UNIVERSITY OF CALIFORNIA, IRVINE

Arylalkane Library Synthesis Enabled by a Stereospecific Nickel-Catalyzed Cross-Coupling Reaction

and

Nickel-Catalyzed Cross-Electrophile Coupling Reactions of Alkyl Mesylates

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Amberly B. Sanford

Dissertation Committee:
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2021

DEDICATION

For Peter James Maraven
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

ACKNOWLEDGEMENTS

I acknowledge Wiley for permission to include Chapter 1, which was originally published in *Israel Journal of Chemistry*. I also acknowledge the American Chemical Society for permission to include Chapter 2, which was originally published in *Journal of the American Chemical Society*. Lastly, I acknowledge Thieme for permission to include Chapter 3, which was originally published in *Synlett*.

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I have had an unusually superb combination of science teachers and professors over the years who have all been crucial in my journey and I feel incredibly fortunate to have been a student of them all. My high school science teacher of 3 years, Lee Strong, played a pivotal role in developing my interest in science. I was lucky enough to have taken earth science, biology, and chemistry courses taught by him, and his unique conceptual-based teaching style gave me an innate understanding of fundamental concepts in science. I greatly appreciate all his encouragement and telling me chemistry was my "thing".

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Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen, P.–P.; Hong, X.; Jarvo, E. R. Nickel-Catalyzed Alkyl–Alkyl Cross-Electrophile Coupling Reaction of 1,3-Dimesylates for the Synthesis of Alkylcyclopropanes. *J. Am. Chem. Soc.* **2020**, *142*, 5017–5023.

Sanford, A. B.; Tollefson, E. J.; Jarvo, E. R. Stereospecific Cross-Coupling Reactions Provide Conformationally-Biased Arylalkanes with Anti-Leukemia Activity. *Isr. J. Chem.* **2020**, *60*, 402–405.

PRESENTATIONS

Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen, P.–P.; Hong, X.; Jarvo, E. R. Nickel-catalyzed cross-electrophile coupling reaction for the synthesis of alkylcyclopropanes. Presented at the GC&E Conference, June 2020 (virtual oral presentation).

Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen, P.–P.; Hong, X.; Jarvo, E. R. Nickel-catalyzed cross-electrophile coupling reaction for the synthesis of alkylcyclopropanes. Presented at Vertex Day Irvine, California, February 2020 (oral presentation).

Sanford, A. B.; Thane, T. A.; Jarvo, E. R. Nickel-catalyzed cross-electrophile coupling of diol derivatives. Presented at the 258th American Chemical Society National Meeting, San Diego, California, August 2019 (oral presentation).

Sanford, A. B.; Thane, T. A.; Jarvo, E. R. Synthesis of alkylcyclopropanes via nickel-catalyzed cross-electrophile coupling. Presented at the UCI Graduate Symposium, Irvine, California, April 2018 (oral presentation).

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ABSTRACT OF THE DISSERTATION

Arylalkane Library Synthesis Enabled by a Stereospecific Nickel-Catalyzed Cross-Coupling Reaction

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By

Amberly B. Sanford

Doctor of Philosophy in Chemistry

University of California, Irvine, 2021

Professor Elizabeth R. Jarvo, Chair

While palladium-catalyzed cross-coupling reactions have unquestionably transformed synthetic organic chemistry, nickel catalysis offers a unique set of advantages. From a reactivity perspective, two advantages of nickel catalysis are the ability to access additional oxidation states and engage a broader range of electrophiles compared to that of palladium catalysis. These properties ultimately allow for multiple mechanisms of oxidative addition to occur. In recent years, it has been established that nickel catalysts undergo stereospecific oxidative additions to C–N or C–O bonds. In contrast, oxidative addition at carbon-halogen bonds, such as C–I, are frequently stereoablative. Both of these modes of oxidative addition occur in the methods reported in this dissertation.

In Chapter 1, the synthesis of an arylalkane library utilizing a stereospecific Kumada cross-coupling reaction is described. The results of biological testing for anti-cancer activity are also reported. Aryltetrahydropyran starting materials are synthesized in a one-step, diastereoselective Prins reaction. A nickel-catalyst engages the benzylic Csp^3–O bond in a stereospecific manner and

undergoes a Kumada cross-coupling reaction with methylmagnesium iodide in solution. The resulting products are acyclic arylalkanes that were tested for anti-cancer activity through a collaboration with the NIH. One compound in the library exhibited micromolar anti-cancer activity.

A limitation of the method above—and similar stereospecific methods—is that the electrophilic Csp^3–O bond must be allylic or benzylic to allow for facile oxidative addition by a nickel catalyst. In an approach to engage alkyl Csp^3–O bonds that are not benzylic or allylic, the cross-electrophile coupling reaction of 1,3-dimesylates for alkylcyclopropane synthesis was developed and discussed in Chapters 2 and 3 of this dissertation. While optimized reaction conditions are similar to the Kumada reaction described above, a key 1,3-diiodide intermediate alters the reaction mechanism leading the nickel catalyst to instead perform a stereoablative oxidative addition. Mono- and 1,2-disubstituted alkylcyclopropanes were synthesized, the latter with moderate diastereoselectivity.

Lastly, the optimization of a cross-electrophile coupling reaction of secondary alkyl mesylates with allylic difluorides is described in Chapter 4. This work builds on the cross-electrophile coupling reaction of 1,3-dimesylates described in Chapters 2 and 3. The resulting β-fluorovinyl cyclopropanes are synthesized as a 1:1 diastereomeric ratio of cis and trans cyclopropanes and one alkene isomer. The currently available evidence is consistent with a stereoablative mechanism for oxidative addition, similar to that previously reported with 1,3-dimesylates. However, the specific details of the mechanism and expansion of scope are currently under investigation.

Chapter One

Stereospecific Cross-Coupling Reactions Provide Conformationally-Biased Arylalkanes with Anti-Leukemia Activity

1.1 Introduction

Drug discovery efforts often show bias towards flat, achiral molecules, however candidates containing multiple sp^3 atoms and stereogenic centers have been associated with increased clinical success.[1,2,3] Biological targets are inherently three-dimensional structures, therefore ligands that extend in all three dimensions may increase interactions to improve potency, while reducing off-target binding.[4] For example, an increase in dimensionality of the core skeleton can be important for assisting appendage π systems to more effectively interact with binding sites.[2]

In contrast to the flat and rigid structures of sp^2-rich molecules, compounds with numerous sp^3 centers exhibit potentially large conformational profiles. Limitation of this profile can be an important attribute for activity by reducing conformational entropic costs upon binding to the biological target.[5] Biologically active natural products, including polyketides, typically inhabit a preferred conformation, while still retaining a degree of flexibility.[6,7] For example, polypropionates often adopt a low-energy conformer to avoid *syn*-pentane interactions.[6]

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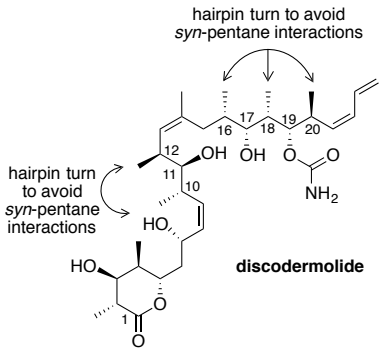
[1] Portions of this Chapter were originally published in Israel Journal of Chemistry: Sanford, A. B.; Tollefson, E. J.; Jarvo, E. R. *Isr. J. Chem.* **2020**, *60*, 402–405.
[2] Lovering, F.; Bikker, J.; Humblet, C. *J. Med. Chem.* **2009**, *52*, 6752–6756.
[3] For recent perspectives on molecular complexity in drug discovery, see: a) Caille, S.; Cui, S.; Faul, M. M.; Mennen, S. M.; Tedrow, J. S.; Walker, S. D. *J. Org. Chem.* **2019**, *84*, 4583–4603. b) Méndez, O.; Medina-Franco, J. L.; *Drug Discov. Today*, **2017**, *22*, 120–126.
[4] Arya, P.; Joseph, R.; Gan, Z.; Rakic, B. *Chem. Biol.* **2005**, *12*, 163–180.
[5] Chang, C. A.; Chen, W.; Gilson, M. K.; *Proc. Natl. Acad. Sci.* **2007**, *104*, 1534–1539.
[6] Hoffmann, R. W. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1124–1134.
[7] Larsen, E. M.; Wilson, M. R.; Taylor, R. E. *Nat. Prod. Rep.* **2015**, *32*, 1183–1206.

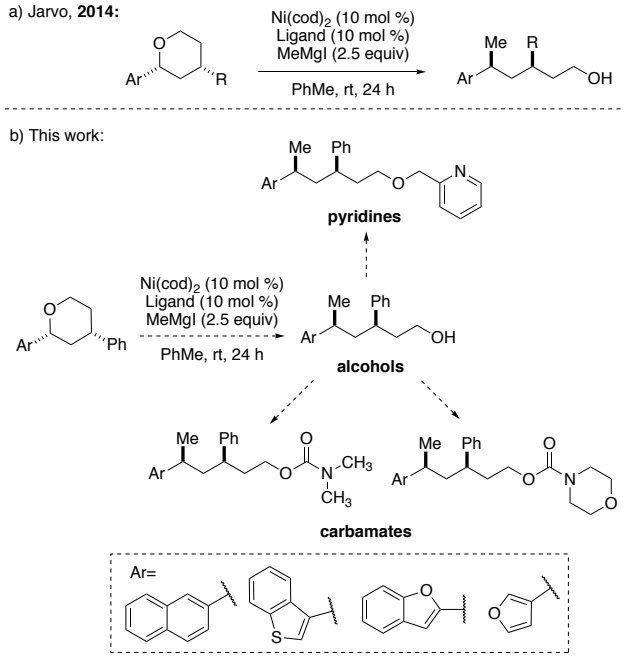
Figure 1.1 Polyketide discodermolide



The polyketide discodermolide is one example where molecular structure reduces the number of populated conformers (Figure 1.1).[7] Extracted from sea sponge *Discodermia dissoluta*,[8] discodermolide has been investigated for its nanomolar ability to inhibit growth of paclitaxel-resistant cancer cells.[9] Discodermolide contains two polypropionate motifs that avoid *syn*-pentane interactions, causing two hairpin-like turns in the linear backbone.[10] Analogues of discodermolide conserve these motifs, as the conformation is critical to its activity.[7] Partly due to this restrictive effect on conformation, methods to access polypropionates and similar structures are of great value.[11,12,13]

[8] Gunasekera, S. P.; Gunasekera, M.; Longley, R. E.; Schulte, G. K. *J. Org. Chem.* **1990**, *55*, 4912–4915.
[9] Kowalski, R. J.; Giannakakou, P.; Gunasekera, S. P.; Longley, R. E.; Day, B. W.; Hamel, E. *Mol. Pharmacol.* **1997**, *52*, 613–622.
[10] Smith, A. B.; LaMarche, M. J.; Falcone-Hindley, M. *Org. Lett.* **2001**, *3*, 695–698.
[11] Hanessian, S.; Giroux, S.; Mascitti, V. *Synthesis* **2006**, 1057–1075.
[12] Li, J.; Menche, D. *Synthesis* **2009**, 2293–2315.
[13] ter Horst, B.; Feringa, B. L.; Minnaard, A. J. *Chem. Commun.* **2010**, *46*, 2535–2547.

Scheme 1.1 a) Stereospecific ring-opening Kumada reaction b) Library synthesis



In 2014, our laboratory reported an C_{sp}^3-C_{sp}^3 Kumada cross-coupling reaction of aryl tetrahydropyrans (THPs) and tetrahydrofurans (Scheme 1.1a).[14,15,16] This ring-opening reaction utilizes an achiral nickel catalyst to couple a benzylic ether with Grignard reagents in a stereospecific manner. Importantly, the THP starting material is generated in a single step from the commercially available aldehyde by a diastereoselective Prins cyclization.[17,18,19] Upon ring-opening of the THP, a compound rich in stereochemical information is generated, including 1,3-substitutients on the linear backbone.

We set out to utilize this ring-opening reaction to synthesize a small library of compounds and test for anticancer activity (Scheme 1.1b). We hypothesized that the sp^3 core skeleton, 1,3-substituent motif, ability to diversify at the alcohol position, and low molecular weight (<500 da)

[14] Tollefson, E. J.; Dawson, D. D.; Osborne, C. A.; Jarvo, E. R. *J. Am. Chem. Soc.* **2014**, *136*, 14951–14958.
[15] Dawson, D. D.; Jarvo, E. R. *Org. Process Res. Dev.* **2015**, *19*, 1356–1359.
[16] Tollefson, E. J.; Hanna, L. E.; Jarvo, E. R. *Acc. Chem. Res.* **2015**, *48*, 2344–2353.
[17] Dintzner, M. R.; Maresh, J. J.; Kinzie, C. R.; Arena, A. F.; Speltz, T. *J. Chem. Educ.* **2012**, *89*, 265–267.
[18] Adams, D. R.; Bhatnagar, S. P. *Synthesis* **1977**, 661–672.
[19] Olier, C.; Kaafarani, M.; Gastaldi, S.; Bertrand, M. P. *Tetrahedron* **2010**, *66*, 413–445.

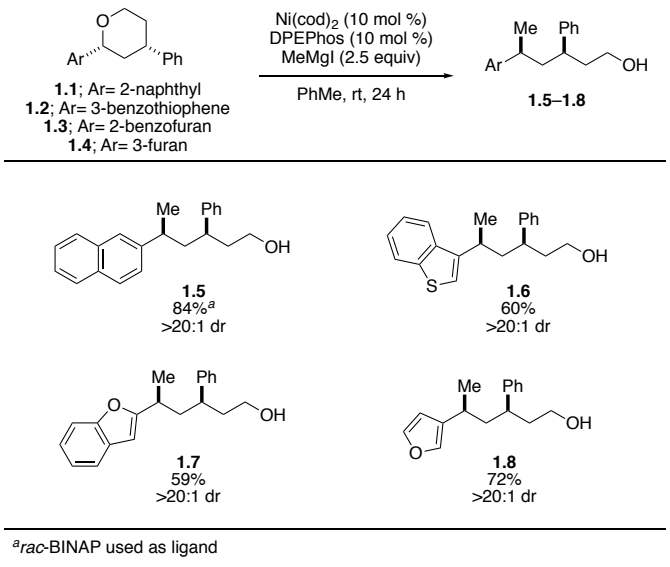
made this scaffold an appropriate candidate for library generation.[20,21]Additionally, this substructure shares similarities to our previously synthesized compounds that demonstrated activity towards breast cancer cell lines, further directing our testing efforts.[22,23] The aryl group was modified to include various heterocycles, and the alcohol was unaltered or further modified to carbamates or hydroxymethyl pyridines. These modifications were chosen due to their prevalence in successful pharmaceutical agents and to improve logP of the series.[21,24,25]

1.2 Results and Discussion

Our four target alcohols were the first compounds in our library to be synthesized (Scheme 1.2). The THP substrates **1.1** to **1.4** were synthesized via a clay-mediated Prins cyclization, employing four different aromatic aldehydes.[17] With THPs in hand, the ring-opening Kumada cross-coupling reactions were performed to yield desired alcohols, **1.5**, **1.6**, **1.7**, and **1.8**. This reaction proceeds reliably with inversion at the benzylic carbon, therefore *cis*-disubstituted tetrahydropyrans produce alcohols with a syn configuration.[14] Each alcohol was tested for anti-cancer activity.

[20] Lipinski, C. A.; Lombardo, F.; Dominy, B. W.; Feeney, P. J. *Adv. Drug Deliv. Rev.* **1997**, *23*, 3–25.
[21] Silverman, R. B.; Holladay, M. W. *The Organic Chemistry of Drug Design and Drug Action*, Elsevier, San Diego, **2014**.
[22] Yonova, I. M.; Johnson, A. G.; Osborne, C. A.; Moore, C. E.; Morrissette, N. S.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 2422–2427.
[23] Johnson, A. G.; Tranquilli, M. M.; Harris, M. R.; Jarvo, E. R. *Tetrahedron Lett.* **2015**, *56*, 3486–3488.
[24] Ghosh, A. K.; Brindisi, M. *J. Med. Chem.* **2015**, *58*, 2895–2940.
[25] Vitaku, E.; Smith, D. T.; Njardarson, J. T. *J. Med. Chem.* **2014**, *57*, 10257–10274.

Scheme 1.2 Alcohols synthesized via Kumada ring-opening cross-coupling reaction

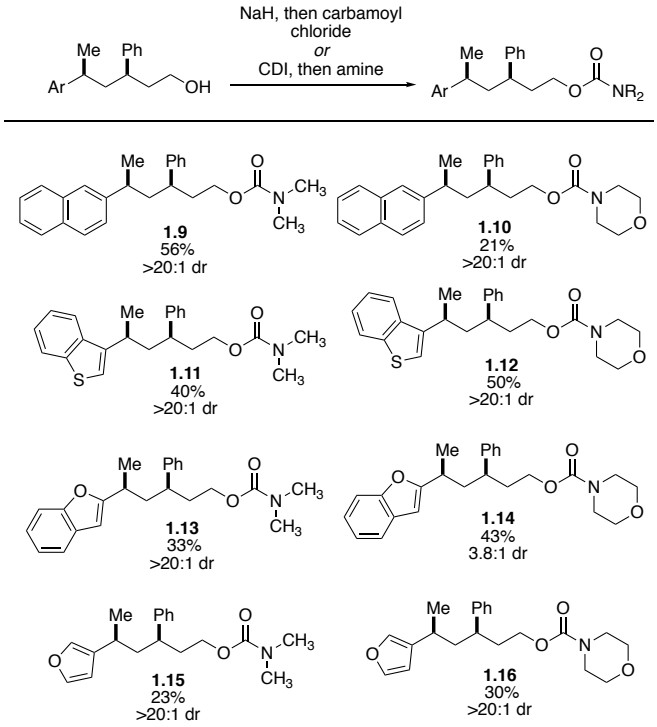


[a]*rac*-BINAP used as ligand

Next, the alcohols were acylated to yield carbamate derivatives (Scheme 1.3). A series of dimethyl carbamates and morpholine carbamates (**1.9**–**1.16**) were synthesized. Either carbamate could be synthesized using sodium hydride and corresponding carbamoyl chloride,[26] however, a more reliable method utilized carbonyldiimidazole (CDI) and the corresponding amine.[27] All carbamate derivatives were subjected to biological testing.

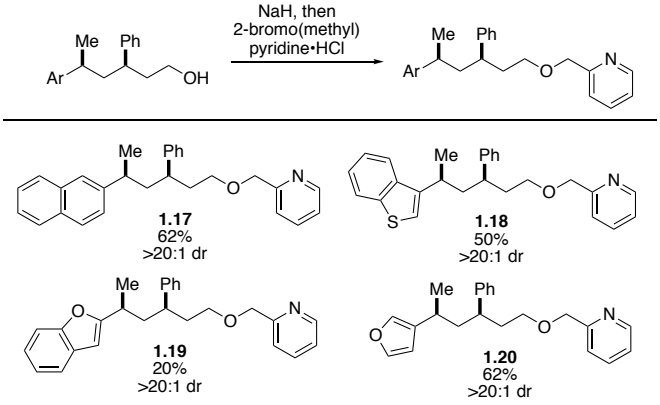
[26] Aikawa, K.; Maruyama, K.; Nitta, J.; Hashimoto, R.; Mikami, K. *Org. Lett.* **2016**, *18*, 3354–3357.
[27] Verma, S. K.; Ghorpade, R.; Pratap, A.; Kaushik, M. P. *Tetrahedron Lett.* **2012**, *53*, 2373–2376.

Scheme 1.3 Dimethyl and morpholine carbamate derivatives



Lastly, our synthetic efforts concluded with transformation of the pendant alcohols to hydroxymethyl pyridines (Scheme 1.4). Compounds **1.17** to **1.20** were synthesized using sodium hydride and 2-bromo(methyl)pyridine. All pyridines were isolated in >20:1 dr and subjected to biological testing.

Scheme 1.4 Pyridine derivatives



With the synthesis of the library complete, we began our evaluation of biological activity. We collaborated with the National Institute of Health Developmental Therapeutics Program (NIH DTP) to evaluate our experimental compounds against 60 human cancer cell lines (at 10 μM).[28,29] If substantial growth inhibition or cell death is detected, the compound is selected by the NIH for further concentration dependent testing.

Results of the initial evaluation are shown in Table 1.1. Each compound is presented with the specific cell line the compound was most active against and associated growth percentages.[30] Untreated cell lines have a growth percentage of 100%, therefore a positive value >100% indicates accelerated growth, a positive value <100% indicates inhibition of growth, and a negative growth percentage indicates cell death.

Table 1.1 Biological data obtained from NIH60 one-dose study. Cell line most susceptible to each tested compound is reported

Compound	Cancer Type	Cell Line	Percent Growth[a]
1.5	Leukemia	MOLT-4	–54
1.6	Renal	CAKI-1	76
1.7	Renal	A498	82
1.8	Renal	A498	67
1.9	Breast	T-47D	75
1.10	Renal	CAKI-1	73
1.11	Melanoma	UACC-62	56
1.12	Leukemia	CCRF-CEM	37
1.13	Melanoma	UACC-62	75
1.14	Renal	UO-31	67
1.15	Renal	HL-60(TB)	78
1.16	Renal	UO-31	75
1.17	Ovarian	OVCAR-8	48
1.18	Leukemia	RPMI-8226	63
1.19	Leukemia	RPMI-8226	75
1.20	Leukemia	HL-60(TB)	70

[a]Percentages are compared to a no-drug control. Positive 0–100% growth indicates growth inhibition, and negative growth percentage indicates lethality

[28] Shoemaker, R. H. *Nat. Rev. Cancer* **2006**, *6*, 813–823.
[29] National Institute of Health, "National Cancer Institute Developmental Therapeutics Program," can be found under https://dtp.cancer.gov/, **2019**.
[30] For full results of each compound against all 60 cell lines, see Experimental Section.

Alcohol **1.5** showed greatest potency, with activity against a range of cell lines, including all leukemia cell lines. For example, it provided –54% growth of leukemia cell line MOLT-4 (acute lymphoblastic leukemia). Alcohol **1.5** was then subjected to concentration dependent testing by the NIH DTP (Table 1.2).[31] Alcohol **1.5** demonstrated micromolar activity towards the range of cell lines, and was most potent towards MOLT-4 with an LC_{50} value of 6.1 μM. Additionally, its activity towards HL-60(TB) at 8.3 μM is intriguing. Cell line HL-60(TB) is an acute promyelocytic leukemia (APL) line, a subtype of acute myeloid leukemia (AML) with a 5-year survival rate for AML of only 24%.[32] Alcohol **1.5** also showed activity towards colon cancer cell lines HCT-116 and KM12.

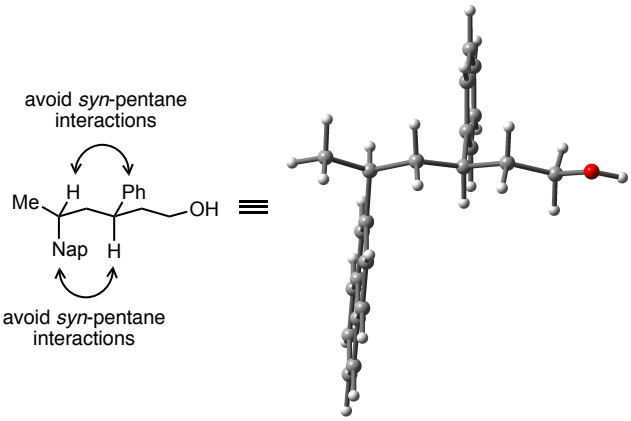
Table 1.2 LC_{50} values for **1.5**

Cancer Type	Cell Line	LC_{50} (μM)
Leukemia	MOLT-4	6.1
Leukemia	CCRF-CEM	5.1
Leukemia	HL-60(TB)	8.3
Colon	HCT-116	5.2
Colon	KM12	5.7

To further investigate the properties of **1.5**, we sought to determine its preferred conformation. We calculated the energy of a series of conformers in a density functional theory (DFT) study at the B3LYP level employing the 6-31G(d) basis set.[33,34,35] The lowest energy conformer (Figure 1.2) confirms our expectations based on hand-held models. The sterically bulky naphthyl and phenyl rings align syn to hydrogen atoms, to adopt a conformation that minimizes *syn*-pentane interactions.

[31] For full results of concentration dependent testing for **1.5** against all 60 cell lines, see Supporting Information.
[32] American Cancer Society, "Cancer Facts and Figures 2019," can be found under https://www.cancer.org/research/cancer-facts-statistics/all-cancer-facts-figures/cancer-facts-figures-2019.html, **2019**.
[33] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[34] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
[35] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.

Figure 1.2 Lowest energy conformer of **1.5** obtained via DFT calculations at the B3LYP/6-31G(d) level



1.3 Conclusion

In summary, we have synthesized a small library of molecules utilizing our previously developed Kumada ring-opening cross-coupling reaction. The molecules in our library contained an sp^3 core scaffold, 1,3-substituents to induce conformational bias, aromatic and heterocyclic rings, along with various alcohol, carbamate, and hydroxymethyl pyridine appendages to provide potential hydrogen bond acceptors and donors. The library compounds were tested for anti-cancer activity in collaboration with the NIH DTP and one alcohol, **1.5**, demonstrated micromolar activity against MOLT-4, CCRF-CEM, and HL-60(TB) leukemia cell lines. Based on the observed structure activity relationships, the naphthyl aromatic ring and primary alcohol were both critical functional groups for anti-leukemia activity of this compound.

1.4 Experimental Details

1.4.1 General Procedures

All reactions were carried out under a N_2 atmosphere, unless otherwise stated. All glassware was either oven-dried or flame-dried prior to use. Toluene (PhMe), diethyl ether (Et_2O), dimethylformamide (DMF), benzene (C_6H_6), and tetrahydrofuran (THF) were degassed with argon

and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 hours) to remove H_2O. ^1H NMR were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C), CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), doublet of triplets (dt), triplet of doublets (td), doublet of doublet of triplets (ddt), quartet (q), quintet (quint), quintet of triplets (quintt), quintet of doublets (quintd), sextet (sext), septet (sept), nonuplet (non), multiplet (m), apparent doublet (ad), apparent triplet (at), apparent quartet (aq), apparent quintet (aquint)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). NMR data were collected at 25 °C, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60Å F254 precoated plates (0.25 mm thickness). Flash chromatography was performed using either SiliaFlash F60 (40- 63 μm, 60 Å) from SiliCycle, a Teledyne Isco Combiflash® Rf+ automated flash chromatography system, or silver impregnated silica gel.[36] High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center.

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (–20 °C) under an atmosphere of N_2 and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored under N_2 atmosphere and used as received. All Grignard reagents

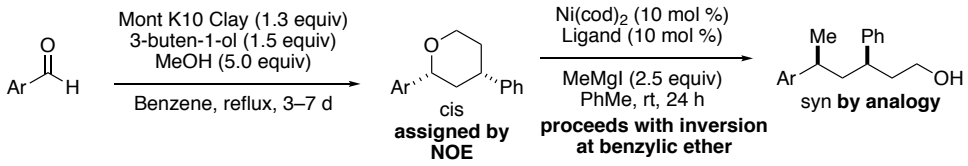
[36] Shaghafi, M. B.; Kohn, B. L.; Jarvo, E. R. *Org. Lett.* **2008**, *10*, 4743–4746.

were titrated with iodine prior to use.[37] All other chemicals were purchased commercially and used as received, unless otherwise noted.

1.4.2 Proof of Relative Configuration

NOE experiments were performed on tetrahydropyrans synthesized in this paper in order to determine the cis relative stereochemistry. It has previously been determined that nickel-catalyzed Kumada ring-opening reactions proceed with inversion, verified through ^{1}H NMR and X-ray crystallography studies.[14] By analogy, final products were assigned syn stereochemistry.

Scheme 1.5 Stereochemical course of the Kumada cross-coupling reaction



1.4.3 General Cross-Coupling Procedures

1.4.3.1 Method A: Cross-Coupling with Methyl Grignard Reagent

In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with substrate (1.0 equiv), $Ni(cod)_2$ (0.10 equiv), *rac*-BINAP or DPEphos (0.10 equiv), and PhMe (2.4 mL). Methylmagnesium iodide (2.5 equiv) was then added dropwise. After 24 h the reaction was removed from the glovebox, quenched with methanol (2 mL), filtered through a plug of silica gel (neat Et_2O), and concentrated in vacuo.[14]

1.4.3.2 Preparation of Methyl Grignard Reagent

Under an N_2 atmosphere, to a 3-necked round bottom flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was added magnesium turnings (2.80 g, 120 mmol,

[37] Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890–891.

1.50 equiv). The flask and magnesium turnings were flame-dried under vacuum and the flask was back-filled with N_2. A crystal of iodine (ca. 2 mg) was added to the flask, followed by anhydrous Et_2O (25 mL). The reaction mixture was brought to 0 °C, and freshly distilled iodomethane (5.0 mL, 82 mmol, 1.0 equiv) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 4 h at room temperature then filtered through the fritted Schlenk filter into a Schlenk bomb under N_2 atmosphere. The magnesium turnings were washed with Et_2O (2 x 1.0 mL) then the Schlenk bomb was sealed, removed, and placed under an argon atmosphere. The resulting methyl Grignard reagent was typically between 2.4 and 3.0 M as titrated by Knochel's method[37] and was stored (sealed under argon atmosphere or in a glovebox) for up to 8 weeks.

1.4.4 Alcohol Modification Procedures

1.4.4.1 Method B: Alcohols to Carbamates Using Carbamoyl Chlorides

The target compounds were prepared using a modified procedure reported by Mikami.[38] In a glove box, a flame-dried round bottom flask was equipped with stir bar and sodium hydride (10. equiv). Anhydrous DMF or THF was added to flask, which was capped with a septum and removed from the glove box. Alcohol (1.0 equiv) was added, and the reaction stirred for 2 h. Dimethylcarbamoyl chloride, or 4-morpholinecarbonyl chloride was added dropwise (20. equiv). The reaction mixture was stirred overnight. Saturated NH_4Cl solution (2 mL) was added to quench. The reaction mixture was diluted with EtOAc (5 mL) and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo.

[38] Aikawa, K.; Maruyama, K.; Nitta, J.; Hashimoto, R.; Mikami, K. *Org. Lett.* **2016**, *18*, 3354–3357.

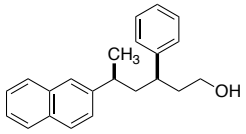
1.4.4.2 Method C: Alcohols to Carbamates Using CDI

The target compounds were prepared using a modified procedure reported by Kaushik.[39] Open to air, a vial was equipped with stir bar and alcohol (1.0 equiv). Carbonyldiimidazole (1.8 equiv) was added, then the mixture was ground with a spatula for 5 min. The vial was capped, purged with N_2, then anhydrous PhMe was added. Amine (17–23 equiv) was added, and the reaction was stirred for 5 min. The reaction was quenched with sat. $NaHCO_3$ solution (2 mL). The reaction was then diluted with EtOAc (5 mL) and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

1.4.4.3 Method D: Alcohols to Hydroxymethyl Pyridines

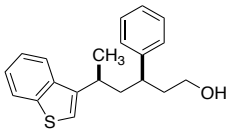
In a glove box, a flame-dried round bottom flask was equipped with a stir bar and sodium hydride (10. equiv). Anhydrous DMF was added to flask, which was capped with a septum and removed from the glove box. Alcohol (1.0 equiv) was added, and the reaction stirred for 2 h. 3-(Bromomethyl)pyridine hydrobromide was added dropwise as a solution in DMF (1.5 equiv). The reaction mixture was stirred overnight. Saturated NH_4Cl solution (2 mL) was added to quench the reaction. The reaction mixture was diluted with EtOAc (5 mL) and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo.

1.4.5 Characterization Data for Products



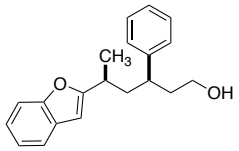
[39] Verma, S. K.; Ghorpade, R.; Pratap, A.; Kaushik, M. P. *Tetrahedron Lett.* **2012**, *53*, 2373–2376.

***syn*-(±)-5-(Naphthalen-2-yl)-3-phenylhexan-1-ol (1.5)** was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (5.5 mg, 20. μmol, 0.10 equiv), *rac*-BINAP (13 mg, 20. μmol, 0.10 equiv), substrate **1.1** (58 mg, 0.20 mmol, 1.0 equiv, dr >20:1), PhMe (1.8 mL), and MeMgI (0.21 mL, 0.50 mmol, 2.4 M in Et_2O, 2.5 equiv). The compound was purified by flash column chromatography with silver-impregnated silica gel (20–50% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (51 mg, 0.17 mmol, 84%, dr >20:1). The dr was determined based on integration of the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.3 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82–7.75 (m, 3H), 7.47–7.40 (m, 3H), 7.33–7.21 (m, 4H), 7.06 (d, *J* = 7.1, 2H), 3.38–3.27 (m, 2H), 2.59 (m, 1H), 2.42 (m, 1H), 2.09–2.03 (m, 1H), 2.00–1.95 (m, 1H), 1.85–1.79 (m, 1H), 1.79–1.72 (m, 1H), 1.22 (d, *J* = 7.0, 3H), 1.00 (br s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 144.7, 144.3, 133.7, 132.4, 128.60, 128.59, 128.2, 128.00, 127.99, 127.7, 127.6, 126.4, 126.0, 125.9, 125.8, 125.3, 61.1, 45.2, 40.40, 40.38, 37.7, 23.8; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{24}ONa$ $[M + Na]^+$ 327.1725, found 327.1727. Compound data is from our previous report.[14]

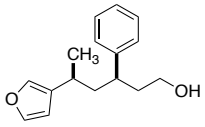


***syn*-(±)-5-(Benzo[*b*]thiophen-3-yl)-3-phenylhexan-1-ol (1.6)** was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (5.5 mg, 20. μmol, 0.10 equiv), DPEPhos (11 mg, 20. μmol, 0.10 equiv), substrate **1.2** (60. mg, 0.20 mmol, 1.0 equiv, 20:1 dr), PhMe (2.4 mL), and MeMgI (0.16 mL, 0.50 mmol, 3.1 M in Et_2O, 2.5 equiv). The compound was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a light yellow oil (37 mg, 0.12 mmol, 60%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.3 (20%

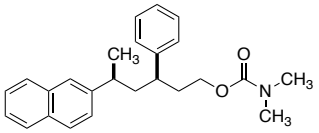
EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.83 (m, 1H), 7.59–7.54 (m, 1H) 7.35–7.16 (m, 5H), 7.07–7.00 (m, 3H) 3.51–3.34 (m, 2H), 3.04–2.94 (m, 1H), 2.71–2.61 (m, 1H) 2.29–2.20 (ddd, *J* = 14.1, 9.5, 5.2 Hz, 1H), 2.01–1.90 (m, 2H), 1.87–1.78 (m, 1H) 1.25 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 144.9, 142.0, 141.0, 138.8, 128.7 (2C), 128.0 (2C), 126.6, 124.3, 123.8, 123.1, 122.2, 120.3, 61.3, 44.6, 40.7, 40.0, 31.3, 22.7; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{26}ONS$ $[M + NH_4]^+$ 328.1735, found 328.1723.



***syn*-(±)-5-(Benzofuran-2-yl)-3-phenylhexan-1-ol (1.7)** was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (5.5 mg, 20. μmol, 0.10 equiv), DPEPhos (11 mg, 20. μmol, 0.10 equiv), substrate **1.3** (56 mg, 0.20 mmol, 1.0 equiv, 20:1 dr), PhMe (2.4 mL), and MeMgI (0.16 mL, 0.50 mmol, 3.1 M in Et_2O, 2.5 equiv). The compound was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a colorless oil (34 mg, 0.12 mmol, 59%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.4 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 1H), 7.47–7.43 (m, 1H) 7.36–7.30 (m, 2H), 7.26–7.15 (m, 5H) 6.31 (s, 1H), 3.51–3.37 (m, 2H), 2.77–2.64 (m, 2H) 1.94–1.82 (ddd, *J* = 13.7, 10.3, 4.5 Hz, 1H), 1.96–1.77 (m, 3H), 1.26 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 163.1, 154.8, 144.6, 129.0, 128.8 (2C), 128.0 (2C), 126.7, 123.3, 122.6, 120.5, 111.1, 101.7, 61.3, 42.9, 40.7, 40.2, 31.9, 20.8; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{20}H_{26}O_2N$ $[M + NH_4]^+$ 312.1964, found 312.1953.

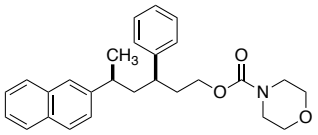


***syn*-(±)-5-(Furan-3-yl)-3-phenylhexan-1-ol (1.8)** was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (5.5 mg, 20. μmol, 0.10 equiv), DPEPhos (11 mg, 20. μmol, 0.10 equiv), substrate **1.4** (46 mg, 0.20 mmol, 1.0 equiv, 20:1 dr), PhMe (2.4 mL), and MeMgI (0.16 mL, 0.50 mmol, 2.5 M in Et_2O, 2.5 equiv). The compound was purified by flash column chromatography (40% EtOAc/hexanes) to afford the title compound as a colorless oil (35 mg, 0.14 mmol, 72%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.7 (40% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.36 (t, *J* = 1.76 Hz, 1H), 7.33–7.27 (m, 2H) 7.23–7.18 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.14–7.10 (m, 3H) 6.26 (s, 1H), 3.50–3.34 (m, 2H), 2.64–2.57 (asept, *J* = 5.2 Hz, 1H) 2.45–2.34 (m, 1H), 1.90–1.71 (m, 4H), 1.1 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 144.9, 143.1, 138.7, 130.2, 128.7 (2C), 128.0 (2C), 126.5, 109.3, 61.3, 44.9, 40.42, 40.37, 27.9, 23.2; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{16}H_{21}O_2$ $[M + H]^+$ 245.1542, found 245.1550.

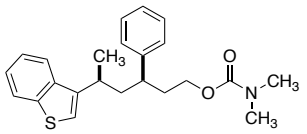


***syn*-(±)-5-(Naphthalen-2-yl)-3-phenylhexyl dimethylcarbamate (1.9)** was prepared according to Method C. The following amounts of reagents were used: substrate **1.5** (29 mg, 0.10 mmol, 1.0 equiv, 20:1 dr) carbonyldiimidazole (29 mg, 0.18 mmol, 1.8 equiv), dimethylamine in EtOH (0.30 mL, 1.7 mmol, 17 equiv, 5.6 M), PhMe (2.0 mL). The compound was purified by flash column chromatography (30% EtOAc/hexanes) to afford the title compound as a colorless oil (11 mg, 0.028 mmol, 56%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.5 (30% EtOAc/hexanes); **^{1}H NMR**

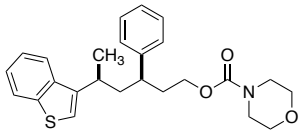
(400 MHz, $CDCl_3$) δ 7.78 (q, *J* = 10.3 Hz, 3H), 7.48–7.38 (m, 3H) 7.33–7.18 (m, 4H), 7.06 (d, *J* = 7.4 Hz, 2H) 3.92–3.86 (m, 1H), 3.77–3.71 (m, 1H), 2.76 (s, 3H) 2.66–2.57 (m, 1H), 2.52–2.39 (m, 4H), 2.07 (ddd, *J* = 14.0, 10.7, 4.2 Hz, 1H), 1.98 (*J* = 13.9, 10.7, 4.50 Hz, 1H), 1.91–1.77 (m, 2H), 1.23 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ156.5, 144.6, 144.3, 133.7, 132.3, 128.5(2C), 128.0, 127.9(2C), 127.6(2C), 126.3, 125.83, 125.80, 125.79, 125.2, 63.4, 44.6, 40.2, 37.7, 36.8, 36.2, 35.4, 23.7; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{25}H_{29}NO_2H$ $[M + H]^+$ 376.2277, found 376.2270.



***syn*-(±)-5-(Naphthalen-2-yl)-3-phenylhexyl morpholinecarbamate (1.10)** was prepared according to Method C. The following amounts of reagents were used: substrate **1.5** (76 mg, 0.25 mmol, 1.0 equiv, 20:1 dr) carbonyldiimidazole (73 mg, 0.45 mmol, 1.8 equiv), morpholine (0.50 mL, 5.8 mmol, 23 equiv). This reaction was run neat. The compound was purified by flash column chromatography (20% EtOAc/hexanes) to afford the title compound as a colorless oil (22 mg, 0.052 mmol, 21%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.4 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82–7.76 (m, 3H), 7.48–7.42 (m, 3H) 7.32–7.21 (m, 4H), 7.05 (d, *J* = 7.5 Hz, 2H) 3.93–3.89 (m, 1H), 3.79–3.74 (m, 1H), 3.63–2.77 (m, 8H) 2.63–2.56 (m, 1H), 2.40 (septet, *J* = 5.3 Hz, 1H), 2.08–1.96 (m, 2H), 1.91–1.79 (m, 2H), 1.23 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 155.2, 144.4, 144.2, 133.6, 132.3, 128.6(2C), 128.0, 127.9(2C), 127.64, 127.55, 126.4, 126.0, 125.9, 125.8, 125.3, 66.5(2C), 63.6, 44.8, 43.8(2C), 40.3, 37.7, 36.8, 23.7; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{27}H_{31}NO_3Na$ $[M + Na]^+$ 440.2202, found 440.2198.

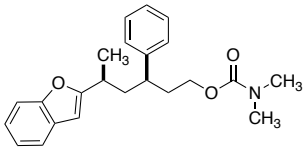


***syn*-(±)-5-(Benzo[*b*]thiophen-3-yl)-3-phenylhexyl dimethylcarbamate (1.11)** was prepared according to Method B. The following amounts of reagents were used: sodium hydride (36 mg, 1.5 mmol, 10. equiv), 4-dimethylcarbamoyl chloride (0.26 mL, 2.8 mmol, 20. equiv), substrate **1.6** (45 mg, 0.15 mmol, 1.0 equiv, 20:1 dr), THF (2.0 mL). The compound was purified by flash column chromatography (0–15% EtOAc/hexanes) to afford the title compound as a light yellow oil (23 mg, 0.060 mmol, 40%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.8 (40% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 1H), 7.58–7.53 (m, 1H) 7.33–7.28 (m, 2H), 7.26–7.15 (m, 3H), 7.04–6.98 (m, 3H), 4.00–3.94 (m, 1H), 3.84–3.76 (m, 1H) 3.03–2.93 (m, 1H), 2.83 (br s, 3H), 2.70–2.58 (m, 4H), 2.70–2.58 (ddd, *J* = 13.9, 6.9, 4.8 Hz, 1H), 2.02–1.83 (m, 3H), 1.25 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 156.6, 144.5, 141.8, 140.8, 128.6, 128.5 (2C), 127.8 (2C), 126.4, 124.1, 123.6, 122.9, 120.1, 120.2, 63.4, 43.9, 40.4, 36.4 (2C), 35.7, 31.2, 22.5; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{23}H_{27}NO_2S$ $[M + Na]^+$ 404.1660, found 404.1671.



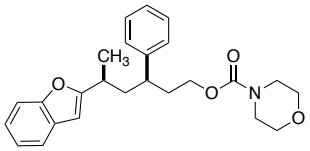
***syn*-(±)-5-(Benzo[*b*]thiophen-3-yl)-3-phenylhexyl morpholine-4-carboxylate (1.12)** was prepared according to Method B. The following amounts of reagents were used: sodium hydride (22 mg, 0.90 mmol, 10. equiv), 4-morpholinecarbonyl chloride (0.21 mL, 1.8 mmol, 20. equiv), substrate **1.6** (27 mg, 0.090 mmol, 1.0 equiv, 20:1 dr), THF (2.0 mL). The compound was purified by flash column chromatography (100% DCM) to afford the title compound as a light yellow oil

(19 mg, 0.045 mmol, 50%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.2 (100% DCM); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.85 (m, 1H), 7.59–7.55 (m, 1H) 7.35–7.28 (m, 2H), 7.28–7.19 (m, 3H), 7.05 (s, 1H), 7.03–6.98 (m, 2H), 4.02–3.97 (m, 1H), 3.88–3.82 (m, 1H) 3.67–3.05 (m, 8H), 3.02–2.93 (m, 1H), 2.61–2.59 (asept, *J* = 5.0 Hz, 1H), 2.29–2.22 (m, 1 H), 2.03–1.86 (m, 3H), 1.25 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 155.5, 144.5, 141.9, 141.0, 138.7, 128.7 (2C), 128.0 (2C), 126.6, 124.4, 123.8, 123.1, 122.3, 120.4, 66.8 (2C), 63.9, 44.3, 44.1 (2C), 40.8, 36.5, 31.4, 22.8; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{25}H_{29}NO_3SNa$ $[M + Na]^+$ 446.1766, found 446.1761.

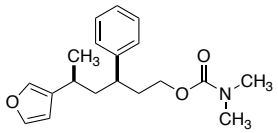


***syn*-(±)-5-(Benzofuran-2-yl)-3-phenylhexyl dimethylcarbamate (1.13)** was prepared according to Method B. The following amounts of reagents were used: sodium hydride (24 mg, 1.0 mmol, 10. equiv), 4-dimethylcarbamoyl chloride (0.18 mL, 2.0 mmol, 20. equiv), substrate **1.7** (28 mg, 0.10 mmol, 1.0 equiv, 20:1 dr), THF (2.0 mL). The compound was purified by flash column chromatography (0–15% EtOAc/hexanes) to afford the title compound as a colorless oil (12 mg, 0.033 mmol, 33%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.7 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 1H), 7.43–7.40 (m, 1H) 7.33–7.27 (m, 2H), 7.23–7.12 (m, 5H) 6.29 (s, 1H), 3.98–3.91 (m, 1H), 3.84–3.77 (m, 1H) 2.85–2.51 (m, 8H), 2.19–2.12 (ddd, *J* = 13.7, 10.3, 4.2 Hz, 1H), 1.98–1.81 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 162.9, 156.5, 154.7, 144.3, 128.8, 128.6 (2C), 127.8 (2C), 126.5, 123.1, 122.4, 120.3, 110.9, 101.6, 63.9, 42.4, 40.5, 36.5, 36.3, 35.8, 31.7, 20.6; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{23}H_{27}NO_3Na$

[M + Na]$^+$ 338.1889, found 338.1898.

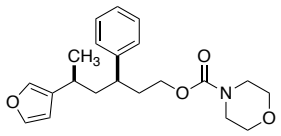


***syn*-(±)-5-(Benzofuran-2-yl)-3-phenylhexyl morpholine-4-carboxylate (1.14)** was prepared according to Method B. The following amounts of reagents were used: sodium hydride (20. mg, 0.80 mmol, 10. equiv), 4-morpholinecarbonyl chloride (0.19 mL, 1.6 mmol, 20. equiv), substrate **1.7** (24 mg, 0.080 mmol, 1.0 equiv, 20:1 dr), THF (2.0 mL). The compound was purified by flash column chromatography (100% DCM) to afford the title compound as a colorless oil (14 mg, 0.034 mmol, 43%, 3.8:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.3 (100% DCM); **^{1}H NMR** (500 MHz, $CDCl_3$, 311 K) δ 7.50–7.46 (ad, *J* = 7.5 Hz, 1H), 7.43–7.40 (ad, *J* = 8.2 Hz, 1H) 7.33–7.27 (m, 2H), 7.23–7.12 (m, 5H) 6.29 (s, 1H), 3.99–3.94 (m, 1H), 3.88–3.83 (m, 1H) 3.60–2.99 (m, 8H), 2.73–2.66 (m, 1H), 2.63–2.57 (asept, *J* = 5.1 Hz, 1H), 2.18–2.12 (m, 1H), 1.97–1.84 (m, 3H), 1.24 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 162.7, 155.3, 154.6, 144.1, 128.7, 128.6 (2C), 127.8 (2C), 126.5, 123.2, 122.5, 120.3, 110.9, 101.7, 66.5 (2C), 63.7, 43.8 (2C), 42.6, 40.6, 36.5, 31.7, 20.6; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{25}H_{29}NO_4Na$ [M + Na]$^+$ 430.1994, found 430.1992.



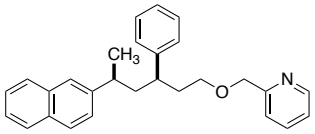
***syn*-(±)-5-(Furan-3-yl)-3-phenylhexyl dimethylcarbamate (1.15)** was prepared according to Method B. The following amounts of reagents were used: sodium hydride (35 mg, 1.5 mmol, 10. equiv), 4-dimethylcarbamoyl chloride (0.26 mL, 2.8 mmol, 20. equiv), substrate **1.8** (35 mg, 0.14

mmol, 1.0 equiv, 20:1 dr), THF (2.0 mL). The compound was purified by flash column chromatography (15–25% EtOAc/hexanes) to afford the title compound as a colorless oil (10. mg, 0.032 mmol, 23%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum **TLC R_f** = 0.8 (40% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.34 (t, *J* = 1.6 Hz, 1H), 7.31–7.26 (m, 2H) 7.22–7.16 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.12–7.08 (m, 3H) 6.26 (s, 1H), 3.97–3.89 (m, 1H), 3.86–3.78 (m, 1H) 2.86 (br s, 3H), 2.75 (br s, 3H), 2.64–2.55 (m, 1H), 2.45–2.37 (m, 1H), 1.95–1.77 (m, 4H), 1.09 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 156.6, 144.5, 142.9, 138.5, 129.9, 128.6 (2C), 127.8 (2C), 126.3, 109.1, 63.5, 44.3, 40.2, 36.6, 36.4, 35.7, 27.7, 23.0; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{25}NO_3Na$ $[M + Na]^+$ 338.1732, found 338.1721.

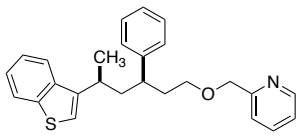


***syn*-(±)-5-(Furan-3-yl)-3-phenylhexyl morpholine-4-carboxylate (1.16)** was prepared according to Method B. The following amounts of reagents were used: sodium hydride (28 mg, 1.2 mmol, 10. equiv), 4-morpholinecarbonyl chloride (0.28 mL, 2.4 mmol, 20. equiv), substrate **1.8** (28 mg, 0.12 mmol, 1.0 equiv, 20:1 dr), THF (2.0 mL). The compound was purified by flash column chromatography (100% DCM) to afford the title compound as a colorless oil (13 mg, 0.036 mmol, 30%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.2 (100% DCM); **^{1}H NMR** (500 MHz, $CDCl_3$, 308 K) δ 7.36–7.33 (m, 1H), 7.31–7.24 (m, 2H) 7.21–7.17 (m, 1H), 7.12–7.02 (m, 3H) 6.25 (s, 1H), 3.98–3.93 (m, 1H), 3.90–3.86 (m, 1H) 3.68–3.52 (m, 4H), 3.42–3.20 (br s, 4H), 2.60–2.54 (asept, *J* = 5.3 Hz, 1H), 2.43–2.36 (m, 1H), 1.94–1.75 (m, 4H), 1.09 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 155.3, 144.4, 142.9, 138.6, 129.9, 128.6 (2C), 127.8 (2C), 126.4,

109.1, 66.6 (2C), 63.9, 44.4 (2C), 43.9, 40.5, 36.6, 27.7, 23.0; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{21}H_{27}NO_4Na$ [M + Na]$^+$ 380.1838, found 380.1832.

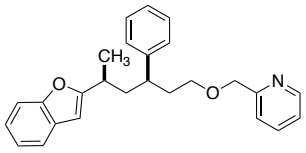


3-((((*syn*-(±))-5-(Naphthalen-2-yl)-2-phenylhexyl)oxy)methyl)pyridine (1.17) was prepared according to Method D. The following amounts of reagents were used: sodium hydride (48 mg, 2.0 mmol, 10. equiv), 2-(bromomethyl)pyridine hydrobromide (140 mg, 0.60 mmol, 3.0 equiv), substrate **1.5** (61 mg, 0.20 mmol, 1.0 equiv, 20:1 dr), DMF (2.0 mL). The compound was purified by flash column chromatography (30% EtOAc/hexanes) to afford the title compound as a colorless oil (49 mg, 0.12 mmol, 62%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.4 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 1H), 7.81–7.74 (m, 3H) 7.46–7.38 (m, 4H), 7.30–7.26 (m, 3H) 7.23–7.19 (m, 1H), 7.10–7.05 (m, 4H), 4.41 (q, *J* = 13 Hz, 2H), 3.34–3.29 (m, 1H) 3.26–2.20 (m, 1H), 2.67–2.58 (m, 1H), 2.52 (septet, *J* = 4.8 Hz, 1H), 2.10 (ddd, *J* = 13.8, 10.6, 4.3 Hz, 1H), 2.02–1.91 (m, 2H), 1.87–1.79 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 159.0, 149.1, 145.0, 144.6, 136.7, 133.9, 132.5, 128.6(2C), 128.3, 128.2(2C), 127.9, 127.8, 126.4, 126.1, 126.03, 126.00, 125.3, 122.3, 121.3, 73.9, 69.3, 45.2, 40.5, 37.9, 37.7, 23.9; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{28}H_{29}NONa$ [M + Na]$^+$ 418.2147, found 418.2157.



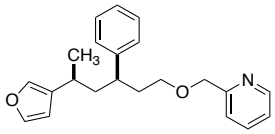
3-((((*syn*-(±))-5-(Benzo[*b*]thiophen-3-yl)-2-phenylhexyl)oxy)methyl)pyridine (1.18) was prepared according to Method D. The following amounts of reagents were used: sodium hydride

(20. mg, 0.80 mmol, 10. equiv), 2-(bromomethyl)pyridine hydrobromide (25 mg, 0.10 mmol, 1.3 equiv), substrate **1.6** (25 mg, 0.080 mmol, 1.0 equiv, 20:1 dr), DMF (2.0 mL). The compound was purified by flash column chromatography (30% EtOAc/hexanes) to afford the title compound as a light yellow oil (15 mg, 0.038 mmol, 48%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.6 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51–8.48 (m, 1H), 7.86–7.82 (m, 1H) 7.63–7.54 (m, 2H), 7.33–7.28 (m, 2H) 7.24–7.11 (m, 5H), 7.05 (s, 1H), 7.04–6.99 (m, 2H), 4.51–4.43 (dd, *J* = 18.7, 13.2 Hz, 2H), 3.42–3.28 (m, 2H) 3.04–2.95 (m, 1H), 2.79–2.70 (asept, *J* = 4.9 Hz, 1H), 3.30–2.23 (ddd, *J* = 14.1, 8.7, 5.1 Hz, 1H), 2.12–2.02 (m, 1H), 2.00–1.82 (m, 2H), 1.25 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 158.8, 149.0, 144.9, 141.9, 140.8, 138.6, 136.6, 128.4 (2C), 127.9 (2C), 126.3, 124.1, 123.6, 122.9, 122.2, 122.1, 121.2, 120.2, 73.8, 69.2, 44.2, 40.5, 36.9, 31.2, 22.5; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{26}H_{27}NOSNa$ $[M + Na]^+$ 424.1711, found 424.1701.



3-((((*syn*-(±))-5-(Benzofuran-2-yl)-2-phenylhexyl)oxy)methyl)pyridine (1.19) was prepared according to Method D. The following amounts of reagents were used: sodium hydride (29 mg, 1.2 mmol, 10. equiv), 2-(bromomethyl)pyridine hydrobromide (38 mg, 0.15 mmol, 1.3 equiv), substrate **1.7** (34 mg, 0.12 mmol, 1.0 equiv, 20:1 dr), and DMF (2.0 mL). The compound was purified by flash column chromatography (30% EtOAc/hexanes) to afford the title compound as a colorless oil (9.2 mg, 0.024 mmol, 20%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.5 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50–8.48 (m, 1H), 7.56–7.47 (m, 2H), 7.45–7.41

(m, 1H) 7.34–7.28 (m, 2H), 7.25–7.18 (m, 4H), 7.18–7.09 (m, 3H), 6.31 (s, 1H), 4.52–4.43 (dd, *J* = 18.1, 13.4 Hz, 2H), 3.43–3.28 (m, 2H), 2.80–2.68 (m, 2H) 2.25–2.15 (ddd, *J* = 13.9, 10.4, 4.6 Hz, 1H), 2.07–1.97 (m, 1H), 1.93–1.83 (m, 2H), 1.25 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 163.0, 158.8, 154.7, 148.9, 144.6, 136.6, 128.9, 128.5 (2C), 127.9 (2C), 126.3, 123.1, 122.4, 122.2, 121.2, 120.3, 110.9, 101.5, 73.7, 69.0, 42.6, 40.4, 37.2, 31.7, 20.7; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{26}H_{27}NO_2Na$ $[M + Na]^+$ 408.1939, found 408.1929.



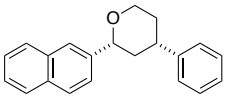
3-((((*syn*-(±))-5-(Furan-3-yl)-2-phenylhexyl)oxy)methyl)pyridine (1.20) was prepared according to Method D. The following amounts of reagents were used: sodium hydride (18 mg, 0.74 mmol, 10. equiv), 2-(bromomethyl)pyridine hydrobromide (36 mg, 0.15 mmol, 2.0 equiv), substrate **1.8** (18 mg, 0.074 mmol, 1.0 equiv, 20:1 dr), DMF (2.0 mL). The compound was purified by flash column chromatography (30% EtOAc/hexanes) to afford the title compound as a colorless oil (15 mg, 0.046 mmol, 62%, 20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.6 (30% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53–8.49 (m, 1H), 7.67–7.62 (td, *J* = 7.7, 1.7 Hz, 1H) 7.35–7.34 (at, *J* = 1.6 Hz, 1H), 7.31–7.26 (m, 3H) 7.22–7.09 (m, 5H), 6.26 (s, 1H), 4.52–4.44 (dd, *J* = 19.2, 13.3 Hz, 2H), 3.39–3.27 (m, 2H), 2.70–2.63 (m, 1H), 2.45–2.36 (asext, *J* = 7.2 Hz, 1H), 2.00–1.92 (m, 1H), 1.88–1.79 (m, 3H), 1.09 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 158.9, 149.0, 144.8, 142.8, 138.5, 136.6, 130.0, 128.4 (2C), 127.9 (2C), 126.2, 122.2, 121.2, 109.2, 73.8, 69.2, 44.7, 40.3, 37.3, 27.8, 23.0; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{22}H_{25}NO_2Na$ $[M + Na]^+$ 358.1783, found 358.1771.

1.4.6 General Procedures for Starting Material Synthesis

1.4.6.1 Method E: Prins Cyclization

The target compounds were prepared using a modified procedure reported by Dintzner.[40] Montmorillonite K10 clay was activated by heating at 200 °C for 2 h immediately prior to use. Aryl aldehyde (1.0 equiv) and Montmorillonite K10 clay (1.3 equiv by mass) were added to a flame-dried round bottom flask equipped with a stir bar. The reaction vessel was evacuated and backfilled with N_2 and then anhydrous benzene (75 mL), MeOH (5.0 equiv), and 3-buten-1-ol (1.5 equiv) were added. The reaction was stirred under reflux for 3–7 days. The reaction mixture was passed through a celite plug (neat Et_2O) and concentrated in vacuo. To remove unreacted aldehyde that was difficult to separate from the desired product, the unpurified mixture was subjected to $NaBH_4$ reduction by a modified procedure reported by Franzén.[41] The unpurified mixture was dissolved in MeOH and $NaBH_4$ (1.6 equiv relative to 1.0 equiv of aldehyde as determined by ^1H NMR integration) was added in one portion and the reaction stirred for 1 hour at room temperature. The reaction was quenched with water and extracted with EtOAc (20 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo.

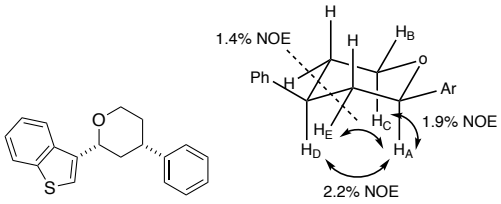
1.4.7 Synthesis and Characterization of Starting Material Tetrahydropyrans



***cis*-(±)-2-(Naphthalen-2-yl)-4-phenyl-tetrahydropyran (1.1)** was prepared according to Method E. The following amounts of reagents were used: Montmorillonite K10 clay (4.9 g, 1.3 equiv by

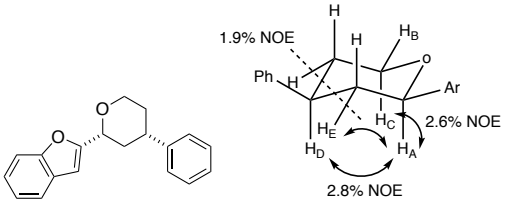
[40] Dintzner, M. R.; Maresh, J. J.; Kinzie, C. R.; Arena, A. F.; Speltz, T. *J. Chem. Educ.* **2012**, *89*, 265–267.
[41] Wang, Y.; Franzén, R. *Synlett.* **2012**, *23*, 925–929.

mass), 2-naphthaldehyde (3.9 g, 25 mmol, 1.0 equiv), 3-buten-1-ol (3.2 mL, 38 mmol, 1.5 equiv), MeOH (3.2 mL, 79 mmol, 3.2 equiv), and benzene (250 mL). The compound was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a yellow oil (1.5 g, 5.1 mmol, 21%, >20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. **TLC R_f** = 0.7 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86–7.81 (m, 4H), 7.51 (d, *J* = 8.3 Hz, 1H) 7.48–7.43 (m, 2H), 7.34–7.30 (m, 2H), 7.28–7.26 (m, 2H), 7.24–7.19 (m, 1H), 4.67 (d, *J* = 10.8 Hz, 1H), 4.36 (d, *J* = 10.8 Hz, 1H), 3.84 (t, *J* = 11.5 Hz, 1H), 3.03 (at, *J* = 11.5 Hz, 1H), 2.19 (d, *J* = 13.1 Hz, 1H), 1.99–1.82 (m, 3H). Analytical data is consistent with literature values.[14]



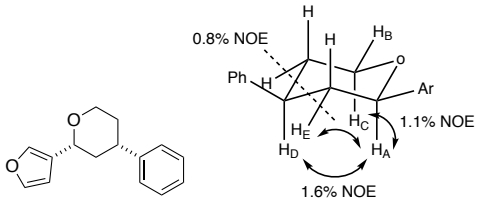
***cis*-(±)-2-(Benzo[*b*]thiophen-3-yl)-4-phenyl-tetrahydropyran** (**1.2**) was prepared according to Method E. The following amounts of reagents were used: Montmorillonite K10 clay (2.0 g, 1.3 equiv by mass), benzo[b]thiophene-3-carboxaldehyde (1.6 g, 10. mmol, 1.0 equiv), 3-buten-1-ol (1.3 mL, 15 mmol, 1.5 equiv), MeOH (2.1 mL, 50. mmol, 5.0 equiv), and benzene (75 mL). The compound was purified by flash column chromatography (10–15% EtOAc/hexanes) to afford the title compound as a light-yellow oil (150 mg, 0.48 mmol, 5%, >20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. The relative configuration was assigned as cis by NOE NMR experiments. Irradiation of the benzylic proton (H_A) gave an NOE enhancement of 1.9% of H_C, an enhancement of 2.2% of H_D, and an enhancement of 1.4% of H_E. **TLC R_f** = 0.7 (20% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.90 (s, *J* = 7.7 Hz, 1H) 7.46–7.26 (m, 8H), 4.93 (d, *J* = 10.7

Hz, 1H), 4.48 (dd, *J* = 4.1, 1.5 Hz, 1H), 3.94–3.88 (td, *J* = 11.4, 3.2 Hz, 1H), 3.12–3.04 (tt, *J* = 11.8, 4.0 Hz, 1H), 2.35–2.29 (m, 1H), 2.12–1.93 (m, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 145.5, 141.0, 137.8, 137.7, 128.8 (2C), 127.0 (2C), 126.7, 124.5, 124.2, 123.1, 122.6, 122.4, 75.7, 69.1, 42.2, 39.7, 33.8; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{18}OS$ $[M + Na]^+$ 317.0976, found 317.0978.



***cis*-(±)-2-(Benzofuran-2-yl)-4-phenyl-tetrahydropyran (1.3)** was prepared according to Method E. The following amounts of reagents were used: Montmorillonite K10 clay (2.0 g, 1.3 equiv by mass), 2-benzofurancarboxaldehyde (1.2 mL, 10. mmol, 1.0 equiv), 3-buten-1-ol (1.3 mg, 15 mmol, 1.5 equiv), MeOH (2.1 mL, 50 mmol, 5.0 equiv), and benzene (50 mL). The compound was purified by flash column chromatography (10–15% EtOAc/hexanes) to afford the title compound as a colorless oil (1.0 g, 3.7 mmol, 37%, 12:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. The relative configuration was assigned as cis by NOE NMR experiments. Irradiation of the benzylic proton (H_A) gave an NOE enhancement of 2.6% of H_C, an enhancement of 2.8% of H_D, and an enhancement of 1.9% of H_E. **TLC R_f** = 0.7 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H) 7.35–7.29 (m, 2H), 7.29–7.15 (m, 5H), 6.64 (s, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.28 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.80–3.75 (td, *J* = 12.1, 1.6 Hz, 1H), 2.96–2.90 (tt, *J* = 12.2, 3.6 Hz, 1H), 2.20 (d, *J* = 12.0 Hz, 1H), 2.10–2.02 (q, *J* = 13.0 Hz, 1H), 1.97–1.89 (qd, *J* = 12.7, 4.7 Hz, 1H), 1.83 (d, *J* = 13.3 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 157.4, 154.9, 145.1, 128.7 (2C), 128.1, 126.9 (2C), 126.7, 124.3, 122.9, 121.1, 111.4,

103.0, 73.7, 68.9, 41.6, 37.4, 34.2; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{19}H_{18}O_2$ [M + Na]$^+$ 301.1205, found 301.1204.



***cis*-(±)-2-(Furan-3-yl)-4-phenyl-tetrahydropyran** (**1.4**) was prepared according to Method E. The following amounts of reagents were used: Montmorillonite K10 clay (3.0 g, 1.3 equiv by mass), 3-furancarboxaldehyde (1.3 mL, 15 mmol, 1.0 equiv), 3-buten-1-ol (1.9 mL, 23 mmol, 1.5 equiv), MeOH (3.0 mL, 75 mmol, 5.0 equiv), and benzene (75 mL). The compound was purified by flash column chromatography (10–15% EtOAc/hexanes) to afford the title compound as a colorless oil (230 mg, 1.0 mmol, 7%, >20:1 dr). The dr was determined based on integration of resonance attributed to the benzylic methines in the ^{1}H NMR spectrum. The relative configuration was assigned as cis by NOE NMR experiments. Irradiation of the benzylic proton (H_A) gave an NOE enhancement of 1.1% of H_C, an enhancement of 1.6% of H_D, and an enhancement of 0.8% of H_E. **TLC R_f** = 0.7 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.38 (s, 1H) 7.34–7.31 (m, 2H), 7.26–7.20 (m, 3H), 6.42 (s, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 4.22 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.76–3.71 (td, *J* = 11.7, 2.8 Hz, 1H), 2.94–2.88 (tt, *J* = 12.1, 4.0 Hz, 1H), 2.09–2.06 (m, 1H), 1.92–1.78 (m, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 145.6, 143.3, 139.2, 128.8 (2C), 127.5, 127.0 (2C), 126.7, 109.0, 73.1, 68.7, 42.0, 40.2, 33.5; **HRMS** (TOF MS ES+) *m / z* calcd for $C_{15}H_{16}O_2$ [M]$^+$ 228.1150, found 228.1156.

1.4.8 Computational Study

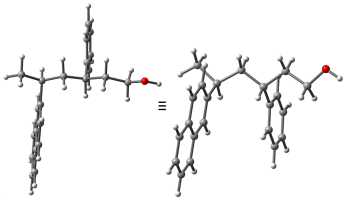
1.4.8.1 Computational Method

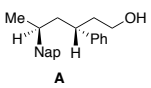
A preliminary conformational search was conducted using MacroModel within Maestro Version 11.7.012 software package.[42] Force field MMFF[43] was used for initial minimization and a conformational search to find lowest energy conformer and all other conformers within 5 kcal/mol. Density functional theory (DFT) calculations using Gaussian 6.0.16 software[44] were then performed on the lowest energy conformer and three other dissimilar structures to further refine their energies. Optimization was performed at the B3LYP[45] level and utilized 6-31G(d) basis set[35] with H_2O has the chosen solvent.

[42] a) Schrödinger Release 2018-3: MacroModel, Schrödinger, LLC, New York, NY, 2018. b) Schrödinger Release 2018-3: Maestro, Schrödinger, LLC, New York, NY, 2018.
[43] Halgren, T. A. *J. Comput. Chem*. **1996**, *17*, 490–519.
[44] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, revision A.03; Gaussian, Inc.: Wallingford, CT, 2016.
[45] a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785–789.

1.4.8.2 Calculated Energies of Conformers

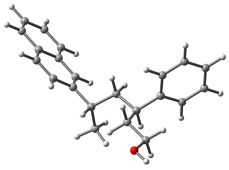
Energies are reported in hartrees, as obtained from Gaussian software. Differences in energies (ΔE) are reported in hartrees and kcal/mol, and are a comparison of a select conformer to the lowest energy conformer ($\Delta E = E_X – E_A$; X = B, C, D).

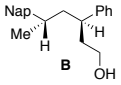




A

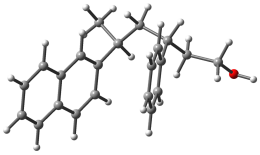
Energy (hartree)	ΔE (hartree)	ΔE (kcal/mol)
-928.039541	0	0

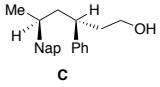




B

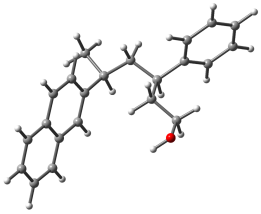
Energy (hartree)	ΔE (hartree)	ΔE (kcal/mol)
-928.036782	0.002759	+1.731

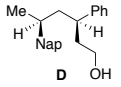




C

Energy (hartree)	ΔE (hartree)	ΔE (kcal/mol)
-928.031776	0.007765	+4.873





D

Energy (hartree)	ΔE (hartree)	ΔE (kcal/mol)
-928.036558	0.002983	+1.815

1.4.8.3 Cartesian Coordinates of Conformers

Conformer A

C	-1.15070800	-0.58454400	1.17665800
C	0.14255000	-0.57005500	1.98106600

C	1.28120300	-1.36672500	1.30413900
C	-1.72798300	0.59062400	0.73561700
C	-2.94786000	0.60524400	0.00461700
C	-3.59862900	-0.63803600	-0.28423300
C	-2.99260400	-1.83938400	0.17537300
C	-1.81168000	-1.81291300	0.88077200
C	-3.54556800	1.81281600	-0.45005900
C	-4.72929800	1.79242700	-1.15545600
C	-5.37231500	0.56151600	-1.44056200
C	-4.81818500	-0.62600500	-1.01396900
C	-0.09019000	-1.08404200	3.41630900
C	1.73818700	-0.83577200	-0.07517900
C	2.73695200	-1.82706400	-0.71531300
C	3.11914400	-1.48289300	-2.14991900
O	3.98589400	-2.51380400	-2.63004500
C	2.30139400	0.57989800	0.00450400
C	1.70064300	1.63078300	-0.70347200
C	2.21033400	2.93080500	-0.64165000
C	3.33769300	3.20492800	0.13435300
C	3.94874100	2.16850400	0.84587500
C	3.43534600	0.87219000	0.78050900
H	0.46614900	0.47573700	2.05543400
H	0.96923500	-2.41317400	1.18633400

H	2.14134700	-1.38380600	1.98687800
H	-1.24260900	1.54127000	0.94763300
H	-3.48040900	-2.78757500	-0.03910400
H	-1.37628800	-2.74890100	1.22109500
H	-3.05152800	2.75648900	-0.23046900
H	-5.17557400	2.72257900	-1.49673600
H	-6.30523200	0.55915100	-1.99761300
H	-5.30829000	-1.57244700	-1.23052300
H	-0.39508900	-2.13735200	3.42090000
H	0.82853000	-1.00008100	4.00858100
H	-0.87368200	-0.50582900	3.91844400
H	0.85297400	-0.79885700	-0.72438100
H	2.29209000	-2.83066400	-0.71185600
H	3.65142700	-1.88644300	-0.11023500
H	3.61860200	-0.50422900	-2.18909000
H	2.21200900	-1.41374900	-2.77172400
H	4.24937500	-2.27406700	-3.53216900
H	0.82063100	1.42810400	-1.30938600
H	1.72513200	3.72703100	-1.20041400
H	3.73703600	4.21429800	0.18533900
H	4.82762500	2.36937300	1.45324600
H	3.92637000	0.07976300	1.34028800

Conformer B

C	1.66242200	-0.94368500	0.21200000
C	0.24641700	-1.28907600	0.66171000
C	-0.73257500	-0.18739900	0.17802000
C	2.41476900	0.03534900	0.83518700
C	3.72348300	0.37073000	0.39484900
C	4.28080100	-0.32345400	-0.72876400
C	3.49518900	-1.32471900	-1.35972500
C	2.23068000	-1.62163600	-0.90330500
C	4.50304700	1.37535500	1.03351100
C	5.76943100	1.67847600	0.58416900
C	6.31969600	0.99035800	-0.52735600
C	5.59103900	0.01219000	-1.16763300
C	0.15556400	-1.53589500	2.17845600
C	-2.24162800	-0.42719700	0.44603900
C	-2.76448500	-1.69907200	-0.25584600
C	-4.21988000	-2.02216200	0.06284400
O	-4.54241000	-3.25803600	-0.57978500
C	-3.03394100	0.82077100	0.06665800
C	-3.14522600	1.24173600	-1.26877600
C	-3.85167600	2.39865900	-1.60176400
C	-4.46227800	3.16313700	-0.60361600
C	-4.35924700	2.75853800	0.72841400

C	-3.65172000	1.59878300	1.05597700
H	-0.02020600	-2.22656100	0.15822800
H	-0.58501500	-0.04133400	-0.90035800
H	-0.44702200	0.75945300	0.65568200
H	2.01209200	0.57505100	1.68938500
H	3.90968200	-1.85905000	-2.21154200
H	1.64729900	-2.39344400	-1.40041500
H	4.08045700	1.90231700	1.88590500
H	6.35361400	2.44817900	1.08126000
H	7.31988000	1.23908100	-0.87150300
H	6.00912700	-0.51796300	-2.02027600
H	0.90587900	-2.26700900	2.49843400
H	0.31850400	-0.61404000	2.74913000
H	-0.82894800	-1.92620900	2.45710300
H	-2.37358200	-0.56856200	1.52665200
H	-2.15943400	-2.56130500	0.04847900
H	-2.65069500	-1.60599600	-1.34405700
H	-4.87831800	-1.21583000	-0.29026300
H	-4.35401000	-2.10206200	1.15375400
H	-5.47750600	-3.44290200	-0.40039200
H	-2.67693300	0.66112000	-2.05983500
H	-3.92503700	2.70363500	-2.64256800
H	-5.01242800	4.06374300	-0.86276000

H	-4.82987400	3.34312700	1.51478900
H	-3.57754500	1.29213300	2.09715300

Conformer C

C	-0.48593900	-1.54311900	0.05536200
C	0.80511500	-2.20278100	-0.41894400
C	1.65674600	-1.37033700	-1.40740600
C	-1.41244400	-1.01786000	-0.82625900
C	-2.64352200	-0.46555200	-0.38191400
C	-2.94052400	-0.46037500	1.02069600
C	-1.98434200	-1.01392300	1.91330900
C	-0.80081100	-1.53723100	1.44344700
C	-3.59748700	0.08267900	-1.28455600
C	-4.78375200	0.61034700	-0.82428400
C	-5.07531500	0.61601000	0.56383700
C	-4.17343300	0.09233800	1.46390400
C	0.47886600	-3.57567300	-1.05037400
C	2.49377500	-0.17430800	-0.86314100
C	3.46661300	-0.61793700	0.24782500
C	4.56368400	0.39961900	0.54095900
O	5.41860700	-0.15481500	1.54366200
C	1.65976300	1.06128000	-0.52527200
C	1.22305000	1.36923000	0.77121100

C	0.45239200	2.50766800	1.02192400
C	0.10136700	3.36672800	-0.02105000
C	0.53237500	3.07774900	-1.31819800
C	1.30498300	1.94111300	-1.56069500
H	1.41463200	-2.40108700	0.47141000
H	1.02197400	-1.00837300	-2.22596500
H	2.37578600	-2.06009400	-1.86935800
H	-1.21186800	-1.01590700	-1.89541000
H	-2.20039700	-1.01803500	2.97929600
H	-0.08326600	-1.95652800	2.14523600
H	-3.37309800	0.07865800	-2.34877500
H	-5.50281600	1.02597600	-1.52505000
H	-6.01458800	1.03559300	0.91371400
H	-4.39314600	0.09417100	2.52910400
H	1.39855700	-4.12253800	-1.28912500
H	-0.11682900	-4.19062100	-0.36674700
H	-0.09397600	-3.45453700	-1.97769500
H	3.11867300	0.11841400	-1.71958300
H	3.94690600	-1.55533500	-0.06196100
H	2.93720000	-0.83922300	1.18204300
H	4.12564700	1.34810500	0.88338400
H	5.12868600	0.61225800	-0.38080500
H	6.09671400	0.50852700	1.74593700

H	1.47895800	0.71708900	1.60061100
H	0.12787800	2.72224700	2.03701300
H	-0.49580500	4.25328100	0.17491200
H	0.27470900	3.74086500	-2.14017100
H	1.64366500	1.73163400	-2.57359100

Conformer D

C	1.30632500	1.28080200	0.17431900
C	0.04087900	1.93688700	0.71118800
C	-1.28148700	1.46469500	0.05311400
C	2.20031000	0.65994100	1.02564300
C	3.41165200	0.08091200	0.55699300
C	3.71698400	0.14763800	-0.84133900
C	2.79115400	0.79633300	-1.70375500
C	1.62898900	1.34489400	-1.21284800
C	4.33215700	-0.56317600	1.42887100
C	5.49741200	-1.11475700	0.94192000
C	5.79802100	-1.04880900	-0.44199800
C	4.92640100	-0.43121300	-1.31267600
C	0.16025800	3.47304800	0.59498500
C	-1.82243100	0.07378100	0.48283100
C	-1.01565500	-1.10825500	-0.10044400
C	-1.46263900	-2.47419500	0.42405600

O	-0.69525300	-3.54677700	-0.12687100
C	-3.30735800	-0.03030000	0.14490800
C	-4.26891400	-0.09851900	1.16293900
C	-5.63290700	-0.16975400	0.86689000
C	-6.06204900	-0.17307500	-0.46145900
C	-5.11592500	-0.10481800	-1.48797600
C	-3.75475400	-0.03463100	-1.18654800
H	-0.02165800	1.69581800	1.78131500
H	-1.19339600	1.50524300	-1.04087800
H	-2.04833000	2.20348100	0.31758300
H	1.98018500	0.60352700	2.09024800
H	3.01680800	0.85440700	-2.76615000
H	0.94394200	1.83756900	-1.89784600
H	4.10051800	-0.61354300	2.49029300
H	6.19228100	-1.60404500	1.61908000
H	6.72005500	-1.48794700	-0.81297500
H	5.15326100	-0.37812400	-2.37499100
H	-0.69283600	3.96450300	1.07670900
H	1.07775600	3.83178600	1.07413500
H	0.18273100	3.79171400	-0.45407600
H	-1.73885000	0.02221700	1.57828600
H	0.04345800	-0.97425100	0.14624600
H	-1.08480800	-1.11025900	-1.19626500

H	-2.49876100	-2.67967800	0.13854000
H	-1.41795700	-2.48761700	1.52512500
H	0.22580400	-3.40954300	0.14726000
H	-3.94508000	-0.09557200	2.20154900
H	-6.35788600	-0.22318300	1.67510400
H	-7.12172900	-0.22856500	-0.69580900
H	-5.43799800	-0.10637400	-2.52623400
H	-3.03403300	0.01807800	-1.99897100

Chapter Two

Nickel-Catalyzed Alkyl–Alkyl Cross-Electrophile Coupling Reaction of 1,3-Dimesylates for the Synthesis of Alkylcyclopropanes

2.1 Introduction

Cross-electrophile coupling (XEC) reactions have the potential to construct carbon-carbon bonds in an efficient manner.[1] To favor cross-reactivity, reactions often pair two substrates of different reactivity, in part to differentiate oxidative addition events.[2] For example, development of aryl-alkyl XEC reactions have been fruitful.[2d,e,3] Reactions that combine two substrates with similar reactivity can be challenging and result in homocoupled products.[4] As such, many known examples of nickel-catalyzed XEC reactions that forge Csp^3–Csp^3 bonds employ one activated substrate as a coupling partner, e.g., allylic or benzylic electrophiles.[2d,e,5,6,7,8] There are few examples of nickel-catalyzed XEC reactions that engage two unactivated alkyl electrophiles.[9,10]

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[1] Portions of this Chapter were originally published in Journal of the American Chemical Society: Sanford, A. B.; Thane, T. T.; McGinnis, T. M.; Chen, P.–P.; Hong, X.; Jarvo, E. R. *J. Am. Chem. Soc.* **2020**, *142*, 5017–5023.

[2] (a) Biswas, S.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 16192–16197. (b) Everson, D. A.; Weix, D. J. *J. Org. Chem*. **2014**, *79*, 4793–4798. (c) Weix, D. J. *Acc. Chem. Res*. **2015**, *48*, 1767–1775. (d) Knappke, C. E. I.; Grupe, S.; Gärtner, D.; Corpet, M.; Gosmini, C.; Jacobi von Wangelin, A. *Chem. Eur. J.* **2014**, *20*, 6828–6842. (e) Wang, X.; Dai, Y.; Gong, H. *Top. Curr. Chem.* **2016**, *374*, 43.

[3] For an example, see: Everson, D. A.; Jones, B. A.; Weix, D. J. *J. Am. Chem. Soc*. **2012**, *134*, 6146–6159.

[4] For a recent discussion and solution in the context of vinyl electrophiles, see: Olivares, A. M.; Weix, D. J. *J. Am. Chem. Soc*. **2018**, *140*, 2446–2449.

[5] Lucas, E. L.; Jarvo, E. R. *Nat. Rev. Chem.* **2017**, *1*, 0065.

[6] (a) Tollefson, E. J.; Erickson, L. W. Jarvo, E. R. *J. Am. Chem. Soc.* **2015**, *137*, 9760. (b) Erickson, L. W. Lucas, E. L.; Tollefson, E. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2016**, *138*, 14006–14011. (c) Konev, M. O.; Hanna, L. E.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2006**, *55*, 6730–6733.

[7] For allylic XEC with alkyl halides, see: (a) Dai, Y.; Wu, F.; Zang, Z.; You, H.; Gong, H. *Chem. Eur. J*. **2012**, *18*, 808–812. (b) Yu, Y.; Chen, H.; Qian, Q.; Yao, K.; Gong, H. *Tetrahedron* **2018**, *74*, 5651–5658.

[8] Examples of other activated C_{sp}^3 electrophiles that have been paired with alkyl halides in Ni-catalyzed XEC reactions: (a) methyl *p*-toluenesulfonate: Liang, Z.; Xue, W.; Lin, K.; Gong, H. *Org. Lett*. **2014**, *16*, 5620–5623. (b) Primary alkyl Katritzky salts: Ni, S.; Li, C.-X.; Mao, L.; Wang, Y.; Han, J.; Pan, Y. *Sci. Adv.* **2019**, *5*: eaaw9516. (c) Togni's reagent: Chen, Y.; Ma, G.; Gong, H. *Org. Lett.* **2018**, *20*, 4677–4680.

[9] (a) Gu, J.; Wang, X.; Xue, W.; Gong, H. *Org. Chem. Front*. **2015**, *2*, 1411–1421. (b) Yu, X.; Yang, T.; Wang, S.; Xu, H.; Gong, H. *Org. Lett*. **2011**, *13*, 2138–2141. (c) Xu, H.; Zhao, C.; Qian, Q.; Deng, W.; Gong, H. *Chem. Sci*. **2013**, *4*, 4022–4029. (d) Xue, W.; Xu, H.; Liang, Z.; Qian, Q.; Gong, H. *Org. Lett*. **2014**, *16*, 4984–4987.

[10] A successful strategy is to employ only one partner that will generate an alkyl radical under photocatalytic conditions. For a lead reference, see: Smith, R. T.; Zhang, X.; Rincón, J. A.; Agejas, J.; Mateos, C.; Barberis, M.; Garcia-Cerrada, S.; de Frutos, O.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2018**, *140*, 17433–17438.

Development of an XEC reaction that employs readily-available, unactivated alkyl electrophiles as ***both*** reactive partners would significantly expand the scope of these transformations.

A 1,3-diol is a compelling functional group motif for use in XEC reactions. Largely due to their prevalence in polyketides, 1,3-diols have robust, well-established synthetic routes for their preparation.[11] For example, substituted 1,3-diols are easily accessed through the reduction of aldol products. We hypothesized that sulfonates derived from 1,3-diols would be engaged by a nickel catalyst and undergo an intramolecular XEC reaction to form cyclopropanes. Furthermore, since aldol reactions can provide outstanding levels of enantioselectivity,[12] this strategy could provide straightforward and predictable access to enantioenriched cyclopropanes, leveraging a well-established and powerful field. Additionally, these reactions would complement traditional asymmetric cyclopropanation routes that typically engage alkene starting materials.[13]

Alkyl sulfonates have a history of use in nickel-catalyzed cross-coupling (XC) and XEC reactions.[14,15,16] Notably, sulfonates utilized in these reactions are frequently generated in situ from

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[11] For selected reviews, see: a) Rychnovsky, S. D. *Chem. Rev*. **1995**, *95*, 2021–2040. b) Bode, S. E.; Wolberg, M.; Müller, M. *Synthesis* **2006**, *4*, 557-588. c) Gupta, P.; Mahajan, N.; Taneja, S. C. *Catal. Sci. Technol*. **2013**, *3*, 2462–2480.

[12] For selected reviews, see: (a) Yamashita, Y.; Yasukawa, T.; Yoo, W. J.; Kitanosono, Kobayashi, S. *Chem Soc. Rev.* **2018**, *47*, 4388–4480. (b) Cowden, C. J.; Paterson, I. Asymmetric Aldol Reactions Using Boron Enolates. *Organic Reactions*; Paquette, L. A., Ed.; Wiley: New York, 1997; Vol. 51; pp 1–200.

[13] Due to their interesting structural and biological properties, several strategies for cyclopropane synthesis have been reported and frequently employ carbenes and carbenoids. For reviews, see: (a) Ebner, C.; Carreira, E. *Chem. Rev*. **2017**, *117*, 11651–11679. (b) Lebel, H.; Marcoux, J. –F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977–1050. (c) Bartoli, G.; Bencivenni, G.; Dalpozzo, R. *Synthesis* **2014**, *46*, 979–1029. (d) Wu, W.; Lin, Z.; Jiang, H. *Org. Biomol. Chem.* **2018**, *16*, 7315–7329.

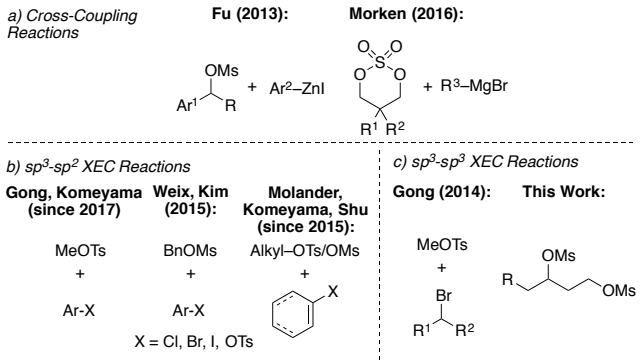
[14] For review of phenol derivatives, ***aryl*** triflates and ***aryl*** sulfonates, in traditional cross-coupling reactions, see: Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. *Chem. Rev*. **2011**, *111*, 1346–1416. (b) for a lead reference, see: Hofmayer, M. S.; Lutter, F. H.; Grokenberger, L.; Hammann, J. M.; Knochel, P. *Org. Lett*. **2019**, *21*, 36–39.

[15] For reviews and a lead reference for ***aryl*** triflates in XEC, see: (a) reference 2 (b) Huang, L.; Ackerman, L. K. G.; Kang, K.; Parson, A. M.; Weix, D. J. *J. Am. Chem. Soc*. **2019**, *141*, 10978–10983.

[16] For representative lead references for XC and XEC reactions of aryl and alkyl sulfonates with alternative metal catalysts, see: (a) reference 2d. Cu: (b) Burns, D. H.; Miller, J. D.; Chan, H.–K.; Delaney, M. O. *J. Am. Chem. Soc*. **1997**, *119*, 2125–2133. (c) Terao, J.; Kambe, N. *Acc. Chem. Res.* **2008**, *41*, 1545–1554. (d) Liu, J.–H. Yang, C.–T.; Lu, X.–Y.; Zhang, Z.–Q.; Xu, L.; Cui, M.; Lu, X.; Xiao, B.; Fu, Y.; Liu, L. *Chem. Eur. J.* **2014**, *20*, 15334–15338. Fe: (e) Furstner, A.; Leitner, A.; Mendez, M.; M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863. (f) Atack, T. C.; Lecker, R. M. Cook, S. P. *J. Am. Chem. Soc.* **2014**, *136*, 9521–9523.

the corresponding alcohols. In the context of cross-coupling reactions, nickel-catalyzed Negishi couplings of benzylic mesylates and Kumada reactions of cyclic sulfates have been reported (Scheme 2.1a). [17,18] The use of alkyl sulfonates as electrophiles in nickel-catalyzed XEC reactions developed contemporaneously, beginning with homocoupling reactions.[19] Chemoselective XEC reactions have utilized alkyl sulfonates with aryl and vinyl halides and pseudohalides (Scheme 2.1b).[20,21,22] Cross-selective pairing of two alkyl sulfonates was demonstrated using methyl tosylate (Scheme 2.1c).[8a,23] However, to the best of our knowledge, no cross-selective XEC reaction of two primary or secondary alkyl sulfonates has been reported. Based on the accessibility of 1,3-diols and reactivity of sulfonates, we sought to develop a nickel-catalyzed XEC reaction of two alkyl mesylates for cyclopropane synthesis (Scheme 2.1c).[13]

Scheme 2.1 Nickel-catalyzed XC and XEC reactions of alkyl sulfates and sulfonates



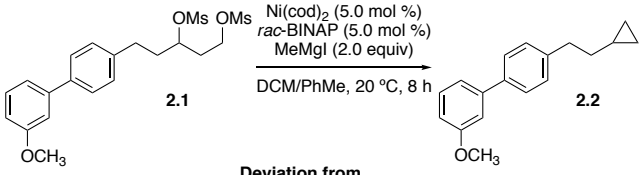
[17] Do, H. Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc*. **2013**, *135*, 16288–16291.
[18] Eno, M. S.; Lu, A.; Morken, J. P. *J. Am. Chem. Soc*. **2016**, *138*, 7824–7827.
[19] (a) Prinsell, M. R.; Everson, D. A.; Weix, D. J. *Chem. Commun*. **2010**, *46*, 5743–5745. (b) Komeyama, K.; Tsunemitsu R.; Michiyuki, T.; Yoshida, H.; Osaka, I. *Molecule*s **2019**, *24*, 1458.
[20] Methyl sulfonates: (a) Wang, J.; Zhao, J.; Gong, H. *Chem. Commun*. **2017**, *53*, 10180–10183. (b) Komeyama, K.; Yamahata, Y.; Osaka, I. *Org. Lett*. **2018**, *20*, 4375–4378.
[21] Benzylic sulfonates (a) Ackerman, L. K. G.; Anka-Lufford, L. L.; Naodovic, M.; Weix, D. J. *Chem. Sci.* **2015**, *6*, 1115–1119. (b) Jung, H.-S.; Kim, S.-H. *Synlett* **2015**, *26*, 666–670.
[22] Primary and secondary alkyl sulfonates: (a) Molander, G. A.; Traister, K. M.; O'Neill, B. T. *J. Org. Chem.* **2015**, *80*, 2907–2911. (b) Komeyama, K.; Ohata, R.; Kiguchi, S.; Osaka, I. *Chem. Commun*. **2017**, *53*, 6401–6404. (c) Duan, J.; Du, Y.-F.; Pang, X.; Shu, X.-Z. *Chem. Sci.* **2019**, *10*, 8706–8712.
[23] XEC of primary alkyl tosylates with secondary alkyl bromides was reported during preparation of this manuscript: Komeyama, K.; Michiyuki, T.; Osaka, I. *ACS Catal.* **2019**, *9*, 9285–9291.

2.2 Results and Discussion

2.2.1 Optimization of Reaction Conditions

I began our investigation by employing 1,3-dimesylate **2.1**. This substrate was designed to provide an alkylcyclopropane with low volatility to facilitate isolation and analysis. I evaluated a series of ligands in the presence of $Ni(cod)_2$ and methylmagnesium iodide (MeMgI) in DCM/PhMe (Table 2.1). The diphosphine ligands *rac*-BINAP and dppm, in addition to the pyridyl ligand Bphen, produced the highest yields of cyclopropane **2.2** (entries 1–3). Additionally, a 70% yield of the desired cyclopropane was achieved utilizing bench-stable ((*R*)-BINAP)$NiCl_2$ as the catalyst (entry 9). In general, across a range of substrates, *rac*-BINAP and dppm provided robust reaction yields, and so we selected these ligands for further experiments.

Table 2.1 Ligand evaluation of XEC reaction of unactivated 1,3-dimesylates



Entry	Deviation from reaction conditions	Yield[a] (%)
1	none	75
2	BPhen	78
3	dppm	71
4	PCy_3	56
5	DPEPhos	44
6	SiMes•HBF_4	33
7	Xantphos	16
8	no ligand	13
9	((*R*)-BINAP)$NiCl_2$	70
10	PhMgBr	5
11	PhMgBr + MgI_2	17
12	no Ni, no ligand	5
13	no MeMgI	0

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

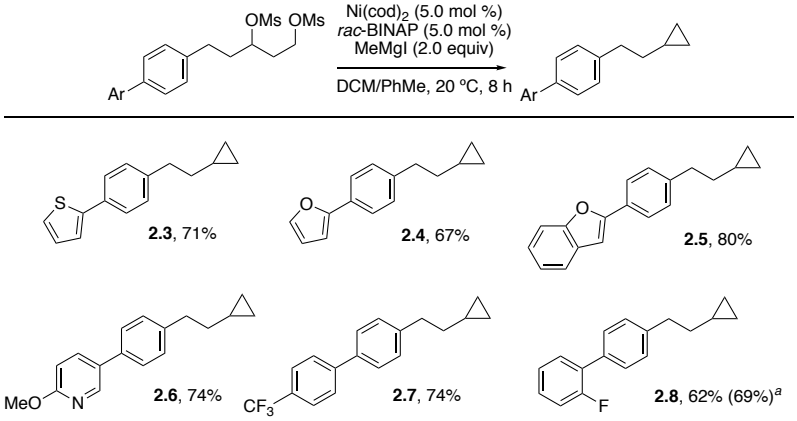
Following the ligand evaluation, I next investigated the importance of the Grignard reagent and nickel catalyst. Modifying the Grignard reagent to phenylmagnesium bromide almost completely shut down the reaction, with 5% of the desired cyclopropane observed (entry 10). Adding MgI_2 to PhMgBr reaction conditions provided a similar result (entry 11). A control

reaction without nickel and ligand (MeMgI only) produced a 5% yield of the desired cyclopropane (entry 12), while a control reaction in the absence of MeMgI provided no conversion to the desired cyclopropane and only recovered starting material (entry 13).

2.2.2 Substrate Scope

With optimized conditions in hand, I investigated the tolerance of various substituted aromatic and heterocyclic groups (Scheme 2.2). Isolated yields are reported, however for certain substrates volatility or polarity complicated isolation. Therefore, yield determined by ^{1}H NMR by comparison to an internal standard is also reported. Heterocycles such as thiophene, furan, and benzofuran were well tolerated under the reaction conditions (**2.3**–**2.5**), as was the substituted heterocycle 2-methoxypyridine (**2.6**). Electron-donating groups were well tolerated in the synthesis of **2.2**, as well as electron-withdrawing groups such as aryl CF_3 and aryl fluoride (**2.7**, **2.8**).

Scheme 2.2 Unbranched alkylcyclopropanes

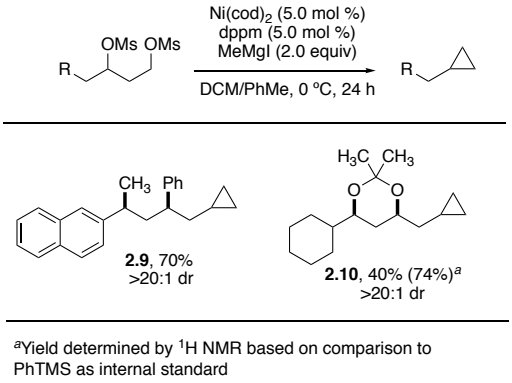


[a]Yield determined by ^{1}H NMR based on comparison to PhTMS as internal standard

Next, I focused on testing the impact of steric bulk near the forming cyclopropane (Scheme 2.3). For compounds such as **2.9**, standard reaction conditions employing *rac*-BINAP as the ligand provided modest yields. Fortunately, we found that for these more hindered substrates,

using dppm as the ligand and performing the reaction at 0 ºC provided good yields.[1] A series of alkyl and aryl groups were well tolerated in the β-position relative to the cyclopropane (**2.9**–**2.10**). For example, the diol precursor for cyclopropane **2.9** was prepared by a stereospecific Kumada ring-opening reaction.[24] Acetonide **2.10** was formed smoothly from the corresponding tetraol derivative, demonstrating tolerance to a typical protecting group employed in polyketide synthesis. These results confirm that—in contrast to our laboratory's previously published XC and XEC reactions—this XEC reaction does not require benzylic or allylic electrophiles to engage the nickel catalyst.[6a,6b,25]

Scheme 2.3 Branched alkylcyclopropanes



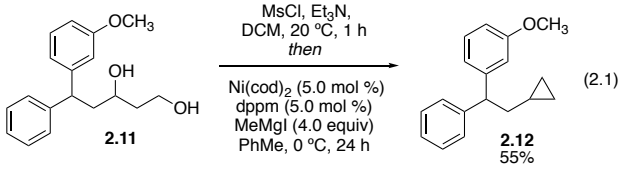
[a]Yield determined by ^{1}H NMR based on comparison to PhTMS as internal standard

2.2.3 1,3-Diol to Cyclopropane

The potential impact of this transformation would be expanded if 1,3-diols could be employed as starting materials for the reaction. We were encouraged that other XC and XEC reactions that employ sulfonates generated in situ have been reported.[17,21a] I developed a procedure where diol **23** was treated with MsCl and base, followed by addition to catalyst and Grignard reagent. Cyclopropane **2.12** was formed in moderate yield, similar to that observed when

[24] Tollefson, E. J.; Dawson, D. D.; Osborne, C. A.; Jarvo, E. R. *J. Am. Chem. Soc.* **2014**, *136*, 14951.
[25] Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, S.; Tollefson, E. J.; Erickson, L. E.; Taylor, B. L.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835–5855.

employing the corresponding 1,3-dimesylate. Therefore, this method allows direct conversion of a 1,3-diol to the corresponding cyclopropane (eq 2.1).

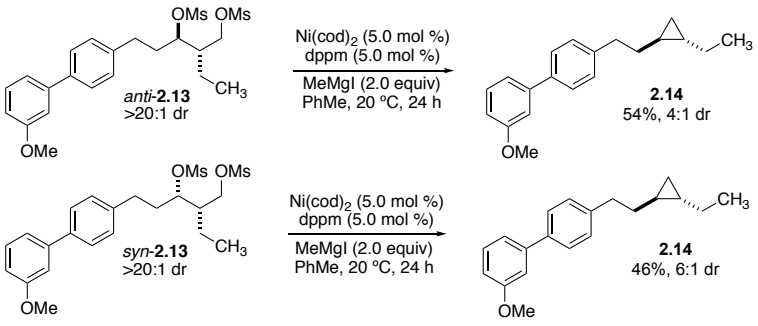


(2.1)

2.2.4 1,2-Disubstituted Alkylcyclopropanes

Computational and experimental data suggests a mechanism that proceeds through a 1,3-diiodide with a stereoablative oxidative addition at the secondary center.[1] To further corroborate our proposed mechanism, I sought to determine the stereochemical outcome of the XEC reaction. Since oxidative addition of the 2° alkyl iodide is predicted to proceed via the alkyl radical, reactions are expected to be stereoablative.[5] Consistent with this hypothesis, I observed a stereoconvergent XEC reaction to form 1,2-disubstituted cyclopropane **2.14** (Scheme 2.4). Either diastereomer of 1,3-dimesylate **2.13** provides *trans*-cyclopropane **2.14**, consistent with epimerization via an alkyl radical intermediate.

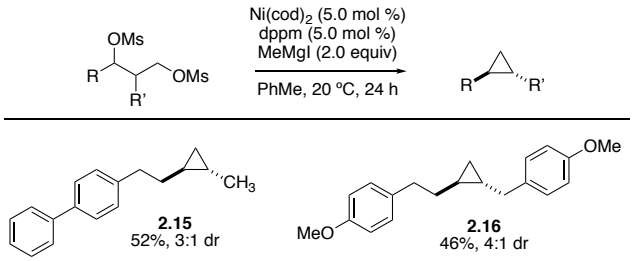
Scheme 2.4 Stereoconvergent XEC reactions



Given the yield and diastereoselectivity observed in Scheme 2.4, I set out to apply our transformation to 1,2-disubstituted alkylcyclopropanes (Scheme 2.5). The corresponding diols

were prepared by aldol or Claisen transformations.[26] Compounds **2.15**–**2.16** were formed in moderate to good yield with preference for the trans diastereomer.

Scheme 2.5 1,2-Disubstituted cyclopropanes

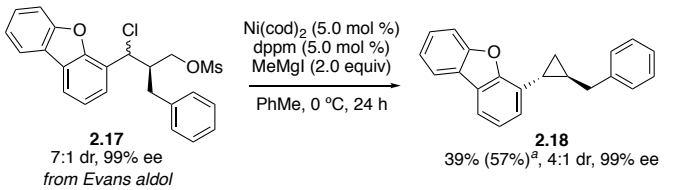


2.2.5 Evans Aldol to Enantioenriched Cyclopropane

Based on our understanding of the reaction mechanism and observed levels of diastereoselectivity, I set out to synthesize enantioenriched 1,2-disubstituted cyclopropanes (Scheme 2.6). An Evans aldol reaction was employed to prepare the corresponding substituted 1,3-diol with high enantioselectivity.[27] Utilizing our transformation, arylcyclopropane **2.18** was formed with high enantiomeric excess. Configuration at C2 is conserved through the XEC reaction. The reaction favors formation of the *trans*-cyclopropane, setting the configuration of C1. Notably, compound **2.18** does not bear the signature directing groups or acyl substitution required for direct synthesis by other asymmetric cyclopropanation methods.[13]

[26] (a) von Richter, V. *Chem. Berichte* **1869**, *2*, 552–553. (b) Claisen, L.; Claparede, A. *Chem. Berichte* **1881**, *14*, 2460–2468. (c) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066–1081.
[27] Evans, D. A.; Bartoli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127–2129.

Scheme 2.6 Enantioenriched 1,2-disubstituted cyclopropane



2.17
7:1 dr, 99% ee
from Evans aldol

2.18
39% (57%)[a], 4:1 dr, 99% ee

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

2.3 Conclusion

In summary, we report a nickel-catalyzed cross-electrophile coupling reaction of 1,3-dimesylates for the synthesis of alkylcyclopropanes. This transformation does not require activation of either electrophilic partner, and engages two alkyl mesylates. Furthermore, direct transformation of a 1,3-diol to the corresponding cyclopropane was established. Synthesis of 1,2-disubstituted cyclopropanes is a stereoconvergent process consistent with the proposed mechanism of oxidative addition, and favors the trans diastereomer. The product of an enantioselective aldol reaction was transformed to the corresponding enantioenriched cyclopropane, therefore capitalizing on outstanding strategies of 1,3-diol synthesis.

2.4 Experimental Details

2.4.1 General Procedures

All reactions were carried out under a N_2 atmosphere, unless otherwise stated. All glassware was either oven-dried or flame-dried prior to use. Toluene (PhMe), diethyl ether (Et_2O), dichloromethane (DCM), hexanes (hex), triethylamine (Et_3N), and tetrahyrdofuran (THF) were degassed with argon and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 hours) to remove H_2O. Other solvents were purchased "anhydrous" commercially, or were purified as described. ^{1}H NMR were recorded on Bruker DRX-400 (400 MHz ^{1}H, 100 MHz ^{13}C), CRYO-500 (500 MHz ^{1}H, 125.7 MHz ^{13}C), GN-500 (500 MHz ^{1}H, 125.7 MHz ^{13}C), or AVANCE-600 (150

MHz ^{13}C, 564.6 MHz ^{19}F) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00) unless otherwise noted. Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), doublet of triplets (dt), triplet of doublets (td), doublet of doublet of triplets (ddt), quartet (q), quintet (quint), quintet of triplets (quintt), quintet of doublets (quintd), sextet (sext), septet (sept), octet (oct), nonuplet (non), multiplet (m), apparent singlet (ap s), apparent doublet (ad), apparent triplet (at), apparent quartet (aq), apparent quintet (aquint)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the solvent resonance as the internal standard ($CDCl_3$, δ 77.16 ppm). NMR data were collected at 25 °C. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60Å F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with *p*-anisaldehyde (PAA), cerium ammonium molybdate (CAM), or potassium permanganate ($KMnO_4$) solutions. Flash chromatography was performed using either SiliaFlash F60 (40- 63 μm, 60 Å) from SiliCycle, or Teledyne Isco Combiflash® Rf+ automated flash chromatography system. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. GC/FID analysis for competition experiments was performed on Agilent 7820A system with helium as carrier gas. For reactions perfomed at rt, average room temperature was 20 ºC.

Bis(1,5-cyclooctadiene)nickel was purchased from Strem, stored in a glove box freezer (–20 °C) under an atmosphere of N_2 and used as received. All ligands were purchased from Strem or Sigma Aldrich and were stored under N_2 atmosphere and used as received. All Grignard reagents were

titrated with iodine prior to use.[28] All other chemicals were purchased commercially and used as received, unless otherwise noted.

2.4.2 General Cross-Electrophile Coupling Procedures

2.4.2.1 Method A: Cross-Electrophile Coupling for Synthesis of Unbranched Alkylcyclopropanes

In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with substrate (1.0 equiv), $Ni(cod)_2$ (5.0 mol %), *rac*-BINAP (5.0 mol %), DCM (up to 0.30 M in substrate), and PhMe (0.10 M in substrate). If substrate was still a precipitate once solvent was added, reaction was stirred until substrate was dissolved, usually ~20 min. Once reaction mixture was homogenous, methylmagnesium iodide (2.0 equiv) was added added slowly over 15–20 seconds. The reaction stirred at rt for 8 h unless otherwise noted. Then the reaction was removed from the glovebox, quenched with methanol (2 mL), filtered through a plug of silica gel (eluting with 100% Et_2O), and concentrated in vacuo.

2.4.2.2 Preparation of Methylmagnesium Iodide

Under an N_2 atmosphere, to a 3-necked round bottom flask equipped with a stir bar, reflux condenser, and Schlenk filtration apparatus was added magnesium turnings (2.80 g, 120 mmol, 1.50 equiv). The flask and magnesium turnings were flame-dried under vacuum and the flask was back-filled with N_2. A crystal of iodine (ca. 2 mg) was added to the flask, followed by anhydrous Et_2O (25 mL). The reaction mixture was brought to 0 °C, and freshly distilled iodomethane (5.0 mL, 82 mmol, 1.0 equiv) was slowly added over 30 min to maintain a gentle reflux. The mixture was stirred for 4 h at room temperature then filtered through the fritted Schlenk filter into a pear-shaped flask under N_2 atmosphere. The magnesium turnings were washed with Et_2O (2 x 1.0 mL)

[28] Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890–891.

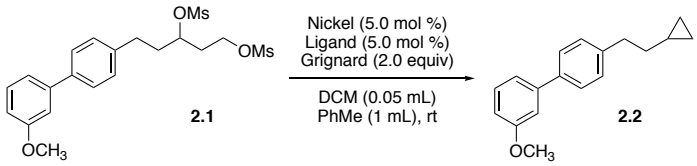
then the Schlenk bomb was sealed, removed, and placed under an argon atmosphere. The resulting methyl Grignard reagent was typically between 2.4 and 3.0 M as titrated by Knochel's method[28] and was stored in a glovebox for up to 8 weeks.

2.4.2.3 Preparation of Phenylmagnesium Bromide

A 2-necked round-bottom flask equipped with a stir bar and reflux condenser was charged with magnesium turnings (3.0 equiv). The reaction apparatus was flame-dried under vacuum and back-filled under N_2. Anhydrous Et_2O and a crystal of iodine (ca. 2 mg) were added to the flask. Aryl or (1.0 equiv) was added slowly over 30 min to maintain a gentle reflux. The mixture was stirred for 2 h at room temperature. The resulting Grignard reagent was typically between 0.8 and 1.5 M as titrated by Knochel's method.[28]

2.4.2.4 XEC Reaction Optimization

Table 2.2 Optimization of 1,3-dimesylate **2.1** in the XEC reaction



	Nickel	Ligand	Grignard[a]	Additive	Time	Yield (%)[b]
Ligand	$Ni(cod)_2$	Xantphos	MeMgI	none	8 h	16
	$Ni(cod)_2$	DPEPhos	MeMgI	none	8 h	44
	$Ni(cod)_2$	bipy	MeMgI	none	8 h	57
	$Ni(cod)_2$	**BPhen**	**MeMgI**	**none**	**8 h**	**78**
	$Ni(cod)_2$	Simes•HBF_4	MeMgI	none	8 h	33
	$Ni(cod)_2$	dppf	MeMgI	none	8 h	66
	$Ni(cod)_2$	PCy_3	MeMgI	none	8 h	56
	$Ni(cod)_2$	dppe	MeMgI	none	8 h	39
	$Ni(cod)_2$	***rac*-BINAP**	**MeMgI**	**none**	**8 h**	**75**
	$Ni(cod)_2$	**dppm**	**MeMgI**	**none**	**8 h**	**71**
	$Ni(cod)_2$	none	MeMgI	none	8 h	13
MeMgI conc.	$Ni(cod)_2$	*rac*-BINAP	MeMgI (2.05 M)	none	24 h	82
	$Ni(cod)_2$	*rac*-BINAP	MeMgI (1 M)	none	24 h	69
Controls	none	none	MeMgI	none	8 h	5
	$Ni(cod)_2$	*rac*-BINAP	none	none	24 h	0[c]
PhMgBr	$Ni(cod)_2$	*rac*-BINAP	PhMgBr	none	8 h	5
	$Ni(cod)_2$	*rac*-BINAP	PhMgBr	MgI_2 (2 equiv)	8 h	17
Pre-formed catalyst	(*R*-BINAP)$NiCl_2$	none	MeMgI	none	8 h	70
Ditosylate	$Ni(cod)_2$	*rac*-BINAP	MeMgI	none	8 h	89 (72)[d]

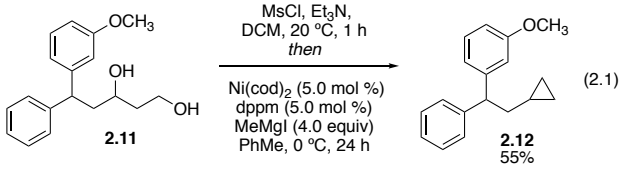
All reactions performed on 0.1 mmol scale. [a]Unless specified, MeMgI concentration is 2.5 M. [b]Yield determined by ^1H NMR by comparison to PhTMS as internal standard. [c]Recovered 90% starting material (dimesylate) by NMR. [d]Isolated yield.

2.4.2.5 Method B: Cross-Electrophile Coupling for Synthesis of Aryl and β-Branched Alkylcyclopropanes and 1,2-Disubsitituted Cyclopropanes

For monosubstituted cyclopropanes: In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with substrate (1.0 equiv), $Ni(cod)_2$ (5.0 mol %), dppm (5.0 mol %), DCM (up to 0.30 M in substrate), and PhMe (0.10–0.20 M in substrate). If substrate was still a precipitate once solvent was added, reaction was stirred until substrate was dissolved, usually ~20 min. Once reaction mixture was homogenous, MeMgI was drawn in a syringe, and both reaction and MeMgI were removed from glovebox and cooled to 0ºC. After 15 min, MeMgI was added slowly over 15–

20 seconds. The reaction stirred at 0 ºC for 24 h. Then the reaction was quenched with methanol (2 mL), filtered through a plug of silica gel (eluted with 100% Et_2O), and concentrated in vacuo. For 1,2-disubstituted alkylcyclopropanes, the same procedure above was used with the exception of temperature. All XECs to synthesize 1,2-disubstituted alkylcyclopropanes were stirred at rt unless otherwise noted.

2.4.2.6 XEC Method of Diol 2.11

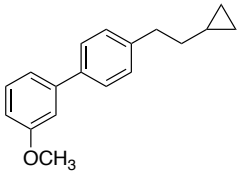


(2.1)

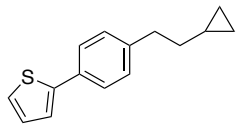
A flame-dried 7 mL vial equipped with a stir bar was charged with substrate **2.11** (1.0 equiv), DCM (0.2 M in substrate), and anhydrous Et_3N (2.0 equiv) under N_2 at rt. Reaction stirred for 5 min, then MsCl (2.0 equiv) was added, and reaction stirred for 1 h. In a glovebox, a separate flame-dried 7 mL vial was charged with $Ni(cod)_2$ (5.0 mol %), dppm (5.0 mol %), and PhMe (0.20 M in substrate). MeMgI (4.0 equiv) was drawn in a syringe, and both vial and syringe were removed from glovebox, and the vial was placed under N_2. The reaction mixture from the mesylation was then transferred via syringe to the vial containing $Ni(cod)_2$ and dppm, and both reaction and MeMgI syringe were cooled to 0ºC. After 15 min, MeMgI was added slowly over 15–20 seconds. Upon addition of MeMgI, the reaction was vented. The reaction stirred at 0 ºC for 24 h. Then the reaction was quenched with methanol (2 mL), filtered through a plug of silica gel (neat Et_2O), and concentrated in vacuo.

2.4.3 Characterization Data for Cyclopropanes 2.2–2.10

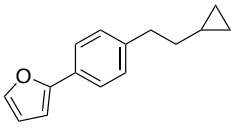
2.4.3.1 Unbranched Alkylcyclopropanes



4'-(2-Cyclopropylethyl)-3-methoxy-1,1'-biphenyl (2.2) was prepared according to Method A. The reaction was performed on a 0.1 mmol scale to obtain a ^{1}H NMR yield and on a 0.2 mmol scale to isolate the product. For 0.1 mmol scale, the following amounts of reagents were used: $Ni(cod)_2$ (1.4 mg, 5.0 μmol, 5.0 mol %), *rac*-BINAP (3.1 mg, 5.0 μmol, 5.0 mol %), substrate **2.1** (44.2 mg, 0.10 mmol, 1.0 equiv), DCM (0.10 mL), PhMe (1.0 mL, 0.10 M in substrate), and MeMgI (0.08 mL, 0.2 mmol, 2.5 M in Et_2O, 2 equiv). A ^{1}H NMR yield of 75% was obtained based on comparison to PhTMS as internal standard. For 0.2 mmol scale, the following amounts of reagents were used: $Ni(cod)_2$ (2.6 mg, 9.5 μmol, 5.0 mol %), *rac*-BINAP (5.9 mg, 9.5 μmol, 5.0 mol %), substrate **2.1** (85 mg, 0.19 mmol, 1.0 equiv), DCM (0.30 mL), PhMe (1.9 mL, 0.10 M in substrate), and MeMgI (0.14 mL, 0.38 mmol, 2.8 M in Et_2O, 2.0 equiv). The compound was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (36 mg, 0.14 mmol, 74%). **TLC R_f** = 0.7 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.11 (s, 1H), 6.87 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.85 (s, 3H), 2.75 (t, *J* = 7.7 Hz, 2H), 1.55 (q, *J* = 7.1 Hz, 2H), 0.78–0.68 (m, 1H), 0.44 (aq, *J* = 5.7 Hz, 2H), 0.06 (q, *J* = 5.1 Hz, 2H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 160.1, 142.9, 142.2, 138.6, 129.8, 129.0 (2C), 127.1 (2C), 119.7, 112.9, 112.5, 55.4, 36.8, 35.8, 10.9, 4.7 (2C); **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{18}H_{20}O$, 252.1514; found, 252.1520.

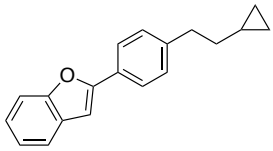


2-(4-(2-Cyclopropylethyl)phenyl)thiophene (2.3) was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), *rac*-BINAP (6.2 mg, 10 μmol, 5.0 mol %), substrate **2.25** (84 mg, 0.20 mmol, 1.0 equiv), DCM (0.30 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.15 mL, 0.40 mmol, 2.6 M in Et_2O, 2.0 equiv). Before purification, a ^1H NMR yield of 75% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (32 mg, 0.14 mmol, 71%). **TLC R_f** = 0.6 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.26 (ad, *J* = 3.3 Hz, 1H), 7.22 (ad, *J* = 4.9 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.05 (dd, *J* = 5.1, 3.5 Hz, 1H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.52 (q, *J* = 7.6 Hz, 2H) 0.76–0.66 (m, 1H), 0.42 (aq, *J* = 4.8 Hz, 2H), 0.05 (q, *J* = 4.7 Hz, 2H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 144.8, 142.3, 132.0, 129.1 (2C), 128.0, 126.0 (2C), 124.4, 122.7, 36.8, 35.8, 10.9, 4.7 (2C); **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{15}H_{16}S$, 228.0973; found, 228.0974.

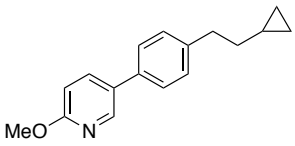


2-(4-(2-Cyclopropylethyl)phenyl)furan (2.4) was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), *rac*-BINAP (6.2 mg, 10. μmol, 5.0 mol %), substrate **2.27** (80. mg, 0.20 mmol, 1.0 equiv), DCM (0.30 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.15 mL, 0.40 mmol, 2.6 M in Et_2O, 2.0 equiv). Before purification, a ^1H NMR yield of 65% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (100% hexanes)

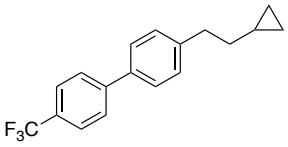
to afford the title compound as a colorless oil (29 mg, 0.13 mmol, 67%). **TLC R_f** = 0.5 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.43 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 3.9 Hz, 1H), 6.44 (dd, *J* = 3.3, 1.8 Hz, 1H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.51 (q, *J* = 7.3 Hz, 2H), 0.75–0.65 (m, 1H), 0.42 (aq, *J* = 5.0 Hz, 2H), 0.04 (q, *J* = 4.8 Hz, 2H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 154.4, 142.1, 141.8, 128.9 (2C), 128.6, 123.9 (2C), 111.7, 104.4, 36.8, 35.9, 10.9, 4.7 (2C); **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{15}H_{16}O$, 212.1201; found, 212.1195.



2-(4-(2-Cyclopropylethyl)phenyl)benzofuran (2.5) was prepared according to modified Method A. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), *rac*-BINAP (6.2 mg, 10. μmol, 5.0 mol %), substrate **2.29** (90. mg, 0.20 mmol, 1.0 equiv), DCM (0.20 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.15 mL, 0.40 mmol, 2.6 M in Et_2O, 2.0 equiv). This reaction was allowed to stir 24 h. Before purification, a ^{1}H NMR yield of 75% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (100% hexanes) to afford the title compound as a white solid (42 mg, 0.16 mmol, 80%). **m.p.** = 67–69 ºC. **TLC R_f** = 0.5 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.28–7.23 (m, 3H), 7.21 (td, *J* = 7.0, 1.4 Hz, 1H), 6.95 (s, 1H), 2.74 (t, *J* = 7.8 Hz, 2H), 1.54 (q, *J* = 7.0 Hz, 2H), 0.76–0.67 (m, 1H), 0.43 (aq, *J* = 4.8 Hz, 2H), 0.05 (q, *J* = 5.0 Hz, 2H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 156.4, 155.0, 143.6, 129.5, 129.1 (2C), 128.1, 125.0 (2C), 124.1, 123.0, 120.9, 111.2, 100.7, 36.7, 36.0, 10.9, 4.7 (2C); **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{19}H_{18}O$, 262.1258; found, 262.1360.

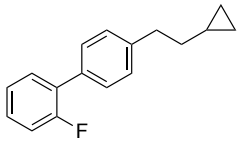


5-(4-(2-Cyclopropylethyl)phenyl)-2-methoxypyridine (2.6) was prepared according to a modified Method A. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), *rac*-BINAP (6.2 mg, 10. μmol, 5.0 mol %), substrate **2.31** (89 mg, 0.20 mmol, 1.0 equiv), DCM (0.30 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.15 mL, 0.40 mmol, 2.6 M in Et_2O, 2.0 equiv). The reaction was allowed to stir for 24 h. Before purification, a ^1H NMR yield of 73% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a light-yellow wax (37 mg, 0.15 mmol, 74%). **m.p.** = 27–30 ºC. **TLC R_f** = 0.7 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.54 (q, *J* = 7.4 Hz, 2H), 0.77–0.69 (m, 1H), 0.44 (ad, *J* = 8.3 Hz, 2H), 0.06 (ad, *J* = 5.0 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 163.6, 144.9, 142.1, 137.5, 135.4, 130.2, 129.2 (2C), 126.6 (2C), 110.9, 53.6, 36.8, 35.8, 10.9, 4.7 (2C); **HRMS** (TOF MS ES+) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{20}NO$, 254.1545; found, 254.1541.



4-(2-Cyclopropylethyl)-4'-(trifluoromethyl)-1,1'-biphenyl (2.7) was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), *rac*-BINAP (6.2 mg, 10. μmol, 5.0 mol %), substrate **2.33** (96 mg, 0.20 mmol, 1.0 equiv), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.15 mL, 0.40 mmol, 2.6 M in Et_2O, 2.0 equiv). Before

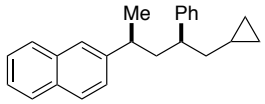
purification, a ^{1}H NMR yield of 73% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (100% hexanes) to afford the title compound as a white solid (43 mg, 0.15 mmol, 74%). **m.p.** = 71–74 ºC. **TLC R_f** = 0.6 (100% hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 1.55 (q, *J* = 7.6 Hz, 2H), 0.77–0.69 (m, 1H), 0.44 (aq, *J* = 5.0 Hz, 2H), 0.07 (q, *J* = 5.1 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 144.8, 143.1, 137.2, 129.3 (2C), 129.1 (q, *J* = 32.4 Hz, 1C), 127.3 (2C), 127.2 (2C), 125.8 (q, *J* = 3.7 Hz, 2C), 124.6 (q, *J* = 271.9 Hz, 1C), 36.8, 35.8, 10.9, 4.7 (2C); **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –62.3; **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{18}H_{17}F_3$, 290.1282; found, 290.1280.



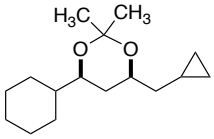
4'-(2-Cyclopropylethyl)-2-fluoro-1,1'-biphenyl (2.8) was prepared according to Method A. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), *rac*-BINAP (6.2 mg, 10. μmol, 5.0 mol %), substrate **2.35** (86 mg, 0.20 mmol, 1.0 equiv), DCM (0.10 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.15 mL, 0.40 mmol, 2.6 M in Et_2O, 2.0 equiv). Before purification, a ^{1}H NMR yield of 69% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (30. mg, 0.12 mmol, 62%). **TLC R_f** = 0.6 (100% hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.42 (td, *J* = 7.7, 1.7 Hz, 1H), 7.30–7.25 (m, 3H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 1H), 2.76 (t, *J* = 7.7 Hz, 2H), 1.55 (q, *J* = 7.3 Hz, 2H), 0.78–0.70 (m, 1H), 0.44 (aq, *J* = 5.5 Hz, 2H), 0.07 (q, *J* = 4.6 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 160.0 (d, *J* = 247.4 Hz, 1C), 142.2, 133.3, 130.8 (d, *J* = 3.7 Hz, 1C), 129.4 (d, *J* = 13.4 Hz, 1C), 129.0 (d, *J* = 3.2 Hz, 2C), 128.8 (d, *J* = 7.9 Hz, 1C), 128.7 (2C),

124.4 (d, J = 3.7 Hz, 1C), 116.2 (d, J = 22.7 Hz, 1C), 36.8, 35.9, 10.9, 4.7 (2C); **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ – 117.98 to –118.02 (m); **HRMS** (TOF MS ES+) *m/z*: $[M + NH_4]^+$ calcd for $C_{17}H_{21}FN$, 258.1658; found, 258.1647.

2.4.3.2 Branched Alkylcyclopropanes



2-((*syn*)-5-Cyclopropyl-4-phenylpentan-2-yl)naphthalene (2.9) was prepared according to Method B. The following amounts of reagents were used: $Ni(cod)_2$ (1.9 mg, 7.0 μmol, 5.0 mol %), dppm (2.7 mg, 7.0 μmol, 5.0 mol %), substrate **2.39** (72 mg, 0.14 mmol, 1.0 equiv), PhMe (1.0 mL, 0.14 M in substrate), and MeMgI (0.09 mL, 0.3 mmol, 2.9 M in Et_2O, 2 equiv). Before purification, a ^{1}H NMR yield of 70% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (100% hexanes) to afford the title compound as a colorless oil (31 mg, 0.10 mmol, 70%). **TLC R_f** = 0.4 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.75 (m, 3H), 7.46–7.40 (m, 3H), 7.31–7.26 (m, 3H), 7.22–7.17 (m, 1H), 7.08 (d, J = 6.9 Hz, 2H), 2.68–2.59 (m, 1H), 2.47–2.38 (m, 1H), 2.14 (ddd, J = 14.4, 10.7, 4.3 Hz, 1H), 1.94 (ddd, J = 14.4, 10.7, 4.4 Hz, 1H), 1.57–1.50 (m, 1H), 1.32–1.25 (m, 1H), 1.22 (d, J = 6.9 Hz, 3H), 0.44–0.37 (m, 1H), 0.27 (sept, J = 3.8 Hz, 1H), 0.19 (sept, J = 3.9 Hz, 1H), –0.13 (sext, J = 4.3 Hz, 1H), –0.20 (sext, J = 4.3 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 146.0, 144.7, 133.8, 132.4, 128.3 (2C), 128.15 (2C), 128.09, 127.74, 127.69, 126.0, 125.94, 125.92, 125.90, 125.2, 44.4, 44.3, 43.1, 37.8, 24.0, 9.3, 4.8, 4.6; **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{24}H_{26}$, 314.2035; found, 314.2033.



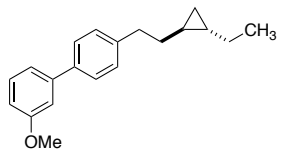
***cis*-4-Cyclohexyl-6-(cyclopropylmethyl)-2,2-dimethyl-1,3-dioxane (2.10)** was prepared according to modified Method B. The reaction was performed on a 0.18 mmol scale to obtain a ^{1}H NMR yield and on a 0.12 mmol scale to isolate the product. For the 0.18 mmol scale: the following amounts of reagents were used: $Ni(cod)_2$ (2.5 mg, 9.0 μmol, 5.0 mol %), dppm (3.5 mg, 9.0 μmol, 5.0 mol %), substrate **2.47** (81 mg, 0.18 mmol, 1.0 equiv), PhMe (1.8 mL, 0.10 M in substrate), and MeMgI (0.13 mL, 0.36 mmol, 2.8 M in Et_2O, 2.0 equiv). An NMR yield of 74% was obtained based on comparison to PhTMS as internal standard. The product was lost during isolation, presumably due to its volatility. For the 0.12 mmol scale: the following amounts of reagents were used: $Ni(cod)_2$ (3.0 mg, 11 μmol, 11 mol %), dppm (4.2 mg, 11 μmol, 11 mol %), substrate **2.47** (55 mg, 0.12 mmol, 1.0 equiv), PhMe (1.0 mL, 0.12 M in substrate), and MeMgI (0.31 mL, 0.44 mmol, 2.8 M in Et_2O, 3.7 equiv). The compound was purified by flash column chromatography (5% EtOAc/hexanes) to afford the title compound as a colorless oil (12 mg, 4.8 μmol, 40%). **TLC** $\mathbf{R_f}$ = 0.7 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.87 (quintd, *J* = 6.1, 2.5 Hz, 1H), 3.54 (ddd, *J* = 11.6, 7.1, 2.3 Hz, 1H), 1.91 (d, *J* = 12.2 Hz, 1H), 1.78–1.62 (m, 4H), 1.54–1.47 (m, 1H), 1.42 (s, 3H), 1.37 (s, 3H), 1.28–1.10 (m, 6H), 0.93 (aquint, *J* = 13.2 Hz, 3H), 0.78–0.68 (m, 1H), 0.43 (ad, *J* = 7.1 Hz, 2H), 0.05 (ap s, 2H); **^{13}C NMR** (100.7 MHz, $CDCl_3$) δ 98.3, 73.4, 69.8, 43.0, 41.8, 34.1, 30.5, 29.1, 28.2, 26.8, 26.3, 26.1, 20.0, 7.0, 4.7, 4.2; **HRMS** (TOF MS ES+) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{29}O_2$, 253.2168; found, 253.2162.

2.4.4 Stereochemical Proof

All 1,2-disubstituted cyclopropanes were isolated as a mixture of diastereomers, with the trans diastereomer as the major. This was determined by NOE spectroscopy performed on the

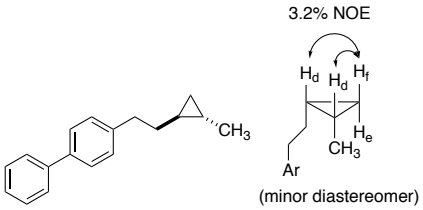
minor diastereomer of compound **2.15** (vide infra). All other 1,2-disubstituted cyclopropanes were assigned by analogy.

2.4.5 Characterization Data for 1,2-Disubstituted Alkylcyclopropanes



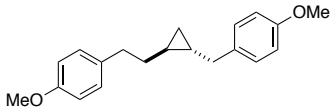
4'-(2-(2-Ethylcyclopropyl)ethyl)-3-methoxy-1,1'-biphenyl (2.14) was prepared according to Method B. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), dppm (3.8 mg, 10. μmol, 5.0 mol %), substrate *trans*-**2.13** (94 mg, 0.20 mmol, 1.0 equiv), DCM (0.20 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.14 mL, 0.40 mmol, 2.8 M in Et_2O, 2.0 equiv). Before purification, a ^{1}H NMR yield of 60% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (30. mg, 0.11 mmol, 54%, 4:1 dr). The compound was characterized as a 4:1 (trans:cis) mixture of diastereomers. **TLC** $\mathbf{R_f}$ = 0.3 (100% hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H, major, 2H, minor), 7.33 (t, *J* = 7.9 Hz, 1H, major, 1H, minor), 7.24 (d, *J* = 8.3 Hz, 2H, major, 2H, minor), 7.16 (d, *J* = 7.4 Hz, 1H, major, 1H, minor), 7.11 (t, *J* = 2.4 Hz, 1H, major, 1H, minor), 6.86 (dd, *J* = 8.1, 2.3 Hz, 1H, major, 1H, minor), 3.85 (s, 3H, major, 3H, minor), 2.72 (t, *J* = 7.7 Hz, 2H, major, 2H, minor), 1.75 (sext, *J* = 7.0 Hz, 1H, minor), 1.59 (sext, *J* = 7.0 Hz, 1H, major), 1.54–1.44 (m, 1H, major), 1.40 (sext, *J* = 6.9 Hz, 1H, minor), 1.30–1.13 (m, 2H, major, 2H, minor), 1.00 (t, *J* = 7.3 Hz, 3H, minor), 0.94 (t, *J* = 7.3 Hz, 3H, major), 0.79–0.66 (m, 2H, minor), 0.64–0.59 (m, 1H, minor), 0.50–0.39 (m, 2H, major), 0.21 (t, *J* = 6.5 Hz, 2H, major), –0.26 (q, *J* = 4.7 Hz, 1H, minor); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 160.1 (both), 142.9 (both), 142.3 (minor), 142.2 (major), 138.6 (minor), 138.5 (major), 129.8 (both), 129.0 (2C major, 2C minor), 127.2 (2C

minor), 127.1 (2C major), 119.7 (both), 112.89 (minor), 112.86 (major), 112.5 (both), 55.4 (both), 36.4 (major), 36.3 (minor), 35.8 (major), 31.0 (minor), 27.4 (major), 22.1 (minor), 21.1 (major), 18.5 (major), 18.1 (minor), 15.9 (minor), 14.6 (minor), 13.9 (major), 11.8 (major), 10.9 (minor); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{20}H_{24}O$, 280.1827; found, 280.1814.



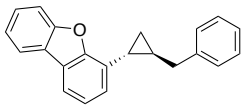
4-(2-(2-Methylcyclopropyl)ethyl)-1,1'-biphenyl (2.15) was prepared according to Method B. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), dppm (3.8 mg, 10. μmol, 5.0 mol %), substrate **2.63** (85 mg, 0.20 mmol, 1.0 equiv), DCM (0.20 mL), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.14 mL, 0.40 mmol, 2.8 M in Et_2O, 2.0 equiv). Before purification, a ^1H NMR yield of 55% was obtained based on comparison to PhTMS as internal standard. To remove the β-hydride elimination byproducts, a dihydroxylation was prepared on unpurified cyclopropane. The following amounts of reagents were used: **2.15** (0.20 mmol, 1.0 equiv), AD mix β (280 mg, 0.36 mmol, 1.8 equiv), *t*BuOH (1 mL), and H_2O (1 mL). The compound was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (25 mg, 0.10 mmol, 52%, 3:1 dr). The compound was characterized as a 3:1 (trans:cis) mixture of diastereomers. The relative configuration of the minor diastereomer was assigned as cis by NOE NMR experiments. Irradiation of the cyclopropane proton (H_f) gave an NOE enhancement of 3.2% of H_d. **TLC R_f** = 0.6 (100% hexanes); **^1H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 2H, major, 2H, minor), 7.51 (d, *J* = 8.1 Hz, 2H, major, 2H, minor), 7.41 (t, *J* = 7.4 Hz, 2H, major, 2H, minor), 7.32–7.23 (m, 3H, major, 3H, minor), 2.73 (m, 2H, major, 2H, minor), 1.70–1.59 (m, 2H, minor), 1.54 (q, *J* = 7.2 Hz, 2H, major), 1.04 (q, *J*

= 6.1 Hz, 3H, minor), 1.00 (d, *J* = 5.5 Hz, 3H, major), 0.81–0.69 (m, 2H, minor), 0.66–0.60 (m, 1H, minor), 0.48–0.38 (m, 2H, major), 0.24–0.18 (m, 1H, major), 0.18–0.13 (m, 1H, major), –0.28 (q, *J* = 5.0 Hz, 1H, minor); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 142.1 (minor), 142.0 (major), 141.3 (both), 138.73 (minor), 138.67 (major), 129.1 (2C, major), 129.0 (2C, minor), 128.8 (2C, major, 2C, minor), 127.12 (2C, major, 2C, minor), 127.08 (3C, major, 3C, minor), 36.4 (major), 36.3 (minor), 35.8 (major), 30.8 (minor), 19.8 (major), 19.1 (major), 15.6 (minor), 13.4 (minor), 13.1 (major), 13.0 (major), 12.2 (minor), 9.71 (minor); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{18}H_{20}$, 236.1565; found, 236.1568.



1-Methoxy-4-(2-(2-(4-methoxybenzyl)cyclopropyl)ethyl)benzene (2.16) was prepared according to Method B. The following amounts of reagents were used: $Ni(cod)_2$ (2.8 mg, 10. μmol, 5.0 mol %), dppm (3.8 mg, 10. μmol, 5.0 mol %), substrate **2.67** (89 mg, 0.20 mmol, 1.0 equiv), PhMe (2.0 mL, 0.10 M in substrate), and MeMgI (0.14 mL, 0.40 mmol, 2.8 M in Et_2O, 2.0 equiv). Before purification, a ^{1}H NMR yield of 47% was obtained based on comparison to PhTMS as internal standard. To remove the β-hydride elimination byproducts, a dihydroxylation was prepared on unpurified cyclopropane. The following amounts of reagents were used: **2.16** (0.20 mmol, 1.0 equiv), AD mix β (280 mg, 0.36 mmol, 1.8 equiv), *t*BuOH (1 mL), and H_2O (1 mL). The compound was purified by flash column chromatography (0–10% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (25 mg, 0.080 mmol, 46%, 5:1 dr). The compound was characterized as a 5:1 (trans:cis) mixture of diastereomers. **TLC R_f** = 0.7 (10% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H, minor), 7.13 (d, *J* = 8.6 Hz, 2H, major, 2H, minor), 7.05 (d, *J* = 8.4 Hz, 2H, major), 6.85–6.78 (m, 4H, major, 4H, minor), 3.78 (s, 6H,

major, 6H, minor), 2.69–2.55 (m, 2H, major, 2H, minor), 2.52–2.42 (m, 2H, major, 1H, minor), 1.80–1.72 (m, 1H, minor), 1.57–1.47 (m, 2H, major, 2H, minor), 1.02 (q, J = 7.3 Hz, 1H, minor), 0.94–0.81 (m, 2H, minor), 0.76–0.67 (m, 1H, major), 0.63–0.55 (m, 1H, major), 0.37–0.32 (m, 1H, major), 0.31–0.27 (m, 1H, major), –0.07 (q, J = 5.3 Hz, 1H, minor); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 157.9 (both), 157.8 (both), 134.9 (minor), 134.8 (major), 134.5 (both), 129.46 (2C, minor), 129.43 (2C, major), 129.3 (2C, major), 129.2 (2C, minor), 113.8 (4C, major, 4C, minor), 55.4 (2C, major, 2C, minor), 39.1 (major), 36.5 (major), 35.6 (minor), 35.1 (major), 33.8 (minor), 31.4 (minor), 20.2 (major), 18.6 (major), 17.2 (minor), 16.1 (minor), 12.0 (major), 11.4 (minor); **HRMS** (TOF MS CI+) *m/z*: $[M]^+$ calcd for $C_{20}H_{24}O_2$, 296.1776; found, 296.1774.

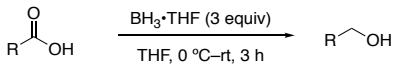


4-((1*R*,2*S*)-2-Benzylcyclopropyl)dibenzo[b,d]furan (2.18) was prepared according to Method B. The following amounts of reagents were used: $Ni(cod)_2$ (1.9 mg, 7.0 μmol, 5.0 mol %), dppm (2.7 mg, 7.0 μmol, 5.0 mol %), substrate **2.17** (60. mg, 0.14 mmol, 1.0 equiv), PhMe (1.4 mL, 0.10 M in substrate), and MeMgI (0.11 mL, 0.40 mmol, 2.5 M in Et_2O, 2.0 equiv). Before purification, a ^{1}H NMR yield of 57% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (0% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (16 mg, 0.055 mmol, 39%, 4:1 dr, 99% ee). The compound was characterized as a 4:1 (trans:cis) mixture of diastereomers. **TLC R_f** = 0.8 (5% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 1H, major, 1H, minor), 7.82 (d, J = 7.6 Hz, 1H, minor), 7.72 (d, J = 7.8 Hz, 1H, major), 7.57 (d, J = 8.2 Hz, 1H major, 1H minor), 7.44 (t, J = 8.0 Hz, 1H, major, 1H, minor), 7.36–7.18 (m, 7H, major, 7H, minor), 7.11 (d, J = 7.7 Hz, 1H, minor), 6.99 (d, J = 7.6 Hz, 1H, major), 2.93 (dd, J = 15.4, 6.7 Hz, 1H, major), 2.79 (dd, J = 15.0, 6.9 Hz, 1H, major), 2.60 (q, J = 8.3 Hz, 1H, minor), 2.54 (dd, J = 15.0, 6.1 Hz, 1H, minor), 2.37–

2.32 (m, 1H, major), 2.19 (dd, J = 15.2, 8.7 Hz, 1H, minor), 1.70–1.58 (m, 1H, major), 1.29–1.21 (m, 1H, major, 2H, minor), 1.21 (q, J = 5.8 Hz, 1H, minor), 1.10–1.04 (m, 1H, major); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 156.2 (both), 155.0 (both), 141.9 (minor), 141.5 (major), 128.6 (2C, major), 128.5 (2C, major), 128.3 (2C, minor), 128.2 (2C, minor), 127.7 (major), 127.08 (major), 127.05 (minor), 126.9 (minor), 126.2 (major), 125.8 (minor), 124.7 (both), 123.9 (both), 123.2 (both), 122.9 (major), 122.70 (minor), 122.69 (major), 122.5 (minor), 120.8 (both), 118.4 (minor), 117.6 (major), 111.88 (minor), 111.83 (major), 40.2 (major), 34.7 (minor), 23.2 (major), 20.0 (minor), 18.2 (major), 16.5 (minor), 15.2 (major), 9.8 (minor); **HRMS** (TOF MS CI+) *m/z*: $[M + NH_4]^+$ calcd for $C_{22}H_{18}ONH_4$, 316.1701; found, 316.1697; **$[\alpha]^{23}_D$** +5.1 (*c* 3.15 mg/mL, $CHCl_3$). **SFC** analysis (Chiralcel OD-H, 10% IPA, 2.0 mL/min, 290 nm) indicated 98% ee (calculated for *minor diastereomer* only): t_R (minor diastereomer, one enantiomer) = 10.8 minutes, t_R (minor diastereomer, other enantiomer) = 11.9 minutes; SFC analysis (Chiralcel AD, 6% IPA, 2.0 mL/min, 290 nm) indicated >99% ee (calculated for *major diastereomer* only): t_R (major diastereomer, one enantiomer) = 12.7 minutes, t_R (major diastereomer, other enantiomer) = 13.8 minutes.

2.4.6 General Procedures for Starting Material Synthesis

2.4.6.1 Method C: Reduction of Carboxylic Acid

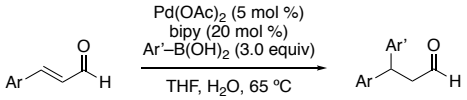


The target compound was prepared using a modified procedure reported by Cole.[29] A flame-dried round bottom flask equipped with stir bar was charged with carboxylic acid (1.0 equiv), and anhydrous THF (1 M) under N_2 atmosphere. The reaction mixture was cooled to 0 ºC and BH_3•THF was added slowly (3.0 equiv). The reaction mixture was allowed to stir for at least 3 h.

[29] Zheng, W.; Cole, P. A. *Bioorg. Chem*. **2003**, *31*, 398–411.

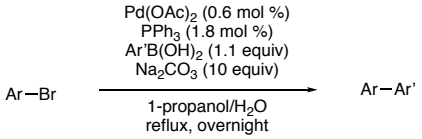
To quench, glacial acetic acid was added dropwise until reaction mixture stopped bubbling. The reaction mixture was diluted with saturated $NaHCO_3$ (10 mL) and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo.

2.4.6.2 Method D: Pd-Catalyzed Conjugate Addition



The target compound was prepared using a modified procedure reported by Lin.[30] A Schlenk flask equipped with stir bar was charged with arylboronic acid (3.0 equiv), $Pd(OAc)_2$ (5 mol %), and bipy (20 mol %) were added, and flask was placed under vacuum and backfilled with N_2 (x 3). Then, THF (2 M in aldehyde), H_2O (3 M in aldehyde), and acetic acid (1 M in aldehyde) were added. Aldehyde (1.0 equiv) was then added, and reaction was heated at 65 ºC and allowed to stir overnight. The reaction was cooled to rt, quenched with sat. $NaHCO_3$, and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.3 Method E: Suzuki-Miyaura Cross-Coupling Reaction with $Pd(OAc)_2$

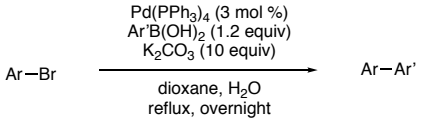


The target compound was prepared using a modified procedure reported by McCarthy.[31] A two-neck round bottom flask was equipped with reflux condenser and stir bar. Aryl bromide (1.0 equiv), $Pd(OAc)_2$ (0.6 mol %), PPh_3 (1.8 mol %), Ar'–$B(OH)_2$ (1.1 equiv), Na_2CO_3 (1.2 equiv),

[30] Lu, X.; Lin, S. *J. Org. Chem*. **2005**, *70*, 9651–9653.
[31] Brooks, D. A.; Etgen, G. J.; Rito, C. J.; Shuker, A. J.; Dominianni, S. J.; Warshawsky, A. M.; Ardecky, R.; Paterniti, J. R.; Tyhonas, J.; Karanewsky, D. S.; Kauffman, R. F.; Broderick, C. J.; Oldham, B. A.; Montrose-Rafizadeh, C.; Winneroski, L. L.; Faul, M. M.; McCarthy, J. R. *J. Med. Chem*. **2001**, *44*, 2061–2064.

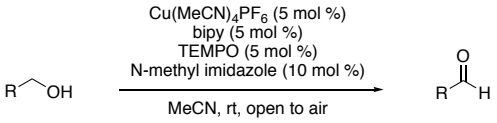
H_2O/1-propanol (1:2 ratio, 0.05 M) were added under N_2. The reaction mixture was allowed to stir at reflux overnight. To quench, 1 M NaOH (10 mL) was added. The reaction mixture was then extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.4 Method F: Suzuki-Miyaura Cross-Coupling Reaction with $Pd(PPh_3)_4$



The target compound was prepared using a modified procedure reported by Nagano.[32] A two-neck round bottom flask was equipped with reflux condenser and stir bar. Aryl bromide (1.0 equiv), $Pd(PPh_3)_4$ (0.030 equiv), Ar'–$B(OH)_2$ (1.2 equiv), K_2CO_3 (10. equiv), and dioxane/H_2O (4:1 ratio, 0.1 M) were added under N_2. The reaction mixture was allowed to stir at reflux overnight. Once complete, H_2O (10 mL) was added. The reaction mixture was then extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.5 Method G: Cu Oxidation of Primary Alcohol to Aldehyde

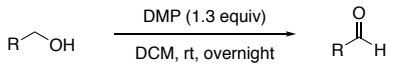


The target compound was prepared using a modified procedure reported by Stahl.[33] A flame-dried round bottom flask equipped with stir bar was charged with alcohol (1.0 equiv), and MeCN (0.2 M). To the reaction flask was added $Cu(MeCN)_4PF_6$ (5.0 mol %), bipy (5.0 mol %), TEMPO (5.0 mol %), and *N*-methyl imidazole (0.10 equiv). The reaction mixture was allowed to stir at rt

[32] Terai, T.; Kohno, M.; Boncompain, G.; Sugiyama, S.; Saito, N.; Fujikake, R.; Ueno, T.; Komatsu, T.; Hanaoka, K.; Okabe, T.; Urano, Y.; Perez, F.; Nagano, T. *J. Am. Chem. Soc.* **2015**, *137*, 33, 10464–10467.
[33] Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc*. **2011**, *133*, 16901–16910.

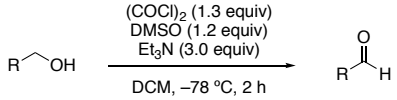
overnight while open to air. To quench, 1 M HCl was added. The reaction mixture was diluted with H_2O (10 mL) and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.6 Method H: DMP Oxidation of Primary Alcohol to Aldehyde



The target compound was prepared using a modified procedure reported by Fernandes.[34] A flame-dried round bottom flask equipped with stir bar was charged with alcohol (1.0 equiv), and DCM (0.2 M). To the reaction flask was added Dess-Martin periodinane (DMP; 1.3 equiv) in one portion. The reaction mixture was stirred overnight. To quench, saturated $NaHCO_3$ (10 mL) was added and the reaction was extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

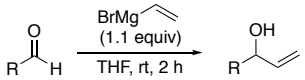
2.4.6.7 Method I: Swern Oxidation of Primary Alcohol to Aldehyde



The target compound was prepared using a modified procedure reported by Kobayashi.[35] A flame-dried round bottom flask equipped with stir bar was charged with alcohol (1.0 equiv), and DCM (0.2 M). The reaction flask was cooled to –78 ºC, then oxalyl chloride (1.3 equiv) and DMSO (1.2 equiv) were added under N_2 with vent. The reaction mixture was allowed to stir at –78 ºC for 2 h. Then, trimethylamine (3.0 equiv) was added and the reaction was warmed to rt. To quench, saturated NH_4Cl (10 mL) was added and the reaction was extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

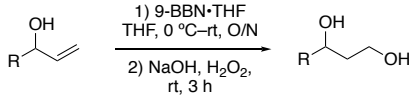
[34] Halle, M. B.; Fernandes, R. A. *RSC. Adv*. **2014**, *4*, 63342–63348.
[35] Shinohara, R.; Morita, M.; Ogawa, N.; Kobayashi, Y. *Org. Lett.* **2019**, *21*, 3247–3251.

2.4.6.8 Method J: Vinyl Grignard Addition into Aldehydes



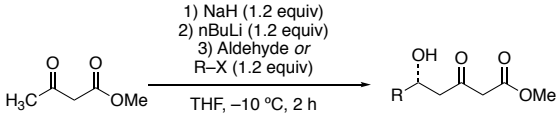
A flame-dried flask with stir bar was charged with vinylmagnesium bromide (1.1 equiv) and cooled to 0 ºC. A solution of aldehyde (1.0 equiv) in anhydrous THF was added in a dropwise. The reaction mixture was stirred at room temperature for at least 2 h. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.9 Method K: Hydroboration/Oxidation



The target compound was prepared using a modified procedure reported by Hartwig.[36] A round bottom flask equipped with stir bar was charged with alkene (1.0 equiv) and THF (0.4 M). The flask was cooled to 0ºC, and 9-BBN•THF (2.5 equiv) was added slowly. The reaction mixture was then warmed to rt and stirred overnight. Then, MeOH (3 mL/mmol), H_2O_2 (30%, 1 mL/mmol) and NaOH (3.0 M, 1 mL/mmol) were added, and the reaction stirred for at least 3 h. Once complete, H_2O (10 mL) was added. The reaction mixture was then extracted with EtOAc (3 x 20 mL) and combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo.

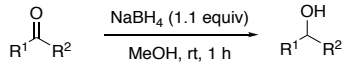
2.4.6.10 Method L: Aldol or Enolate Alkylation



[36] Stanley, L. M.; Hartwig, J. F. *J. Am. Chem. Soc*. **2009**, *131*, 8971–8983.

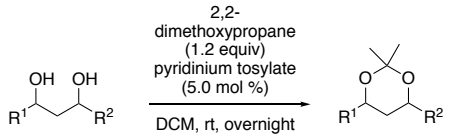
The target compound was prepared using a modified procedure reported by Xie.[37] In a glove box, a flame-dried flask with stir bar was charged with sodium hydride (1.2 equiv), capped with stopper and removed from glove box. An N_2 inlet and anhydrous THF (0.2 M) were added. Methyl acetoacetate (1.0 equiv) was added as a solution in anhydrous THF at rt, and a vent in the stopper was placed to allow release of H_2 gas. The reaction was allowed to stir at rt for 30 min. The reaction flask was then cooled to –10 ºC. It is imperative to keep flask close to this temperature for the remaining reaction duration. *n*-Butyllithium (1.2 equiv) was added, and reaction stirred for an additional 30 min. Then, aldehyde or benzyl halide (1.2 equiv) was added and reaction continued to stir for 1 h. To quench, sat. NH_4Cl (5 mL) was added and the reaction mixture was then extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.11 Method M: $NaBH_4$ Reduction



Open to air, β-keto ester (1.0 equiv) and MeOH (0.2 M) were added to a flask equipped with a stir bar. Sodium borohydride ($NaBH_4$; 1.1 equiv) was added and reaction stirred at rt for 1 h. Reaction was quenched with water (10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

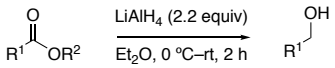
2.4.6.12 Method N: Acetonide Formation



[37] Wu, Y.; Du, C.; Hu, C.; Li, Y.; Xie, Z. *J. Org. Chem*. **2011**, *76*, 4075–4081.

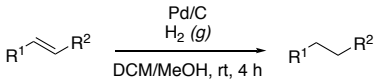
The target compound was prepared using a modified procedure reported by Urpí.[38] To a flame-dried flask equipped with stir bar, diol (1.0 equiv) and DCM (0.3 M) were added. Pyridinium tosylate (5.0 mol %) and 2,2-dimethoxypropane (1.2 equiv) were added and reaction was allowed to stir overnight. Reaction was then quenched with sat. $NaHCO_3$ and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.13 Method O: $LiAlH_4$ Reduction



In a glove box, a flame-dried flask was charged with $LiAlH_4$ (2.2 equiv), capped with stopper and removed from glovebox. An N_2 inlet and anhydrous Et_2O (0.2 M) were added. The reaction flask was cooled to 0 ºC and substrate (1.0 equiv) was added as a solution in Et_2O (1.0 M). The reaction was warmed to rt and stirred for 2 h. To quench, saturated NH_4Cl was added and reaction was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.14 Method P: Pd/C Reduction of Alkenes

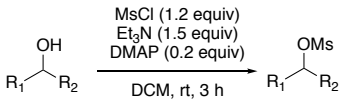


A round-bottom flask with stir bar was charged with palladium on carbon (1.0 mg/ 3.5 mmol of substrate), flushed with N_2, and capped with septum. Slowly DCM was added, until Pd/C was fully submerged. Then, MeOH or EtOH (0.2 M in substrate), and alkene (1.0 equiv) were added. Vacuum was pulled on the flask until the solvent began to bubble, at which point the flask was backfilled with N_2 (x 3). An H_2 balloon was added and the reaction mixture was allowed to stir

[38] Pellicena, M.; Solsona, J. G.; Romea, P.; Urpí, F. *Tetrahedron* **2012**, *68*, 10338–10350.

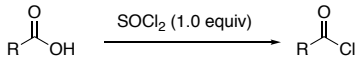
vigorously for 4 h. The balloon was then removed, and the flask was purged with N_2 for 30 min. The septum was removed, and the reaction mixture was filtered through celite using MeOH (100 mL). The collected solvent was then concentrated in vacuo.

2.4.6.15 Method Q: Mesylation



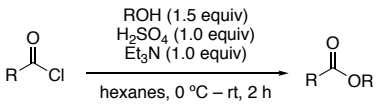
A round bottom flask equipped with stir bar was charged with alcohol (1.0 equiv) and DCM (0.2 M) under N_2. Then, Et_3N (1.5 equiv), DMAP (0.2 equiv), and MsCl (2.2 equiv) were added. The reaction mixture was then stirred at rt for at least 3 h. Once complete by TLC, sat. $NaHCO_3$ (5 mL) was added and the reaction mixture was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

2.4.6.16 Method R: $SOCl_2$ Chlorination



The target compound was prepared using a modified procedure reported by Ramachandran.[39] To a flame-dried flask equipped with a stir bar was added carboxylic acid (1.0 equiv) and the flask was flushed with N_2. Next, a vent was placed, and thionyl chloride (1.0 equiv) was added over 15 min. The reaction was allowed to stir until gas evolution stopped. The flask was then heated to 80 ºC for 2 h to ensure completion. The desired product was distilled.

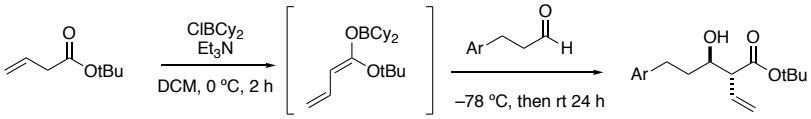
2.4.6.17 Method S: Esterification from Acid Chloride



[39] Ramachandran, P. V.; Nicponski, D.; Kim, B. Total Regio- and Diastereocontrol in the Aldol Reactions of Dienolborinates. *Org. Lett.* **2013**, *15*, 1398–1401.

The target compound was prepared using a modified procedure reported by Ramachandran.[39] A flask was equipped with a stir bar then flame-dried. Under N_2, alcohol (1.5 equiv), Et_3N (1.0 equiv), and hexanes (0.2 M in substrate) were added, and the flask was cooled to 0 ºC. Then the acid chloride (1.0 equiv) was added. The reaction mixture formed a precipitate and was allowed to stir for at least 2 h. The reaction was slowly quenched with sat. $NaHCO_3$ and extracted with Et_2O (3x). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo.

2.4.6.18 Method T: Diastereoselective Anti Aldol



Dicyclohexylboron chloride

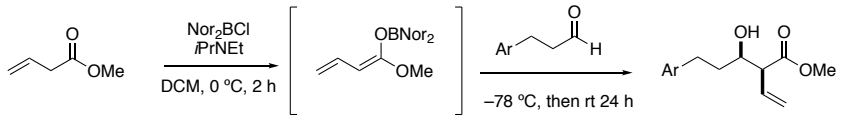
The target compound was prepared using a modified procedure reported by Ramachandran.[39] Freshly distilled cyclohexene (2.0 equiv) was added to a flame-dried flask with stir bar under N_2. Diethyl ether (45 mL, 2.3 M) was added, and the flask was cooled to 0 ºC. Once cooled, BH_2Cl•DMS (1.0 equiv) was slowly added (under N_2) and the flask was allowed to vent. Once addition was complete, the vent was removed, and the reaction was allowed to warm to rt and stir for 4 h. The Et_2O was then distilled away from desired product. Once complete, the dicyclohexylboron chloride product was distilled (5 torr, oil bath ~130 ºC, distillation head ~110 ºC). The product was stored in a Schlenk flask as a 2 M solution in anhydrous DCM at –20 ºC.

Aldol

The target compound was prepared using a modified procedure reported by Ramachandran.[39] To a flame-dried flask with stir bar, DCM (0.20–0.30 M in aldehyde), ester (1.5–2.0 equiv), and amine base (1.5 equiv) were added under N_2. The flask was cooled to 0 ºC, and the boron Lewis acid (1.3

equiv) was added over 5 min. The reaction was allowed to stir at 0 ºC for 2 h. The solution was then cooled to –78 ºC, and aldehyde (1.0 equiv) was slowly added. Once complete, the flask was allowed to warm to rt slowly overnight (achieved by allowing the dry ice to slowly evaporate and the dewar was never removed from the reaction flask–this is critical to achieve best possible dr). To workup, MeOH (5 mL/ mmol), and phosphate buffer (1 mL/mmol) was added and the reaction was allowed to vigorously stir. The flask was cooled to 0 ºC, and H_2O_2 (1 mL/mmol, 30% w/v) was added via syringe pump over 1 h. The reaction mixture was then extracted with DCM, and combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo.

2.4.6.19 Method U: Diastereoselective Syn Aldol



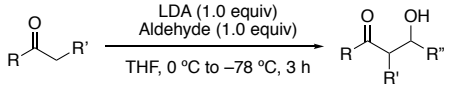
Di(bicyclo[2.2.1]heptan-2-yl)chloroborane

The target compound was prepared using a modified procedure reported by Ramanchandran.[39] Norbornene (2.0 equiv) was added to a flame-dried flask with stir bar. The flask was placed under vacuum and backfilled with N_2 (x 3). Diethyl ether (35 mL, 2.6 M in substrate) was added, and the flask was cooled to 0 ºC. Once cooled, BH_2Cl•DMS (1.0 equiv) was slowly added (under N_2) and the flask was allowed to vent. Once addition was complete, the vent was removed, and the reaction was allowed to warm to rt and stir overnight. The Et_2O was then distilled from desired product. Once complete, the di(bicyclo[2.2.1]heptan-2-yl)chloroborane product was distilled (5 torr, oil bath ~150 ºC, distillation head ~125 ºC). The product was stored in a Schlenk flask as a 2 M solution in anhydrous DCM at –20 ºC.

Aldol

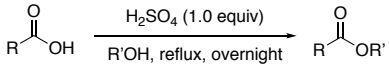
Followed procedure from Method AA.

2.4.6.20 Method V: Nonselective Aldol using LDA



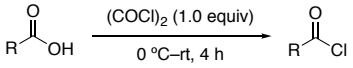
The target compound was prepared using a modified procedure reported by Heathcock.[26c] To a flame-dried flask with stir bar, diisopropylamine (1.0 equiv) and THF (0.50 M in amine) were added under N_2. The flask was then cooled to 0 ºC and *n*-BuLi (1.0 equiv) was added slowly. The reaction stirred for 1 h at 0 ºC, then was cooled to –78 ºC and ester or aldehyde (1.0 equiv) was added dropwise. The reaction stirred for 1 h, then electrophile (1.0 equiv) was added and reaction continued to stir for 2 h. The reaction was quenched with sat. NH_4Cl (10 mL) and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo.

2.4.6.21 Method W: Esterification from Carboxylic Acid



The target compound was prepared using a modified procedure reported by Alexakis.[40] A 2-neck round-bottom flask was equipped with reflux condenser and stir bar then flame-dried. Under N_2, carboxylic acid (1.0 equiv), alcohol (0.80 M in substrate) and H_2SO_4 (1.0 equiv) were added. The reaction mixture was allowed to reflux overnight. After heat was removed, the reaction was slowly quenched with sat. $NaHCO_3$ and extracted with EtOAc (3x). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo.

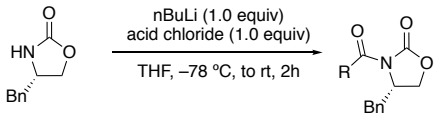
2.4.6.22 Method X: $(COCl)_2$ Chlorination



[40] Perron, Q.; Alexakis, A. *Adv. Synth. Catal*. **2010**, *352*, 2611–2620.

The target compound was prepared using a modified procedure reported by Spivey.[41] To a flame-dried flask equipped with stir bar, carboxylic acid (1.0 equiv) and DCM (0.83 M in substrate) were added under N_2. The flask was cooled to 0 ºC, and oxalyl chloride was added (1.5 equiv). The flask was allowed to warm to rt, a vent was placed, and the reaction stirred for 4 h. When gas evolution stopped, a distillation apparatus was attached and DCM was removed first, followed by distillation of desired product.

2.4.6.23 Method Y: Acid Chloride to Oxazolidinone



The target compound was prepared using a modified procedure reported by Evans.[42] A flame-dried flask equipped with stir bar was charged with oxazolidinone (1.0 equiv) and THF (0.30 M in substrate). The reaction flask was cooled to –78 ºC, and *n*-BuLi (1.0 equiv) was added slowly. The reaction was allowed to stir for 1 h, and then acid chloride (1.0 equiv) was added. The reaction was then warmed to rt and stirred for 1 h, quenched with sat. NH_4Cl, extracted with EtOAc (3x), dried over Na_2SO_4, and concentrated in vacuo.

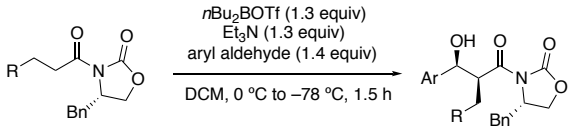
2.4.6.24 Method Z: Evans Aldol

Dibutylboron Triflate

The target compound was prepared using a modified procedure reported by Evans.[42] A two-neck flask equipped with stir bar, septum, and distillation apparatus was flame-dried and allowed to cool under vaccum. The apparatus was back-filled with N_2 (and kept under positive N_2 pressure the remaining time of the reaction), tributylborane (1.0 equiv) was added, and the flask was heated

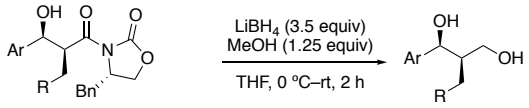
[41] Murray, J. I.; Spivey, A. C. *Adv. Synth. Catal*. **2015**, *357*, 3825–3830.
[42] Gage, J. R.; Evans, D. A. *Org. Synth*. **1990**, *68*, 83.

to 50 ºC. Once to heated temperature, a vent was placed in septum, and triflic acid (1.0 equiv) was added slowly. Fleeting bubbles indicated initiation of reaction (generation of butane), and the reaction mixture continued to stir for 30 min at 50 ºC. After stirring, the vent was removed, vacuum was applied to the apparatus, and the reaction mixture was heated to 86 ºC. The desired product distilled off as a clear, very light-yellow liquid (5 torr, distillation head at 60 ºC). The title compound was stored neat in a Schlenk flask at –20 ºC.



The target compound was prepared using a modified procedure reported by Evans.[42] A flame-dried flask equipped with stir bar was charged with oxazolidinone complex (1.0 equiv), Et_3N (1.3 equiv), and DCM (0.5 M in substrate) under N_2 and cooled to 0 ºC. Then, *n*Bu_2BOTf (1.3 equiv) was then added to the mixture dropwise and reaction stirred for 30 min. The reaction mixture was then cooled to –78 ºC, and the aldehyde (1.4 equiv) was slowly added. The reaction continued to stir at –78 ºC for 1 h. The reaction was then quenched with phosphate pH 7 buffer and stirred at 0 ºC for 1 h. To workup, DCM (20 mL) was added and the layers were separated. The aqueous layer was washed with DCM (3x) and the combined organic layers were dried with Na_2SO_4, and concentrated in vacuo. Then, MeOH (1.5 mL/mmol) was added, the flask was cooled to 0 ºC, and H_2O_2 (30% w/v, 0.5 mL/mmol) was added dropwise over 1 h. The reaction continued to stir at 0 ºC for an additional hr. Then, H_2O and Et_2O were added. The layers were separated and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated in vacuo.

2.4.6.25 Method AA: $LiBH_4$ Cleavage of Auxiliary

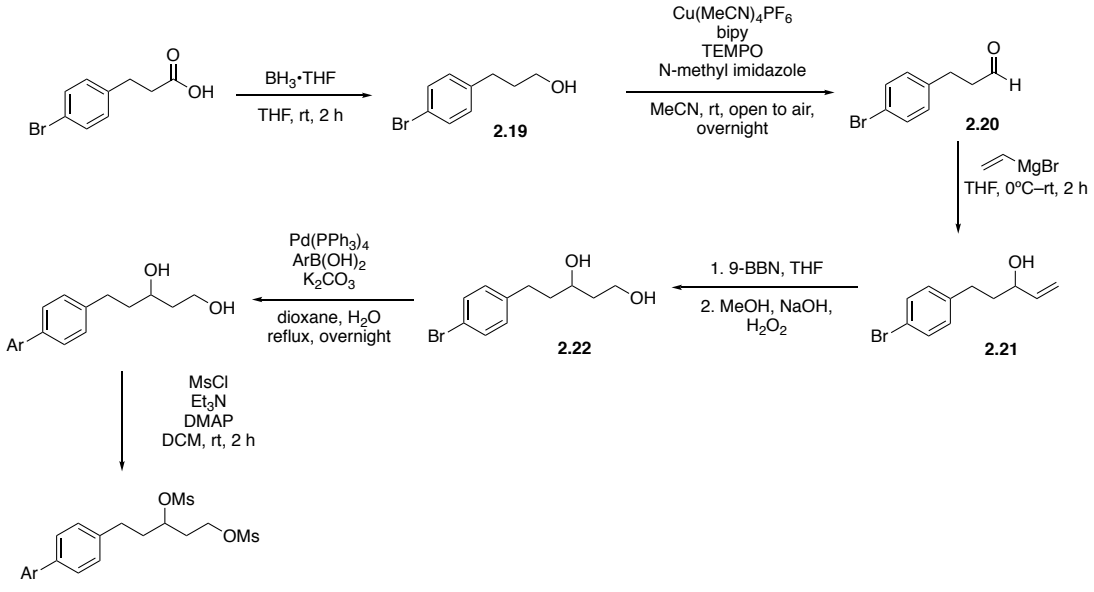


The target compound was prepared using a modified procedure reported by Day.[43] To a flame-dried flask with stir bar, oxazolidinone complex (1.0 equiv), MeOH (1.25 equiv), and THF (0.20 M in substrate) were added under N_2. The flask was cooled to 0 ºC, then $LiBH_4$ (3.5 equiv, 0.20 M in substrate) was slowly added. The reaction was allowed to warm to rt and stirred for 2 h. The reaction was then quenched with sat. NH_4Cl (10 mL) slowly and extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and concentrated in vacuo.

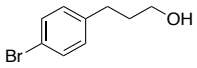
2.4.7 Synthesis and Characterization Data for Intermediates and 1,3-Dimesylates

2.4.7.1 Intermediates and 1,3-Dimesylates for Unbranched Alkylcyclopropanes

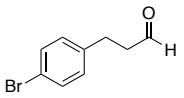
Scheme 2.7 Synthesis of unbranched 1,3-dimesylates



[43] Choy, N.; Shin, Y.; Nguyen, P. Q.; Curran, D. P.; Balachandran, R.; Madiraju, C.; Day, B. W. *J. Med. Chem.* **2003**, *46*, 2846–2864.

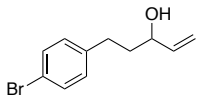


3-(4-Bromophenyl)propan-1-ol (2.19) was prepared according to Method C. The following amounts of reagents were used: 3-(4-bromophenyl)propionic acid (6.8 g, 30. mmol, 1.0 equiv), BH_3•THF (90. mL, 90. mmol, 3.0 equiv, 1.0 M), and THF (10. mL, 3.0 M in substrate). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (5.9 g, 28 mmol, 93%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.86 (tt, *J* = 7.8, 6.4 Hz, 2H), 1.42 (s, 1H). Analytical data is consistent with literature values.[44]

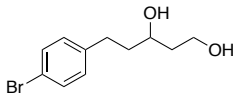


3-(4-Bromophenyl)propanal (2.20) was prepared according to Method G. The following amounts of reagents were used: **2.19** (5.9 g, 27 mmol, 1.0 equiv), $Cu(MeCN)_4PF_6$ (1.0 g, 2.8 mmol, 0.10 equiv), bipy (0.44 g, 2.8 mmol, 0.10 equiv), TEMPO (0.44 g, 2.8 mmol, 0.10 equiv), *N*-methyl imidazole (0.44 mL, 5.5 equiv, 0.20 equiv), and MeCN (20. mL, 1.4 M in substrate). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (2.7 g, 40%, 10% EtOAc by NMR, 4% DCM by NMR). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.3 Hz, 2H). Analytical data is consistent with literature values.[45]

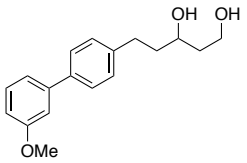
[44]Andersen, C.; Ferey, V.; Daumas, M.; Bernardelli, P.; Guérinot, A.; Cossy, J. *Org. Lett.* **2019**, *21*, 2285–2289.
[45] McGorry, R. J.; Allen, S. K.; Pitzen, M. D.; Coombs, T. C. *Tetrahedron Lett.* **2017**, *58,* 4623–4627.



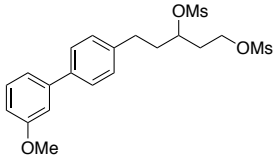
5-(4-Bromophenyl)pent-1-en-3-ol (2.21) was prepared according to Method J. The following amounts of reagents were used: **2.20** (2.7 g, 13 mmol, 1.0 equiv), vinylmagnesium bromide (20. mL, 14 mmol, 1.1 equiv), and THF (10. mL, 1.4 M in substrate). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (2.1 g, 8.8 mmol, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.89 (ddd, *J* = 16.9, 10.5, 6.2 Hz, 1H), 5.24 (dt, *J* = 17.4, 1.1 Hz, 1H), 5.14 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.11 (quint, *J* = 5.6, Hz 1H), 2.73–2.62 (m, 2H), 1.88–1.87 (m, 2H), 1.49 (d, *J* = 4.4 Hz, 1H).



5-(4-Bromophenyl)pentane-1,3-diol (2.22) was prepared according to Method K. The following amounts of reagents were used: **2.21** (1.7 g, 7.1 mmol, 1.0 equiv), 9-BBN (35 mL, 18 mmol, 2.5 equiv), MeOH (21 mL, 3.0 mL/mmol), H_2O_2 (11 mL, 1.5 mL/mmol, 30% w/w), NaOH (11 mL, 1.5 mL/mmol, 3.0 M), and THF (20. mL, 0.36 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white solid (1.7 g, 6.4 mmol, 91%). **m.p.** = 87–88 ºC; **TLC R_f** = 0.3 (60% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.95–3.79 (m, 3H), 2.79–2.70 (m, 1H), 2.69–2.60 (m, 1H), 2.56 (s, 1H), 2.14 (s, 1H), 1.86–1.69 (m, 4H); **^{13}C NMR** (500 MHz, $CDCl_3$) δ 141.0, 131.6 (2C), 130.4 (2C), 119.7, 71.4, 62.0, 39.3, 38.5, 31.4; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{11}H_{15}BrO_2Na$, 281.0153; found, 281.0145.

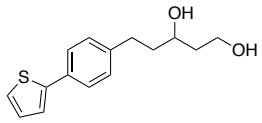


5-(3'-Methoxy-[1,1'-biphenyl]-4-yl)pentane-1,3-diol (2.23) was prepared according to Method F. The following amounts of reagents were used: **2.22** (0.97 g, 3.8 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol, 3.0 mol %), K_2CO_3 (5.2 g, 38. mmol, 10. equiv), (3-methoxyphenyl)boronic acid (0.68 g, 4.5 mmol, 1.2 equiv), 1,4-dioxane (20.0 mL), and DI water (5.0 mL). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to yield the title compound as a white solid (0.63 g, 2.2 mmol, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 7.7, 1H), 7.11 (s, 1H), 6.88 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.97–3.89 (m, 2H), 3.87–3.82 (m, 4H), 2.87–2.80 (m, 1H), 2.77–2.70 (m, 1H), 2.36 (d, *J* = 3.9 Hz, 1H), 2.06 (t, *J* = 4.9 Hz, 1H), 1.90–1.82 (m, 2H), 1.78–1.73 (m, 2H).

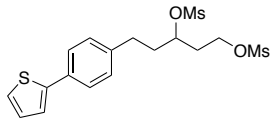


5-(3'-Methoxy-[1,1'-biphenyl]-4-yl)pentane-1,3-diyl dimethanesulfonate (2.1) was prepared according to Method Q. The following amounts of reagents were used: **2.23** (0.70 g, 2.4 mmol, 1.0 equiv), Et_3N (1.0 mL, 7.3 mmol, 3.0 equiv), DMAP (60. mg, 0.49 mmol, 0.20 equiv), MsCl (0.42 mL, 5.4 mmol, 2.2 equiv), and DCM (10. mL, 0.24 M in substrate). The compound was purified by flash column chromatography (0–50% EtOAc/hexanes) to afford the title compound as a white solid (0.93 g, 2.1 mmol, 86%). **m.p.** = 71–72 ºC; **TLC R_f** = 0.7 (50% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 4.97–4.93 (m, 1H), 4.40–4.33 (m,

2H), 3.85 (s, 3H), 3.04 (s, 3H), 3.03 (s, 3H), 2.82–2.74 (m, 2H), 2.24–2.05 (m, 4H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 160.1, 142.4, 139.7, 139.3, 129.9, 128.9 (2C), 127.5 (2C), 119.6, 112.9, 112.7, 78.4, 65.7, 55.4, 38.8, 37.5, 36.6, 34.2, 30.8; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{26}O_7S_2Na$, 465.1018; found, 465.0995.

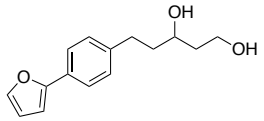


5-(4-(Thiophen-2-yl)phenyl)pentane-1,3-diol (2.24) was prepared according to Method F. The following amounts of reagents were used: **2.22** (0.21 g, 0.82 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (28 mg, 25 μmol, 3.0 mol %), 2-thienylboronic acid (0.14 g, 1.1 mmol, 1.3 equiv), K_2CO_3 (1.1 g, 8.2 mmol, 10. equiv), and 1,4-dioxane/H_2O (8.8 mL, 4:1 ratio, 0.10 M). The compound was purified by flash column chromatography (0–5% MeOH/DCM) to afford the title compound as a white solid (0.16 g, 0.63 mmol, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.27–7.22 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.05 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.93–3.86 (m, 2H), 3.85–3.78 (m, 1H), 2.79 (ddd, *J* = 14.3, 9.5, 5.8 Hz, 1H), 2.69 (ddd, *J* = 13.9, 9.3, 6.9 Hz, 1H), 2.75 (s, 1H), 2.56 (s, 1H), 1.89–1.67 (m, 4H).

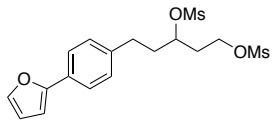


5-(4-(Thiophen-2-yl)phenyl)pentane-1,3-diyl dimethanesulfonate (2.25) was prepared according to Method Q. The following amounts of reagents were used: **2.24** (0.16 g, 0.63 mmol, 1.0 equiv), Et_3N (0.26 mL, 1.9 mmol, 3.0 equiv), DMAP (15 mg, 0.13 mmol, 0.20 equiv), MsCl (0.11 mL, 1.4 mmol, 2.2 equiv), and DCM (3.0 mL, 0.21 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white solid (0.20 g, 0.48 mmol, 76%). **m.p.** = 77–80 ºC; **TLC R_f** = 0.7 (60% EtOAc/hexanes);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 4.1 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.92 (quint, *J* = 6.9 Hz, 1H), 4.37–4.31 (m, 2H), 3.03 (s, 3H), 3.01 (s, 3H), 2.75 (td, *J* = 8.6, 2.4 Hz, 2H), 2.22–1.99 (m, 4H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 144.2, 139.8, 132.6, 128.9 (2C), 128.1, 126.2 (2C), 124.7, 123.0, 78.3, 65.7, 38.7, 37.4, 36.4, 34.1, 30.8; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{22}O_7S_2Na$, 441.0476; found, 441.0462.

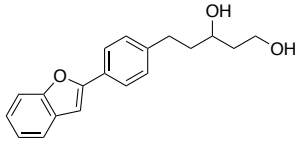


5-(4-(Furan-2-yl)phenyl)pentane-1,3-diol (2.26) was prepared according to Method F. The following amounts of reagents were used: **2.22** (0.26 g, 1.0 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (35 mg, 30 μmol, 3.0 mol %), 2-furanylboronic acid (0.26 g, 1.5 mmol, 1.2 equiv), K_2CO_3 (1.4 g, 10. mmol, 10. equiv), and 1,4-dioxane/H_2O (8.8 mL, 4:1 ratio, 0.100 M). The compound was purified by flash column chromatography (0–5% MeOH/DCM) to afford the title compound as a white solid (0.21 g, 0.85 mmol, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 3.0 Hz, 1H), 6.45 (dd, *J* = 3.4, 1.9 Hz, 1H), 3.94–3.86 (m, 2H), 3.85–3.78 (m, 1H), 2.79 (ddd, *J* = 14.1, 9.4, 6.1 Hz, 1H), 2.60 (ddd, *J* = 14.2, 9.2, 6.9 Hz, 1H), 2.64 (s, 1H), 2.39 (s, 1H), 1.89–1.66 (m, 4H).

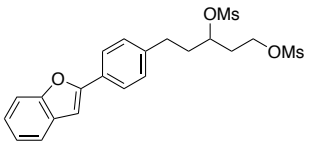


5-(4-(Furan-2-yl)phenyl)pentane-1,3-diyl dimethanesulfonate (2.27) was prepared according to Method Q. The following amounts of reagents were used: **2.26** (0.21 g, 0.85 mmol, 1.0 equiv), Et_3N (0.35 mL, 2.6 mmol, 3.0 equiv), DMAP (21 mg, 0.17 mmol, 0.20 equiv), MsCl (0.14 mL, 1.9 mmol, 2.2 equiv), and DCM (3.0 mL, 0.28 M in substrate). The compound was purified by

flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white solid (0.11 g, 0.28 mmol, 33%). **m.p.** = 107–109 ºC; **TLC R_f** = 0.6 (60% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.61 (dd, *J* = 3.3, 0.7 Hz, 1H), 6.46 (dd, *J* = 3.4, 1.9 Hz, 1H), 4.95–4.89 (m, 1H), 4.39–4.30 (m, 2H), 3.03 (s, 3H), 3.02 (s, 3H), 2.75 (td, *J* = 8.0, 2.2 Hz, 2H), 2.22–2.00 (m, 4H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 153.9, 142.0, 139.6, 129.3, 128.8 (2C), 124.2 (2C), 111.7, 104.8, 78.3, 65.7, 38.7, 37.5, 36.5, 34.2, 30.9; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{22}O_7S_2Na$, 425.0705; found, 425.0688.

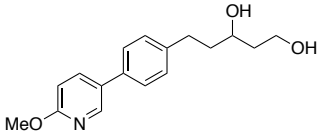


5-(4-(Benzofuran-2-yl)phenyl)pentane-1,3-diol (2.28) was prepared according to Method E. The following amounts of reagents were used: **2.22** (0.26 g, 1.0 mmol, 1.0 equiv), $Pd(OAc)_2$ (1.4 mg, 6.0 μmol, 0.60 mol %), PPh_3 (4.7 mg, 1.8 μmol 1.8 mol %), 2-benzofuranylboronic acid (0.18 g, 1.1 mmol, 1.1 equiv), Na_2CO_3 (0.13 g, 1.2 mmol, 1.2 equiv), and 1-propanol/H_2O (2:1, 15 mL, 0.050 M in substrate). The compound was purified by flash column chromatography (100% EtOAc) to afford the title compound as a pale-yellow solid (0.16 g, 0.52 mmol, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.31–7.18 (m, 4H), 6.97 (s, 1H), 3.95–3.87 (m, 2H), 3.87–3.78 (m, 1H), 2.86–2.79 (m, 1H), 2.76–2.69 (m, 1H), 2.61 (s, 1H), 2.27 (s, 1H), 1.91–1.69 (m, 4H).

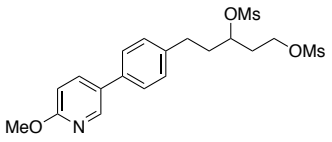


5-(4-(Benzofuran-2-yl)phenyl)pentane-1,3-diyl dimethanesulfonate (2.29) was prepared according to Method Q. The following amounts of reagents were used: **2.28** (0.14 g, 0.47 mmol,

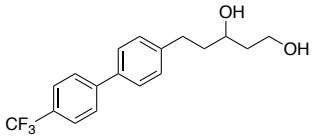
1.0 equiv), Et_3N (0.20 mL, 1.4 mmol, 3.0 equiv), DMAP (11 mg, 0.094 mmol, 0.20 equiv), MsCl (0.08 mL, 1 mmol, 2 equiv), and DCM (5.0 mL, 0.094 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white, fluffy solid (0.14 g, 0.31 mmol, 66%). **m.p.** = 131–133 ºC; **TLC** $\mathbf{R_f}$ = 0.6 (60% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.29–7.26 (m, 3H), 7.22 (td, *J* = 7.7, 1.2 Hz, 1H), 6.99 (s, 1H), 4.99–4.92 (m, 1H), 4.91–4.32 (m, 2H), 3.05 (s, 3H), 3.03 (s, 3H), 2.80 (t, *J* = 7.8 Hz, 2H), 2.25–2.04 (m, 4H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 155.9, 155.0, 141.0, 129.4, 128.94 (2C), 128.88, 125.4 (2C), 124.4, 123.1, 121.0, 111.3, 101.2, 78.3, 65.6, 38.8, 37.6, 36.5, 34.3, 31.1; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{24}O_7S_2Na$, 475.0861; found, 475.0855.



5-(4-(6-Methoxypyridin-3-yl)phenyl)pentane-1,3-diol (2.30) was prepared according to Method F. The following amounts of reagents were used: **2.22** (0.26 g, 1.0 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (35 mg, 30 μmol, 3.0 mol %), 2-methoxypyridine-5-boronic acid (0.18 g, 1.2 mmol, 1.2 equiv), K_2CO_3 (1.4 g, 10. mmol, 10. equiv), and 1,4-dioxane/H_2O (8.8 mL, 4:1 ratio, 0.1 M). The compound was purified by flash column chromatography (0–5% MeOH/DCM) to afford the title compound as a white solid (0.20 g, 0.78 mmol, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.5 Hz, 1H), 7.78 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 3.99 (s, 3H), 3.97–3.89 (m, 2H), 3.89–3.82 (m, 1H), 2.84 (ddd, *J* = 14.2, 9.7, 6.0 Hz, 1H), 2.74 (ddd, *J* = 14.1, 9.4, 6.9 Hz, 1H), 2.63 (s, 1H), 2.35 (s, 1H), 1.93–1.74 (m, 4H).

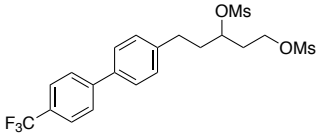


5-(4-(6-methoxypyridin-3-yl)phenyl)pentane-1,3-diyl dimethanesulfonate (2.31) was prepared according to Method Q. The following amounts of reagents were used: **2.30** (0.21 g, 0.78 mmol, 1.0 equiv), Et_3N (0.33 mL, 2.3 mmol, 3.0 equiv), DMAP (19 mg, 0.16 mmol, 0.20 equiv), MsCl (0.13 mL, 1.7 mmol, 2.2 equiv), and DCM (4.0 mL, 0.20 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white solid (0.20 g, 0.46 mmol, 59%). **m.p.** = 118–119 ºC; **TLC** $\mathbf{R_f}$ = 0.5 (60% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 2.5, 0.7 Hz, 1H), 7.77 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.80 (dd, *J* = 8.6, 0.7 Hz, 1H), 4.99–4.93 (m, 1H), 4.41–4.33 (m, 2H), 3.97 (s, 3H), 3.06 (s, 3H), 3.03 (s, 3H), 2.79 (ddd, *J* = 9.5, 6.9, 2.8 Hz, 2H), 2.25–2.03 (m, 4H); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 163.7, 144.9, 139.6, 137.4, 136.2, 129.8, 129.1 (2C), 127.0 (2C), 110.9, 78.3, 65.7, 53.6, 38.8, 37.5, 36.6, 34.2, 30.8; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{25}NO_7S_2Na$, 466.0970; found, 466.0964.

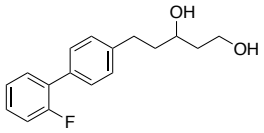


5-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)pentane-1,3-diol (2.32) was prepared according to Method F. The following amounts of reagents were used: **2.22** (0.26 g, 1.0 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol, 0.10 equiv), 4-(trifluoromethyl)phenylboronic acid (0.23 g, 1.2 mmol, 1.2 equiv), K_2CO_3 (1.4 g, 10. mmol, 10. equiv), and 1,4-dioxane/H_2O (8.75 mL, 4:1 ratio, 0.1 M). The compound was purified by flash column chromatography (0–5% MeOH/DCM) to afford the title compound as a white solid (0.21 g, 0.63 mmol, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.98–3.82 (m, 3H), 2.86 (ddd, *J*

= 13.8, 9.2, 5.8 Hz, 1H), 2.76 (ddd, *J* = 14.2, 9.3, 6.9 Hz, 1H), 2.42 (s, 1H), 2.03 (s, 1H), 1.94–1.74 (m, 4H).

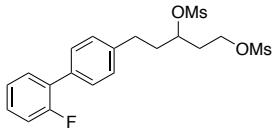


5-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)pentane-1,3-diyl dimethanesulfonate (2.33) was prepared according to Method Q. The following amounts of reagents were used: **2.32** (83 mg, 0.26 mmol, 1.0 equiv), Et_3N (0.04 mL, 0.6 mmol, 3 equiv), DMAP (6.3 mg, 52 μmol, 0.20 equiv), MsCl (0.04 mL, 0.6 mmol, 2 equiv), and DCM (5.0 mL, 0.052 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white, waxy foam (0.11 g, 0.23 mmol, 91%). **TLC R_f** = 0.6 (60% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.99–4.93 (m, 1H), 4.42–4.33 (m, 2H), 3.06 (s, 3H), 3.03 (s, 3H), 2.81 (td, *J* = 6.9, 2.8 Hz, 2H), 2.25–2.04 (m, 4H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 144.5, 140.6, 138.0, 129.4 (q, *J* = 32.4 Hz, 1C), 129.1 (2C), 127.6 (2C), 127.4 (2C), 125.9 (q, *J* = 3.7 Hz, 2C), 124.4 (q, *J* = 271.9 Hz, 1C), 78.2, 65.6, 38.8, 37.6, 36.6, 34.3, 31.7 (unknown impurity), 30.9; **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –62.6; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{23}F_3O_6S_2Na$, 503.0786; found, 503.0775.



5-(2'-Fluoro-[1,1'-biphenyl]-4-yl)pentane-1,3-diol (2.34) was prepared according to Method E. The following amounts of reagents were used: **2.22** (0.13 g, 0.50 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.7 mg, 3.0 μmol, 0.60 mol %), PPh_3 (2.4 mg, 9.0 μmol, 1.8 mol %), 2-fluorophenylboronic acid (77 mg, 0.55 mmol, 1.1 equiv), Na_2CO_3 (63 mg, 0.60 mmol, 1.2 equiv), and 1-propanol/H_2O (2:1, 15 mL, 0.050 M in substrate). The compound was purified by flash column chromatography (100%

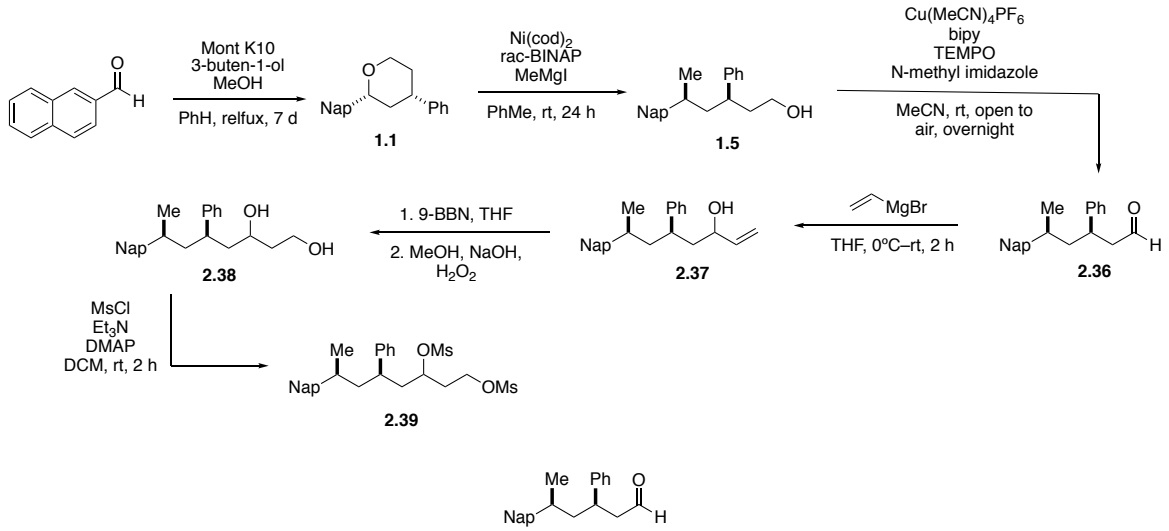
EtOAc) to afford the title compound as a white, waxy solid (0.11 g, 0.40 mmol, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.41 (td, *J* = 8.3, 1.8 Hz, 1H), 7.31–7.25 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.13 (dd, *J* = 10.9, 8.1 Hz, 1H), 3.95–3.87 (m, 2H), 3.85–3.78 (m, 1H), 3.09 (s, 1H), 2.93 (s, 1H), 2.83 (ddd, *J* = 14.2, 9.9, 5.9 Hz, 1H), 2.72 (ddd, *J* = 16.3, 9.7, 6.7 Hz, 1H), 1.91–1.71 (m, 4H).



5-(2'-Fluoro-[1,1'-biphenyl]-4-yl)pentane-1,3-diyl dimethanesulfonate (2.35) was prepared according to Method Q. The following amounts of reagents were used: **2.34** (94 mg, 0.34 mmol, 1.0 equiv), Et_3N (0.14 mL, 1.0 mmol, 3.0 equiv), DMAP (8.3 mg, 68 μmol, 0.20 equiv), MsCl (0.06 mL, 0.8 mmol, 2 equiv), and DCM (5.0 mL, 0.068 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a white, waxy solid (0.10 g, 0.24 mmol, 70%). **m.p.** = 80–82 ºC; **TLC R_f** = 0.8 (60% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.32–7.25 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H) 7.13 (t, *J* = 10.0 Hz, 1H), 4.98–4.94 (m, 1H), 4.39–4.33 (m, 2H), 3.04 (s, 3H), 3.02 (s, 3H), 2.82–2.78 (m, 2H), 2.24–2.06 (m, 4H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 159.9 (d, *J* = 247.4 Hz, 1C), 140.0, 134.0, 130.7 (d, *J* = 3.7 Hz, 1C), 129.4 (d, *J* = 2.8 Hz, 2C), 129.0 (d, *J* = 7.9 Hz, 1C), 128.8 (d, *J* = 13.4 Hz, 1C), 128.6 (2C), 124.5 (d, *J* = 3.7 Hz, 1C), 116.2 (d, *J* = 22.7 Hz, 1C), 78.4, 65.7, 38.7, 37.5, 36.5, 34.2, 30.9; **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –118.05 to –118.10 (m); **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{23}FO_6S_2Na$, 453.0818; found, 453.0807.

2.4.7.2 Intermediates and 1,3-Dimesylates for Branched Alkylcyclopropanes

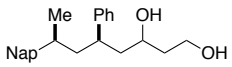
Scheme 2.8 Synthesis of 1,3-dimesylate **2.39**



***syn*-(±)-5-(Naphthalen-2-yl)-3-phenylhexanal (2.36)** was prepared according to Method G. The following amounts of reagents were used: **1.5** (0.32 g, 1.1 mmol, 1.0 equiv), $Cu(MeCN)_4PF_6$ (39 mg, 0.11 mmol, 0.10 equiv), bipy (16 mg, 0.11 mmol, 0.10 equiv), TEMPO (16 mg, 0.11 mmol, 0.10 equiv), *N*-methyl imidazole (20. μL, 0.20 mmol, 0.20 equiv), and MeCN (5.0 mL, 0.20 M in substrate). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a pale pink wax (0.28 g, 0.92 mmol, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.46 (t, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.47 (s, 1H), 7.43 (t, *J* = 7.0 Hz, 2H), 7.32–7.20 (m, 4H), 7.07 (d, *J* = 7.2 Hz, 2H), 2.95–2.87 (m, 1H), 2.65–2.53 (m, 3H), 2.08 (ddd, *J* = 14.0, 10.7, 4.1 Hz, 1H), 1.97 (ddd, *J* = 15.0, 10.9, 4.2 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H).

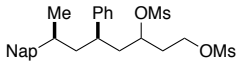
7-(Naphthalen-2-yl)-5-phenyloct-1-en-3-ol (2.37) was prepared according to Method J. The following amounts of reagents were used: **2.36** (0.21 g, 0.70 mmol, 1.0 equiv), vinylmagnesium

bromide (2.0 mL, 0.14 mmol, 2.0 equiv), and THF (2.0 mL, 0.35 M in substrate). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a colorless oil (0.16 g, 0.48 mmol, 69%, 1:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.73 (m, 6H, both diastereomers), 7.46–7.38 (m, 6H, both diastereomers), 7.32–7.19 (m, 8H, both diastereomers), 7.09–7.04 (m, 4H, both diastereomers), 5.70–5.61 (m, 2H, both diastereomers), 4.95 (addd, *J* = 24.3, 17.3, 6.4 Hz, 4H, both diastereomers), 3.81 (q, *J* = 6.8 Hz, 1H, one diastereomer), 3.70–3.65 (m, 1H, other diastereomer), 2.65–2.55 (m, 3H, both diastereomers), 2.42 (sept, *J* = 5.3 Hz, 1H, one diastereomer), 2.13–2.02 (m, 2H, both diastereomers), 1.98–1.89 (m, 2H, both diastereomers), 1.87–1.80 (m, 2H, both diastereomers), 1.76–1.66 (m, 3H, both diastereomers), 1.29 (s, 1H, one diastereomer), 1.20 (at, *J* = 6.0 Hz, 6H, both diastereomers).



7-(Naphthalen-2-yl)-5-phenyloctane-1,3-diol (2.38) was prepared according to Method K. The following amounts of reagents were used: **2.37** (0.16 g, 0.48 mmol, 1.0 equiv), 9-BBN (2.4 mL, 1.2 mmol, 2.5 equiv), MeOH (1.4 mL, 3.0 mL/mmol), H_2O_2 (0.72 mL, 1.5 mL/mmol, 30% w/w), NaOH (0.72 mL, 1.5 mL/mmol, 3.0 M aqueous solution), and THF (3.0 mL, 0.16 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a colorless oil (0.15 g, 0.42 mmol, 87%, 1:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.22 (m, 6H, both diastereomers), 7.47–7.36 (m, 6H, both diastereomers), 7.33–7.18 (m, 8H, both diastereomers), 7.08–7.03 (m, 4H, both diastereomers), 3.63–3.46 (m, 5H, both diastereomers), 3.36 (tt, *J* = 9.1, 3.2 Hz, 1H, one diastereomer), 2.64–2.30 (m, 6H, both diastereomers), 2.11–2.00 (m, 2H, both diastereomers), 1.97–1.89 (m, 2H, both diastereomers),

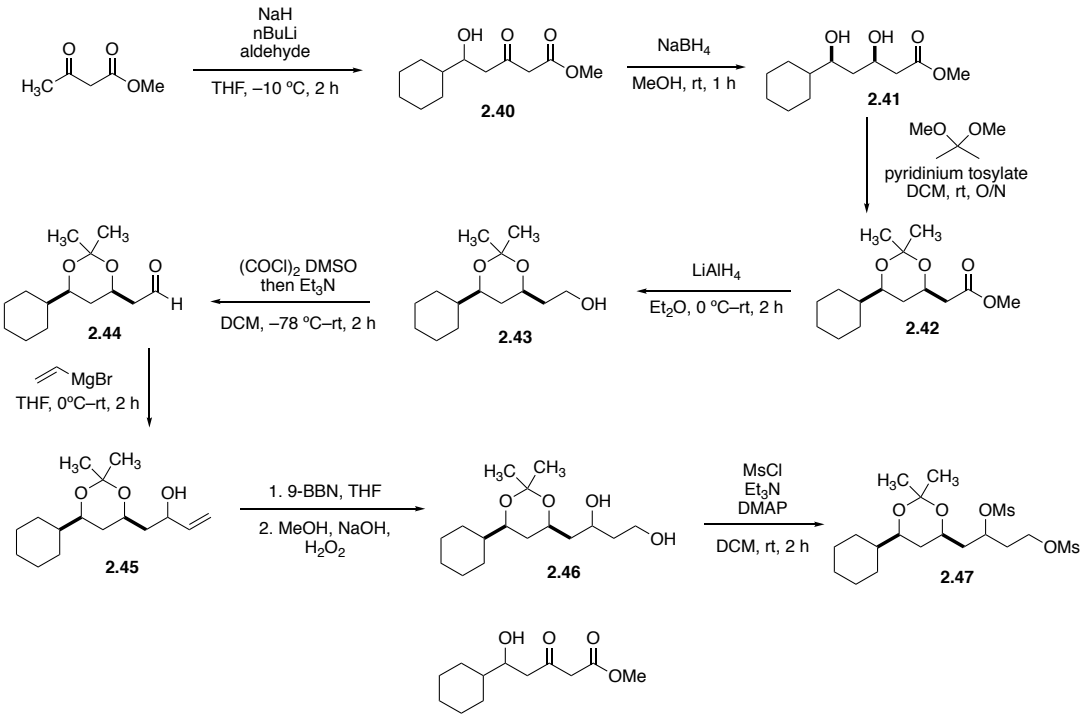
1.81–1.54 (m, 6H, both diastereomers), 1.52–1.32 (m, 4H, both diastereomers), 1.20 (d, J = 6.8 Hz, 6H, both diastereomers).



7-(Naphthalen-2-yl)-5-phenyloctane-1,3-diyl dimethanesulfonate (2.39) was prepared according to Method Q. The following amounts of reagents were used: **2.38** (0.15 g, 0.42 mmol, 1.0 equiv), Et_3N (0.18 mL, 1.3 mmol, 3.0 equiv), DMAP (10. mg, 84 μmol, 0.20 equiv), MsCl (0.07 mL, 1 mmol, 2 equiv), and DCM (2.0 mL, 0.21 M in substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a pale yellow oil (0.15 g, 0.29 mmol, 69%, 1:1 dr). **TLC R_f** = 0.8 (60% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81–7.77 (m, 6H, both diastereomers), 7.49–7.41 (m, 6H, both diastereomers), 7.36–7.31 (m, 4H, both diastereomers), 7.28–7.24 (m, 4H, both diastereomers), 7.08 (t, J = 6.9 Hz, 4H, both diastereomers), 4.60–4.49 (m, 2H, both diastereomers), 4.13 (s, 4H, both diastereomers), 2.85 (s, 3H, one diastereomer), 2.81 (s, 3H, other diastereomer), 2.60–2.51 (m, 2H, both diastereomers), 2.53 (s, 3H, one diastereomer), 2.50 (s, 3H, other diastereomer), 2.46–2.32 (m, 2H, both diastereomers), 2.16–2.08, (m, 2H, both diastereomers), 2.05–1.74 (m, 10H, both diastereomers), 1.23 (d, J = 6.8 Hz, 3H, one diastereomer), 1.22 (d, J = 6.8 Hz, 3H, other diastereomer); **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ 144.0 (one diastereomer), 143.8 (other diastereomer), 143.6 (one diastereomer), 143.2 (other diastereomer), 133.69 (one diastereomer), 133.67 (other diastereomer), 132.40 (one diastereomer), 132.37 (other diastereomer), 128.9 (one diastereomer, 2C), 128.8 (other diastereomer, 2C), 128.31 (one diastereomer), 128.26 (other diastereomer), 128.2 (one diastereomer, 2C), 127.9 (other diastereomer, 2C), 127.7 (one diastereomer, 2C; other diastereomer 1C), 127.6 (other diastereomer, 2C), 127.0 (one diastereomer), 126.9 (other diastereomer), 126.11 (one diastereomer), 126.07 (other diastereomer),

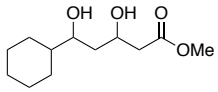
125.93 (one diastereomer), 125.89 (both diastereomers, 2C), 125.7 (one diastereomer), 125.4 (both diastereomers, 2C), 77.7 (one diastereomer), 77.5 (other diastereomer), 65.6 (one diastereomer), 65.4 (other diastereomer), 45.3 (one diastereomer), 45.1 (other diastereomer), 42.9 (one diastereomer), 42.3 (other diastereomer), 40.0 (one diastereomer), 39.9 (other diastereomer), 38.3 (one diastereomer), 38.1 (other diastereomer), 37.7 (one diastereomer), 37.5 (other diastereomer), 37.3 (both diastereomers), 34.4 (one diastereomer), 33.7 (other diastereomer), 23.8 (one diastereomer), 23.6 (other diastereomer); **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{32}O_6S_2Na$, 527.1538; found, 527.1520.

Scheme 2.9 Synthesis of 1,3-dimesylate **2.47**

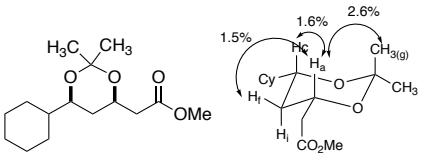


Methyl 5-cyclohexyl-5-hydroxy-3-oxopentanoate (2.40) was prepared according to Method L. The following amounts of reagents were used: methyl acetoacetate (0.54 mL, 5.0 mmol, 1.0 equiv), NaH (0.14 g, 6.0 mmol, 1.2 equiv), *n*-BuLi (2.4 mL, 6.0 mmol, 1.2 equiv, 2.5 M in hexanes), cyclohexanecarboxaldehyde (0.73 mL, 6.0 mmol, 1.2 equiv), and THF (10. mL, 0.20 M in

substrate). The compound was purified by flash column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a colorless oil (0.48 g, 2.1 mmol, 42%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.88–3.81 (m, 1H), 3.75 (s, 3H), 3.50 (s, 2H), 2.73 (dd, *J* = 17.4, 3.0 Hz, 1H), 2.65 (dd, *J* = 17.1 9.1 Hz, 1H), 2.57 (s, 1H), 1.88–1.72 (m, 3H), 1.70–1.61 (m, 2H), 1.41–1.32 (m, 1H), 1.29–1.11 (m, 3H), 1.04 (quintd, *J* = 12.2, 3.3 Hz, 2H).

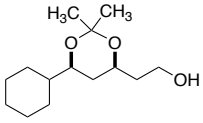


Methyl 5-cyclohexyl-3,5-dihydroxypentanoate (2.41) was prepared according to Method M. The following amounts of reagents were used: **2.40** (0.34 g, 1.5 mmol, 1.0 equiv), $NaBH_4$ (62 mg, 1.6 mmol, 1.1 equiv), and MeOH (7.0 mL, 0.23 M in substrate). The compound was purified by flash column chromatography as one diastereomer (0–50% EtOAc/hexanes) to afford the title compound as a colorless oil (0.15 g, 43%, >20:1 dr, 4% EtOAc by ^{1}H NMR). **TLC R_f** = 0.5 (50% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.29–4.23 (m, 1H), 3.79 (s, 1H), 3.72 (s, 3H), 3.68–3.63 (m, 1H), 3.02 (s, 1H), 2.51 (d, *J* = 2.5 Hz, 1H), 2.50 (s, 1H), 1.82–1.72 (m, 3H), 1.71–1.63 (m, 2H), 1.59 (d, *J* = 9.2 Hz, 1H), 1.39–1.30 (m, 1H), 1.27–1.11 (m, 4H), 1.03 (quintd, *J* = 12.3, 3.3 Hz, 2H).

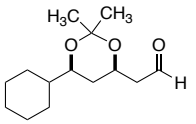


***cis*-Methyl 2-(6-cyclohexyl-2,2-dimethyl-1,3-dioxan-4-yl)acetate (2.42)** was prepared according to Method N. The following amounts of reagents were used: **2.41** (0.22 g, 0.93 mmol, 1.0 equiv), 2,2-dimethoxypropane (0.14 mL, 1.1 mmol, 1.2 equiv), pyridinium tosylate (12 mg, 47 μmol, 5.0 mol %), and DCM (3.0 mL, 0.31 M in substrate). The compound was purified by flash column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a white,

crystalline solid (0.17 g, 66%, >20:1 dr, 2% DCM by ^{1}H NMR). The relative configuration was assigned as cis by NOE NMR experiments. Irradiation of the acetonide proton (H_a) gave an NOE enhancement of 1.6% of H_c, an enhancement of 2.6% of H_g, and an enhancement of 1.5% of H_f. **TLC R_f** = 0.8 (20% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.30–4.23 (adtd, *J* = 13.5, 6.6, 2.3 Hz, 1H), 3.68 (s, 3H), 3.56 (ddd, *J* = 11.5, 6.9, 2.3 Hz, 1H), 2.55 (dd, *J* = 15.6, 6.9 Hz, 1H), 2.38 (dd, *J* = 15.6, 6.2 Hz, 1H), 1.89 (d, *J* = 12.3 Hz, 1H), 1.77–1.62 (m, 4H), 1.56 (dt, *J* = 12.5, 2.5 Hz, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.33–1.27 (m, 1H), 1.27–1.11 (m, 4H), 0.93 (aquint, *J* = 12.7 Hz, 2H).

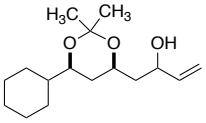


2-(*cis*)-6-Cyclohexyl-2,2-dimethyl-1,3-dioxan-4-yl)ethan-1-ol (2.43) was prepared according to Method O. The following amounts of reagents were used: **2.42** (0.17 g, 0.63 mmol, 1.0 equiv), $LiAlH_4$ (53 mg, 1.4 mmol, 2.2 equiv), and Et_2O (6.3 mL, 0.10 M in substrate). The compound was used in the next synthetic step without further purification. **TLC R_f** = 0.5 (20% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.13–4.05 (m, 1H), 3.81–3.76 (m, 2H), 3.56 (ddd, *J* = 11.4, 6.9, 2.3 Hz, 1H), 2.56 (at, *J* = 5.3 Hz, 1H), 1.91 (d, *J* = 13.4 Hz, 1H), 1.76–1.65 (m, 6H), 1.44 (s, 3H), 1.38 (s, 3H), 1.34–1.13 (m, 6H), 1.02–0.86 (m, 2H).

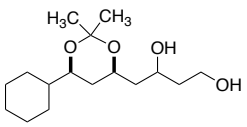


2-(*cis*)-6-Cyclohexyl-2,2-dimethyl-1,3-dioxan-4-yl)acetaldehyde (2.44) was prepared according to Method I. The following amounts of reagents were used: **2.43** (0.14 g, 0.58 mmol, 1.0 equiv), oxalyl chloride (0.06 mL, 0.8 mmol, 1 equiv), DMSO (0.05 mL, 0.7 mmol, 1 equiv), Et_3N (0.24 mL, 1.7 mmol, 3.0 equiv), and DCM (5.8 mL, 0.10 M in substrate). The compound was purified

by column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a clear yellow oil (131.5 mg, 3% DMSO by ^{1}H NMR, 90% yield). **TLC R_f** = 0.8 (25% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.78 (t, *J* = 2.2 Hz, 1H), 4.37–4.33 (m, 1H), 3.59–3.55 (m, 1H), 2.59 (ddd, *J* = 16.4, 7.2, 2.3 Hz, 1H), 2.49 (ddd, *J* = 16.5, 4.5, 1.7 Hz, 1H), 1.93–1.86 (m, 1H), 1.75–1.61 (m, 4H), 1.55 (td, *J* = 12.7, 2.5 Hz, 1H), 1.43 (s, 3H), 1.36 (s, 3H), 1.34–1.12 (m, 5H), 0.98–0.86 (m, 2H).

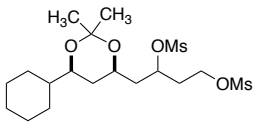


1-(*cis*)-6-Cyclohexyl-2,2-dimethyl-1,3-dioxan-4-yl)but-3-en-2-ol (2.45) was prepared according to Method J. The following amounts of reagents were used: **2.44** (130 mg, 0.54 mmol, 1.0 equiv), vinylmagnesium bromide (1.1 mL, 1.1 mmol, 2.0 equiv), and THF (3 mL, 0.2 M in substrate). The compound was purified by column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a clear oil (82 mg, 19% Et_2O by ^{1}H NMR, 54% yield). The NMR data was characterized as a 1:1 ratio of diastereomers: **TLC R_f** = 0.7 (25% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.92–5.80 (m, 2H, both diastereomers), 5.31–5.23 (m, 2H, both diastereomers), 5.13–5.07 (m, 2H, both diastereomers), 4.43–4.36 (br s, 1H, one diastereomer), 4.35–4.30 (br s, 1H, other diastereomer), 4.16 (t, *J* = 10.3 Hz, 1H, one diastereomer), 4.09 (t, *J* = 10.6 Hz, 1H, other diastereomer) 3.56–3.46 (m, 2H, both diastereomers), 3.36 (s, 1H), 3.09 (s, 1H), 1.94–0.86 (m, 42H, both diastereomers).



4-(*cis*)-6-Cyclohexyl-2,2-dimethyl-1,3-dioxan-4-yl)butane-1,3-diol (2.46) was prepared according to Method K. The following amounts of reagents were used: **2.45** (77 mg, 0.29 mmol,

1.0 equiv), 9-BBN (1.5 mL, 0.73 mmol, 2.5 equiv), THF (1.0 mL, 0.30 M in substrate), MeOH (0.90 mL, 3.0 mL/mmol), NaOH (0.45 mL, 1.5 mL/mmol, 3.0 M aqueous solution), and H_2O_2 (0.45 mL, 1.5 mL/mmol, 30% w/w). The compound was purified by flash column chromatography (0–5% MeOH/DCM) to afford the title compound as a clear, colorless oil (0.072 g, 80% yield, 33% DCM by ^{1}H NMR). The NMR data was characterized a 1:1 mixture of diastereomers). **TLC** $\mathbf{R_f}$ = 0.3 (50% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.22–4.15 (m, 2H, both diastereomers), 4.15–4.07 (m, 2H, both diastereomers), 3.91 (s, 1H, one diastereomer), 3.87–3.79 (m, 4H, both diastereomers), 3.58–3.53 (m, 2H, both diastereomers), 3.50 (d, *J* = 3.5 Hz, 1H, other diastereomer), 2.77 (t, *J* = 2.8 Hz, 1H, one diastereomer), 2.71 (t, *J* = 2.7 Hz, 1H, other diastereomer), 1.93–1.86 (m, 2H, both diastereomers), 1.78–1.60 (m, 14H, both diastereomers), 1.57–1.09 (m, 26H, both diastereomers), 0.98–0.86 (m, 4H, both diastereomers).

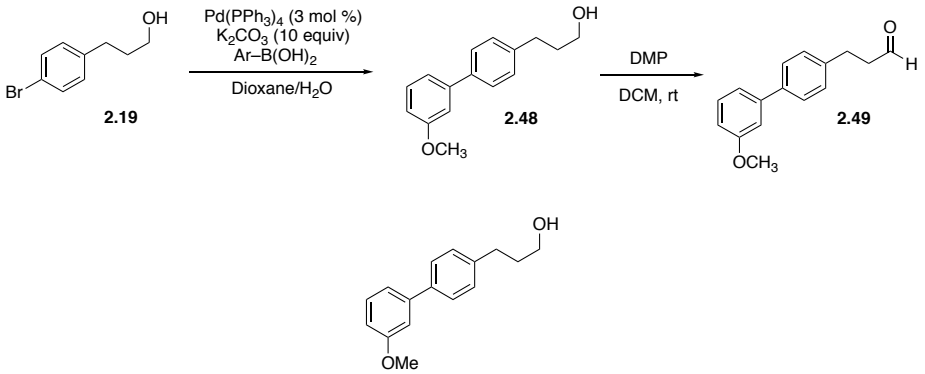


4-(*cis*)-6-Cyclohexyl-2,2-dimethyl-1,3-dioxan-4-yl)butane-1,3-diyl dimethanesulfonate (2.47) was prepared according to Method Q. The following amounts of reagents were used: **2.46** (71.8 mg, 0.250 mmol, 1.00 equiv), methanesulfonyl chloride (0.05 mL, 0.6 mmol, 2 equiv), dimethylaminopyridine (6 mg, 0.05 mmol, 0.2 equiv), Et_3N (0.09 mL, 0.6 mmol, 2 equiv), and DCM (2 mL). The compound was purified by flash column chromatography (0–50% EtOAc/hexanes) to afford a clear oil (55 mg, 0.22 mmol, 88% yield). **TLC** $\mathbf{R_f}$ = 0.5 (40% EtOAc/hexanes; CAM stain); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.06 (octet, *J* = 4.0 Hz, 1H, one diastereomer), 5.00 (septet, *J* = 4.1 Hz, 1H, other diastereomer), 4.40–4.31 (m, 4H, both diastereomers), 3.99 (t, *J* = 10.5 Hz, 2H, both diastereomers), 3.99 (t, *J* = 10.5 Hz, 2H, both diastereomers), 3.55 (ddd, *J* = 11.4, 6.9, 2.3 Hz, 2H, both diastereomers), 3.06 (s, 3H, one

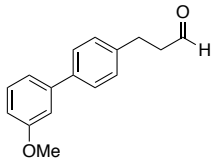
diastereomer), 3.05 (s, 3H, other diastereomer), 3.04 (s, 6H, both diastereomers), 2.32–2.19 (m, 2H, both diastereomers), 2.17–2.07 (m, 2H, both diastereomers), 1.92–1.84 (m, 4H, both diastereomers), 1.77–1.61 (m, 10H, both diastereomers), 1.48 (ddt, J = 15.0, 12.7, 2.4 Hz, 2H, both diastereomers), 1.41 (s, 6H, both diastereomers), 1.35 (s, 6H, both diastereomers), 1.31–1.11 (m, 10H, both diastereomers), 1.00–0.84 (m, 2H, both diastereomers); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 98.8 (one diastereomer), 98.6 (other diastereomer), 76.6 (one diastereomer), 76.3 (other diastereomer), 73.2 (one diastereomer), 73.1 (other diastereomer), 65.9 (one diastereomer), 65.8 (other diastereomer), 65.6 (one diastereomer), 65.2 (other diastereomer), 42.8 (2C, both diastereomers), 42.3 (one diastereomer), 41.4 (other diastereomer), 38.7 (one diastereomer), 38.6 (other diastereomer), 37.55 (one diastereomer), 37.51 (other diastereomer), 35.1 (one diastereomer), 34.2 (other diastereomer), 34.1 (one diastereomer), 34.0 (other diastereomer), 30.3 (2C, both diastereomers), 28.93 (one diastereomer), 28.88 (other diastereomer), 28.0 (2C, both diastereomers), 26.7 (2C, both diastereomers), 26.1 (2C, both diastereomers), 26.0 (2C, both diastereomers), 20.0 (one diastereomer), 19.8 (other diastereomer); **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{34}O_8S_2Na$, 465.1593; found, 465.1606.

2.4.7.3 Intermediates and 1,3-Dimesylates for 1,2-Disubstituted Alkylcyclopropanes

Scheme 2.10 Synthesis of aldehyde **2.49** used in diastereoselective aldol reactions

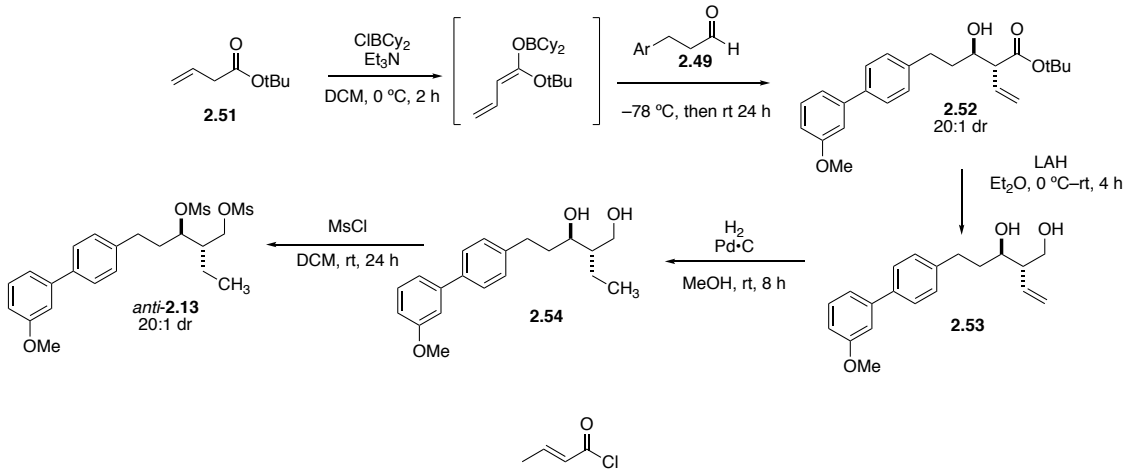


3-(3'-methoxy-[1,1'-biphenyl]-4-yl)propan-1-ol (2.48) was prepared according to Method F. The following amounts of reagents were used: **2.19** (2.5 g, 12 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.41 g, 0.35 mmol, 3.0 mol %), K_2CO_3 (16 g, 120 mmol, 10. equiv), 3-methoxyphenyl boronic acid (2.1 g, 14 mmol, 1.2 equiv), dioxane (60 mL), and H_2O (15 mL). The compound was purified by flash column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a yellow oil in EtOAc (2.8 g, 12 mmol, 77% yield, 40% EtOAc by ^{1}H NMR); **^{1}H NMR** (400 MHz, CDCl3) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.13 (s, 1H), 6.89 (d, *J* = 6.8 Hz, 1H), 3.87 (s, 3H), 3.71 (br s, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 1.95 (quint, *J* = 7.5 Hz, 2H), 1.40 (s, 1H).

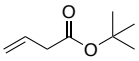


3-(3'-methoxy-[1,1'-biphenyl]-4-yl)propanal (2.49) was prepared according to Method H. The following amounts of reagents were used: **2.48** (2.8 g, 12 mmol, 1.0 equiv), DMP (5.5 g, 13 mmol, 1.1 equiv), and DCM (50 mL). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a yellow oil (1.6 g, 6.8 mmol, 53% yield, 15% EtOAc by ^{1}H NMR); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 3.87 (s, 3H), 3.02 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H).

Scheme 2.11 Synthesis of 1,3-dimesylate *anti*-**2.13**

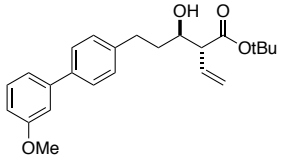


(*E*)-But-2-enoyl chloride (2.50) was prepared according to Method R. The following amounts of reagents were used: *trans*-crotonic acid (3.19 g, 37.2 mmol, 1.00 equiv) and $SOCl_2$ (2.70 mL, 37.2 mmol, 1.00 equiv). The compound was distilled (distillation head temperature ~115 ºC) to afford the title compound as a colorless oil. Yield was determined in next synthetic step. **TLC R_f** = 0.7 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (dq, *J* = 15.1, 6.9 Hz, 1H), 6.10 (dq, *J* = 15.1, 1.7 Hz, 1H), 1.99 (dd, *J* = 6.9, 1.7 Hz, 3H). Analytical data is consistent with literature values.[39]

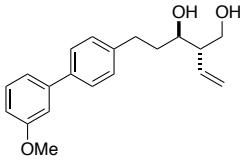


***tert*-Butyl but-3-enoate (2.51)** was prepared according to Method S. The following amounts of reagents were used: acid chloride **2.50** (37.2 mmol), *t*BuOH (5.32 mL, 55.7 mmol, 1.5 equiv), Et_3N (5.17 mL, 37.2 mmol, 1.00 equiv), and hexanes (37 mL, 0.10 M). The compound was purified by flash column chromatography (15% Et_2O/pentane) to afford the title compound as a clear, colorless oil (0.75 g, 4.9 mmol, 13% over two steps, 7% Et_2O by ^{1}H NMR). **TLC R_f** = 0.8 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.96–5.85 (m, 1H), 5.13 (ddt, *J* = 13.8, 2.2, 1.6

Hz, 2H), 3.00 (dt, *J* = 6.9, 1.4, 2H), 1.45 (s, 9H). Analytical data is consistent with literature values.[19]

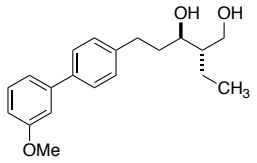


***tert*-Butyl (*anti*)-3-hydroxy-5-(3'-methoxy-[1,1'-biphenyl]-4-yl)-2-vinylpentanoate (2.52)** was prepared according to Method T. The following amounts of reagents were used: aldehyde **2.49** (0.50 g, 2.1 mmol, 1.0 equiv), ester **2.51** (0.44 g, 3.1 mmol, 1.5 equiv), dicyclohexylboron chloride (1.4 mL, 2.7 mmol, 1.3 equiv, 2.0 M), Et_3N (0.43 mL, 3.1 mmol, 1.5 equiv) and DCM (10. mL, 0.20 M). The compound was purified by flash column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (0.68 g, 1.8 mmol, 86%). **TLC R_f** = 0.7 (40% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 2.2 Hz, 1H), 6.87 (dd, *J* = 8.0, 2.5 Hz, 1H), 5.86–5.77 (m, 1H), 5.23 (d, *J* = 5.6 Hz, 1H), 5.19 (s, 1H), 3.86 (s, 3H), 3.86–3.81 (m, 1H), 3.03 (dd, *J* = 9.4, 7.9 Hz, 1H), 2.90 (ddd, *J* = 14.1, 9.9, 5.1 Hz, 1H), 2.76–2.69 (m, 2H), 1.92–1.84 (m, 1H), 1.78–1.68 (m, 1H), 1.46 (s, 9H).

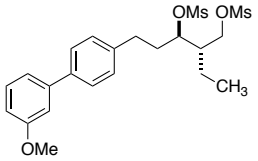


***anti*-5-(3'-Methoxy-[1,1'-biphenyl]-4-yl)-2-vinylpentane-1,3-diol (2.53)** was prepared according to Method O. The following amounts of reagents were used: ester **2.52** (0.68 g, 1.8 mmol, 1.0 equiv), $LiAlH_4$ (0.16 g, 4.2 mmol, 2.3 equiv), and Et_2O (9.0 mL, 0.20 M). The compound was used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.10 (t, *J* =

2.0 Hz, 1H), 6.87 (dd, *J* = 7.8, 2.5 Hz, 1H), 5.70–5.61 (m, 1H), 5.21 (d, *J* = 5.7 Hz, 1H), 5.17 (s, 1H), 3.86 (s, 3H), 3.84–3.74 (m, 3H), 2.89 (ddd, *J* = 14.3, 10.1, 5.5 Hz, 1H), 2.77–2.68 (m, 1H), 2.50 (d, *J* = 4.9 Hz, 1H), 2.41–2.34 (m, 2H), 1.98–1.90 (m, 1H), 1.98–1.72 (m, 1H).



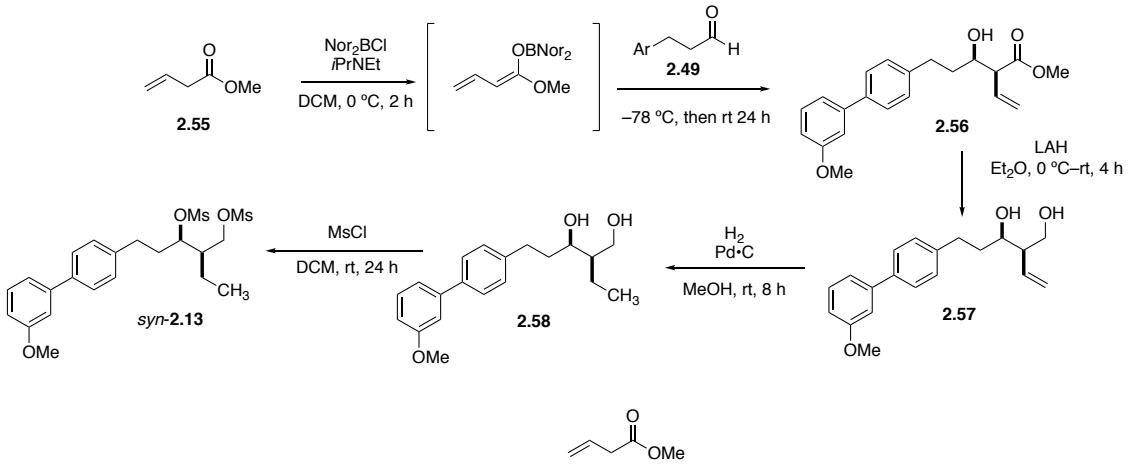
***anti*-2-Ethyl-5-(3'-methoxy-[1,1'-biphenyl]-4-yl)pentane-1,3-diol (2.54)** was prepared according to Method P. The following amounts of reagents were used: diol **2.53** (1.8 mmol, 1.0 equiv), Pd/C (70 mg), H_2 balloon (excess), DCM (3.0 mL, 0.6 M in substrate), and MeOH (9.0 mL, 0.20 M in substrate). The compound was used without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.96 (ap d, *J* = 11.6, 1H), 3.86 (s, 3H), 3.79–3.68 (m, 2H), 2.89 (quint, *J* = 7.3 Hz, 1H), 2.78–2.69 (m, 1H), 2.48 (d, *J* = 5.0 Hz, 1H), 2.35 (s, 1H), 1.97–1.89 (m, 2H), 1.53–1.42 (m, 3H), 0.95 (t, *J* = 7.3 Hz, 3H).



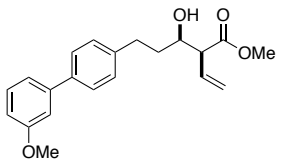
***anti*-2-Ethyl-5-(3'-methoxy-[1,1'-biphenyl]-4-yl)pentane-1,3-diyl dimethanesulfonate (*anti*-2.13)** was prepared according to Method Q. The following amounts of reagents were used: diol **2.54** (1.8 mmol, 1.0 equiv), MsCl (0.30 mL, 3.9 mmol, 2.2 equiv), Et_3N (0.75 mL, 5.4 mmol, 3.0 equiv), DMAP (43 mg, 0.36 mmol, 0.2 equiv), and DCM (9.0 mL, 0.20 M). The compound was purified by flash column chromatography (0–35% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (0.34 g, 0.72 mmol, 40% over three steps). **TLC R_f** = 0.5 (40% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H),

7.28 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 7.7 Hz, 1H), 7.10 (t, J = 2.5 Hz, 1H), 6.88 (dd, J = 8.0, 2.5 Hz, 1H), 4.92 (q, J = 5.7 Hz, 1H), 4.32–4.25 (m, 2H), 3.86 (s, 3H), 3.06 (s, 3H), 3.00 (s, 3H), 2.80 (td, J = 8.3, 4.7 Hz, 2H), 2.16–2.09 (m, 3H), 1.61 (septet, J = 7.0 Hz, 1H), 1.46 (septet, J = 7.0 Hz, 1H), 1.02 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (500 MHz, $CDCl_3$) δ 160.1, 142.5, 139.9, 139.3, 129.9, 129.0 (2C), 127.5 (2C), 119.6, 112.9, 112.7, 81.9, 67.8, 55.5, 43.4, 39.0, 37.6, 33.6, 30.9, 20.0, 11.6. **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{30}O_7S_2Na$, 493.1331; found, 493.1310.

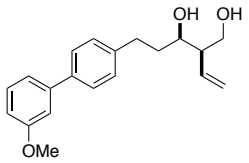
Scheme 2.12 Synthesis of 1,3-dimesylate *syn*-**2.13**



Methyl but-3-enoate (2.55) was prepared according to Method S. The following amounts of reagents were used: acid chloride **2.50** (75 mmol, 10 equiv), MeOH (4.5 mL, 113 mmol, 1.5 equiv), Et_3N (10. mL, 75 mmol, 1.0 equiv), and hexanes (200 mL, 0.4 M). The desired compound was inseparable from internal alkene isomer. The compound used in the next synthetic step unpurified. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.98–5.90 (m, 1H), 5.20–5.14 (m, 2H), 3.70 (s, 3H), 1.88 (dd, J = 6.6 Hz, 1.8 Hz, 2H). Analytical data is consistent with literature values.[39]

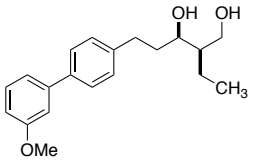


Methyl (*syn*)-3-hydroxy-5-(3'-methoxy-[1,1'-biphenyl]-4-yl)-2-vinylpentanoate (2.56) was prepared according to Method U. The following amounts of reagents were used: aldehyde **2.49** (0.33 g, 1.4 mmol, 1.0 equiv), ester **2.55** (1.0 mL, excess), dinorbornylboron chloride (0.90 mL, 1.8 mmol, 1.3 equiv, 2.0 M), diisopropylethylamine (0.36 mL, 2.1 mmol, 1.5 equiv), and DCM (5 mL, 0.3 M in substrate). The compound was purified by flash column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (0.14 g, 0.43 mmol, 31%, 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.11 (s, 1H), 6.88 (dd, *J* = 7.9, 2.6 Hz, 1H), 5.96 (dt, *J* = 16.4, 9.8 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 3.98 (sext, *J* = 3.9 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.10 (dd, *J* = 8.9, 4.2 Hz, 1H), 2.89 (ddd, *J* = 14.3, 9.6, 5.3 Hz, 1H), 2.76–2.66 (m, 2H), 1.89–1.79 (m, 1H), 1.77–1.67 (m, 1H).

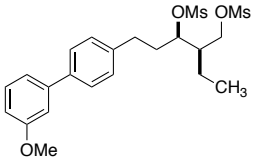


***syn*-5-(3'-Methoxy-[1,1'-biphenyl]-4-yl)-2-vinylpentane-1,3-diol (2.57)** was prepared according to Method O. The following amounts of reagents were used: ester **2.56** (0.14 g, 0.43 mmol, 1.0 equiv), $LiAlH_4$ (52 mg, 1.4 mmol, 3.2 equiv), and Et_2O (2.2 mL, 0.20 M). The compound was used in the next synthetic step without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.12 (s, 1H), 6.89 (dd, *J* = 9.0, 1.9 Hz, 1H), 5.95–5.84 (m, 1H), 5.30 (d, *J* = 9.8 Hz, 1H), 5.23 (d, *J* =

18.0 Hz, 1H), 3.93–3.75 (m, 6H), 2.92–2.82 (m, 1H), 2.78–2.68 (m, 1H), 2.42–2.33 (m, 1H), 2.10 (s, 1H), 1.92–1.77 (m, 3H).



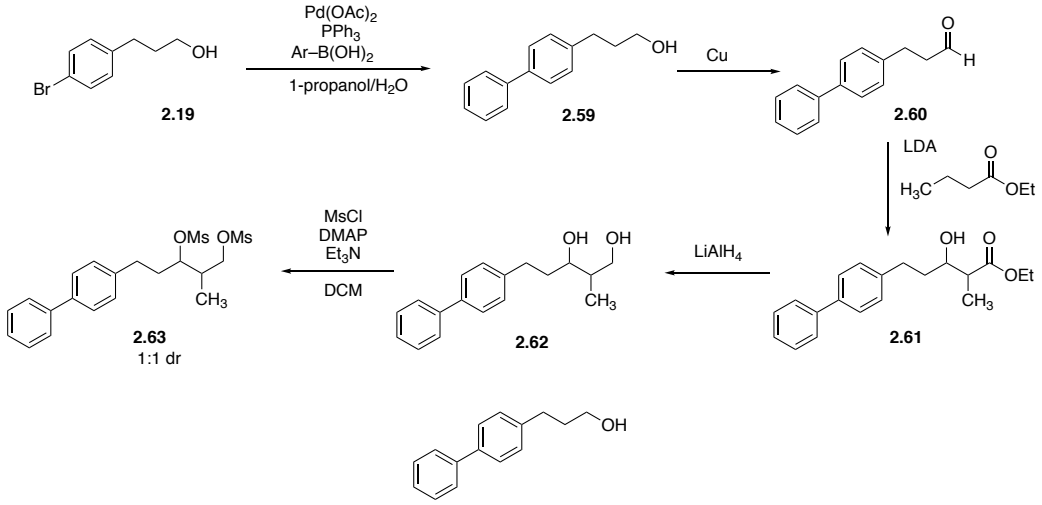
***syn*-2-Ethyl-5-(3'-methoxy-[1,1'-biphenyl]-4-yl)pentane-1,3-diol (2.58)** was prepared according to Method P. The following amounts of reagents were used: diol **2.57** (0.77 mmol, 1.0 equiv), Pd/C (44 mg), H_2 balloon (excess), DCM (5.0 mL, 0.15 M in substrate), and MeOH (20. mL, 0.038 M in substrate). The compound was used in the next synthetic step without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.88 (dd, *J* = 7.0, 2.0 Hz, 1H), 3.94–3.87 (m, 1H), 3.86 (s, 3H), 3.85–3.73 (m, 2H), 2.92 (ddd, *J* = 14.2, 10.2, 5.5 Hz, 1H), 2.74–2.65 (m, 1H), 2.50 (d, *J* = 5.2 Hz, 1H), 2.24 (t, *J* = 4.8 Hz, 1H), 1.94–1.85 (m, 1H), 1.81–1.72 (m, 1H), 1.68–1.61 (m, 1H), 1.36 (quint, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).



***syn*-2-Ethyl-5-(3'-methoxy-[1,1'-biphenyl]-4-yl)pentane-1,3-diyl dimethanesulfonate (*syn*-2.13)** was prepared according to Method Q. The following amounts of reagents were used: diol **2.58** (0.77 mmol), MsCl (0.13 mL, 1.7 mmol, 2.2 equiv), Et_3N (0.32 mL, 2.3 mmol, 3.0 equiv), DMAP (18 mg, 0.15 mmol, 0.20 equiv), and DCM (3.9 mL, 0.20 M). The compound was purified by flash column chromatography (0–40% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (0.21 g, 0.43 mmol, 57% over three steps, 8% EtOAc by NMR, 20:1 dr). **TLC R_f** = 0.6 (40% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* =

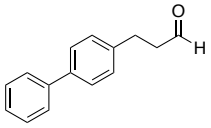
8.0 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.89 (dd, *J* = 8.1, 2.3 Hz, 1H), 4.96 (quint, *J* = 4.0 Hz, 1H), 4.32–4.24 (m, 2H), 3.86 (s, 3H), 3.05 (s, 3H), 3.02 (s, 3H), 2.86–2.80 (m, 1H), 2.75–2.69 (m, 1H), 2.17–2.09 (m, 2H), 2.03–1.97 (m, 1H), 1.56 (sept, *J* = 7.3 Hz, 1H), 1.41 (sept, *J* = 7.7 Hz, 1H), 0.98 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (500 MHz, $CDCl_3$) δ 160.1, 142.4, 139.7, 139.3, 129.9, 128.9 (2C), 127.5 (2C), 119.6, 112.9, 112.7, 81.4, 68.3, 55.4, 43.7, 38.9, 37.5, 37.3, 31.7, 19.1, 12.0. **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{30}O_7S_2Na$, 493.1331; found, 493.1337.

Scheme 2.13 Synthesis of 1,3-dimesylate **2.63**

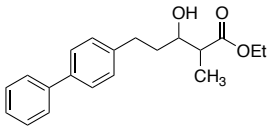


3-([1,1'-Biphenyl]-4-yl)propan-1-ol (2.59) was prepared according to Method E. The following amounts of reagents were used: alcohol **2.19** (1.9 g, 8.6 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mg, 0.05 mmol, 0.6 mol %), PPh_3 (40. mg, 0.16 mmol, 1.8 mol %), phenylboronic acid (1.2 g, 9.5 mmol, 1.1 equiv), Na_2CO_3 (1.1 g, 10. mmol, 1.1 equiv), 1-propanol (20. mL, 0.43 M in substrate) and H_2O (8.0 mL). The compound was purified by flash column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a white solid (1.6 g, 7.4 mmol, 86%). **TLC R_f** = 0.2 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 3.72 (q, *J*

= 6.0 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 1.94 (quint, *J* = 6.9 Hz, 2H). Analytical data is consistent with literature values.[46]

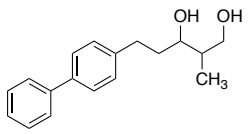


3-([1,1'-Biphenyl]-4-yl)propanal (2.60) was prepared according to Method G. The following amounts of reagents were used: alcohol **2.59** (1.3 g, 6.2 mmol, 1.0 equiv), Cu(MeCN)OTf (0.12 g, 0.31 mmol, 5.0 mol %), bipy (48 mg, 0.31 mmol, 5.0 mol %), TEMPO (48 mg, 0.31 mmol, 5.0 mol %), *N*-methyl imidazole (0.05 mL, 0.6 mmol, 0.1 equiv), and MeCN (30 mL, 0.20 M in substrate). The compound was purified by flash column chromatography (0–20% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (1.1 g, 5.2 mmol, 85%). **TLC R_f** = 0.2 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H). Analytical data is consistent with literature values.[47]

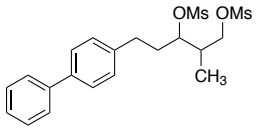


Ethyl 5-([1,1'-biphenyl]-4-yl)-3-hydroxy-2-methylpentanoate (2.61) was prepared according to Method V. The following amounts of reagents were used: *n*-BuLi (19 mL, 48 mmol, 3.4 equiv, 2.5M), diisopropylamine (6.8 mL 48 mmol, 3.4 equiv), ethyl propionate (3.3 mL, 28 mmol, 2.0 equiv), aldehyde **2.60** (3.0 g, 14 mmol, 1.0 equiv), and THF (15 mL, 0.93 M in substrate). The compound was used in the next synthetic step without further purification.

[46] Ni, S.; Wei, H.; Li, B.; Chen, F.; Liu, Y.; Chen, W.; Xu, Y.; Qiu, X.; Li, X.; Lu, Y.; Liu, W.; Hu, L.; Lin, D.; Wang, M.; Zheng, X.; Mao, F.; Zhu, J.; Lan, L.; Li, J. *J. Med. Chem*. **2017**, *60*, 8145–8159.
[47] Zha, G.-F.; Fang, W.-Y.; Leng, J.; Qin, H.-L. *Adv. Synth. Catal*. **2019**, *361*, 2262–2267.



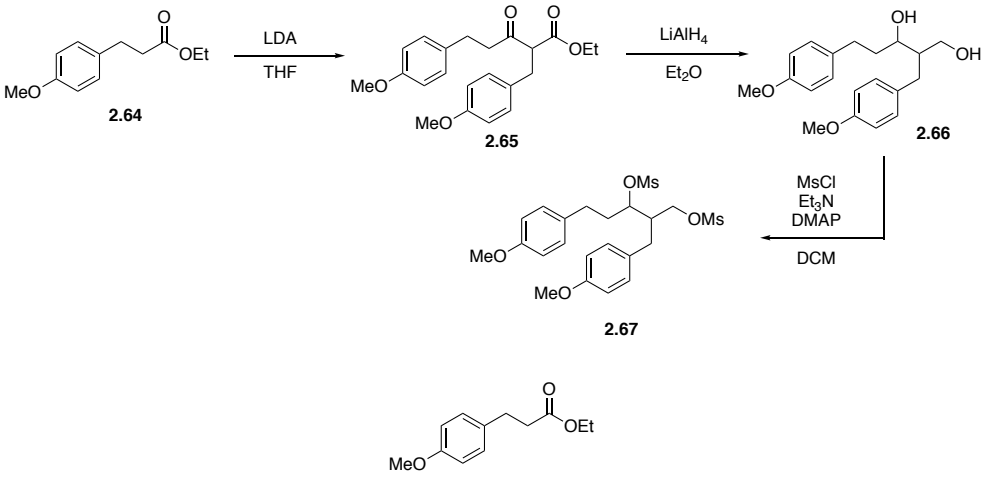
5-([1,1'-Biphenyl]-4-yl)-2-methylpentane-1,3-diol (2.62) was prepared according to Method M. The following amounts of reagents were used: beta-keto ester **2.61** (14 mmol, 1.0 equiv), $NaBH_4$ (1.3 g, 35 mmol, 2.5 equiv), I_2 (1.1 g, 4.2 mmol, 0.3 equiv), and THF (50 mL, 0.28 M substrate). The compound was purified by flash column chromatography (0–25% EtOAc/hexanes) to afford the title compound as a white solid (0.41 g, 1.5 mmol, 11% over two steps, 1:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 4H, both diastereomers), 7.51 (d, *J* = 8.2 Hz, 4H, both diastereomers), 7.41 (t, *J* = 7.5 Hz, 4H, both diastereomers), 7.32 (dt, *J* = 7.4, 1.4 Hz, 2H, both diastereomers), 7.27 (d, *J* = 8.1 Hz, 4H, both diastereomers), 3.90–3.84 (m, 1H, one diastereomer), 3.78 (dd, *J* = 10.9, 3.8 Hz, 1H, other diastereomer), 3.71–3.67 (m, 3H, both diastereomers), 3.65–3.57 (m, 1H, one diastereomer), 3.33 (br s, one diastereomer), 3.18 (br s, one diastereomer), 2.93–2.76 (m, 4H, both diastereomers), 2.75–2.64 (m, 2H, both diastereomers), 1.95–1.71 (m, 6H, both diastereomers), 0.92 (d, *J* = 7.1 Hz, 3H, one diastereomer), 0.89 (d, *J* = 7.0 Hz, 3H, other diastereomer).



5-([1,1'-Biphenyl]-4-yl)-2-methylpentane-1,3-diyl dimethanesulfonate (2.63) was prepared according to Method Q. The following amounts of reagents were used: diol **2.62** (0.53 g, 2.0 mmol, 1.0 equiv), MsCl (0.33 mL, 4.3 mL, 2.2 equiv), Et_3N (0.82 mL, 5.9 mmol, 3.0 equiv), DMAP (48 mg, 0.39 mmol, 0.20 equiv), and DCM (9.8 mL, 0.20 M substrate). The compound was purified by flash column chromatography (0–50% EtOAc/hexanes) to afford the title compound as a white solid (0.65 g, 1.5 mmol, 77%, 3:1 dr). The compound was characterized as a 3:1 mixture of

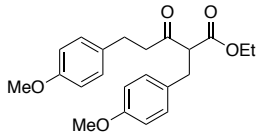
diastereomers. **m.p.** = 78–80 ºC; **TLC** $\mathbf{R_f}$ = 0.6 (50% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 4H, major, 4H, minor), 7.43 (t, *J* = 7.6 Hz, 2H, major, 2H, minor), 7.33 (t, *J* = 7.4 Hz, 1H, major, 1H, minor), 7.28 (d, *J* = 8.2 Hz, 2H, major, 2H, minor), 4.97 (ddd, *J* = 8.3, 5.8, 2.6 Hz, 1H, major), 4.85 (q, *J* = 6.0 Hz, 1H, minor), 4.24–4.15 (m, 2H, major, 2H, minor), 3.06 (s, 3H, minor), 3.05 (s, 3H, major), 3.03 (s, 3H, major), 3.01 (s, 3H, minor), 2.85–2.70 (m, 2H, major, 2H, minor), 2.42 (quint, *J* = 6.4 Hz, 1H, minor), 2.34 (ap q, *J* = 7.0 Hz, 1H, major), 2.22–2.13 (m, 1H, major), 2.11–1.97 (m, 1H, major, 2H, minor), 1.12 (d, *J* = 6.9 Hz, 3,H minor), 1.05 (d, *J* = 7.05 Hz, 3H, major); **^{13}C NMR** (500 MHz, $CDCl_3$) δ 140.9 (both), 139.8 (minor), 139.51 (major), 139.49 (major), 139.46 (minor), 129.0 (minor), 128.9 (4C major, 3C minor), 127.5 (2C major, 2C minor), 127.3 (both), 127.1 (2C major, 2C minor), 82.4 (minor), 81.2 (major), 70.4 (major), 70.2 (minor), 38.9 (both), 37.6 (minor), 37.5 (major), 36.8 (both), 33.9 (major), 33.2 (minor), 31.6 (major), 30.6 (minor), 12.8 (minor), 10.3 (major). **HRMS** (TOF MS ES+) *m/z*: $[M]^+$ calcd for $C_{20}H_{26}O_6S_2$, 449.1068; found, 449.1054.

Scheme 2.14 Synthesis of 1,3-dimesylate **2.67**

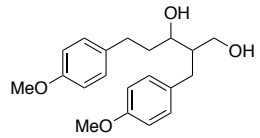


Ethyl 3-(4-methoxyphenyl)propanoate (2.64) was prepared according to Method W. The following amounts of reagents were used: 3-(4-methoxyphenyl)propanoic acid (5.4 g, 30. mmol, 1.0 equiv), H_2SO_4 (1.6 g, 30. mmol, 1.0 equiv), and EtOH (37 mL, 0.81 M in substrate). The

compound was purified by flash column chromatography (0–30% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (5.7 g, 27 mmol, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.12 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). Analytical data is consistent with literature values.[48]



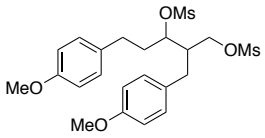
Ethyl 2-(4-methoxybenzyl)-5-(4-methoxyphenyl)-3-oxopentanoate (2.65) was prepared according to Method V. The following amounts of reagents were used: *n*-BuLi (11 mL, 28 mmol, 1.0 equiv, 2.5M), diisopropylamine (3.8 mL 28 mmol, 1.0 equiv), ester **2.64** (5.7 g, 28 mmol, 1.0 equiv), and THF (10. mL, 2.8 M in substrate). The compound was used in the next synthetic step unpurified.



2-(4-Methoxybenzyl)-5-(4-methoxyphenyl)pentane-1,3-diol (2.66) was prepared according to Method O. The following amounts of reagents were used: beta-keto ester **2.65** (11 mmol, 1.0 equiv), $LiAlH_4$ (1.5 g, 39 mmol, 3.5 equiv), and Et_2O (50. mL, 0.22 M substrate). The compound was purified by flash column chromatography (0–50% EtOAc/hexanes) to afford the title compound as a clear, colorless oil (0.88 g, 2.7 mmol, 25% over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H, major), 7.09 (d, *J* = 8.2 Hz, 4H, minor), 7.03 (d, *J* = 8.5 Hz, 2H, major), 6.86–6.76 (m, 4H, major, 4H, minor), 3.93–3.86 (1H, major, 1H, minor), 3.79 (s, 3H,

[48] Zhang, J.; Zhen, X.; Zeng, J.; Pu, K. *Anal. Chem*. **2018**, *90*, 9301–9307.

major), 3.78 (s, 3H, minor), 3.77 (3H, major; 3H, minor), 3.73–3.55 (m, 2H, major; 2H, minor), 2.85–2.50 (m, 5H, major; 5H, minor), 2.36 (t, J = 4.3 Hz, 1H, major), 1.97–1.75 (m, 3H, major; 2H, minor).

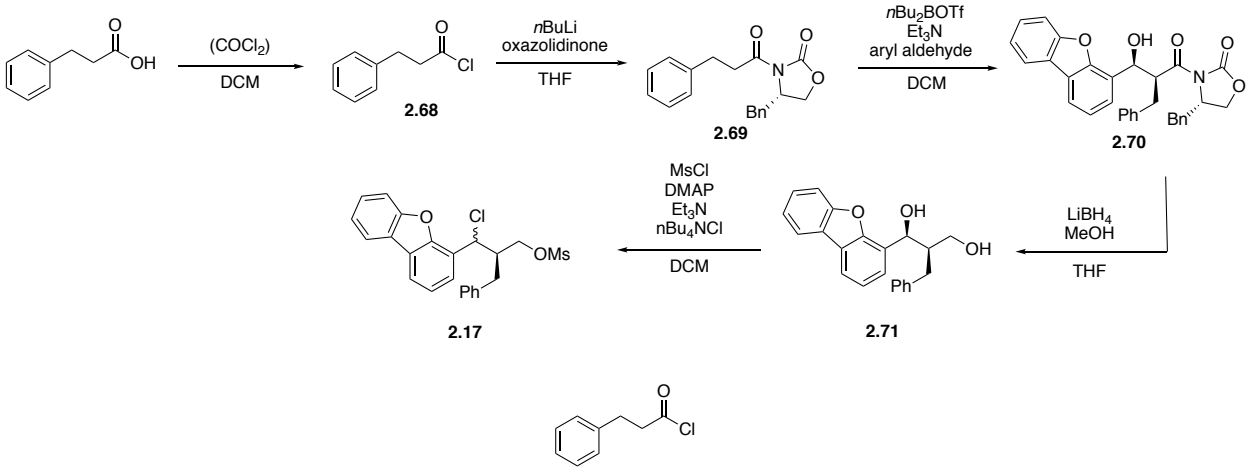


2-(4-Methoxybenzyl)-5-(4-methoxyphenyl)pentane-1,3-diyl dimethanesulfonate (2.67) was prepared according to Method Q. The following amounts of reagents were used: diol **2.66** (1.1 g, 3.4 mmol, 1.0 equiv), MsCl (0.58 mL, 7.5 mL, 2.2 equiv), Et_3N (1.4 mL, 10. mmol, 3.0 equiv), DMAP (83 mg, 0.68 mmol, 0.20 equiv), and DCM (10. mL, 0.34 M substrate). The compound was purified by flash column chromatography (0–60% EtOAc/hexanes) to afford the title compound as a clear, light yellow oil (1.5 g, 3.1 mmol, 92% over two steps). The compound was characterized as a 3:1 mixture of diastereomers. **TLC R_f** = 0.6 (50% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11–7.06 (m, 2H major, 2H minor), 7.00 (d, J = 8.6 Hz, 2H major, 2H minor), 6.83 (t, J = 8.5 Hz, 17H, 4H major, 4H minor), 4.95–4.88 (m, 1H major, 1H minor), 4.21–4.14 (m, 2H major, 2H minor), 3.79–3.88 (m, 6H major, 6H minor), 3.04 (s, 3H, minor), 3.03 (s, 3H, major), 2.97 (s, 3H, major), 2.95 (s, 3H, minor), 2.85–2.52 (m, 4H major, 4H minor), 2.50–2.41 (m, 1H major, 1H minor), 2.18–1.97 (m, 2H major, 2H minor); **^{13}C NMR** (500 MHz, $CDCl_3$) δ 158.6 (both), 158.3 (major), 158.2 (minor), 132.4 (minor), 132.3 (major), 130.2 (both), 129.8 (2C, major), 129.7 (2C, minor), 129.49 (2C, major), 129.45 (2C, minor), 114.4 (2C, major), 114.3 (2C, minor), 114.19 (2C, major), 114.16 (2C, minor), 81.6 (minor), 81.1 (major), 68.2 (major), 67.6 (minor), 55.40 (4C, both), 44.0 (minor), 43.8 (major), 39.0 (minor), 38.8 (major), 37.45 (minor), 37.39 (major), 33.8 (minor), 33.7 (major), 32.1 (minor), 31.3 (major), 31.0 (major), 30.3

(minor). **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{30}O_8S_2Na$, 509.1280; found, 509.1299.

2.4.7.4 Intermediates and 1,3-Chloromesylate for Enantioenriched 1,2-Disubstituted Alkylcyclopropane

Scheme 2.15 Synthesis of benzylic chloride **2.72**

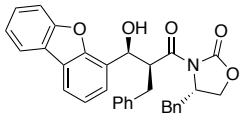


3-Phenylpropanoyl chloride (2.68) was prepared according to Method X. The following amounts of reagents were used: 3-phenylpropanoic acid (3.8 g, 25 mmol, 1.0 equiv) and $(COCl)_2$ (3.2 mL, 38 mmol, 1.5 equiv). The compound was distilled (distillation head temperature ~90 ºC) to afford the title compound as a colorless oil (3.5 g, 21 mmol, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (tt, *J* = 7.1, 1.7 Hz, 2H), 7.25–7.20 (m, 1H), 7.18 (d, *J* = 6.9 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H). Analytical data is consistent with literature values.[49]

(*S*)-4-Benzyl-3-(3-phenylpropanoyl)oxazolidin-2-one (2.69) was prepared according to Method Y. The following amounts of reagents were used: **2.68** (3.5 g, 21 mmol, 1.0 equiv), *n*-BuLi (8.3

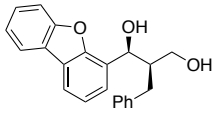
[49] Greenberg, J. A.; Sammakia, T. *J. Org. Chem.* **2017**, *82*, 3245–3251.

mL, 21 mmol, 1.0 equiv, 2.5 M in hexanes), (*S*)-4-benzyl-2-oxazolidinone (3.7 g, 21 mmol, 1.0 equiv), and THF (69 mL, 0.30 M in substrate). The compound was purified by flash column chromatography to afford the title compound as a white solid (1.8 g, 5.9 mmol, 28%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.12 (m, 10H), 4.65 (octet, *J* = 3.3 Hz, 1H), 4.18–4.10 (m, 2H), 3.37–3.19 (m, 3H), 3.02 (td, *J* = 8.0, 3.2 Hz, 2H), 2.75 (dd, *J* = 13.5, 9.5 Hz, 1H). Analytical data is consistent with literature values.[50]

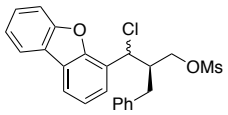


(*S*)-4-Benzyl-3-((2*S*,3*S*)-2-benzyl-3-(dibenzo[*b*,*d*]furan-4-yl)-3-hydroxypropanoyl)oxazolidin-2-one (2.70) was prepared according to Method Z. The following amounts of reagents were used: **2.69** (1.8 g, 5.9 mmol, 1.0 equiv), nBu_2BOTf (1.1 mL, 7.7 mmol, 1.3 equiv), Et_3N (1.1 mL, 7.7 mmol, 1.3 equiv), dibenzofuran-4-carboxaldehyde (1.6 g, 8.3 mmol, 1.3 equiv), and DCM (10. mL, 0.59 M in substrate). The compound was purified by flash column chromatography to afford the title compound as a white foam (1.5 g, 2.9 mmol, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (*J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.38–7.31 (m, 2H), 7.27–7.11 (m, 8H), 6.90–6.84 (m, 2H), 5.63 (t, *J* = 5.2 Hz, 1H), 5.24 (dt, *J* = 9.5, 6.3 Hz, 1H), 4.35–4.27 (m, 1H), 3.81 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.70 (t, *J* = 8.5 Hz, 1H), 3.41 (d, *J* = 4.7 Hz, 1H), 3.26 (d, *J* = 2.9 Hz, 1H), 3.24 (s, 1H), 2.78 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.12 (dd, *J* = 14.7, 9.5 Hz, 1H).

[50] Edmonds, M. K. Graichen, F. H. M.; Gardiner, J.; Abell, A. D. *Org. Lett*. **2008**, *10*, 885–887.



(1*S*,2*R*)-2-Benzyl-1-(dibenzo[*b*,*d*]furan-4-yl)propane-1,3-diol (2.71) was prepared according to Method AA. The following amounts of reagents were used: **2.70** (1.35 g, 2.77 mmol, 1.00 equiv), $LiBH_4$ (4.3 mL, 8.7 mmol, 3.1 equiv), MeOH (0.13 mL, 3.1 mmol, 1.2 equiv), and THF (12 mL, 0.22 M in substrate). The compound was purified by flash column chromatography (0–40% EtOAc/hexanes) to afford the title compound as a white solid (0.93 g, 2.68 mmol, 96%, 15% EtOAc, 3% Et_2O by ^1H NMR, >20:1 dr). **m.p. =** 111–114 ºC; **TLC Rf** = 0.5 (40% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.1 Hz, 1H), 7.83 (d, *J* = 6.9 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.35 (td, *J* = 7.4, 2.0 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.10 (t, *J* = 7.1 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 5.70 (d, *J* = 3.8 Hz, 1H), 3.78 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.68 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.54 (br s, 1H), 2.80–2.70 (m, 2H), 2.53–2.46 (m, 1H), 2.39 (br s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 156.1, 152.8, 140.5, 129.2 (2C), 128.4 (2C), 127.3, 127.0, 126.0, 125.0, 124.3, 124.2, 123.0 (2C), 120.8, 119.7, 111.9, 72.6, 63.7, 47.2, 31.0. **HRMS** (TOF MS ES+) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{20}O_3Na$, 355.1310; found, 355.1307. **$[\alpha]^{23}_D$** –189 (*c* 2.0 mg/mL, $CHCl_3$). **SFC** analysis (Chiralcel AS-H, 10% IPA, 2.0 mL/min, 290 nm) indicated >99% ee: t_R (only diastereomer, one enantiomer) = 10.8 minutes, t_R (only diastereomer, other enantiomer) = 13.6 minutes.



(2*R*)-2-Benzyl-3-chloro-3-(dibenzo[*b*,*d*]furan-4-yl)propyl methanesulfonate (2.17) was prepared according to Method Q. The following amounts of reagents were used: **2.71** (260 mg, 0.78 mmol, 1.0 equiv), MsCl (0.13 mL, 1.7 mmol, 2.2 equiv), Et_3N (0.33 mL, 2.3 mmol, 3.0 equiv),

DMAP (19 mg, 0.16 mmol, 0.20 equiv), and DCM (1.6 mL, 0.50 M in substrate). The compound was purified by flash column chromatography (0–40% EtOAc/hexanes) to afford the title compound as a white foam (60. mg, 0.14 mmol, 18%, 6.7:1 dr, 99% ee). The title compound showed minor traces of dichloride product. The compound was assumed to have an enantiomeric excess of 99% based on enantiomeric excess of preceding diol **2.71** and subsequent cyclopropane **42**. The compound was characterized as a 6.7:1 dr of the desired benzylic chloride products. **TLC Rf** = 0.6 (25% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 1H, major, 1H, minor), 7.93 (d, *J* = 8.6 Hz, 1H, major, 1H, minor), 7.61 (d, *J* = 8.2 Hz, 1H, major, 1H, minor), 7.58 (d, *J* = 7.6 Hz, 1H, major, 1H, minor), 7.50 (t, *J* = 7.3 Hz, 1H, major, 1H, minor), 7.41–7.34 (m, 2H, major, 2H, minor), 7.27–7.22 (m, 2H, major, 2H, minor), 7.20–7.13 (m, 1H, major, 1H, minor), 7.10 (d, *J* = 7.3 Hz, 2H, major, 2H, minor), 5.62 (d, *J* = 10.0 Hz, 1H, minor), 5.57 (d, *J* = 8.9 Hz, 1H, major), 4.65 (dd, *J* = 9.7, 3.7 Hz, 1H, major), 4.25 (dd, *J* = 9.5, 2.6 Hz, 1H, major), 4.15 (dd, *J* = 9.9, 5.9 Hz, 1H, minor), 3.89 (dd, *J* = 10.2, 3.8 Hz, 1H, minor), 3.28 (dd, *J* = 14.3, 3.3 Hz, 1H, minor), 3.12–3.06 (m, 1H, major), 3.00 (s, 3H, major), 2.78 (dd, *J* = 13.3, 10.9 Hz, 1H, minor), 2.73 (s, 3H, minor), 2.72 (dd, *J* = 15.4, 9.8 Hz, 1H, major), 2.63 (dd, *J* = 13.7, 3.7 Hz, 1H, minor), 2.58 (dd, *J* = 13.4, 5.3 Hz, 1H, major); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 156.2 (both), 153.1 (both), 138.2 (both), 129.22 (2C, minor), 129.16 (2C, major), 128.83 (2C, minor), 128.76 (2C, major), 127.84 (minor), 127.8 (major), 126.8 (major), 126.6 (minor), 126.3 (both), 125.0 (both), 124.0 (both), 123.7 (both), 123.48 (minor), 123.40 (major), 123.3 (major), 123.2 (minor), 121.4 (minor), 121.3 (major), 121.2 (minor), 121.0 (major), 112.03 (minor), 111.97 (major), 69.6 (minor), 68.4 (major), 58.9 (minor), 58.1 (major), 47.0 (major), 46.8 (minor), 37.1 (major), 36.9 (minor), 34.4 (major), 33.4 (minor); **HRMS** (TOF MS ES+) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{21}ClO_4SNa$, 451.0747; found, 451.0744. **$[\alpha]^{23}_D$** + 4.9 (*c* 3.25 mg/mL, $CHCl_3$).

Chapter Three

Harnessing C–O Bonds is Stereoselective Cross-Coupling and Cross-Electrophile Coupling Reactions

3.1 Introduction

The secondary alcohol is a cornerstone functional group in organic synthesis, serving both as a building block and a target.[1,2,3,4,5] Its notable function as a building block is partly based on its capability to be transformed into a wide range of electrophiles. From a broad perspective, this transformation primes alcohols to undergo reactions that forge new tertiary stereogenic centers (Scheme 3.1a). Strategic deployment of secondary alcohols as key synthetic intermediates has been showcased in the synthesis of natural products,[4] for example, in the [2,3]-Wittig rearrangement towards punctatin A, the Eschenmoser-Claisen rearrangement towards tuberostemonine, and the ring contraction to form the fused cyclopropane in the last synthetic step to make yatakemycin (Scheme 3.1b).[6,7,8]

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[1] Portions of this Chapter were originally published in Synlett: Sanford, A. B.; Jarvo, E. R. *Synlett* **2020**, DOI: 10.1055/s-0040-1705987

[2] Cramer, J.; Sager, C. P.; Ernst, B. *J. Med. Chem.* **2019**, *62*, 8915.

[3] Trader, D. J.; Carlson, E. E. *Mol. BioSyst.* **2012**, *8*, 2484.

[4] (a) Nicolaou, K. C.; Sorensen, E. J. *Classics in Total Synthesis: Targets, Strategies, and Methods*, Vol. 1; Wiley-VCH: Weinheim, **1996**. (b) Hanessian, S.; Giroux, S.; Merner, B. L. *Design and Strategy in Organic Synthesis*; Wiley-VCH: Weinheim, **2013**. (c) Dryzhakov, M.; Richmond, E.; Moran, J. *Synthesis* **2016**, *48*, 935. (d) Ajvazi, N.; Stavber, S. *Arkivoc* **2018**, *ii*, 288.

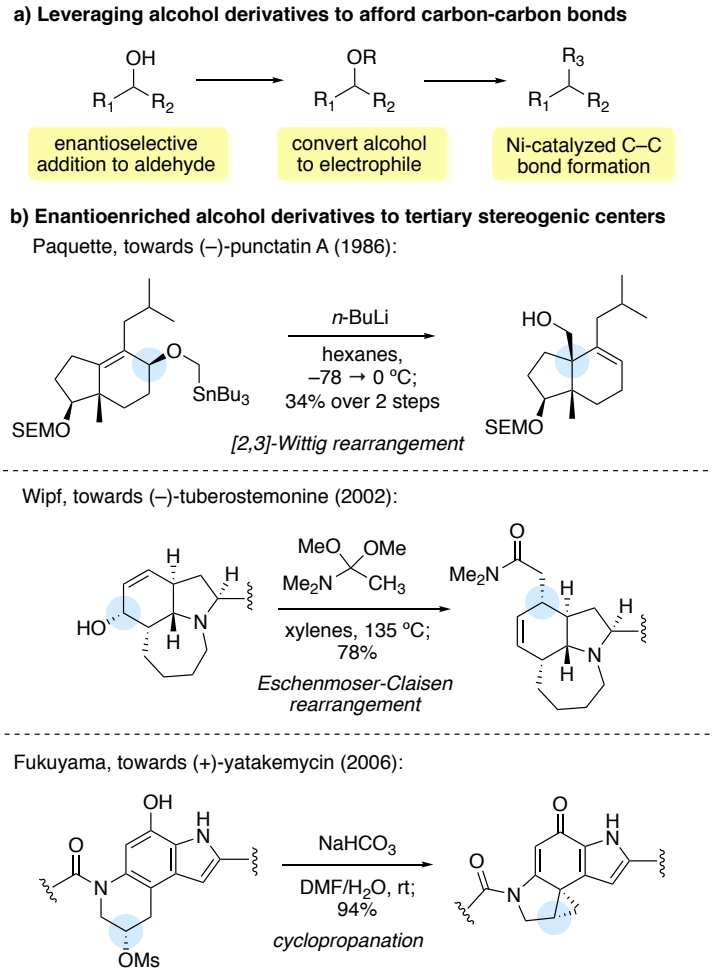
[5] (a) For representative asymmetric strategies for synthesis of secondary alcohols, see: *Comprehensive Asymmetric Catalysis*, Vol. I–III; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. Ed.; Springer-Verlag: Heildelberg, **1999**. (b) For enzymatic strategies, see: Chen, B.-S.; de Souza, F. Z. R. *RSC Adv*. **2019**, *9*, 2102.

[6] (a) Paquette, L. A.; Sugimura, T. *J. Am. Chem. Soc.* **1986**, *108*, 3841. (b) Sugimura, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1987**, *109*, 3017.

[7] Wipf, P.; Rector, S. R.; Takahashi, H. *J. Am. Chem. Soc*. **2002**, *124*, 14848.

[8] Okano, K.; Tokuyama, H.; Fukuyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 7136.

Scheme 3.1 Stereospecific reactions of asymmetric alcohol derivatives in total syntheses

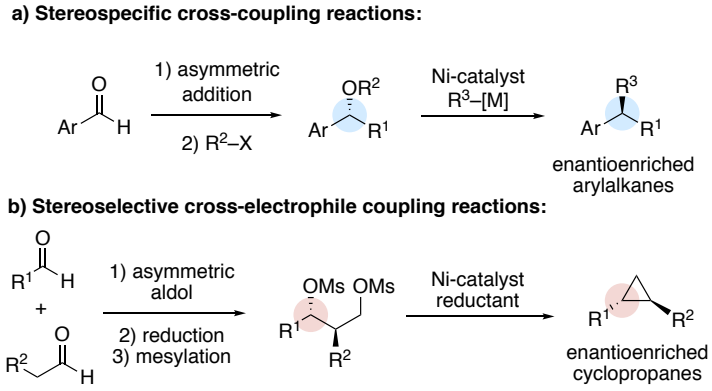


Beginning in 2009, our laboratory focused on engaging C(sp^3)–O bonds in nickel-catalyzed stereospecific reactions, a new strategy to parlay readily accessible enantioenriched building blocks to tertiary stereogenic centers (Scheme 3.2a). We selected nickel catalysts for reaction development due to lower propensity for β-hydride elimination and high rate of oxidative addition, both critical features for reactions involving alkylmetal intermediates.[9,10] These efforts resulted in the development of stereospecific nickel-catalyzed Kumada, Suzuki-Miyaura, and Negishi

[9] (a) Tasker, S. Z.; Standley, R. A.; Jamison, T. F. *Nature*, **2014**, *509*, 299. (b) *Modern Organonickel Chemistry*; Yamaru, Y., Ed.; Wiley-VCH: Weinheim, **2005**. (c) Diccianni, J. B.; Diao, T. *Trends Chem.* **2019**, *1*, 830.
[10] For a discussion of the merits of nickel catalysts in activation of C(sp^2)–O bonds, see: Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. *Chem. Rev*. **2011**, *111*, 1346.

reactions.[11,12,13] From a synthetic perspective, we applied these methods toward syntheses of 1,1-diarylalkanes and triarylmethanes—moieties that appear in commercial and investigative medicinal compounds.[14] From an organometallic perspective, these reactions provided key examples of stereospecific oxidative addition reactions of nickel catalysts.

Scheme 3.2 Stereospecific reactions of asymmetric alcohol derivatives in total syntheses



To further expand the range of nickel-catalyzed reactions that utilize alcohol derivatives, our laboratory began developing cross-electrophile coupling (XEC) reactions of alcohol derivatives in 2015.[15] In addition to alcohol-alkyl halide XEC reactions, we envisioned cross-

[11] Kumada: (a) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo. E. R. *J. Am. Chem. Soc.* **2011**, *133*, 389. (b) Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. *Org. Lett.* **2012**, *14*, 4293. (c) Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 7790. (d) Yonova, I. M.; Johnson, A. G.; Osborne, C. A.; Moore, C. E.; Morrissette, N. S.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 2422. (e) Tollefson, E. J.; Dawson, D. D.; Osborne, C. A.; Jarvo, E. R. J. *Am. Chem. Soc.* **2014**, *136*, 14951. (f) Dawson, D. D.; Jarvo, E. R. *Org. Proc. Res. Dev.* **2015**, *19*, 1356. (g) Sanford, A. B.; Tollefson, E. J. Jarvo, E. R. *Isr. J. Chem*. **2020**, *60*, 402.

[12] Suzuki-Miyaura: (a) Harris, M. R.; Hanna, L. E.; Greene, M. A.; Moore, C. E.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 3303. (b) Johnson, A. G.; Tranquilli, M. M.; Harris, M. R.; Jarvo, E. R. *Tetrahedron Lett.* **2015**, *56*, 3486. (c) Zhang, S.; Taylor, B. L. H.; Ji, C.; Gao, Y.; Harris, M. R.; Hanna, L. E.; Jarvo, E. R.; Houk, K. N.; Hong, X. *J. Am. Chem. Soc.* **2017**, *139*, 12994.

[13] Negishi: Wisniewska, H. M.; Swift, E. C.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 9083.

[14] For representative examples, see: (a) Palchaudhuri, R.; Nesterenko, V.; Hergenrother, P. J. *J. Am. Chem. Soc*. **2008**, *130*, 10274. (b) Huang, Z.; Ducharme, Y.; MacDonald, D.; Robichaud, A. *Curr. Opin. Chem. Biol*. **2001**, *5*, 432. (c) Mondal, S.; Panda, G. *RSC Adv*. **2014**, *4*, 28317.

[15] (a) Tollefson, E. J.; Erickson, L. W.; Jarvo, E. R. *J. Am. Chem. Soc.* **2015**, *137*, 9760. (b) Konev, M. O.; Hanna, L. E.; Jarvo, E. R. *Angew. Chem. Int. Ed.* **2016**, *55*, 6730. (c) Erickson, L. W.; Lucas, E. L.; Tollefson, E. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2016**, *138*, 14006. (d) Chen, P.-P.; Lucas, E. L.; Greene, M. A.; Zhang, S.; Tollefson, E. J.; Erickson, L. W.; Taylor, B. L.; Jarvo, E. R.; Hong, X. *J. Am. Chem. Soc.* **2019**, *141*, 5835.

electrophile coupling reactions of diol derivatives.[16] While various diol substitution patterns are imaginable, we focused on 1,3-diols for two important reasons: the accessibility of enantioenriched starting materials and the generation of enantioenriched cyclopropanes as products (Scheme 3.2b). We envisioned an asymmetric aldol reaction followed by carbonyl reduction to provide the desired 1,3-diols quickly and efficiently. Key aspects of the method development, not previously reported, are discussed in this Chapter.

Shifting the medicinal chemistry landscape towards compounds that extend in three-dimensions will require synthetic reactions that provide command over absolute and relative configuration.[17] Toward this goal, the methods outlined in this Chapter provide products containing pharmaceutically relevant motifs with robust stereochemical control. Both methods begin with an alcohol derivative prepared by a well-established asymmetric alcohol synthesis. Functionalization to provide the requisite leaving group, followed by selective nickel-catalyzed transformation, provides the new C–C bond and a new tertiary stereogenic center. During development of these transformations, mechanistic experiments uncovered multiple roles for the magnesium reagent beyond serving simply as a transmetallating agent.[15d,16] This understanding has enabled us to successfully activate less-reactive substrates, expanding the scope and utility of the respective reactions.

3.2 Cross-Coupling Reactions

Over the past decade, our group has developed multiple stereospecific nickel-catalyzed cross-coupling reactions of benzylic electrophiles. In this Chapter, the discussion is focused on

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

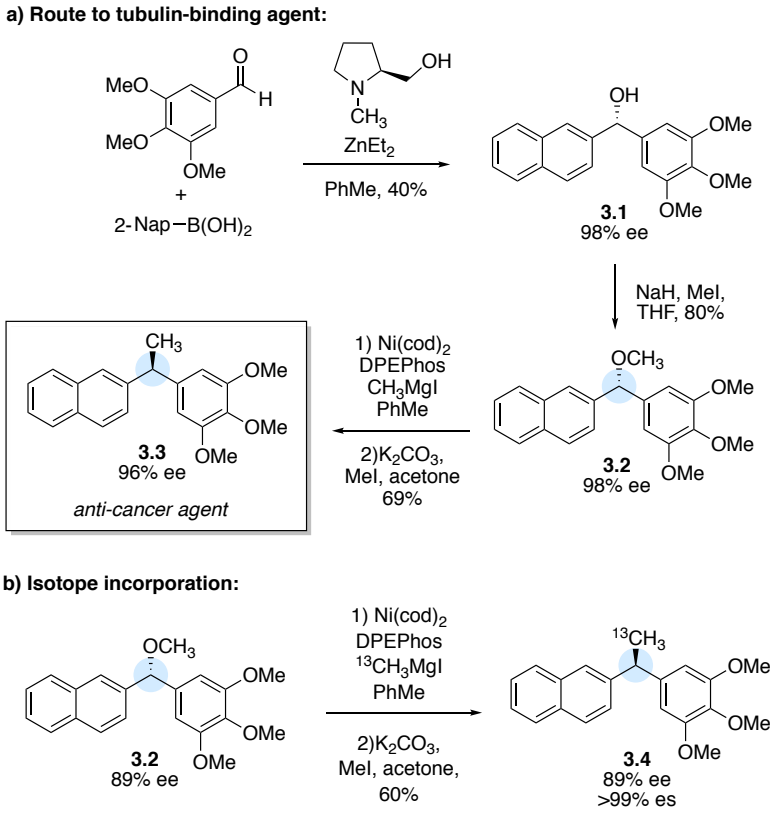
[17] (a) Lovering, F.; Bikker, J.; Humblet, C. *J. Med. Chem*. **2009**, *52*, 6752. (b) Caille, S.; Cui, S.; Faul, M. M.; Mennen, S. M.; Tedrow, J. S.; Walker, S. D. *J. Org. Chem*. **2019**, *84*, 4583. (c) Méndez-Lucio, O.; Medina-Franco, J. L. *Drug Discovery Today*, **2017**, *22*, 120. (d) Birudukota, N. V. S.; Franke, R.; Hofer, B. *Org. Biomol. Chem*. **2016**, *14*, 3821. (e) Ruddigkeit, L.; Van Deursen, R.; Blum, L. C.; Reymond, J.-L. *J. Chem. Inf. Model.* **2012**, *52*, 2864. (f) Feher, M.; Schmidt, J. M. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 218.

Kumada reactions as a representative example of stereospecific cross-coupling (XC) reactions. These Kumada reactions also provided a steppingstone toward cross-electrophile coupling (XEC) reactions. Since the stereospecific XC employed benzylic ethers, we focused many of our synthetic applications on the 1,1-diarylalkane moiety. Compounds containing 1,1-diarylalkanes and triarylmethanes have been shown to have anti-cancer, anti-malarial, and anti-inflammatory properties,[14] however, their enantioselective synthesis remained a challenge at the time.

Our first report in this domain was in 2011, when we disclosed the stereospecific Kumada reaction of secondary benzylic methyl ethers.[11a] This method was utilized to synthesize two compounds with biological activity: an anti-cancer agent (**3.3**) and an anti-insomnia agent (not shown). The route to tubulin-binding compound **3.3** is shown in Scheme 3.3a.[18] We frequently employed Bolm-type arylation reactions for synthesis of enantioenriched benzhydril alcohols.[19] For this example, a procedure reported by Chan was utilized to synthesize alcohol **1** in high ee.[20] Alcohol **3.1** was methylated to form the benzylic ether **3.2**, that was then subjected to the nickel-catalyzed Kumada XC reaction. The anti-cancer agent **3.3** was synthesized in high ee, and the cross-coupling reaction occurred with inversion. Additionally, an isotopically-labeled Grignard reagent was used to quickly and efficiency incorporate an isotope into the final product (**3.4**) as is often required for pharmacokinetic experiments (Scheme 3.3b).[11f,21]

[18] Alami, M.; Messaoudi, S.; Hamze, A.; Provot, O.; Brion, J.-D.; Liu, J.- M.; Bignon, J.; Bakala, J. Patent WO/2009/147217 A1, Dec 10, 2009.
[19] Bolm, C.; Rudolph, J. *J. Am. Chem. Soc*. **2002**, *124*, 14850.
[20] Zhang, F.-Y.; Yip, C.-W.; Cao, R.; Chan, A. S. C. *Tetrahedron: Asymmetry* **1997**, *8*, 585.
[21] (a) Haskins, N. J. *Biomed. Mass Spectrom.* **1982**, *9*, 269. (b) Wolfe, R. R.; Chinkes, D. L. Basic Characteristics of Isotopic Tracers. In *Isotopic Tracers in Metabolic Research: Principles and Practice of Kinetic Analysis*; 2nd ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2005; pp 1–9.

Scheme 3.3 Bioactive 1,1-diarylalkane synthesized via stereospecific cross-coupling reaction

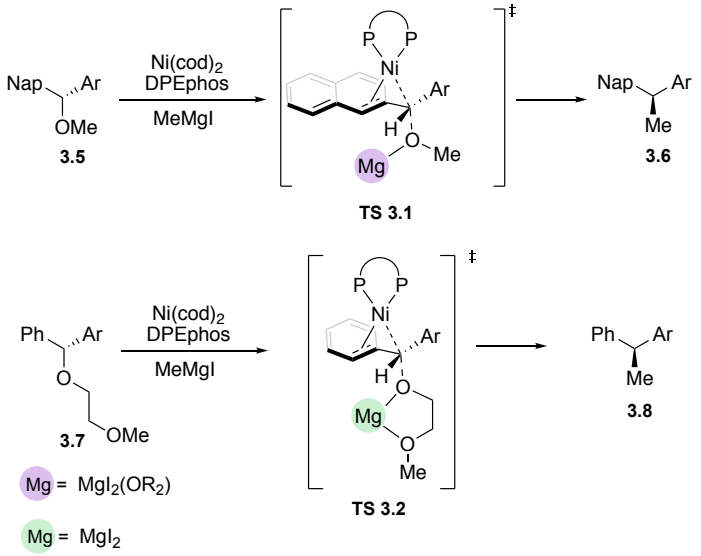


While the synthesis of bioactive compounds demonstrated the utility of the Kumada reaction, a limitation of this transformation was that extended aromatic groups were necessary for successful oxidative addition at the benzylic C–O bond. In 2012, our group expanded the scope of this transformation to include non-extended aromatic groups.[11b] We hypothesized that the Grignard reagent played dual roles in the catalytic system, serving both as transmetallating agent and providing Lewis acidic magnesium salts.[22] The Lewis acids were thought to activate the C–O bond for rate-determining oxidative addition. This working hypothesis was based on an early proposal by Felkin and co-workers.[23] Eventually, this hypothesis was supported by our own kinetic experiments and density functional theory (DFT) calculations performed by our collaborators,

[22] (a) Schlenk, W.; Schlenk, W. *Ber. Dtsch. Chem. Ges. B* **1929**, *62*, 920. (b) Wurtz, A. *Ann. Chim. Phys.* **1855**, *44*, 275. (c) Wurtz, A. *Ann. Chim. Pharm.* **1855**, *96*, 364.
[23] Felkin, H.; Swierczewski, G. *Tetrahedron Lett.* **1972**, *13*, 1433.

Professor Hong and co-workers.[24] At the time, we proposed that improved coordination to the Lewis acid, via a chelating leaving group, could compensate for decreased binding of the arene to the nickel catalyst (Scheme 3.4). This would stabilize the transition state for oxidative addition and therefore allow the less stabilizing, simple arene substrates to be reactive.

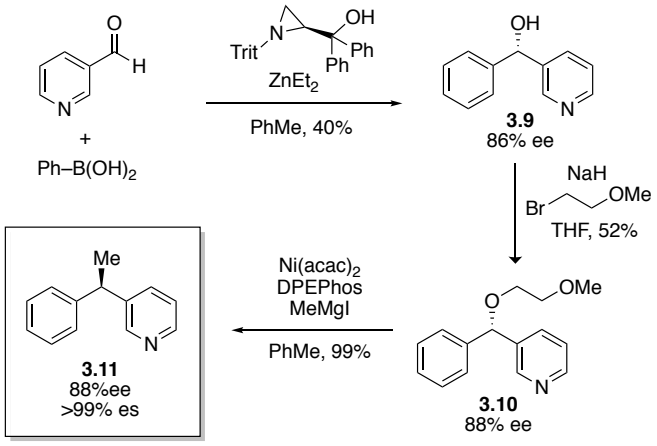
Scheme 3.4 Oxidative addition is accelerated by Lewis acidic magnesium salts



Benzhydrylic alcohols now participated in the Kumada reaction when equipped with the traceless directing group (Scheme 3.5).[11b] Enantioenriched alcohol **3.9** was prepared by asymmetric addition of phenylboronic acid into 3-pyridinecarboxaldehyde.[25] Alcohol **3.9** was subjected to Williamson ether synthesis to afford benzylic ether **3.10**. The stereospecific Kumada cross-coupling reaction proceeded smoothly to afford pyridine-containing 1,1-diarylalkane **3.11** in good yield and high stereochemical fidelity.

[24] (a) See ref. 15d (b) Dawson, D. D.; Oswald, V. F.; Borovik, A. S.; Jarvo, E. R. *Chem. Eur. J.* **2020**, *26*, 3044.
[25] Braga, A. L.; Paixão, M. W.; Westermann, B.; Schneider P. H.; Wessjohan, L. A. *J. Org. Chem*. **2008**, *73*, 2879.

Scheme 3.5 Cross-coupling reaction using traceless directing group



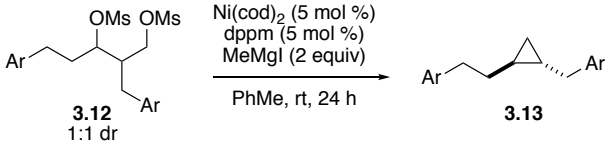
3.3 Cross-Electrophile Coupling Reactions

In 2020, our laboratory reported the cross-electrophile coupling reaction of 1,3-dimesylates.[16] This work built on our prior development of intramolecular XEC reactions of carbinol derivatives with alkyl and aryl halides.[15] However, despite the apparent similarities of the transformations, we discovered significant mechanistic differences that had important implications for the stereochemical outcome of these reactions. In this Chapter, key details of reaction development, mechanistic experiments, and application in the synthesis of enantioenriched alkyl- and arylcyclopropanes are discussed. Cyclopropanes appear frequently in both natural products and pharmaceutical compounds, fueling our motivation to design new methods for their synthesis.[26] The inclusion of a cyclopropyl motif can provide a wide range of benefits to medicinal agents, such as increased metabolic stability, decreased lipophilicity, and increased passage through the blood-brain barrier.[26a] The cyclopropane has notable features, including conformational rigidity and projection of the substituents in a nonplanar fashion.[17]

[26] (a) Talele, T. T. *J. Med. Chem*. **2016**, *59*, 8712. (b) Gagnon, A.; Duplessis, M.; Fader, L. *Org. Prep. Proced. Int.* **2010**, *42*, 1. (c) Bartoli, G.; Bencivenni, G.; Dalpozzo, R. *Synthesis* **2014**, *46*, 979. (d) Ebner, C.; Carreira, E. *Chem. Rev.* **2017**, *117*, 11651.

To begin our investigations on an XEC of diol derivatives, 1,3-dimesylate **3.12** was employed as it could be easily accessed through a large-scale Claisen condensation.[27] Sulfonation to form the 1,3-dimesylate was more facile than formation of the corresponding 1,3-ditosylate, likely due to significant steric interactions in the latter. We selected reaction conditions similar to those we had employed for related XC and XEC reactions, employing MeMgI as the terminal reducing agent. The bidentate phosphine ligand dppm proved to perform best with respect to conversion and dr (Table 3.1, entry 1), while monodentate PPh_3 gave similar conversion but lower dr (entry 3). For top-performing ligands, β-hydride elimination was observed as the major byproduct. Based on the product distribution and yield, the stereochemical course of this transformation was not clear, although, preliminary experiments showed that both diastereomers of the starting material were consumed.

Table 3.1 Optimization of XEC reaction of substituted 1,3-dimesylates. Ar = *p*-MeO-C_6H_4



3.12 1:1 dr

3.13

entry	deviation from std conditions	conversion (%)[a]	dr (trans:cis)
1	none	50	9:1
2	*rac*-BINAP	37	14:1
3	PPh_3	58	5:1
4	RuPhos	39	4:1
5	4,4'-ditert bipy	35	9:1
6	SIMes•HBF_4	31	>20:1
7	$Ni(acac)_2$	53	9:1
8	$NiCl_2$	23	12:1
9	$Ni(OTf)_2$	0	—
10	0 °C	41	8:1

[a]Conversion determined by ^{1}H NMR. Integration of peaks attributed to cyclopropanes were compared to integration of the peak attributed to methoxy groups.

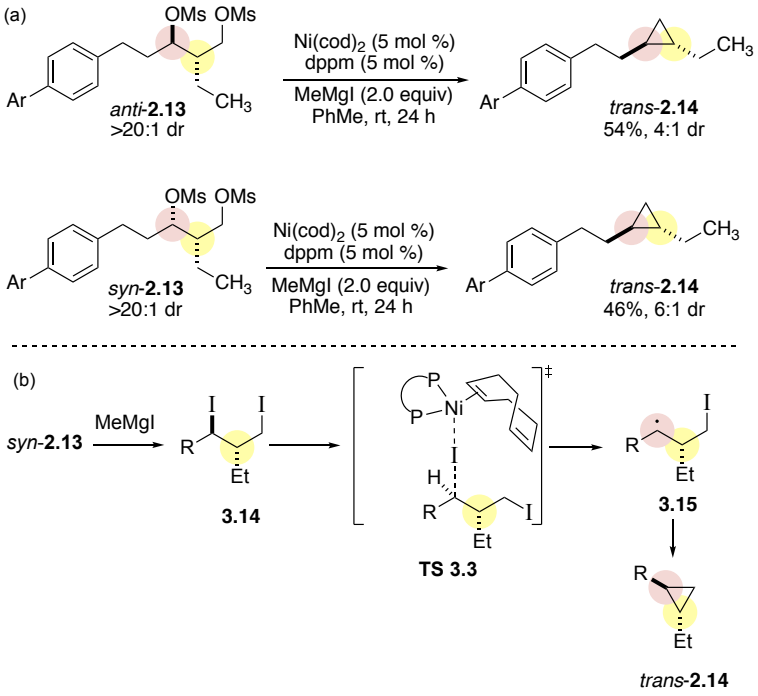
[27] (a) Claisen, L.; Claparede, A. *Ber. Dtsch. Chem. Ges*. **1881**, *14*, 2460. (b) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem*. **1980**, *45*, 1066.

To determine the stereochemical outcome of this reaction, we prepared both diastereomers of 1,3-dimesylate **2.13** and subjected them to the reaction conditions (Scheme 3.6a).[16,28] Both *syn*- and *anti*-1,3-dimesylate **2.13** provided *trans*-cyclopropane **2.14** with similar yields and diastereoselectivity. Therefore, the proposed mechanism should account for a stereoconvergent transformation. Based on our experiments and DFT calculations by our collaborators, we proposed a mechanism where MeMgI once again played a dual role (Scheme 3.6b).[16] We determined that 1,3-dimesylates react with MeMgI to form 1,3-diiodides (**3.14**) in situ. Activation of the secondary C–I bond by nickel proceeds via halogen atom abstraction (**TS 3.3**) and is stereoablative. Fortunately, product formation is diastereoselective, favoring the *trans*-cyclopropane. This mechanism ablates and re-sets the stereochemical information at the secondary center, leading to an overall stereoselective reaction.[9]

The implications of this dual role of MeMgI are worth noting. We previously demonstrated that the Lewis acidity of MgI_2 salts in the MeMgI solution allowed us to activate less-reactive substrates in our cross-coupling reactions (Scheme 3.4). In this cross-electrophile coupling method, the multiple roles of the Grignard reagent similarly provide an avenue to activate sluggish substrates (Scheme 3.6). Our previous XEC methods required the use of a benzylic or allylic electrophile. This new method now provides activation of simple alkyl substrates by transformation of alkyl mesylates to alkyl iodides in situ.[29]

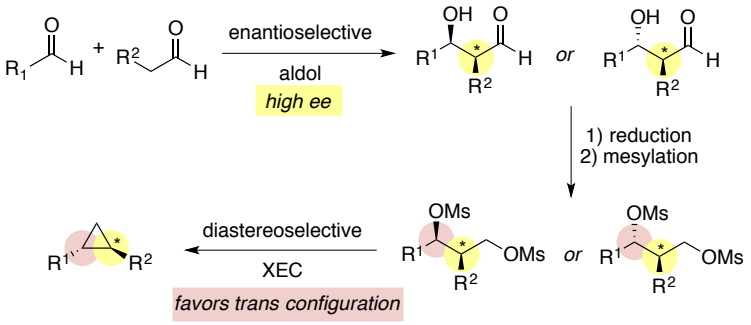
[28] For selective syntheses of diastereomers, see: Ramachandran, P. V.; Nicponski, D.; Kim, B. *Org. Lett*. **2013**, *15*, 1398.
[29] (a) Do, H. Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 16288. (b) Liang, Z.; Xue, W.; Lin, K.; Gong, H. *Org. Lett***. 2014**, *16*, 5620. (c) Yu, X.; Yang, T.; Wang, S.; Xu, H.; Gong, H. *Org. Lett***. 2011**, *13*, 2138.

Scheme 3.6 XEC reaction of 1,3-dimesylates is stereoablative and diastereoselective. Ar = *m*-MeO-C_6H_4



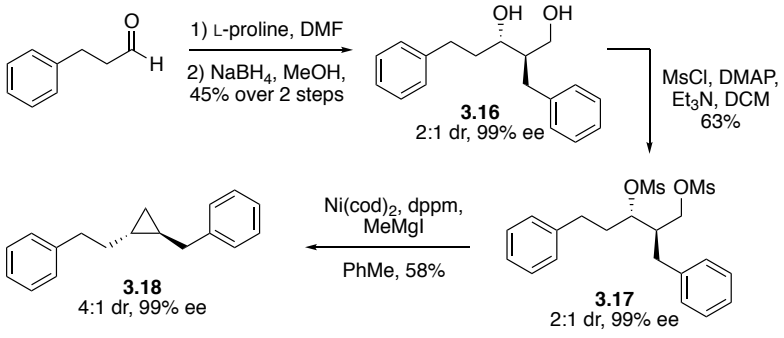
Building upon the knowledge that this transformation was stereoconvergent and provides access to *trans*-cyclopropanes, we envisioned a strategy for enantioselective cyclopropane formation (Scheme 3.7).[16] An enantioselective aldol reaction would need to provide high control of configuration at the α-stereocenter, since this stereocenter would be retained in the product. The configuration of the β-hydroxy group would be irrelevant, since this center is ablated and re-set over the course of the XEC reaction. We moved forward with two well-established syntheses that reliably control the configuration of R^2, namely Evans and proline-catalyzed aldol reactions, followed by simple reduction and mesylation to yield our desired 1,3-dimesylates.[30,31]

Scheme 3.7 XEC reaction of 1,3-dimesylates to afford enantioenriched cyclopropanes



We prepared a test substrate employing a proline-catalyzed aldol reaction.[30] Hydrocinnamaldehyde was utilized in the self-aldol reaction, followed an $NaBH_4$ reduction of the unpurified mixture to afford 1,3-diol **3.16** with excellent ee (Scheme 3.8). The 1,3-diol was converted to 1,3-dimesylate **3.17** in good yield. 1,3-Dimesylate **3.17** was subjected to our optimized conditions and, gratifyingly, alkylcyclopropane **3.18** was isolated in good yield with excellent enantioenrichment. Notably, cyclopropane **3.18** was formed with greater diastereoselectivity than the starting diol derivative, consistent with the proposed stereoablative mechanism.

Scheme 3.8 Enantioenriched alkylcyclopropane **3.18** synthesized via proline-catalyzed aldol route

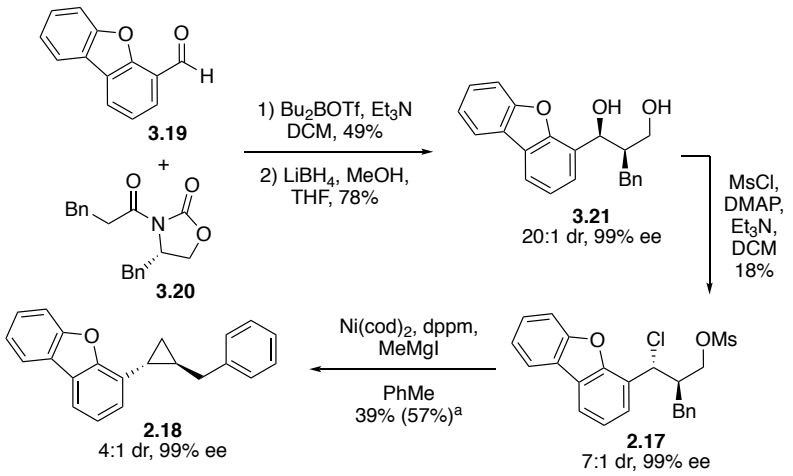


As a second test, we performed an Evans aldol reaction with aldehyde **3.19** and oxazolidinone **3.20**.[31] After cleavage of the auxiliary, the 1,3-diol **3.21** was isolated in moderate

[30] Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2002**, *124*, 6798.
[31] Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc*. **1981**, *103*, 2127.

yield with excellent dr and ee (Scheme 3.9). Mesylation provided the 1,3-chloromesylate **2.17** which was subjected to our XEC conditions. Arylcyclopropane **2.18** was generated with excellent enantioselectivity and good diastereoselectivity.

Scheme 3.9 Enantioenriched arylcyclopropane **2.18** synthesized via Evans aldol route



[a]Yield determined by NMR based on comparison to PhTMS as internal standard

3.4 Conclusion

This Chapter highlighted representative efforts by our laboratory to transform the C–O bonds of readily available carbinols into new C–C bonds with control of configuration. Enantioselective additions into aldehydes produced the building blocks that were employed in both our cross-coupling and cross-electrophile coupling methods. Our successes provide new cross-coupling strategies for synthesis of stereochemically-rich alkyl moieties—critical features for non-planar medicinal compounds. Development of these nickel-catalyzed reactions has also furthered our understanding of closed-shell mechanisms for oxidative addition using base metal catalysts and new mechanisms for XEC reactions. Along the way, the Grignard reagent has provided multiple roles, some surprising, serving as transmetallating agent, Lewis acid, and halide source.

Chapter Four

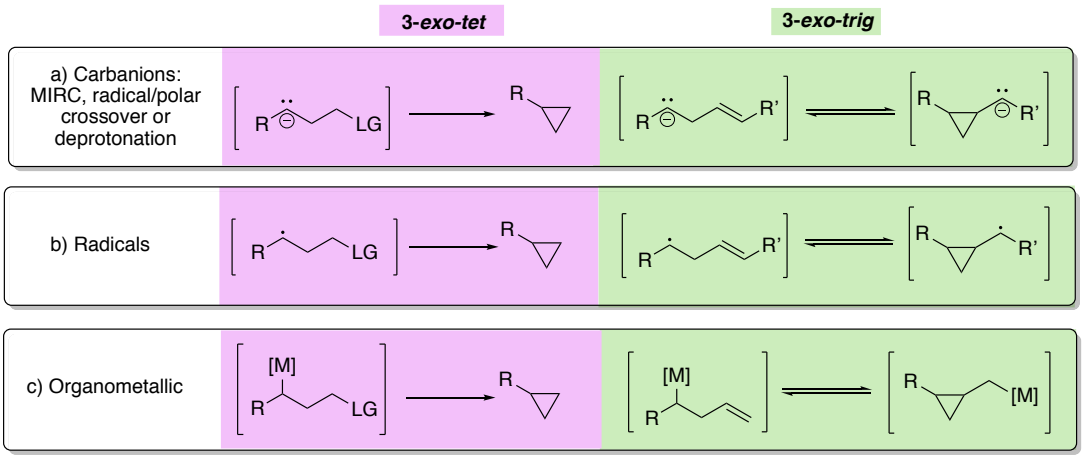
β-Fluorovinyl Cyclopropane Synthesis via Nickel-Catalyzed Cross-Electrophile Coupling Reaction of Alkyl Mesylates with Allylic Difluorides

4.1 Introduction

Continued interest in new methods for cyclopropane synthesis is driven by their favorable pharmaceutical properties and occurrence in natural products.[1,2] A complement to traditional intermolecular reactions utilizing alkenes and carbenoids is the intramolecular cyclization. Cyclization strategies have historically been developed and continue to be investigated, partly due to the fact that both the 3-*exo*-*tet* and 3-*exo*-*trig* cyclizations are favorable, enabling a wide array of transformations.[3] Mechanistically, 3-*exo*-*tet* cyclizations are usually irreversible while 3-*exo*-*trig* cyclizations are reversible, the latter requiring a subsequent step to push the intermediate forward along the reaction pathway. Many groups over the last few decades have explored these cyclizations with varying mechanistic strategies, substitution patterns, and steroselectivity. Most of these cyclopropanation methods fit into one of the general categories shown in Scheme 4.1.[4]

[1] Talele, T. T. *J. Med. Chem*. **2016**, *59*, 8712–8756.
[2] For representative reviews, see: (a) Ebner, C.; Carreira, E. *Chem. Rev.* **2017**, *117*, 11651−11679. (b) Lebel, H.; Marcoux, J. − F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977−1050. (c) Bartoli, G.; Bencivenni, G.; Dalpozzo, R. *Synthesis* **2014**, *46*, 979−1029. (d) Wu, W.; Lin, Z.; Jiang, H. *Org. Biomol. Chem.* **2018**, *16*, 7315−7329.
[3] Baldwin, J. E. *J. C. S. Chem. Comm.* **1976**, *18*, 734–736.
[4] Cyclopropanations that proceed through carbocation intermediates have also been reported. For lead references, see: (a) Mercadante, M. A.; et. al. *Chem. Sci.* **2014**, *5*, 3983–3994. (b) Kelly, C. B.; Mercadante, M. A.; Carnaghan, E. R.; Doherty, M. J.; Fager, D. C.; Hauck, J. J.; MacInnis, A. E.; Tilley, L. J.; Leadbeater, N. E. *Eur. J. Org. Chem*. **2015**, *19*, 4071–4076. (c) Sarabia, F. J.; Ferreira, E. M. *Org. Lett.* **2017**, *19*, 2865–2868. (d) Hardee, D. J.; Lambert, T. H. *J. Am. Chem. Soc.* **2009**, *131*, 7536–7537.

Scheme 4.1 Cyclization strategies for cyclopropane synthesis



Carbanions that react in a 3-*exo-tet* manner encompass many widely applied transformations (Scheme 4.1a). Michael-initiated ring closures (MIRC) were formally named by Little in 1980, however one of the earliest examples and articulation of this strategy can be traced to McCoy in 1958.[5,6,7] Since first reported, MIRCs have been extensively developed and employed in numerous natural product syntheses.[8,9,2] Another method to access relevant carbanions is a

[5] Little, R. D.; Dawson, J. R. *Tetrahedron Lett.* **1980**, *21*, 2609–2612.
[6] McCoy, L. L. *J. Am. Chem. Soc.* **1958**, *80*, 6568–6572.
[7] For an electroreductive coupling, see: Baizer, M. M.; Chruma, J. L. *J. Org. Chem*. **1972**, *37*, 1951–1960.
[8] For recent lead reference of MIRC, see: Tobrman, T.; Krupička, M.; Polák, P.; Dvořáková, H.; Čubiňák, M.; Babor, M.; Dvořák, D. *Eur. J. Org. Chem*. **2020**, *4*, 429–436.
[9]Amputch, M. A.; Matamoros, R.; Little, R. D. *Tetrahedron* **1994**, *50*, 5591–5614.

radical/polar crossover.[10] Simple deprotonation of acidic protons has also been utilized.[2c,11] Additionally, the 3-*exo-trig* variant has been reported, often incorporated as an S_N2' elimination.[12]

Closely related but mechanistically distinct is the radical cyclization (Scheme 4.1b). Cyclizations reported by the Suero group and others have demonstrated the utility of this 3-*exo-tet* pathway, while mechanistic studies are often necessary to distinguish this S_H2 mechanism from one via a carbanion intermediate.[13] Radical 3-*exo-trig* cyclizations have also been investigated, however, in a more kinetics context. The cyclopropylcarbinyl radical intermediate must be trapped in order to drive the reaction forward as the equilibrium favors the uncyclized radical.[14]

Lastly, transition metal-mediated ring closures have also been reported (Scheme 4.1c). Our group has demonstrated organonickel complexes that undergo 3-*exo-tet* closures to yield aryl-,

---

[10] (a) Shu, C.; Mega, R. S.; Andreassen, B. L.; Noble, A.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2018**, *57*, 15430–15434. (b) Zhang, Y.; Qian, R.; Zheng, X.; Zeng, Y.; Sun, J.; Chen, Y.; Ding, A.; Guo, H. *Chem. Commun*. **2015**, *51*, 54–57. (c) Phelan, J. P.; Lang, S. B.; Compton, J. S.; Kelly, C. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A. *J. Am. Chem. Soc.* **2018**, *140*, 8037–8047. (d) Milligan, J. A.; Phelan, J. P.; Polites, V. C.; Kelly, C. B.; Molander, G. A. *Org. Lett.* **2018**, *20*, 6840–6844. (e) Milligan, J. A.; Burns, K. L.; Le, A. V.; Polites, V. C.; Wang, Z.-J.; Molander, G. A.; Kelly, C. B. *Adv. Synth. Catal.* **2020**, *362*, 242–247. (f) Njue, C. K.; Nuthakki, B.; Vaze, A.; Bobbitt, J. M.; Rusling, J. F. *Electrochem. Commun.* **2001**, *3*, 733–736. (g) Guo, T.; Zhang, L.; Liu, X.; Fang, Y.; Jin, X.; Yang, Y.; Li, Y.; Chen, B.; Ouyang, M. *Adv. Synth. Catal.* **2018**, *360*, 4459–4463. (h) Luo, W.; Yang, Y.; Fang, Y.; Zhang, X.; Jin, X.; Zhao, G.; Zhang, L.; Li, Y.; Zhou, W.; Xia, T.; Chen, B. *Adv. Synth. Catal.* **2019**, *361*, 4215–4221.

[11] Electroreductive couplings can also access necessary anions. For lead examples, see: (a) Léonel, E.; Paugam, J. P.; Condon-Gueugnot, S.; Nédélec, J.-Y. *Tetrahedron* **1998**, *54*, 3207–3218. (b) Lu, Y.-W.; Nédélec, J. Y.; Folest, J.-C.; Perichon, J. *J. Org. Chem*. **1990**, *55*, 2503–2507.

[12] Paquette, L. A.; Stirling, C. J. M. *Tetrahedron* **1992**, *48*, 7383–7423.

[13] (a) Herraiz, A. G.; Suero, M. G. *Synthesis* **2019**, *51*, 2821–2828. (b) Sayes, M.; Benoit, G.; Charette, A. B. *Angew. Chem. Int. Ed.* **2018**, *57*, 13514–13518. (c) Curran, D. P.; Gabarda, A. E. *Tetrahedron*, **1999**, *55*, 3327–3336. (d) Léonel, E.; Dolhem, E.; Devaud, M.; Paugam, J. P.; Nédélec, J. Y. *Electrochimica Acta* **1997**, *42*, 2125–2132. (e) Ohtani, T.; Tsuchiya, Y.; Uraguchi, D.; Ooi, T. *Org. Chem. Front*. **2019**, *6*, 1734–1737. (f) Li, P.; Zhao, J.; Shi, L.; Wang, J.; Shi, X.; Li, F. *Nat. Commun.* **2018**, *9*, 1–9. (g) Ohkita, T.; Tsuchiya, Y.; Togo, H. *Tetrahedron* **2008**, *64*, 7247–7251. (h) Kawabata, N.; Tanimoto, M. *Tetrahedron* **1980**, *36*, 3517–3522.

[14] (a) Čeković, Ž.; Saičić, R. *Tetrahedron Lett*. **1990**, *31*, 6085–6088. (b) Saičić, R. N.; Čeković, Ž. *Tetrahedron* **1992**, *48*, 8975–8992. (c) Fletcher, R. J.; Lampard, C.; Murphy, J. A.; Lewis, N. *J. Chem. Soc. Perkin. Trans*. 1 **1995**, *6*, 623–633. (d) Giese, B.; Kopping, B.; Göbel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K. J.; Trach, F. Radical Cyclization Methods. *Organic Reactions*; Paquette, L. A., Ed.; Wiley: New York, 1996; Vol. *48*; pp 301−856. (e) David, H.; Afonso, C.; Bonin, M.; Doisneau, G.; Guillerez, M.-G.; Guibé, F. *Tetrahedron Lett.* **1999**, *40*, 8557–8561.

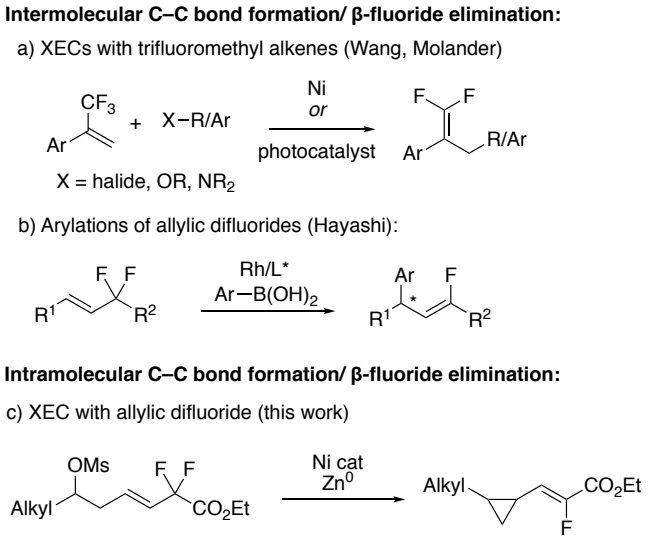
vinyl, and alkylcyclopropanes.[15] For *3-exo-trig* cyclizations, the Krische group has reported organonickel complexes that undergo a migratory insertion pathway.[16,17] This transformation occurs in a stereoselective manner—thought to be a result of a reversible migratory insertion where only one resulting diastereomer leads to the desired product.[16]

Built upon our previous cross-electrophile (XEC) reaction employing 1,3-dimesylates for cyclopropane synthesis, we envisioned an intramolecular XEC of alkyl mesylates with allylic difluorides that involves a 3-*exo-trig* cyclization (Scheme 4.2c).[15c] An interesting feature of the cyclization step is that all three mechanistic pathways shown in Scheme 4.1 are plausible, with the radical or organometallic pathway most likely. We chose to incorporate the β-fluoride elimination step to provide a terminal, irreversible event in an otherwise reversible mechanism.[18] Cross-electrophile coupling (XEC) reactions of trifluoromethyl alkenes with electrophilic radical precursors have been reported (Scheme 4.2a).[19,20,21] To the best of our knowledge, similar XEC transformations that employ allylic difluorides have not been realized. However, allylic difluorides have been utilized in other C–C bond forming/β-fluoride elimination reactions, such as rhodium-catalyzed arylations (Scheme 4.2b) and organocopper-mediated alkylations.[22,23] Our motivation to

[15] (a) Tollefson, E. J.; Erickson, L. W.; Jarvo, E. R. *J. Am. Chem. Soc*. **2015**, *137*, 9760−9763. (b) Erickson, L. W.; Lucas, E. L.; Tollefson, E. J.; Jarvo, E. R. *J. Am. Chem. Soc*. **2016**, *138*, 14006−14011. (c) Sanford, A. B.; Thane, T. A.; McGinnis, T. M.; Chen. P.-P.; Hong, X.; Jarvo, E. R. *J. Am. Chem. Soc*. **2020**, *142*, 5017−5023.
[16] Guo, Y.-A.; Liang, T.; Kim, S. W.; Xiao, H.; Krische, M. J. *J. Am. Chem. Soc*. **2017**, *139*, 6847–6850.
[17] Fiser, B.; Cuerva, J. M.; Gómez-Bengoa, E. *Organometallics* **2018**, *37*, 390–395.
[18] Nickel-catalyzed cyclizations followed by β-fluoride elimination have been reported for the synthesis of 5- and 6-membered rings. For lead references, see: (a) Ichitsuka, T.; Fujita, T.; Arita, T.; Ichikawa, J. *Angew. Chem. Int. Ed*. **2014**, *53*, 7564–7568. (b) Fujita, T.; Watabe, Y.; Ichitsuka, T.; Inchikawa, J. *Chem. Eur. J.* **2015**, *21*, 13225–13228. (c) Fujita, T.; Arita, T.; Ichitsuka, T.; Ichikawa, J. *Dalton Trans*. **2015**, *44*, 19460–19463.
[19] Lan, Y.; Yang, F.; Wang, C. *ACS Catal*. **2018**, *8*, 9245–9251.
[20] (a) Ding, D.; Lan, Y.; Lin, Z.; Wang, C. *Org. Lett*. **2019**, *21*, 2723–2730. (b) Lin, Z.; Lan, Y.; Wang, C. *ACS Catal*. **2019**, *9*, 775–780.
[21] Wiles, R. J.; Phelan, J. P.; Molander, G. A. *Chem. Commun.* **2019**, *55*, 7599–7602.
[22] Pan, Y.; Lu, X.; Qiu, H.; Hayashi, T.; Huang, Y. *Org. Lett.* **2020**, *22*, 8413–8418.
[23] For representative examples, see: (a) Okada, M.; Nakamura, Y.; Saito, A.; Sato, A.; Horikawa, H.; Taguchi, T. *Chem. Lett.* **2002**, *31*, 28–29. (b) Otaka, A.; Watanabe, J.; Yukimasa, A.; Sasaki, Y.; Watanabe, H.; Kinoshita, T.; Oishi, S.; Tamamura, H.; Fuiji, N. *J. Org. Chem*. **2004**, *69*, 1634–1645.

design this transformation is two-fold: demonstrate XEC reactions of allylic difluorides and provide a new strategy to transform an inexpensive and commercially available fluorinated building block, ethyl bromodifluoroacetate, to vinylfluorides.

Scheme 4.2 C–C bond formation/β-fluoride elimination reactions



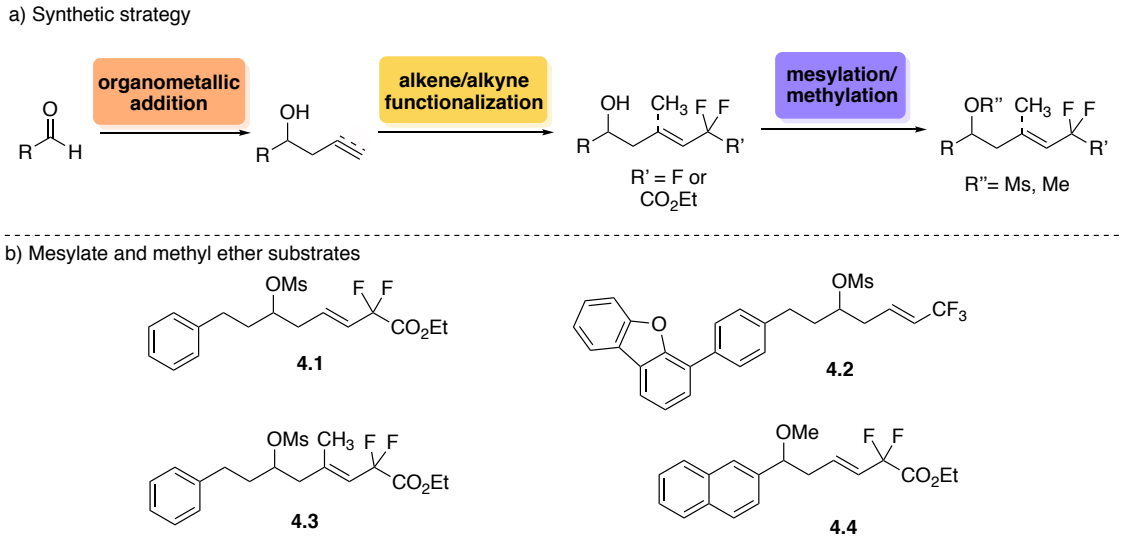
4.2 Results and Discussion

4.2.1 Substrate Synthesis

To begin my investigations, I created a general synthetic strategy in order to provide substrates containing the necessary functional group core constructed of a secondary mesylate and allylic di- or trifluoride. While individual procedures varied depending on the specific substrate at aim, the overall strategy remained consistent and followed the sequence of organometallic addition, alkene/alkyne functionalization, and lastly alcohol derivatization (Scheme 4.3a).[24] The four substrates described in this Chapter are summarized in Scheme 4.3b.

[24] (a) Wang, X.; Zhao, S.; Liu, J.; Zhu, D.; Guo, M.; Tang, X.; Wang, G. *Org. Lett*. **2017**, *19*, 4187–4190. (b) Gao, P.; Yuan, C.; Zhao, Y.; Shi, Z. *Chem* **2018**, *4*, 2201–2211. (c) Thaliji, R. K.; Roush, W. R. *J. Am. Chem. Soc.* **2005**, *127*, 16778–16779. (d) Sato, K.; Omote, M.; Ando, A.; Kumadaki, I. *J. Fluorine Chem*. **2004**, *125*, 509–515.

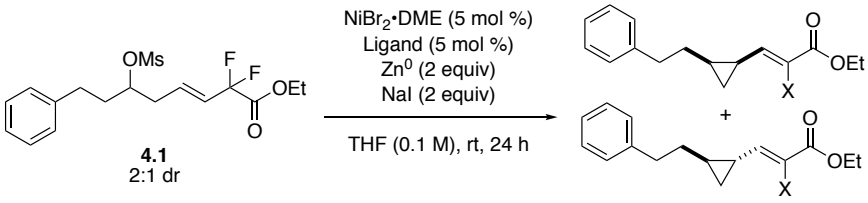
Scheme 4.3 Allylic di- and trifluoride substrates



4.2.2 Reaction Optimization

To begin my examination of the proposed transformation, mesylate **4.1** was synthesized and subjected to various nickel conditions. Mesylate **4.1** was chosen for initial evaluation studies as it does not contain a sterically hindered alkene (as opposed to **4.3**) but does contain an ester, a functional group not tolerated in our previous XEC conditions. First, a ligand evaluation was performed with $NiBr_2$•DME as the nickel source, zinc powder, and sodium iodide in THF (Table 4.1). The optimal ligand in this evaluation was BPhen (entry 1), which provided a 50% yield of the desired cyclopropane **4.5**, and defluorinated cyclopropane **4.6** in an 11% yield. It was determined that both cyclopropanes, **4.5** and **4.6,** were synthesized as a 1:1 mixture of cyclopropane diastereomers, and only one alkene isomer (Z) was observed. Related nitrogen-based ligands, Phen and bipy, resulted in low yields (entries 2–3). No cyclopropane product was observed with bidentate phosphine, BOX, and *N*-heterocyclic carbene ligands (entries 4–7). A control reaction without nickel generated no cyclopropane products (entry 8).

Table 4.1 Reaction optimization via ligand evaluation with $NiBr_2$•DME



4.5: X= F
4.6: X= H

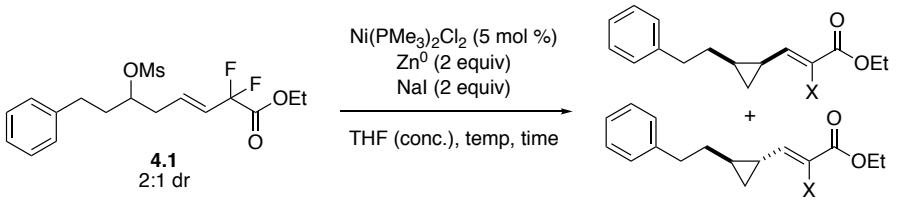
Entry	Ligand	4.5 (trans:cis)[a]	4.6 (trans:cis)[a]	SM
1	BPhen	50 (1.5:1)	11 (1:1)	9
2	Phen	26 (2:1)	6 (2:1)	15
3	bipy	<10	<5	58
4	Xantphos	0	0	54
5	pybox	0	0	50
6	Indabox	0	0	33
7	SIMes•HBF_4	0	0	76
8[b]	none	0	0	71

[a]Yields determined by ^{1}H NMR by comparison to PhTMS as internal standard. Trans:cis refers to cyclopropane diastereomers. One alkene isomer (Z) observed.
[b]No nickel

In an effort to further increase yield and decrease remaining starting material, mesylate **4.1** was subjected to other nickel catalysts (Table 4.2). The commercially available, pre-formed complex $Ni(PMe_3)_2Cl_2$ resulted in a 48% yield of **4.5** and full consumption of starting material (entry 1).[25] Next, the concentration was lowered to reduce the likelihood of possible polymerization (entry 2). Under these conditions, the yield of cyclopropane **4.5** increased to 77%. In order to reduce the reaction time from entry 2, the reaction was heated to 40 ºC for 24 h, in which a 75% of the desired cyclopropane **4.5** was obtained.

[25] The decreased yield of defluorinated product **4.6** is attributed to the rigorous drying of THF used in the reactions reported in Table 4.2.

Table 4.2 Reaction optimization with nickel catalyst $Ni(PMe_3)_2Cl_2$



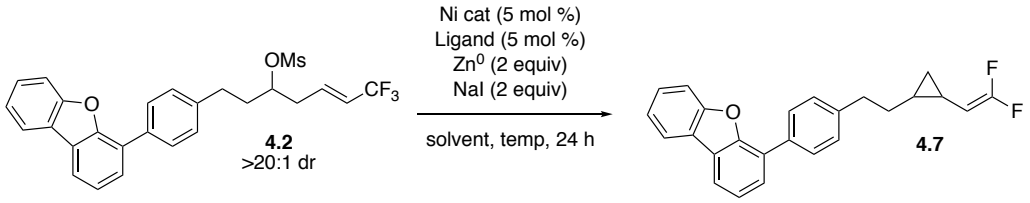
Entry	Conc.	Temp	Time	4.5 (trans:cis)[a]	4.6 (trans:cis)[a]	SM
1	0.1	rt	24	48 (1:1)	<5	0
2	0.025	rt	72	77 (1:1)	<5	0
3	0.025	40 ºC	24	75 (1:1)	<5	0

[a]Yields determined by ^1H NMR by comparison to PhTMS as internal standard.
Trans:cis refers to cyclopropane diastereomers. One alkene isomer (Z) observed.

4.2.3 β-Difluoro Vinyl Cyclopropane

Next, structural modifications were made to the allylic difluoride motif to determine the breadth of functional group reactivity. In accordance with previous reported XECs employing trifluoromethyl alkenes, mesylate **4.2** was synthesized.[19,20,21] A dibenzofuran ring was added to the structure to reduce volatility. Mesylate **4.2** was subjected to various one-electron reducing conditions (Table 4.3). For all experiments under these conditions, consumption of starting material occurred but no cyclopropane formation was observed. It should be noted that, to the best of our knowledge, all previously reported trifluoromethyl alkenes that participate in XEC reactions are trifluoromethyl substituted styrenes.[19,20,21]

Table 4.3 Trifluoromethyl alkene substrate under one-electron reducing conditions



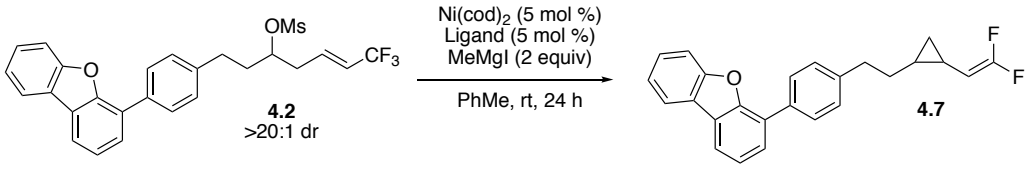
Entry	Ni cat	Ligand	Solvent	Temp	Yield[a]	SM[a]
1	$Ni(PMe_3)_2Cl_2$	none	THF	rt	0	45
2	$Ni(PMe_3)_2Cl_2$	none	THF	40 °C	0	21
3	$Ni(PMe_3)_2Cl_2$	none	DMA	rt	0	35
4	$Ni(cod)_2$	bipy	THF	40 °C	0	10
5	$Ni(cod)_2$	BPhen	THF	40 °C	0	16

[a]Yields determined by ^1H NMR by comparison to PhTMS as internal standard.

Inspired by our previous cyclopropanations utilizing MeMgI, mesylate **4.2** was subjected to similar reaction conditions. When mesylate **4.2** was reacted with $Ni(cod)_2$, dppm, and MeMgI, an 8% yield of the desired cyclopropane **4.7** was obtained (Table 4.4, entry 1). Since reduction of the mesylate moiety in **4.8** was a major competitive reaction, we hypothesized that hydrogen atom abstraction from solvent, toluene, could be occurring. However, a similar yield was obtained when the solvent was changed to benzene (entry 2). Unfortunately, employing other ligands (entries 3–4) or the addition of AgOTf (entry 5) resulted in little to no cyclopropane formation.[26] It should be noted when BPhen was employed as the ligand (entry 4), a 46% yield of iodide byproduct **4.9** was observed. This result suggests a potential iodide intermediate, consistent with our previous research.[15c]

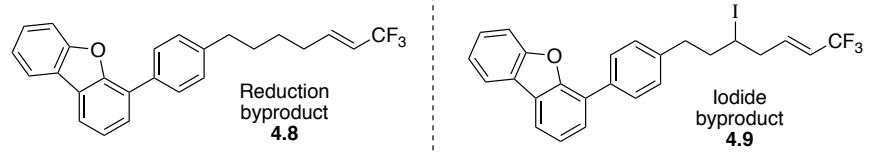
[26] Silver salts are known to increase rates of reactions involving electrophilic fluorine. For a lead reference, see: Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc*. **2009**, *131*, 1662–1663.

Table 4.4 Trifluoromethyl alkene substrate under MeMgI conditions



Entry	Ligand	Additive	Solvent	Yield (trans:cis)[a]	SM %[a]	Reduction %[a]
1	dppm	none	PhMe	8 (1:1)	0	53
2	dppm	none	benzene	9 (1:1)	0	N/A
3	*rac*-BINAP	none	PhMe	0	25	43
4[b]	BPhen	none	PhMe	<5	0	N/A
5	dppm	AgOTf	PhMe	0	0	50

[a]Yields determined by ^{1}H NMR by comparison to PhTMS as internal standard.
Trans:cis refers to cyclopropane diastereomers.
[b]46% yield of iodide byproduct **4.9**
N/A= unable to quantify



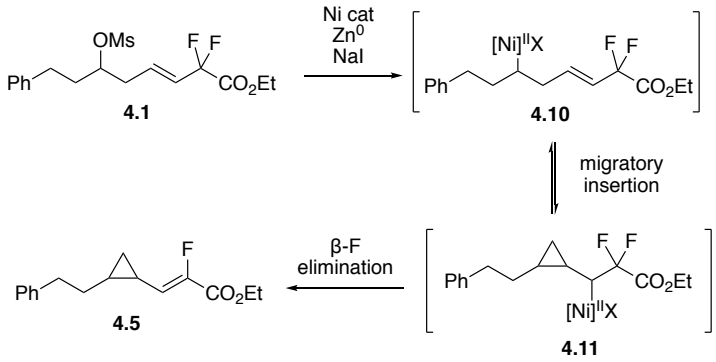
4.2.4 A Plausible Mechanism

In 2020, the Jarvo lab reported the XEC reaction of 1,3-dimesylates for cyclopropane synthesis. Both experimental and computational evidence suggested the reaction proceeds through a 1,3-diiodide that is formed in situ.[15c] Further computational investigation is consistent with formation of a carbon-nickel bond at the secondary iodide center that then displaces the primary iodide in a 3-*exo*-*tet* closure.[15c] In a mechanistically distinct cyclopropanation, the Krische group has reported the migratory insertion of an alkene into an alkylnickel intermediate.[27,16] This migratory insertion is thought to be reversible but only one diastereomer continues on the reaction pathway to form product. On these two bases, a plausible mechanism for our transformation is reported below (Scheme 4.4). It was hypothesized that under reaction conditions, mesylate **4.1**

[27] See "4.1 Introduction" section for details.

would form organonickel complex **4.10**. Migratory insertion of the alkene into the carbon-nickel bond would form intermediate **4.11**, and finally β-fluoride elimination forms the observable cyclopropane product **4.5**.

Scheme 4.4 Plausible Mechanism

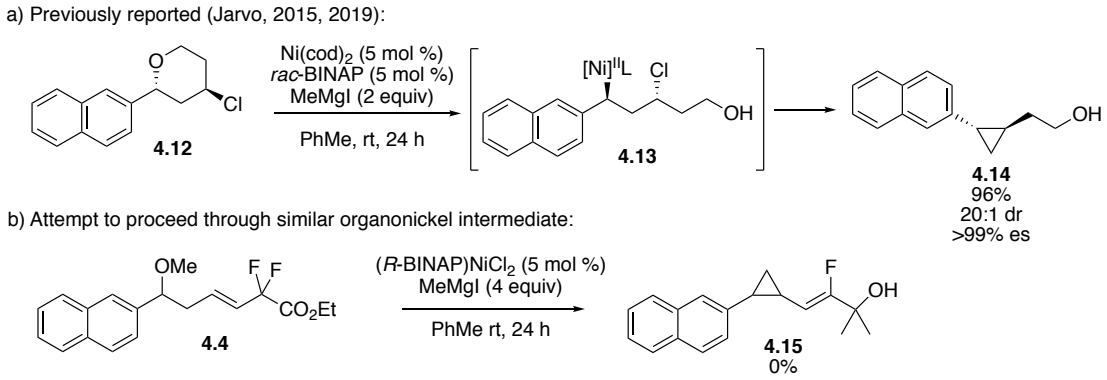


4.2.5 Naphthylic Ether Substrate

To test if the XEC reactions of allylic difluorides proceed through an organonickel intermediate, naphthylic ether **4.4** was synthesized. The Jarvo lab has previously reported the XEC ring contraction of 4-chloro-2-aryl-tetrahydropyrans when treated with a nickel catalyst and MeMgI.[15a] Experimental and computational data suggests this reaction of 4-chloro-2-aryl-tetrahydropyrans, which utilizes a naphthylic ether, proceeds through an organonickel intermediate (**4.13**, Scheme 4.5a).[28] I proposed if a cyclopropane product was observed from a similar reaction with naphthylic ether **4.4**, our XEC reaction with allylic difluorides under single-electron reducing conditions (Table 4.1–4.2) may also be proceeding through an organonickel intermediate. When naphthylic ether **4.4** was subjected to our previously developed cyclopropanation conditions, all starting material was consumed but no cyclopropane product was observed (Scheme 4.5b).

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

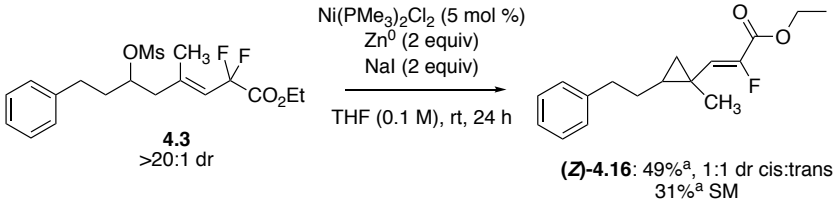
Scheme 4.5 Testing for an organonickel intermediate



4.2.6 Trisubstituted Cyclopropane

To further test the hypothesis of a migratory insertion mechanism, I synthesized mesylate **4.3**. I hypothesized that if the reaction proceeds as proposed in Scheme 4.4, increasing alkene substitution would induce diastereoselectivity. To investigate, mesylate **4.3** was synthesized and subjected to reaction conditions. After 24 h, trisubstituted cyclopropane **(*Z*)-4.16** was obtained in a 49% yield, which is comparable to the results from mesylate **4.1** (Table 4.2, entry 1). Surprisingly, there was no observable effect on the diastereoselectivity. While the results from Scheme 4.5–4.6 do not completely rule out a migratory insertion pathway, the currently available evidence is most consistent with cyclization of an organoradical intermediate.

Scheme 4.6 Synthesis of a trisubstituted cyclopropane



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

4.3 Conclusion

In conclusion, the XEC reaction of secondary mesylates with allylic difluorides has been developed. Completed work includes reaction optimization, an attempt to engage an allylic

trifluoride, and investigation into an organonickel intermediate. A trisubstituted cyclopropane with a quaternary center has also been synthesized. The currently available evidence suggests the cyclization proceeds via an organoradical intermediate. Presently, research is being performed to explore alternate substitution patterns and to expand the scope of this transformation.

4.4 Experimental Details

4.4.1 General Procedures

All reactions were carried out under a N_2 atmosphere, unless otherwise stated. All glassware was either oven-dried or flame-dried prior to use. Dichloromethane (DCM), triethylamine (Et_3N), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), and tetrahydrofuran (THF) were degassed with argon and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 °C for 12 hours) to remove H_2O. Other solvents were purchased "anhydrous" commercially, or were purified as described. ^1H NMR were recorded on Bruker DRX-400 (400 MHz ^1H, 100 MHz ^{13}C), CRYO-500 (500 MHz ^1H, 125.7 MHz ^{13}C), GN-500 (500 MHz ^1H, 125.7 MHz ^{13}C), or AVANCE-600 (150 MHz ^{13}C, 564.6 MHz ^{19}F) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00) unless otherwise noted. Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), doublet of triplets (dt), triplet of doublets (td), doublet of doublet of triplets (ddt), quartet (q), quintet (quint), quintet of triplets (quintt), quintet of doublets (quintd), sextet (sext), septet (sept), octet (oct), nonuplet (non), multiplet (m), apparent singlet (ap s), apparent doublet (ad), apparent triplet (at), apparent quartet (aq), apparent quintet (aquint)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the solvent resonance as the internal standard ($CDCl_3$, δ

77.16 ppm). NMR data were collected at 25 °C. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60Å F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or cerium ammonium molybdate (CAM), or potassium permanganate ($KMnO_4$) solutions. Flash chromatography was performed using either SiliaFlash F60 (40- 63 μm, 60 Å) from SiliCycle, or Teledyne Isco Combiflash® Rf+ automated flash chromatography system. High resolution mass spectrometry was performed by the University of California, Irvine Mass Spectrometry Center. For reactions performed at rt, average room temperature was 20 ºC. All ligands were purchased from Strem or Sigma Aldrich and were stored under N_2 atmosphere and used as received. All other chemicals were purchased commercially and used as received, unless otherwise noted.

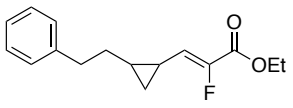
4.4.2 General Cross-Electrophile Coupling Procedures

4.4.2.1 Method A: Cross-Electrophile Coupling on Allylic Difluorides

In a glovebox, a flame-dried 7 mL vial equipped with a stir bar was charged with substrate (1.0 equiv), $Ni(PMe_3)_2Cl_2$ (5.0 mol %), Zn powder (2.0 equiv), NaI (2.0 equiv), and THF (0.025–0.1 M in substrate. The reaction stirred at rt for 24–72 h. The reaction was removed from the glovebox, the stir bar was removed, reaction mixture was concentrated in vacuo to remove THF, and loaded onto silica plug with DCM. After 10 min, the silica plug was flushed with 10% EtOAc/hexanes and concentrated in vacuo.

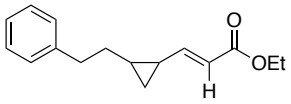
4.4.3 Characterization Data for Cyclopropanes 4.5, 4.6, 4.16

4.4.3.1 β-Fluorovinyl Cyclopropanes

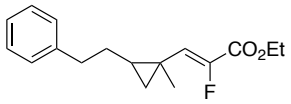


Ethyl (*Z*)-2-fluoro-3-(2-phenethylcyclopropyl)acrylate (4.5) was prepared according to Method A. The following amounts of reagents were used: $Ni(PMe_3)_2Cl_2$ (3.3 mg, 5.0 μmol, 5.0 mol %),

Zn powder (13 mg, 0.20 mmol, 2.0 equiv), NaI (30. mg, 0.20 mmol, 2.0 equiv), substrate **4.1** (37.6 mg, 0.10 mmol, 1.0 equiv), and THF (4.0 mL, 0.025 M in substrate). Before purification, a ^{1}H NMR yield of 77% was obtained based on comparison to PhTMS as internal standard. The compound was purified by flash column chromatography (0–5% EtOAc/hex) to afford the title compound as a colorless oil (17 mg, 0.065 mmol, 65%, 1:1 dr). The reported NMR data is a 1.2:1 mixture of diastereomers. **TLC R_f** = 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 4H, both), 7.21–7.12 (m, 6H, both), 5.82 (dd, *J* = 31.7, 11.0 Hz, 1H, cis), 5.59 (dd, *J* = 31.9, 10.7 Hz, 1H, trans), 4.30–4.21 (m, 4H, both), 2.74–2.66 (m, 4H, both), 1.93–1.83 (m, 1H, cis), 1.80–1.61 (m, 4H, both), 1.60–1.52 (m, 1H, trans), 1.33–1.31 (m, 7H, both), 1.15 (td, *J* = 8.6, 4.8 Hz, 1H, cis), 1.05–0.96 (m, 1H, trans), 0.83–0.76 (m, 2H, trans), 0.45 (q, *J* = 5.4 Hz, 1H, cis); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 160.9 (d, *J* = 33.8 Hz, one diastereomer), 160.7 (d, *J* = 33.8 Hz, other diastereomer), 148.9 (d, *J* = 253.4 Hz, one diastereomer), 147.7 (d, *J* = 252.5 Hz, other diastereomer), 141.8 (2C, both diastereomers), 128.60 (2C, one diastereomer), 128.56 (2C, other diastereomer), 128.48 (4C, both diastereomers), 125.9 (2C, both diastereomers), 125.7 (d, *J* = 10.6 Hz, one diastereomer), 122.4 (d, *J* = 9.7 Hz, other diastereomer), 61.46 (one diastereomer), 61.43 (other diastereomer), 35.9 (one diastereomer), 35.57 (one diastereomer), 35.54 (other diastereomer), 32.0 (other diastereomer), 22.3 (one diastereomer), 20.4 (other diastereomer), 15.7 (one diastereomer), 15.6 (one diastereomer), 15.5 (2C, other diastereomer), 14.4 (other diastereomer), 12.8 (one diastereomer); **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –135.2 (d, *J* = 31.3 Hz), –136.9 (d, *J* = 31.3 Hz); **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{19}FO_2$, 285.1267; found, 285.1266.



Ethyl (*E*)-3-(2-phenethylcyclopropyl)acrylate (4.6) was prepared according to Method A. The following amounts of reagents were used: $Ni(PMe_3)_2Cl_2$ (6.6 mg, 10. μmol, 5.0 mol %), Zn powder (26 mg, 0.40 mmol, 2.0 equiv), NaI (60. mg, 0.40 mmol, 2.0 equiv), substrate **4.1** (75.2 mg, 0.20 mmol, 1.0 equiv), and THF (8.0 mL, 0.025 M in substrate, THF was not freshly dried). The compound was purified by flash column chromatography (0–2% EtOAc/hex) to afford the title compound as a colorless oil (11 mg, 18% Et_2O by ^1H NMR, 0.022 mmol, 11%, 1.4:1 dr cis:trans). The reported NMR data is a 1.2:1 mixture of diastereomers. **TLC R_f** = 0.4 (5% EtOAc/hexanes); **^1H NMR** (400 MHz, $CDCl_3$) δ 7.31–7.22 (m, 4H, both), 7.21–7.12 (m, 6H, both), 6.68 (dd, *J* = 16.1, 10.4 Hz, 1H, cis), 6.44 (dd, *J* = 15.9, 10.3 Hz, 1H, trans), 5.90 (d, *J* = 15.5 Hz, 1H, cis), 5.78 (d, *J* = 15.5 Hz, 1H, trans), 4.22–4.13 (m, 4H, both), 2.74–2.64 (m, 4H, both), 1.83–1.58 (m, 6H, both), 1.31–1.26 (m, 7H, both), 1.10 (td, *J* = 8.1, 4.7 Hz, 1H, cis), 1.06–0.99 (m, 1H, cis), 0.84–0.78 (m, 1H, trans), 0.78–0.72 (m, 1H, trans), 0.52 (ap q, *J* = 5.6 Hz, 1H, cis); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 167.0 (one diastereomer), 166.7 (other diastereomer), 153.5 (one diastereomer), 150.5 (other diastereomer), 142.04 (one diastereomer), 141.98 (other diastereomer), 128.6 (4C, both diastereomers), 128.5 (4C, both diastereomers), 126.0 (2C, both diastereomers), 120.3 (one diastereomer), 117.9 (other diastereomer), 60.1 (2C, both diastereomers), 36.0 (one diastereomer), 35.6 (2C, both diastereomers), 31.6 (other diastereomer), 22.9 (one diastereomer), 22.3 (other diastereomer), 21.3 (one diastereomer), 19.6 (other diastereomer), 16.0 (one diastereomer), 15.5 (other diastereomer), 14.5 (2C, both diastereomers); **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{20}O_2$, 267.1361; found, 267.1371.



Ethyl (*Z*)-2-fluoro-3-(1-methyl-2-phenethylcyclopropyl)acrylate (4.16) was prepared according to Method A. The following amounts of reagents were used: $Ni(PMe_3)_2Cl_2$ (3.3 mg, 5.0 μmol, 5.0 mol %), Zn powder (13 mg, 0.20 mmol, 2.0 equiv), NaI (30. mg, 0.20 mmol, 2.0 equiv), substrate **4.3** (39.0 mg, 0.10 mmol, 1.0 equiv), and THF (1.0 mL, 0.1 M in substrate). A ^{1}H NMR yield of 49% was obtained based on comparison to PhTMS as internal standard. A small sample was obtained by flash column chromatography (0–2% EtOAc/hex) for characterization. The reported NMR data is a 1:1 mixture of diastereomers. **TLC R_f** = 0.4 (5% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.23 (m, 4H, both), 7.21–7.13 (m, 6H, both), 5.86 (d, *J* = 35.8 Hz, 1H, one diastereomer), 5.72 (d, *J* = 35.8 Hz, 1H, other diastereomer), 4.26 (q, *J* = 7.1 Hz, 2H, one diastereomer), 4.25 (q, *J* = 7.0 Hz, 2H, other diastereomer), 2.74–2.65 (m, 4H, both diastereomers), 1.78–1.59 (m, 4H, both diastereomers), 1.33 (t, *J* = 7.0 Hz, 3H, one diastereomer), 1.32 (t, *J* = 7.0 Hz, 3H, other diastereomer), 1.29 (d, *J* = 2.8 Hz, 3H, one diastereomer), 1.27 (d, *J* = 2.5 Hz, 3H, other diastereomer), 1.06–1.02 (m, 2H, one diastereomer), 0.94–0.84 (m, 1H, other diastereomer), 0.84–0.82 (m, 1H, other diastereomer), 0.64 (t, *J* = 5.3 Hz, 1H, other diastereomer), 0.39 (ap t, *J* = 4.3 Hz, 1H, one diastereomer); **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –131.3 (d, *J* = 36.8 Hz), –135.2 (d, *J* = 36.8 Hz); **HRMS** (TOF MS ES+) *m/z*: *submitted*.

4.4.4 General Procedures for Starting Material Synthesis

4.4.4.1 Method A: Grignard Addition

A solution of aldehyde (1.0 equiv) in anhydrous THF was added in a dropwise manner to allylmagnesium bromide (1.1 equiv) at 0˚C. The reaction mixture was stirred at room temperature for at least 2 h. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the mixture

was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

4.4.4.2 Method B: TMS Protection of Alcohol

To a flame-dried flask with stir bar was added alcohol (1.0 equiv) and DCM (0.20 M). Then, imidazole (2.0 equiv) and TMSCl (1.2 equiv) were added. The reaction continued to stir overnight. The reaction was quenched with DI H_2O (10 mL) and the mixture was extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

4.4.4.3 Method C: Cu-Catalyzed C–H Difluoroalkylation of Alkenes

The target compound was prepared using a modified procedure by Wang.[24a] Copper iodide (CuI) powder (0.10 equiv) was added to a flame dried Schlenk flask with stir bar. Under N_2, *N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA, 1.5 equiv), $BrCF_2CO_2Et$ (1.5 equiv), alkene (1.0 equiv), and acetonitrile (0.20–0.50 M) were added. The flask was sealed at heated to 65–70 ºC overnight. Once complete, the flask was cooled and the MeCN was removed in vacuo.

4.4.4.4 Method D: TMS Removal

To a flame-dried flask with stir bar was added silyl ether (1.0 equiv) and THF (0.5 M). The flask was cooled to 0 ºC, and TBAF was slowly added (1.1 equiv). The reaction continued to stir at 0 ºC for 1 h. The reaction was quenched with DI H_2O (10 mL) and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

4.4.4.5 Method E: Mesylation of Alcohol

A round bottom flask equipped with stir bar was charged with alcohol (1.0 equiv) and DCM (0.20 M) under N_2. Then, Et_3N (1.5 equiv), DMAP (0.1 equiv), and MsCl (1.2 equiv) were added. The

reaction mixture was then stirred at rt for at least 3 h. Once complete by TLC, saturated aqueous $NaHCO_3$ (5 mL) was added and the reaction mixture was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

4.4.4.6 Method F. Barbier Reaction

The target compound was prepared using a modified procedure by Sarkar.[29] A round bottom flask equipped with stir bar was charged with zinc powder (1.1 equiv) and THF (0.20 M) under N_2. Then, aldehyde (1.0 equiv), and propargylic/allylic halide (1.1 equiv) were added. The reaction mixture was then stirred at rt overnight. To workup, saturated aqueous NH_4Cl (10 mL) was added and the reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

4.4.4.7 Method G. 1,2-Difunctionalization of Alkyne

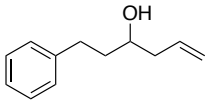
The target compound was prepared using a modified procedure by Roush.[24c] A round bottom flask equipped with stir bar was charged Cp_2ZrCl_2 (1.0 equiv) and DCM (1.2 M in Cp_2ZrCl_2) then cooled to 0 ºC. Once cooled, $AlMe_3$ (3.0 equiv) was added dropwise, and the mixture was allowed to warm to rt, stirred for 2 h, then cooled down to –20 ºC. A solution of alkyne in DCM (1.0 M) was added dropwise and the reaction was allowed to stir at rt overnight. The reaction was then cooled to –40 ºC and a solution of I_2 (1.3 equiv) in THF (1.8 M in I_2) was added dropwise. The reaction then stirred at rt for 2 h. To quench, the reaction was cooled to 0 ºC and DI H_2O was added very slowly. Once quench was completed, Et_2O (20 mL) was added and the mixture was filtered through a pad of celite. Then, 1M HCl (10 mL) was added and the mixture was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, aqueous Rochelle's salt, brine, then dried with Na_2SO_4 and concentrated in vacuo.

[29] Sahoo, S. R.; Sarkar, D. *Eur. J. Org. Chem*. **2020**, *11*, 1727–1731.

4.4.4.8 Method H. Cu-Catalyzed XEC of Vinyl Iodide with $BrCF_2CO_2Et$

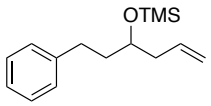
The target compound was prepared using a modified procedure by Kumadaki.[24d] A round bottom flask equipped with stir bar was charged with copper powder (2.8 equiv) and DMSO (0.20 M) under N_2. Then, vinyl iodide (1.0 equiv) and $BrCF_2CO_2Et$ (1.0 equiv) were added. The reaction mixture was then heated to 45 ºC and stirred at overnight. To workup, reaction mixture was poured into a separatory funnel with ice and saturated aqueous NH_4Cl (10 mL). The organic layer was separated, then the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo.

4.4.5 Synthesis and Characterization Data for Intermediates and Mesylate Starting Materials

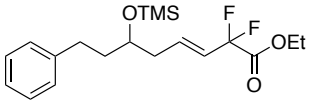


1-Phenylhex-5-en-3-ol (4.17) was prepared according to Method A. The following amounts of reagents were used: aldehyde (2.6 mL, 20. mmol, 1.0 equiv) and allylmagnesium bromide (24 mL, 24 mmol, 1.2 equiv). The compound was purified by flash column chromatography (0–20% EtOAc/hex) to afford the title compound as a colorless oil (2.6 g, 15 mmol, 75%). **TLC R_f =** 0.5 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.31–7.23 (m, 2H), 7.22–7.15 (m, 3H), 5.88–5.76 (m, 1H), 5.17–5.13 (m, 1H), 5.13–5.10 (m, 1H), 3.73–3.63 (m, 1H), 2.86–2.76 (m, 1H), 2.74–2.64 (m, 1H), 2.37–2.28 (m, 1H), 2.23–2.14 (m, 1H), 1.83–1.75 (m, 2H), 1.60 (s, 1H). Analytical data is consistent with literature values.[30]

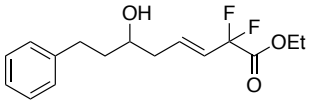
[30] Zhang, Y.-X.; Zhang, A.-Q.; Tian, J.-S.; Loh, T.-P. *Org. Biomol. Chem*. **2013**, *11*, 8387–8394.



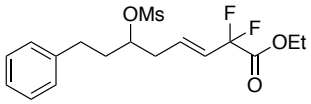
Trimethyl((1-phenylhex-5-en-3-yl)oxy)silane (4.18) was prepared according to Method B. The following amounts of reagents were used: alcohol **4.17** (2.6 g, 15 mmol, 1.0 equiv), TMSCl (3.3 mL, 18 mmol, 1.2 equiv), imidazole (2.0 g, 30. mmol, 2.0 equiv), and DCM (50. mL, 0.20 M in substrate). The compound was used in the next synthetic step unpurified. **TLC R_f =** 0.7 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.31–7.22 (m, 2H), 7.21–7.16 (m, 3H), 5.87–5.74 (m, 1H), 5.09–5.00 (m, 2H), 3.74 (quint, *J* = 5.9 Hz, 1H), 2.73 (ddd, *J* = 13.8, 10.3, 6.1 Hz, 1H), 2.56 (ddd, *J* = 13.8, 10.3, 6.1 Hz, 1H), 2.26 (t, *J* = 6.6 Hz, 2H), 1.83–1.68 (m, 2H), 0.13 (s, 9H).



Ethyl (*E*)-2,2-difluoro-8-phenyl-6-((trimethylsilyl)oxy)oct-3-enoate (4.19) was prepared according to Method C. The following amounts of reagents were used: silane **4.18** (1.9 g, 7.5 mmol, 1.0 equiv), CuI (0.14 g, 0.75 mmol, 0.10 equiv), PMDETA (2.3 mL, 11 mmol, 1.5 equiv), $BrCF_2CO_2Et$ (1.4 mL, 11 mmol, 1.5 equiv), and MeCN (15 mL, 0.5 M in substrate). The compound was purified by flash column chromatography (0–5% EtOAc/hex) to afford the title compound as a colorless oil (1.1 g, 2.9 mmol, 39% over two steps, 1.5:1 dr). The reported NMR data is a 1.5:1 mixture of diastereomers. **TLC R_f =** 0.5 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.32–7.26 (m, 4H, both), 7.21–7.13 (6H, both), 6.35–6.23 (m, 1H, major), 6.12–6.00 (m, 1H, minor), 5.78–5.62 (m, 2H, both), 4.30 (q, *J* = 7.2 Hz, 2H, major), 4.28 (q, *J* = 7.1 Hz, 2H minor), 3.78 (quint, *J* = 5.8 Hz, 2H, both), 2.75–2.65 (m, 2H, both), 2.62–2.54 (m, 2H, both), 2.53–2.48 (m, 2H, both), 2.37–2.29 (m, 2H, both), 1.78–1.70 (m, 4H, both), 1.32 (t, *J* = 7.2 Hz, 3H, major), 1.30 (t, *J* = 7.2 Hz, 3H, minor), 0.12 (s, 18H, both).

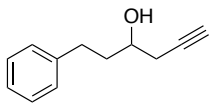


Ethyl (*E*)-2,2-difluoro-6-hydroxy-8-phenyloct-3-enoate (4.20) was prepared according to Method D. The following amounts of reagents were used: ester **4.19** (1.1 g, 2.9 mmol, 1.0 equiv), TBAF (3.2 mL, 3.2 mmol, 1.1 equiv, 1.0 M in THF), and THF (5.8 mL, 0.5 M in substrate). The compound was purified by flash column chromatography (0–15% EtOAc/hex) to afford the title compound as a colorless oil (0.65 g, 2.2 mmol, 75%, 2.3:1 dr). The reported NMR data is a 2.3:1 mixture of diastereomers. **TLC R_f =** 0.2 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.31–7.26 (m, 4H, both), 7.22–7.16 (m, 6H, both), 6.31 (dtt, *J* = 16.0, 7.3, 2.6 Hz, 1H, major), 6.07 (dtt, *J* = 11.7, 7.1, 1.9 Hz, 1H, minor), 5.84–5.66 (m, 2H, both), 4.31 (q, *J* = 7.1 Hz, 2H, major), 4.29 (q, *J* = 7.1 Hz, 2H, minor), 3.79–2.68 (m, 2H, both), 2.84–2.75 (m, 2H, both), 2.73–2.64 (m, 2H, both), 2.55–2.48 (m, 1H, major), 2.42–2.25 (m, 1H, major, 2H, minor), 1.83–1.75 (m, 4H, both), 1.53 (d, *J* = 4.9 Hz, 1H, major), 1.50 (d, *J* = 5.5 Hz, 1H, minor), 1.33 (t, *J* = 7.1 Hz, 3H, major), 1.32 (t, *J* = 7.1 Hz, 3H, minor).



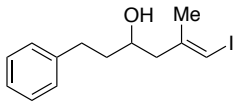
Ethyl-2,2-difluoro-6-((methylsulfonyl)oxy)-8-phenyloct-3-enoate (4.1) was prepared according to Method E. The following amounts of reagents were used: alcohol **4.20** (0.35 g, 1.2 mmol, 1.0 equiv), MsCl (0.11 mL, 1.4 mmol, 1.2 equiv), DMAP (14 mg, 0.12 mmol, 0.10 equiv), Et3N (0.24 mL, 1.8 mmol, 1.5 equiv), and DCM (5.9 mL, 0.20 M in substrate). The compound was purified by flash column chromatography (0–25% EtOAc/hex) to afford the title compound as a colorless oil (0.39 g, 1.0 mmol, 88%, 2.3:1 dr). The reported NMR data is a 2.3:1 mixture of diastereomers. **TLC R_f =** 0.3 (15% EtOAc/hexanes); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4H, both),

7.23–7.16 (m, 6H, both), 6.37–6.22 (m, 1H, major), 6.07–5.99 (m, 1H, minor), 5.88–5.73 (m, 2H, both), 4.82 (quint, J = 5.7 Hz, 2H, both), 4.34–4.27 (m, 4H, both), 3.00 (s, 3H, minor), 2.99 (s, 3H, major), 2.85–2.52 (m, 8H, both), 2.11–1.92 (m, 4H, both), 1.33 (t, J = 7.1 Hz, 3H, major), 1.32 (t, J = 7.0 Hz, 3H, minor); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 163.7 (t, J = 34.5 Hz, major), 163.9 (t, J = 34.2 Hz, minor), 140.6 (minor), 140.4 (minor), 135.3 (t, J = 6.9 Hz, minor), 133.4 (t, J = 9.3 Hz, major), 128.73 (2C, major), 128.69 (2C, minor), 128.4 (4C, both), 126.45 (major), 126.37 (minor), 125.4 (t, J = 25.7 Hz, major), 124.3 (t, J = 26.2 Hz, minor), 112.7 (t, J = 249.7 Hz, minor), 111.9 (t, J = 247.8 Hz, major), 81.0 (minor), 80.4 (major), 63.35 (minor), 63.25 (major), 38.8 (both), 37.3 (both), 36.2 (minor), 26.1 (major), 33.5 (minor), 31.3 (major), 14.00 (2C, both); **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –103.4 (d, J = 10.9 Hz), –103.5 (d, J = 10.9 Hz); **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{22}F_2O_5S$, 344.1054; found, 344.1044.

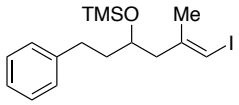


1-Phenylhex-5-yn-3-ol (4.21) was prepared according to Method F. The following amounts of reagents were used: zinc (0.72 g, 11 mmol, 1.1 equiv), propargyl bromide (0.83 mL, 11 mmol, 1.1 equiv), 3-phenylpropionaldehyde (1.3 mL, 10. mmol, 1.0 equiv) and THF (50 mL, 0.2 M in substrate). The compound was purified by flash column chromatography (0–15% EtOAc/hex) to afford the title compound as a colorless oil (1.0 g, 5.9 mmol, 59%). **TLC R_f =** 0.4 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.31–7.24 (m, 2H), 7.21–7.16 (m, 3H), 3.82–3.72 (m, 1H), 2.86–2.76 (m, 1H), 2.74–2.64 (m, 1H), 2.44 (ddd, J = 16.7, 4.9, 2.7 Hz, 1H), 2.34 (ddd, J = 17.1, 7.0, 2.6 Hz, 1H), 2.05 (t, J = 2.6 Hz, 1H), 2.01 (br s, 1H), 1.90–1.83 (m, 2H). Analytical data is consistent with literature values.[31]

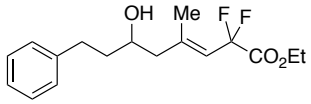
[31] Liang, T.; Woo, S. K.; Krische, M. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 9207–9211.



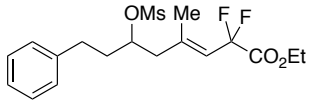
(*E*)-6-Iodo-5-methyl-1-phenylhex-5-en-3-ol (4.22) was prepared according to Method G. The following amounts of reagents were used: Cp_2ZrCl_2 (0.82 g, 2.8 mmol, 1.0 equiv), DCM (2.4 mL, 1.2 M in Cp_2ZrCl_2), alkyne **4.21** (0.49 g, 2.8 mmol, 1.0 equiv), $AlMe_3$ (4.2 mL, 8.4 mmol, 2.8 equiv), I_2 (0.92 g, 3.7 mmol, 1.3 equiv) and THF (2.0 mL, 1.8 M in I_2). The compound was purified by flash column chromatography (0–15% EtOAc/hex) to afford the title compound as a colorless oil (0.29 g, 0.93 mmol, 33%). **TLC R_f =** 0.6 (20% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.31–7.25 (m, 2H), 7.19 (d, *J* = 7.3 Hz, 3H), 6.01 (s, 1H), 3.80–3.70 (m, 1H), 2.86–2.77 (m, 1H), 2.73–2.64 (m, 1H), 2.42–2.30 (m, 2H), 1.84 (s, 3H), 1.76 (ap q, *J* = 7.5 Hz, 2H), 1.57 (d, *J* = 3.7 Hz, 1H).



(*E*)-((6-Iodo-5-methyl-1-phenylhex-5-en-3-yl)oxy)trimethylsilane (4.23) was prepared according to method B. The following amounts of reagents were used: alcohol **4.22** (0.18 g, 0.56 mmol, 1.0 equiv), TMSCl (0.06 mL, 0.5 mmol, 1 equiv), imidazole (56 mg, 0.82 mmol, 2.0 equiv), and DCM (1.4 mL, 0.30 M in substrate). The compound was purified by flash column chromatography (0–10% EtOAc/hex) to afford the title compound as a colorless oil (0.18 g, 0.46 mmol, 82%). **TLC R_f =** 0.6 (5% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.28 (ap t, *J* = 7.6 Hz, 2H), 7.21–7.12 (m, 3H), 5.93 (s, 1H), 3.80 (quint, *J* = 6.0 Hz, 1H), 2.76–2.67 (m, 1H), 2.62–2.53 (m, 1H), 2.41–2.32 (m, 2H), 1.83 (s, 3H), 1.78–1.67 (m, 2H), 0.10 (s, 9H).



Ethyl (*E*)-2,2-difluoro-6-hydroxy-4-methyl-8-phenyloct-3-enoate (4.24) was prepared according to method H. The following amounts of reagents were used: vinyl iodide **4.23** (0.18 g, 0.46 mmol, 1.0 equiv), Cu powder (82 mg, 1.3 mmol, 2.8 equiv), $BrCF_2CO_2Et$ (0.07 mL, 0.6 mmol, 1 equiv), and DMSO (2.3 mL, 0.20 M in substrate). The compound was purified by flash column chromatography (0–15% EtOAc/hex) to afford the title compound as a colorless oil (85 mg, 0.27 mmol, 60%). **TLC R_f =** 0.7 (30% EtOAc/hexanes); **^{1}H NMR** (400 MHz) $CDCl_3$ δ 7.32–7.26 (m, 2H), 7.22–7.16 (m, 3H), 5.54 (t, *J* = 13.7 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.84–3.75 (m, 1H), 2.87–2.77 (m, 1H), 2.74–2.64 (m, 1H), 2.31–3.16 (m, 2H), 1.86 (s, 3H), 1.80 (t, *J* = 7.8 Hz, 1H), 1.78 (t, *J* = 8.1 Hz, 1H), 1.57 (d, *J* = 4.1 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H).



ethyl (*E*)-2,2-difluoro-4-methyl-6-((methylsulfonyl)oxy)-8-phenyloct-3-enoate (4.3) was prepared according to Method E. The following amounts of reagents were used: alcohol **4.24** (85 mg, 0.27 mmol, 1.0 equiv), MsCl (0.02 mL, 0.3 mmol, 1 equiv), DMAP (3.3 mg, 0.027 mmol, 0.10 equiv), Et_3N (0.06 mL, 0.4 mmol, 1 equiv), and DCM (2.7 mL, 0.10 M in substrate). The compound was purified by flash column chromatography (0–15% EtOAc/hex) to afford the title compound as a colorless oil (87 mg, 0.22 mmol, 82%). **TLC R_f =** 0.2 (15% EtOAc/hexanes); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.26 (m, 2H), 7.23–7.16 (m, 3H), 5.54 (t, *J* = 13.6 Hz, 1H), 4.88 (quint, *J* = 6.4 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.98 (s, 3H), 2.84–2.66 (m, 2H), 2.55 (dd, *J* = 13.4, 8.1 Hz, 1H), 2.46–2.37 (m, 1H), 2.10–1.94 (m, 2H), 1.92–1.87 (m, 3H), 1.32 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δ 164.2 (t, *J* = 35.1 Hz), 144.9 (t, *J* = 6.9 Hz), 140.5, 128.7 (2C), 128.5 (2C), 126.4, 121.1 (t, *J* = 26.6 Hz), 120.5 (t, *J* = 248.8 Hz), 79.8, 63.2, 45.5, 38.8, 36.5,

31.3, 17.9, 14.0; **^{19}F NMR** (564.6 MHz, $CDCl_3$) δ –98.3; **HRMS** (TOF MS ES+) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{24}F_2O_5S$, 413.1210; found, 413.1225.

Developmental Therapeutics Program

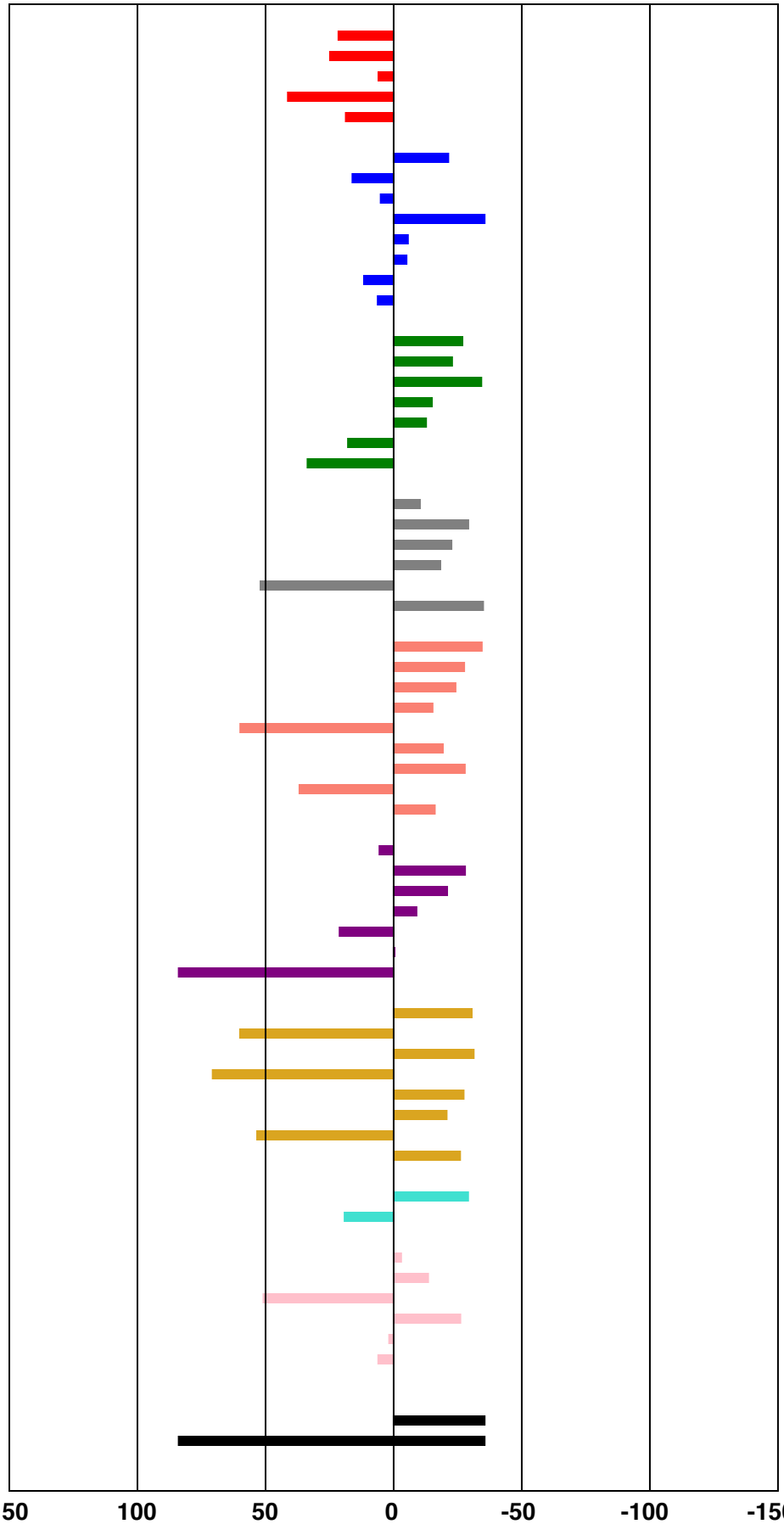
One Dose Mean Graph

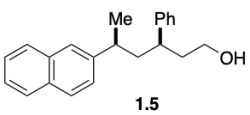
NSC: D-785438 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Jul 20, 2015

Experiment ID: 1507OS27 | **Report Date:** Aug 07, 2015

Panel/Cell Line	Growth Percent
Leukemia	
HL-60(TB)	-38.55
K-562	-35.25
MOLT-4	-54.16
RPMI-8226	-18.82
SR	-41.41
Non-Small Cell Lung Cancer	
A549/ATCC	-81.43
EKVX	-44.00
HOP-62	-55.03
HOP-92	-95.60
NCI-H226	-65.67
NCI-H23	-65.12
NCI-H460	-48.52
NCI-H522	-53.88
Colon Cancer	
COLO 205	-86.94
HCC-2998	-82.91
HCT-116	-94.32
HCT-15	-75.03
HT29	-72.76
KM12	-42.27
SW-620	-26.47
CNS Cancer	
SF-268	-70.36
SF-295	-89.23
SF-539	-82.66
SNB-19	-78.32
SNB-75	-8.12
U251	-95.02
Melanoma	
LOX IMVI	-94.50
MALME-3M	-87.63
M14	-84.25
MDA-MB-435	-75.29
SK-MEL-2	-0.23
SK-MEL-28	-79.31
SK-MEL-5	-87.88
UACC-257	-23.33
UACC-62	-76.16
Ovarian Cancer	
IGROV1	-54.55
OVCAR-3	-87.97
OVCAR-4	-80.98
OVCAR-5	-69.01
OVCAR-8	-38.99
NCI/ADR-RES	-60.45
SK-OV-3	23.80
Renal Cancer	
786-0	-90.57
A498	-0.13
ACHN	-91.34
CAKI-1	10.54
RXF 393	-87.41
SN12C	-80.78
TK-10	-6.80
UO-31	-86.04
Prostate Cancer	
PC-3	-89.16
DU-145	-40.94
Breast Cancer	
MCF7	-63.02
MDA-MB-231/ATCC	-73.55
HS 578T	-9.29
BT-549	-86.13
T-47D	-58.34
MDA-MB-468	-54.09
Mean	-60.10
Delta	35.50
Range	119.40

Mean Growth Percent - Growth Percent





1.5

Developmental Therapeutics Program

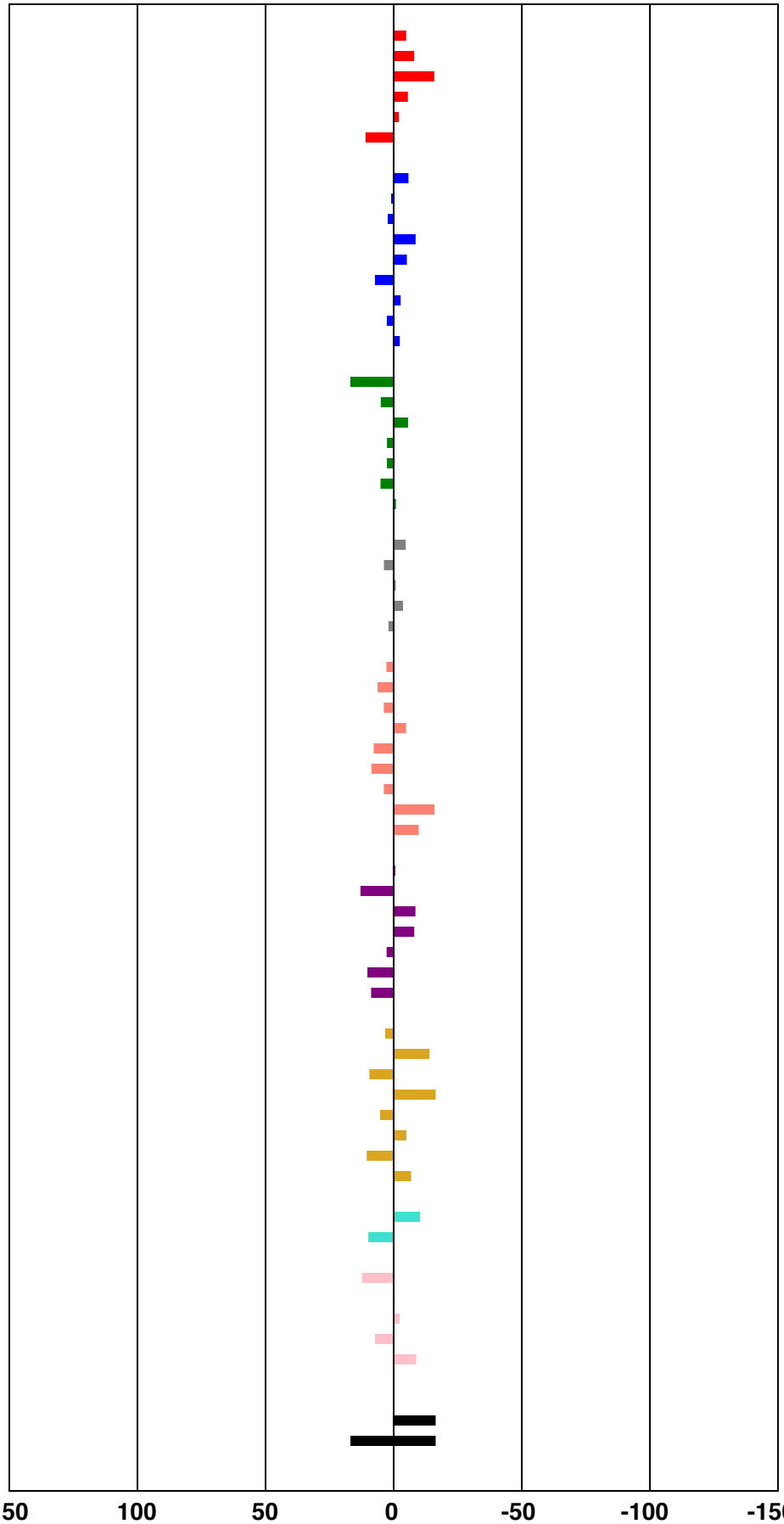
One Dose Mean Graph

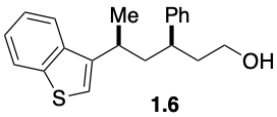
NSC: D-800496 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Sep 11, 2017

Experiment ID: 1709OS67 | **Report Date:** Oct 04, 2017

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	87.78
HL-60(TB)	84.64
K-562	76.83
MOLT-4	87.12
RPMI-8226	90.63
SR	102.97
Non-Small Cell Lung Cancer	
A549/ATCC	86.89
EKVX	92.99
HOP-62	94.32
HOP-92	84.10
NCI-H226	87.53
NCI-H23	99.32
NCI-H322M	89.94
NCI-H460	94.68
NCI-H522	90.27
Colon Cancer	
COLO 205	108.89
HCC-2998	97.03
HCT-116	87.05
HCT-15	94.62
HT29	94.66
KM12	97.13
SW-620	91.78
CNS Cancer	
SF-268	87.98
SF-295	95.80
SF-539	91.85
SNB-19	89.02
U251	94.01
Melanoma	
LOX IMVI	94.84
MALME-3M	98.26
M14	95.86
MDA-MB-435	87.81
SK-MEL-2	99.82
SK-MEL-28	100.67
SK-MEL-5	95.84
UACC-257	76.75
UACC-62	82.89
Ovarian Cancer	
IGROV1	92.03
OVCAR-3	104.97
OVCAR-4	84.16
OVCAR-5	84.64
OVCAR-8	94.76
NCI/ADR-RES	102.25
SK-OV-3	100.81
Renal Cancer	
786-0	95.34
A498	78.65
ACHN	101.48
CAKI-1	76.28
RXF 393	97.31
SN12C	87.74
TK-10	102.53
UO-31	85.87
Prostate Cancer	
PC-3	82.40
DU-145	101.89
Breast Cancer	
MCF7	104.36
MDA-MB-231/ATCC	92.20
HS 578T	90.34
BT-549	99.25
T-47D	83.87
Mean	92.34
Delta	16.06
Range	32.61

Mean Growth Percent - Growth Percent





1.6

Developmental Therapeutics Program

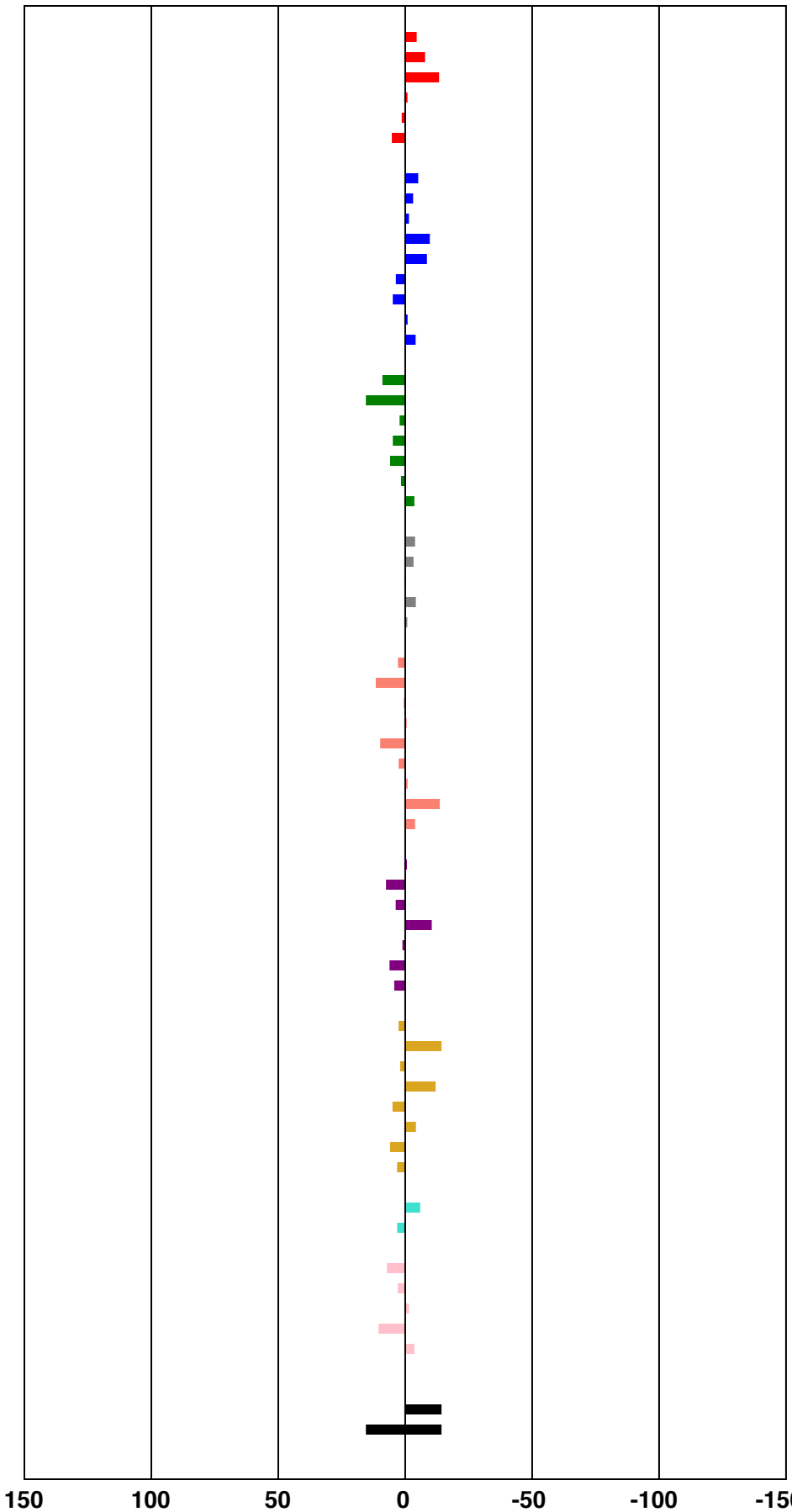
One Dose Mean Graph

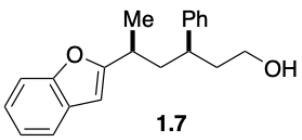
NSC: D-800495 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Sep 11, 2017

Experiment ID: 1709OS67 | **Report Date:** Oct 04, 2017

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	91.74
HL-60(TB)	88.43
K-562	82.92
MOLT-4	95.35
RPMI-8226	96.96
SR	100.85
Non-Small Cell Lung Cancer	
A549/ATCC	91.12
EKVX	93.13
HOP-62	94.78
HOP-92	86.55
NCI-H226	87.70
NCI-H23	99.27
NCI-H322M	100.48
NCI-H460	95.31
NCI-H522	92.15
Colon Cancer	
COLO 205	104.57
HCC-2998	111.08
HCT-116	97.80
HCT-15	100.46
HT29	101.54
KM12	97.24
SW-620	92.63
CNS Cancer	
SF-268	92.37
SF-295	92.97
SF-539	95.90
SNB-19	92.07
U251	95.43
Melanoma	
LOX IMVI	98.43
MALME-3M	107.19
M14	96.12
MDA-MB-435	95.69
SK-MEL-2	105.44
SK-MEL-28	98.17
SK-MEL-5	95.31
UACC-257	82.62
UACC-62	92.36
Ovarian Cancer	
IGROV1	95.58
OVCAR-3	103.15
OVCAR-4	99.33
OVCAR-5	85.79
OVCAR-8	96.69
NCI/ADR-RES	101.76
SK-OV-3	99.91
Renal Cancer	
786-0	98.20
A498	81.95
ACHN	97.57
CAKI-1	84.27
RXF 393	100.59
SN12C	92.03
TK-10	101.56
UO-31	98.78
Prostate Cancer	
PC-3	90.34
DU-145	98.76
Breast Cancer	
MCF7	102.79
MDA-MB-231/ATCC	98.52
HS 578T	94.78
BT-549	106.08
T-47D	92.64
Mean	95.92
Delta	13.97
Range	29.13

Mean Growth Percent - Growth Percent





1.7

Developmental Therapeutics Program

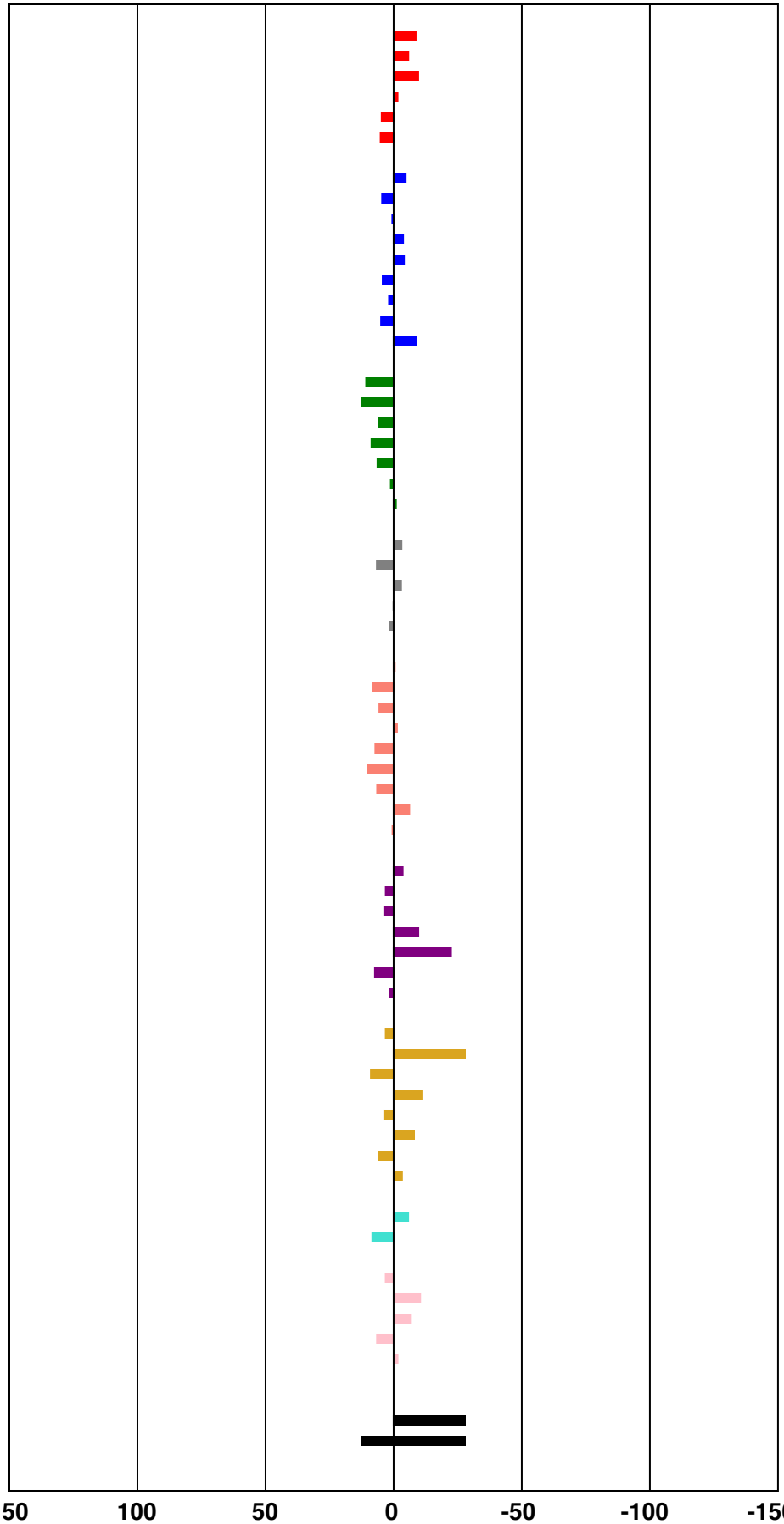
One Dose Mean Graph

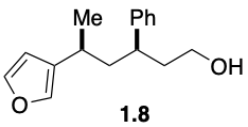
NSC: D-800497 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Sep 11, 2017

Experiment ID: 1709OS67 | **Report Date:** Oct 04, 2017

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	86.41
HL-60(TB)	89.29
K-562	85.43
MOLT-4	93.49
RPMI-8226	99.69
SR	100.11
Non-Small Cell Lung Cancer	
A549/ATCC	90.32
EKVX	99.53
HOP-62	95.54
HOP-92	91.32
NCI-H226	90.98
NCI-H23	99.30
NCI-H322M	96.83
NCI-H460	99.93
NCI-H522	86.37
Colon Cancer	
COLO 205	105.75
HCC-2998	107.33
HCT-116	100.65
HCT-15	103.67
HT29	101.33
KM12	96.13
SW-620	94.13
CNS Cancer	
SF-268	91.96
SF-295	101.58
SF-539	92.13
SNB-19	95.08
U251	96.42
Melanoma	
LOX IMVI	94.57
MALME-3M	102.97
M14	100.60
MDA-MB-435	93.71
SK-MEL-2	102.17
SK-MEL-28	104.95
SK-MEL-5	101.47
UACC-257	88.91
UACC-62	95.46
Ovarian Cancer	
IGROV1	91.49
OVCAR-3	98.11
OVCAR-4	98.69
OVCAR-5	85.38
OVCAR-8	72.64
NCI/ADR-RES	102.33
SK-OV-3	96.36
Renal Cancer	
786-0	98.12
A498	67.19
ACHN	103.91
CAKI-1	84.11
RXF 393	98.69
SN12C	87.06
TK-10	100.78
UO-31	91.76
Prostate Cancer	
PC-3	89.34
DU-145	103.35
Breast Cancer	
MCF7	98.13
MDA-MB-231/ATCC	84.66
HS 578T	88.60
BT-549	101.52
T-47D	93.49
Mean	95.02
Delta	27.83
Range	40.14

Mean Growth Percent - Growth Percent





1.8

Developmental Therapeutics Program

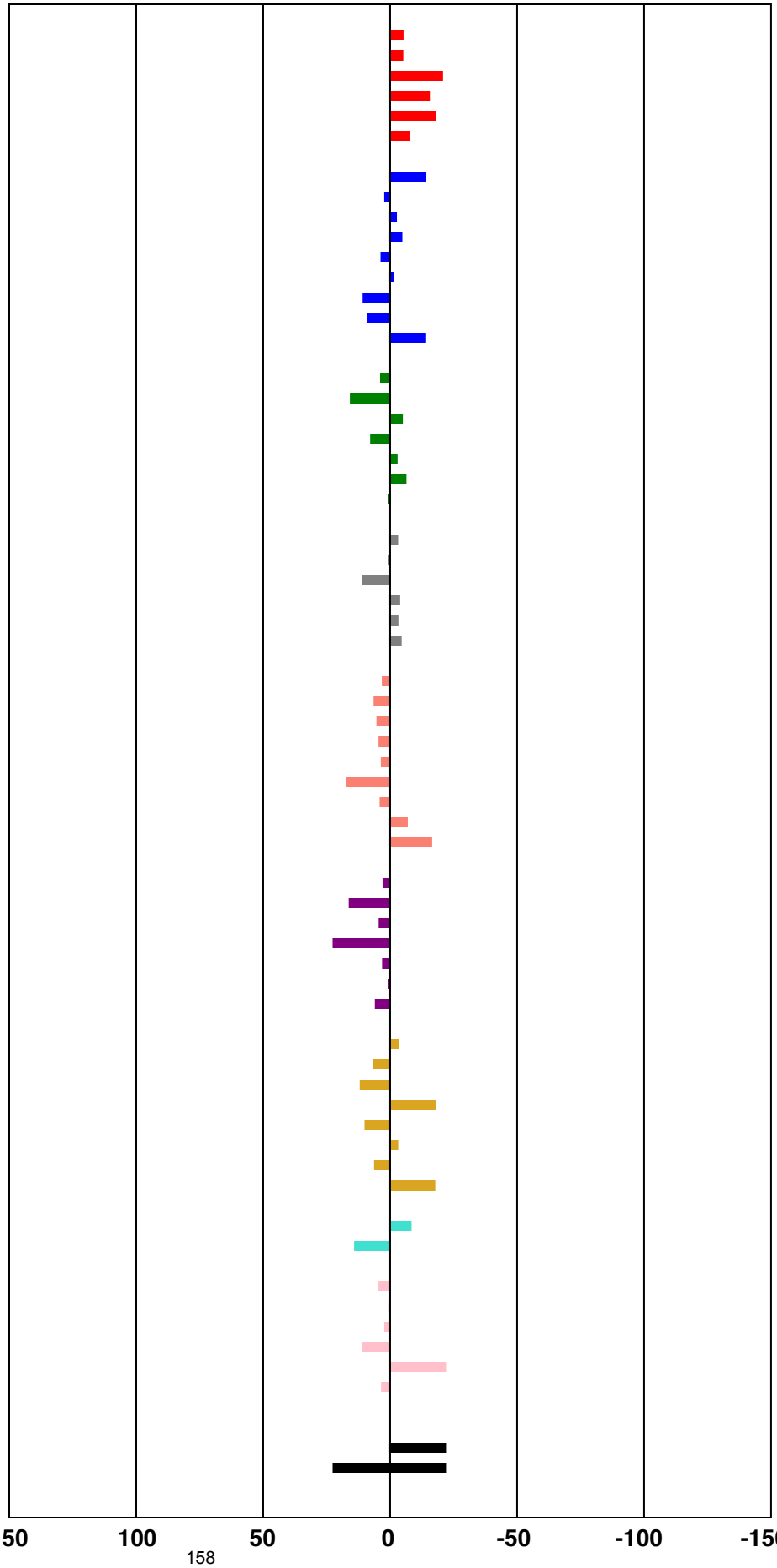
One Dose Mean Graph

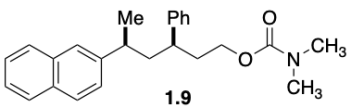
NSC: D-813868 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Apr 08, 2019

Experiment ID: 1904OS92 | **Report Date:** Apr 29, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	91.73
HL-60(TB)	91.82
K-562	76.19
MOLT-4	81.35
RPMI-8226	78.84
SR	89.20
Non-Small Cell Lung Cancer	
A549/ATCC	82.75
EKVX	98.68
HOP-62	94.34
HOP-92	92.19
NCI-H226	100.13
NCI-H23	95.40
NCI-H322M	107.18
NCI-H460	105.51
NCI-H522	82.83
Colon Cancer	
COLO 205	100.32
HCC-2998	112.20
HCT-116	91.99
HCT-15	104.22
HT29	94.07
KM12	90.58
SW-620	97.28
CNS Cancer	
SF-268	93.85
SF-295	97.11
SF-539	107.26
SNB-19	93.06
SNB-75	93.75
U251	92.47
Melanoma	
LOX IMVI	99.62
MALME-3M	102.87
M14	101.74
MDA-MB-435	100.92
SK-MEL-2	100.01
SK-MEL-28	113.58
SK-MEL-5	100.49
UACC-257	90.06
UACC-62	80.48
Ovarian Cancer	
IGROV1	99.34
OVCAR-3	112.67
OVCAR-4	100.87
OVCAR-5	119.02
OVCAR-8	99.52
NCI/ADR-RES	96.99
SK-OV-3	102.38
Renal Cancer	
786-0	93.57
A498	103.10
ACHN	108.33
CAKI-1	78.92
RXF 393	106.44
SN12C	93.83
TK-10	102.68
UO-31	79.24
Prostate Cancer	
PC-3	88.58
DU-145	110.54
Breast Cancer	
MCF7	100.94
MDA-MB-231/ATCC	96.73
HS 578T	98.68
BT-549	107.49
T-47D	75.00
MDA-MB-468	99.91
Mean	96.68
Delta	21.68
Range	44.02

Mean Growth Percent - Growth Percent





1.9

Developmental Therapeutics Program

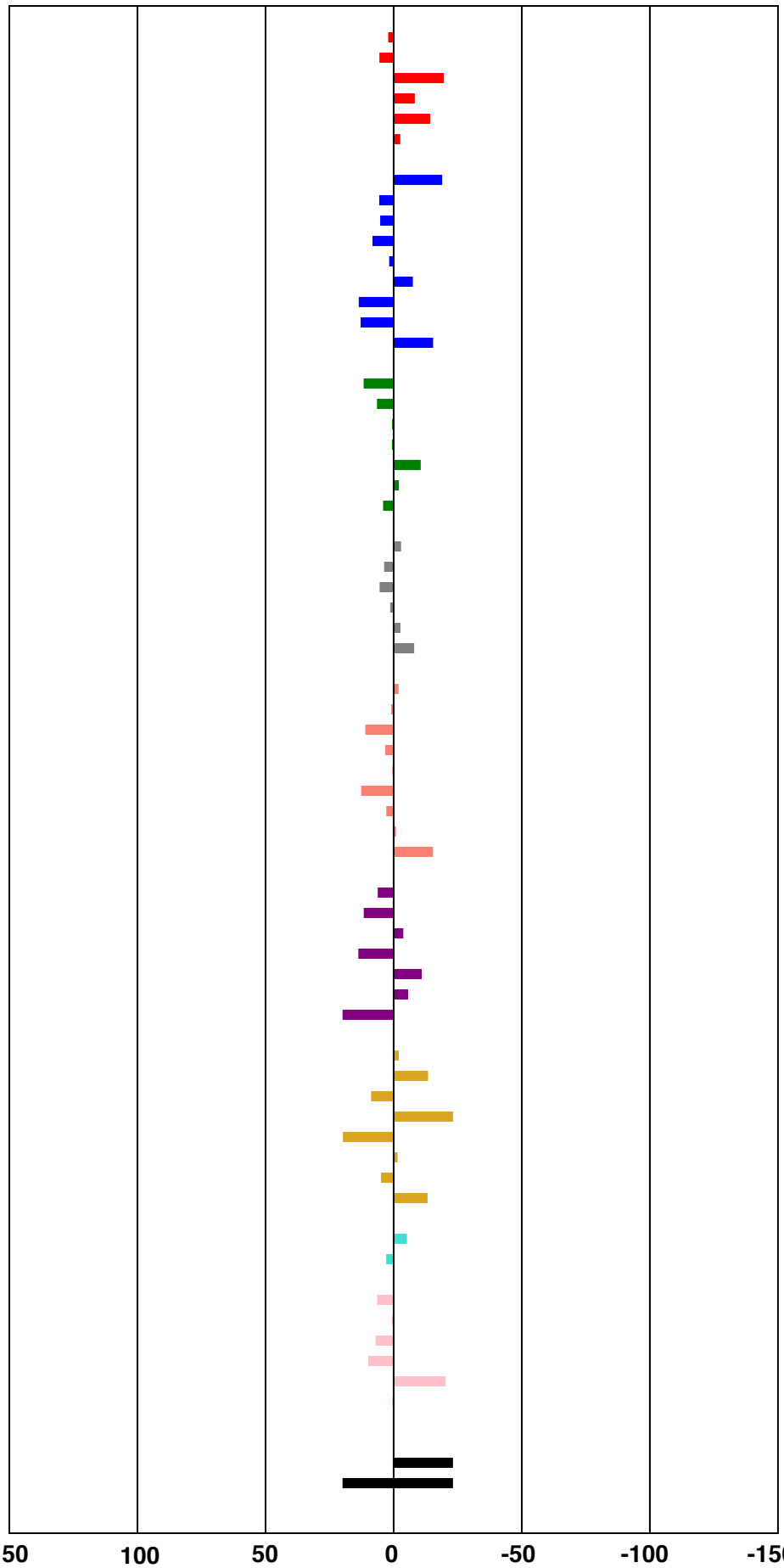
One Dose Mean Graph

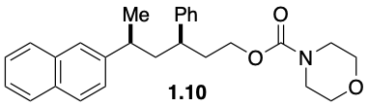
NSC: D-813866 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Apr 08, 2019

Experiment ID: 1904OS92 | **Report Date:** Apr 29, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	97.60
HL-60(TB)	101.03
K-562	76.56
MOLT-4	87.88
RPMI-8226	81.88
SR	93.54
Non-Small Cell Lung Cancer	
A549/ATCC	77.19
EKVX	101.10
HOP-62	100.72
HOP-92	103.74
NCI-H226	97.20
NCI-H23	88.63
NCI-H322M	109.08
NCI-H460	108.35
NCI-H522	80.73
Colon Cancer	
COLO 205	107.19
HCC-2998	101.97
HCT-116	96.06
HCT-15	96.16
HT29	85.56
KM12	94.10
SW-620	99.59
CNS Cancer	
SF-268	93.23
SF-295	99.19
SF-539	100.96
SNB-19	96.83
SNB-75	93.48
U251	88.12
Melanoma	
LOX IMVI	94.18
MALME-3M	96.44
M14	106.52
MDA-MB-435	98.79
SK-MEL-2	95.95
SK-MEL-28	108.16
SK-MEL-5	98.34
UACC-257	95.20
UACC-62	80.79
Ovarian Cancer	
IGROV1	101.68
OVCAR-3	107.14
OVCAR-4	92.36
OVCAR-5	109.24
OVCAR-8	85.16
NCI/ADR-RES	90.47
SK-OV-3	115.41
Renal Cancer	
786-0	94.10
A498	82.68
ACHN	104.26
CAKI-1	72.98
RXF 393	115.26
SN12C	94.63
TK-10	100.38
UO-31	82.90
Prostate Cancer	
PC-3	90.94
DU-145	98.38
Breast Cancer	
MCF7	101.92
MDA-MB-231/ATCC	96.20
HS 578T	102.50
BT-549	105.37
T-47D	75.77
MDA-MB-468	95.98
Mean	95.80
Delta	22.82
Range	42.43

Mean Growth Percent - Growth Percent





1.10

Developmental Therapeutics Program

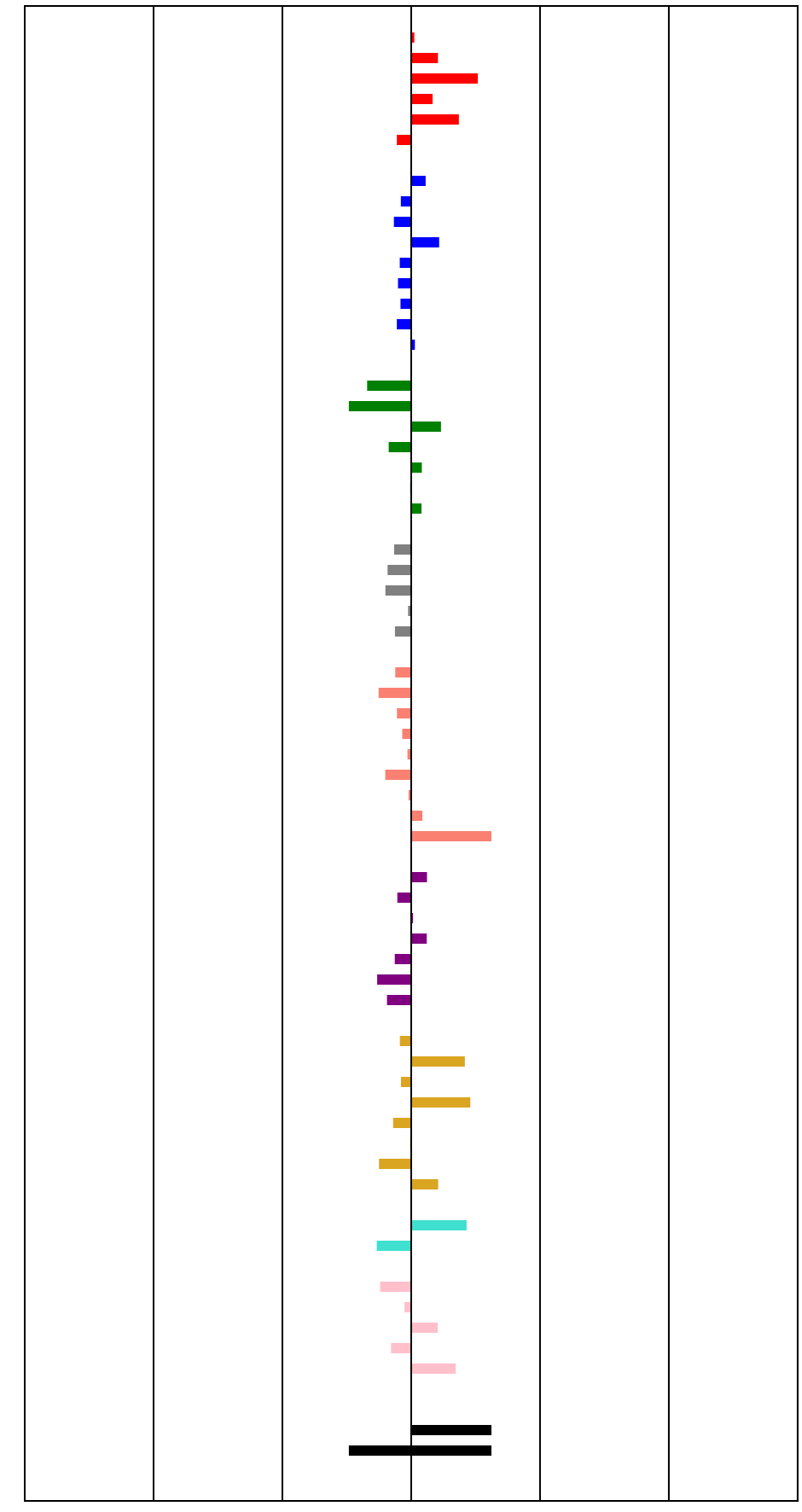
One Dose Mean Graph

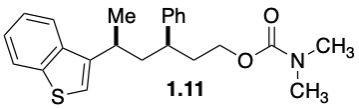
NSC: D-800499 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Sep 11, 2017

Experiment ID: 1709OS67 | **Report Date:** Oct 04, 2017

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	85.65
HL-60(TB)	76.48
K-562	61.02
MOLT-4	78.56
RPMI-8226	68.36
SR	91.77
Non-Small Cell Lung Cancer	
A549/ATCC	81.26
EKVX	90.22
HOP-62	92.92
HOP-92	76.02
NCI-H226	90.64
NCI-H23	91.32
NCI-H322M	90.35
NCI-H460	91.77
NCI-H522	85.43
Colon Cancer	
COLO 205	103.30
HCC-2998	110.40
HCT-116	75.30
HCT-15	94.93
HT29	82.73
KM12	86.56
SW-620	82.86
CNS Cancer	
SF-268	92.82
SF-295	95.37
SF-539	96.21
SNB-19	87.41
U251	92.51
Melanoma	
LOX IMVI	92.38
MALME-3M	98.85
M14	91.72
MDA-MB-435	89.67
SK-MEL-2	87.65
SK-MEL-28	96.26
SK-MEL-5	87.21
UACC-257	82.52
UACC-62	55.73
Ovarian Cancer	
IGROV1	80.73
OVCAR-3	91.58
OVCAR-4	86.15
OVCAR-5	80.83
OVCAR-8	92.58
NCI/ADR-RES	99.41
SK-OV-3	95.60
Renal Cancer	
786-0	90.59
A498	66.04
ACHN	90.18
CAKI-1	63.93
RXF 393	93.21
SN12C	86.58
TK-10	98.71
UO-31	76.40
Prostate Cancer	
PC-3	65.36
DU-145	99.57
Breast Cancer	
MCF7	98.27
MDA-MB-231/ATCC	88.78
HS 578T	76.54
BT-549	94.03
T-47D	69.58
Mean	86.53
Delta	30.80
Range	54.67

Mean Growth Percent - Growth Percent





1.11

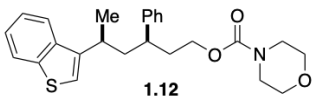
Developmental Therapeutics Program

One Dose Mean Graph

NSC: D-803734 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Feb 12, 2018

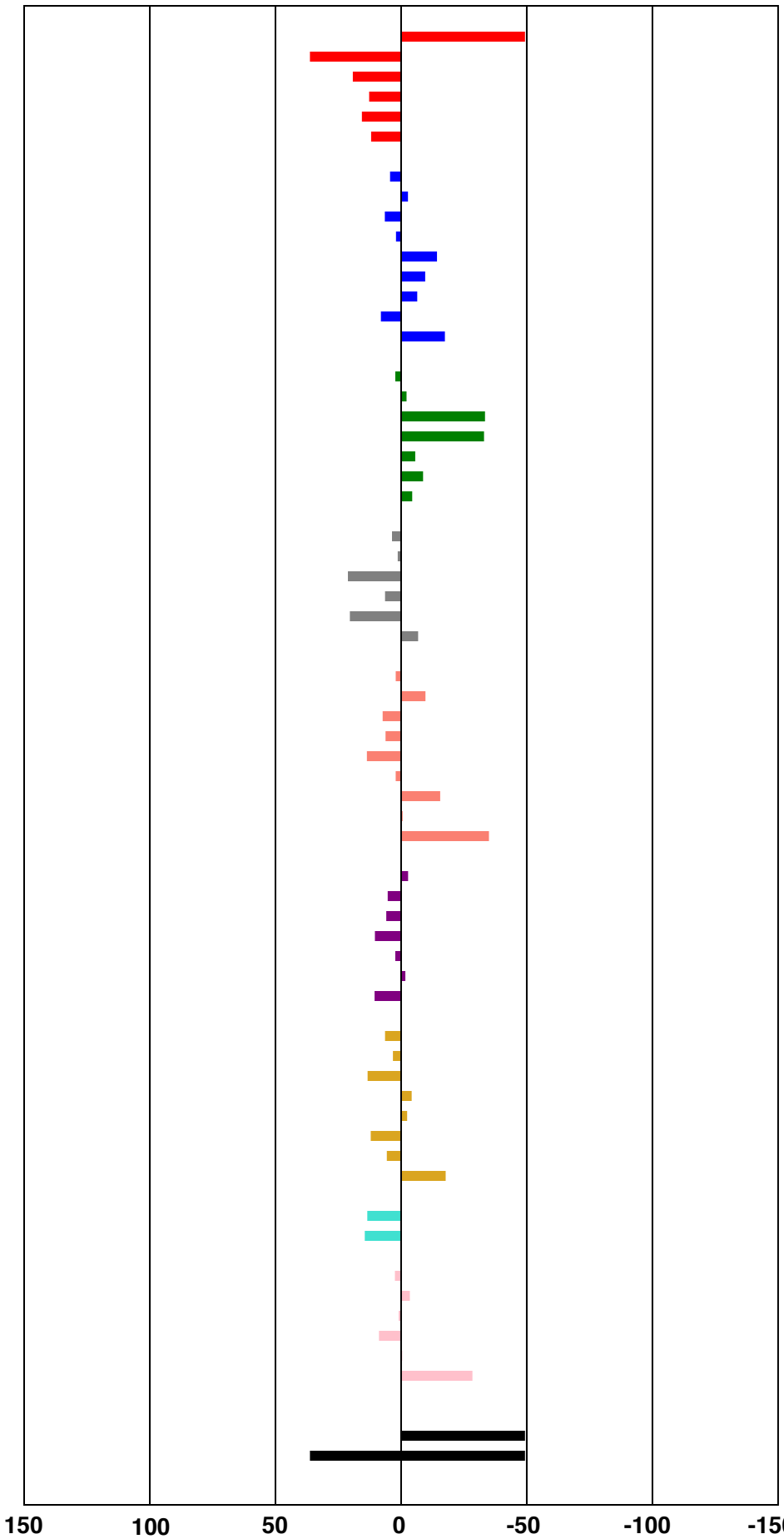
Experiment ID: 1802OS40 | **Report Date:** Jun 08, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	37.19
HL-60(TB)	122.09
K-562	105.03
MOLT-4	98.53
RPMI-8226	101.42
SR	97.75
Non-Small Cell Lung Cancer	
A549/ATCC	90.21
EKVX	83.75
HOP-62	92.29
HOP-92	87.85
NCI-H226	72.20
NCI-H23	76.90
NCI-H322M	80.06
NCI-H460	93.86
NCI-H522	69.06
Colon Cancer	
COLO 205	88.13
HCC-2998	84.32
HCT-116	53.10
HCT-15	53.49
HT29	80.86
KM12	77.74
SW-620	82.06
CNS Cancer	
SF-268	89.44
SF-295	87.16
SF-539	106.98
SNB-19	92.21
SNB-75	106.20
U251	79.71
Melanoma	
LOX IMVI	87.96
MALME-3M	76.79
M14	93.16
MDA-MB-435	92.01
SK-MEL-2	99.43
SK-MEL-28	87.97
SK-MEL-5	70.93
UACC-257	85.86
UACC-62	51.53
Ovarian Cancer	
IGROV1	83.70
OVCAR-3	91.15
OVCAR-4	91.72
OVCAR-5	96.24
OVCAR-8	88.14
NCI/ADR-RES	84.79
SK-OV-3	96.37
Renal Cancer	
786-0	92.21
A498	89.07
ACHN	99.15
CAKI-1	82.28
RXF 393	84.08
SN12C	97.90
TK-10	91.50
UO-31	68.75
Prostate Cancer	
PC-3	99.27
DU-145	100.27
Breast Cancer	
MCF7	88.28
MDA-MB-231/ATCC	83.00
HS 578T	86.79
BT-549	94.62
T-47D	86.03
MDA-MB-468	58.10
Mean	86.14
Delta	48.95
Range	84.90



1.12

Mean Growth Percent - Growth Percent



Developmental Therapeutics Program

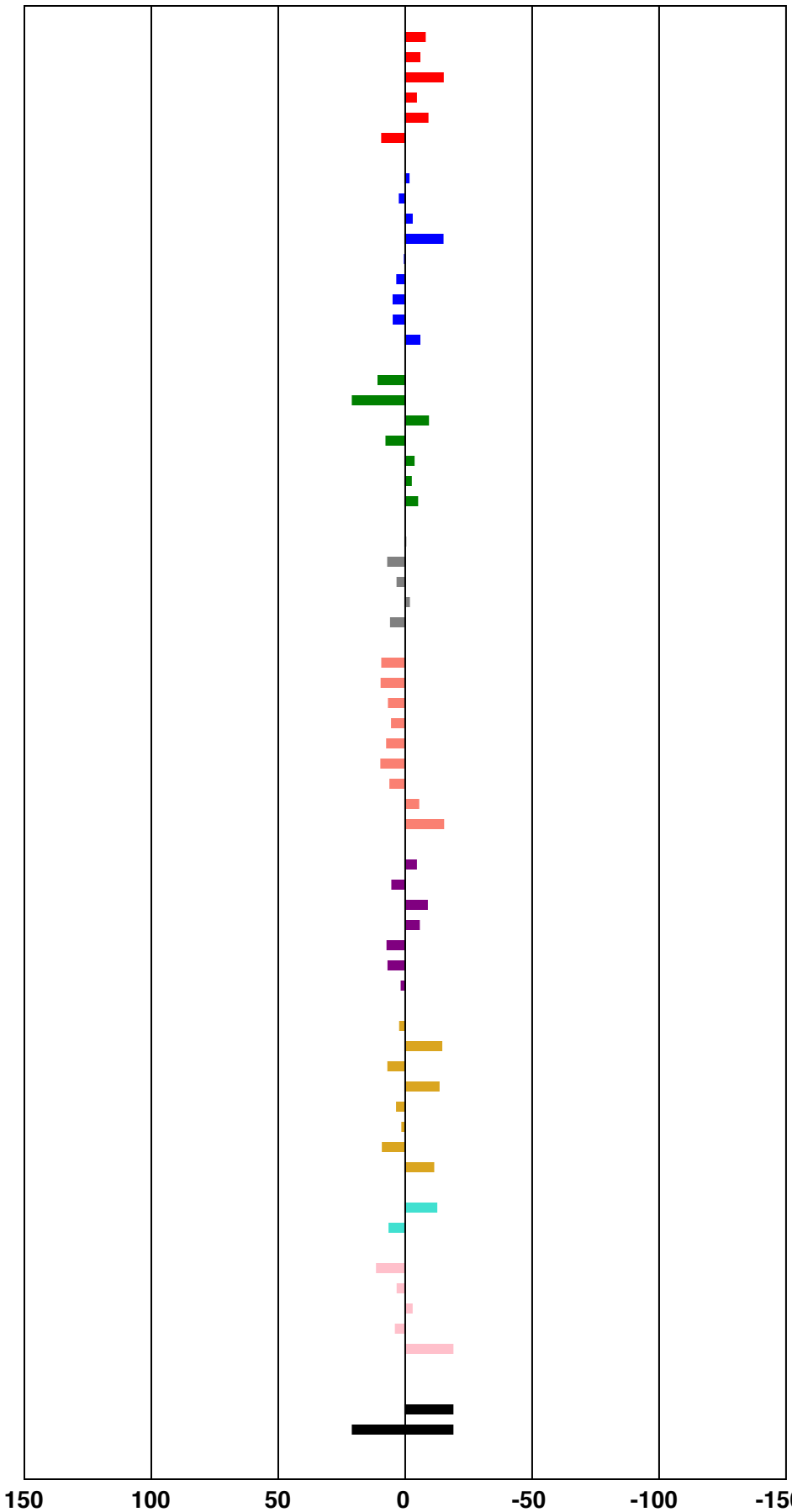
One Dose Mean Graph

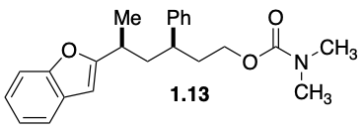
NSC: D-800498 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Sep 11, 2017

Experiment ID: 1709OS67 | **Report Date:** Oct 04, 2017

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	82.73
HL-60(TB)	84.84
K-562	75.63
MOLT-4	86.19
RPMI-8226	81.65
SR	99.62
Non-Small Cell Lung Cancer	
A549/ATCC	89.11
EKVX	92.69
HOP-62	87.85
HOP-92	75.72
NCI-H226	90.70
NCI-H23	93.67
NCI-H322M	95.13
NCI-H460	95.08
NCI-H522	84.84
Colon Cancer	
COLO 205	101.07
HCC-2998	111.20
HCT-116	81.45
HCT-15	97.93
HT29	87.12
KM12	88.21
SW-620	85.72
CNS Cancer	
SF-268	90.35
SF-295	97.25
SF-539	93.57
SNB-19	88.97
U251	96.14
Melanoma	
LOX IMVI	99.58
MALME-3M	99.85
M14	96.96
MDA-MB-435	95.74
SK-MEL-2	97.67
SK-MEL-28	99.95
SK-MEL-5	96.39
UACC-257	85.29
UACC-62	75.48
Ovarian Cancer	
IGROV1	86.20
OVCAR-3	95.62
OVCAR-4	81.89
OVCAR-5	85.06
OVCAR-8	97.52
NCI/ADR-RES	97.14
SK-OV-3	91.95
Renal Cancer	
786-0	92.55
A498	76.21
ACHN	97.19
CAKI-1	77.28
RXF 393	93.76
SN12C	91.68
TK-10	99.36
UO-31	79.38
Prostate Cancer	
PC-3	78.18
DU-145	96.73
Breast Cancer	
MCF7	101.66
MDA-MB-231/ATCC	93.53
HS 578T	87.88
BT-549	94.23
T-47D	71.82
Mean	90.49
Delta	18.67
Range	39.38

Mean Growth Percent - Growth Percent





1.13

Developmental Therapeutics Program

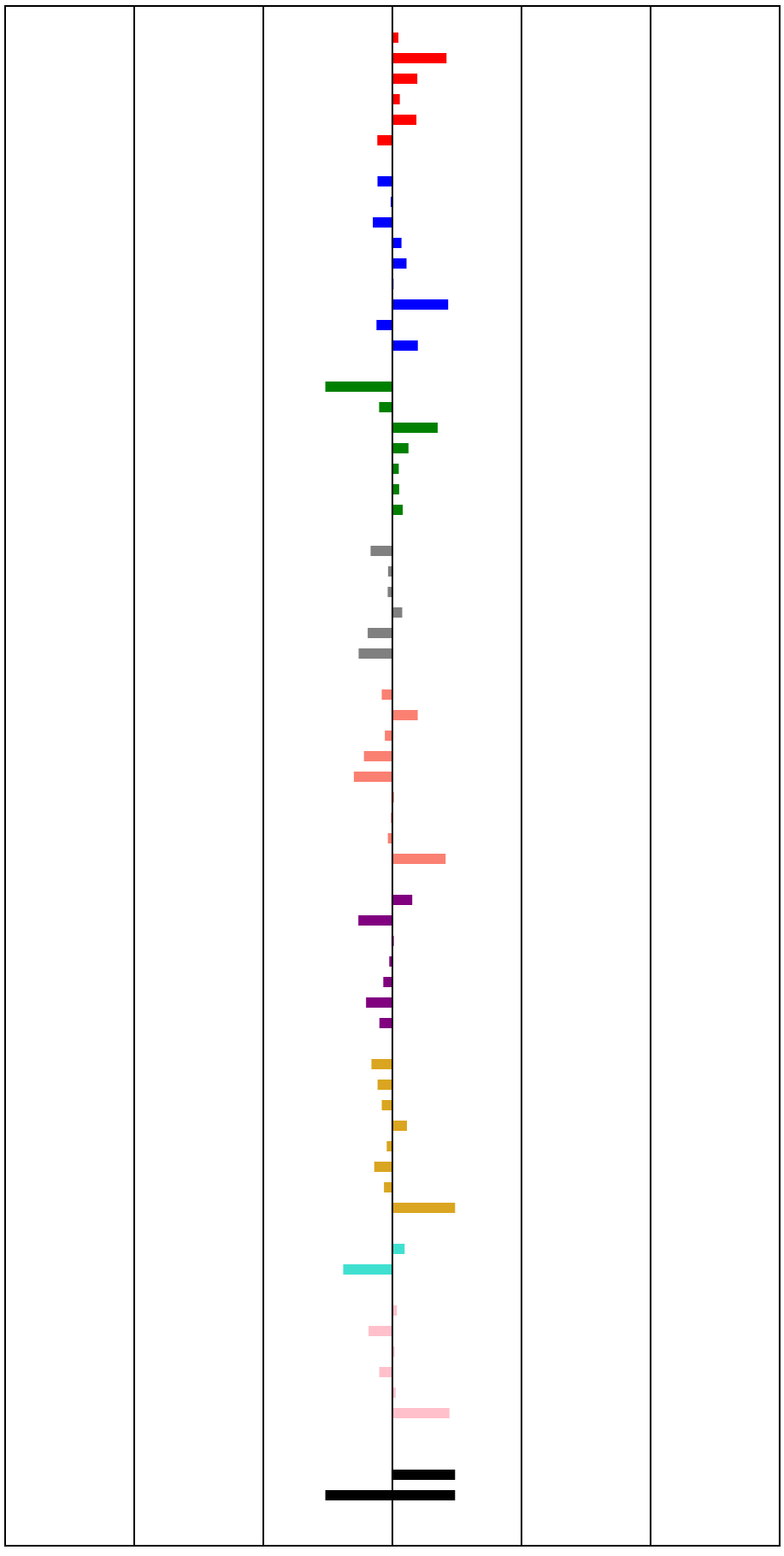
One Dose Mean Graph

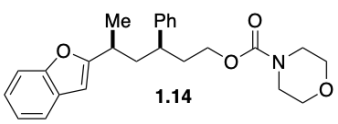
NSC: D-803735 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Feb 12, 2018

Experiment ID: 1802OS40 | **Report Date:** Jun 08, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	88.96
HL-60(TB)	70.32
K-562	81.63
MOLT-4	88.41
RPMI-8226	81.98
SR	96.46
Non-Small Cell Lung Cancer	
A549/ATCC	96.39
EKVX	91.28
HOP-62	98.19
HOP-92	87.76
NCI-H226	85.81
NCI-H23	90.83
NCI-H322M	69.68
NCI-H460	96.78
NCI-H522	81.43
Colon Cancer	
COLO 205	116.59
HCC-2998	95.76
HCT-116	73.74
HCT-15	85.05
HT29	88.81
KM12	88.66
SW-620	87.28
CNS Cancer	
SF-268	99.07
SF-295	92.30
SF-539	92.44
SNB-19	87.47
SNB-75	100.18
U251	103.70
Melanoma	
LOX IMVI	94.75
MALME-3M	81.48
M14	93.53
MDA-MB-435	101.64
SK-MEL-2	105.55
SK-MEL-28	90.66
SK-MEL-5	91.17
UACC-257	92.38
UACC-62	70.66
Ovarian Cancer	
IGROV1	83.59
OVCAR-3	103.80
OVCAR-4	90.73
OVCAR-5	91.83
OVCAR-8	94.14
NCI/ADR-RES	100.82
SK-OV-3	95.65
Renal Cancer	
786-0	98.74
A498	96.36
ACHN	94.74
CAKI-1	85.65
RXF 393	92.81
SN12C	97.66
TK-10	93.88
UO-31	67.00
Prostate Cancer	
PC-3	86.55
DU-145	109.66
Breast Cancer	
MCF7	89.54
MDA-MB-231/ATCC	99.85
HS 578T	90.43
BT-549	95.70
T-47D	90.03
MDA-MB-468	69.18
Mean	90.95
Delta	23.95
Range	49.59

Mean Growth Percent - Growth Percent





1.14

Developmental Therapeutics Program

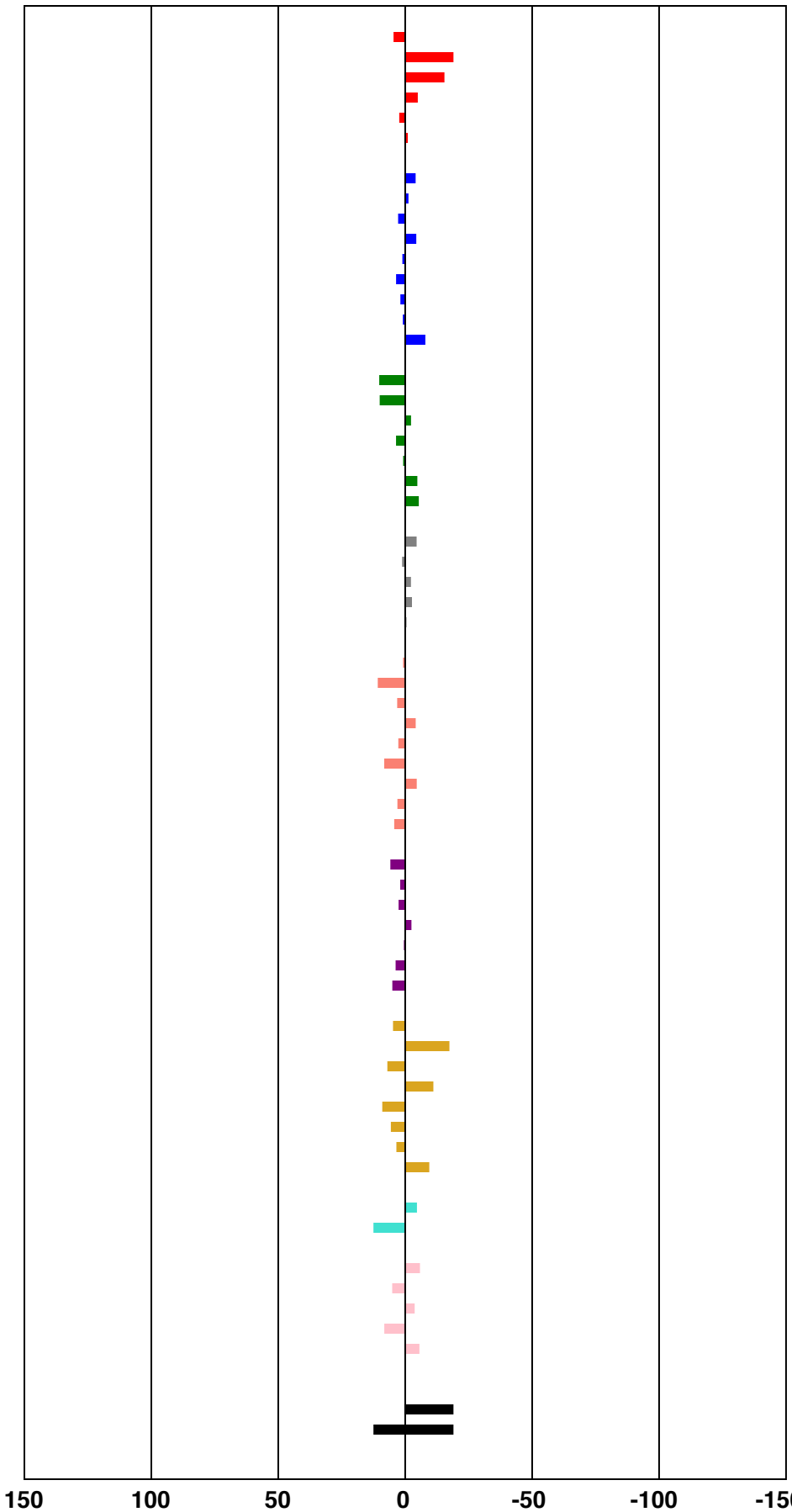
One Dose Mean Graph

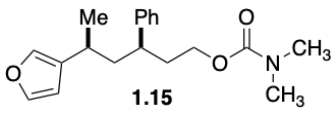
NSC: D-800500 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Sep 11, 2017

Experiment ID: 1709OS67 | **Report Date:** Oct 04, 2017

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	101.14
HL-60(TB)	78.20
K-562	81.75
MOLT-4	92.25
RPMI-8226	98.89
SR	96.17
Non-Small Cell Lung Cancer	
A549/ATCC	93.10
EKVX	95.92
HOP-62	99.33
HOP-92	92.84
NCI-H226	97.66
NCI-H23	100.13
NCI-H322M	98.44
NCI-H460	97.48
NCI-H522	89.27
Colon Cancer	
COLO 205	106.77
HCC-2998	106.59
HCT-116	94.91
HCT-15	100.15
HT29	97.35
KM12	92.42
SW-620	91.85
CNS Cancer	
SF-268	92.71
SF-295	97.76
SF-539	94.94
SNB-19	94.54
U251	96.69
Melanoma	
LOX IMVI	97.37
MALME-3M	107.35
M14	99.70
MDA-MB-435	93.07
SK-MEL-2	99.25
SK-MEL-28	104.81
SK-MEL-5	92.66
UACC-257	99.61
UACC-62	100.87
Ovarian Cancer	
IGROV1	102.39
OVCAR-3	98.51
OVCAR-4	99.15
OVCAR-5	94.75
OVCAR-8	97.05
NCI/ADR-RES	100.32
SK-OV-3	101.61
Renal Cancer	
786-0	101.34
A498	79.79
ACHN	103.57
CAKI-1	86.11
RXF 393	105.57
SN12C	102.19
TK-10	100.01
UO-31	87.72
Prostate Cancer	
PC-3	92.58
DU-145	109.05
Breast Cancer	
MCF7	91.39
MDA-MB-231/ATCC	101.66
HS 578T	93.48
BT-549	104.78
T-47D	91.61
Mean	96.87
Delta	18.67
Range	30.85

Mean Growth Percent - Growth Percent





1.15

Developmental Therapeutics Program

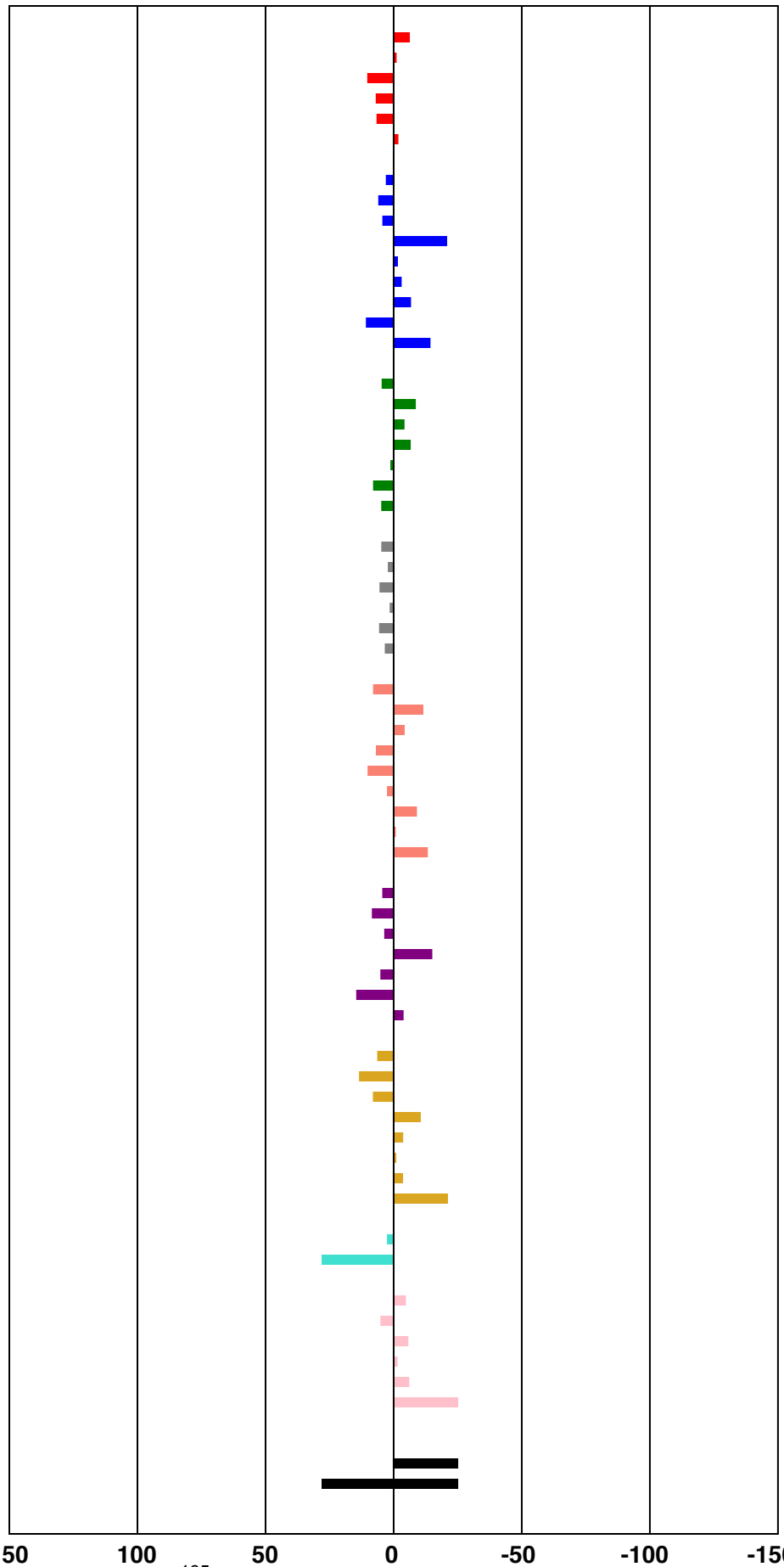
One Dose Mean Graph

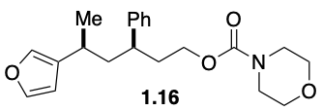
NSC: D-803733 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Feb 12, 2018

Experiment ID: 1802OS40 | **Report Date:** Jun 08, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	89.62
HL-60(TB)	94.79
K-562	105.58
MOLT-4	102.27
RPMI-8226	101.96
SR	94.08
Non-Small Cell Lung Cancer	
A549/ATCC	98.33
EKVX	101.28
HOP-62	99.69
HOP-92	75.06
NCI-H226	94.27
NCI-H23	92.81
NCI-H322M	89.16
NCI-H460	106.11
NCI-H522	81.56
Colon Cancer	
COLO 205	99.96
HCC-2998	87.28
HCT-116	91.69
HCT-15	89.27
HT29	96.56
KM12	103.31
SW-620	100.12
CNS Cancer	
SF-268	100.10
SF-295	97.55
SF-539	100.81
SNB-19	96.83
SNB-75	100.96
U251	98.74
Melanoma	
LOX IMVI	103.32
MALME-3M	84.35
M14	91.63
MDA-MB-435	102.21
SK-MEL-2	105.46
SK-MEL-28	97.87
SK-MEL-5	86.84
UACC-257	95.09
UACC-62	82.59
Ovarian Cancer	
IGROV1	99.72
OVCAR-3	103.78
OVCAR-4	98.96
OVCAR-5	80.85
OVCAR-8	100.46
NCI/ADR-RES	109.89
SK-OV-3	92.06
Renal Cancer	
786-0	101.69
A498	108.79
ACHN	103.38
CAKI-1	85.35
RXF 393	92.22
SN12C	94.92
TK-10	92.26
UO-31	74.74
Prostate Cancer	
PC-3	97.87
DU-145	123.40
Breast Cancer	
MCF7	91.14
MDA-MB-231/ATCC	100.46
HS 578T	90.20
BT-549	94.41
T-47D	89.83
MDA-MB-468	70.74
Mean	95.60
Delta	24.86
Range	52.66

Mean Growth Percent - Growth Percent





1.16

Developmental Therapeutics Program

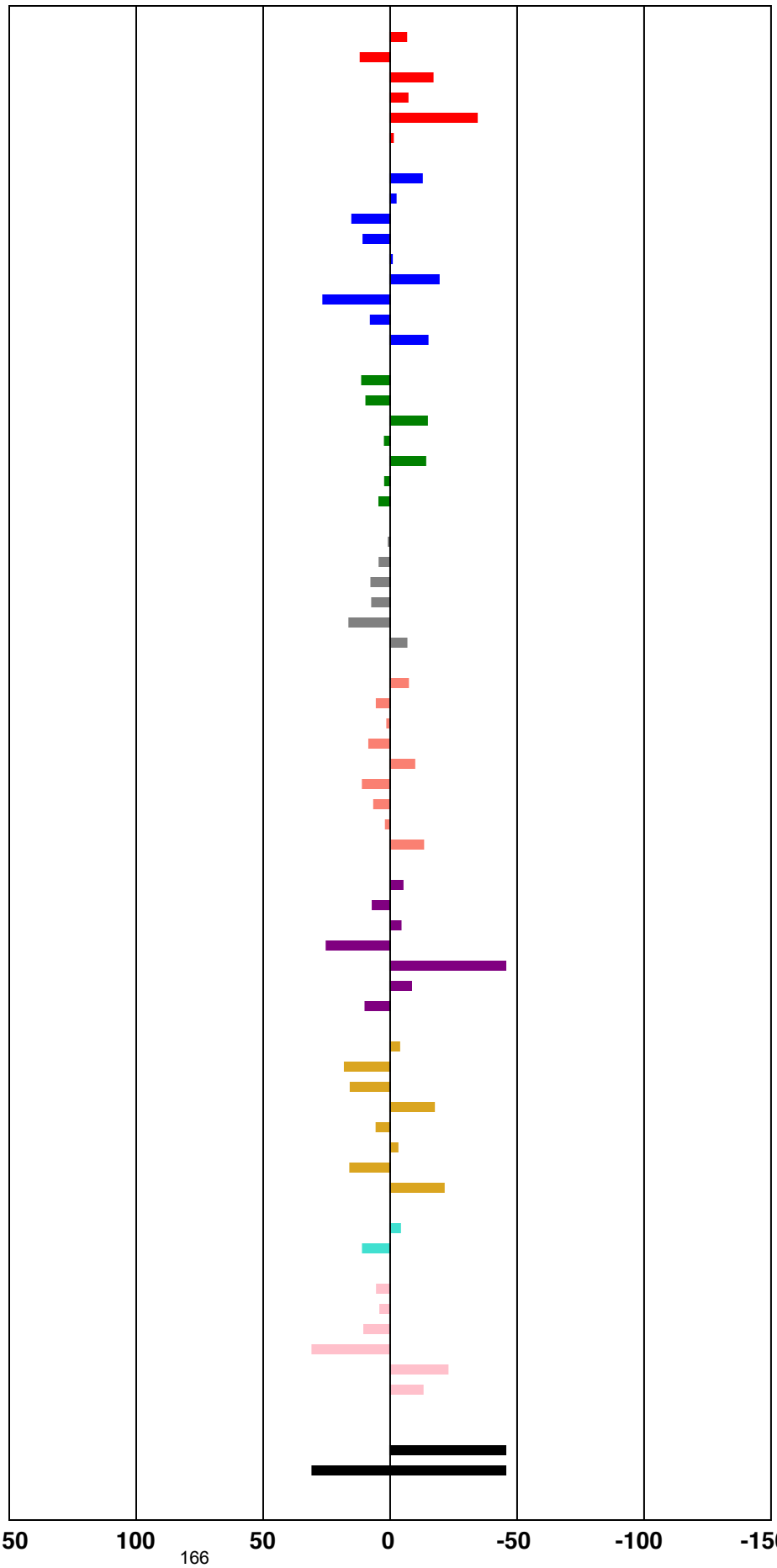
One Dose Mean Graph

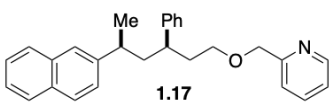
NSC: D-813867 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Apr 08, 2019

Experiment ID: 1904OS92 | **Report Date:** Apr 29, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	87.10
HL-60(TB)	105.15
K-562	76.72
MOLT-4	86.59
RPMI-8226	59.32
SR	92.37
Non-Small Cell Lung Cancer	
A549/ATCC	80.95
EKVX	91.27
HOP-62	108.45
HOP-92	104.03
NCI-H226	92.77
NCI-H23	74.32
NCI-H322M	119.85
NCI-H460	101.15
NCI-H522	78.70
Colon Cancer	
COLO 205	104.56
HCC-2998	102.89
HCT-116	78.93
HCT-15	95.61
HT29	79.61
KM12	95.52
SW-620	97.78
CNS Cancer	
SF-268	94.11
SF-295	97.70
SF-539	100.92
SNB-19	100.61
SNB-75	109.59
U251	87.01
Melanoma	
LOX IMVI	86.42
MALME-3M	98.80
M14	94.66
MDA-MB-435	101.76
SK-MEL-2	83.93
SK-MEL-28	104.28
SK-MEL-5	99.83
UACC-257	95.22
UACC-62	80.43
Ovarian Cancer	
IGROV1	88.55
OVCAR-3	100.40
OVCAR-4	89.33
OVCAR-5	118.54
OVCAR-8	48.07
NCI/ADR-RES	85.19
SK-OV-3	103.24
Renal Cancer	
786-0	89.87
A498	111.37
ACHN	109.07
CAKI-1	76.19
RXF 393	98.88
SN12C	90.56
TK-10	109.23
UO-31	72.34
Prostate Cancer	
PC-3	89.55
DU-145	104.24
Breast Cancer	
MCF7	98.71
MDA-MB-231/ATCC	97.41
HS 578T	103.72
BT-549	124.13
T-47D	70.83
MDA-MB-468	80.65
Mean	93.48
Delta	45.41
Range	76.06

Mean Growth Percent - Growth Percent





1.17

Developmental Therapeutics Program

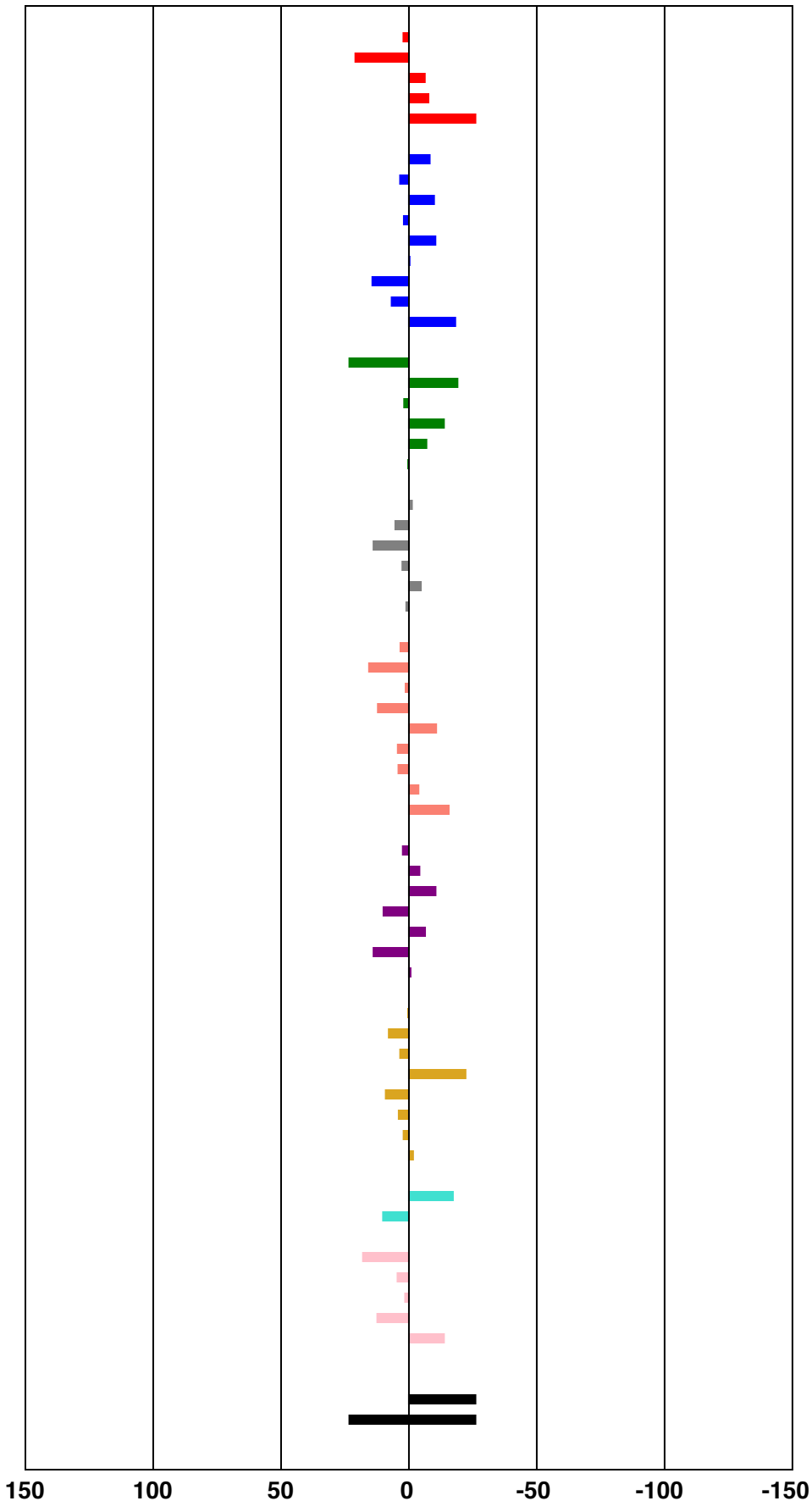
One Dose Mean Graph

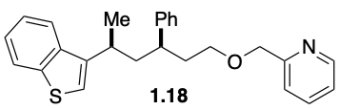
NSC: D-802028 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Nov 27, 2017

Experiment ID: 1711OS06 | **Report Date:** Jun 08, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	91.69
HL-60(TB)	110.48
K-562	83.31
MOLT-4	81.89
RPMI-8226	63.51
Non-Small Cell Lung Cancer	
A549/ATCC	81.40
EKVX	92.99
HOP-62	79.70
HOP-92	91.52
NCI-H226	79.16
NCI-H23	89.27
NCI-H322M	103.83
NCI-H460	96.29
NCI-H522	71.40
Colon Cancer	
HCC-2998	112.83
HCT-116	70.53
HCT-15	91.40
HT29	75.83
KM12	82.68
SW-620	89.81
CNS Cancer	
SF-268	88.35
SF-295	94.85
SF-539	103.39
SNB-19	92.10
SNB-75	84.86
U251	90.56
Melanoma	
LOX IMVI	92.85
MALME-3M	105.14
M14	90.83
MDA-MB-435	101.68
SK-MEL-2	78.86
SK-MEL-28	93.89
SK-MEL-5	93.64
UACC-257	85.79
UACC-62	73.96
Ovarian Cancer	
IGROV1	91.93
OVCAR-3	85.41
OVCAR-4	79.11
OVCAR-5	99.48
OVCAR-8	83.21
NCI/ADR-RES	103.38
SK-OV-3	88.89
Renal Cancer	
786-0	89.87
A498	97.41
ACHN	92.96
CAKI-1	67.39
RXF 393	98.60
SN12C	93.52
TK-10	91.63
UO-31	87.91
Prostate Cancer	
PC-3	72.32
DU-145	99.65
Breast Cancer	
MCF7	107.51
MDA-MB-231/ATCC	94.00
HS 578T	91.02
BT-549	101.90
MDA-MB-468	75.82
Mean	89.53
Delta	26.02
Range	49.32

Mean Growth Percent - Growth Percent





1.18

Developmental Therapeutics Program

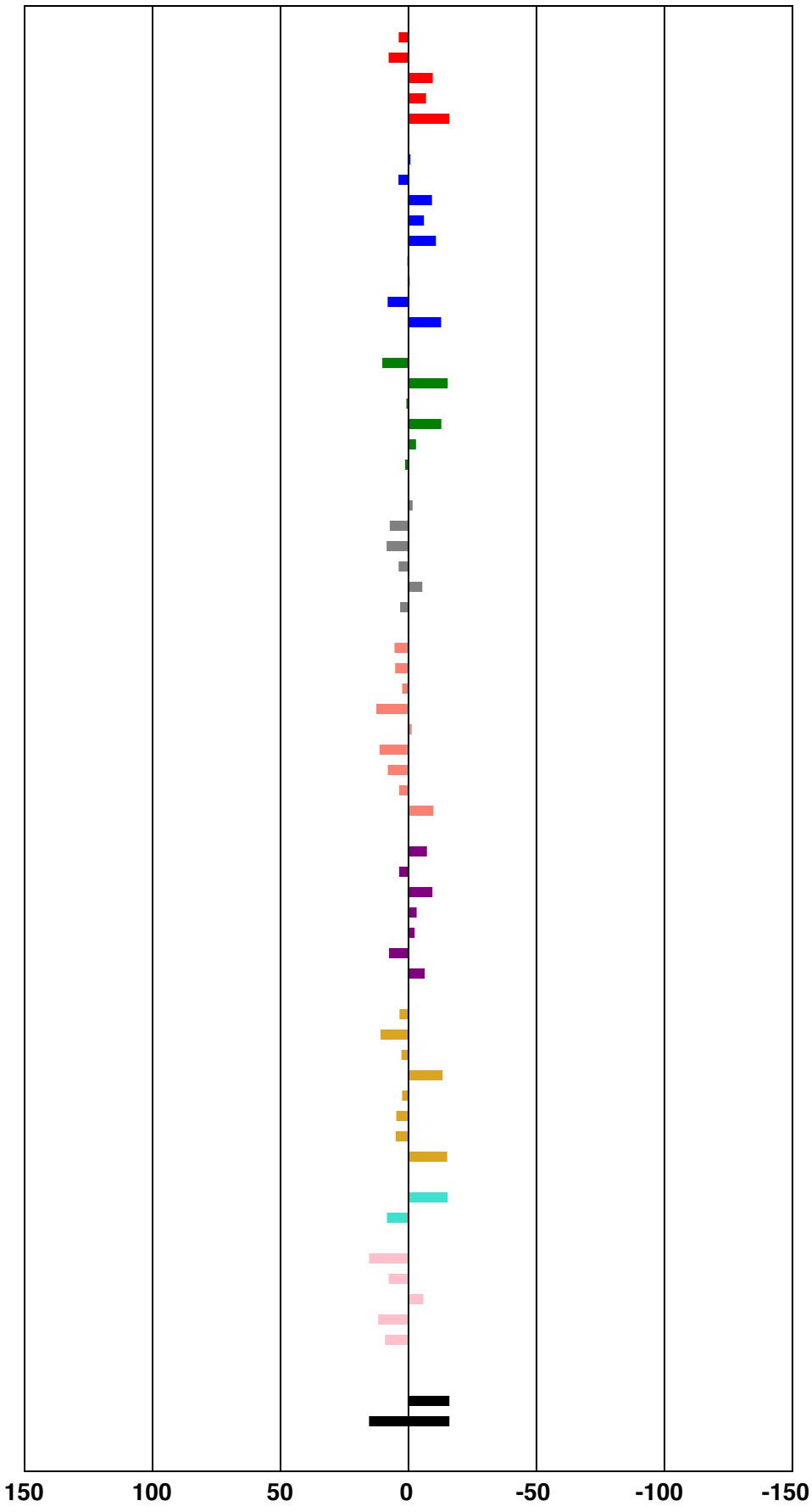
One Dose Mean Graph

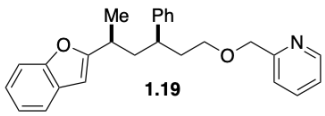
NSC: D-802029 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Nov 27, 2017

Experiment ID: 1711OS06 | **Report Date:** Jun 08, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	94.13
HL-60(TB)	98.05
K-562	81.47
MOLT-4	84.11
RPMI-8226	74.98
Non-Small Cell Lung Cancer	
A549/ATCC	90.20
EKVX	94.22
HOP-62	81.78
HOP-92	84.91
NCI-H226	80.24
NCI-H23	90.69
NCI-H322M	90.52
NCI-H460	98.45
NCI-H522	78.21
Colon Cancer	
HCC-2998	100.53
HCT-116	75.63
HCT-15	91.12
HT29	78.13
KM12	88.02
SW-620	91.65
CNS Cancer	
SF-268	89.34
SF-295	97.62
SF-539	98.84
SNB-19	94.16
SNB-75	85.56
U251	93.57
Melanoma	
LOX IMVI	95.76
MALME-3M	95.52
M14	92.78
MDA-MB-435	102.87
SK-MEL-2	89.71
SK-MEL-28	101.63
SK-MEL-5	98.38
UACC-257	93.96
UACC-62	81.20
Ovarian Cancer	
IGROV1	83.76
OVCAR-3	93.96
OVCAR-4	81.61
OVCAR-5	87.77
OVCAR-8	88.56
NCI/ADR-RES	97.92
SK-OV-3	84.66
Renal Cancer	
786-0	93.80
A498	101.20
ACHN	93.05
CAKI-1	77.61
RXF 393	92.79
SN12C	95.09
TK-10	95.33
UO-31	75.85
Prostate Cancer	
PC-3	75.64
DU-145	98.72
Breast Cancer	
MCF7	105.71
MDA-MB-231/ATCC	98.06
HS 578T	85.12
BT-549	102.18
MDA-MB-468	99.47
Mean	90.63
Delta	15.65
Range	30.73

Mean Growth Percent - Growth Percent





1.19

Developmental Therapeutics Program

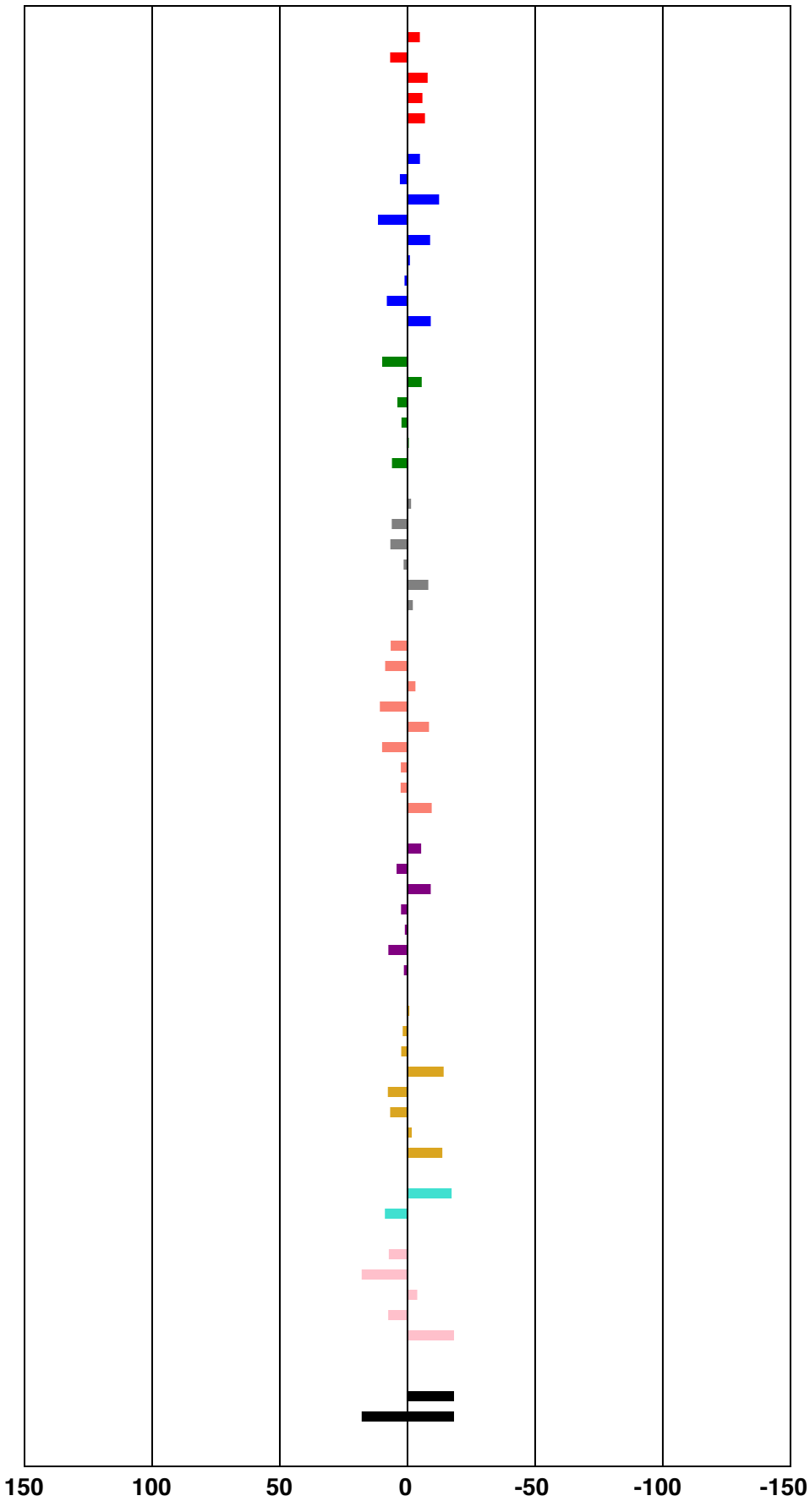
One Dose Mean Graph

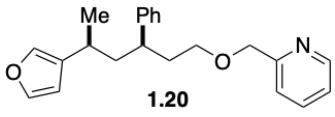
NSC: D-802030 / 1 | **Conc:** 1.00E-5 Molar | **Test Date:** Nov 27, 2017

Experiment ID: 1711OS06 | **Report Date:** Jun 08, 2019

Panel/Cell Line	Growth Percent
Leukemia	
CCRF-CEM	89.47
HL-60(TB)	100.44
K-562	86.42
MOLT-4	88.46
RPMI-8226	87.47
Non-Small Cell Lung Cancer	
A549/ATCC	89.43
EKVX	96.63
HOP-62	81.93
HOP-92	105.21
NCI-H226	85.45
NCI-H23	93.37
NCI-H322M	94.81
NCI-H460	101.74
NCI-H522	85.20
Colon Cancer	
HCC-2998	103.56
HCT-116	88.74
HCT-15	97.61
HT29	96.00
KM12	93.78
SW-620	99.73
CNS Cancer	
SF-268	92.91
SF-295	99.81
SF-539	100.36
SNB-19	95.17
SNB-75	86.16
U251	92.22
Melanoma	
LOX IMVI	100.23
MALME-3M	102.40
M14	91.20
MDA-MB-435	104.47
SK-MEL-2	85.89
SK-MEL-28	103.60
SK-MEL-5	96.25
UACC-257	96.33
UACC-62	84.83
Ovarian Cancer	
IGROV1	88.96
OVCAR-3	97.93
OVCAR-4	85.21
OVCAR-5	96.18
OVCAR-8	94.69
NCI/ADR-RES	101.14
SK-OV-3	95.07
Renal Cancer	
786-0	93.58
A498	95.53
ACHN	96.10
CAKI-1	80.15
RXF 393	101.34
SN12C	100.44
TK-10	92.65
UO-31	80.67
Prostate Cancer	
PC-3	77.03
DU-145	102.50
Breast Cancer	
MCF7	100.96
MDA-MB-231/ATCC	111.59
HS 578T	90.49
BT-549	101.20
MDA-MB-468	76.09
Mean	93.98
Delta	17.89
Range	35.50

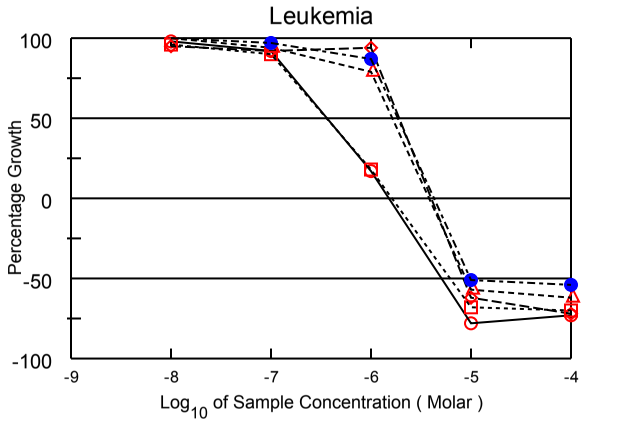
Mean Growth Percent - Growth Percent

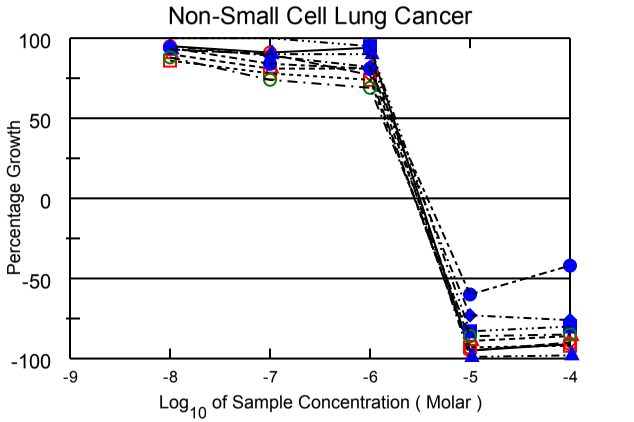


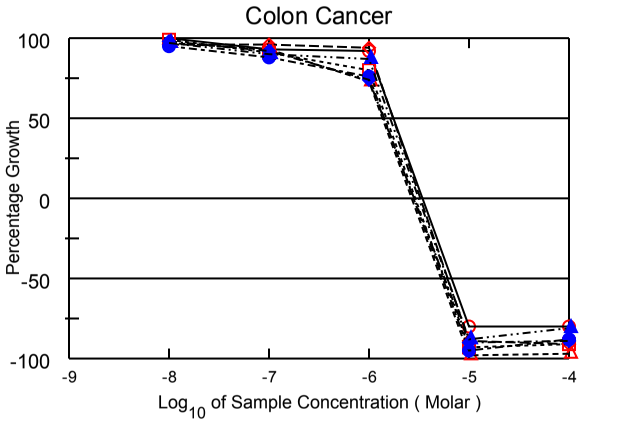


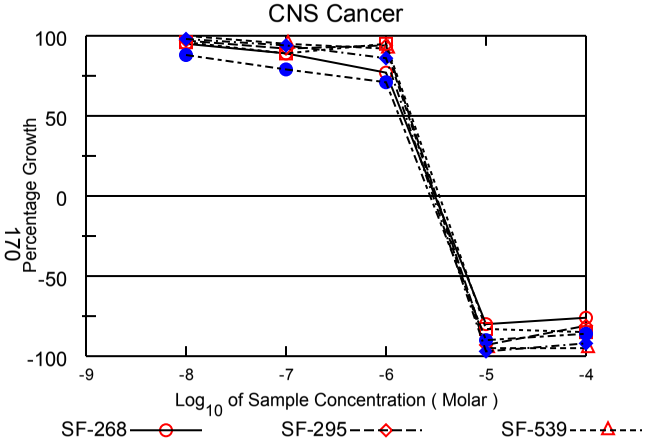
1.20

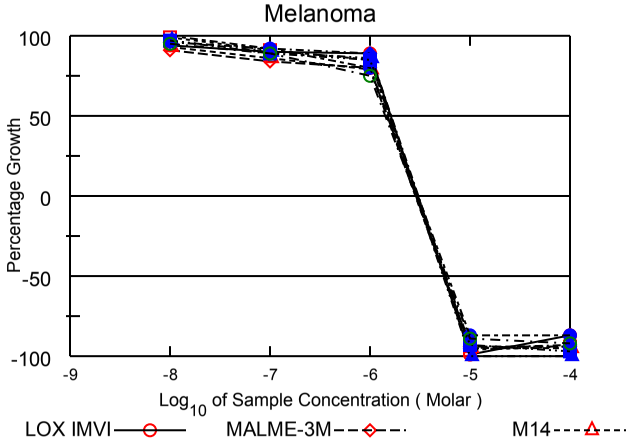
National Cancer Institute Developmental Therapeutics Program Dose Response Curves	NSC: D - 785438 / 1	SSPL: 0ZML	EXP. ID: 1508NS40
	Report Date: October 24, 2015	Test Date: August 17, 2015	

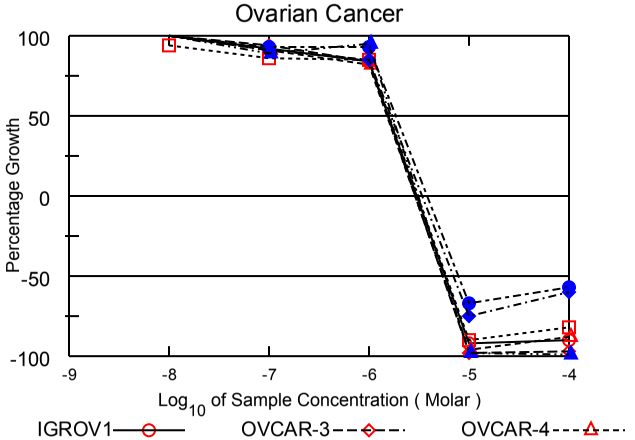


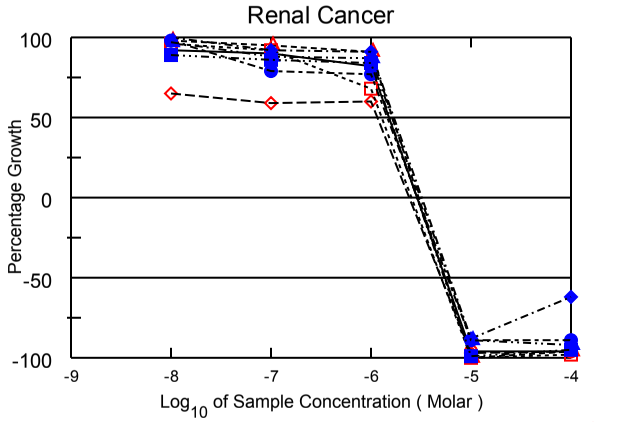


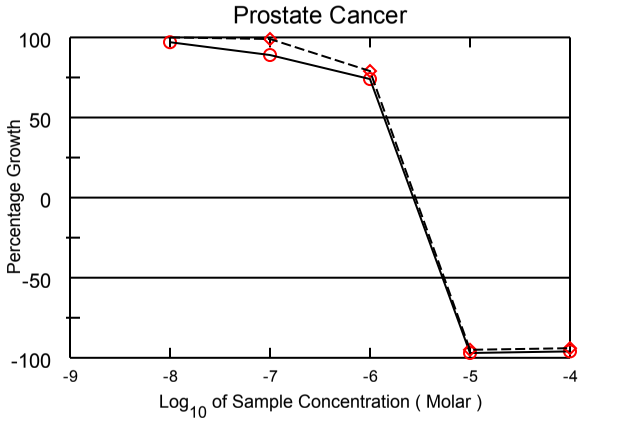


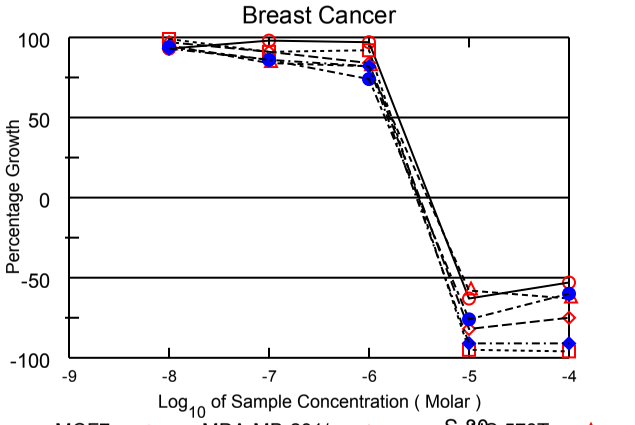












National Cancer Institute Developmental Therapeutics Program
In-Vitro Testing Results

NSC : D - 785438 / 1	Experiment ID : 1508NS40	Test Type : 08	Units : Molar
Report Date : October 24, 2015	Test Date : August 17, 2015	QNS :	MC :
COMI : EJT-III-137	Stain Reagent : SRB Dual-Pass Related	SSPL : 0ZML	

			Log10 Concentration												
	Time		Mean Optical Densities					Percent Growth							
Panel/Cell Line	Zero	Ctrl	-8.0	-7.0	-6.0	-5.0	-4.0	-8.0	-7.0	-6.0	-5.0	-4.0	GI50	TGI	LC50
Leukemia															
CCRF-CEM	0.775	3.022	2.977	2.848	1.156	0.174	0.207	98	92	17	-78	-73	3.64E-7	1.51E-6	5.11E-6
HL-60(TB)	0.866	3.042	2.934	2.859	2.909	0.328	0.241	95	92	94	-62	-72	1.91E-6	4.00E-6	8.36E-6
K-562	0.299	2.340	2.335	2.210	1.908	0.130	0.114	100	94	79	-57	-62	1.63E-6	3.82E-6	8.95E-6
MOLT-4	0.563	2.446	2.369	2.250	0.897	0.181	0.170	96	90	18	-68	-70	3.56E-7	1.61E-6	6.19E-6
RPMI-8226	0.922	2.522	2.529	2.474	2.315	0.449	0.428	100	97	87	-51	-54	1.85E-6	4.26E-6	9.79E-6
Non-Small Cell Lung Cancer															
A549/ATCC	0.557	2.563	2.458	2.392	2.446	0.027	0.051	95	91	94	-95	-91	1.71E-6	3.14E-6	5.77E-6
EKVX	0.560	2.352	2.222	2.167	1.947	0.030	0.055	93	90	77	-95	-90	1.44E-6	2.82E-6	5.50E-6
HOP-62	0.812	2.041	1.916	1.810	1.806	0.088	0.118	90	81	81	-89	-86	1.52E-6	2.99E-6	5.88E-6
HOP-92	1.053	1.435	1.380	1.350	1.335	0.076	0.087	86	78	74	-93	-92	1.39E-6	2.77E-6	5.53E-6
NCI-H226	0.865	2.381	2.283	2.143	2.087	0.349	0.502	94	84	81	-60	-42	1.65E-6	3.75E-6	.
NCI-H23	0.580	2.286	2.202	2.094	1.972	0.158	0.138	95	89	82	-73	-76	1.60E-6	3.38E-6	7.11E-6
NCI-H322M	0.659	2.138	2.034	1.983	1.985	0.009	0.010	93	90	90	-99	-98	1.62E-6	2.99E-6	5.52E-6
NCI-H460	0.246	2.788	2.843	2.789	2.654	0.043	0.049	102	100	95	-83	-80	1.79E-6	3.42E-6	6.55E-6
NCI-H522	0.900	2.179	2.024	1.852	1.784	0.122	0.137	88	74	69	-86	-85	1.33E-6	2.78E-6	5.83E-6
Colon Cancer															
COLO 205	0.405	1.788	1.826	1.695	1.673	0.079	0.083	103	93	92	-80	-80	1.75E-6	3.41E-6	6.65E-6
HCC-2998	0.560	2.357	2.283	2.279	2.252	0.062	0.049	96	96	94	-89	-91	1.74E-6	3.27E-6	6.12E-6
HCT-116	0.281	2.364	2.294	2.220	1.806	0.005	0.009	97	93	73	-98	-97	1.36E-6	2.67E-6	5.22E-6
HCT-15	0.234	1.919	1.900	1.774	1.589	0.017	0.021	99	91	80	-93	-91	1.50E-6	2.91E-6	5.65E-6
HT29	0.203	1.524	1.453	1.369	1.213	0.011	0.024	95	88	76	-95	-88	1.43E-6	2.80E-6	5.49E-6
KM12	0.426	2.482	2.438	2.309	1.947	0.045	0.047	98	92	74	-90	-89	1.40E-6	2.83E-6	5.73E-6
SW-620	0.269	2.150	2.093	1.959	1.913	0.031	0.051	97	90	87	-88	-81	1.63E-6	3.14E-6	6.04E-6
CNS Cancer															
SF-268	0.469	1.835	1.771	1.680	1.519	0.095	0.113	95	89	77	-80	-76	1.48E-6	3.09E-6	6.45E-6
SF-295	0.632	2.199	2.154	2.067	2.109	0.047	0.118	97	92	94	-93	-81	1.72E-6	3.19E-6	5.92E-6
SF-539	0.835	2.638	2.644	2.539	2.497	0.041	0.040	100	95	92	-95	-95	1.68E-6	3.11E-6	5.74E-6
SNB-19	0.604	2.201	2.139	2.028	2.117	0.105	0.090	96	89	95	-83	-85	1.79E-6	3.42E-6	6.55E-6
SNB-75	0.719	1.423	1.337	1.274	1.217	0.075	0.100	88	79	71	-90	-86	1.35E-6	2.76E-6	5.67E-6
U251	0.364	2.007	1.977	1.914	1.770	0.011	0.030	98	94	86	-97	-92	1.57E-6	2.94E-6	5.52E-6
Melanoma															
LOX IMVI	0.363	2.789	2.638	2.550	2.511	0.002	0.048	94	90	89	-99	-87	1.60E-6	2.96E-6	5.46E-6
MALME-3M	0.779	1.499	1.437	1.386	1.354	0.049	0.050	91	84	80	-94	-94	1.49E-6	2.89E-6	5.60E-6
M14	0.513	1.982	1.884	1.775	1.668	0.028	0.027	93	86	79	-95	-95	1.46E-6	2.84E-6	5.53E-6
MDA-MB-435	0.432	2.453	2.427	2.279	2.147	0.019	0.024	99	91	85	-96	-94	1.56E-6	2.95E-6	5.59E-6
SK-MEL-2	0.988	2.443	2.503	2.324	2.156	0.127	0.126	104	92	80	-87	-87	1.52E-6	3.02E-6	6.00E-6
SK-MEL-28	0.567	1.920	1.867	1.817	1.775	0.031	0.040	96	92	89	-95	-93	1.64E-6	3.06E-6	5.72E-6
SK-MEL-5	0.529	3.031	2.956	2.770	2.690	-0.003	-0.004	97	90	86	-100	-100	1.57E-6	2.91E-6	5.39E-6
UACC-257	0.903	2.192	2.148	2.055	1.995	0.062	0.030	97	89	85	-93	-97	1.57E-6	3.00E-6	5.72E-6
UACC-62	0.961	2.951	2.848	2.740	2.457	0.102	0.082	95	89	75	-89	-92	1.42E-6	2.86E-6	5.76E-6
Ovarian Cancer															
IGROV1	0.737	2.430	2.434	2.296	2.165	0.059	0.076	100	92	84	-92	-90	1.57E-6	3.01E-6	5.78E-6
OVCAR-3	0.492	1.529	1.545	1.466	1.367	0.011	0.013	101	94	84	-98	-97	1.54E-6	2.91E-6	5.47E-6
OVCAR-4	0.604	1.587	1.607	1.495	1.409	0.022	0.075	102	91	82	-96	-88	1.51E-6	2.88E-6	5.49E-6
OVCAR-5	0.567	1.613	1.550	1.462	1.451	0.054	0.101	94	86	85	-90	-82	1.57E-6	3.04E-6	5.87E-6
OVCAR-8	0.454	2.140	2.179	2.019	2.017	0.152	0.194	102	93	93	-67	-57	1.85E-6	3.82E-6	7.87E-6
NCI/ADR-RES	0.357	1.673	1.676	1.559	1.480	0.089	0.144	100	91	85	-75	-60	1.66E-6	3.40E-6	6.98E-6
SK-OV-3	0.962	2.220	2.238	2.076	2.151	0.018	0.011	101	89	95	-98	-99	1.70E-6	3.10E-6	5.63E-6
Renal Cancer															
786-0	0.670	2.333	2.206	2.158	2.028	0.030	0.027	92	90	82	-96	-96	1.51E-6	2.89E-6	5.53E-6
A498	1.356	1.910	1.715	1.681	1.690	0.040	0.057	65	59	60	-97	-96	1.16E-6	2.42E-6	5.02E-6
ACHN	0.336	1.634	1.609	1.571	1.522	0.001	0.012	98	95	91	-100	-96	1.65E-6	3.01E-6	5.49E-6
CAKI-1	0.325	2.206	2.136	2.063	1.602	0.001	0.008	96	92	68	-100	-98	1.28E-6	2.54E-6	5.04E-6
RXF 393	0.568	1.301	1.287	1.145	1.131	0.065	0.062	98	79	77	-89	-89	1.45E-6	2.91E-6	5.85E-6
SN12C	0.531	2.279	2.271	2.138	2.115	0.066	0.203	100	92	91	-88	-62	1.69E-6	3.22E-6	6.15E-6
TK-10	0.856	2.832	2.780	2.603	2.571	0.096	0.068	97	88	87	-89	-92	1.62E-6	3.12E-6	6.01E-6
UO-31	0.686	2.486	2.284	2.232	2.205	0.006	0.038	89	86	84	-99	-95	1.54E-6	2.88E-6	5.40E-6
Prostate Cancer															
PC-3	0.732	2.451	2.401	2.255	2.009	0.025	0.027	97	89	74	-97	-96	1.39E-6	2.72E-6	5.34E-6
DU-145	0.332	1.667	1.775	1.657	1.388	0.015	0.022	108	99	79	-95	-94	1.47E-6	2.84E-6	5.49E-6
Breast Cancer															
MCF7	0.406	2.733	2.565	2.687	2.671	0.150	0.190	93	98	97	-63	-53	1.97E-6	4.04E-6	8.28E-6
MDA-MB-231/ATCC	0.541	1.644	1.612	1.546	1.464	0.096	0.138	97	91	84	-82	-75	1.60E-6	3.19E-6	6.39E-6
HS 578T	0.766	1.799	1.749	1.638	1.615	0.319	0.284	95	84	82	-58	-63	1.69E-6	3.84E-6	8.71E-6
BT-549	0.905	1.860	1.850	1.777	1.784	0.045	0.036	99	91	92	-95	-96	1.68E-6	3.10E-6	5.74E-6
T-47D	0.504	1.177	1.137	1.082	1.001	0.121	0.202	94	86	74	-76	-60	1.44E-6	3.11E-6	6.71E-6
MDA-MB-468	0.652	1.565	1.504	1.437	1.399	0.059	0.056	93	86	82	-91	-91	1.53E-6	2.98E-6	5.79E-6

National Cancer Institute Developmental Therapeutics Program

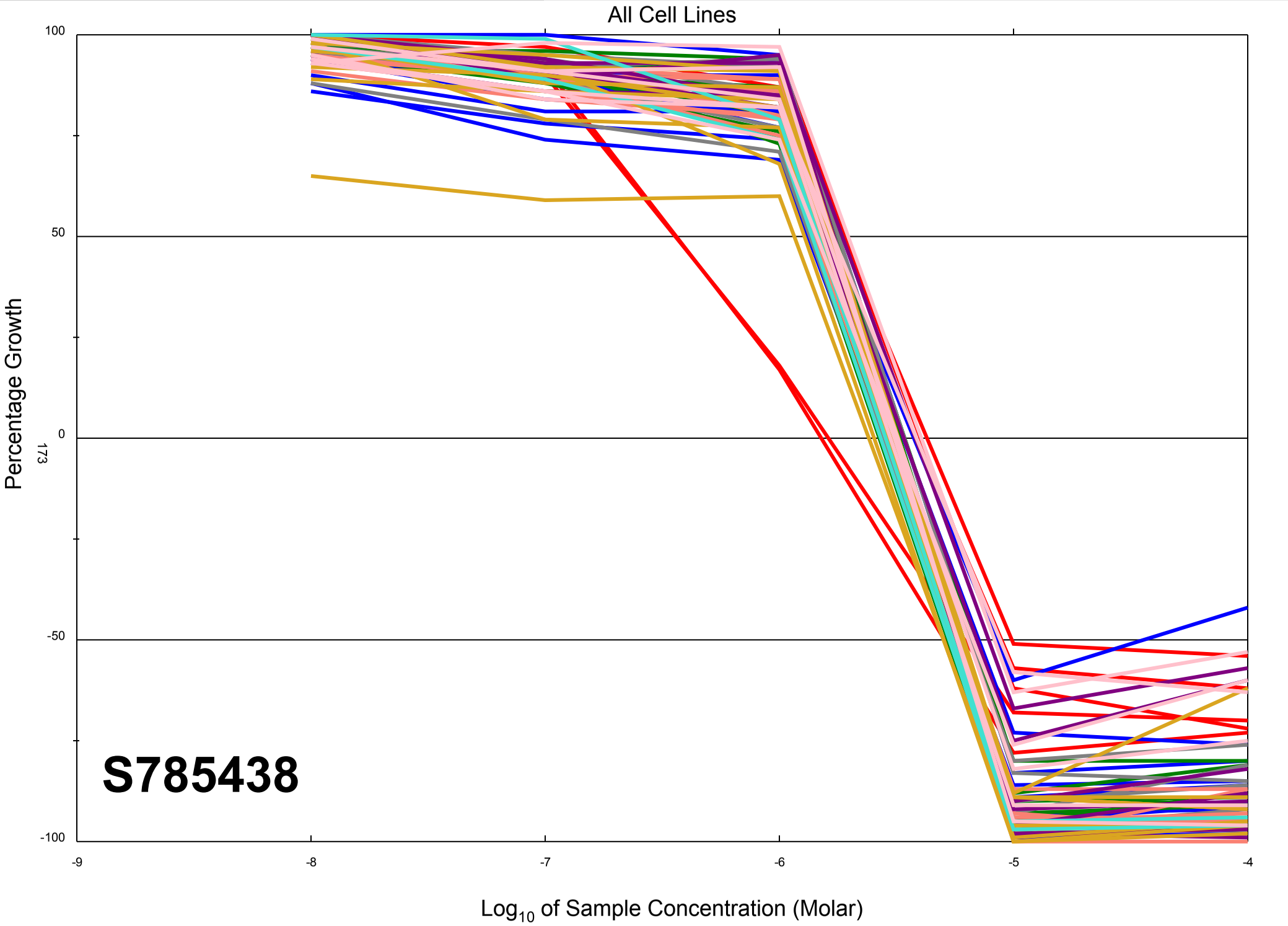
Mean Graphs

NSC : D - 785438/1 | Units :Molar | SSPL :0ZML | EXP. ID :1508NS40

Report Date :October 24, 2015 | Test Date :August 17, 2015

Panel/Cell Line	Log_{10}GI50	GI50	Log_{10}TGI	TGI	Log_{10}LC50	LC50
Leukemia						
CCRF-CEM	-6.44		-5.82		-5.29	
HL-60(TB)	-5.72		-5.40		-5.08	
K-562	-5.79		-5.42		-5.05	
MOLT-4	-6.45		-5.79		-5.21	
RPMI-8226	-5.73		-5.37		-5.01	
Non-Small Cell Lung Cancer						
A549/ATCC	-5.77		-5.50		-5.24	
EKVX	-5.84		-5.55		-5.26	
HOP-62	-5.82		-5.52		-5.23	
HOP-92	-5.86		-5.56		-5.26	
NCI-H226	-5.78		-5.43			
NCI-H23	-5.80		-5.47		-5.15	
NCI-H322M	-5.79		-5.52		-5.26	
NCI-H460	-5.75		-5.47		-5.18	
NCI-H522	-5.88		-5.56		-5.23	
Colon Cancer						
COLO 205	-5.76		-5.47		-5.18	
HCC-2998	-5.76		-5.49		-5.21	
HCT-116	-5.86		-5.57		-5.28	
HCT-15	-5.82		-5.54		-5.25	
HT29	-5.85		-5.55		-5.26	
KM12	-5.85		-5.55		-5.24	
SW-620	-5.79		-5.50		-5.22	
CNS Cancer						
SF-268	-5.83		-5.51		-5.19	
SF-295	-5.76		-5.50		-5.23	
SF-539	-5.77		-5.51		-5.24	
SNB-19	-5.75		-5.47		-5.18	
SNB-75	-5.87		-5.56		-5.25	
U251	-5.81		-5.53		-5.26	
Melanoma						
LOX IMVI	-5.80		-5.53		-5.26	
MALME-3M	-5.83		-5.54		-5.25	
M14	-5.83		-5.55		-5.26	
MDA-MB-435	-5.81		-5.53		-5.25	
SK-MEL-2	-5.82		-5.52		-5.22	
SK-MEL-28	-5.79		-5.51		-5.24	
SK-MEL-5	-5.80		-5.54		-5.27	
UACC-257	-5.80		-5.52		-5.24	
UACC-62	-5.85		-5.54		-5.24	
Ovarian Cancer						
IGROV1	-5.81		-5.52		-5.24	
OVCAR-3	-5.81		-5.54		-5.26	
OVCAR-4	-5.82		-5.54		-5.26	
OVCAR-5	-5.80		-5.52		-5.23	
OVCAR-8	-5.73		-5.42		-5.10	
NCI/ADR-RES	-5.78		-5.47		-5.16	
SK-OV-3	-5.77		-5.51		-5.25	
Renal Cancer						
786-0	-5.82		-5.54		-5.26	
A498	-5.93		-5.62		-5.30	
ACHN	-5.78		-5.52		-5.26	
CAKI-1	-5.89		-5.60		-5.30	
RXF 393	-5.84		-5.54		-5.23	
SN12C	-5.77		-5.49		-5.21	
TK-10	-5.79		-5.51		-5.22	
UO-31	-5.81		-5.54		-5.27	
Prostate Cancer						
PC-3	-5.86		-5.57		-5.27	
DU-145	-5.83		-5.55		-5.26	
Breast Cancer						
MCF7	-5.71		-5.39		-5.08	
MDA-MB-231/ATCC	-5.80		-5.50		-5.19	
HS 578T	-5.77		-5.42		-5.06	
BT-549	-5.78		-5.51		-5.24	
T-47D	-5.84		-5.51		-5.17	
MDA-MB-468	-5.82		-5.53		-5.24	
_MID	-5.83		-5.52		-5.22	
Delta	0.62		0.3		0.08	
Range	0.74		0.45		0.29	

National Cancer Institute Developmental Therapeutics Program Dose Response Curves	NSC : D - 785438/1	SSPL:0ZML	EXP. ID:1508NS40
	Report Date:October 24, 2015	Test Date:August 17, 2015	



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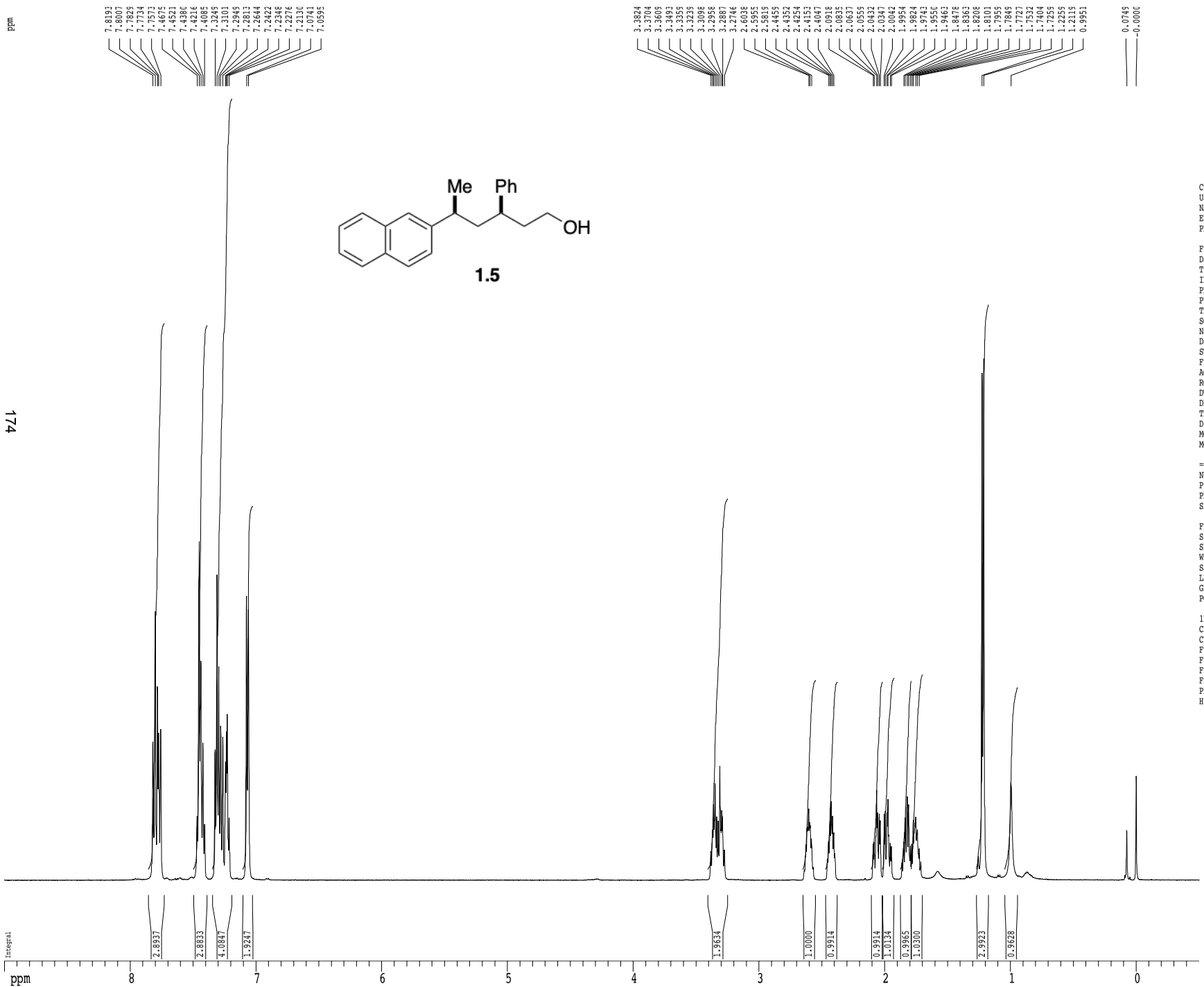


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PROCNO                 1

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TD                 81728
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TE                298.0 K
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MCWRK        0.01500000 sec

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NUC1                  1H
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PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
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1D NMR plot parameters
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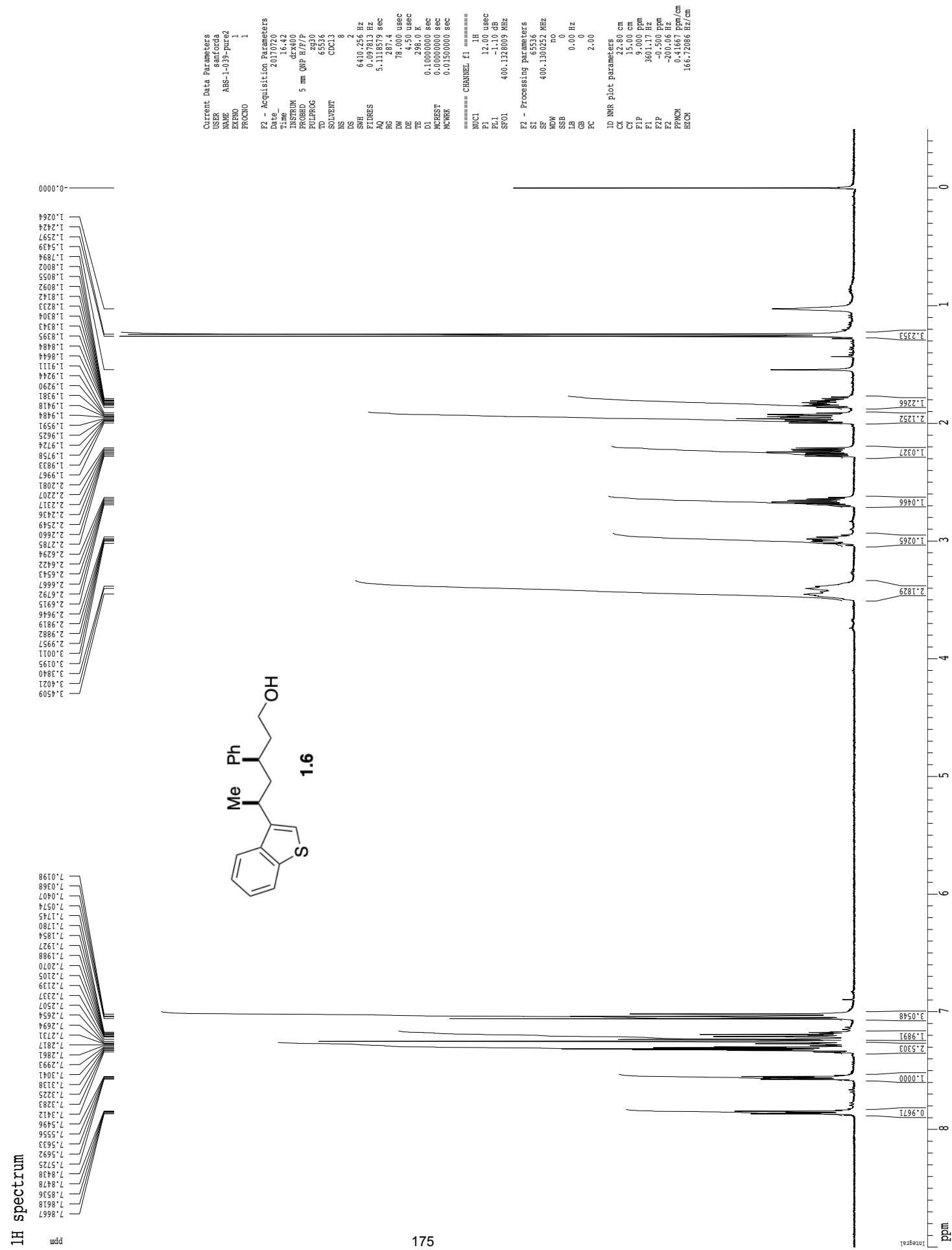
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FIDRES 0.097813 Hz
AQ 5.1118579 sec
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TE 298.0 K
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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LB 0.00 Hz
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Me
Ph
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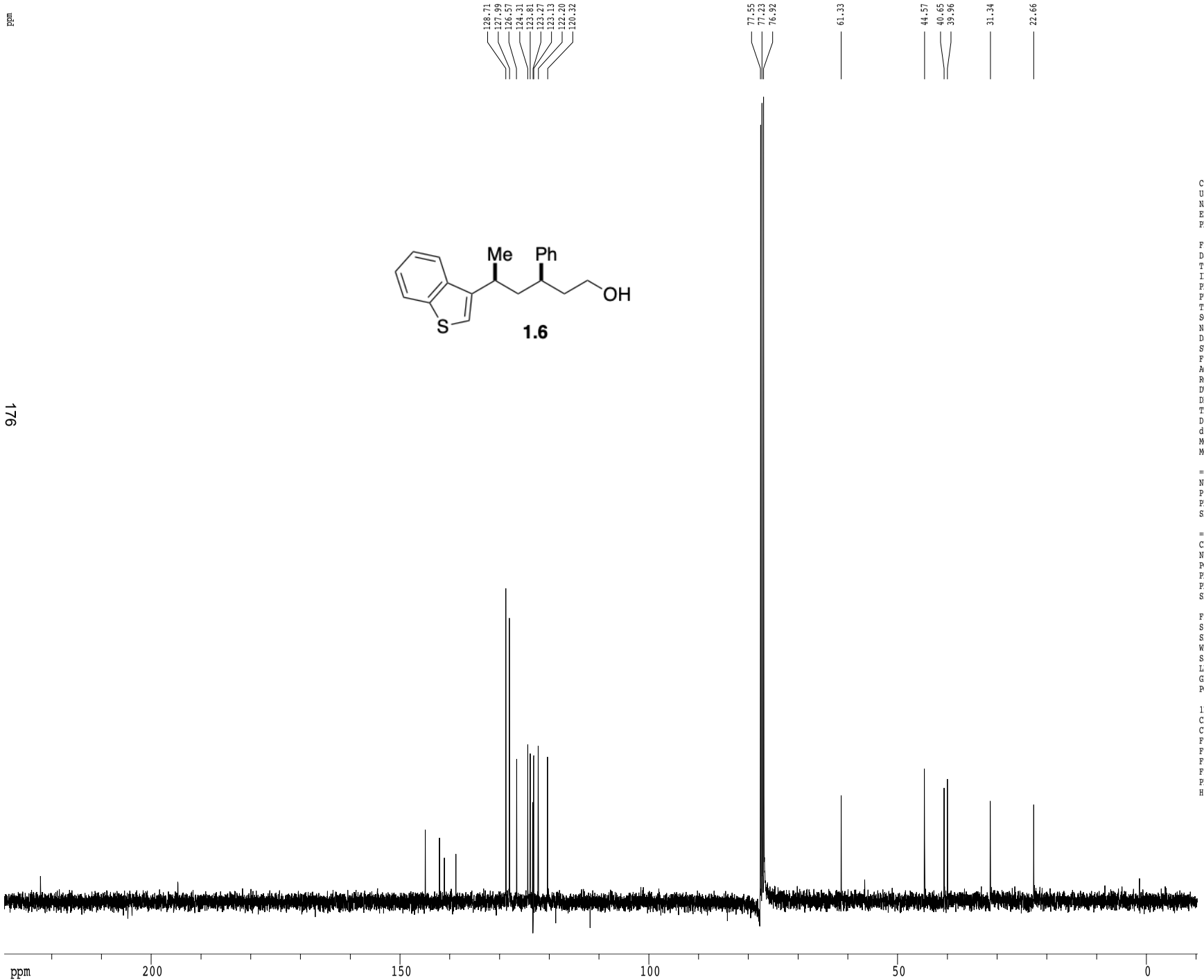
S
1.6
ppm
Integral

13C spectrum with 1H decoupling



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NAME ABS-1-039-carbon
EXPNO 1
PROCNO 1

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SOLVENT CDCl3
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======== CHANNEL f1 ========
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P1 7.60 usec
PL1 -3.00 dB
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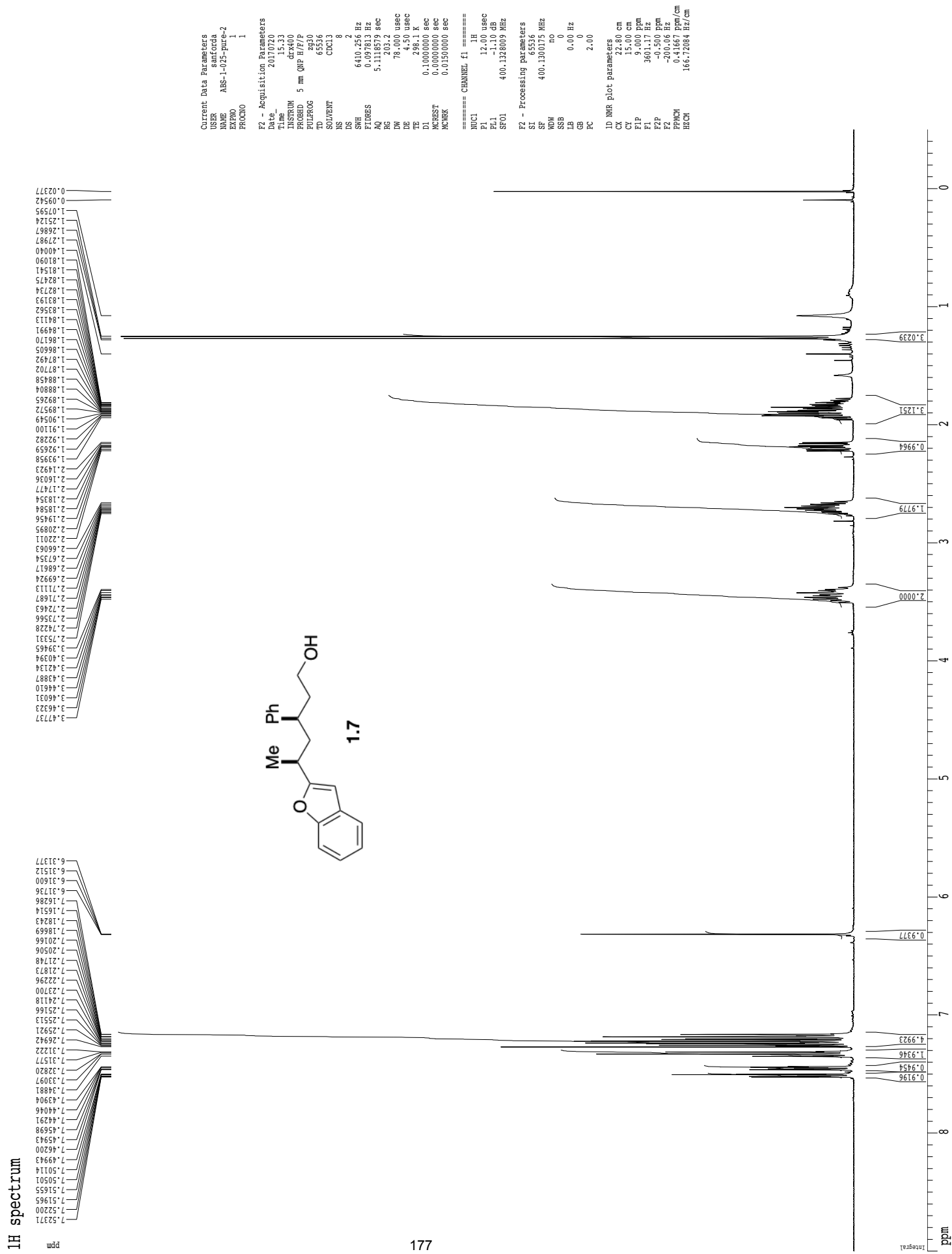
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PULPROG zg30
TD 65536
SOLVENT CDCl3
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DS 2
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FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 203.2
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
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MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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LB 0.00 Hz
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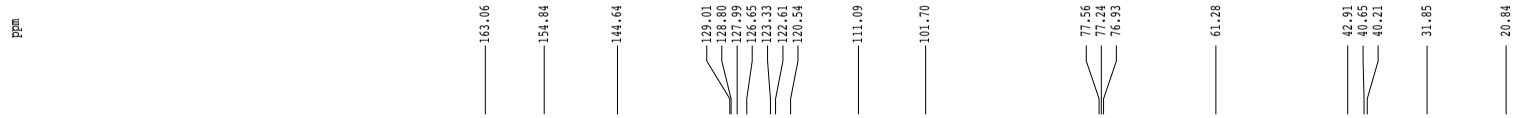
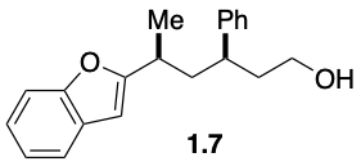
Integral
ppm

13C spectrum with 1H decoupling





1.7

178

Current Data Parameters
USER sanforda
NAME ABS-1-025-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170720
Time 15.35
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 171
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 11585.2
DW 20.700 usec
DE 20.39 usec
TE 297.9 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

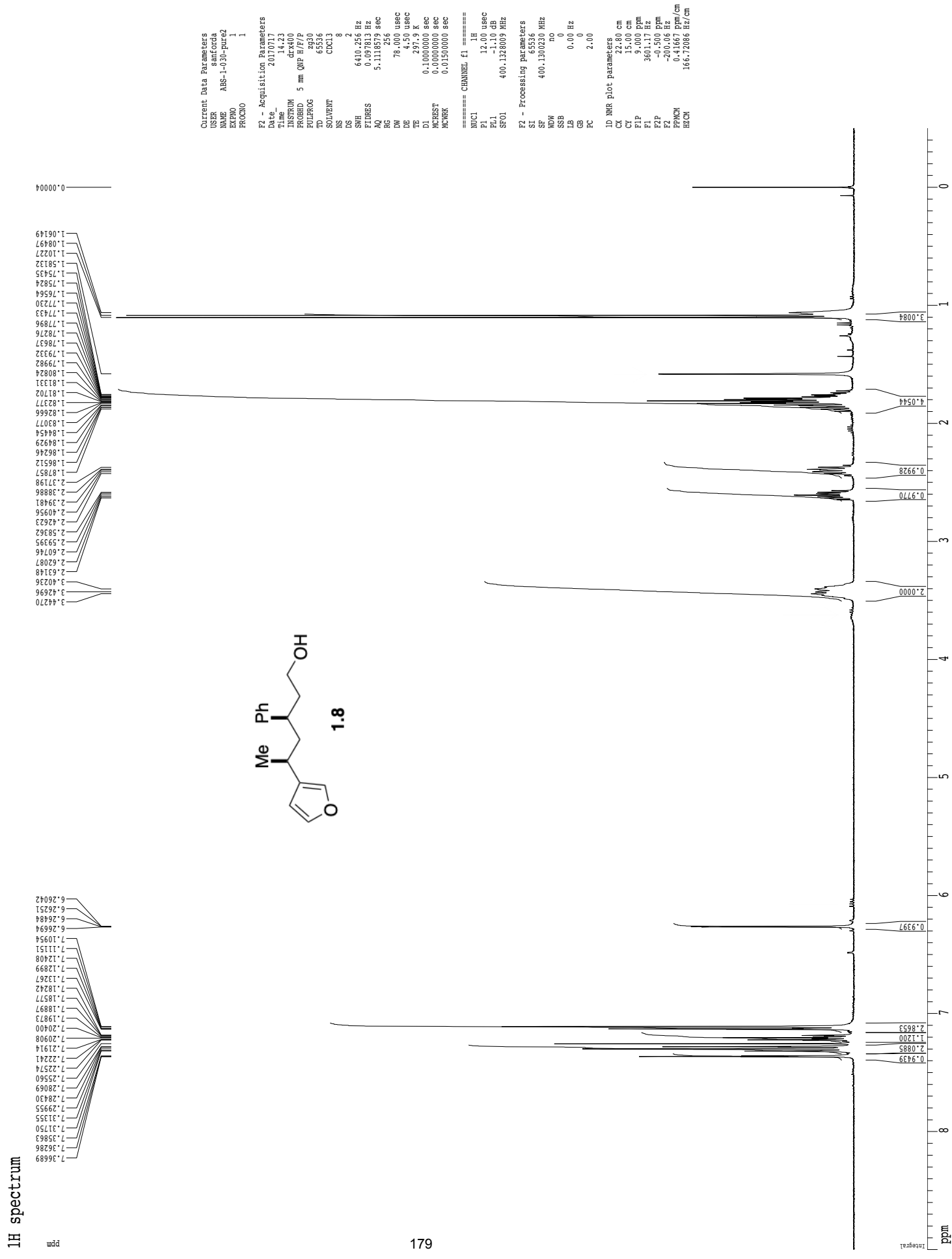
======== CHANNEL f1 ========
NUC1 13C
P1 7.60 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 mlev16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

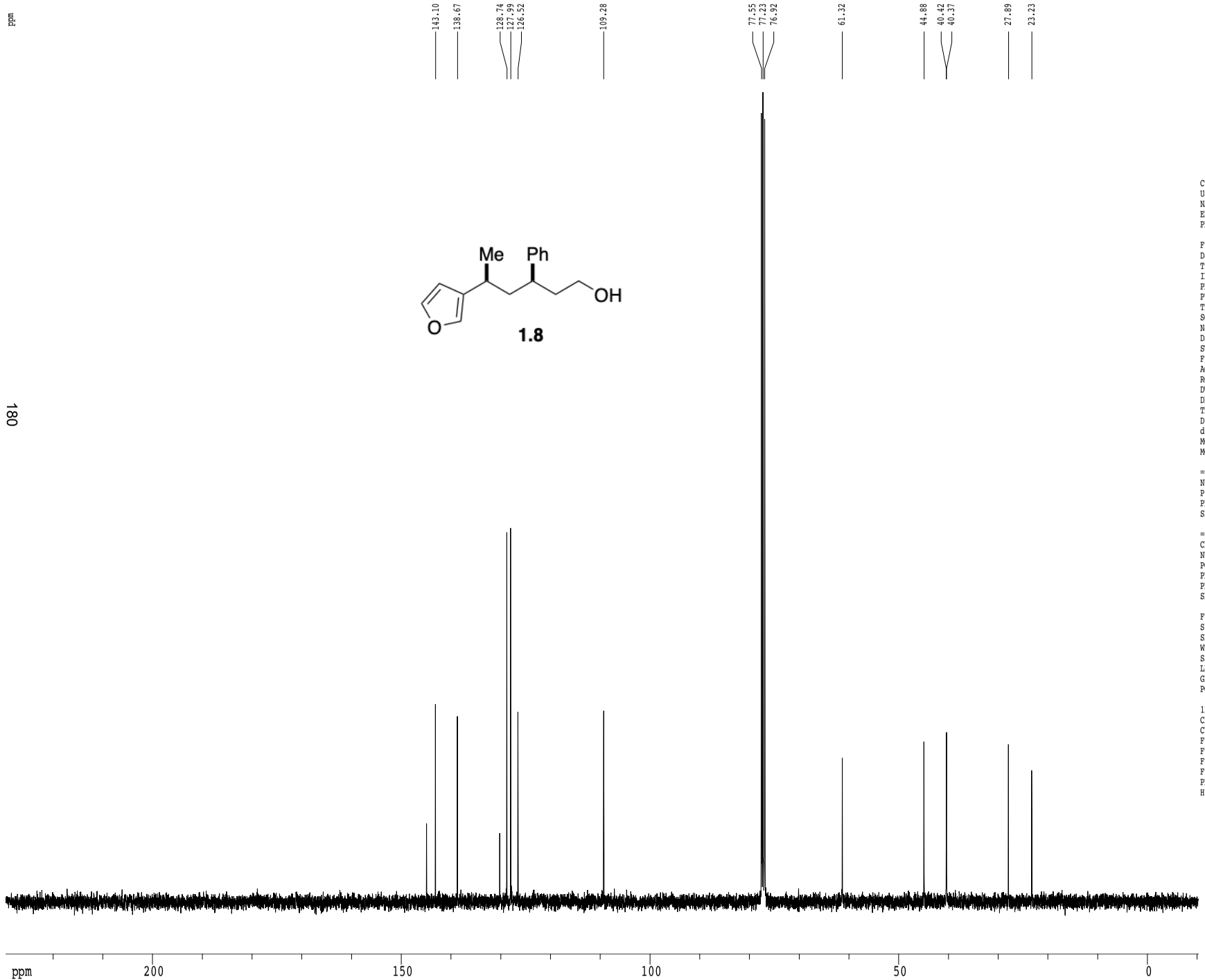
F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 229.496 ppm
F1 23090.21 Hz
F2P -10.579 ppm
F2 -1064.37 Hz
PPMCM 10.52959 ppm/cm
HZCM 1059.41138 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-1-030-pure2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170717
Time_ 14.23
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 256
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300230 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Me
Ph
OH
O
1.8
3.008
4.054
0.992
0.977
2.000
0.939
7.853
1.120
2.088
0.943
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-1-030-pure-c
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170717
Time 14.27
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 550
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 16384
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

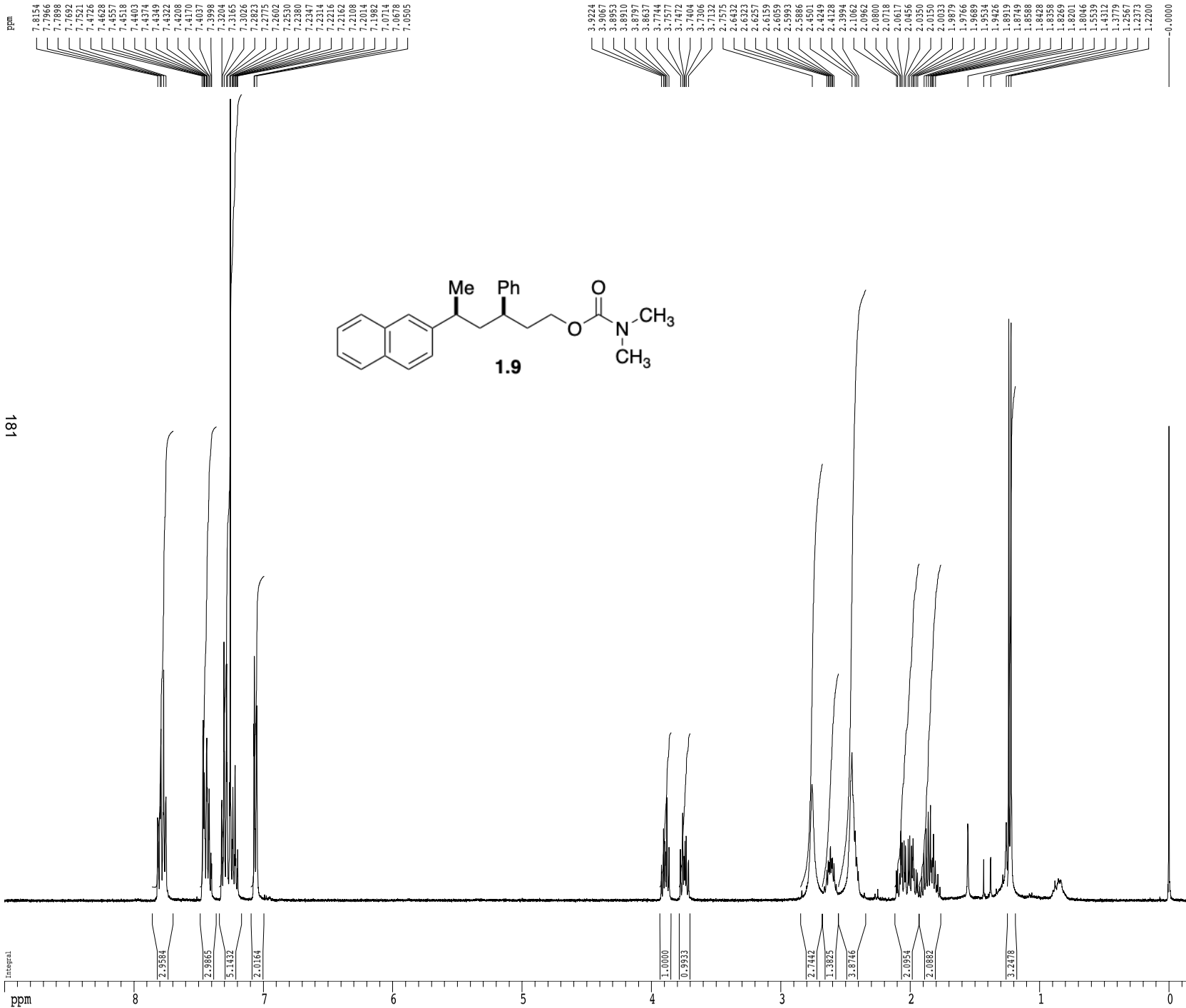
======== CHANNEL f1 ========
NUC1 13C
P1 7.60 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 mlev16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 229.496 ppm
F1 23090.21 Hz
F2P -10.579 ppm
F2 -1064.37 Hz
PPMCM 10.52959 ppm/cm
HZCM 1059.41138 Hz/cm

1H spectrum




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-158-proton
EXPNO                  1
PROCNO                 1

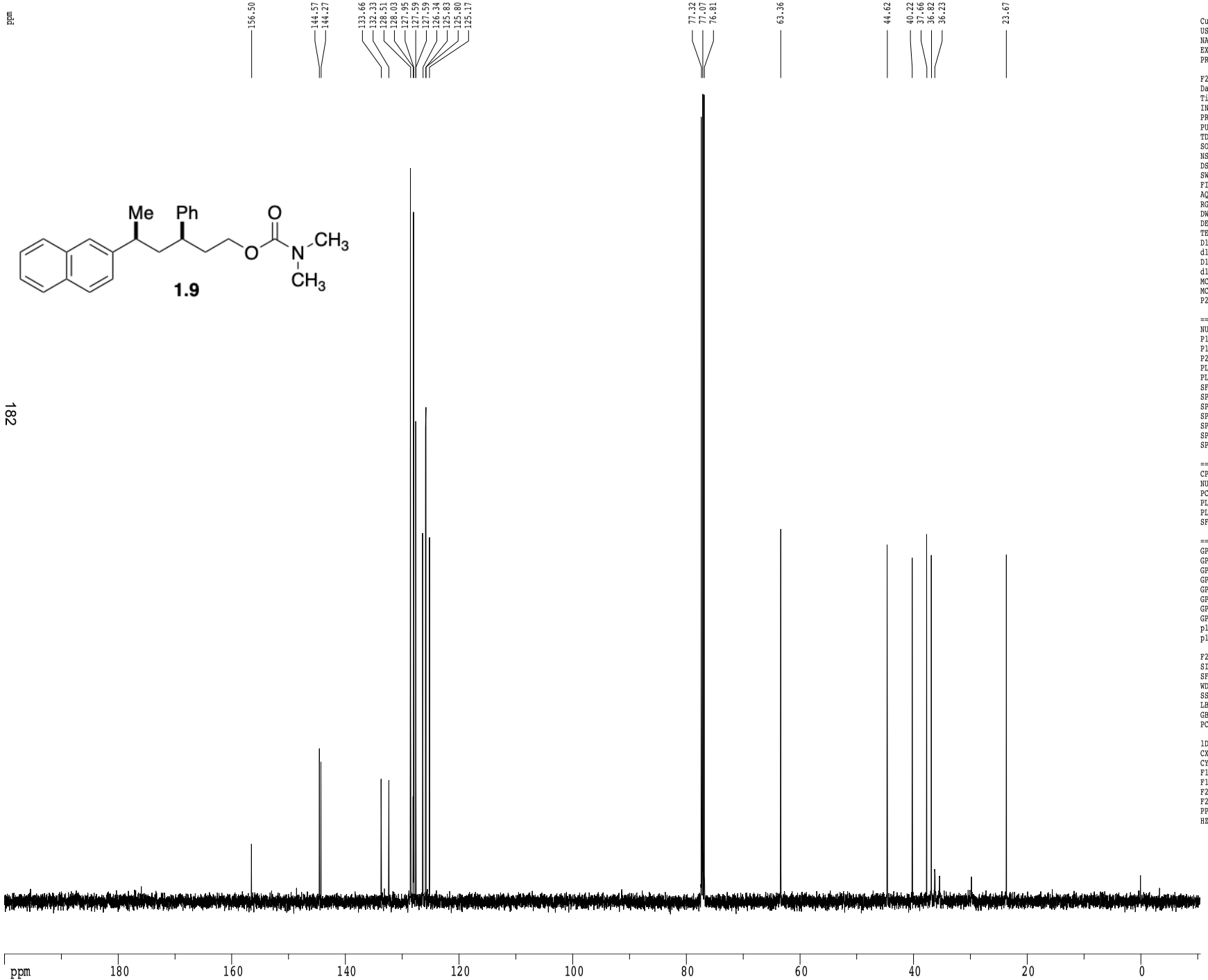
F2 - Acquisition Parameters
Date_           20190221
Time              14.11
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES        0.097813 Hz
AQ            5.1118579 sec
RG                322.5
DW               78.000 usec
DE                4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======= CHANNEL f1 =======
NUC1                  1H
P1                12.00 usec
PL1               -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                65536
SF           400.1300239 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P                9.000 ppm
F1              3601.17 Hz
F2P               -0.500 ppm
F2              -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-2-158-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190221
Time 14.58
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 824
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

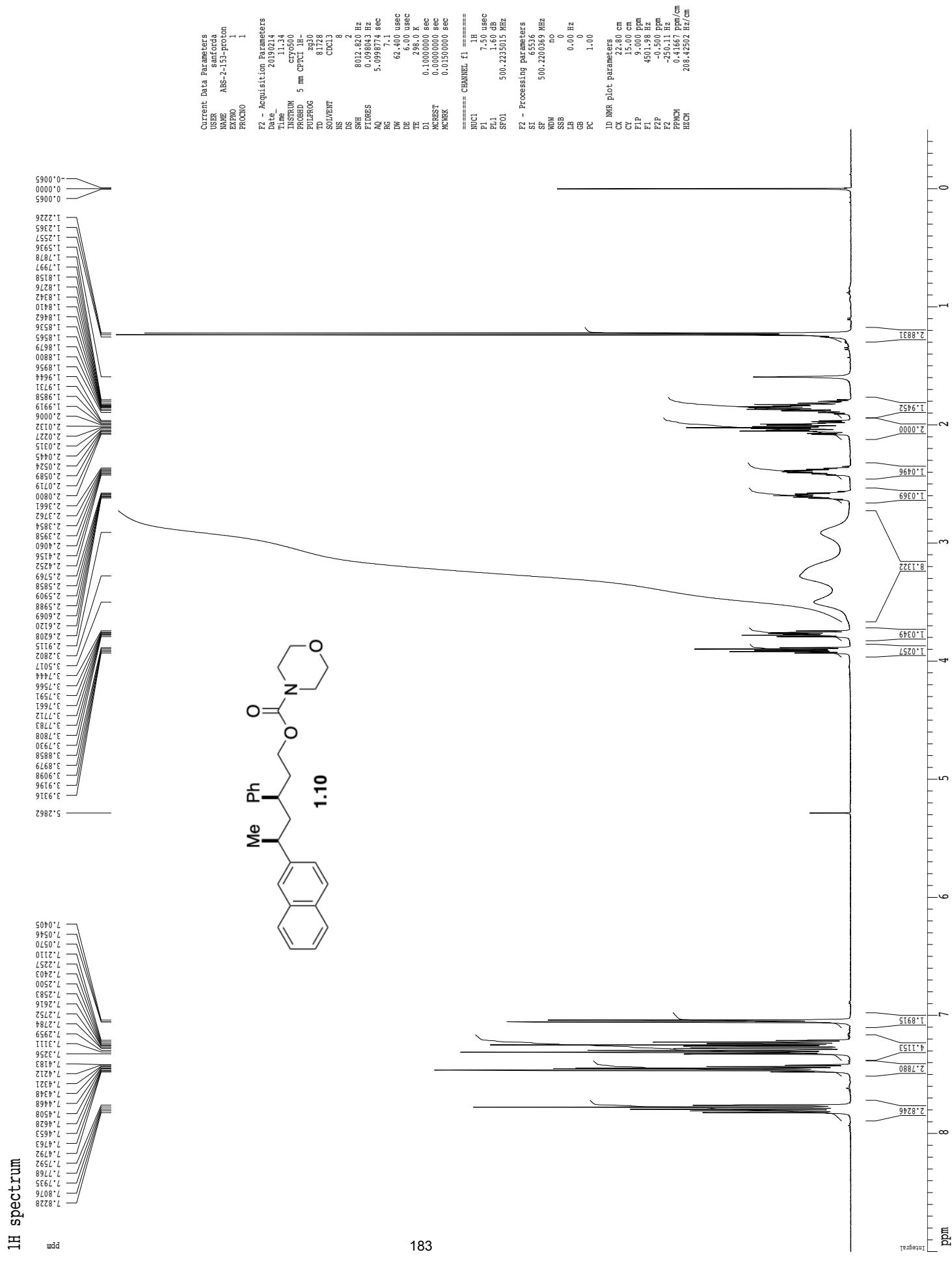
======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

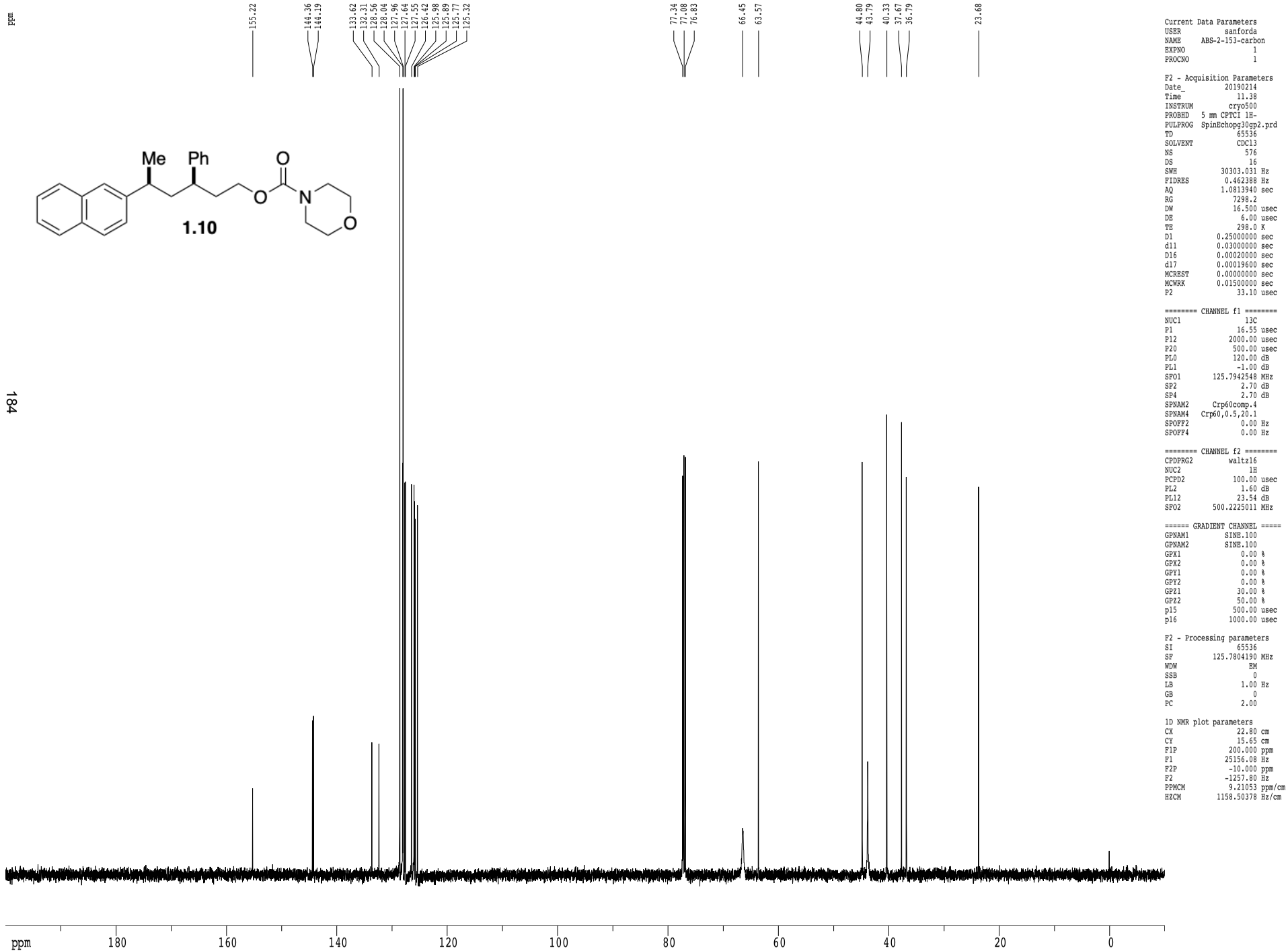
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P -10.460 ppm
F2 -1315.66 Hz
PPMCM 9.23070 ppm/cm
HZCM 1161.04163 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-153-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190214
Time_ 11.34
INSTRUM CRYO500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200369 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Me
Ph
1.10
ppm
Integral

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




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-153-carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190214
Time                11.38
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT             CDCl3
NS                    576
DS                     16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                33.10 usec

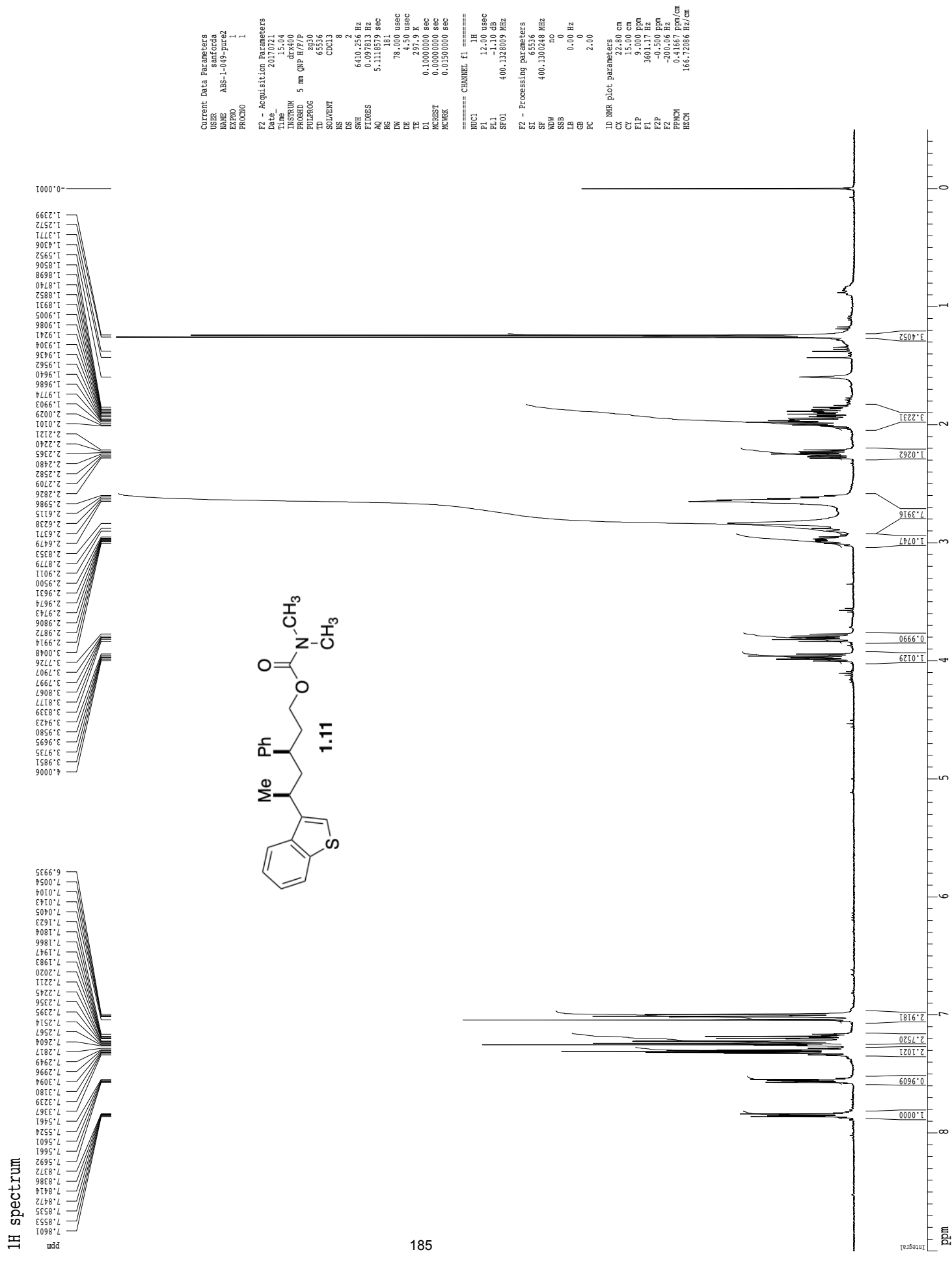
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

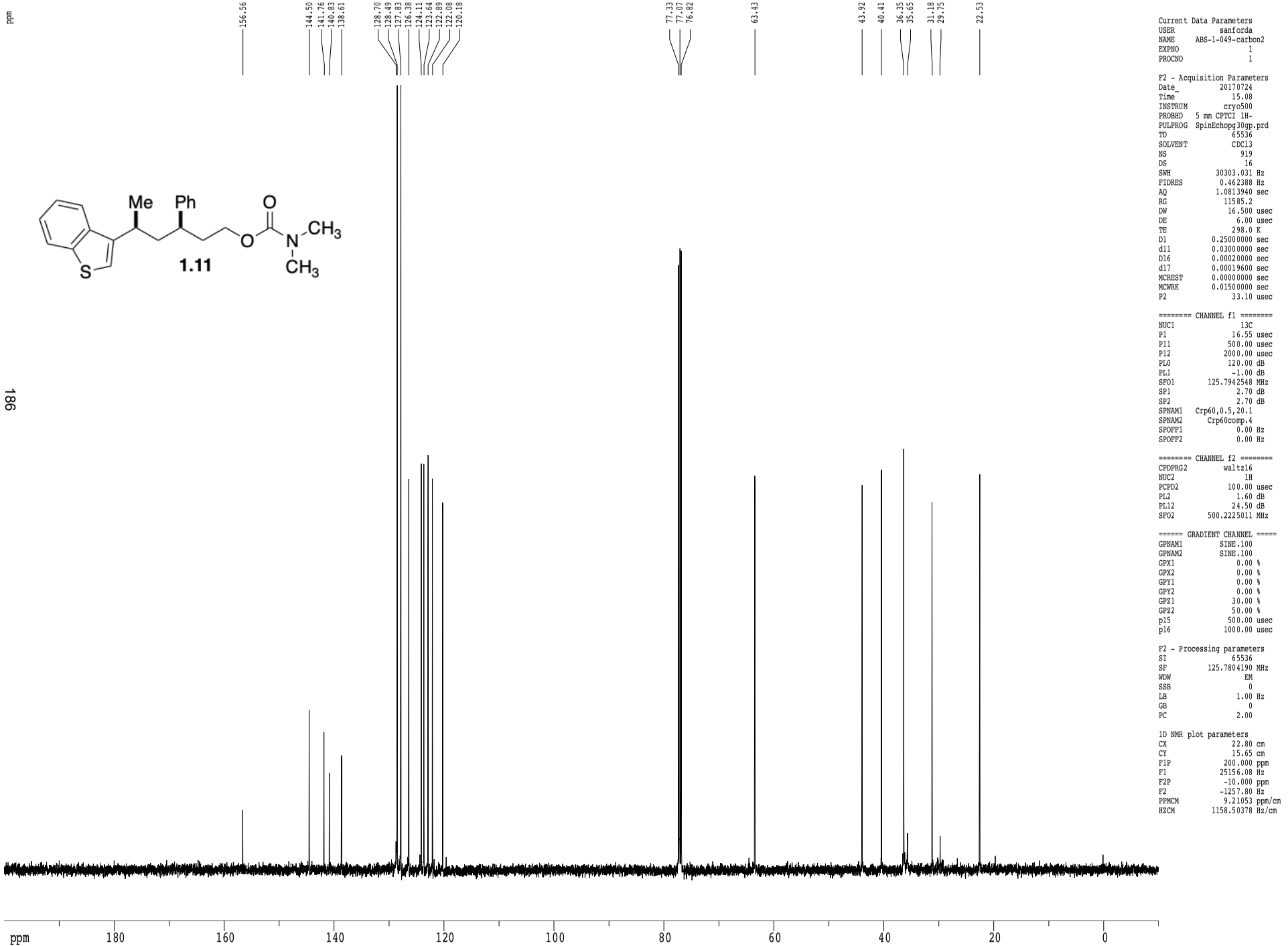
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                  65536
SF          125.7804190 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1             25156.08 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM            9.21053 ppm/cm
HZCM          1158.50378 Hz/cm
```


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-1-049-pure2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170721
Time_ 15.04
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 181
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300248 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Me
Ph
1.11
N
CH3
CH3
O
O
S
3.4052
3.2231
1.0262
7.3916
1.0747
0.9990
1.0129
2.9181
2.7520
2.1021
0.9609
1.0000
Integral
ppm

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




```
Current Data Parameters
USER                sanforda
NAME      ABS-1-049-carbon2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20170724
Time               15.08
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65536
SOLVENT            CDCl3
NS                   919
DS                    16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                11585.2
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                16.55 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP1               2.70 dB
SP2               2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

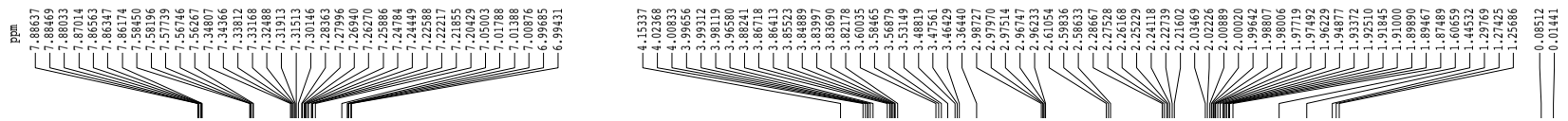
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.50 dB
SFO2         500.2225011 MHz

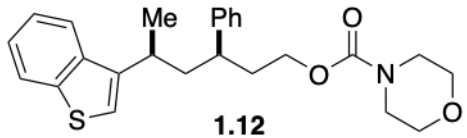
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                  65536
SF           125.7804190 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1              25156.08 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM             9.21053 ppm/cm
HZCM           1158.50378 Hz/cm
```

1H spectrum

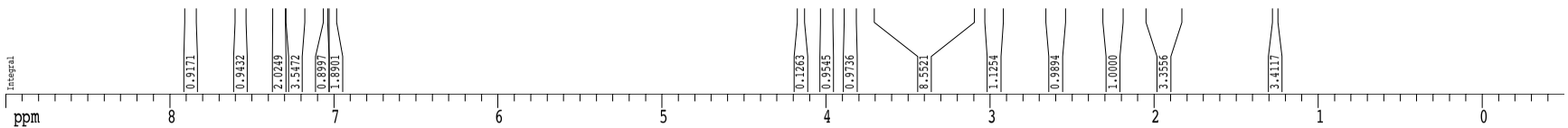




1.12

187

impurity



Current Data Parameters
USER sanforda
NAME ABS-1-051-pure2
EXPNO 1
PROCNO 1

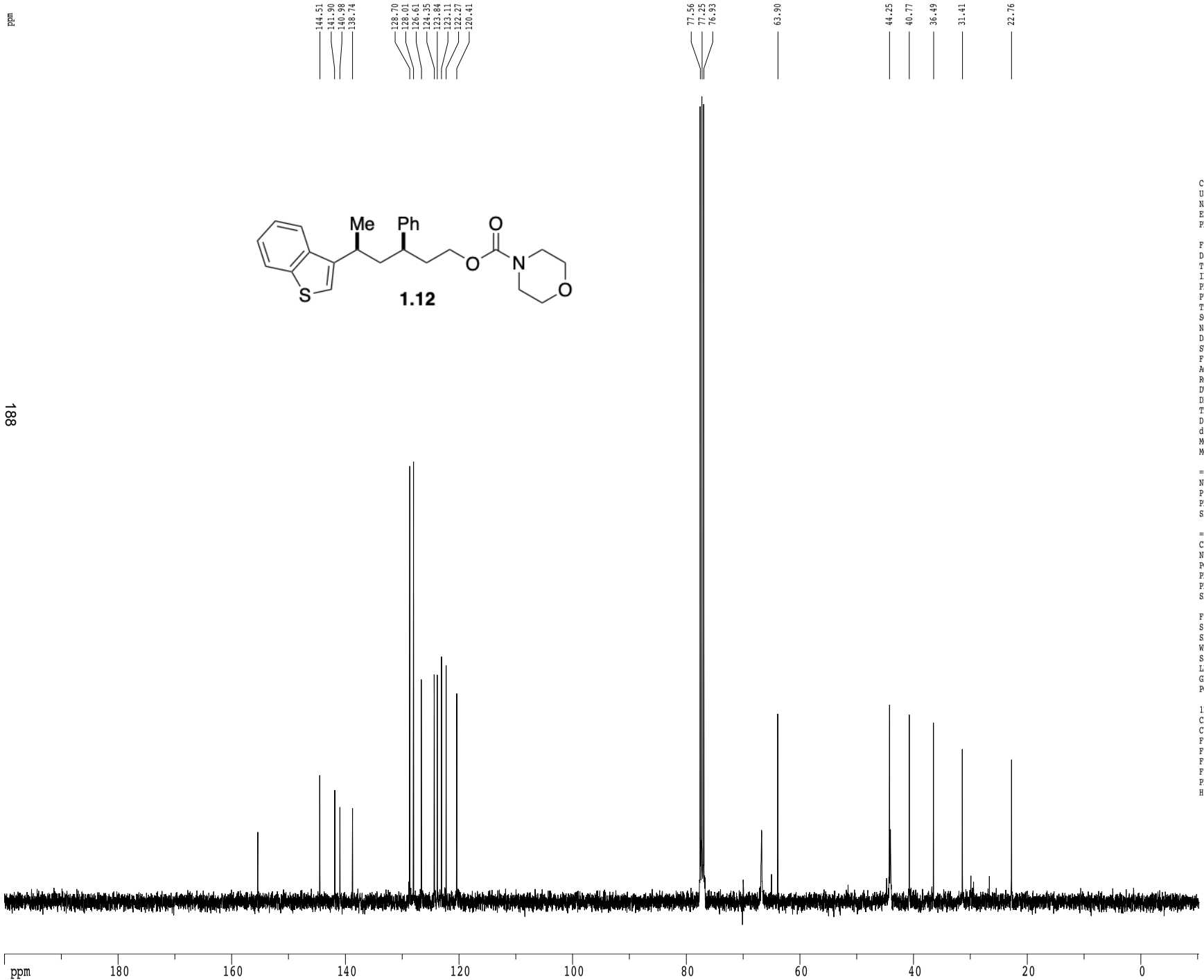
F2 - Acquisition Parameters
Date_ 20170717
Time 9.34
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 203.2
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-1-051-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170713
Time 13.26
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 768
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

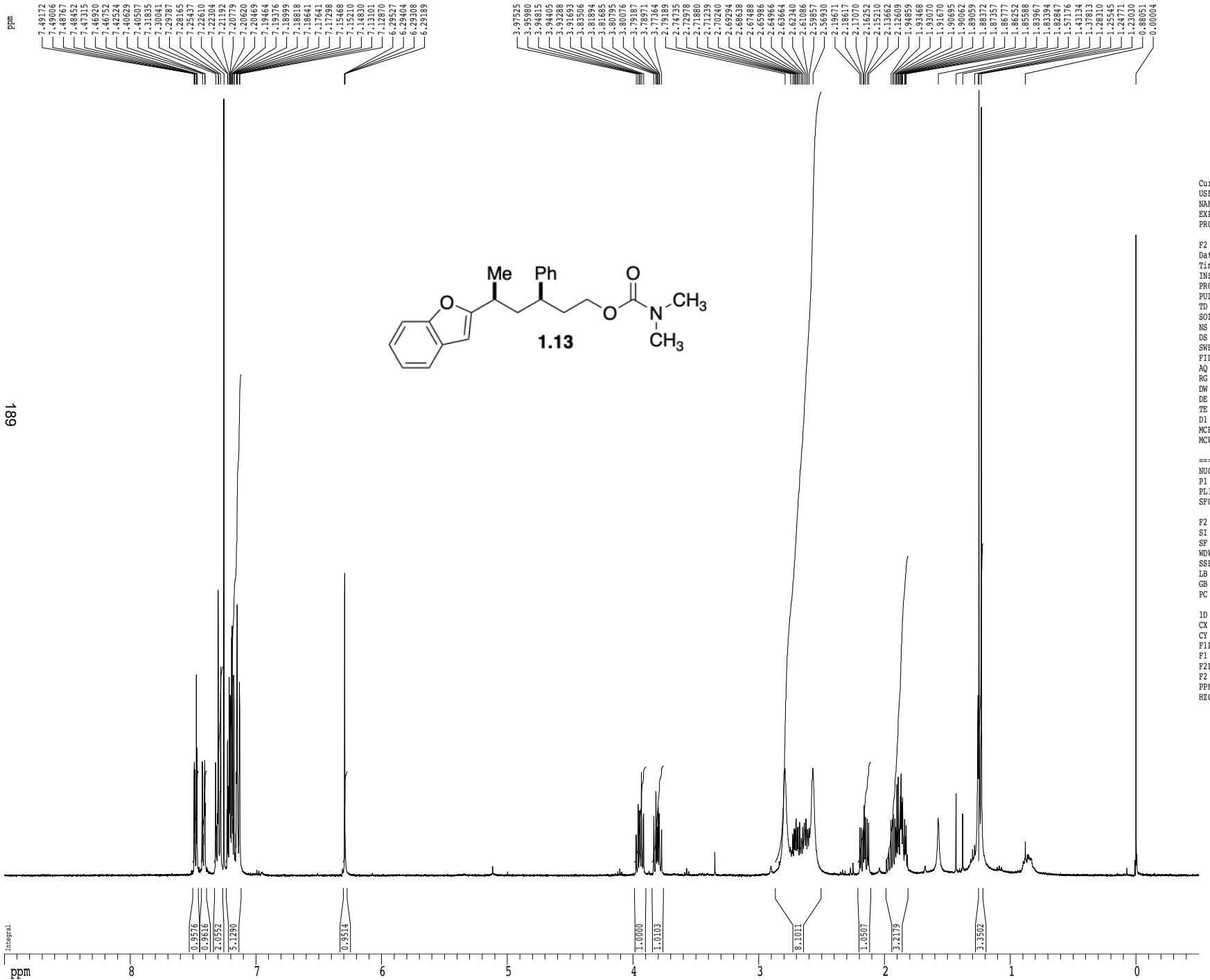
======== CHANNEL f1 ========
NUC1 13C
P1 7.60 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 mlev16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.246 ppm
F2 -1030.87 Hz
PPMCM 9.22131 ppm/cm
HZCM 927.78168 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-1-048-pure2
EXPNO 1
PROCNO 1

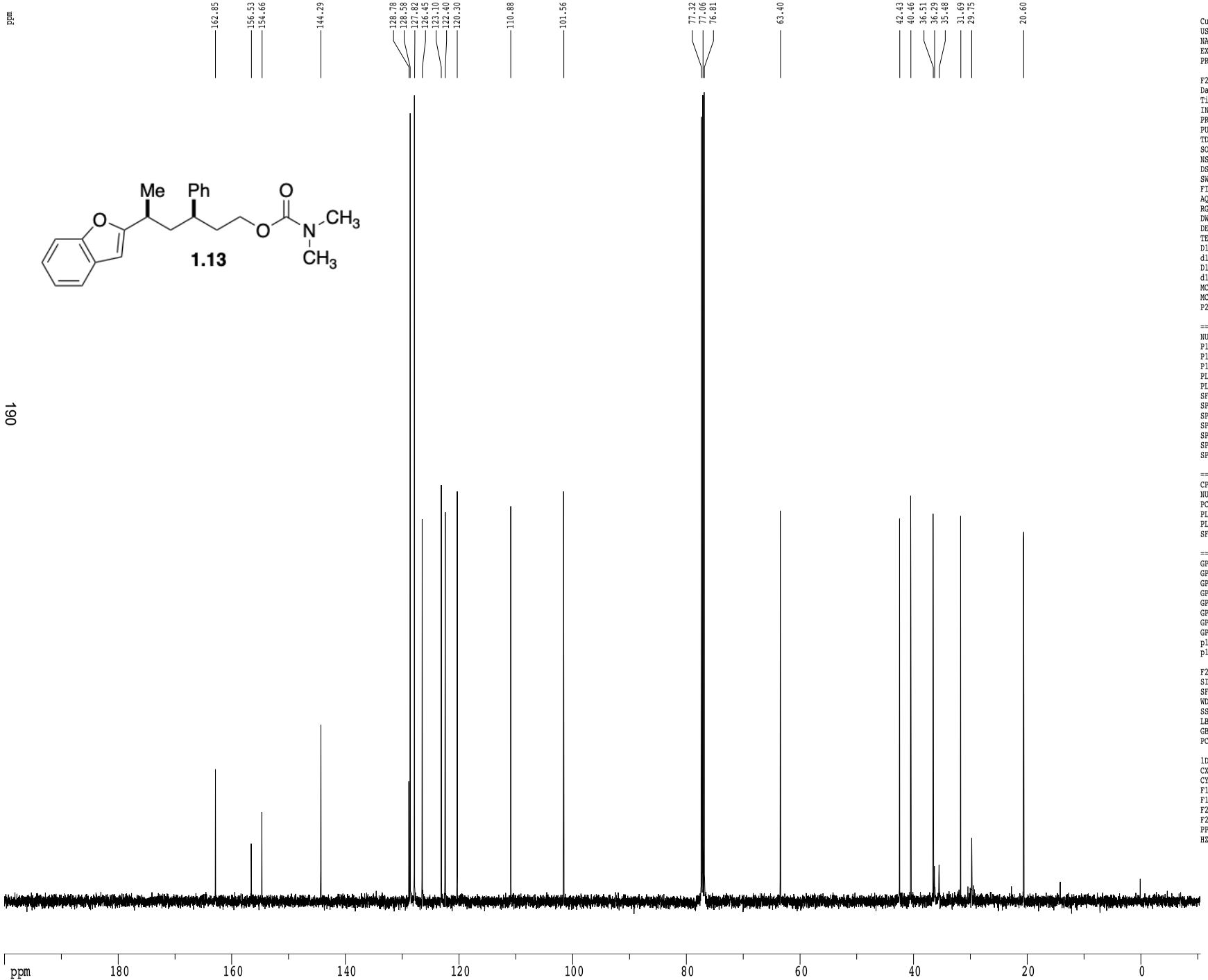
F2 - Acquisition Parameters
Date_ 20170724
Time 13.02
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 256
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300235 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

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



Current Data Parameters
USER sanforda
NAME ABS-1-048-carbon2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170724
Time 14.04
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 706
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 3649.1
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

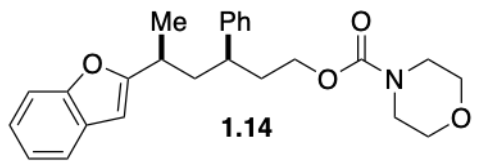
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P -10.460 ppm
F2 -1315.66 Hz
PPMCM 9.23070 ppm/cm
HZCM 1161.04163 Hz/cm

1H spectrum



1.14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Current Data Parameters
USER            sanforda
NAME      ABS-1-052-temp2
EXPNO                  3
PROCNO                 1

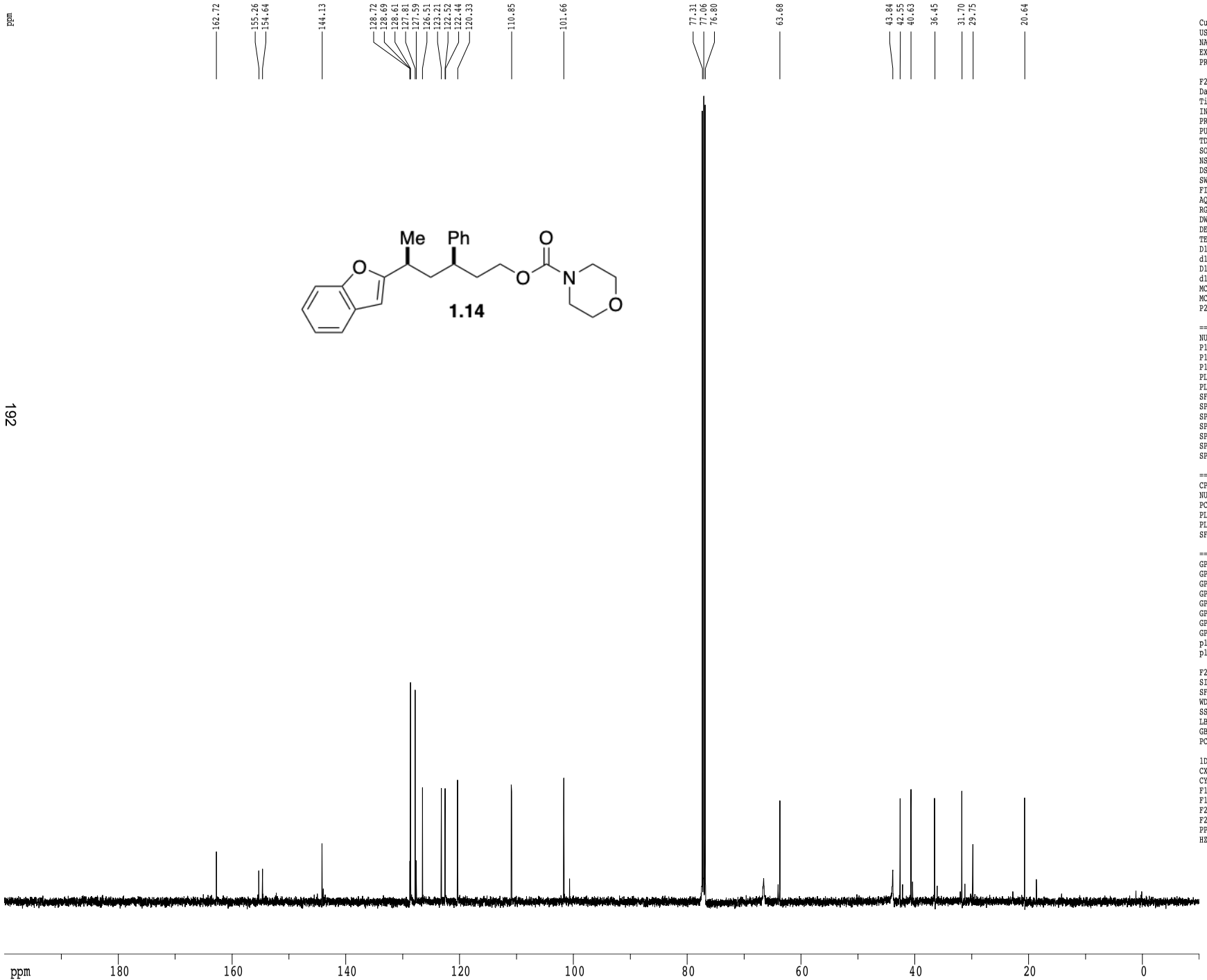
F2 - Acquisition Parameters
Date_           20171106
Time               12.10
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 sec
RG                   5.7
DW                62.400 usec
DE                 6.00 usec
TE                311.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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

F2 - Processing parameters
SI                 65536
SF          500.2200347 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P               -0.500 ppm
F2               -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-1-052-carbon2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171107
Time 10.55
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 90904
SOLVENT CDCl3
NS 787
DS 16
SWH 30303.031 Hz
FIDRES 0.333352 Hz
AQ 1.4999660 sec
RG 5160.6
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

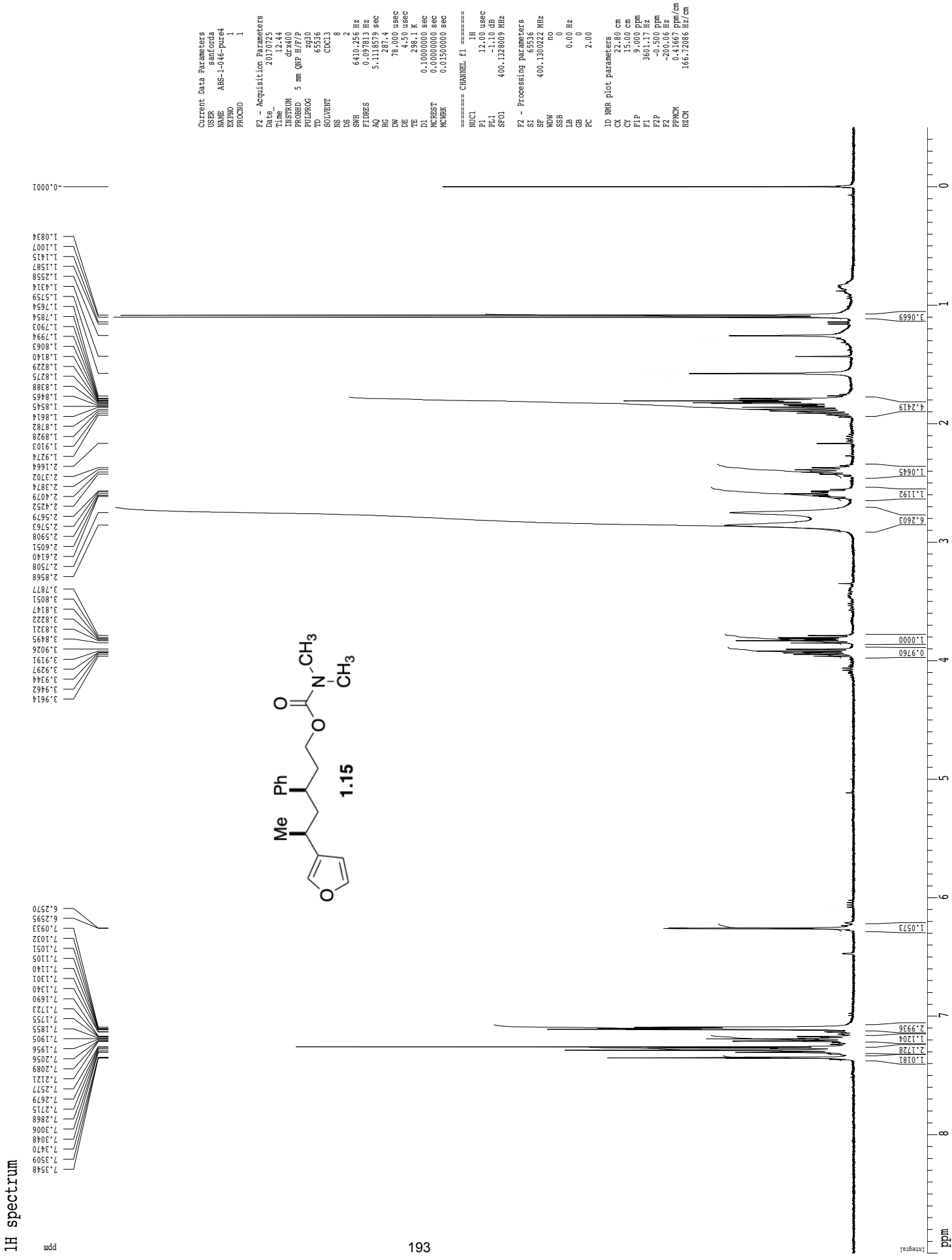
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

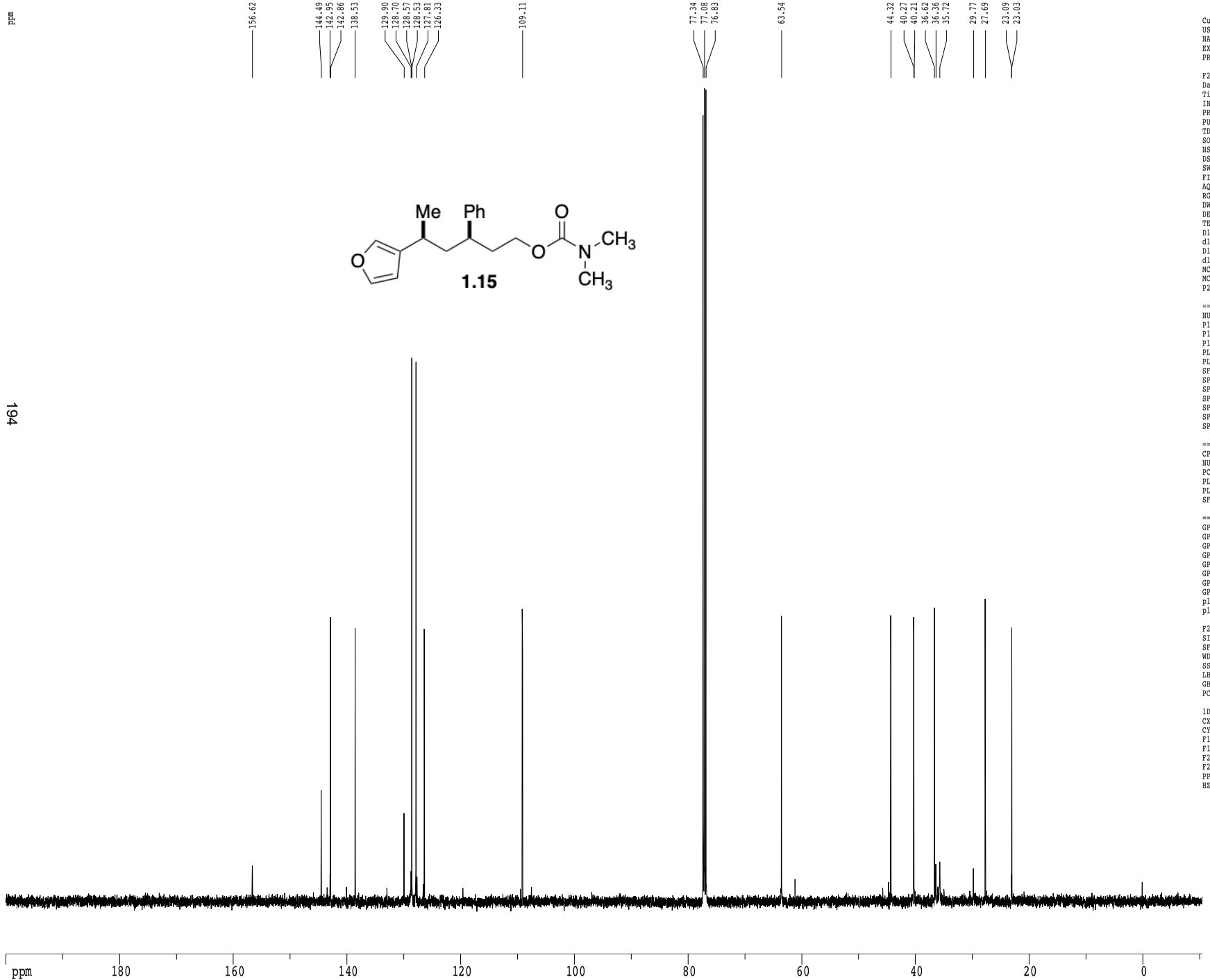
F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-1-046-pure4
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170725
Time_ 12.44
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 287.4
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300222 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Me
Ph
1.15
O
N
CH3
CH3
O
O
3.9614
3.9344
3.9297
3.9191
3.9026
3.8495
3.8321
3.8222
3.8147
3.8051
3.7877
2.8568
2.7508
2.6140
2.6051
2.5908
2.5763
2.5679
2.4252
2.4079
2.3874
2.3702
2.1664
1.9274
1.9103
1.8928
1.8782
1.8614
1.8545
1.8465
1.8388
1.8275
1.8229
1.8140
1.8063
1.7994
1.7903
1.7854
1.7654
1.5759
1.4314
1.2558
1.1587
1.1415
1.1007
1.0834
7.3548
7.3509
7.3470
7.3048
7.3006
7.2868
7.2715
7.2679
7.2577
7.2121
7.2089
7.2056
7.1956
7.1905
7.1855
7.1755
7.1723
7.1690
7.1340
7.1301
7.1140
7.1105
7.1051
7.1032
7.0933
6.2595
6.2570
3.0669
4.2419
1.0645
1.1192
6.2603
1.0000
0.9760
1.0573
2.9936
1.1204
2.1728
1.0181
0.0001
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-1-046-pure-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170725
Time 18.40
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 953
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 4597.6
DW 16.500 usec
DE 6.00 usec
TE 293.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======= CHANNEL f1 =======
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

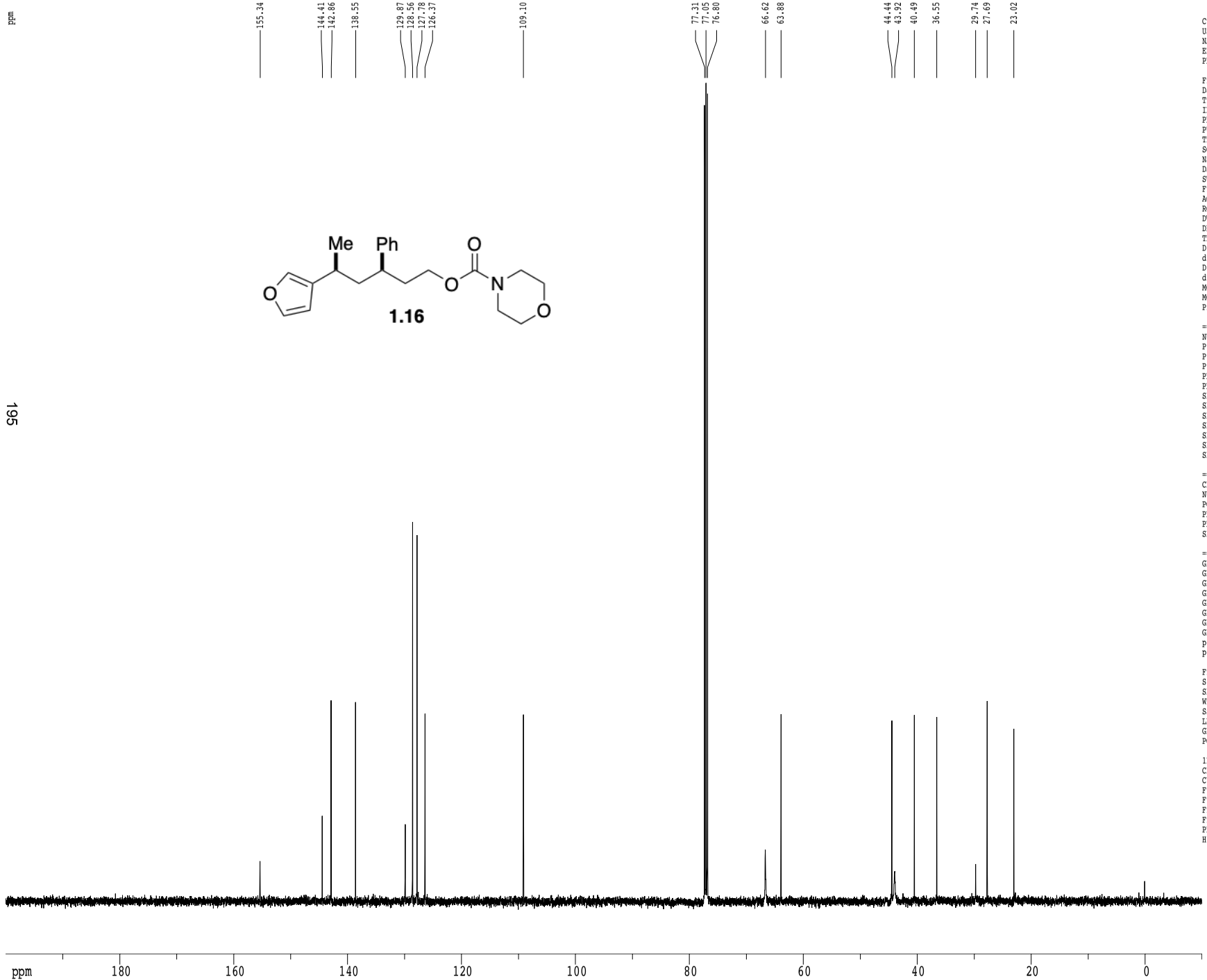
======= CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

===== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P -10.460 ppm
F2 -1315.66 Hz
PPMCM 9.23070 ppm/cm
HZCM 1161.04163 Hz/cm

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



Current Data Parameters
USER sanforda
NAME ABS-1-050-carbon2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171108
Time 14.26
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 869
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 8192
DW 16.500 usec
DE 6.00 usec
TE 298.1 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

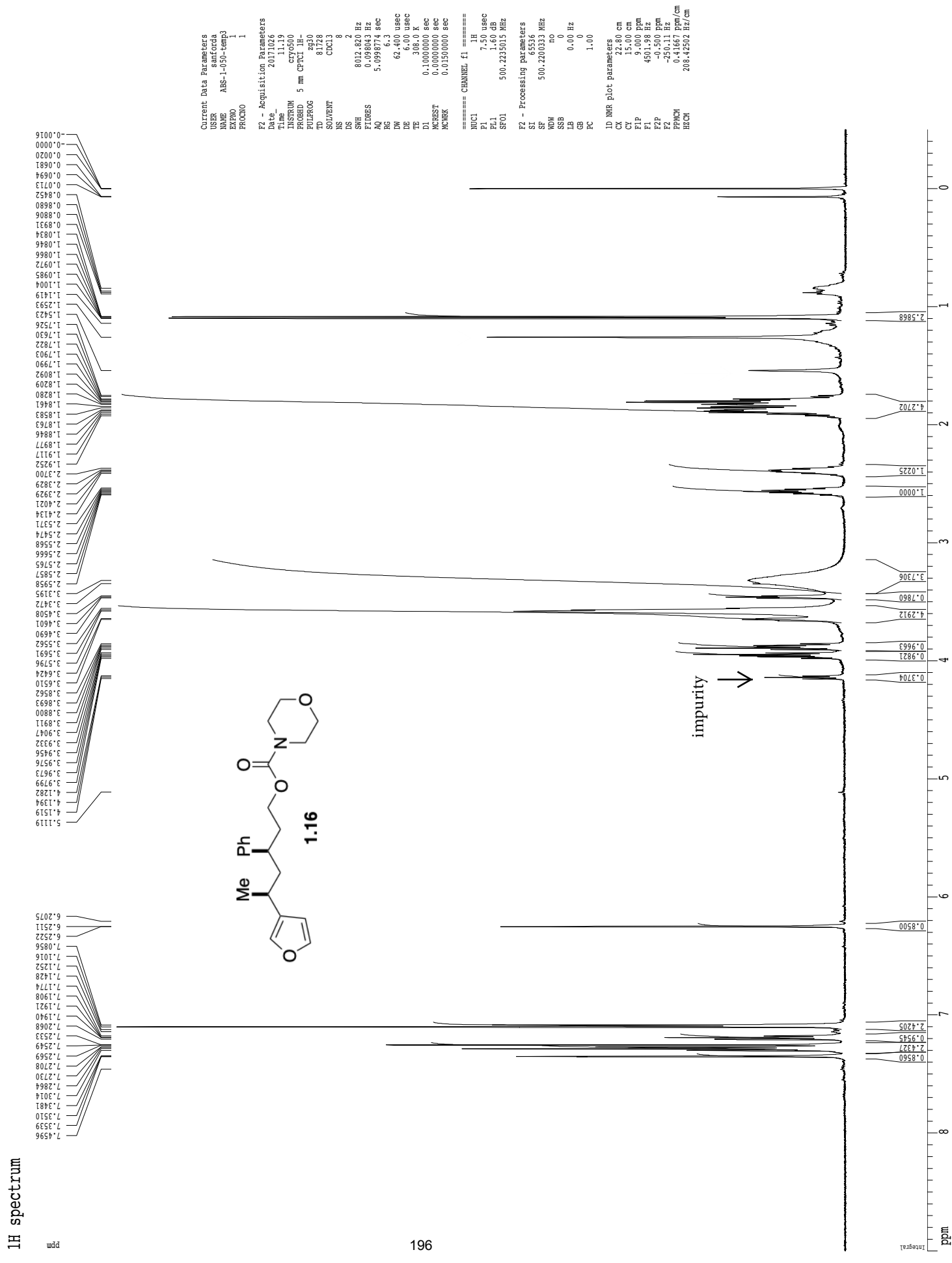
======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

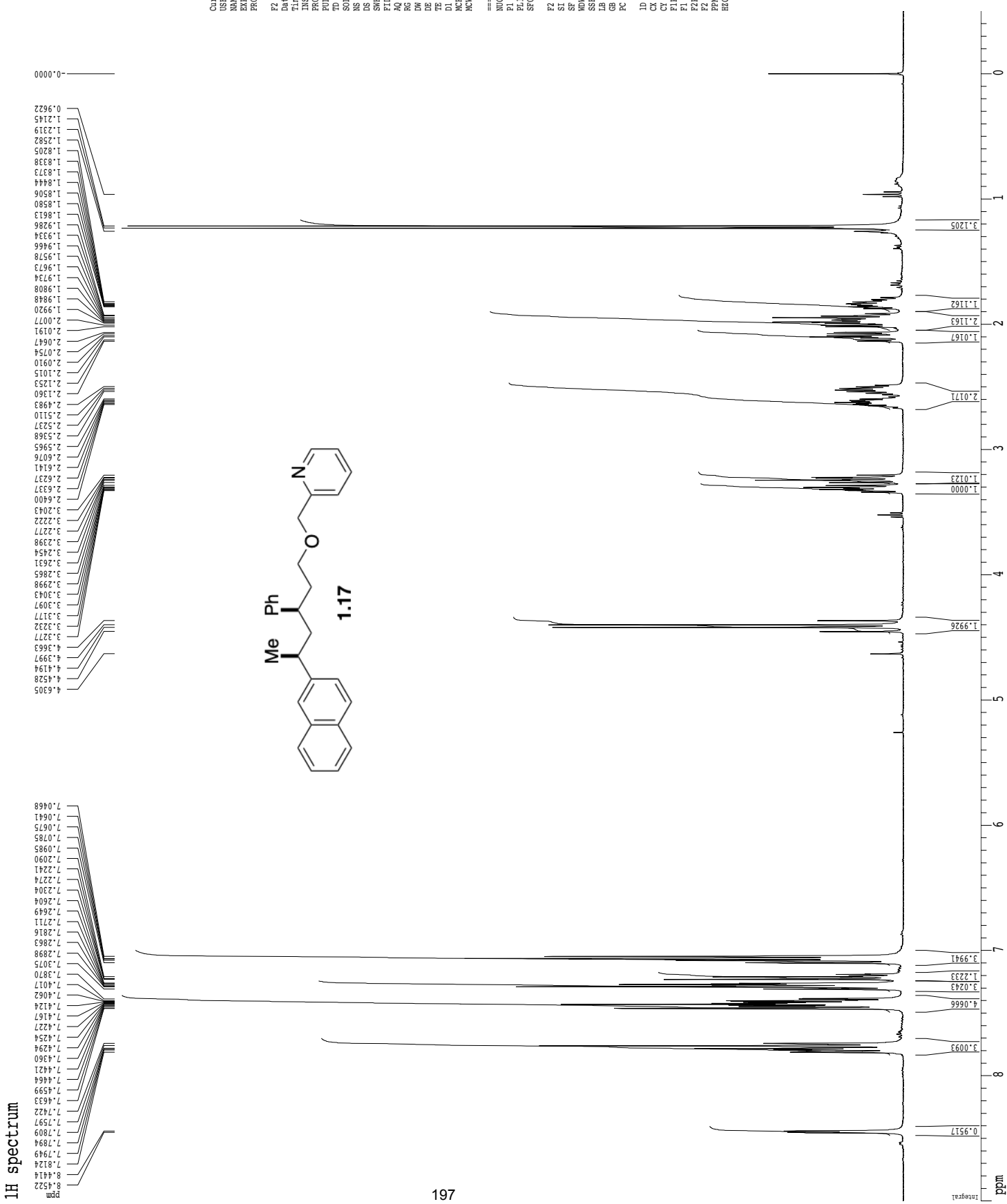
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

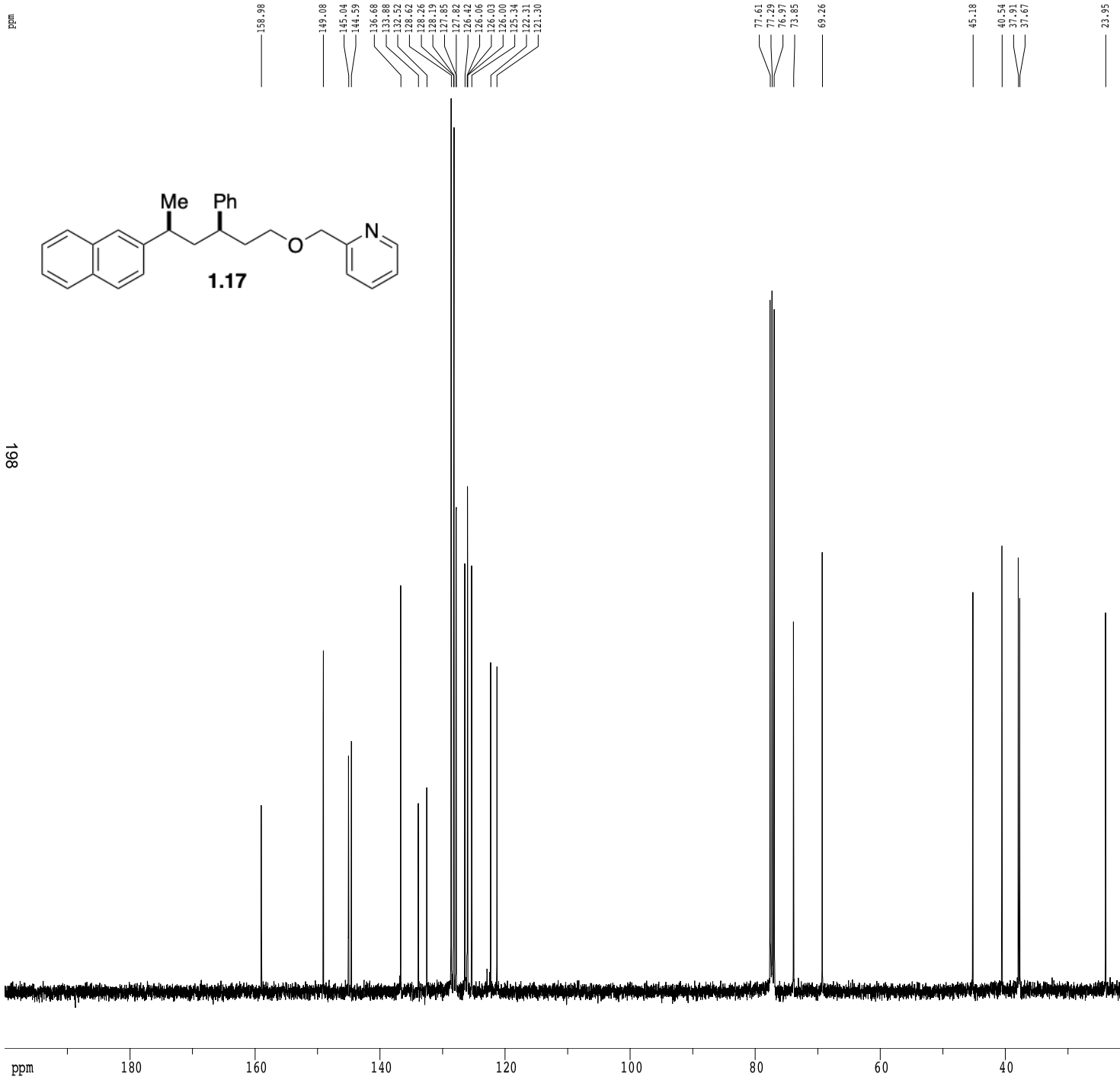
F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-1-050-temp3
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171026
Time_ 11.19
INSTRUM CRYO500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 308.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200333 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Me
Ph
O
N
O
O
O
1.16
impurity
ppm
Integral


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-125-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190112
Time_ 14.01
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 80.6
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300330 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Me
Ph
O
N
1.17
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-2-125-carbon
EXPNO 1
PROCNO 1

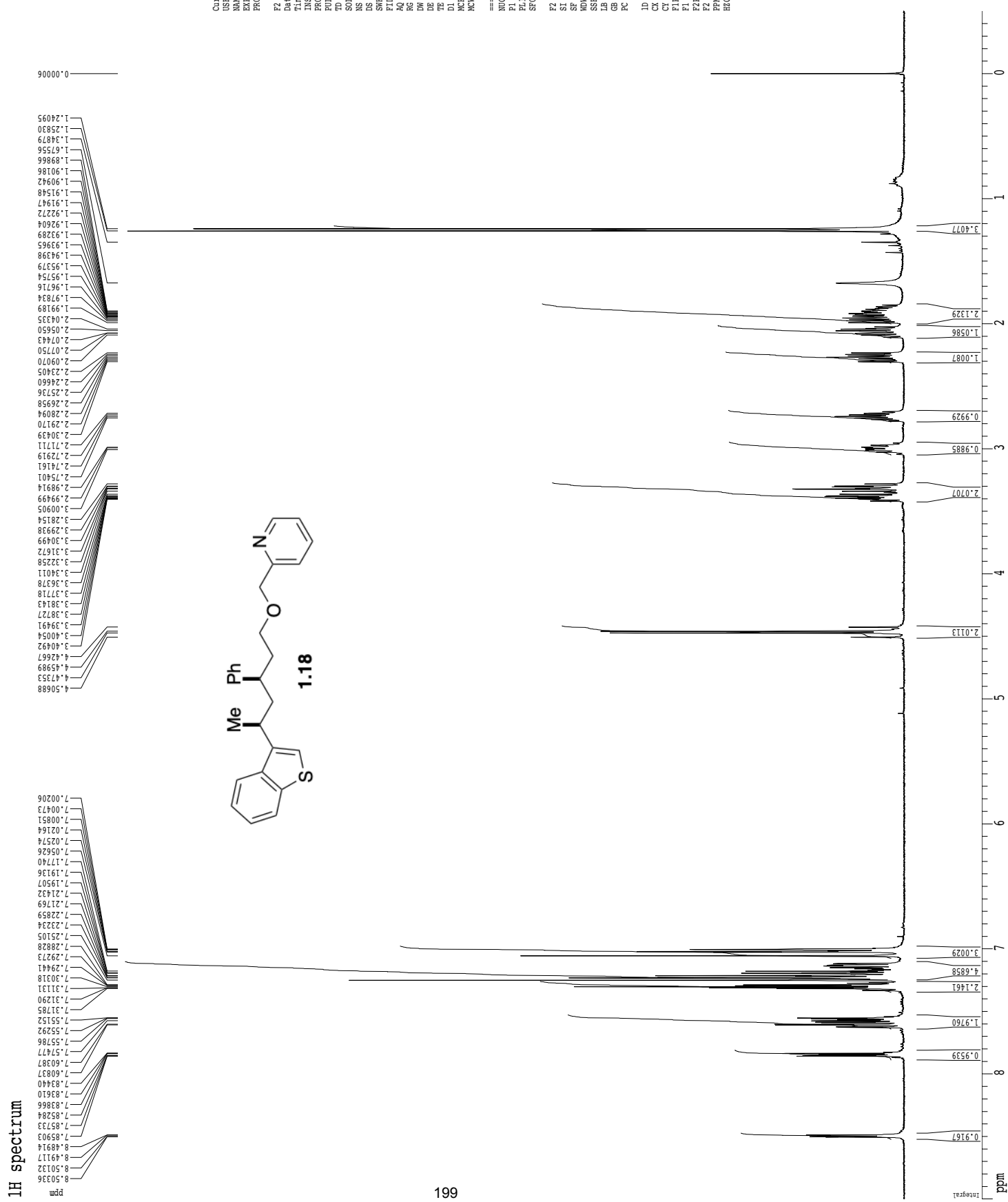
F2 - Acquisition Parameters
Date_ 20190112
Time 14.05
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 496
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 5160.6
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

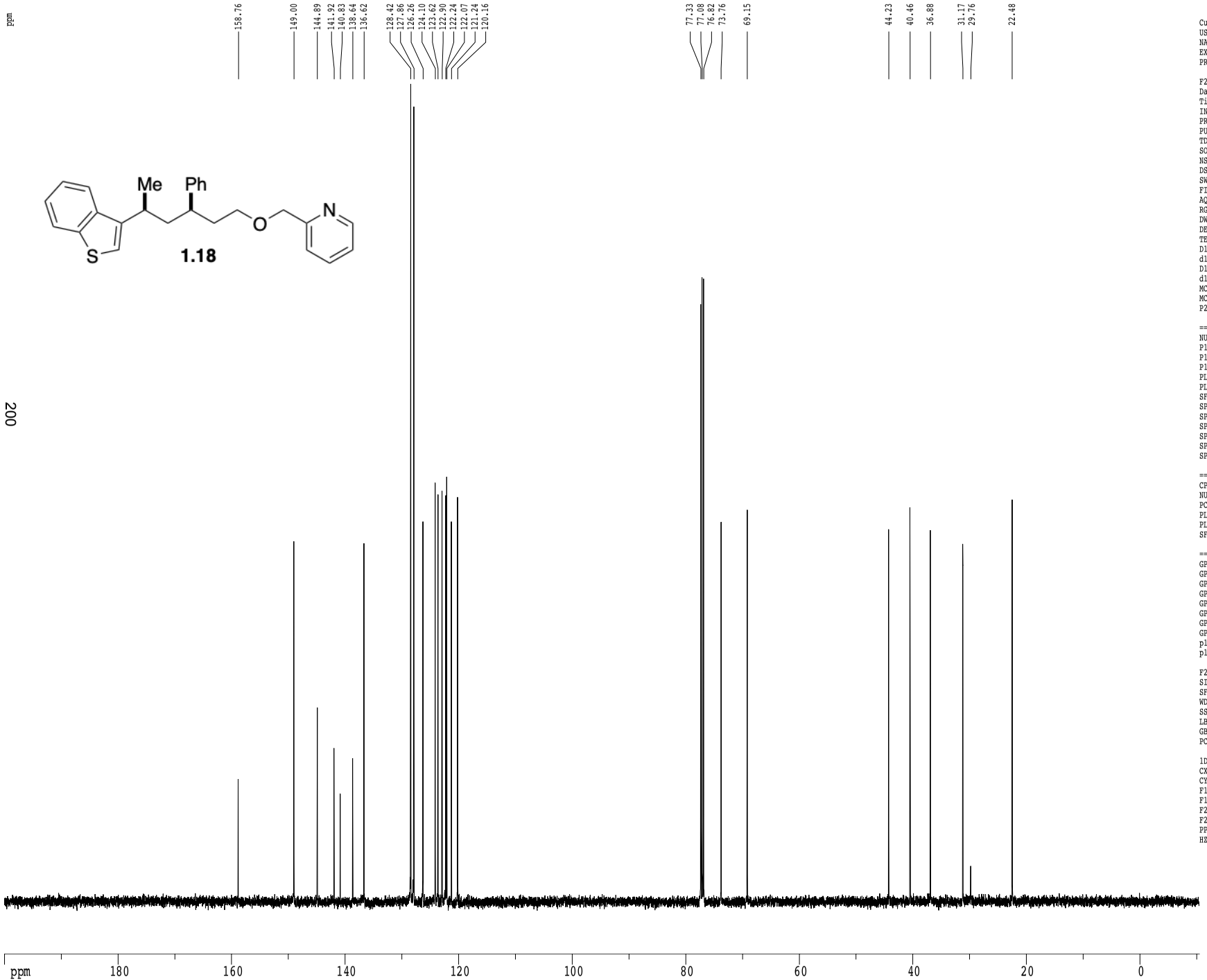
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69629 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-1-060
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170808
Time_ 9.43
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 203.2
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300249 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Me
Ph
1.18
N
O
S
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-1-060-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170808
Time 18.15
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 504
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

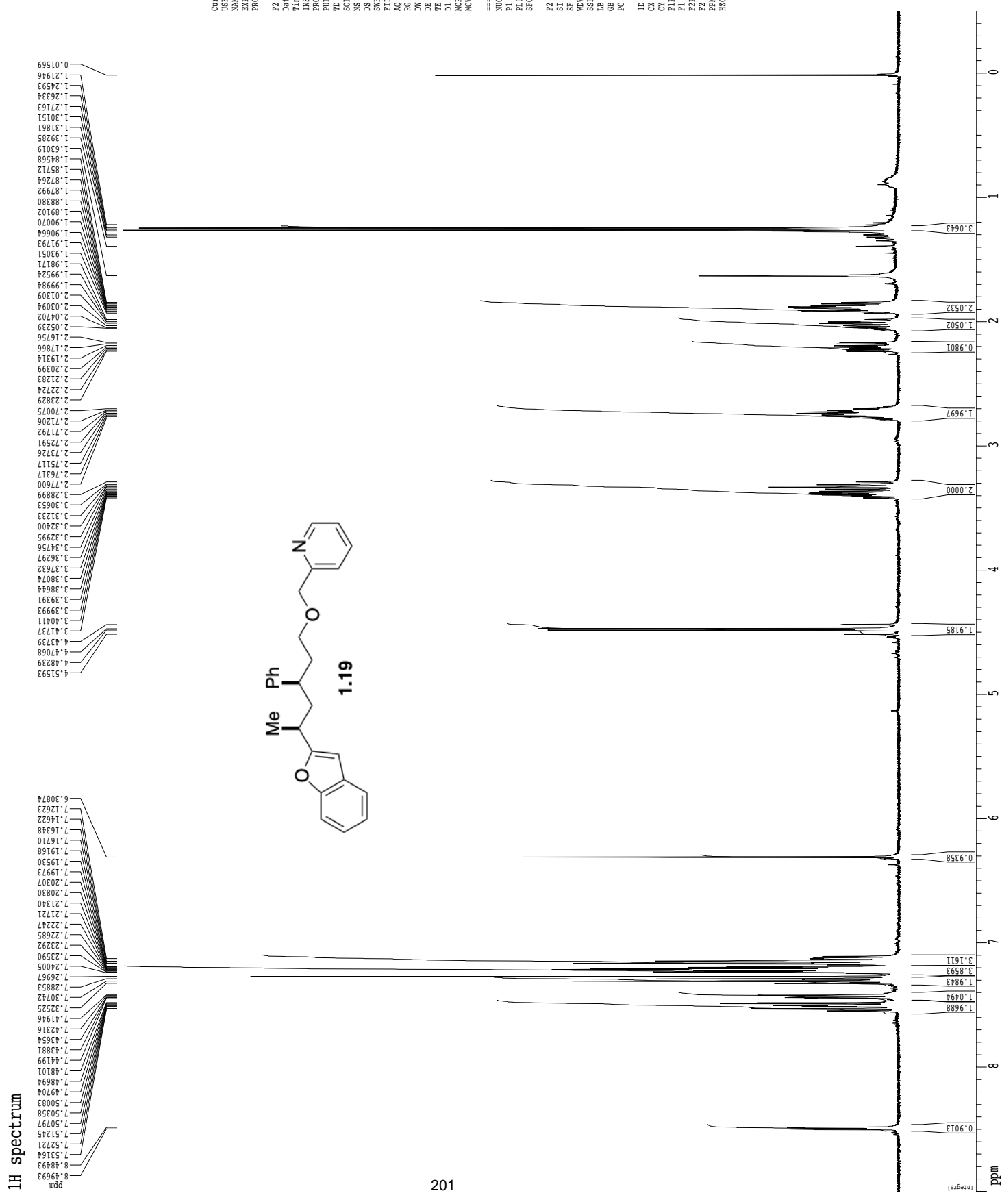
======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

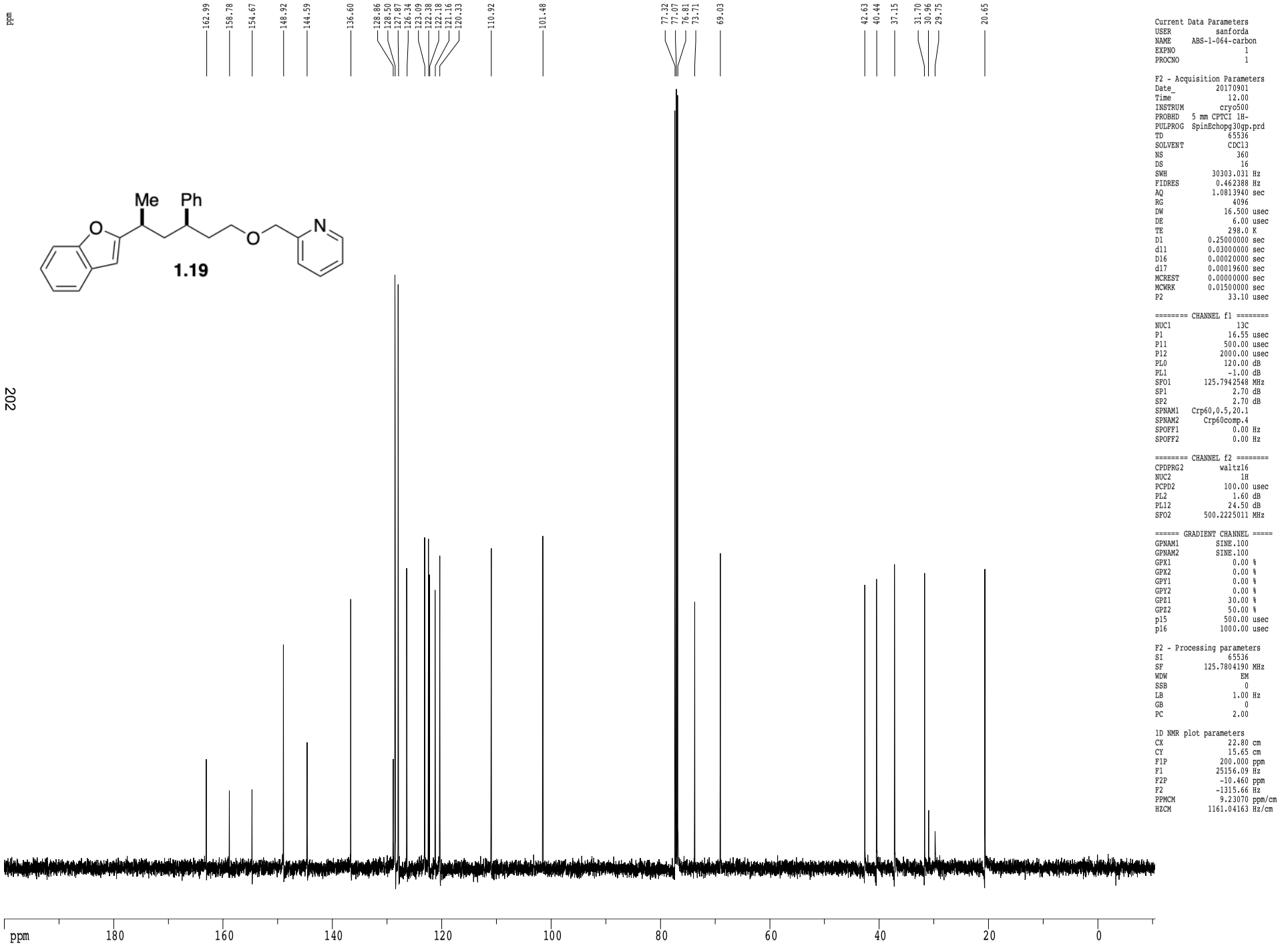
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P -10.460 ppm
F2 -1315.66 Hz
PPMCM 9.23070 ppm/cm
HZCM 1161.04163 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-1-064-3A
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170823
Time_ 13.14
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 322.5
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
Me
Ph
1.19
3.0643
2.0532
1.0502
0.9801
1.9697
2.0000
1.9185
0.9358
3.1611
3.8593
1.9843
1.0494
1.9688
0.9013
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-1-064-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170901
Time 12.00
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 360
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 4096
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

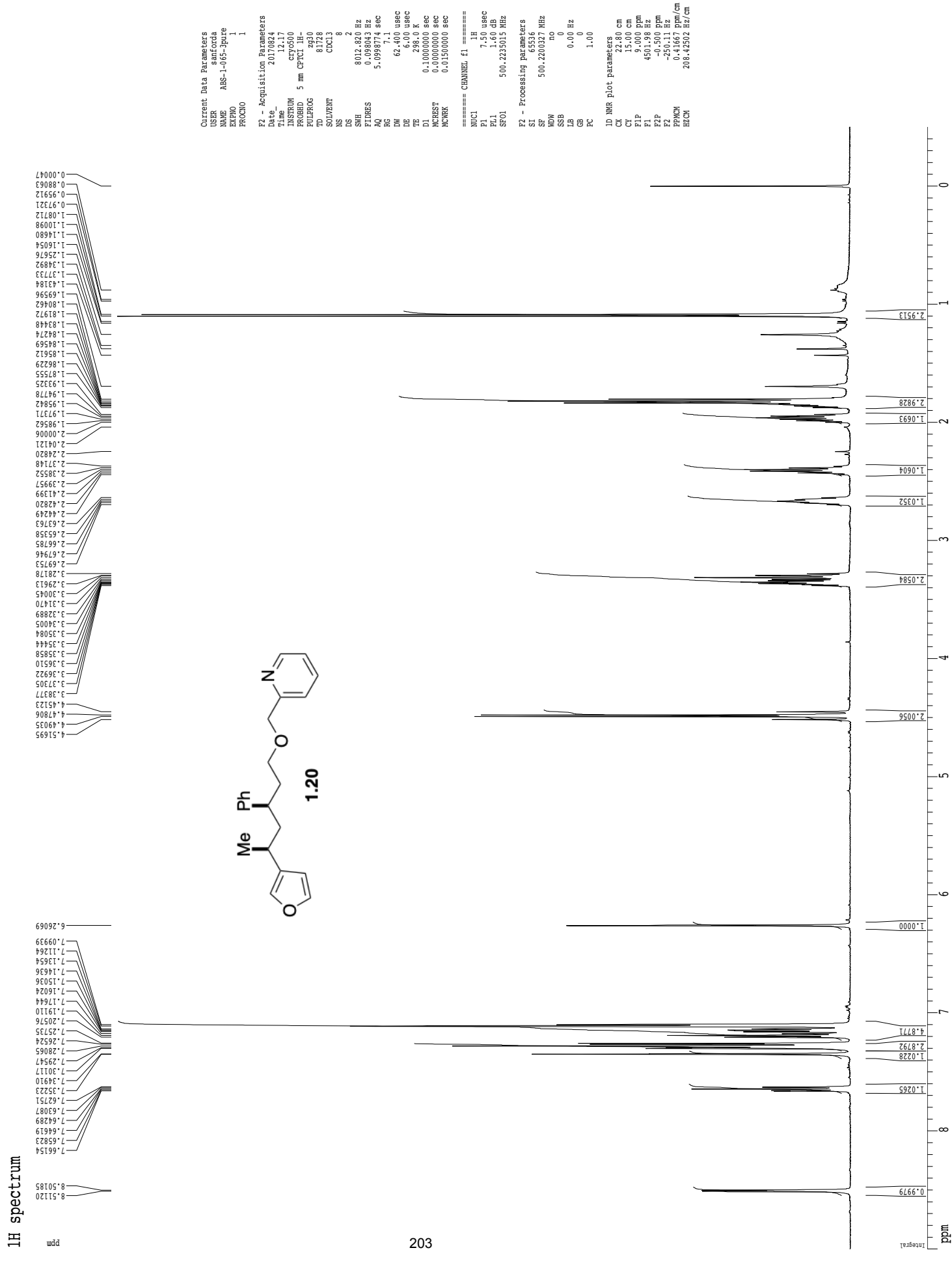
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

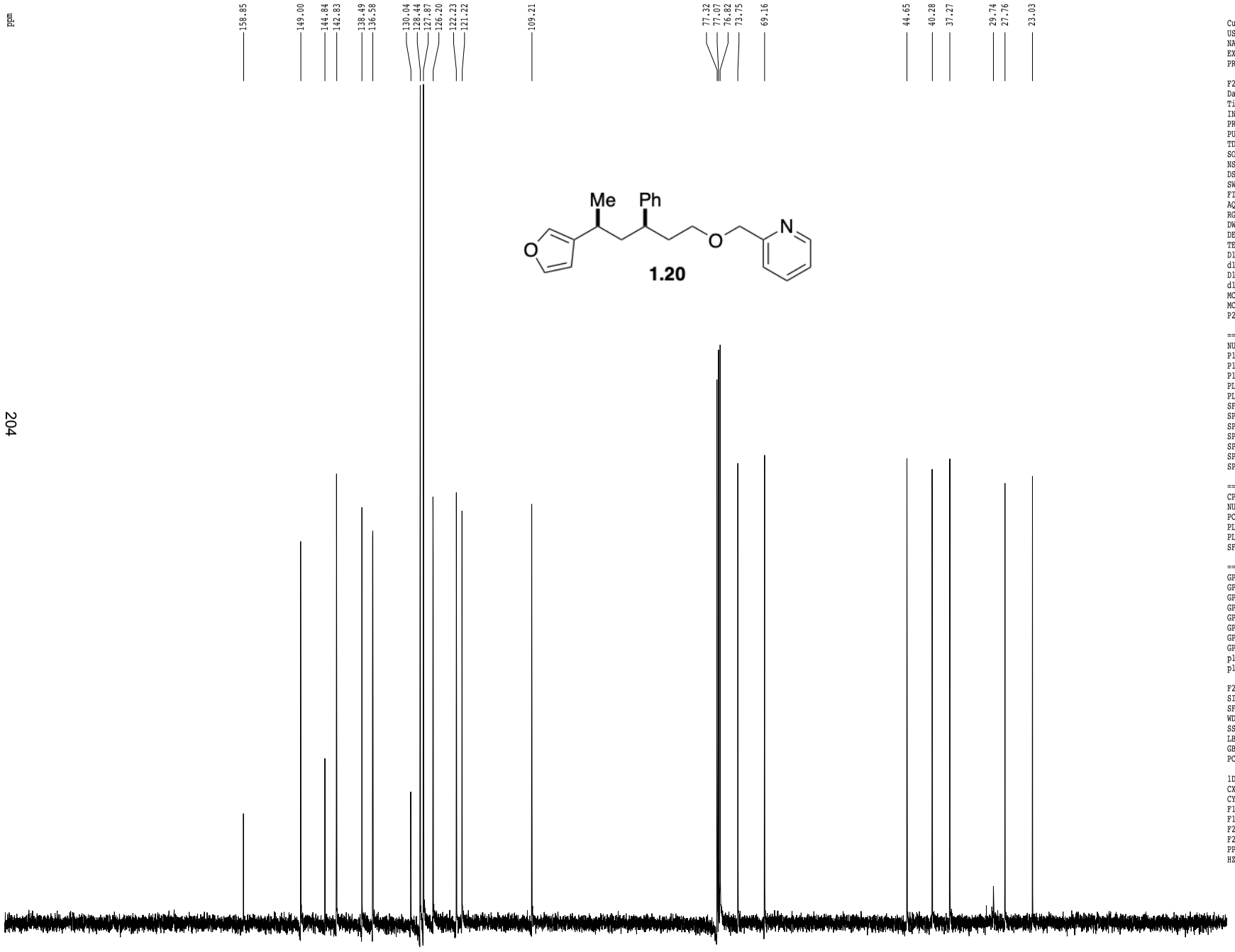
F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P -10.460 ppm
F2 -1315.66 Hz
PPMCM 9.23070 ppm/cm
HZCM 1161.04163 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-1-065-3pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170824
Time_ 12.17
INSTRUM CRYO500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200327 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
Me
Ph
1.20
O
N
O
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-1-070-carbo
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170901
Time 12.13
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp.prd
TD 65536
SOLVENT CDCl3
NS 249
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP1 2.70 dB
SP2 2.70 dB
SPNAM1 Crp60,0.5,20.1
SPNAM2 Crp60comp.4
SPOFF1 0.00 Hz
SPOFF2 0.00 Hz

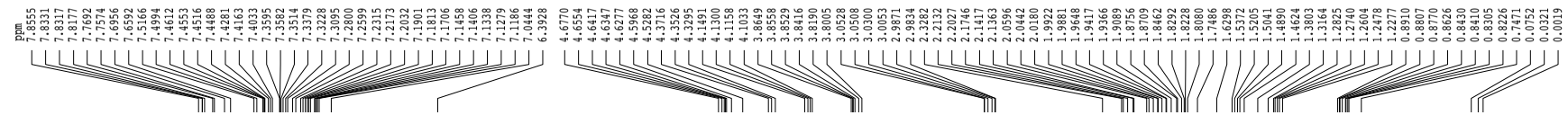
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 24.50 dB
SFO2 500.2225011 MHz

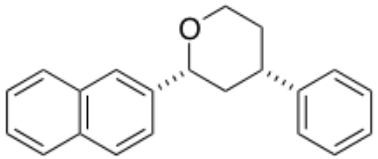
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P -10.460 ppm
F2 -1315.66 Hz
PPMCM 9.23070 ppm/cm
HZCM 1161.04163 Hz/cm

1H spectrum





1.1

205


```
Current Data Parameters
USER            sanforda
NAME      ABS-2-102-pure
EXPNO                   1
PROCNO                  1

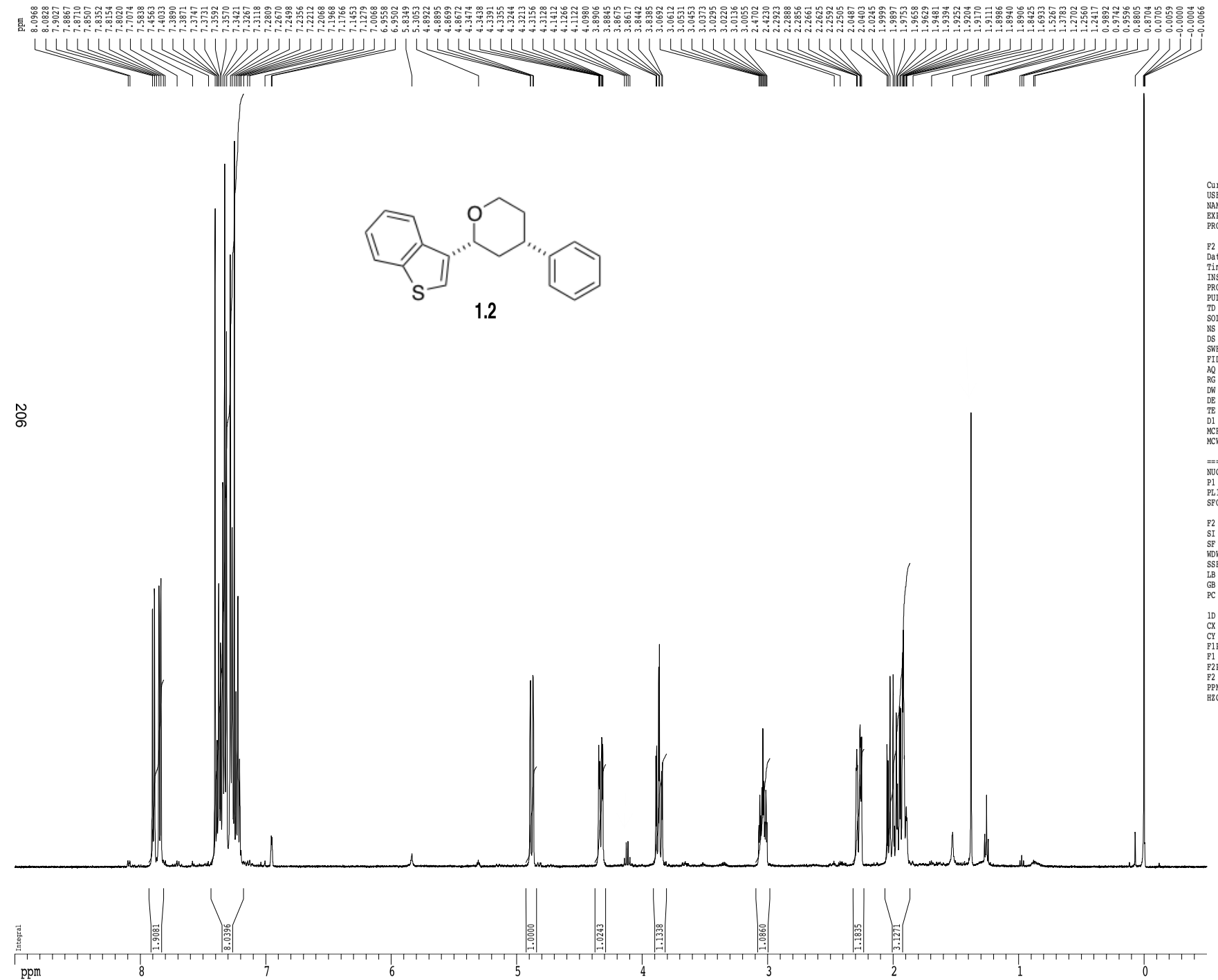
F2 - Acquisition Parameters
Date_            20181204
Time                11.14
INSTRUM             gn500
PROBHD   5 mm broadband
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                  1824.6
DW                 62.400 usec
DE                  6.00 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======= CHANNEL f1 =======
NUC1                   1H
P1                 12.00 usec
PL1                -5.80 dB
SFO1         498.9534926 MHz

F2 - Processing parameters
SI                  65536
SF           498.9500312 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               4490.55 Hz
F2P               -0.500 ppm
F2               -249.47 Hz
PPMCM           0.41667 ppm/cm
HZCM          207.89586 Hz/cm
```

1H spectrum



Current Data Parameters

USER	sanforda
NAME	ABS-1-098-proton
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20171010
Time	15.36
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	81728
SOLVENT	CDCl3
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.098043 Hz
AQ	5.0998774 sec
RG	5.7
DW	62.400 usec
DE	6.00 usec
TE	298.0 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======= CHANNEL f1 =======

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

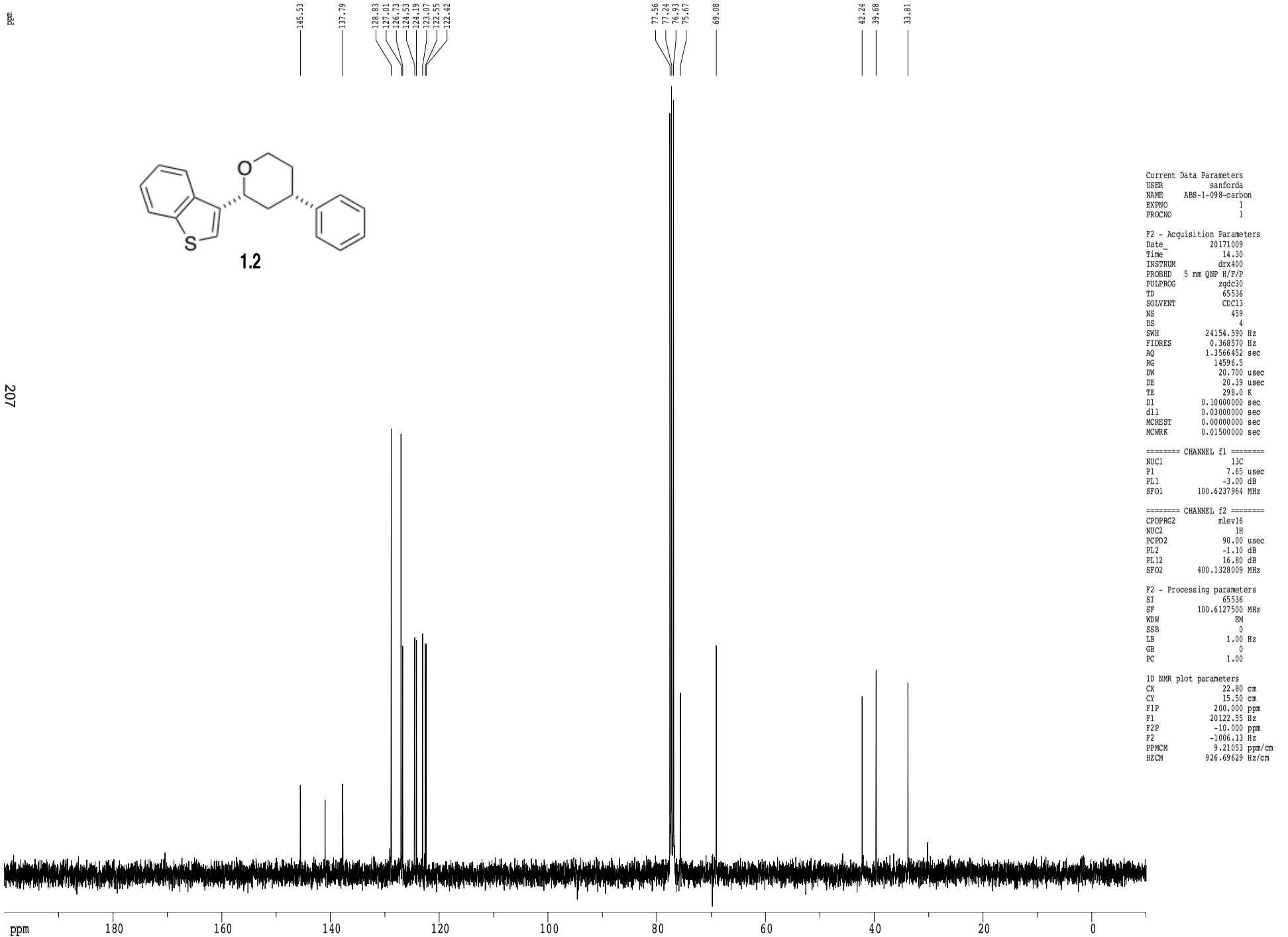
F2 - Processing parameters

SI	65536
SF	500.2200362 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
CY	15.00 cm
F1P	9.000 ppm
F1	4501.98 Hz
F2P	-0.500 ppm
F2	-250.11 Hz
PPMCM	0.41667 ppm/cm
HZCM	208.42502 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-1-098-carbon
EXPNO 1
PROCNO 1

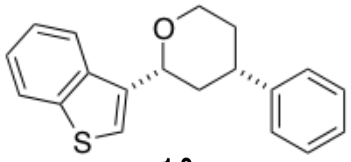
F2 - Acquisition Parameters
Date_ 20171009
Time 14.30
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 459
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 14596.5
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 mlev16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

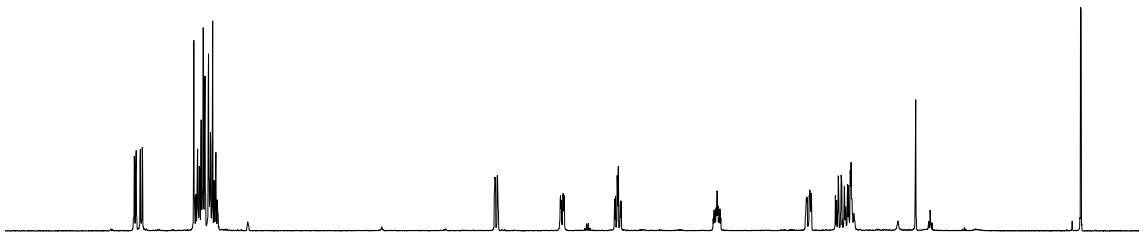
F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

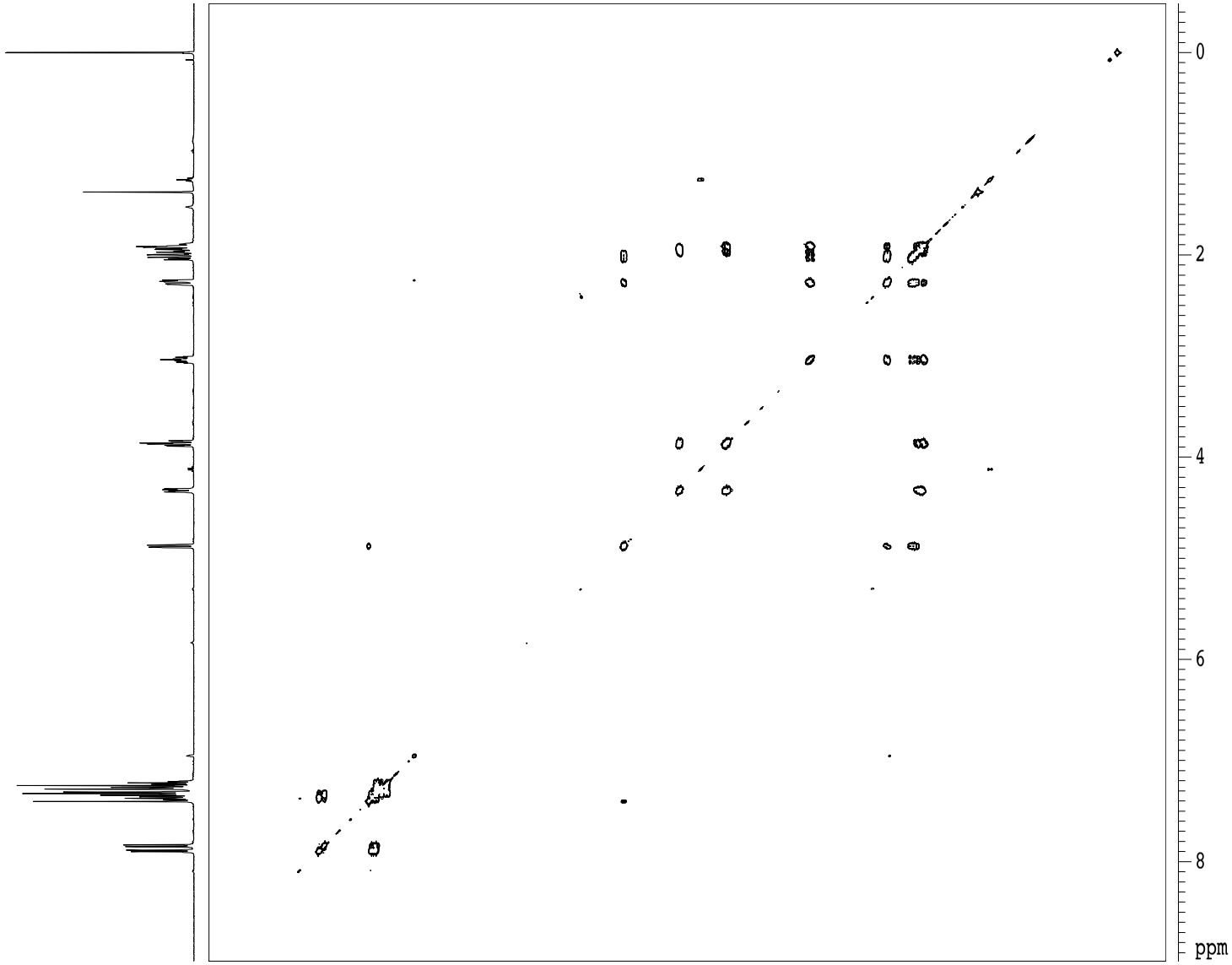
1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69629 Hz/cm



1.2

gcosy60





Current Data Parameters

USER	sanforda
NAME	ABS-1-098-proton
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20171010
Time	15.39
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	2
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	287.4
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221621 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2222 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	undefined

F2 - Processing parameters

SI	1024
SF	500.2200362 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

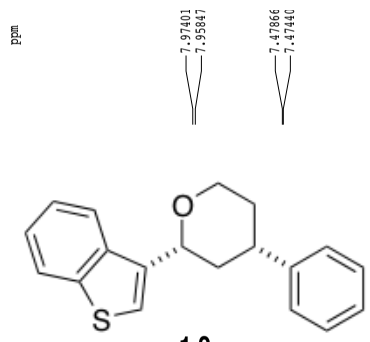
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200362 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.983 ppm
F2LO	4493.36 Hz
F2PHI	-0.483 ppm
F2HI	-241.49 Hz
F1PLO	8.983 ppm
F1LO	4493.36 Hz
F1PHI	-0.483 ppm
F1HI	-241.49 Hz
F2PPMCM	0.63104 ppm/cm
F2HZCM	315.65656 Hz/cm
F1PPMCM	0.63104 ppm/cm
F1HZCM	315.65656 Hz/cm

gnoe



1.2

Current Data Parameters
USER sanforda
NAME ABS-1-098-proton
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171010
Time 16.28
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoelcc.wu
TD 65536
SOLVENT CDCl3
NS 256
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec

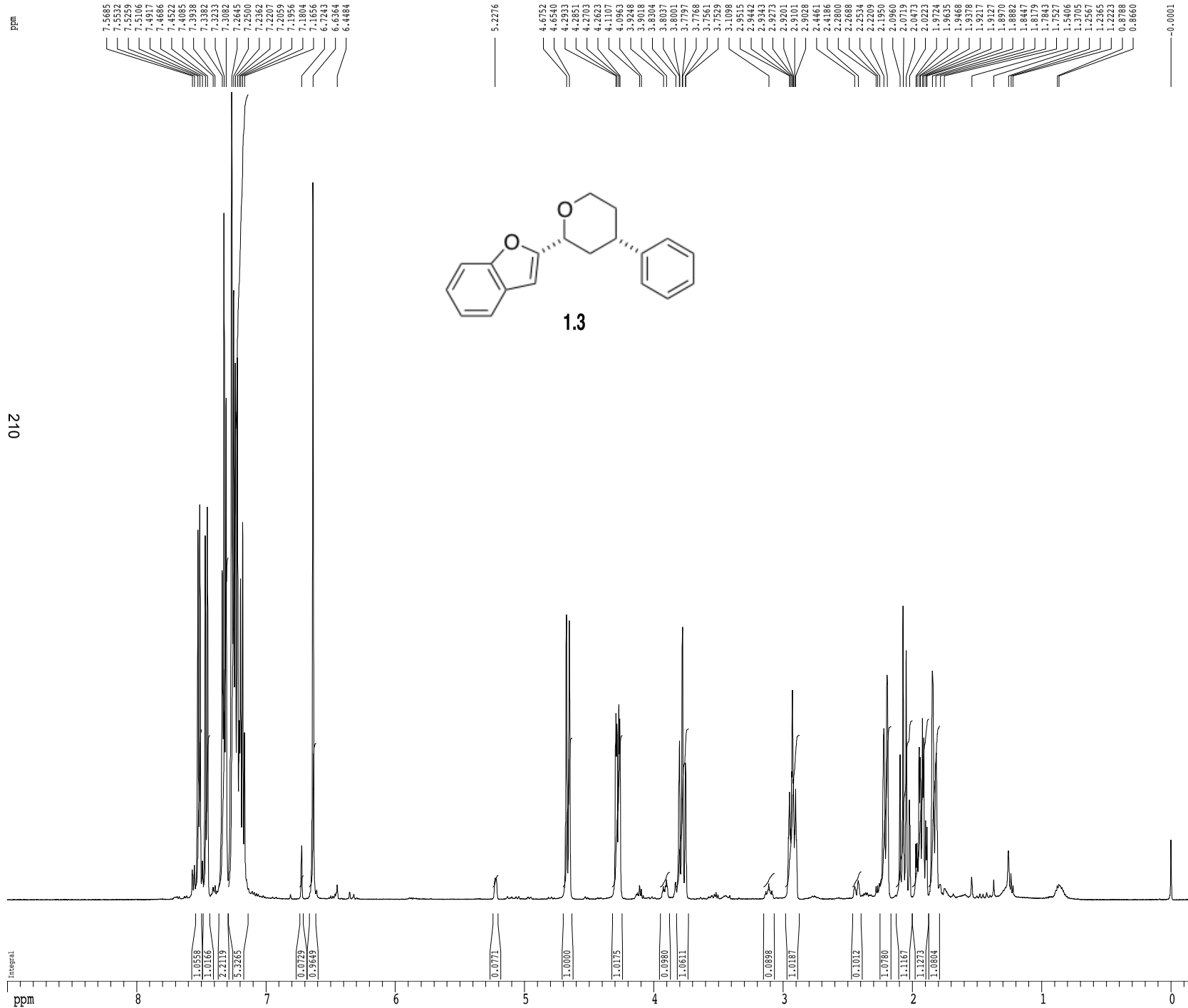
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P12 40000.00 usec
PL1 1.60 dB
SFO1 500.2224772 MHz
SP1 61.60 dB
SPNAM1 gauss1.512
SPOFF1 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm

1H spectrum




```
Current Data Parameters
USER            sanforda
NAME      ABS-1-053-proton3
EXPNO                   1
PROCNO                  1

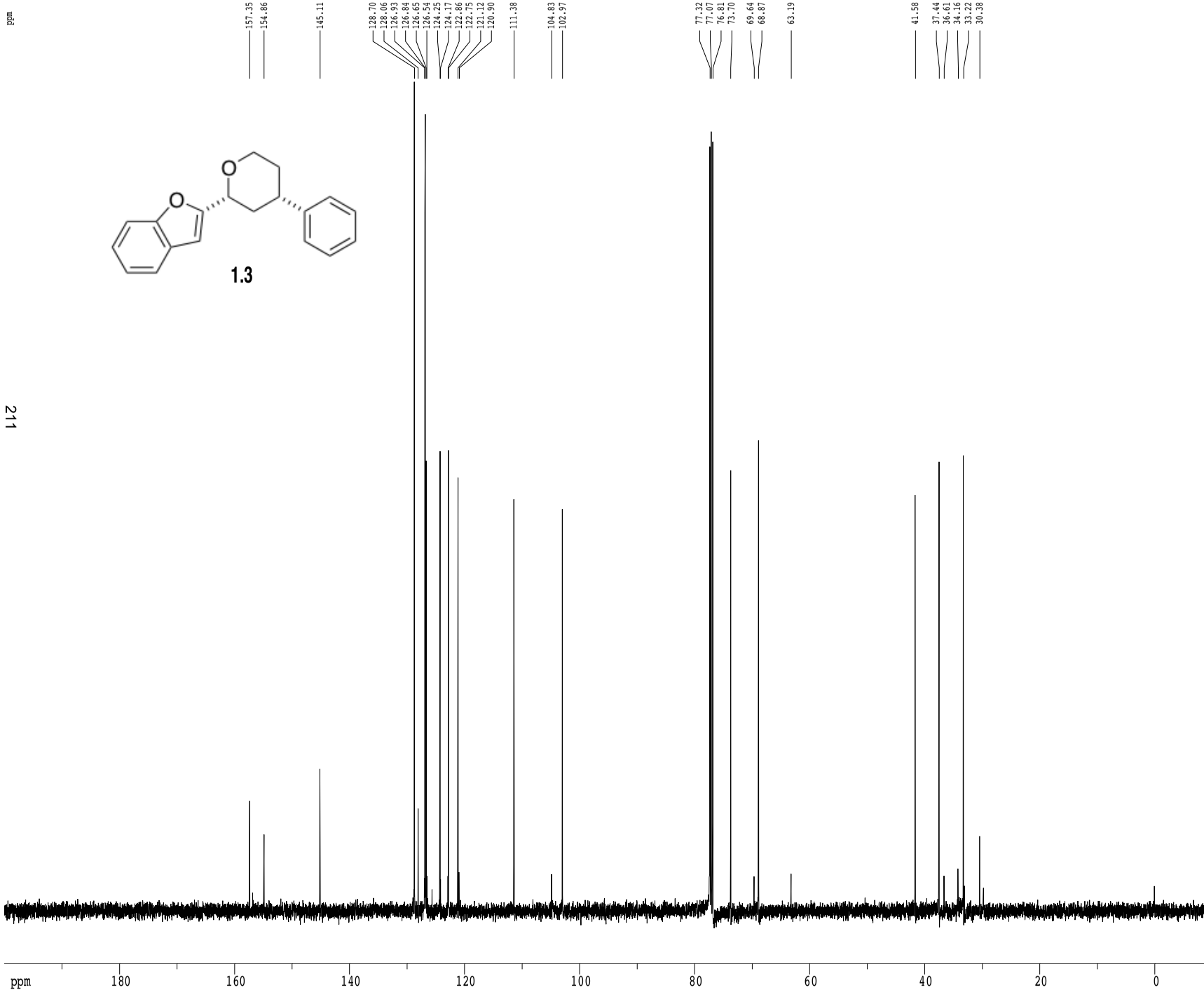
F2 - Acquisition Parameters
Date_          20171025
Time              12.08
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                    4
DW               62.400 usec
DE                6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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

F2 - Processing parameters
SI                 65536
SF          500.2200618 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42503 Hz/cm
```

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




```
Current Data Parameters
USER                 sanforda
NAME       ABS-1-053-carbon2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_             20171020
Time                 14.44
INSTRUM           cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   SpinEchopg30gp.prd
TD                   65536
SOLVENT              CDCl3
NS                     512
DS                      16
SWH               30303.031 Hz
FIDRES            0.462388 Hz
AQ                1.0813940 sec
RG                  7298.2
DW                  16.500 usec
DE                   6.00 usec
TE                  298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  33.10 usec

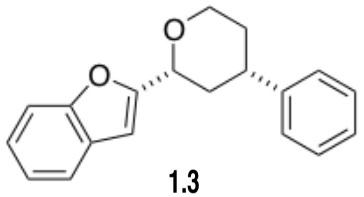
======== CHANNEL f1 ========
NUC1                   13C
P1                  16.55 usec
P11                500.00 usec
P12               2000.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP1                  2.70 dB
SP2                  2.70 dB
SPNAM1    Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1               0.00 Hz
SPOFF2               0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.50 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15               500.00 usec
p16              1000.00 usec

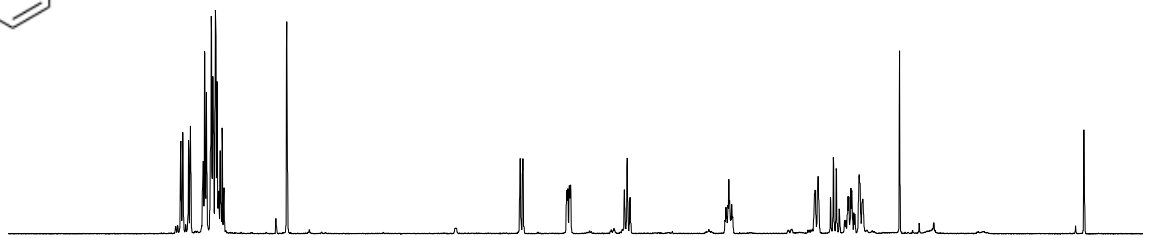
F2 - Processing parameters
SI                   65536
SF            125.7804190 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   2.00

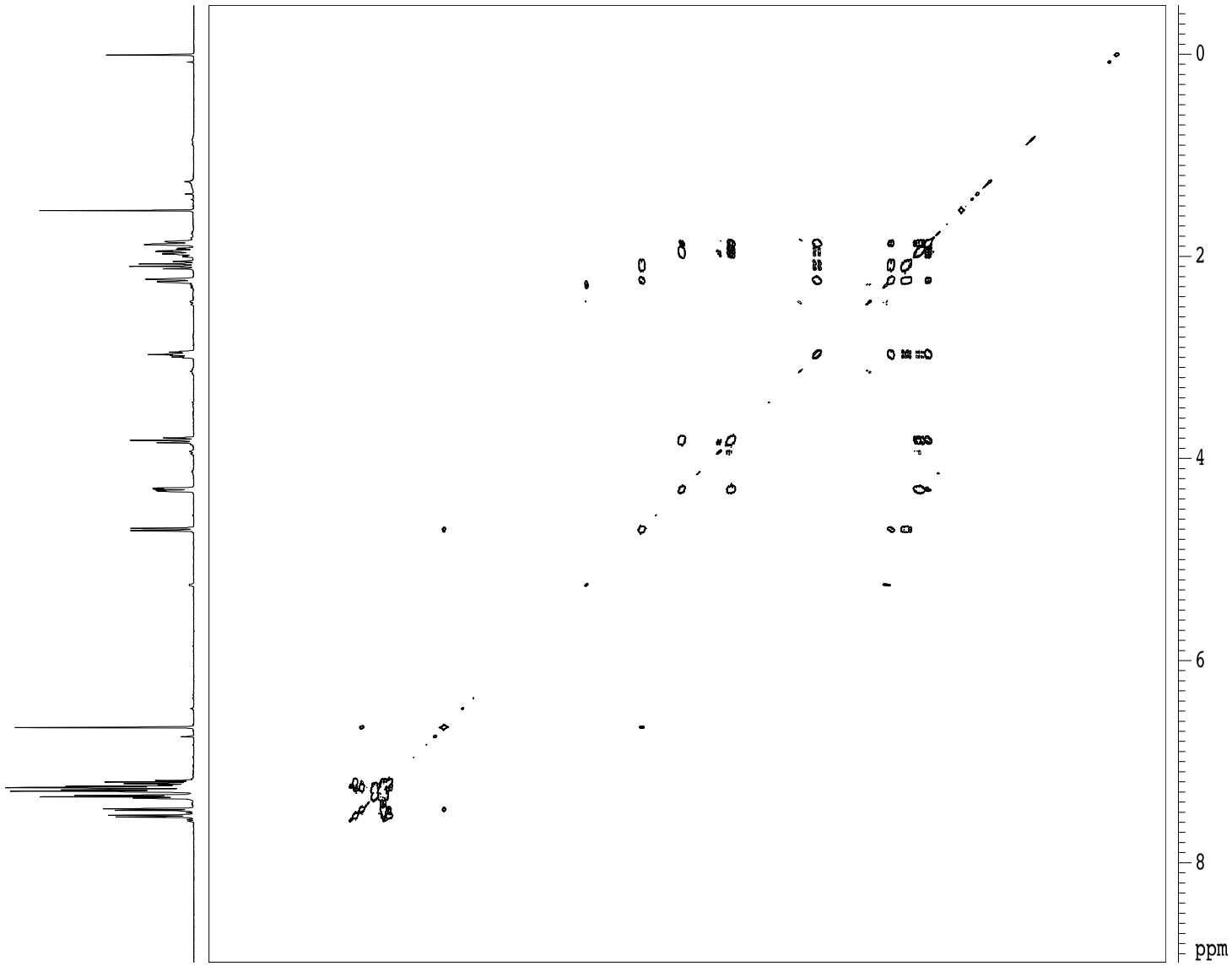
1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               200.000 ppm
F1              25156.08 Hz
F2P               -10.000 ppm
F2              -1257.80 Hz
PPMCM             9.21053 ppm/cm
HZCM           1158.50378 Hz/cm
```



1.3

gcosy60





212

Current Data Parameters

USER	sanforda
NAME	ABS-1-053-proton
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20171013
Time	10.19
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	2
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	228.1
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221605 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2222 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	undefined

F2 - Processing parameters

SI	1024
SF	500.2200346 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

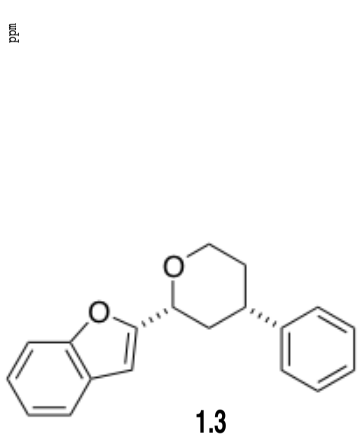
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200346 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.983 ppm
F2LO	4493.36 Hz
F2PHI	-0.483 ppm
F2HI	-241.49 Hz
F1PLO	8.983 ppm
F1LO	4493.36 Hz
F1PHI	-0.483 ppm
F1HI	-241.49 Hz
F2PPMCM	0.63104 ppm/cm
F2HZCM	315.65656 Hz/cm
F1PPMCM	0.63104 ppm/cm
F1HZCM	315.65656 Hz/cm

gnoe



1.3

Current Data Parameters
USER sanforda
NAME ABS-1-053-proton
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171013
Time 13.29
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoelcc.wu
TD 65536
SOLVENT CDCl3
NS 256
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec

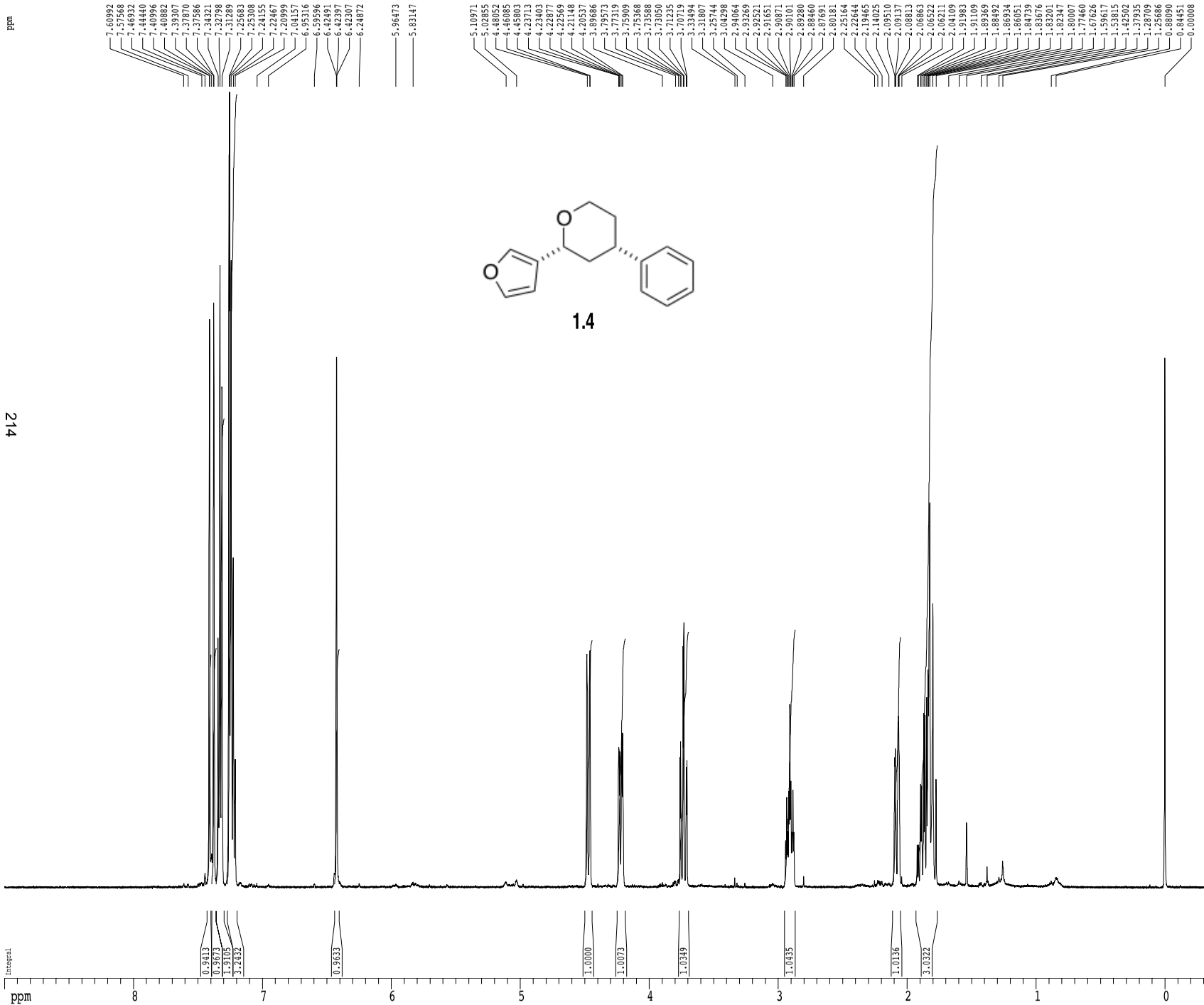
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P12 40000.00 usec
PL1 1.60 dB
SFO1 500.2223861 MHz
SP1 61.60 dB
SPNAM1 gauss1.512
SPOFF1 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-1-099-proton
EXPNO 1
PROCNO 1

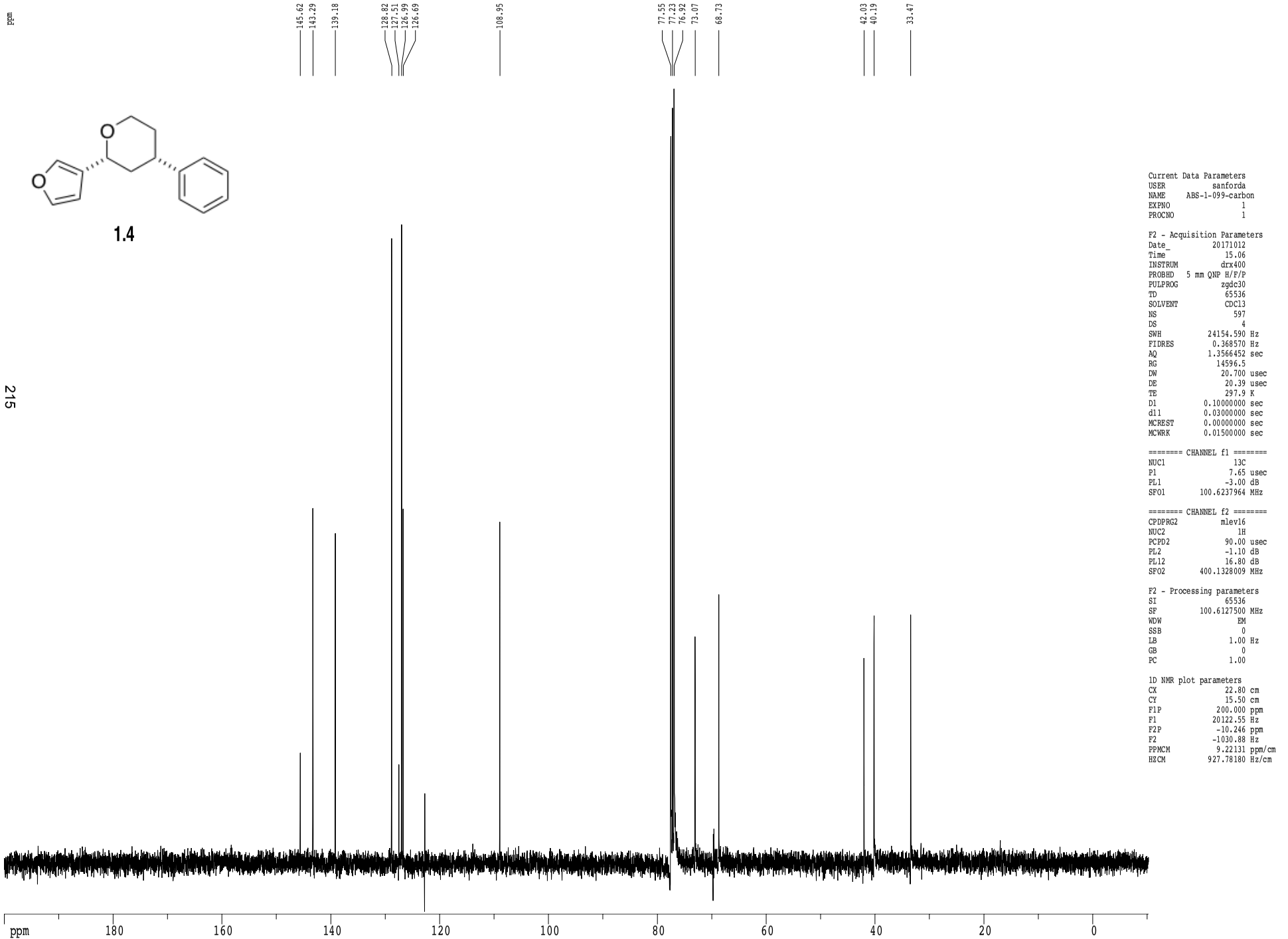
F2 - Acquisition Parameters
Date_ 20171012
Time 9.23
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200348 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

13C spectrum with 1H decoupling



1.4

Current Data Parameters
USER sanforda
NAME ABS-1-099-carbon
EXPNO 1
PROCNO 1

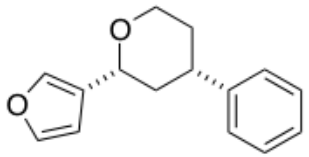
F2 - Acquisition Parameters
Date_ 20171012
Time 15.06
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 597
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 14596.5
DW 20.700 usec
DE 20.39 usec
TE 297.9 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 mlev16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

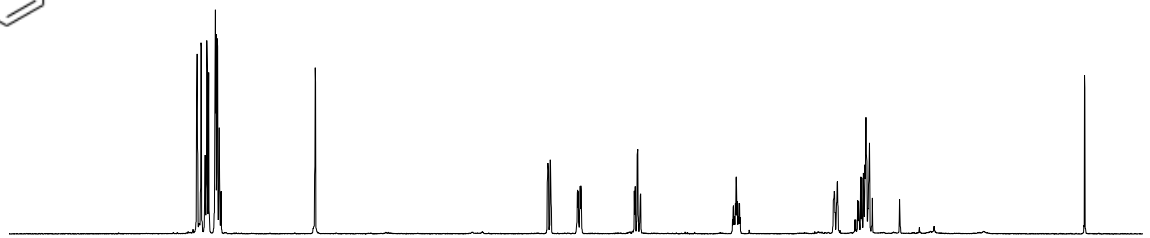
F2 - Processing parameters
SI 65536
SF 100.6127500 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

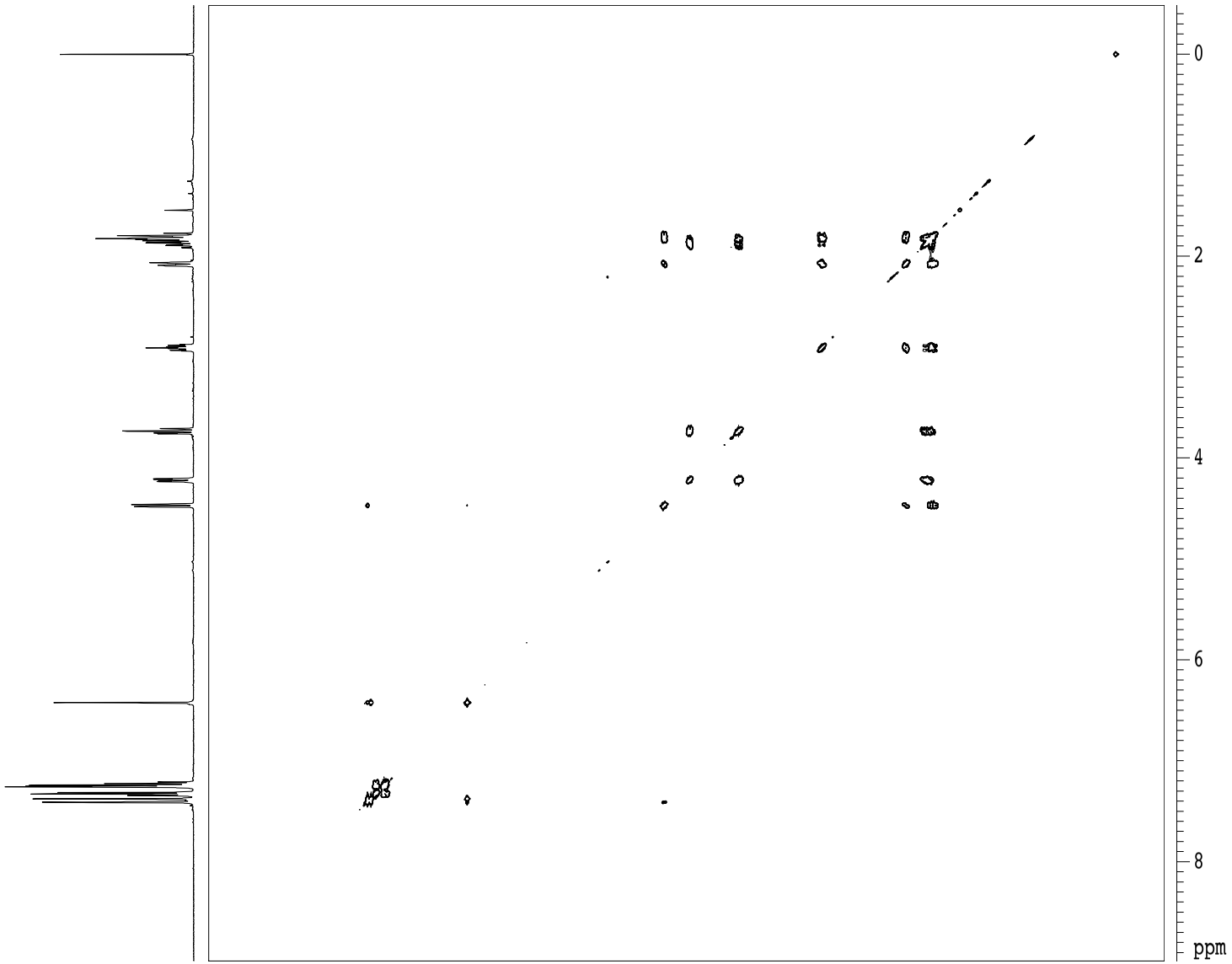
1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.246 ppm
F2 -1030.88 Hz
PPMCM 9.22131 ppm/cm
HZCM 927.78180 Hz/cm



1.4

gcosy60





216

Current Data Parameters

USER	sanforda
NAME	ABS-1-099-proton
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

Date_	20171012
Time	12.07
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	2
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	512
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221612 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2222 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	undefined

F2 - Processing parameters

SI	1024
SF	500.2200353 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

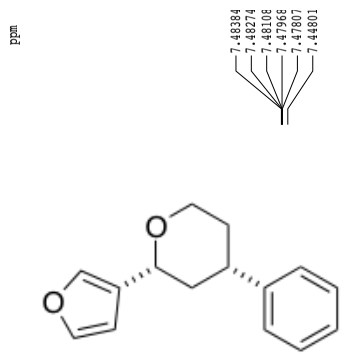
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200353 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.983 ppm
F2LO	4493.36 Hz
F2PHI	-0.483 ppm
F2HI	-241.49 Hz
F1PLO	8.983 ppm
F1LO	4493.36 Hz
F1PHI	-0.483 ppm
F1HI	-241.49 Hz
F2PPMCM	0.63104 ppm/cm
F2HZCM	315.65656 Hz/cm
F1PPMCM	0.63104 ppm/cm
F1HZCM	315.65656 Hz/cm

gnoe



1.4

Current Data Parameters
USER sanforda
NAME ABS-1-099-proton
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171012
Time 9.50
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoelcc.wu
TD 65536
SOLVENT CDCl3
NS 256
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec

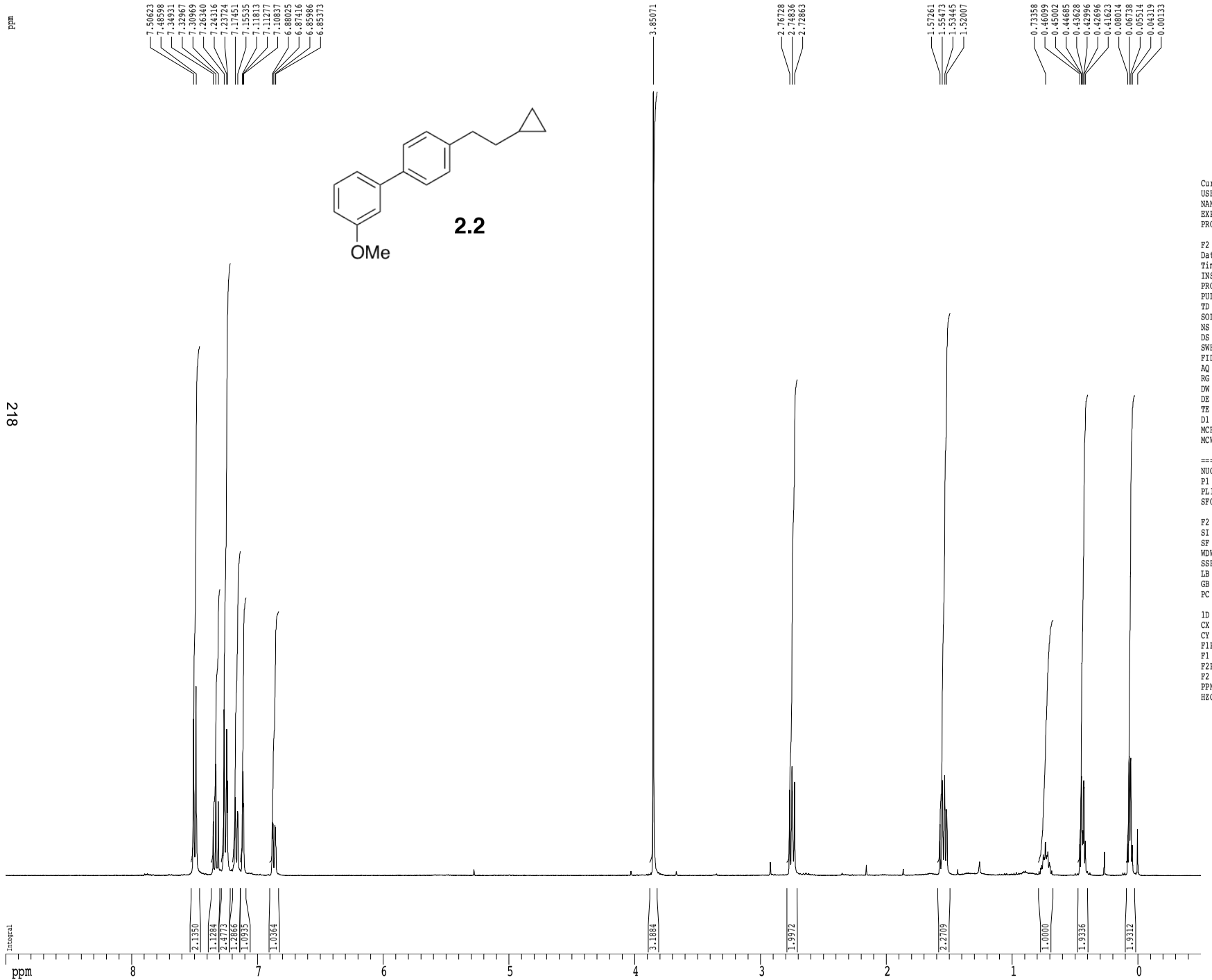
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P12 40000.00 usec
PL1 1.60 dB
SFO1 500.2222712 MHz
SP1 61.60 dB
SPNAM1 gauss1.512
SPOFF1 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm

1H spectrum




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-065-pure
EXPNO                   1
PROCNO                  1

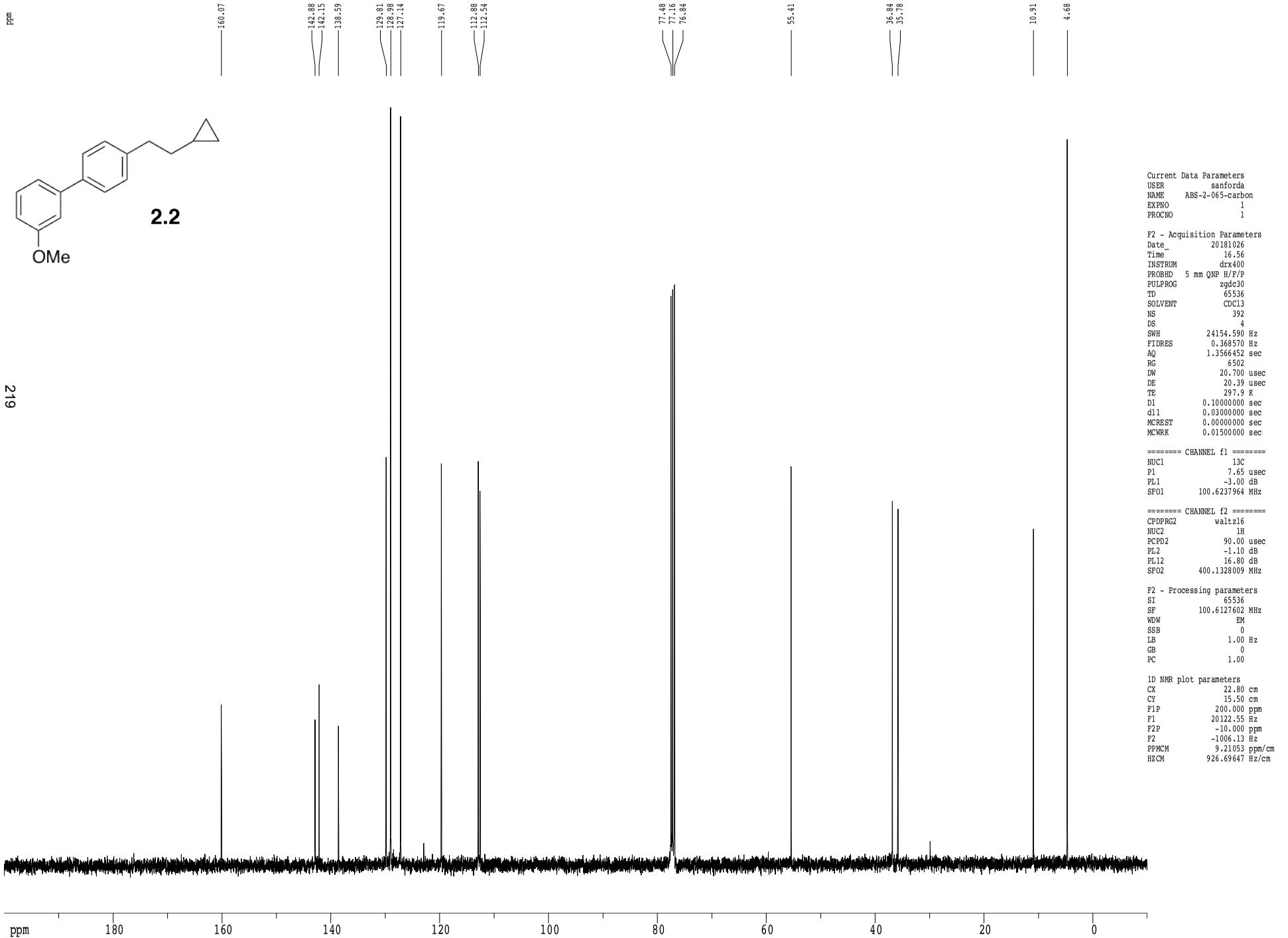
F2 - Acquisition Parameters
Date_            20181025
Time                19.24
INSTRUM            drx400
PROBHD   5 mm QNP H/F/P
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              6410.256 Hz
FIDRES           0.097813 Hz
AQ               5.1118579 sec
RG                  161.3
DW                 78.000 usec
DE                  4.50 usec
TE                 298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======= CHANNEL f1 =======
NUC1                   1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                  65536
SF           400.1300304 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                 2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                 9.000 ppm
F1               3601.17 Hz
F2P                -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-2-065-carbon
EXPNO 1
PROCNO 1

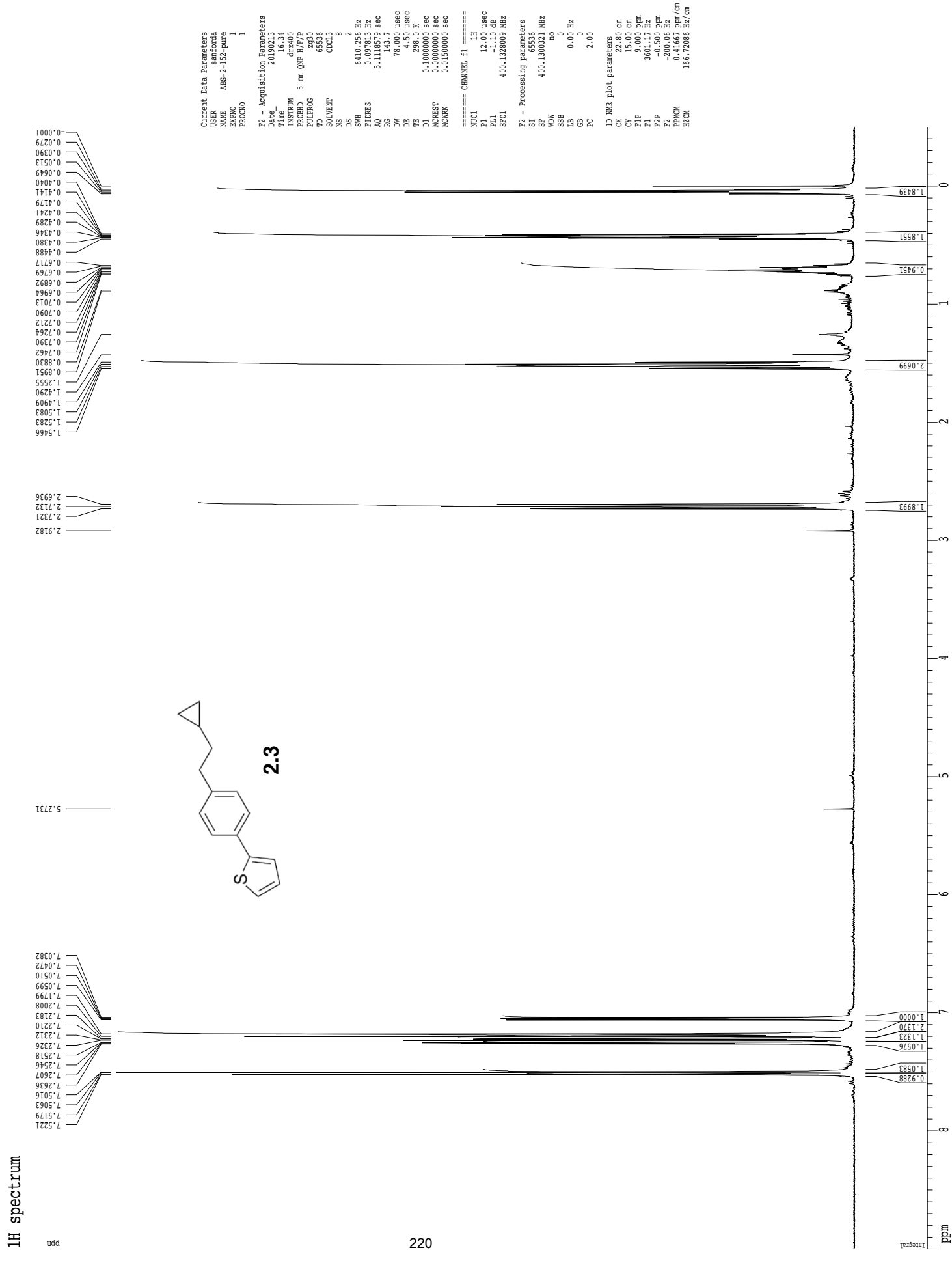
F2 - Acquisition Parameters
Date_ 20181026
Time 16.56
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 392
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 6502
DW 20.700 usec
DE 20.39 usec
TE 297.9 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

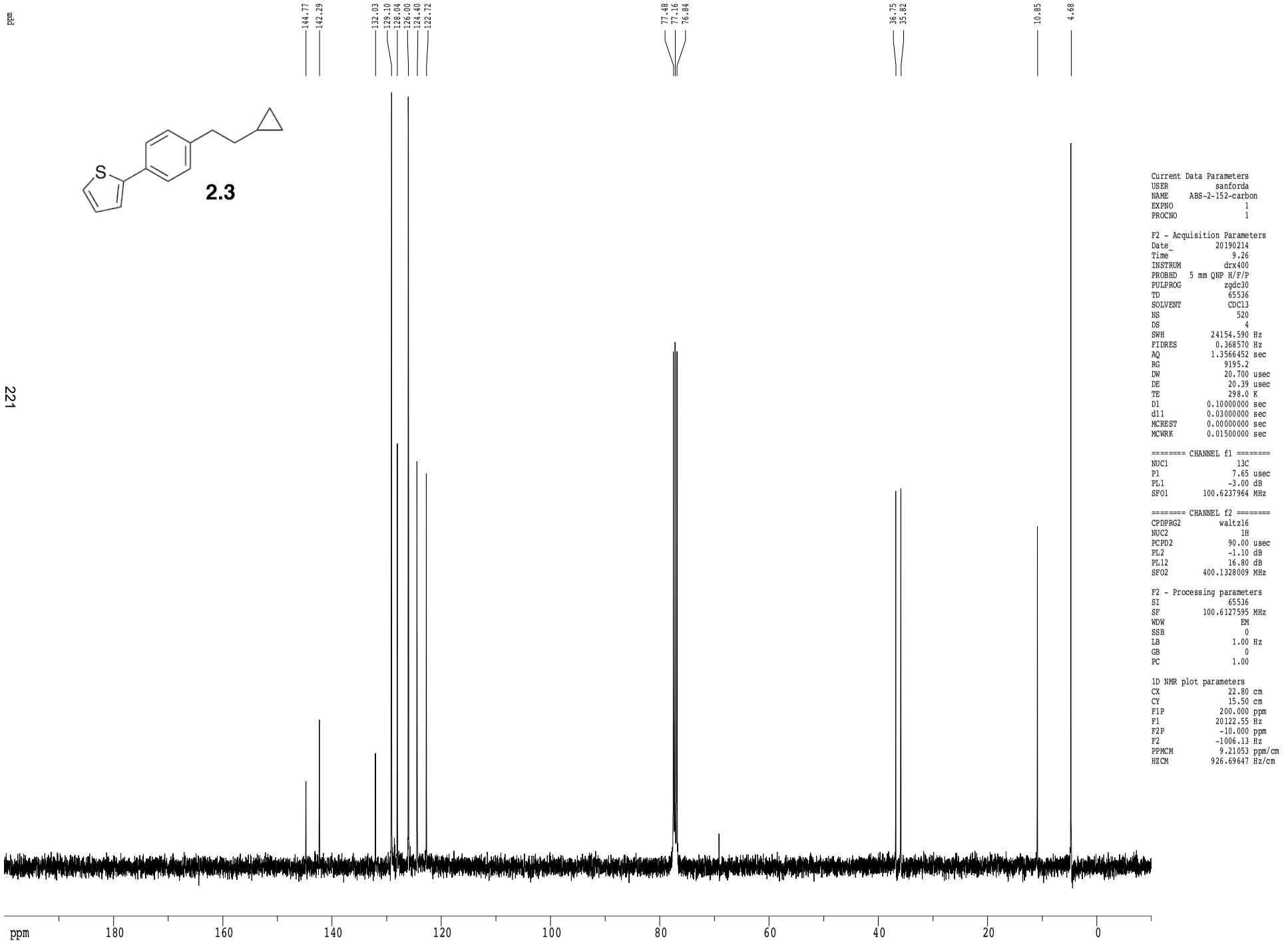
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127602 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69647 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-152-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190213
Time_ 16.34
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 143.7
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300321 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
2.3
S
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-2-152-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190214
Time 9.26
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 520
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

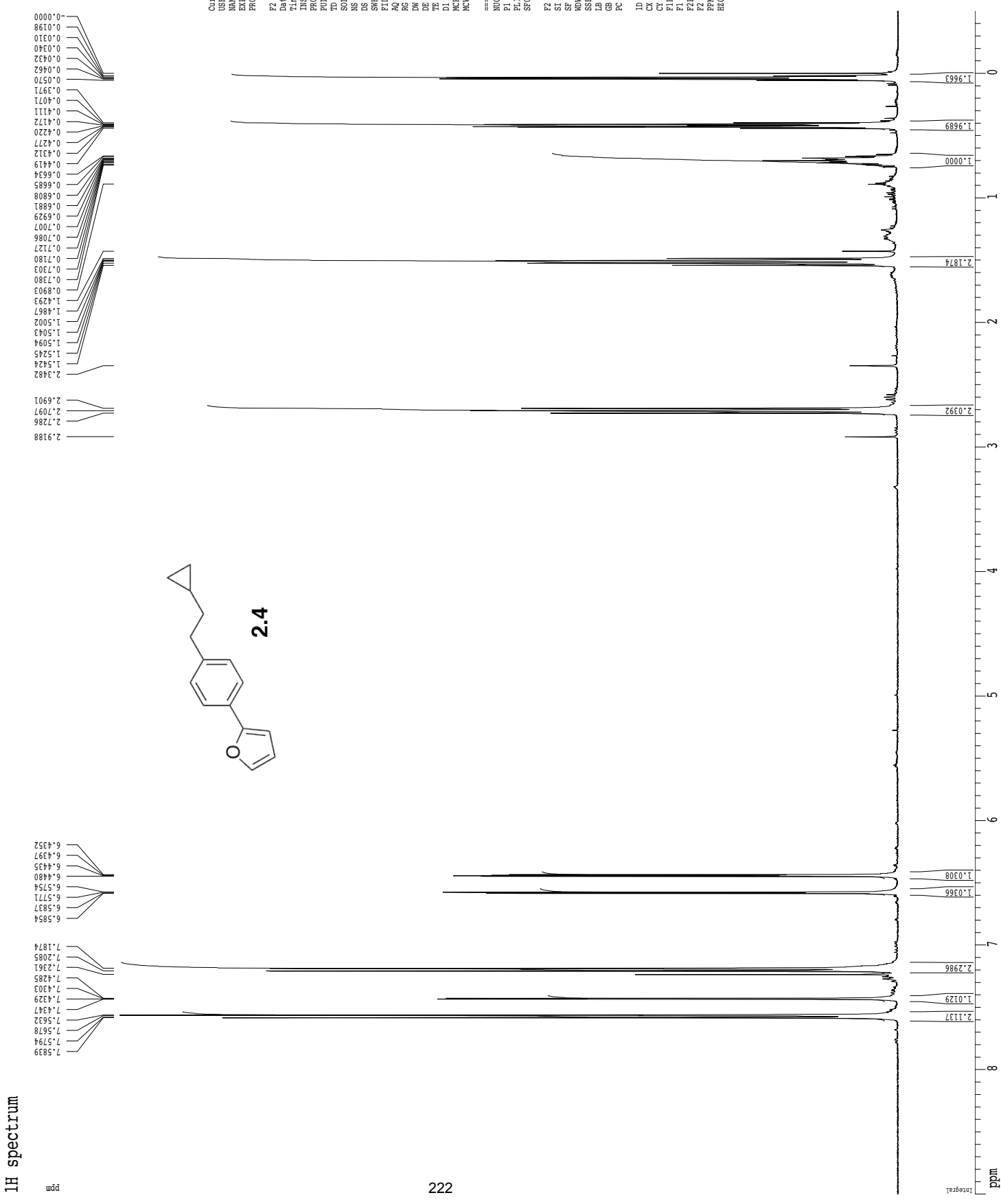
======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

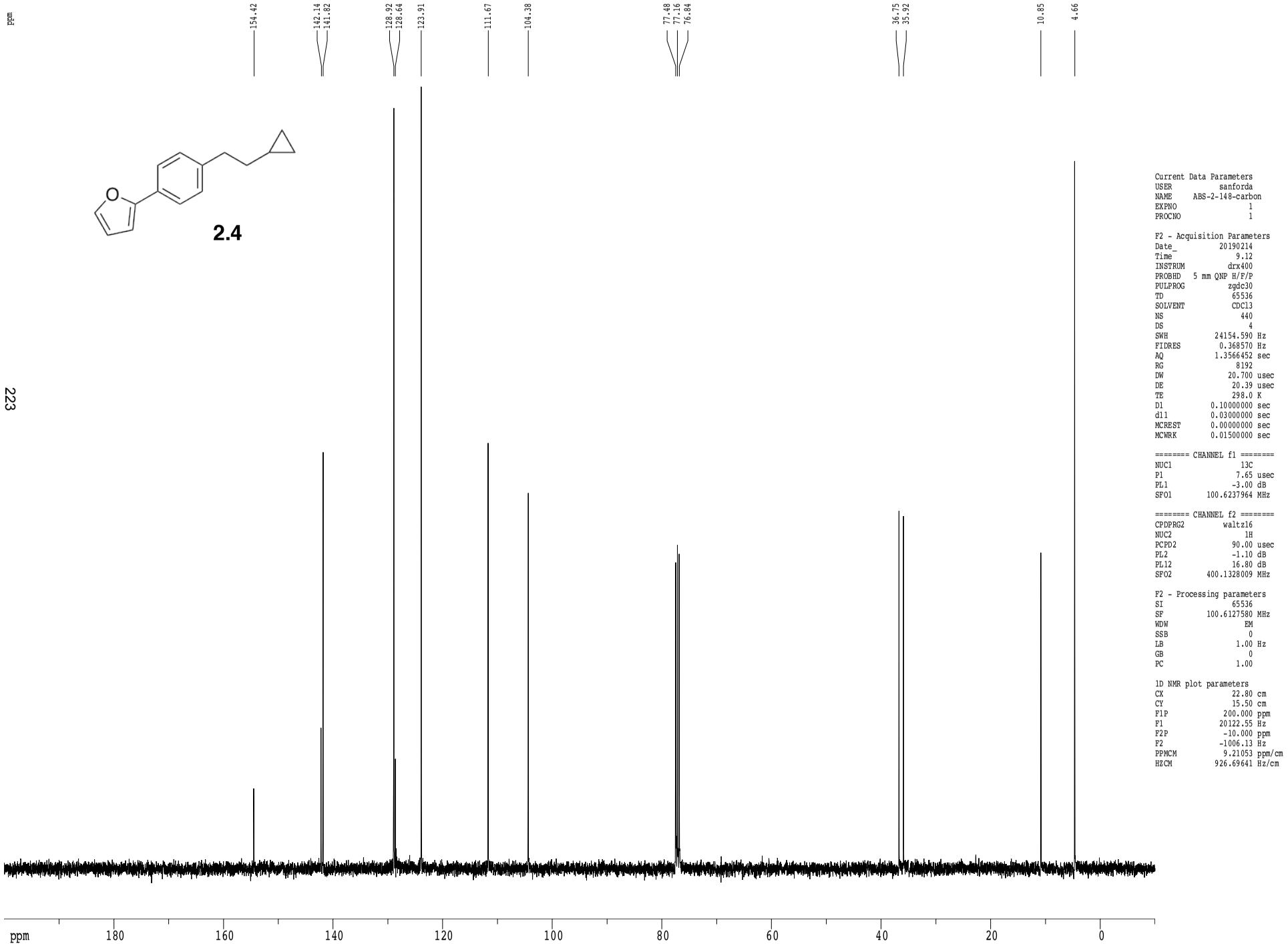
F2 - Processing parameters
SI 65536
SF 100.6127595 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69647 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-148-pure-2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190213
Time_ 16.38
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 143.7
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300307 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.0000
0.0198
0.0310
0.0340
0.0432
0.0462
0.0570
0.3971
0.4071
0.4111
0.4172
0.4220
0.4277
0.4312
0.4419
0.6634
0.6685
0.6808
0.6881
0.6929
0.7007
0.7086
0.7127
0.7180
0.7303
0.7380
0.8903
1.4293
1.4867
1.5002
1.5043
1.5094
1.5245
1.5424
2.3482
2.6901
2.7097
2.7286
2.9188
6.4352
6.4397
6.4435
6.4480
6.5754
6.5771
6.5837
6.5854
7.1874
7.2085
7.2361
7.4285
7.4303
7.4329
7.4447
7.5632
7.5678
7.5794
7.5839
2.4
O
1.9663
1.9689
1.0000
2.1874
2.0392
1.0308
1.0356
2.2986
1.0129
2.1137
ppm
Integral

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-2-148-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190214
Time 9.12
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 440
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 8192
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

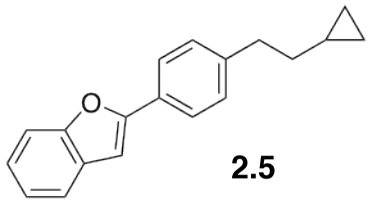
======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127580 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69641 Hz/cm

1H spectrum



2.5

224

Current Data Parameters
USER sanforda
NAME ABS-2-131-pure
EXPNO 1
PROCNO 1

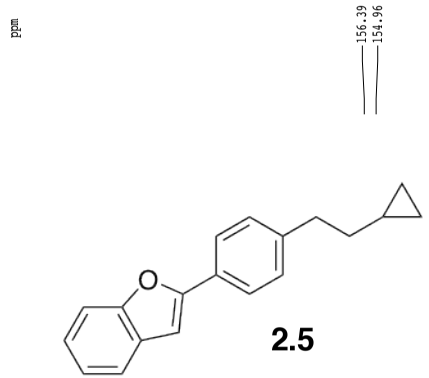
F2 - Acquisition Parameters
Date_ 20190119
Time 13.13
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 143.7
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300324 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

13C spectrum with 1H decoupling



2.5

Current Data Parameters
USER sanforda
NAME ABS-2-131-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190119
Time 13.17
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 352
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

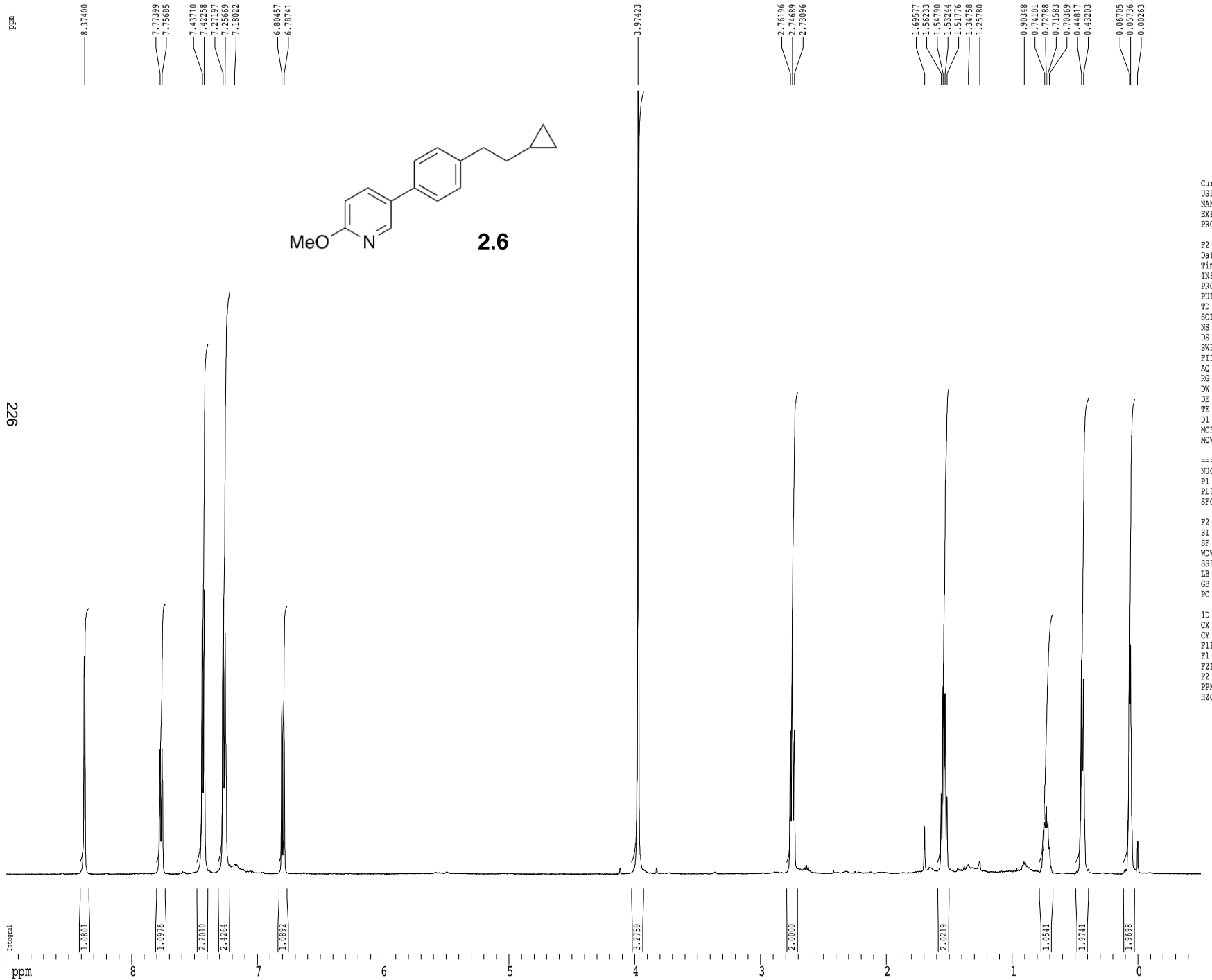
======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127591 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69647 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-141-proton
EXPNO 1
PROCNO 1

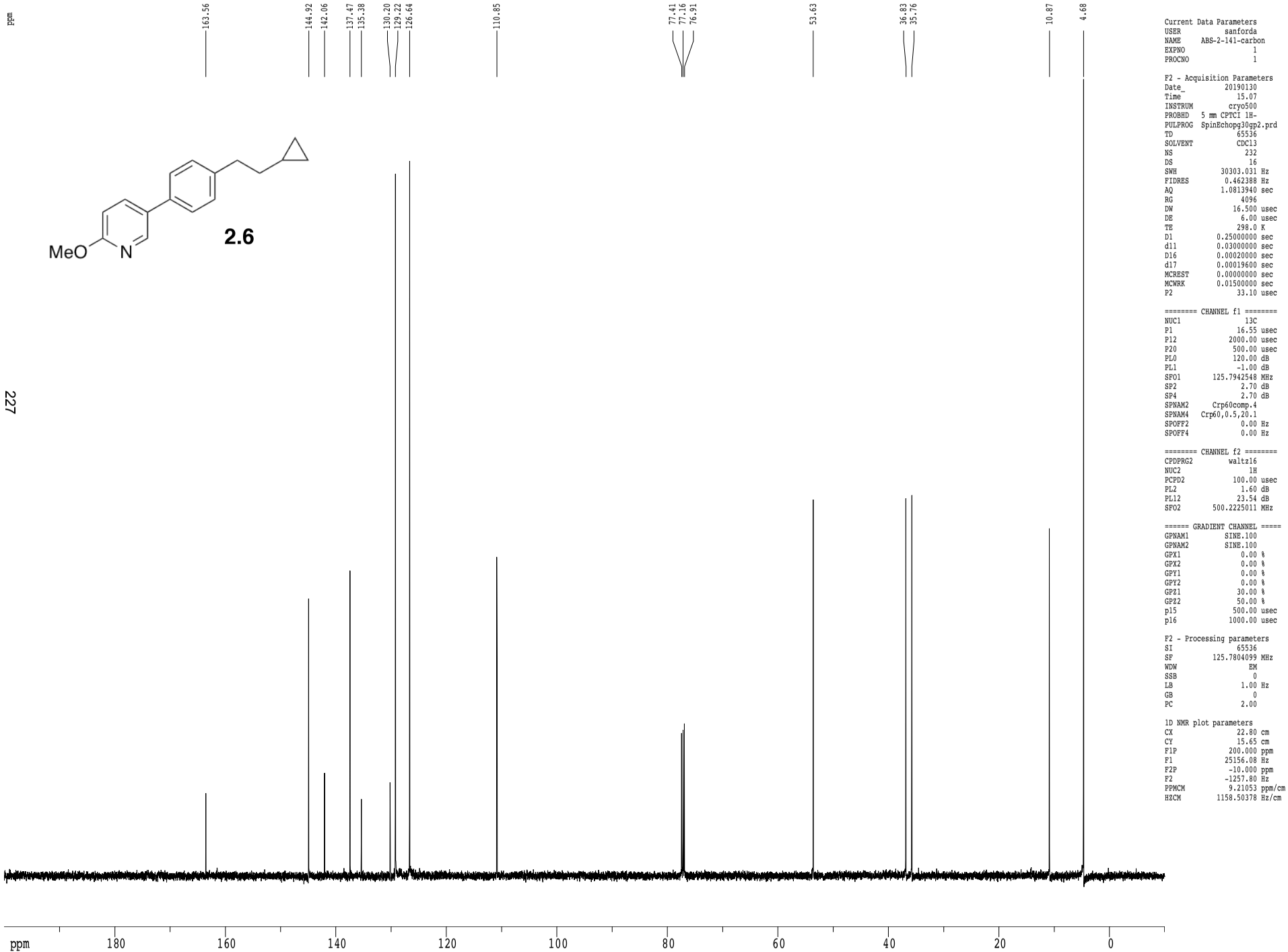
F2 - Acquisition Parameters
Date_ 20190130
Time 15.04
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200381 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

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



Current Data Parameters
USER sanforda
NAME ABS-2-141-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190130
Time 15.07
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 232
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 4096
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

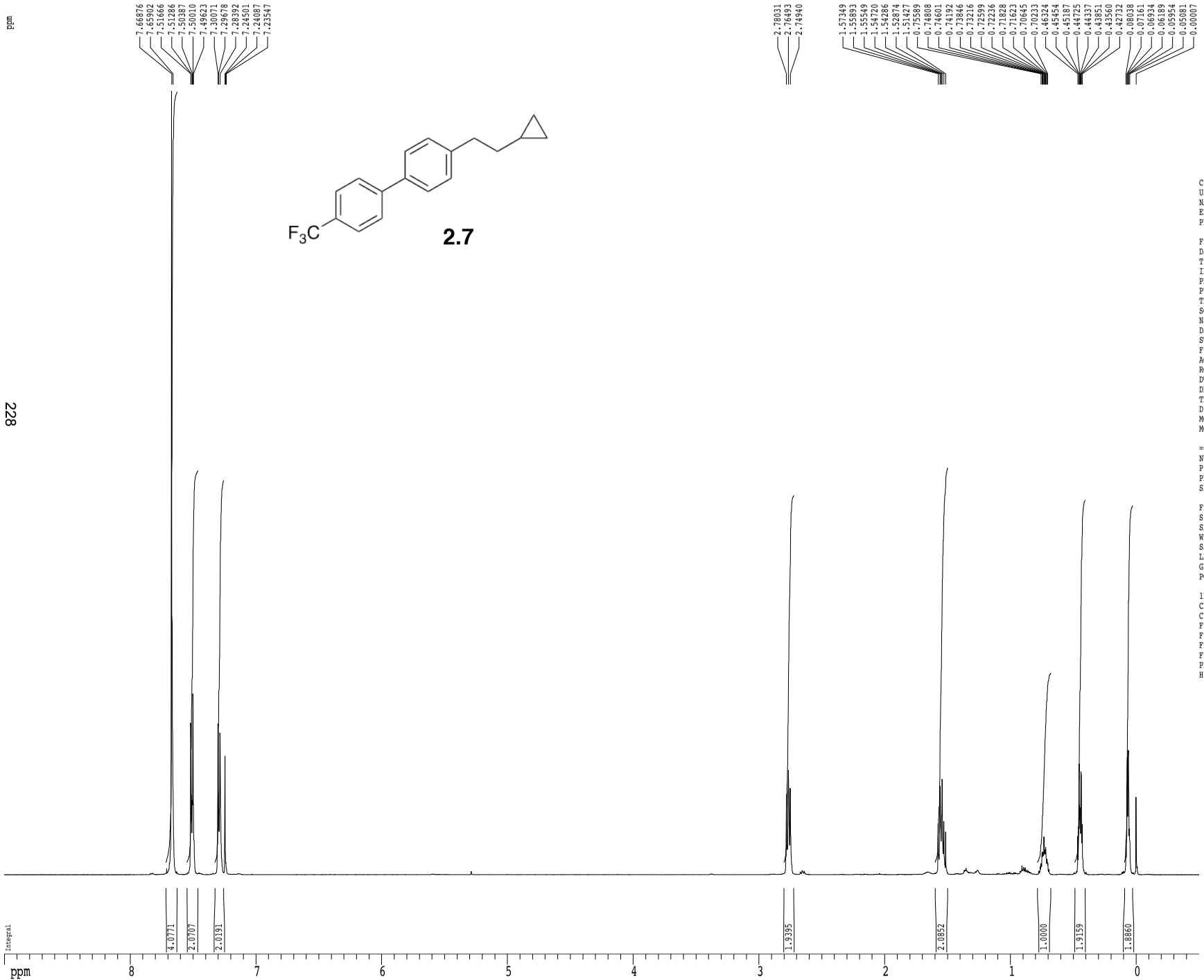
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804099 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-133-proton-2
EXPNO 1
PROCNO 1

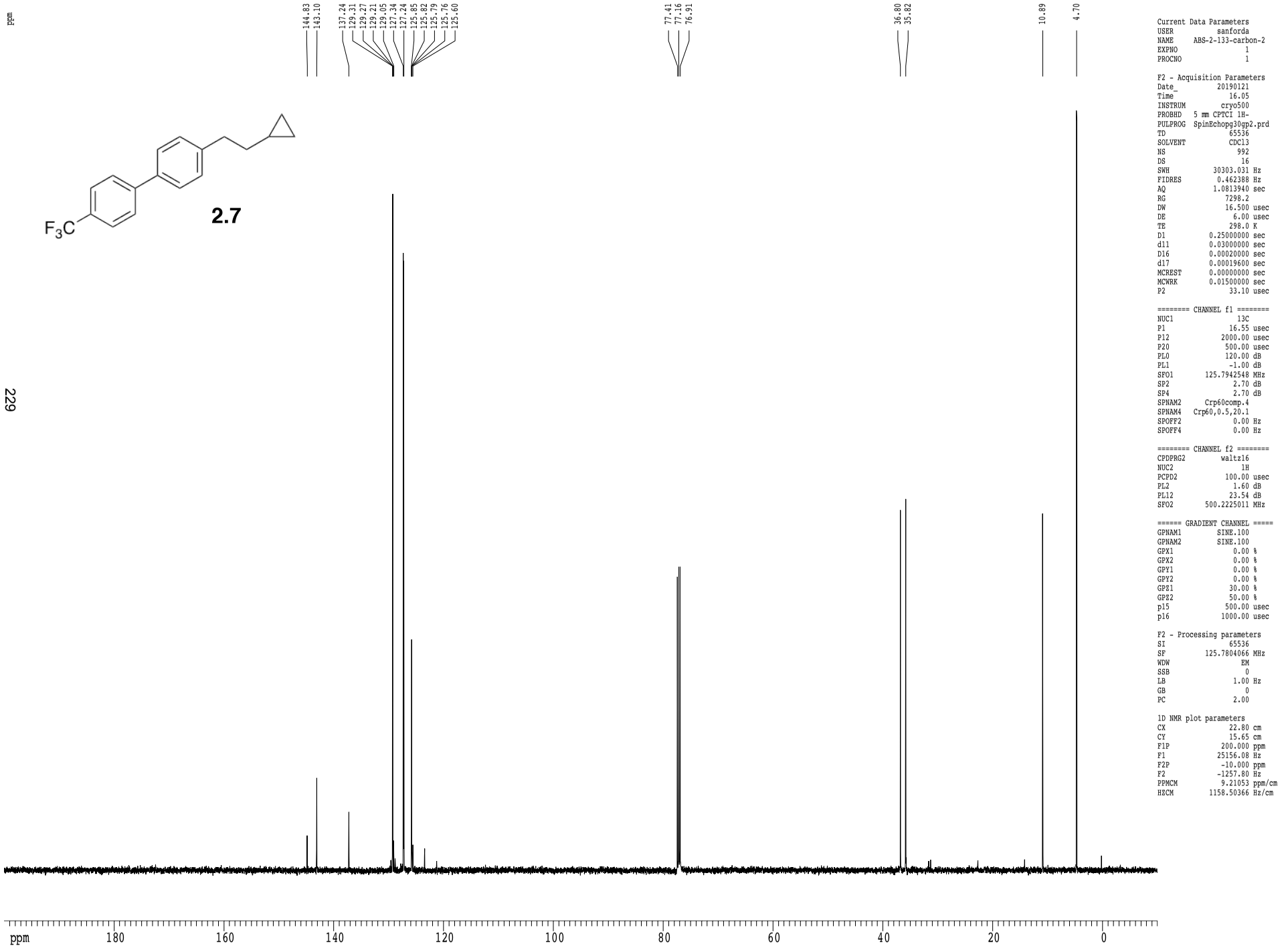
F2 - Acquisition Parameters
Date_ 20190121
Time 16.29
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 11.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200402 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

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



Current Data Parameters
USER sanforda
NAME ABS-2-133-carbon-2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190121
Time 16.05
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 992
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

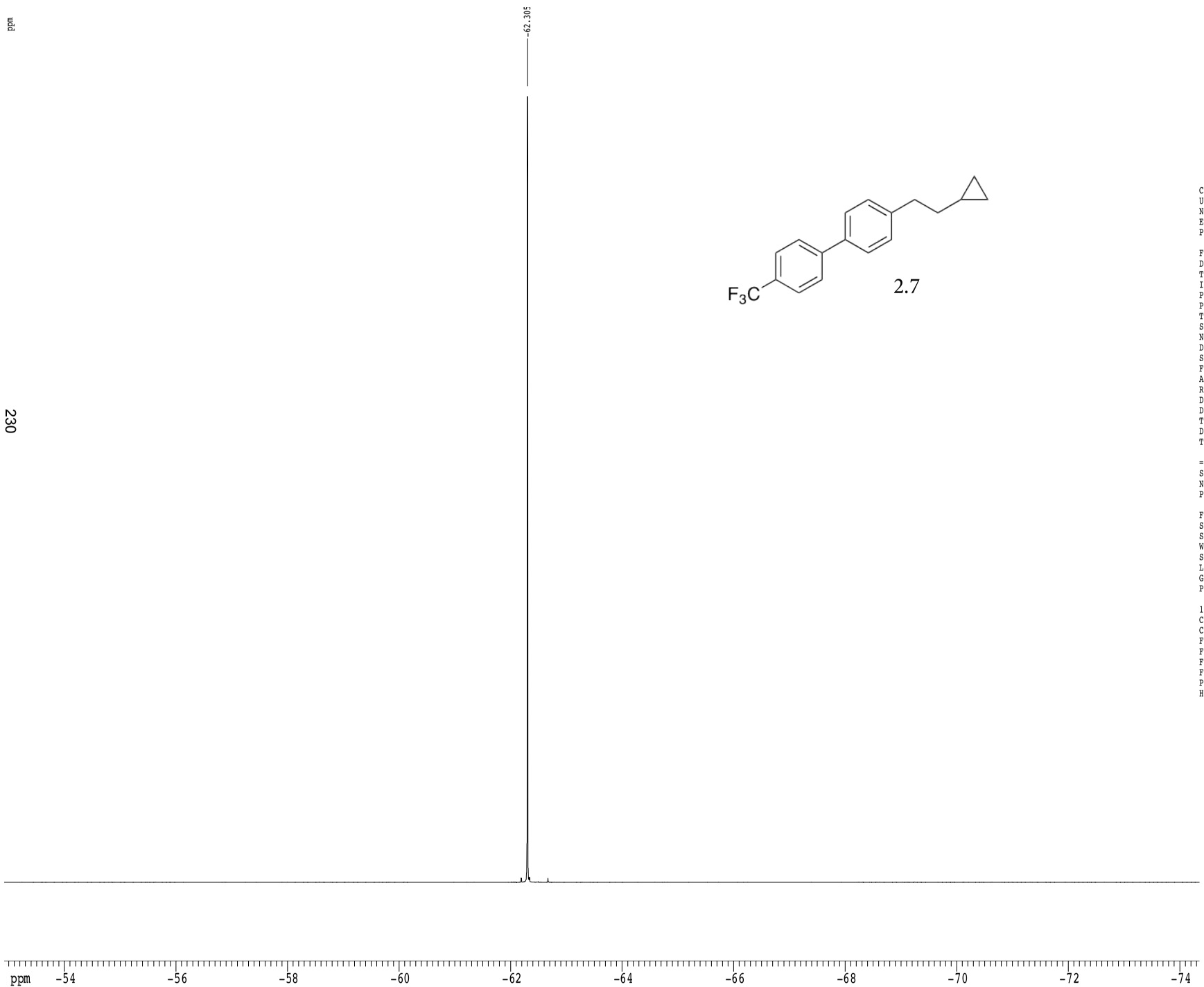
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804066 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50366 Hz/cm

19F spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-133-F
EXPNO 2
PROCNO 1

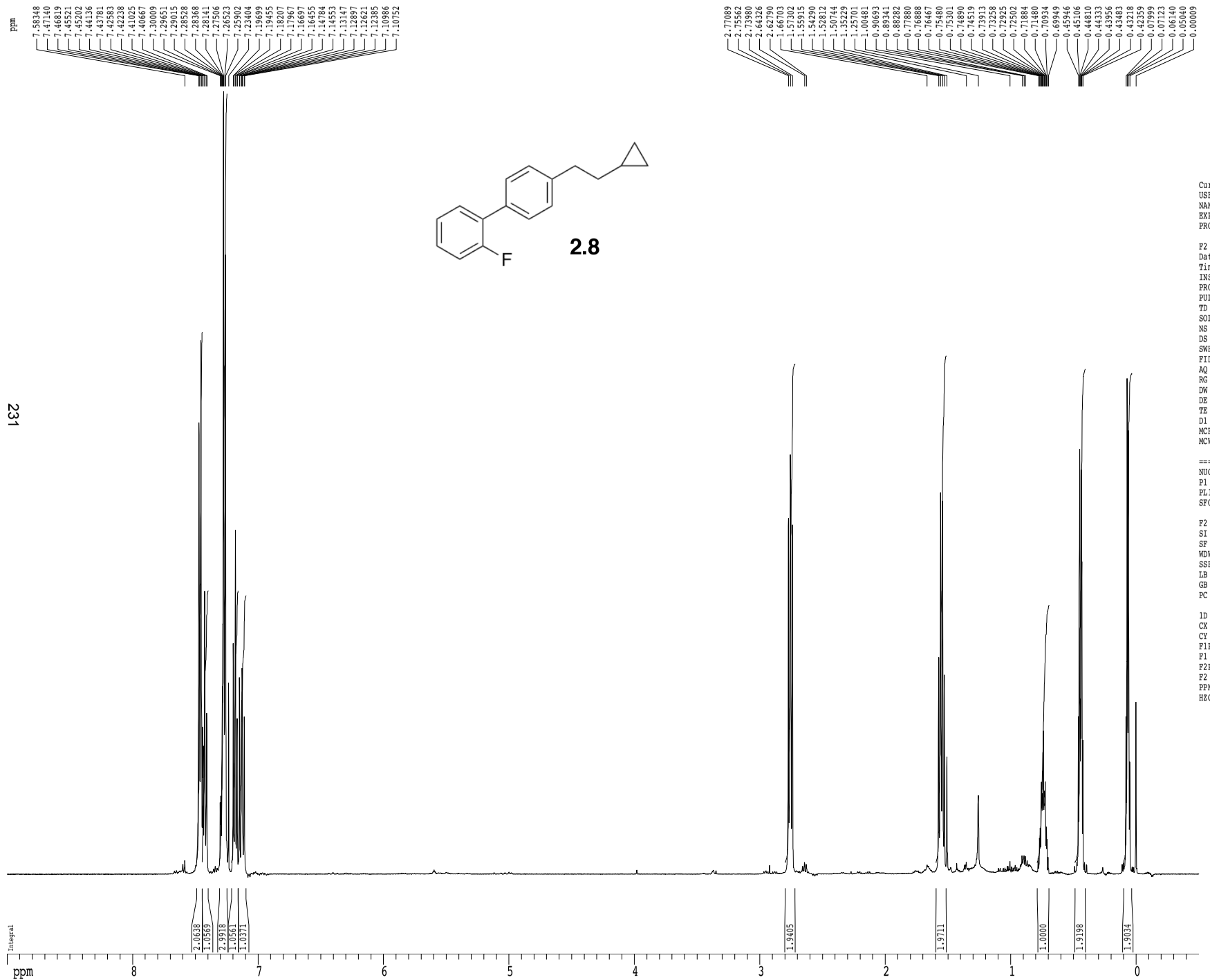
F2 - Acquisition Parameters
Date_ 20191220
Time 12.29
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgflqn30
TD 36288
SOLVENT CDCl3
NS 16
DS 2
SWH 12096.774 Hz
FIDRES 0.333355 Hz
AQ 1.4999540 sec
RG 575
DW 41.333 usec
DE 18.00 usec
TE 298.0 K
D1 3.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 564.6504512 MHz
NUC1 19F
P1 17.50 usec

F2 - Processing parameters
SI 131072
SF 564.6863858 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P -52.925 ppm
F1 -29886.19 Hz
F2P -74.347 ppm
F2 -41982.96 Hz
PPMCM 0.93957 ppm/cm
HZCM 530.56024 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-097-proton
EXPNO 1
PROCNO 1

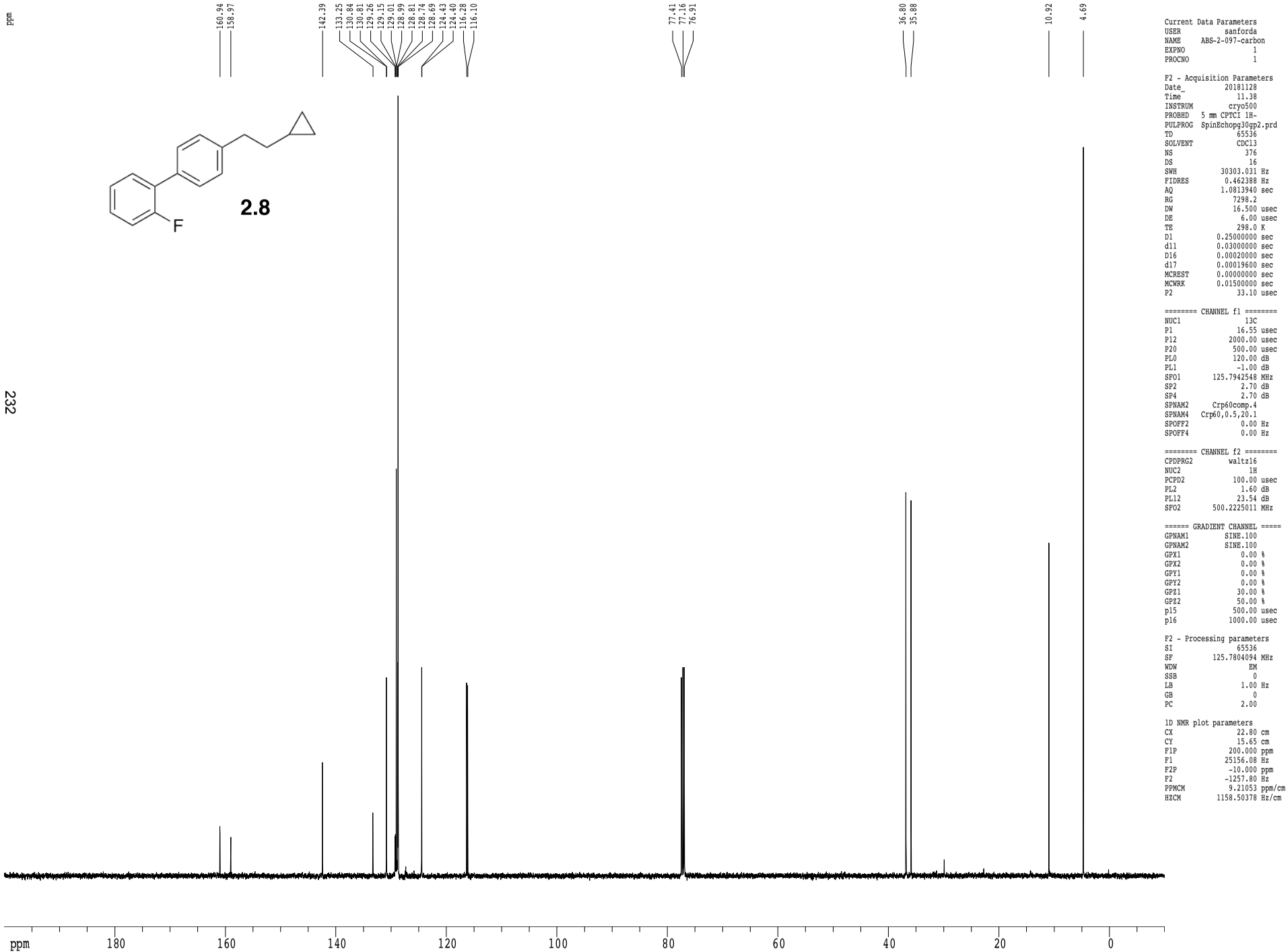
F2 - Acquisition Parameters
Date_ 20181128
Time 11.46
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200451 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

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



Current Data Parameters
USER sanforda
NAME ABS-2-097-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181128
Time 11.38
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 376
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

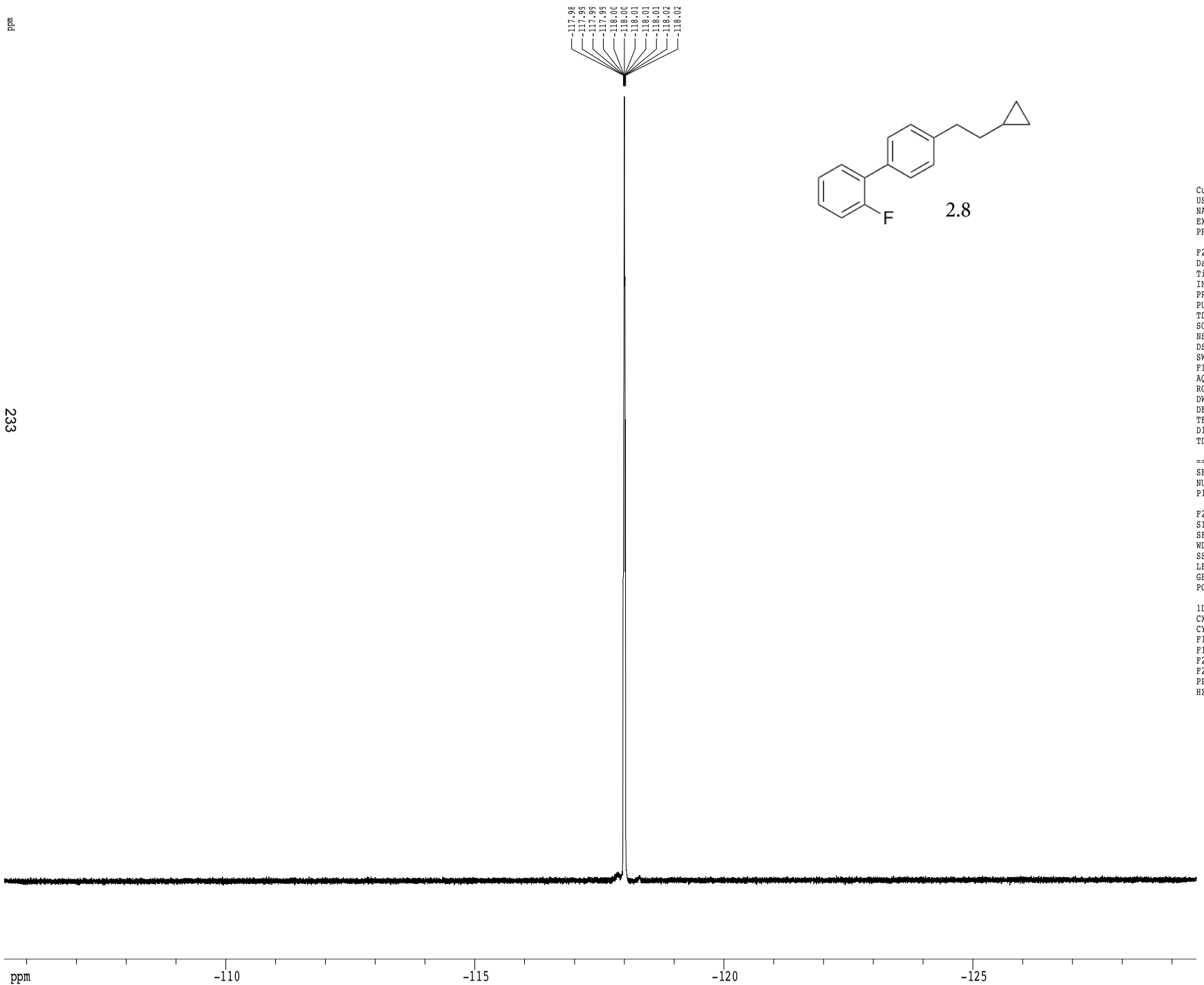
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804094 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

19F spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-097-F
EXPNO 4
PROCNO 1

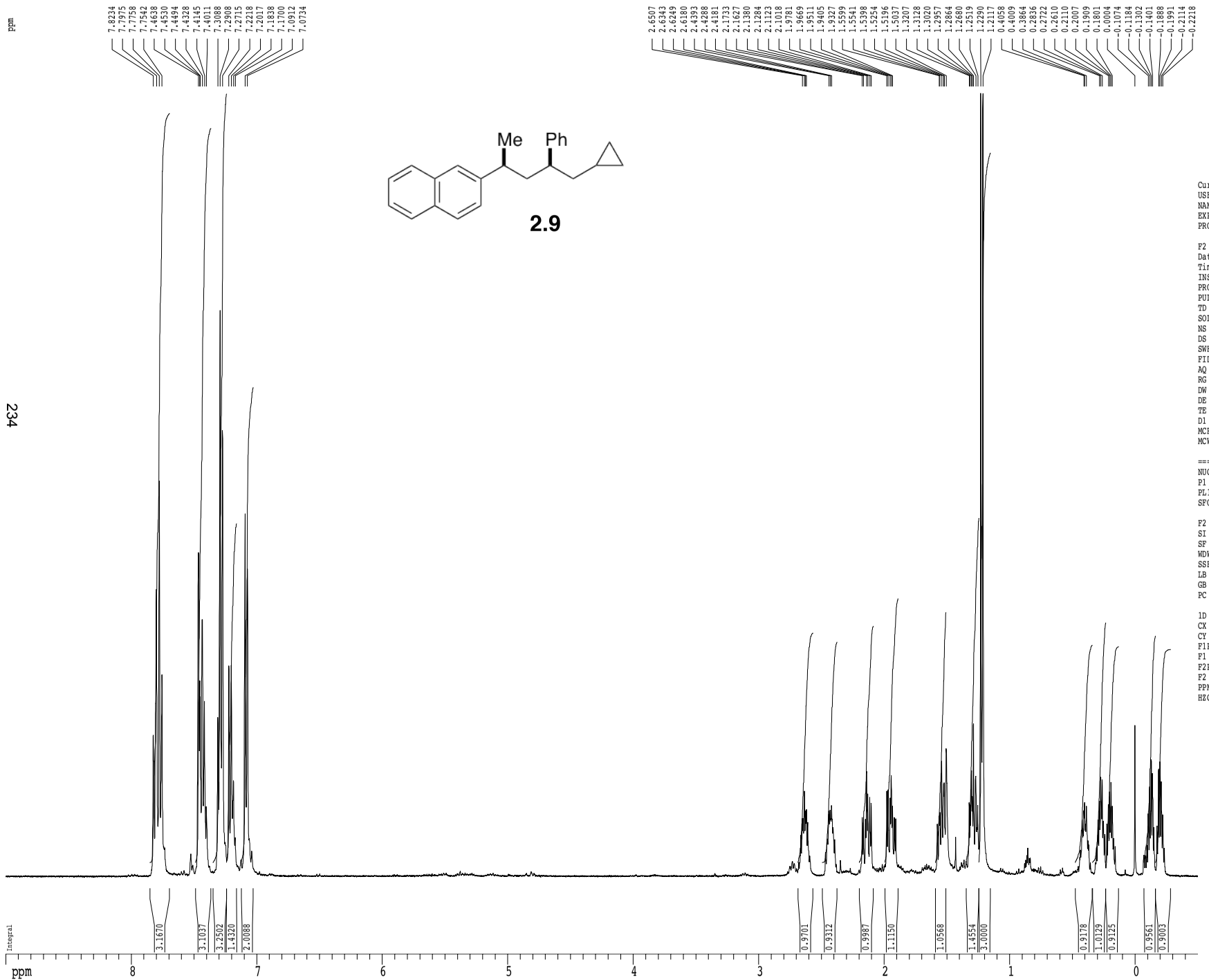
F2 - Acquisition Parameters
Date_ 20191220
Time 12.38
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgflqn30
TD 40538
SOLVENT CDCl3
NS 16
DS 2
SWH 13513.514 Hz
FIDRES 0.333354 Hz
AQ 1.4999560 sec
RG 575
DW 37.000 usec
DE 18.00 usec
TE 298.0 K
D1 3.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 564.6200238 MHz
NUC1 19F
P1 17.50 usec

F2 - Processing parameters
SI 131072
SF 564.6863858 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P -105.554 ppm
F1 -59605.18 Hz
F2P -129.486 ppm
F2 -73118.70 Hz
PPMCM 1.04961 ppm/cm
HZCM 592.69818 Hz/cm

1H spectrum




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-206-pure
EXPNO                   1
PROCNO                  1

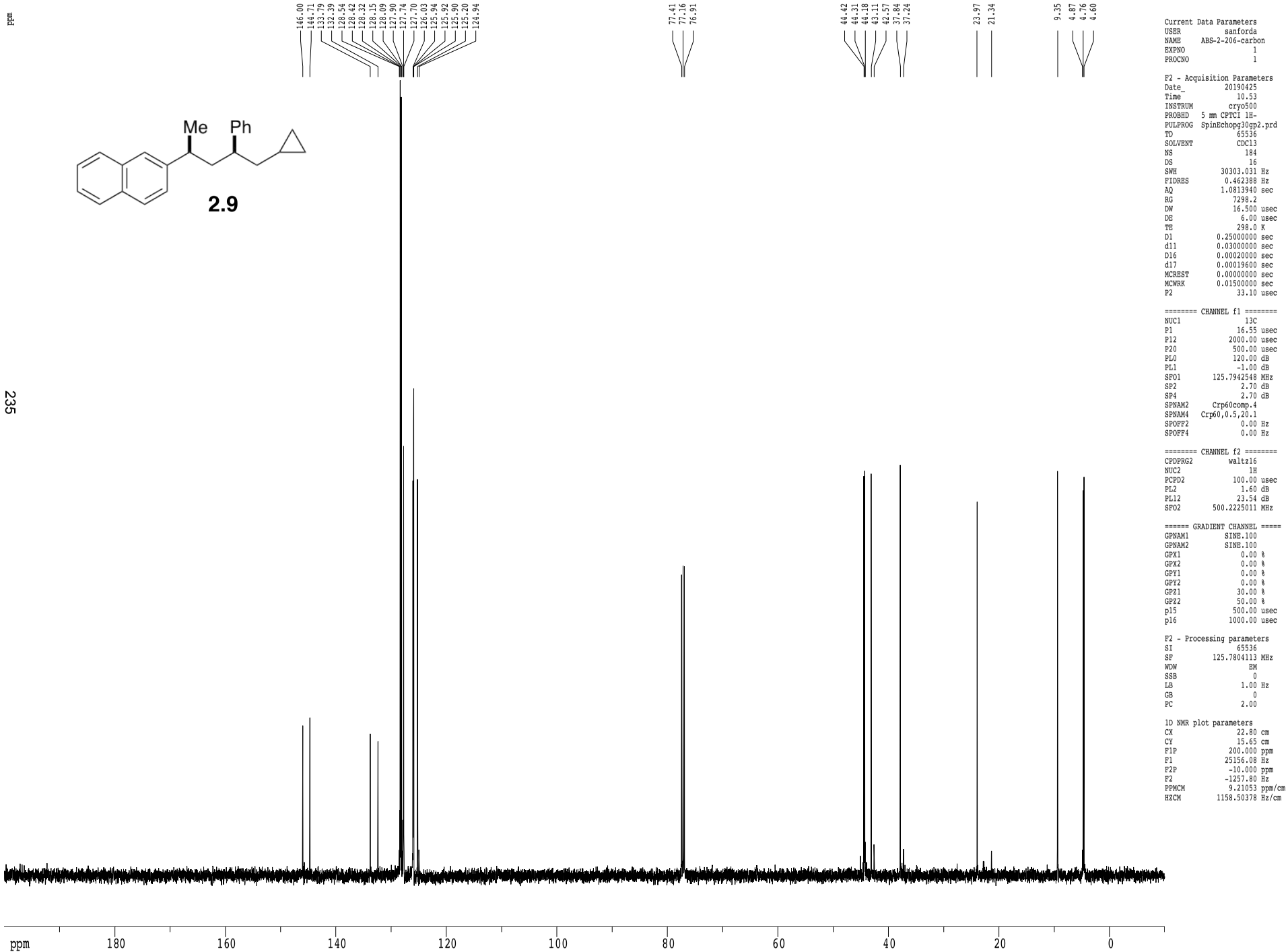
F2 - Acquisition Parameters
Date_            20190425
Time                10.05
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ              5.1118579 sec
RG                   128
DW                78.000 usec
DE                 4.50 usec
TE                298.1 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======= CHANNEL f1 =======
NUC1                   1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300361 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                 9.000 ppm
F1               3601.17 Hz
F2P                -0.500 ppm
F2               -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-2-206-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190425
Time 10.53
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 184
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

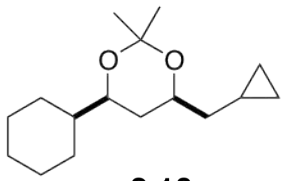
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804113 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



2.10


```
Current Data Parameters
USER            sanforda
NAME      ABS-2-ace-proton
EXPNO                  1
PROCNO                 1

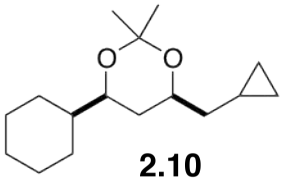
F2 - Acquisition Parameters
Date_           20190906
Time              16.24
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES         0.097813 Hz
AQ            5.1118579 sec
RG                203.2
DW             78.000 usec
DE              4.50 usec
TE              298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======= CHANNEL f1 =======
NUC1                 1H
P1              12.00 usec
PL1             -1.10 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                65536
SF          400.1300203 MHz
WDW                  no
SSB                   0
LB              0.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX              22.80 cm
CY              15.00 cm
F1P              9.000 ppm
F1            3601.17 Hz
F2P             -0.500 ppm
F2            -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM         166.72086 Hz/cm
```

13C spectrum with 1H decoupling



2.10

Current Data Parameters
USER sanforda
NAME ABS-2-acetonide-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190904
Time 14.32
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 248
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3564452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 297.9 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

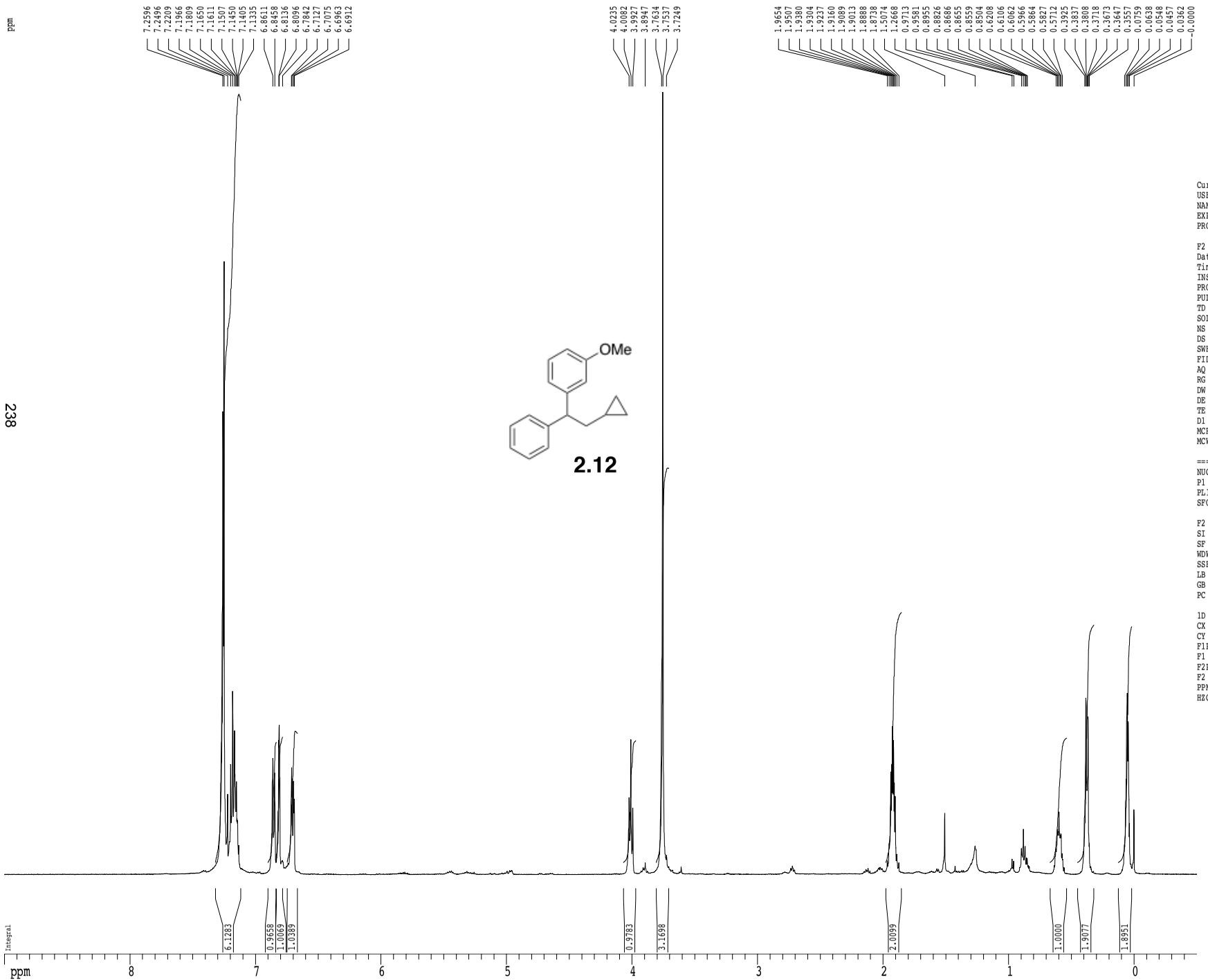
======= CHANNEL f1 =======
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======= CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127569 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69641 Hz/cm

1H spectrum



Current Data Parameters
USER tthane
NAME TATii58c
EXPNO 1
PROCNO 1

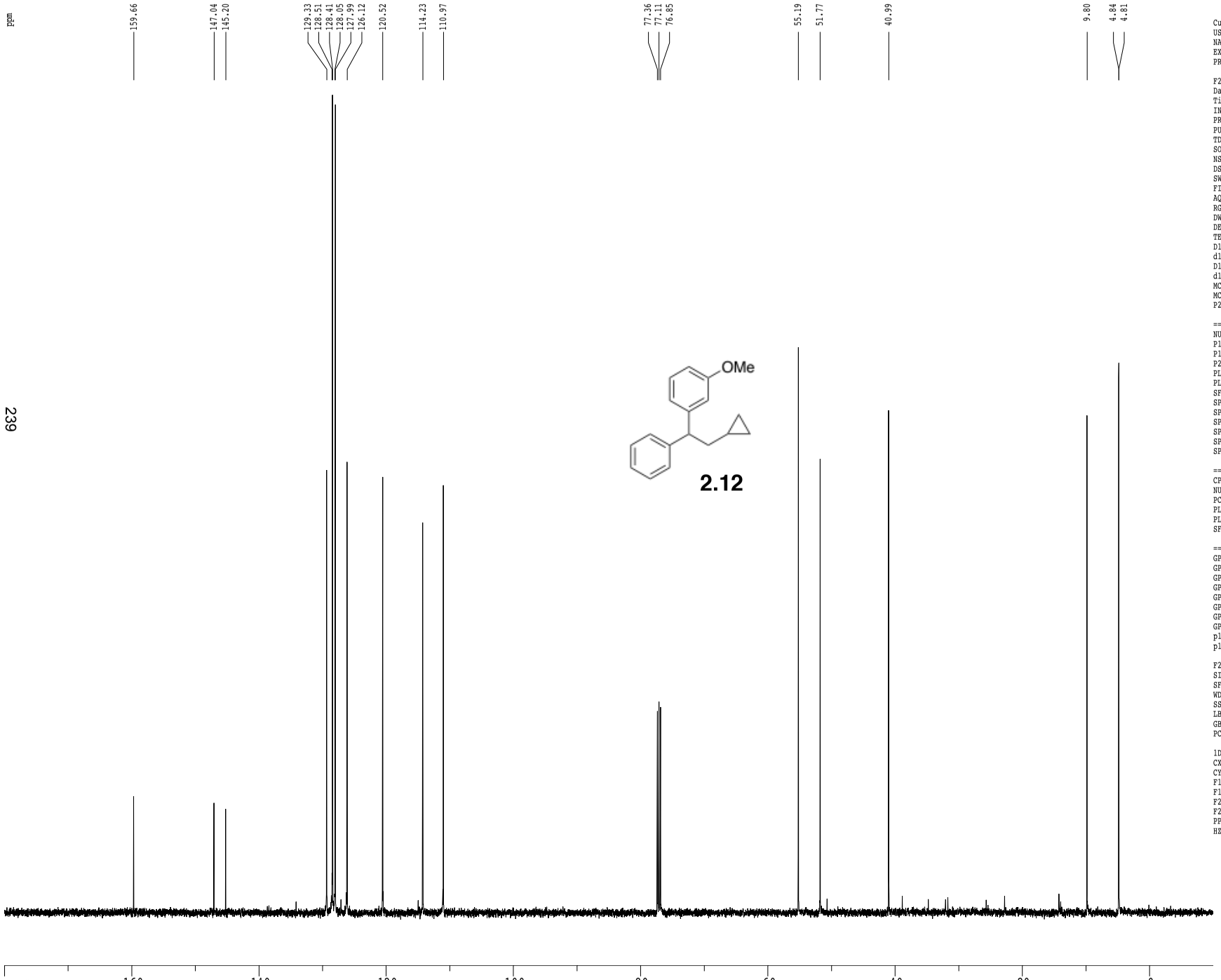
F2 - Acquisition Parameters
Date_ 20190110
Time 18.01
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3T
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 3.2
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200513 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42503 Hz/cm

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




```
Current Data Parameters
USER                tthane
NAME              TATii58c
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20190110
Time                 18.03
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     376
DS                      16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                 7298.2
DW                16.500 usec
DE                 6.00 usec
TE                 298.0 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                 33.10 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2                0.00 Hz
SPOFF4                0.00 Hz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                 1H
PCPD2              100.00 usec
PL2                 1.60 dB
PL12               23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

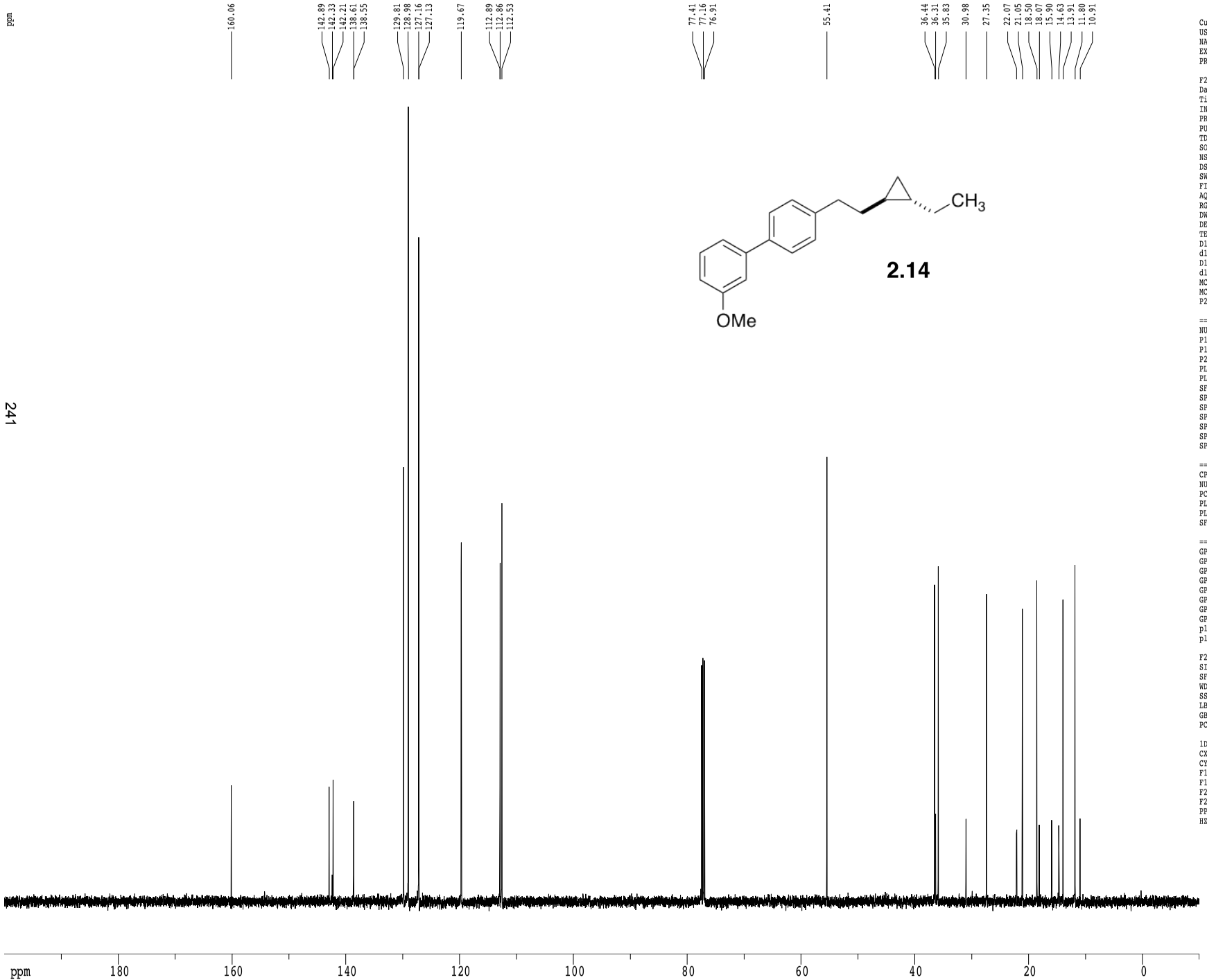
F2 - Processing parameters
SI                   65536
SF           125.7804190 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                  22.80 cm
CY                  15.65 cm
F1P               180.000 ppm
F1              22640.47 Hz
F2P               -10.000 ppm
F2              -1257.80 Hz
PPMCM             8.33333 ppm/cm
HZCM          1048.17017 Hz/cm
```

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-3-063-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191111
Time_ 14.16
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 114
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300322 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
2.14
CH3
OMe
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-3-063-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191111
Time 15.50
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 256
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 6502
DW 16.500 usec
DE 6.00 usec
TE 298.2 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

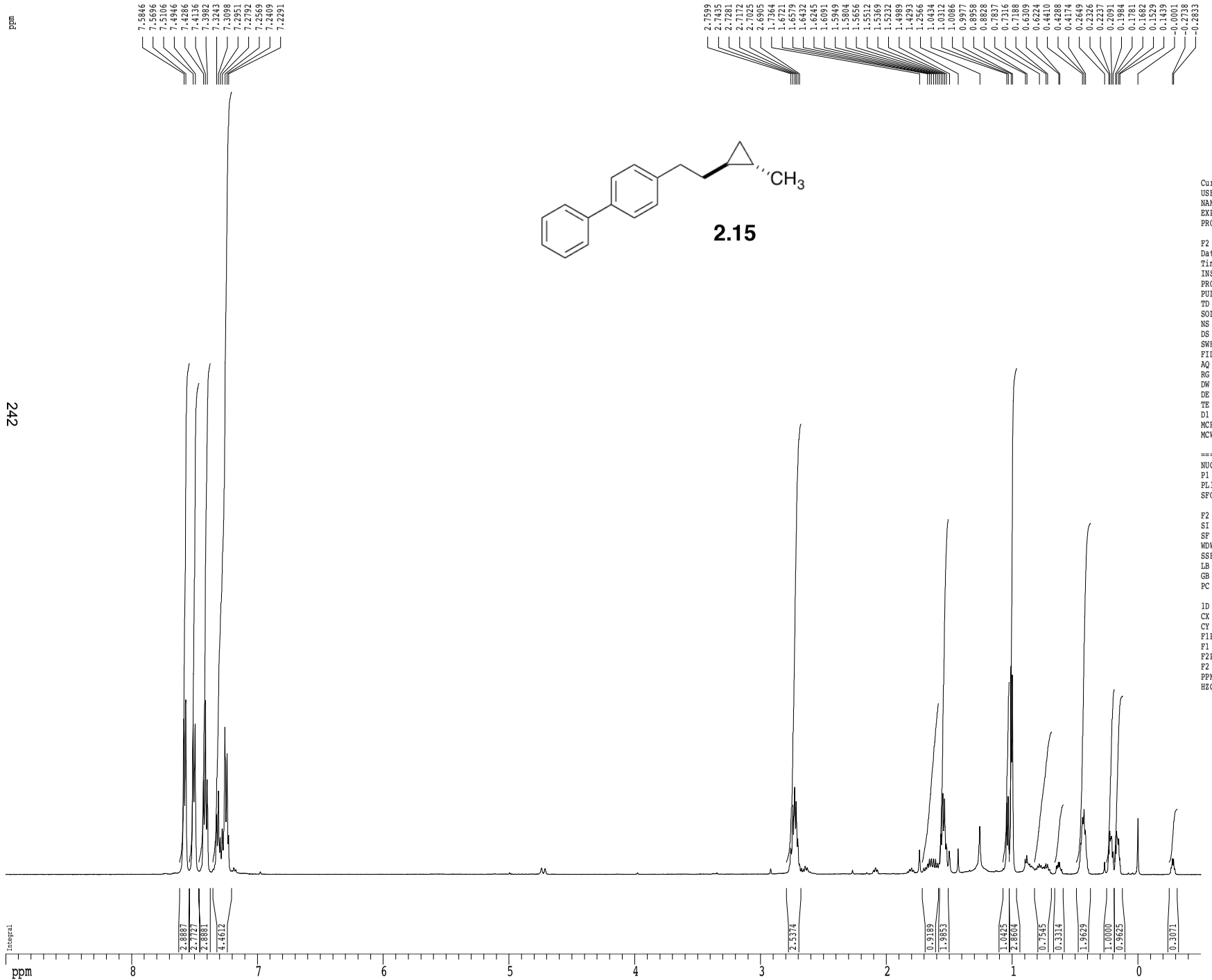
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804094 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



2.15

```
Current Data Parameters
USER            sanforda
NAME      ABS-3-062-proton2
EXPNO                   1
PROCNO                  1

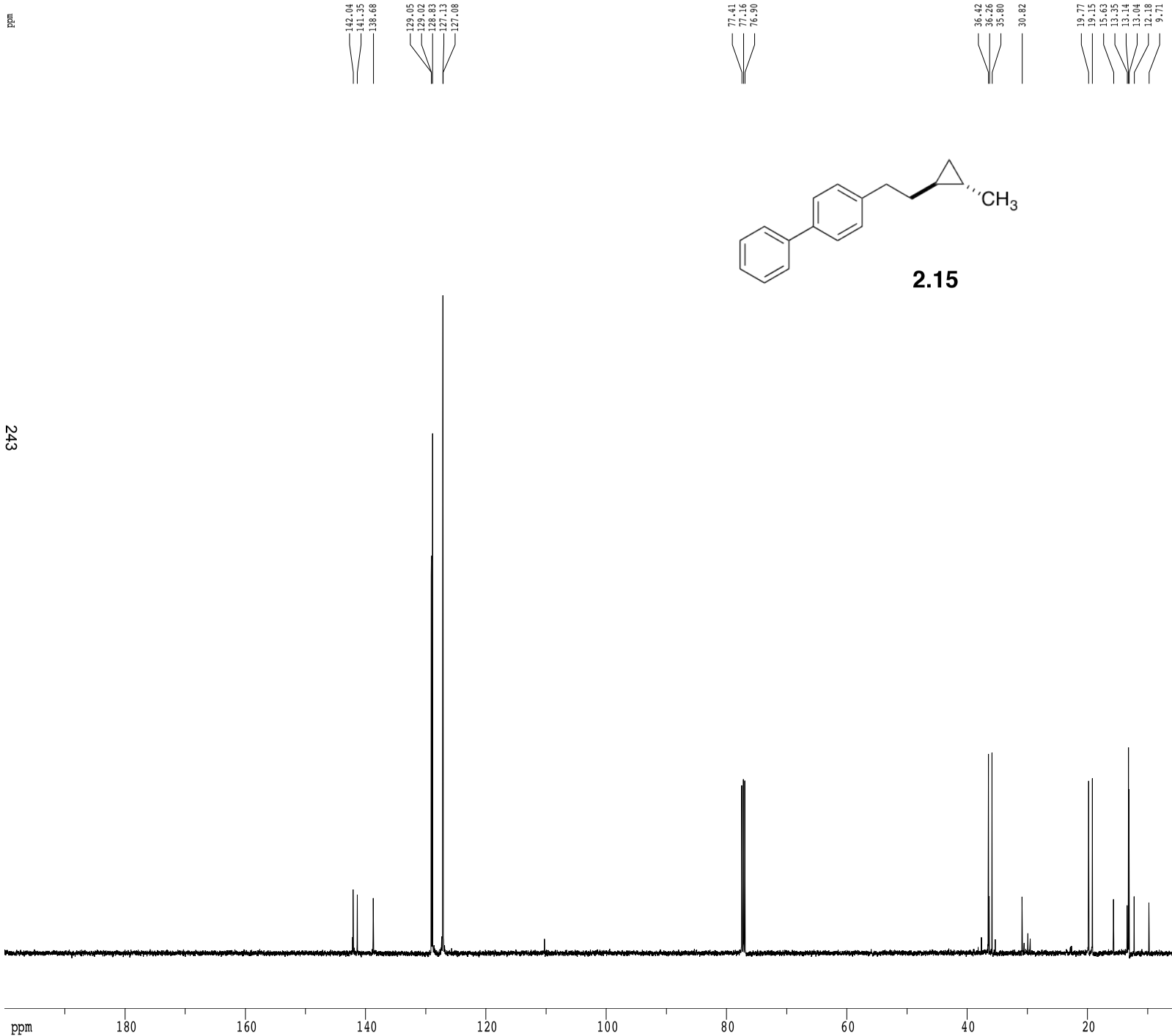
F2 - Acquisition Parameters
Date_            20191111
Time                15.35
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  81728
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.098043 Hz
AQ               5.0998774 sec
RG                    6.3
DW                62.400 usec
DE                 6.00 usec
TE                298.2 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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

F2 - Processing parameters
SI                  65536
SF           500.2200466 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  4.00 cm
F1P                9.000 ppm
F1               4501.98 Hz
F2P                -0.500 ppm
F2               -250.11 Hz
PPMCM            0.41667 ppm/cm
HZCM           208.42502 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-3-062-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191111
Time 15.39
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 432
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.2 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

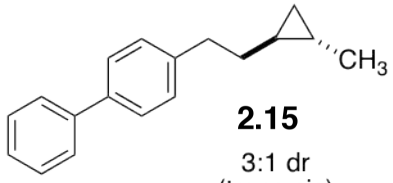
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804094 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

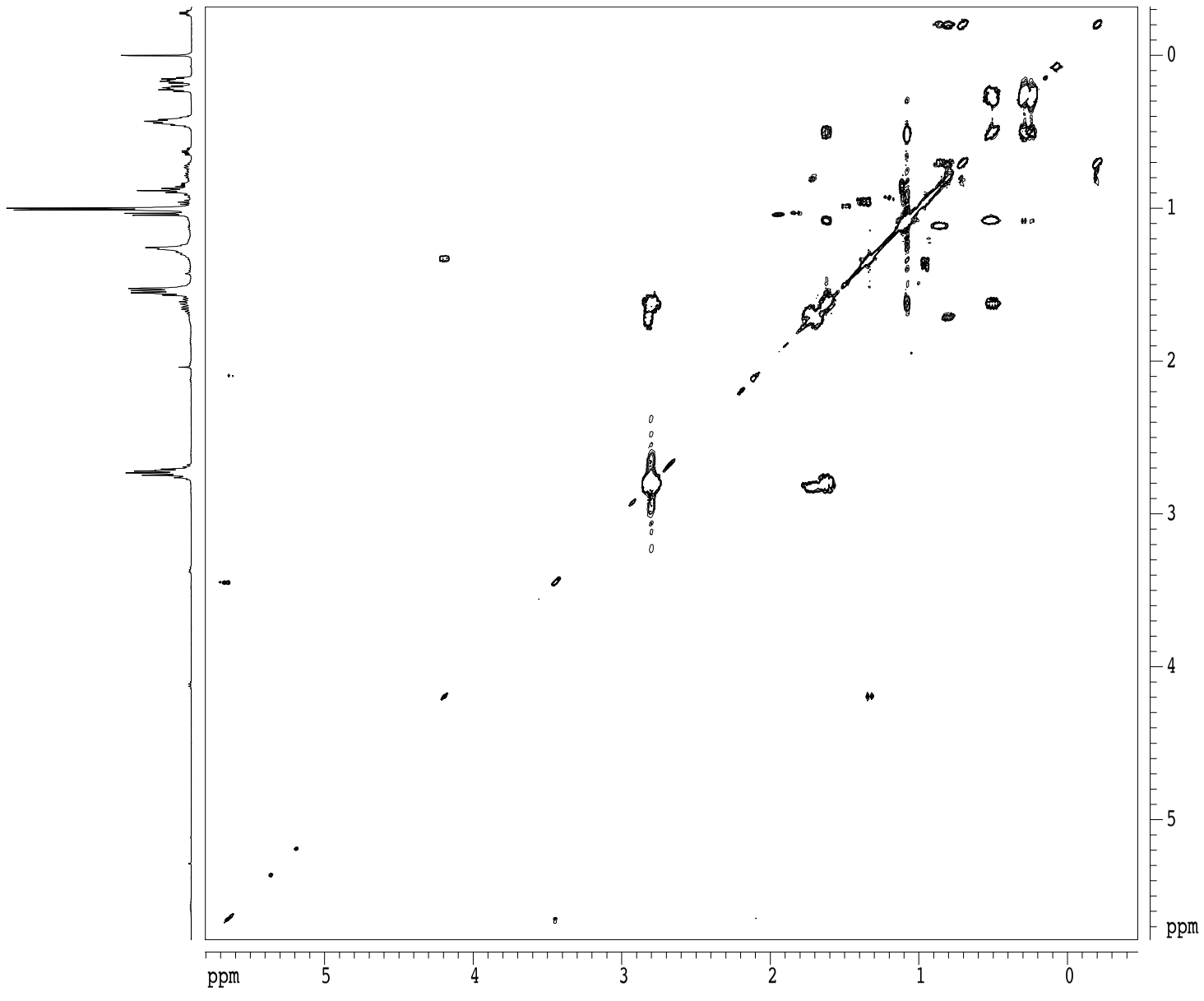
1D NMR plot parameters
CX 22.80 cm
CY 12.00 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

gcosy60



2.15

3:1 dr
(trans:cis)



Current Data Parameters

USER	sanforda
NAME	ABS-1-255-proton
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20180713
Time	10.10
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	1
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	228.1
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221259 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2221 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	QF

F2 - Processing parameters

SI	1024
SF	500.2200000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

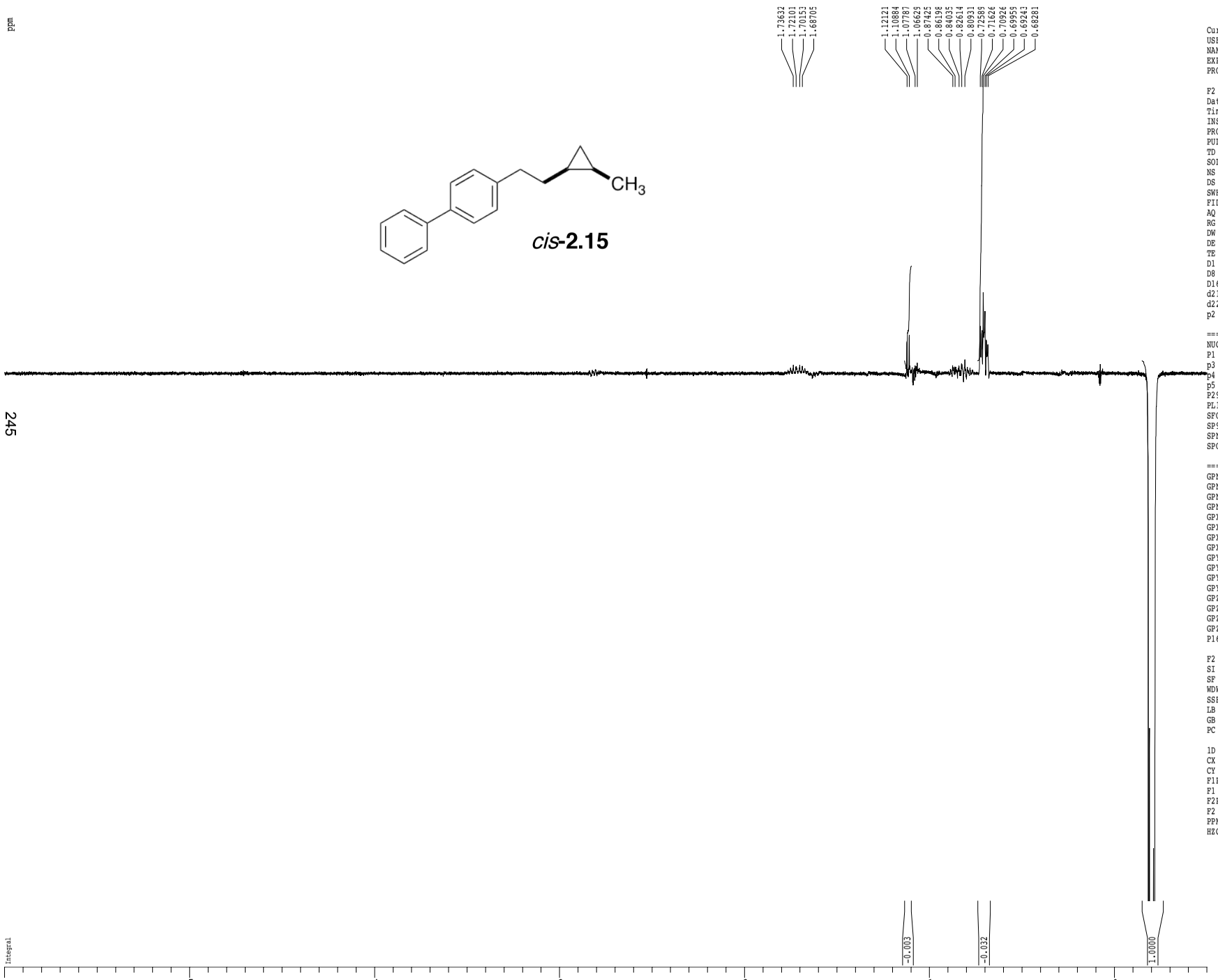
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	5.803 ppm
F2LO	2902.74 Hz
F2PHI	-0.474 ppm
F2HI	-236.87 Hz
F1PLO	5.784 ppm
F1LO	2893.50 Hz
F1PHI	-0.316 ppm
F1HI	-158.26 Hz
F2PPMCM	0.41843 ppm/cm
F2HZCM	209.30745 Hz/cm
F1PPMCM	0.40672 ppm/cm
F1HZCM	203.45052 Hz/cm

gnoe



Current Data Parameters
USER sanforda
NAME ABS-1-255-proton2
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180713
Time 11.59
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoelcc22.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec

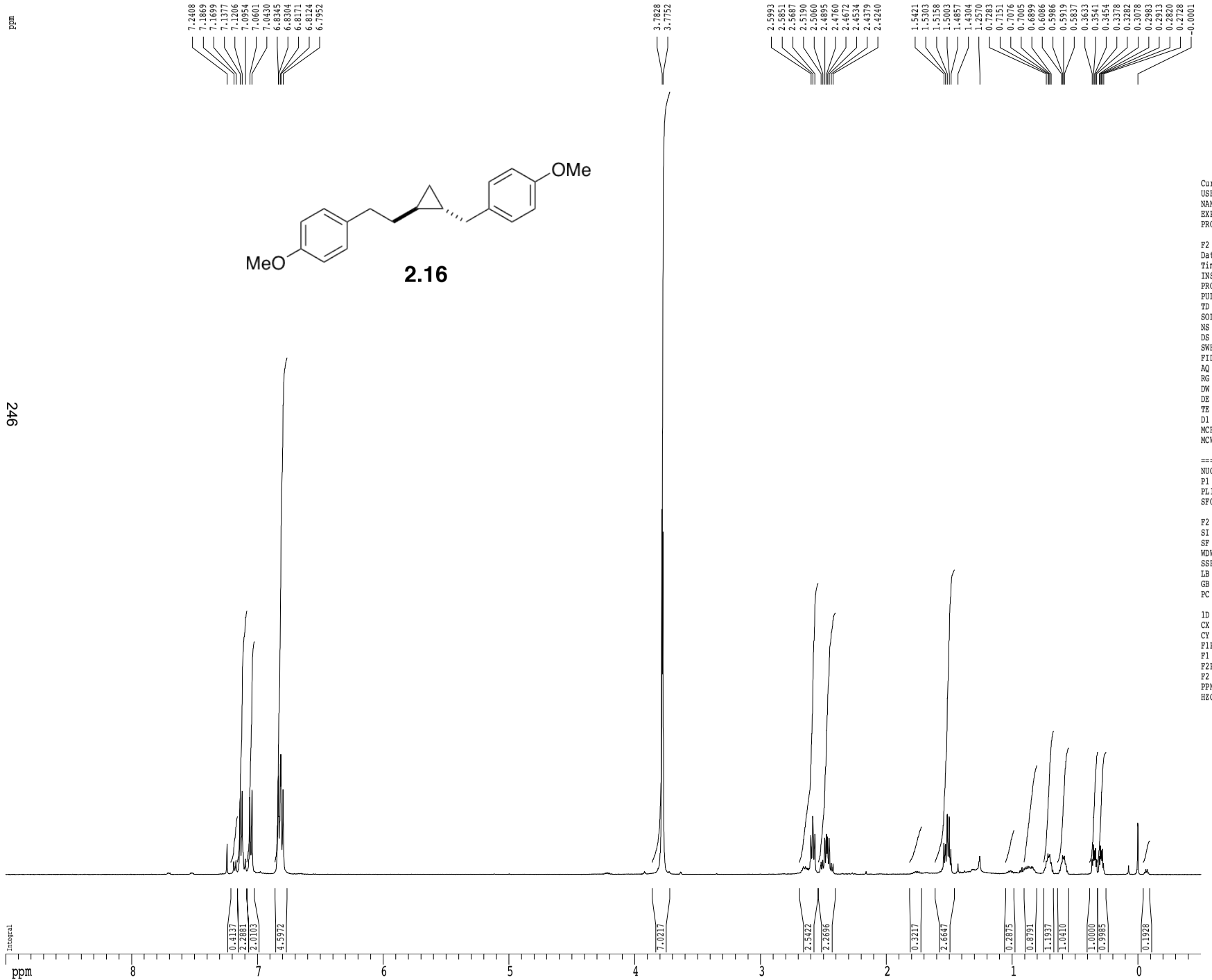
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2198996 MHz
SP9 61.60 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 6.000 ppm
F1 3001.32 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.28509 ppm/cm
HZCM 142.60658 Hz/cm

1H spectrum




```
Current Data Parameters
USER            sanforda
NAME      ABS-3-059-proton
EXPNO                  1
PROCNO                 1

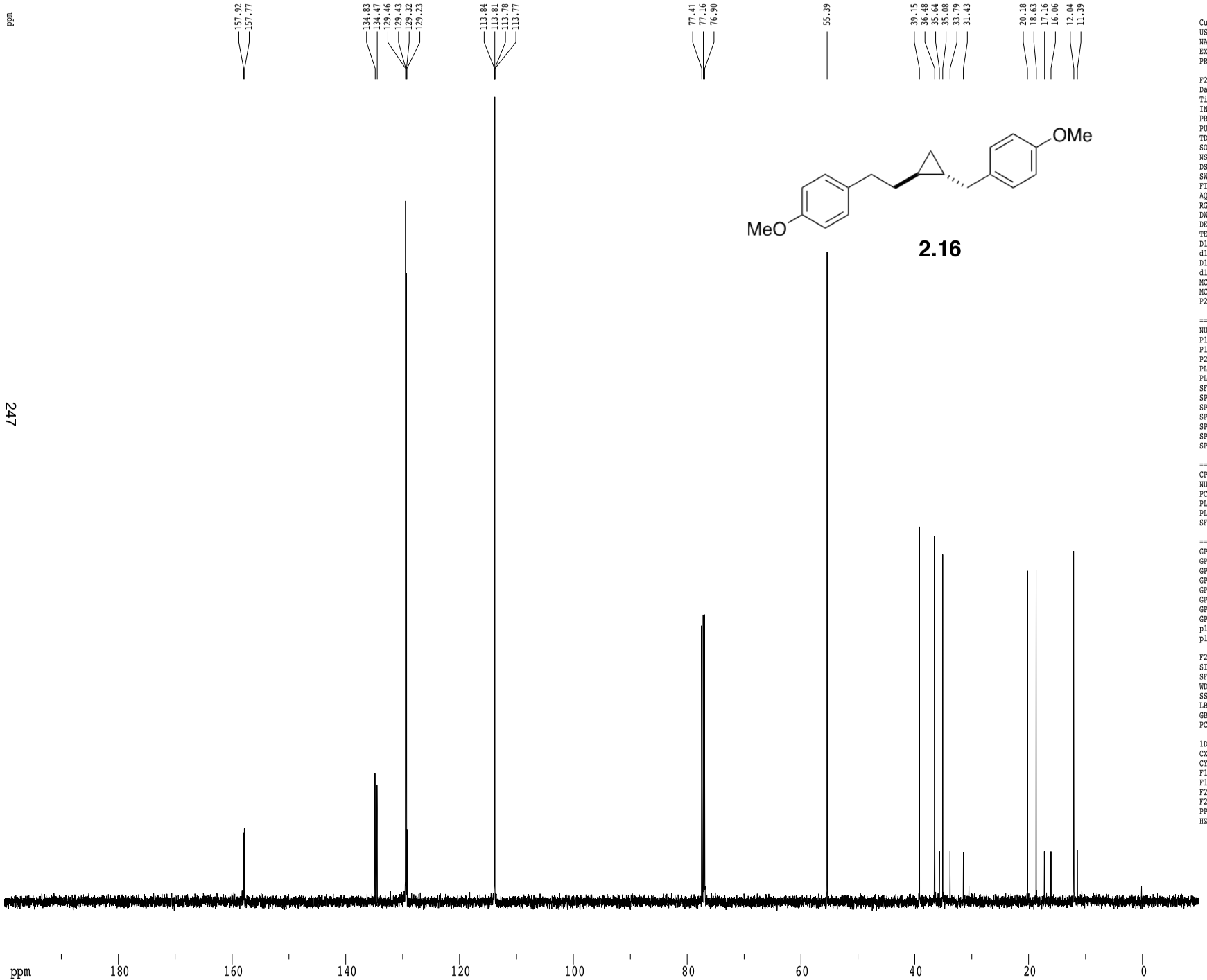
F2 - Acquisition Parameters
Date_           20191112
Time              17.04
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                    4
DW               62.400 usec
DE                6.00 usec
TE                298.2 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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

F2 - Processing parameters
SI                 65536
SF           500.2200404 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                 7.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-3-064-carbon2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191122
Time 11.38
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 344
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 18390.4
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

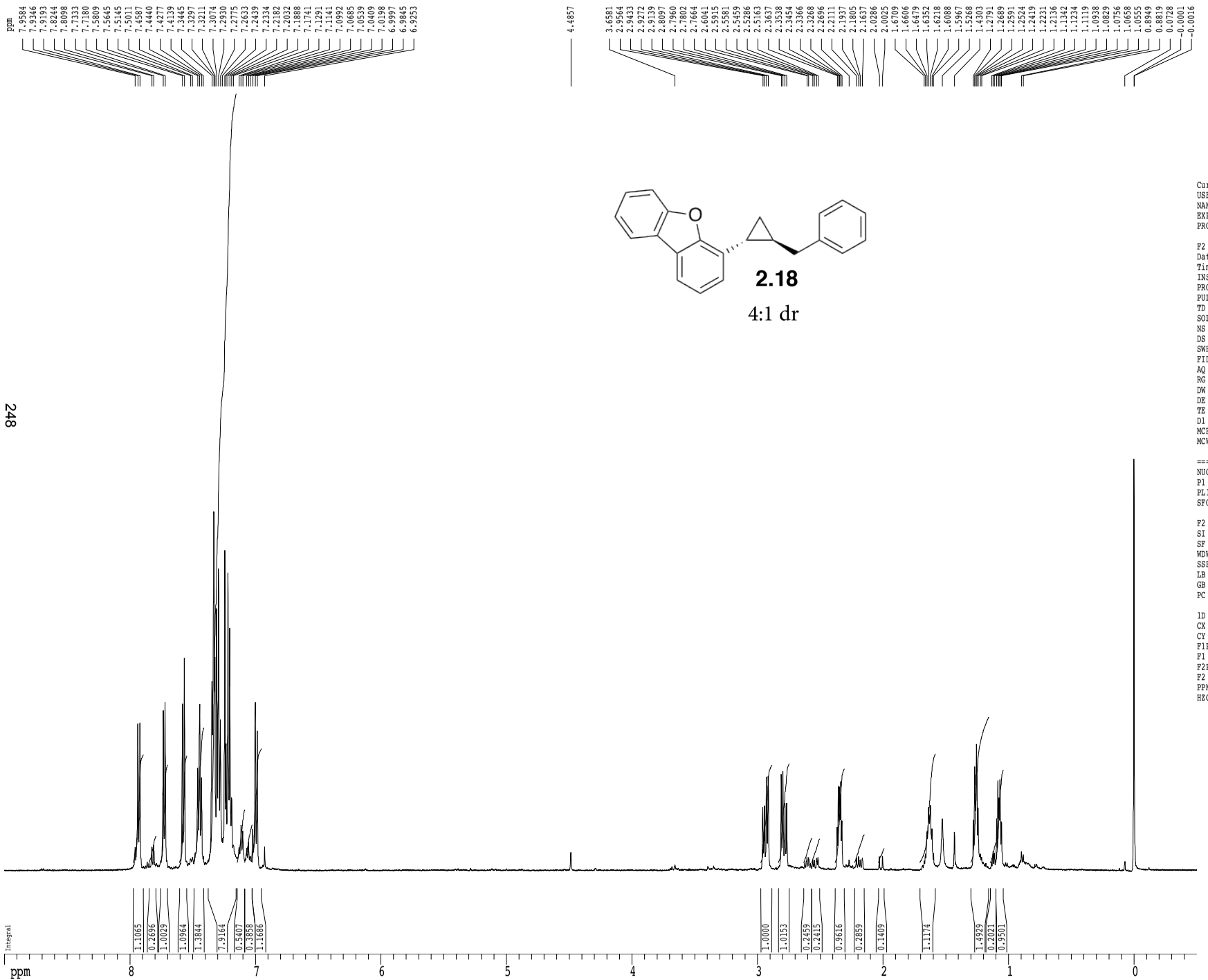
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804094 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



248

2.18

4:1 dr

```
Current Data Parameters
USER            sanforda
NAME      ABS-3-104-proton
EXPNO                  1
PROCNO                 1

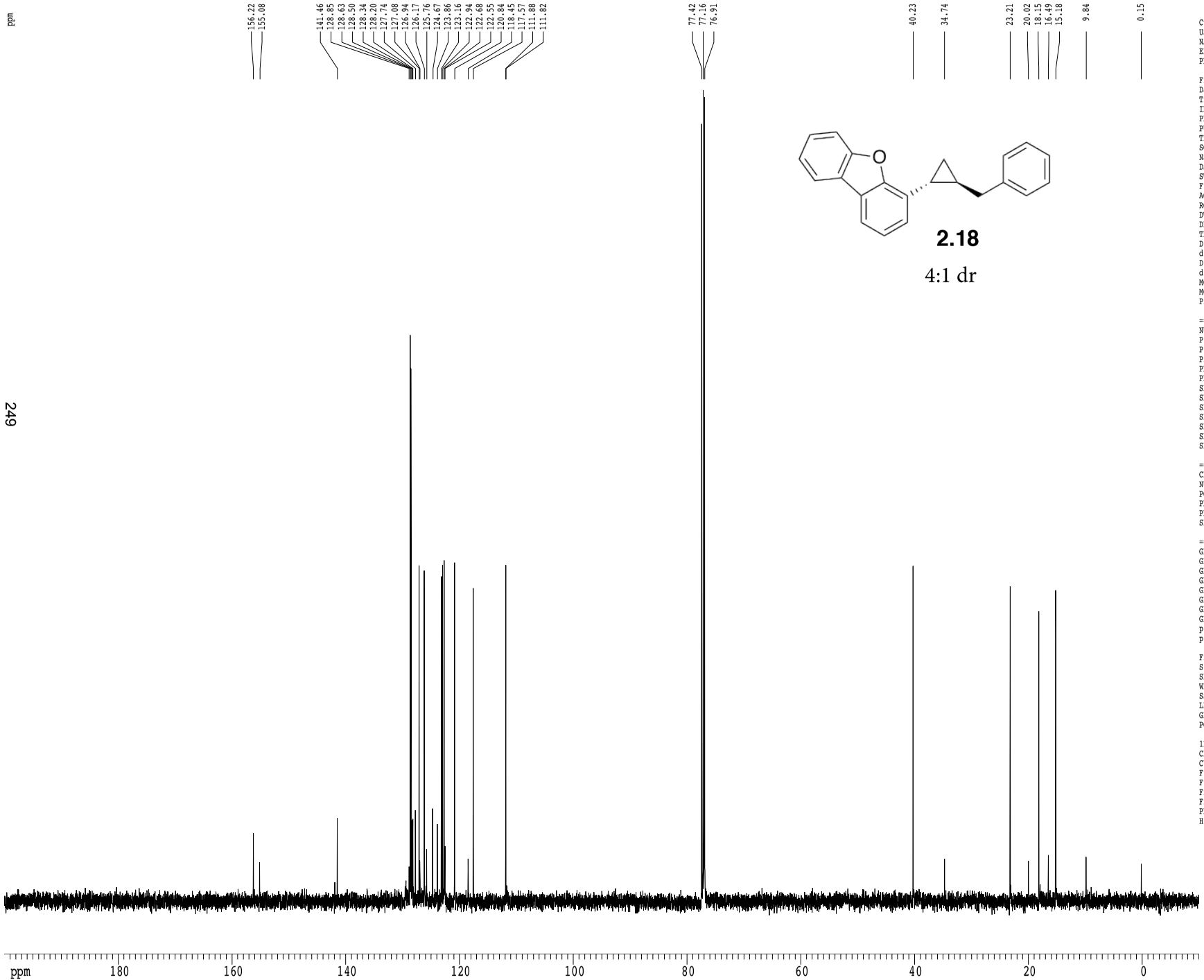
F2 - Acquisition Parameters
Date_           20200114
Time               13.39
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 sec
RG                   7.1
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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

F2 - Processing parameters
SI                 65536
SF           500.2200393 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                  8.00 cm
F1P                9.000 ppm
F1              4501.98 Hz
F2P               -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

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



2.18

4:1 dr

```
Current Data Parameters
USER            sanforda
NAME      ABS-3-105-carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200114
Time              13.42
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT            CDCl3
NS                   392
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                7298.2
DW               16.500 usec
DE                6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2               33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

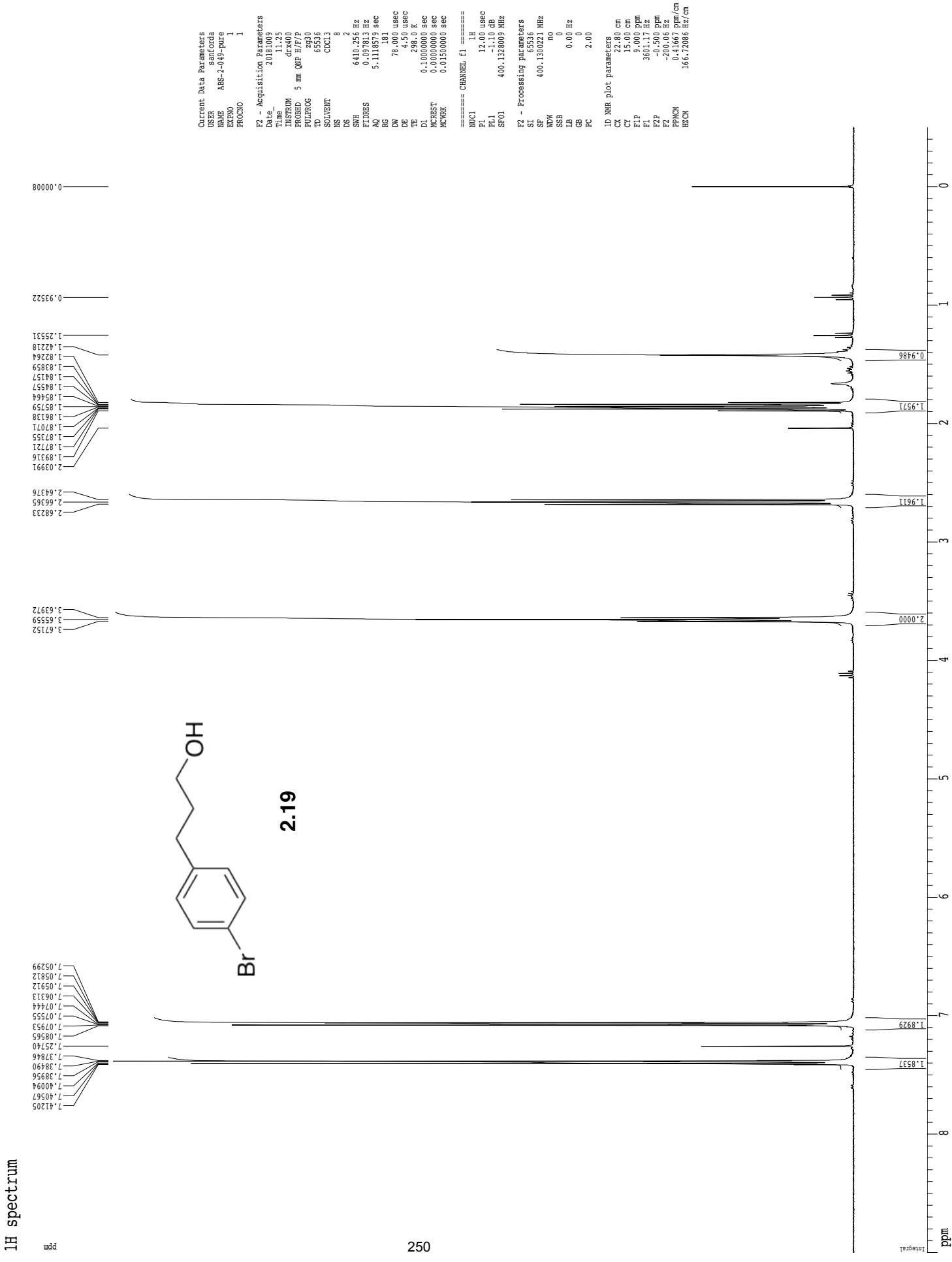
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

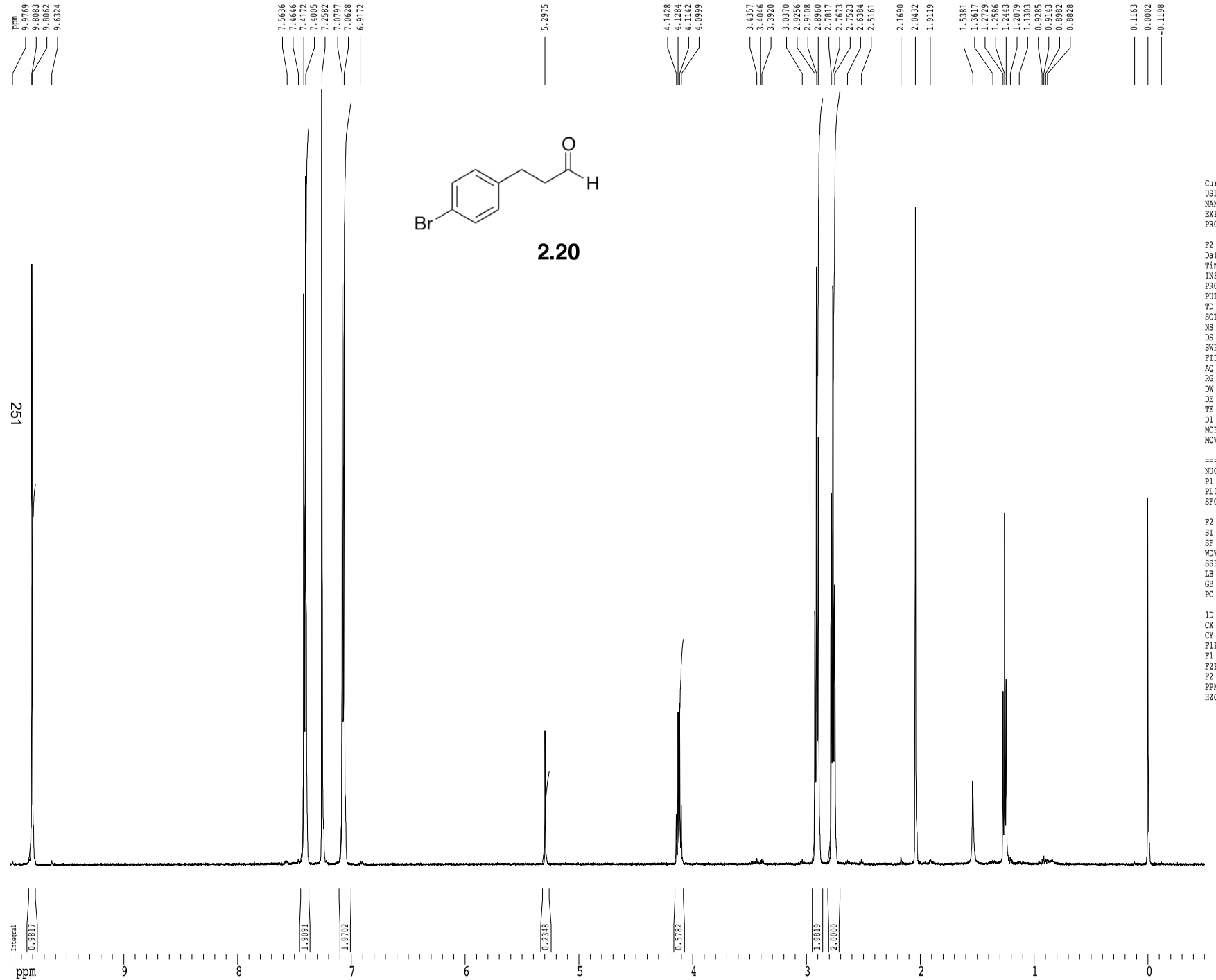
F2 - Processing parameters
SI                65536
SF           125.7804071 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P              200.000 ppm
F1             25156.08 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM             9.21053 ppm/cm
HZCM          1158.50378 Hz/cm
```

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-049-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181009
Time_ 11.25
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 181
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300221 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.000 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.00008
0.93522
1.25531
1.42218
1.82264
1.83859
1.84157
1.84557
1.85464
1.85759
1.86138
1.87071
1.87355
1.87721
1.89316
2.03991
2.64376
2.66365
2.68233
3.63972
3.65559
3.67152
7.05299
7.05812
7.05912
7.06313
7.07444
7.07555
7.07953
7.08565
7.25740
7.37846
7.38490
7.38956
7.40094
7.40567
7.41205
0.9486
1.9571
1.9611
2.0000
1.8929
1.8537
Integral
ppm
0
1
2
3
4
5
6
7
8
ppm
OH
Br
2.19

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-081-pure
EXPNO 1
PROCNO 1

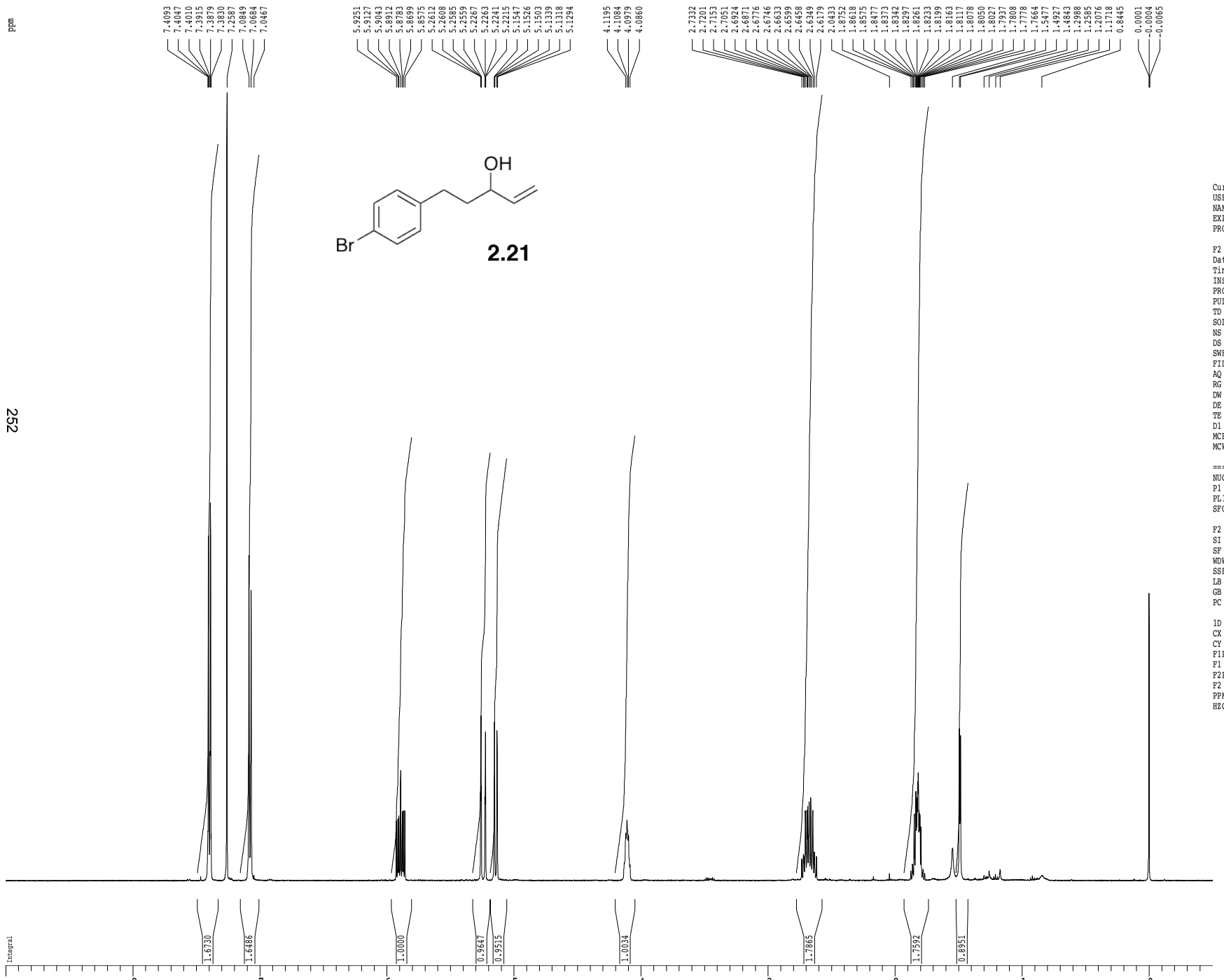
F2 - Acquisition Parameters
Date_ 20181107
Time 13.18
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 7.1
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200342 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.46053 ppm/cm
HZCM 230.36450 Hz/cm

1H spectrum




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-084-pure
EXPNO                 1
PROCNO                1

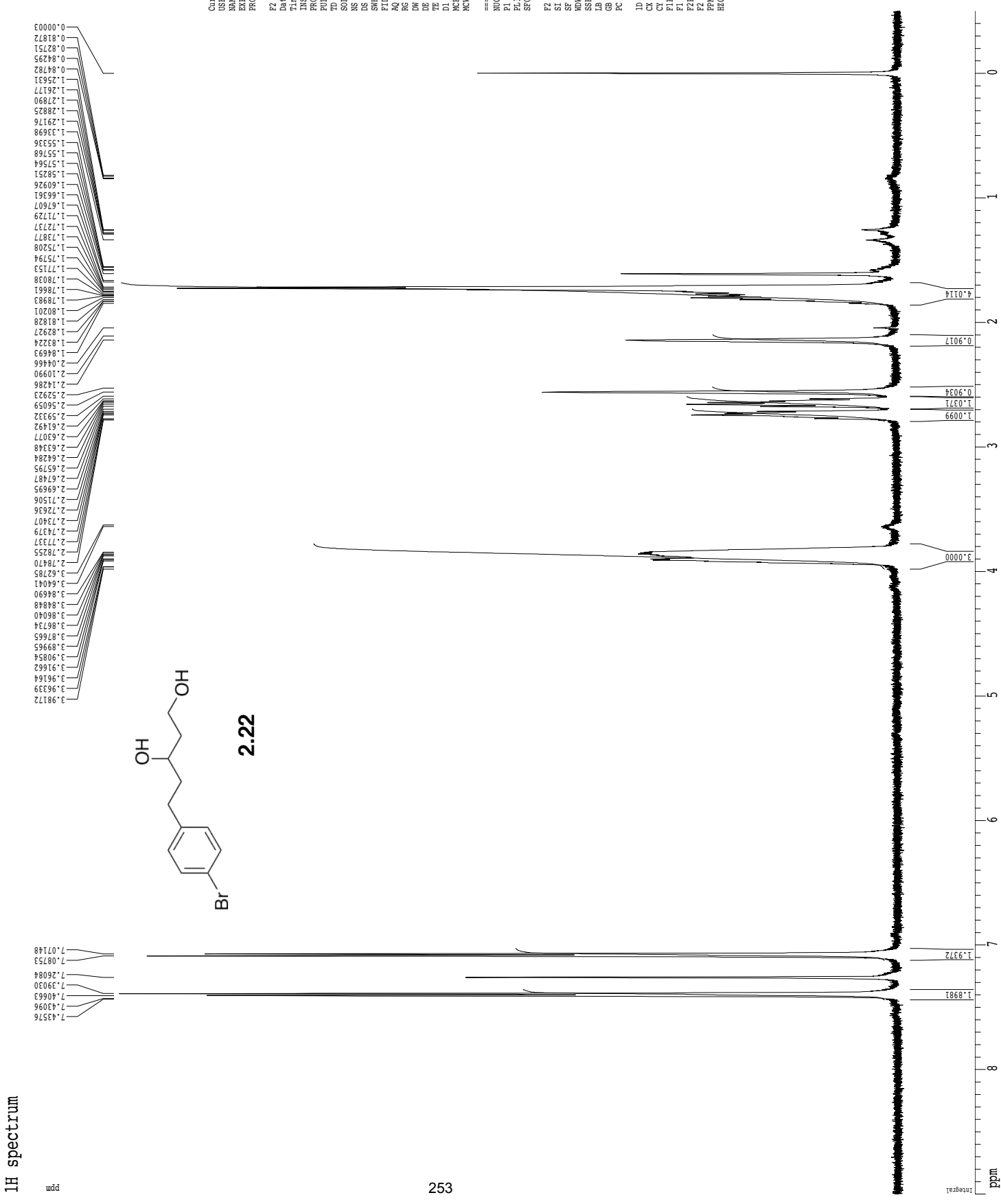
F2 - Acquisition Parameters
Date_          20181108
Time               9.04
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG            zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                    8
DW               62.400 usec
DE                6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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

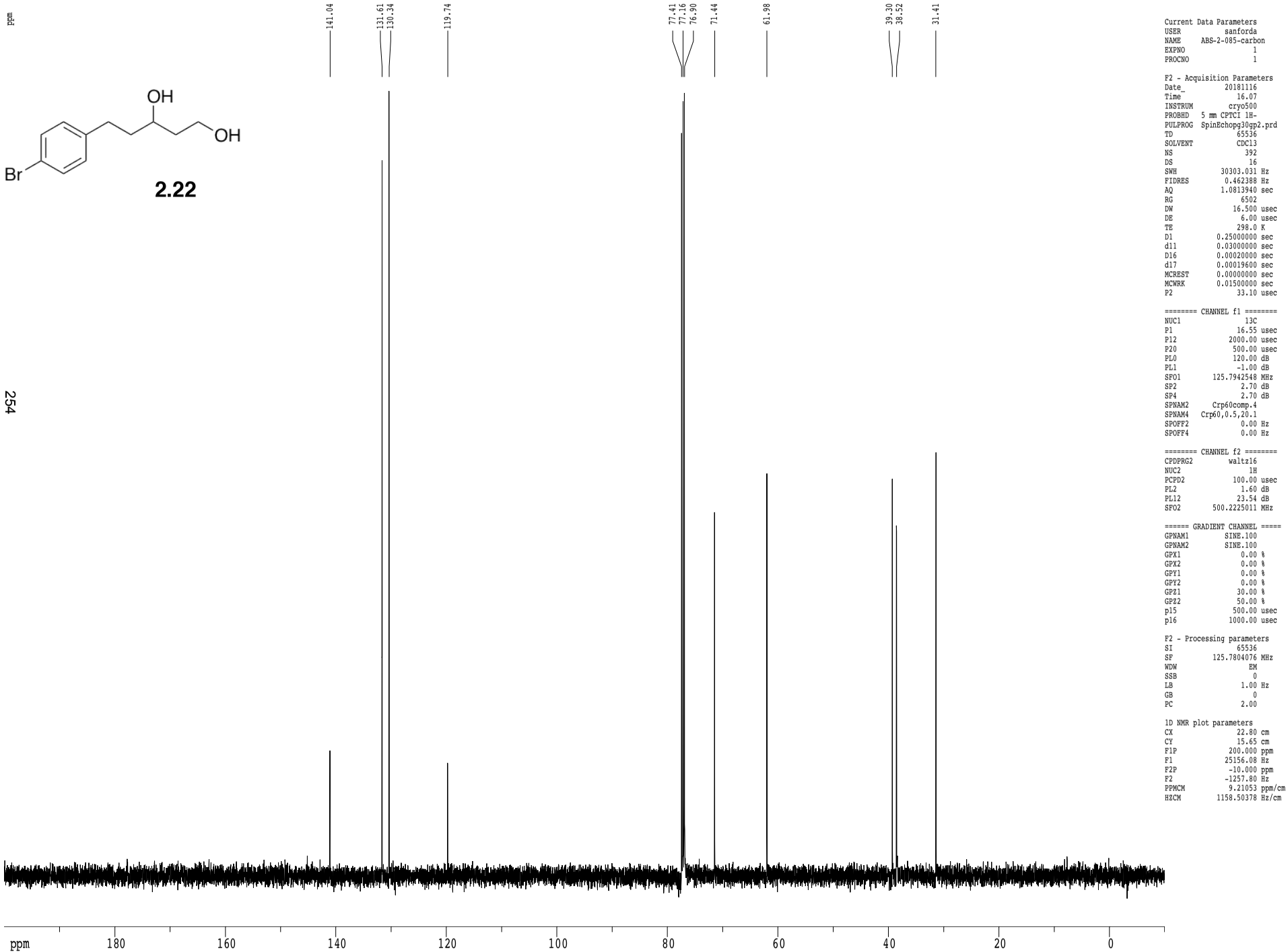
F2 - Processing parameters
SI                65536
SF          500.2200331 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                1.00

1D NMR plot parameters
CX               22.80 cm
CY               15.00 cm
F1P               9.000 ppm
F1             4501.98 Hz
F2P              -0.500 ppm
F2             -250.11 Hz
PPMCM          0.41667 ppm/cm
HZCM         208.42502 Hz/cm
```

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-085-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181115
Time_ 17.13
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 1290.2
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 498.9534926 MHz
F2 - Processing parameters
SI 65536
SF 498.9500302 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4490.55 Hz
F2P -0.500 ppm
F2 -249.47 Hz
PPMCM 0.41667 ppm/cm
HZCM 207.89586 Hz/cm
OH
OH
Br
2.22
4.0114
0.9017
0.9034
1.0371
1.0099
3.0000
1.9372
1.8981
Integral
ppm

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



Current Data Parameters
USER sanforda
NAME ABS-2-085-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181116
Time 16.07
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 392
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 6502
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

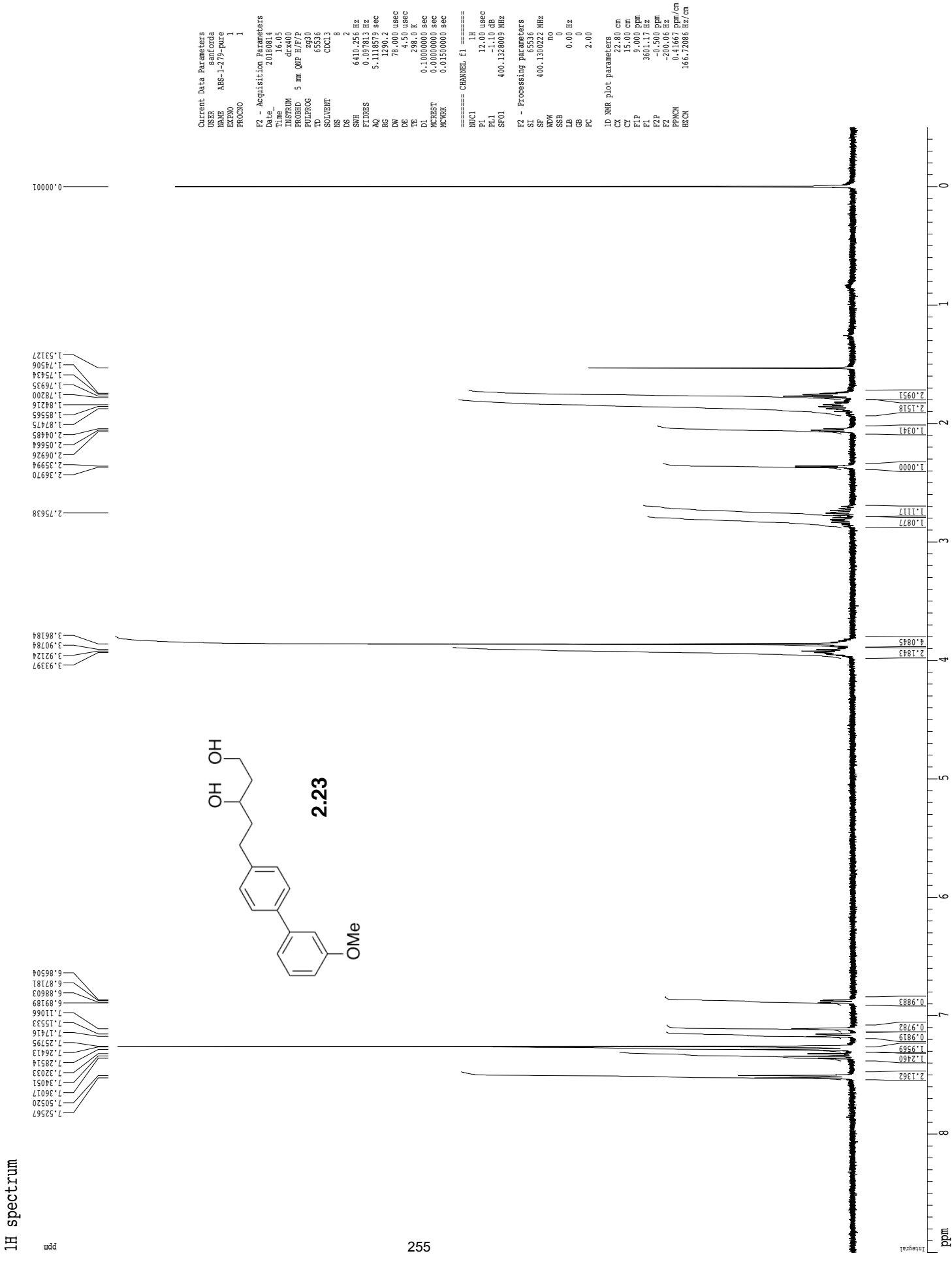
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

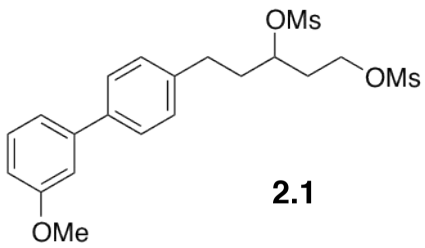
F2 - Processing parameters
SI 65536
SF 125.7804076 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-1-279-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180814
Time_ 16.05
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 1290.2
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300222 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
OH
2.23
OMe
ppm
Integral

1H spectrum



2.1

Current Data Parameters
USER sanforda
NAME ABS-2-025-proton
EXPNO 1
PROCNO 1

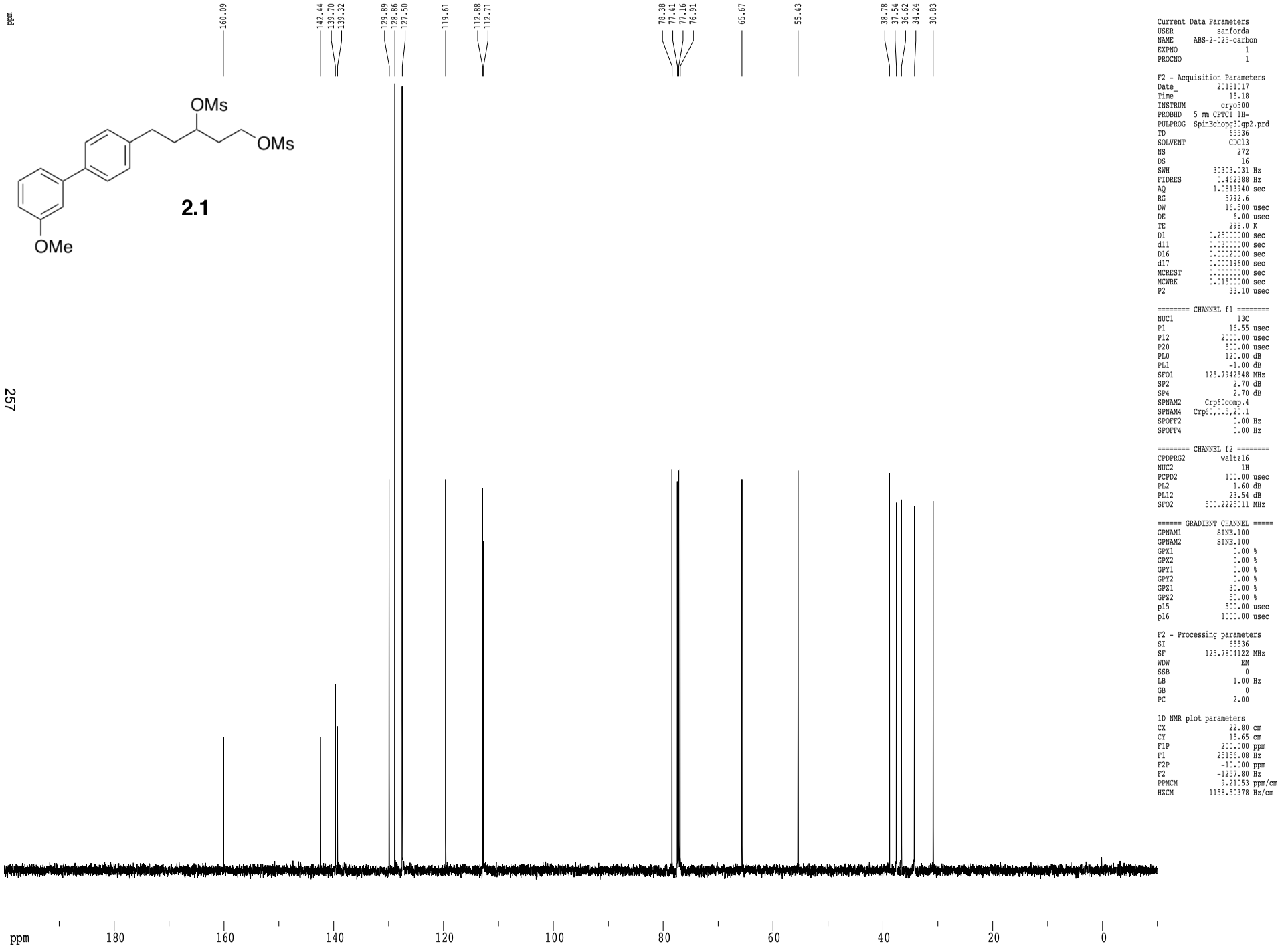
F2 - Acquisition Parameters
Date_ 20181017
Time 15.15
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200371 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

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




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-025-carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20181017
Time              15.18
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT            CDCl3
NS                   272
DS                    16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG                5792.6
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

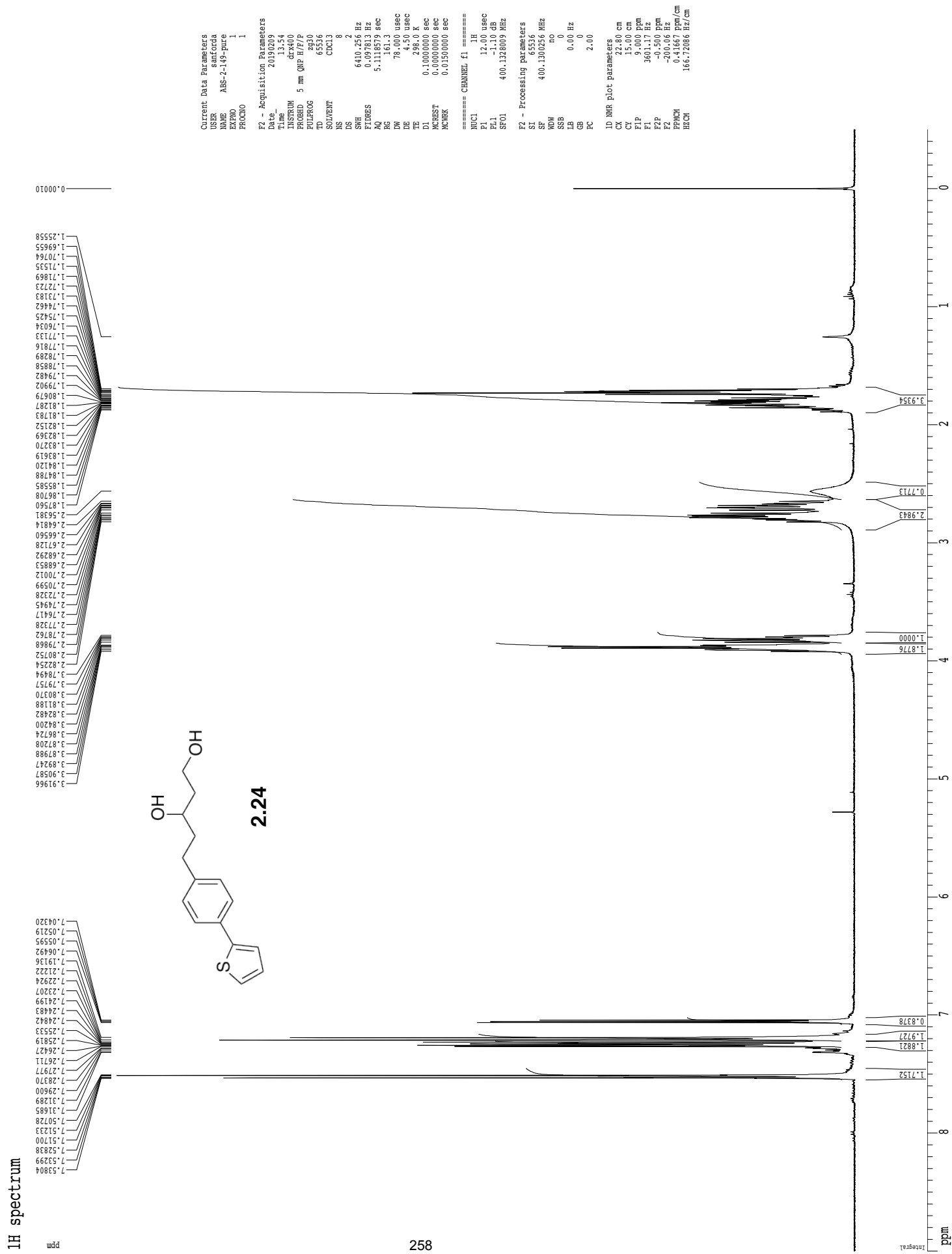
======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2         500.2225011 MHz

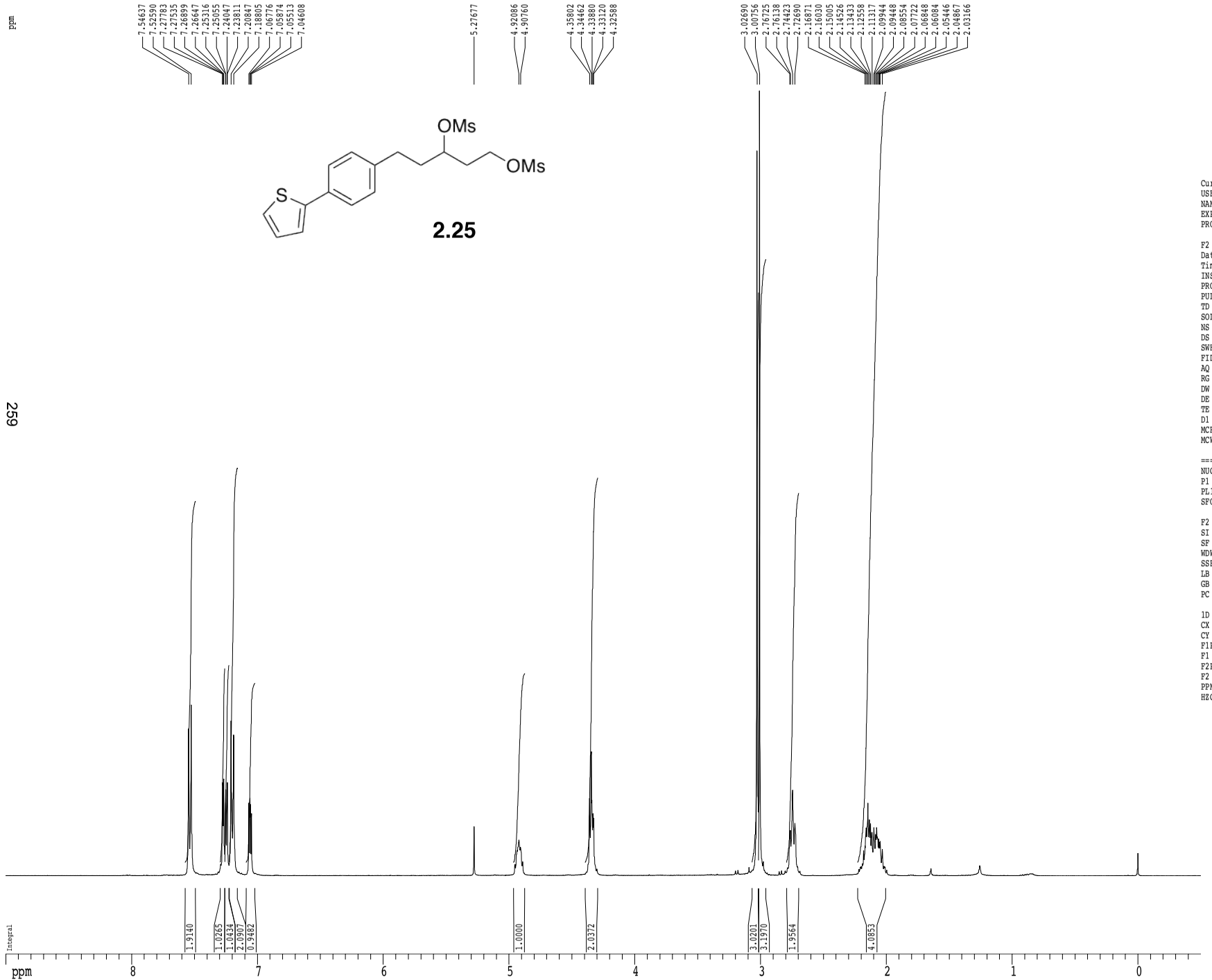
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804122 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             200.000 ppm
F1             25156.08 Hz
F2P             -10.000 ppm
F2             -1257.80 Hz
PPMCM           9.21053 ppm/cm
HZCM         1158.50378 Hz/cm
```


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-149-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190209
Time_ 13.54
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 161.3
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300256 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
2.24
OH
OH
S
3.9354
0.7713
2.9843
1.8776
1.0000
0.8378
1.8821
1.9727
1.7152
Integral
ppm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-150-proton
EXPNO 1
PROCNO 1

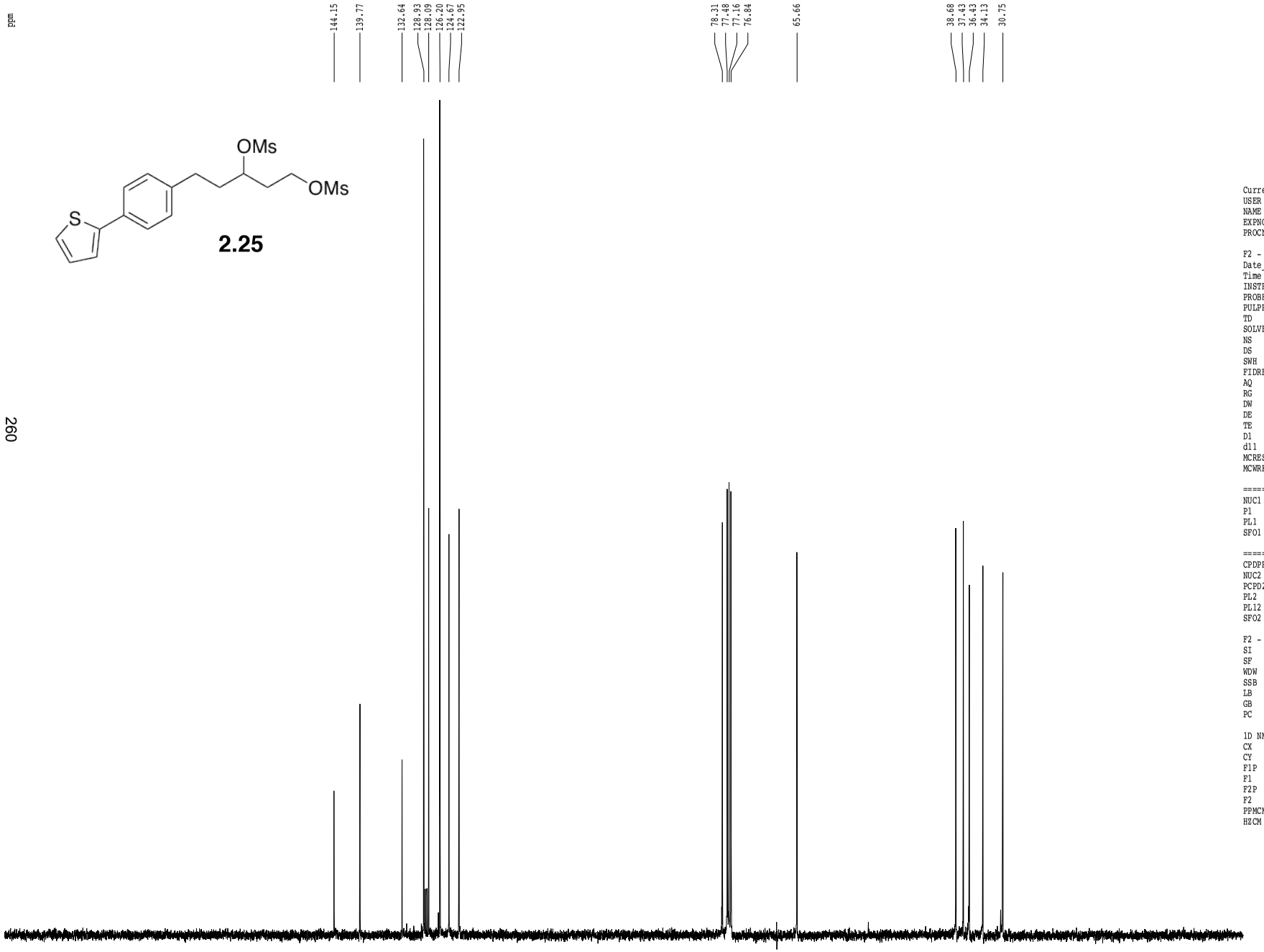
F2 - Acquisition Parameters
Date_ 20190211
Time 18.16
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 71.8
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300253 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-2-150-carbon
EXPNO 1
PROCNO 1

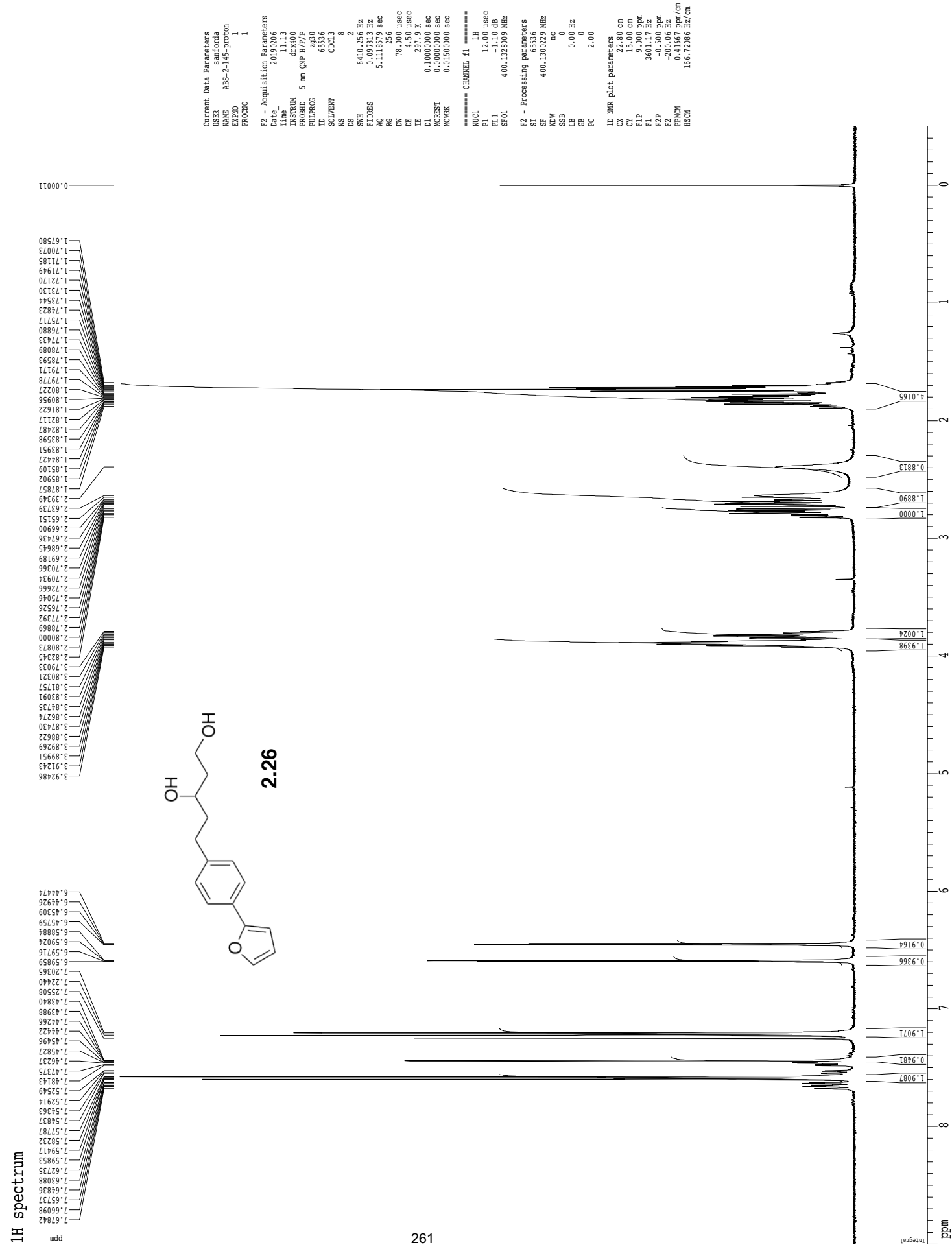
F2 - Acquisition Parameters
Date_ 20190211
Time 18.18
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 424
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 298.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

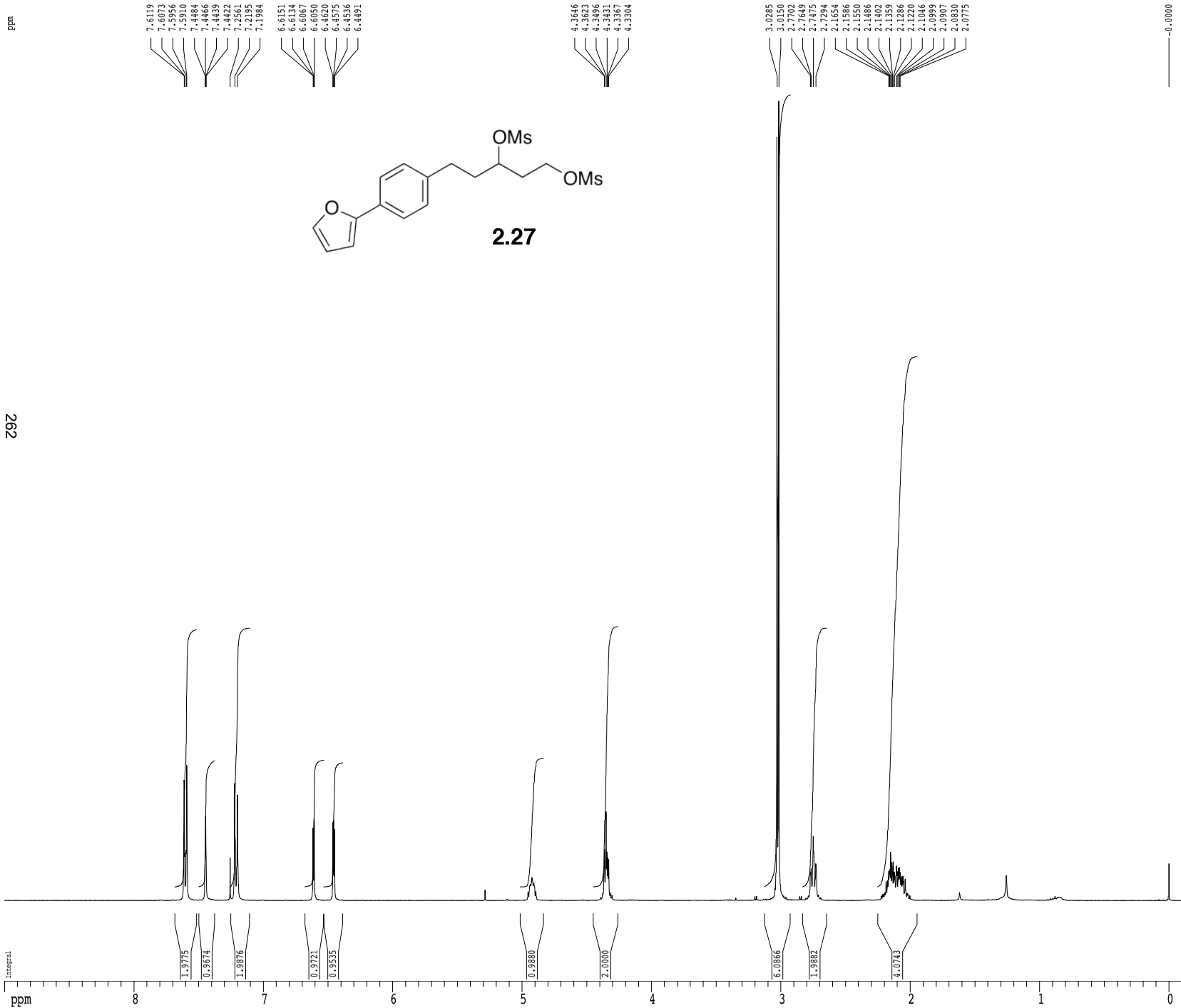
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69653 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-145-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190206
Time_ 11.13
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 256
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300229 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
2.26
OH
OH
O
ppm
Integral
4.0165
0.8813
1.8890
1.0000
1.0024
1.9398
0.9164
0.9366
1.9071
0.9481
1.9087

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-147-proton-2
EXPNO 1
PROCNO 1

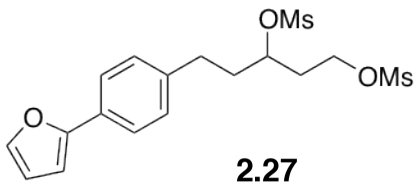
F2 - Acquisition Parameters
Date_ 20190208
Time 12.56
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 101.6
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300224 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

13C spectrum with 1H decoupling



2.27

263

```
Current Data Parameters
USER            sanforda
NAME      ABS-2-147-carbon
EXPNO                  1
PROCNO                 1

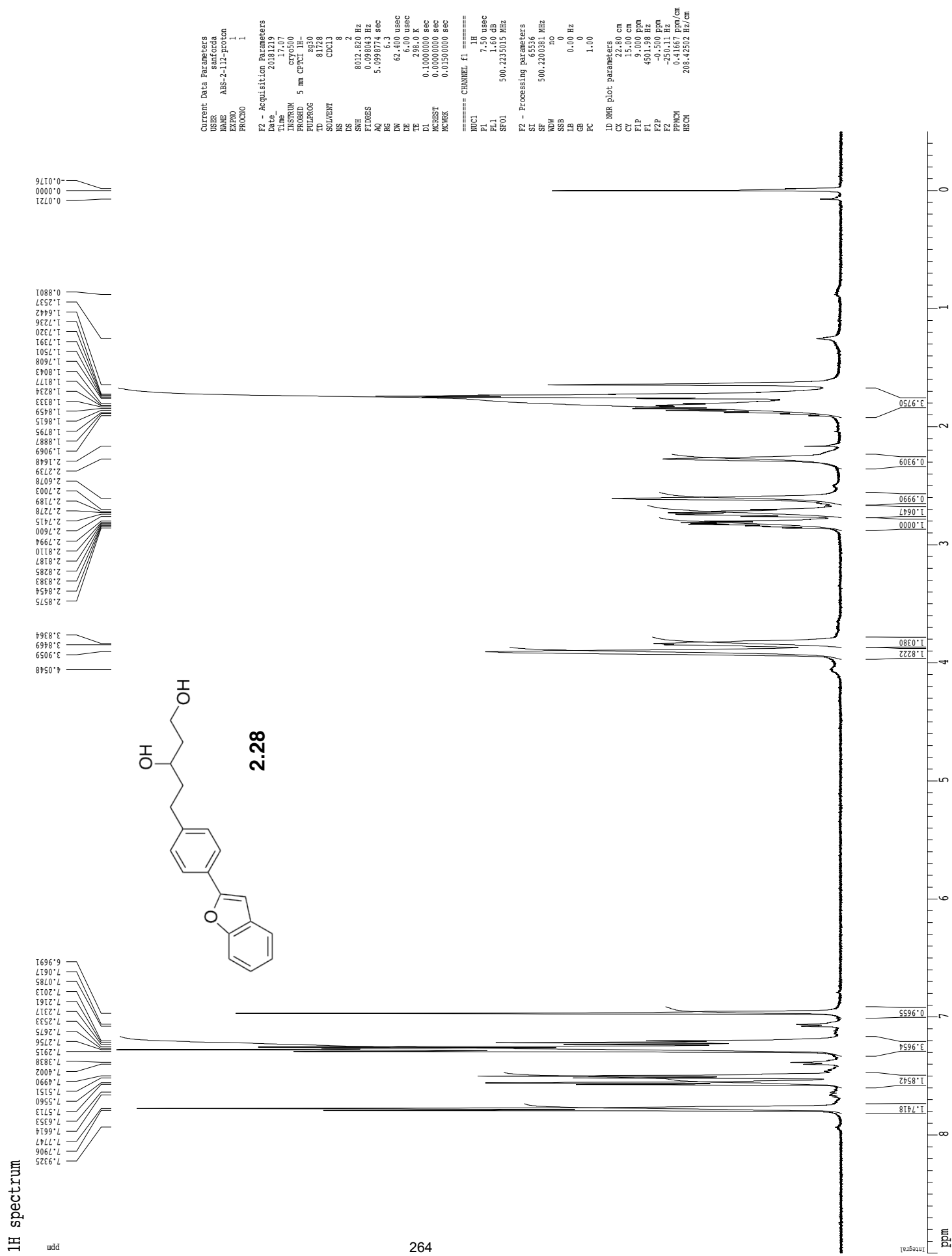
F2 - Acquisition Parameters
Date_           20190208
Time              12.59
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  424
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ             1.3566452 sec
RG                7298.2
DW               20.700 usec
DE                20.39 usec
TE                298.1 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 7.65 usec
PL1               -3.00 dB
SFO1         100.6237964 MHz

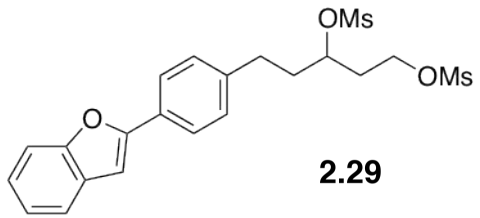
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               -1.10 dB
PL12              16.80 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                65536
SF           100.6127646 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P              200.000 ppm
F1             20122.55 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM           9.21053 ppm/cm
HZCM          926.69647 Hz/cm
```


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-112-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181219
Time_ 17.07
INSTRUM CRYO500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200381 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
2.28
OH
OH
O
ppm
Integral

1H spectrum



2.29

```
Current Data Parameters
USER            sanforda
NAME      ABS-2-128-proton-2
EXPNO                    1
PROCNO                   1

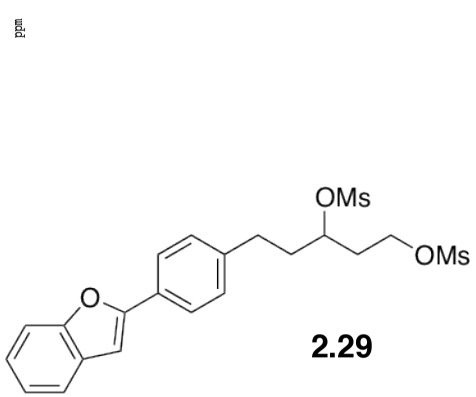
F2 - Acquisition Parameters
Date_          20190115
Time              17.55
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ              5.1118579 sec
RG                 203.2
DW                78.000 usec
DE                 4.50 usec
TE                298.1 K
D1            0.10000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300233 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P                -0.500 ppm
F2               -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

13C spectrum with 1H decoupling



2.29


```
Current Data Parameters
USER            sanforda
NAME      ABS-2-128-carbon-2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_          20190115
Time              17.59
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                  544
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ             1.3566452 sec
RG                9195.2
DW                20.700 usec
DE                20.39 usec
TE                298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

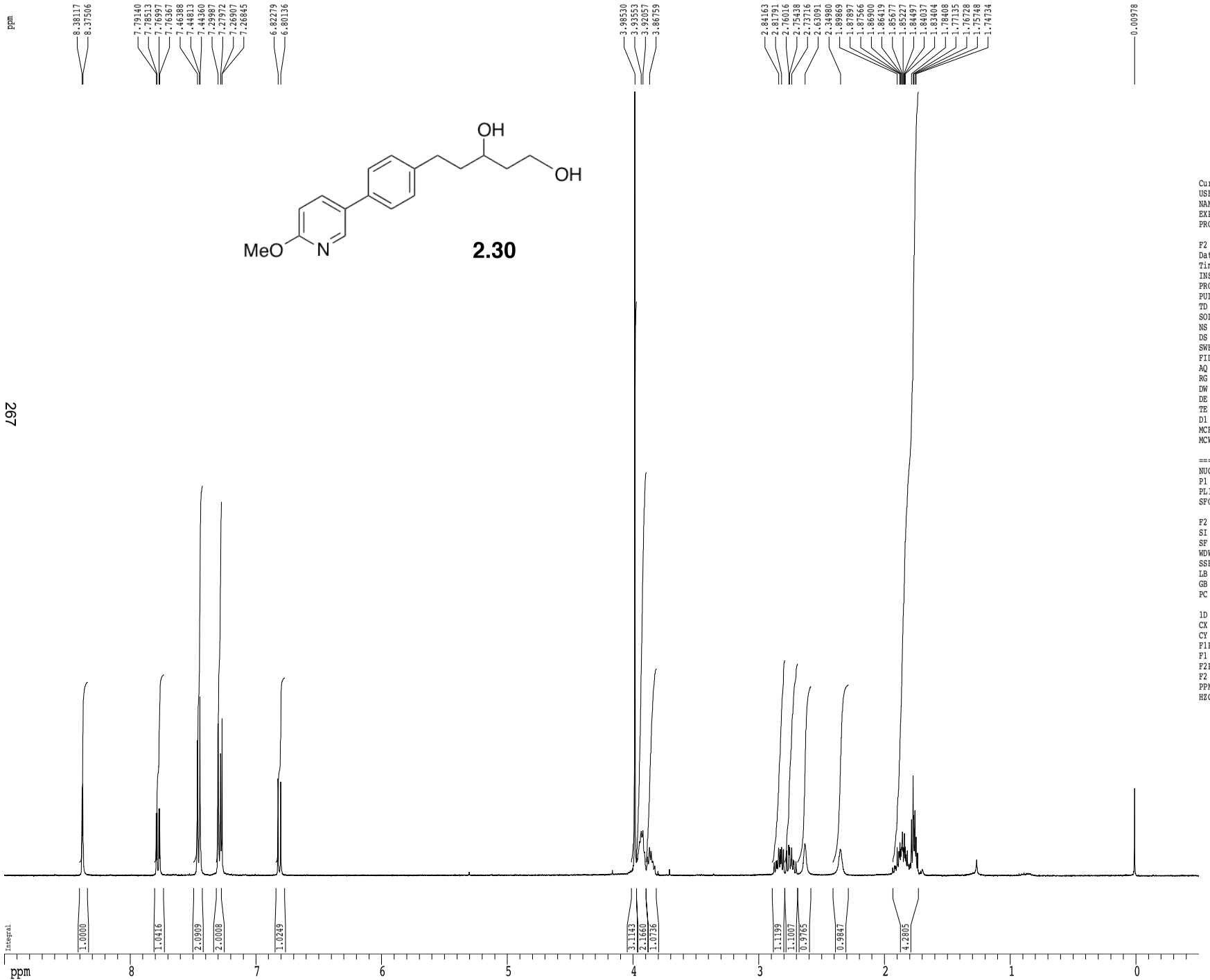
======== CHANNEL f1 ========
NUC1                 13C
P1                  7.65 usec
PL1                -3.00 dB
SFO1         100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                -1.10 dB
PL12               16.80 dB
SFO2         400.1328009 MHz

F2 - Processing parameters
SI                65536
SF           100.6127591 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P              200.000 ppm
F1             20122.55 Hz
F2P              -10.000 ppm
F2             -1006.13 Hz
PPMCM            9.21053 ppm/cm
HZCM           926.69647 Hz/cm
```

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-137-proton
EXPNO 1
PROCNO 1

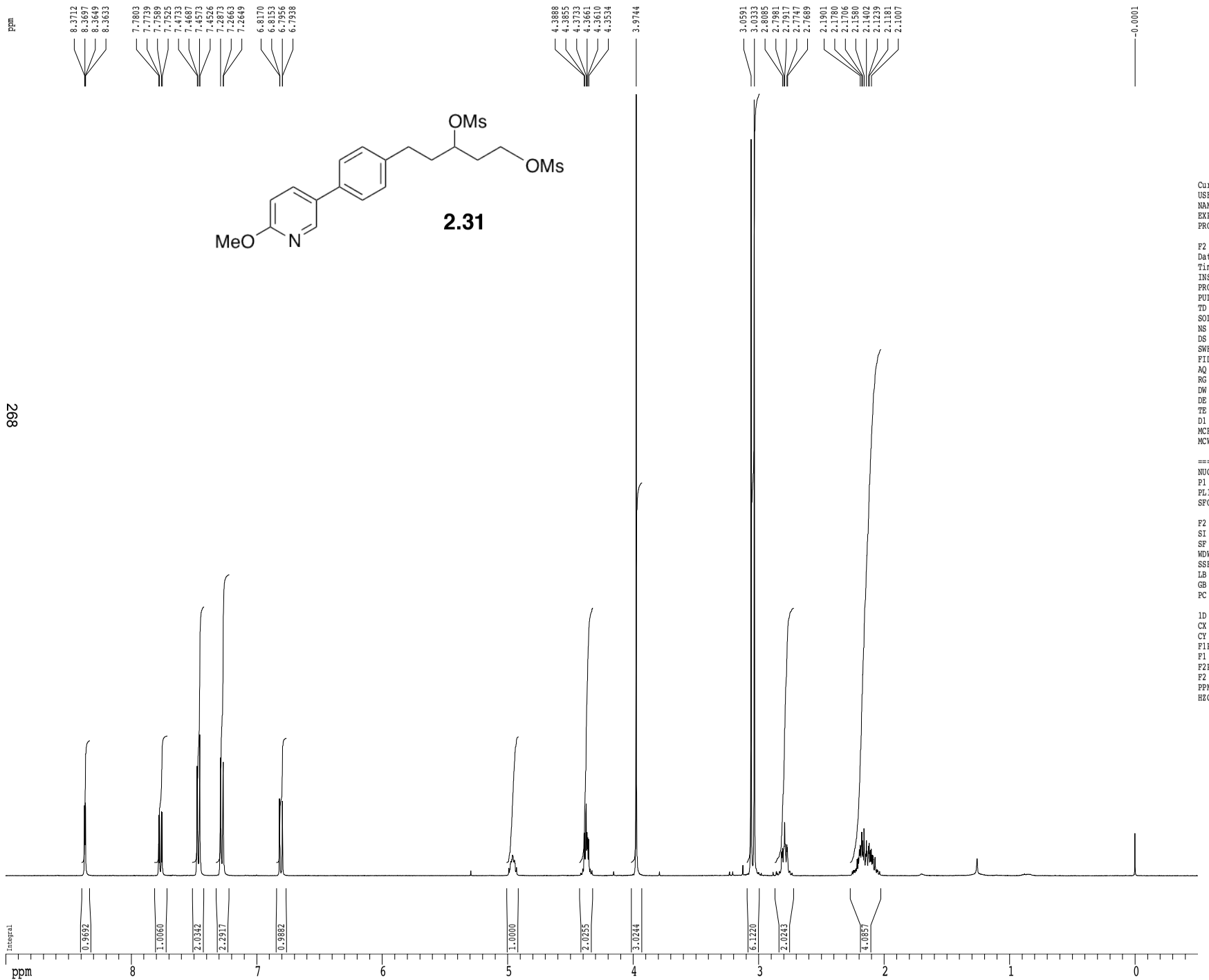
F2 - Acquisition Parameters
Date_ 20190126
Time 13.35
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 362
DW 78.000 usec
DE 4.50 usec
TE 298.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-138-proton
EXPNO 1
PROCNO 1

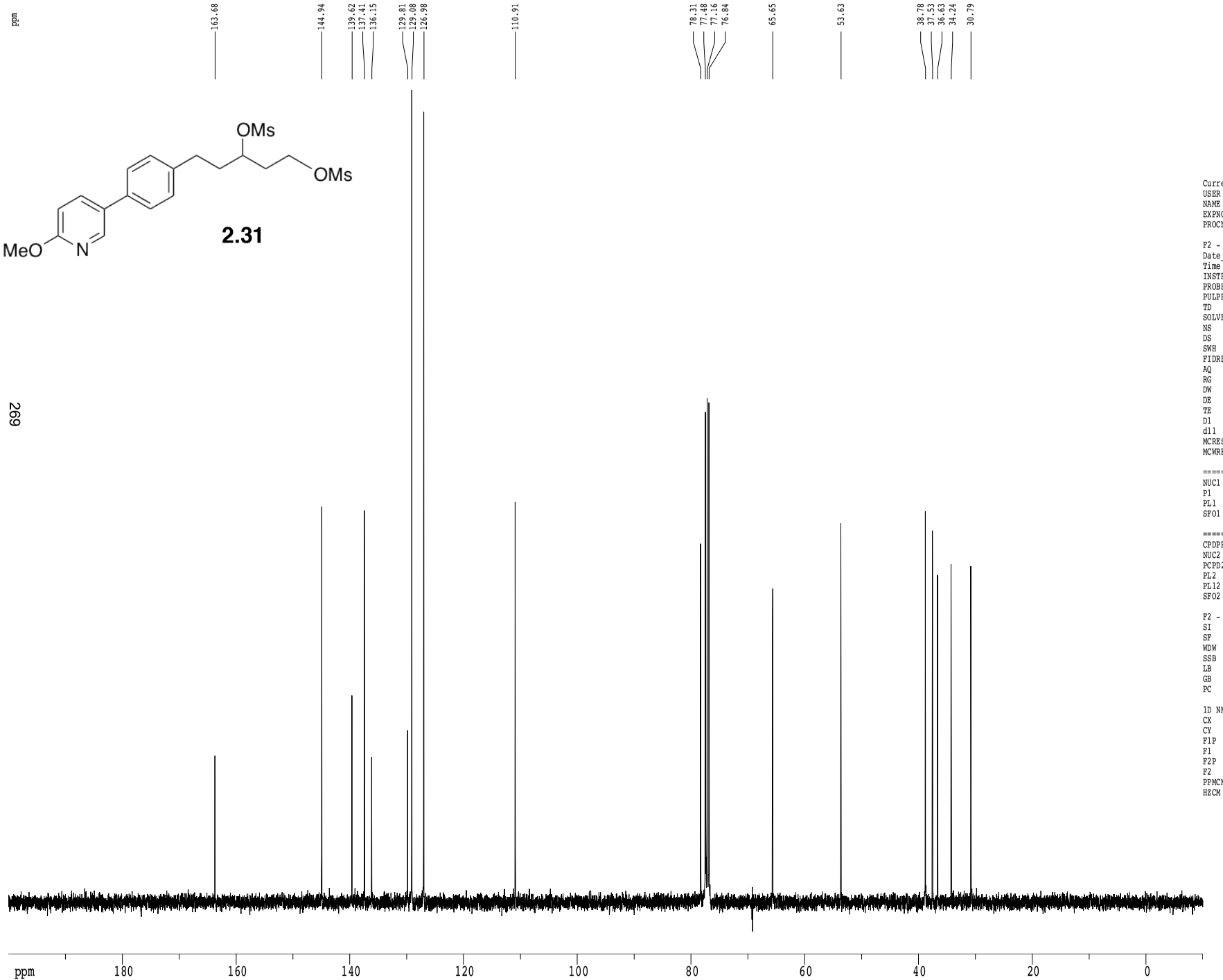
F2 - Acquisition Parameters
Date_ 20190126
Time 15.40
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 128
DW 78.000 usec
DE 4.50 usec
TE 298.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300191 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER sanforda
NAME ABS-2-138-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190126
Time 15.47
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 472
DS 4
SWH 24154.590 Hz
FIDRES 0.368570 Hz
AQ 1.3566452 sec
RG 9195.2
DW 20.700 usec
DE 20.39 usec
TE 299.0 K
D1 0.10000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

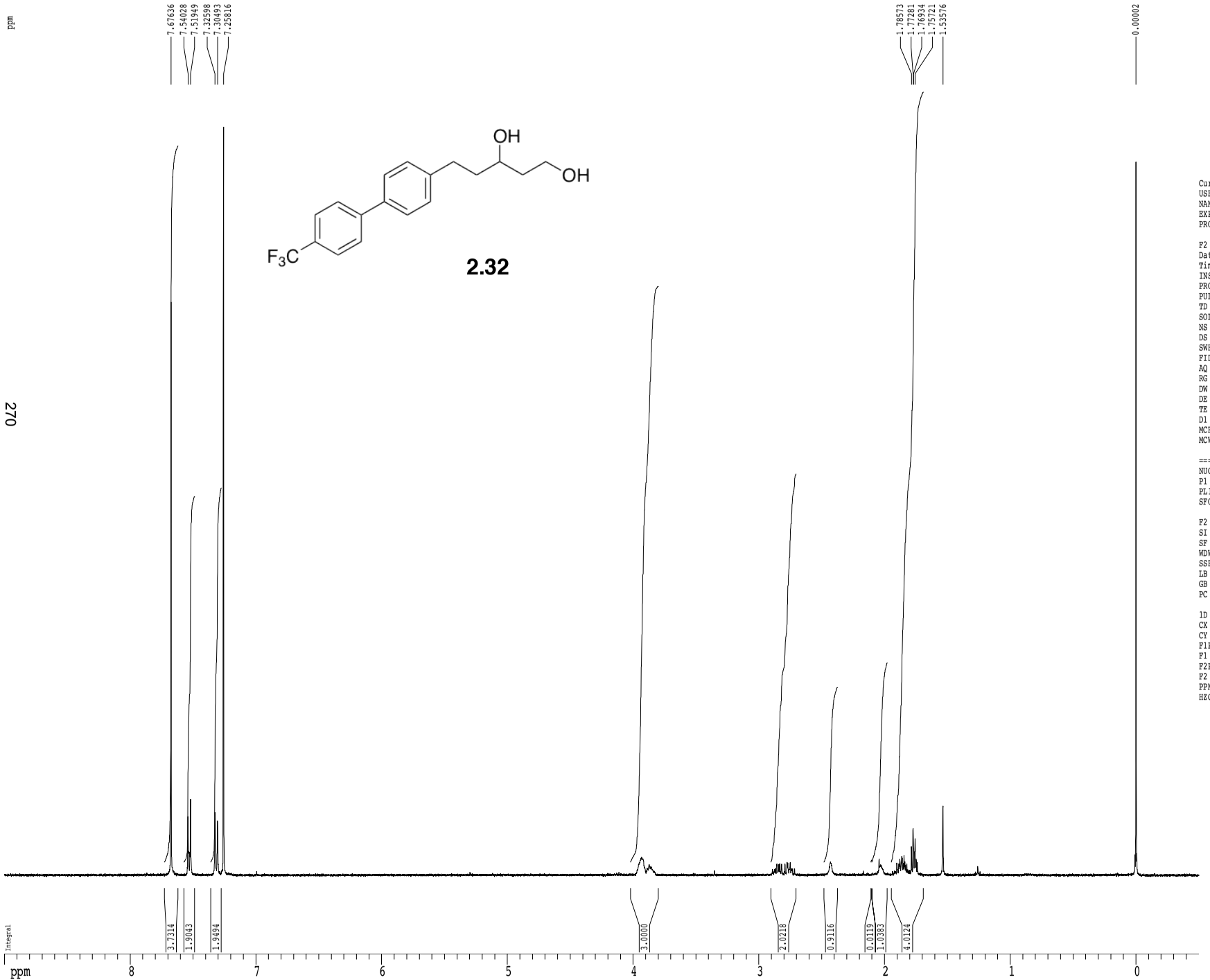
======== CHANNEL f1 ========
NUC1 13C
P1 7.65 usec
PL1 -3.00 dB
SFO1 100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.10 dB
PL12 16.80 dB
SFO2 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 100.6127617 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.50 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 9.21053 ppm/cm
HZCM 926.69647 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-122-pure-2
EXPNO 1
PROCNO 1

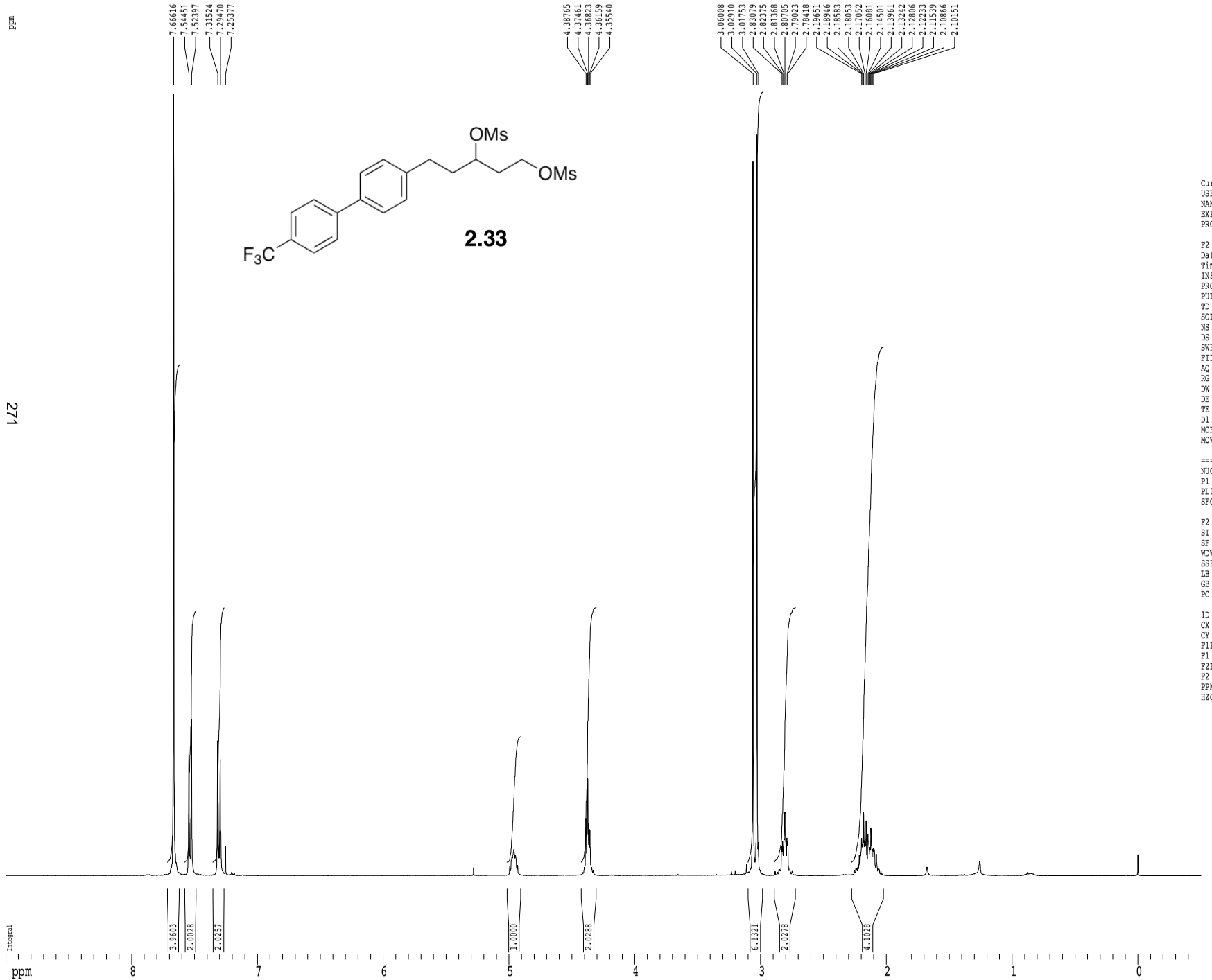
F2 - Acquisition Parameters
Date_ 20190115
Time 15.18
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 912.3
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300221 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-130-pure
EXPNO 1
PROCNO 1

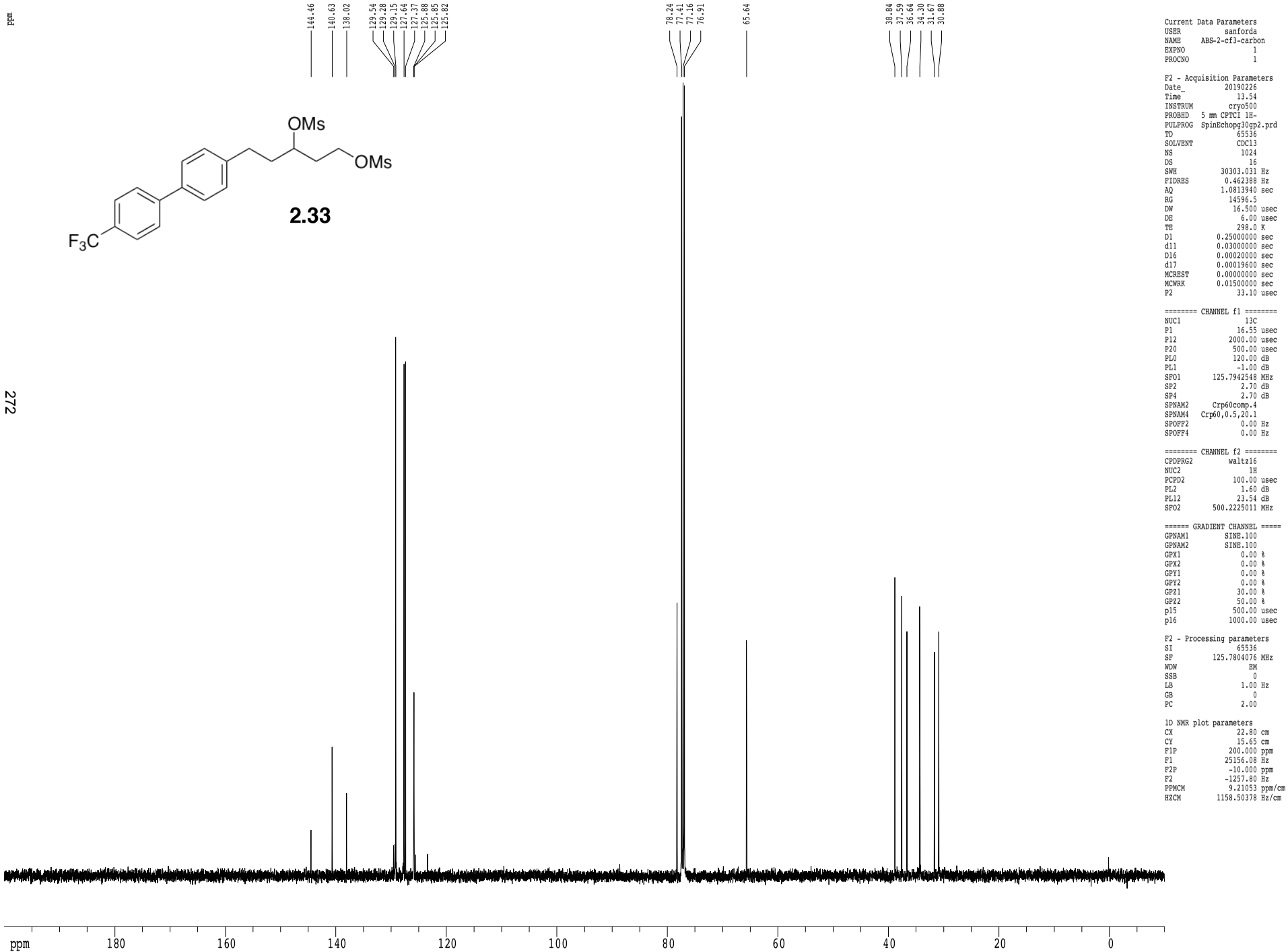
F2 - Acquisition Parameters
Date_ 20190116
Time 18.24
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 50.8
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300235 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

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




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-cf3-carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190226
Time                13.54
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                     16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ            1.0813940 sec
RG              14596.5
DW               16.500 usec
DE                6.00 usec
TE              298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

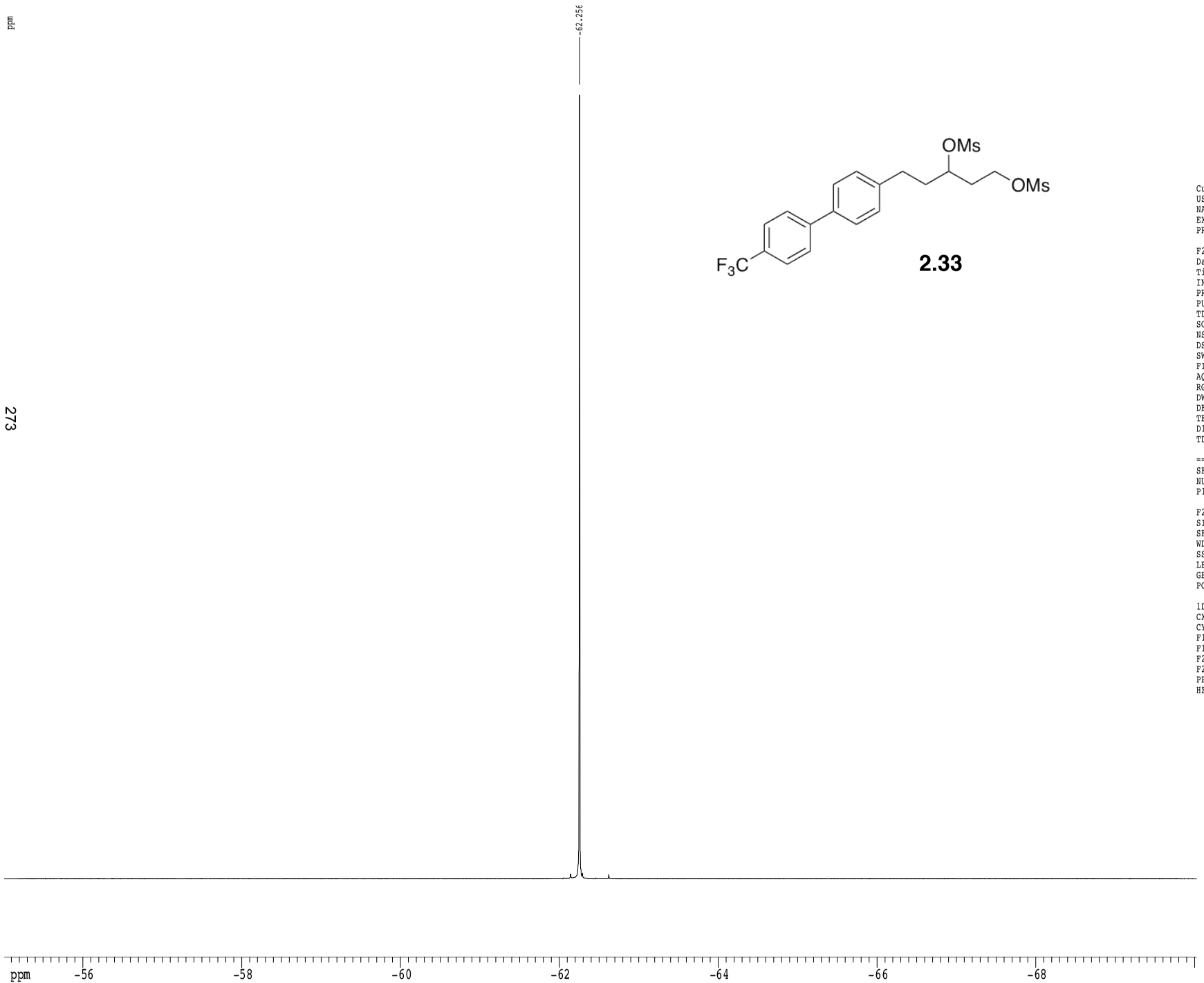
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                  65536
SF          125.7804076 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1             25156.08 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM             9.21053 ppm/cm
HZCM         1158.50378 Hz/cm
```

19F spectrum



2.33

```
Current Data Parameters
USER            mcginnit
NAME          tmm-2-030
EXPNO                 3
PROCNO                1

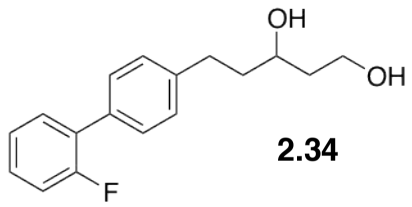
F2 - Acquisition Parameters
Date_          20200108
Time              17.34
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgflqn30
TD                25422
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8474.576 Hz
FIDRES         0.333356 Hz
AQ             1.4999480 sec
RG                  406
DW               59.000 usec
DE               18.00 usec
TE                298.0 K
D1           3.00000000 sec
TD0                   1

======== CHANNEL f1 =======
SFO1         564.6510827 MHz
NUC1               19F
P1               17.50 usec

F2 - Processing parameters
SI               131072
SF           564.6863858 MHz
WDW                 no
SSB                  0
LB                0.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              -55.014 ppm
F1            -31065.78 Hz
F2P              -70.022 ppm
F2            -39540.36 Hz
PPMCM           0.65823 ppm/cm
HZCM          371.69205 Hz/cm
```

1H spectrum



2.34

274

Current Data Parameters
USER sanforda
NAME ABS-2-087-pure2
EXPNO 1
PROCNO 1

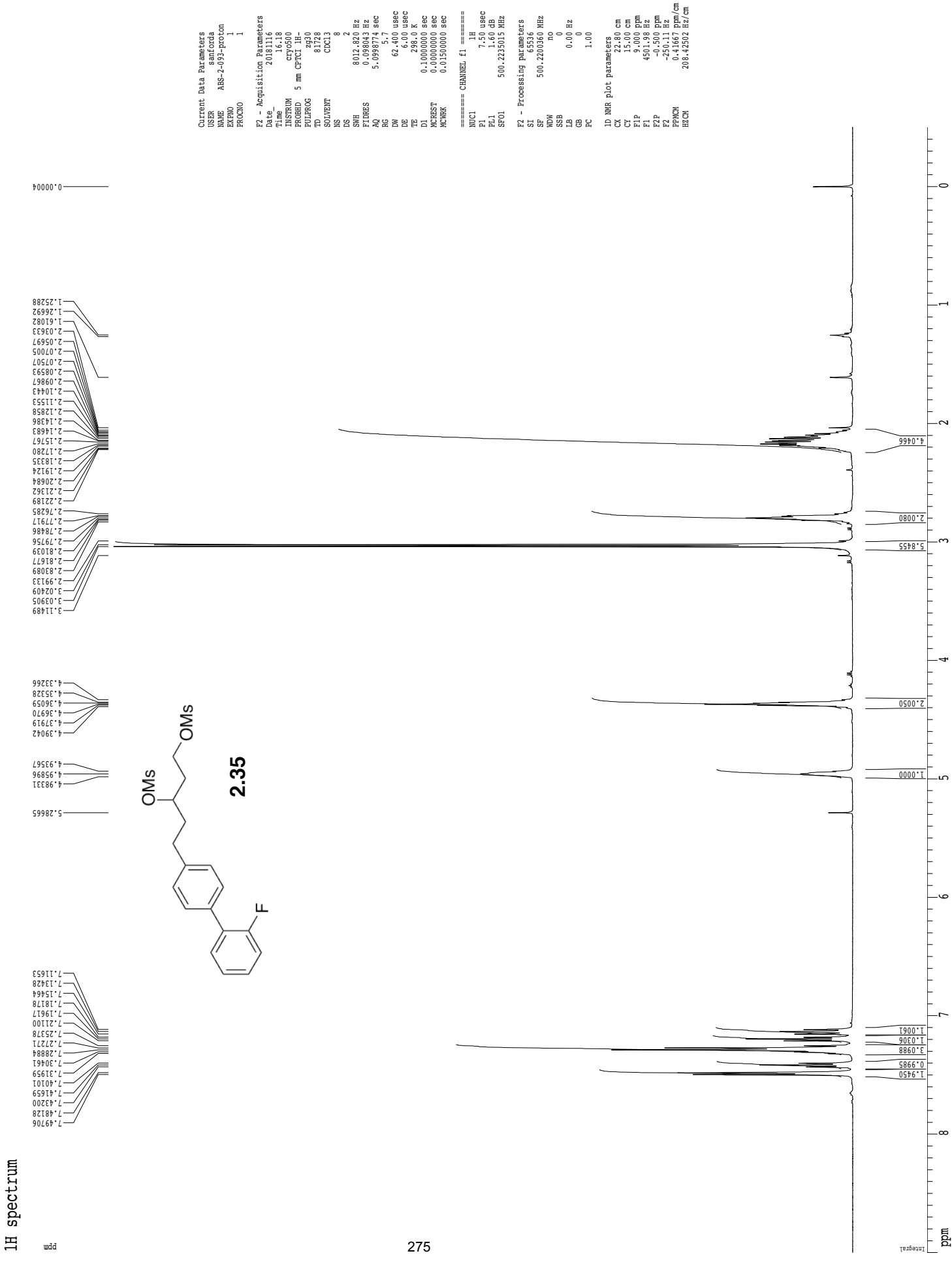
F2 - Acquisition Parameters
Date_ 20181115
Time 12.24
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 4.5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

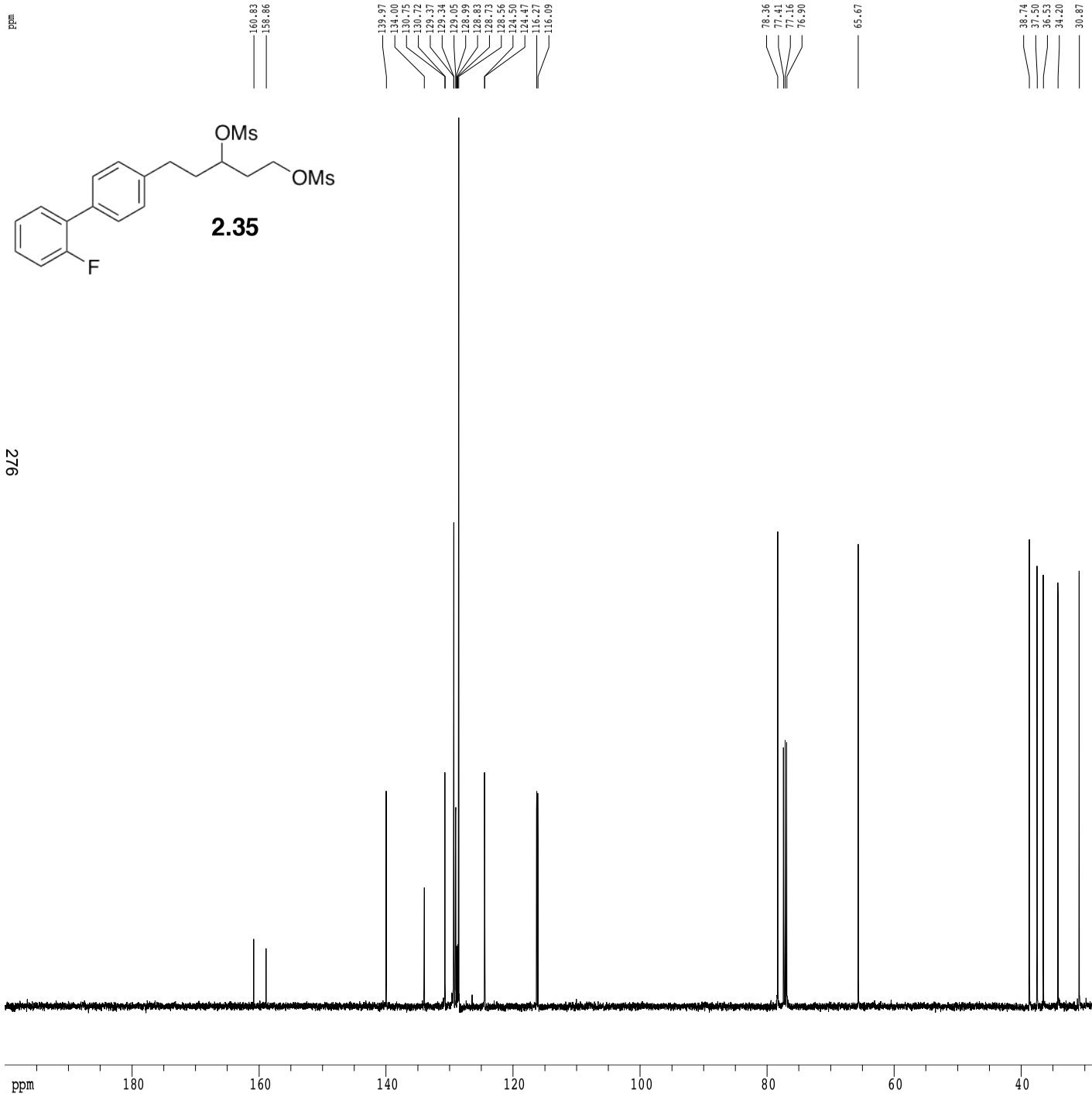
F2 - Processing parameters
SI 65536
SF 500.2200395 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-093-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181116
Time_ 16.18
INSTRUM CTYo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200360 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
OMs
OMs
F
2.35
4.0466
2.0080
5.8455
2.0050
1.0000
1.0061
1.0306
3.0988
0.9985
1.9450
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-2-093-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181116
Time 16.22
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 288
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 6502
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

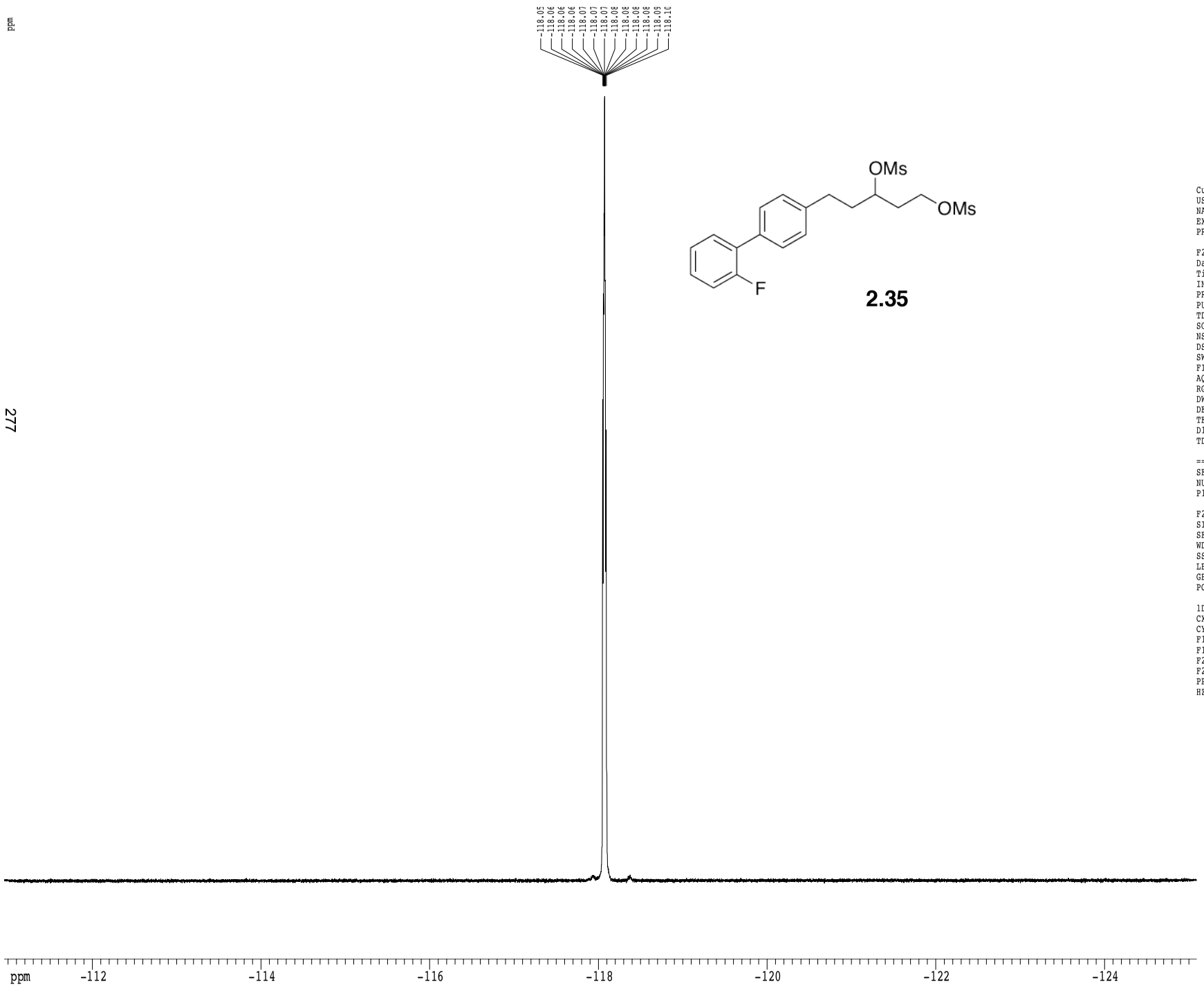
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804150 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

19F spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-093-F
EXPNO 2
PROCNO 1

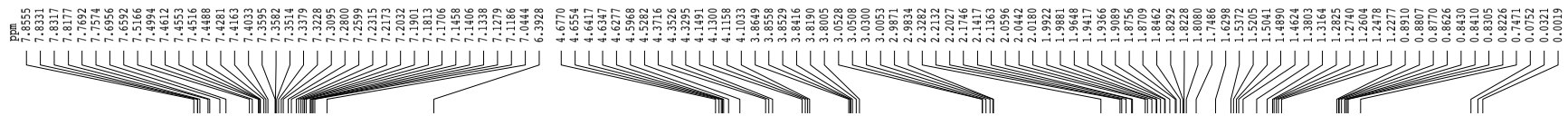
F2 - Acquisition Parameters
Date_ 20191220
Time 12.15
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgflqn30
TD 23934
SOLVENT CDCl3
NS 16
DS 2
SWH 7978.724 Hz
FIDRES 0.333364 Hz
AQ 1.4999141 sec
RG 575
DW 62.667 usec
DE 18.00 usec
TE 298.0 K
D1 3.00000000 sec
TD0 1

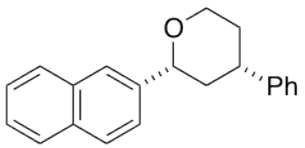
======== CHANNEL f1 ========
SFO1 564.6197387 MHz
NUC1 19F
P1 17.50 usec

F2 - Processing parameters
SI 131072
SF 564.6863858 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P -110.960 ppm
F1 -62657.71 Hz
F2P -125.090 ppm
F2 -70636.44 Hz
PPMCM 0.61971 ppm/cm
HZCM 349.94406 Hz/cm

1H spectrum





1.1

278

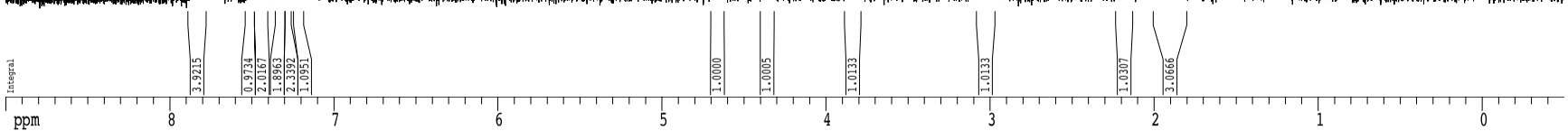
Current Data Parameters
USER sanforda
NAME ABS-2-102-pure
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181204
Time 11.14
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 1824.6
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

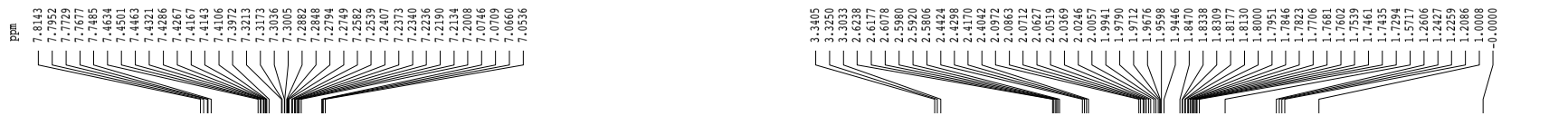
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -5.80 dB
SFO1 498.9534926 MHz

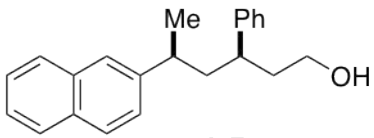
F2 - Processing parameters
SI 65536
SF 498.9500312 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4490.55 Hz
F2P -0.500 ppm
F2 -249.47 Hz
PPMCM 0.41667 ppm/cm
HZCM 207.89586 Hz/cm



1H spectrum





1.5

279


```
Current Data Parameters
USER            sanforda
NAME       ABS-2-114-f11
EXPNO                   1
PROCNO                  1

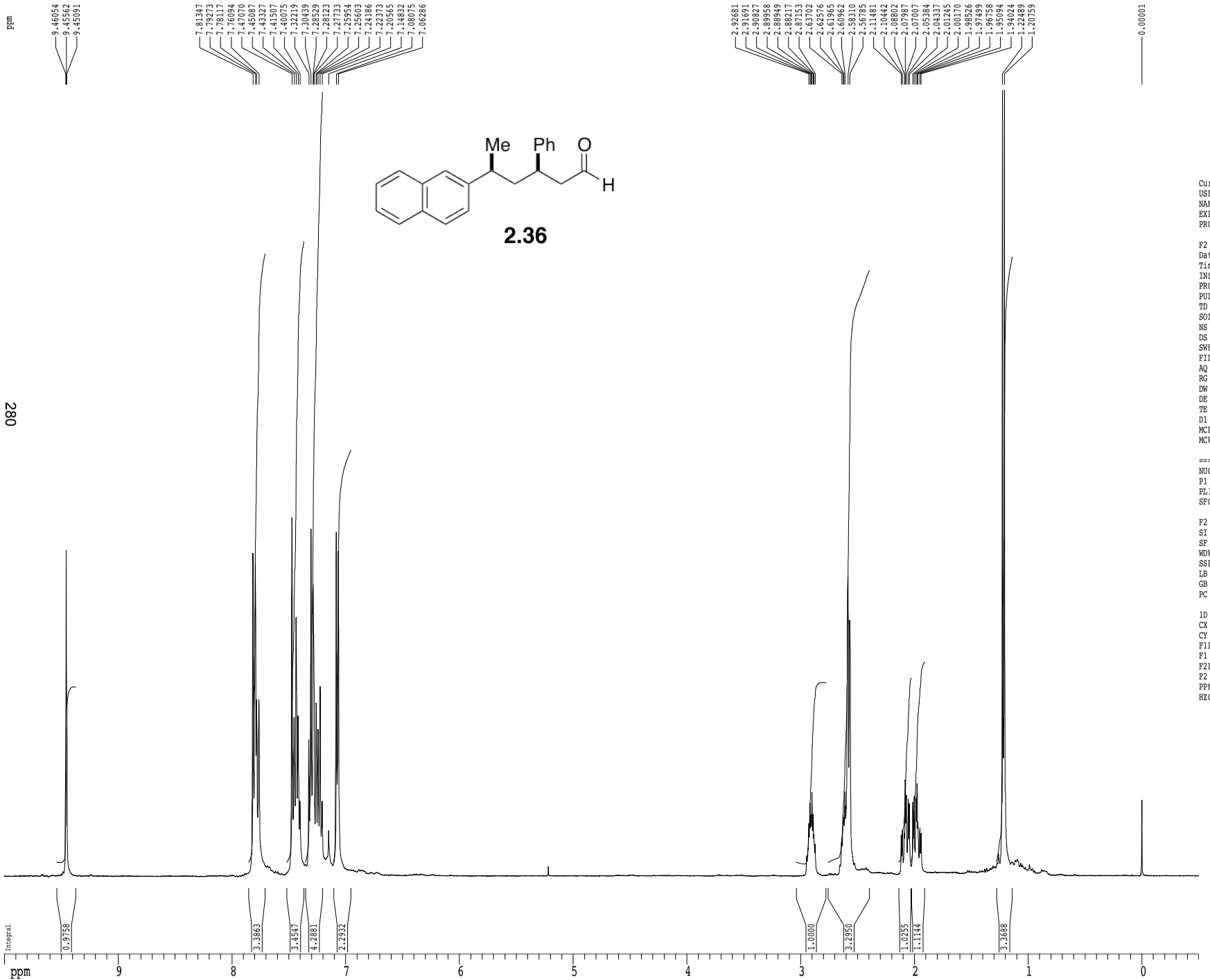
F2 - Acquisition Parameters
Date_            20181220
Time                14.35
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ              5.1118579 sec
RG                  80.6
DW                78.000 usec
DE                 4.50 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======= CHANNEL f1 =======
NUC1                   1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300356 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                 9.000 ppm
F1               3601.17 Hz
F2P                -0.500 ppm
F2               -200.06 Hz
PPMCM           0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

1H spectrum



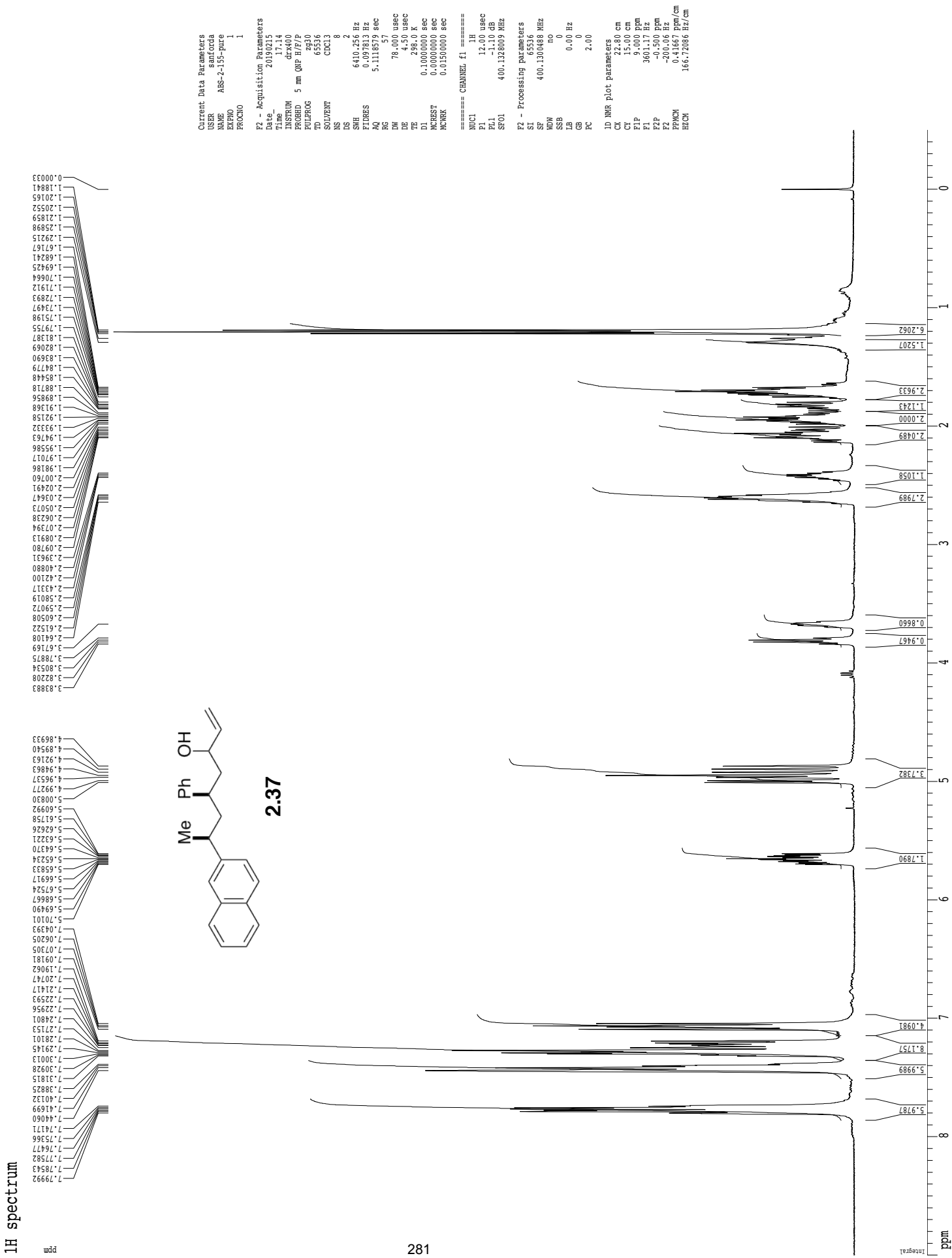

```
Current Data Parameters
USER            sanforda
NAME      ABS-2-151-pure
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20190215
Time                9.54
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ              5.1118579 sec
RG                    64
DW                78.000 usec
DE                 4.50 usec
TE                297.9 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

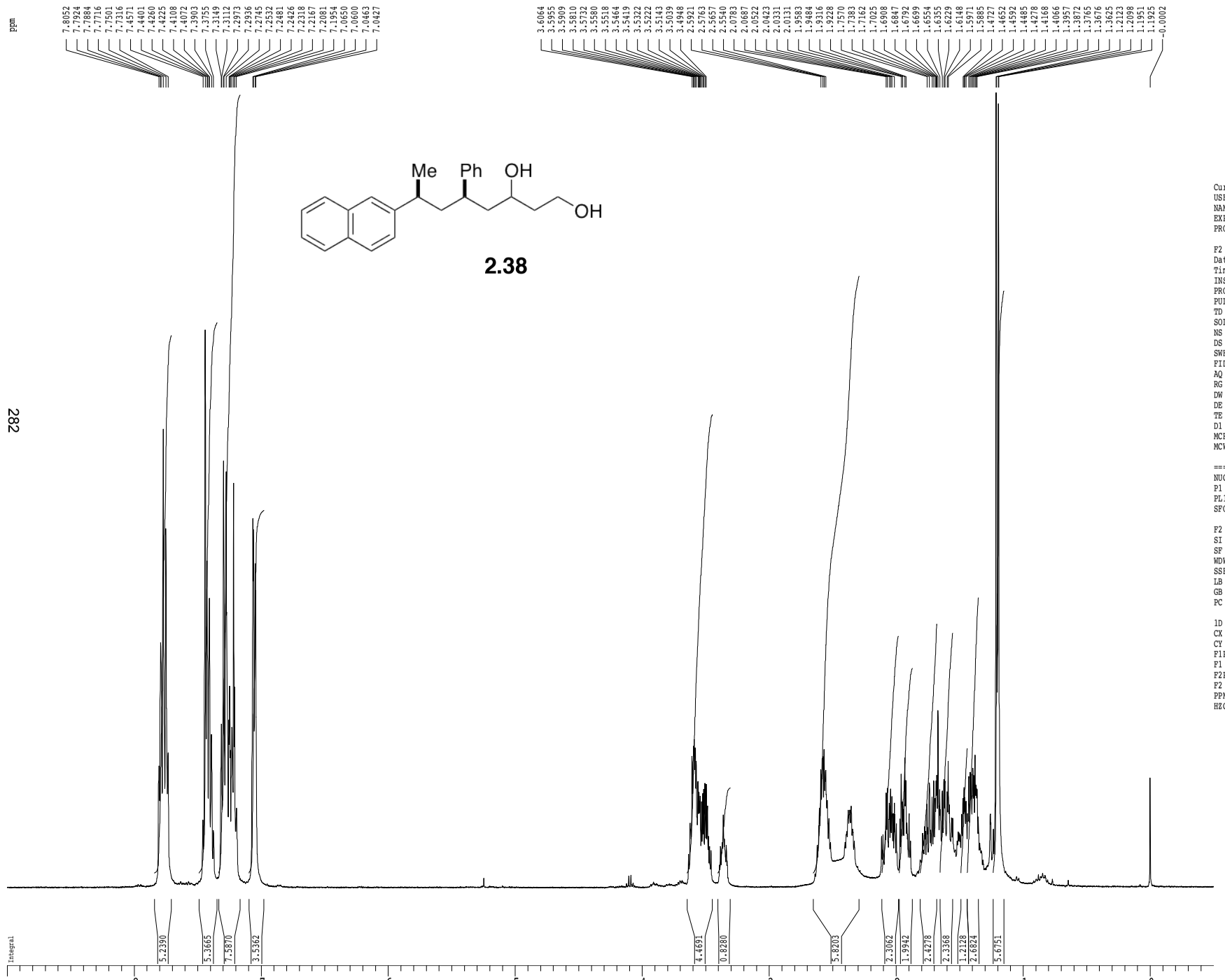
======= CHANNEL f1 =======
NUC1                  1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300644 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P               10.000 ppm
F1              4001.30 Hz
F2P                -0.500 ppm
F2               -200.07 Hz
PPMCM           0.46053 ppm/cm
HZCM          184.27043 Hz/cm
```


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-2-155-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190215
Time_ 17.14
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 57
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300488 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
Me
Ph
OH
2.37
6.2062
1.5207
2.9633
1.1243
2.0000
2.0489
1.1058
2.7989
0.8660
0.9467
3.7382
1.7890
4.0981
8.1757
5.9989
5.9787
ppm
Integral

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-156-pure
EXPNO 1
PROCNO 1

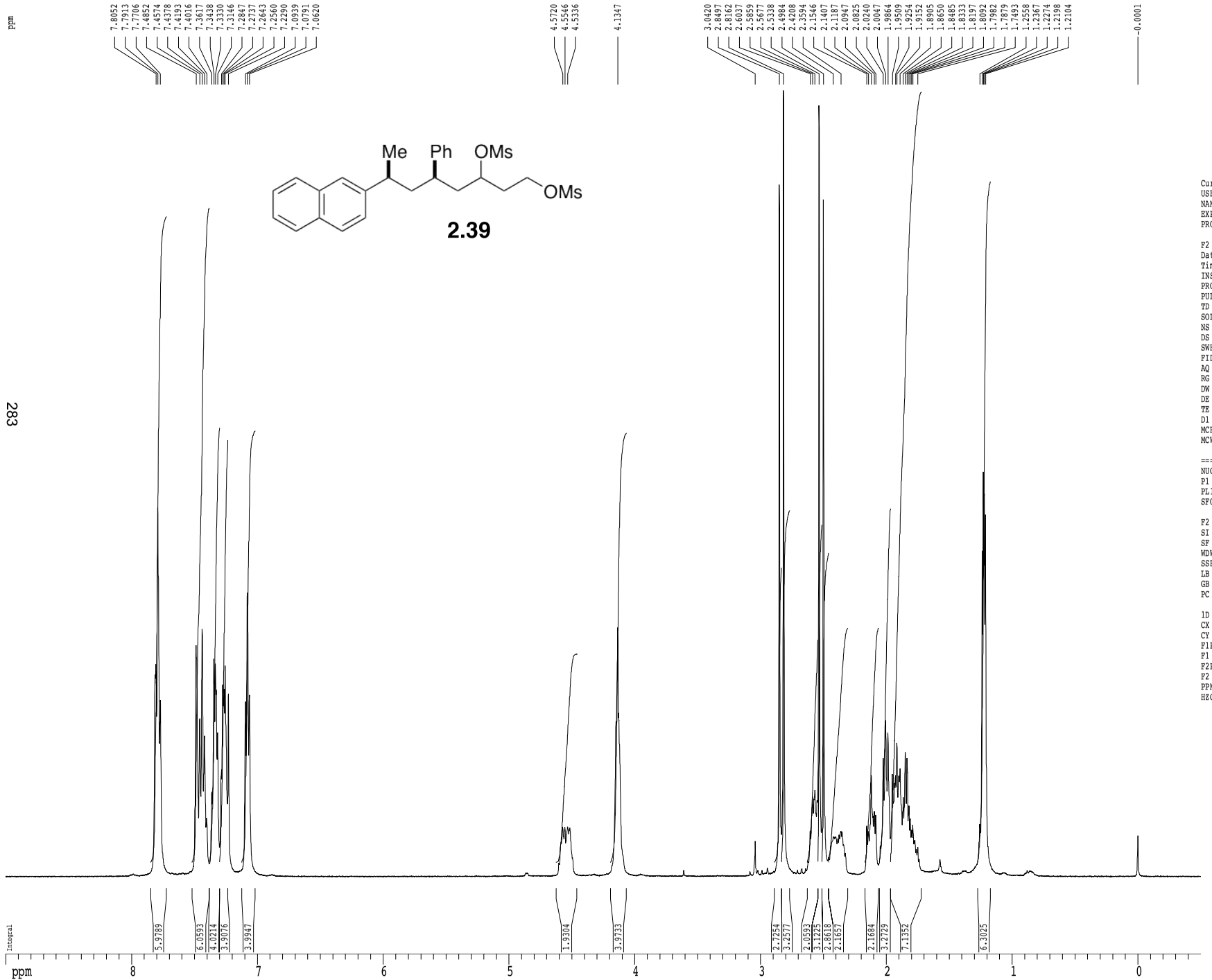
F2 - Acquisition Parameters
Date_ 20190218
Time 15.14
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 64
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300382 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-2-157-proton
EXPNO 1
PROCNO 1

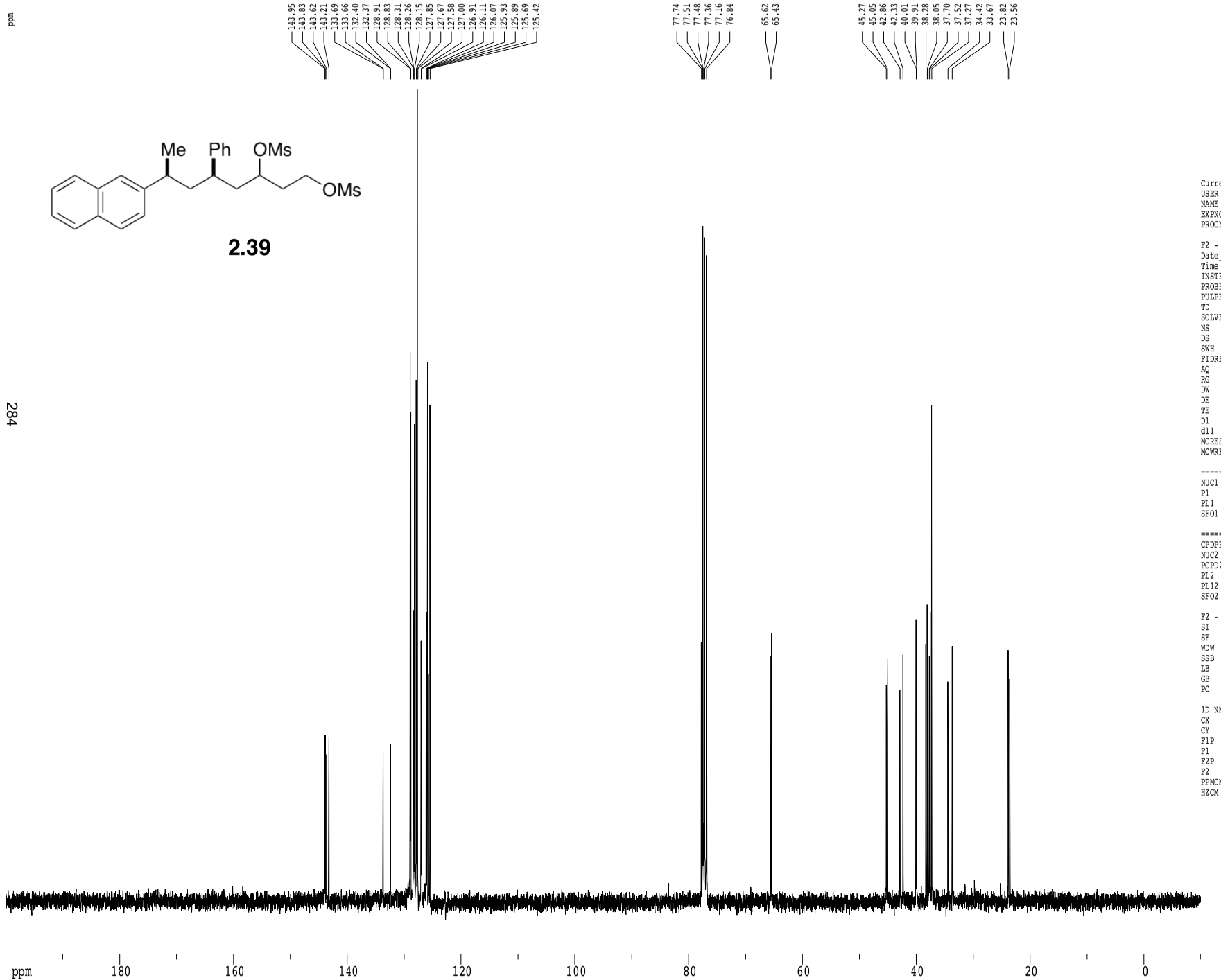
F2 - Acquisition Parameters
Date_ 20190219
Time 17.01
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 64
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300331 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

13C spectrum with 1H decoupling




```
Current Data Parameters
USER            sanforda
NAME      ABS-2-157-carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190219
Time              17.04
INSTRUM           drx400
PROBHD   5 mm QNP H/F/P
PULPROG           zgdc30
TD                65536
SOLVENT           CDCl3
NS                  688
DS                    4
SWH           24154.590 Hz
FIDRES         0.368570 Hz
AQ             1.3566452 sec
RG                9195.2
DW               20.700 usec
DE               20.39 usec
TE                298.0 K
D1            0.10000000 sec
d11           0.03000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

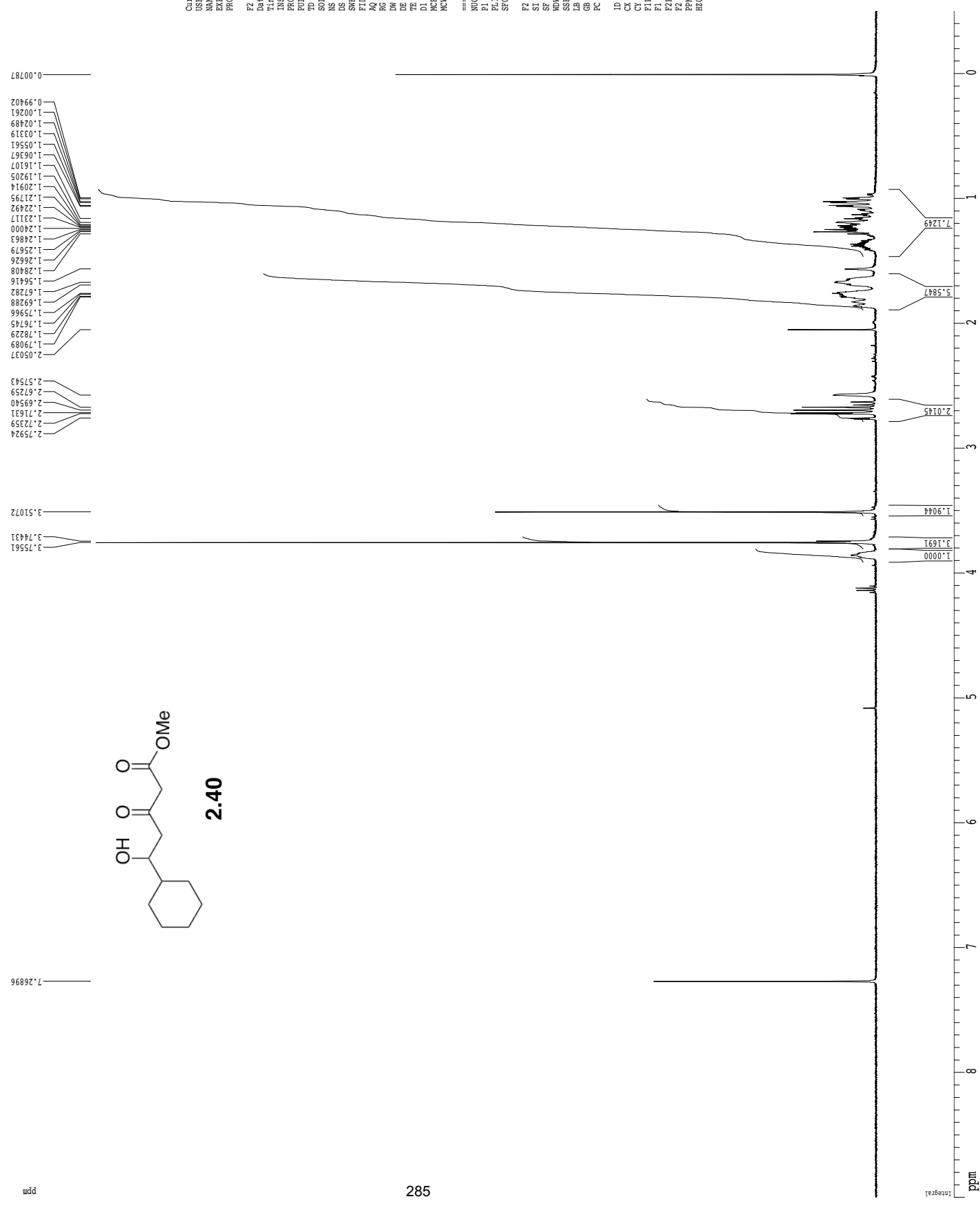
======== CHANNEL f1 ========
NUC1                13C
P1                7.65 usec
PL1              -3.00 dB
SFO1        100.6237964 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            90.00 usec
PL2              -1.10 dB
PL12             16.80 dB
SFO2        400.1328009 MHz

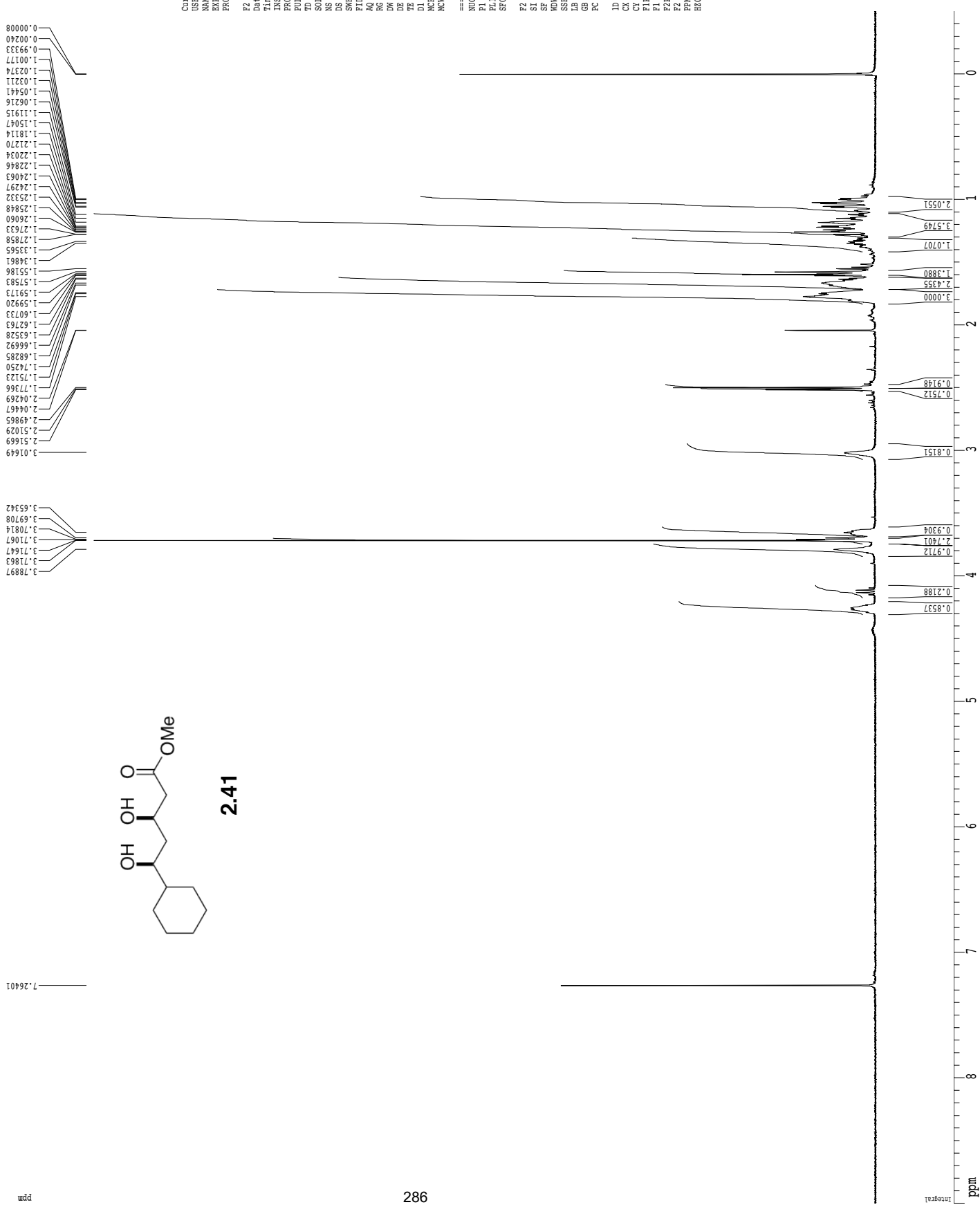
F2 - Processing parameters
SI                65536
SF          100.6127680 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.50 cm
F1P             200.000 ppm
F1             20122.55 Hz
F2P             -10.000 ppm
F2             -1006.13 Hz
PPMCM           9.21053 ppm/cm
HZCM          926.69653 Hz/cm
```

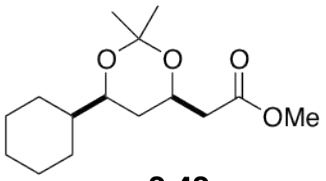
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-238-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190605
Time_ 16.26
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 645.1
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
0.00787
0.99402
1.00261
1.02489
1.03319
1.05561
1.06367
1.16107
1.19205
1.20914
1.21795
1.22492
1.23117
1.24000
1.24863
1.25679
1.26626
1.28408
1.56416
1.67282
1.69288
1.75966
1.76745
1.78229
1.79089
2.05037
2.57543
2.67259
2.69540
2.71631
2.72359
2.75924
3.51072
3.74431
3.75561
7.26896
7.1249
5.5847
2.0145
1.9044
3.1691
1.0000
OMe
O
O
OH
2.40
ppm
Integral

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-252-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190704
Time_ 9.18
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 322.5
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300197 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.000 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
7.26401
3.78897
3.71863
3.71647
3.71067
3.70814
3.69708
3.65342
3.01649
2.51669
2.51029
2.49865
2.04269
2.04467
1.77366
1.75123
1.74250
1.68285
1.66692
1.63528
1.62763
1.60733
1.59920
1.59173
1.57583
1.55186
1.34861
1.33565
1.27858
1.27633
1.26060
1.25848
1.25332
1.24297
1.24063
1.22846
1.22034
1.21270
1.18114
1.15047
1.11915
1.06216
1.05441
1.03211
1.02374
1.00177
0.99333
0.00240
0.00008
2.0551
3.5749
1.0707
1.3880
2.4355
3.0000
0.9148
0.7512
0.8151
0.9304
2.7401
0.9712
0.2188
0.8537
OH
OH
O
OMe
2.41
ppm
Integral

1H spectrum



2.42

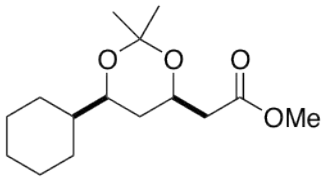
Current Data Parameters
USER sanforda
NAME ABS-2-253-crude
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190705
Time 11.57
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 50.8
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300108 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

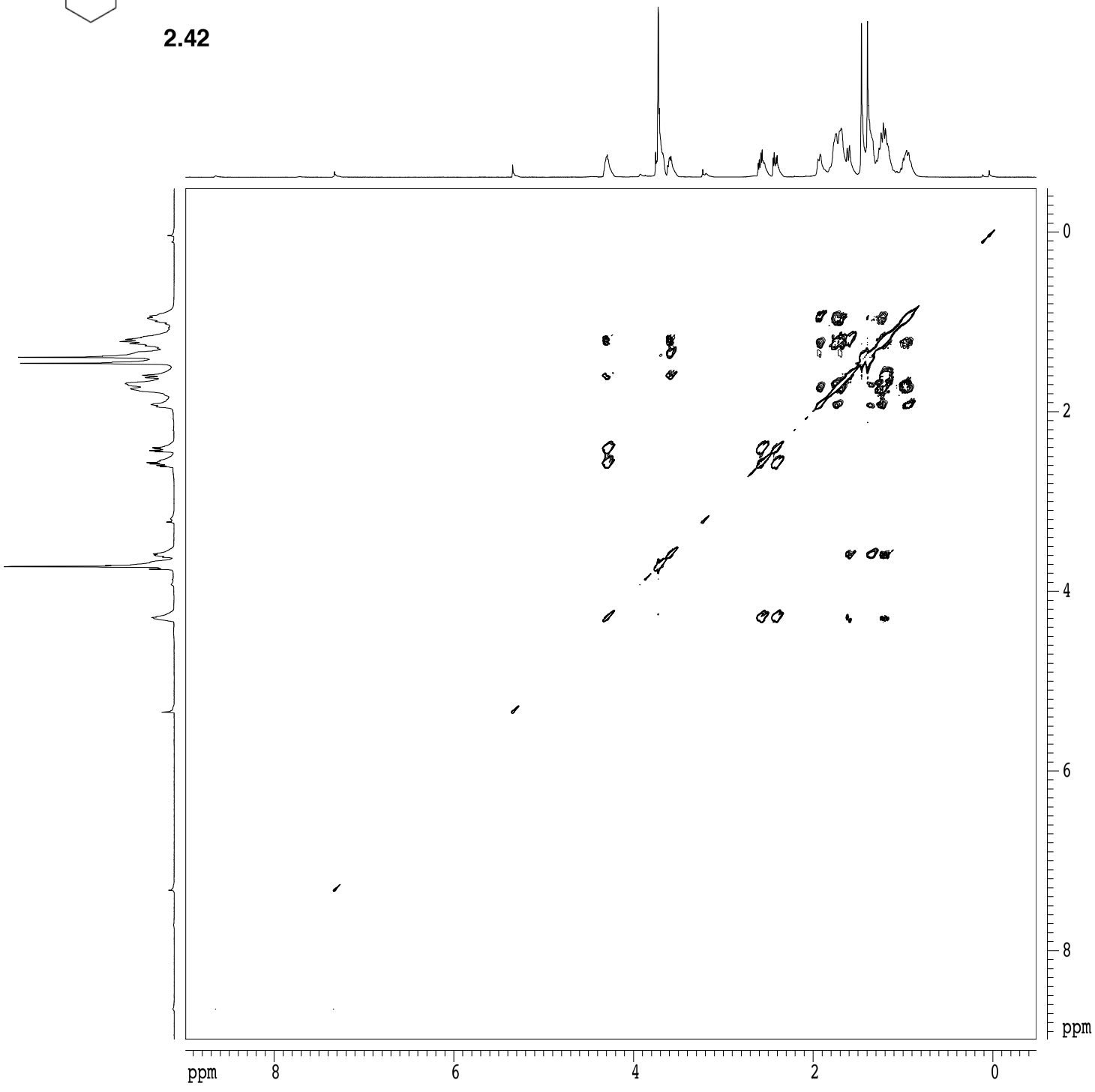
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm



2.42

gcosy60

288



Current Data Parameters

USER	sanforda
NAME	ABS-2-253-proton
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20190705
Time	13.27
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	1
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	25.4
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221259 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2221 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	QF

F2 - Processing parameters

SI	1024
SF	500.2200000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

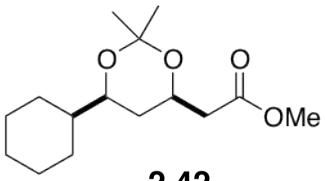
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200000 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.983 ppm
F2LO	4493.36 Hz
F2PHI	-0.483 ppm
F2HI	-241.49 Hz
F1PLO	8.983 ppm
F1LO	4493.36 Hz
F1PHI	-0.483 ppm
F1HI	-241.49 Hz
F2PPMCM	0.63104 ppm/cm
F2HZCM	315.65659 Hz/cm
F1PPMCM	0.63104 ppm/cm
F1HZCM	315.65659 Hz/cm

gnoe



2.42

Current Data Parameters
USER sanforda
NAME ABS-2-253-proton
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190705
Time 13.55
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoelcc22.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 35.9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33376500 sec
d22 0.16399699 sec
p2 15.00 usec

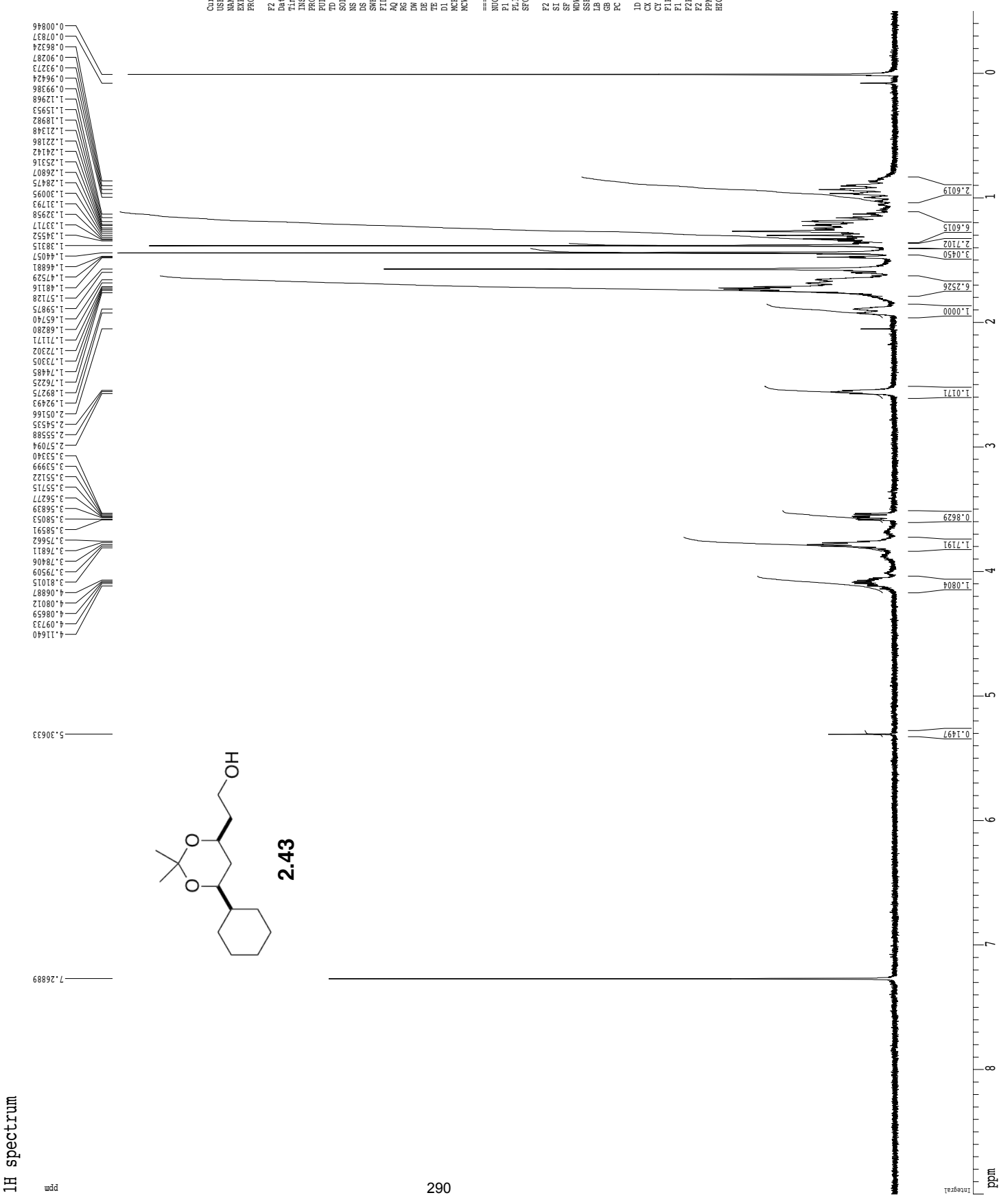
======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
p3 22.50 usec
p4 30.00 usec
p5 20.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2221474 MHz
SP9 61.60 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPNAM3 sine.100
GPNAM4 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

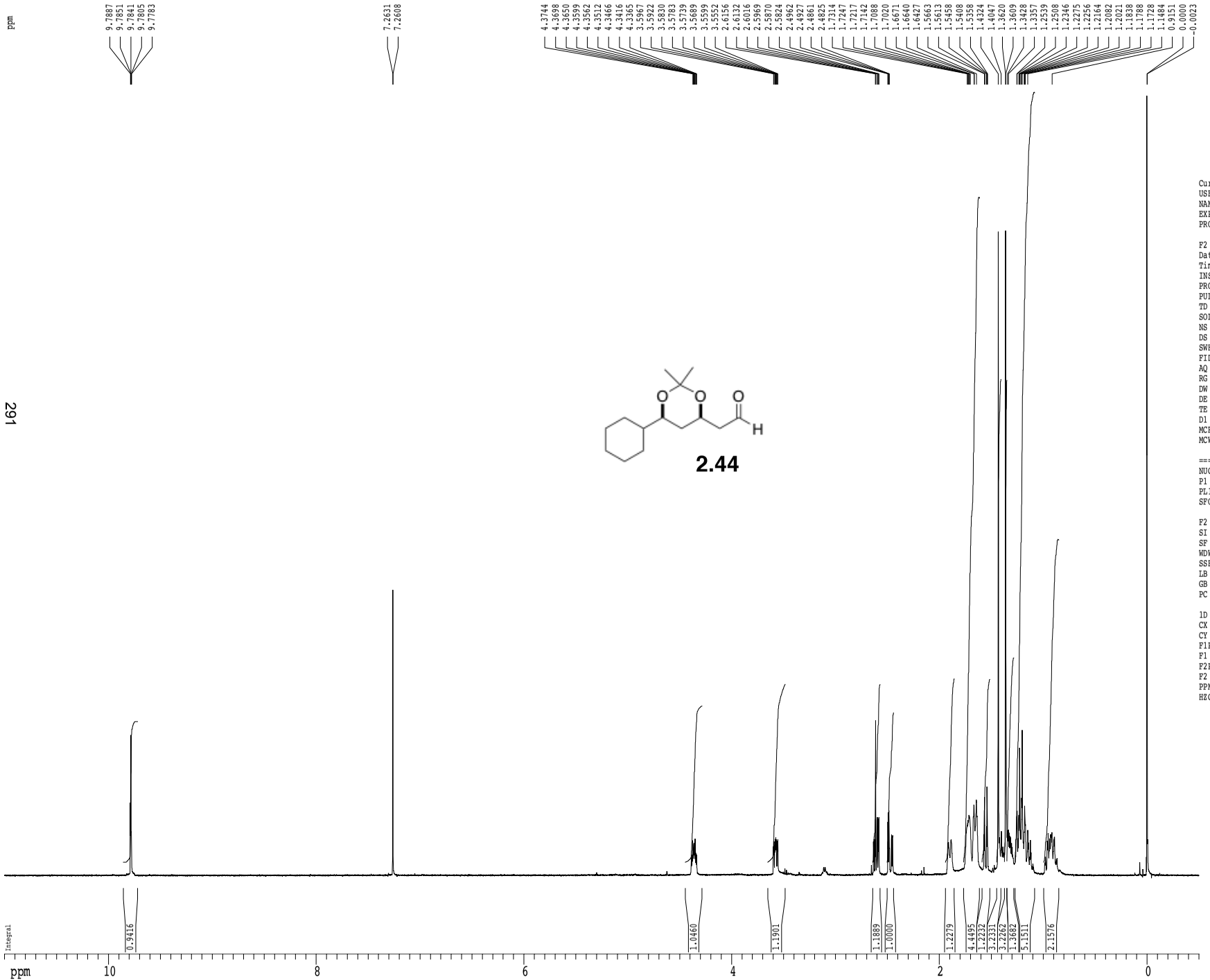
F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-297-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190830
Time_ 11.44
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 724.1
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
OH
2.43
ppm
Integral

1H spectrum



Current Data Parameters

USER	tthane
NAME	ABS-TATswern
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

Date_	20190822
Time	18.04
INSTRUM	gn500
PROBHD	5 mm broadband
PULPROG	zg30
TD	81728
SOLVENT	CDCl3T
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.098043 Hz
AQ	5.0998774 sec
RG	645.1
DW	62.400 usec
DE	6.00 usec
TE	298.0 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======= CHANNEL f1 =======

NUC1	1H
P1	12.00 usec
PL1	-5.00 dB
SFO1	498.8534919 MHz

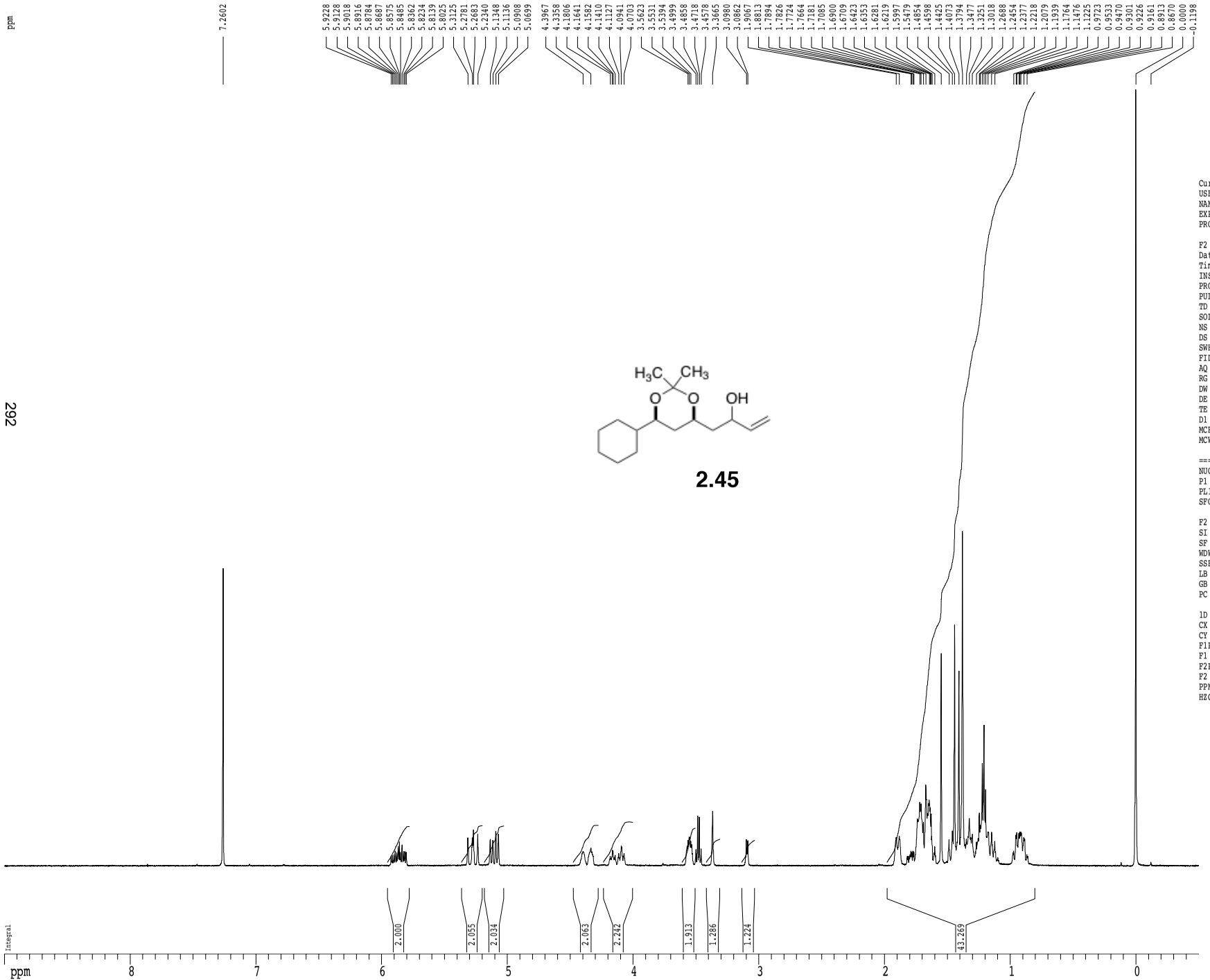
F2 - Processing parameters

SI	65536
SF	498.8500260 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
CY	15.00 cm
F1P	11.000 ppm
F1	5487.35 Hz
F2P	-0.500 ppm
F2	-249.43 Hz
PPMCM	0.50439 ppm/cm
HZCM	251.61296 Hz/cm

1H spectrum



Current Data Parameters
USER tthane
NAME TATiii20c
EXPNO 2
PROCNO 1

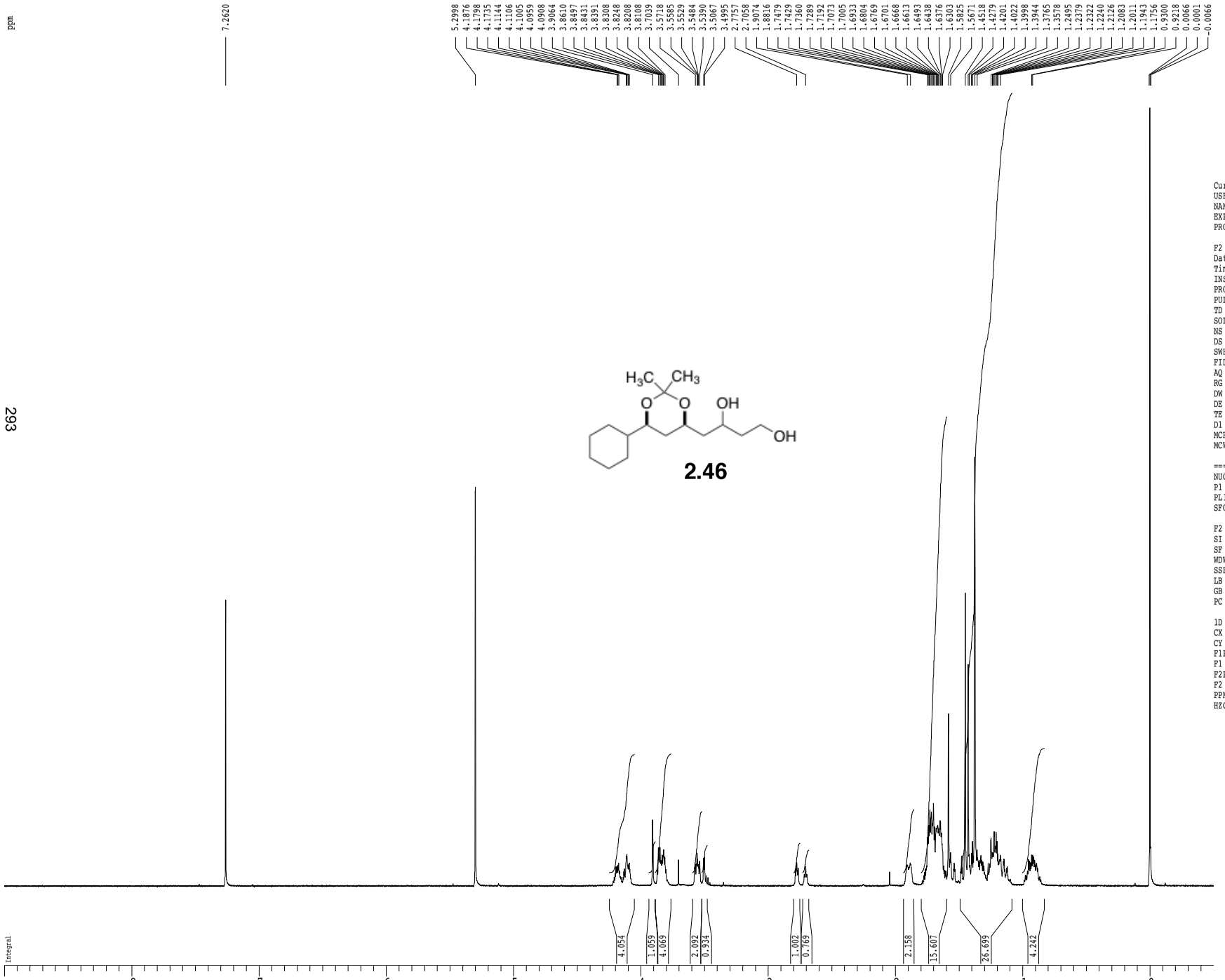
F2 - Acquisition Parameters
Date_ 20190823
Time 16.17
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 9
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

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

F2 - Processing parameters
SI 65536
SF 500.2200310 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm

1H spectrum



Current Data Parameters
USER tthane
NAME TATiii21
EXPNO 1
PROCNO 1

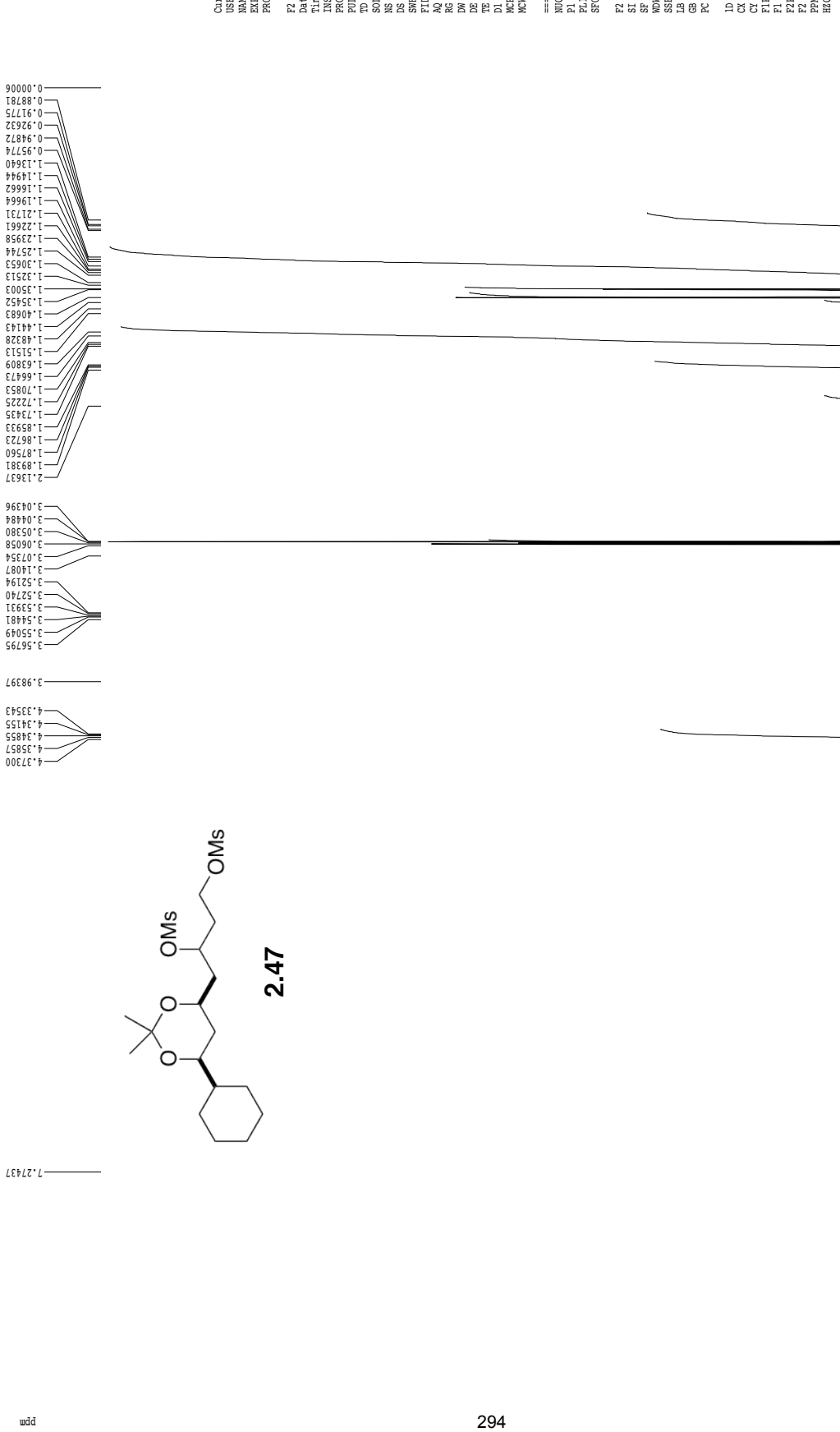
F2 - Acquisition Parameters
Date_ 20190830
Time 12.33
INSTRUM gn500
PROBHD 5 mm broadband
PULPROG zg30
TD 81728
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 1024
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -5.00 dB
SFO1 498.8534919 MHz

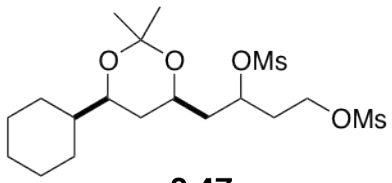
F2 - Processing parameters
SI 65536
SF 498.8500261 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4489.65 Hz
F2P -0.500 ppm
F2 -249.42 Hz
PPMCM 0.41667 ppm/cm
HZCM 207.85419 Hz/cm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-287-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190802
Time_ 9.54
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 101.6
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300153 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
7.27437
4.37300
4.35857
4.34855
4.34155
4.33543
3.98397
3.56795
3.55049
3.54481
3.53931
3.52740
3.52194
3.14087
3.07354
3.06058
3.05380
3.04484
3.04396
2.13637
1.89381
1.87560
1.86723
1.85933
1.74435
1.72225
1.70853
1.66473
1.63809
1.51513
1.48328
1.44143
1.40683
1.35452
1.35003
1.32513
1.30653
1.25744
1.23958
1.22661
1.21731
1.19664
1.16662
1.14944
1.13640
0.95774
0.94872
0.92632
0.91775
0.88781
0.00006
4.215
10.254
6.262
6.212
2.221
10.129
4.127
2.222
1.912
5.993
2.668
3.077
2.000
2.001
4.063
2.028
OMs
OMs
O
O
2.47
ppm
Integral

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



2.47

Current Data Parameters
USER sanforda
NAME ABS-2-287-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190802
Time 10.34
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 616
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.2 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

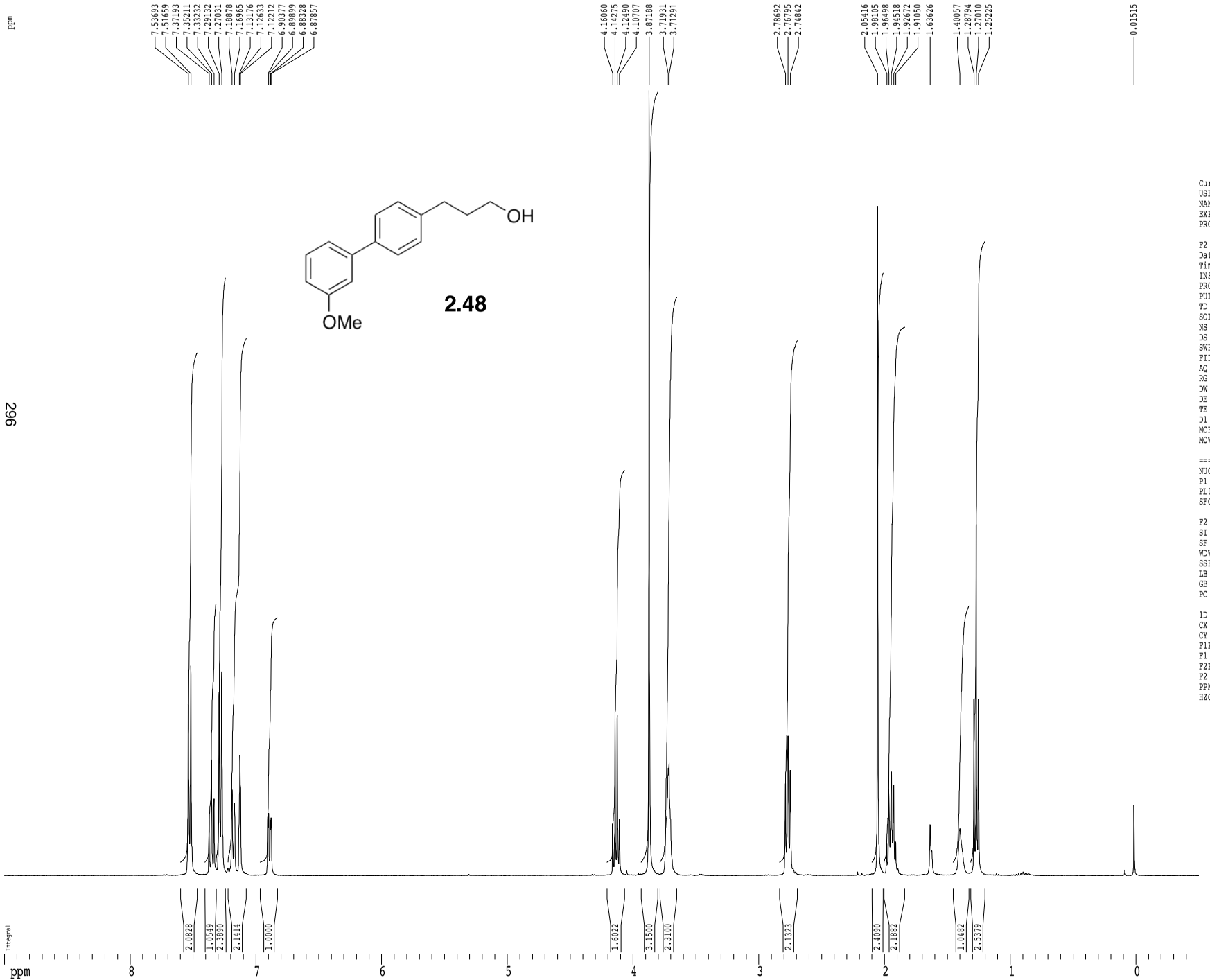
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804117 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



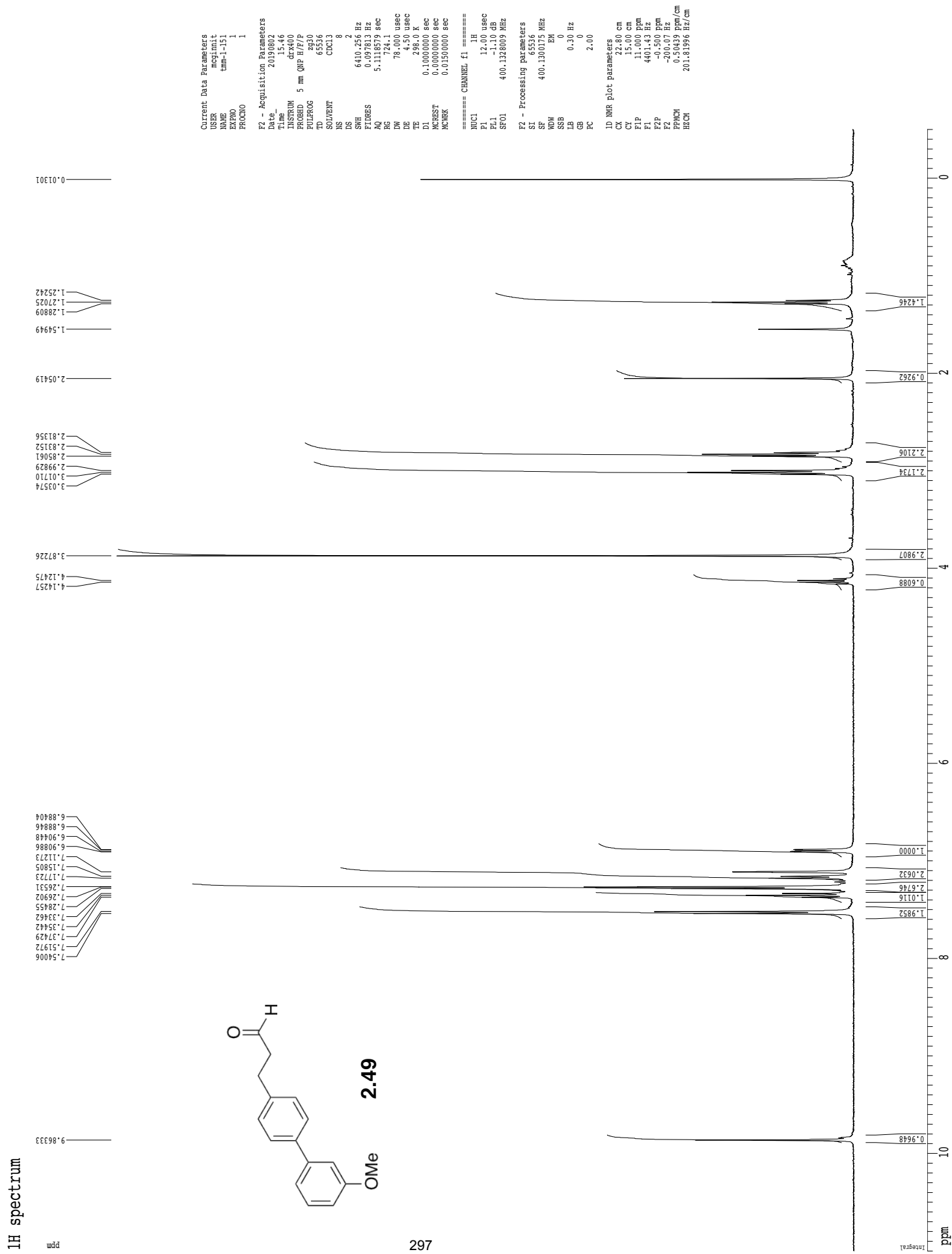
Current Data Parameters
USER mcginnit
NAME tmm-1-148-24
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190801
Time 9.46
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 256
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

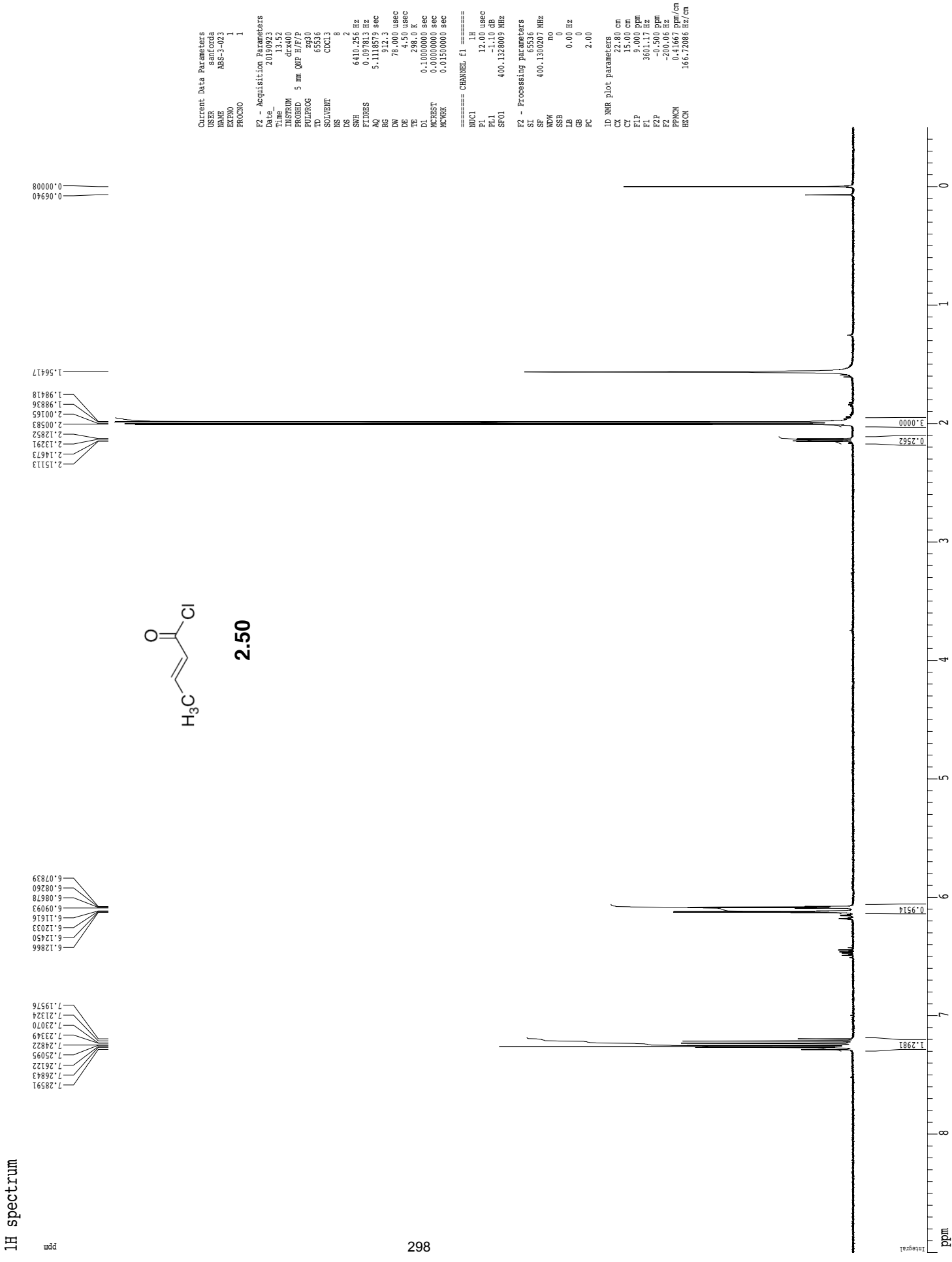
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm


1H spectrum
Current Data Parameters
USER mcginnit
NAME tmm-1-151
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190802
Time_ 15.46
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 724.1
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.50439 ppm/cm
HZCM 201.81996 Hz/cm
0.01301
1.25242
1.27025
1.28809
1.54949
2.05419
2.81356
2.83152
2.85061
2.99829
3.01710
3.03574
3.87226
4.12475
4.14257
6.88404
6.88846
6.90448
6.90986
7.11273
7.15805
7.17723
7.26531
7.26902
7.28455
7.33462
7.35442
7.37429
7.51972
7.54006
9.86333
1.4246
0.9262
2.2106
2.1734
2.9807
0.6088
1.0000
2.0632
2.6746
1.0116
1.9852
0.9648
O
H
OMe
2.49
ppm
Integral

1H spectrum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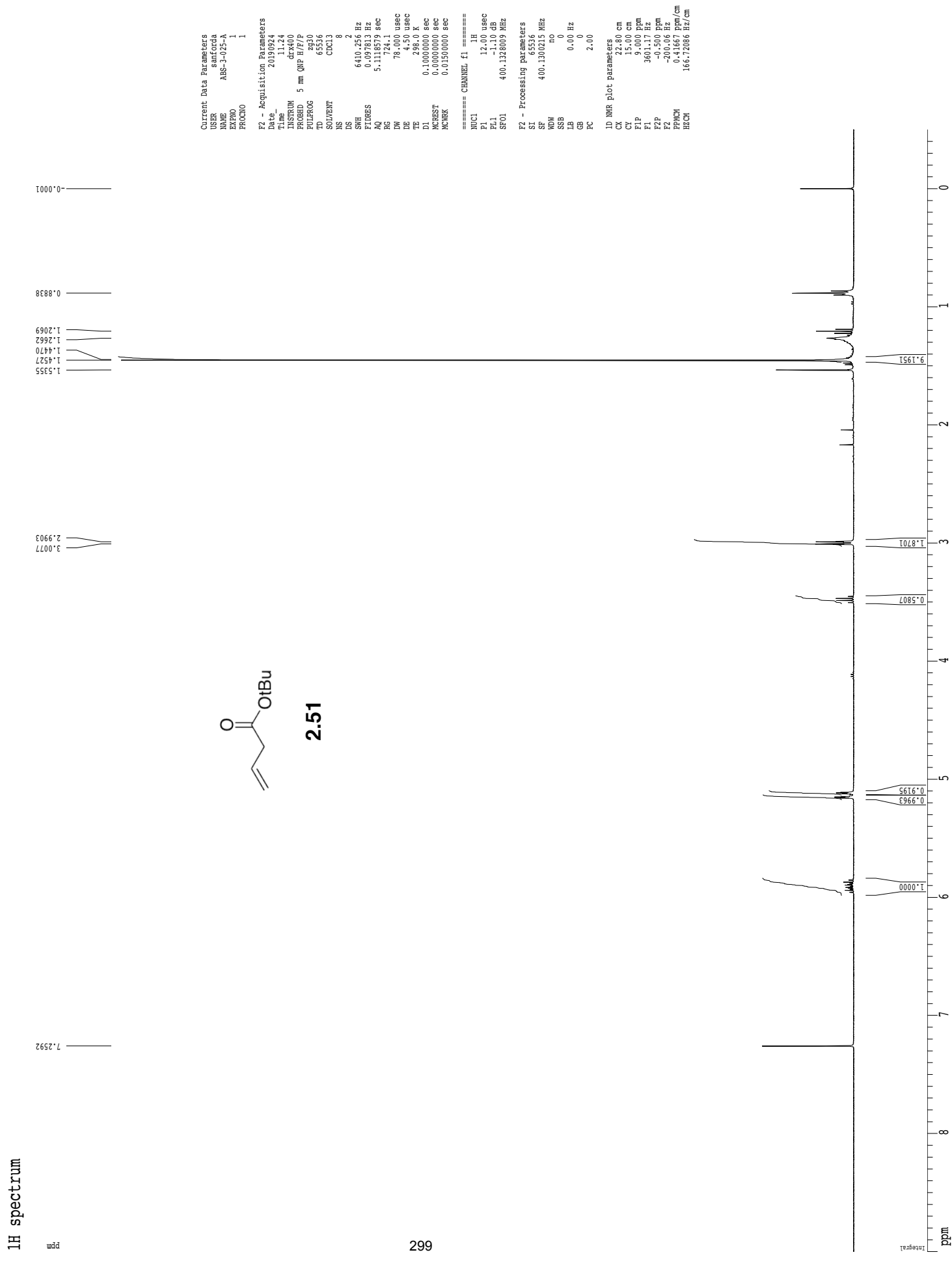
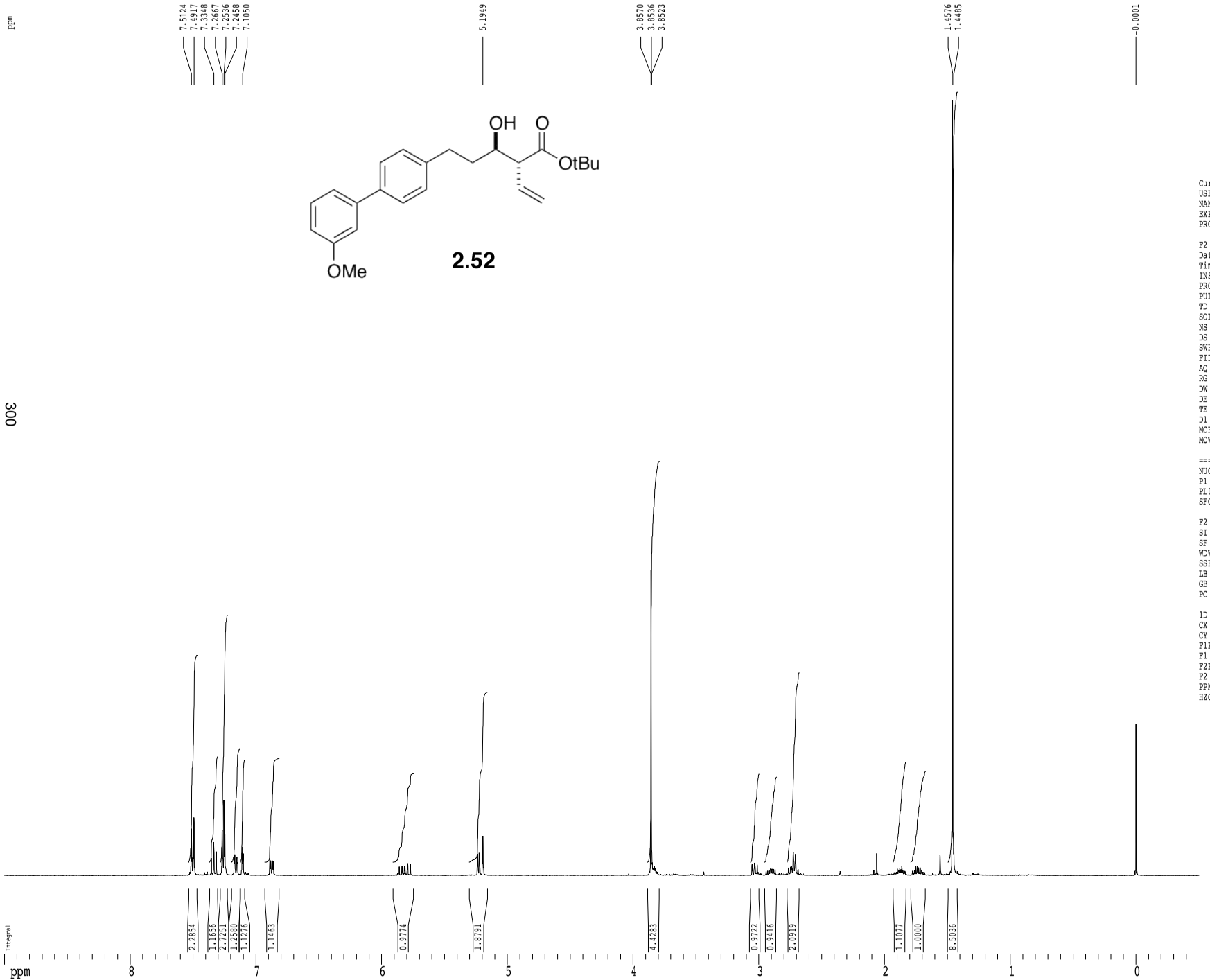
USER sanforda
NAME ABS-3-023
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190923
Time_ 13.52
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 912.3
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300207 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.00008
0.06940
1.56417
1.98418
1.98836
2.00165
2.00583
2.12852
2.13291
2.14673
2.15113
6.07839
6.08260
6.08678
6.09093
6.11616
6.12033
6.12450
6.12866
7.28591
7.26843
7.26122
7.25095
7.24822
7.23349
7.23170
7.21324
7.19576
3.0000
0.2562
0.9514
1.2981
2.50
O
Cl
H3C
ppm
Integral


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-3-025-A
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190924
Time_ 11.24
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 724.1
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300215 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.0001
0.8838
1.2069
1.2662
1.4470
1.4527
1.5355
2.9903
3.0077
7.2592
9.1951
1.8701
0.5807
0.9195
0.9963
1.0000
OtBu
O
2.51
ppm
Integral

1H spectrum



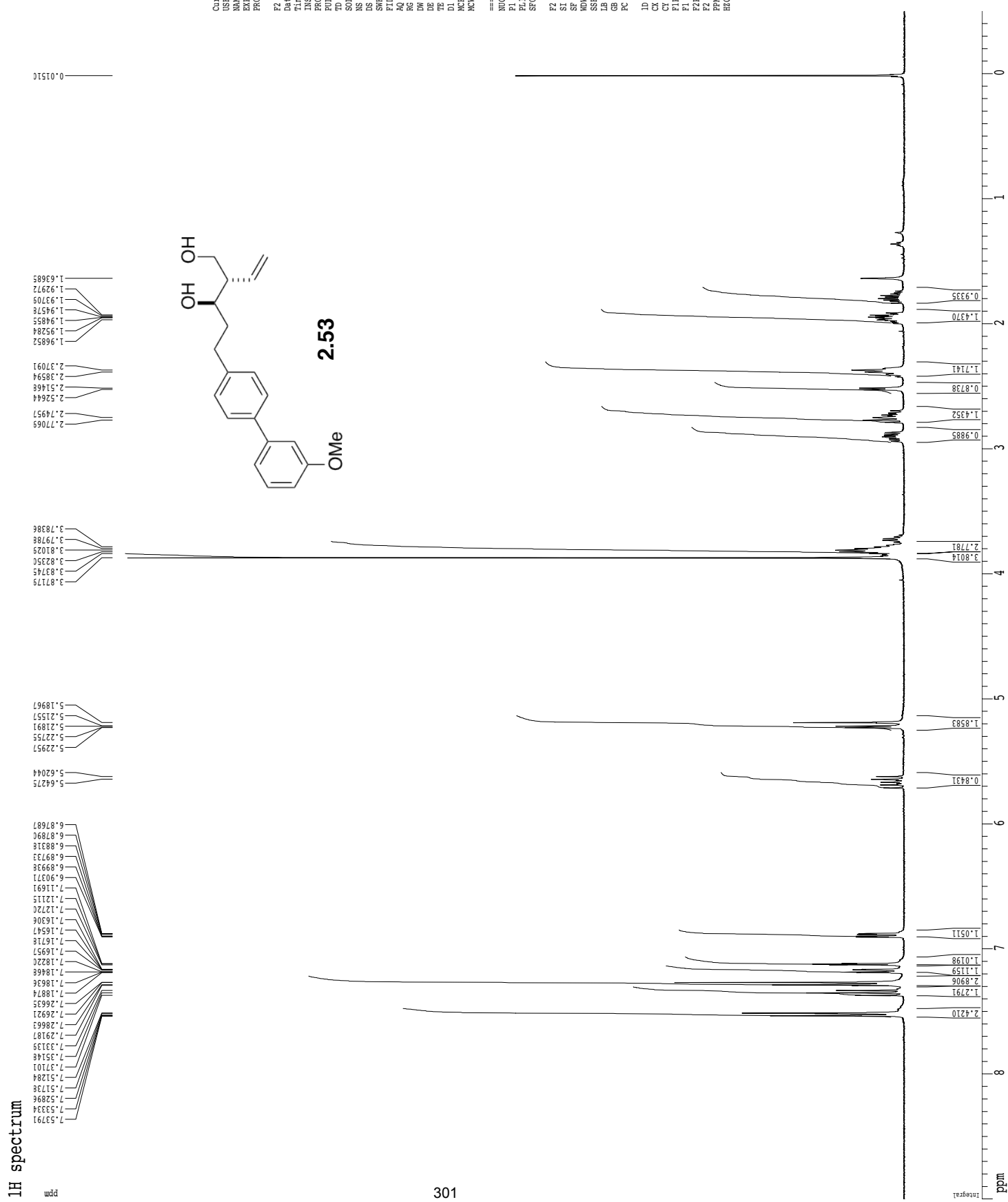
Current Data Parameters
USER sanforda
NAME ABS-3-043-proton
EXPNO 1
PROCNO 1

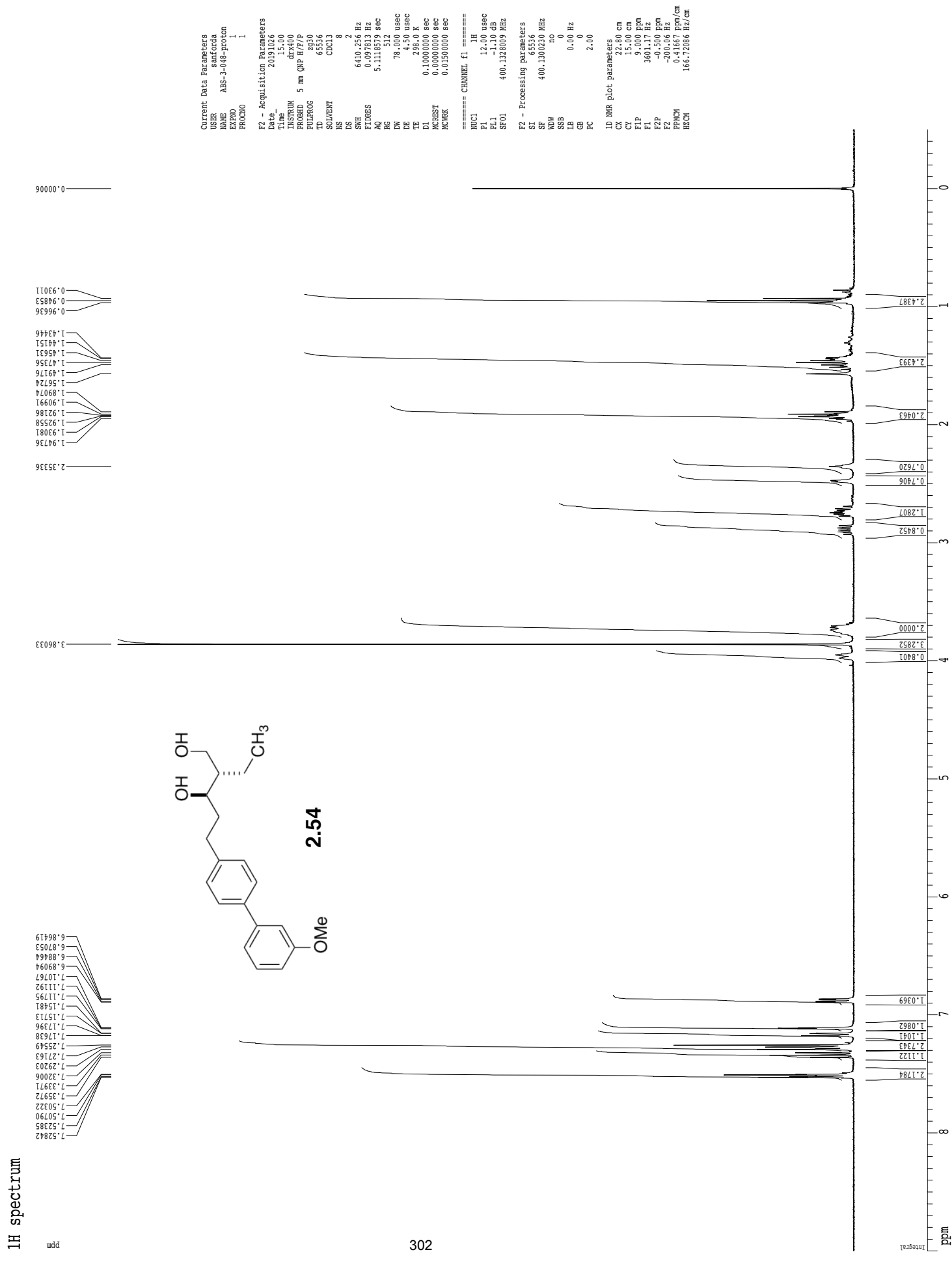
F2 - Acquisition Parameters
Date_ 20191026
Time 14.53
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 287.4
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

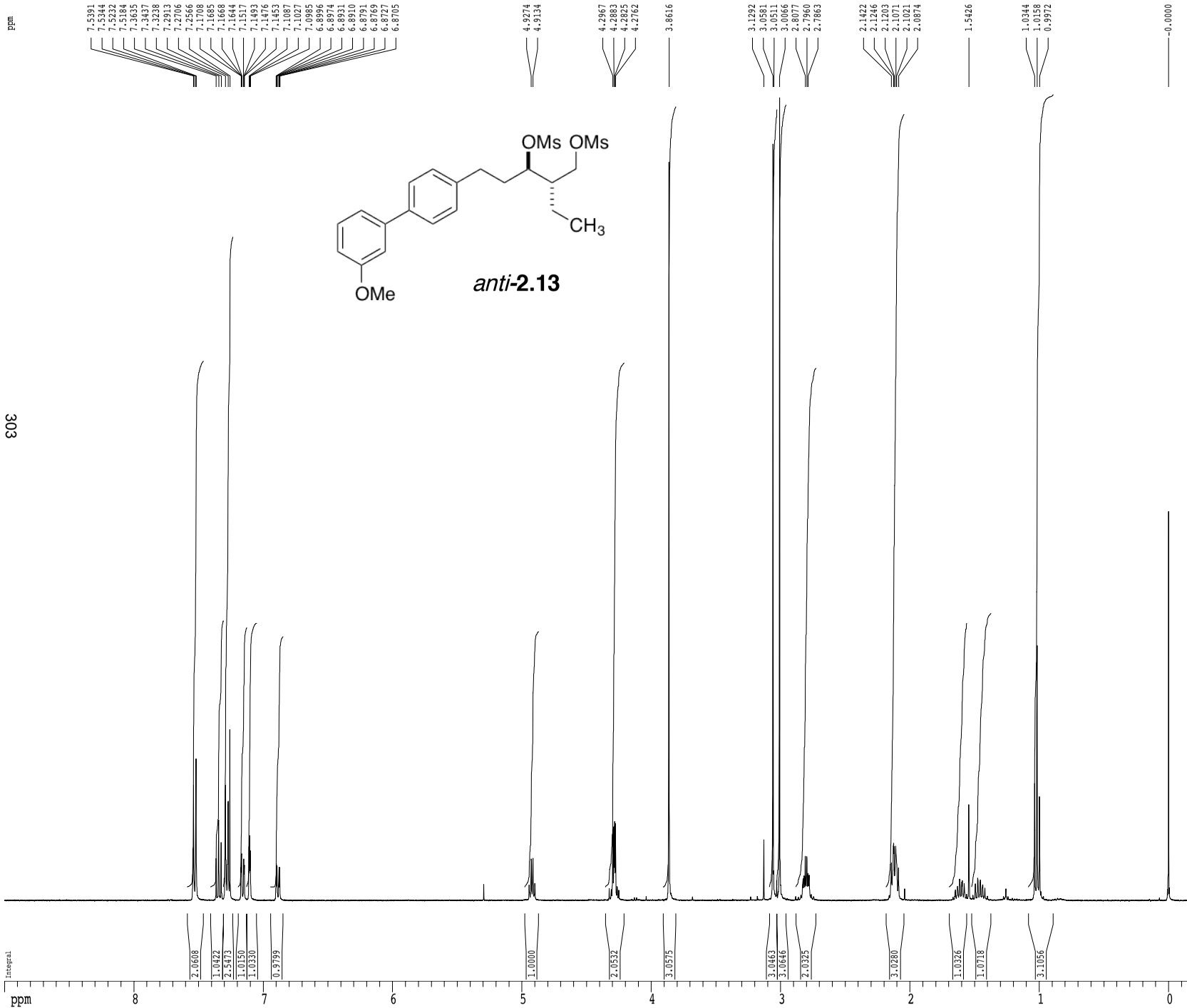
F2 - Processing parameters
SI 65536
SF 400.1300237 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-3-046-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191026
Time_ 14.56
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 322.5
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72084 Hz/cm
OH
OH
OMe
2.53
ppm
Integral


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-3-048-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191026
Time_ 15.00
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 512
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300230 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
OH
CH3
OMe
2.54
ppm
Integral
302

1H spectrum

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Current Data Parameters
USER            sanforda
NAME      ABS-3-049-proton
EXPNO                  1
PROCNO                 1

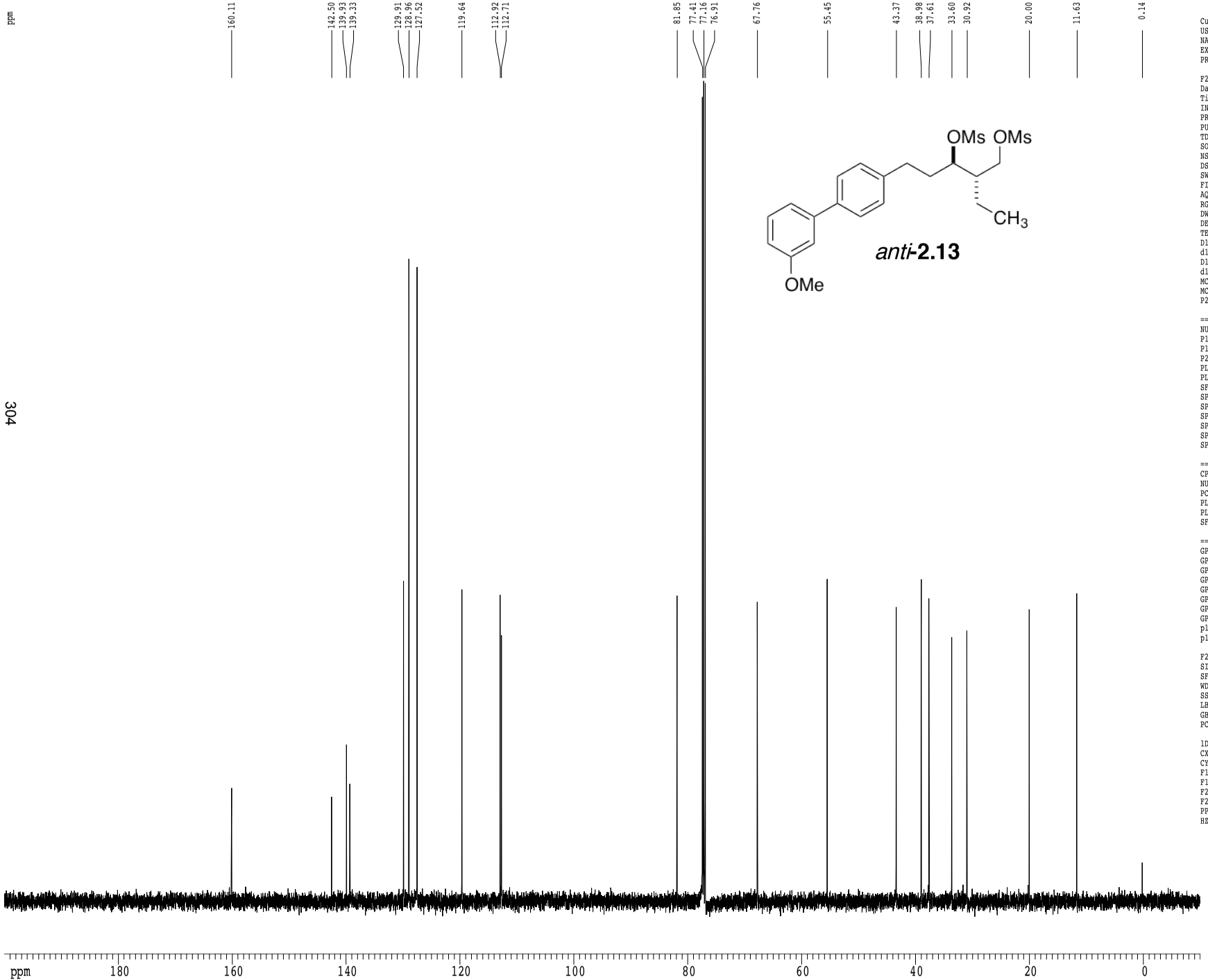
F2 - Acquisition Parameters
Date_          20191025
Time               9.55
INSTRUM          drx400
PROBHD   5 mm QNP H/F/P
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            6410.256 Hz
FIDRES        0.097813 Hz
AQ            5.1118579 sec
RG                287.4
DW               78.000 usec
DE                4.50 usec
TE                297.9 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======= CHANNEL f1 =======
NUC1                  1H
P1                12.00 usec
PL1               -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                65536
SF           400.1300224 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              3601.17 Hz
F2P              -0.500 ppm
F2              -200.06 Hz
PPMCM          0.41667 ppm/cm
HZCM          166.72086 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-3-049-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191025
Time 10.17
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 480
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2896.3
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

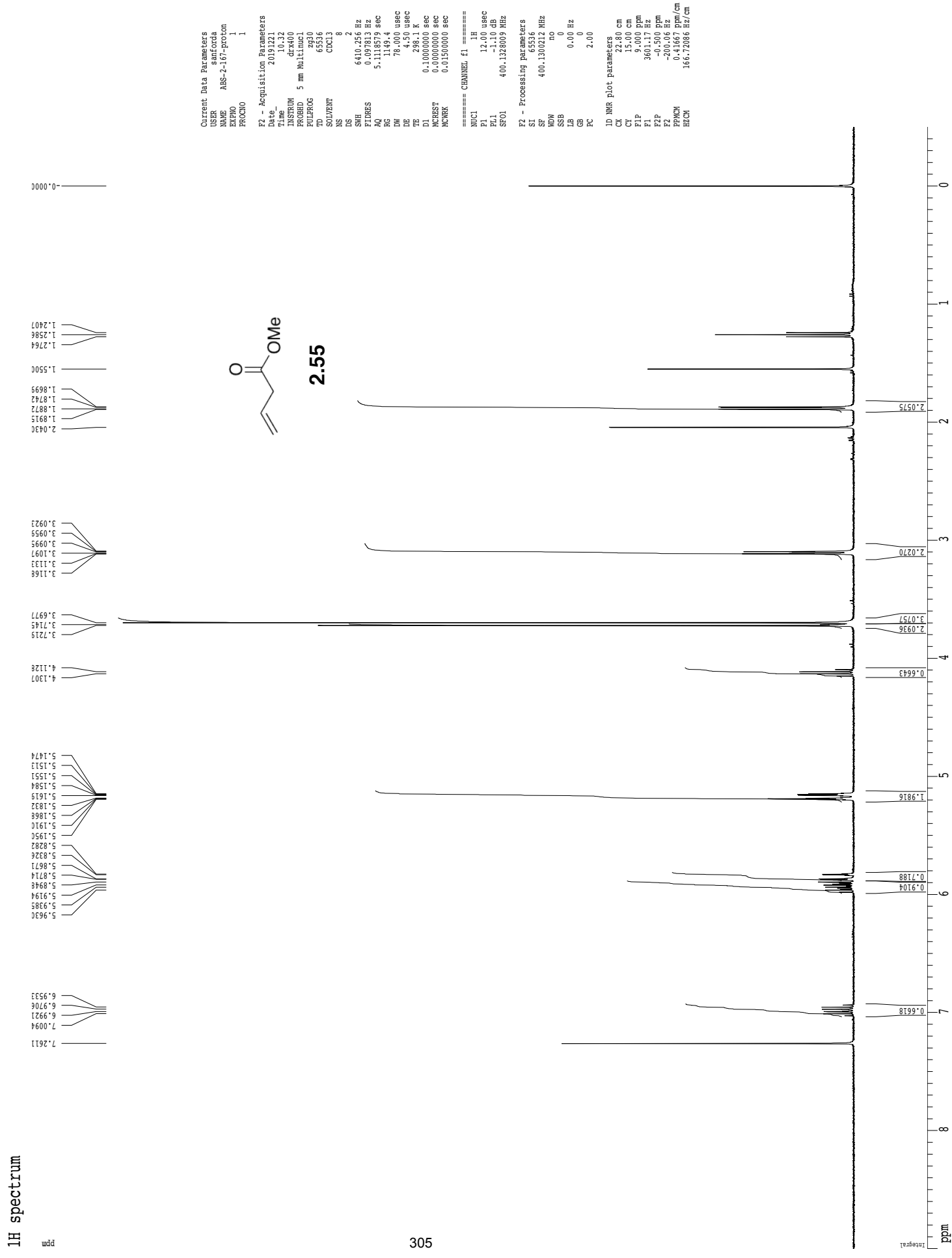
======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804071 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm


1H spectrum
ppm
Integral
Current Data Parameters
USER sanforda
NAME ABS-2-167-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191221
Time_ 10.32
INSTRUM drx400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 1149.4
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300212 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OMe
2.55
0.0000
1.2407
1.2586
1.2764
1.5500
1.8699
1.8742
1.8872
1.8915
2.0430
3.0923
3.0959
3.0995
3.1097
3.1133
3.1168
3.6971
3.7145
3.7219
4.1128
4.1307
5.1474
5.1513
5.1551
5.1584
5.1619
5.1832
5.1868
5.1910
5.1950
5.8282
5.8326
5.8671
5.8714
5.8948
5.9194
5.9385
5.9630
6.9533
6.9706
6.9921
7.0094
7.2611
2.0575
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3.0757
2.0936
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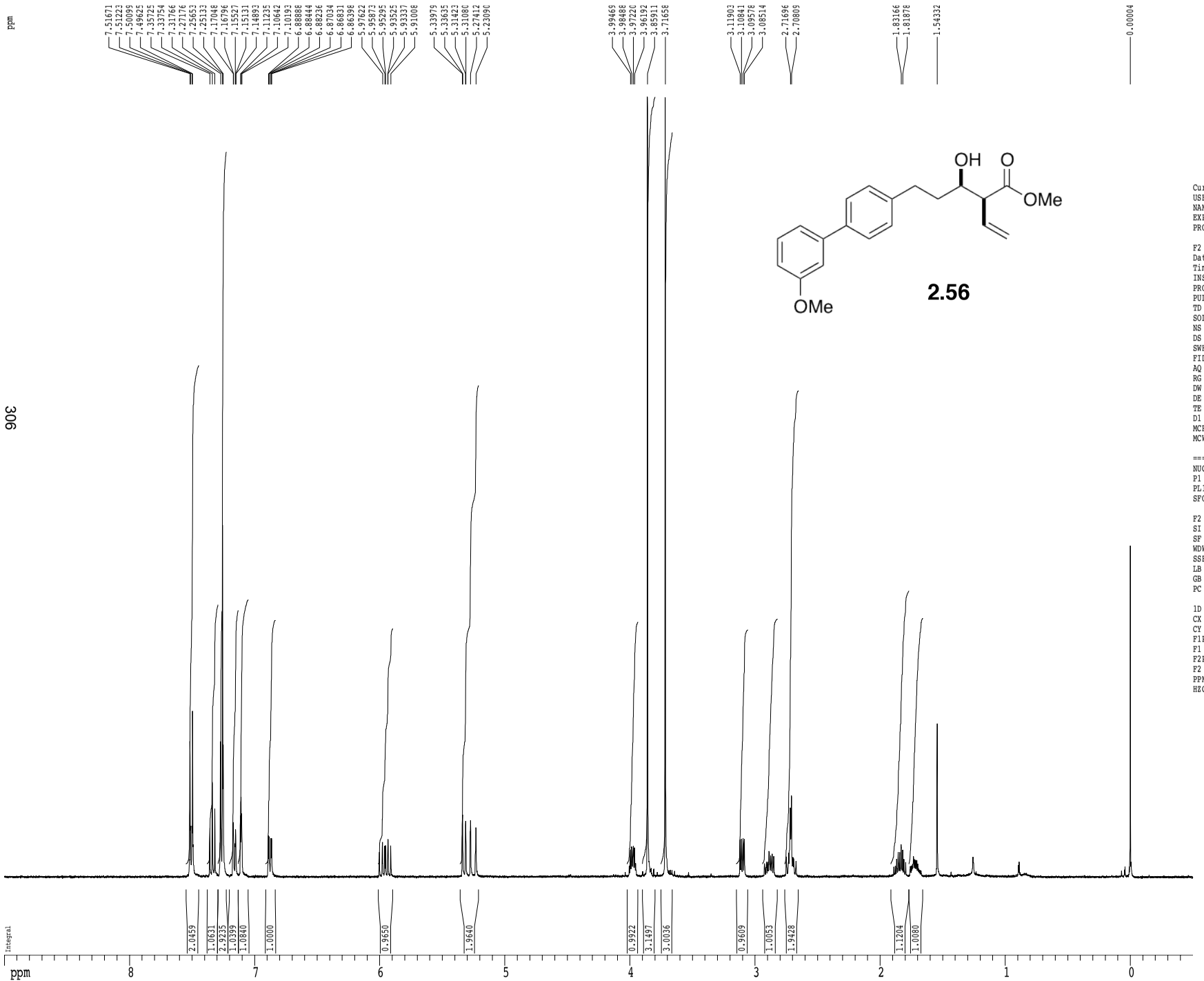
0.7188
0.9104
0.6618

1H spectrum

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Current Data Parameters
USER            sanforda
NAME      ABS-3-069-proton3
EXPNO                   1
PROCNO                  1

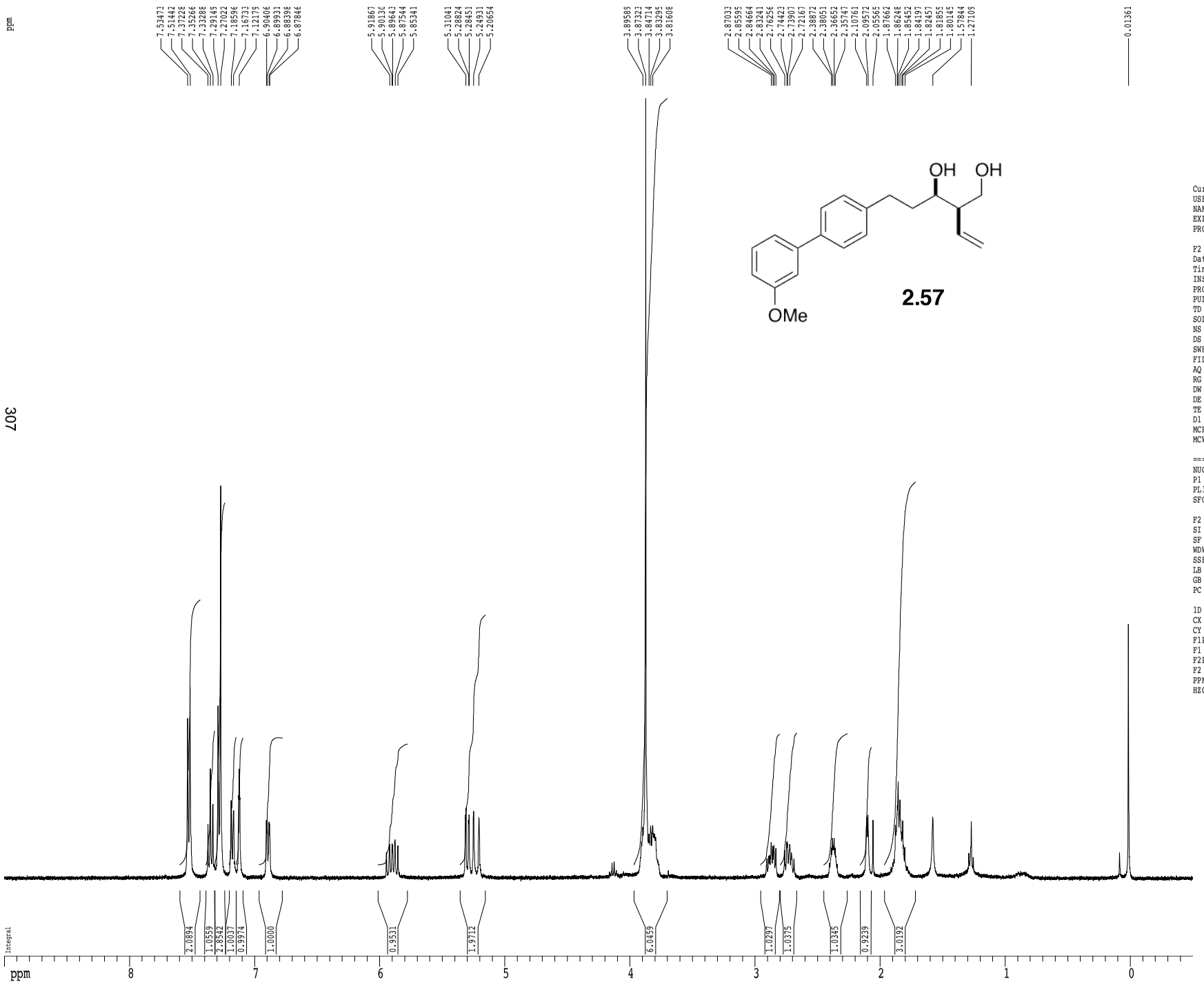
F2 - Acquisition Parameters
Date_            20191221
Time               14.58
INSTRUM           drx400
PROBHD   5 mm Multinucl
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6410.256 Hz
FIDRES          0.097813 Hz
AQ              5.1118579 sec
RG                 724.1
DW                78.000 usec
DE                 4.50 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -1.10 dB
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300230 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                9.000 ppm
F1               3601.17 Hz
F2P                -0.500 ppm
F2               -200.06 Hz
PPMCM            0.41667 ppm/cm
HZCM           166.72086 Hz/cm
```

1H spectrum



Current Data Parameters

USER	sanforda
NAME	ABS-3-050-proton2
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20191221
Time	10.39
INSTRUM	drx400
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	6410.256 Hz
FIDRES	0.097813 Hz
AQ	5.1118579 sec
RG	645.1
DW	78.000 usec
DE	4.50 usec
TE	298.0 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

NUC1	1H
P1	12.00 usec
PL1	-1.10 dB
SFO1	400.1328009 MHz

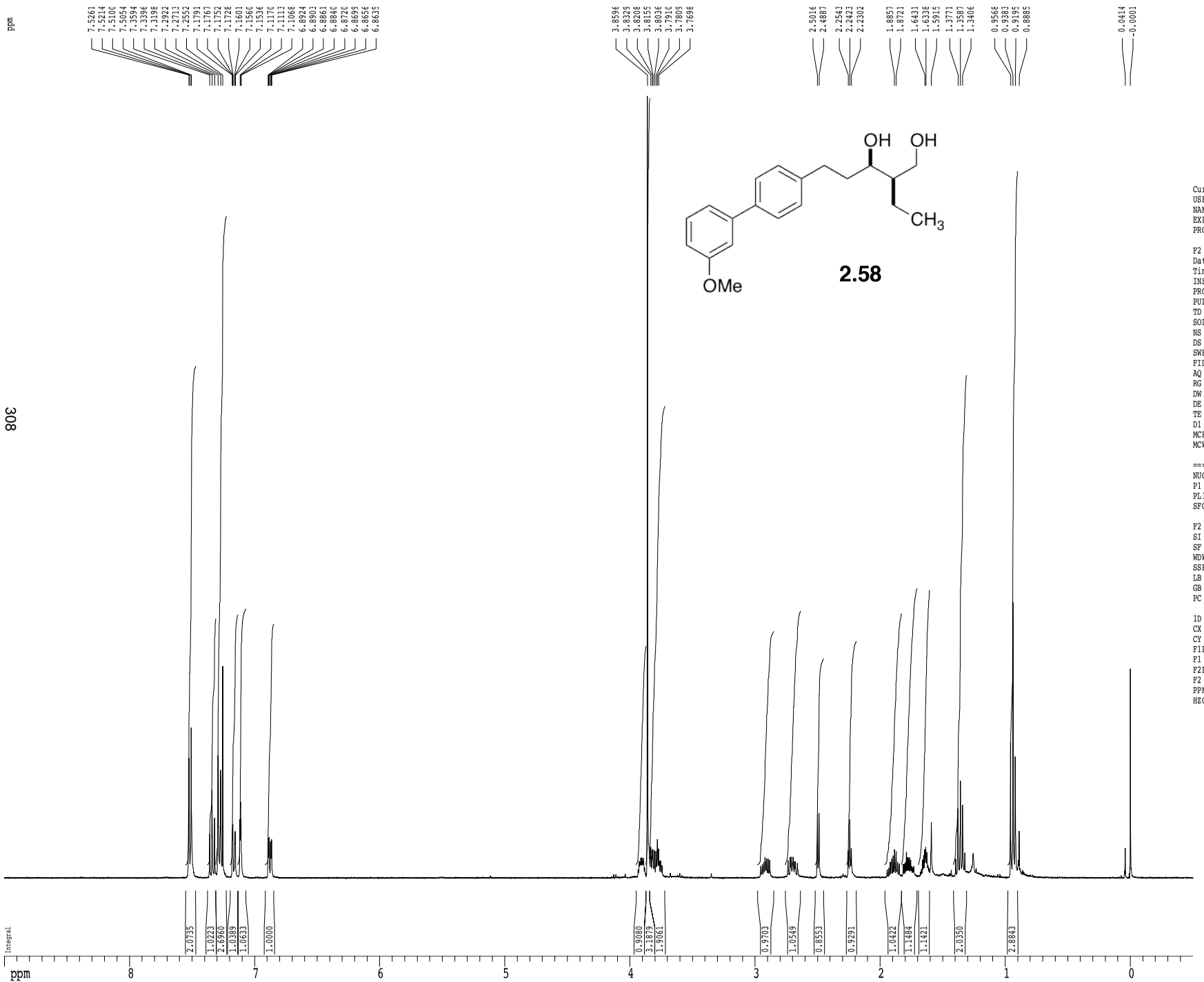
F2 - Processing parameters

SI	65536
SF	400.1300175 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
CY	15.00 cm
F1P	9.000 ppm
F1	3601.17 Hz
F2P	-0.500 ppm
F2	-200.06 Hz
PPMCM	0.41667 ppm/cm
HZCM	166.72084 Hz/cm

1H spectrum



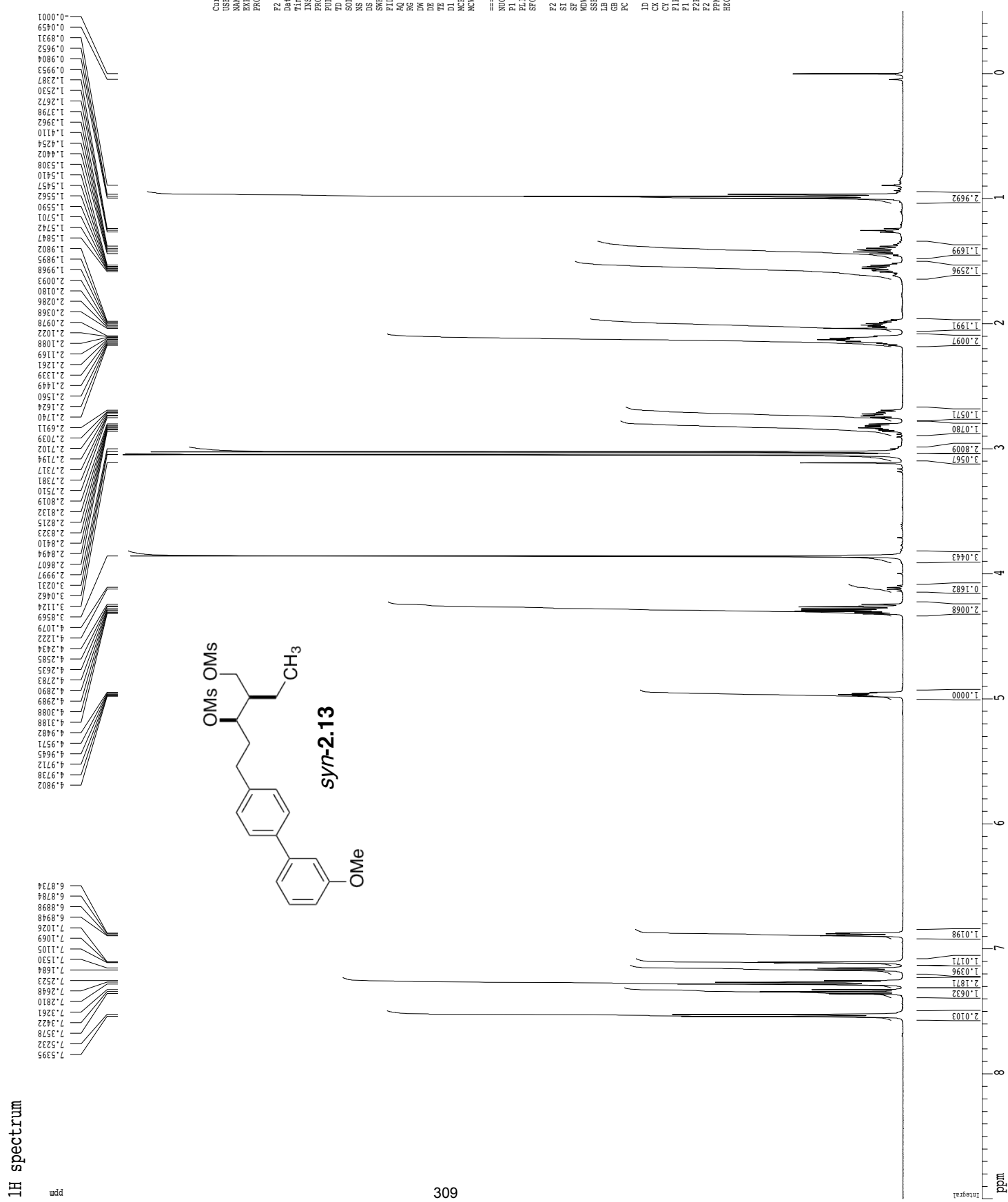
Current Data Parameters
USER sanforda
NAME ABS-3-073-proton
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191221
Time 15.02
INSTRUM drx400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 406.4
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

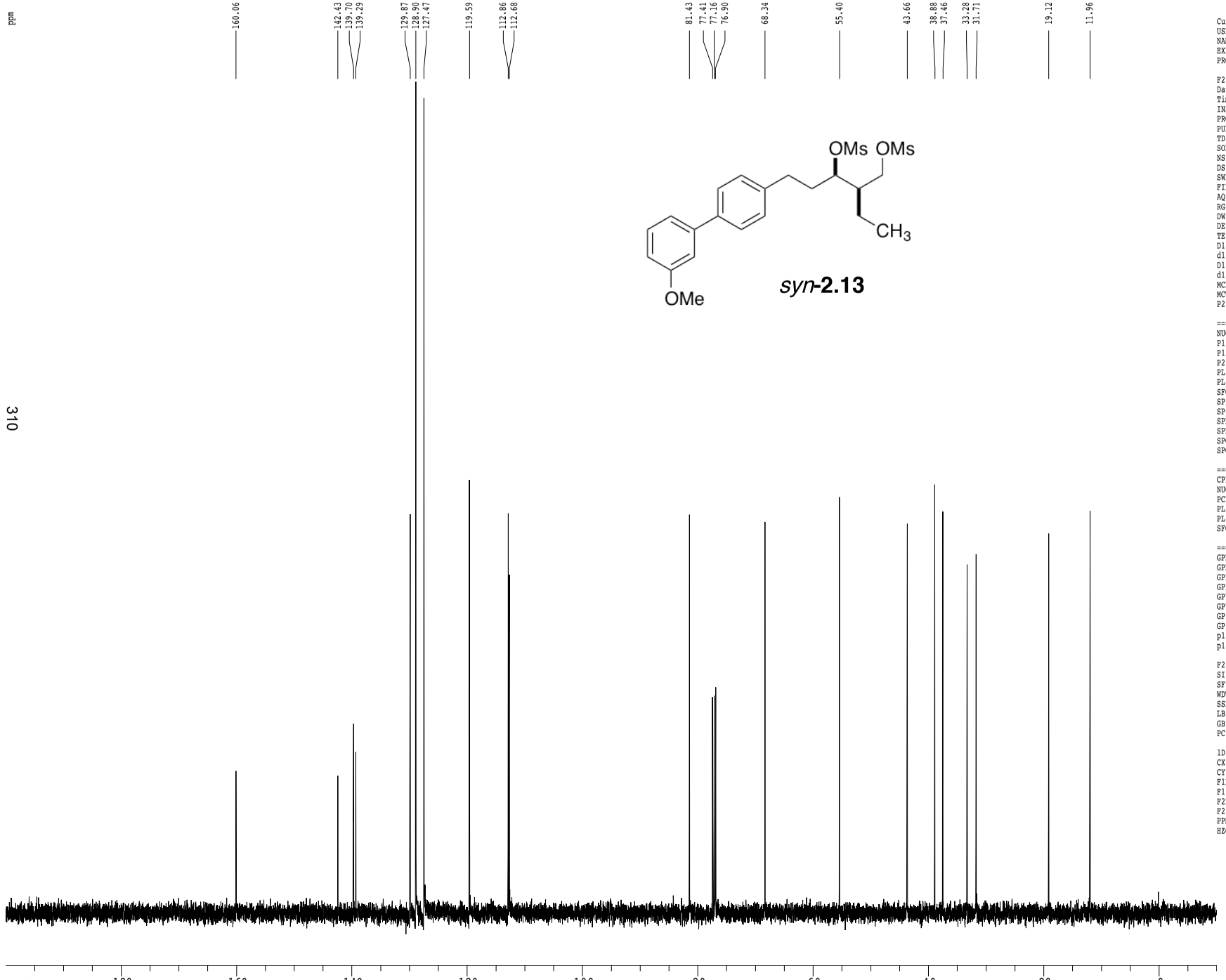
======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300235 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm


1H spectrum
ppm
Integral
OMs OMs
CH3
OMe
syn-2.13

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




```
Current Data Parameters
USER            sanforda
NAME      ABS-3-074-carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20191125
Time                14.48
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                  65536
SOLVENT             CDCl3
NS                     88
DS                     16
SWH           30303.031 Hz
FIDRES         0.462388 Hz
AQ             1.0813940 sec
RG               10321.3
DW                16.500 usec
DE                 6.00 usec
TE                298.0 K
D1             0.25000000 sec
d11            0.03000000 sec
D16            0.00020000 sec
d17            0.00019600 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec
P2                33.10 usec

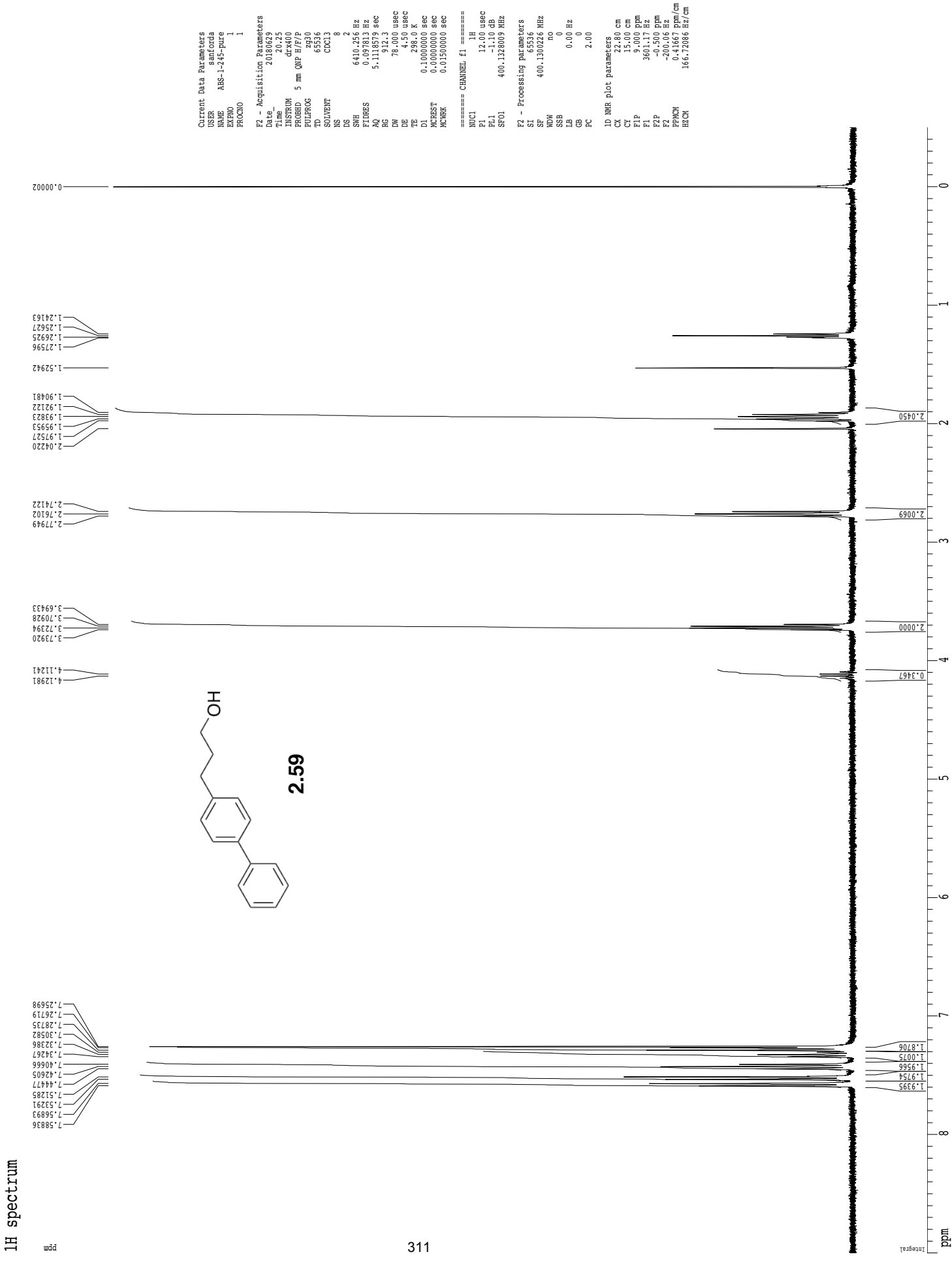
======== CHANNEL f1 ========
NUC1                  13C
P1                 16.55 usec
P12              2000.00 usec
P20               500.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP2                2.70 dB
SP4                2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2              0.00 Hz
SPOFF4              0.00 Hz

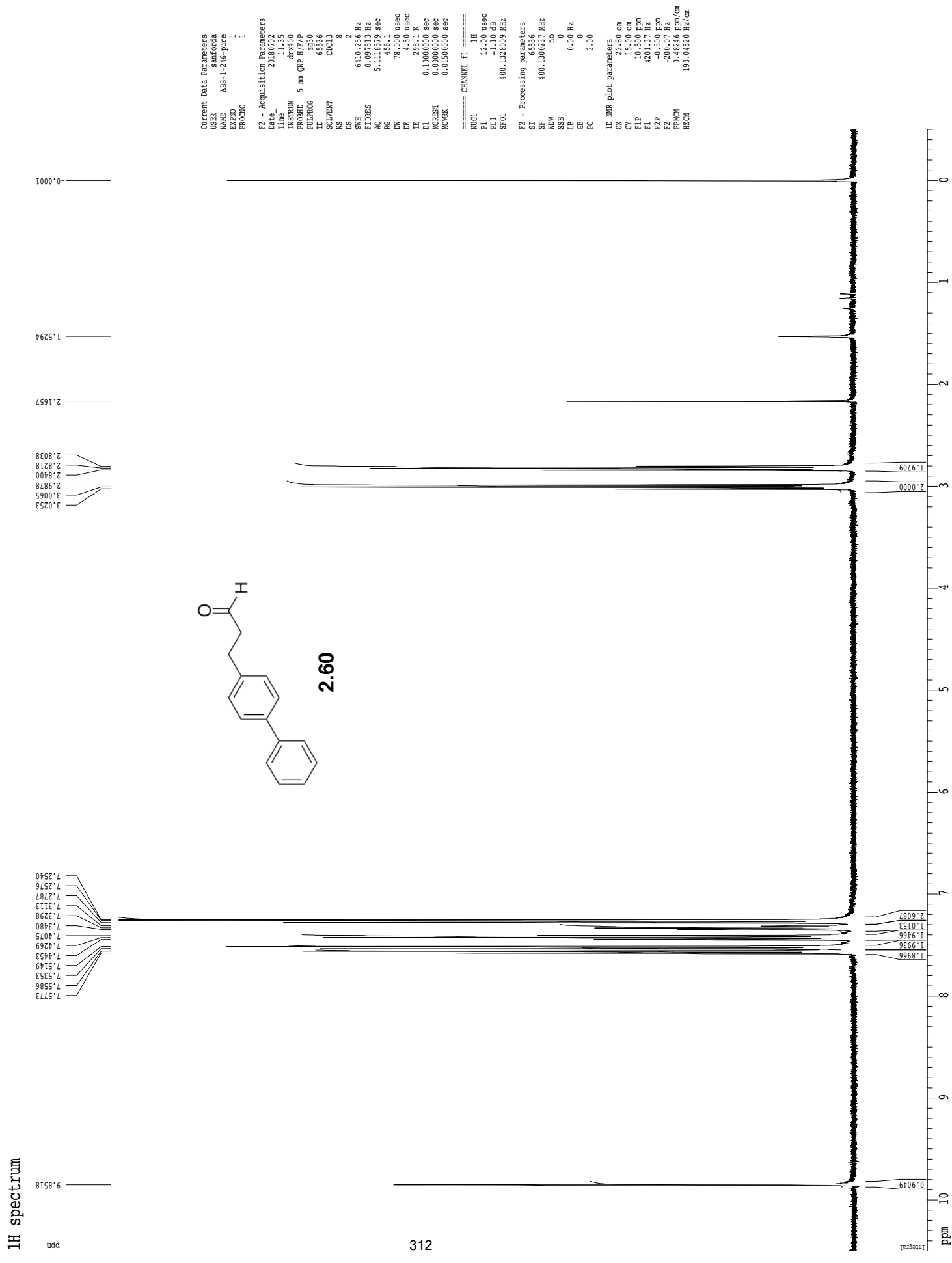
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                1.60 dB
PL12              23.54 dB
SFO2         500.2225011 MHz

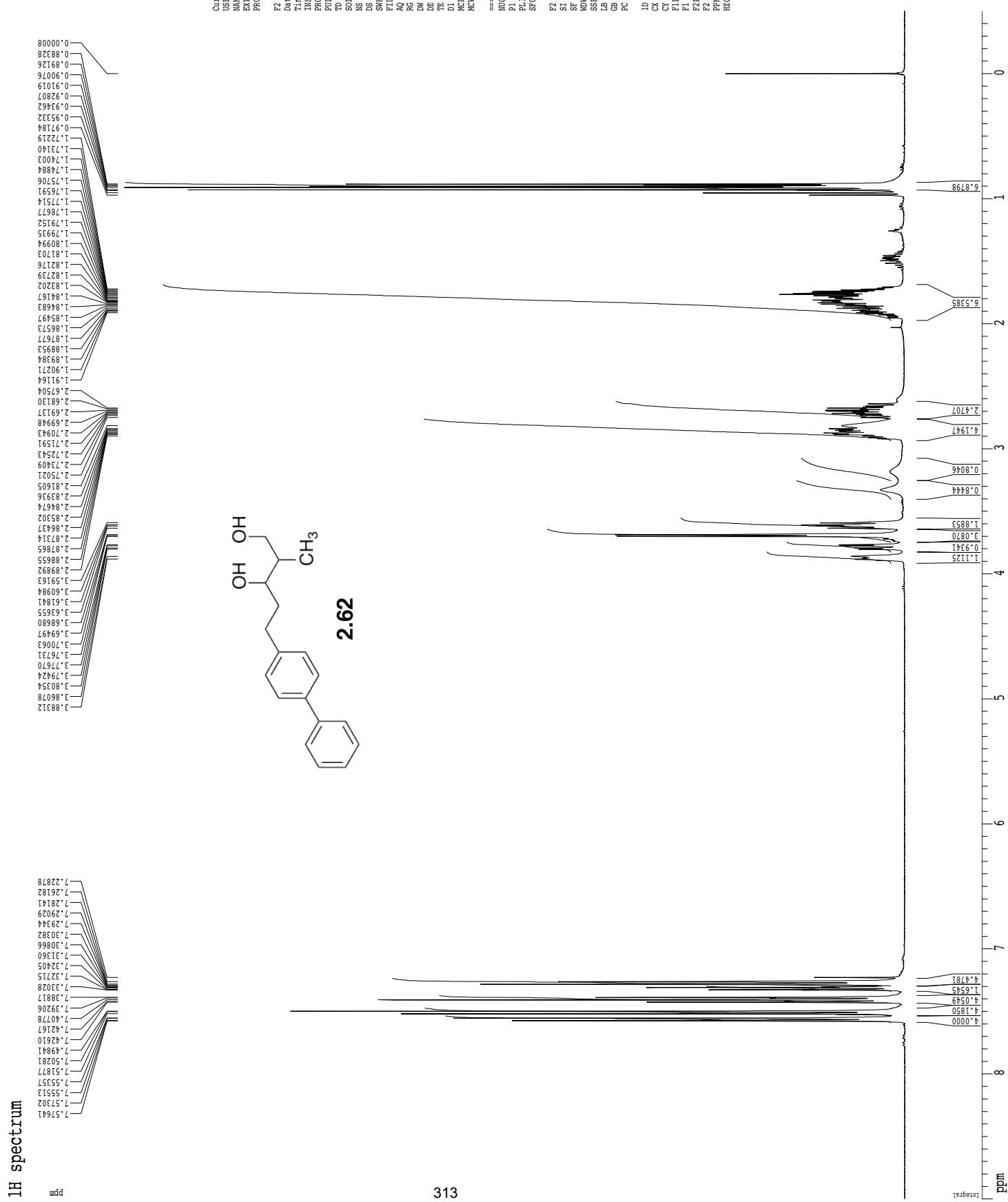
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

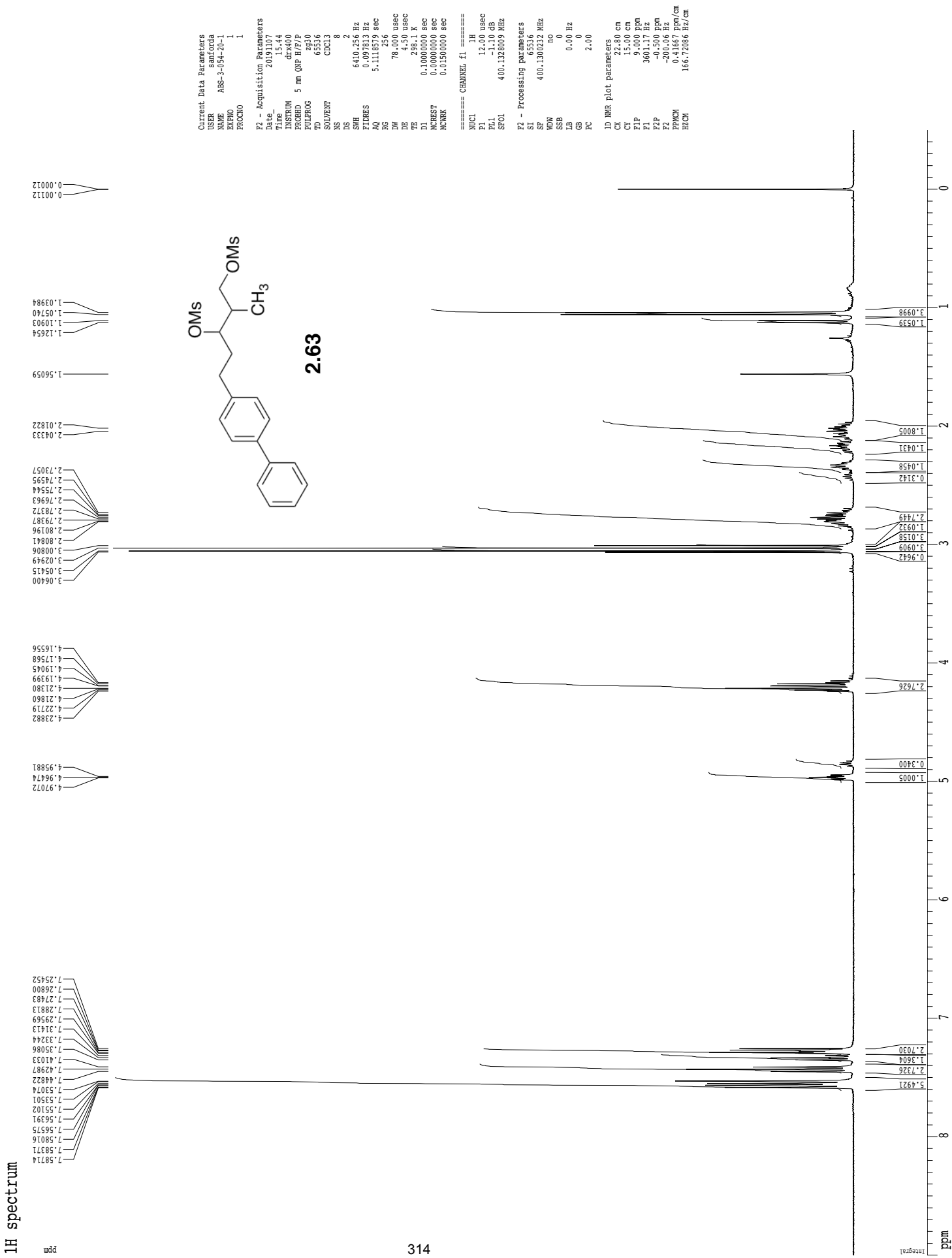
F2 - Processing parameters
SI                  65536
SF           125.7804140 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.65 cm
F1P              200.000 ppm
F1             25156.08 Hz
F2P              -10.000 ppm
F2             -1257.80 Hz
PPMCM            9.21053 ppm/cm
HZCM          1158.50378 Hz/cm
```

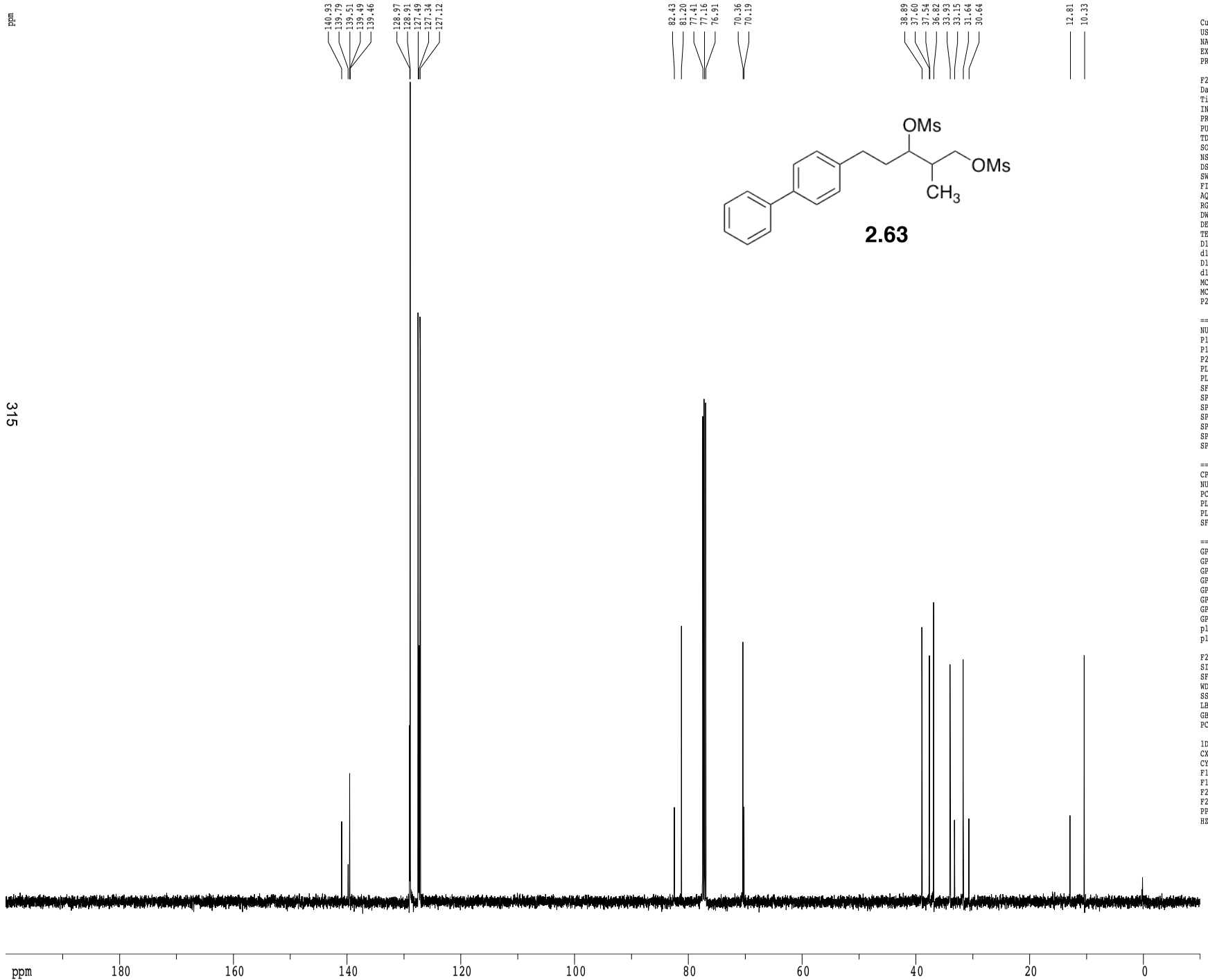

1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-1-245-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180629
Time_ 20.25
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 912.3
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300226 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.00002
1.24163
1.25627
1.26925
1.27596
1.52942
1.90481
1.92122
1.93823
1.95953
1.97527
2.04220
2.74122
2.76102
2.77949
3.69433
3.70928
3.72394
3.73920
4.11241
4.12981
7.25698
7.26719
7.28735
7.30582
7.32386
7.34267
7.40666
7.42605
7.44477
7.51285
7.53291
7.56893
7.58836
1.8706
1.0075
1.9566
1.9754
1.9395
0.3467
2.0000
2.0069
2.0450
OH
2.59
ppm
Integral


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-1-246-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180702
Time_ 11.35
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 456.1
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300237 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.48246 ppm/cm
HZCM 193.04520 Hz/cm
0.0001
1.5294
2.1657
2.8038
2.8218
2.8400
2.9878
3.0065
3.0253
7.2540
7.2576
7.2787
7.3113
7.3298
7.3480
7.4075
7.4269
7.4453
7.5149
7.5353
7.5586
7.5773
9.8518
1.9709
2.0000
2.6087
1.0153
1.9466
1.9936
1.8996
0.9049
O
H
2.60
ppm
Integral


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-3-sub-diol
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191030
Time_ 17.33
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 71.8
DW 78.000 usec
DE 4.50 usec
TE 297.9 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300335 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
OH
CH3
2.62
6.8798
6.5385
2.4707
4.1947
0.8046
0.8444
1.8853
3.0870
0.9341
1.1125
4.4781
1.6545
4.0549
4.1850
4.0000
ppm
Integral


1H spectrum
2.63
OMs
OMs
CH3
Current Data Parameters
USER sanforda
NAME ABS-3-054-20-1
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191107
Time_ 15.44
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 256
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300232 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.000 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
ppm
Integral

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




```
Current Data Parameters
USER            sanforda
NAME      ABS-3-054-carbon2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20191108
Time                 10.07
INSTRUM            cryo500
PROBHD    5 mm CPTCI 1H-
PULPROG   SpinEchopg30gp2.prd
TD                   65536
SOLVENT              CDCl3
NS                     544
DS                      16
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0813940 sec
RG                   8192
DW                 16.500 usec
DE                  6.00 usec
TE                 298.1 K
D1              0.25000000 sec
d11             0.03000000 sec
D16             0.00020000 sec
d17             0.00019600 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec
P2                  33.10 usec

======== CHANNEL f1 ========
NUC1                  13C
P1                  16.55 usec
P12               2000.00 usec
P20                500.00 usec
PL0                120.00 dB
PL1                 -1.00 dB
SFO1          125.7942548 MHz
SP2                  2.70 dB
SP4                  2.70 dB
SPNAM2       Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2               0.00 Hz
SPOFF4               0.00 Hz

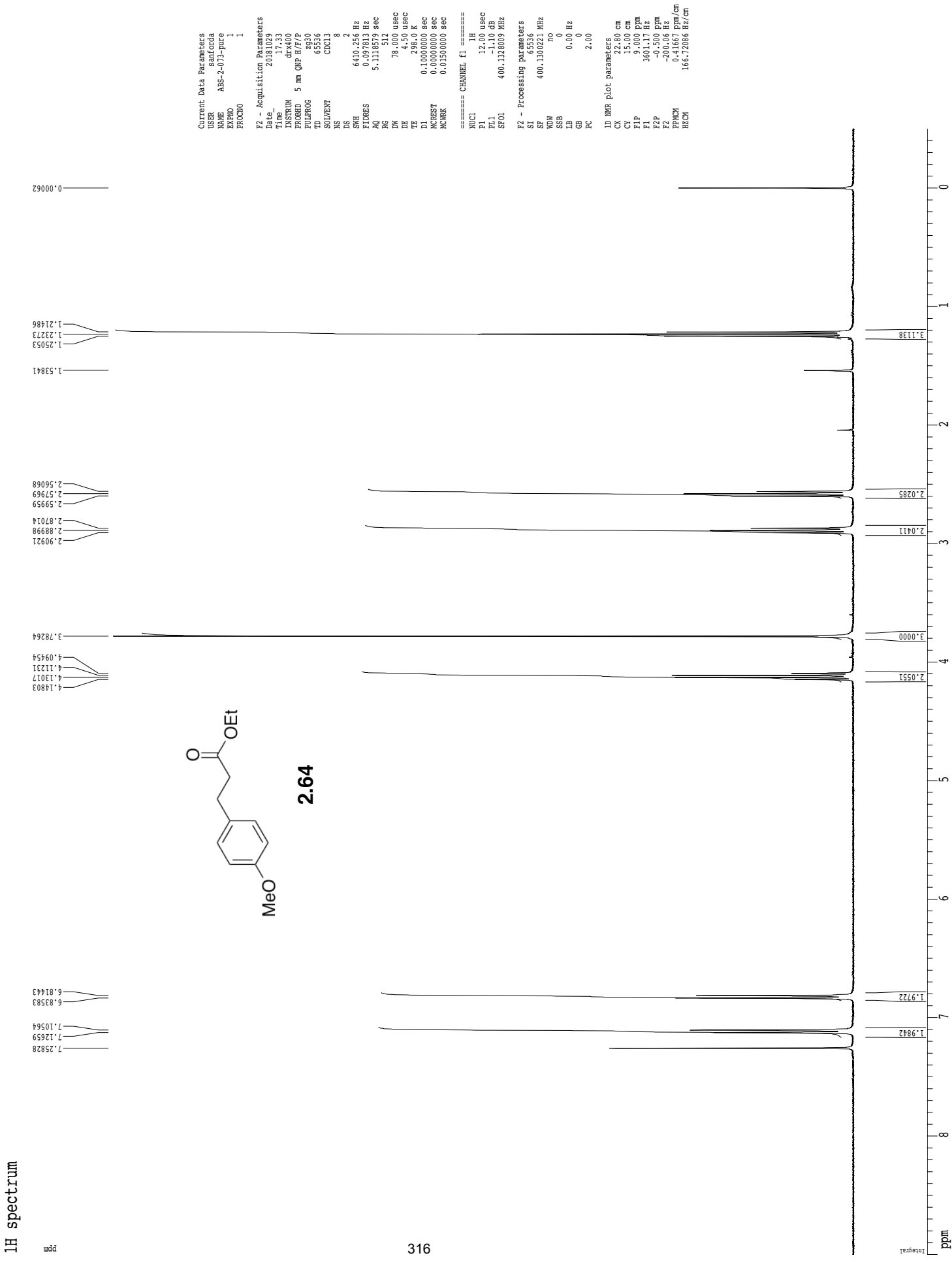
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              100.00 usec
PL2                  1.60 dB
PL12                23.54 dB
SFO2          500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                30.00 %
GPZ2                50.00 %
p15                500.00 usec
p16               1000.00 usec

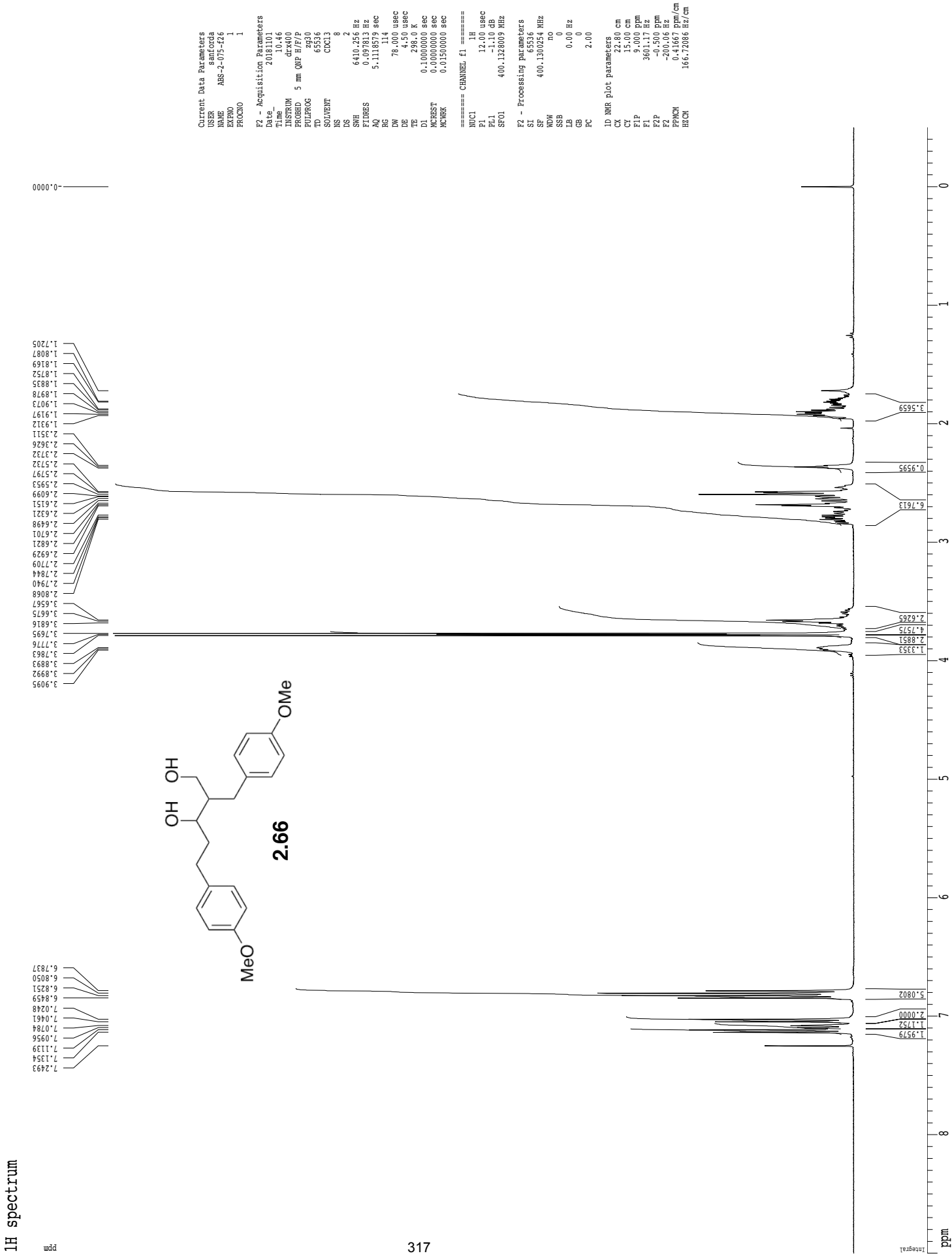
F2 - Processing parameters
SI                   65536
SF            125.7804090 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    2.00

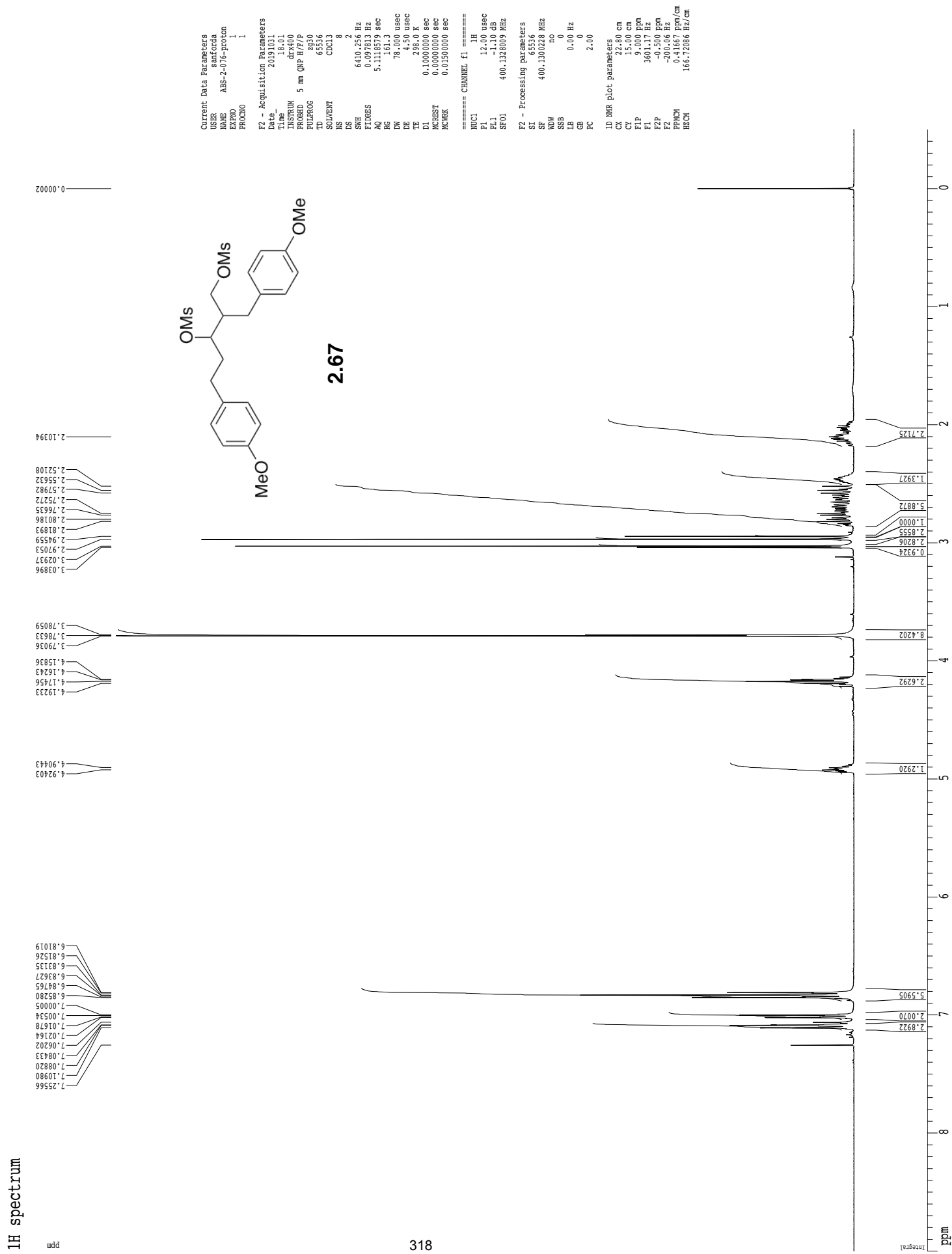
1D NMR plot parameters
CX                   22.80 cm
CY                   15.65 cm
F1P                200.000 ppm
F1              25156.08 Hz
F2P                -10.000 ppm
F2              -1257.80 Hz
PPMCM              9.21053 ppm/cm
HZCM            1158.50378 Hz/cm
```

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-073-pure
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181029
Time_ 17.33
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 512
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300221 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.00062
1.21486
1.23273
1.25053
1.53841
2.56068
2.57969
2.59959
2.87014
2.88998
2.90921
3.78264
4.09454
4.11231
4.13017
4.14803
6.81443
6.83583
7.10564
7.12659
7.25828
3.1138
2.0285
2.0411
3.0000
2.0551
1.9722
1.9842
OEt
O
MeO
2.64
ppm
Integral

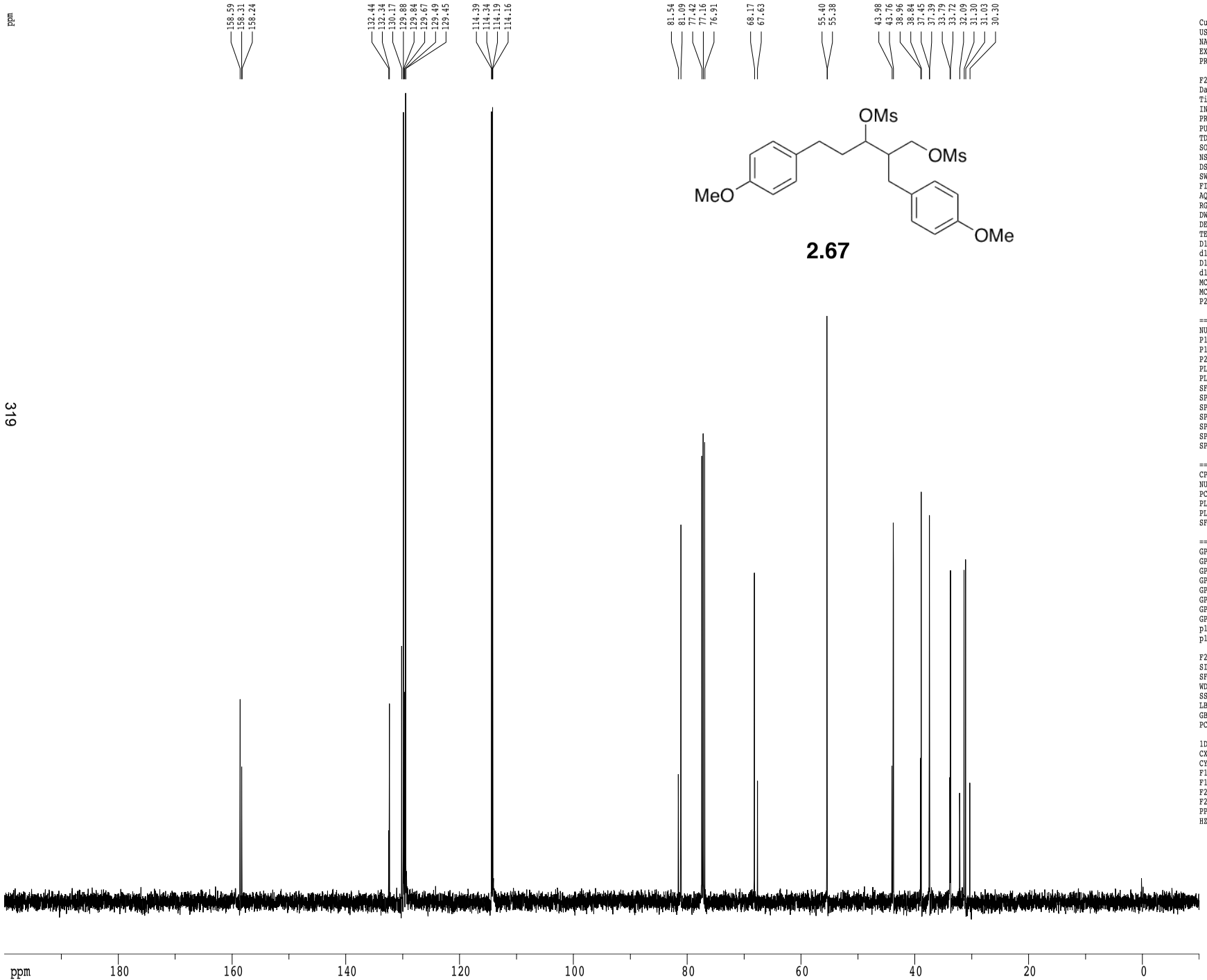
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-2-075-F26
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181101
Time_ 10.46
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 114
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300254 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
OH
OMe
MeO
2.66
ppm
Integral


Current Data Parameters
USER sanforda
NAME ABS-2-076-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191031
Time_ 18.01
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 161.3
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300228 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OMs
OMs
OMe
MeO
2.67
0.00002
2.10394
2.52108
2.55632
2.57982
2.75272
2.76635
2.80186
2.81893
2.94559
2.97053
3.02937
3.03896
3.78059
3.78633
3.79036
4.15836
4.16243
4.17456
4.19233
4.90443
4.92403
6.81019
6.81526
6.83135
6.83627
6.84765
6.85280
7.00005
7.00534
7.01678
7.02164
7.06202
7.08433
7.08820
7.10980
7.25566
2.7125
1.3927
5.8872
1.0000
2.8555
2.8206
0.9324
8.4202
2.6292
1.2920
5.5905
2.0070
2.8922
ppm
Integral

1H spectrum

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



Current Data Parameters
USER sanforda
NAME ABS-2-076-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191102
Time 16.02
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 192
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 14596.5
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

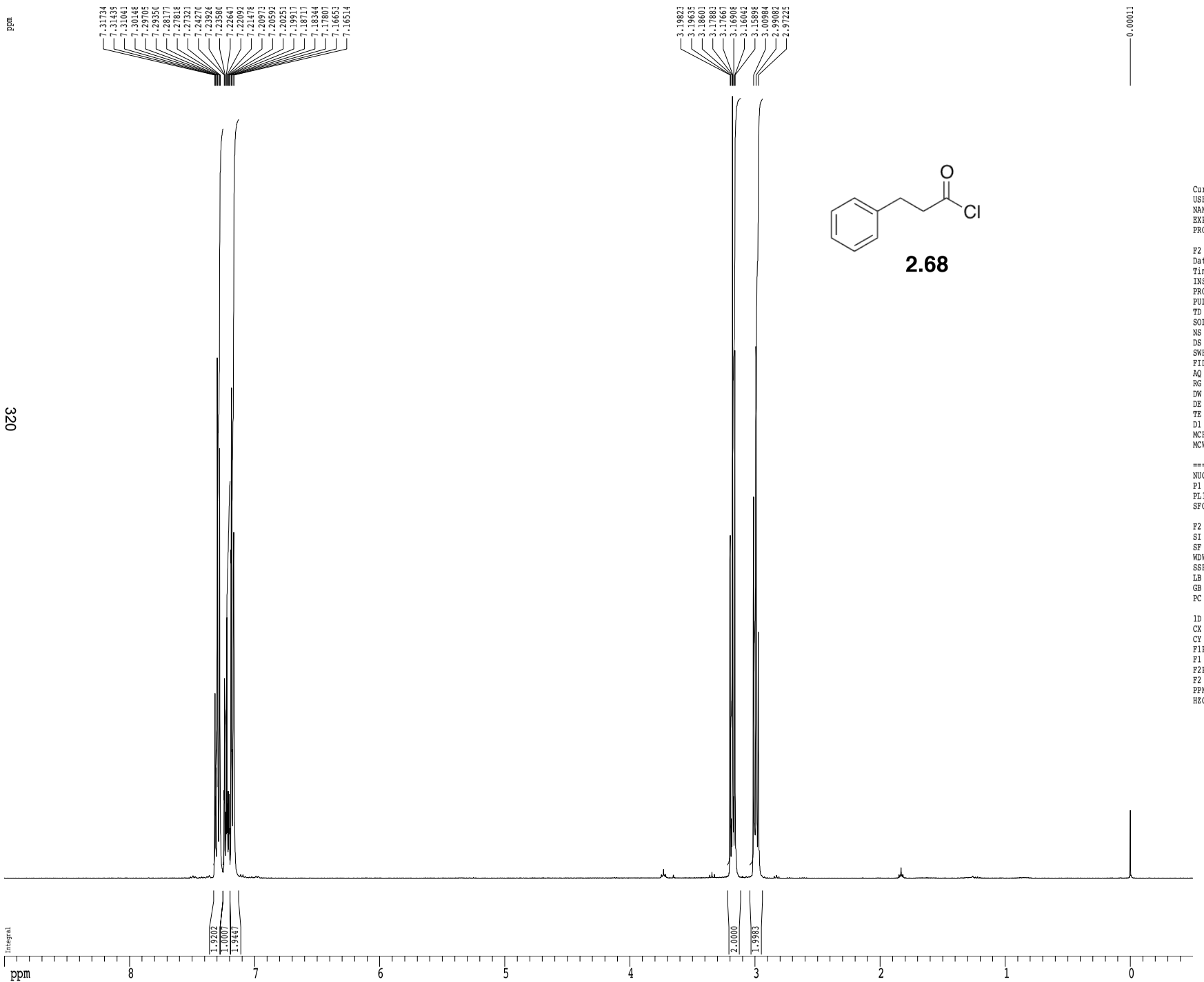
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804117 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

1H spectrum



2.68

Current Data Parameters

USER	sanforda
NAME	ABS-3-090
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20191210
Time	17.24
INSTRUM	drx400
PROBHD	5 mm Multinucl
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	6410.256 Hz
FIDRES	0.097813 Hz
AQ	5.1118579 sec
RG	90.5
DW	78.000 usec
DE	4.50 usec
TE	297.9 K
D1	0.10000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======= CHANNEL f1 =======

NUC1	1H
P1	12.00 usec
PL1	-1.10 dB
SFO1	400.1328009 MHz

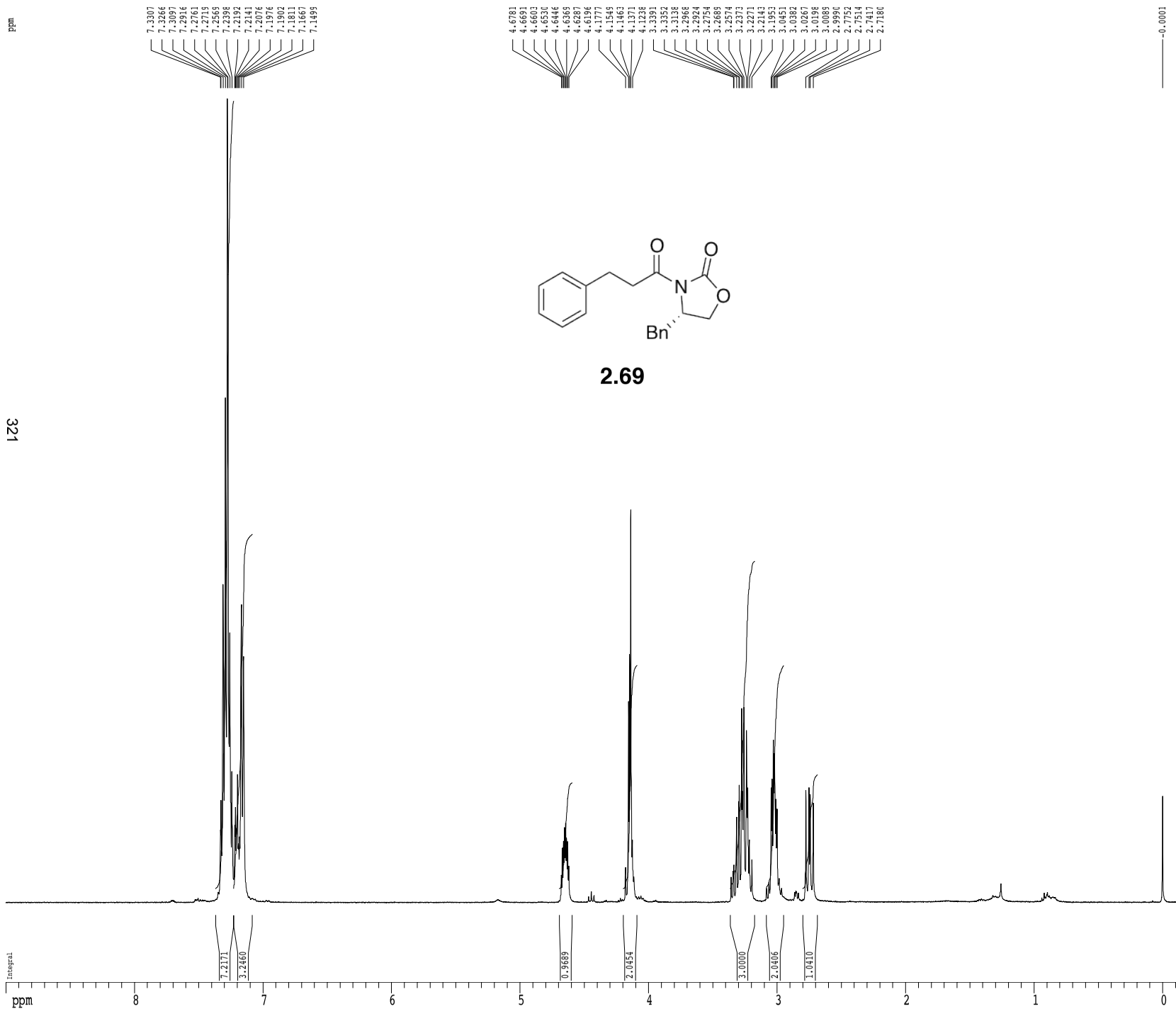
F2 - Processing parameters

SI	65536
SF	400.1300416 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
CY	15.00 cm
F1P	9.000 ppm
F1	3601.17 Hz
F2P	-0.500 ppm
F2	-200.06 Hz
PPMCM	0.41667 ppm/cm
HZCM	166.72086 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-3-091-proton
EXPNO 1
PROCNO 1

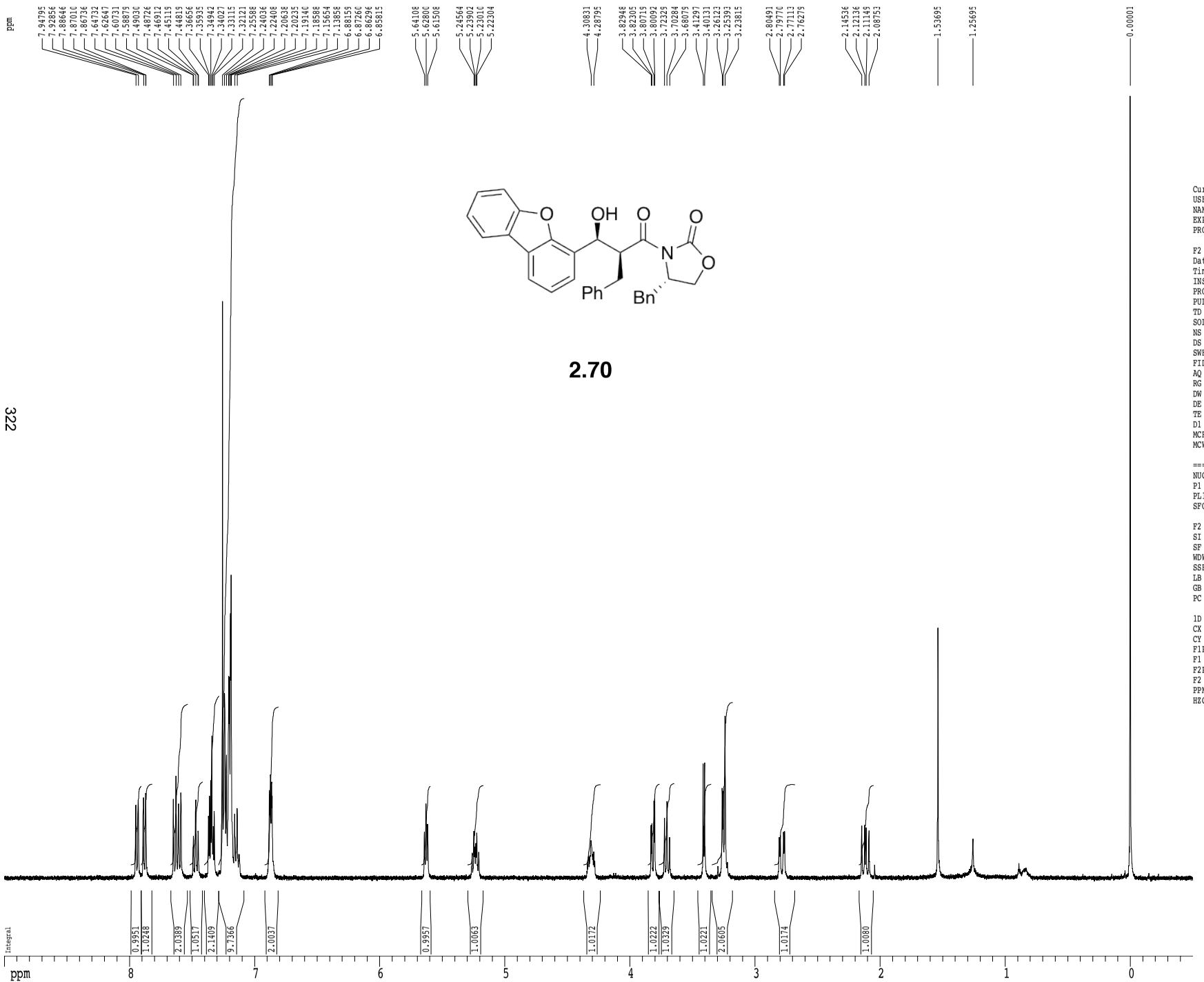
F2 - Acquisition Parameters
Date_ 20200103
Time 17.13
INSTRUM drx400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 128
DW 78.000 usec
DE 4.50 usec
TE 298.2 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300296 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

1H spectrum



2.70

322

Current Data Parameters
USER sanforda
NAME ABS-3-092-proton
EXPNO 1
PROCNO 1

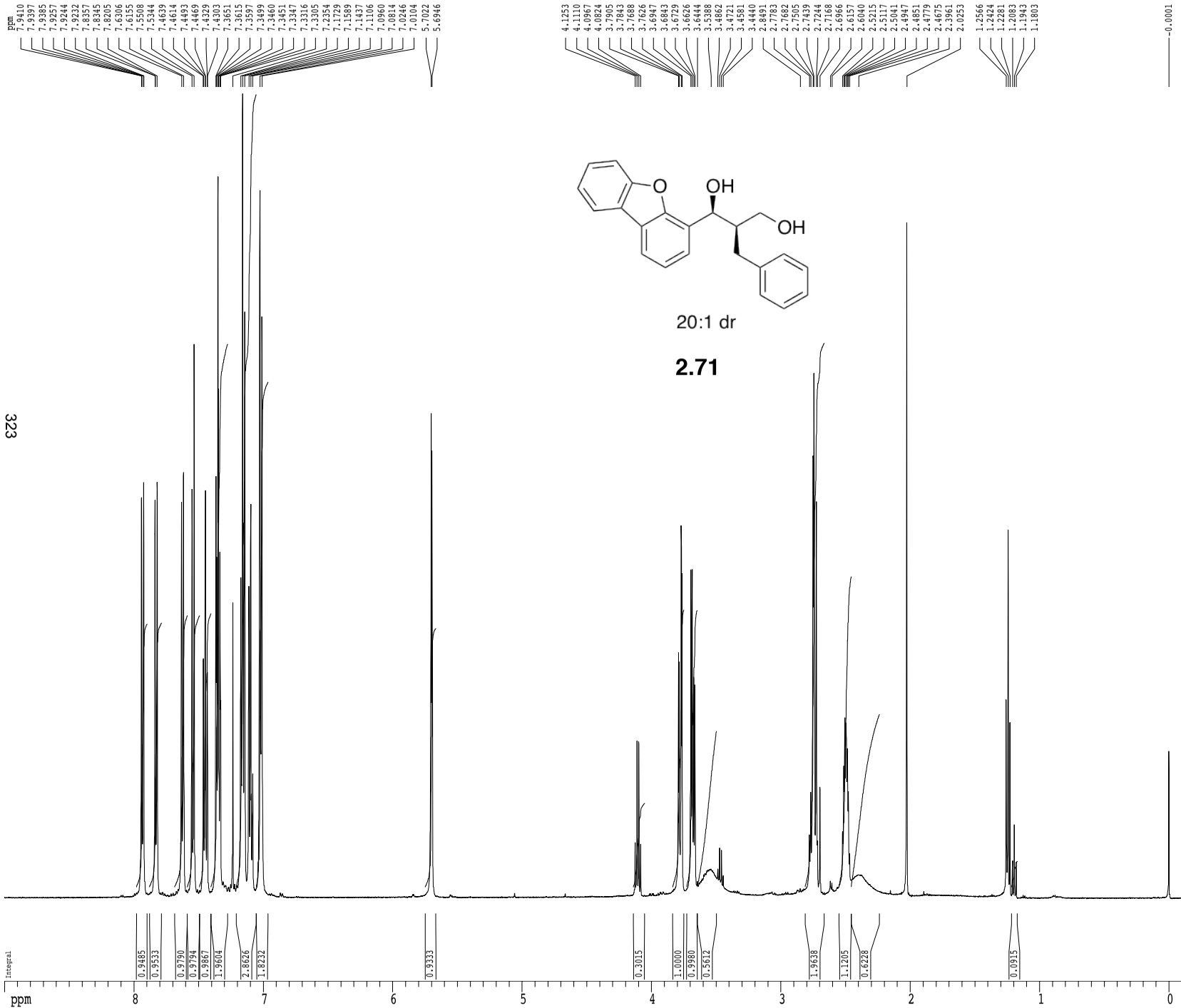
F2 - Acquisition Parameters
Date_ 20200104
Time 11.46
INSTRUM drx400
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 812.7
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300233 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

1H spectrum

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Current Data Parameters
USER            sanforda
NAME      ABS-3-094-proton
EXPNO                  1
PROCNO                 1

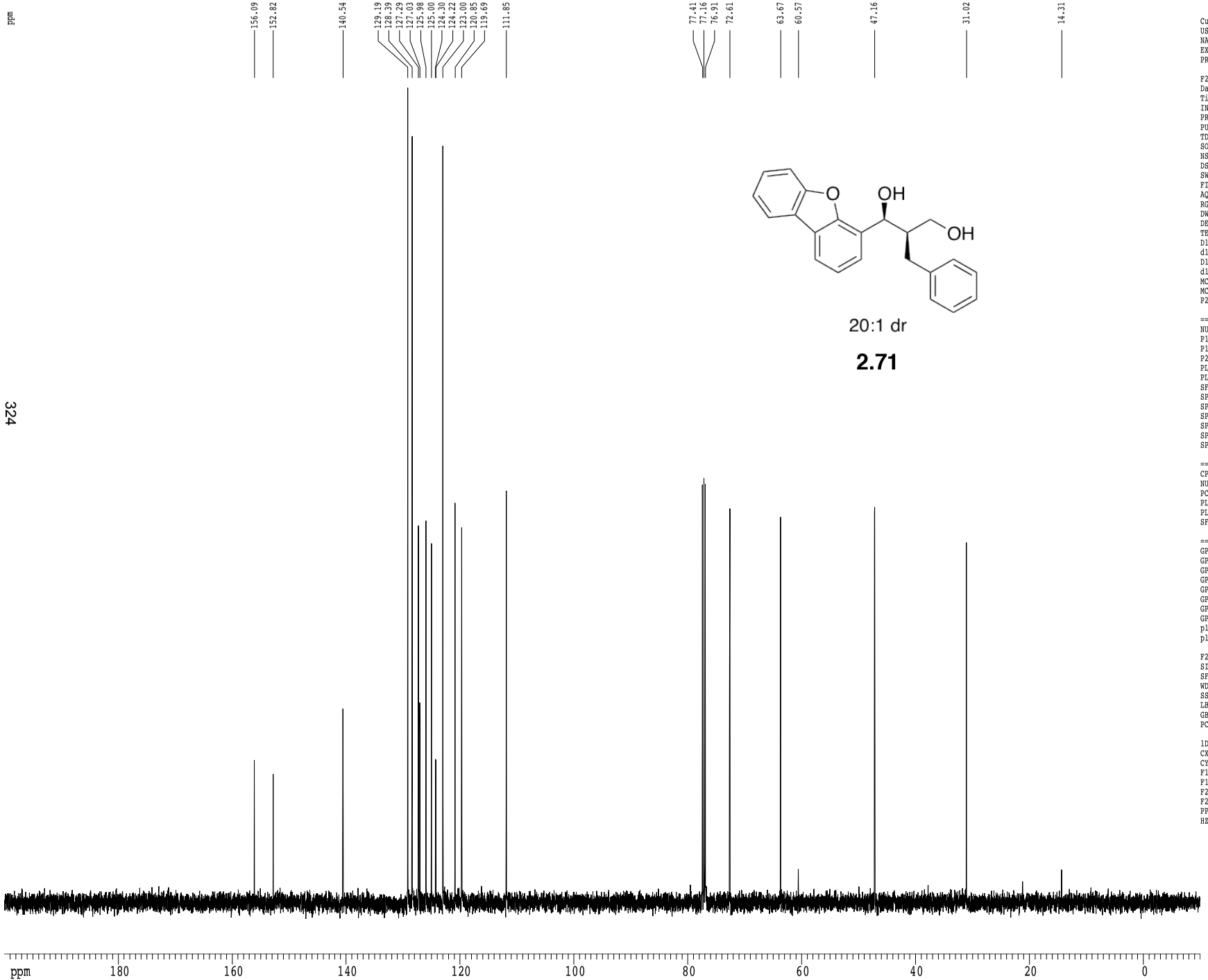
F2 - Acquisition Parameters
Date_           20200102
Time                13.04
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES             0.098043 Hz
AQ              5.0998774 sec
RG                   7.1
DW                62.400 usec
DE                 6.00 usec
TE                298.0 K
D1             0.10000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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

F2 - Processing parameters
SI                 65536
SF            500.2200435 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                 9.000 ppm
F1               4501.98 Hz
F2P                -0.500 ppm
F2               -250.11 Hz
PPMCM              0.41667 ppm/cm
HZCM             208.42502 Hz/cm
```

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

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Current Data Parameters
USER            sanforda
NAME      ABS-3-094-carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20200102
Time              13.06
INSTRUM           cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp2.prd
TD                65536
SOLVENT           CDCl3
NS                   80
DS                   16
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG               7298.2
DW               16.500 usec
DE                6.00 usec
TE                298.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                33.10 usec

======== CHANNEL f1 ========
NUC1                13C
P1                16.55 usec
P12             2000.00 usec
P20              500.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1         125.7942548 MHz
SP2               2.70 dB
SP4               2.70 dB
SPNAM2      Crp60comp.4
SPNAM4    Crp60,0.5,20.1
SPOFF2             0.00 Hz
SPOFF4             0.00 Hz

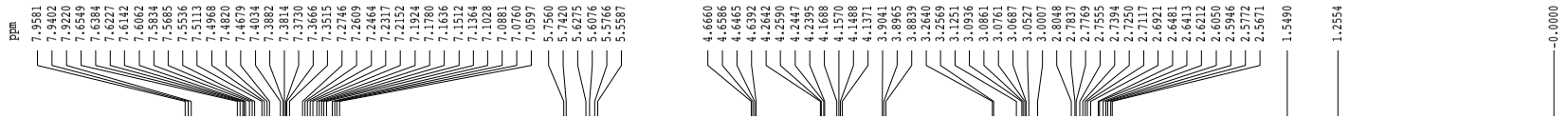
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               1.60 dB
PL12             23.54 dB
SFO2         500.2225011 MHz

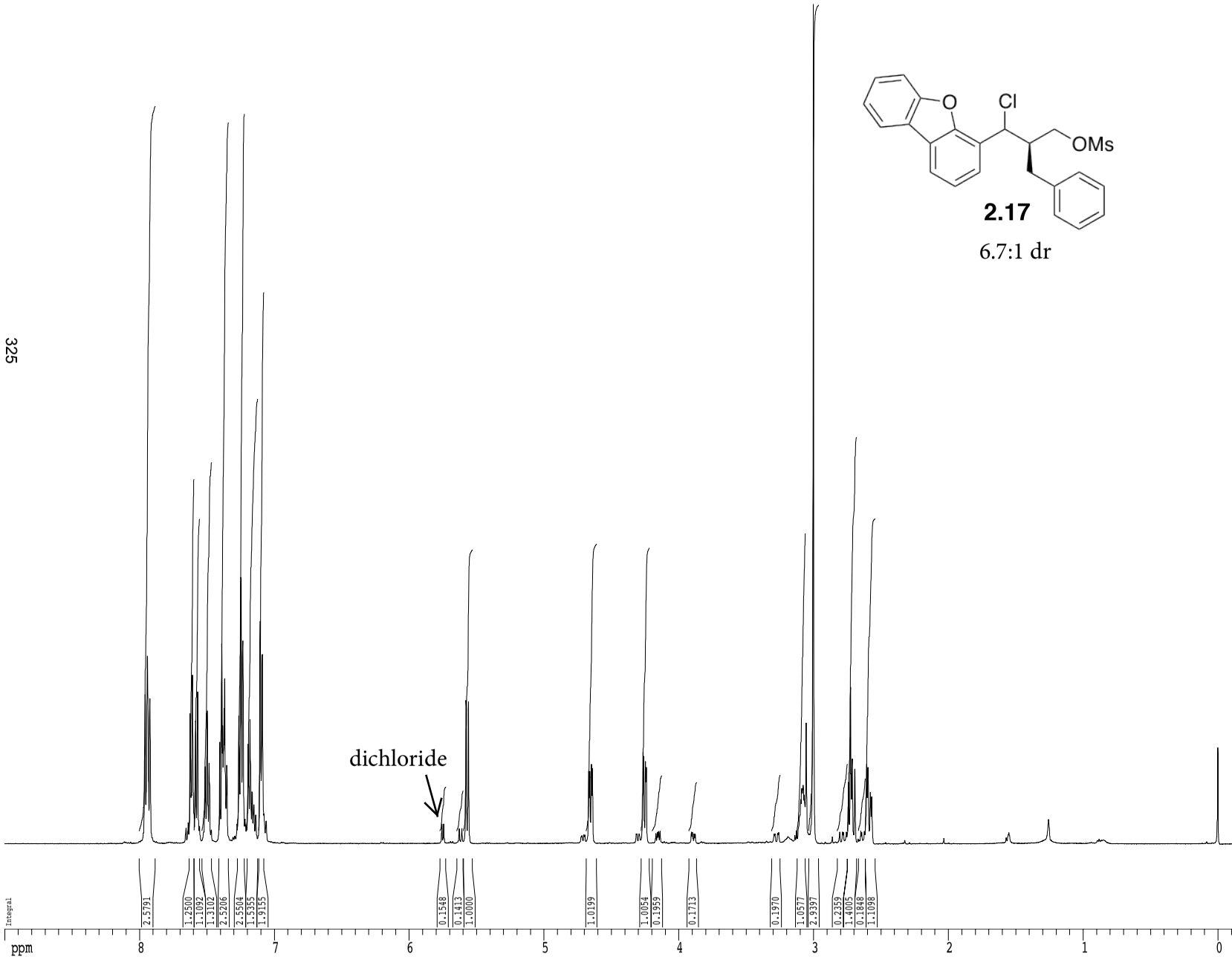
====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7804122 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                2.00

1D NMR plot parameters
CX                22.80 cm
CY                15.65 cm
F1P             200.000 ppm
F1              25156.08 Hz
F2P              -10.000 ppm
F2              -1257.80 Hz
PPMCM             9.21053 ppm/cm
HZCM          1158.50378 Hz/cm
```

1H spectrum





2.17

6.7:1 dr

```
Current Data Parameters
USER            sanforda
NAME      ABS-3-105-cl-proton
EXPNO                  1
PROCNO                 1

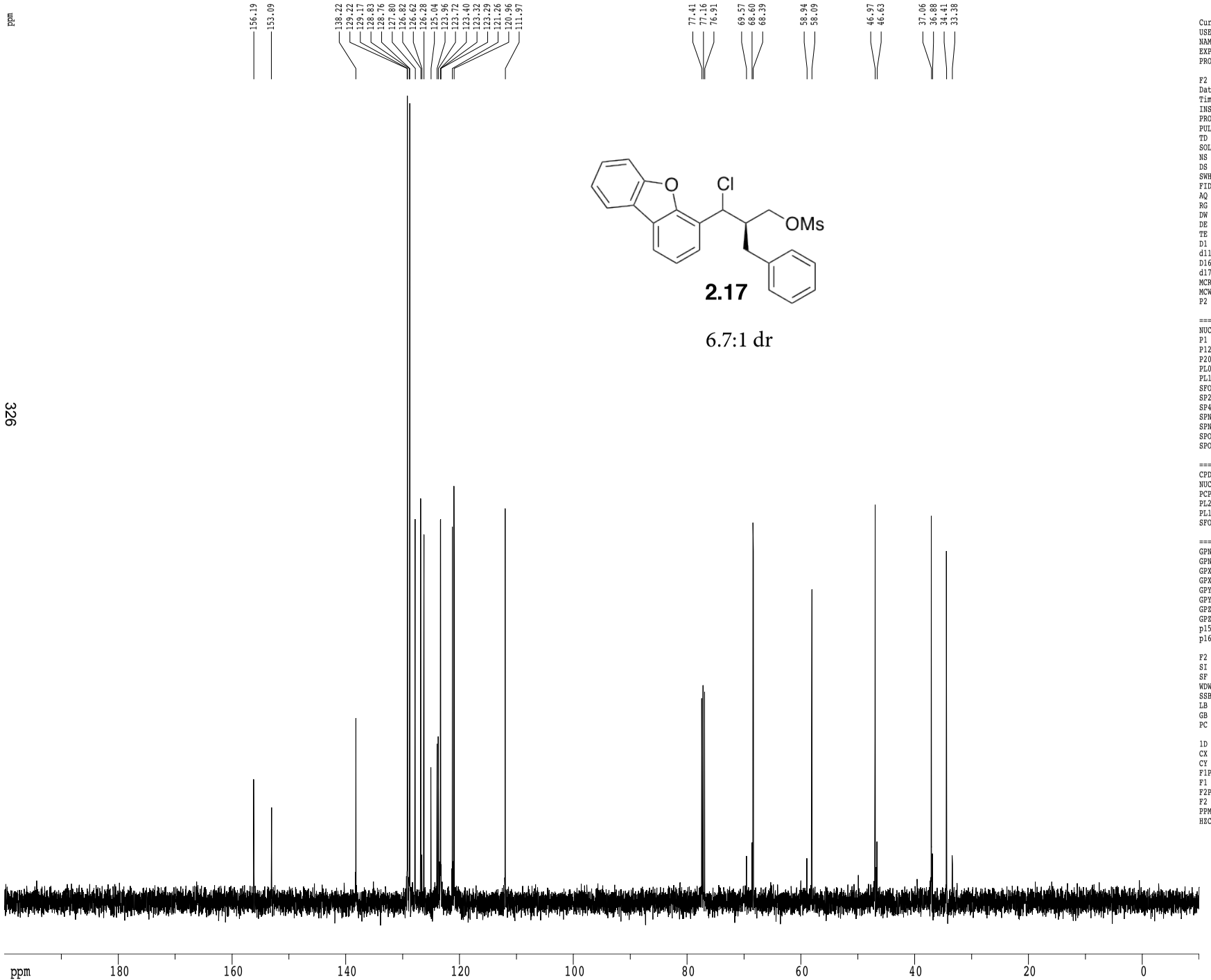
F2 - Acquisition Parameters
Date_           20200114
Time              13.34
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG             zg30
TD                81728
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ             5.0998774 sec
RG                    5
DW               62.400 usec
DE                6.00 usec
TE                298.0 K
D1           0.10000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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

F2 - Processing parameters
SI                 65536
SF           500.2200437 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00

1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P               9.000 ppm
F1              4501.98 Hz
F2P              -0.500 ppm
F2              -250.11 Hz
PPMCM           0.41667 ppm/cm
HZCM          208.42502 Hz/cm
```

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



Current Data Parameters
USER sanforda
NAME ABS-3-105-cl-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200114
Time 13.35
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 56
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 33.10 usec

======== CHANNEL f1 ========
NUC1 13C
P1 16.55 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 2.70 dB
SP4 2.70 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 23.54 dB
SFO2 500.2225011 MHz

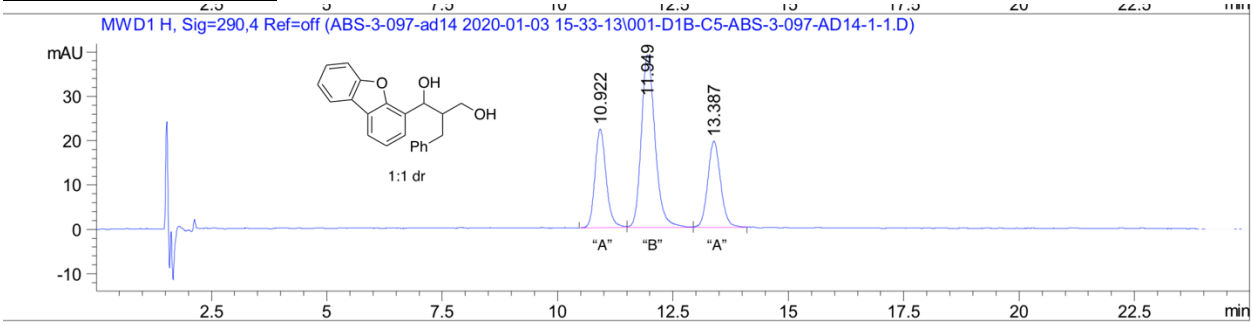
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804145 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

SFC DATA: COMPOUND 2.71

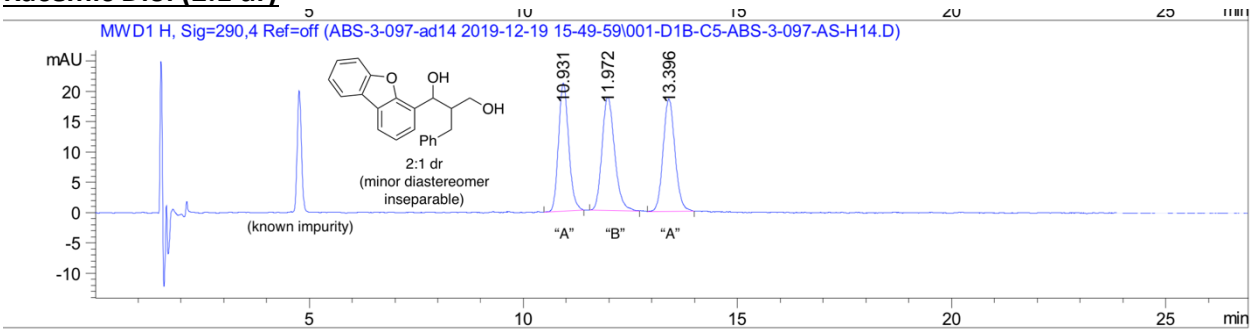
Racemic Diol (1:1 dr)



Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.922	BV	0.2603	374.05426	22.22932	24.0009
2	11.949	VV	0.3142	808.98389	38.97200	51.9078
3	13.387	VB	0.3037	375.46368	19.40884	24.0913
Totals :				1558.50183	80.61016	

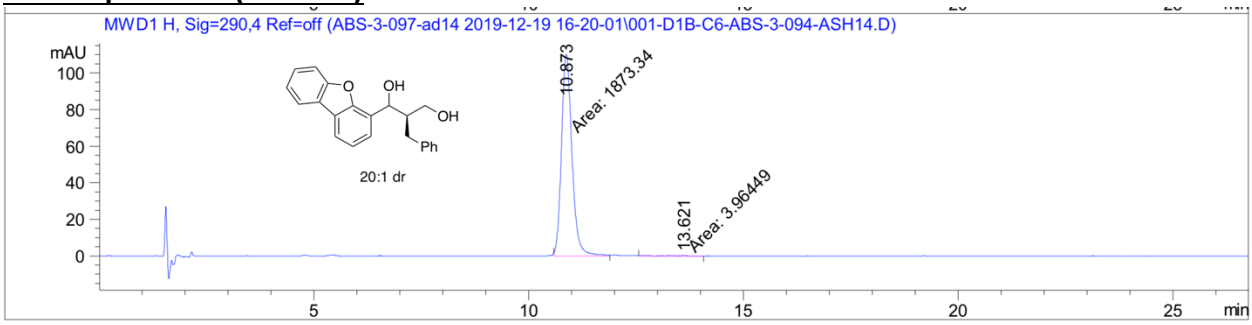
Racemic Diol (2:1 dr)



Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.931	VB R	0.2552	349.67221	21.11995	32.1480
2	11.972	BB	0.3138	380.45923	18.66255	34.9785
3	13.396	BB	0.2950	357.56464	18.53786	32.8736
Totals :				1087.69608	58.32036	

Enantiopure Diol (>20:1 dr)

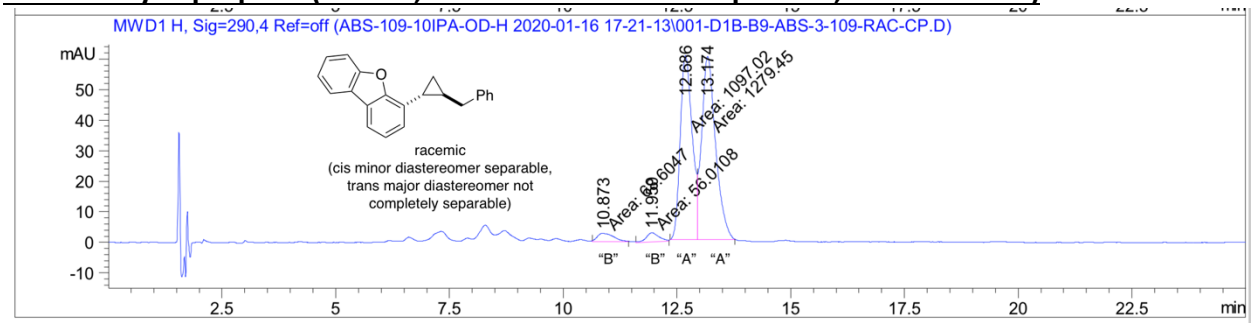


Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.873	MM	0.2834	1873.34485	110.18804	99.7888
2	13.621	MM	0.6003	3.96449	1.10067e-1	0.2112

SFC DATA: COMPOUND 2.18

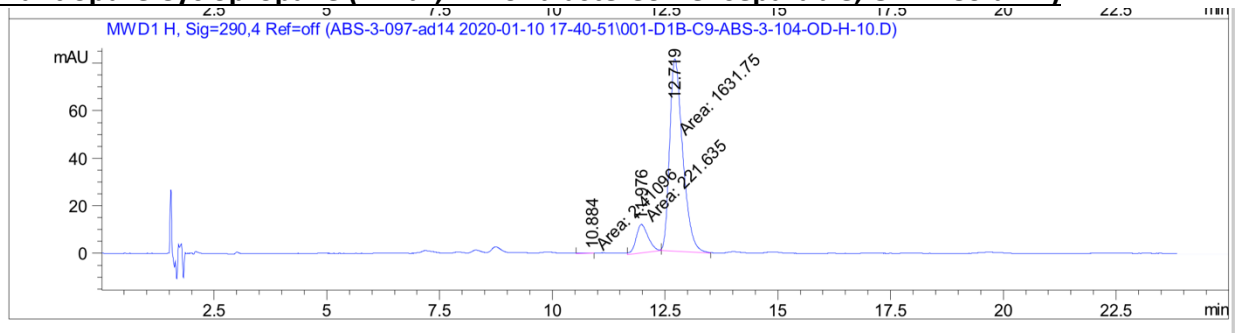
Racemic Cyclopropane (20:1 dr; minor diastereomer separable; OD-H Column)



Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.873	MM	0.4164	68.60468	2.74578	2.7430
2	11.950	MM	0.3168	56.01078	2.94664	2.2395
3	12.686	MM	0.3035	1097.01843	60.23377	43.8617
4	13.174	MM	0.3557	1279.45093	59.95268	51.1558
Totals :				2501.08481	125.87888	

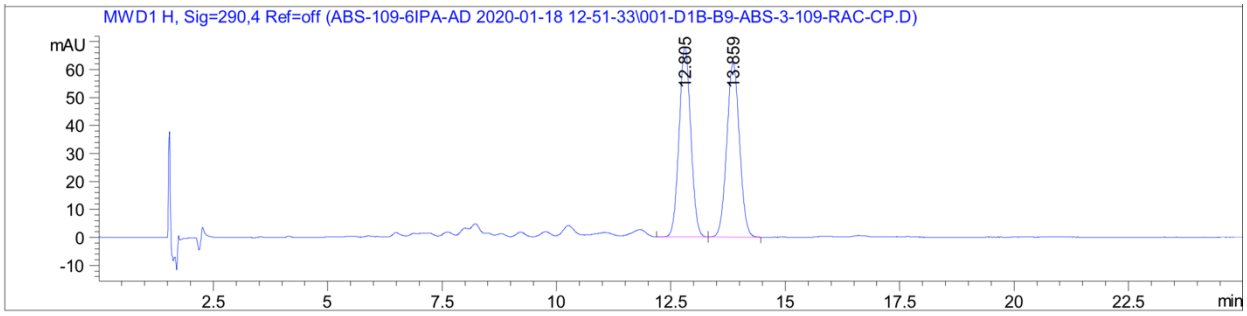
Enantiopure Cyclopropane (7:1 dr; minor diastereomer separable; OD-H Column)



Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.884	MM	0.3871	2.41096	1.03806e-1	0.1299
2	11.976	MM	0.3091	221.63527	11.95211	11.9429
3	12.719	MM	0.3359	1631.74744	80.95510	87.9272
Totals :				1855.79367	93.01102	

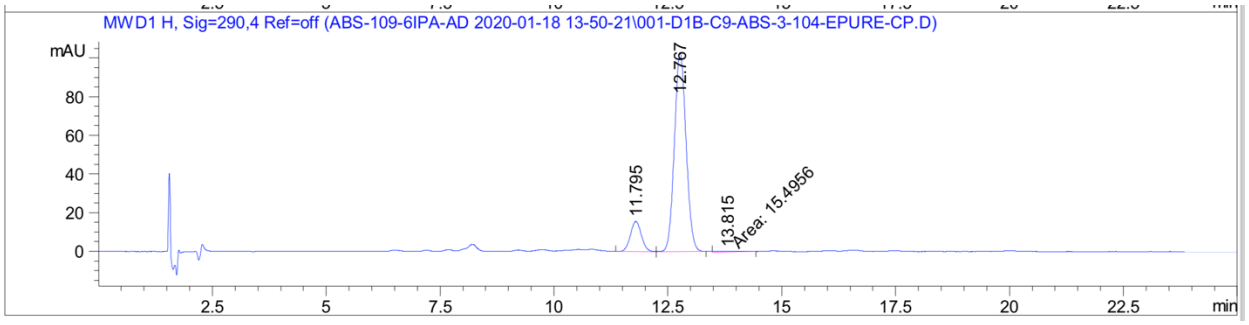
Racemic Cyclopropane (major diastereomer separable; AD Column)



Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.805	BB	0.2757	1208.46973	67.88329	50.0251
2	13.859	VV R	0.3040	1207.25879	62.33078	49.9749
Totals :				2415.72852	130.21406	

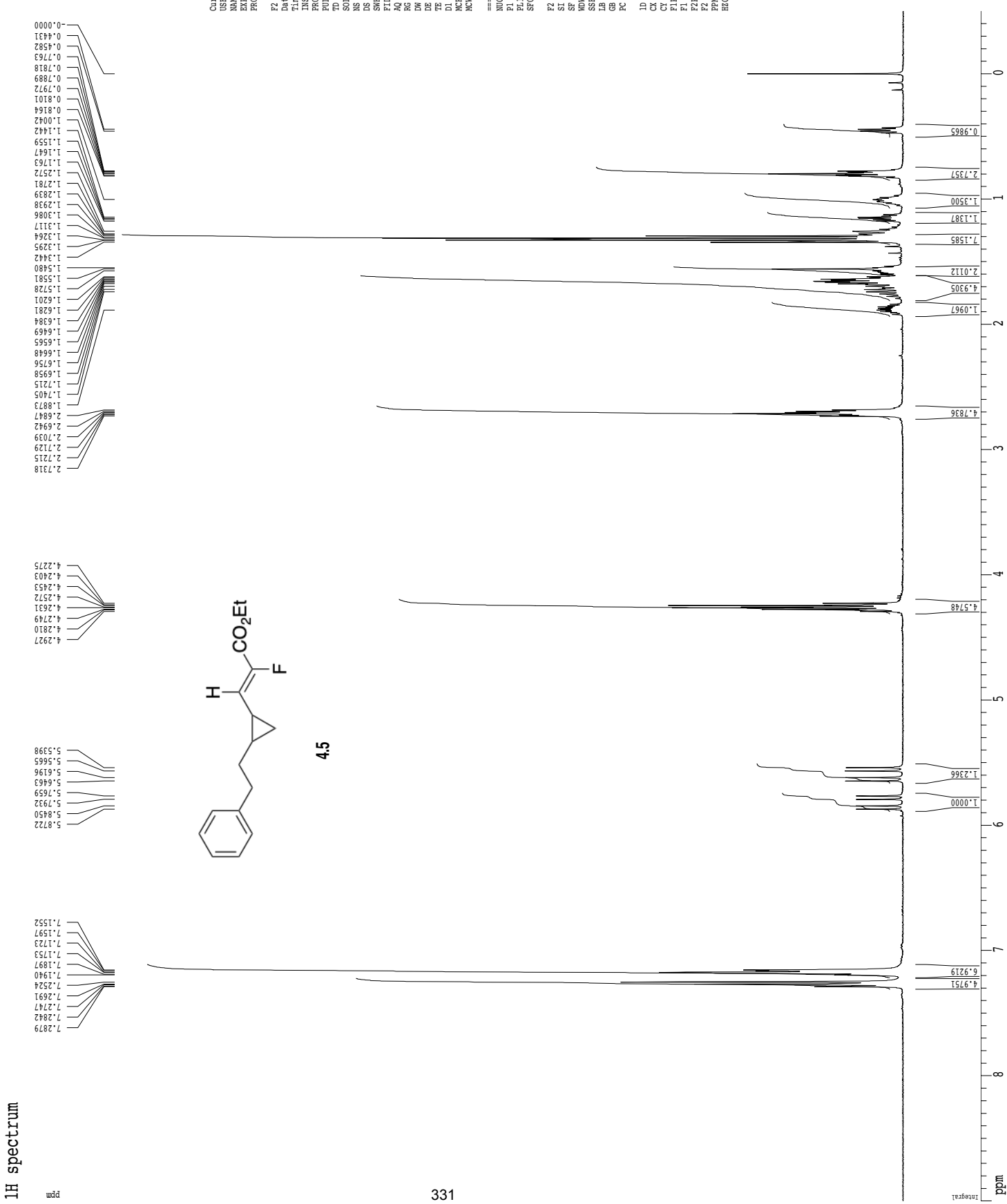
Enantiopure Cyclopropane (7:1 dr; major diastereomer separable; AD Column)



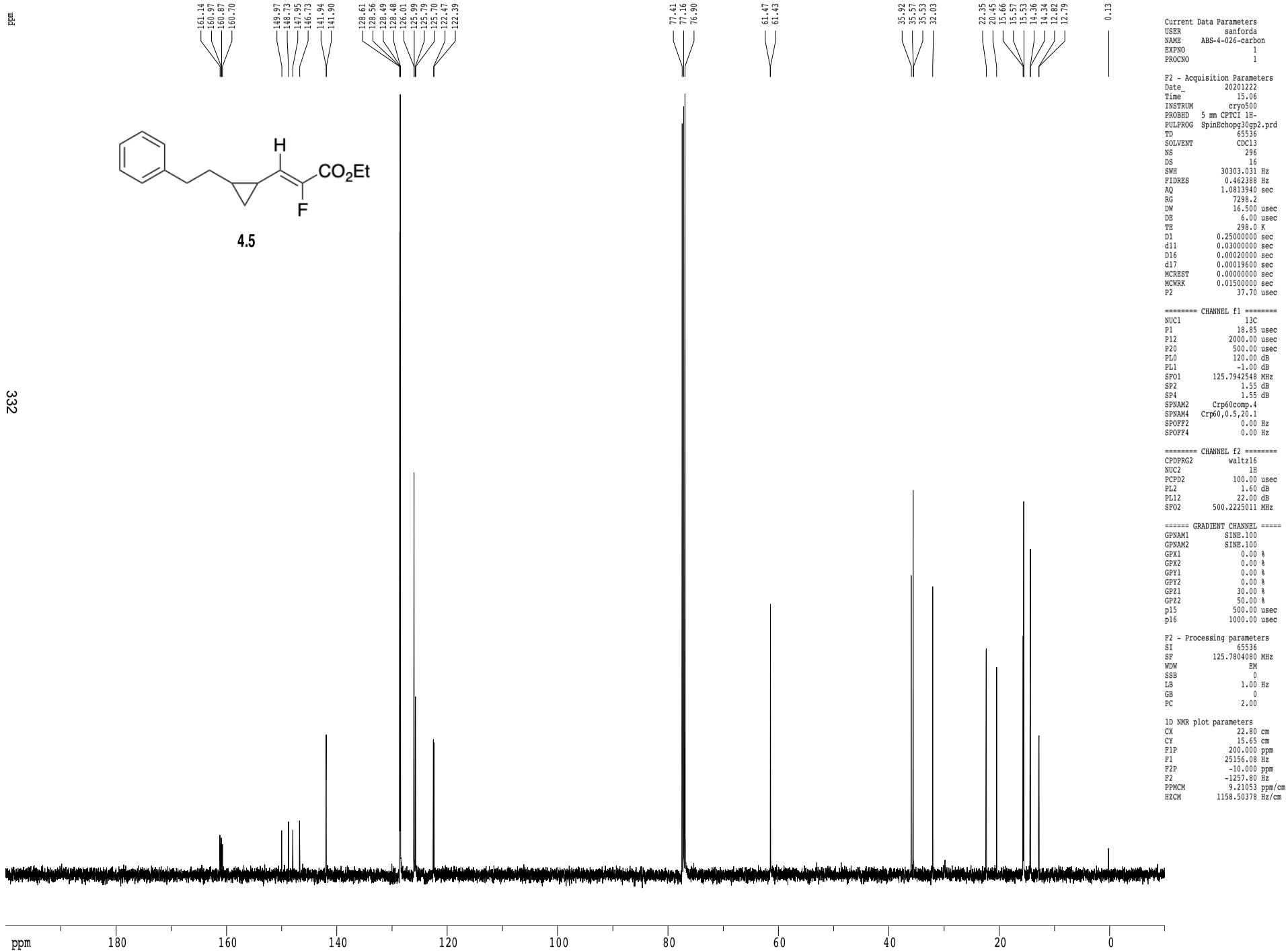
Signal 8: MWD1 H, Sig=290,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.795	BB	0.2571	260.90823	15.60549	12.3619
2	12.767	BB	0.2779	1834.17700	102.91557	86.9039
3	13.815	MM	0.5975	15.49565	4.32228e-1	0.7342
Totals :				2110.58088	118.95328	

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-4-026-F22
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201222
Time_ 13.45
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 203.2
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.60 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300246 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 10.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.0000
0.4431
0.4582
0.7763
0.7818
0.7889
0.7972
0.8101
0.8164
1.0042
1.1442
1.1559
1.1647
1.1763
1.2572
1.2781
1.2839
1.2938
1.3086
1.3117
1.3264
1.3295
1.3442
1.5480
1.5581
1.5728
1.6201
1.6281
1.6384
1.6469
1.6565
1.6648
1.6756
1.6958
1.7215
1.7405
1.8873
2.6847
2.6942
2.7039
2.7129
2.7215
2.7318
4.2275
4.2403
4.2453
4.2572
4.2631
4.2749
4.2810
4.2927
5.3398
5.5665
5.6196
5.6463
5.7659
5.7932
5.8450
5.8722
7.1552
7.1597
7.1723
7.1753
7.1897
7.1940
7.2524
7.2691
7.2747
7.2842
7.2879
0.9865
2.7357
1.3500
1.1387
7.1585
2.0112
4.9305
1.0967
4.7836
4.5748
1.2366
1.0000
6.9219
4.9751
H
CO2Et
F
4.5
ppm
Integral
331

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



Current Data Parameters
USER sanforda
NAME ABS-4-026-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201222
Time 15.06
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 296
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 37.70 usec

======== CHANNEL f1 ========
NUC1 13C
P1 18.85 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 1.55 dB
SP4 1.55 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

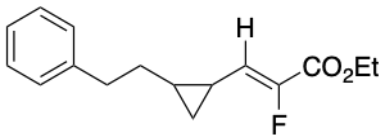
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 22.00 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

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

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

19F spectrum



4.5

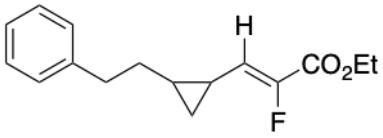

```
Current Data Parameters
USER            sanforda
NAME         ABS-4-056-f
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20210212
Time              12.47
INSTRUM           av600
PROBHD   5 mm CPBBO BB-
PULPROG        zgflqn30
TD               131072
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           178571.422 Hz
FIDRES          1.362392 Hz
AQ              0.3670516 sec
RG                   575
DW                2.800 usec
DE               18.00 usec
TE                298.1 K
D1            3.00000000 sec
TD0                   1

======== CHANNEL f1 =======
SFO1         564.6299196 MHz
NUC1                19F
P1                18.25 usec

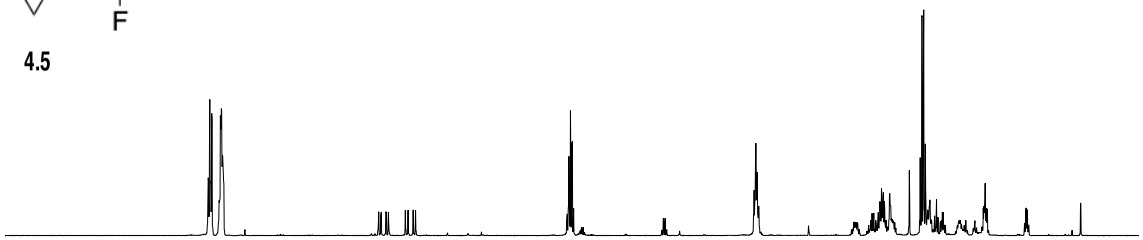
F2 - Processing parameters
SI               131072
SF           564.6863858 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

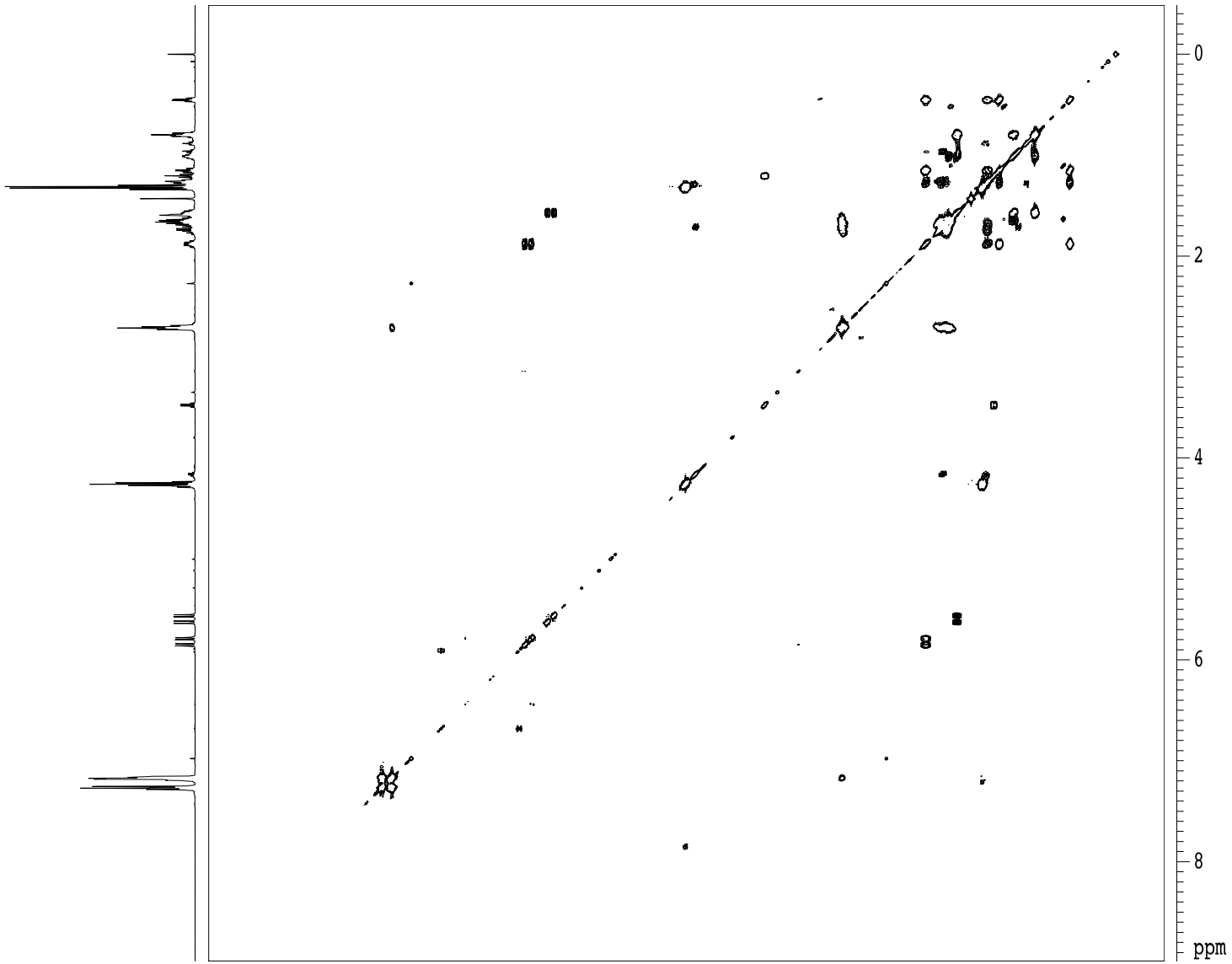
1D NMR plot parameters
CX                22.80 cm
CY                15.00 cm
F1P              58.120 ppm
F1             32819.54 Hz
F2P             -258.111 ppm
F2           -145751.91 Hz
PPMCM          13.86979 ppm/cm
HZCM         7832.08105 Hz/cm
```



4.5

gcosy60





334

Current Data Parameters

USER	sanforda
NAME	ABS-3-194-cosy
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20200727
Time	13.06
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	2
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	143.7
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221611 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2222 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	QF

F2 - Processing parameters

SI	1024
SF	500.2200352 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

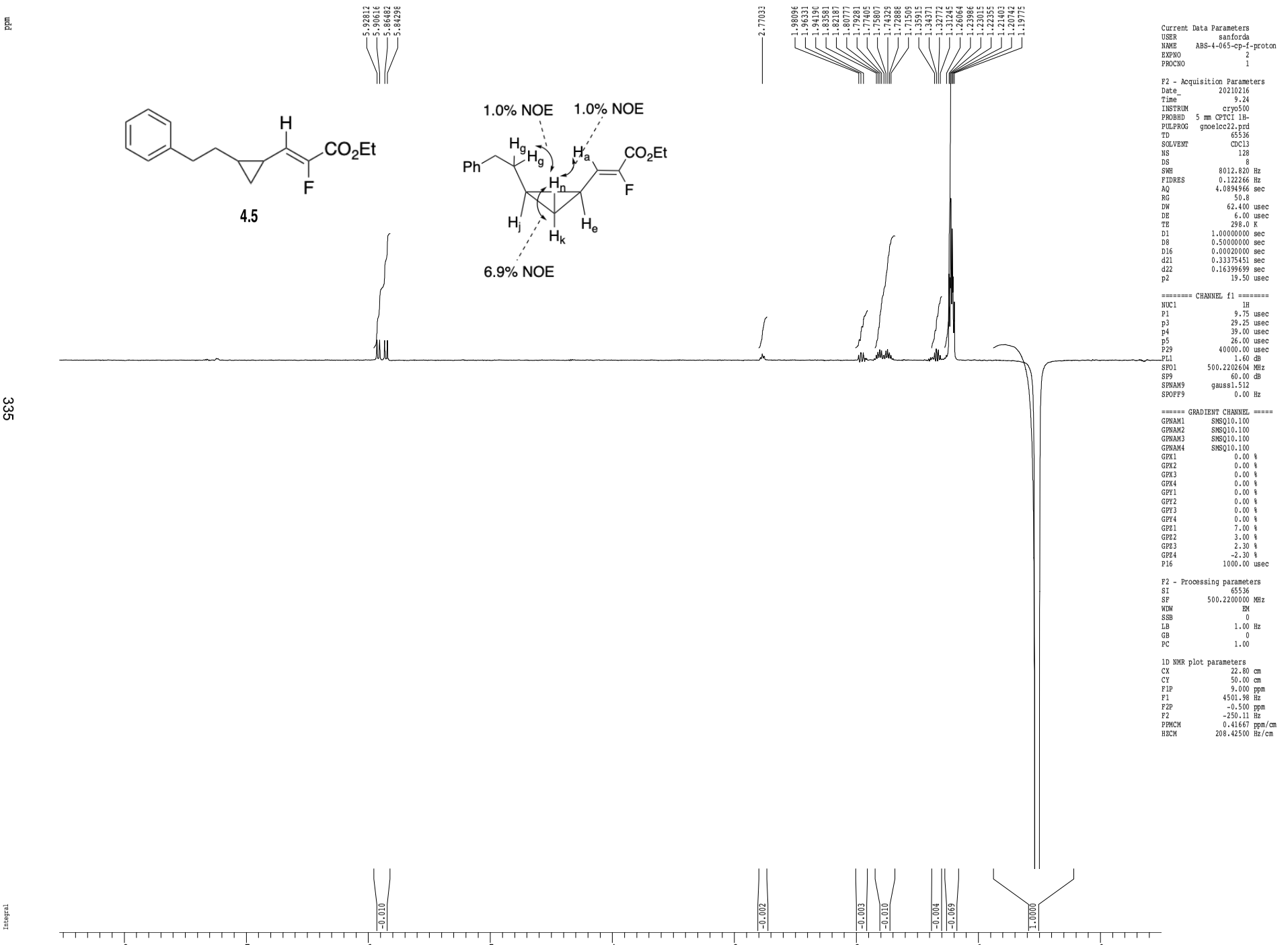
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200352 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.983 ppm
F2LO	4493.36 Hz
F2PHI	-0.483 ppm
F2HI	-241.49 Hz
F1PLO	8.983 ppm
F1LO	4493.36 Hz
F1PHI	-0.483 ppm
F1HI	-241.49 Hz
F2PPMCM	0.63104 ppm/cm
F2HZCM	315.65656 Hz/cm
F1PPMCM	0.63104 ppm/cm
F1HZCM	315.65656 Hz/cm

gnoe



Current Data Parameters
USER sanforda
NAME ABS-4-065-cp-f-proton
EXPNO 2
PROCNO 1

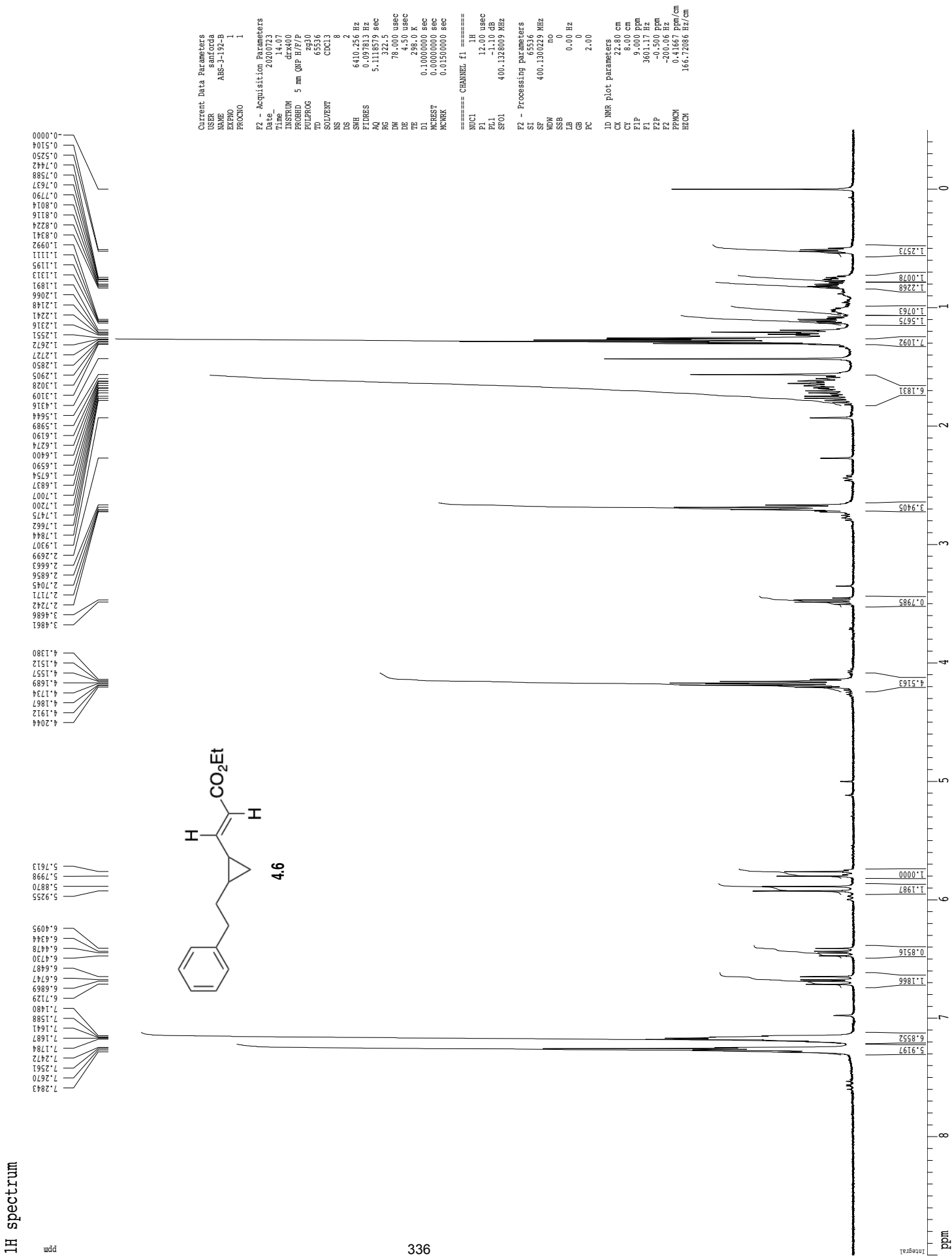
F2 - Acquisition Parameters
Date_ 20210216
Time 9.24
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG gnoelcc22.prd
TD 65536
SOLVENT CDCl3
NS 128
DS 8
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 50.8
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
D8 0.50000000 sec
D16 0.00020000 sec
d21 0.33375451 sec
d22 0.16399699 sec
p2 19.50 usec

======= CHANNEL f1 =======
NUC1 1H
P1 9.75 usec
p3 29.25 usec
p4 39.00 usec
p5 26.00 usec
P29 40000.00 usec
PL1 1.60 dB
SFO1 500.2202604 MHz
SP9 60.00 dB
SPNAM9 gauss1.512
SPOFF9 0.00 Hz

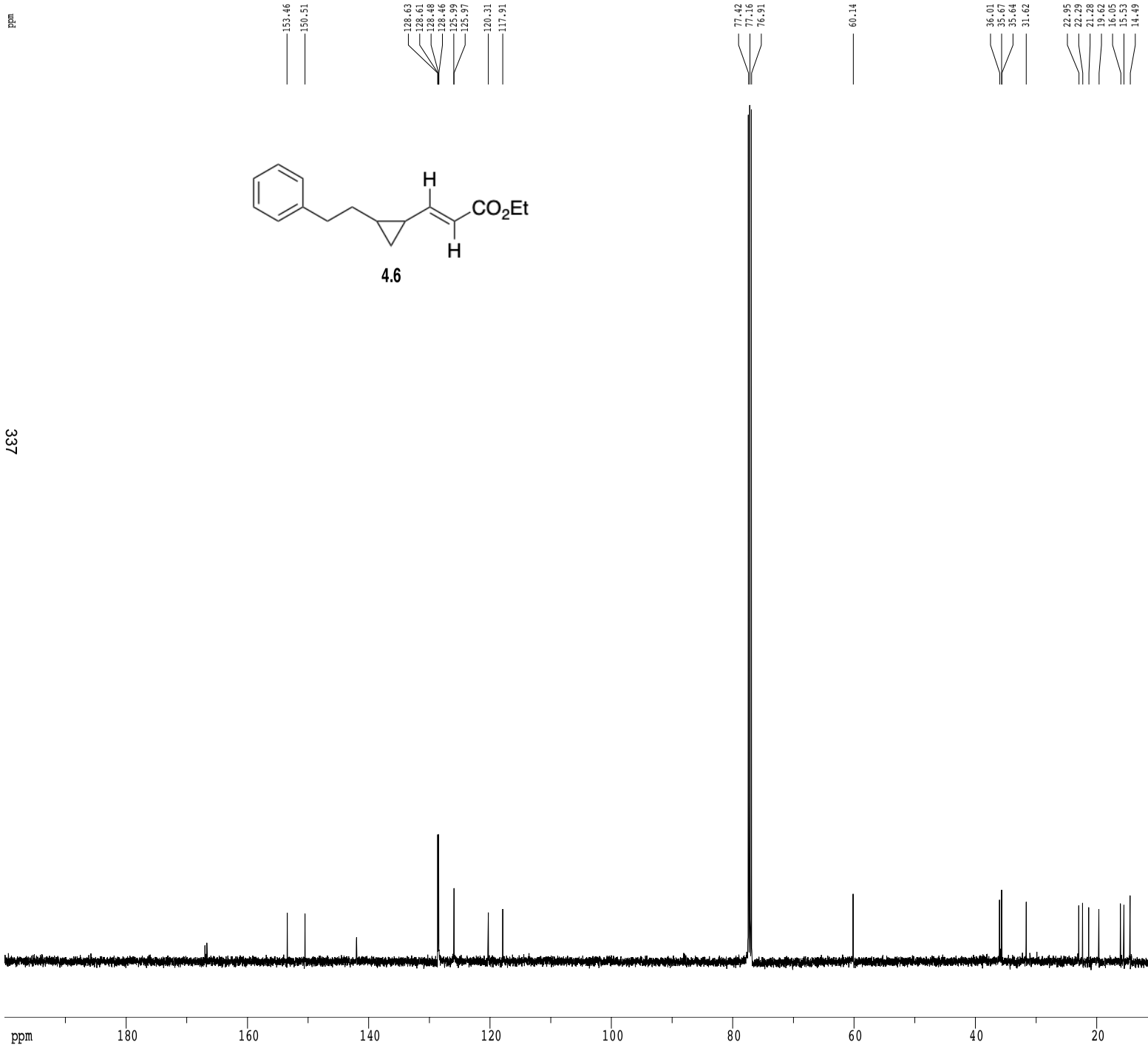
====== GRADIENT CHANNEL =====
GPNAM1 SMSQ10.100
GPNAM2 SMSQ10.100
GPNAM3 SMSQ10.100
GPNAM4 SMSQ10.100
GPX1 0.00 %
GPX2 0.00 %
GPX3 0.00 %
GPX4 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPY3 0.00 %
GPY4 0.00 %
GPZ1 7.00 %
GPZ2 3.00 %
GPZ3 2.30 %
GPZ4 -2.30 %
P16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 500.2200000 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 50.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42500 Hz/cm


1H spectrum
Current Data Parameters
USER sanforda
NAME ABS-3-192-B
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20200723
Time_ 14.07
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 322.5
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300229 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 8.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
CO2Et
H
H
4.6
ppm
Integral

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



Current Data Parameters
USER sanforda
NAME ABS-4-042-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210202
Time 15.20
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 769
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 37.70 usec

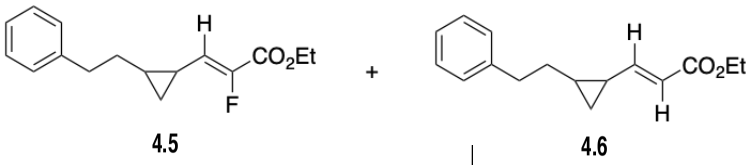
======== CHANNEL f1 ========
NUC1 13C
P1 18.85 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 1.55 dB
SP4 1.55 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 22.00 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804057 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

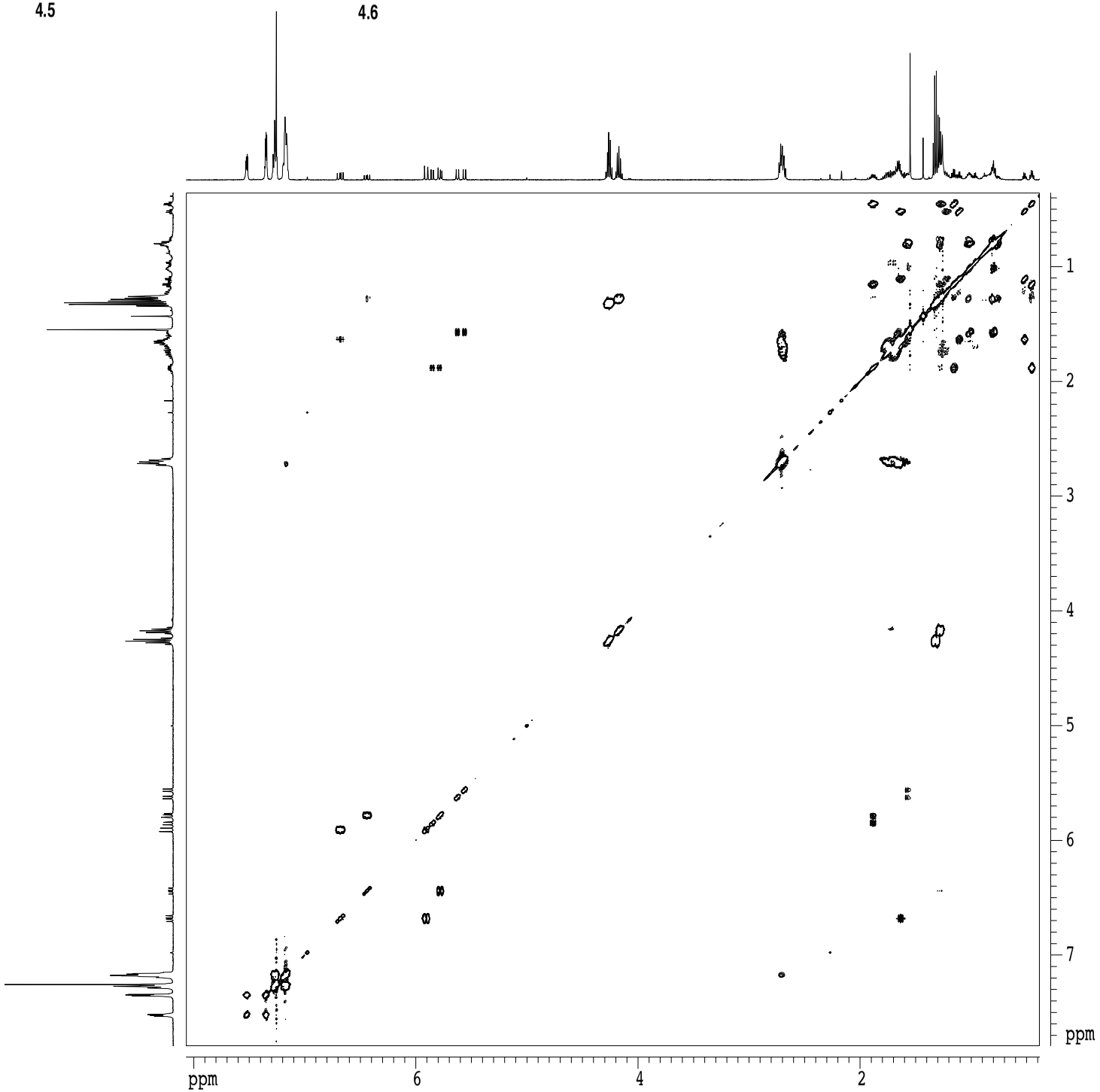
1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50366 Hz/cm



4.5 + 4.6

gcosy60

338



Current Data Parameters

USER	sanforda
NAME	ABS-3-184-cosy
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20200713
Time	10.15
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	2
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	362
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	7.50 usec
PL1	1.60 dB
SFO1	500.2221598 MHz

====== GRADIENT CHANNEL =====

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2222 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	QF

F2 - Processing parameters

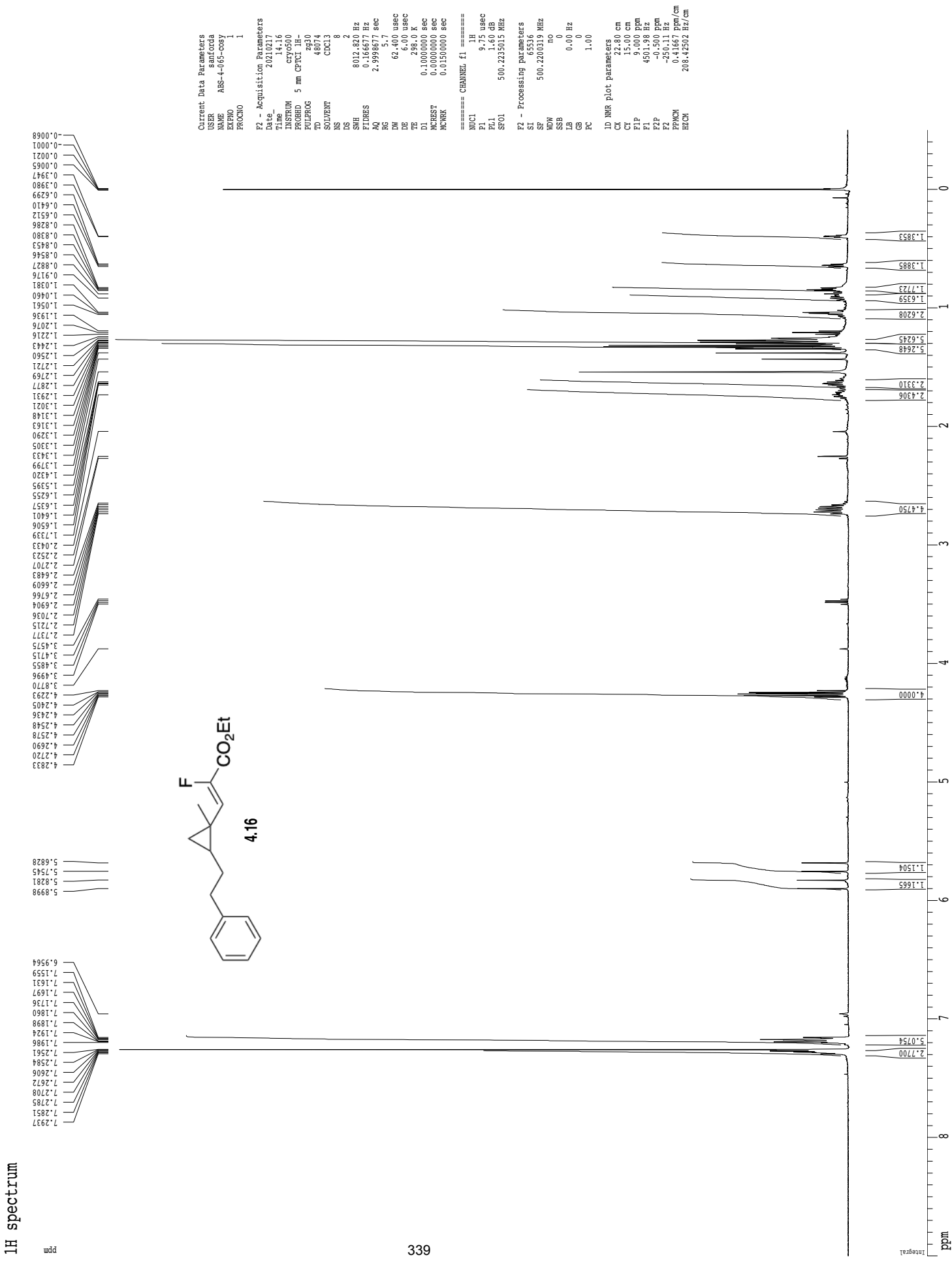
SI	1024
SF	500.2200338 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

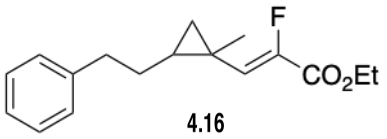
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200338 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	8.068 ppm
F2LO	4035.59 Hz
F2PHI	0.386 ppm
F2HI	193.15 Hz
F1PLO	7.790 ppm
F1LO	3896.87 Hz
F1PHI	0.358 ppm
F1HI	179.28 Hz
F2PPMCM	0.51210 ppm/cm
F2HZCM	256.16272 Hz/cm
F1PPMCM	0.49546 ppm/cm
F1HZCM	247.83974 Hz/cm

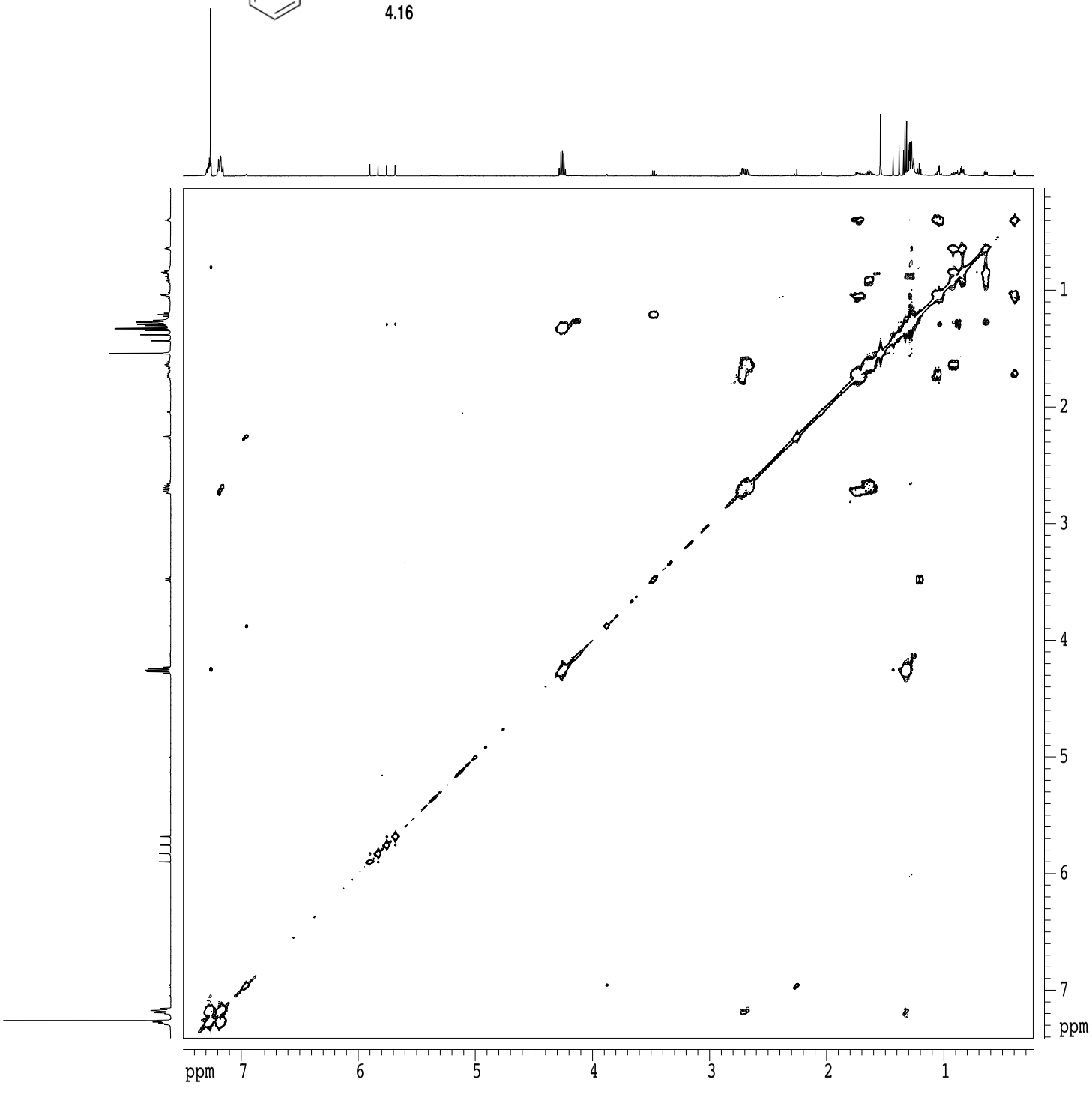

1H spectrum
ppm
Integral
Current Data Parameters
USER sanforda
NAME ABS-4-065-cosy
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210217
Time_ 14.16
INSTRUM CTYc500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 48074
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.9998677 sec
RG 5.7
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======= CHANNEL f1 =======
NUC1 1H
P1 9.75 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200319 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
F
CO2Et
4.16



4.16

gcosy60

340



Current Data Parameters

USER	sanforda
NAME	ABS-4-065-cosy
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20210217
Time	14.19
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	cosygp60.prd
TD	2048
SOLVENT	CDCl3
NS	2
DS	16
SWH	4734.849 Hz
FIDRES	2.311938 Hz
AQ	0.2163188 sec
RG	512
DW	105.600 usec
DE	6.00 usec
TE	298.0 K
d0	0.00000300 sec
D1	1.00000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00021120 sec

======== CHANNEL f1 ========

NUC1	1H
P1	9.75 usec
PL1	1.60 dB
SFO1	500.2221578 MHz

====== GRADIENT CHANNEL =====

GPNAM1	SMSQ10.100
GPNAM2	SMSQ10.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	17.00 %
GPZ2	17.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	1
TD	512
SFO1	500.2222 MHz
FIDRES	9.247751 Hz
SW	9.465 ppm
FnMODE	QF

F2 - Processing parameters

SI	1024
SF	500.2200319 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

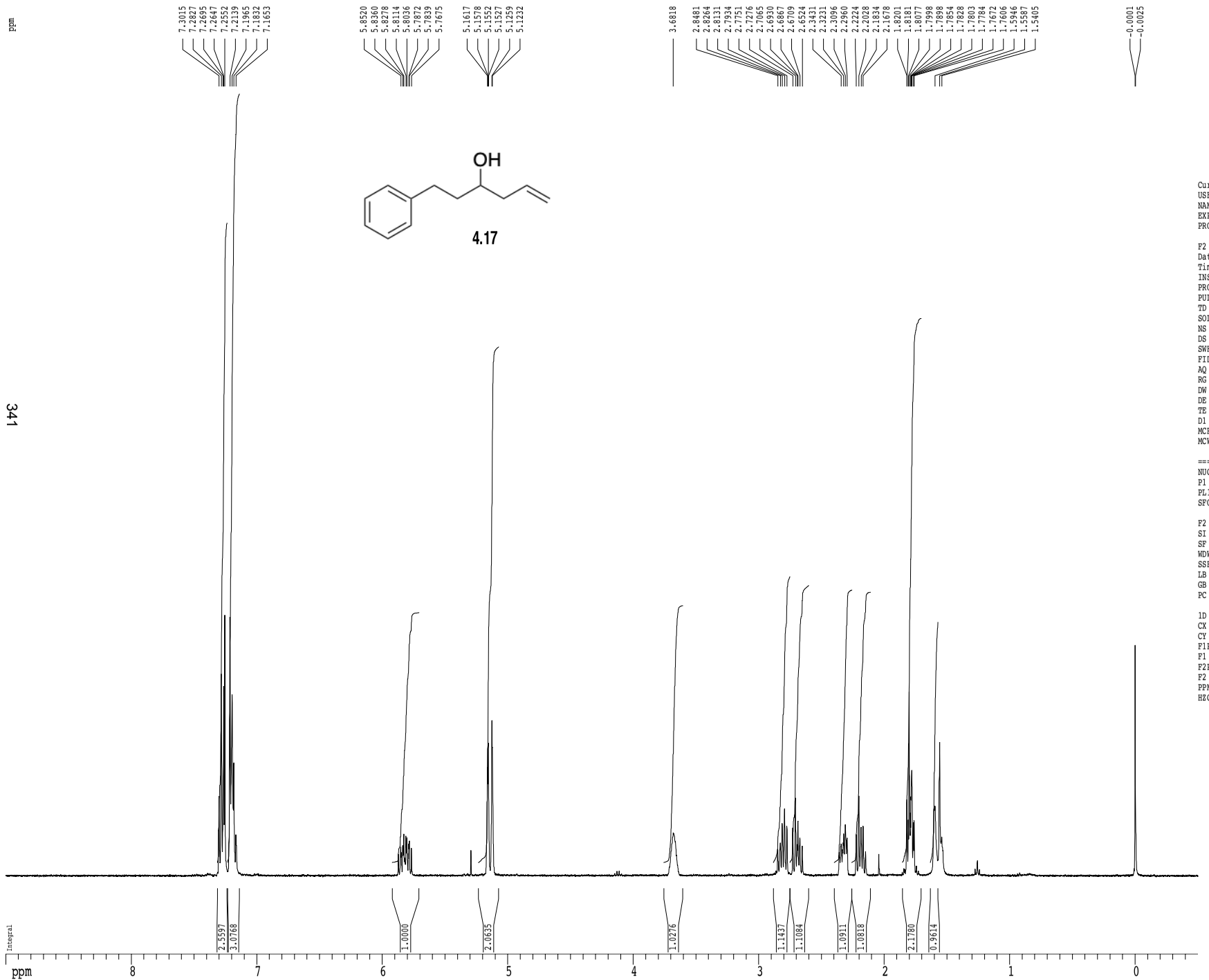
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.2200319 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.494 ppm
F2LO	3748.43 Hz
F2PHI	0.237 ppm
F2HI	118.68 Hz
F1PLO	7.410 ppm
F1LO	3706.81 Hz
F1PHI	0.126 ppm
F1HI	63.20 Hz
F2PPMCM	0.48375 ppm/cm
F2HZCM	241.98283 Hz/cm
F1PPMCM	0.48560 ppm/cm
F1HZCM	242.90761 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-3-287
EXPNO 1
PROCNO 1

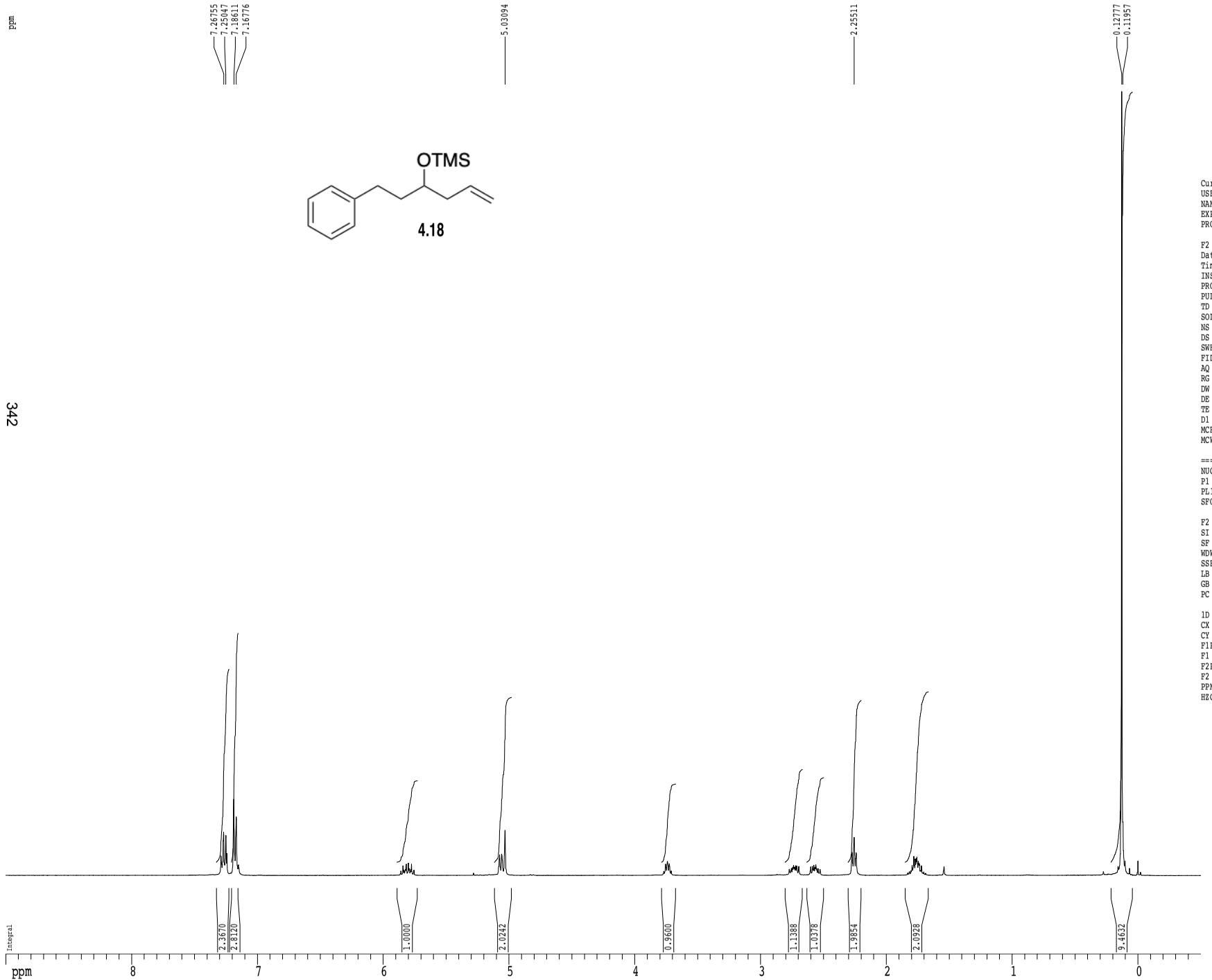
F2 - Acquisition Parameters
Date_ 20201120
Time 15.49
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 32050
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.200008 Hz
AQ 2.4999499 sec
RG 645.1
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.60 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300235 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 5.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

1H spectrum



Current Data Parameters
USER sanforda
NAME ABS-3-186
EXPNO 1
PROCNO 1

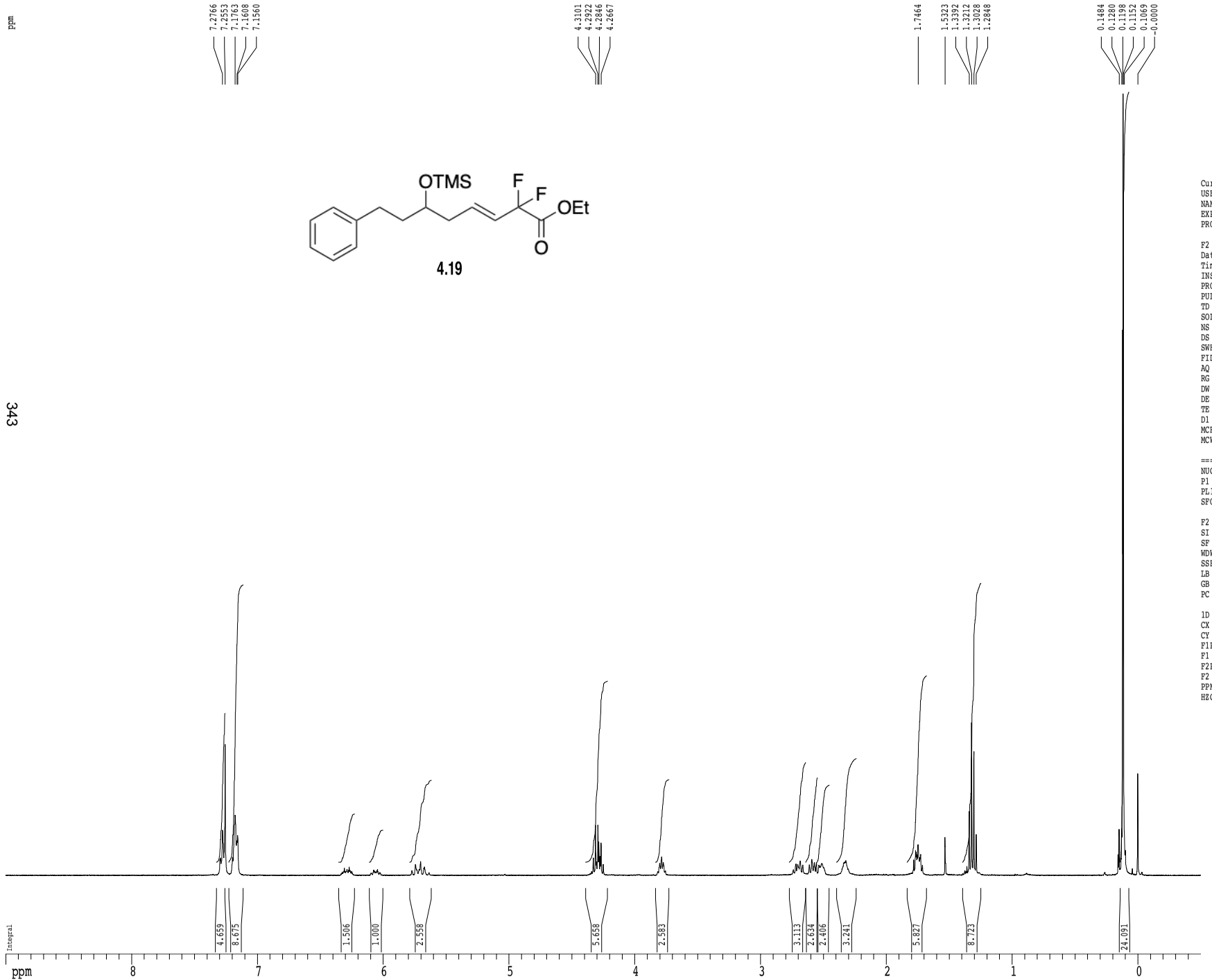
F2 - Acquisition Parameters
Date_ 20200715
Time 10.35
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 128
DW 78.000 usec
DE 4.50 usec
TE 298.1 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 65536
SF 400.1300288 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

1H spectrum



343

Current Data Parameters
USER sanforda
NAME ABS-3-187
EXPNO 1
PROCNO 1

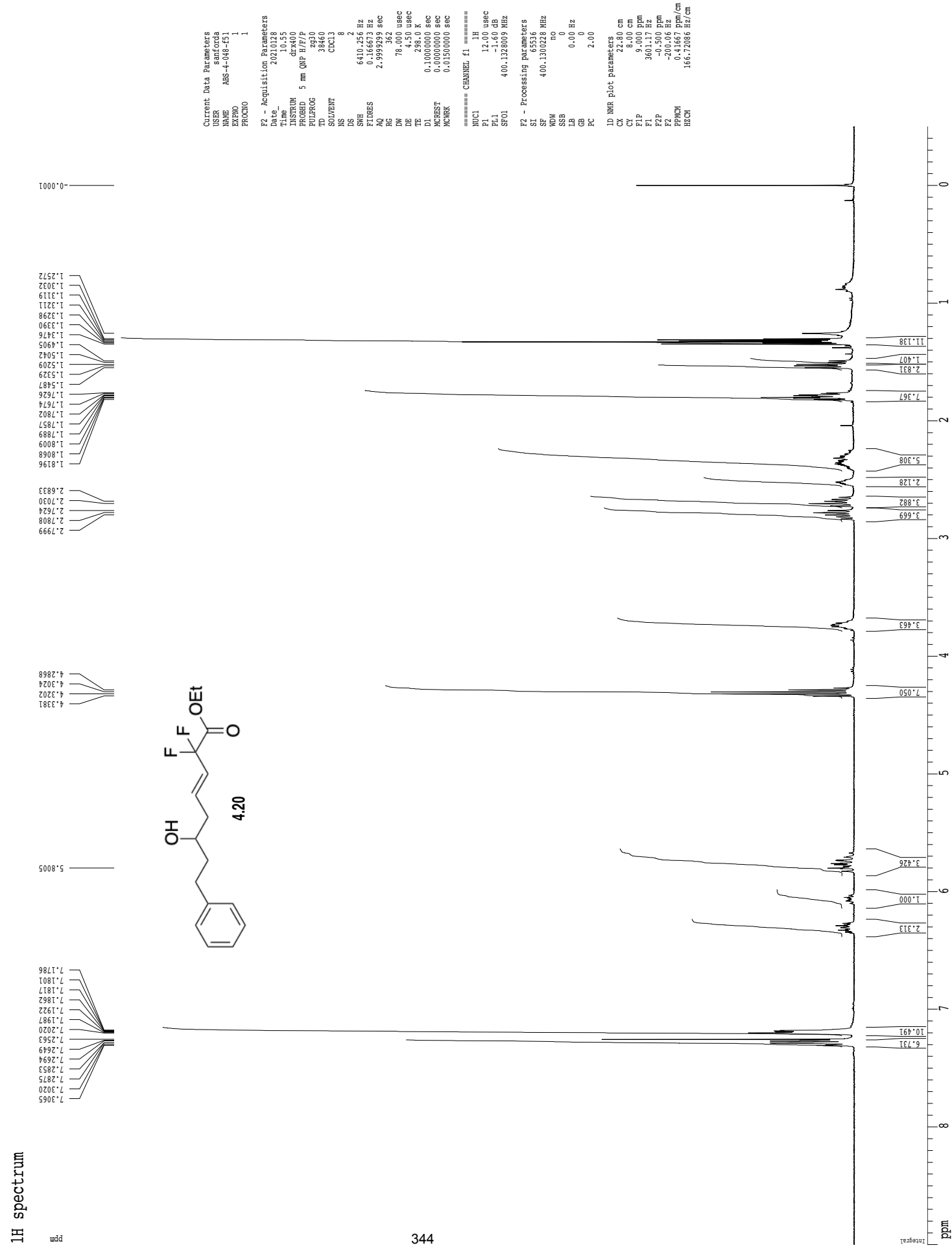
F2 - Acquisition Parameters
Date_ 20200717
Time 13.06
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.097813 Hz
AQ 5.1118579 sec
RG 322.5
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======= CHANNEL f1 =======
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz

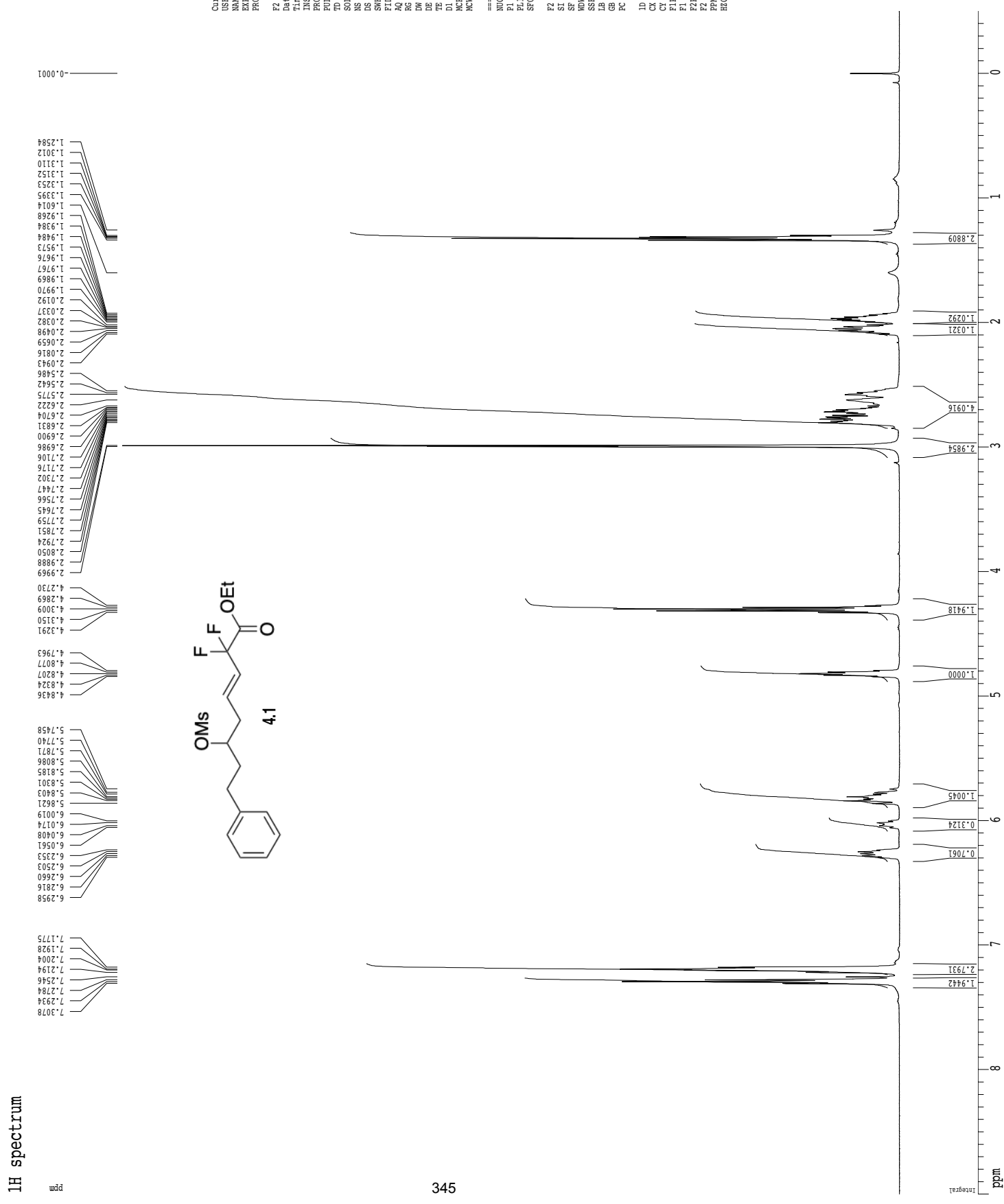
F2 - Processing parameters
SI 65536
SF 400.1300233 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm

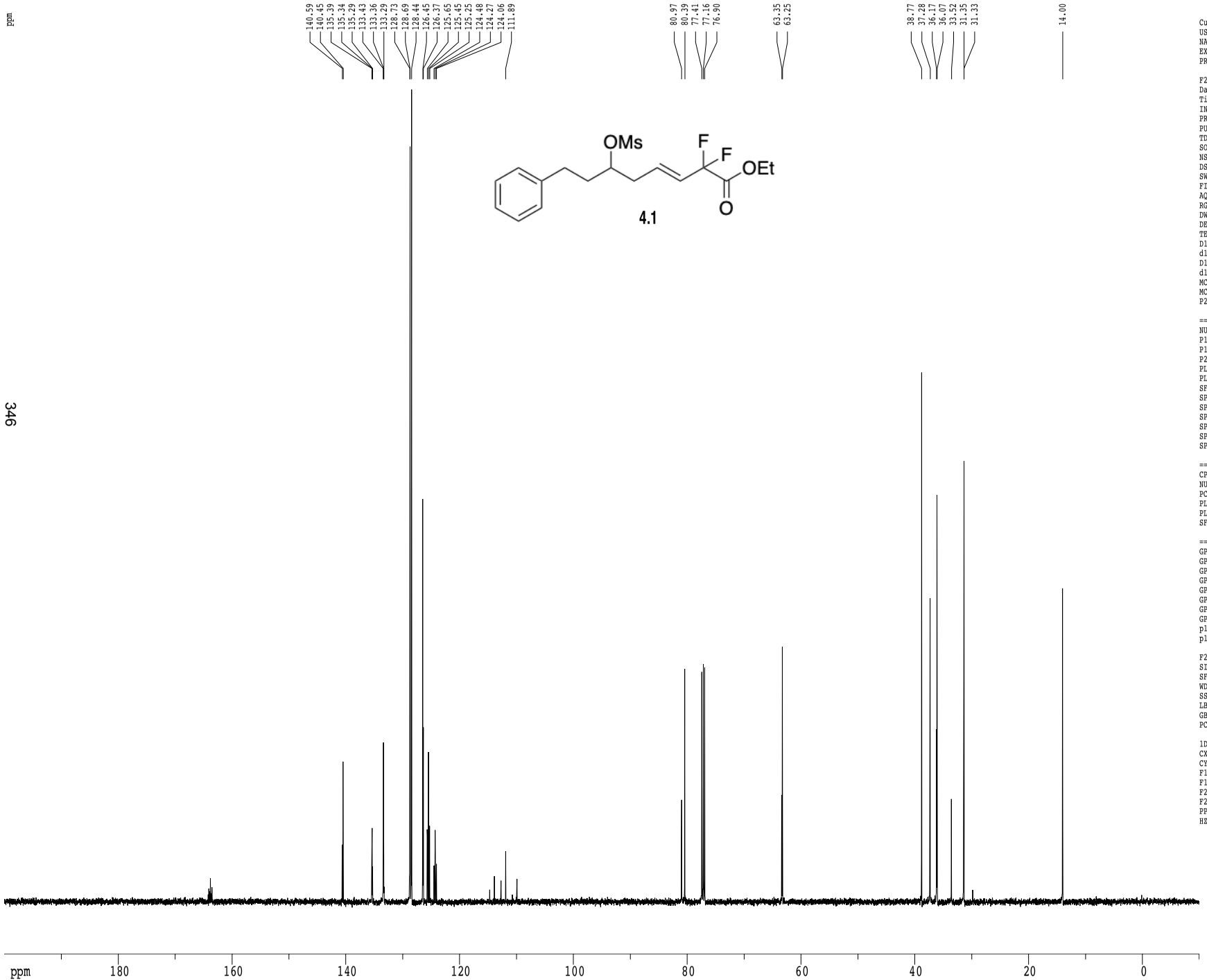
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-4-049-f51
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210128
Time_ 10.55
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 362
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.60 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300228 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 8.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
F
F
OEt
O
4.20
ppm
Integral
ppm

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-3-303-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201214
Time_ 16.56
INSTRUM CTYo500
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 48074
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.166677 Hz
AQ 2.9998677 sec
RG 5
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.75 usec
PL1 1.60 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200337 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 4501.98 Hz
F2P -0.500 ppm
F2 -250.11 Hz
PPMCM 0.41667 ppm/cm
HZCM 208.42502 Hz/cm
F
F
OEt
O
OMs
4.1
ppm
Integral
2.8809
1.0292
1.0321
4.0916
2.9854
1.9418
1.0000
1.0045
0.3124
0.7061
2.7931
1.9442

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



Current Data Parameters
USER sanforda
NAME ABS-3-303-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201214
Time 16.58
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 336
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 6502
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 37.70 usec

======== CHANNEL f1 ========
NUC1 13C
P1 18.85 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 1.55 dB
SP4 1.55 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

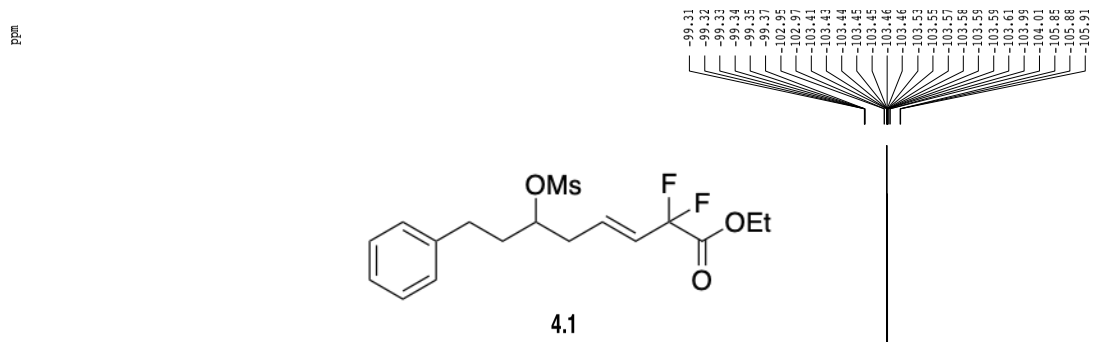
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 22.00 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.65 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

19F spectrum



4.1

Current Data Parameters
USER sanforda
NAME ABS-4-050-f
EXPNO 1
PROCNO 1

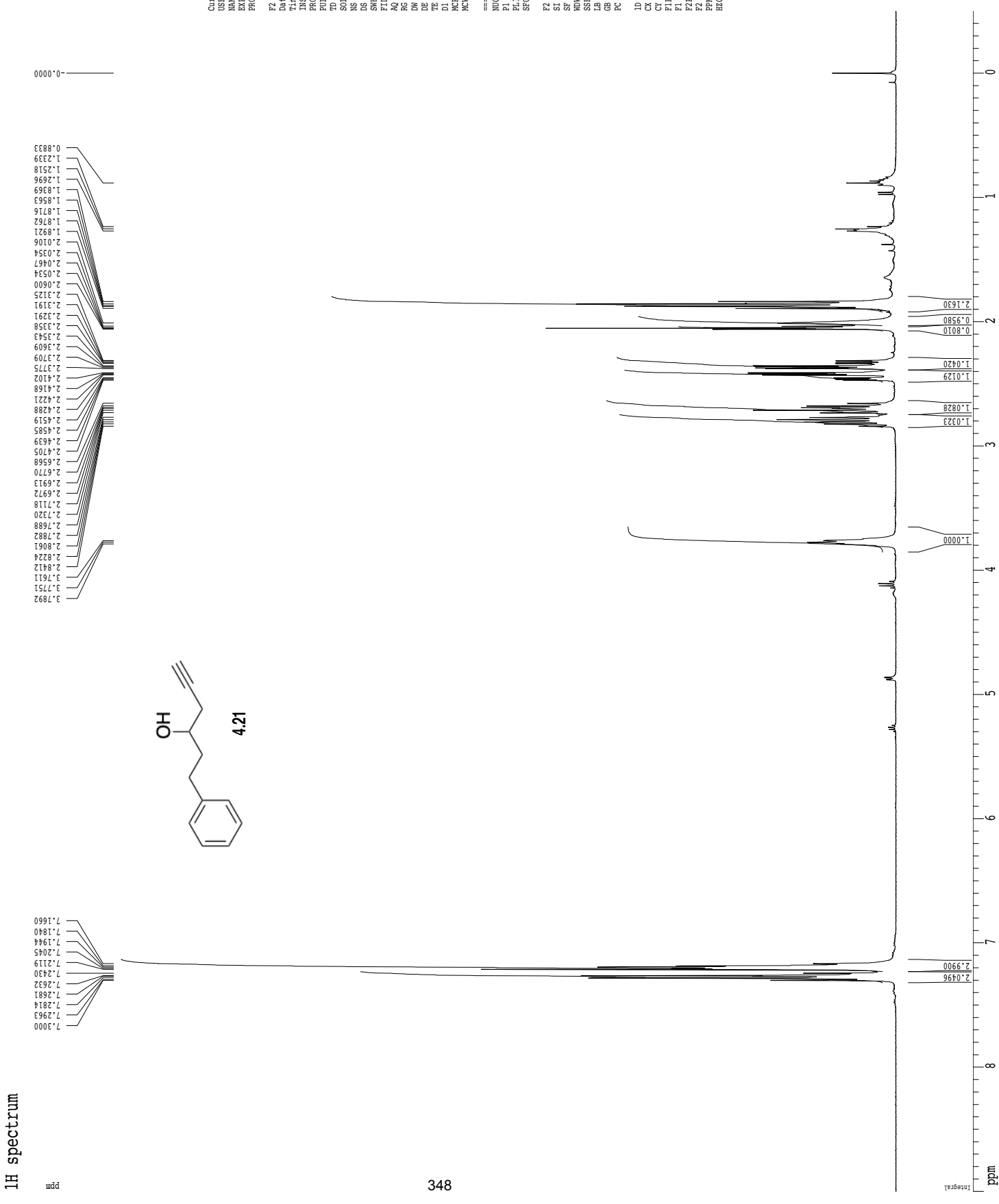
F2 - Acquisition Parameters
Date_ 20210212
Time 12.39
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgflqn30
TD 131072
SOLVENT CDCl3
NS 16
DS 2
SWH 178571.422 Hz
FIDRES 1.362392 Hz
AQ 0.3670516 sec
RG 575
DW 2.800 usec
DE 18.00 usec
TE 298.2 K
D1 3.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 564.6299196 MHz
NUC1 19F
P1 18.25 usec

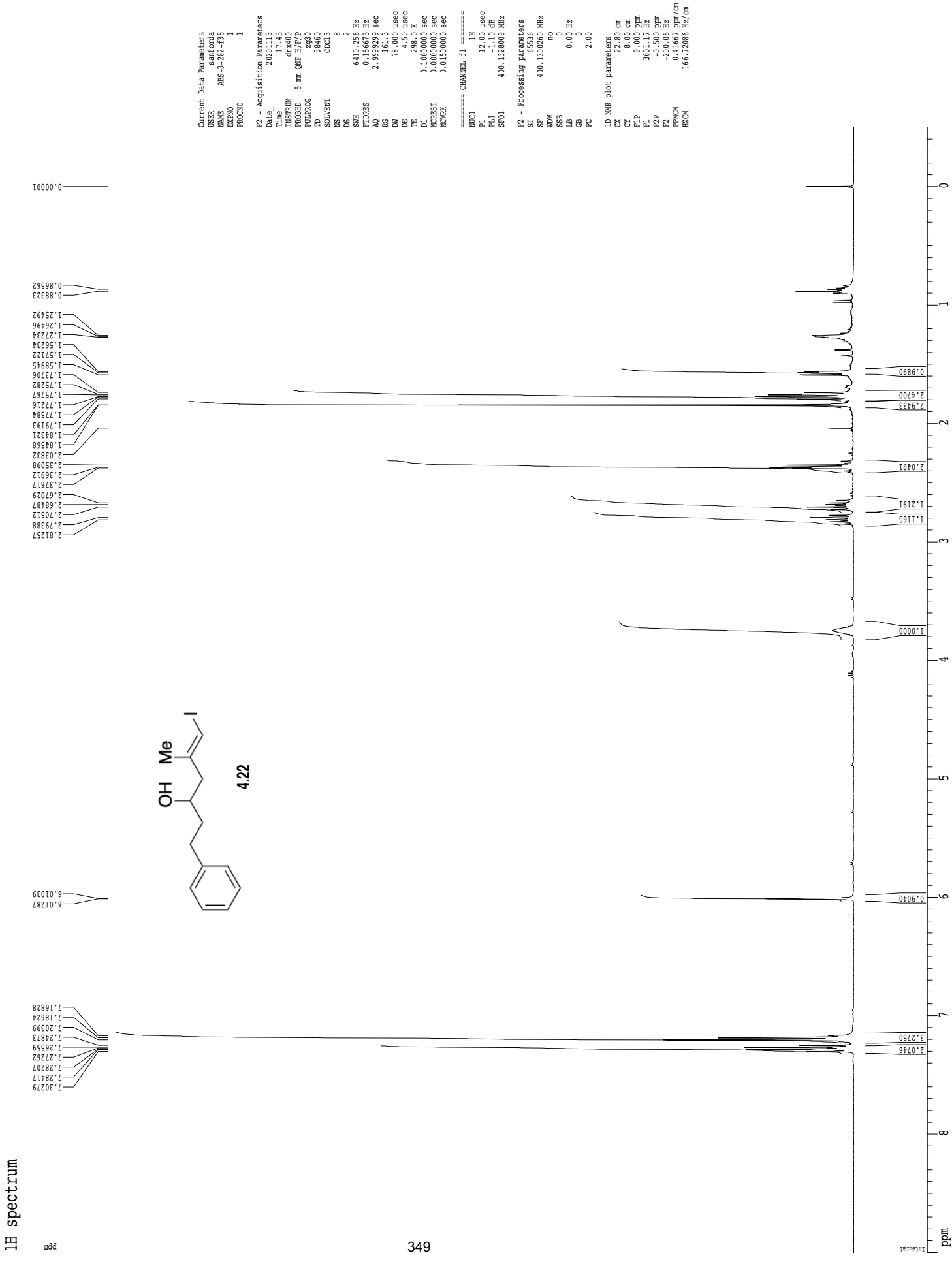
F2 - Processing parameters
SI 131072
SF 564.6863858 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 58.120 ppm
F1 32819.54 Hz
F2P -258.111 ppm
F2 -145751.91 Hz
PPMCM 13.86979 ppm/cm
HZCM 7832.08105 Hz/cm

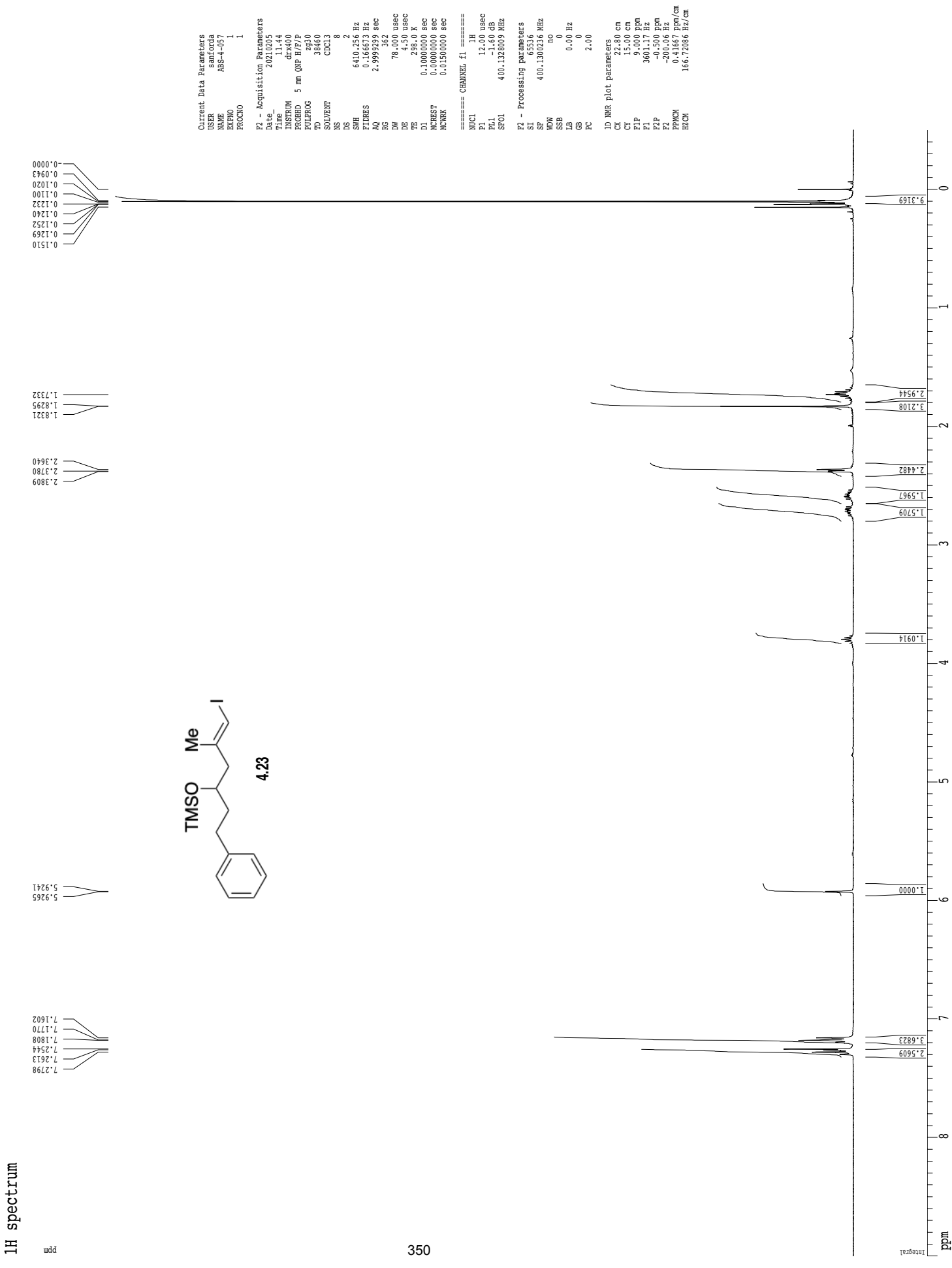
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-3-279-f50
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201110
Time_ 14.36
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 114
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300282 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 8.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
4.21
ppm
Integral

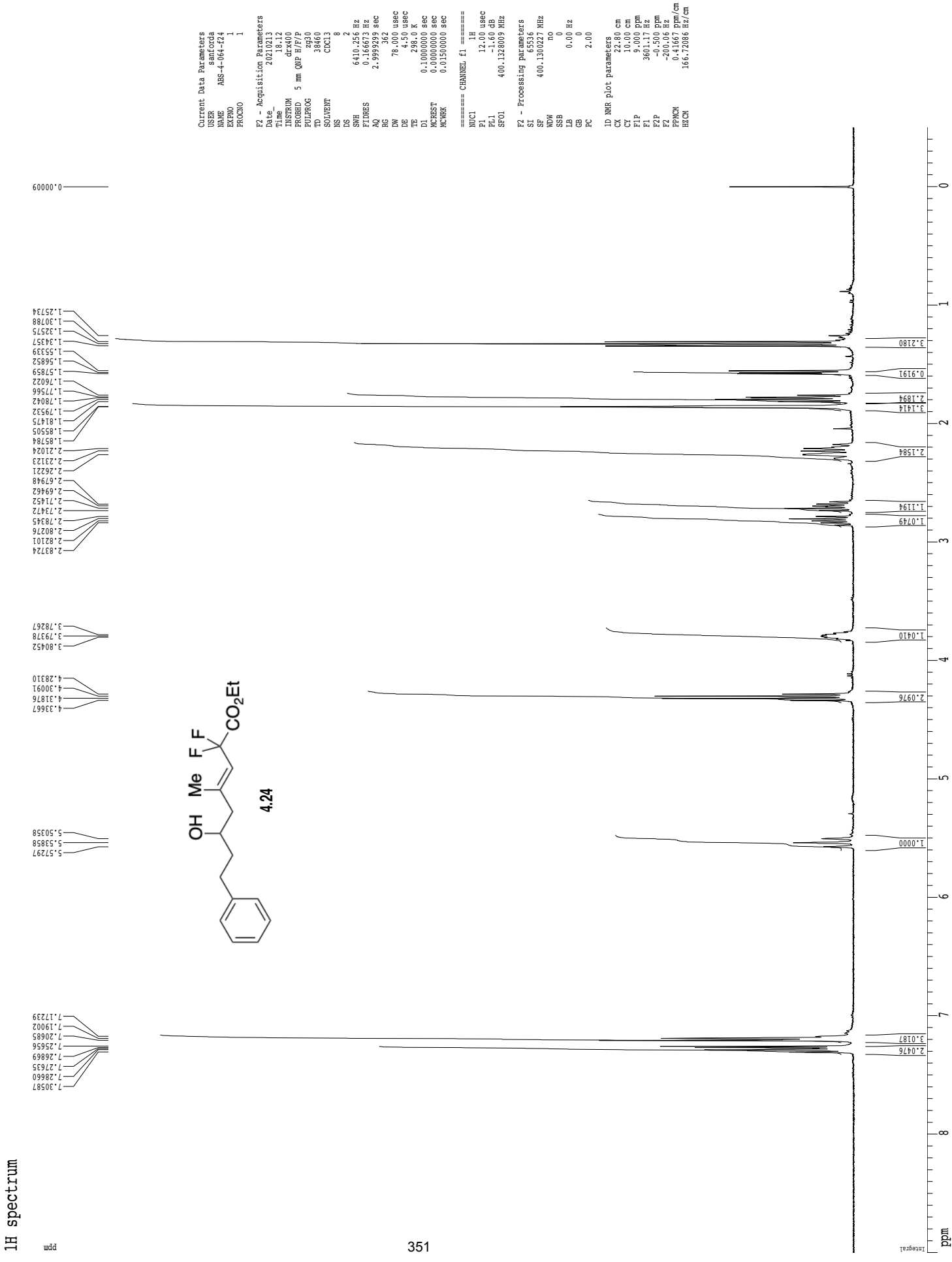
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-3-282-f38
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201113
Time_ 17.45
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 161.3
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.10 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300260 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 8.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH
Me
I
4.22
ppm
Integral

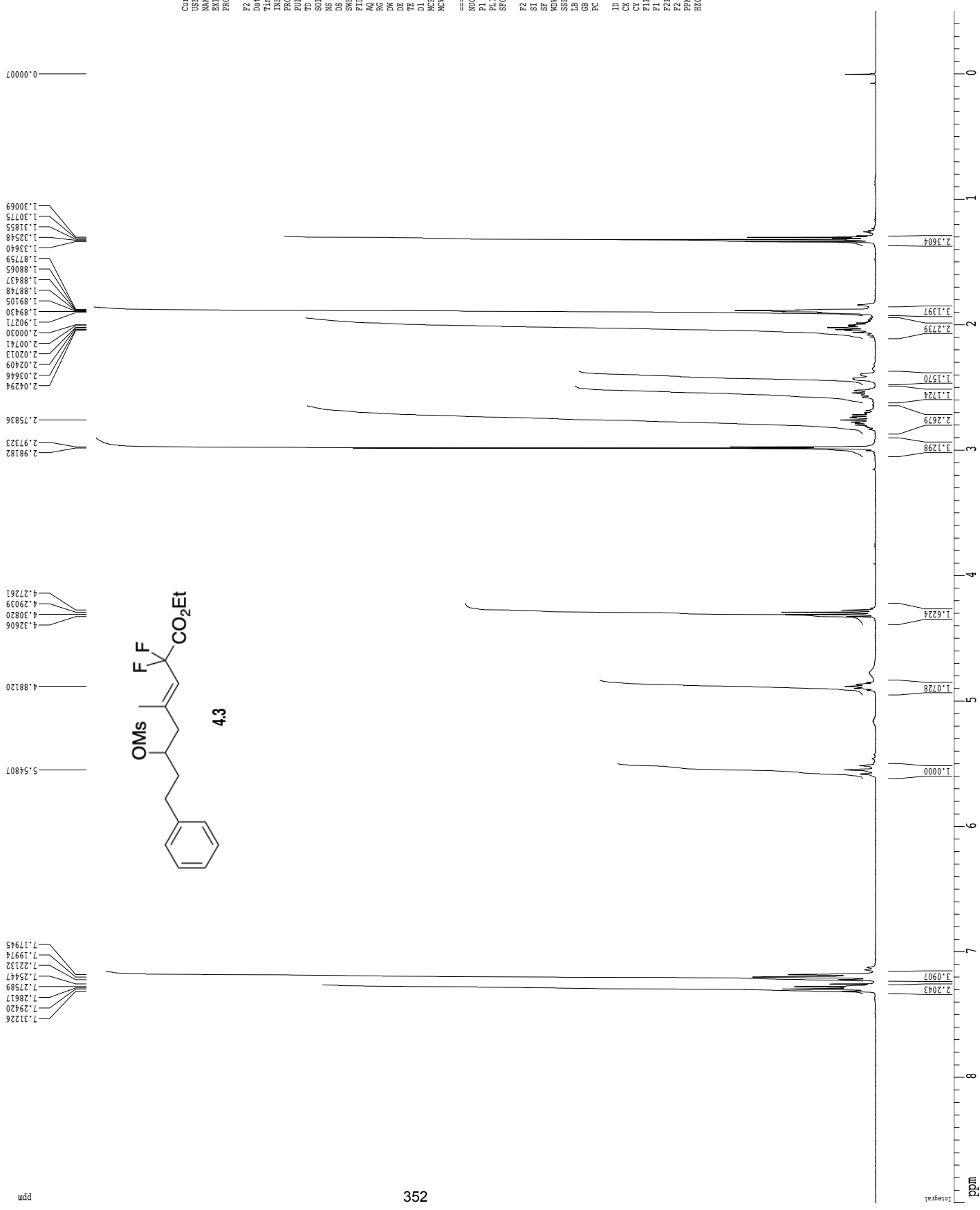
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-4-057
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210205
Time_ 11.44
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 362
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.60 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300236 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.0000
0.0943
0.1020
0.1100
0.1232
0.1240
0.1252
0.1269
0.1510
1.7332
1.8295
1.8321
2.3640
2.3780
2.3809
5.9241
5.9265
7.1602
7.1770
7.1808
7.2544
7.2613
7.2798
9.3169
2.9544
3.2108
2.4482
1.5967
1.5709
1.0914
1.0000
3.6823
2.5609
TMSO
Me
I
4.23
ppm
Integral

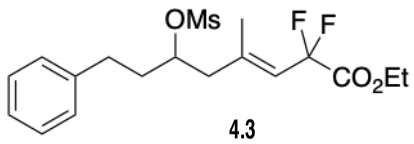
1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-4-064-F24
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210213
Time_ 18.12
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 362
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.60 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300227 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 10.00 cm
F1P 9.000 ppm
F1 3601.17 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
OH Me F F CO2Et
4.24
ppm
Integral

1H spectrum


Current Data Parameters
USER sanforda
NAME ABS-3-397-proton
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20210213
Time_ 11.45
INSTRUM drx400
PROBHD 5 mm QNP H/F/P
PULPROG zg30
TD 38460
SOLVENT CDCl3
NS 8
DS 2
SWH 6410.256 Hz
FIDRES 0.166673 Hz
AQ 2.9999299 sec
RG 114
DW 78.000 usec
DE 4.50 usec
TE 298.0 K
D1 0.10000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 -1.60 dB
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 65536
SF 400.1300233 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 10.00 cm
F1P 9.000 ppm
F1 3601.117 Hz
F2P -0.500 ppm
F2 -200.06 Hz
PPMCM 0.41667 ppm/cm
HZCM 166.72086 Hz/cm
0.00007
1.30069
1.30775
1.31855
1.32548
1.33640
1.87759
1.88065
1.88437
1.88748
1.89105
1.89430
1.90271
2.00030
2.00741
2.02013
2.02409
2.03646
2.04294
2.75836
2.97323
2.98182
4.22606
4.23082
4.29039
4.27261
4.88120
5.54807
7.17945
7.19974
7.22132
7.25447
7.27589
7.28617
7.29420
7.31226
2.3604
3.1397
2.2739
1.1570
1.1724
2.2679
3.1298
1.6224
1.0728
1.0000
3.0907
2.2043
OMs
F F
CO2Et
4.3
ppm
Integral

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



4.3

353

Current Data Parameters
USER sanforda
NAME ABS-3-297-carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210213
Time 12.35
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG SpinEchopg30gp2.prd
TD 65536
SOLVENT CDCl3
NS 152
DS 16
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2580.3
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.25000000 sec
d11 0.03000000 sec
D16 0.00020000 sec
d17 0.00019600 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
P2 37.70 usec

======== CHANNEL f1 ========
NUC1 13C
P1 18.85 usec
P12 2000.00 usec
P20 500.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SP2 1.55 dB
SP4 1.55 dB
SPNAM2 Crp60comp.4
SPNAM4 Crp60,0.5,20.1
SPOFF2 0.00 Hz
SPOFF4 0.00 Hz

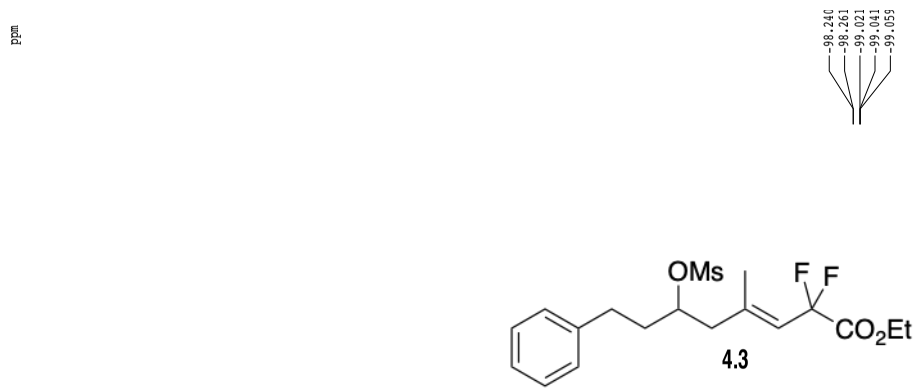
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 1.60 dB
PL12 22.00 dB
SFO2 500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 30.00 %
GPZ2 50.00 %
p15 500.00 usec
p16 1000.00 usec

F2 - Processing parameters
SI 65536
SF 125.7804103 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
CY 15.00 cm
F1P 200.000 ppm
F1 25156.08 Hz
F2P -10.000 ppm
F2 -1257.80 Hz
PPMCM 9.21053 ppm/cm
HZCM 1158.50378 Hz/cm

19F spectrum



Current Data Parameters
USER sanforda
NAME ABS-3-297-f
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210213
Time 12.48
INSTRUM av600
PROBHD 5 mm CPBBO BB-
PULPROG zgflqn30
TD 131072
SOLVENT CDCl3
NS 16
DS 2
SWH 178571.422 Hz
FIDRES 1.362392 Hz
AQ 0.3670516 sec
RG 575
DW 2.800 usec
DE 18.00 usec
TE 298.1 K
D1 3.00000000 sec
TD0 1

======= CHANNEL f1 =======
SFO1 564.6299196 MHz
NUC1 19F
P1 18.25 usec

F2 - Processing parameters
SI 131072
SF 564.6863858 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
CY 10.00 cm
F1P 0.000 ppm
F1 0.00 Hz
F2P -200.000 ppm
F2 -112937.28 Hz
PPMCM 8.77193 ppm/cm
HZCM 4953.38965 Hz/cm