
PL71 120.00 dB
PL72 120.00 dB
PL73 120.00 dB
PL74 120.00 dB
PL75 120.00 dB
PL76 120.00 dB
PL77 120.00 dB
PL78 120.00 dB
PL79 120.00 dB
PL80 120.00 dB
PL81 120.00 dB
PL82 120.00 dB
PL83 120.00 dB
PL84 120.00 dB
PL85 120.00 dB
PL86 120.00 dB
PL87 120.00 dB
PL88 120.00 dB
PL89 120.00 dB
PL90 120.00 dB
PL91 120.00 dB
PL92 120.00 dB
PL93 120.00 dB
PL94 120.00 dB
PL95 120.00 dB
PL96 120.00 dB
PL97 120.00 dB
PL98 120.00 dB
PL99 120.00 dB
PL100 120.00 dB
===== GRADIENT CHANNEL =====
GPNAM[1] GRADIENT CHANNEL
GPNAM[2] GRADIENT CHANNEL
GPP1 0 %
GPP2 0 %
GPP3 0 %
GPP4 0 %
GPP5 0 %
GPP6 0 %
GPP7 0 %
GPP8 0 %
GPP9 0 %
GPP10 0 %
GPP11 0 %
GPP12 0 %
GPP13 0 %
GPP14 0 %
GPP15 0 %
GPP16 0 %
GPP17 0 %
GPP18 0 %
GPP19 0 %
GPP20 0 %
GPP21 0 %
GPP22 0 %
GPP23 0 %
GPP24 0 %
GPP25 0 %
GPP26 0 %
GPP27 0 %
GPP28 0 %
GPP29 0 %
GPP30 0 %
GPP31 0 %
GPP32 0 %
GPP33 0 %
GPP34 0 %
GPP35 0 %
GPP36 0 %
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GPP38 0 %
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GPP79 0 %
GPP80 0 %
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GPP83 0 %
GPP84 0 %
GPP85 0 %
GPP86 0 %
GPP87 0 %
GPP88 0 %
GPP89 0 %
GPP90 0 %
GPP91 0 %
GPP92 0 %
GPP93 0 %
GPP94 0 %
GPP95 0 %
GPP96 0 %
GPP97 0 %
GPP98 0 %
GPP99 0 %
GPP100 0 %
===== Processing Parameters =====
SI 45336
SF 125.7604080 MHz
SFO 125.7604080 MHz
SSB 0
GB 0
PC 2.00



DJT-III-135

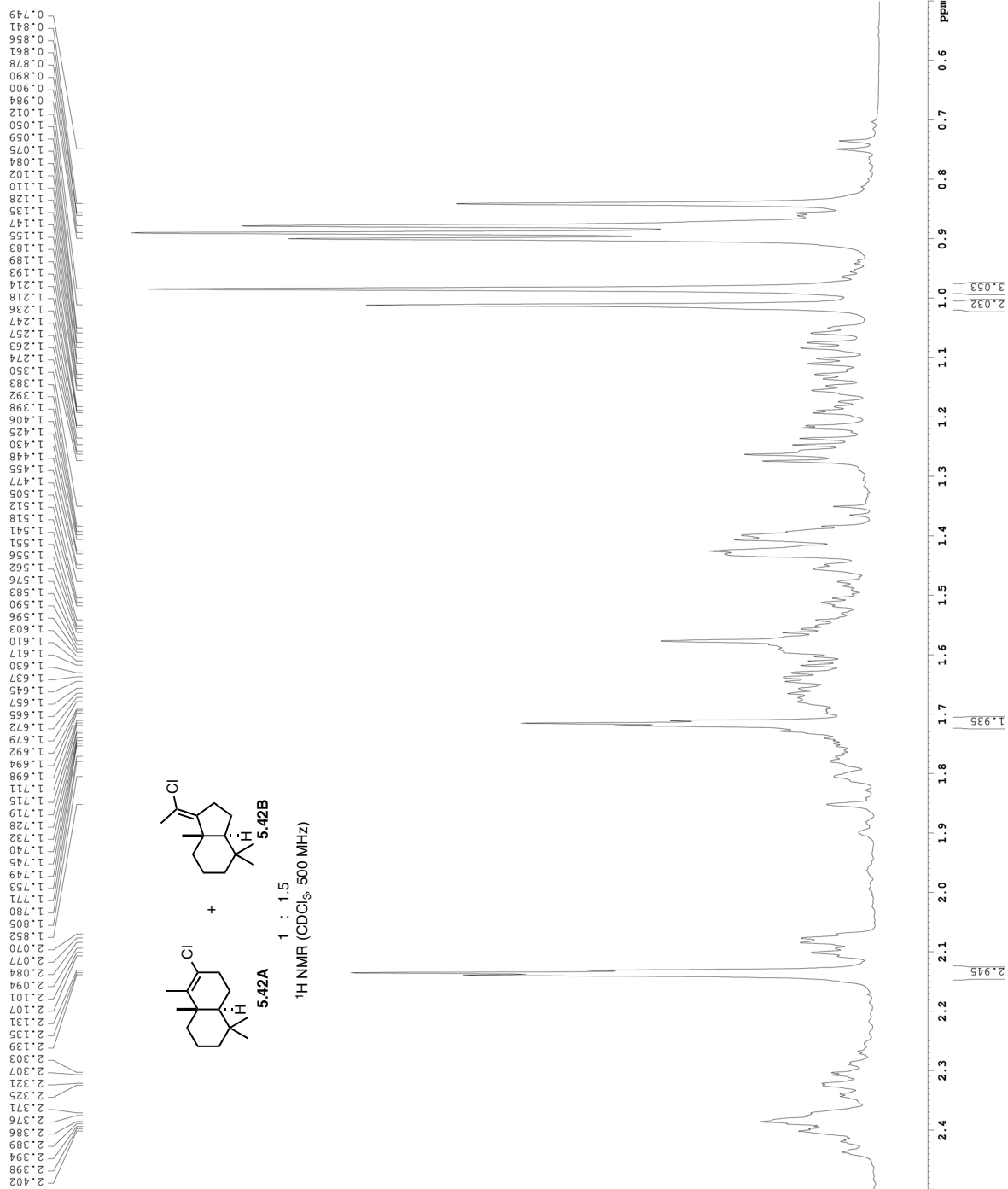
Current Data Parameters

NAME DJT-III-135
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Time 20111526
INSTRUM cryo500
PROBHD 5 mm CPXI 1H
TD 65536
SOLVENT CDCl3
NS 20
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 3.0398274 sec
RG 62.400 usec
DR 2.000 usec
DE 98.00 usec
DI 0.10000000 sec
MCREST 0 sec
PCPRGK 0.15000000 sec
===== CHANNEL f1 =====
NUC1 1H
PULPROG zgpg30
PL1 7.00 usec
PL12 1.60 dB
PL13 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

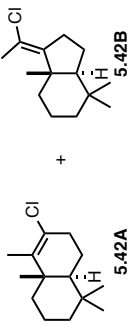
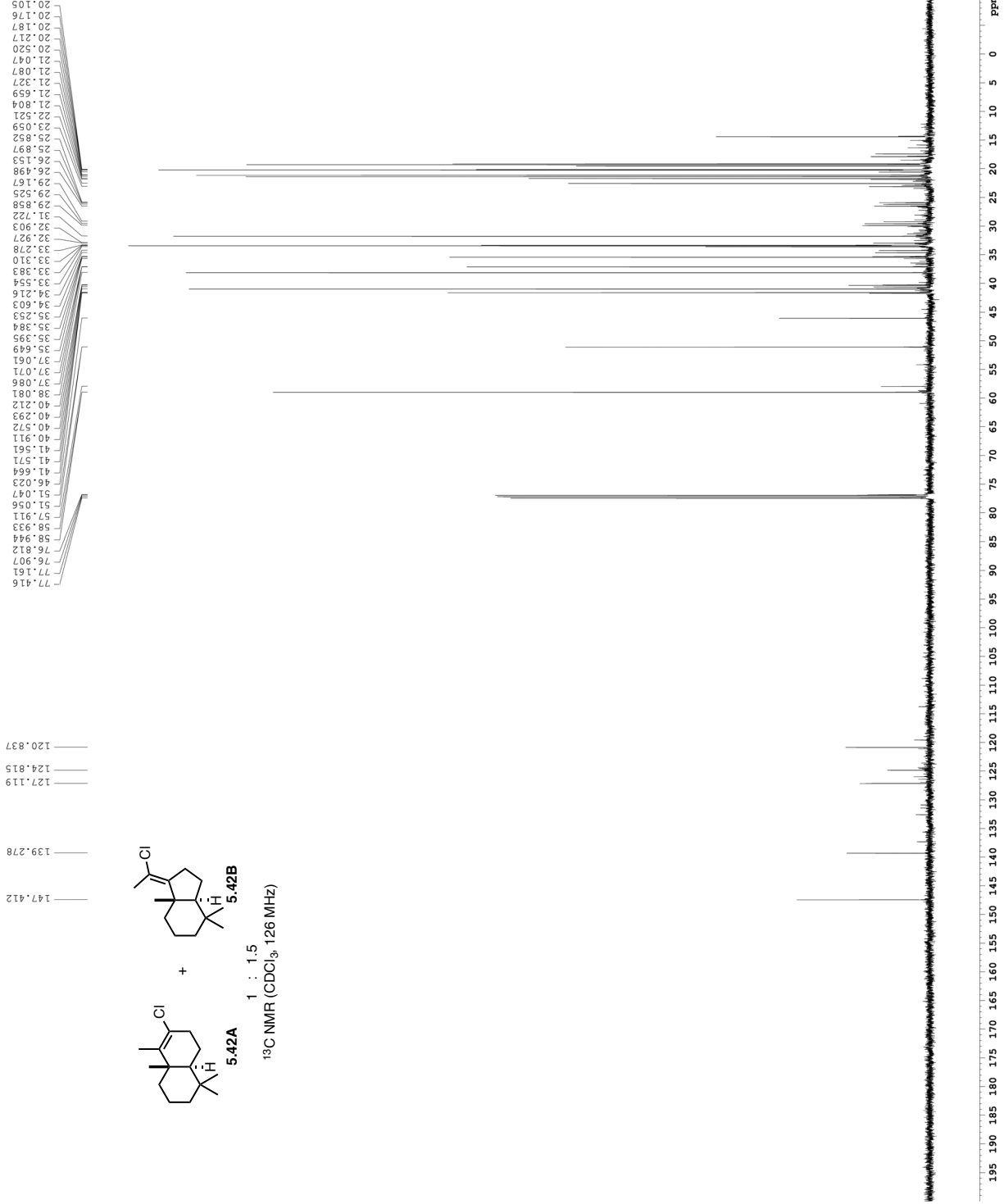


DJT-III-135

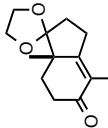
Current Data Parameters
NAME DJT-III-135
PROCNO 1
PROBHD 5 mm CPY500
Time 20111115.26
INSTRUM cpym500
PROBHD 5 mm CPY500
TDPROC 8128
SOLVENT CDCl3
NS 20
SRH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 3.0398274 sec
RG 4
DR 62.400 usec
DE 96.00 usec
D1 0.10000000 sec
MCREST 0 sec
PCWRRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H 7.18 usec
PUL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200306 MHz
SFX
SSB 0
LB 0.30 Hz
GB 0
PC 4.00



Percent Data Parameters
NAME DJT-III-135
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Time 20.11.33
INSTRUM s sm cryo500
PULPROG zgpg30
FUPROG Spinchoptop-prd
SOLVENT cdcl3
NS 317
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.026166 sec
RG 328.2
DM 16.500 usec
DE 2.000 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.05000000 sec
D16 0.00200000 sec
MCWEST 0
MCWEST 0.00019600 sec
MCWBK 0
MCWBK 0.01500000 sec
F2 31.00 usec
===== CHANNEL f1 =====
NUC1 13
P1 15.50 usec
PL1 500.00 usec
PC1 19.00 dB
PL2 220.00 usec
PL3 120.00 dB
PL4 120.00 dB
PL5 120.00 dB
PL6 120.00 dB
SFO 125.791420 MHz
SFO2 500.222911 MHz
===== CHANNEL f2 =====
NUC2 1H
P2 100.00 usec
PC2 19.00 dB
PL2 24.60 dB
PL3 24.60 dB
SFO2 500.222911 MHz
===== GRADIENT CHANNEL =====
GEMM1(1) SINE.100
GEMM1(2) SINE.100
GEMM2(1) SINE.100
GEMM2(2) SINE.100
GEX1 0 %
GEX2 0 %
GEX3 0 %
GEX4 0 %
GEX5 0 %
GEX6 0 %
GEX7 0 %
GEX8 0 %
GEX9 0 %
GEX10 0 %
GEX11 0 %
GEX12 0 %
GEX13 0 %
GEX14 0 %
GEX15 0 %
GEX16 0 %
GEX17 0 %
GEX18 0 %
GEX19 0 %
GEX20 0 %
GEX21 0 %
GEX22 0 %
GEX23 0 %
GEX24 0 %
GEX25 0 %
GEX26 0 %
GEX27 0 %
GEX28 0 %
GEX29 0 %
GEX30 0 %
GEX31 0 %
GEX32 0 %
GEX33 0 %
GEX34 0 %
GEX35 0 %
GEX36 0 %
GEX37 0 %
GEX38 0 %
GEX39 0 %
GEX40 0 %
GEX41 0 %
GEX42 0 %
GEX43 0 %
GEX44 0 %
GEX45 0 %
GEX46 0 %
GEX47 0 %
GEX48 0 %
GEX49 0 %
GEX50 0 %
GEX51 0 %
GEX52 0 %
GEX53 0 %
GEX54 0 %
GEX55 0 %
GEX56 0 %
GEX57 0 %
GEX58 0 %
GEX59 0 %
GEX60 0 %
GEX61 0 %
GEX62 0 %
GEX63 0 %
GEX64 0 %
GEX65 0 %
GEX66 0 %
GEX67 0 %
GEX68 0 %
GEX69 0 %
GEX70 0 %
GEX71 0 %
GEX72 0 %
GEX73 0 %
GEX74 0 %
GEX75 0 %
GEX76 0 %
GEX77 0 %
GEX78 0 %
GEX79 0 %
GEX80 0 %
GEX81 0 %
GEX82 0 %
GEX83 0 %
GEX84 0 %
GEX85 0 %
GEX86 0 %
GEX87 0 %
GEX88 0 %
GEX89 0 %
GEX90 0 %
GEX91 0 %
GEX92 0 %
GEX93 0 %
GEX94 0 %
GEX95 0 %
GEX96 0 %
GEX97 0 %
GEX98 0 %
GEX99 0 %
GEX100 0 %
===== Processing Parameters =====
SI 65336
SF 125.7804085 MHz
WDW EM
SSB 0
GB 1.00 Hz
PC 2.00

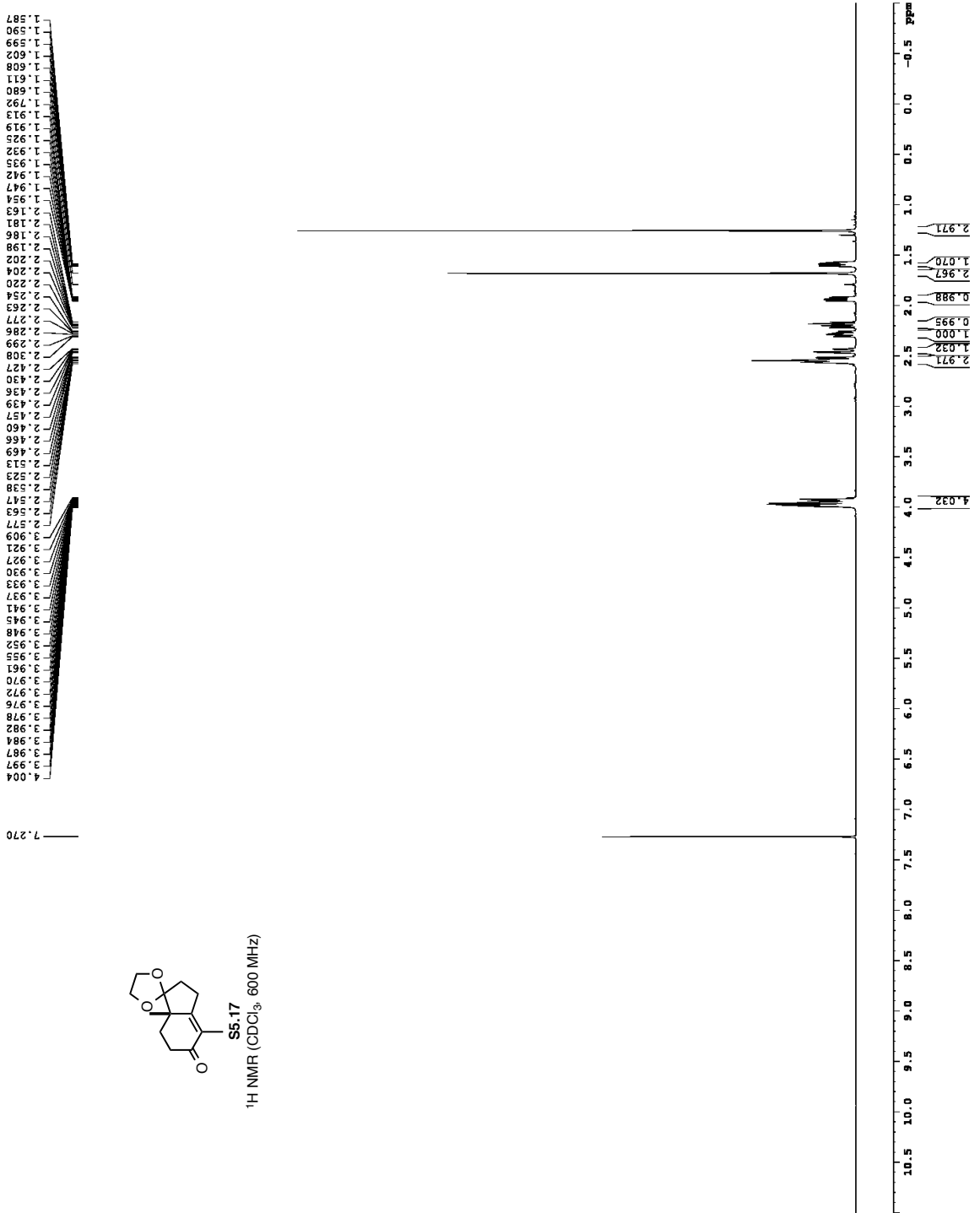


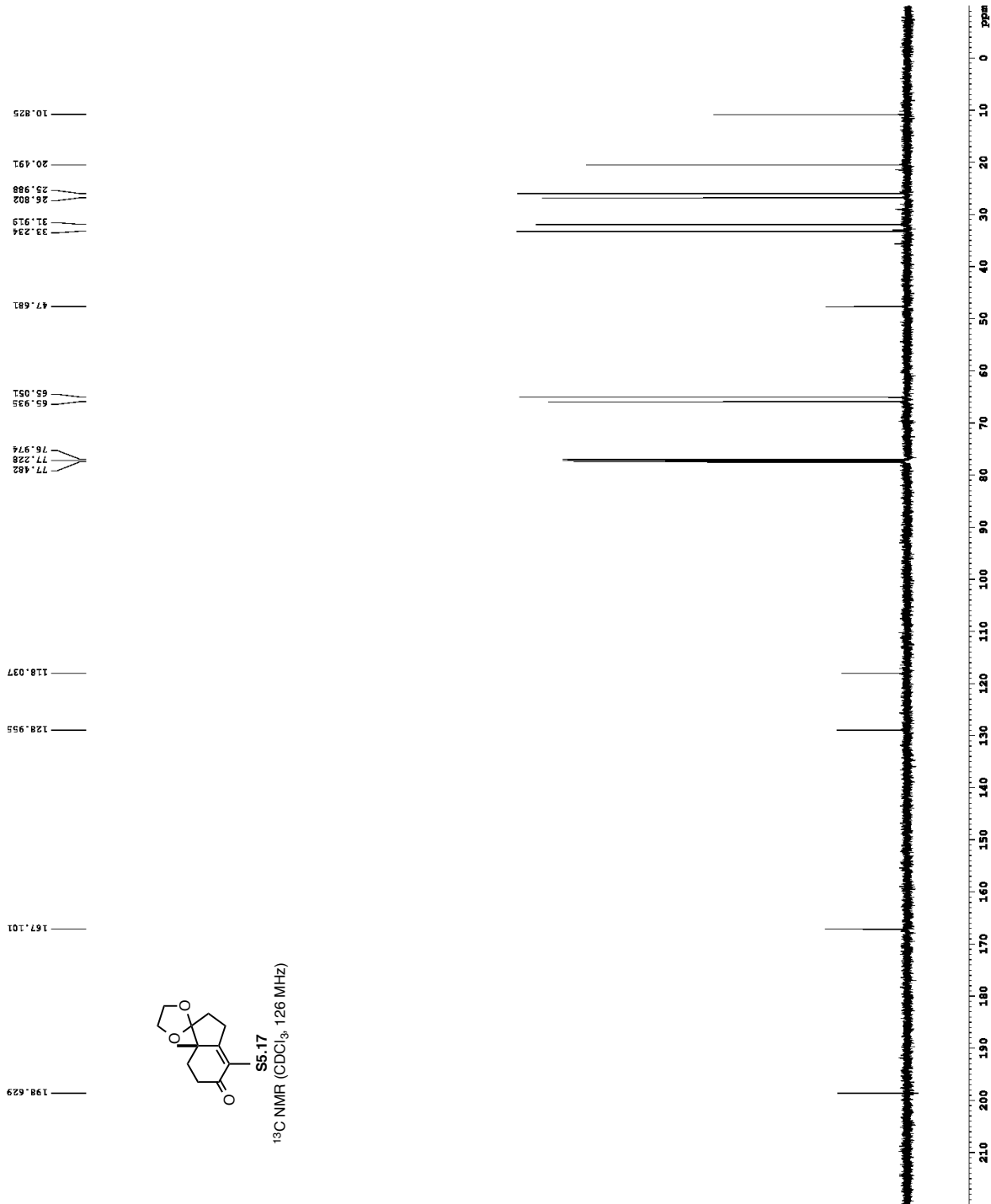
1 : 1.5
¹³C NMR (CDCl₃, 126 MHz)



S5.17
¹H NMR (CDCl₃, 600 MHz)

Current Data Parameters
 NAME S5.17
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 201309
 Time 11:50:50
 INSTRUM spect
 PULPROG zgpg30
 PROCES 2D
 FIDRES 0.1000000
 AQ 0.0000000
 SFO 600.1362009 MHz
 P1 24.0000000
 FWHM 24.0000000
 SFO 600.1362009 MHz
 P2 - Processing parameters
 SF 600.1362009 MHz
 DS 4
 SSF 0
 GB 0
 CB 0
 CC 0
 CD 0
 CE 0
 CF 0
 CG 0
 CH 0
 CI 0
 CJ 0
 CK 1.00





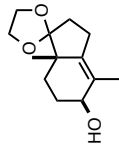
Current Data Parameters
 NAME YS-IV-18
 EXPNO 5
 F2PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151216
 Time 15.42
 INSTRUM cryo500
 PROBRD 5 mm CPYI 1H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 152
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.084288 sec
 RG 2896.3
 DW 16.500 usec
 DE 6.00 usec
 IE 288.0 K
 D1 0.25000000 sec
 D11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 F2 33.10 usec

CHANNEL f1
 NUC1 13C
 P1 16.35 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 125.7962500 dB
 SP1 2.70 dB
 SP2 2.70 dB
 SFNAM[1] Crp60,0.5,20.1
 SFNAM[2] Crp60comp.4
 SFOF1 0 Hz
 SFOF2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 2.50 dB
 SP2 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
 NDM EM
 SSB 0
 GB 1.00 Hz
 PC 0
 GC 2.00

YS-III-292

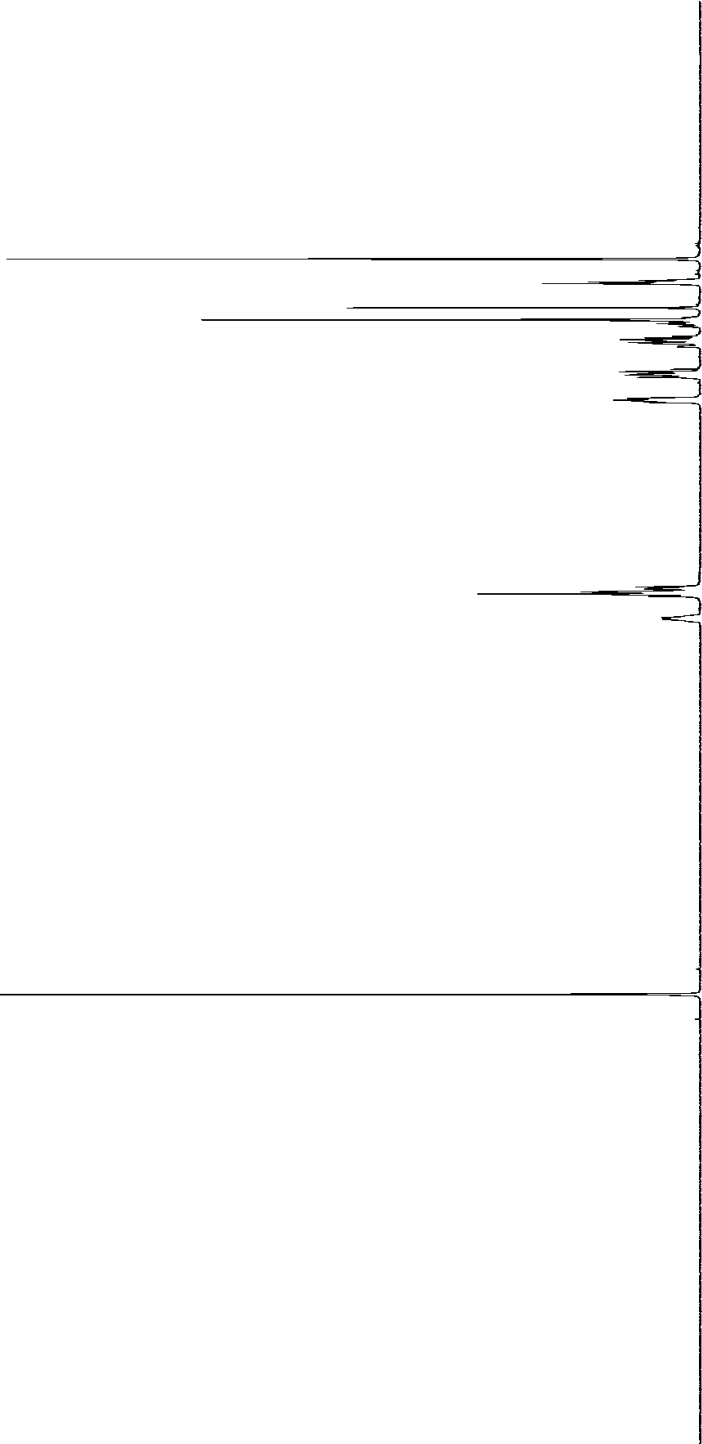


5.45
¹H NMR (CDCl₃, 500 MHz)

Concent Data Parameters
NAME YS-III-292
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ Acq 20041122
Time 11:52
PROBHD 5 mm CP NCT 1B
PULPROG zgpg30
SOLVENT CDCl3
DS 2
SMBUS 0.131625 Hz
AQ 1.599752 sec
DM 62.400 use
D1 28.00 use
D11 0.1005000 sec
D12 0.0150000 sec
NAME: CHANNEL f1
NUC1 ¹H
P1 1.00 use
PL1 1.20 dB
SFO1 500.235015 MHz
F2 - Processing parameters
WDW EM
SSP 500.235334 MHz
SFO 500.235015 MHz
GB 0
PC 4.00

4.139
4.125
3.957
3.948
3.938
3.934
3.928
3.919
3.915
3.909
3.905
3.888
3.880
3.869
3.857
2.331
2.315
2.300
2.126
2.120
2.113
2.106
2.099
2.087
2.079
2.058
1.871
1.865
1.836
1.821
1.822
1.810
1.796
1.784
1.705
1.698
1.686
1.679
1.647
1.625
1.540
1.532
1.519
1.512
1.411

7.260



10.5 10.0 9.5 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 ppm

3.000
1.995
4.009
2.031
2.012
2.000
0.936
0.921

Current Data Parameters
 NAME YS-IV-20
 EXPNO 4
 PROCNO 1

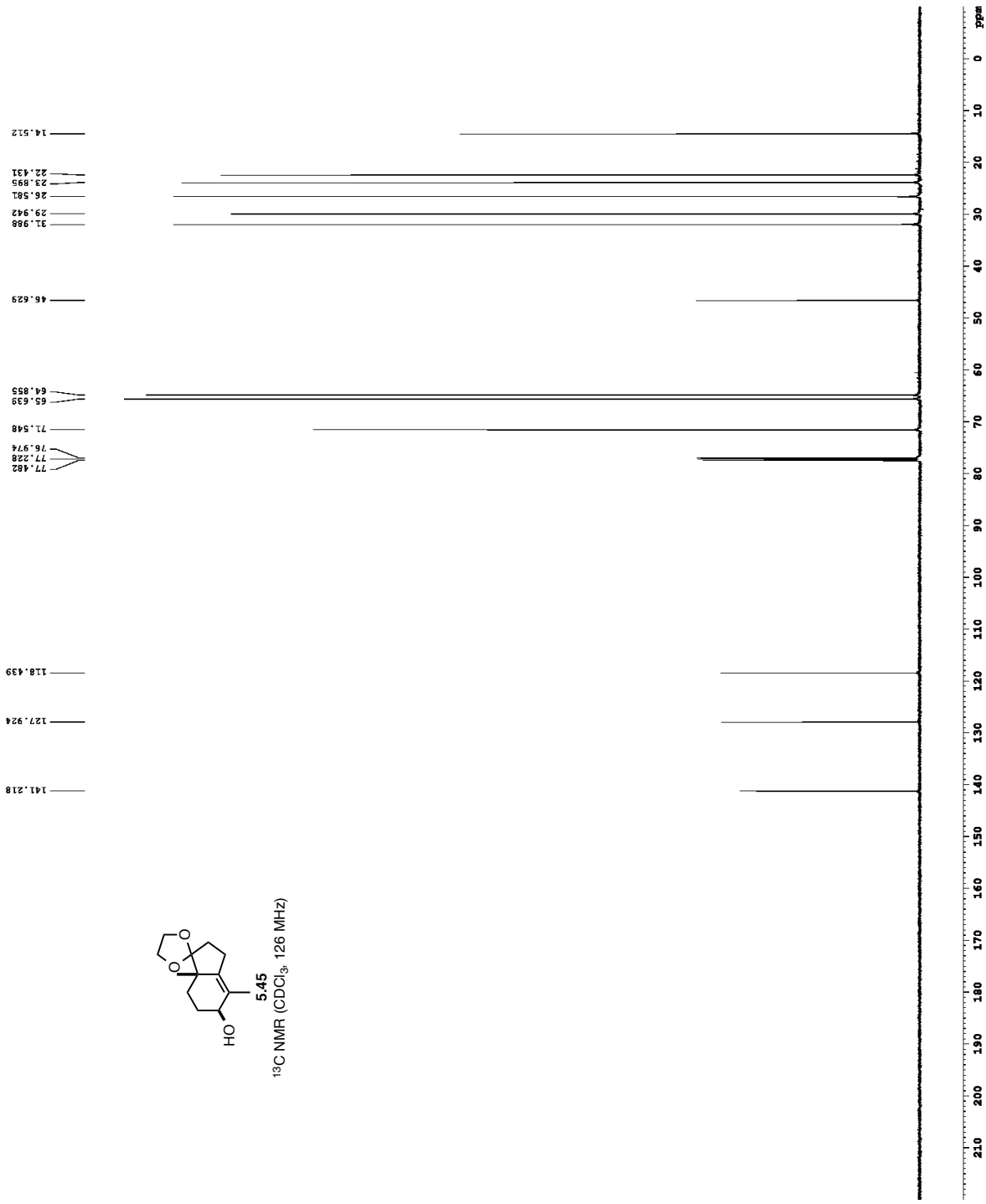
F2 - Acquisition Parameters
 Date_ 20151209
 Time 17.41
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 640
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.487244 Hz
 AQ 1.0813440 sec
 RG 7298.2
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 D11 0.0000000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 F2 33.10 usec

CHANNEL f1 13C
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P10 120.00 dB
 SFO1 125.764268 MHz
 SF2 125.764268 MHz
 SF1 125.764268 MHz
 SF2 125.764268 MHz
 SFOFF 0 Hz
 SFOFF2 0 Hz

CHANNEL f2 1H
 NUC2 1H
 P2 10.00 usec
 P21 100.00 usec
 P20 1.80 dB
 SFO2 500.136450 MHz
 SFOFF 0 Hz

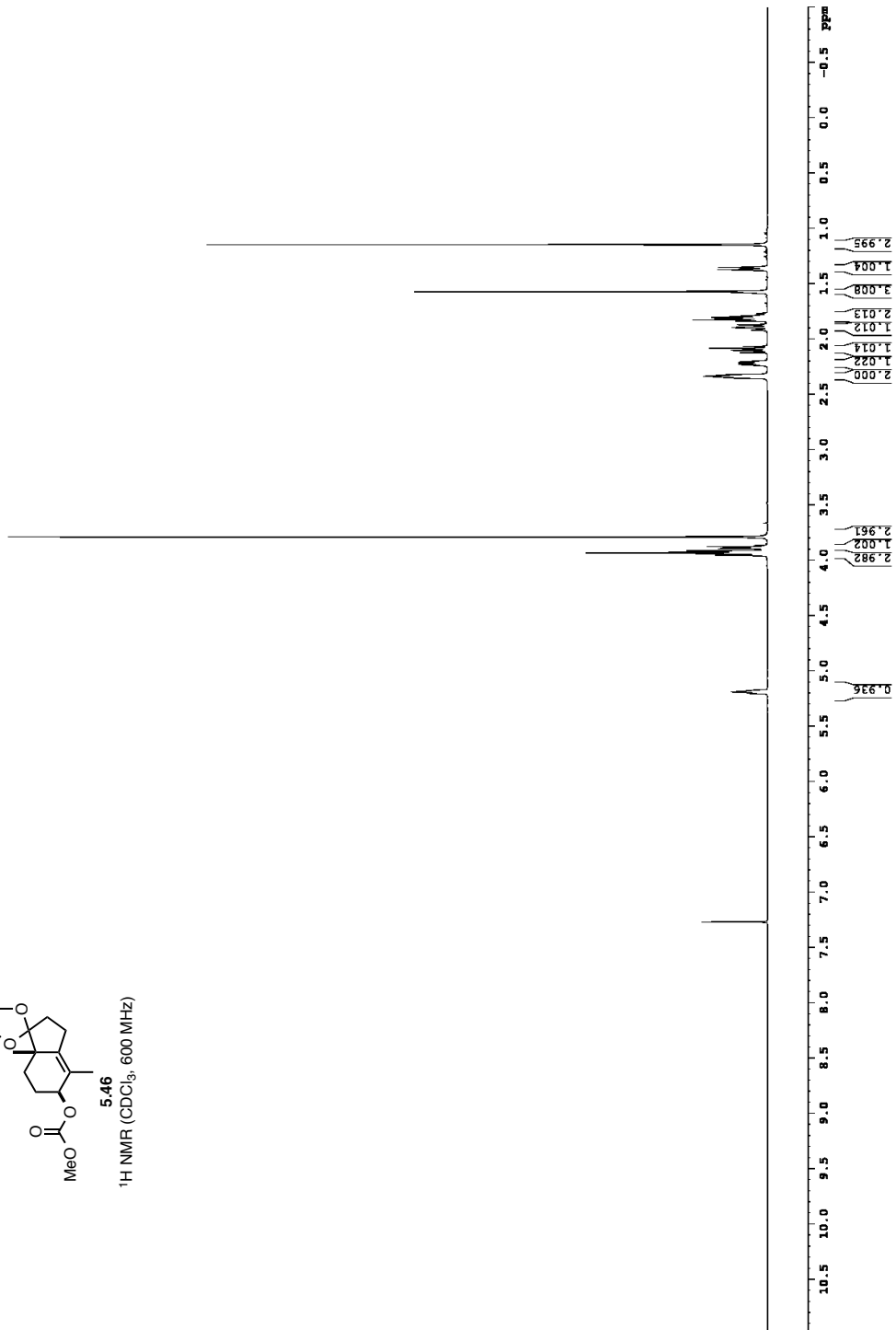
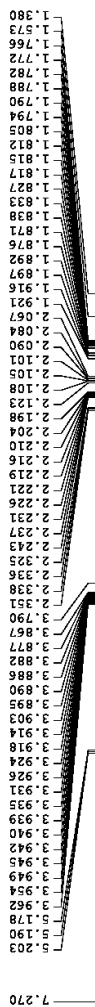
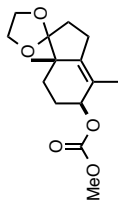
GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GZ1 30.00 %
 GZ2 50.00 %
 P15 500.00 usec
 P16 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7604059 MHz
 RM EM
 SSB 0
 GB 0
 GC 0
 PC 2.00



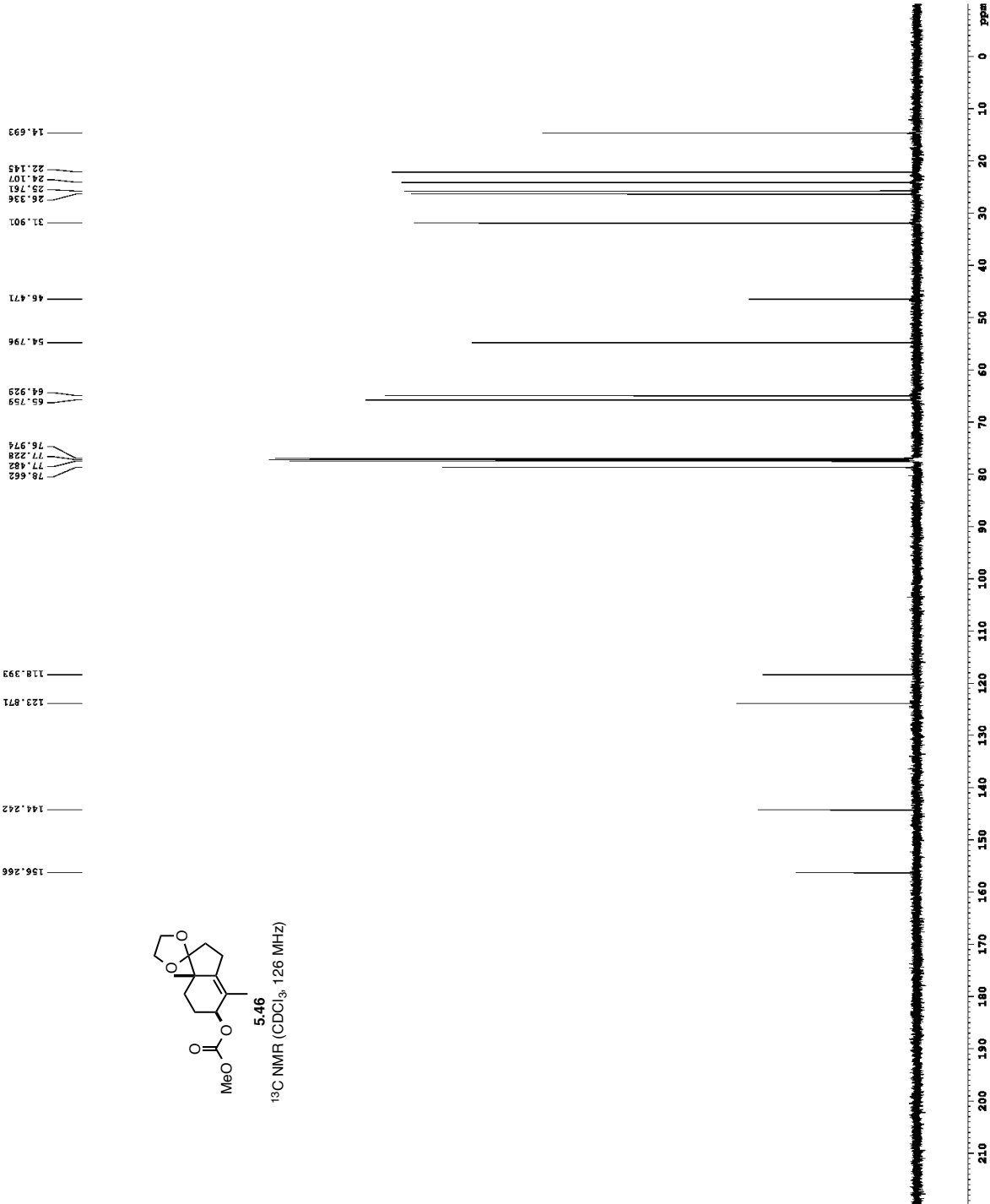
YS-III-293

Current Data Parameters
NAME YS-III-293
PROCNO 1
EXPNO 1
F2 - Acquisition Parameters
Date_ 20111117
Time 10:06:57
INSTRUM spect
PROBHD 5 mm TBI 13130
PULPROG zgpg30
TD 38400
SFO 400.136260
WDW EM
SS 4
RG 8
DE 1
AQ 0.100000000
FIDRES 0.000300000
AQC 1.000000000
RG 8
SOLVENT CDCl3
NS 4
DS 4
SWH 9615.385 Hz
F2 - Processing Parameters
Date_ 20111117
Time 10:06:57
INSTRUM spect
PROBHD 5 mm TBI 13130
PULPROG zgpg30
TD 38400
SFO 400.136260
WDW EM
SS 4
RG 8
DE 1
AQ 0.100000000
FIDRES 0.000300000
AQC 1.000000000
RG 8
SOLVENT CDCl3
NS 4
DS 4
SWH 9615.385 Hz
F2 - Processing Parameters
Date_ 20111117
Time 10:06:57
INSTRUM spect
PROBHD 5 mm TBI 13130
PULPROG zgpg30
TD 38400
SFO 400.136260
WDW EM
SS 4
RG 8
DE 1
AQ 0.100000000
FIDRES 0.000300000
AQC 1.000000000
RG 8
SOLVENT CDCl3
NS 4
DS 4
SWH 9615.385 Hz





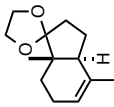
¹³C-NMR (CDCl₃, 126 MHz)



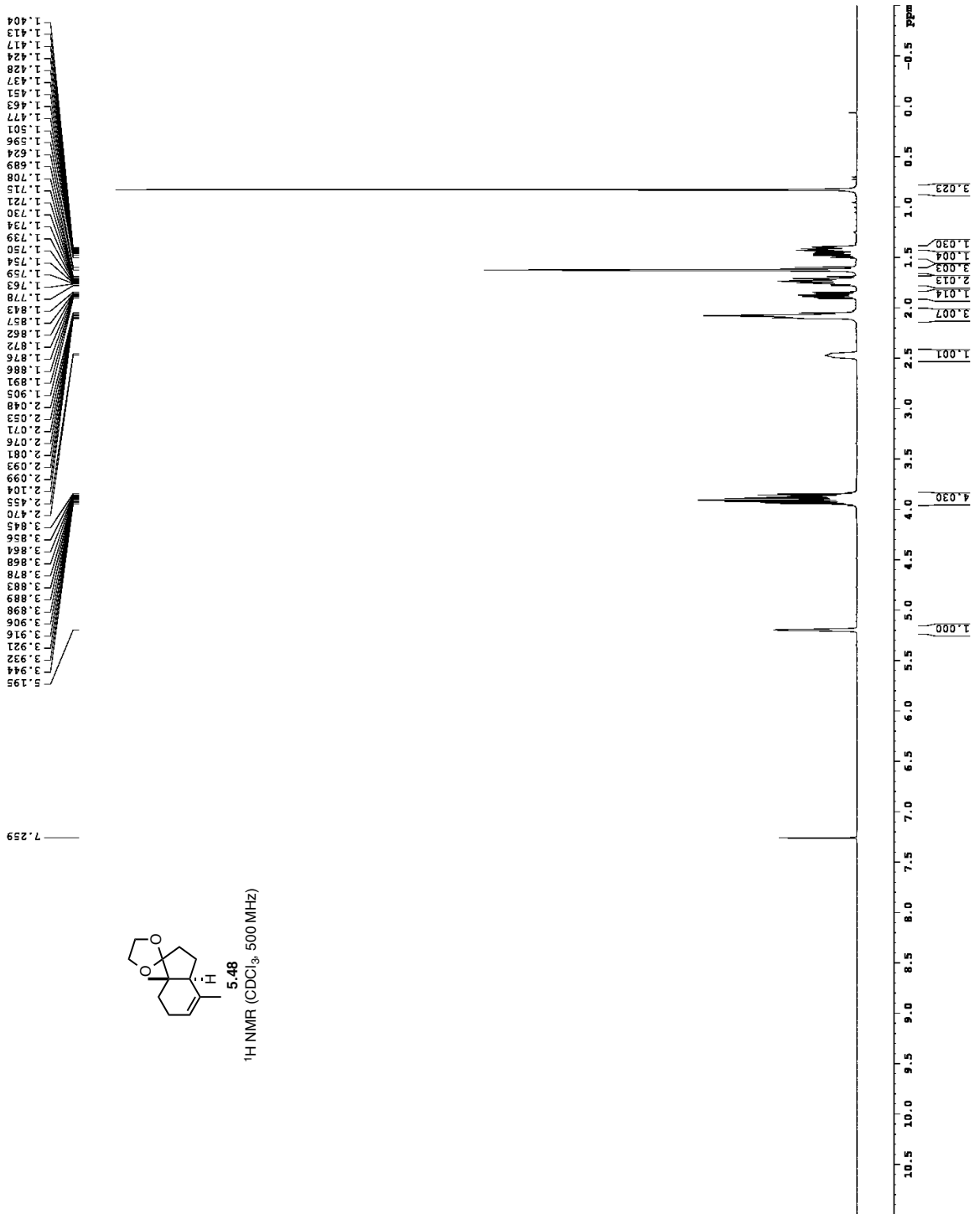
Current Data Parameters
 NAME XS-III-293
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151117
 Time 17.20
 INSTRUM cryo500
 PULPROG zgpg30
 PROCNO 5
 GAMMA 5 mm CPIC13.1K
 F2PRG0 SpinEchoes30.Prd
 TD 65536
 SOLVENT CDCl3
 NS 424
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.24278 Hz
 AQRES 1.081346 sec
 RG 5792.8
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 d11 0.0000000 sec
 d12 0.0000000 sec
 d16 0.0020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWEX 0.01500000 sec
 P2 33.10 usec
 CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P10 120.00 dB
 P11 120.00 dB
 SFO1 125.762549 MHz
 SFO2 2.70 dB
 SFO3 2.70 dB
 SPNAM[1] Crp60,0.5,20.1
 SPNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz
 CHANNEL f2
 CPDPRG12 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 2.00 dB
 SFO2 500.225011 MHz
 GRADIENT CHANNEL
 GPMAM[1] SINE.100
 GPMAM[2] SINE.100
 GPC1 0 %
 GPC2 0 %
 GPC3 0 %
 GPC4 0 %
 GPC5 0 %
 GPC6 30.00 %
 GPC7 50.00 %
 GPC8 500.00 usec
 P15 1000.00 usec
 F2 - Processing Parameters
 SI 65536
 SF 125.7804002 MHz
 MDW EM
 SSB 0
 GB 1.00 Hz
 GC 0
 PC 2.00

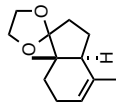
Current Data Parameters
 NAME YS-III-296
 PACNO 1
 F2 - Acquisition Parameters
 Date_ 2011119
 Time_ 11:18
 INSTRUM spect
 PULPROG zgpg30
 PROCNO 5
 ID 128272
 EXPTNO 1
 NS 4
 DS 4
 SWH 812.820 Hz
 FIDRES 0.088502 Hz
 AQ 7.2394623 sec
 RG 6.2
 DB 62.00 Hz
 UC 288.0 K
 UPR 0.100000 sec
 MCHRES 0 sec
 ACHRES 0.0150000 sec
 CHANNEL_ F1
 NUC1 1H
 P1 7.50 Hz
 PL1 500.2331015 MHz
 F2 - Processing Parameters
 SI 65516
 SF 500.2331015 MHz
 DS 4
 SSF 0
 GB 0
 CB 0
 PC 4.00

1.404
1.413
1.417
1.424
1.428
1.437
1.451
1.463
1.477
1.501
1.596
1.624
1.689
1.708
1.715
1.721
1.730
1.734
1.739
1.750
1.754
1.759
1.763
1.778
1.843
1.857
1.862
1.872
1.876
1.886
1.891
1.905
2.048
2.053
2.071
2.076
2.081
2.093
2.099
2.104
2.455
2.470
3.845
3.856
3.864
3.868
3.878
3.883
3.889
3.898
3.906
3.916
3.921
3.932
3.944
5.195



5.48
¹H NMR (CDCl₃, 500 MHz)





5.48
¹³C-NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME      YS-III-296
EXPNO    5
PROCNO   1

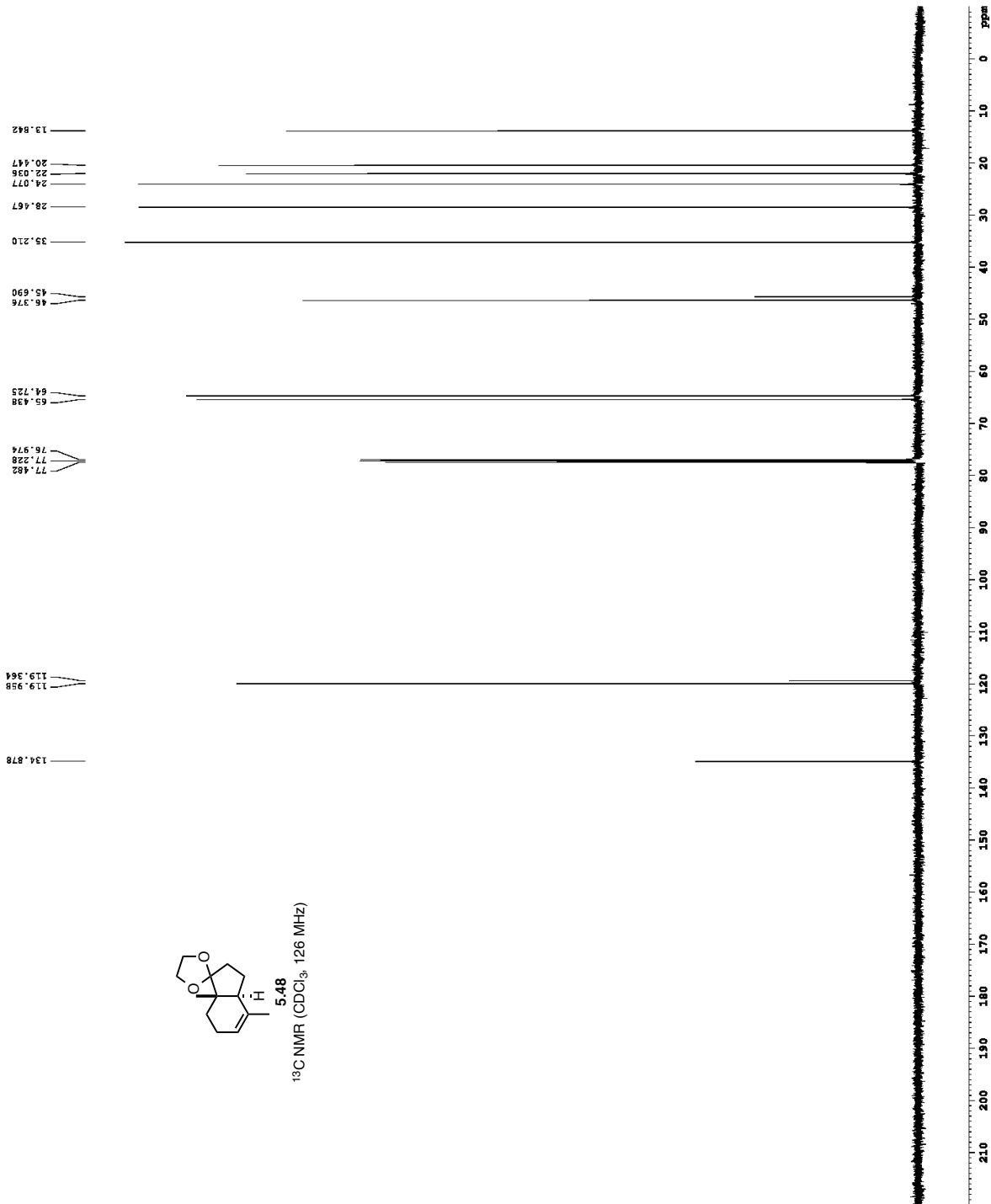
F2 - Acquisition Parameters
Data_    20151119
Time     16.57
INSTRUM  cryo500
PROBHD   5 mm CPIC1-H
PULPROG  zgpg30
SOLVENT  CDCl3
NS       504
DS       16
SWH      30303.031 Hz
AQ       0.487248 Hz
RG       1.0613440 sec
RG       6502
DM       16.500 usec
DE       6.00 usec
TE       298.0 K
D1       0.25000000 sec
d11      0.00000000 sec
d16      0.00020000 sec
d17      0.00019600 sec
MCREST   0 sec
MCWRRK   0.01500000 sec
P2       33.10 usec

===== CHANNEL f1 =====
NUC1      13C
P1        16.55 usec
P11       500.00 usec
P12       2000.00 usec
P10       120.00 dB
P110      10.00 dB
FREQ1     125.764568 MHz
SE1       2.70 dB
SE2       2.70 dB
SFO1      Crp60,0.5,20.1
SFO2      Crp60comp-.4
SFOF1     0 Hz
SFOF2     0 Hz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
P2        100.00 usec
P21       1.60 dB
P22       1.60 dB
P20       120.00 dB
FREQ2     500.2223011 MHz

===== GRADIENT CHANNEL =====
GPRAM[1]  SINE.100
GPRAM[2]  SINE.100
GPX1      0 *
GPY1      0 *
GPZ1      0 *
GPRAM[1]  30.00 *
GPRAM[2]  50.00 *
GPX2      0 *
GPY2      0 *
GPZ2      0 *
P15       500.00 usec
P16       1000.00 usec

F2 - Processing parameters
SI        65536
SF        125.760398 MHz
EM
NDM       0
SSB       0
CB        0
GB        0
PC        2.00
    
```

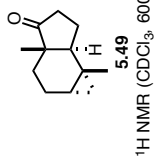
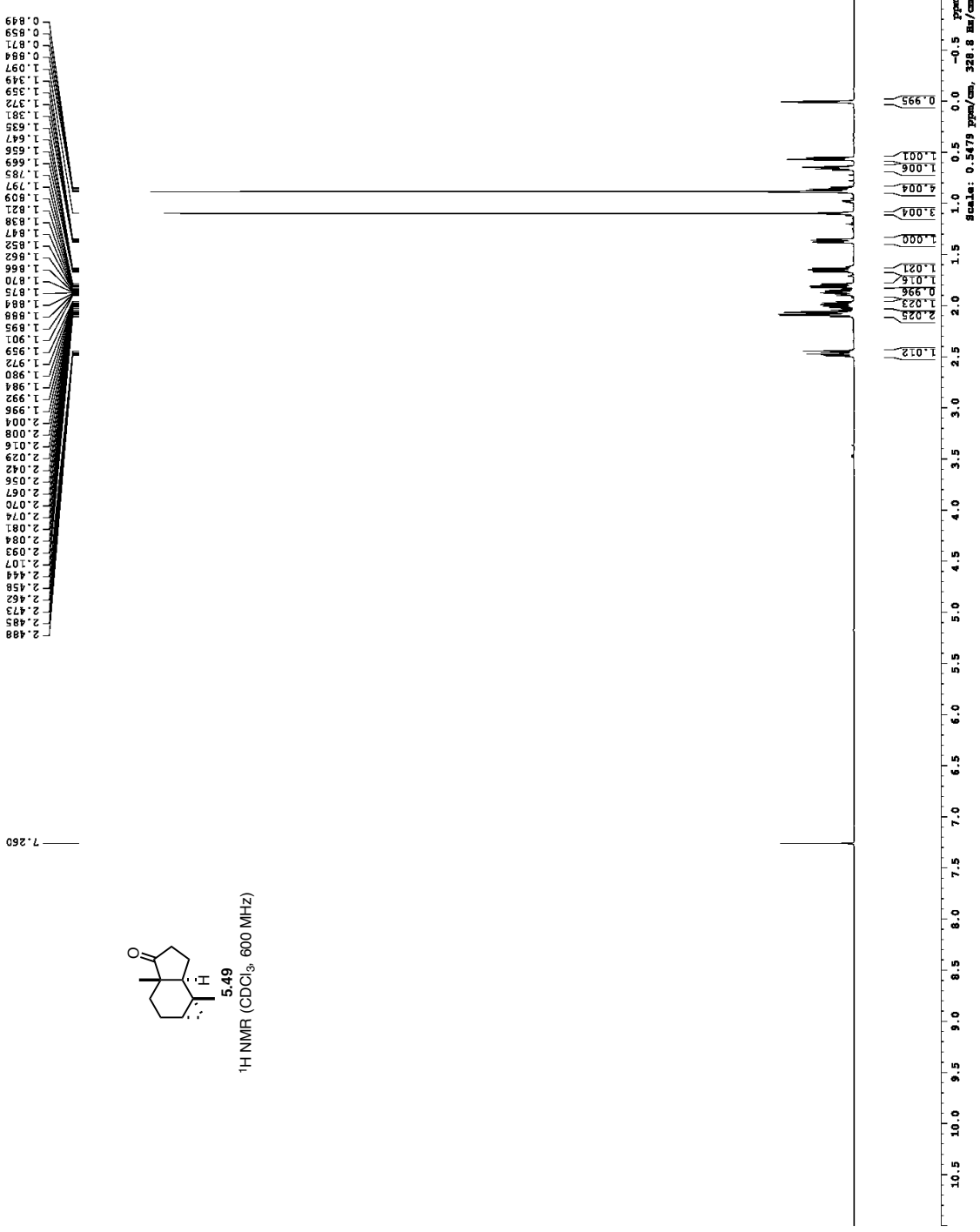


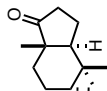
YS-IV-29

Current Data Parameters
 NAME YS-IV-29
 PROCNO 1
 P2 - Acquisition Parameters
 DATE_ 20160903
 TIME 16:39
 INSTRUM 5 mm TRX 5030
 PULPROG zgpg30
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 9615.345 Hz
 FIDRES 0.08842 Hz
 AQ 3.19597886 sec
 RG 322 chg
 DW 52.000 usec
 DE 1.500 usec
 TE 298.1 K usec
 D1 0.10000000 sec
 D0 1

===== CHANNEL f1 =====
 NUCL1 13C
 P1 100.626126 MHz
 PL1 24.0000000 W
 PR1 1.00000000 sec

P2 - Processing Parameters
 SI 655216
 SF 600.1300354 MHz
 DS 2
 SW 0
 ZG 0.30 Hz
 GB 0
 PC 1.00





5.49
¹³C NMR (CDCl₃, 126 MHz)

221.098

77.482
77.228
76.974

50.651

47.316

36.606

27.977
22.945
22.195
19.716
17.824
16.287
13.312

Current Data Parameters
NAME YS-IV-29
EXPNO 4
PROCNO 1

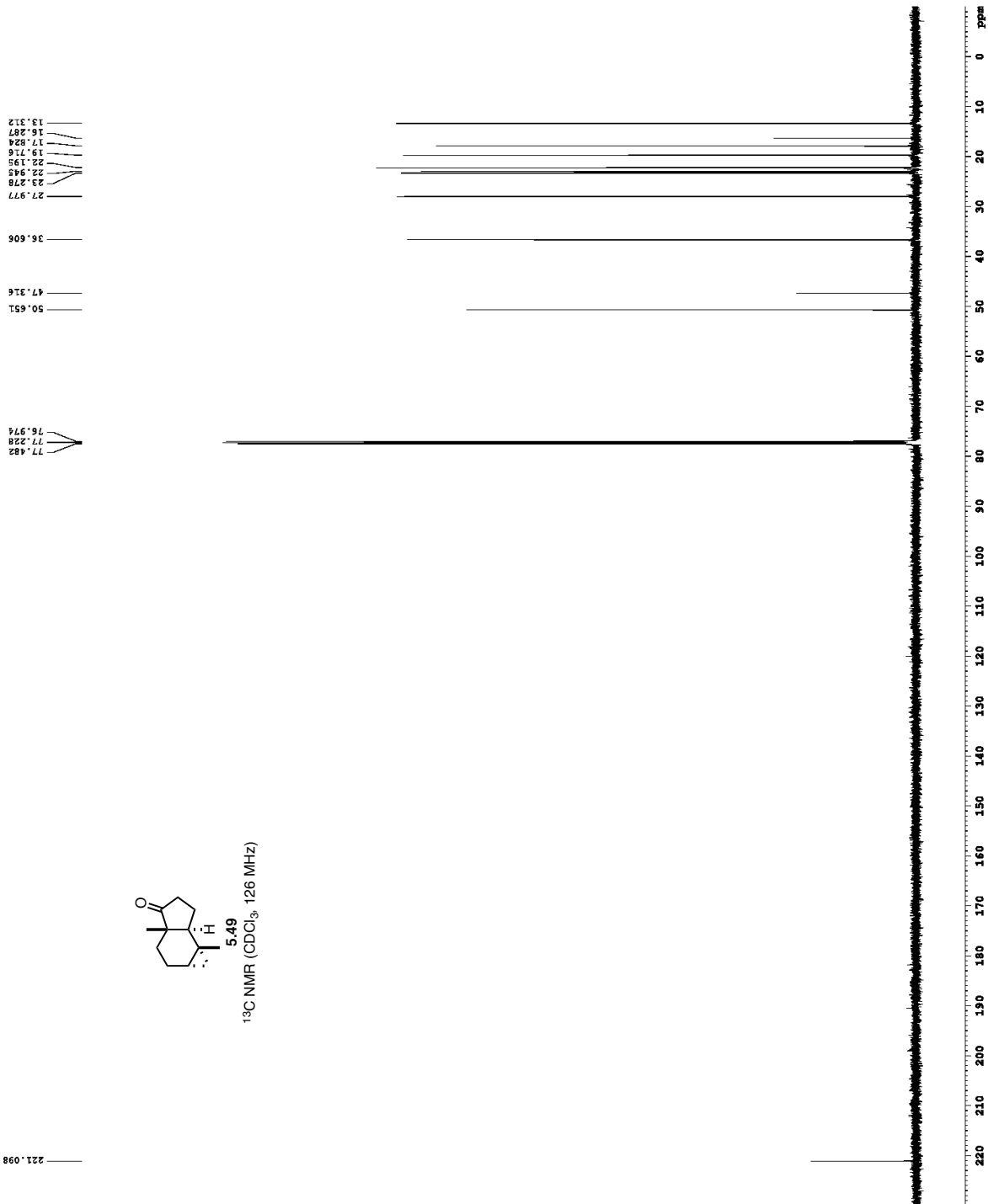
F2 - Acquisition Parameters
Date_ 20160107
Time 16.47
INSTRUM cryo500
PULPROG zgpg30
SOLVENT CDCl₃
NS 832
DS 2
SWH 30303.031 Hz
AQ 0.6477328 Hz
RG 1.0813440 sec
RG 7298.2
DM 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.2300000 sec
d11 0.0300000 sec
d16 0.0002000 sec
d17 0.00019600 sec
MCRET1 0 sec
MCRRK 0.01500000 sec
F2 33.10 usec

CHANNEL f1 13C
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 120.00 dB
PL2 120.00 dB
SFO1 125.764568 MHz
SFO2 125.764568 MHz
SFO3 125.764568 MHz
SFO4 125.764568 MHz
SFO5 125.764568 MHz
SFO6 125.764568 MHz
SFO7 125.764568 MHz
SFO8 125.764568 MHz
SFO9 125.764568 MHz
SFO10 125.764568 MHz
SFO11 125.764568 MHz
SFO12 125.764568 MHz
SFO13 125.764568 MHz
SFO14 125.764568 MHz
SFO15 125.764568 MHz
SFO16 125.764568 MHz
SFO17 125.764568 MHz
SFO18 125.764568 MHz
SFO19 125.764568 MHz
SFO20 125.764568 MHz
SFO21 125.764568 MHz
SFO22 125.764568 MHz
SFO23 125.764568 MHz
SFO24 125.764568 MHz
SFO25 125.764568 MHz
SFO26 125.764568 MHz
SFO27 125.764568 MHz
SFO28 125.764568 MHz
SFO29 125.764568 MHz
SFO30 125.764568 MHz
SFO31 125.764568 MHz
SFO32 125.764568 MHz
SFO33 125.764568 MHz
SFO34 125.764568 MHz
SFO35 125.764568 MHz
SFO36 125.764568 MHz
SFO37 125.764568 MHz
SFO38 125.764568 MHz
SFO39 125.764568 MHz
SFO40 125.764568 MHz
SFO41 125.764568 MHz
SFO42 125.764568 MHz
SFO43 125.764568 MHz
SFO44 125.764568 MHz
SFO45 125.764568 MHz
SFO46 125.764568 MHz
SFO47 125.764568 MHz
SFO48 125.764568 MHz
SFO49 125.764568 MHz
SFO50 125.764568 MHz

CHANNEL f2
CFPRAG2 waitz16
NUC2 13C
PCPD2 100.00 usec
PL0 120.00 dB
PL1 120.00 dB
PL2 120.00 dB
SFO1 500.2223011 MHz

GRADIENT CHANNEL
GPNAM[1] SINE.100
GPNAM[2] SINE.100
GPA1 0 %
GPA2 0 %
GPX1 0 %
GPX2 0 %
GPY1 0 %
GPY2 0 %
GFZ1 30.00 %
GFZ2 30.00 %
PL5 50.00 usec
PL6 500.00 usec
PL7 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7603979 MHz
WDW EM
SSB 0
GB 0
PC 2.00



```

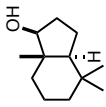
Current Data Parameters
NAME      YS-IV-24
PROCNO    1
Date_     201114
INSTRUM   cryo-500
PULPROG   zgpg30
TD         65536
AQ         8.178
RG         4096
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         4.00

F2 - Acquisition Parameters
Date_     201114
INSTRUM   cryo-500
PULPROG   zgpg30
TD         65536
AQ         8.178
RG         4096
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         4.00

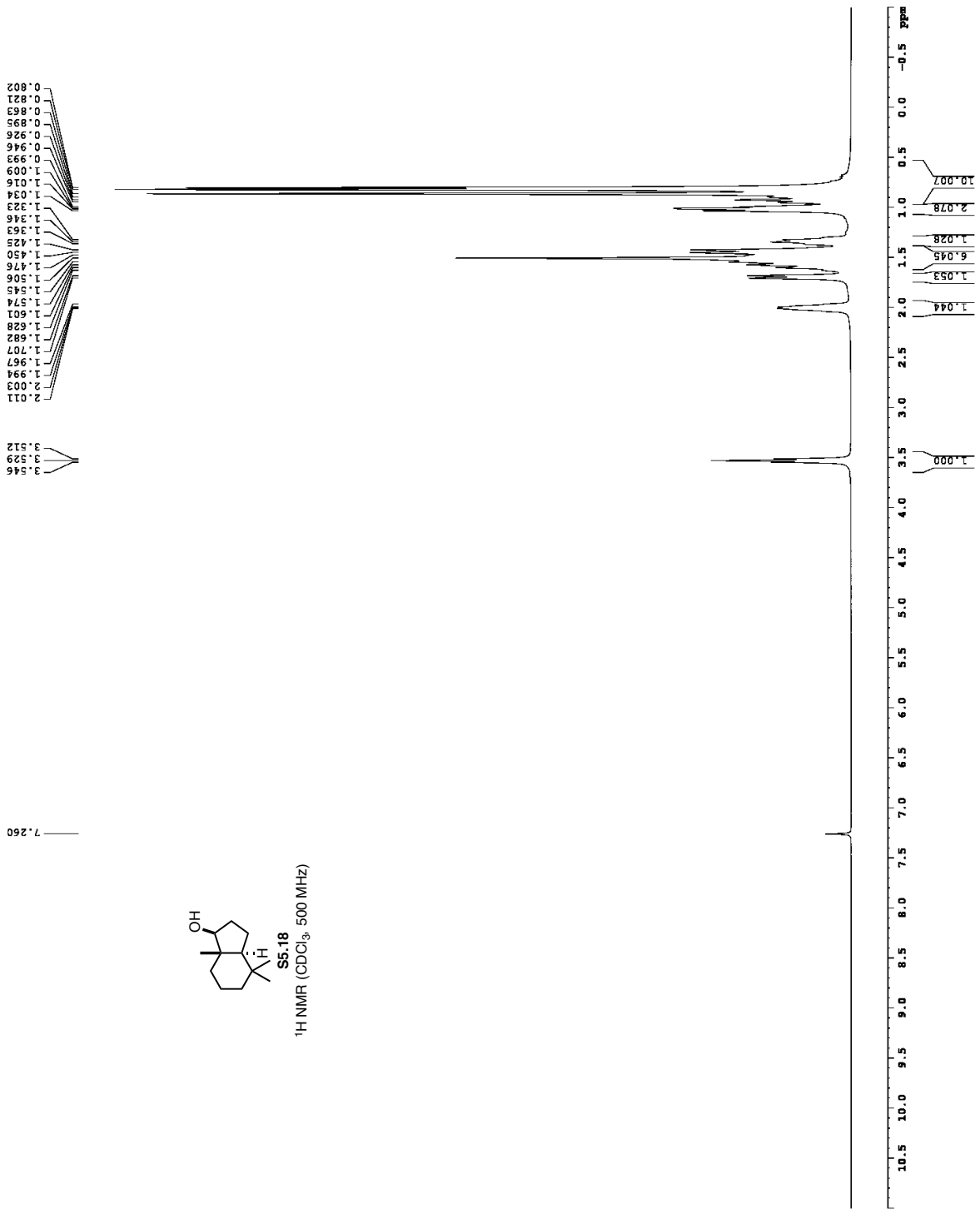
F1 - Processing parameters
Date_     201114
INSTRUM   cryo-500
PULPROG   zgpg30
TD         65536
AQ         8.178
RG         4096
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         4.00

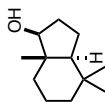
===== CHANNEL f1 =====
NUC1       13C
P1         7.50 uSec
PL1        0.00 dB
SFO1       500.2282500 MHz

===== CHANNEL f2 =====
NUC2       1H
P2         13.00 uSec
PL2        19.00 dB
SFO2       500.1364500 MHz
  
```

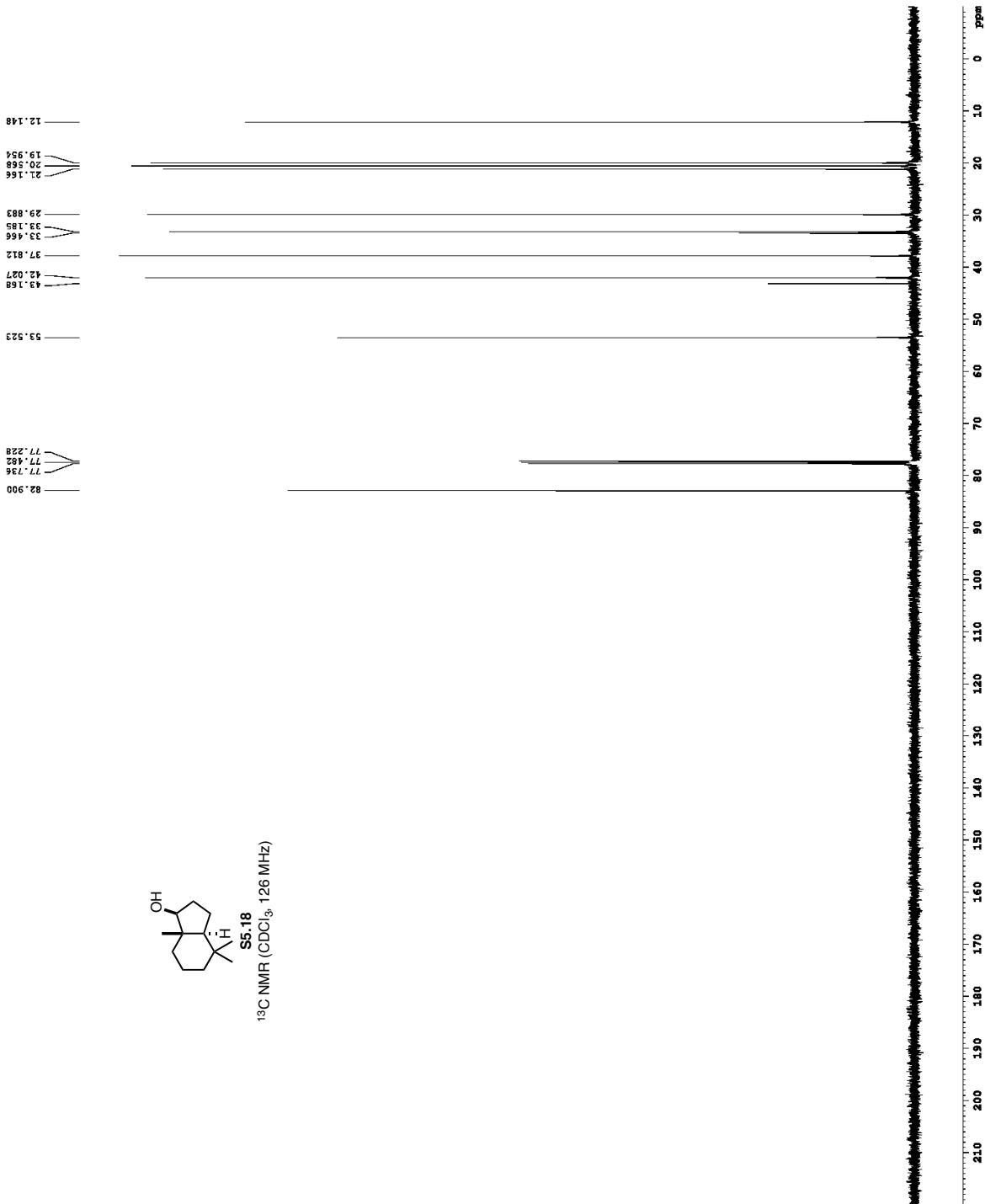


S5.18
¹H NMR (CDCl₃, 500 MHz)





S5.18
¹³C NMR (CDCl₃, 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 CPIC1 H-
PULPROG  zgpg30
SOLVENT  CDCl3
NS       248
DS       2
SWH      30303.031 Hz
FIDRES   0.46280 Hz
AQ       1.0613440 sec
RG       7298.2
DM       16.500 usec
DE       6.00 usec
TE       298.0 K
D1       0.25000000 sec
d11      0.00000000 sec
d16      0.00020000 sec
d17      0.00019600 sec
MCREST   0 sec
MCWRRK   0.01500000 sec
P2       33.10 usec

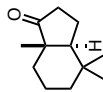
===== CHANNEL f1 =====
NUC1     13C
P1       16.55 usec
P11      500.00 usec
P12      2000.00 usec
P10      120.00 dB
P15      1.00 dB
SFO1     125.762569 MHz
SF2      2.70 dB
SF21     2.70 dB
SF22     2.70 dB
SFOF1[1] Crp60,0.5,20.1
SFOF1[2] Crp60comp.4
SFOF2    0 Hz
SFOFZ    0 Hz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
P2       100.00 usec
P21      1.60 dB
P22      1.60 dB
SFO2     500.2223031 MHz

===== GRADIENT CHANNEL =====
GPRAM[1] SINE.100
GPRAM[2] SINE.100
GPX1     0 *
GPY1     0 *
GPZ1     0 *
GPRAM[1] 30.00 *
GPRAM[2] 50.00 *
P15      500.00 usec
P16      1000.00 usec

F2 - Processing parameters
SI       65536
SF       125.7603692 MHz
WDW      EM
SSB      0
CB       0
GC       0
PC       2.00
    
```

XS-IV-25

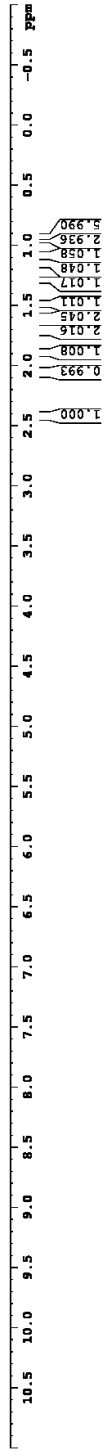


5.31
¹H NMR (CDCl₃, 600 MHz)

```
Current Data Parameters
NAME XS-IV-25
PROCNO 1
DATE_ 2011217
INSTRUM spect
PROBHD 5 mm TBI 1H/13
PULPROG zgpg30
TD 65536
F2 - Acquisition Parameters
Date_ 2011217
Time 15.00
INSTRUM spect
PROBHD 5 mm TBI 1H/13
PULPROG zgpg30
TD 65536
F2 - Processing parameters
Date_ 2011217
Time 15.00
INSTRUM spect
PROBHD 5 mm TBI 1H/13
PULPROG zgpg30
TD 65536
F2 - Processing parameters
Date_ 2011217
Time 15.00
INSTRUM spect
PROBHD 5 mm TBI 1H/13
PULPROG zgpg30
TD 65536
```

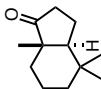
2.443
2.429
2.428
2.411
2.397
2.091
2.076
2.061
2.048
2.029
1.915
1.906
1.900
1.894
1.886
1.881
1.872
1.741
1.735
1.733
1.718
1.713
1.711
1.703
1.696
1.690
1.681
1.675
1.674
1.618
1.612
1.606
1.601
1.598
1.594
1.592
1.585
1.580
1.504
1.499
1.495
1.487
1.477
1.473
1.306
1.296
1.283
1.274
1.177
1.169

7.270



YS-IV-25

221.551



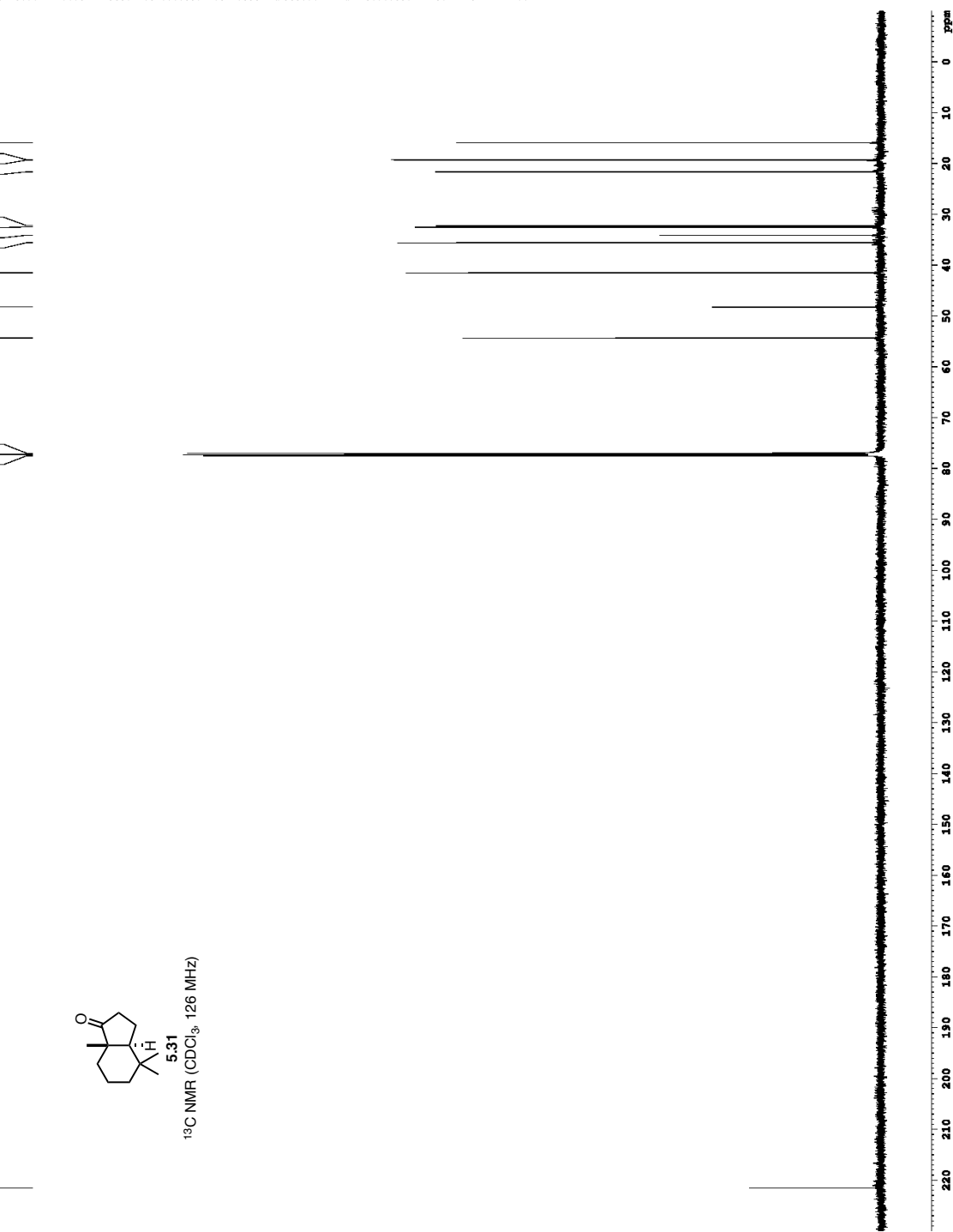
5.31
¹³C NMR (CDCl₃, 126 MHz)

77.483
77.228
76.973
54.329
48.220
41.495
35.564
34.104
32.496
32.208
21.622
19.334
19.226
15.882

Current Data Parameters
NAME YS-IV-25
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20151217
Time 10.53
INSTRUM gn-500
PROBHD 5 mm broadband
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 800
DS 2
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.083940 sec
RG 383.00
DM 16.500 usec
DE 4.50 usec
TE 298.0 K
D1 0.2500000 sec
SOLVENT CDCl3
ACQRES 0.0500000 sec
SCANS 1
FREQ 125.518000 MHz
XCRS 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 0.00 dB
SFO1 125.537181 MHz
===== CHANNEL f2 =====
CPDPRG12 waltz16
NUC2 1H
P2 18.00 usec
PL2 12.00 dB
PL12 12.00 dB
SFO2 499.1824859 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

Current Data Parameters
NAME DJT-V-036
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20150203
Time 18:19
PROBHD 5 mm CPIC-1H
PULPROG zgpg30
TD 65536
FIDRES 0.999728 sec
AQ 0.500114 Hz
RG 327.5
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0 sec
MCWRK 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.00 usec
PL1 0 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

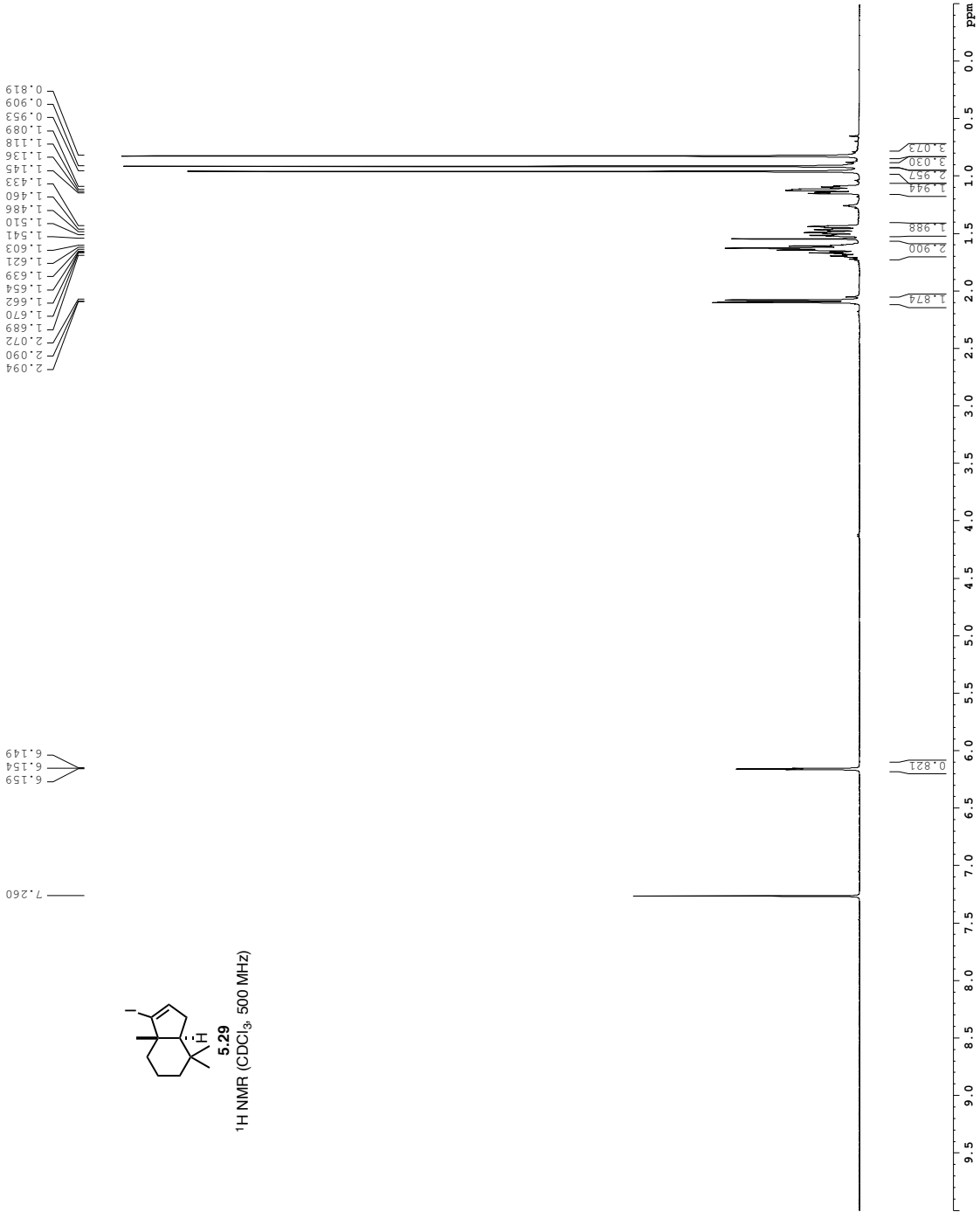
2.094
2.090
2.072
1.689
1.670
1.662
1.654
1.639
1.621
1.603
1.541
1.510
1.486
1.460
1.433
1.414
1.356
1.118
1.089
0.953
0.909
0.819

6.159
6.154
6.149

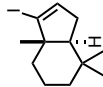
7.260



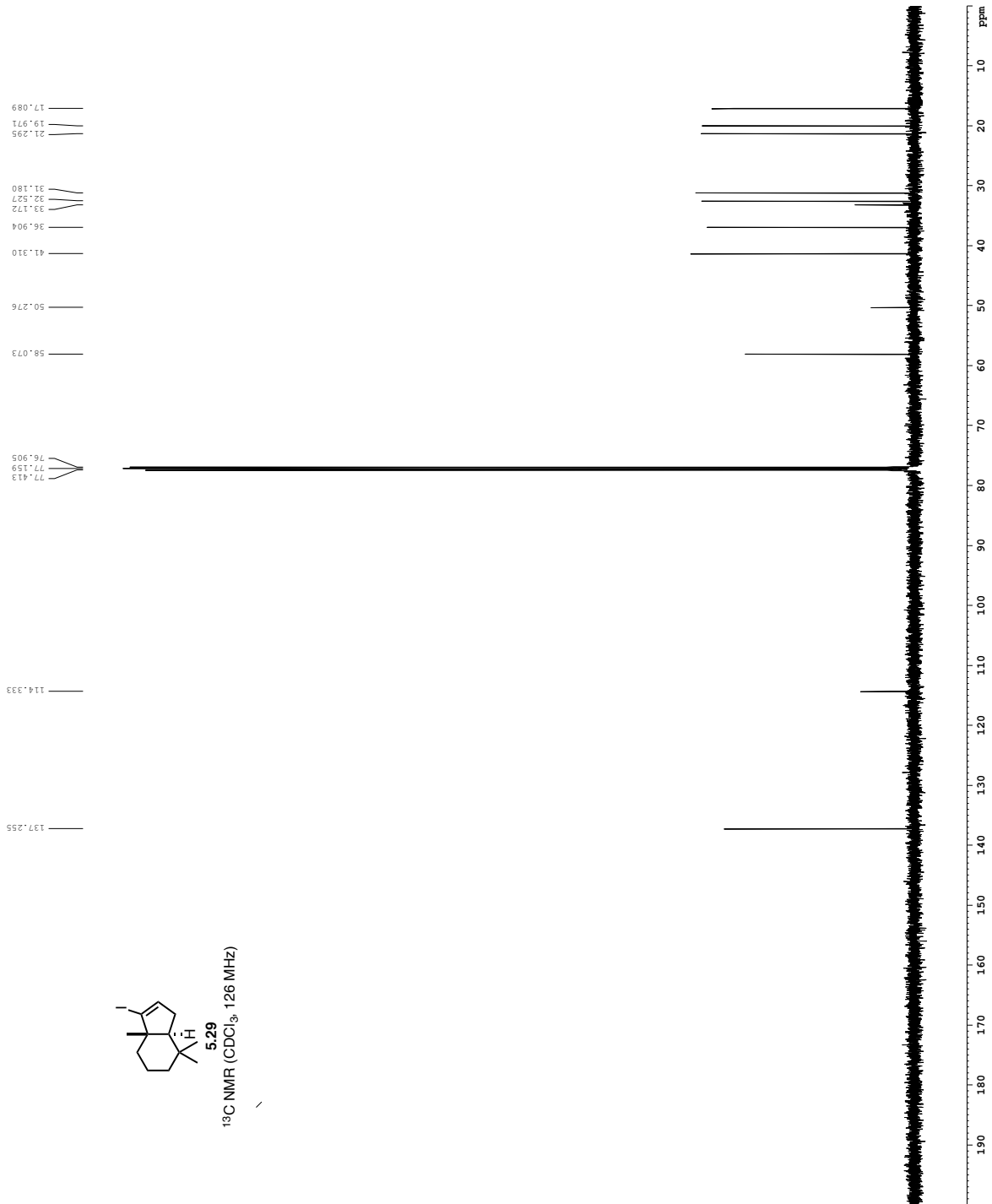
5.29
1H NMR (CDCl₃, 500 MHz)



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



5.29
¹³C NMR (CDCl₃, 126 MHz)



Current Data Parameters
 NAME DJT-V-036
 PROCNO 2
 F2 - Acquisition Parameters
 Date_ 20150203
 Time 18.24
 INSTRUM ctye500
 PULPROG zgpg30
 F1PRG SpinEchoPrg30CPD.prd
 TD 65536
 SOLVENT CDCl3
 NS 391
 DS 0
 SWH 30300.00 Hz
 FWH 0.66238 Hz
 AQ 1.0813440 sec
 RG 13004
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 d11 0.0300000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRK 0.01500000 sec
 F2 33.10 usec

==== CHANNEL f1 =====
 NUC1 ¹³C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P13 120.00 dB
 P14 0.00 dB
 SFO1 125.7942548 MHz
 SFO2 500.2225011 MHz
 SF2 2.70 dB
 SF2 2.70 dB
 SPNAM[1] Cp60.0.5.20.1
 SPNAM[2] Cp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 ¹H
 P1 100.00 usec
 P11 4.50 dB
 P12 4.50 dB
 SFO2 500.2225011 MHz

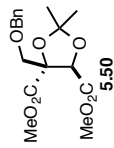
==== GRADIENT CHANNEL =====
 GENAM[1] SINE.100
 GENAM[2] SINE.100
 GP1 0 %
 GP2 0 %
 GP3 0 %
 GP4 0 %
 GP5 0 %
 GP6 0 %
 GP7 0 %
 GP8 0 %
 GP9 0 %
 GP10 0 %
 GP11 0 %
 GP12 0 %
 GP13 0 %
 GP14 0 %
 GP15 0 %
 GP16 0 %
 GP17 0 %
 GP18 0 %
 GP19 0 %
 GP20 0 %
 GP21 30.00 %
 GP22 50.00 %
 GP23 50.00 usec
 P15 1000.00 usec
 P16 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7804074 MHz
 WDW EM
 SSB 0
 GB 0
 CB 0
 PC 2.00

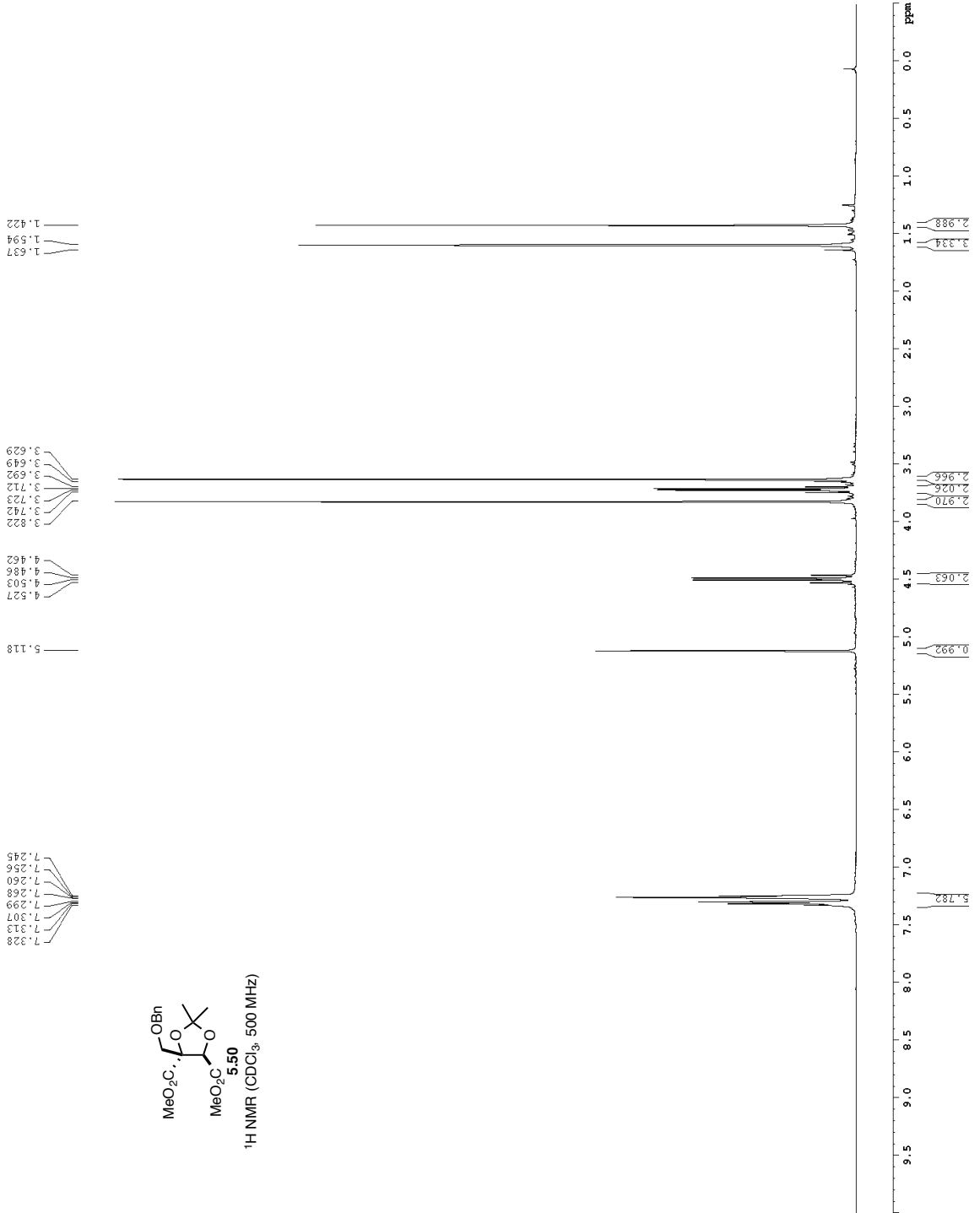
¹H spectrum

```

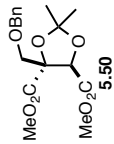
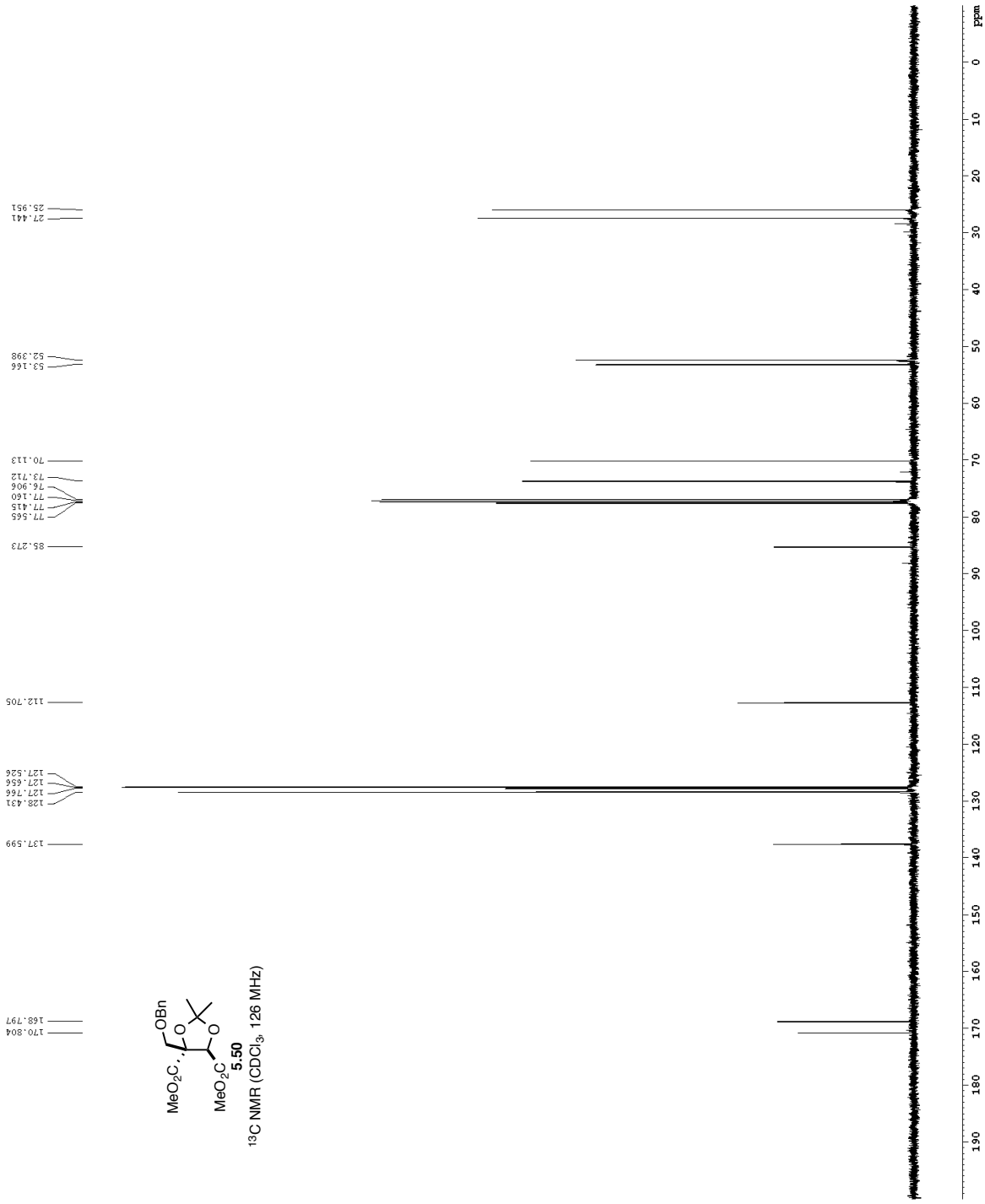
Current Data Parameters
NAME          D01-VI-104
PROCNO       1
F2 - Acquisition Parameters
Date_        20131108
Time         09:54:00
INSTRUM      spect
PROBHD       5 mm CPYBBO
PULPROG      zgpg30
SOLVENT      CDCl3
NS           30
SH1          8012.620 Hz
NUC1         13
NUC2         13
NUC3         13
PC           4.00
===== CHANNEL f1 =====
P1          7.50 usec
PL          0.00 dB
SFO1        500.2252615 MHz
F2 - Processing parameters
SI          500.2252615 MHz
WDW         EM
SSB         0
GB          0.30 Hz
PC          4.00
  
```



5.50
¹H NMR (CDCl₃, 500 MHz)



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



¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME DFT-VI-104
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151118
 Time 7.42
 INSTRUM spect
 PULPROG zgpg30cp.prd
 TD 65536
 SOLVENT CDCl₃
 NS 374
 DS 30303.07 Hz
 SFO1 125.7942548 MHz
 ETRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 6502
 DW 16.500 usec
 DE 6.00 usec
 TE 300.2 K
 FL1 0.2500000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRR 0.01500000 sec
 F2 33.10 usec

===== CHANNEL f1 =====
 NUC1 13C
 F1 16.55 usec
 P1 500.00 usec
 PL1 0.00 dB
 PL2 2000.00 usec
 PL2 1.00 dB
 PL1 1.00 dB
 SF01 125.7942548 MHz
 SF1 2.70 dB
 SF2 2.70 dB
 SFO2 500.2225011 MHz
 SFNM[1] Crp60, 0.5, 20.1
 SFNM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

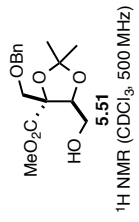
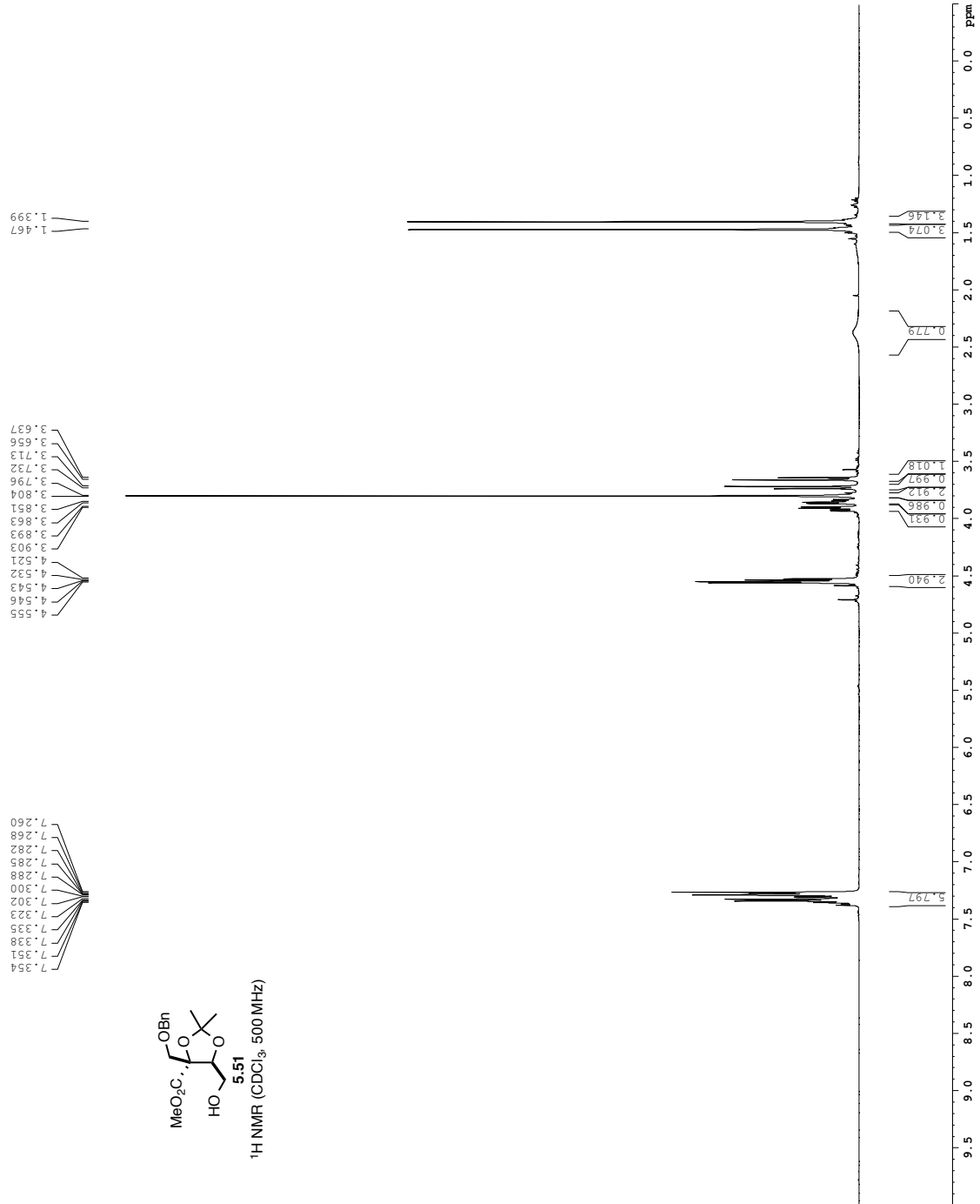
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 P0 100.00 usec
 PL1 1.60 dB
 PL12 24.50 dB
 SF02 500.2225011 MHz
 ===== GRADIENT CHANNEL =====
 GSNM[1] SINE.100
 GSNM[2] SINE.100
 GF1 0 %
 GF2 0 %
 GF3 0 %
 GF4 0 %
 GF5 0 %
 GF6 0 %
 GF7 0 %
 GF8 0 %
 GF9 0 %
 GF10 0 %
 GF11 0 %
 GF12 0 %
 GF13 0 %
 GF14 0 %
 GF15 0 %
 GF16 0 %
 P15 500.00 usec
 P16 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7604100 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 2.00

¹H spectrum

```

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
PCMRK     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-III-303

Current Data Parameters
NAME YS-III-303
PROCNO 1
PZ - Acquisition Parameters
Date_ 2011128
Time_ 14:52:00
INSTRUM spect
PROBHD 5 mm TBI
PULPROG zgpg30
TD 32768
AQ 0.10000000
RG 327.68
WDW EM
SSB 0
LB 0
GB 0
PC 1.00

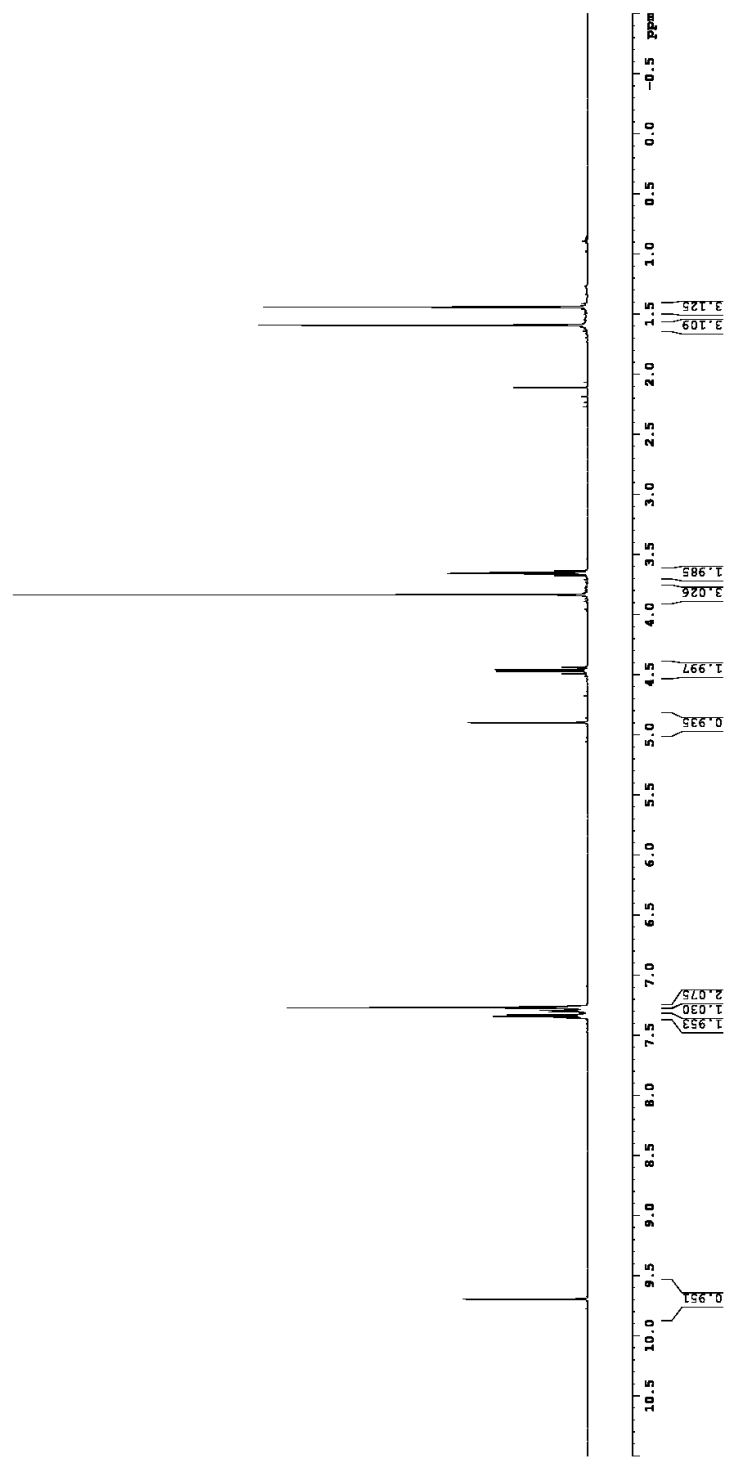
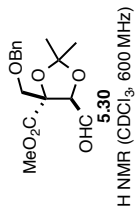
Channel: F1
RF01 600.132019 MHz
P1 8.00 use
PL1 24.0000000 W
F2 - Processing parameters
SF 600.1300297 MHz
WDW EM
SSB 0
LB 0
GB 0
PC 1.00

1.440
1.591
2.110

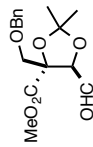
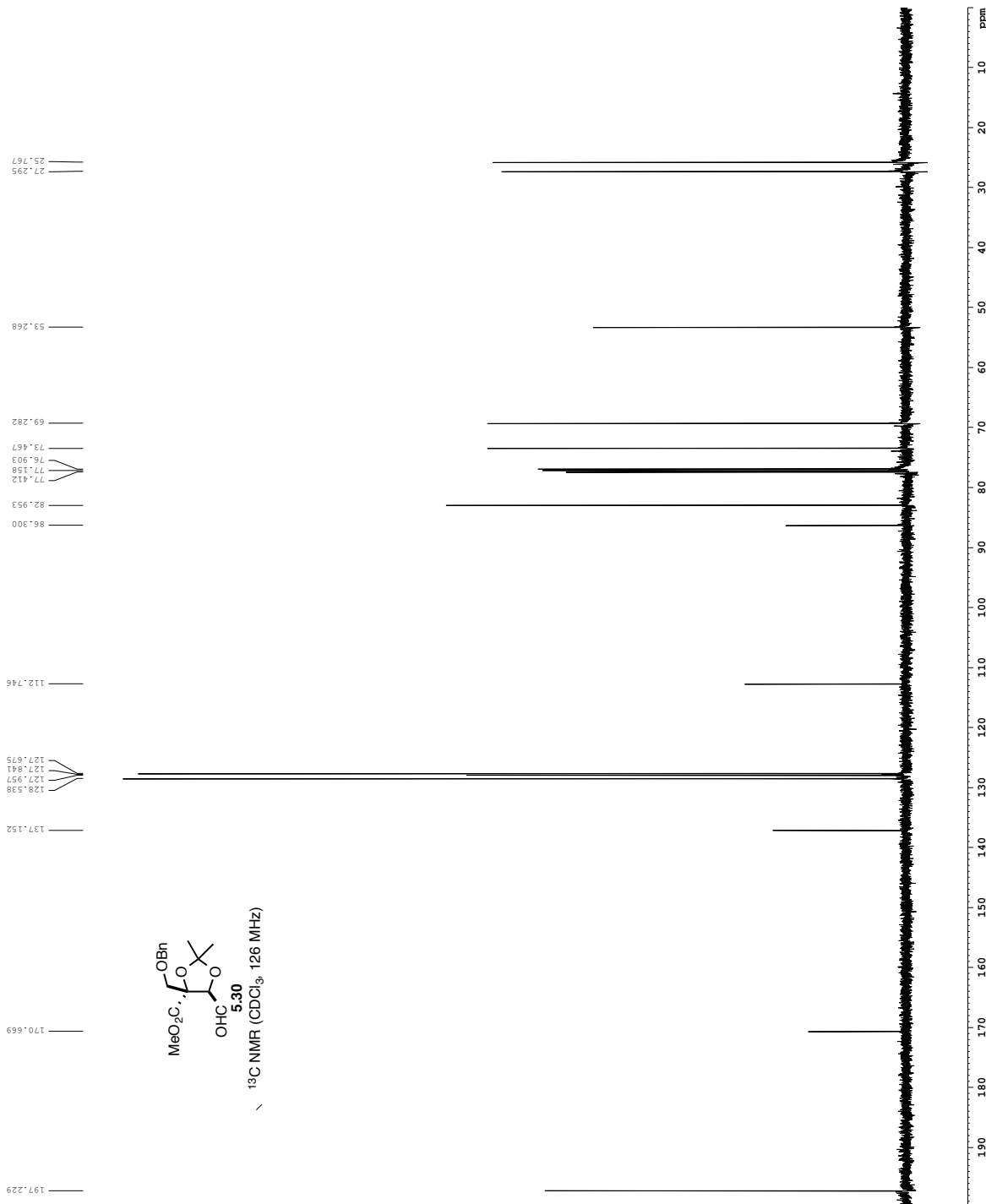
3.634
3.650
3.659
3.676
3.834
3.843
4.437
4.457
4.471
4.491
4.898
4.900

7.260
7.270
7.279
7.292
7.302
7.304
7.329
7.340
7.342
7.351
7.354

9.695
9.696



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



13C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME      DJT-IV-040
PROCNO    2
PROCNO    1

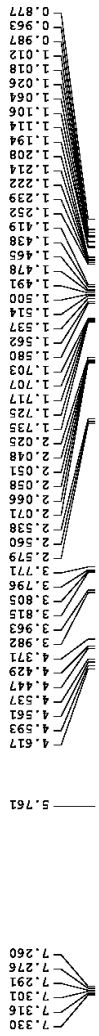
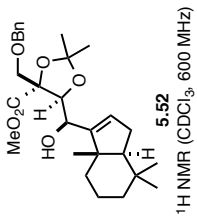
F2 - Acquisition Parameters
Date_     20140616
Time      16.32
INSTRUM   cryo500
PROBHD    5 mm CPYACQ300
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         101
DS         1
SWH        30303.0 Hz
FIDRES     0.252381 Hz
AQ         1.0813440 sec
RG         6502
DW         16.500 usec
DE         6.00 usec
TE         298.0 K
d1         0.250000 sec
d11        0.0300000 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
P13        120.00 dB
P14        120.00 dB
SFO1       125.7942548 MHz
SF1        3.20 dB
SF2        3.20 dB
SFO2       500.2225011 MHz

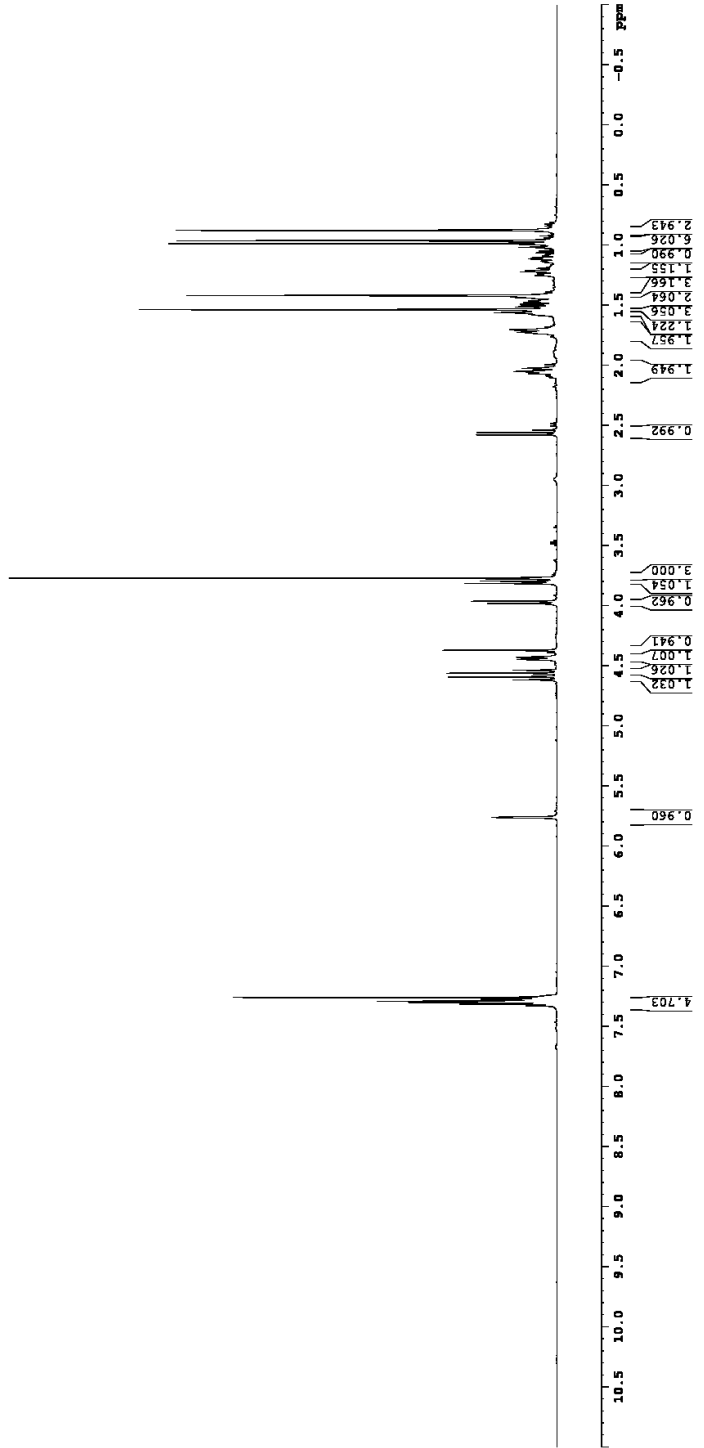
===== CHANNEL f2 =====
CFDPRG[2] waltz16
NUC2       1H
PCPD2      100.00 usec
P13        24.60 dB
P14        24.60 dB
SFO2       500.2225011 MHz

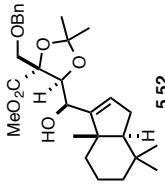
===== GRADIENT CHANNEL =====
GENAM[1]   SINE.100
GENAM[2]   SINE.100
GXY1       0 *
GXY2       0 *
GXY3       0 *
GXY4       0 *
GXY5       0 *
GXY6       0 *
GZ1        30.00 %
GZ2        50.00 %
GZ3        500.00 usec
P13        1000.00 usec
P14        1000.00 usec

F2 - Processing parameters
SI         65536
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         2.00
    
```



Current Data Parameters
 NAME YS-III-303
 FNAME I
 F2 - Acquisition Parameters
 Date 10/31/02
 Time 11:14
 INSTRUM spect
 PULPROG zgpg30
 PCPRG05 5 mm CPTC
 TD 65536
 SFO 600.1354
 AQC 1.0000000
 AS 327.28
 AV 327.28
 CH 1
 DE 0.0010000
 DS 4
 EB 832.402 Hz
 FIDRES 0.000463 Hz
 NS 512
 DSF 5.0000000 sec
 SFO 600.1354 MHz
 SWH 67.400 MHz
 FWH 2984.0 Hz
 LB 0.3000000 Hz
 GB 0
 PC 4.00
 MCORET 0 sec
 MCHOPK 0.0150000 sec
 ===== CHANNEL f1 =====
 NUC1 13C
 P1 7.50 uSec
 PL1 0 dB
 SFO1 500.125000 MHz
 ===== CHANNEL f2 =====
 NUC2 1H
 P2 13.00 uSec
 PL2 0 dB
 SFO2 400.146400 MHz
 ===== Processing parameters =====
 SI 32
 SF 600.1354 MHz
 DSF 67.400 MHz
 SSB 0
 GB 0
 PC 4.00





Current Data Parameters
 NAME XS-III-303
 EXPNO 6
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151202
 Time 13.57
 INSTRUM cryo500
 PULPROG zgpg30
 PROCPRG 5 mm CPIC130k
 F2 - Processing Parameters
 SI 65536
 SF 125.7803996 MHz
 WDW EM
 SSF 0
 LB 1.00 Hz
 GB 0
 PC 2.00

Acquisition Parameters
 Date_ 20151202
 Time 13.57
 INSTRUM cryo500
 PULPROG zgpg30
 PROCPRG 5 mm CPIC130k
 F2 - Processing Parameters
 SI 65536
 SF 125.7803996 MHz
 WDW EM
 SSF 0
 LB 1.00 Hz
 GB 0
 PC 2.00

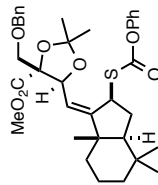
CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P10 120.00 dB
 P11 125.792549 MHz
 SFO1 2.70 dB
 SFO2 2.70 dB
 SFO3 2.70 dB
 SFO4 2.70 dB
 SFO5 2.70 dB
 SFO6 2.70 dB
 SFO7 2.70 dB
 SFO8 2.70 dB
 SFO9 2.70 dB
 SFO10 2.70 dB
 SFO11 2.70 dB
 SFO12 2.70 dB
 SFO13 2.70 dB
 SFO14 2.70 dB
 SFO15 2.70 dB
 SFO16 2.70 dB
 SFO17 2.70 dB
 SFO18 2.70 dB
 SFO19 2.70 dB
 SFO20 2.70 dB
 SFO21 2.70 dB
 SFO22 2.70 dB
 SFO23 2.70 dB
 SFO24 2.70 dB
 SFO25 2.70 dB
 SFO26 2.70 dB
 SFO27 2.70 dB
 SFO28 2.70 dB
 SFO29 2.70 dB
 SFO30 2.70 dB
 SFO31 2.70 dB
 SFO32 2.70 dB
 SFO33 2.70 dB
 SFO34 2.70 dB
 SFO35 2.70 dB
 SFO36 2.70 dB
 SFO37 2.70 dB
 SFO38 2.70 dB
 SFO39 2.70 dB
 SFO40 2.70 dB
 SFO41 2.70 dB
 SFO42 2.70 dB
 SFO43 2.70 dB
 SFO44 2.70 dB
 SFO45 2.70 dB
 SFO46 2.70 dB
 SFO47 2.70 dB
 SFO48 2.70 dB
 SFO49 2.70 dB
 SFO50 2.70 dB
 SFO51 2.70 dB
 SFO52 2.70 dB
 SFO53 2.70 dB
 SFO54 2.70 dB
 SFO55 2.70 dB
 SFO56 2.70 dB
 SFO57 2.70 dB
 SFO58 2.70 dB
 SFO59 2.70 dB
 SFO60 2.70 dB
 SFO61 2.70 dB
 SFO62 2.70 dB
 SFO63 2.70 dB
 SFO64 2.70 dB
 SFO65 2.70 dB
 SFO66 2.70 dB
 SFO67 2.70 dB
 SFO68 2.70 dB
 SFO69 2.70 dB
 SFO70 2.70 dB
 SFO71 2.70 dB
 SFO72 2.70 dB
 SFO73 2.70 dB
 SFO74 2.70 dB
 SFO75 2.70 dB
 SFO76 2.70 dB
 SFO77 2.70 dB
 SFO78 2.70 dB
 SFO79 2.70 dB
 SFO80 2.70 dB
 SFO81 2.70 dB
 SFO82 2.70 dB
 SFO83 2.70 dB
 SFO84 2.70 dB
 SFO85 2.70 dB
 SFO86 2.70 dB
 SFO87 2.70 dB
 SFO88 2.70 dB
 SFO89 2.70 dB
 SFO90 2.70 dB
 SFO91 2.70 dB
 SFO92 2.70 dB
 SFO93 2.70 dB
 SFO94 2.70 dB
 SFO95 2.70 dB
 SFO96 2.70 dB
 SFO97 2.70 dB
 SFO98 2.70 dB
 SFO99 2.70 dB
 SFO100 2.70 dB

CHANNEL f2
 CPDPRG12 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 2.00 dB
 P23 2.00 dB
 P24 2.00 dB
 P25 2.00 dB
 P26 2.00 dB
 P27 2.00 dB
 P28 2.00 dB
 P29 2.00 dB
 P30 2.00 dB
 P31 2.00 dB
 P32 2.00 dB
 P33 2.00 dB
 P34 2.00 dB
 P35 2.00 dB
 P36 2.00 dB
 P37 2.00 dB
 P38 2.00 dB
 P39 2.00 dB
 P40 2.00 dB
 P41 2.00 dB
 P42 2.00 dB
 P43 2.00 dB
 P44 2.00 dB
 P45 2.00 dB
 P46 2.00 dB
 P47 2.00 dB
 P48 2.00 dB
 P49 2.00 dB
 P50 2.00 dB
 P51 2.00 dB
 P52 2.00 dB
 P53 2.00 dB
 P54 2.00 dB
 P55 2.00 dB
 P56 2.00 dB
 P57 2.00 dB
 P58 2.00 dB
 P59 2.00 dB
 P60 2.00 dB
 P61 2.00 dB
 P62 2.00 dB
 P63 2.00 dB
 P64 2.00 dB
 P65 2.00 dB
 P66 2.00 dB
 P67 2.00 dB
 P68 2.00 dB
 P69 2.00 dB
 P70 2.00 dB
 P71 2.00 dB
 P72 2.00 dB
 P73 2.00 dB
 P74 2.00 dB
 P75 2.00 dB
 P76 2.00 dB
 P77 2.00 dB
 P78 2.00 dB
 P79 2.00 dB
 P80 2.00 dB
 P81 2.00 dB
 P82 2.00 dB
 P83 2.00 dB
 P84 2.00 dB
 P85 2.00 dB
 P86 2.00 dB
 P87 2.00 dB
 P88 2.00 dB
 P89 2.00 dB
 P90 2.00 dB
 P91 2.00 dB
 P92 2.00 dB
 P93 2.00 dB
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 P96 2.00 dB
 P97 2.00 dB
 P98 2.00 dB
 P99 2.00 dB
 P100 2.00 dB

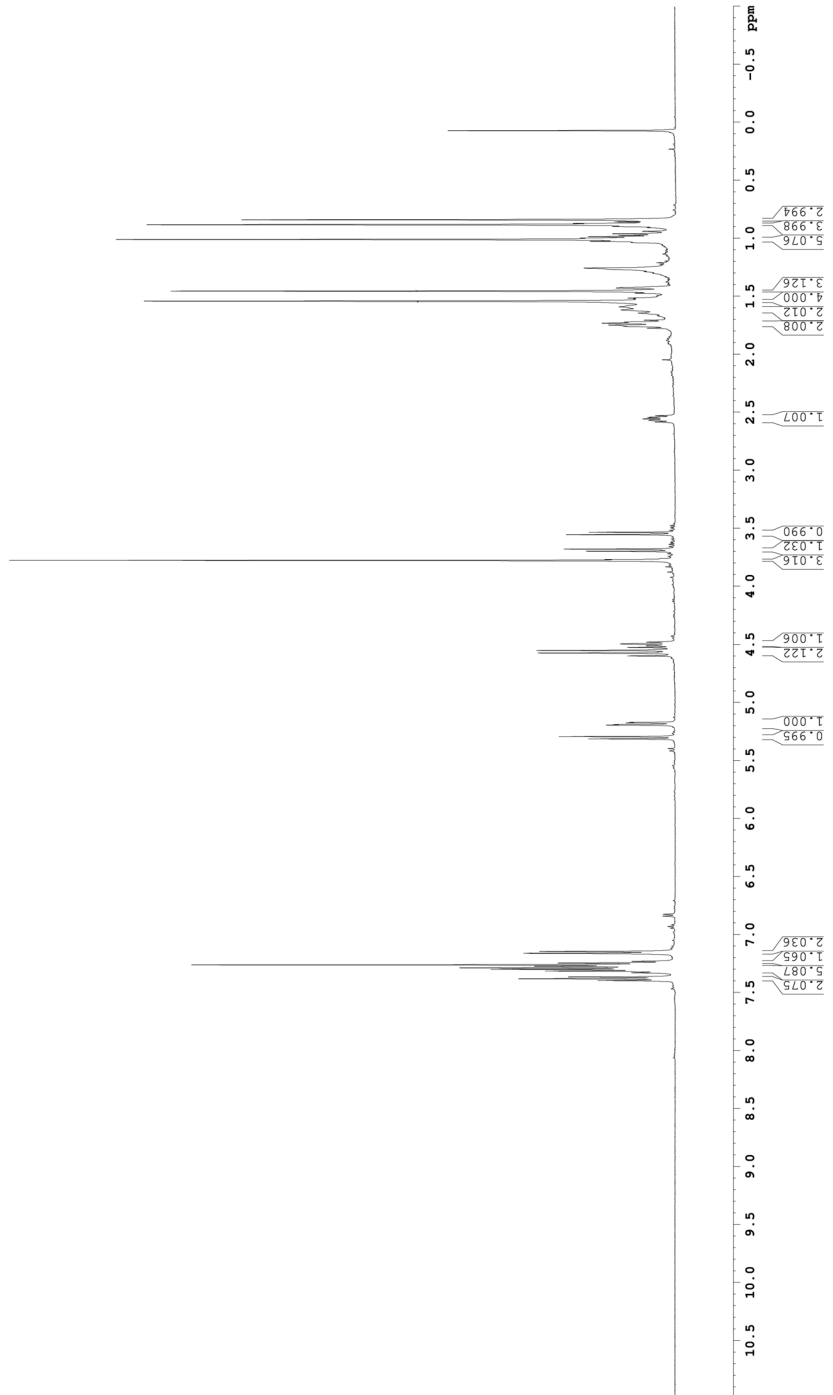
DJT-IV-123

Current Data Parameters
NAME DJT-IV-123
PROCNO 1
PROCNO 1
F2 - Acquisition Parameters
Time 21.48.05
INSTRUM ctyo500
PROBHD 5 mm CFC113H
PULPROG zgpg30
TD 81728
SOLVENT CDCl3
DS 0
SS 0
SMH 8012.820 Hz
FIDRES 0.098043 Hz
RG 5.0395673 sec
RG 6.3
DM 62.400 usec
DE 288.0 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0 sec
ACQPRG CHANNEL F1
NUC1 1H
P1 7.10 usec
PL1 1.80 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200308 MHz
AQ 6.50
SGB 0
LB 0.30 Hz
GB 0
PC 4.00

7.396
7.381
7.364
7.328
7.313
7.299
7.286
7.273
7.260
7.244
7.229
7.162
7.144
5.312
5.293
5.193
5.174
5.170
4.596
4.572
4.549
4.524
4.510
4.493
4.479
3.776
3.768
3.697
3.678
3.552
3.533
2.569
2.565
2.556
2.544
1.773
1.758
1.747
1.731
1.721
1.705
1.644
1.616
1.589
1.540
1.454
1.205
1.008
0.997
0.881
0.838



5.55
1H NMR (CDCl₃, 500 MHz)

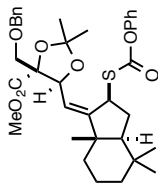


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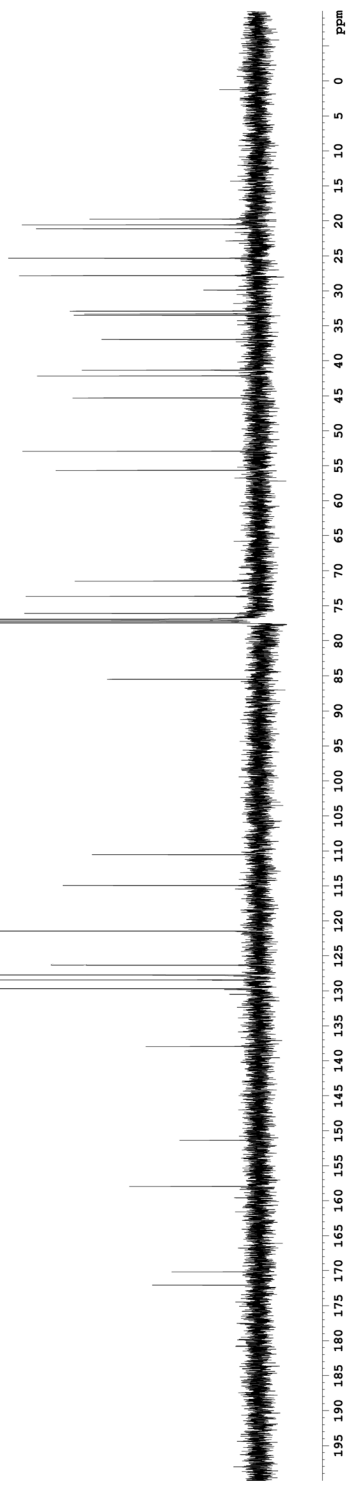
Current Data Parameters
NAME      DJT-IV-123
PROCNO    4
F2 - Acquisition Parameters
Time      9.01
INSTRUM   5 mm cryo-100
PULPROG   zgpg30
PROBHD    5 mm 1H/13
SOLVENT   CDCl3
NS        636
DS        4
SWH        30303.031 Hz
FIDRES     0.462288 Hz
AQ         1.175256 sec
RG         16.500 usec
DM         16.500 usec
DC         298.0 K
TE         298.0 K
D1         0.2500000 sec
d11        0.0000000 sec
d15        0.0000000 sec
d16        0.0000000 sec
d17        0.0000000 sec
d18        0.0000000 sec
d19        0.0000000 sec
d20        0.0000000 sec
d21        0.0000000 sec
d22        0.0000000 sec
d23        0.0000000 sec
d24        0.0000000 sec
d25        0.0000000 sec
d26        0.0000000 sec
d27        0.0000000 sec
d28        0.0000000 sec
d29        0.0000000 sec
d30        0.0000000 sec
d31        0.0000000 sec
d32        0.0000000 sec
d33        0.0000000 sec
d34        0.0000000 sec
d35        0.0000000 sec
d36        0.0000000 sec
d37        0.0000000 sec
d38        0.0000000 sec
d39        0.0000000 sec
d40        0.0000000 sec
d41        0.0000000 sec
d42        0.0000000 sec
d43        0.0000000 sec
d44        0.0000000 sec
d45        0.0000000 sec
d46        0.0000000 sec
d47        0.0000000 sec
d48        0.0000000 sec
d49        0.0000000 sec
d50        0.0000000 sec
d51        0.0000000 sec
d52        0.0000000 sec
d53        0.0000000 sec
d54        0.0000000 sec
d55        0.0000000 sec
d56        0.0000000 sec
d57        0.0000000 sec
d58        0.0000000 sec
d59        0.0000000 sec
d60        0.0000000 sec
d61        0.0000000 sec
d62        0.0000000 sec
d63        0.0000000 sec
d64        0.0000000 sec
d65        0.0000000 sec
d66        0.0000000 sec
d67        0.0000000 sec
d68        0.0000000 sec
d69        0.0000000 sec
d70        0.0000000 sec
d71        0.0000000 sec
d72        0.0000000 sec
d73        0.0000000 sec
d74        0.0000000 sec
d75        0.0000000 sec
d76        0.0000000 sec
d77        0.0000000 sec
d78        0.0000000 sec
d79        0.0000000 sec
d80        0.0000000 sec
d81        0.0000000 sec
d82        0.0000000 sec
d83        0.0000000 sec
d84        0.0000000 sec
d85        0.0000000 sec
d86        0.0000000 sec
d87        0.0000000 sec
d88        0.0000000 sec
d89        0.0000000 sec
d90        0.0000000 sec
d91        0.0000000 sec
d92        0.0000000 sec
d93        0.0000000 sec
d94        0.0000000 sec
d95        0.0000000 sec
d96        0.0000000 sec
d97        0.0000000 sec
d98        0.0000000 sec
d99        0.0000000 sec
d100       0.0000000 sec
=====
CHANNEL f1
NUC1       13C
P1         15.00 usec
PL1        0.00 dB
PL12       0.00 dB
PL13       0.00 dB
PL14       0.00 dB
PL15       0.00 dB
PL16       0.00 dB
PL17       0.00 dB
PL18       0.00 dB
PL19       0.00 dB
PL20       0.00 dB
PL21       0.00 dB
PL22       0.00 dB
PL23       0.00 dB
PL24       0.00 dB
PL25       0.00 dB
PL26       0.00 dB
PL27       0.00 dB
PL28       0.00 dB
PL29       0.00 dB
PL30       0.00 dB
PL31       0.00 dB
PL32       0.00 dB
PL33       0.00 dB
PL34       0.00 dB
PL35       0.00 dB
PL36       0.00 dB
PL37       0.00 dB
PL38       0.00 dB
PL39       0.00 dB
PL40       0.00 dB
PL41       0.00 dB
PL42       0.00 dB
PL43       0.00 dB
PL44       0.00 dB
PL45       0.00 dB
PL46       0.00 dB
PL47       0.00 dB
PL48       0.00 dB
PL49       0.00 dB
PL50       0.00 dB
PL51       0.00 dB
PL52       0.00 dB
PL53       0.00 dB
PL54       0.00 dB
PL55       0.00 dB
PL56       0.00 dB
PL57       0.00 dB
PL58       0.00 dB
PL59       0.00 dB
PL60       0.00 dB
PL61       0.00 dB
PL62       0.00 dB
PL63       0.00 dB
PL64       0.00 dB
PL65       0.00 dB
PL66       0.00 dB
PL67       0.00 dB
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PL69       0.00 dB
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PL74       0.00 dB
PL75       0.00 dB
PL76       0.00 dB
PL77       0.00 dB
PL78       0.00 dB
PL79       0.00 dB
PL80       0.00 dB
PL81       0.00 dB
PL82       0.00 dB
PL83       0.00 dB
PL84       0.00 dB
PL85       0.00 dB
PL86       0.00 dB
PL87       0.00 dB
PL88       0.00 dB
PL89       0.00 dB
PL90       0.00 dB
PL91       0.00 dB
PL92       0.00 dB
PL93       0.00 dB
PL94       0.00 dB
PL95       0.00 dB
PL96       0.00 dB
PL97       0.00 dB
PL98       0.00 dB
PL99       0.00 dB
PL100      0.00 dB
=====
CHANNEL f2
CPDPRG2    waltz16
NUC2       13C
P2         100.00 usec
PL2        1.60 dB
PL22       24.60 dB
PL23       24.60 dB
PL24       24.60 dB
PL25       24.60 dB
PL26       24.60 dB
PL27       24.60 dB
PL28       24.60 dB
PL29       24.60 dB
PL30       24.60 dB
PL31       24.60 dB
PL32       24.60 dB
PL33       24.60 dB
PL34       24.60 dB
PL35       24.60 dB
PL36       24.60 dB
PL37       24.60 dB
PL38       24.60 dB
PL39       24.60 dB
PL40       24.60 dB
PL41       24.60 dB
PL42       24.60 dB
PL43       24.60 dB
PL44       24.60 dB
PL45       24.60 dB
PL46       24.60 dB
PL47       24.60 dB
PL48       24.60 dB
PL49       24.60 dB
PL50       24.60 dB
PL51       24.60 dB
PL52       24.60 dB
PL53       24.60 dB
PL54       24.60 dB
PL55       24.60 dB
PL56       24.60 dB
PL57       24.60 dB
PL58       24.60 dB
PL59       24.60 dB
PL60       24.60 dB
PL61       24.60 dB
PL62       24.60 dB
PL63       24.60 dB
PL64       24.60 dB
PL65       24.60 dB
PL66       24.60 dB
PL67       24.60 dB
PL68       24.60 dB
PL69       24.60 dB
PL70       24.60 dB
PL71       24.60 dB
PL72       24.60 dB
PL73       24.60 dB
PL74       24.60 dB
PL75       24.60 dB
PL76       24.60 dB
PL77       24.60 dB
PL78       24.60 dB
PL79       24.60 dB
PL80       24.60 dB
PL81       24.60 dB
PL82       24.60 dB
PL83       24.60 dB
PL84       24.60 dB
PL85       24.60 dB
PL86       24.60 dB
PL87       24.60 dB
PL88       24.60 dB
PL89       24.60 dB
PL90       24.60 dB
PL91       24.60 dB
PL92       24.60 dB
PL93       24.60 dB
PL94       24.60 dB
PL95       24.60 dB
PL96       24.60 dB
PL97       24.60 dB
PL98       24.60 dB
PL99       24.60 dB
PL100      24.60 dB
=====
CHANNEL GRADIENT CHANNEL
CPDPRG2    waltz16
NUC2       13C
P2         100.00 usec
PL2        1.60 dB
PL22       24.60 dB
PL23       24.60 dB
PL24       24.60 dB
PL25       24.60 dB
PL26       24.60 dB
PL27       24.60 dB
PL28       24.60 dB
PL29       24.60 dB
PL30       24.60 dB
PL31       24.60 dB
PL32       24.60 dB
PL33       24.60 dB
PL34       24.60 dB
PL35       24.60 dB
PL36       24.60 dB
PL37       24.60 dB
PL38       24.60 dB
PL39       24.60 dB
PL40       24.60 dB
PL41       24.60 dB
PL42       24.60 dB
PL43       24.60 dB
PL44       24.60 dB
PL45       24.60 dB
PL46       24.60 dB
PL47       24.60 dB
PL48       24.60 dB
PL49       24.60 dB
PL50       24.60 dB
PL51       24.60 dB
PL52       24.60 dB
PL53       24.60 dB
PL54       24.60 dB
PL55       24.60 dB
PL56       24.60 dB
PL57       24.60 dB
PL58       24.60 dB
PL59       24.60 dB
PL60       24.60 dB
PL61       24.60 dB
PL62       24.60 dB
PL63       24.60 dB
PL64       24.60 dB
PL65       24.60 dB
PL66       24.60 dB
PL67       24.60 dB
PL68       24.60 dB
PL69       24.60 dB
PL70       24.60 dB
PL71       24.60 dB
PL72       24.60 dB
PL73       24.60 dB
PL74       24.60 dB
PL75       24.60 dB
PL76       24.60 dB
PL77       24.60 dB
PL78       24.60 dB
PL79       24.60 dB
PL80       24.60 dB
PL81       24.60 dB
PL82       24.60 dB
PL83       24.60 dB
PL84       24.60 dB
PL85       24.60 dB
PL86       24.60 dB
PL87       24.60 dB
PL88       24.60 dB
PL89       24.60 dB
PL90       24.60 dB
PL91       24.60 dB
PL92       24.60 dB
PL93       24.60 dB
PL94       24.60 dB
PL95       24.60 dB
PL96       24.60 dB
PL97       24.60 dB
PL98       24.60 dB
PL99       24.60 dB
PL100      24.60 dB
=====
F2 - Processing Parameters
SI         655536
SF         125.760460 MHz
WDW        EM
SSB        0
GB         0
PC         2.00
=====

```

- 172.019
- 170.146
- 157.932
- 151.350
- 137.924
- 129.635
- 128.414
- 127.729
- 127.702
- 126.294
- 121.424
- 114.905
- 110.485
- 85.430
- 77.413
- 77.159
- 76.905
- 76.058
- 73.621
- 71.446
- 55.600
- 52.879
- 45.261
- 42.116
- 41.304
- 36.912
- 33.427
- 33.262
- 32.861
- 27.791
- 25.285
- 21.078
- 20.515
- 19.639



5.55
¹³C NMR (CDCl₃, 126 MHz)

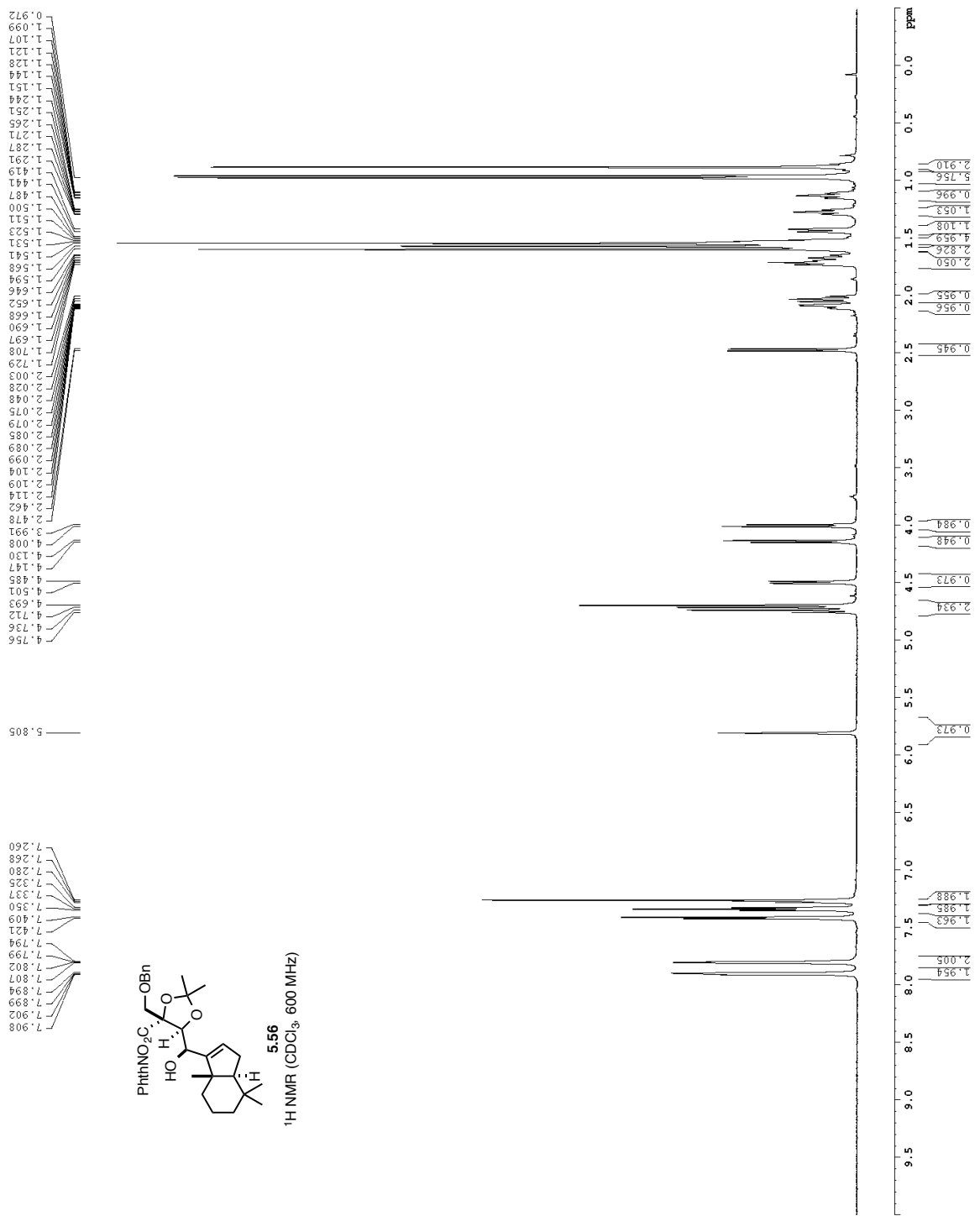


1H spectrum

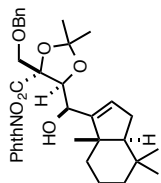
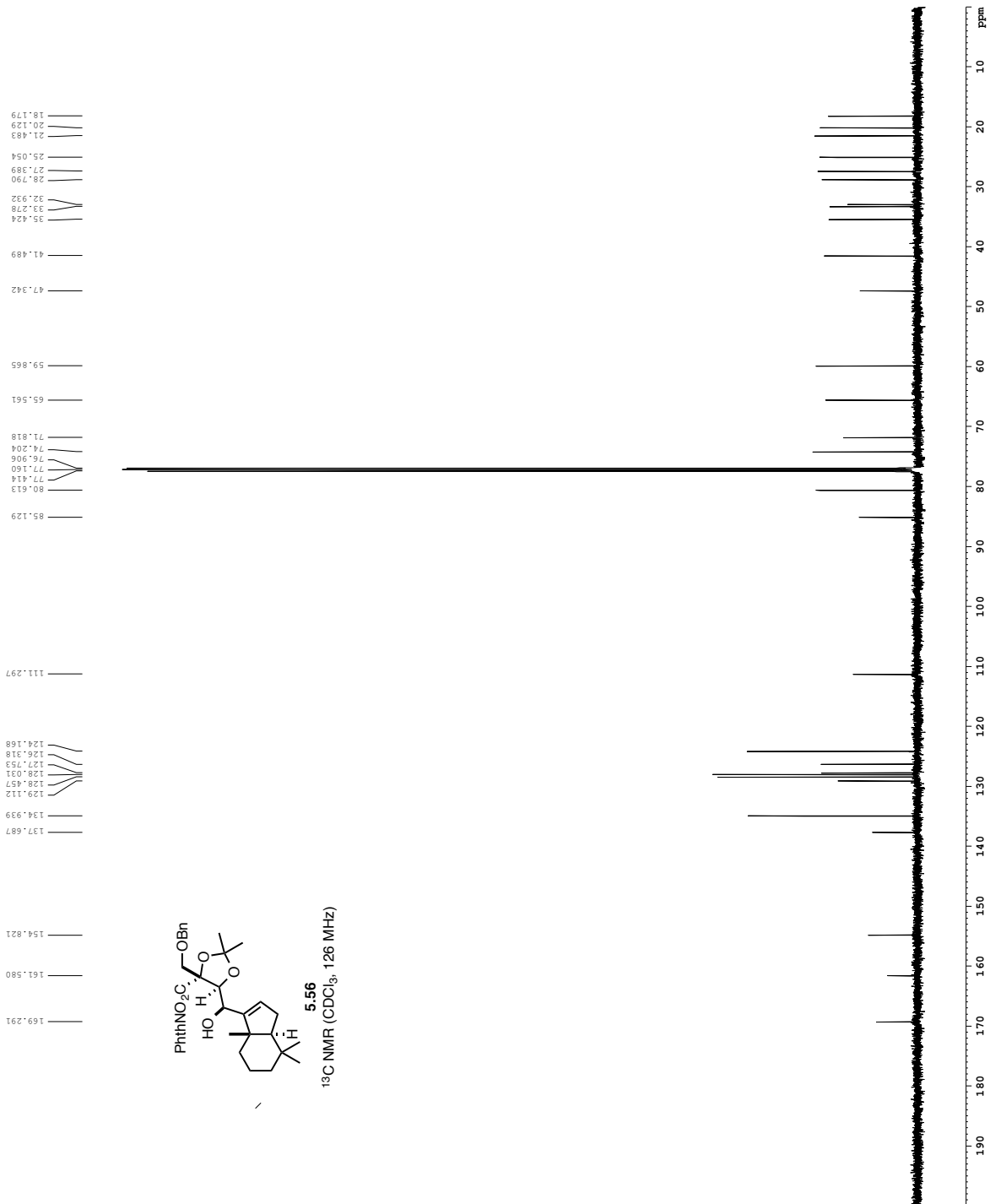
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Current Data Parameters
NAME      D1F1V-03
PROCNO    1
Date_     201103
EX - Acquisition Parameters
INSTRUM   spect
PROBHD    5 mm TBI 1H/13
PULPROG   zgpg30
AQ        9.874
RG        12
SOLVENT   CDCl3
NS        12
DS        4
SWH        9633.380 Hz
FIDRES    0.098042 Hz
AQ        3.0999999 sec
PC        322
RG        513.000 uses
NUC1       13
NUC2       13
NUC3       13
NUC4       13
NUC5       13
NUC6       13
NUC7       13
NUC8       13
NUC9       13
NUC10      13
NUC11      13
NUC12      13
===== CHANNEL f1 =====
SFO1      600.1340009 MHz
PC1       8.000 usec
PL1       0.00 dB
PL2       23.0441656 dB
===== CHANNEL f2 =====
SFO2      600.1300343 MHz
PC2       8.000 usec
PL3       0.00 dB
PL4       23.0441656 dB
===== Processing parameters =====
SI        1
SF        600.1300343 MHz
WDW        EM
SSB        0
GB        0
PC        0
RG        0
DS        4
SWH        9633.380 Hz
FIDRES    0.098042 Hz
AQ        3.0999999 sec
PC        322
RG        513.000 uses
NUC1       13
NUC2       13
NUC3       13
NUC4       13
NUC5       13
NUC6       13
NUC7       13
NUC8       13
NUC9       13
NUC10      13
NUC11      13
NUC12      13

```



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



5.56
¹³C NMR (CDCl₃, 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 CPIC1H-
PULPROG      Spinechopep2d
TD           65536
SOLVENT      CDCl3
NS           857
DS           0
SWH          30303.031 Hz
AQ           0.8491666 Hz
RG           1.0813480 sec
RG           7298.2
DM           16.500 usec
DE           6.00 usec
TE           298.0 K
D1           0.25000000 sec
d11          0.00000000 sec
D16          0.00000000 sec
d17          0.00020000 sec
MCREST       0 sec
MCWRK        0.01500000 sec
F2           33.10 usec

===== CHANNEL f1 =====
NUC1          13C
P1           16.55 usec
P11          500.00 usec
P12          2000.00 usec
PL0          120.00 dB
PL1          20.00 dB
PL2          20.00 dB
SFO1         125.7942548 MHz
SF02         2.70 dB
SF01         2.70 dB
SF02         2.70 dB
SFO1         0 Hz
SFO2         0 Hz
SFO1         0 Hz
SFO2         0 Hz

===== CHANNEL f2 =====
CFPRG2       waltz16
NUC2         1H
PCPD2        100.00 usec
PL0          120.00 dB
PL1          20.00 dB
PL2          20.00 dB
SFO2         500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]     SINE.100
GPNAM[2]     SINE.100
GPA1         0 %
GPA2         0 %
GPX1         0 %
GPX2         0 %
GPY1         0 %
GPY2         0 %
GPZ1         30.00 %
GPZ2         50.00 %
P15          500.00 usec
P16          1000.00 usec

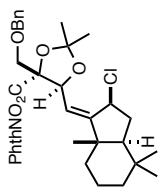
F2 - Processing parameters
SI           65536
SF           125.7604076 MHz
WDW          EM
SSB          0
GB           0
PC           2.00
    
```

1H spectrum

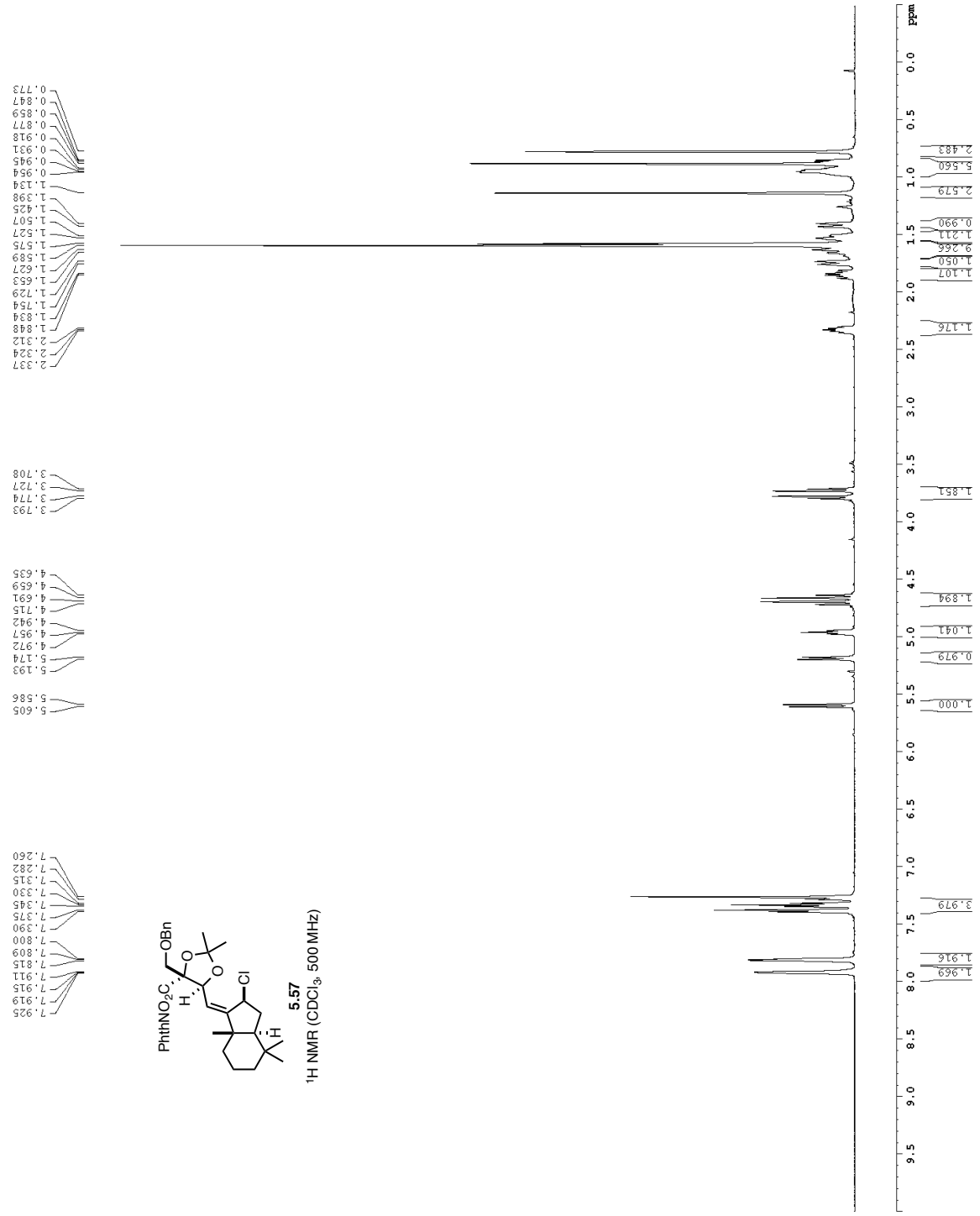
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=====
Name: PhthNO2C-OBn
Date_ Acquired: 20110808
Time: 11.09
PROCIN: 5 mm QNP1H-
PROBHD: 5 mm QNP1H-
PULPROG: zgpg30
SOLVENT: CDCl3
NS: 2
DS: 4
AQ: 0.098973 sec
RG: 0.098973 sec
INJ: 10.00 nsec
EM: 62.500 usec
TE: 296.2 K
NUC1: 13C
NUC2: 1H
PC: 4.00
===== CHANNEL f1 =====
NUC1: 13C
P1: 7.18 usec
PL1: 0.00 dB
PL12: 1.40 dB
RF1: 500.225015 MHz
===== CHANNEL f2 =====
NUC2: 1H
P2: 13.00 usec
PL2: 0.00 dB
RF2: 500.2200345 MHz
===== Processing parameters =====
SI: 32768
SF: 500.2200345 MHz
WDW: EM
SSB: 0
GB: 0
PC: 4.00
=====

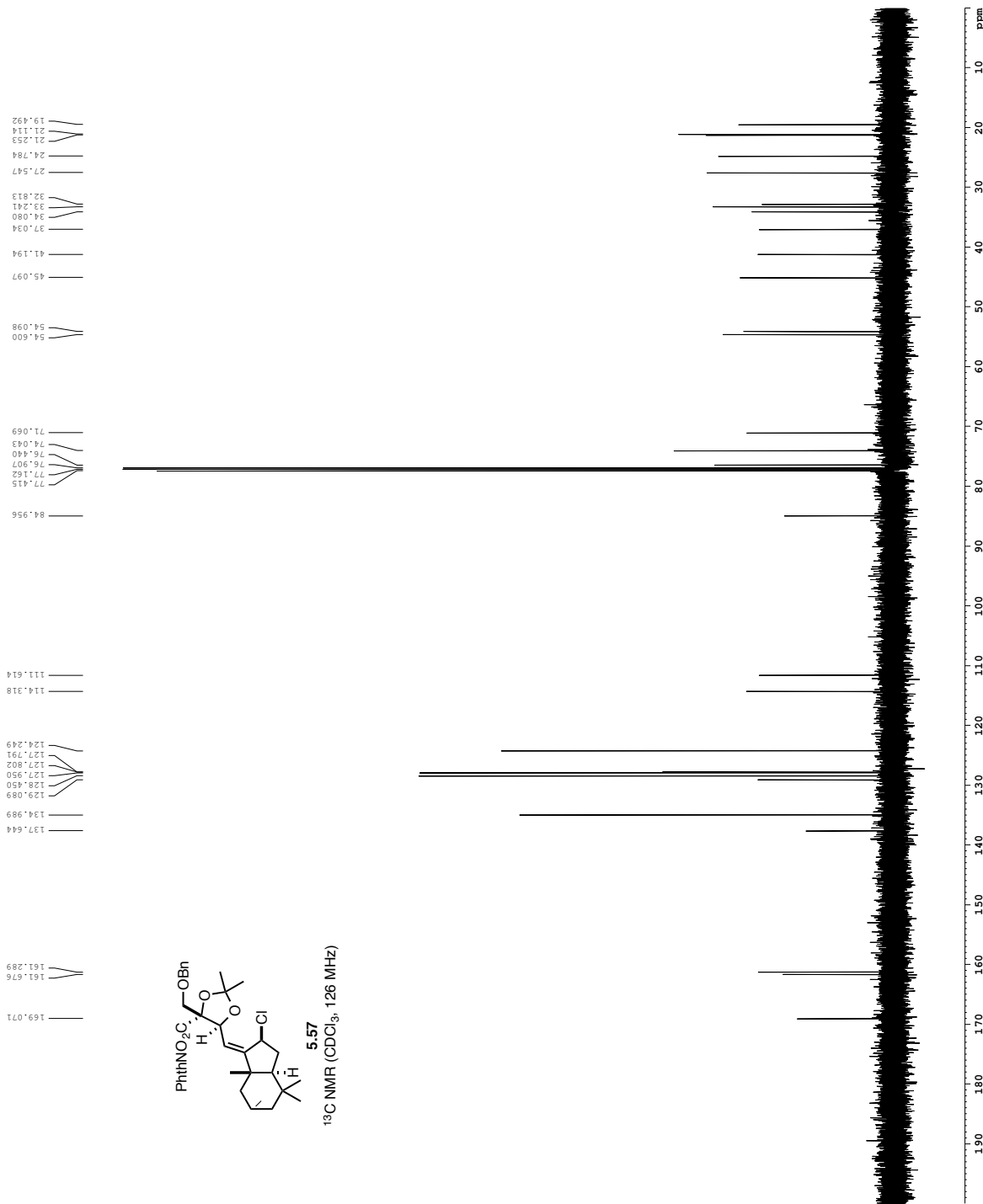
```



¹H NMR (CDCl₃, 500 MHz)



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



```

Current Data Parameters
NAME          DUT-IV-271
PROCNO       1
PROBNO       1
F2 - Acquisition Parameters
Date_        20141206
Time         11.49
INSTRUM      cryo500
PROBHD       5 mm cryoProbe
PULPROG      zgpg30
SOLVENT      CDCl3
NS           269
DS           16
SWH           30303.06 Hz
AQ           1.0813440 sec
RG           7298.2
DM           16.500 usec
DE           6.00 usec
TE           298.0 K
D1           0.95000000 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
P13          120.00 dB
P14          120.00 dB
SFO1         125.7942548 MHz
SF1          2.70 dB
SF2          2.70 dB
SFO2         500.2225011 MHz

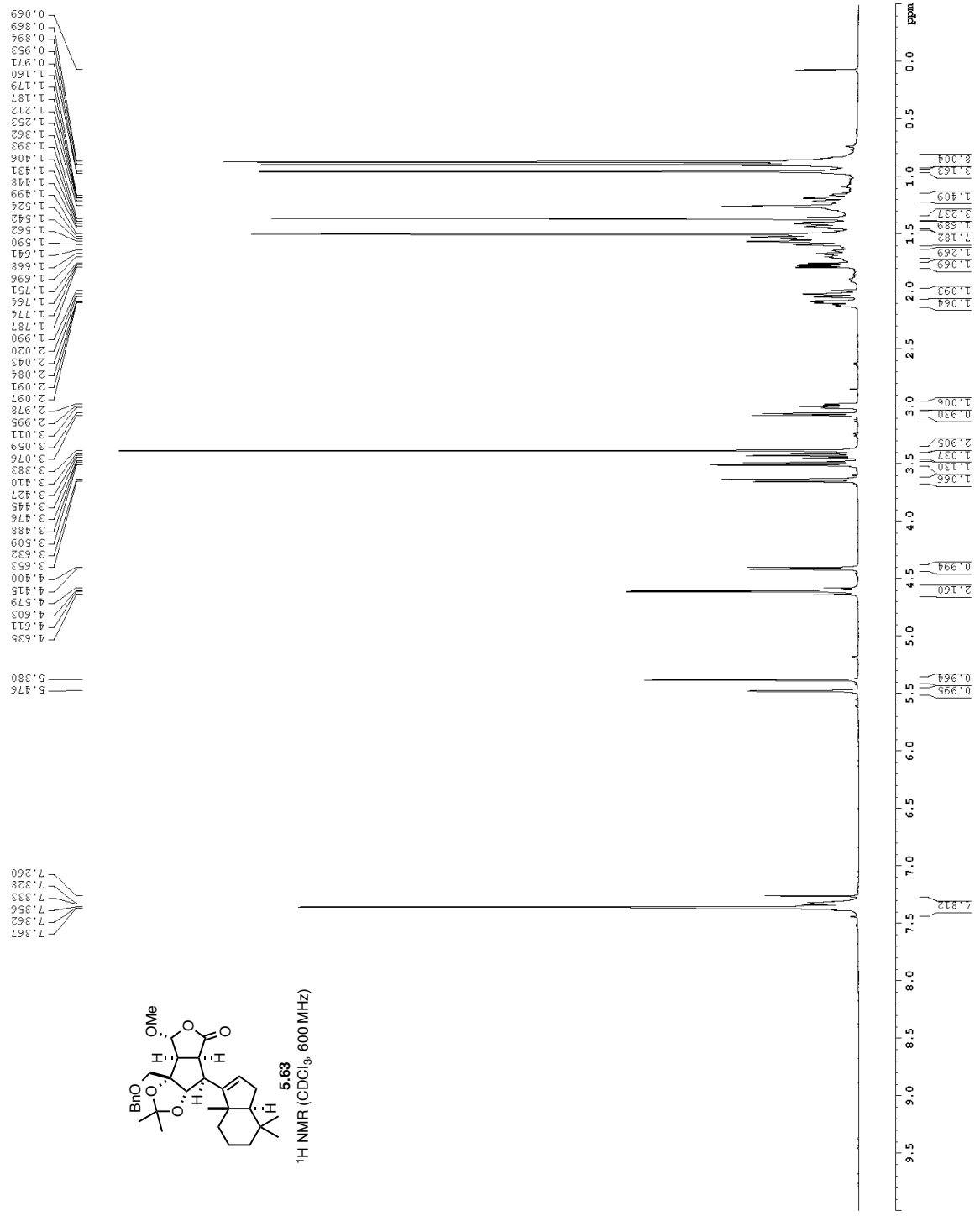
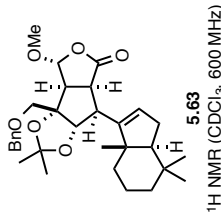
===== CHANNEL f2 =====
CFDPRG[2]    waltz16
NUC2         1H
PCPDZ        100.00 usec
P2           24.50 dB
P11          24.50 dB
P12          24.50 dB
SFO2         500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]     SINE.100
GPNAM[2]     SINE.100
GZX         0 %
GZY         0 %
GFY1        0 %
GFY2        0 %
GEZ1        30.00 %
GEZ2        50.00 %
P13         100.00 usec
P14         100.00 usec
F2 - Processing parameters
SI           65536
WDW          no
SSB          0
GB           0
PC           2.00
  
```

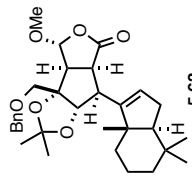
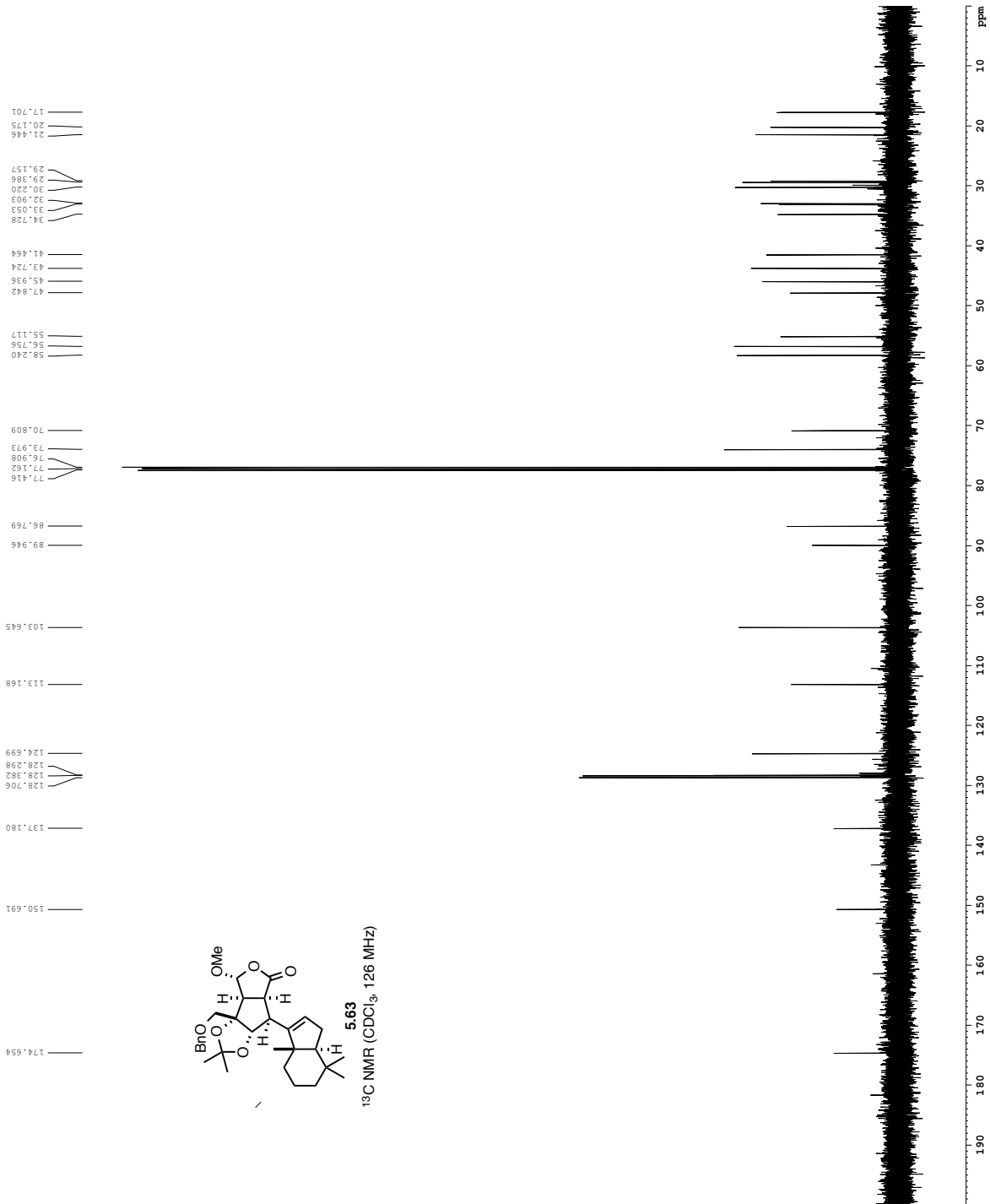
1H spectrum

```

===== Data Parameters
NAME      217-V-103
PROCNO    1
PR      20
PC - Acquisition Parameters
Date_     20150228
Time     07:30:06
INSTRUM   spect
PROBHD    5 mm QNP1H-M
TD        65536
SOLVENT   CDCl3
NS       30
DS       0
AQ       0.81300000 sec
FIDRES   0.450014 Hz
AQRES    0.399772 sec
RG        62.400 usec
IN       2962.0 K
TE        296.200 K
===== CHANNEL f1 =====
NUC1      1H
PULPROG  zgpg30
PCPD1     500.130000 MHz
SFO1     500.130000 MHz
GPA1     1.600 dB
===== Processing parameters =====
SI      65536
SF      500.130000 MHz
WDW     EM
SSB     0
GB      0
PC      4.00
  
```



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



¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME DJI-V-07
 EXPNO 6
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20150128
 Time 8.37
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 260
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.813480 Hz
 AQ 1.0813480 sec
 RG 6502
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 D11 0.0020000 sec
 D16 0.0020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRR 0.01500000 sec
 F2 33.10 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 120.00 dB
 SFO1 125.7942568 MHz
 SFO2 2.70 dB
 SF2 2.70 dB
 SFNAM[1] Cfp60,0.5,20.1
 SFNAM[2] Cfp60 comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CFPDPRG[2] waltz16
 NUC2 1H
 P2 100.00 usec
 P21 4.50 dB
 P22 4.50 dB
 P12 2.70 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 Hz
 GB 0
 PC 2.00

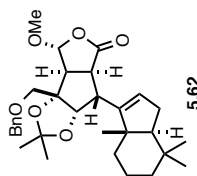
1H spectrum

```

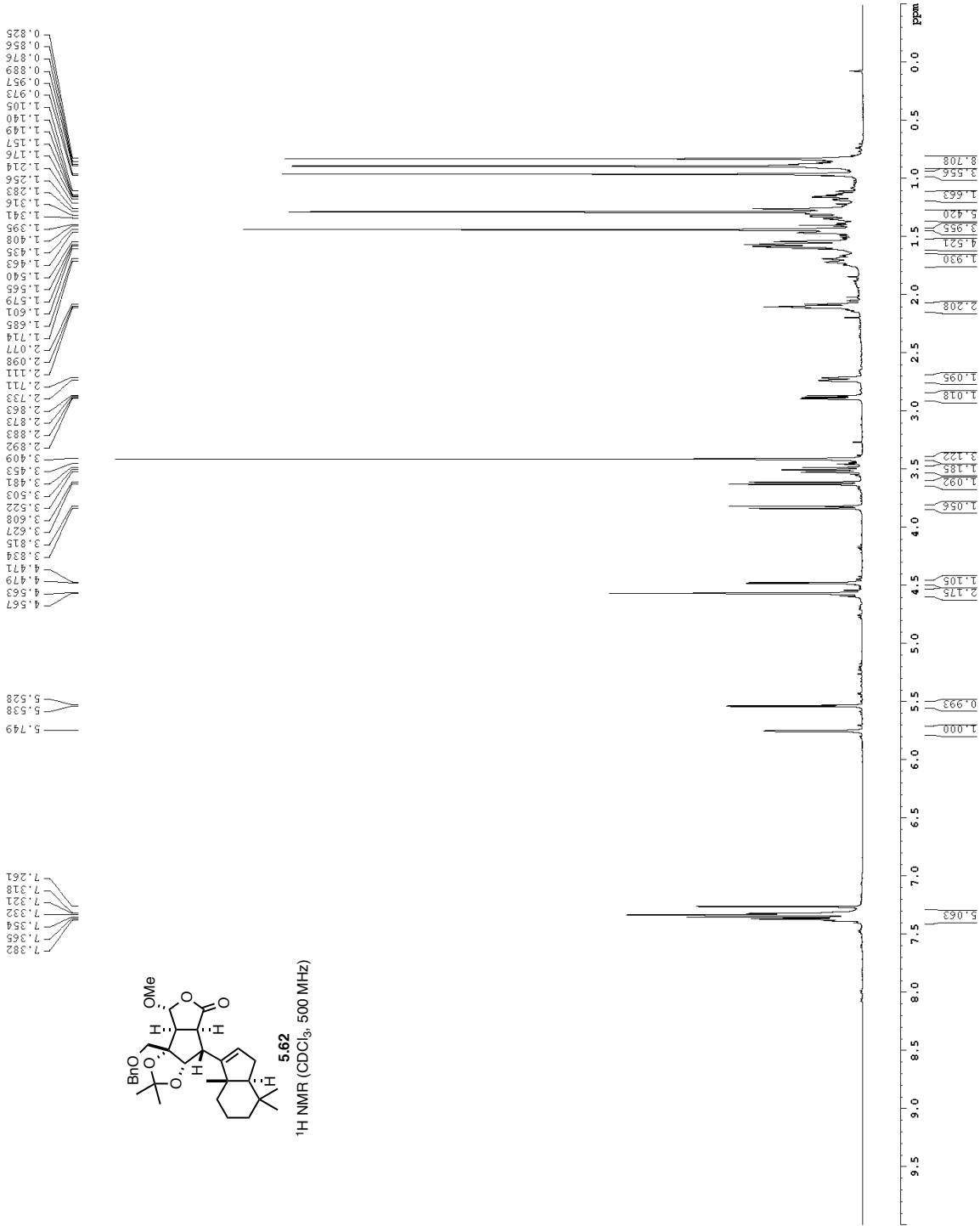
=====
Output Data Parameters
NAME      2JTY-103
PROCNO    1
Date_    20150228
Time     17:20:00
PROGRAM   5 nm QNP1 JC
ID        16202
INSTRUM   CPDPR07
NUC1      13C
NUC2      13C
P1        0.01500000 sec
===== CHANNEL f1 =====
PULPROG  zgpg30
PC        7.00 uSFC
PR        500.2620000 MHz
RG        16.00 dB
SI        32768
SF        500.2620000 MHz
SSB       0
===== CHANNEL f2 =====
PC        0.00000000 sec
=====

```

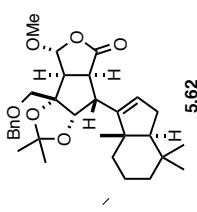
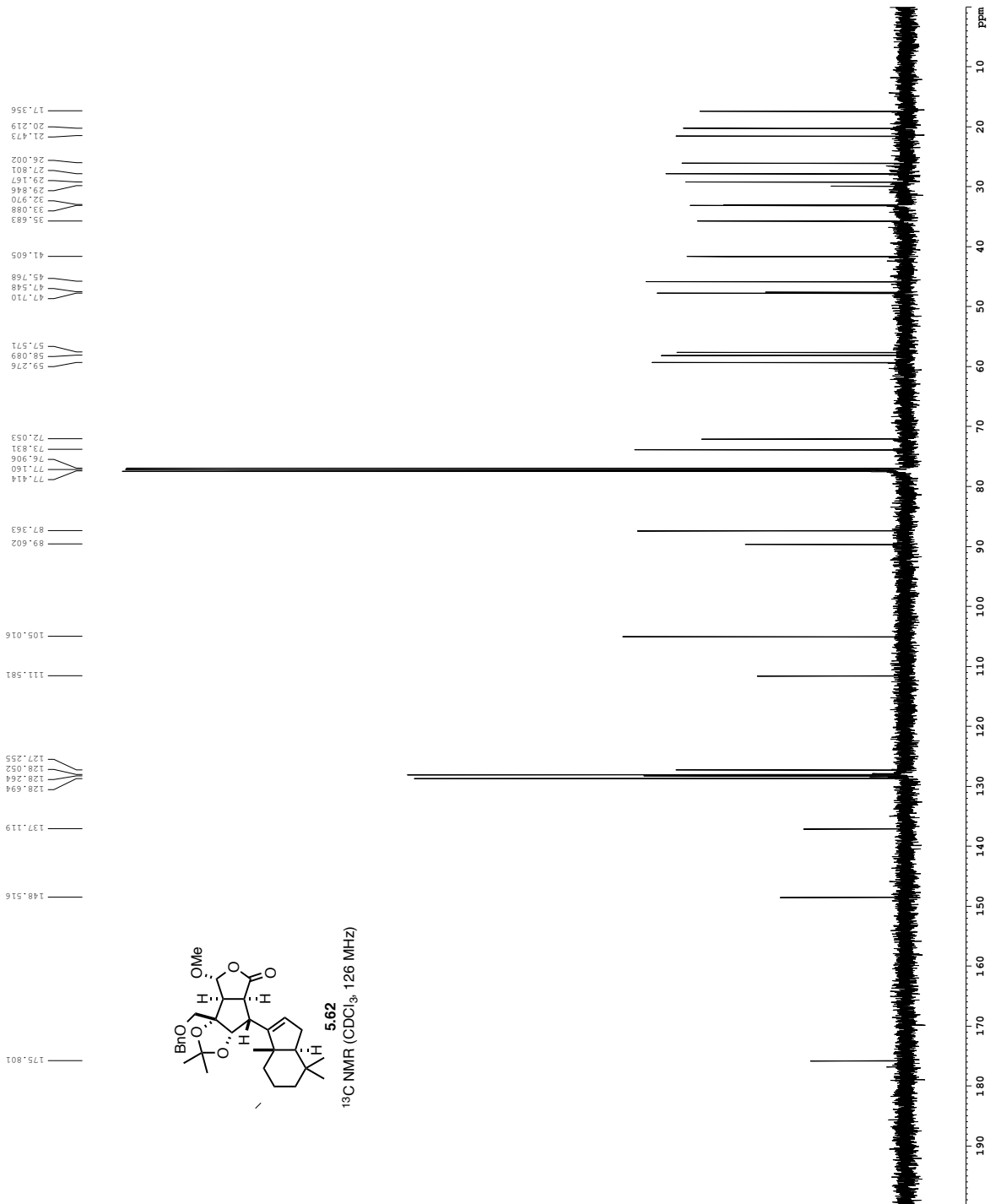
4.567, 4.563, 4.479, 4.471, 3.834, 3.815, 3.627, 3.608, 3.522, 3.503, 3.481, 3.453, 3.409, 2.892, 2.883, 2.873, 2.759, 2.711, 2.098, 2.077, 1.714, 1.685, 1.601, 1.579, 1.565, 1.540, 1.463, 1.435, 1.408, 1.395, 1.341, 1.316, 1.283, 1.214, 1.157, 1.149, 1.140, 1.105, 0.973, 0.957, 0.889, 0.876, 0.825



5.62
 1H NMR (CDCl₃, 500 MHz)



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



5.62
13C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME          DUT-V-056
EXPNO        6
PROCNO       1
F2 - Acquisition Parameters
Date_        20150225
Time         16.33
INSTRUM      cryo500
PROBHD       5 mm CPIC1H-
PULPROG      Spinechop200.prd
TD           65536
SOLVENT      CDCl3
NS           135
DS           0
SWH           30303.031 Hz
AQ           0.8613460 Hz
RG           1.0813440 sec
RG           3251
DM           16.500 usec
DE           6.00 usec
TE           298.0 K
D1           0.2500000 sec
d11          0.0000000 sec
D16          0.0020000 sec
d17          0.0019600 sec
MCREST       0 sec
MCWRK        0.01500000 sec
F2           33.10 usec

===== CHANNEL f1 =====
NUC1         13C
P1           16.55 usec
P11          500.00 usec
P12          2000.00 usec
PL0          120.00 dB
PL1          20.00 dB
PL2          24.50 dB
SFO1         125.7942548 MHz
SF02         2.70 dB
SF2          2.70 dB
SFO1         125.7942548 MHz
SFO2         2.70 dB
SFO1         125.7942548 MHz
SFO2         2.70 dB
SFO1         125.7942548 MHz
SFO2         2.70 dB
===== CHANNEL f2 =====
CFPPRG2      waltz16
NUC2         1H
PCPD2        100.00 usec
PL0          120.00 dB
PL1          20.00 dB
PL2          24.50 dB
SFO1         500.2225011 MHz
SFO2         500.2225011 MHz

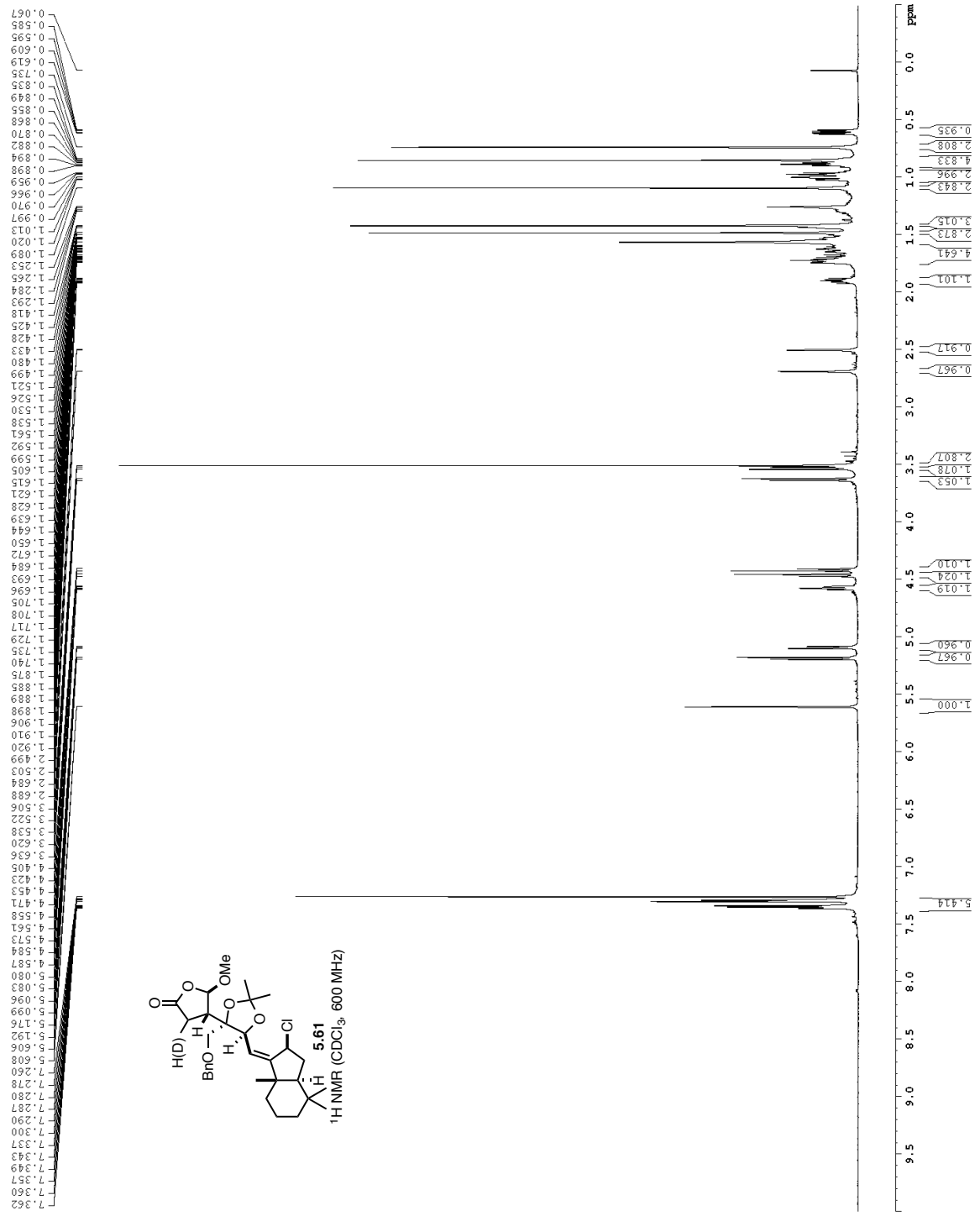
===== GRADIENT CHANNEL =====
GPNAM[1]     SINE.100
GPNAM[2]     SINE.100
GPA1         0 %
GPA2         0 %
GPX1         0 %
GPX2         0 %
GPY1         0 %
GPY2         0 %
GFZ1         30.00 %
GFZ2         50.00 %
P15          500.00 usec
P16          1000.00 usec

F2 - Processing parameters
SI           65536
SF           125.7604085 MHz
WDW          EM
SSB          0
GB           0
PC           2.00
    
```

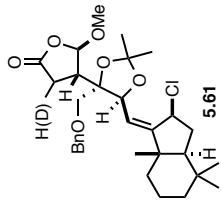
1H spectrum

```

Operator: 141101
NAME: 20211109
PROCNO: 1
PR: 1
PC: 1
Date_: 20211109
TIME: 11:00
INSTRUM: spect
PROBHD: 5 mm TRL HLT3
TD: 65536
AQ: 0.16600000 sec
RG: 327.680
DELTA: 0.10000000 sec
NS: 0
DS: 0
SFO1: 601.500 MHz
FIDRES: 0.099842 Hz
AQ: 0.16600000 sec
RG: 327.680
IN: 32.000 usec
TE: 298.2 K
TD: 0.10000000 sec
===== CHANNEL f1 =====
NUC1: 1H
PULPROG: zgpg30
PC: 8.000 usec
PUL1: 24.00000000 usec
===== Processing parameters =====
SI: 32768
SF: 600.136257 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
  
```



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



¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME DDT-V-263
 EXPNO 21
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 2015_08_22
 Time 9:12
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG SpinEcho309p.prd
 TD 65536
 SOLVENT CDCl₃
 NS 842
 DS 0
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.081340 sec
 RG 5792.6
 KB 16.00 usec
 DB 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 ACQPRG 1
 MCHST 0 sec
 MCHCK 0.01500000 sec
 P2 33.10 usec

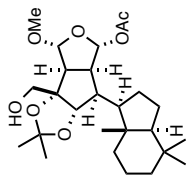
===== CHANNEL f1 =====
 NUC1 13C
 P1 16.50 usec
 PL1 500.00 usec
 P12 2000.00 usec
 PL2 120.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF2 2.70 dB
 SFNAM[1] Cry60_0.5.20.1
 SFNAM[2] Cry60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 100.00 usec
 PL2 1.60 dB
 PL12 24.50 dB
 SFO2 500.2225011 MHz

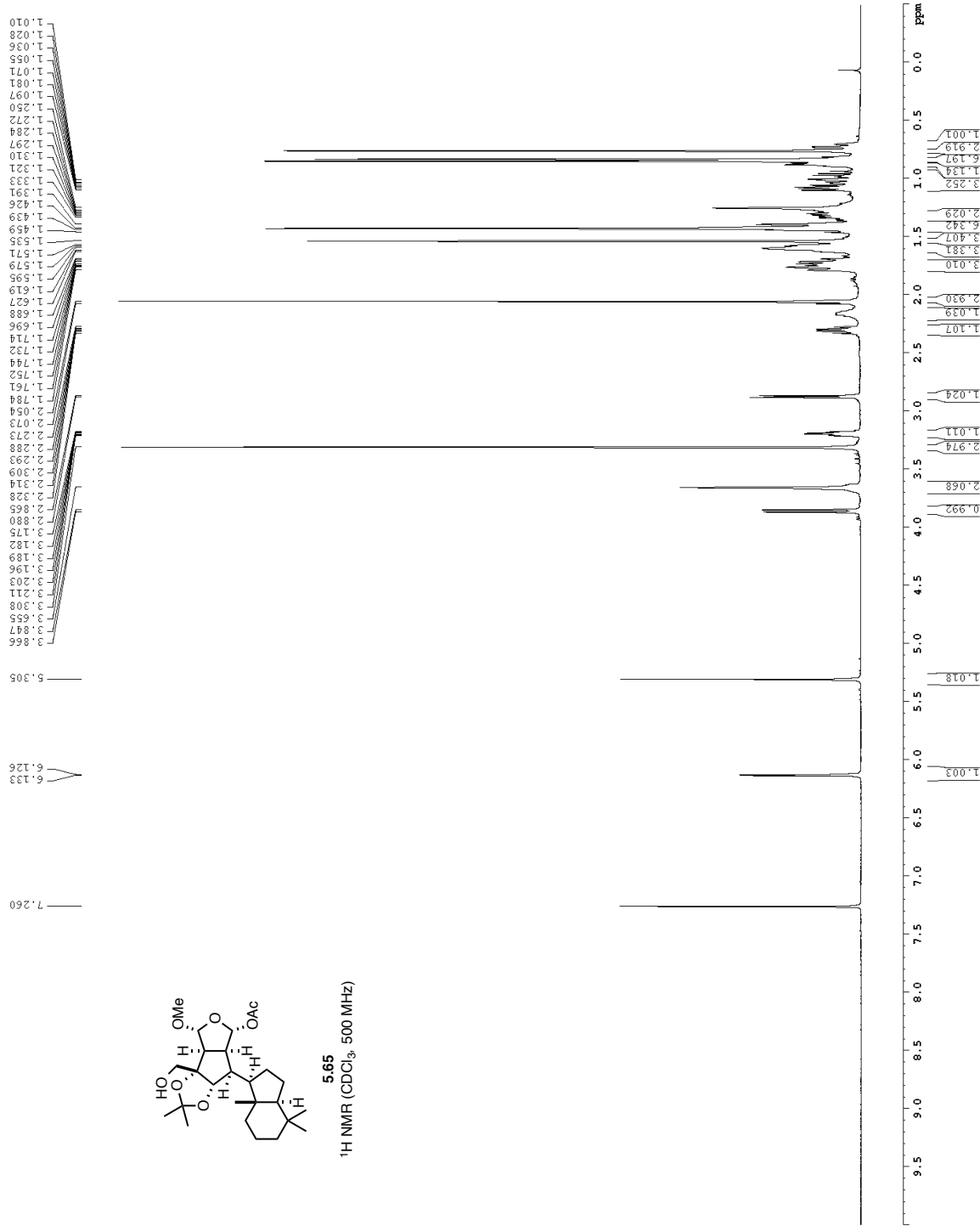
===== GRADIENT CHANNEL =====
 GFNAM[1] SINE.100
 GFNAM[2] SINE.100
 GF1 0 %
 GF2 0 %
 GF3 0 %
 GF4 0 %
 GF21 30.00 %
 GF22 50.00 %
 PL5 500.00 usec
 PL6 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.7804080 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GC 0
 PC 2.00

1H spectrum

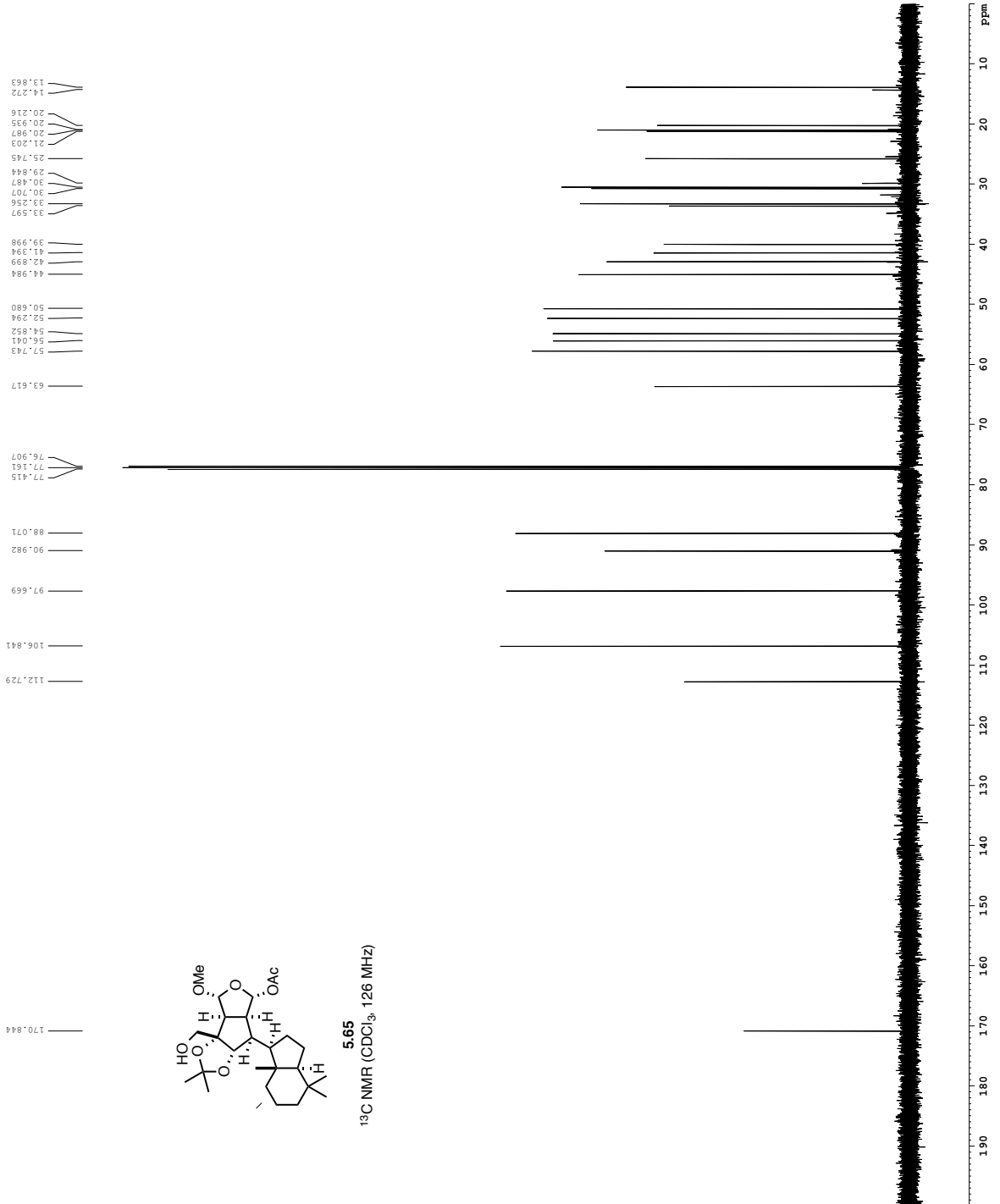
```
===== Data Parameters =====
NAME      517-7-210
EXPNO     5
PROCNO    1
Date_      20150808
Time      13:07
Date Acq   20150808
Time Acq   13:07
PROBHD    5 mm QNP1H-H
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        4096
DS        4
AQ        0.00000000 sec
RG        655.36
FIDRES    0.00000000 Hz
AQ        0.00000000 sec
SFO1      500.225015 MHz
SFO2      125.761155 MHz
SFO3      125.761155 MHz
SFO4      125.761155 MHz
SFO5      125.761155 MHz
SFO6      125.761155 MHz
SFO7      125.761155 MHz
SFO8      125.761155 MHz
SFO9      125.761155 MHz
SFO10     125.761155 MHz
SFO11     125.761155 MHz
SFO12     125.761155 MHz
SFO13     125.761155 MHz
SFO14     125.761155 MHz
SFO15     125.761155 MHz
SFO16     125.761155 MHz
SFO17     125.761155 MHz
SFO18     125.761155 MHz
SFO19     125.761155 MHz
SFO20     125.761155 MHz
SFO21     125.761155 MHz
SFO22     125.761155 MHz
SFO23     125.761155 MHz
SFO24     125.761155 MHz
SFO25     125.761155 MHz
SFO26     125.761155 MHz
SFO27     125.761155 MHz
SFO28     125.761155 MHz
SFO29     125.761155 MHz
SFO30     125.761155 MHz
SFO31     125.761155 MHz
SFO32     125.761155 MHz
SFO33     125.761155 MHz
SFO34     125.761155 MHz
SFO35     125.761155 MHz
SFO36     125.761155 MHz
SFO37     125.761155 MHz
SFO38     125.761155 MHz
SFO39     125.761155 MHz
SFO40     125.761155 MHz
SFO41     125.761155 MHz
SFO42     125.761155 MHz
SFO43     125.761155 MHz
SFO44     125.761155 MHz
SFO45     125.761155 MHz
SFO46     125.761155 MHz
SFO47     125.761155 MHz
SFO48     125.761155 MHz
SFO49     125.761155 MHz
SFO50     125.761155 MHz
SFO51     125.761155 MHz
SFO52     125.761155 MHz
SFO53     125.761155 MHz
SFO54     125.761155 MHz
SFO55     125.761155 MHz
SFO56     125.761155 MHz
SFO57     125.761155 MHz
SFO58     125.761155 MHz
SFO59     125.761155 MHz
SFO60     125.761155 MHz
SFO61     125.761155 MHz
SFO62     125.761155 MHz
SFO63     125.761155 MHz
SFO64     125.761155 MHz
SFO65     125.761155 MHz
SFO66     125.761155 MHz
SFO67     125.761155 MHz
SFO68     125.761155 MHz
SFO69     125.761155 MHz
SFO70     125.761155 MHz
SFO71     125.761155 MHz
SFO72     125.761155 MHz
SFO73     125.761155 MHz
SFO74     125.761155 MHz
SFO75     125.761155 MHz
SFO76     125.761155 MHz
SFO77     125.761155 MHz
SFO78     125.761155 MHz
SFO79     125.761155 MHz
SFO80     125.761155 MHz
SFO81     125.761155 MHz
SFO82     125.761155 MHz
SFO83     125.761155 MHz
SFO84     125.761155 MHz
SFO85     125.761155 MHz
SFO86     125.761155 MHz
SFO87     125.761155 MHz
SFO88     125.761155 MHz
SFO89     125.761155 MHz
SFO90     125.761155 MHz
SFO91     125.761155 MHz
SFO92     125.761155 MHz
SFO93     125.761155 MHz
SFO94     125.761155 MHz
SFO95     125.761155 MHz
SFO96     125.761155 MHz
SFO97     125.761155 MHz
SFO98     125.761155 MHz
SFO99     125.761155 MHz
SFO100    125.761155 MHz
===== Processing parameters =====
RG1       655.36
RG2       655.36
RG3       655.36
RG4       655.36
RG5       655.36
RG6       655.36
RG7       655.36
RG8       655.36
RG9       655.36
RG10      655.36
RG11      655.36
RG12      655.36
RG13      655.36
RG14      655.36
RG15      655.36
RG16      655.36
RG17      655.36
RG18      655.36
RG19      655.36
RG20      655.36
RG21      655.36
RG22      655.36
RG23      655.36
RG24      655.36
RG25      655.36
RG26      655.36
RG27      655.36
RG28      655.36
RG29      655.36
RG30      655.36
RG31      655.36
RG32      655.36
RG33      655.36
RG34      655.36
RG35      655.36
RG36      655.36
RG37      655.36
RG38      655.36
RG39      655.36
RG40      655.36
RG41      655.36
RG42      655.36
RG43      655.36
RG44      655.36
RG45      655.36
RG46      655.36
RG47      655.36
RG48      655.36
RG49      655.36
RG50      655.36
RG51      655.36
RG52      655.36
RG53      655.36
RG54      655.36
RG55      655.36
RG56      655.36
RG57      655.36
RG58      655.36
RG59      655.36
RG60      655.36
RG61      655.36
RG62      655.36
RG63      655.36
RG64      655.36
RG65      655.36
RG66      655.36
RG67      655.36
RG68      655.36
RG69      655.36
RG70      655.36
RG71      655.36
RG72      655.36
RG73      655.36
RG74      655.36
RG75      655.36
RG76      655.36
RG77      655.36
RG78      655.36
RG79      655.36
RG80      655.36
RG81      655.36
RG82      655.36
RG83      655.36
RG84      655.36
RG85      655.36
RG86      655.36
RG87      655.36
RG88      655.36
RG89      655.36
RG90      655.36
RG91      655.36
RG92      655.36
RG93      655.36
RG94      655.36
RG95      655.36
RG96      655.36
RG97      655.36
RG98      655.36
RG99      655.36
RG100     655.36
===== CDANDEL f1 =====
RG1       655.36
RG2       655.36
RG3       655.36
RG4       655.36
RG5       655.36
RG6       655.36
RG7       655.36
RG8       655.36
RG9       655.36
RG10      655.36
RG11      655.36
RG12      655.36
RG13      655.36
RG14      655.36
RG15      655.36
RG16      655.36
RG17      655.36
RG18      655.36
RG19      655.36
RG20      655.36
RG21      655.36
RG22      655.36
RG23      655.36
RG24      655.36
RG25      655.36
RG26      655.36
RG27      655.36
RG28      655.36
RG29      655.36
RG30      655.36
RG31      655.36
RG32      655.36
RG33      655.36
RG34      655.36
RG35      655.36
RG36      655.36
RG37      655.36
RG38      655.36
RG39      655.36
RG40      655.36
RG41      655.36
RG42      655.36
RG43      655.36
RG44      655.36
RG45      655.36
RG46      655.36
RG47      655.36
RG48      655.36
RG49      655.36
RG50      655.36
RG51      655.36
RG52      655.36
RG53      655.36
RG54      655.36
RG55      655.36
RG56      655.36
RG57      655.36
RG58      655.36
RG59      655.36
RG60      655.36
RG61      655.36
RG62      655.36
RG63      655.36
RG64      655.36
RG65      655.36
RG66      655.36
RG67      655.36
RG68      655.36
RG69      655.36
RG70      655.36
RG71      655.36
RG72      655.36
RG73      655.36
RG74      655.36
RG75      655.36
RG76      655.36
RG77      655.36
RG78      .030 Hz
RG79      0
RG80      4.00
```



5.65
1H NMR (CDCl₃, 500 MHz)



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



```

Current Data Parameters
NAME          DJT-V-270
EXPNO         6
PROCNO        1
F2 - Acquisition Parameters
Date_         20150824
Time          13.11
INSTRUM       cryo500
PROBHD        5 mm CPICHH-
PULPROG       SPHrEcho30-ppd
TD            65536
SOLVENT       CDCl3
NS            498
DS            0
SWH           30303.031 Hz
AQ           0.461346 Hz
RG           1.081346 sec
RG           4096
DM           16.500 usec
DE           6.00 usec
TE           298.0 K
D1           0.2500000 sec
d11          0.0000000 sec
d16          0.0020000 sec
d17          0.00019600 sec
MCREST        0 sec
MCWRK        0.01500000 sec
F2           33.10 usec

===== CHANNEL f1 =====
NUC1          13C
P1           16.55 usec
P11          500.00 usec
P12          2000.00 usec
PL0          120.00 dB
PL1          19.00 dB
PL2          125.7942548 MHz
SF01         500.1363011 MHz
SF2          2.70 dB
SFNAM[1]     Crp60.0.5.20.1
SFNAM[2]     Crp60comp.4
SFOPE1       0 Hz
SFOPE2       0 Hz

===== CHANNEL f2 =====
CFPPRG[2]    waltz16
NUC2          1H
PCPD2        100.00 usec
PL0          120.00 dB
PL1          19.00 dB
PL2          125.7942548 MHz
SF02         500.2225011 MHz

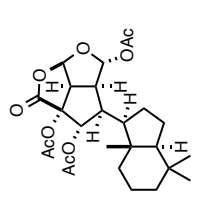
===== GRADIENT CHANNEL =====
GPNAM[1]     SINE.100
GPNAM[2]     SINE.100
GPA1         0 %
GPA2         0 %
GPX1         0 %
GPX2         0 %
GPF1         30.00 %
GPF2         50.00 %
P15          500.00 usec
P16          1000.00 usec

F2 - Processing parameters
SI           125.7804080 MHz
WDW          no
SSB          0 Hz
GB          0
PC          2.00
    
```

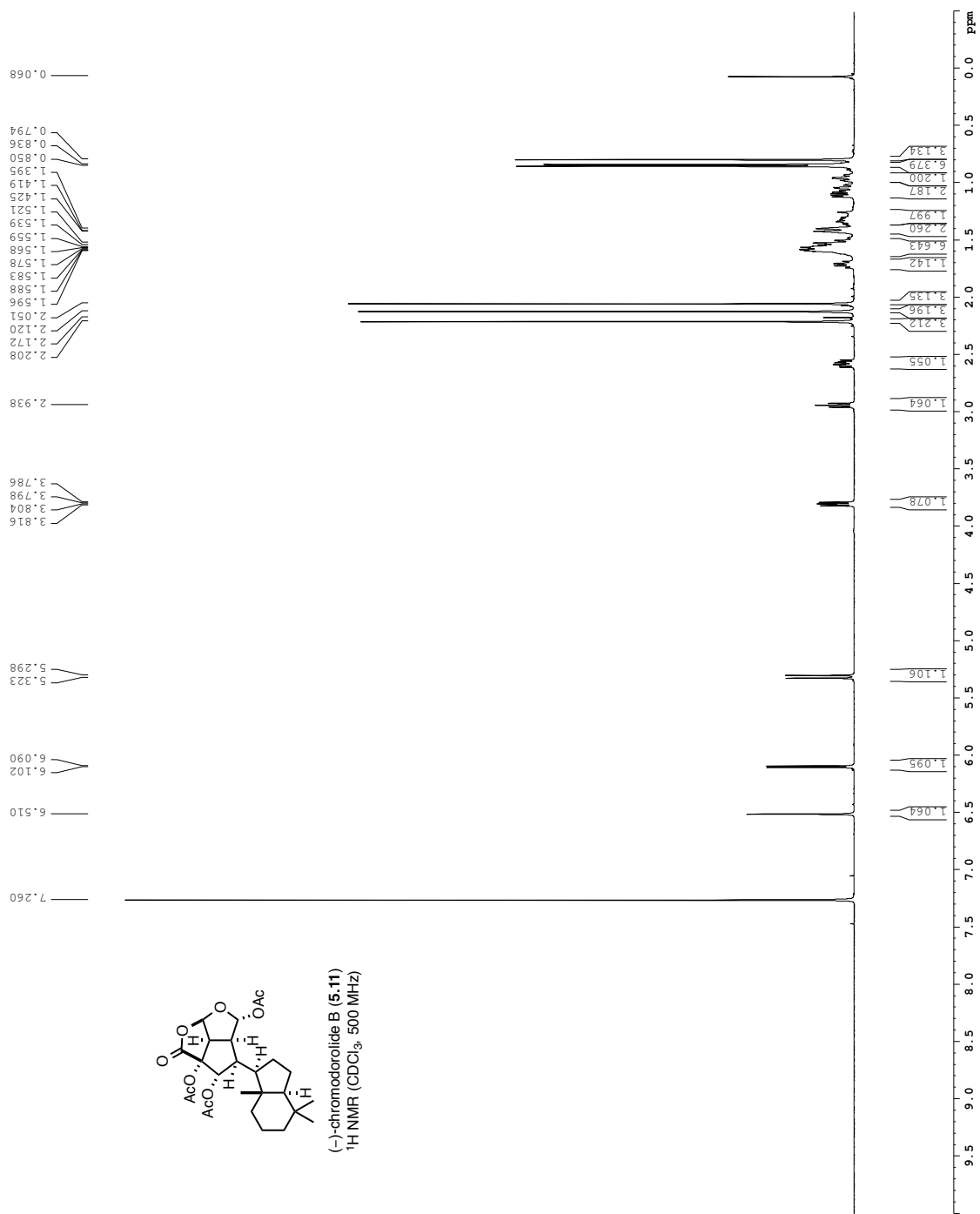
1H spectrum

```

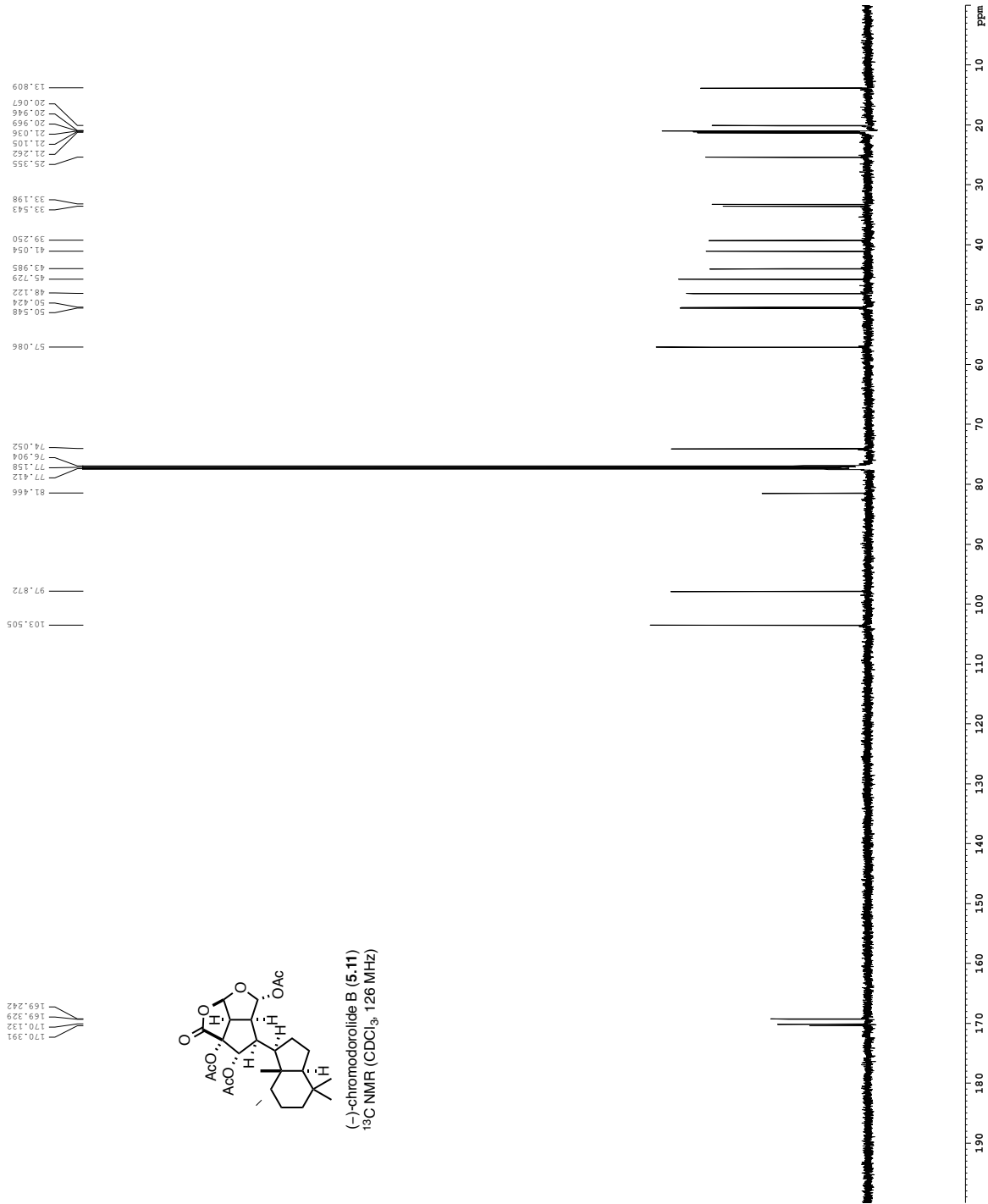
Current Data Parameters
NAME          DJT-V-272
EXPNO         5
PROCNO        1
F2 - Acquisition Parameters
Data_         20150907
Time_         9.43
INSTRUM       cryo500
PROBHD        5 mm CPTCI 1H-
PULPROG       zg30
TD            81728
SOLVENT       CDCl3
NS            140
DS            4
SFO1          500.136261 MHz
SFO2          500.136261 MHz
SFO3          500.136261 MHz
SFO4          500.136261 MHz
SFO5          500.136261 MHz
SFO6          500.136261 MHz
SFO7          500.136261 MHz
SFO8          500.136261 MHz
SFO9          500.136261 MHz
SFO10         500.136261 MHz
SFO11         500.136261 MHz
SFO12         500.136261 MHz
SFO13         500.136261 MHz
SFO14         500.136261 MHz
SFO15         500.136261 MHz
SFO16         500.136261 MHz
SFO17         500.136261 MHz
SFO18         500.136261 MHz
SFO19         500.136261 MHz
SFO20         500.136261 MHz
===== CHANNEL f1 =====
NUC1          1H
P1            7.50 usec
PL1           1.60 dB
SFO1         500.2235015 MHz
F2 - Processing parameters
SI            65536
SF           500.2235015 MHz
WDW           EM
SSB           0
LB           0.30 Hz
GB           0
PC           4.00
  
```



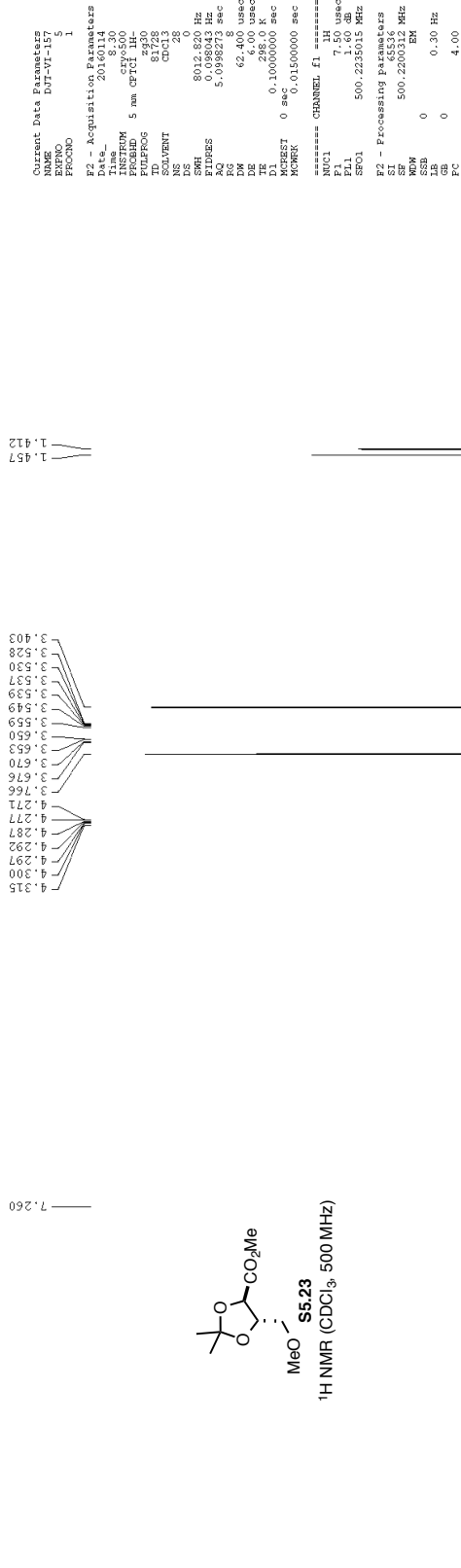
(-)-chromodorolide B (5.11)
¹H NMR (CDCl₃, 500 MHz)



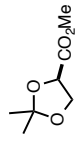
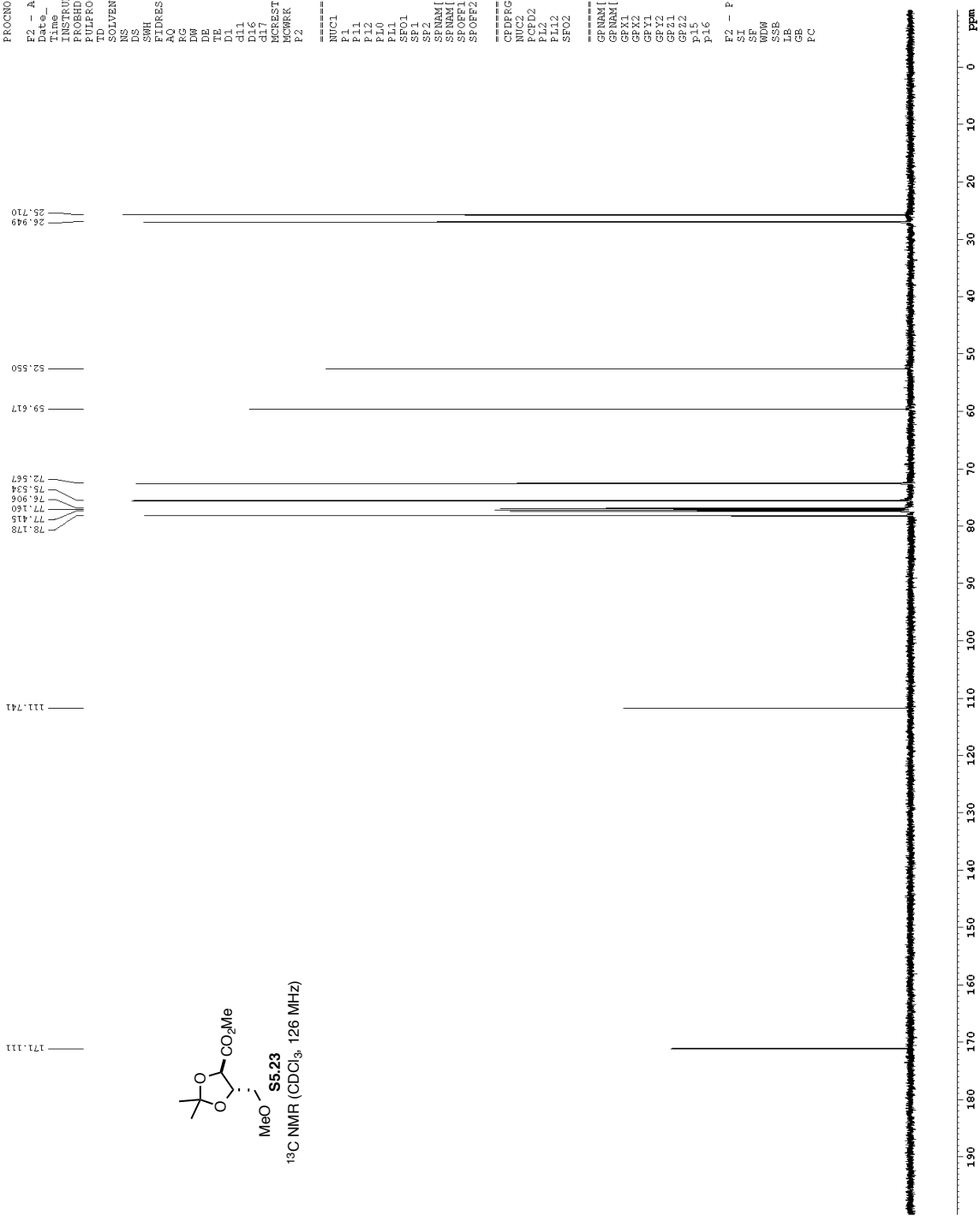
Z-restored spin-echo ¹³C spectrum with ¹H decoupling



1H spectrum



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



MeO S5.23
13C NMR (CDCl₃, 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   Spinechop930pp.prd
D1        6.5216
SOLVENT   CDCl3
NS         411
DS         1
SS        30303.031 Hz
SF         0.462388 Hz
AQ         1.0813440 sec
RG         512.6
RG2        162.60 usec
DE         6.00 usec
TE         298.0 K
D11        0.25000000 sec
d11        0.03000000 sec
p15        0.00200000 sec
p16        0.0019600 sec
MCREST    0 sec
MCORRK    0.01500000 sec
P2         33.10 usec

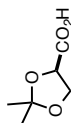
===== CHANNEL f1 =====
NUC1       13C
P1         16.15 usec
PL1        500.00 usec
P12        2000.00 usec
PL2        120.00 dB
PL11       -1.00 dB
SF01       125.7942548 MHz
SFO1        1.00 dB
SFO2        2.70 dB
SFOFF1     0 Hz
SFOFF2     0 Hz
SFNAM[1]   Cyp60.0.5.20.1
SFNAM[2]   Cyp60comp.4
SFOFF1     0 Hz
SFOFF2     0 Hz

===== CHANNEL f2 =====
CPDPRG2    waitz16
NUC2        1H
P2         100.00 usec
PCPD2      1.60 dB
PL2        24.50 dB
SFO2       500.2225011 MHz

===== GRADIENT CHANNEL =====
GFNAM[1]   SINE.100
GFNAM[2]   SINE.100
GX1        0 %
GX2        0 %
GY1        0 %
GY2        0 %
GZ1        30.00 %
GZ2        50.00 %
p15        500.00 usec
p16        1000.00 usec

F2 - Processing Parameters
SI         65536
SF         125.7804140 MHz
WDW        EM
SSB        0
LB         0
GB         1.00 Hz
PC         2.00
    
```

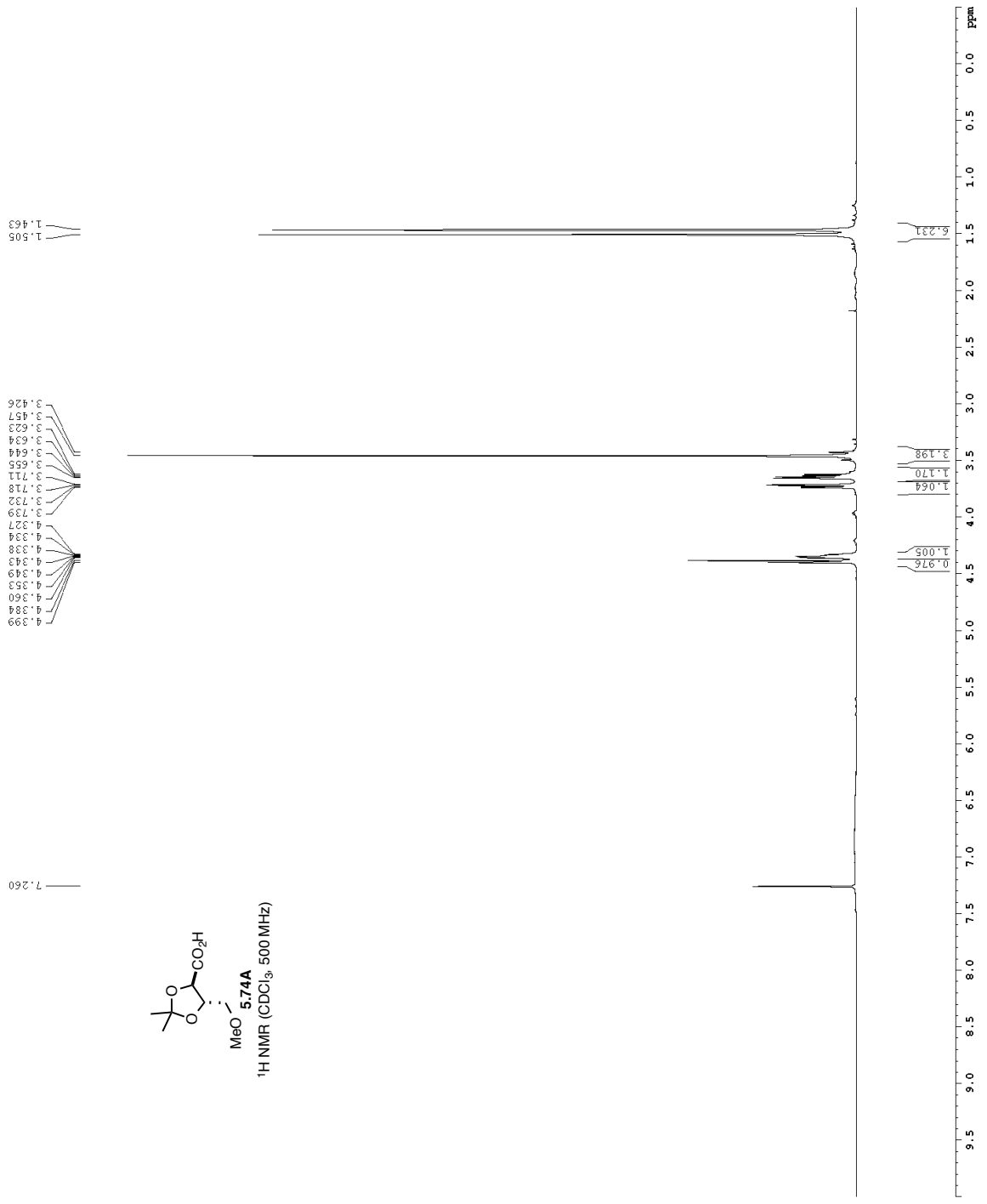
1H spectrum



MeO 5.74A
 1H NMR (CDCl₃, 500 MHz)

```

Current Data Parameters
NAME      DAT-1410
EXPNO     1
PROCNO    1
Date_     20160113
Data_     CHY-500
INSTRUM   spect
PROBHD    5 mm QNP1H-
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         20
DS         2
SWH        8012.820 Hz
FIDRES     1.955956 Hz
AQ         1.9397956 sec
RG          62.400 usec
DM          0.10000000 sec
DE         298.20 K
TE         0.10000000 sec
D1         0.10000000 sec
d11        0.01500000 sec
HWDW      EM
SFO        500.2200301 MHz
NUC1       13C
NUC2       1H
PC         4.00
===== CHANNEL f1 =====
P1         7.50 usec
PL1        0.00 dB
SFO1       500.225015 MHz
===== CHANNEL f2 =====
P2 - Processing parameters
SFO2       500.2200301 MHz
NUC1       1H
PC         4.00
    
```



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

```

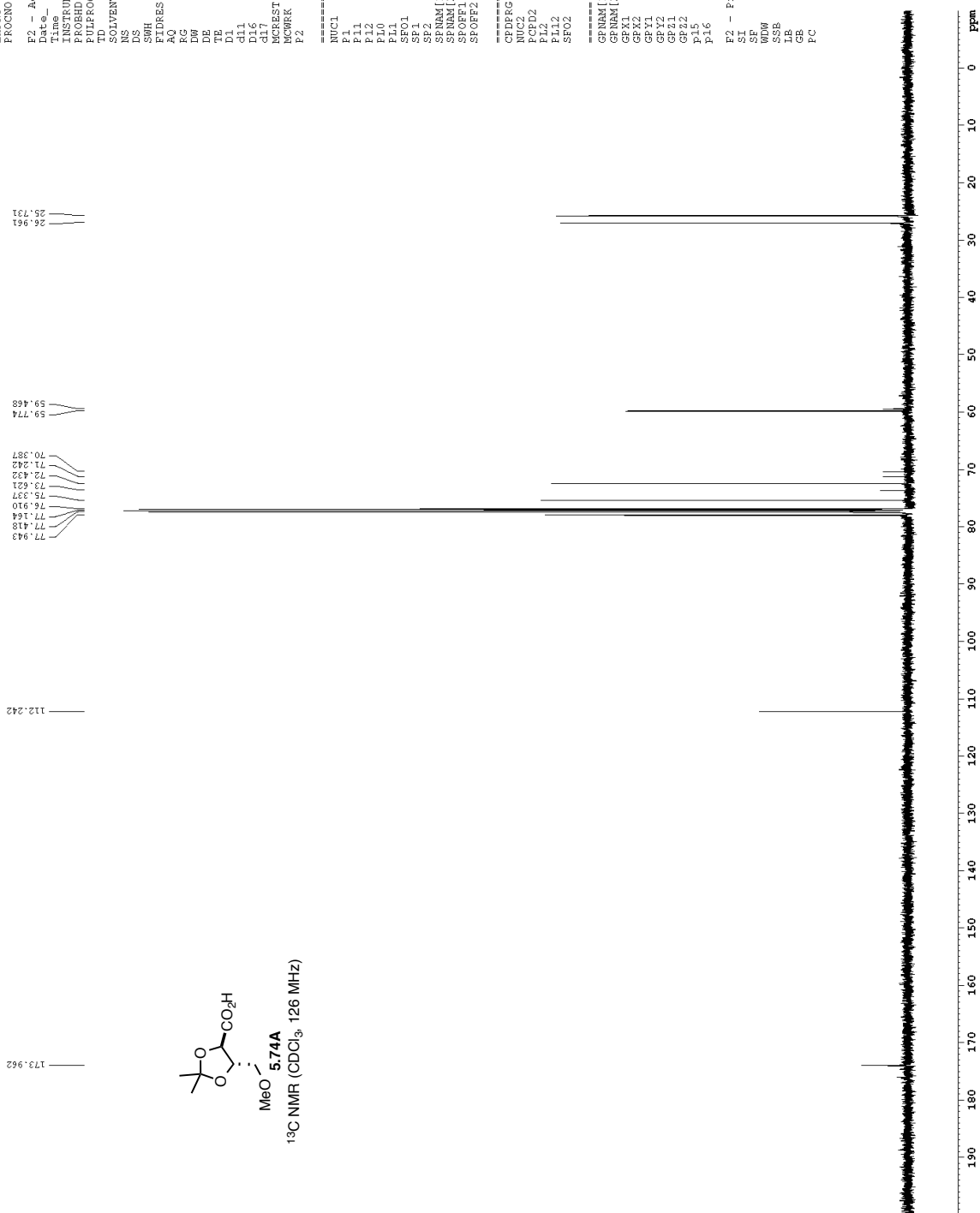
Current Data Parameters
NAME      DFT-VI-160
PROCNO    2
PROBHD    5 mm cryo500
PULPROG   Spinchop30Prd
TD         65536
SOLVENT   CDCl3
NS         328
DS         0
SWH        30303.0 Hz
FIDRES     0.46238 Hz
AQ         1.0813440 sec
RG         4597.6
DW         16.500 usec
DE         6.00 usec
TE         298.10 K
d11        0.0300000 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
P13        12.00 dB
P14        12.00 dB
SFO1       125.7942548 MHz
SF1        2.70 dB
SF2        2.70 dB
SFO2       500.00 usec
SF11       500.00 usec
SF12       24.50 dB
SF13       24.50 dB
SF14       24.50 dB
SFO2       500.2225011 MHz

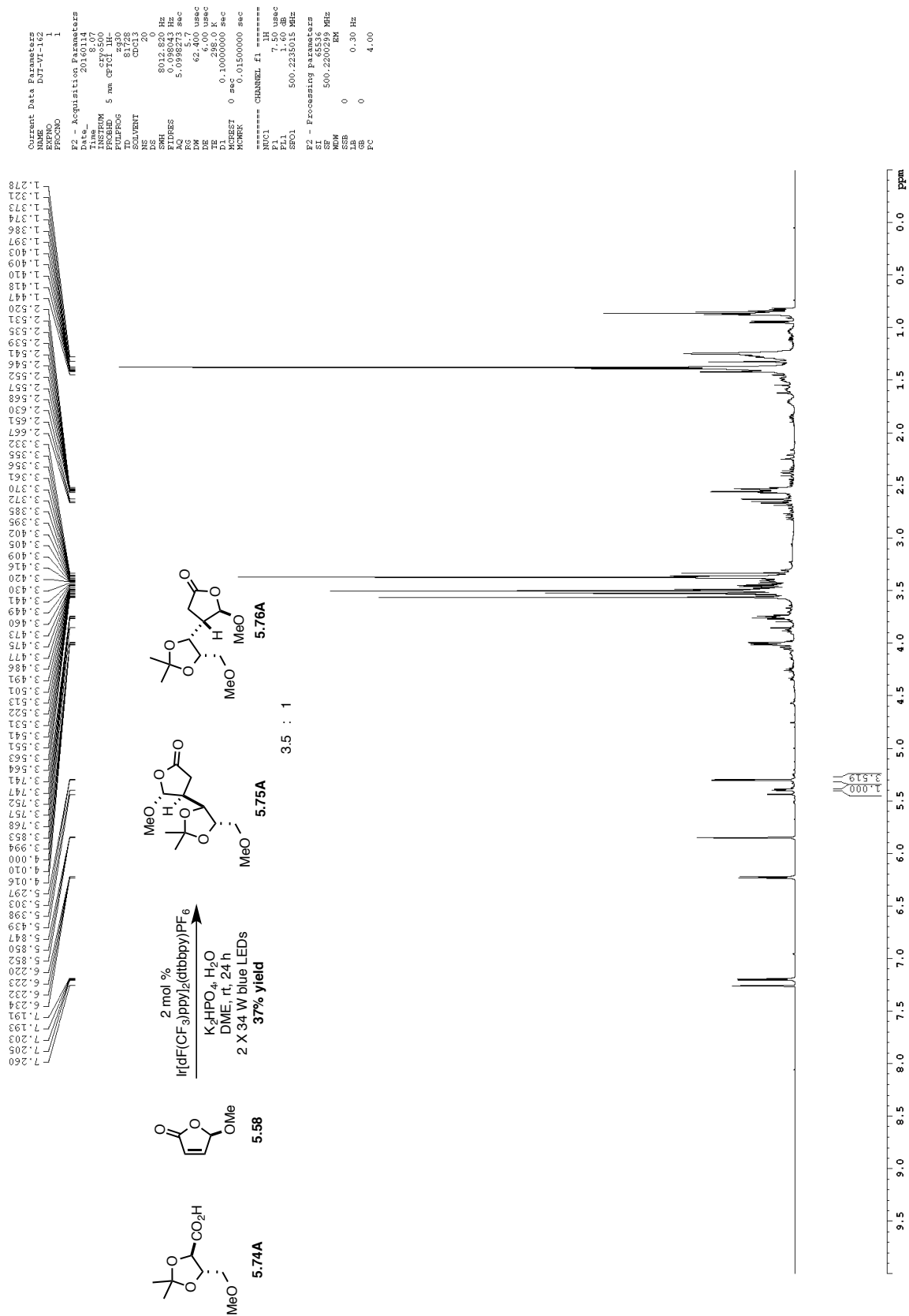
===== CHANNEL f2 =====
CFDEFG[2] waltz16
NUC2       1H
P2         100.00 usec
P21        100.00 usec
P22        100.00 usec
P23        24.50 dB
P24        24.50 dB
SFO2       500.2225011 MHz

===== GRADIENT CHANNEL =====
GPRAM[1]  SINE.100
GPRAM[2]  SINE.100
GXY1      0 %
GXY2      0 %
GZY1      0 %
GZY2      0 %
GZ1       30.00 %
GZ2       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
    
```

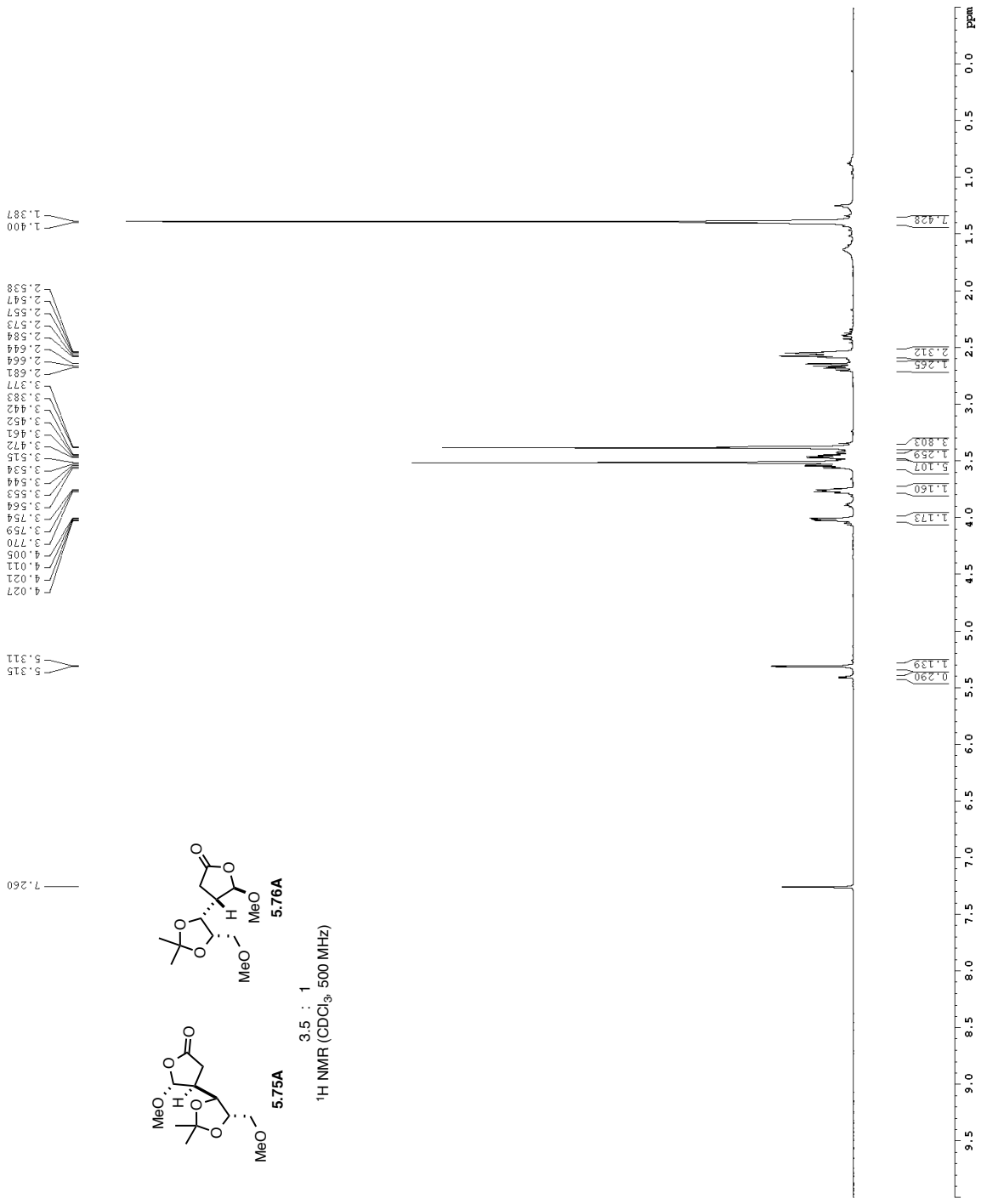
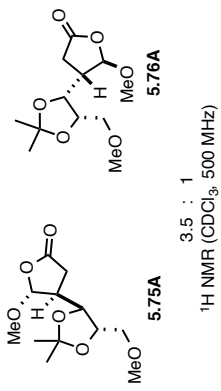


¹H spectrum

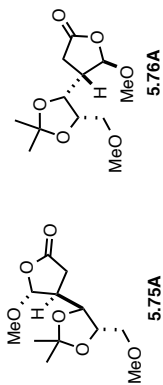


¹H spectrum

Current Data Parameters
NAME D17-VI-162
PROCNO 1
Date_ 20160603
INSTRUM cty-500
PROBHD 5 mm CPXI 1HC
TD 81728
SOLVENT CDCl3
NS 20
SRH 8012.820 Hz
NUC1 1H
PULPROG zgpg30
AQ 5.0988273 sec
RG 6.3
DE 62.400 usec
TE 298.0 K
D1 0.10000000 sec
D12REST 0 sec
D12 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 0.00 dB
SFO1 500.2235015 MHz
===== CHANNEL f2 =====
NUC1 13C
P2 16.00 usec
PL2 0.00 dB
SFO2 125.7613500 MHz



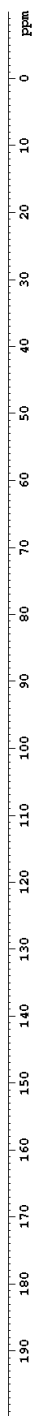
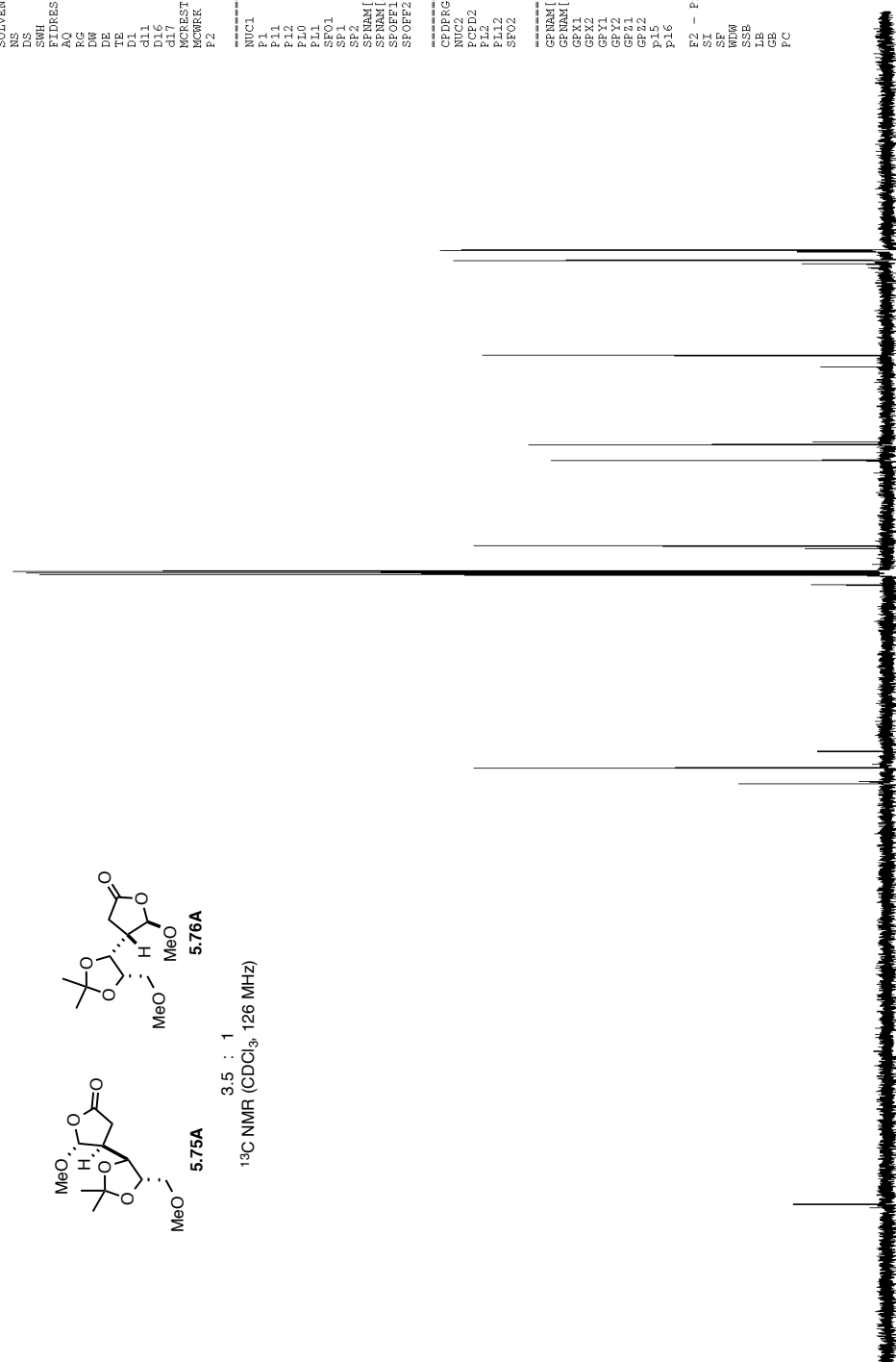
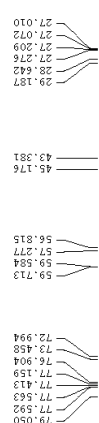
Z-restored spin-echo 13C spectrum with 1H decoupling



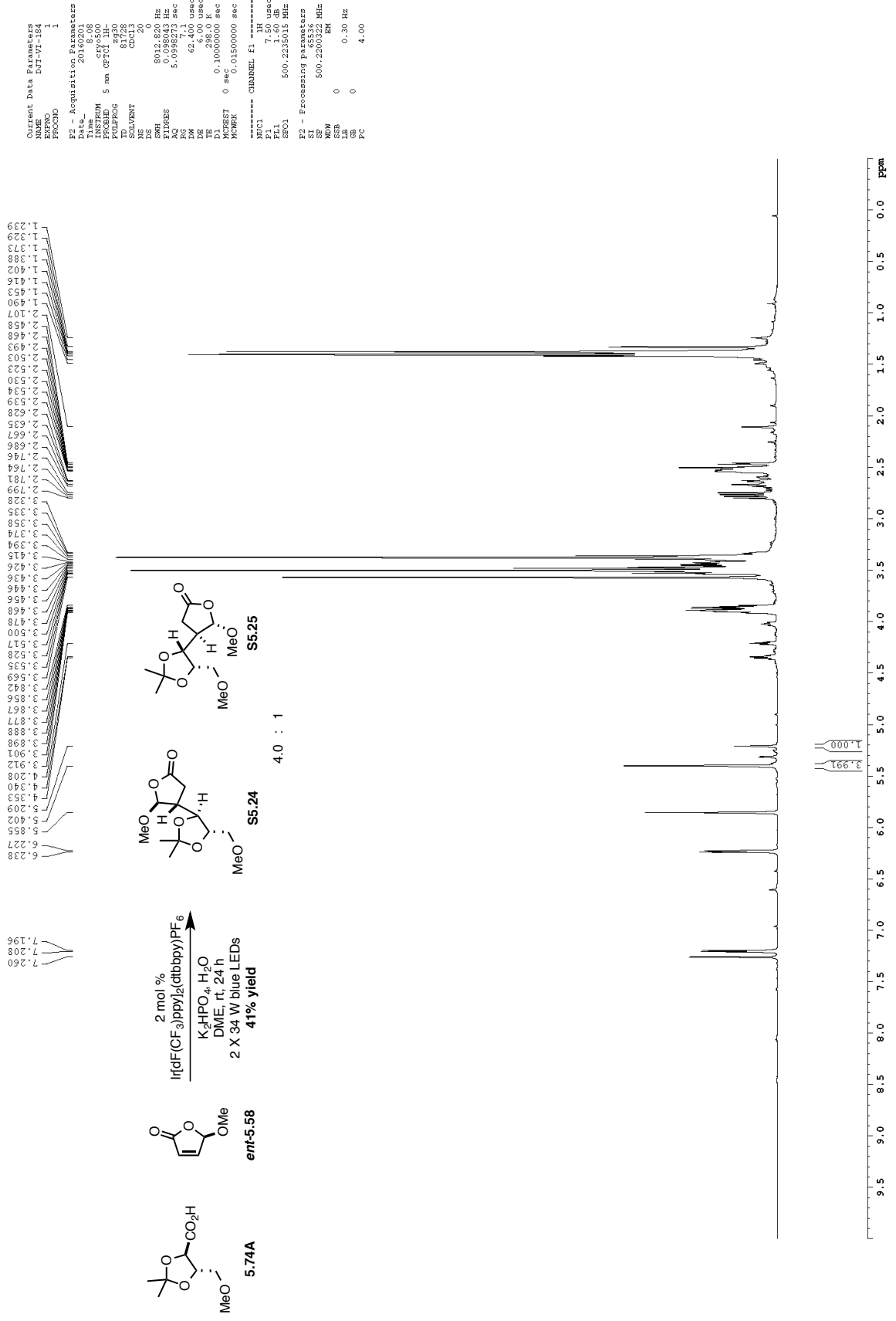
3.5 : 1
13C NMR (CDCl₃, 126 MHz)

```

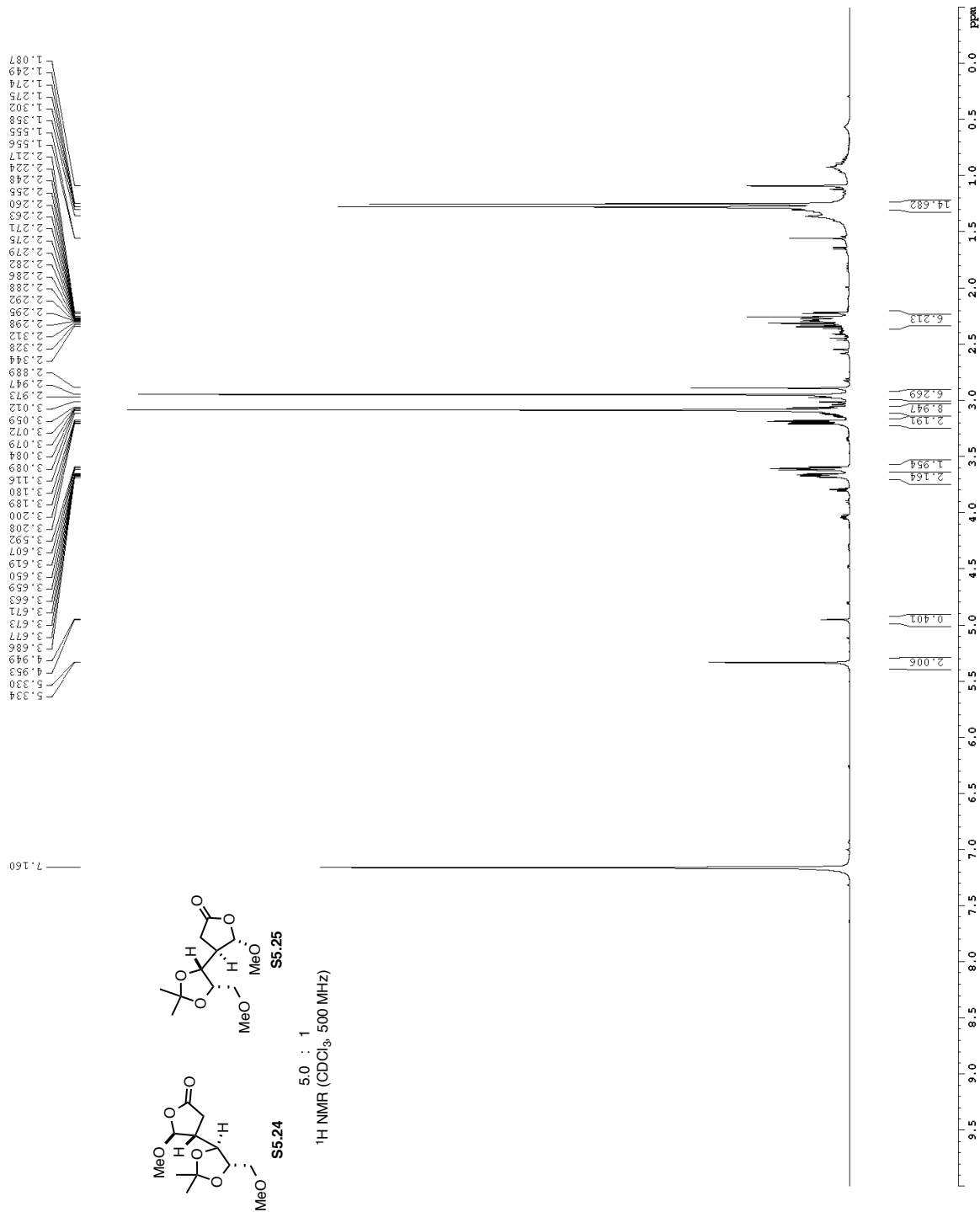
Current Data Parameters
NAME          D01-VI-162
EXPNO         0
PROCNO       1
F2 - Acquisition Parameters
Date_         20160115
Time         9:08
PROBHD       cryo-1H
PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           314
DS           0
SWH           30302.031 Hz
FIDRES       0.462388 Hz
AQ           1.0813440 sec
RG           7298.2
DE           16.500 usec
TE           300.2 K
D1           0.25000000 sec
d11          0.03000000 sec
d16          0.00020000 sec
d17          0.00019600 sec
MCREST       0 sec
MCMRR        0.01500000 sec
F2           33.10 usec
===== CHANNEL f1 =====
NUC1          13C
P1           16.55 usec
PL1          500.00 usec
PL2          200.00 usec
PL3          19.00 dB
PL4          -1.00 dB
SFO1         125.7942548 MHz
SF1          2.70 dB
SF2          2.70 dB
SFO2         500.2225011 MHz
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
P2           100.00 usec
PL2          1.60 dB
PL3          24.50 dB
SFO2         500.2225011 MHz
===== GRADIENT CHANNEL =====
GPRAM[1]     SINE.100
GPRAM[2]     SINE.100
GFX1         0 %
GFX2         0 %
GFY1         0 %
GFY2         0 %
GZ1          20.00 %
GZ2          20.00 %
P15          500.00 usec
P16          1000.00 usec
F2 - Processing parameters
SI           65536
SF           125.7804085 MHz
SFO          EN
SSB          0
LB           1.00 Hz
GB           0
PC           2.00
    
```



¹H spectrum



¹H spectrum



Current Data Parameters
NAME D17-VI-184
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160202
INSTRUM crys-500
PROBHD 5 mm CPCL H-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 0
DS 0
SWH 802.820 Hz
AQ 1.0000000 sec
RG 4.15
FIDRES 62.440 usec
AQ 6.000 usec
TE 298.0 K
DE 0.10000000 sec
PC 0.15000000 sec
MCMRES 0 sec

----- CHANNEL f1 -----
NUC1 ¹H
P1 7.50 usec
PL 0.00 dB
SFO1 500.2255015 MHz

F2 - Processing parameters
SI 65536
SF 500.2250007 MHz
WDW EM
SS 0
LB 0
GB 0
PC 4.00

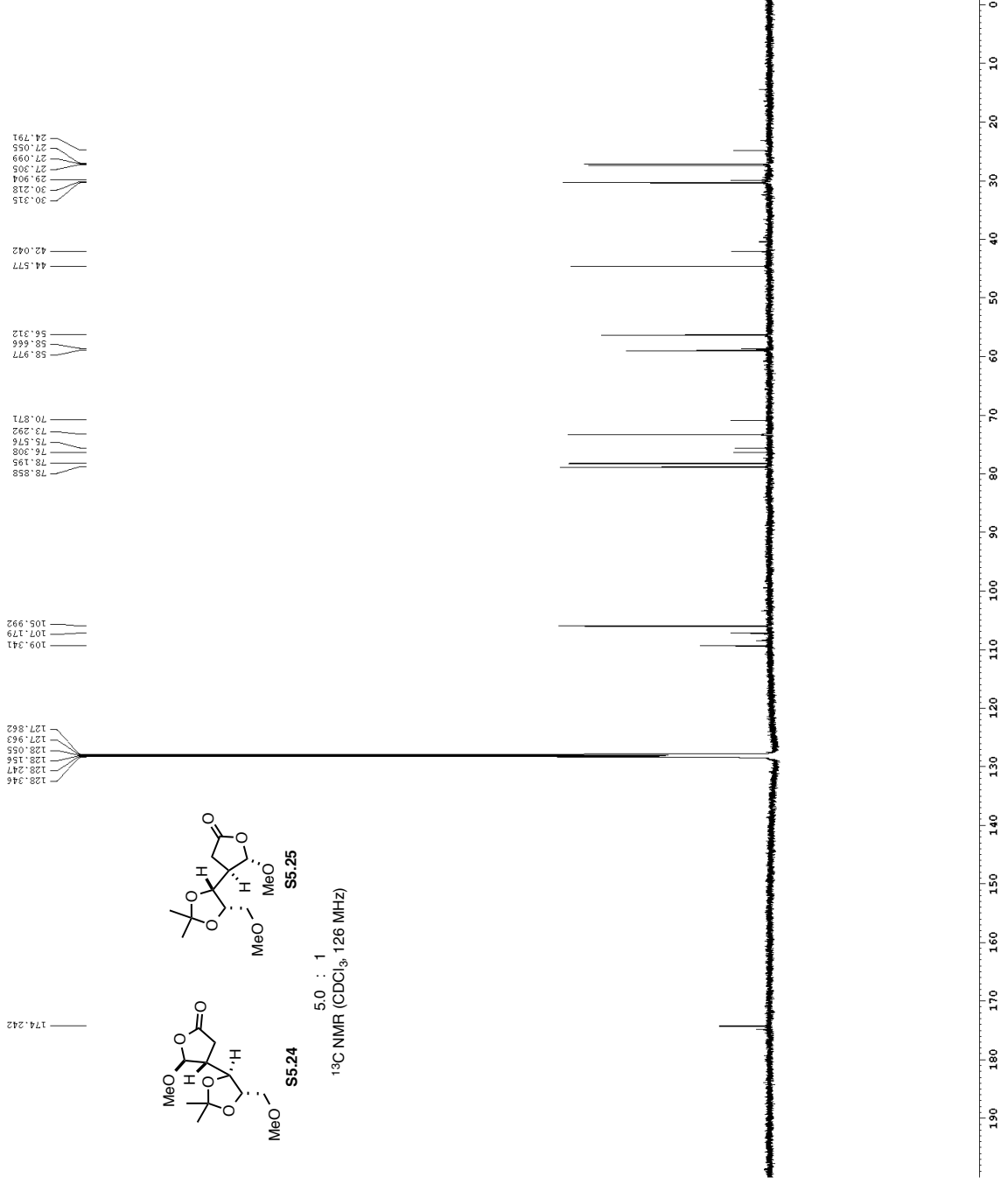
Z-restored spin-echo ¹³C spectrum with ¹H decoupling

Current Data Parameters
 NAME DUT-VI-184
 EXPNO 8
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160902
 Time 9.32
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG SpinEcho93upg.prd
 TD 65536
 SOLVENT CDCl3
 NS 603
 DS 40
 SRH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 4096
 RM 1638.0 usec
 DE 16.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 SFO1 125.7942548 MHz
 SF 2.70 usec
 SFNAM[1] Crys60.0_5_20.1
 SFNAM[2] Crys60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz
 P2 0.01500000 sec
 MCREG 33.10 usec

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 100.00 usec
 PL1 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF 2.70 usec
 SFNAM[1] Crys60.0_5_20.1
 SFNAM[2] Crys60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 ¹H
 P1 100.00 usec
 PCPD2 1.60 dB
 PL2 24.50 dB
 SF02 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPC1 0 %
 GPC2 0 %
 GPT1 0 %
 GPT2 0 %
 GPC1 30.00 %
 GPC2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec
 F2 - Processing parameters
 SI 32768
 SF 125.7803755 MHz
 WDM 0
 SSE 0
 LE 1.00 Hz
 GB 0
 PC 2.00



```

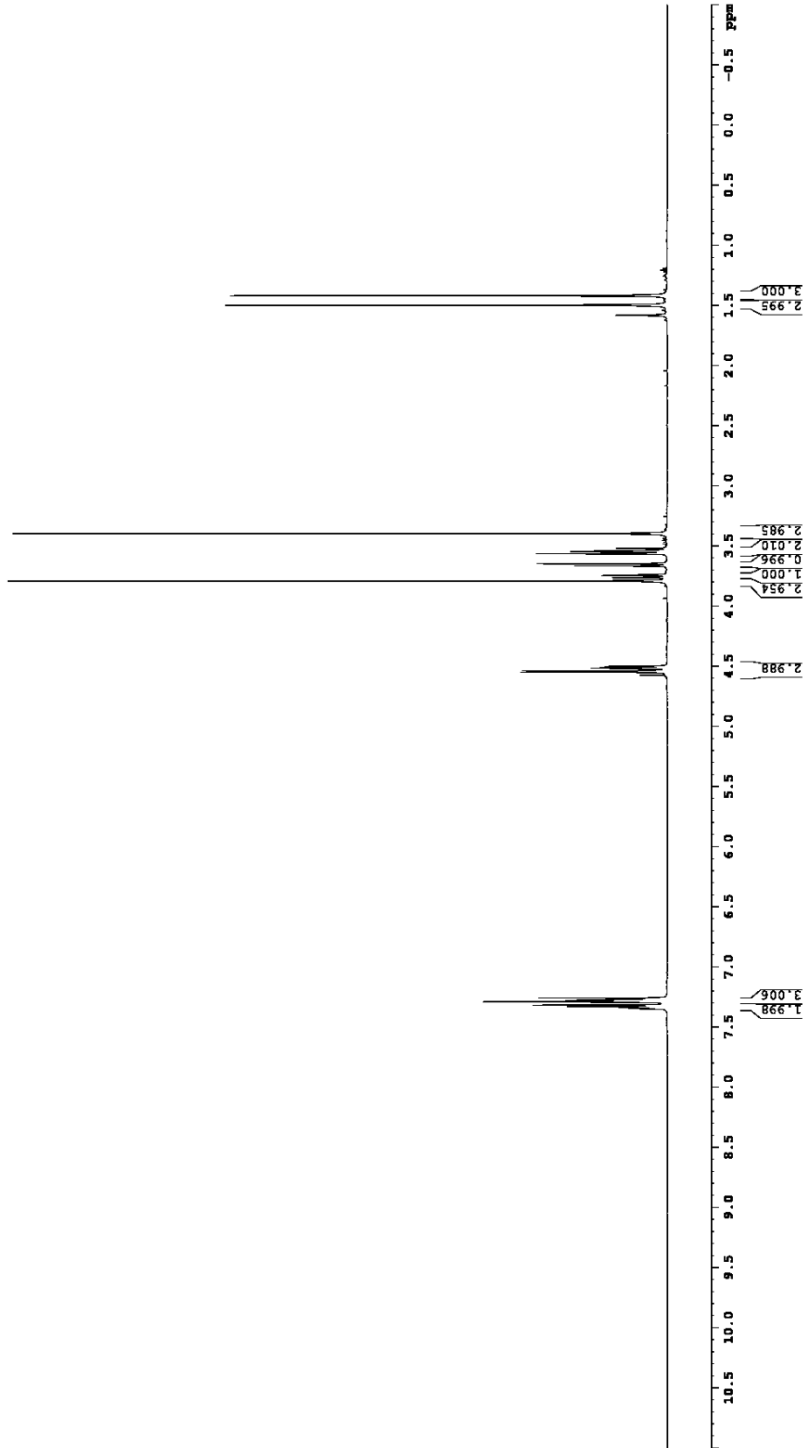
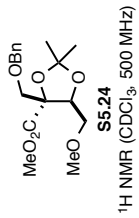
Current Data Parameters
NAME      XS-IV-39
PULPROG  zgpg30
PROCNO   1
F2 - Acquisition Parameters
Date_    20160114
Time     11.00
INSTRUM  spect
PROBHD   5 mm CPY131
PULPROG  zgpg30
TD       65536
SFO      500.136260
AQ       0.1150000
RG       4096
DS        4
SS       0
FIDRES   0.12420 Hz
AQRES    0.008043 Hz
FIDRES   6.7 Hz
RGRES    0.000000 Hz
AQRES    0.000000 Hz
FIDRES   0.12420 Hz
RGRES    0.000000 Hz
AQRES    0.000000 Hz
INSTRUM  spect
PROBHD   5 mm CPY131
PULPROG  zgpg30
TD       65536
SFO      500.136260
AQ       0.1150000
RG       4096
DS        4
SS       0
FIDRES   0.12420 Hz
AQRES    0.008043 Hz
FIDRES   6.7 Hz
RGRES    0.000000 Hz
AQRES    0.000000 Hz
INSTRUM  spect
PROBHD   5 mm CPY131
PULPROG  zgpg30
TD       65536
SFO      500.136260
AQ       0.1150000
RG       4096
DS        4
SS       0
FIDRES   0.12420 Hz
AQRES    0.008043 Hz
FIDRES   6.7 Hz
RGRES    0.000000 Hz
AQRES    0.000000 Hz

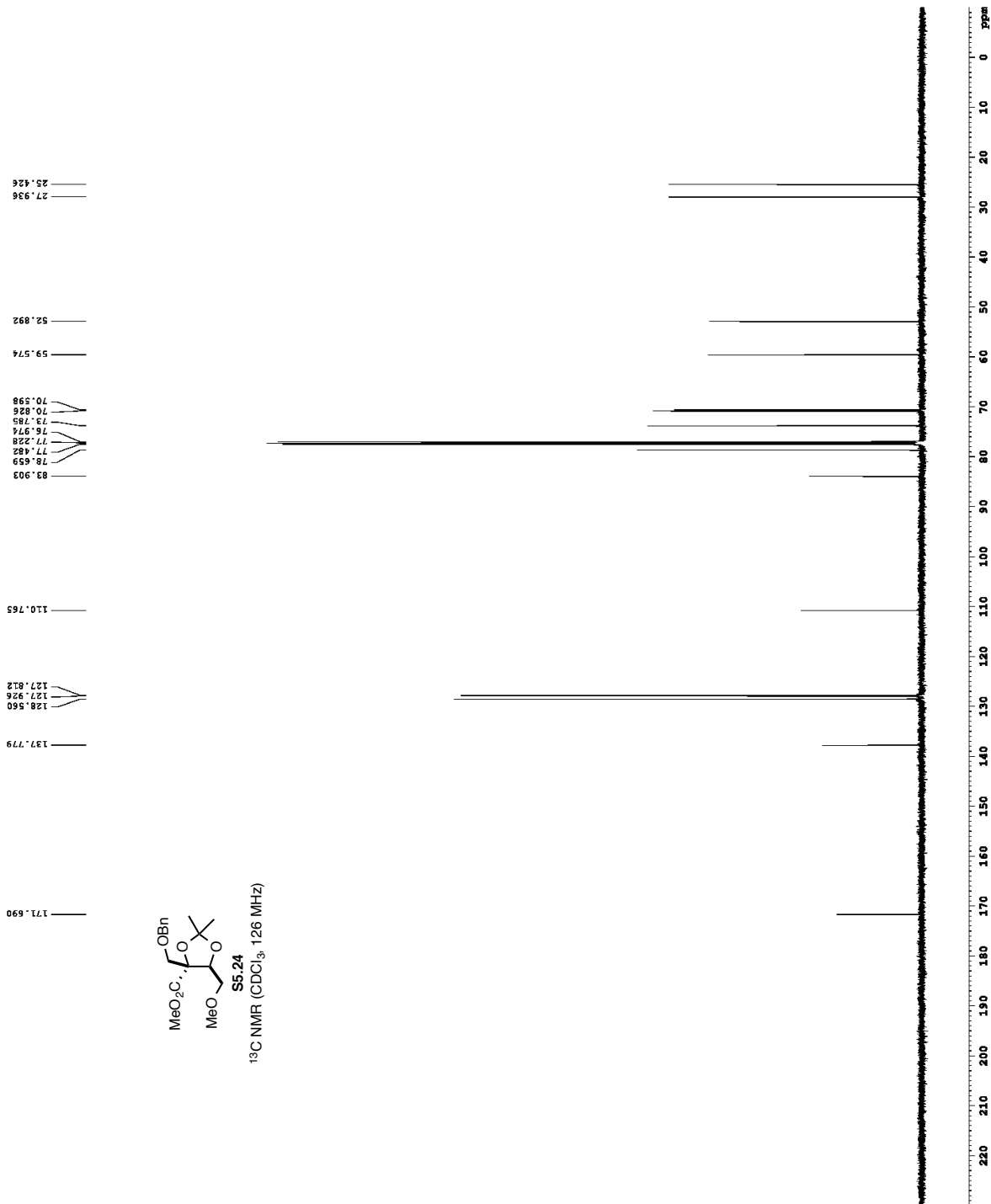
```

1.497
1.416

3.397
3.520
3.536
3.540
3.546
3.557
3.564
3.647
3.666
3.740
3.745
3.760
3.766
3.791
4.499
4.504
4.515
4.520
4.538
4.549
4.573

7.259
7.265
7.275
7.278
7.284
7.290
7.318
7.330
7.334
7.347



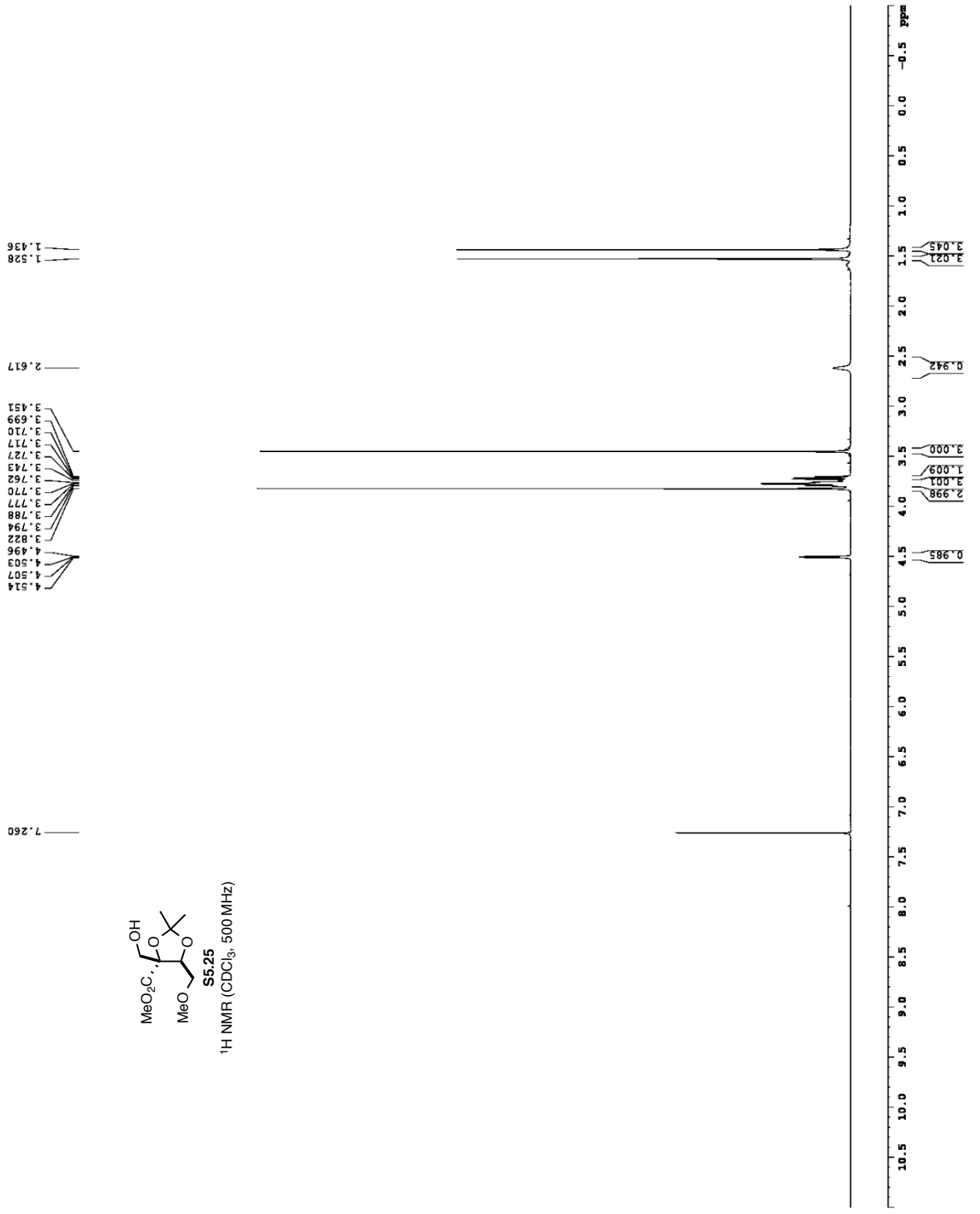
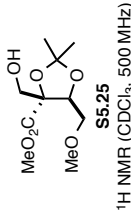


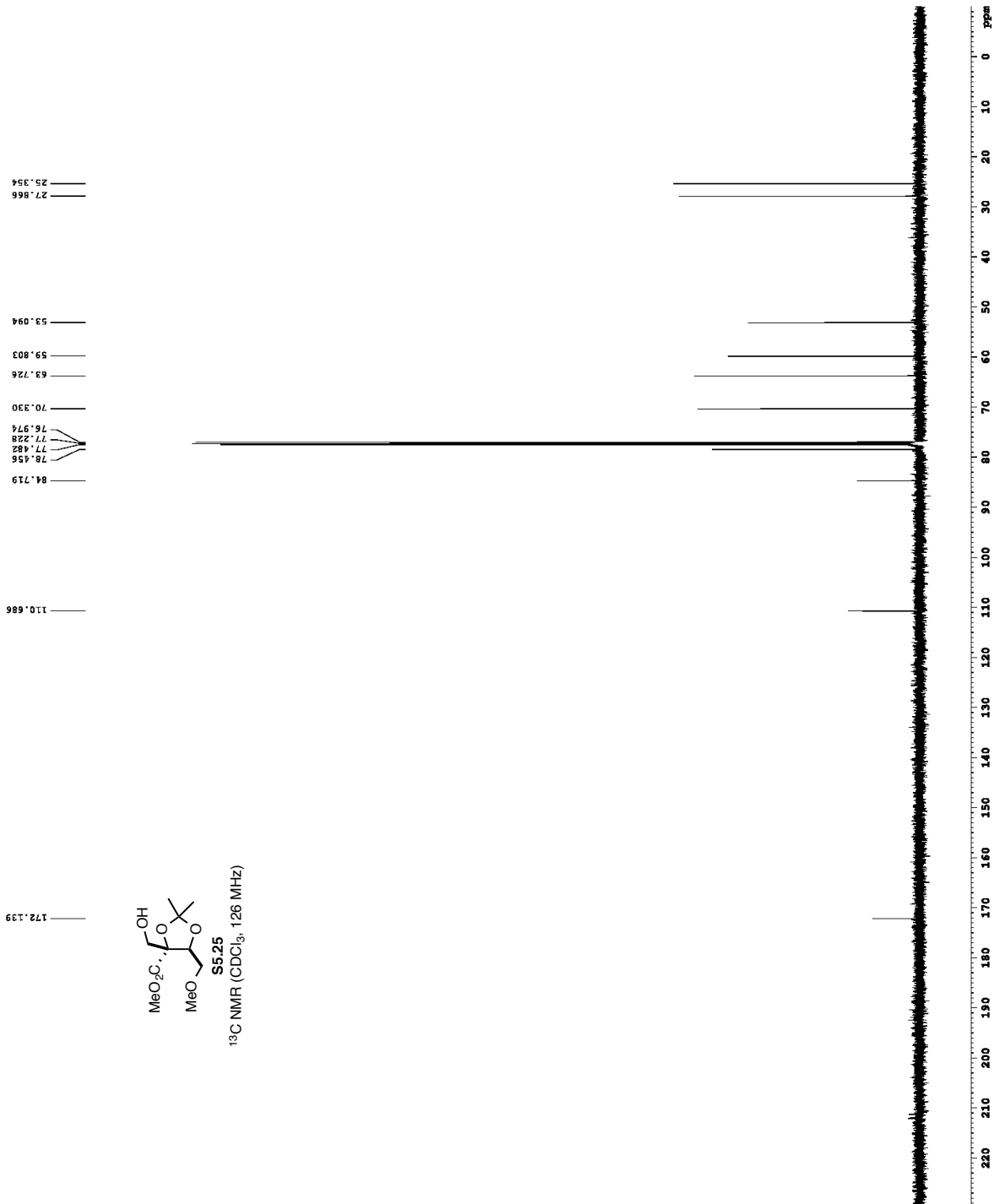
Current Data Parameters
 NAME YS-IV-39
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160114
 Time 9.13
 INSTRUM cryo-500
 PROBHD 5 mm CPXI 1H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 568
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.442368 Hz
 AQ 1.081236 sec
 RG 4597.6
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.000000 sec
 d12 0.000000 sec
 d15 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 P2 33.10 usec
 CHANNEL f1 13C
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 1.00 dB
 PL2 125.792508 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SPNAM[1] Crp60.0.5.20.1
 SPNAM[2] Crp60comp.4
 SFOF1 0 Hz
 SFOF2 0 Hz
 CHANNEL f2 1H
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 4.50 dB
 PL0 500.00 usec
 PL1 500.2225011 MHz
 SP02
 GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 0 %
 GPY2 0 %
 GPZ2 0 %
 P15 50.00 %
 P16 500.00 usec
 P17 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.7804000 MHz
 WDM 0 RM
 SSB 0
 LB 0
 GB 0
 PC 2.00

```

Current Data Parameters
NAME      XS-IV-41
PROCNO    1
DATE_     20160116
INSTRUM   spect
PROBHD    5 mm TBI 1H/13
PULPROG   zgpg30
TD        65536
AQ        0.100000000
RG        655.362 Hz
RG2       5.098042 Hz
RG3       5.098042 Hz
RG4       5.098042 Hz
RG5       5.098042 Hz
RG6       5.098042 Hz
RG7       5.098042 Hz
RG8       5.098042 Hz
RG9       5.098042 Hz
RG10      5.098042 Hz
RG11      5.098042 Hz
RG12      5.098042 Hz
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RG15      5.098042 Hz
RG16      5.098042 Hz
RG17      5.098042 Hz
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RG19      5.098042 Hz
RG20      5.098042 Hz
RG21      5.098042 Hz
RG22      5.098042 Hz
RG23      5.098042 Hz
RG24      5.098042 Hz
RG25      5.098042 Hz
RG26      5.098042 Hz
RG27      5.098042 Hz
RG28      5.098042 Hz
RG29      5.098042 Hz
RG30      5.098042 Hz
RG31      5.098042 Hz
RG32      5.098042 Hz
RG33      5.098042 Hz
RG34      5.098042 Hz
RG35      5.098042 Hz
RG36      5.098042 Hz
RG37      5.098042 Hz
RG38      5.098042 Hz
RG39      5.098042 Hz
RG40      5.098042 Hz
RG41      5.098042 Hz
RG42      5.098042 Hz
RG43      5.098042 Hz
RG44      5.098042 Hz
RG45      5.098042 Hz
RG46      5.098042 Hz
RG47      5.098042 Hz
RG48      5.098042 Hz
RG49      5.098042 Hz
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RG64      5.098042 Hz
RG65      5.098042 Hz
RG66      5.098042 Hz
RG67      5.098042 Hz
RG68      5.098042 Hz
RG69      5.098042 Hz
RG70      5.098042 Hz
RG71      5.098042 Hz
RG72      5.098042 Hz
RG73      5.098042 Hz
RG74      5.098042 Hz
RG75      5.098042 Hz
RG76      5.098042 Hz
RG77      5.098042 Hz
RG78      5.098042 Hz
RG79      5.098042 Hz
RG80      5.098042 Hz
RG81      5.098042 Hz
RG82      5.098042 Hz
RG83      5.098042 Hz
RG84      5.098042 Hz
RG85      5.098042 Hz
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RG91      5.098042 Hz
RG92      5.098042 Hz
RG93      5.098042 Hz
RG94      5.098042 Hz
RG95      5.098042 Hz
RG96      5.098042 Hz
RG97      5.098042 Hz
RG98      5.098042 Hz
RG99      5.098042 Hz
RG100     5.098042 Hz

```





```

Current Data Parameters
NAME      YS-IV-41
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20160116
Time     10.28
INSTRUM cryo500
PROBHD   5 mm CPICR1H-
PULPROG zgpg30
TD        65536
SOLVENT  CDCl3
NS        500
DS        2
SWH       30303.031 Hz
AQ        0.4824748 Hz
RG        1.0813440 sec
RG        7298.2
DM        16.500 usec
DE        6.00 usec
TE        298.0 K
D1        0.2500000 sec
d11       0.0000000 sec
d12       0.0000000 sec
d13       0.0002000 sec
d14       0.00019600 sec
d15       0.00019600 sec
d16       0.00019600 sec
d17       0.00019600 sec
MCRESTI  0 sec
MCWRK    0.01500000 sec
F2        33.10 usec

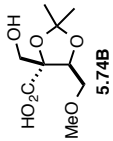
===== CHANNEL f1 =====
NUC1      13C
P1        16.55 usec
P11       500.00 usec
P12       2000.00 usec
P13       120.00 dB
P14       120.00 dB
P15       120.00 dB
P16       120.00 dB
SFO1      125.7642568 MHz
SFO2      2.70 dB
SFO3      2.70 dB
SFO4      2.70 dB
SFO5      2.70 dB
SFO6      2.70 dB
SFO7      2.70 dB
SFO8      2.70 dB
SFO9      2.70 dB
SFO10     2.70 dB
SFO11     2.70 dB
SFO12     2.70 dB
SFO13     2.70 dB
SFO14     2.70 dB
SFO15     2.70 dB
SFO16     2.70 dB
SFO17     2.70 dB
SFO18     2.70 dB
SFO19     2.70 dB
SFO20     2.70 dB
SFO21     2.70 dB
SFO22     2.70 dB
SFO23     2.70 dB
SFO24     2.70 dB
SFO25     2.70 dB
SFO26     2.70 dB
SFO27     2.70 dB
SFO28     2.70 dB
SFO29     2.70 dB
SFO30     2.70 dB
SFO31     2.70 dB
SFO32     2.70 dB
SFO33     2.70 dB
SFO34     2.70 dB
SFO35     2.70 dB
SFO36     2.70 dB
SFO37     2.70 dB
SFO38     2.70 dB
SFO39     2.70 dB
SFO40     2.70 dB
SFO41     2.70 dB
SFO42     2.70 dB
SFO43     2.70 dB
SFO44     2.70 dB
SFO45     2.70 dB
SFO46     2.70 dB
SFO47     2.70 dB
SFO48     2.70 dB
SFO49     2.70 dB
SFO50     2.70 dB

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2      1H
P2        100.00 usec
P21       100.00 usec
P22       100.00 usec
P23       1.80 dB
P24       1.80 dB
P25       1.80 dB
P26       1.80 dB
P27       1.80 dB
P28       1.80 dB
P29       1.80 dB
P30       1.80 dB
P31       1.80 dB
P32       1.80 dB
P33       1.80 dB
P34       1.80 dB
P35       1.80 dB
P36       1.80 dB
P37       1.80 dB
P38       1.80 dB
P39       1.80 dB
P40       1.80 dB
P41       1.80 dB
P42       1.80 dB
P43       1.80 dB
P44       1.80 dB
P45       1.80 dB
P46       1.80 dB
P47       1.80 dB
P48       1.80 dB
P49       1.80 dB
P50       1.80 dB
P51       1.80 dB
P52       1.80 dB
P53       1.80 dB
P54       1.80 dB
P55       1.80 dB
P56       1.80 dB
P57       1.80 dB
P58       1.80 dB
P59       1.80 dB
P60       1.80 dB
P61       1.80 dB
P62       1.80 dB
P63       1.80 dB
P64       1.80 dB
P65       1.80 dB
P66       1.80 dB
P67       1.80 dB
P68       1.80 dB
P69       1.80 dB
P70       1.80 dB
P71       1.80 dB
P72       1.80 dB
P73       1.80 dB
P74       1.80 dB
P75       1.80 dB
P76       1.80 dB
P77       1.80 dB
P78       1.80 dB
P79       1.80 dB
P80       1.80 dB
P81       1.80 dB
P82       1.80 dB
P83       1.80 dB
P84       1.80 dB
P85       1.80 dB
P86       1.80 dB
P87       1.80 dB
P88       1.80 dB
P89       1.80 dB
P90       1.80 dB
P91       1.80 dB
P92       1.80 dB
P93       1.80 dB
P94       1.80 dB
P95       1.80 dB
P96       1.80 dB
P97       1.80 dB
P98       1.80 dB
P99       1.80 dB
P100      1.80 dB

===== GRADIENT CHANNEL =====
GPRAM[1] SINE.100
GPRAM[2] SINE.100
GPA1     0 %
GPA2     0 %
GPA3     0 %
GPA4     0 %
GPA5     0 %
GPA6     0 %
GPA7     0 %
GPA8     0 %
GPA9     0 %
GPA10    0 %
GPA11    0 %
GPA12    0 %
GPA13    0 %
GPA14    0 %
GPA15    0 %
GPA16    0 %
GPA17    0 %
GPA18    0 %
GPA19    0 %
GPA20    0 %
GPA21    0 %
GPA22    0 %
GPA23    0 %
GPA24    0 %
GPA25    0 %
GPA26    0 %
GPA27    0 %
GPA28    0 %
GPA29    0 %
GPA30    0 %
GPA31    0 %
GPA32    0 %
GPA33    0 %
GPA34    0 %
GPA35    0 %
GPA36    0 %
GPA37    0 %
GPA38    0 %
GPA39    0 %
GPA40    0 %
GPA41    0 %
GPA42    0 %
GPA43    0 %
GPA44    0 %
GPA45    0 %
GPA46    0 %
GPA47    0 %
GPA48    0 %
GPA49    0 %
GPA50    0 %
GPA51    0 %
GPA52    0 %
GPA53    0 %
GPA54    0 %
GPA55    0 %
GPA56    0 %
GPA57    0 %
GPA58    0 %
GPA59    0 %
GPA60    0 %
GPA61    0 %
GPA62    0 %
GPA63    0 %
GPA64    0 %
GPA65    0 %
GPA66    0 %
GPA67    0 %
GPA68    0 %
GPA69    0 %
GPA70    0 %
GPA71    0 %
GPA72    0 %
GPA73    0 %
GPA74    0 %
GPA75    0 %
GPA76    0 %
GPA77    0 %
GPA78    0 %
GPA79    0 %
GPA80    0 %
GPA81    0 %
GPA82    0 %
GPA83    0 %
GPA84    0 %
GPA85    0 %
GPA86    0 %
GPA87    0 %
GPA88    0 %
GPA89    0 %
GPA90    0 %
GPA91    0 %
GPA92    0 %
GPA93    0 %
GPA94    0 %
GPA95    0 %
GPA96    0 %
GPA97    0 %
GPA98    0 %
GPA99    0 %
GPA100   0 %

F2 - Processing parameters
SI        65536
SF        125.7603988 MHz
EM
NSB       0
SSB       0
DSB       0
GB        0
GC        0
PC        2.00
    
```

XS-IV-43



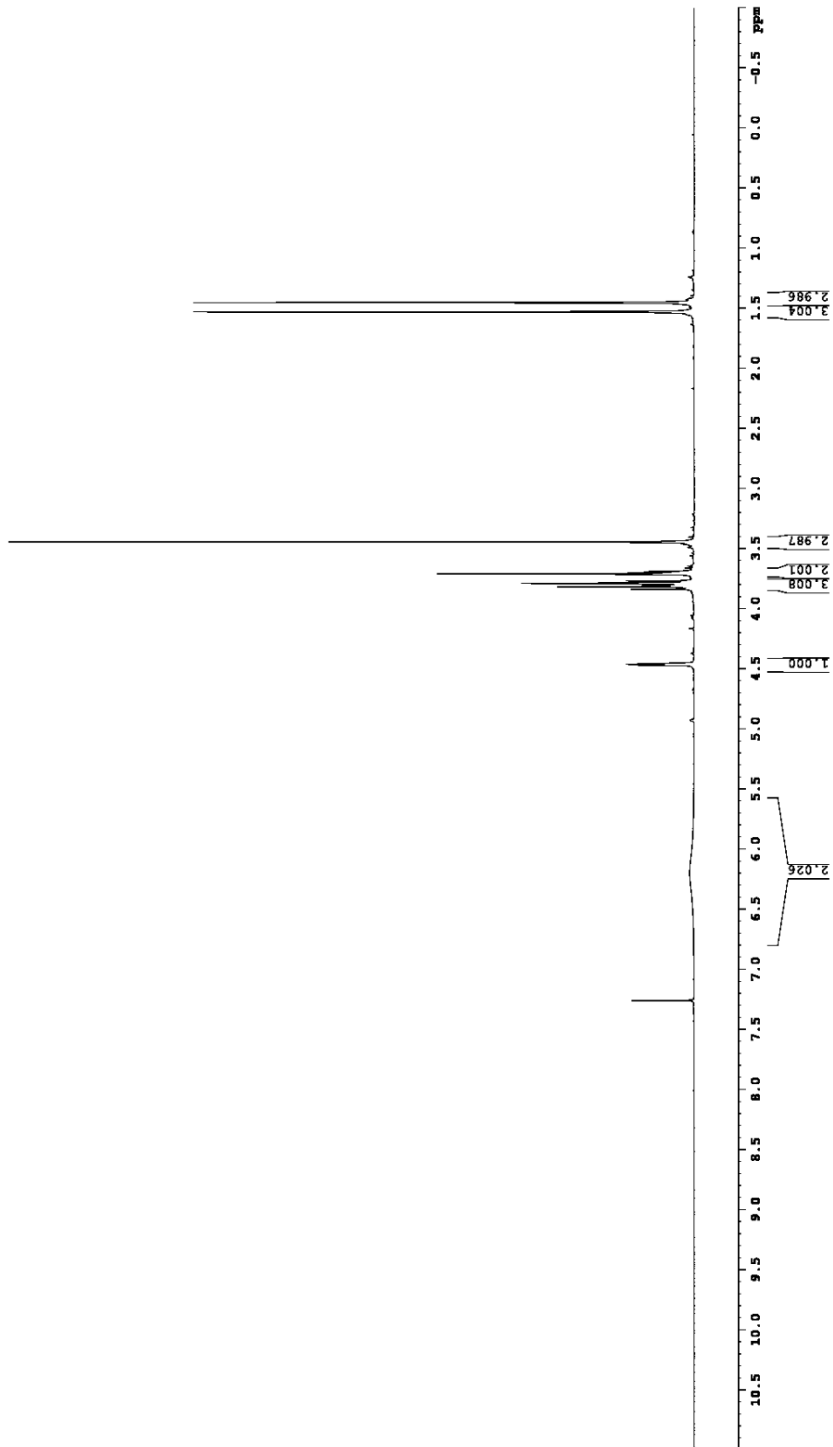
¹H NMR (CDCl₃, 600 MHz)

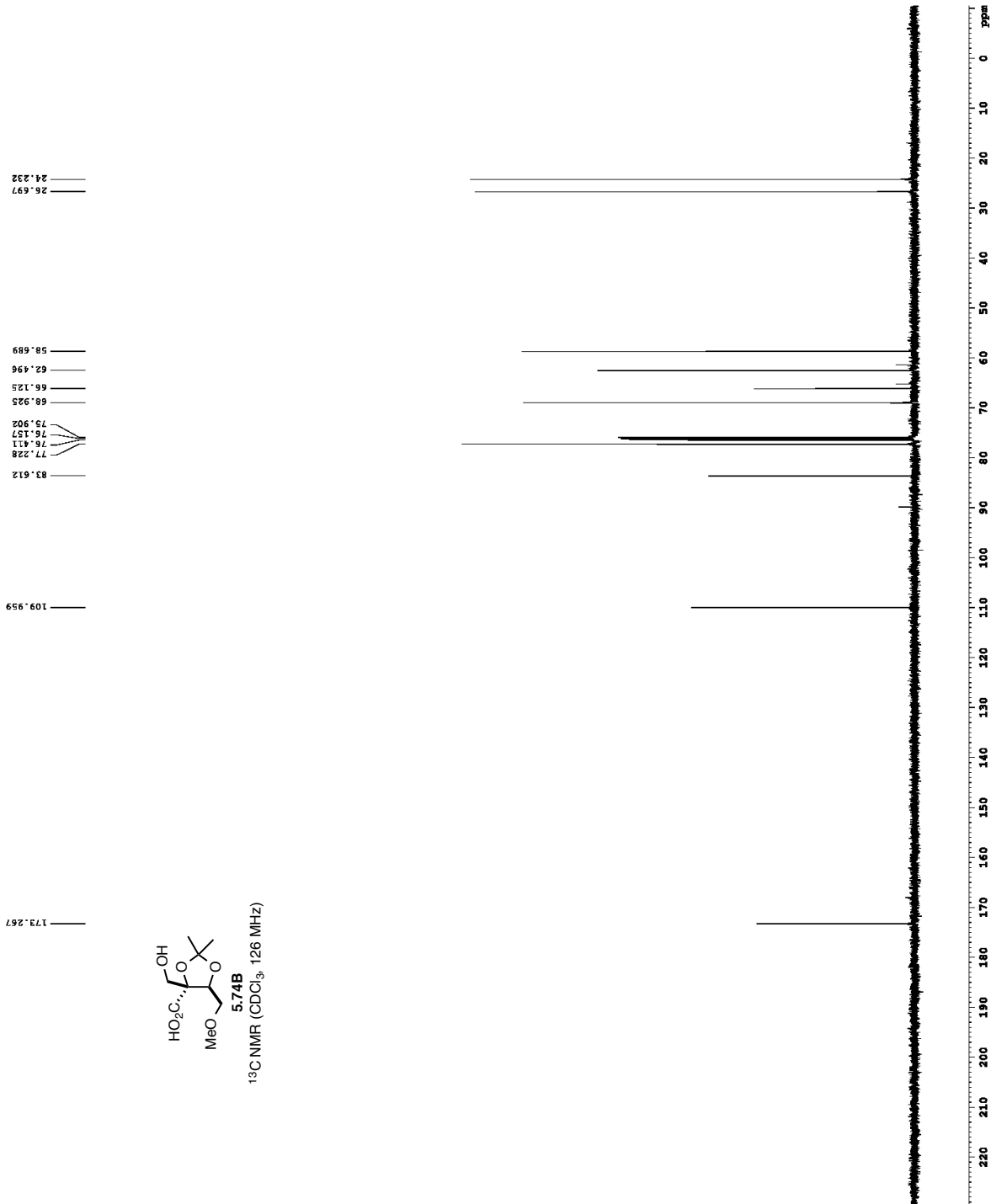
Current Data Parameters
NAME XS-IV-43
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160119
Time_ 14:55:00
INSTRUM spect
PULPROG zgpg30
TD 65536
SFO 600.136209
AQ 0.100000000
RG 327
GB 0
PC 1.00
CHNAME_ f1
SFO1 600.136209 MHz
P1 8.00 use
PL1 21.0000000 W
P2 - Processing parameters
SI 32768
SF 600.136202 MHz
WDW EM
SS 0
LB 0.30 Hz
GB 0
PC 1.00

1.530
1.453

3.445
3.464
3.661
3.687
3.698
3.705
3.710
3.715
3.769
3.785
3.802
3.809
3.818
3.838
4.455
4.461
4.465
4.471

7.260





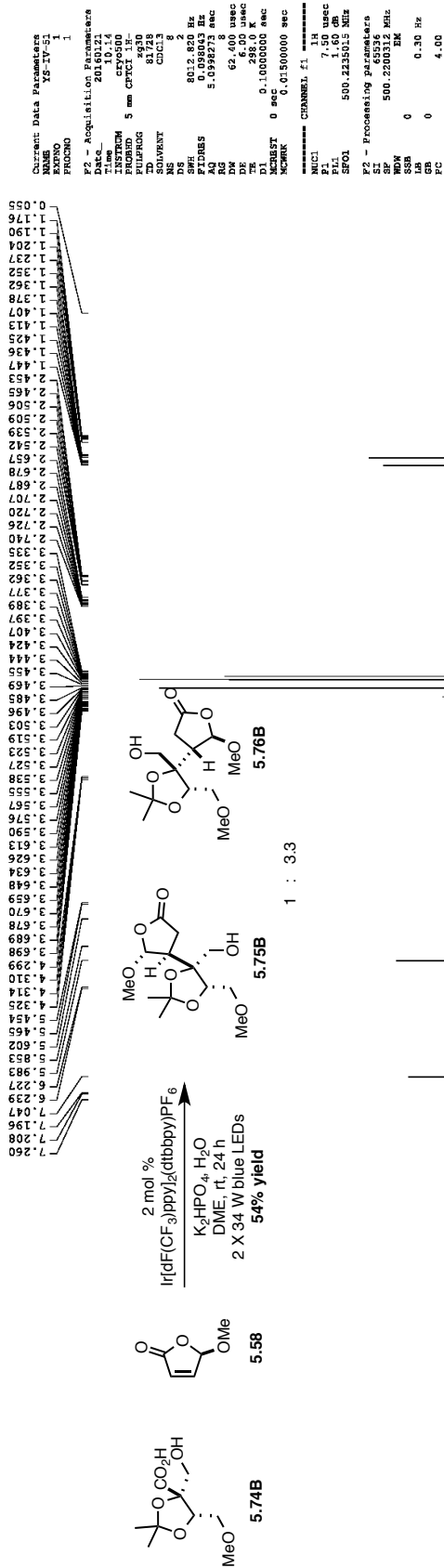
Current Data Parameters
 NAME YS-IV-43
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160119
 Time 16.58
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 168
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.4817440 Hz
 AQ 1.00817440 sec
 RG 3251
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCNRRK 0.01500000 sec
 F2 33.10 usec

CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P14 120.00 dB
 SFL1 0.00000000 MHz
 SF1 125.7642560 MHz
 SS1 2.70 dB
 SP2 2.70 dB
 SFNAM[1] Crp60,0.5,20.1
 SFNAM[2] Crp60comp.4
 SFOF1 0 Hz
 SFOF2 0 Hz

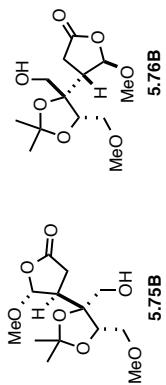
CHANNEL f2
 CPDPRG[2] waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.80 dB
 P22 2.00 dB
 SF2 500.1364570 MHz
 SF22 500.2225031 MHz

GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GFZ1 30.00 %
 GFZ2 50.00 %
 P15 500.00 usec
 P16 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.7805370 MHz
 NDM EM
 SSB 0
 GB 1.00 Hz
 PC 2.00

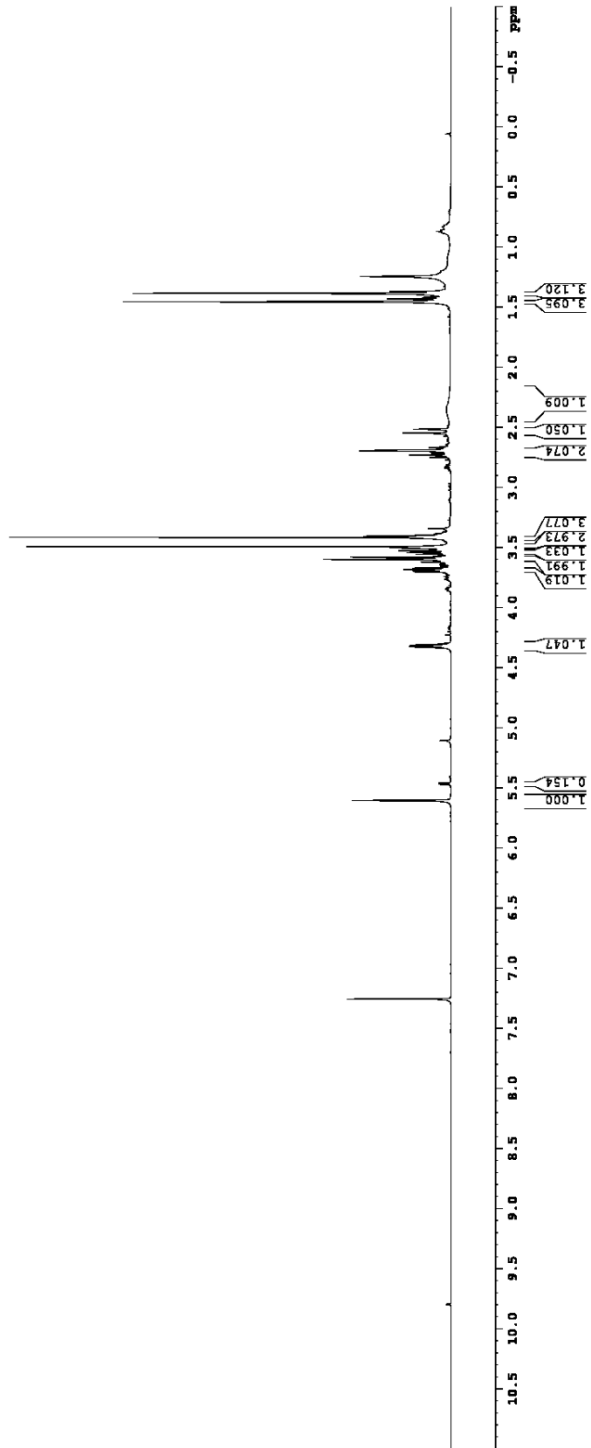


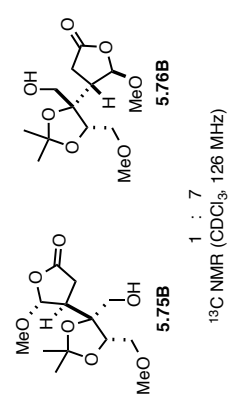
Current Data Parameters
 NAME YS-TV-51
 PACNO 1
 F2 - Acquisition Parameters
 Date_ 2016022
 TIME 14:07:40
 INSTRUM 5 mm CPY130
 PULPROG zgpg30
 ID 8178
 VS UNIT C13H
 CHAN 4
 SWH 502.820 Hz
 FIDRES 0.098003 Hz
 AQC 5.029999 sec
 RG 5.7
 DB 62.00 Hz
 CB 4.00 Hz
 CR 288.0 K
 INJECT 0 sec
 ACQSTRT 0.100000 sec
 ACQSTP 0.0150010 sec
 CHANNEL f1
 NUC1 13C
 P1 7.00 usec
 PL1 0.00 dB
 SFO1 500.261015 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.261015 MHz
 DSF 0
 BPF 0
 GB 0
 PC 4.00

4.332
4.321
4.317
4.305
3.701
3.690
3.682
3.671
3.620
3.598
3.579
3.556
3.542
3.523
3.525
3.453
3.415
2.750
2.735
2.729
2.717
2.696
2.690
2.668
2.548
2.516
2.355
1.454
1.385



1 : 7
¹H NMR (CDCl₃, 500 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 CPXI IH-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 112
 DS 1
 SWH 30303.031 Hz
 FIDRES 0.492488 Hz
 AQ 1.068248 sec
 RG 8192
 DW 16.500 usec
 DE 6.00 usec
 IE 298.0 K
 D1 0.25000000 sec
 d11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 P2 33.10 usec

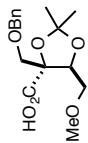
CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 100.00 dB
 PL2 125.79425600 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SFNAM[1] Crp60.0.5.20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

CHANNEL f2
 CPDPRG[2] waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 1.60 dB
 SF02 500.22250011 MHz

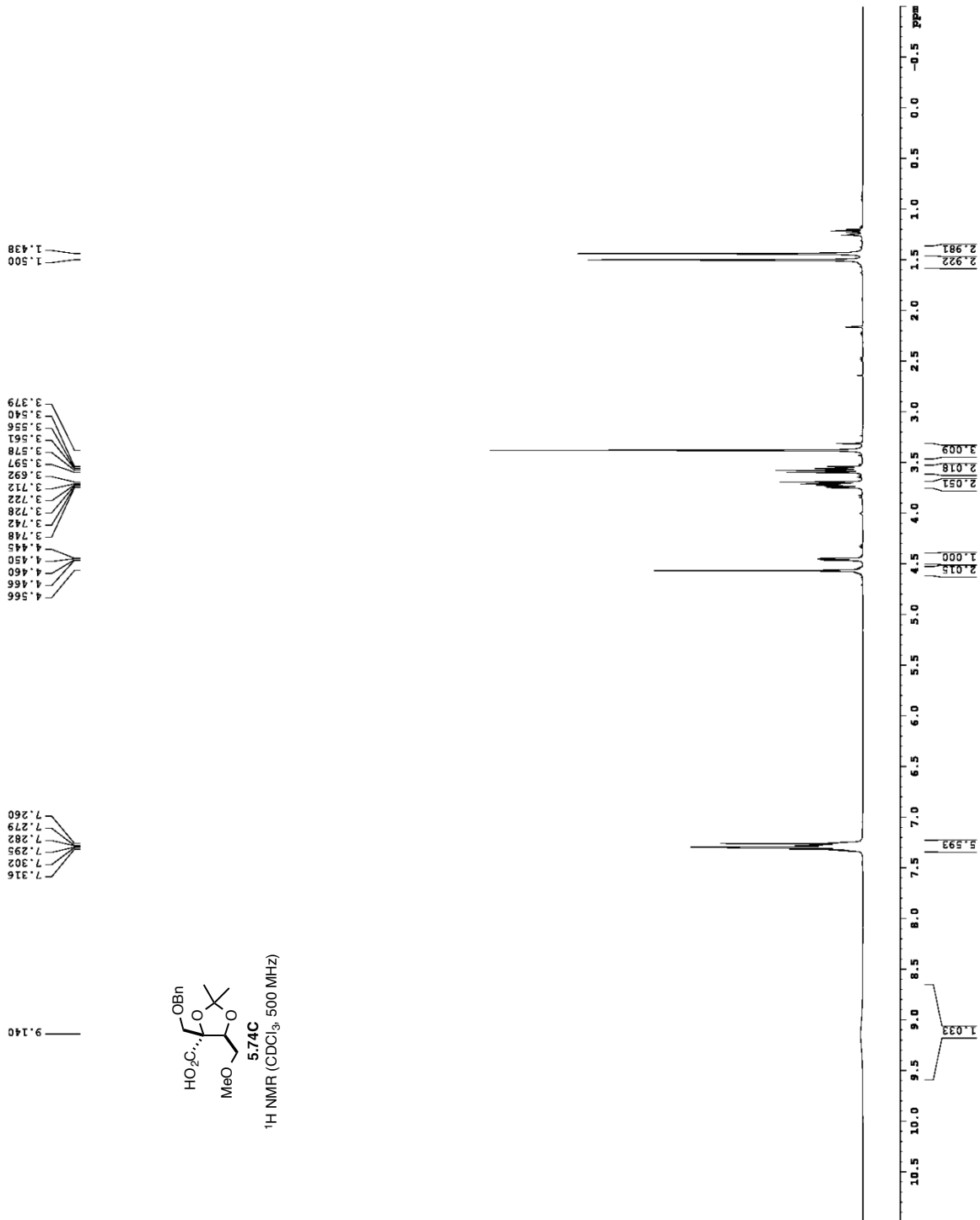
GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 *
 GPY1 0 *
 GPZ1 0 *
 GPX2 0 *
 GPY2 0 *
 GPZ2 0 *
 P15 50.00 *
 P16 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.7604004 MHz
 NDM 0
 SSB 0
 GB 1.00 Hz
 GC 0
 PC 2.00

YS-IV-58

Current Data Parameters
NAME YS-IV-58
PROCNO 1
F2 - Acquisition Parameters
Date_ 2016116
Time_ 10:02:00
INSTRUM spect
PROBHD 5 mm CPY130
PULPROG zgpg30
ID 81728
RS1PRMT 4
SFB 802.820 Hz
F1THRU 5.088013 Hz
SFOFF 5.079987 Hz
RG 5.7
EN 62.500 MHz
TE 298.0 K
PC 0.100000 sec
MCXST 0 sec
MCXSK 0.0150000 sec
SOLVENT CHANNEL F1
P1 7.00 usec
PL 0.00 dB
PCP1 500.2335015 MHz
F2 - Processing parameters
SI 32768
SF 500.2653536 MHz
SFO 500.2653536 MHz
WDW EM
SSB 0
GB 0
PC 4.00



¹H NMR (CDCl₃, 500 MHz)



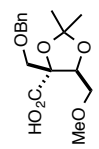
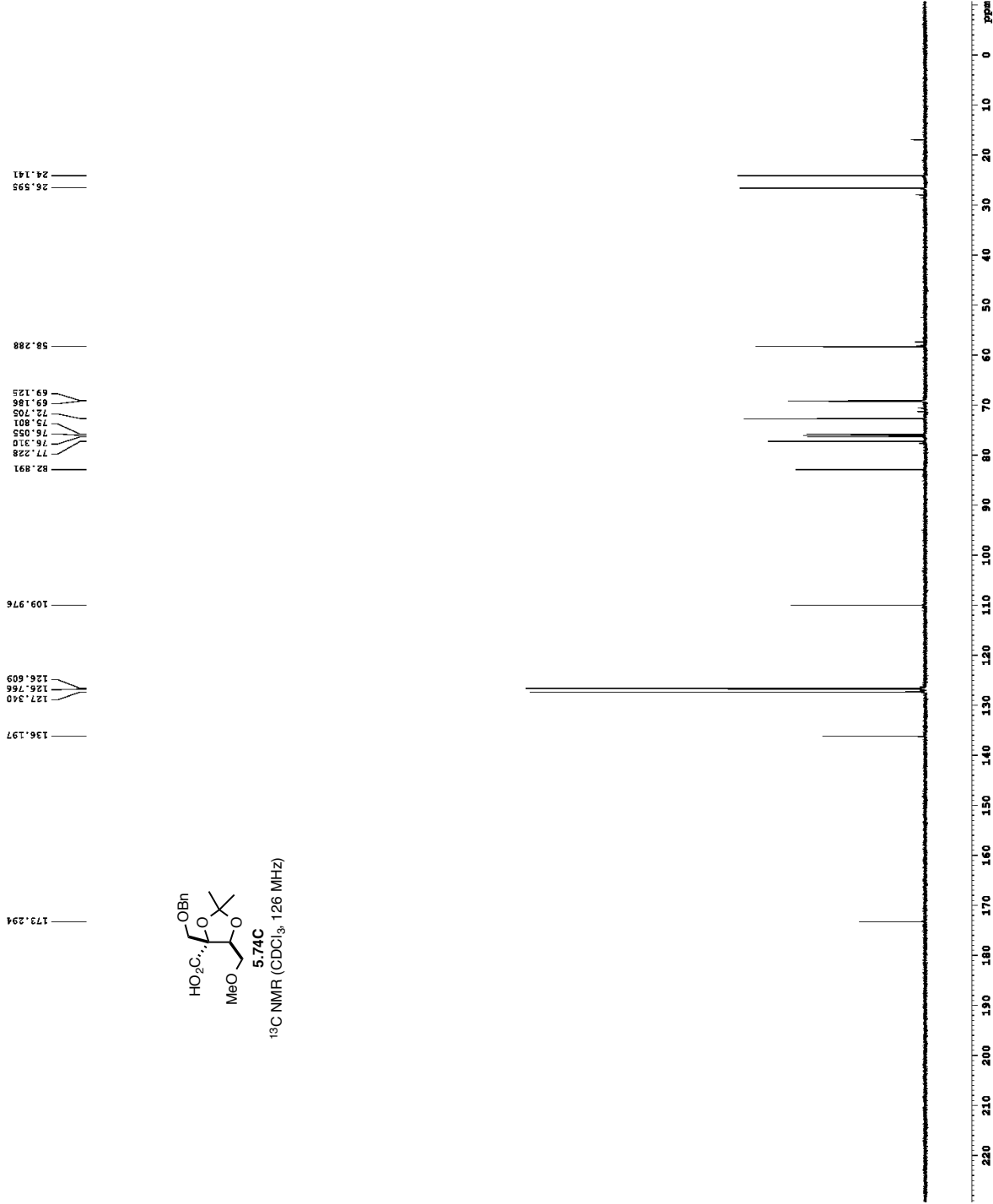
Current Data Parameters
 NAME XS-IV-58
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160126
 Time 17.15
 INSTRUM cryo500
 PROBRD 5 mm CPICL 4H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 1
 SWH 30303.031 Hz
 FIDRES 0.462368 Hz
 RG 1.0625603 sec
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.5000000 sec
 D11 0.3000000 sec
 D16 0.0020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWEX 0.01500000 sec
 P2 33.10 usec

CHANNEL f1 13C
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P10 120.00 dB
 P11 1.00 dB
 P12 125.794538 MHz
 SFO2 2.70 dB
 SFO1 2.70 dB
 SFO2 2.70 dB
 SPNAM[1] Crp60,0.5,20.1
 SPNAM[2] Crp60comp.4
 SFOE1 0 Hz
 SFOE2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2P02 100.00 usec
 P2 1.60 dB
 P12 2.30 dB
 SFO2 500.2225011 MHz

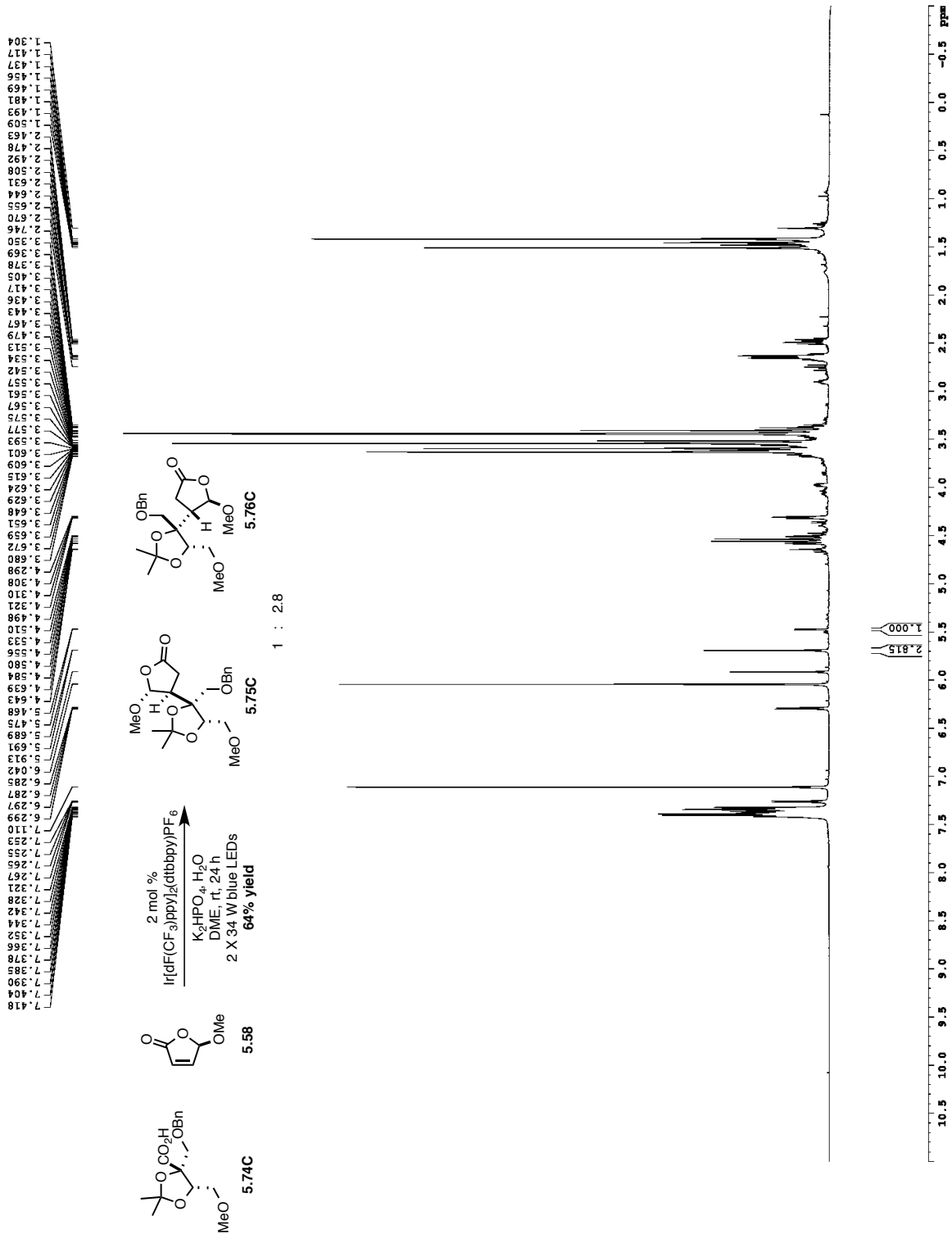
GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GX1 0 %
 GX2 0 %
 GY1 0 %
 GY2 0 %
 GZ1 30.00 %
 GZ2 50.00 %
 P15 500.00 usec
 P16 1000.00 usec

F2 - Processing Parameters
 SI 65536
 SF 125.7805602 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

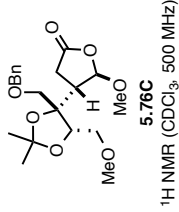


¹³C NMR (CDCl₃, 126 MHz)

YS-IV-61

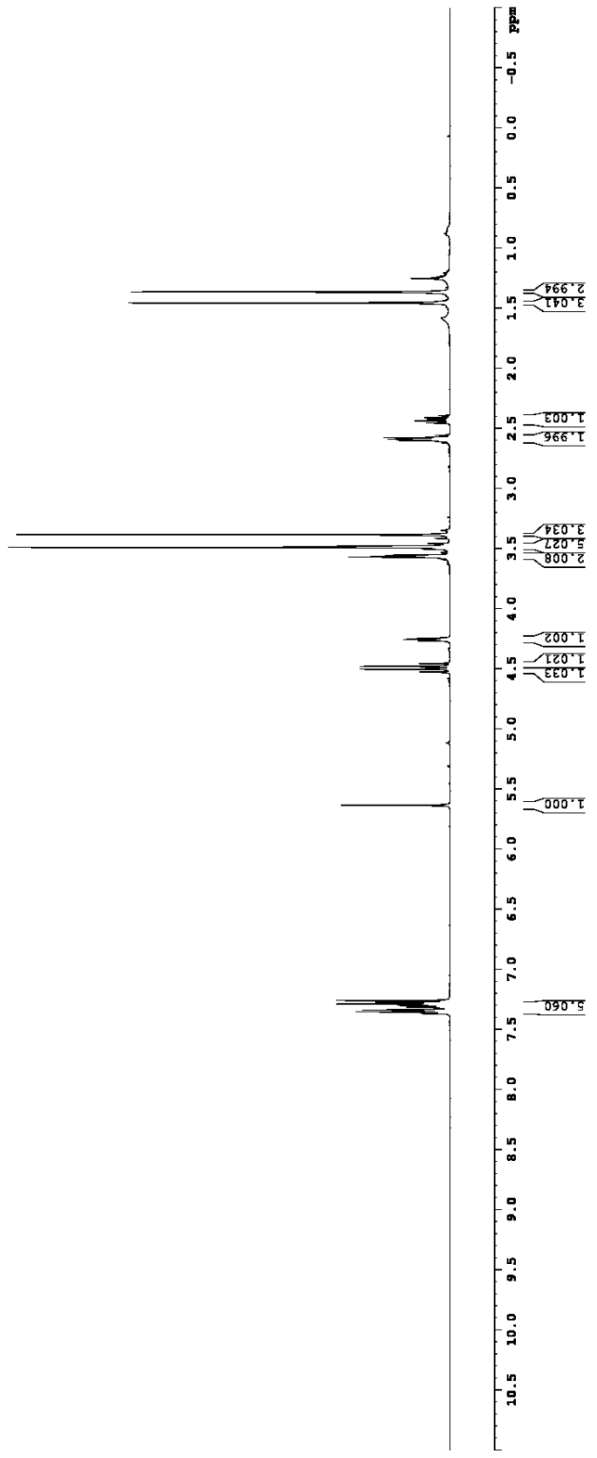


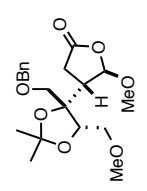
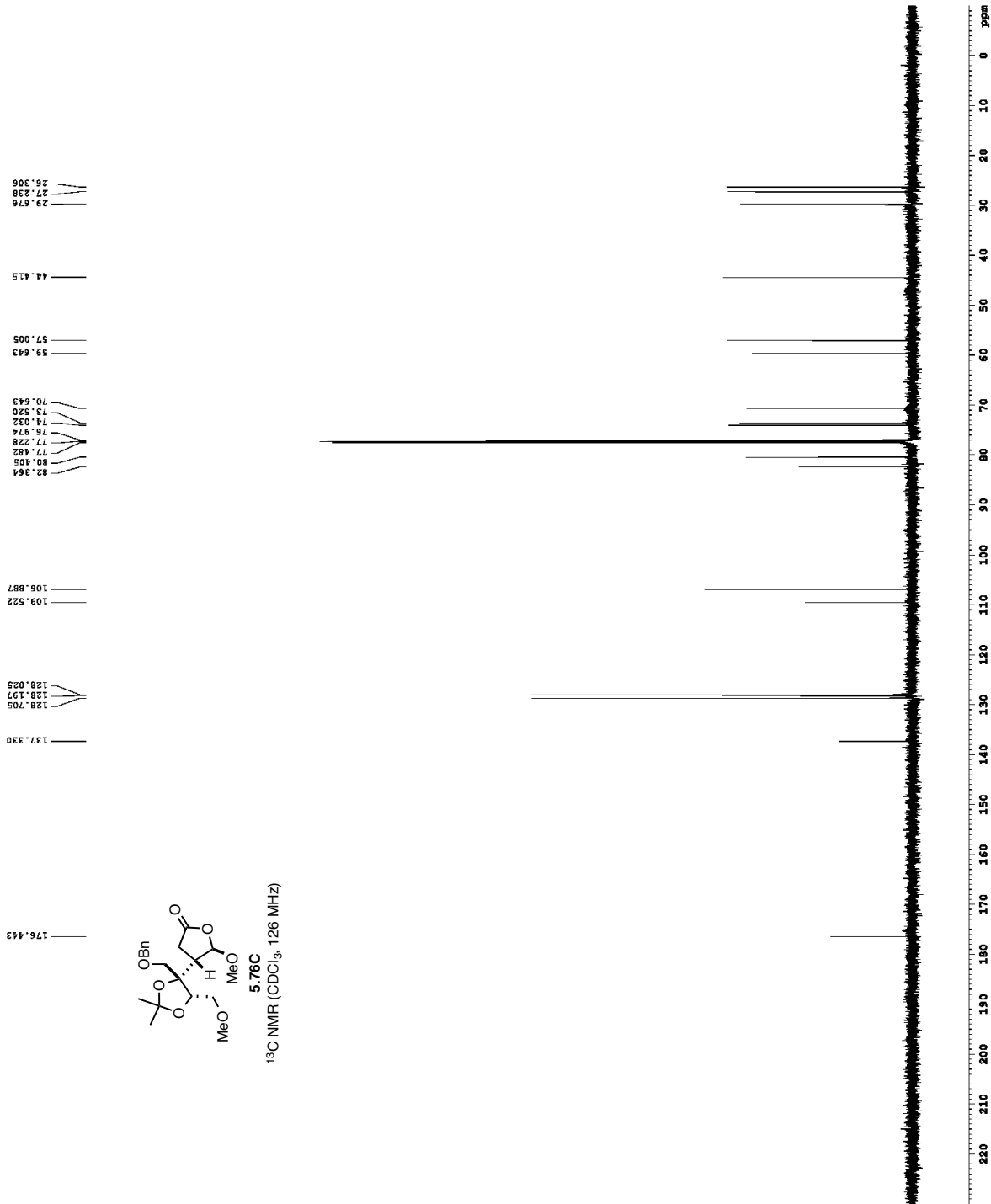
Current Data Parameters
 NAME XS-IV-61
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160127
 TIME 08:00:00
 INSTRUM spect
 PULPROG zgpg30
 ID 8172
 VS SWHT CUCI2
 F1 8012.820 Hz
 F2 509.8043 Hz
 RG 5.0398279 MHz
 DM 62.400 Hz
 SFO 500.136260 MHz
 T1 298.0 K
 T2 0.1000000 sec
 ACHSET 0 sec
 ACQMSK 0.0150000 sec
 CHANNEL f1
 NUC1 13C
 P1 1.20 sec
 PL1 0.000000 dB
 SFO1 500.136260 MHz
 F2 - Processing parameters
 SI 6558
 SF 500.136260 MHz
 SFO 500.136260 MHz
 ZSR 0
 GB 0
 PC 4.00



5.76C
¹H NMR (CDCl₃, 500 MHz)

- 7.367
- 7.354
- 7.339
- 7.316
- 7.302
- 7.290
- 7.275
- 7.259
- 5.636
- 4.528
- 4.504
- 4.480
- 4.456
- 4.268
- 4.257
- 4.244
- 3.570
- 3.561
- 3.555
- 3.490
- 3.478
- 3.384
- 2.601
- 2.590
- 2.577
- 2.454
- 2.438
- 2.424
- 2.409
- 1.456
- 1.364





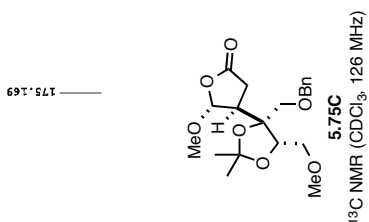
5.76C
¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME YS-IV-61
 EXPNO 5
 F2PROCNO 1
 F2 - Acquisition Parameters
 Data_ 20160127
 Time 17.07
 INSTRUM cryo500
 PROBRD 5 mm CPXI IH
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 200
 DS 1
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.08228 sec
 RG 7288.2
 DW 16.500 usec
 DE 6.00 usec
 TE 288.0 K
 DL 0.25000000 sec
 D1 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 F2 33.10 usec

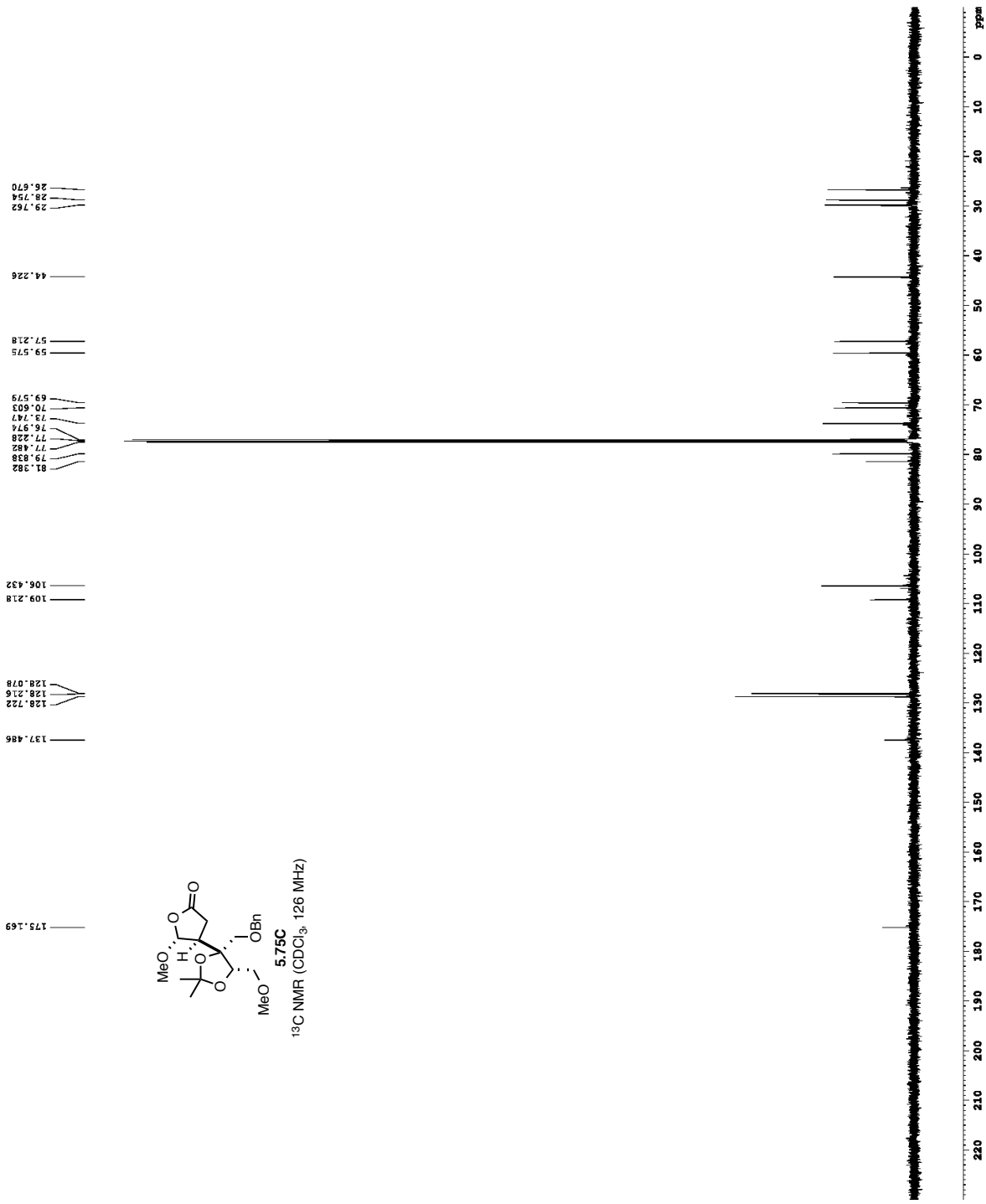
CHANNEL f1
 NUC1 13C
 P1 16.35 usec
 P11 500.00 usec
 P12 2000.00 usec
 P14 120.00 dB
 P15 125.7942500 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SFNAM[1] Crp60.0.5.20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 2.00 dB
 P23 2.00 dB
 SFO2 500.2228011 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
 NDM EM
 SSB 0
 GB 1.00 Hz
 PC 0
 GC 2.00

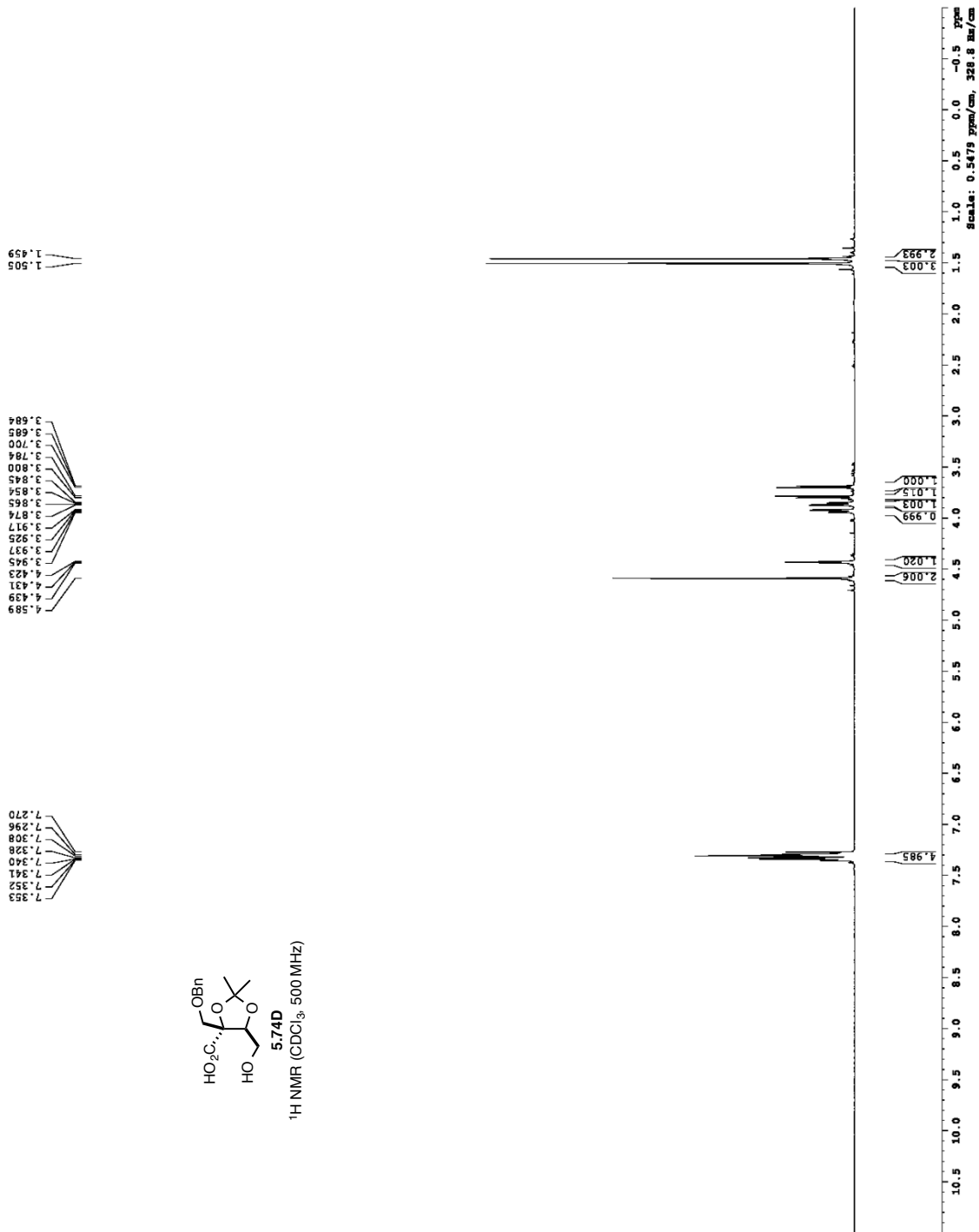
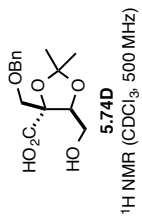


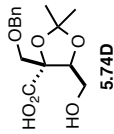
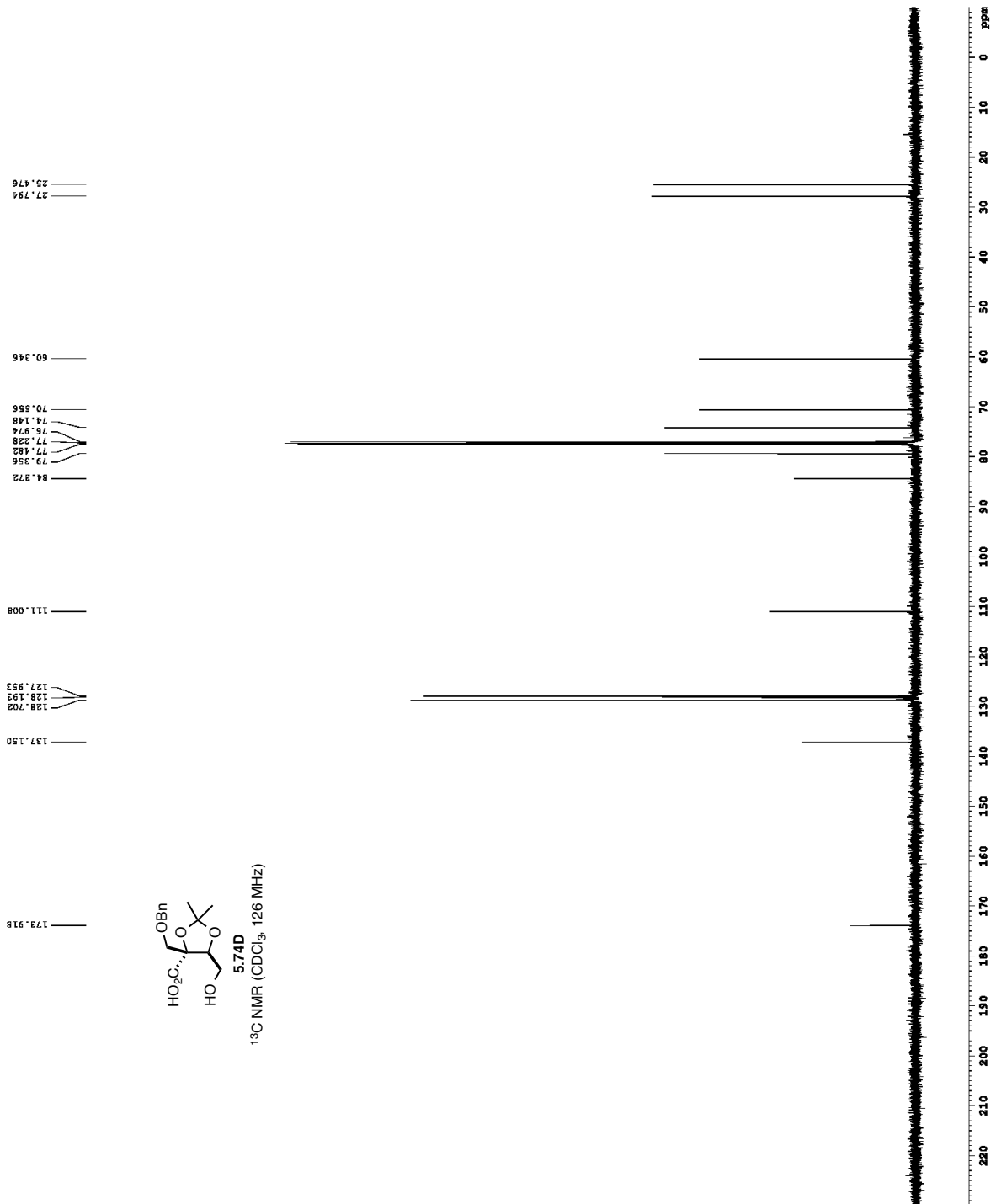
Current Data Parameters
 NAME YS-IV-61
 EXPNO 9
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160127
 Time 17:26
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 584
 DS 1
 SFO 303.031 Hz
 FIDRES 0.4828 Hz
 AQRES 1.081440 sec
 RG 5160.6
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 D11 0.0000000 sec
 D15 0.0020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 P2 33.10 usec
 CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P10 170.00 dB
 P12 10.00 dB
 SFO1 125.762548 MHz
 SF1 2.70 dB
 SF2 2.70 dB
 SPNAM[1] Crp60.0.5.20.1
 SPNAM[2] Crp60comp.4
 SFOF1 0 Hz
 SFOF2 0 Hz
 CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.50 dB
 P22 1.50 dB
 SFO2 500.2225011 MHz
 GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 0 %
 GPY2 0 %
 GPZ2 0 %
 P15 50.00 %
 P16 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.762548 MHz
 WDM 0 RM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00



YS-IV-37

Current Data Parameters
NAME: YS-IV-37
EXPNO: 2
PROCNO: 1
F2 - Acquisition Parameters
Date_ Acq: 2016_08_24
Time: 8.44
INSTRUM: spect
PULPROG: zgpg30
AQ: 9.671 s
RG: 327.5
SI: 8
SF: 9615.282 Hz
FIDRES: 0.09842 Hz
AQRES: 5.1595942 sec
RG: 4.616 sec
DE: 52.000 usec
TE: 298.2 K
D1: 0.10000000 sec
D11: 0.10000000 sec
CHUNK1: 1
SFO1: 600.132409 MHz
NUC1: 13C
P1: 24.0000000 usec
PC: 24.0000000 usec
F2 - Processing parameters
SI: 327.5
SF: 600.1300281 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00





¹³C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME YS-IV-37
 EXPNO 3
 F2PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160116
 Time 14.23
 INSTRUM cryo-500
 PROBHD 5 mm CPXI 1H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 304
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.442468 Hz
 AQ 1.081248 sec
 RG 728.2
 DW 16.500 usec
 DE 6.00 usec
 IE 298.0 K
 D1 0.25000000 sec
 d11 0.000000 sec
 d12 0.00020000 sec
 d15 0.00019600 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 P2 33.10 usec

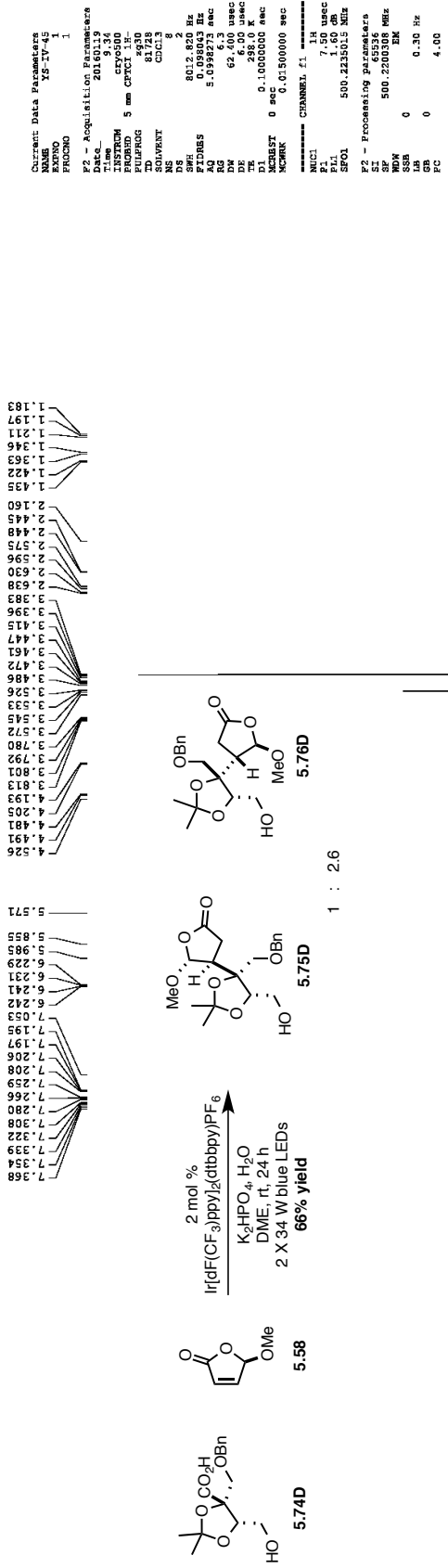
CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P1O 120.00 dB
 P1L 1.00 dB
 P1S 125.792508 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SPNAM[L1] Crp60.0.5.20.1
 SPNAM[L2] Crp60comp.4
 SFOF1 0 Hz
 SFOF2 0 Hz

CHANNEL f2
 CPDPRG[2] waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 4.00 dB
 P2O 500.00 MHz
 P2S 500.2225011 MHz

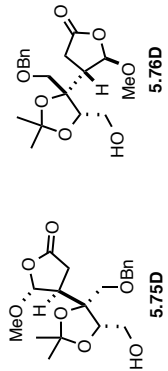
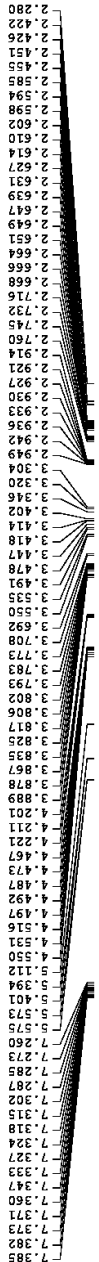
GRADIENT CHANNEL
 GPNAM[L1] SINE.100
 GPNAM[L2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 0 %
 GPY2 0 %
 GPZ2 0 %
 P15 50.00 %
 P16 500.00 usec
 P17 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7803997 MHz
 WDM 0
 SSB 0
 GB 0
 PC 2.00

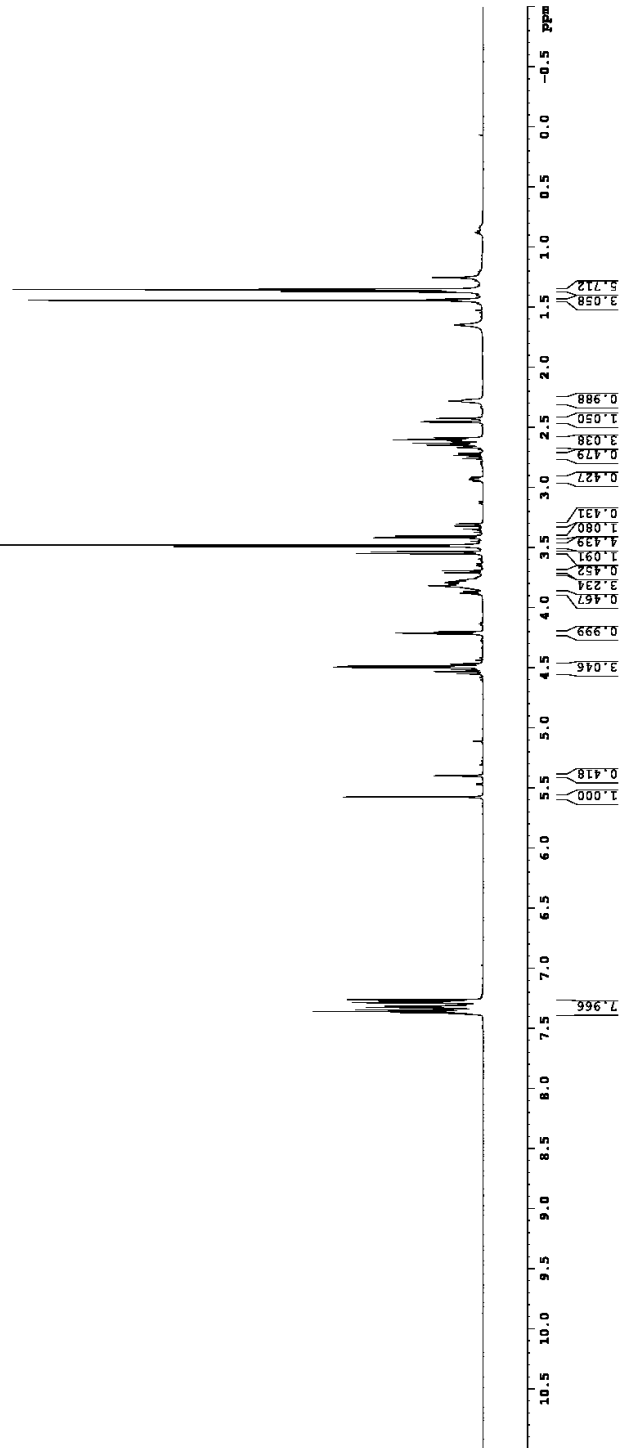
YS-IV-45

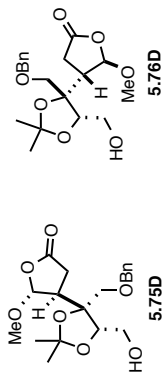


Current Data Parameters
 NAME YS-TV-45
 PACNO 1
 F2 - Acquisition Parameters
 Date_ 20161119
 Time_ 11:24:46
 INSTRUM 5 mm TFS 16SD
 PULPROG zgpg30
 ID 9874
 NS 1024
 DS 4
 SWH 9453.345 Hz
 FIDRES 0.098002 Hz
 AQ 5.029999 sec
 RG 382
 BK 21.024 MHz
 EQ 288.1 K
 TS 0.1000000 sec
 TD0 1
 CHANNEL f1
 RF01 600.1362009 MHz
 NUC1 13C
 P1 8.00 usec
 PL1 24.0000000 W
 F2 - Processing parameters
 SI 32768
 SF 600.1362009 MHz
 DS 4
 SWH 9453.345 Hz
 FIDRES 0.098002 Hz
 AQ 5.029999 sec
 RG 382
 BK 21.024 MHz
 EQ 288.1 K
 TS 0.1000000 sec
 TD0 1



1 : 2.6
¹H NMR (CDCl₃, 500 MHz)





1 : 2.6
¹³C NMR (CDCl₃, 126 MHz)

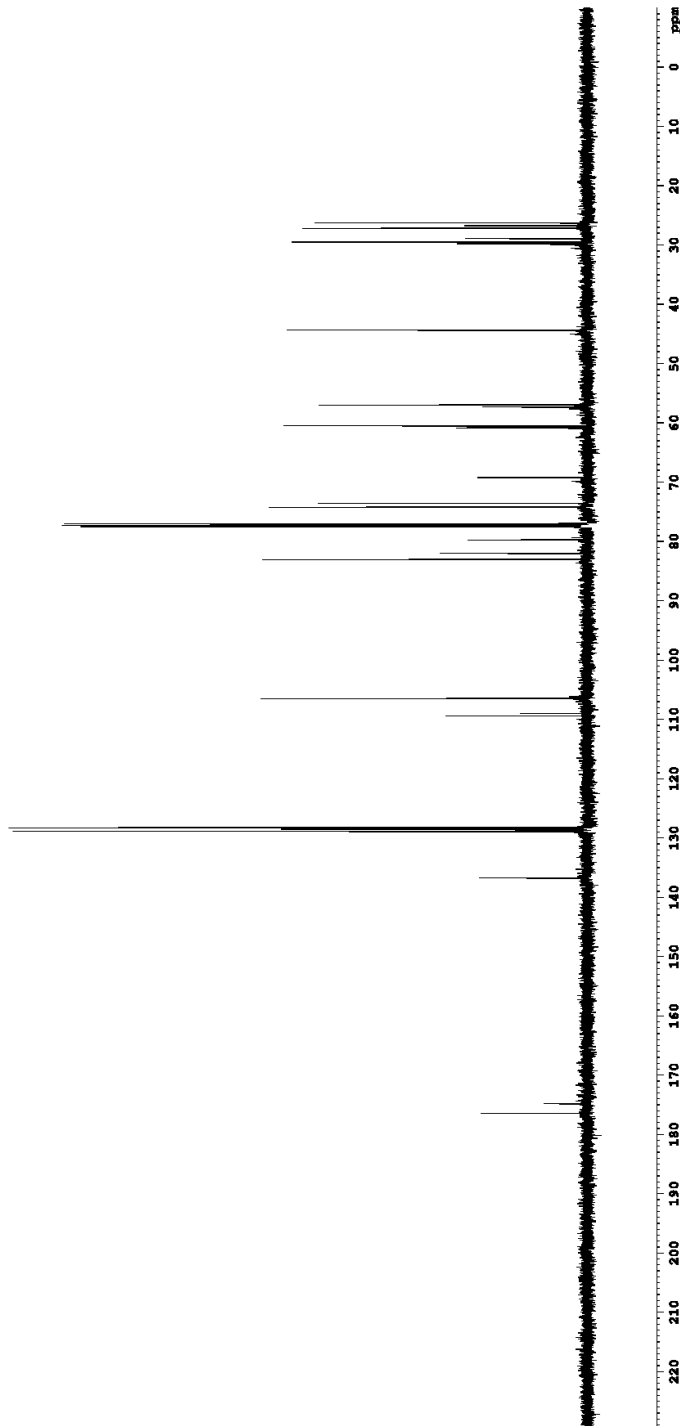
Current Data Parameters
 NAME YS-IV-45
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 File_ 2016112
 Date_ 15
 INSTRUM cryo500
 PROBDH 5 mm CPIC1 1H-
 PULPROG Sp1rEcho930pp.prd
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 9195.2
 DW 16.500 usec
 DE 298.0 K
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 ACQRES 0 sec
 WPCW 0.01500000 sec
 WPRK 33.10 usec

CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 PL1 0.00 dB
 P2 200.00 usec
 PL2 120.00 dB
 PL3 -1.00 dB
 PL4
 SF01 125.7942548 MHz
 SF2 2.70 dB
 SF3
 SPAN[M] C1P60.0 2.70 dB
 SPAN[F] 0 Hz
 SFOFF1 0 Hz
 SFOFF2 0 Hz

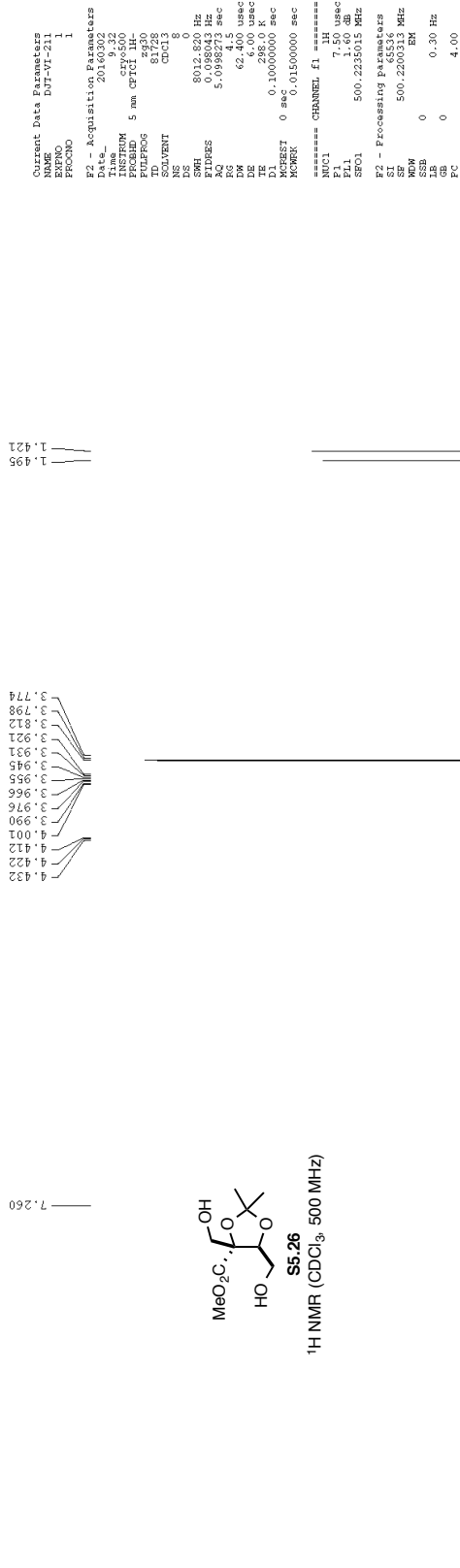
CHANNEL f2
 CPDPRG2 waltz16
 Mode
 PCPD2 100.00 usec
 PL2 1.60 dB
 PL12 24.50 dB
 SF02 500.2225011 MHz

GRADIENT CHANNEL
 GENAM[1] SINE.100
 GENAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GZ1 30.00 %
 GZ2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

F2 - Processing Parameters
 SI 65536
 SF 125.760482 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 2.00



¹H spectrum

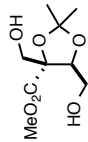


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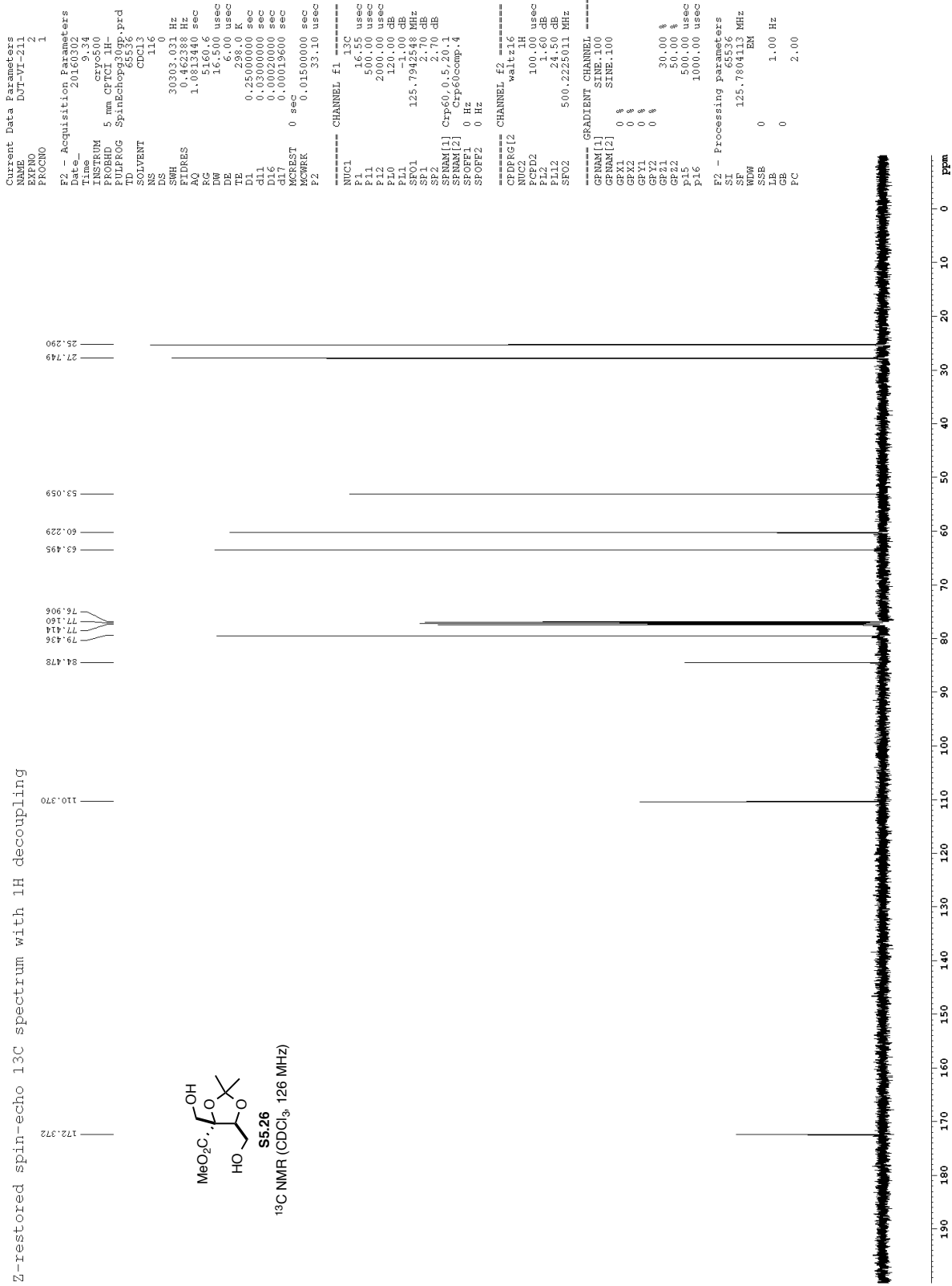
Current Data Parameters
NAME      DAT-WU-211
EXPNO    1
PROCNO   1
Date_    20160302
Time     0
INSTRUM  cryo500
PROBHD   5 mm QNP1H-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS       0
DS       0
SWH       8012.820 Hz
F2       500.136199 MHz
AQ       5.0988273 sec
RG       4.5
WDW       EM
SSB       0
LB        62.00 usec
GB        0.00 usec
TE        298.0 K
D1        0.10000000 sec
d11       0.01500000 sec
d12       0.01500000 sec
d13       0.01500000 sec
===== CHANNEL f1 =====
NUC1      1H
P1        7.50 usec
PL1       0.00 dB
SFO1      500.225015 MHz
===== CHANNEL f2 =====
NUC2      13C
P2        15.00 usec
PL2       0.00 dB
SFO2      125.760350 MHz
===== CHANNEL f3 =====
NUC3      13C
P3        15.00 usec
PL3       0.00 dB
SFO3      125.760350 MHz
===== CHANNEL f4 =====
NUC4      13C
P4        15.00 usec
PL4       0.00 dB
SFO4      125.760350 MHz
===== CHANNEL f5 =====
NUC5      13C
P5        15.00 usec
PL5       0.00 dB
SFO5      125.760350 MHz
===== CHANNEL f6 =====
NUC6      13C
P6        15.00 usec
PL6       0.00 dB
SFO6      125.760350 MHz
===== CHANNEL f7 =====
NUC7      13C
P7        15.00 usec
PL7       0.00 dB
SFO7      125.760350 MHz
===== CHANNEL f8 =====
NUC8      13C
P8        15.00 usec
PL8       0.00 dB
SFO8      125.760350 MHz
===== CHANNEL f9 =====
NUC9      13C
P9        15.00 usec
PL9       0.00 dB
SFO9      125.760350 MHz
===== CHANNEL f10 =====
NUC10     13C
P10       15.00 usec
PL10      0.00 dB
SFO10     125.760350 MHz
===== CHANNEL f11 =====
NUC11     13C
P11       15.00 usec
PL11      0.00 dB
SFO11     125.760350 MHz
===== CHANNEL f12 =====
NUC12     13C
P12       15.00 usec
PL12      0.00 dB
SFO12     125.760350 MHz
===== CHANNEL f13 =====
NUC13     13C
P13       15.00 usec
PL13      0.00 dB
SFO13     125.760350 MHz
===== CHANNEL f14 =====
NUC14     13C
P14       15.00 usec
PL14      0.00 dB
SFO14     125.760350 MHz
===== CHANNEL f15 =====
NUC15     13C
P15       15.00 usec
PL15      0.00 dB
SFO15     125.760350 MHz
===== CHANNEL f16 =====
NUC16     13C
P16       15.00 usec
PL16      0.00 dB
SFO16     125.760350 MHz
===== CHANNEL f17 =====
NUC17     13C
P17       15.00 usec
PL17      0.00 dB
SFO17     125.760350 MHz
===== CHANNEL f18 =====
NUC18     13C
P18       15.00 usec
PL18      0.00 dB
SFO18     125.760350 MHz
===== CHANNEL f19 =====
NUC19     13C
P19       15.00 usec
PL19      0.00 dB
SFO19     125.760350 MHz
===== CHANNEL f20 =====
NUC20     13C
P20       15.00 usec
PL20      0.00 dB
SFO20     125.760350 MHz
===== CHANNEL f21 =====
NUC21     13C
P21       15.00 usec
PL21      0.00 dB
SFO21     125.760350 MHz
===== CHANNEL f22 =====
NUC22     13C
P22       15.00 usec
PL22      0.00 dB
SFO22     125.760350 MHz
===== CHANNEL f23 =====
NUC23     13C
P23       15.00 usec
PL23      0.00 dB
SFO23     125.760350 MHz
===== CHANNEL f24 =====
NUC24     13C
P24       15.00 usec
PL24      0.00 dB
SFO24     125.760350 MHz
===== CHANNEL f25 =====
NUC25     13C
P25       15.00 usec
PL25      0.00 dB
SFO25     125.760350 MHz
===== CHANNEL f26 =====
NUC26     13C
P26       15.00 usec
PL26      0.00 dB
SFO26     125.760350 MHz
===== CHANNEL f27 =====
NUC27     13C
P27       15.00 usec
PL27      0.00 dB
SFO27     125.760350 MHz
===== CHANNEL f28 =====
NUC28     13C
P28       15.00 usec
PL28      0.00 dB
SFO28     125.760350 MHz
===== CHANNEL f29 =====
NUC29     13C
P29       15.00 usec
PL29      0.00 dB
SFO29     125.760350 MHz
===== CHANNEL f30 =====
NUC30     13C
P30       15.00 usec
PL30      0.00 dB
SFO30     125.760350 MHz
===== CHANNEL f31 =====
NUC31     13C
P31       15.00 usec
PL31      0.00 dB
SFO31     125.760350 MHz
===== CHANNEL f32 =====
NUC32     13C
P32       15.00 usec
PL32      0.00 dB
SFO32     125.760350 MHz
===== CHANNEL f33 =====
NUC33     13C
P33       15.00 usec
PL33      0.00 dB
SFO33     125.760350 MHz
===== CHANNEL f34 =====
NUC34     13C
P34       15.00 usec
PL34      0.00 dB
SFO34     125.760350 MHz
===== CHANNEL f35 =====
NUC35     13C
P35       15.00 usec
PL35      0.00 dB
SFO35     125.760350 MHz
===== CHANNEL f36 =====
NUC36     13C
P36       15.00 usec
PL36      0.00 dB
SFO36     125.760350 MHz
===== CHANNEL f37 =====
NUC37     13C
P37       15.00 usec
PL37      0.00 dB
SFO37     125.760350 MHz
===== CHANNEL f38 =====
NUC38     13C
P38       15.00 usec
PL38      0.00 dB
SFO38     125.760350 MHz
===== CHANNEL f39 =====
NUC39     13C
P39       15.00 usec
PL39      0.00 dB
SFO39     125.760350 MHz
===== CHANNEL f40 =====
NUC40     13C
P40       15.00 usec
PL40      0.00 dB
SFO40     125.760350 MHz
===== CHANNEL f41 =====
NUC41     13C
P41       15.00 usec
PL41      0.00 dB
SFO41     125.760350 MHz
===== CHANNEL f42 =====
NUC42     13C
P42       15.00 usec
PL42      0.00 dB
SFO42     125.760350 MHz
===== CHANNEL f43 =====
NUC43     13C
P43       15.00 usec
PL43      0.00 dB
SFO43     125.760350 MHz
===== CHANNEL f44 =====
NUC44     13C
P44       15.00 usec
PL44      0.00 dB
SFO44     125.760350 MHz
===== CHANNEL f45 =====
NUC45     13C
P45       15.00 usec
PL45      0.00 dB
SFO45     125.760350 MHz
===== CHANNEL f46 =====
NUC46     13C
P46       15.00 usec
PL46      0.00 dB
SFO46     125.760350 MHz
===== CHANNEL f47 =====
NUC47     13C
P47       15.00 usec
PL47      0.00 dB
SFO47     125.760350 MHz
===== CHANNEL f48 =====
NUC48     13C
P48       15.00 usec
PL48      0.00 dB
SFO48     125.760350 MHz
===== CHANNEL f49 =====
NUC49     13C
P49       15.00 usec
PL49      0.00 dB
SFO49     125.760350 MHz
===== CHANNEL f50 =====
NUC50     13C
P50       15.00 usec
PL50      0.00 dB
SFO50     125.760350 MHz
===== CHANNEL f51 =====
NUC51     13C
P51       15.00 usec
PL51      0.00 dB
SFO51     125.760350 MHz
===== CHANNEL f52 =====
NUC52     13C
P52       15.00 usec
PL52      0.00 dB
SFO52     125.760350 MHz
===== CHANNEL f53 =====
NUC53     13C
P53       15.00 usec
PL53      0.00 dB
SFO53     125.760350 MHz
===== CHANNEL f54 =====
NUC54     13C
P54       15.00 usec
PL54      0.00 dB
SFO54     125.760350 MHz
===== CHANNEL f55 =====
NUC55     13C
P55       15.00 usec
PL55      0.00 dB
SFO55     125.760350 MHz
===== CHANNEL f56 =====
NUC56     13C
P56       15.00 usec
PL56      0.00 dB
SFO56     125.760350 MHz
===== CHANNEL f57 =====
NUC57     13C
P57       15.00 usec
PL57      0.00 dB
SFO57     125.760350 MHz
===== CHANNEL f58 =====
NUC58     13C
P58       15.00 usec
PL58      0.00 dB
SFO58     125.760350 MHz
===== CHANNEL f59 =====
NUC59     13C
P59       15.00 usec
PL59      0.00 dB
SFO59     125.760350 MHz
===== CHANNEL f60 =====
NUC60     13C
P60       15.00 usec
PL60      0.00 dB
SFO60     125.760350 MHz
===== CHANNEL f61 =====
NUC61     13C
P61       15.00 usec
PL61      0.00 dB
SFO61     125.760350 MHz
===== CHANNEL f62 =====
NUC62     13C
P62       15.00 usec
PL62      0.00 dB
SFO62     125.760350 MHz
===== CHANNEL f63 =====
NUC63     13C
P63       15.00 usec
PL63      0.00 dB
SFO63     125.760350 MHz
===== CHANNEL f64 =====
NUC64     13C
P64       15.00 usec
PL64      0.00 dB
SFO64     125.760350 MHz
===== CHANNEL f65 =====
NUC65     13C
P65       15.00 usec
PL65      0.00 dB
SFO65     125.760350 MHz
===== CHANNEL f66 =====
NUC66     13C
P66       15.00 usec
PL66      0.00 dB
SFO66     125.760350 MHz
===== CHANNEL f67 =====
NUC67     13C
P67       15.00 usec
PL67      0.00 dB
SFO67     125.760350 MHz
===== CHANNEL f68 =====
NUC68     13C
P68       15.00 usec
PL68      0.00 dB
SFO68     125.760350 MHz
===== CHANNEL f69 =====
NUC69     13C
P69       15.00 usec
PL69      0.00 dB
SFO69     125.760350 MHz
===== CHANNEL f70 =====
NUC70     13C
P70       15.00 usec
PL70      0.00 dB
SFO70     125.760350 MHz
===== CHANNEL f71 =====
NUC71     13C
P71       15.00 usec
PL71      0.00 dB
SFO71     125.760350 MHz
===== CHANNEL f72 =====
NUC72     13C
P72       15.00 usec
PL72      0.00 dB
SFO72     125.760350 MHz
===== CHANNEL f73 =====
NUC73     13C
P73       15.00 usec
PL73      0.00 dB
SFO73     125.760350 MHz
===== CHANNEL f74 =====
NUC74     13C
P74       15.00 usec
PL74      0.00 dB
SFO74     125.760350 MHz
===== CHANNEL f75 =====
NUC75     13C
P75       15.00 usec
PL75      0.00 dB
SFO75     125.760350 MHz
===== CHANNEL f76 =====
NUC76     13C
P76       15.00 usec
PL76      0.00 dB
SFO76     125.760350 MHz
===== CHANNEL f77 =====
NUC77     13C
P77       15.00 usec
PL77      0.00 dB
SFO77     125.760350 MHz
===== CHANNEL f78 =====
NUC78     13C
P78       15.00 usec
PL78      0.00 dB
SFO78     125.760350 MHz
===== CHANNEL f79 =====
NUC79     13C
P79       15.00 usec
PL79      0.00 dB
SFO79     125.760350 MHz
===== CHANNEL f80 =====
NUC80     13C
P80       15.00 usec
PL80      0.00 dB
SFO80     125.760350 MHz
===== CHANNEL f81 =====
NUC81     13C
P81       15.00 usec
PL81      0.00 dB
SFO81     125.760350 MHz
===== CHANNEL f82 =====
NUC82     13C
P82       15.00 usec
PL82      0.00 dB
SFO82     125.760350 MHz
===== CHANNEL f83 =====
NUC83     13C
P83       15.00 usec
PL83      0.00 dB
SFO83     125.760350 MHz
===== CHANNEL f84 =====
NUC84     13C
P84       15.00 usec
PL84      0.00 dB
SFO84     125.760350 MHz
===== CHANNEL f85 =====
NUC85     13C
P85       15.00 usec
PL85      0.00 dB
SFO85     125.760350 MHz
===== CHANNEL f86 =====
NUC86     13C
P86       15.00 usec
PL86      0.00 dB
SFO86     125.760350 MHz
===== CHANNEL f87 =====
NUC87     13C
P87       15.00 usec
PL87      0.00 dB
SFO87     125.760350 MHz
===== CHANNEL f88 =====
NUC88     13C
P88       15.00 usec
PL88      0.00 dB
SFO88     125.760350 MHz
===== CHANNEL f89 =====
NUC89     13C
P89       15.00 usec
PL89      0.00 dB
SFO89     125.760350 MHz
===== CHANNEL f90 =====
NUC90     13C
P90       15.00 usec
PL90      0.00 dB
SFO90     125.760350 MHz
===== CHANNEL f91 =====
NUC91     13C
P91       15.00 usec
PL91      0.00 dB
SFO91     125.760350 MHz
===== CHANNEL f92 =====
NUC92     13C
P92       15.00 usec
PL92      0.00 dB
SFO92     125.760350 MHz
===== CHANNEL f93 =====
NUC93     13C
P93       15.00 usec
PL93      0.00 dB
SFO93     125.760350 MHz
===== CHANNEL f94 =====
NUC94     13C
P94       15.00 usec
PL94      0.00 dB
SFO94     125.760350 MHz
===== CHANNEL f95 =====
NUC95     13C
P95       15.00 usec
PL95      0.00 dB
SFO95     125.760350 MHz
===== CHANNEL f96 =====
NUC96     13C
P96       15.00 usec
PL96      0.00 dB
SFO96     125.760350 MHz
===== CHANNEL f97 =====
NUC97     13C
P97       15.00 usec
PL97      0.00 dB
SFO97     125.760350 MHz
===== CHANNEL f98 =====
NUC98     13C
P98       15.00 usec
PL98      0.00 dB
SFO98     125.760350 MHz
===== CHANNEL f99 =====
NUC99     13C
P99       15.00 usec
PL99      0.00 dB
SFO99     125.760350 MHz
===== CHANNEL f100 =====
NUC100    13C
P100      15.00 usec
PL100     0.00 dB
SFO100    125.760350 MHz

```

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



S5.26
¹³C NMR (CDCl₃, 126 MHz)



```

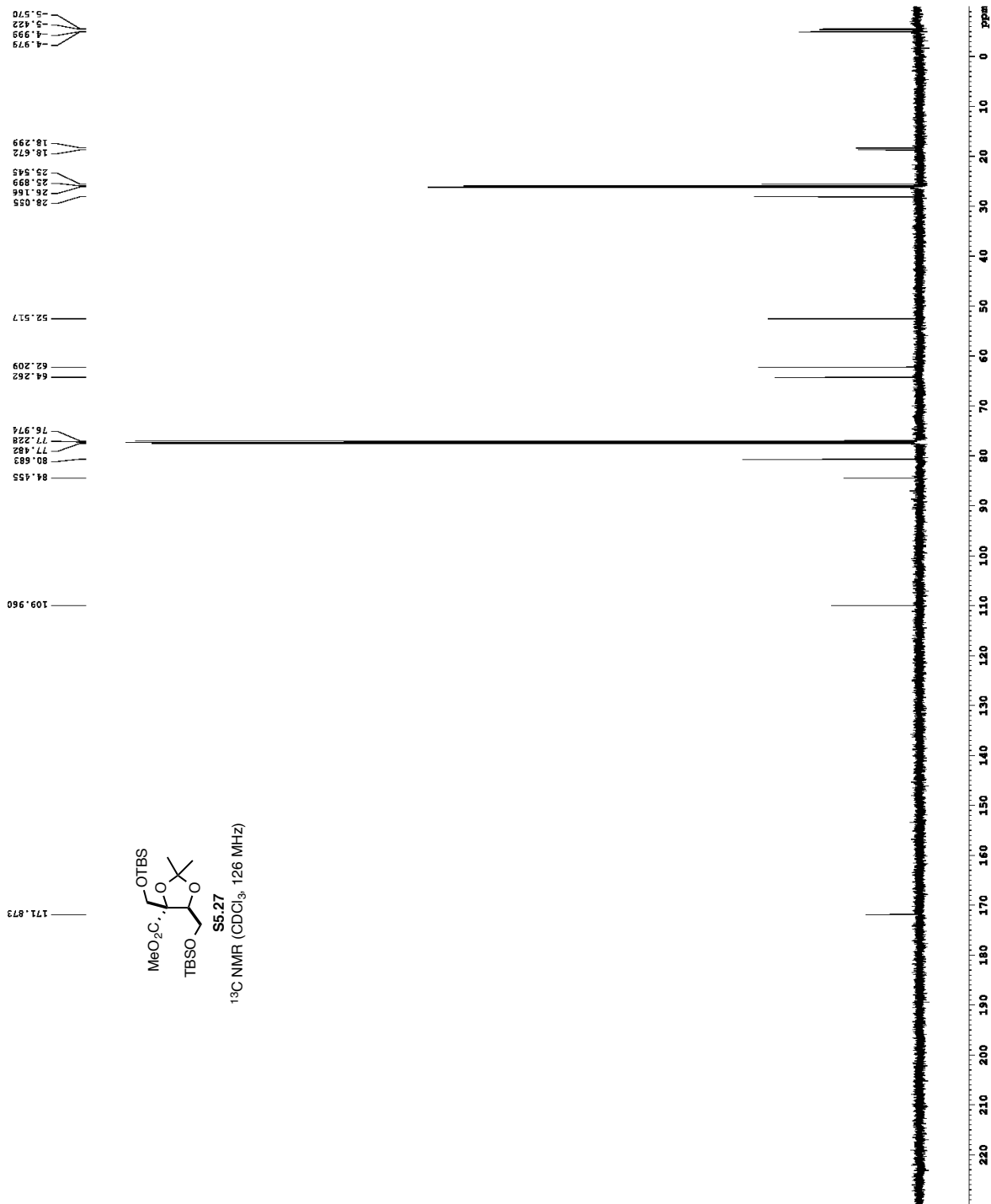
Current Data Parameters
NAME          DUT-VI-211
EXPNO         2
PROCNO        1
F2 - Acquisition Parameters
Date_         20160302
Time          9.34
INSTRUM       cryo500
PROBHD        5 mm CFTCI 1H-
PULPROG       SpinEchoq20sp.prd
TD            65536
SOLVENT       CDCl3
NS            1116
DS            10
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813440 sec
RG            516.00 usec
DE            16.00 usec
TE            298.0 K
DL            0.25000000 sec
dL1           0.03000000 sec
dL6           0.00020000 sec
MGREEST       0 sec
MGREK         0.01500000 sec
P2            33.10 usec

===== CHANNEL F1 =====
NUC1          13C
P1            16.00 usec
PL1           500.00 usec
P12           2000.00 usec
PL2           120.00 dB
PL0           120.00 dB
PL11          -1.00 dB
SFO1         125.7942548 MHz
SF1          2.70 dB
SF2          2.70 dB
SFNAM[1]     Cry60-0.5.20.1
SFNAM[2]     Cry60comp.4
SFOFF1       0 Hz
SFOFF2       0 Hz

===== CHANNEL F2 =====
CPDPRG12     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
GFX1         0 %
GFX2         0 %
GFI1         0 %
GFI2         0 %
GFZ1         30.00 %
GFZ2         50.00 %
p15          500.00 usec
p16          1000.00 usec

F2 - Processing Parameters
SI           65536
SF           125.7804113 MHz
WDW          EM
SSB          0
GB           0
PC           2.00
  
```

Current Data Parameters
 NAME DJT-VI-110
 EXPNO 2
 F2PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160202
 Time 8.59
 INSTRUM cryo500
 PROBHD 5 mm CPXI 1H-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 328
 DS 1
 SWH 30303.031 Hz
 FIDRES 0.491248 Hz
 AQ 1.087248 sec
 RG 2288.8
 DW 16.500 usec
 DE 6.00 usec
 IE 288.0 K
 D1 0.25000000 sec
 d11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 F2 33.10 usec

CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 125.7942500 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SFOF1 Crp60,0.5,20.1
 SFOF2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.60 dB
 P22 1.60 dB
 SFO2 500.2225011 MHz

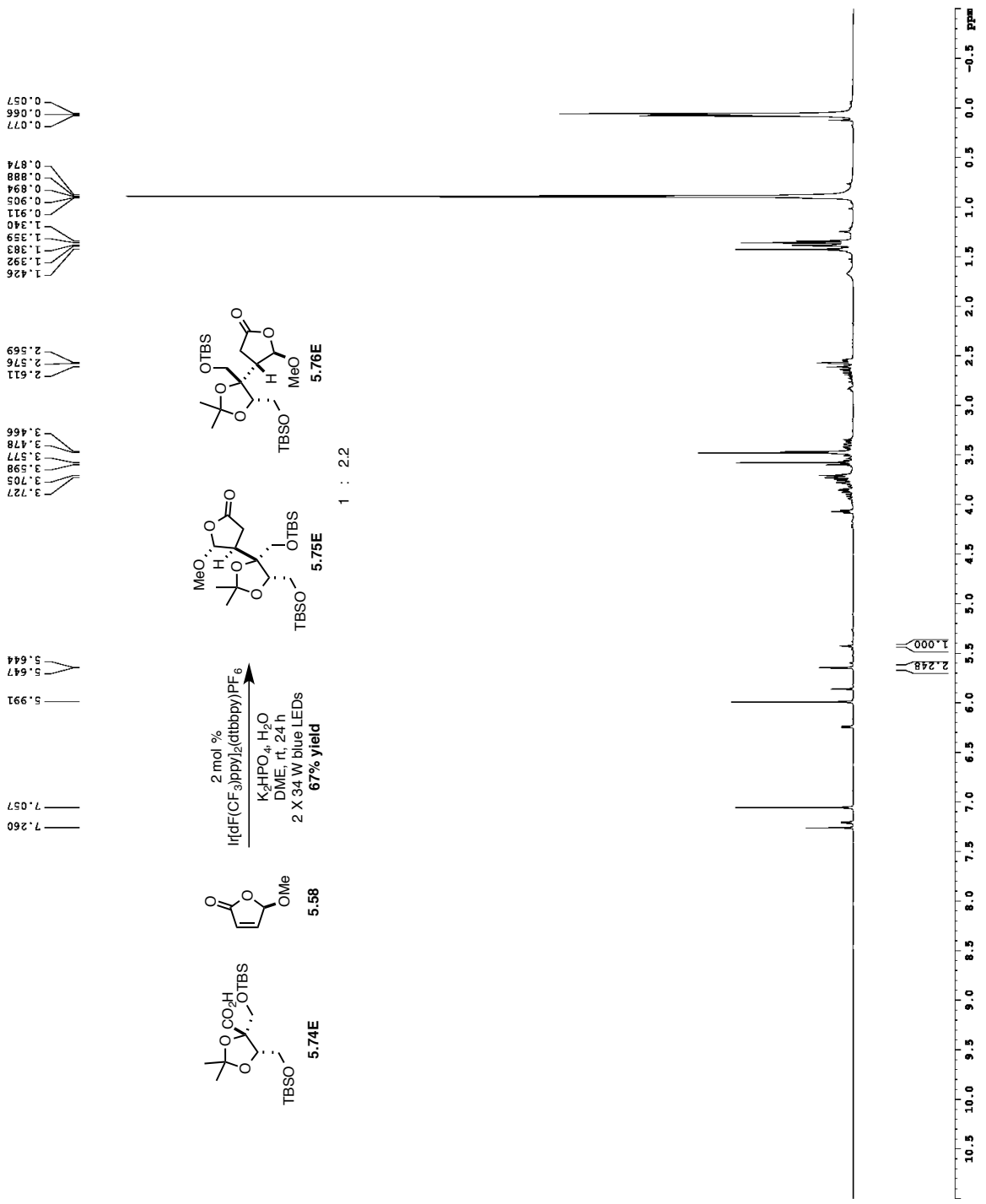
GRADIENT CHANNEL
 GPMAM[1] SINE.100
 GPMAM[2] SINE.100
 GPX1 0 *
 GPY1 0 *
 GPZ1 0 *
 GPX2 0 *
 GPY2 0 *
 GPZ2 0 *
 P15 30.00 *
 P16 50.00 *
 P17 500.00 usec
 P18 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7603989 MHz
 NDM 0
 SSB 0
 GB 0
 CB 0
 SC 2.00

YS-IV-44

```

Comment: Data Parameters
NAME      YS-IV-44
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Date_     20160119
Time      11.00
INSTRUM   spect
PROBHD    5 mm CPXI 1H-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         2
DS         2
SWH        8012.820 Hz
FIDRES     0.098043 Hz
AQ          5.1394657 sec
RG          51.7
RG2         51.7
DM          62.400 usec
DE          298.0 K
TE          298.0 K
D1          0.10000000 sec
d11        0.10000000 sec
d12        0.10000000 sec
d13        0.10000000 sec
d14        0.10000000 sec
d15        0.10000000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL1        0.00 dB
SFO1       500.253015 MHz
F2 - Processing parameters
SI         32768
SF          500.253014 MHz
WDW         EM
SSB         0
GB          0
PC          0
  
```



```

Current Data Parameters
NAME          YS-TV-44
PROCNO       1
F2 - Acquisition Parameters
Date_        20161119
Time_        11:01:19
INSTRUM      5 mm TFS 16SD
PROBHD       5102
PULPROG      zgpg30
ID           98074
VS UNIT      CACD 4
NS          4
DS          4
SFO1        600.1362009 MHz
P1          8.00 use
P2          24.0000000 W
P3
P4
F2 - Processing parameters
SI          0
SF          600.1362009 MHz
WDW         EM
SSB         0
LB          0
GB          0
PC          1.00
  
```

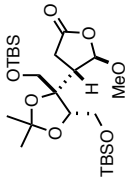
0.084
0.081
0.077
0.070
0.062
0.061

0.889
0.894
0.904
0.909
1.251
1.363
1.430
1.577

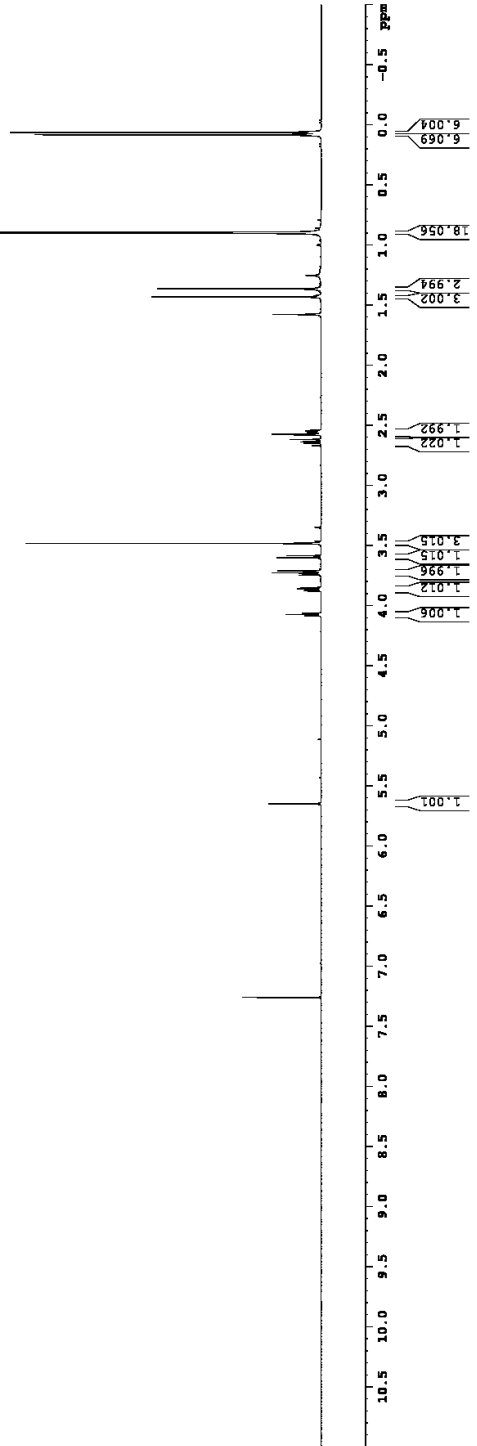
2.547
2.557
2.560
2.572
2.576
2.578
2.617
2.636
2.648
3.482
3.584
3.601
3.709
3.716
3.727
3.734
3.745
3.849
3.859
3.867
3.877
4.074
4.074
4.084

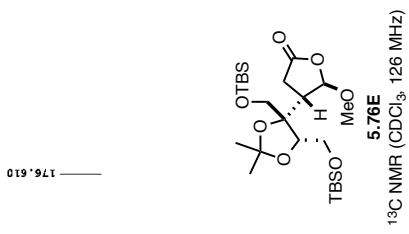
5.647
5.649

7.260



¹H NMR (CDCl₃, 600 MHz)





Current Data Parameters
 NAME YS-IV-44
 EXPNO 3
 F2PROC 1

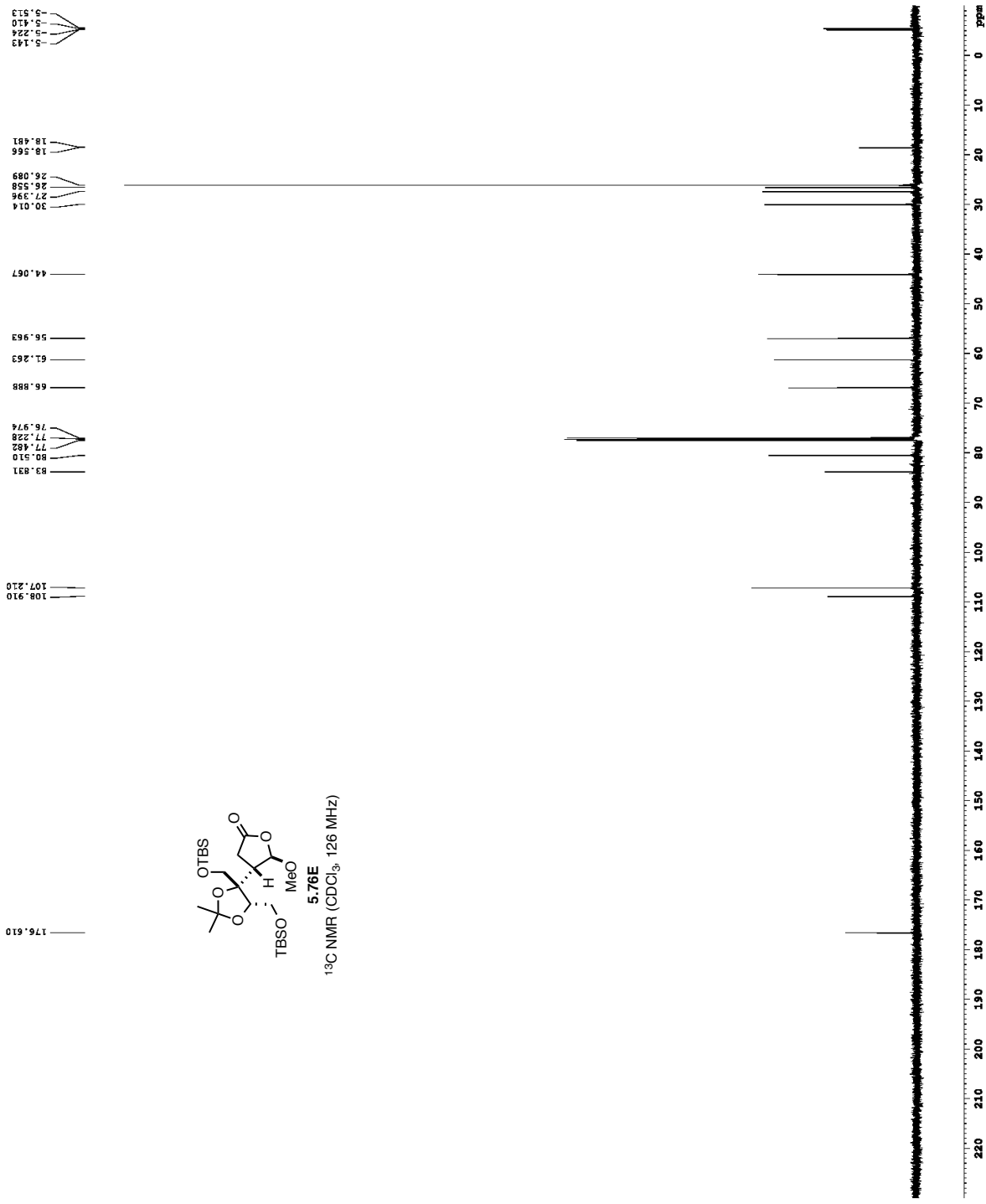
F2 - Acquisition Parameters
 Date_ 20160119
 Time 16.13
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 200
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.4817440 Hz
 AQ 1.0817440 sec
 RG 7298.2
 DM 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 F2 33.10 usec

CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P10 120.00 dB
 P11 0.00 dB
 P12 125.7942560 MHz
 SP1 2.70 dB
 SP2 2.70 dB
 SFNAM[1] Crp60,0.5,20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.80 dB
 P22 2.00 dB
 SFOFF 500.2225031 MHz

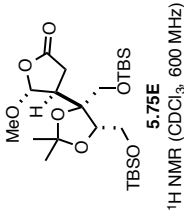
GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 30.00 %
 GPY2 50.00 %
 GPZ2 50.00 usec
 P15 500.00 usec
 P16 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7803991 MHz
 NDM 0
 SSB 0
 GB 1.00 Hz
 PC 0
 GC 2.00

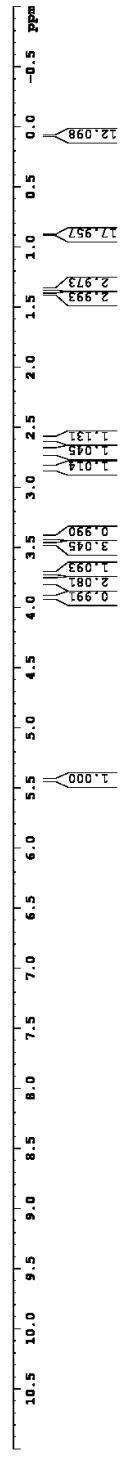


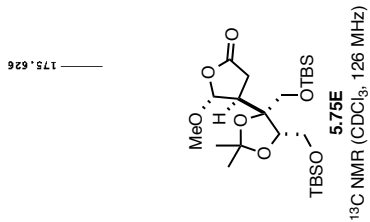
Current Data Parameters
 NAME YS-TV-44
 PACNO 1
 F2 - Acquisition Parameters
 Date_ 20161119
 Time_ 11:51:00
 INSTRUM 5 mm TET 143Q
 PULPROG zgpg30
 ID 98074
 EX 1
 NS 1000
 DS 4
 SWH 9653.385 Hz
 FIDRES 0.0988042 Hz
 AQ 5.0299999 sec
 RG 512
 BK 27.024 sec
 DM 327.680 sec
 TS 288.0 K
 TD 61.0000000 sec
 F0 60.1362009 MHz
 CHANNEL f1
 RF01 60.1362009 MHz
 P1 8.00 usec
 PL1 24.0000000 W
 F2 - Processing parameters
 SI 32768
 SF 600.136201 MHz
 SWH 9653.385 Hz
 DS 4
 SSF 0
 SC 0
 EC 1.00

0.048
 0.057
 0.063
 0.071
 0.075
 0.082
 0.880
 0.884
 0.895
 0.905
 0.906
 1.253
 1.346
 1.365
 1.377
 1.389
 1.400
 1.432
 1.568
 2.576
 2.586
 2.605
 2.615
 2.678
 2.693
 2.707
 2.722
 2.827
 2.831
 2.837
 3.349
 3.404
 3.421
 3.465
 3.472
 3.483
 3.560
 3.705
 3.722
 3.753
 3.766
 3.783
 3.787
 3.804
 3.902
 3.906
 3.919
 3.923
 5.431
 5.436

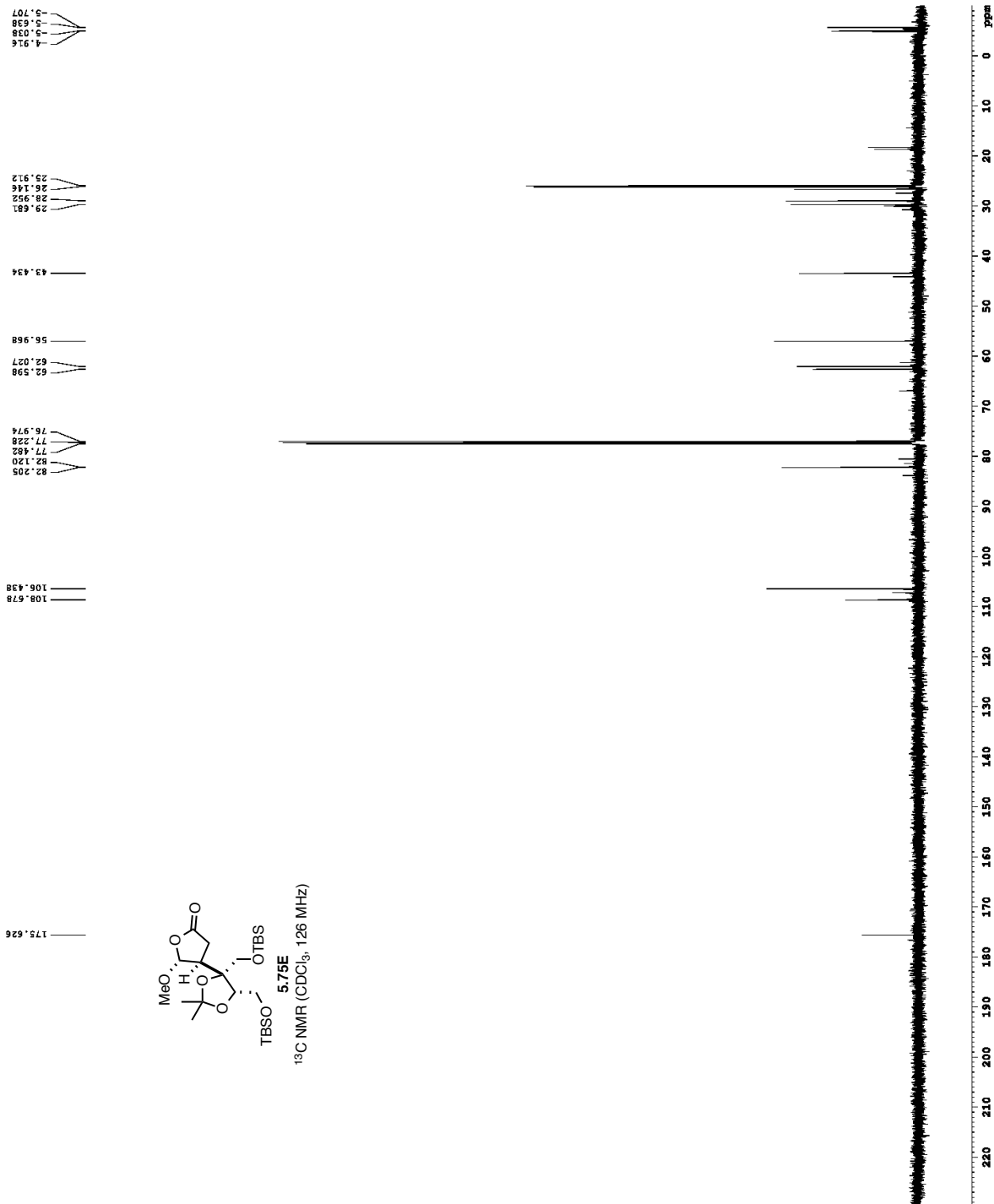


7.260

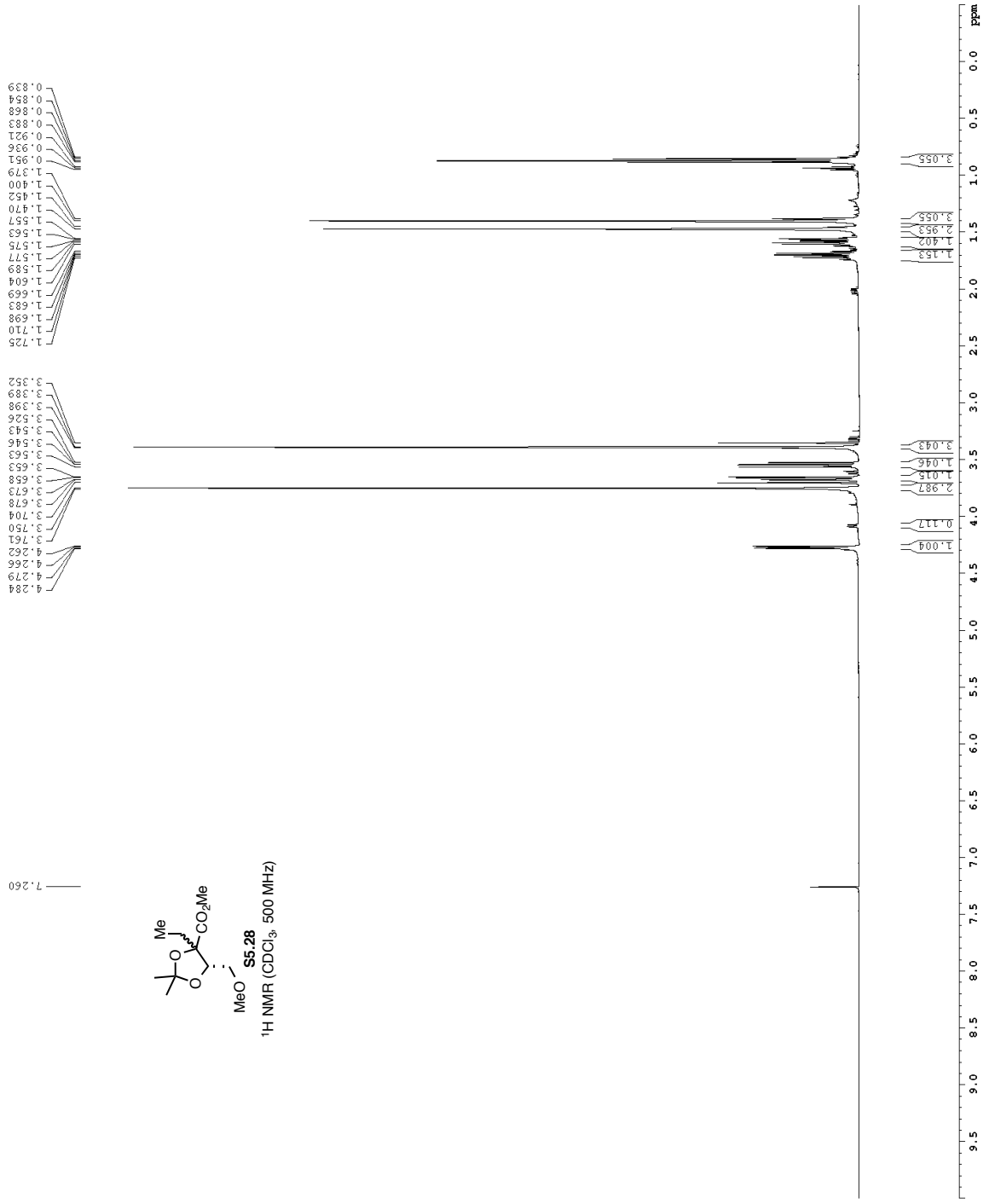




Current Data Parameters
 NAME YS-IV-44
 EXPNO 5
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160119
 Time 16.31
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 320
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.4817440 Hz
 AQ 1.0817440 sec
 RG 7298.2
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 D11 0.00000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCNRRK 0.01500000 sec
 F2 33.10 usec
 CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 P14 120.00 dB
 P15 0.00000000 sec
 SFO1 125.7642500 MHz
 SF2 2.70 dB
 SF21 2.70 dB
 SF22 2.70 dB
 SFNAM[1] Crp60, 0.5, 20.1
 SFNAM[2] Crp60comp.4
 SFOF1 0 Hz
 SFOF2 0 Hz
 CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.80 dB
 P22 2.00 dB
 SFO2 500.2225011 MHz
 GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 30.00 %
 GPY2 50.00 %
 GPZ2 50.00 usec
 P15 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.7803990 MHz
 NDM 0 EM
 SSB 0
 GB 0
 PC 2.00



¹H spectrum



Current Data Parameters
 NAME DT-VI-161
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ Time 20160112 15:17
 INSTRUM spect
 PROBRD 5 mm CPXI 1H
 PULPROG zgpg30
 SFO1 500.2235015 MHz
 AQ 5.098273 sec
 RG 62.400 usec
 NS 10
 DS 0
 EQ 8012.820 Hz
 FIDRES 0.098043 Hz
 AQ 5.098273 sec
 RG 62.400 usec
 DE 6.00 usec
 TE 300.2 K
 D1 0.10000000 sec
 MCHRES1 0 sec
 MCHRES2 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 7.15 usec
 PL1 1.40 dB
 SFO1 500.2235015 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.2235015 MHz
 KW 0
 SSB 0
 GB 0
 PC 4.00

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

```

Current Data Parameters
NAME      DOT-VI-161
EXPNO    6
PROCNO   1
F2 - Acquisition Parameters
Date_    20160117
Time     15.21
INSTRUM  cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  Spinecho90upg.prd
D1       6.500000
SOLVENT  CDCl3
NS       253
DS       0
SWH      30303.031 Hz
FIDRES   0.462388 Hz
AQ       1.081340 sec
RG       128.82
DE       16.500 usec
TE       298.0 K
D1       0.25000000 sec
d11      0.03000000 sec
D16      0.00020000 sec
MCREST   0 sec
MORPH    0
MORPHK   0
P2       0.01500000 sec
P2       33.10 usec
    
```

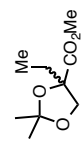
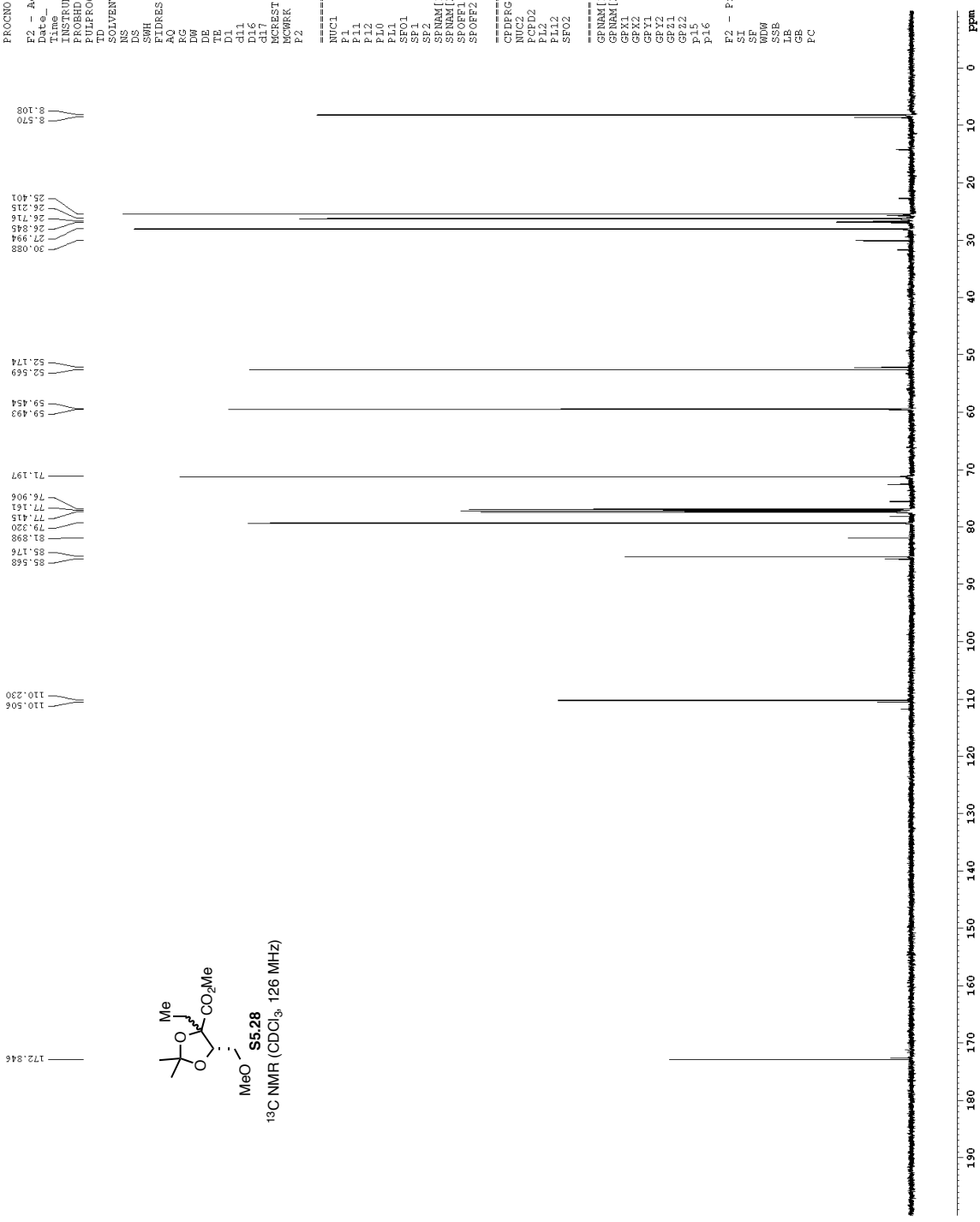
```

===== CHANNEL f1 =====
NUC1     13C
NUC2     1H
P1       500.00 usec
P2       2000.00 usec
PL1      120.00 dB
PL2      -1.00 dB
SFO1     125.7942548 MHz
SFO2     500.1362600 MHz
SFNAM[1] Cyp60_0_5_20_1
SFNAM[2] Cyp60comp_4
SFOFF1   0 Hz
SFOFF2   0 Hz

===== CHANNEL f2 =====
CFDPRG[2] waltz16
NUC2     1H
PCPD2    100.00 usec
PL2      1.60 dB
PL12     24.50 dB
SFO2     500.2225011 MHz

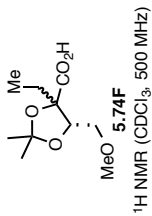
===== GRADIENT CHANNEL =====
GFNAM[1] SINE.100
GFNAM[2] SINE.100
GX1      0 %
GX2      0 %
GY1      0 %
GY2      0 %
GZ1      0 %
GZ2      0 %
P15      30.00 %
P16      50.00 %
P16      500.00 usec
P16      1000.00 usec

F2 - Processing Parameters
SI        65336
SF        125.7804145 MHz
WDW       EM
SSB       0
LB        0
GB        0
PC        2.00
    
```

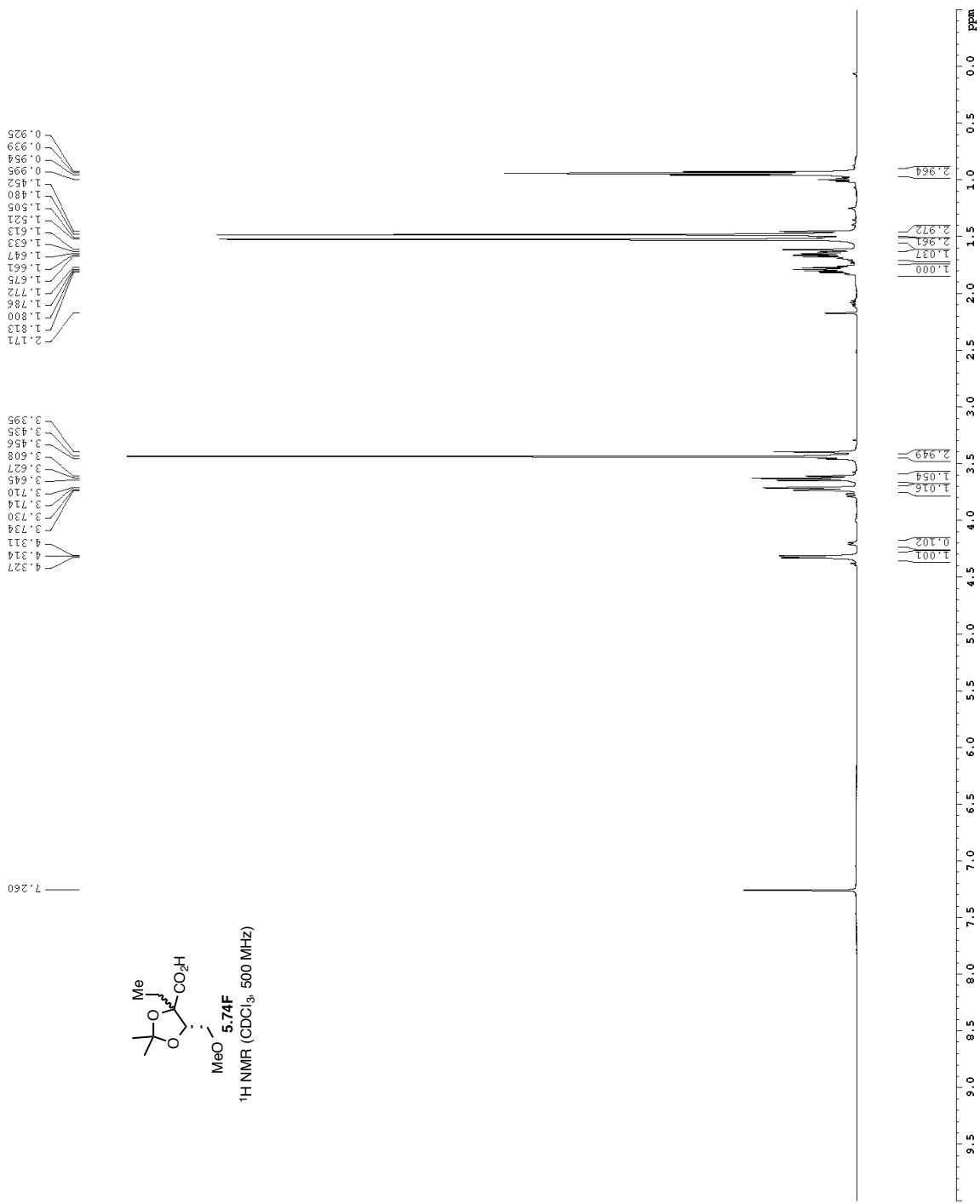


MeO S5.28
¹³C NMR (CDCl₃, 126 MHz)

¹H spectrum



Current Data Parameters
NAME: 077-VI-144
EXPNO: 2
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20160115
Time: 11:00:00
INSTRUM: cryo500
PROBHD: 5 mm CPXI_HH-
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
DS: 4
SWH: 801.520 Hz
AQ: 0.098273 sec
RG: 62.400 usec
DW: 62.400 usec
TE: 298.0 K
DPRST: 0 sec
MORPH: 0.01500000 sec
----- CHANNEL f1 -----
NUC1: ¹H
P1: 7.50 usec
PL1: 0.00 dB
SFO1: 500.2235015 MHz
F2 - Processing parameters
SI: 32768
SF: 500.22302299 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 4.00



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

```

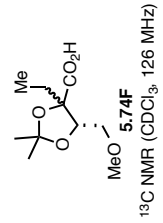
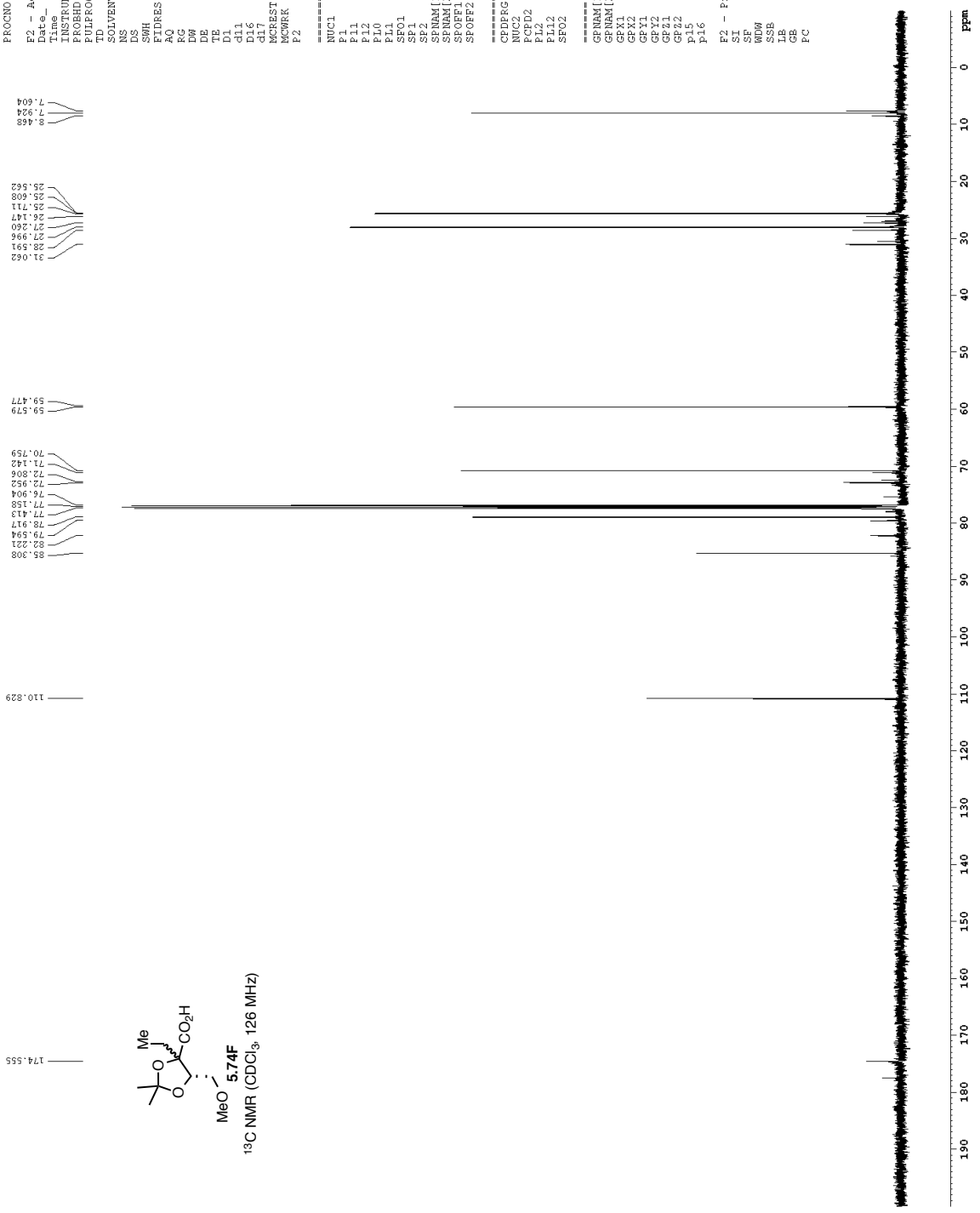
Current Data Parameters
NAME      DOT-VI-164
EXPNO    4
PROCNO   1
F2 - Acquisition Parameters
Date_    20160115
Time     14.44
INSTRUM  cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  Spinecho90upr.prd
D1       6.5000000
SOLVENT  CDCl3
NS       234
DS       0
SWH      30303.031 Hz
FIDRES   0.462388 Hz
AQ       1.0813440 sec
RG       6562
RG2      16.500 usec
DE       6.000 usec
TE       298.0 K
D11      0.25000000 sec
d111     0.03000000 sec
D16      0.00200000 sec
DELTA    0.0013600 sec
MCREST   0 sec
MORPH    0.01500000 sec
P2       33.10 usec
  
```

```

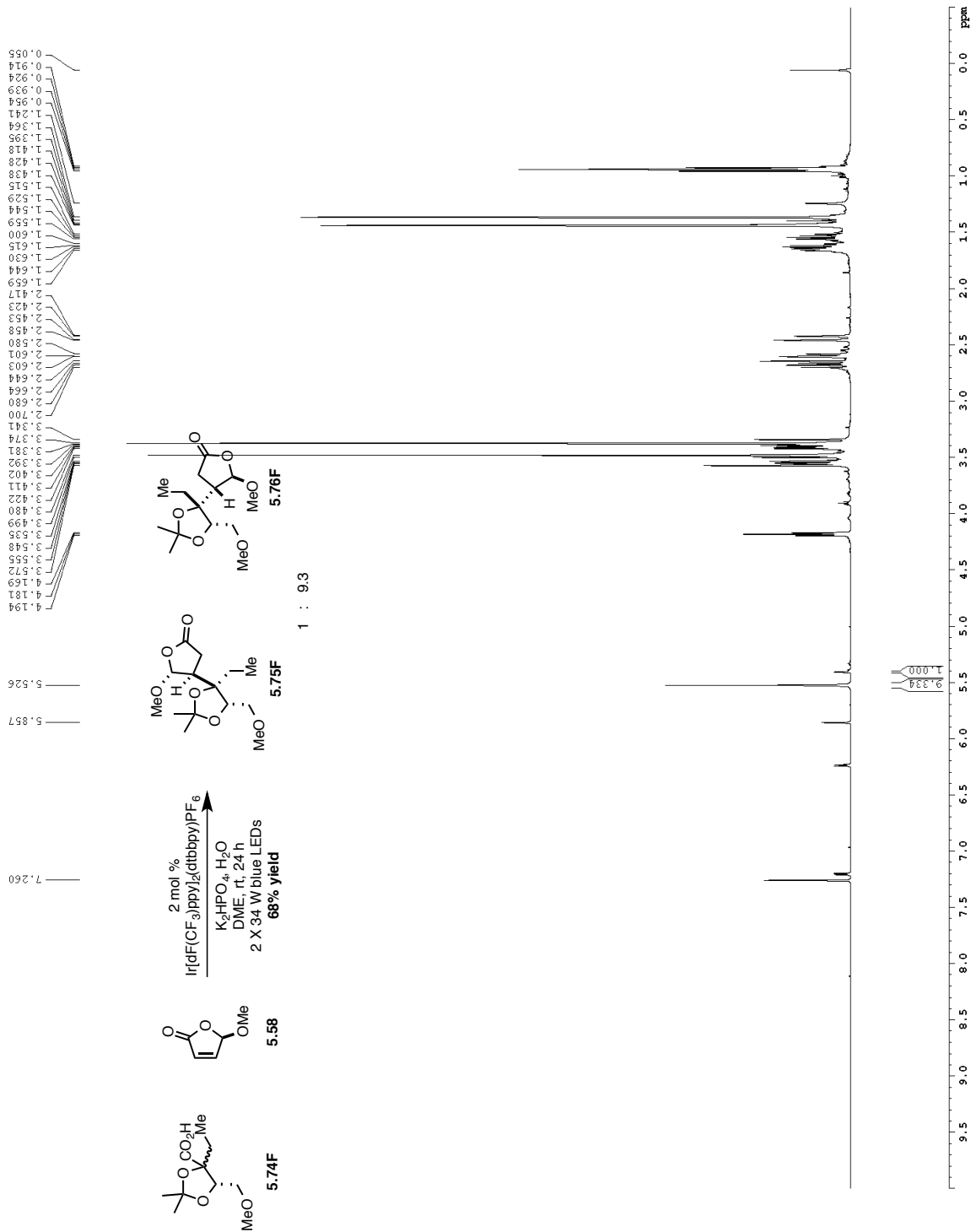
===== CHANNEL f1 =====
NUC1     13C
NUC2     1H
P1       500.00 usec
P2       2000.00 usec
PL0      120.00 dB
PL1      -1.00 dB
SFO1     125.7942548 MHz
SFO2     500.1362500 MHz
SFNAM[1] Cyp60_0_5_20_1
SFNAM[2] Cyp60comp_4
SFOFF1   0 Hz
SFOFF2   0 Hz
  
```

```

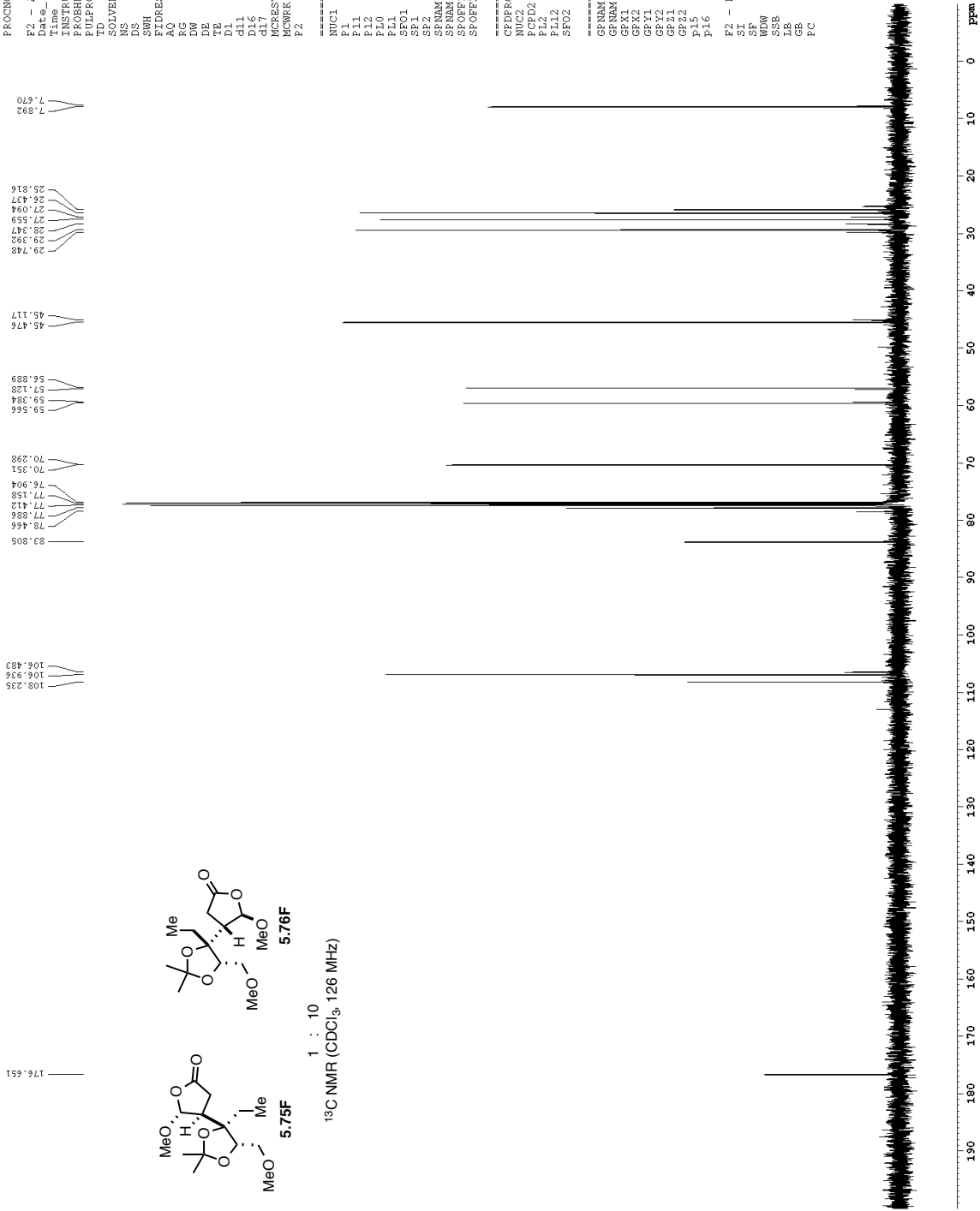
===== CHANNEL f2 =====
CFDPRG[2] waltz16
NUC2     1H
PCPD2    100.00 usec
PL2      1.60 dB
PL12     24.50 dB
SFO2     500.2225011 MHz
===== GRADIENT CHANNEL =====
GFNAM[1] SINE.100
GFNAM[2] SINE.100
GX1      0 %
GX2      0 %
GY1      0 %
GY2      0 %
p15      30.00 %
p16      50.00 %
p16      500.00 usec
p16      1000.00 usec
F2 - Processing Parameters
SI        65336
SF        125.7804095 MHz
WDW       EM
SSB       0
LB        0
GB        0
PC        2.00
  
```



1H spectrum



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



```

Current Data Parameters
NAME          DWT-VI-165
EXPNO         3
PROCNO        1
F2 - Acquisition Parameters
Date_         20160118
Time         10.05
INSTRUM       cryo500
PROBHD        5 mm CFTCI 1H-
PULPROG       SpinEcho9209p.prd
TD            65536
SOLVENT       CDCl3
NS            1124
DS            4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.081340 sec
RG            595.00
MG            15.500 usec
DE            6.00 usec
TE            298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
d15           0.00200000 sec
d16           0.00196000 sec
MCPRST        0 sec
MCORREK       0.01500000 sec
P2            33.10 usec

===== CHANNEL f1 =====
NUC1          13C
PC            15.00 usec
PL1           500.00 usec
PL2           2000.00 usec
PL0           120.00 dB
PL1           -1.00 dB
SFO1          125.7542548 MHz
SF           125.7542548 MHz
SF2           2.70 dB
SPNAM[1]      Cry60_0_5_20_1
SPNAM[2]      Cry60comp_4
SFOFF1        0 Hz
SFOFF2        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

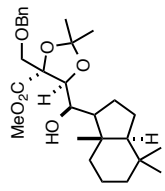
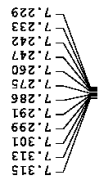
===== GRADIENT CHANNEL =====
GPNAM[1]      SINE.100
GPNAM[2]      SINE.100
GFX1          0 %
GFX2          0 %
GFL1          0 %
GFL2          0 %
GPD2          30.00 %
p15           50.00 usec
p16           1000.00 usec

F2 - Processing parameters
SI            65536
SF           125.7804039 MHz
WDW           EM
SSB           0
LB            0
GB            1.00 Hz
PC            2.00
  
```

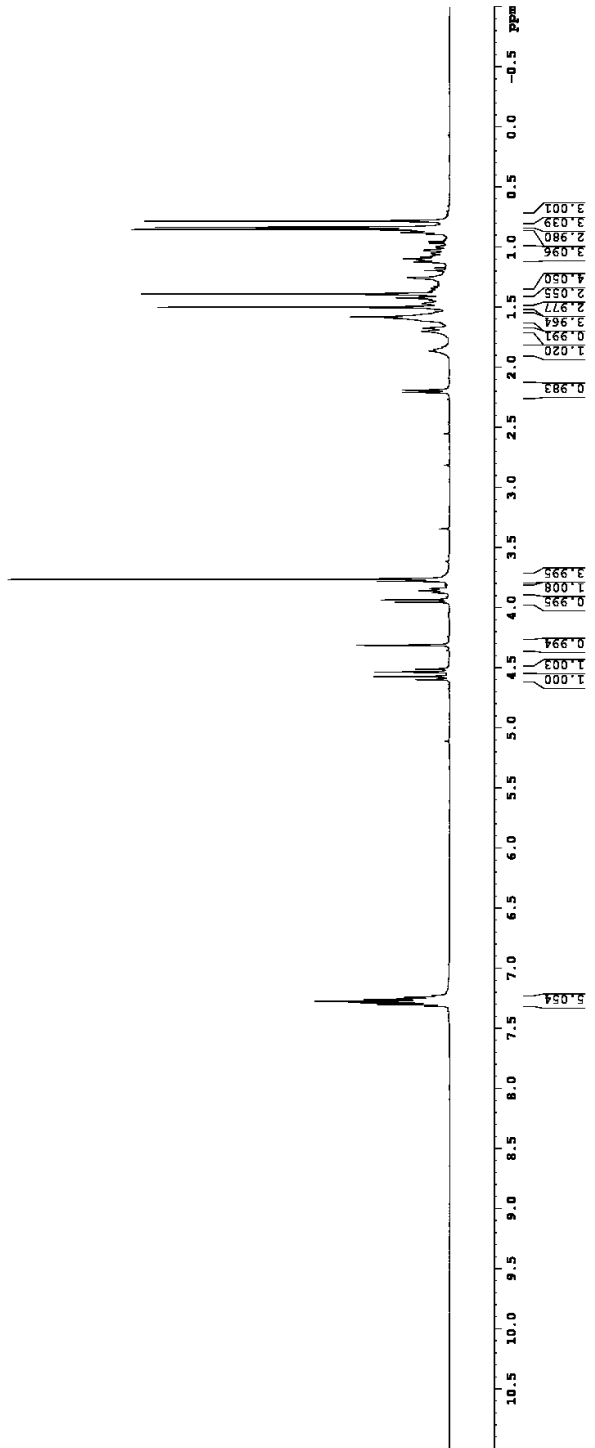


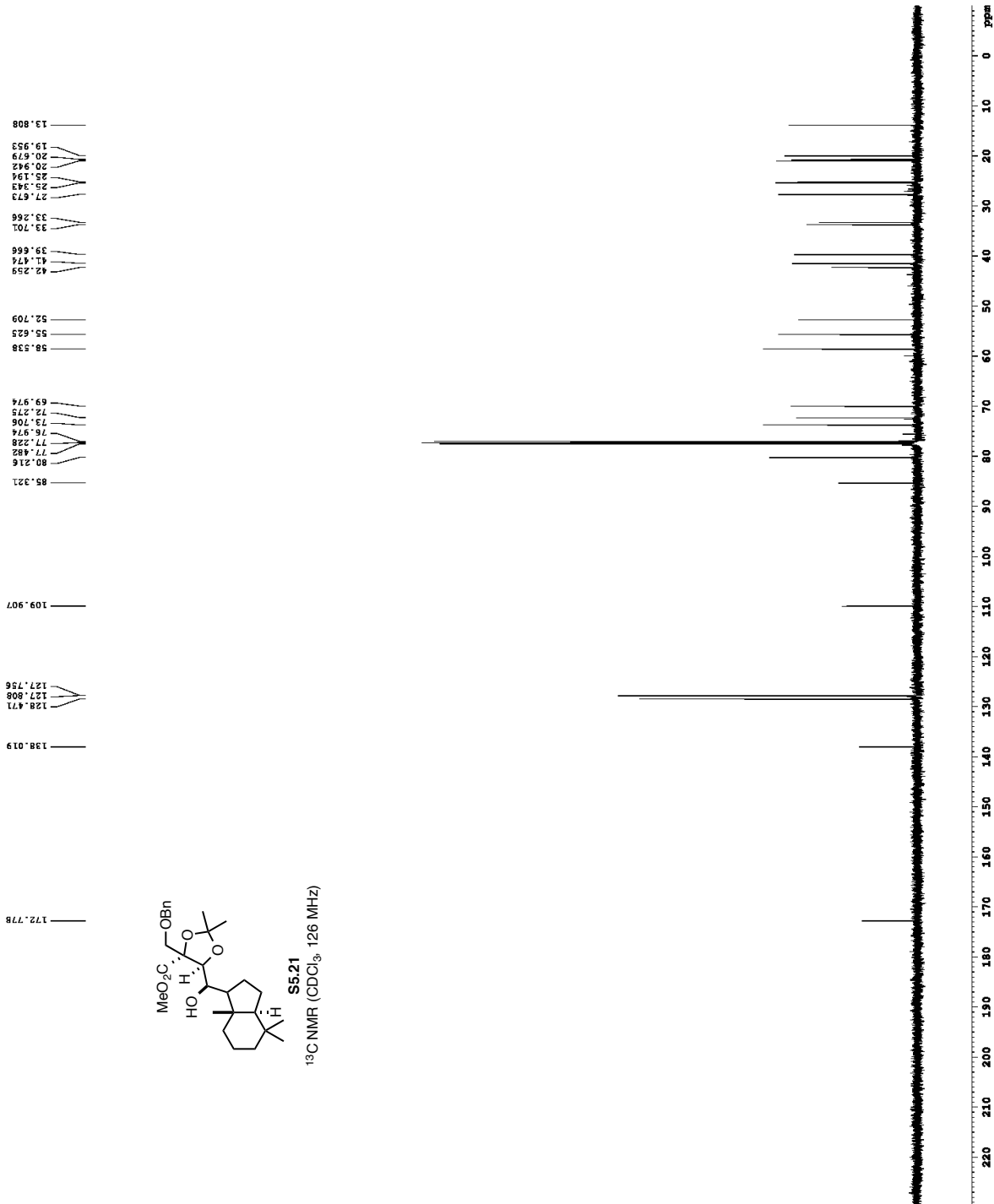
```

Current Data Parameters
NAME: S5-21
EXPNO: 1
PROCNO: 1
F2 - Acquisition Parameters
Time: 11.10
Date_Time: 11-11-00
INSTRUM: spect
PROBHD: 5 mm broadband
PULPROG: zgpg30
SFO: 500
AQ: 0.1929
RG: 327
SOLVENT: CDCl3
SS: 2
DS: 4
SFRATE: 0.152420 Hz
AQ: 5.4398273 sec
RG: 5.4398273 sec
DM: 62.400 use
DS: 2.00 use
SI: 2.00 use
D1: 0.1000000 sec
d11: 0.1000000 sec
d12: 0.1000000 sec
d13: 0.1000000 sec
d14: 0.1000000 sec
===== CHANNEL f1 =====
NUC1: 13C
P1: 1.00 use
PL1: -2.00 dB
SFO1: 499.1831943 MHz
F2 - Processing parameters
SI: 327
SF: 499.1831943 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
  
```



¹H NMR (CDCl₃, 500 MHz)





Current Data Parameters
 NAME YS-IV-55
 EXPNO 4
 F2PROCNO 1

F2 - Acquisition Parameters
 Date_ 20160125
 Time 16.51
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 1
 SWH 30303.031 Hz
 FIDRES 0.481340 Hz
 AQ 1.081340 sec
 RG 7298.2
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.5000000 sec
 d11 0.0000000 sec
 d16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCNRRK 0.01500000 sec
 F2 33.10 usec

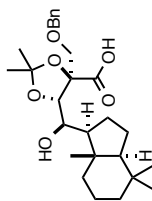
CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 0.00 dB
 PL2 125.7942500 MHz
 SF1 2.70 dB
 SF2 2.70 dB
 SFNAM[1] Crp60,0.5,20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.80 dB
 P22 2.00 dB
 PL0 500.13000 MHz
 SF02 500.2225031 MHz

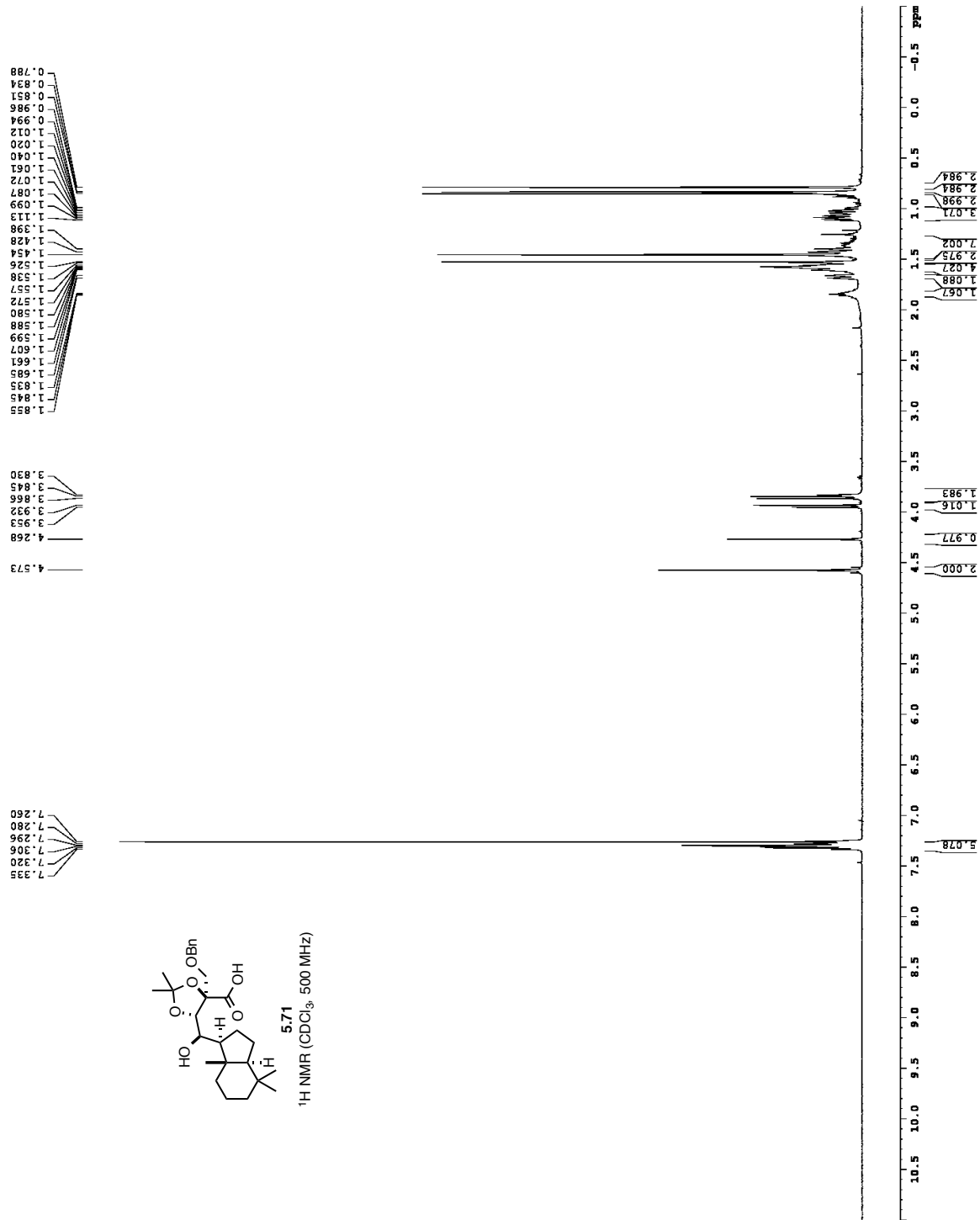
GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPX2 30.00 %
 GPY2 50.00 %
 GPZ2 50.00 usec
 PL5 1000.00 usec
 PL6 1000.00 usec

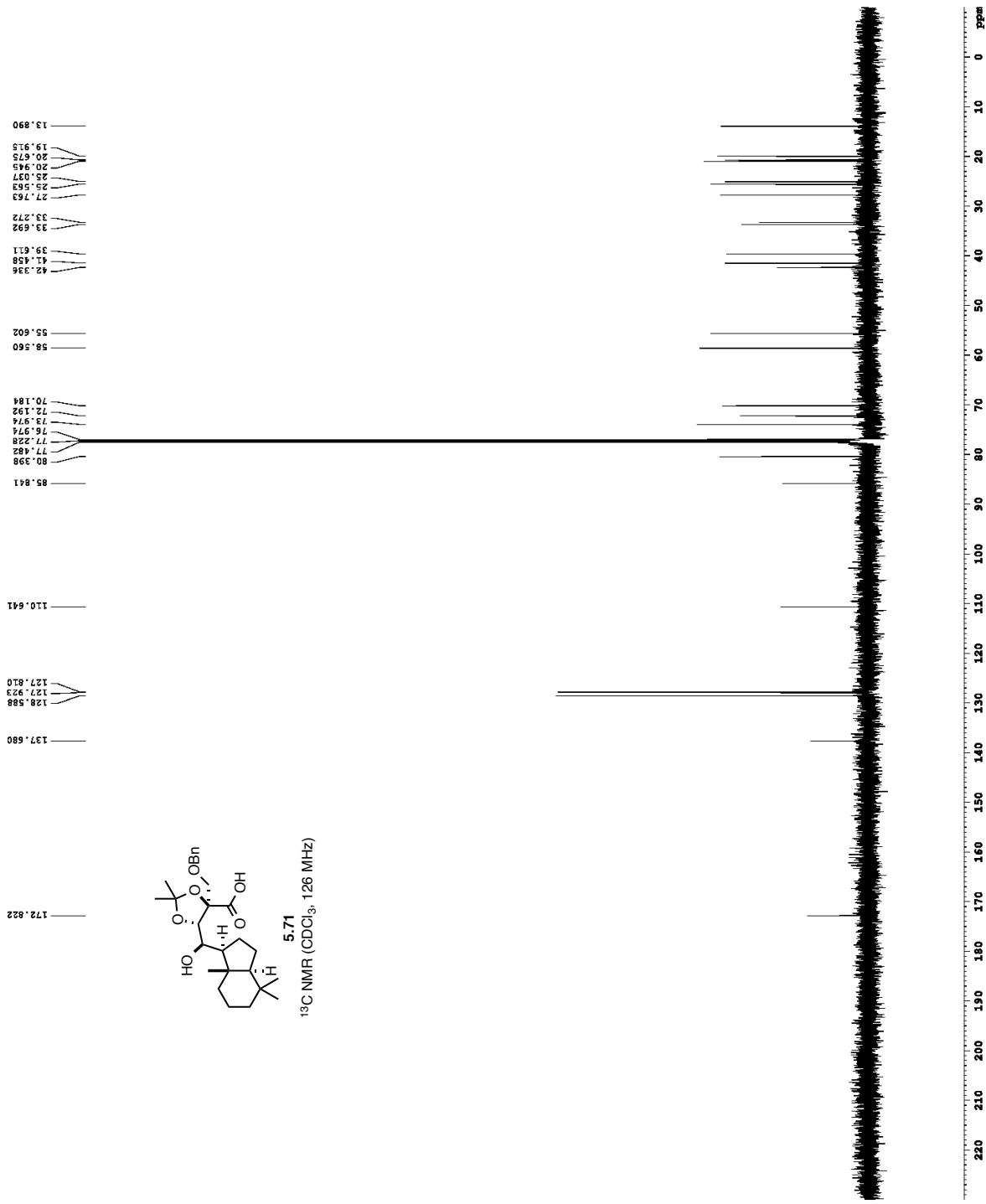
F2 - Processing parameters
 SI 65536
 SF 125.7803998 MHz
 NDM EM
 SSB 0
 GB 1.00 Hz
 PC 2.00

Current Data Parameters
 NAME YS-IV-56
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 2010128
 Time_ 17:02
 INSTRUM spect
 PULPROG zgpg30
 TD 65536
 NS 4096
 DS 4
 SWH 832.842 Hz
 FIDRES 0.098803 Hz
 RG 32768
 Acq 3.59747 sec
 NS2 4096
 DS2 4
 SWH2 832.842 Hz
 FIDRES2 0.098803 Hz
 RG2 32768
 Acq2 3.59747 sec
 TR 0.29840 K
 TE 300.2 K
 DE 0.1000000 sec
 MCHRESZ 0 sec
 MCHRES 0.0150000 sec
 ===== CHANNEL f1 =====
 NUC1 13C
 P1 7.50 usec
 PL1 0 dB
 SFO1 500.252515 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.252515 MHz
 DSF 0
 AS 0
 GB 0
 HC 4.00



¹H NMR (CDCl₃, 500 MHz)





13.890
19.915
20.675
21.949
23.037
25.563
27.763
33.272
33.692
39.611
41.458
42.336
55.602
58.560
70.184
72.192
72.974
76.974
77.228
77.482
80.598
85.841
110.641
127.810
127.923
128.588
137.680
172.822

Current Data Parameters
NAME YS-IV-56
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160128
Time 12.24

INSTRUM 5 mm CPXI 1H-
PROBHD SPHSCNCP0303
TD 65536
SOLVENT CDCl3
NS 700
DS 1
SWH 30303.031 Hz
FIDRES 0.452468 Hz
AQ 1.081248 sec
RG 5792.6
DM 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.00000000 sec
d12 0.00200000 sec
d15 0.00000000 sec
d17 0.00019600 sec
MCREST 0 sec
MCWRRK 0.01500000 sec
P2 33.10 usec

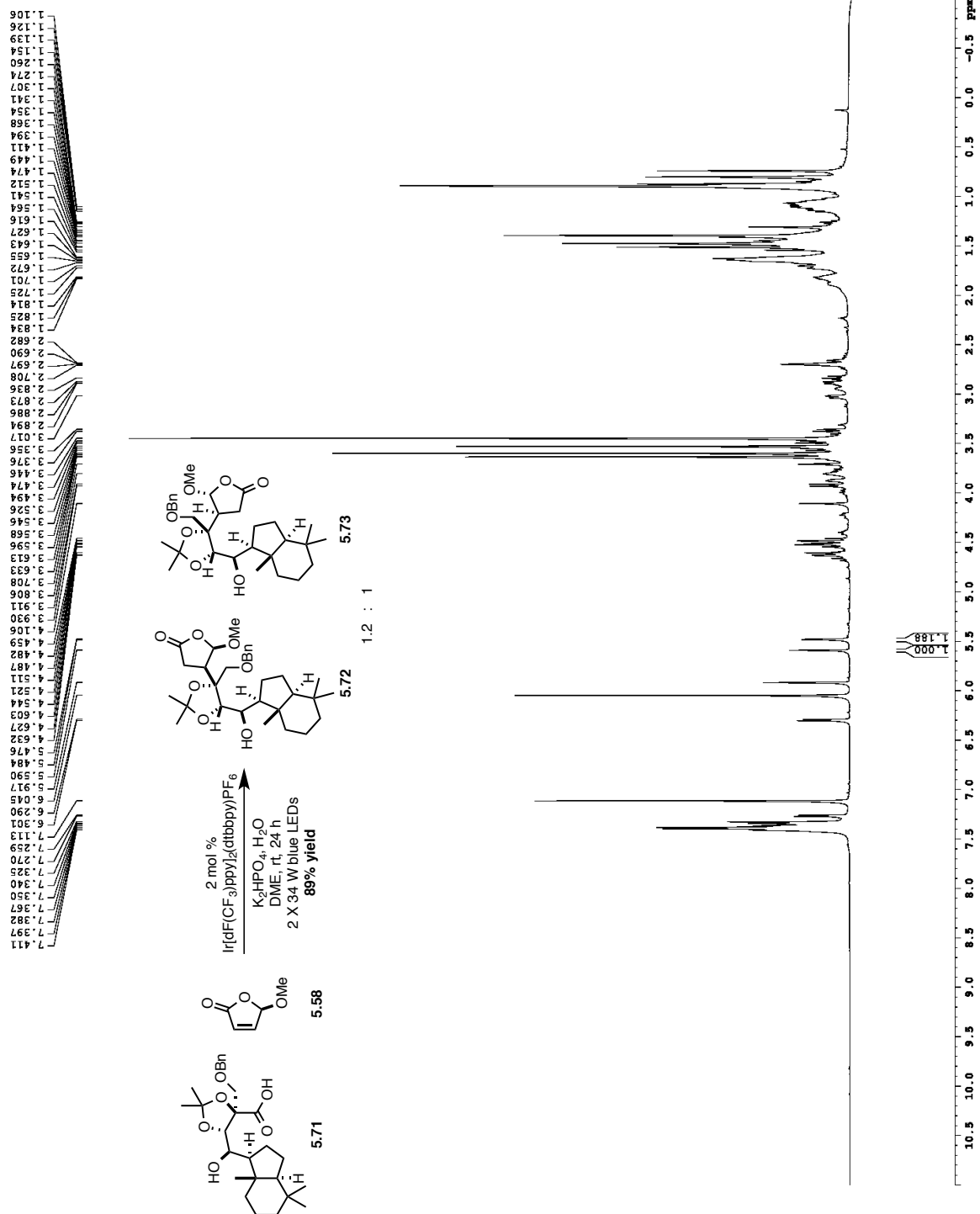
CHANNEL f1
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 1.00 dB
PL2 125.792568 MHz
PL3 1.00 dB
PL4 2.70 dB
PL5 2.70 dB
SFOF1 Crp60.0.5.20.1
SFOF2 Crp60comp.4
SFOF3 0 Hz
SFOF4 0 Hz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL3 48.50 dB
SFO2 500.2225011 MHz

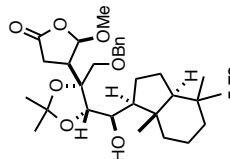
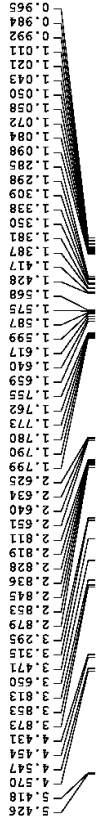
GRADIENT CHANNEL
GPMAM[1] SINE.100
GPMAM[2] SINE.100
GPX1 0 *
GPX2 0 *
GPY1 0 *
GPY2 0 *
GZ1 30.00 *
GZ2 50.00 *
P15 500.00 usec
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7803992 MHz
WDW EM
SSB 0
GB 1.00 Hz
PC 2.00

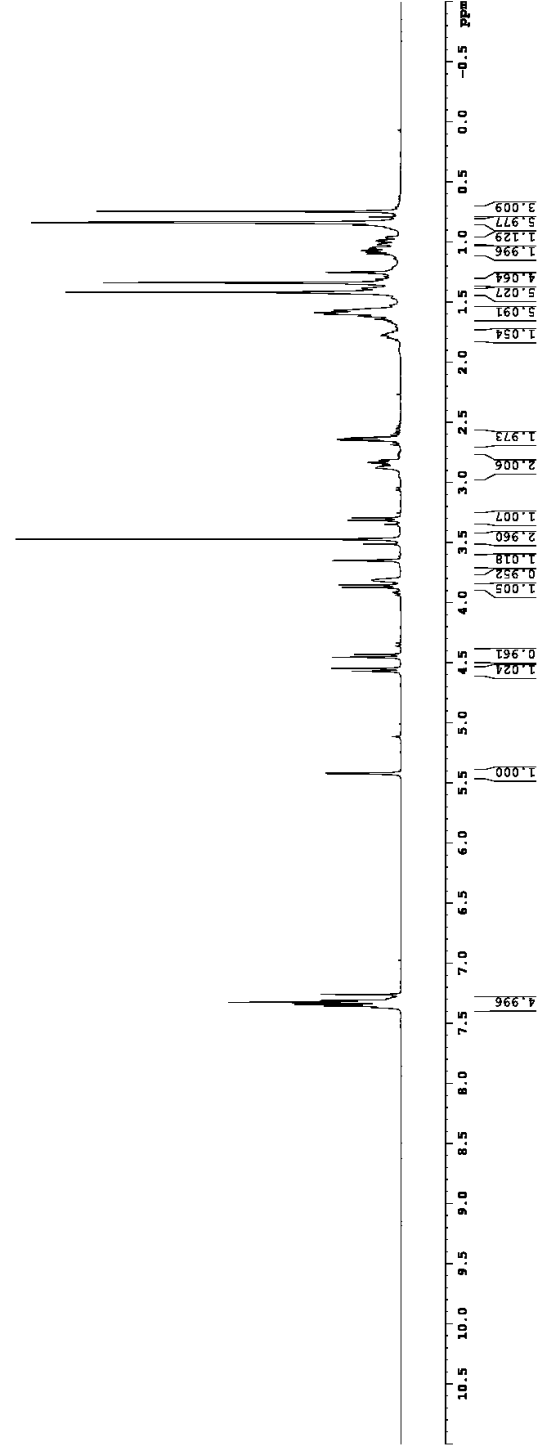
YS-IV-63

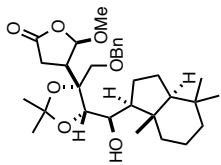
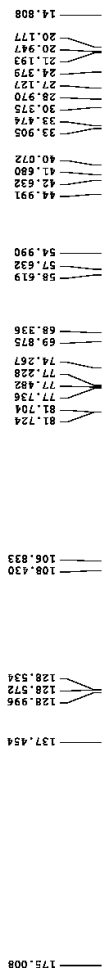


Current Data Parameters
 NAME XS-IV-63
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160211
 TIME 17:00:00
 INSTRUM crys300
 PULPROG zgpg30
 ID 81728
 NS 4
 DS 4
 SWH 8012.826 Hz
 FIDRES 0.098043 Hz
 AQ 5.77 sec
 RG 624.00
 DB 288.00
 UC 288.00
 UG 288.00
 SFO 500.136299 MHz
 ACQST 0 sec
 ACQPR 0.0150000 sec
 CHANNEL f1
 NUCL 1H
 P1 7.50 nsec
 PL1 0.00 dB
 SFO1 500.136299 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.136299 MHz
 DS 4
 SWH 8012.826 Hz
 FWHM 0.30 Hz
 GB 0
 PC 4.00



5.72
¹H NMR (CDCl₃, 500 MHz)





5.72
13C NMR (CDCl₃, 126 MHz)

Current Data Parameters
 NAME Y8-IV-63
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20161201
 Time 8:01
 INSTRUM crys500
 PROBRD 5 mm CPIC1 1H-
 PULPROG Spinechop30pr.prd
 ID 65536
 SOLVENT CDCl3
 NS 96
 DS 4
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 7298.2
 DW 16.500 usec
 DE 282.0 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 d17 0.00019600 sec
 ACQST 0 sec
 MCNRS1 0.01500000 sec
 SFOFF1 0 Hz
 P2 33.10 usec

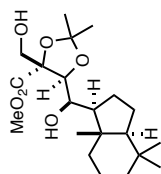
===== CHANNEL F1 =====
 NUC1 13C
 P1 16.55 usec
 PL1 200.00 usec
 PL2 200.00 usec
 PL0 120.00 dB
 PL1 1.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF1 2.70 dB
 SF2 2.70 dB
 SFOFF1 Cpf60, 0.5, 20.1
 SFOFF2 Cpf60comp, 4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL F2 =====
 CDPRG2 waltz16
 NUC2 13C
 P2 100.00 usec
 PL2 1.60 dB
 PL12 24.50 dB
 SFO2 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GENAM[1] 0 %
 GENAM[2] 0 %
 GPX1 0 %
 GPX2 0 %
 GPY1 0 %
 GPY2 0 %
 GZ1 30.00 %
 GZ2 50.00 %
 GZ3 500.00 usec
 PL6 1000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7803892 MHz
 NS 96
 DS 4
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

¹H spectrum



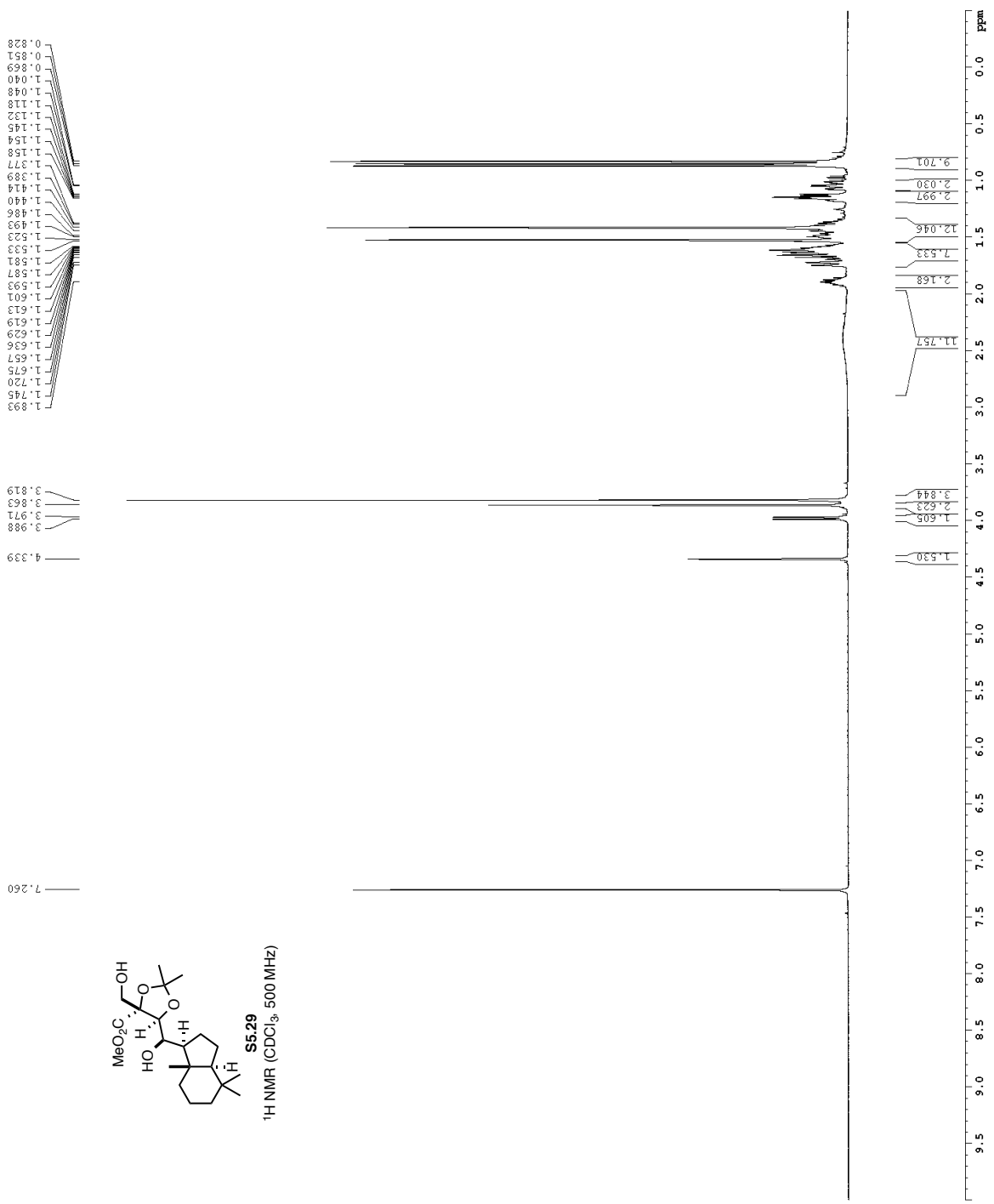
S5.29
¹H NMR (CDCl₃, 500 MHz)

```

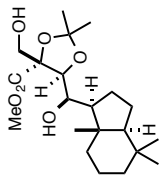
Current Data Parameters
NAME      D171-V1-123
EXPNO     5
PROCNO    1

F2 - Acquisition Parameters
Date_     20130216
Time     17:07:00
INSTRUM   crys500
PROBHD    5 mm CPYCI 1H-
PULPROG   zgpg30
TD         81728
SOLVENT   CDCl3
DS         0
SWH        8012.820 Hz
AQ         0.0998273 sec
RG         5.0498273 sec
FIDRES     7.1
AQ         7.1 usec
RG         62.47 usec
TE         298.0 K
DE         0.10000000 sec
D1         0.01500000 sec
MCNREK    0
===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL         0.00 dB
SFO1       500.225015 MHz

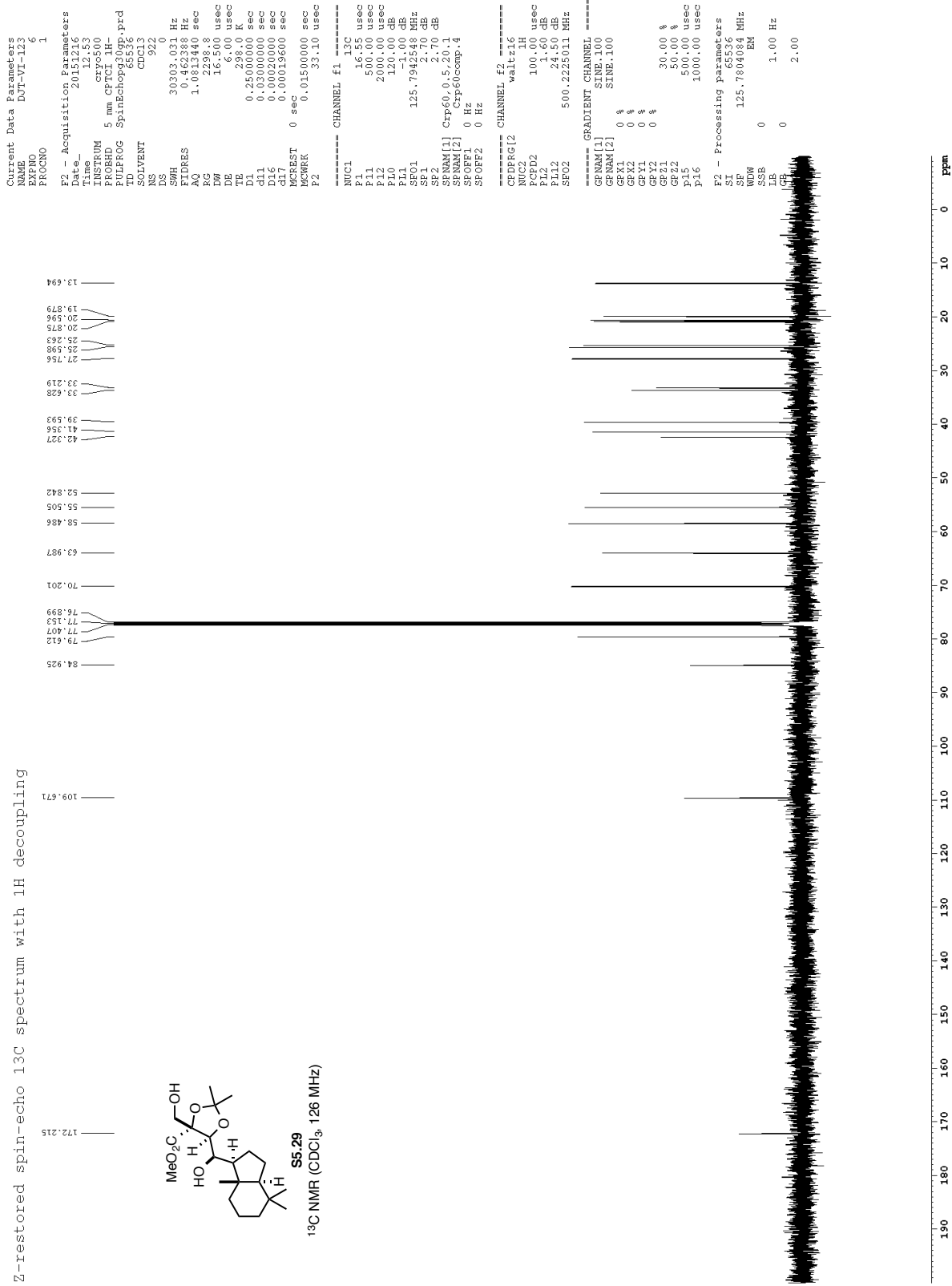
F2 - Processing parameters
SI         32768
SF         500.2200316 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         4.00
    
```



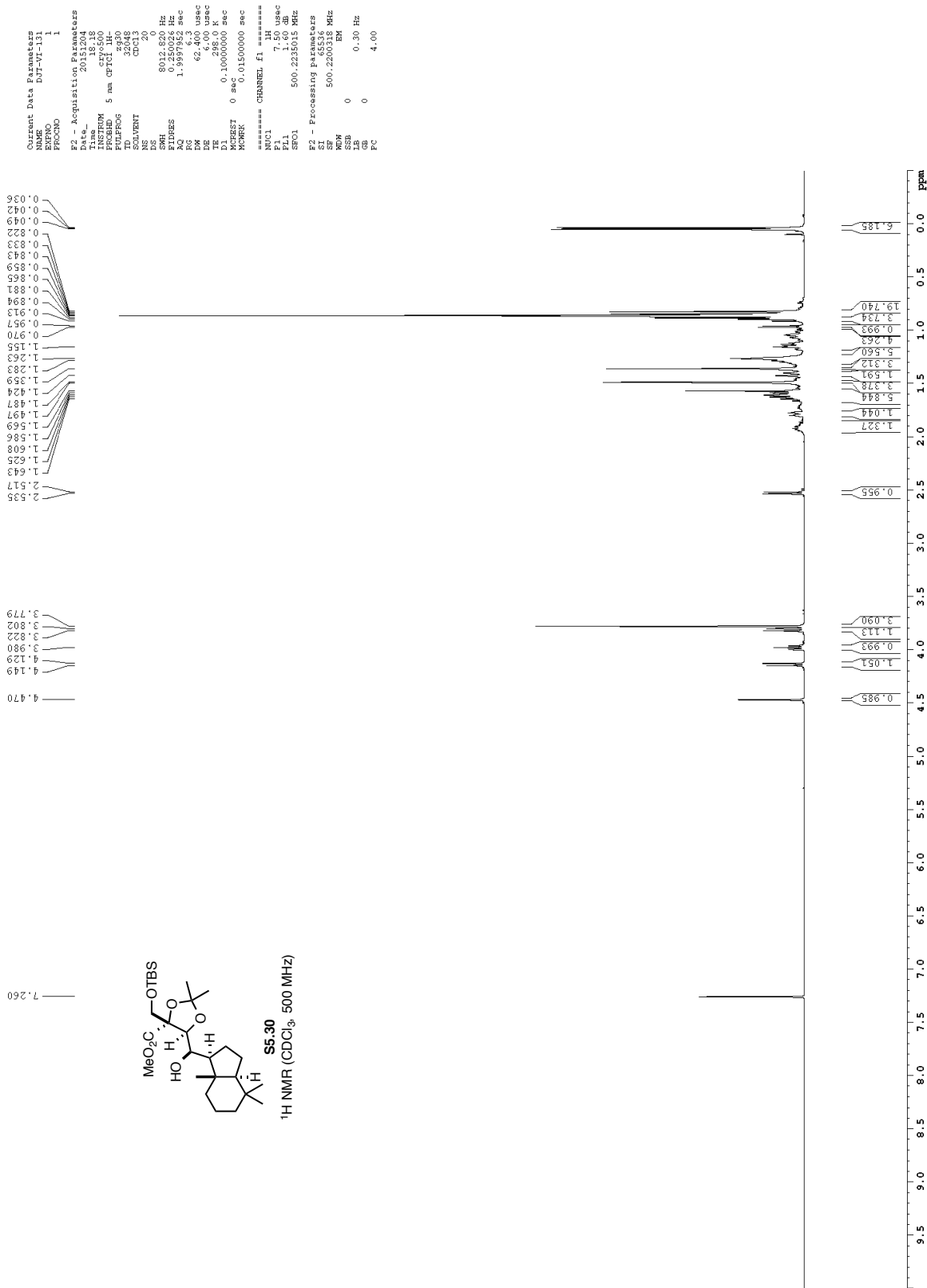
Z-restored spin-echo ¹³C spectrum with ¹H decoupling



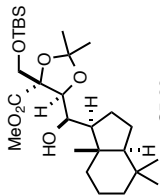
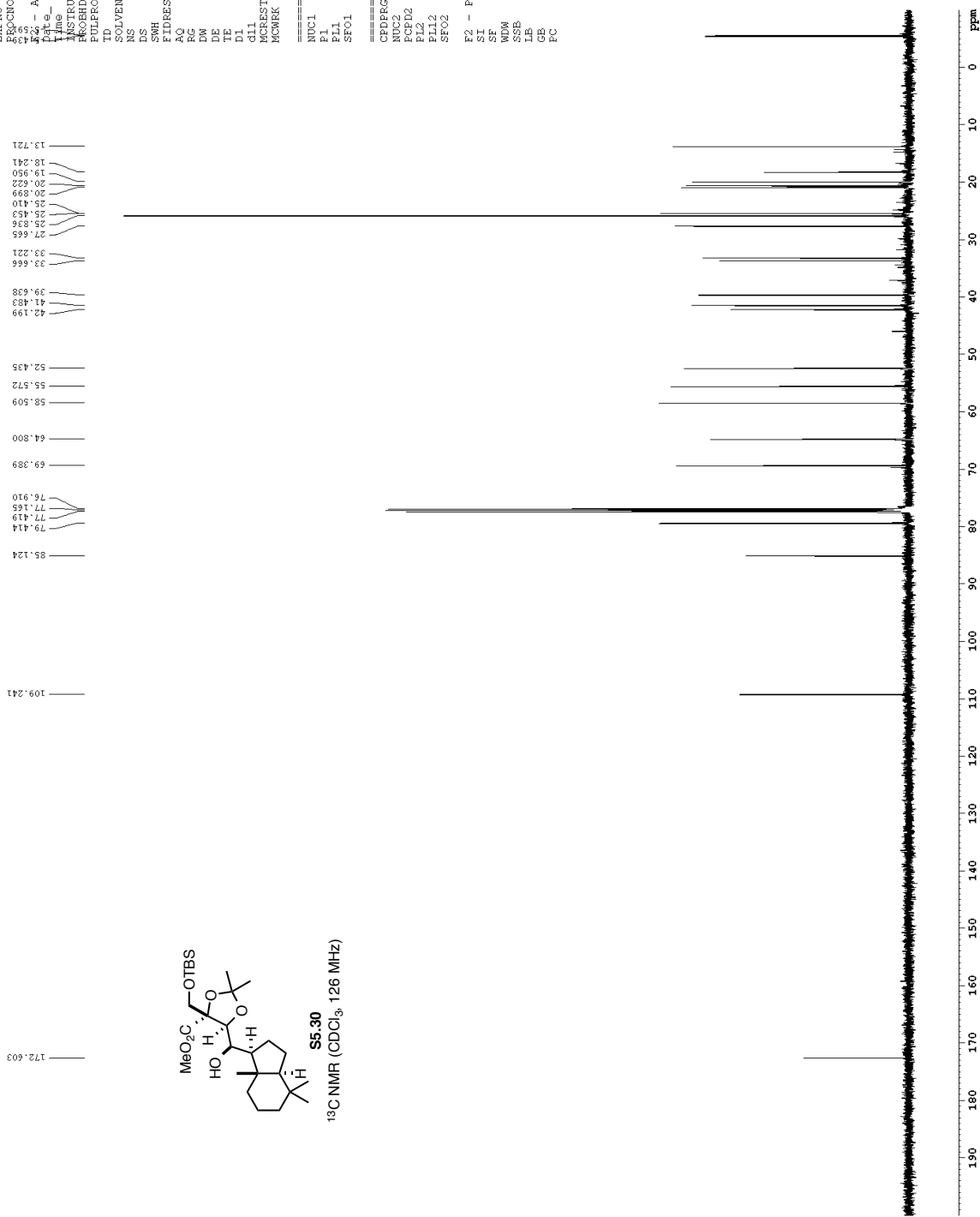
S5.29
¹³C NMR (CDCl₃, 126 MHz)



¹H spectrum



13C spectrum with 1H decoupling



S5.30
¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME      DJT-VI-131
EXPNO     4
PROCNO    1
Date_     20151218
Time      8:47
INSTRUM   spect
PROBHD    5 mm broadband
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         622
DS         0
SWH        30303.031 Hz
AQ         1.0842388 sec
RG         1.0813440 sec
RG         4597.6
DM         16.500 usec
DE         4.50 usec
TE         298.0 K
D1         0.25000000 sec
d11        0.03000000 sec
DELTA     0 sec
ACQST      0.01500000 sec
MCWPRK    0.01500000 sec

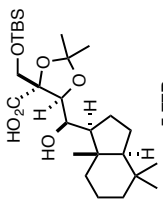
===== CHANNEL f1 =====
NUC1       13C
P1         9.00 usec
PL1        -0.60 dB
SFO1       125.5327181 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -3.00 dB
PL12       12.80 dB
SFO2       499.1824959 MHz

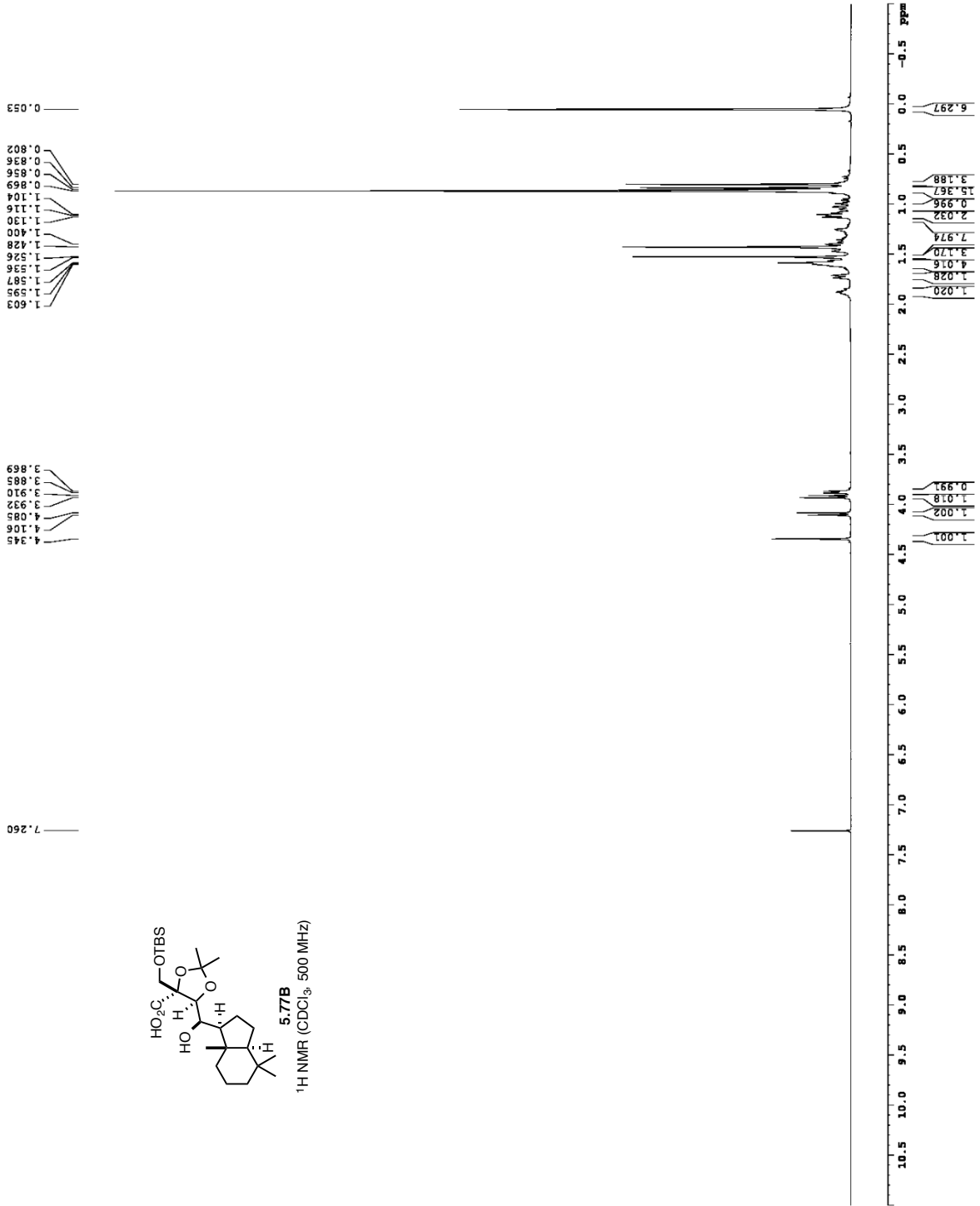
F2 - Processing parameters
SI         65536
SF         125.5188974 MHz
WDW        EM
SSE        0
LB         1.00 Hz
GB         0
PC         2.00
    
```

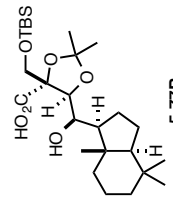
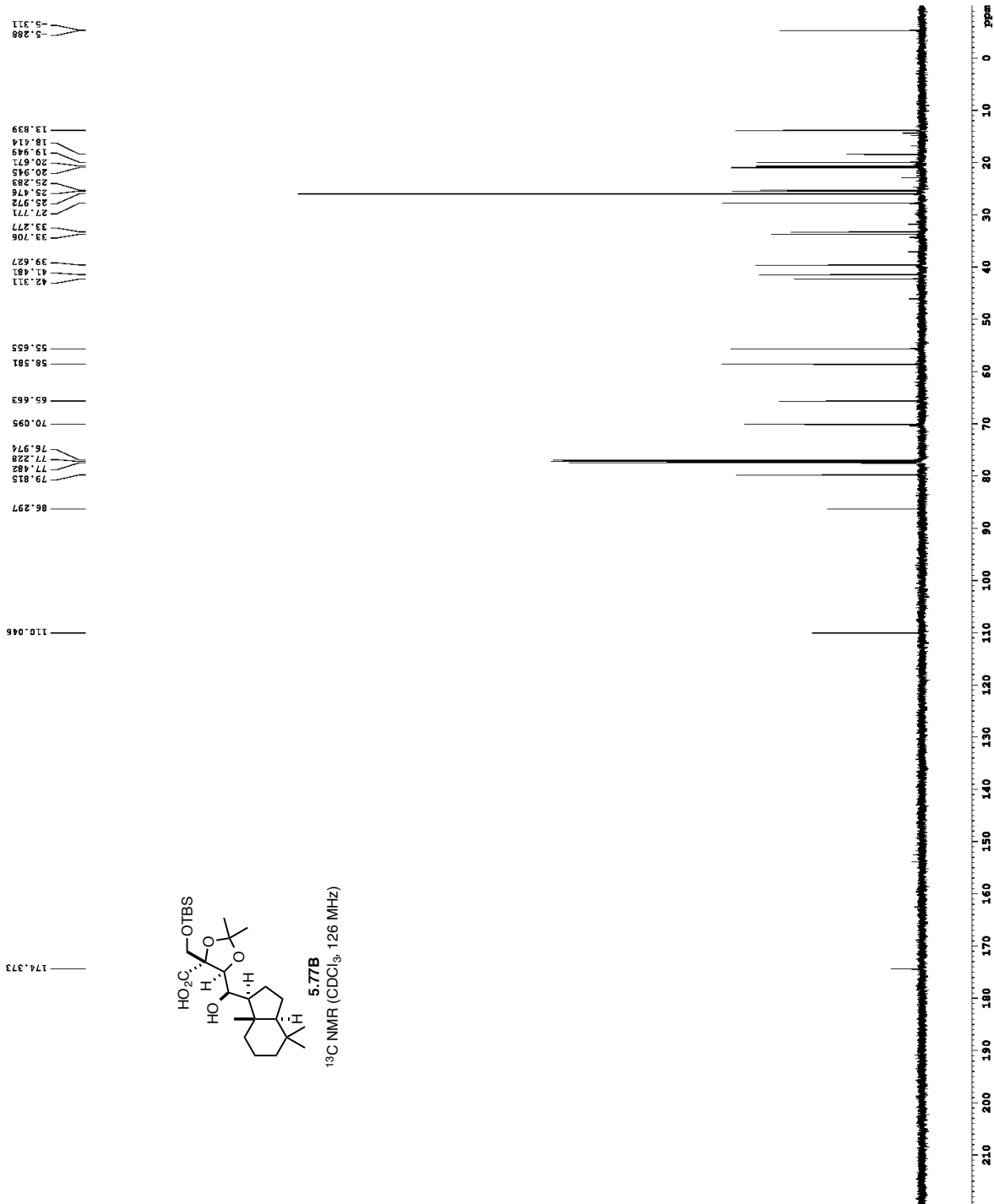
```

Current Data Parameters
NAME          XS-IV-17
PROCNO       1
F2 - Acquisition Parameters
Date_        20111213
TIME        17:05:55
INSTRUM     5 mm CPYX500
PROBHD      513
PULPROG     zgpg30
AQ          8.172
RG          655
SFO         500.136260 MHz
NUC1        13C
NUC2        13C
SOLVENT     CDCl3
DMS
ORIG        5012.620 Hz
FIDRES      0.098003 Hz
AQRES       5.039947 Hz
RGRES       6.2 Hz
ORIGRES     62.400 Hz
NUC1RES     288.0 K
INTEGRST    0 sec
INTEGRMT    0.0150010 sec
===== CHANNEL f1 =====
NUC1        13C
P1          7.00 usec
PL1         0 dB
SFO1        500.136260 MHz
===== CHANNEL f2 =====
F2 - Processing parameters
SI          65536
SF          500.136260 MHz
WDW         EM
SSB         0
GB          0
PC          4.00
  
```



¹H NMR (CDCl₃, 500 MHz)



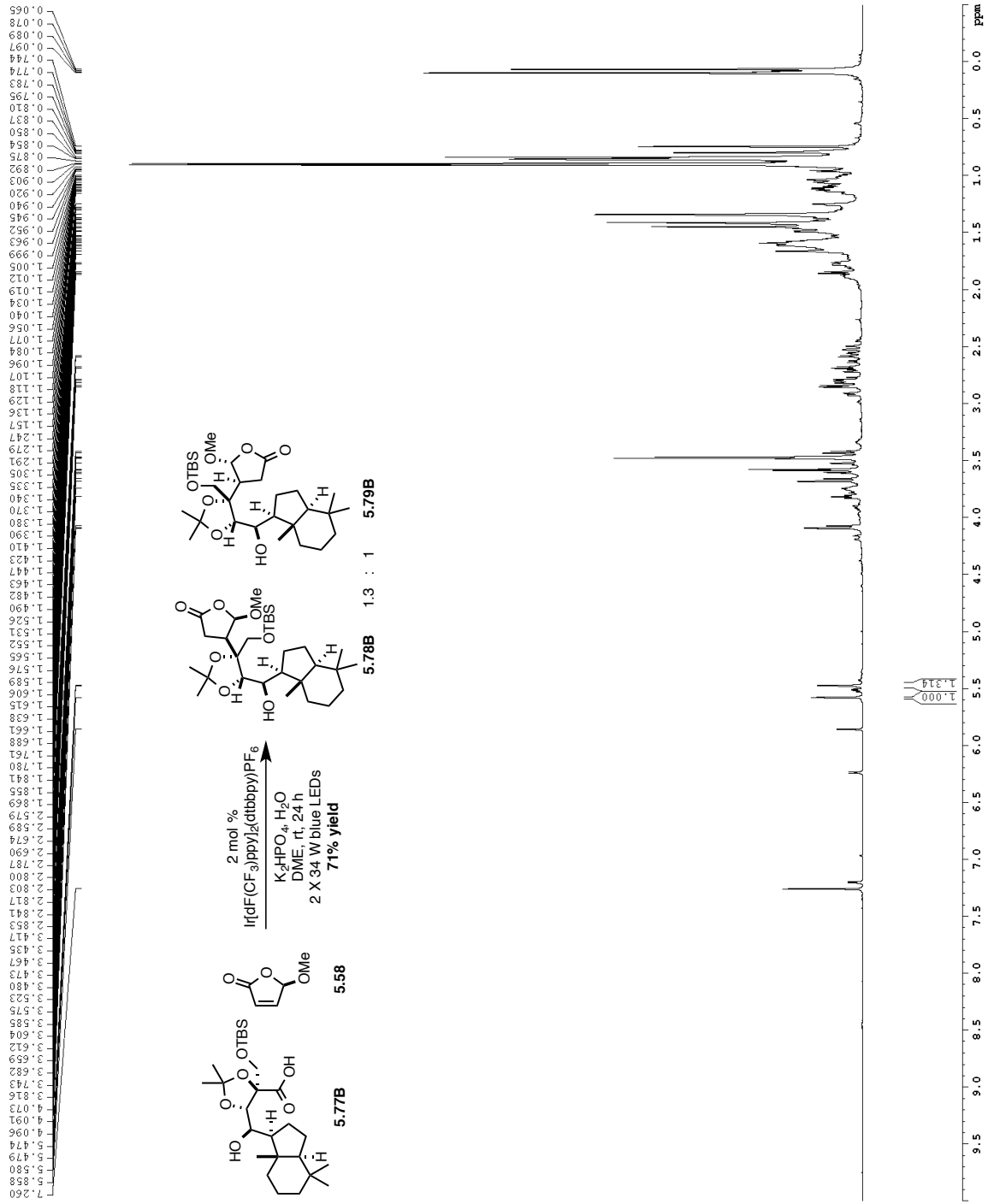


Current Data Parameters
 NAME YS-IV-17
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151215
 Time 15.48
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 216
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.813440 Hz
 AQ 1.081340 sec
 RG 3649.1
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 d11 0.0000000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 F2 33.10 usec

CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 0.00 dB
 PL2 125.7942560 dB
 PL3 0.00 dB
 SF1 2.70 dB
 SF2 2.70 dB
 SFNAM[1] Crp60,0.5,20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

CHANNEL f2
 CPDPRG[2] waltz16
 NUC2 1H
 FCPD2 100.00 usec
 PL2 1.80 dB
 PL3 2.10 dB
 SF02 500.2225031 MHz
 SF02 500.2225031 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
 NDM EM
 SSB 0
 GB 1.00 Hz
 GC 0
 PC 2.00

1H spectrum



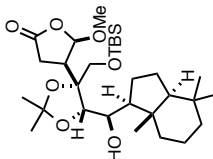
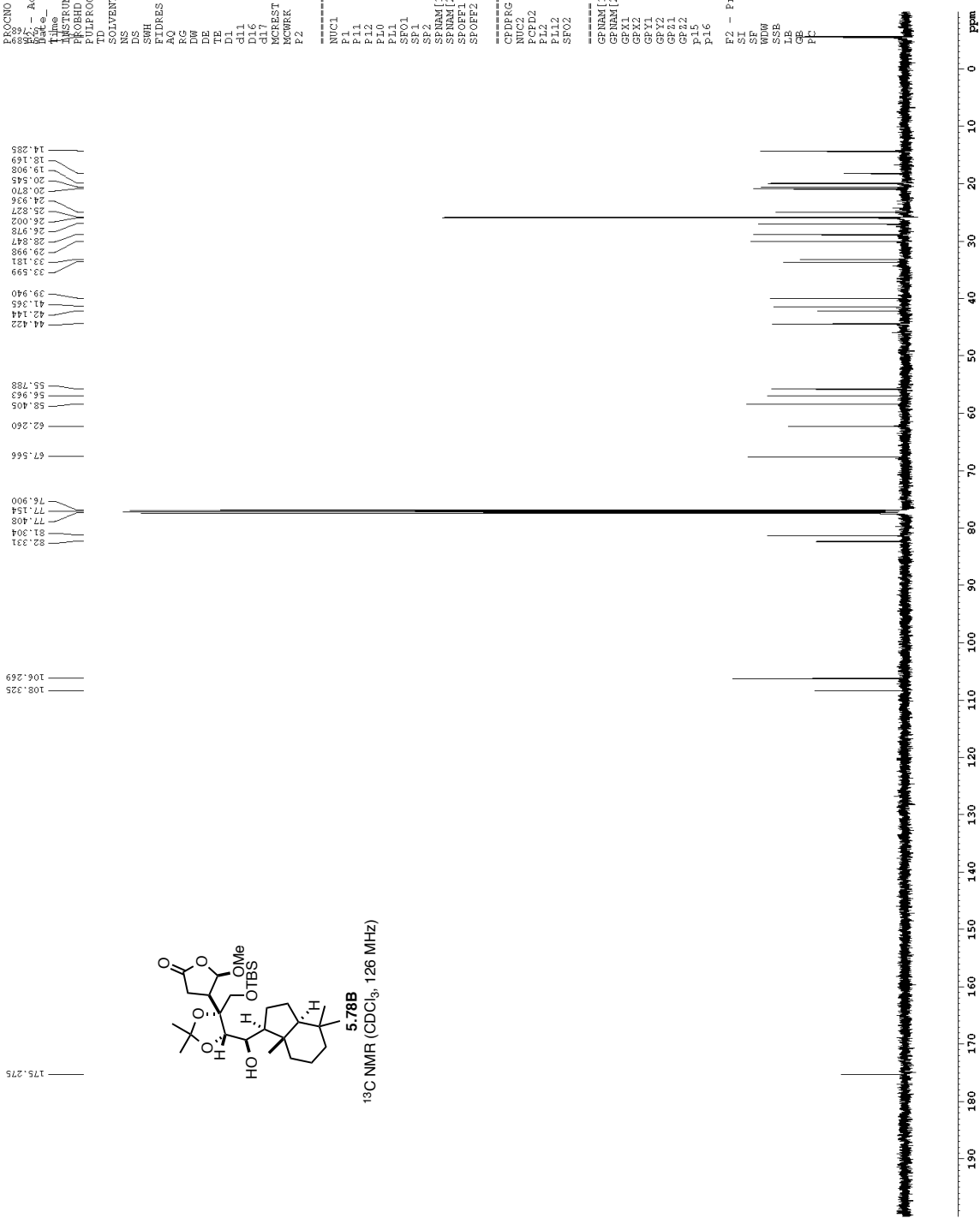
Current Data Parameters
 NAME DJT-VI-141
 PROBO 1

F2 - Acquisition Parameters
 Date 20151211
 Time 8:59
 Name 141-000000
 PROBO 1
 PULPROG 5 mm TBI H1/3
 PC 2830
 SFO1 1
 SOLVENT CDCl3
 NS 20
 DS 2
 SW 8615.365 Hz
 FIDRES 0.038042 Hz
 AQ 5.098478 sec
 DW 52.000 usec
 DE 14.54 usec
 DI 3.00 usec
 D1 0.1000000 sec
 TE0 1

***** CHANNEL f1 *****
 SFO1 600.1342009 MHz
 PFC1 8 dB
 PL1 24.00000000 W
 FLM1

F2 - Processing Parameters
 SI 65536
 SF 600.1300368 MHz
 SFO 0
 SSB 0
 LB 0
 GB 0
 PC 1.00

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



5.78B
¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME          DUT-VI-14
EXPNO        1
PROCNO       1
F2          20151214
F3          20151214
Acquisition Parameters
Date_       8.13
Time       8.13
INSTRUM     cryo500
PROBHD      5 mm CFTCI 1H-
PULPROG     SpinEchoq20p.prd
TD          65536
SOLVENT     CDCl3
NS          511
DS          4
SWH          30303.031 Hz
FIDRES      0.462388 Hz
AQ          1.0813440 sec
RG          1024.00
AQ          16.00 usec
DE          6.00 usec
TE          298.0 K
DL          0.25000000 sec
dL1         0.03000000 sec
dL6         0.00020000 sec
MGREFT      0 sec
MGREK       0.00019600 sec
MCOREK      0.01500000 sec
P2          33.10 usec

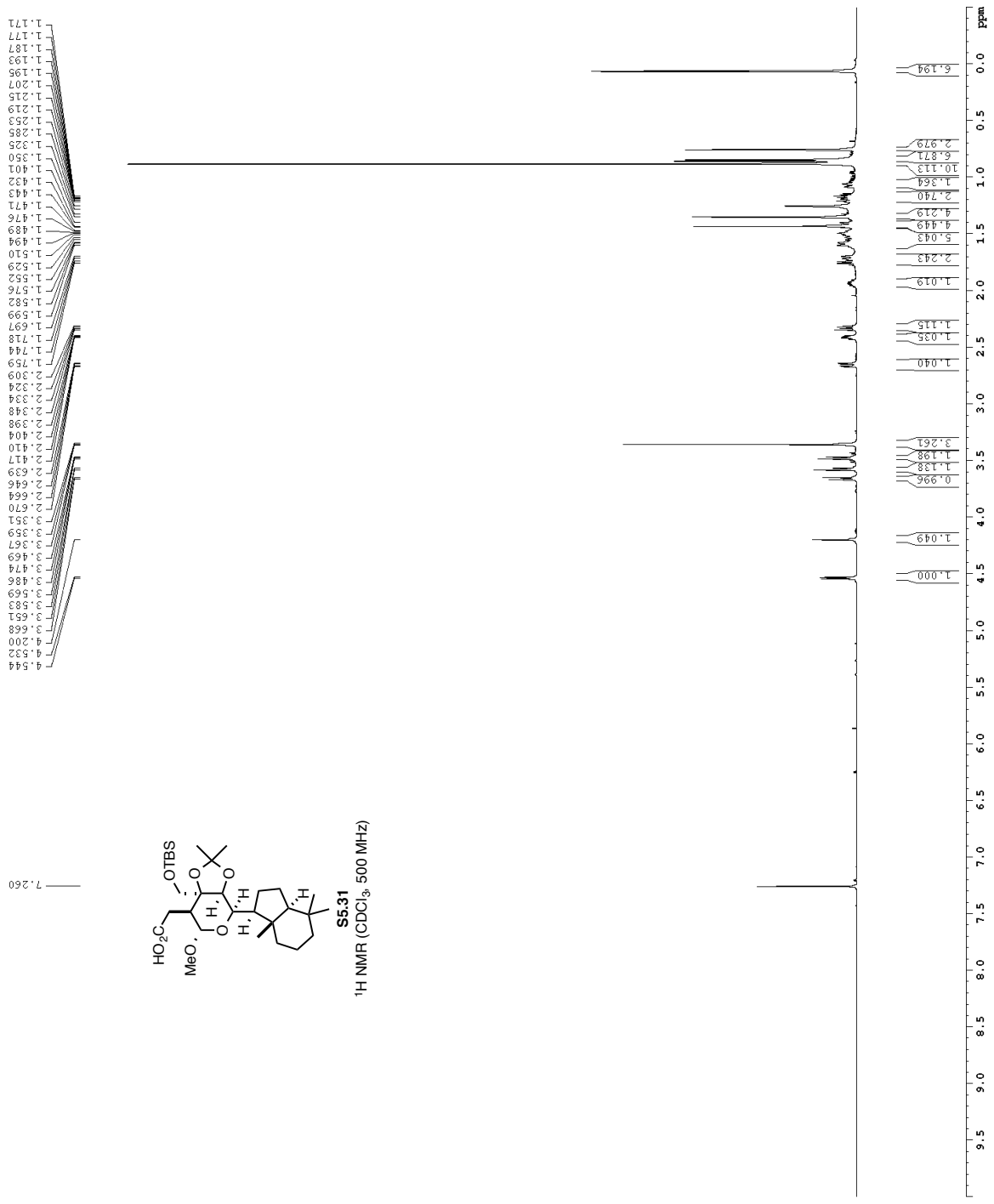
===== CHANNEL F1 =====
NUC1         13C
P1          16.00 usec
PL1         500.00 usec
P12         2000.00 usec
PL12        120.00 dB
SFO1        125.7942548 MHz
SF1         -1.00 dB
SF2         2.70 dB
SFOFF1      0 Hz
SFOFF2      0 Hz

===== CHANNEL F2 =====
CPDPRG12    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
GFX1        0 %
GFX2        0 %
GFI1        0 %
GFI2        0 %
GFZ1        30.00 %
GFZ2        50.00 %
p15         500.00 usec
p16         1000.00 usec

P2 - Processing Parameters
SI          65536
SF          125.7804085 MHz
WDW         EM
SSB         0
ZB          0
GB          0
PC          2.00
    
```


1H spectrum



```

Current Data Parameters
NAME      547-14-152
PROCNO    1
Date_     20160107
INSTRUM   av600
PROBHD    5 mm BBI HH/13
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         20
DS         2
SWH        9615.385 Hz
FIDRES     0.000100 Hz
AQ         1.959200 sec
RG         456
DM         52.00 usec
DE         298.0 K
TE         298.0 K
D1         0.10000000 sec
D10        1
===== CHANNEL f1 =====
NUC1       13C
P1         8.00 usec
PL1        24.00000000 W
===== CHANNEL f2 =====
NUC2       1H
P2         8.00 usec
PL2        24.00000000 W
===== Processing Parameters =====
SI         65536
SF         600.1360356 MHz
WDW        EM
SSB        0
GB         0
PC         1.00
  
```

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

Current Data Parameters
 NAME DOT-VI-152
 EXPNO 1
 PROCNO 1

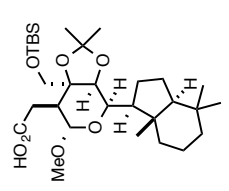
F2 - Acquisition Parameters
 Date_ 20161017
 Time 14.14
 INSTRUM spect
 PROBM 5 mm CPY 13C QNP 1H
 PULPROG SpinEcho30pp-prd
 TD 65536
 SOLVENT CDCl3
 NS 253
 DS 30303.030 Hz
 SH 0.462388 Hz
 FIDRES 1.0813440 sec
 AQ 4096
 RG 16.500 usec
 DE 6.00 usec
 TE 300.2 K
 D1 0.2500000 sec
 d11 0.0300000 sec
 D16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCWRR 0.01500000 sec
 F2 33.10 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 16.55 usec
 F1 500.00 usec
 P12 2000.00 usec
 F12 10.00 dB
 P13 1.00 dB
 F13 1.00 dB
 SF01 125.7942548 MHz
 SF2 2.70 dB
 SF2 2.70 dB
 SFO1 Cyp60.0.5.20.1
 SFO2 Cyp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

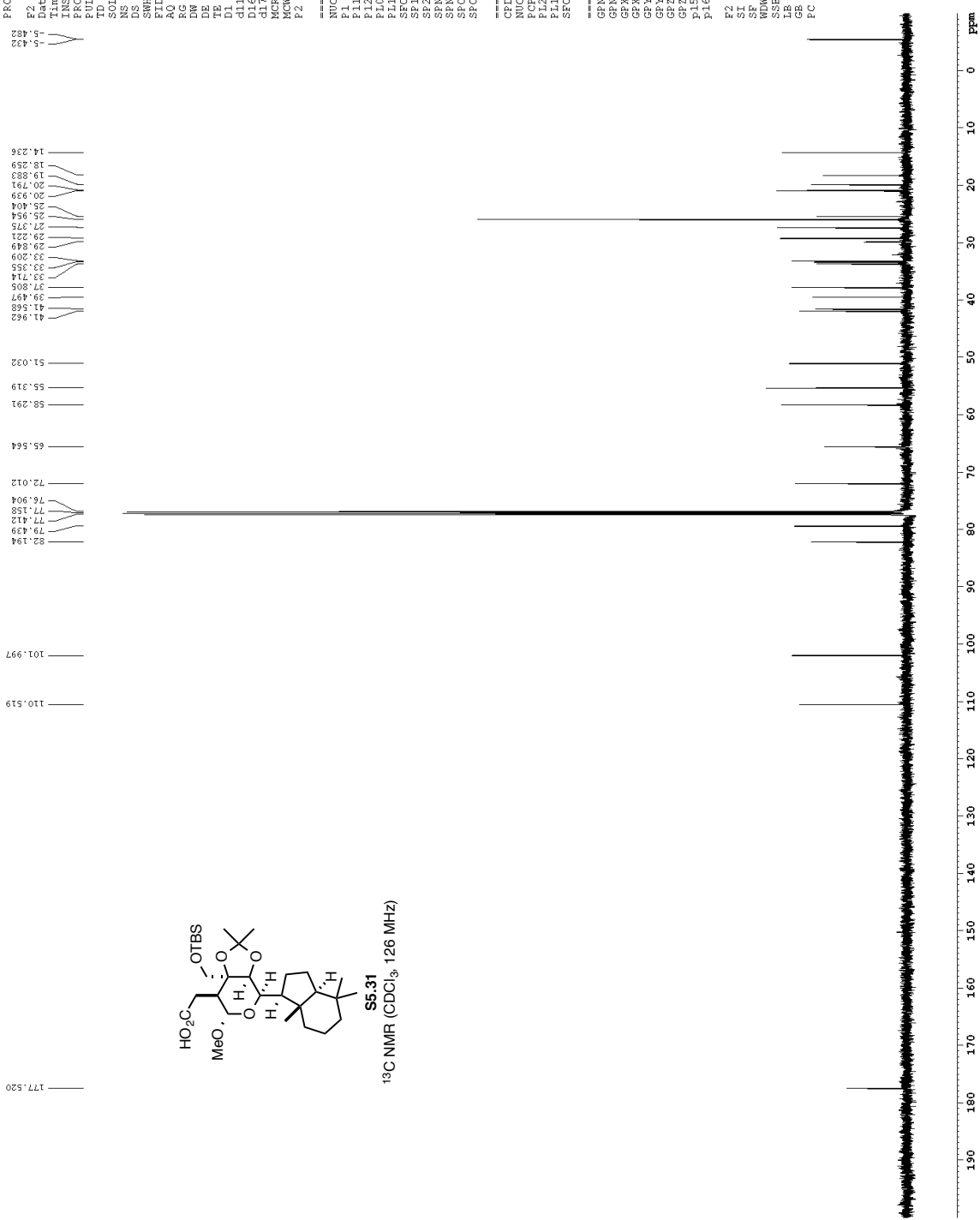
===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 1H
 P2 100.00 usec
 F2 200.00 dB
 F22 24.50 dB
 SF02 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GRAM[1] SINE.100
 GRAM[2] SINE.100
 GPX1 0 %
 GPX2 0 %
 GY1 0 %
 GY2 0 %
 GF1 30.00 %
 GF2 30.00 %
 P1 500.00 usec
 P16 10000.00 usec

F2 - Processing parameters
 SI 65536
 SF 125.7804071 MHz
 GRM EN
 SSB 0
 LB 1.00 Hz
 GB 0
 FC 2.00

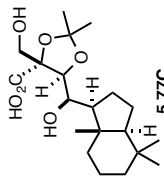


S5.31
¹³C NMR (CDCl₃, 126 MHz)

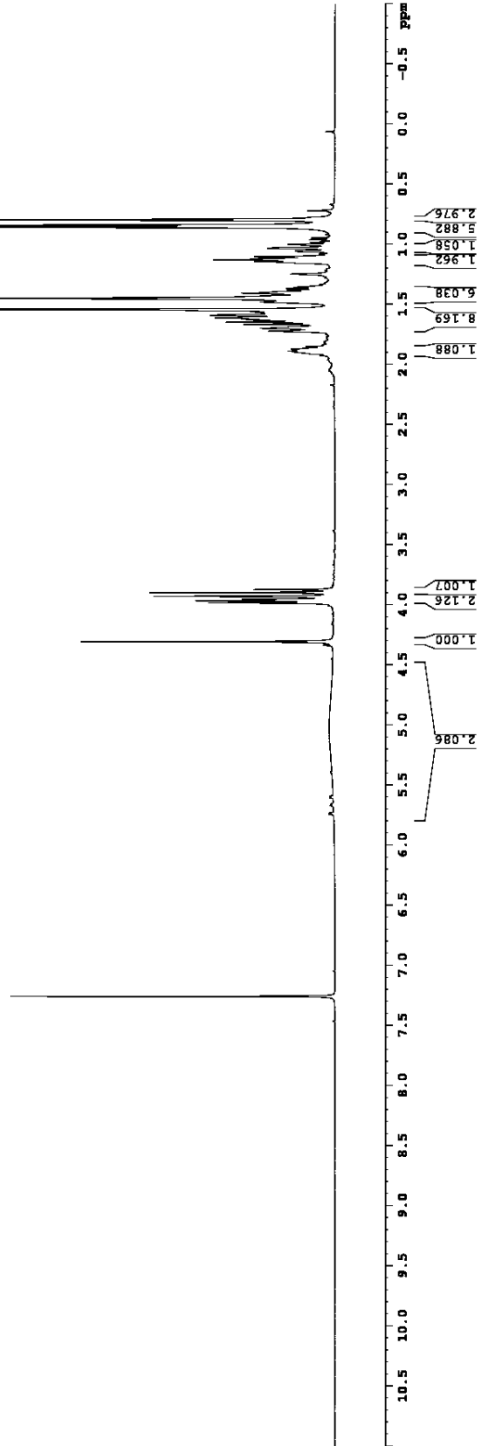


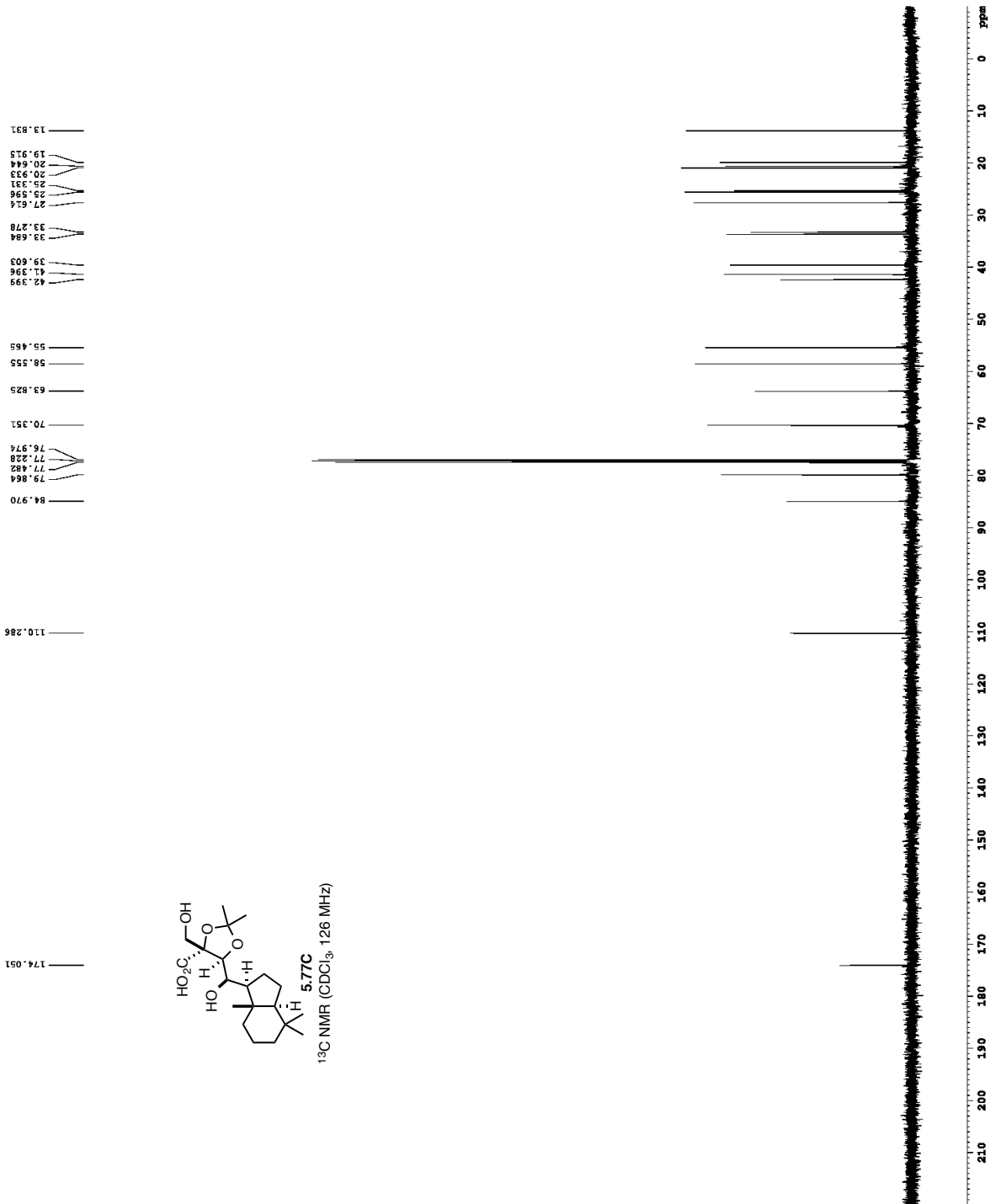
```

Current Data Parameters
NAME      YS-IV-13
PROCNO    1
DATE_     20121216
INSTRUM   spect
PROBHD    5 mm CPYX500
PULPROG   zgpg30
AQ        8.1728
RG        655.36
RES       0.125000000
SOLVENT   CDCl3
DMS       8032.820 Hz
FIDRES    0.000000000 Hz
AQRES     0.000000000 Hz
RGRES     7.71 MHz
RGRES     62.400000000 Hz
RGRES     288.00 K
RGRES     0.100000000 sec
RGRES     0.015000000 sec
===== CHANNEL f1 =====
NUC1       13C
P1         7.00 usec
PL1        0.00 dB
RG1        500.233000000 MHz
===== CHANNEL f2 =====
NUC2       1H
P2         12.00 usec
PL2        19.00 dB
RG2        500.233000000 MHz
===== Processing parameters =====
SI         32768
SF         500.233000000 MHz
WDW        EM
SSB        0
GB         0
PC         4.00
  
```

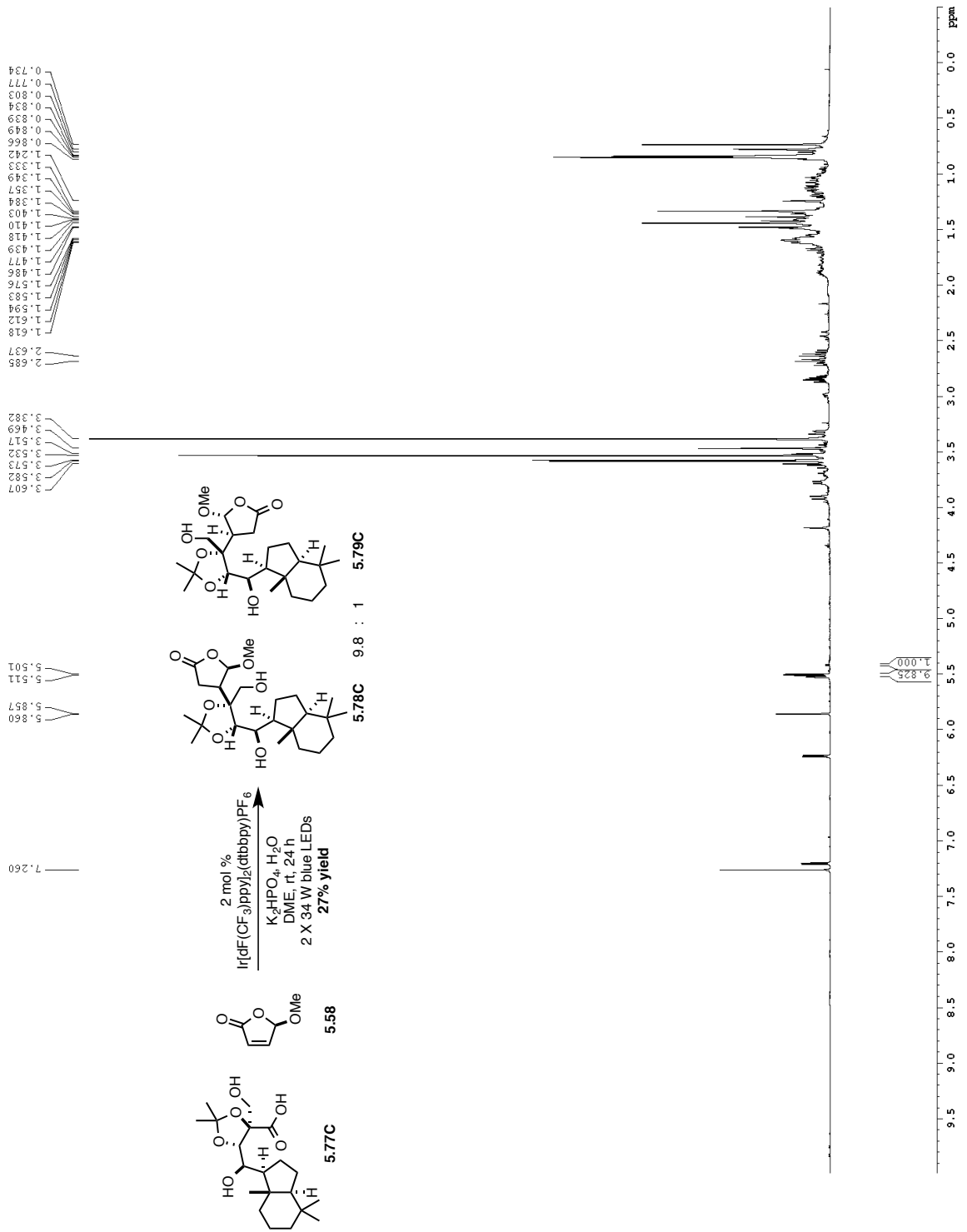


¹H NMR (CDCl₃, 500 MHz)





¹H spectrum



Current Data Parameters
 NAME: 217-173
 EXPNO: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20160121
 Time: 6.00
 INSTRUM: cryo500
 PROBHD: 5 mm QNP1H-
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 20
 DS: 2
 SWH: 8012.820 Hz
 FIDRES: 0.098273 Hz
 AQ: 5.1938273 sec
 RG: 61.3
 DM: 62.400 usec
 DE: 1.000 usec
 TE: 298.0 K
 D1: 0.10000000 sec
 D11: 0.01500000 sec
 D12: 0.01500000 sec
 D13: 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1: 1H
 P1: 7.50 usec
 PL1: 0.00 dB
 SFO1: 500.225015 MHz
 F2 - Processing parameters
 SI: 32768
 SF: 500.2200312 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 4.00

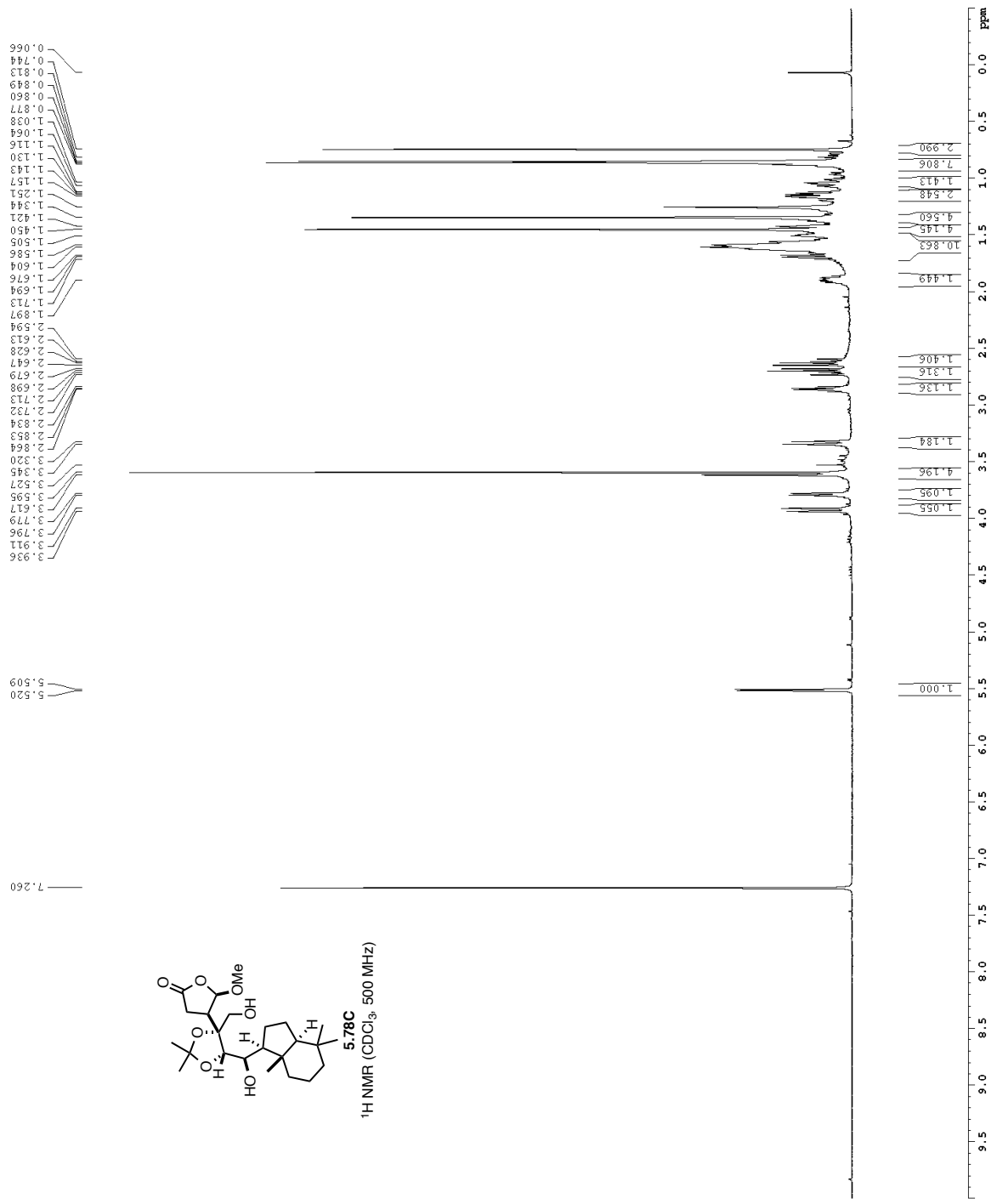
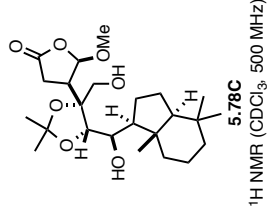
1H spectrum

```

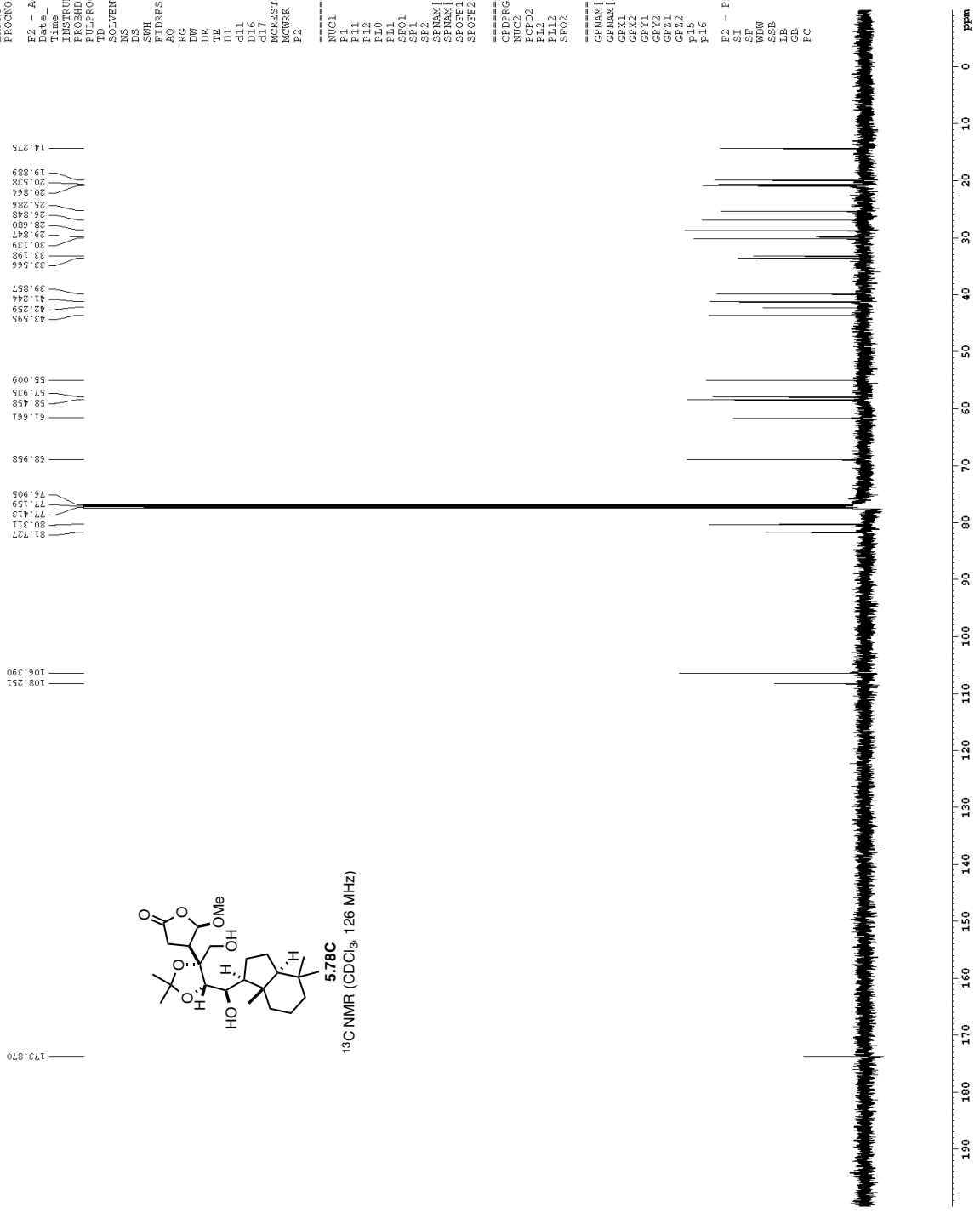
Current Data Parameters
NAME      DAT-VI-173
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20160921
Time      09:11
INSTRUM   cryo500
PROBHD    5 mm CPXI 1H
PULPROG   zgpg30
TD        81728
SOLVENT   CDCl3
DS        20
SS        20
SMH       8012.820 Hz
NUC1       13C
NUC2       1H
AQ        5.098273 sec
RG         5.17
DE        62.400 usec
TE        298.0 K
D1        0.10000000 sec
DELTA     0.01500000 sec
===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL1        0.00 dB
SFO1       500.225015 MHz

F2 - Processing Parameters
SI         45853
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



Current Data Parameters
 NAME DJT-VI-173
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160118
 Time 9:59
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG SpinEcho93upg.prd
 TD 65536
 SOLVENT CDCl3
 NS 633
 DS 0
 SRH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813440 sec
 RG 2298.8
 RW 163.0 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 D16 0.00020000 sec
 SFOFF 0.00019600 sec
 MCREST 0
 MCBRE 0.01500000 sec
 P2 33.10 usec

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 100.00 usec
 PL1 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 -1.00 dB
 SFO1 125.7942548 MHz
 SF1 2.70 dB
 SFNAM[1] Crys60_0_5_20_1 dB
 SFNAM[2] Crys60comp_4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

===== CHANNEL f2 =====
 CPDPRG2 waitz16
 NUC2 ¹H
 PCPD2 100.00 usec
 PL2 1.60 dB
 PL12 24.50 dB
 SFO2 500.2225011 MHz

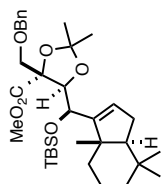
===== GRADIENT CHANNEL =====
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPC1 0 %
 GPC2 0 %
 GPT1 0 %
 GPT2 0 %
 GPC3 30.00 %
 GPC4 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

F2 - Processing parameters
 SI 32768
 SF 125.7804780 MHz
 WDW EM
 SSE 0
 LE 1.00 Hz
 GB 0
 PC 2.00

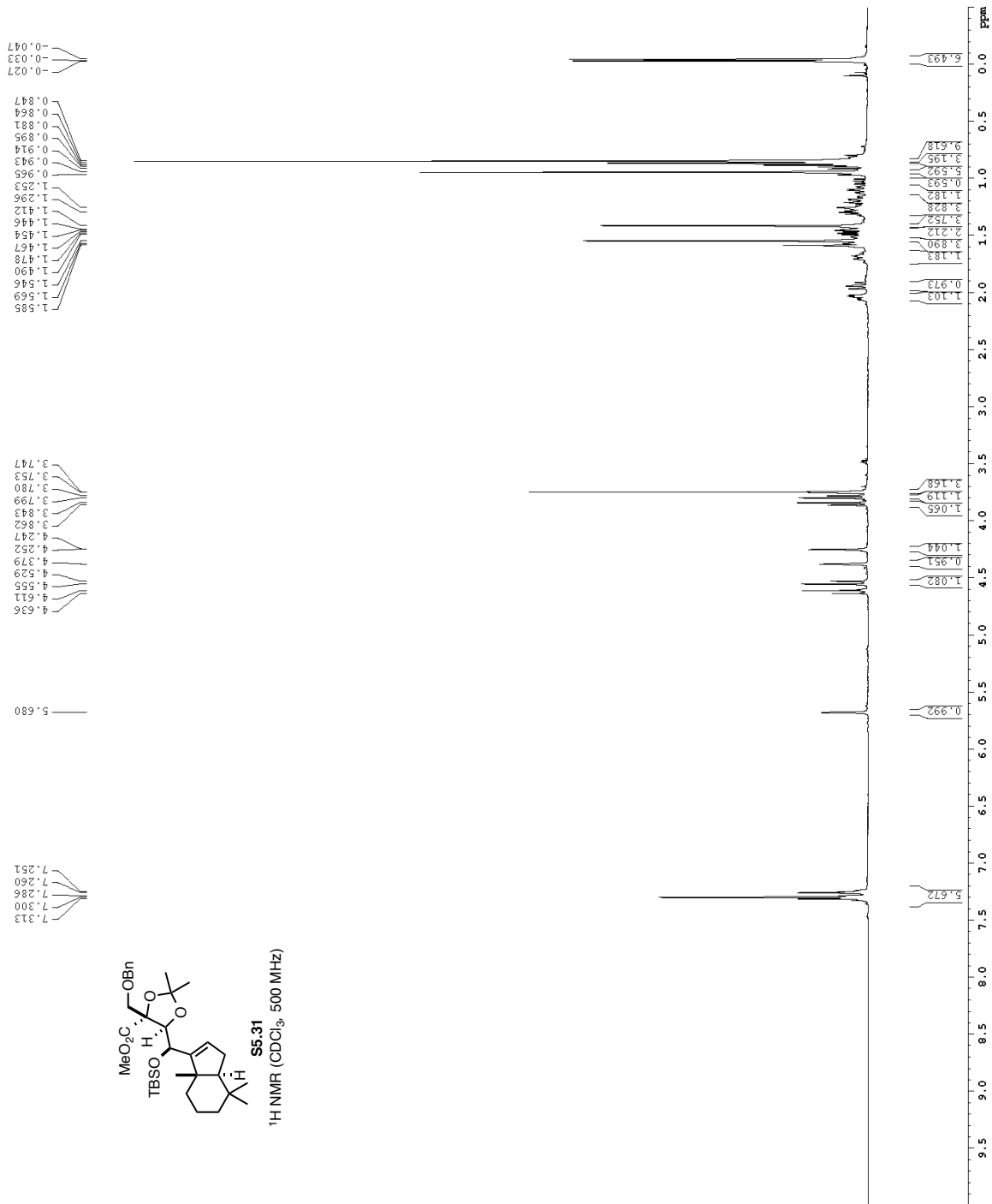
¹H spectrum

```

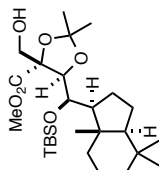
Current Data Parameters
NAME      DAT-VU-135
EXPNO    1
PROCNO   1
Date_    20151208
INSTRUM  crys500
PROBHD   5 mm QNP1H-
PULPROG  zgpg30
TD        32768
SOLVENT  CDCl3
NS        30
DS        4
SWH       8012.820 Hz
FIDRES    0.0979542 Hz
AQ         1.997952 sec
RG         655.57
BW         62.00 usec
TE         298.0 K
D1         0.10000000 sec
DELTA     0.01500000 sec
===== CHANNEL f1 =====
NUC1      1H
P1        7.50 usec
PL1       0.00 dB
SFO1      500.225015 MHz
===== CHANNEL f2 =====
NUC2      13C
P2        12.00 usec
PL2       19.00 dB
SFO2      125.760350 MHz
===== Processing parameters =====
SI         32768
SF         500.2200318 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         4.00
  
```



55.31
¹H NMR (CDCl₃, 500 MHz)



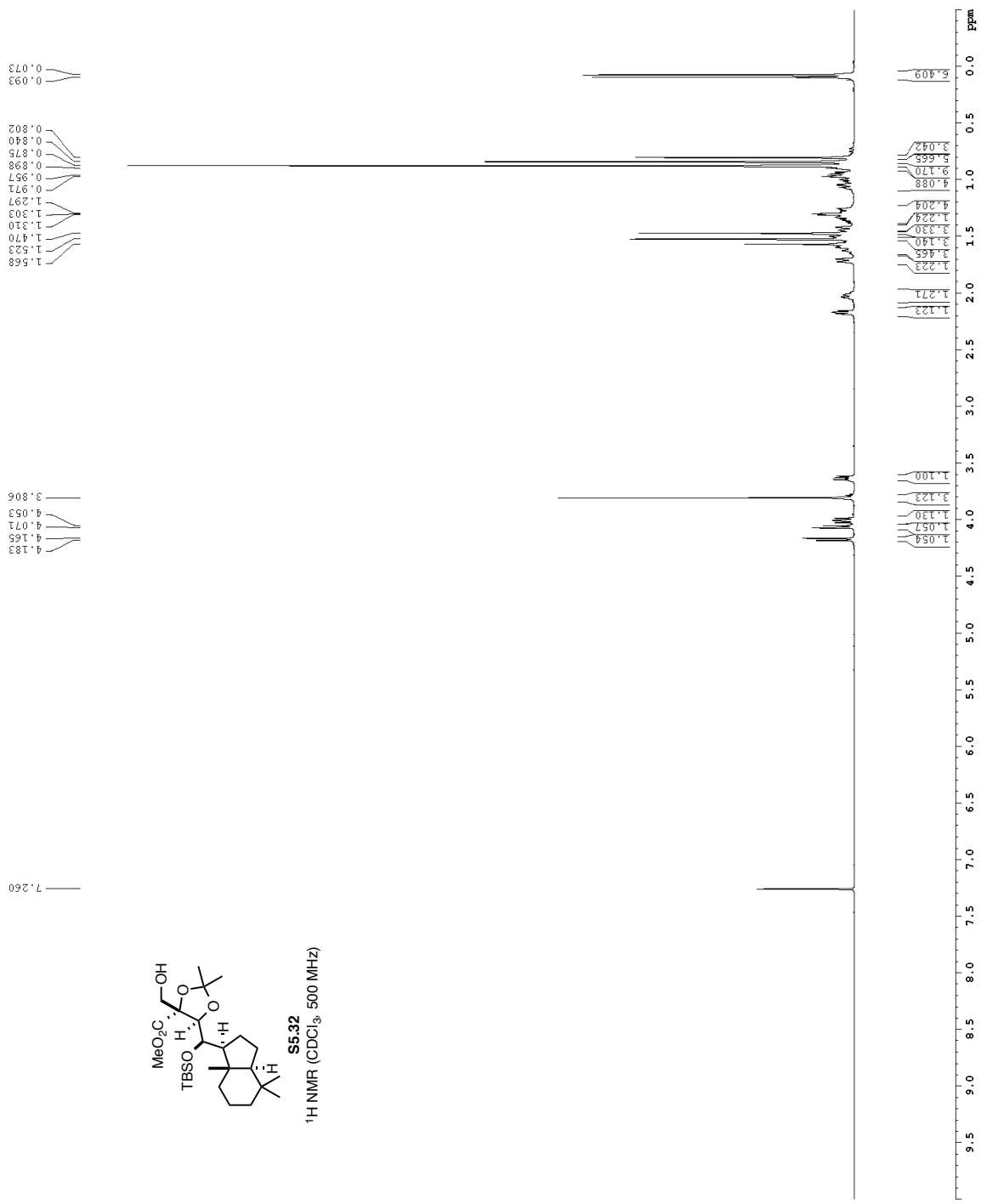
¹H spectrum



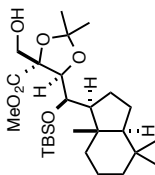
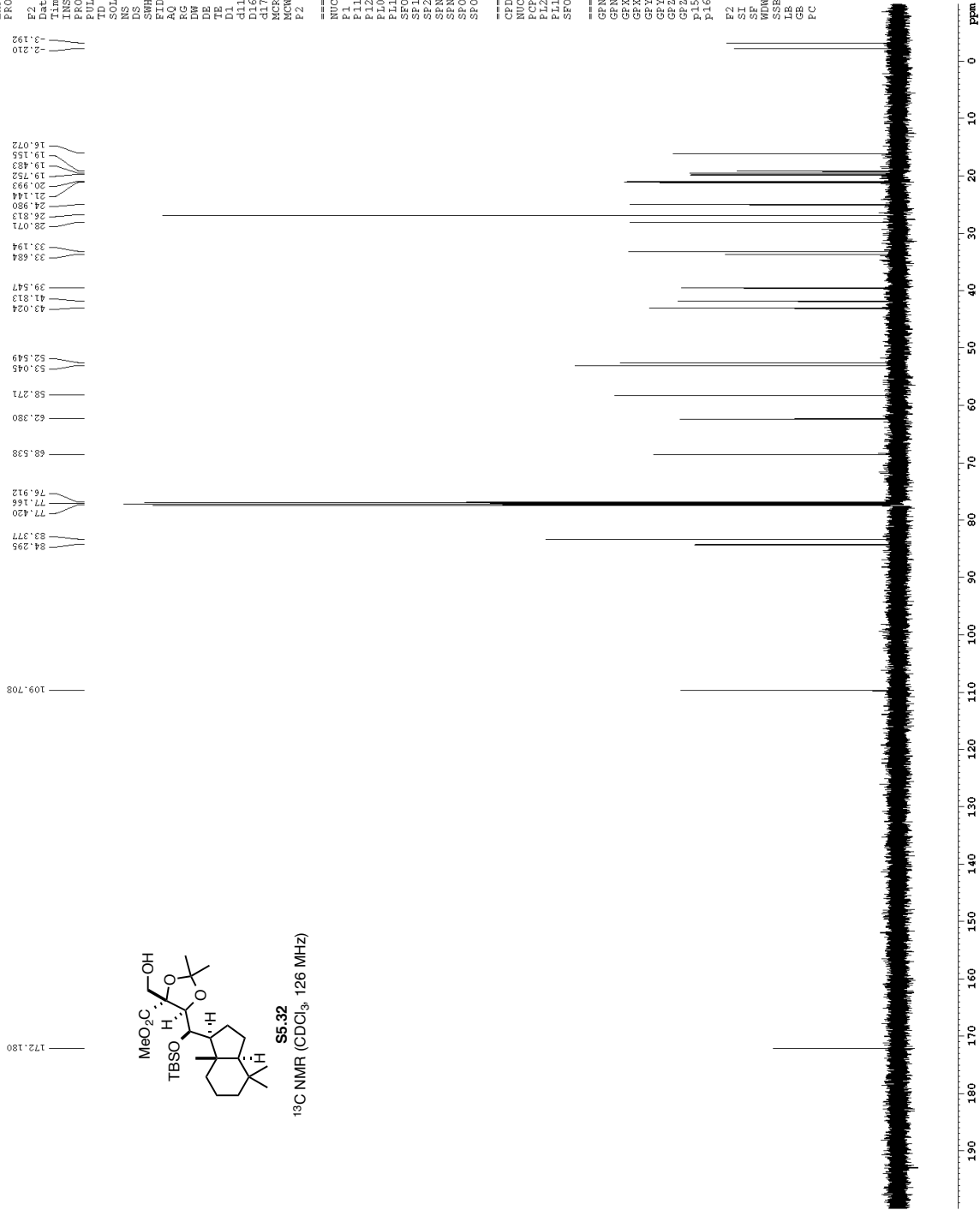
S5.32
¹H NMR (CDCl₃, 500 MHz)

Current Data Parameters
NAME: S5.32
EXPNO: 2
PROCNO: 1
Date_ : 20151207
Time: 11:00:00
INSTRUM: cryo500
PROBHD: 5 mm CPYCI H-
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
DS: 4
SWH: 8012.520 Hz
FIDRES: 0.7490000 Hz
AQ: 0.0000000 sec
RG: 2.1489800
DW: 62.400 usec
DE: 0.1500000 usec
TE: 298.2 K
D1: 0.10000000 sec
DELTA: 0.00000000 sec
AQC: 0.015000000 sec
----- CHANNEL f1 -----
NUC1: ¹H
P1: 7.50 usec
PL1: 0.00 dB
SFO1: 500.225015 MHz

F2 - Processing parameters
SI: 32768
SF: 500.2250317 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
¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME      DDT-VI-133
EXPNO     3
PROCNO    1
F2 - Acquisition Parameters
Date_     20151207
Time      13.36
INSTRUM   cryo500
PROBHD    5 mm CFTCI 1H-
PULPROG   SpinEchoy20dp.prd
TD         65536
SOLVENT   CDCl3
DS         3
SMH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.0813440 sec
RG         3849.1
DB         16.00 usec
TE         288.0 K
D1         0.25000000 sec
d11        0.03000000 sec
D16        0.00020000 sec
MCB1ST    0 sec
MCB2ST    0.00196000 sec
MCB3ST    0.01500000 sec
PC         33.10 usec

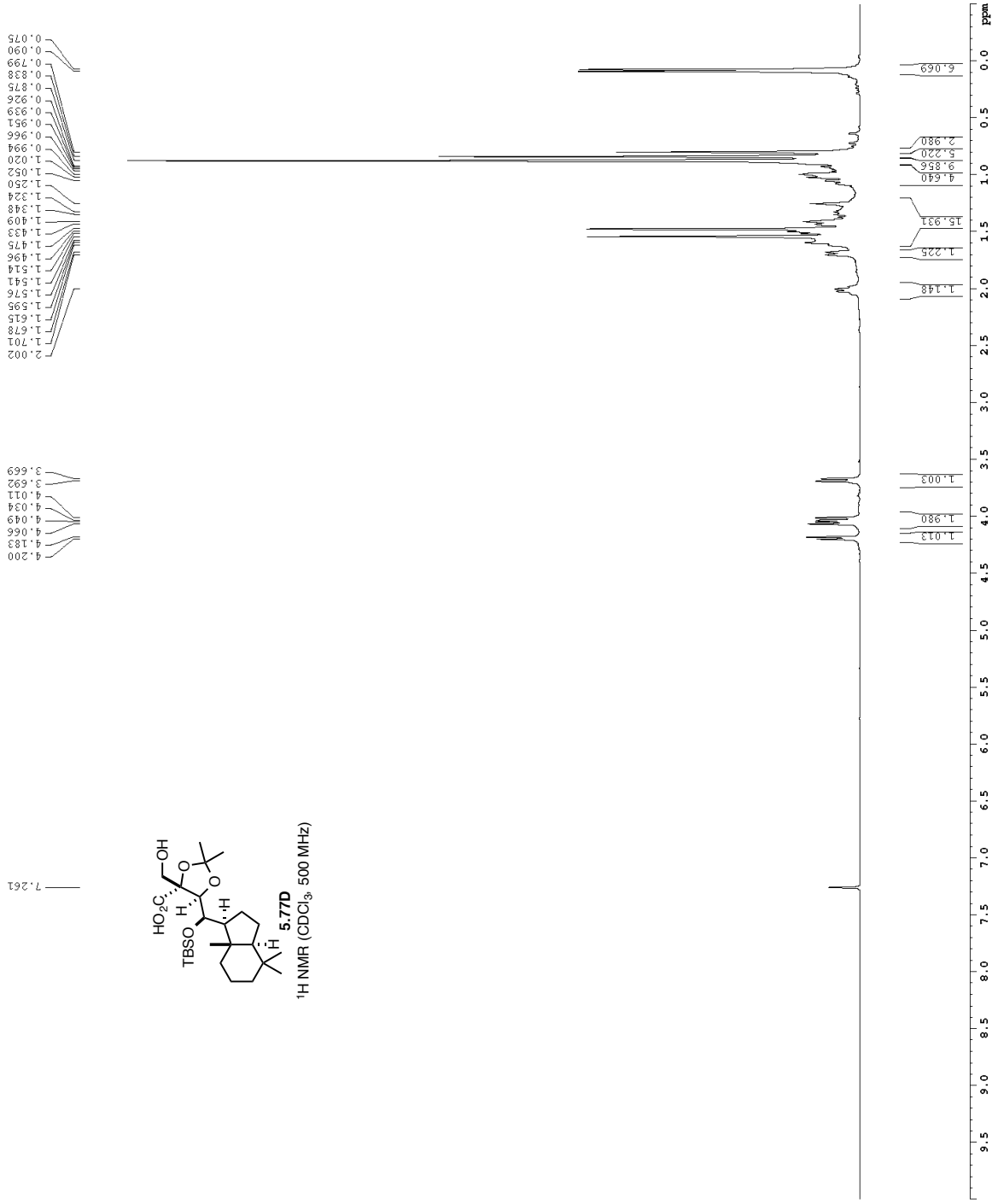
===== CHANNEL f1 =====
NUC1       13C
P1         16.00 usec
PL1        2000.00 usec
PL2        2000.00 usec
PL0        120.00 dB
PL1        -1.00 dB
SF01       125.7942548 MHz
SF         125.7600000 MHz
SFOFF      0 Hz
SFOFF1     0 Hz
SFOFF2     0 Hz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        1.60 dB
PL12       24.50 dB
SF02       500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GFX1       0 %
GFX2       0 %
GFY1       0 %
GFY2       0 %
GFZ1       0 %
GFZ2       0 %
P15        30.00 %
P16        50.00 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



Current Data Parameters
 NAME: 017-VI-12
 EXPNO: 3
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20151214
 Time: 11:25:00
 INSTRUM: cryo500
 PROBHD: 5 mm CETCI 1H-
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 DS: 4
 SFO: 500.1350600 MHz
 SWH: 8012.520 Hz
 FIDRES: 0.092533 Hz
 AQ: 0.0012500 sec
 RG: 415
 RW: 4.15
 DR: 62.400 usec
 DK: 2.000 usec
 TR: 285.0 K
 D1: 0.1000000 sec
 D11: 0.0000000 sec
 D12: 0.01500000 sec
 D13: 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1: 1H
 P1: 7.50 usec
 PL1: 0.00 dB
 SFO1: 500.2235015 MHz
 F2 - Processing parameters
 SI: 32768
 SF: 500.2230318 MHz
 DD: 0
 LB: 0
 GB: 0
 PC: 4.00

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

```

Current Data Parameters
NAME          DDT-VI-142
EXPNO        4
PROCNO       1
F2 - Acquisition Parameters
Date_         20151204
Time         13.11
INSTRUM      cryo500
PROBHD       5 mm CFTCI 1H-
PULPROG      SpinEchoy20dp.prd
TD           65536
SOLVENT      CDCl3
DS           2
DS           16
SMH          30303.031 Hz
FIDRES       0.462388 Hz
AQ           1.0813440 sec
RG           6502
DB           16.000 usec
DE           6.000 usec
TE           298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
MGZST        0 sec
MGZBK        0.01500000 sec
P2           33.10 usec

```

```

===== CHANNEL f1 =====
NUC1          13C
P1           16.00 usec
PL1          0.00 dB
P12          2000.00 usec
PL2          120.00 dB
PL0          120.00 dB
PL1          -1.00 dB
SF01         125.7942548 MHz
SFO1         2.70 dB
SFO2         2.70 dB
SFOFF1       0 Hz
SFOFF2       0 Hz
SFOFF3       0 Hz
SFOFF4       0 Hz
SFOFF5       0 Hz
SFOFF6       0 Hz
SFOFF7       0 Hz
SFOFF8       0 Hz
SFOFF9       0 Hz
SFOFF10      0 Hz
SFOFF11      0 Hz
SFOFF12      0 Hz
SFOFF13      0 Hz
SFOFF14      0 Hz
SFOFF15      0 Hz
SFOFF16      0 Hz
SFOFF17      0 Hz
SFOFF18      0 Hz
SFOFF19      0 Hz
SFOFF20      0 Hz
SFOFF21      0 Hz
SFOFF22      0 Hz
SFOFF23      0 Hz
SFOFF24      0 Hz
SFOFF25      0 Hz
SFOFF26      0 Hz
SFOFF27      0 Hz
SFOFF28      0 Hz
SFOFF29      0 Hz
SFOFF30      0 Hz
SFOFF31      0 Hz
SFOFF32      0 Hz
SFOFF33      0 Hz
SFOFF34      0 Hz
SFOFF35      0 Hz
SFOFF36      0 Hz
SFOFF37      0 Hz
SFOFF38      0 Hz
SFOFF39      0 Hz
SFOFF40      0 Hz
SFOFF41      0 Hz
SFOFF42      0 Hz
SFOFF43      0 Hz
SFOFF44      0 Hz
SFOFF45      0 Hz
SFOFF46      0 Hz
SFOFF47      0 Hz
SFOFF48      0 Hz
SFOFF49      0 Hz
SFOFF50      0 Hz
SFOFF51      0 Hz
SFOFF52      0 Hz
SFOFF53      0 Hz
SFOFF54      0 Hz
SFOFF55      0 Hz
SFOFF56      0 Hz
SFOFF57      0 Hz
SFOFF58      0 Hz
SFOFF59      0 Hz
SFOFF60      0 Hz
SFOFF61      0 Hz
SFOFF62      0 Hz
SFOFF63      0 Hz
SFOFF64      0 Hz
SFOFF65      0 Hz
SFOFF66      0 Hz
SFOFF67      0 Hz
SFOFF68      0 Hz
SFOFF69      0 Hz
SFOFF70      0 Hz
SFOFF71      0 Hz
SFOFF72      0 Hz
SFOFF73      0 Hz
SFOFF74      0 Hz
SFOFF75      0 Hz
SFOFF76      0 Hz
SFOFF77      0 Hz
SFOFF78      0 Hz
SFOFF79      0 Hz
SFOFF80      0 Hz
SFOFF81      0 Hz
SFOFF82      0 Hz
SFOFF83      0 Hz
SFOFF84      0 Hz
SFOFF85      0 Hz
SFOFF86      0 Hz
SFOFF87      0 Hz
SFOFF88      0 Hz
SFOFF89      0 Hz
SFOFF90      0 Hz
SFOFF91      0 Hz
SFOFF92      0 Hz
SFOFF93      0 Hz
SFOFF94      0 Hz
SFOFF95      0 Hz
SFOFF96      0 Hz
SFOFF97      0 Hz
SFOFF98      0 Hz
SFOFF99      0 Hz
SFOFF100     0 Hz

```

```

===== CHANNEL f2 =====
CPDPRG12      waltz16
NUC2          13C
P2           16.00 usec
PL2          0.00 dB
P12          2000.00 usec
PL12         120.00 dB
SF02         125.7942548 MHz
SFO2         2.70 dB
SFOFF1       0 Hz
SFOFF2       0 Hz
SFOFF3       0 Hz
SFOFF4       0 Hz
SFOFF5       0 Hz
SFOFF6       0 Hz
SFOFF7       0 Hz
SFOFF8       0 Hz
SFOFF9       0 Hz
SFOFF10      0 Hz
SFOFF11      0 Hz
SFOFF12      0 Hz
SFOFF13      0 Hz
SFOFF14      0 Hz
SFOFF15      0 Hz
SFOFF16      0 Hz
SFOFF17      0 Hz
SFOFF18      0 Hz
SFOFF19      0 Hz
SFOFF20      0 Hz
SFOFF21      0 Hz
SFOFF22      0 Hz
SFOFF23      0 Hz
SFOFF24      0 Hz
SFOFF25      0 Hz
SFOFF26      0 Hz
SFOFF27      0 Hz
SFOFF28      0 Hz
SFOFF29      0 Hz
SFOFF30      0 Hz
SFOFF31      0 Hz
SFOFF32      0 Hz
SFOFF33      0 Hz
SFOFF34      0 Hz
SFOFF35      0 Hz
SFOFF36      0 Hz
SFOFF37      0 Hz
SFOFF38      0 Hz
SFOFF39      0 Hz
SFOFF40      0 Hz
SFOFF41      0 Hz
SFOFF42      0 Hz
SFOFF43      0 Hz
SFOFF44      0 Hz
SFOFF45      0 Hz
SFOFF46      0 Hz
SFOFF47      0 Hz
SFOFF48      0 Hz
SFOFF49      0 Hz
SFOFF50      0 Hz
SFOFF51      0 Hz
SFOFF52      0 Hz
SFOFF53      0 Hz
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SFOFF55      0 Hz
SFOFF56      0 Hz
SFOFF57      0 Hz
SFOFF58      0 Hz
SFOFF59      0 Hz
SFOFF60      0 Hz
SFOFF61      0 Hz
SFOFF62      0 Hz
SFOFF63      0 Hz
SFOFF64      0 Hz
SFOFF65      0 Hz
SFOFF66      0 Hz
SFOFF67      0 Hz
SFOFF68      0 Hz
SFOFF69      0 Hz
SFOFF70      0 Hz
SFOFF71      0 Hz
SFOFF72      0 Hz
SFOFF73      0 Hz
SFOFF74      0 Hz
SFOFF75      0 Hz
SFOFF76      0 Hz
SFOFF77      0 Hz
SFOFF78      0 Hz
SFOFF79      0 Hz
SFOFF80      0 Hz
SFOFF81      0 Hz
SFOFF82      0 Hz
SFOFF83      0 Hz
SFOFF84      0 Hz
SFOFF85      0 Hz
SFOFF86      0 Hz
SFOFF87      0 Hz
SFOFF88      0 Hz
SFOFF89      0 Hz
SFOFF90      0 Hz
SFOFF91      0 Hz
SFOFF92      0 Hz
SFOFF93      0 Hz
SFOFF94      0 Hz
SFOFF95      0 Hz
SFOFF96      0 Hz
SFOFF97      0 Hz
SFOFF98      0 Hz
SFOFF99      0 Hz
SFOFF100     0 Hz

```

```

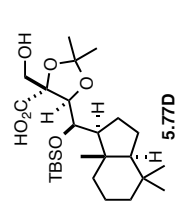
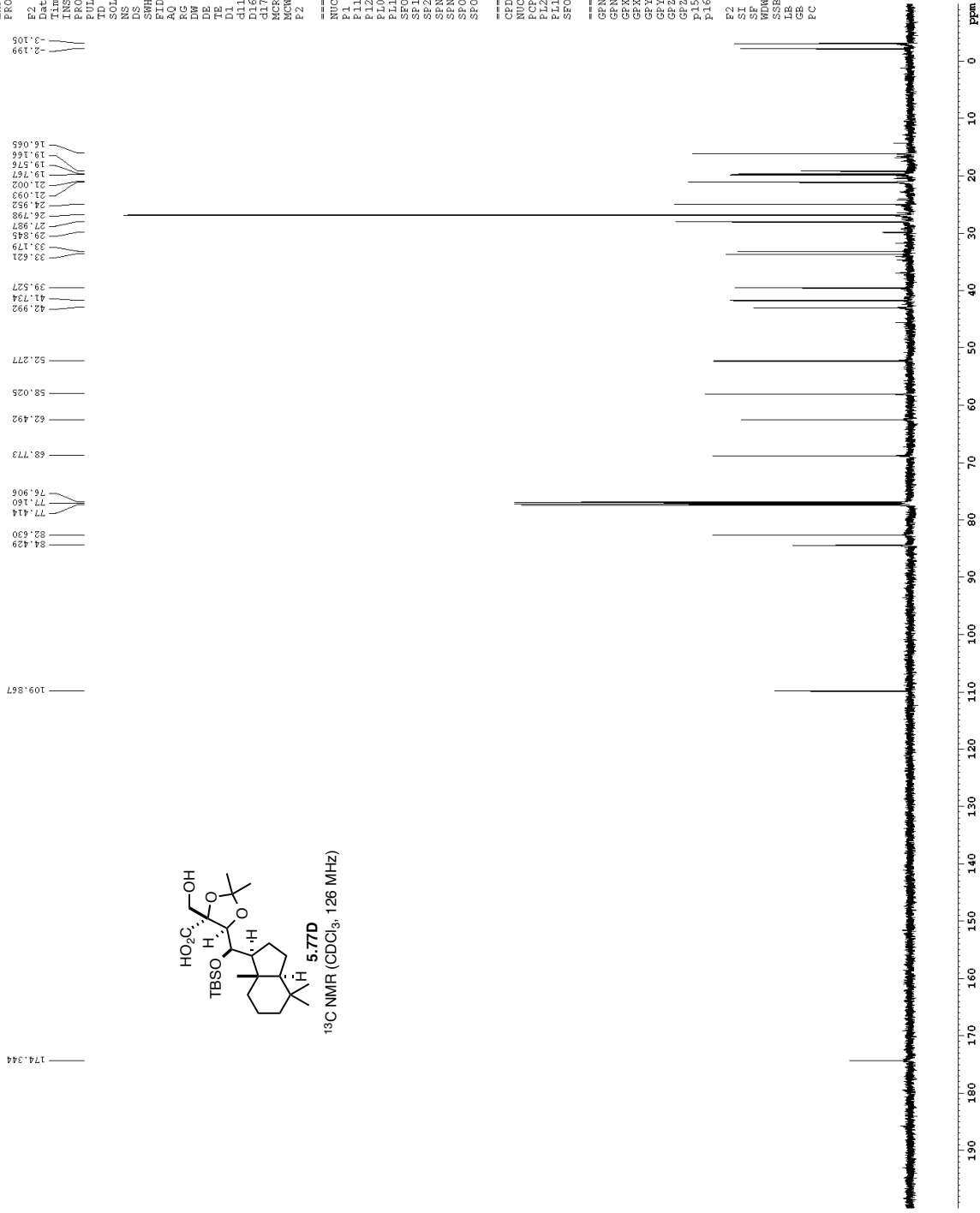
===== GRADIENT CHANNEL =====
GFNAM[1]      SINE.100
GFNAM[2]      SINE.100
GFEX1         0 %
GFEX2         0 %
GFEX3         0 %
GFEX4         0 %
GFEX5         0 %
GFEX6         0 %
GFEX7         0 %
GFEX8         0 %
GFEX9         0 %
GFEX10        0 %
GFEX11        0 %
GFEX12        0 %
GFEX13        0 %
GFEX14        0 %
GFEX15        0 %
GFEX16        0 %
GFEX17        0 %
GFEX18        0 %
GFEX19        0 %
GFEX20        0 %
GFEX21        0 %
GFEX22        0 %
GFEX23        0 %
GFEX24        0 %
GFEX25        0 %
GFEX26        0 %
GFEX27        0 %
GFEX28        0 %
GFEX29        0 %
GFEX30        0 %
GFEX31        0 %
GFEX32        0 %
GFEX33        0 %
GFEX34        0 %
GFEX35        0 %
GFEX36        0 %
GFEX37        0 %
GFEX38        0 %
GFEX39        0 %
GFEX40        0 %
GFEX41        0 %
GFEX42        0 %
GFEX43        0 %
GFEX44        0 %
GFEX45        0 %
GFEX46        0 %
GFEX47        0 %
GFEX48        0 %
GFEX49        0 %
GFEX50        0 %
GFEX51        0 %
GFEX52        0 %
GFEX53        0 %
GFEX54        0 %
GFEX55        0 %
GFEX56        0 %
GFEX57        0 %
GFEX58        0 %
GFEX59        0 %
GFEX60        0 %
GFEX61        0 %
GFEX62        0 %
GFEX63        0 %
GFEX64        0 %
GFEX65        0 %
GFEX66        0 %
GFEX67        0 %
GFEX68        0 %
GFEX69        0 %
GFEX70        0 %
GFEX71        0 %
GFEX72        0 %
GFEX73        0 %
GFEX74        0 %
GFEX75        0 %
GFEX76        0 %
GFEX77        0 %
GFEX78        0 %
GFEX79        0 %
GFEX80        0 %
GFEX81        0 %
GFEX82        0 %
GFEX83        0 %
GFEX84        0 %
GFEX85        0 %
GFEX86        0 %
GFEX87        0 %
GFEX88        0 %
GFEX89        0 %
GFEX90        0 %
GFEX91        0 %
GFEX92        0 %
GFEX93        0 %
GFEX94        0 %
GFEX95        0 %
GFEX96        0 %
GFEX97        0 %
GFEX98        0 %
GFEX99        0 %
GFEX100       0 %

```

```

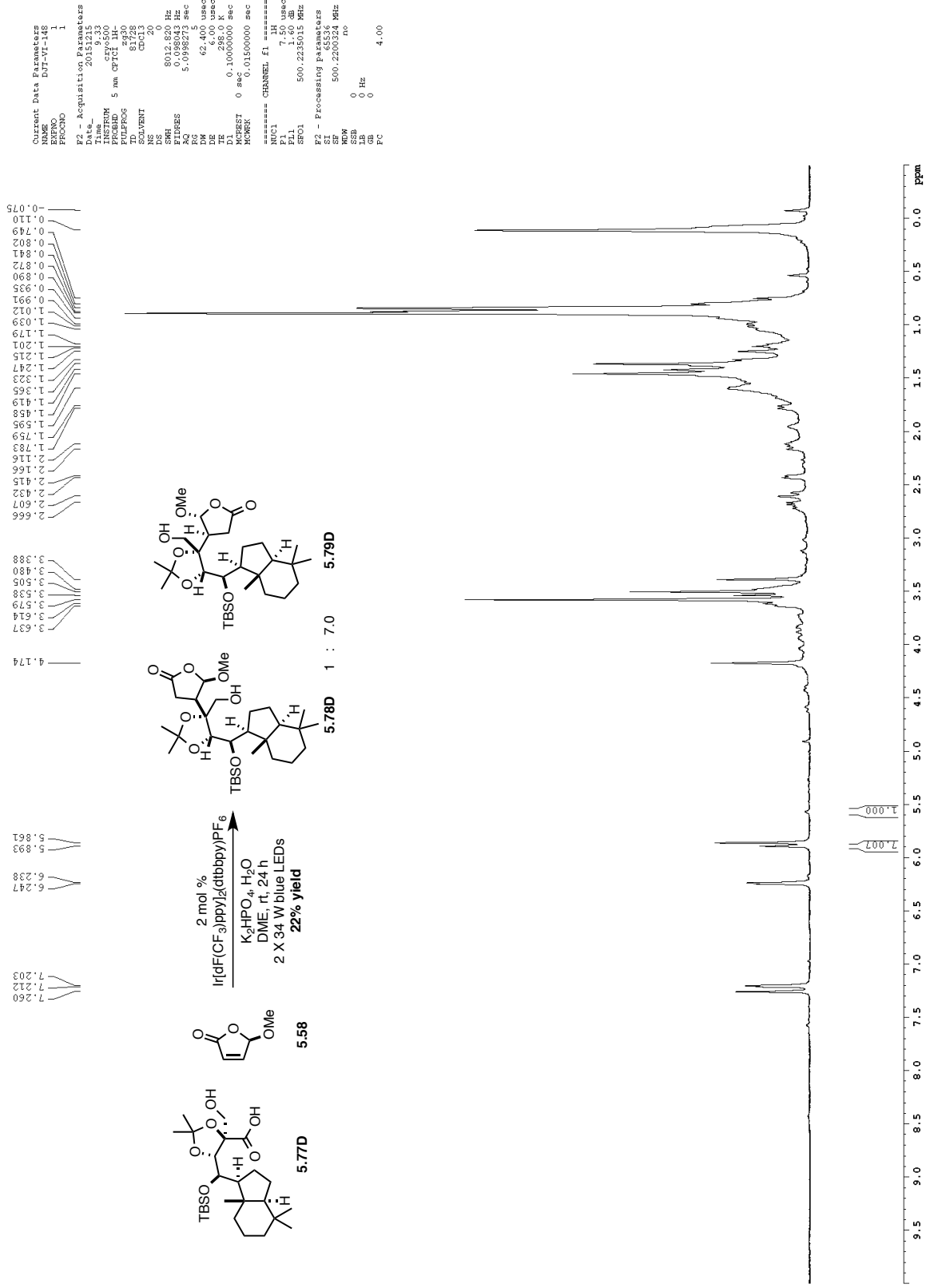
F2 - Processing Parameters
SF           125.7604085 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           2.00

```

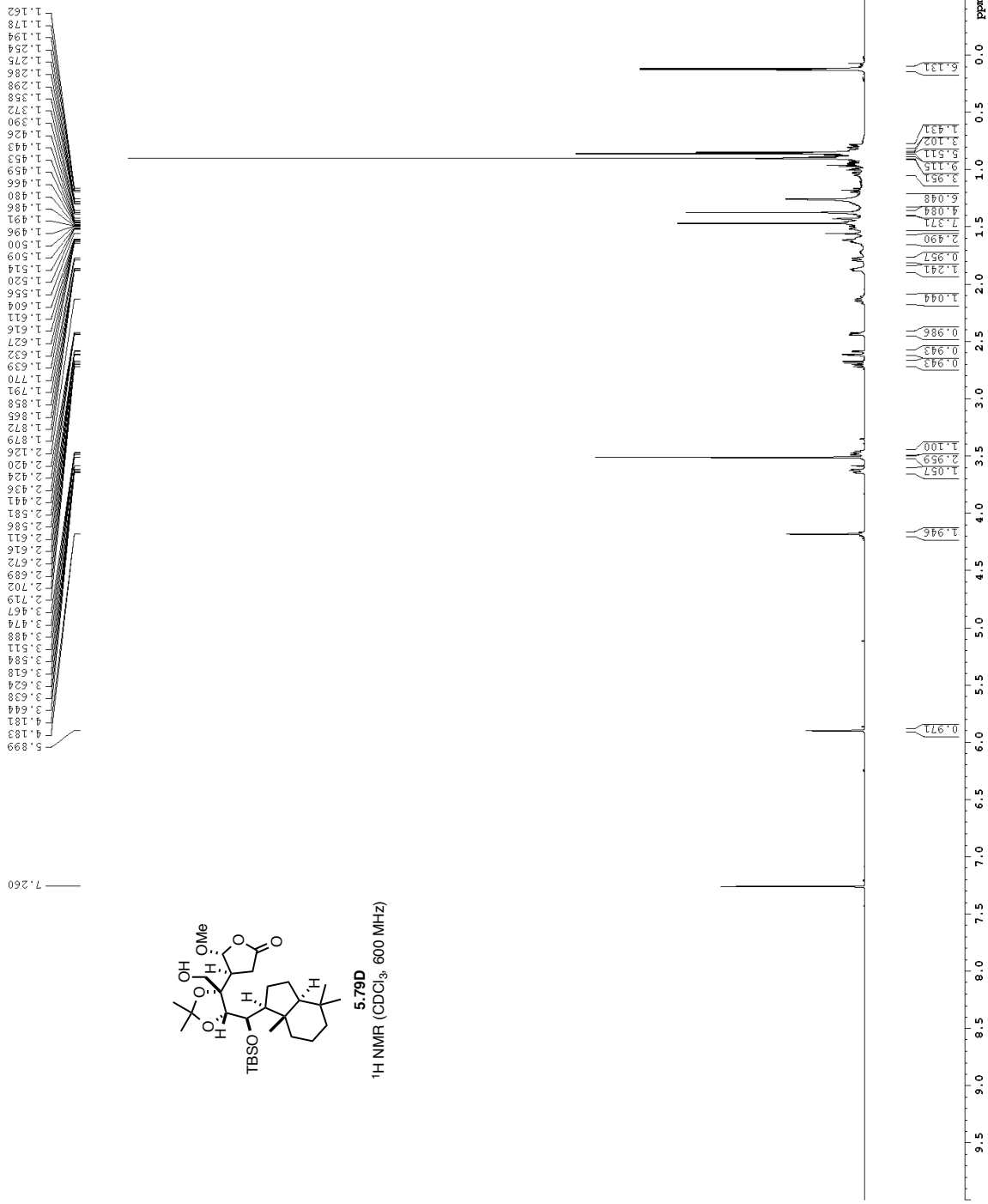


¹³C NMR (CDCl₃, 126 MHz)

1H spectrum



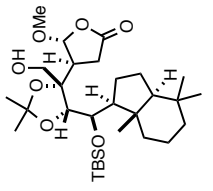
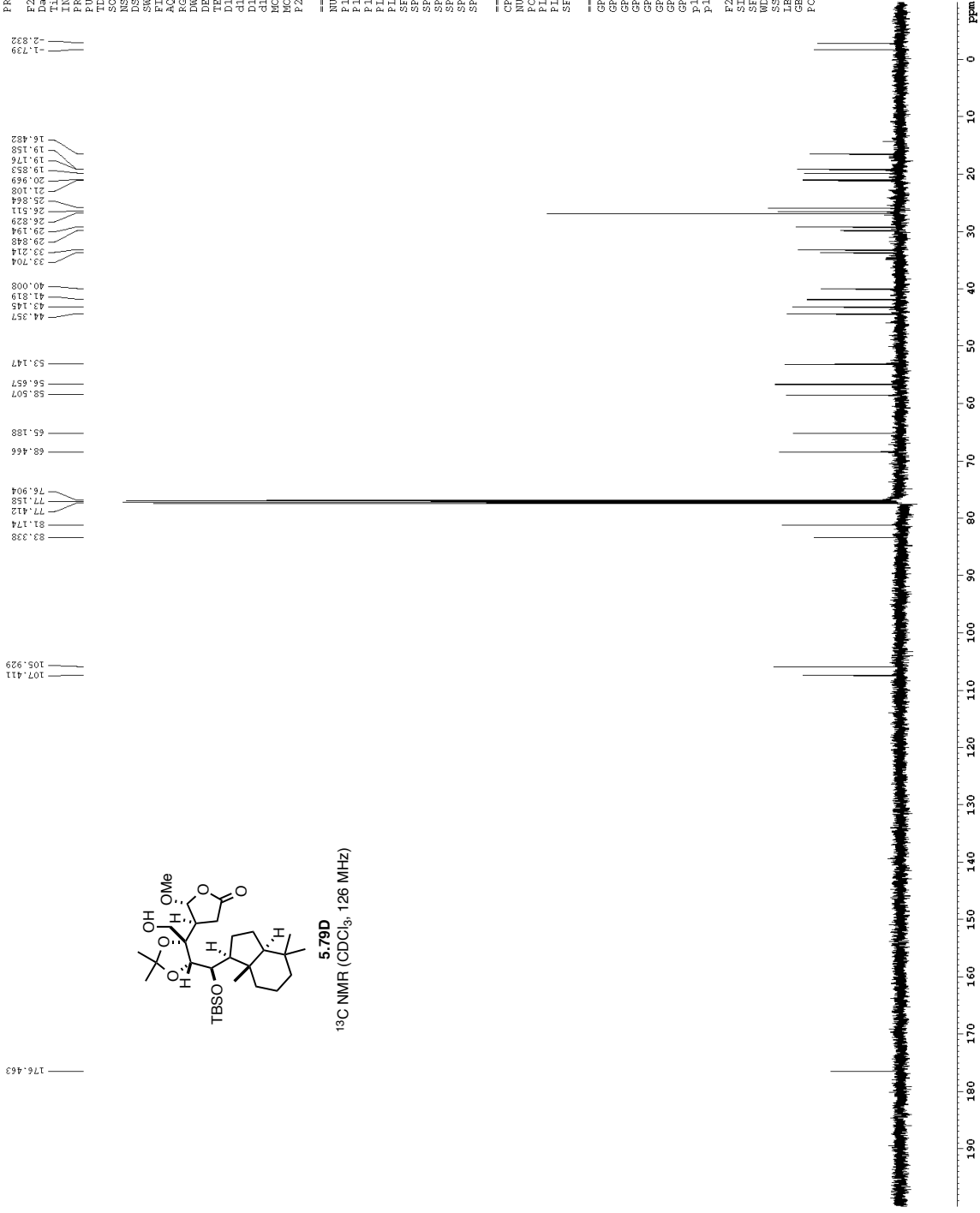
¹H spectrum



```

=====
Constant Data Parameters
NAME      D07-VI-148
PROCNO    1
E2 - Acquisition Parameters
Date_     2015-07-05
INSTRUM   AV600
PROBHD    5 mm TBI 1H/13
PULPROG   zgpg30
TD         65536
SOLVENT    CDCl3
DS         20
SS         20
SMH        9615.385 Hz
NUC1       13C
AQ         5.0988478 sec
RG         50.181
DE         14.450 usec
TE         298.0 K
D1         0.10000000 sec
=====
===== CHANNEL F1 =====
NUC1       1H
P1         8.00 usec
PL1        24.00000000 W
=====
E2 - Processing Parameters
SI         32768
SF         600.1300357 MHz
WDW        EM
SSB        0
GB         0
PC         1.00
  
```

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



5.79D
¹³C NMR (CDCl₃, 126 MHz)

```

Current Data Parameters
NAME      DUT-VI-148
EXPNO     20
PROCNO    1
F2 - Acquisition Parameters
Date_     20160127
Time      13.12
INSTRUM   cryo500
PROBHD    5 mm CFTCI 1H-
PULPROG   SpinEchoq20sp.prd
TD         65536
SOLVENT   CDCl3
NS         421
DS         0
SMH        30303.031 Hz
FIDRES     0.462388 Hz
AQ         1.0513440 sec
RG         1250.00
AQ         1250.00 usec
DE         6.00 usec
TE         298.0 K
D1         0.25000000 sec
dH1        0.03000000 sec
D16        0.00020000 sec
DELTA     0.00019600 sec
MAGREST    0 sec
MORPH      0.01500000 sec
P2         33.10 usec

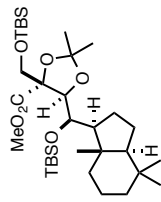
===== CHANNEL F1 =====
NUC1       13C
P1         16 usec
PL1        500.00 usec
PL2        2000.00 usec
PL0        120.00 dB
PL1        -1.00 dB
SFO1       125.7942548 MHz
SF         125.7600000 MHz
SF2        2.70 dB
SFNAM[1]   Cry60-0.5.20.1
SFNAM[2]   Cry60comp.4
SFOFF1     0 Hz
SFOFF2     0 Hz

===== CHANNEL F2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      100.00 usec
PL2        1.60 dB
PL12       24.50 dB
SFO2       500.2225011 MHz

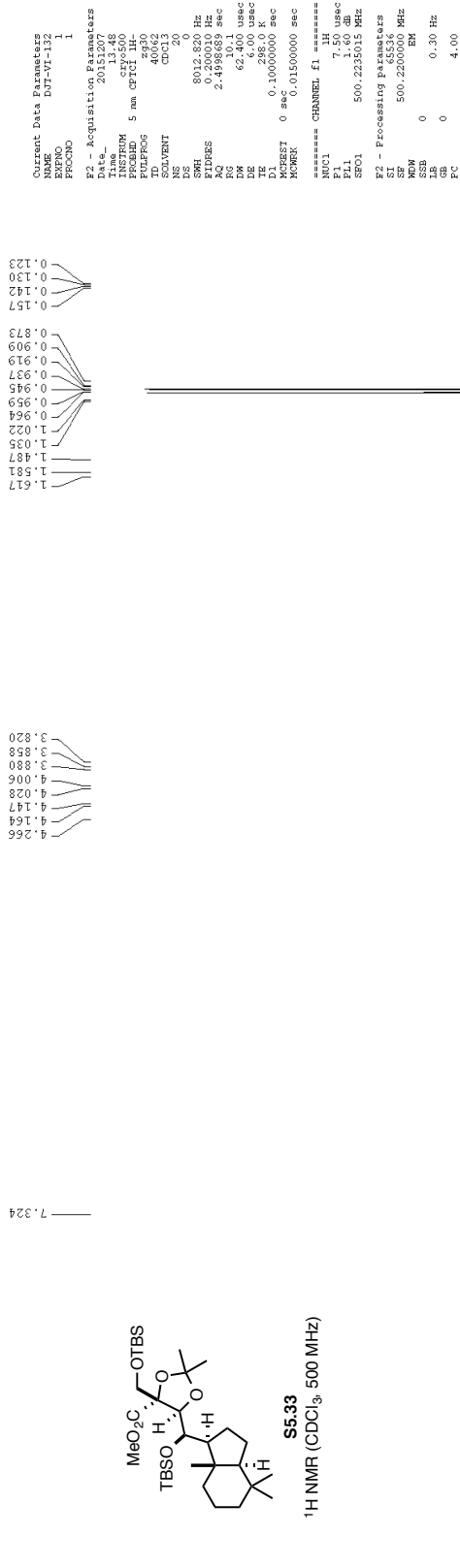
===== GRADIENT CHANNEL =====
GPNAM[1]   SINE.100
GPNAM[2]   SINE.100
GFX1       0 %
GFX2       0 %
GFY1       0 %
GFY2       0 %
GFZ1       0 %
GFZ2       30.00 %
p15        50.00 %
p16        500.00 usec
p16        1000.00 usec

F2 - Processing parameters
SI         65536
SF         125.7804076 MHz
MORPH      EM
SSB        0
LB         0
GB         0
PC         1.00 Hz
FC         2.00
    
```

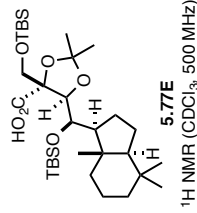

¹H spectrum



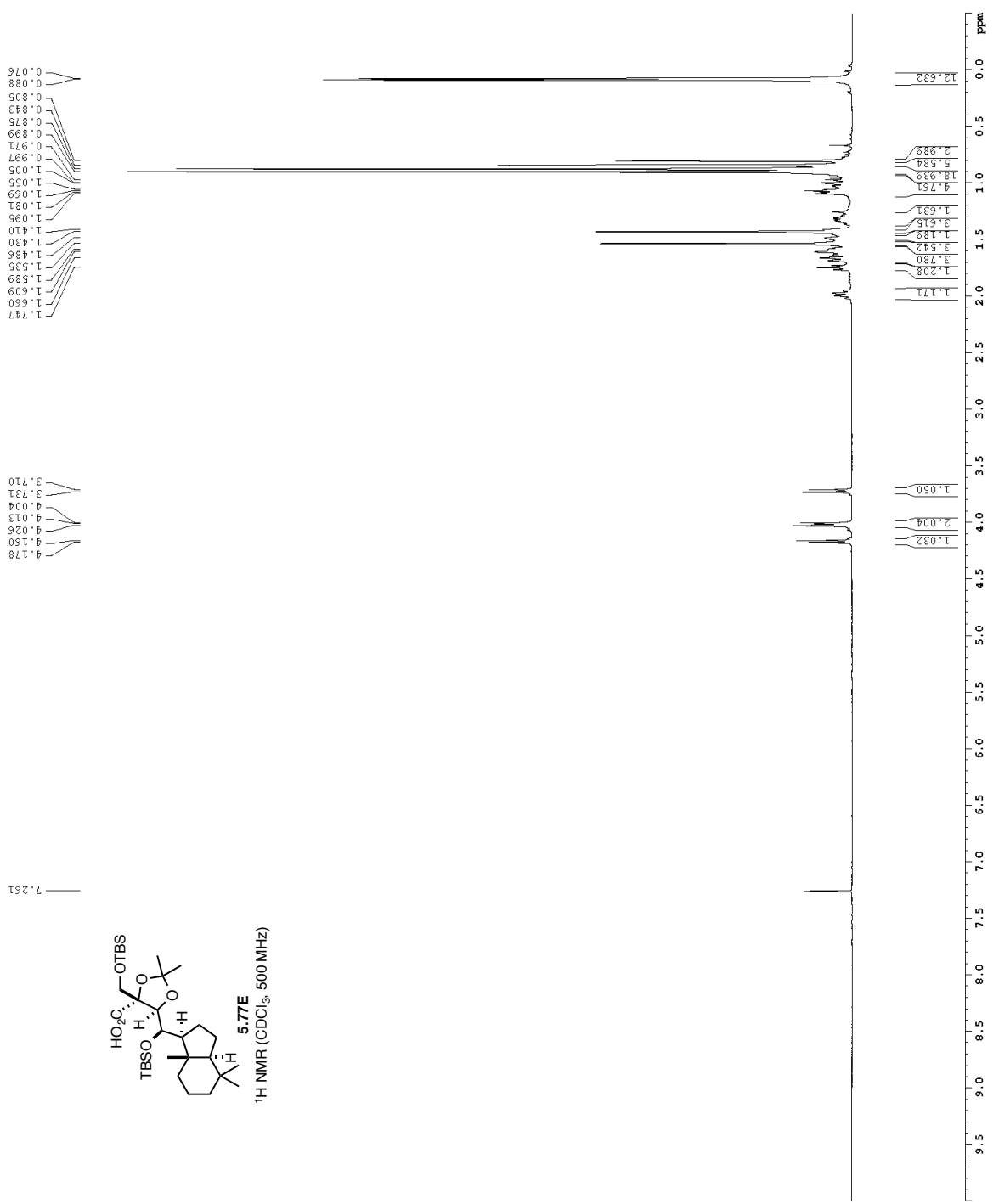
S5.33
¹H NMR (CDCl₃, 500 MHz)



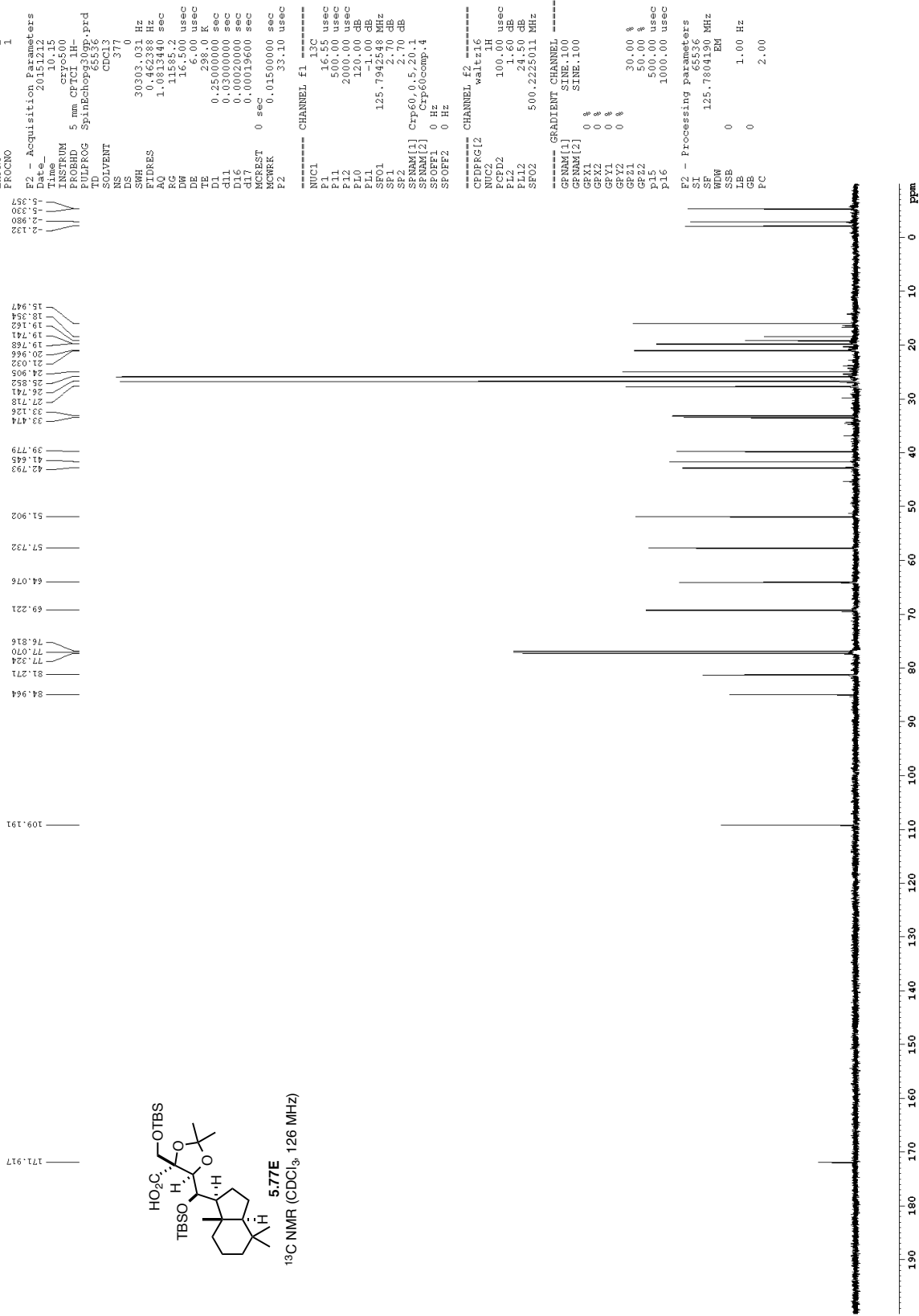
1H spectrum



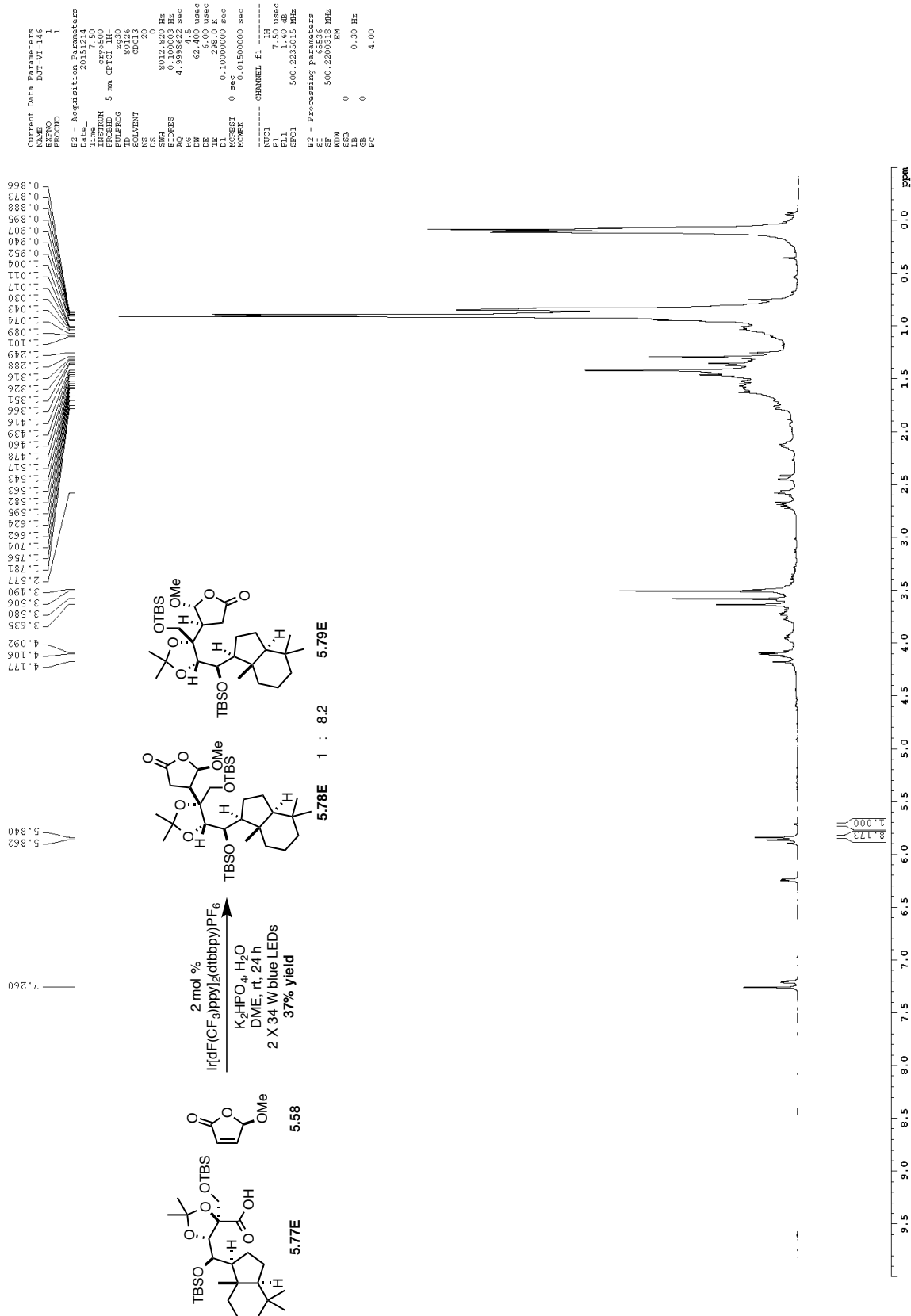
Current Data Parameters
 NAME: 217142443
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20151212
 Time: 11.33
 INSTRUM: cryo500
 PROBRD: 5 mm CPY1H-
 PULPROG: zgpg30
 ZD: 0.226
 SOLVENT: CDCl3
 NS: 20
 DS: 2
 SWH: 8012.820 Hz
 FIDRES: 0.998023 Hz
 RG: 4.15
 DM: 62.400 usec
 DE: 288.0 Hz
 TE: 300.2 K
 D1: 0.10000000 sec
 ACQRES: 0.01500000 sec
 HWDW: EM
 L1: 0
 L2: 0
 L3: 0
 L4: 0
 PC: 4.00



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

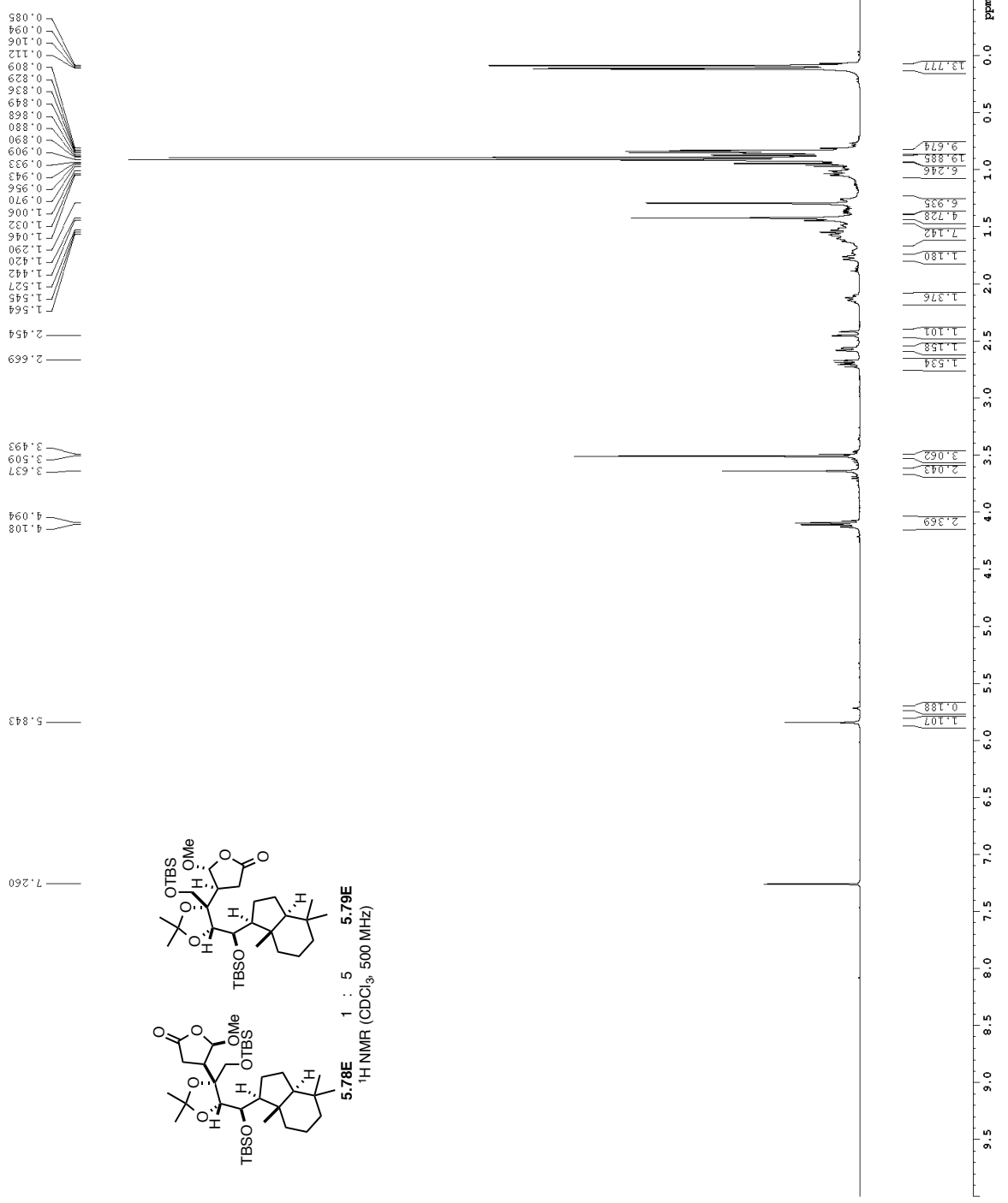


1H spectrum



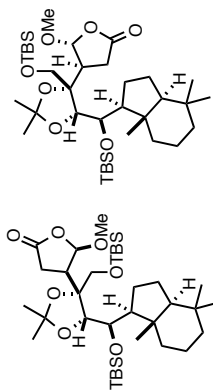
1H spectrum

Current Data Parameters
 NAME: 20151215_142
 EXPNO: 3
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20151215
 Time: 10:46:56
 INSTRUM: cryo500
 PROBHD: 5 mm QNP1H-
 ZULP05
 ZD: 0.0000
 ZD2: 0.0000
 SOLVENT: CDCl3
 NS: 20
 DS: 2
 SWH: 8012.820 Hz
 FIDRES: 0.098213 Hz
 AQRES: 0.000015 sec
 RG: 519.92715
 DM: 62.400 usec
 DE: 0.000000 usec
 TE: 298.0 K
 D1: 0.10000000 sec
 DELTA: 0.000000 sec
 HONEST: 0.01500000 sec
 HOREK: 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1: 1H
 P1: 7.50 usec
 PL1: 0.00 dB
 SFO1: 500.225010 MHz
 =====
 F2 - Processing parameters
 SI: 32768
 SF: 500.2200316 MHz
 EQ: EM
 AS: 0
 LA: 0.30 Hz
 GB: 0
 PC: 4.00



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

176.908
106.911
106.720
106.214



5.78E 1 : 5 5.79E
13C NMR (CDCl₃, 126 MHz)

```

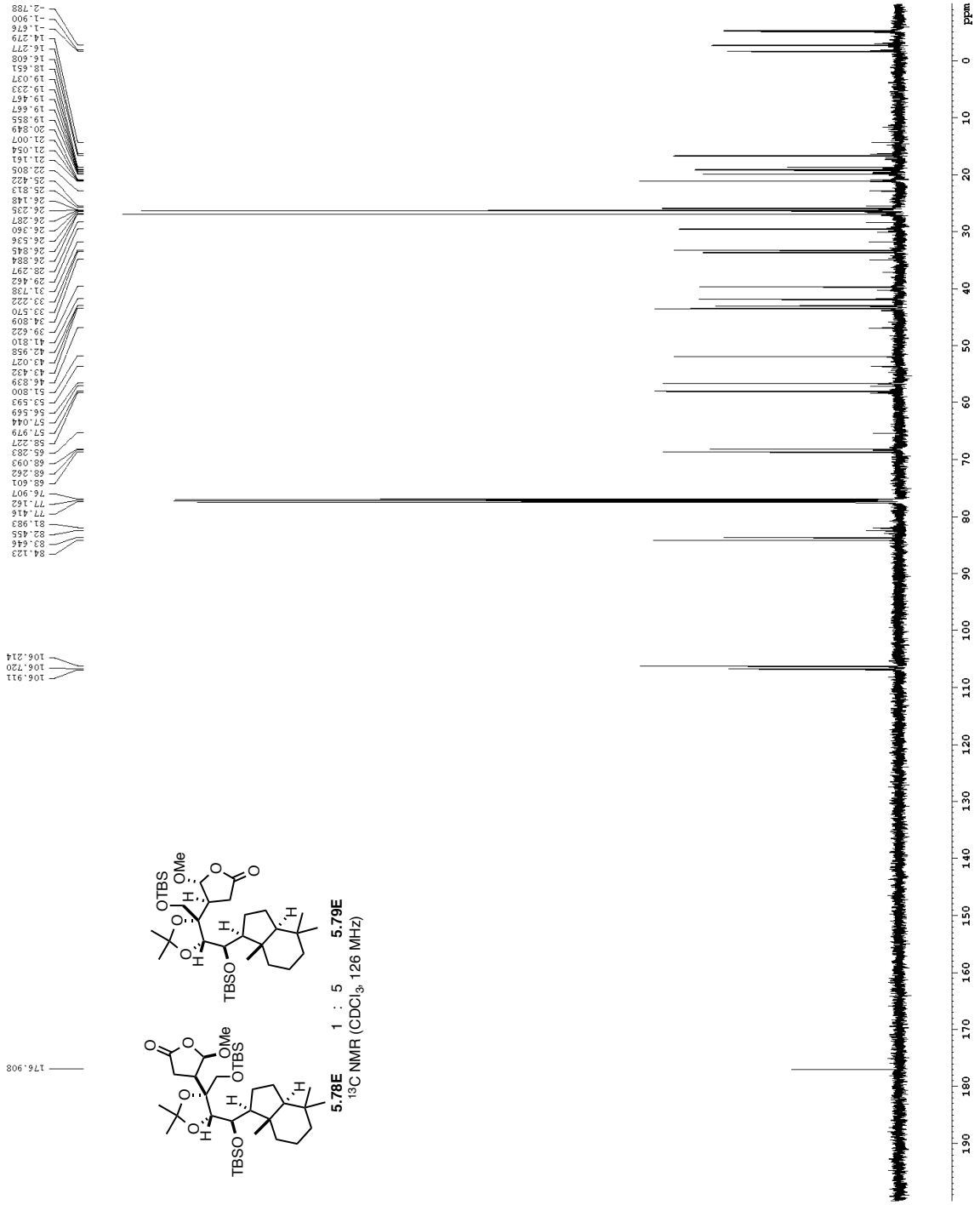
Current Data Parameters
NAME          DVT-VI-146
EXPNO         1
PROCNO        1
F2 - Acquisition Parameters
Date_         20151215
Time          7.46
INSTRUM       cryo600
PROBHD        5 mm CFC1 1H-
PULPROG       SpinEchoPrp.prd
SOLVENT       CDCl3
DS            239
SWH            30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813440 sec
RG            12.500
AQ            12.500 usec
DE            6.00 usec
TE            298.10 K
D1            0.25000000 sec
d11           0.03000000 sec
D15           0.00020000 sec
DELTA        0.00019600 sec
MCREST       0 sec
MCWRRK       0.01500000 sec
F2            33.10 usec

===== CHANNEL f1 =====
NUC1          13C
P1            16.155 usec
PL1           500.00 usec
PL2           2000.00 usec
PL0           120.00 dB
PL1           -1.00 dB
PL2           -1.00 dB
SFO1          125.7942548 MHz
SFO2          27.7000000 MHz
SF            27.7000000 MHz
SFOFF1        0 Hz
SFOFF2        0 Hz

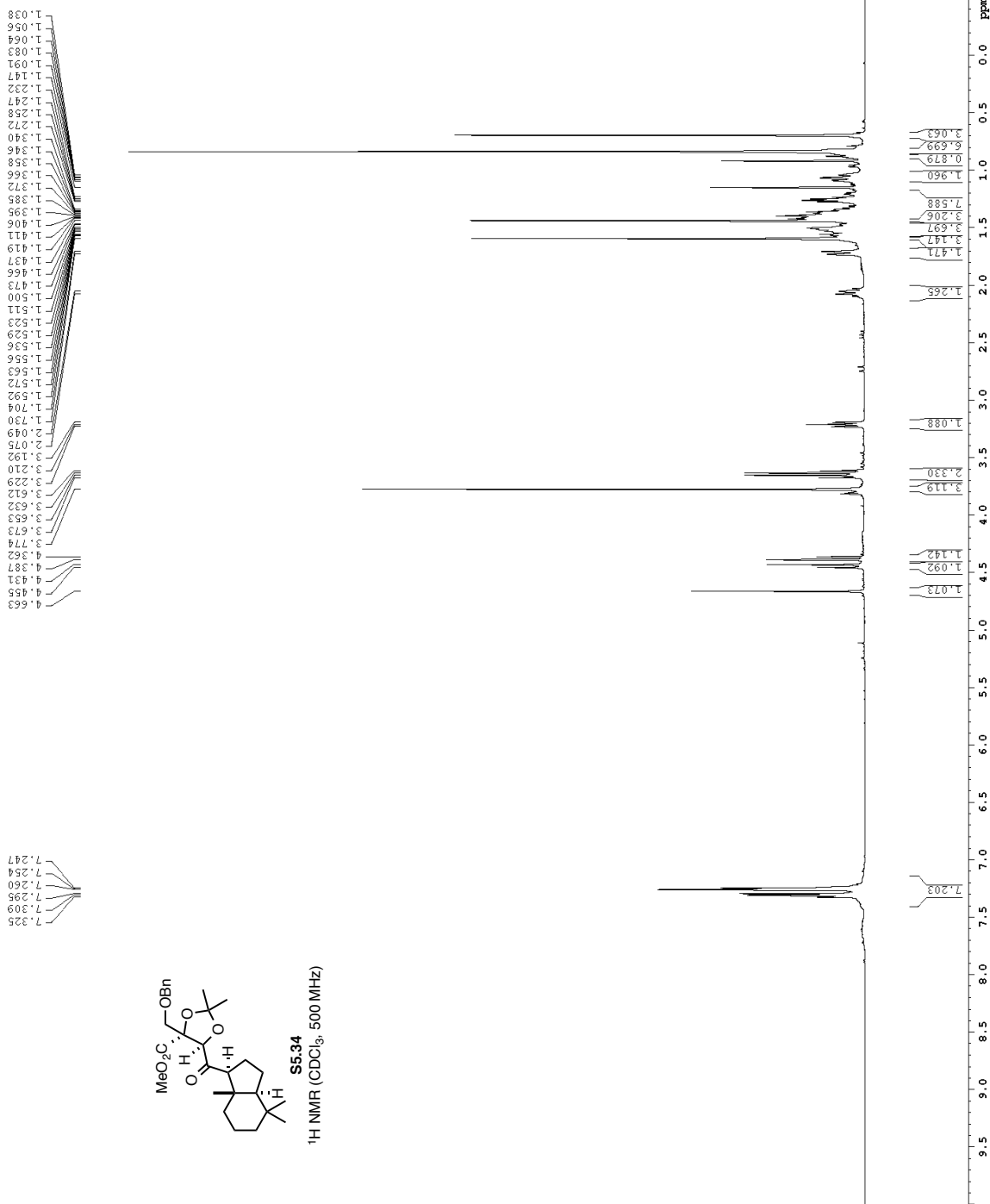
===== CHANNEL f2 =====
CPDPRG2       waitz16
NUC2          1H
P2            100.00 usec
PL2           1.60 dB
PL0           24.50 dB
SFO2          500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]      SINE.100
GPNAM[2]      SINE.100
GFX1          0 %
GFX2          0 %
GFX3          0 %
GFX4          0 %
GFX5          30.00 %
GFX6          50.00 %
P15           500.00 usec
P16           1000.00 usec

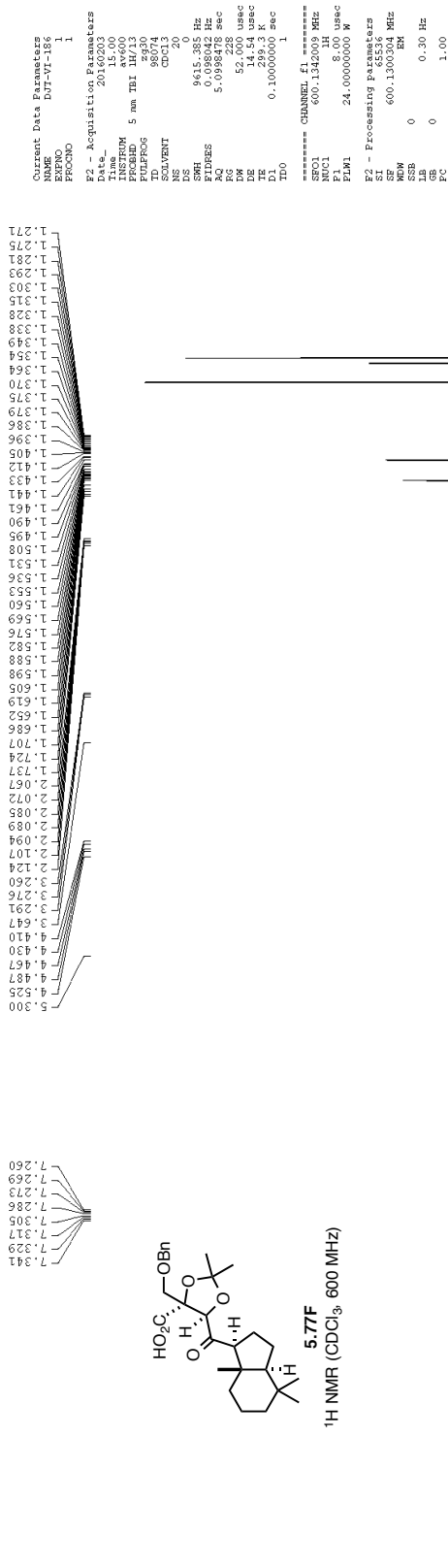
F2 - Processing parameters
SI            656336
SF            125.7804076 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            2.00
  
```



¹H spectrum



1H spectrum



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

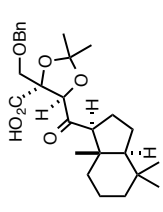
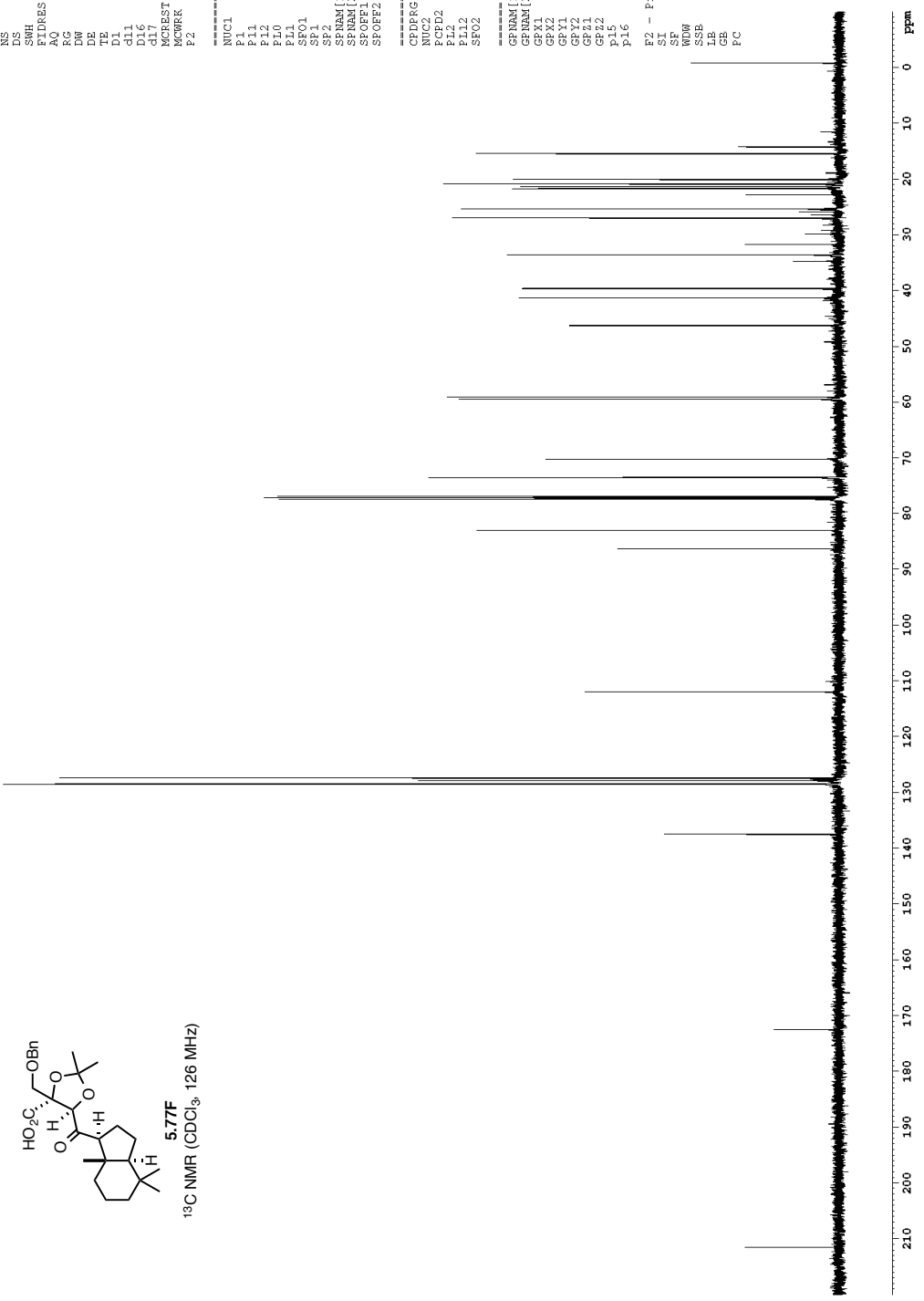
Current Data Parameters
 NAME DUT-VI-186
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20160204
 Time 7.22
 INSTRUM crys500
 PROBDH 5 mm CPTCI 1H-
 PULPROG SpinEchozgpgprd
 PCPRG2 6536
 SOLVENT CDCl3
 NS 200
 DS 0
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.081340 sec
 RG 327
 DE 16.500 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 d12 0.00200000 sec
 d13 0.00150000 sec
 MCREST 0 sec
 MCWRRK 0.01500000 sec
 P2 33.10 usec

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 16.15 usec
 P11 500.00 usec
 P12 2000.00 usec
 PLO 120.00 dB
 P1L -1.00 dB
 SF01 125.7942548 MHz
 SFO1 125.7942548 MHz
 SF2 2.70 dB
 SFNAM[1] Crp50.0.5.20.1
 SFNAM[2] Crp50comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

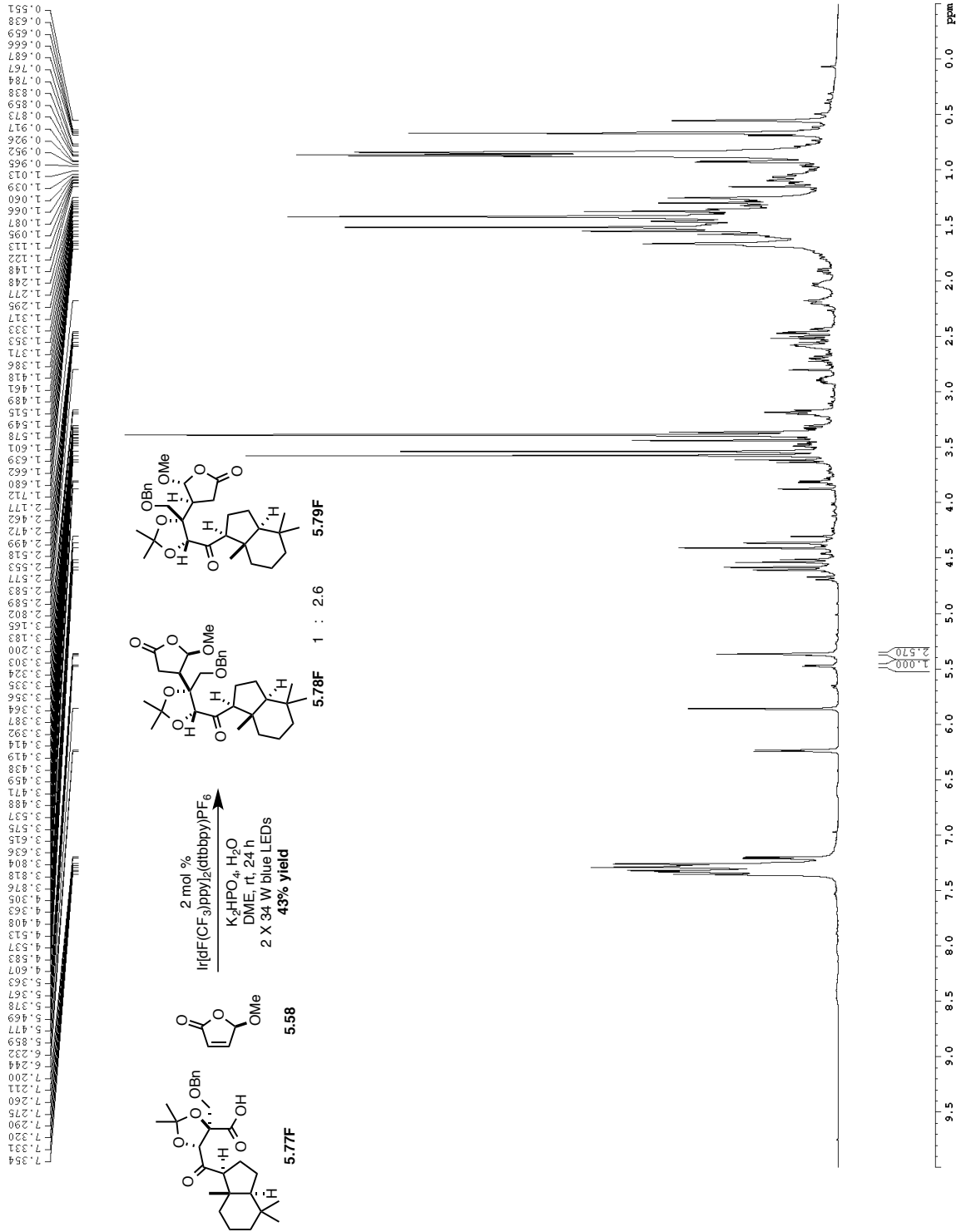
===== CHANNEL f2 =====
 NUC2 ¹H
 P2 100.00 usec
 P21 1.60 dB
 P22 24.50 dB
 SFO2 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GFNAM[1] STINE.100
 GFNAM[2] STINE.100
 GX1 0 %
 GX2 0 %
 GY1 0 %
 GY2 0 %
 GFZ1 30.00 %
 GFZ2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

F2 - Processing Parameters
 SI 6536
 SF 125.7804113 MHz
 WDM 0
 LB 0
 GB 0
 PC 2.00

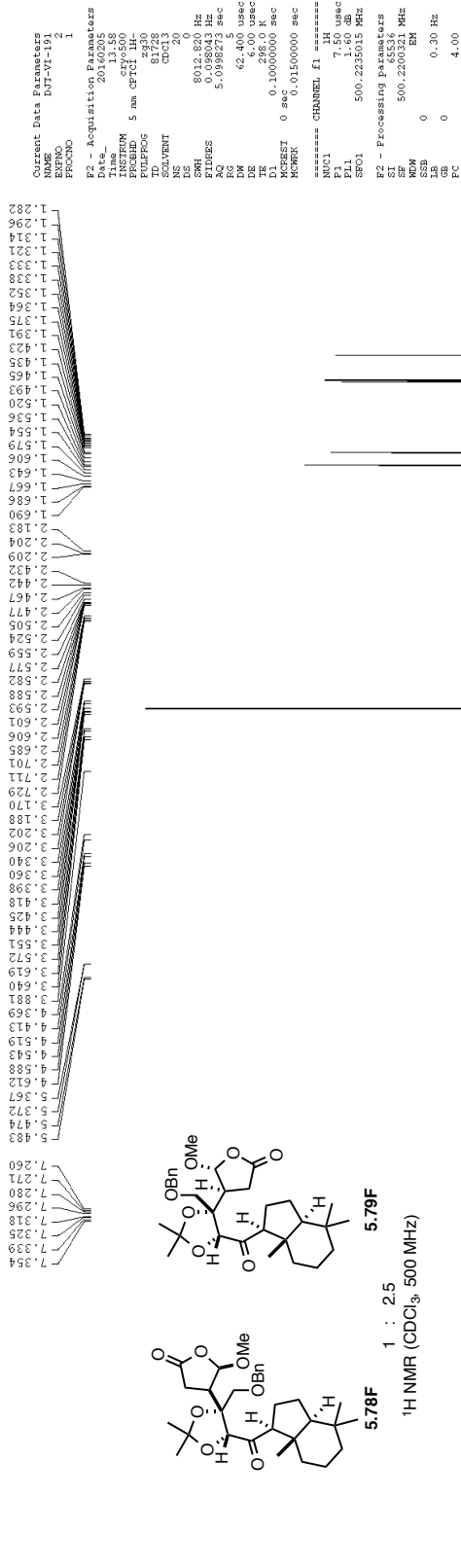


¹H spectrum



Content Data Parameters
 NAME: 247-14-19
 EXPNO: 1
 PROCNO: 1
 Date_ 20160205
 Time: 11:00:00
 INSTRUM: cryo500
 PROBHD: 5 mm QNP1H-
 PULPROG: zgpg30
 TD: 65536
 SOLVENT: CDCl3
 NS: 40
 DS: 4
 SWH: 8012.820 Hz
 FIDRES: 0.001000 Hz
 RG: 4.5
 DWDW: 62.400 usec
 DE: 0.001000 usec
 TE: 298.2 K
 D1: 0.1000000 sec
 D11: 0.0000000 sec
 D12: 0.01500000 sec
 D13: 0.01500000 sec
 D14: 0.01500000 sec
 D15: 0.01500000 sec
 ===== CHANNEL f1 =====
 NUC1: 1H
 P1: 7.50 usec
 PL1: 0.00 dB
 SFO1: 500.225015 MHz
 ===== CHANNEL f2 =====
 NUC2: 13C
 P2: 1.50 usec
 PL2: 19.00 dB
 SFO2: 125.761150 MHz
 ===== Processing parameters =====
 SI: 32768
 SF: 500.2200323 MHz
 DSF: 128
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 4.00

1H spectrum



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

```

Current Data Parameters
NAME      DOT-VI-191
EXPNO     3
PROCNO    1
F2 - Acquisition Parameters
Date_     20160205
Time      14.04
INSTRUM   crys500
PROBHD    5 mm CPTCI 1H-
PULPROG   Spinecho90upg.prd
D1        6.500000
SOLVENT   CDCl3
NS         137
DS         16
SFOFF     30303.031 Hz
FIDRES    0.462388 Hz
AQ         1.081340 sec
RG         128.82
DE         16.500 usec
TE         298.0 K
D1         0.25000000 sec
d11        0.03000000 sec
D16        0.00020000 sec
DELTA     0.00019600 sec
MORREST   0 sec
MORPH     0.01500000 sec
P2         33.10 usec
  
```

```

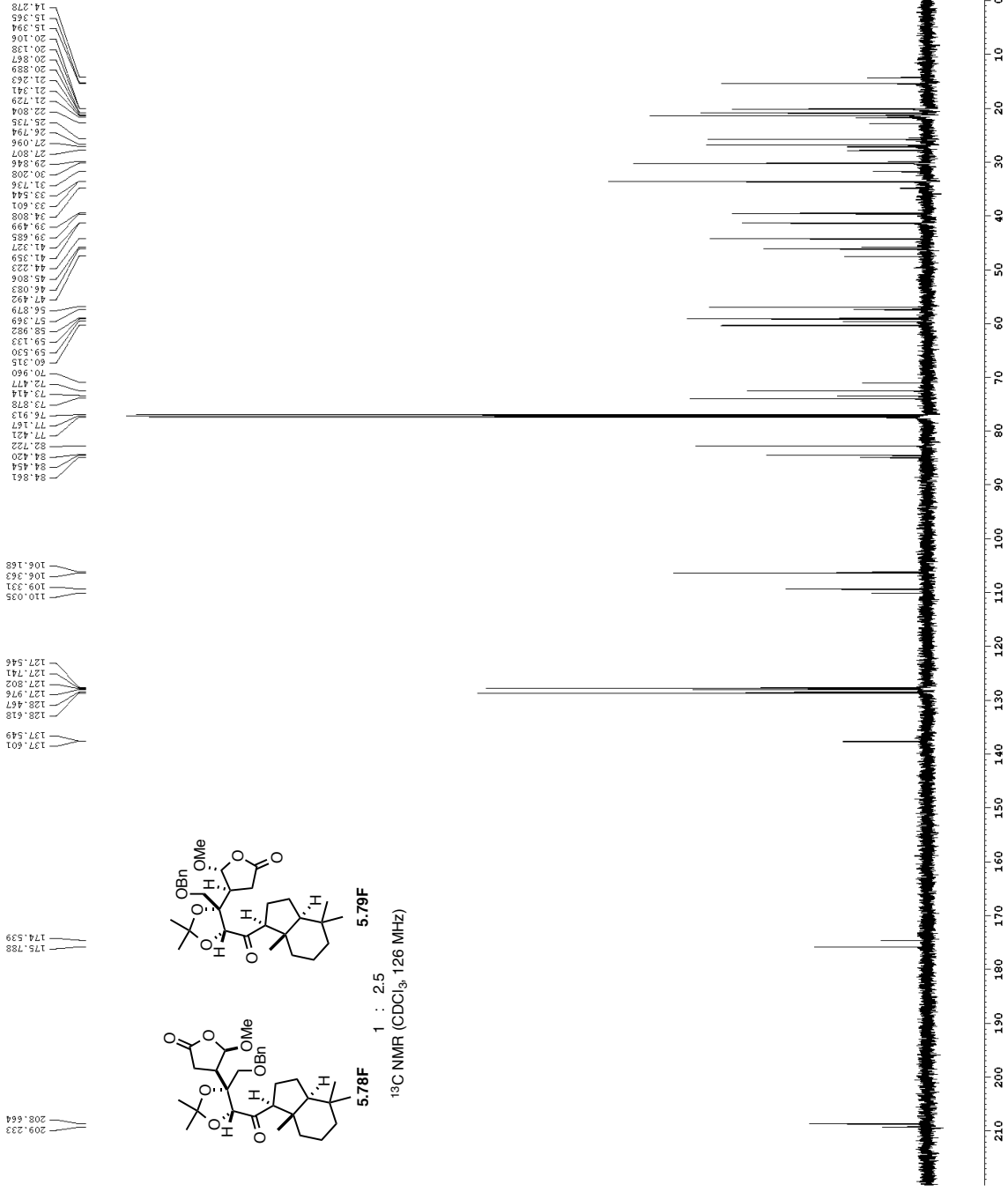
===== CHANNEL f1 =====
NUC1      13C
P1        16.15 usec
P11       500.00 usec
P12       2000.00 usec
PL0       120.00 dB
PL1       -1.00 dB
SFO1      125.7942548 MHz
SFOFF     0 Hz
SFNAM[1]  Cryp60.0.5.20.1
SFNAM[2]  Cryp60comp.4
SFOFF1    0 Hz
SFOFF2    0 Hz
  
```

```

===== CHANNEL f2 =====
CFDPRG[2] waltz16
NUC2      1H
PCPD2     100.00 usec
PL2       1.60 dB
PL12      24.50 dB
SFO2      500.2225011 MHz
  
```

```

===== GRADIENT CHANNEL =====
GFNAM[1]  SINE.100
GFNAM[2]  SINE.100
GX1       0 %
GX2       0 %
GY1       0 %
GY2       0 %
GFZ1      30.00 %
GFZ2      50.00 %
p15       500.00 usec
p16       1000.00 usec
F2 - Processing Parameters
SI         65536
SF         125.7804085 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         2.00
  
```



YS-IV-15

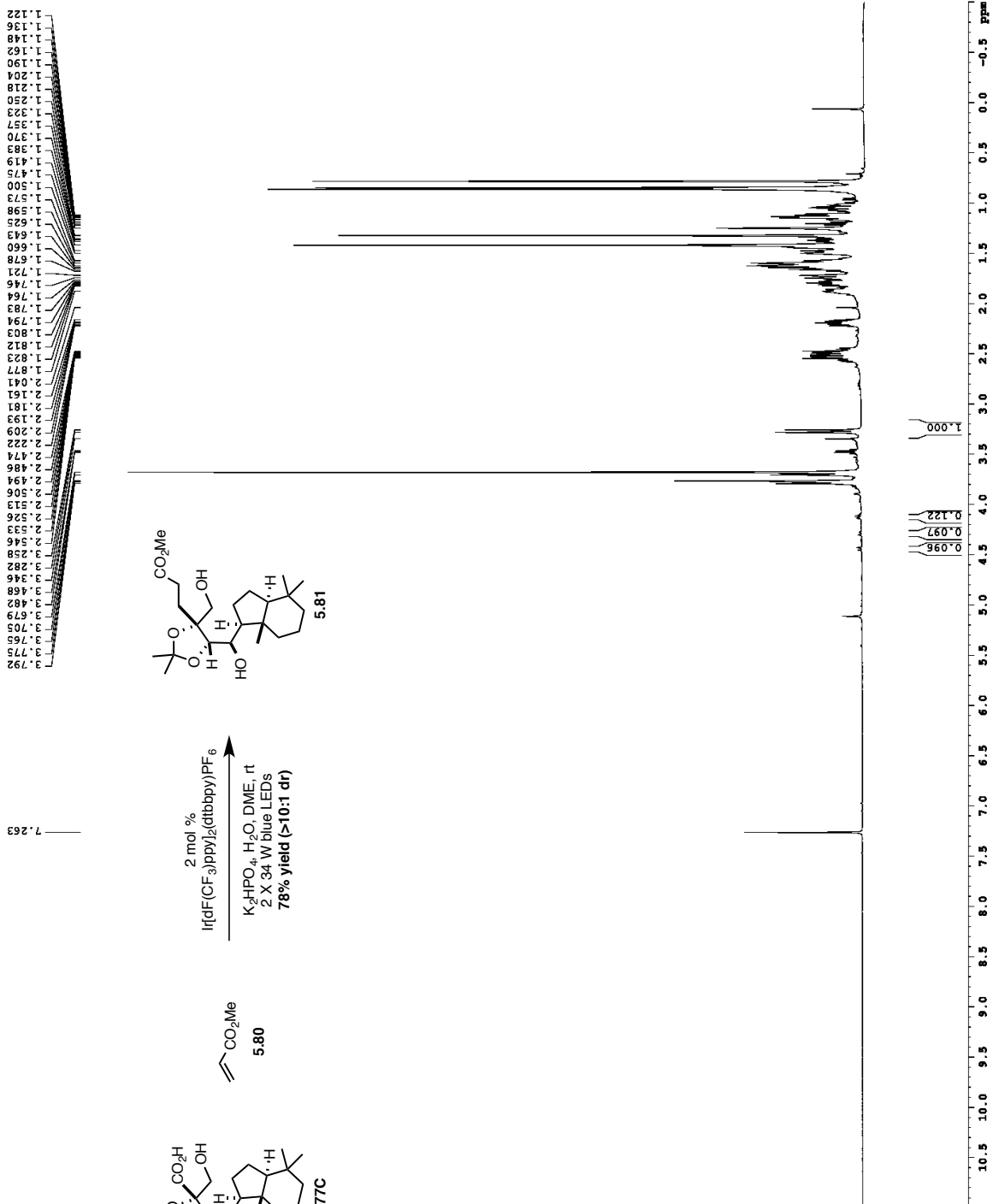
```

Comment: Data Parameters
NAME      YS-IV-15
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_     20151204
Time      11:24:30
INSTRUM   cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   zgpg30
TD         81928
SOLVENT   CDCl3
NS         2
DS         2
SWH        8012.820 Hz
FIDRES     0.098043 Hz
AQ         5.1397661 sec
RG         6.13
AQ2        62.400 usec
DM         288.0000000 sec
TE         298.00 K
D1         0.10000000 sec
MCWRRK    0.01500000 sec

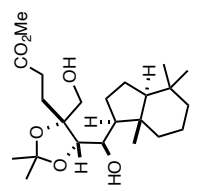
===== CHANNEL f1 =====
NUC1       1H
P1         7.50 usec
PL1        1.60 dB
SFO1       500.2635015 MHz

F2 - Processing parameters
SI         32768
SF         500.260312 MHz
WDW        EM
SSB        0
GB         0
PC         0
  
```

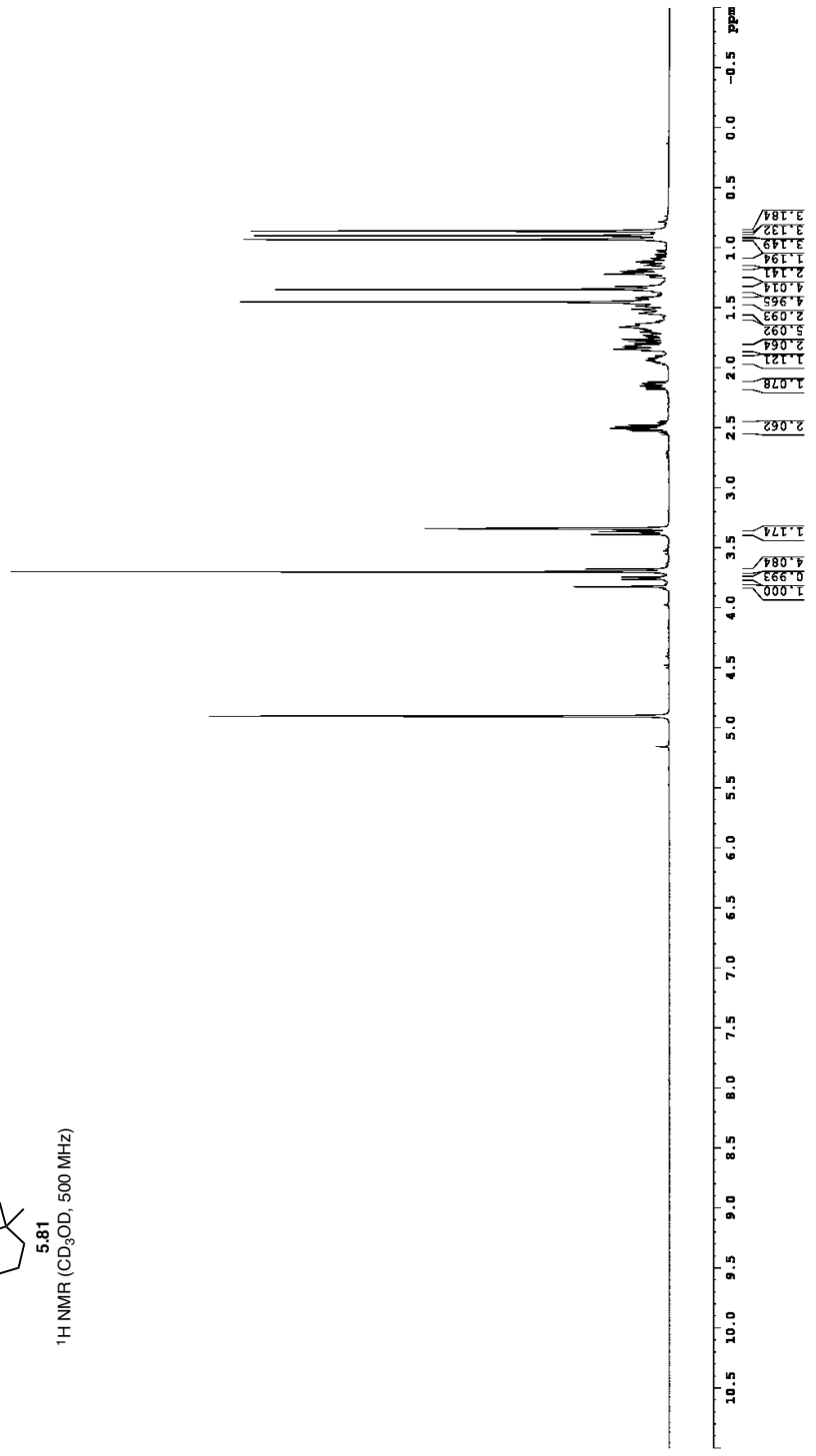


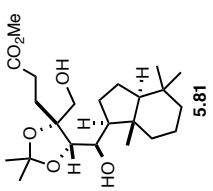
Current Data Parameters
 NAME XS-IV-15
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20151216
 TIME 11:00:00
 INSTRUM spect
 PULPROG zgpg30
 ID 81728
 NS 4
 DS 4
 SWH 8012.820 Hz
 FIDRES 0.098043 Hz
 AQ 3.0398279 sec
 RG 624.00
 DB 288.00
 UC 288.00
 UG 288.00
 VZ 0.1000000 sec
 ACQRES 0.0150000 sec
 CHANNEL f1
 NUCL 13C
 P1 1.50 sec
 PL1 0.00
 SFO1 500.23500 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.235002 MHz
 DF 65536
 AS 0.500000
 SR 0.000000
 GB 0
 PC 4.00

1.207
1.210
1.221
1.321
1.347
1.436
1.424
1.438
1.451
1.485
1.511
1.516
1.539
1.545
1.636
1.813
1.647
1.658
1.661
1.680
1.686
1.692
1.700
1.728
1.744
1.752
1.780
1.798
1.812
1.817
1.827
1.839
1.846
1.858
1.937
1.944
1.944
2.131
2.137
2.147
2.150
2.160
2.165
2.179
2.476
2.482
2.506
2.510
2.524
2.530
3.340
3.365
3.374
3.388
3.677
3.700
3.746
3.763
3.823
4.903



5.81
¹H NMR (CD₃OD, 500 MHz)





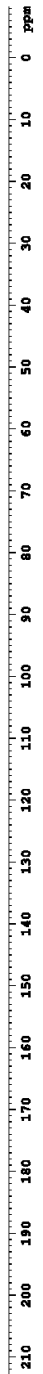
¹³C NMR (CD₃OD, 126 MHz)

Current Data Parameters
 NAME YS-IV-15
 EXPNO 16
 F2PROC 1
 F2 - Acquisition Parameters
 Date_ 20151216
 Time 8.57
 INSTRUM cryo500
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 320
 DS 2
 SWH 30303.031 Hz
 FIDRES 0.81340 Hz
 AQ 1.081340 sec
 RG 4597.6
 DW 16.500 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.2500000 sec
 d11 0.0000000 sec
 d16 0.0002000 sec
 d17 0.00019600 sec
 MCREST 0 sec
 MCNRRK 0.01500000 sec
 F2 33.10 usec

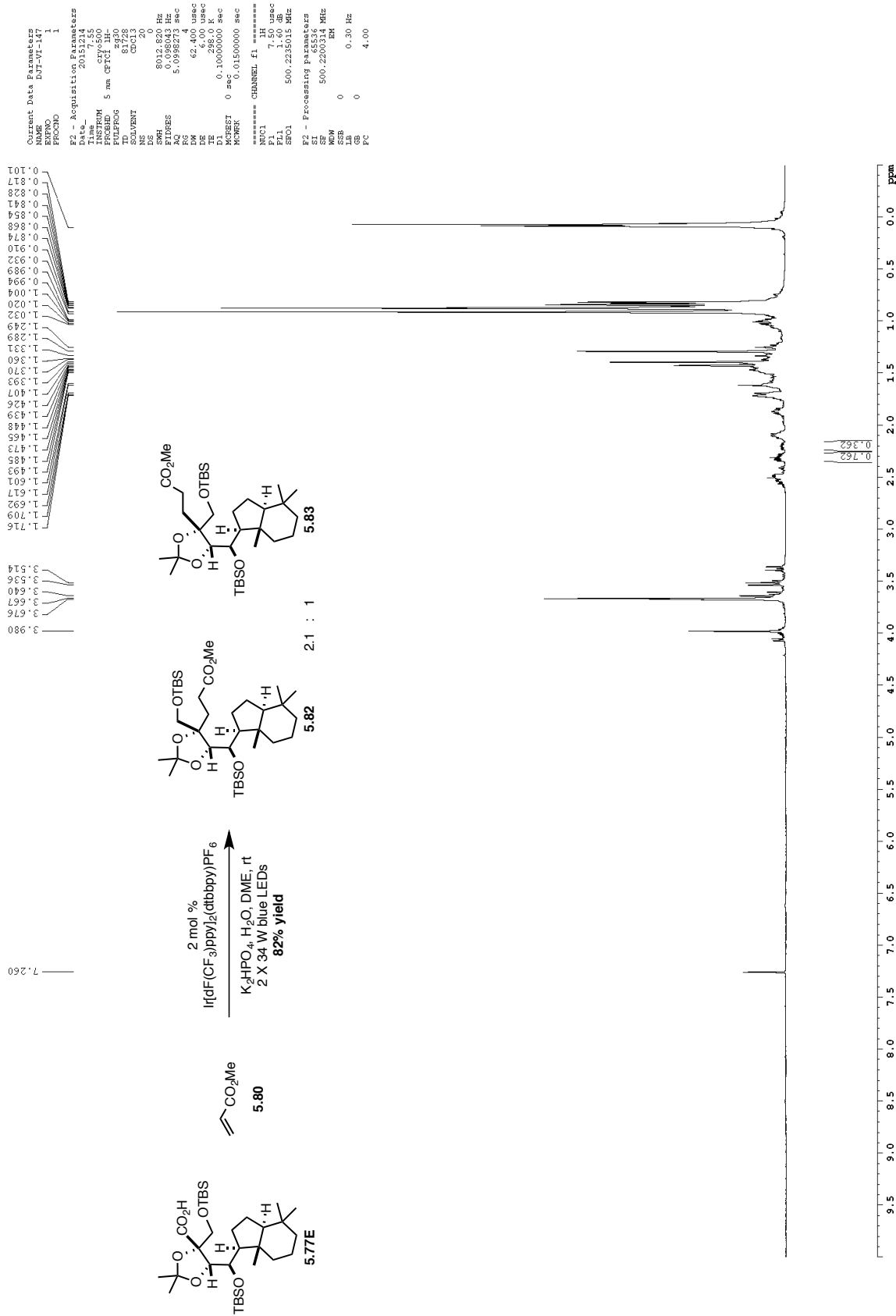
CHANNEL f1
 NUC1 13C
 P1 16.55 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 0.00 dB
 PL2 125.7942500 dB
 PL3 0.00 dB
 SP1 2.70 dB
 SP2 2.70 dB
 SFNAM[1] Crp60,0.5,20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

CHANNEL f2
 CPDPRG2 waltz16
 NUC2 1H
 P2 100.00 usec
 P21 1.80 dB
 P22 2.00 dB
 SF02 500.2225011 MHz

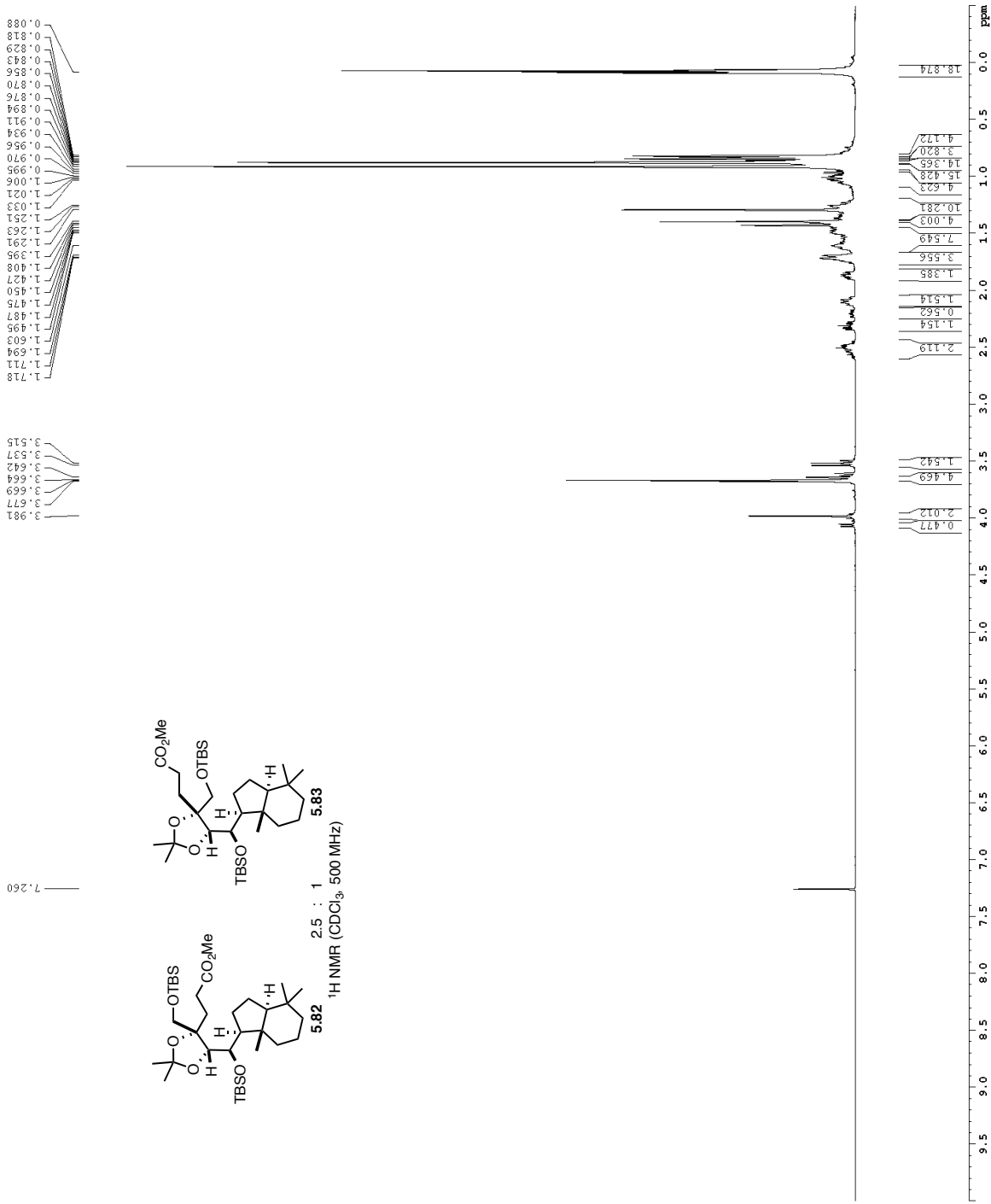
GRADIENT CHANNEL
 GPNAM[1] SINE.100
 GPNAM[2] SINE.100
 GPX1 0 %
 GPY1 0 %
 GPZ1 0 %
 GPC1 30.00 %
 GPC2 50.00 %
 GPC3 50.00 usec
 P15 1000.00 usec
 P16 1000.00 usec
 F2 - Processing parameters
 SI 65536
 SF 125.7801371 MHz
 NDM EM
 SSB 0
 GB 1.00 Hz
 PC 0
 GC 2.00



1H spectrum



¹H spectrum



Current Data Parameters
 NAME D17-VF-17
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 2013.11.14
 INSTRUM crys-500
 PULPROG zgpg30
 FREQH0 500.136455
 TD 65536
 SFO1 500.136455
 SOLVENT CDCl3
 NS 0
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.15000000 sec
 AQ 5.0998273 sec
 RG 517
 RW 62.40 usec
 TX 6.00 usec
 TE 298.0 K
 DE 0.10000000 sec
 ACQRES 0.15000000 sec
 MCMRES 0.01500000 sec
 ===== CHANNEL f1 =====
 NUCl1 1H
 P1 7.50 usec
 SFO1 500.2235015 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.2235017 MHz
 EQ 0
 EM 0
 GB 0
 PC 4.00

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

Current Data Parameters
 NAME DJT-VI-147
 EXPNO 20
 PROCNO 1

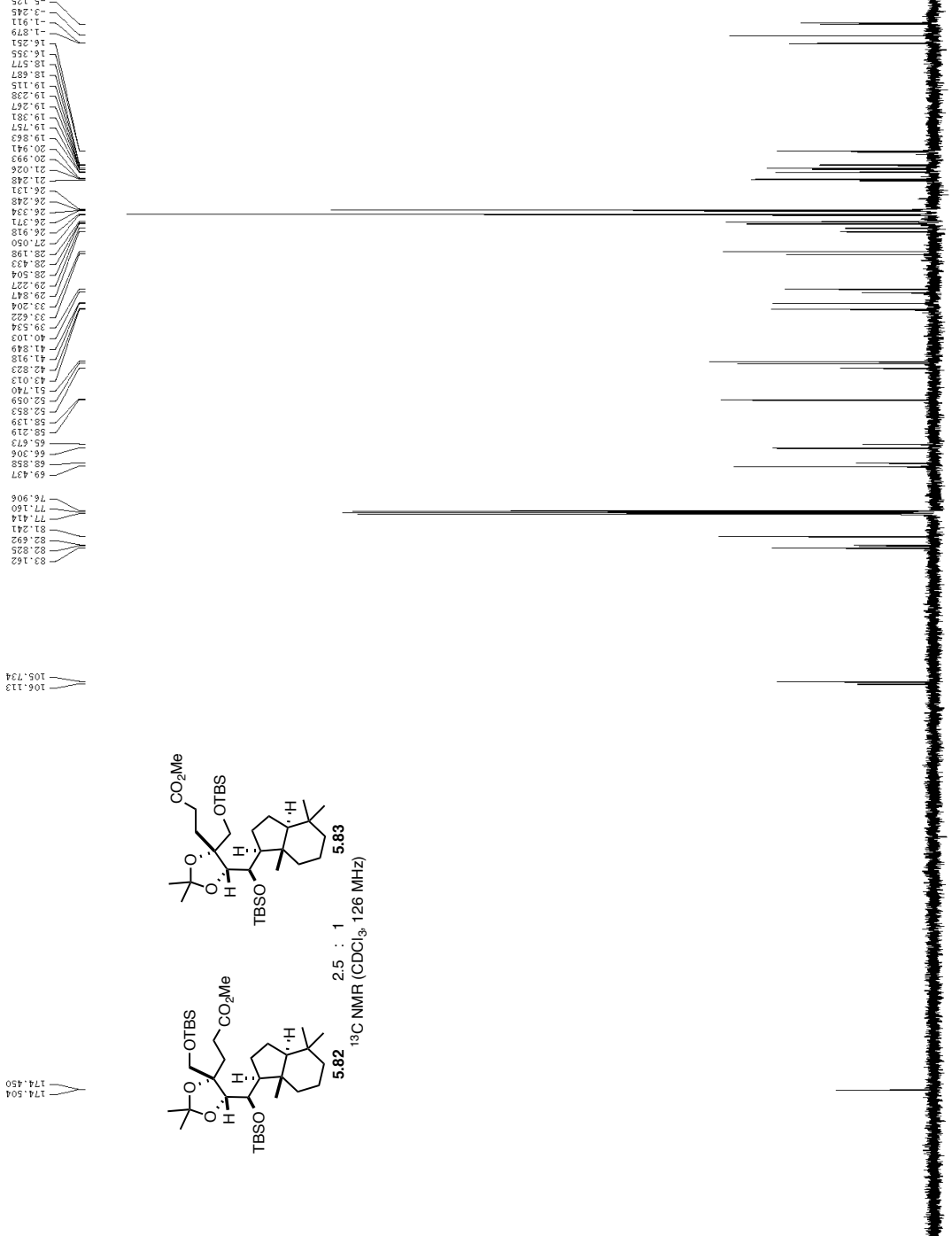
F2 - Acquisition Parameters
 Date_ 20160127
 Time 13:06
 INSTRUM crys500
 PROBHD 5 mm CPTCI LH-
 PULPROG SpinEchozgpgprd
 TD 65536
 SOLVENT CDCl3
 NS 151
 DS 0
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.081340 sec
 RG 682
 DW 16.500 usec
 DE 6.000 usec
 TE 298.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 d12 0.00020000 sec
 d13 0.00020000 sec
 d17 0.00015000 sec
 MCREST 0 sec
 MCWRR 0.01500000 sec
 P2 33.10 usec

CHANNEL f1
 NUCL1 13C
 P1 16.15 usec
 P11 500.00 usec
 P12 2000.00 usec
 PL0 120.00 dB
 PL1 -1.00 dB
 SF01 125.7942548 MHz
 SFO1 125.7942548 MHz
 SF2 2.70 dB
 SFNAM[1] Crp60.0.5.20.1
 SFNAM[2] Crp60comp.4
 SFOFF1 0 Hz
 SFOFF2 0 Hz

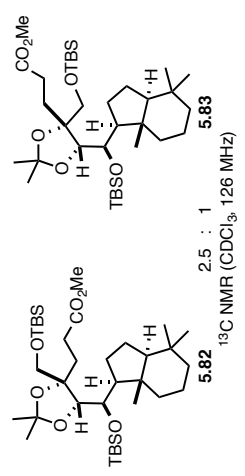
CHANNEL f2
 CFDFRG12 waltz16
 NUCL2 1H
 PCPD2 100.00 usec
 PL2 1.60 dB
 PL12 24.50 dB
 SF02 500.2225011 MHz

GRADIENT CHANNEL
 GFNAM[1] SINE.100
 GFNAM[2] SINE.100
 GEX1 0 %
 GEX2 0 %
 GXY1 0 %
 GXY2 0 %
 GFZ1 30.00 %
 GFZ2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

F2 - Processing Parameters
 SI 65536
 SF 125.7804071 MHz
 WDW EM
 SSB 0
 LB 0
 GB 0
 PC 2.00



174.504
106.113
105.734

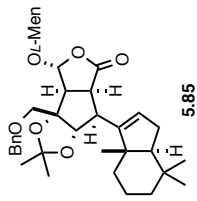


YS-V-312B

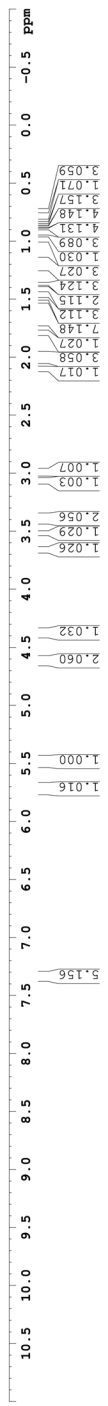
Current Data Parameters
NAME YS-V-312B
PROCNO 1
PROBHD 5 mm CPBBO BP
PULPROG zgpg30
SOLVENT CDCl3
NS 8
DS 8
SWH 9615.385 Hz
FIDRES 0.098042 Hz
AQ 3.0398160 sec
RG 10
DR 52.000 usec
DE 236.0 usec
TE 300.2 K
D1 0.10000000 sec
TD0 1

===== CHANNEL f1 =====
SF01 600.1342009 MHz
NUC1 13C
P1 12.00 usec
PL1 20.00000000 W
=====

SF - Processing parameters
SF 600.1300349 MHz
WDW EM
SSB 0
GB 0
PC 1.00



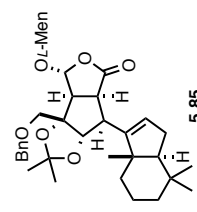
¹H NMR (CDCl₃, 600 MHz)



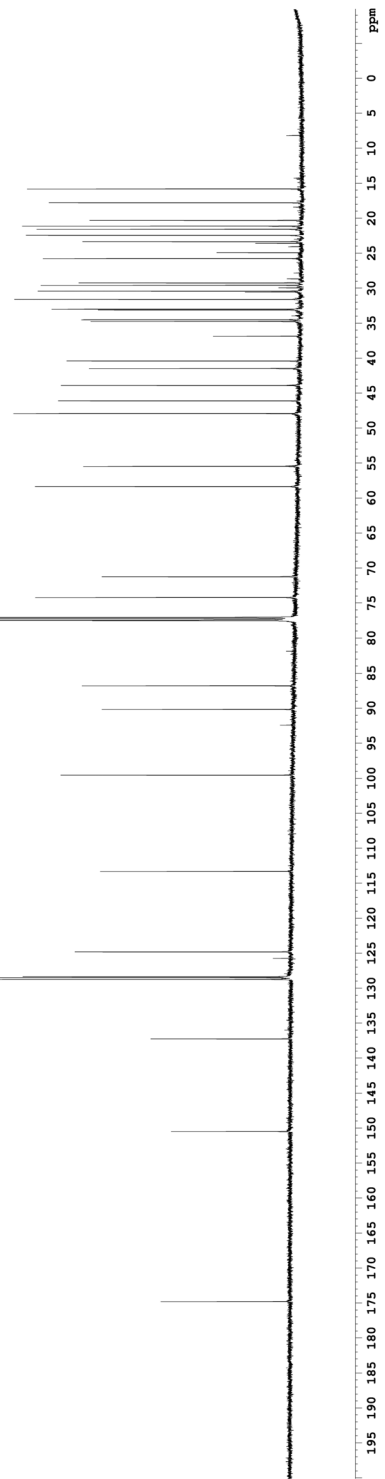
YS-V-312B

Current Data Parameters
NAME YS-V-312B
PROCNO 3
F2 - Acquisition Parameters
NAME YS-V-312B
INSTRUM av600
PULPROG zgpg30
SOLVENT CDCl3
NS 96
SRH 36231.8883 Hz
FIDRES 0.532853 Hz
AQ 0.9902670 sec
RG 2000 sec
DM 13.800 usec
DE 2.000 usec
TE 298.20 K
D1 0.4000001 sec
D11 0.050000000 sec
TD0 1
===== CHANNEL f1 =====
SF01 150.9194880 MHz
NUC1 13C
P1 10.00 usec
PL1 64.00000000 N
===== CHANNEL f2 =====
SF02 600.1330110 MHz
CPDPRG2 waltz16
PCPD2 20.00000000 sec
PLM12 0.36000001 W
===== Processing Parameters =====
SI 65536
RG 150.9027864 MHz
SFO 600.1330110 MHz
SSB 0
GB 0
PC 1.00

174.761
150.474
137.217
128.707
128.472
128.339
124.793
113.297
99.514
90.131
86.741
77.488
77.440
77.228
77.016
74.179
71.201
58.295
55.419
47.875
47.853
46.058
43.655
41.434
40.365
36.823
34.723
34.475
33.070
32.956
31.544
30.369
29.530
29.198
25.703
24.878
23.309
22.288
21.536
21.079
20.261
17.745
15.762

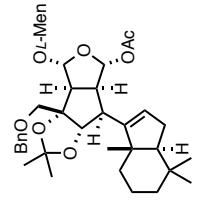


¹³C NMR (CDCl₃, 151 MHz)

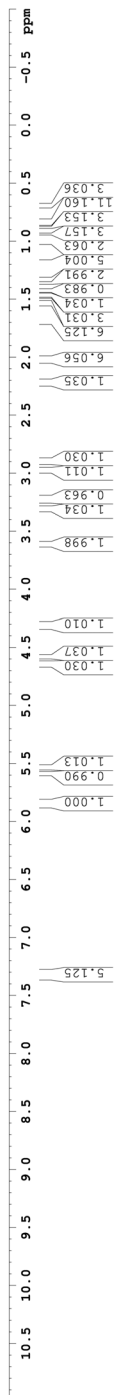


YS-VI-2

Current Data Parameters
NAME YS-VI-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Time_ 20110715
Time 14:15
INSTRUM AV600
PROBHD 5 mm CPBBO
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 9615.385 Hz
FIDRES 0.100002 Hz
AQ 4.3399999 sec
RG 16
DR 52.000 usec
DE 236.0 usec
TE 300.2 K
D1 0.10000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 600.1342009 MHz
NUC1 1H
P1 12.00 usec
PLM1 20.00000000 W
===== Processing parameters =====
SF 600.1300348 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

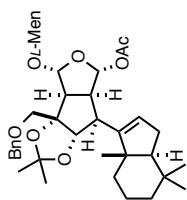


5.86
¹H NMR (CDCl₃, 600 MHz)

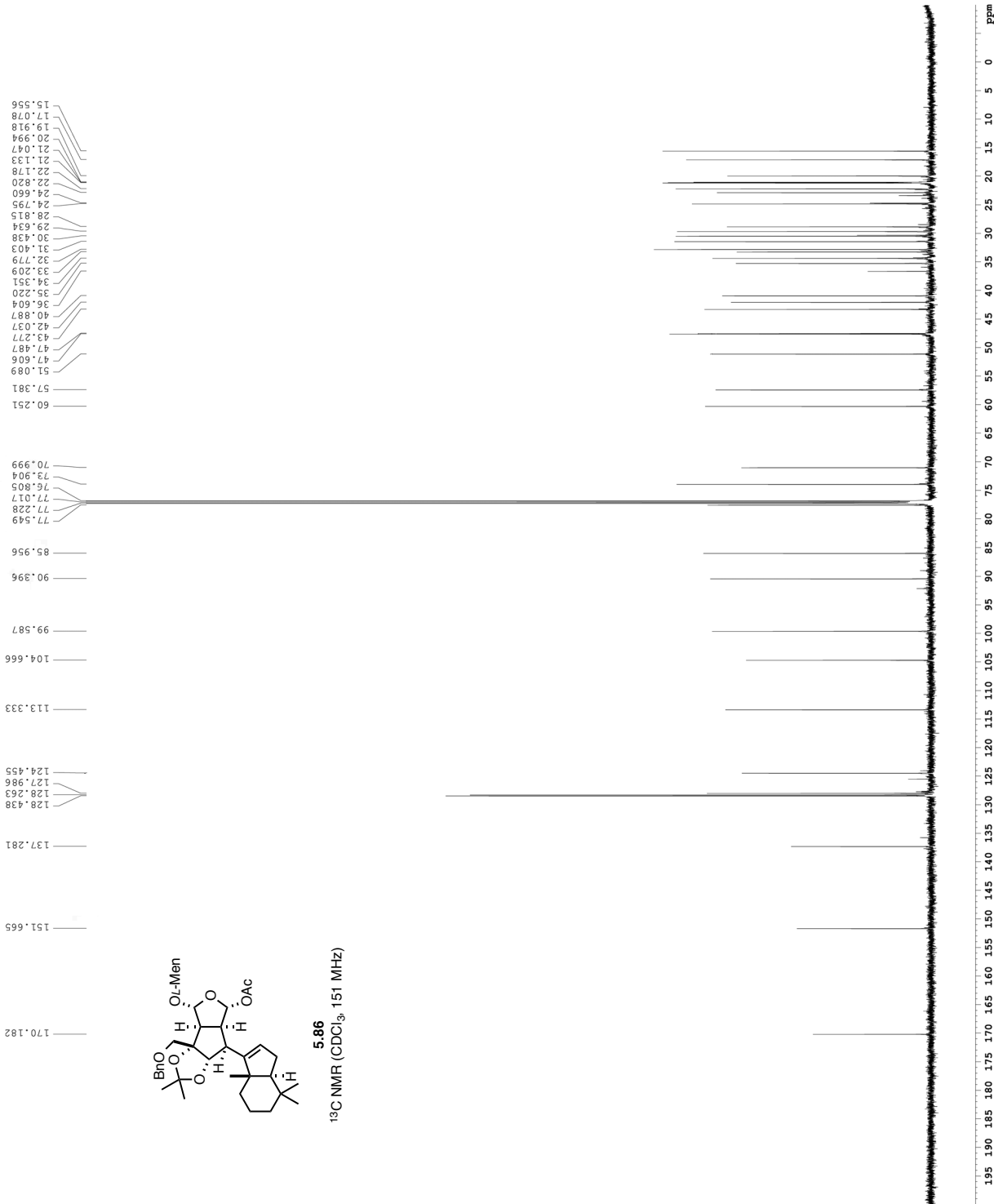


YS-VI-2

Current Data Parameters
NAME 3S-VI-2
PROCNO 3
F2 - Acquisition Parameters
Time 20:14:04
INSTRUM av600
PULPROG zgpg30
SOLVENT CDCl3
NS 320
SI 36231.863 Hz
FIDRES 0.55265 Hz
AQ 0.900000 sec
RG 2280
DM 13.800 usec
TE 298.2 K
D1 0.6000000 sec
D11 0.1500000 sec
TD0 1
===== CHANNEL f1 =====
SF01 150.919480 MHz
NUC1 13C
P1 10.00 usec
PLM1 64.00000000 M
===== CHANNEL f2 =====
SF02 600.133010 MHz
NUC2 1H
P2 19.00 usec
PLM2 0.36000001 M
===== CHANNEL f3 =====
SF03 600.133010 MHz
NUC3 1H
P3 19.00 usec
PLM3 0.36000001 M
===== Processing parameters =====
SI 65536
SF 150.902824 MHz
WDW 0
SSB 0
GB 0
PC 1.00



5.86
13C NMR (CDCl₃, 151 MHz)



YS-VI-13

```

Current Data Parameters
NAME      YS-VI-13
EXPNO     1
PROCNO    1
F2 - Acquisition Parameters
Time      2011053
INSTRUM   av600
PROBHD    5 mm CPBBO BB
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         1
SWH        9615.385 Hz
FIDRES     0.100002 Hz
RG          4.33999916
AQ          16.000 usec
DM          52.000 usec
DE          236.000 usec
TE          300.2 K
D1          0.10000000 sec
TD0         1
===== CHANNEL f1 =====
SF01      600.1342009 MHz
NUC1       13
PULPROG   zgpg30
PL1        20.00000000 M
===== Processing parameters =====
SI         65536
WDW         EM
SSB         0
LB          0.30 Hz
GB          0
EC          1.00
  
```

