Stereoselective Synthesis of High-Value Alkenes through Catalytic Olefin Metathesis:

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STEREOSELECTIVE SYNTHESIS OF HIGH-VALUE ALKENES THROUGH CATALYTIC OLEFIN METATHESIS

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Abstract

■ ***Chapter 1. Development of Ru-Based Catechothiolate Complexes for Z-selective Ring-Opening/Cross-Metathesis and Cross-Metathesis***

We have developed a broadly applicable Ru-catalyzed protocol for *Z*-selective ring-opening/cross-metathesis (ROCM). Transformations are promoted by 2.0–5.0 mol % of a Ru-based catechothiolate complex, furnishing products in up to 97 % yield and >98:2 *Z*:*E* ratio. The *Z*-selective ROCM processes are found to be compatible with terminal alkenes of different sizes that include the first examples involving heteroaryl olefins, 1,3-dienes, and O- and S-substituted alkenes as well as allylic and homoallylic alcohols. Reactions with an enantioenriched α-substituted allylic alcohol are shown to afford congested *Z*-olefins with high diastereoselectivity. The insights gained from these investigations provided the impetus to develop electronically modified Ru catechothiolate catalysts that are readily accessible from a commercially available dichloro-Ru carbene and an easily generated air-stable zinc catechothiolate. The new complex is effective in catalyzing *Z*-selective cross-metathesis (CM) of terminal alkenes and inexpensive *Z*-2-butene-1,4-diol to directly generate linear *Z*-allylic alcohols, including those that bear a hindered

neighboring substituent or reactive functionalities such as a phenol, an aldehyde or a carboxylic acid. Transformations typically proceed with 5.0 mol % of the catalyst within 4–8 hours under ambient conditions, and products are obtained in up to 80% yield and 98:2 *Z*:*E* selectivity. Utility is highlighted through synthesis of a molecular fragment en route to anti-tumor agent neopeltolide and in a single-step stereoselective gram-scale conversion of renewable feedstock to synthetically valuable *Z*-allylic alcohols.

■ ***Chapter 2. Kinetically Controlled Z- and E-Selective Cross-Metathesis to Access 1,2-Disubstituted Alkenyl Halides***

We have discovered that previously unknown halo-substituted molybdenum alkylidenes are capable of participating in highly efficient olefin metathesis reactions that afford linear 1,2-disubstituted *Z*-alkenyl halides. Transformations are promoted by 1.0–10.0 mol % of a Mo-based pentafluorophenylimido monoaryloxide pyrrolide (MAP) complex that is generated *in situ* and used with unpurified, commercially available and easy-to-handle liquid 1,2-dihaloethene reagents, delivering a myriad of alkenyl chlorides, bromides and fluorides in up to 91% yield and >98:2 *Z*:*E* ratio. Through mechanism-based modification of the aryloxide ligand, a newly synthesized Mo-based MAP complex was shown to be effective in promoting kinetically controlled *E*-selective CM to access the corresponding thermodynamically less favored *E*-isomers of alkenyl chlorides and fluorides. Reactions typically proceed within 4 hours at ambient temperature with 1.0–5.0 mol % of the catalyst, which may be utilized in the form of air- and moisture-stable paraffin pellets. Utility of the aforementioned protocols is demonstrated through

preparation of biologically active compounds and related analogues as well as late-stage site- and stereoselective fluorination of complex organic molecules.

■ ***Chapter 3. Molybdenum-Based Chloride Catalysts for Z-Selective Olefin Metathesis***

A new class of Mo-based monoaryloxide chloride (MAC) complexes for *Z*-selective olefin metathesis has been developed. The MAC catalysts are capable of promoting CM with commercially available, inexpensive and typically inert *Z*-1,1,1,4,4,4-hexafluoro-2-butene to furnish the higher-energy *Z*-isomers of trifluoromethyl-substituted alkenes in up to 95% yield and >98:2 *Z*:*E* selectivity. Furthermore, otherwise inefficient and non-stereoselective transformations with *Z*-1,2-dichloroethene and 1,2-dibromoethene can be accomplished with appreciably improved efficiency and *Z*-selectivity. The method enables synthesis of biologically active compounds and CF_3-analogues of medicinally relevant molecules. Density functional theory (DFT) calculations shed light on the origins of the activity and selectivity levels observed in these transformations.

■ ***Chapter 4. Stereoselective Synthesis of Z- and E-Trisubstituted Alkenes by Merging Cross-Coupling with Cross-Metathesis***

We have discovered that challenging acyclic *E*- and *Z*-trisubstituted alkenes, particularly alkenyl chlorides and bromides, can be accessed efficiently and in high stereoisomeric purity (up to >98% *E* and 95% *Z*) through a sequence involving catalytic cross-coupling followed by stereoretentive CM promoted by Mo-based catalysts. Initial exploratory studies with 1,1-disubstiuted alkenes revealed crucial mechanistic features of the transformations that led us to utilize readily accessible trisubstituted olefins as substrates,

in combination with commercially available 1,2-dihaloethenes as cross-partners for CM. Applications to synthesis of biologically active compounds and synthetic precursors underscore utility. The stereoretentive transformations may be extended to trisubstituted non-halogenated alkenes such as aliphatic olefins.

Acknowledgements

My graduate career in the States has been an incredible journey, a journey that left lasting memories through the people I met and interacted with as well as the activities I participated. First, I would like to express my sincere gratitude to Professor Amir H. Hoveyda for accepting me as part of his group. I remember when I met him in late Summer of 2012 shortly after arriving in Boston. I had requested to work on copper catalysis, one of the areas of research that the group is known for which I was initially interested. Professor Hoveyda insisted me to work on catalytic olefin metathesis, and told me to trust his judgment in a calm, almost prophetic fashion. In retrospect, even I could not have predicted myself to be involved in the discovery and development of new transformations in olefin metathesis that culminated in a fruitful haul of publications in top journals. During the last 5 years, I was given ample opportunities to partake in various research conferences and presentations and collaborate with distinguished group members to tackle compelling problems in Chemistry. I was especially honored to be selected as the recipient of the 2016–2017 Bristol-Myers Squibb Graduate Fellowship on the blessing of Professor Hoveyda. He has instilled in me a sense of responsibility as a scientist in doing "what you have to" and not "what you can do", something that I will always adhere to in my future career as an aspiring academic. I owe him a great deal. I would also like to take this opportunity to thank Professor James P. Morken and Professor Masayuki Wasa for kindly agreeing to serve as members of my doctoral defense committee, spending time to read my dissertation and giving me valuable suggestions.

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who is now a Professor in China. He was my mentor in Professor Chan's group and was instrumental in teaching me fundamental skills as a laboratory researcher. In addition, I would like to acknowledge Professors Teck Peng Loh and Xuewei Liu for inspiring me in Chemistry and providing me recommendation letters for my graduate school applications.

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A successful graduate career is not possible without friends who supported me through the years. My first friends/classmates when I officially began graduate school in Fall 2012 were KyungA (Stella) Lee and Jaehee Lee. It has been a blessing to meet these amazing people and I thank them for their support and friendship through these years. I would also like to show my appreciation to Thach, Farid Van Der Mei, Ying Shi and Yucheng Mu, friends whom have helped me in one way or another. To all my friends and colleagues from the Hoveyda group, I wish them the best in their future endeavors.

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As I embark on my independent academic career hopefully in the near future, I look forward to continue contributing to scientific research and educating the next generation of budding chemists to honor the legacy of Merkert Chemistry.

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Chapter One

Development of Ru-Based Catechothiolate Complexes for Z-selective Ring-Opening/Cross-Metathesis and Cross-Metathesis

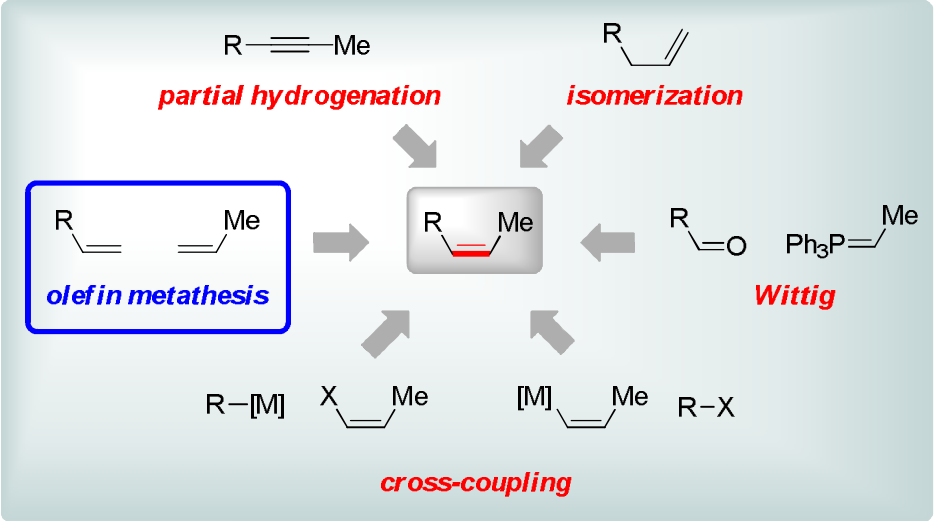
1.1. Introduction

Development of efficient and reliable protocols to construct stereochemically defined C=C double bonds has important implications in chemical synthesis, since such functionalities are prevalent in biologically active compounds and serve as versatile precursors for myriad of chemical transformations.[1] In this context, methods that preferentially furnish *Z*-alkenes[2] selectively are highly desirable but less established than those for the *E*-alkenes due to complicating issues of thermodynamics that tend to favor the lower-energy *E*-isomers in many instances. Nonetheless, the ingenuity of chemists has led to the introduction of several notable strategies that reliably afford *cis*-olefins over the years (Scheme 1.1).[2, 3] Despite these advances, a number of significant shortcomings still remains. For example, stoichiometric waste generation and poor atom economy are issues that plague *Z*-selective Wittig[3a] and Still-Gennari[3b] transformations. Partial hydrogenation of alkynes[3c] sometimes suffers from over-reduction whereas terminal alkene isomerization strategies[3d,e] are limited in scope and often result in

(1) Negishi, E.-i.; Huang, Z.; Wang, G.; Mohan, S.; Wang, C.; Hattori, H. *Acc. Chem. Res.* **2008**, *41*, 1474–1485.
(2) For a review on synthesis of *Z*-alkenes, see: Siau, W.-Y.; Zhang, Y.; Zhao, Y. *Top. Curr. Chem.* **2012**, *327*, 33–58.
(3) (a) For a representative report, see: Bergelson, L. D.; Shemyakin, M. M. *Tetrahedron* **1963**, *19*, 149–159. (b) For a representative report, see: Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405–4408. (c) For a representative report, see: Lindlar, H.; Dubuis, R. *Org. Synth.* **1966**, *46*, 89. For representative reports on olefin isomerization to obtain *Z*-alkenes, see: (d) Chen, C.; Dugan, T. R.; Brennessel, W. W.; Weix, D. J.; Holland, P. L. *J. Am. Chem. Soc.* **2014**, *136*, 945–955. (e) Zhuo, L.-G.; Yao, Z.-K.; Yu, Z.-X. *Org. Lett.* **2013**, *15*, 4634–4637. (f) Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules*, 3rd ed.; University Science Books: Sausalito, CA, **2009**.

difficult-to-separate olefin mixtures. Catalytic cross-coupling to obtain *Z*-olefins entails the use of *Z*-alkenyl halides or *Z*-alkenyl organometallic reagents as precursors that can be challenging to prepare.[3f]

Scheme 1.1. Common Strategies to Access *Z*-Alkenes.

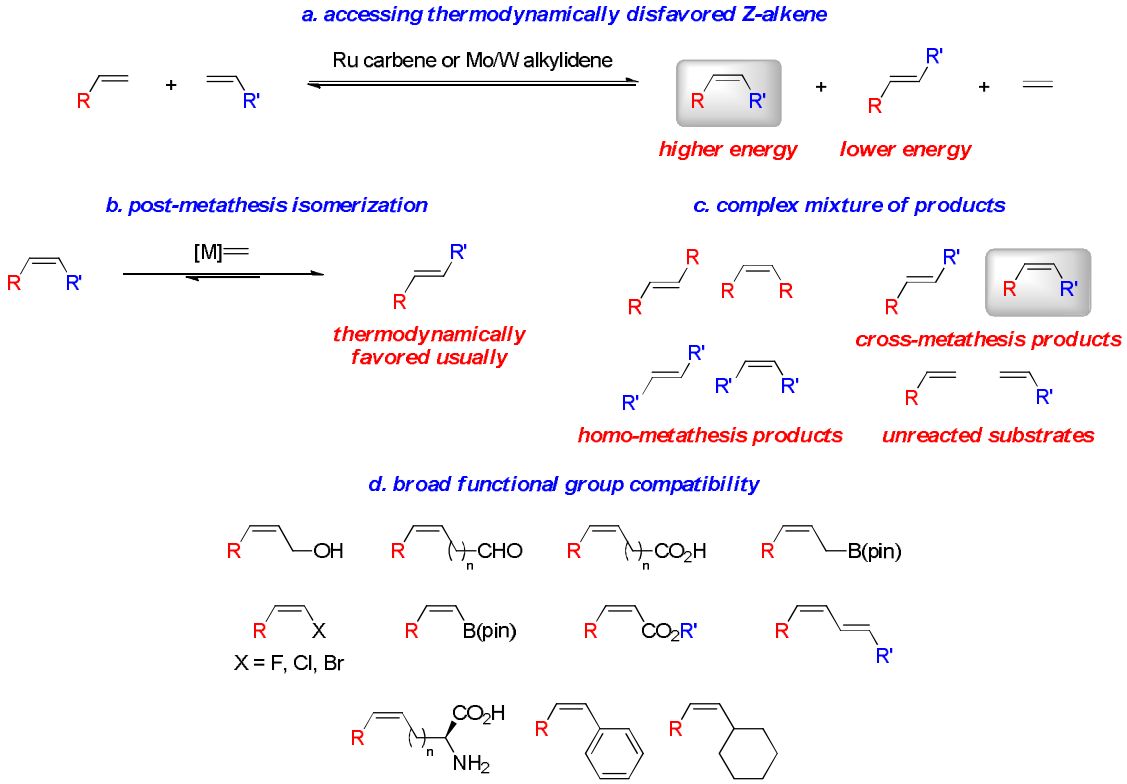


Catalytic olefin metathesis (OM) represents one of the most attractive tools for stereoselective preparation of C=C double bonds.[4] This process offers a distinct synthesis approach by utilizing two olefins as substrates, available in abundant quantities as by-products of petroleum purification or readily accessed by a plethora of methods, to generate a more functionalized alkene product with defined geometry. This unique nature of OM coupled with minimal waste generation and broad functional group compatibility has resulted in extensive applications in natural product synthesis and materials

(4) For selected reviews on stereoselective olefin metathesis, see: (a) Hoveyda, A. H. *J. Org. Chem.* **2014**, *79*, 4763−4792. (b) "Catalyst-Controlled Stereoselective Olefin Metathesis Reactions," Hoveyda, A. H.; Khan, R. K. M.; Torker, S.; Malcolmson, S. J.; in *Handbook of Olefin Metathesis*; Grubbs, R. H.; O'Leary, D. Eds; VCH–Wiley, **2014**, in press. (c) Fürstner, A. *Science* **2013**, *341*, 1357–1344. (d) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243–251.

science.[4,5] To achieve both high efficiency and *Z* selectivity in catalyst-controlled OM, however, a number of challenges have to be overcome (Scheme 1.2).

Scheme 1.2. Challenges in Catalyst-Controlled *Z*-Selective Olefin Metathesis.



The inherent reversibility of OM means that any product that is generated can revert back to the starting alkenes. Since the product olefin can potentially re-enter the catalytic cycle, any kinetic selectivity that is initially obtained can be eroded. A competent *Z*-selective catalyst must be capable of delivering the thermodynamically less favored (in most instances) *Z*-stereoisomer (vs. lower-energy *E*-alkene) efficiently without engendering significant erosion of *Z* selectivity through post-OM isomerization.[6]

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(5) (a) Fürstner, A. *Angew. Chem. Int. Ed.* **2014**, *53*, 8587–8598. (b) *Metathesis in Natural Product Synthesis: Strategies, Substrates and Catalysts*; Cossy, J.; Arseniyadis, S.; Meyer, C.; Grubbs, R. H. Eds.; Wiley–VCH, Weinheim, Germany, **2010**. (c) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem. Int. Ed.* **2005**, *44*, 4490–4527.

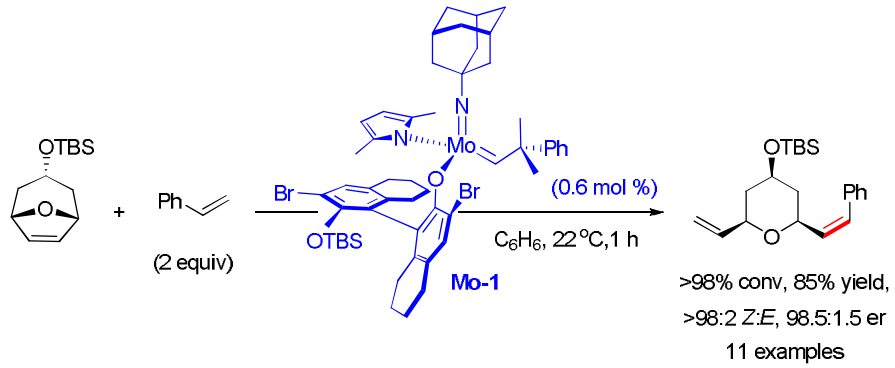
(6) For the importance of interplay between kinetic *Z* selectivity and post-metathesis isomerization, see: (a) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, 471, 461–466. (b)

Furthermore, it has to do so without promoting significant formation of undesired homocoupling by-products, especially in cross-metathesis (CM) and ring-closing metathesis (RCM). An added challenge is that the OM catalyst has to exhibit high functional group tolerance for broad applicability in chemical synthesis.

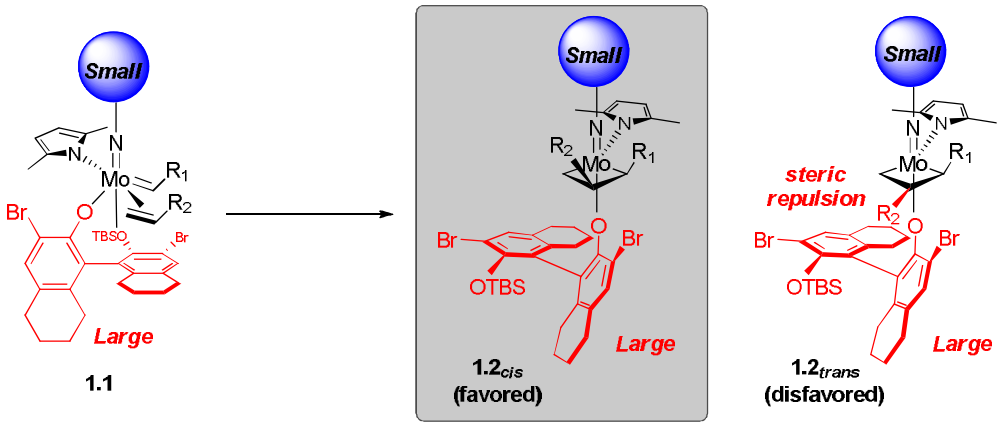
1.2. Ru-Based Catechothiolates for Z Selectivity in Olefin Metathesis

1.2.1. The Advent of Z-Selective Olefin Metathesis

Scheme 1.3.1 The First Case of *Z*-Selective Olefin Metathesis Involving a Mo-Based Alkylidene.



Scheme 1.3.2 Origin of *Z*-Selectivity Based on Ligand Steric Factors.



Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88–93. (c) Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740–5745.

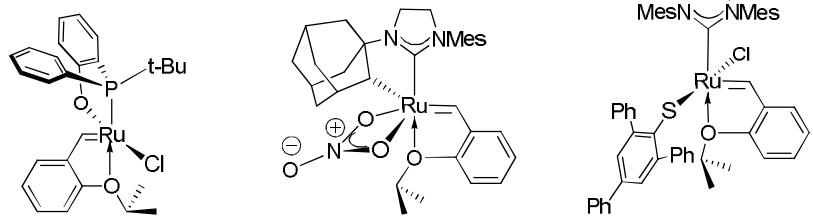
The first examples of kinetically controlled *Z*-selective OM were disclosed in 2009,[7] wherein a high-oxidation-state stereogenic-at-Mo imido monoaryloxide pyrrolide (MAP) complex (**Mo-1**) was shown to promote efficient and *Z*-selective ring-opening/cross-metathesis (ROCM) with strained oxabicyclic alkenes and styrenes (Scheme 1.3.1). The mechanistic principle for *Z* selectivity can be rationalized in Scheme 1.3.2. The incoming olefin approaches *trans* to the pyrrolide (strong σ-donor)[8] due to its ability to stabilize the vacant coordination site to afford complex **1.1**. The high *Z* selectivity originates from the size difference between the freely rotating sizeable aryloxide and the (comparatively) smaller imido ligand, which favors formation of metallacyclobutane $\mathbf{1.2}_{cis}$ wherein R^1 and R^2 are pointing away from the aryloxide to minimize steric repulsion (vs. $\mathbf{1.2}_{trans}$ wherein one R group has severe steric clash with aryloxide). Subsequent [2+2] cycloreversion of $\mathbf{1.2}_{cis}$ gives the desired *Z*-olefin product. *Z*-Selective ring-opening metathesis polymerization (ROMP),[9] homo-metathesis,[10] CM[11] and macrocyclic RCM[12] transformations catalyzed by related Mo- and W-based MAP complexes were subsequently reported.

The design principles from *Z*-selective MAP alkylidenes inspired efforts to develop low-oxidation-state Ru carbenes as viable catalysts for *Z*-selective OM. The

(7) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844–3845.
(8) (a) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129*, 8207–8216. (b) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H *J. Am. Chem. Soc.* **2009**, *131*, 58–59.
(9) For example, see: Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962–7963.
(10) For example, see: Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630–16631.
(11) For example, see: Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, 471, 461–466.
(12) For example, see: Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88–93.

impetus for such studies stemmed from the complementary[13] attributes of Ru carbenes (vs. Mo/W alkylidenes) which could potentially enhance the impact of *Z*-selective OM in chemical synthesis. Since 2010, different classes of *Z*-selective stereogenic-at-Ru catalysts have been developed (Scheme 1.4). These include complexes that bear a bidendate phosphine ligand such as **Ru-2**,[14] a bidendate *N*-heterocyclic carbene (NHC)-chelating ligand such as **Ru-3**[15] as well as Ru arylthiolates exemplified by **Ru-4**.[16]

Scheme 1.4. Previously Reported Ru Complexes That Could Promote *Z*-Selective Olefin Metathesis.



Ru-2 **Ru-3** **Ru-4**

Despite these advances, the reported Ru-based catalysts tend to suffer from limited substrate scope, poor efficiency and/or diminished stereoselectivity at high conversions. For instance, **Ru-2** and related analogues can promote co-polymerization of norbornene with cyclooctene but only up to 51% *Z* selectivity.[14] **Ru-4** has been shown to

(13) (a) Cortez, G. A.; Baxter, C. A.; Schrock, R. R.; Hoveyda, A. H. *Org. Lett.* **2007**, *9*, 2871–2874. (b) A. H. Hoveyda, A. R. Zhugralin, *Nature* **2007**, *450*, 243–251.
(14) Torker, S.; Müller, A.; Chen, P. *Angew. Chem. Int. Ed.* **2010**, *49*, 3762–3766.
(15) (a) Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8525–8527. (b) Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9686–9688. (c) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693–699. (d) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 2040–2043. (e) Marx, V. M.; Herbert, M. B.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 94–97. (f) Herbert, M. B.; Marx, V. M.; Pederson, R. L.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 310–314. (g) Rosebrugh, L. E.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 1276–1279. (h) Cannon, J. S.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 9001–9004. (i) Rosebrugh, L. E.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 10032–10035. (j) Chong, W.; Carlson, J. S.; Bedke, D. K.; Vanderwal, C. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 10052–10055. (k) Hartung, J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 10183–10185. (l) Quigley, B. L.; Grubbs, R. H. *Chem. Sci.* **2014**, *5*, 501–506. (m) Hartung, J.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2014**, *53*, 3885–3888. (n) Mangold, S. L.; O'Leary, D. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2014**, *136*, 12469–12478.
(16) (a) Occhipinti, G.; Hansen, F. R.; Törnroos, K. W.; Jensen, V. R. *J. Am. Chem. Soc.* **2013**, *135*, 3331–3334. (b) Occhipinti, G.; Koudriavtsev, V.; Törnroos, K. W.; Jensen, V. R. *Dalton Trans.* **2014**, *43*, 11106–11117.

promote *Z*-selective homocoupling of simple terminal alkenes such as allylbenzene (82% *Z* selectivity at 44% conversion),[16a] but stereoselectivity plunges as reaction progresses (45% *Z* selectivity at >98% conversion), presumably due to post-metathesis isomerization of the product.[6] Although **Ru-3** and its analogues have been demonstrated to be effective in a range of *Z*-selective OM transformations,[15] blatant shortcomings in functional group tolerance remain. Notably, the lack of reactivity with sterically encumbered alkenes like styrenes and those that carry important functionalities such as carboxylic acids,[15b,j] as well as the frequent need for alcohol protection especially with proximal hydroxyl groups[15k,n] limit the general applicability of these catalysts. In this regard, a more general, readily accessible and modifiable class of Ru carbenes that is capable of promoting highly efficient and *Z*-selective OM with broad functional group compatibility remains to be conceived.

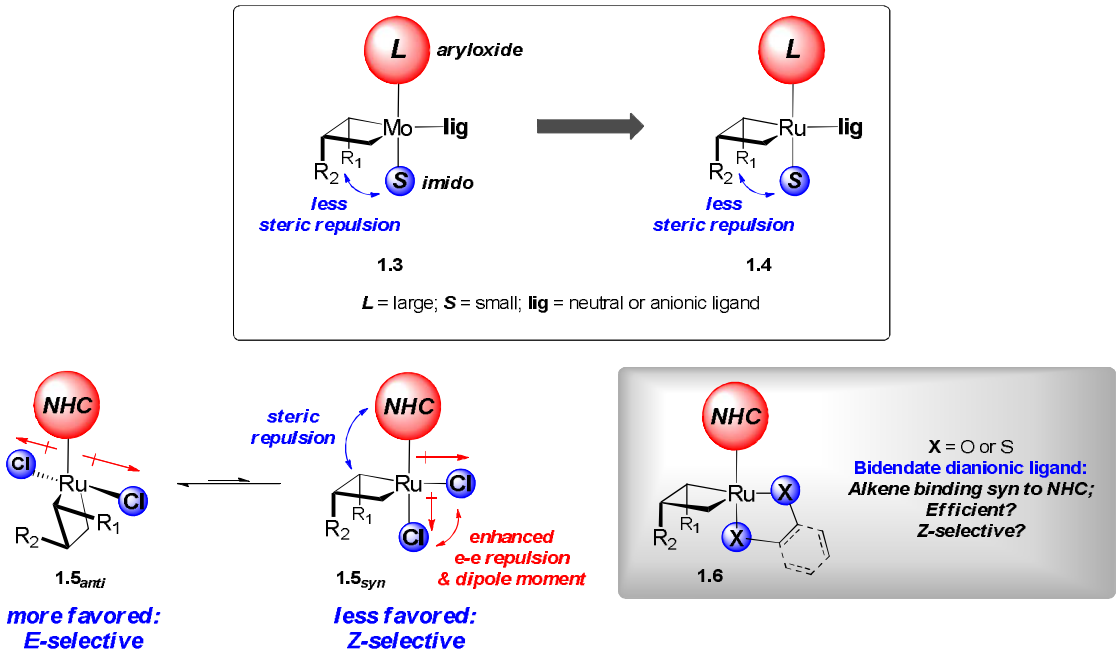
1.2.2. Rational Design of Catechothiolate Complexes as Z-Selective Catalysts

Inspired by the design principles for *Z* selectivity in high-oxidation-state MAP alkylidenes, our group hypothesized that high *Z* selectivity could be attained if the trigonal bipyramidal ruthenacyclobutane intermediate **1.4** bears axial ligands that are significantly different in size (Scheme 1.5). This will enforce *cis* orientation of both metallacycle substituents (i.e. R^1 and R^2) away from the large ligand to minimize steric repulsion. In the context of commonly used dichloro-Ru carbenes, **1.5**$_{syn}$ would possess the required ligand environment for *Z* selectivity (larger NHC vs. smaller Cl). However, the intermediacy of **1.5**$_{syn}$ is disfavored for several reasons: (i) electron-electron repulsion between the two Cl ligands (*syn* to each other),[17] (ii) unfavorably high dipole

(17) *Syn* orientation of a donor group and an NHC in dichloro-Ru complexes has been observed, likely arising from donor properties of the chelating groups. For example, see: (a) Ung, T.; Hejl, A.; Grubbs, R.

moment[18,19] and (iii) steric repulsion between the NHC and the metallacyclobutane (*syn* to each other).

Scheme 1.5. Rational Design of New Ru-Based Catalysts for *Z*-Selective Olefin Metathesis.



As a result, the transformation tends to proceed through **1.5**$_{anti}$, wherein the metallacyclobutane is formed *anti* to the large NHC. In this scenario, the NHC plays minimal role in determining stereoselectivity and the observed *E*:*Z* ratio largely depends on the size difference between substituents R^1 and R^2, resulting in predominant formation of the *E*-alkene in most instances. In order to favor the formation of ruthenacyclobutane

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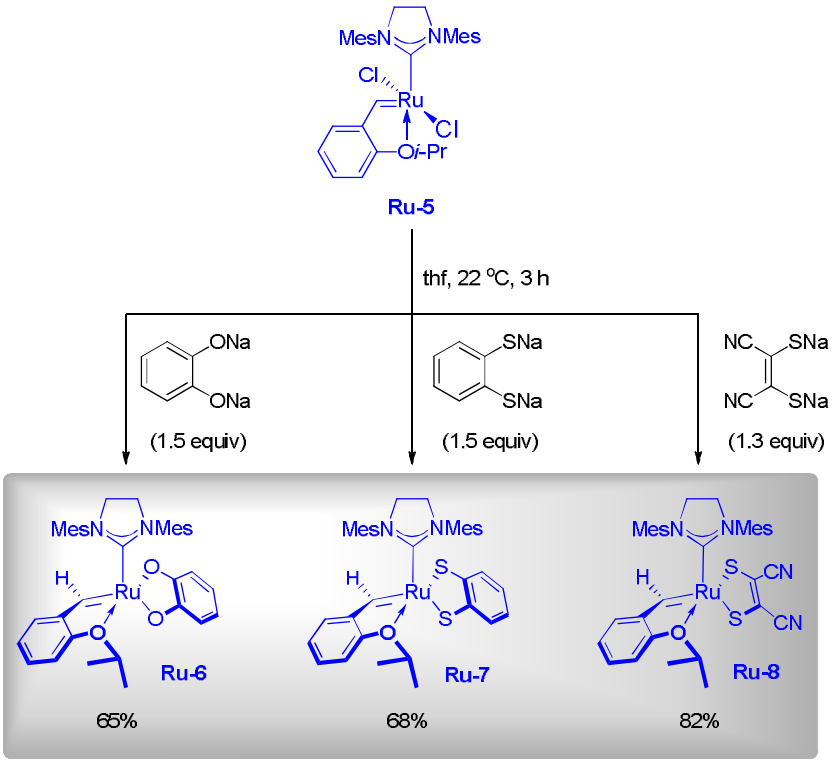
H.; Schrodi, Y. *Organometallics* **2004**, *23*, 5399–5401. (b) Slugovc, C.; Perner, B.; Stelzer, F.; Mereiter, K. *Organometallics* **2004**, *23*, 3622–3626. (c) Barbasiewicz, M.; Szadkowska, A.; Bujok, R.; Grela, K. Straub, B. F.; Lemcoff, N. G. *Inorg. Chem.* **2009**, *48*, 10819–10825. (e) Tzur, E.; Szadkowska, A.; Ben-Asuly, A.; Makal, A.; Goldberg, I.; Wozniak, K.; Grela, K.; Lemcoff, N. G. *Chem.–Eur. J.* **2010**, *16*, 8726–8737. For a study involving *syn*/*anti* isomerization, see: (f) Poater, A.; Ragone, F.; Correa, A.; Szadkowska, A.; Barbasiewicz, M.; Grela, K.; Cavallo, L. *Chem.–Eur. J.* **2010**, *16*, 14354–14364.

(18) Polar solvents have been proposed to stabilize the high dipole moment of *syn* alkene–NHC complexes and the related metallacyclobutanes. See: (a) Benitez, D.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2005**, *127*, 12218−12219. (b) Correa, A.; Cavallo, L. *J. Am. Chem. Soc.* **2006**, *128*, 13352−13353.

(19) For the significance of minimizing donor−donor interactions in Ru-catalyzed OM, see: (a) Khan, R. K. M.; Zhugralin, A. R.; Torker, S.; O'Brien, R. V.; Lombardi, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 12438−12441. (b) Torker, S.; Khan, R. K. M.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 3439−3455.

1.5$_{syn}$, our group envisioned replacing the two Cl with a bidendate dianion such as a catecholate or dithiolate as depicted in **1.6**. This would allow us to achieve the aforementioned objective as the two anionic ligands would be forced to adopt a *syn* orientation.[17] A practical synthesis route to the aforementioned complexes was thus devised by treating commercially available dichloro-Ru carbene **Ru-5** with disodium salts of catechol and dithiols to give **Ru-6**–**Ru-8** (Scheme 1.6).[20]

Scheme 1.6. Synthesis of New Ru-Based Complexes for *Z*-Selective Olefin Metathesis.

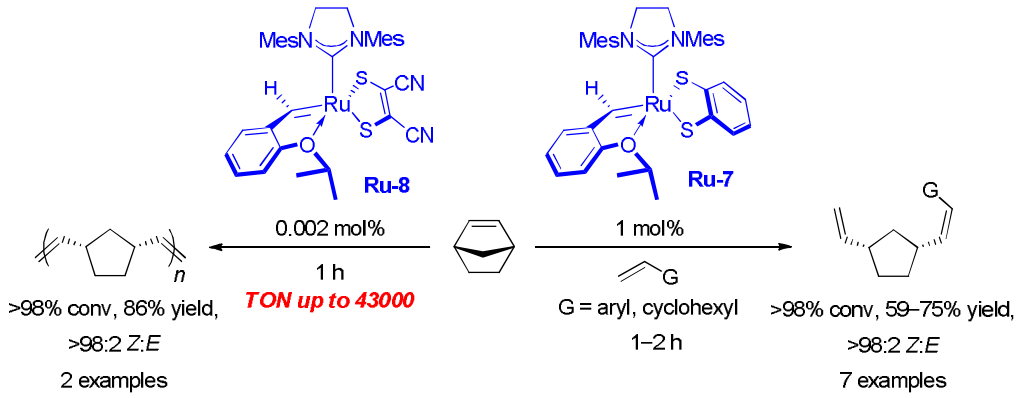


1.2.3. Exceptional Efficiency and Z Selectivity in Ring-Opening Metathesis Polymerization and Ring-Opening/Cross-Metathesis with Hindered Alkenes

(20) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2013**, *135*, 10258–10261.

As a proof-of-concept, ROMP[21] and ROCM[22] reactions with representative cyclic alkene substrates were investigated for efficiency and stereoselectivity using the new Ru carbenes in hand (Scheme 1.7). It was found that Ru dithiolates **Ru-7** and **Ru-8** are effective in promoting highly efficient and *Z*-selective ROMP with norbornene and cyclooctadiene (up to 43000 turnover number (TON) in 1 h with **Ru-8**). **Ru-7** was also demonstrated to catalyze ROCM with norbornenes and cyclobutenes and sterically bulky olefins such as styrenes and vinylcyclohexane with exceptional efficiency and stereochemical control. In contrast, **Ru-6** was shown to promote similarly efficient ROMP with norbornene but with minimal stereoselectivity (58:42 *Z*:*E* ratio).

Scheme 1.7. Exceptional Efficiency and *Z*-Selectivity in ROMP and ROCM with Ru Dithiolates.



The reasons for the observed selectivity difference between Ru diolates and dithiolates were later elucidated through a series of mechanistic and density functional theory (DFT) investigations.[23] It was revealed that Ru complexes containing sulfide ligands are better able to preserve their structural integrity under standard reaction

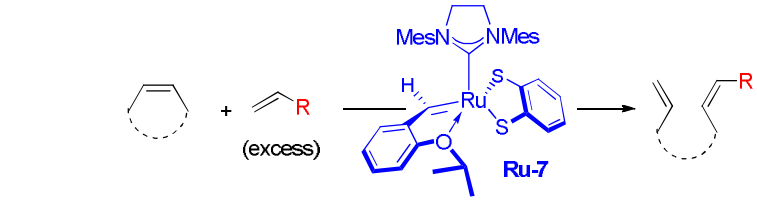
(21) For representative reviews on the importance of stereoregular ROMP, see: (a) Schrock, R. R. *Dalton Trans.* **2011**, *40*, 7484–7495. (b) Sutthasupa, S.; Shiotsuki, M; Sanda, F. *Polymer Journal* **2010**, *42*, 905–915. (c) Xia, Y.; Kornfield, J. A.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 3761–3766. (d) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565–1604.
(22) For the importance of ROCM in chemical synthesis, see: Grela, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 5504–5507.
(23) For studies that shed light on the importance of *S*-based (vs *O*-based) bidentate ligands, see: Khan, R. K. M.; Torker, S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 14337–14340.

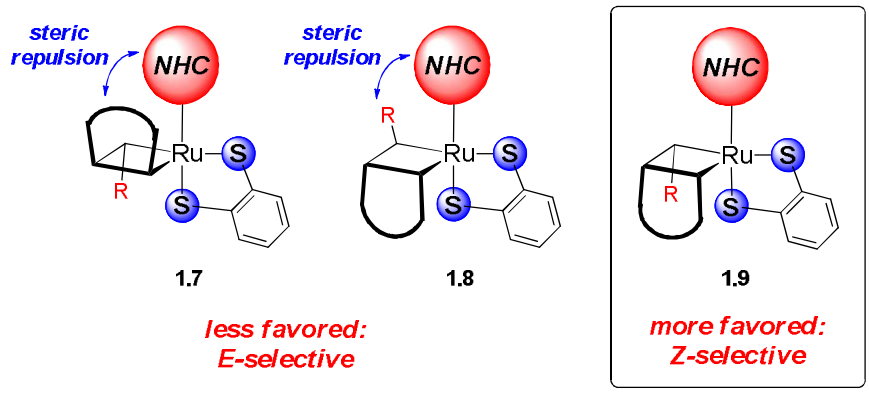
conditions, while the *O*-based variants decompose more readily to inactive entities that may promote non-selective transformations. DFT calculations further suggested that whereas olefin coordination is the rate-determining step with Ru diolates, it is the metallacyclobutane formation step that controls the identity of the major isomer with the dithiolate system. Stereochemical differentiation through formation of a metal–olefin complex is less likely since the more loosely associated alkene is too distal for steric interactions to exert a significant influence (vs. metallacyclobutane formation, see Scheme 1.5), hence offering an additional rationale for the selectivity trends in the aforementioned processes.

1.3. Examining Functional Group Compatibility of Ru-Based Catechothiolates Through Ring-Opening/Cross-Metathesis

1.3.1. Z-Selective ROCM with Broad Substrate Scope

Scheme 1.8. *Z*-Selective ROCM with Ru Catechothiolates as Catalysts.





- How small can the alkene substituents be for high *Z*-selectivity?
- Broad substrate scope: allylic or homoallylic alcohols, enol ethers, 1,3-dienes, heteroaryl olefins?

Encouraged by the first successful cases of catalytic ROCM with the newly discovered catechothiolate system, we aimed to gain further insights on the functional group tolerance of this class of Ru catalysts. Prior to our studies, it was shown that Mo-based MAP alkylidenes are capable of promoting highly efficient and *Z*-selective ROCM of various cyclic alkenes with styrenes[7] and enol ethers[24] as the olefin cross-partner, albeit with hydroxyl groups on the substrates protected due to the inherent sensitivity of alkylidenes toward protic groups.[13b] On the other hand, the only examples of Ru-catalyzed *Z*-selective ROCM with *O*- and *S*-substituted alkenes are promoted by a Ru carbene that affords *trans* products with other olefin cross-partners.[25] An enantioenriched **Ru-3** was shown to catalyze *Z*- and enantioselective ROCM transformations with various norborene derivatives and terminal aliphatic alkenes such as allylic acetate; however, all reported cases do not involve unprotected hydroxyl groups.[15k]

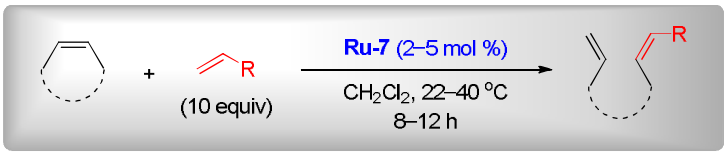
In light of the aforementioned ROCM results with hindered terminal alkenes, we wondered if Ru dithiolates such as **Ru-7** can promote reactions with olefins bearing smaller groups in spite of the diminished steric repulsion with the mesityl moieties of the NHC ligand (cf. **1.7** and **1.8**, Scheme 1.8). Although ROCM with hindered alkenes was shown to be efficient, the corresponding reactions with smaller substrates present new challenges since these undergo more facile homocoupling to generate ethylene and the somewhat unstable methylidene complex,[26] which has been implicated to decompose and lower catalyst lifetime. In addition, ROCM with smaller alkenes furnish products that are

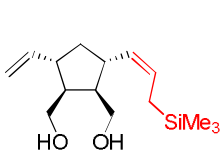
(24) Yu, M.; Ibrahem, I.; Hasegawa, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 2788–2799.
(25) Khan, R. K. M.; O'Brien, R. V.; Torker, S.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 12774–12779.
(26) Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 7961−7968.

relatively more exposed and hence are more susceptible to post-OM isomerization.[6] The final issue is whether ROCM can proceed efficiently and stereoselectively with a wide substrate range that include sparsely examined enol ethers,[27] 1,3-dienes,[28] heteroaryl olefins as well as unprotected allylic and homoallylic alcohols.

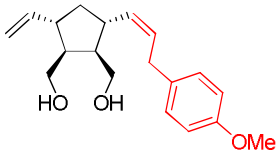
1.3.2. Z-Selective ROCM with Unhindered Aliphatic Alkenes[29]

Scheme 1.9. *Z*-Selective ROCM with Primaryl Alkyl Olefins.

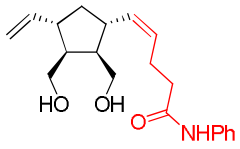




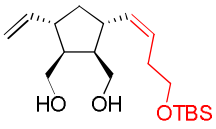
1.10
>98% conv, 89% yield,
>98:2 *Z*:*E*



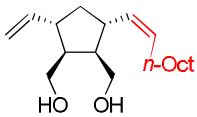
1.11
>98% conv, 83% yield,
>98:2 *Z*:*E*



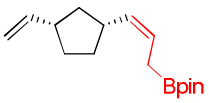
1.12
>98% conv, 65% yield,
>98:2 *Z*:*E*



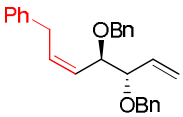
1.13
87% conv, 68% yield,
>98:2 *Z*:*E*



1.14
91% conv, 58% yield,
>98:2 *Z*:*E*



1.15
98% conv, 64% yield,
90:10 *Z*:*E*



1.16
75% conv, 58% yield,
>98:2 *Z*:*E*

We first examined the influence of the terminal alkene cross-partner size on the efficiency and stereoselectivity of the ROCM transformations using **Ru-7** as catalyst (Scheme 1.9). With cross-partners that bear bulky β-substituents (where the alkene and sizeable moiety are linked by a methylene unit), ROCM proceeds efficiently to afford

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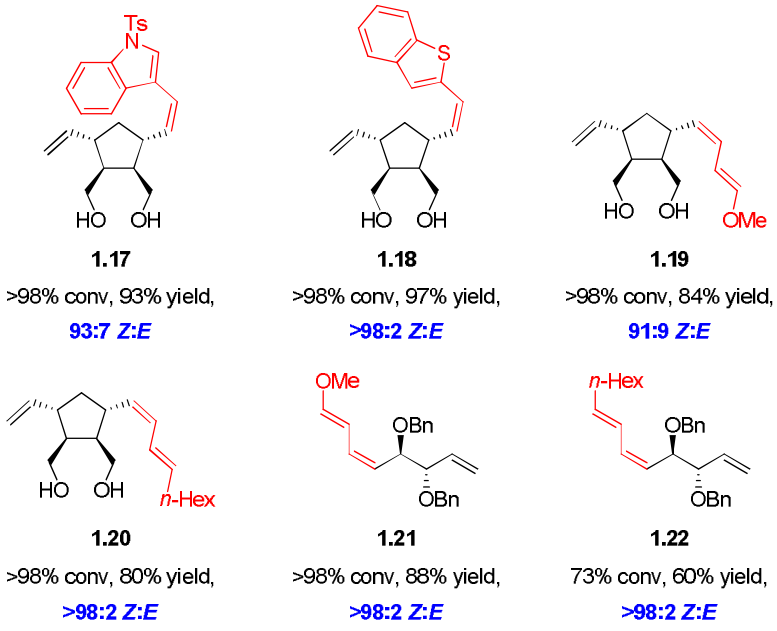
(27) Enol ethers are usually employed to terminate Ru-catalyzed OM due to their "irreversible" formation of Fischer-type carbenes. See: (a) Maynard, H. D.; Okada, S. Y.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6239–6248. (b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.
(28) Prior to our studies, *Z*-selective OM with 1,3-dienes is scarce and existing cases involve MAP alkylidenes: (a) Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 11334–11337. (b) Kiesewetter, E. T.; O'Brien, R. V.; Yu, E. C.; Meek, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2013**, *135*, 6026–6029.
(29) Koh, M. J.; Khan, R. K. M.; Torker, S.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2014**, *53*, 1968–1972.

1.10 and **1.11** in 89% and 83% yield, respectively with complete *Z* selectivity. Transformations with the less hindered γ,δ-unsaturated amide and homoallylic silyl ether are similarly *Z*-selective but somewhat less efficient (**1.12** and **1.13** generated in 65% and 68% yield, respectively), presumably due to more competitive homo-metathesis of the cross-partner and formation of the unstable Ru methylidene.[26]

In further support of this hypothesis, ROCM with the least hindered 1-decene proceeds to 91% conversion and **1.14** was obtained in 58% yield and >98:2 *Z*:*E* ratio. The reactions can also be extended to different cyclic olefins as highlighted by the synthesis of **1.15** and **1.16**. The above results indicate that steric repulsion between the mesityl moieties of the NHC and the metallacyclobutane substituents appears to be sufficient to favor the intermediacy of **1.9** (vs. **1.7** and **1.8**, Scheme 1.8) even when R is relatively small.

1.3.3. Z-Selective ROCM with Heterocyclic and Conjugated Alkenes

Scheme 1.10. Z-Selective ROCM with Heterocyclic Alkenes and 1,3-Dienes.



1.17
>98% conv, 93% yield,
93:7 *Z*:*E*

1.18
>98% conv, 97% yield,
>98:2 *Z*:*E*

1.19
>98% conv, 84% yield,
91:9 *Z*:*E*

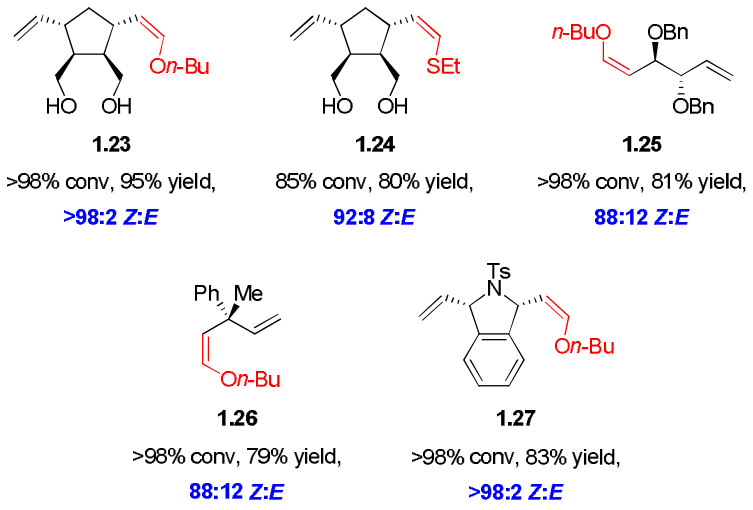
1.20
>98% conv, 80% yield,
>98:2 *Z*:*E*

1.21
>98% conv, 88% yield,
>98:2 *Z*:*E*

1.22
73% conv, 60% yield,
>98:2 *Z*:*E*

We next examined the reaction scope with various functionalized heterocyclic alkenes and 1,3-dienes (Scheme 1.10). Heterocyclic olefins are found to be compatible under the ROCM conditions as represented by the synthesis of **1.17** and **1.18**; products are generated in 93–97% yield and ≥93% *Z* selectivity. 1,3-Dienes[28] also serve as efficient cross-partners in the ROCM protocol. Transformations with (*E*)-1-methoxy-1,3-butadiene or (*E*)-deca-1,3-diene with norbornene- and cyclobutene-derived substrates proceeded efficiently to give the desired products **1.18**–**1.22** in 60–88% yield and >98:2 *Z*:*E* ratio in most instances; the reaction to deliver **1.19** gave somewhat lower *Z* selectivity (91:9 *Z*:*E* ratio), the exact origin of which remains to be determined.[30]

Scheme 1.11. *Z*-Selective ROCM with *O*- and *S*-Substituted Alkenes.

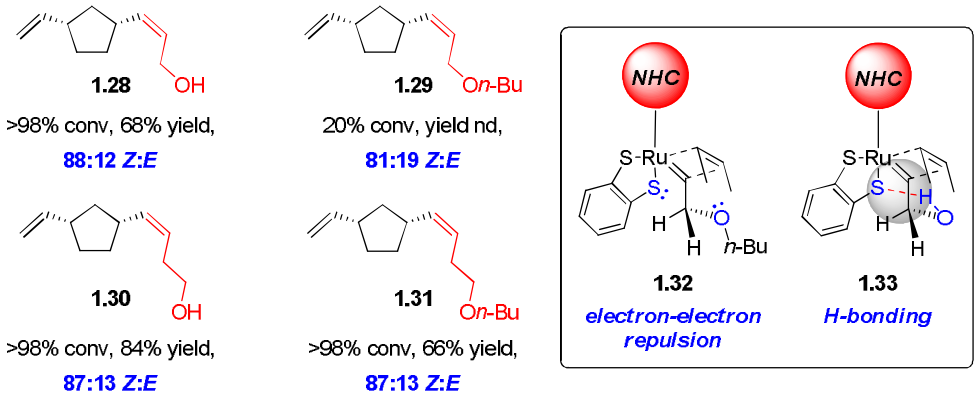


ROCM transformations employing enol ethers and vinyl sulfides, olefins that are capable of forming less reactive Fischer-type carbene species with Ru complexes,[27] are shown to be similarly efficient and stereoselective with a range of cyclic alkene substrates possessing different strain energies, furnishing products **1.23**–**1.27** in 79–95% yield and ≥88% *Z* selectivity (Scheme 1.11).

(30) Examination of selectivity as a function of time indicates that the *E*-isomer is not generated by post-metathesis isomerization.

1.3.4. Positive Influence of Allylic Alcohol-Induced Electrostatic (H-Bonding) Interactions on Reaction Efficiency and Selectivity

Scheme 1.12. *Z*-Selective ROCM with Allyl and Homoallyl Alcohols and Their Derived Ethers.

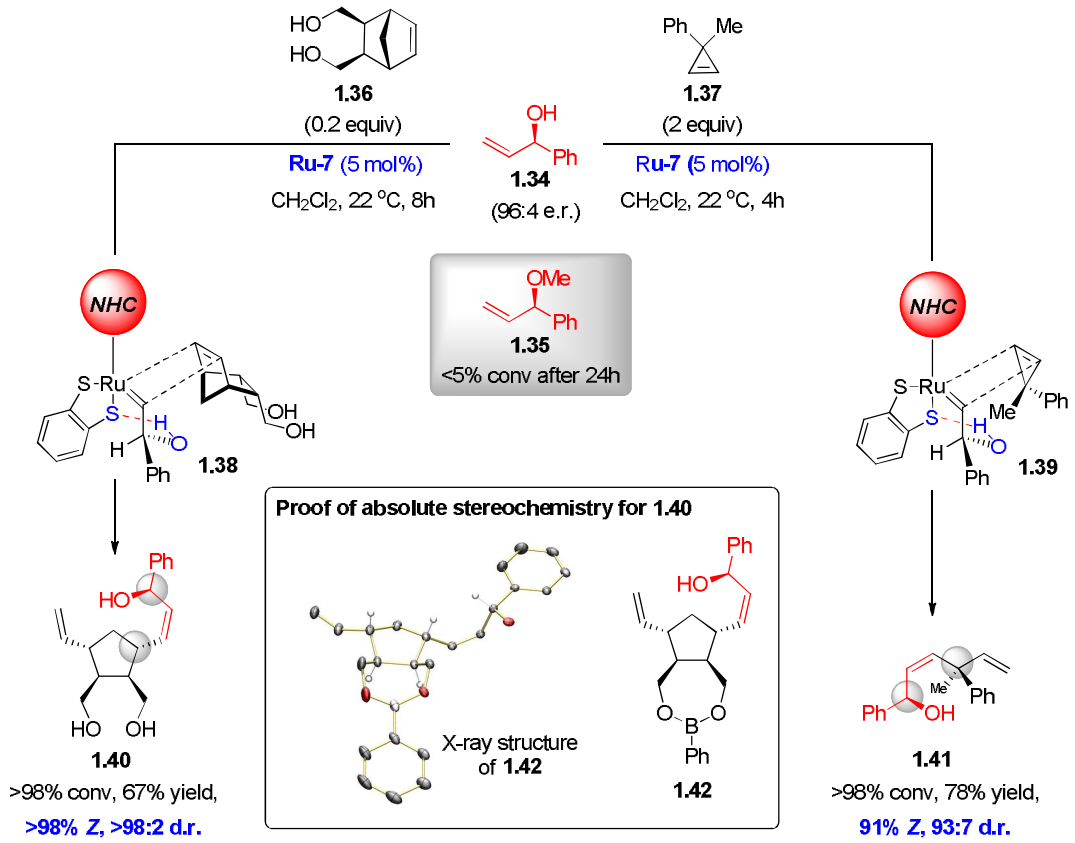


Given the sensitivity of high-oxidation-state alkylidene complexes toward hydroxyl groups[13b] and the persisting lack of examples with previously reported Ru-catalyzed methods, we turned to the possibility of using allylic and homoallylic alcohols as cross-partners in our ROCM regime (Scheme 1.12). Interestingly, whereas the reactions of norbornene with homoallyl alcohol and its derived *n*-butyl ether proceeded to give **1.30** and **1.31** as a mixture of 87:13 *Z*:*E* isomers in 84% and 66% yield, respectively, ROCM with allyl alcohol to give **1.28** (>98% conversion, 68% yield) was appreciably more efficient than its protected variant (20% conversion). In view of the efficiency of reactions with primary alkyl olefins (Scheme 1.9), it appears that incorporation of an allylic ether oxygen induces a detrimental effect, one that is no longer present when allyl alcohol is used (cf. **1.28**). A plausible rationale for these observations is that electron-electron repulsion[31] may exist between the allylic ether oxygen and the neighboring sulfide unit *trans* to the NHC, consequently raising the energy of the ruthenacyclobutane

(31) Similar unfavorable repulsive forces between the oxygen substitent and the sulfide unit are unlikely in effect for vinyl (Scheme 1.11) and homoallylic ethers (cf. **1.13** in Scheme 1.9 and **1.30** in Scheme 1.12); it appears that it is the heteroatom within an allylic ether that engenders repulsive electronic interactions.

and the preceding transition state (cf. **1.32**, Scheme 1.12). On the other hand, such unfavorable repulsive interactions could be dispensed with through electrostatic (H-bonding) interactions between the allylic hydroxyl unit and the sulfide *trans* to the NHC,[32] which could also contribute to stabilizing the ruthenacyclobutane and the preceding transition state by minimizing the *trans* influence[19] arising from placement of the NHC and sulfide groups (cf. **1.33**, Scheme 1.12).

Scheme 1.13. *Z*- and diastereoselective ROCM with an Enantioenriched Secondary Allylic Alcohol.



To gain more insights, we chose to examine the reaction of an enantiomerically enriched secondary allylic alcohol (Scheme 1.13), since the facility with which the

(32) For studies on H-bonding interactions with *S*-containing functional groups, see: (a) Wennmohs, F.; Staemmler, V; Schindler, M. *J. Chem. Phys.* **2003**, *119*, 3208–3218. (b) Tsogoeva, S. B.; Yalalov, D. A; Hateley, M. J.; Weckbecker, C.; Hutchmacher, K. *Eur. J. Org. Chem.* **2005**, 4995–5000. (c) Schreiner, E.; Nair, N. N.; Pollet, R.; Staemmler, V.; Marx, D.; *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 20725–20730. (d) Zhou, P.; Tian, F.; Lv, F.; Shang, Z. *Proteins Struct. Funct. Bioinf.* **2008**, *76*, 151–163.

sterically congested *Z*-olefin is formed could further substantiate the positive influence of the hydroxyl group. Furthermore, whether the ROCM proceeds diastereoselectively would shed further light on the nature of the aforementioned electrostatic interactions. Treatment of commercially available allylic alcohol **1.34** (96:4 enantiomeric ratio (e.r.)) with cyclic alkene **1.36** (5:1 ratio) in the presence of 5 mol % of **Ru-7** gave **1.40** (via **1.38**) in 67% yield as a single diastereomer (>98:2 *Z*:*E* and >98:2 diastereomeric ratio (d.r.)). The identity of the major enantiomer was ascertained by the X-ray structure of the phenylboronate derivative **1.42**. When **1.34** was subjected to cyclopropene **1.37** (1:2 ratio), under otherwise the same reaction conditions, **1.41** was obtained in 78% yield, 91:9 *Z*:*E* and 93:7 d.r. (via **1.39**). Perhaps unsurprisingly, there was <5% conversion after 24 hours when the allylic methyl ether **1.35** was reacted with either **1.36** or **1.37**. These observations highlight a crucial mechanistic attribute. Previously, allylic alcohols have been shown to react with greater efficiency and diastereoselectivity than their protected derivatives in ROCM transformations catalyzed by dichloro-Ru complexes,[33] and electrostatic attraction (H-bonding) between the alcohol and the anionic Cl ligands were invoked to rationalize these results. It is likely that similar principles are operative in the Ru dithiolate system.[32] As illustrated by **1.33** in Scheme 1.12, such electrostatic interactions between the allylic hydroxyl group and the sulfide *anti* to the NHC not only alleviate *trans* influence, but also induce structural organization leading to high diastereofacial differentiation in reactions with enantioenriched allylic alcohols. These data underscore the unique ability of Ru dithiolates to promote OM with alkenes

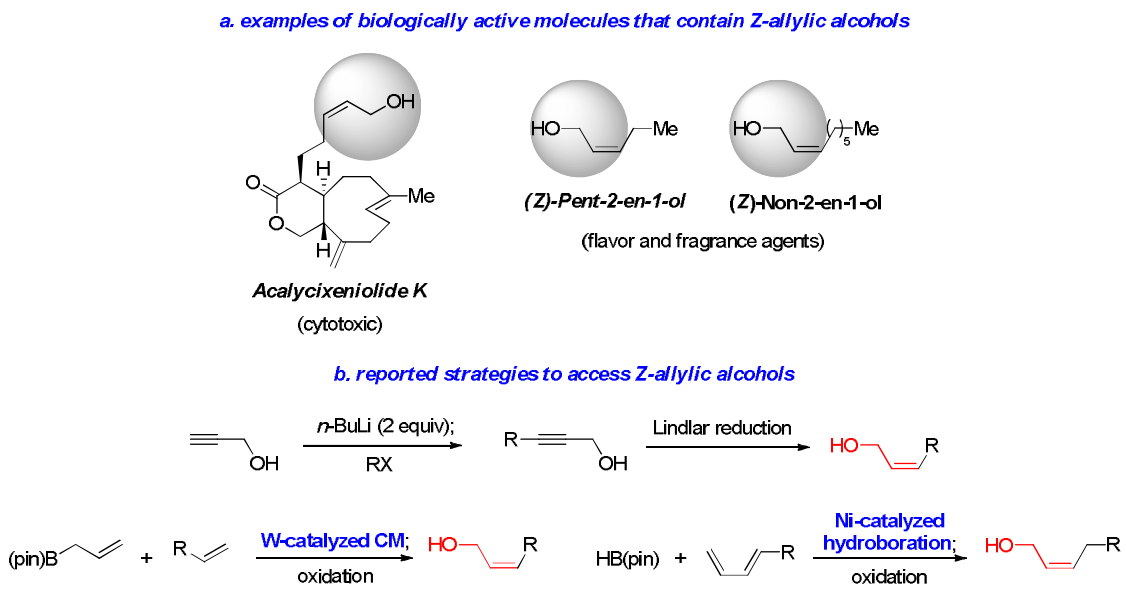
(33) (a) Hoveyda, A. H.; Lombardi, P. J.; O'Brien, R. V.; Zhugralin, A. R. *J. Am. Chem. Soc.* **2009**, *131*, 8378–8379. For related studies, see: (b) Hoye, T. R.; Zhao, H. *Org. Lett.* **1999**, *1*, 1123–1125. (c) Fuwa, H.; Saito, A.; Sasaki, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 3041–3044. (d) Lin, Y. A.; Chalker, J. M.; Davis, B. G. *J. Am. Chem. Soc.* **2010**, *132*, 16805–16811. (e) Donohoe, T. J.; Basutto, J. A.; Bower, J. F.; Rathi, A. *Org. Lett.* **2011**, *13*, 1036–1039.

containing a proximal alcohol unit, which provided the impetus for us to address a longstanding limitation in CM for the preparation of synthetically valuable *Z*-allylic alcohols.

1.4. Cross-Metathesis to Access Functionalized Z-Allylic Alcohols

1.4.1. Significance of Z-Allylic Alcohols in Chemical Synthesis

Scheme 1.14. Importance of *Z*-Allylic Alcohols in Nature and Common Methods to Prepare Them.



The *Z*-allylic hydroxyl motif is commonly found in biologically active compounds[34] including fragrance agents such as (*Z*)-pent-2-en-1-ol and (*Z*)-non-2-en-1-ol (Scheme 1.14a). In addition, it also serves as a convenient handle for further elaboration in organic synthesis.[35] The traditional route to synthesize 1,2-disubstituted *Z*-allylic alcohols involves partial hydrogenation[3c] of disubstituted propargylic alcohols that are in turn accessed from alkylation of propargyl alcohol. More recently, catalytic methods that afford such moieties have been developed (Scheme 1.14b). For instance, in 2010, Morken

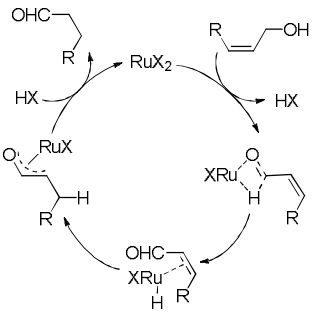
(34) For examples, see: (a) Yadav, J. S.; Bhanu, L. R. M.; Dutta, D. *Tetrahedron* **1998**, *54*, 3929–3934. (b) Rho, J.-R.; Oh, M.-S.; Jang, K. H.; Cho, K. W.; Shin, J. *J. Nat. Prod.* **2001**, *64*, 540–543.
(35) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307–1370.

and Ely have reported a Ni-catalyzed 1,4-hydroboration protocol using 1,3-dienes and HB(pin) followed by oxidation to afford allylic alcohols efficiently and *Z*-selectively.[36] In 2013, our group has shown that W-based MAP-catalyzed *Z*-selective CM of terminal alkenes with allylboronic pinacol ester followed by oxidation enables access to a variety of *Z*-allylic alcohols efficiently.[28b] Despite these advances, a catalytic method that directly affords *Z*-allylic alcohols with a wide substrate range, especially those that bear important functional units such as carboxylic acids, phenols and carbonyl groups, under ambient conditions in a single step (without oxidation in between) would be highly coveted.

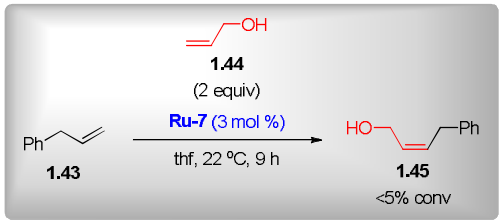
1.4.2. Challenges in CM to Access Z-Allylic Alcohols

Scheme 1.15. Challenges in *Z*-Selective CM to Access Allylic Alcohols with Ru Dithiolate Complexes.

a. Ru-catalyzed redox isomerization as potential complication

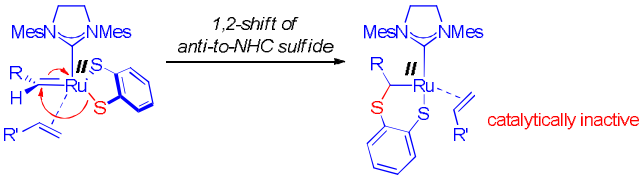


b. CM between 2 terminal alkenes inefficient with Ru dithiolates



c. possible pathways for decomposition of Ru dithiolate species

1. Rearrangement of disulfide ligand



2. Bimolecular decomposition

OM with allylic alcohols lies in the exclusive purview of low-oxidation-state Ru carbene catalysis. However, studies in *Z*-selective OM with allylic alcohols are thus far

(36) Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534–2535.

limited to ROCM,[15m,29] processes that benefit from the driving force of strain release. Catalytic CM provides a strategically distinct and highly versatile approach to linear *Z*-allylic alcohols by utilizing readily available alkenes as starting materials. Direct *Z*-selective CM between an olefin and a commercially available allylic alcohol would undeniably represent one of the most straightforward ways to generate these products.

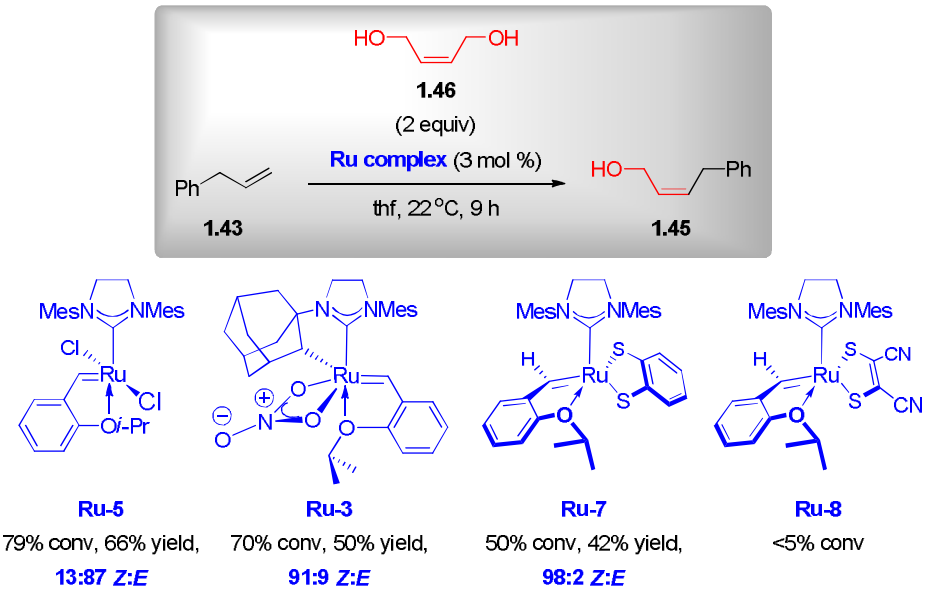
However, in addition to the challenges associated with catalyst-controlled *Z*-selective OM as illustrated in Scheme 1.2, the propensity of the allylic hydroxyl unit to undergo undesired redox isomerization under Ru catalysis is documented (Scheme 1.15a).[37] Further exacerbating the situation is the observation that a typical CM between a terminal olefin such as allylbenzene **1.43** and 2 equivalents of allyl alcohol **1.44** using **Ru-7** as catalyst failed to furnish appreciable amounts of the desired product **1.45** (<5% conversion) (Scheme 1.15b). Additional control experiments confirmed that Ru-based dithiolates like **Ru-7** are inefficient in promoting reactions with two mono-substituted olefins. We hypothesized that the inevitable formation of unstable Ru methylidene complexes during the course of the reaction (either from CM or homocoupling of the alkene substrates) is the main culprit for catalyst decomposition leading to poor efficiency. Two conceivable modes of catalyst decomposition are presented in Scheme 1.15c. First, the possibly enhanced electron density of the sulfide positioned opposite to the NHC ligand as a result of *trans* influence[19] may cause an intramolecular 1,2-sulfide shift into the carbene[38] leading to a catalytically inactive species, particularly when an

(37) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 2027–2036.
(38) For an example of 1,2-thio group migration into carbenoids, see: Feng, X.; Shi, W.; Wang, J. *J. Org. Chem.* **2005**, *70*, 4191–4194.

exposed methylidene is involved (R = H). Second, biomolecular decomposition of the relatively unhindered methylidene[39] can further diminish the catalyst lifetime.

1.4.3. Preliminary Results in CM with Z-2-Butene-1,4-Diol

Scheme 1.16. CM of Allylbenzene and *Z*-2-Butene-1,4-diol with representative Ru complexes.



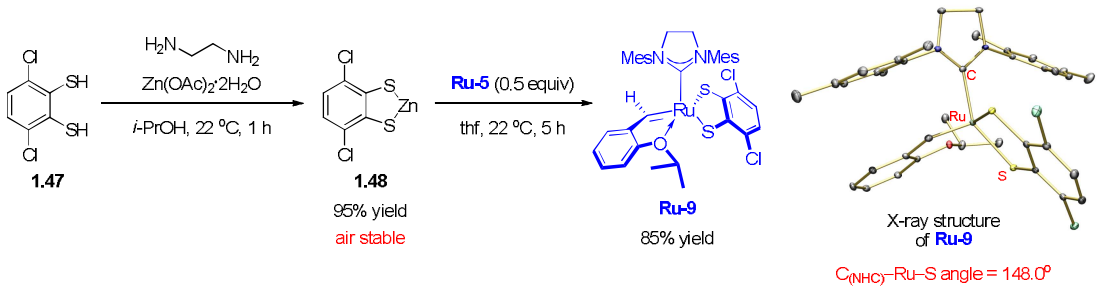
Since allyl alcohol was found to be inefficient in CM with Ru dithiolates, we turned to commercially available, inexpensive and stereoisomerically pure *Z*-2-butene-1,4-diol as the cross-partner instead. We envisioned that the use of a 1,2-disubstituted olefin should diminish ethylene generation and discourage the formation of unstable methylidene complexes, which are adept at causing post-metathesis isomerization[6] and lowering catalyst life time (Scheme 1.15). CM of allylbenzene **1.43** with excess *Z*-2-butene-1,4-diol **1.46** was carried out with various reported Ru catalysts and results are summarized in Scheme 1.16. With dichloro-Ru carbene, **1.45** was obtained in 66% yield as a 87:13 *E*:*Z* mixture of isomers, presumably due to substrate control. With the NHC-chelating complex **Ru-3**, which has been shown to promote a range of Z-selective OM

(39) Vougioukalakis, G. C.; Grubbs, R. H. *Chem Rev.* **2010**, *110*, 1746–1787.

transformations,[15] **1.45** was generated with decent *Z* selectivity (91:9 *Z*:*E* ratio) albeit in moderate yield (70% conversion, 50% yield). Catechothiolate **Ru-7** was slightly less efficient in promoting CM (50% conversion, 42% yield), but appreciably more *Z*-selective (98% *Z* selectivity) compared to **Ru-3**. This result is in stark contrast to the corresponding CM with allyl alcohol **1.44** (Scheme 1.15b), and lends credence to the detrimental effect of the putative Ru methylidene. On the other hand, dithiolate **Ru-8** failed to catalyze the CM transformation (<5% conversion).

1.4.4. Development of New Ru Catechothiolates for CM with Z-2-Butene-1,4-Diol[40]

Scheme 1.17. Synthesis of New Ru-Based Catechothiolates Exemplified by **Ru-9**.

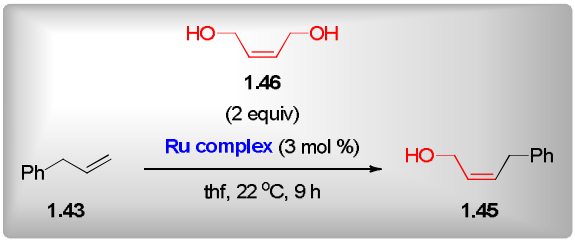


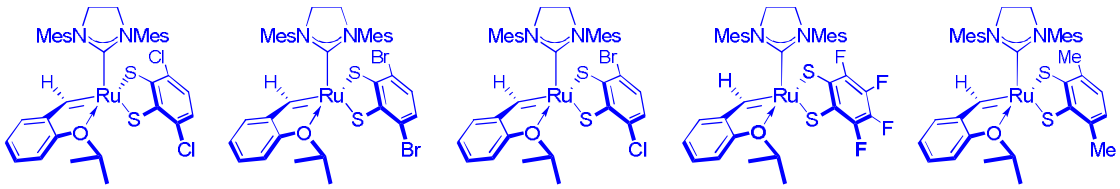
We pondered whether incorporation of electronegative atoms (for example, Cl) within the catechothiolate ligand in **Ru-7** might slow down the rate of 1,2-sulfide shift leading to catalyst decomposition by reducing *trans* influence with the NHC as illustrated in Scheme 1.15c. Efforts to prepare **Ru-9**, the dichloro derivative of the parent complex **Ru-7**, using the corresponding disodium dithiolate precursor (Scheme 1.6) proved to be unsatisfactory as the desired Ru complex was difficult to purify from unidentified side products (>98% conversion, 5% yield). A more practical synthesis route would have to be developed, which led us to discover that treatment of 3,6-dichloro-catechothiol **1.47** with ethylenediamine and $Zn(OAc)_2 \cdot 2H_2O$ under ambient conditions for 1 hour affords

(40) Koh, M. J.; Khan, R. K. M.; Torker, S.; Yu, M.; Mikus, M. S.; Hoveyda, A. H. *Nature* **2015**, *517*, 181–186.

the air-stable Zn dithiolate **1.48** in 95% yield as a white solid (Scheme 1.17). Subjecting **1.48** to commercially available **Ru-5** gave the desired **Ru-9** in 85% yield with little byproduct formation, improving the ease of purification. The X-ray structure of **Ru-9** reveals a wider $C_{(NHC)}$–Ru–S angle of 148.0° (vs. 143.4° for **Ru-7**), supporting the aforementioned effect of the electron-withdrawing Cl in reducing electron density at the sulfide site and hence lowering *trans* influence between the NHC and the sulfide anion.

Scheme 1.18. CM of Allylbenzene and *Z*-2-Butene-1,4-diol with Modified Ru Catechothiolate Complexes.





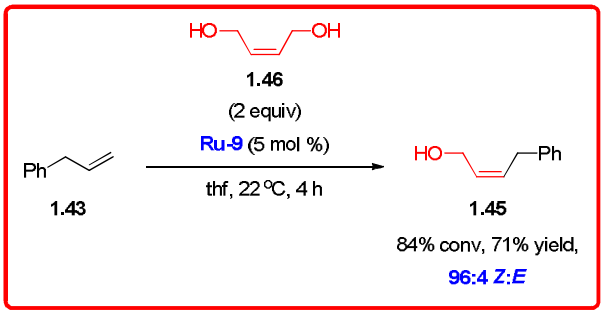
Ru-9 77% conv, 61% yield, **96:4 *Z*:*E***

Ru-10 75% conv, 60% yield, **94:6 *Z*:*E***

Ru-11 76% conv, 57% yield, **95:5 *Z*:*E***

Ru-12 75% conv, 58% yield, **96:4 *Z*:*E***

Ru-13 56% conv, 47% yield, **96:4 *Z*:*E***



Various Ru complexes **Ru-10**–**Ru-12** were subsequently prepared from the corresponding halogenated catechothiols using the procedure established in Scheme 1.17. Examination of CM using **1.43** as the model substrate showed that these catalysts were similarly efficient and *Z*-selective compared to **Ru-9**, furnishing the desired product in

58–61% yield and 94:6–96:4 *Z*:*E* ratios (Scheme 1.18). The lower efficiency of **Ru-13** (56% conversion, 47% yield) is consistent with the positive electronic influence of the halogen substituents in **Ru-9**–**Ru-12**. Eventually, we selected **Ru-9** was the optimal catalyst due to its ease of preparation (3,6-dichloro-catechothiol **1.47** is commercially available, but other halogenated catechothiols have to be synthesized). Further optimization using 5 mol % **Ru-9** led to 84% conversion within four hours, delivering **1.45** in 71% yield and 96% *Z* selectivity.

1.4.5. CM to Access Functionalized Z-Allylic Alcohols Using Ru-9 as Catalyst

With the established conditions in hand, we proceeded to examine the scope of the catalytic protocol (Scheme 1.19). Reactions with various terminal olefins, including those that possess heterocyclic and Lewis basic functional groups, furnishing the desired products **1.49**–**1.55** in 57–80% yield and ≥91% *Z* selectivity. **1.49** is an intermediate used to synthesized (+)-disparlure, a female sex pheromone of the gypsy moth *Porthertria dispar* (L).[41] CM transformations are compatible with substrates that contain a hydroxyl unit (**1.56**), a *p*-keto-phenol (**1.57**), an aldehyde (**1.58**) and a carboxylic acid (**1.59** and **1.60**). The method is applicable to CM with sizeable α-branched alkenes (**1.61** and **1.62**) and styrenes (**1.63** and **1.64**), affording the *Z*-allylic alcohols in 53–63% yield and 93:7–98:2 *Z*:*E* ratios. **Ru-11** gave slightly higher yields in the cases of **1.63** and **1.64**. Electron-rich and electron-deficient 1,3-*Z*,*E*-dienes **1.65**–**1.67** as well as sterically congested 1,3-*Z*,*Z*-diene **1.68** could also be prepared with good efficiency and stereoselectivity (54–66% yield, 87:13–96:4 *Z*:*E*).

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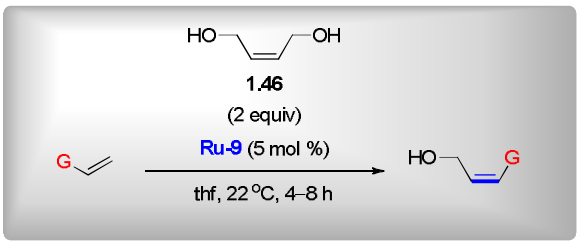
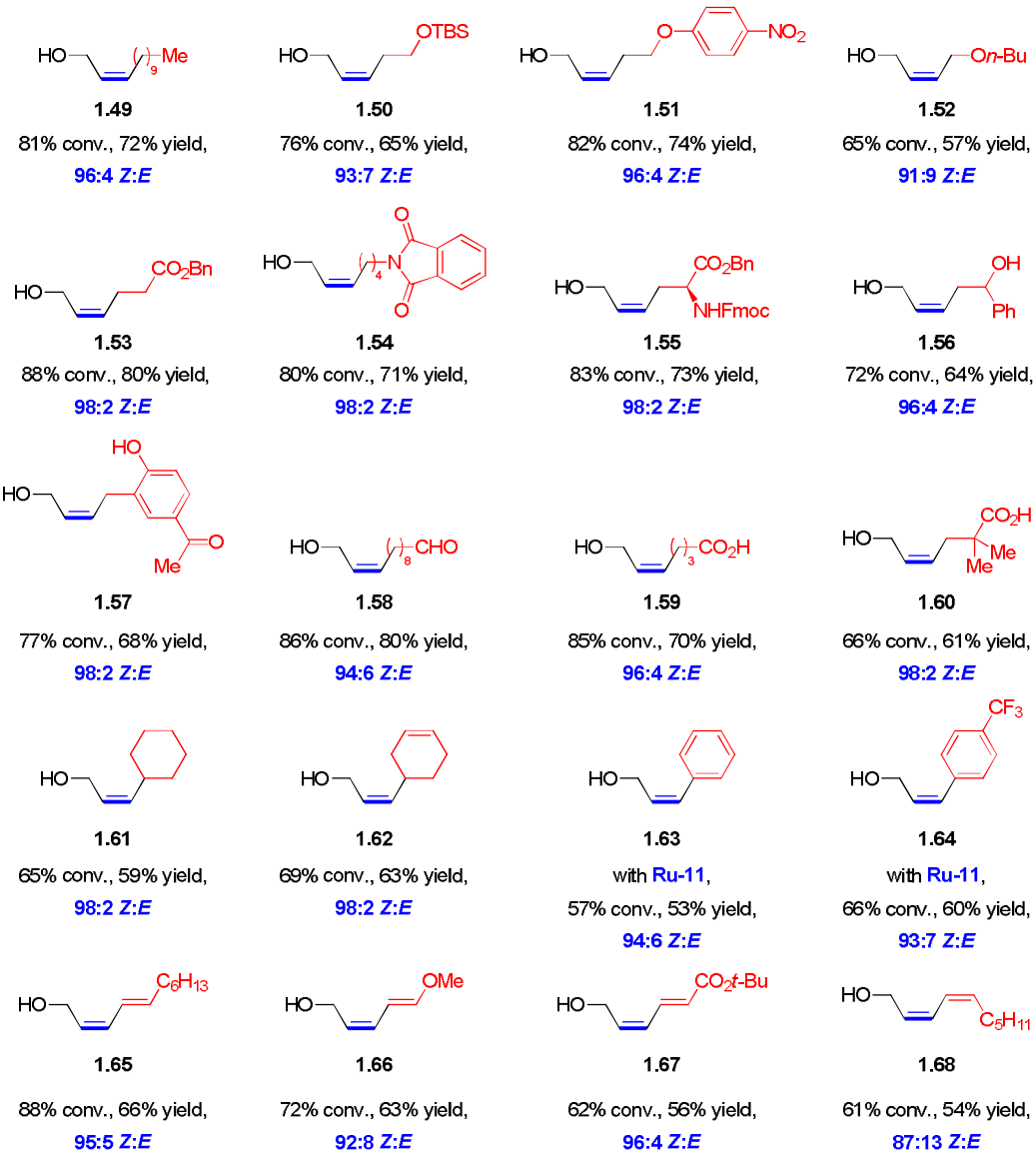
(41) Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 464–465.

Scheme 1.19. The range of *Z*-Allylic alcohols Accessed through *Z*-Selective CM with **Ru-9**.



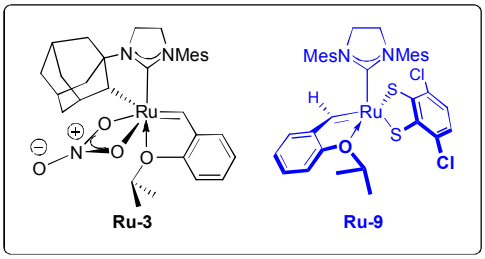


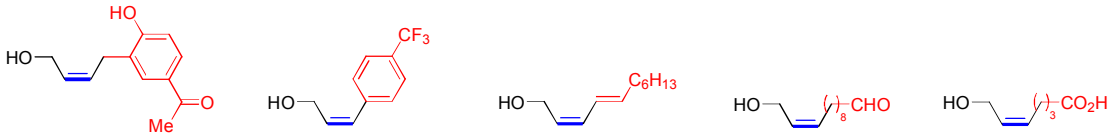
1.4.6. Comparison of Ru-3 and Ru-9 in CM to Access Z-Allylic Alcohols

Dichloro-Ru carbene complexes are well-documented to be robust in the presence of a broad assortment of functionalities that include sterically hindered alkenes as well as

those containing Brønsted acids and carbonyl groups. The development of *Z*-selective Ru catalysts has involved substitution of one or both chlorides with other anionic ligands (cf. Schemes 1.4, 1.6 and 1.17). The findings showcased in Scheme 1.19 with catechothiolate **Ru-9** illustrate that replacing the chlorides with a bidendate disulfide ligand does not alter the ability of the catalyst to promote CM with the aforementioned functional groups. However, it is not a given that other *Z*-selective Ru catalysts exhibit the same degree of functional group tolerance as Ru dichloride complexes such as **Ru-5**.

Scheme 1.20. Comparison of **Ru-3** and **Ru-9** in *Z*-Selective CM.





1.57	**1.64**	**1.65**	**1.58**	**1.59**
with **Ru-3**, 58% conv., 50% yield, **82:18 *Z*:*E***	with **Ru-3**, 19% conv., yield ND, *Z*:*E* ND	with **Ru-3**, 59% conv., 53% yield, **93:7 *Z*:*E***	with **Ru-3**, 41% conv., 30% yield, **87:13 *Z*:*E***	with **Ru-3**, <5% conv.
with **Ru-9**, 77% conv., 68% yield, **98:2 *Z*:*E***	with **Ru-9**, 60% conv., 55% yield, **93:7 *Z*:*E***	with **Ru-9**, 88% conv., 66% yield, **95:5 *Z*:*E***	with **Ru-9**, 86% conv., 80% yield, **94:6 *Z*:*E***	with **Ru-9**, 85% conv., 70% yield, **96:4 *Z*:*E***

To evaluate this, we carried out CM studies with a number of substrates using **Ru-3** as the catalyst for comparison (Scheme 1.20). Whereas **1.57** was generated in 68% yield and 98:2 *Z*:*E* ratio with **Ru-9**, the reaction was less efficient and stereoselective with **Ru-3** (50% yield, 82:18 *Z*:*E*). A larger difference in efficiency was observed with sterically demanding aryl olefin **1.64** (19% conversion with **Ru-3** vs. 60% conversion, 55% yield with **Ru-9**). Similarly, the transformation leading to 1,3-*Z*,*E*-diene **1.65** was

more efficient with **Ru-9** (66% yield) than with **Ru-3** (53% yield). Intriguingly, the aldehyde-containing **1.58** was only obtained in 30% yield and 87% *Z* selectivity with **Ru-3** (vs. 80% yield and 94% *Z* selectivity with **Ru-9**). Carboxylic acids are incompatible with **Ru-3** as highlighted by the CM leading to **1.59** (<5% conversion), an observation that is consistent with a previous report.[15b] Presumably, the highly polarized and nucleophilic Ru–alkyl bond in **Ru-3** causes complications with acidic or electrophilic functional groups leading to catalyst decomposition,[42] reminiscent of high-oxidation-state Mo- and W-based alkylidenes.

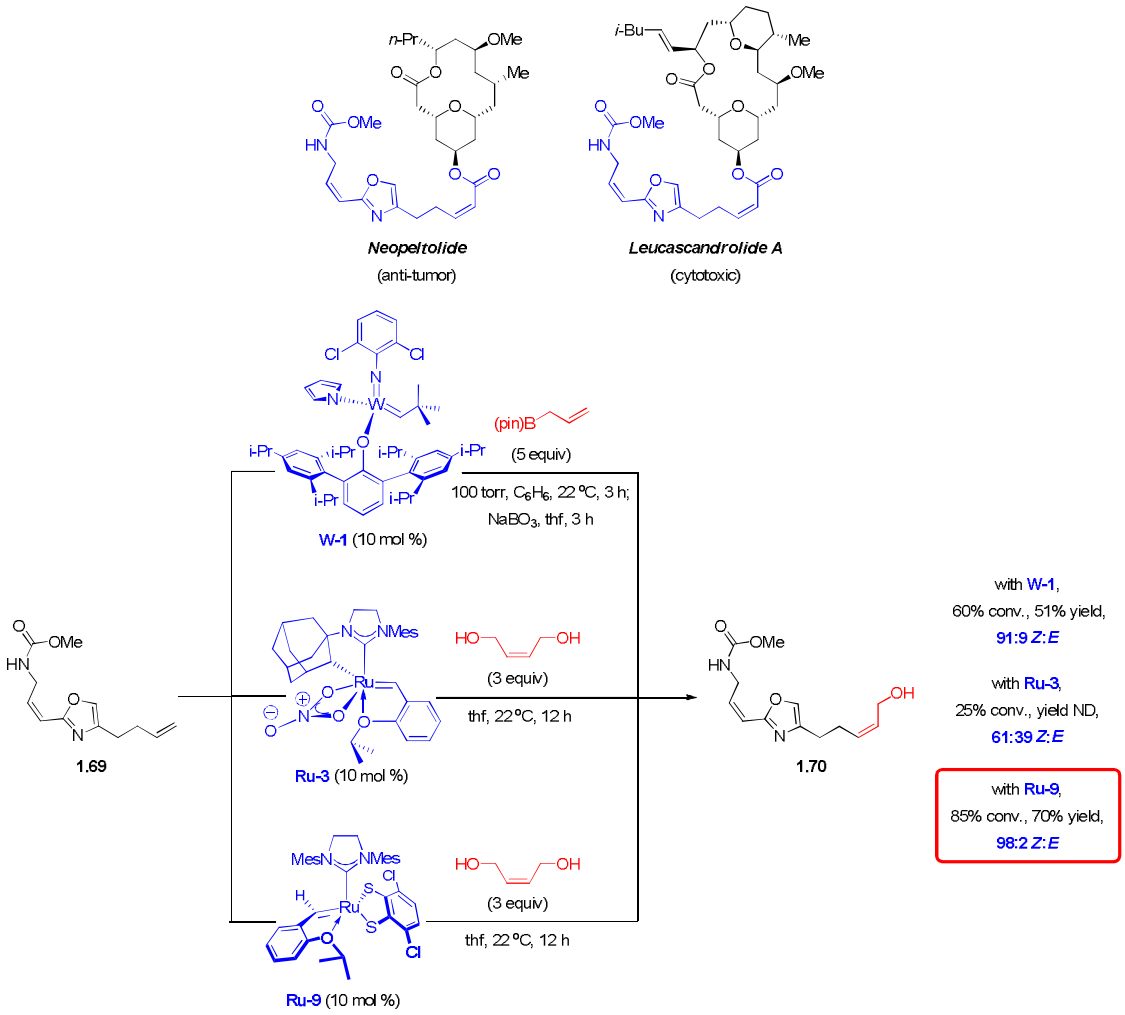
1.4.7. Application to Stereoselective Synthesis of Neopeltolide and Leucascandrolide A Side Chain

An opportunity to demonstrate the utility of the CM strategy revealed itself during the course of the total synthesis of the anti-tumor agent neopeltolide.[43] The same *Z*,*Z*-diene appendage exists in the cytotoxic natural product leucascandrolide A.[44] The best conditions to obtain the requisite *Z*-allylic alcohol precursor **1.70** with a W-based MAP complex involved CM of **1.69** with allylboronic acid pinacol ester followed by oxidation,[28b] delivering the product in 51% overall yield and 91:9 *Z*:*E* ratio. A more direct approach to **1.70** would entail CM of **1.69** and *Z*-2-butene-1,4-diol using Ru carbene complexes. However, using **Ru-3** as catalyst, there was only 25% conversion and the product was formed in poor stereoselectivity (61% *Z* selectivity). In contrast, with **Ru-9**, the required transformation proceeded efficiently to give **1.70** in 70% yield and

(42) Herbert, M. B.; Lan, Y.; Keitz, B. K.; Liu, P.; Endo, K.; Day, M. W.; Houk, K .N.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 7861–7866.
(43) Wright, A. E.; Botelho, J. C.; Guzman, E.; Harmody, D.; Linley, P.; McCarthy, P. J.; Pitts, T. P.; Pomponi, S. A.; Reed, J. K. *J. Nat. Prod.* **2007**, *70*, 412–416.
(44) D'Ambrosio, M.; Guerriero, A.; Debitus, C.; Peitra, F. *Helv. Chim. Acta* **1996**, *79*, 51–60.

98:2 *Z*:*E* ratio. The neopeltolide side chain was obtained following oxidation of the allylic alcohol, allowing for completion of the total synthesis.[45]

Scheme 1.21. *Z*-Selective CM for Stereoselective Synthesis of Neopeltolide and Leucascandrolide A Side Chain.



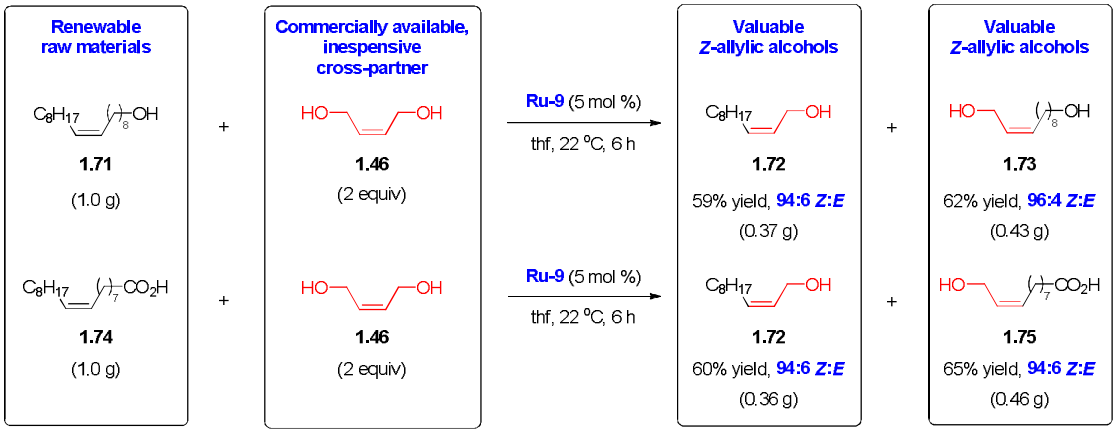
1.4.8. Application to Transformation of Renewable Raw Materials

To further challenge our catalytic system, we wondered if the newly developed Ru catechothiolates are sufficiently reactive to promote CM between two *Z*-1,2-disubstituted alkenes. To the best of our knowledge, there are no prior reports with previously disclosed *Z*-selective Ru carbenes. A compelling application in this context

(45) Yu, M.; Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2014**, *54*, 215–220.

relates to transformations involving animal fats and vegetable oils, which are inexpensive and abundant compounds that could serve as viable replacements for the gradually depleting petrochemicals.[46] These feedstock which includes oleochemicals like oleic acid and oleyl alcohol, naturally occurring sources of *Z*-alkenes, are being utilized more frequently.[47] The ability of OM to directly such renewable raw materials to higher-value products efficiently and stereoselectively would be highly coveted and expected to play an increasingly important role for various oleochemical industries.[48]

Scheme 1.22. Transformation of Renewable Raw Materials to Valuable *Z*-Allylic Alcohols by Stereoselective CM.



As shown in Scheme 1.22, subjecting one gram of oleyl alcohol **1.71** to 2 equivalents of **1.46** and 5 mol % of **Ru-9** delivers *Z*-allylic alcohol **1.72** (0.37 g, 59% yield, 94:6 *Z*:*E*) and diol **1.73** (0.43 g, 62% yield, 96:4 *Z*:*E*), both of which are easily separable. Likewise, one gram of oleic acid **1.74** can be converted by CM to 0.36 g of **1.72** (60% yield, 94:6 *Z*:*E*) and 0.46 g of hydroxy-acid **1.75** (65% yield, 94:6 *Z*:*E*). **1.75** is

(46) Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J.; Schäfer, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 3854–3871.
(47) Gunstone, F. D. in Oleochemical Manufacture and Applications (eds Gunstone, F. D.& Hamilton, R. J.) Vol. 1 (Academic Press, 2001).
(48) Behr, A.; Gomes, J. P. Beilstein *J. Org. Chem.* **2011**, *7*, 1–8.

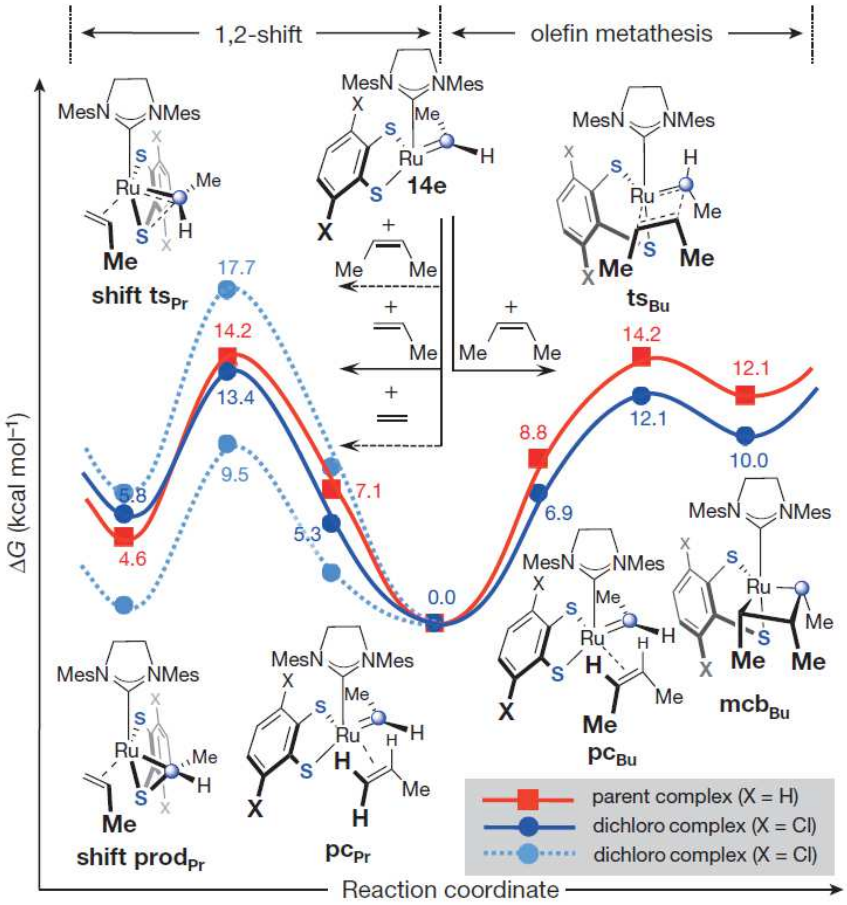
an anti-fungal agent[49] and **1.72** has been used as a precursor for natural product synthesis.[50] The efficiency of these transformations stands in contrast to previous attempts of CM using dichloro-Ru carbenes as catalysts. In a recent effort, CM involving oleic acid or methyl oleate with **1.46** or its bis-acetate derivative in the presence of a Ru-based complex afforded products as complex mixtures of difficult-to-separate stereoisomers (70–85% *E*) with substantial amounts of self-metathesis products (~20%).[51] Moreover, these reactions were performed at 50 °C with added $PhSiCl_3$ (100 equivalents) to ensure high activity. In light of these data, the advantage of Ru catechothiolates extends beyond promoting OM with stereochemcial control.

1.4.9. Investigation of 1,2-Sulfide Shift and OM Pathways Through DFT Calculations

DFT calculations were performed to shed further light on the origin of the improved efficiency with the dichlorocatechothiolate system (vs. the non-chlorinated parent system). Specifically, the non-productive OM pathway involving *Z*-2-butene (Bu) and catalyst decomposition processes entailing competitive 1,2-shift of the more electron-rich *trans*-to-NHC sulfide ligand (cf. Scheme 1.15c) to the electrophilic ethylidene in the presence of ethylene, propene and *Z*-2-butene were investigated (Scheme 1.23). The turnover-limiting barrier (transition state derived from *Z*-2-butene and the dichloro complex $\mathbf{ts_{Bu,Cl}}$) for the OM reaction of the active 14-electron dichlorocatechothiolate species ($\mathbf{14e_{Cl}}$) with *Z*-2-butene to generate the metallacyclobutane ($\mathbf{mcb_{Bu,Cl}}$) was found to be 2.1 kcal mol^{-1} lower in energy compared to $\mathbf{ts_{Bu,H}}$ (14.2 kcal mol^{-1} vs. 12.1 kcal mol^{-}

(49) Suzuki, Y.; Kurita, O.; Kono, Y.; Hyakutake, H.; Sakurai, A. *Biosci. Biotechnol. Biochem.* **1995**, *59*, 2049–2051.
(50) (a) Uehara, H.; Oishi, T.; Yoshikawa, K.; Mochida, K.; Hirama, M. *Tetrahedron Lett.* **1999**, *40*, 8641–8645. (b) Gries, R.; Khaskin, G.; Gotoh, T.; Schaefer, P. W.; Gries, G. *J. Chem. Ecol.* **2005**, *31*, 879–891.
(51) Kajetanowicz, A.; Sytniczuk, A.; Grela, K. *Green Chem.* **2014**, *16*, 1579–1585.

[1]; red vs. blue curve). In addition, the more stabilized metallacycle derived from dichlorocatechothiolate species could be due to a weakened *trans* influence (10.0 kcal mol^{-1} vs. 12.1 kcal mol^{-1} for **mcb$_{Bu,Cl}$** vs. **mcb$_{Bu,H}$**).

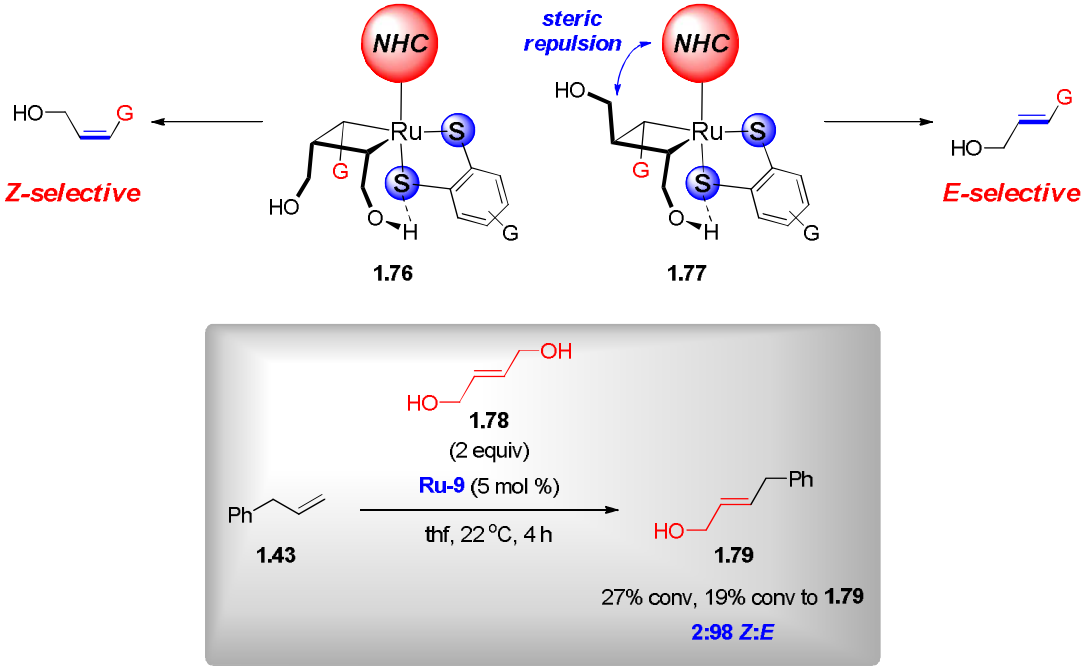


Overall, comparison of the energy barriers for the model OM pathway involving Ru ethylidene and *Z*-2-butene (proceeding through transition state **ts$_{Bu}$**) vs. the 1,2-shift induced by propene (via transition state **shift ts$_{Pr}$**) implies a favorable differentiation between productive and decomposition processes in the case of **Ru-9** (12.1 kcal mol^{-1} and 13.4 kcal mol^{-1} for the transition states derived from OM with *Z*-2-butene (**ts$_{Bu,Cl}$**) vs. the 1,2-shift in the presence of bound propene (**shift ts$_{Pr,Cl}$**), respectively); for **Ru-7**, the two processes are equally preferred (14.2 kcal mol^{-1} for **ts$_{Bu,H}$** and **shift ts$_{Pr,H}$**). It merits

mention that the significantly lower barrier (9.5 kcal mol^{-1}) for the 1,2-shift induced by the π-acidic ethylene (structure of complex not shown; vs. 13.4 kcal mol^{-1} for propene and 17.7 kcal mol^{-1} for *Z*-2-butene) suggests that CM between two terminal alkenes (leading to ethylene formation as byproduct) is detrimental compared to when a 1,2-disubstituted olefin (such as **1.46**) is used.

1.4.10. Preliminary Observation in Kinetically Controlled E-Selective CM

Scheme 1.24. Preliminary Result in *E*-Selective CM of Allylbenzene with *E*-2-Butene-1,4-diol.



CM between a terminal alkene and *Z*-2-butene-1,4-diol **1.46** likely proceeds through metallacyclobutane **1.76** (Scheme 1.24) wherein the metallacycle substituents are oriented away from the sizeable NHC ligand and the alcohol possibly engaging in stabilizing electrostatic interaction with the sulfide ligand (cf. Scheme 1.12). In the same fashion, we wondered if it is possible to develop a kinetically controlled *E*-selective CM by utilizing stereoisomerically pure *E*-2-butene-1,4-diol **1.78** as the cross-partner. We envisioned that the reaction would likely entail the formation of metallacyclobutane **1.77**,

where one methylenehydroxyl motif has to be oriented towards the NHC ligand (probably resulting in unfavorable steric repulsion); collapse of **1.77** will lead to the corresponding *E*-isomer of the product.

To test our hypothesis, we performed the CM transformation of model substrate **1.43** with **1.78** using the conditions established in Scheme 1.19. Even though there was only 19% conversion to *E*-allylic alcohol **1.79**, the almost complete reversal of stereoselectivity (98% *E* selectivity) lends credence to the concept of olefin "stereoretention",[52] where the stereochemistry of the 1,2-disubstituted alkene reagent can be preserved in the catalytic OM process, in the design of *E*-selective OM transformations.

1.5. Conclusions

The discovery of Ru-based dithiolate complexes in 2013 provided us the opportunity of developing broad-scope Ru-catalyzed *Z*-selective OM protocols with complementary reactivity profiles to high-oxidation-state alkylidene catalysts. The investigations described herein are designed with the goal of gaining a deeper understanding of this new class of Ru catalysts. In addition to catalyzing ROMP and ROCM with sterically hindered olefins, we have shown that Ru catechothiolate **Ru-7** is capable of promoting highly efficient and *Z*-selective ROCM transformations with an unprecedented scope of cross-partners including heterocyclic alkenes, enol ethers and vinyl sulfides, 1,3-dienes as well as allylic and homoallylic alcohols. The studies with allyl alcohol and its derived ether revealed a mechanistically significant attribute of Ru dithiolate complexes that arises from stabilizing electrostatic (H-bonding) interactions

(52) For a recent review, see: Montgomery, T. P.; Ahmed, T. S.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 11024–11036.

between the unprotected allylic hydroxyl group and the sulfide *trans* to the NHC. On the other hand, protecting the hydroxyl group proved to be detrimental to reaction efficiency. The first successful cases of *Z*- and diastereoselective ROCM with an enantioenriched secondary allylic alcohol further substantiate the positive influence of the hydroxyl unit, where it is postulated to engage in electrostatic attraction that induces structural organization leading to high diastereofacial differentiation.

Taking advantage of the unique ability of Ru dithiolate complexes in catalyzing OM with alkenes bearing a proximal hydroxyl group, we proceeded to develop a CM method that enables access to synthetically valuable *Z*-allylic alcohols. Preliminary experiments showed that these catalysts are ineffective in promoting CM between two terminal alkenes presumably due to generation of the unstable methylidene complex, which led us to using *Z*-2-butene-1,4-diol **1.46** as a cross-partner to deliver the allylic hydroxyl unit. Based on our understanding of the possible modes of catalyst decomposition that is supported by DFT calculations, different electronically modified catechothiolate complexes **Ru-9**–**13** were subsequently prepared in high yields through a new synthesis route that involved readily accessible and air-stable zinc dithiolate precursors. **Ru-9** was shown to promote CM with a wide array of substrates including sterically encumbered α-branched alkenes, styrenes, 1,3-dienes as well as those that possess commonly occurring functionalities such as a ketone, an aldehyde, a phenol and a carboxylic acid. The high functional group compatibility of **Ru-9** was further highlighted by comparing a number of these CM reactions using the alternative *Z*-selective **Ru-3** catalyst. In all cases, **Ru-9** proved to be superior in both efficiency and stereoselectivity. Utility of the CM protocol was underscored through applications to the stereoselective

synthesis of the side chain of biologically active compounds neopeltolide and leucascandrolide A. Transformation of renewable oleochemical feedstock such as oleic acid and oleyl alcohol through *Z*-selective CM enables efficient access to two different synthetically valuable *Z*-allylic alcohols simultaneously; it merits mention that the analogous reactions with commonly used dichloro-Ru carbenes gave more complicated reaction mixtures with substantial self-metathesis of the starting material. These results also indicate that Ru dithiolate complexes are capable of promoting CM between two *Z*-1,2-disubstituted alkenes, a characteristic not exhibited by previously disclosed *Z*-selective Ru catalysts.

The concept of utilizing a readily available and stereoisomerically pure *Z*-1,2-disubstituted olefin reagent for improved efficiency and *Z* selectivity (by reducing the amount of undesired methylidene complex formation) inspired us to investigate different commercially available *Z*-alkenes to address other unresolved problems in OM, which will be presented in subsequent chapters. The same principle of olefin stereoretention can be potentially extended to kinetically controlled *E*-selective CM, which we have shown herein by switching the cross-partner (**1.46**) to a stereodefined *E*-1,2-disubstituted olefin (**1.78**).

1.6. Experimentals

1.6.1. General

Unless otherwise noted, all transformations were performed with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum line techniques. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.16 ppm, CD_2Cl_2: δ 5.32 ppm, CD_3OD: δ 3.31 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm, C_6D_6: δ 128.00 ppm, CD_2Cl_2: δ 54.00 ppm, CD_3OD: δ 49.00 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS and JEOL Accu TOF Dart (positive mode) at the Boston College Mass Spectrometry Facility. Values for *Z:E* ratios of products were determined by analysis of ^1H NMR spectra.

Solvents:

Solvents (CH_2Cl_2, pentane, benzene) were purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system. Tetrahydrofuran was distilled

from Na/benzophenone. Methanol was distilled over $MgSO_4$. 2-propanol and acetonitrile were used as received. All purification procedures of CM and ROCM products were carried out with reagent grade solvents (purchased from Fisher) under bench-top conditions.

Deuterated solvents:

$CDCl_3$, CD_2Cl_2, C_6D_6 and CD_3OD were purchased from Cambridge Isotope Laboratories and used as received.

Reagents (for *Z*-selective ROCM protocol):

Styrene (Aldrich), allylbenzene (Aldrich), allyl alcohol (Aldrich), allyl(pinacolato)boronate (Frontier Scientific), 3-buten-1-ol (Aldrich), butyl vinyl ether (Aldrich), allyltrimethylsilane (Aldrich), 4-allylanisole (Aldrich), ethyl vinyl sulfide (Aldrich), 1-decene (Aldrich) and (*E*)-1-methoxy-1,3-butadiene (Aldrich) were distilled from CaH_2 under vacuum prior to use. (*E*)-Deca-1,3-diene was prepared according to a literature procedure[28a] and was distilled from CaH_2 under vacuum prior to use. 1-(*tert*-butyldimethylsilyoxy)-3-butene, [53] *N*-phenylpent-4-enamide, [54] 1-tosyl-3-vinyl-1*H*-indole,[55] 2-vinylbenzo[*b*]thiophene[56] and 4-butoxybut-1-ene[57] were prepared according to literature procedures. 5-Norbornene-2-*exo*,3-*exo*-dimethanol **1.36** (Aldrich) and norbornene (Aldrich) were used as received. *(R)*-1-Phenyl-2-propen-1-ol **1.34** (Fluka) was purified by column chromatography prior to use; enantiomeric ratio was determined

(53) Pirrung, M. C.; Webster, N. J. G. *J. Org. Chem.* **1987**, *52*, 3603–3613.
(54) Nicolai, S.; Sedigh-Zadeh, R.; Waser, J. *J. Org. Chem.* **2013**, *78*, 3783–3801.
(55) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693–11712.
(56) Marrocchi, A.; Minuti, L.; Taticchi, A.; Scheeren, H. W. *Tetrahedron* **2001**, *57*, 4959–4965.
(57) Kaur, S.; Crivello, J. V.; Pascuzzi, N. *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 199–209.

by HPLC analysis to be 96:04 (Chiracel OD-H column, 98:2 hexanes:2-propanol, 1 mL/min, 220 nm) in comparison with authentic racemic material.

Reagents (for *Z*-selective CM protocol):

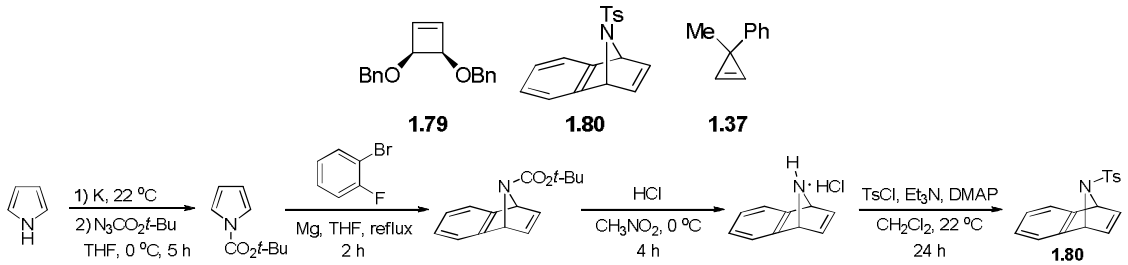
Allylbenzene (Aldrich), allyl butyl ether (Aldrich), 1-dodecene (Aldrich), 4-phenyl-1-buten-4-ol (Aldrich), 5-hexenoic acid (Aldrich), 2,2-dimethyl-4-pentenoic acid (Acros), undecylenic aldehyde (Aldrich), vinylcyclohexane (Aldrich), 4-vinyl-1-cyclohexene (Aldrich), styrene (Aldrich), 4-(trifluoromethyl)styrene (Aldrich), 4-methylstyrene (Aldrich), (*E*)-1-methoxy-1,3-butadiene (Aldrich), vinylboronic acid pinacol ester (Aldrich) and 2,6-lutidine were either distilled (from CaH_2 or $CaCl_2$) under vacuum or dried by azeotropic distillation (with C_6H_6) prior to use. (*E*)-Deca-1,3-diene,[52] (*Z*)-nona-1,3-diene,[58] 1-(*tert*-butyldimethylsilyoxy)-3-butene,[53] 1-(3-butenoxyl)-4-nitrobenzoate,[59] (*E*)-*tert*-butyl penta-2,4-dienoate,[59] benzyl 4-pentenoate,[60] 2-(5-hexenyl)isoindoline-1,3-dione [61] and (*S*,*Z*)-benzyl 2-(((9*H*-fluoren-9-yl)methoxy)carbonylamino)-6-hydroxy4-hexenoate [62] were prepared according to literature procedures. 3,6-Dichloro-1,2-benzenedthiol (Aldrich), 2,5-dimethylbenzenethiol (Aldrich), 2-bromo-5-chlorobenzenethiol (Oakwood), 1,2,3,4-tetrafluorobenzene (Oakwood), 2,5-dibromoaniline (Aldrich), diethyl malonate (Aldrich), thiophosgene (Aldrich), sodium hydride (Aldrich), sodium nitrite (Aldrich), sulfuric acid (Aldrich), hydrochloric acid (Aldrich), zinc acetate dihydrate (Alfa Aesar), ethylenediamine (Aldrich), *n*-butyllithium (Strem), sulfur (Aldrich), potassium ethyl xanthogenate (Aldrich), lithium aluminum

(58) Kliman, L. T.; Mlynarski, S. N.; Ferris, G. E.; Morken, J. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 521–524.
(59) Lipshutz, B. H.; Ghorai, S.; Bošković, Z. *Tetrahedron* **2008**, *64*, 6949–6954.
(60) Kusuma, B. R.; Peterson, L. B.; Zhao, H.; Vielhauer, G.; Holzbeierlein, J.; Blagg, B. S. J. *J. Med. Chem.* **2011**, *54*, 6234–6253.
(61) Smith, B. J.; Sulikowski, G. A. *Angew. Chem. Int. Ed.* **2010**, *49*, 1599–1602.
(62) Ryan, S. J.; Zhang, Y.; Kennan, A. J. *Org. Lett.* **2005**, *7*, 4765–4767.

hydride (Aldrich), second-generation Hoveyda-Grubbs catalyst (Aldrich), *Z*-2-butene-1,4-diol (Fluka), 3'-Allyl-4'-hydroxyacetophenone (Aldrich), oleic acid (Aldrich), oleyl alcohol (Aldrich), ethyl 4-oxazolecarboxylate (TCI), diisobutylaluminum hydride (Strem), iodine (Aldrich), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Strem), potassium phosphate tribasic (Alfa Aesar), triphenylphosphine (Aldrich), tetrabromomethane (Aldrich), allylmagnesium chloride (Aldrich) and copper(I) cyanide (Strem) were used as received.

1.6.2. Preparation of Cyclic Olefin Substrates

Cyclobutene **1.79**[19a] and cyclopropene **1.37**[63] were prepared in analogy to previously reported procedures.



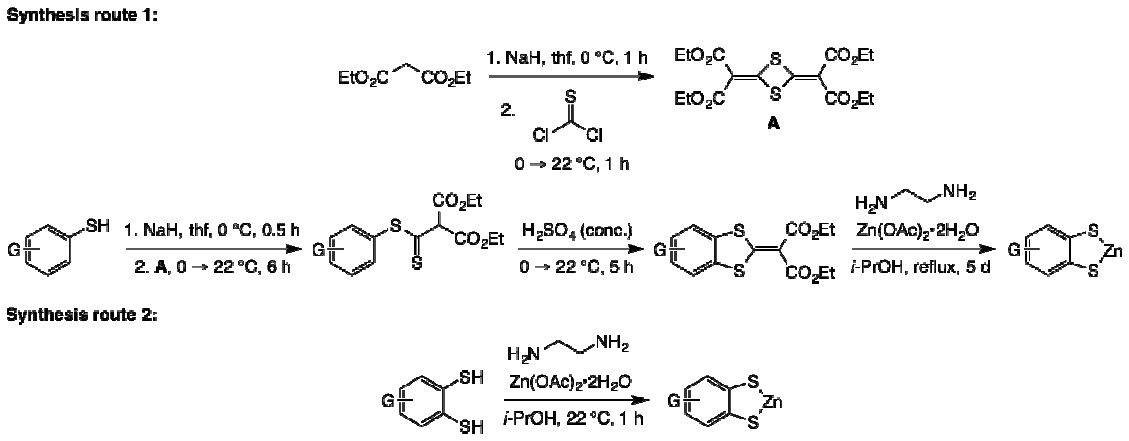
***N*-Tosyl-2,3-Benzo-7-azabicyclo[2.2.1]hepta-2,5-diene 1.80**: 2,3-Benzo-7-azabicyclo[2.2.1]hepta-2,5-diene hydrochloride (precursor to **1.80**) was prepared based on a reported procedure.[64] The ammonium salt (100 mg, 0.557 mmol, 1.00 equiv) was added to a flame-dried round-bottom flask equipped with a stir bar, followed by *p*-toluenesulfonyl chloride (159 mg, 0.835mmol, 1.50 equiv), triethylamine (233 μL, 1.67 mmol, 3.00 equiv), dimethylaminopyridine (6.8 mg, 0.056 mmol, 0.10 equiv) and CH_2Cl_2 (3 mL). The mixture was allowed to stir at 22 °C for 24 hours. The resulting mixture was

(63) M. Rubin, V. Gevorgyan, *Synthesis* **2004**, 796–800.
(64) Carpino, L. A.; Barr, D. E. *J. Org. Chem.* **1966**, *31*, 764–767.

washed with H_2O (3 x 5 mL). The aqueous layers were combined and back-washed with dichloromethane (2 x 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a brown residue, which was purified by silica gel chromatography (10% EtOAc in hexanes to 20% EtOAc in hexanes) to afford **1.80** as brown solid (124 mg, 0.417 mmol, 75% yield); mp: 152–154 ^oC; **IR (CH_2Cl_2)**: 3052 (w), 2920 (w), 1597 (w), 1448 (w), 1339 (m), 1157 (m), 1092 (s), 599 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.46 (2H, d, J = 8.4 Hz), 7.09 (2H, dd, J = 8.0, 0.5 Hz), 7.03 (2H, dd, J = 5.1, 3.0 Hz), 6.80–6.77 (4H, m), 5.44 (2H, s), 2.34 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 147.4, 143.4, 142.5, 135.4, 129.5, 128.4, 125.2, 121.3, 67.9, 21.7; **HRMS $[M+H]^+$** calcd for $C_{17}H_{16}NO_2S$: 298.0902, found: 298.0893.

1.6.3. Synthesis of Ru-Based Complexes

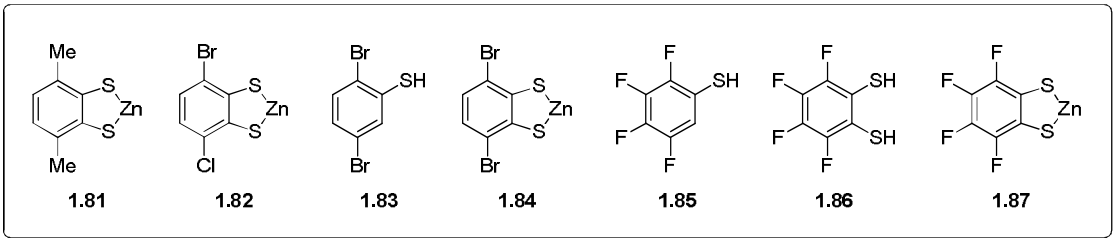
a. Preparation of zinc dithiolates



Zinc dithiolate salts were prepared either in analogy to a previously reported procedure (synthesis route 1)[65] or through synthesis route 2 as shown above.

(65) Yeung, C. M.; Klein, L. L. *Tetrahedron Lett.* **1990**, *31*, 2121–2124.

Zinc 3,6-dichlorobenzene-1,2-dithiolate (1.48): Prepared through synthesis route 2 starting from 3,6-dichlorobenzene-1,2-dithiol **1.47**. A mixture of 3,6-dichlorobenzene-1,2-dithiol (211 mg, 1.00 mmol, 1.00 equiv), $Zn(OAc)_2 \bullet 2H_2O$ (878 mg, 4.00 mmol, 4.00 equiv) and ethylenediamine (0.40 mL, 6.00 mmol, 6.00 equiv) in *i*-PrOH (8 mL) was allowed to stir for 1 hour at 22 °C. The precipitated solid was filtered, washed with methanol (5.0 mL) and hot chloroform (5.0 mL), and dried in a vacuum dessicator overnight to afford **1.48** (261 mg, 0.95 mmol, 95% yield) as white solid.



Zinc 3,6-dimethylbenzene-1,2-dithiolate (1.81): Prepared through route 1 starting from 2,5-dimethylbenzenethiol and isolated as white solid in 21% overall yield.

Zinc 3-bromo-6-chlorobenzene-1,2-dithiolate (1.82): Prepared through route 1 starting from 2-bromo-5-chlorobenzenethiol and isolated as white solid in 28% overall yield.

2,5-Dibromobenzenethiol (1.83): Prepared in analogy to a previously reported procedure.[66] To a suspension of 2,5-dibromoaniline (1.25 g, 5.00 mmol, 1.00 equiv) in 6M HCl (9.1 mL) at –5 °C was added dropwise a solution of $NaNO_2$ (0.380 g, 5.50 mmol, 1.10 equiv) in water (2.5 mL), and the mixture was allowed to stir for 1 hour at –5 °C. To the mixture was added a solution of $EtOCS_2K$ (1.36 g, 8.50 mmol, 1.70 equiv) in water (2.5 mL), and the mixture was allowed to stir for 4 hours at 80 °C. The aqueous layer was washed with Et_2O (3 x 20.0 mL) and the combined organic layers were dried

(66) Agou, T.; Kobayashi, J.; Kawashima, T. J. *Chem. Eur. J.* **2007**, *13*, 8051–8060.

over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a solid. A solution of the unpurified product in tetrahydrofuran (2.5 mL) was slowly added to a suspension of $LiAlH_4$ (0.455 g, 12.0 mmol, 2.40 equiv) in tetrahydrofuran (5 mL) at 0 °C. The mixture was allowed to stir for 12 hours at 22 °C. The reaction was quenched by pouring into a mixture of conc. HCl (2.5 mL) and crushed ice and washing with Et_2O (3 x 20.0 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford **1.83** (0.805 g, 3.00 mmol, 60% yield) as yellow oil, which was used in the next step without purification.

Zinc 3,6-dibromobenzene-1,2-dithiolate (1.84): Prepared through route 1 starting from **1.83** and isolated as white solid in 15% overall yield.

2,3,4,5-Tetrafluorobenzenethiol (1.85): To a stirred solution of *n*-BuLi (0.69 mL, 1.10 mmol, 1.10 equiv) in tetrahydrofuran (2 mL) at –78 °C was added 1,2,3,4-tetrafluorobenzene (150 mg, 1.00 mmol, 1.00 equiv) over 30 minutes. The solution was allowed to stir for a further 45 minutes at the same temperature, after which dry, powdered sulfur (35.3 mg, 1.10 mmol, 1.10 equiv) was added in portions over 30 minutes. The solution was allowed to stir for a further 30 minutes at –78 °C. The reaction was quenched with 6M HCl (1.5 mL) and washed with Et_2O (3 x 5.0 mL). The combined organic layers were washed with water (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford **1.85** (75.0 mg, 0.41 mmol, 41% yield) as yellow oil, which was used in the next step without purification.

3,4,5,6-Tetrafluorobenzene-1,2-dithiol (1.86): To a stirred solution of *n*-BuLi (0.28 mL, 0.45 mmol, 1.10 equiv) in tetrahydrofuran (1 mL) at –78 °C was added **1.85** (75.0 mg, 0.41 mmol, 1.00 equiv) in tetrahydrofuran (1 mL) over 30 minutes. The solution was

allowed to stir for a further 45 minutes at –78 °C, after which dry, powdered sulfur (14.4 mg, 0.45 mmol, 1.10 equiv) was added in portions over 30 minutes. The solution was allowed to stir for a further 30 minutes at –78 °C. The reaction was quenched with 6M HCl (0.6 mL) and washed with Et_2O (3 x 3.0 mL). The combined organic layers were washed with water (5.0 mL), dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford **1.86** (39.5 mg, 0.18 mmol, 45% yield) as brown oil, which was used in the next step without purification.

Zinc 3,4,5,6-tetrafluorobenzene-1,2-dithiolate (1.87): Prepared through route 2 starting from **1.86**. A mixture of **1.86** (214 mg, 1.00 mmol, 1.00 equiv), $Zn(OAc)_2•2H_2O$ (878 mg, 4.00 mmol, 4.00 equiv) and ethylenediamine (0.40 mL, 6.00 mmol, 6.00 equiv) in *i*-PrOH (8 mL) was allowed to stir for 1 hour at 22 °C. The precipitated solid was filtered, washed with methanol (5.0 mL) and hot chloroform (5.0 mL), and dried in a vacuum dessicator overnight to afford **1.87** (155 mg, 0.56 mmol, 56% yield) as white solid.

b. Preparation of Ru-based dithiolate complexes

Complex Ru-9: To a 2-dram vial charged with a stir bar and zinc dithiolate **1.48** (26.9 mg, 0.098 mmol, 2.00 equiv) under N_2 atmosphere, a solution of second-generation complex **Ru-5** (30.7 mg, 0.049 mmol, 1.00 equiv) in tetrahydrofuran (610 μL) is added. The resulting mixture is allowed to stir for 5 hours at 22 °C, at which time the solvent is evaporated under vacuum. Residual tetrahydrofuran is removed through co-evaporation with pentane (2 x 2 mL). The obtained solid is dissolved in dichloromethane and passed through a short column of Celite (4 cm in height) in a pipette (~0.5 cm diameter) with dichloromethane (10 mL). After removal of dichloromethane from the filtrate and co-evaporation with pentane, **Ru-9** is isolated as brown solid (31.9 mg, 0.042 mmol, 85%

yield); **^{1}H NMR (400 MHz, CD_2Cl_2)**: δ 14.30 (1H, s), 7.32–7.26 (1H, m), 7.10 (1H, d, J = 8.1 Hz), 6.96 (2H, s), 6.87 (1H, dd, J = 8.1, 0.6 Hz), 6.82–6.76 (2H, m), 6.61 (1H, dd, J = 7.5, 1.6 Hz), 6.45–6.00 (2H, br s), 5.29–5.25 (1H, m), 3.92 (4H, br s), 2.52 (6H, br s), 2.30–2.10 (3H, br s), 2.20 (6H, s), 1.75–1.55 (3H, br s), 1.68 (3H, d, J = 6.6 Hz), 1.50 (3H, d, J = 6.6 Hz); **^{13}C NMR (100 MHz, CD_2Cl_2)**: δ 253.9 (d, J = 13.6 Hz), 218.0, 154.9, 154.2, 142.4, 141.9, 138.8 (br), 136.6 (br), 136.3 (br), 131.6, 130.0, 130.0, 129.7, 128.0, 124.7, 123.4, 122.6, 121.9, 115.9, 82.2, 52.0, 24.5, 21.6, 21.3, 19.4 (br), 18.0 (br).

Complex Ru-10: To a 2-dram vial charged with a stir bar and zinc dithiolate **1.84** (35.6 mg, 0.098 mmol, 2.00 equiv) under N_2 atmosphere, a solution of second-generation complex **Ru-5** (30.7 mg, 0.049 mmol, 1.00 equiv) in tetrahydrofuran (610 μL) is added. The resulting mixture is allowed to stir for 5 hours at 22 °C, at which time the solvent is evaporated under vacuum. Residual tetrahydrofuran is removed through co-evaporation with pentane (2 x 2 mL). The obtained solid is dissolved in dichloromethane and passed through a short column of Celite (4 cm in height) in a pipette (~0.5 cm diameter) with dichloromethane (10 mL). After removal of dichloromethane from the filtrate and co-evaporation with pentane, **Ru-10** is isolated as brown solid (33.5 mg, 0.039 mmol, 80% yield); **^{1}H NMR (400 MHz, CD_2Cl_2)**: δ 14.29 (1H, s), 7.35–7.27 (1H, m), 7.11 (1H, d, J = 8.3 Hz), 7.00–6.96 (3H, m), 6.90 (1H, dd, J = 8.1, 0.7 Hz), 6.81 (1H, t, J = 7.4 Hz), 6.63 (1H, dd, J = 7.6, 1.6 Hz), 6.57–5.87 (2H, br s), 5.31–5.22 (1H, m), 3.94 (4H, br s), 2.54 (6H, br s), 2.38–2.03 (3H, br s), 2.21 (6H, s), 1.73–1.45 (3H, br s), 1.68 (3H, d, J = 6.6 Hz), 1.51 (3H, d, J = 6.5 Hz); **^{13}C NMR (100 MHz, CD_2Cl_2)**: δ 254.0 (d, J = 23.8 Hz), 218.2, 155.5, 154.9, 144.0, 141.9, 137.1, 136.6 (br), 136.2, 130.1 (br), 129.7 (br),

128.0, 126.9, 125.5, 124.7, 123.2, 122.6, 121.2, 115.8, 82.0, 52.0, 24.5, 21.7, 21.3, 19.4 (br), 18.6.

Complex Ru-11: To a 2-dram vial charged with a stir bar and zinc dithiolate **1.82** (31.3 mg, 0.098 mmol, 2.00 equiv) under N_2 atmosphere, a solution of second-generation Hoveyda-Grubbs catalyst (30.7 mg, 0.049 mmol, 1.00 equiv) in tetrahydrofuran (610 μL) is added. The resulting mixture is allowed to stir for 5 hours at 22 °C, at which time the solvent is evaporated under vacuum. Residual tetrahydrofuran is removed through co-evaporation with pentane (2 x 2 mL). The obtained solid is dissolved in dichloromethane and passed through a short column of Celite (4 cm in height) in a pipette (~0.5 cm diameter) with dichloromethane (10 mL). After removal of dichloromethane from the filtrate and co-evaporation with pentane, **Ru-11** is isolated as brown solid (33.3 mg, 0.041 mmol, 84% yield) as mixture of carbene isomers; **^{1}H NMR (400 MHz, CD_2Cl_2)**: δ 14.31 (0.5H, 1s), 14.30 (0.5H, s), 7.35–7.28 (1H, m), 7.11 (1H, d, J = 8.3 Hz), 7.06 (0.5H, d, J = 8.1 Hz), 7.01–6.96 (2.5H, m), 6.87–6.78 (1.5H, m), 6.80 (0.5H, d, J = 8.0 Hz), 6.73 (0.5H, d, J = 8.1 Hz), 6.68–6.60 (1.5H, m), 6.39–6.01 (1H, br s), 5.32–5.24 (1H, m), 3.94 (4H, br s), 2.54 (6H, br s), 2.35–2.10 (3H, br s), 2.21 (6H, s), 1.77–1.48 (3H, br s), 1.69 (3H, dd, J = 6.6, 3.0 Hz), 1.56–1.50 (3H, m); **^{13}C NMR (100 MHz, CD_2Cl_2)**: δ 254.1, 253.9, 218.2, 218.0, 156.1, 154.9, 153.6, 144.3, 142.1, 141.9, 138.8 (br), 136.7, (br), 132.4, 130.8, 129.9, 129.7, 128.0, 126.7, 125.2, 124.7, 123.6, 122.6, 122.3, 122.3, 120.3, 115.9, 82.2, 82.1, 52.0, 26.2, 24.5, 24.5, 21.7, 21.6, 21.3, 19.6 (br), 19.4 (br).

Complex Ru-12: To a 2-dram vial charged with a stir bar and zinc dithiolate **1.87** (27.2 mg, 0.098 mmol, 2.00 equiv) under N_2 atmosphere, a solution of **Ru-5** (30.7 mg, 0.049

mmol, 1.00 equiv) in tetrahydrofuran (610 μL) is added. The resulting mixture is allowed to stir for 5 hours at 22 °C, at which time the solvent is evaporated under vacuum. Residual tetrahydrofuran is removed through co-evaporation with pentane (2 x 2 mL). The obtained solid is dissolved in dichloromethane and passed through a short column of Celite (4 cm in height) in a pipette (~0.5 cm diameter) with dichloromethane (10 mL). After removal of dichloromethane from the filtrate and co-evaporation with pentane, **Ru-12** is isolated as brown solid (30.7 mg, 0.040 mmol, 82% yield); **^{1}H NMR (400 MHz, CD_2Cl_2)**: δ 14.43 (1H, s), 7.32–7.26 (1H, m), 7.12 (1H, d, J = 8.4 Hz), 6.95 (2H, s), 6.80 (1H, t, J = 7.4 Hz), 6.70–6.50 (1H, br s), 6.60 (1H, dd, J = 7.5, 1.6 Hz), 6.11 (1H, br s), 5.32–5.29 (1H, m), 3.92 (4H, br s), 2.49 (6H, br s), 2.37–2.15 (3H, br s), 2.18 (6H, s), 1.73 (3H, d, J = 6.7 Hz), 1.62 (3H, br s), 1.47 (3H, d, J = 6.6 Hz); **^{13}C NMR (100 MHz, CD_2Cl_2)**: 255.2 (d, J = 28.3 Hz), 216.8, 144.5 (ddd, J = 236.0, 43.8, 10.5 Hz), 141.9, 139.9–137.6 (m), 138.9 (d, J = 17.6 Hz), 138.6 (br), 136.6 (br), 134.9 (dt, J = 129.0, 18.0 Hz), 130.0, 129.7, 129.7, 128.9, 128.2, 126.9 (d, J = 18.1 Hz), 124.8, 122.8, 116.3, 83.3, 52.0, 24.8, 21.5, 21.2, 19.8 (br), 19.0 (br).

1.6.4. Z-Selective Ring-Opening/Cross-Metathesis (ROCM) Reactions

General Procedure

In an N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar is charged with strained alkene substrate (1.0 equiv) and terminal olefin cross partner (10 equiv). To this vial, a solution of Ru complex **Ru-7** (2.0–5.0 mol %) in dichloromethane is added. The resulting solution is allowed to stir for 2–12 hours at 22–40 °C, after which the reaction is quenched by addition of wet diethyl ether and concentrated *in vacuo*

(percent conversion determined by 400 MHz or 500 MHz ^{1}H NMR analysis). Purification is performed through silica gel chromatography.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-3-(Trimethylsilyl)prop-1-enyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.10):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-*exo*,3-*exo*-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and allyltrimethylsilane (111 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 30% EtOAc in hexanes) to afford **1.10** (23.2 mg, 0.0864 mmol, 89% yield) as colorless oil; **IR (CH_2Cl_2)**: 3274 (br), 2951 (w), 2918 (w), 1640 (w), 1398 (w), 1048 (w), 993 (w), 850 (s), 837 (s), 663 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.74 (1H, ddd, J = 17.1, 10.1, 7.9 Hz), 5.48–5.31 (1H, m), 5.15 (1H, dd, J = 12.0, 10.8 Hz), 5.00 (1H, ddd, J = 17.0, 1.8, 0.9 Hz), 4.95 (1H, dd, J = 10.1, 1.3 Hz), 3.75–3.62 (4H, m), 3.32 (2H, s), 2.42 (1H, ddd, J = 20.5, 12.7, 7.8 Hz), 2.21– 1.98 (3H, m), 1.85 (1H, dt, J = 12.3, 6.1 Hz), 1.53 (1H, ddd, J = 13.6, 9.7, 1.3 Hz), 1.36 (1H, ddd, J = 13.6, 7.5, 1.5 Hz), 1.22 (1H, t, J = 12.0 Hz), 0.00 (9H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.8, 130.9, 126.4, 114.4, 62.3, 62.3, 50.3, 48.6, 46.6, 39.9, 39.5, 18.8, -1.7; **HRMS [M+H-H_2O]$^+$** calcd for $C_{15}H_{27}OSi$: 251.1831, found: 251.1837.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-3-(4-Methoxyphenyl)prop-1-enyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.11):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and 4-allylanisole (144 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 40% EtOAc in hexanes) to afford **1.11** (24.4 mg, 0.0807 mmol, 83% yield) as yellow oil; **IR (CH_2Cl_2)**: 3286 (br), 2917 (m), 1610 (w), 1509 (s), 1463 (w), 1243 (s), 1175 (m), 1033 (s), 995 (m), 911 (m), 816 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.09 (2H, d, J = 8.7 Hz), 6.83 (2H, d, J = 8.6 Hz), 5.75 (1H, ddd, J = 16.0, 12.0, 8.0 Hz), 5.57 (1H, dt, J = 10.7, 7.5 Hz), 5.37 (1H, t, J = 10.2 Hz), 5.05–4.99 (1H, m), 4.98–4.95 (1H, m), 3.78 (3H, s), 3.75–3.64 (4H, m), 3.34 (1H, dd, J = 10.9, 7.6 Hz), 3.29–3.26 (2H, m), 2.69–2.56 (1H, m), 2.27–2.19 (1H, m), 2.16–2.03 (2H, m), 1.93 (1H, dt, J = 12.3, 6.2 Hz), 1.33–1.22 (2H, m); **^{13}C NMR (100 MHz, C_6D_6)**: δ 158.6, 142.1, 134.1, 133.2, 129.5, 129.5, 114.3, 114.2, 61.8, 54.8, 50.3, 48.8, 46.4, 40.1, 39.7, 33.2; **HRMS $[M+H]^+$** calcd for $C_{19}H_{27}O_3$: 303.1960, found: 303.1955.

(*Z*)-5-((1*R*,2*R*,3*S*,4*S*)-2,3-Bis(hydroxymethyl)-4-vinylcyclopentyl)-*N*-phenylpent-4-enamide (1.12):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-

2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and *N*-phenylpent-4-enamide (320 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed >98% conv of **1.36**, and the ROCM product was obtained in >98:02 *Z*/*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 50% EtOAc in hexanes) to afford **1.12** (20.8 mg, 0.0631 mmol, 65% yield) as colorless oil; **IR (CH_2Cl_2)**: 3299 (br), 2920 (m), 2853 (m), 1663 (m), 1599 (m), 1545 (m), 1443 (s), 1027 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.61 (1H, s), 7.50 (2H, d, J = 7.7 Hz), 7.31 (2H, t, J = 7.9 Hz), 7.10 (1H, t, J = 7.4 Hz), 5.75 (1H, ddd, J = 17.1, 10.1, 8.1 Hz), 5.45–5.36 (1H, m), 5.25 (1H, t, J = 10.2 Hz), 5.02 (1H, ddd, J = 17.1, 1.8, 1.0 Hz), 4.94 (1H, ddd, J = 10.1, 1.8, 0.5 Hz), 3.79 (1H, dd, J = 11.6, 2.7 Hz), 3.71 (1H, dd, J = 12.0, 2.5 Hz), 3.67–3.61 (2H, m), 2.92–2.80 (1H, m), 2.75–2.65 (1H, m), 2.57–2.43 (2H, m), 2.36–2.28 (2H, m), 2.03–1.81 (4H, m), 1.23–1.16 (2H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.4, 142.1, 138.0, 135.1, 129.2, 128.5, 124.5, 119.9, 114.1, 61.8, 60.4, 50.1, 48.7, 45.6, 39.8, 39.2, 38.0, 23.9; **HRMS $[M+H]^+$** calcd for $C_{20}H_{28}NO_3$: 330.2069, found: 330.2076.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-4-(*tert*-Butyldimethylsilyloxy)but-1-enyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.13):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and 1-(*tert*-butyldimethylsilyoxy)-3-butene (181 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed 89% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The

resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 30% EtOAc in hexanes) to afford **1.13** (22.5 mg, 0.0661 mmol, 68% yield) as yellow oil; **IR (CH_2Cl_2)**: 3299 (br), 2926 (s), 2856 (m), 1639 (w), 1463 (w), 1095 (m), 1046 (m), 836 (s); **^{1}H NMR (500 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.76 (1H, ddd, J = 17.8, 10.3, 8.3 Hz), 5.43–5.36 (1H, m), 5.30 (1H, t, J = 10.3 Hz), 5.04–4.98 (1H, m), 4.94 (1H, ddd, J = 10.1, 1.7, 0.8 Hz), 3.75–3.71 (1H, m), 3.69 (1H, d, J = 10.6 Hz), 3.67–3.58 (4H, m), 2.67– 2.57 (1H, m), 2.42– 2.28 (2H, m), 2.25– 2.16 (2H, m), 2.08– 2.00 (1H, m), 1.95 (1H, tdd, J = 10.3, 7.7, 2.8 Hz), 1.89 (1H, dt, J = 12.3, 6.3 Hz), 1.27–1.19 (2H, m), 0.90 (9H, d, J = 0.7 Hz), 0.07 (6H, s); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 142.1, 134.8, 127.2, 114.1, 63.4, 62.3, 61.3, 50.1, 48.6, 46.1, 39.8, 39.7, 31.5, 26.2, –5.1, –5.1; **HRMS [M+Na]$^+$** calcd for $C_{19}H_{36}O_3NaSi$: 363.2326, found: 363.2330.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-Dec-1-enyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.14):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and 1-decene (136 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed 91% consumption of **1.36**, and the ROCM product was obtained in 92:8 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 30% EtOAc in hexanes) to afford **1.14** (16.6 mg, 0.0564 mmol, 58% yield) as colorless oil; **IR (CH_2Cl_2)**: 3274 (br), 2921 (s), 2853 (m), 1640 (w), 1458 (w), 1029 (m), 993 (m), 911 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.74 (1H, ddd, J = 17.2, 10.1, 7.9 Hz), 5.39 (1H, dt, J = 10.8, 7.3 Hz), 5.22 (1H, dd, J = 10.8, 9.5 Hz), 5.01 (1H, dd, J = 17.0, 1.8, 0.9 Hz), 4.96 (1H, ddd, J =

10.1, 1.8, 0.6 Hz), 3.79– 3.58 (4H, m), 2.84 (2H, s), 2.54–2.41 (1H, m), 2.19–1.97 (5H, m), 1.86 (1H, dt, *J* = 12.3, 6.1, Hz), 1.34–1.19 (13H, m), 0.88 (3H, t, *J* = 6.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.7, 132.9, 131.0, 114.5, 62.3, 62.3, 50.1, 48.6, 46.6, 40.0, 39.8, 32.1, 30.1, 29.7, 29.5, 29.5, 27.8, 22.8, 14.3; **HRMS $[M+H]^+$** calcd for $C_{19}H_{35}O_2$: 295.2637, found: 295.2634.

((3*S*,4*R*,*Z*)-7-Phenylhepta-1,5-diene-3,4-diyl)bis(oxy)bis(methylene)dibenzene (1.16):

Following the general procedure, a solution of **Ru-7** (1.9 mg, 2.8 μmol, 5.0 mol %) in dichloromethane (113 μL) was transferred by syringe to a vial containing cyclobutene **1.79** (15.0 mg, 0.0563 mmol, 1.00 equiv) and allylbenzene (67.0 mg, 0.563 mmol, 10.0 equiv). The resulting solution was allowed to stir for 12 hours at 40 °C. Analysis of the unpurified mixture revealed 75% consumption of **1.79**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) followed by passing through a plug of activated charcoal with 50% Et_2O in pentane to afford **1.16** (12.6 mg, 0.0328 mmol, 58% yield) as colorless oil; **IR (CH_2Cl_2)**: 3027 (w), 2918 (w), 2860 (w), 1602 (w), 1495 (w), 1453 (m), 1088 (s), 1069 (s), 1028 (m), 927 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.36–7.27 (10H, m), 7.25–7.17 (3H, m), 7.12 (2H, d, *J* = 7.3 Hz), 5.96–5.83 (2H, m), 5.56 (1H, ddt, *J* = 11.0, 9.4, 1.7 Hz), 5.35–5.29 (2H, m), 4.67 (2H, d, *J* = 12.2 Hz), 4.46 (2H, dd, *J* = 12.2, 8.2 Hz), 4.36 (1H, ddd, *J* = 9.4, 4.7, 1.0 Hz), 3.92–3.85 (1H, m), 3.33 (2H, t, *J* = 6.9 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.4, 138.8, 135.7, 133.5, 128.6, 128.6, 128.4, 128.4, 128.4, 128.3, 127.8, 127.8, 127.5, 127.5, 126.2, 119.0, 82.7, 76.3, 70.6, 70.3, 34.3; **HRMS $[M+NH_4]^+$** calcd for $C_{27}H_{32}NO_2$: 402.2433, found: 402.2443.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-2-(1-Tosyl-1*H*-indol-3-yl)vinyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.17):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and 1-tosyl-3-vinyl-1*H*-indole (289 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.36**, and the ROCM product was obtained in 93:7 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 40% EtOAc in hexanes) to afford 1.17 (40.9 mg, 0.0906 mmol, 93% yield) as off-white wax; **IR (CH_2Cl_2)**: 3308 (br), 3076 (w), 2922 (m), 1639 (w), 1597 (w), 1447 (m), 1370 (m), 1173 (s), 965 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.99 (1H, d, J = 8.3 Hz), 7.76 (2H, d, J = 8.4 Hz), 7.59 (1H, s), 7.47 (1H, d, J = 7.8 Hz), 7.35–7.30 (1H, m), 7.22 (3H, t, J = 7.2 Hz), 6.38 (1H, d, J = 11.3 Hz), 5.76 (1H, ddd, J = 17.1, 10.1, 8.1 Hz), 5.68 (1H, dd, J = 11.3, 10.1 Hz), 5.09–5.02 (1H, m), 5.00 (1H, dd, J = 10.1, 1.3 Hz), 3.73–3.68 (2H, m), 3.61–3.59 (2H, m), 3.10 (2H, s), 2.82–2.73 (1H, m), 2.33 (3H, s), 2.32–2.22 (1H, m), 2.17–2.12 (2H, m), 2.00 (1H, dt, J = 12.5, 6.3 Hz), 0.90–0.83 (1H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.1, 141.4, 138.0, 135.2, 134.9, 131.0, 130.0, 126.9, 125.1, 123.5, 123.3, 119.6, 119.1, 118.5, 114.8, 113.8, 61.9, 61.9, 50.2, 48.6, 46.3, 41.3, 39.7, 21.7; **HRMS $[M+H]^+$** calcd for $C_{26}H_{30}NO_4S$: 452.1896, found: 452.1887.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-2-(Benzo[*b*]thiophen-2-yl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.18):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and 2-vinylbenzo[*b*]thiophene (156 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 40% EtOAc in hexanes) to afford **1.18** (29.6 mg, 0.0941 mmol, 97% yield) as yellow oil; **IR (CH_2Cl_2)**: 3275 (br), 3070 (w), 2917 (m), 2850 (w), 1638 (w), 1456 (w), 1015 (m), 993 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.77 (1H, dd, J = 7.6, 0.8 Hz), 7.73–7.68 (1H, m), 7.38–7.26 (2H, m), 7.16 (1H, s), 6.61 (1H, dd, J = 11.5, 0.6 Hz), 5.77 (1H, ddd, J = 17.4, 10.0, 8.0 Hz), 5.56 (1H, t, J = 10.8 Hz), 5.11–5.02 (1H, m), 5.00 (1H, dd, J = 10.1, 1.7 Hz), 3.82–3.76 (2H, m), 3.73–3.65 (2H, m), 3.26–2.97 (3H, m), 2.37–2.29 (1H, m), 2.21–2.17 (2H, m), 2.11 (1H, dt, J = 12.4, 6.3 Hz), 1.39–1.31 (1H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.4, 140.0, 139.8, 139.3, 136.4, 124.7, 124.7, 123.5, 123.0, 122.1, 122.1, 114.8, 62.3, 62.2, 50.8, 48.7, 46.6, 41.6, 39.5; **HRMS $[M+H]^+$** calcd for $C_{19}H_{23}O_2S$: 315.1419, found: 315.1410.

((1*S*,2*R*,3*R*,5*S*)-3-((1*Z*,3*E*)-4-Methoxybuta-1,3-dienyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.19):

Following the general procedure, a solution of **Ru-7** (1.4 mg, 1.9 μmol, 2.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-

2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and (*E*)-1-methoxy-1,3-butadiene (82.0 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the ^{1}H NMR (400 MHz) spectrum revealed >98% consumption of **1.36**, and the ROCM product was obtained in 91:9 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 40% EtOAc in hexanes) to afford **1.19** (19.5 mg, 0.0818 mmol, 84% yield) as colorless oil; **IR (CH_2Cl_2)**: 3305 (br), 2920 (m), 1648 (m), 1608 (m), 1452 (w), 1210 (s), 1027 (s), 993 (s), 912 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.56 (1H, d, J = 12.3 Hz), 5.88 (1H, t, J = 11.0 Hz), 5.80–5.66 (2H, m), 5.09–4.98 (2H, m), 4.96 (1H, dd, J = 10.1, 1.7 Hz), 3.76–3.63 (4H, m), 3.60 (3H, s), 3.28 (2H, s), 2.64–2.52 (1H, m), 2.28–2.19 (1H, m), 2.15–1.99 (2H, m), 1.93 (1H, dt, J = 12.4, 6.2 Hz), 1.24 (1H, d, J = 11.2 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 152.1, 141.7, 129.9, 125.3, 114.5, 101.7, 62.2, 62.0, 56.9, 50.3, 48.5, 46.5, 40.3, 39.9; **HRMS $[M+H-H_2O]^+$** calcd for $C_{14}H_{21}O_2$: 221.1542, found: 221.1545.

((1*S*,2*R*,3*R*,5*S*)-3-((1*Z*,3*E*)-Deca-1,3-dienyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.20):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and (*E*)-deca-1,3-diene (134 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the ^{1}H NMR (400 MHz) spectrum revealed >98% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 30% EtOAc in

hexanes) to afford **1.20** (22.8 mg, 0.0780 mmol, 80% yield) as colorless oil; **IR (CH_2Cl_2)**: 3276 (br), 2922 (s), 2854 (m), 1639 (w), 1455 (m), 1027 (s), 983 (s), 946 (s), 910 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.25 (1H, ddd, J = 13.6, 11.5, 6.0 Hz), 5.97 (1H, t, J = 10.9 Hz), 5.82–5.61 (2H, m), 5.16 (1H, t, J = 10.2 Hz), 5.04–4.98 (1H, m), 4.96 (1H, dd, J = 10.1, 1.8, Hz), 3.77–3.61 (4H, m), 3.22 (2H, s), 2.70–2.61 (1H, m), 2.28–2.16 (1H, m), 2.15–1.99 (4H, m), 1.93 (1H, dt, J = 12.3, 6.2 Hz), 1.42–1.24 (9H, m), 0.88 (3H, t, J = 6.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.6, 136.0, 132.6, 129.6, 125.5, 114.5, 62.2, 62.1, 50.2, 48.6, 46.5, 40.2, 40.0, 33.1, 31.9, 29.5, 29.1, 22.8, 14.3; **HRMS $[M+H]^+$** calcd for $C_{19}H_{33}O_2$: 293.2481, found: 293.2473.

((3*S*,4*R*,5*Z*,7*E*)-8-Methoxyocta-1,5,7-triene-3,4-diyl)bis(oxy)bis(methylene)dibenzene (1.21):

Following the general procedure, a solution of **Ru-7** (1.9 mg, 2.8 μmol, 5.0 mol %) in dichloromethane (113 μL) was transferred by syringe to a vial containing cyclobutene **1.79** (15.0 mg, 0.0563 mmol, 1.00 equiv) and (*E*)-1-methoxy-1,3-butadiene (47.0 mg, 0.563 mmol, 10.0 equiv). The resulting solution was allowed to stir for 12 hours at 40 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.79**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **1.21** (17.4 mg, 0.0497 mmol, 88% yield) as colorless oil; **IR (CH_2Cl_2)**: 2918 (w), 2850 (w), 1649 (m), 1608 (w), 1453 (w), 1335 (w), 1210 (s), 1168 (m), 1087 (s), 1065 (s), 925 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.38–7.29 (8H, m), 7.27–7.23 (2H, m), 6.63 (1H, d, J = 12.3 Hz), 6.16 (1H, t, J = 11.2 Hz), 5.89 (1H, ddd, J = 17.3, 10.4, 7.7 Hz), 5.56 (1H, t, J = 12.1 Hz), 5.35–5.25 (2H, m), 5.21 (1H, t, J = 10.3 Hz), 4.66 (2H, d, J =

12.3 Hz), 4.45 (2H, dd, *J* = 12.3, 5.5, Hz), 4.31–4.24 (1H, m), 3.87 (1H, dd, *J* = 7.7, 4.5 Hz), 3.49 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.3, 138.9, 138.9, 135.7, 129.7, 128.3, 128.3, 127.9, 127.7, 127.4, 127.4, 123.0, 119.0, 101.4, 82.8, 76.5, 70.6, 69.9, 56.6; **HRMS $[M+NH_4]^+$** calcd for $C_{23}H_{30}NO_3$: 368.2226, found: 368.2243.

(3*S*,4*R*,5*Z*,7*E*)-Tetradeca-1,5,7-triene-3,4-diylbis(oxy)bis(methylene)dibenzene (1.22):

Following the general procedure, a solution of **Ru-7** (1.9 mg, 2.8 μmol, 5.0 mol %) in dichloromethane (113 μL) was transferred by syringe to a vial containing cyclobutene **1.79** (15.0 mg, 0.0563 mmol, 1.00 equiv) and (*E*)-deca-1,3-diene (78.0 mg, 0.563 mmol, 10.0 equiv). The resulting solution was allowed to stir for 12 hours at 40 °C. Analysis of the unpurified mixture revealed 73% consumption of **1.79**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (100% hexanes to 5% Et_2O in hexanes) followed by passing through a plug of activated charcoal with 50% Et_2O in pentane to afford **1.22** (13.7 mg, 0.0339 mmol, 60% yield) as colorless oil; **IR (CH_2Cl_2)**: 3028 (w), 2955 (m), 2925 (s), 2855 (m), 1653 (w), 1496 (w), 1455 (m), 1090 (s), 1070 (s), 1028 (w), 988 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.37–7.26 (10H, m), 6.24 (1H, t, *J* = 11.0 Hz), 6.18–6.07 (1H, m), 5.87 (1H, ddd, *J* = 16.0, 12.0, 8.0 Hz), 5.74 (1H, dt, *J* = 14.2, 6.9 Hz), 5.34–5.25 (3H, m), 4.64 (2H, dd, *J* = 12.3, 2.2 Hz), 4.44 (2H, dd, *J* = 12.2, 9.0 Hz), 4.35 (1H, dd, *J* = 9.3, 4.6 Hz), 3.86 (1H, dd, *J* = 7.7, 4.6 Hz), 2.05 (2H, q, *J* = 7.0 Hz), 1.38–1.25 (8H, m), 0.89 (3H, t, *J* = 6.7 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.8, 138.8, 137.8, 135.6, 133.6, 128.3, 128.3, 127.9, 127.7, 127.5, 127.4, 126.0, 125.6, 120.0, 82.8,

76.3, 70.6, 70.1, 33.0, 31.9, 29.3, 29.1, 22.8, 14.3; **HRMS $[M+NH_4]^+$** calcd for $C_{28}H_{40}NO_2$: 422.3059, found: 422.3072.

((1*S*,2*R*,3*S*,5*S*)-3-((*Z*)-2-Butoxyvinyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.23):

Following the general procedure, a solution of **Ru-7** (1.4 mg, 1.9 μmol, 2.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and butyl vinyl ether (97.0 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 40% EtOAc in hexanes) to afford **1.23** (23.5 mg, 0.0924 mmol, 95% yield) as colorless oil; **IR (CH_2Cl_2)**: 3414 (br), 2920 (m), 2987 (m), 1639 (w), 1455 (w), 1367 (w), 1135 (m), 1038 (s), 907 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.00 (1H, dd, J = 6.2, 0.8 Hz), 5.76 (1H, ddd, J = 17.2, 10.1, 8.1 Hz), 5.00 (1H, ddd, J = 17.0, 1.8, 1.0 Hz), 4.94–4.89 (1H, m), 4.27 (1H, dd, J = 9.1, 6.2 Hz), 3.77–3.70 (5H, m), 3.60 (1H, dd, J = 11.9, 6.7 Hz), 2.79–2.70 (1H, m), 2.42 (1H, dq, J = 11.2, 7.9 Hz), 2.03–1.90 (2H, m), 1.87–1.76 (1H, m), 1.68–1.52 (3H, m), 1.43–1.31 (2H, m), 1.28–1.15 (2H, m), 0.93 (3H, t, J = 7.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.7, 142.5, 113.8, 109.6, 72.5, 62.2, 61.1, 50.2, 48.5, 45.6, 39.6, 36.5, 31.8, 19.1, 13.9; **HRMS $[M+H-H_2O]^+$** calcd for $C_{15}H_{25}O_2$: 237.1860, found: 237.1855.

((1*S*,2*R*,3*R*,5*S*)-3-((*Z*)-2-(Ethylthio)vinyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.24):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and ethyl vinyl sulfide (86.0 mg, 0.973 mmol, 10.0 equiv). The resulting solution was allowed to stir for 12 hours at 40 °C. Analysis of the unpurified mixture revealed 85% consumption of **1.36**, and the ROCM product was obtained in 92:8 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 40% EtOAc in hexanes) to afford **1.24** (18.9 mg, 0.0780 mmol, 80% yield) as colorless oil; **IR (CH_2Cl_2)**: 3284 (br), 2919 (m), 2871 (w), 1639 (w), 1450 (m), 1047 (s), 1029 (s), 993 (s), 912 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.95 (1H, d, J = 9.4 Hz), 5.75 (1H, ddd, J = 17.1, 10.1, 8.1 Hz), 5.46 (1H, t, J = 9.4 Hz), 5.02 (1H, dd, J = 17.1, 1.0 Hz), 4.98–4.92 (1H, m,), 3.76–3.66 (4H, m), 3.27 (1H, s), 2.72–2.54 (3H, m), 2.37–2.26 (1H, m), 2.11–1.95 (3H, m), 1.31–1.25 (5H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.8, 132.8, 125.3, 114.4, 62.1, 61.7, 50.1, 48.6, 46.0, 41.7, 40.0, 28.1, 15.6; **HRMS [M+H-H_2O]$^+$** calcd for $C_{13}H_{21}OS$: 225.1313, found: 225.1324.

((3*R*,4*S*,*Z*)-1-Butoxyhexa-1,5-diene-3,4-diyl)bis(oxy)bis(methylene)dibenzene (1.25):

Following the general procedure, a solution of **Ru-7** (1.9 mg, 2.8 μmol, 5.0 mol %) in dichloromethane (113 μL) was transferred by syringe to a vial containing cyclobutene **1.79** (15.0 mg, 0.0563 mmol, 1.00 equiv) and butyl vinyl ether (56.0 mg, 0.563 mmol, 10.0 equiv). The resulting solution was allowed to stir for 12 hours at 40 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.79**, and the ROCM product was

obtained in 88:12 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) followed by passing through a plug of activated charcoal with 100% Et_2O to afford **1.25** (16.7 mg, 0.0456 mmol, 81% yield) as a colorless oil; **IR (CH_2Cl_2)**: 2957 (w), 2926 (m), 2858 (w), 1659 (m), 1454 (w), 1377 (m), 1085 (s), 1068 (s), 1028 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.37–7.29 (8H, m), 7.26–7.22 (2H, m), 6.20 (1H, d, J = 6.2 Hz), 5.87 (1H, ddd, J = 17.1, 10.7, 7.5 Hz), 5.29–5.28 (1H, m), 5.27–5.22 (1H, m), 4.65 (2H, dd, J = 12.3, 4.6 Hz), 4.55 (1H, dd, J = 9.4, 3.7 Hz), 4.51–4.45 (3H, m), 3.91–3.87 (1H, m), 3.74 (2H, t, J = 6.5 Hz), 1.60–1.52 (2H, m), 1.41–1.30 (2H, m), 0.91 (3H, t, J = 7.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 149.0, 139.5, 139.1, 135.8, 128.3, 128.2, 127.8, 127.7, 127.3, 127.2, 118.5, 103.3, 82.7, 74.5, 72.5, 70.5, 70.3, 32.0, 19.1, 14.0; **HRMS $[M+NH_4]^+$** calcd for $C_{24}H_{34}NO_3$: 384.2539, found: 384.2544.

(*R*,*Z*)-(1-Butoxy-3-methylpenta-1,4-dien-1,3-diyl)dibenzene (1.26):

Following the general procedure, a solution of **Ru-7** (1.6 mg, 2.3 μmol, 2.0 mol %) in dichloromethane (230 μL) was transferred by syringe to a vial containing cyclopropene **1.37** (15.0 mg, 0.115 mmol, 1.00 equiv) and butyl vinyl ether (115 mg, 1.15 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.37**, and the ROCM product was obtained in 88:12 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (5% Et_2O in hexanes to 10% Et_2O in hexanes) to afford **1.26** (20.9 mg, 0.0907 mmol, 79% yield) as colorless oil; **IR (CH_2Cl_2)**: 2960 (w), 2932 (w), 2872 (w), 1655 (m), 1372 (w), 1095 (s), 909 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.42–7.37 (2H, m), 7.30–7.25 (2H, m), 7.19–7.14 (1H, m), 6.29 (1H, ddd, J = 17.7,

10.2, 1.3 Hz), 5.95 (1H, dd, *J* = 6.8, 1.3 Hz), 5.09–5.08 (1H, m), 5.05 (1H, dt, *J* = 4.8, 1.4 Hz), 4.49 (1H, dd, *J* = 6.8, 1.2 Hz), 3.66–3.60 (2H, m), 1.58 (3H, d, *J* = 1.2 Hz), 1.47 (1H, d, *J* = 6.9 Hz), 1.45–1.41 (1H, m), 1.29–1.19 (2H, m), 0.86 (3H, td, *J* = 7.2, 1.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.8, 146.1, 145.3, 128.0, 126.8, 125.7, 112.1, 110.8, 72.4, 45.9, 31.9, 27.4, 19.1, 13.9; **HRMS [M+H]$^+$** calcd for $C_{16}H_{23}O$: 231.1749, found: 231.1752.

(1*R*,3*S*)-1-((*Z*)-2-Butoxyvinyl)-2-tosyl-3-vinylisoindoline (1.27):

Following the general procedure, a solution of **Ru-7** (0.70 mg, 1.0 mol, 2.0 mol %) in dichloromethane (100 μL) was transferred by syringe to a vial containing 7-azanorbornene **1.80** (15.0 mg, 0.0504 mmol, 1.00 equiv) and butyl vinyl ether (51.0 mg, 0.504 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.80**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) to afford **1.27** (16.6 mg, 0.0418 mmol, 83% yield) as colorless oil; **IR (CH_2Cl_2)**: 2957 (w), 2928 (m), 1661 (m), 1460 (w), 1352 (m), 1164 (s), 1095 (s), 1039 (s), 578 (s), 551 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.80 (2H, d, *J* = 8.3 Hz), 7.26–7.19 (4H, m), 7.17–7.00 (2H, m), 6.14 (1H, dd, *J* = 6.1, 1.1 Hz), 5.99–5.90 (1H, m), 5.88 (1H, d, *J* = 9.8 Hz), 5.42 (1H, dt, *J* = 17.0, 1.0 Hz), 5.28 (1H, d, *J* = 7.5 Hz), 5.22 (1H, dt, *J* = 10.1, 1.0 Hz), 4.56 (1H, dd, *J* = 8.9, 6.1 Hz), 3.97–3.81 (2H, m), 2.38 (3H, s), 1.75–1.68 (2H, m), 1.49 (2H, q, *J* = 8.0 Hz), 1.00 (3H, t, *J* = 7.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.9, 139.5, 139.1, 135.8, 128.3, 128.2, 127.8, 127.7, 127.3, 127.2, 118.5, 103.3, 82.7, 74.5,

72.5, 70.5, 70.3, 32.0, 19.1, 14.0; **HRMS [M+H]$^+$** calcd for $C_{23}H_{28}NO_3S$: 398.1784, found: 398.1792.

(*Z*)-3-((1*R*,3*S*)-3-Vinylcyclopentyl)prop-2-en-1-ol (1.28):

Following the general procedure, Following the general procedure, a solution of **Ru-7** (5.5 mg, 8.0 μmol, 5.0 mol %) in dichloromethane (320 μL) was transferred by syringe to a vial containing norbornene (15.0 mg, 0.159 mmol, 1.00 equiv) and allyl alcohol (93.0 mg, 1.59 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of norbornene, and the ROCM product was obtained in 88:12 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 30% Et_2O in hexanes) to afford **1.28** (16.4 mg, 0.108 mmol, 68% yield) as colorless oil; **IR (CH_2Cl_2)**: 3319 (br), 2943 (m), 2864 (m), 1639 (w), 1447 (w), 1012 (s), 993 (s), 907 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.79 (1H, ddd, J = 17.4, 10.2, 7.5 Hz), 5.53 (1H, dt, J = 10.8, 6.8 Hz), 5.43 (1H, dd, J = 10.6, 9.4 Hz), 4.98 (1H, ddd, J = 17.1, 1.9, 1.2 Hz), 4.88 (1H, ddd, J = 10.2, 1.9, 1.0 Hz), 4.20 (2H, d, J = 5.6 Hz), 2.89–2.76 (1H, m), 2.61–2.46 (1H, m), 1.96–1.89 (1H, m), 1.87–1.77 (2H, m), 1.51–1.32 (3H, m), 1.12 (1H, dt, J = 12.4, 10.5 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: δ 143.1, 137.1, 128.4, 112.7, 58.7, 44.7, 41.4, 38.4, 32.8, 32.0; **HRMS [M+H-H_2O]$^+$** calcd for $C_{10}H_{15}$: 135.1174, found: 135.1179.

For the synthesis of **1.28** from the ROCM reaction of norbornene and allyl(pinacolato)boronate, a solution of **Ru-7** (2.2 mg, 3.2 μmol, 2.0 mol %) in dichloromethane (320 μL) was transferred by syringe to a vial containing norbornene (15.0 mg, 0.159 mmol, 1.00 equiv) and allyl(pinacolato)boronate (268 mg, 1.59 mmol,

10.0 equiv). The resulting mixture was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of norbornene; **1.15** was obtained in 90:10 *Z*:*E* ratio. The mixture was concentrated and dissolved in tetrahydrofuran (1 mL) and cooled to 0 ºC in an ice bath. A 2.0 M aqueous solution of NaOH (880 μL, 1.75 mmol, 11.0 equiv) was added, followed by H_2O_2 (170 μL, 1.75 mmol, 11.0 equiv). The mixture was allowed to warm to 22 °C over 0.5 h. The solution was treated with a 2.0 M solution of HCl and washed with CH_2Cl_2 (3 x 1 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a yellow oil, which was purified by silica gel chromatography (10% Et_2O in hexanes to 30% Et_2O in hexanes) to obtain **1.28** (15.5 mg, 0.102 mmol, 64% yield) as colorless oil. The spectra data for this compound were identical to those reported above.

(*Z*)-4-((1*R*,3*S*)-3-Vinylcyclopentyl)but-3-en-1-ol (1.30):

Following the general procedure, a solution of **Ru-7** (5.5 mg, 8.0 μmol, 5.0 mol %) in dichloromethane (320 μL) was transferred by syringe to a vial containing norbornene (15.0 mg, 0.159 mmol, 1.00 equiv) and 3-buten-1-ol (115 mg, 1.59 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of norbornene, and the product was obtained in 87:13 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (5% Et_2O in hexanes to 10% Et_2O in hexanes) to afford **1.30** (23.3 mg, 0.140 mmol, 88% yield) as colorless oil; **IR (CH_2Cl_2)**: 3334 (br), 2944 (s), 2864 (m), 1639 (w), 1447 (w), 1045 (s), 907 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.80 (1H, ddd, J = 17.3, 10.1, 7.5 Hz), 5.50 (1H, t, J = 10.1 Hz), 5.29 (1H, dt, J = 10.8, 7.5 Hz), 4.97 (1H, dd, J = 17.1, 1.1 Hz), 4.91–4.83 (1H, m), 3.63 (2H, t, J = 6.3 Hz), 2.90–2.76 (1H, m),

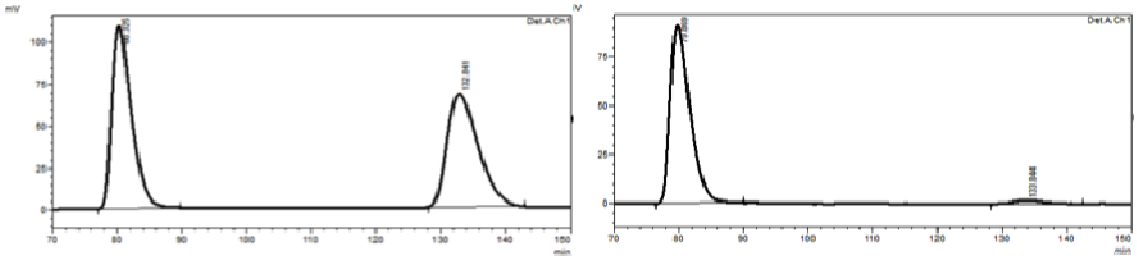
2.62–2.47 (1H, m), 2.34 (2H, qd, J = 6.5, 1.3 Hz), 1.99–1.87 (1H, m), 1.86–1.78 (2H, m), 1.49–1.35 (3H, m), 1.18–1.04 (1H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 143.3, 138.8, 123.9, 112.6, 62.5, 44.6, 41.3, 38.3, 32.8, 31.9, 31.2; **HRMS [M+H]$^+$** calcd for $C_{11}H_{19}O$: 167.1436, found: 167.1431.

(1*R*,3*S*)-1-((*Z*)-4-butoxybut-1-enyl)-3-vinylcyclopentane (1.31):

Following the general procedure, a solution of **Ru-7** (5.5 mg, 8.0 μmol, 5.0 mol %) in dichloromethane (320 μL) was transferred by syringe to a vial containing norbornene (15.0 mg, 0.159 mmol, 1.00 equiv) and 4-butoxybut-1-ene (204 mg, 1.59 mmol, 10.0 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of norbornene, and the product was obtained in 87:13 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **1.31** (23.4 mg, 0.105 mmol, 66% yield) as colorless oil; **IR (CH_2Cl_2)**: 3078 (s), 2861 (s), 1640 (w), 1464 (w), 1361 (w), 908 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.80 (1H, ddd, J = 17.3, 9.9, 7.6 Hz), 5.39 (1H, t, J = 9.9 Hz), 5.30 (1H, dt, J = 10.4, 7.1 Hz), 4.97 (1H, d, J = 17.2 Hz), 4.87 (1H, d, J = 10.2 Hz), 3.47–3.36 (4H, m), 2.87–2.76 (1H, m), 2.58–2.46 (1H, m), 2.34 (2H, q, J = 6.9 Hz), 1.96–1.87 (1H, m), 1.82–1.80 (2H, m), 1.62–1.50 (2H, m), 1.40–1.30 (4H, m), 1.14–1.04 (1H, m), 0.92 (3H, t, J = 7.3 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: δ 143.4, 136.9, 125.2, 112.6, 71.0, 70.8, 44.8, 41.4, 38.5, 32.8, 32.4, 32.1, 28.9. 19.8, 14.1; **HRMS [M+H]$^+$** calcd for $C_{15}H_{27}O$: 223.2062, found: 223.2066.

((1*S*,2*R*,3*R*,5*S*)-3-((*R*,*Z*)-3-Hydroxy-3-phenylprop-1-enyl)-5-vinylcyclopentane-1,2-diyl)dimethanol (1.40):

Following the general procedure, a solution of **Ru-7** (3.4 mg, 4.9 μmol, 5.0 mol %) in dichloromethane (195 μL) was transferred by syringe to a vial containing 5-norbornene-2-exo,3-exo-dimethanol **1.36** (15.0 mg, 0.0973 mmol, 1.00 equiv) and (*R*)-1-phenyl-2-propen-1-ol **1.34** (65.2 mg, 0.486 mmol, 5.0 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.36**, and the ROCM product was obtained in >98:2 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (20% EtOAc in hexanes to 80% EtOAc in hexanes) to afford **1.40** (18.8 mg, 0.0652 mmol, 67% yield) as colorless oil; **IR (CH_2Cl_2)**: 3299 (br), 2961 (w), 2921 (m), 2856 (m), 1639 (w), 1492 (m), 1021 (m), 913 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.42–7.33 (4H, m), 7.31–7.26 (1H, m), 5.78 (1H, ddd, J = 17.6, 10.2, 8.2 Hz), 5.72 (1H, dd, J = 10.8, 8.4 Hz), 5.55 (1H, d, J = 7.9 Hz), 5.43 (1H, t, J = 10.5 Hz), 5.04 (1H, ddt, J = 17.1, 1.8, 1.0 Hz), 4.99–4.92 (1H, m), 4.20 (1H, s), 3.82 (3H, s); 3.69–3.50 (2H, m), 3.14–3.03 (2H, m), 2.62–2.52 (1H, m), 2.03–1.94 (2H, m), 1.33–1.23 (2H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 143.7, 142.0, 136.6, 132.9, 128.7, 127.7, 126.1, 114.2, 69.7, 61.9, 60.1, 50.1, 48.4, 45.6, 39.9, 39.5; **HRMS [M+H-H_2O]$^+$** calcd for $C_{18}H_{23}O_2$: 271.1698, found: 271.1701; diastereomeric ratio was established by HPLC analysis in comparison with authentic racemic material prepared from **1.36** and *rac*-1-phenyl-2-propen-1-ol under standard conditions (97:03 e.r. shown for **1.40**; after correction for 96:04 e.r. of the starting material, results in a diastereoselectivity of >98:02 d.r.; Daicel Chiralpak OD-H column (97:3 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm) was used.)



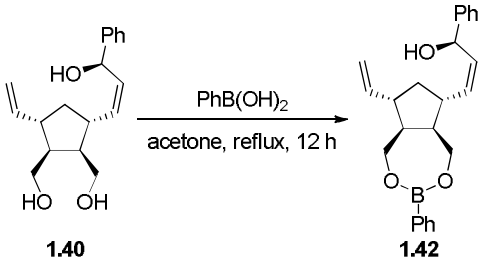
Peak #	Retention time (min)	Area	Area %	Peak #	Retention time (min)	Area	Area %
1	80.33	23060079	50.39	1	79.87	19429049	97.06
2	132.84	22706960	49.61	2	133.84	588688	2.94

(1*R*,4*R*,*Z*)-4-Methyl-1,4-diphenylhexa-2,5-dien-1-ol (1.41):

Following the general procedure, a solution of **Ru-7** (3.9 mg, 5.6 μmol, 5.0 mol %) in dichloromethane (224 μL) was transferred by syringe to a vial containing (*R*)-1-phenyl-2-propen-1-ol **1.34** (15.0 mg, 0.112 mmol, 1.00 equiv) and cyclopropene **1.37** (29.0 mg, 0.224 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed >98% consumption of **1.34**, and the product was obtained in 91:9 *Z*:*E* ratio. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 20% Et_2O in hexanes) after which it was passed through a plug of activated charcoal with 50% Et_2O in pentane to afford **1.41** (23.1 mg, 0.0870 mmol, 78% yield) as colorless oil; **IR (CH_2Cl_2)**: 3408 (br), 2961 (w), 2924 (m), 2852 (w), 1616 (w), 1579 (w), 1491 (w), 1446 (w), 1005 (w), 914 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.37 (2H, dd, J = 8.1, 1.0 Hz), 7.34–7.26 (3H, m), 7.26–7.17 (4H, m), 7.06–7.04 (2H, m), 6.34 (1H, dd, J = 17.3, 10.5 Hz), 5.90 (1H, dd, J = 11.5, 0.8 Hz), 5.68 (1H, dd, J = 11.5, 9.9 Hz), 5.16 (2H, ddd, J = 18.4, 13.9, 1.0 Hz), 5.08 (1H, d, J = 9.8 Hz), 1.58 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.0,

146.2, 142.9, 139.1, 133.1, 128.6, 128.4, 127.6, 127.3, 126.5, 126.3, 112.9, 69.3, 47.5, 29.3; **HRMS [M+H-H_2O]$^+$** calcd for $C_{19}H_{19}$: 247.1487, found: 247.1485.

1.6.5 Proof of the Stereochemical Identity of ROCM Products 1.40 and 1.41



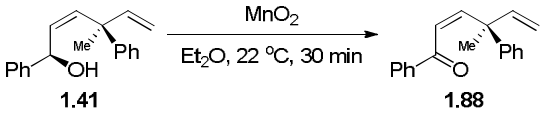
1.40 **1.42**

(*R*,*Z*)-1-Phenyl-3-((5a*R*,6*R*,8*S*,8a*S*)-3-phenyl-8-vinylhexahydro-1*H* cyclopenta[*e*][1,3,2]dioxaborepin-6-yl)prop-2-en-1-ol (1.42):

A previously reported procedure was adopted.[67] A flame-dried round-bottom flask, equipped with a stir bar and reflux condenser, was charged with **1.40** (20.0 mg, 0.069 mmol, 1.00 equiv), phenylboronic acid (20.0 mg, 0.069 mmol, 1.00 equiv) and acetone (0.5 mL). The solution was allowed to stir at reflux for 12 hours. The resulting mixture was concentrated *in vacuo* to afford **1.42** as yellow solid, which was recrystallized from hexane, affording colorless crystals (24.4 mg, 0.0652 mmol, 94% yield); mp: 84–86 ^oC; **IR (CH_2Cl_2)**: 3386 (br), 3075 (w), 2919 (w), 1640 (w), 1599 (w), 1479 (m), 1439 (m), 1141 (m), 1030 (m), 915 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.84–7.79 (2H, m), 7.44–7.37 (1H, m), 7.36–7.32 (2H, m), 7.32–7.30 (3H, m), 7.26–7.25 (2H, m), 5.80–5.69 (2H, m), 5.52–5.47 (1H, m), 5.43 (1H, t, J = 10.3 Hz), 5.08 (1H, ddd, J = 17.1, 1.7, 1.0 Hz), 5.01 (1H, ddd, J = 10.1, 1.7, 0.6 Hz), 4.42 (1H, d, J = 12.2 Hz), 4.37 (1H, d, J = 12.1 Hz), 4.30–4.22 (1H, m), 4.20–4.13 (1H, m), 2.98–2.84 (1H, m), 2.58–2.44 (1H, m), 2.27 (2H, s), 2.15–2.09 (1H, m), 1.86 (1H, dt, J = 11.6, 5.7 Hz), 1.34 (1H,

(67) Sugihara, J. M.; Bowman, C. M. *J. Am. Chem. Soc.* **1958**, *80*, 2443–2446.

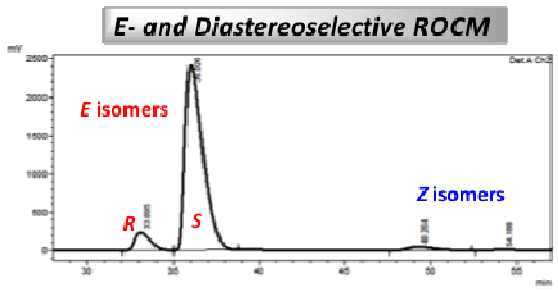
q, J = 12.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 143.7, 140.6, 134.4, 134.0, 133.7, 130.7, 128.7, 127.7, 127.6, 126.1, 115.3, 69.9, 64.3, 64.1, 49.6, 48.4, 46.3, 40.3, 39.9; **HRMS [M+H-H_2O]$^+$** calcd for $C_{24}H_{26}BO_2$: 357.2026, found: 357.2021.

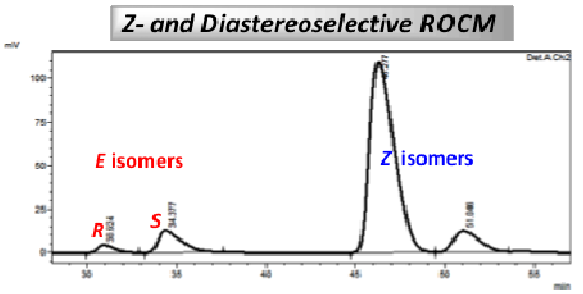


(*R*,*Z*)-4-Methyl-1,4-diphenylhexa-2,5-dien-1-one (1.88):

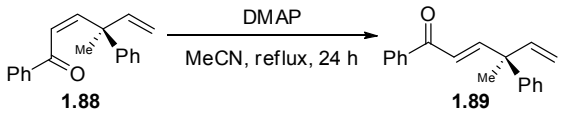
A previously reported procedure was adopted.[33a] An oven-dried vial equipped with a stir bar was charged with **1.41** (16.0 mg, 0.0610 mmol, 1.00 equiv). Diethyl ether (1.8 mL) was added through a syringe followed by manganese dioxide (160 mg, 10 mg/mg of substrate, ~30 equiv). The resulting suspension was allowed to stir vigorously until the reaction was determined to be complete according to TLC analysis (30 min). The mixture was filtered through a short pad of celite, which was then washed with diethyl ether (3 x 5.0 mL). The volatiles were removed *in vacuo*, affording yellow oil which was purified by silica gel chromatography (5% Et_2O in hexanes). **1.88** was obtained in 91:09 *Z*/*E* ratio and as colorless oil (14.3 mg, 0.0550 mmol, 90% yield); **IR (CH_2Cl_2)**: 2965 (w), 2926 (w), 1670 (s), 1580 (w), 1492 (w), 1448 (m), 1007 (m), 919 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.84–7.79 (2H, m), 7.55–7.49 (1H, m), 7.40 (2H, t, J = 7.7 Hz), 7.33–7.28 (2H, m), 7.17 (2H, t, J = 7.6 Hz), 7.12–7.05 (1H, m), 6.49 (1H, d, J = 13.2 Hz), 6.23 (1H, d, J = 12.8 Hz), 6.20 (1H, dd, J = 17.2, 10.8 Hz), 5.09 (1H, d, J = 10.6 Hz), 5.05 (1H, d, J = 17.4 Hz), 1.55 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 194.9, 146.2, 146.0, 144.4, 137.4, 133.1, 128.9, 128.5, 128.2, 127.2, 126.9, 126.3, 113.7, 48.9, 26.8; **HRMS [M+H]$^+$** calcd for $C_{19}H_{19}O$: 263.1436, found: 263.1438; diastereomeric ratio was established by HPLC analysis in comparison with authentic material prepared

according to a previously reported procedure[33a] where the absolute stereochemistry of the major *E*-enone isomers[33a] had been formerly established [89.5:10.5 e.r. shown for **1.88**; after correction for 96:4 e.r. of the starting material, diastereoselectivity is measured to be 93:7 d.r.; Daicel Chiralpak OD-H column (99.5:0.5 hexanes:*i*-PrOH, 0.7 mL/min, 254 nm) was used].





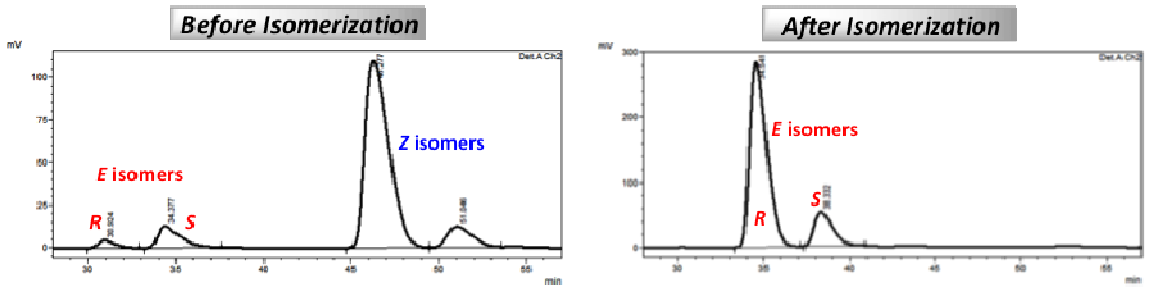
Peak #	Retention time (min)	Area	Area %	Peak #	Retention time (min)	Area	Area %
1	33.10	14469688	7.42	1	30.92	296306	2.26
2	36.03	175303050	89.84	2	34.38	1131722	8.62
3	49.26	4660845	2.39	3	46.28	10474729	79.80
4	54.19	688395	0.35	4	51.05	1223446	9.32



To ascertain the absolute stereochemistry of the diastereoselective ROCM product, *Z*-enone **1.88** was isomerized to its corresponding *E* isomer through a modified reported procedure.[68] An oven-dried vial equipped with a stir bar was charged with **1.88** (12.0 mg, 0.046 mmol, 1.00 equiv, 91:09 *Z*/*E*). Dry MeCN (0.2 mL) was added through syringe followed by *N*,*N*-dimethylaminopyridine (1.1 mg, 5.6 μmol, 20 mol %). The resulting solution was allowed to reflux for 24 hours in a sealed vial. After addition of H_2O, the mixture was washed with Et_2O (3 x 2.0 mL). The combined organic layers were dried

(68) Könning, D.; Hiller, W.; Christmann, M. *Org. Lett.* **2012**, *14*, 5258–5261.

over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford **1.89** in >98:2 *E*:*Z* as yellow oil, which was purified by silica gel chromatography (5% Et_2O in hexanes) to afford colorless oil (11.3 mg, 0.0430 mmol, 94% yield). Comparison of the HPLC retention times for the *E* isomers before and after isomerization allowed us to establish the absolute configuration at the all-carbon quaternary stereogenic center of the product [Daicel Chiralpak OD-H column (99.5:0.5 hexanes:*i*-PrOH, 0.7 mL/min, 254 nm) was used].



Peak #	Retention time (min)	Area	Area %	Peak #	Retention time (min)	Area	Area %
1	30.92	296306	2.26	1	34.54	19774970	83.09
2	34.38	1131722	8.62	2	38.33	4024481	16.91
3	46.28	10474729	79.80	-	-	-	-
4	51.05	1223446	9.32	-	-	-	-

1.6.6. Z-Selective Cross-Metathesis (CM) Reactions

General Procedure: An oven-dried 8 mL vial equipped with a magnetic stir bar is charged with alkene substrate (1.0 equiv) and *Z*-2-butene-1,4-diol (2.0–5.0 equiv) in a fume hood. The vial is then sealed, evacuated and purged with N_2. To this vessel, a solution of **Ru-9** (5.0 mol %) in tetrahydrofuran is added. The resulting solution is allowed to stir for 4–12 hours at 22 °C, after which the reaction is quenched by addition of wet diethyl ether and concentrated *in vacuo* (percent conversion determined by 400

MHz ^{1}H NMR analysis). Purification is performed through silica gel chromatography and/or Kugelrohr distillation.

(*Z*)-4-Phenyl-2-butene-1-ol (1.45): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with allylbenzene (15.0 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 84% consumption of allylbenzene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.45** (13.4 mg, 0.0904 mmol, 71% yield) as pale yellow oil in 96:4 *Z*/*E* ratio. The spectral data for this compound were identical to those reported in the literature.[36]

(*Z*)-2-Tridecene-1-ol (1.49): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 1-dodecene (21.4 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 81% consumption of 1-dodecene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.49** (18.1 mg, 0.091 mmol, 72% yield) as pale yellow oil in 96:4 *Z*/*E* ratio The spectral data for this compound were identical to those reported in the literature.[69]

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(69) Wang, Z.; Zheng, J.; Huang, P. *Chin. J. Chem.* **2012**, *30*, 23–28.

(*Z*)-5-(*tert*-Butyldimethylsiloxy)-2-pentene-1-ol (1.50): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 1-(*tert*-butyldimethylsilyoxy)-3-butene (23.7 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 76% consumption of 1-(*tert*-butyldimethylsilyoxy)-3-butene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.50** (17.8 mg, 0.0823 mmol, 65% yield) as pale yellow oil in 93:7 *Z*/*E* ratio. The spectral data for this compound were identical to those reported in the literature.[70]

(*Z*)-5-(4-Nitrophenoxy)-2-pentene-1-ol (1.51): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 1-(but-3-enoxyl)-4-nitrobenzoate (24.6 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 82% consumption of 1-(but-3-enoxyl)-4-nitrobenzoate. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.51** (21.0 mg, 0.0941 mmol, 74% yield) as pale yellow oil in 96:04 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3365 (br), 2923 (m), 1606 (m), 1591 (s), 1508 (s), 1497 (s), 1468 (s), 1331 (s), 1255 (s), 1110 (m), 1019 (s), 844 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 8.20 (2H, d, J = 9.3 Hz), 6.94 (2H, d, J = 9.3 Hz), 5.88–5.77 (1H, m), 5.65 (1H, dddd, J = 10.9, 7.5, 6.2,

(70) Manning, P. T.; Misko, T. P. *PCT Int. Appl.* WO 2005025620, 2005.

1.2 Hz), 4.28–4.22 (2H, br s), 4.09 (2H, t, J = 6.4 Hz), 2.68–2.60 (2H, m), 1.43 (1H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 163.9, 131.9, 127.6, 126.1, 114.6, 68.0, 58.6, 27.5; **HRMS [M+H-H_2O]$^+$** calcd for $C_{11}H_{12}NO_3$: 206.0817, found: 206.0815.

(*Z*)-4-Butoxy-2-butene-1-ol (1.52): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 4-butoxybut-1-ene (14.5 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 12 hours at 22 °C. Analysis of the unpurified mixture revealed 65% consumption of 4-butoxybut-1-ene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.52** (10.5 mg, 0.073 mmol, 57% yield) as pale yellow oil in 91:9 *Z*/*E* ratio The spectral data for this compound were identical to those reported in the literature.[71]

(*Z*)-Benzyl 6-hydroxy-4-hexenoate (1.53): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with benzyl pent-4-enoate (22.4 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 88% consumption of benzyl pent-4-enoate. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.53** (22.5 mg, 0.102 mmol, 80% yield) as pale yellow oil in 98:2 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3402 (br), 3018 (w), 2922 (m), 1732 (s), 1455

(71) Gansäuer, A.; Fan, C.-A.; Keller, F.; Keil, J. *J. Am. Chem. Soc.* **2007**, *129*, 3484–3485.

(m), 1382 (w), 1352 (w), 1154 (s), 1025 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.40–7.30 (5H, m), 5.74–5.64 (1H, m), 5.49 (1H, dt, J = 10.9, 6.4 Hz), 5.11 (2H, s), 4.18 (2H, t, J = 6.1 Hz), 2.50–2.40 (4H, m), 1.76 (1H, t, J = 5.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.2, 135.9, 130.8, 130.2, 128.7, 128.5, 128.5, 66.6, 58.4, 33.9, 22.8; **HRMS [M+H-H_2O]$^+$** calcd for $C_{13}H_{15}O_2$: 203.1072, found: 203.1071.

(*S*,*Z*)-Benzyl 2-(((9H-9-fluorenyl)methoxy)carbonylamino)-6-hydroxy-4-hexenoate (1.55): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with (*S*,*Z*)-benzyl 2-(((9*H*-fluoren-9-yl)methoxy)carbonylamino)-6-hydroxy-4-hexenoate (54.3 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (24.2 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 83% consumption of (*S*,*Z*)-benzyl 2-(((9*H*-fluoren-9-yl)methoxy)carbonylamino)-6-hydroxy-4-hexenoate. The resulting brown residue was purified by silica gel chromatography (10% Et_2O in hexanes to 60% Et_2O in hexanes) to afford **1.55** (42.4 mg, 0.0927 mmol, 73% yield) as white solid in 98:2 *Z*/*E* ratio; mp: 75–77 °C; **IR (CH_2Cl_2)**: 3332 (br), 3064 (w), 3033 (w), 2947 (m), 1720 (s), 1530 (m), 1450 (m), 1251 (m), 1213 (m), 1188 (m), 1048 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.77 (2H, d, J = 7.5 Hz), 7.59 (2H, d, J = 7.5 Hz), 7.43–7.27 (9H, m), 5.78 (1H, dt, J = 10.6, 7.1 Hz), 5.61 (1H, d, J = 7.3 Hz), 5.49–5.38 (1H, m), 5.26–5.10 (2H, m), 4.54–4.45 (1H, m), 4.40 (2H, d, J = 7.0 Hz), 4.21 (1H, t, J = 6.5 Hz), 4.08 (2H, s), 2.74–2.62 (1H, m), 2.62–2.52 (1H, m), 1.39 (1H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.7, 155.9, 144.0, 143.9, 141.5, 141.4, 135.3, 132.8, 128.8, 128.7, 128.6, 127.9, 127.2,

126.3, 125.2, 120.1, 67.5, 67.1, 58.2, 53.5, 47.3, 30.4; **HRMS [M+H]$^+$** calcd for $C_{28}H_{28}NO_5$: 458.1968, found: 458.1969.

(*Z*)-5-Phenyl-2-pentene-1,5-diol (1.56): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 4-phenyl-1-buten-4-ol (18.8 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 72% consumption of 4-phenyl-1-buten-4-ol. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.56** (14.5 mg, 0.0814 mmol, 64% yield) as yellow oil in 96:4 *Z*/*E* ratio The spectral data for this compound were identical to those reported in the literature.[72]

(*Z*)-1-(4-Hydroxy-3-(4-hydroxy-2-butenyl)phenyl)ethanone (1.57): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 3'-allyl-4'-hydroxyacetophenone (22.4 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 77% consumption of 3'-allyl-4'-hydroxyacetophenone. The resulting brown residue was purified by silica gel chromatography (10% Et_2O in hexanes to 60% Et_2O in hexanes) to afford **1.57** (17.8 mg, 0.0863 mmol, 68% yield) as off-white solid in 98:2 *Z*/*E* ratio; mp: 97–99 °C; **IR (CH_2Cl_2)**: 3251 (br), 3018 (w), 2962 (m), 2925 (m), 1656 (s), 1592 (s), 1509 (w), 1426

(72) Fujiwara, T.; Yanai, K.; Shimane, K.; Takamori, M.; Takeda, T. *Eur. J. Org. Chem.* **2001**, 155–161.

(w), 1360 (m), 1281 (s), 1120 (w), 1020 (w), 824 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.80 (1H, d, J = 2.2 Hz), 7.77 (1H, dd, J = 8.4, 2.3 Hz), 6.86 (1H, d, J = 8.4 Hz), 5.79 (1H, dt, J = 10.9, 6.2 Hz), 5.69 (1H, dt, J = 10.8, 7.6 Hz),[18] 4.42 (2H, d, J = 6.2 Hz), 3.56 (2H, d, J = 7.8 Hz), 2.55 (3H, s), 1.25 (2H, br s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.9, 132.6, 131.5, 130.1, 129.6, 127.1, 127.1, 125.5, 116.3, 58.7, 30.3, 26.5; **HRMS $[M+H]^+$** calcd for $C_{12}H_{15}O_3$: 207.1021, found: 207.1015.

(*Z*)-12-Hydroxy-10-dodecenal (1.58): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with undecylenic aldehyde (21.4 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 86% consumption of undecylenic aldehyde. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.58** (20.1 mg, 0.101 mmol, 80% yield) as pale yellow oil in 94:6 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3408 (br), 2924 (s), 2854 (s), 1725 (m), 1558 (m), 1462 (m), 1265 (w), 1027 (w); **^{1}H NMR (400 MHz, C_6D_6)**: *Z*-isomer (major): δ 9.33 (1H, s), 5.58 (1H, dt, J = 11.4, 6.3 Hz), 5.56–5.36 (1H, m), 4.01 (2H, d, J = 6.4 Hz), 1.98–1.89 (2H, m), 1.87–1.78 (2H, m), 1.33–1.05 (13H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 203.1, 133.3, 128.5, 58.8, 44.1, 29.7, 29.4, 29.4, 29.3, 29.2, 27.5, 22.2; **HRMS $[M+H-H_2O]^+$** calcd for $C_{12}H_{21}O$: 181.1592, found: 181.1598.

(*Z*)-7-Hydroxy-5-heptenoic acid (1.59): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 5-hexenoic acid (14.5 mg, 0.127 mmol, 1.00 equiv) and *Z*-

2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 85% consumption of 5-hexenoic acid. The resulting brown oil was purified by silica gel chromatography (100% CH_2Cl_2 to 5% MeOH in CH_2Cl_2) and filtered through a small plug of activated charcoal to afford **1.59** (12.8 mg, 0.0890 mmol, 70% yield) as pale yellow oil in 96:4 *Z*/*E* ratio The spectral data for this compound were identical to those reported in the literature.[73]

(*Z*)-6-Hydroxy-2,2-dimethyl-4-hexenoic acid (1.60): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 2,2-dimethyl-4-pentenoic acid (16.3 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 66% consumption of 2,2-dimethyl-4-pentenoic acid. The resulting brown oil was purified by silica gel chromatography (100% CH_2Cl_2 to 5% MeOH in CH_2Cl_2) and filtered through a small plug of activated charcoal to afford **1.60** (12.3 mg, 0.0778 mmol, 61% yield) as pale yellow oil in 98:2 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3316 (br), 3021 (w), 2963 (w), 2923 (m), 2854 (w), 1698 (s), 1473 (m), 1389 (w), 1366 (w), 1197 (m), 1146 (m), 1021 (m), 866 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.42 (1H, br s), 5.80–5.70 (1H, m), 5.56 (1H, dtt, J = 12.0, 8.0, 1.2 Hz), 4.19 (2H, d, J = 6.8 Hz), 2.33 (2H, d, J = 7.9 Hz), 1.29 (1H, s), 1.23 (6H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 183.0, 131.4, 127.9, 58.4, 42.8, 37.9, 24.5; **HRMS $[M+H]^+$** calcd for $C_8H_{15}O_3$: 159.1021, found: 159.1029.

(73) Taber, D. F.; Herr, R. J.; Gleave, D. M. *J. Org. Chem.* **1997**, *62*, 194–198.

(*Z*)-3-Cyclohexyl-2-propene-1-ol (1.61): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with vinylcyclohexane (14.0 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (56.0 mg, 0.635 mmol, 5.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 65% consumption of vinylcyclohexane. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.61** (10.5 mg, 0.075 mmol, 59% yield) as pale yellow oil in 98:2 *Z*/*E* ratio The spectral data for this compound were identical to those reported in the literature.[74]

(*Z*)-3-(3-Cyclohexenyl)-2-propene-1-ol (1.62): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 4-vinyl-1-cyclohexene (13.7 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (56.0 mg, 0.635 mmol, 5.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 69% consumption of 4-vinyl-1-cyclohexene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.62** (11.0 mg, 0.0796 mmol, 63% yield) as pale yellow oil in 98:2 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3311 (br), 3021 (w), 2915 (m), 2851 (w), 2835 (w), 1652 (w), 1435 (w), 1264 (m), 1024 (m), 999 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.73–5.63 (2H, m), 5.56 (1H, dt, J = 11.0, 6.6 Hz), 5.47 (1H, t, J = 10.6 Hz), 4.26–4.20 (2H, m), 2.64–2.53 (1H, m), 2.12–

(74) Reed, S. A.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 3316–3318.

1.99 (3H, m), 1.87–1.75 (1H, m), 1.71–1.63 (1H, m), 1.46–1.37 (1H, m), 1.26–1.21 (1H, m); **^{13}C NMR (100 MHz, C_6D_6)**: δ 138.4, 127.4, 127.1, 126.0, 58.9, 32.5, 31.9, 29.2, 24.6; **HRMS [M+H-H_2O]$^+$** calcd for C_9H_{13}: 121.1017, found: 121.1017.

(*Z*)-3-Phenyl-2-propene-1-ol (1.63): Following the general procedure, a solution of **Ru-11** (5.1 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with styrene (13.2 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (56.0 mg, 0.635 mmol, 5.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 57% consumption of styrene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.63** (9.0 mg, 0.0671 mmol, 53% yield) as pale yellow oil in 94:6 *Z*/*E* ratio. Spectral data for this compound were identical to those reported in the literature.[75]

(*Z*)-3-(4-(Trifluoromethyl)phenyl)-2-propene-1-ol (1.64): Following the general procedure, a solution of **Ru-11** (5.1 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 4-(trifluoromethyl)styrene (21.9 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (56.0 mg, 0.635 mmol, 5.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 66% consumption of 4-(trifluoromethyl)styrene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.64** (15.4 mg, 0.0762 mmol, 60% yield) as pale yellow oil in 93:7 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3334 (br), 3022 (w), 2924 (m), 1617 (m), 1403 (w), 1322 (s), 1163 (m), 1111 (s), 1066 (s), 1014

(75) Singh, K.; Staig, S. J.; Weaver, J. D. *J. Am. Chem. Soc.* **2014**, *136*, 5275–5278.

(m), 851 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.60 (2H, d, J = 8.0 Hz), 7.32 (2H, d, J = 8.0 Hz), 6.60 (1H, d, J = 11.8 Hz), 6.00 (1H, dt, J = 12.4, 6.4 Hz), 4.42 (2H, s), 1.50 (1H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.9, 133.3, 130.0, 129.1, 125.4, 125.3, 125.3, 59.6; **HRMS [M+H-H_2O]$^+$** calcd for $C_{10}H_8F_3$: 185.0578, found: 185.0580.

(2*Z*,4*E*)-Undeca-2,4-dien-1-ol (1.65): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with deca-1,3-diene (17.6 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed 88% consumption of deca-1,3-diene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.65** (14.1 mg, 0.0838 mmol, 66% yield) as colorless oil in 95:5 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3320 (br), 3023 (w), 2956 (m), 2924 (s), 2854 (m), 1653 (w), 1459 (m), 1264 (m), 1027 (m), 985 (m), 952 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.35–6.25 (1H, m), 6.07 (1H, t, J = 11.0 Hz), 5.76 (1H, dt, J = 14.5, 7.0 Hz), 5.49 (1H, dt, J = 10.9, 7.0 Hz), 4.30 (2H, d, J = 7.0 Hz), 2.15–2.06 (2H, m), 1.42–1.34 (2H, m), 1.32–1.25 (7H, m), 0.88 (3H, t, J = 6.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.8, 131.5, 127.2, 124.9, 59.0, 33.0, 31.9, 29.3, 29.1, 22.8, 14.2; **HRMS [M+H-H_2O]$^+$** calcd for $C_{11}H_{19}$: 151.1487, found: 151.1487.

(2*Z*,4*E*)-5-Methoxypenta-2,4-dien-1-ol (1.66): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with (*E*)-1-methoxy-1,3-butadiene (10.7 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The

resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed 72% consumption of (*E*)-1-methoxy-1,3-butadiene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.66** (9.1 mg, 0.0797 mmol, 63% yield) as colorless oil in 92:8 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3416 (br), 2928 (m), 1688 (m), 1438 (m), 1054 (s), 977 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.64 (1H, d, J = 12.3 Hz), 6.00 (1H, t, J = 11.1 Hz), 5.75 (1H, t, J = 11.8 Hz), 5.40 (1H, dt, J = 10.8, 7.0 Hz), 4.26 (2H, d, J = 7.0 Hz), 3.62 (3H, s), 1.28 (1H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.3, 127.9, 124.2, 100.9, 59.1, 56.8; **HRMS [M+H-H_2O]$^+$** calcd for C_6H_9O: 97.0653, found: 97.0648.

(2*E*,4*Z*)-*tert*-Butyl 6-hydroxyhexa-2,4-dienoate (1.67): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with (*E*)-*tert*-butyl penta-2,4-dienoate (19.6 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed 62% consumption of (*E*)-*tert*-butyl penta-2,4-dienoate. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.67** (13.1 mg, 0.0711 mmol, 56% yield) as colorless oil in 96:4 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3399 (br), 2977 (m), 2927 (m), 1706 (s), 1688 (s), 1638 (m), 1605 (m), 1367 (m), 1310 (m), 1276 (s), 1152 (s), 1121 (s), 1034 (m), 994 (m), 871 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.47 (1H, ddd, J = 15.2, 11.8, 1.1 Hz), 6.18 (1H, td, J = 11.3, 0.7 Hz), 5.94 (1H, dt, J = 11.0, 6.7 Hz), 5.86 (1H, d, J = 15.2 Hz), 4.43 (2H, d, J = 4.6 Hz), 1.50–

1.48 (1H, br s), 1.49 (9H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.4, 137.4, 128.0, 125.4, 80.7, 59.1, 36.7, 28.3; **HRMS $[M+H]^+$** calcd for $C_{10}H_{17}O_3$: 185.1178, found: 185.1176.

(2*Z*,4*Z*)-Deca-2,4-dien-1-ol (1.68): Following the general procedure, a solution of **Ru-9** (4.9 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with (*Z*)-nona-1,3-diene (15.8 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (22.4 mg, 0.254 mmol, 2.00 equiv). The resulting solution was allowed to stir for 8 hours at 22 °C. Analysis of the unpurified mixture revealed 61% consumption of (*Z*)-nona-1,3-diene. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.68** (10.6 mg, 0.0687 mmol, 54% yield) as colorless oil in 87:13 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3332 (br), 3008 (m), 2956 (s), 2924 (s), 2856 (s), 1683 (w), 1458 (m), 1378 (w), 1089 (m), 985 (s), 950 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 6.39 (1H, ddd, J = 11.4, 11.0, 1.2 Hz), 6.29–6.19 (1H, m), 5.66–5.59 (1H, m), 5.59–5.52 (1H, m), 4.40–4.28 (2H, m), 2.22–2.14 (2H, m), 1.42–1.37 (2H, m), 1.33–1.25 (5H, m), 0.89 (3H, t, J = 6.9 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 134.9, 129.2, 126.0, 122.8, 58.9, 31.6, 29.3, 27.6, 22.7, 14.2; **HRMS $[M+H-H_2O]^+$** calcd for $C_{10}H_{17}$: 137.1330, found: 137.1327.

(*Z*)-3-(4-methylphenyl)-2-propene-1-ol (1.90; not shown in the text): Following the general procedure, a solution of **Ru-10** (5.4 mg, 6.3 μmol, 5.0 mol %) in tetrahydrofuran (255 μL) was transferred by syringe to a vial charged with 4-methylstyrene (15.0 mg, 0.127 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (56.0 mg, 0.635 mmol, 5.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 55% consumption of 4-methylstyrene. The resulting brown oil was

purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) to afford **1.90** (9.8 mg, 0.0661 mmol, 52% yield) as pale yellow oil in 95:5 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3312 (br), 3018 (w), 2920 (m), 2857 (w), 1611 (w), 1512 (m), 1449 (m), 1119 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.16 (2H, d, J = 8.1 Hz), 7.11 (2H, d, J = 8.1 Hz), 6.54 (1H, d, J = 12.0 Hz), 5.88–5.79 (1H, m), 4.45 (2H, s), 2.35 (3H, s), 1.45 (1H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.3, 133.8, 131.1, 130.5, 129.1, 128.9, 60.0, 21.3; **HRMS [M+H-H_2O]$^+$** calcd for $C_{10}H_{11}$: 131.0861, found: 131.0860.

1.6.7. Synthesis of Precursor 1.70 en route to (+)-Neopeltolide

Methyl (*Z*)-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate (1.70): In a N_2-filled glove box, a 25 mL flask with a magnetic stir bar was charged with **1.69**[45] (160 mg, 0.672 mmol) and *Z*-2-butene-1,4-diol (178 mg, 2.02 mmol, 3.00 equiv) and tetrahydrofuran (6.7 mL). A catalyst solution of **Ru-9** (10 mg/mL in tetrahydrofuran, 2.57 mL, 25.7 mg, 0.034 mmol, 5 mol %) was added and the mixture was allowed to stir at 22 °C for two hours under 100 torr vacuum. Additional catalyst (10 mg/mL in tetrahydrofuran, 2.57 mL, 25.7 mg, 0.034 mmol, 5 mol %) was added and the mixture was allowed to stir for additional 10 hours. The reaction mixture was taken out of the glove box and filtered through a thin pad of silica gel (EtOAc). The filtrate was concentrated by vacuum and the resulting brown oil was purified by silica gel chromatography (1:2 hexanes: ethyl acetate) to afford **1.70** as colorless oil (128 mg, 0.478 mmol, 71% yield). **IR (neat)**: 3329 (br), 2920 (m), 2850 (m), 1701 (s), 1589 (w), 1521 (s), 1462 (m), 1261 (s), 1193 (w), 1023 (s), 778 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.34 (1H, s), 6.28 (1H, dt, J = 11.6, 1.6 Hz), 6.10–6.04 (1H, m), 5.68–5.62 (1H, m), 5.60 (1H, br s), 5.55–5.49 (1H, m), 4.32 (2H, t, J = 5.6 Hz), 4.15 (2H,

d, J = 6.8 Hz), 3.68 (3H, s), 2.62 (2H, t, J = 7.2 Hz), 2.48 (2H, q, J = 7.2 Hz), 1.97 (1H, br s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 160.2, 157.3, 141.2, 136.4, 134.1, 131.6, 129.7, 116.7, 58.4, 52.3, 39.5, 26.0, 25.9; **HRMS [M+H]$^+$** calcd for $C_{13}H_{19}N_2O_4$: 267.1345, found: 267.1341.

1.6.8. Gram-Scale Z-Selective Cross-Metathesis (CM) Reactions

General Procedure: An oven-dried 40 mL vial equipped with a magnetic stir bar is charged with alkene substrate (1.0 equiv) and *Z*-2-butene-1,4-diol (2.0 equiv) in a fume hood. The vial is then sealed, evacuated and purged with N_2. To this vial, a solution of **Ru-9** (5.0 mol %) in tetrahydrofuran is added. The resulting solution is allowed to stir for 4 or 6 hours at 22°C, after which the reaction is quenched by addition of wet diethyl ether and concentrated *in vacuo* (percent conversion determined by 400 MHz ^{1}H NMR analysis). Purification is performed through silica gel chromatography and/or Kugelrohr distillation.

(*Z*)-2-(7-Hydroxy-5-heptenyl)isoindoline-1,3-dione (1.54): Following the general procedure, a solution of **Ru-9** (167 mg, 0.218 mmol, 5.0 mol %) in tetrahydrofuran (8.7 mL) was transferred by syringe to a vial charged with 2-(hex-5-enyl)isoindoline-1,3-dione (1.00 g, 4.36 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (0.769 g, 8.72 mmol, 2.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C. Analysis of the unpurified mixture revealed 73% consumption of 2-(hex-5-enyl)isoindoline-1,3-dione. The resulting brown oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) and filtered through a small plug of activated charcoal to afford **1.54** (0.724 g, 2.79 mmol, 64% yield) as yellow oil in 98:2 *Z*/*E* ratio The spectral data for this compound were identical to those reported in the literature.[70]

(*Z*)-2-Undecene-1,11-diol (1.73): Following the general procedure, a solution of **Ru-9** (142 mg, 0.186 mmol, 5.0 mol %) in tetrahydrofuran (7.4 mL) was transferred by syringe to a vial charged with oleyl alcohol (1.00 g, 3.72 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (0.656 g, 7.45 mmol, 2.00 equiv). The resulting solution was allowed to stir for 6 hours at 22 °C. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 60% EtOAc in hexanes) and filtered through a small plug of activated charcoal to afford an inseparable mixture of unreacted oleyl alcohol and **1.72**, as well as **1.73** (0.431 g, 2.31 mmol, 62% yield) as yellow oil in 96:4 *Z*/*E* ratio; **IR (CH_2Cl_2)**: 3331 (br), 3054 (w), 2926 (m), 2854 (m), 1684 (w), 1458 (w), 1264 (m), 1021 (m), 909 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.60 (1H, dt, J = 11.2, 6.4 Hz), 5.56–5.49 (1H, m), 4.19 (2H, d, J = 6.3 Hz), 3.63 (2H, t, J = 6.6 Hz), 2.10–2.02 (2H, m), 1.59–1.50 (2H, m), 1.38–1.27 (12H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 133.3, 128.5, 63.2, 58.8, 32.9, 29.7, 29.5, 29.5, 29.2, 27.5, 25.8; **HRMS $[M+H-H_2O]^+$** calcd for $C_{11}H_{21}O$: 169.1592, found: 169.1585. The mixture of oleyl alcohol and **1.72** was further purified by Kugelrohr distillation to afford **1.72** (0.374 g, 2.20 mmol, 59% yield) as colorless oil in 94:06 *Z*/*E* ratio. The spectral data for **1.72** were identical to those reported in the literature.[28b]

(*Z*)-11-Hydroxy-9-undecenoic acid (1.75): Following the general procedure, a solution of **Ru-9** (135 mg, 0.177 mmol, 5.0 mol %) in tetrahydrofuran (7.1 mL) was transferred by syringe to a vial charged with oleic acid (1.00 g, 3.54 mmol, 1.00 equiv) and *Z*-2-butene-1,4-diol (0.624 g, 7.08 mmol, 2.00 equiv). The resulting solution was allowed to stir for 6 hours at 22 °C. The resulting brown oil was purified by silica gel chromatography (10% EtOAc in hexanes to 60% EtOAc in hexanes) and filtered through

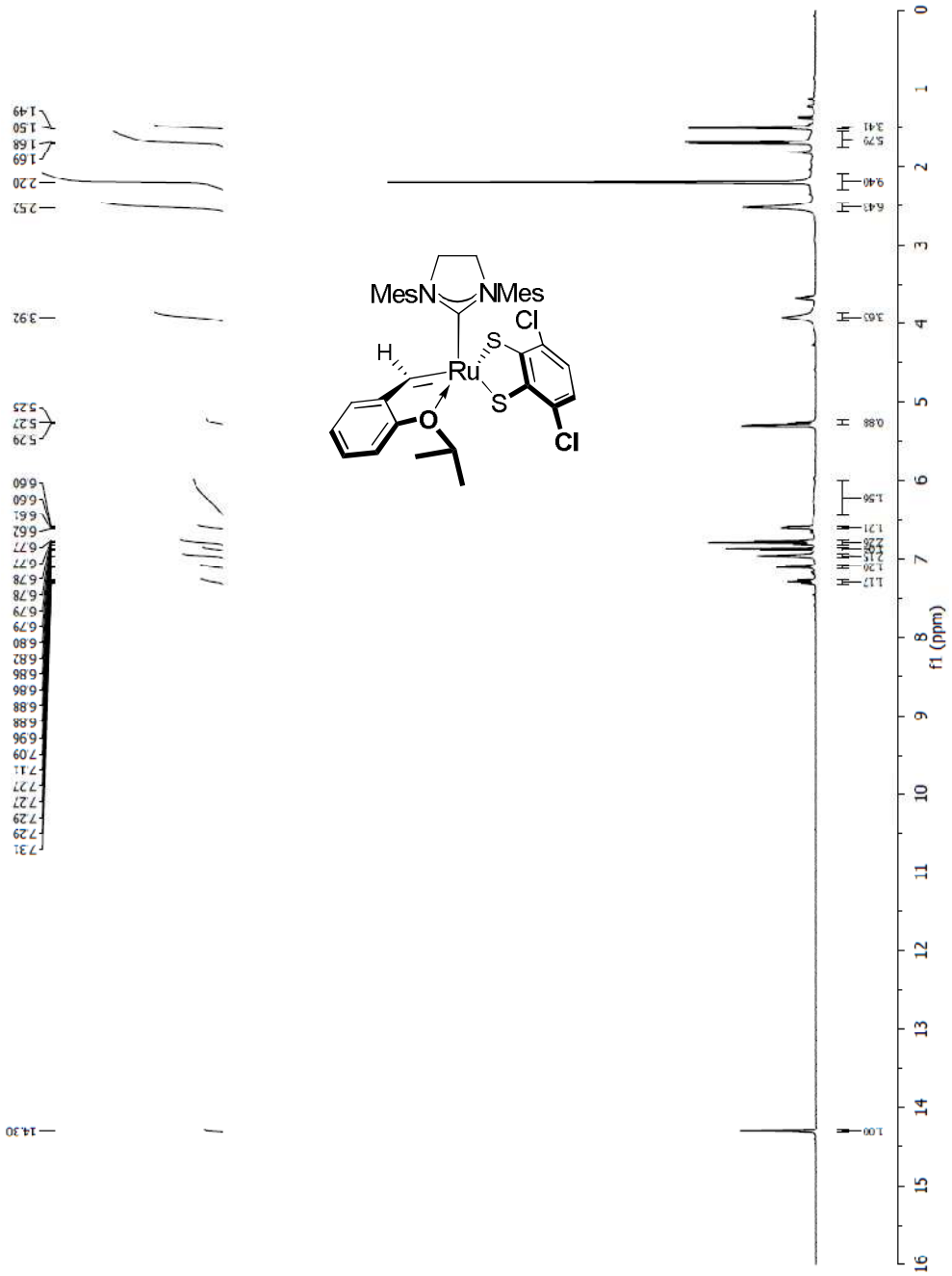
a small plug of activated charcoal to afford an inseparable mixture of unreacted oleic acid and **1.72**, as well as **1.75** (0.461 g, 2.30 mmol, 65% yield) as yellow oil in 94:06 *Z*/*E* ratio. The spectral data for **1.75** were identical to those reported in the literature.[76] The mixture of oleic acid and **1.72** was further purified by Kugelrohr distillation to afford **1.72** (0.362 g, 2.13 mmol, 60% yield) as colorless oil in 94:6 *Z*/*E* ratio. The spectral data for **1.72** were identical to those reported in the literature.[28b]

(76) Suzuki, Y.; Kurita, O.; Kono, Y.; Hyakutake, H.; Sakurai, A. *Biosci. Biotech. Biochem.* **59**, 2049–2051 (1995).

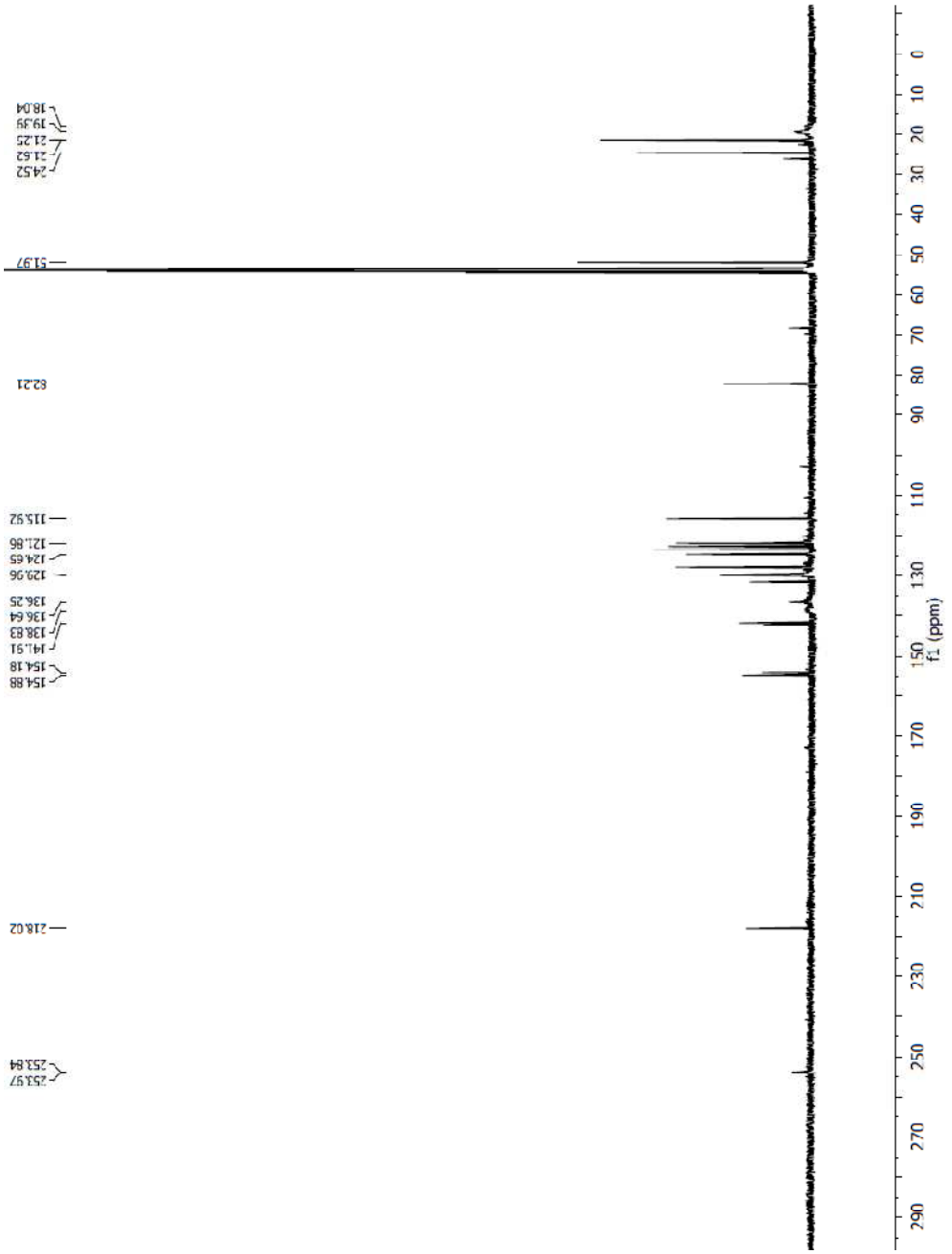
1.6.9. NMR Spectra

a. NMR spectra of Ru-based complexes

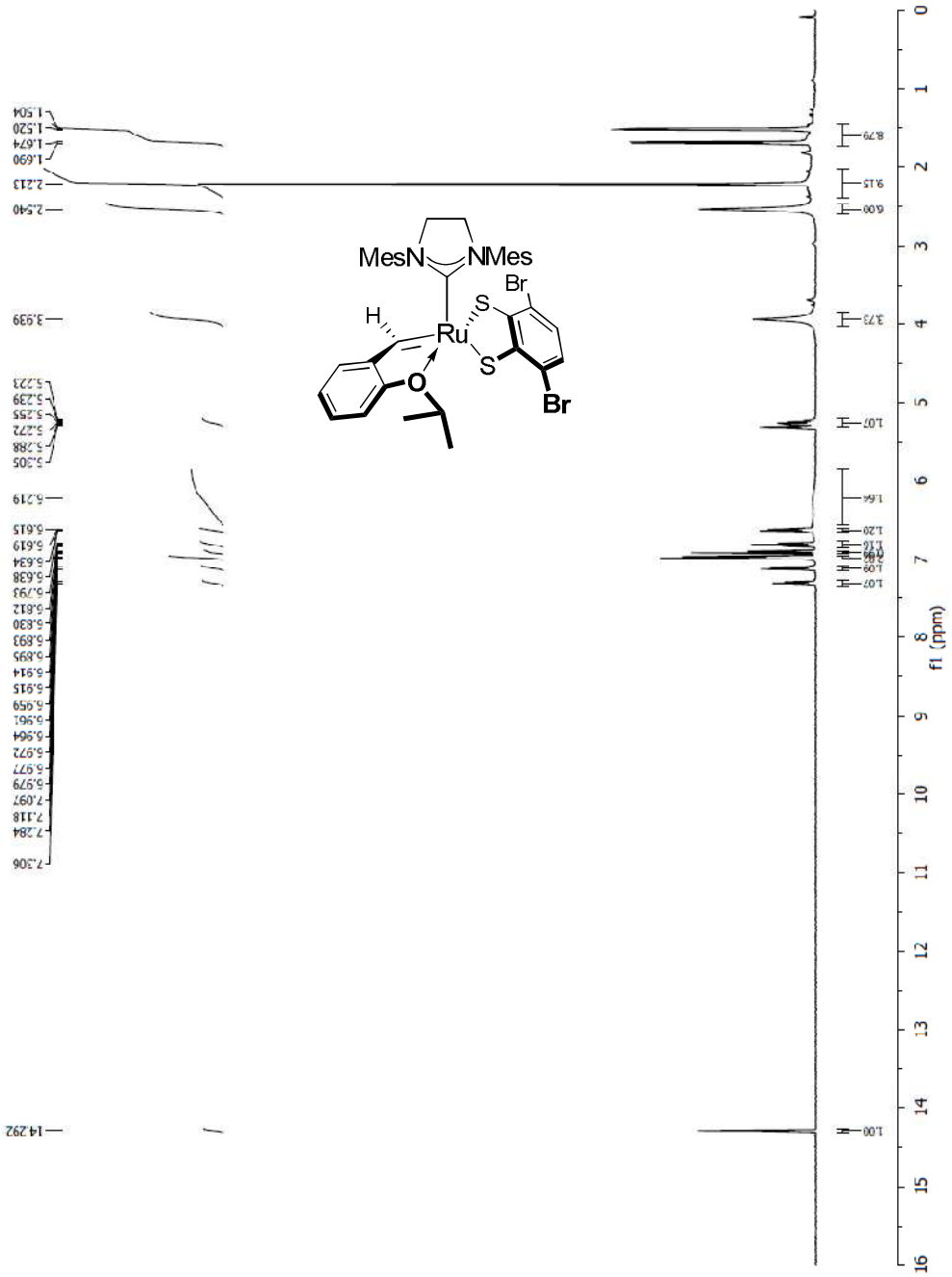
^{1}H NMR spectrum of Ru-9



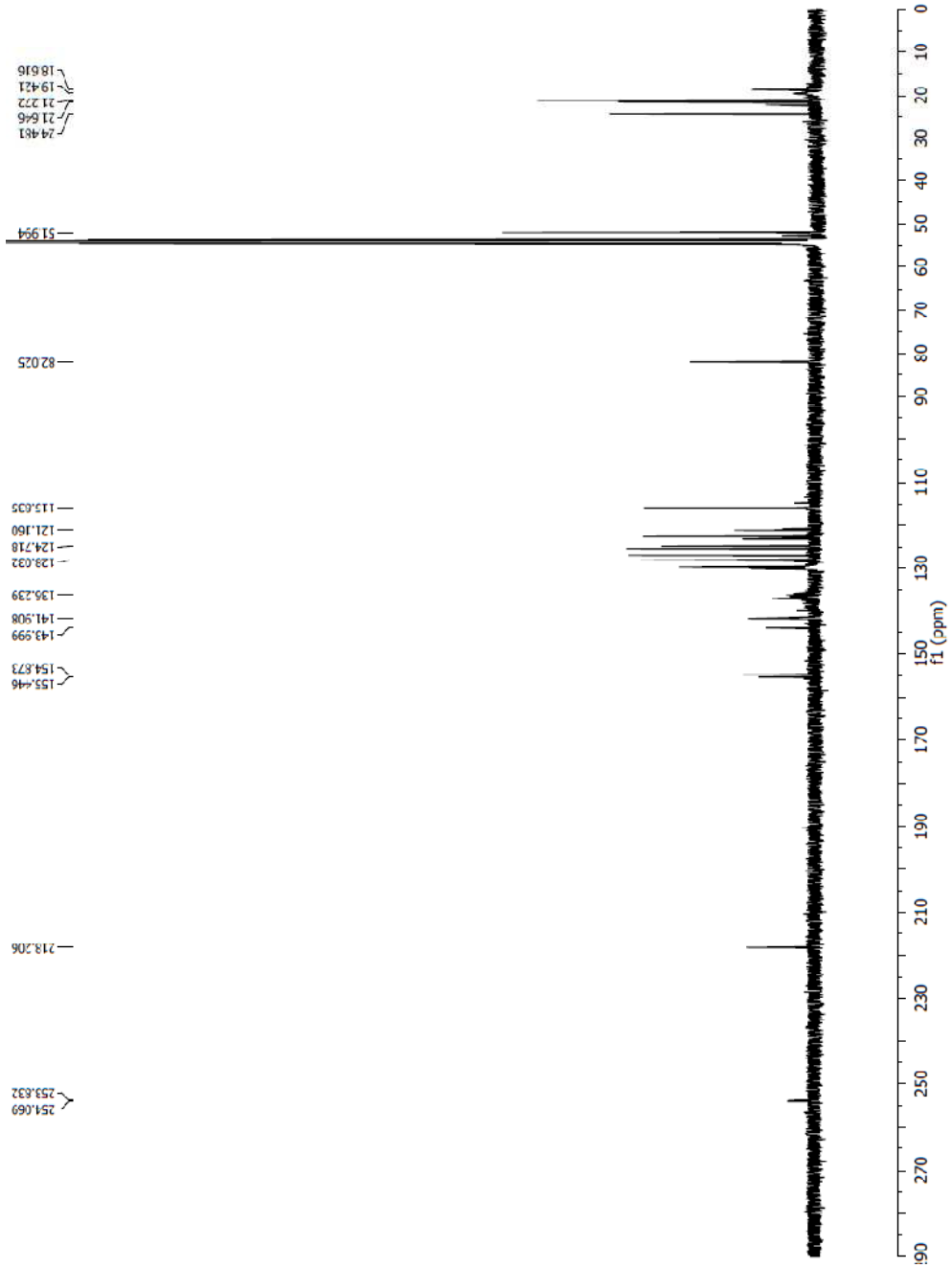
^{13}C NMR spectrum of Ru-9



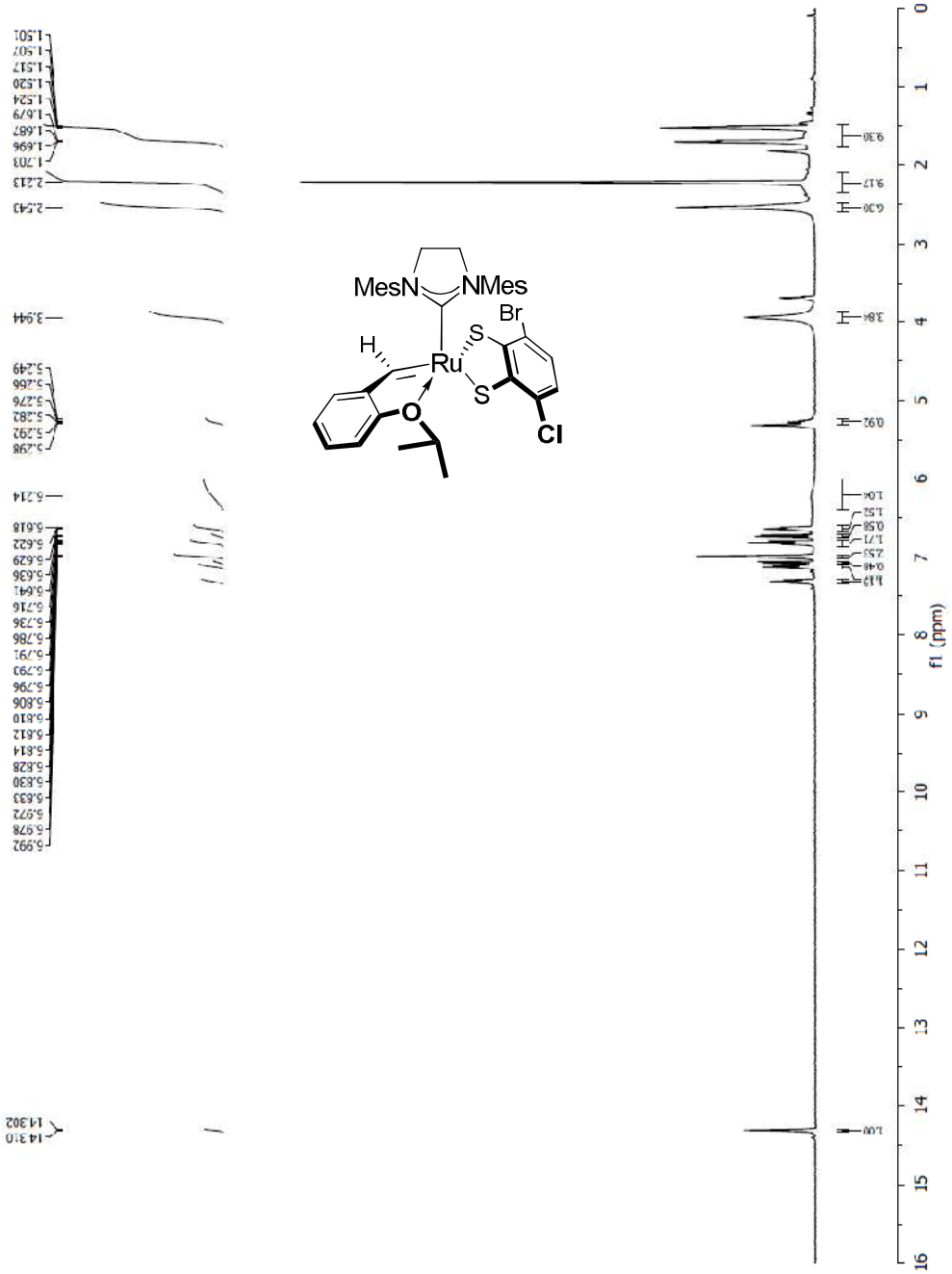
^{1}H NMR spectrum of Ru-10



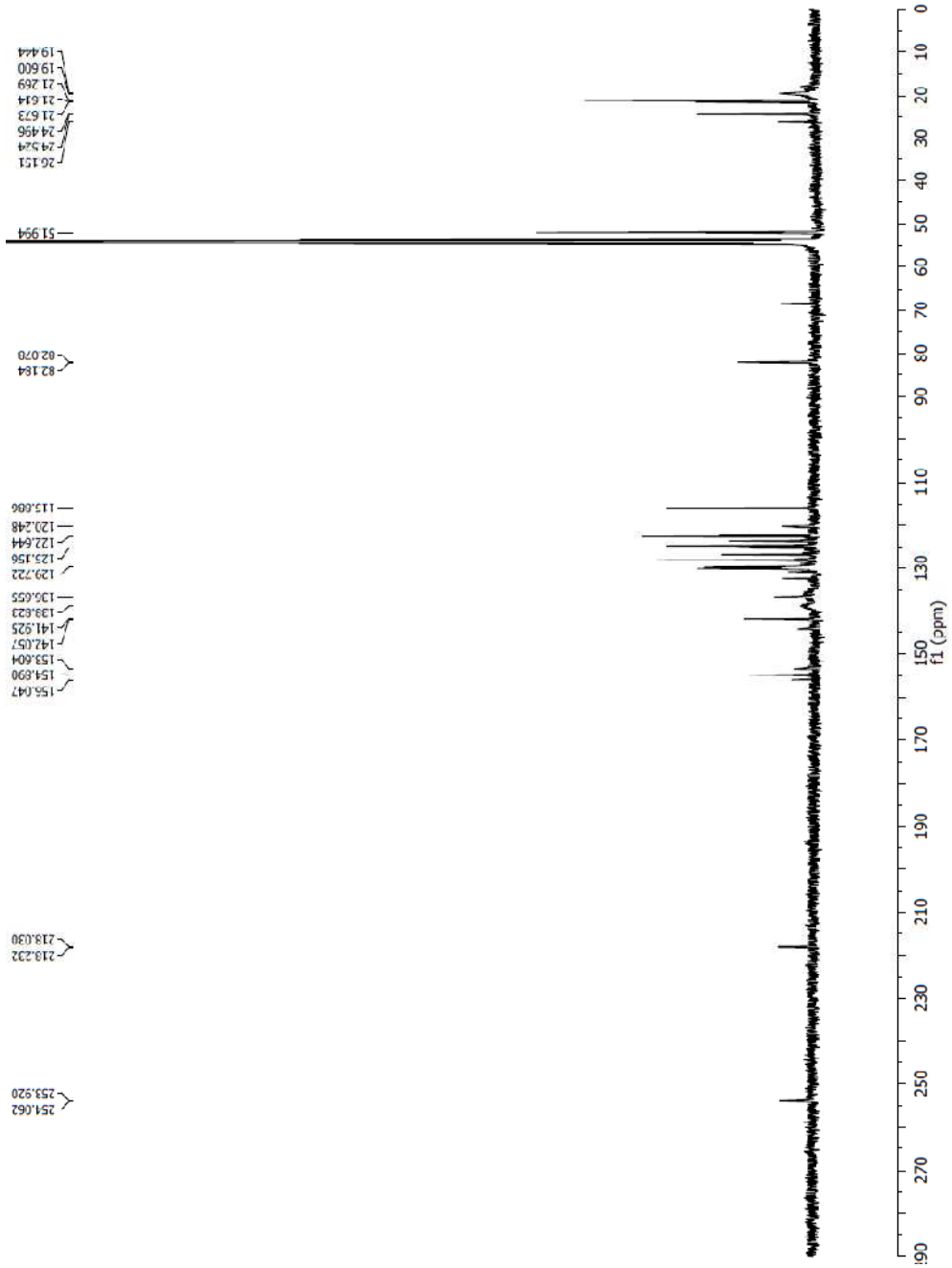
^{13}C NMR spectrum of Ru-10



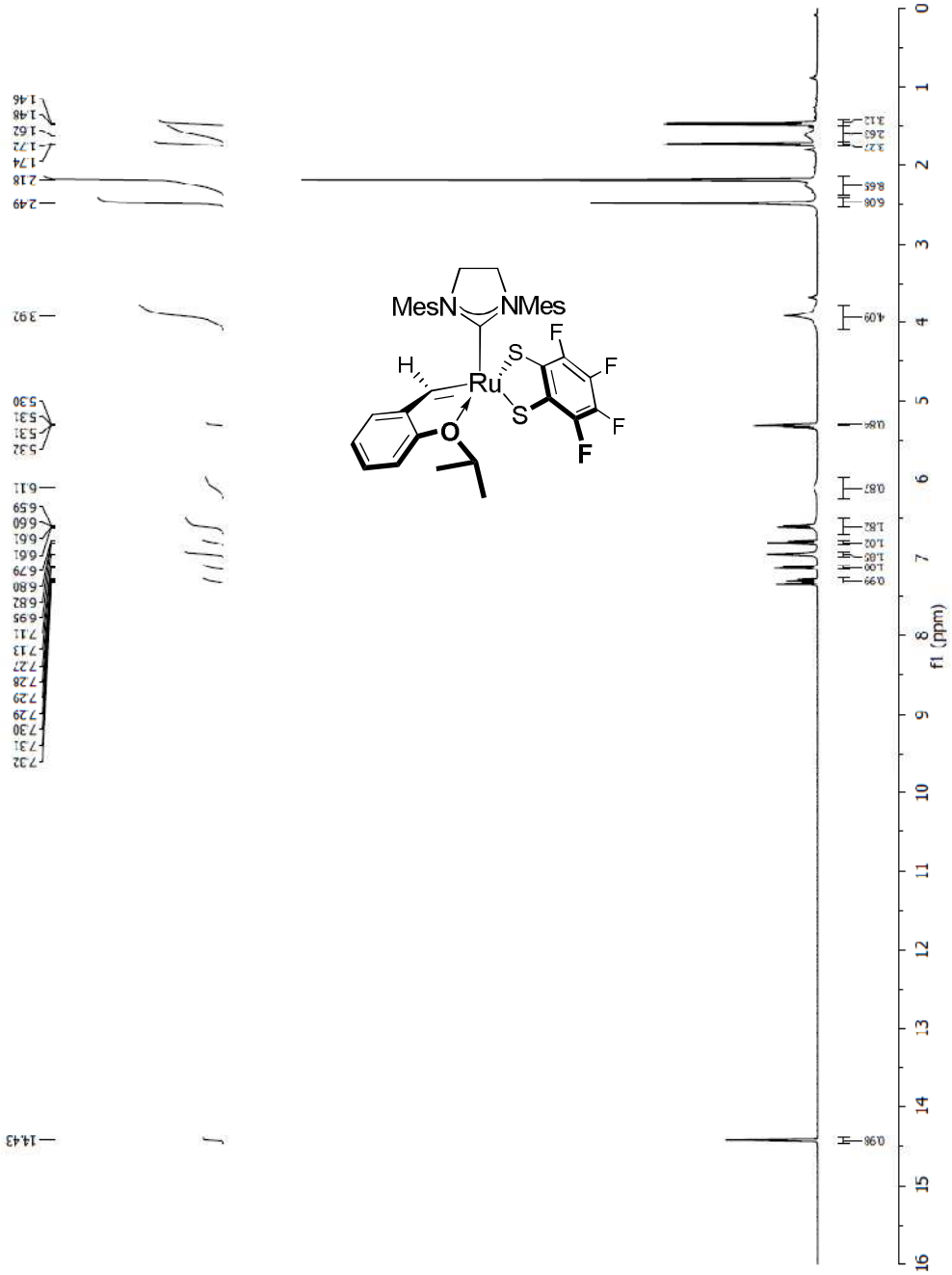
^{1}H NMR spectrum of Ru-11



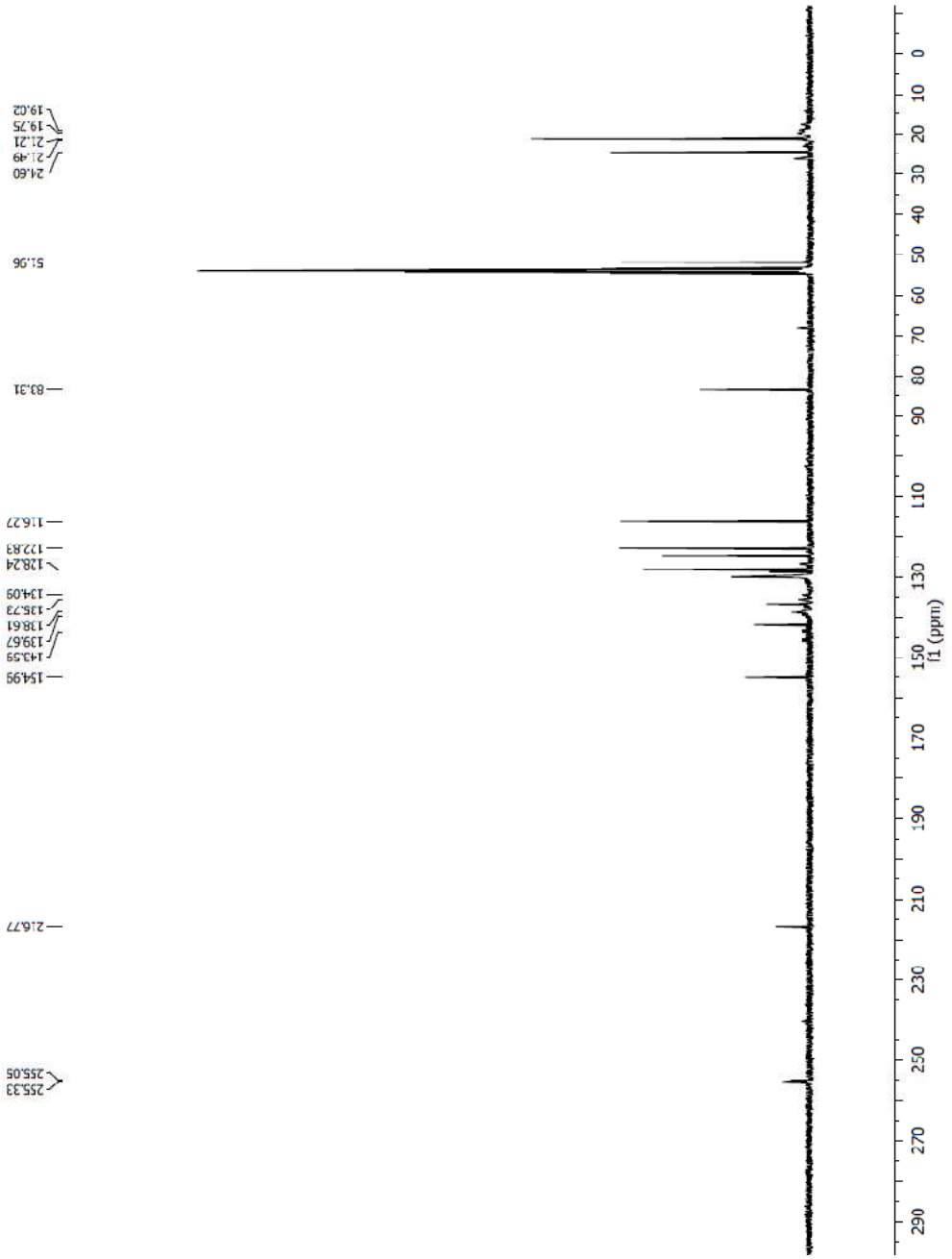
^{13}C NMR spectrum of Ru-11



^{1}H NMR spectrum of Ru-12

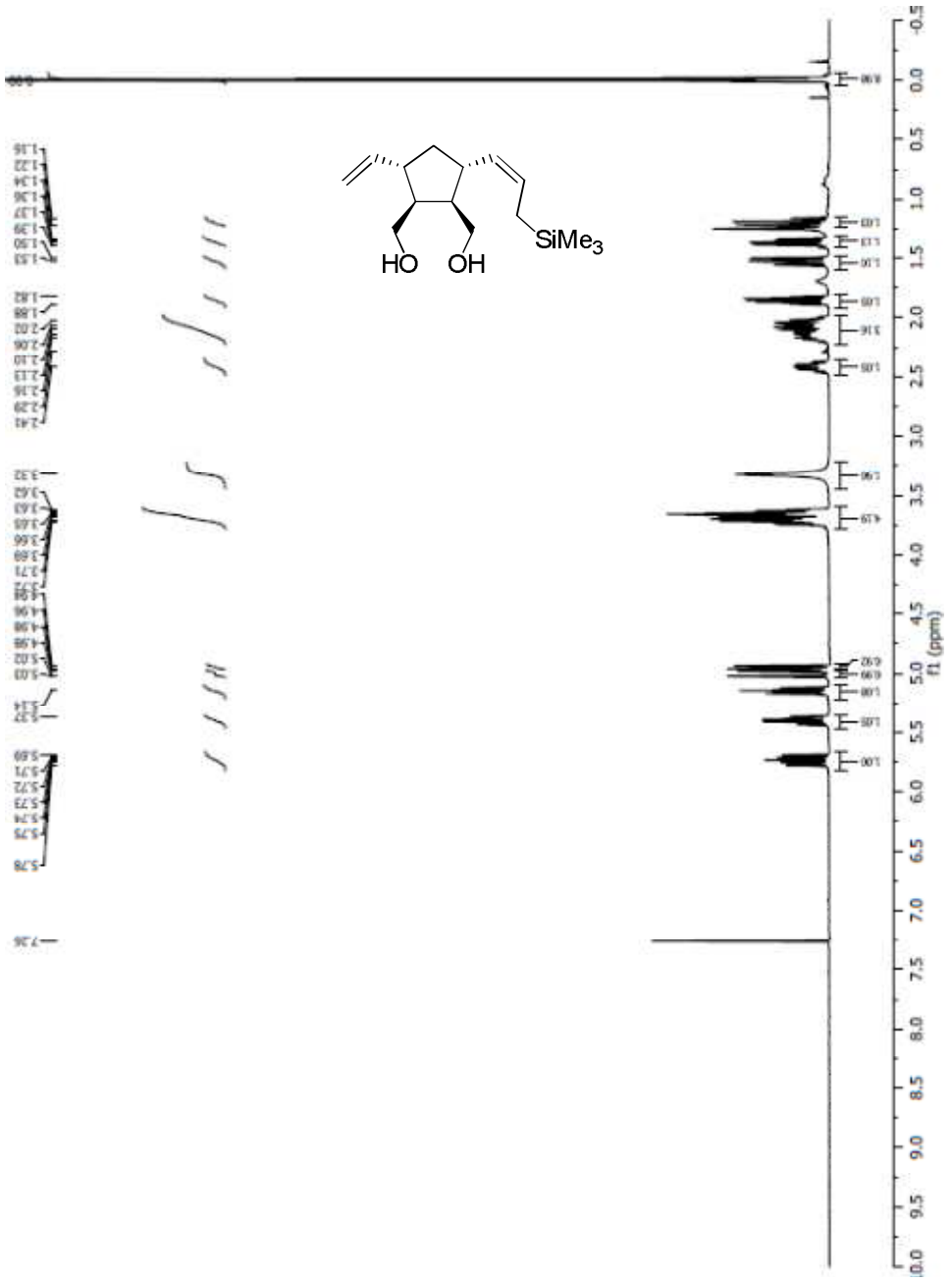


^{13}C NMR spectrum of Ru-12

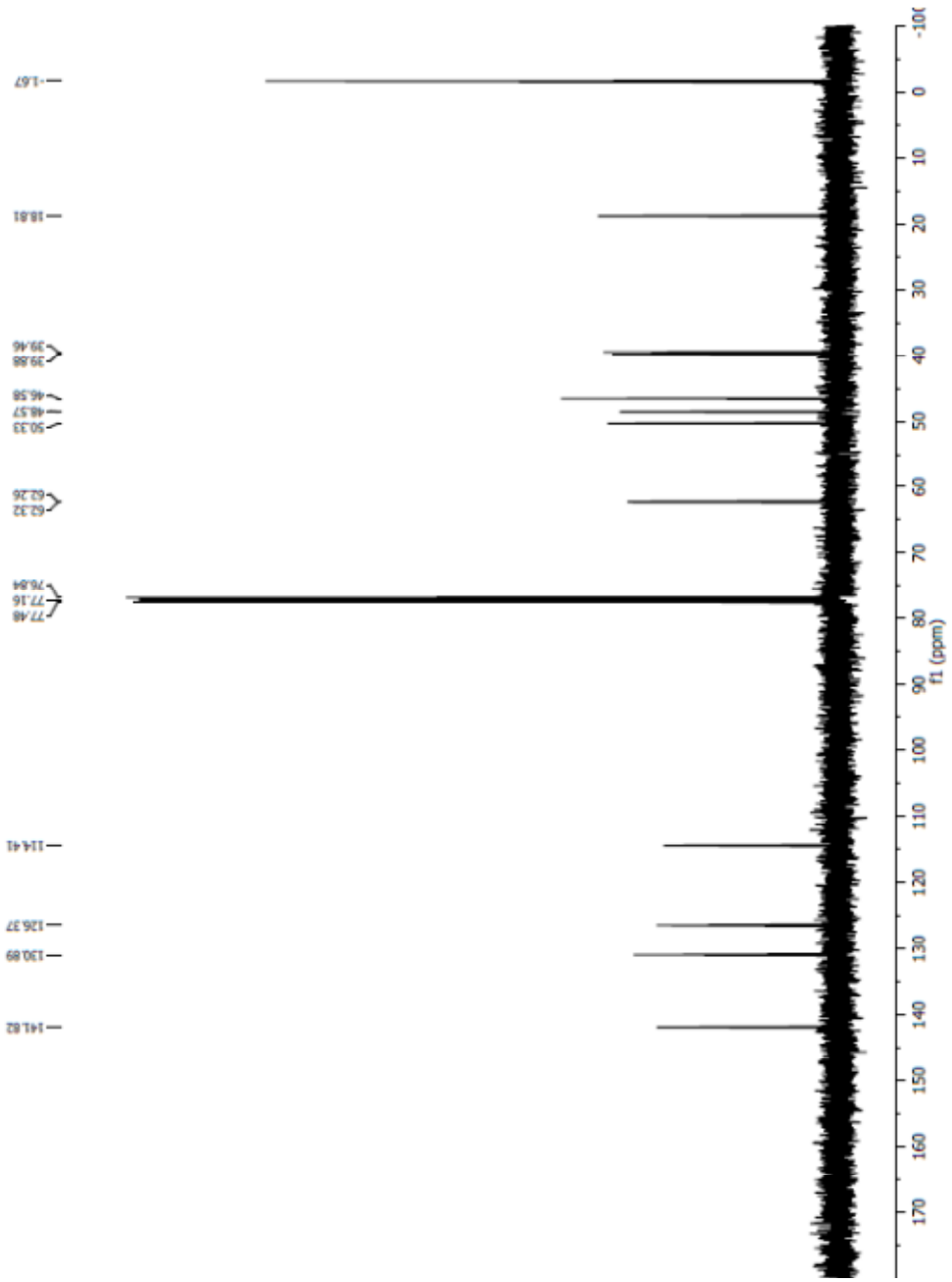


b. NMR spectra of ROCM products

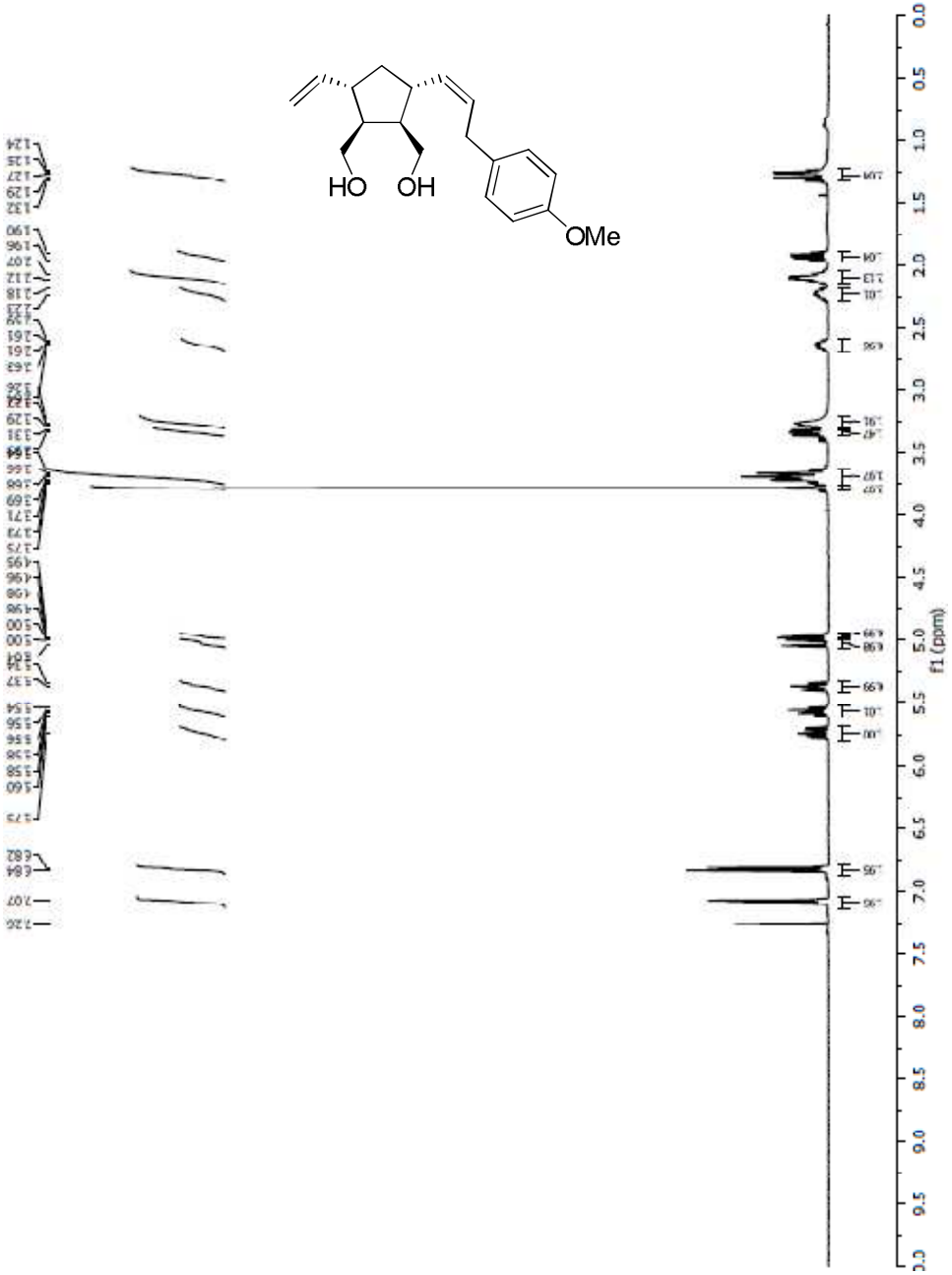
^{1}H NMR spectrum of 1.10



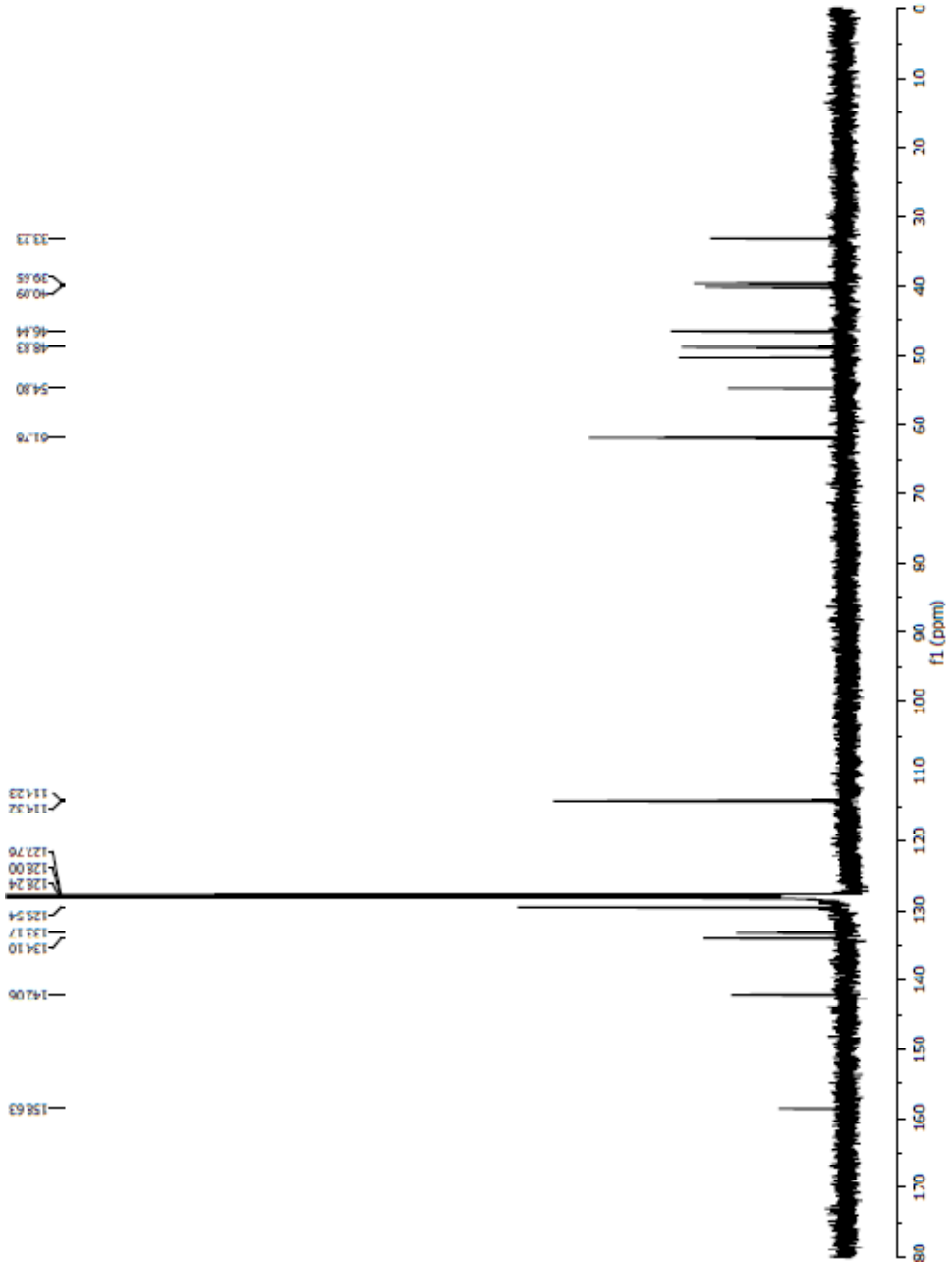
^{13}C NMR spectrum of 1.10



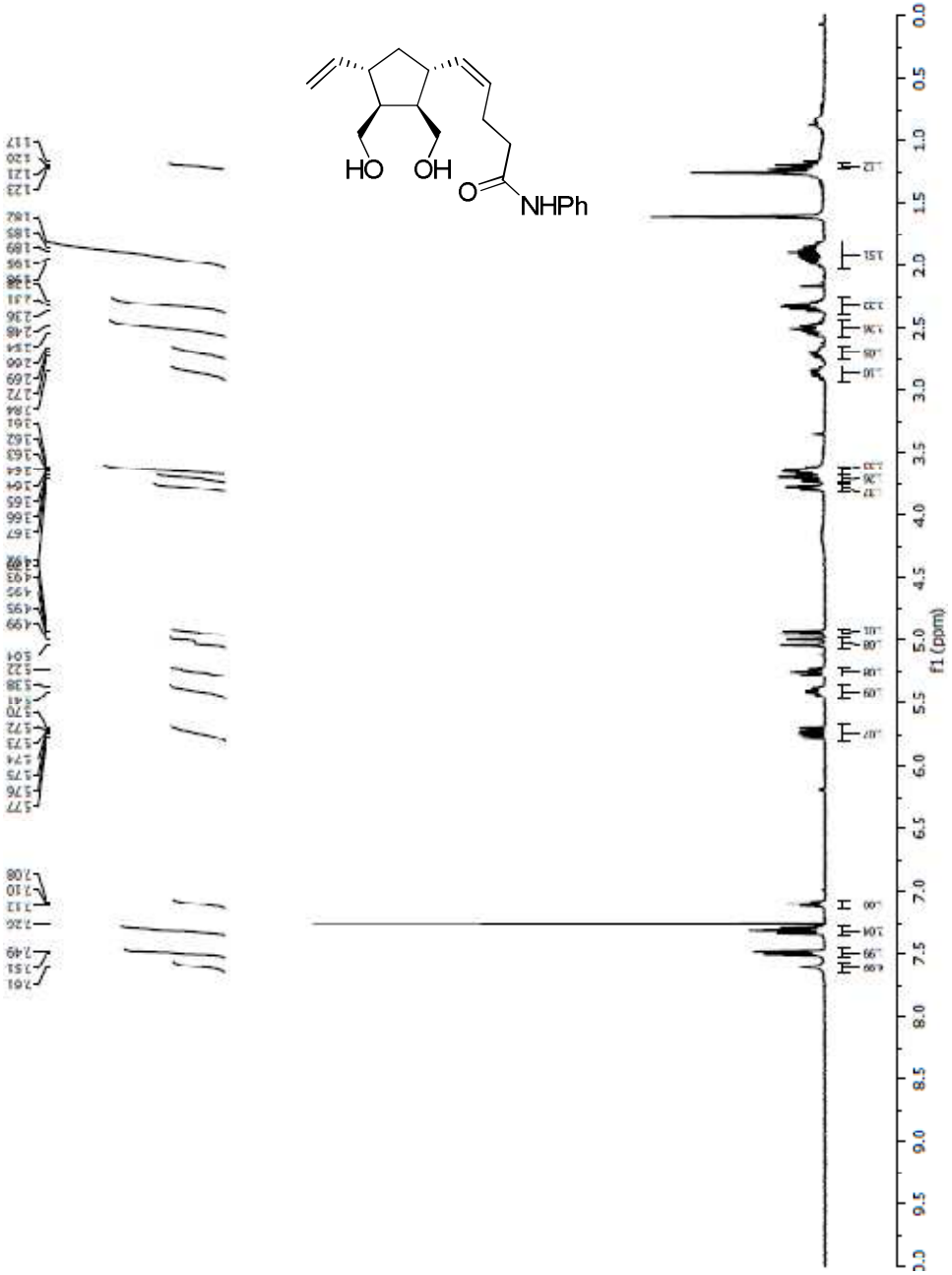
^{1}H NMR spectrum of 1.11



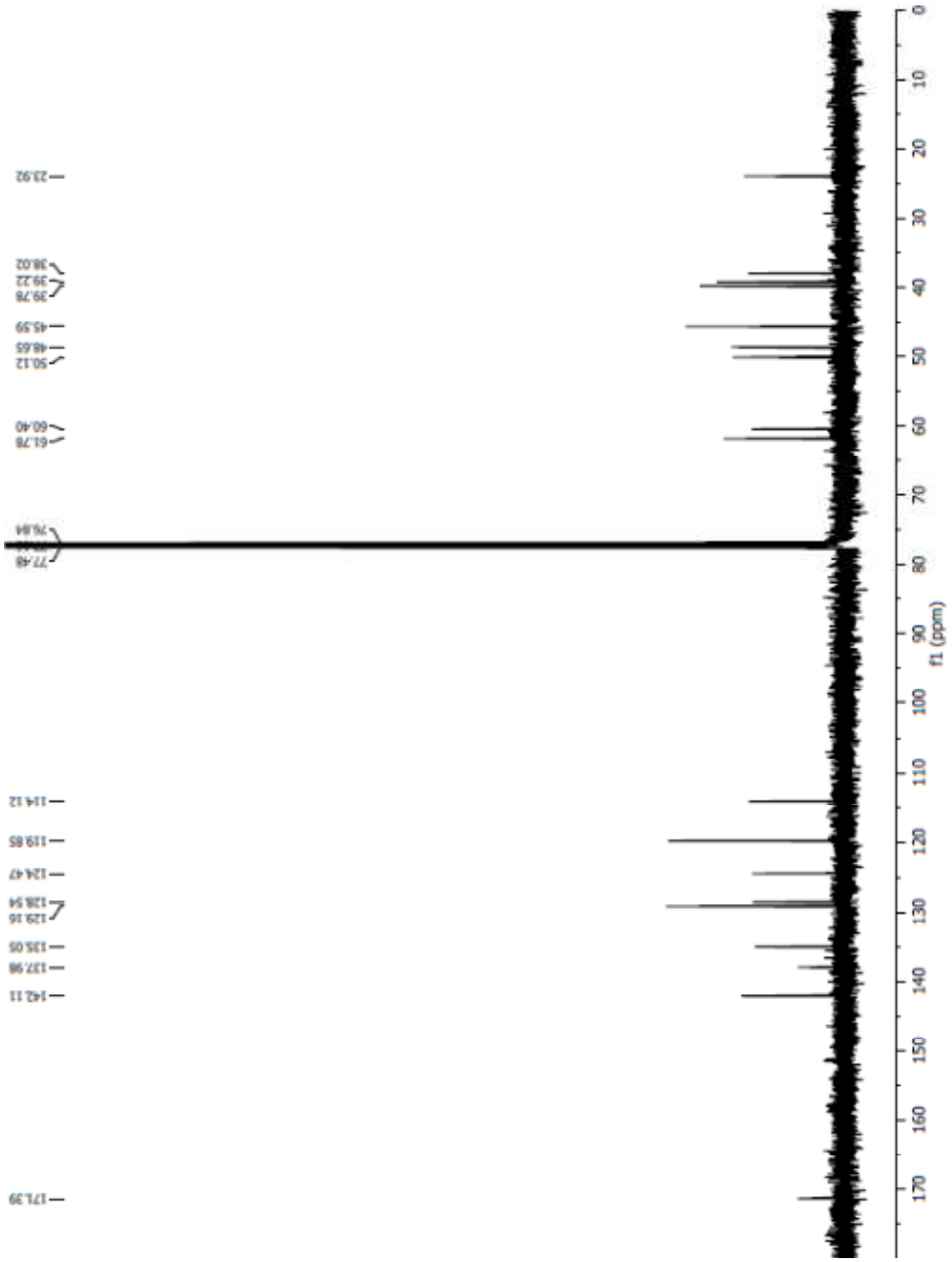
^{13}C NMR spectrum of 1.11



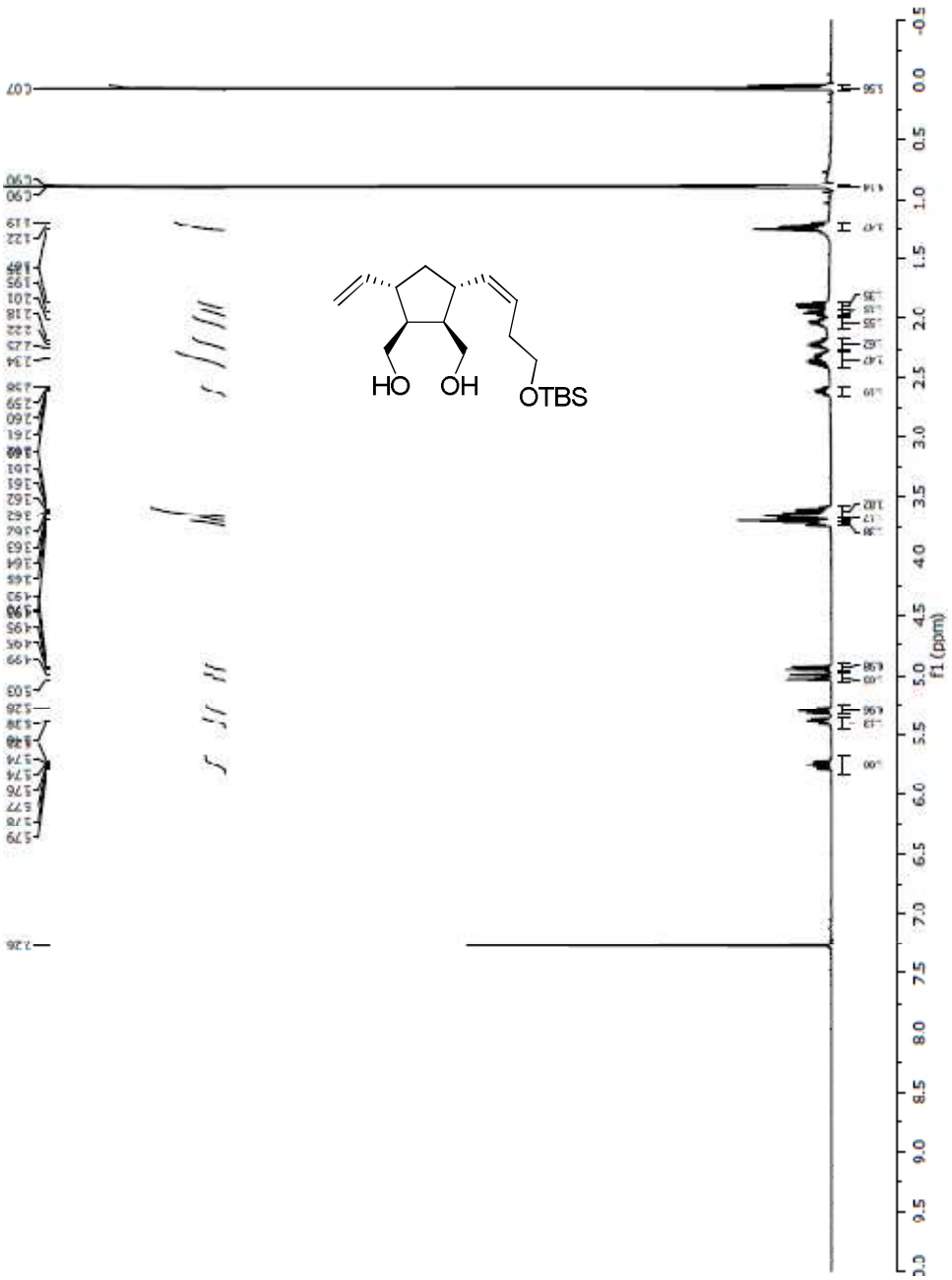
^{1}H NMR spectrum of 1.12



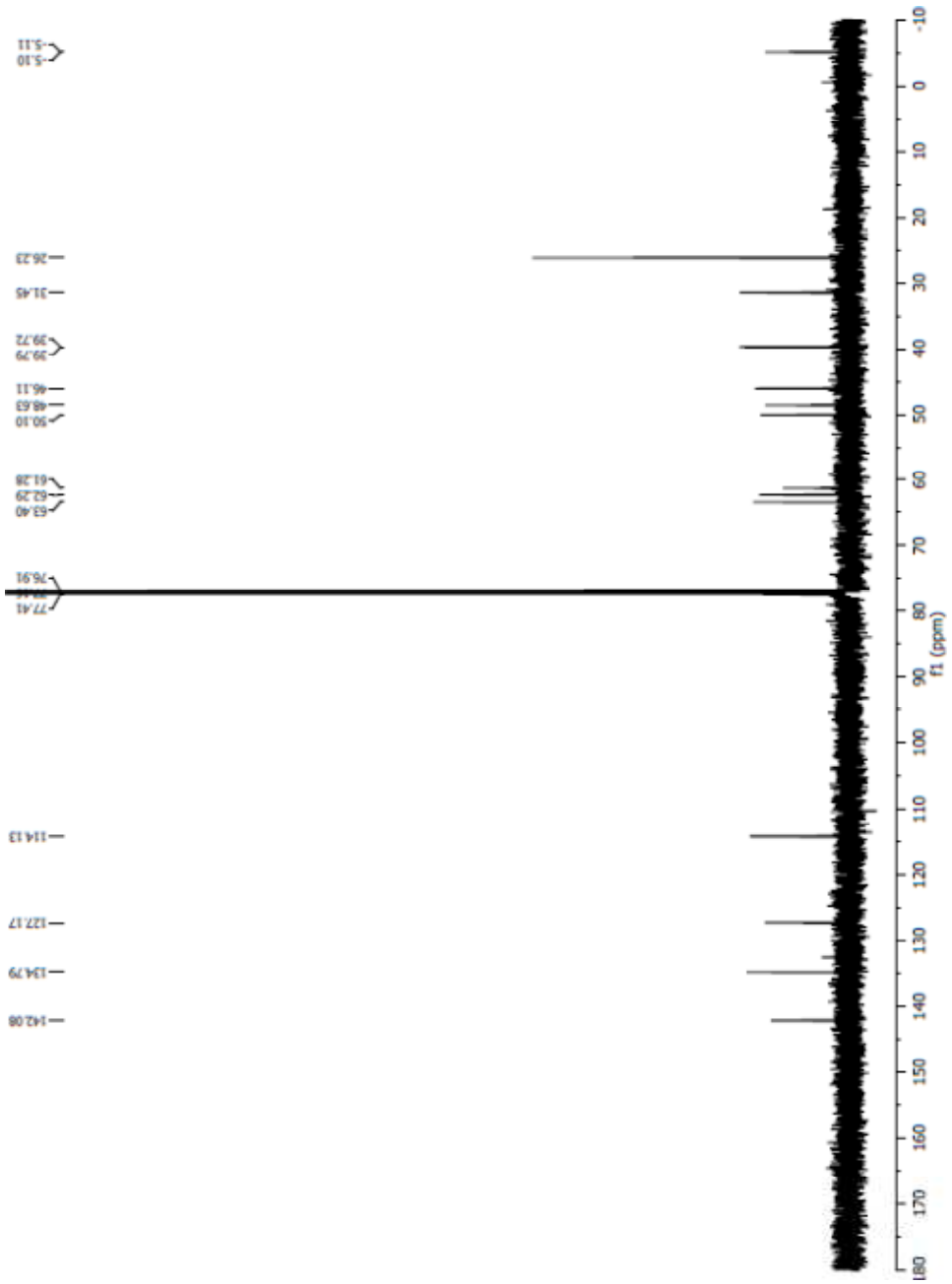
^{13}C NMR spectrum of 1.12



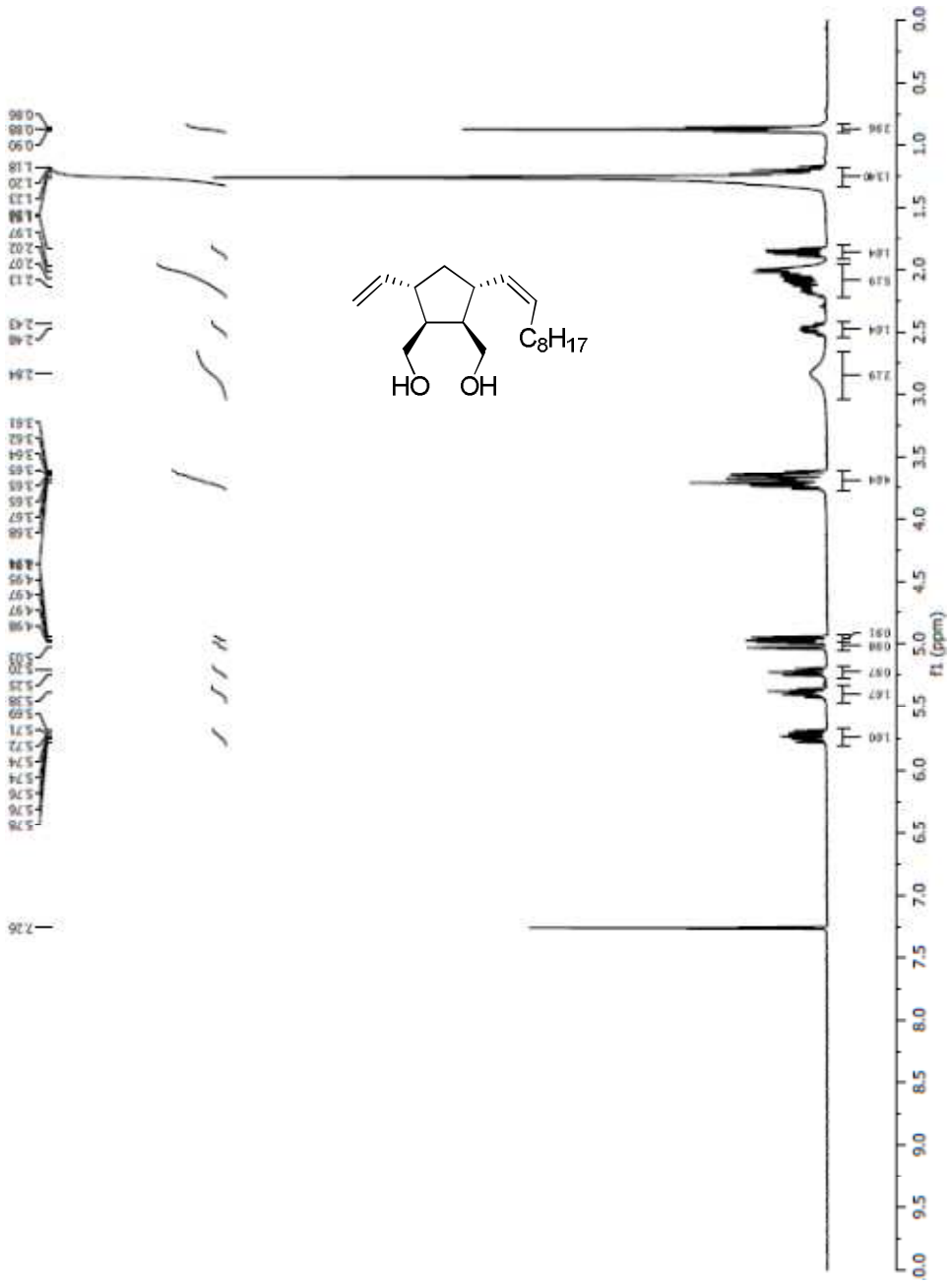
^{1}H NMR spectrum of 1.13



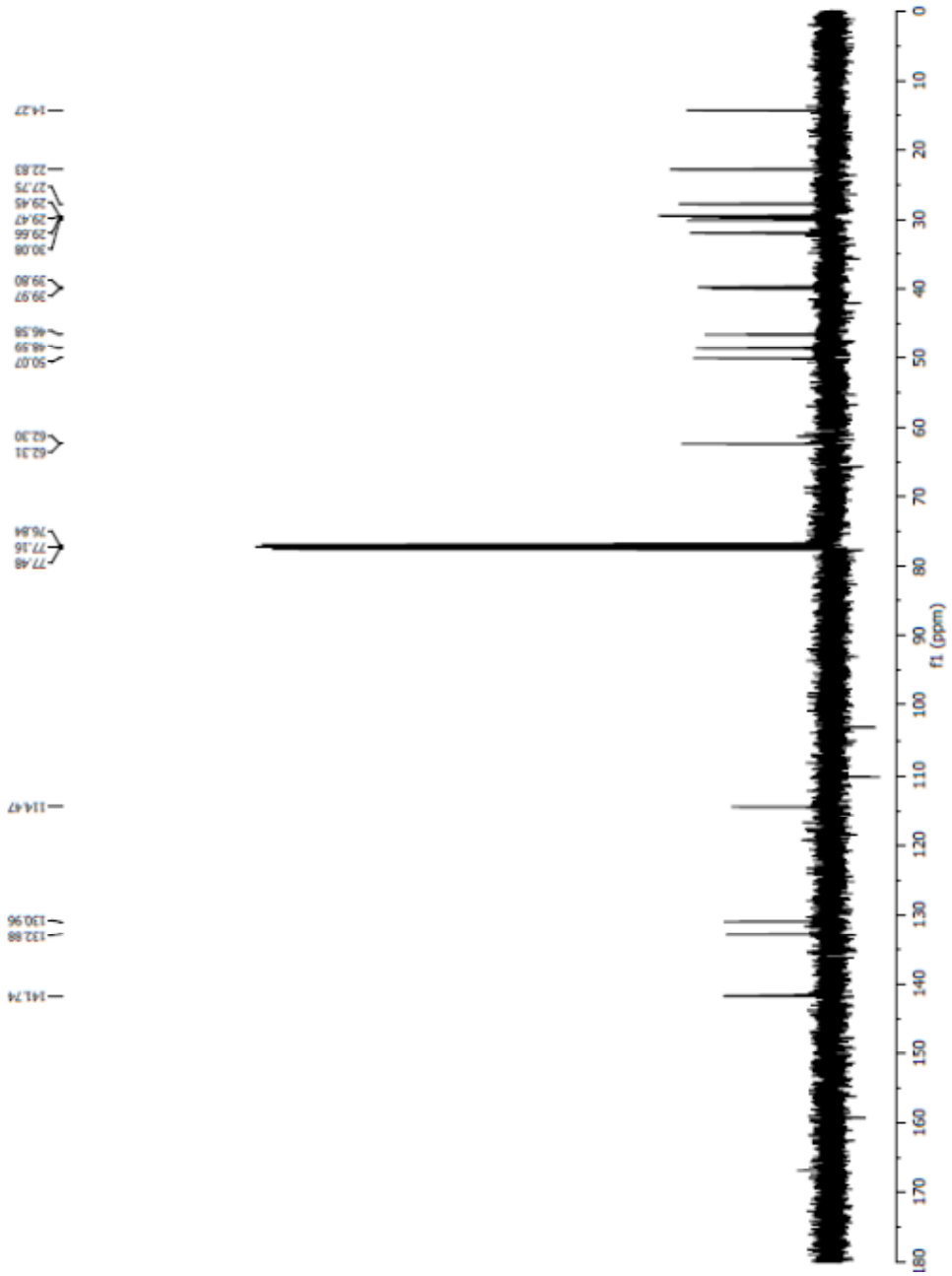
^{13}C NMR spectrum of 1.13



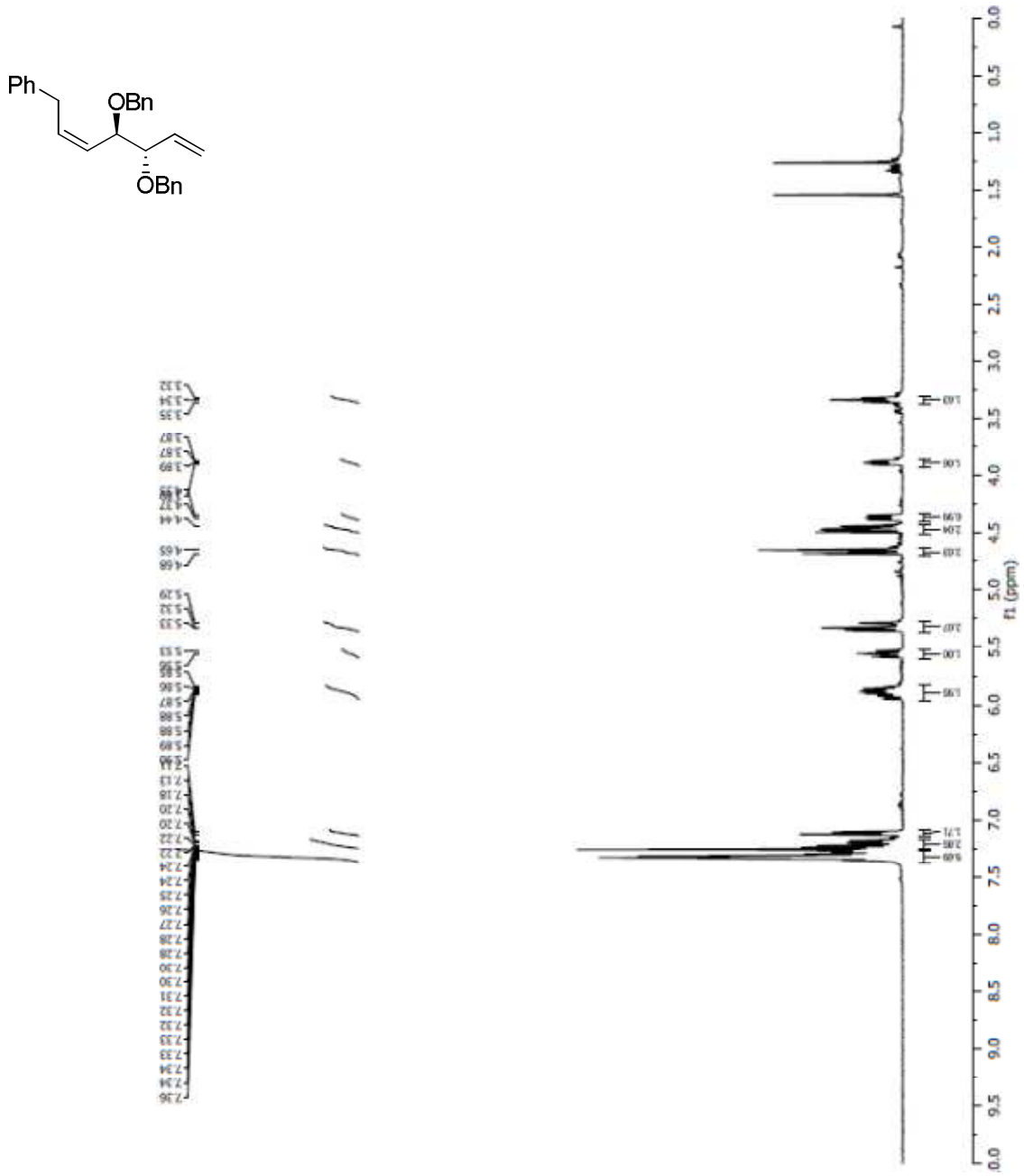
^{1}H NMR spectrum of 1.14



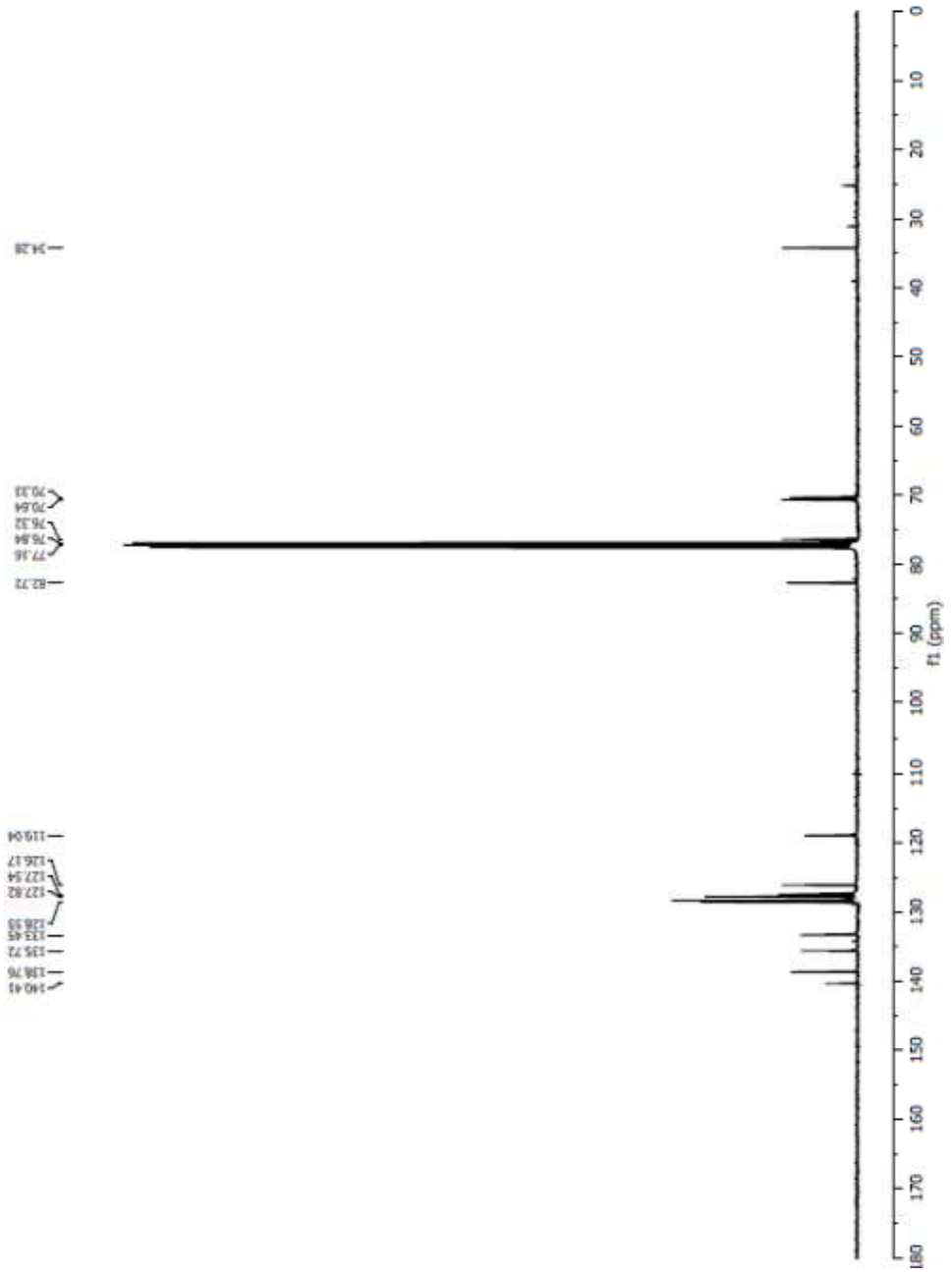
^{13}C NMR spectrum of 1.14



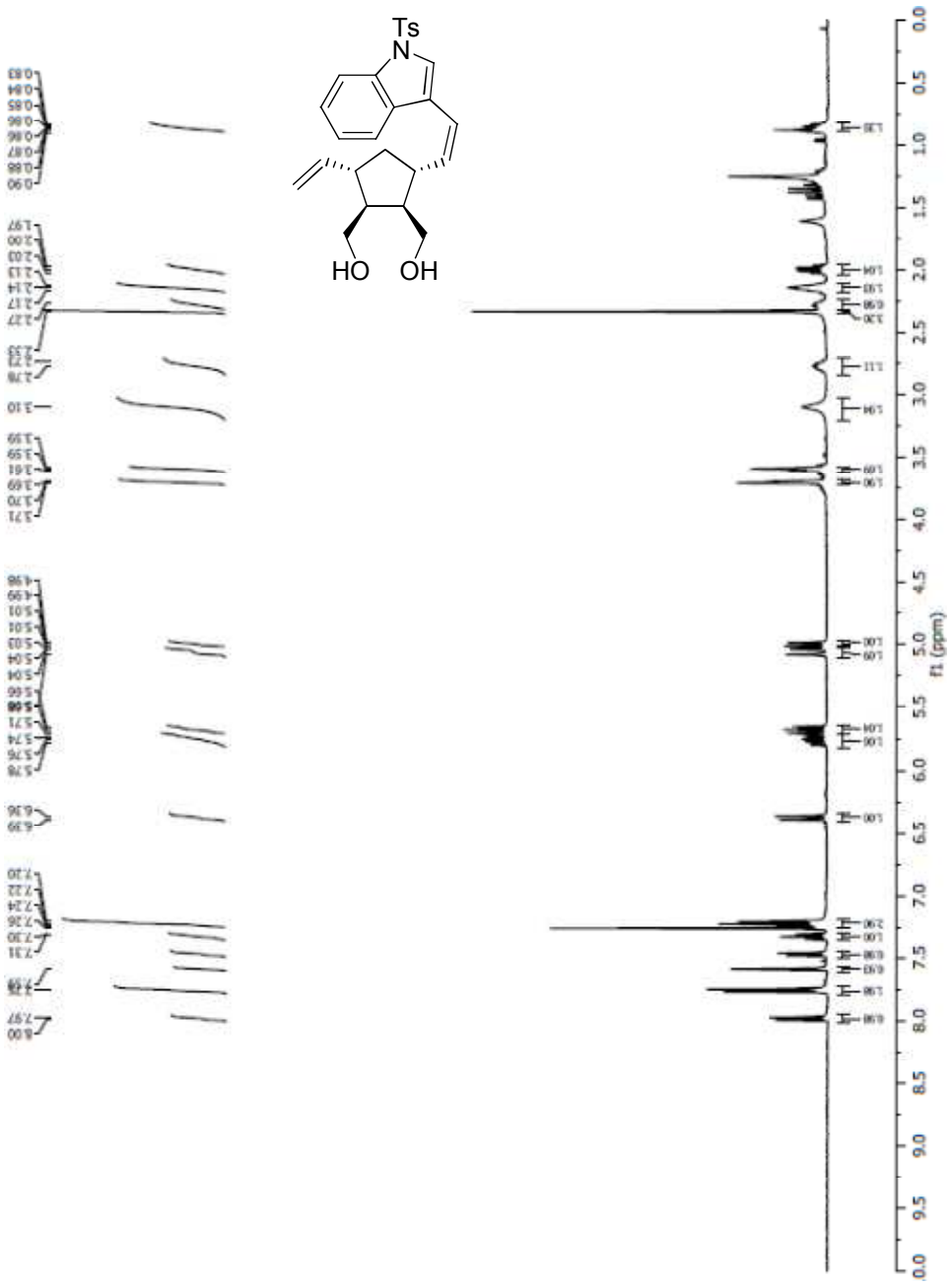
^{1}H NMR spectrum of 1.16



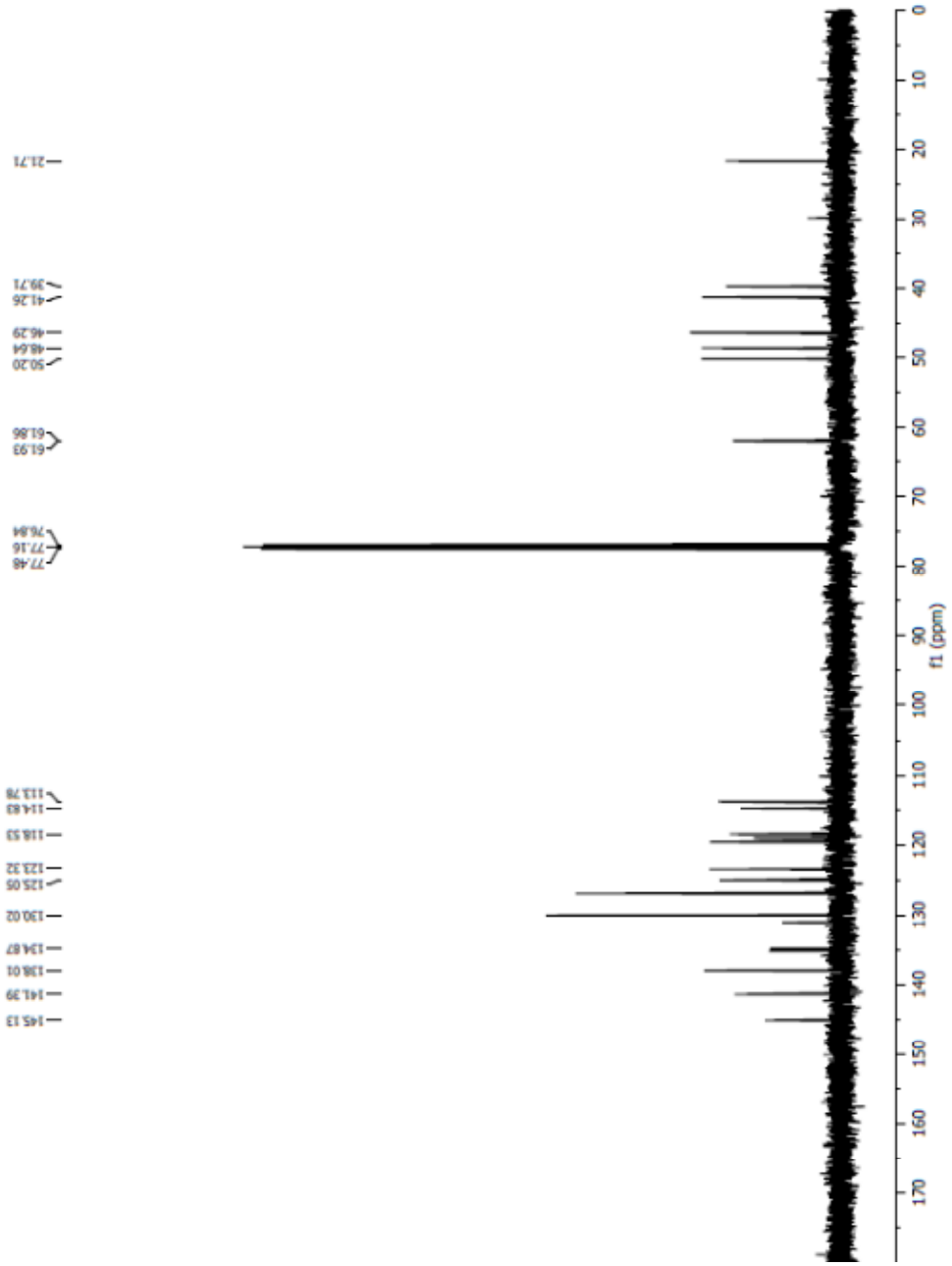
^{13}C NMR spectrum of 1.16



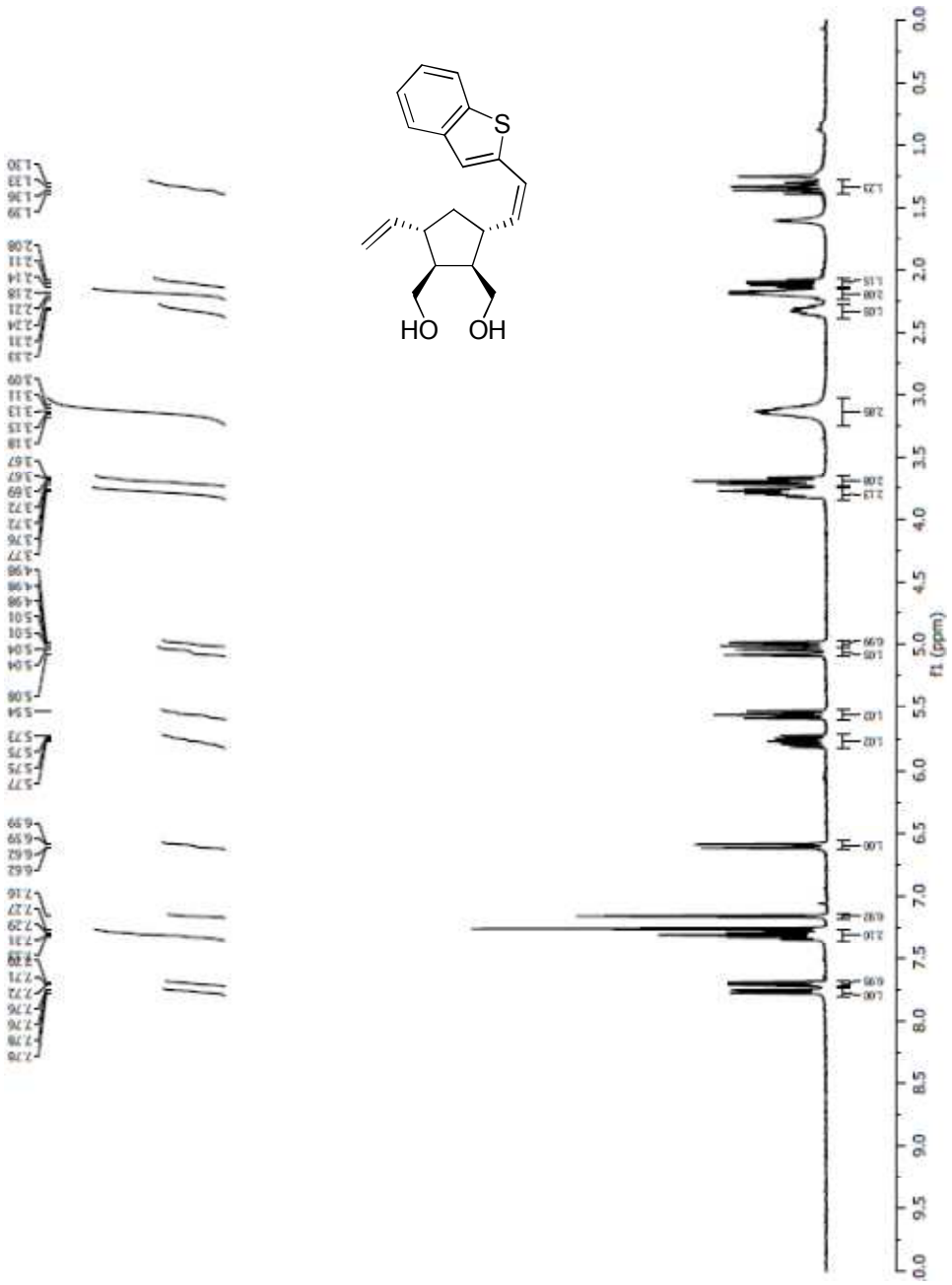
^{1}H NMR spectrum of 1.17



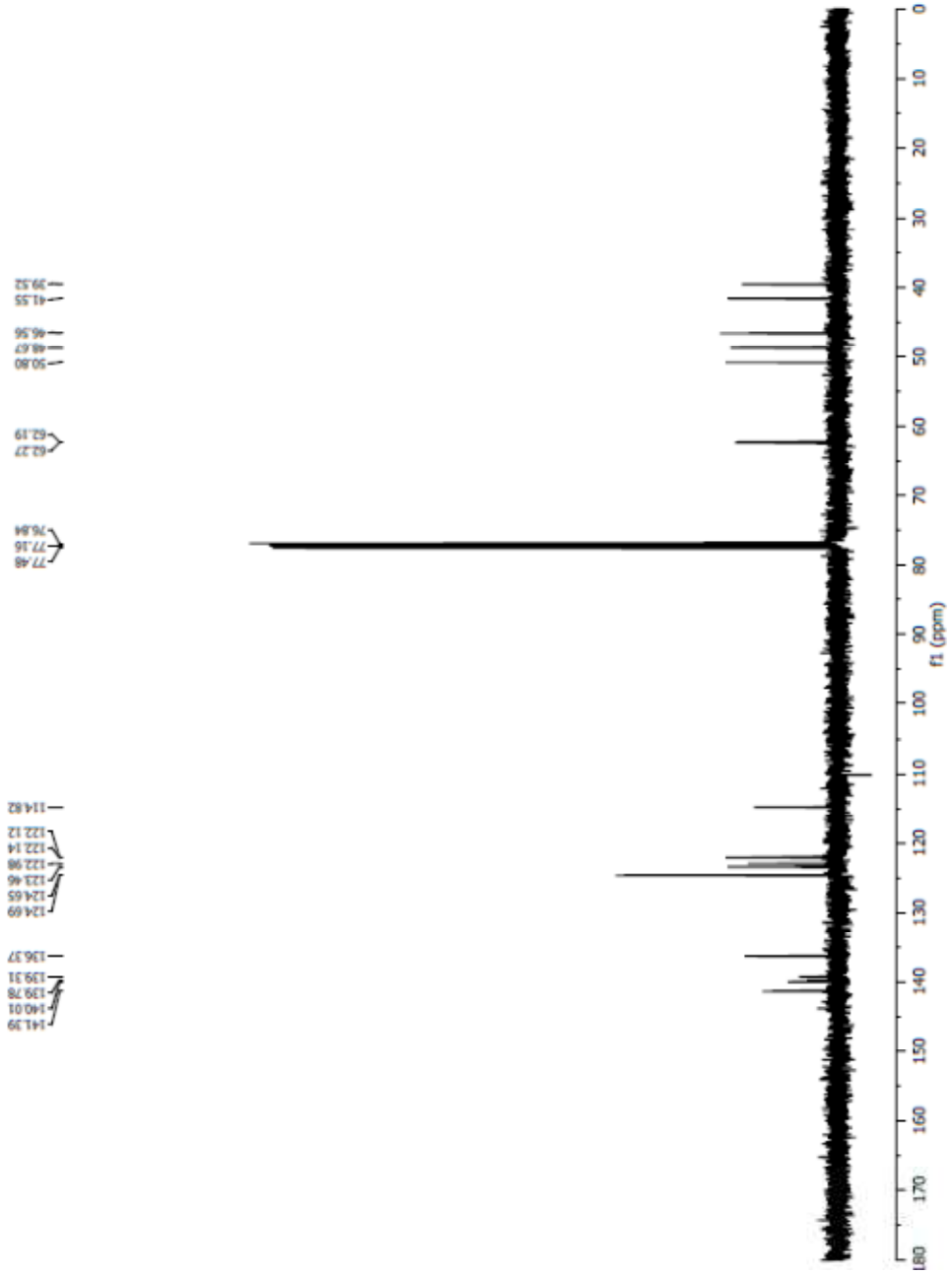
^{13}C NMR spectrum of 1.17



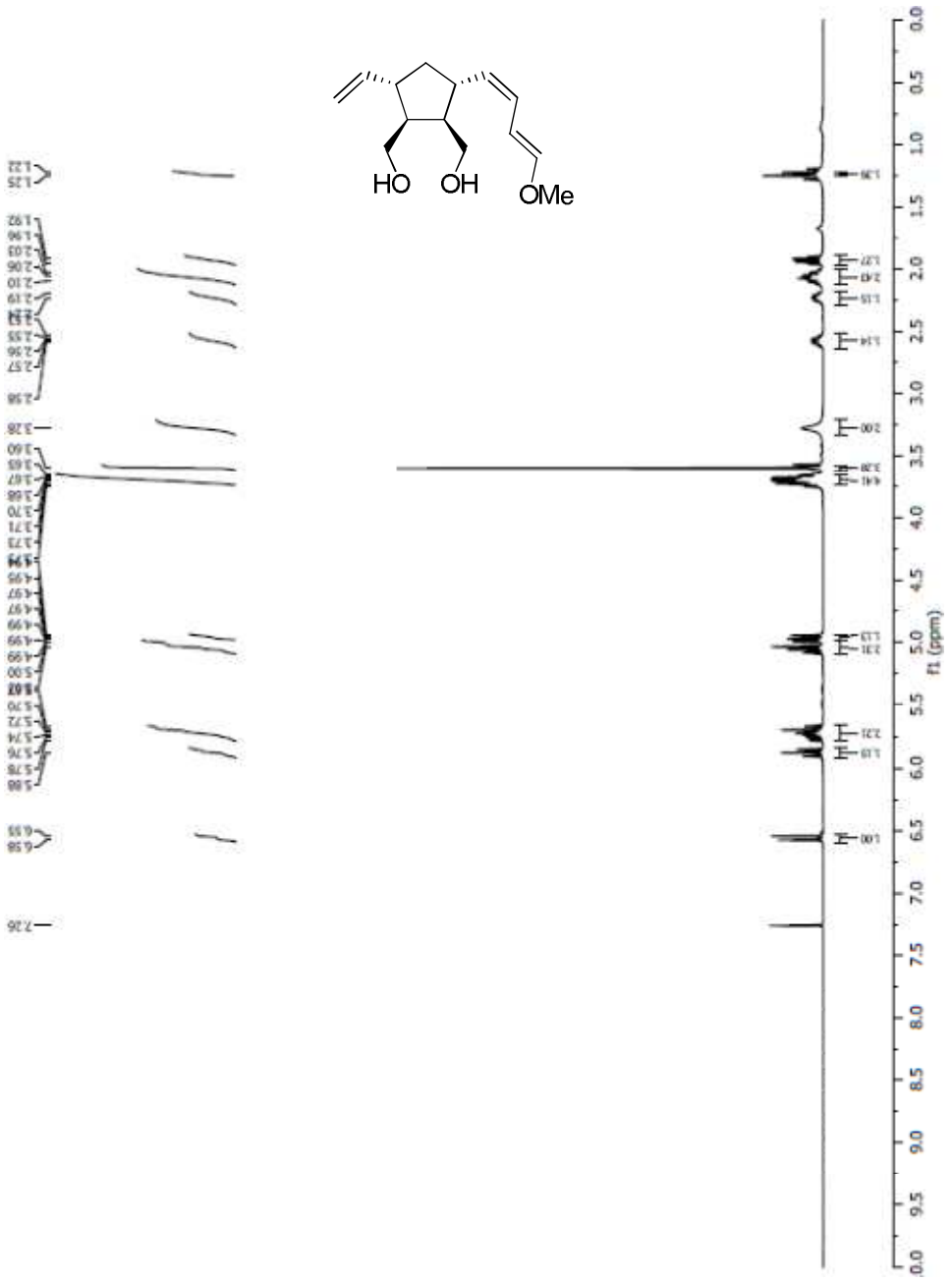
^{1}H NMR spectrum of 1.18



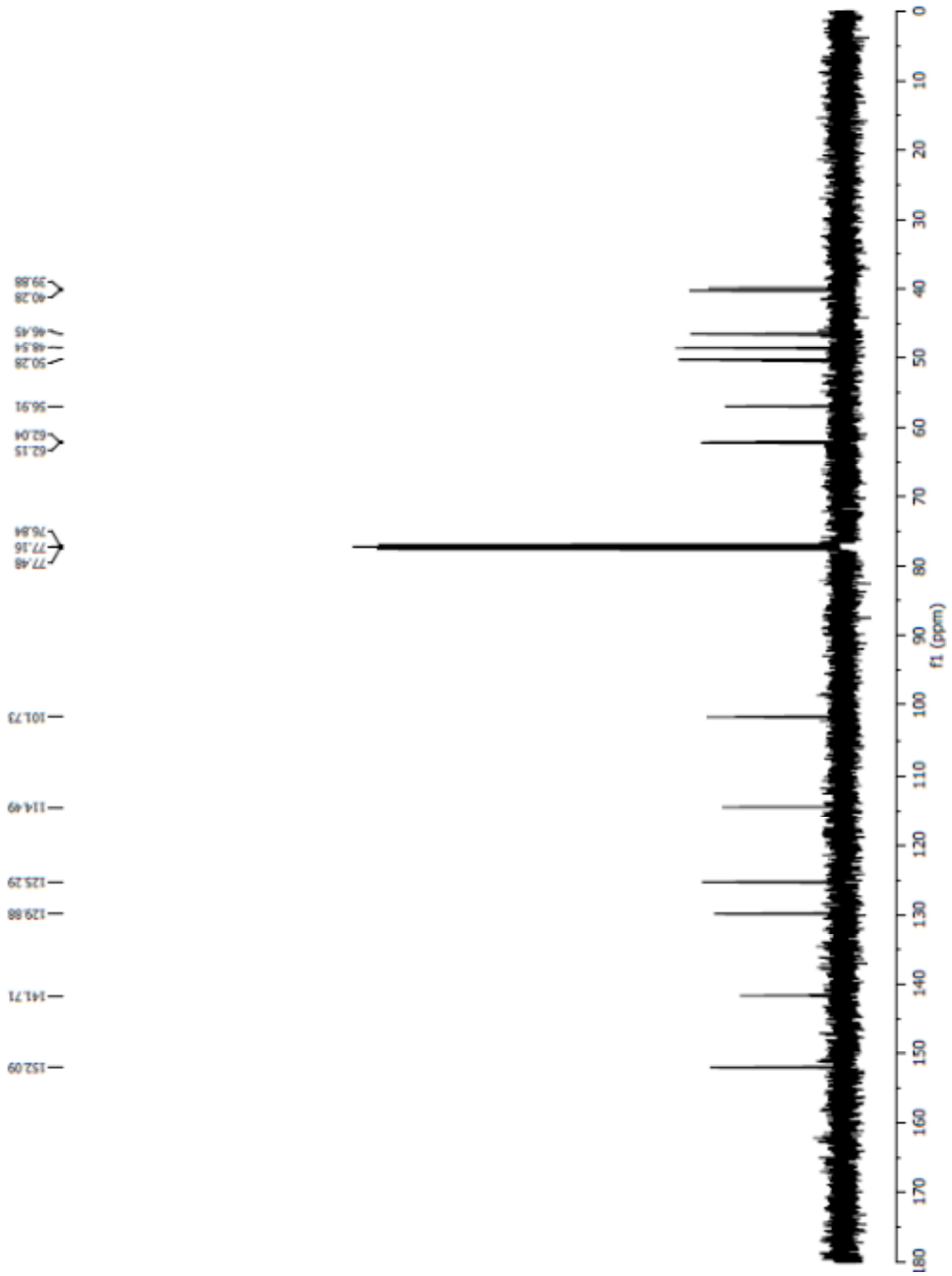
^{13}C NMR spectrum of 1.18



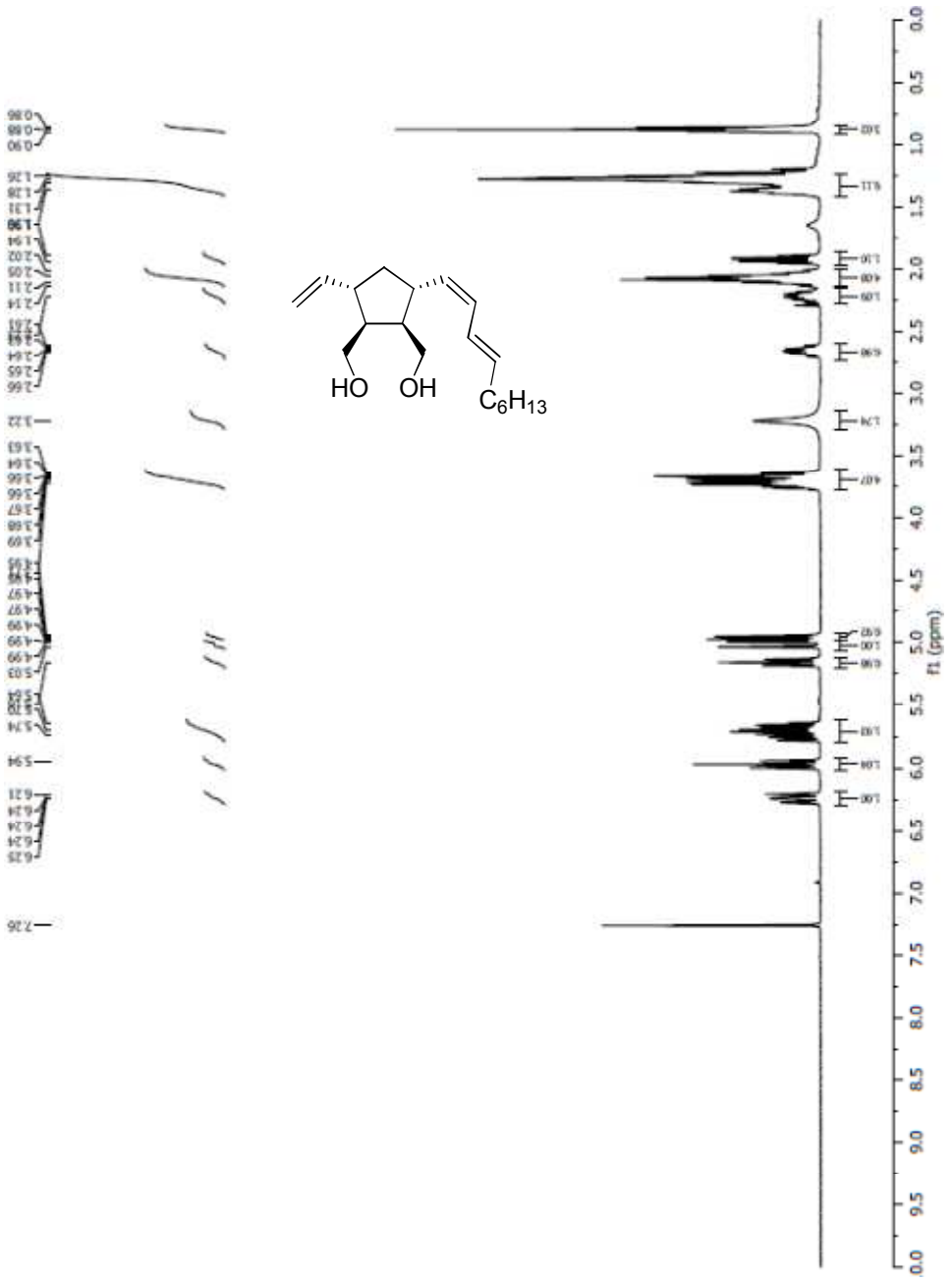
^{1}H NMR spectrum of 1.19



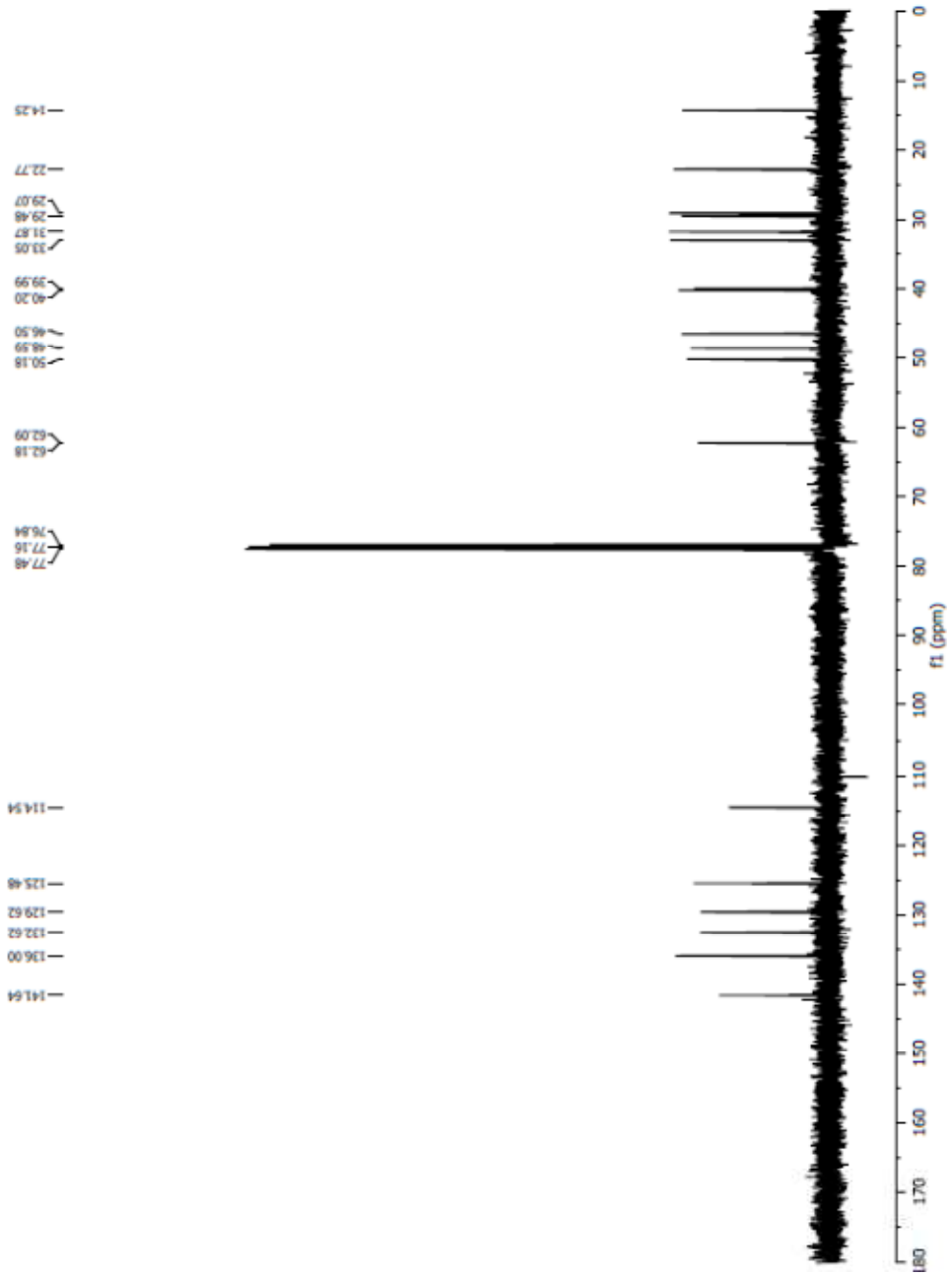
^{13}C NMR spectrum of 1.19



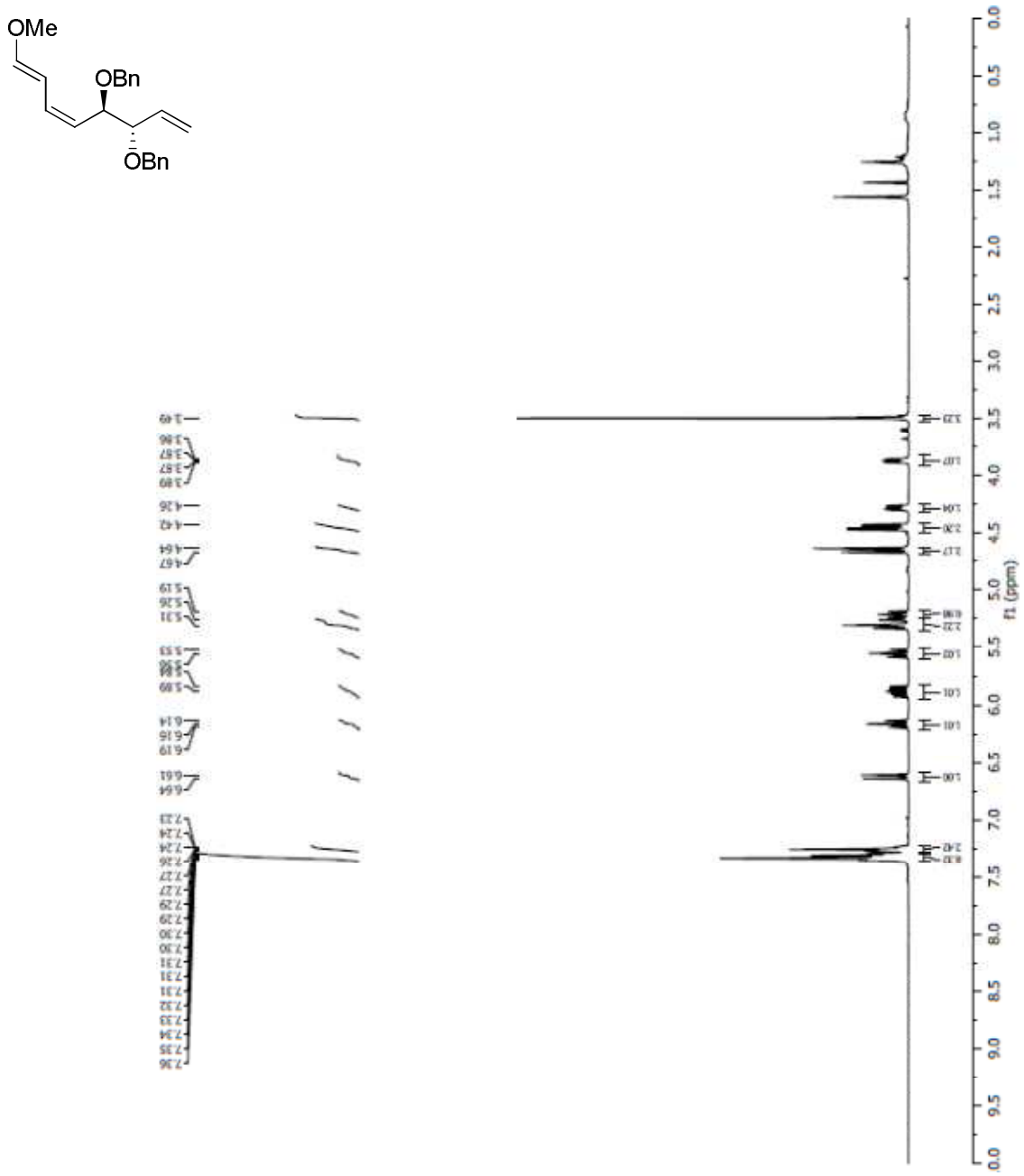
^{1}H NMR spectrum of 1.20



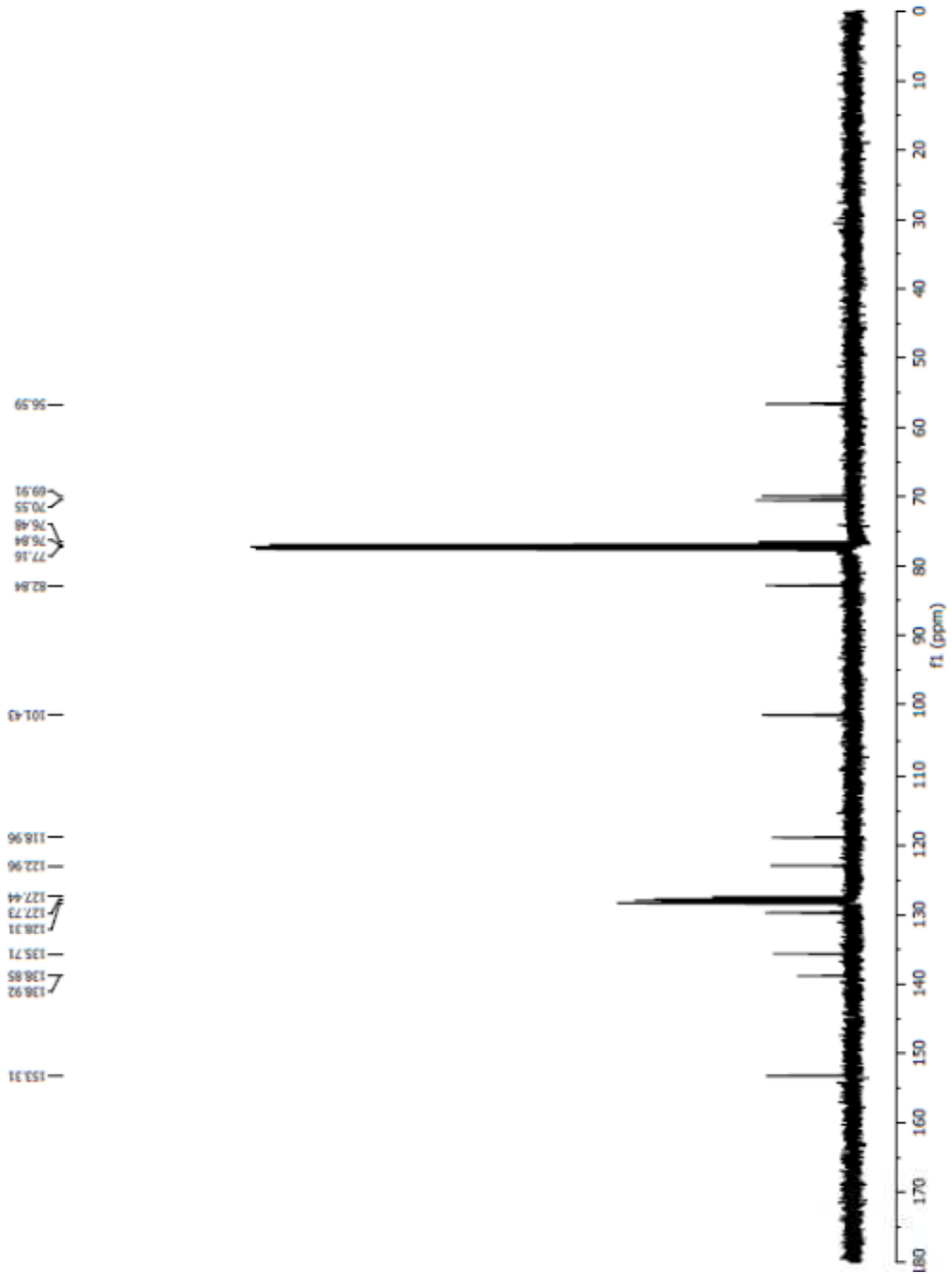
^{13}C NMR spectrum of 1.20



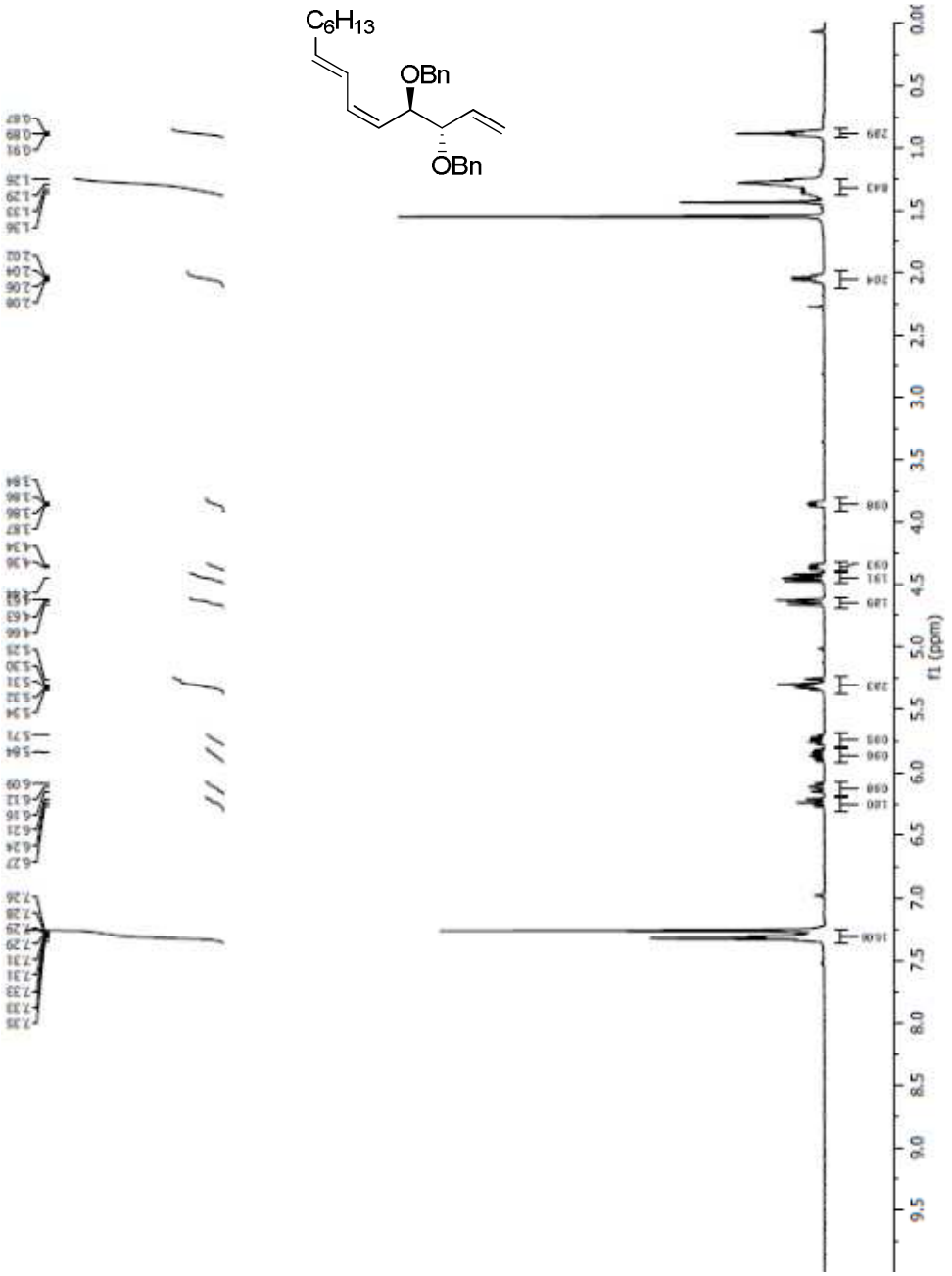
^{1}H NMR spectrum of 1.21



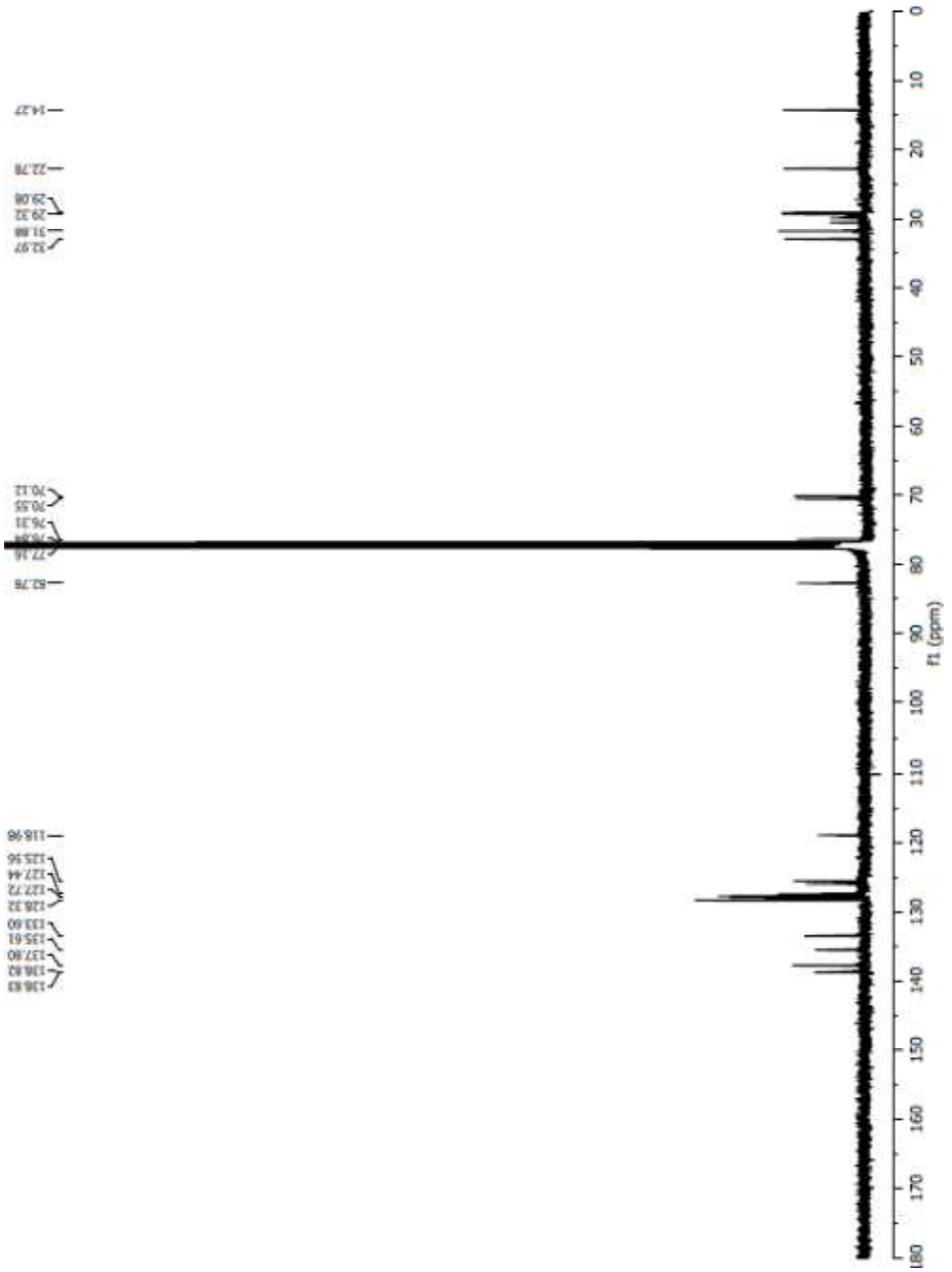
^{13}C NMR spectrum of 1.21



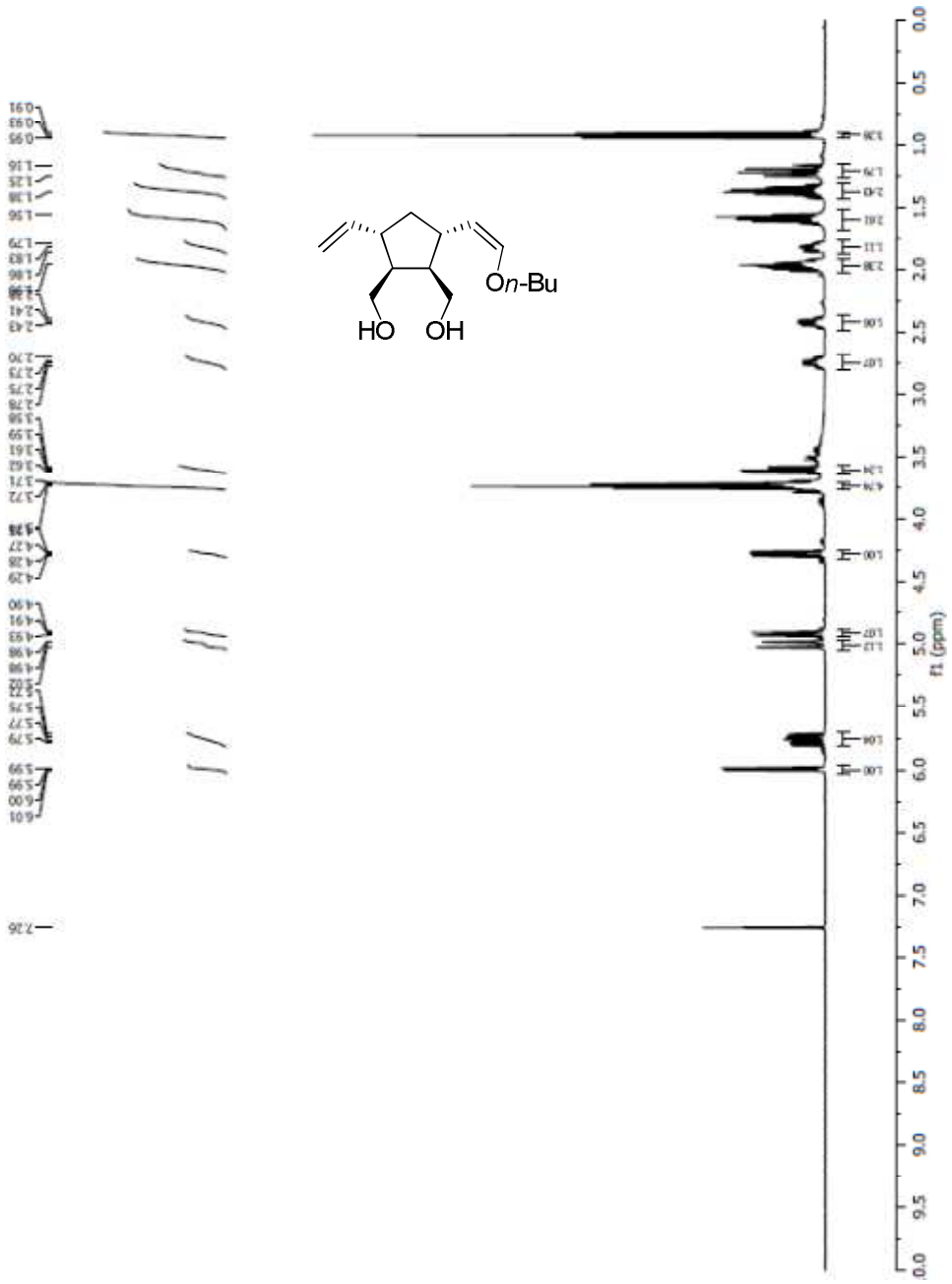
^{1}H NMR spectrum of 1.22



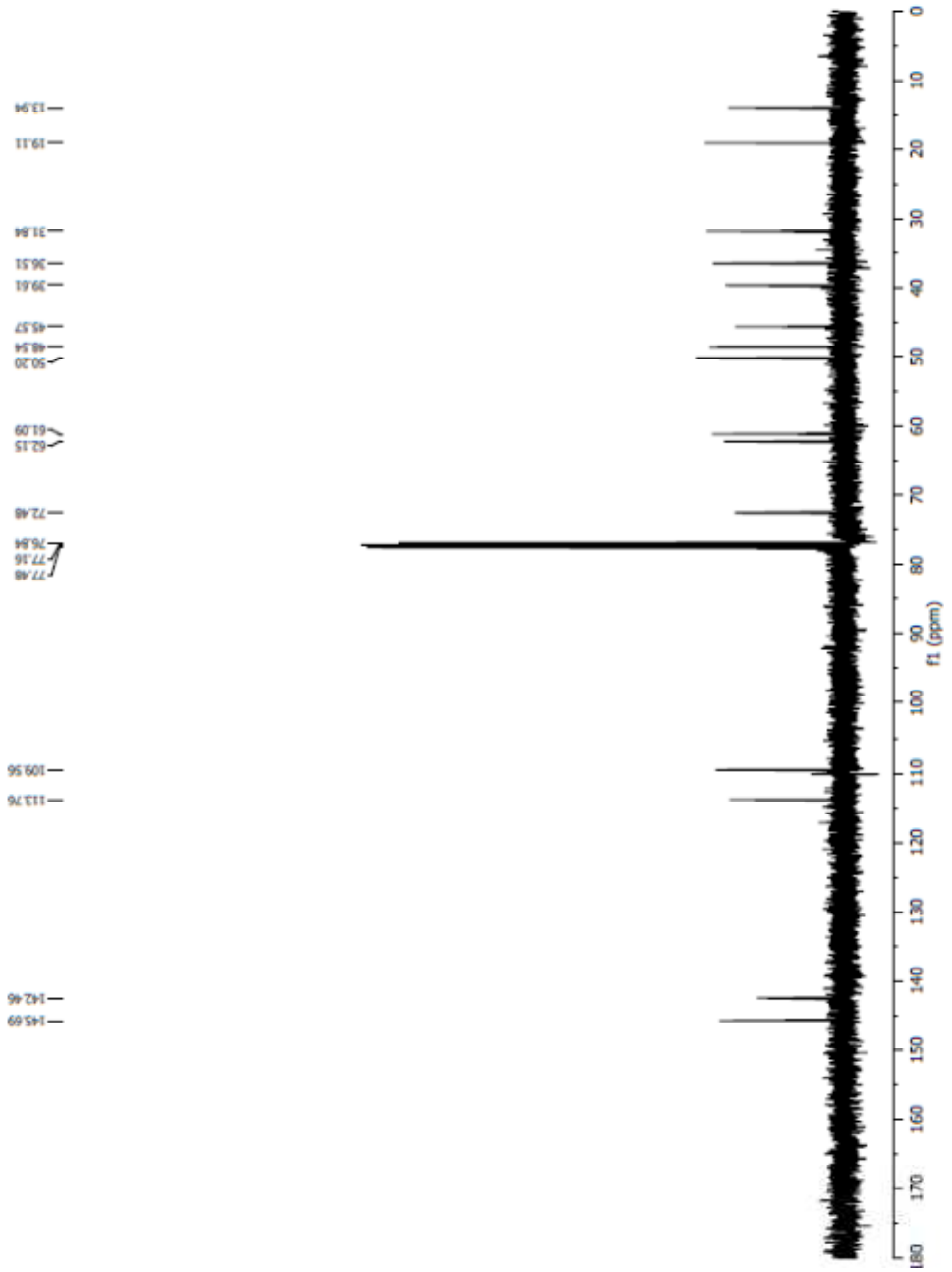
^{13}C NMR spectrum of 1.22



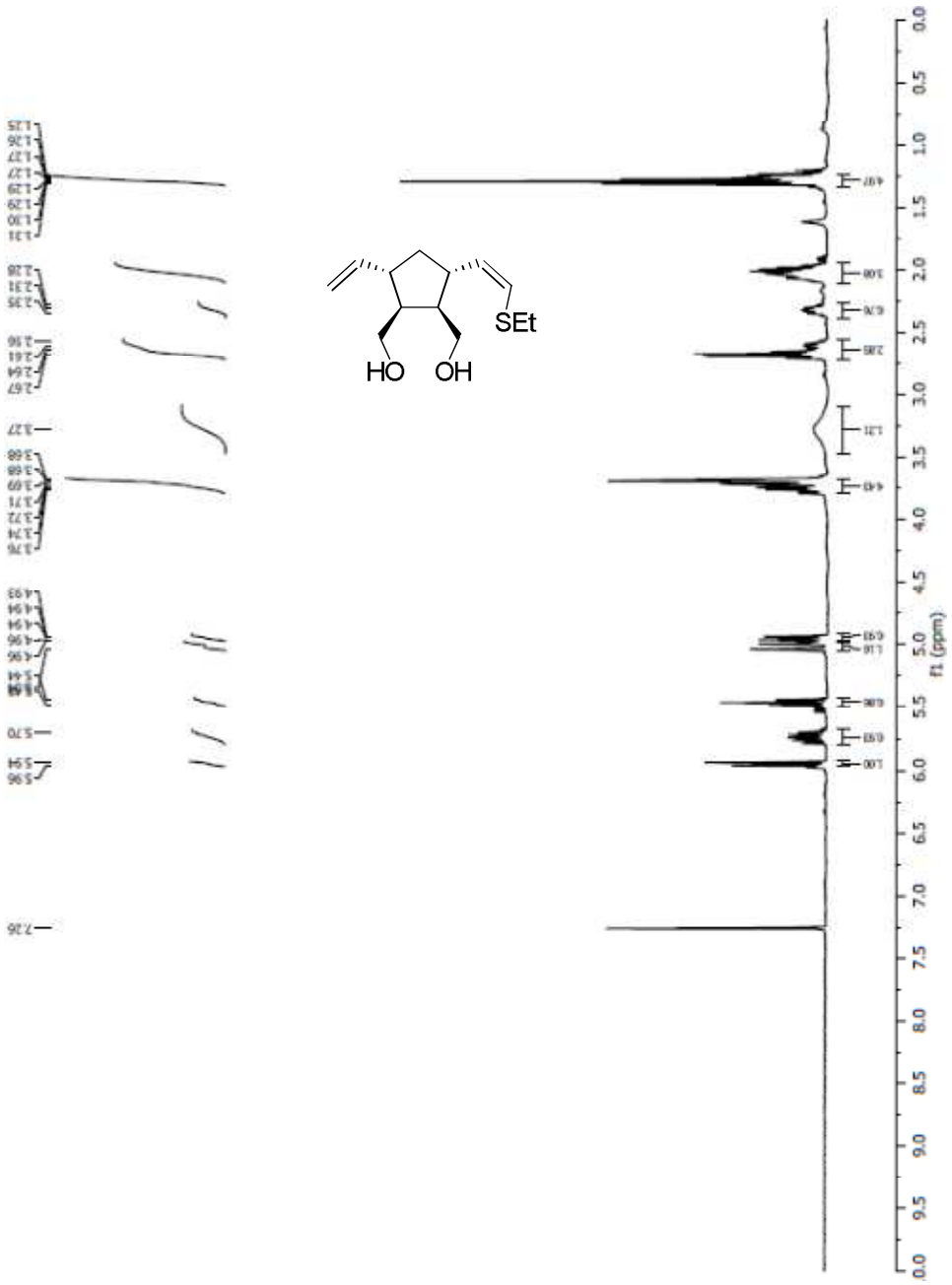
^{1}H NMR spectrum of 1.23



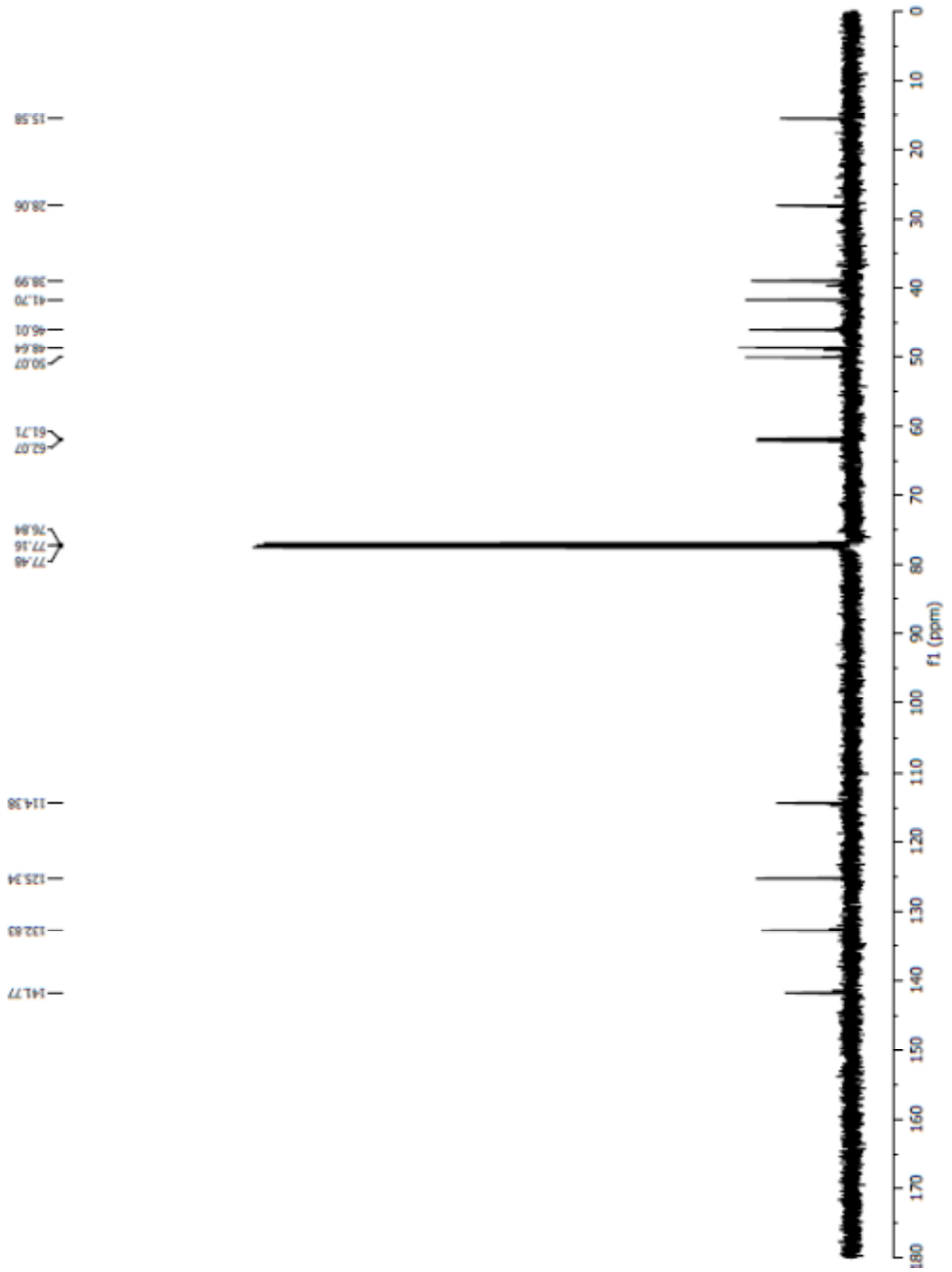
^{13}C NMR spectrum of 1.23



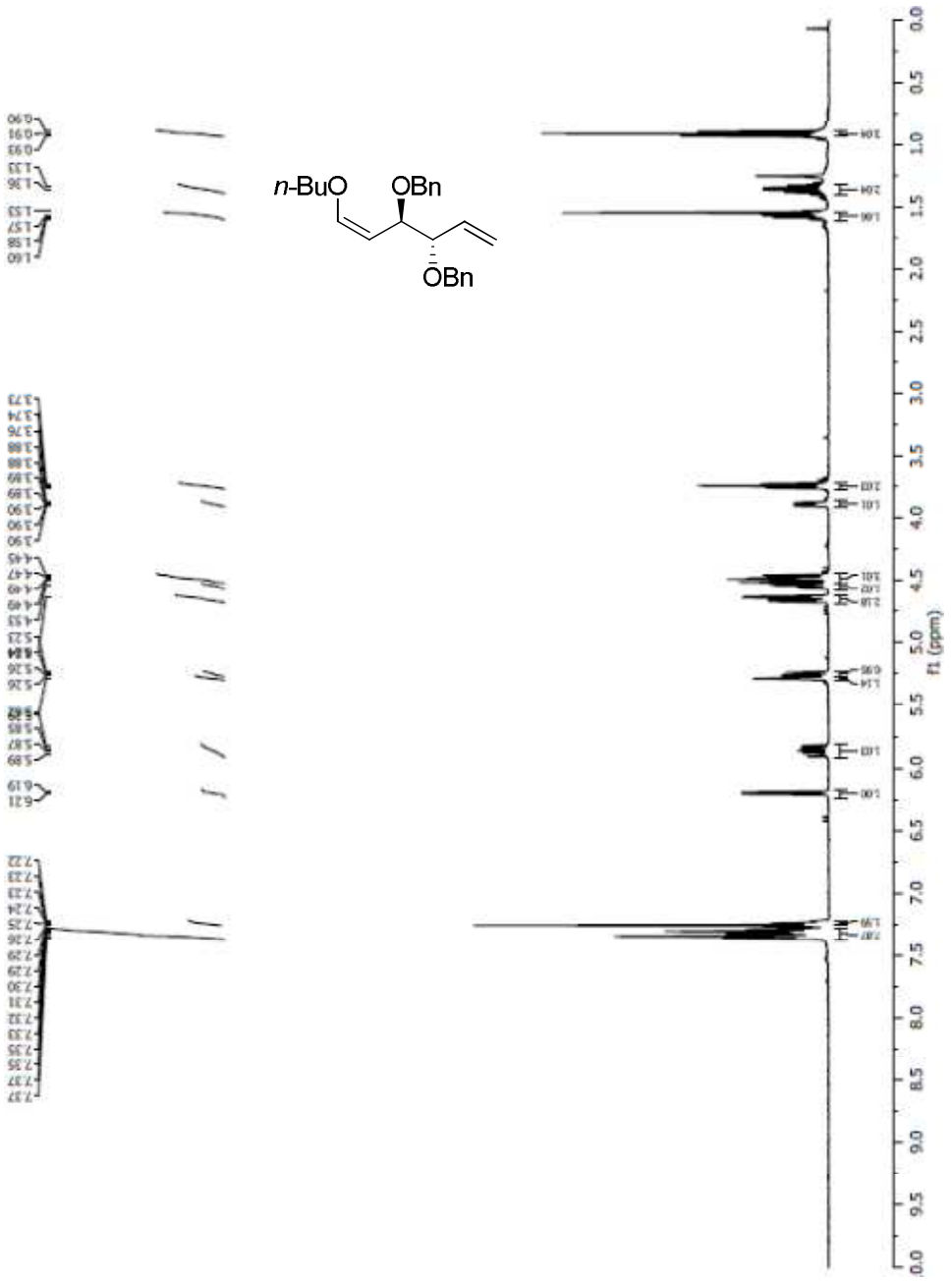
^{1}H NMR spectrum of 1.24



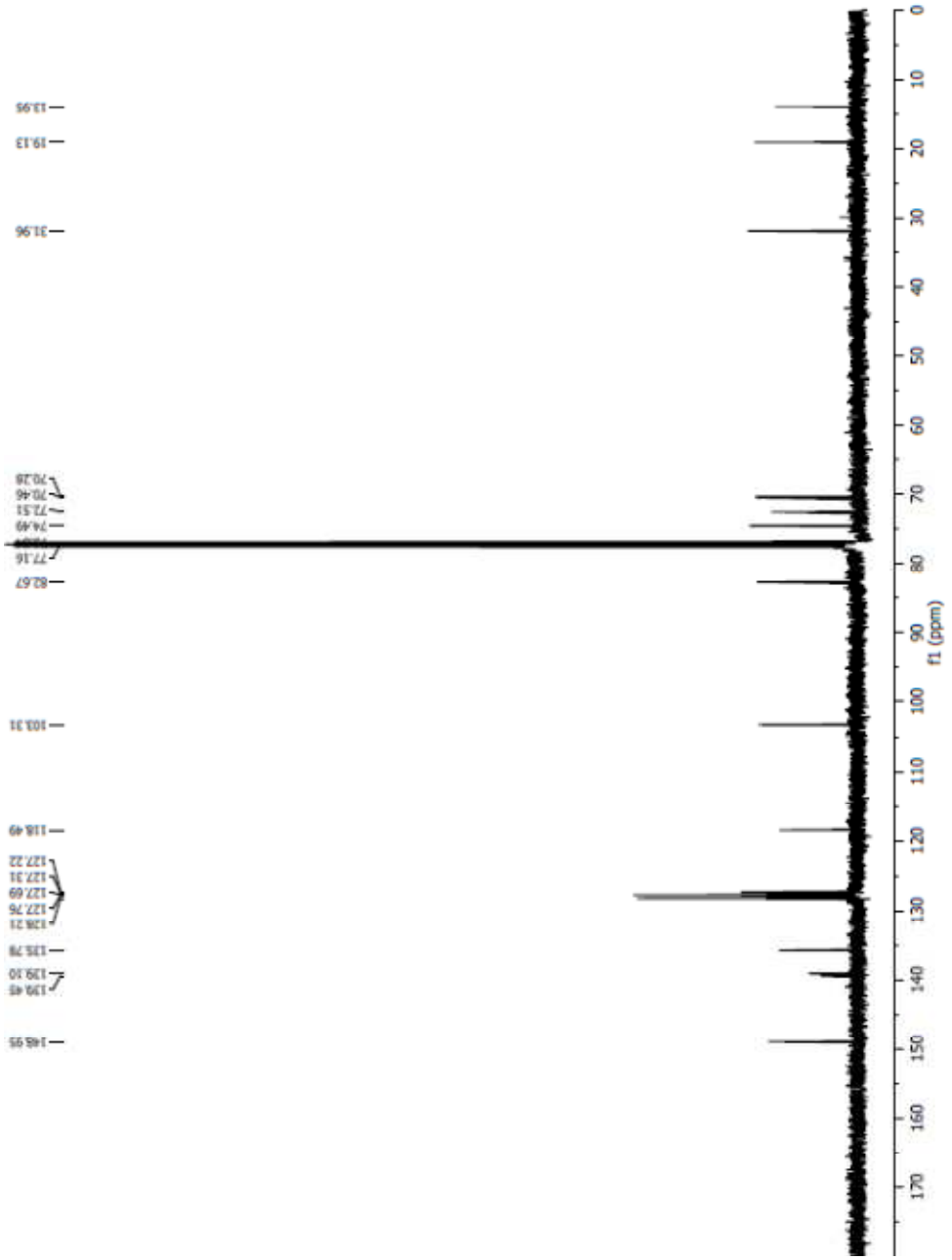
^{13}C NMR spectrum of 1.24



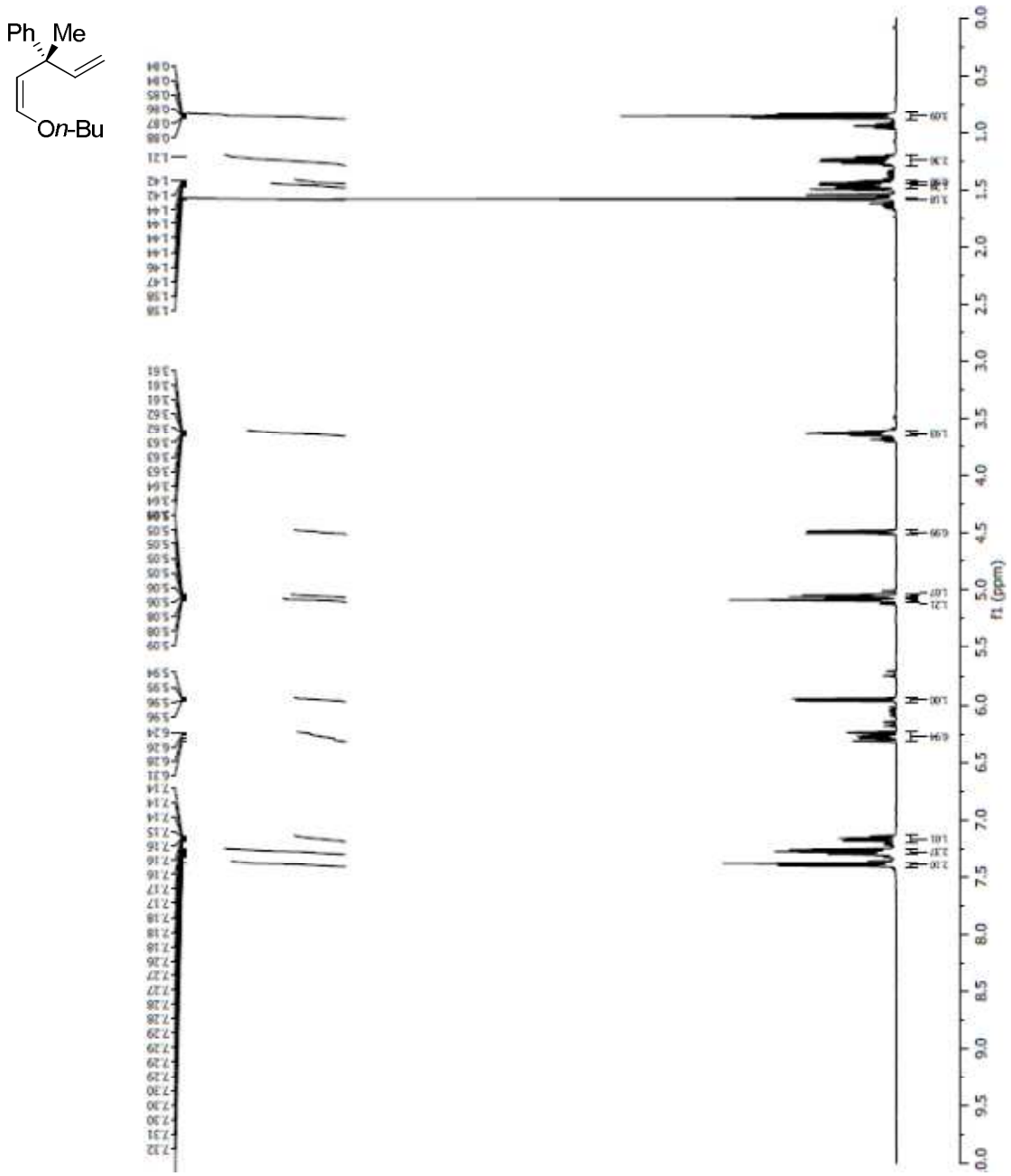
^{1}H NMR spectrum of 1.25



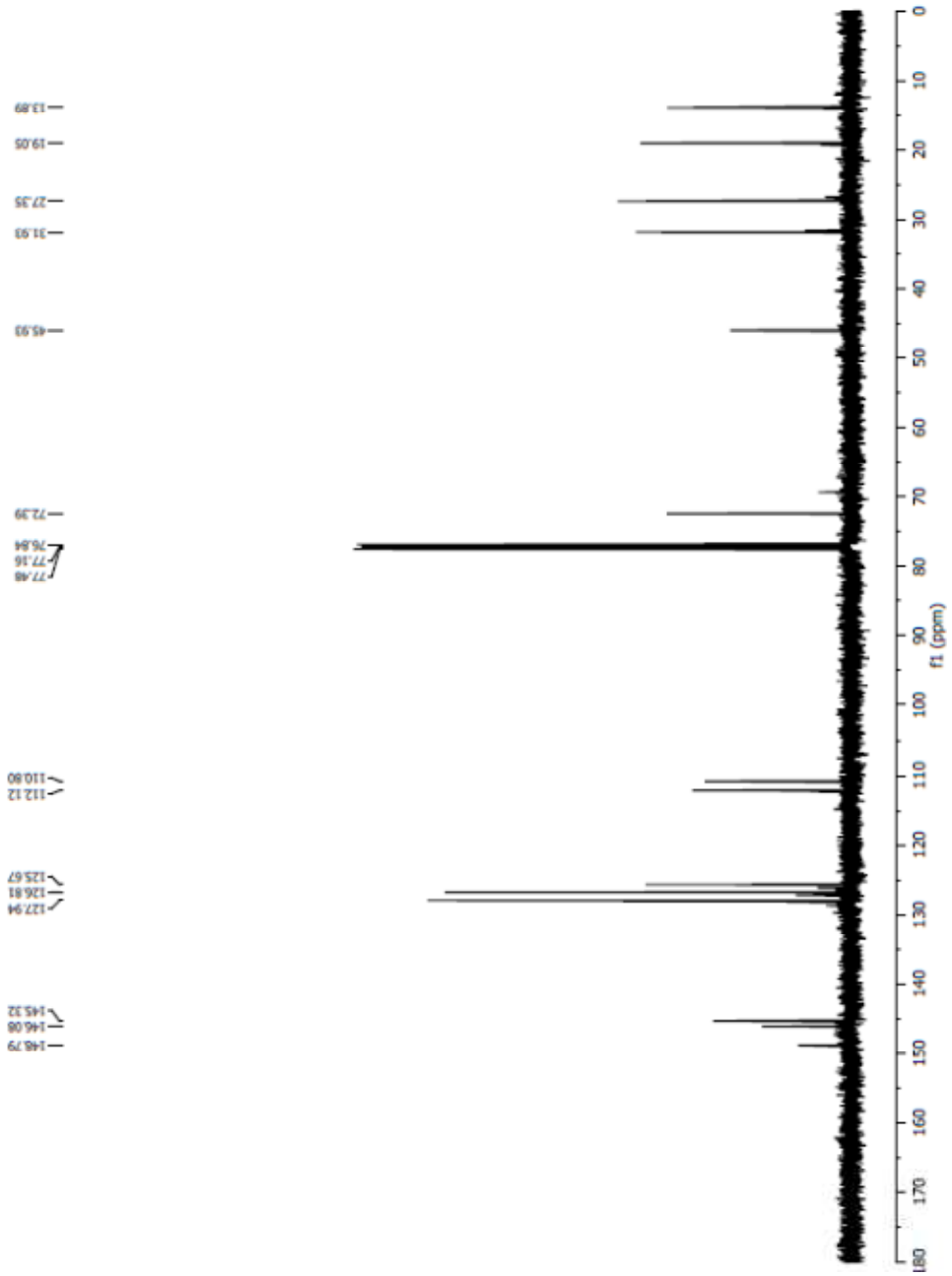
^{13}C NMR spectrum of 1.25



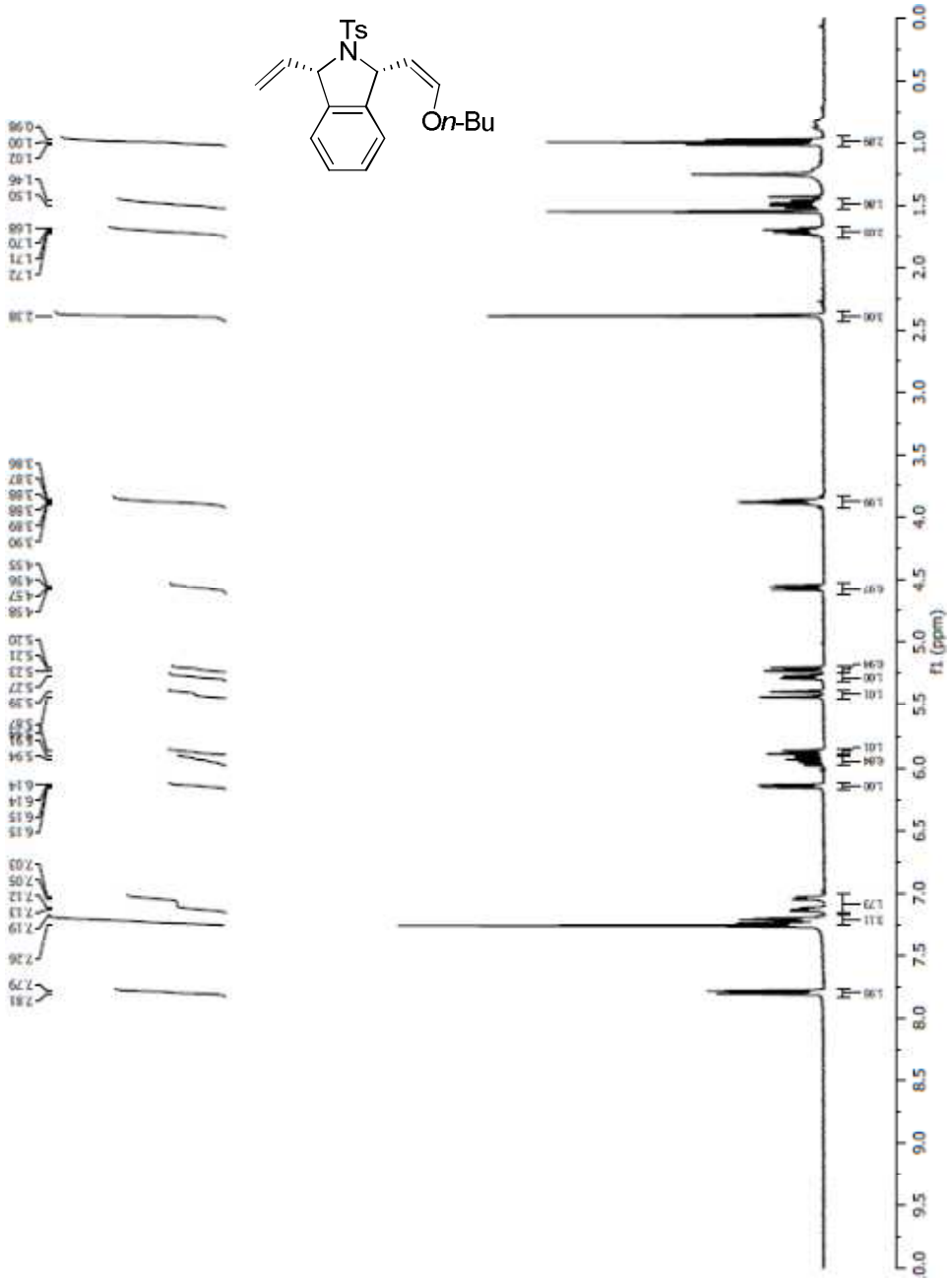
^{1}H NMR spectrum of 1.26



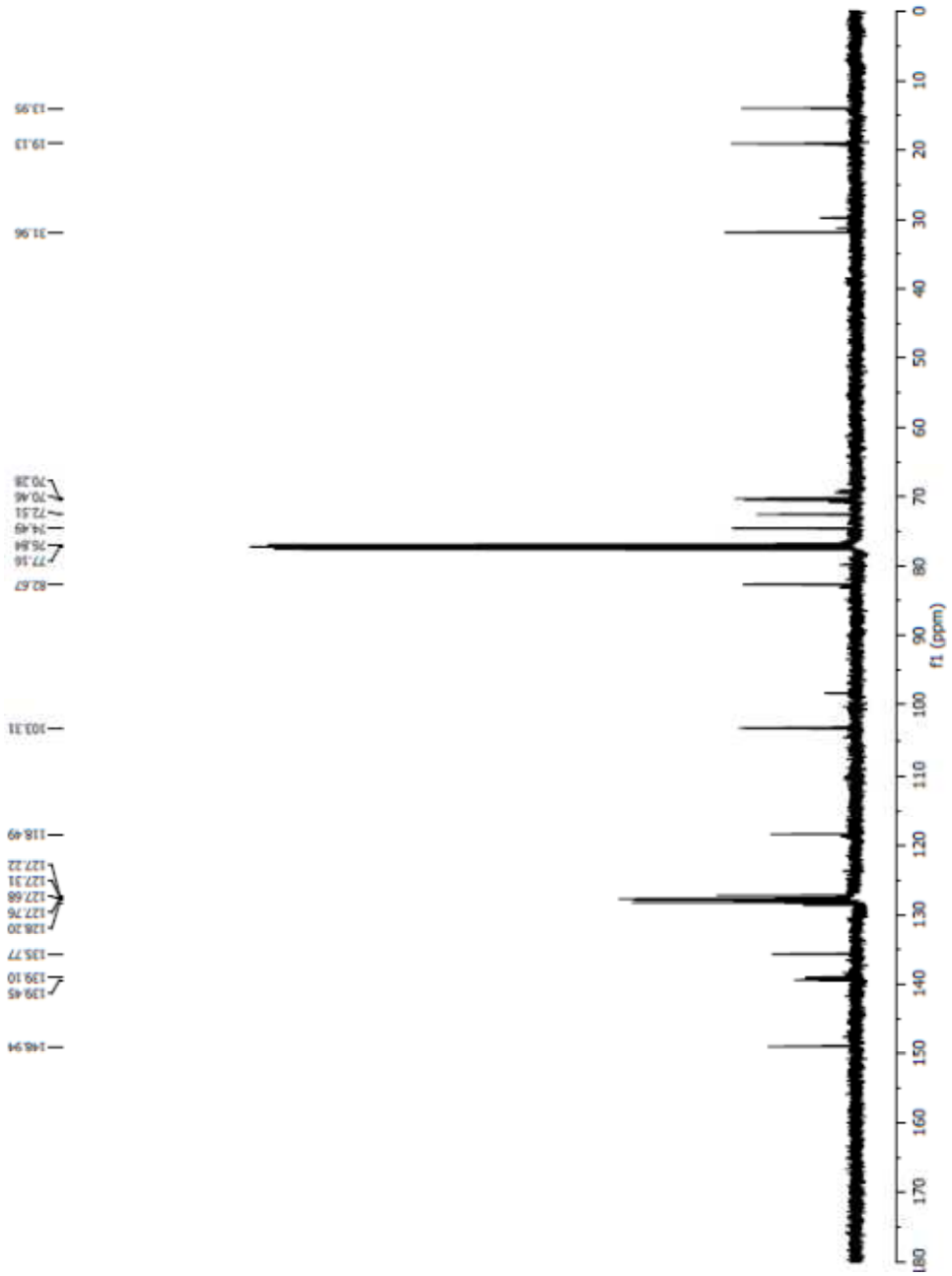
^{13}C NMR spectrum of 1.26



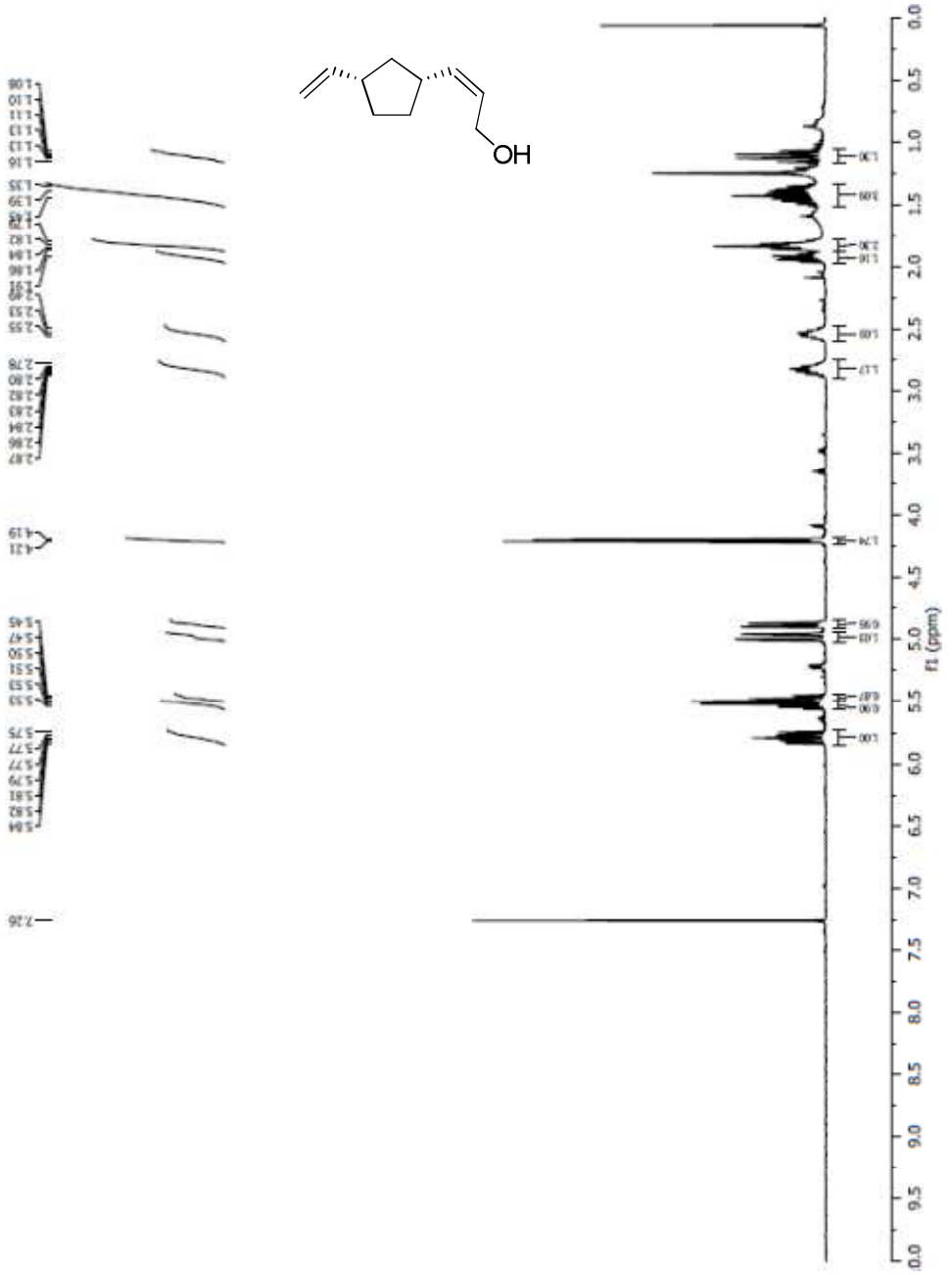
^{1}H NMR spectrum of 1.27



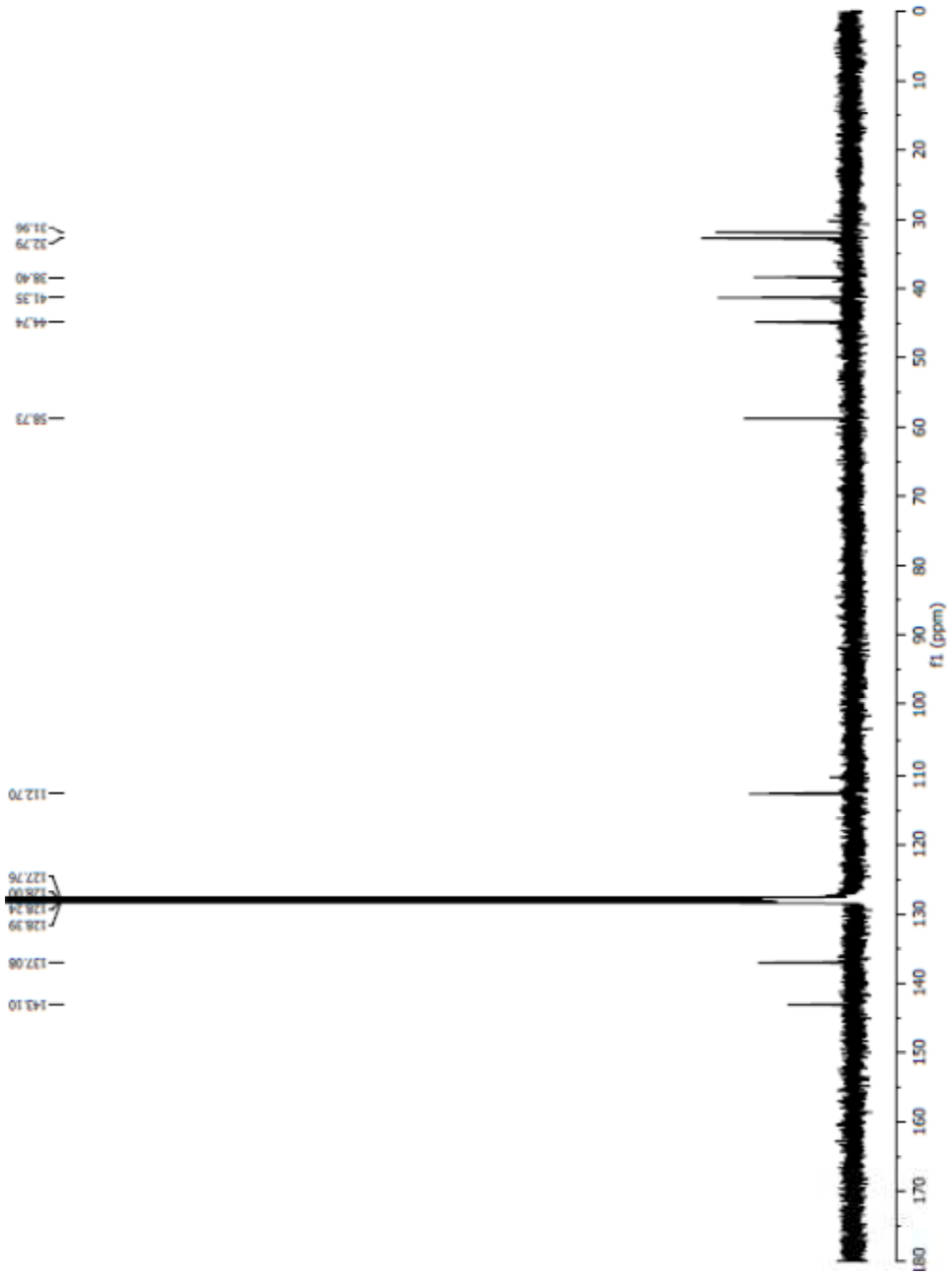
^{13}C NMR spectrum of 1.27



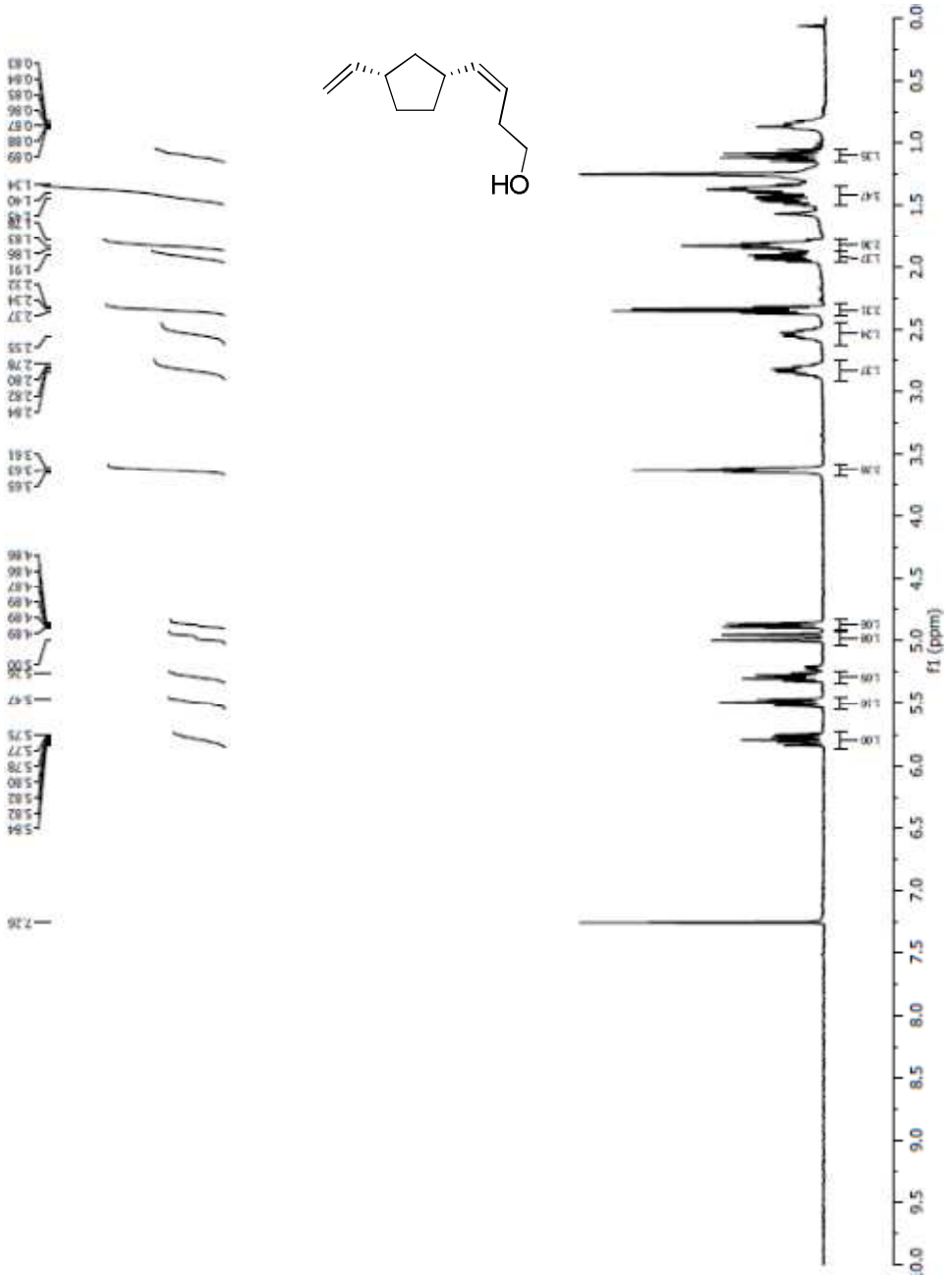
^{1}H NMR spectrum of 1.28



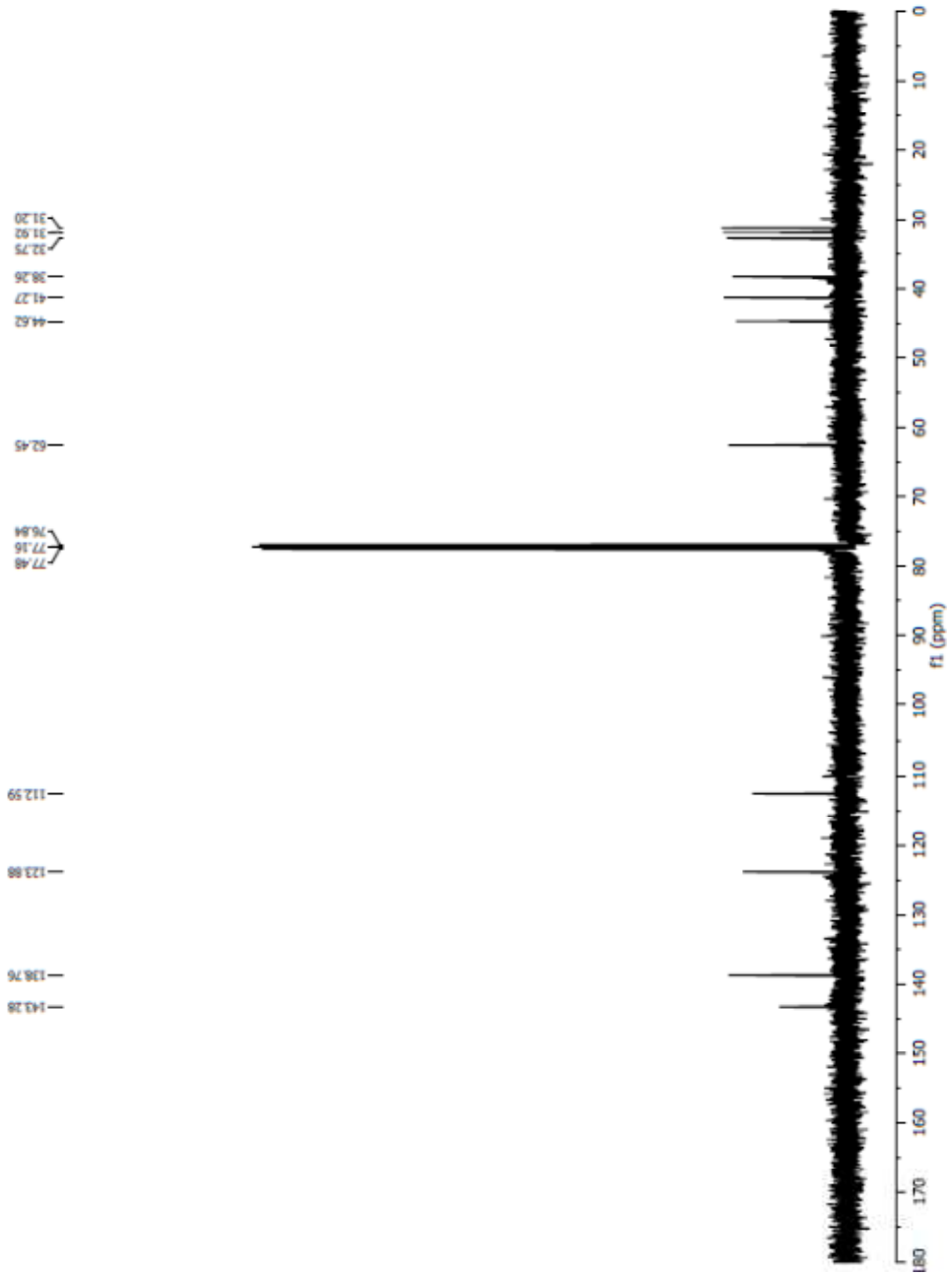
^{13}C NMR spectrum of 1.28



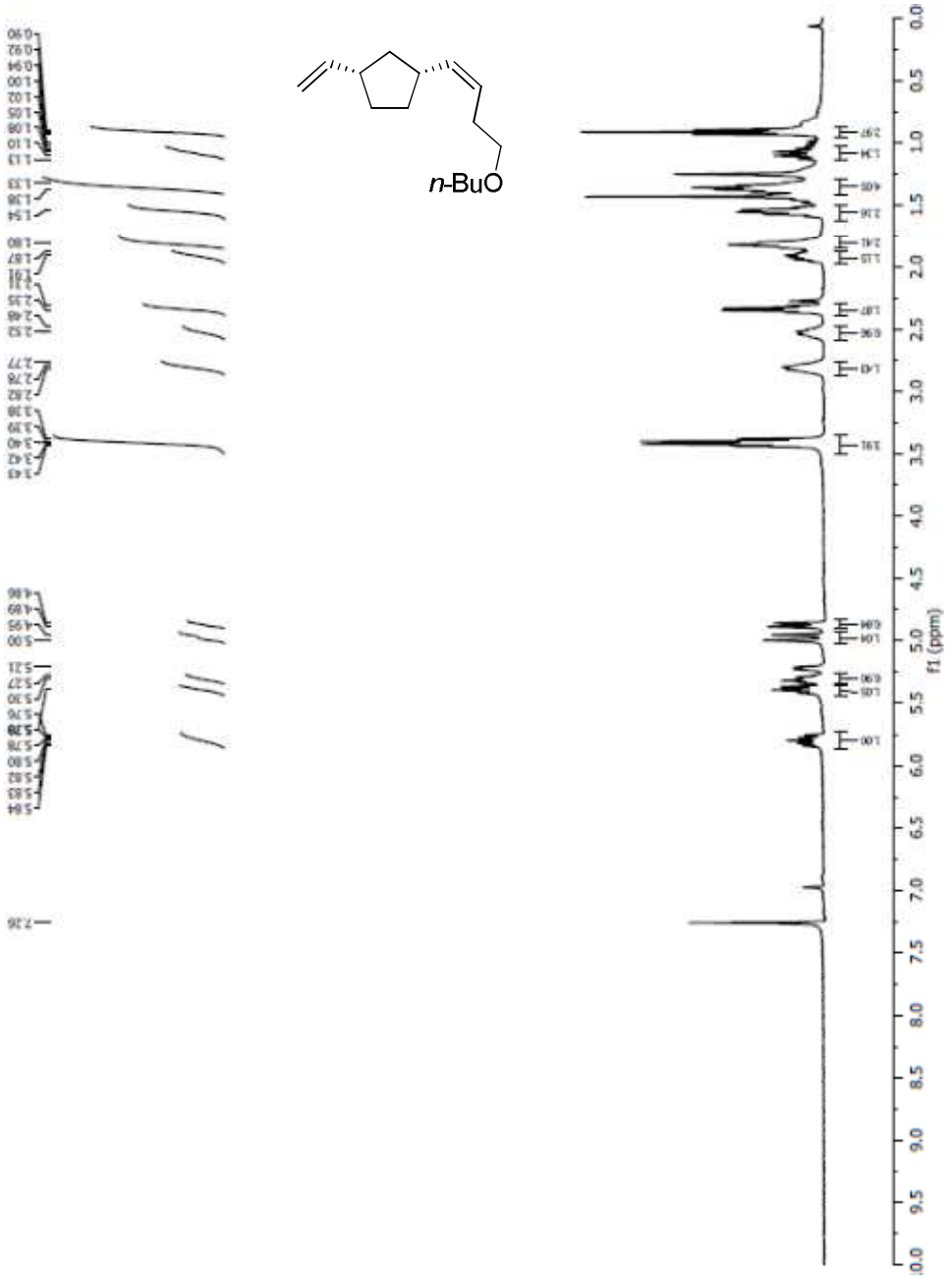
^{1}H NMR spectrum of 1.30



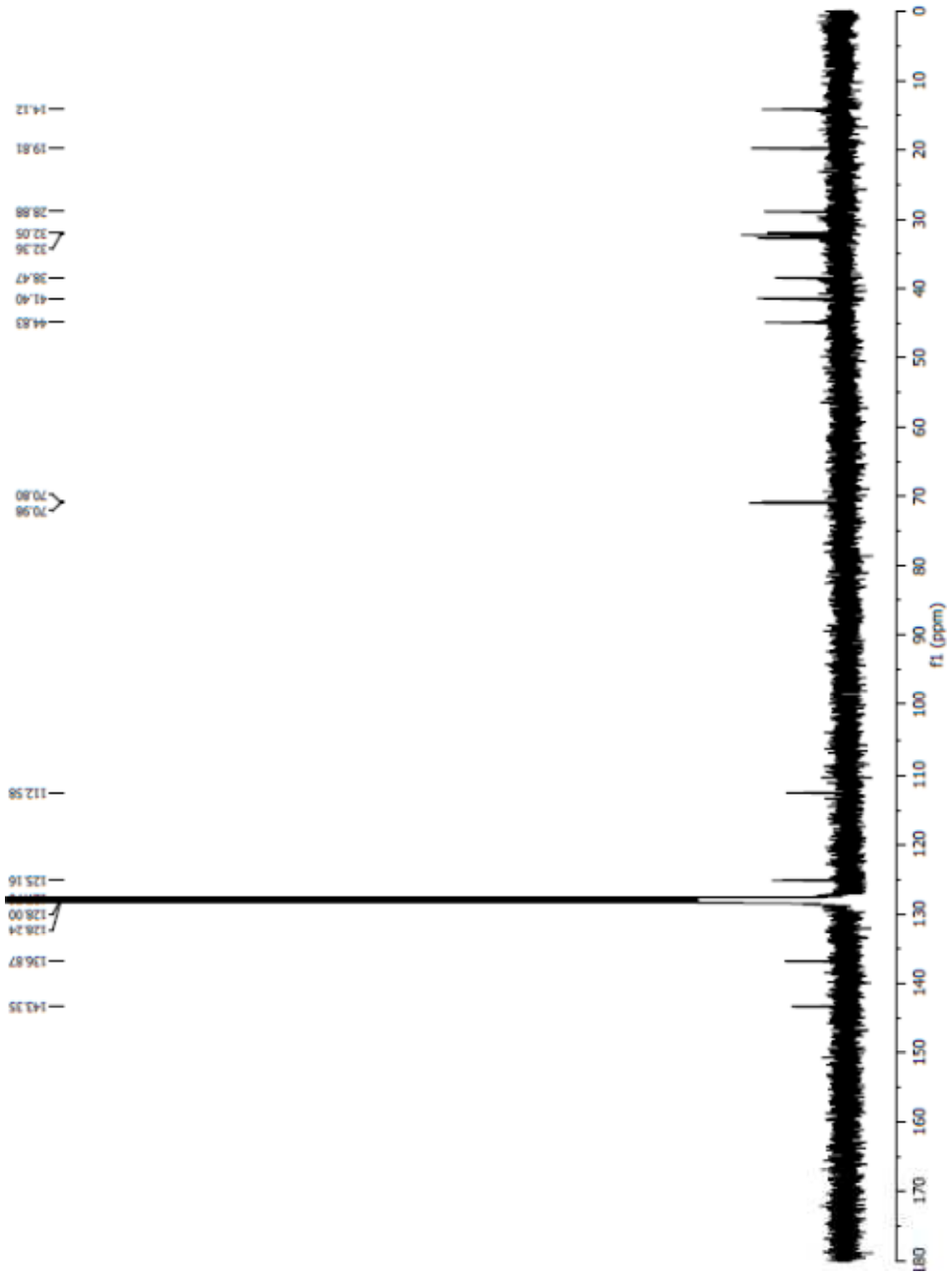
^{13}C NMR spectrum of 1.30



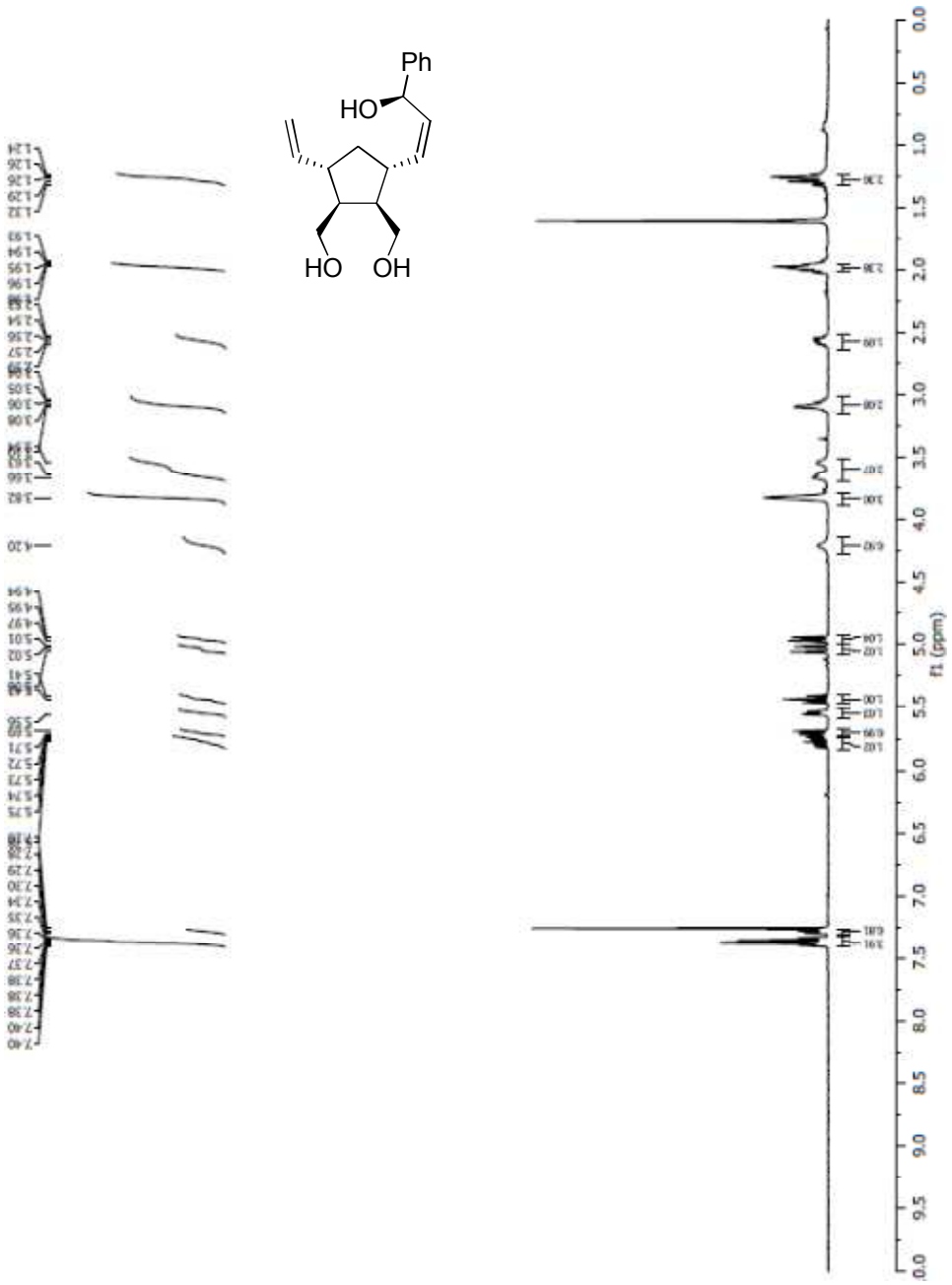
^{1}H NMR spectrum of 1.31



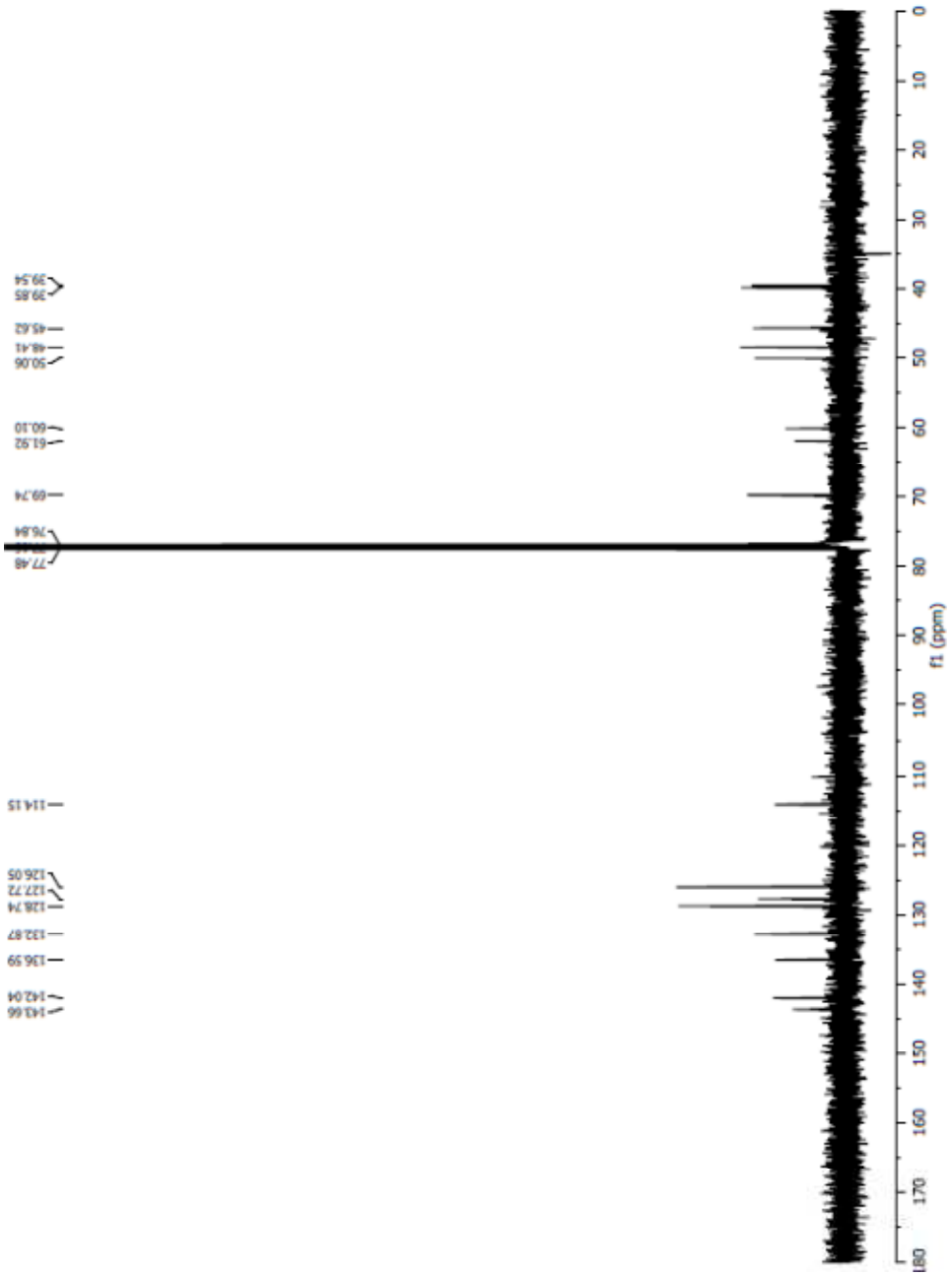
^{13}C NMR spectrum of 1.31



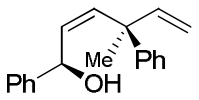
^{1}H NMR spectrum of 1.40

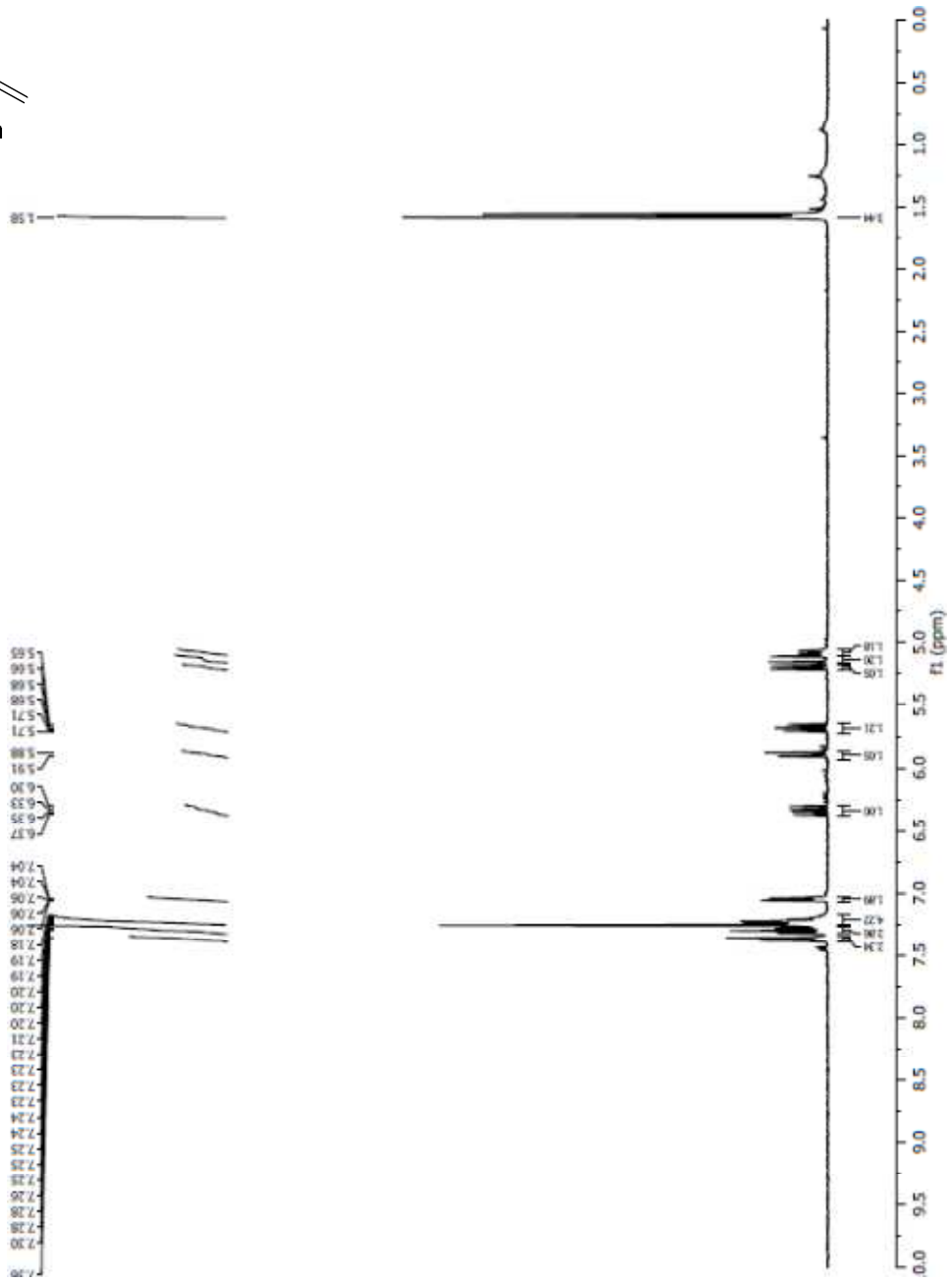


^{13}C NMR spectrum of 1.40

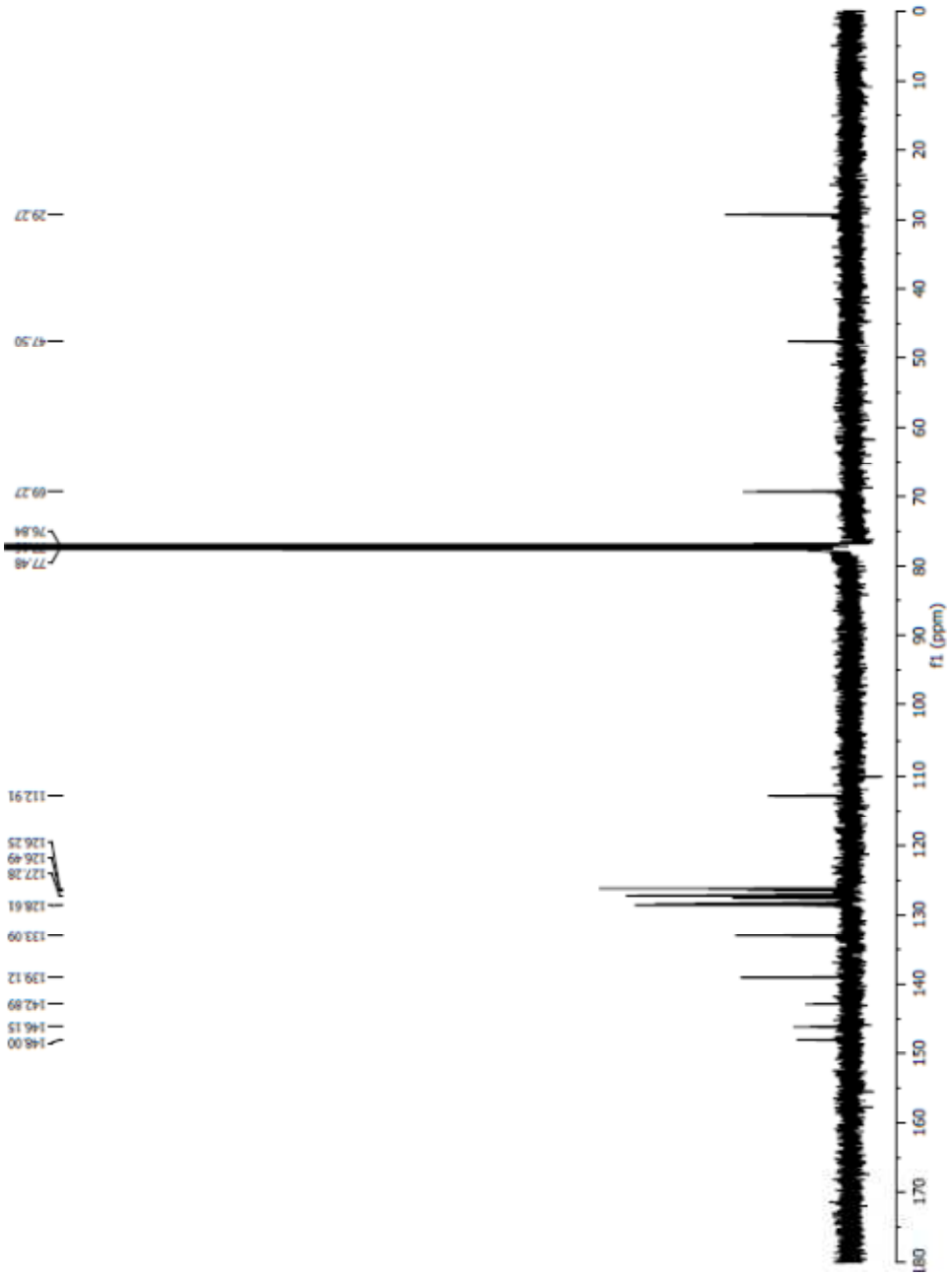


^{1}H NMR spectrum of 1.41

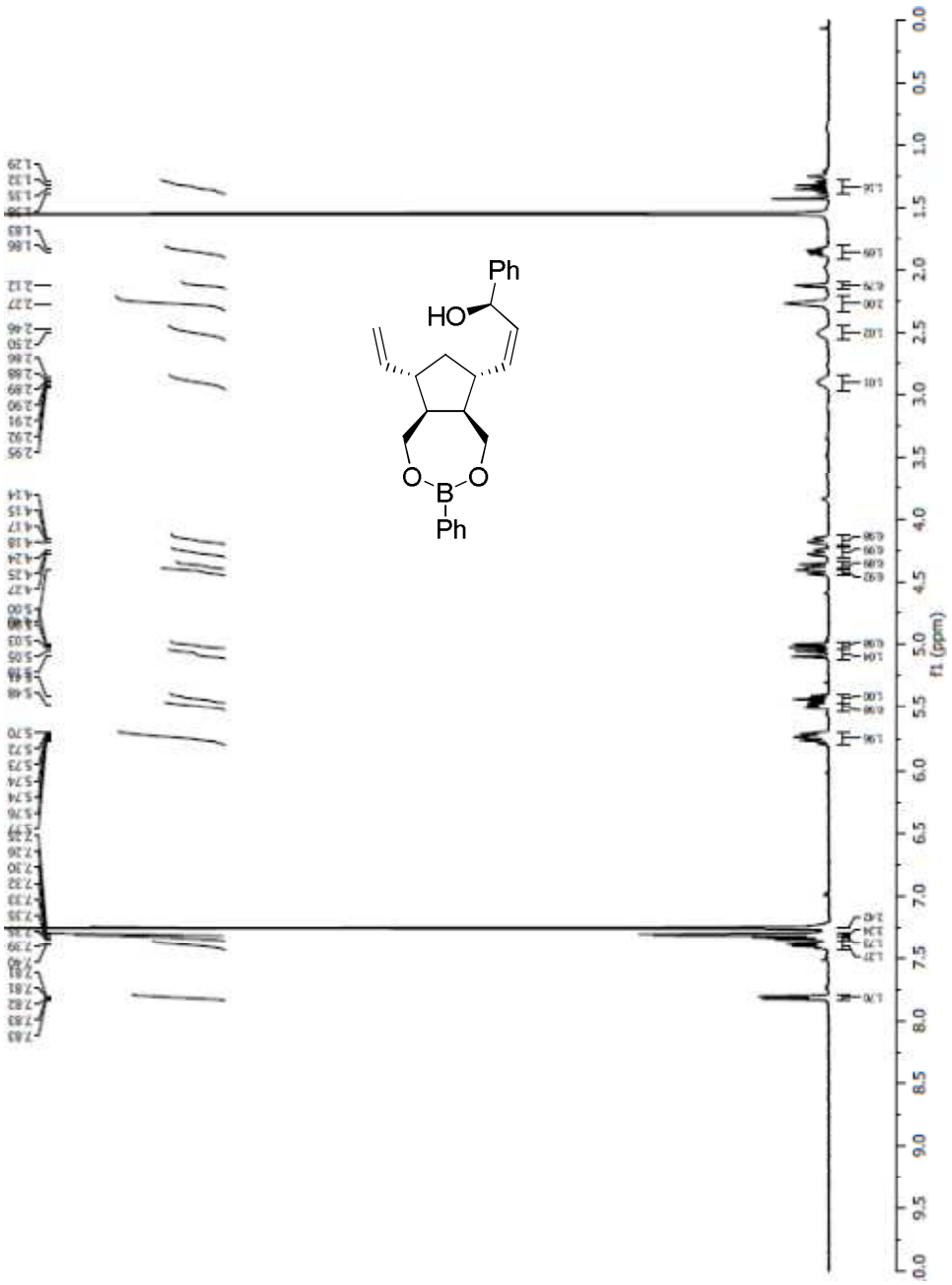




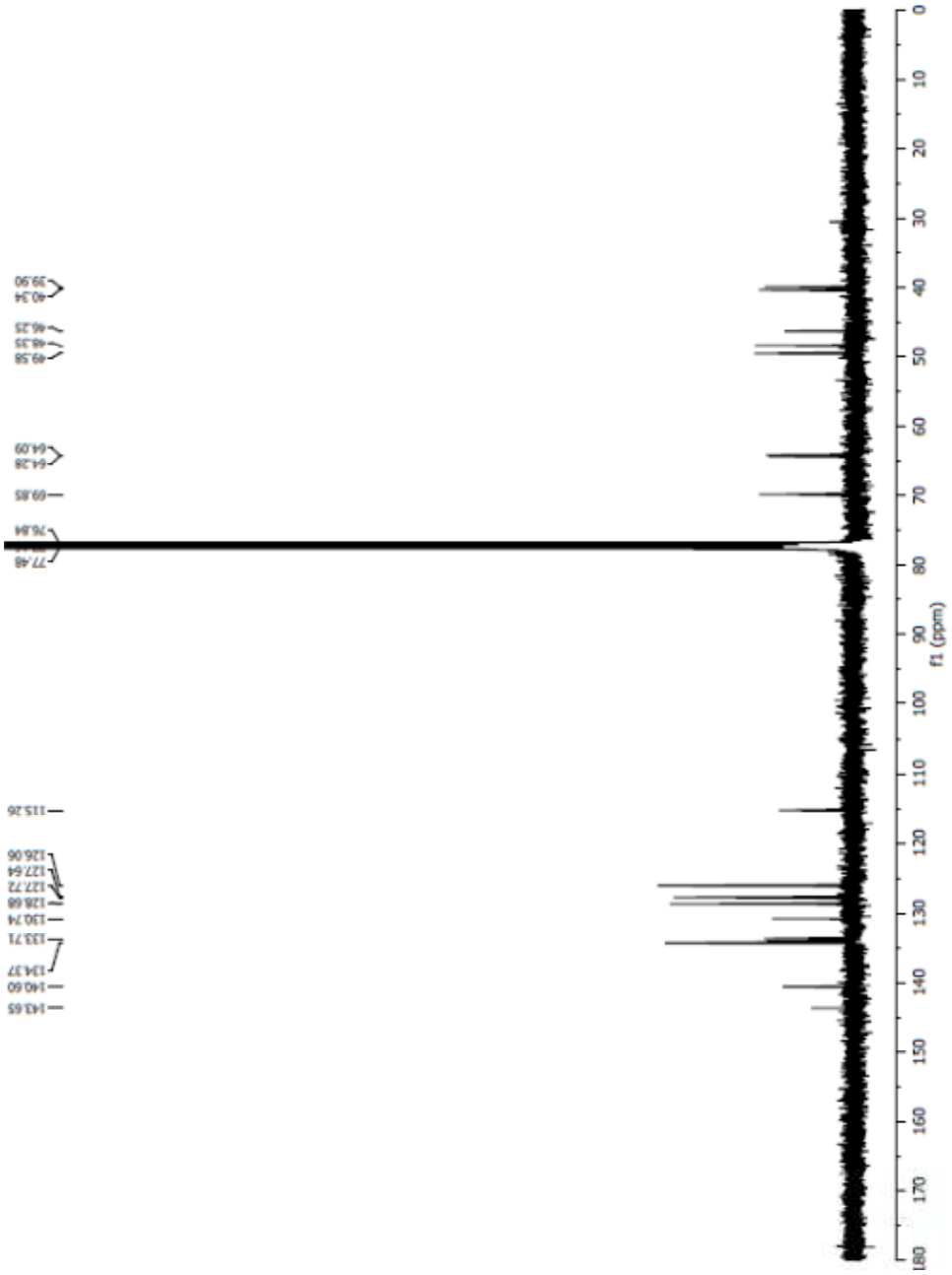
^{13}C NMR spectrum of 1.41



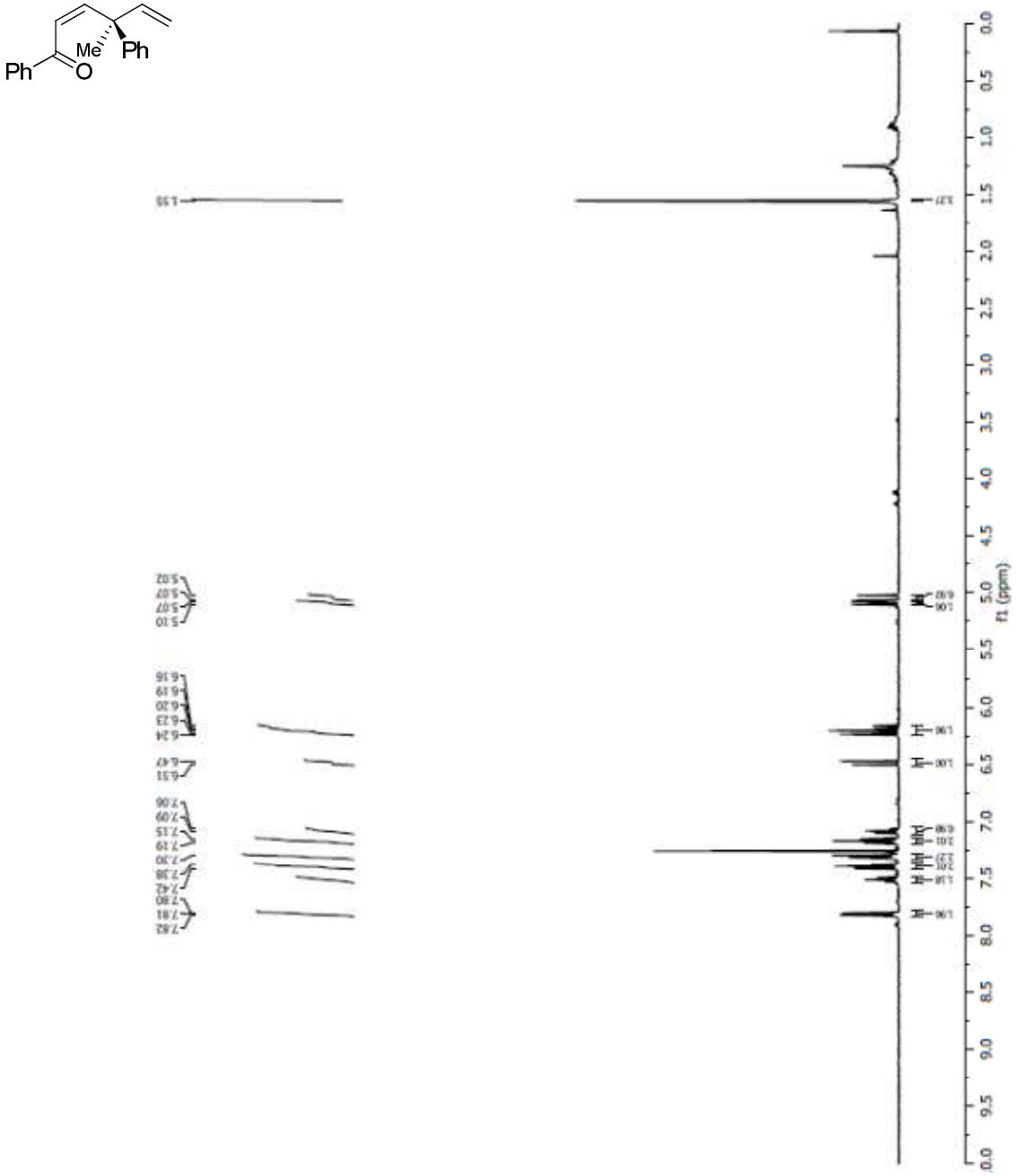
^{1}H NMR spectrum of 1.42



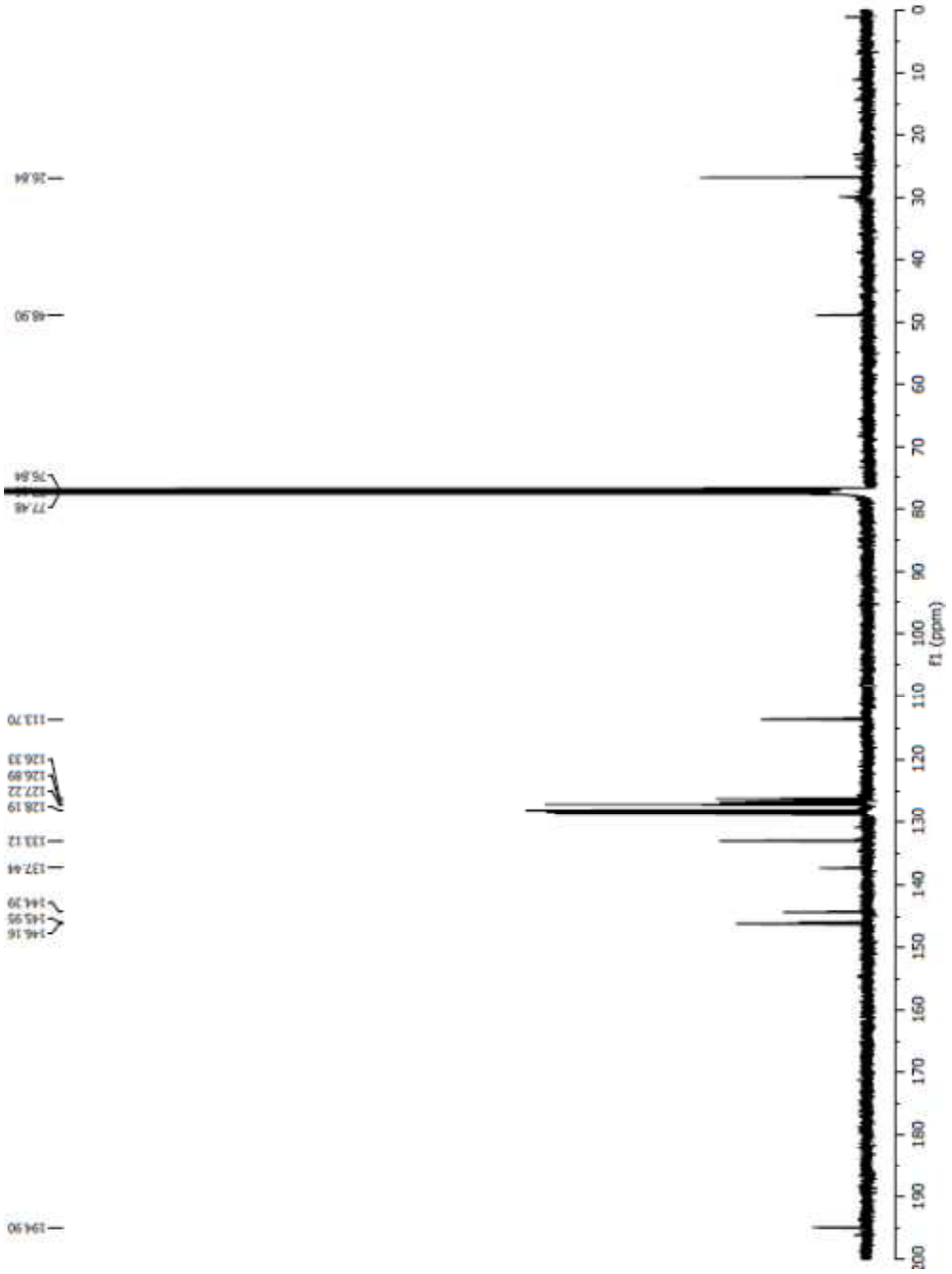
^{13}C NMR spectrum of 1.42



^{1}H NMR spectrum of 1.88

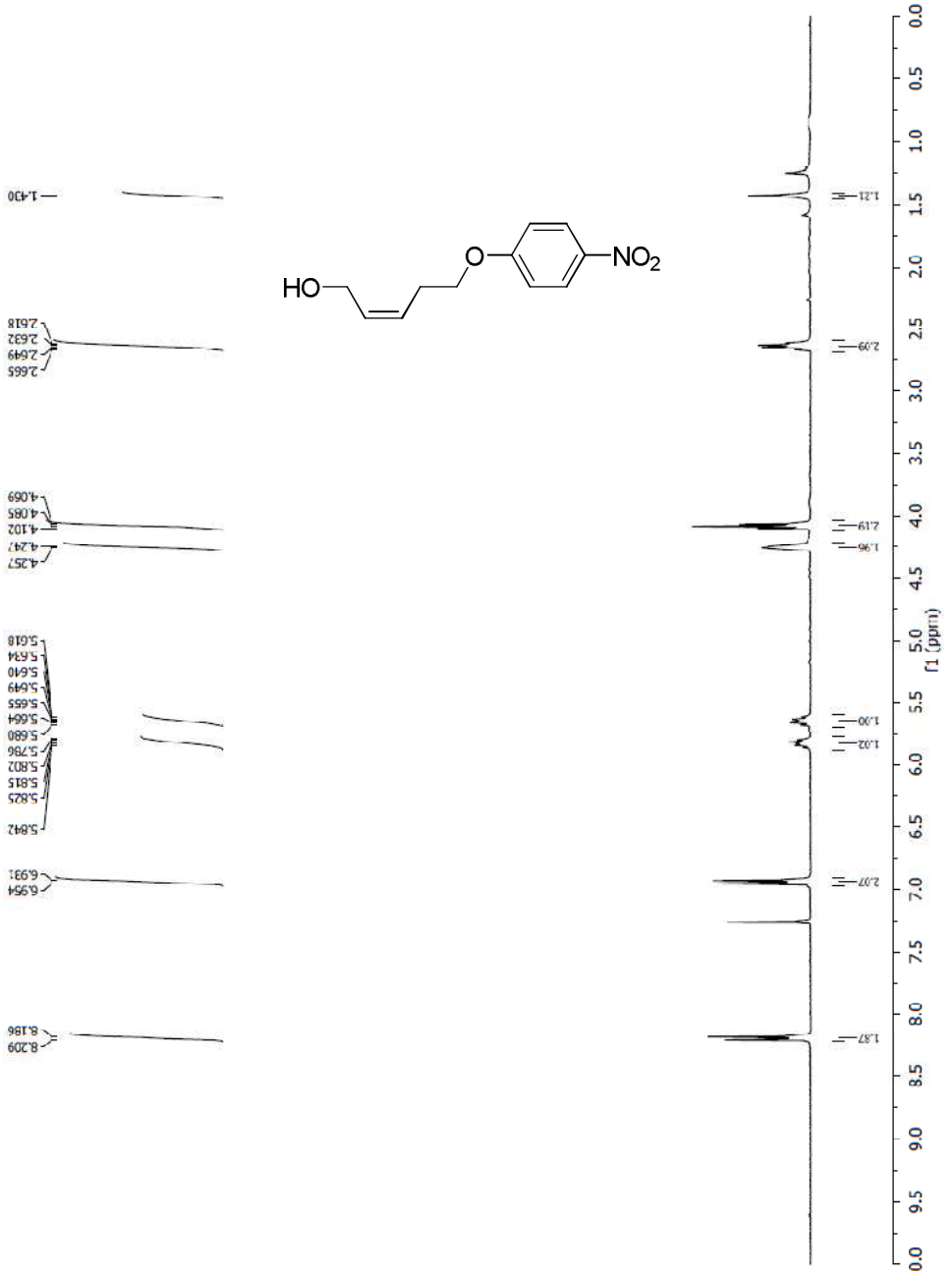


^{13}C NMR spectrum of 1.88

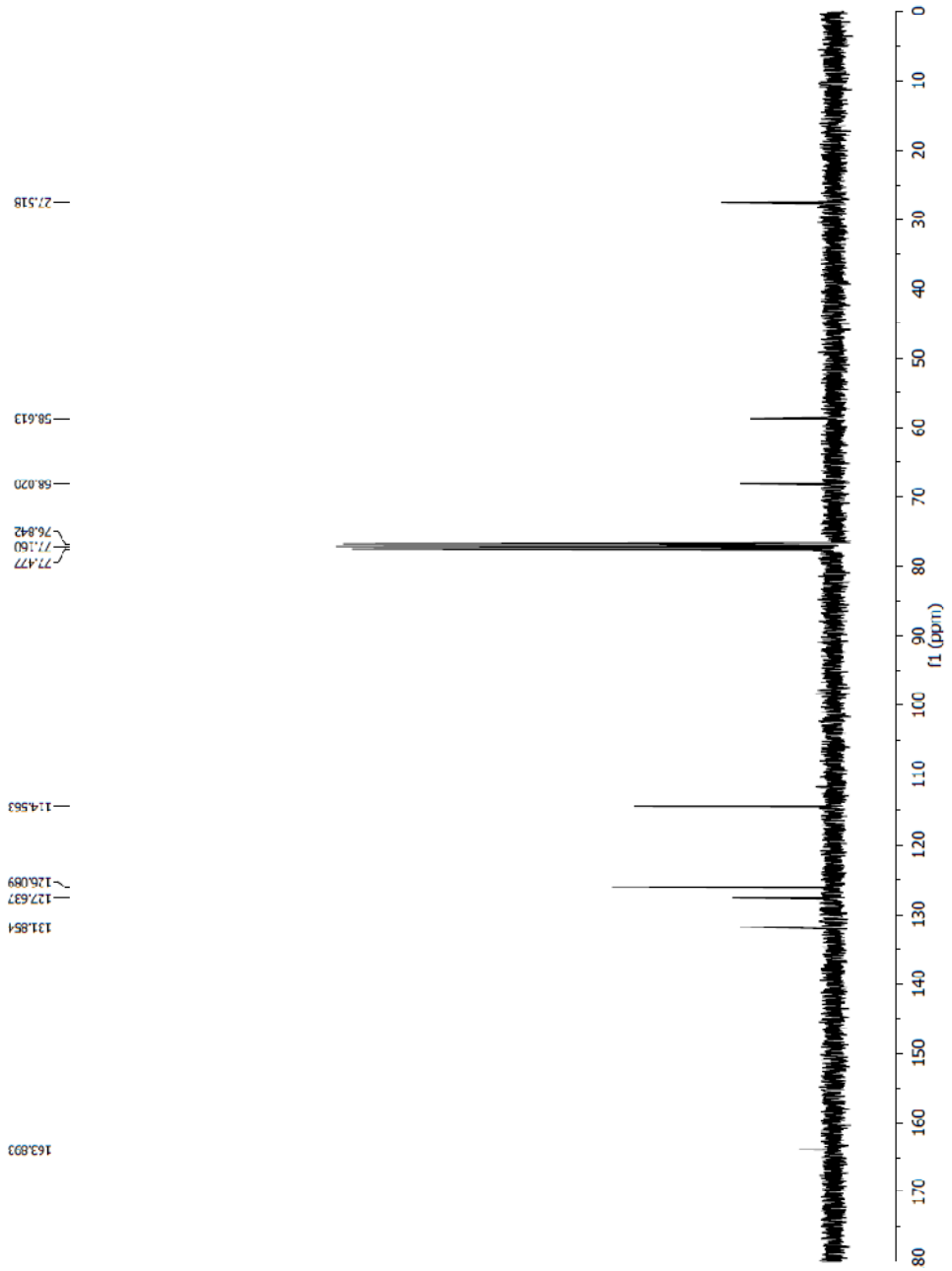


c. NMR spectra of CM products

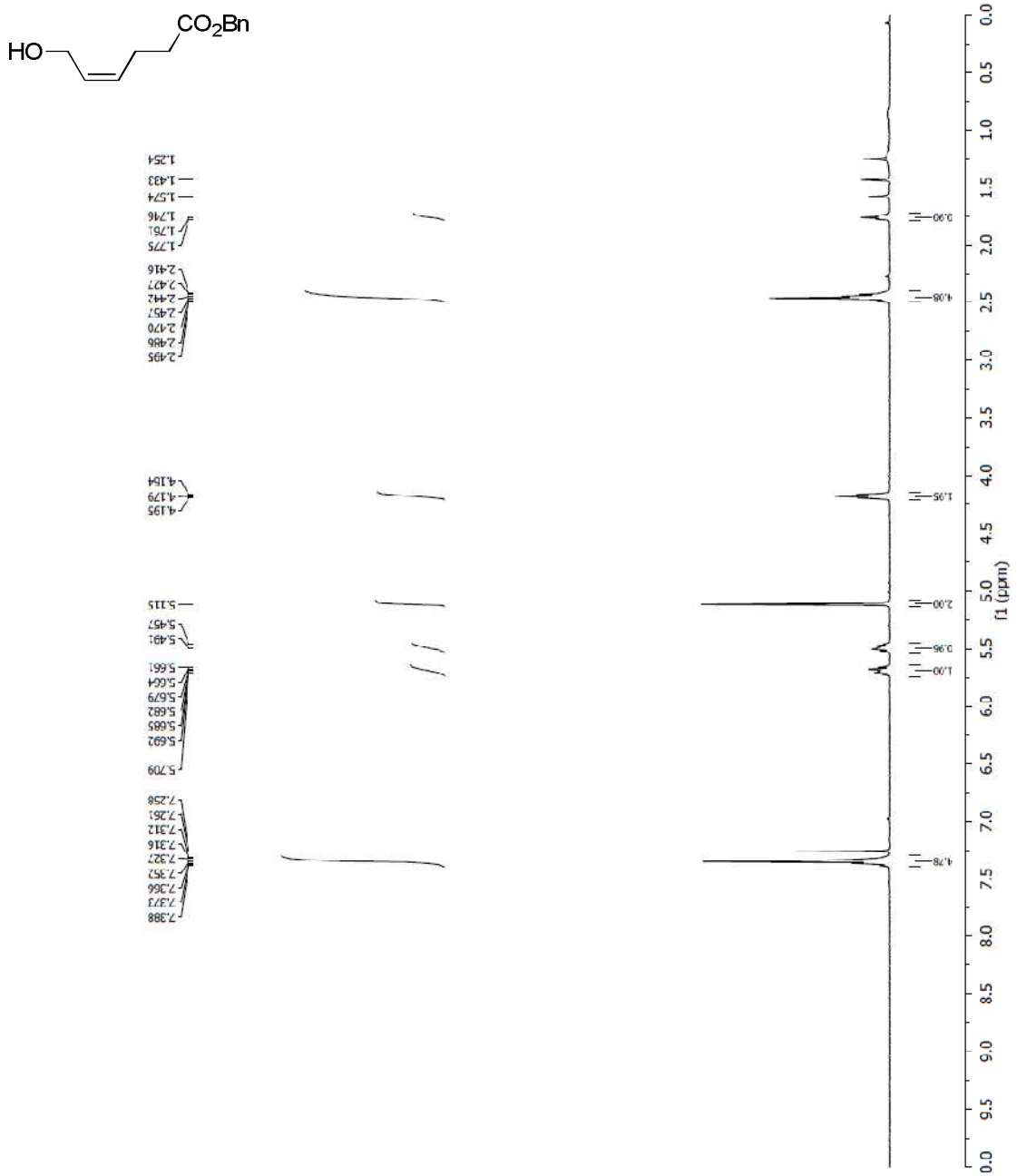
^{1}H NMR spectrum of 1.51



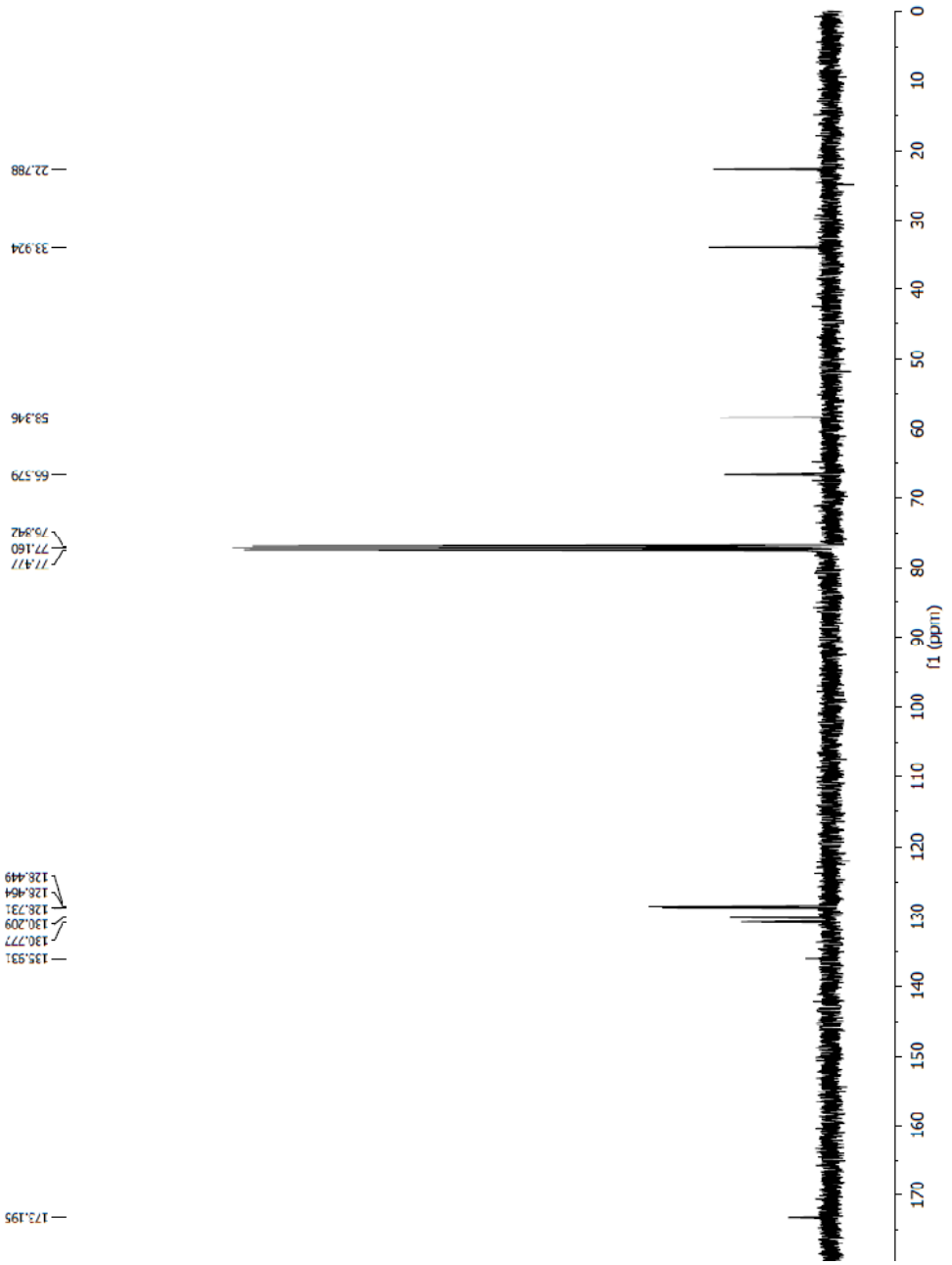
^{13}C NMR spectrum of 1.51



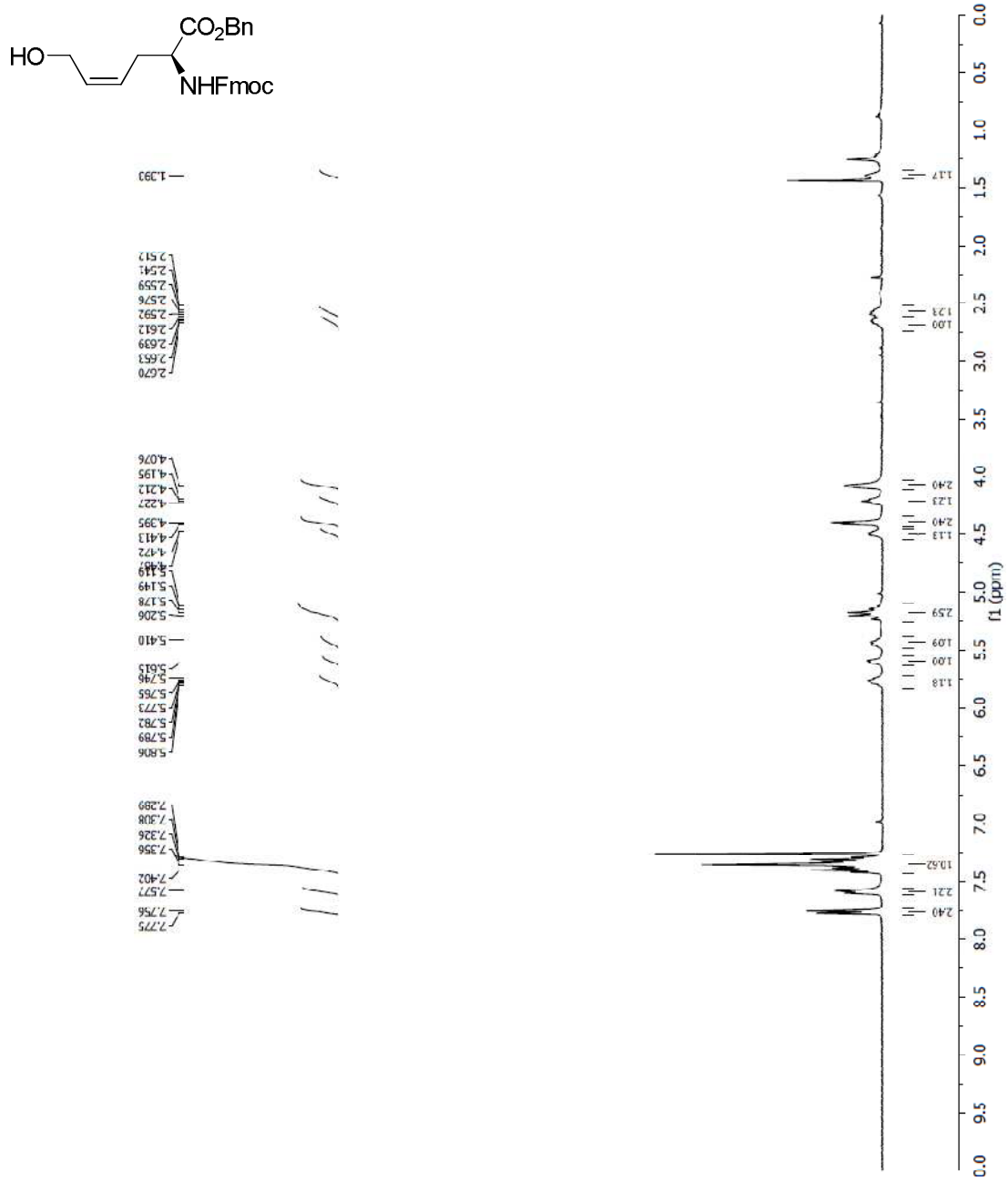
^{1}H NMR spectrum of 1.53



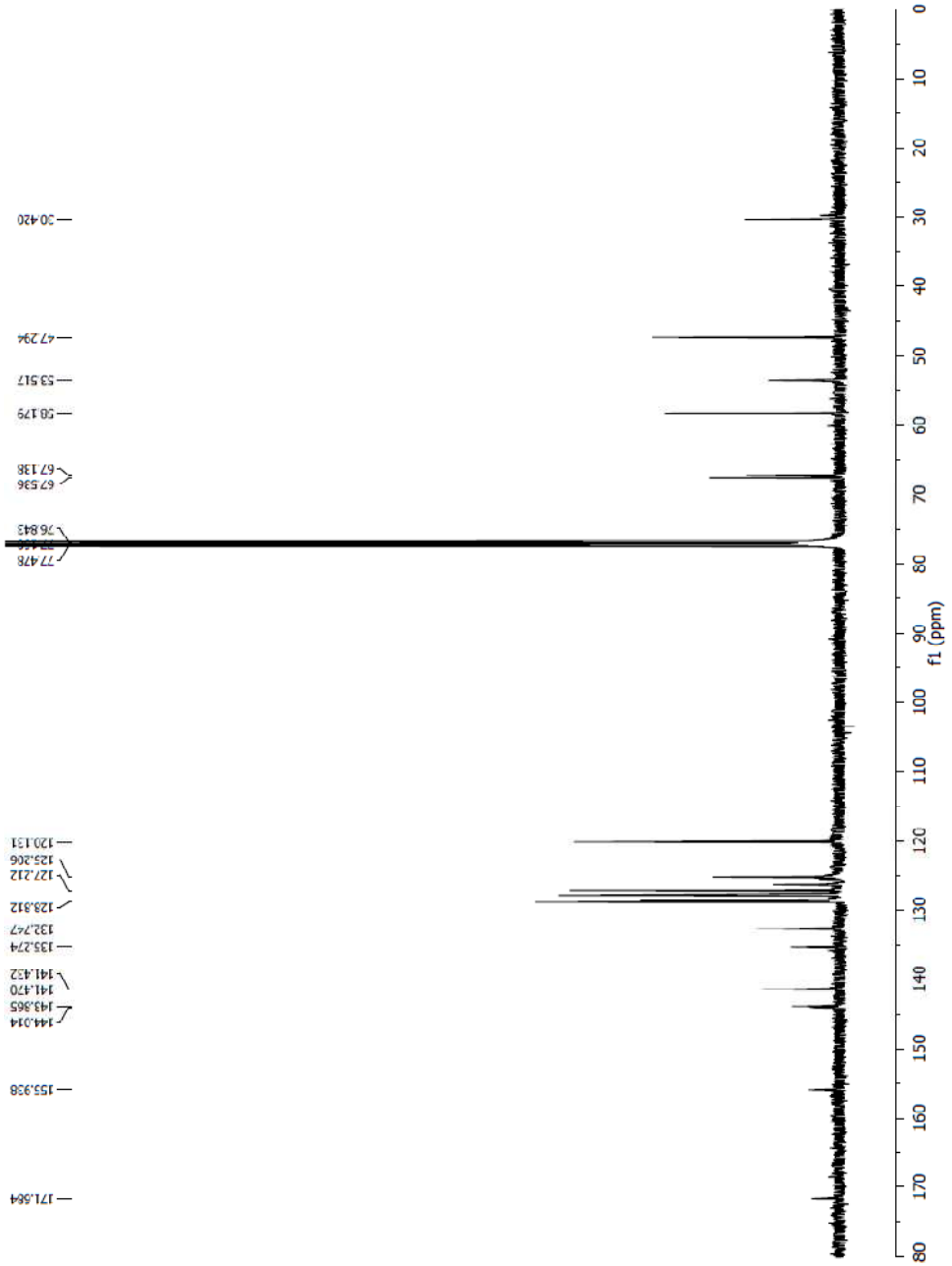
^{13}C NMR spectrum of 1.53



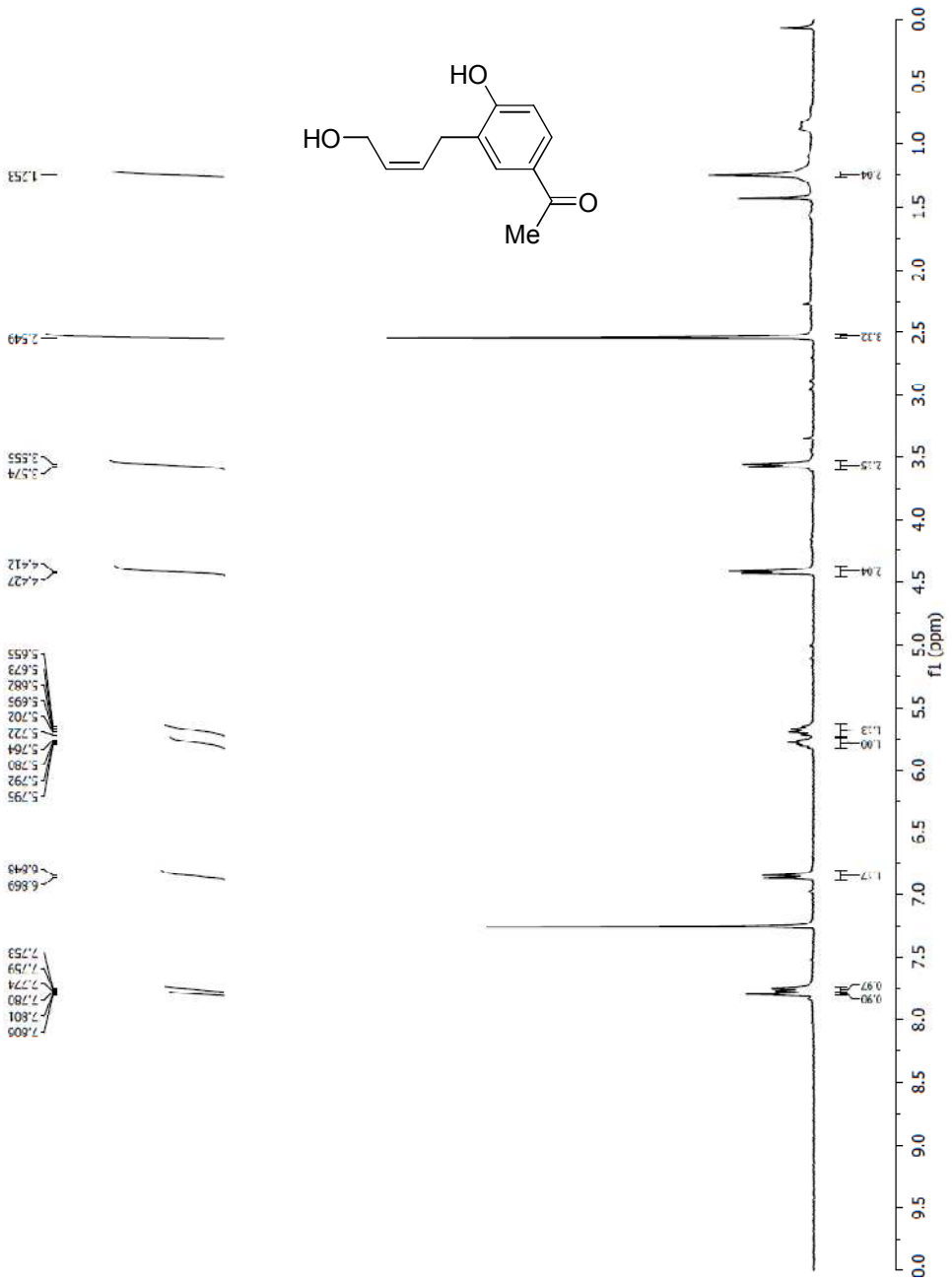
^{1}H NMR spectrum of 1.55



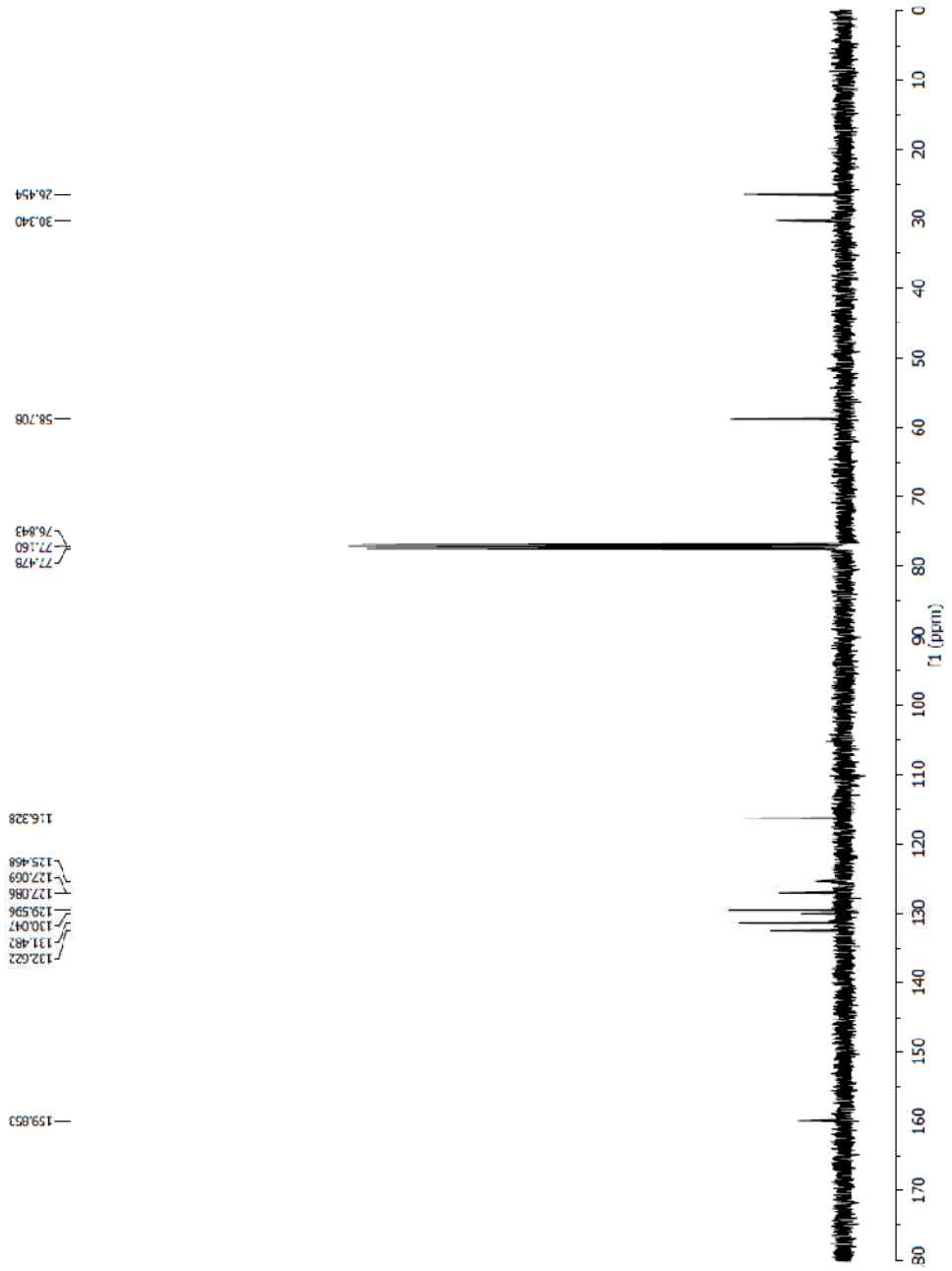
^{13}C NMR spectrum of 1.55



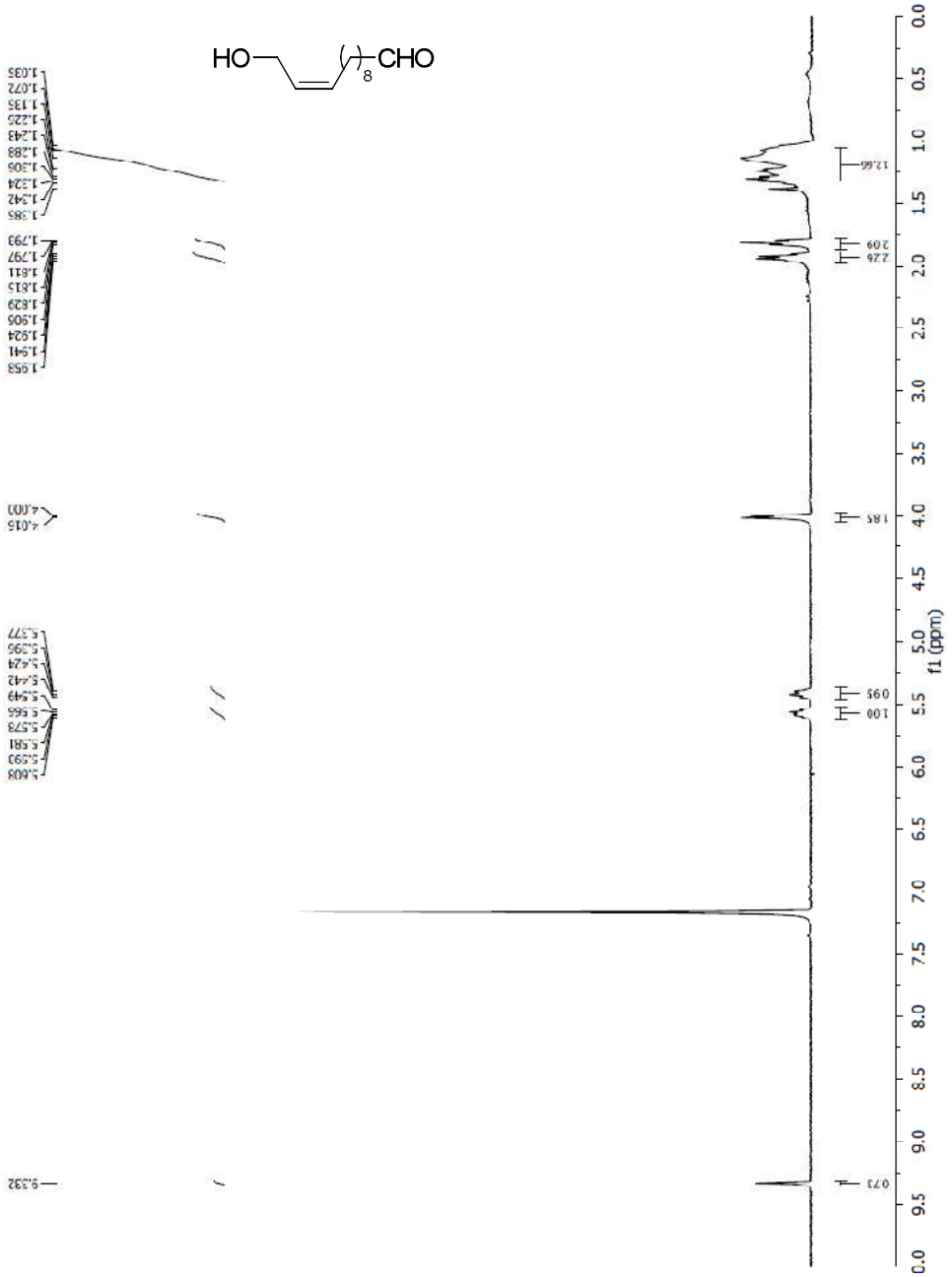
^{1}H NMR spectrum of 1.57



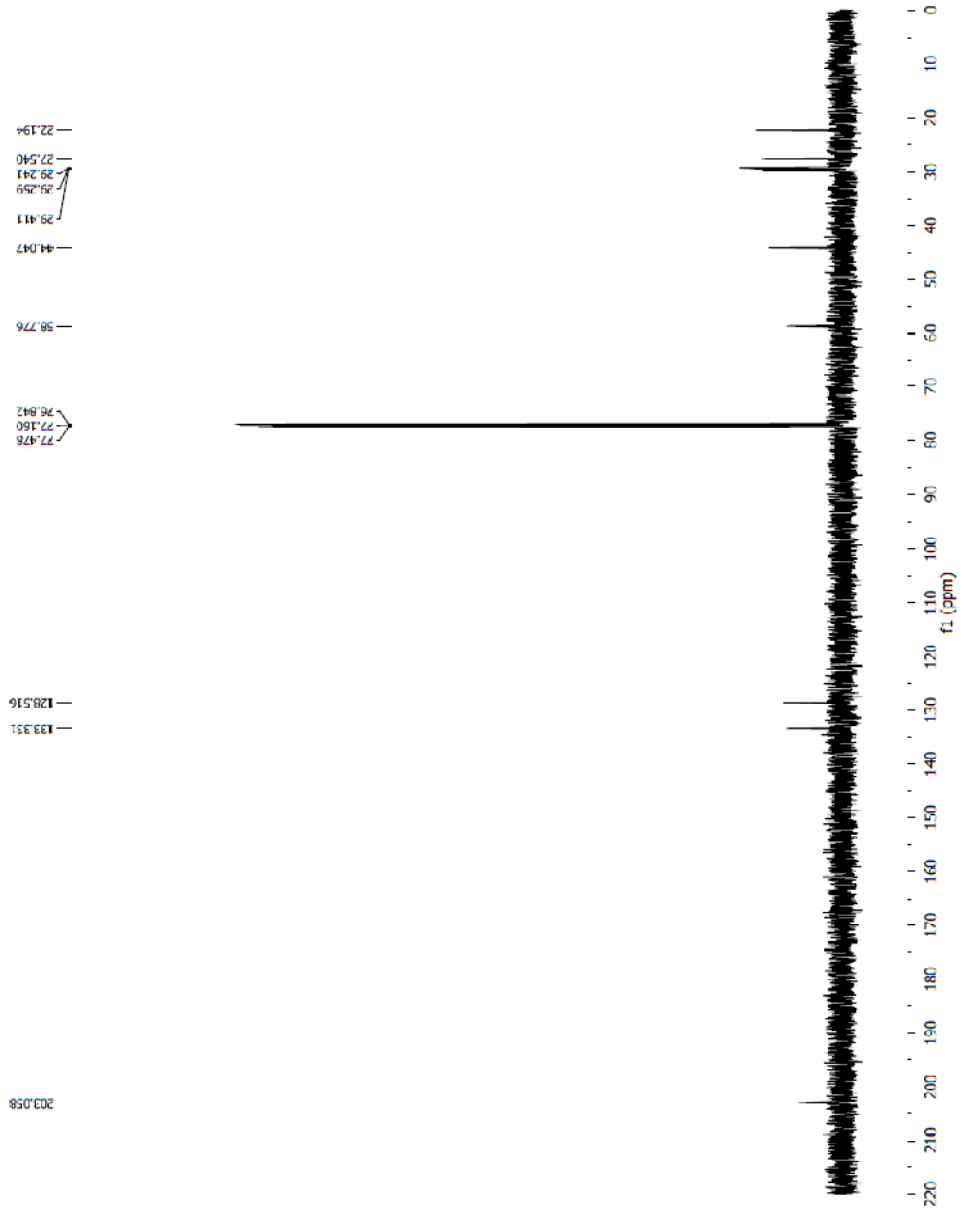
^{13}C NMR spectrum of 1.57



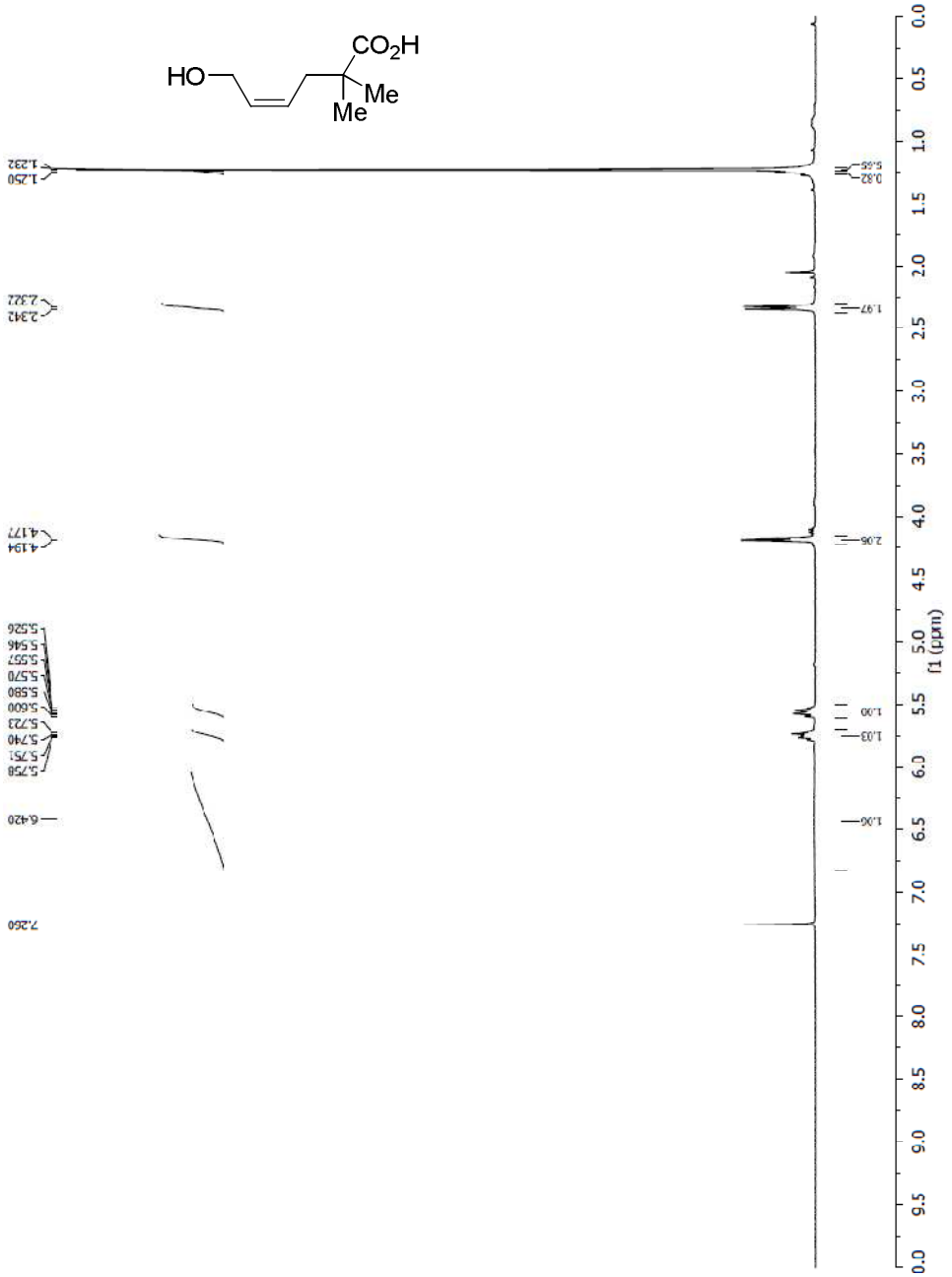
^{1}H NMR spectrum of 1.58



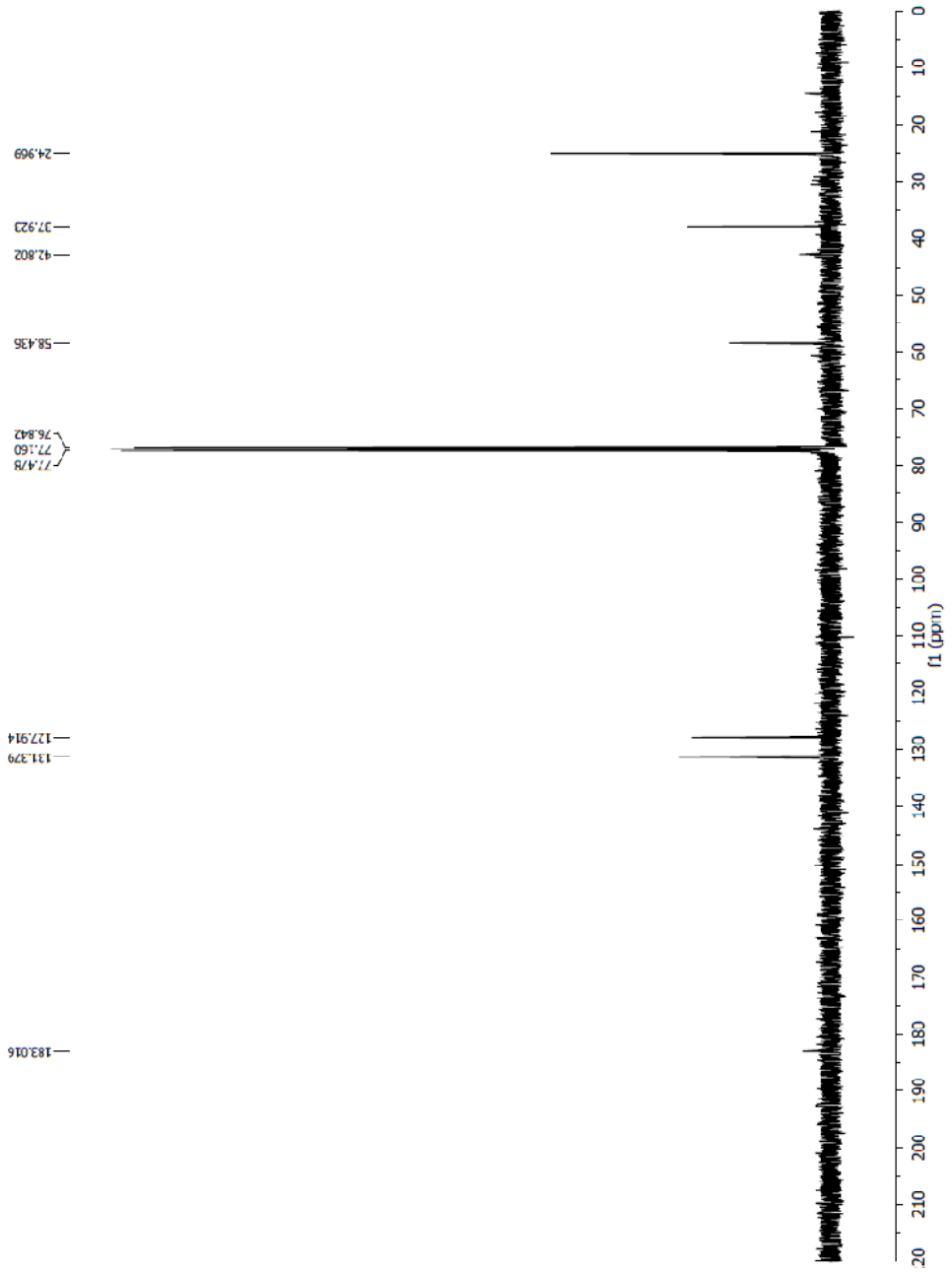
^{13}C NMR spectrum of 1.58



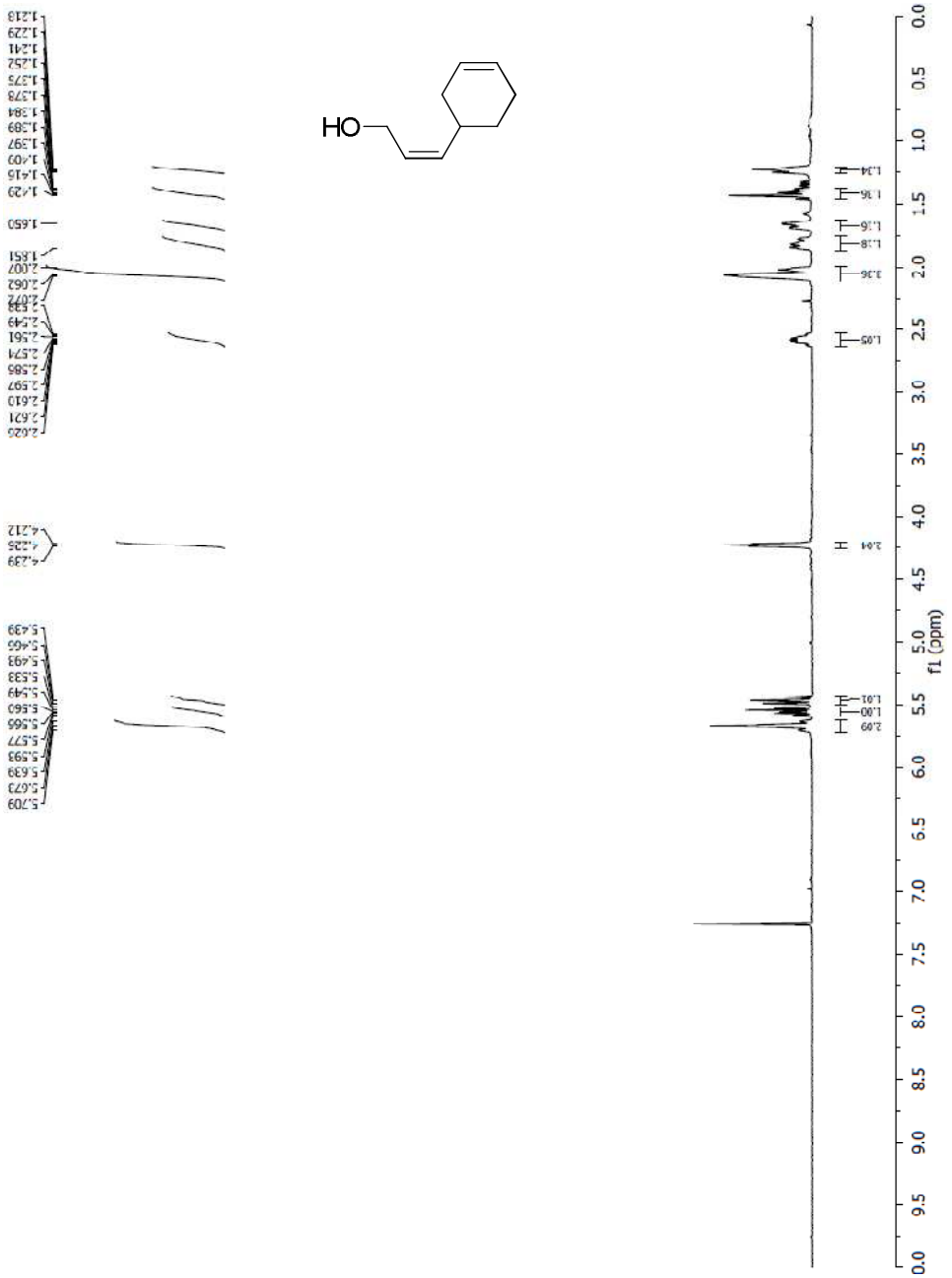
^{1}H NMR spectrum of 1.60



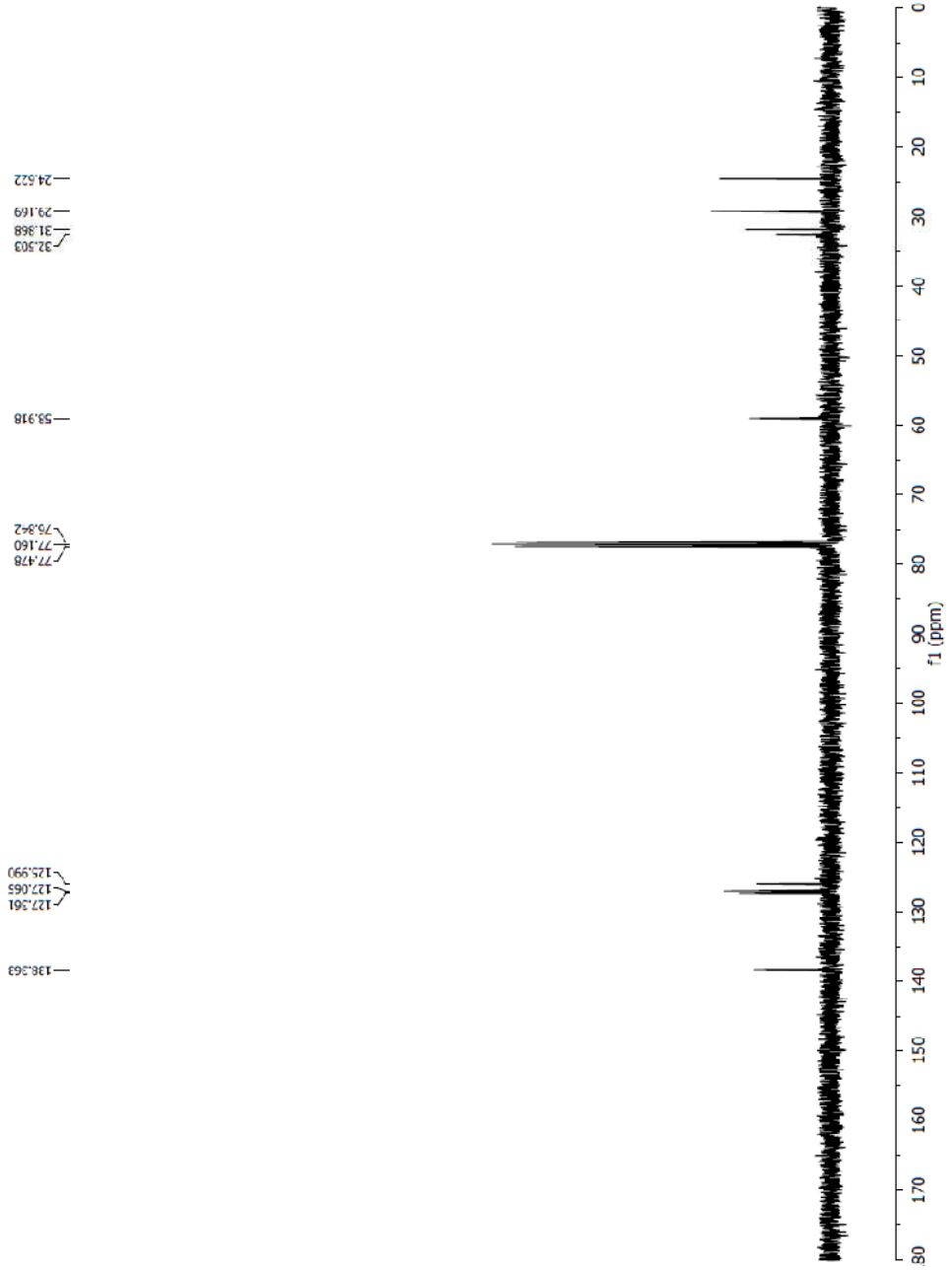
^{13}C NMR spectrum of 1.60



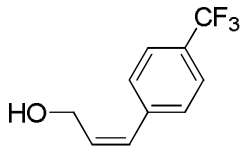
^{1}H NMR spectrum of 1.62

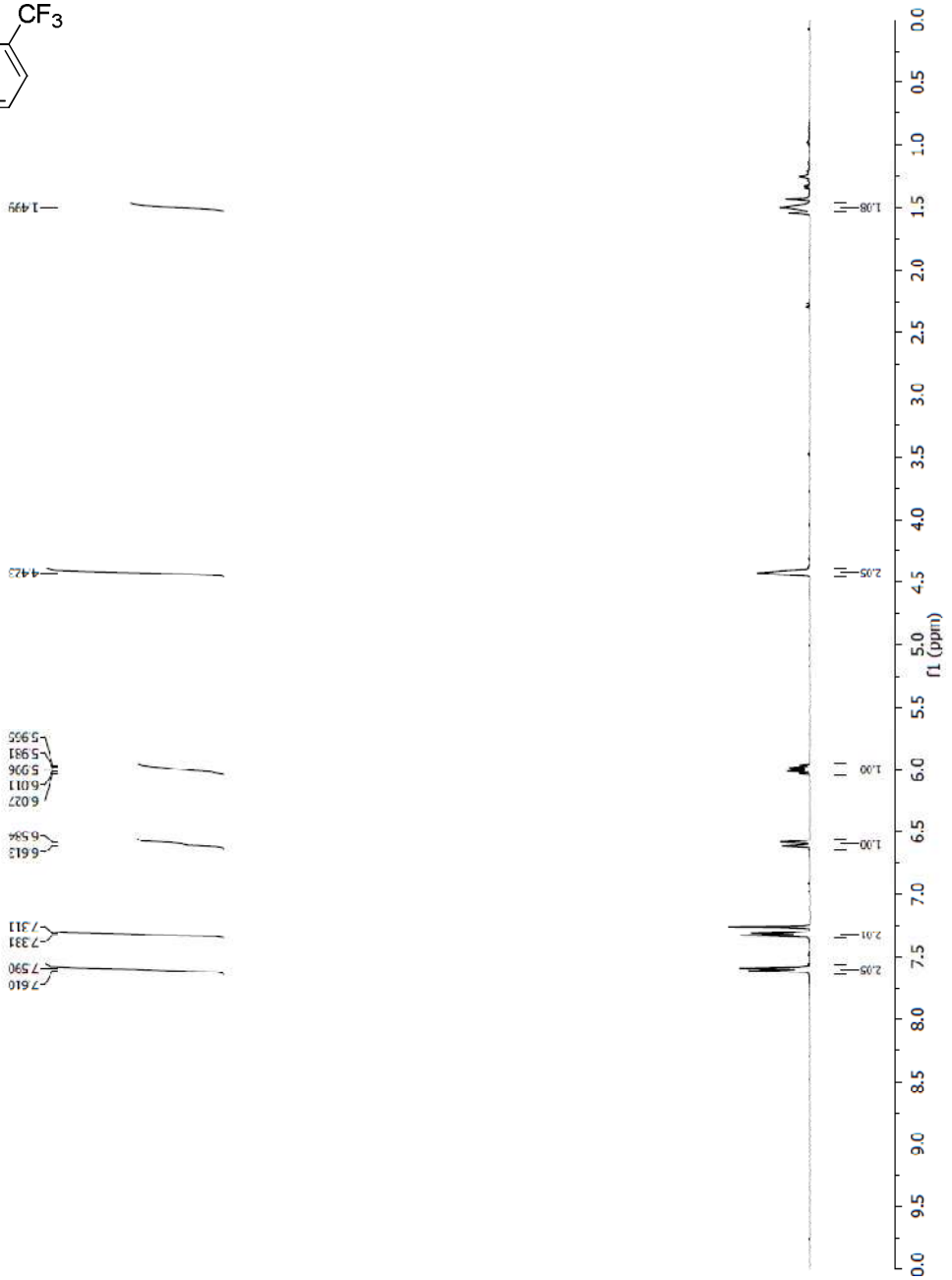


^{13}C NMR spectrum of 1.62

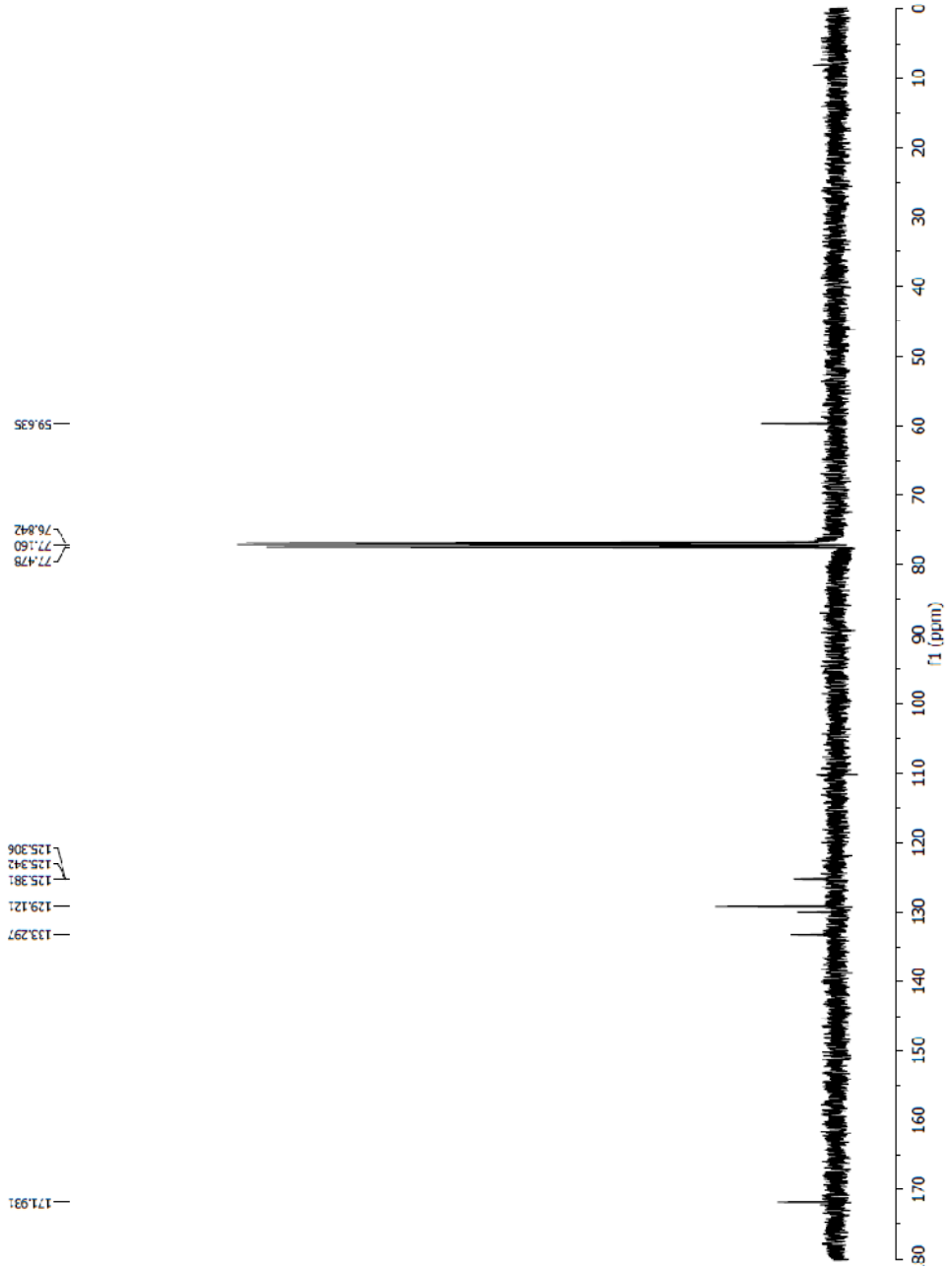


^{1}H NMR spectrum of 1.64

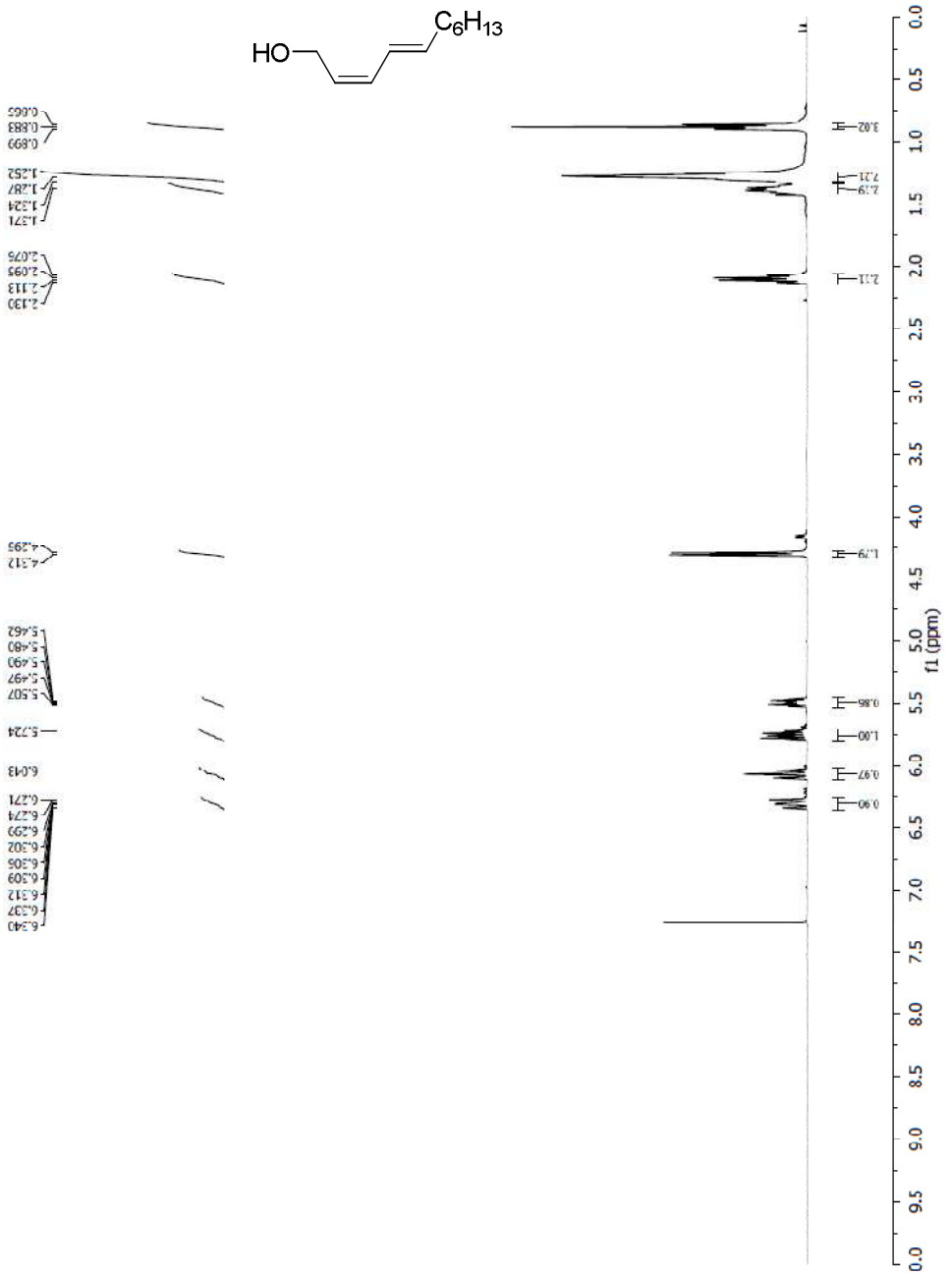




^{13}C NMR spectrum of 1.64



^{1}H NMR spectrum of 1.65



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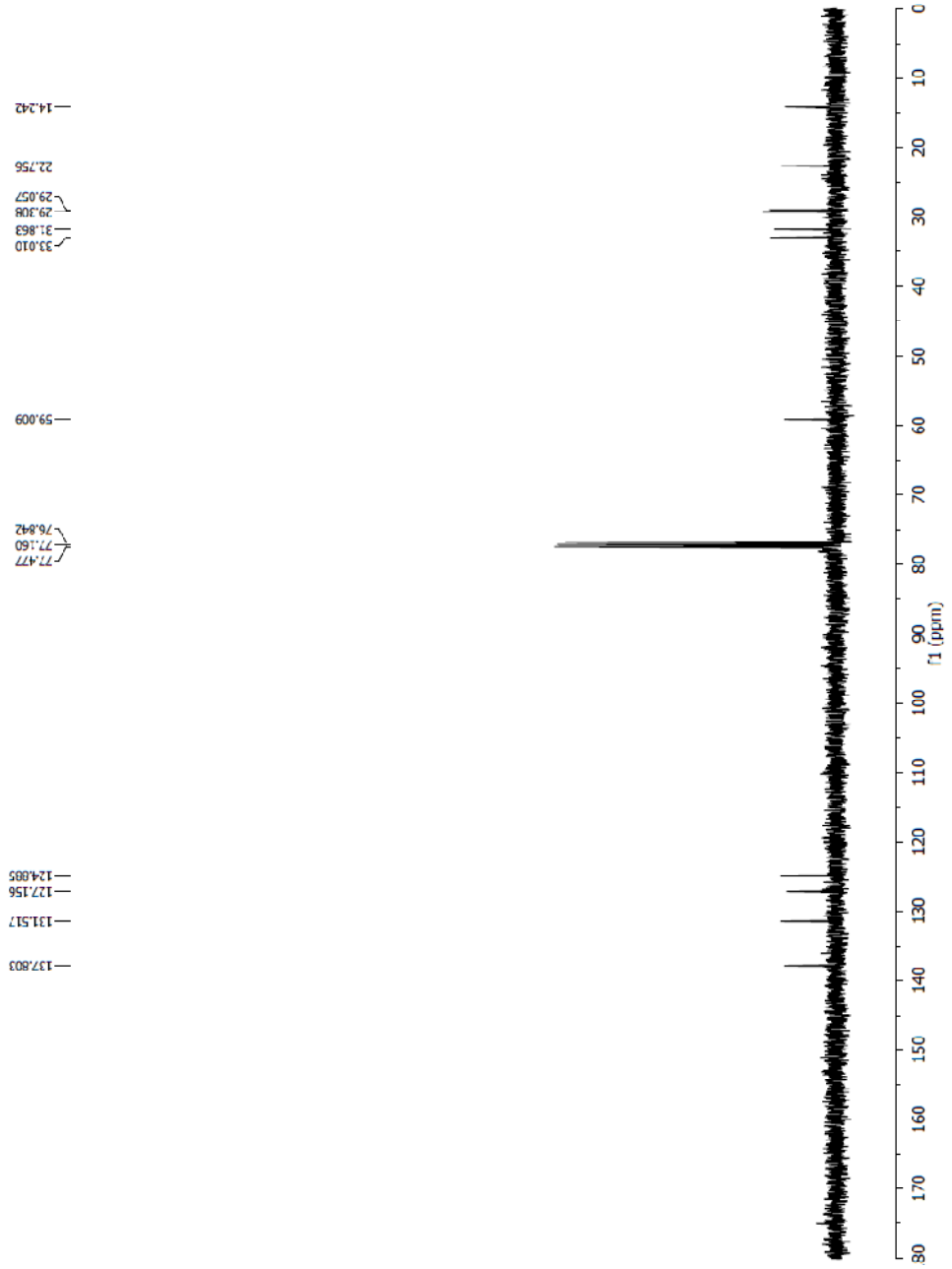

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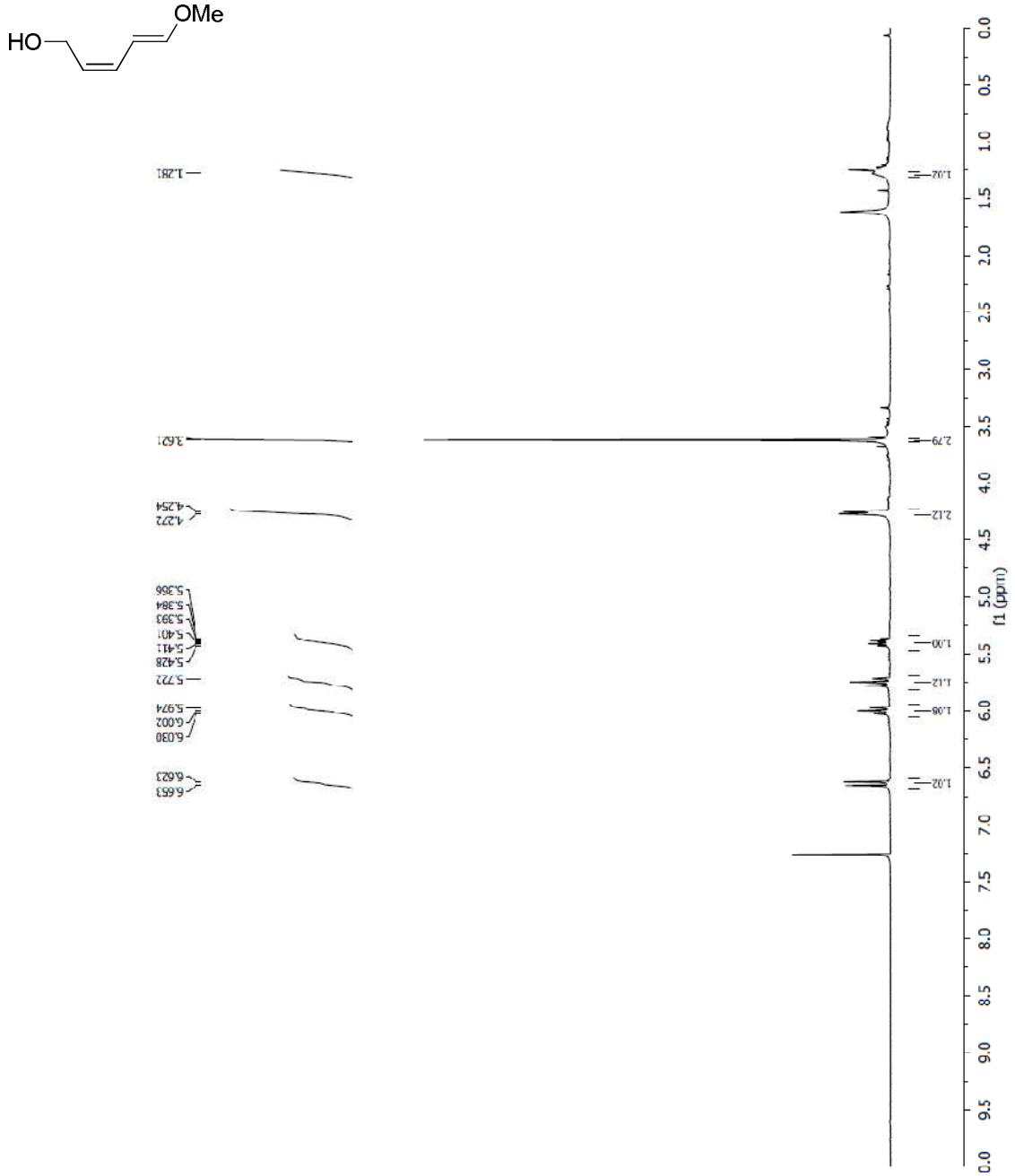

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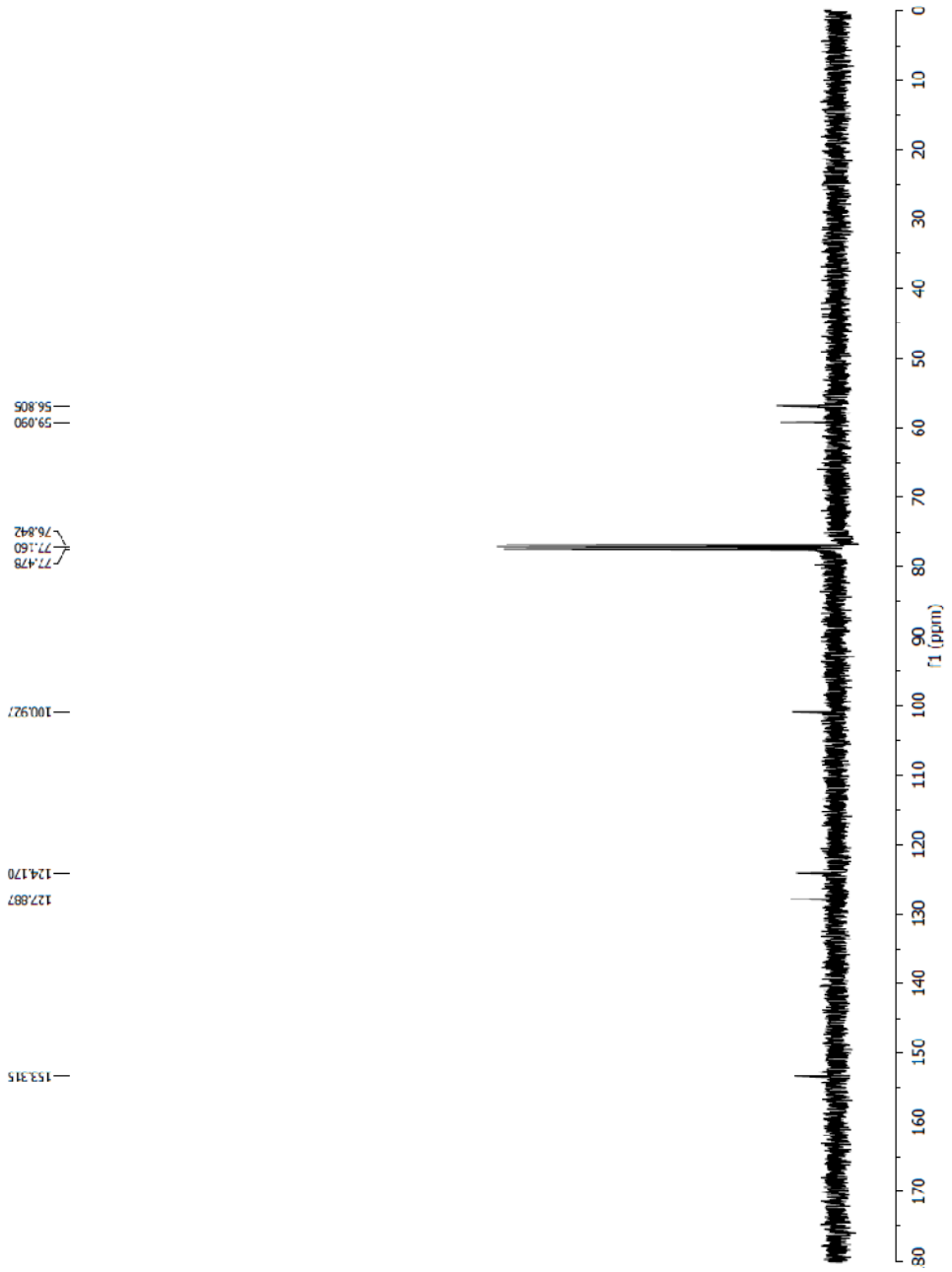

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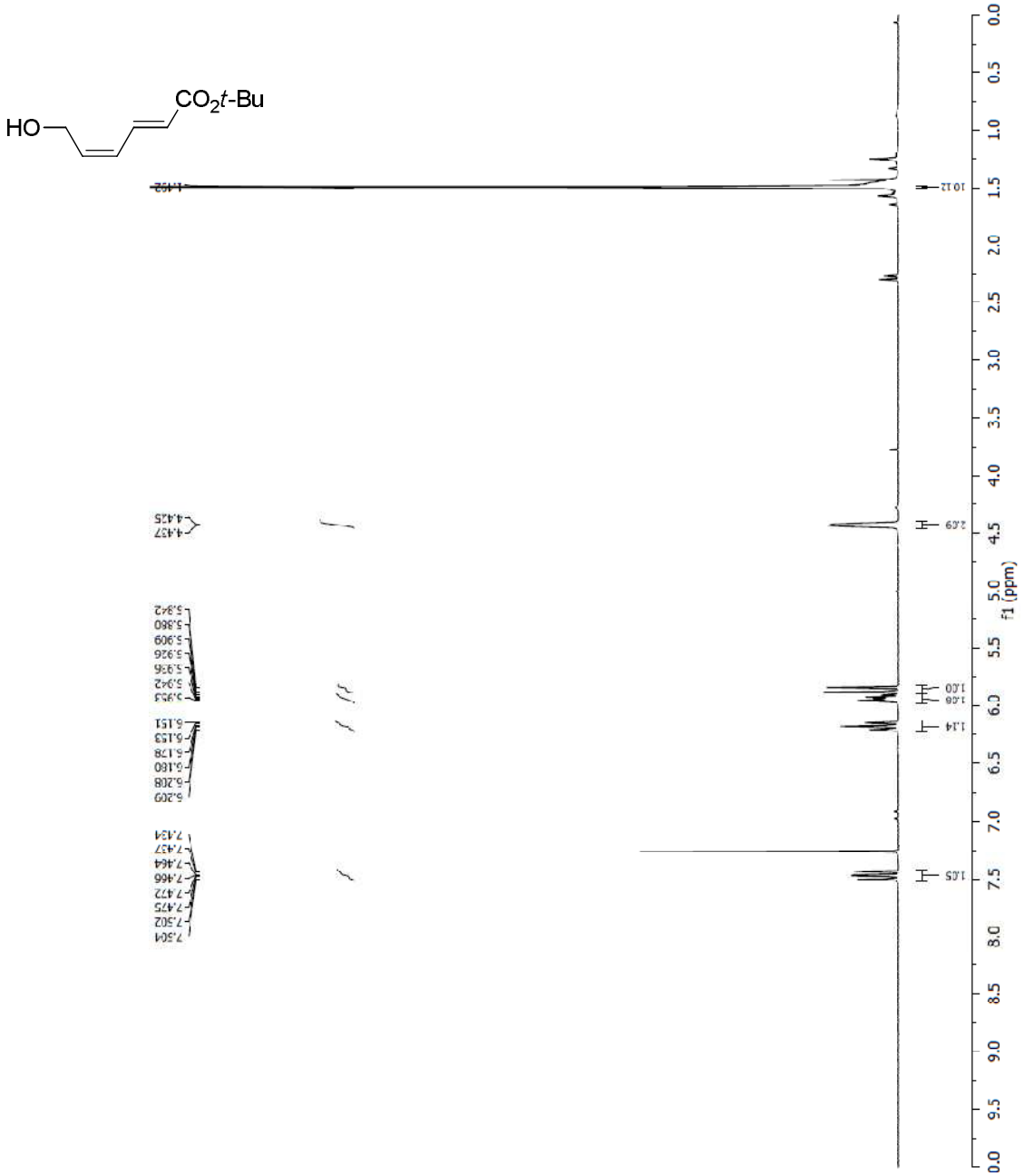

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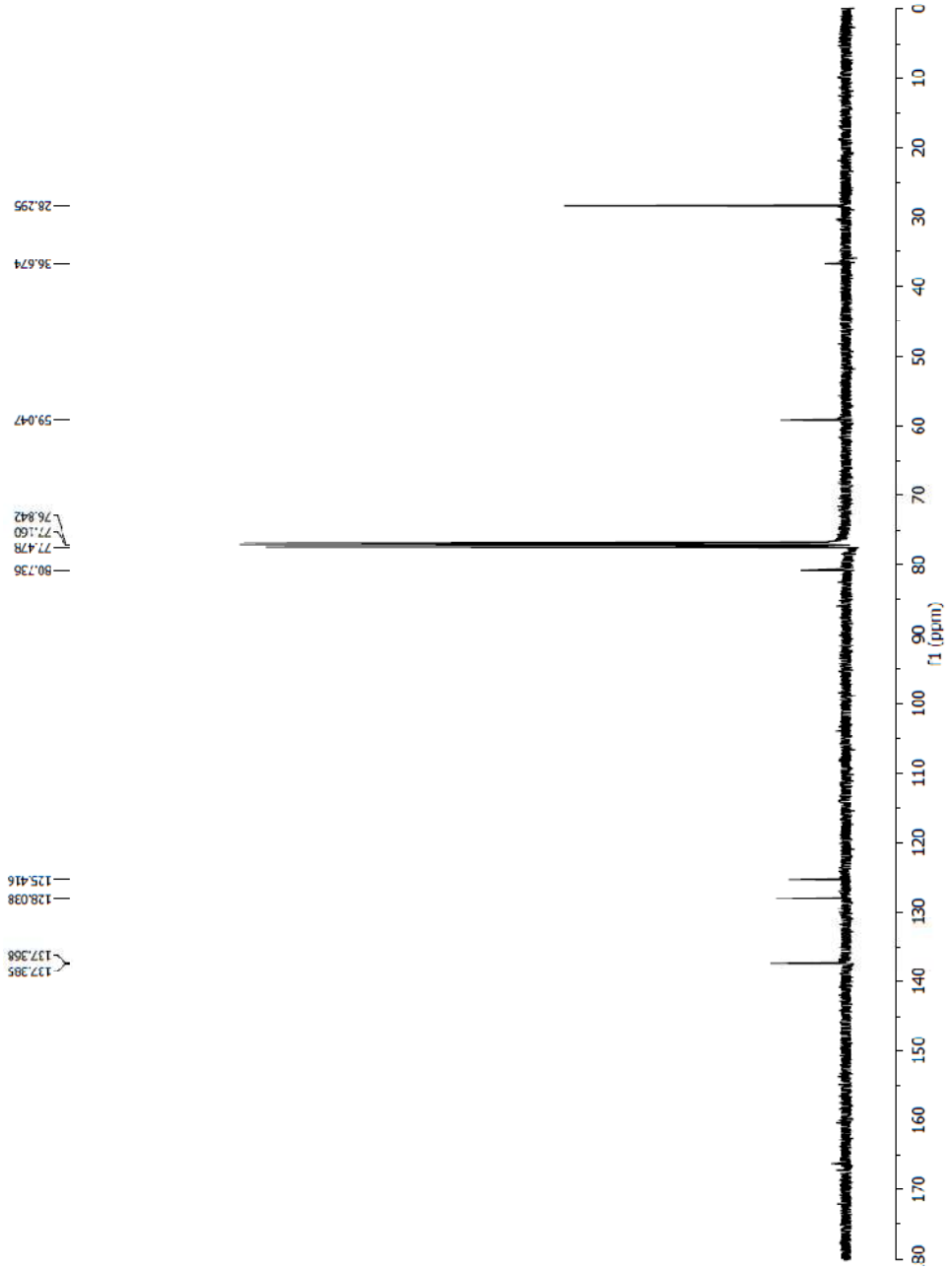
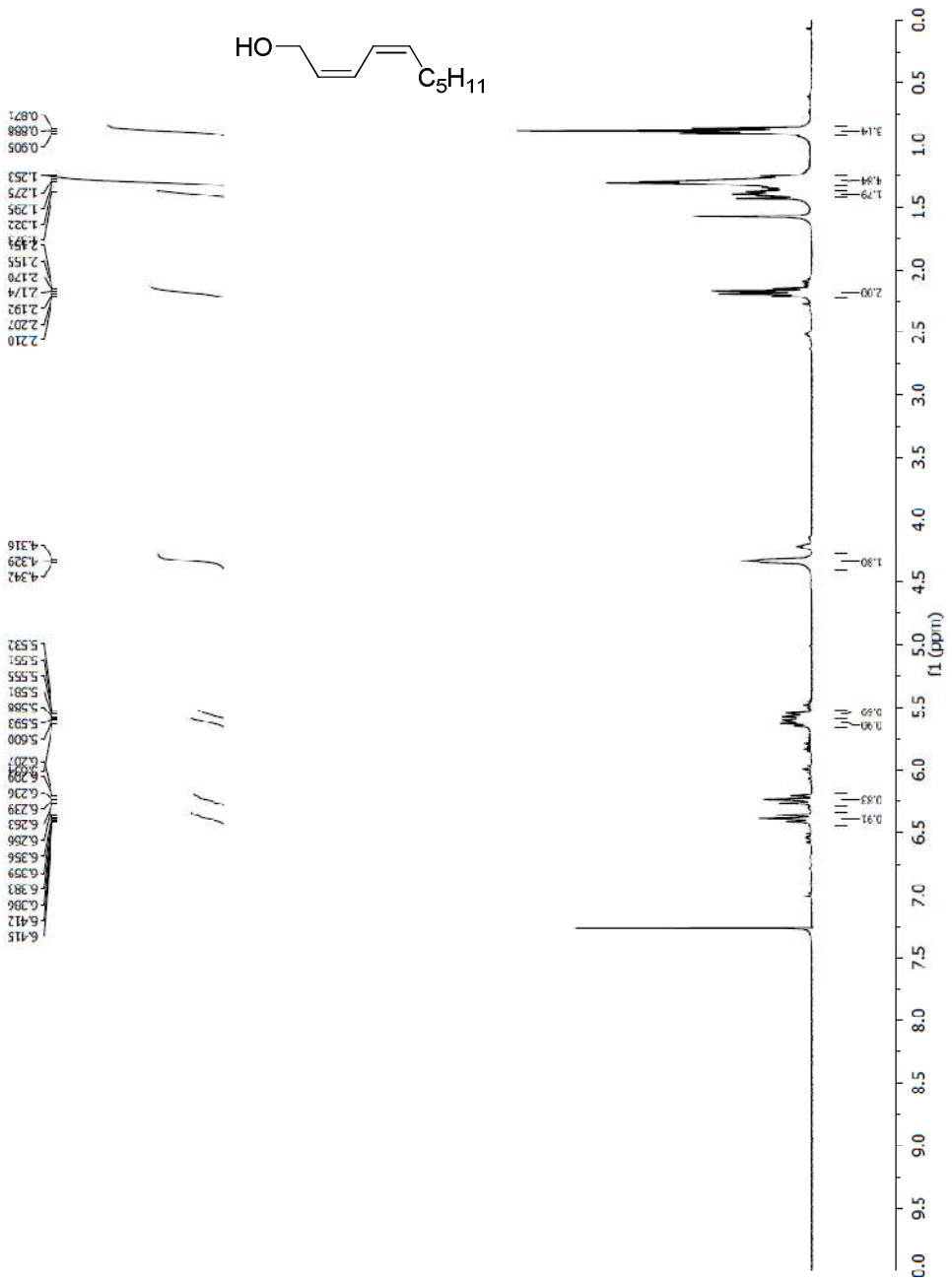


^{1}H NMR spectrum of 1.68



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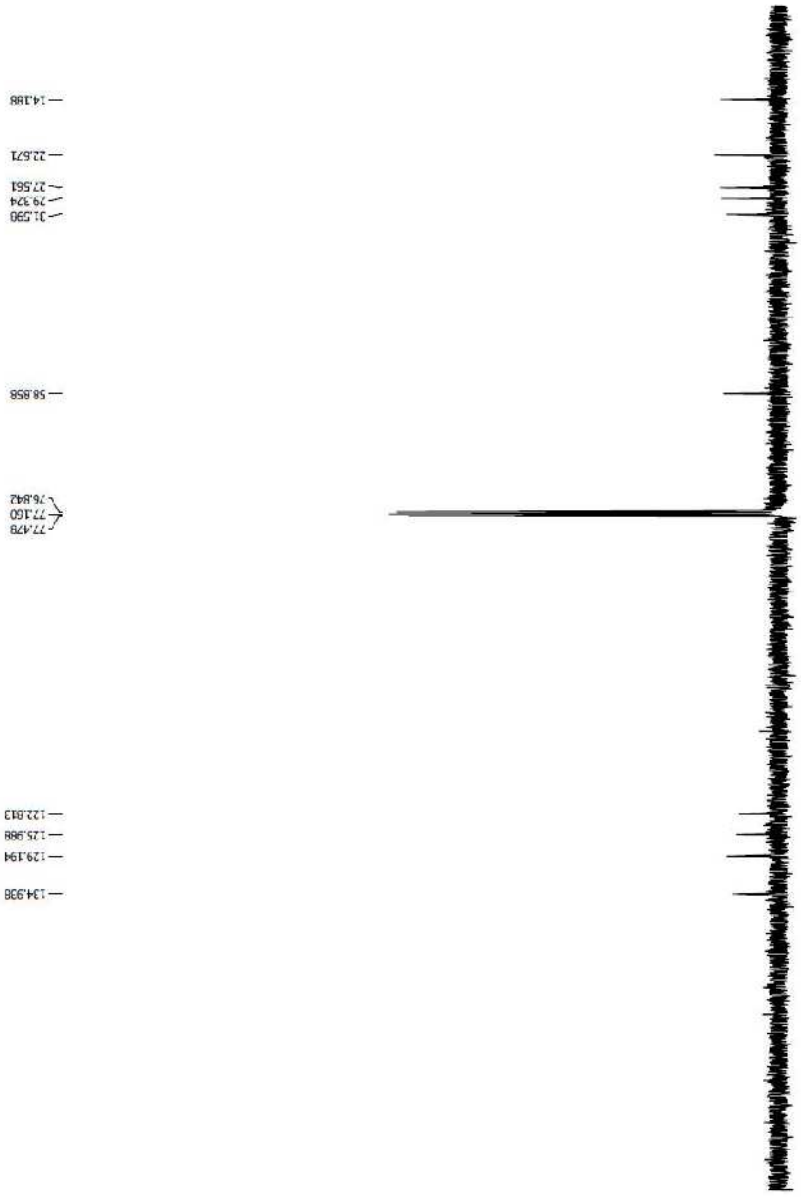
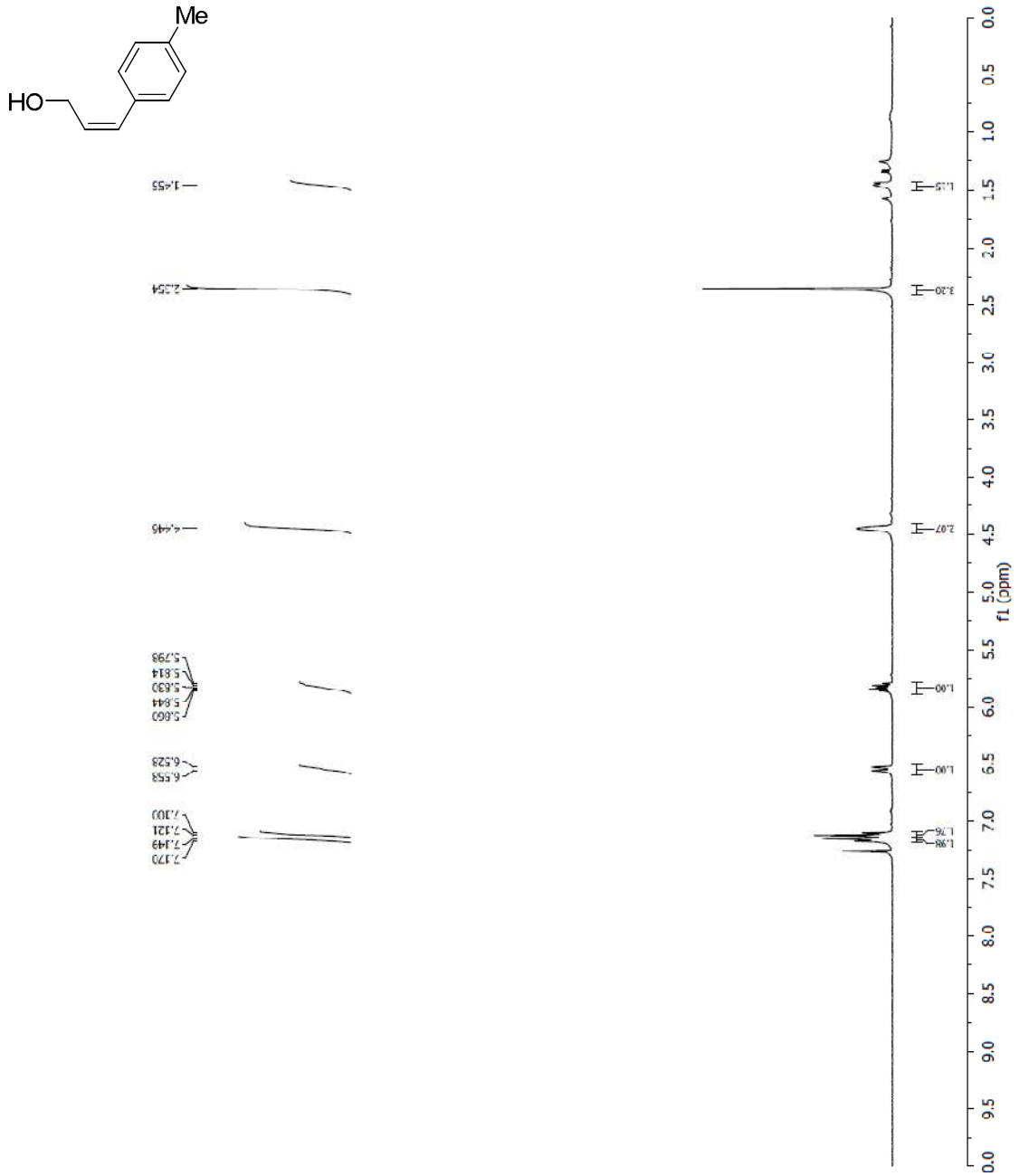


^{1}H NMR spectrum of 1.90



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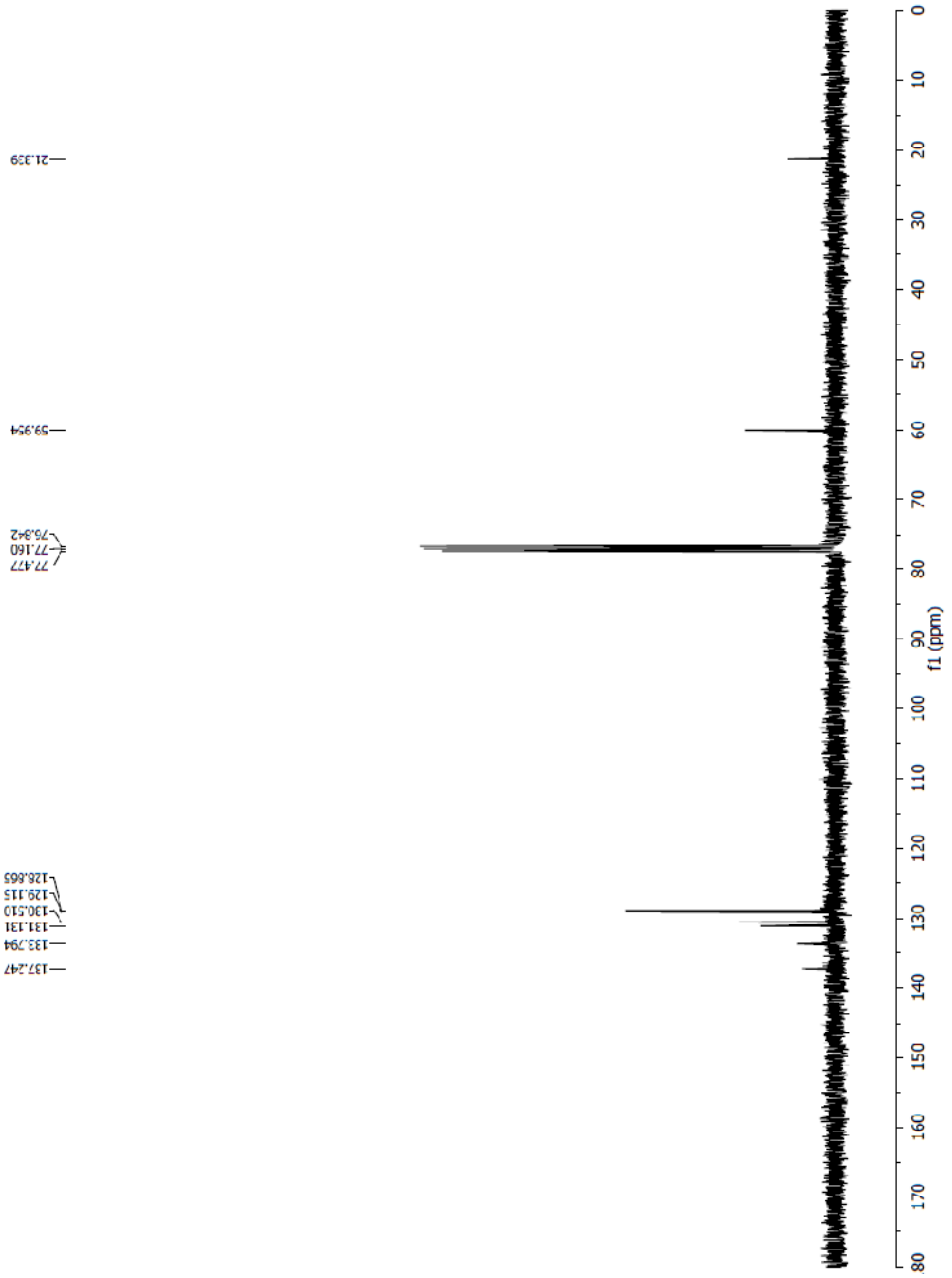

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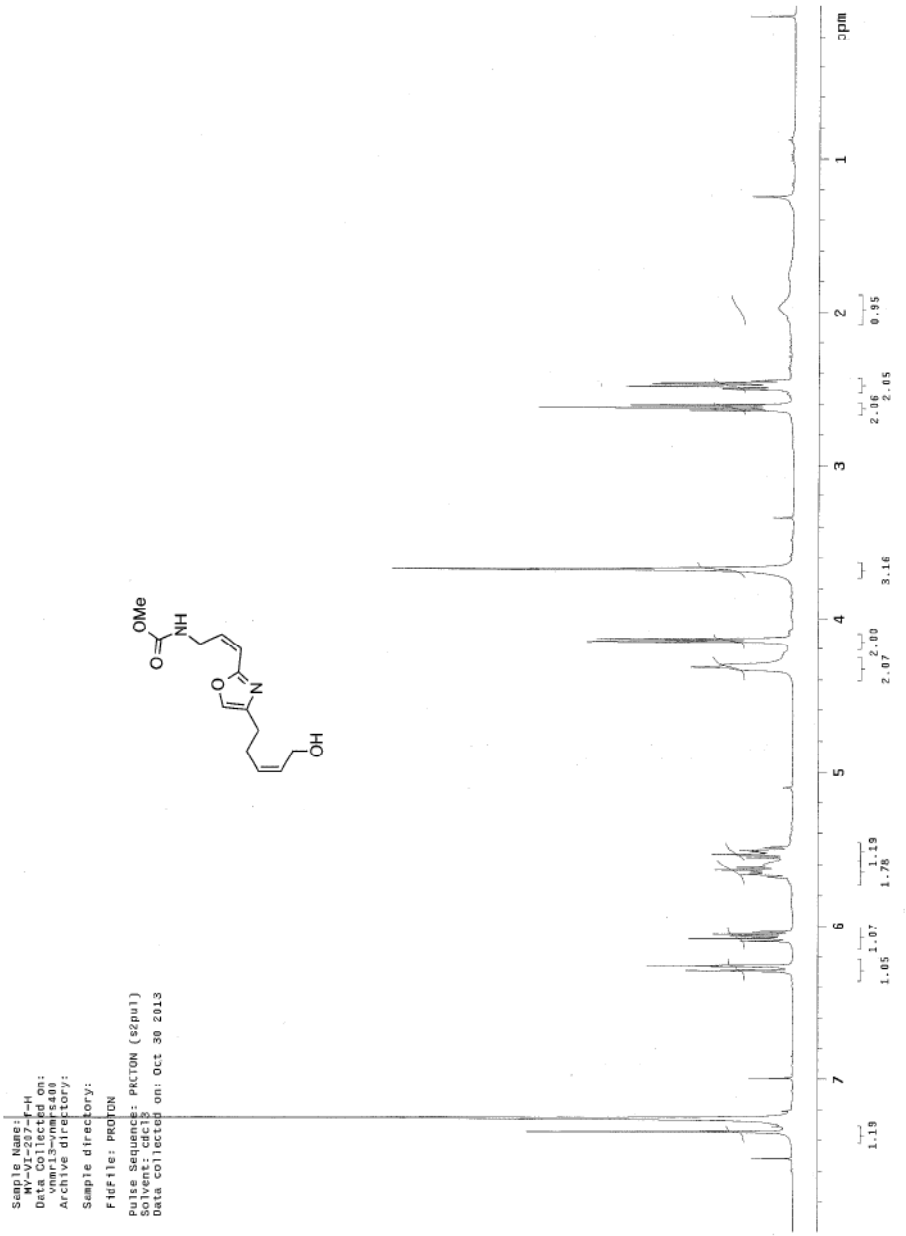

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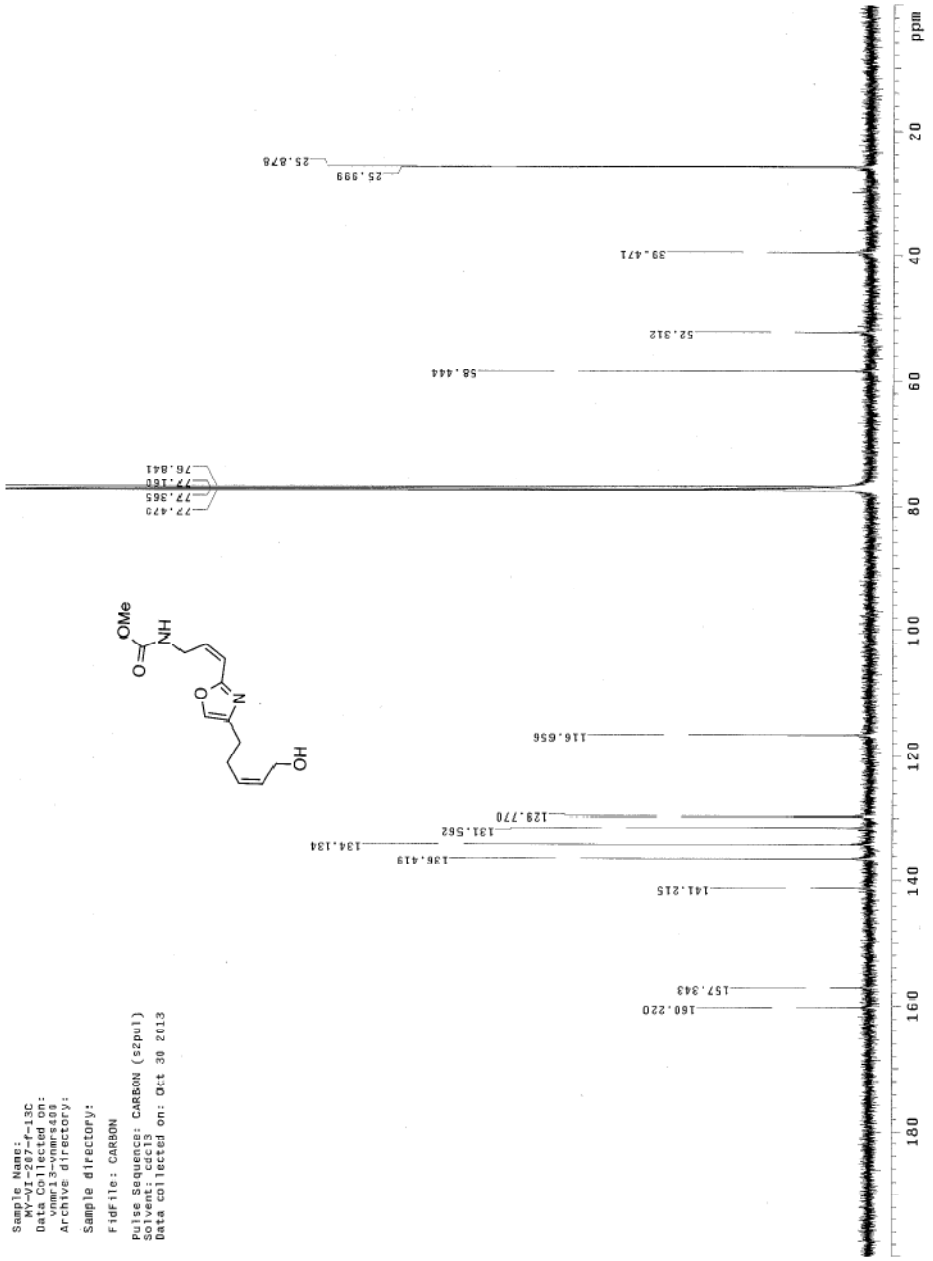
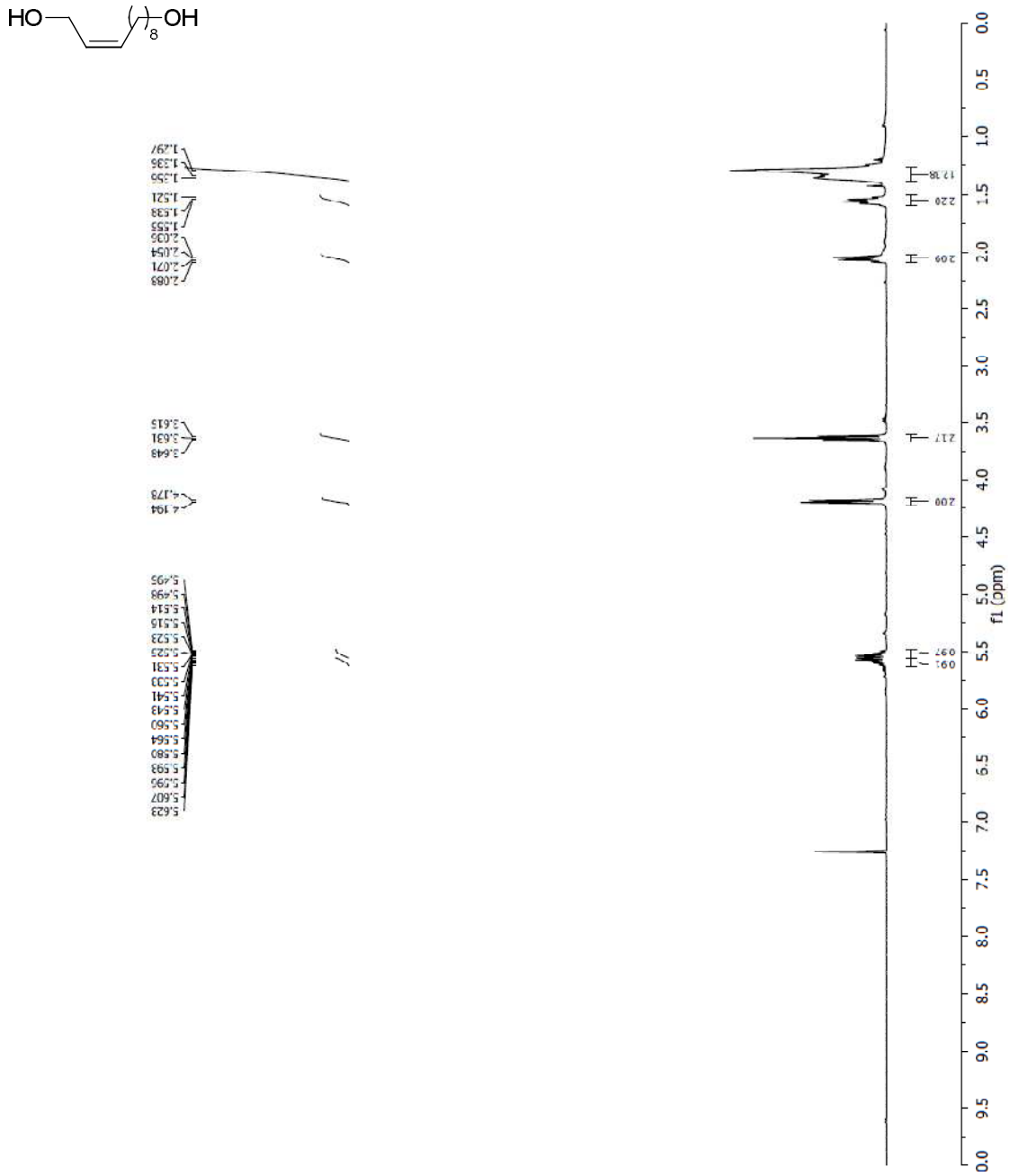
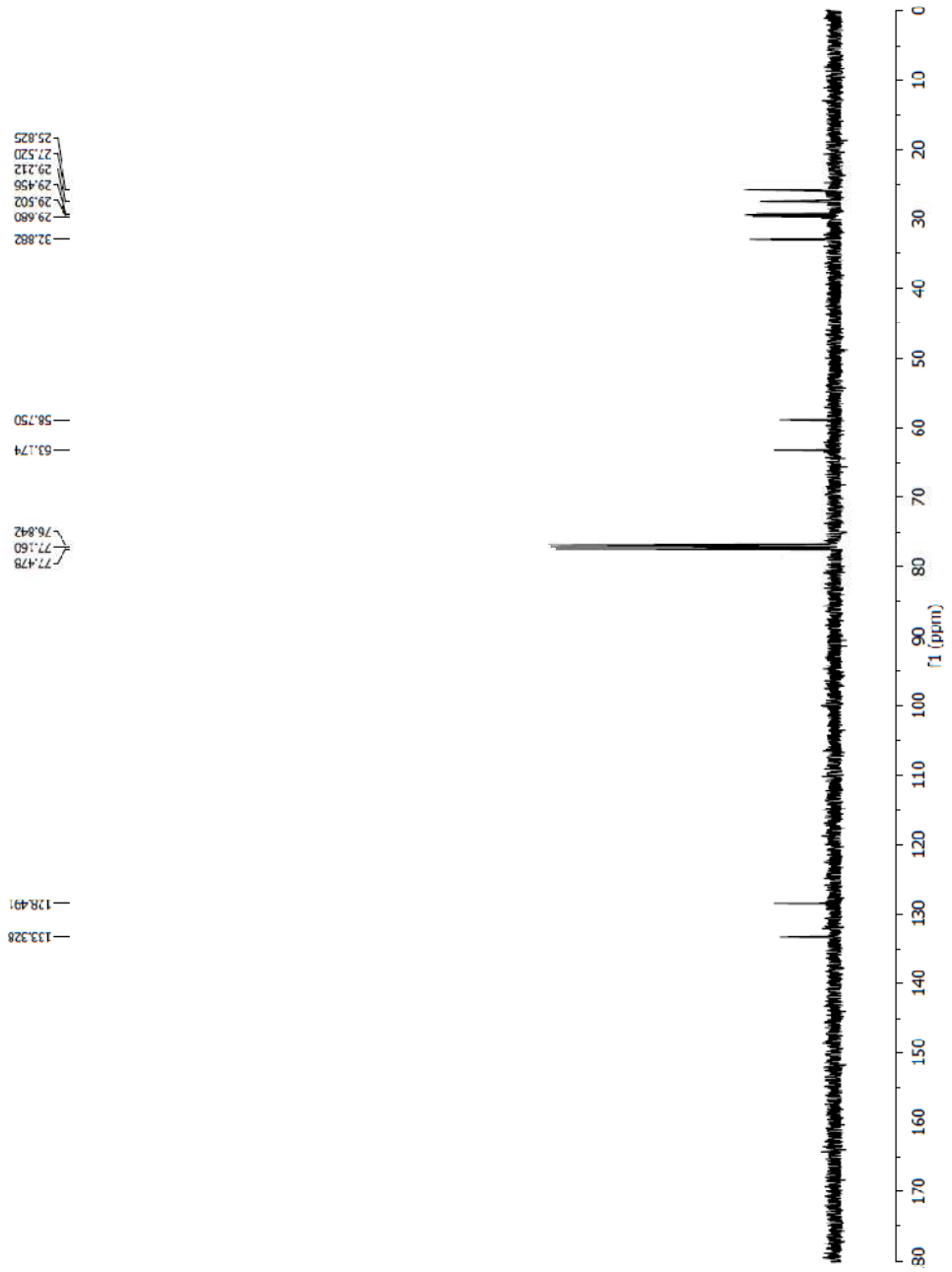


^{1}H NMR spectrum of 1.73



^{13}C NMR spectrum of 1.73



1.6.10. Density Functional Theory (DFT) Calculations

DFT[77] computations were performed with the Gaussian 09 suite of programs,[78] applying the dispersion corrected functional ωB97XD[79, 80]. The following basis set (termed "basis1") was used for geometry optimizations and evaluation of thermal corrections to the Gibbs free energy at 298.15 K and 24 atm[81]: 6-31G(d,p) basis set for hydrogen and carbon atoms, including additional diffuse functions (+) on heteroatoms (oxygen, nitrogen and sulfur). A quasi-relativistic effective core potential (ECP) of the Stuttgart-Dresden type[82] was used for ruthenium (MWB28 keyword in Gaussian for basis set and ECP). The nature of all stationary points was checked through vibrational analysis. Single point electronic energy (ΔE_{sp}) calculations in solution (tetrahydrofuran) were performed on the gas phase geometries obtained with basis1 through application of an integral equation formalism variant of the polarizable continuum model (IEFPCM)[83], as well as the SMD solvation model[84] and the larger basis set termed "basis2": 6-311+G(2df,2p) on H, C, N, S and MWB28 on ruthenium. The single point electronic energies (ΔE_{sp}) at the basis2 level were corrected by addition of thermal corrections to the Gibbs free energy obtained at the corresponding basis1 level. Therefore, the relative gas phase thermal correction to the free energy (ΔG_{corr}) obtained at the ωB97XD/basis1 level has been averaged for the dithiocatecholate and the dichlorodithiocatecholate ($\Delta G_{corr,avg}$, Tables

(77) For a recent review on the application of DFT to complexes containing transition metals, see: Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757.
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(79) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.
(80) For selected references applying dispersion correction in DFT calculations of OM processes promoted by ruthenium carbenes, see: (a) Zhao, Y.; Truhlar, D. G. *Org. Lett.* **2007**, *9*, 1967. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157. (c) Torker, S.; Merki, D.; Chen. P. *J. Am. Chem. Soc.* **2008**, *130*, 4808. (d) Minenkov, Y.; Occhipinti, G.; Heyndrickx, W.; Jensen, V. R. *Eur. J. Inorg. Chem.* **2012**, 1507. (e) Minenkov, Y.; Occhipinti, G.; Jensen, V. R. *Organometallics* **2013**, *32*, 2099−2111. (f) Urbina-Blanco, C. A.; Poater, A.; Lebl, T.; Manzini, S.; Slawin, A. M. Z.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2013**, *135*, 7073−7079.
(81) (a) Urbina-Blanco, C. A.; Poater, A.; Lebl, T.; Manzini, S.; Slawin, A. M. Z.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2013**, *135*, 7073−7079. (b) Martin, R. L.; Hay, P. J.; Pratt, L. R. *J. Phys. Chem. A* **1998**, *102*, 3565−3573.
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S1–S2 and Figure S2). The electronic and free energy surfaces (Figures S1, S3, S4) and tables of energies (Tables S1–S2) are given below. For geometries and energies of computed structures in gas-phase, refer to supplementary information in reference 40.

Analysis of the potential energy and free energy surfaces as a function of basis set and solvation

In order to gain a more detailed understanding of the significantly better performance of the dichloro-dithiolate complex **Ru-9** vs the unsubstituted parent version **Ru-7**, we compared the energy barriers for degenerate OM of propene and *cis*-butene to the corresponding barriers for a plausible decomposition pathway, i.e. a 1,2-shift of the sulfur anion (which is trans to the NHC) to the electrophilic ethylidene (cf. Figures S1–S4).

Treatment of thermal correction to the Gibbs free energy

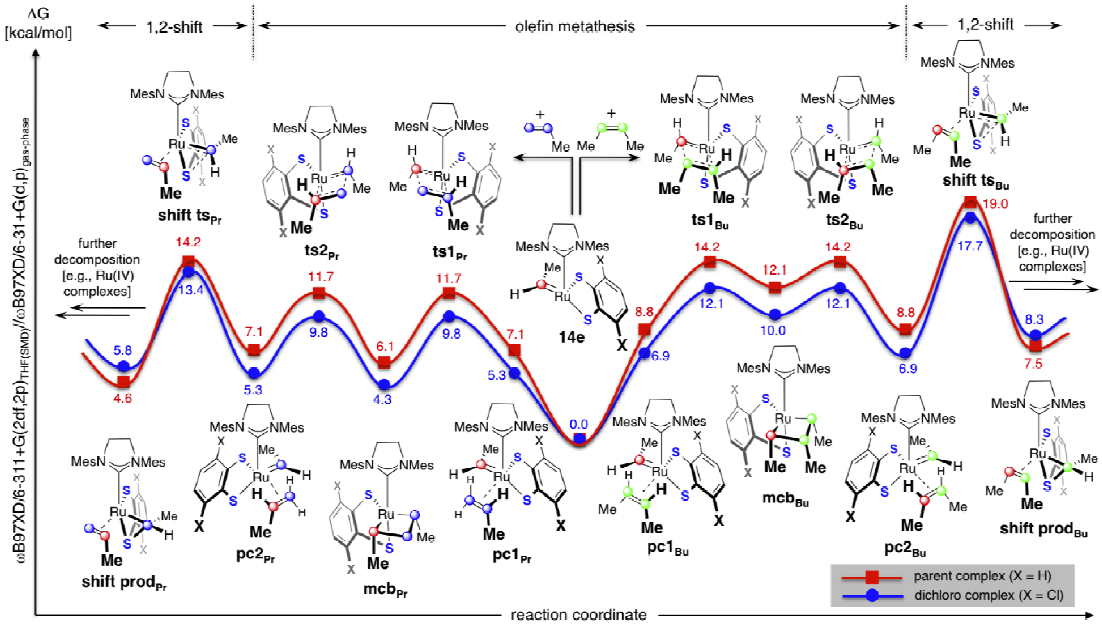
Based on comparison of various electronic and free energy surfaces we have identified a systematic pattern for the thermal correction to the Gibbs free energy ($\Delta G_{corr,avg}$) and decided to apply an average value for **Ru-7** and **Ru-9** (Figure S2). *Note that not all of the investigated pathways are presented in this Supporting Information [which furthermore include metallacyclobutane intermediates with a different degree of methyl substitution (i.e. either unsubstituted or symmetrically and unsymmetrically substituted mono-, di-, and trisubstituted variants)]*. On average, we observed an increase in $\Delta G_{corr,avg}$ from either **pc1** → **mcb** or **pc2** → **shift prod**, a trend that one would expect on the basis of increased rigidity, with the π-complexes **pc** being most flexible (Figure S2). Furthermore we hypothesize that such a trend should not be significantly different between complexes **Ru-7** and **Ru-9** and should argue for the validity of this approach. Such treatment eliminates errors in the relative ΔG values, which exhibit a far less systematic pattern than the corresponding ΔE surfaces (cf. Figure S1).

Detailed Discussion of Computational Investigations

As previously observed with the current model of theory (ωB97XD/basis2$_{THF(PCM/SMD)}$//ωB97XD/basis1$_{gas\text{-}phase}$), changing the solvation model from PCM to SMD results in a ~3 kcal/mol increase in energies for assemblies (**pc1** → **shift prod**) relative to the unbound state (**14e** + olefin, cf. Figures S3–4).[23] Below, the following processes are investigated in detail at the ωB97XD/basis2$_{THF(SMD)}$//ωB97XD/basis1$_{gas\text{-}phase}$ level of theory (Scheme S1 = Figure S4): nonproductive OM involving propene (Pr) and *Z*-2-butene (Bu), and competitive decomposition entailing 1,2-shift of the more electron rich trans-to-NHC sulfide ligand to the electrophilic ethylidene. The turnover-limiting barrier (**ts1$_{Pr,Cl}$**) for the OM reaction of the electronically altered complex with propene (**14e$_{Cl}$** → **pc2$_{Pr,Cl}$**; Scheme S1, left segment) was calculated to be 1.9 kcal/mol lower in energy compared to **ts1$_{Pr,H}$** (11.7 vs. 9.8 kcal/mol; blue vs. red curve in Scheme S1); this finding points to

increased Lewis acidity of the Ru center in halogenated species **14e$_{Cl}$** and a less endergonic olefin coordination (5.3 vs. 7.1 kcal/mol for **pc1$_{Pr,Cl}$** vs. **pc1$_{Pr,H}$**). Additionally, the more stabilized metallacyclobutane derived from the dichlorocatechothiolate species hints at a weakened trans influence between the NHC and the sulfur of the less electron-rich derivative (4.3 vs. 6.1 kcal/mol for **mcb$_{Pr,Cl}$** vs. **mcb$_{Pr,H}$**). There is a similar trend for the transformation with *Z*-2-butene (Scheme S1, right segment), although the additional methyl group disfavors substrate association by ~2–3 kcal/mol. Equally noteworthy is that, whereas a 1,2-shift within the modified complex (i.e., **pc2$_{Pr,Cl}$** → **shift prod$_{Pr,Cl}$**) is endergonic by 0.5 kcal/mol, the same process in the parent system (i.e., **pc2$_{Pr,H}$** → **shift prod$_{Pr,H}$**) is appreciably exergonic (–2.5 kcal/mol). We attribute the latter energetic discrepancy to the alleviation of a stronger trans influence between the Lewis basic NHC and non-chlorinated sulfide ligands upon cleavage of the Ru–S bond, hence affording complexes **shift prod$_{Pr/Bu}$** that can further react through as yet unidentified pathways. *[Note that we find higher barriers for **shift ts$_{Pr}$** when the bound propene adopts the orientation in **pc2$_{Pr}$** (structure of this alternative **shift ts$_{Pr}$** not shown) (Figure S4). A more detailed investigation regarding the above-mentioned decomposition pathways leading to a 1,2-shift in presence of a bound (π-acidic) olefin is presented below.]*

Scheme S1. Examination of the energetics of OM vs. sulfide shift by DFT calculations



When comparing barriers **ts1$_{Bu}$/ts2$_{Bu}$** for OM involving *Z*-2-butene (which is directly relevant to OM of oleic acid described in the current report) and the 1,2-shift induced by propene (**shift ts$_{Pr}$**), a more favorable partitioning is predicted in case of the dichlorodithiolate complex (12.1 vs 13.4 kcal/mol for **ts1$_{Bu,Cl}$** and **shift ts$_{Pr,Cl}$**,

respectively). In contrast, both processes are predicted to be equally likely when catalyst **Ru-7** is involved (14.2 kcal/mol for $\mathbf{ts1_{Bu,H}}$ and **shift** $\mathbf{ts_{Pr,H}}$, respectively), which rationalizes its poorer performance compared to **Ru-9**.

Error assessment of energy surfaces

Since the energy surfaces are referenced to the 14e-complexes (0.0 kcal/mol), the difference in barrier for non-productive OM of propene between **Ru-9** and **Ru-7** (= difference between $\mathbf{ts1_{Pr,Cl}}$ and $\mathbf{ts1_{Pr,H}}$ = 1.9 kcal/mol) is dependent on the accurate determination of the reference points ($\mathbf{14e_{Cl}}$ and $\mathbf{14e_H}$). In other words, an error in the energies of $\mathbf{14e_{Cl}}$ and $\mathbf{14e_H}$ will result in addition or subtraction of a constant term X to/from the blue (vs red) curve in Figure S4 (bottom). In contrast, the difference in exo-/endothermicity of the $\mathbf{pc2_{Pr,H}} \rightarrow$ **shift** $\mathbf{prod_{Pr,H}}$ (–2.5 kcal/mol) vs $\mathbf{pc2_{Pr,Cl}} \rightarrow$ **shift** $\mathbf{prod_{Pr,Cl}}$ (+0.5 kcal/mol) transformation, which amounts to –3.0 kcal/mol (= –2.5 – 0.5 kcal/mol), is independent of term X (due to cancellation of X). Similarly, the difference in exo-/endothermicity between $\mathbf{pc2_{Bu,H}} \rightarrow$ **shift** $\mathbf{prod_{Bu,H}}$ (–1.3 kcal/mol) vs $\mathbf{pc2_{Bu,Cl}} \rightarrow$ **shift** $\mathbf{prod_{Bu,Cl}}$ (+1.4 kcal/mol) is –2.7 kcal/mol. Furthermore, such a systematic trend appears in all other above-mentioned pathways, which are not included in the Supporting Information. Based on this analysis it can be concluded with some confidence that the larger driving force for formation of **shift** $\mathbf{prod_{Pr,H}}$ from $\mathbf{pc2_{Pr,H}}$ is real and can most likely be attributed to the release of trans influence between the sulfur anion and the NHC. Furthermore, in agreement with the Hammond postulate, the difference in barrier heights between $\mathbf{pc2_{Pr,H}} \rightarrow$ **shift** $\mathbf{ts_{Pr,H}}$ (+7.1 kcal/mol) vs $\mathbf{pc2_{Pr,Cl}} \rightarrow$ **shift** $\mathbf{ts_{Pr,Cl}}$ (+8.1 kcal/mol) is only –1.0 kcal/mol (= 7.1 – 8.1 kcal/mol), most likely due to partial reduction of unfavorable trans influence in the transition state.

Facility of the 1,2-shift as a function of the bound ligand

In addition to the processes described above, we have investigated the nature of the 1,2-shift in greater detail and observed a significant dependence on the type of the bound ligand (see Tables S3–S4 and Figures S5–S8). The 5 different investigated cases include a unimolecular process (**14e → shift prod**) as well as bimolecular variants with a π-donor (THF, $\mathbf{14e_{THF}} \rightarrow$ **shift** $\mathbf{prod_{THF}}$) and π-acidic olefins of different size (L = ethylene (Et), propene (Pr) and *Z*-2-butene (Bu); $\mathbf{pc_L} \rightarrow$ **shift** $\mathbf{prod_L}$). As expected, the increase in basis set (basis1 → basis2) and the inclusion of solvation (PCM or SMD model) leads to destabilization of the bimolecular processes relative to the unimolecular scenario (e.g. the free energy of **shift** $\mathbf{ts_{Et,H}}$ increases from 1.8 to 8.7 to 10.1 kcal/mol in Figures S5, S7 and S8 relative to reference point **14e**). Nonetheless, during this progression the unimolecular decomposition via 1,2-shift (**shift** $\mathbf{ts_H}$) does not become competitive (18.0, 18.2 and 17.0 kcal/mol, respectively). Furthermore, comparison of the 1,2-shift in presence of a bound

THF molecule (**14e$_{THF}$ → shift prod$_{THF}$**) with the series of olefin induced rearrangements strongly suggests that the 1,2-shift might be catalyzed by π-acceptors (compare free energy barriers of 19.2 and 10.1 kcal/mol for **shift ts$_{THF}$** and **shift ts$_{Et,H}$** in Figure S8). In agreement with this hypothesis is the increase in barrier upon the concomitant decrease in π-acceptor ability during transition from ethylene → propene → *cis*-butene (10.1, 14.2 and 19.0 kcal/mol for **shift ts$_{Et,H}$**, **shift ts$_{Pr,H}$** and **shift ts$_{Bu,H}$**). Such an effect has been described in decomposition of Ru carbenes in presence of π-acceptors like CO, likely leading to an increase in electrophilicity of the carbene p-orbital.[85] Finally we conclude, that regardless of the nature of these 5 different pathways the 1,2-shift is either less endergonic or more exergonic in case of the more electron rich dithiolate in **Ru-7** vs **Ru-9**, supporting the better performance of the latter (X = H; e.g. −4.6 kcal/mol for **pc$_{Et,H}$ → shift prod$_{Et,H}$** vs −1.8 kcal/mol for **pc$_{Et,Cl}$ → shift prod$_{Et,Cl}$** in Figure S8).

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Comparison of 1,2-shift vs Olefin Metathesis (Tables of energies)

Table of energies and free energies after geometry optimizations with B97XD/basis 1

Table S1. Energies and free energies (298.15 K, 24 atm) for the surfaces shown in Figure S1 at the ωB97XD/basis1$_{\text{gas phase}}$ level of theory.

	E [hartree]	ΔE [kcal/mol]	G [hartree]	ΔG [kcal/mol]	ΔG_{corr} [kcal/mol]	$\Delta G_{corr,avg}$ [kcal/mol]	FREQ
shift							
prod$_{Pr,H}$	-2322.52721449	-26.1	-2321.904913	-7.0	19.1	18.5	16.19
shift	-		-				-
ts$_{Pr,H}$	**2322.50563358**	**-12.6**	**2321.886580**	**4.5**	**17.1**	**17.1**	**208.66**
pc2$_{Pr,H}$	-2322.51757632	-20.1	-2321.900145	-4.0	16.1	16.8	21.95
ts2$_{Pr,H}$	-		-				-
	2322.50818664	**-14.2**	**2321.889535**	**2.7**	**16.8**	**16.4**	**144.54**
mcb$_{Pr,H}$	-2322.51838401	-20.6	-2321.898244	-2.8	17.8	17.1	18.99
ts1$_{Pr,H}$	-		-				-
	2322.50818662	**-14.2**	**2321.889535**	**2.7**	**16.8**	**16.4**	**144.54**
pc1$_{Pr,H}$	-2322.51757628	-20.1	-2321.900147	-4.0	16.1	16.8	21.95
14e	-2322.48559715	0.0	-2321.893774	0.0	0.0	0.0	16.76
pc1$_{Bu,H}$	-2322.51585314	-19.0	-2321.896393	-1.6	17.3	17.1	18.50
ts1$_{Bu,H}$	-		-				-
	2322.50662065	**-13.2**	**2321.886475**	**4.6**	**17.8**	**17.0**	**126.95**
mcb$_{Bu,H}$	-2322.51438221	-18.1	-2321.889804	2.5	20.6	19.5	-6.58
ts2$_{Bu,H}$	-		-				-
	2322.50662067	**-13.2**	**2321.886474**	**4.6**	**17.8**	**17.0**	**126.95**
pc2$_{Bu,H}$	-2322.51585314	-19.0	-2321.896393	-1.6	17.3	17.1	18.50
shift	-		-				-
ts$_{Bu,H}$	**2322.50136856**	**-9.9**	**2321.879247**	**9.1**	**19.0**	**19.2**	**201.04**
shift							
prod$_{Bu,H}$	-2322.52494349	-24.7	-2321.900637	-4.3	20.4	19.4	24.51
shift							
prod$_{Pr,Cl}$	-3241.67794441	-23.1	-3241.080678	-5.2	17.9	18.5	16.79
shift	-		-				-
ts$_{Pr,Cl}$	**3241.66016208**	**-12.0**	**3241.064185**	**5.2**	**17.1**	**17.1**	**215.79**
pc2$_{Pr,Cl}$	-3241.67305486	-20.0	-3241.076281	-2.4	17.6	16.8	19.11
ts2$_{Pr,Cl}$	-		-				-
	3241.66393738	**-14.3**	**3241.069814**	**1.6**	**16.0**	**16.4**	**147.60**
mcb$_{Pr,Cl}$	-3241.67410626	-20.7	-3241.079138	-4.2	16.5	17.1	14.12
ts1$_{Pr,Cl}$	-		-				-
	3241.66393740	**-14.3**	**3241.069817**	**1.6**	**16.0**	**16.4**	**147.58**
pc1$_{Pr,Cl}$	-3241.67305486	-20.0	-3241.076281	-2.4	17.6	16.8	19.11
14e	-3241.64110754	0.0	-3241.072426	0.0	0.0	0.0	5.07
pc1$_{Bu,Cl}$	-3241.67166412	-19.2	-3241.076030	-2.3	16.9	17.1	14.92
ts1$_{Bu,Cl}$	-		-				-
	3241.66271565	**-13.6**	**3241.068056**	**2.7**	**16.3**	**17.0**	**127.87**
mcb$_{Bu,Cl}$	-3241.67043755	-18.4	-3241.072351	0.0	18.5	19.5	15.87
ts2$_{Bu,Cl}$	-		-				-
	3241.66271566	**-13.6**	**3241.068055**	**2.7**	**16.3**	**17.0**	**127.88**
pc2$_{Bu,Cl}$	-3241.67166412	-19.2	-3241.076030	-2.3	16.9	17.1	14.92
shift	-		-				-
ts$_{Bu,Cl}$	**3241.65639947**	**-9.6**	**3241.056921**	**9.7**	**19.3**	**19.2**	**233.03**
shift							
prod$_{Bu,Cl}$	-3241.67568891	-21.7	-3241.077809	-3.4	18.3	19.4	15.89

E …….... gas phase electronic energy in hartree
G ……. sum of electronic and thermal free energies in hartree at 298.15 K and 24 atm
ΔE …….. relative electronic energy in kcal/mol
ΔG …….. relative free energy in kcal/mol
ΔG_{corr} ….. relative gas phase thermal correction to free energy in kcal/mol ($\Delta G = \Delta E + \Delta G_{corr}$)
$\Delta G_{corr,avg}$ .. average relative gas phase thermal correction to free energy in kcal/mol {e.g.: $\Delta G_{corr,avg} = [\Delta G_{corr}(ts2_{Pr,H}) + \Delta G_{corr}(ts2_{Pr,Cl})] *1/2$}
FREQ …. lowest frequency of stationary point

Tables of energies after single point energy calculations with B97XD/basis2 in THF (PCM, SMD)

Table S2. Energies and free energies for the surfaces shown in Figures S3–S4 at the ωB97XD/basis2$_{THF(PCM/SMD)}$//
ωB97XD/basis1$_{gas\ phase}$ levels of theory.

	ωB97XD/basis2$_{THF(PCM)}$//ωB97XD/basis1$_{gas\text{-}phase}$			**ωB97XD/basis2$_{THF(SMD)}$//ωB97XD/basis1$_{gas\ phase}$**		
	E_{sp} [hartree]	**ΔE_{sp} [kcal/mol]**	**ΔG_{sp} [kcal/mol]**	**E_{sp} [hartree]**	**ΔE_{sp} [kcal/mol]**	**ΔG_{sp} [kcal/mol]**
shift prod$_{Pr,H}$	-2322.98386246	-16.9	1.6	-2323.00822805	-13.9	4.6
shift ts$_{Pr,H}$	**-2322.96510207**	**-5.2**	**11.9**	**-2322.99064800**	**-2.9**	**14.2**
pc2$_{Pr,H}$	-2322.97723004	-12.8	4.1	-2323.00149867	-9.7	7.1
ts2$_{Pr,H}$	**-2322.96875477**	**-7.5**	**8.9**	**-2322.99351234**	**-4.7**	**11.7**
mcb$_{Pr,H}$	-2322.97835644	-13.5	3.6	-2323.00355031	-11.0	6.1
ts1$_{Pr,H}$	**-2322.96875481**	**-7.5**	**8.9**	**-2322.99351238**	**-4.7**	**11.7**
pc1$_{Pr,H}$	-2322.97723002	-12.8	4.1	-2323.00149859	-9.7	7.1
14e	-2322.95686041	0.0	0.0	-2322.98600811	0.0	0.0
pc1$_{Bu,H}$	-2322.97568702	-11.8	5.3	-2322.99932259	-8.4	8.8
ts1$_{Bu,H}$	**-2322.96666894**	**-6.2**	**10.9**	**-2322.99057008**	**-2.9**	**14.2**
mcb$_{Bu,H}$	-2322.97417457	-10.9	8.6	-2322.99775577	-7.4	12.1
ts2$_{Bu,H}$	**-2322.96666899**	**-6.2**	**10.9**	**-2322.99057013**	**-2.9**	**14.2**
pc2$_{Bu,H}$	-2322.97568702	-11.8	5.3	-2322.99932259	-8.4	8.8
shift ts$_{Bu,H}$	**-2322.96156189**	**-3.0**	**16.2**	**-2322.98631629**	**-0.2**	**19.0**
shift prod$_{Bu,H}$	-2322.98164908	-15.6	3.8	-2323.00495284	-11.9	7.5

shift prod$_{Pr,Cl}$	-3242.20465414	-15.0	3.5	-3242.23013568	-12.7	5.8
shift ts$_{Pr,Cl}$	**-3242.18958209**	**-5.5**	**11.6**	**-3242.21580980**	**-3.7**	**13.4**
pc2$_{Pr,Cl}$	-3242.20297337	-14.0	2.9	-3242.22830626	-11.6	5.3
ts2$_{Pr,Cl}$	**-3242.19449419**	**-8.6**	**7.8**	**-3242.22035846**	**-6.6**	**9.8**
mcb$_{Pr,Cl}$	-3242.20404315	-14.6	2.5	-3242.23024980	-12.8	4.3
ts1$_{Pr,Cl}$	**-3242.19449384**	**-8.6**	**7.8**	**-3242.22035846**	**-6.6**	**9.8**
pc1$_{Pr,Cl}$	-3242.20297337	-14.0	2.9	-3242.22830626	-11.6	5.3
14e	-3242.18074205	0.0	0.0	-3242.20987796	0.0	0.0
pc1$_{Bu,Cl}$	-3242.20167166	-13.1	4.0	-3242.22618526	-10.2	6.9
ts1$_{Bu,Cl}$	**-3242.19310179**	**-7.8**	**9.3**	**-3242.21779310**	**-5.0**	**12.1**
mcb$_{Bu,Cl}$	-3242.20011373	-12.2	7.3	-3242.22507506	-9.5	10.0
ts2$_{Bu,Cl}$	**-3242.19310167**	**-7.8**	**9.3**	**-3242.21779293**	**-5.0**	**12.1**
pc2$_{Bu,Cl}$	-3242.20167166	-13.1	4.0	-3242.22618526	-10.2	6.9
shift ts$_{Bu,Cl}$	**-3242.18638261**	**-3.5**	**15.6**	**-3242.21215394**	**-1.4**	**17.7**
shift prod$_{Bu,Cl}$	-3242.20271852	-13.8	5.6	-3242.22748382	-11.0	8.3

E_{sp} …….. single point electronic energy in THF in hartree
ΔE_{sp} …… relative single point electronic energy in THF in kcal/mol
ΔG_{sp} …… relative free energy in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}$/basis2 + $\Delta G_{corr,avg}$/basis1)

Comparison of 1,2-shift as a function of the bound ligand (Tables of energies)

Table of energies and free energies after geometry optimizations with B97XD/basis 1

Table S3. Energies and free energies (298.15 K, 24 atm) for various 1,2-shifts shown in Figure S5 at the ωB97XD/basis1$_{\text{gas phase}}$ level of theory.

	E [hartree]	ΔE [kcal/mol]	G [hartree]	ΔG [kcal/mol]	ΔG_{corr} [kcal/mol]	$\Delta G_{corr,avg}$ [kcal/mol]	FREQ
14e$_H$	-2322.48559715	0.0	-2321.893774	0.0	0.0	0.0	16.76
shift ts$_H$	- **2322.45786297**	**17.4**	- **2321.865019**	**18.0**	**0.6**	**1.0**	**-273.32**
shift prod$_H$	-2322.46847417	10.7	-2321.876098	11.1	0.3	1.0	12.18
14e$_{THF,H}$	-2322.51457899	-18.2	-2321.897705	-2.5	15.7	16.4	18.15
shift ts$_{THF,H}$	- **2322.49422250**	**-5.4**	- **2321.877368**	**10.3**	**15.7**	**15.8**	**-276.75**
shift prod$_{THF,H}$	-2322.50784611	-14.0	-2321.890276	2.2	16.2	16.5	23.09
pc$_{Et,H}$	-2322.52001742	-21.6	-2321.901902	-5.1	16.5	16.1	23.63
shift ts$_{Et,H}$	- **2322.50869686**	**-14.5**	- **2321.890955**	**1.8**	**16.3**	**16.2**	**-213.95**
shift prod$_{Et,H}$	-2322.53179170	-29.0	-2321.910739	-10.6	18.3	17.7	25.51
pc$_{Pr,H}$	-2322.51757632	-20.1	-2321.900145	-4.0	16.1	16.8	21.95
shift ts$_{Pr,H}$	- **2322.50563358**	**-12.6**	- **2321.886580**	**4.5**	**17.1**	**17.1**	**-208.66**
shift prod$_{Pr,H}$	-2322.52721449	-26.1	-2321.904913	-7.0	19.1	18.5	16.19
pc$_{Bu,H}$	-2322.51585314	-19.0	-2321.896393	-1.6	17.3	17.1	18.50
shift ts$_{Bu,H}$	- **2322.50136856**	**-9.9**	- **2321.879247**	**9.1**	**19.0**	**19.2**	**-201.04**
shift prod$_{Bu,H}$	-2322.52494349	-24.7	-2321.900637	-4.3	20.4	19.4	24.51
14e$_{Cl}$	-3241.64110754	0.0	-3241.072426	0.0	0.0	0.0	5.07
shift ts$_{Cl}$	- **3241.61140101**	**18.6**	- **3241.040592**	**20.0**	**1.3**	**1.0**	**-295.61**
shift prod$_{Cl}$	-3241.61983765	13.3	-3241.048605	14.9	1.6	1.0	16.09
14e$_{THF,C}$	-3241.67236873	-19.6	-3241.076598	-2.6	17.0	16.4	16.24
shift ts$_{THF,Cl}$	- **3241.64850915**	**-4.6**	- **3241.054351**	**11.3**	**16.0**	**15.8**	**-285.00**
shift prod$_{THF,Cl}$	-3241.65973152	-11.7	-3241.064249	5.1	16.8	16.5	19.91
pc$_{Et,Cl}$	-3241.67495822	-21.2	-3241.081337	-5.6	15.6	16.1	18.73
shift ts$_{Et,Cl}$	- **3241.66300087**	**-13.7**	- **3241.068454**	**2.5**	**16.2**	**16.2**	**-250.45**

shift prod$_{Et,Cl}$	-3241.68242207	-25.9	-3241.086450	-8.8	17.1	17.7	17.67
pc$_{Pr,Cl}$	-3241.67305486	-20.0	-3241.076281	-2.4	17.6	16.8	19.11
shift ts$_{Pr,Cl}$	**-3241.66016208**	**-12.0**	**-3241.064185**	**5.2**	**17.1**	**17.1**	**-215.79**
shift prod$_{Pr,Cl}$	-3241.67794441	-23.1	-3241.080678	-5.2	17.9	18.5	16.79
pc$_{Bu,Cl}$	-3241.67166412	-19.2	-3241.076030	-2.3	16.9	17.1	14.92
shift ts$_{Bu,Cl}$	**-3241.65639947**	**-9.6**	**-3241.056921**	**9.7**	**19.3**	**19.2**	**-233.03**
shift prod$_{Bu,Cl}$	-3241.67568891	-21.7	-3241.077809	-3.4	18.3	19.4	15.89

E …….... gas phase electronic energy in hartree
G ……. sum of electronic and thermal free energies in hartree at 298.15 K and 24 atm
ΔE …….. relative electronic energy in kcal/mol
ΔG …….. relative free energy in kcal/mol
ΔG_{corr} ….. relative gas phase thermal correction to free energy in kcal/mol ($\Delta G = \Delta E + \Delta G_{corr}$)
$\Delta G_{corr,avg}$ .. average relative gas phase thermal correction to free energy in kcal/mol {e.g.: $\Delta G_{corr,avg} = [\Delta G_{corr}(14e_H) + \Delta G_{corr}(14e_{Cl})] *1/2$}
FREQ …. lowest frequency of stationary point

Tables of energies after single point energy calculations with B97XD/basis2 in THF (PCM, SMD)

Table S4. Energies and free energies for various 1,2-shifts shown in Figures S7–S8 at the ωB97XD/basis2$_{THF(PCM/SMD)}$//ωB97XD/basis1$_{gas\ phase}$ levels of theory.

	ωB97XD/basis2$_{THF(PCM)}$//ωB97XD/basis1$_{gas-phase}$			**ωB97XD/basis2$_{THF(SMD)}$//ωB97XD/basis1$_{gas\ phase}$**		
	E_{sp} [hartree]	**ΔE_{sp} [kcal/mol]**	**ΔG_{sp} [kcal/mol]**	**E_{sp} [hartree]**	**ΔE_{sp} [kcal/mol]**	**ΔG_{sp} [kcal/mol]**
14e$_H$	-2322.95686041	0.0	0.0	-2322.98600811	0.0	0.0
shift ts$_H$	**-2322.92946726**	**17.2**	**18.2**	**-2322.96053647**	**16.0**	**17.0**
shift prod$_H$	-2322.93716018	12.4	13.3	-2322.96887349	10.8	11.7
14e$_{THF,H}$	-2322.97808081	-13.3	3.0	-2323.00206548	-10.1	6.3
shift ts$_{THF,H}$	**-2322.95586327**	**0.6**	**16.5**	**-2322.98072130**	**3.3**	**19.2**
shift prod$_{THF,H}$	-2322.96805312	-7.0	9.5	-2322.99198747	-3.8	12.7
pc$_{Et,H}$	-2322.97966429	-14.3	1.8	-2323.00516434	-12.0	4.1
shift ts$_{Et,H}$	**-2322.96885800**	**-7.5**	**8.7**	**-2322.99580132**	**-6.1**	**10.1**
shift prod$_{Et,H}$	-2322.98880124	-20.0	-2.3	-2323.01511307	-18.3	-0.5
pc$_{Pr,H}$	-2322.97723004	-12.8	4.1	-2323.00149867	-9.7	7.1
shift ts$_{Pr,H}$	**-2322.96510207**	**-5.2**	**11.9**	**-2322.99064800**	**-2.9**	**14.2**
shift prod$_{Pr,H}$	-2322.98386246	-16.9	1.6	-2323.00822805	-13.9	4.6
pc$_{Bu,H}$	-2322.97568702	-11.8	5.3	-2322.99932259	-8.4	8.8
shift ts$_{Bu,H}$	**-2322.96156189**	**-3.0**	**16.2**	**-2322.98631629**	**-0.2**	**19.0**
shift prod$_{Bu,H}$	-2322.98164908	-15.6	3.8	-2323.00495284	-11.9	7.5
14e$_{Cl}$	-3242.18074205	0.0	0.0	-3242.20987796	0.0	0.0
shift ts$_{Cl}$	**-3242.15318129**	**17.3**	**18.3**	**-3242.18530122**	**15.4**	**16.4**
shift prod$_{Cl}$	-3242.15883527	13.7	14.7	-3242.19148211	11.5	12.5
14e$_{THF,C}$	-3242.20404885	-14.6	1.7	-3242.22874914	-11.8	4.5
shift ts$_{THF,Cl}$	**-3242.18017734**	**0.4**	**16.2**	**-3242.20619897**	**2.3**	**18.2**
shift prod$_{THF,Cl}$	-3242.19008995	-5.9	10.6	-3242.21550716	-3.5	13.0
pc$_{Et,Cl}$	-3242.20460343	-15.0	1.1	-3242.23123952	-13.4	2.7
shift ts$_{Et,Cl}$	**-3242.19266401**	**-7.5**	**8.8**	**-3242.22060887**	**-6.7**	**9.5**
shift prod$_{Et,Cl}$	-3242.20946131	-18.0	-0.3	-3242.23664500	-16.8	0.9

pc$_{Pr,Cl}$	-3242.20297337	-14.0	2.9	-3242.22830626	-11.6	5.3
shift ts$_{Pr,Cl}$	**-3242.18958209**	**-5.5**	**11.6**	**-3242.21580980**	**-3.7**	**13.4**
shift prod$_{Pr,Cl}$	-3242.20465414	-15.0	3.5	-3242.23013568	-12.7	5.8
pc$_{Bu,Cl}$	-3242.20167166	-13.1	4.0	-3242.22618526	-10.2	6.9
shift ts$_{Bu,Cl}$	**-3242.18638261**	**-3.5**	**15.6**	**-3242.21215394**	**-1.4**	**17.7**
shift prod$_{Bu,Cl}$	-3242.20271852	-13.8	5.6	-3242.22748382	-11.0	8.3

E_{sp} …….. single point electronic energy in THF in hartree
ΔE_{sp} …… relative single point electronic energy in THF in kcal/mol
ΔG_{sp} …… relative free energy in kcal/mol ($\Delta G_{sp} = \Delta E_{sp}$/basis2 + $\Delta G_{corr,avg}$/basis1)

Comparison of 1,2-shift vs Olefin Metathesis (energy surfaces)

Potential energy and free energy surfaces with B97XD/basis1

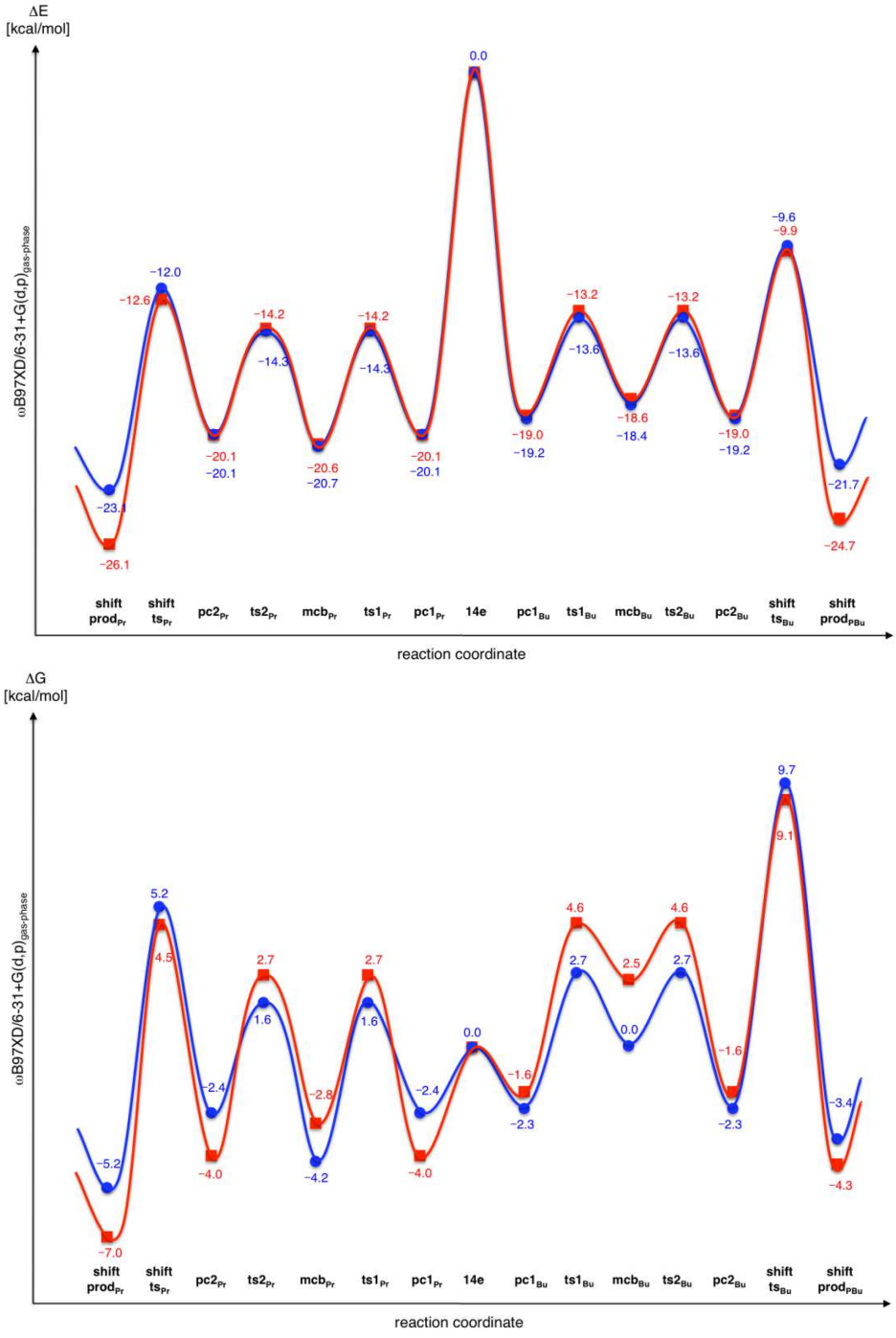

Figure S1. Potential energy surface (top) and free energy surface with ωB97XD/basis1; blue and red curves correspond to the dichlorodithiolate complex **Ru-9** or the unsubstituted variant **Ru-7**, respectively.

Relative thermal correction (G_{corr}) to the free energy with B97XD/basis1$_{gas-phase}$

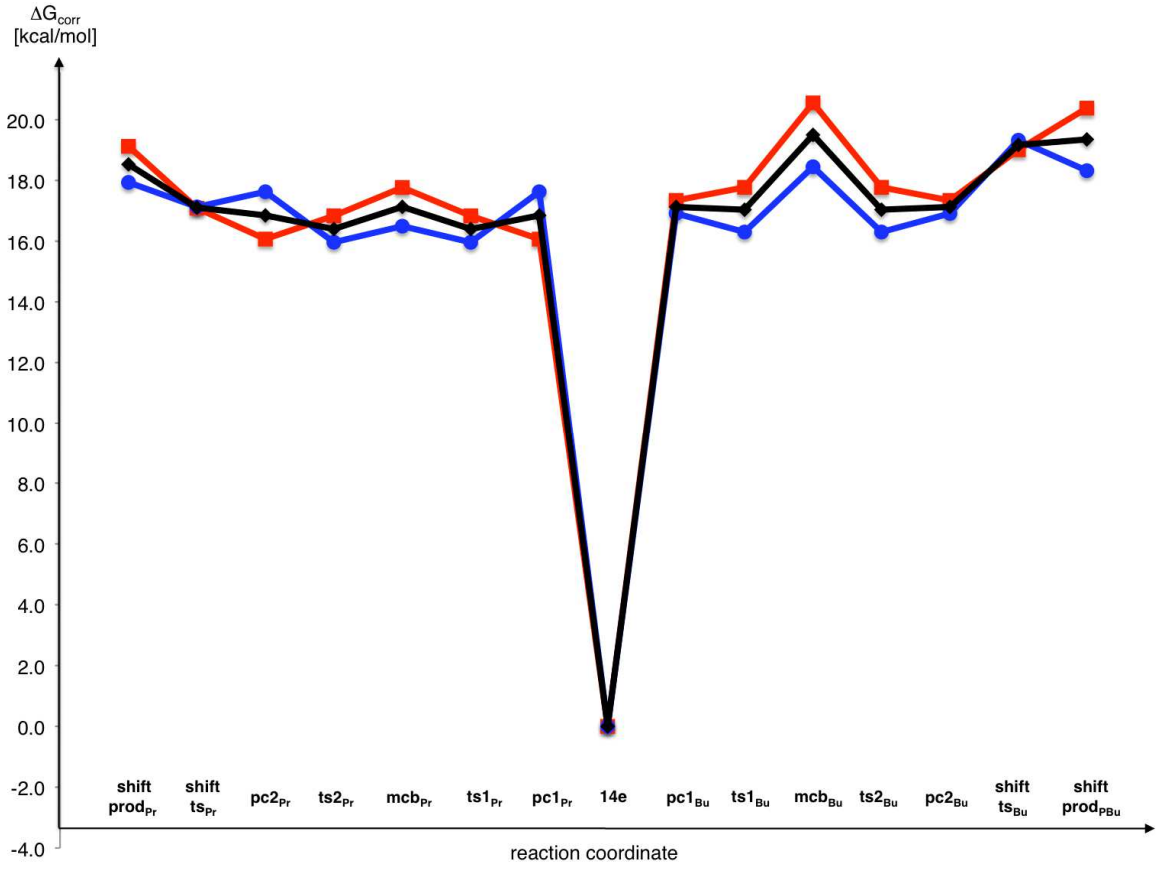

Figure S2. Relative thermal correction (ΔG_{corr}) to the free energy with ωB97XD/basis1 for dithiocatecholate (red), dichlorodithiocatecholate (blue) and the average value ($\Delta G_{corr,avg}$, black).

Potential energy and free energy surfaces with B97XD/basis2$_{THF(PCM)}$// B97XD/basis1$_{gas-phase}$

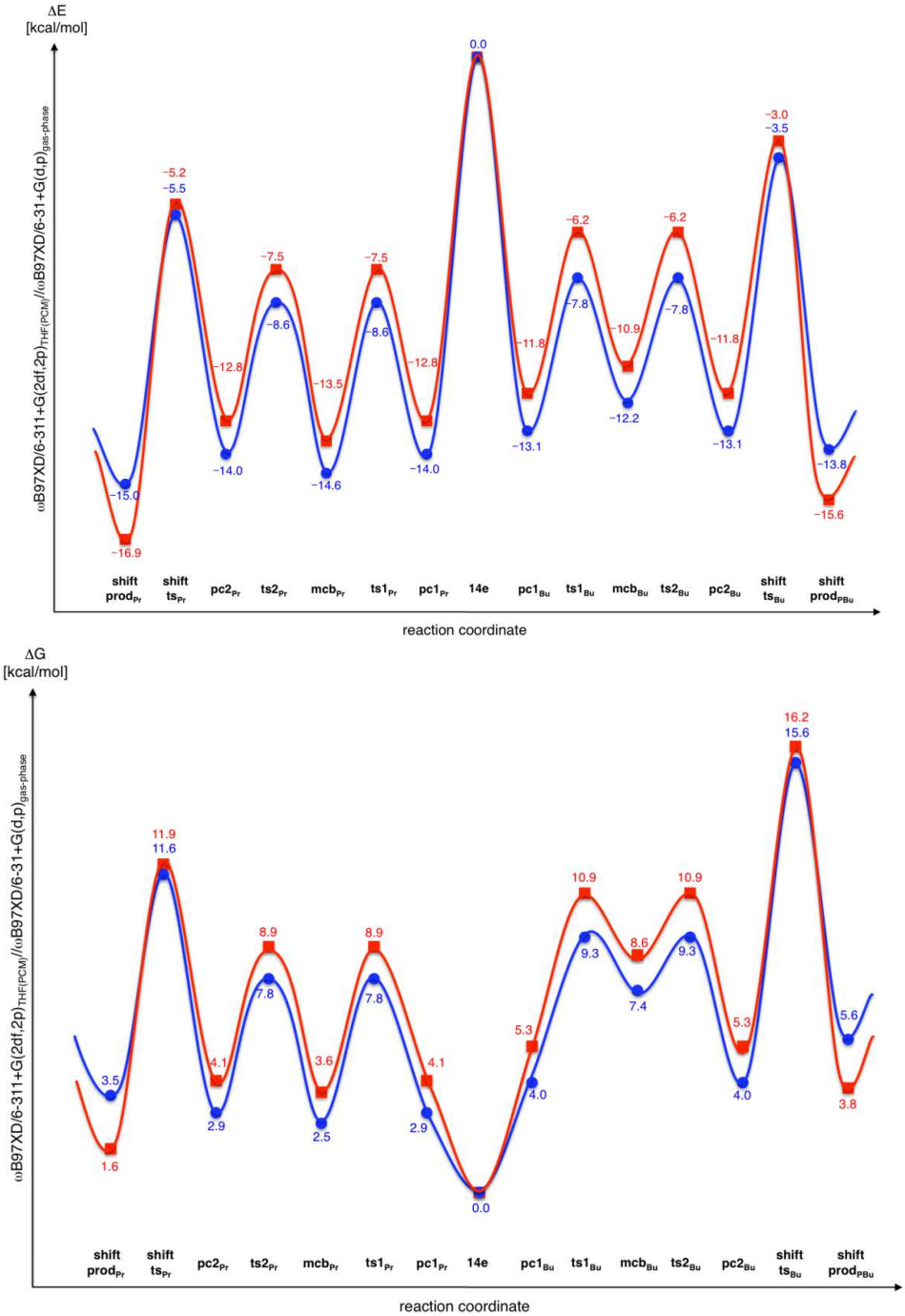

Figure S3. Potential energy surface (top) and free energy surface with ωB97XD/basis2$_{THF(PCM)}$//ωB97XD/basis1$_{gas-phase}$; blue and red curves correspond to the dichlorodithiolate complex **Ru-9** or the unsubstituted variant **Ru-7**, respectively.

Potential energy and free energy surfaces with B97XD/basis2$_{THF(SMD)}$// B97XD/basis1$_{gas-phase}$

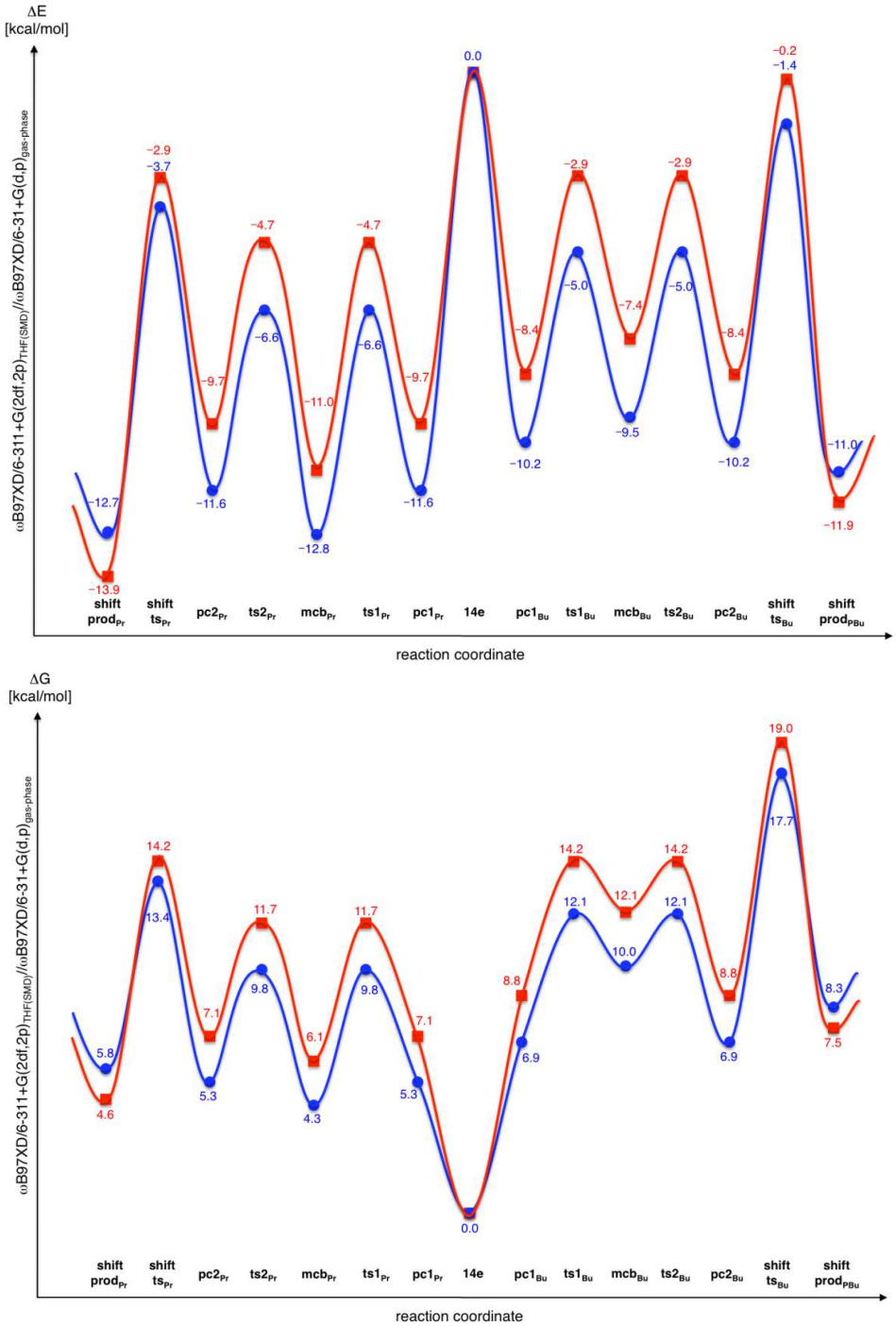

Figure S4. Potential energy surface (top) and free energy surface with ωB97XD/basis2$_{THF(SMD)}$//ωB97XD/basis1$_{gas-phase}$; blue and red curves correspond to the dichlorodithiolate complex **Ru-9** or the unsubstituted variant **Ru-7**, respectively.

Comparison of 1,2-shift as a function of the bound ligand (energy surfaces)

Potential energy and free energy surfaces with B97XD/basis1

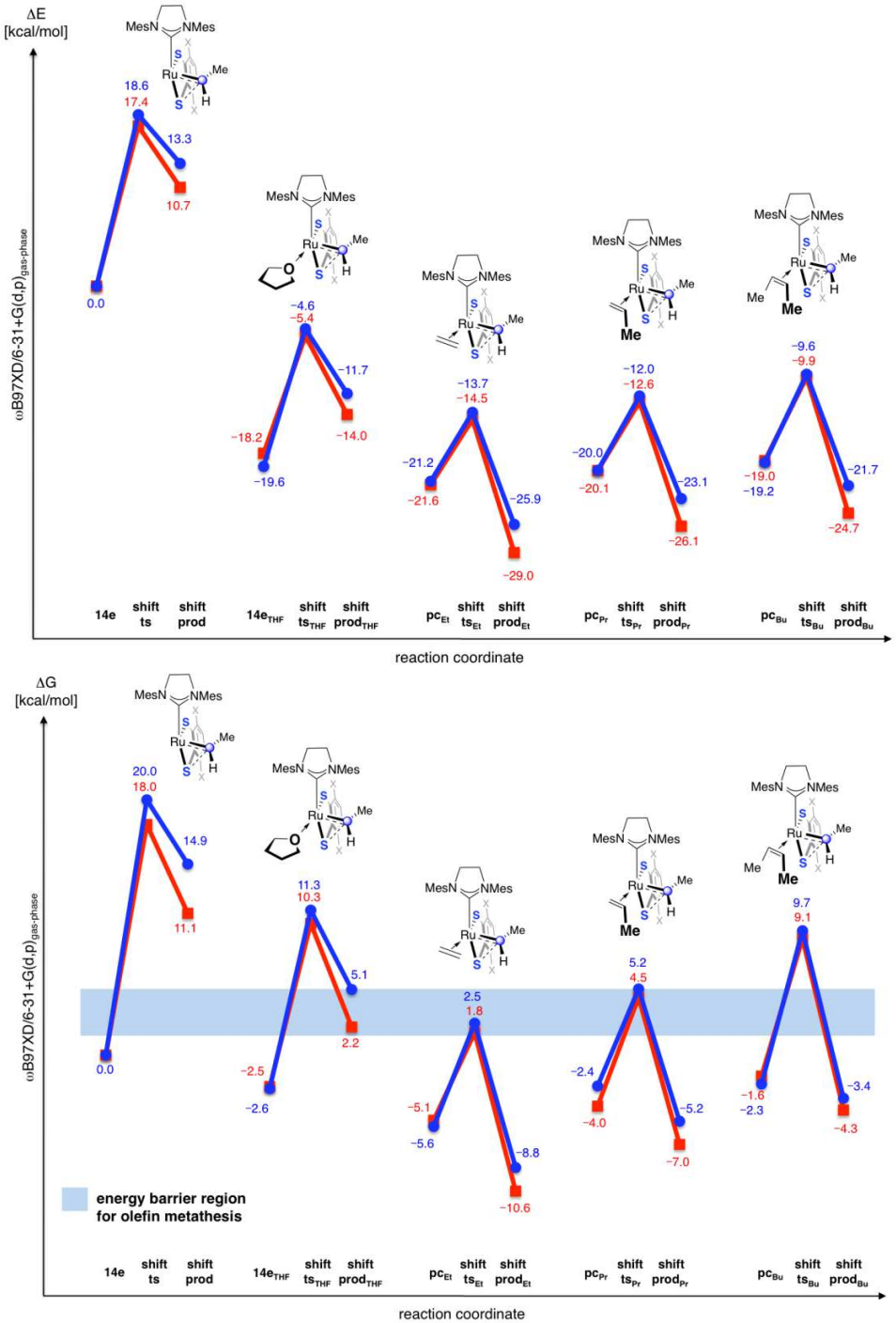

Figure S5. Potential energy surfaces (top) and free energy surfaces for various 1,2-shifts with ωB97XD/basis2$_{THF(SMD)}$//ωB97XD/basis1$_{gas\text{-}phase}$; blue and red curves correspond to the dichlorodithiolate complex **Ru-9** or the unsubstituted variant **Ru-7**, respectively.

Relative thermal correction (G_{corr}) to the free energy with B97XD/basis1$_{gas\text{-}phase}$

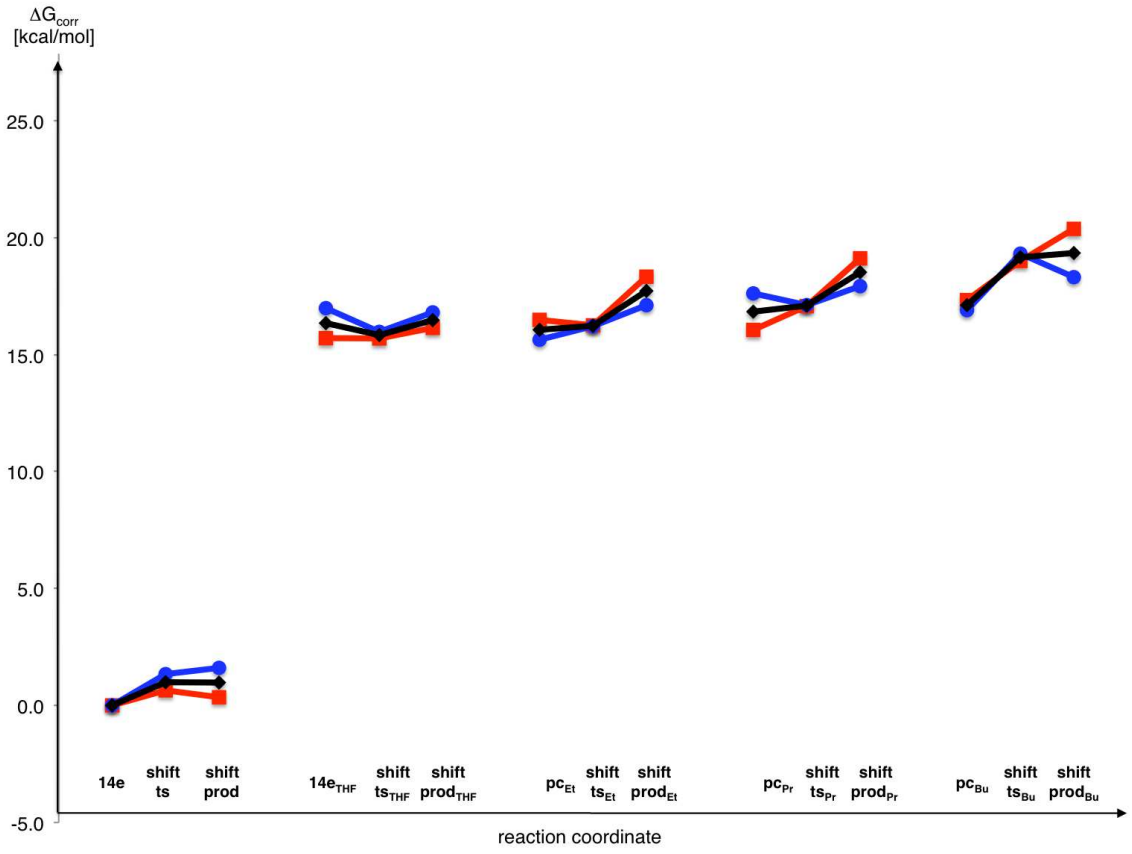

Figure S6. Relative thermal correction (ΔG_{corr}) to the free energy with ωB97XD/basis1 for dithiocatecholate (red), dichlorodithiocatecholate (blue) and the average value ($\Delta G_{corr,avg}$, black).

Potential energy and free energy surfaces with B97XD/basis2$_{THF(PCM)}$// B97XD/basis1$_{gas-phase}$

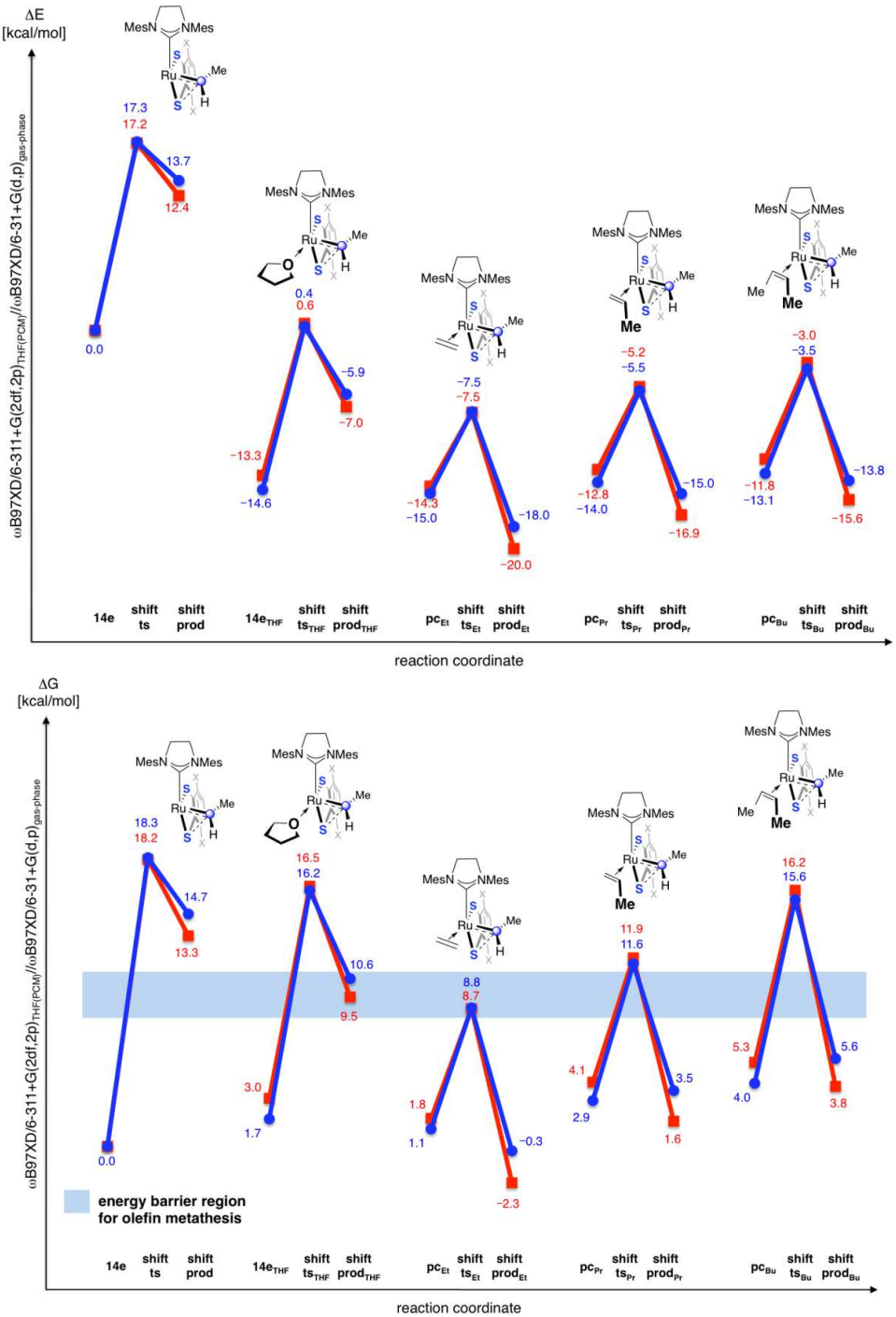

Figure S7. Potential energy surfaces (top) and free energy surfaces for various 1,2-shifts with ωB97XD/basis2$_{THF(PCM)}$//ωB97XD/basis1$_{gas-phase}$; blue and red curves correspond to the dichlorodithiolate complex **Ru-9** or the unsubstituted variant **Ru-7**, respectively.

Potential energy and free energy surfaces with B97XD/basis2$_{THF(SMD)}$// B97XD/basis1$_{gas-phase}$

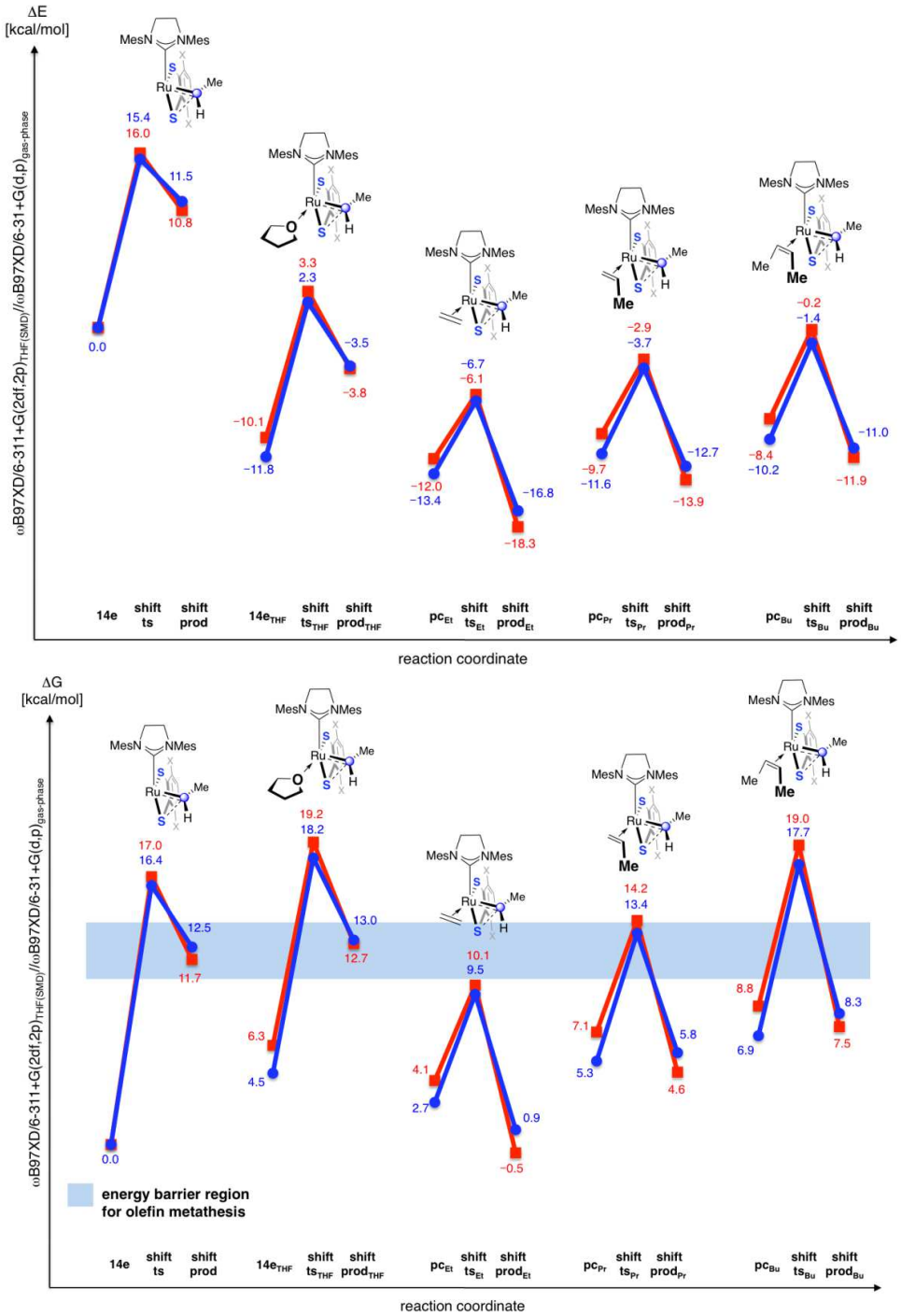

Figure S8. Potential energy surfaces (top) and free energy surfaces for various 1,2-shifts with ωB97XD/basis2$_{THF(SMD)}$//ωB97XD/basis1$_{gas-phase}$; blue and red curves correspond to the dichlorodithiolate complex **Ru-9** or the unsubstituted variant **Ru-7**, respectively.

1.6.11. X-ray Crystallographic Data

X-ray Crystal Structure for Ru-9

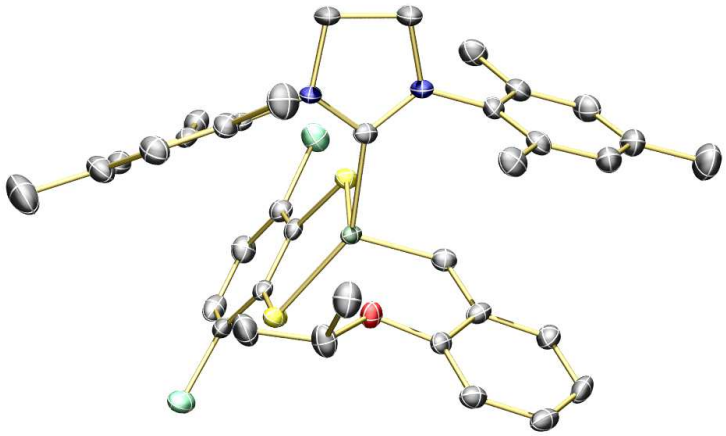

Table 1. **Crystal data and structure refinement for Ru-9**

Identification code	$C_{37}H_{40}Cl_2N_2ORuS_2(CH_2Cl_2)$	
Empirical formula	$C_{38}H_{42}Cl_4N_2ORuS_2$	
Formula weight	849.72	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 19.3211(8) Å	α= 90°.
	b = 17.4846(7) Å	β= 90°.
	c = 22.8338(8) Å	γ = 90°.
Volume	7713.8(5) $Å^3$	
Z	8	
Density (calculated)	1.463 Mg/m^3	
Absorption coefficient	0.825 mm^{-1}	
F(000)	3488	
Crystal size	0.200 x 0.100 x 0.080 mm^3	
Theta range for data collection	1.784 to 28.364°.	
Index ranges	-25<=h<=24, -23<=k<=23, -27<=l<=30	
Reflections collected	100010	
Independent reflections	9598 [R(int) = 0.1107]	
Completeness to theta = 25.242°	100.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.6187
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9598 / 0 / 441
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1060
R indices (all data)	R1 = 0.0922, wR2 = 0.1259
Extinction coefficient	na
Largest diff. peak and hole	1.166 and -0.999 e.$Å^{-3}$

Table 2. **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Ru-9. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	x	y	z	U(eq)
Ru(1)	1991(1)	9678(1)	3053(1)	16(1)
Cl(1)	658(1)	12215(1)	2281(1)	31(1)
Cl(2)	-329(1)	10112(1)	4309(1)	32(1)
S(1)	1058(1)	9697(1)	3658(1)	19(1)
S(2)	1560(1)	10755(1)	2609(1)	22(1)
O(1)	3018(1)	9899(1)	2555(1)	21(1)
N(1)	1667(2)	8035(2)	2740(1)	20(1)
N(2)	2085(2)	8075(2)	3622(1)	20(1)
C(1)	1956(2)	8500(2)	3144(2)	18(1)
C(2)	1505(2)	7269(2)	2973(2)	27(1)
C(3)	1935(2)	7251(2)	3529(2)	27(1)
C(4)	1506(2)	8221(2)	2144(2)	18(1)
C(5)	1922(2)	7899(2)	1701(2)	24(1)
C(6)	1749(2)	8055(2)	1120(2)	29(1)
C(7)	1183(2)	8506(2)	970(2)	29(1)
C(8)	783(2)	8793(2)	1414(2)	25(1)
C(9)	915(2)	8644(2)	2003(2)	19(1)
C(10)	2518(2)	7379(3)	1835(2)	35(1)
C(11)	997(3)	8653(3)	338(2)	49(1)
C(12)	394(2)	8894(2)	2451(2)	26(1)
C(13)	2481(2)	8294(2)	4126(2)	20(1)
C(14)	3205(2)	8332(2)	4069(2)	22(1)
C(15)	3590(2)	8526(2)	4561(2)	27(1)
C(16)	3278(2)	8673(2)	5100(2)	30(1)
C(17)	2566(2)	8616(2)	5140(2)	30(1)
C(18)	2155(2)	8421(2)	4659(2)	25(1)
C(19)	3562(2)	8165(2)	3499(2)	28(1)
C(20)	3715(3)	8884(3)	5625(2)	45(1)
C(21)	1382(2)	8359(2)	4734(2)	30(1)
C(22)	2580(2)	9917(2)	3654(2)	21(1)

C(23)	3284(2)	10142(2)	3529(2)	20(1)
C(24)	3746(2)	10367(2)	3966(2)	23(1)
C(25)	4414(2)	10581(2)	3832(2)	26(1)
C(26)	4630(2)	10568(2)	3254(2)	26(1)
C(27)	4187(2)	10347(2)	2809(2)	22(1)
C(28)	3517(2)	10132(2)	2948(2)	18(1)
C(29)	3214(2)	9835(2)	1928(2)	28(1)
C(30)	2573(2)	9908(3)	1570(2)	34(1)
C(31)	3601(2)	9095(2)	1835(2)	32(1)
C(32)	587(2)	10507(2)	3456(2)	18(1)
C(33)	-31(2)	10704(2)	3751(2)	23(1)
C(34)	-404(2)	11356(2)	3618(2)	28(1)
C(35)	-177(2)	11829(2)	3170(2)	28(1)
C(36)	408(2)	11639(2)	2862(2)	22(1)
C(37)	809(2)	10986(2)	2998(2)	20(1)
C(1S)	1214(3)	1426(3)	4697(2)	53(2)
Cl(1S)	2013(1)	1328(1)	5028(1)	92(1)
Cl(2S)	592(1)	1816(1)	5163(1)	78(1)

Table 3. **Bond lengths [Å] and angles [°] for Ru-9.**

Ru(1)-C(22)	1.830(4)
Ru(1)-C(1)	2.071(3)
Ru(1)-S(1)	2.2706(10)
Ru(1)-S(2)	2.2954(9)
Ru(1)-O(1)	2.319(3)
Cl(1)-C(36)	1.734(4)
Cl(2)-C(33)	1.739(4)
S(1)-C(32)	1.747(4)
S(2)-C(37)	1.749(4)
O(1)-C(28)	1.380(4)
O(1)-C(29)	1.484(5)
N(1)-C(1)	1.352(5)
N(1)-C(4)	1.433(5)
N(1)-C(2)	1.475(4)
N(2)-C(1)	1.344(5)
N(2)-C(13)	1.434(5)
N(2)-C(3)	1.484(4)
C(2)-C(3)	1.517(5)
C(4)-C(9)	1.399(5)
C(4)-C(5)	1.410(5)
C(5)-C(6)	1.394(6)
C(5)-C(10)	1.498(5)
C(6)-C(7)	1.391(6)
C(7)-C(8)	1.370(6)
C(7)-C(11)	1.509(6)
C(8)-C(9)	1.393(5)
C(9)-C(12)	1.500(5)
C(13)-C(18)	1.390(5)
C(13)-C(14)	1.406(5)
C(14)-C(15)	1.389(5)
C(14)-C(19)	1.503(5)
C(15)-C(16)	1.393(6)
C(16)-C(17)	1.382(6)
C(16)-C(20)	1.513(6)

C(17)-C(18)	1.398(6)
C(18)-C(21)	1.508(6)
C(22)-C(23)	1.445(5)
C(23)-C(24)	1.395(5)
C(23)-C(28)	1.399(5)
C(24)-C(25)	1.377(6)
C(25)-C(26)	1.385(6)
C(26)-C(27)	1.384(6)
C(27)-C(28)	1.386(5)
C(29)-C(30)	1.489(6)
C(29)-C(31)	1.511(6)
C(32)-C(37)	1.407(5)
C(32)-C(33)	1.413(5)
C(33)-C(34)	1.382(5)
C(34)-C(35)	1.388(6)
C(35)-C(36)	1.371(6)
C(36)-C(37)	1.414(5)
C(1S)-Cl(1S)	1.726(6)
C(1S)-Cl(2S)	1.745(6)

C(22)-Ru(1)-C(1)	99.91(15)
C(22)-Ru(1)-S(1)	91.98(13)
C(1)-Ru(1)-S(1)	85.87(10)
C(22)-Ru(1)-S(2)	111.69(11)
C(1)-Ru(1)-S(2)	148.03(11)
S(1)-Ru(1)-S(2)	88.23(3)
C(22)-Ru(1)-O(1)	78.36(14)
C(1)-Ru(1)-O(1)	104.03(12)
S(1)-Ru(1)-O(1)	167.13(7)
S(2)-Ru(1)-O(1)	87.49(7)
C(32)-S(1)-Ru(1)	105.37(13)
C(37)-S(2)-Ru(1)	105.43(13)
C(28)-O(1)-C(29)	118.1(3)
C(28)-O(1)-Ru(1)	109.1(2)
C(29)-O(1)-Ru(1)	132.8(2)
C(1)-N(1)-C(4)	127.0(3)

C(1)-N(1)-C(2)	112.8(3)
C(4)-N(1)-C(2)	120.2(3)
C(1)-N(2)-C(13)	127.0(3)
C(1)-N(2)-C(3)	112.6(3)
C(13)-N(2)-C(3)	118.6(3)
N(2)-C(1)-N(1)	107.3(3)
N(2)-C(1)-Ru(1)	128.7(3)
N(1)-C(1)-Ru(1)	122.9(3)
N(1)-C(2)-C(3)	101.8(3)
N(2)-C(3)-C(2)	101.9(3)
C(9)-C(4)-C(5)	120.8(3)
C(9)-C(4)-N(1)	121.1(3)
C(5)-C(4)-N(1)	117.8(3)
C(6)-C(5)-C(4)	117.8(4)
C(6)-C(5)-C(10)	119.9(4)
C(4)-C(5)-C(10)	122.2(4)
C(7)-C(6)-C(5)	122.3(4)
C(8)-C(7)-C(6)	118.0(4)
C(8)-C(7)-C(11)	120.7(4)
C(6)-C(7)-C(11)	121.2(4)
C(7)-C(8)-C(9)	122.8(4)
C(8)-C(9)-C(4)	118.1(4)
C(8)-C(9)-C(12)	118.7(3)
C(4)-C(9)-C(12)	123.0(3)
C(18)-C(13)-C(14)	121.6(4)
C(18)-C(13)-N(2)	120.2(3)
C(14)-C(13)-N(2)	118.1(3)
C(15)-C(14)-C(13)	118.1(4)
C(15)-C(14)-C(19)	120.2(4)
C(13)-C(14)-C(19)	121.7(3)
C(14)-C(15)-C(16)	121.7(4)
C(17)-C(16)-C(15)	118.5(4)
C(17)-C(16)-C(20)	121.3(4)
C(15)-C(16)-C(20)	120.2(4)
C(16)-C(17)-C(18)	122.1(4)
C(13)-C(18)-C(17)	118.0(4)

C(13)-C(18)-C(21)	122.5(4)
C(17)-C(18)-C(21)	119.5(4)
C(23)-C(22)-Ru(1)	120.0(3)
C(24)-C(23)-C(28)	118.4(4)
C(24)-C(23)-C(22)	122.5(4)
C(28)-C(23)-C(22)	119.1(3)
C(25)-C(24)-C(23)	121.2(4)
C(24)-C(25)-C(26)	119.2(4)
C(27)-C(26)-C(25)	121.2(4)
C(26)-C(27)-C(28)	119.1(4)
O(1)-C(28)-C(27)	125.7(3)
O(1)-C(28)-C(23)	113.4(3)
C(27)-C(28)-C(23)	120.9(3)
O(1)-C(29)-C(30)	108.1(3)
O(1)-C(29)-C(31)	109.0(3)
C(30)-C(29)-C(31)	114.1(4)
C(37)-C(32)-C(33)	117.9(3)
C(37)-C(32)-S(1)	121.3(3)
C(33)-C(32)-S(1)	120.8(3)
C(34)-C(33)-C(32)	122.4(4)
C(34)-C(33)-Cl(2)	118.6(3)
C(32)-C(33)-Cl(2)	119.0(3)
C(33)-C(34)-C(35)	119.2(4)
C(36)-C(35)-C(34)	119.7(4)
C(35)-C(36)-C(37)	122.3(4)
C(35)-C(36)-Cl(1)	118.7(3)
C(37)-C(36)-Cl(1)	119.0(3)
C(32)-C(37)-C(36)	118.5(4)
C(32)-C(37)-S(2)	119.6(3)
C(36)-C(37)-S(2)	122.0(3)
Cl(1S)-C(1S)-Cl(2S)	112.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. **Anisotropic displacement parameters ($Å^2 \times 10^3$) for Ru-9. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	14(1)	14(1)	21(1)	1(1)	-1(1)	-1(1)
Cl(1)	28(1)	21(1)	43(1)	9(1)	-5(1)	0(1)
Cl(2)	26(1)	39(1)	30(1)	6(1)	6(1)	4(1)
S(1)	17(1)	17(1)	23(1)	2(1)	1(1)	1(1)
S(2)	17(1)	18(1)	30(1)	5(1)	-1(1)	0(1)
O(1)	16(1)	28(1)	21(1)	0(1)	-1(1)	0(1)
N(1)	24(2)	11(1)	26(2)	4(1)	-7(1)	-3(1)
N(2)	24(2)	14(1)	23(2)	2(1)	-3(1)	-3(1)
C(1)	15(2)	15(2)	24(2)	1(1)	2(2)	1(1)
C(2)	37(2)	16(2)	29(2)	5(2)	-8(2)	-8(2)
C(3)	35(2)	17(2)	30(2)	4(2)	-8(2)	-5(2)
C(4)	22(2)	11(2)	22(2)	1(1)	-4(2)	-3(1)
C(5)	24(2)	18(2)	29(2)	0(2)	-4(2)	2(2)
C(6)	34(2)	26(2)	27(2)	1(2)	2(2)	2(2)
C(7)	39(3)	22(2)	25(2)	4(2)	-2(2)	2(2)
C(8)	29(2)	17(2)	30(2)	2(2)	-9(2)	-2(2)
C(9)	21(2)	14(2)	22(2)	-3(1)	-4(2)	-3(1)
C(10)	29(2)	37(2)	39(3)	-2(2)	0(2)	10(2)
C(11)	68(4)	45(3)	32(3)	7(2)	-7(3)	12(3)
C(12)	23(2)	26(2)	31(2)	-4(2)	-4(2)	-1(2)
C(13)	23(2)	17(2)	21(2)	2(2)	-4(2)	0(2)
C(14)	26(2)	19(2)	22(2)	3(2)	0(2)	4(2)
C(15)	25(2)	28(2)	26(2)	3(2)	-2(2)	-3(2)
C(16)	32(2)	31(2)	26(2)	2(2)	-5(2)	-5(2)
C(17)	37(3)	30(2)	22(2)	0(2)	2(2)	-1(2)
C(18)	28(2)	21(2)	25(2)	6(2)	-1(2)	0(2)
C(19)	24(2)	28(2)	31(2)	2(2)	3(2)	7(2)
C(20)	45(3)	57(3)	34(3)	-4(2)	-10(2)	-8(3)
C(21)	26(2)	34(2)	29(2)	7(2)	6(2)	-1(2)
C(22)	22(2)	18(2)	23(2)	0(2)	2(2)	1(2)
C(23)	16(2)	16(2)	29(2)	-2(2)	0(2)	-1(1)

C(24)	25(2)	20(2)	25(2)	-2(2)	-4(2)	-1(2)
C(25)	19(2)	26(2)	34(2)	-5(2)	-9(2)	-3(2)
C(26)	17(2)	19(2)	41(2)	1(2)	-1(2)	-2(2)
C(27)	20(2)	21(2)	27(2)	3(2)	2(2)	-2(2)
C(28)	16(2)	16(2)	23(2)	2(1)	-2(2)	2(1)
C(29)	26(2)	37(2)	20(2)	1(2)	2(2)	6(2)
C(30)	37(3)	38(2)	27(2)	7(2)	-6(2)	3(2)
C(31)	28(2)	37(2)	30(2)	-6(2)	-2(2)	7(2)
C(32)	17(2)	17(2)	19(2)	-5(1)	-4(2)	0(1)
C(33)	22(2)	21(2)	25(2)	-2(2)	-1(2)	-1(2)
C(34)	25(2)	28(2)	30(2)	-4(2)	-1(2)	6(2)
C(35)	24(2)	19(2)	41(3)	-6(2)	-10(2)	6(2)
C(36)	19(2)	20(2)	27(2)	1(2)	-7(2)	-4(2)
C(37)	20(2)	15(2)	25(2)	-1(2)	-6(2)	-2(1)
C(1S)	77(4)	43(3)	40(3)	0(2)	-15(3)	-7(3)
Cl(1S)	63(1)	115(2)	97(1)	-28(1)	-21(1)	-11(1)
Cl(2S)	79(1)	54(1)	102(1)	14(1)	20(1)	-16(1)

Table 5. **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for Ru-9.**

	x	y	z	U(eq)
H(2A)	1648	6861	2697	33
H(2B)	1006	7215	3059	33
H(3A)	1670	7033	3860	33
H(3B)	2366	6953	3474	33
H(6)	2027	7847	817	35
H(8)	399	9107	1316	30
H(10A)	2727	7529	2209	52
H(10B)	2864	7418	1523	52
H(10C)	2352	6851	1862	52
H(11A)	648	8282	211	73
H(11B)	1412	8601	94	73
H(11C)	811	9172	298	73
H(12A)	443	9445	2520	40
H(12B)	474	8617	2818	40
H(12C)	-74	8785	2308	40
H(15)	4080	8560	4529	32
H(17)	2350	8712	5506	36
H(19A)	3448	7645	3372	41
H(19B)	4064	8210	3551	41
H(19C)	3407	8532	3202	41
H(20A)	4149	8596	5615	68
H(20B)	3462	8761	5985	68
H(20C)	3816	9433	5616	68
H(21A)	1178	8133	4381	45
H(21B)	1186	8870	4797	45
H(21C)	1278	8034	5073	45
H(22)	2423	9893	4048	25
H(24)	3598	10372	4362	28
H(25)	4723	10735	4134	31
H(26)	5091	10713	3161	31

H(27)	4340	10343	2414	27
H(29)	3530	10270	1829	33
H(30A)	2242	9512	1686	51
H(30B)	2689	9847	1154	51
H(30C)	2368	10414	1633	51
H(31A)	4028	9099	2068	48
H(31B)	3717	9039	1420	48
H(31C)	3310	8665	1959	48
H(34)	-810	11480	3832	33
H(35)	-425	12281	3076	34
H(1S1)	1054	917	4563	64
H(1S2)	1263	1758	4349	64

Table 6. **Torsion angles [°] for Ru-9.**

C(13)-N(2)-C(1)-N(1)	169.9(3)
C(3)-N(2)-C(1)-N(1)	5.4(4)
C(13)-N(2)-C(1)-Ru(1)	-21.5(6)
C(3)-N(2)-C(1)-Ru(1)	174.1(3)
C(4)-N(1)-C(1)-N(2)	-173.4(3)
C(2)-N(1)-C(1)-N(2)	7.6(4)
C(4)-N(1)-C(1)-Ru(1)	17.1(5)
C(2)-N(1)-C(1)-Ru(1)	-161.9(3)
C(1)-N(1)-C(2)-C(3)	-16.5(4)
C(4)-N(1)-C(2)-C(3)	164.4(3)
C(1)-N(2)-C(3)-C(2)	-15.2(4)
C(13)-N(2)-C(3)-C(2)	178.9(3)
N(1)-C(2)-C(3)-N(2)	17.5(4)
C(1)-N(1)-C(4)-C(9)	-78.8(5)
C(2)-N(1)-C(4)-C(9)	100.1(4)
C(1)-N(1)-C(4)-C(5)	107.7(4)
C(2)-N(1)-C(4)-C(5)	-73.4(5)
C(9)-C(4)-C(5)-C(6)	4.0(5)
N(1)-C(4)-C(5)-C(6)	177.5(3)
C(9)-C(4)-C(5)-C(10)	-173.7(4)
N(1)-C(4)-C(5)-C(10)	-0.2(5)
C(4)-C(5)-C(6)-C(7)	-0.7(6)
C(10)-C(5)-C(6)-C(7)	177.1(4)
C(5)-C(6)-C(7)-C(8)	-0.8(6)
C(5)-C(6)-C(7)-C(11)	-178.7(4)
C(6)-C(7)-C(8)-C(9)	-0.9(6)
C(11)-C(7)-C(8)-C(9)	177.0(4)
C(7)-C(8)-C(9)-C(4)	4.0(6)
C(7)-C(8)-C(9)-C(12)	-171.9(4)
C(5)-C(4)-C(9)-C(8)	-5.6(5)
N(1)-C(4)-C(9)-C(8)	-178.9(3)
C(5)-C(4)-C(9)-C(12)	170.1(3)
N(1)-C(4)-C(9)-C(12)	-3.2(5)
C(1)-N(2)-C(13)-C(18)	110.1(4)

C(3)-N(2)-C(13)-C(18)	-86.3(4)
C(1)-N(2)-C(13)-C(14)	-73.6(5)
C(3)-N(2)-C(13)-C(14)	90.1(4)
C(18)-C(13)-C(14)-C(15)	-2.1(5)
N(2)-C(13)-C(14)-C(15)	-178.4(3)
C(18)-C(13)-C(14)-C(19)	177.5(3)
N(2)-C(13)-C(14)-C(19)	1.3(5)
C(13)-C(14)-C(15)-C(16)	0.7(6)
C(19)-C(14)-C(15)-C(16)	-178.9(4)
C(14)-C(15)-C(16)-C(17)	0.5(6)
C(14)-C(15)-C(16)-C(20)	-179.9(4)
C(15)-C(16)-C(17)-C(18)	-0.3(6)
C(20)-C(16)-C(17)-C(18)	180.0(4)
C(14)-C(13)-C(18)-C(17)	2.2(5)
N(2)-C(13)-C(18)-C(17)	178.4(3)
C(14)-C(13)-C(18)-C(21)	-178.0(3)
N(2)-C(13)-C(18)-C(21)	-1.8(5)
C(16)-C(17)-C(18)-C(13)	-1.0(6)
C(16)-C(17)-C(18)-C(21)	179.3(4)
C(1)-Ru(1)-C(22)-C(23)	106.0(3)
S(1)-Ru(1)-C(22)-C(23)	-167.9(3)
S(2)-Ru(1)-C(22)-C(23)	-79.0(3)
O(1)-Ru(1)-C(22)-C(23)	3.6(3)
Ru(1)-C(22)-C(23)-C(24)	176.7(3)
Ru(1)-C(22)-C(23)-C(28)	-3.6(5)
C(28)-C(23)-C(24)-C(25)	0.5(5)
C(22)-C(23)-C(24)-C(25)	-179.8(3)
C(23)-C(24)-C(25)-C(26)	-0.4(6)
C(24)-C(25)-C(26)-C(27)	0.3(6)
C(25)-C(26)-C(27)-C(28)	-0.4(6)
C(29)-O(1)-C(28)-C(27)	3.0(5)
Ru(1)-O(1)-C(28)-C(27)	-177.1(3)
C(29)-O(1)-C(28)-C(23)	-177.5(3)
Ru(1)-O(1)-C(28)-C(23)	2.4(3)
C(26)-C(27)-C(28)-O(1)	180.0(3)
C(26)-C(27)-C(28)-C(23)	0.6(5)

C(24)-C(23)-C(28)-O(1)	179.9(3)
C(22)-C(23)-C(28)-O(1)	0.2(5)
C(24)-C(23)-C(28)-C(27)	-0.6(5)
C(22)-C(23)-C(28)-C(27)	179.7(3)
C(28)-O(1)-C(29)-C(30)	-156.2(3)
Ru(1)-O(1)-C(29)-C(30)	23.9(5)
C(28)-O(1)-C(29)-C(31)	79.2(4)
Ru(1)-O(1)-C(29)-C(31)	-100.7(3)
Ru(1)-S(1)-C(32)-C(37)	0.5(3)
Ru(1)-S(1)-C(32)-C(33)	-179.2(3)
C(37)-C(32)-C(33)-C(34)	-2.3(5)
S(1)-C(32)-C(33)-C(34)	177.4(3)
C(37)-C(32)-C(33)-Cl(2)	178.7(3)
S(1)-C(32)-C(33)-Cl(2)	-1.6(4)
C(32)-C(33)-C(34)-C(35)	1.8(6)
Cl(2)-C(33)-C(34)-C(35)	-179.2(3)
C(33)-C(34)-C(35)-C(36)	0.6(6)
C(34)-C(35)-C(36)-C(37)	-2.4(6)
C(34)-C(35)-C(36)-Cl(1)	177.0(3)
C(33)-C(32)-C(37)-C(36)	0.5(5)
S(1)-C(32)-C(37)-C(36)	-179.2(3)
C(33)-C(32)-C(37)-S(2)	-178.6(3)
S(1)-C(32)-C(37)-S(2)	1.8(4)
C(35)-C(36)-C(37)-C(32)	1.8(5)
Cl(1)-C(36)-C(37)-C(32)	-177.6(3)
C(35)-C(36)-C(37)-S(2)	-179.2(3)
Cl(1)-C(36)-C(37)-S(2)	1.4(4)
Ru(1)-S(2)-C(37)-C(32)	-3.0(3)
Ru(1)-S(2)-C(37)-C(36)	178.0(3)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure for Ru-10

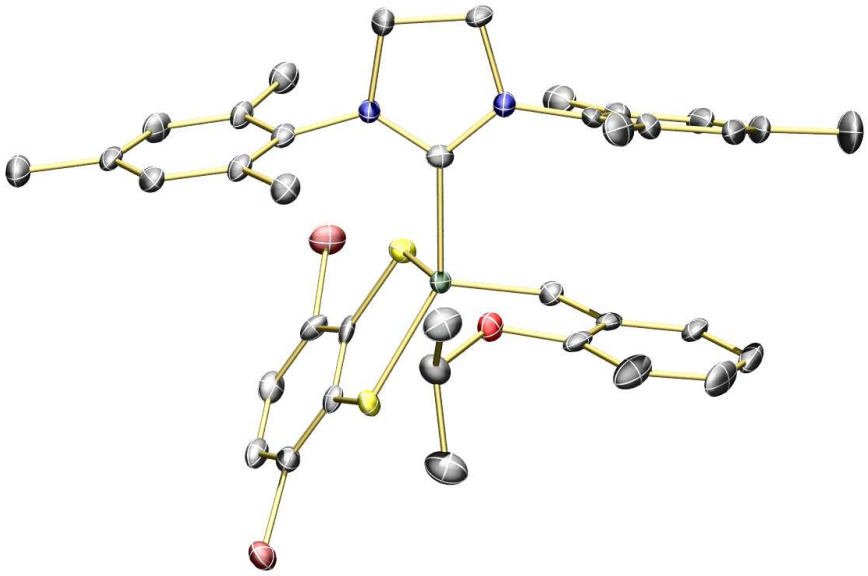

Table 1. **Crystal data and structure refinement for Ru-10.**

Identification code	$C_{37}H_{40}Br_2N_2ORuS_2(CH_2Cl_2)0.5$	
Empirical formula	$C_{37.50}H_{41}Br_2ClN_2ORuS_2$	
Formula weight	896.18	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 16.165(6) Å	α= 90°.
	b = 13.391(5) Å	β= 102.771(6)°.
	c = 17.344(6) Å	γ = 90°.
Volume	3662(2) $Å^3$	
Z	4	
Density (calculated)	1.626 Mg/m^3	
Absorption coefficient	2.831 mm^{-1}	
F(000)	1804	
Crystal size	0.450 x 0.260 x 0.070 mm^3	
Theta range for data collection	1.940 to 28.640°.	
Index ranges	-21<=h<=21, -18<=k<=14, -21<=l<=23	
Reflections collected	53449	
Independent reflections	16921 [R(int) = 0.0780]	

Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4728
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16921 / 4 / 864
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.0891
R indices (all data)	R1 = 0.0801, wR2 = 0.0983
Absolute structure parameter	0.009(6)
Extinction coefficient	na
Largest diff. peak and hole	1.593 and -0.871 e.$Å^{-3}$

Table 2. **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Ru-10. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	x	y	z	U(eq)
Ru(1)	7381(1)	9295(1)	8768(1)	15(1)
Br(1)	6882(1)	6388(1)	10903(1)	26(1)
Br(2)	10054(1)	6744(1)	9174(1)	32(1)
S(1)	6978(1)	8201(1)	9636(1)	18(1)
S(2)	8568(1)	8387(1)	8862(1)	20(1)
O(1)	6232(3)	10257(4)	8808(3)	20(1)
N(1)	7598(4)	10521(4)	7314(4)	18(1)
N(2)	7274(4)	8976(5)	7029(3)	17(1)
C(1)	7430(4)	9643(5)	7622(4)	16(2)
C(2)	7585(5)	10476(6)	6464(4)	22(2)
C(3)	7300(5)	9403(5)	6250(4)	21(2)
C(4)	7965(5)	11414(6)	7714(5)	22(2)
C(5)	7471(5)	12239(6)	7711(5)	25(2)
C(6)	7847(6)	13112(6)	8041(5)	35(2)
C(7)	8710(6)	13154(7)	8372(5)	37(2)
C(8)	9192(6)	12307(7)	8362(5)	33(2)
C(9)	8847(5)	11419(6)	8032(5)	24(2)
C(10)	6530(5)	12205(6)	7357(5)	30(2)
C(11)	9113(7)	14126(7)	8699(6)	58(3)
C(12)	9378(5)	10536(7)	7982(5)	31(2)
C(13)	7008(5)	7954(5)	7013(4)	18(2)
C(14)	7593(5)	7210(5)	6945(5)	19(2)
C(15)	7301(5)	6228(6)	6811(5)	24(2)
C(16)	6453(5)	5992(5)	6734(4)	21(2)
C(17)	5887(5)	6741(6)	6800(4)	20(2)
C(18)	6152(4)	7729(5)	6936(4)	17(2)
C(19)	8505(5)	7435(6)	6970(5)	27(2)
C(20)	6156(5)	4934(6)	6585(5)	29(2)
C(21)	5512(5)	8531(6)	6975(5)	22(2)
C(22)	7874(5)	10430(5)	9250(4)	18(2)

C(23)	7363(5)	11256(5)	9399(4)	19(2)
C(24)	7688(5)	12153(6)	9743(5)	23(2)
C(25)	7158(6)	12920(6)	9863(5)	31(2)
C(26)	6304(6)	12797(6)	9643(5)	34(2)
C(27)	5954(5)	11917(7)	9309(5)	30(2)
C(28)	6486(5)	11154(6)	9176(4)	21(2)
C(29)	5381(4)	9839(6)	8762(5)	23(2)
C(30)	5147(5)	9789(7)	9559(5)	32(2)
C(31)	4729(5)	10341(6)	8111(5)	27(2)
C(32)	7824(4)	7348(5)	9893(4)	16(2)
C(33)	7812(5)	6564(6)	10412(4)	21(2)
C(34)	8447(5)	5843(6)	10573(5)	23(2)
C(35)	9122(5)	5921(6)	10213(5)	24(2)
C(36)	9154(4)	6692(6)	9700(4)	21(2)
C(37)	8517(5)	7424(5)	9528(4)	19(2)
Ru(2)	7411(1)	-46(1)	3645(1)	14(1)
Br(3)	5171(1)	727(1)	5544(1)	27(1)
Br(4)	7182(1)	4009(1)	3878(1)	37(1)
S(3)	6365(1)	40(1)	4338(1)	18(1)
S(4)	7422(1)	1634(1)	3624(1)	19(1)
O(2)	7538(3)	-1746(3)	3814(3)	17(1)
N(3)	8335(3)	-258(5)	2276(4)	18(1)
N(4)	7059(4)	304(4)	1903(3)	16(1)
C(38)	7633(4)	-29(5)	2522(4)	14(1)
C(39)	8265(4)	-56(7)	1428(4)	23(2)
C(40)	7338(5)	207(6)	1156(5)	28(2)
C(41)	9149(4)	-584(5)	2739(4)	16(2)
C(42)	9337(5)	-1591(6)	2772(5)	20(2)
C(43)	10130(5)	-1886(6)	3183(5)	25(2)
C(44)	10735(5)	-1197(6)	3550(5)	26(2)
C(45)	10521(4)	-198(6)	3504(5)	22(2)
C(46)	9723(5)	129(6)	3089(5)	20(2)
C(47)	8702(5)	-2347(6)	2365(5)	27(2)
C(48)	11599(5)	-1550(7)	3993(5)	37(2)
C(49)	9516(5)	1222(5)	3031(5)	22(2)
C(50)	6162(5)	404(6)	1845(4)	19(2)

C(51)	5783(5)	1343(5)	1701(4)	18(2)
C(52)	4903(5)	1390(6)	1539(4)	20(2)
C(53)	4403(4)	552(6)	1524(4)	19(2)
C(54)	4796(5)	-363(6)	1675(4)	20(2)
C(55)	5679(4)	-457(5)	1821(4)	18(2)
C(56)	6287(5)	2277(5)	1700(5)	25(2)
C(57)	3448(5)	622(6)	1331(5)	28(2)
C(58)	6059(5)	-1480(6)	1888(5)	29(2)
C(59)	8474(4)	-158(5)	4265(4)	18(2)
C(60)	8830(5)	-1137(6)	4523(4)	19(2)
C(61)	9646(5)	-1263(6)	4981(5)	26(2)
C(62)	9968(5)	-2218(7)	5166(5)	32(2)
C(63)	9467(5)	-3027(7)	4900(5)	32(2)
C(64)	8657(5)	-2920(6)	4452(5)	26(2)
C(65)	8339(4)	-1974(5)	4269(5)	19(2)
C(66)	6801(5)	-2360(5)	3880(5)	21(2)
C(67)	6727(5)	-3284(6)	3363(5)	29(2)
C(68)	6775(5)	-2576(6)	4723(5)	28(2)
C(69)	6279(4)	1311(5)	4543(4)	17(2)
C(70)	5760(4)	1657(6)	5035(4)	19(2)
C(71)	5661(5)	2661(6)	5182(5)	26(2)
C(72)	6102(5)	3339(6)	4835(5)	27(2)
C(73)	6600(5)	3030(5)	4358(5)	22(2)
C(74)	6728(5)	2022(6)	4207(5)	19(2)
C(1S)	8902(10)	3649(8)	2819(8)	45(3)
Cl(1S)	8864(3)	4901(3)	3085(3)	48(1)
Cl(2S)	8520(5)	3402(3)	1809(2)	62(2)
C(1T)	8290(20)	3820(20)	2380(30)	45(3)
Cl(1T)	9025(12)	3502(9)	1821(9)	48(1)
Cl(2T)	8628(16)	4964(15)	2834(11)	62(2)

Table 3. **Bond lengths [Å] and angles [°] for Ru-10.**

Ru(1)-C(22)	1.831(7)
Ru(1)-C(1)	2.060(7)
Ru(1)-S(2)	2.247(2)
Ru(1)-O(1)	2.273(5)
Ru(1)-S(1)	2.295(2)
Br(1)-C(33)	1.900(7)
Br(2)-C(36)	1.882(7)
S(1)-C(32)	1.762(7)
S(2)-C(37)	1.746(8)
O(1)-C(28)	1.380(9)
O(1)-C(29)	1.471(8)
N(1)-C(1)	1.345(9)
N(1)-C(4)	1.443(9)
N(1)-C(2)	1.471(9)
N(2)-C(1)	1.343(9)
N(2)-C(13)	1.433(9)
N(2)-C(3)	1.476(9)
C(2)-C(3)	1.529(10)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.362(11)
C(4)-C(9)	1.411(11)
C(5)-C(6)	1.382(11)
C(5)-C(10)	1.509(11)
C(6)-C(7)	1.388(13)
C(6)-H(6)	0.9500
C(7)-C(8)	1.378(13)
C(7)-C(11)	1.510(12)
C(8)-C(9)	1.382(11)
C(8)-H(8)	0.9500
C(9)-C(12)	1.474(11)
C(10)-H(10A)	0.9800

C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(18)	1.393(10)
C(13)-C(14)	1.397(10)
C(14)-C(15)	1.399(10)
C(14)-C(19)	1.496(10)
C(15)-C(16)	1.383(10)
C(15)-H(15)	0.9500
C(16)-C(17)	1.380(10)
C(16)-C(20)	1.500(11)
C(17)-C(18)	1.395(10)
C(17)-H(17)	0.9500
C(18)-C(21)	1.503(10)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.437(10)
C(22)-H(22)	0.9500
C(23)-C(24)	1.391(10)
C(23)-C(28)	1.392(10)
C(24)-C(25)	1.383(11)
C(24)-H(24)	0.9500
C(25)-C(26)	1.359(12)
C(25)-H(25)	0.9500

C(26)-C(27)	1.379(12)
C(26)-H(26)	0.9500
C(27)-C(28)	1.386(10)
C(27)-H(27)	0.9500
C(29)-C(30)	1.512(11)
C(29)-C(31)	1.521(10)
C(29)-H(29)	1.0000
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-C(33)	1.386(10)
C(32)-C(37)	1.406(10)
C(33)-C(34)	1.391(10)
C(34)-C(35)	1.377(11)
C(34)-H(34)	0.9500
C(35)-C(36)	1.371(11)
C(35)-H(35)	0.9500
C(36)-C(37)	1.405(10)
Ru(2)-C(59)	1.821(7)
Ru(2)-C(38)	2.058(7)
Ru(2)-S(4)	2.250(2)
Ru(2)-S(3)	2.284(2)
Ru(2)-O(2)	2.299(5)
Br(3)-C(70)	1.899(8)
Br(4)-C(73)	1.908(8)
S(3)-C(69)	1.749(7)
S(4)-C(74)	1.747(8)
O(2)-C(65)	1.392(8)
O(2)-C(66)	1.473(8)
N(3)-C(38)	1.332(8)
N(3)-C(41)	1.449(9)
N(3)-C(39)	1.475(9)
N(4)-C(38)	1.332(9)

N(4)-C(50)	1.436(9)
N(4)-C(40)	1.469(9)
C(39)-C(40)	1.509(10)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(46)	1.376(10)
C(41)-C(42)	1.381(10)
C(42)-C(43)	1.381(11)
C(42)-C(47)	1.502(11)
C(43)-C(44)	1.392(11)
C(43)-H(43)	0.9500
C(44)-C(45)	1.380(11)
C(44)-C(48)	1.513(11)
C(45)-C(46)	1.401(10)
C(45)-H(45)	0.9500
C(46)-C(49)	1.500(10)
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-C(55)	1.389(10)
C(50)-C(51)	1.396(10)
C(51)-C(52)	1.389(10)
C(51)-C(56)	1.493(10)
C(52)-C(53)	1.379(10)
C(52)-H(52)	0.9500
C(53)-C(54)	1.378(10)
C(53)-C(57)	1.509(10)
C(54)-C(55)	1.399(10)

C(54)-H(54)	0.9500
C(55)-C(58)	1.496(10)
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
C(57)-H(57A)	0.9800
C(57)-H(57B)	0.9800
C(57)-H(57C)	0.9800
C(58)-H(58A)	0.9800
C(58)-H(58B)	0.9800
C(58)-H(58C)	0.9800
C(59)-C(60)	1.461(10)
C(59)-H(59)	0.9500
C(60)-C(65)	1.389(10)
C(60)-C(61)	1.392(10)
C(61)-C(62)	1.392(11)
C(61)-H(61)	0.9500
C(62)-C(63)	1.371(12)
C(62)-H(62)	0.9500
C(63)-C(64)	1.374(11)
C(63)-H(63)	0.9500
C(64)-C(65)	1.378(10)
C(64)-H(64)	0.9500
C(66)-C(68)	1.501(11)
C(66)-C(67)	1.518(10)
C(66)-H(66)	1.0000
C(67)-H(67A)	0.9800
C(67)-H(67B)	0.9800
C(67)-H(67C)	0.9800
C(68)-H(68A)	0.9800
C(68)-H(68B)	0.9800
C(68)-H(68C)	0.9800
C(69)-C(74)	1.401(10)
C(69)-C(70)	1.401(10)
C(70)-C(71)	1.385(11)
C(71)-C(72)	1.372(11)

C(71)-H(71)	0.9500
C(72)-C(73)	1.341(11)
C(72)-H(72)	0.9500
C(73)-C(74)	1.400(10)
C(1S)-Cl(1S)	1.743(12)
C(1S)-Cl(2S)	1.755(14)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(1T)-Cl(1T)	1.74(3)
C(1T)-Cl(2T)	1.75(3)
C(1T)-H(1T1)	0.9900
C(1T)-H(1T2)	0.9900

C(22)-Ru(1)-C(1)	98.4(3)
C(22)-Ru(1)-S(2)	97.9(2)
C(1)-Ru(1)-S(2)	88.73(19)
C(22)-Ru(1)-O(1)	78.0(3)
C(1)-Ru(1)-O(1)	96.2(2)
S(2)-Ru(1)-O(1)	173.98(14)
C(22)-Ru(1)-S(1)	112.8(2)
C(1)-Ru(1)-S(1)	148.7(2)
S(2)-Ru(1)-S(1)	88.17(7)
O(1)-Ru(1)-S(1)	89.44(14)
C(32)-S(1)-Ru(1)	105.3(3)
C(37)-S(2)-Ru(1)	106.5(3)
C(28)-O(1)-C(29)	122.3(6)
C(28)-O(1)-Ru(1)	110.3(4)
C(29)-O(1)-Ru(1)	122.9(4)
C(1)-N(1)-C(4)	129.1(6)
C(1)-N(1)-C(2)	113.8(6)
C(4)-N(1)-C(2)	115.5(6)
C(1)-N(2)-C(13)	130.9(6)
C(1)-N(2)-C(3)	113.9(6)
C(13)-N(2)-C(3)	114.9(6)
N(2)-C(1)-N(1)	107.3(6)
N(2)-C(1)-Ru(1)	123.2(5)

N(1)-C(1)-Ru(1)	129.5(5)
N(1)-C(2)-C(3)	102.6(6)
N(1)-C(2)-H(2A)	111.2
C(3)-C(2)-H(2A)	111.2
N(1)-C(2)-H(2B)	111.2
C(3)-C(2)-H(2B)	111.2
H(2A)-C(2)-H(2B)	109.2
N(2)-C(3)-C(2)	102.1(6)
N(2)-C(3)-H(3A)	111.3
C(2)-C(3)-H(3A)	111.3
N(2)-C(3)-H(3B)	111.3
C(2)-C(3)-H(3B)	111.3
H(3A)-C(3)-H(3B)	109.2
C(5)-C(4)-C(9)	122.6(7)
C(5)-C(4)-N(1)	119.5(7)
C(9)-C(4)-N(1)	117.6(7)
C(4)-C(5)-C(6)	118.7(8)
C(4)-C(5)-C(10)	120.9(7)
C(6)-C(5)-C(10)	120.4(8)
C(5)-C(6)-C(7)	121.0(8)
C(5)-C(6)-H(6)	119.5
C(7)-C(6)-H(6)	119.5
C(8)-C(7)-C(6)	118.8(8)
C(8)-C(7)-C(11)	121.1(9)
C(6)-C(7)-C(11)	120.1(9)
C(7)-C(8)-C(9)	122.4(8)
C(7)-C(8)-H(8)	118.8
C(9)-C(8)-H(8)	118.8
C(8)-C(9)-C(4)	116.5(8)
C(8)-C(9)-C(12)	121.8(8)
C(4)-C(9)-C(12)	121.7(7)
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5

H(10B)-C(10)-H(10C)	109.5
C(7)-C(11)-H(11A)	109.5
C(7)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(7)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	120.9(7)
C(18)-C(13)-N(2)	119.7(6)
C(14)-C(13)-N(2)	118.5(6)
C(13)-C(14)-C(15)	118.3(7)
C(13)-C(14)-C(19)	122.3(7)
C(15)-C(14)-C(19)	119.3(7)
C(16)-C(15)-C(14)	121.4(7)
C(16)-C(15)-H(15)	119.3
C(14)-C(15)-H(15)	119.3
C(17)-C(16)-C(15)	119.2(7)
C(17)-C(16)-C(20)	120.4(7)
C(15)-C(16)-C(20)	120.3(7)
C(16)-C(17)-C(18)	121.2(7)
C(16)-C(17)-H(17)	119.4
C(18)-C(17)-H(17)	119.4
C(13)-C(18)-C(17)	118.9(7)
C(13)-C(18)-C(21)	121.3(7)
C(17)-C(18)-C(21)	119.7(7)
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5

H(19B)-C(19)-H(19C)	109.5
C(16)-C(20)-H(20A)	109.5
C(16)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(16)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-Ru(1)	120.7(5)
C(23)-C(22)-H(22)	119.6
Ru(1)-C(22)-H(22)	119.6
C(24)-C(23)-C(28)	117.9(7)
C(24)-C(23)-C(22)	124.3(7)
C(28)-C(23)-C(22)	117.8(7)
C(25)-C(24)-C(23)	121.3(8)
C(25)-C(24)-H(24)	119.4
C(23)-C(24)-H(24)	119.4
C(26)-C(25)-C(24)	119.5(8)
C(26)-C(25)-H(25)	120.3
C(24)-C(25)-H(25)	120.3
C(25)-C(26)-C(27)	121.2(8)
C(25)-C(26)-H(26)	119.4
C(27)-C(26)-H(26)	119.4
C(26)-C(27)-C(28)	119.2(8)
C(26)-C(27)-H(27)	120.4
C(28)-C(27)-H(27)	120.4
O(1)-C(28)-C(27)	125.9(7)
O(1)-C(28)-C(23)	113.2(6)
C(27)-C(28)-C(23)	120.9(7)
O(1)-C(29)-C(30)	112.8(6)
O(1)-C(29)-C(31)	111.0(6)

C(30)-C(29)-C(31)	115.2(6)
O(1)-C(29)-H(29)	105.6
C(30)-C(29)-H(29)	105.6
C(31)-C(29)-H(29)	105.6
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(33)-C(32)-C(37)	118.3(6)
C(33)-C(32)-S(1)	122.3(6)
C(37)-C(32)-S(1)	119.3(6)
C(32)-C(33)-C(34)	122.8(7)
C(32)-C(33)-Br(1)	120.7(6)
C(34)-C(33)-Br(1)	116.4(6)
C(35)-C(34)-C(33)	118.7(7)
C(35)-C(34)-H(34)	120.7
C(33)-C(34)-H(34)	120.7
C(36)-C(35)-C(34)	119.9(7)
C(36)-C(35)-H(35)	120.1
C(34)-C(35)-H(35)	120.1
C(35)-C(36)-C(37)	122.2(7)
C(35)-C(36)-Br(2)	119.1(6)
C(37)-C(36)-Br(2)	118.7(6)
C(36)-C(37)-C(32)	118.2(7)
C(36)-C(37)-S(2)	121.1(6)
C(32)-C(37)-S(2)	120.7(5)
C(59)-Ru(2)-C(38)	102.7(3)
C(59)-Ru(2)-S(4)	94.7(2)

C(38)-Ru(2)-S(4)	88.2(2)
C(59)-Ru(2)-S(3)	113.9(2)
C(38)-Ru(2)-S(3)	143.33(19)
S(4)-Ru(2)-S(3)	88.13(7)
C(59)-Ru(2)-O(2)	78.3(3)
C(38)-Ru(2)-O(2)	95.9(2)
S(4)-Ru(2)-O(2)	172.49(13)
S(3)-Ru(2)-O(2)	92.25(13)
C(69)-S(3)-Ru(2)	104.9(3)
C(74)-S(4)-Ru(2)	106.2(3)
C(65)-O(2)-C(66)	120.0(5)
C(65)-O(2)-Ru(2)	109.6(4)
C(66)-O(2)-Ru(2)	120.7(4)
C(38)-N(3)-C(41)	128.7(6)
C(38)-N(3)-C(39)	113.2(6)
C(41)-N(3)-C(39)	117.9(5)
C(38)-N(4)-C(50)	126.9(6)
C(38)-N(4)-C(40)	112.7(6)
C(50)-N(4)-C(40)	116.7(6)
N(4)-C(38)-N(3)	108.1(6)
N(4)-C(38)-Ru(2)	122.0(5)
N(3)-C(38)-Ru(2)	129.7(5)
N(3)-C(39)-C(40)	101.9(6)
N(3)-C(39)-H(39A)	111.4
C(40)-C(39)-H(39A)	111.4
N(3)-C(39)-H(39B)	111.4
C(40)-C(39)-H(39B)	111.4
H(39A)-C(39)-H(39B)	109.2
N(4)-C(40)-C(39)	102.9(6)
N(4)-C(40)-H(40A)	111.2
C(39)-C(40)-H(40A)	111.2
N(4)-C(40)-H(40B)	111.2
C(39)-C(40)-H(40B)	111.2
H(40A)-C(40)-H(40B)	109.1
C(46)-C(41)-C(42)	122.7(7)
C(46)-C(41)-N(3)	118.4(6)

C(42)-C(41)-N(3)	118.8(6)
C(41)-C(42)-C(43)	118.1(7)
C(41)-C(42)-C(47)	121.2(7)
C(43)-C(42)-C(47)	120.7(7)
C(42)-C(43)-C(44)	121.7(7)
C(42)-C(43)-H(43)	119.2
C(44)-C(43)-H(43)	119.2
C(45)-C(44)-C(43)	118.4(7)
C(45)-C(44)-C(48)	121.6(8)
C(43)-C(44)-C(48)	120.0(8)
C(44)-C(45)-C(46)	121.5(7)
C(44)-C(45)-H(45)	119.2
C(46)-C(45)-H(45)	119.2
C(41)-C(46)-C(45)	117.7(7)
C(41)-C(46)-C(49)	122.0(7)
C(45)-C(46)-C(49)	120.4(7)
C(42)-C(47)-H(47A)	109.5
C(42)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(42)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(44)-C(48)-H(48A)	109.5
C(44)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(44)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(46)-C(49)-H(49A)	109.5
C(46)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(46)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(55)-C(50)-C(51)	121.4(7)
C(55)-C(50)-N(4)	118.5(6)

C(51)-C(50)-N(4)	119.5(6)
C(52)-C(51)-C(50)	117.8(7)
C(52)-C(51)-C(56)	119.7(7)
C(50)-C(51)-C(56)	122.5(6)
C(53)-C(52)-C(51)	122.5(7)
C(53)-C(52)-H(52)	118.8
C(51)-C(52)-H(52)	118.8
C(54)-C(53)-C(52)	118.4(7)
C(54)-C(53)-C(57)	120.2(7)
C(52)-C(53)-C(57)	121.4(7)
C(53)-C(54)-C(55)	121.6(7)
C(53)-C(54)-H(54)	119.2
C(55)-C(54)-H(54)	119.2
C(50)-C(55)-C(54)	118.4(7)
C(50)-C(55)-C(58)	122.6(6)
C(54)-C(55)-C(58)	118.9(7)
C(51)-C(56)-H(56A)	109.5
C(51)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(51)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
C(53)-C(57)-H(57A)	109.5
C(53)-C(57)-H(57B)	109.5
H(57A)-C(57)-H(57B)	109.5
C(53)-C(57)-H(57C)	109.5
H(57A)-C(57)-H(57C)	109.5
H(57B)-C(57)-H(57C)	109.5
C(55)-C(58)-H(58A)	109.5
C(55)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5
C(55)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58C)	109.5
H(58B)-C(58)-H(58C)	109.5
C(60)-C(59)-Ru(2)	120.7(5)
C(60)-C(59)-H(59)	119.7

Ru(2)-C(59)-H(59)	119.7
C(65)-C(60)-C(61)	119.1(7)
C(65)-C(60)-C(59)	118.0(6)
C(61)-C(60)-C(59)	122.9(7)
C(62)-C(61)-C(60)	120.1(8)
C(62)-C(61)-H(61)	119.9
C(60)-C(61)-H(61)	119.9
C(63)-C(62)-C(61)	119.1(8)
C(63)-C(62)-H(62)	120.5
C(61)-C(62)-H(62)	120.5
C(62)-C(63)-C(64)	121.8(8)
C(62)-C(63)-H(63)	119.1
C(64)-C(63)-H(63)	119.1
C(63)-C(64)-C(65)	119.1(8)
C(63)-C(64)-H(64)	120.4
C(65)-C(64)-H(64)	120.4
C(64)-C(65)-C(60)	120.7(7)
C(64)-C(65)-O(2)	125.8(7)
C(60)-C(65)-O(2)	113.4(6)
O(2)-C(66)-C(68)	112.4(6)
O(2)-C(66)-C(67)	111.5(6)
C(68)-C(66)-C(67)	113.8(7)
O(2)-C(66)-H(66)	106.1
C(68)-C(66)-H(66)	106.1
C(67)-C(66)-H(66)	106.1
C(66)-C(67)-H(67A)	109.5
C(66)-C(67)-H(67B)	109.5
H(67A)-C(67)-H(67B)	109.5
C(66)-C(67)-H(67C)	109.5
H(67A)-C(67)-H(67C)	109.5
H(67B)-C(67)-H(67C)	109.5
C(66)-C(68)-H(68A)	109.5
C(66)-C(68)-H(68B)	109.5
H(68A)-C(68)-H(68B)	109.5
C(66)-C(68)-H(68C)	109.5
H(68A)-C(68)-H(68C)	109.5

H(68B)-C(68)-H(68C)	109.5
C(74)-C(69)-C(70)	117.7(7)
C(74)-C(69)-S(3)	120.3(6)
C(70)-C(69)-S(3)	122.0(6)
C(71)-C(70)-C(69)	122.8(7)
C(71)-C(70)-Br(3)	117.4(6)
C(69)-C(70)-Br(3)	119.7(6)
C(72)-C(71)-C(70)	118.0(7)
C(72)-C(71)-H(71)	121.0
C(70)-C(71)-H(71)	121.0
C(73)-C(72)-C(71)	120.5(7)
C(73)-C(72)-H(72)	119.7
C(71)-C(72)-H(72)	119.7
C(72)-C(73)-C(74)	123.2(8)
C(72)-C(73)-Br(4)	118.5(6)
C(74)-C(73)-Br(4)	118.3(6)
C(73)-C(74)-C(69)	117.8(7)
C(73)-C(74)-S(4)	122.4(6)
C(69)-C(74)-S(4)	119.8(6)
Cl(1S)-C(1S)-Cl(2S)	114.8(7)
Cl(1S)-C(1S)-H(1S1)	108.6
Cl(2S)-C(1S)-H(1S1)	108.6
Cl(1S)-C(1S)-H(1S2)	108.6
Cl(2S)-C(1S)-H(1S2)	108.6
H(1S1)-C(1S)-H(1S2)	107.5
Cl(1T)-C(1T)-Cl(2T)	106.8(18)
Cl(1T)-C(1T)-H(1T1)	110.4
Cl(2T)-C(1T)-H(1T1)	110.4
Cl(1T)-C(1T)-H(1T2)	110.4
Cl(2T)-C(1T)-H(1T2)	110.4
H(1T1)-C(1T)-H(1T2)	108.6

Symmetry transformations used to generate equivalent atoms:

Table 4. **Anisotropic displacement parameters ($Å^2$ x 10^3) for Ru-10. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	18(1)	12(1)	15(1)	0(1)	4(1)	1(1)
Br(1)	31(1)	19(1)	30(1)	4(1)	11(1)	-2(1)
Br(2)	26(1)	37(1)	36(1)	3(1)	11(1)	12(1)
S(1)	20(1)	12(1)	23(1)	2(1)	8(1)	0(1)
S(2)	21(1)	19(1)	22(1)	3(1)	8(1)	4(1)
O(1)	21(3)	16(3)	23(3)	-1(2)	6(2)	2(2)
N(1)	26(3)	14(3)	16(3)	-1(3)	4(3)	-2(3)
N(2)	24(3)	13(3)	13(3)	0(3)	2(3)	-2(3)
C(1)	15(3)	18(3)	15(4)	3(3)	3(3)	5(3)
C(2)	34(4)	20(4)	10(4)	0(3)	4(3)	0(3)
C(3)	26(4)	17(4)	19(4)	-3(3)	3(3)	-5(3)
C(4)	41(5)	14(4)	15(4)	0(3)	12(4)	-8(3)
C(5)	41(5)	15(4)	20(5)	1(3)	9(4)	-5(3)
C(6)	71(7)	14(4)	22(5)	-1(4)	20(5)	-5(4)
C(7)	66(7)	26(5)	21(5)	-11(4)	14(5)	-27(4)
C(8)	47(5)	34(5)	18(5)	-8(4)	9(4)	-22(4)
C(9)	34(4)	23(4)	17(4)	0(3)	8(3)	-10(4)
C(10)	43(5)	17(4)	30(5)	5(4)	10(4)	9(4)
C(11)	92(8)	32(6)	52(7)	-18(5)	22(6)	-31(6)
C(12)	31(5)	38(5)	22(5)	-1(4)	1(4)	-8(4)
C(13)	25(4)	16(4)	11(4)	0(3)	0(3)	2(3)
C(14)	23(4)	14(4)	18(4)	-3(3)	2(3)	4(3)
C(15)	28(4)	18(4)	26(5)	-3(3)	8(4)	8(3)
C(16)	35(4)	15(4)	11(4)	-2(3)	2(3)	-1(3)
C(17)	24(4)	21(4)	15(4)	-2(3)	2(3)	-4(3)
C(18)	18(4)	17(4)	14(4)	-3(3)	-1(3)	3(3)
C(19)	28(4)	25(4)	29(5)	-4(4)	7(4)	5(3)
C(20)	45(5)	17(4)	24(5)	-2(4)	5(4)	-5(4)
C(21)	21(4)	22(4)	22(5)	-1(3)	3(3)	3(3)
C(22)	20(4)	19(4)	15(4)	-1(3)	2(3)	-2(3)
C(23)	32(4)	17(4)	10(4)	2(3)	9(3)	2(3)

C(24)	36(5)	21(4)	12(4)	-4(3)	7(3)	0(3)
C(25)	64(6)	15(4)	14(4)	-2(3)	6(4)	4(4)
C(26)	59(6)	18(4)	25(5)	0(4)	10(4)	19(4)
C(27)	34(5)	33(5)	23(5)	-2(4)	4(4)	15(4)
C(28)	33(4)	21(4)	10(4)	-1(3)	8(3)	5(3)
C(29)	20(4)	22(4)	26(4)	4(4)	6(3)	1(3)
C(30)	26(4)	39(5)	32(5)	12(4)	7(4)	5(4)
C(31)	25(4)	31(4)	23(5)	3(4)	1(3)	10(3)
C(32)	15(4)	14(3)	15(4)	-4(3)	-4(3)	2(3)
C(33)	27(4)	18(4)	18(4)	-1(3)	4(3)	-1(3)
C(34)	34(4)	13(4)	19(4)	0(3)	-1(3)	5(3)
C(35)	26(4)	18(4)	25(5)	1(3)	-3(3)	8(3)
C(36)	20(4)	26(4)	18(4)	-7(3)	4(3)	6(3)
C(37)	24(4)	11(3)	16(4)	-6(3)	-5(3)	1(3)
Ru(2)	19(1)	8(1)	14(1)	0(1)	4(1)	0(1)
Br(3)	26(1)	25(1)	34(1)	-4(1)	14(1)	-1(1)
Br(4)	70(1)	9(1)	34(1)	3(1)	17(1)	0(1)
S(3)	24(1)	10(1)	20(1)	-1(1)	6(1)	0(1)
S(4)	31(1)	9(1)	18(1)	1(1)	10(1)	1(1)
O(2)	17(3)	9(2)	23(3)	-1(2)	2(2)	2(2)
N(3)	14(3)	24(3)	13(3)	-2(3)	-1(2)	1(2)
N(4)	23(3)	18(3)	7(3)	4(2)	4(3)	3(2)
C(38)	15(3)	12(3)	15(4)	0(3)	5(3)	-2(3)
C(39)	21(4)	34(4)	14(4)	5(4)	5(3)	0(4)
C(40)	31(5)	34(5)	19(5)	1(4)	9(4)	4(4)
C(41)	16(3)	19(4)	15(4)	-5(3)	8(3)	0(3)
C(42)	24(4)	23(4)	16(4)	-3(3)	10(3)	2(3)
C(43)	31(4)	21(4)	27(5)	0(4)	11(4)	8(3)
C(44)	21(4)	38(5)	20(5)	1(4)	8(3)	9(4)
C(45)	15(4)	30(5)	21(4)	2(4)	1(3)	-3(3)
C(46)	23(4)	22(4)	18(4)	-2(3)	9(3)	2(3)
C(47)	34(5)	18(4)	34(5)	-3(4)	14(4)	-1(3)
C(48)	24(5)	54(6)	30(6)	3(5)	-3(4)	12(4)
C(49)	27(4)	15(4)	27(5)	-4(3)	10(4)	-7(3)
C(50)	27(4)	20(4)	9(4)	1(3)	4(3)	-1(3)
C(51)	26(4)	17(4)	12(4)	4(3)	6(3)	3(3)

C(52)	28(4)	14(3)	18(4)	0(3)	6(3)	9(3)
C(53)	23(4)	20(4)	14(4)	1(3)	5(3)	2(3)
C(54)	24(4)	19(4)	16(4)	3(3)	1(3)	-4(3)
C(55)	21(4)	18(4)	14(4)	-2(3)	0(3)	0(3)
C(56)	35(5)	14(4)	23(5)	6(3)	1(4)	0(3)
C(57)	27(4)	27(4)	26(5)	3(4)	-2(3)	-3(4)
C(58)	39(5)	12(4)	32(5)	-1(3)	-2(4)	1(3)
C(59)	22(4)	13(4)	20(4)	-3(3)	5(3)	-3(3)
C(60)	25(4)	19(4)	12(4)	2(3)	3(3)	1(3)
C(61)	24(4)	29(5)	25(5)	5(4)	6(4)	2(3)
C(62)	27(5)	39(5)	26(5)	13(4)	1(4)	8(4)
C(63)	41(5)	27(4)	29(5)	12(4)	7(4)	17(4)
C(64)	34(5)	17(4)	29(5)	6(3)	12(4)	6(3)
C(65)	20(4)	12(3)	24(5)	1(3)	4(3)	0(3)
C(66)	23(4)	11(3)	29(5)	0(3)	5(4)	-2(3)
C(67)	43(5)	16(4)	23(5)	-4(4)	-2(4)	-2(4)
C(68)	38(5)	22(4)	27(5)	-2(4)	9(4)	-9(4)
C(69)	18(4)	16(3)	12(4)	2(3)	-5(3)	3(3)
C(70)	19(4)	19(4)	18(4)	-5(3)	1(3)	0(3)
C(71)	34(5)	24(4)	18(5)	-5(4)	4(4)	9(4)
C(72)	41(5)	15(4)	23(5)	-1(3)	3(4)	7(3)
C(73)	31(4)	13(4)	19(4)	3(3)	1(3)	6(3)
C(74)	26(4)	16(3)	15(4)	-2(3)	1(3)	0(3)
C(1S)	77(10)	19(5)	44(9)	6(5)	27(7)	-5(6)
Cl(1S)	73(3)	21(1)	60(3)	3(2)	35(2)	1(2)
Cl(2S)	106(5)	34(2)	42(2)	12(2)	7(2)	0(2)
C(1T)	77(10)	19(5)	44(9)	6(5)	27(7)	-5(6)
Cl(1T)	73(3)	21(1)	60(3)	3(2)	35(2)	1(2)
Cl(2T)	106(5)	34(2)	42(2)	12(2)	7(2)	0(2)

Table 5. **Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Ru-10.**

	x	y	z	U(eq)
H(2A)	8155	10604	6363	26
H(2B)	7178	10963	6163	26
H(3A)	6734	9384	5887	25
H(3B)	7713	9045	6005	25
H(6)	7509	13692	8042	41
H(8)	9782	12335	8590	39
H(10A)	6429	12330	6787	44
H(10B)	6243	12717	7605	44
H(10C)	6308	11545	7449	44
H(11A)	9619	13987	9114	87
H(11B)	8707	14513	8922	87
H(11C)	9275	14509	8274	87
H(12A)	9978	10722	8141	46
H(12B)	9256	10288	7437	46
H(12C)	9253	10013	8334	46
H(15)	7693	5712	6772	29
H(17)	5305	6580	6753	24
H(19A)	8591	7488	6430	40
H(19B)	8861	6897	7249	40
H(19C)	8661	8068	7249	40
H(20A)	6016	4660	7065	44
H(20B)	6606	4533	6442	44
H(20C)	5650	4919	6152	44
H(21A)	5315	8828	6451	33
H(21B)	5775	9048	7350	33
H(21C)	5029	8239	7151	33
H(22)	8475	10474	9403	22
H(24)	8285	12239	9898	28
H(25)	7390	13529	10097	38
H(26)	5941	13327	9721	40

H(27)	5356	11833	9171	37
H(29)	5412	9130	8590	27
H(30A)	5571	9391	9923	48
H(30B)	4588	9477	9499	48
H(30C)	5131	10465	9770	48
H(31A)	4578	10994	8296	40
H(31B)	4220	9923	7975	40
H(31C)	4968	10431	7643	40
H(34)	8414	5308	10925	28
H(35)	9566	5441	10320	29
H(39A)	8412	-653	1150	28
H(39B)	8633	507	1347	28
H(40A)	7264	842	857	33
H(40B)	7022	-328	822	33
H(43)	10267	-2577	3217	30
H(45)	10925	280	3759	27
H(47A)	8160	-2241	2518	41
H(47B)	8910	-3021	2520	41
H(47C)	8621	-2273	1791	41
H(48A)	11952	-972	4195	56
H(48B)	11870	-1932	3634	56
H(48C)	11534	-1976	4435	56
H(49A)	9485	1452	2489	34
H(49B)	9958	1595	3396	34
H(49C)	8968	1334	3171	34
H(52)	4636	2022	1435	24
H(54)	4459	-943	1680	24
H(56A)	6506	2499	2245	38
H(56B)	5923	2799	1406	38
H(56C)	6762	2148	1448	38
H(57A)	3277	1315	1391	41
H(57B)	3220	193	1692	41
H(57C)	3226	403	785	41
H(58A)	6149	-1691	1371	44
H(58B)	5674	-1950	2065	44
H(58C)	6604	-1471	2272	44

H(59)	8802	427	4422	22
H(61)	9984	-695	5168	31
H(62)	10528	-2308	5472	38
H(63)	9685	-3680	5029	39
H(64)	8321	-3491	4272	31
H(66)	6288	-1945	3661	26
H(67A)	6867	-3111	2857	44
H(67B)	6146	-3541	3267	44
H(67C)	7122	-3796	3629	44
H(68A)	7220	-3059	4945	43
H(68B)	6220	-2855	4745	43
H(68C)	6868	-1957	5031	43
H(71)	5298	2875	5512	31
H(72)	6055	4032	4934	33
H(1S1)	8566	3253	3124	54
H(1S2)	9497	3417	2974	54
H(1T1)	8274	3306	2780	54
H(1T2)	7720	3892	2033	54

Table 6. **Torsion angles [°] for Ru-10.**

C(13)-N(2)-C(1)-N(1)	-175.3(7)
C(3)-N(2)-C(1)-N(1)	-2.2(8)
C(13)-N(2)-C(1)-Ru(1)	3.7(10)
C(3)-N(2)-C(1)-Ru(1)	176.8(5)
C(4)-N(1)-C(1)-N(2)	-166.4(7)
C(2)-N(1)-C(1)-N(2)	-1.7(8)
C(4)-N(1)-C(1)-Ru(1)	14.7(11)
C(2)-N(1)-C(1)-Ru(1)	179.3(5)
C(1)-N(1)-C(2)-C(3)	4.6(8)
C(4)-N(1)-C(2)-C(3)	171.4(6)
C(1)-N(2)-C(3)-C(2)	4.8(8)
C(13)-N(2)-C(3)-C(2)	179.1(6)
N(1)-C(2)-C(3)-N(2)	-5.2(7)
C(1)-N(1)-C(4)-C(5)	-110.0(9)
C(2)-N(1)-C(4)-C(5)	85.6(9)
C(1)-N(1)-C(4)-C(9)	75.7(10)
C(2)-N(1)-C(4)-C(9)	-88.7(8)
C(9)-C(4)-C(5)-C(6)	-0.9(12)
N(1)-C(4)-C(5)-C(6)	-174.8(7)
C(9)-C(4)-C(5)-C(10)	179.4(7)
N(1)-C(4)-C(5)-C(10)	5.4(11)
C(4)-C(5)-C(6)-C(7)	0.0(13)
C(10)-C(5)-C(6)-C(7)	179.7(8)
C(5)-C(6)-C(7)-C(8)	0.4(13)
C(5)-C(6)-C(7)-C(11)	177.5(8)
C(6)-C(7)-C(8)-C(9)	0.2(13)
C(11)-C(7)-C(8)-C(9)	-176.9(9)
C(7)-C(8)-C(9)-C(4)	-1.0(12)
C(7)-C(8)-C(9)-C(12)	176.2(8)
C(5)-C(4)-C(9)-C(8)	1.4(12)
N(1)-C(4)-C(9)-C(8)	175.5(7)
C(5)-C(4)-C(9)-C(12)	-175.9(8)
N(1)-C(4)-C(9)-C(12)	-1.8(11)
C(1)-N(2)-C(13)-C(18)	81.9(10)

C(3)-N(2)-C(13)-C(18)	-91.1(8)
C(1)-N(2)-C(13)-C(14)	-108.5(9)
C(3)-N(2)-C(13)-C(14)	78.5(8)
C(18)-C(13)-C(14)-C(15)	-1.1(11)
N(2)-C(13)-C(14)-C(15)	-170.6(7)
C(18)-C(13)-C(14)-C(19)	175.8(7)
N(2)-C(13)-C(14)-C(19)	6.3(11)
C(13)-C(14)-C(15)-C(16)	1.1(12)
C(19)-C(14)-C(15)-C(16)	-176.0(7)
C(14)-C(15)-C(16)-C(17)	-0.8(12)
C(14)-C(15)-C(16)-C(20)	179.6(8)
C(15)-C(16)-C(17)-C(18)	0.6(11)
C(20)-C(16)-C(17)-C(18)	-179.8(7)
C(14)-C(13)-C(18)-C(17)	1.0(11)
N(2)-C(13)-C(18)-C(17)	170.3(7)
C(14)-C(13)-C(18)-C(21)	-177.5(7)
N(2)-C(13)-C(18)-C(21)	-8.1(11)
C(16)-C(17)-C(18)-C(13)	-0.7(11)
C(16)-C(17)-C(18)-C(21)	177.8(7)
C(1)-Ru(1)-C(22)-C(23)	94.8(6)
S(2)-Ru(1)-C(22)-C(23)	-175.3(6)
O(1)-Ru(1)-C(22)-C(23)	0.2(6)
S(1)-Ru(1)-C(22)-C(23)	-84.0(6)
Ru(1)-C(22)-C(23)-C(24)	-178.3(6)
Ru(1)-C(22)-C(23)-C(28)	1.0(9)
C(28)-C(23)-C(24)-C(25)	0.2(11)
C(22)-C(23)-C(24)-C(25)	179.4(7)
C(23)-C(24)-C(25)-C(26)	0.2(13)
C(24)-C(25)-C(26)-C(27)	0.6(13)
C(25)-C(26)-C(27)-C(28)	-1.7(14)
C(29)-O(1)-C(28)-C(27)	-22.7(11)
Ru(1)-O(1)-C(28)-C(27)	-179.4(7)
C(29)-O(1)-C(28)-C(23)	158.9(6)
Ru(1)-O(1)-C(28)-C(23)	2.2(7)
C(26)-C(27)-C(28)-O(1)	-176.2(8)
C(26)-C(27)-C(28)-C(23)	2.1(12)

C(24)-C(23)-C(28)-O(1)	177.1(7)
C(22)-C(23)-C(28)-O(1)	-2.2(10)
C(24)-C(23)-C(28)-C(27)	-1.4(11)
C(22)-C(23)-C(28)-C(27)	179.4(7)
C(28)-O(1)-C(29)-C(30)	-51.7(9)
Ru(1)-O(1)-C(29)-C(30)	102.1(6)
C(28)-O(1)-C(29)-C(31)	79.3(8)
Ru(1)-O(1)-C(29)-C(31)	-126.9(6)
Ru(1)-S(1)-C(32)-C(33)	-179.8(6)
Ru(1)-S(1)-C(32)-C(37)	-3.6(6)
C(37)-C(32)-C(33)-C(34)	-1.2(11)
S(1)-C(32)-C(33)-C(34)	175.0(6)
C(37)-C(32)-C(33)-Br(1)	-178.0(5)
S(1)-C(32)-C(33)-Br(1)	-1.8(9)
C(32)-C(33)-C(34)-C(35)	1.2(11)
Br(1)-C(33)-C(34)-C(35)	178.1(6)
C(33)-C(34)-C(35)-C(36)	-0.8(11)
C(34)-C(35)-C(36)-C(37)	0.6(12)
C(34)-C(35)-C(36)-Br(2)	-176.8(6)
C(35)-C(36)-C(37)-C(32)	-0.6(11)
Br(2)-C(36)-C(37)-C(32)	176.8(5)
C(35)-C(36)-C(37)-S(2)	-179.2(6)
Br(2)-C(36)-C(37)-S(2)	-1.8(9)
C(33)-C(32)-C(37)-C(36)	0.9(10)
S(1)-C(32)-C(37)-C(36)	-175.4(6)
C(33)-C(32)-C(37)-S(2)	179.5(5)
S(1)-C(32)-C(37)-S(2)	3.1(8)
Ru(1)-S(2)-C(37)-C(36)	177.6(5)
Ru(1)-S(2)-C(37)-C(32)	-0.9(6)
C(50)-N(4)-C(38)-N(3)	163.7(6)
C(40)-N(4)-C(38)-N(3)	6.4(8)
C(50)-N(4)-C(38)-Ru(2)	-20.2(10)
C(40)-N(4)-C(38)-Ru(2)	-177.5(5)
C(41)-N(3)-C(38)-N(4)	175.5(7)
C(39)-N(3)-C(38)-N(4)	1.3(9)
C(41)-N(3)-C(38)-Ru(2)	-0.3(11)

C(39)-N(3)-C(38)-Ru(2)	-174.4(6)
C(38)-N(3)-C(39)-C(40)	-7.8(9)
C(41)-N(3)-C(39)-C(40)	177.3(6)
C(38)-N(4)-C(40)-C(39)	-10.9(8)
C(50)-N(4)-C(40)-C(39)	-170.7(6)
N(3)-C(39)-C(40)-N(4)	10.4(8)
C(38)-N(3)-C(41)-C(46)	-85.0(9)
C(39)-N(3)-C(41)-C(46)	89.0(8)
C(38)-N(3)-C(41)-C(42)	98.8(9)
C(39)-N(3)-C(41)-C(42)	-87.2(9)
C(46)-C(41)-C(42)-C(43)	1.0(12)
N(3)-C(41)-C(42)-C(43)	177.0(6)
C(46)-C(41)-C(42)-C(47)	-178.4(7)
N(3)-C(41)-C(42)-C(47)	-2.4(11)
C(41)-C(42)-C(43)-C(44)	-0.8(12)
C(47)-C(42)-C(43)-C(44)	178.6(7)
C(42)-C(43)-C(44)-C(45)	0.9(12)
C(42)-C(43)-C(44)-C(48)	-179.7(7)
C(43)-C(44)-C(45)-C(46)	-1.1(12)
C(48)-C(44)-C(45)-C(46)	179.5(7)
C(42)-C(41)-C(46)-C(45)	-1.2(11)
N(3)-C(41)-C(46)-C(45)	-177.2(6)
C(42)-C(41)-C(46)-C(49)	178.6(7)
N(3)-C(41)-C(46)-C(49)	2.5(11)
C(44)-C(45)-C(46)-C(41)	1.2(11)
C(44)-C(45)-C(46)-C(49)	-178.5(8)
C(38)-N(4)-C(50)-C(55)	-69.0(10)
C(40)-N(4)-C(50)-C(55)	87.5(8)
C(38)-N(4)-C(50)-C(51)	120.2(8)
C(40)-N(4)-C(50)-C(51)	-83.3(9)
C(55)-C(50)-C(51)-C(52)	0.6(11)
N(4)-C(50)-C(51)-C(52)	171.1(6)
C(55)-C(50)-C(51)-C(56)	-178.1(7)
N(4)-C(50)-C(51)-C(56)	-7.6(11)
C(50)-C(51)-C(52)-C(53)	0.6(11)
C(56)-C(51)-C(52)-C(53)	179.3(7)

C(51)-C(52)-C(53)-C(54)	-0.1(11)
C(51)-C(52)-C(53)-C(57)	-178.9(7)
C(52)-C(53)-C(54)-C(55)	-1.7(11)
C(57)-C(53)-C(54)-C(55)	177.2(7)
C(51)-C(50)-C(55)-C(54)	-2.2(11)
N(4)-C(50)-C(55)-C(54)	-172.9(6)
C(51)-C(50)-C(55)-C(58)	173.4(8)
N(4)-C(50)-C(55)-C(58)	2.8(11)
C(53)-C(54)-C(55)-C(50)	2.8(11)
C(53)-C(54)-C(55)-C(58)	-173.0(8)
C(38)-Ru(2)-C(59)-C(60)	-93.3(6)
S(4)-Ru(2)-C(59)-C(60)	177.4(6)
S(3)-Ru(2)-C(59)-C(60)	87.4(6)
O(2)-Ru(2)-C(59)-C(60)	0.1(6)
Ru(2)-C(59)-C(60)-C(65)	1.2(10)
Ru(2)-C(59)-C(60)-C(61)	178.4(6)
C(65)-C(60)-C(61)-C(62)	1.3(12)
C(59)-C(60)-C(61)-C(62)	-175.9(8)
C(60)-C(61)-C(62)-C(63)	-0.9(13)
C(61)-C(62)-C(63)-C(64)	0.4(14)
C(62)-C(63)-C(64)-C(65)	-0.4(13)
C(63)-C(64)-C(65)-C(60)	0.8(12)
C(63)-C(64)-C(65)-O(2)	179.1(7)
C(61)-C(60)-C(65)-C(64)	-1.2(12)
C(59)-C(60)-C(65)-C(64)	176.1(7)
C(61)-C(60)-C(65)-O(2)	-179.8(6)
C(59)-C(60)-C(65)-O(2)	-2.4(10)
C(66)-O(2)-C(65)-C(64)	37.6(11)
Ru(2)-O(2)-C(65)-C(64)	-176.1(7)
C(66)-O(2)-C(65)-C(60)	-144.0(6)
Ru(2)-O(2)-C(65)-C(60)	2.3(8)
C(65)-O(2)-C(66)-C(68)	45.3(9)
Ru(2)-O(2)-C(66)-C(68)	-97.2(6)
C(65)-O(2)-C(66)-C(67)	-83.9(8)
Ru(2)-O(2)-C(66)-C(67)	133.6(5)
Ru(2)-S(3)-C(69)-C(74)	7.6(6)

Ru(2)-S(3)-C(69)-C(70)	-173.1(5)
C(74)-C(69)-C(70)-C(71)	1.7(11)
S(3)-C(69)-C(70)-C(71)	-177.6(6)
C(74)-C(69)-C(70)-Br(3)	-177.4(5)
S(3)-C(69)-C(70)-Br(3)	3.3(9)
C(69)-C(70)-C(71)-C(72)	-0.9(12)
Br(3)-C(70)-C(71)-C(72)	178.2(6)
C(70)-C(71)-C(72)-C(73)	1.2(12)
C(71)-C(72)-C(73)-C(74)	-2.4(13)
C(71)-C(72)-C(73)-Br(4)	178.9(6)
C(72)-C(73)-C(74)-C(69)	3.2(12)
Br(4)-C(73)-C(74)-C(69)	-178.1(5)
C(72)-C(73)-C(74)-S(4)	-176.6(6)
Br(4)-C(73)-C(74)-S(4)	2.1(9)
C(70)-C(69)-C(74)-C(73)	-2.7(10)
S(3)-C(69)-C(74)-C(73)	176.7(6)
C(70)-C(69)-C(74)-S(4)	177.1(5)
S(3)-C(69)-C(74)-S(4)	-3.5(9)
Ru(2)-S(4)-C(74)-C(73)	177.2(6)
Ru(2)-S(4)-C(74)-C(69)	-2.6(7)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure for Ru-11

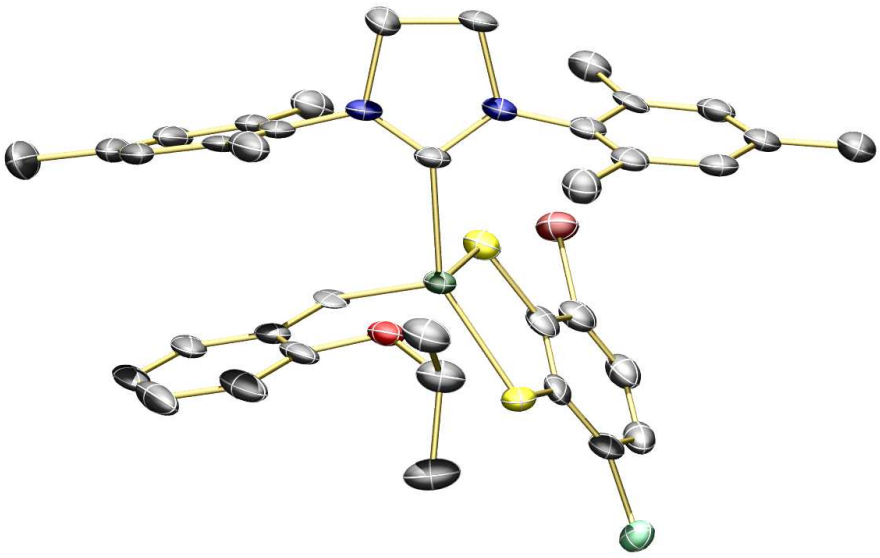

Table 1. **Crystal data and structure refinement for Ru-11.**

Identification code	$C_{37}H_{40}BrClN_2ORuS_2(CH_2Cl_2)0.5$	
Empirical formula	$C_{37.50}H_{41}BrCl_2N_2ORuS_2$	
Formula weight	851.72	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 16.1481(9) Å	α= 90°.
	b = 13.3717(7) Å	β= 102.263(3)°.
	c = 17.4135(9) Å	γ = 90°.
Volume	3674.3(3) $Å^3$	
Z	4	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	7.378 mm^{-1}	
F(000)	1732	
Crystal size	0.600 x 0.180 x 0.090 mm^3	
Theta range for data collection	2.597 to 66.620°.	
Index ranges	-19<=h<=19, -15<=k<=15, -20<=l<=20	
Reflections collected	40357	
Independent reflections	12422 [R(int) = 0.0630]	

Completeness to theta = 66.500°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.4876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12422 / 966 / 852
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1168
R indices (all data)	R1 = 0.0542, wR2 = 0.1222
Absolute structure parameter	0.033(5)
Extinction coefficient	na
Largest diff. peak and hole	1.655 and -0.890 e.Å^{-3}

Table 2. **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Ru-11. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	x	y	z	U(eq)
Ru(1)	7578(1)	9348(1)	6351(1)	24(1)
Cl(1)	9822(10)	8364(5)	4515(5)	30(1)
Br(1)	7780(2)	5306(5)	6113(3)	42(1)
Cl(1X)	8009(4)	5290(11)	6140(6)	30(1)
Br(1X)	9812(6)	8593(2)	4444(3)	42(1)
S(1)	8630(1)	9251(2)	5660(1)	28(1)
S(2)	7563(2)	7656(2)	6373(1)	31(1)
O(1)	7459(4)	11054(5)	6187(4)	27(1)
N(1)	6626(5)	9578(6)	7723(4)	30(1)
N(2)	7912(5)	8992(6)	8096(4)	27(2)
C(1)	7331(6)	9329(8)	7472(5)	26(2)
C(2)	6693(6)	9373(10)	8560(5)	37(2)
C(3)	7609(7)	9092(9)	8844(6)	40(3)
C(4)	5831(5)	9893(8)	7250(5)	29(2)
C(5)	5637(7)	10901(8)	7203(6)	36(2)
C(6)	4841(7)	11207(8)	6791(6)	37(2)
C(7)	4254(7)	10499(10)	6433(6)	42(2)
C(8)	4455(6)	9503(9)	6491(5)	35(2)
C(9)	5250(6)	9178(8)	6904(5)	33(2)
C(10)	6279(7)	11679(8)	7617(6)	37(2)
C(11)	3389(7)	10850(10)	5986(7)	48(3)
C(12)	5463(7)	8087(8)	6976(7)	38(2)
C(13)	8805(6)	8882(8)	8158(5)	28(2)
C(14)	9182(6)	7932(7)	8294(6)	29(2)
C(15)	10055(6)	7883(7)	8454(5)	29(2)
C(16)	10569(6)	8718(7)	8474(6)	32(2)
C(17)	10176(6)	9643(7)	8331(5)	29(2)
C(18)	9305(6)	9739(7)	8173(5)	31(2)
C(19)	8664(7)	7007(8)	8299(6)	37(2)
C(20)	11516(7)	8635(9)	8667(6)	38(2)

C(21)	8921(7)	10767(8)	8103(7)	41(3)
C(22)	6497(6)	9478(8)	5722(5)	27(1)
C(23)	6161(7)	10439(8)	5457(6)	33(1)
C(24)	5348(7)	10573(9)	5018(6)	38(2)
C(25)	5038(7)	11533(10)	4830(7)	45(3)
C(26)	5531(7)	12348(9)	5088(7)	46(3)
C(27)	6351(7)	12232(9)	5544(7)	40(2)
C(28)	6663(6)	11287(8)	5718(6)	32(2)
C(29)	8199(7)	11681(8)	6103(6)	34(2)
C(30)	8270(8)	12613(9)	6625(7)	46(3)
C(31)	8224(8)	11884(9)	5266(6)	42(3)
C(32)	8725(6)	7963(8)	5450(6)	31(2)
C(33)	9246(6)	7622(9)	4976(6)	35(2)
C(34)	9351(7)	6632(8)	4829(6)	39(2)
C(35)	8922(7)	5941(8)	5179(6)	39(2)
C(36)	8399(7)	6262(8)	5648(6)	38(2)
C(37)	8261(7)	7266(8)	5796(6)	33(2)
Ru(2)	2376(1)	4978(1)	8767(1)	27(1)
Cl(2)	4977(12)	7682(10)	9245(6)	33(2)
Br(2)	1861(3)	7840(7)	10886(3)	45(1)
Cl(2X)	2012(6)	7956(13)	10912(7)	33(2)
Br(2X)	5037(6)	7508(5)	9184(3)	45(1)
S(3)	3557(2)	5913(2)	8852(2)	35(1)
S(4)	1959(2)	6065(2)	9633(1)	33(1)
O(2)	1244(4)	3986(5)	8814(4)	31(1)
N(3)	2606(5)	3752(6)	7310(4)	30(1)
N(4)	2268(5)	5301(6)	7033(4)	29(2)
C(38)	2431(6)	4636(7)	7616(5)	28(2)
C(39)	2591(7)	3797(8)	6464(6)	36(2)
C(40)	2292(6)	4857(8)	6252(5)	34(2)
C(41)	2966(7)	2851(8)	7715(6)	36(2)
C(42)	2437(7)	2029(8)	7704(6)	36(2)
C(43)	2822(9)	1145(8)	8030(6)	47(3)
C(44)	3684(10)	1097(10)	8356(7)	55(3)
C(45)	4178(8)	1950(9)	8364(6)	45(3)
C(46)	3828(7)	2830(9)	8020(6)	40(2)

C(47)	1511(8)	2070(9)	7347(7)	44(3)
C(48)	4075(12)	110(11)	8697(9)	81(5)
C(49)	4380(7)	3714(10)	7984(7)	46(3)
C(50)	1998(6)	6331(8)	7019(5)	31(2)
C(51)	2571(6)	7078(8)	6935(5)	30(2)
C(52)	2267(7)	8045(8)	6810(6)	35(2)
C(53)	1422(7)	8294(8)	6729(5)	34(2)
C(54)	855(7)	7518(8)	6796(6)	33(2)
C(55)	1131(6)	6537(8)	6933(5)	30(2)
C(56)	3487(7)	6873(9)	6971(7)	43(3)
C(57)	1106(7)	9346(9)	6576(6)	45(2)
C(58)	507(6)	5725(8)	6988(6)	36(2)
C(59)	2907(6)	3854(7)	9251(5)	27(1)
C(60)	2388(7)	3013(8)	9411(6)	33(1)
C(61)	2744(8)	2125(8)	9764(6)	40(2)
C(62)	2243(9)	1342(9)	9886(6)	46(3)
C(63)	1374(9)	1427(9)	9658(7)	51(3)
C(64)	998(8)	2302(9)	9304(6)	45(3)
C(65)	1512(7)	3076(8)	9185(6)	35(2)
C(66)	388(6)	4395(10)	8784(6)	40(2)
C(67)	-267(7)	3878(9)	8139(6)	41(3)
C(68)	160(7)	4405(11)	9584(6)	48(3)
C(69)	2818(7)	6928(7)	9895(6)	33(2)
C(70)	2793(7)	7702(8)	10406(6)	39(2)
C(71)	3427(7)	8425(8)	10583(6)	39(2)
C(72)	4100(7)	8356(8)	10217(6)	42(2)
C(73)	4129(7)	7605(9)	9706(6)	40(2)
C(74)	3490(6)	6863(8)	9523(6)	32(2)
C(1S)	6079(19)	5668(15)	7172(12)	62(5)
Cl(1S)	6410(8)	5893(7)	8199(5)	76(3)
Cl(2S)	6073(13)	4431(13)	6847(11)	70(4)
C(1T)	6640(20)	5510(20)	7500(20)	62(5)
Cl(1T)	5952(12)	5801(12)	8142(9)	76(3)
Cl(2T)	6310(20)	4370(20)	7035(19)	70(4)

Table 3. **Bond lengths [Å] and angles [°] for Ru-11.**

Ru(1)-C(22)	1.862(9)
Ru(1)-C(1)	2.074(8)
Ru(1)-S(2)	2.263(3)
Ru(1)-S(1)	2.285(2)
Ru(1)-O(1)	2.303(7)
Cl(1)-C(33)	1.677(14)
Br(1)-C(36)	1.905(13)
Cl(1X)-C(36)	1.746(18)
Br(1X)-C(33)	1.934(12)
S(1)-C(32)	1.773(10)
S(2)-C(37)	1.741(11)
O(1)-C(28)	1.404(12)
O(1)-C(29)	1.492(12)
N(1)-C(1)	1.347(11)
N(1)-C(4)	1.433(12)
N(1)-C(2)	1.463(12)
N(2)-C(1)	1.353(12)
N(2)-C(13)	1.432(12)
N(2)-C(3)	1.491(11)
C(2)-C(3)	1.504(14)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.383(15)
C(4)-C(9)	1.385(14)
C(5)-C(6)	1.393(16)
C(5)-C(10)	1.535(16)
C(6)-C(7)	1.392(16)
C(6)-H(6)	0.9500
C(7)-C(8)	1.370(16)
C(7)-C(11)	1.521(15)
C(8)-C(9)	1.400(14)
C(8)-H(8)	0.9500

C(9)-C(12)	1.498(15)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(18)	1.398(13)
C(13)-C(14)	1.407(14)
C(14)-C(15)	1.379(14)
C(14)-C(19)	1.494(14)
C(15)-C(16)	1.388(14)
C(15)-H(15)	0.9500
C(16)-C(17)	1.388(14)
C(16)-C(20)	1.498(14)
C(17)-C(18)	1.381(13)
C(17)-H(17)	0.9500
C(18)-C(21)	1.503(14)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.432(14)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(15)
C(23)-C(28)	1.413(14)
C(24)-C(25)	1.391(16)
C(24)-H(24)	0.9500

C(25)-C(26)	1.367(17)
C(25)-H(25)	0.9500
C(26)-C(27)	1.400(16)
C(26)-H(26)	0.9500
C(27)-C(28)	1.370(15)
C(27)-H(27)	0.9500
C(29)-C(31)	1.491(14)
C(29)-C(30)	1.533(15)
C(29)-H(29)	1.0000
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-C(33)	1.377(14)
C(32)-C(37)	1.409(15)
C(33)-C(34)	1.365(16)
C(34)-C(35)	1.372(16)
C(34)-H(34)	0.9500
C(35)-C(36)	1.364(15)
C(35)-H(35)	0.9500
C(36)-C(37)	1.395(15)
Ru(2)-C(59)	1.844(10)
Ru(2)-C(38)	2.075(9)
Ru(2)-S(3)	2.259(3)
Ru(2)-O(2)	2.273(7)
Ru(2)-S(4)	2.297(3)
Cl(2)-C(73)	1.73(2)
Br(2)-C(70)	1.881(13)
Cl(2X)-C(70)	1.719(19)
Br(2X)-C(73)	1.887(14)
S(3)-C(74)	1.745(11)
S(4)-C(69)	1.788(11)
O(2)-C(65)	1.403(12)
O(2)-C(66)	1.478(12)

N(3)-C(38)	1.351(13)
N(3)-C(41)	1.453(13)
N(3)-C(39)	1.469(12)
N(4)-C(38)	1.333(12)
N(4)-C(50)	1.444(13)
N(4)-C(40)	1.493(12)
C(39)-C(40)	1.517(14)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(46)	1.382(16)
C(41)-C(42)	1.390(16)
C(42)-C(43)	1.399(16)
C(42)-C(47)	1.493(17)
C(43)-C(44)	1.389(19)
C(43)-H(43)	0.9500
C(44)-C(45)	1.391(19)
C(44)-C(48)	1.528(16)
C(45)-C(46)	1.385(15)
C(45)-H(45)	0.9500
C(46)-C(49)	1.490(17)
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-C(51)	1.390(14)
C(50)-C(55)	1.403(14)
C(51)-C(52)	1.383(14)
C(51)-C(56)	1.493(15)
C(52)-C(53)	1.383(15)

C(52)-H(52)	0.9500
C(53)-C(54)	1.404(15)
C(53)-C(57)	1.501(16)
C(54)-C(55)	1.390(15)
C(54)-H(54)	0.9500
C(55)-C(58)	1.499(14)
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
C(57)-H(57A)	0.9800
C(57)-H(57B)	0.9800
C(57)-H(57C)	0.9800
C(58)-H(58A)	0.9800
C(58)-H(58B)	0.9800
C(58)-H(58C)	0.9800
C(59)-C(60)	1.464(14)
C(59)-H(59)	0.9500
C(60)-C(65)	1.388(15)
C(60)-C(61)	1.402(15)
C(61)-C(62)	1.367(17)
C(61)-H(61)	0.9500
C(62)-C(63)	1.380(19)
C(62)-H(62)	0.9500
C(63)-C(64)	1.399(18)
C(63)-H(63)	0.9500
C(64)-C(65)	1.371(15)
C(64)-H(64)	0.9500
C(66)-C(68)	1.515(14)
C(66)-C(67)	1.534(14)
C(66)-H(66)	1.0000
C(67)-H(67A)	0.9800
C(67)-H(67B)	0.9800
C(67)-H(67C)	0.9800
C(68)-H(68A)	0.9800
C(68)-H(68B)	0.9800
C(68)-H(68C)	0.9800

C(69)-C(70)	1.370(15)
C(69)-C(74)	1.380(15)
C(70)-C(71)	1.394(16)
C(71)-C(72)	1.375(16)
C(71)-H(71)	0.9500
C(72)-C(73)	1.349(16)
C(72)-H(72)	0.9500
C(73)-C(74)	1.417(14)
C(1S)-Cl(2S)	1.75(2)
C(1S)-Cl(1S)	1.78(2)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(1T)-Cl(2T)	1.76(2)
C(1T)-Cl(1T)	1.78(3)
C(1T)-H(1T1)	0.9900
C(1T)-H(1T2)	0.9900

C(22)-Ru(1)-C(1)	102.2(4)
C(22)-Ru(1)-S(2)	95.2(3)
C(1)-Ru(1)-S(2)	88.1(3)
C(22)-Ru(1)-S(1)	113.9(3)
C(1)-Ru(1)-S(1)	143.9(3)
S(2)-Ru(1)-S(1)	87.94(9)
C(22)-Ru(1)-O(1)	78.0(4)
C(1)-Ru(1)-O(1)	95.8(3)
S(2)-Ru(1)-O(1)	172.72(18)
S(1)-Ru(1)-O(1)	92.44(17)
C(32)-S(1)-Ru(1)	105.7(4)
C(37)-S(2)-Ru(1)	106.2(4)
C(28)-O(1)-C(29)	118.2(7)
C(28)-O(1)-Ru(1)	109.5(5)
C(29)-O(1)-Ru(1)	121.4(6)
C(1)-N(1)-C(4)	127.0(8)
C(1)-N(1)-C(2)	112.8(8)
C(4)-N(1)-C(2)	119.7(7)
C(1)-N(2)-C(13)	127.6(8)

C(1)-N(2)-C(3)	111.9(8)
C(13)-N(2)-C(3)	117.1(7)
N(1)-C(1)-N(2)	108.1(8)
N(1)-C(1)-Ru(1)	130.4(7)
N(2)-C(1)-Ru(1)	121.5(6)
N(1)-C(2)-C(3)	103.6(7)
N(1)-C(2)-H(2A)	111.0
C(3)-C(2)-H(2A)	111.0
N(1)-C(2)-H(2B)	111.0
C(3)-C(2)-H(2B)	111.0
H(2A)-C(2)-H(2B)	109.0
N(2)-C(3)-C(2)	102.5(8)
N(2)-C(3)-H(3A)	111.3
C(2)-C(3)-H(3A)	111.3
N(2)-C(3)-H(3B)	111.3
C(2)-C(3)-H(3B)	111.3
H(3A)-C(3)-H(3B)	109.2
C(5)-C(4)-C(9)	121.5(10)
C(5)-C(4)-N(1)	119.0(9)
C(9)-C(4)-N(1)	119.2(9)
C(4)-C(5)-C(6)	119.3(10)
C(4)-C(5)-C(10)	120.7(10)
C(6)-C(5)-C(10)	120.0(10)
C(7)-C(6)-C(5)	119.8(11)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(8)-C(7)-C(6)	120.0(10)
C(8)-C(7)-C(11)	121.1(11)
C(6)-C(7)-C(11)	118.9(11)
C(7)-C(8)-C(9)	121.2(10)
C(7)-C(8)-H(8)	119.4
C(9)-C(8)-H(8)	119.4
C(4)-C(9)-C(8)	118.1(10)
C(4)-C(9)-C(12)	120.9(9)
C(8)-C(9)-C(12)	120.9(9)
C(5)-C(10)-H(10A)	109.5

C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(7)-C(11)-H(11A)	109.5
C(7)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(7)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(18)-C(13)-C(14)	120.7(9)
C(18)-C(13)-N(2)	119.1(9)
C(14)-C(13)-N(2)	119.8(9)
C(15)-C(14)-C(13)	117.6(9)
C(15)-C(14)-C(19)	120.6(9)
C(13)-C(14)-C(19)	121.8(9)
C(14)-C(15)-C(16)	123.2(9)
C(14)-C(15)-H(15)	118.4
C(16)-C(15)-H(15)	118.4
C(17)-C(16)-C(15)	117.6(9)
C(17)-C(16)-C(20)	120.8(9)
C(15)-C(16)-C(20)	121.5(9)
C(18)-C(17)-C(16)	121.7(9)
C(18)-C(17)-H(17)	119.1
C(16)-C(17)-H(17)	119.1
C(17)-C(18)-C(13)	119.1(9)
C(17)-C(18)-C(21)	119.1(9)
C(13)-C(18)-C(21)	121.4(9)
C(14)-C(19)-H(19A)	109.5

C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(16)-C(20)-H(20A)	109.5
C(16)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(16)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-Ru(1)	121.1(7)
C(23)-C(22)-H(22)	119.4
Ru(1)-C(22)-H(22)	119.4
C(24)-C(23)-C(28)	119.1(10)
C(24)-C(23)-C(22)	123.0(10)
C(28)-C(23)-C(22)	117.7(9)
C(23)-C(24)-C(25)	120.1(11)
C(23)-C(24)-H(24)	119.9
C(25)-C(24)-H(24)	119.9
C(26)-C(25)-C(24)	120.2(11)
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9
C(25)-C(26)-C(27)	120.8(11)
C(25)-C(26)-H(26)	119.6
C(27)-C(26)-H(26)	119.6
C(28)-C(27)-C(26)	119.1(11)
C(28)-C(27)-H(27)	120.4
C(26)-C(27)-H(27)	120.4
C(27)-C(28)-O(1)	125.6(10)

C(27)-C(28)-C(23)	120.7(10)
O(1)-C(28)-C(23)	113.7(9)
C(31)-C(29)-O(1)	112.7(8)
C(31)-C(29)-C(30)	114.7(9)
O(1)-C(29)-C(30)	111.0(9)
C(31)-C(29)-H(29)	105.9
O(1)-C(29)-H(29)	105.9
C(30)-C(29)-H(29)	105.9
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(33)-C(32)-C(37)	119.1(10)
C(33)-C(32)-S(1)	122.4(9)
C(37)-C(32)-S(1)	118.5(8)
C(34)-C(33)-C(32)	123.3(11)
C(34)-C(33)-Cl(1)	112.4(9)
C(32)-C(33)-Cl(1)	124.2(10)
C(34)-C(33)-Br(1X)	118.2(8)
C(32)-C(33)-Br(1X)	118.4(9)
C(33)-C(34)-C(35)	118.4(10)
C(33)-C(34)-H(34)	120.8
C(35)-C(34)-H(34)	120.8
C(36)-C(35)-C(34)	119.3(10)
C(36)-C(35)-H(35)	120.4
C(34)-C(35)-H(35)	120.4
C(35)-C(36)-C(37)	123.8(11)
C(35)-C(36)-Cl(1X)	113.2(9)

C(37)-C(36)-Cl(1X)	122.5(9)
C(35)-C(36)-Br(1)	119.4(9)
C(37)-C(36)-Br(1)	116.7(8)
C(36)-C(37)-C(32)	116.0(10)
C(36)-C(37)-S(2)	122.9(9)
C(32)-C(37)-S(2)	121.1(8)
C(59)-Ru(2)-C(38)	98.6(4)
C(59)-Ru(2)-S(3)	96.7(3)
C(38)-Ru(2)-S(3)	88.6(3)
C(59)-Ru(2)-O(2)	78.9(4)
C(38)-Ru(2)-O(2)	96.1(3)
S(3)-Ru(2)-O(2)	173.96(19)
C(59)-Ru(2)-S(4)	112.9(3)
C(38)-Ru(2)-S(4)	148.5(3)
S(3)-Ru(2)-S(4)	88.17(10)
O(2)-Ru(2)-S(4)	89.76(18)
C(74)-S(3)-Ru(2)	106.0(4)
C(69)-S(4)-Ru(2)	104.8(4)
C(65)-O(2)-C(66)	122.1(8)
C(65)-O(2)-Ru(2)	110.6(6)
C(66)-O(2)-Ru(2)	122.4(6)
C(38)-N(3)-C(41)	129.0(8)
C(38)-N(3)-C(39)	113.6(8)
C(41)-N(3)-C(39)	116.1(8)
C(38)-N(4)-C(50)	131.3(8)
C(38)-N(4)-C(40)	112.9(8)
C(50)-N(4)-C(40)	115.5(7)
N(4)-C(38)-N(3)	107.9(8)
N(4)-C(38)-Ru(2)	123.1(7)
N(3)-C(38)-Ru(2)	129.1(7)
N(3)-C(39)-C(40)	102.7(8)
N(3)-C(39)-H(39A)	111.2
C(40)-C(39)-H(39A)	111.2
N(3)-C(39)-H(39B)	111.2
C(40)-C(39)-H(39B)	111.2
H(39A)-C(39)-H(39B)	109.1

N(4)-C(40)-C(39)	102.6(8)
N(4)-C(40)-H(40A)	111.3
C(39)-C(40)-H(40A)	111.3
N(4)-C(40)-H(40B)	111.3
C(39)-C(40)-H(40B)	111.3
H(40A)-C(40)-H(40B)	109.2
C(46)-C(41)-C(42)	123.7(10)
C(46)-C(41)-N(3)	118.0(10)
C(42)-C(41)-N(3)	117.9(10)
C(41)-C(42)-C(43)	116.3(11)
C(41)-C(42)-C(47)	122.4(10)
C(43)-C(42)-C(47)	121.3(11)
C(44)-C(43)-C(42)	121.8(12)
C(44)-C(43)-H(43)	119.1
C(42)-C(43)-H(43)	119.1
C(43)-C(44)-C(45)	119.3(11)
C(43)-C(44)-C(48)	119.7(14)
C(45)-C(44)-C(48)	121.0(14)
C(46)-C(45)-C(44)	120.8(12)
C(46)-C(45)-H(45)	119.6
C(44)-C(45)-H(45)	119.6
C(41)-C(46)-C(45)	118.0(11)
C(41)-C(46)-C(49)	122.0(10)
C(45)-C(46)-C(49)	120.0(11)
C(42)-C(47)-H(47A)	109.5
C(42)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(42)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(44)-C(48)-H(48A)	109.5
C(44)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(44)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5

C(46)-C(49)-H(49A)	109.5
C(46)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(46)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(51)-C(50)-C(55)	121.2(9)
C(51)-C(50)-N(4)	118.9(9)
C(55)-C(50)-N(4)	118.7(9)
C(52)-C(51)-C(50)	117.8(9)
C(52)-C(51)-C(56)	119.6(9)
C(50)-C(51)-C(56)	122.6(9)
C(53)-C(52)-C(51)	123.4(10)
C(53)-C(52)-H(52)	118.3
C(51)-C(52)-H(52)	118.3
C(52)-C(53)-C(54)	117.4(10)
C(52)-C(53)-C(57)	122.3(10)
C(54)-C(53)-C(57)	120.3(10)
C(55)-C(54)-C(53)	121.3(10)
C(55)-C(54)-H(54)	119.3
C(53)-C(54)-H(54)	119.3
C(54)-C(55)-C(50)	118.7(9)
C(54)-C(55)-C(58)	119.9(9)
C(50)-C(55)-C(58)	121.3(9)
C(51)-C(56)-H(56A)	109.5
C(51)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(51)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
C(53)-C(57)-H(57A)	109.5
C(53)-C(57)-H(57B)	109.5
H(57A)-C(57)-H(57B)	109.5
C(53)-C(57)-H(57C)	109.5
H(57A)-C(57)-H(57C)	109.5
H(57B)-C(57)-H(57C)	109.5

C(55)-C(58)-H(58A)	109.5
C(55)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58B)	109.5
C(55)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58C)	109.5
H(58B)-C(58)-H(58C)	109.5
C(60)-C(59)-Ru(2)	119.0(7)
C(60)-C(59)-H(59)	120.5
Ru(2)-C(59)-H(59)	120.5
C(65)-C(60)-C(61)	118.3(10)
C(65)-C(60)-C(59)	119.3(9)
C(61)-C(60)-C(59)	122.4(10)
C(62)-C(61)-C(60)	121.1(12)
C(62)-C(61)-H(61)	119.5
C(60)-C(61)-H(61)	119.5
C(61)-C(62)-C(63)	119.4(11)
C(61)-C(62)-H(62)	120.3
C(63)-C(62)-H(62)	120.3
C(62)-C(63)-C(64)	121.0(11)
C(62)-C(63)-H(63)	119.5
C(64)-C(63)-H(63)	119.5
C(65)-C(64)-C(63)	118.6(12)
C(65)-C(64)-H(64)	120.7
C(63)-C(64)-H(64)	120.7
C(64)-C(65)-C(60)	121.7(11)
C(64)-C(65)-O(2)	126.0(10)
C(60)-C(65)-O(2)	112.3(8)
O(2)-C(66)-C(68)	112.3(9)
O(2)-C(66)-C(67)	110.7(9)
C(68)-C(66)-C(67)	114.4(9)
O(2)-C(66)-H(66)	106.3
C(68)-C(66)-H(66)	106.3
C(67)-C(66)-H(66)	106.3
C(66)-C(67)-H(67A)	109.5
C(66)-C(67)-H(67B)	109.5
H(67A)-C(67)-H(67B)	109.5

C(66)-C(67)-H(67C)	109.5
H(67A)-C(67)-H(67C)	109.5
H(67B)-C(67)-H(67C)	109.5
C(66)-C(68)-H(68A)	109.5
C(66)-C(68)-H(68B)	109.5
H(68A)-C(68)-H(68B)	109.5
C(66)-C(68)-H(68C)	109.5
H(68A)-C(68)-H(68C)	109.5
H(68B)-C(68)-H(68C)	109.5
C(70)-C(69)-C(74)	119.2(10)
C(70)-C(69)-S(4)	121.6(9)
C(74)-C(69)-S(4)	119.0(8)
C(69)-C(70)-C(71)	123.1(11)
C(69)-C(70)-Cl(2X)	127.5(10)
C(71)-C(70)-Cl(2X)	109.5(9)
C(69)-C(70)-Br(2)	120.0(9)
C(71)-C(70)-Br(2)	116.9(9)
C(72)-C(71)-C(70)	117.8(10)
C(72)-C(71)-H(71)	121.1
C(70)-C(71)-H(71)	121.1
C(73)-C(72)-C(71)	119.8(11)
C(73)-C(72)-H(72)	120.1
C(71)-C(72)-H(72)	120.1
C(72)-C(73)-C(74)	123.0(11)
C(72)-C(73)-Cl(2)	113.8(10)
C(74)-C(73)-Cl(2)	123.1(10)
C(72)-C(73)-Br(2X)	120.5(9)
C(74)-C(73)-Br(2X)	116.5(9)
C(69)-C(74)-C(73)	117.2(10)
C(69)-C(74)-S(3)	121.8(8)
C(73)-C(74)-S(3)	121.0(8)
Cl(2S)-C(1S)-Cl(1S)	117.7(13)
Cl(2S)-C(1S)-H(1S1)	107.9
Cl(1S)-C(1S)-H(1S1)	107.9
Cl(2S)-C(1S)-H(1S2)	107.9
Cl(1S)-C(1S)-H(1S2)	107.9

H(1S1)-C(1S)-H(1S2)	107.2
Cl(2T)-C(1T)-Cl(1T)	108(2)
Cl(2T)-C(1T)-H(1T1)	110.1
Cl(1T)-C(1T)-H(1T1)	110.1
Cl(2T)-C(1T)-H(1T2)	110.1
Cl(1T)-C(1T)-H(1T2)	110.1
H(1T1)-C(1T)-H(1T2)	108.5

Symmetry transformations used to generate equivalent atoms:

Table 4. **Anisotropic displacement parameters ($Å^2$ x 10^3) for Ru-11. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	34(1)	26(1)	14(1)	0(1)	10(1)	0(1)
Cl(1)	32(2)	29(2)	35(3)	3(2)	18(2)	2(3)
Br(1)	62(1)	30(1)	38(1)	3(1)	23(1)	2(2)
Cl(1X)	32(2)	29(2)	35(3)	3(2)	18(2)	2(3)
Br(1X)	62(1)	30(1)	38(1)	3(1)	23(1)	2(2)
S(1)	36(1)	33(1)	19(1)	-1(1)	13(1)	2(1)
S(2)	51(1)	24(1)	21(1)	1(1)	13(1)	2(1)
O(1)	37(3)	25(3)	24(4)	-2(3)	15(3)	-6(3)
N(1)	40(3)	37(3)	15(3)	0(2)	12(2)	1(2)
N(2)	35(4)	33(4)	13(4)	-1(3)	9(3)	1(3)
C(1)	37(4)	28(4)	17(4)	1(4)	13(3)	1(4)
C(2)	44(5)	53(6)	18(4)	-3(5)	16(4)	-1(5)
C(3)	47(6)	58(8)	20(5)	-1(5)	17(4)	9(5)
C(4)	31(4)	41(5)	18(4)	-2(4)	15(3)	-2(4)
C(5)	59(4)	40(4)	16(4)	0(3)	23(3)	4(3)
C(6)	53(5)	42(6)	22(5)	-4(4)	20(4)	11(4)
C(7)	41(5)	64(7)	26(6)	-3(5)	20(4)	5(5)
C(8)	39(5)	53(6)	17(5)	-6(4)	14(4)	-5(4)
C(9)	44(5)	43(5)	18(5)	-6(4)	16(4)	-9(4)
C(10)	53(6)	34(5)	28(6)	-7(5)	19(4)	4(4)
C(11)	46(6)	74(9)	27(6)	-2(6)	13(5)	7(5)
C(12)	44(6)	42(5)	33(6)	-1(5)	17(5)	-10(4)
C(13)	40(4)	36(4)	12(4)	2(4)	11(4)	0(4)
C(14)	50(5)	25(5)	18(5)	0(4)	17(4)	3(4)
C(15)	50(5)	28(5)	13(4)	6(4)	14(4)	12(4)
C(16)	46(5)	32(5)	20(5)	2(4)	14(4)	4(4)
C(17)	41(4)	31(5)	16(4)	-2(4)	8(4)	-5(4)
C(18)	44(5)	29(5)	19(5)	-1(4)	7(4)	2(4)
C(19)	53(6)	33(5)	25(6)	0(5)	10(5)	0(4)
C(20)	47(5)	41(6)	27(5)	3(5)	9(4)	-1(5)
C(21)	48(6)	38(6)	39(7)	0(5)	11(5)	4(4)

C(22)	38(3)	39(3)	4(3)	-3(3)	2(2)	0(3)
C(23)	52(4)	35(3)	18(3)	-1(3)	19(3)	0(3)
C(24)	43(5)	49(6)	27(6)	-2(5)	17(4)	1(4)
C(25)	44(6)	65(7)	30(6)	7(5)	15(5)	6(5)
C(26)	58(6)	46(6)	39(7)	7(5)	21(5)	16(5)
C(27)	54(6)	39(5)	32(6)	1(5)	18(4)	6(4)
C(28)	43(5)	35(5)	24(5)	3(4)	19(4)	3(4)
C(29)	42(5)	34(5)	23(5)	3(4)	6(4)	-3(4)
C(30)	72(8)	35(6)	28(6)	-7(5)	4(5)	-6(5)
C(31)	59(7)	43(6)	27(6)	-2(5)	18(5)	-11(5)
C(32)	29(5)	41(5)	20(5)	-5(4)	-3(3)	9(4)
C(33)	39(5)	46(5)	22(5)	-3(4)	9(4)	1(4)
C(34)	45(6)	44(5)	29(6)	-5(5)	10(4)	13(4)
C(35)	56(6)	37(5)	19(5)	-4(4)	0(4)	14(4)
C(36)	56(6)	39(5)	21(5)	2(4)	11(4)	6(4)
C(37)	47(6)	35(4)	15(5)	0(4)	4(4)	9(4)
Ru(2)	36(1)	30(1)	16(1)	0(1)	9(1)	0(1)
Cl(2)	33(3)	30(3)	40(4)	-6(2)	17(2)	-4(2)
Br(2)	48(2)	54(2)	40(2)	-5(1)	22(1)	-7(2)
Cl(2X)	33(3)	30(3)	40(4)	-6(2)	17(2)	-4(2)
Br(2X)	48(2)	54(2)	40(2)	-5(1)	22(1)	-7(2)
S(3)	39(1)	41(1)	28(1)	2(1)	10(1)	-6(1)
S(4)	46(1)	34(1)	21(1)	-3(1)	14(1)	3(1)
O(2)	40(3)	34(3)	21(3)	0(3)	15(3)	-4(3)
N(3)	40(3)	37(3)	15(3)	0(2)	12(2)	1(2)
N(4)	39(4)	35(4)	16(4)	3(3)	10(3)	1(3)
C(38)	35(5)	39(5)	14(4)	1(3)	10(3)	1(4)
C(39)	52(6)	36(5)	19(5)	3(4)	6(4)	5(4)
C(40)	45(5)	44(6)	14(4)	2(4)	12(4)	1(5)
C(41)	60(5)	38(5)	14(5)	0(4)	18(4)	9(4)
C(42)	59(4)	40(4)	16(4)	0(3)	23(3)	4(3)
C(43)	96(7)	30(5)	25(6)	-1(4)	35(5)	3(5)
C(44)	101(8)	46(6)	26(6)	10(5)	32(6)	33(6)
C(45)	61(6)	59(6)	21(5)	10(5)	21(5)	28(5)
C(46)	59(6)	48(6)	19(5)	5(5)	22(4)	16(5)
C(47)	73(7)	37(6)	27(6)	-2(5)	20(5)	-10(5)

C(48)	148(14)	53(8)	55(9)	25(7)	48(9)	51(9)
C(49)	44(6)	65(7)	32(6)	11(6)	14(5)	12(5)
C(50)	41(5)	39(5)	12(4)	0(4)	7(4)	0(4)
C(51)	42(5)	39(5)	9(4)	6(4)	6(4)	-5(4)
C(52)	51(5)	38(5)	19(5)	1(4)	16(4)	-7(4)
C(53)	49(5)	40(5)	14(5)	4(4)	10(4)	3(4)
C(54)	45(5)	41(5)	16(5)	-2(4)	13(4)	1(4)
C(55)	40(5)	38(5)	13(5)	-1(4)	6(4)	-3(4)
C(56)	46(6)	53(7)	31(6)	5(5)	13(5)	-7(5)
C(57)	65(7)	44(6)	27(5)	6(5)	15(5)	8(5)
C(58)	41(5)	36(5)	31(6)	-1(5)	8(4)	-4(4)
C(59)	38(3)	39(3)	4(3)	-3(3)	2(2)	0(3)
C(60)	52(4)	35(3)	18(3)	-1(3)	19(3)	0(3)
C(61)	73(7)	36(5)	14(5)	2(4)	17(5)	4(5)
C(62)	90(7)	37(6)	16(5)	2(4)	20(5)	-3(5)
C(63)	94(8)	37(6)	25(6)	0(5)	20(6)	-25(6)
C(64)	64(7)	51(6)	21(6)	0(5)	12(5)	-20(5)
C(65)	56(5)	37(5)	15(5)	1(4)	16(4)	-11(4)
C(66)	37(5)	57(6)	28(5)	-1(5)	10(4)	-7(5)
C(67)	44(5)	53(7)	27(5)	1(5)	8(4)	-9(5)
C(68)	44(6)	72(8)	33(6)	-15(6)	17(4)	-9(6)
C(69)	50(5)	26(5)	20(5)	8(4)	4(4)	5(4)
C(70)	58(6)	41(6)	18(5)	5(4)	11(4)	4(4)
C(71)	62(6)	30(5)	24(5)	-1(4)	5(4)	1(4)
C(72)	56(6)	38(6)	29(6)	4(4)	3(4)	-7(5)
C(73)	48(5)	47(6)	23(5)	6(4)	4(4)	-4(5)
C(74)	39(5)	38(5)	15(5)	6(4)	-6(4)	-4(4)
C(1S)	105(15)	38(8)	44(9)	12(7)	16(9)	1(10)
Cl(1S)	128(9)	51(3)	47(3)	8(2)	14(5)	-1(5)
Cl(2S)	102(12)	49(3)	71(9)	-1(5)	43(7)	1(5)
C(1T)	105(15)	38(8)	44(9)	12(7)	16(9)	1(10)
Cl(1T)	128(9)	51(3)	47(3)	8(2)	14(5)	-1(5)
Cl(2T)	102(12)	49(3)	71(9)	-1(5)	43(7)	1(5)

Table 5. **Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Ru-11.**

	x	y	z	U(eq)
H(2A)	6315	8817	8637	44
H(2B)	6549	9973	8837	44
H(3A)	7924	9621	9183	48
H(3B)	7666	8454	9138	48
H(6)	4701	11898	6755	45
H(8)	4049	9024	6248	42
H(10A)	6378	11580	8187	55
H(10B)	6054	12352	7486	55
H(10C)	6813	11600	7443	55
H(11A)	3063	10275	5737	73
H(11B)	3462	11332	5582	73
H(11C)	3086	11169	6352	73
H(12A)	6001	7970	6815	57
H(12B)	5013	7702	6637	57
H(12C)	5515	7875	7523	57
H(15)	10317	7247	8556	35
H(17)	10516	10225	8343	35
H(19A)	8727	6575	7860	55
H(19B)	8067	7190	8244	55
H(19C)	8859	6649	8795	55
H(20A)	11736	8892	9199	58
H(20B)	11752	9028	8289	58
H(20C)	11680	7933	8640	58
H(21A)	8735	10933	8588	62
H(21B)	8433	10783	7659	62
H(21C)	9344	11256	8015	62
H(22)	6161	8898	5575	33
H(24)	5001	10009	4844	46
H(25)	4483	11623	4522	54
H(26)	5314	13000	4957	55

H(27)	6687	12801	5729	48
H(29)	8714	11270	6318	40
H(30A)	8847	12881	6708	70
H(30B)	8141	12435	7133	70
H(30C)	7867	13121	6368	70
H(31A)	8180	11252	4976	62
H(31B)	8759	12215	5241	62
H(31C)	7748	12319	5032	62
H(34)	9712	6427	4493	47
H(35)	8989	5246	5094	46
H(39A)	2192	3300	6170	43
H(39B)	3162	3681	6358	43
H(40A)	2694	5220	5996	40
H(40B)	1724	4861	5899	40
H(43)	2485	563	8028	57
H(45)	4763	1929	8607	54
H(47A)	1283	2719	7462	67
H(47B)	1219	1534	7567	67
H(47C)	1424	1983	6776	67
H(48A)	4055	71	9255	122
H(48B)	4666	75	8642	122
H(48C)	3756	-449	8414	122
H(49A)	4297	3947	7439	69
H(49B)	4975	3526	8175	69
H(49C)	4231	4251	8313	69
H(52)	2659	8565	6778	41
H(54)	270	7667	6746	40
H(56A)	3607	6945	6445	64
H(56B)	3623	6191	7161	64
H(56C)	3833	7350	7329	64
H(57A)	571	9341	6185	67
H(57B)	1527	9741	6378	67
H(57C)	1013	9642	7066	67
H(58A)	6	6016	7136	54
H(58B)	768	5237	7387	54
H(58C)	338	5390	6479	54

H(59)	3508	3821	9394	33
H(61)	3342	2067	9920	47
H(62)	2491	745	10127	55
H(63)	1025	884	9743	61
H(64)	399	2358	9150	54
H(66)	405	5110	8621	48
H(67A)	-33	3802	7667	62
H(67B)	-783	4284	8014	62
H(67C)	-402	3218	8323	62
H(68A)	94	3716	9755	72
H(68B)	-374	4768	9552	72
H(68C)	611	4736	9964	72
H(71)	3395	8948	10945	47
H(72)	4544	8836	10324	50
H(1S1)	5498	5938	6999	74
H(1S2)	6451	6059	6900	74
H(1T1)	6614	6048	7101	74
H(1T2)	7232	5458	7800	74

Table 6. **Torsion angles [°] for Ru-11.**

C(4)-N(1)-C(1)-N(2)	-174.6(9)
C(2)-N(1)-C(1)-N(2)	-2.3(12)
C(4)-N(1)-C(1)-Ru(1)	2.7(15)
C(2)-N(1)-C(1)-Ru(1)	175.0(8)
C(13)-N(2)-C(1)-N(1)	-163.0(9)
C(3)-N(2)-C(1)-N(1)	-4.9(12)
C(13)-N(2)-C(1)-Ru(1)	19.4(14)
C(3)-N(2)-C(1)-Ru(1)	177.4(7)
C(1)-N(1)-C(2)-C(3)	8.3(12)
C(4)-N(1)-C(2)-C(3)	-178.8(9)
C(1)-N(2)-C(3)-C(2)	9.7(12)
C(13)-N(2)-C(3)-C(2)	170.2(9)
N(1)-C(2)-C(3)-N(2)	-10.0(11)
C(1)-N(1)-C(4)-C(5)	-100.6(12)
C(2)-N(1)-C(4)-C(5)	87.6(12)
C(1)-N(1)-C(4)-C(9)	84.7(12)
C(2)-N(1)-C(4)-C(9)	-87.1(11)
C(9)-C(4)-C(5)-C(6)	-0.8(14)
N(1)-C(4)-C(5)-C(6)	-175.4(8)
C(9)-C(4)-C(5)-C(10)	177.7(9)
N(1)-C(4)-C(5)-C(10)	3.1(13)
C(4)-C(5)-C(6)-C(7)	0.1(15)
C(10)-C(5)-C(6)-C(7)	-178.5(9)
C(5)-C(6)-C(7)-C(8)	0.6(15)
C(5)-C(6)-C(7)-C(11)	180.0(9)
C(6)-C(7)-C(8)-C(9)	-0.4(15)
C(11)-C(7)-C(8)-C(9)	-179.8(9)
C(5)-C(4)-C(9)-C(8)	1.0(14)
N(1)-C(4)-C(9)-C(8)	175.5(8)
C(5)-C(4)-C(9)-C(12)	-178.5(9)
N(1)-C(4)-C(9)-C(12)	-4.0(13)
C(7)-C(8)-C(9)-C(4)	-0.3(14)
C(7)-C(8)-C(9)-C(12)	179.2(9)
C(1)-N(2)-C(13)-C(18)	68.3(13)

C(3)-N(2)-C(13)-C(18)	-88.8(11)
C(1)-N(2)-C(13)-C(14)	-119.0(11)
C(3)-N(2)-C(13)-C(14)	83.9(11)
C(18)-C(13)-C(14)-C(15)	1.0(14)
N(2)-C(13)-C(14)-C(15)	-171.5(8)
C(18)-C(13)-C(14)-C(19)	178.7(9)
N(2)-C(13)-C(14)-C(19)	6.1(14)
C(13)-C(14)-C(15)-C(16)	-1.0(14)
C(19)-C(14)-C(15)-C(16)	-178.7(9)
C(14)-C(15)-C(16)-C(17)	0.5(14)
C(14)-C(15)-C(16)-C(20)	178.7(9)
C(15)-C(16)-C(17)-C(18)	-0.1(14)
C(20)-C(16)-C(17)-C(18)	-178.2(9)
C(16)-C(17)-C(18)-C(13)	0.2(14)
C(16)-C(17)-C(18)-C(21)	174.0(9)
C(14)-C(13)-C(18)-C(17)	-0.6(14)
N(2)-C(13)-C(18)-C(17)	172.0(8)
C(14)-C(13)-C(18)-C(21)	-174.4(9)
N(2)-C(13)-C(18)-C(21)	-1.7(13)
C(1)-Ru(1)-C(22)-C(23)	94.9(8)
S(2)-Ru(1)-C(22)-C(23)	-175.9(7)
S(1)-Ru(1)-C(22)-C(23)	-85.9(7)
O(1)-Ru(1)-C(22)-C(23)	1.4(7)
Ru(1)-C(22)-C(23)-C(24)	-177.1(7)
Ru(1)-C(22)-C(23)-C(28)	-2.9(12)
C(28)-C(23)-C(24)-C(25)	0.8(15)
C(22)-C(23)-C(24)-C(25)	175.0(9)
C(23)-C(24)-C(25)-C(26)	-0.9(16)
C(24)-C(25)-C(26)-C(27)	-0.1(17)
C(25)-C(26)-C(27)-C(28)	1.2(17)
C(26)-C(27)-C(28)-O(1)	-177.8(9)
C(26)-C(27)-C(28)-C(23)	-1.2(16)
C(29)-O(1)-C(28)-C(27)	-39.9(13)
Ru(1)-O(1)-C(28)-C(27)	175.3(8)
C(29)-O(1)-C(28)-C(23)	143.2(8)
Ru(1)-O(1)-C(28)-C(23)	-1.5(9)

C(24)-C(23)-C(28)-C(27)	0.3(14)
C(22)-C(23)-C(28)-C(27)	-174.2(9)
C(24)-C(23)-C(28)-O(1)	177.2(8)
C(22)-C(23)-C(28)-O(1)	2.8(12)
C(28)-O(1)-C(29)-C(31)	-44.5(12)
Ru(1)-O(1)-C(29)-C(31)	95.9(9)
C(28)-O(1)-C(29)-C(30)	85.7(10)
Ru(1)-O(1)-C(29)-C(30)	-133.8(7)
Ru(1)-S(1)-C(32)-C(33)	173.8(7)
Ru(1)-S(1)-C(32)-C(37)	-7.4(8)
C(37)-C(32)-C(33)-C(34)	-1.1(15)
S(1)-C(32)-C(33)-C(34)	177.6(8)
C(37)-C(32)-C(33)-Cl(1)	178.9(9)
S(1)-C(32)-C(33)-Cl(1)	-2.3(14)
C(37)-C(32)-C(33)-Br(1X)	175.5(7)
S(1)-C(32)-C(33)-Br(1X)	-5.8(12)
C(32)-C(33)-C(34)-C(35)	-0.7(16)
Cl(1)-C(33)-C(34)-C(35)	179.2(9)
Br(1X)-C(33)-C(34)-C(35)	-177.3(8)
C(33)-C(34)-C(35)-C(36)	1.0(15)
C(34)-C(35)-C(36)-C(37)	0.6(17)
C(34)-C(35)-C(36)-Cl(1X)	-172.5(9)
C(34)-C(35)-C(36)-Br(1)	178.4(8)
C(35)-C(36)-C(37)-C(32)	-2.3(16)
Cl(1X)-C(36)-C(37)-C(32)	170.1(8)
Br(1)-C(36)-C(37)-C(32)	179.8(7)
C(35)-C(36)-C(37)-S(2)	177.9(8)
Cl(1X)-C(36)-C(37)-S(2)	-9.7(14)
Br(1)-C(36)-C(37)-S(2)	0.0(12)
C(33)-C(32)-C(37)-C(36)	2.5(14)
S(1)-C(32)-C(37)-C(36)	-176.3(7)
C(33)-C(32)-C(37)-S(2)	-177.7(7)
S(1)-C(32)-C(37)-S(2)	3.5(11)
Ru(1)-S(2)-C(37)-C(36)	-177.8(8)
Ru(1)-S(2)-C(37)-C(32)	2.4(9)
C(50)-N(4)-C(38)-N(3)	175.8(9)

C(40)-N(4)-C(38)-N(3)	2.5(11)
C(50)-N(4)-C(38)-Ru(2)	-2.7(14)
C(40)-N(4)-C(38)-Ru(2)	-176.0(6)
C(41)-N(3)-C(38)-N(4)	167.9(9)
C(39)-N(3)-C(38)-N(4)	1.8(11)
C(41)-N(3)-C(38)-Ru(2)	-13.6(15)
C(39)-N(3)-C(38)-Ru(2)	-179.7(7)
C(38)-N(3)-C(39)-C(40)	-5.1(11)
C(41)-N(3)-C(39)-C(40)	-173.1(9)
C(38)-N(4)-C(40)-C(39)	-5.5(11)
C(50)-N(4)-C(40)-C(39)	-179.9(8)
N(3)-C(39)-C(40)-N(4)	5.8(10)
C(38)-N(3)-C(41)-C(46)	-77.2(13)
C(39)-N(3)-C(41)-C(46)	88.6(11)
C(38)-N(3)-C(41)-C(42)	109.0(11)
C(39)-N(3)-C(41)-C(42)	-85.2(11)
C(46)-C(41)-C(42)-C(43)	0.3(15)
N(3)-C(41)-C(42)-C(43)	173.8(8)
C(46)-C(41)-C(42)-C(47)	-178.1(10)
N(3)-C(41)-C(42)-C(47)	-4.7(14)
C(41)-C(42)-C(43)-C(44)	0.9(15)
C(47)-C(42)-C(43)-C(44)	179.3(10)
C(42)-C(43)-C(44)-C(45)	0.4(16)
C(42)-C(43)-C(44)-C(48)	-179.4(10)
C(43)-C(44)-C(45)-C(46)	-2.8(16)
C(48)-C(44)-C(45)-C(46)	176.9(10)
C(42)-C(41)-C(46)-C(45)	-2.7(15)
N(3)-C(41)-C(46)-C(45)	-176.1(9)
C(42)-C(41)-C(46)-C(49)	176.8(10)
N(3)-C(41)-C(46)-C(49)	3.4(14)
C(44)-C(45)-C(46)-C(41)	3.9(15)
C(44)-C(45)-C(46)-C(49)	-175.6(10)
C(38)-N(4)-C(50)-C(51)	108.8(12)
C(40)-N(4)-C(50)-C(51)	-78.0(11)
C(38)-N(4)-C(50)-C(55)	-83.7(13)
C(40)-N(4)-C(50)-C(55)	89.5(10)

C(55)-C(50)-C(51)-C(52)	3.8(14)
N(4)-C(50)-C(51)-C(52)	170.9(8)
C(55)-C(50)-C(51)-C(56)	-175.9(9)
N(4)-C(50)-C(51)-C(56)	-8.7(14)
C(50)-C(51)-C(52)-C(53)	-3.0(14)
C(56)-C(51)-C(52)-C(53)	176.6(9)
C(51)-C(52)-C(53)-C(54)	1.4(15)
C(51)-C(52)-C(53)-C(57)	-178.6(9)
C(52)-C(53)-C(54)-C(55)	-0.4(14)
C(57)-C(53)-C(54)-C(55)	179.6(9)
C(53)-C(54)-C(55)-C(50)	1.1(14)
C(53)-C(54)-C(55)-C(58)	-179.1(9)
C(51)-C(50)-C(55)-C(54)	-2.9(14)
N(4)-C(50)-C(55)-C(54)	-170.1(8)
C(51)-C(50)-C(55)-C(58)	177.3(9)
N(4)-C(50)-C(55)-C(58)	10.2(13)
C(38)-Ru(2)-C(59)-C(60)	-95.7(7)
S(3)-Ru(2)-C(59)-C(60)	174.7(7)
O(2)-Ru(2)-C(59)-C(60)	-1.1(7)
S(4)-Ru(2)-C(59)-C(60)	83.9(7)
Ru(2)-C(59)-C(60)-C(65)	0.9(12)
Ru(2)-C(59)-C(60)-C(61)	178.8(7)
C(65)-C(60)-C(61)-C(62)	-0.3(15)
C(59)-C(60)-C(61)-C(62)	-178.2(9)
C(60)-C(61)-C(62)-C(63)	0.1(16)
C(61)-C(62)-C(63)-C(64)	-0.1(17)
C(62)-C(63)-C(64)-C(65)	0.3(17)
C(63)-C(64)-C(65)-C(60)	-0.5(16)
C(63)-C(64)-C(65)-O(2)	177.5(10)
C(61)-C(60)-C(65)-C(64)	0.5(15)
C(59)-C(60)-C(65)-C(64)	178.5(10)
C(61)-C(60)-C(65)-O(2)	-177.7(8)
C(59)-C(60)-C(65)-O(2)	0.3(12)
C(66)-O(2)-C(65)-C(64)	25.0(14)
Ru(2)-O(2)-C(65)-C(64)	-179.2(9)
C(66)-O(2)-C(65)-C(60)	-156.9(8)

Ru(2)-O(2)-C(65)-C(60)	-1.1(9)
C(65)-O(2)-C(66)-C(68)	49.7(13)
Ru(2)-O(2)-C(66)-C(68)	-103.2(10)
C(65)-O(2)-C(66)-C(67)	-79.5(11)
Ru(2)-O(2)-C(66)-C(67)	127.5(8)
Ru(2)-S(4)-C(69)-C(70)	179.5(8)
Ru(2)-S(4)-C(69)-C(74)	5.1(8)
C(74)-C(69)-C(70)-C(71)	-1.4(15)
S(4)-C(69)-C(70)-C(71)	-175.8(8)
C(74)-C(69)-C(70)-Cl(2X)	178.0(9)
S(4)-C(69)-C(70)-Cl(2X)	3.6(14)
C(74)-C(69)-C(70)-Br(2)	177.3(8)
S(4)-C(69)-C(70)-Br(2)	2.9(12)
C(69)-C(70)-C(71)-C(72)	0.8(16)
Cl(2X)-C(70)-C(71)-C(72)	-178.6(9)
Br(2)-C(70)-C(71)-C(72)	-177.9(8)
C(70)-C(71)-C(72)-C(73)	-0.1(16)
C(71)-C(72)-C(73)-C(74)	-0.2(17)
C(71)-C(72)-C(73)-Cl(2)	175.5(9)
C(71)-C(72)-C(73)-Br(2X)	179.0(8)
C(70)-C(69)-C(74)-C(73)	1.1(14)
S(4)-C(69)-C(74)-C(73)	175.6(7)
C(70)-C(69)-C(74)-S(3)	-178.8(7)
S(4)-C(69)-C(74)-S(3)	-4.3(12)
C(72)-C(73)-C(74)-C(69)	-0.3(15)
Cl(2)-C(73)-C(74)-C(69)	-175.6(9)
Br(2X)-C(73)-C(74)-C(69)	-179.5(7)
C(72)-C(73)-C(74)-S(3)	179.5(9)
Cl(2)-C(73)-C(74)-S(3)	4.3(13)
Br(2X)-C(73)-C(74)-S(3)	0.4(11)
Ru(2)-S(3)-C(74)-C(69)	1.0(9)
Ru(2)-S(3)-C(74)-C(73)	-178.8(7)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure for Ru-12

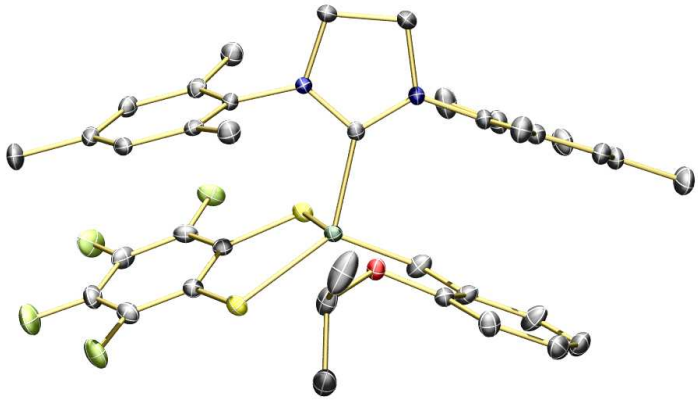

Table 1. **Crystal data and structure refinement for Ru-12.**

Identification code	$C_{37}H_{38}F_4N_2ORuS_2$	
Empirical formula	$C_{37}H_{38}F_4N_2ORuS_2$	
Formula weight	767.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.1440(5) Å	α= 92.458(3)°.
	b = 10.9170(5) Å	β= 102.025(3)°.
	c = 17.5734(8) Å	γ = 116.998(2)°.
Volume	1674.75(14) $Å^3$	
Z	2	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	0.649 mm^{-1}	
F(000)	788	
Crystal size	0.400 x 0.120 x 0.060 mm^3	
Theta range for data collection	2.120 to 28.416°.	
Index ranges	-13<=h<=13, -14<=k<=14, -23<=l<=23	
Reflections collected	62314	
Independent reflections	8397 [R(int) = 0.0461]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6403	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	8397 / 0 / 436
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0582
R indices (all data)	R1 = 0.0359, wR2 = 0.0613
Extinction coefficient	na
Largest diff. peak and hole	0.419 and -0.522 e.$Å^{-3}$

Table 2. **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Ru-12. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.**

	x	y	z	U(eq)
Ru(1)	3624(1)	276(1)	2741(1)	12(1)
S(1)	1141(1)	-138(1)	2214(1)	16(1)
S(2)	2717(1)	-2060(1)	2700(1)	16(1)
F(1)	620(1)	-5042(1)	2066(1)	24(1)
F(2)	-2298(1)	-6213(1)	1205(1)	31(1)
F(3)	-3649(1)	-4590(1)	773(1)	32(1)
F(4)	-2106(1)	-1828(1)	1280(1)	27(1)
O(1)	4501(1)	2617(1)	2966(1)	15(1)
N(1)	6917(2)	943(2)	2672(1)	16(1)
N(2)	5188(2)	49(2)	1557(1)	16(1)
C(1)	5416(2)	434(2)	2330(1)	13(1)
C(2)	7806(2)	925(2)	2108(1)	23(1)
C(3)	6604(2)	380(2)	1318(1)	17(1)
C(4)	7637(2)	1219(2)	3499(1)	17(1)
C(5)	8553(2)	2596(2)	3872(1)	17(1)
C(6)	9304(2)	2836(2)	4665(1)	20(1)
C(7)	9166(2)	1758(2)	5087(1)	22(1)
C(8)	8261(2)	398(2)	4694(1)	24(1)
C(9)	7506(2)	103(2)	3899(1)	20(1)
C(10)	8735(2)	3800(2)	3435(1)	22(1)
C(11)	9952(2)	2046(2)	5954(1)	31(1)
C(12)	6596(2)	-1384(2)	3485(1)	29(1)
C(13)	3732(2)	-602(2)	985(1)	14(1)
C(14)	2972(2)	-2049(2)	771(1)	16(1)
C(15)	1537(2)	-2654(2)	240(1)	18(1)
C(16)	874(2)	-1863(2)	-87(1)	17(1)
C(17)	1699(2)	-426(2)	105(1)	16(1)
C(18)	3144(2)	229(2)	630(1)	14(1)
C(19)	3663(2)	-2957(2)	1077(1)	22(1)
C(20)	-690(2)	-2561(2)	-654(1)	25(1)

C(21)	4082(2)	1788(2)	772(1)	20(1)
C(22)	4518(2)	686(2)	3805(1)	21(1)
C(23)	5237(2)	2108(2)	4209(1)	18(1)
C(24)	5989(2)	2518(2)	5012(1)	25(1)
C(25)	6693(2)	3895(2)	5355(1)	24(1)
C(26)	6657(2)	4887(2)	4900(1)	23(1)
C(27)	5921(2)	4520(2)	4101(1)	20(1)
C(28)	5222(2)	3131(2)	3762(1)	16(1)
C(29)	3627(2)	3246(2)	2514(1)	22(1)
C(30)	4672(3)	4581(2)	2256(1)	38(1)
C(31)	2546(2)	3373(2)	2949(1)	31(1)
C(32)	108(2)	-1958(2)	1950(1)	15(1)
C(33)	812(2)	-2787(2)	2156(1)	15(1)
C(34)	-35(2)	-4212(2)	1895(1)	18(1)
C(35)	-1518(2)	-4824(2)	1446(1)	21(1)
C(36)	-2206(2)	-4007(2)	1237(1)	21(1)
C(37)	-1400(2)	-2599(2)	1500(1)	19(1)

Table 3. **Bond lengths [Å] and angles [°] for Ru-12.**

Ru(1)-C(22)	1.836(2)
Ru(1)-C(1)	2.0317(17)
Ru(1)-S(2)	2.2759(5)
Ru(1)-O(1)	2.2770(12)
Ru(1)-S(1)	2.3160(5)
S(1)-C(32)	1.7571(18)
S(2)-C(33)	1.7464(18)
F(1)-C(34)	1.356(2)
F(2)-C(35)	1.349(2)
F(3)-C(36)	1.351(2)
F(4)-C(37)	1.353(2)
O(1)-C(28)	1.392(2)
O(1)-C(29)	1.481(2)
N(1)-C(1)	1.346(2)
N(1)-C(4)	1.435(2)
N(1)-C(2)	1.477(2)
N(2)-C(1)	1.344(2)
N(2)-C(13)	1.437(2)
N(2)-C(3)	1.471(2)
C(2)-C(3)	1.528(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.395(2)
C(4)-C(9)	1.401(3)
C(5)-C(6)	1.391(3)
C(5)-C(10)	1.509(3)
C(6)-C(7)	1.386(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.391(3)
C(7)-C(11)	1.511(3)
C(8)-C(9)	1.390(3)
C(8)-H(8)	0.9500

C(9)-C(12)	1.509(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.397(2)
C(13)-C(18)	1.398(2)
C(14)-C(15)	1.391(2)
C(14)-C(19)	1.511(3)
C(15)-C(16)	1.391(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.386(2)
C(16)-C(20)	1.506(2)
C(17)-C(18)	1.393(2)
C(17)-H(17)	0.9500
C(18)-C(21)	1.503(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.452(3)
C(22)-H(22)	0.93(3)
C(23)-C(28)	1.397(3)
C(23)-C(24)	1.400(3)
C(24)-C(25)	1.379(3)
C(24)-H(24)	0.9500

C(25)-C(26)	1.382(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.391(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.388(2)
C(27)-H(27)	0.9500
C(29)-C(31)	1.512(3)
C(29)-C(30)	1.519(3)
C(29)-H(29)	1.0000
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-C(37)	1.390(2)
C(32)-C(33)	1.403(2)
C(33)-C(34)	1.389(2)
C(34)-C(35)	1.371(3)
C(35)-C(36)	1.380(3)
C(36)-C(37)	1.373(3)

C(22)-Ru(1)-C(1)	99.88(8)
C(22)-Ru(1)-S(2)	94.10(6)
C(1)-Ru(1)-S(2)	90.93(5)
C(22)-Ru(1)-O(1)	78.62(7)
C(1)-Ru(1)-O(1)	94.29(5)
S(2)-Ru(1)-O(1)	171.66(3)
C(22)-Ru(1)-S(1)	122.85(6)
C(1)-Ru(1)-S(1)	137.19(5)
S(2)-Ru(1)-S(1)	88.740(16)
O(1)-Ru(1)-S(1)	91.82(3)
C(32)-S(1)-Ru(1)	103.47(6)
C(33)-S(2)-Ru(1)	104.34(6)
C(28)-O(1)-C(29)	119.61(13)
C(28)-O(1)-Ru(1)	109.90(10)

C(29)-O(1)-Ru(1)	120.27(10)
C(1)-N(1)-C(4)	127.19(15)
C(1)-N(1)-C(2)	113.04(14)
C(4)-N(1)-C(2)	118.52(14)
C(1)-N(2)-C(13)	125.59(14)
C(1)-N(2)-C(3)	113.84(14)
C(13)-N(2)-C(3)	120.56(14)
N(2)-C(1)-N(1)	107.71(15)
N(2)-C(1)-Ru(1)	119.18(12)
N(1)-C(1)-Ru(1)	133.00(13)
N(1)-C(2)-C(3)	102.90(13)
N(1)-C(2)-H(2A)	111.2
C(3)-C(2)-H(2A)	111.2
N(1)-C(2)-H(2B)	111.2
C(3)-C(2)-H(2B)	111.2
H(2A)-C(2)-H(2B)	109.1
N(2)-C(3)-C(2)	102.18(14)
N(2)-C(3)-H(3A)	111.3
C(2)-C(3)-H(3A)	111.3
N(2)-C(3)-H(3B)	111.3
C(2)-C(3)-H(3B)	111.3
H(3A)-C(3)-H(3B)	109.2
C(5)-C(4)-C(9)	121.42(17)
C(5)-C(4)-N(1)	119.18(16)
C(9)-C(4)-N(1)	119.20(16)
C(6)-C(5)-C(4)	118.09(17)
C(6)-C(5)-C(10)	120.40(17)
C(4)-C(5)-C(10)	121.51(16)
C(7)-C(6)-C(5)	122.16(18)
C(7)-C(6)-H(6)	118.9
C(5)-C(6)-H(6)	118.9
C(6)-C(7)-C(8)	118.26(18)
C(6)-C(7)-C(11)	121.10(18)
C(8)-C(7)-C(11)	120.63(19)
C(9)-C(8)-C(7)	121.79(18)
C(9)-C(8)-H(8)	119.1

C(7)-C(8)-H(8)	119.1
C(8)-C(9)-C(4)	118.23(17)
C(8)-C(9)-C(12)	120.21(18)
C(4)-C(9)-C(12)	121.55(17)
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(7)-C(11)-H(11A)	109.5
C(7)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(7)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(18)	121.60(15)
C(14)-C(13)-N(2)	119.06(16)
C(18)-C(13)-N(2)	119.27(15)
C(15)-C(14)-C(13)	117.71(16)
C(15)-C(14)-C(19)	119.59(16)
C(13)-C(14)-C(19)	122.68(16)
C(16)-C(15)-C(14)	122.08(16)
C(16)-C(15)-H(15)	119.0
C(14)-C(15)-H(15)	119.0
C(17)-C(16)-C(15)	118.56(16)
C(17)-C(16)-C(20)	121.03(17)
C(15)-C(16)-C(20)	120.39(17)
C(16)-C(17)-C(18)	121.52(17)
C(16)-C(17)-H(17)	119.2

C(18)-C(17)-H(17)	119.2
C(17)-C(18)-C(13)	118.26(16)
C(17)-C(18)-C(21)	120.67(16)
C(13)-C(18)-C(21)	120.97(15)
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(16)-C(20)-H(20A)	109.5
C(16)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(16)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-Ru(1)	120.21(14)
C(23)-C(22)-H(22)	113.5(15)
Ru(1)-C(22)-H(22)	125.9(16)
C(28)-C(23)-C(24)	118.32(17)
C(28)-C(23)-C(22)	117.77(17)
C(24)-C(23)-C(22)	123.88(17)
C(25)-C(24)-C(23)	121.05(19)
C(25)-C(24)-H(24)	119.5
C(23)-C(24)-H(24)	119.5
C(24)-C(25)-C(26)	119.52(18)
C(24)-C(25)-H(25)	120.2
C(26)-C(25)-H(25)	120.2
C(25)-C(26)-C(27)	121.11(18)
C(25)-C(26)-H(26)	119.4

C(27)-C(26)-H(26)	119.4
C(28)-C(27)-C(26)	118.81(18)
C(28)-C(27)-H(27)	120.6
C(26)-C(27)-H(27)	120.6
C(27)-C(28)-O(1)	125.27(16)
C(27)-C(28)-C(23)	121.20(17)
O(1)-C(28)-C(23)	113.49(15)
O(1)-C(29)-C(31)	110.92(16)
O(1)-C(29)-C(30)	111.74(17)
C(31)-C(29)-C(30)	114.88(18)
O(1)-C(29)-H(29)	106.2
C(31)-C(29)-H(29)	106.2
C(30)-C(29)-H(29)	106.2
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(37)-C(32)-C(33)	118.61(16)
C(37)-C(32)-S(1)	120.69(14)
C(33)-C(32)-S(1)	120.63(13)
C(34)-C(33)-C(32)	118.15(16)
C(34)-C(33)-S(2)	120.30(14)
C(32)-C(33)-S(2)	121.52(13)
F(1)-C(34)-C(35)	117.79(16)
F(1)-C(34)-C(33)	119.80(16)
C(35)-C(34)-C(33)	122.40(17)
F(2)-C(35)-C(34)	120.38(17)
F(2)-C(35)-C(36)	120.14(17)

C(34)-C(35)-C(36)	119.48(16)
F(3)-C(36)-C(37)	120.75(17)
F(3)-C(36)-C(35)	120.10(17)
C(37)-C(36)-C(35)	119.15(17)
F(4)-C(37)-C(36)	117.60(16)
F(4)-C(37)-C(32)	120.16(16)
C(36)-C(37)-C(32)	122.18(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. **Anisotropic displacement parameters ($Å^2$ x 10^3) for Ru-12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	13(1)	12(1)	13(1)	2(1)	4(1)	7(1)
S(1)	15(1)	13(1)	21(1)	4(1)	4(1)	8(1)
S(2)	16(1)	13(1)	20(1)	4(1)	4(1)	9(1)
F(1)	27(1)	14(1)	37(1)	6(1)	11(1)	12(1)
F(2)	26(1)	14(1)	44(1)	-4(1)	6(1)	2(1)
F(3)	18(1)	28(1)	36(1)	-1(1)	-3(1)	4(1)
F(4)	20(1)	25(1)	36(1)	6(1)	-1(1)	14(1)
O(1)	18(1)	13(1)	14(1)	2(1)	1(1)	9(1)
N(1)	12(1)	21(1)	13(1)	-2(1)	0(1)	8(1)
N(2)	12(1)	22(1)	12(1)	-2(1)	2(1)	8(1)
C(1)	13(1)	11(1)	15(1)	1(1)	2(1)	6(1)
C(2)	14(1)	34(1)	19(1)	-5(1)	2(1)	11(1)
C(3)	14(1)	22(1)	17(1)	0(1)	4(1)	9(1)
C(4)	14(1)	22(1)	14(1)	-1(1)	0(1)	10(1)
C(5)	16(1)	20(1)	16(1)	1(1)	2(1)	9(1)
C(6)	17(1)	23(1)	16(1)	-3(1)	2(1)	8(1)
C(7)	17(1)	32(1)	15(1)	2(1)	0(1)	11(1)
C(8)	21(1)	26(1)	24(1)	8(1)	1(1)	13(1)
C(9)	16(1)	20(1)	22(1)	1(1)	0(1)	9(1)
C(10)	23(1)	21(1)	20(1)	1(1)	2(1)	9(1)
C(11)	26(1)	44(1)	17(1)	3(1)	0(1)	15(1)
C(12)	26(1)	19(1)	35(1)	1(1)	-5(1)	11(1)
C(13)	12(1)	19(1)	11(1)	0(1)	2(1)	6(1)
C(14)	18(1)	18(1)	13(1)	4(1)	5(1)	9(1)
C(15)	18(1)	15(1)	15(1)	-2(1)	3(1)	4(1)
C(16)	14(1)	22(1)	11(1)	0(1)	2(1)	6(1)
C(17)	15(1)	22(1)	13(1)	3(1)	4(1)	11(1)
C(18)	15(1)	17(1)	12(1)	0(1)	5(1)	7(1)
C(19)	25(1)	22(1)	22(1)	3(1)	4(1)	14(1)
C(20)	16(1)	29(1)	20(1)	-3(1)	-3(1)	8(1)
C(21)	21(1)	16(1)	22(1)	2(1)	4(1)	9(1)

C(22)	33(1)	18(1)	17(1)	5(1)	7(1)	16(1)
C(23)	25(1)	19(1)	15(1)	2(1)	7(1)	13(1)
C(24)	40(1)	27(1)	15(1)	4(1)	6(1)	22(1)
C(25)	29(1)	28(1)	17(1)	-5(1)	1(1)	17(1)
C(26)	20(1)	20(1)	24(1)	-5(1)	1(1)	9(1)
C(27)	20(1)	16(1)	21(1)	2(1)	2(1)	8(1)
C(28)	15(1)	17(1)	15(1)	0(1)	3(1)	9(1)
C(29)	32(1)	19(1)	16(1)	2(1)	-2(1)	17(1)
C(30)	66(2)	17(1)	20(1)	5(1)	2(1)	15(1)
C(31)	34(1)	39(1)	27(1)	-8(1)	-5(1)	29(1)
C(32)	16(1)	15(1)	16(1)	4(1)	6(1)	7(1)
C(33)	15(1)	15(1)	15(1)	3(1)	6(1)	7(1)
C(34)	22(1)	15(1)	22(1)	6(1)	10(1)	11(1)
C(35)	22(1)	13(1)	24(1)	-1(1)	7(1)	3(1)
C(36)	14(1)	22(1)	21(1)	1(1)	2(1)	4(1)
C(37)	19(1)	20(1)	22(1)	7(1)	6(1)	11(1)

Table 5. **Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for Ru-12.**

	x	y	z	U(eq)
H(2A)	8255	296	2228	28
H(2B)	8635	1870	2114	28
H(3A)	6818	1101	970	21
H(3B)	6552	-459	1045	21
H(6)	9932	3769	4926	24
H(8)	8157	-351	4976	29
H(10A)	8896	4588	3800	34
H(10B)	7810	3519	3010	34
H(10C)	9619	4075	3212	34
H(11A)	9342	2234	6261	46
H(11B)	10969	2858	6058	46
H(11C)	10055	1235	6106	46
H(12A)	6629	-2011	3862	43
H(12B)	7037	-1509	3060	43
H(12C)	5532	-1597	3262	43
H(15)	993	-3637	95	21
H(17)	1270	124	-127	19
H(19A)	2853	-3849	1143	33
H(19B)	4409	-2489	1585	33
H(19C)	4176	-3122	700	33
H(20A)	-767	-3300	-1026	37
H(20B)	-850	-1873	-944	37
H(20C)	-1472	-2964	-361	37
H(21A)	4616	2111	1331	30
H(21B)	3409	2204	620	30
H(21C)	4834	2066	456	30
H(22)	4460(30)	40(30)	4143(15)	40(7)
H(24)	6016	1838	5325	30
H(25)	7199	4160	5901	29
H(26)	7143	5835	5138	27

H(27)	5898	5207	3793	24
H(29)	2970	2569	2020	26
H(30A)	5005	5373	2665	57
H(30B)	4116	4707	1764	57
H(30C)	5568	4524	2170	57
H(31A)	1955	2482	3117	47
H(31B)	1846	3621	2600	47
H(31C)	3135	4098	3413	47

Table 6. **Torsion angles [°] for Ru-12.**

C(13)-N(2)-C(1)-N(1)	177.18(16)
C(3)-N(2)-C(1)-N(1)	-4.1(2)
C(13)-N(2)-C(1)-Ru(1)	-6.2(2)
C(3)-N(2)-C(1)-Ru(1)	172.54(12)
C(4)-N(1)-C(1)-N(2)	-166.60(16)
C(2)-N(1)-C(1)-N(2)	0.3(2)
C(4)-N(1)-C(1)-Ru(1)	17.4(3)
C(2)-N(1)-C(1)-Ru(1)	-175.67(14)
C(1)-N(1)-C(2)-C(3)	3.2(2)
C(4)-N(1)-C(2)-C(3)	171.38(15)
C(1)-N(2)-C(3)-C(2)	5.9(2)
C(13)-N(2)-C(3)-C(2)	-175.33(16)
N(1)-C(2)-C(3)-N(2)	-5.02(19)
C(1)-N(1)-C(4)-C(5)	-109.7(2)
C(2)-N(1)-C(4)-C(5)	84.1(2)
C(1)-N(1)-C(4)-C(9)	75.5(2)
C(2)-N(1)-C(4)-C(9)	-90.8(2)
C(9)-C(4)-C(5)-C(6)	-1.9(3)
N(1)-C(4)-C(5)-C(6)	-176.64(16)
C(9)-C(4)-C(5)-C(10)	178.03(17)
N(1)-C(4)-C(5)-C(10)	3.3(3)
C(4)-C(5)-C(6)-C(7)	-0.1(3)
C(10)-C(5)-C(6)-C(7)	179.99(17)
C(5)-C(6)-C(7)-C(8)	1.0(3)
C(5)-C(6)-C(7)-C(11)	-177.93(18)
C(6)-C(7)-C(8)-C(9)	0.0(3)
C(11)-C(7)-C(8)-C(9)	178.94(19)
C(7)-C(8)-C(9)-C(4)	-1.9(3)
C(7)-C(8)-C(9)-C(12)	177.12(18)
C(5)-C(4)-C(9)-C(8)	2.8(3)
N(1)-C(4)-C(9)-C(8)	177.59(16)
C(5)-C(4)-C(9)-C(12)	-176.13(17)
N(1)-C(4)-C(9)-C(12)	-1.4(3)
C(1)-N(2)-C(13)-C(14)	-97.4(2)

C(3)-N(2)-C(13)-C(14)	83.9(2)
C(1)-N(2)-C(13)-C(18)	85.3(2)
C(3)-N(2)-C(13)-C(18)	-93.3(2)
C(18)-C(13)-C(14)-C(15)	-5.4(3)
N(2)-C(13)-C(14)-C(15)	177.45(16)
C(18)-C(13)-C(14)-C(19)	172.92(17)
N(2)-C(13)-C(14)-C(19)	-4.2(3)
C(13)-C(14)-C(15)-C(16)	1.2(3)
C(19)-C(14)-C(15)-C(16)	-177.16(17)
C(14)-C(15)-C(16)-C(17)	2.3(3)
C(14)-C(15)-C(16)-C(20)	-179.33(17)
C(15)-C(16)-C(17)-C(18)	-1.8(3)
C(20)-C(16)-C(17)-C(18)	179.83(17)
C(16)-C(17)-C(18)-C(13)	-2.2(3)
C(16)-C(17)-C(18)-C(21)	174.20(16)
C(14)-C(13)-C(18)-C(17)	5.9(3)
N(2)-C(13)-C(18)-C(17)	-176.97(15)
C(14)-C(13)-C(18)-C(21)	-170.46(16)
N(2)-C(13)-C(18)-C(21)	6.7(2)
C(1)-Ru(1)-C(22)-C(23)	92.70(16)
S(2)-Ru(1)-C(22)-C(23)	-175.64(15)
O(1)-Ru(1)-C(22)-C(23)	0.27(15)
S(1)-Ru(1)-C(22)-C(23)	-84.49(16)
Ru(1)-C(22)-C(23)-C(28)	-0.1(2)
Ru(1)-C(22)-C(23)-C(24)	-177.66(16)
C(28)-C(23)-C(24)-C(25)	0.3(3)
C(22)-C(23)-C(24)-C(25)	177.90(19)
C(23)-C(24)-C(25)-C(26)	-0.1(3)
C(24)-C(25)-C(26)-C(27)	0.1(3)
C(25)-C(26)-C(27)-C(28)	-0.3(3)
C(26)-C(27)-C(28)-O(1)	-177.16(16)
C(26)-C(27)-C(28)-C(23)	0.5(3)
C(29)-O(1)-C(28)-C(27)	-36.4(2)
Ru(1)-O(1)-C(28)-C(27)	178.31(14)
C(29)-O(1)-C(28)-C(23)	145.84(16)
Ru(1)-O(1)-C(28)-C(23)	0.51(17)

C(24)-C(23)-C(28)-C(27)	-0.5(3)
C(22)-C(23)-C(28)-C(27)	-178.25(17)
C(24)-C(23)-C(28)-O(1)	177.39(16)
C(22)-C(23)-C(28)-O(1)	-0.3(2)
C(28)-O(1)-C(29)-C(31)	-48.8(2)
Ru(1)-O(1)-C(29)-C(31)	92.92(16)
C(28)-O(1)-C(29)-C(30)	80.8(2)
Ru(1)-O(1)-C(29)-C(30)	-137.50(14)
Ru(1)-S(1)-C(32)-C(37)	-170.09(14)
Ru(1)-S(1)-C(32)-C(33)	6.90(16)
C(37)-C(32)-C(33)-C(34)	0.5(3)
S(1)-C(32)-C(33)-C(34)	-176.52(13)
C(37)-C(32)-C(33)-S(2)	178.45(14)
S(1)-C(32)-C(33)-S(2)	1.4(2)
Ru(1)-S(2)-C(33)-C(34)	168.84(13)
Ru(1)-S(2)-C(33)-C(32)	-9.04(16)
C(32)-C(33)-C(34)-F(1)	178.37(16)
S(2)-C(33)-C(34)-F(1)	0.4(2)
C(32)-C(33)-C(34)-C(35)	0.0(3)
S(2)-C(33)-C(34)-C(35)	-177.99(15)
F(1)-C(34)-C(35)-F(2)	1.6(3)
C(33)-C(34)-C(35)-F(2)	180.00(17)
F(1)-C(34)-C(35)-C(36)	-177.83(17)
C(33)-C(34)-C(35)-C(36)	0.6(3)
F(2)-C(35)-C(36)-F(3)	-1.7(3)
C(34)-C(35)-C(36)-F(3)	177.68(17)
F(2)-C(35)-C(36)-C(37)	178.94(17)
C(34)-C(35)-C(36)-C(37)	-1.7(3)
F(3)-C(36)-C(37)-F(4)	0.3(3)
C(35)-C(36)-C(37)-F(4)	179.62(17)
F(3)-C(36)-C(37)-C(32)	-177.12(17)
C(35)-C(36)-C(37)-C(32)	2.2(3)
C(33)-C(32)-C(37)-F(4)	-178.98(16)
S(1)-C(32)-C(37)-F(4)	-1.9(2)
C(33)-C(32)-C(37)-C(36)	-1.7(3)
S(1)-C(32)-C(37)-C(36)	175.40(15)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure for Cyclic Boronate 1.42

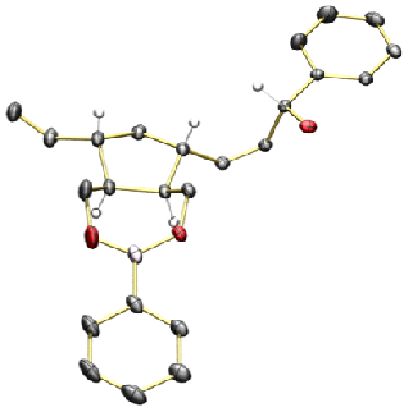

Table 1: **Crystal data and structure refinement for cyclic boronate 1.42**

Identification code	$C_{24}H_{27}BO_3$	
Empirical formula	$C_{24}H_{27}BO_3$	
Formula weight	374.26	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	C 2 2 21	
Unit cell dimensions	a = 21.808(2) Å	α= 90°.
	b = 24.164(2) Å	β= 90°.
	c = 9.1450(8) Å	γ = 90°.
Volume	4819.2(8) $Å^3$	
Z	8	
Density (calculated)	1.032 Mg/m^3	
Absorption coefficient	0.519 mm^{-1}	
F(000)	1600	
Crystal size	0.420 x 0.040 x 0.020 mm^3	
Theta range for data collection	2.729 to 68.517°.	
Index ranges	-26<=h<=25, -29<=k<=27, -10<=l<=10	
Reflections collected	21415	
Independent reflections	4309 [R(int) = 0.0431]	
Completeness to theta = 67.679°	99.3 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.6403
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4309 / 2 / 261
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0732
R indices (all data)	R1 = 0.0326, wR2 = 0.0748
Absolute structure parameter	0.17(8)
Extinction coefficient	na
Largest diff. peak and hole	0.103 and -0.101 e.$Å^{-3}$

Table 2: **Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1.42. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor**

	x	y	z	U(eq)
B(1)	7034(1)	-263(1)	7775(2)	48(1)
O(1)	7640(1)	-270(1)	7432(2)	44(1)
O(2)	6703(1)	181(1)	8166(2)	80(1)
O(3)	9774(1)	358(1)	6136(2)	40(1)
C(1)	6691(1)	-834(1)	7722(2)	53(1)
C(2)	6088(1)	-883(1)	8223(3)	71(1)
C(3)	5789(1)	-1390(1)	8215(3)	84(1)
C(4)	6078(1)	-1852(1)	7699(3)	80(1)
C(5)	6675(1)	-1818(1)	7194(3)	68(1)
C(6)	6975(1)	-1313(1)	7228(2)	56(1)
C(7)	8043(1)	200(1)	7344(2)	41(1)
C(8)	7794(1)	670(1)	6428(2)	37(1)
C(9)	8301(1)	1116(1)	6197(2)	38(1)
C(10)	7959(1)	1669(1)	6316(2)	47(1)
C(11)	7466(1)	1568(1)	7469(2)	46(1)
C(12)	7238(1)	980(1)	7110(2)	46(1)
C(13)	6966(1)	716(1)	8457(3)	67(1)
C(14)	8634(1)	1049(1)	4772(2)	36(1)
C(15)	9229(1)	972(1)	4552(2)	34(1)

C(16)	9703(1)	927(1)	5742(2)	32(1)
C(17)	10304(1)	1188(1)	5277(2)	33(1)
C(18)	10791(1)	880(1)	4763(2)	36(1)
C(19)	11330(1)	1130(1)	4301(2)	46(1)
C(20)	11385(1)	1689(1)	4342(3)	60(1)
C(21)	10911(1)	2003(1)	4861(3)	79(1)
C(22)	10369(1)	1756(1)	5330(3)	64(1)
C(23)	6965(1)	1989(1)	7485(3)	59(1)
C(24)	6766(1)	2253(1)	8645(3)	68(1)

Table 3: **Bond lengths [Å] and angles [°] for 1.42**

B(1)-O(2)	1.342(3)
B(1)-O(1)	1.360(2)
B(1)-C(1)	1.570(3)
O(1)-C(7)	1.439(2)
O(2)-C(13)	1.439(3)
O(3)-C(16)	1.429(2)
O(3)-H(3O)	0.81(2)
O(3)-H(3OA)	0.81(2)
C(1)-C(6)	1.388(3)
C(1)-C(2)	1.398(3)
C(2)-C(3)	1.387(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.364(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.385(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.510(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(12)	1.557(2)

C(8)-C(9)	1.559(3)
C(8)-H(8)	1.0000
C(9)-C(14)	1.500(2)
C(9)-C(10)	1.534(2)
C(9)-H(9)	1.0000
C(10)-C(11)	1.525(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(23)	1.494(3)
C(11)-C(12)	1.541(3)
C(11)-H(11)	1.0000
C(12)-C(13)	1.508(3)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.326(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.505(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.517(2)
C(16)-H(16)	1.0000
C(17)-C(22)	1.380(3)
C(17)-C(18)	1.380(2)
C(18)-C(19)	1.389(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.356(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.366(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.392(3)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.311(3)
C(23)-H(23)	0.9500
C(24)-H(24A)	0.9500
C(24)-H(24B)	0.9500

O(2)-B(1)-O(1)	126.5(2)
O(2)-B(1)-C(1)	117.08(17)
O(1)-B(1)-C(1)	116.42(19)
B(1)-O(1)-C(7)	126.56(16)
B(1)-O(2)-C(13)	123.61(17)
C(16)-O(3)-H(3O)	118(3)
C(16)-O(3)-H(3OA)	110(4)
H(3O)-O(3)-H(3OA)	126(4)
C(6)-C(1)-C(2)	117.1(2)
C(6)-C(1)-B(1)	122.03(17)
C(2)-C(1)-B(1)	120.9(2)
C(3)-C(2)-C(1)	121.0(3)
C(3)-C(2)-H(2)	119.5
C(1)-C(2)-H(2)	119.5
C(4)-C(3)-C(2)	120.5(2)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.0(3)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	119.2(3)
C(4)-C(5)-H(5)	120.4
C(6)-C(5)-H(5)	120.4
C(5)-C(6)-C(1)	122.1(2)
C(5)-C(6)-H(6)	118.9
C(1)-C(6)-H(6)	118.9
O(1)-C(7)-C(8)	113.96(14)
O(1)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7A)	108.8
O(1)-C(7)-H(7B)	108.8
C(8)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(7)-C(8)-C(12)	114.79(15)
C(7)-C(8)-C(9)	109.92(13)
C(12)-C(8)-C(9)	105.89(14)

C(7)-C(8)-H(8)	108.7
C(12)-C(8)-H(8)	108.7
C(9)-C(8)-H(8)	108.7
C(14)-C(9)-C(10)	112.99(15)
C(14)-C(9)-C(8)	112.72(14)
C(10)-C(9)-C(8)	104.34(14)
C(14)-C(9)-H(9)	108.9
C(10)-C(9)-H(9)	108.9
C(8)-C(9)-H(9)	108.9
C(11)-C(10)-C(9)	104.64(15)
C(11)-C(10)-H(10A)	110.8
C(9)-C(10)-H(10A)	110.8
C(11)-C(10)-H(10B)	110.8
C(9)-C(10)-H(10B)	110.8
H(10A)-C(10)-H(10B)	108.9
C(23)-C(11)-C(10)	114.47(17)
C(23)-C(11)-C(12)	113.19(16)
C(10)-C(11)-C(12)	103.18(15)
C(23)-C(11)-H(11)	108.6
C(10)-C(11)-H(11)	108.6
C(12)-C(11)-H(11)	108.6
C(13)-C(12)-C(11)	110.07(17)
C(13)-C(12)-C(8)	115.42(16)
C(11)-C(12)-C(8)	106.11(15)
C(13)-C(12)-H(12)	108.3
C(11)-C(12)-H(12)	108.3
C(8)-C(12)-H(12)	108.3
O(2)-C(13)-C(12)	112.69(19)
O(2)-C(13)-H(13A)	109.1
C(12)-C(13)-H(13A)	109.1
O(2)-C(13)-H(13B)	109.1
C(12)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.8
C(15)-C(14)-C(9)	128.33(16)
C(15)-C(14)-H(14)	115.8
C(9)-C(14)-H(14)	115.8

C(14)-C(15)-C(16)	124.90(16)
C(14)-C(15)-H(15)	117.5
C(16)-C(15)-H(15)	117.5
O(3)-C(16)-C(15)	109.14(13)
O(3)-C(16)-C(17)	112.17(13)
C(15)-C(16)-C(17)	111.13(13)
O(3)-C(16)-H(16)	108.1
C(15)-C(16)-H(16)	108.1
C(17)-C(16)-H(16)	108.1
C(22)-C(17)-C(18)	118.06(18)
C(22)-C(17)-C(16)	119.50(17)
C(18)-C(17)-C(16)	122.42(15)
C(17)-C(18)-C(19)	121.31(17)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(20)-C(19)-C(18)	120.00(19)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	119.73(19)
C(19)-C(20)-H(20)	120.1
C(21)-C(20)-H(20)	120.1
C(20)-C(21)-C(22)	120.8(2)
C(20)-C(21)-H(21)	119.6
C(22)-C(21)-H(21)	119.6
C(17)-C(22)-C(21)	120.1(2)
C(17)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9
C(24)-C(23)-C(11)	125.6(2)
C(24)-C(23)-H(23)	117.2
C(11)-C(23)-H(23)	117.2
C(23)-C(24)-H(24A)	120.0
C(23)-C(24)-H(24B)	120.0
H(24A)-C(24)-H(24B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4: **Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1.42. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$**

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	38(1)	68(1)	36(1)	9(1)	6(1)	3(1)
O(1)	32(1)	53(1)	48(1)	5(1)	1(1)	-2(1)
O(2)	53(1)	75(1)	111(2)	1(1)	43(1)	4(1)
O(3)	46(1)	34(1)	40(1)	10(1)	-10(1)	-7(1)
C(1)	36(1)	79(2)	46(1)	14(1)	3(1)	-5(1)
C(2)	39(1)	98(2)	77(2)	20(1)	8(1)	-7(1)
C(3)	40(1)	120(2)	91(2)	34(2)	3(1)	-21(2)
C(4)	60(1)	98(2)	84(2)	28(2)	-5(1)	-35(2)
C(5)	63(1)	76(2)	65(1)	16(1)	5(1)	-24(1)
C(6)	44(1)	73(1)	51(1)	12(1)	6(1)	-16(1)
C(7)	31(1)	49(1)	43(1)	1(1)	-1(1)	2(1)
C(8)	31(1)	50(1)	30(1)	-2(1)	-2(1)	7(1)
C(9)	35(1)	45(1)	33(1)	1(1)	-3(1)	6(1)
C(10)	50(1)	47(1)	43(1)	-2(1)	-2(1)	10(1)
C(11)	43(1)	57(1)	40(1)	-4(1)	-4(1)	15(1)
C(12)	34(1)	62(1)	43(1)	-4(1)	-1(1)	14(1)
C(13)	60(1)	68(2)	72(2)	-5(1)	32(1)	12(1)
C(14)	39(1)	38(1)	30(1)	3(1)	-4(1)	1(1)
C(15)	39(1)	33(1)	31(1)	0(1)	0(1)	-2(1)
C(16)	37(1)	30(1)	31(1)	-1(1)	0(1)	-1(1)
C(17)	36(1)	33(1)	31(1)	-2(1)	-3(1)	-4(1)
C(18)	38(1)	38(1)	34(1)	1(1)	-3(1)	1(1)
C(19)	36(1)	67(1)	36(1)	1(1)	-2(1)	-4(1)
C(20)	51(1)	73(2)	57(1)	4(1)	1(1)	-28(1)
C(21)	84(2)	44(1)	109(2)	-2(1)	20(2)	-28(1)
C(22)	62(1)	35(1)	94(2)	-9(1)	18(1)	-8(1)
C(23)	58(1)	66(1)	54(1)	-4(1)	-1(1)	24(1)
C(24)	62(1)	69(1)	71(2)	-12(1)	6(1)	25(1)

Table 5: **Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1.42**

	x	y	z	U(eq)
H(3O)	9950(20)	289(15)	6890(30)	48(12)
H(3OA)	9780(20)	168(17)	5410(40)	56(15)
H(2)	5879	-565	8575	86
H(3)	5381	-1416	8571	100
H(4)	5868	-2196	7687	97
H(5)	6877	-2138	6829	82
H(6)	7388	-1294	6902	67
H(7A)	8440	80	6928	49
H(7B)	8122	339	8345	49
H(8)	7670	520	5453	44
H(9)	8604	1090	7015	45
H(10A)	8240	1968	6625	56
H(10B)	7772	1771	5367	56
H(11)	7665	1562	8453	56
H(12)	6909	1009	6352	56
H(13A)	7291	677	9207	80
H(13B)	6645	963	8859	80
H(14)	8386	1063	3918	43
H(15)	9366	944	3569	41
H(16)	9548	1132	6617	39
H(18)	10757	488	4725	44
H(19)	11661	910	3956	55
H(20)	11751	1862	4011	72
H(21)	10952	2394	4903	95
H(22)	10043	1979	5687	76
H(23)	6774	2073	6578	71
H(24A)	6944	2182	9574	81
H(24B)	6443	2515	8556	81

Table 6: **Torsion angles [°] for 1.42**

O(2)-B(1)-O(1)-C(7)	-3.5(3)
C(1)-B(1)-O(1)-C(7)	177.20(17)
O(1)-B(1)-O(2)-C(13)	-8.0(4)
C(1)-B(1)-O(2)-C(13)	171.3(2)
O(2)-B(1)-C(1)-C(6)	175.1(2)
O(1)-B(1)-C(1)-C(6)	-5.5(3)
O(2)-B(1)-C(1)-C(2)	-7.1(3)
O(1)-B(1)-C(1)-C(2)	172.3(2)
C(6)-C(1)-C(2)-C(3)	-0.3(3)
B(1)-C(1)-C(2)-C(3)	-178.2(2)
C(1)-C(2)-C(3)-C(4)	-0.8(4)
C(2)-C(3)-C(4)-C(5)	0.8(4)
C(3)-C(4)-C(5)-C(6)	0.3(4)
C(4)-C(5)-C(6)-C(1)	-1.5(4)
C(2)-C(1)-C(6)-C(5)	1.4(3)
B(1)-C(1)-C(6)-C(5)	179.3(2)
B(1)-O(1)-C(7)-C(8)	-50.0(2)
O(1)-C(7)-C(8)-C(12)	69.8(2)
O(1)-C(7)-C(8)-C(9)	-171.01(14)
C(7)-C(8)-C(9)-C(14)	96.35(17)
C(12)-C(8)-C(9)-C(14)	-139.12(15)
C(7)-C(8)-C(9)-C(10)	-140.68(15)
C(12)-C(8)-C(9)-C(10)	-16.16(17)
C(14)-C(9)-C(10)-C(11)	157.90(15)
C(8)-C(9)-C(10)-C(11)	35.11(18)
C(9)-C(10)-C(11)-C(23)	-163.74(17)
C(9)-C(10)-C(11)-C(12)	-40.31(18)
C(23)-C(11)-C(12)-C(13)	-80.5(2)
C(10)-C(11)-C(12)-C(13)	155.25(16)
C(23)-C(11)-C(12)-C(8)	153.98(17)
C(10)-C(11)-C(12)-C(8)	29.71(18)
C(7)-C(8)-C(12)-C(13)	-9.1(2)
C(9)-C(8)-C(12)-C(13)	-130.52(18)
C(7)-C(8)-C(12)-C(11)	113.11(17)

C(9)-C(8)-C(12)-C(11)	-8.33(18)
B(1)-O(2)-C(13)-C(12)	66.7(3)
C(11)-C(12)-C(13)-O(2)	175.64(16)
C(8)-C(12)-C(13)-O(2)	-64.3(2)
C(10)-C(9)-C(14)-C(15)	120.5(2)
C(8)-C(9)-C(14)-C(15)	-121.53(19)
C(9)-C(14)-C(15)-C(16)	1.1(3)
C(14)-C(15)-C(16)-O(3)	91.07(19)
C(14)-C(15)-C(16)-C(17)	-144.72(17)
O(3)-C(16)-C(17)-C(22)	-158.52(19)
C(15)-C(16)-C(17)-C(22)	79.0(2)
O(3)-C(16)-C(17)-C(18)	23.0(2)
C(15)-C(16)-C(17)-C(18)	-99.44(17)
C(22)-C(17)-C(18)-C(19)	-0.5(3)
C(16)-C(17)-C(18)-C(19)	177.95(16)
C(17)-C(18)-C(19)-C(20)	-0.3(3)
C(18)-C(19)-C(20)-C(21)	1.0(3)
C(19)-C(20)-C(21)-C(22)	-0.9(4)
C(18)-C(17)-C(22)-C(21)	0.6(4)
C(16)-C(17)-C(22)-C(21)	-177.9(2)
C(20)-C(21)-C(22)-C(17)	0.1(5)
C(10)-C(11)-C(23)-C(24)	-129.8(3)
C(12)-C(11)-C(23)-C(24)	112.3(3)

Symmetry transformations used to generate equivalent atoms:

Chapter Two

Kinetically Controlled Z- and E-Selective Cross-Metathesis to Access 1,2-Disubstituted Alkenyl Halides

2.1. Introduction

Alkenes substituted with a halogen represent as one of the most important classes of compounds in chemistry (Scheme 2.1). Alkenyl chlorides and bromides are prevalent in biologically active natural products,[1] or serve as substrates for a variety of organic transformations (for example, catalytic cross-coupling[2]). Alkenyl fluorides are prized due to the importance of organofluorine compounds in medicine,[3] agrochemicals[4] and materials science.[5] A fluorine-substituted alkene can also influence the properties of a molecule (for example, the *Z*-isomer of F-vigabatrin (γ-aminobutyric acid (GABA) transaminase inhibitor) is more active than the corresponding *E*-isomer but similarly potent and exhibits a distinct mechanism of action compared to the parent non-fluorinated alkene (vigabatrin).[6] Functionalization of a stereochemically defined alkenyl fluoride can enable access to a wider range of desirable fluorine-containing molecules.[7]

A number of methods have been reported for the preparation of 1,2-disubstituted *Z*-halo-alkenes. One option is the Wittig reaction of an aldehyde with a halogen-

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substituted phosphonium salt,[8] but stereoselectivities are variable and toxic hexamethylphosphoramide and/or cryogenic conditions are sometimes necessary.[9] Alternative strategies that furnish *Z*-alkenyl chlorides and bromides entail multi-step sequences involving synthesis of a *Z*-alkenylmetal intermediate (for example, through CM with an alkenyl boronate[10] or *trans*-metal-hydride additions to an alkyne[11]) followed by treatment with an electrophilic halogen source.[12] To access the corresponding *E*-isomers, a similar synthesis route demanding prior generation of *E*-alkenylmetal precursors followed by halogenation[13] has been disclosed. Alternatively, treatment of an aldehyde with excess chromium chloride and chloroform under Takai olefination conditions[14] affords *E*-alkenyl chlorides selectively. Approaches to synthesis of 1,2-disubstituted alkenyl fluorides in either isomeric form have been scarce[8b,15] and generally suffer from limited scope.

Despite these advances, there is a persisting lack of catalytic protocols that directly furnish a broad assortment of functionalized alkenyl halides efficiently and

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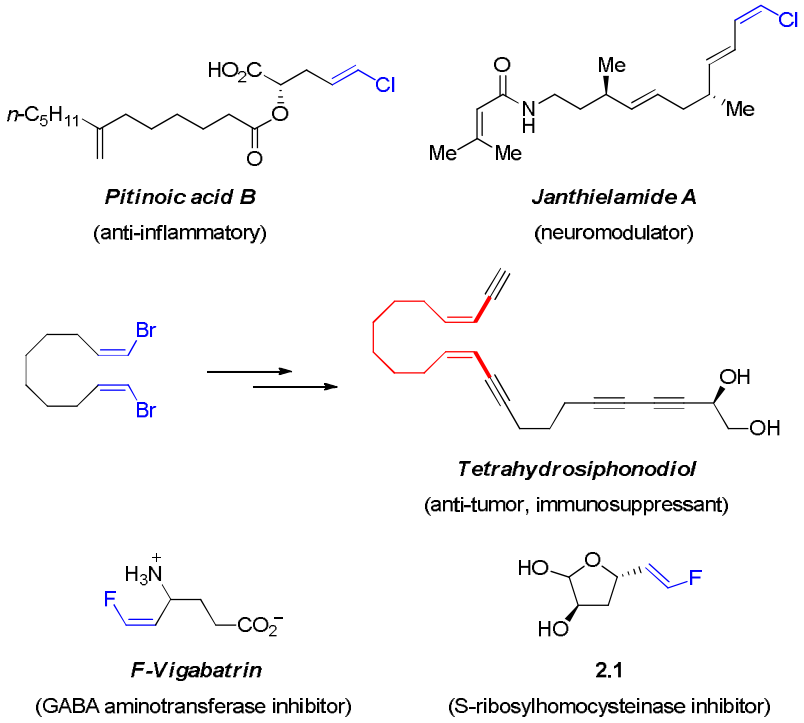
stereoselectively under mild reaction conditions, particularly those that do not entail the generation of synthetic intermediates and stochiometric waste. This provided the impetus for us to explore stereoselective catalytic OM as a viable solution to the aforementioned challenge.

Scheme 2.1. Stereochemically Defined Alkenyl Halides in Chemical Synthesis.



2.2. The Potential and Challenges of Alkenyl Halide Cross-Metathesis

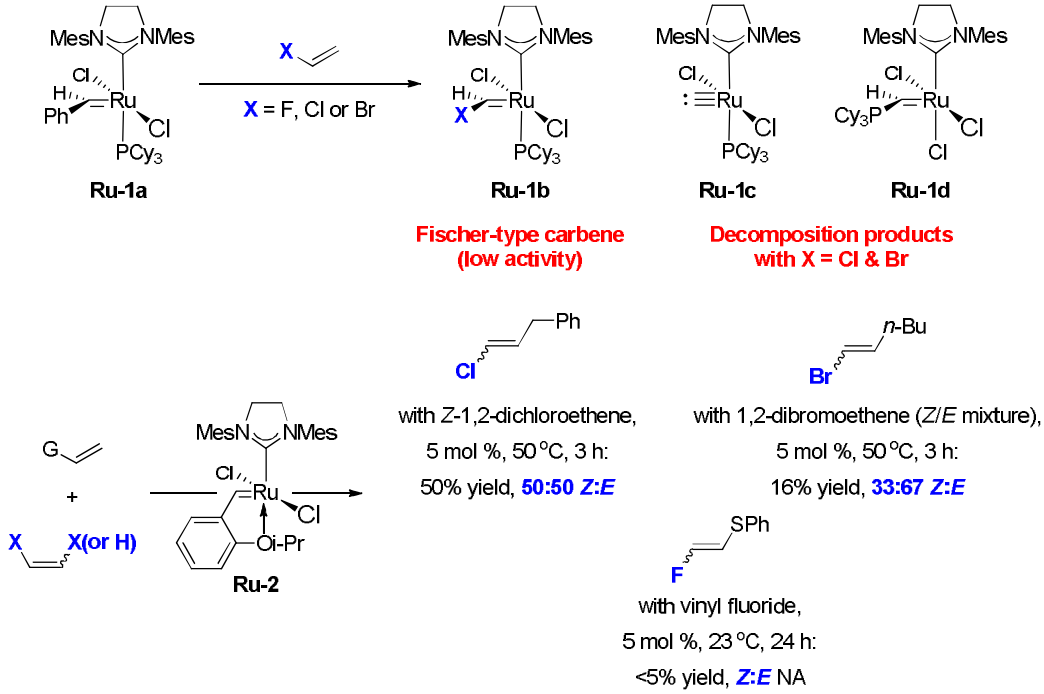
2.2.1. Advances in Alkenyl Halide OM with Ru-Based Complexes

Prior to our investigations, previous reports of OM with alkenyl halides are limited to Ru-catalyzed transformations (Scheme 2.2) Halogen-substituted Fischer-type carbene complexes (**Ru-1b**) generally exhibit poor metathesis activity.[16] Moreover, phosphine-containing Ru systems (X= Cl or Br) tend to form decomposition products

(16) (a) Macnaughtan, M. L.; Johnson, M. J. A.; Kampf, J. W. *J. Am. Chem. Soc.* **2007**, *129*, 7708–7709. (b) Macnaughtan, M. L.; Gary, J. B.; Gerlach, D. L.; Johnson, M. J. A.; Kampf, J. W. *Organometallics* **2009**, *28*, 2880–2887.

such as phosphoniomethylidene **Ru-1c** and carbide **Ru-1d**. Phosphine-free Ru carbenes (for example, **Ru-2**) show improved reactivity[16b,17] but reactions are still plagued by poor efficiency and stereoselectivity even at elevated temperatures (for example, 50 °C) and prolonged reaction times (for example, 24 h).

Scheme 2.2. State-of-the-art in CM with Alkenyl Halides Using Ru-Based Complexes.



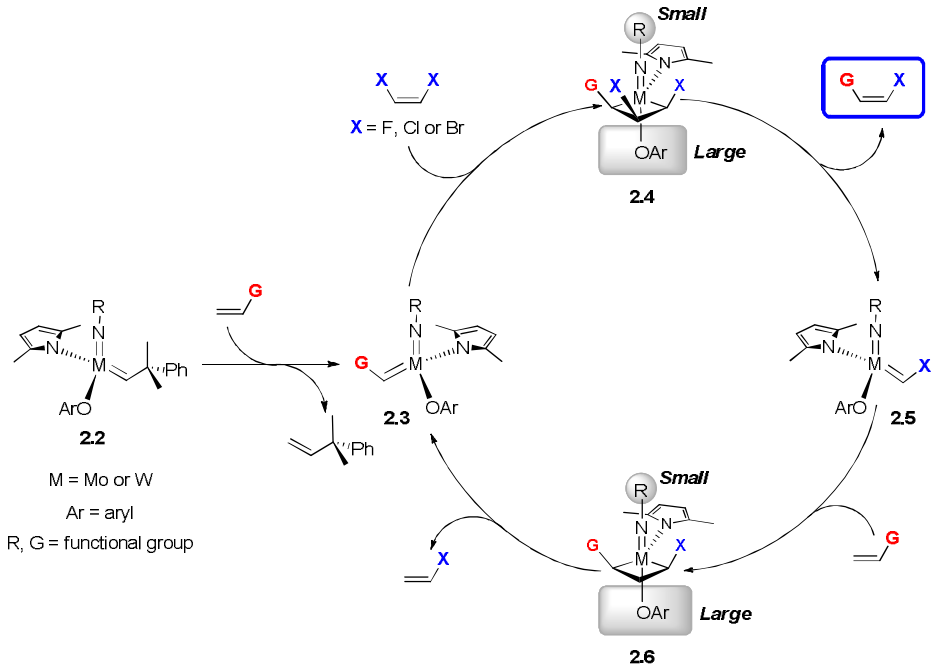
2.2.2. Z-Selective CM with Alkenyl Halides and High-Oxidation-State Alkylidenes

In light of the limited success of alkenyl halide OM with Ru-based complexes, we wondered whether the corresponding high-oxidation-state (Mo/W-based) halo-substituted alkylidenes would be less susceptible to the aforementioned problems and hence more adept in promoting OM with alkenyl halides. Given the precedence that alkoxy-substituted Mo alkylidenes are more reactive than the related Ru carbenes to participate in efficient CM,[18] we hoped that the same might apply to halogen-substituted alkenes.

(17) Sashuk, V.; Samojłowicz, C.; Szadkowska, A.; Grela, K. *Chem. Commun.* **2008**, 2468–2470.
(18) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, 471, 461–466.

However, to the best of our knowledge, no information is known about the structure, reactivity or stability profiles of halo-substituted alkylidene complexes. Adding to the uncertainty is a disclosed computational study suggesting that fluoro-substituted alkylidenes are even less stable than methylidene complexes.[19]

Scheme 2.3. Possible Catalytic Cycle for *Z*-Selective CM with *Z*-Dihaloethene with High-Oxidation-State Alkylidenes.



Nonetheless, we proceeded to develop a *Z*-selective CM protocol for the preparation of 1,2-disubstituted alkenyl halides. As illustrated in Scheme 2.3, we envisioned that treatment of a Mo or W monoaryloxide pyrrolide (MAP) neophylidene complex **2.2** with a terminal alkene could generate **2.3** which might then react with a *Z*-dihaloethene cross-partner to deliver the desired *Z*-alkenyl halide product and halo-substituted alkylidene **2.5** via the all-*syn* metallacyclobutane **2.4** where all substituents are oriented towards the smaller imido group (cf. Chapter 1, Scheme 1.3.2). **2.5** and the olefin substrate could then react to afford **2.6**, which would collapse to regenerate the

(19) Vasiliu, M.; Li, S.; Arduengo, A. J. III; Dixon, D. A. *J. Phys. Chem. C* **2011**, *115*, 12106–12120.

propagating alkylidene **2.3** and release vinyl halide as byproduct. The use of *Z*-dihaloethene as reagent (vs. vinyl halide) in CM offers a number of advantages: (1) In addition to being commercially available and inexpensive, *Z*-dihaloethenes are typically liquids at ambient conditions (for example, boiling point for *Z*-1,2-dichloroethene = 60 ^{o}C vs. 13 ^{o}C for vinyl chloride), thus rendering them more convenient to handle. (2) The use of 1,2-disubstituted *Z*-dihaloethene should diminish ethylene generation and discourage the formation of unstable methylidene complexes, which can lower reaction efficiency and cause post-metathesis isomerization (cf. Chapter 1).

2.3. Z-Selective Cross-Metathesis to Access 1,2-Disubstituted Alkenyl Halides[20]

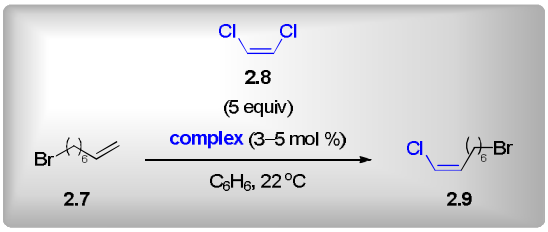
2.3.1. Identification of an Effective Catalyst for CM

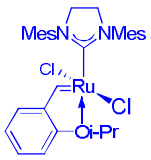
We began by probing the ability of a variety of OM catalysts to promote Z-selective CM between 8-bromo-1-octene **2.7** and commercially available *Z*-1,2-dichloroethene **2.8** (Scheme 2.4.1). CM with 5 mol % dichloro complex **Ru-2** required 50 ^{o}C to afford the desired product **2.9** in 59% yield after four hours, albeit with poor stereoselectivity (58% *Z* selectivity). Reaction was minimal with previously reported *Z*-selective Ru carbenes **Ru-3**[21] and **Ru-4**.[22] Transformation with bis-alkoxide **Mo-1** led to 67% conversion (22 ^{o}C, 4 h) but mostly to undesired homocoupling products without any detectable alkenyl chloride. Similarly, **W-1** and **Mo-2** promoted homocoupling of **2.7** with no desired **2.9** observed. The breakthrough arrived in the form of adamantylimido complex **Mo-3**, which resulted in 60% conversion and 27% yield of the desired CM

(20) Koh, M. J.; Nguyen, T. T.; Zhang, H.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2016**, *531*, 459–465.
(21) Rosebrugh, L. E.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *1 35*, 1276–1279.
(22) Koh, M. J.; Khan, R. K. M.; Torker, S.; Yu, M.; Mikus, M. S.; Hoveyda, A. H. *Nature* **2015**, *517*, 181–186.

product was obtained as a single stereoisomer (>98:2 *Z*:*E*). Homo-metathesis of **2.7** was still a competitive pathway in this case.

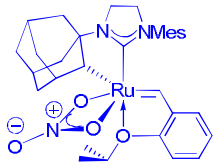
Scheme 2.4.1 CM of 8-Bromo-1-Octene and *Z*-1,2-Dichloroethene with Various Complexes.





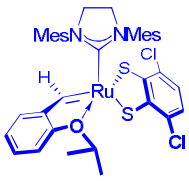
Ru-2

with 5 mol %, 50 °C, 4 h,
82% conv, 59% yield,
58:42 *Z*:*E*



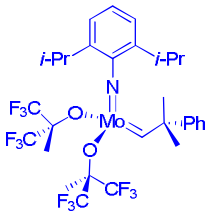
Ru-3

with 5 mol %, 50 °C, 4 h,
10% conv, <5% yield,
Z*:*E NA



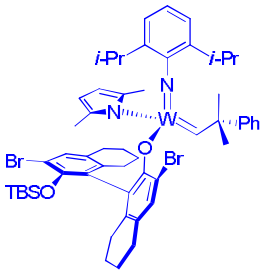
Ru-4

with 5 mol %, 50 °C, 4 h,
<10% conv, <5% yield,
Z*:*E NA



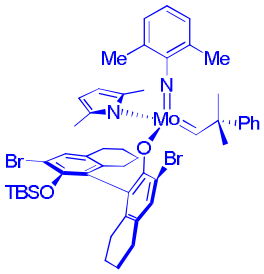
Mo-1

with 5 mol %, 22 °C, 4 h,
67% conv, <5% yield,
Z*:*E NA



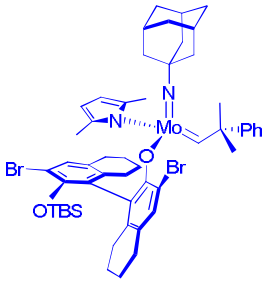
W-1

with 5 mol %, 22 °C, 4 h,
45% conv, <10% yield,
Z*:*E ND



Mo-2

with 5 mol %, 22 °C, 4 h,
43% conv, <5% yield,
Z*:*E NA



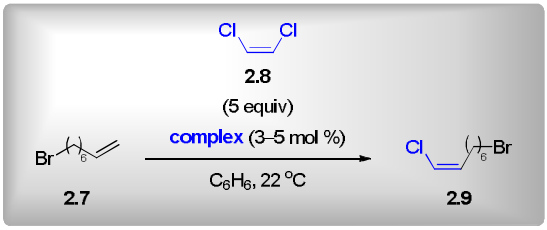
Mo-3

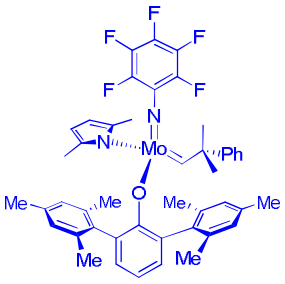
with 5 mol %, 22 °C, 4 h,
60% conv, 27% yield,
>98:2 *Z*:*E*

In order to improve the efficiency of CM, we surmised that more active variants of Mo MAP complexes could serve as better catalysts. As such, we turned to pentafluorophenylimido complexes **Mo-4a**–**c** to promote CM (Scheme 2.4.2). Efficiency did improve as the transformation with **Mo-4a** provided **2.9** in 60% yield and complete *Z* selectivity. We reasoned that a complex bearing a more sterically encumbered aryloxide ligand, although likely to be less active, could prolong catalyst lifetime and improve

reaction efficiency. Hence, we examined the CM with **Mo-4b**, but found that while high stereocontrol could still be retained (98% *Z* selectivity), conversion and yield were diminished (62% conversion, 40% yield). Repeating the same reaction for 12 hours appreciably improved efficiency and **2.9** was isolated in 84% yield but as a mixture of 93:7 *Z*:*E* isomers, presumably due to post-metathesis isomerization. To achieve a more effective balance between reaction rate and robustness without compromising stereochemical control, we switched to **Mo-4b** that contains a 2,4,6-triethyl-substituted aryloxide ligand. Optimal results could finally be obtained and **2.9** was generated in 75% yield and >98:2 *Z*:*E* ratio after four hours at ambient temperature.

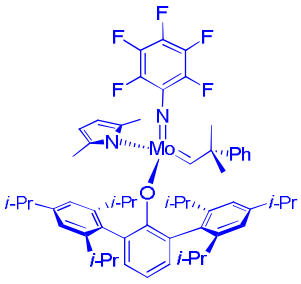
Scheme 2.4.2 Further Optimization of CM with C_6F_5-Imido Alkylidenes Complexes.





Mo-4a

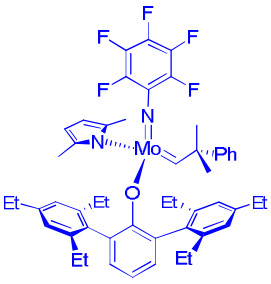
with 5 mol %, 22 °C, 4 h,
87% conv, 60% yield,
>98:2 *Z*:*E*



Mo-4b

with 5 mol %, 22 °C, 4 h,
62% conv, 40% yield,
98:2 *Z*:*E*

with 5 mol %, 22 °C, 12 h,
95% conv, 84% yield,
93:7 *Z*:*E*

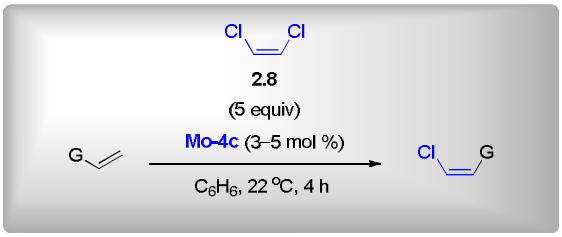


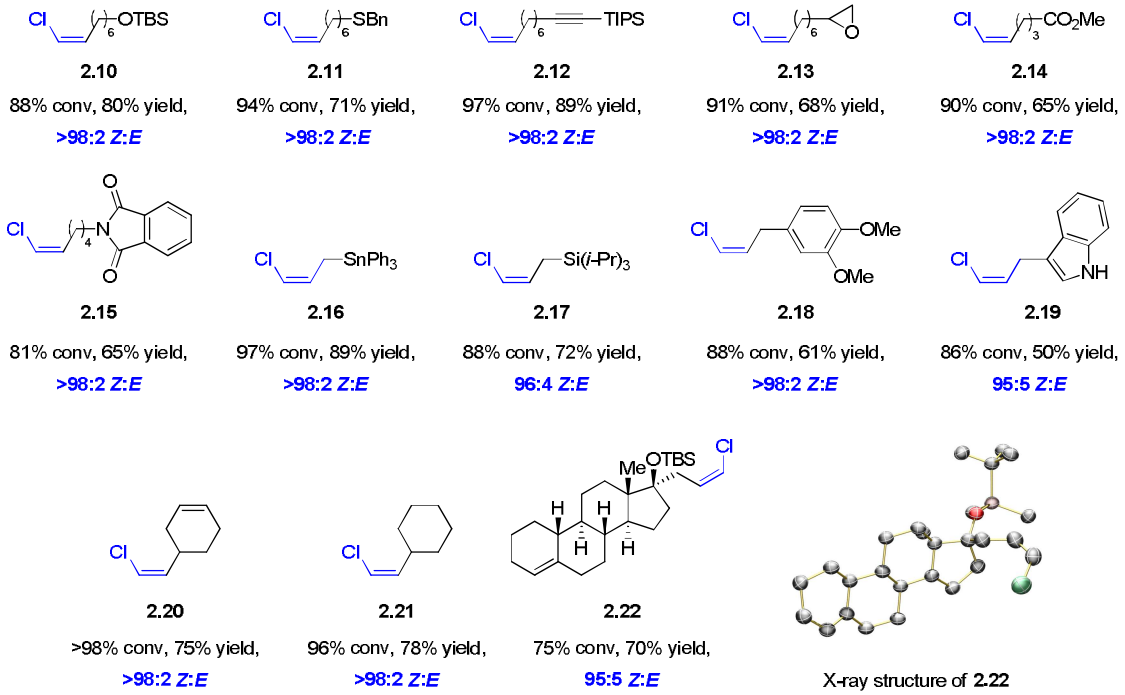
Mo-4c

with 5 mol %, 22 °C, 4 h,
90% conv, 75% yield,
>98:2 *Z*:*E*

2.3.2. CM to Access Functionalized Z-Alkenyl Chlorides

Scheme 2.5. The range of *Z*-Alkenyl Chlorides Accessed through *Z*-Selective CM with **Mo-4c**.





With the optimal conditions in hand, we proceeded to explore the scope of our protocol (Scheme 2.5). A variety of *Z*-alkenyl chlorides can be accessed in 50–91% yield and 95 to >98% *Z* selectivity. These include those bearing common functionalities such as a silyl ether (**2.10**), a sulfide (**2.11**), an alkyne (**2.12**), an epoxide (**2.13**), an ester (**2.14**) or a phthalimide (**2.15**). Allylstannane **2.16** and allylsilane **2.17**, potential allylating agents for C–C bond forming reactions, can be obtained in 72–89% yield and ≥96:4 *Z*:*E* ratio. Substrates bearing an aryl or heteroaryl group at the allylic position were tolerated (**2.18** and **2.19**), and sterically congested α-branched aliphatic alkenes could also

participate in CM efficiently (**2.20** and **2.21**). It merits mention that transformations with styrenes (regardless of their electronic attributes) were found to be inefficient. This is probably due to excessive steric hindrance within the requisite trisubstituted all-*syn* metallacyclobutane for CM (cf. **2.4** in Scheme 2.3), which causes homocoupling of the aryl olefin to be more competitive and the resulting stilbenes do not re-enter the catalytic cycle easily. In contrast, CM with α-branched aliphatic olefins is more efficient because these alkenes do not undergo facile homocoupling. The reaction to afford **2.22** underscores applicability to alkenes that contain a homoallylic quaternary stereogenic center.

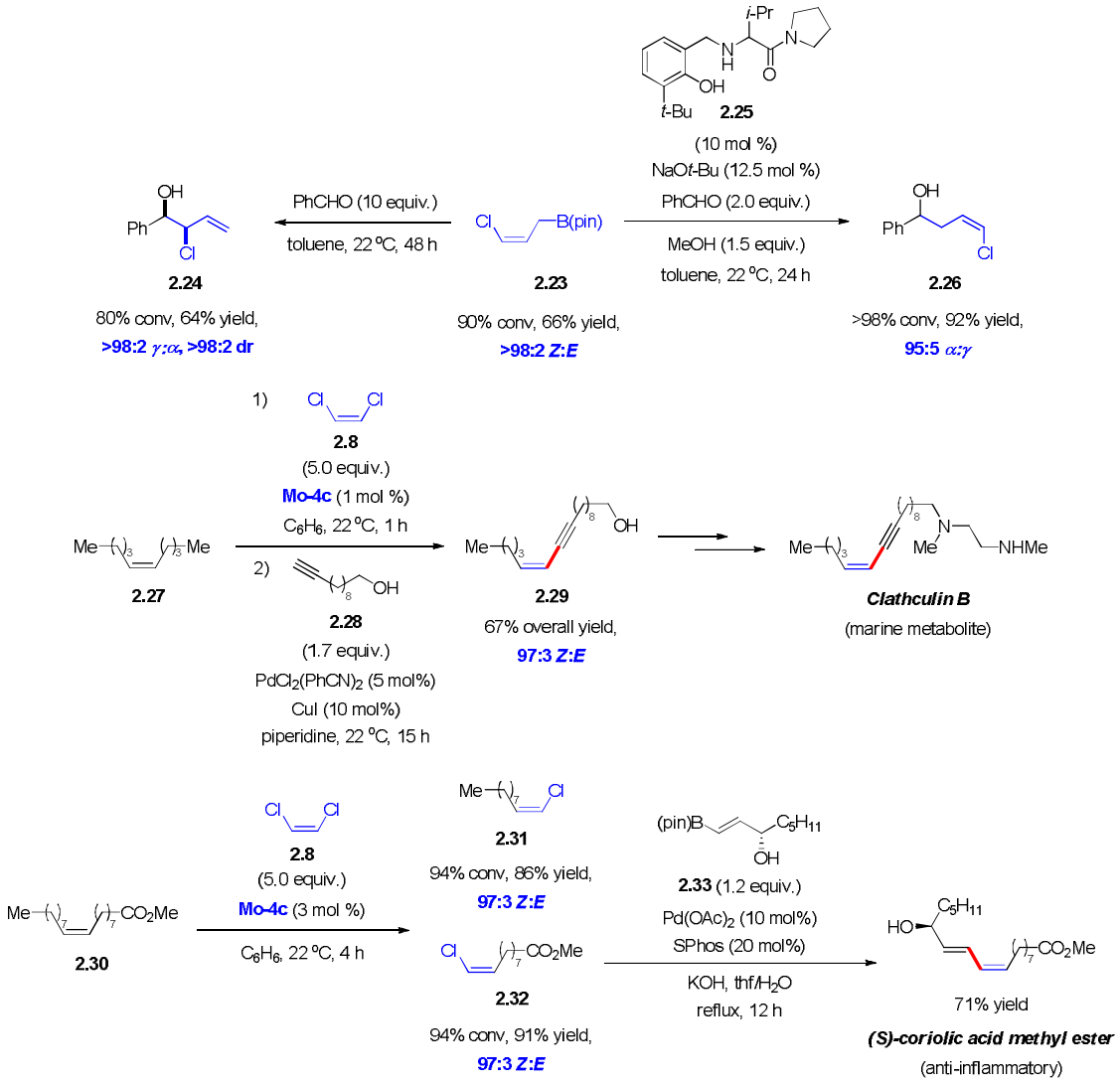
2.3.3. Application of Z-Alkenyl Chlorides in Organic Synthesis

A number of key transformations were performed to demonstrate utility of the *Z*-alkenyl chlorides obtained from CM (Scheme 2.6). Allylboronate **2.23**, isolated in 66% yield and complete *Z* selectivity by CM between commercially available allylboronic pinacol ester and *Z*-1,2-dichloroethene **2.8**, was used as a reagent in two representative additions to benzaldehyde. In one case, **2.24** was formed in 64% yield and >98% γ- and diastereoselectivity. On the other hand, **2.26** was obtained in 92% yield and 95:5 α:γ ratio without loss in *Z*:*E* ratio (>98% *Z* selectivity) in the presence of 10 mol % aminophenol **2.25**.[23] It is noteworthy that access to *Z*-alkenyl chlorides such as sulfide **2.11**,[24] indole **2.19**[25] and allylboron **2.23** by the alternative two-step procedure involving vinyl-B(pin)

(23) (a) Silverio, D. L.; Torker, S.; Pilyugina, T.; Vieira, E. M.; Snapper, M. L.; Haeffner, F.; Hoveyda, A. H. *Nature* **2013**, *494*, 216–221. For the use of **2.23** in other C–C bond forming reactions, see: (b) van der Mei, F. W.; Miyamoto, H.; Silverio, D. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2016**, *55*, 4701–4706. (c) Land ry, M. L.; Hu, D. X.; McKenna, G. M.; Burns, N. Z. *J. Am. Chem. Soc.* **2016**, *138*, 5150–5158.
(24) Gensch, K. H.; Pitman, I. H.; Higuchi, T. *J. Am. Chem. Soc.* **1968**, *90*, 2096–2104.
(25) Hamri, S.; Rodríguez, J.; Basset, J.; Guillaumet, G.; Pujol, M. D. *Tetrahedron* **2012**, *68*, 6269–6275.

CM/boron-to-halogen exchange[10,12] is likely to be problematic due to sensitivity of the aforementioned functional groups under basic halogenation conditions.

Scheme 2.6. Representative Applications Involving *Z*-Alkenyl Chlorides Obtained by *Z*-Selective CM.



1,2-Disubstituted *Z*-olefins also serve as effective substrates in the CM protocol. Subjection of commercially available *Z*-5-decene **2.27** and excess **2.8** to 1 mol % of **Mo-4c** for two hours followed by Sonogashira coupling with alkyne **2.28** furnished enyne **2.29** in 67% overall yield and 97% *Z* selectivity without the need for isolation of the volatile *Z*-alkenyl chloride intermediate. **2.29** has been used for the preparation of marine

metabolite clathculin B.[26] In another example, treatment of *Z*-methyl oleate **2.30** under the established CM conditions afforded readily separable *Z*-alkenyl chlorides **2.31** and **2.32** in 86% and 91% yield, respectively, and 97:3 *Z*:*E* ratio. **2.32** was further elaborated to anti-inflammatory (*S*)-coriolic acid methyl ester through Suzuki coupling with alkenylboronate **2.33** (obtained from site- and *E*-selective protoboryl addition of commercially available (*S*)-1-octyn-3-ol).[27] Overall, the target compound was accessed from a renewable resource in 65% overall yield and 97% *Z* selectivity, which compares favorably with previous synthesis methods.[28]

2.3.4. CM & ROCM to Access Functionalized Z-Alkenyl Bromides

To access *Z*-alkenyl bromides by CM, we envisioned the use of commercially available and inexpensive 1,2-dibromoethene **2.34** which exists as a mixture of 64:36 *Z*:*E* isomers (pure *Z*-1,2-dibromoethene is not readily available and difficult to purify from the mixture). We surmised that the *Z*-isomer of 1,2-dibromoethene should react faster with MAP complexes[29] to give the corresponding *Z*-olefin CM product predominantly. As depicted in Scheme 2.7, an array of *Z*-alkenyl bromides **2.35**–**2.40** were obtained in 57–83% yield, albeit with somewhat lower stereoselectivity (87–91% *Z* selectivity).

The present strategy can be applied to ROCM as well. In the presence of 10 mol % **Mo-4c**, dibromoalkene **2.41** was generated in 88% yield and 89:11 *Z*,*Z*:*Z*,*E* ratio within 1 hour through ROCM of cyclooctene and excess **2.34**. **2.41** is a reported precursor for the synthesis of biologically active tetrahydrosiphonodiol.[30] In this case,

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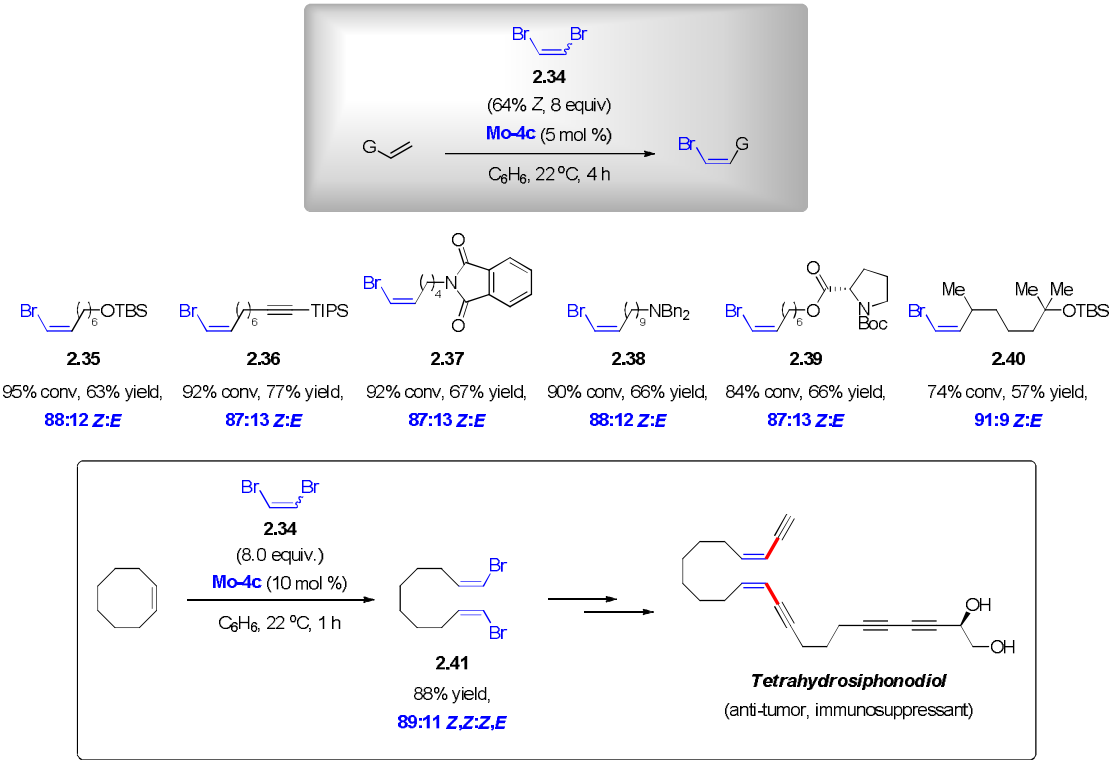
(26) Hoye, R. C.; Andersen, G. L.; Brown, S. G.; Schultz, E. E. *J. Org. Chem.* **2010**, *75*, 7400–7403.
(27) Jang, H.; Zhugralin, A. R.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 7859–7871.
(28) (a) Stille, J. K.; Sweet, M. P. *Tetrahedron Lett.* **1989**, *30*, 3645–3648. (b) Kang, S.-K.; Kim, K.-S. *Bull. Korean Chem. Soc.* **1990**, *11*, 475–477.
(29) Hoveyda, A. H. *J. Org. Chem.* **2014**, *79*, 4763–4792.
(30) López, S.; Fernández-Trillo, F.; Midón, P.; Castedo, L.; Saá, C. *J. Org. Chem.* **2005**, *70*, 6346–6352.

higher catalyst loading was necessary for maximal conversion of the ring-opening metathesis polymerization (ROMP) byproduct to **2.41**. It is worth mentioning that ROCM can also be performed between cyclooctene and *Z*-1,2-dichloroethene **2.8** to give the corresponding *Z*,*Z*-dichloroalkene in 75% yield as a stereoisomer using less active **Mo-3** as the catalyst (**Mo-3** is sufficient for the more facile ROCM with less hindered **2.8** to compete with ROMP for attaining maximal *Z* selectivity). With **Mo-3**, ROCM with the more sizeable **2.34** is relatively sluggish (~35% conversion to product, ~20% ROMP).

Scheme 2.7. Synthesis of *Z*-Alkenyl Bromides through *Z*-Selective CM and ROCM.

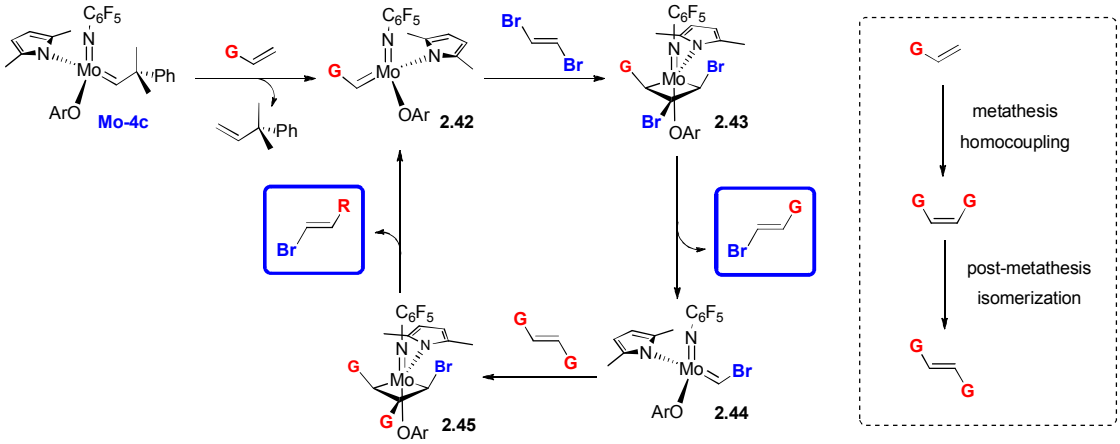


2.3.5. Rationale for Incomplete Z Selectivity in OM with 1,2-Dibromoethene

Two plausible reasons can be used to explain the lower *Z* selectivities observed in the OM transformations leading to alkenyl bromides in Scheme 2.7. As illustrated by the pathways in Scheme 2.8, the *E*-isomer of 1,2-dibromoethene, even though reacting more slowly than its *Z*-isomer counterpart, can potentially partake in the catalytic cycle to give

E-alkenyl bromide via metallacyclobutane **2.43** where all substituents are oriented *anti* to each other. This latter process is reminiscent of the CM transformation between a terminal olefin and *E*-2-butene-1,4-diol (cf. Chapter 1, Scheme 1.24), which we further exploit in the development of kinetically *E*-selective CM (see Section 2.4 for further discussion). The resulting bromo-substituted alkylidene **2.44** can further react with the *E*-homocoupling byproduct (from competitive *Z*-selective homocoupling of the terminal olefin substrate followed by post-metathesis isomerization) via all-*anti* metallacyclobutane **2.45** (where the substituents are oriented away from each other to minimize eclipsing interactions) to furnish more of the *E*-alkenyl bromide minor product.

Scheme 2.8. Possible Pathways Leading to Formation of *E*-Alkenyl Bromide Minor Product.

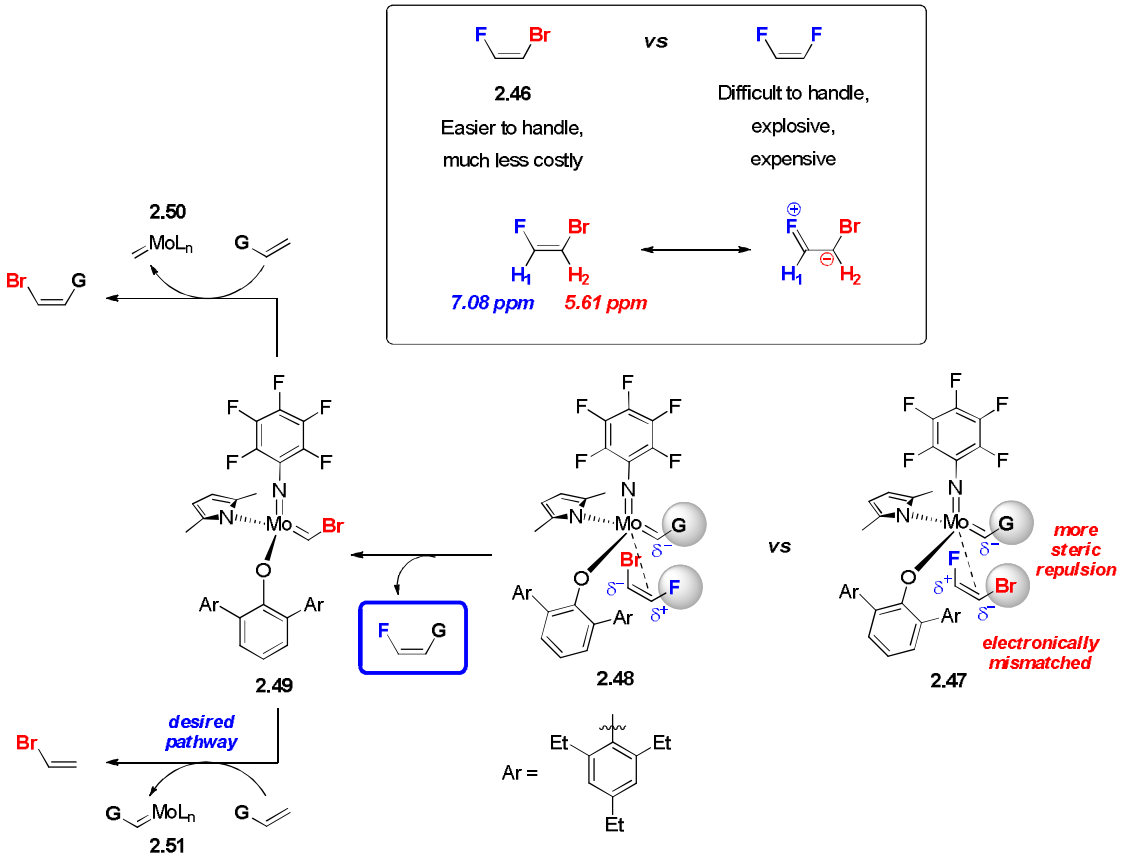


2.3.6. Identification of a Suitable Alkenyl Fluoride Reagent for CM

Synthesis of *Z*-alkenyl fluorides by CM presents a new complication pertaining to selection of a suitable fluorine-containing cross-partner (Scheme 2.9). For reasons listed in Section 2.2.2, we chose to avoid vinyl fluoride (boiling point = -72 °C). *Z*-1,2-Difluoroethene is expensive, similarly challenging to handle and explosive. Hence, we envisioned the use of *Z*-1-bromo-2-fluoroethene **2.46**, a more economically viable and less volatile reagent (boiling point = 36 °C). However, the use of dissymmetrical alkene

2.46 raises a potential regioselectiviy problem: it could react with the Mo alkylidene via two competing modes of addition (**2.47** and **2.48**). Analysis of the ^{1}H NMR spectrum ($CDCl_3$) of **2.46** shows that the C–H adjacent to Br is appreciably more shielded, implying enhanced electron density at this carbon (greater π donating and σ withdrawing inductive effect of fluorine), consequently favoring its association with the Lewis acidic Mo center via **2.48** (electronic matching). Furthermore, the metallacycle formed via **2.47** would likely suffer from greater steric repulsion between the larger bromine (vs. fluorine in **2.48**) and the alkylidene substituent (G). The resulting Br-substituted alkylidene **2.49** could then react with the olefin substrate to regenerate the propagating alkylidene species **2.51** and release vinyl bromide as byproduct.

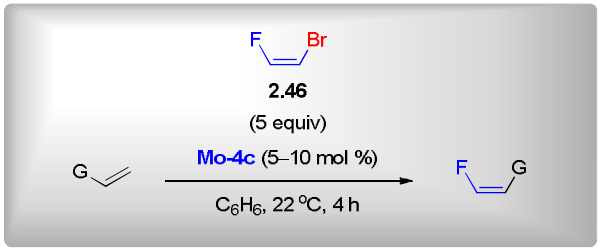
Scheme 2.9. Identification of a Practical and Effective Alkenyl Fluoride Reagent for CM.

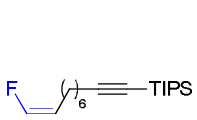


2.3.7. CM to Access Functionalized Z-Alkenyl Fluorides

As a testament to our aforementioned hypothesis, *Z*-alkenyl fluoride **2.52** was formed as the major product (72:28 Br:F ratio) and >98% *Z* selectivity (Scheme 2.10). Consistent with the suggested model in Scheme 2.9, CM with a sterically encumbered α-branched alkene gave 96:4 Br:F selectivity and **2.53** was isolated in 70% yield and >98:2 *Z*:*E* ratio (mode of addition **2.47** is disfavored to a greater extent due to enhanced steric repulsion between the larger G substituent and bromine). Another reason for the lower Br:F selectivity observed with sterically unhindered olefins (**2.52**) could be facile homocoupling of the substrate to give products that can react with Br-alkylidene **2.49** to give more of the bromo-alkene product.

Scheme 2.10. Synthesis of *Z*-Alkenyl Fluorides through *Z*-Selective CM.



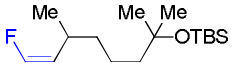


2.52

>98% conv, **72:28 F:Br**

64% yield (F),

>98:2 *Z*:*E*

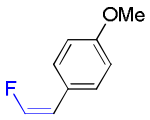


2.53

>98% conv, **96:4 F:Br**

70% yield (F),

>98:2 *Z*:*E*

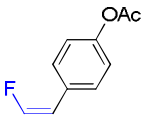


2.54

>98% conv, **93:7 F:Br**

71% yield (F),

95:5 *Z*:*E*

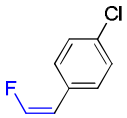


2.55

84% conv, **96:4 F:Br**

72% yield (F),

94:6 *Z*:*E*

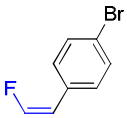


2.56

78% conv, **96:4 F:Br**

64% yield (F),

97:3 *Z*:*E*

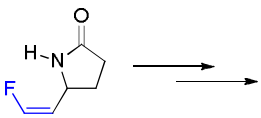


2.57

88% conv, **95:5 F:Br**

66% yield (F),

93:7 *Z*:*E*



2.58

(CM with TBS-amide/ deprotection)

60% conv, **>98:2 F:Br**

55% overall yield,

>98:2 *Z*:*E*

F-Vigabatrin

(GABA aminotransferase inhibitor with unique mode of action)

In contrast to transformations with dichloro- or dibromoethene (**2.8** and **2.34**), CM between styrenes and **2.46** proceeded efficiently to afford *Z*-β-fluorostyrenes **2.54**–**2.57** in 64–72% yield and ≥93% *Z* selectivity. This is likely due to diminished eclipsing interaction between fluorine and G within the all-*syn* metallacyclobutane for CM (cf. **2.4** in Scheme 2.3) compared to the more sizeable chlorine and bromine atoms, such that CM now competes more effectively with styrene homocoupling. To showcase utility, **2.58** was prepared via CM with the *tert*-butyldimethylsilyl (TBS)-protected amide substrate followed by desilylation in 55% overall yield as a single *Z*-isomer. This compound has been elaborated to *Z*-fluoro-vigabatrin, a GABA transaminase inhibitor[6] described in Section 2.1. There was <5% conversion with the unprotected amide substrate, presumably due to internal chelation of the Lewis basic amide group with the Mo center in the intermediate alkylidene complex.[31]

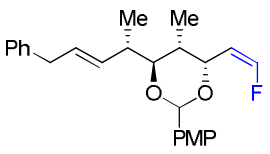
2.3.8. Demonstration of Functional Group Compatibility and Late-Stage Fluorination

A useful corollary of the present CM strategy is the possibility of performing a late-stage stereoselective conversion of an alkenyl C–H to a C–F bond within a complex molecule.[32] This would enable access to a myriad of stereodefined fluorine-labeled analogues for potential bioassay screening in medicinal chemistry programs. As shown in Scheme 2.11, efficient and stereoselective synthesis of *Z*-alkenyl fluorides **2.59** and **2.60** (63% and 70% yield, respectively) highlights the point that CM transformations can be used to transform olefin-containing biologically relevant molecules to their fluorinated derivatives. The reactions that afford **2.61** (derived from anti-depressant perphenazine)

(31) Zhang, H.; Yu, E. C.; Torker, S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 16493–16496.
(32) Campbell, M. G.; Ritter, T. *Org. Process Res. Dev.* **2014**, *18*, 474–480.

and **2.62** (derived from β-lactamase inhibitor sulbactam) demonstrate compatibility with functional motifs that are commonly found in bioactive compounds.

Scheme 2.11. *Z*-Selective Alkenyl Fluoride CM with Complex Molecules.



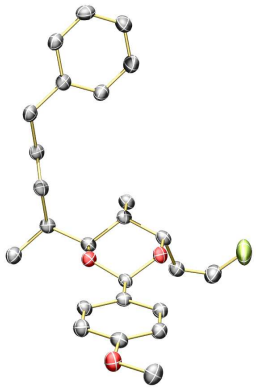
2.59

80% conv, **>98:2 F:Br**

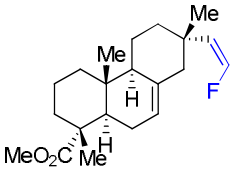
63% yield,

>98:2 *Z*:*E*

(from intermediate in synthesis of ***Baconipyrone C***)



X-ray structure of **2.59**



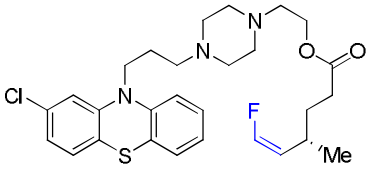
2.60

83% conv, **95:5 F:Br**

70% yield (F),

>98:2 *Z*:*E*

(from methyl ester of ***Isopimaric acid***, potassium channel opener)



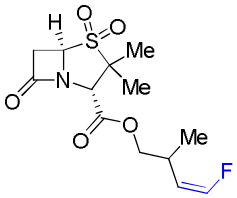
2.61

88% conv, **91:9 F:Br**

78% yield (F),

>98:2 *Z*:*E*

(from ***Perphenazine***, anti-depressant)



2.62

86% conv, **>98:2 F:Br**

80% yield,

>98:2 *Z*:*E*

(from ***Sulbactam***, ß-lactamase inhibitor)

One remarkable attribute of CM that allows access to highly elaborate *Z*-alkenyl fluorides is that these transformations can be conducted under mild reaction conditions. For example, synthesis of **2.62** by the alternative two-step sequence of *Z*-selective CM with vinyl-B(pin)[10] using **Mo-4c** as catalyst followed by C–B to C–F bond conversion[33] resulted in substrate decomposition. The first CM step delivered the required *Z*-alkenyl-B(pin) (22°C, 24 h, 70% conversion, >98% *Z* selectivity), but treatment with NaOH and

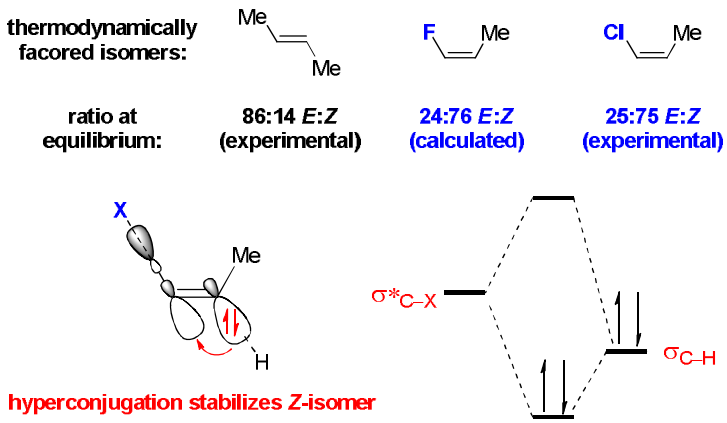
(33) Furuya, T.; Ritter, T. *Org. Lett.* **2009**, *11*, 2860–2863.

AgOTf and then Selectfluor led to an unidentifiable mixture of compounds, probably due to the sensitivity of the molecule's bicyclic core.[34] On the contrary, *Z*-alkenyl fluoride **2.62** was efficiently generated by direct CM in 80% yield (>98:2 Br:F) as a single stereoisomer with our established method.

2.4. Development of Kinetically Controlled E-Selective Cross-Metathesis

2.4.1. Key Challenges in CM to Access E-Alkenyl Halides

Scheme 2.12. Thermodynamic Parameters of 2-Butene and Selected 1-Halopropenes.



Kinetically controlled *Z*-selective OM was first introduced in 2009,[35] but the corresponding transformations through which *E*-alkenes can be obtained in high yields with broad scope remains a longstanding limitation in the field. This is particularly the case for acyclic halogen-substituted olefins (Scheme 2.12), where the *Z*-isomer is thermodynamically favored in many instances due to stabilizing hyperconjugative donation of electron density from a filled σ_{C-H} orbital to a low-lying vacant $\sigma^*_{C-halogen}$ orbital.[36] Nevertheless, the energy difference between *E*- and *Z*-isomers of alkenyl halides is often too small to ensure high selectivity by thermodynamic control

(34) Haginaka, J.; Yasuda, H.; Uno, T.; Nakagawa, T. *Chem. Pharm. Bull.* **1984**, *32*, 2752–2758.
(35) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844–3845.
(36) Wiberg, K. B.; Wang, Y. G.; Petersson, G. A.; Bailey, W. F. *J. Chem. Theory Comput.* **2009**, *5*, 1033–1037.

and separation of these two geometric forms is challenging in many cases. As such, it becomes apparent that developing a kinetically controlled CM protocol to access *E*-alkenyl halides constitutes a compelling research objective, in addition to the tremendous utility of such moieties in organic chemistry (Scheme 2.1).

As illustrated in Chapter 1 (Scheme 1.24) as well as Section 2.3.5 (Scheme 2.8), a conceptually feasible solution to the aforementioned problem is the application of olefin stereoretention by employing a *trans*-1,2-disubstituted olefin reagent to deliver high kinetic *E* selectivity.[37] In addition to these preliminary observations, the only other report on kinetically *E*-selective CM reactions involving Ru-based catechothiolate complexes was disclosed in 2016, wherein thermodynamically favored *E*-isomers of simple (unfunctionalized) 1,2-disubstituted aliphatic olefins could be obtained in 3–31% yield.[38] These results underscore the need for identifying a catalyst that is sufficiently active to promote stereoretentive OM with *trans*-alkenes.

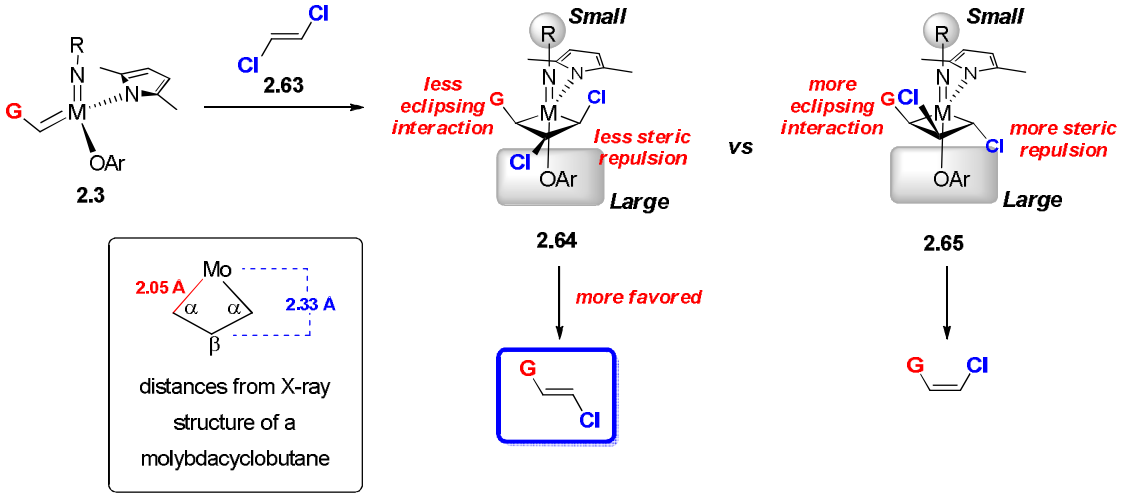
2.4.2. Design Principles for Kinetically E-Selective CM[39]

To achieve kinetically controlled *E*-selective CM, we envisioned the use of *E*-1,2-dihaloethene such as commercially available and inexpensive *E*-1,2-dichloroethene **2.63** as cross-partner (Scheme 2.13). Treatment of a MAP complex with a terminal olefin substrate generates **2.3** which should engage with **2.63** to generate two conceivable metallacyclobutanes **2.64** and **2.65**. We reasoned that formation of all-*anti* metallacycle **2.64** (cf. Scheme 2.8) should be favored to avoid the eclipsing interaction (G and Cl) inherent in **2.65**. Furthermore, information regarding the bond distances from the X-ray

(37) For a recent review, see: Montgomery, T. P.; Ahmed, T. S.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 11024–11036.
(38) Johns, A. M.; Ahmed, T. S.; Jackson, B. W.; Grubbs, R. H. *Org. Lett.* **2016**, *18*, 772–775.
(39) Nguyen, T. T.; Koh, M. J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. *Science* **2016**, *352*, 569–575.

structure of a molybdacyclobutane[40] shows that the Mo–C_α bond length is shorter than the Mo–C_β bond length (2.05 vs. 2.33 Å). This implies that there might be less steric repulsion between chlorine and the sizeable aryloxide ligand in **2.64** compared to **2.65**, further increasing the likelihood of generating the former metallacycle. Subsequent cleavage of **2.64** affords the desired *E*-olefin product.

Scheme 2.13. Kinetically *E*-Selective CM with *E*-Dihaloethene and High-Oxidation-State Alkylidenes.

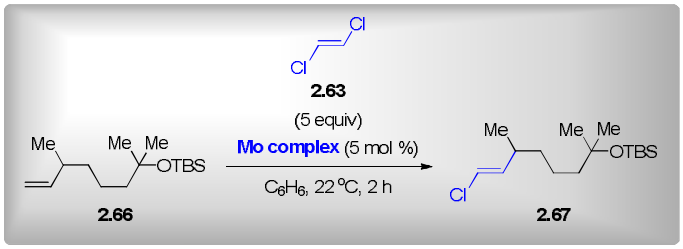


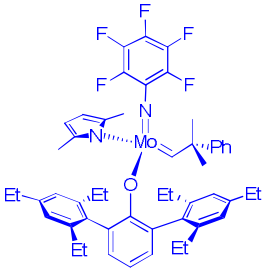
In testing our hypothesis, we subjected **2.68** to 5 equivalents of **2.63** and 5 mol % of **Mo-4c** (Scheme 2.14). Within two hours, the desired CM product **2.67** was obtained in 70% yield and 80:20 *E*:*Z* ratio. Although stereoselectivity remains to be improved, this result is encouraging since it lends credence to our proposed model described in Scheme 2.13. In contemplating ways to improve the *E*:*Z* ratio, we envisaged that removing *ortho*-aryl substituents within the aryloxide ligand might alleviate steric repulsion with chlorine at the C_β , thus favoring reaction via **2.64**. In the event, CM with **Mo-4d** led to substantially improved stereoselectivity (91:9 *E*:*Z*) but lower efficiency (41% conversion vs. 72% conversion to **2.67** for **Mo-4c**), possibly due to competitive bimolecular

(40) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10840–10841.

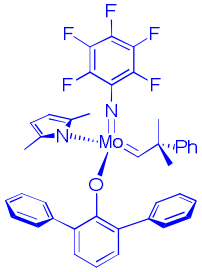
decomposition.[41] To retain high selectivity without compromising efficiency, we evaluated the performance of **Mo-4e** and **Mo-4f**, both of which contain aryloxides bearing *meta*-aryl substituents to provide sufficient steric protection around the Mo center for better catalyst lifetime. The best balance of efficiency and selectivity could be obtained with **Mo-4f**, delivering **2.67** in 93% yield and 89% *E* selectivity. Selectivity improved to 93:7 *E*:*Z* with 20 equivalents of **2.63**, probably due to reduced competitive non-stereoselective CM involving the vinyl chloride byproduct (cf. Scheme 2.3).

Scheme 2.14. Identification of an Effective Catalyst for *E*-Selective CM with *E*-1,2-Dichloroethene.

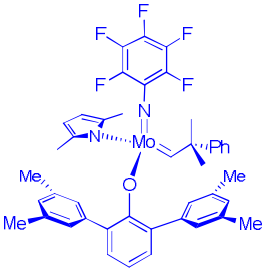




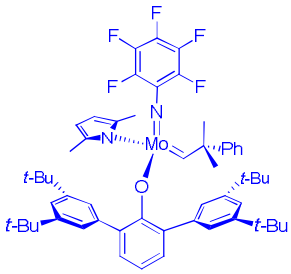
92% conv, 72% conv to **2.67**, 70% yield. **80:20 *E*:*Z***



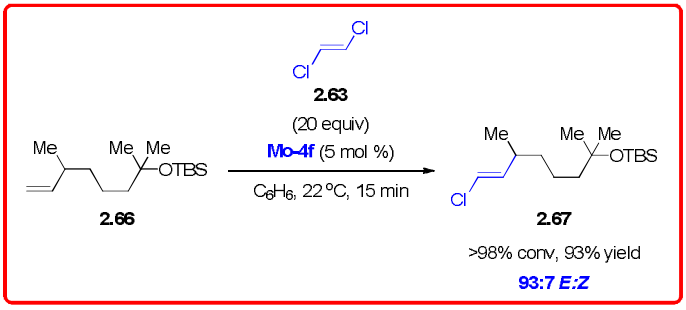
52% conv, 41% conv to **2.67**, yield ND, **91:9 *E*:*Z***



78% conv, 70% conv to **2.67**, yield ND, **90:10 *E*:*Z***



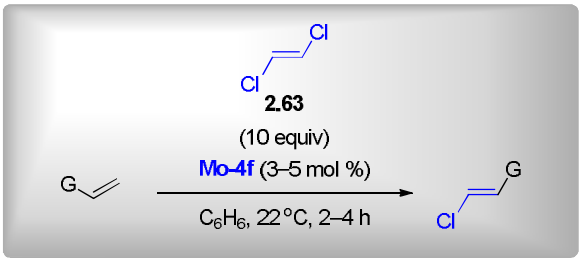
>98% conv, 93% conv to **2.67**, 93% yield, **89:11 *E*:*Z***

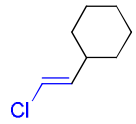


(41) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633.

2.4.3. CM to Access Functionalized E-Alkenyl Chlorides

Scheme 2.15. Synthesis of *E*-Alkenyl Chlorides through *E*-Selective CM.

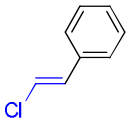




2.68

>98% conv, 80% yield,

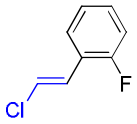
92:8 *E*:*Z*



2.69

>98% conv, 65% yield,

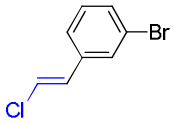
>98:2 *E*:*Z*



2.70

>98% conv, 54% yield,

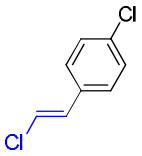
>98:2 *E*:*Z*



2.71

>98% conv, 60% yield,

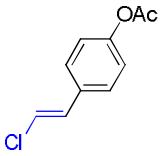
>98:2 *E*:*Z*



2.72

>98% conv, 69% yield,

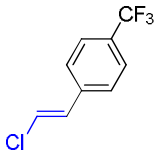
>98:2 *E*:*Z*



2.73

>98% conv, 75% yield,

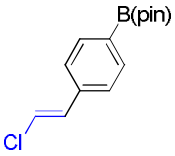
>98:2 *E*:*Z*



2.74

96% conv, 59% yield,

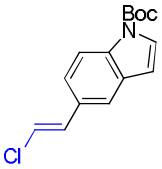
>98:2 *E*:*Z*



2.75

>98% conv, 61% yield,

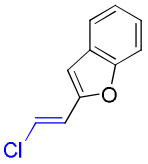
>98:2 *E*:*Z*



2.76

>98% conv, 85% yield,

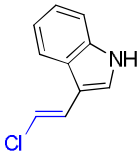
>98:2 *E*:*Z*



2.77

>98% conv, 62% yield,

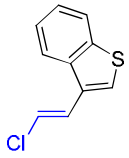
>98:2 *E*:*Z*



2.78

>98% conv, 85% yield,

>98:2 *E*:*Z*



2.79

85% conv, 69% yield,

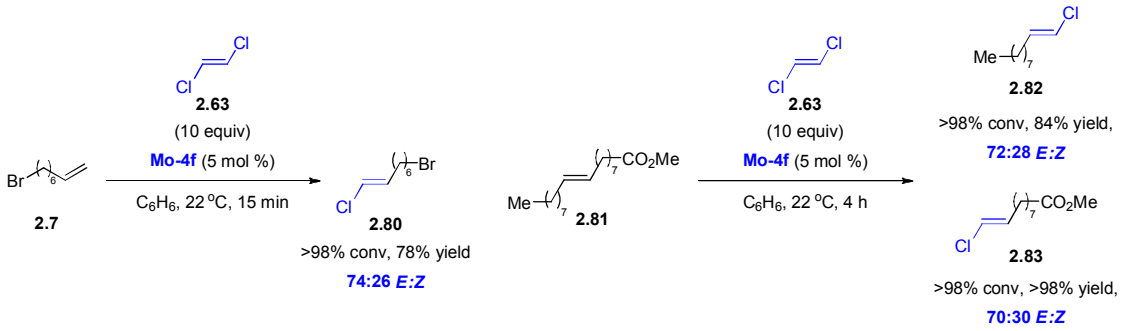
>98:2 *E*:*Z*

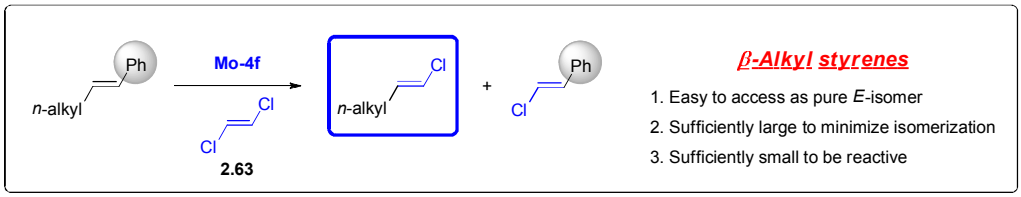
With the optimal catalyst in hand, we surveyed the scope of our catalytic protocol (Scheme 2.15). In general, CM reactions with sterically hindered α-branched aliphatic alkenes (**2.68**) as well as electronically diverse aryl and heteroaryl olefins (**2.69**–**2.79**) proceeded efficiently to give the desired products in 54–85% yield and ≥92:8 *E*:*Z* ratio (the difference between conversion and isolated yield is largely due to formation of homocoupling products). Notably, *E*-alkenyl chlorides containing an aryl halide or

boronate motif such as **2.71**, **2.72** and **2.75**, the synthesis of which by alternative cross-coupling methods may suffer from chemoselectivity issues,[42] can be readily accessed by CM.

2.4.4. CM with Unhindered Aliphatic Olefins

Scheme 2.16. Complications in *E*-Selective CM with Unhindered Aliphatic Olefins & Possible Solution.





CM with unhindered aliphatic alkenes (vs. α-branched aliphatic alkenes like **2.66**) posed an unforeseen complication (Scheme 2.16). For example, reaction of **2.7** and excess **2.63** under standard CM conditions provided the desired alkenyl chloride **2.80** in 78% yield, but stereoselectivity was moderate (74% *E* selectivity). The origin of this discrepancy may be rooted in more competitive and moderately selective generation of 1,2-disubstituted homocoupling products, which can re-enter the catalytic cycle and react with **2.63** to give isomeric mixtures of **2.80**. In another instance, CM with *E*-methyl oleate **2.81** with **2.63** delivered the expected CM products **2.82** and **2.83** with similar selectivity (~70:30 *E*:*Z*). These findings imply that *trans*-1,2-disubstituted alkyl olefins

(42) (a) Barluenga, J.; Moriel, P.; Aznar, P.; Valdés, C. *Adv. Synth. Catal.* **2006**, *348*, 347–353. (b) Billingsley, K. L.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 5589–5591.

may undergo facile *E*-to-*Z* isomerization through moderately selective self-metathesis before reaction with **2.63**.

In order to address the problem with unhindered alkyl olefins, we surmised that an appropriate *E*-1,2-disubstituted alkene may be used as substrate for CM, which would be equivalent to a stereospecific group exchange to generate the desired *E*-alkenyl chloride (Scheme 2.16, box). The ideal substituent should be readily accessible and sufficiently sizeable to minimize substrate self-metathesis and adventitious *E*-to-*Z* isomerization, but not so large as to inhibit CM with **2.63**. One such class of substrates are β-alkyl styrenes and these robust compounds can be efficiently prepared by a variety of methods (see Section 2.4.5).

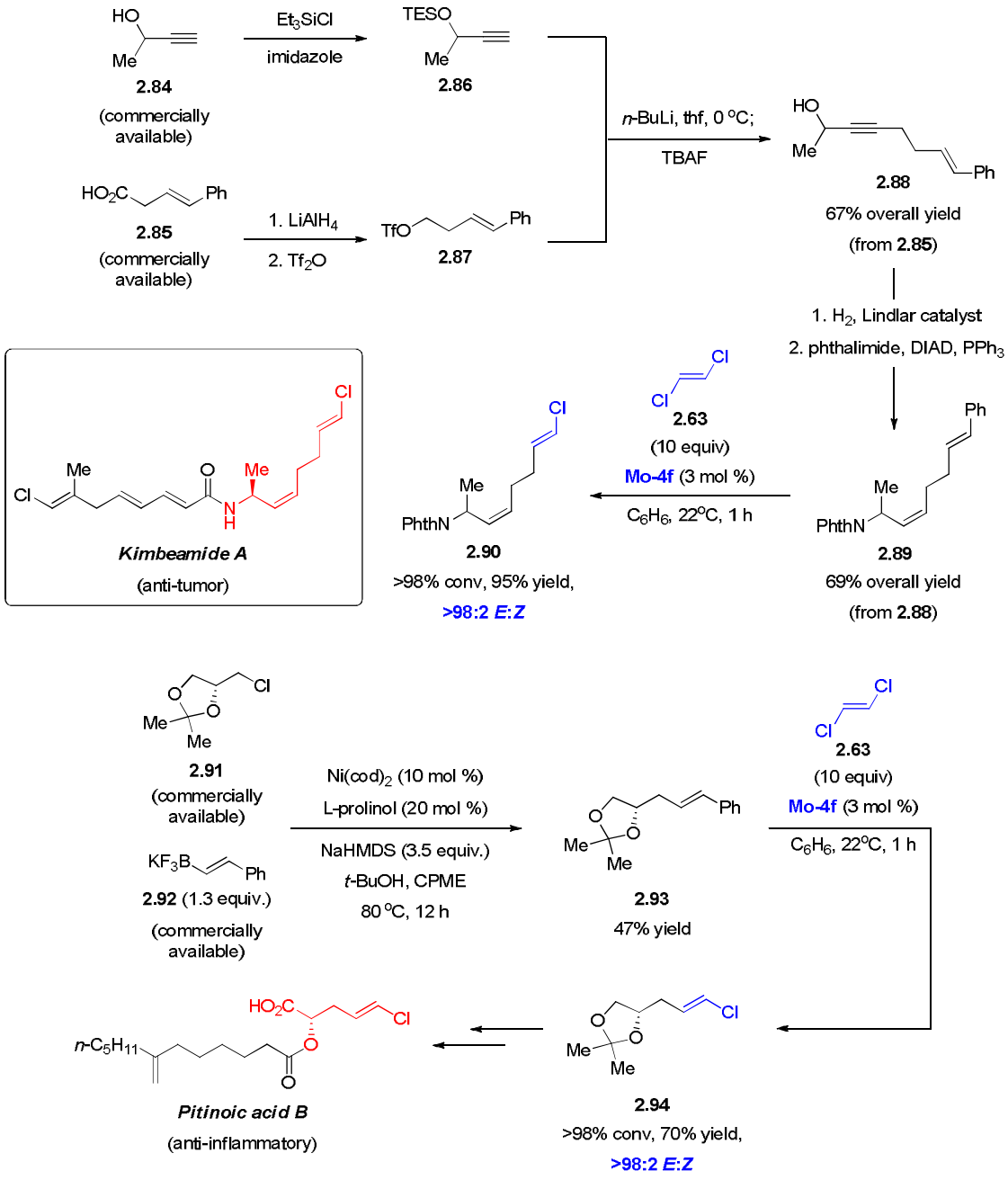
2.4.5. Application to Natural Product Synthesis

We chose to demonstrate the utility of *E*-selective CM using β-alkyl styrenes as substrates in the context of natural product synthesis (Scheme 2.17). The first example relates to a concise preparation of the amine fragment of anti-tumor kimbeamide A (**2.90**). 1,5-Enyne **2.88** was obtained from coupling **2.86** and **2.87**, which were derived from commercially available 3-butyn-2-ol **2.84** and carboxylic acid **2.85**. Partial hydrogenation of **2.88** followed by Mitsunobu reaction afforded 1,5-diene **2.89** in 69% overall yield, which was subjected to CM with excess **2.63** in the presence of 3 mol % **Mo-4f** to furnish *E*-alkenyl chloride **2.90** in 95% yield and >98:2 *E*:*Z* ratio within 1 hour. It merits mention that CM occurred chemoselectively at the styrenyl site without reacting with the internal *Z*-allylic amine (>98% *Z*).

Another exemplary case corresponds to anti-inflammatory pitinoic acid B. β-Alkyl styrene **2.93** was accessed by catalytic cross-coupling from commercially available

alkyl chloride **2.91** and alkenyl trifluoroborate **2.92** in 47% yield.[43] CM of **2.93** with **2.63** under the established conditions delivered *E*-alkenyl chloride **2.94** in 70% yield as a single stereoisomer; **2.94** is a reported precursor to pitinoic acid B.[44]

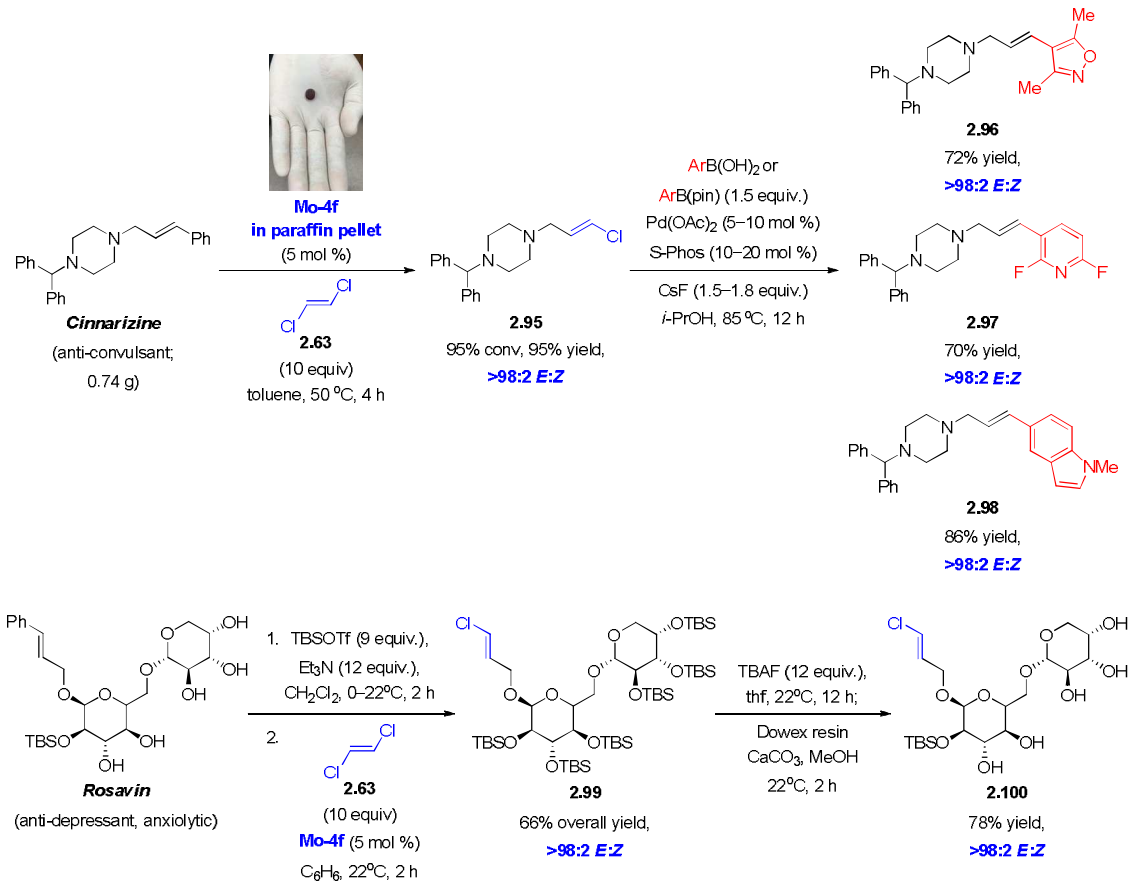
Scheme 2.17. Application of *E*-Selective CM with Unhindered Alkenes to Natural Product Synthesis.



(43) Molander, G. A.; Argintaru, O. A. *Org. Lett.* **2014**, *16*, 1904–1907.
(44) Montaser, R.; Paul, V. J.; Luesch, H. *Org. Lett.* **2013**, *15*, 4050–4053.

2.4.6. Application to Preparation of Analogues of Bioactive Compounds

Scheme 2.18. Modification of Therapeutic Agents through *E*-Selective CM.

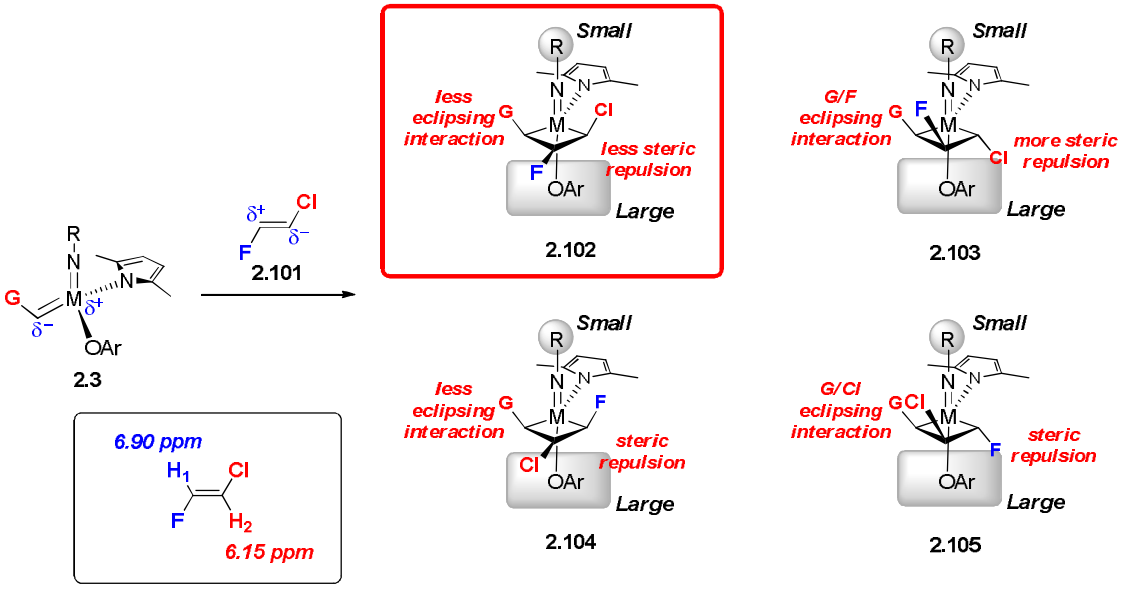


Another useful application of the CM strategy pertains to modification of biologically active compounds (Scheme 2.18). Conversion of 0.74 g of anti-convulsant cinnarizine to *E*-alkenyl chloride **2.95** (95% yield, >98% *E* selectivity) shows that CM transformations are scalable. In addition, the Mo-based Mo complexes may be delivered in the form of air- and moisture-resistant paraffin pellets, allowing reactions to be performed in the fume hood (CM was performed at 50 °C in toluene under nitrogen atmosphere to ensure complete release of the MAP complex). **2.95** serves as a convenient entry to derivatives that may be difficult to access efficiently and/or high *E* selectivity by alternative synthesis routes (including direct CM). Illustrative examples are highlighted

through Suzuki coupling of **2.95** with various commercially available heterocyclic boronic acids or pinacol esters to afford **2.96**–**2.98** in 70–86% yield. In another case, the persilylated analogue of anti-depressant rosavin was transformed to *E*-alkenyl chloride **2.99** in 90% yield and >98:2 *E*:*Z* ratio. In analogy to cinnarizine-derived **2.95**, **2.99** or its deprotected variant **2.100** may be further converted to an array of different analogues.

2.4.7. Design of E-Selective CM Reactions that Afford Alkenyl Fluorides

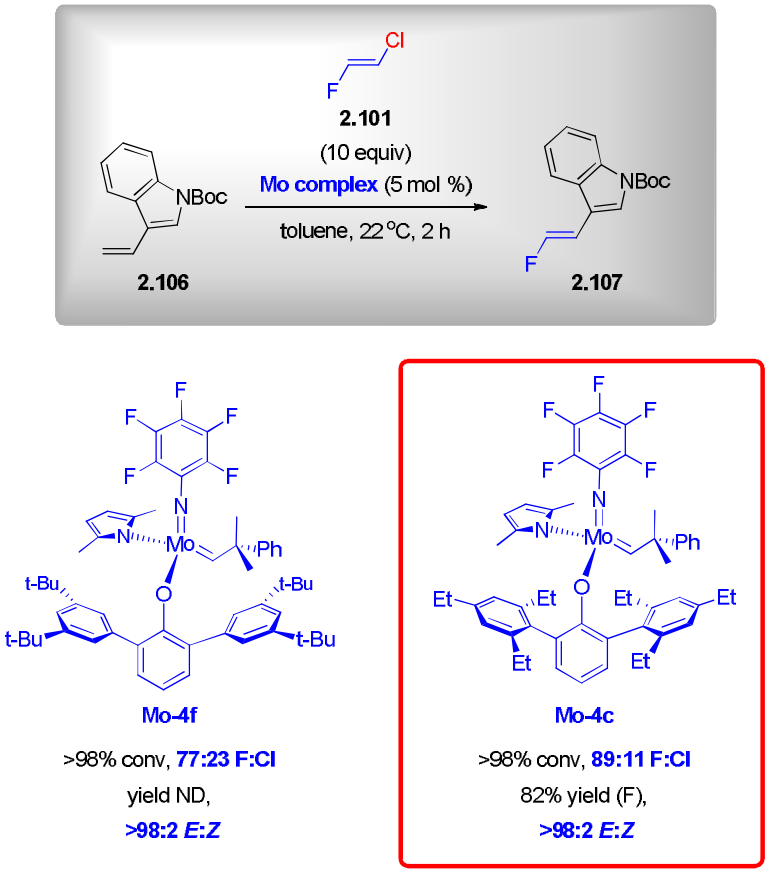
Scheme 2.19. Design of *E*-Selective CM with *E*-1-Chloro-2-fluoroethene to Access Alkenyl Fluorides.



As with the case for *Z*-alkenyl fluorides, a suitable and practical *E*-1,2-disubstituted fluoroalkene cross-partner needs to be identified for CM reactions that furnish *E*-alkenyl fluorides (Scheme 2.19). *E*-1,2-Difluoroethene is costly and volatile (boiling point = -42 ^{o}C), whereas dissymmetrical *E*-1-chloro-2-fluoro-ethene **2.101** is economically more viable and more convenient to handle (boiling point = -4 ^{o}C). **2.101** is polarized in a similar fashion as *Z*-1-bromo-2-fluoroethene **2.46** (Scheme 2.9), where there is greater electron density at the carbon adjacent to chlorine (from analysis of ^{1}H NMR spectrum ($CDCl_3$)). The same issue of regioselectivity thus arises since CM can

potentially proceed via four different metallacyclobutanes (**2.102**–**2.105**). We reasoned that CM should preferentially proceed via **2.102** on the basis of electronic matching between the alkylidene species **2.3** and **2.101**, and that there should be less steric strain within metallacycle **2.102** (vs. **2.103** and **2.104** where eclipsing interactions between substituents and steric repulsion between the aryloxide and a halogen at C_α exist).

Scheme 2.20. Identification of an Effective Catalyst for *E*-Selective CM with *E*-1-Chloro-2-fluoroethene.



To test our hypothesis, CM between aryl olefin **2.106** and 10 equivalents of **2.101** (dispensed as a solution in toluene) was carried out (Scheme 2.20). Indeed, the desired *E*-alkenyl fluoride **2.107** was obtained as the major product (77:23 F:Cl ratio). Intriguingly, both fluoro- and chloro-alkene products were generated with >98% *E* selectivity. These observations imply that reaction via metallacyclobutane **2.104** is likely to be the major

competing pathway (since cleavage of **2.103** and **2.105** should lead to a *Z*-alkenyl fluoride and a *Z*-alkenyl chloride, respectively). In order to improve the F:Cl regioselectivity, we thought that reverting to **Mo-4c**, which contains 2,4,6-triethyl-aryl groups (vs. 3,5-di-*tert*-butyl-aryl moieties in **Mo-4f**) could increase the steric repulsion between the halogen at C_β and the aryloxide in **2.104** (C_β–Cl) compared with **2.102** (C_β–F), since C–F bond length is shorter (1.35 Å vs. 1.80 Å for C–Cl) and fluorine atom is smaller (0.42 Å atomic radius vs. 0.79 Å for Cl). Gratifyingly, repeating the CM with **Mo-4c** led to improved F:Cl selectivity (89:11) and *E*-alkenyl fluoride **2.107** could be isolated in 82% yield. It merits mention Mo complexes with more hindered aryloxide ligands (for example, **Mo-4b**) gave lower substrate conversions.

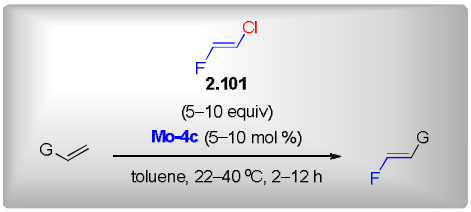
2.4.8. CM to Access Functionalized E-Alkenyl Fluorides

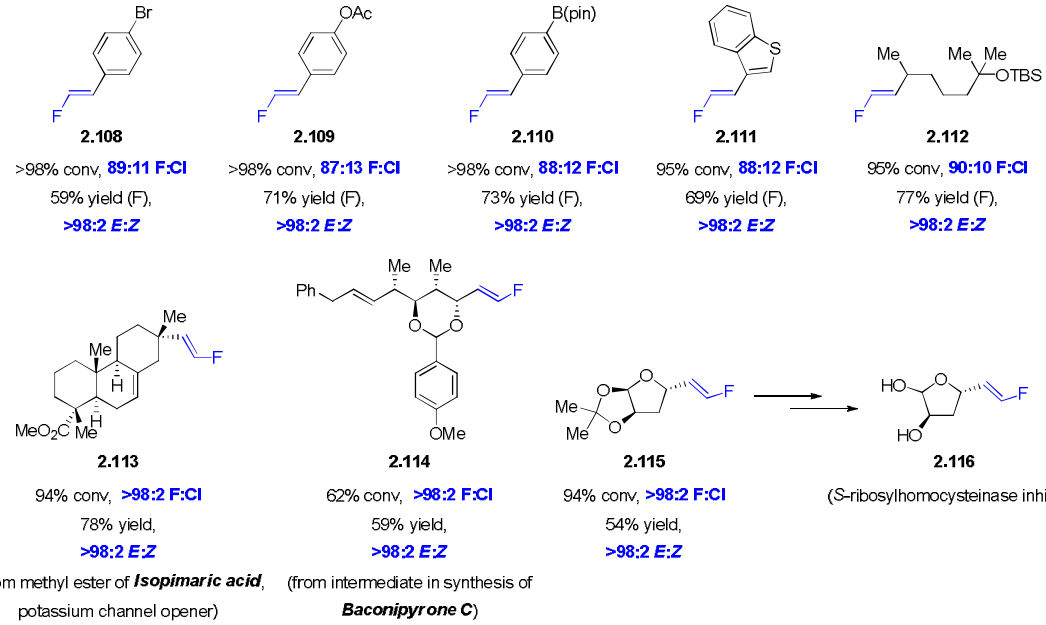
Using **Mo-4c** as the optimal catalyst, an assortment of *E*-alkenyl fluorides could be prepared in 54–79% yield as single stereoisomers (Scheme 2.21). In all cases, F:Cl selectivity is high (≥87:13 F:Cl). Functionalized aryl and heteroaryl alkenes (**2.108**–**2.111**) and sterically congested α-branched aliphatic olefins (**2.112**–**2.115**) are tolerated under the CM conditions. Similar to the *Z*-alkenyl fluoride cases presented in Scheme 2.11, access to **2.113** and **2.114** demonstrates that CM can be used to introduce a fluorine site- and stereoselectively within complex molecules to obtain fluorine-tagged derivatives.[32] An additional compelling example relates to the synthesis of *E*-alkenyl fluoride **2.115** (54% yield, >98:2 *E*:*Z* ratio), an intermediate used to prepare *S*-ribosylhomocysteinase inhibitor **2.116**.[45] Analogous to alkenyl fluoride **2.52** in Scheme

(45) Wnuk, S. F.; Lalama, J.; Robert, J.; Garmendia, C. A. *Bioorg. Med. Chem.* **2008**, *16*, 5090–5102.

2.10, CM of **2.101** with unhindered alkyl olefins suffers from moderate F:Cl selectivity (~70:30 F:Cl).

Scheme 2.21. Synthesis of *E*-Alkenyl Fluorides through *E*-Selective CM.





2.5. Conclusions

We have addressed key shortcomings in OM through development of catalytic protocols for kinetically controlled *Z*- and *E*-selective CM to access 1,2-disubstituted alkenyl halides. Prior to our investigations, OM with halo-alkenes primarily involved Ru-based complexes and transformations have been plagued by poor efficiency and/or stereoselectivity as a consequence of the undesirable formation of Fischer-type halo-substituted Ru carbenes that are less active towards OM and prone to decomposition

pathways. Taking advantage of the complementary[46] attributes of high-oxidation-state alkylidenes (vs. low-oxidation-state Ru carbenes), we found that halo-substituted alkylidenes are viable species to participate in OM to deliver a variety of functionalized alkenyl halides with high efficiency and selectivity. Utility of our developed methods is highlighted through synthesis of a number of biologically active targets and related analogues including fluorine-labeled derivatives.

The key players for the success of our methodology is the availability of inexpensive and easy-to-handle stereochemically defined *Z*- and *E*-1,2-disubstituted haloethene reagents as well as easily modifiable Mo-based MAP catalysts that are capable of reacting with the former to facilitate stereoretentive CM using readily available mono- or disubstituted alkenes as substrates. As already mentioned, use of 1,2-disubstituted haloethenes as cross-partners (vs. volatile vinyl halide) is beneficial in terms of practicality and reaction efficiency by reducing generation of ethylene and unstable methylidene complexes that can potentially lower catalyst lifetime and cause post-metathesis isomerization. During the course of our studies, we have shown that polarized dissymmetrical alkenes such as *Z*-1-bromo-2-fluoroethene **2.46** and *E*-1-chloro-2-fluoro-ethene **2.101** can serve as effective cross-partners by engaging with the polarized Mo alkylidene species to deliver the desired fluoro-alkene product predominantly.

We have also disclosed one of the first instances of highly efficient and kinetically controlled *E*-selective CM reactions that afford alkenyl chlorides and fluorides selectively. Based on our understanding of the possible competing pathways pertaining to metallacyclobutane formation as well as the associated stereoelectronic factors, different

(46) (a) Cortez, G. A.; Baxter, C. A.; Schrock, R. R.; Hoveyda, A. H. *Org. Lett.* **2007**, *9*, 2871–2874. (b) A. H. Hoveyda, A. R. Zhugralin, Nature **2007**, *450*, 243–251.

optimal Mo complexes (**Mo-4c** or **Mo-4f**) bearing distinct aryloxide ligands were identified to catalyze transformations leading to *E*-alkenyl fluorides and chlorides. These results show that the same MAP catalyst scaffold for *Z* selectivity can be readily tuned to meet the requirements for kinetic *E* selectivity by varying the aryloxide ligand within the complex.

Despite the advances delineated in this chapter, there remains a number of drawbacks to be addressed. For example, in *Z*- and *E*-selective CM with dissymmetrical fluorine-containing reagents **2.46** and **2.101**, unhindered alkyl olefins tend to result in moderate regioselectivity due to rapid homocoupling. CM of styrenes with *Z*-1,2-dichloroethene **2.8** also suffers from poor efficiency as a result of competitive styrene homocoupling, whereas transformations with 1,2-dibromoethene leading to *Z*-alkenyl bromides give somewhat lower selectivity (87–91% *Z* selectivity) than those that afford chloro- or fluoro-alkenes. Development of a new class of OM catalysts that exhibits distinct reactivity and chemoselectivity attributes favoring CM to our desired product (vs. self-metathesis) may allow us to solve some of the aforementioned limitations to broaden the applicability of our catalytic strategies.

2.6. Experimentals

2.6.1. General

Unless otherwise noted, transformations were performed with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum line techniques. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz), 500 (500 MHz) or 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.16 ppm, CD_2Cl_2: δ 5.32 ppm, CD_3OD: δ 3.31 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm, C_6D_6: δ 128.00 ppm, CD_2Cl_2: δ 54.00 ppm, CD_3OD: δ 49.00 ppm). ^{19}F NMR spectra were recorded on a Varian Unity INOVA 400 (376 MHz) spectrometer with complete proton decoupling. High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS and JEOL Accu TOF Dart (positive mode) at the Boston College Mass Spectrometry Facility. Melting points were determined using a Thomas Hoover Uni-melt capillary melting point apparatus. Values for *Z:E* ratios of products were determined by analysis of ^1H NMR spectra.

Solvents:

Solvents (CH_2Cl_2, pentane, benzene and toluene) were purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system. Tetrahydrofuran was distilled from Na/benzophenone. Methanol was distilled over $MgSO_4$. Acetone was used as received. All purification procedures of CM products were carried out with reagent grade solvents (purchased from Fisher) under bench-top conditions.

Reagents (for *Z*-selective CM):

8-Bromo-1-octene (Aldrich), 4-allyl-1,2-dimethoxybenzene (Aldrich), 3-(2-propenyl)indole (Combi-blocks), allylboronic acid pinacol ester (Frontier Scientific), allyltriisopropylsilane (Aldrich), allyltriphenylstannane (Aldrich), methyl 5-hexenoate (Aldrich), 1,2-epoxy-9-decene (Aldrich), vinylcyclohexane (Aldrich), vinylcyclohexene (Aldrich), methyl oleate (Aldrich), *Z*-5-decene (Aldrich), *Z*-cyclooctene (Aldrich), 10-undecyn-1-ol (Aldrich), piperidine (Aldrich), (*S*)-1-octyn-3-ol (Aldrich), benzaldehyde (Aldrich), 4-methoxystyrene (Aldrich), 4-acetoxystyrene (Aldrich), 4-bromostyrene (Aldrich) and 4-chlorostyrene (Aldrich) were either distilled (from CaH_2 or $CaCl_2$) under vacuum or dried by azeotropic distillation (with benzene) prior to use.

2-(5-Hexenyl)isoindoline-1,3-dione,[47] 1-(*tert*-butyldimethylsilyoxy)-7-octene,[48] 9-decen-1-ynyltriisopropylsilane,[18] benzyl(7-octenyl)sulfane,[49] 2-(3-*tert*-butyl-2-hydroxybenzylamino)-3-methyl-1-(1-pyrrolidinyl)-1-butanone[23a] and *N*,*N*-dibenzyl-10-undecen-1-amine[50] were prepared in analogy to reported procedures. *tert*-Butyl(2,6-

(47) Smith, B. J.; Sulikowski, G. A. *Angew. Chem. Int. Edn* **2010**, *49*, 1599–1602.
(48) Pirrung, M. C.; Webster, N. J. G. *J. Org. Chem.* **1987**, *52*, 3603–3613.
(49) Lin, Y. A.; Chalker, J. M.; Floyd, N.; Bernardes, G. J. L.; Davis, B. G. *J. Am. Chem. Soc.* **2008**, *130*, 9642–9643.
(50) Bélanger, G.; Doré, M.; Ménard, F.; Darsigny, V. *J. Org. Chem.* **2006**, *71*, 7481–7484.

dimethyl-7-octen-2-yloxy)dimethylsilane and allylestrenol *tert*-butyldimethylsilyl ether (from allylestrenol (TCI)) were prepared in analogy to a reported procedure.[51] (*S*)-1-*tert*-Butyl 1-oct-7-enyl pyrrolidine-1,2-dicarboxylate (from 7-octen-1-ol (TCI) and *N*-(*tert*-butoxycarbonyl)-L-proline (Advanced Chemtech)), 2-methyl-3-butenyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (from 2-methyl-3-buten-1-ol (Aldrich) and sulbactam (TCI)) and (*S*)-2-(4-(3-(2-chloro-10*H*-phenothiazin-10-yl)propyl)piperazin-1-yl)ethyl 4-methylhex-5-enoate (from (*S*)-4-methyl-5-hexenoic acid[52] and perphenazine (Aldrich)) were prepared by esterification in analogy to a reported procedure.[53] 1-(*tert*-Butyldimethylsilyl)-5-vinylpyrrolidin-2-one (from 5-vinyl-2-pyrrolidinone (Focus Synthesis)) was prepared in analogy to a reported procedure.[48] Isopimaric acid methyl ester[54] (from isopimaric acid (Aldrich)) and (4*S*,5*R*,6*S*)-2-(4-methoxyphenyl)-5-methyl-4-((*S*,*E*)-5-phenyl-3-penten-2-yl)-6-vinyl-1,3-dioxane[55] were prepared according to reported procedures.

Z-1,2-Dichloroethene (Aldrich), 1,2-dibromoethene (TCI), *Z*-1-bromo-2-fluoroethene (Synquest), 1,3-bis(1-adamantyl)imidazolinium tetrafluoroborate (Aldrich), copper(I) chloride (Strem), copper(I) iodide (Aldrich), sodium *tert*-butoxide (Strem), palladium(II) acetate (Strem), dichloro bis(benzonitrile)palladium(II) (Strem), SPhos (Strem) and potassium hydroxide (Aldrich) were used as received. Bis(pinacolato)diboron (Frontier Scientific) was recrystallized from pentane prior to use.

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(52) Barrett, A. G. M.; Carr, R. A. E. *J. Org. Chem.* **1986**, *51*, 4840–4856.
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Reagents (for *E*-selective CM):

Vinylcylohexane (Aldrich), *trans*-β-methylstyrene (TCI), 2-fluorostyrene (Aldrich), 3-bromostyrene (Aldrich), 4-chlorostyrene (Aldrich), 4-bromostyrene (Aldrich), 4-acetoxystyrene (Aldrich), 4-trifluoromethylstyrene (Aldrich), 4-vinylphenylboronic acid pinacol ester (Aldrich), 8-bromo-1-octene (Aldrich), *trans*-methyl oleate (TCI), cinnarizine (AK Scientific) were either distilled (from CaH_2 or $CaCl_2$) under vacuum or dried by azeotropic distillation (with benzene) prior to use.

3-Vinylbenzo[*b*]thiophene, [56] 2-vinylbenzofuran, [57] *tert*-butyl 5-vinyl-1*H*-indole-1-carboxylate,[58] 3-vinyl-1*H*-indole,[59] *tert*-butyl 3-vinyl-1*H*-indole-1-carboxylate,[60] *tert*-butyl((2,6-dimethyl-7-octen-2-yl)oxy)dimethylsilane[51] and rosavin persilylated ether[51] (from rosavin (AK Scientific)) were prepared in analogy to reported procedures. Isopimaric acid methyl ester[54] (from isopimaric acid (Aldrich)) and (4*S*,5*R*,6*S*)-2-(4-methoxyphenyl)-5-methyl-4-((*S*,*E*)-5-phenyl-3-penten-2-yl)-6-vinyl-1,3-dioxane[55] were prepared according to reported procedures.

E-1,2-Dichloroethene (Aldrich), 3,5-dimethylphenylboronic acid (Aldrich), 3,5-di-*tert*-butylphenylboronic acid (Combi-blocks), *E*-1-chloro-2-fluoroethene (Synquest), (*R*)-(+)-4-(chloromethyl)-2,2-dimethyl-1,3-dioxolane (Aldrich), potassium *trans*-β-styryltrifluoroborate (Alfa Aesar), 1-methylindole-5-boronic acid (Combi-Blocks), 2,6-difluoropyridine-3-boronic acid (Combi-Blocks), 3,5-Dimethylisoxazole-4-boronic acid

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(57) Falk, A.; Cavalieri, A.; Nichol, G. S.; Vogt, D.; Schmalz, H. *Adv. Synth. Catal.* **2015**, *357*, 3317–3320.
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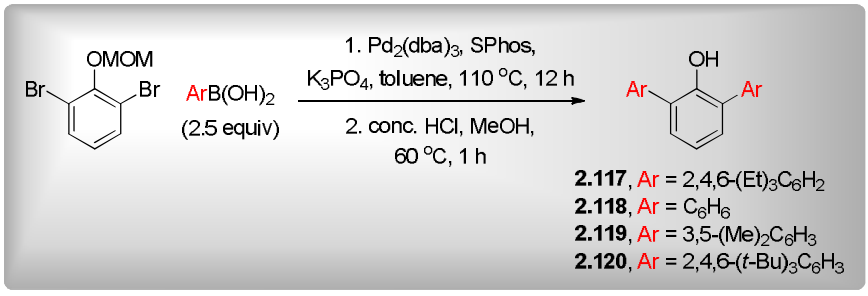
(60) Silva Jr., L. F.; Craveiro, M. V.; Gambardella, M. T. P. *Synthesis* **2007**, 3851–3857.

pinacol ester (Combi-Blocks), cesium fluoride (Alfa Aesar) , palladium(II) acetate (Strem), SPhos (Strem) were used as received.

Organometallic Complexes:

Complexes **Ru-2** and **Ru-3** were purchased from Sigma-Aldrich. Complex **Ru-4** was prepared according to a previously reported procedure.[22] Bisalkoxide complex **Mo-1** was prepared according to a previously reported procedure.[61] Mo monoaryloxide pyrrolide (MAP) complexes **Mo-2** and **Mo-3** were prepared *in situ* according to a previously reported procedure.[35] Mo complexes **Mo-4a** and **Mo-4b** were prepared *in situ* according to a previously reported procedure.[31] **Mo-4c–f** were prepared *in situ* from Mo bis-pyrrolide precursor and the corresponding terphenol according to a previously reported procedure.[35] W complex **W-1** was prepared according to a previously reported procedure.[62] Mo and W complexes were manipulated under an atmosphere of N_2 in a glove box. Paraffin pellets were received from XiMo, AG.

2.6.2. General Synthesis of 2,6-Diarylphenols



(61) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.
(62) Jiang, A. J.; Zhao, Y.; Schrock, R. R; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630–16631.

2.117 was prepared according to previously reported procedures.[63] An oven-dried round-bottom flask equipped with a magnetic stir bar was charged with 1,3-dibromo-2-(methoxymethyl)benzene [64] (148.0 mg, 0.500 mmol, 1.00 equiv), 2,4,6-triethylphenylboronic acid[65] (257.6 mg, 1.25 mmol, 2.50 equiv), K_3PO_4 (636.8 mg, 3.00 mmol, 6.00 equiv), $Pd_2(dba)_3$ (22.9 mg, 0.0250 mmol, 5.0 mol %), SPhos (41.1 mg, 0.100 mmol, 20 mol %) and toluene (5 mL). The mixture was allowed to stir for 12 h at 100 °C. The mixture was then allowed to cool to room temperature, diluted with EtOAc, filtered through a pad of Celite and concentrated under vacuum. The resulting residue obtained was re-dissolved in MeOH (2.5 mL) and concentrated HCl (150 μL) was added. The solution was allowed to stir for 1 h at 60 °C, after which it was allowed to cool to room temperature and concentrated under vacuum. The resulting yellow oil was purified by silica gel chromatography (2% EtOAc in hexanes) to afford **2.117** (145.0 mg, 0.350 mmol, 70% yield) as colorless gum. **IR (CH_2Cl_2)**: 3526 (m), 2963 (m), 2931 (m), 2871 (m), 1606 (w), 1436 (s), 1323 (m), 1220 (s), 1168 (m), 872 (s), 433 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.10–7.06 (2H, m), 7.06 –7.00 (5H, m), 4.54 (1H, s), 2.68 (4H, q, J = 7.6 Hz), 2.48–2.32 (8H, m), 1.29 (6H, t, J = 7.6 Hz), 1.06 (12H, t, J = 7.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 150.4, 144.2, 143.5, 132.2, 130.4, 126.5, 125.8, 120.1, 28.9, 26.9, 15.5, 15.4; **HRMS $[M+H]^+$** calcd for $C_{30}H_{39}O$: 415.3001, found: 415.2994.

2.118 (Aldrich) was used as received.

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(63) (a) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696. (b) Radlauer, M. R.; Day, M. W.; Agapie, T. *Organometallics* **2012**, *31*, 2231–2243.
(64) Prepared in analogy to a reported procedure: Hussein, L.; Purkait, N.; Biyikal, M.; Tausch, E.; Roesky, P. W.; Blechert, S. *Chem. Commun.* **2014**, *50*, 3862–3864.
(65) Prepared in analogy to a reported procedure: Sickert, M.; Abels, F.; Lang, M.; Sieler, J.; Birkemeyer, C.; Schneider, C. *Chem. Eur. J.* **2010**, *16*, 2806–2818.

2.119 was prepared according to previously reported procedures.[63a] An oven-dried round-bottom flask equipped with a magnetic stir bar was charged with 1,3-dibromo-2-(methoxymethyl)benzene[64] (296 mg, 1.00 mmol, 1.00 equiv), 3,5-dimethylphenylboronic acid (375 mg, 2.50 mmol, 2.50 equiv), K_3PO_4 (1274 mg, 6.00 mmol, 6.00 equiv), $Pd_2(dba)_3$ (45.8 mg, 0.0500 mmol, 5.0 mol %), SPhos (82.1 mg, 0.200 mmol, 20 mol %) and toluene (10 mL). The mixture was allowed to stir for 12 h at 110 °C, was then allowed to cool to 22 °C, diluted with EtOAc, filtered through a pad of Celite and concentrated in vacuo. The residue was purified by silica gel chromatography (20:1 hexanes:EtOAc) to obtain the MOM-protected ether as waxy off-white solid, which was then dissolved in hot MeOH (25 mL) and concentrated HCl (1.0 mL) was added. The solution was allowed to stir for 1 h at 60 °C, after which it was allowed to cool to 22 °C, causing off-white crystalline solid to precipitate. The mixture was allowed to stand at 0 °C for 12 h. The solid was collected by vacuum filtration, washed with cold methanol (3 x 5 mL), and dried under vacuum to obtain pure **2.119** (147 mg, 0.486 mmol, 49% yield) as off-white solid. The spectral data for this compound were identical to those reported previously.[66]

2.120 was prepared in analogy to **2.119** from 1,3-dibromo-2-(methoxymethyl)benzene (296 mg, 1.00 mmol, 1.00 equiv), 3,5-di-*tert*-butylphenylboronic acid (585 mg, 2.50 mmol, 2.50 equiv), K_3PO_4 (1274 mg, 6.00 mmol, 6.00 equiv), $Pd_2(dba)_3$ (91.6 mg, 0.100 mmol, 10 mol %), SPhos (164 mg, 0.400 mmol, 40 mol %) to obtain pure **2.120** (436 mg, 0.926 mmol, 93% yield) as off-white crystalline solid. **IR (in CH_2Cl_2)**: 3534 (m), 2961 (s), 2905 (m), 2867 (m), 1593 (m), 1409 (m), 1393 (w), 1362 (m), 1258 (m), 1222 (m),

(66) Ito, H.; Nagahara, T.; Ishihara, K.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2004**, *43*, 994–997.

1204 (m), 877 (m), 796 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.45 (2H, t, J = 1.9 Hz), 7.40 (4H, dd, J = 1.9, 0.6 Hz), 7.30 (2H, d, J = 7.6 Hz), 7.10−7.04 (1H, m), 5.56 (1H, s), 1.37 (36H, s); **^{13}C NMR (151 MHz, $CDCl_3$)**: δ 151.3, 149.6, 136.9, 129.9, 129.8, 123.8, 121.8, 120.5, 35.2, 31.7; **HRMS $[M+H]^+$** calcd for $C_{34}H_{47}O$: 471.3628, found: 471.3627.

Synthesis of Mo MAP Complexes ***2.6.2. General Synthesis of 2,6-Diarylphenols***

2.6.3. Synthesis of Mo MAP Complexes

General procedure for *in situ* preparation of Mo-4c for NMR analysis: In a N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with pentafluorophenylimido Mo bispyrrolide complex[67] (16.7 mg, 0.0280 mmol, 1.00 equiv), **1.117** (11.6 mg, 0.0280 mmol, 1.00 equiv) and C_6D_6 (1 mL), resulting in a dark red solution. The vial was capped and the mixture was allowed to stir for 2 h at 22 °C, at which time it was transferred to a screw cap NMR tube by a pipette. The NMR tube was capped and sealed with Teflon tape. For *in situ* generated complexes, only the diagnostic signal of α carbon of the *syn*-alkylidene is shown. Diagnostic NMR data for **Mo-4c**: **^{1}H NMR (400 MHz, C_6D_6)**: δ 11.38 (1H, s).

General procedure for *in situ* preparation of Mo-4c for catalytic reactions: In a N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with pentafluorophenylimido Mo bispyrrolide complex (59.8 mg, 0.100 mmol, 1.00 equiv), **1.117** (41.5 mg, 0.100 mmol, 1.00 equiv) and C_6H_6 (1 mL), resulting in a dark red solution. The vial was capped and the mixture was allowed to stir for 2 h at 22 °C, after which the catalyst solution was transferred to the reaction mixture by syringe (dried at 65 °C).

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(67) Yuan, J.; Schrock, R. R.; Müller, P.; Axtell, J. C.; Dobereiner, G. E. *Organometallics* **2012**, *31*, 4650–4653.

General procedure for *in situ* preparation of Mo-4f for NMR analysis: In a N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with pentafluorophenylimido Mo bispyrrolide complex (*52*) (15.0 mg, 0.0251 mmol, 1.00 equiv), **1.120** (11.8 mg, 0.0251 mmol, 1.00 equiv) and C_6D_6 (1 mL), generating a dark-red solution. The vial was capped and the mixture was allowed to stir for 2 h at 22 °C, after which it was transferred to a screw cap NMR tube by a pipette. The NMR tube was capped and sealed with Teflon tape. Diagnostic NMR data for **Mo-4f**: **^{1}H NMR (400 MHz, C_6D_6)**: δ 11.88 (1H, s).

General procedure for *in situ* preparation of Mo-4f for catalytic reactions: In a N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with pentafluorophenylimido Mo bispyrrolide complex (59.8 mg, 0.100 mmol, 1.00 equiv), **1.120** (47.1 mg, 0.100 mmol, 1.00 equiv) and C_6H_6 (1 mL), resulting in a dark red solution. The vial was capped and the mixture was allowed to stir for 2 h at 22 °C, after which the solution was transferred to the reaction mixture by syringe (dried at 65 °C).

2.6.4. Z-Selective Cross-Metathesis (CM) Reactions

General Procedure: In a N_2-filled glove box, an oven-dried 8 mL vial equipped with a magnetic stir bar was charged with alkene substrate (1.0 equiv) and the corresponding organohalide reagent (*Z*-1,2-dichloroethene (5.0 equiv), *Z*-1-bromo-2-fluoroethene (5.0 equiv) or 1,2-dibromoethene (8.0 equiv)). To this vessel, a solution of **Mo-4c** in benzene (3.0–10 mol %) was added. The resulting solution was allowed to stir for 4–12 h at 22–40 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ (% conversion was determined by ^{1}H NMR analysis of the unpurified mixture). Purification was performed through silica gel chromatography.

(*Z*)-8-Bromo-1-chloro-1-octene (2.9): Following the general procedure, a solution of **Mo-3b** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 5.00 equiv), 8-bromo-1-octene (19.1 mg, 0.100 mmol, 1.00 equiv) and benzene (470 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed ~90% consumption of 8-bromo-1-octene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.9** (17.4 mg, 0.0770 mmol, 77% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR ($CDCl_3$)**: 2930 (s), 2856 (m), 1630 (w), 1462 (w), 1438 (w), 1295 (w), 1258 (w), 741 (w), 726 (w), 710 (w), 646 (w), 564 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.02 (1H, dt, J = 7.1, 1.5 Hz), 5.74 (1H, q, J = 7.2 Hz), 3.41 (2H, t, J = 6.8 Hz), 2.23 (2H, qd, J = 7.2, 1.5 Hz), 1.90–1.82 (2H, m), 1.47–1.33 (6H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 131.5, 118.1, 33.9, 32.7, 28.2, 28.1, 27.9, 26.8; **HRMS $[M+H]^+$** calcd for $C_8H_{15}BrCl$: 225.0046, found: 225.0043.

(*Z*)-*tert*-Butyl(8-chloro-7-octenyloxy)dimethylsilane (2.10): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.5 mmol, 5.00 equiv), *tert*-butyldimethyl(7-octenyloxy)silane (24.2 mg, 0.1 mmol, 1.00 equiv) and benzene (470 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 88% consumption of *tert*-butyldimethyl(7-octenyloxy)silane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.10** (22.2 mg, 0.0802 mmol, 80% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR**

(CH_2Cl_2): 2930 (s), 2856 (m), 1630 (w), 1462 (w), 1438 (w), 1295 (w), 1258 (w), 733 (s), 705 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.00 (1H, dd, J = 7.0, 1.4 Hz), 5.74 (1H, qd, J = 7.2, 2.2 Hz), 3.60 (2H, td, J = 6.5, 2.2 Hz), 2.22 (2H, q, J = 7.0 Hz), 1.55–1.47 (2H, m), 1.44–1.29 (6H, m), 0.89 (9H, d, J = 2.3 Hz), 0.04 (6H, d, J = 2.3 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 132.0, 118.0, 63.4, 32.9, 29.1, 28.5, 27.1, 26.1, 25.8, 18.5, –5.1; **HRMS [M+H]$^+$** calcd for $C_{14}H_{30}ClOSi$: 277.1754, found: 277.1766.

(*Z*)-Benzyl(8-chloro-7-octenyl)sulfane (2.11): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 50 μL, 5.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.5 mmol, 5.00 equiv) and benzyl(7-octenyl)sulfane (23.4 mg, 0.1 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 94% consumption of benzyl(7-octenyl)sulfane. The resulting orange oil was purified by silica gel chromatography (100% hexanes to 2% Et_2O in hexanes) to afford **2.11** (19.1 mg, 0.0710 mmol, 71% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2924 (s), 2853 (m), 1629 (w), 1494 (w), 1453 (m), 734 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.33–7.30 (5H, m), 6.01 (1H, d, J = 7.0 Hz), 5.73 (1H, q, J = 7.1 Hz), 3.70 (2H, s), 2.41 (2H, t, J = 7.4 Hz), 2.23–2.17 (2H, m), 1.37–1.27 (8H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 131.9, 129.0, 128.6, 127.0, 127.0, 118.1, 36.4, 31.5, 29.3, 28.8, 28.7, 28.3, 27.0; **HRMS [M+H]$^+$** calcd for $C_{15}H_{22}ClS$: 269.1131, found: 269.1133.

(*Z*)-(10-Chlorodec-9-en-1-yn-1-yl)triisopropylsilane (2.12): Following the general procedure, a solution of **Mo-4c** in benzene (0.022 M, 45 μL, 1.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (16.0 mg,

0.165 mmol, 5.00 equiv) and 9-decen-1-ynyltriisopropylsilane (9.6 mg, 0.0328 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 97% consumption of 9-decen-1-ynyltriisopropylsilane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.12** (9.6 mg, 0.0294 mmol, 89% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (neat)**: 2938 (s), 2862 (s), 2171 (m), 1630 (w), 1462 (m), 995 (w), 882 (s), 771 (m), 674 (s), 659 (s), 619 (m); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.01 (1H, dt, J = 7.1, 1.6 Hz), 5.74 (1H, q, J = 7.1 Hz), 2.30–2.18 (4H, m), 1.59–0.98 (29H, m); **^{13}C NMR (400 MHz, $CDCl_3$)**: δ 131.9, 118.1, 28.9, 28.7, 28.6, 28.4, 27.1, 19.9, 18.8, 18.8, 11.5, 11.3; **HRMS [M]$^+$** calcd for $C_{19}H_{35}ClSi$: 326.2197, found: 326.2083.

(*Z*)-2-(8-Chloro-7-octenyl)oxirane (2.13): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.5 mmol, 5.00 equiv) and 1,2-epoxy-9-decene (23.4 mg, 0.1 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 91% consumption of 1,2-epoxy-9-decene. The resulting orange oil was purified by silica gel chromatography (100% hexanes to 5% Et_2O in hexanes) to afford **2.13** (12.9 mg, 0.0684 mmol, 68% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2928 (s), 2857 (m), 1630 (w), 1463 (w), 1100 (m), 734 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.01 (1H, dd, J = 7.1, 1.5 Hz), 5.74 (1H, q, J = 7.2 Hz), 2.93–2.87 (1H, m), 2.75 (1H, dd, J = 5.0, 4.0 Hz), 2.46 (1H, dd, J = 5.0, 2.7 Hz), 2.25–2.18 (2H, m), 1.53–1.35 (10H, m); **^{13}C NMR (100**

MHz, $CDCl_3$): δ 131.9, 118.1, 52.5, 47.3, 32.6, 29.3, 29.2, 28.4, 27.1, 26.1; **HRMS [M+H]$^+$** calcd for $C_{10}H_{18}ClO$: 189.1046, found: 189.1046.

(*Z*)-Methyl 6-chloro-5-hexenoate (2.14): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 5.00 equiv) and methyl 5-hexenoate (12.8 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 90% consumption of methyl 5-hexenoate. The resulting orange oil was purified by silica gel chromatography (5% Et_2O in hexanes) to afford **2.14** (10.6 mg, 0.0652 mmol, 65% yield) in >98:2 *Z*:*E* ratio as pale yellow oil. **IR (CH_2Cl_2)**: 2952 (w), 2850 (w), 1734 (s), 1630 (w), 1437 (m), 1315 (w), 1150 (m), 1003 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.06 (1H, dt, J = 7.1, 1.5 Hz), 5.74 (1H, q, J = 7.2 Hz), 3.67 (3H, s), 2.34 (2H, t, J = 7.5 Hz), 2.31–2.22 (2H, m), 1.81–1.72 (2H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.9, 130.6, 119.2, 51.7, 33.5, 26.5, 23.8; **HRMS [M+H]$^+$** found for $C_7H_{12}ClO_2$: 163.0532.

(*Z*)-2-(6-Chloro-5-hexenyl)isoindoline-1,3-dione (2.15): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 5.00 equiv), 2-(5-hexenyl)isoindoline-1,3-dione (22.9 mg, 0.100 mmol, 1.00 equiv) and benzene (470 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 81% consumption of 2-(5-hexenyl)isoindoline-1,3-dione. The resulting orange oil was purified by silica gel chromatography (100% hexanes to

10% Et_2O in hexanes) to afford **2.15** (17.2 mg, 0.0652 mmol, 65 % yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2926 (w), 2861 (w), 1706 (s), 1395 (m), 1363 (m), 1039 (w), 529 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.84 (1H, dd, *J* = 5.5, 3.0 Hz), 7.71 (2H, dd, *J* = 5.4, 3.1 Hz), 6.02 (1H, dt, *J* = 7.1, 1.5 Hz), 5.73 (1H, q, *J* = 7.2 Hz), 3.70 (2H, t, *J* = 7.2 Hz), 2.28 (2H, qd, *J* = 7.4, 1.5 Hz), 1.77–1.67 (2H, m), 1.52–1.44 (2H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 168.6, 134.0, 132.2, 131.2, 123.3, 118.7, 37.9, 28.2, 26.6, 25.8; **HRMS [M+H]$^+$** calcd for $C_{14}H_{15}ClNO_2$: 264.0791, found: 264.0790.

(*Z*)-(3-Chloroallyl)triphenylstannane (2.16): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 20 μL, 2.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (19.3 mg, 0.199 mmol, 5.00 equiv) and allyltriphenylstannane (15.6 mg, 0.0399 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 97% consumption of allyltriphenylstannane. The resulting orange oil was purified by silica gel chromatography (50:1 hexanes/EtOAc) to afford **2.16** (15.1 mg, 0.0355 mmol, 89% yield) in >98:2 *Z*:*E* ratio as clear crystalline solid. M.p. 71–73 °C; **IR ($CDCl_3$)**: 3060 (w), 1617 (w), 1479 (w), 1426 (m), 1321 (m), 1073 (m), 992 (m), 729 (s), 712 (s), 695 (s), 656 (m); **^{1}H NMR (600 MHz, C_6D_6)**: *Z* isomer (major): δ 7.63–7.50 (6H, m), 7.41–7.35 (9H, m), 6.05 (1H, tdd, *J* = 8.9, 6.8, 0.6 Hz), 5.81 (1H, dtd, *J* = 6.8, 1.2, 0.5 Hz), 2.55 (2H, dt, *J* = 8.9, 0.9 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.2, 137.17, 129.3, 128.7, 115.0, 12.5; **HRMS [M+H]$^+$** calcd for $C_{21}H_{20}ClSn$: 427.0275, found: 427.0272.

(*Z*)-(3-Chloroallyl)triisopropylsilane (2.17): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol, 5.00 equiv) and allyltriisopropylsilane (9.9 mg, 0.0499 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 90% consumption of allyltriisopropylsilane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.17** (9.8 mg, 0.0421 mmol, 84% yield) in 96:4 *Z*:*E* ratio as colorless oil. **IR ($CDCl_3$)**: 2941 (s), 2890 (m), 2866 (s), 1622 (w), 1462 (m), 1326 (m), 1154 (m), 998 (m), 881 (s), 749 (m), 721 (s), 674 (s); **^{1}H NMR (600 MHz, C_6D_6)**: *Z* isomer (major): δ 5.61 (1H, dt, J = 6.9, 1.5 Hz), 5.50 (1H, td, J = 8.4, 7.0 Hz), 1.67 (2H, dd, J = 8.4, 1.5 Hz), 0.97 (18H, d, J = 6.7 Hz), 0.93–0.85 (3H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 129.5, 115.3, 77.5, 77.2, 76.8, 18.8, 11.4, 11.1.

(*Z*)-4-(3-Chloroallyl)-1,2-dimethoxybenzene (2.18): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 5.00 equiv) and 4-allyl-1,2-dimethoxybenzene (17.8 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 88% consumption of 4-allyl-1,2-dimethoxybenzene. The resulting orange oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **2.18** (13.0 mg, 0.0611 mmol, 61% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2917 (m), 2834 (m), 1606 (m), 1512 (s), 1463 (m), 1259 (s), 1234 (s), 1139 (s), 1028 (s),

688 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.81 (1H, d, J = 8.0 Hz), 6.77–6.72 (2H, m), 6.15 (1H, ddd, J = 7.0, 2.0, 0.9 Hz), 5.95 (1H, q, J = 7.1 Hz), 3.87 (3H, s), 3.86 (3H, s), 3.53 (2H, d, J = 7.2 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 149.2, 147.7, 131.7, 130.8, 120.3, 118.7, 111.8, 111.5, 56.1, 56.0, 33.0; **HRMS $[M+H]^+$** calcd for $C_{11}H_{14}ClO_2$: 213.0682, found: 213.0675.

(*Z*)-3-(3-Chloroallyl)-1H-indole (2.19): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 32 μL, 3.2 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (30.8 mg, 0.318 mmol, 5.00 equiv), 3-(2-propenyl)indole (10.0 mg, 0.0636 mmol, 1.00 equiv) and benzene (260 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched with wet $CDCl_3$ and analysis of the unpurified mixture revealed 86% consumption of 3-(2-propenyl)indole. The resulting orange oil was purified by silica gel chromatography (15% Et_2O in hexanes) to afford **2.19** (6.1 mg, 0.0318 mmol, 50% yield) in 95:5 *Z*:*E* ratio as colorless oil. **IR ($CDCl_3$)**: 3416 (m), 2919 (w), 1627 (w), 1456 (m), 1420 (w), 1353 (w), 1334 (w), 1226 (w), 1091 (w), 1101 (w), 778 (w), 742 (s), 686 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.94 (1H, brs), 7.61 (1H, dd, J = 7.7, 0.7 Hz), 7.35 (1H, d, J = 8.1 Hz), 7.20 (1H, td, J = 7.6, 1.2 Hz), 7.12 (1H, ddd, J = 8.0, 7.1, 1.0 Hz), 7.03–6.99 (1H, m), 6.13 (1H, dt, J = 7.0, 1.6 Hz), 6.01 (1H, q, J = 7.0 Hz), 3.69 (2H, ddd, J = 7.0, 1.5, 1.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.3, 130.6, 127.2, 122.2, 121.5, 119.4, 118.9, 118.1, 113.4, 111.1, 23.3; **HRMS $[M+H]^+$** calcd for $C_{11}H_{11}ClN$: 192.0580, found: 192.0590.

(*Z*)-4-(2-Chlorovinyl)-1-cyclohexene (2.20): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by

syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.5 mmol, 5.00 equiv), 4-vinyl-1-cyclohexene (11.0 mg, 0.1 mmol, 1.00 equiv) and benzene (470 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 96% consumption of 4-vinyl-1-cyclohexene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.20** (10.9 mg, 0.0754 mmol, 75% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 3022 (m), 2914 (s), 2854 (m), 2836 (m), 1629 (w), 1435 (m), 1330 (w), 720 (m), 653 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 5.99 (1H, dd, J = 7.1, 1.1 Hz), 5.74–5.62 (3H, m), 2.94–2.81 (1H, m), 2.20–2.05 (3H, m), 1.87–1.71 (2H, m), 1.50–1.42 (1H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.5, 127.1, 125.8, 117.0, 32.2, 30.4, 27.6, 24.4; **HRMS $[M+H]^+$** calcd for $C_8H_{12}Cl$: 143.0628, found: 143.0624.

(*Z*)-(2-Chlorovinyl)cyclohexane (2.21): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.5 mmol, 5.00 equiv), vinylcyclohexane (11.0 mg, 0.1 mmol, 1.00 equiv) and benzene (470 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of vinylcyclohexane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.21** (11.3 mg, 0.0781 mmol, 78% yield) in >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[13a]

***tert*-Butyl(((8*R*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-((*Z*)-3-chloroallyl)-13-methyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)oxy)dimethylsilane (2.22):** Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.3 mg, 0.251 mmol, 5.00 equiv) and (((8*R*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-allyl-13-methyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)oxy) (*tert*-butyl)dimethylsilane (20.7 mg, 0.0499 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 75% consumption of (((8*R*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-allyl-13-methyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)oxy) (*tert*-butyl)dimethylsilane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.22** (15.7 mg, 0.0349 mmol, 70% yield) in 95:5 *Z*:*E* ratio as off-white solid. M.p. 110–112 °C; **IR ($CDCl_3$)**: 2950 (s), 2926 (s), 2855 (s), 1626 (w), 1253 (m), 1086 (m), 1072 (m), 834 (s), 772 (s); **^{1}H NMR (400 MHz, C_6D_6)**: *Z* isomer (major): δ 5.97 (1H, q, J = 6.6 Hz), 5.81 (1H, dt, J = 7.1, 1.9 Hz), 5.49 (1H, brs), 2.60 (1H, ddd, J = 16.4, 6.1, 1.2 Hz), 2.47 (1H, ddd, J = 16.2, 6.6, 2.1 Hz), 2.30–2.22 (1H, m), 2.10–0.80 (32H, m), 0.63–0.51 (1H, m), 0.12 (3H, s), 0.09 (3H, s); **^{13}C NMR (100 MHz, C_6D_6)**: δ 140.7, 130.8, 120.6, 118.7, 86.5, 50.6, 49.4, 48.7, 42.7, 42.6, 38.3, 37.2, 36.3, 33.2, 32.5, 29.5, 26.7, 26.3, 24.2, 23.0, 19.2, 16.0, –1.1, –1.5; **HRMS $[M+H]^+$** calcd for $C_{27}H_{45}ClOSi$: 449.3006, found: 449.3003.

(*Z*)-2-(3-Chloroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.23): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 50 μL, 5.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 5.00 equiv) and allylboronic acid pinacol ester (16.8 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched with wet $CDCl_3$ and analysis of the unpurified mixture revealed 90% consumption of allylboronic acid pinacol ester. The resulting orange oil was purified by silica gel chromatography (2% Et_2O in pentane to 5% Et_2O in pentane) to afford **2.23** (13.4 mg, 0.0662 mmol, 66% yield) in >98:2 *Z*:*E* ratio as pale yellow oil. **IR (CH_2Cl_2)**: 2978 (m), 2930 (w), 1628 (w), 1460 (w), 1317 (s), 1142 (s), 967 (m), 746 (m), 686 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.02 (1H, dt, J = 6.9, 1.5 Hz), 5.94–5.85 (1H, m), 1.86 (2H, d, J = 7.5 Hz), 1.26 (12H, s); **^{13}C NMR (100 MHz, C_6D_6)**: δ 117.8, 83.3, 24.8; **HRMS [M+H]$^+$** calcd for $C_9H_{17}BClO_2$: 203.1010, found: 203.1020.

(*Z*)-1-Chloro-1-decene (2.31) & (*Z*)-Methyl 10-chloro-9-decenoate (2.32): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 1.00 mL, 0.100 mmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (1.63 g, 16.9 mmol, 5.00 equiv), methyl oleate (1.00 g, 3.37 mmol, 1.00 equiv) and benzene (5.70 mL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 94% consumption of methyl oleate. The resulting orange oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **2.31** (0.508 g, 2.91 mmol, 86% yield) in 97:3 *Z*:*E* as colorless oil and **2.32** (0.671 g, 3.07 mmol, 91% yield) in 97:3 *Z*:*E* ratio as colorless oil. The spectral data for **2.31**

were identical to those previously reported.[68] Spectral data for **2.32**: **IR (CH_2Cl_2)**: 2927 (m), 2856 (w), 1737 (s), 1629 (w), 1436 (m), 1171 (m), 967 (m), 709 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.01 (1H, dd, J = 7.1, 1.6 Hz), 5.74 (1H, q, J = 7.1 Hz), 3.67 (3H, s), 2.30 (2H, t, J = 7.5 Hz), 2.21 (2H, qd, J = 7.2, 1.4 Hz), 1.67–1.58 (2H, m), 1.43–1.35 (2H, m), 1.34–1.30 (6H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 174.4, 131.9, 118.1, 51.6, 34.2, 29.2, 29.1, 29.1, 28.4, 27.1, 25.1; **HRMS $[M+H]^+$** calcd for $C_{11}H_{20}ClO_2$: 219.1152, found: 219.1160.

(*Z*)-((8-Bromooct-7-en-1-yl)oxy)(*tert*-butyl)dimethylsilane (2.35): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 21 μL, 2.1 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (61.0 mg, 0.330 mmol, 8.00 equiv), *tert*-butyldimethyl(oct-7-en-1-yloxy)silane (10.0 mg, 0.0410 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 95% consumption of *tert*-butyldimethyl(oct-7-en-1-yloxy)silane. The resulting orange oil was purified by silica gel chromatography (2% Et_2O in hexanes to 5% Et_2O in hexanes) to afford **2.35** (8.3 mg, 0.0260 mmol, 63% yield) in 88:12 *Z*:*E* ratio as colorless oil. **IR ($CDCl_3$)**: 2928 (s), 2856 (m), 1471 (w), 1463 (w), 1254 (m), 1100 (s), 1006 (w), 835 (s), 812 (w), 775 (s), 701 (w), 662 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.14 (1H, dt, J = 7.2, 1.2 Hz), 6.08 (1H, q, J = 6.8 Hz), 3.60 (2H, t, J = 6.4 Hz), 2.19 (2H, q, J = 7.2 Hz), 1.55–1.26 (8H, m), 0.90 (9H, s), 0.05 (6H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 135.0, 107.6, 63.2, 32.7, 29.6, 28.9, 28.1, 26.0, 25.6, 18.3, –5.3; **HRMS $[M+H]^+$** calcd for $C_{14}H_{30}BrOSi$: 321.1249, found: 321.1261.

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(*Z*)-(10-Bromodec-9-en-1-yn-1-yl)triisopropylsilane (2.36): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 15 μL, 1.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (44.6 mg, 0.240 mmol, 8.00 equiv) and 9-decen-1-ynyltriisopropylsilane (8.8 mg, 0.0301 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 98% consumption of 9-decen-1-ynyltriisopropylsilane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.36** (9.3 mg, 0.0250 mmol, 83% yield) in 87:13 *Z*:*E* ratio as colorless oil. **IR (neat)**: 2934 (s), 2862 (s), 2170 (m), 1622 (w), 1462 (m), 995 (w), 882 (s), 771 (m), 659 (s), 620 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.14 (1H, dt, J = 6.9, 1.3 Hz), 6.08 (1H, q, J = 6.8 Hz), 2.28–2.16 (4H, m), 1.58–1.00 (29H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 135.1, 107.8, 29.8, 28.9, 28.7, 28.6, 28.2, 19.9, 18.8, 11.5; **HRMS $[M]^+$** calcd for $C_{19}H_{35}BrSi$: 370.1691, found: 370.1602.

(*Z*)-2-(6-Bromohex-5-en-1-yl)isoindoline-1,3-dione (2.37): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 22 μL, 2.2 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (65.0 mg, 0.350 mmol, 8.00 equiv), 2-(hex-5-en-1-yl)isoindoline-1,3-dione (10.0 mg, 0.0440 mmol, 1.00 equiv) and benzene (50 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 92% consumption of 2-(hex-5-en-1-yl)isoindoline-1,3-dione. The resulting orange oil was purified by silica gel chromatography (15% Et_2O in hexanes) to afford **2.37** (9.0 mg, 0.0290 mmol, 67% yield) in 87:13 *Z*:*E* ratio as colorless

oil. **IR ($CDCl_3$)**: 2938 (w), 2861 (w), 1771 (w), 1706 (s), 1618 (w), 1466 (w), 1437 (w), 1396 (m), 1372 (m), 1338 (w), 1287 (w), 1188 (w), 1172 (w), 1113 (w), 1040 (w), 719 (m), 665 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.85–7.82 (2H, m), 7.72–7.69 (2H, m), 6.16 (1H, dt, J = 7.2, 1.2 Hz), 6.07 (1H, q, J = 6.8 Hz), 3.70 (2H, t, J = 7.2 Hz), 2.25 (2H, qd, J = 7.2, 1.2 Hz), 1.76–1.69 (2H, m), 1.52–1.45 (2H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 168.4, 134.2, 133.9, 132.1, 123.2, 108.2, 37.8, 29.2, 28.0, 25.4; **HRMS $[M+H]^+$** calcd for $C_{14}H_{15}BrNO_2$: 308.0286, found: 308.0291.

(*Z*)-*N*,*N*-Dibenzyl-11-bromo-10-undecen-1-amine (2.38): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 14 μL, 1.4 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (42.5 mg, 0.229 mmol, 8.00 equiv) and *N*,*N*-dibenzyl-10-undecen-1-amine (10.0 mg, 0.0286 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 hours at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 90% consumption of *N*,*N*-dibenzyl-10-undecen-1-amine. The resulting orange oil was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **2.38** (8.1 mg, 0.0189 mmol, 66% yield) in 88:12 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2924 (m), 2852 (w), 2792 (w), 1621 (w), 1494 (w), 1452 (w), 1028 (w), 696 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 7.38–7.35 (4H, m), 7.31–7.28 (4H, m), 7.24–7.20 (2H, m), 6.14 (1H, d, J = 6.9 Hz), 6.08 (1H, q, J = 6.8 Hz), 3.54 (4H, s), 2.42–2.36 (2H, m), 2.22–2.14 (2H, m), 1.31–1.18 (14H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.3, 135.2, 128.9, 128.2, 126.8, 107.7, 58.4, 53.6, 29.9, 29.7, 29.6, 29.5, 29.3, 28.3, 27.4, 27.1; **HRMS $[M+H]^+$** calcd for $C_{25}H_{35}BrN$: 428.1953, found: 428.1959.

(*S*,*Z*)-2-(8-Bromo-7-octenyl) 1-*tert*-butyl pyrrolidine-1,2-dicarboxylate (2.39): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 15 μL, 1.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (45.7 mg, 0.246 mmol, 8.00 equiv) and (*S*)-1-*tert*-butyl-1-oct-7-enyl pyrrolidine-1,2-dicarboxylate (10.0 mg, 0.0307 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 84% consumption of (*S*)-1-*tert*-butyl 1-oct-7-enyl pyrrolidine-1,2-dicarboxylate. The resulting orange oil was purified by silica gel chromatography (5% Et_2O in hexanes to 15% Et_2O in hexanes) to afford **2.39** (8.2 mg, 0.0203 mmol, 66% yield) in 87:13 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2956 (m), 2929 (m), 2855 (w), 1744 (s), 1697 (s), 1477 (w), 1391 (s), 1365 (s), 1159 (s), 1120 (s), 1087 (m), 702 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.15 (1H, d, J = 7.1 Hz), 6.07 (1H, q, J = 6.9 Hz), 4.29–4.08 (3H, m), 3.56–3.36 (2H, m), 2.25–2.16 (3H, m), 2.05–1.83 (4H, m), 1.67–1.61 (2H, m), 1.46 (3H, s), 1.41 (6H, s), 1.38–1.33 (5H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.5, 154.0, 134.9, 108.0, 80.0, 65.1, 59.4, 46.5, 31.1, 29.7, 28.8, 28.7, 28.6, 28.5, 28.1, 25.8, 24.5, 23.8; **HRMS [M+H]$^+$** calcd for $C_{18}H_{31}BrNO_4$: 404.1437, found: 404.1425.

(*Z*)-(8-Bromo-2,6-dimethyl-7-octen-2-yloxy)(*tert*-butyl)dimethylsilane (2.40): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 18 μL, 1.8 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (55.0 mg, 0.296 mmol, 8.00 equiv) and *tert*-butyl(2,6-dimethyl-7-octen-2-yloxy)dimethylsilane (10.0 mg, 0.0370 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of

wet $CDCl_3$ and analysis of the unpurified mixture revealed 71% consumption of *tert*-butyl(2,6-dimethyl-7-octen-2-yloxy)dimethylsilane. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.40** (7.4 mg, 0.0212 mmol, 57% yield) in 91:9 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2930 (m), 2858 (w), 1621 (w), 1462 (w), 1343 (m), 1039 (s), 833 (s), 770 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.09 (1H, dd, J = 7.0, 0.8 Hz), 5.85 (1H, dd, J = 9.2, 7.0 Hz), 2.76–2.64 (1H, m), 1.39–1.31 (6H, m), 1.17 (6H, s), 0.99 (3H, d, J = 6.7 Hz), 0.85 (9H, s), 0.06 (6H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.9, 106.2, 73.6, 45.2, 37.1, 34.7, 30.1, 29.8, 26.0, 22.1, 19.8, –1.9; **HRMS $[M+H]^+$** calcd for $C_{16}H_{34}BrOSi$: 349.1562, found: 349.1573.

(1*Z*,9*Z*)-1,10-Dibromodeca-1,9-diene (2.41): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 100 μL, 10.0 μmol, 10 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (148.7 mg, 0.800 mmol, 8.00 equiv) and *Z*-cyclooctene (11.0 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 1 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *Z*-cyclooctene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.41** (26.1 mg, 0.0880 mmol, 88% yield) in 89:11 *Z*,*Z*:*Z*,*E* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[30]

(1*Z*,9*Z*)-1,10-Dichlorodeca-1,9-diene (2.121; not shown in the text): Following the general procedure, a solution of **Mo-3** in benzene (0.1 M, 50 μL, 5.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.5 mmol, 5.00 equiv), *Z*-cyclooctene (11.0 mg, 0.100 mmol, 1.00 equiv) and

benzene (450 μL). The resulting solution was allowed to stir for 2 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *Z*-cyclooctene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.121** (15.6 mg, 0.0750 mmol, 75% yield) in >98:2 *Z*,*Z*:*Z*,*E* ratio as colorless oil. **IR ($CDCl_3$)**: 2926 (s), 2855 (m), 1630 (w), 1462 (w), 736 (w), 724 (w), 700 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.01 (2H, dt, J = 7.2 Hz, 1.6 Hz), 5.75 (2H, q, J = 7.2 Hz), 2.22 (4H, qd, J = 7.2, 1.6 Hz), 1.45–1.38 (4H, m), 1.36–1.31 (4H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 131.8, 117.9, 28.8, 28.2, 26.9.

(*Z*)-(10-Fluorodec-9-en-1-yn-1-yl)triisopropylsilane (2.52): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (62.5 mg, 0.500 mmol, 5.00 equiv) and 9-decen-1-ynyltriisopropylsilane (29.3 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 9-decen-1-ynyltriisopropylsilane that resulted in the formation of a mixture of F- and Br-alkenes (72:28 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.52** (26.3 mg, 0.0638 mmol, 64% yield of F-alkene by mass) in >98:2 *Z*:*E* ratio and 74:26 fluoro:bromo mixture as colorless oil. **IR (neat)**: 2938 (s), 2863 (s), 2171 (m), 1672 (w), 1462 (m), 994 (m), 882 (s), 770 (m), 735(m), 674 (s), 659 (s), 620 (m); **^{1}H NMR (600 MHz, $CDCl_3$**: *Z* isomer (major): δ 6.44 (F-alkene, 1H, ddt, J = 86.0, 4.7, 1.5 Hz), 6.17–6.04 (Br-alkene, 2H, m), 4.71 (F-alkene, 1H, dtd, J = 43.5, 7.6, 4.7 Hz), 2.29–2.04 (4H,

m), 1.59–1.20 (8H, m), 1.12–0.97 (21H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.6, 146.9, 135.1, 111.1, 111.1, 109.3, 107.8, 80.2, 29.8, 29.3, 29.2, 28.9, 28.9, 28.7, 28.7, 28.6, 28.6, 28.2, 22.8, 22.7, 20.0, 18.8, 18.8, 11.5, 11.3; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –131.33 (1F, dd, J = 86.1, 43.5 Hz); **HRMS $[M+NH_4]^+$** calcd for $C_{19}H_{39}FNSi$: 328.2836, found: 328.2849.

(*Z*)-*tert*-Butyl((8-fluoro-2,6-dimethyloct-7-en-2-yl)oxy)dimethylsilane (2.53): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.3 mg, 0.251 mmol, 5.00 equiv) and *tert*-butyl(2,6-dimethyl-7-octen-2-yloxy)dimethylsilane (13.5 mg, 0.0499 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *tert*-butyl(2,6-dimethyl-7-octen-2-yloxy)dimethylsilane that resulted in the formation of a mixture of F- and Br-alkenes (96:4 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.53** (10.1 mg, 0.0350 mmol, 70% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (neat)**: 2956 (m), 2930 (m), 2856 (m), 1670 (m), 1462 (m), 1382 (m), 1364 (m), 1251 (m), 1159 (m), 1039 (s), 833 (s), 769 (s), 688 (m); **^{1}H NMR (600 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.41 (1H, ddd, J = 86.0, 4.8, 0.8 Hz), 4.52 (1H, ddd, J = 43.9, 9.8, 4.8 Hz), 2.73–2.63 (1H, m), 1.46–1.19 (6H, m), 1.18 (3H, s), 1.17 (3H, s), 0.99 (3H, d, J = 6.8 Hz), 0.85 (9H, s), 0.06 (6H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 146.8 (d, J = 255.2 Hz), 117.3 (d, J = 5.0 Hz), 77.4, 45.1, 37.9, 37.9, 30.1, 29.8, 28.4, 28.3, 26.01, 26.0, 22.2, 21.2, 21.2, 18.3, –1.9; **^{19}F NMR (376**

MHz, $CDCl_3$): δ –131.74 (1F, dd, J = 86.2, 43.9 Hz); **HRMS $[M+H]^+$** calcd for $C_{16}H_{34}FOSi$: 289.2375, found: 289.2363.

(*Z*)-1-(2-Fluorovinyl)-4-methoxybenzene (2.54): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (62.5 mg, 0.500 mmol, 10.0 equiv) and 4-methoxystyrene (6.8 mg, 0.0507 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 4-methoxystyrene that resulted in the formation of a mixture of F- and Br-alkenes (93:7 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (20:1 hexanes/Et_2O) to afford **2.54** (5.4 mg, 0.0355 mmol, 71% yield) in 95:5 *Z*:*E* ratio as pale yellow oil. The spectral data for this compound were identical to those previously reported.[15e]

(*Z*)-4-(2-Fluorovinyl)phenyl acetate (2.55): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (62.5 mg, 0.500 mmol, 10.0 equiv) and 4-acetoxystyrene (8.1 mg, 0.0499 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 84% consumption of 4-acetoxystyrene that resulted in the formation of a mixture of F- and Br-alkenes (96:4 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (10:1 hexanes/Et_2O) to afford **2.55** (6.5 mg, 0.0361 mmol, 72% yield) in 94:6 *Z*:*E* ratio as pale yellow oil. **IR ($CDCl_3$):** 2929 (w), 2869 (m), 1758 (s), 1662 (m), 1506 (m), 1369 (m),

1189 (s), 1167 (s), 1009 (s), 911 (s), 852 (s), 616 (m), 533(m); **^{1}H NMR (600 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.52 (2H, d, J = 8.6 Hz), 7.07 (2H, d, J = 8.7 Hz), 6.65 (1H, dd, J = 82.6, 5.4 Hz), 5.60 (1H, dd, J = 44.3, 5.4 Hz), 2.30 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 169.5, 149.7, 147.0, 130.5, 130.1, 130.0, 121.8, 110.1, 77.5, 77.2, 76.8, 21.3; **^{19}F NMR (376 MHz, $CDCl_3$)**: *Z* isomer (major): δ –122.66 (1F, dd, J = 82.5, 44.3 Hz); **HRMS $[M+H]^+$** calcd for $C_{10}H_{10F}O_2$: 180.0665, found: 180.0667.

(*Z*)-1-Chloro-4-(2-fluorovinyl)benzene (2.56): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 36 μL, 3.6 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (90.2 mg, 0.722 mmol, 10.0 equiv) and 4-chlorostyrene (10.0 mg, 0.0722 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$. Analysis of the unpurified mixture revealed 78% consumption of 4-chlorostyrene that resulted in the formation of a mixture of F- and Br-alkenes (96:4 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (100% hexanes to 2% Et_2O in hexanes) to afford **2.56** (7.2 mg, 0.0460 mmol, 64% yield) in 97:3 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[69]

(*Z*)-1-Bromo-4-(2-fluorovinyl)benzene (2.57): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 27 μL, 2.7 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (68.3 mg, 0.546 mmol, 10.0 equiv) and 4-bromostyrene (10.0 mg, 0.0546 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was

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quenched by the addition of wet $CDCl_3$. Analysis of the unpurified mixture revealed 88% consumption of 4-bromostyrene that resulted in the formation of a mixture of F- and Br-alkenes (95:5 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (100% hexanes to 2% Et_2O in hexanes) to afford **2.57** (7.2 mg, 0.0358 mmol, 66% yield) in 93:7 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[24]

(*Z*)-5-(2-Fluorovinyl)pyrrolidin-2-one (2.58): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 89 μL, 8.9 μmol, 10 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (55.4 mg, 0.444 mmol, 5.00 equiv) and 1-(*tert*-butyldimethylsilyl)-5-vinylpyrrolidin-2-one (20.0 mg, 0.0887 mmol, 1.00 equiv). The resulting solution was allowed to stir for 12 h at 40 °C, after which the reaction was quenched by the addition of wet $CDCl_3$. Subsequent analysis of the unpurified mixture revealed 60% consumption of 1-(*tert*-butyldimethylsilyl)-5-vinylpyrrolidin-2-one that resulted in the exclusive formation of F-alkene (>98:2 fluoro:bromo). The mixture was concentrated and the unpurified residue was re-dissolved in MeOH (1.0 mL) and treated with an aqueous 1.0 M solution of HCl (0.25 mL). The solution was allowed to stir for 2 h at 22 °C. The solution was then diluted with EtOAc (2 mL) and H_2O (2 mL) and the organic layer was separated. The aqueous layer was further washed with EtOAc (3 x 2 mL); the organic layers were combined and dried over $MgSO_4$. The volatiles were removed in vacuo to afford yellow oil, which was purified by silica gel chromatography (30% EtOAc in hexanes to 100% EtOAc) to afford **2.58** (6.3 mg, 0.0488 mmol, 55% yield over two steps) in >98:2 *Z*:*E* ratio as pale yellow oil. The spectral data for this compound were identical to those previously reported.[6a]

(4*R*,5*S*,6*S*)-4-((*Z*)-2-Fluorovinyl)-2-(4-methoxyphenyl)-5-methyl-6-((*S*,*E*)-5-phenylpent-3-en-2-yl)-1,3-dioxane (2.59): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 40 μL, 4.0 μmol, 10 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (25.0 mg, 0.200 mmol, 5.00 equiv) and (4*R*,5*S*,6*R*)-2-(4-methoxyphenyl)-5-methyl-4-((*R*,*E*)-5-phenylpent-3-en-2-yl)-6-vinyl-1,3-dioxane (15.1 mg, 0.0399 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 80% consumption of (4*R*,5*S*,6*R*)-2-(4-methoxyphenyl)-5-methyl-4-((*R*,*E*)-5-phenylpent-3-en-2-yl)-6-vinyl-1,3-dioxane that resulted in the exclusive formation of F-alkene alkene (>98:2 fluoro:bromo). The resulting orange oil was purified by preparative thin layer chromatography (1:8 EtOAc/hexanes) to afford **2.59** (10.0 mg, 0.0252 mmol, 63% yield) in >98:2 *Z*:*E* ratio as off-white solid. M.p. 80–82 °C; **IR ($CDCl_3$)**: 3029 (m), 2962 (m), 1665 (m), 1615 (m), 1586 (s), 1246 (s), 1079 (s), 1014 (s), 826 (s), 727 (s), 696 (s); **^{1}H NMR (500 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.41 (2H, d, J = 8.7 Hz), 7.33–7.27 (4H, m), 7.22–7.15 (2H, m), 6.89 (2H, d, J = 8.7 Hz), 6.66 (1H, ddd, J = 84.2, 4.9, 1.1 Hz), 5.75 (1H, s), 5.74–5.65 (1H, m), 5.60 (1H, dt, J = 15.3, 6.6 Hz), 5.40 (1H, ddd, J = 40.8, 9.6, 5.0 Hz), 5.06 (1H, dd, J = 9.8, 5.6 Hz), 3.81 (3H, s), 3.55 (1H, dd, J = 10.6, 2.1 Hz), 3.38 (2H, d, J = 6.4 Hz), 2.51–2.41 (1H, m), 2.34–2.24 (1H, m), 1.40–1.19 (4H, m), 1.16 (3H, d, J = 7.0 Hz), 0.73 (3H, d, J = 7.0 Hz); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 159.9, 151.3, 149.5, 141.1, 132.2, 130.0, 128.6, 128.5, 126.0, 113.64, 105.6, 105.5, 94.9, 81.1, 70.0, 70.0, 39.3, 38.6, 34.1, 18.5, 11.9; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –121.39 (1F, dd, J = 84.2, 40.8 Hz); **HRMS $[M+H]^+$** calcd for $C_{25}H_{30}FO_3$: 397.2179, found: 397.2194.

Methyl (1*R*,4a*R*,4b*S*,7*S*,10a*R*)-7-((*Z*)-2-fluorovinyl)-1,4a,7-trimethyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxylate (2.60): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 27 μL, 2.7 μmol, 10 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (16.2 mg, 0.130 mmol, 5.00 equiv) and isopimaric acid methyl ester (8.2 mg, 0.0259 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$. Analysis of the unpurified mixture revealed 83% consumption of isopimaric acid methyl ester that resulted in the formation of a mixture of F- and Br-alkenes (94:6 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (1:1 hexanes/benzene, then 20:1 hexanes/Et_2O) to afford **2.60** (6.4 mg, 0.0191 mmol, 70% yield) in 96:4 *Z*:*E* ratio as colorless oil. **IR (neat)**: 2923 (m), 2869 (m), 1724 (s), 1665 (m), 1432 (m), 1385 (m), 1368 (m), 1241 (s), 1184 (m), 1144 (s), 1016 (s), 753(m), 733(m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.26 (1H, dd, J = 85.0, 5.4 Hz), 5.35–5.28 (1H, m), 4.49 (1H, dd, J = 50.1, 5.4 Hz), 3.64 (3H, s), 2.13 (2H, d, J = 2.1 Hz), 2.05–1.66 (6H, m), 1.65–1.45 (6H, m), 1.44–1.28 (1H, m), 1.26 (3H, d, J = 0.7 Hz), 1.18–1.05 (1H, m), 1.02 (3H, s), 0.89 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 179.*4*, 147.44658, 145.0, 135.5, 121.5, 121.4, 52.0, 51.9, 46.9, 46.9, 46.7, 45.4, 38.9, 37.1, 36.9, 36.9, 35.2, 35.0, 25.3, 22.6, 22.6, 19.9, 18.1, 17.6, 15.4; **^{19}F NMR (376 MHz, $CDCl_3$)**: *Z*-isomer (major): δ –125.90 (1F, dd, J = 85.0, 50.1 Hz); **HRMS [M+H]$^+$** calcd for $C_{21}H_{32}FO_2$: 335.2386, found: 335.2391.

(*S*,*Z*)-2-(4-(3-(2-Chloro-10*H*-phenothiazin-10-yl)propyl)piperazin-1-yl)ethyl 6-fluoro-4-methyl-5-hexenoate (2.61): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 10 μL, 1.0 μmol, 5.0 mol %) was transferred by syringe to an

oven-dried vial containing *Z*-1-bromo-2-fluoroethene (12.0 mg, 0.0970 mmol, 5.00 equiv), (*S*)-2-(4-(3-(2-chloro-10*H*-phenothiazin-10-yl)propyl)piperazin-1-yl)ethyl 4-methylhex-5-enoate (10.0 mg, 0.0200 mmol, 1.00 equiv) and benzene (40 μL). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 88% consumption of (*S*)-2-(4-(3-(2-chloro-10*H*-phenothiazin-10-yl)propyl)piperazin-1-yl)ethyl 4-methylhex-5-enoate that resulted in the formation of a mixture of F- and Br-alkenes (91:9 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (5% MeOH in CH_2Cl_2) to afford **2.61** (8.3 mg, 0.0156 mmol, 78% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR ($CDCl_3$)**: 2930 (w), 2874 (w), 2850 (w), 2812 (w), 1733 (m), 1669 (w), 1458 (s), 1408 (w), 1377 (w), 1326 (w), 1279 (w), 1246 (w), 1164 (m), 1145 (w), 1129 (w), 1099 (w), 1038 (w), 1004 (w), 802 (w), 750 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.15 (1H, t, J = 7.6 Hz), 7.11 (1H, d, J = 7.6 Hz), 7.01 (1H, d, J = 8.0 Hz), 6.94–6.84 (4H, m), 6.44 (1H, dd, J = 85.6, 4.8 Hz), 4.51 (1H, dq, J = 43.2, 4.8 Hz), 4.18 (2H, t, J = 6.4 Hz), 3.89 (2H, t, J = 6.8 Hz), 2.71–2.28 (15H, m), 1.94 (2H, quint, J = 7.2 Hz), 1.76–1.68 (1H, m), 1.55–1.47 (1H, m), 1.02 (3H, d, J = 6.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.5, 147.3 (d, $J_{C\text{-}F}$ = 255.0 Hz), 146.4, 144.5, 133.2, 127.8, 127.5, 127.4, 124.8, 123.5, 122.8, 122.2, 115.8 (d, $J_{C\text{-}F}$ = 9.0 Hz), 115.8, 61.7, 56.6, 55.5, 53.3, 53.2, 45.3, 32.3, 31.9, 31.9, 27.9, 27.9, 24.2, 20.9, 20.9; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –130.23 (1F, dd, J = 86.1, 43.6 Hz); **HRMS $[M+NH_4]^+$** calcd for $C_{28}H_{36}N_3O_2Si$: 532.2201, found: 532.2202.

(*Z*)-4-Fluoro-2-methyl-3-butenyl (2*S*,5*R*)-3,3-Dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (2.62): Following the general

procedure, a solution of **Mo-4c** in benzene (0.1 M, 10 μL, 1.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (20.7 mg, 0.166 mmol, 5.00 equiv) and 2-methyl-3-butenyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (10.0 mg, 0.0332 mmol, 1.00 equiv, 60:40 mixture of diastereomers). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$. Analysis of the unpurified mixture revealed 86% consumption of 2-methyl-3-butenyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide that resulted in the exclusive formation of F-alkene (>98:2 fluoro:bromo). The resulting orange oil was purified by silica gel chromatography (10% Et_2O in hexanes to 40% Et_2O in hexanes) to afford **2.62** (8.5 mg, 0.0266 mmol, 80% yield) in >98:2 *Z*:*E* ratio and 60:40 mixture of diastereomers as yellow oil. **IR (CH_2Cl_2)**: 2971 (w), 2936 (w), 1794 (s), 1753 (s), 1672 (w), 1464 (w), 1320 (s), 1265 (m), 1189 (s), 1119 (s), 1003 (m), 709 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.51 (1H, dd, J = 84.4, 4.6 Hz), 4.64–4.59 (1H, m), 4.62 (1H, ddd, J = 41.8, 9.5, 4.6 Hz), 4.43–4.37 (1H, m), 4.20–3.98 (2H, m), 3.53–3.42 (2H, m), 3.17–3.03 (1H, m), 1.62 (3H, s), 1.42 (3H, s), 1.08 (3H, d, J = 3.3 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 170.8, 170.8, 167.1, 167.1, 148.8 (d, $J_{C\text{-}F}$ = 258.0 Hz), 148.8 (d, $J_{C\text{-}F}$ = 259.0 Hz), 112.6, 112.5, 70.1, 70.1, 63.5, 63.4, 62.8, 62.8, 61.2, 61.2, 38.5, 38.5, 28.2, 28.2, 20.5, 20.5, 18.6, 18.6, 17.3, 17.3; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –127.13 (0.6F, dd, J = 89.6, 44.8 Hz), –127.26 (0.4F, dd, J = 89.6, 43.2 Hz); **HRMS $[M+H]^+$** calcd for $C_{13}H_{19}FNO_5S$: 320.0968, found: 320.0979.

2.6.5. Chloro-allyl Addition to Benzaldehyde with 2.23

***syn*-2-Chloro-1-phenyl-3-buten-1-ol (2.24):** In a N_2-filled glove box, an oven-dried vial with magnetic stir bar was charged with **2.23** (10.0 mg, 0.0494 mmol, 1.00 equiv), benzaldehyde (52.4 mg, 0.494 mmol, 10.0 equiv) and toluene (0.2 mL). The resulting solution was allowed to stir for 48 h at 22 °C. The reaction mixture was concentrated in vacuo to afford pale yellow oil, which was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **2.24** (5.8 mg, 0.0318 mmol, 64% yield) in >98:2 diastereomeric ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[70]

2.6.6. Chloro-allyl Addition to Benzaldehyde with 2.23 in the Presence of rac-2.25

(*Z*)-4-Chloro-1-phenyl-3-buten-1-ol (2.26): In a N_2-filled glove box, an oven-dried vial with magnetic stir bar was charged with aminophenol *rac*-**2.25**[23a] (1.6 mg, 4.9 μmol, 10 mol %), NaO*t*-Bu (0.6 mg, 6.2 μmol, 12.5 mol %), toluene (0.2 mL) and MeOH (3.0 μmol, 0.0741 mmol, 1.50 equiv). The resulting solution was allowed to stir for 5 min at 22 °C and then transferred to another oven-dried vial charged with magnetic stir bar, **2.23** (10.0 mg, 0.0494 mmol, 1.00 equiv) and benzaldehyde (10.5 mg, 0.0988 mmol, 2.00 equiv). The resulting solution was allowed to stir for 24 h at 22 °C. The reaction mixture was concentrated by vacuum to afford pale yellow oil, which was purified by silica gel chromatography (100% hexanes to 10% Et_2O in hexanes) to afford **2.26** (8.3 mg, 0.0454 mmol, 92% yield) in 95:5 α:γ ratio and >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[71]

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(70) Julia, M.; Verpeaux, J. N.; Zahneisen, T. *Bull. Soc. Chim. Fr.* **1994**, *131*, 539–554.
(71) (a) Hu, S.; Jayaraman, S.; Oehlschlager, A. C. *J. Org. Chem.* **1996**, *61*, 7513–7520. (b) Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039–1053.

2.6.7. Synthesis of Enyne 2.29 en route to Clathculin B

(*Z*)-12-Heptadecen-10-yn-1-ol (2.29): In a N_2-filled glove box, a solution of **Mo-4c** in benzene (0.1 M, 36 μL, 3.6 μmol, 1.0 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 3.00 equiv) and *Z*-5-decene (50.5 mg, 0.360 mmol, 0.60 equiv). The resulting solution was allowed to stir for 2 h at 22 °C. The mixture was exposed to air out of the glove box and *carefully* concentrated in vacuo. To the resulting orange oil was added 10-undecyn-1-ol **2.28** (101.0 mg, 0.600 mmol, 1.00 equiv), dichlorobis(benzonitrile)palladium(II) (11.5 mg, 0.0300 mmol, 5.0 mol %)) and copper(I) iodide (11.4 mg, 0.0600 mmol, 10 mol %)). The vial was then sealed, evacuated and purged with N_2. To this vial was added piperidine (1.8 mL) and the resulting mixture was allowed to stir for 15 h at 22 °C, after which the reaction was quenched by the addition of a saturated solution of NH_4Cl. The aqueous layer was then washed with ether (3 x 10 mL) and the combined organic layers were washed successively with 0.2 M HCl (10 mL), saturated $NaHCO_3$ (10 mL) and water (2 x 10 mL), then dried over $MgSO_4$ and concentrated in vacuo to afford yellow oil, which was purified by silica gel chromatography (10% Et_2O in hexanes to 20% Et_2O in hexanes) to afford **2.29** (100.7 mg, 0.402 mmol, 67% yield over two steps) in 97:3 *Z*:*E* ratio as pale yellow oil. The spectral data for this compound were identical to those previously reported.[26]

2.6.8. Synthesis of (S)-Coriolic Acid Methyl Ester

(*S*,*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-octen-3-ol (2.33): Prepared in analogy to a previously reported procedure.[27] In a N_2-filled glove box, an oven-dried vial with a magnetic stir bar was charged with 1,3-bis(1-adamantyl)imidazolinium

tetrafluoroborate (12.8 mg, 0.0300 mmol, 5.0 mol %), copper(I) chloride (3.0 mg, 0.0300 mmol, 5.0 mol %), NaO*t*-Bu (11.5 mg, 0.120 mmol, 20 mol %) and thf (1.5 mL). The vial was sealed and allowed to stir for 10 min at 22 °C. Bis(pinacolato)diboron (152.4 mg, 0.600 mmol, 1.00 equiv) was then added, causing the solution to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone) and removed from the glove box. The mixture was allowed to stir at 22 °C for 30 min under N_2 atm. At this time, (*S*)-1-octyn-3-ol (88.0 μL, 0.600 mmol, 1.00 equiv) and MeOH (49.0 μL, 1.20 mmol, 2.00 equiv) were added by syringe. The solution was allowed to stir for 12 h at 22 °C, after which the reaction was quenched by the addition of HCl (1M in diethyl ether), passed through a short plug of silica gel, and washed with Et_2O (3 x 5 mL). The filtrate was concentrated in vacuo to afford brown oil, which was purified by silica gel chromatography (5% EtOAc in hexanes to 30% EtOAc in hexanes) to afford **2.33** as pale yellow oil (135.7 mg, 0.534 mmol, 89% yield). The spectral data for **2.33** are identical to those previously reported.[72]

(*S*)-Coriolic acid methyl ester: In a N_2-filled glove box, an oven-dried vial with magnetic stir bar was charged with **2.32** (87.5 mg, 0.400 mmol, 1.00 equiv), **2.33** (122.0 mg, 0.480 mmol, 1.20 equiv), palladium(II) acetate (9.0 mg, 0.0400 mmol, 10 mol %), SPhos (32.8 mg, 0.0800 mmol, 20 mol %) and KOH (31.4 mg, 0.560 mmol, 1.40 equiv). A 10:1 thf/H_2O mixture (4 mL) was subsequently added. The vial was sealed and removed from the glove box. The mixture was allowed to stir at 65 °C for 12 h, after which the reaction was quenched by passing through a short plug of silica gel and washed with Et_2O (3 x 5 mL). The filtrate was concentrated in vacuo to afford yellow oil, which

(72) Berrée, F.; Gernigon, N.; Hercouet, A.; Lin, C. H.; Carboni, B. *Eur. J. Org. Chem.* **2009**, 329–333.

was purified by silica gel chromatography (10% Et_2O in hexanes to 15% Et_2O in hexanes) to afford (*S*)-coriolic acid methyl ester as colorless oil (88.2 mg, 0.284 mmol, 71% yield). **IR (CH_2Cl_2)**: 3443 (br), 2927 (m), 2855 (w), 1736 (m), 1563 (w), 1420 (w), 1174 (w), 950 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 6.48 (1H, ddd, J = 15.2, 11.0, 1.0 Hz), 5.97 (1H, t, J = 10.9 Hz), 5.67 (1H, dd, J = 15.1, 6.9 Hz), 5.43 (1H, dt, J = 10.1, 7.7 Hz), 4.20–4.12 (1H, m), 3.66 (3H, s), 2.30 (2H, t, J = 7.5 Hz), 2.17 (2H, q, J = 6.9 Hz), 1.64–1.52 (3H, m), 1.35–1.26 (16H, m), 1.46 (3H, t, J = 5.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 174.5, 136.1, 133.0, 128.0, 125.9, 110.2, 73.1, 51.6, 37.5, 34.2, 31.9, 29.6, 29.2, 29.1, 27.8, 25.3, 25.0, 22.8, 14.2; **HRMS $[M+H-H_2O]^+$** calcd for $C_{19}H_{33}O_2$: 293.2481, found: 293.2483.

2.6.9. Kinetically E-Selective Cross-Metathesis (CM) Reactions

General Procedure: In a N_2-filled glove box, an oven-dried 8 mL vial equipped with a magnetic stir bar was charged with alkene substrate (1.0 equiv) and the corresponding *E*-1,2-dihaloethene (5–20 equiv). A solution of **Mo-4c** or **Mo-4f** in benzene (3.0–5.0 mol %) was then added. The resulting mixture was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ (% conversion determined by ^{1}H NMR analysis of the unpurified mixture). Purification was performed through silica gel chromatography.

(*E*)-*tert*-Butyl((8-chloro-2,6-dimethyloct-7-en-2-yl)oxy)dimethylsilane (2.67): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 20 μL, 2.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (77.6 mg, 0.800 mmol, 20.0 equiv), *tert*-butyl((2,6-dimethyl-7-octen-2-yl)oxy)dimethylsilane (10.8 mg, 0.0400 mmol, 1.00 equiv). The resulting solution was

allowed to stir for 15 min at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting alkene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.67** (11.4 mg, 0.0374 mmol, 93% yield) in 93:7 *E:Z* ratio as colorless oil. **IR (neat):** 2956 (m), 2929 (m), 2956 (m), 1633 (w), 1461 (m), 1381 (m), 1363 (m), 1251 (s), 1080 (m), 1039 (s), 1005 (m), 935 (m), 832 (s), 806 (m), 770 (s), 688 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** *E* isomer (major): δ 5.89 (1H, dd, J = 13.3, 0.8 Hz), 5.76 (1H, dd, J = 13.3, 8.3 Hz), 2.24–2.11 (1H, m), 1.42–1.21 (6H, m), 1.16 (6H, s), 0.99 (3H, d, J = 6.7 Hz), 0.83 (9H, s), 0.04 (6H, s); *Z* isomer (minor, resolved signals only): δ 5.95 (1H, dd, J = 7.1, 0.8 Hz), 5.51 (1H, dd, J = 9.4, 7.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.8, 115.8, 73.5, 45.1, 37.3, 36.1, 30.0, 29.9, 26.0, 22.0, 20.4, 18.3, -1.9; **HRMS $[M+H]^+$** calcd for $C_{16}H_{34}ClOSi$: 305.2067, found: 305.2061.

(*E*)-(2-Chlorovinyl)cyclohexane (2.68): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (96.9 mg, 1.00 mmol, 20.0 equiv), vinylcyclohexane (5.5 mg, 0.0500 mmol, 1.00 equiv). The resulting solution was allowed to stir for 15 min at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of vinylcyclohexane. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **2.68** (5.8 mg, 0.0401 mmol, 80% yield) in 92:8 *E:Z* ratio as colorless oil. **IR (neat)**: 2924 (s), 2852 (m), 1621 (w), 1448 (m), 937 (s), 818 (s), 776 (m); **^{1}H NMR (600 MHz, $CDCl_3$)**: *E* isomer (major): δ 5.91 (1H, dd, J = 13.3, 0.9 Hz), 5.86 (1H, dd, J = 13.3, 7.0 Hz), 2.07–1.98 (1H, m), 1.76–1.61 (6H, m), 1.31 – 1.20 (2H,

m), 1.21–1.05 (2H, m); *Z* isomer (minor, resolved signals only): δ 5.59 (1H, dd, J = 9.0, 7.1 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 139.8, 115.8, 40.0, 32.7, 26.1, 25.9.

(*E*)-(2-Chlorovinyl)benzene (2.69): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 30 μL, 3.0 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (96.9 mg, 1.00 mmol, 10.0 equiv), *trans*-β-methylstyrene (11.8 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting alkene. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **2.69** (9.0 mg, 0.0649 mmol, 65% yield) in >98:2 *E:Z* ratio as colorless oil. The spectral data for this compound were identical to those previously reported (*53*).

(*E*)-1-(2-Chlorovinyl)-2-fluorobenzene (2.70): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 50 μL, 5.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (96.9 mg, 1.00 mmol, 10.0 equiv) and 2-fluorostyrene (12.2 mg, 0.100 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting alkene. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **2.70** (8.4 mg, 0.0536 mmol, 54% yield) in >98:2 *E:Z* ratio as colorless oil. **IR (neat)**: 3076 (w), 1606 (s), 1575 (w), 1483 (s), 1455 (m), 1231 (s) 1199 (m), 941 (s), 932 (s), 842 (m), 826 (s), 749 (s); **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (1H, td, J = 10.9, 8.2, 1.8 Hz), 7.25 (1H, dddd, J = 8.2, 7.2, 5.3, 1.8 Hz), 7.10 (1H, td, J = 7.2, 1.2 Hz), 7.06 (1H, ddd, J = 10.9, 8.2, 1.2 Hz), 6.90 (1H, d, J = 13.8 Hz), 6.81 (1H, d, J = 13.8 Hz);

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.0 (d, J = 250.3 Hz), 129.6 (d, J = 8.7 Hz), 128.2 (d, J = 3.5 Hz), 126.9 (d, J = 1.7 Hz), 124.5 (d, J = 3.6 Hz), 122.8 (d, J = 12.7 Hz), 121.8 (d, J = 8.7 Hz), 116.1 (d, J = 22.0 Hz); **HRMS [M+H]$^+$** calcd for C_8H_6ClF: 156.0142, found: 156.0147.

(*E*)-1-Bromo-3-(2-chlorovinyl)benzene (2.71): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 16 μL, 1.6 μmol, 3 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (53.0 mg, 0.546 mmol, 10.0 equiv) and 3-bromostyrene (10.0 mg, 0.0546 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 3-bromostyrene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.71** (7.1 mg, 0.0326 mmol, 60% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 3072 (w), 2926 (w), 1610 (m), 1586 (w), 1561 (m), 1470 (w), 1242 (w), 1072 (w), 933 (s), 831 (m), 768 (s), 672 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.45 (1H, s), 7.40 (1H, ddd, J = 6.7, 2.5, 1.5 Hz), 7.24−7.17 (2H, m), 6.77 (1H, d, J = 13.7 Hz), 6.66 (1H, d, J = 13.7 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 137.0, 132.1, 131.2, 130.4, 129.1, 124.9, 123.1, 120.5; **HRMS [M+H]$^+$** calcd for C_8H_6BrCl: 215.9341, found: 215.9338.

(*E*)-1-Chloro-4-(2-chlorovinyl)benzene (2.72): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 40 μL, 4.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (77.6 mg, 0.800 mmol, 10.0 equiv) and 4-chlorostyrene (11.2 mg, 0.808 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of

wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 4-chlorostyrene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **2.72** (9.7 mg, 0.0560 mmol, 69% yield) in >98:2 *E*:*Z* ratio as colorless oil. The spectral data for this compound were identical to those previously reported (*54*).

(*E*)-4-(2-Chlorovinyl)phenyl acetate (2.73): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 24 μL, 2.4 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (77.6 mg, 0.800 mmol, 10.0 equiv) and 4-acetoxystyrene (13.0 mg, 0.802 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 4-acetoxystyrene. The resulting orange oil was purified by silica gel chromatography (5% EtOAc/hexanes) to afford **2.73** (11.8 mg, 0.0600 mmol, 75% yield) in >98:2 *E*:*Z* ratio as off-white crystalline solid. **Mp:** 61−63 °C; **IR (neat)**: 3081 (w), 2927 (w), 2852 (w), 1736 (s), 1740 (s), 1614 (w), 1601 (w), 1580 (m), 1506 (m), 1219 (s), 1204 (s), 1185 (s), 1166 (s), 1011 (m), 937 (s), 909 (s), 846 (m), 819 (m), 800 (s), 778 (m), 650 (s), 519 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.30 (2H, d, J = 8.8 Hz), 7.06 (2H, d, J = 8.8 Hz), 6.82 (1H, d, J = 13.7 Hz), 6.61 (1H, d, J = 13.7 Hz), 2.30 (3H, s); **^{13}C NMR (151 MHz, $CDCl_3$)**: δ 169.4, 150.6, 132.8, 132.5, 127.3, 122.1, 119.0, 21.3; **HRMS $[M+H]^+$** calcd for $C_{10}H_{10}ClO_2$: 197.0369, found: 197.0373.

(*E*)-1-(2-Chlorovinyl)-4-(trifluoromethyl)benzene (2.74) : Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 30 μL, 3.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (58.2 mg, 0.600 mmol, 10.0 equiv) and 4-trifluoromethylstyrene (10.3 mg, 0.0598 mmol, 1.00

equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 84% consumption of alkene. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **2.74** (7.3 mg, 0.0353 mmol, 59% yield) in >98:2 *E*:*Z* ratio as clear colorless oil. **IR (neat):** 3074 (w), 2869 (m), 1614 (m), 1574 (w), 1412 (m), 1321 (s), 1164 (m), 1120 (s), 1108 (s), 1066 (s), 1017 (m), 930 (s), 823(m), 794 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (2H, d, J = 8.1 Hz), 7.40 (2H, d, J = 8.1 Hz), 6.87 (1H, d, J = 13.7 Hz), 6.76 (1H, d, J = 13.7 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 132.2, 126.4, 125.9 (q, J =3.8 Hz), 121.6, 101.1; **HRMS $[M+H]^+$** calcd for $C_9H_6ClF_3$: 206.0110, found: 206.0110.

(*E*)-2-(4-(2-Chlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2.75): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 22 μL, 2.2 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (41.7 mg, 0.430 mmol, 10.0 equiv) and 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3-dioxolane (10.0 mg, 0.0430 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3-dioxolane. The resulting orange oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **2.75** (7.0 mg, 0.0262 mmol, 61% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 2978 (m), 2930 (w), 1607 (m), 1398 (m), 1359 (s), 1323 (m), 1271 (m), 1143 (m), 1089 (m), 933 (w), 857 (m), 793 (m), 636 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.76 (1H, d, J = 8.1 Hz), 7.29 (2H, d, J = 7.9 Hz), 6.84 (1H, d, J = 13.7 Hz), 6.71 (1H, d, J = 13.7 Hz), 1.34 (12H, s); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 137.6,

135.4, 133.5, 125.5, 119.9, 84.0, 25.0; **HRMS [M+H]$^+$** calcd for $C_{14}H_{19}BClO_2$: 265.1158, found: 265.1167.

(*E*)-*tert*-Butyl 6-(2-chlorovinyl)-1*H*-indole-1-carboxylate (2.76): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 12 μL, 1.2 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (39.8 mg, 0.411 mmol, 10.0 equiv) and *tert*-butyl 6-vinyl-1*H*-indole-1-carboxylate (10.0 mg, 0.0411 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *tert*-butyl 6-vinyl-1*H*-indole-1-carboxylate. The resulting orange oil was purified by silica gel chromatography (5% Et_2O/hexanes) to afford **2.76** (9.1 mg, 0.0328 mmol, 80% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 3073 (w), 2979 (w), 2934 (w), 1731 (s), 1437 (m), 1336 (s), 1263 (m), 1148 (s), 1126 (s), 932 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.12 (1H, s), 7.58–7.53 (1H, m), 7.47 (1H, d, J = 8.1 Hz), 7.17 (1H, d, J = 8.1 Hz), 6.92 (1H, d, J = 13.7 Hz), 6.67 (1H, d, J = 13.7 Hz), 6.53–6.48 (1H, m), 1.66 (9H, s); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 134.2, 131.3, 130.6, 126.9, 121.3, 121.1, 117.7, 113.3, 107.4, 84.1, 28.3; **HRMS [M+H]$^+$** calcd for $C_{16}H_{17}ClNO_2$: 278.0948, found: 278.0937.

(*E*)-2-(2-Chlorovinyl)benzofuran (2.77): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 35 μL, 3.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (67.2 mg, 0.694 mmol, 10.0 equiv) and 2-vinylbenzofuran (10.0 mg, 0.0694 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 84% consumption of 2-vinylbenzofuran. The

resulting orange oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **2.77** (7.7 mg, 0.0431 mmol, 62% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 3084 (w), 2979 (w), 2925 (w), 2853 (w), 1625 (w), 1450 (m), 1254 (m), 949 (m), 924 (m), 823 (s), 786 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.52 (1H, ddd, J = 7.6, 1.3, 0.7 Hz), 7.42 (1H, ddd, J = 8.2, 1.7, 0.9 Hz), 7.31–7.26 (1H, m), 7.23–7.18 (1H, m), 6.91 (1H, dd, J = 13.5, 0.5 Hz), 6.75 (1H, d, J = 13.4, 1.3 Hz), 6.59 (1H, s); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 155.0, 151.9, 128.6, 125.2, 123.2, 122.1, 121.2, 121.2, 111.1, 105.4; **HRMS $[M+H]^+$** calcd for $C_{10}H_8ClO$: 179.0264, found: 179.0264.

(*E*)-3-(2-Chlorovinyl)-1H-indole (2.78): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 40 μL, 4.0 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (77.6 mg, 0.800 mmol, 10.0 equiv) and 3-vinyl-1*H*-indole (11.5 mg, 0.0803 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of alkene precursor. The resulting orange oil was purified by silica gel chromatography (10% EtOAc/hexanes then 20% EtOAc/hexanes) to afford **2.78** (12.1 mg, 0.0681 mmol, 85% yield) in >98:2 *E*:*Z* ratio as slight brown solid. **Mp:** >250 °C; **IR (in $CDCl_3$)**: 3382 (s), 2984 (w), 1730 (s), 1457 (m), 1373 (m), 1243 (s), 1099 (s), 1044 (s), 751 (s), 732 (s).; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (1H, s), 7.79–7.71 (1H, m), 7.43–7.35 (1H, m), 7.30–7.16 (3H, m), 7.01 (1H, dd, J = 13.7, 0.6 Hz), 6.66 (1H, d, J = 13.7 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 136.7, 126.3, 125.1, 123.6, 123.0, 120.9, 120.0, 114.9, 112.9, 111.6.; **HRMS $[M+H]^+$** calcd for $C_{10}H_9ClN$: 178.0424, found: 178.0421.

(*E*)-3-(2-Chlorovinyl)benzo[*b*]thiophene (2.79): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 31 μL, 3.1 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (60.5 mg, 0.624 mmol, 10.0 equiv) and 3-vinylbenzo[*b*]thiophene (10.0 mg, 0.0624 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 85% consumption of 3-vinylbenzo[*b*]thiophene. The resulting orange oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **2.79** (8.4 mg, 0.0431 mmol, 69% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 3067 (w), 2979 (w), 2920 (w), 2849 (w), 1607 (w), 1425 (m), 1263 (m), 1221 (w), 926 (m); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.87 (1H, d, J = 8.0 Hz), 7.84 (1H, d, J = 8.0 Hz), 7.43 (1H, td, J = 7.7, 1.2 Hz), 7.40–7.37 (2H, m), 7.10 (1H, d, J = 13.6 Hz), 6.73 (1H, d, J = 13.6 Hz); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 126.2, 124.9, 124.7, 123.1, 123.0, 122.0, 120.0; **HRMS $[M+H]^+$** calcd for $C_{10}H_8ClS$: 195.0035, found: 195.0036.

2-((3*Z*,7*E*)-8-Chloroocta-3,7-dien-2-yl)isoindoline-1,3-dione (2.90): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 25 μL, 2.5 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (78.9 mg, 0.814 mmol, 10.0 equiv) and **2.89** (93% by mass, 29.0 mg, 0.0814 mmol, 1.00 equiv). The resulting solution was allowed to stir for 1 h at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting alkene. The resulting orange oil was purified by silica gel chromatography (5% EtOAc/hexanes) to afford a 83:17 mixture of **2.90** and unreacted **2.89** (26.9 mg, 0.0771 mmol, 95% yield by mass) in >98:2 *E*:*Z* ratio

as yellow oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.81 (2H, dd, J = 5.4, 3.0 Hz), 7.69 (2H, dd, J = 5.4, 3.0 Hz), 6.01 (1H, ddt, J = 10.9, 9.3, 1.6 Hz), 5.92 (1H, dt, J = 13.2, 1.3 Hz), 5.83 (1H, dt, J = 13.2, 7.2 Hz, 0H), 5.44 (1H, dtd, J = 10.7, 7.5, 1.2 Hz), 5.19 (1H, dqd, J = 9.3, 7.0, 1.1 Hz), 2.29–2.17 (2H, m), 2.12–2.07 (2H, m), 1.53 (3H, d, J = 6.9 Hz); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 168.1, 134.0, 132.8, 132.2, 131.1, 129.8, 123.3, 117.9, 43.6, 30.7, 27.0, 19.5; **HRMS $[M+H]^+$** calcd for $C_{16}H_{17}ClNO_2$: 290.0948, found: 290.0956.

(*S*,*E*)-4-(3-Chloroallyl)-2,2-dimethyl-1,3-dioxolane (2.94): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 14 μL, 1.4 μmol, 3.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (48.5 mg, 0.500 mmol, 10.0 equiv) and **2.93**[43] (*33*) (10.3 mg, 0.0472 mmol, 1.00 equiv). The resulting solution was allowed to stir for 1 hour at 22 °C, after which the reaction was quenched by the addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting alkene. The resulting orange oil was purified by silica gel chromatography (50:1 pentane/Et_2O then 10:1 pentane/Et_2O) to afford **2.94** (6.2 mg, 0.0351 mmol, 70% yield) in >98:2 *E*:*Z* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[44]

(*E*)-1-Benzhydryl-4-(3-chloroallyl)piperazine (2.95): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 1.00 mL, 0.1 mmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (1.94 g, 20.0 mmol, 10.0 equiv) and cinnarizine (737 mg, 2.00 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 94% consumption of cinnarizine. The resulting orange oil was purified by silica gel chromatography (100% CH_2Cl_2 to 1%

MeOH/CH_2Cl_2) to afford **2.95** (614 mg, 1.88 mmol, 94% yield) in >98:2 *E*:*Z* ratio as yellow oil. **IR (in CH_2Cl_2)**: 2807 (m), 2765 (w), 1635 (w), 1598 (w), 1491 (w), 1302 (m), 1450 (m), 1264 (m), 1006 (m), 929 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.43−7.38 (4H, m), 7.29−7.23 (4H, m), 7.20−7.14 (2H, m), 6.12 (1H, dt, J = 13.3, 1.2 Hz), 5.97 (1H, dt, J = 13.3, 7.1 Hz), 4.22 (1H, s), 3.00 (2H, dd, J = 7.1, 1.2 Hz), 2.59−2.32 (8H, m); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 142.8, 130.4, 128.6, 128.1, 127.1, 120.6, 76.3, 58.4, 53.3, 51.9; **HRMS $[M+H]^+$** calcd for $C_{20}H_{24}ClN_2$: 327.1628, found: 327.1626.

((2*S*,3*R*,4*S*,5*R*)-2-((*E*)-3-Chloroallyloxy)-6-(((2*R*,3*R*,4*S*,5*S*)-3,4,5-tris(*tert*-butyldimethylsilyloxy)tetrahydro-2*H*-pyran-2-yloxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triyl)tris(oxy)tris(*tert*-butyldimethylsilane) (2.99): Following the general procedure, a solution of **Mo-4f** in benzene (0.1 M, 15 μL, 1.5 μmol, 5 mol %) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (29.1 mg, 0.300 mmol, 10.0 equiv) and rosavin per-silyl ether (33.4 mg, 0.0300 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting alkene**.** The resulting orange oil was purified by silica gel chromatography (100% hexanes to 2% Et_2O/hexanes) to afford **2.99** (28.9 mg, 0.0270 mmol, 90% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 2954 (m), 2929 (m), 2887 (w), 2857 (m), 1472 (w), 1463 (w), 1359 (w), 1252 (m), 1095 (s), 1037 (m), 862 (m), 832 (s), 774 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 6.23 (1H, d, J = 13.4 Hz), 6.04 (1H, d, J = 12.7, 6.2 Hz), 4.70 (1H, d, J = 6.4 Hz), 4.43 (1H, s), 4.37 (1H, ddd, J = 12.6, 5.7, 1.2 Hz), 4.08–4.01 (1H, m), 3.98–3.91 (2H, m), 3.88 (1H, t, J = 10.1 Hz), 3.78–3.67 (4H, m), 3.61 (1H, d, J = 6.2 Hz), 3.57 (2H, dd, J = 10.1, 8.7 Hz), 3.23 (1H,

dd, J = 9.9, 4.3 Hz), 0.93–0.84 (54H, m), 0.10–0.01 (36H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 129.8, 121.1, 101.6, 100.6, 81.4, 78.3, 77.4, 77.3, 72.6, 72.1, 70.0, 67.1, 26.2, 26.1, 26.0, 25.9, 25.9, 18.5, 18.4, 18.2, 18.2, 18.1, 18.0, –4.0, –4.3, –4.3, –4.3, –4.3, –4.5, –4.5, –4.8, –4.8; **HRMS [M+Na]$^+$** found for $C_{50}H_{107}ClO_{10}Si_6Na$: 1093.6085.

(2*S*,3*R*,4*S*,5*R*)-2-((*E*)-3-chloroallyloxy)-6-(((2*R*,3*R*,4*S*,5*S*)-3,4,5-trihydroxytetrahydro-2*H*-pyran-2-yloxy)methyl)tetrahydro-2*H*-pyran-3,4,5-triol (2.100): Prepared in analogy to a previously reported procedure.[73] A mixture of **2.99** (22.2 mg, 0.0207 mmol, 1.00 equiv) and (n-Bu)$_4$NF (1.0 M in THF, 0.25 mL, 0.248 mmol, 12.0 equiv) was allowed to stir for 12 hours at 22 °C under N_2 atm. $CaCO_3$ (51.5 mg), Dowex 50WX8-400 (154.6 mg) and MeOH (0.37 mL) were then added and the resulting suspension was allowed to stir for 2 hours at 22 °C. The mixture was filtered through a pad of celite and the filter cake was washed with MeOH (2 mL). The filtrate was concentrated under vacuum to give off-white solid. EtOH (2 mL) was added and the resulting mixture was filtered and concentrated in vacuo to afford **2.100** (6.3 mg, 0.0163 mmol, 79% yield) in >98:2 E:Z ratio as off-white solid. **Mp:** 68–70 °C; **IR (in CH_3OH)**: 3333 (br), 2925 (w), 1638 (w), 1580 (m), 1410 (m), 1363 (m), 1255 (m); **^{1}H NMR (400 MHz, CD_3OD)**: δ 6.46 (1H, d, J = 13.3 Hz), 6.11–6.02 (1H, m), 4.37–4.27 (3H, m), 4.17 (1H, dd, J = 12.9, 6.6 Hz), 4.10 (1H, d, J = 10.6 Hz), 3.87 (1H, d, J = 12.2 Hz), 3.81 (1H, s); 3.72 (1H, dd, J = 11.3, 5.9 Hz), 3.62–3.50 (3H, m), 3.48–3.42 (1H, m), 3.38–3.32 (2H, m), 3.20 (1H, t, J = 8.0 Hz); **^{13}C NMR (100 MHz, CD_3OD)**: δ 131.0, 122.4, 105.2, 103.3, 77.9, 76.9, 75.0, 74.2, 72.4, 71.6, 69.6, 69.5, 68.2, 66.8; **HRMS [M+NH_4]$^+$** calcd for $C_{14}H_{27}ClNO_{10}$: 404.1324, found: 404.1343.

(73) Kaburagi, Y.; Kishi, Y. *Org. Lett.* **2007**, *9*, 723–726.

***tert*-Butyl (*E*)-3-(2-fluorovinyl)-1*H*-indole-1-carboxylate (2.107):** Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M in toluene, 215 μL mmol, 0.507 mmol, 10.0 equiv) and *tert*-butyl 3-vinyl-1*H*-indole-1-carboxylate (12.3 mg, 0.0506 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was then quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *tert*-butyl 3-vinyl-1*H*-indole-1-carboxylate that resulted in the formation of a mixture of F- and Cl-alkenes (89:11 F:Cl). The resulting red oil was purified by silica gel chromatography (50:1 pentane/Et_2O) to afford **2.107** (10.9 mg, 0.0417 mmol, 82% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 2981 (w), 2932 (w), 1732 (s), 1717 (s), 1454 (m), 1368 (s), 1253 (s), 1149 (s), 1090 (s), 736 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.15 (1H, d, J = 8.3 Hz), 7.57 – 7.50 (2H, m), 7.29 (1H, ddd, J = 83.7, 11.5, 0.6 Hz), 7.34 (2H, ddd, J = 8.5, 7.2, 1.3 Hz), 7.28 (1H, d, J = 1.2 Hz), 7.28 – 7.25 (1H, m), 6.46 (1H, ddd, J = 19.3, 11.4, 0.9 Hz), 1.66 (9H, s); **^{19}F NMR (376 MHz, $CDCl_3$):** δ –126.49 (1F, dd, $J_{C\text{-}F}$ = 83.7, 19.3 Hz); **^{13}C NMR (151 MHz, $CDCl_3$)**: δ 150.1 (d, $J_{C\text{-}F}$ = 258.2 Hz), 149.6, 135.9, 128.6, 125.0, 123.3, 123.1, 119.8, 115.6, 113.1 (d, $J_{C\text{-}F}$ = 12.9 Hz), 105.5 (d, $J_{C\text{-}F}$ = 18.3 Hz), 84.1, 28.3; **HRMS [M+H]$^+$** calcd for $C_{15}H_{17}FNO_2$: 262.1243, found: 262.1246.

(*E*)-1-Bromo-4-(2-fluorovinyl)benzene (2.108): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1-chloro-2-fluoroethene (2.36 M in toluene, 110 μL mmol, 0.260, 5.07 equiv) and 4-bromostyrene (9.4 mg, 0.0513 mmol, 1.00

equiv). The solution was allowed to stir for 2 h at 22 °C, after which the reaction was quenched with wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of styrene that resulted in the formation of a mixture of fluoro- and chloro-alkenes (89:11 F:Cl). The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **2.108** (6.1 mg, 0.0303 mmol, 59% yield) in >98:2 *E*:*Z* ratio as colorless oil. The spectral data for this compound were in accordance with those reported previously.[15e]

(*E*)-4-(2-Fluorovinyl)phenyl acetate (2.109): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 25 μL, 2.5 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing *E*-1-chloro-2-fluoroethene (2.36 M in toluene, 105 μL, 0.248 mmol, 5.00 equiv) and 4-acetoxystyrene (8.1 mg, 0.0499 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C, after which the reaction was quenched with wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of styrene that resulted in the formation of a mixture of fluoro- and chloro-alkenes (87:13 F:Cl). The resulting orange oil was purified by silica gel chromatography (10:1 pentane/Et_2O) to afford **2.109** (6.4 mg, 0.0355 mmol, 71% yield) in >98:2 *E*:*Z* ratio as needle-like crystalline solid. **Mp:** 57–59 C; **IR (in CH_2Cl_2):** 3096 (w), 1740 (s), 1656 (m), 1603 (w), 1508 (m), 1362 (m), 1209 (s), 1185 (s), 1165 (s), 1080 (s), 1007 (m), 918 (s), 668 (m), 530 (s); **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.25 (2H, d, J = 8.6 Hz), 7.13 (1H, dd, J = 83.0, 11.3 Hz), 7.04 (2H, d, J = 8.6 Hz), 6.38 (1H, dd, J = 19.1, 11.3 Hz), 2.30 (3H, d, J = 0.6 Hz); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 169.6, 150.3 (d, $J_{C\text{-}F}$ = 259.5 Hz), 127.3, 122.10, 113.24 (d, $J_{C\text{-}F}$ = 16.6 Hz), 21.26; **^{19}F NMR (376 MHz,**

$CDCl_3$): δ –129.42 (1F, dd, J = 83.0, 19.1 Hz); **HRMS [M+H]$^+$** calcd for $C_{10}H_{10}FO_2$: 181.0664, found: 181.0661.

(*E*)-2-(4-(2-Fluorovinyl)phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.110): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 22 μL, 2.2 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M, 185 μL, 0.435 mmol, 10.0 equiv) and 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (10.0 mg, 0.0435 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane that resulted in the formation of a mixture of fluoro- and chloro-alkenes (88:12 F:Cl). The resulting red oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **2.110** (7.9 mg, 0.0318 mmol, 73% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 2980 (w), 1657 (w), 1610 (w), 1360 (m), 1264 (m), 1092 (m), 912 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.74 (2H, d, J = 8.0 Hz), 7.25 (2H, d, J = 8.3 Hz), 7.22 (1H, dd, J = 83.0, 11.3 Hz), 6.39 (1H, dd, J = 19.3, 11.3 Hz), 1.34 (12H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –128.46 (1F, dd, J = 83.1, 19.3 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 150.9 (d, $J_{C\text{-}F}$ = 260.6 Hz), 135.4, 125.6, 125.5, 114.2, 114.0, 84.0, 25.0; **HRMS [M+H]$^+$** calcd for $C_{14}H_{19}BFO_2$: 249.1462, found: 249.1462.

(*E*)-3-(2-Fluorovinyl)benzo[*b*]thiophene (2.111): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 31 μL, 3.1 μmol, 5.0 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M, 265 μL, 0.624 mmol, 10.0 equiv) and 3-vinylbenzo[*b*]thiophene (10.0

mg, 0.0624 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 95% consumption of 3-vinylbenzo[*b*]thiophene that resulted in the formation of a mixture of fluoro- and chloro-alkenes (88:12 F:Cl). The resulting red oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **2.111** (7.3 mg, 0.0410 mmol, 66% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 3057 (w), 2921 (w), 1657 (m), 1426 (w), 1264 (m), 1111 (m), 908 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.89−7.85 (1H, m), 7.80−7.76 (1H, m), 7.45−7.36 (2H, m), 7.30 (1H, s), 7.23 (1H, dd, J = 83.5, 11.3 Hz), 6.63 (1H, ddd, J = 18.1, 11.3, 1.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ −125.14 (1F, dd, J = 83.5, 18.1 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 150.8 (d, $J_{C\text{-}F}$ = 261.9 Hz), 124.8, 124.6, 123.1, 122.0, 122.0, 122.0, 107.2, 107.0; **HRMS $[M+H]^+$** calcd for $C_{10}H_8FS$: 179.0331, found: 179.0335.

(*E*)-*tert*-Butyl(8-fluoro-2,6-dimethyl-7-octen-2-yloxy)dimethylsilane (2.112): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 18 μL, 1.8 μmol, 5 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M, 78 μL, 0.185 mmol, 5.00 equiv) and *tert*-butyl(2,6-dimethyl-7-octen-2-yloxy)dimethylsilane (10.0 mg, 0.0370 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 95% consumption of *tert*-butyl(2,6-dimethyl-7-octen-2-yloxy)dimethylsilane (that resulted in the formation of a mixture of fluoro- and chloro-alkenes (90:10 F:Cl). The resulting red oil was purified by silica gel chromatography (100% pentane) to afford **2.112** (8.2 mg, 0.0284 mmol, 77% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (in CH_2Cl_2)**: 2956 (m), 2930 (m), 2856 (w),

1672 (w), 1462 (w), 1252 (m), 1039 (s), 917 (m), 833 (s), 770 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 6.48 (1H, ddd, J = 86.3, 11.1, 0.8 Hz), 5.22 (1H, ddd, J = 20.0, 11.1, 9.0 Hz), 2.05 (1H, qt, J = 10.9, 7.3 Hz), 2.01–1.99 (1H, m), 1.37–1.23 (6H, m), 1.17 (6H, s), 1.00 (3H, s), 0.85 (9H, s), 0.05 (6H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ −133.34 (1F, dd, J = 86.3, 20.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.0 (d, $J_{C\text{-}F}$ = 252.3 Hz), 117.7, 73.6, 45.1, 37.9, 30.8, 30.0, 26.0, 22.0, 21.2, 18.3, -1.9; **HRMS $[M+H]^+$** calcd for $C_{16}H_{34}FOSi$: 289.2363, found: 289.2371.

Methyl (1*R*,4a*R*,4b*S*,7*S*,10a*R*)-7-((*E*)-2-fluorovinyl)-1,4a,7-trimethyl-1,2,3,4,4a,4b,5,6,7, 8,10,10a-dodecahydrophenanthrene-1-carboxylate (2.113): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 14 μL, 1.4 μmol, 10.0 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M, 30 μL, 0.0711 mmol, 5.00 equiv) and methyl (1*R*,4a*R*,4b*S*,7*S*,10a*R*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene-1-carboxylate (4.5 mg, 0.0142 mmol, 1.00 equiv). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 94% consumption of alkene precursor that resulted in the exclusive formation of fluoro-alkene. The resulting orange oil was purified by silica gel chromatography (10 mL of 1:1 hexanes/benzene then 15 mL of 20:1 hexanes/Et_2O) to afford **2.113** (3.7 mg, 0.0111 mmol, 78% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2916 (m), 2868 (m), 2847 (m), 1724 (s), 1667 (m), 1432 (m), 1385 (m), 1241 (s), 1184 (m), 1143 (m), 1069 (s), 920 (s).; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.47 (1H, dd, J = 86.1, 11.2 Hz), 5.37 (1H, dd, J = 22.9, 11.2 Hz), 5.32 (1H, m), 3.64 (3H, s), 2.03–1.69 (8H, m), 1.64–1.47 (6H, m),

1.42–1.23 (5H, m), 1.17–1.06 (1H, m), 0.89 (3H, s), 0.88 (3H, s).; **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 179.3, 149.1, 146.6, 135.0, 123.9, 123.87, 121.7, 52.1, 51.9, 46.8, 46.8, 46.7, 45.4, 39.0, 37.1, 36.8, 36.8, 35.2, 33.6, 33.5, 25.3, 22.2, 19.9, 18.1, 17.6, 15.4.; **^{19}F NMR (376 MHz, $CDCl_3$):** δ –138.07 (1F, dd, J = 86.1, 22.8 Hz).; **HRMS $[M+H]^+$** calcd for $C_{21}H_{32}FO_2$: 335.2386, found: 335.2382.

(4*R*,5*S*,6*S*)-4-((*E*)-2-Fluorovinyl)-2-(4-methoxyphenyl)-5-methyl-6-((*S*,*E*)-5-phenyl-3-penten-2-yl)-1,3-dioxane (2.114): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 26 μL, 2.6 μmol, 10.0 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M, 56 μL, 0.132 mmol, 5.0 equiv) and (4*S*,5*R*,6*S*)-2-(4-methoxyphenyl)-5-methyl-4-((*S*,*E*)-5-phenyl-3-penten-2-yl)-6-vinyl-1,3-dioxane (10.0 mg, 0.0264 mmol, 1.00 equiv). The resulting solution was allowed to stir for 2 hours at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 62% consumption of (4*S*,5*R*,6*S*)-2-(4-methoxyphenyl)-5-methyl-4-((*S*,*E*)-5-phenyl-3-penten-2-yl)-6-vinyl-1,3-dioxane that resulted in the exclusive formation of fluoro-alkene (>98:2 F:Cl). The resulting red oil was purified by preparative thin layer chromatography (1:8 EtOAc/hexanes) to afford **2.114** (6.2 mg, 0.0156 mmol, 59% yield) in >98:2 *E*:*Z* ratio as white solid. **Mp:** 62–64 ^{o}C; **IR (in CH_2Cl_2)**: 2960 (w), 2925 (m), 2849 (w), 1667 (m), 1615 (w), 1517 (m), 1248 (s), 1076 (s), 1032 (s), 828 (m), 699 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.40 (2H, d, J = 8.8 Hz), 7.3 –7.26 (2H, m), 7.22–7.17 (3H, m), 6.89 (2H, d, J = 8.8 Hz), 6.78 (1H, dd, J = 84.2, 11.0 Hz), 5.97 (1H, ddd, J = 18.3, 11.0, 9.7 Hz), 5.75 (1H, s), 5.72–5.56 (2H, m), 4.45 (1H, dd, J = 9.6, 5.7 Hz), 3.81 (3H, s), 3.56 (1H, dd, J = 10.6, 2.2 Hz), 3.38 (2H, d, J = 6.3 Hz), 2.51–2.41 (1H, m), 2.34–2.23 (1H, m), 1.16 (3H,

d, J = 7.0 Hz), 0.70 (3H, d, J = 7.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –121.53 (1F, ddd, J = 84.2, 18.3, 2.2 Hz); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 160.0, 153.4 (d, $J_{C\text{-}F}$ = 263.4 Hz), 141.1, 132.1, 131.7, 130.1, 128.6, 128.5, 127.5, 126.1, 113.7, 106.7, 94.8, 81.2, 73.6, 55.5, 39.3, 38.7, 34.4, 18.5, 12.6; **HRMS $[M+H]^+$** calcd for $C_{25}H_{30}FO_3$: 397.2179, found: 397.2174.

(3a*R*,5*S*,6a*R*)-5-((*E*)-2-Fluorovinyl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (2.116): Following the general procedure, a solution of **Mo-4c** in benzene (0.1 M, 42 μL, 4.2 μmol, 10.0 mol %) was transferred by syringe to an oven-dried vial containing a solution of *E*-1-chloro-2-fluoroethene in toluene (2.36 M, 90 μL, 0.212 mmol, 5.00 equiv) and (3a*R*,5*S*,6a*R*)-2,2-dimethyl-5-vinyltetrahydrofuro[2,3-*d*][1,3]dioxole (*13*, *56*) (7.1 mg, 0.0422 mmol, 1.00 equiv). The resulting solution was allowed to stir for 12 h at 40 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 94% consumption of alkene precursor that resulted in the exclusive formation of fluoro-alkene (>98:2 F:Cl). The resulting orange oil was purified by silica gel chromatography (100 mL of 20:1 pentane/Et_2O then 100 mL of 10:1 pentane/Et_2O) to afford **2.116** (4.3 mg, 0.0228 mmol, 54% yield) in >98:2 *E*:*Z* ratio as colorless oil. The spectral data for this compound were identical to those previously reported.[45]

2.6.10. Synthesis of the Amine Fragment of Kimbeamide A

(But-3-yn-2-yloxy)triethylsilane (2.86): Triethylsilyl chloride (1.48 mL, 8.80 mmol, 1.10 equiv) was added to a solution of 3-butyn-2-ol **2.84** (627 μL, 8.00 mmol, 1.00 equiv) and imidazole (1.09 g, 16.0 mmol. 2.00 equiv) in CH_2Cl_2 (25 mL) at 0 °C. Once the addition was complete, the mixture was allowed to stir at 22 °C for 3 h before addition of

a saturated solution of aqueous $NaHCO_3$ (25 mL). The phases were separated and the aqueous phase was back-washed with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with 1 M solution of aqueous HCl (25 mL) and 5% w/v aqueous $CuSO_4$ (25 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was purified by silica gel chromatography (200:1 hexanes/EtOAc) to afford silyl ether **2.86** (1.42 g, 7.70 mmol, 96% yield) as colorless oil. The spectral data for this compound were identical to those previously reported.[74]

(*E*)-8-Phenyloct-7-en-3-yn-2-ol (2.88): $LiAlH_4$ (617 mg, 16.2 mmol, 2.6 equiv) was added to a solution of *trans*-3-styryl acetic acid **2.85** (1.00 g, 6.17 mmol, 1.00 equiv) in THF (5 mL) at 0 °C. The mixture was allowed to stir at 0 °C for 20 min, then at 22 °C for 1 h. The reaction was cooled to 0 °C and quenched by addition of H_2O (617 μL), followed by 1 M solution of aqueous NaOH (617 μL). The resulting mixture was allowed to stir at 0 °C for 5 min, then H_2O (2 mL) was added. The mixture was allowed to stir at 22 °C for an additional 15 min before introducing $MgSO_4$. The mixture was filtered through celite and the filtrate was concentrated under reduced pressure. The product was purified by silica gel chromatography (4:1 hexanes/EtOAc) to afford (*E*)-4-phenylbut-3-en-1-ol (859 mg, 5.80 mmol, 94% yield) as colorless oil. Trifluoromethanesulfonic anhydride (269 μL, 1.60 mmol, 1.07 equiv) was added to a solution of pyridine (129 μL, 1.60 mmol, 1.07 equiv) in CH_2Cl_2 (5 mL) at –20 °C and the resulting mixture was allowed to stir for 10 min before a solution of (*E*)-4-phenylbut-3-en-1-ol (222 mg, 1.50 mmol, 1.00 equiv) in CH_2Cl_2 (1 mL) was slowly added. The mixture was allowed to

(74) Spivey, A. C.; Laraia, L.; Bayly, A. R.; Rzepa, H. S.; White, A. J. P. *Org. Lett.* **2010**, *12*, 900–903.

reach 22 °C over 10 min before it was concentrated on a rotary evaporator (water bath temperature ≤20 °C). Unpurified triflate **2.87** was immediately used in the next step.

n-BuLi (1.6 M in hexanes, 4.88 mL, 7.80 mmol) was added to a solution of alkyne **2.86** (1.38 g, 7.50 mmol) in THF (10 mL) at –20 °C. The mixture was allowed to stir at –20 °C for 15 min, then a solution of triflate **2.87** in THF (5 mL) was added. Once the addition was complete, the mixture was allowed to stir at 0 °C for 30 min before $(n\text{-Bu})_4\text{NF}$ (1.0 M in THF, 10 mL, 10.0 mmol) was added. The mixture was allowed to stir at 0 °C for another 5 min, after which the reaction was quenched by the addition of H_2O (20 mL) and diluted with Et_2O (20 mL). The phases were separated and the aqueous phase was back-washed with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was purified by silica gel chromatography (20:1 to 9:1 hexanes/EtOAc) to afford propargylic alcohol **2.88** (213 mg, 1.06 mmol, 71% yield over 2 steps) as colorless solid. R_f = 0.14 (hexane/EtOAc, 9:1). **Mp**: 36–38 °C; **IR (neat):** 3331 (w), 2980 (m), 2928 (m), 1152 (m), 1070 (s), 962 (m), 741 (m); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 (2H, dt, J = 7.6, 1.6 Hz), 7.31 (2H, td, J = 7.6, 1.6 Hz), 7.24–7.19 (1H, m), 6.45 (1H, d, J = 15.9 Hz), 6.25 (1H, dt, J = 15.9, 6.1 Hz), 4.53 (1H, qd, J = 6.6, 2.7 Hz), 2.59 (1H, d, J = 2.7 Hz), 2.47–2.31 (4H, m), 1.45 (3H, d, J = 6.6 Hz); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 137.4, 131.0, 128.6, 128.5, 127.1, 126.0, 83.6, 83.1, 58.3, 32.1, 24.7, 18.9; **HRMS $[M+H-H_2O]^+$** calcd for $C_{14}H_{15}$: 183.11738; found: 183.11671.

2-((3*Z*,7*E*)-8-Phenylocta-3,7-dien-2-yl)isoindoline-1,3-dione (2.89): A mixture of alkyne **2.88** (61 mg, 0.30 mmol), Lindlar's catalyst (12.0 mg) and quinoline (21 μL, 0.18 mmol) in MeOH (2.5 mL) was purged three times with H_2 and then allowed to stir under

atmosphere of H_2 at 22 °C for 1 h. The reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure. Unpurified *Z*-allylic alcohol was used in the next step.

Diisopropyl azodicarboxylate (89 μL, 0.45 mmol) was added to a solution of crude alcohol, phthalimide (53 mg, 0.36 mmol) and triphenylphosphine (118 mg, 0.45 mmol) in THF (4 mL) at rt. The mixture was allowed to stir at 22 °C for 18 h, then concentrated under reduced pressure and triturated with Et_2O. The precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The product was purified by silica gel chromatography on silica gel (20:1 hexane/Et_2O) to afford a 93:7 mixture of **2.89** and over-reduced (*Z*)-2-(8-phenyloct-3-en-2-yl)isoindoline-1,3-dione (74 mg, 69% yield by mass over 2 steps) as colorless oil. R_f = 0.46 (hexane/EtOAc, 9:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 (2H, dd, *J* = 5.5, 3.1 Hz), 7.66 (2H, dd, *J* = 5.5, 3.1 Hz), 7.31–7.19 (4H, m), 7.15 (1H, tt, *J* = 7.0, 1.6 Hz), 6.35 (1H, d, *J* = 15.9 Hz), 6.16 (1H, dt, *J* = 15.9, 6.5 Hz), 6.00 (1H, ddt, *J* = 10.7, 9.1, 1.5 Hz), 5.53 (1H, dtd, *J* = 10.7, 7.2, 1.0 Hz), 5.25 (1H, dqd, *J* = 9.1, 7.0, 1.0 Hz), 2.37–2.29 (2H, m), 2.29–2.23 (2H, m), 1.52 (3H, d, *J* = 7.0 Hz); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.0, 137.6, 133.9, 132.1, 131.9, 130.7, 129.6, 129.2, 128.5, 126.9, 126.0, 123.1, 43.7, 32.8, 27.4, 19.6; **HRMS $[M+H]^+$** calcd for $C_{22}H_{22}NO_2$: 332.16505; found: 332.16342.

2.6.11. Synthesis of Cinnarizine Derivatives

General procedure for Pd-catalyzed Suzuki cross-coupling: In a N_2-filled glove box, an oven-dried vial with magnetic stir bar was charged with **2.95** (1.00 equiv), arylboronic acid or pinacol ester (1.50 equiv) and CsF (1.50–1.80 equiv). $Pd(OAc)_2$/SPhos (1:2 solution in *i*-PrOH, 0.01 M in Pd) was subsequently added. The vial was sealed and

removed from the glove box. The mixture was allowed to stir at 85 °C for 12 h, after which the reaction was quenched by passing the solution through a short plug of silica gel and washed with 5% MeOH/CH_2Cl_2 or Et_2O (3 x 2 mL). The filtrate was concentrated *in vacuo* to afford brown oil, which was purified by silica gel chromatography to afford the products in 70–86% yield.

(*E*)-4-(3-(4-Benzhydrylpiperazin-1-yl)prop-1-en-1-yl)-3,5-dimethylisoxazole (2.96): Following the general procedure, an oven-dried vial with magnetic stir bar was charged with **2.95** (16.3 mg, 0.0499 mmol, 1.00 equiv), 3,5-dimethylisoxazole-4-boronic acid pinacol ester (16.47 mg, 0.0749 mmol, 1.50 equiv) and CsF (11.4 mg, 0.0750 mmol, 1.50 equiv). $Pd(OAc)_2$/SPhos (1:2 solution in *i*-PrOH, 0.01 M in Pd, 0.38 mL, 3.8 μmol, 7.5 mol %) was subsequently added. The vial was sealed and removed from the glove box. The mixture was allowed to stir at 85 °C for 12 h, after which the reaction was quenched by passing through a short plug of silica gel and washed with 5% MeOH/CH_2Cl_2 (3x2 mL). The filtrate was concentrated *in vacuo* to afford brown oil, which was purified by silica gel chromatography (100% CH_2Cl_2 to 2% MeOH/CH_2Cl_2) to afford **2.96** (13.9 mg, 0.0359 mmol, 72% yield) as yellow oil. **IR (in CH_2Cl_2)**: 2931 (w), 2806 (m), 2763 (w), 1671 (w), 1598 (w), 1491 (w), 1450 (m), 1426 (w), 1136 (m), 1004 (m), 966 (m), 909 (m), 730 (s), 705 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.41 (4H, d, J = 8.3 Hz), 7.30–7.22 (4H, m), 7.17 (2H, t, J = 7.3 Hz), 6.18 (1H, d, J = 16.3 Hz), 5.92 (1H, dt, J = 16.4, 6.8 Hz), 4.24 (1H, s), 3.14 (2H, d, J = 6.8 Hz), 2.77–2.32 (8H, m), 2.38 (3H, s), 2.28 (3H, s); **^{13}C NMR (151 MHz, $CDCl_3$)**: δ 165.5, 158.4, 142.8, 128.6, 128.0, 127.1, 120.8, 112.5, 76.3, 61.8, 53.6, 51.9, 11.8, 11.6 ; **HRMS $[M+H]^+$** calcd for $C_{25}H_{30}N_3O$: 388.2389, found: 388.2392.

(*E*)-1-Benzhydryl-4-(3-(2,6-difluoropyridin-3-yl)allyl)piperazine (2.97): Following the general procedure, an oven-dried vial with magnetic stir bar was charged with **2.95** (14.7 mg, 0.0450 mmol, 1.00 equiv), 2,6-difluoro-3-pyridineboronic acid (10.7 mg, 0.0675 mmol, 1.50 equiv) and CsF (12.3 mg, 0.0810 mmol, 1.80 equiv). $Pd(OAc)_2$/SPhos (1:2 solution in *i*-PrOH, 0.01 M in Pd, 0.45 mL, 4.50 μmol, 10 mol %) was subsequently added. The vial was sealed and removed from the glove box. The mixture was allowed to stir at 85 °C for 12 h, after which the reaction was quenched by passing through a short plug of silica gel and washed with Et_2O (3x2 mL). The filtrate was concentrated *in vacuo* to afford yellow oil, which was purified by silica gel chromatography (100% CH_2Cl_2 to 1% MeOH/CH_2Cl_2) to afford **2.97** (12.7 mg, 0.0313 mmol, 70% yield) as yellow oil. **IR (in CH_2Cl_2)**: 2924 (m), 2852 (w), 2765 (w), 1602 (m), 1586 (m), 1469 (s), 1452 (m), 1411 (m), 1302 (m), 1246 (w), 1136 (w), 993 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.91 (1H, dd, J = 17.0, 8.1 Hz), 7.42–7.39 (4H, m), 7.28–7.23 (4H, m), 7.19–7.16 (2H, m), 6.78 (1H, dd, J = 8.1, 2.8 Hz), 6.55 (1H, d, J = 16.0 Hz), 6.39–6.28 (1H, m), 4.24 (1H, s), 3.19 (2H, d, J = 5.8 Hz), 2.56–2.38 (8H, m); **^{13}C NMR (101 MHz, C_6D_6)**: δ 143.3, 141.2 (dd, $J_{C\text{-}F}$ = 7.4, 4.5 Hz), 132.0, 131.6, 130.2, 128.8, 127.9, 127.2, 122.4, 116.7 (d, $J_{C\text{-}F}$ = 18.9 Hz), 106.2 (dd, $J_{C\text{-}F}$ = 35.2, 5.5 Hz), 76.6, 60.7, 53.6, 52.3; **HRMS $[M+H]^+$** calcd for $C_{25}H_{26}F_2N_3$: 406.2095, found: 406.2114.

(*E*)-5-(3-(4-Benzhydrylpiperazin-1-yl)prop-1-en-1-yl)-1-methyl-1*H*-indole (2.98): Following the general procedure, an oven-dried vial with magnetic stir bar was charged with **2.95** (16.3 mg, 0.0499 mmol, 1.00 equiv), 1-methylindole-5-boronic acid (13.1 mg, 0.0749 mmol, 1.50 equiv) and CsF (11.4 mg, 0.0750 mmol, 1.50 equiv). A mixture of $Pd(OAc)_2$/SPhos (1:2 solution in *i*-PrOH, 0.01 M in Pd, 0.25 mL, 2.50 μmol, 5.0 mol %)

was subsequently added. The vial was sealed and removed from the glove box. The mixture was allowed to stir at 85 °C for 12 h, after which the reaction was quenched by passing through a short plug of silica gel and washed with 5% MeOH/CH_2Cl_2 (3 x 2 mL). The filtrate was concentrated in vacuo to afford brown oil, which was purified by silica gel chromatography (100% CH_2Cl_2 to 2% MeOH/CH_2Cl_2) to afford **2.98** (18.2 mg, 0.0432 mmol, 86% yield) as yellow oil. **IR (in CH_2Cl_2)**: 3024 (w), 2806 (m), 2764 (w), 1597 (w), 1489 (m), 1450 (m), 1332 (m), 1244 (m), 1135 (m), 1005 (m), 966 (m), 907 (m), 727 (s), 704 (s); **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.56 (1H, d, J = 1.5 Hz), 7.41 (4H, dt, J = 8.0, 1.6 Hz), 7.31 (1H, dd, J = 8.6, 1.6 Hz), 7.25 (5H, q, J = 7.6 Hz), 7.16 (2H, ddt, J = 7.8, 6.8, 1.3 Hz), 7.01 (1H, d, J = 3.1 Hz), 6.62 (1H, d, J = 15.7 Hz), 6.44 (1H, dd, J = 3.1, 0.8 Hz), 6.21 (1H, dt, J = 15.7, 6.9 Hz), 4.24 (1H, s), 3.77 (3H, s), 3.20 (2H, d, J = 6.4 Hz), 2.77 – 2.25 (8H, m); **^{13}C NMR (151 MHz, $CDCl_3$)**: δ 142.9, 136.6, 129.4, 128.8, 128.6, 128.1, 127.0, 109.4, 101.4, 76.3, 61.4, 53.5, 51.9, 33.0; **HRMS $[M+H]^+$** calcd for $C_{29}H_{32}N_3$: 422.2596, found: 422.2599.

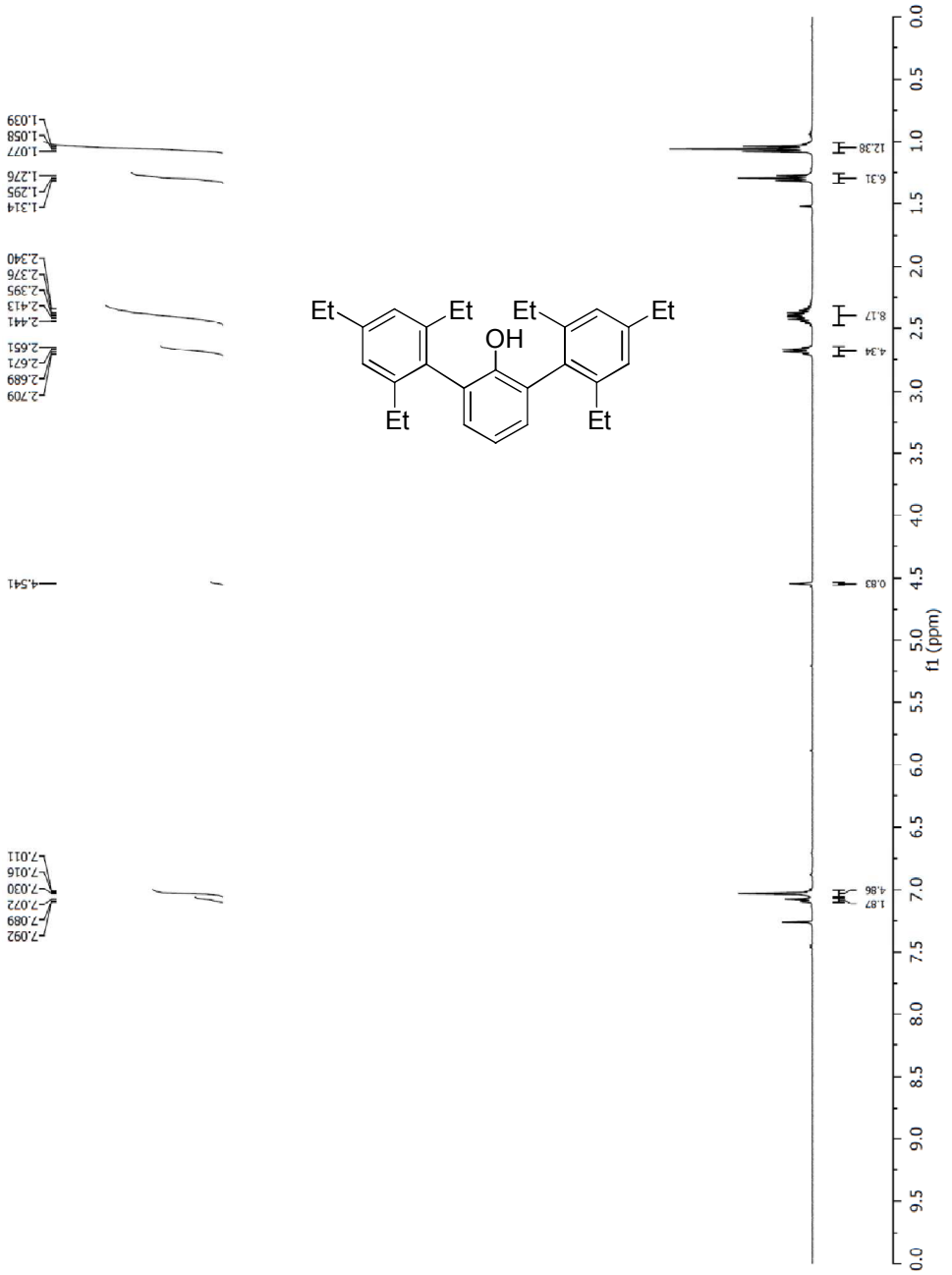
2.6.12. Representative Example of E-Selective CM with Air- and Moisture-Resistant Paraffin Tablets

Representative procedure: An oven-dried 5-mL Schlenk tube was charged with a paraffin tablet (4.4 wt% in **Mo-4f**, 126.8 mg, 0.573 mmol, 5 mol %) and cinnarizine (42.6 mg, 0.116 mmol, 1.00 equiv). The tube was sealed with a rubber septum, then evacuated and back-filled with N_2 three times to remove oxygen. *E*-1,2-Dichloroethene (90 mL, 1.17 mmol, 10.0 equiv) and 0.2 mL toluene were added via syringe and the resulting mixture was allowed to stir at 50 °C for 4 h. At this time, the mixture was diluted with CH_2Cl_2 and the resulting residue (yellow oil) was purified by silica gel chromatography

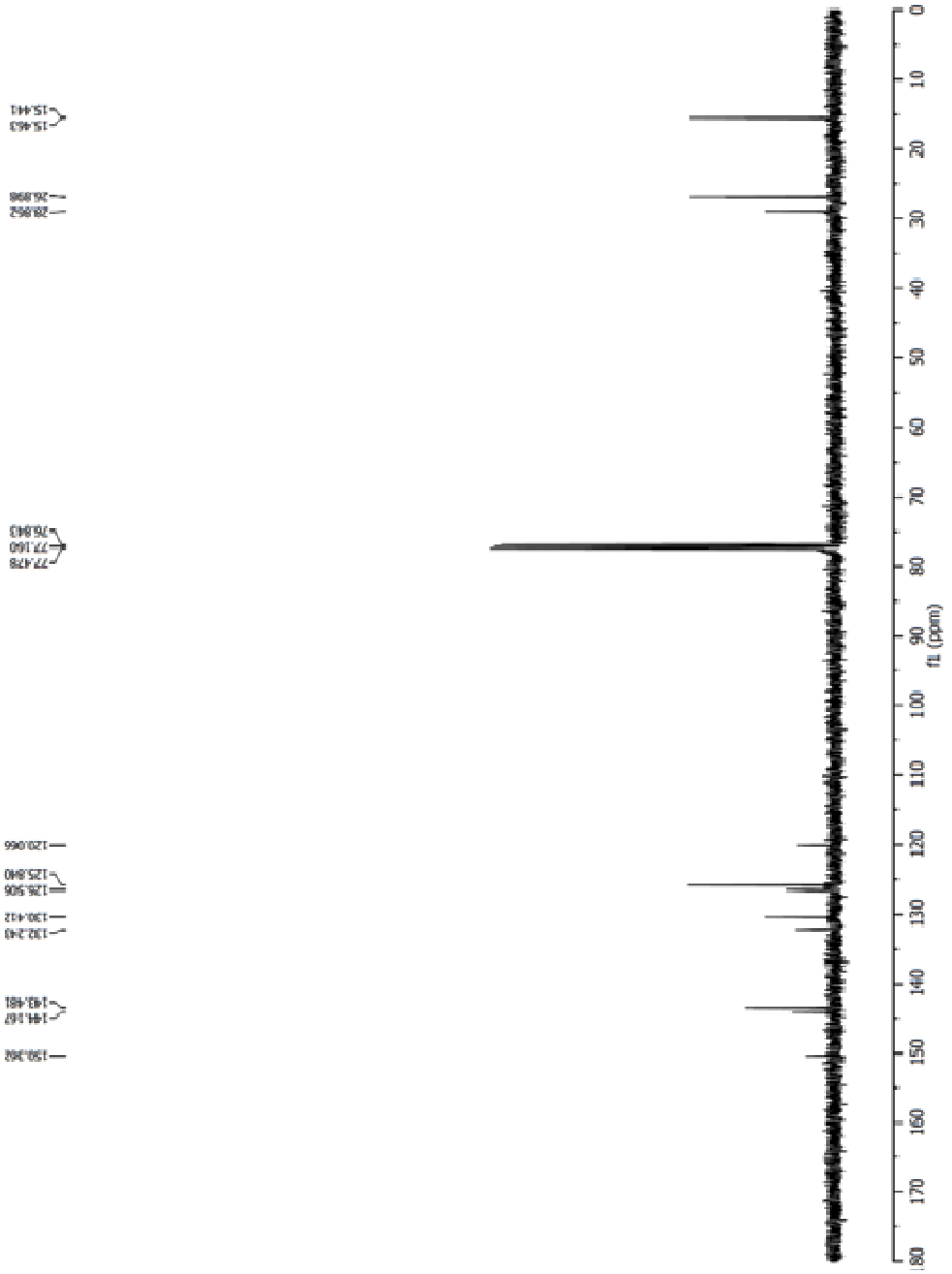
(100% CH_2Cl_2 to 1% MeOH/CH_2Cl_2) to afford **2.95** (36.0 mg, 0.110 mmol, 95% yield) in >98:2 *E*:*Z* ratio as yellow oil.

2.6.13. NMR Spectra

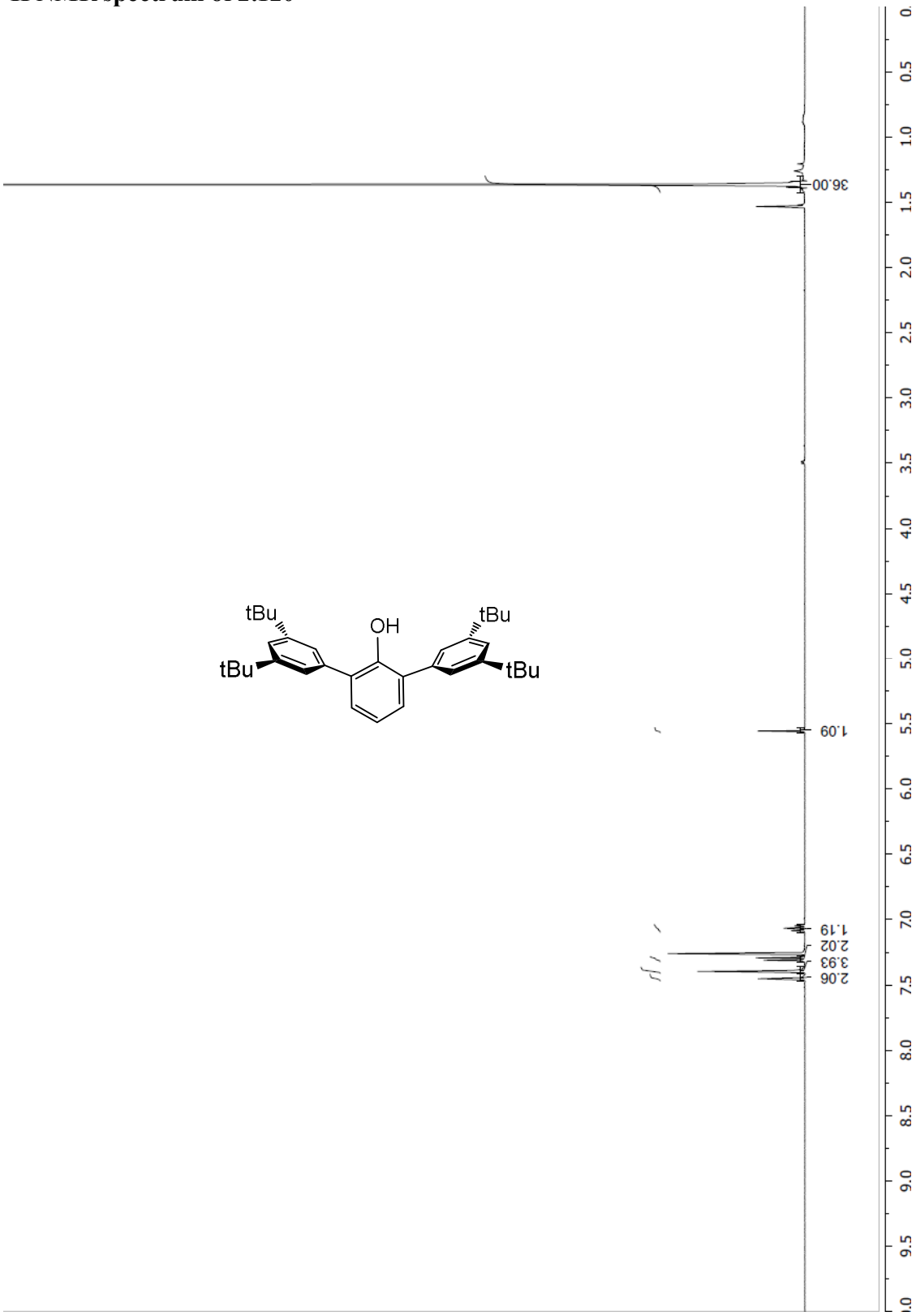
^{1}H NMR spectrum of 2.117



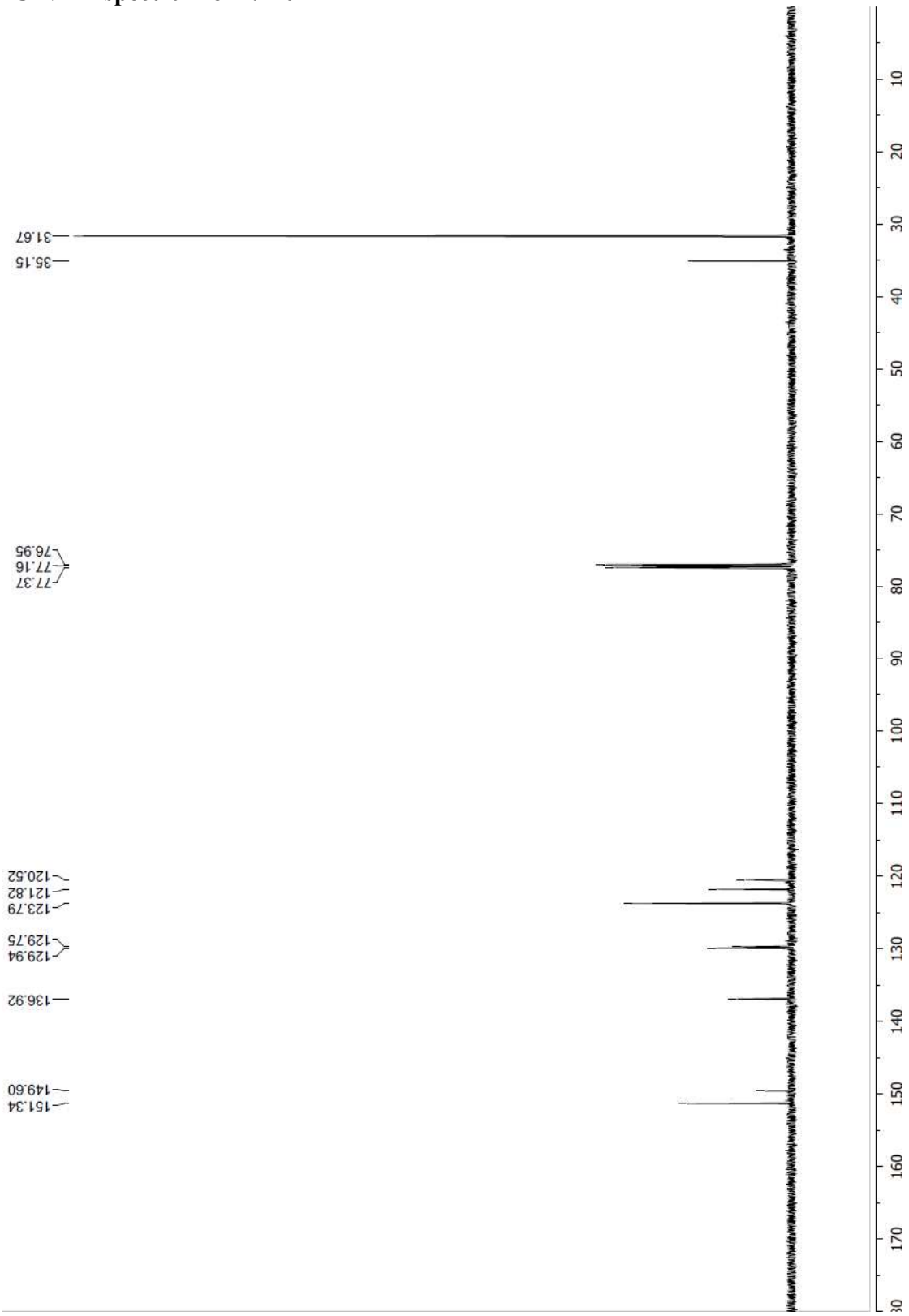
^{13}C NMR spectrum of 2.117



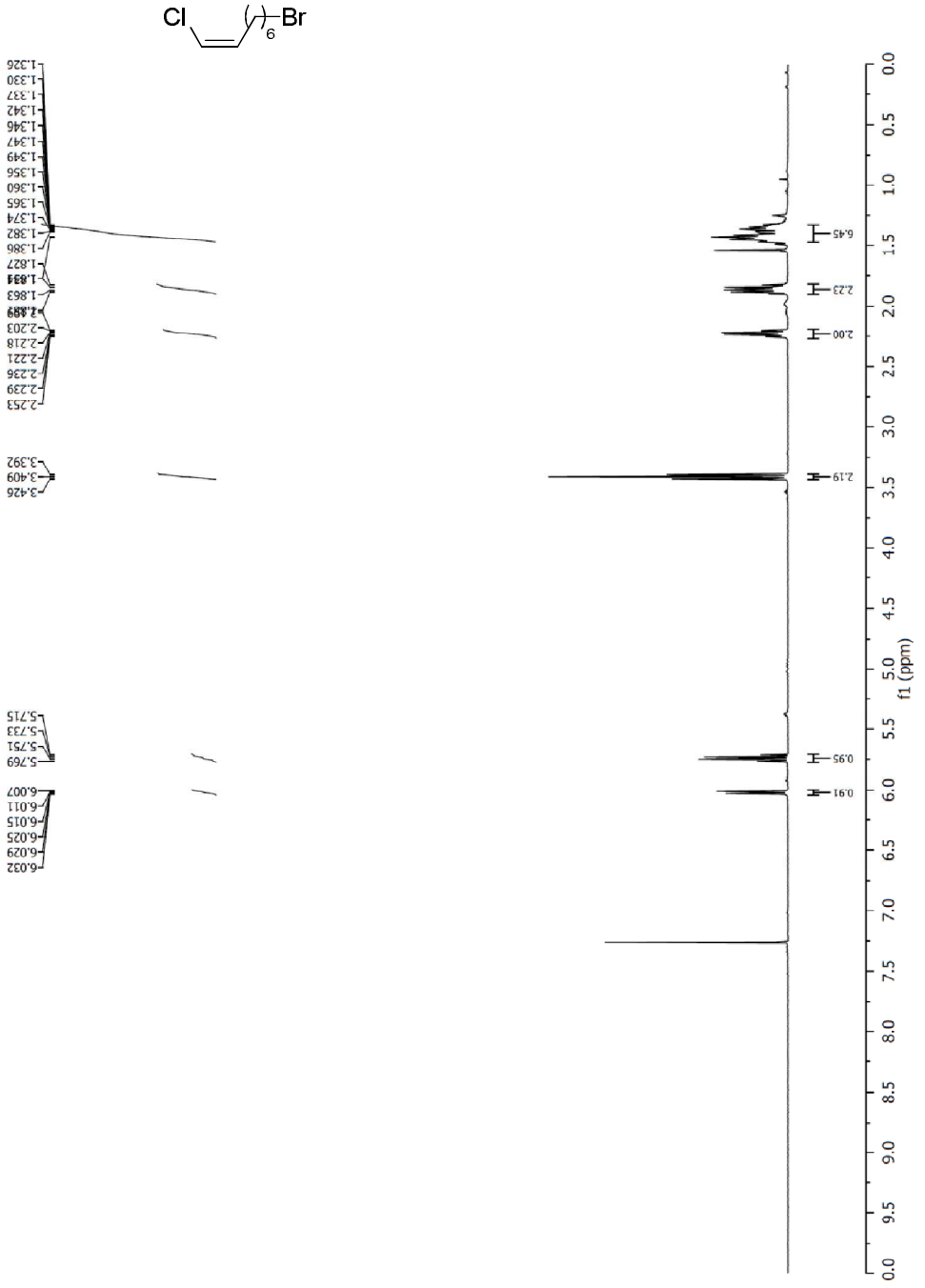
^{1}H NMR spectrum of 2.120



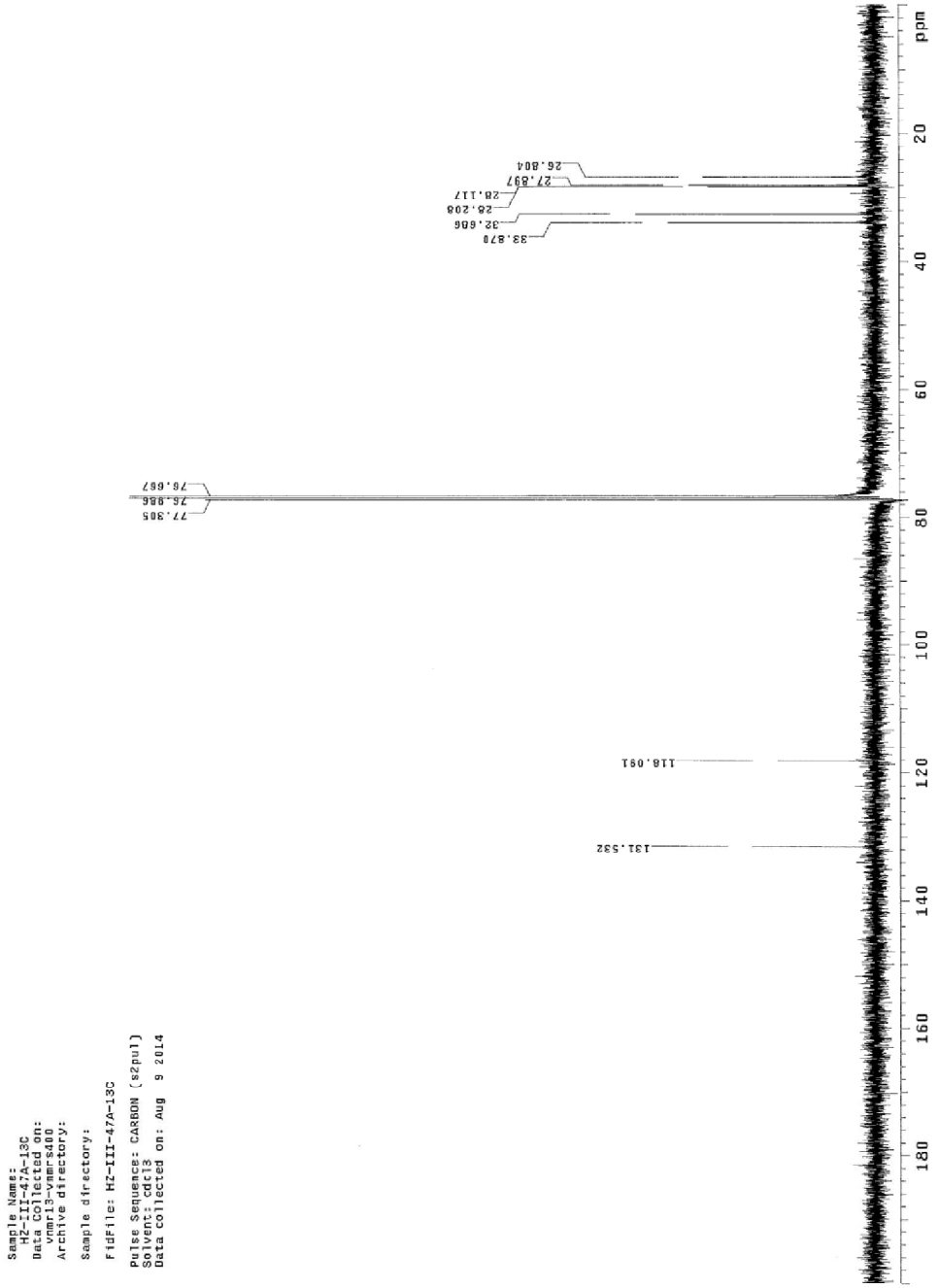
^{13}C NMR spectrum of 2.120



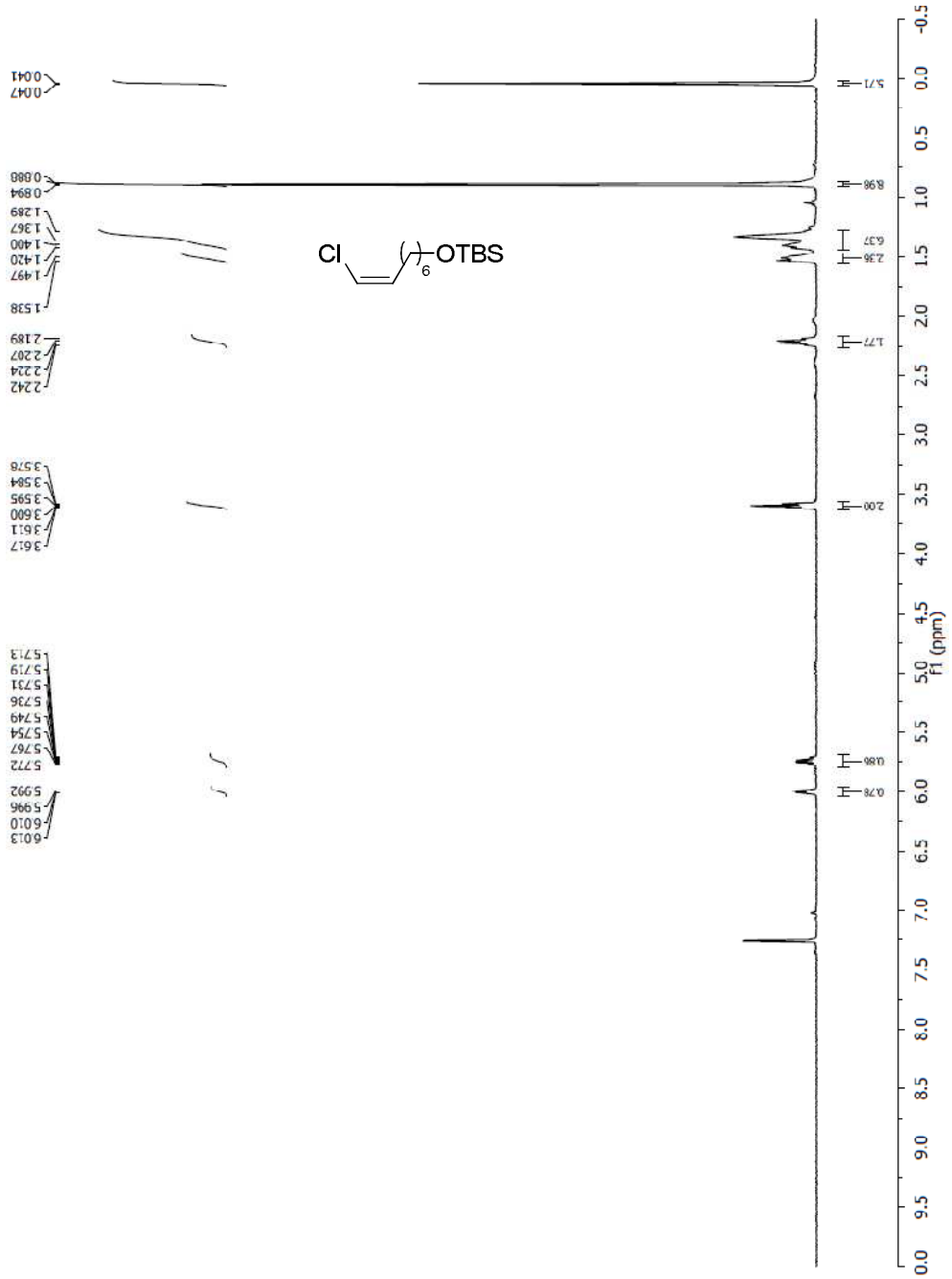
^{1}H NMR spectrum of 2.9



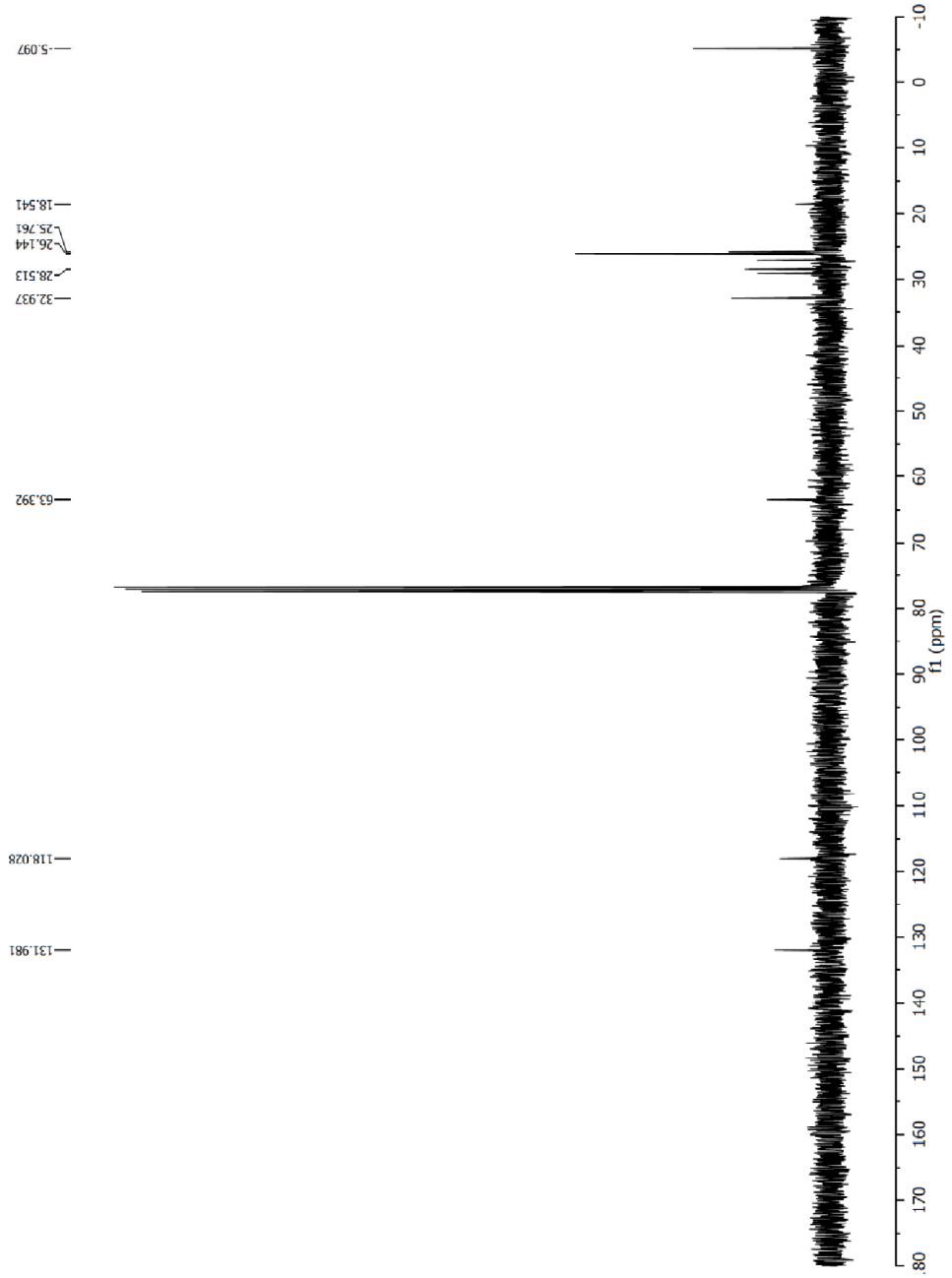
^{13}C NMR spectrum of 2.9



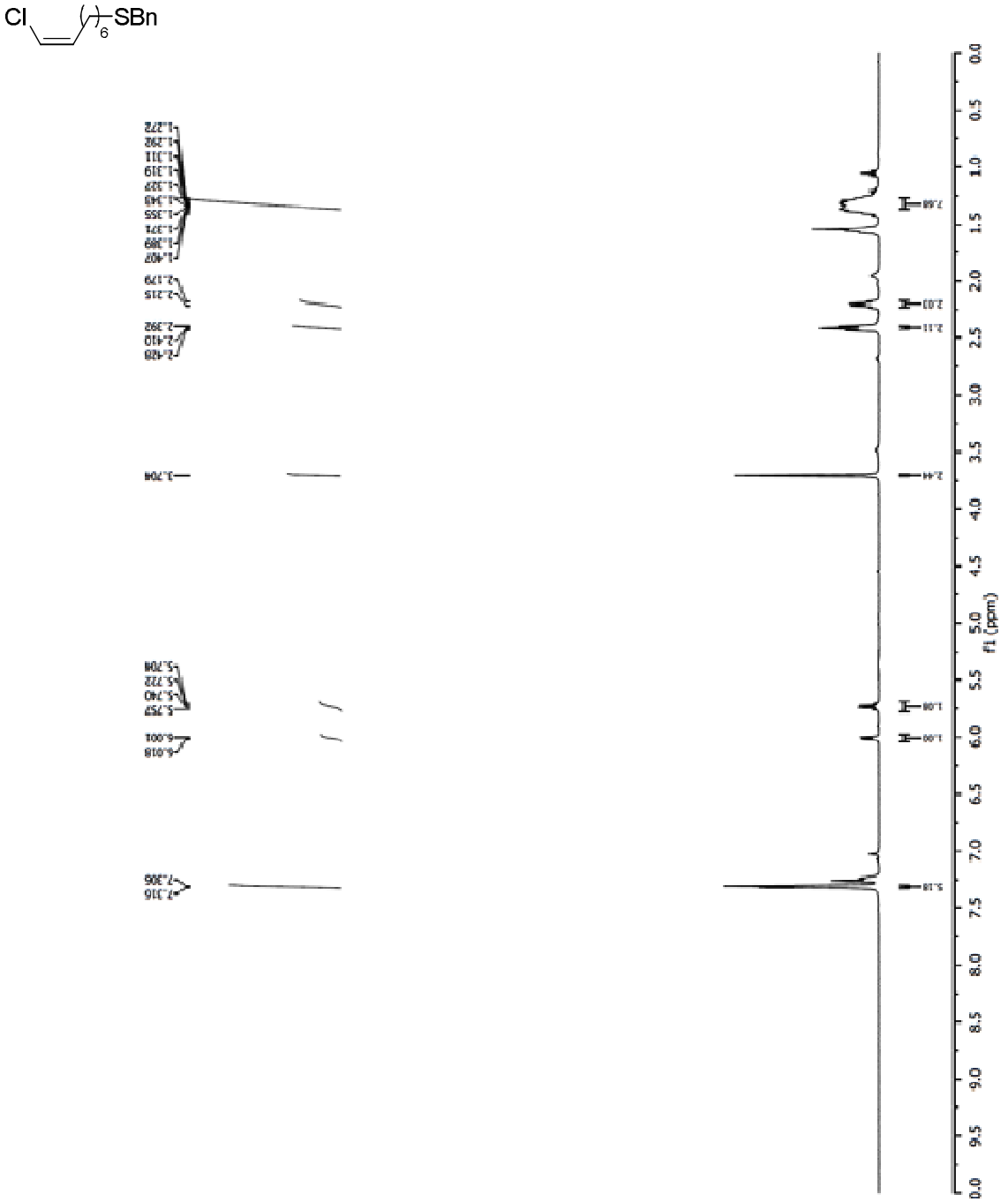
^{1}H NMR spectrum of 2.10



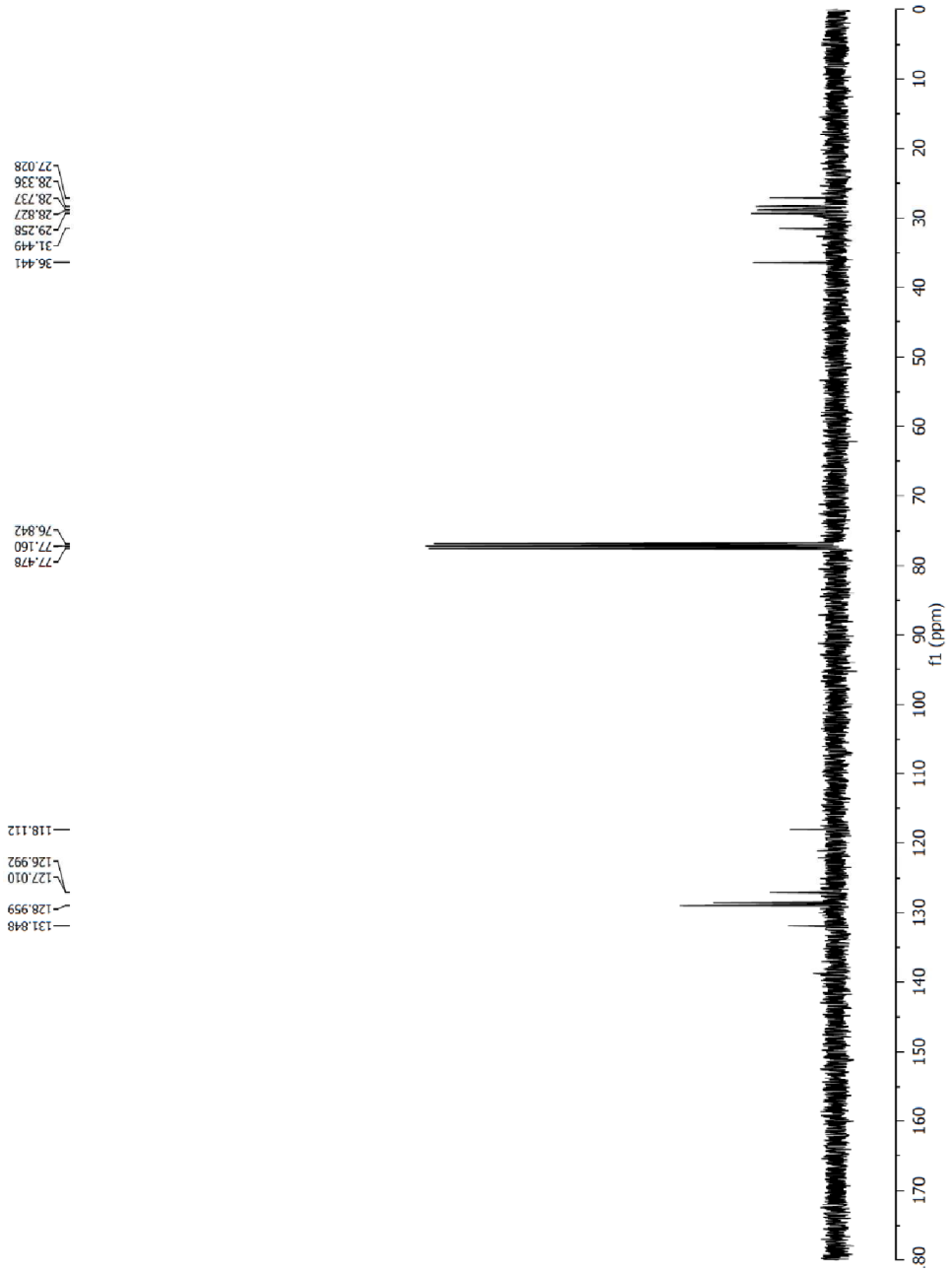
^{13}C NMR spectrum of 2.10



^{1}H NMR spectrum of 2.11



^{13}C NMR spectrum of 2.11



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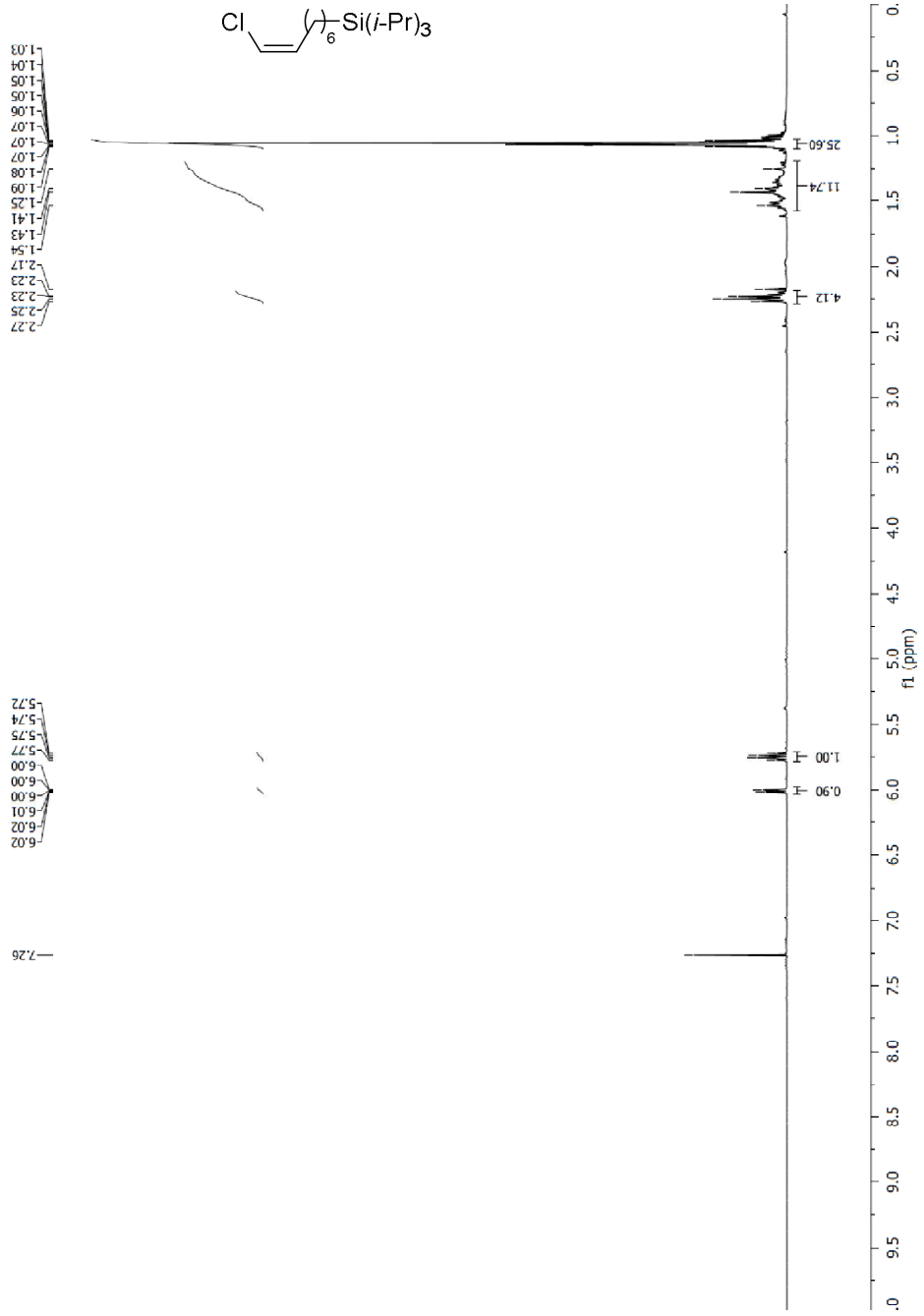
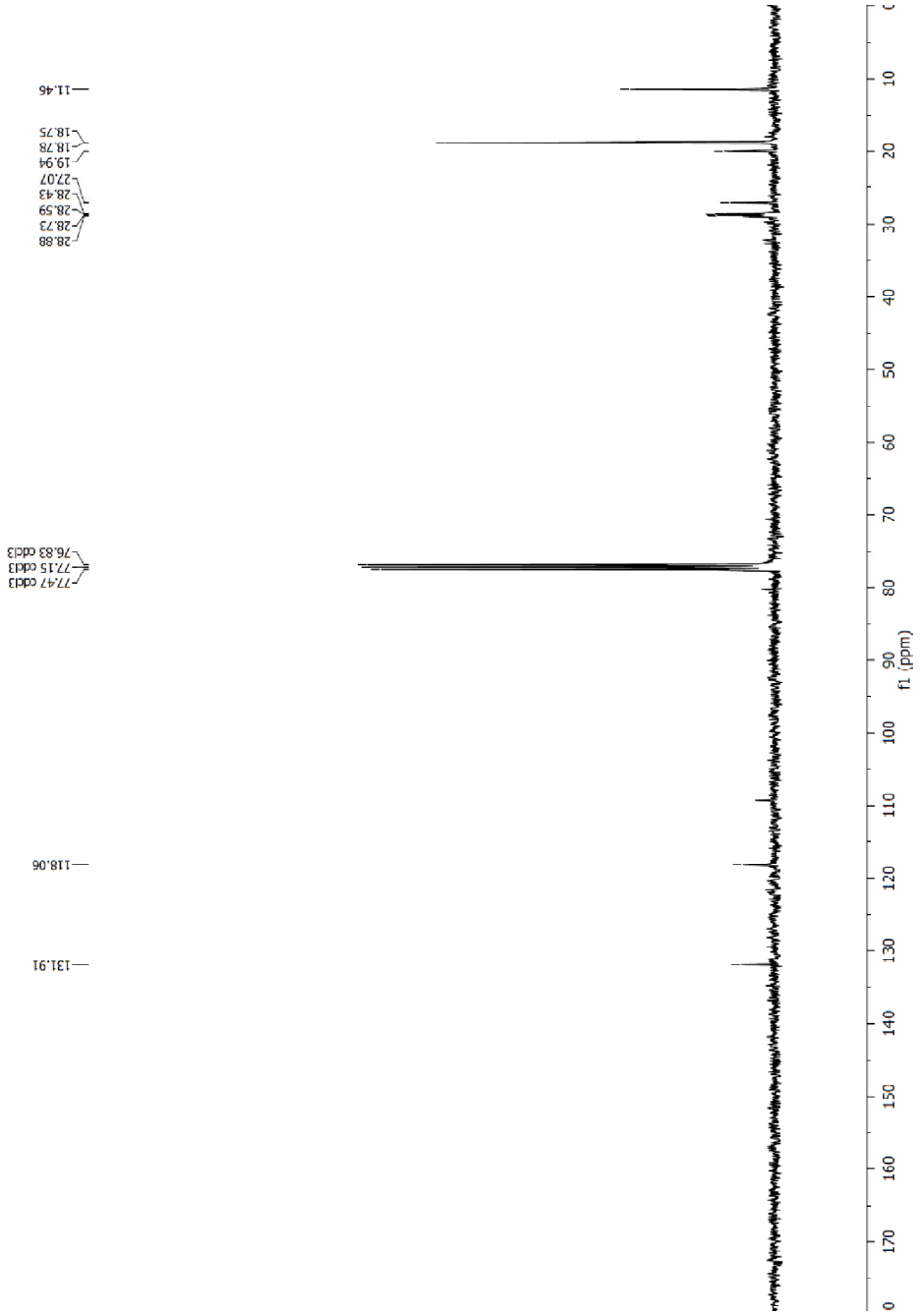
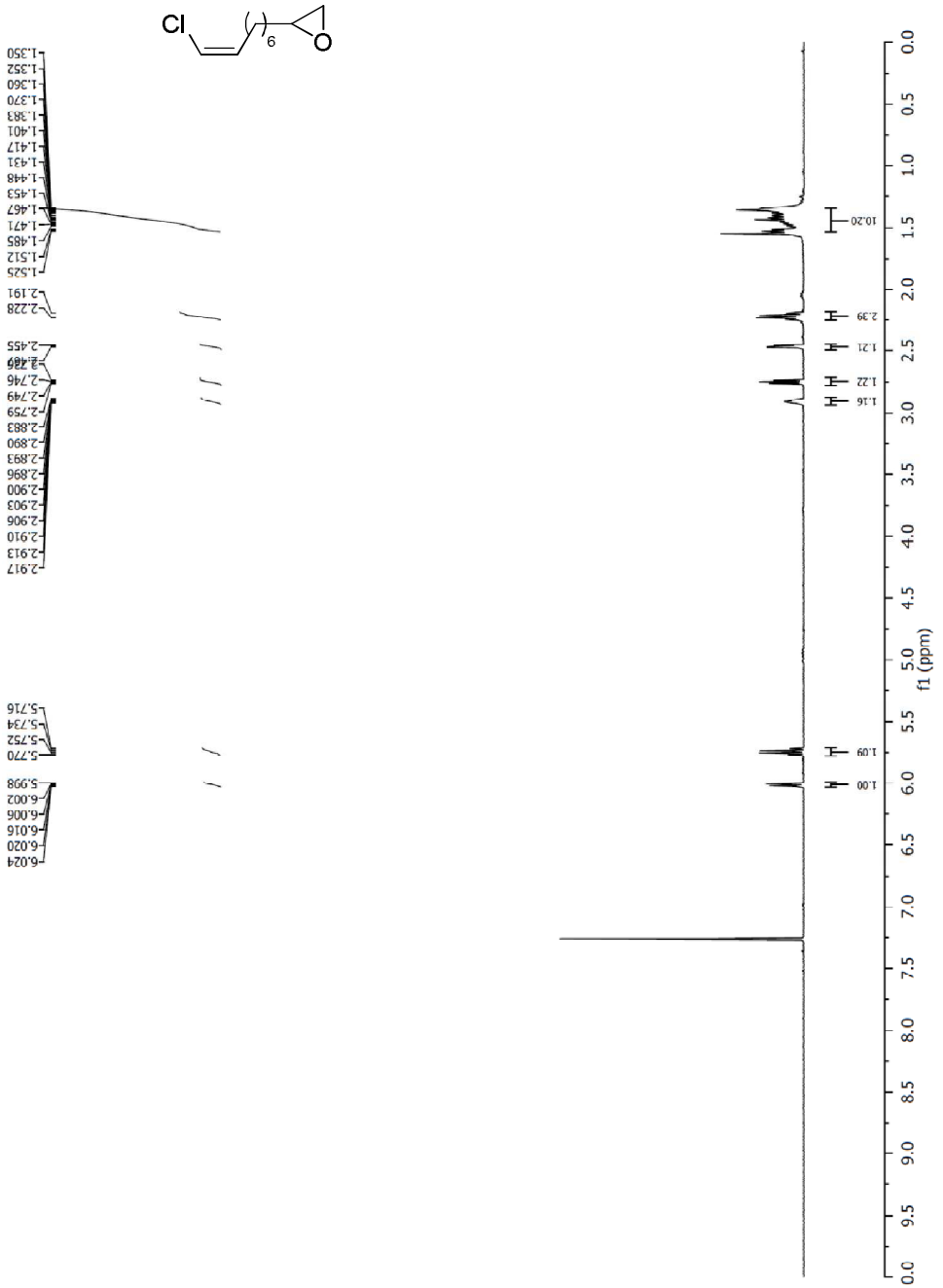


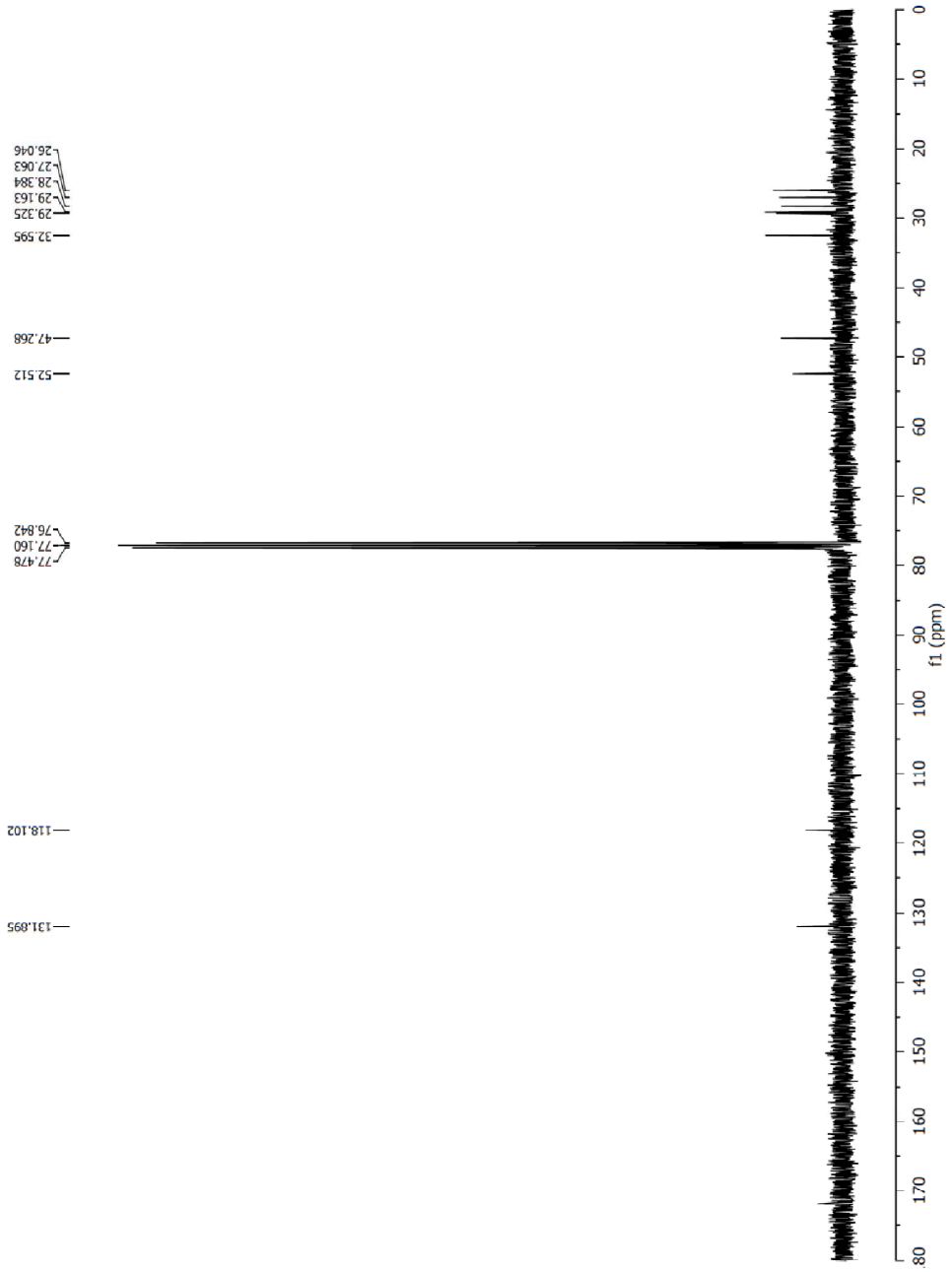
^{13}C NMR spectrum of 2.12



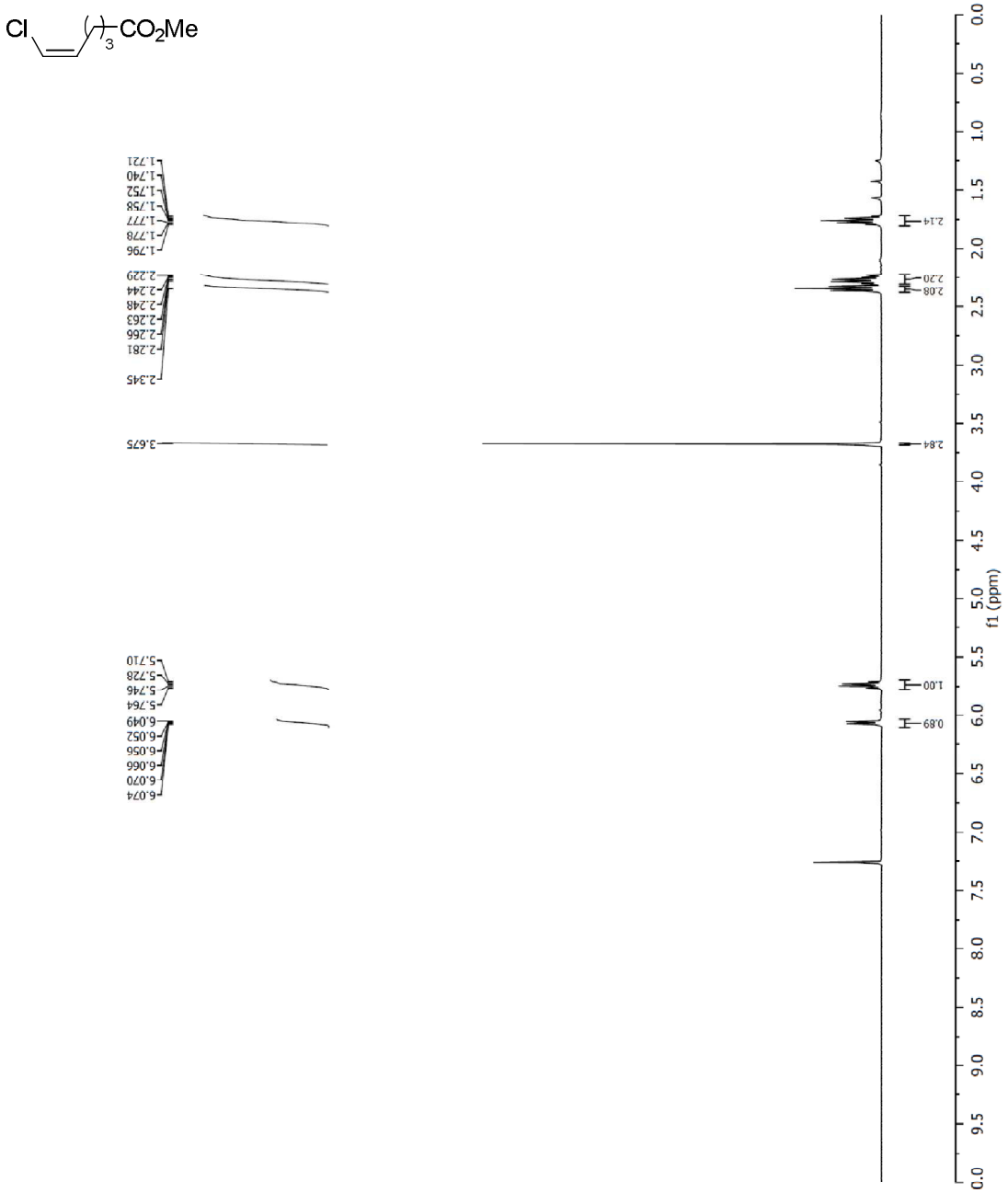
^{1}H NMR spectrum of 2.13



^{13}C NMR spectrum of 2.13



^{1}H NMR spectrum of 2.14



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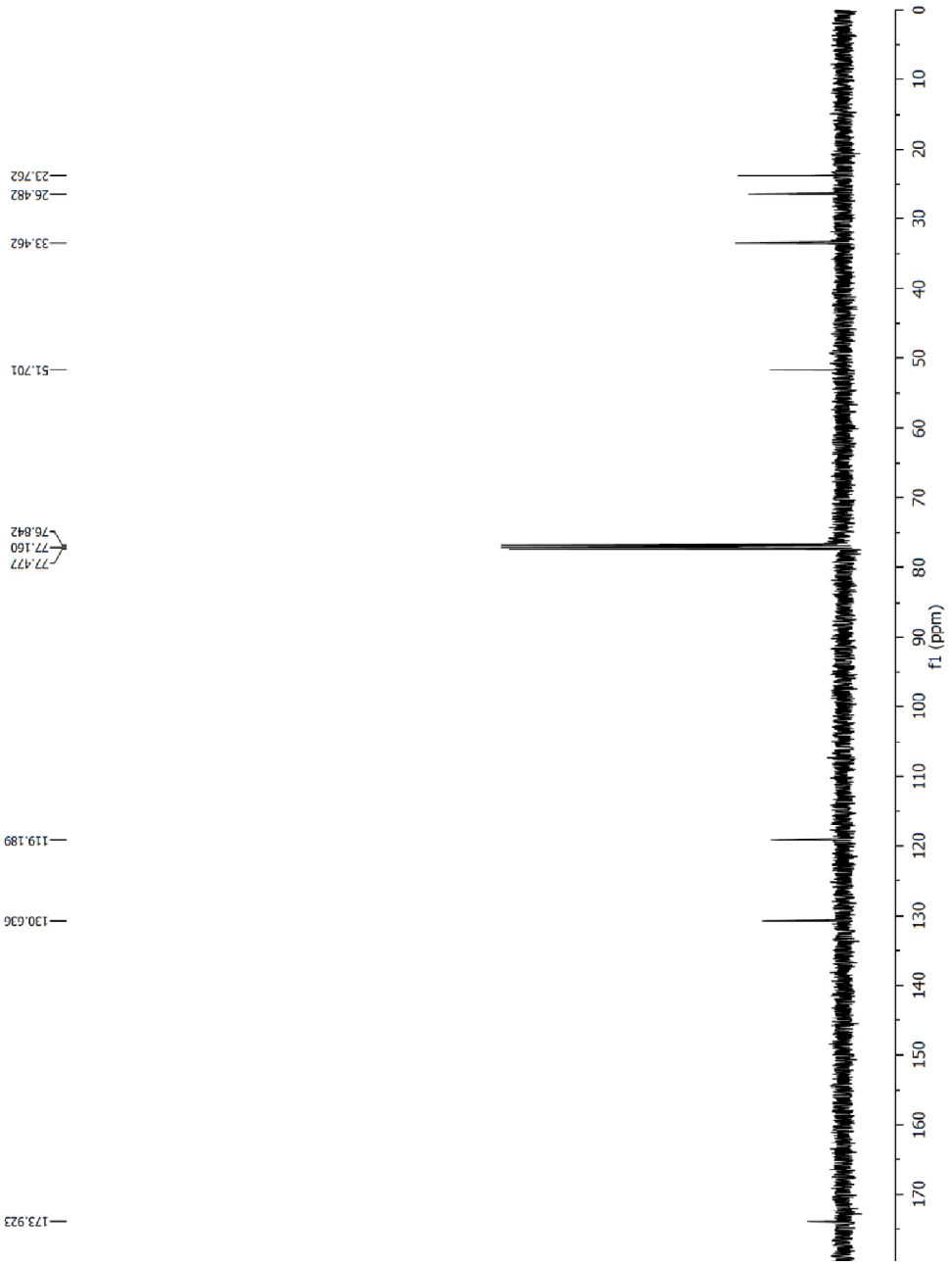
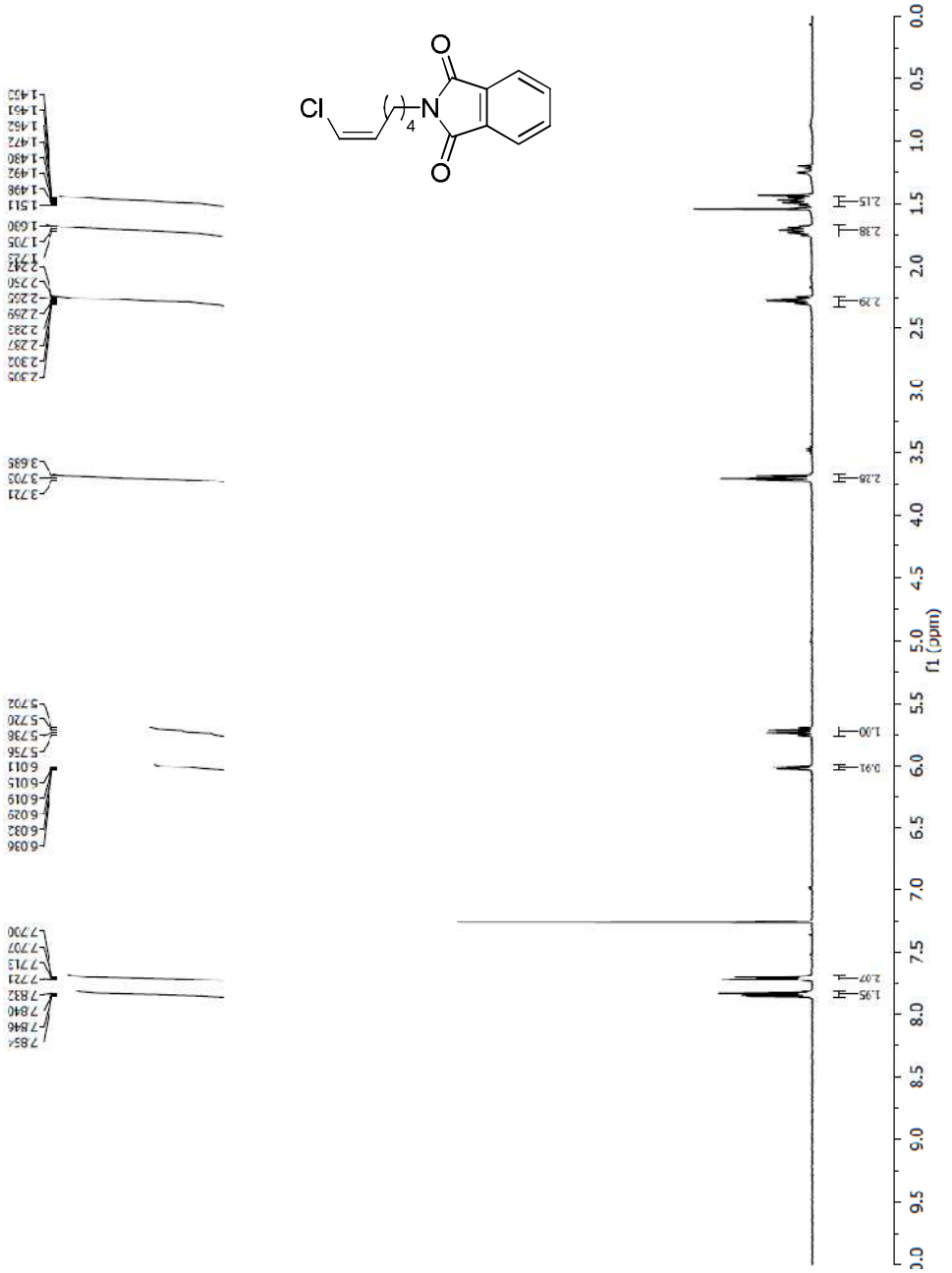
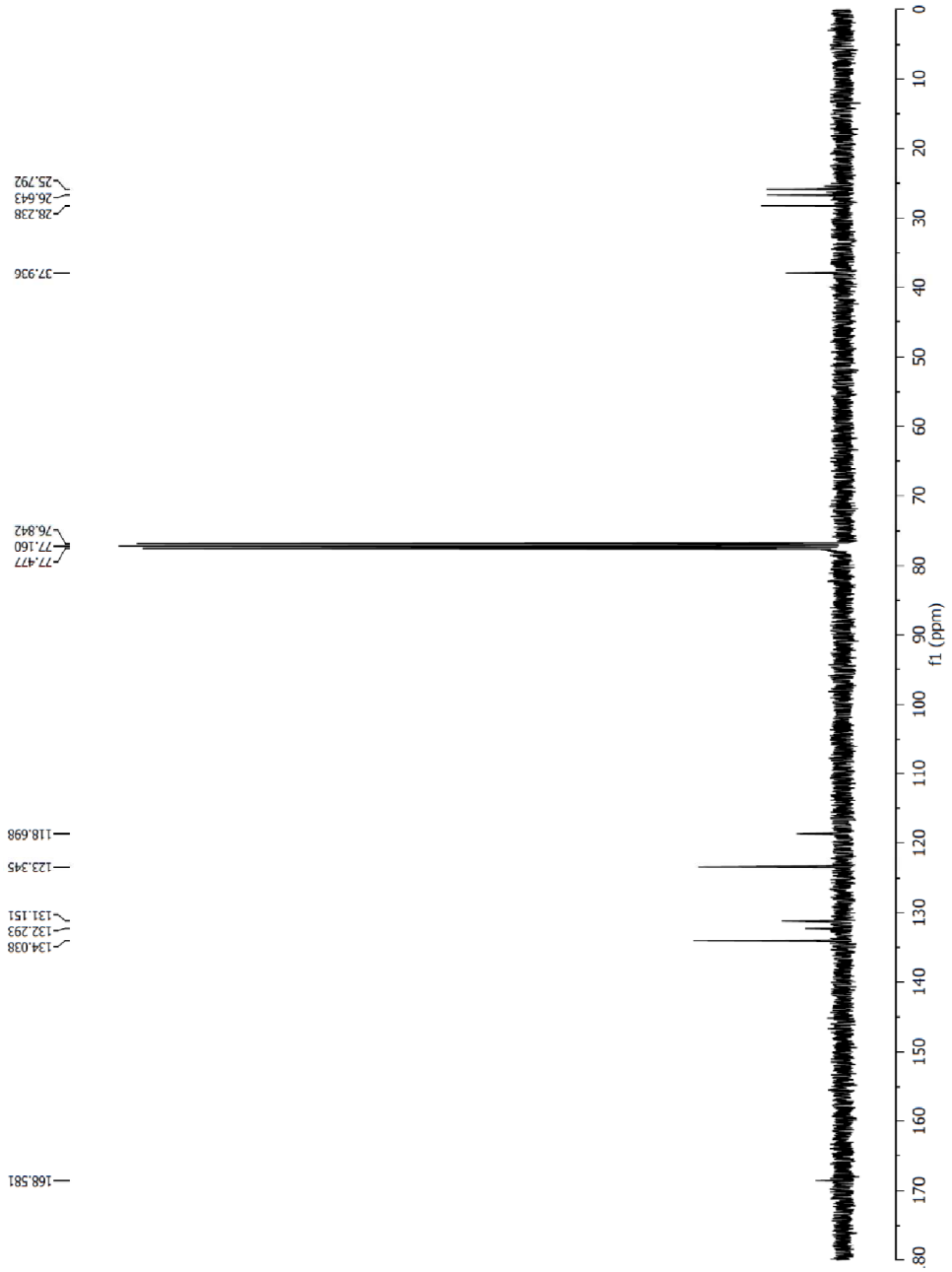


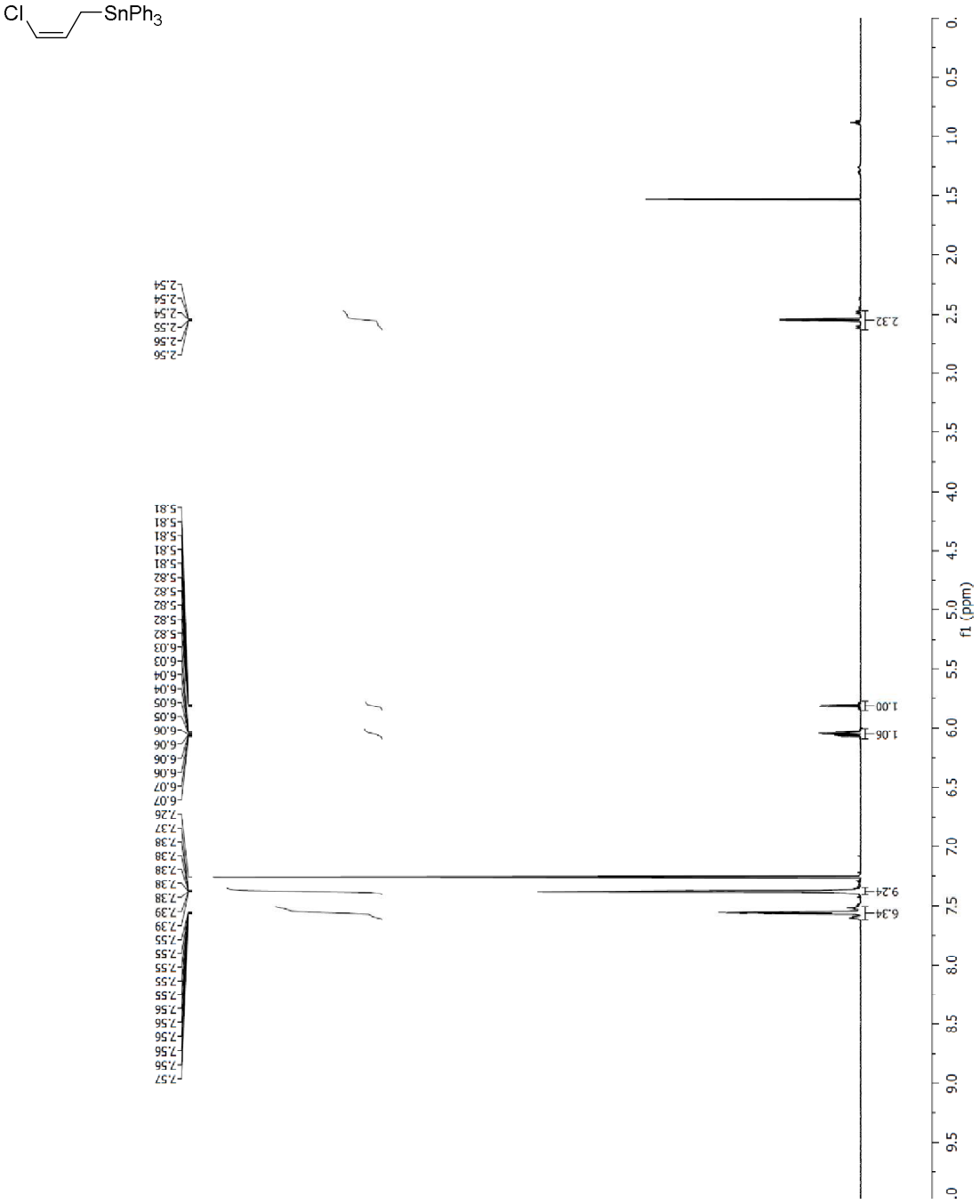
^{1}H NMR spectrum of 2.15



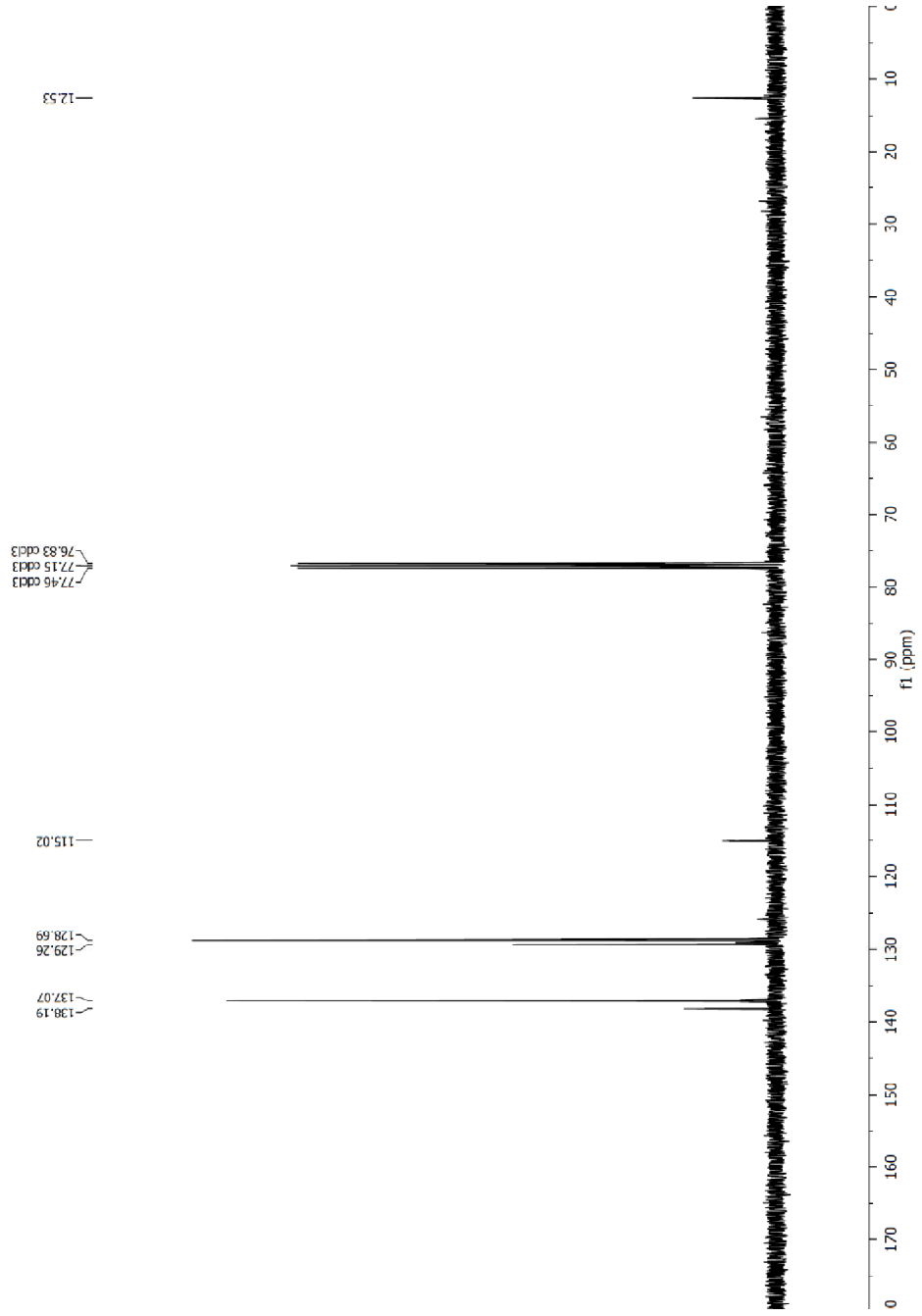
^{13}C NMR spectrum of 2.15



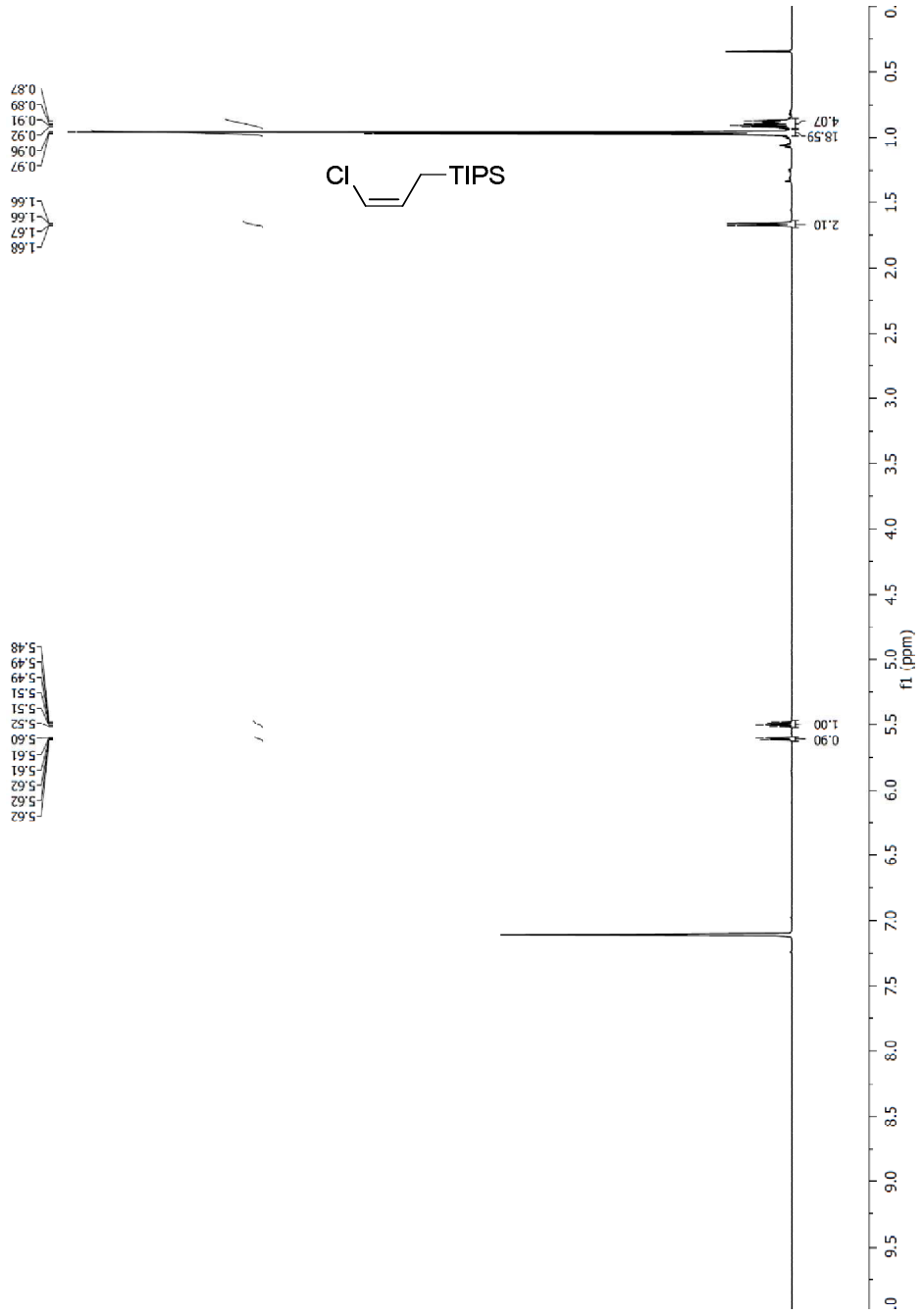
^{1}H NMR spectrum of 2.16



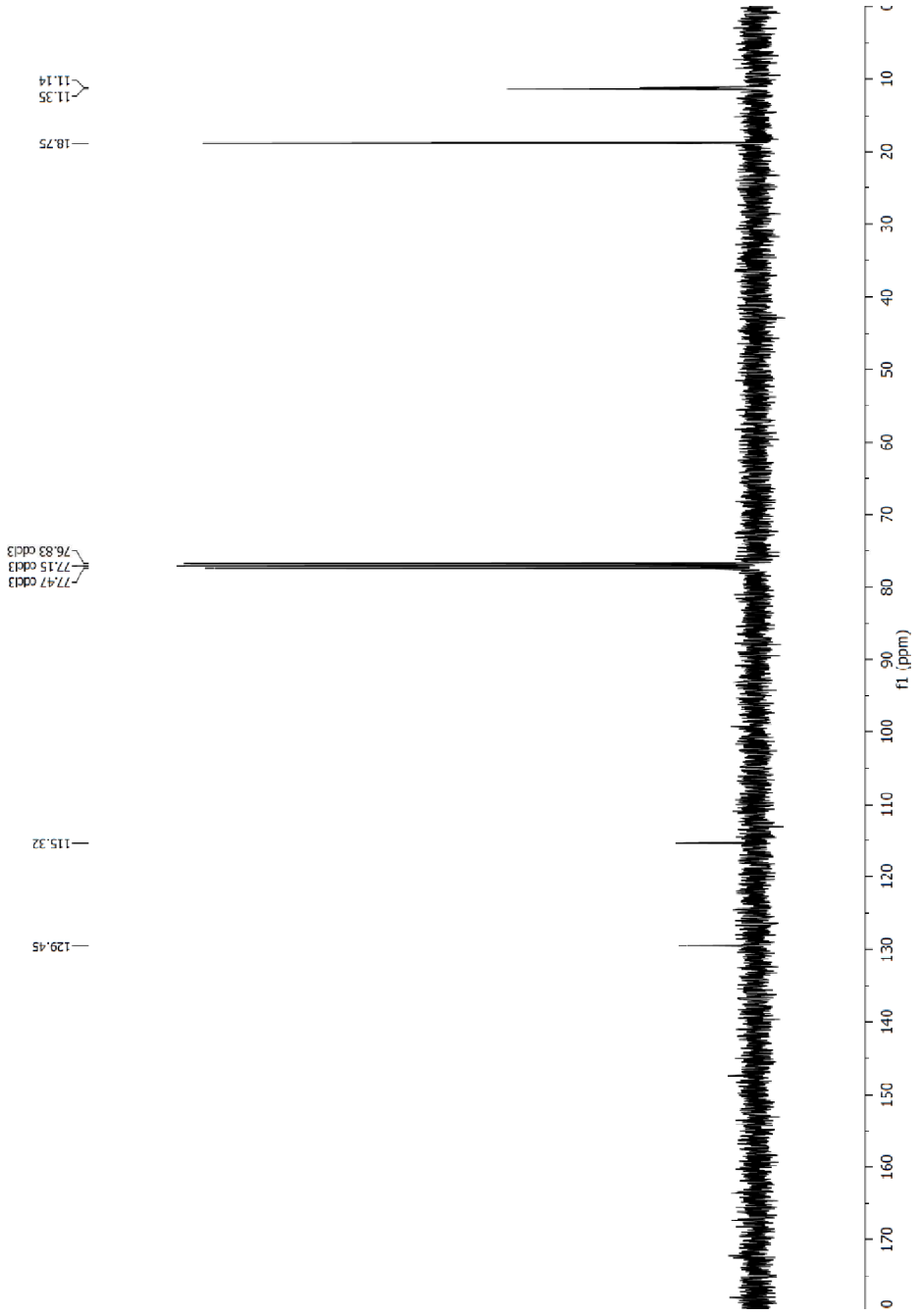
^{13}C NMR spectrum of 2.16



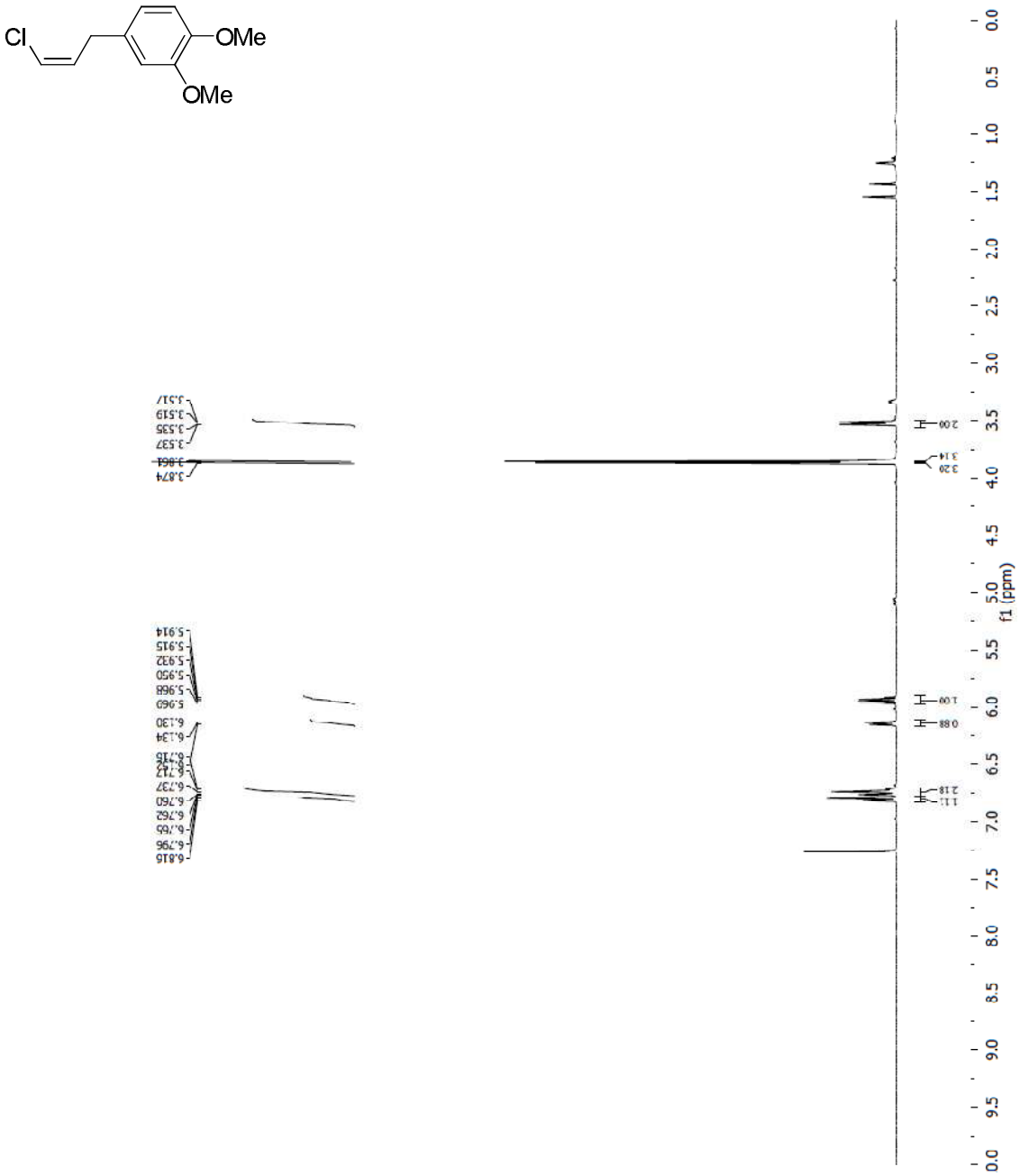
^{1}H NMR spectrum of 2.17



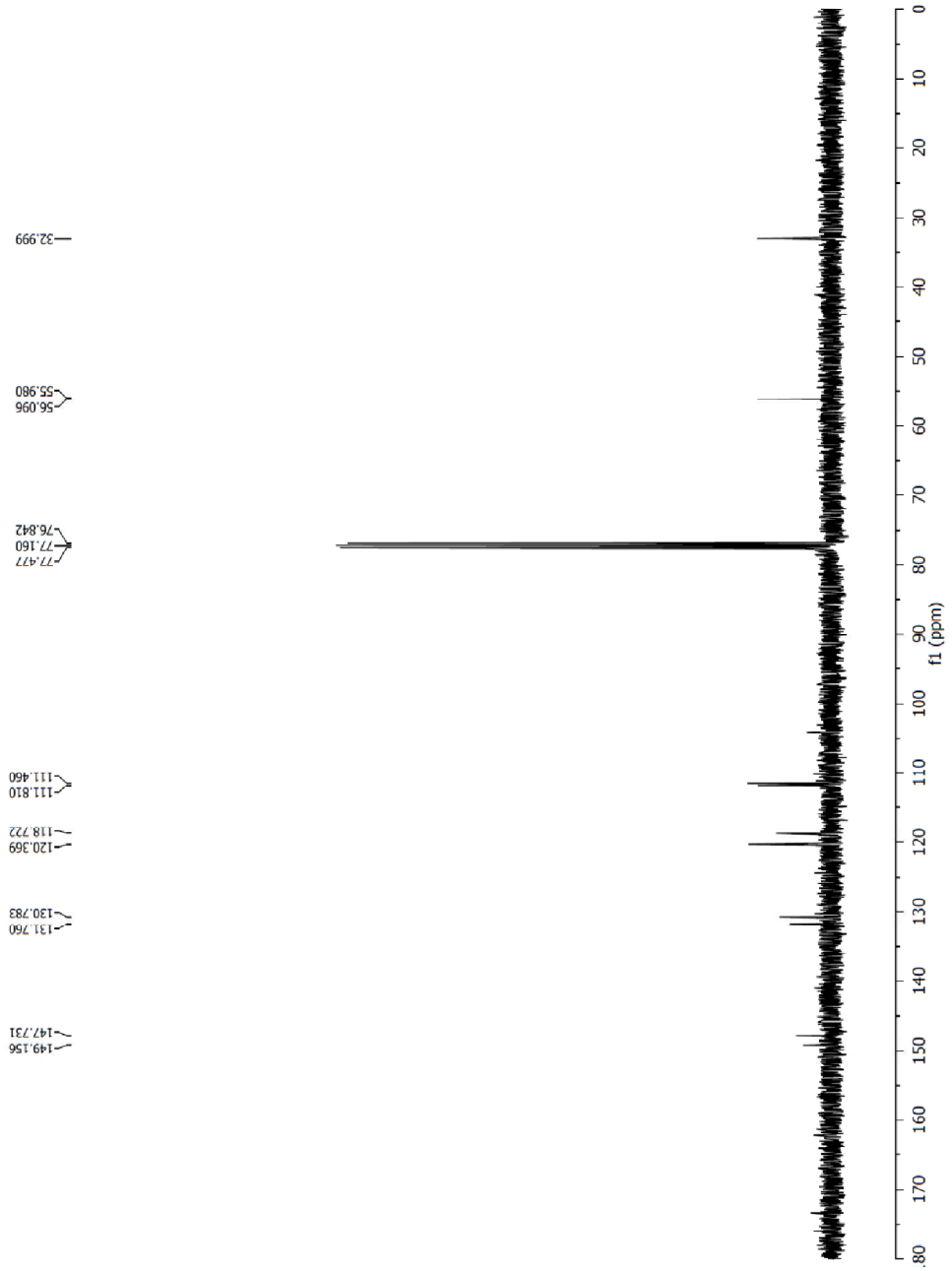
^{13}C NMR spectrum of 2.17



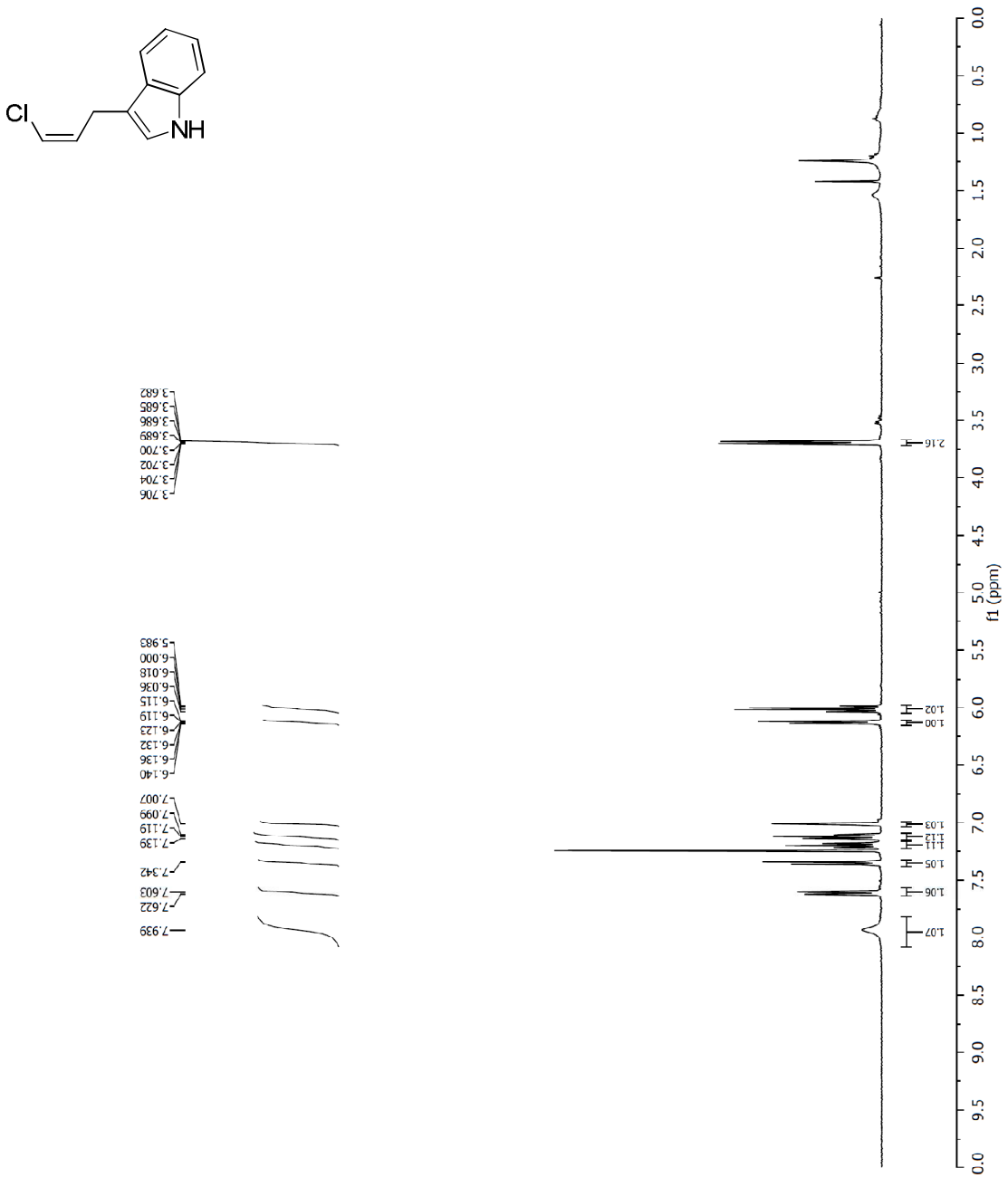
^{1}H NMR spectrum of 2.18



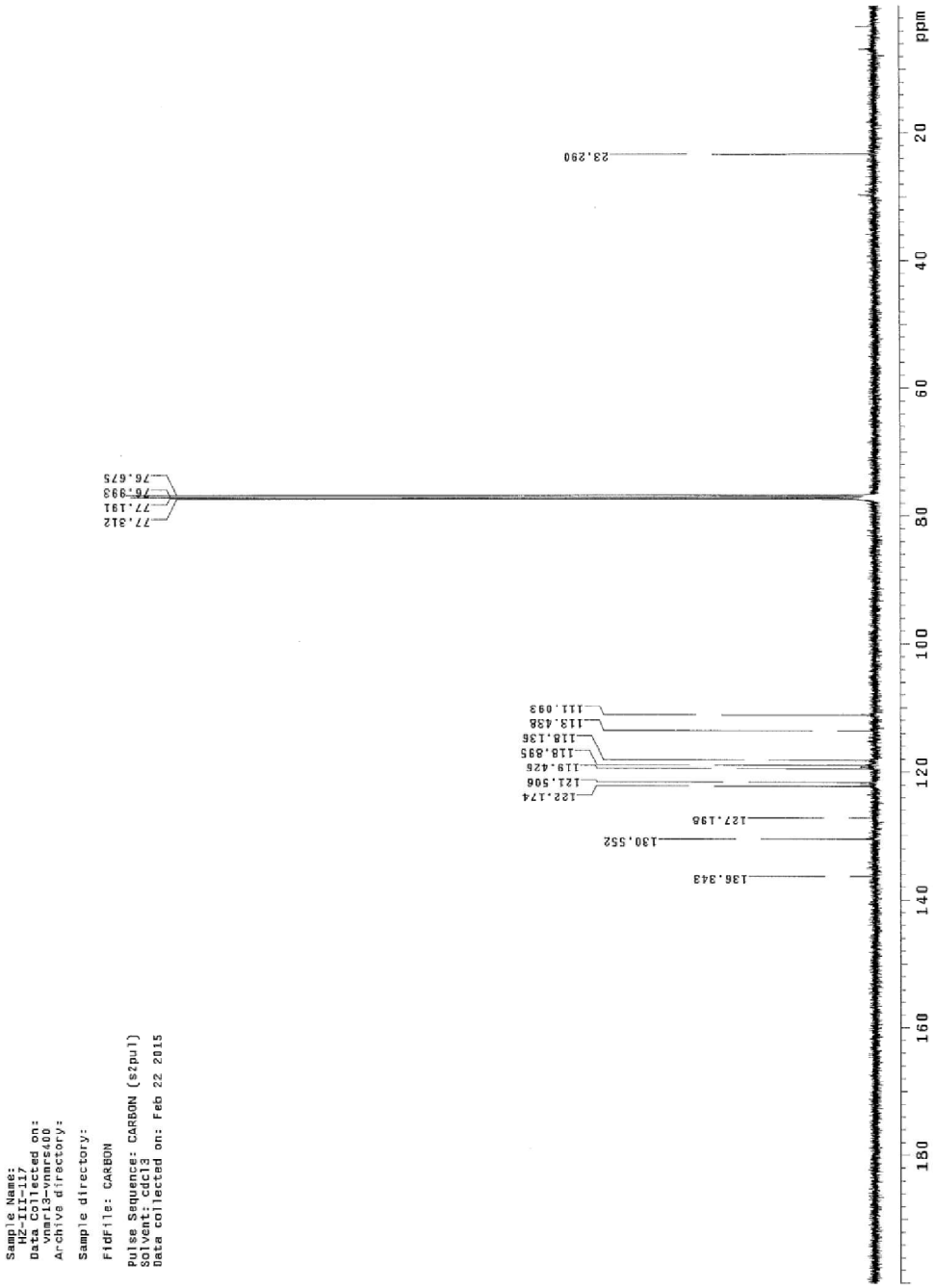
^{13}C NMR spectrum of 2.18



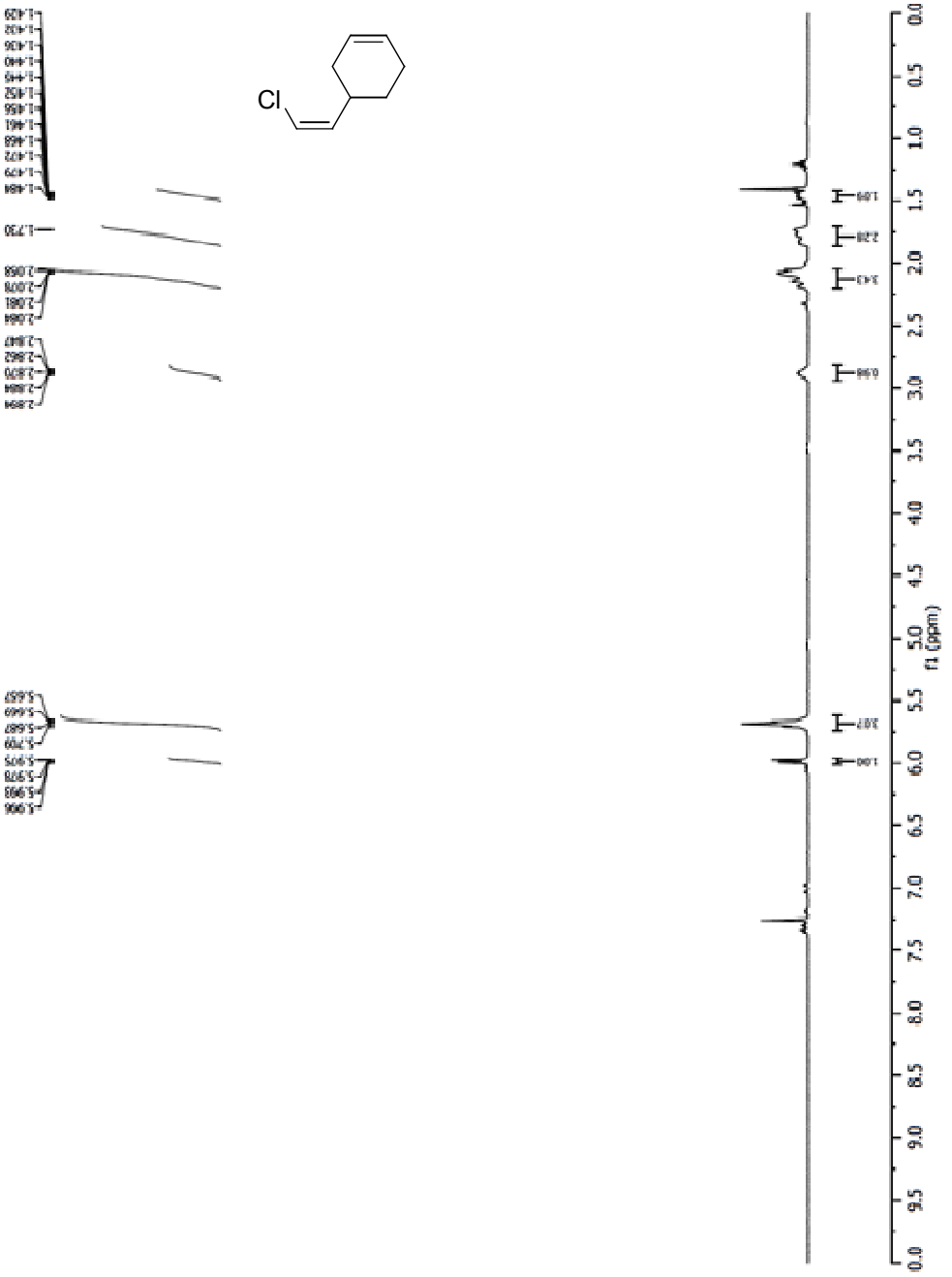
^{1}H NMR spectrum of 2.19



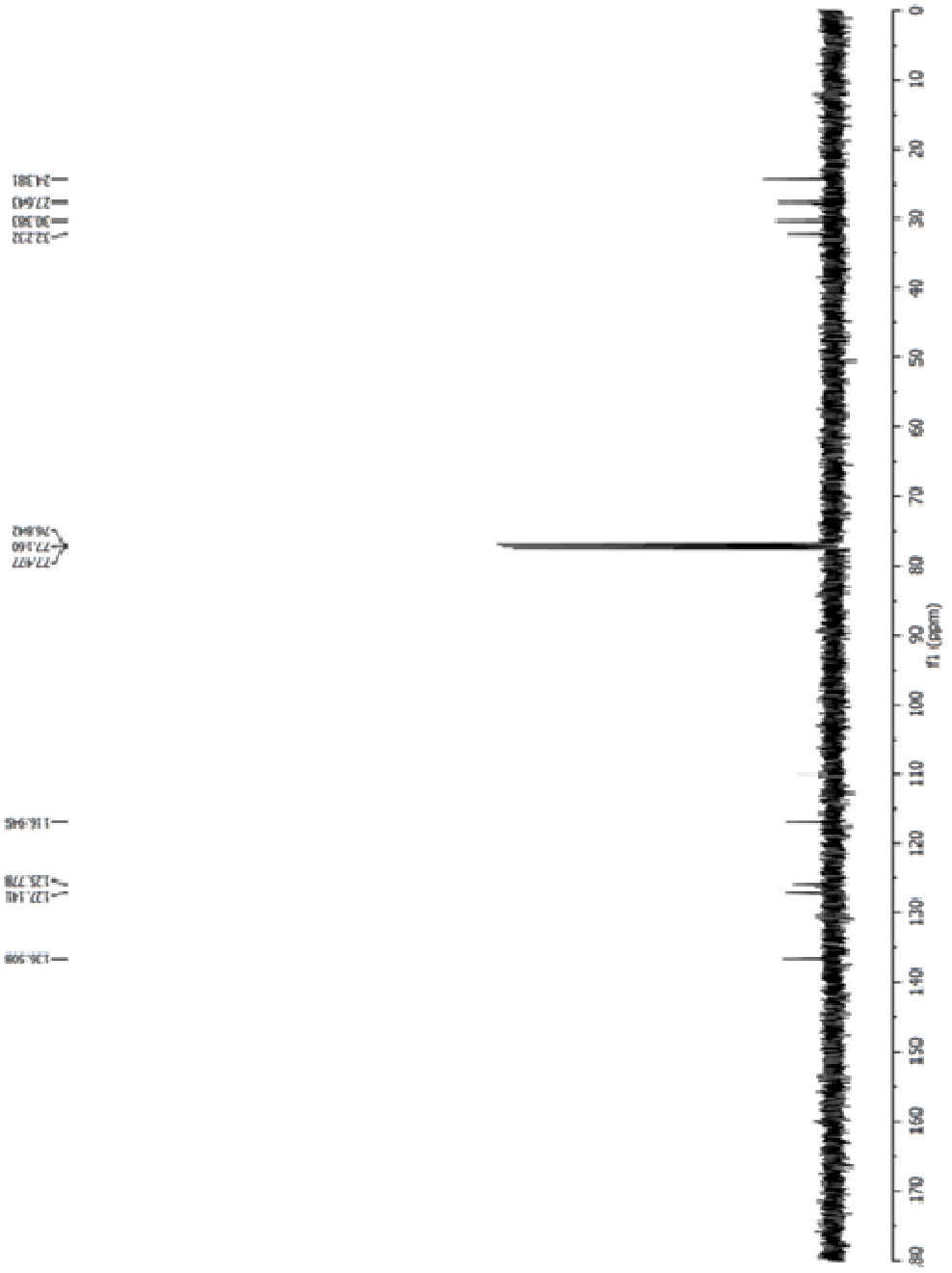
^{13}C NMR spectrum of 2.19



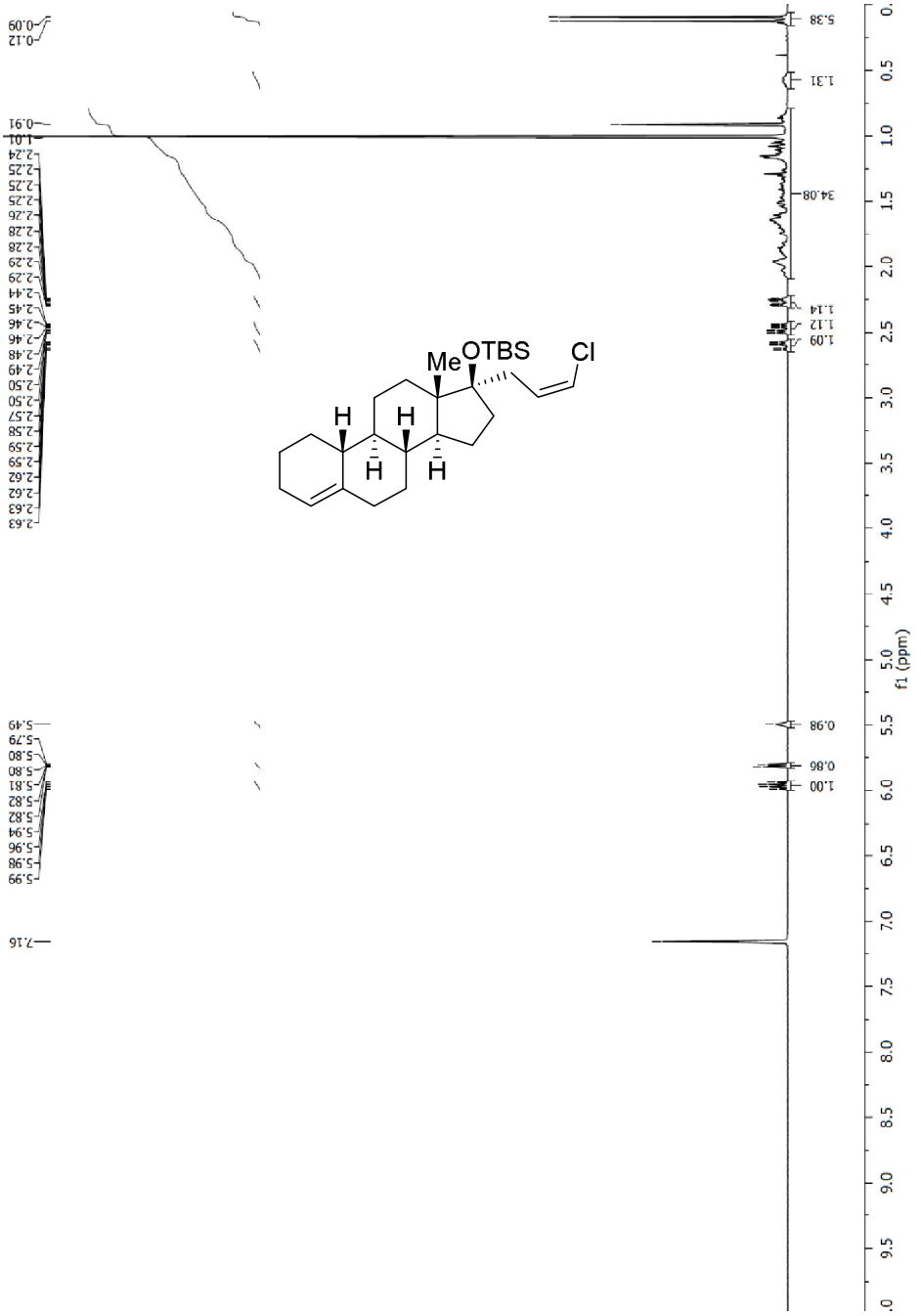
^{1}H NMR spectrum of 2.20



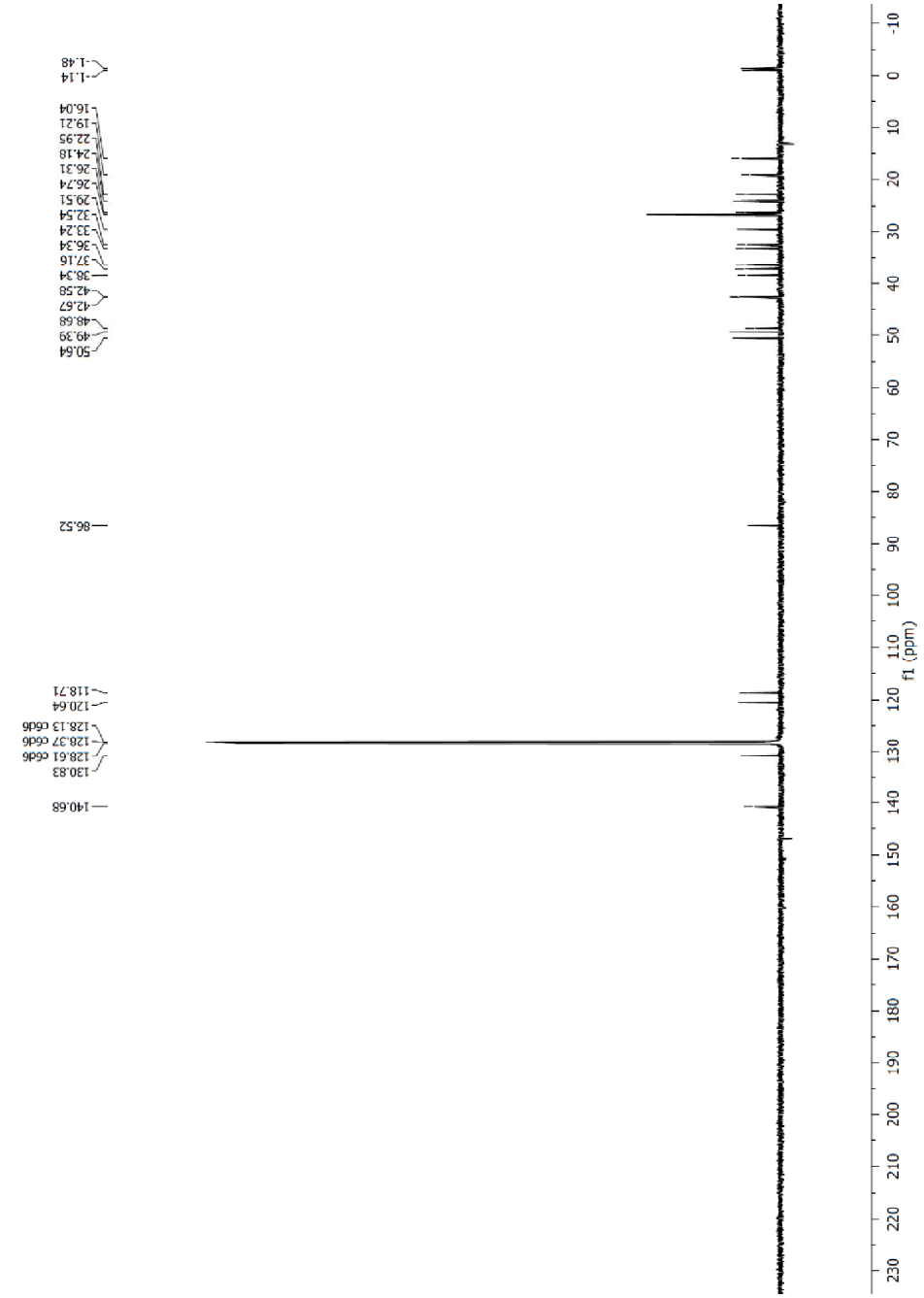
^{13}C NMR spectrum of 2.20



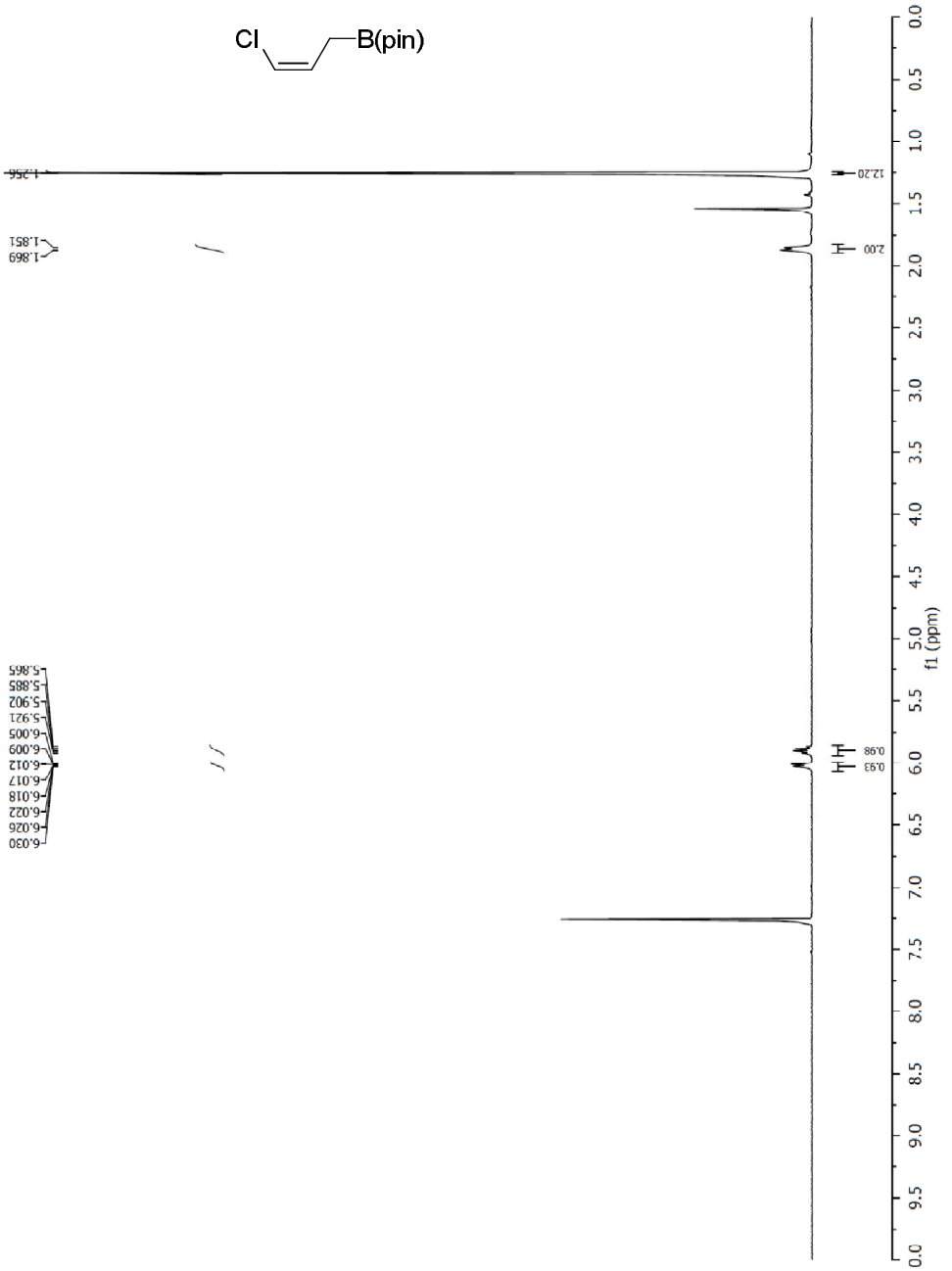
^{1}H NMR spectrum of 2.22



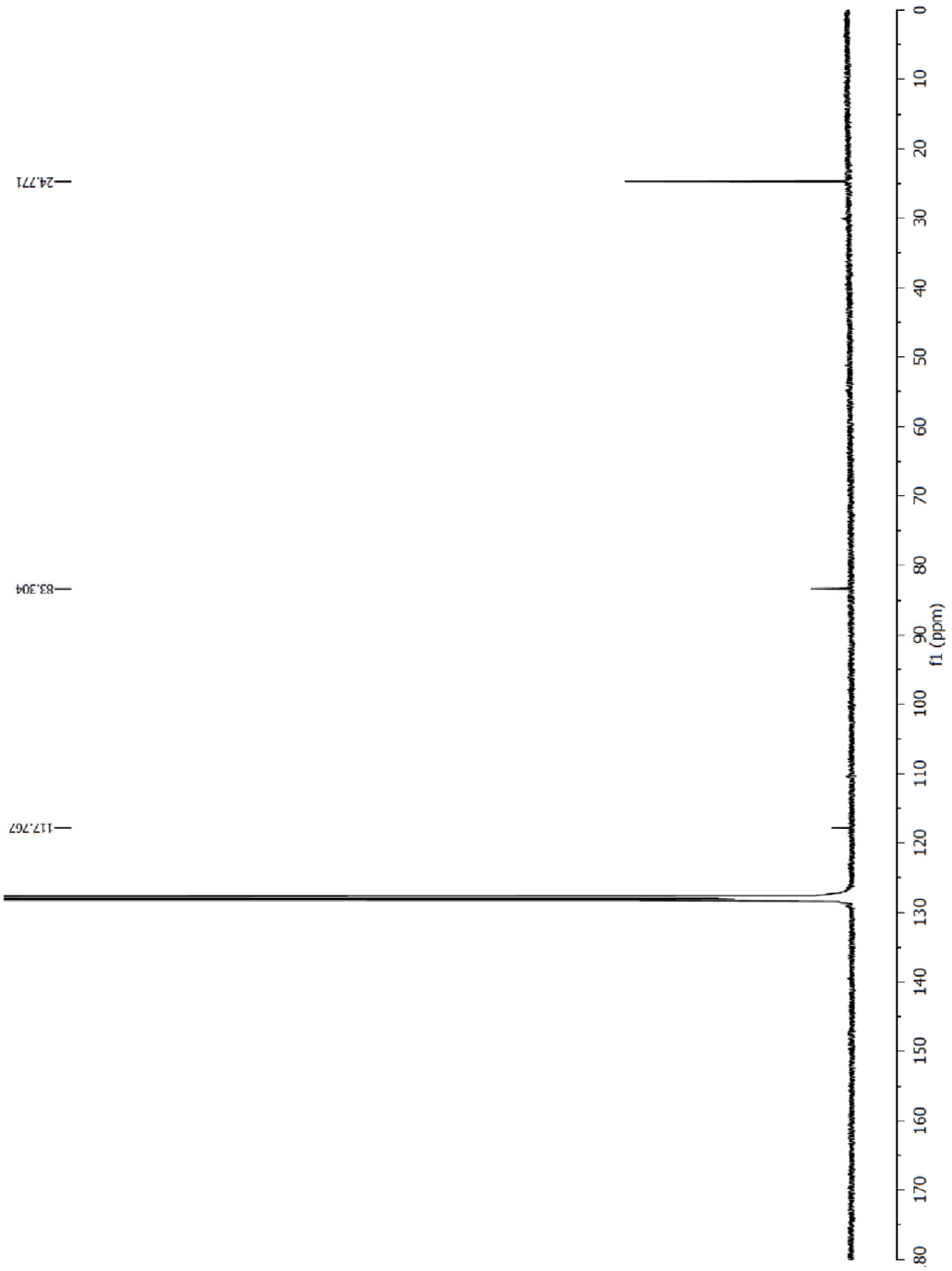
^{13}C NMR spectrum of 2.22



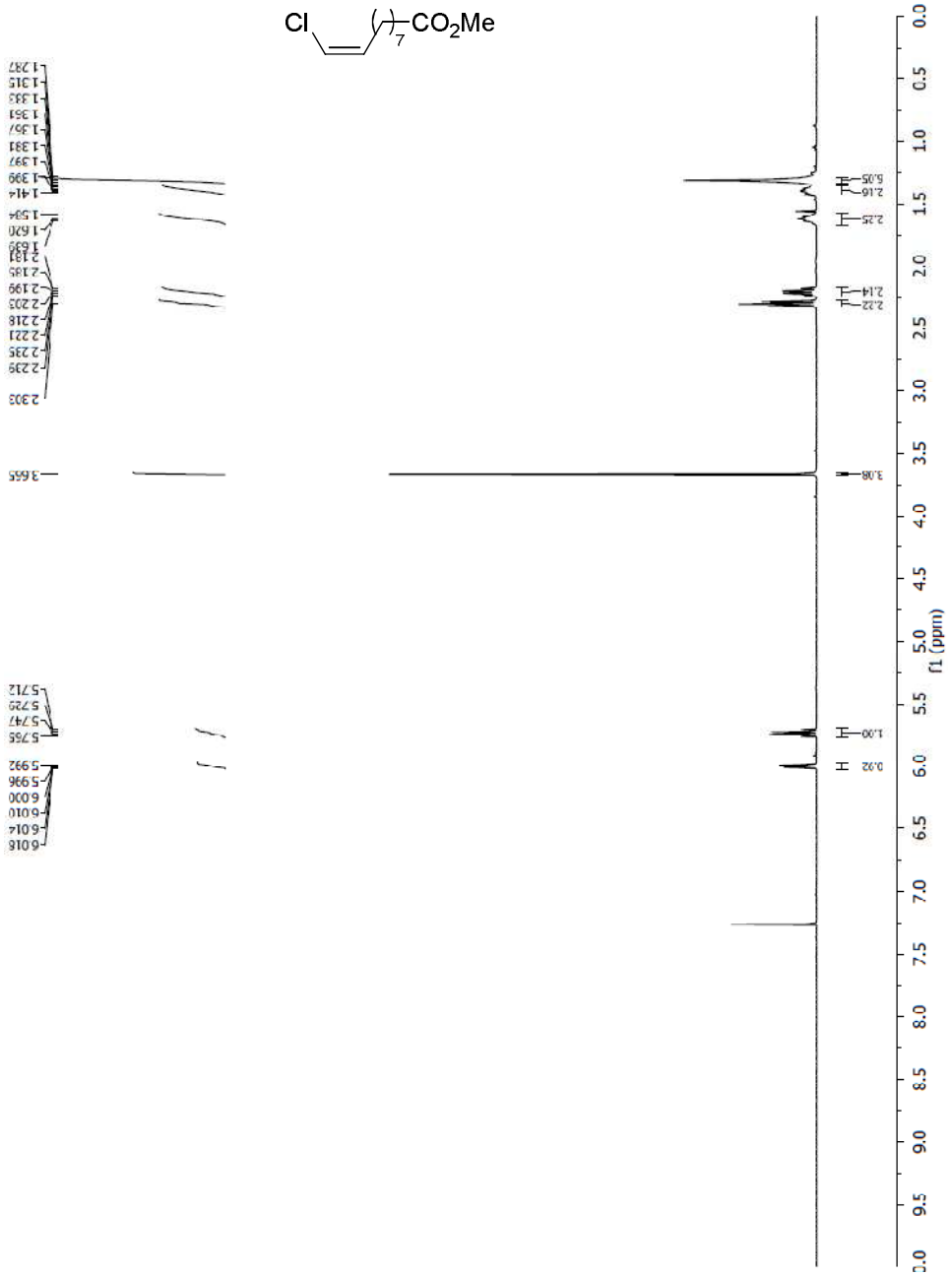
^{1}H NMR spectrum of 2.23



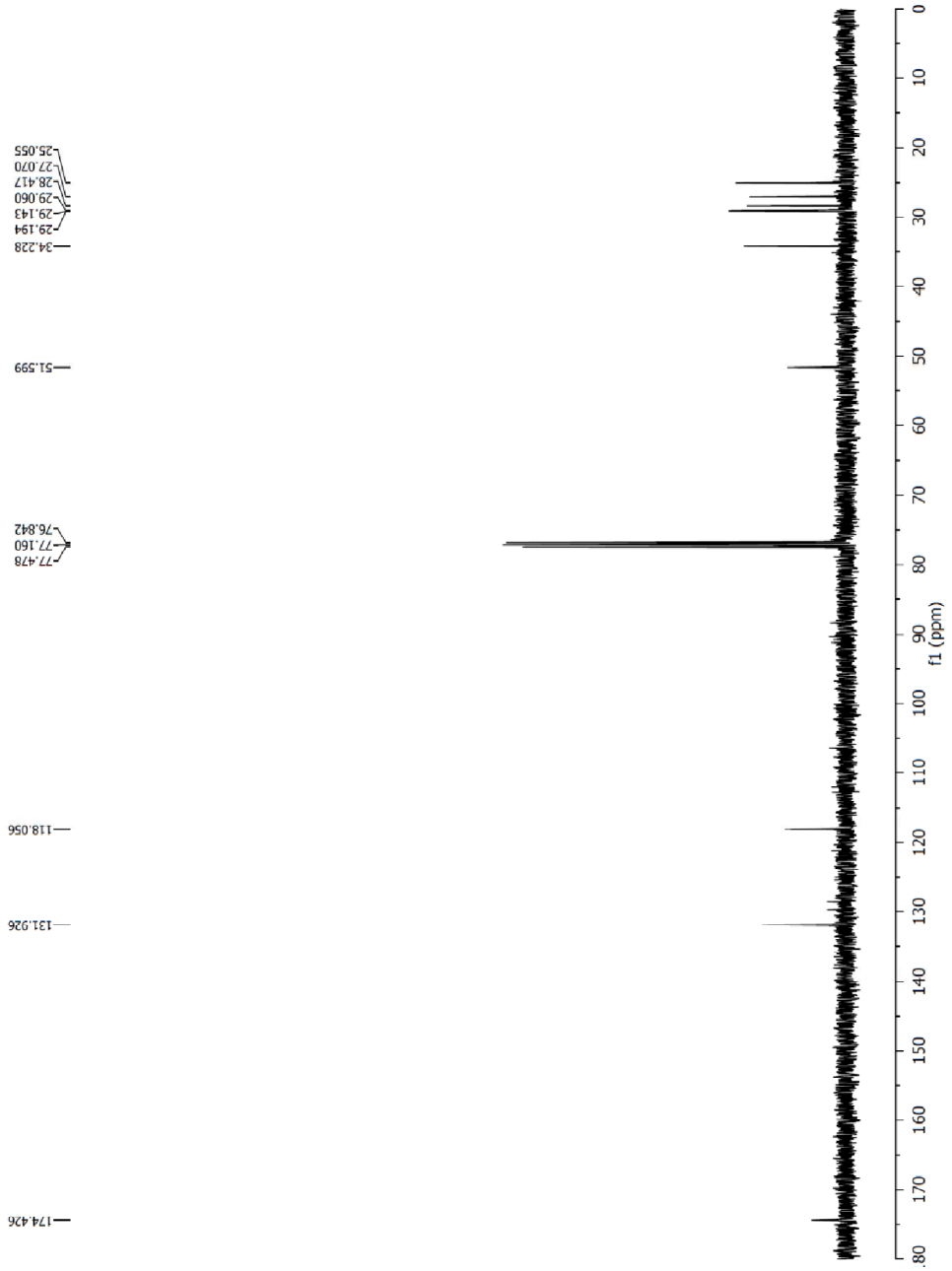
^{13}C NMR spectrum of 2.23



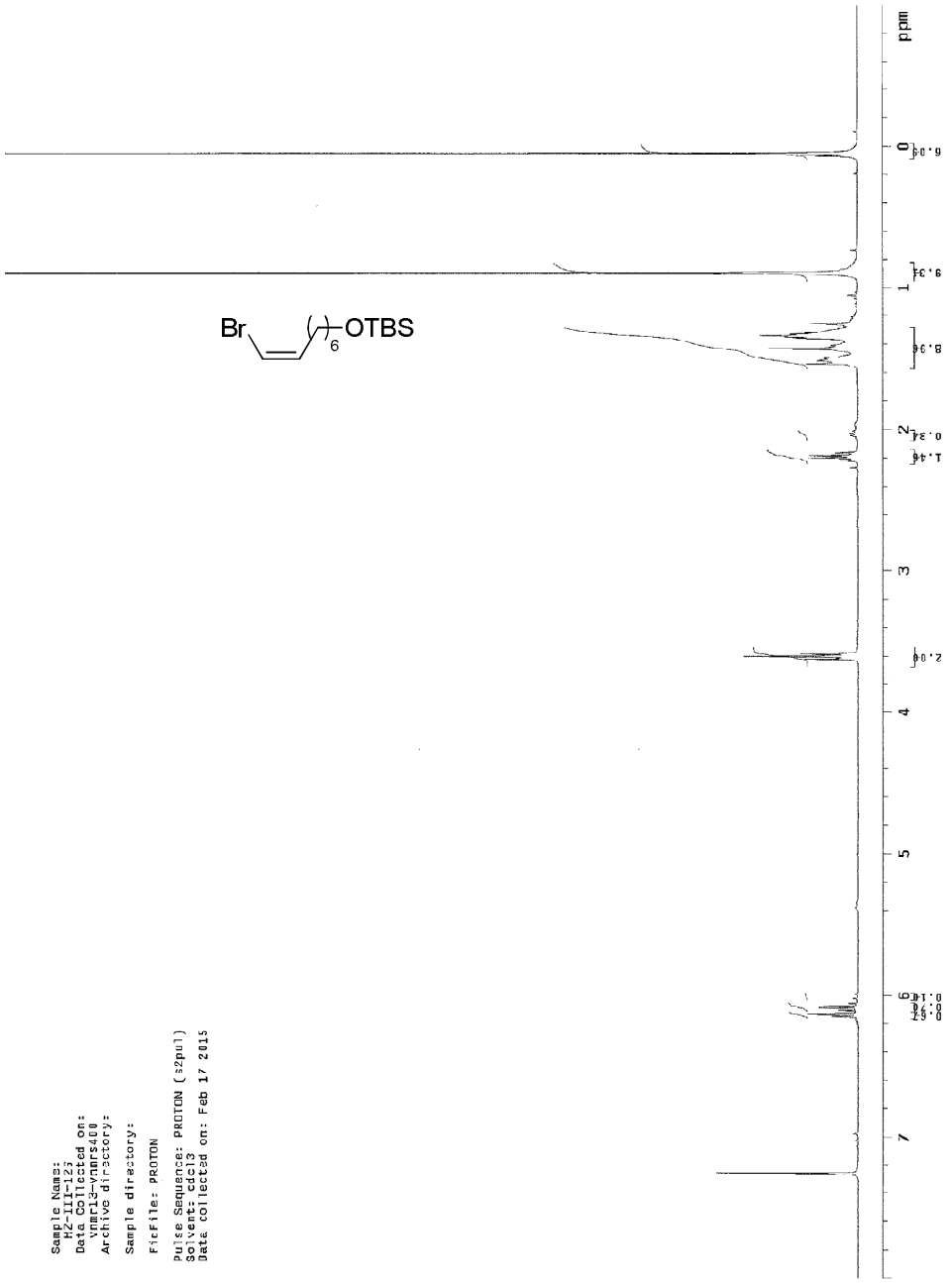
^{1}H NMR spectrum of 2.32



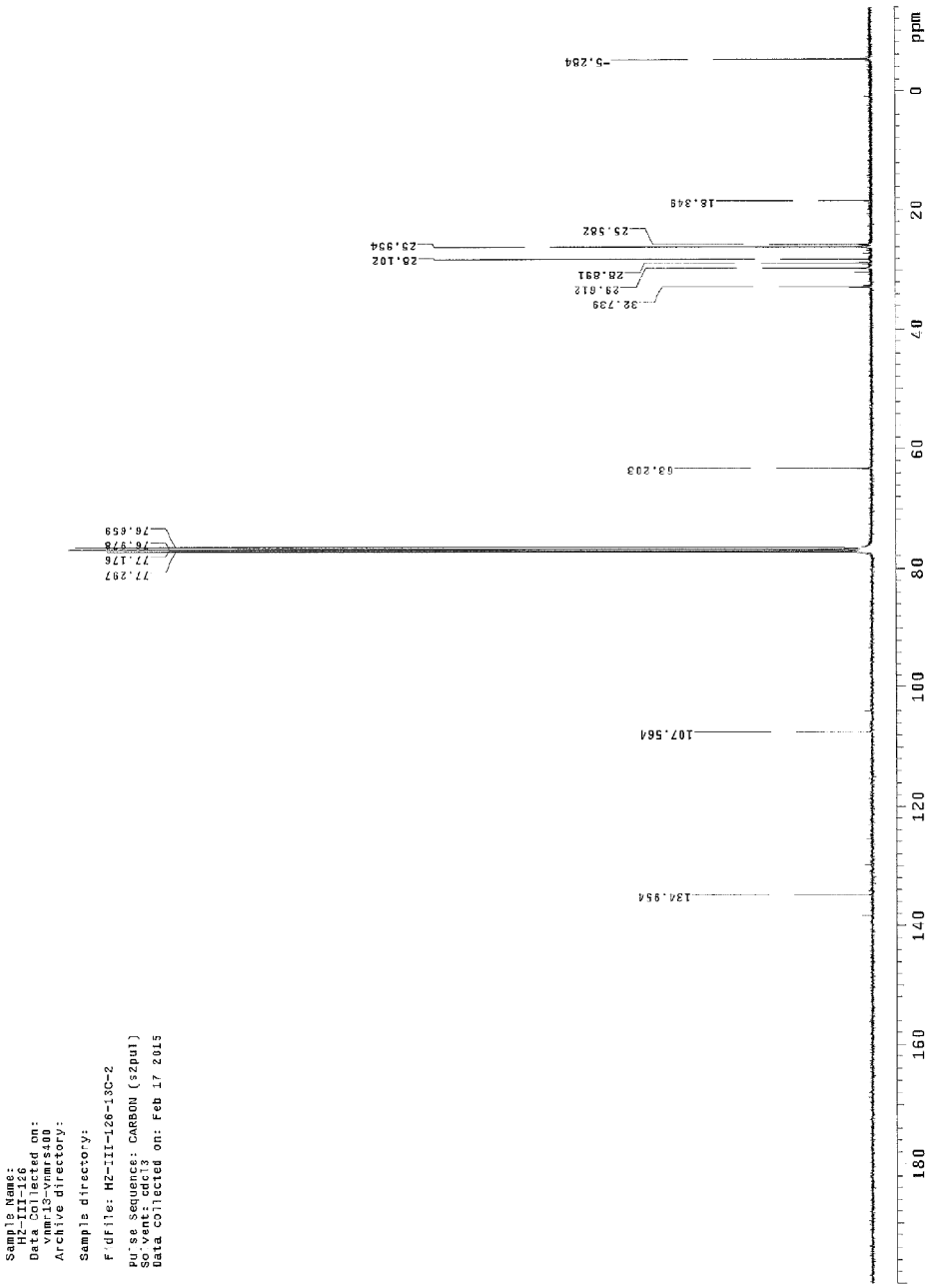
^{13}C NMR spectrum of 2.32



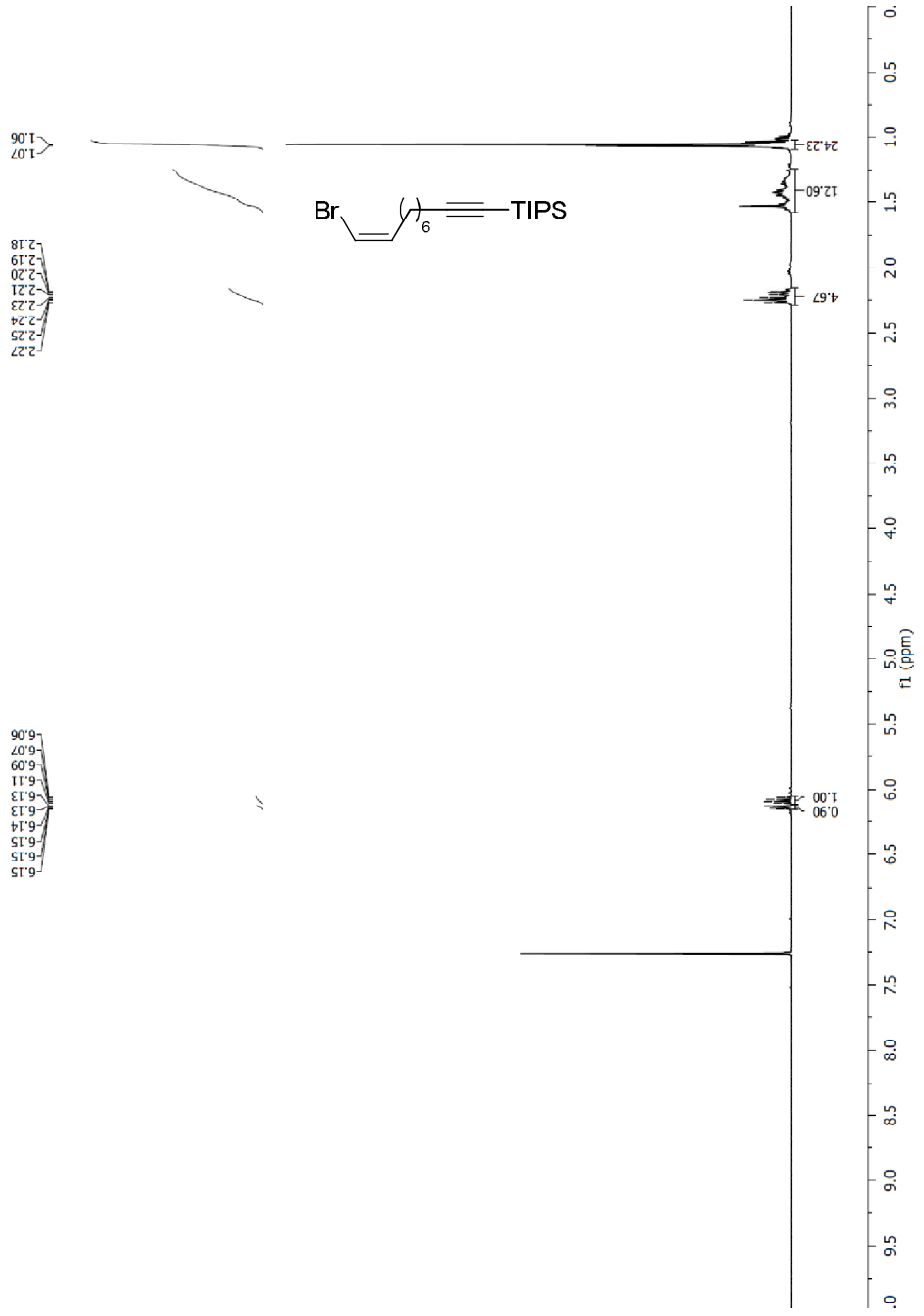
^{1}H NMR spectrum of 2.35



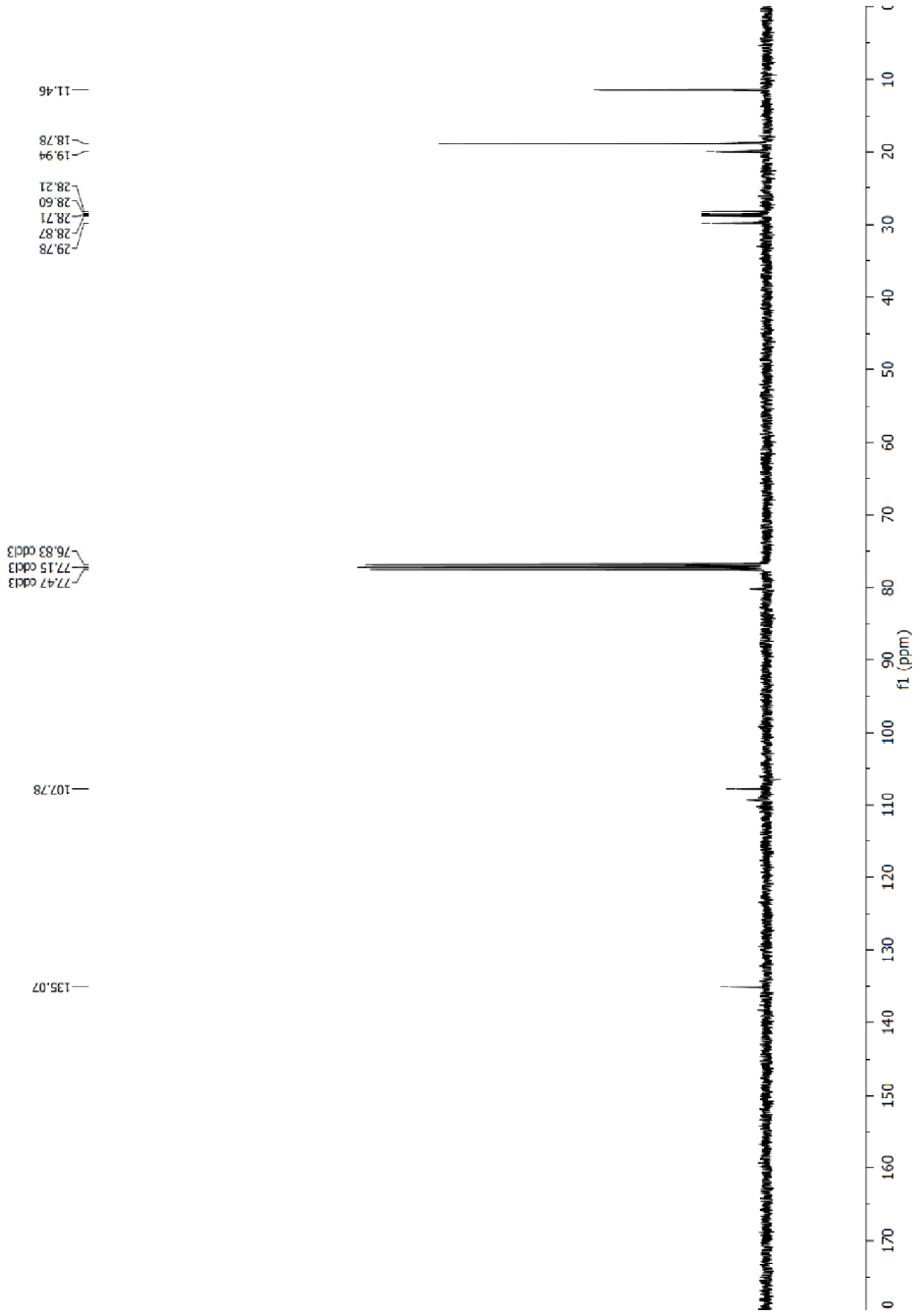
^{13}C NMR spectrum of 2.35



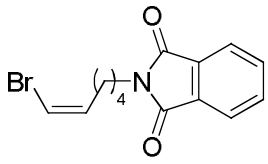
^{1}H NMR spectrum of 2.36

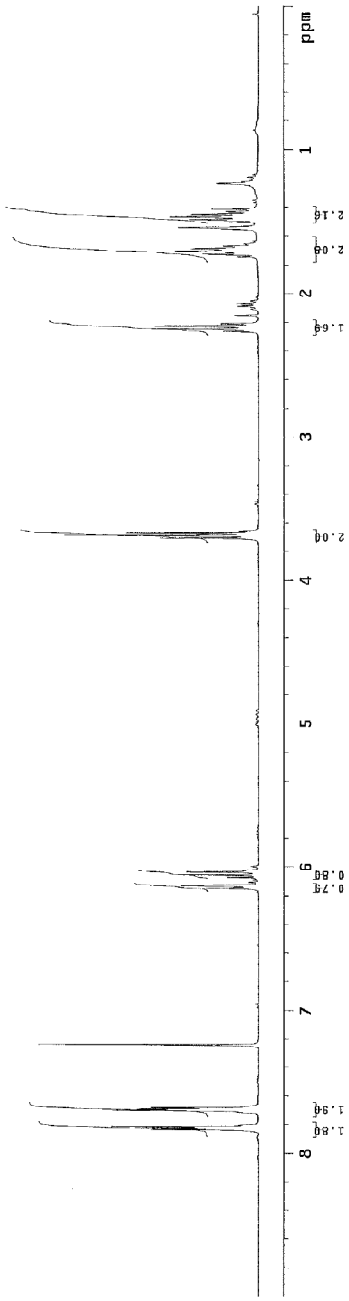


^{13}C NMR spectrum of 2.36



^{1}H NMR spectrum of 2.37





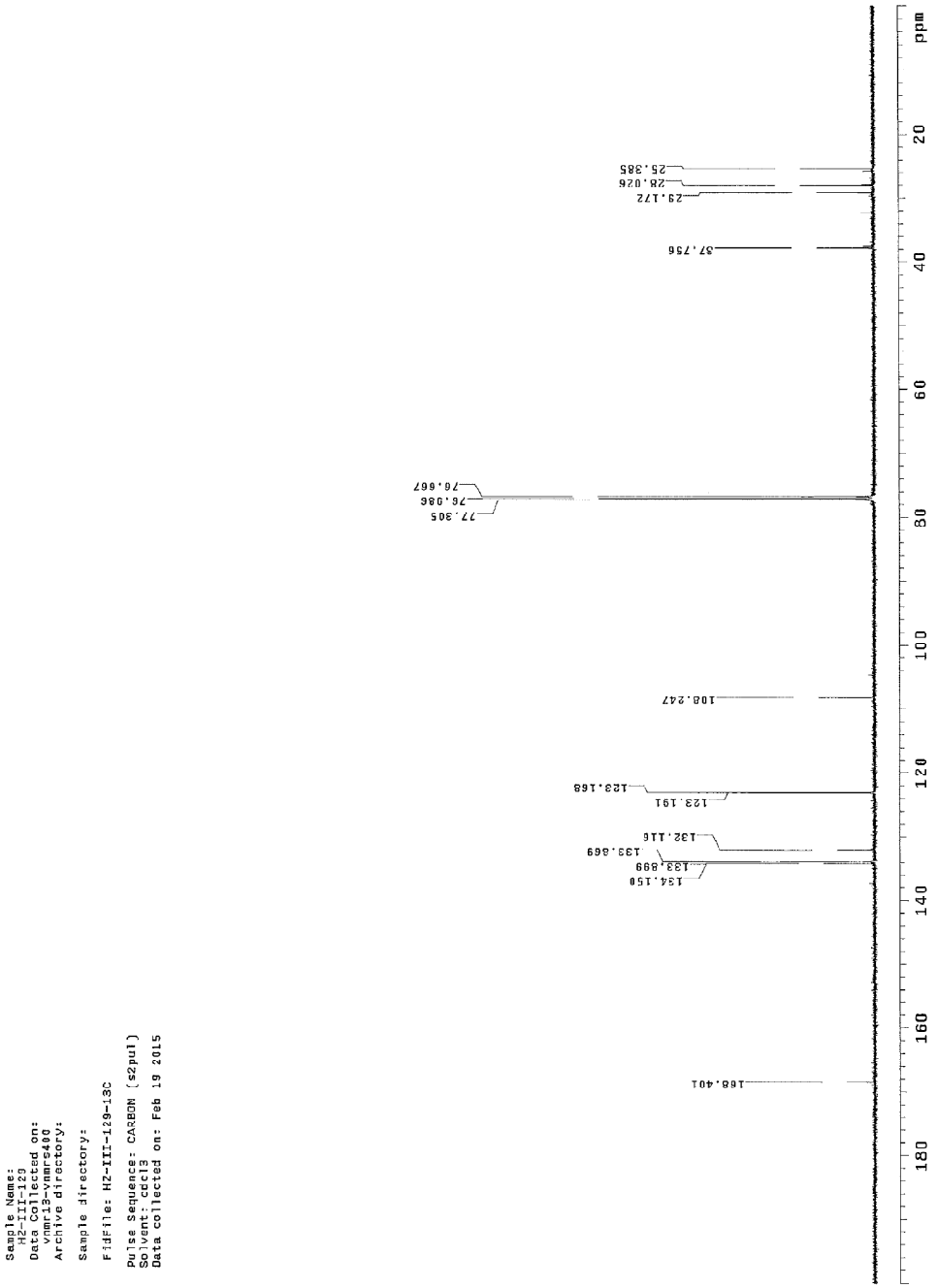
Sample Name:
HZ-III-1298-11-3-14
Data Collected on:
ynmr13-ynmrs400
Archive directory:

Sample directory:

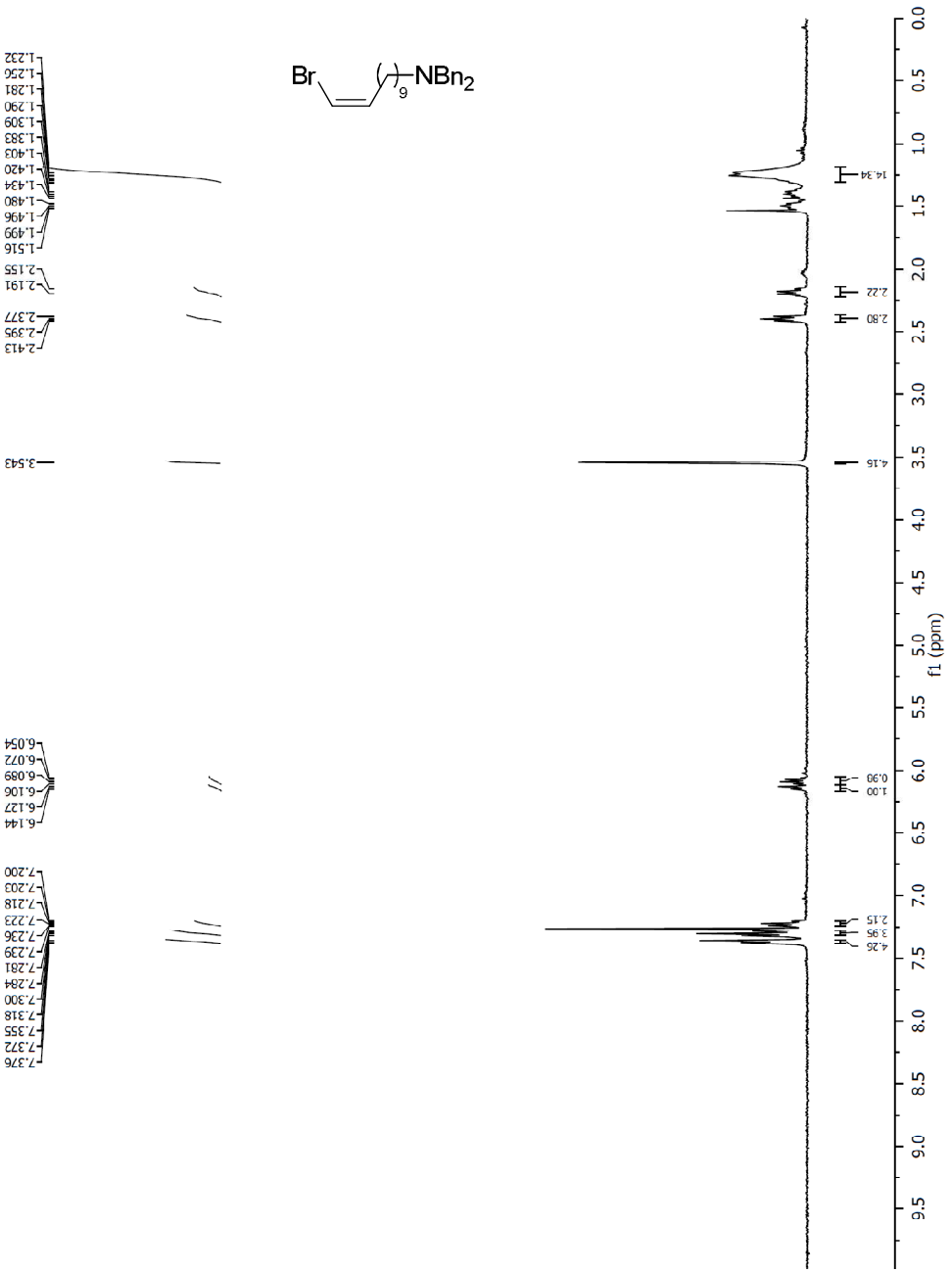
Fidfile: HZ-III-1298-11-3-14

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov 3 2014

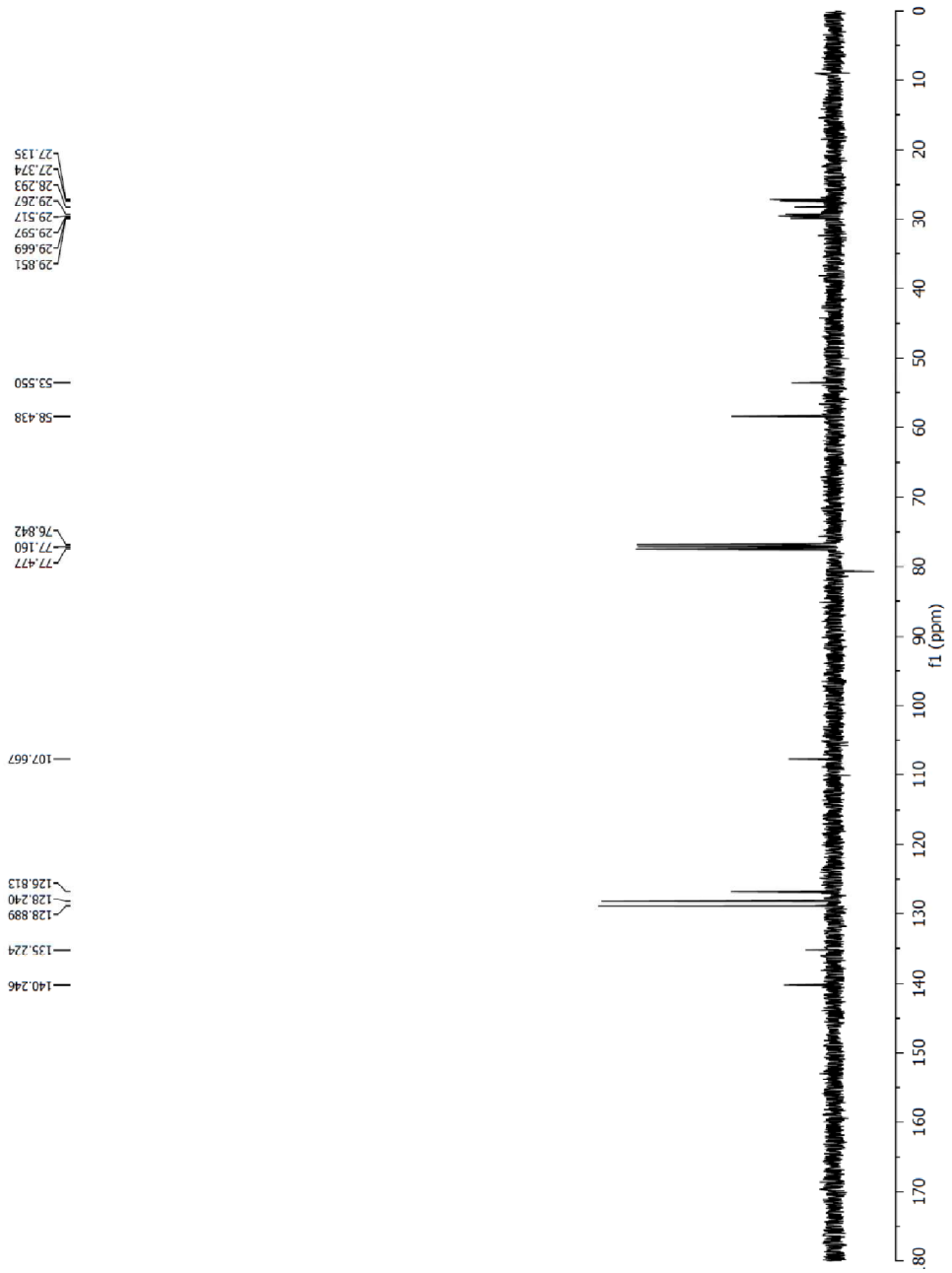
^{13}C NMR spectrum of 2.37



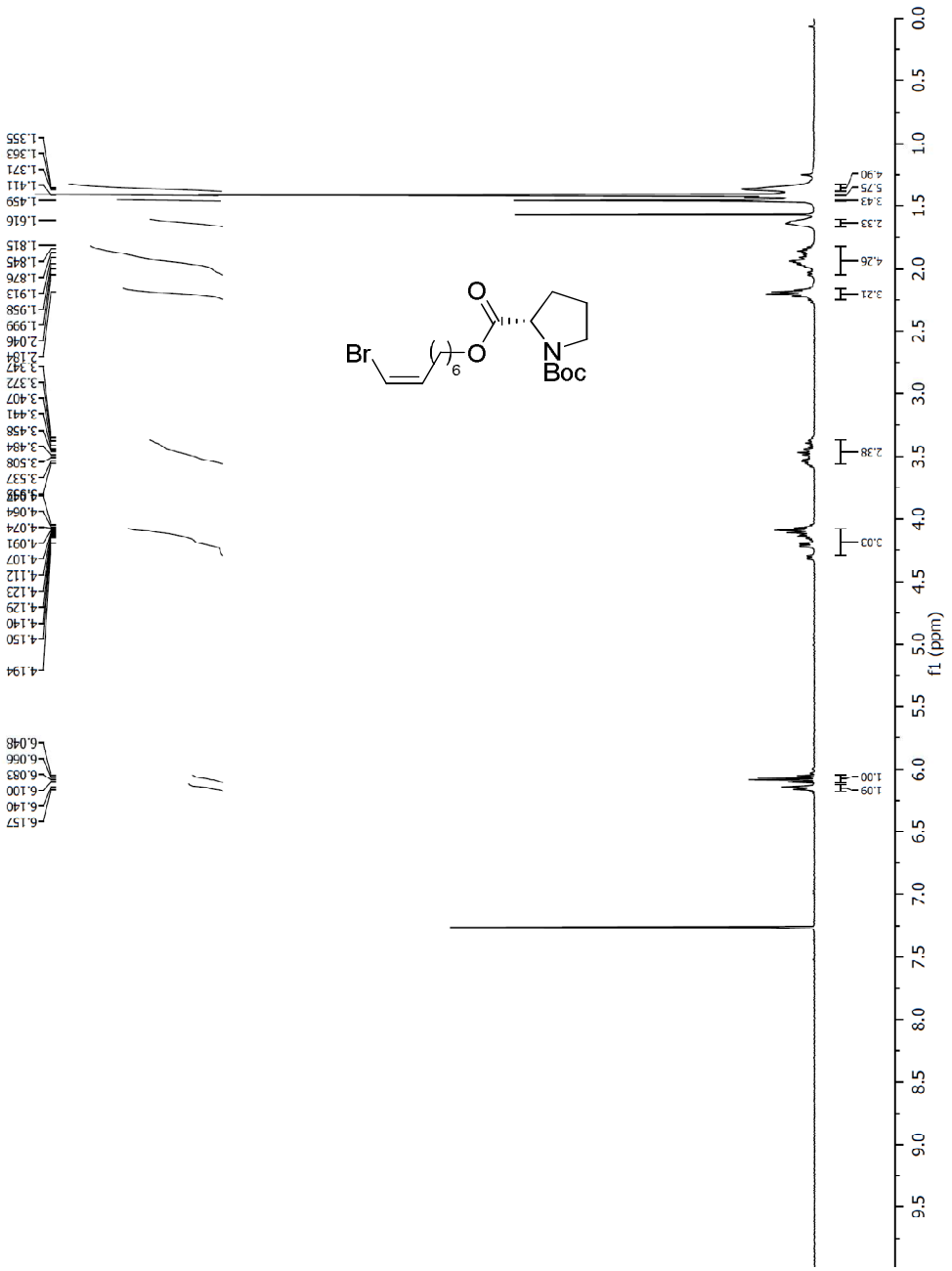
^{1}H NMR spectrum of 2.38



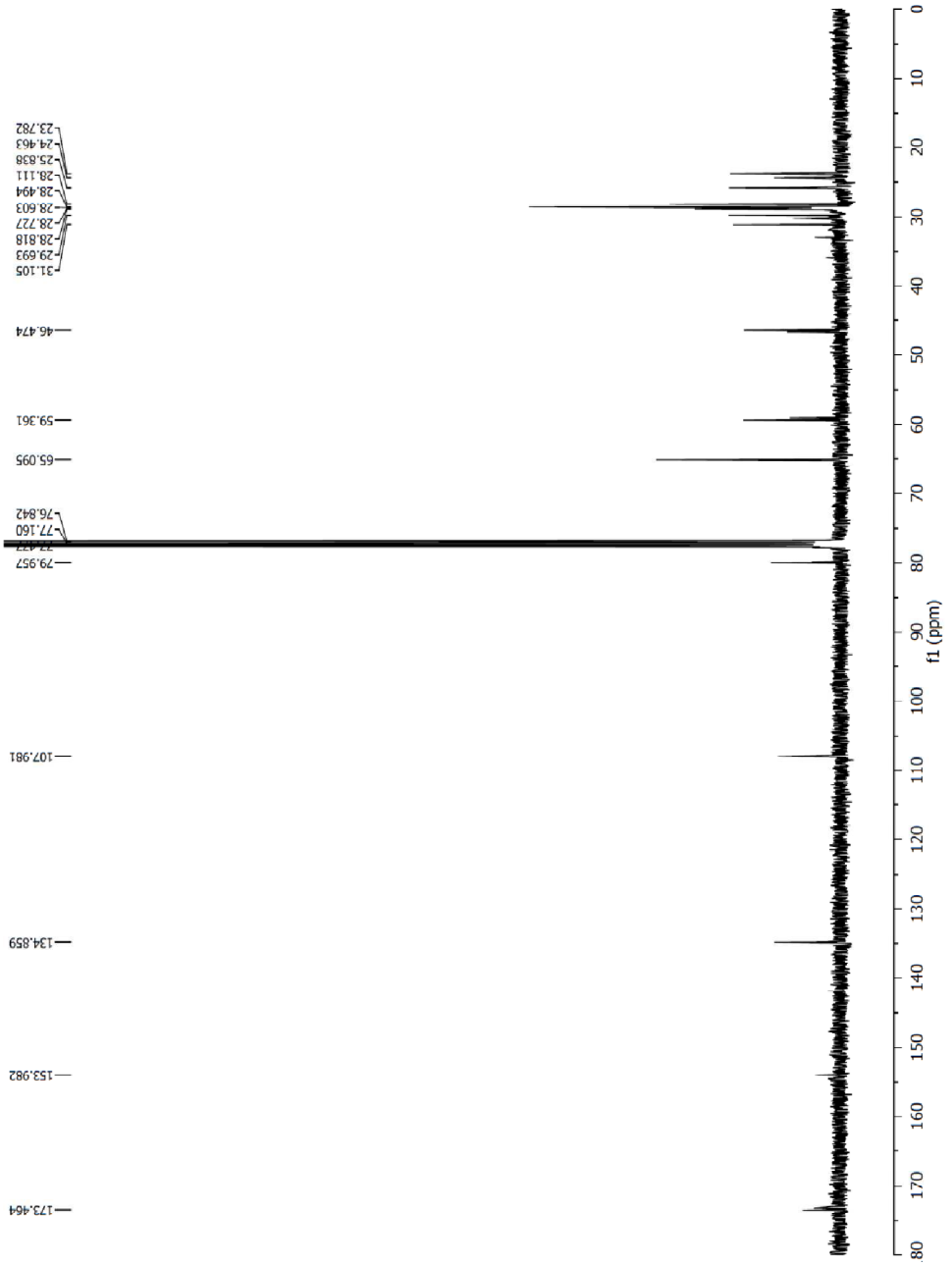
^{13}C NMR spectrum of 2.38



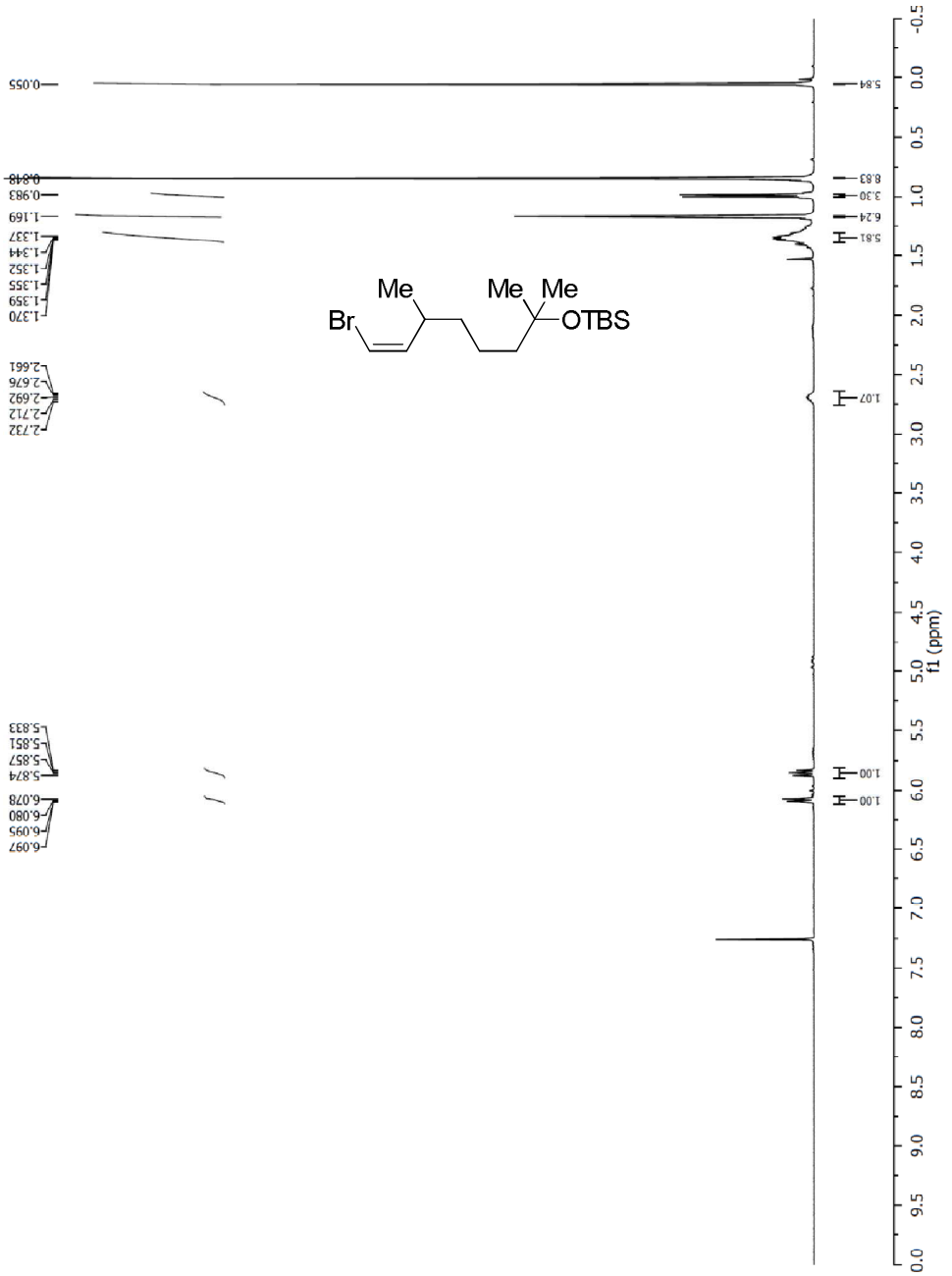
^{1}H NMR spectrum of 2.39



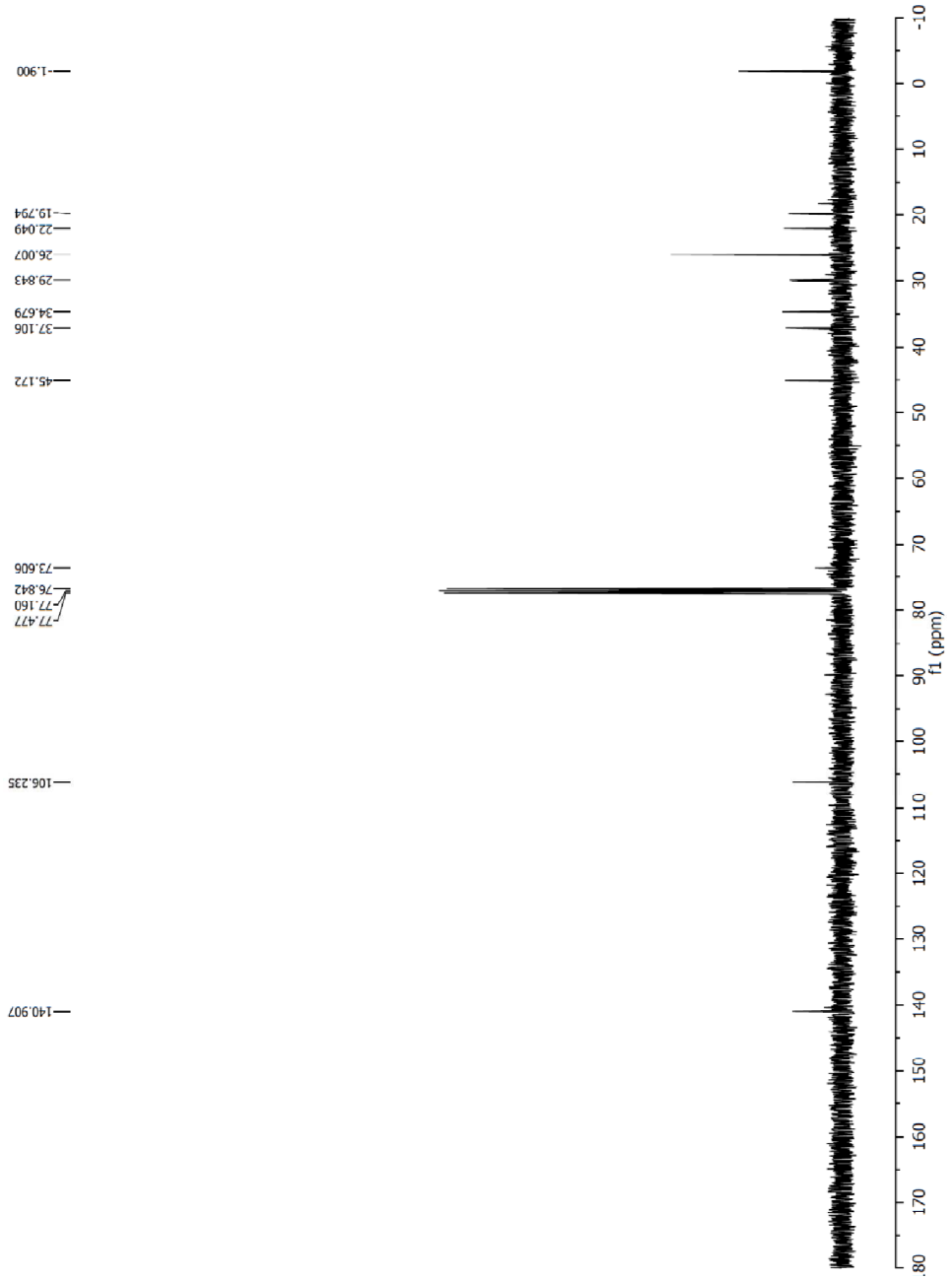
^{13}C NMR spectrum of 2.39



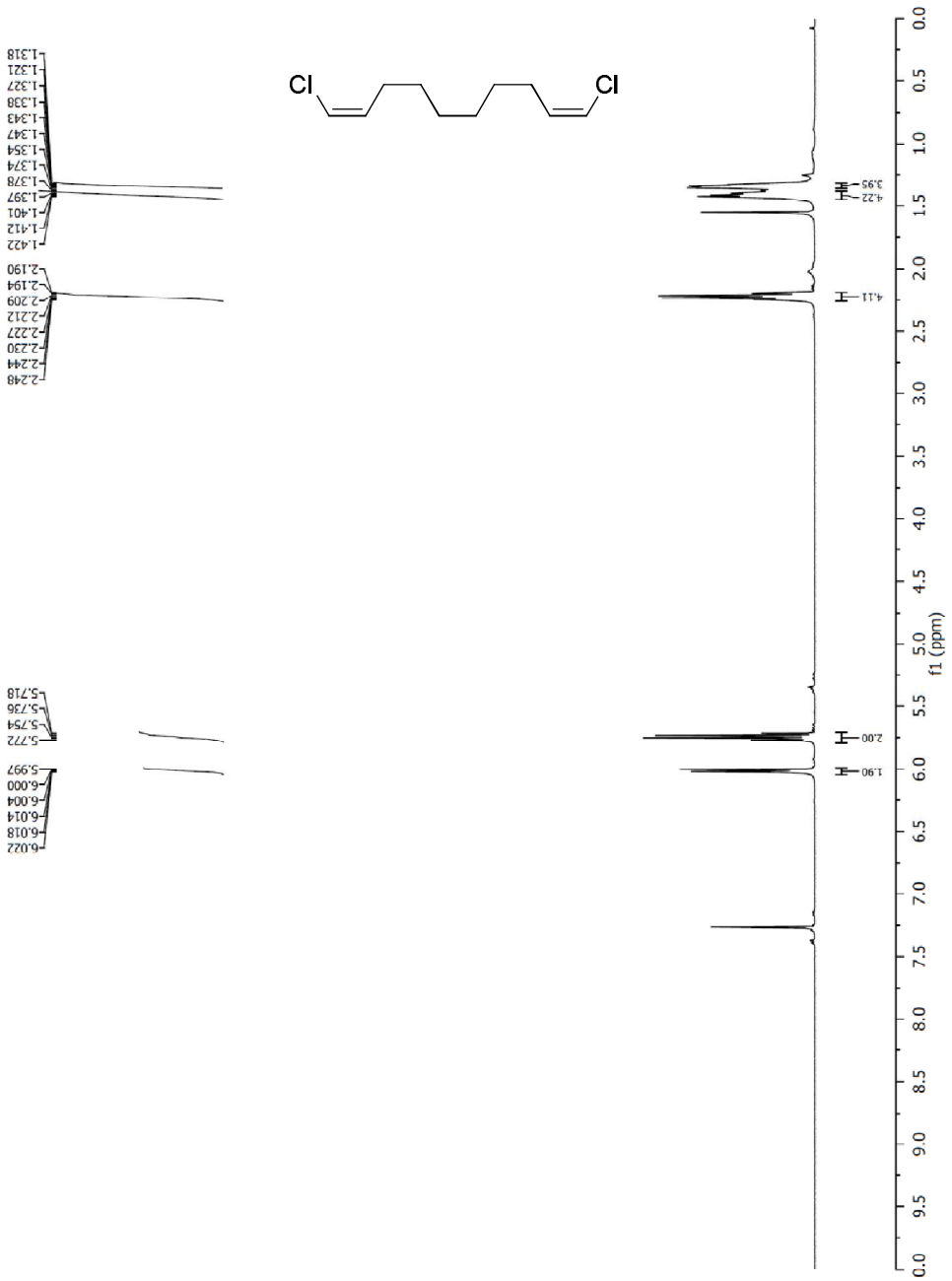
^{1}H NMR spectrum of 2.40



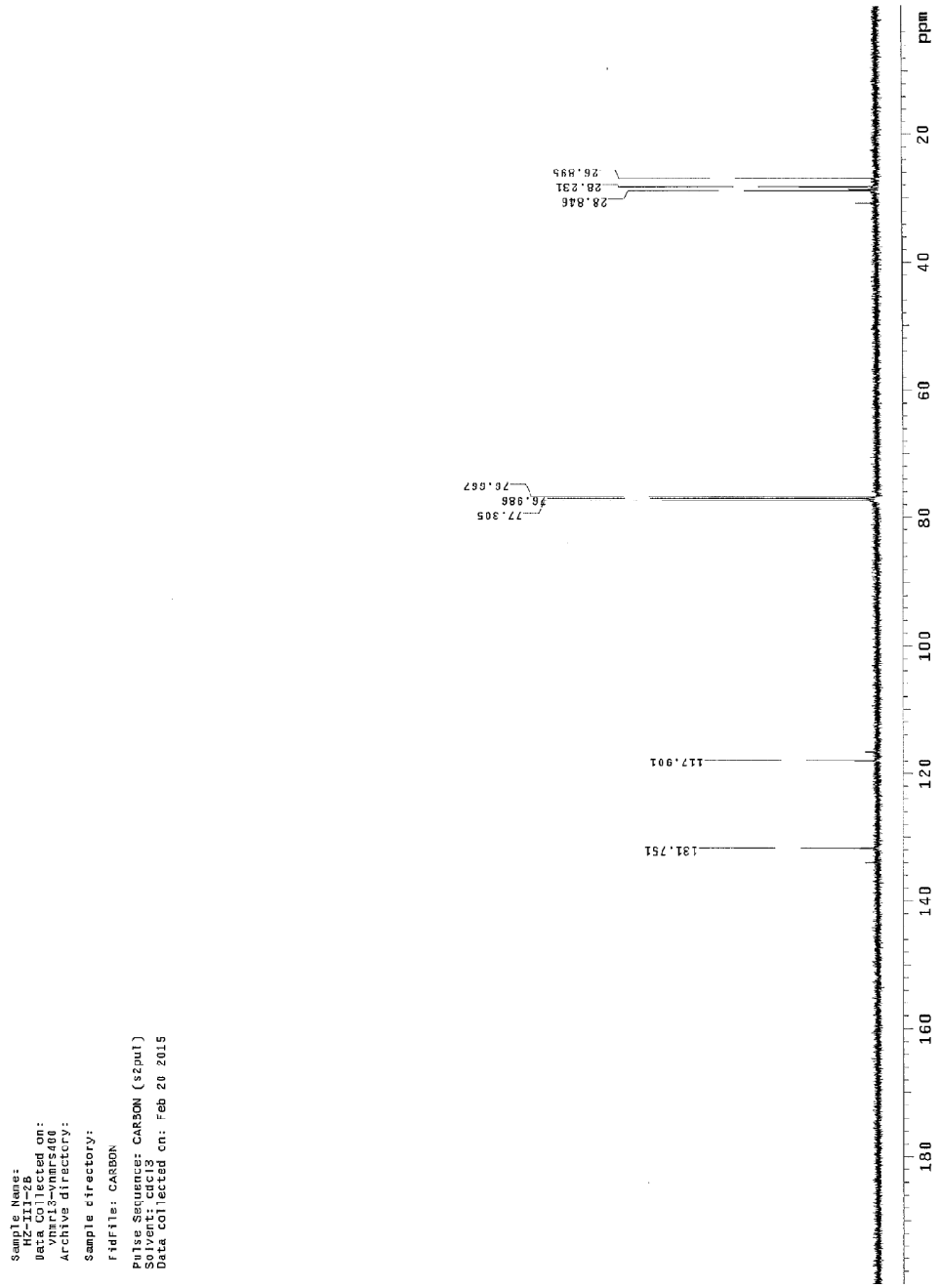
^{13}C NMR spectrum of 2.40



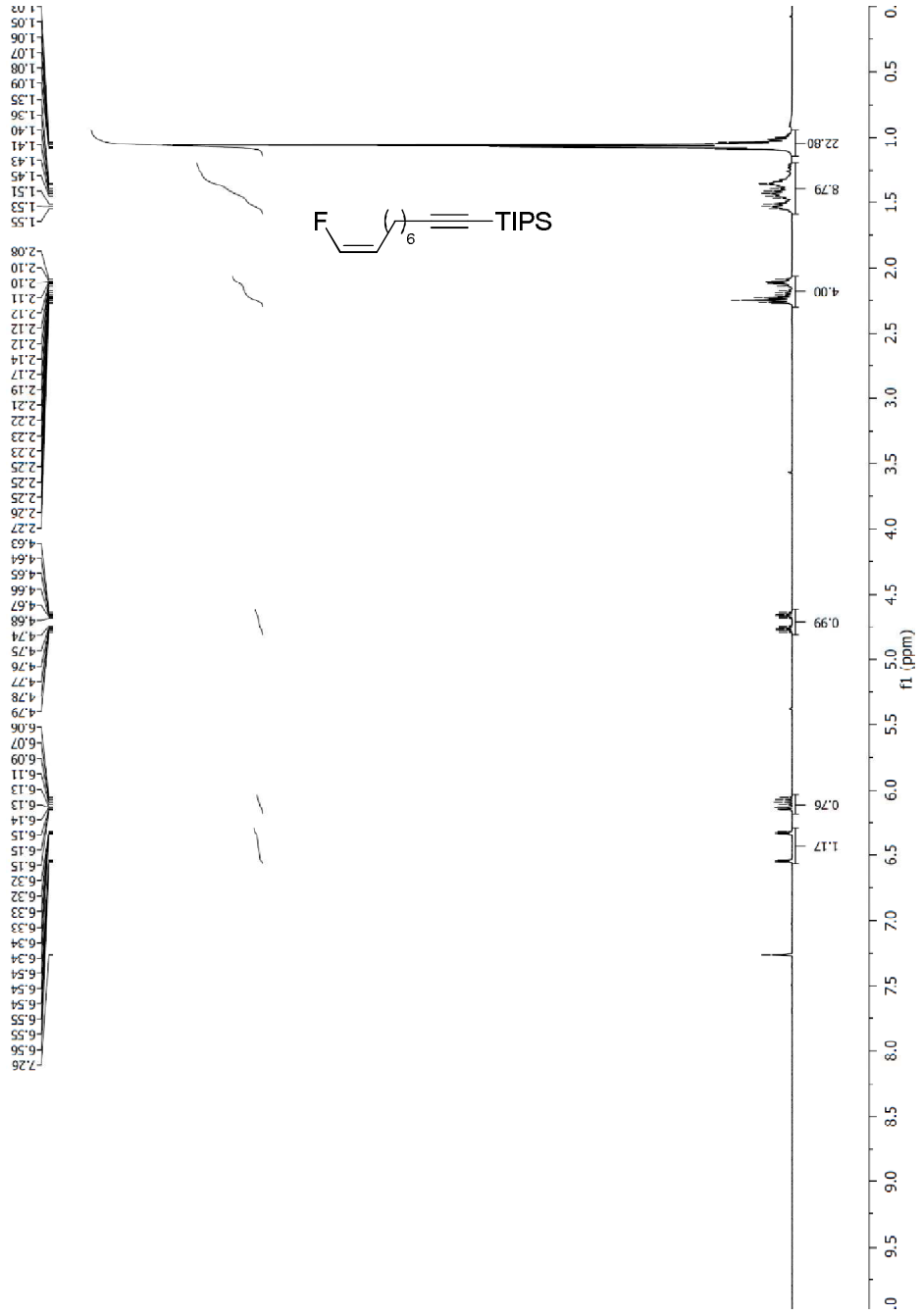
^{1}H NMR spectrum of 2.121



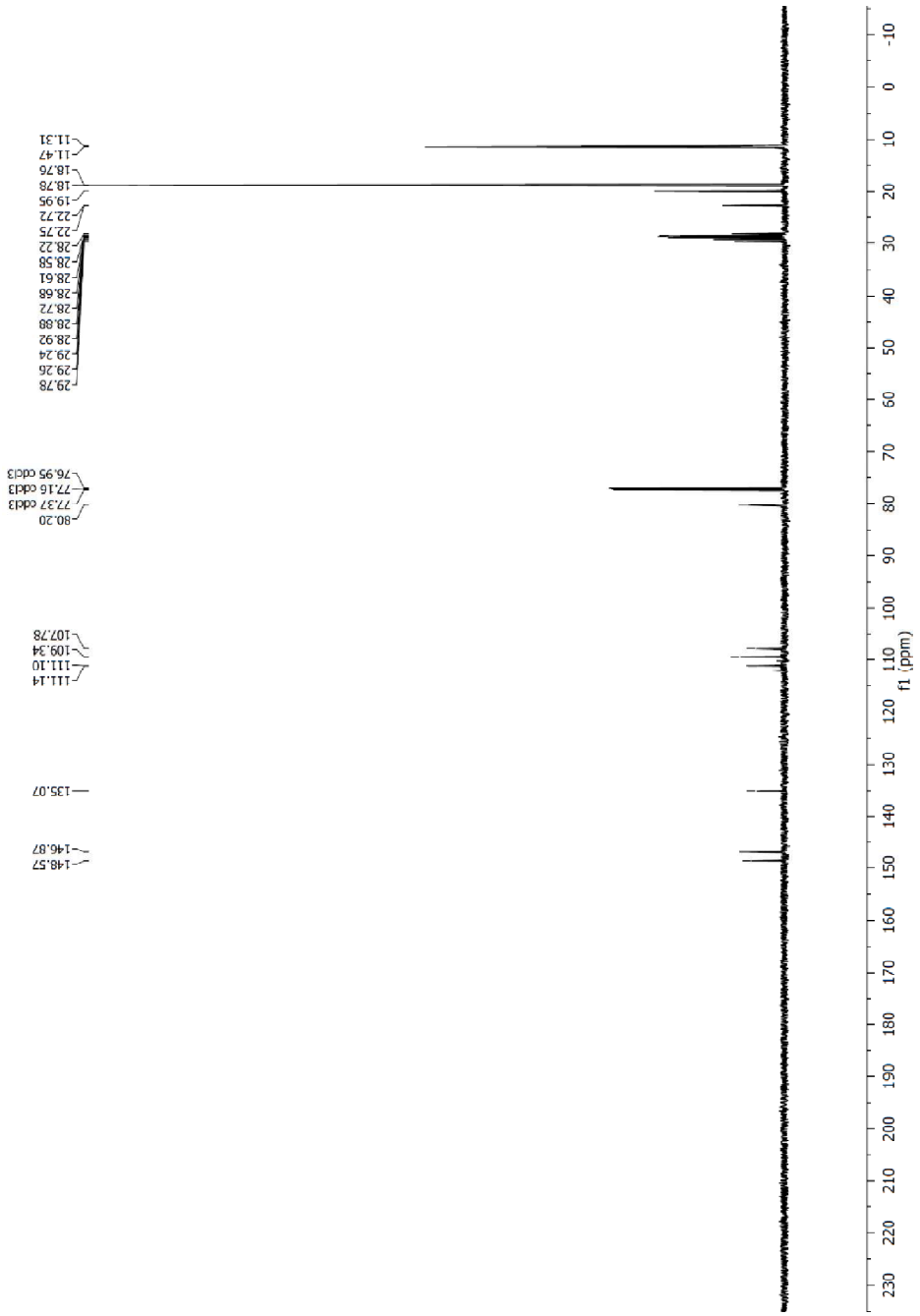
^{13}C NMR spectrum of 2.121



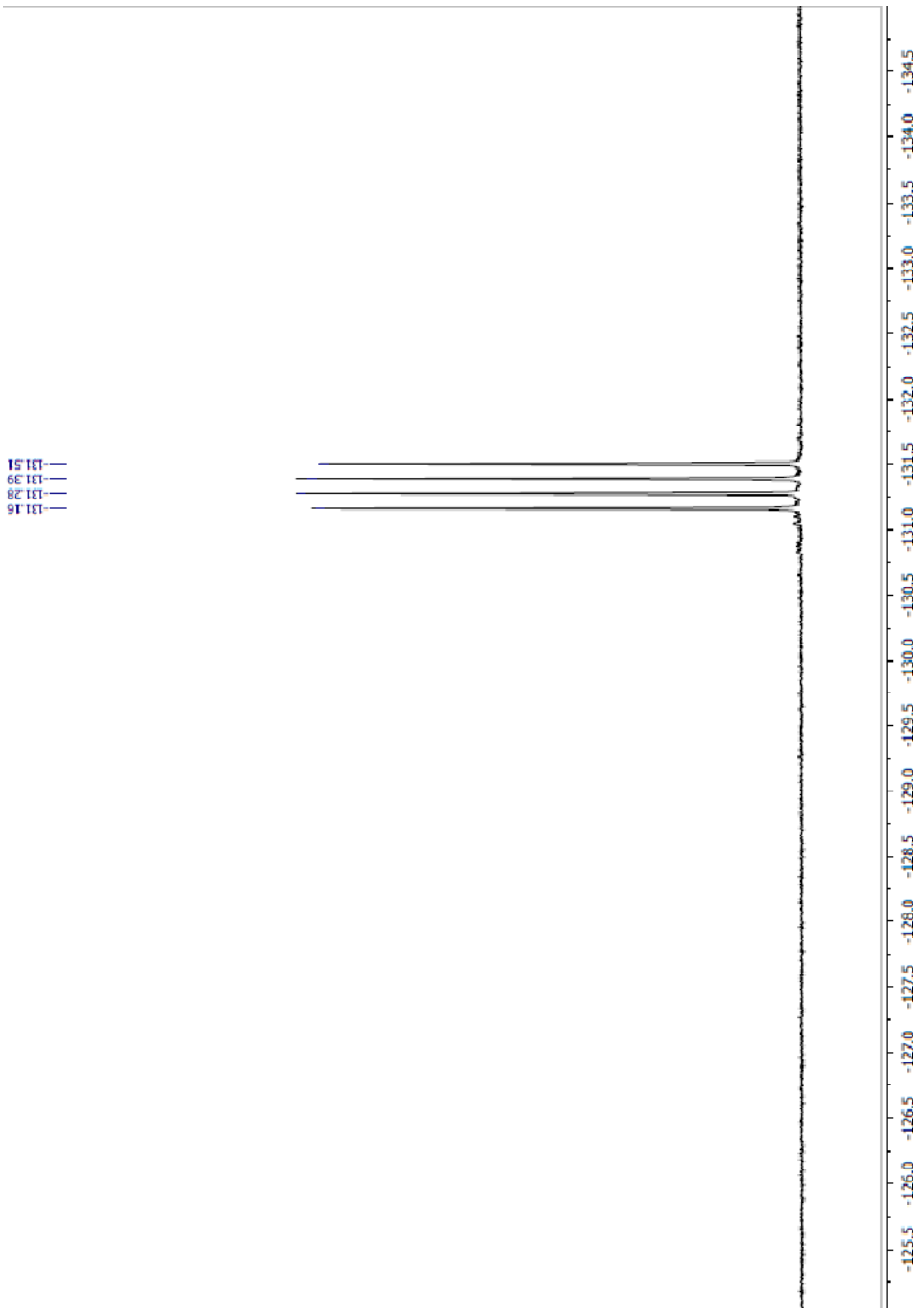
^{1}H NMR spectrum of 2.52



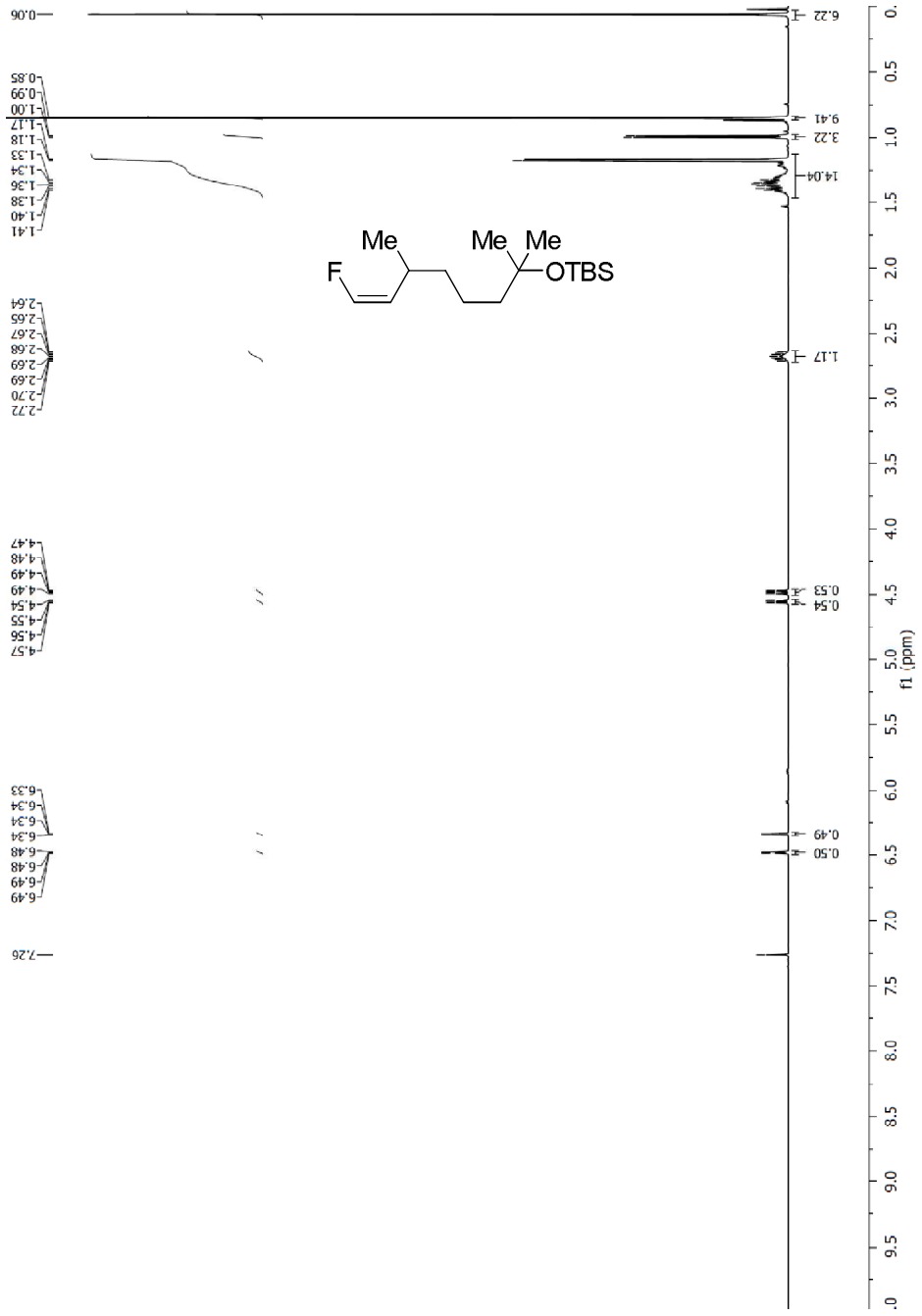
^{13}C NMR spectrum of 2.52



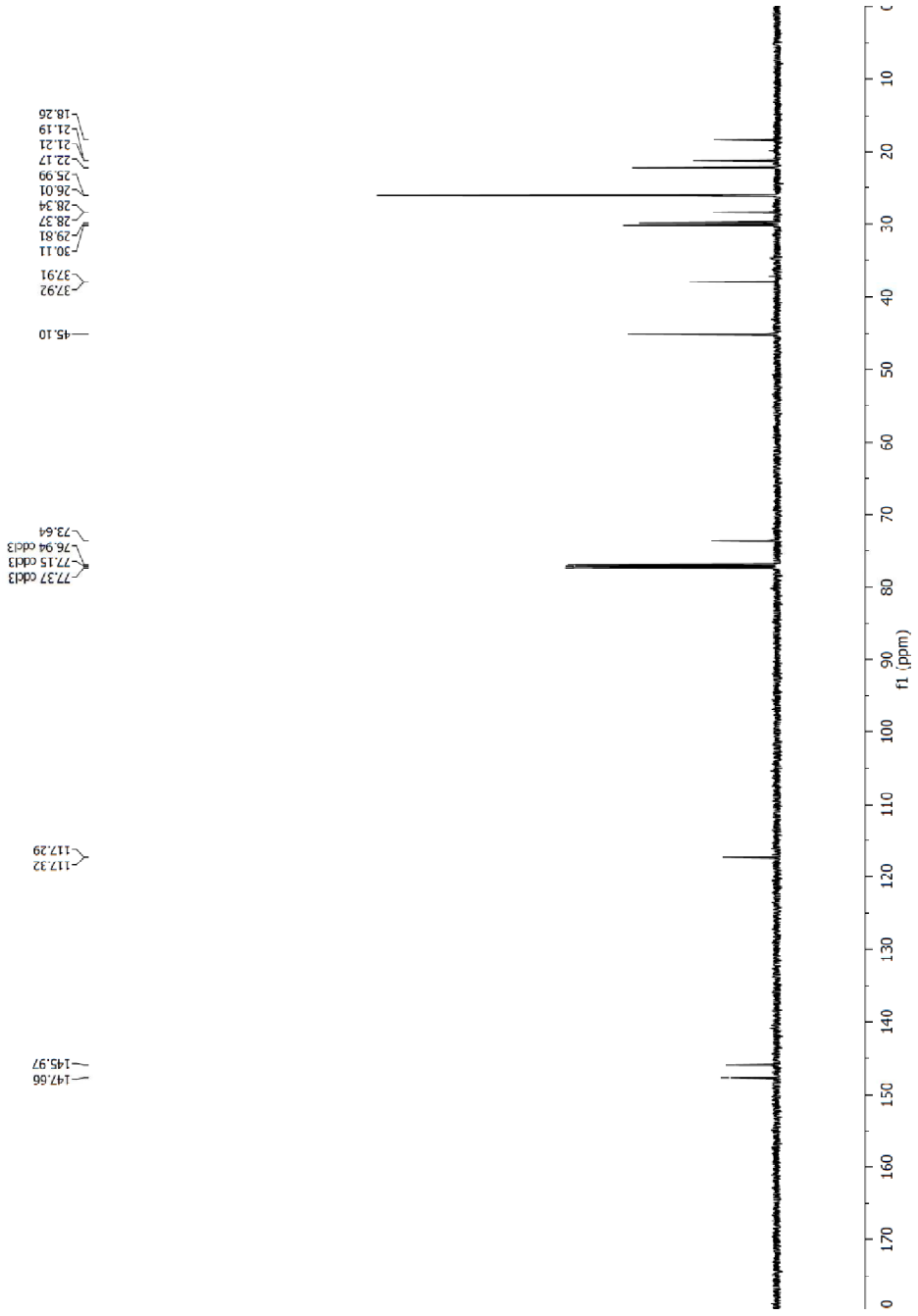
^{19}F NMR spectrum of 2.52



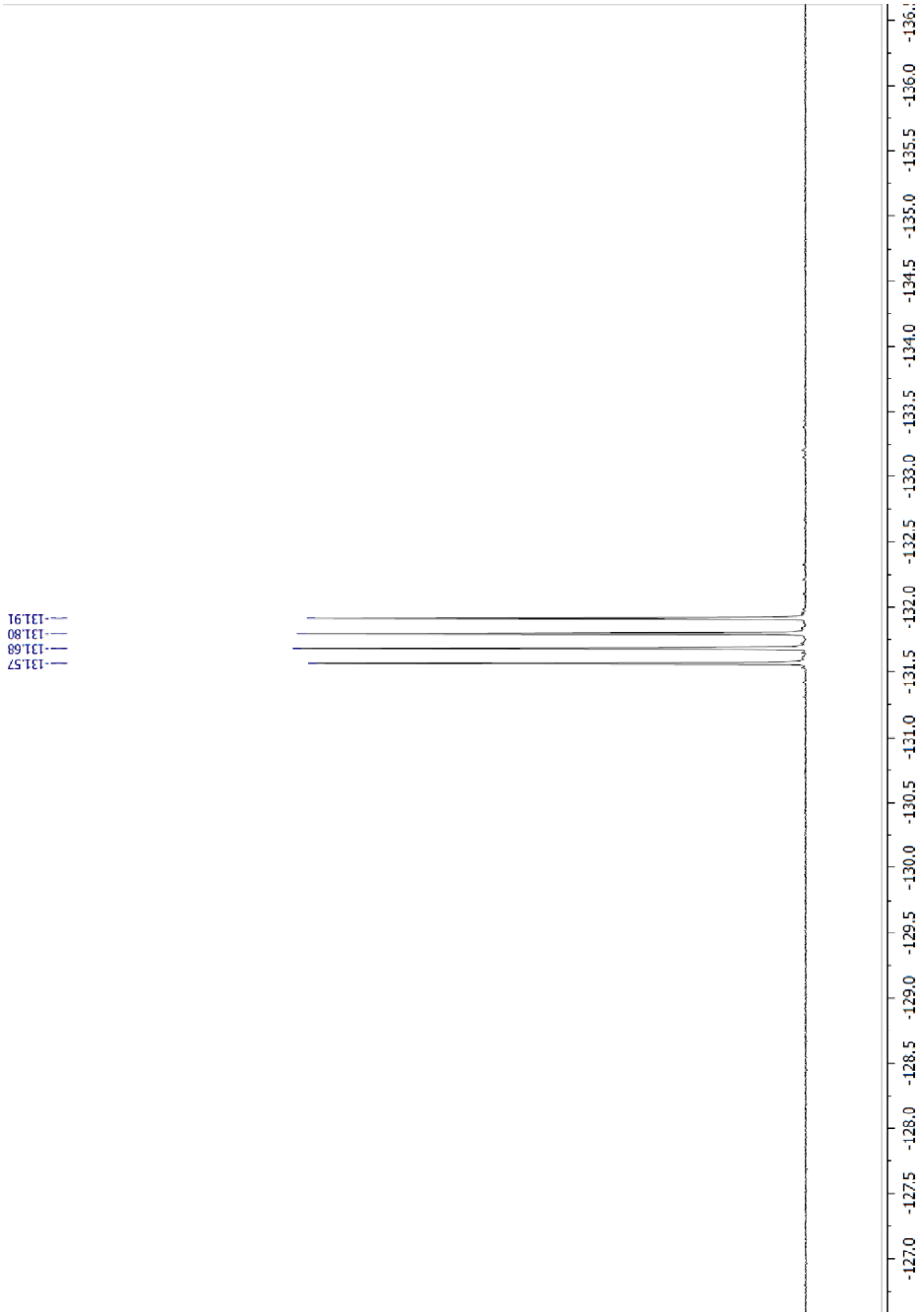
^{1}H NMR spectrum of 2.53



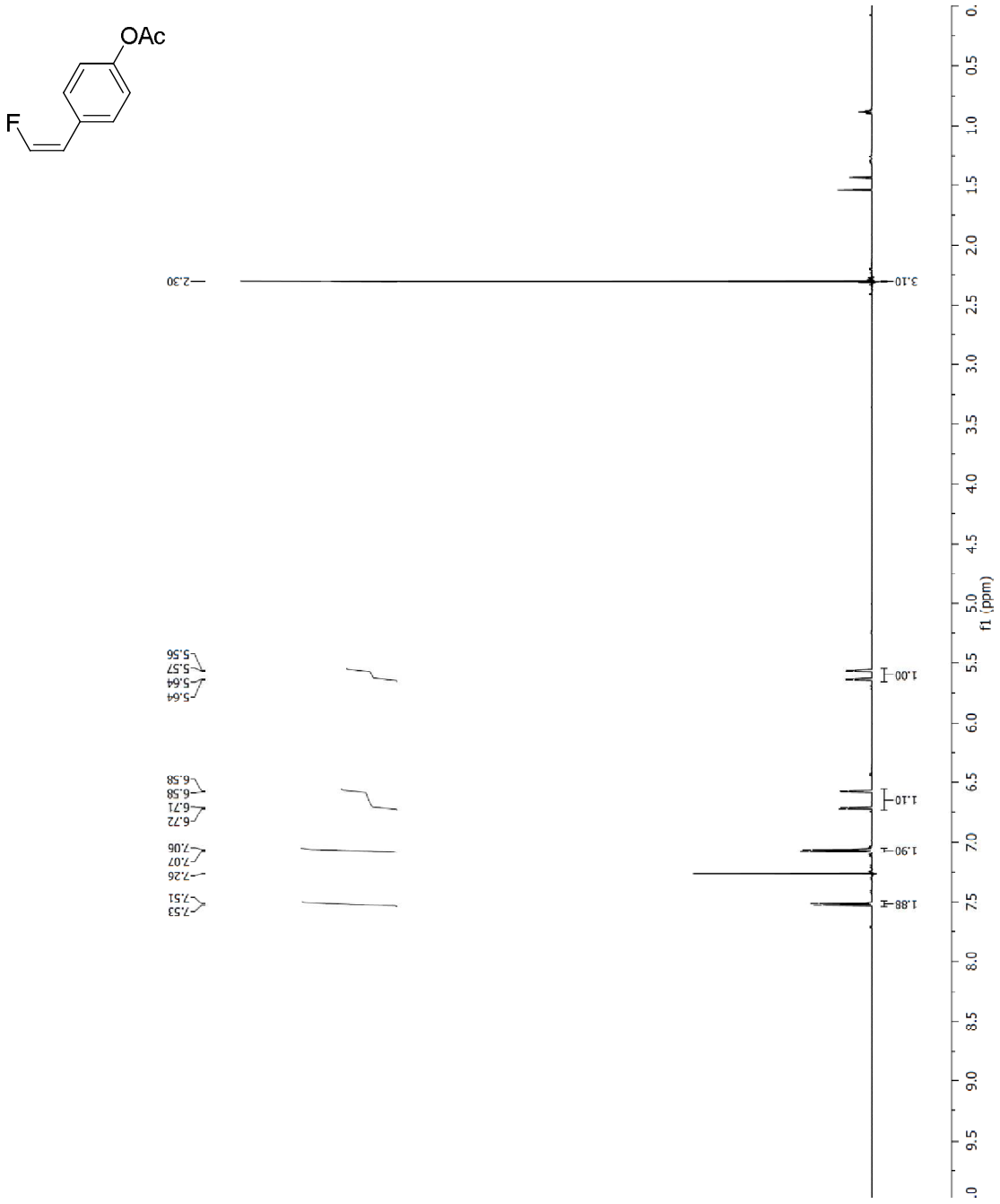
^{13}C NMR spectrum of 2.53



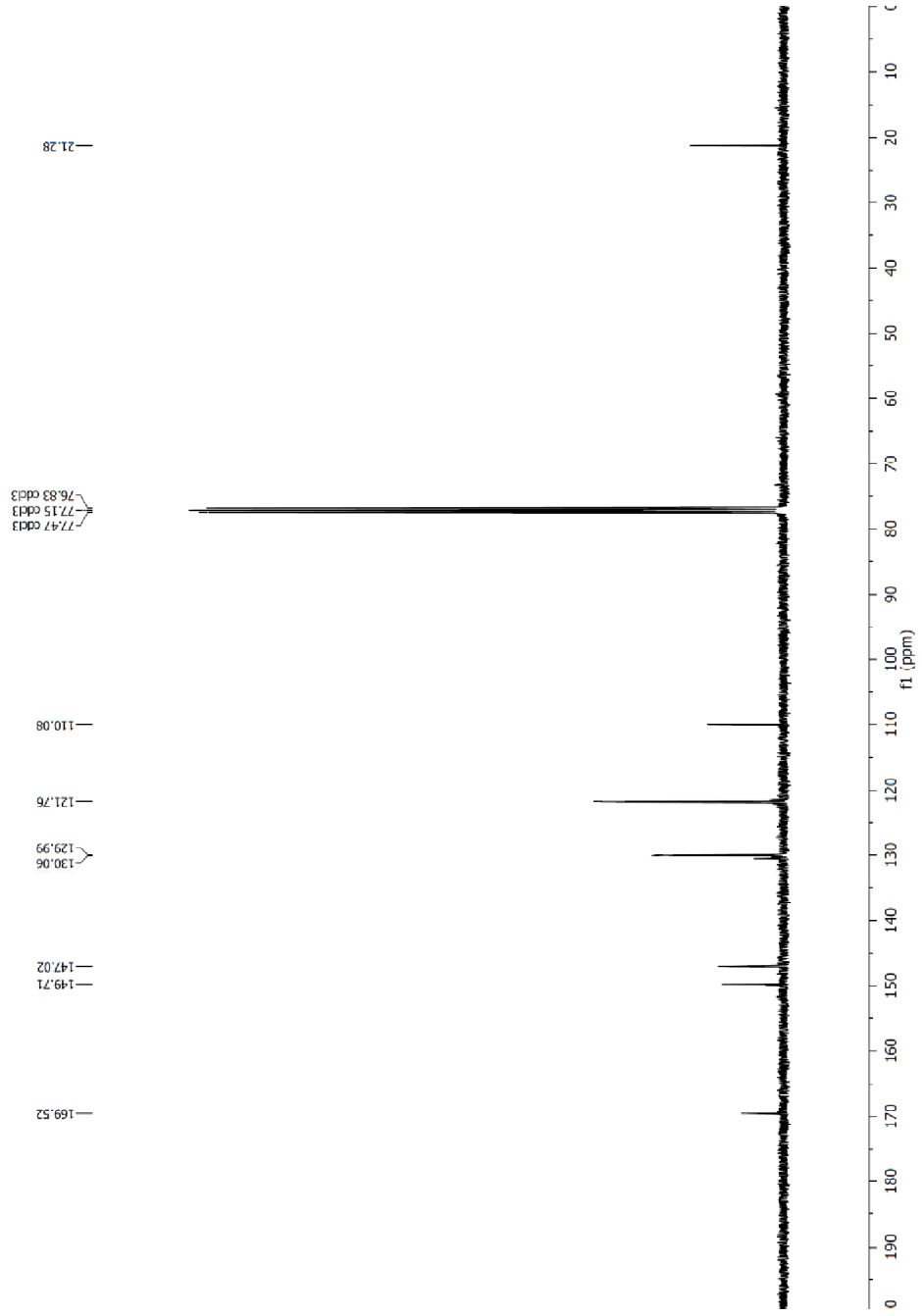
^{19}F NMR spectrum of 2.53



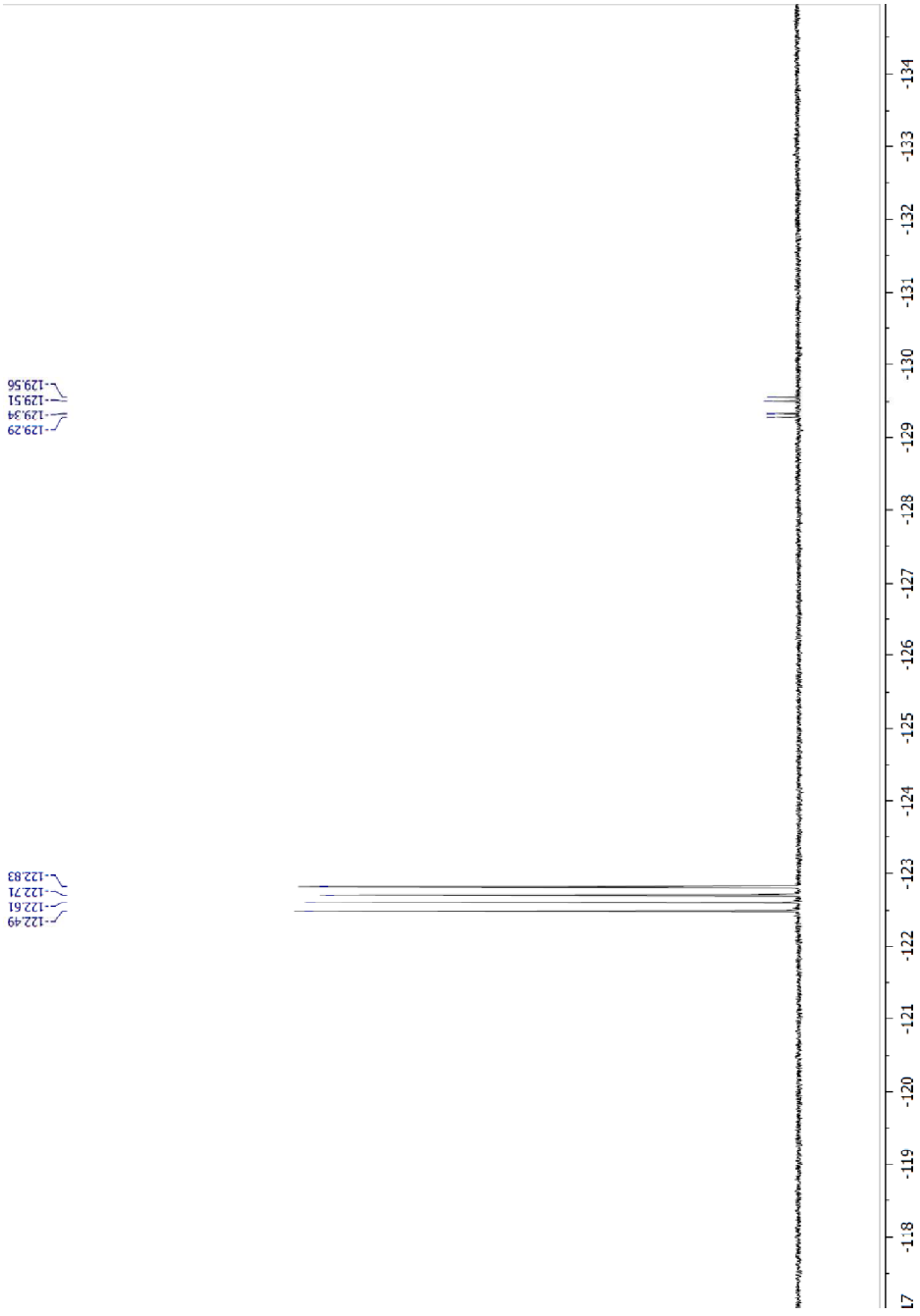
^{1}H NMR spectrum of 2.55



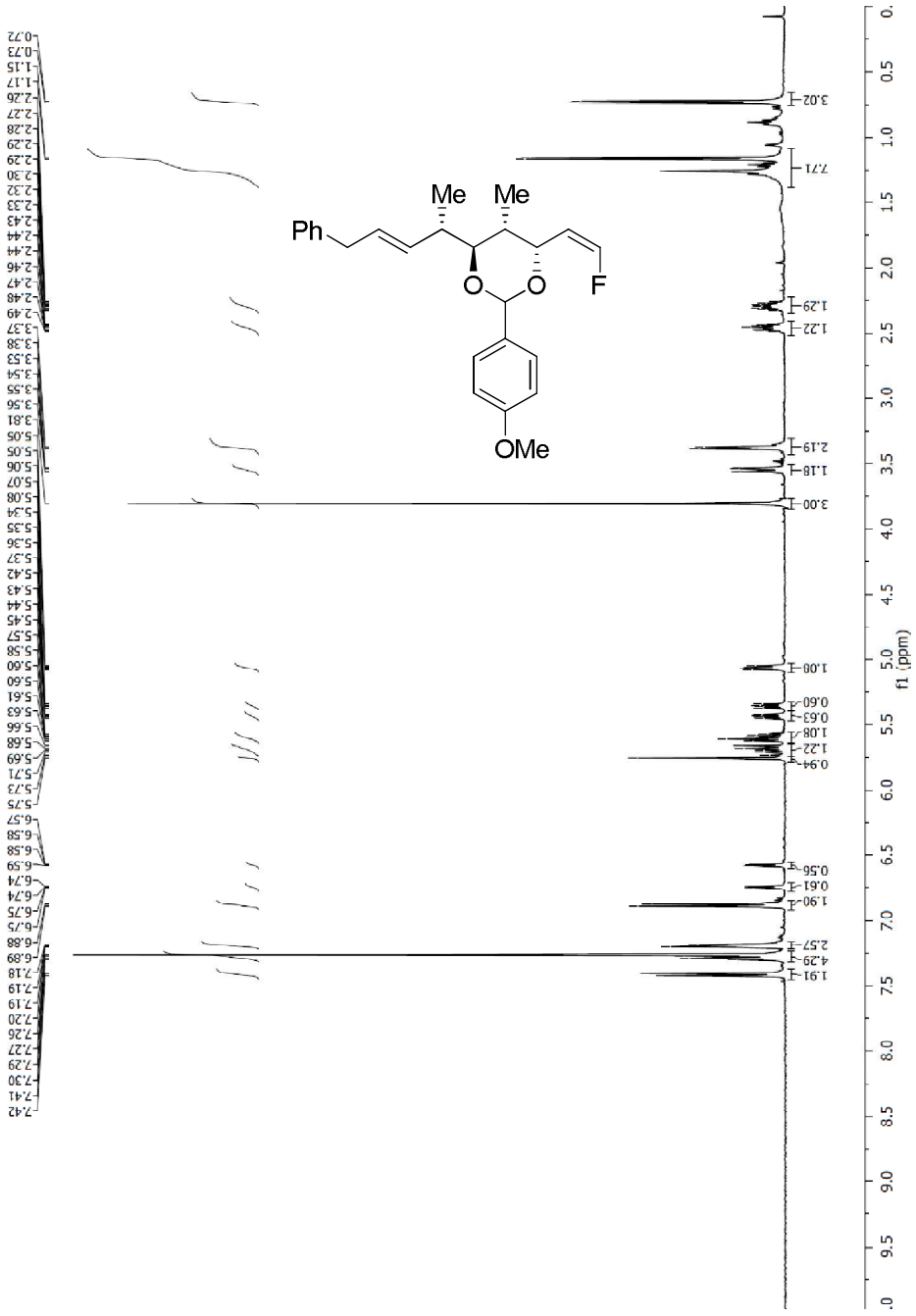
^{13}C NMR spectrum of 2.55



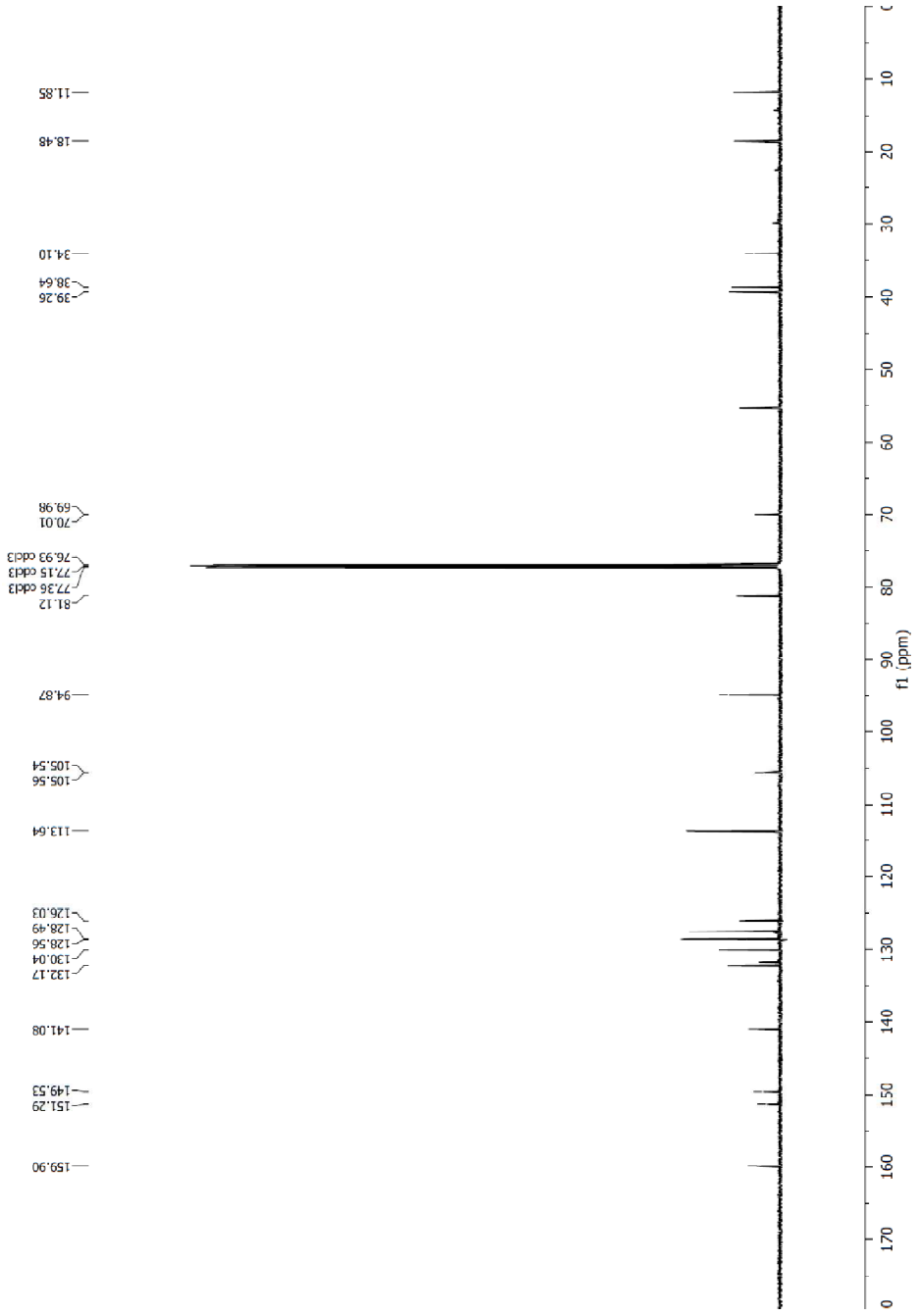
^{19}F NMR spectrum of 2.55



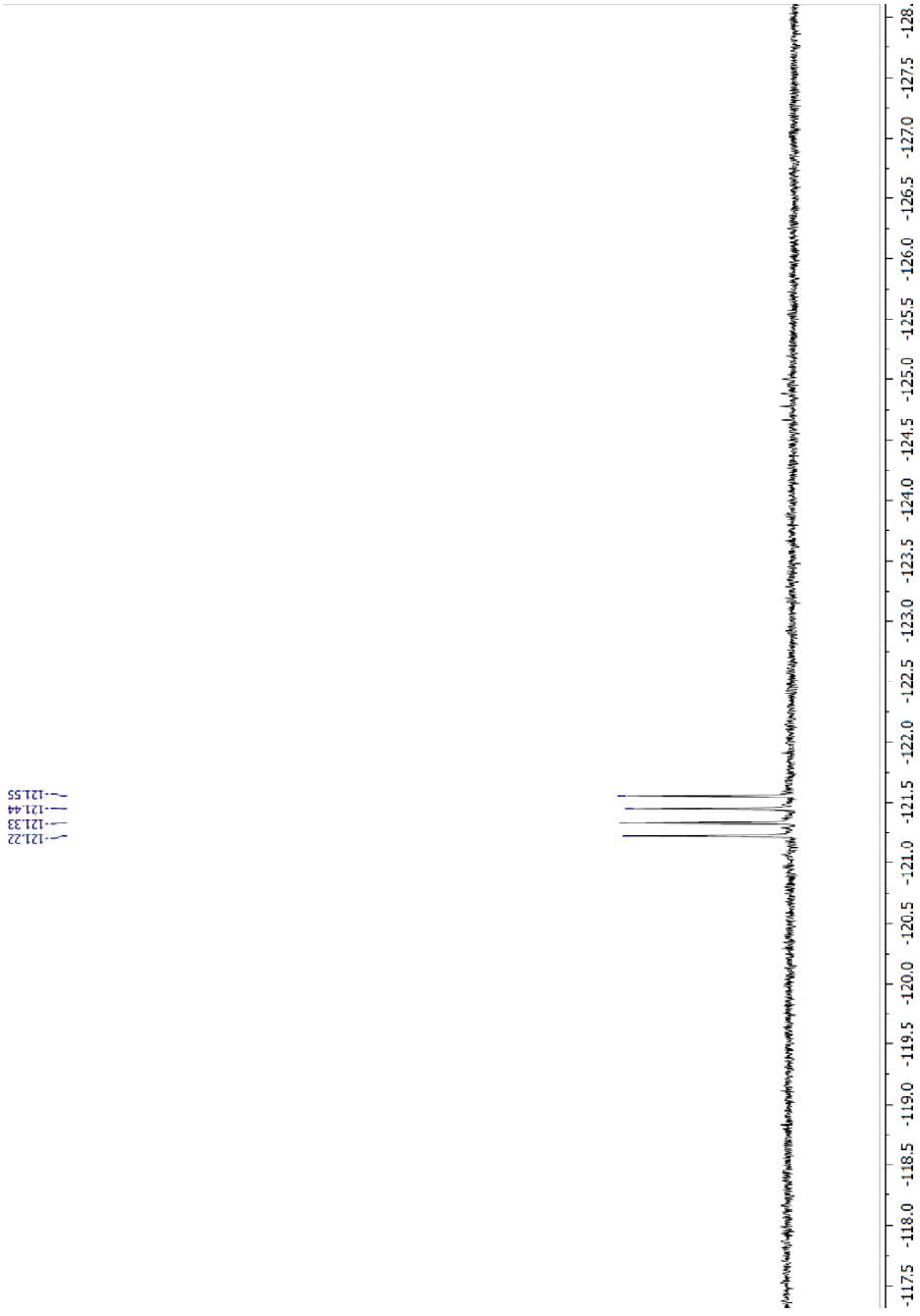
^{1}H NMR spectrum of 2.59



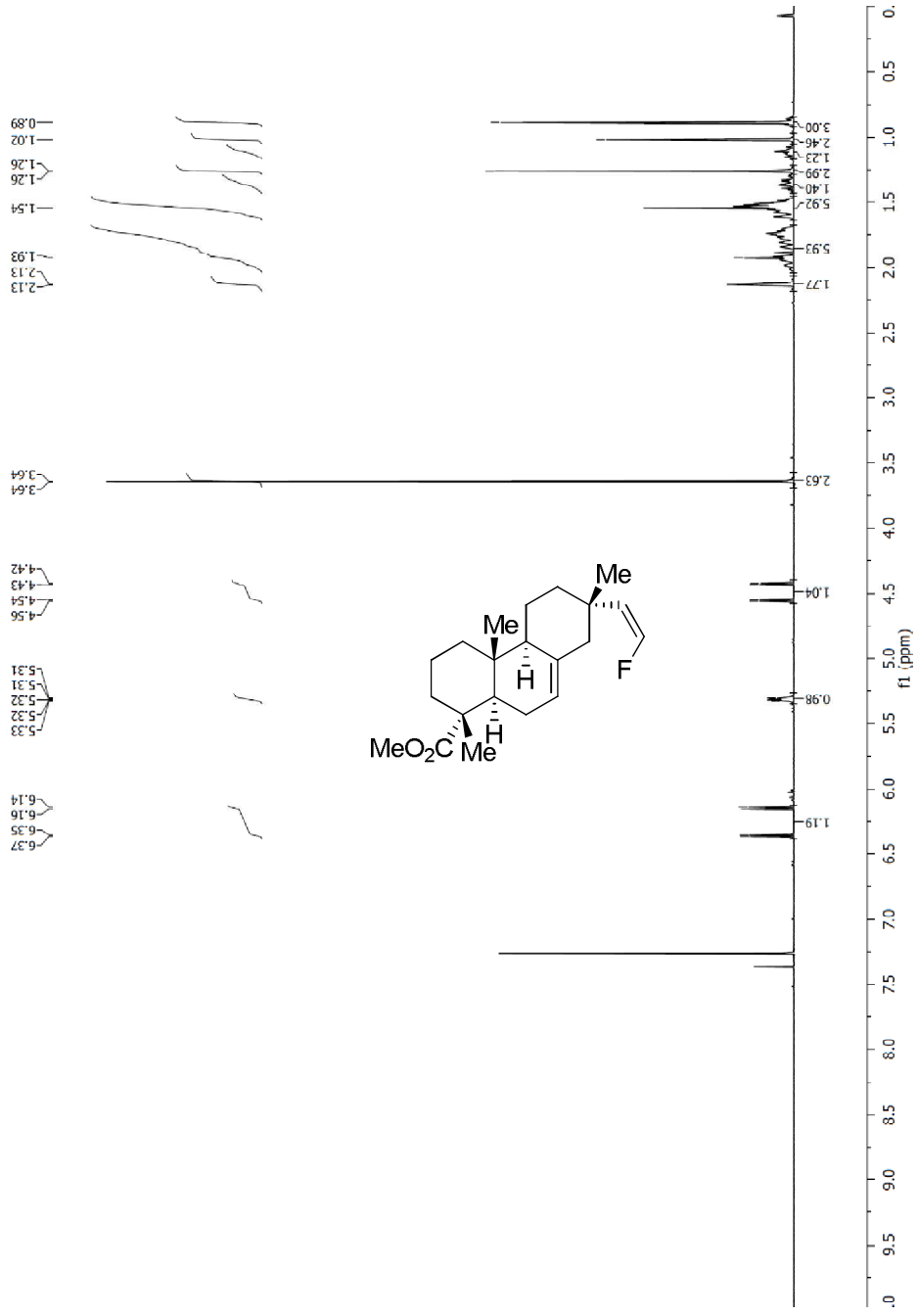
^{13}C NMR spectrum of 2.59



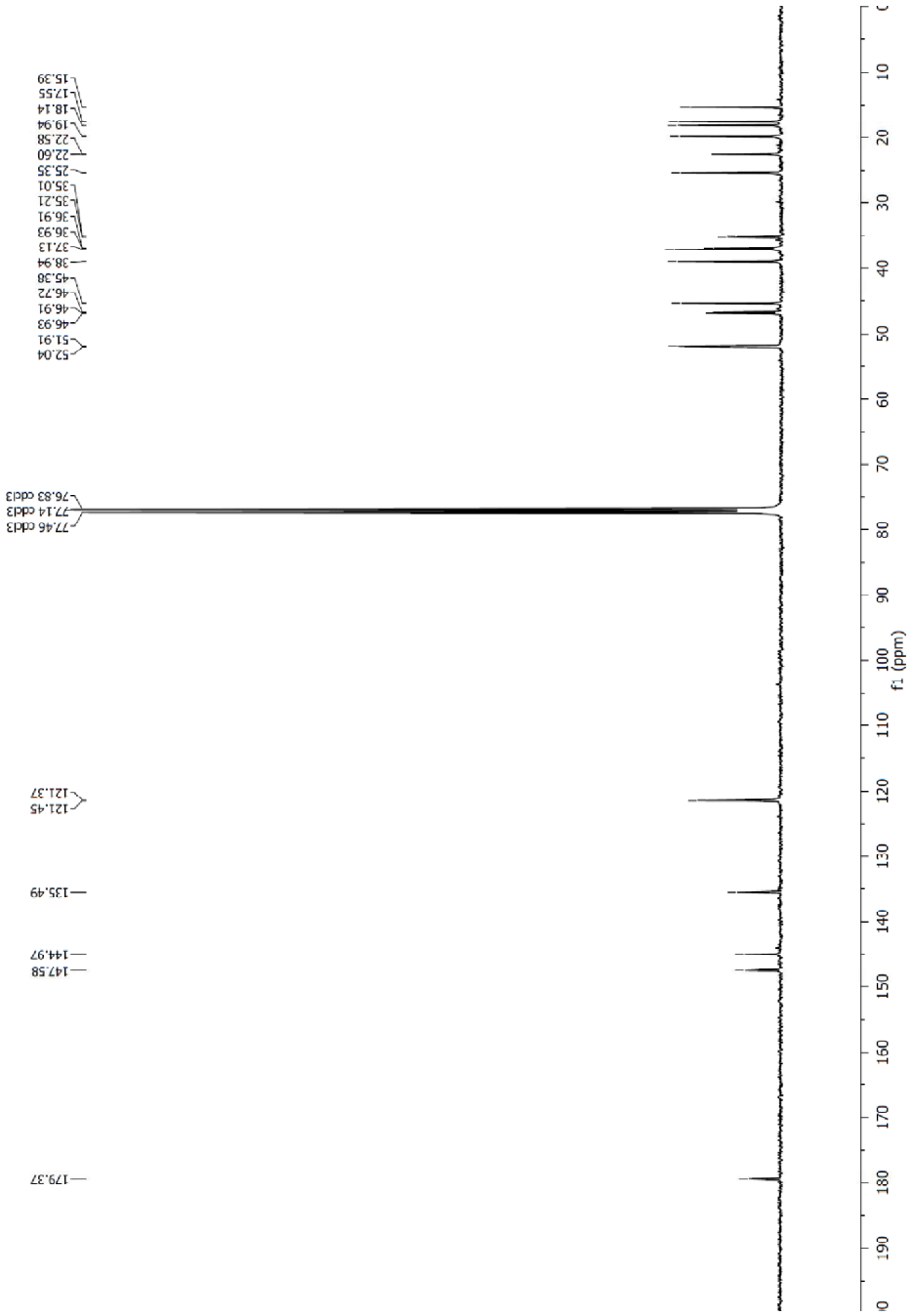
^{19}F NMR spectrum of 2.59



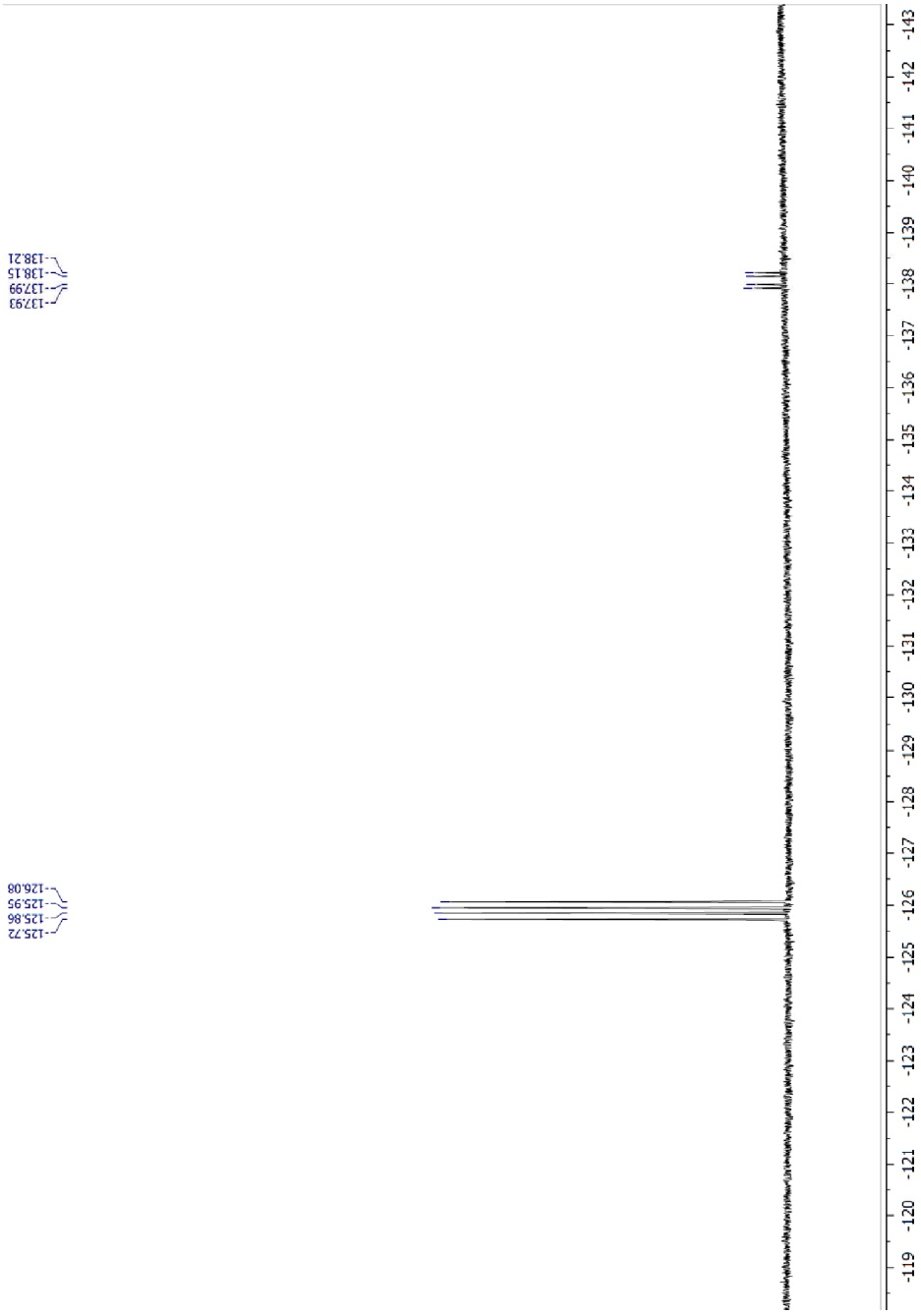
^{1}H NMR spectrum of 2.60



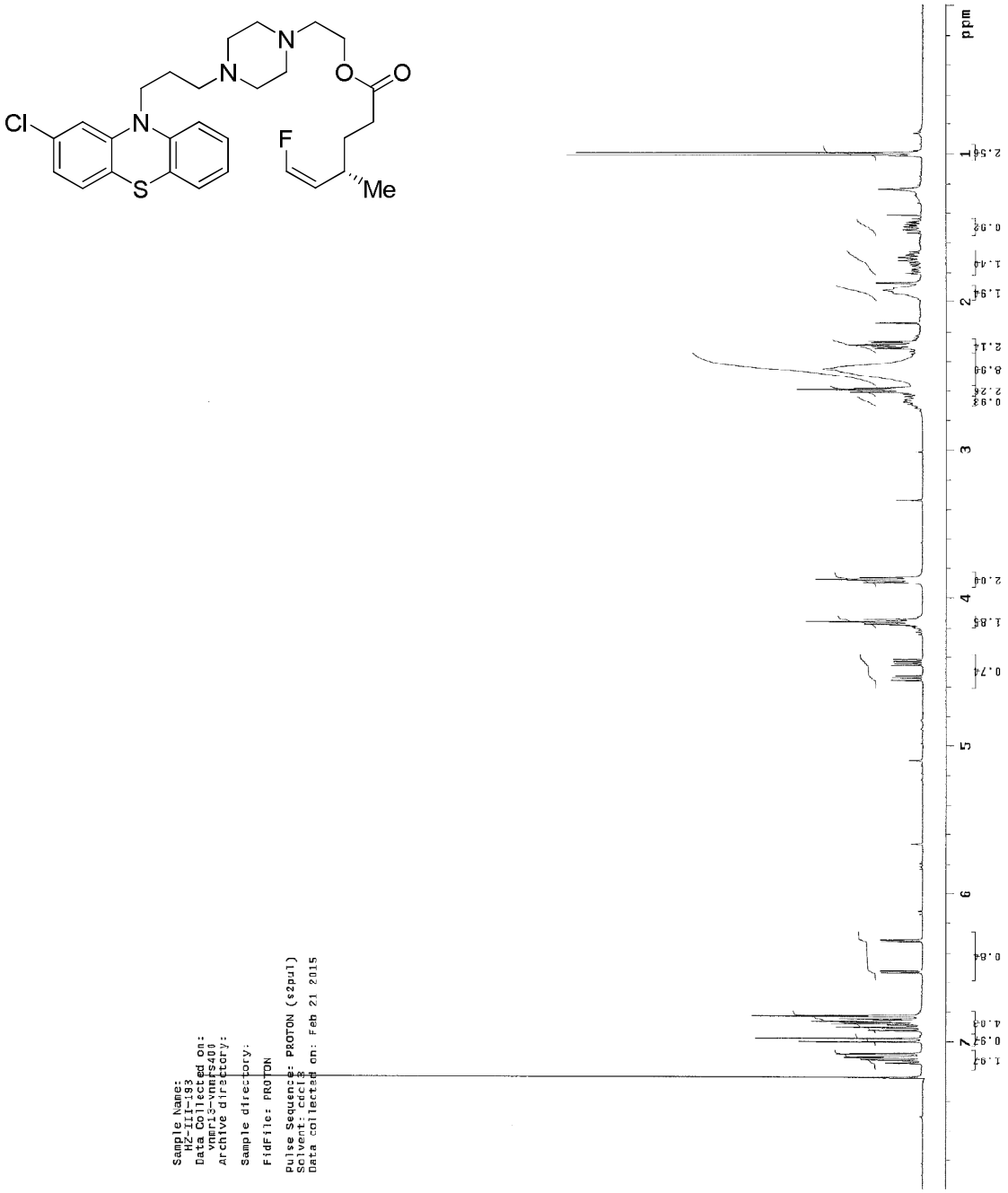
^{13}C NMR spectrum of 2.60



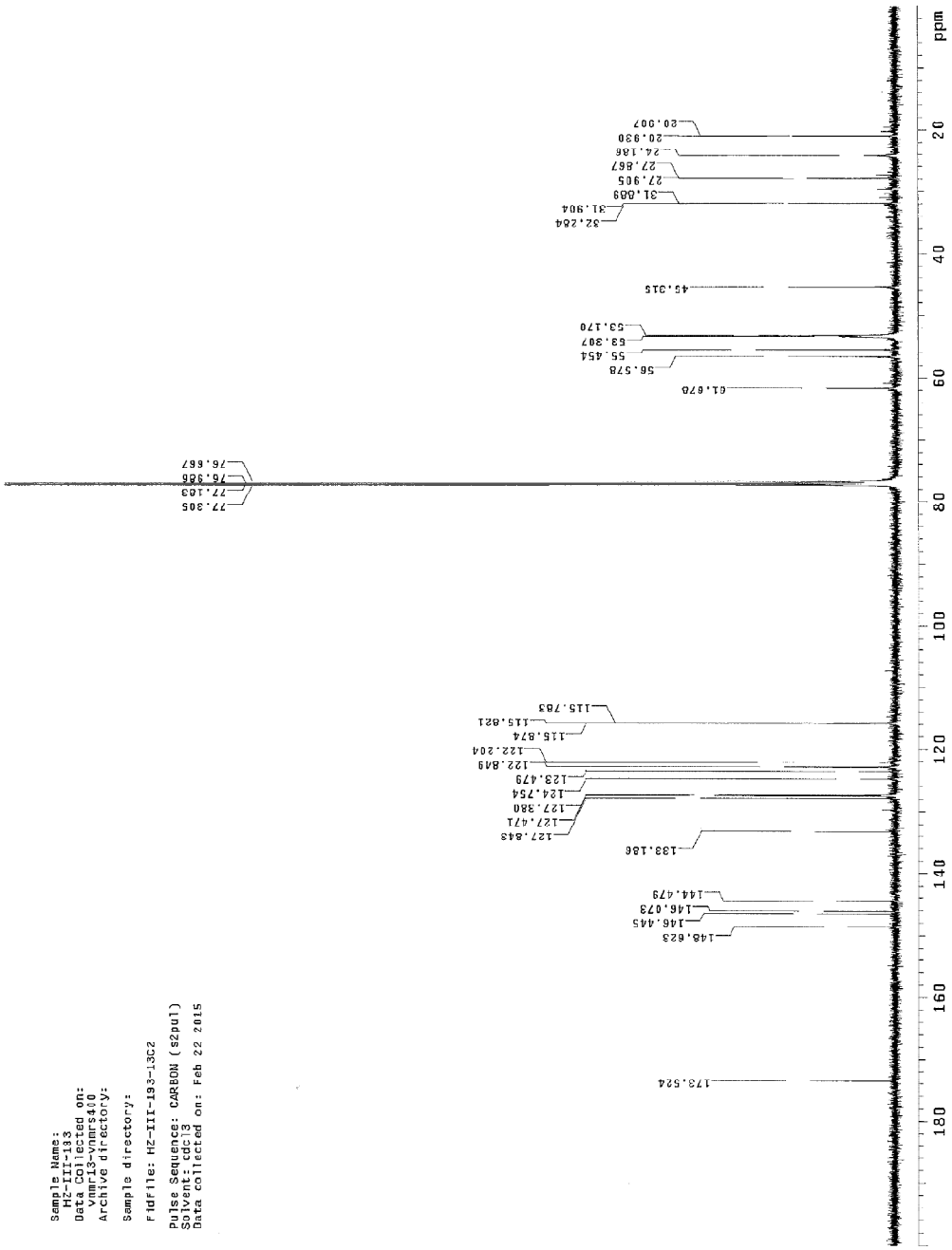
^{19}F NMR spectrum of 2.60



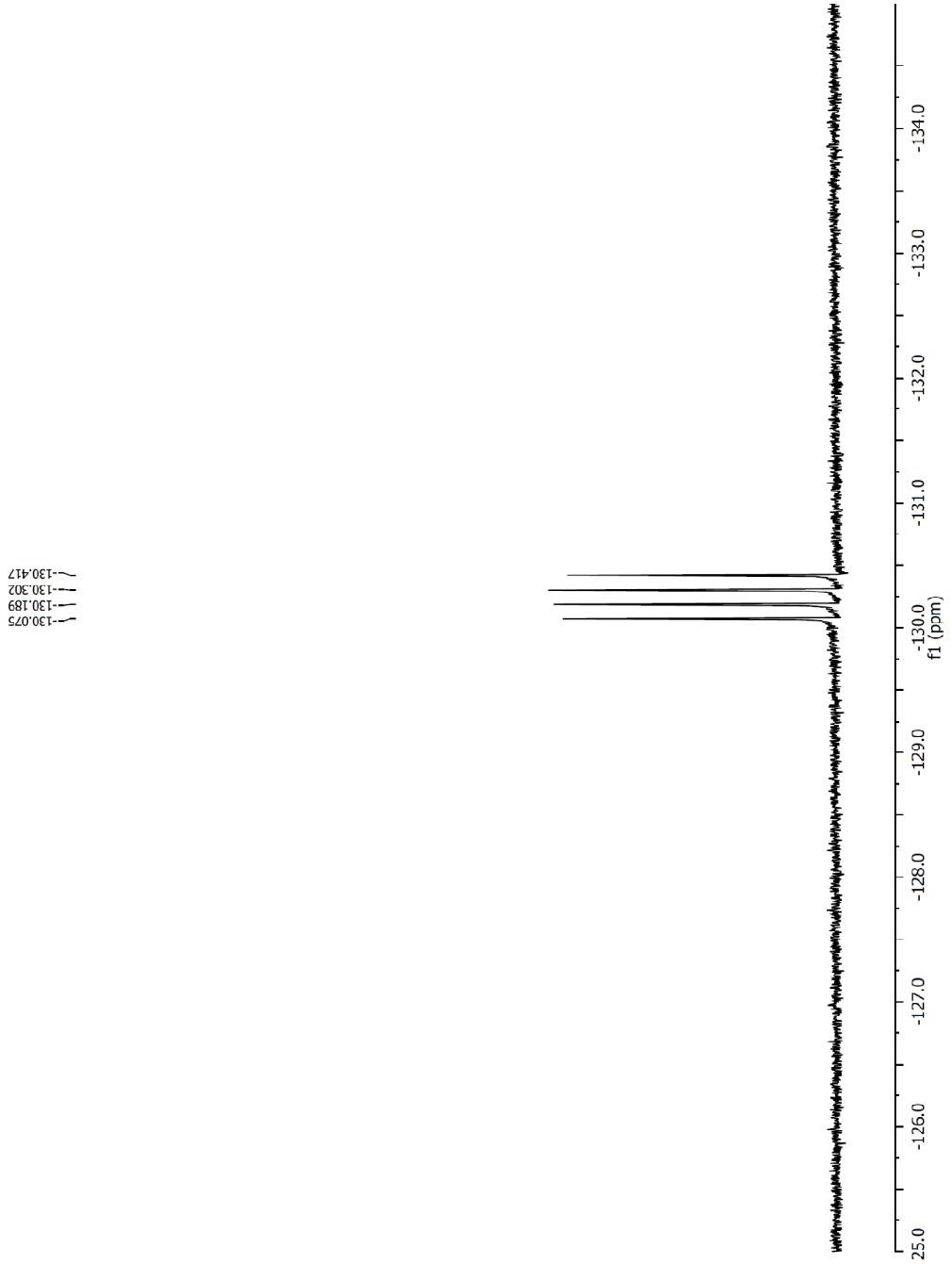
^{1}H NMR spectrum of 2.61



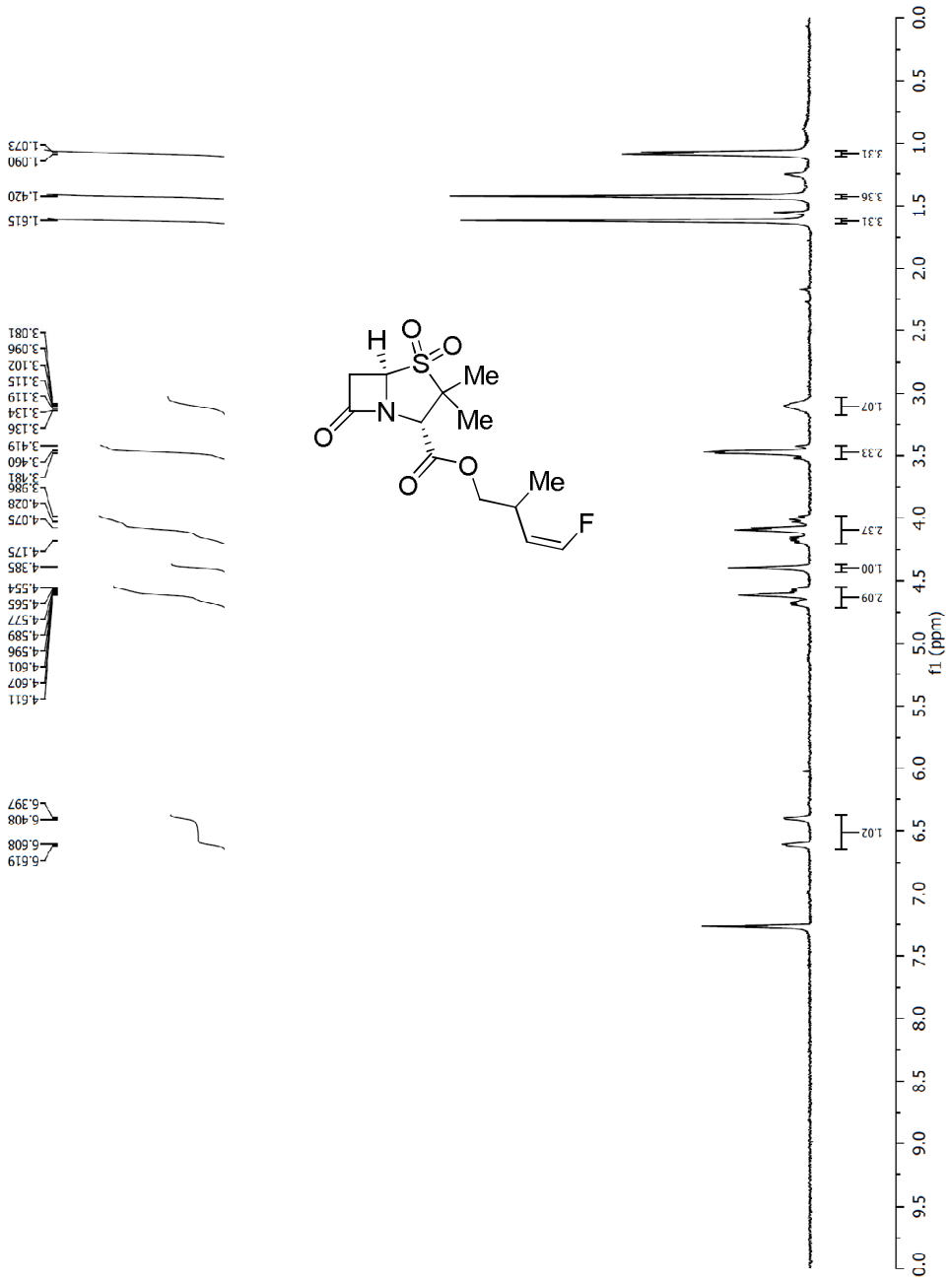
^{13}C NMR spectrum of 2.61



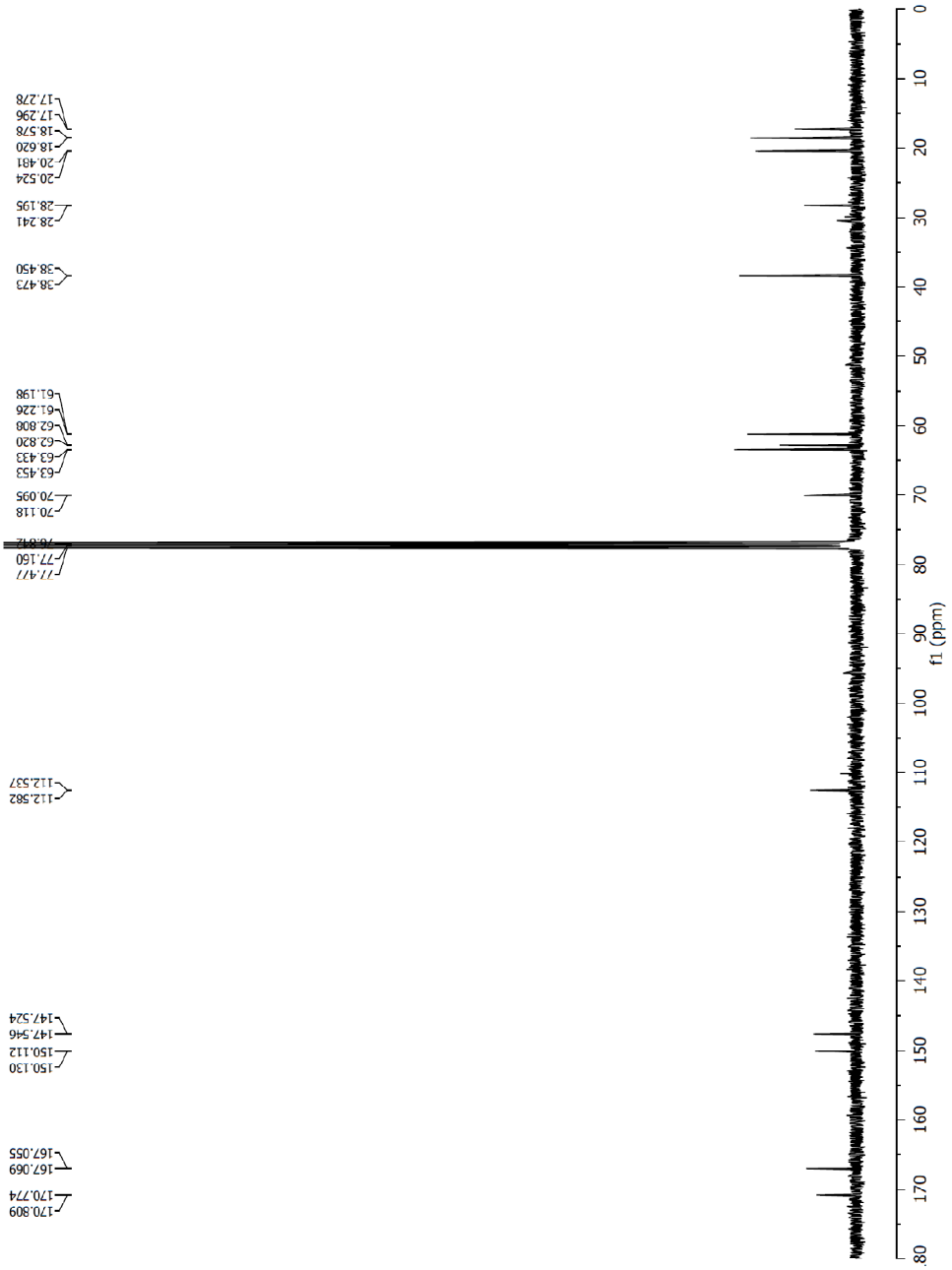
^{19}F NMR spectrum of 2.61



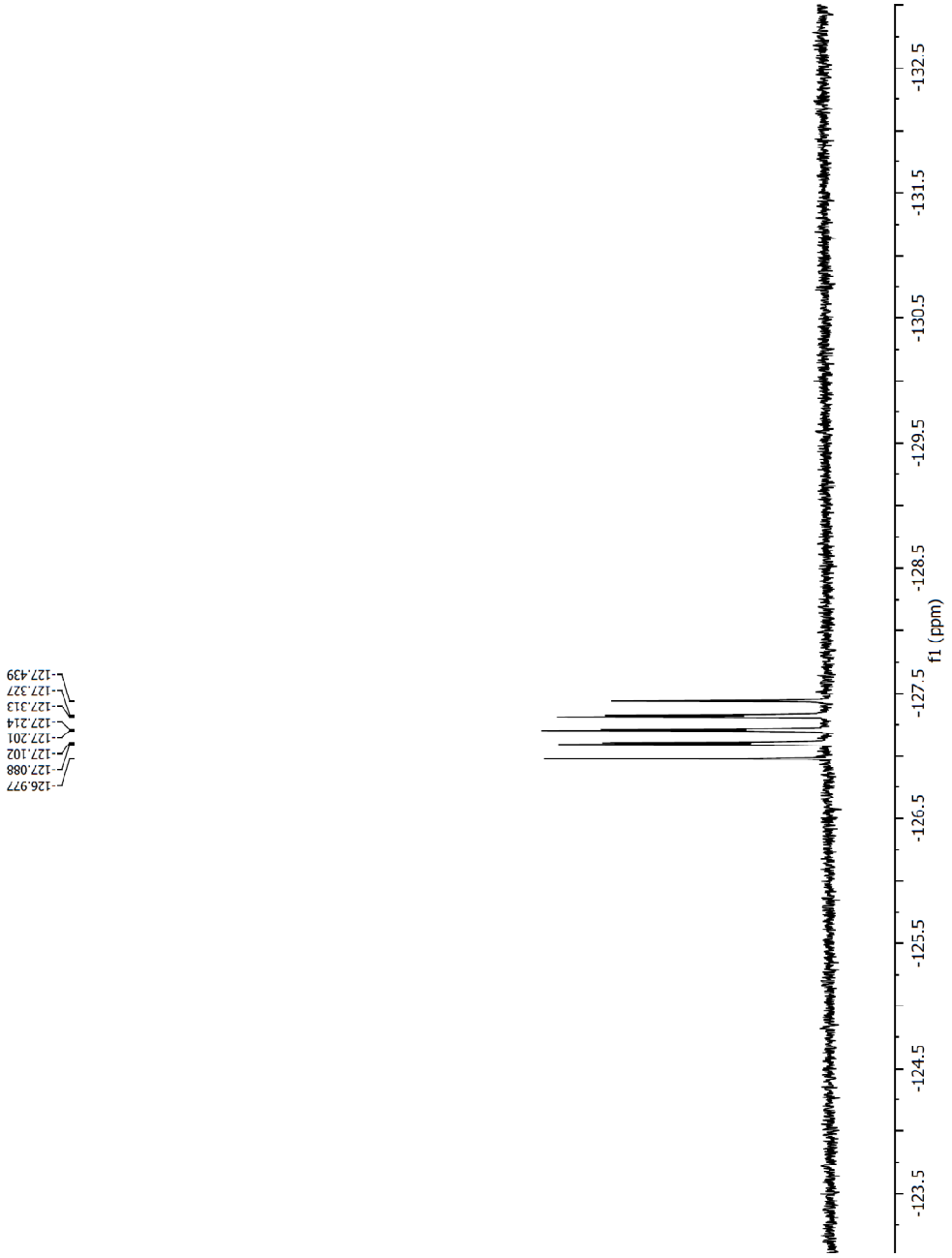
^{1}H NMR spectrum of 2.62



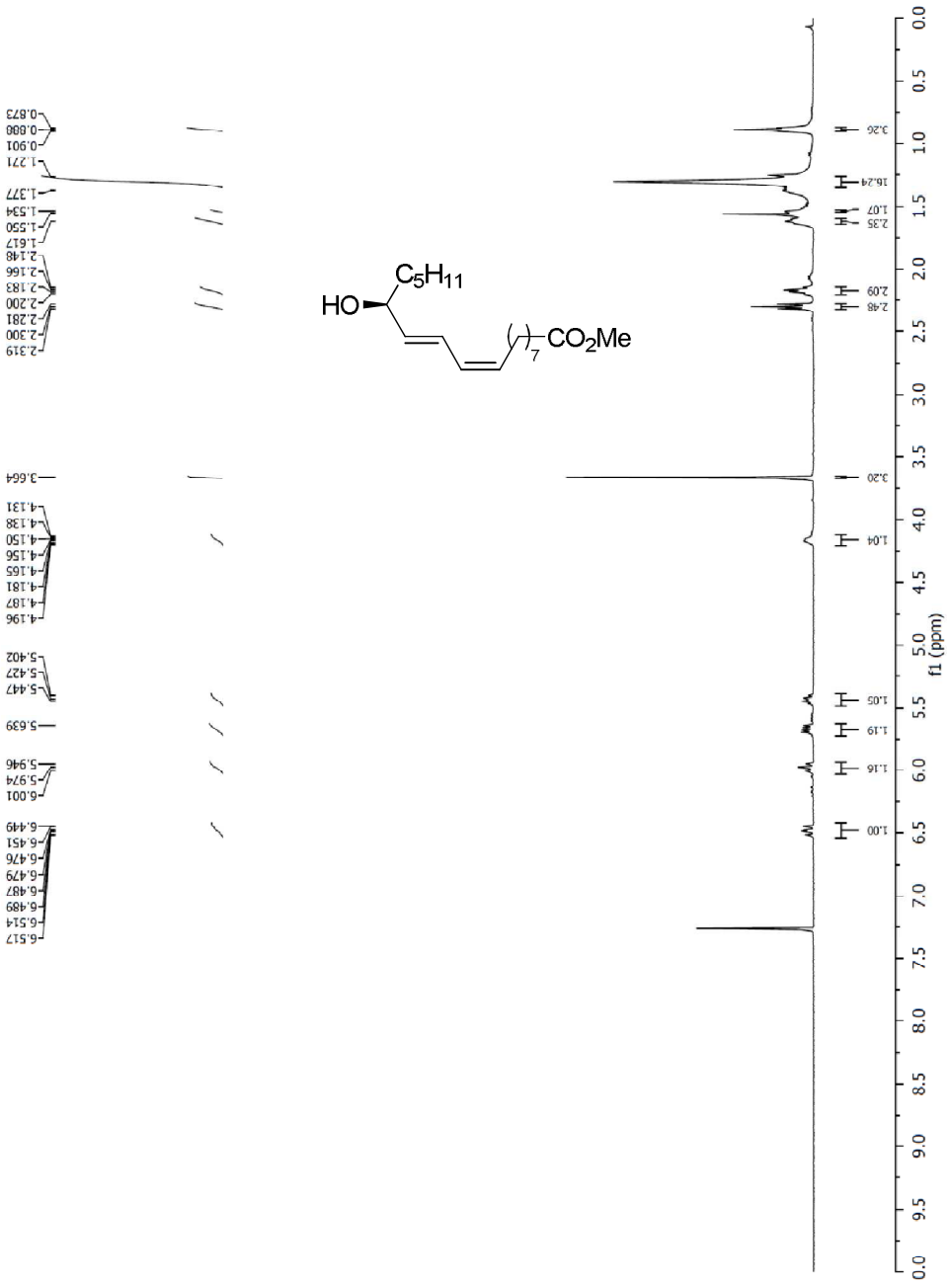
^{13}C NMR spectrum of 2.62



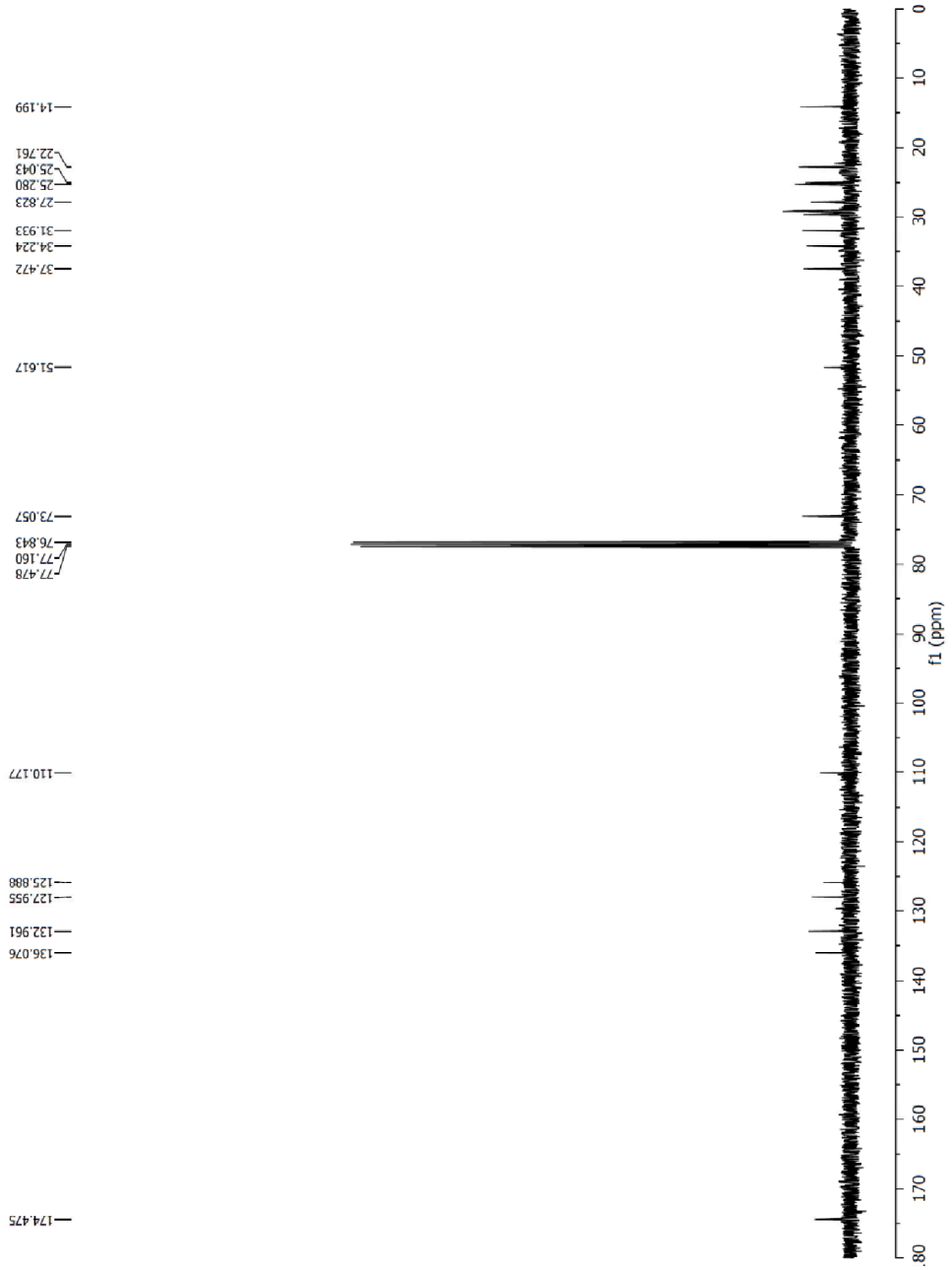
^{19}F NMR spectrum of 2.62



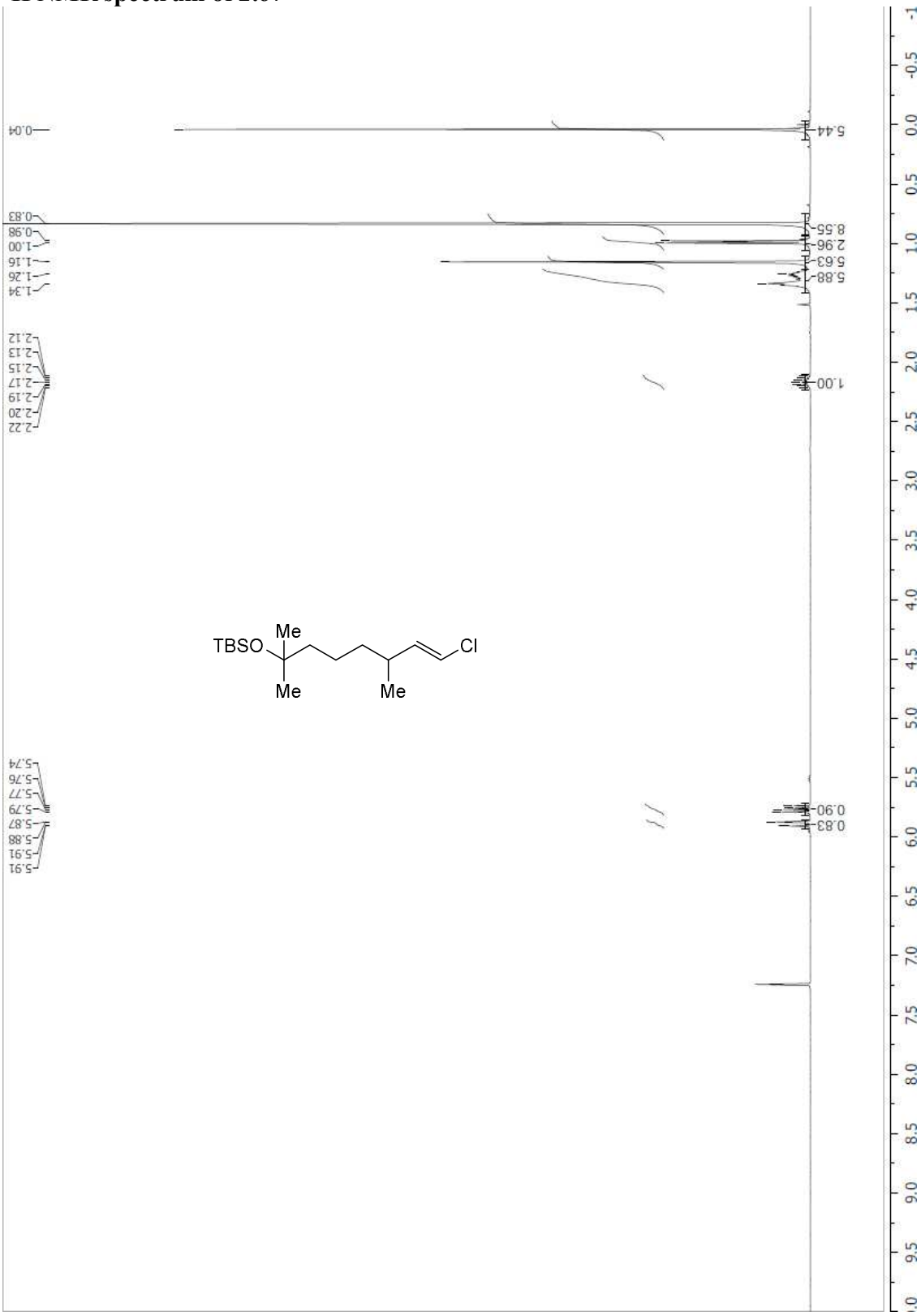
^{1}H NMR spectrum of (*S*)-coriolic acid methyl ester



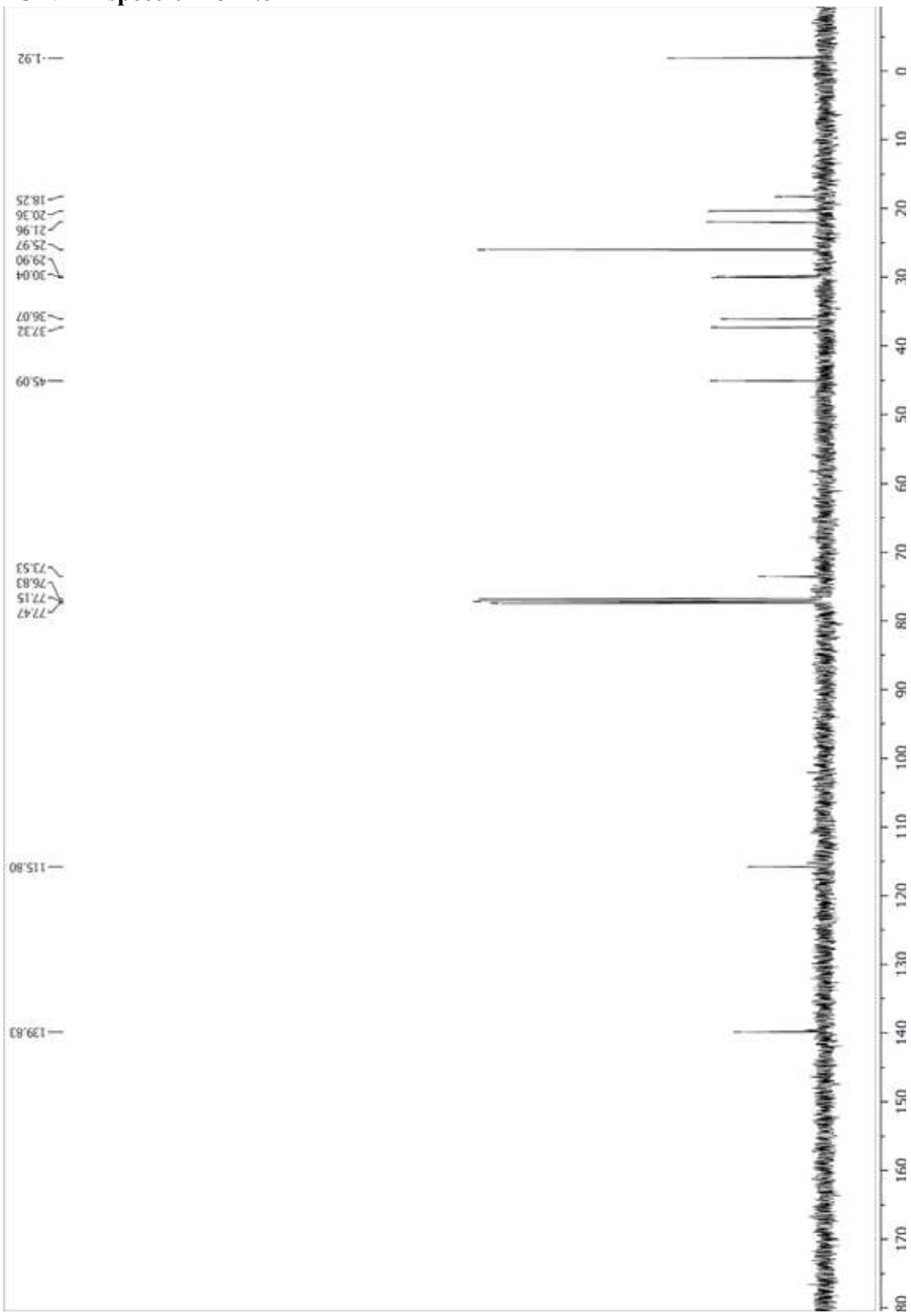
^{13}C NMR spectrum of (*S*)-coriolic acid methyl ester



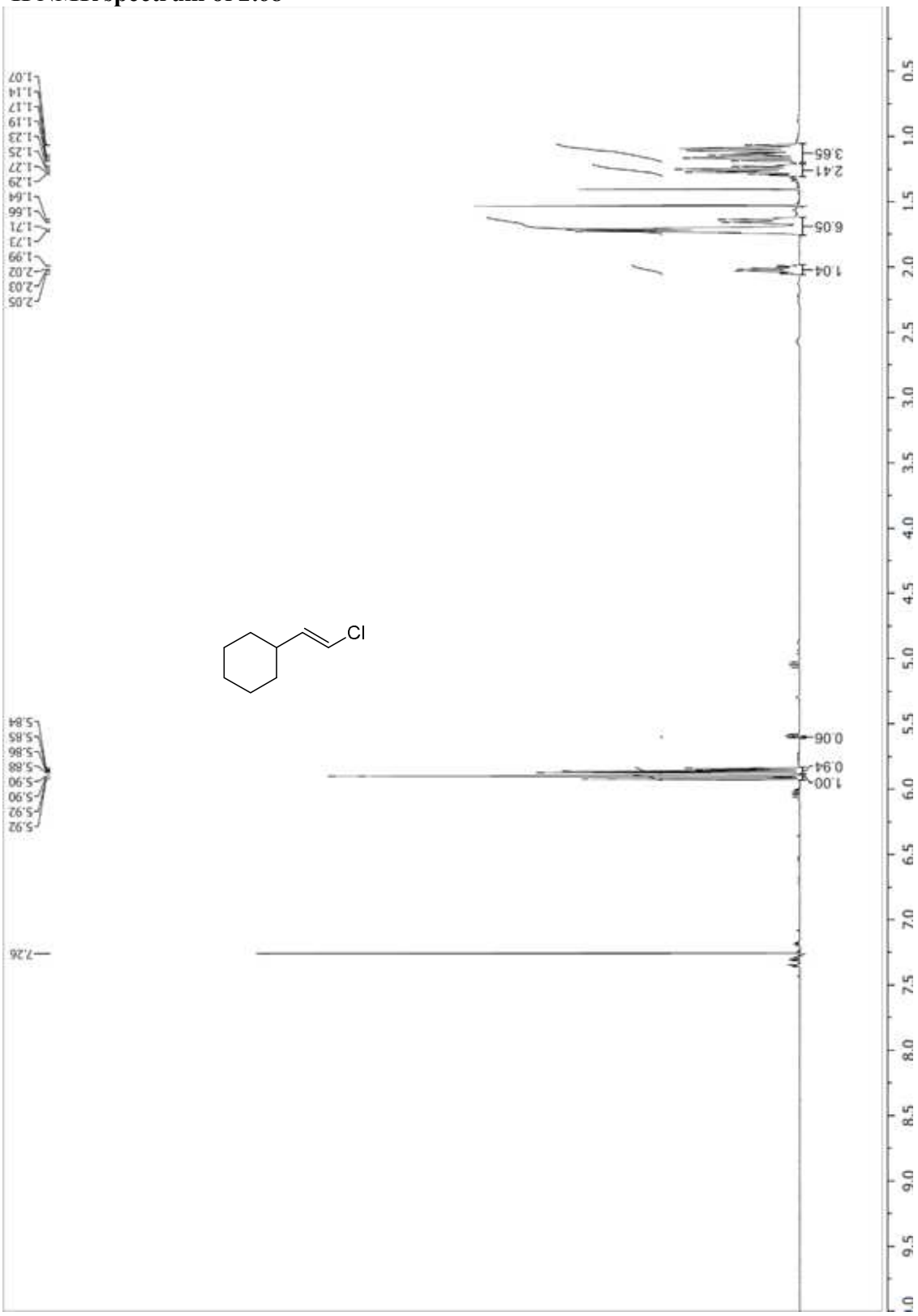
^{1}H NMR spectrum of 2.67



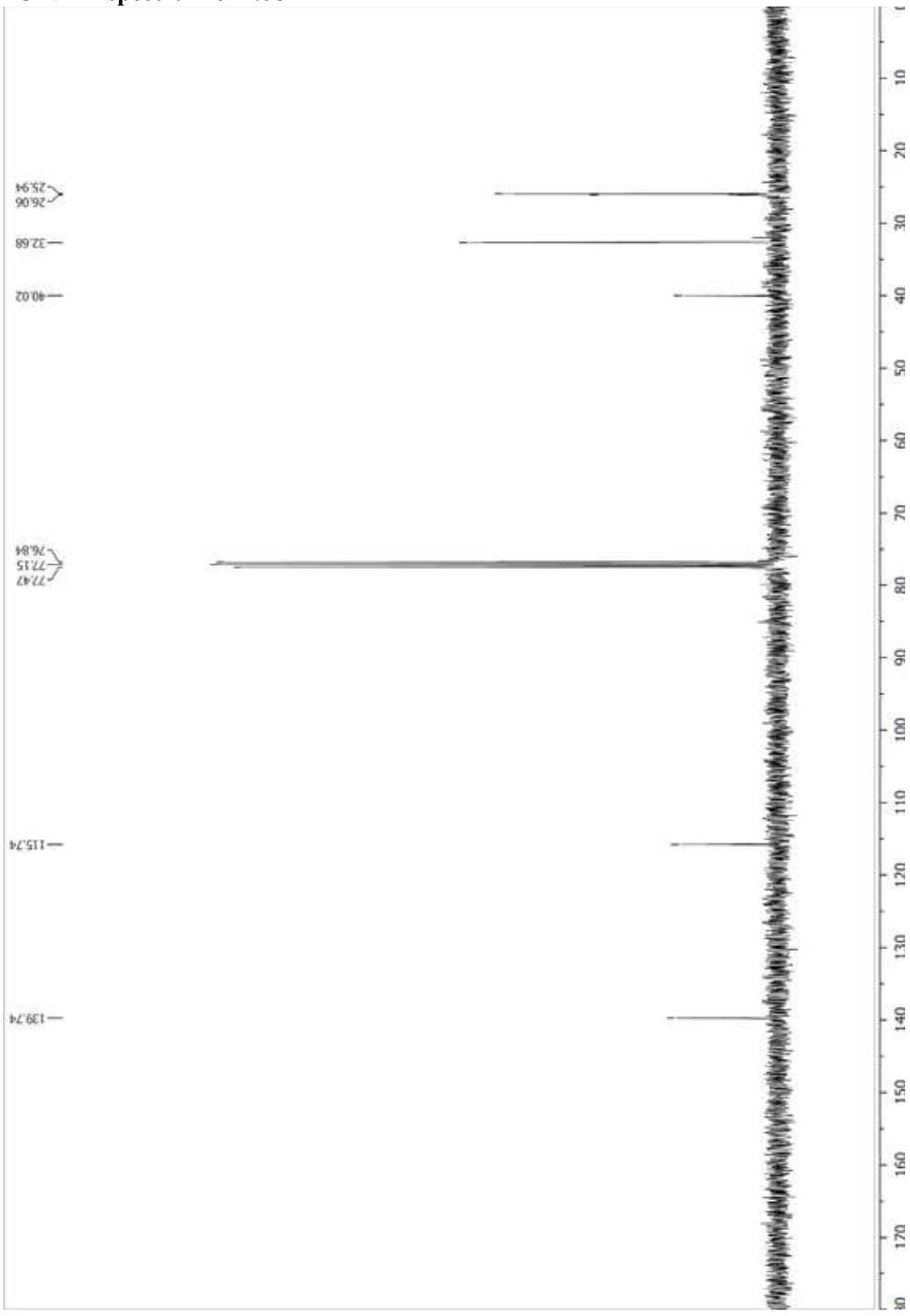
^{13}C NMR spectrum of 2.67



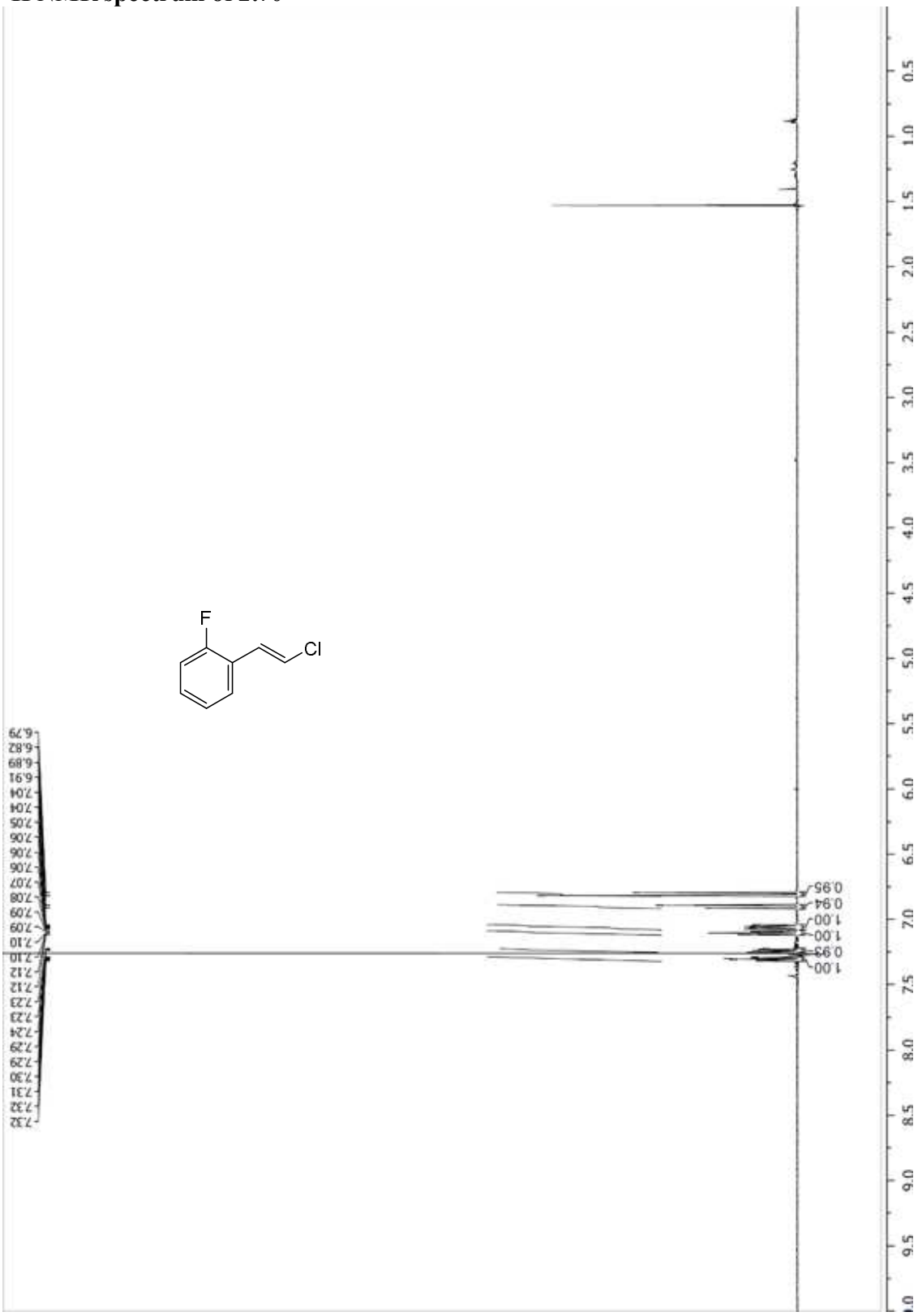
^{1}H NMR spectrum of 2.68



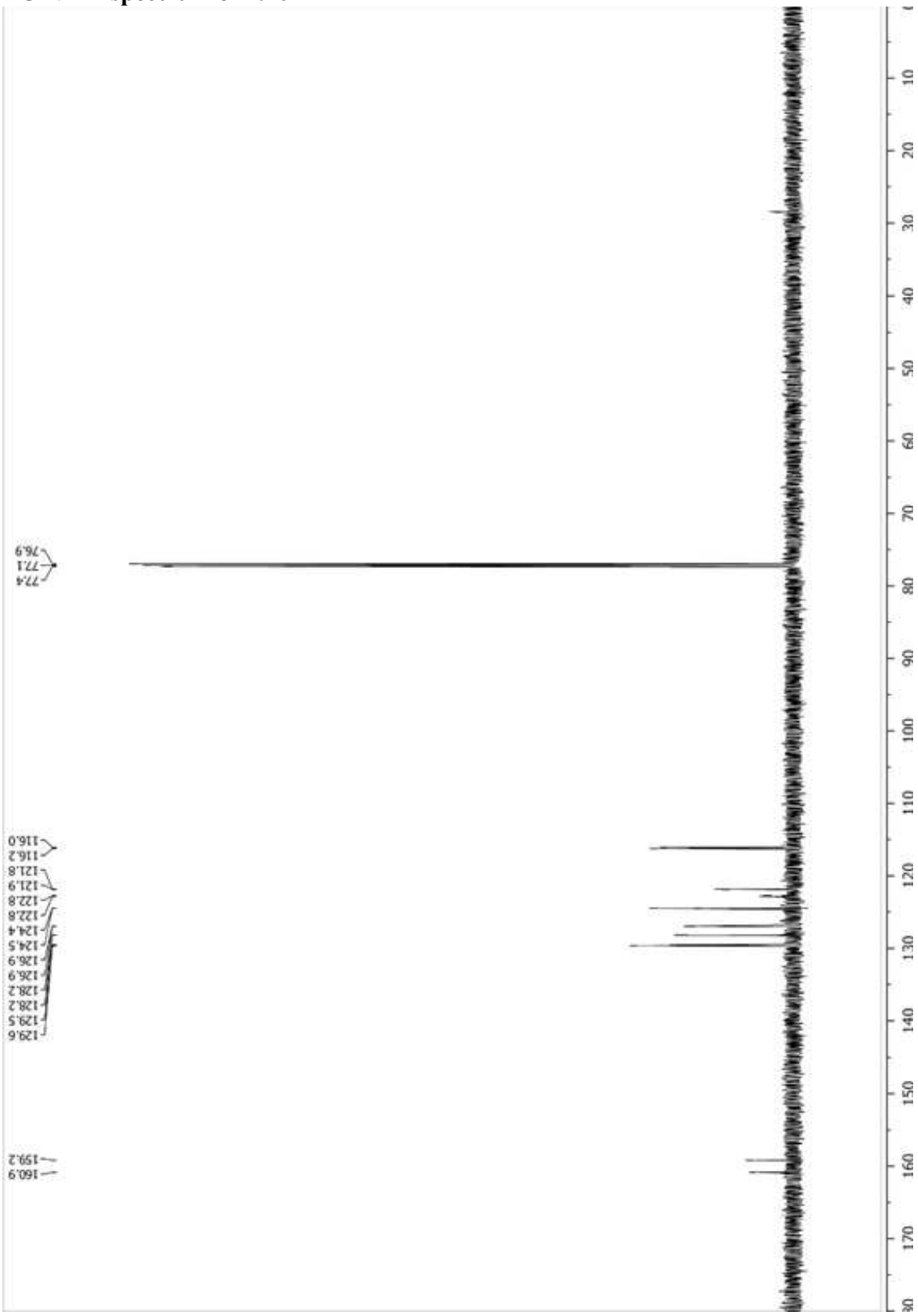
^{13}C NMR spectrum of 2.68



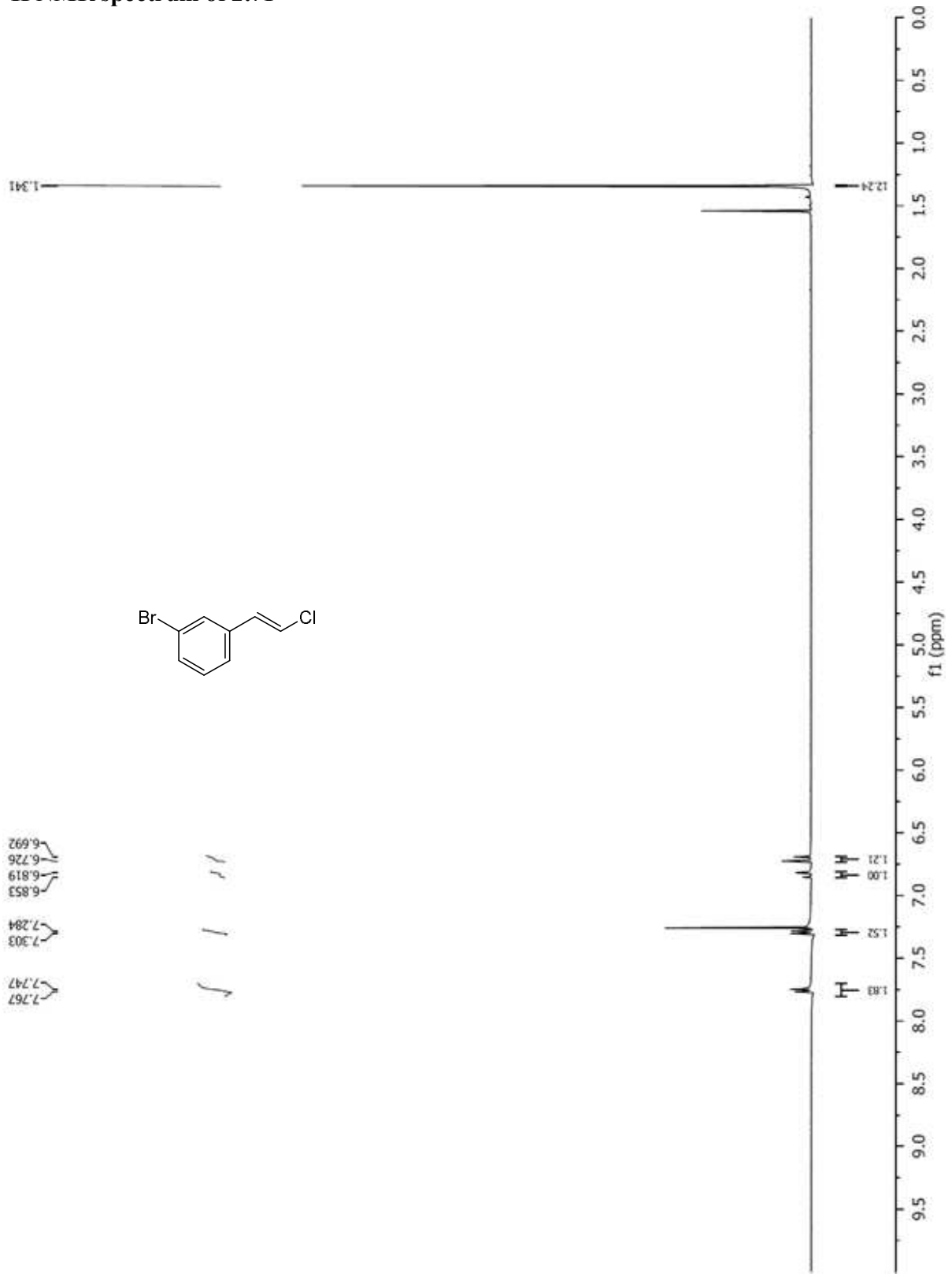
^{1}H NMR spectrum of 2.70



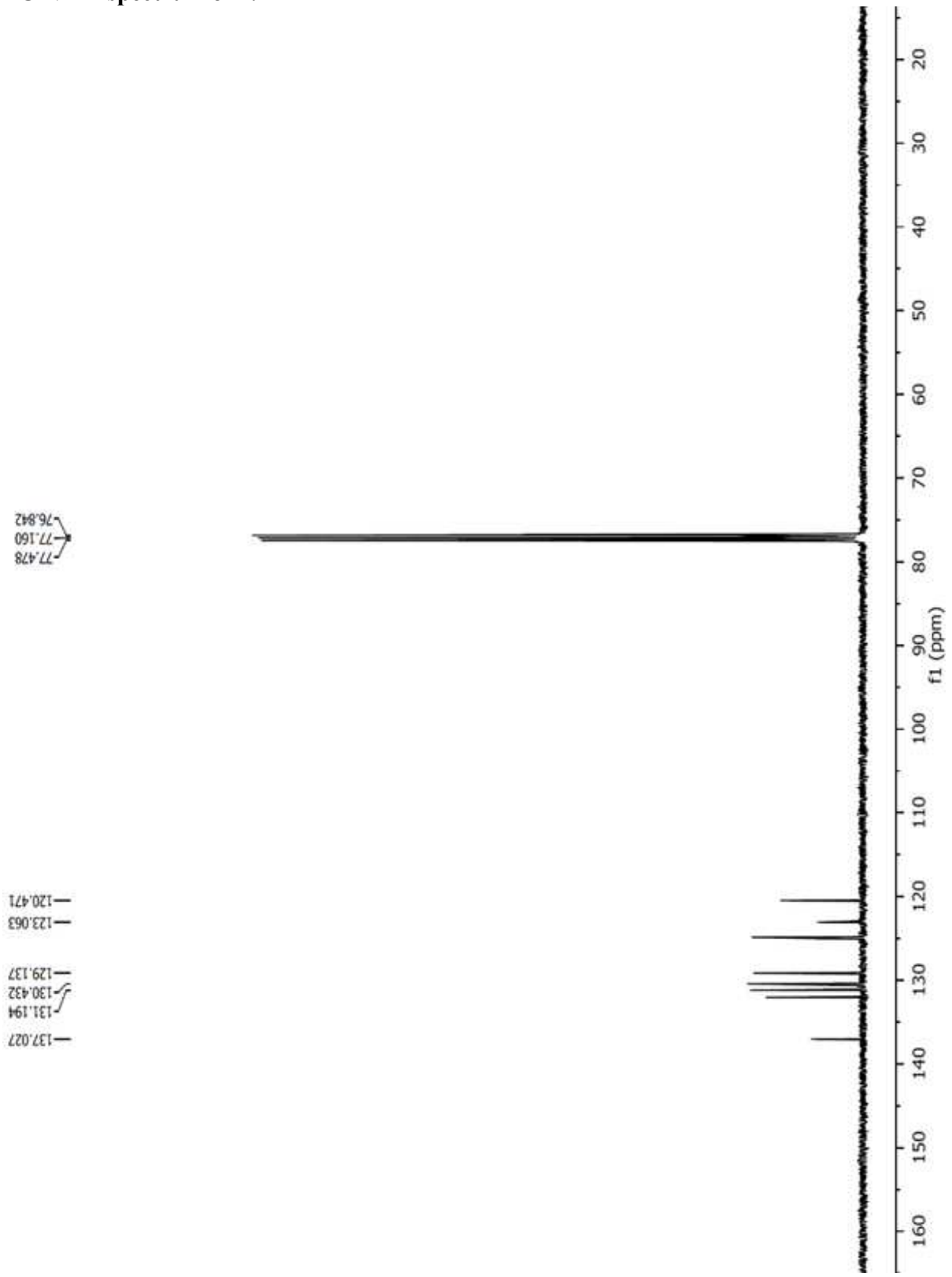
^{13}C NMR spectrum of 2.70



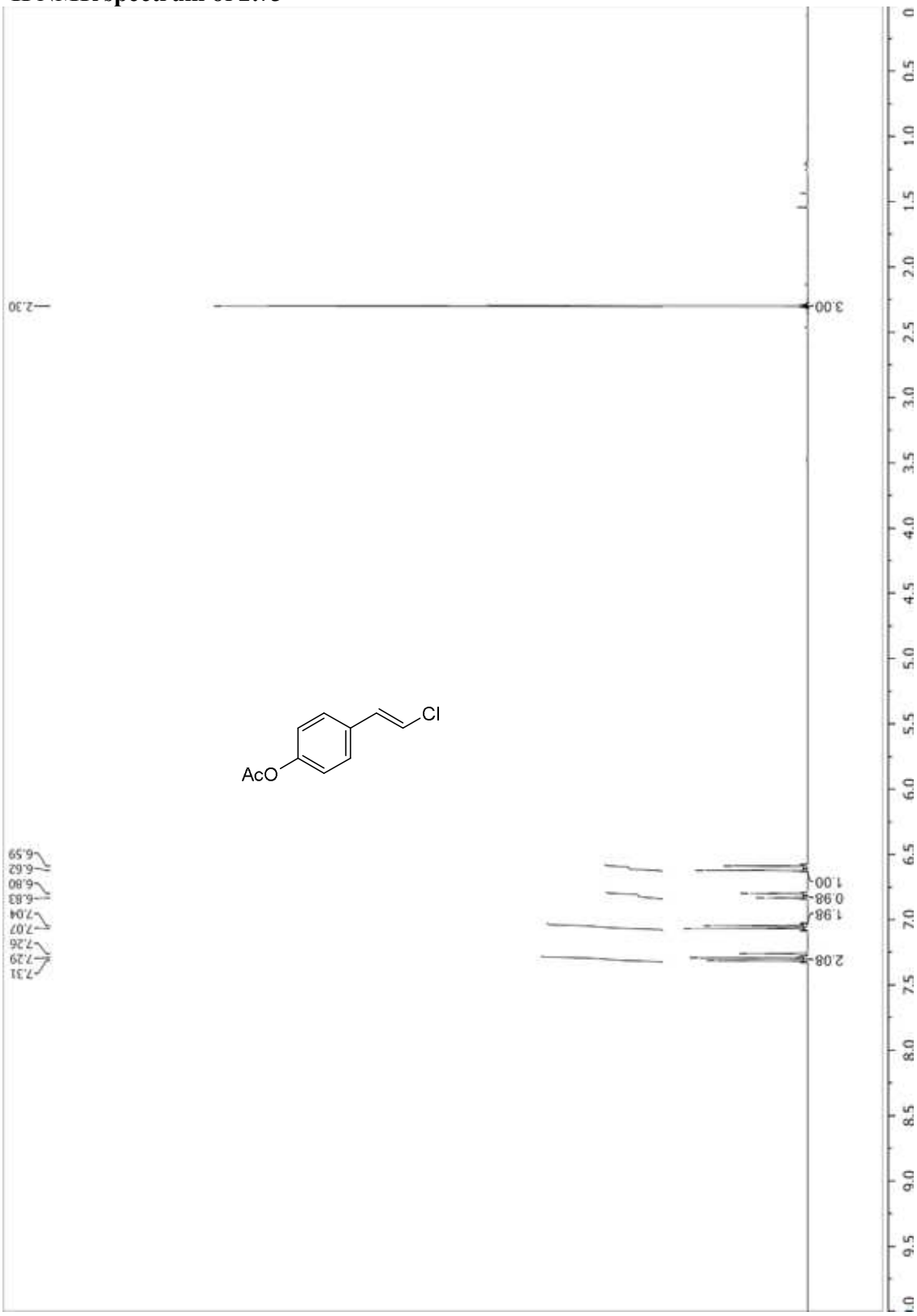
^{1}H NMR spectrum of 2.71



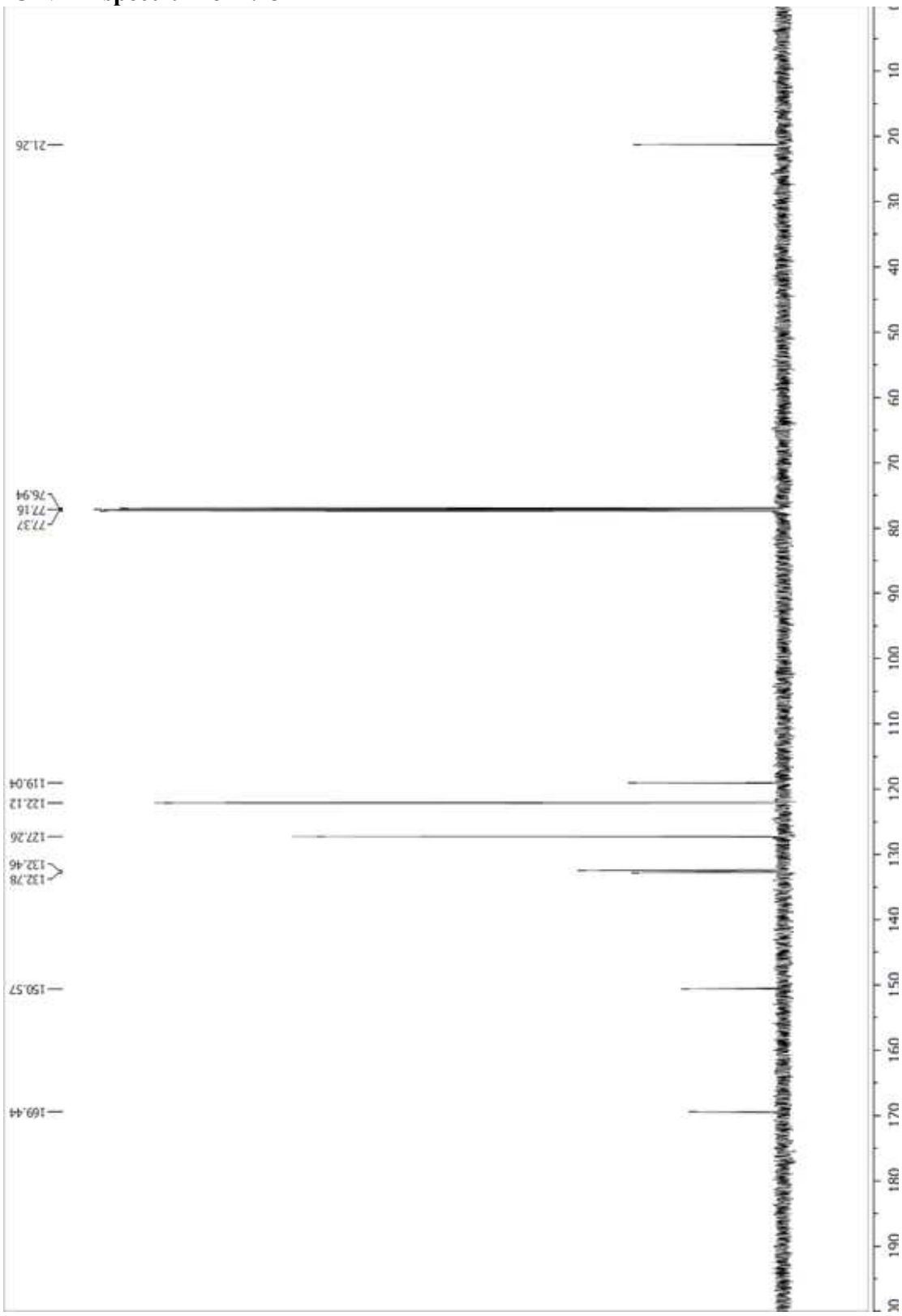
^{13}C NMR spectrum of 2.71



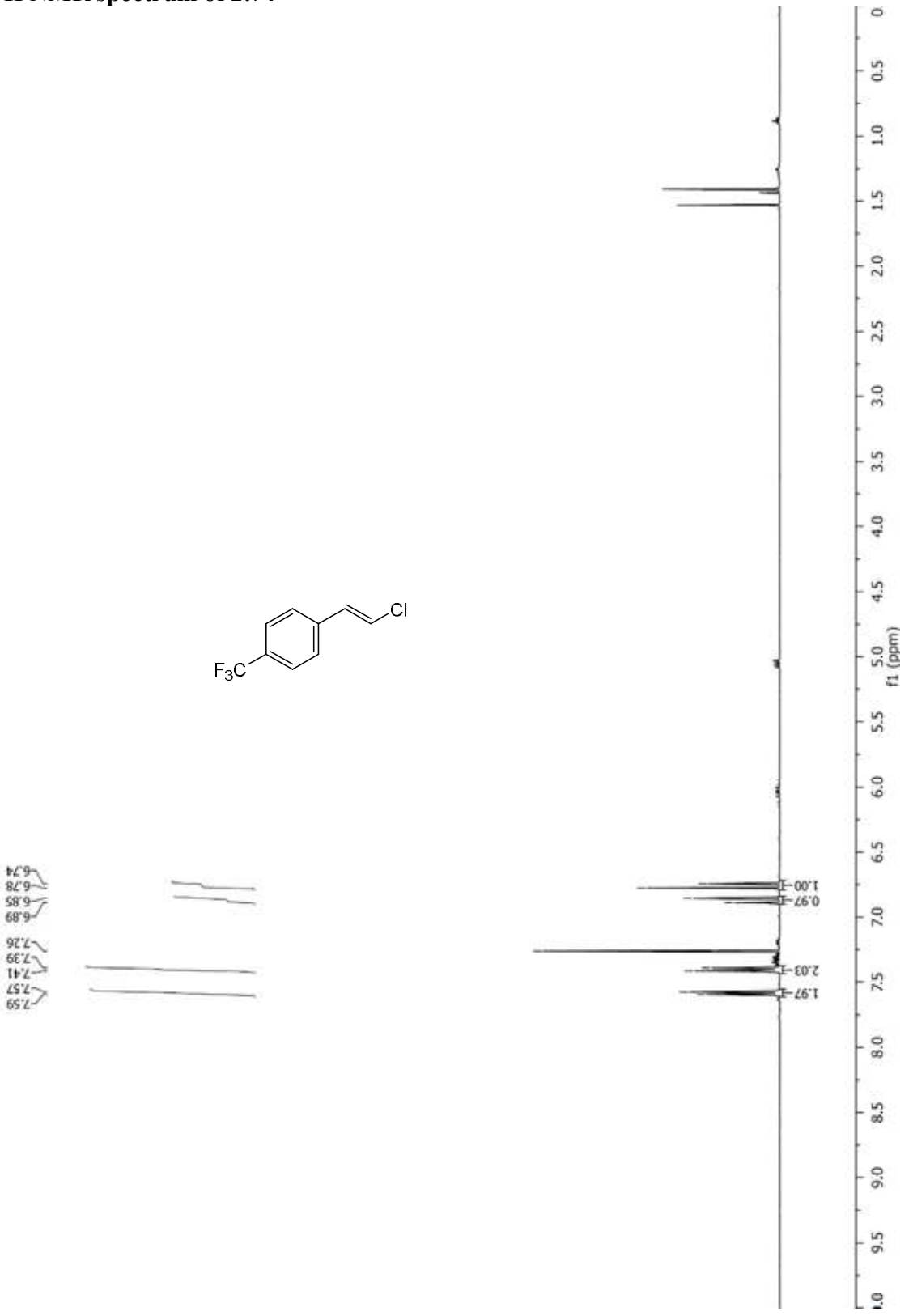
^{1}H NMR spectrum of 2.73



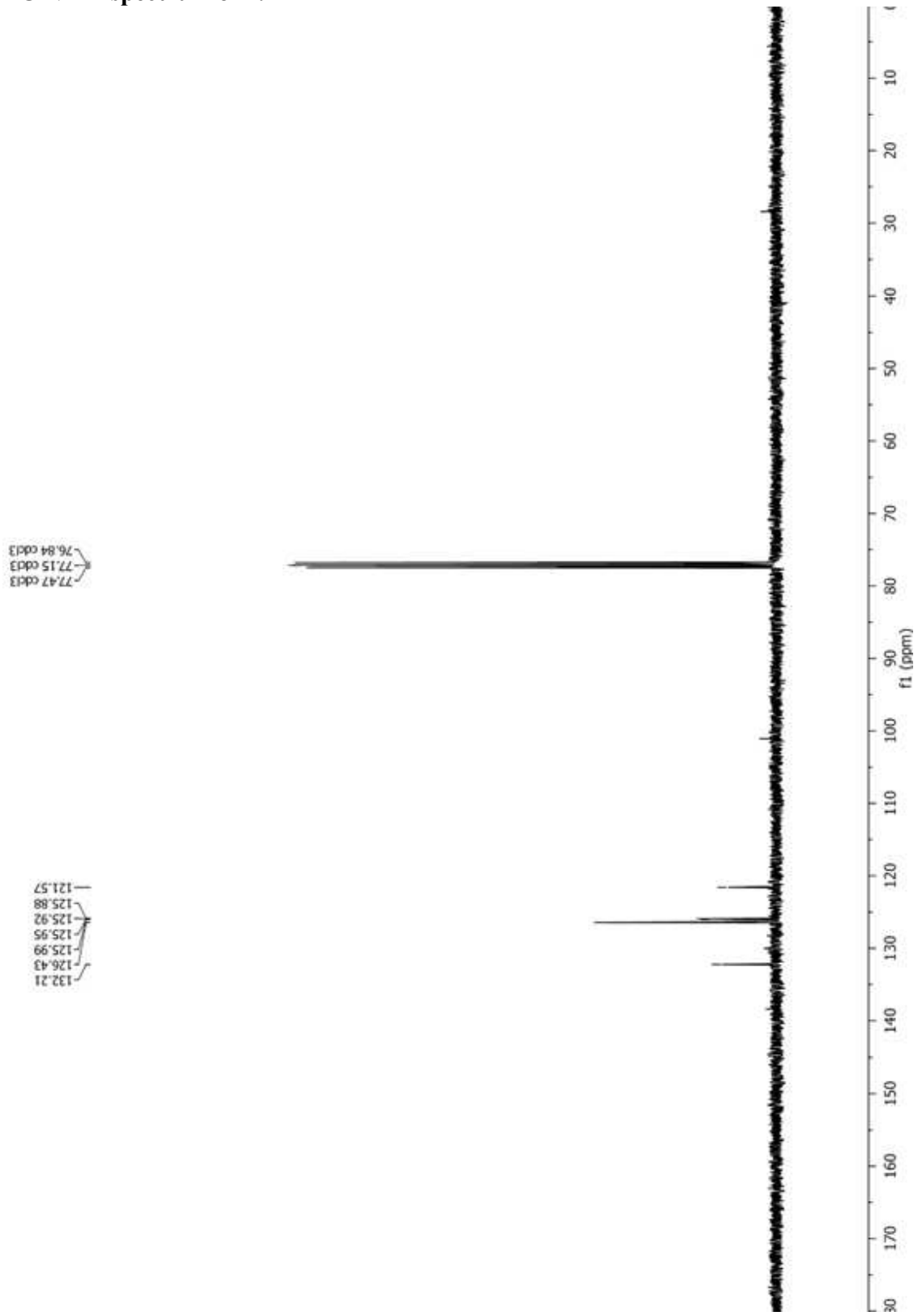
^{13}C NMR spectrum of 2.73



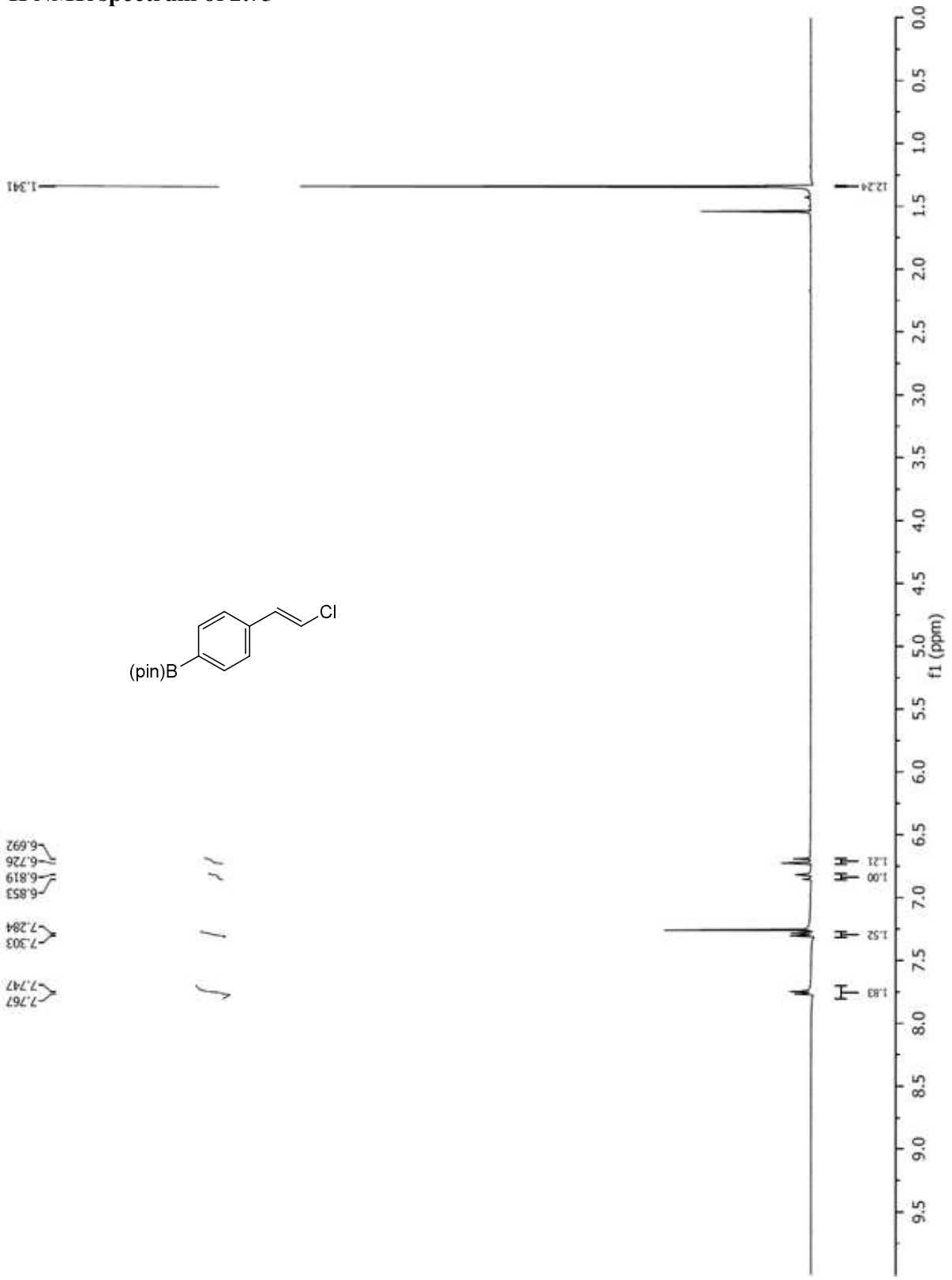
^{1}H NMR spectrum of 2.74



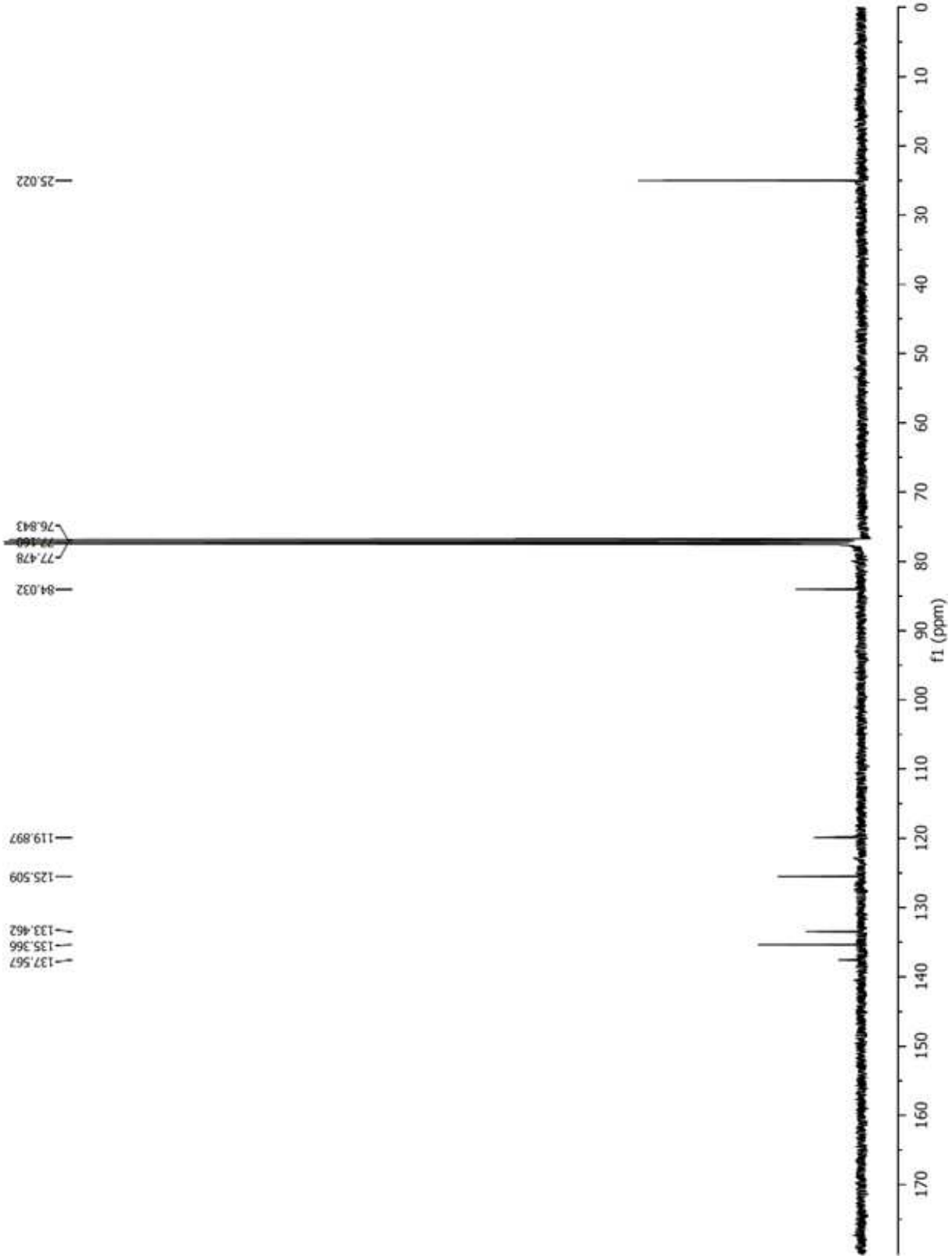
^{13}C NMR spectrum of 2.74



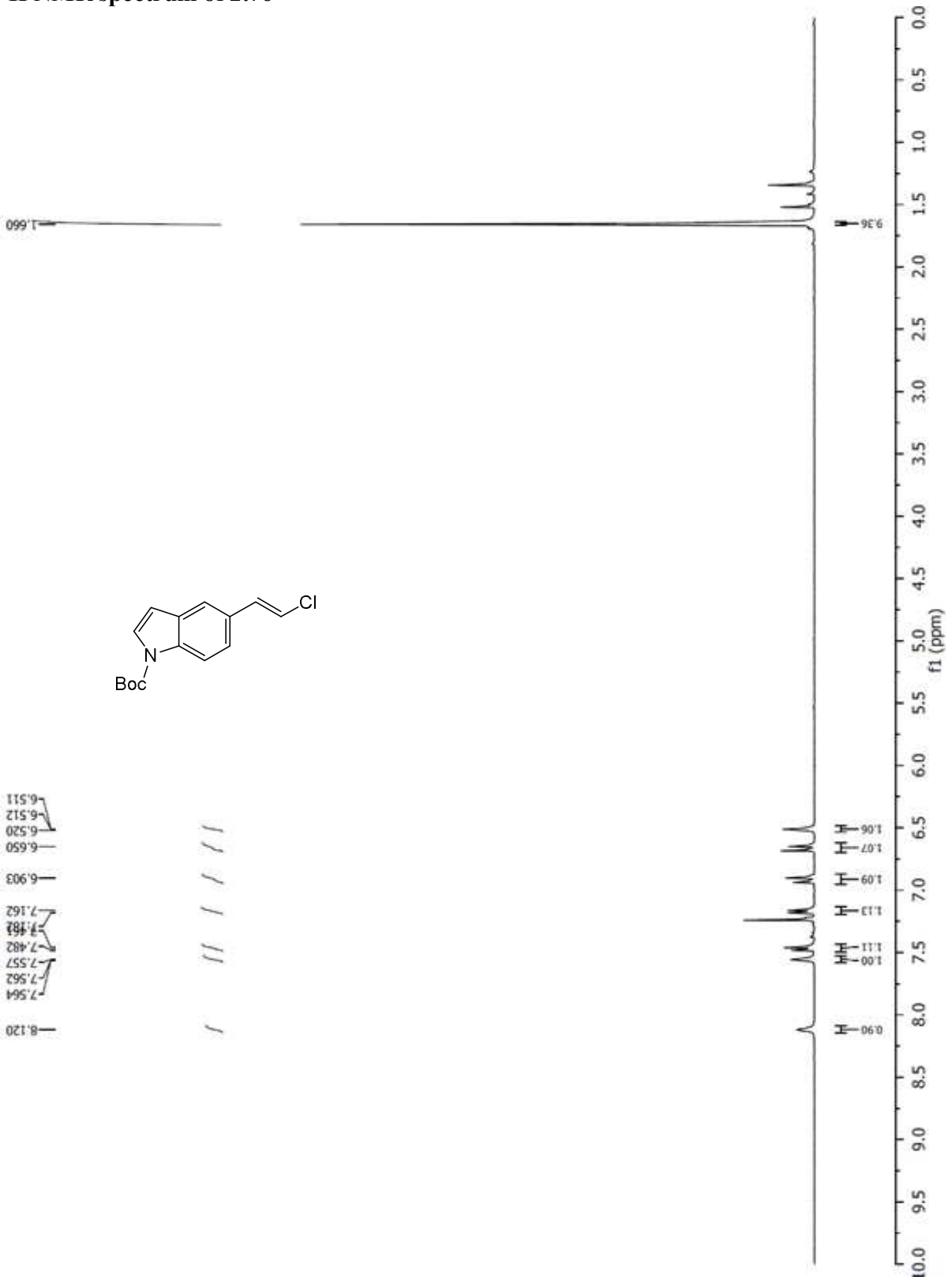
^{1}H NMR spectrum of 2.75



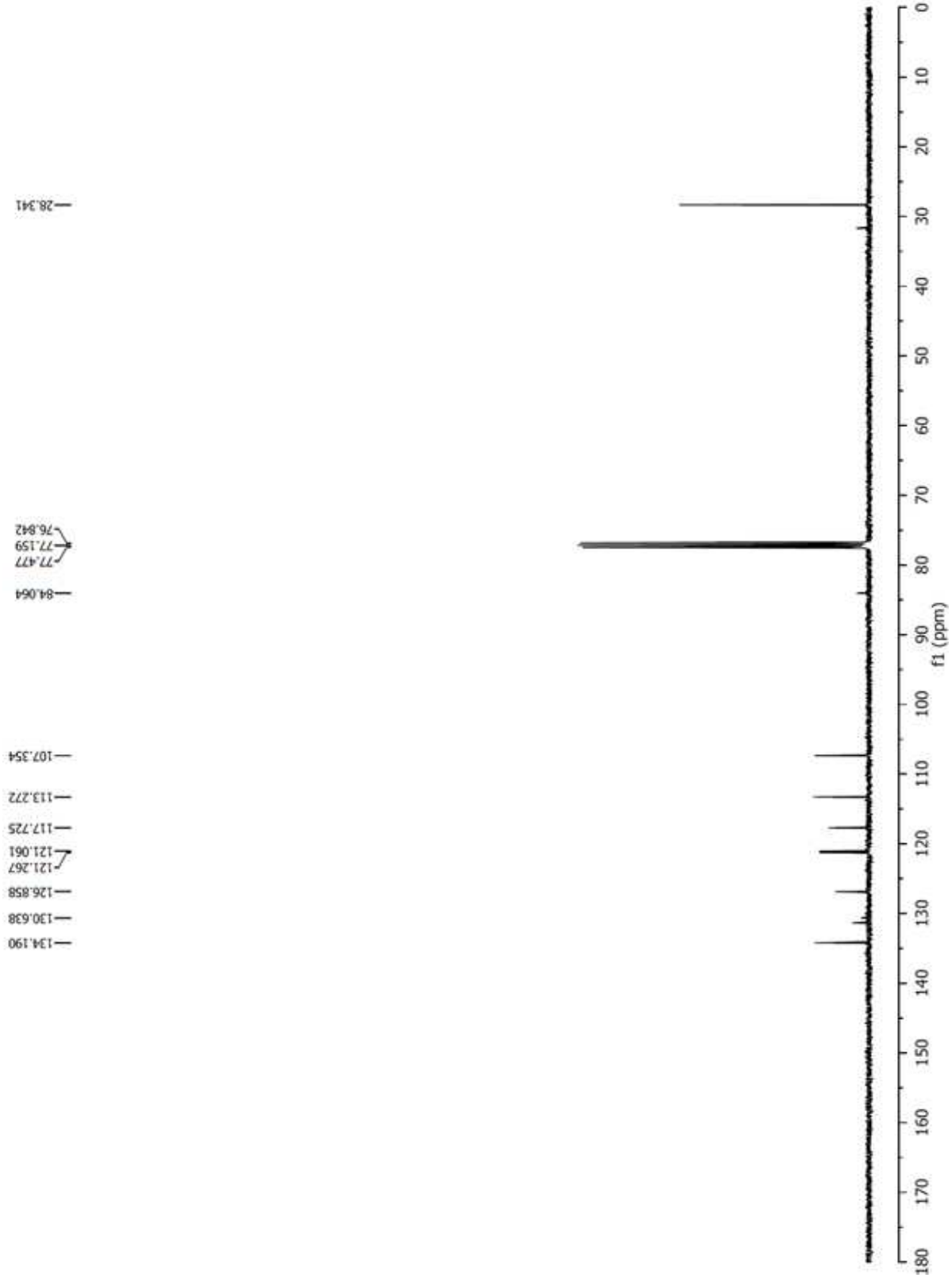
^{13}C NMR spectrum of 2.75



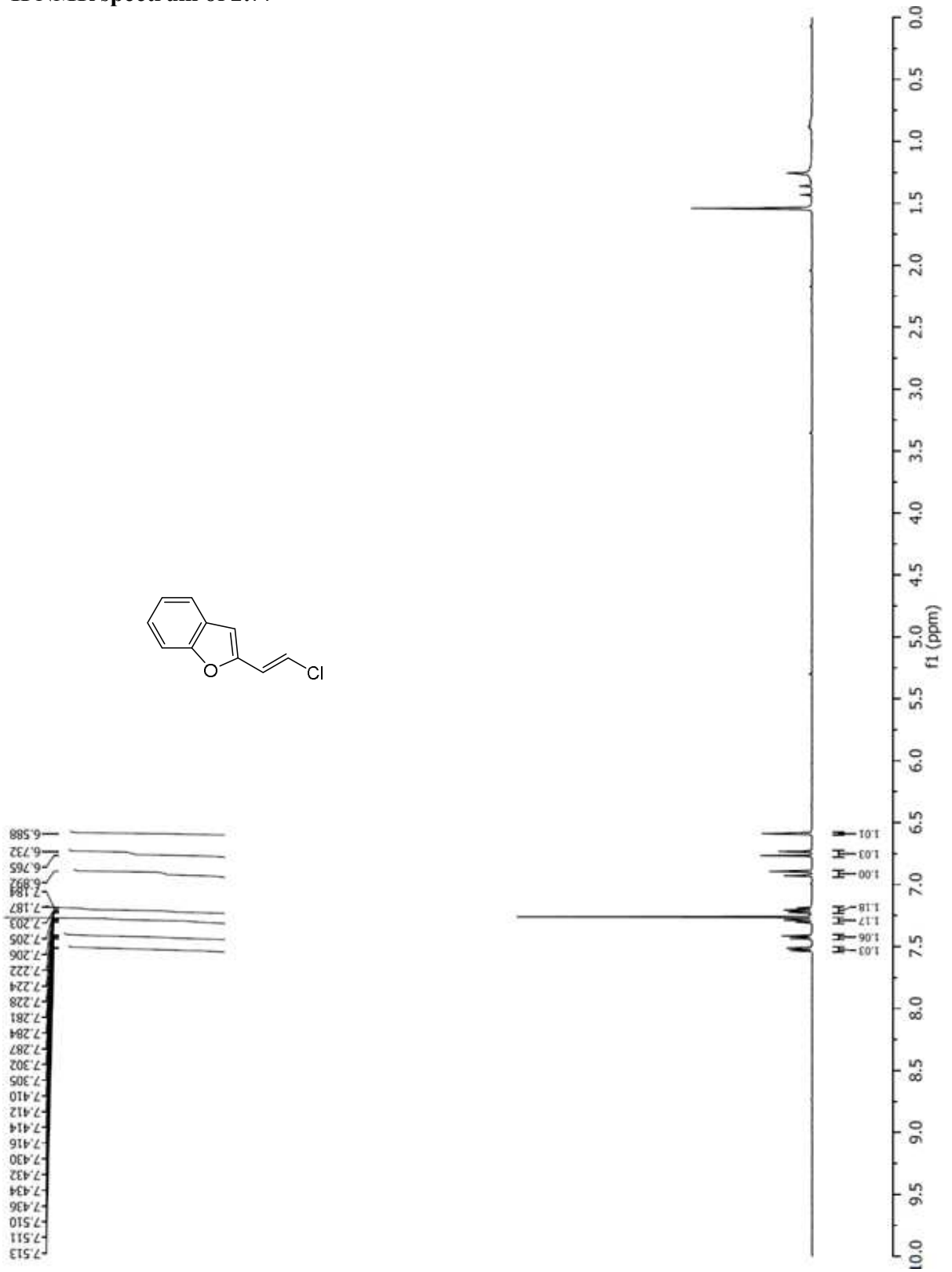
^{1}H NMR spectrum of 2.76



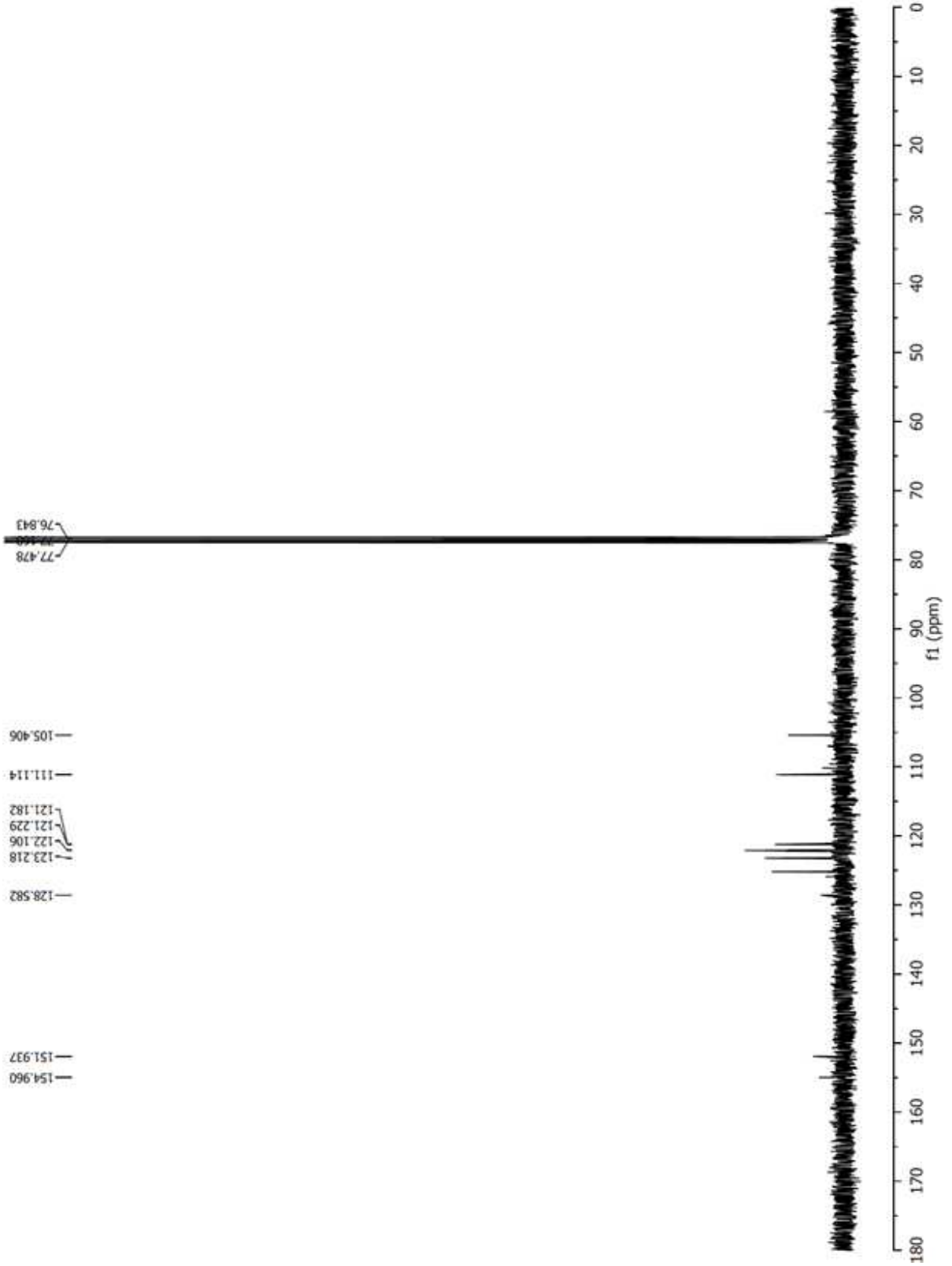
^{13}C NMR spectrum of 2.76



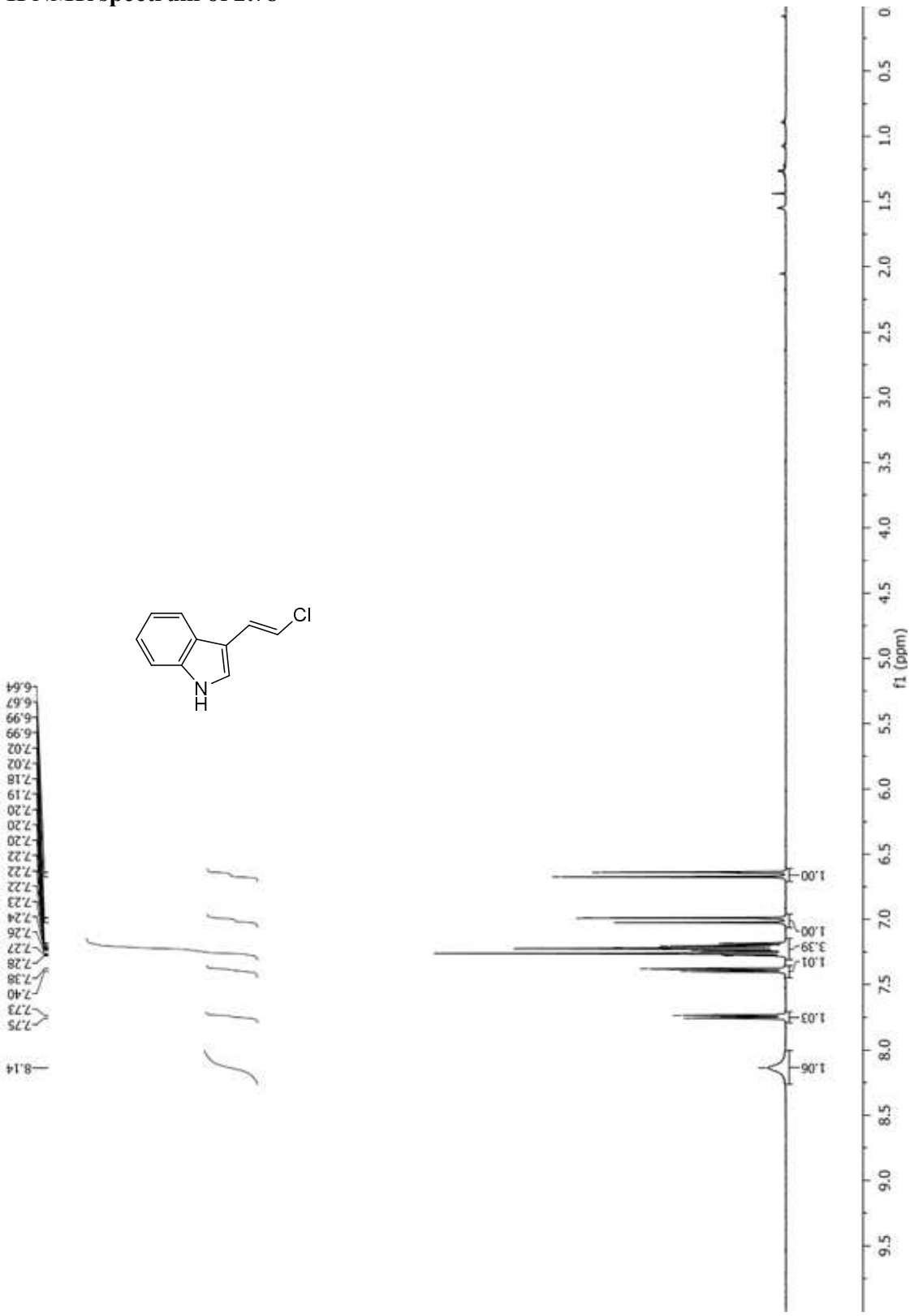
^{1}H NMR spectrum of 2.77



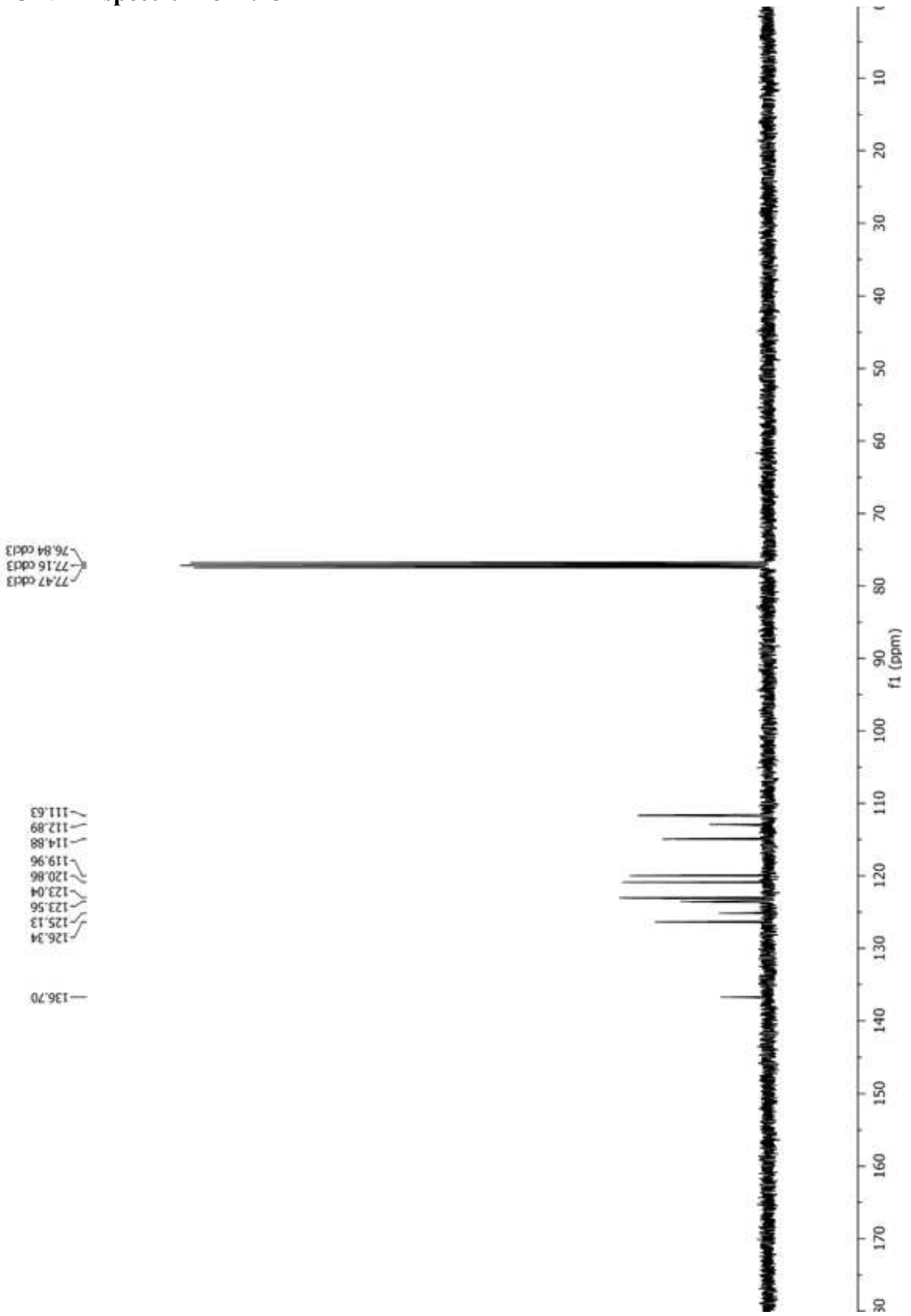
^{13}C NMR spectrum of 2.77



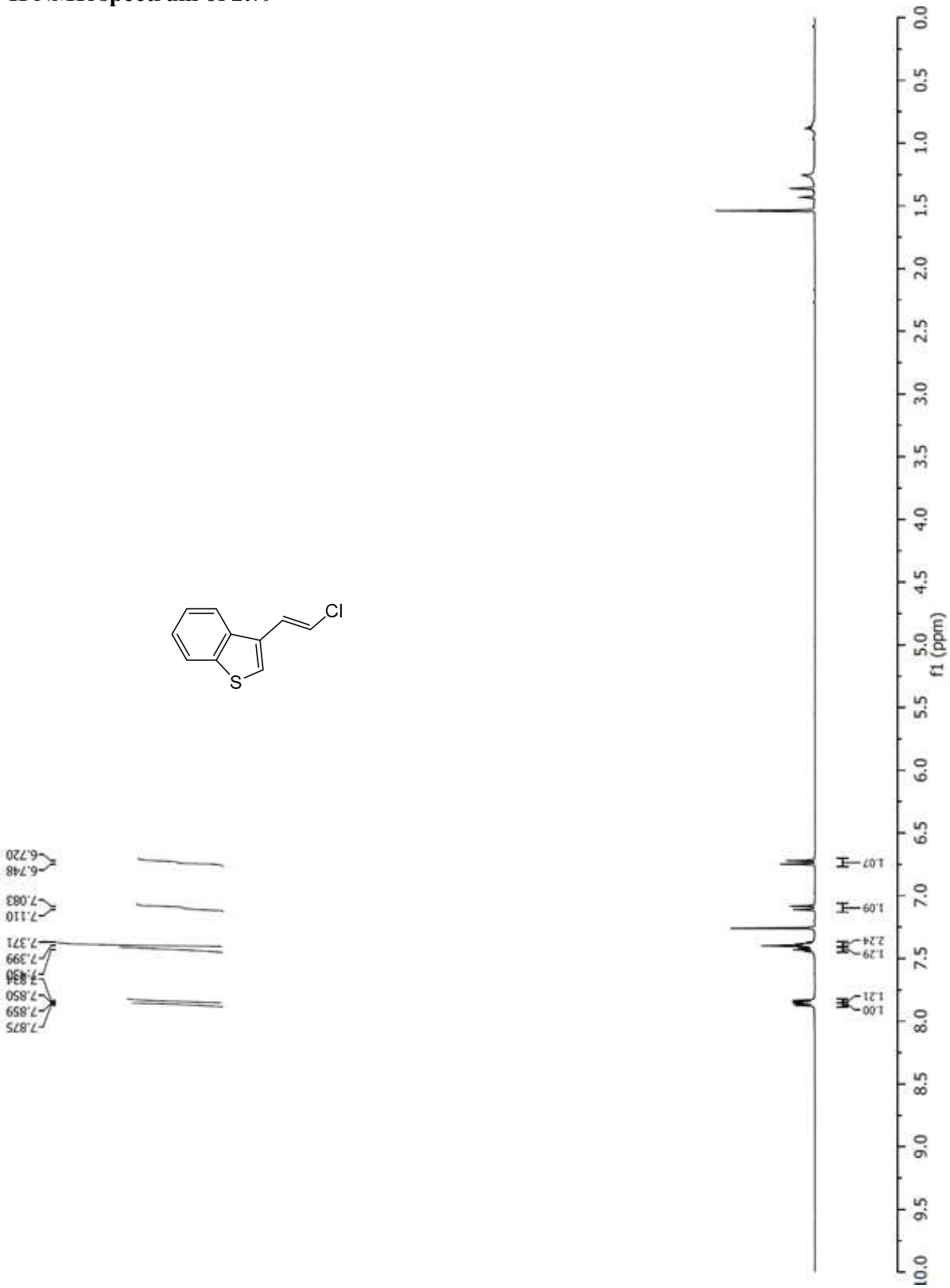
^{1}H NMR spectrum of 2.78



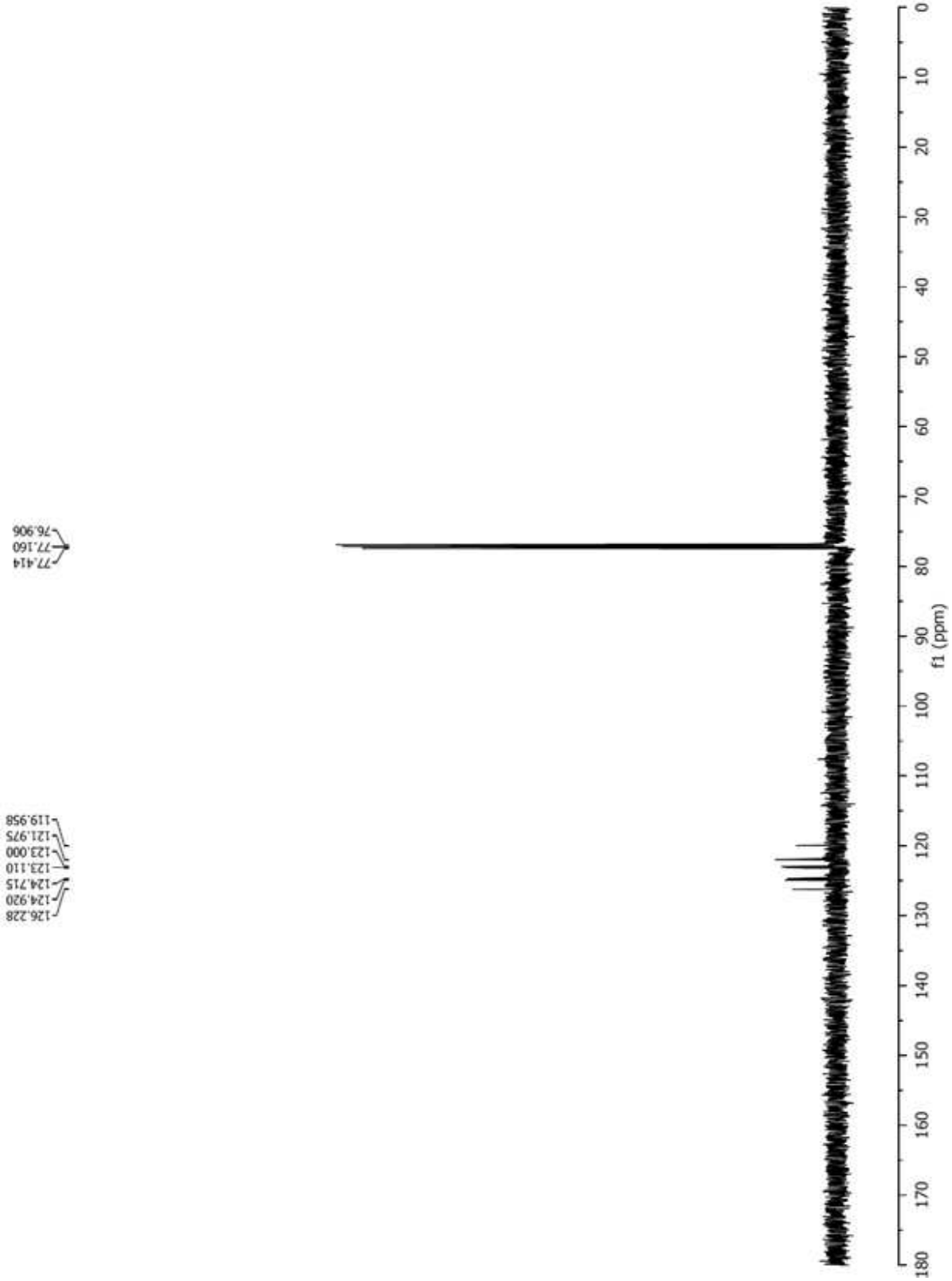
^{13}C NMR spectrum of 2.78



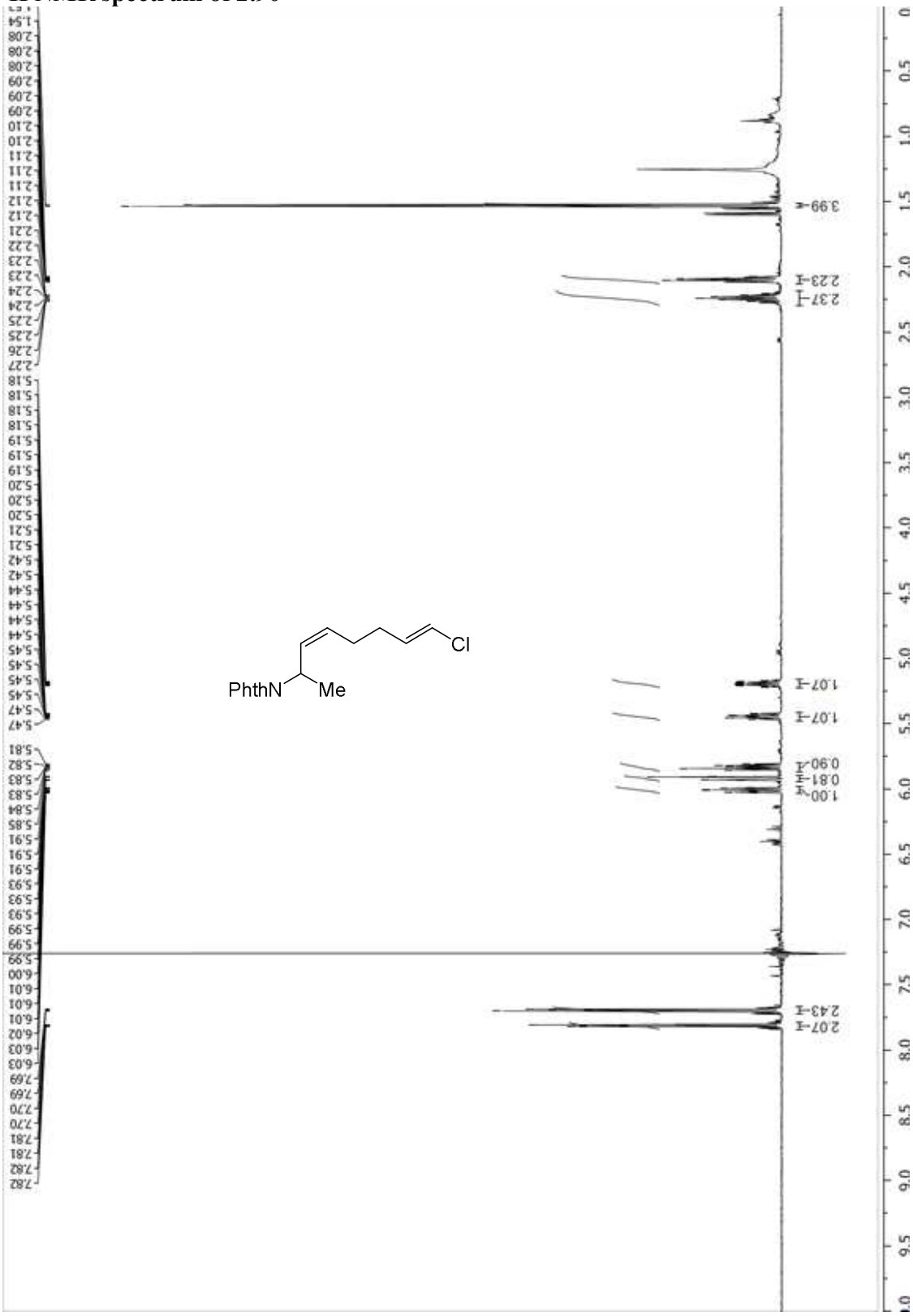
^{1}H NMR spectrum of 2.79



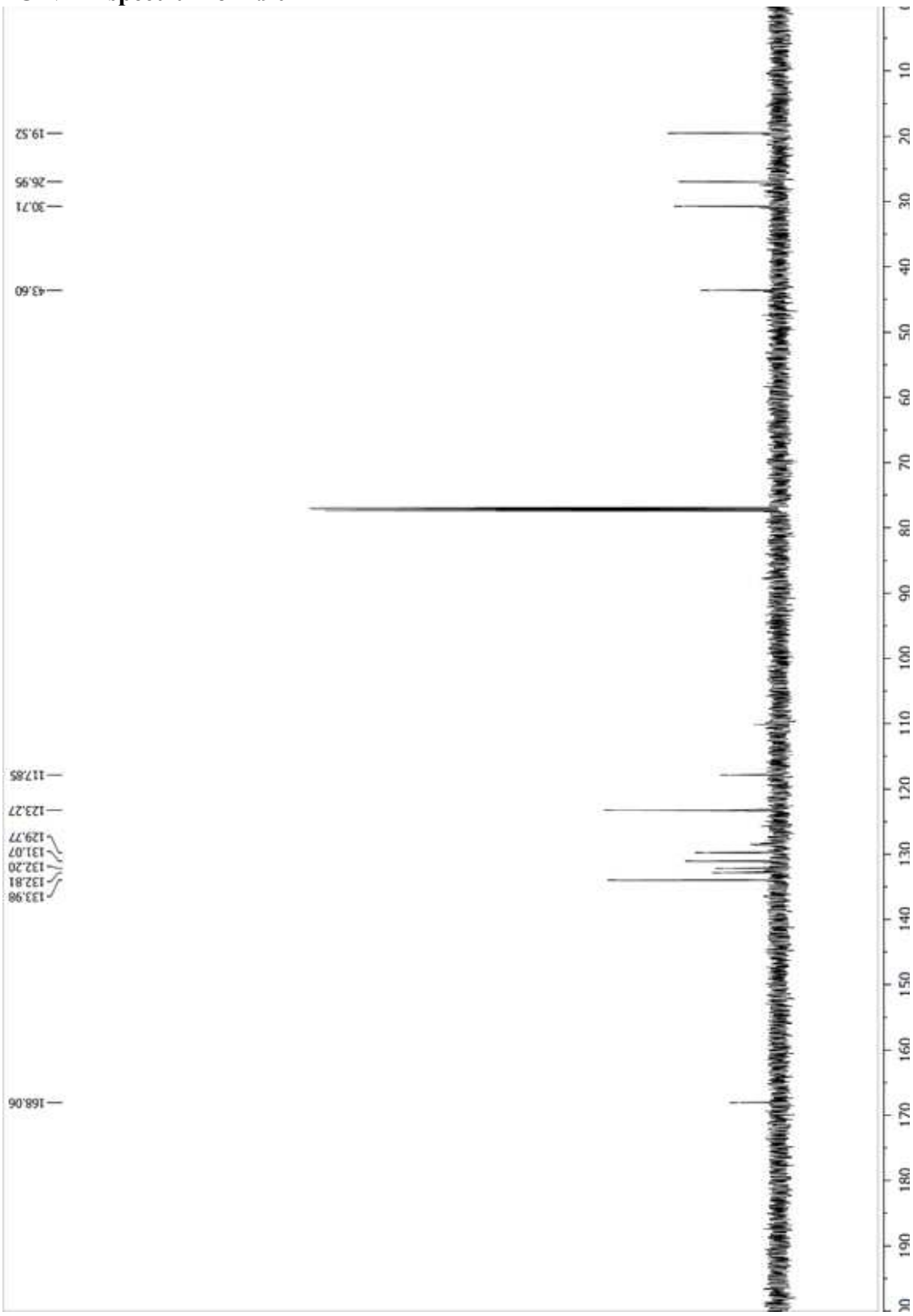
^{13}C NMR spectrum of 2.79



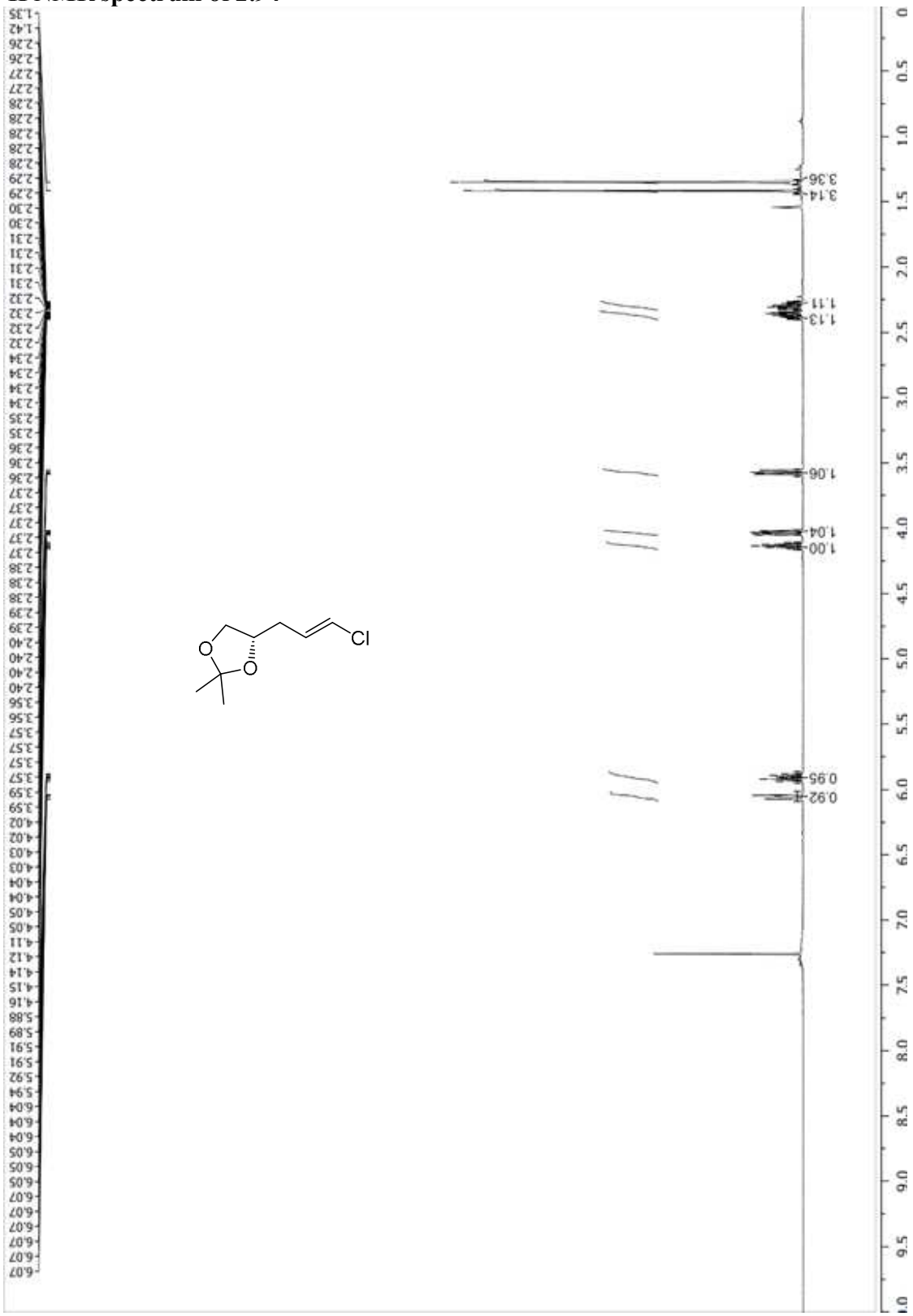
^{1}H NMR spectrum of 2.90



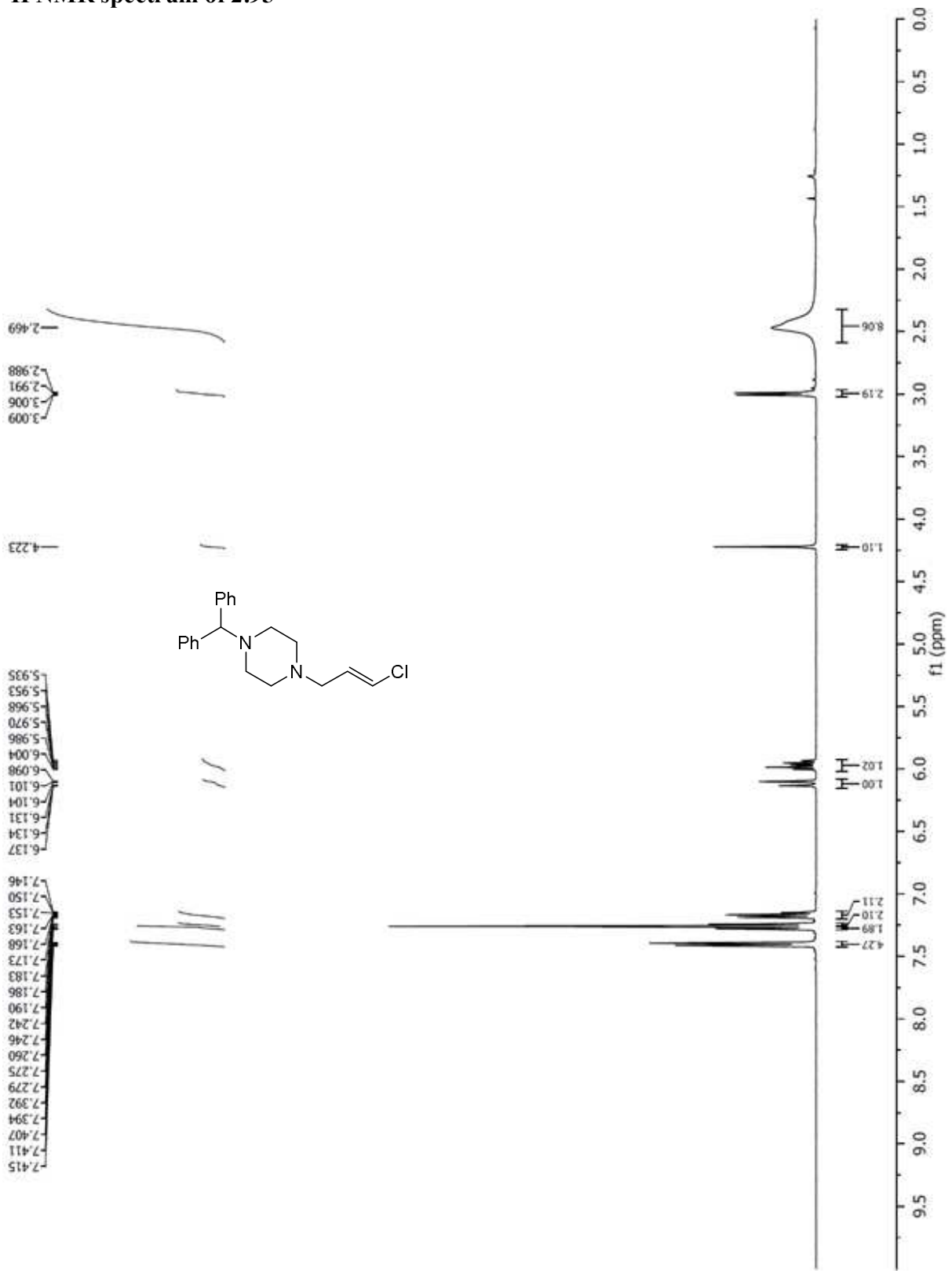
^{13}C NMR spectrum of 2.90



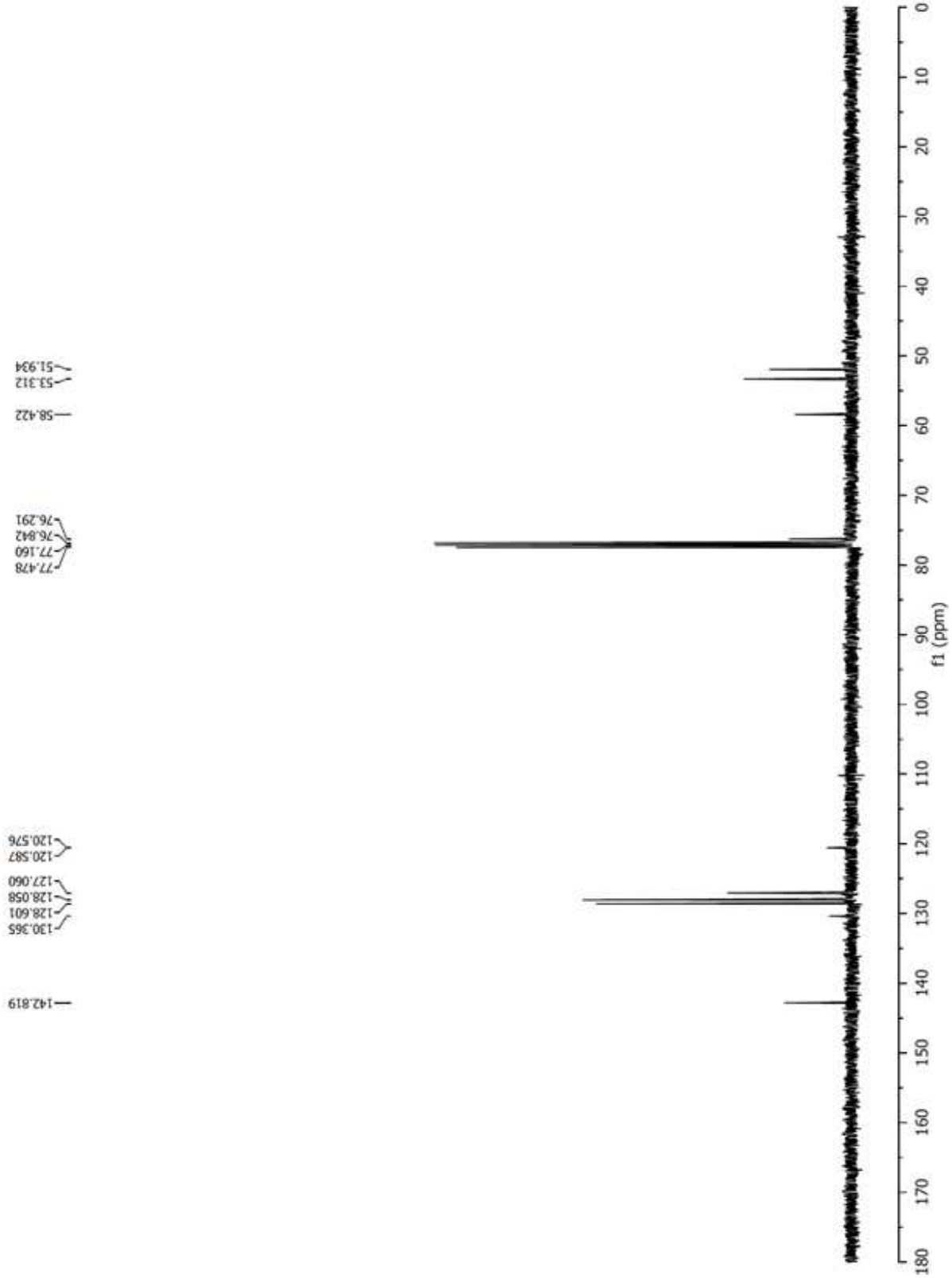
^{1}H NMR spectrum of 2.94



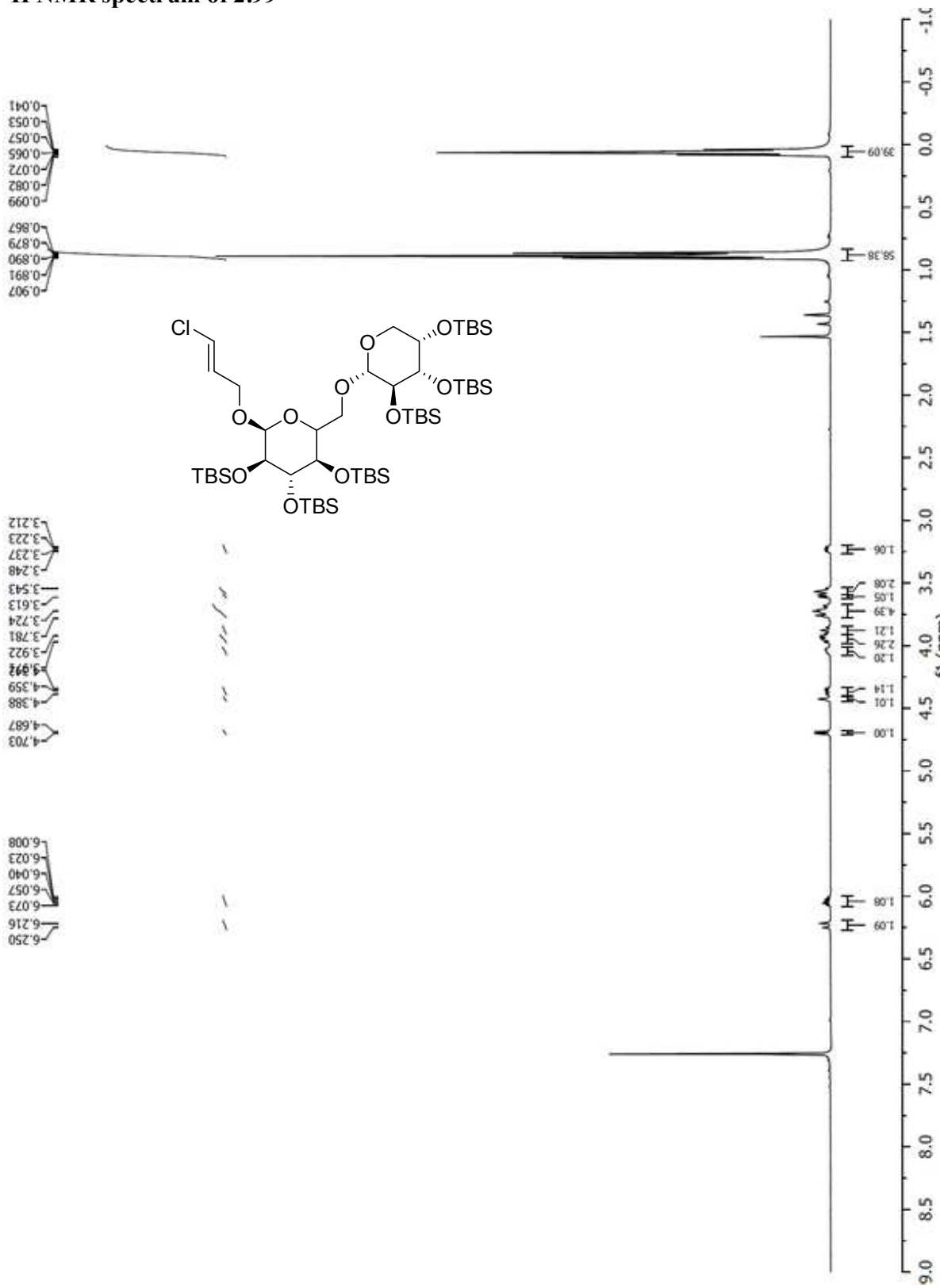
^{1}H NMR spectrum of 2.95



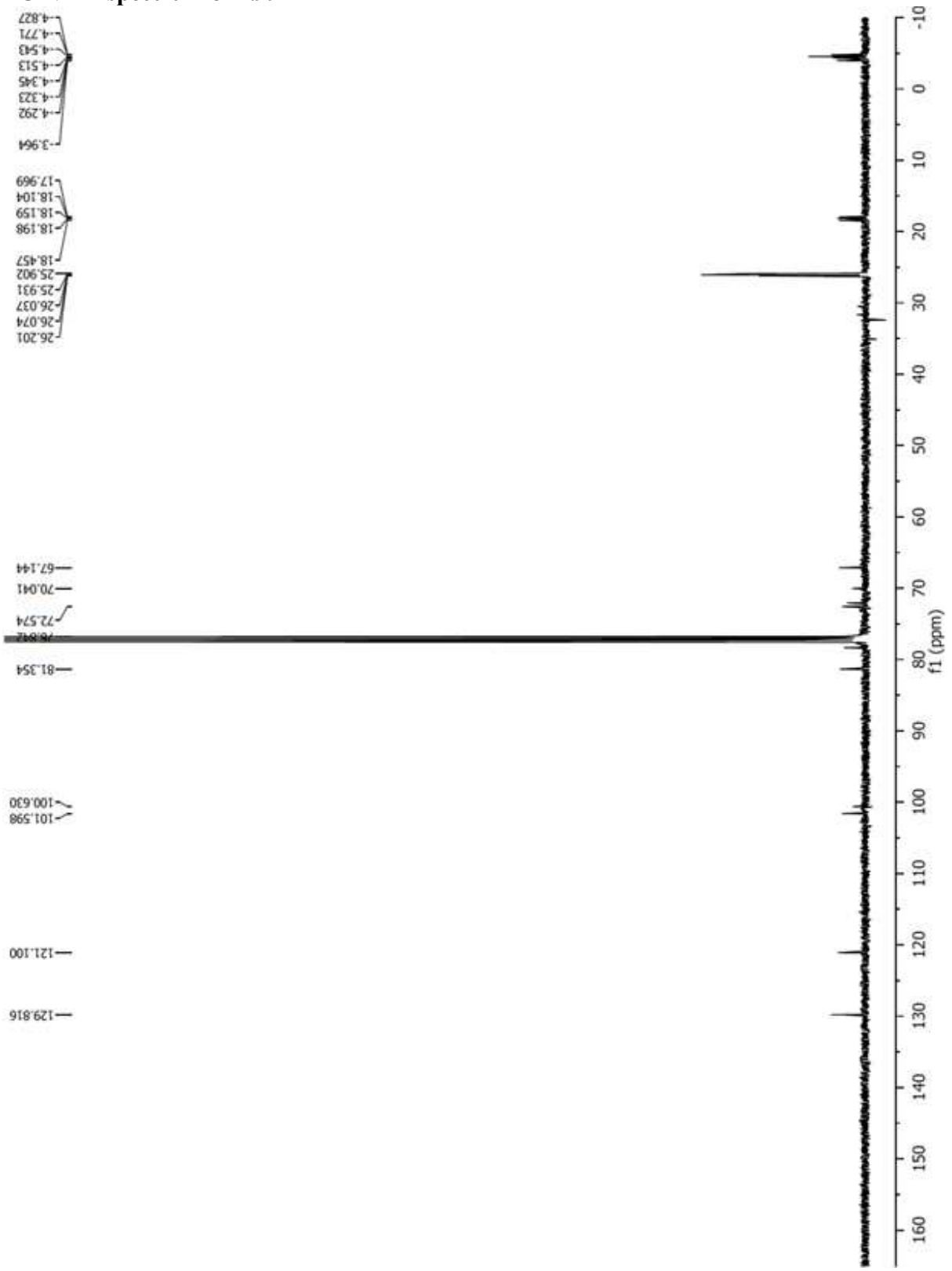
^{13}C NMR spectrum of 2.95



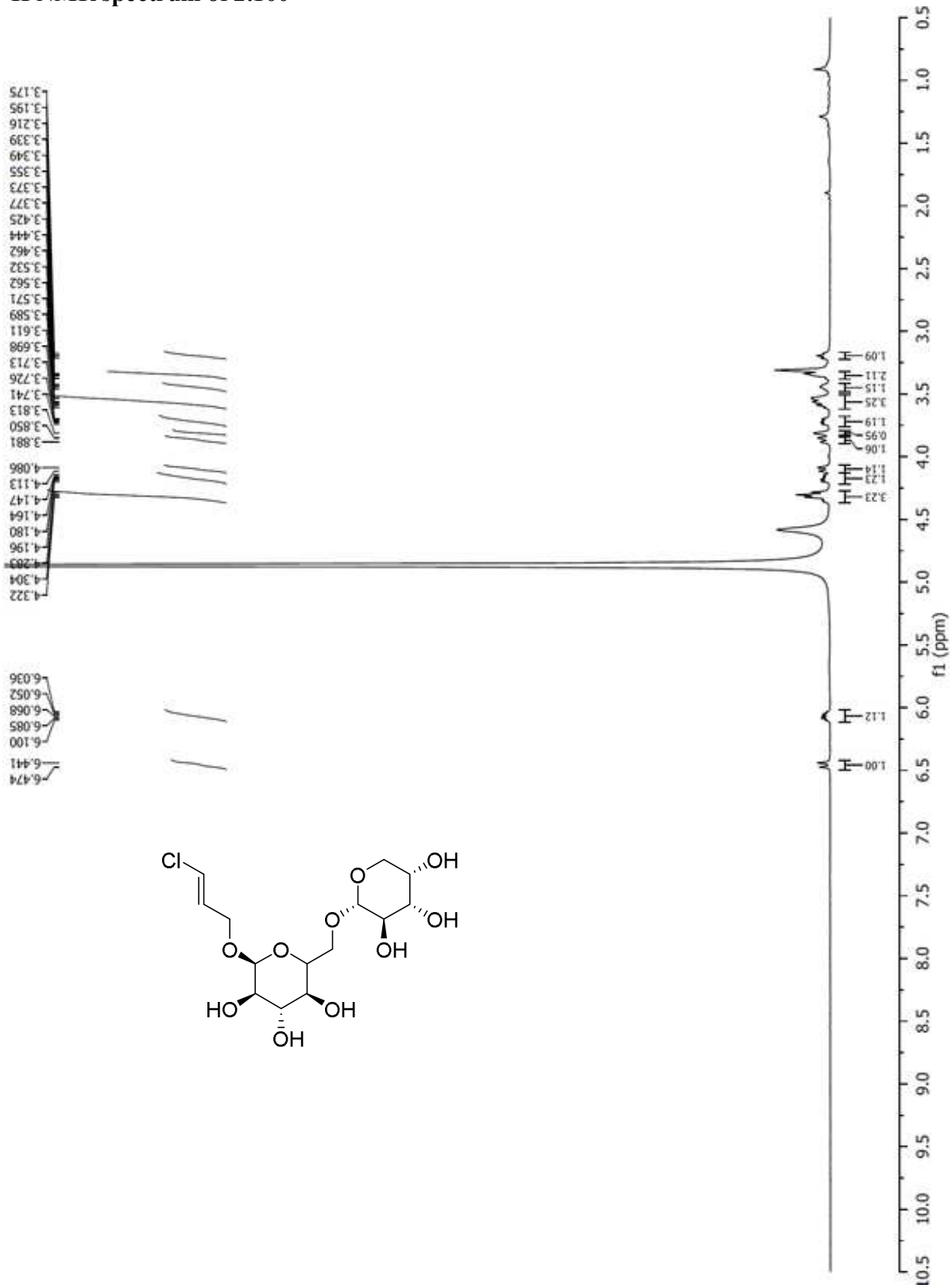
^{1}H NMR spectrum of 2.99



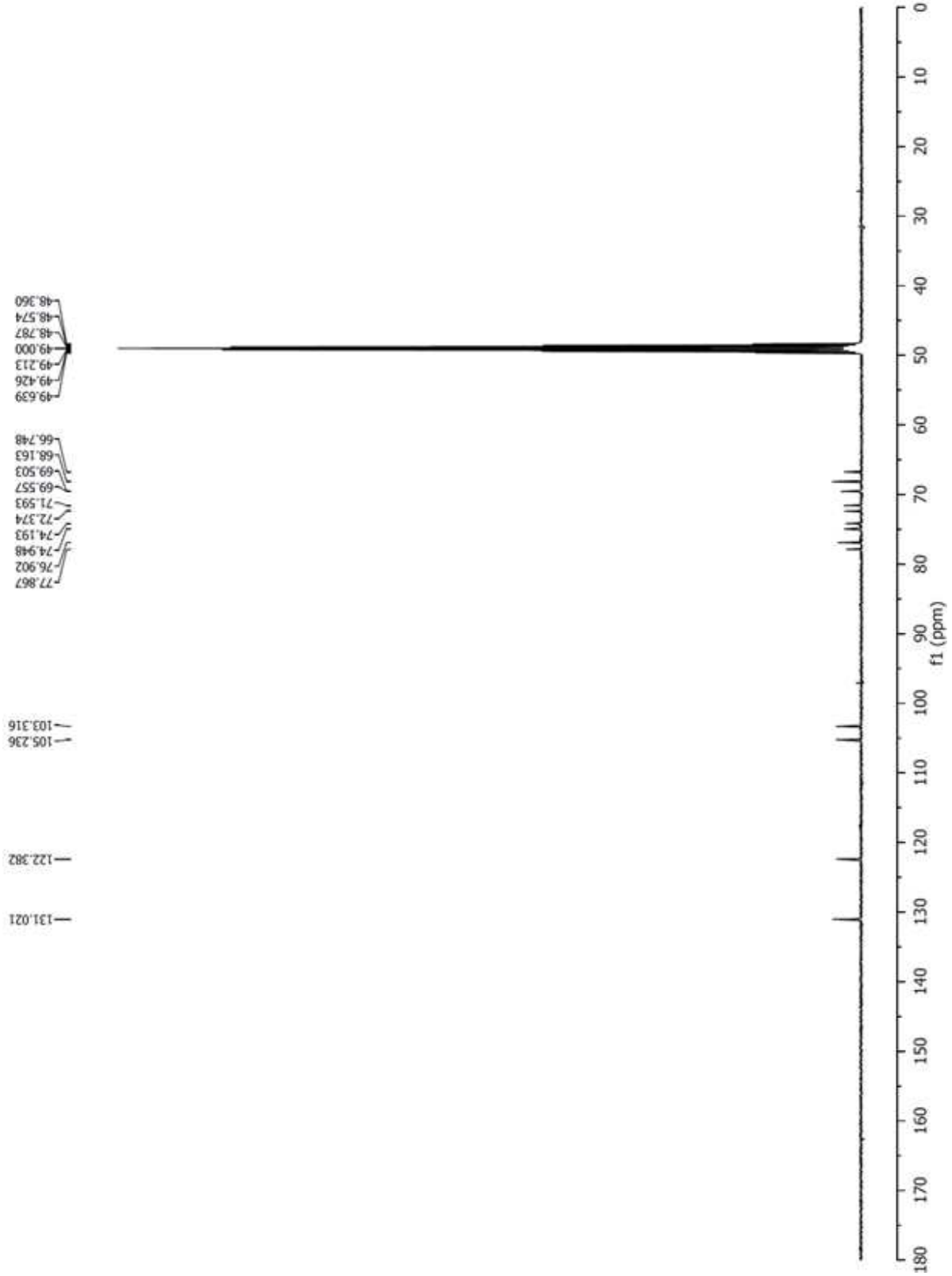
^{13}C NMR spectrum of 2.99



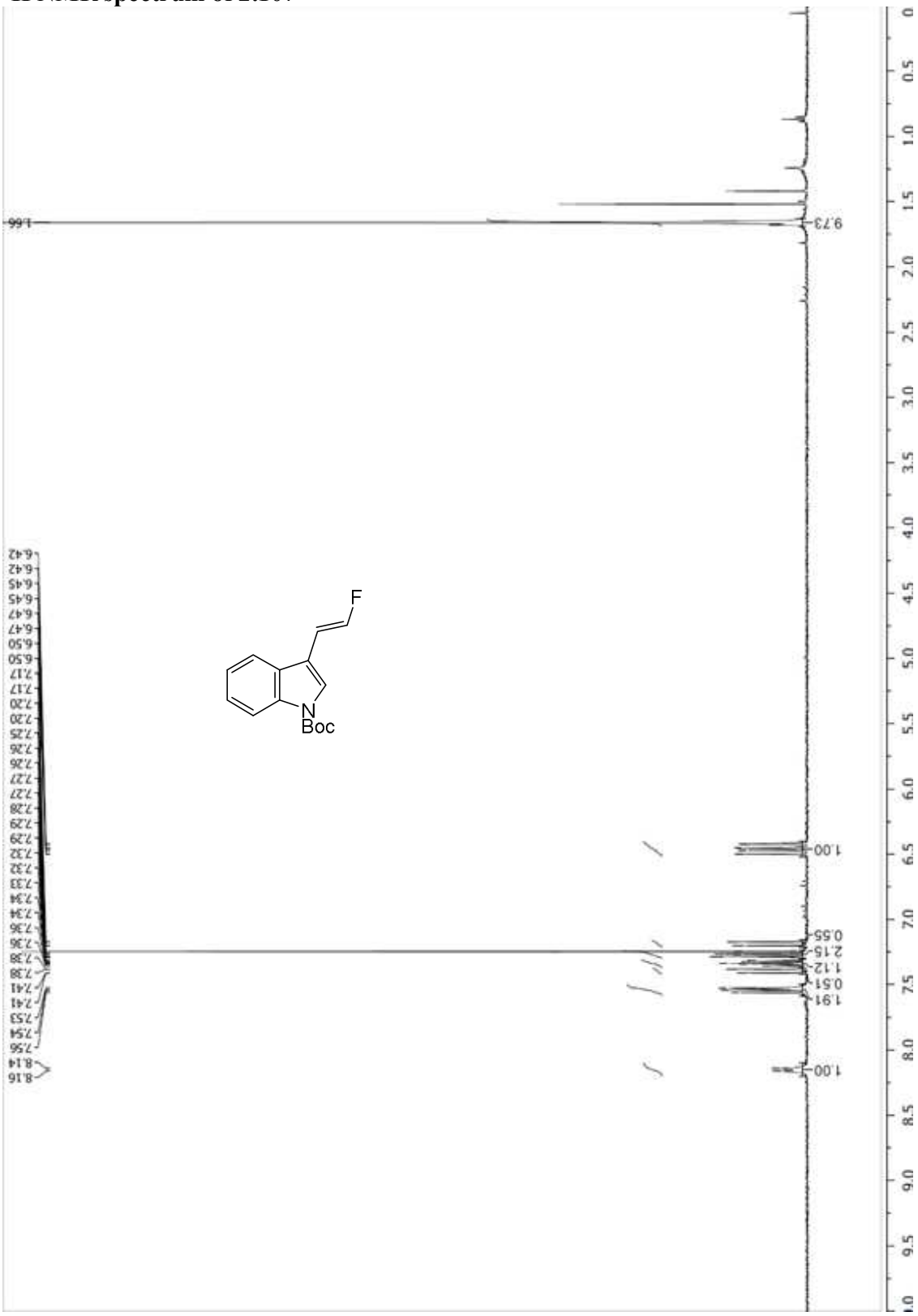
^{1}H NMR spectrum of 2.100



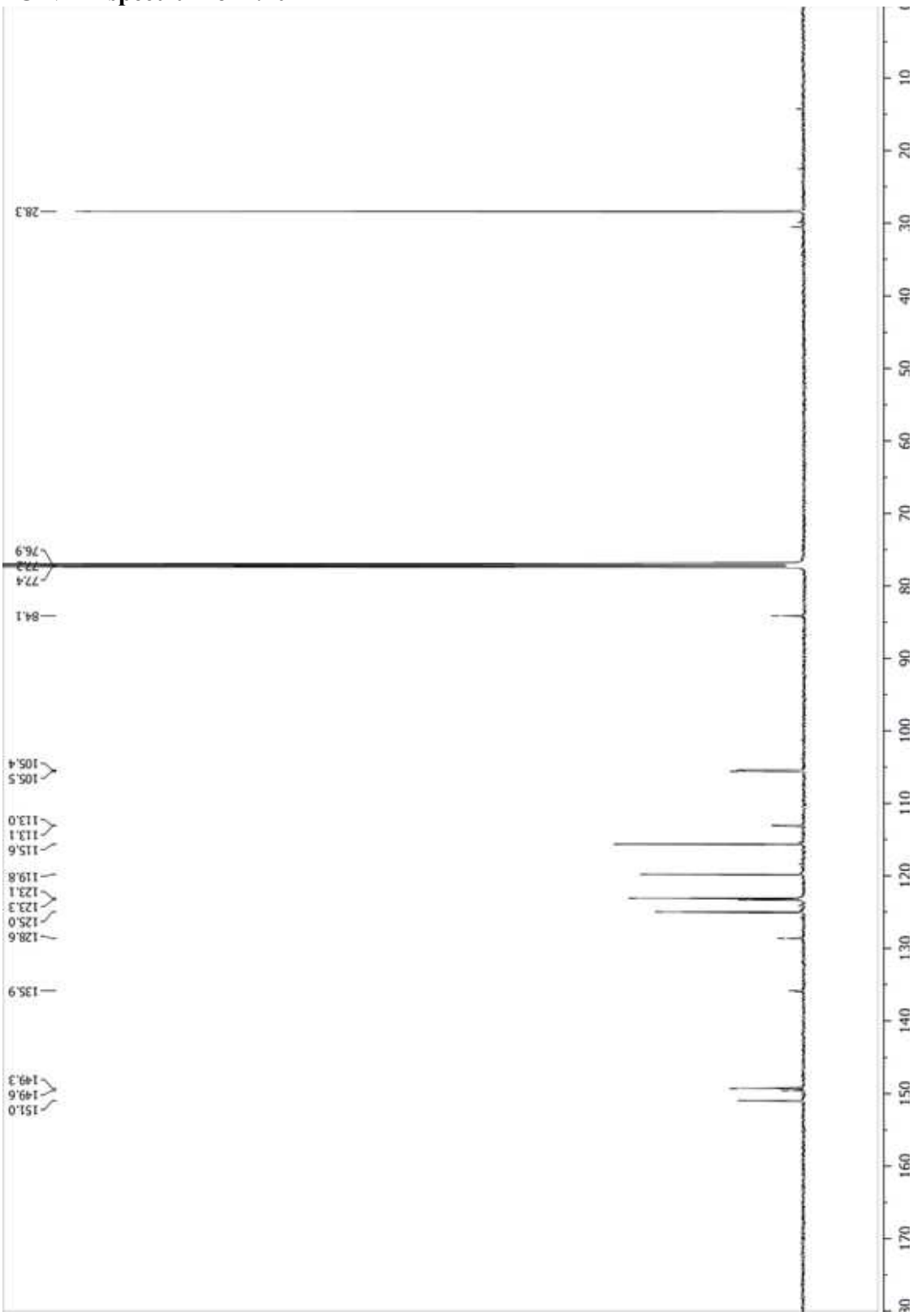
^{13}C NMR spectrum of 2.100



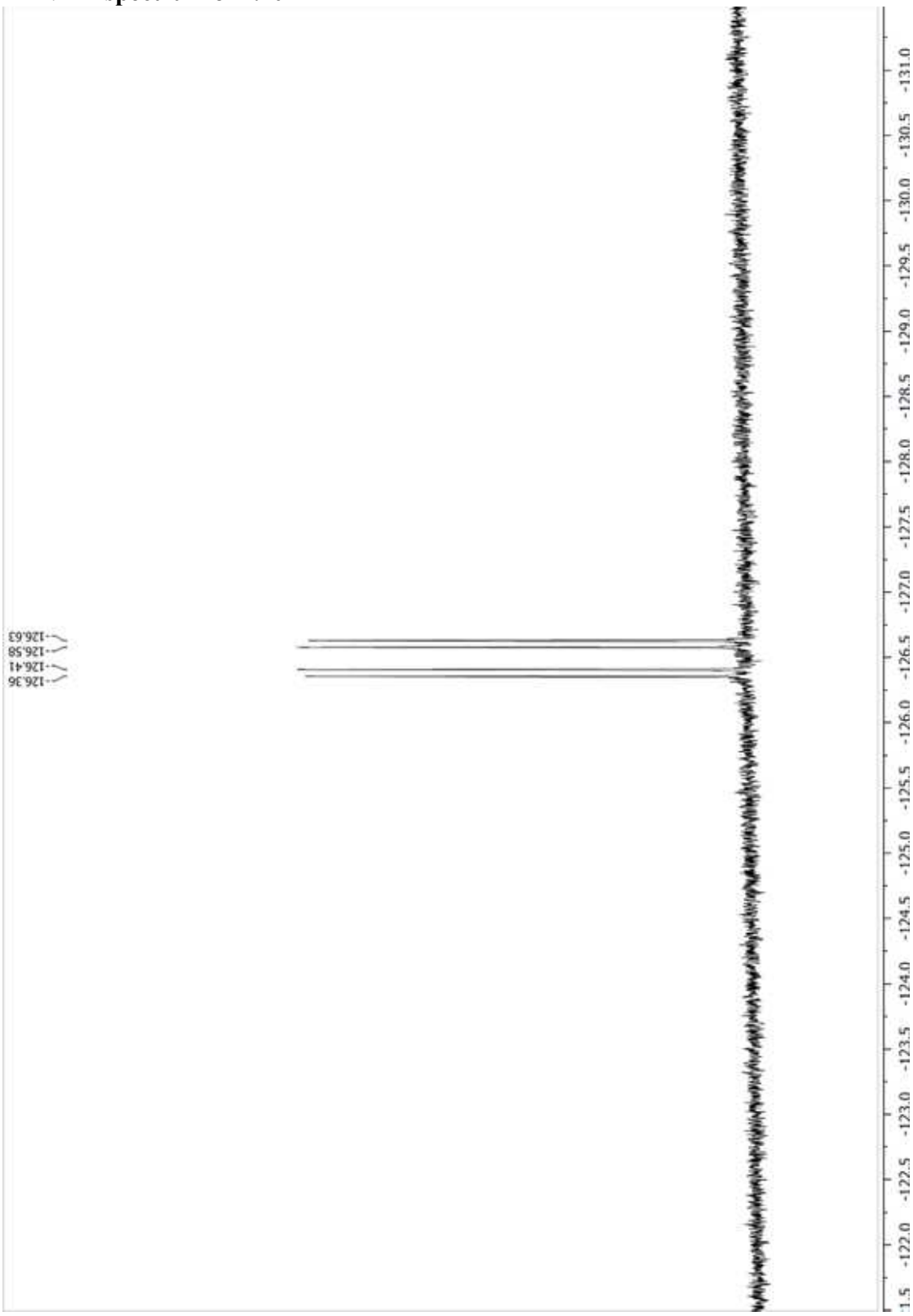
^{1}H NMR spectrum of 2.107



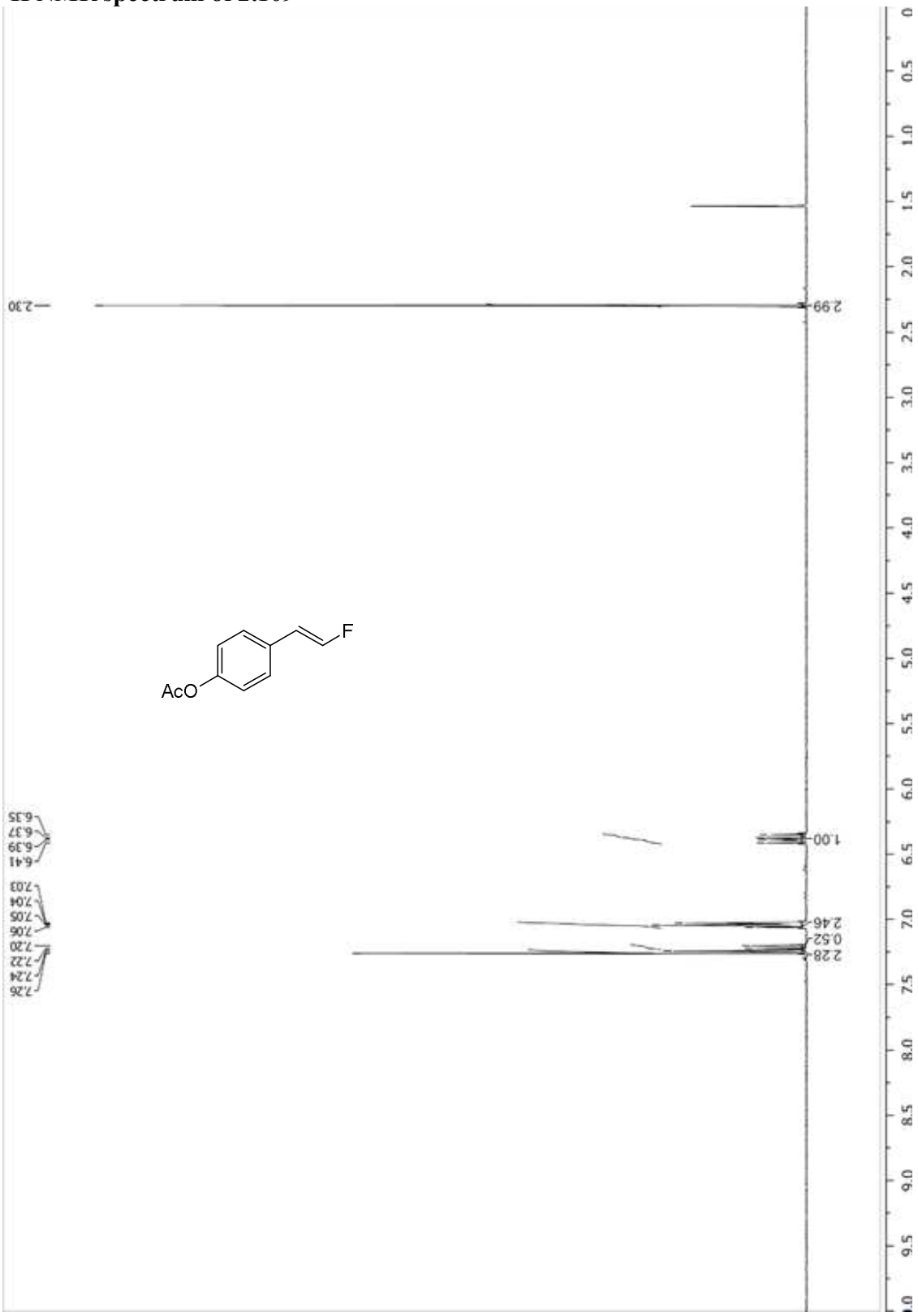
^{13}C NMR spectrum of 2.107



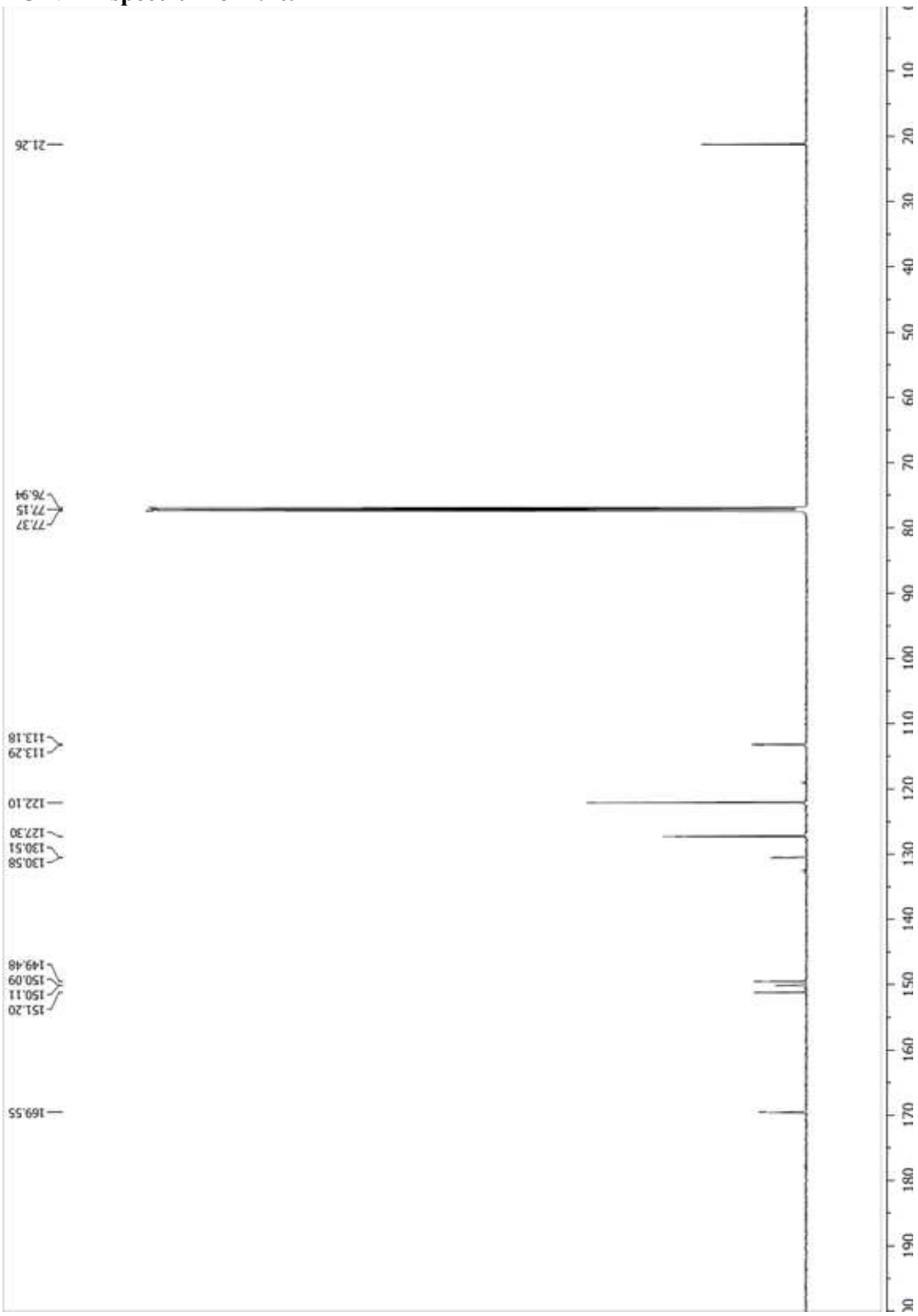
^{19}F NMR spectrum of 2.107



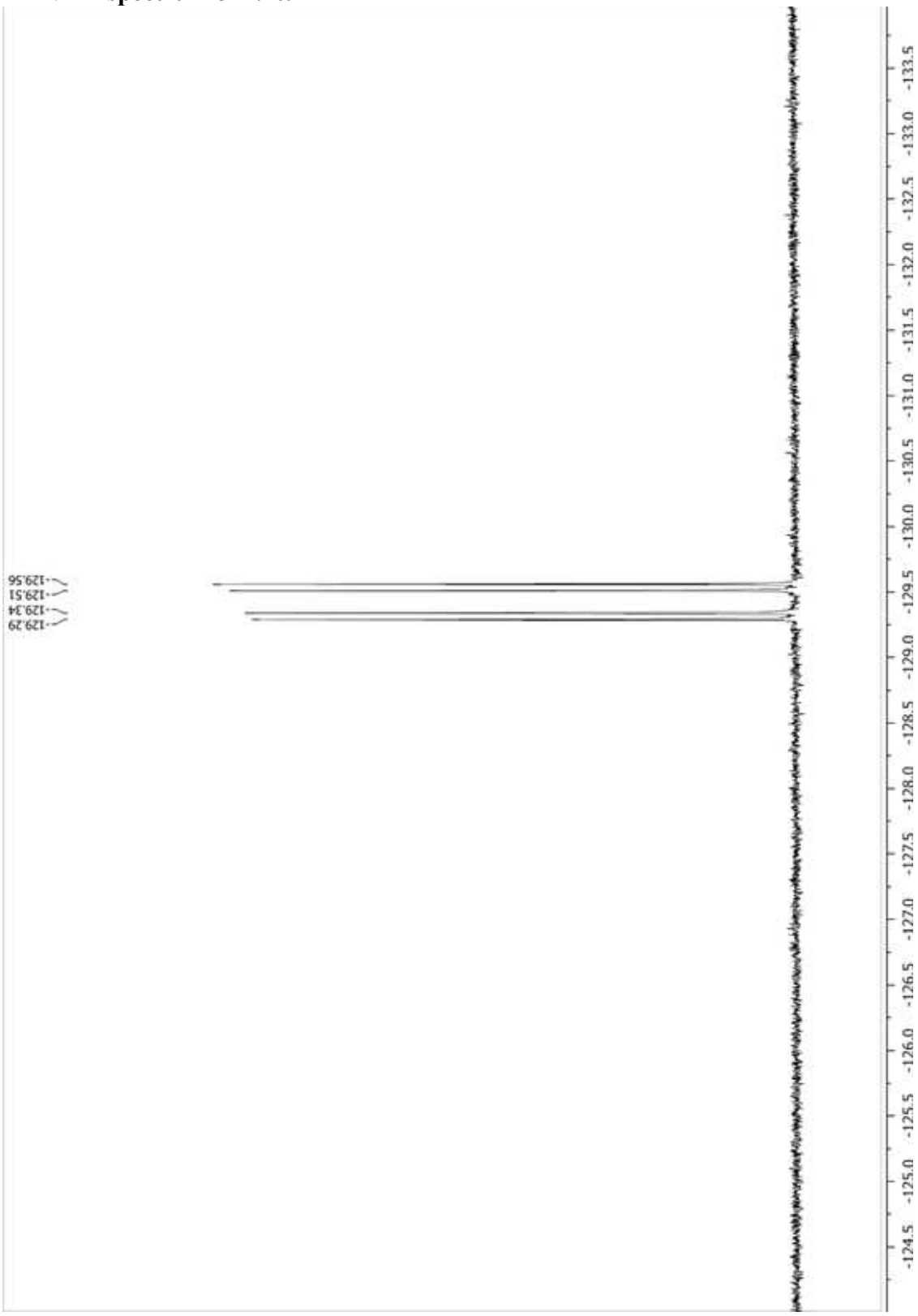
^{1}H NMR spectrum of 2.109



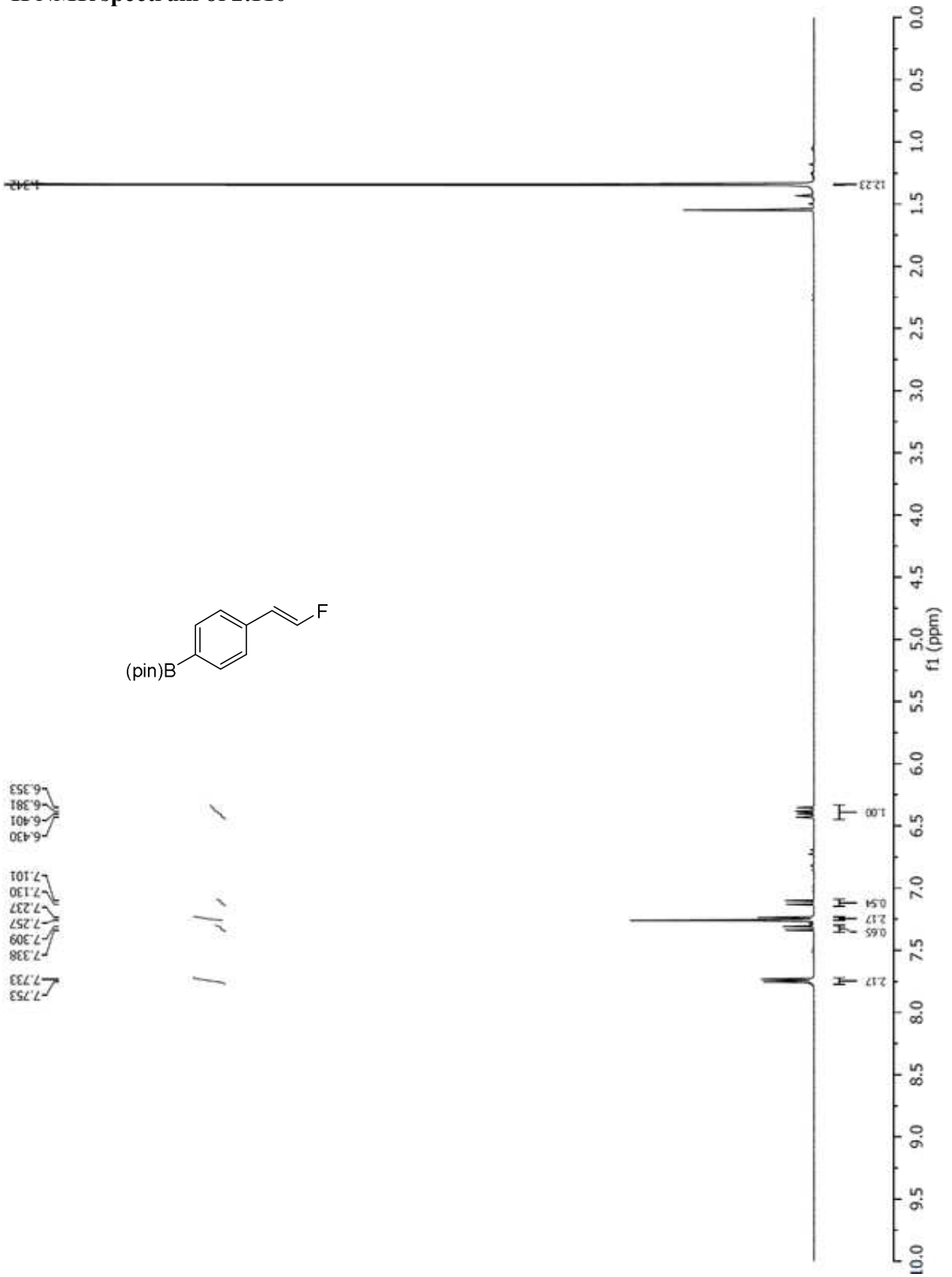
^{13}C NMR spectrum of 2.109



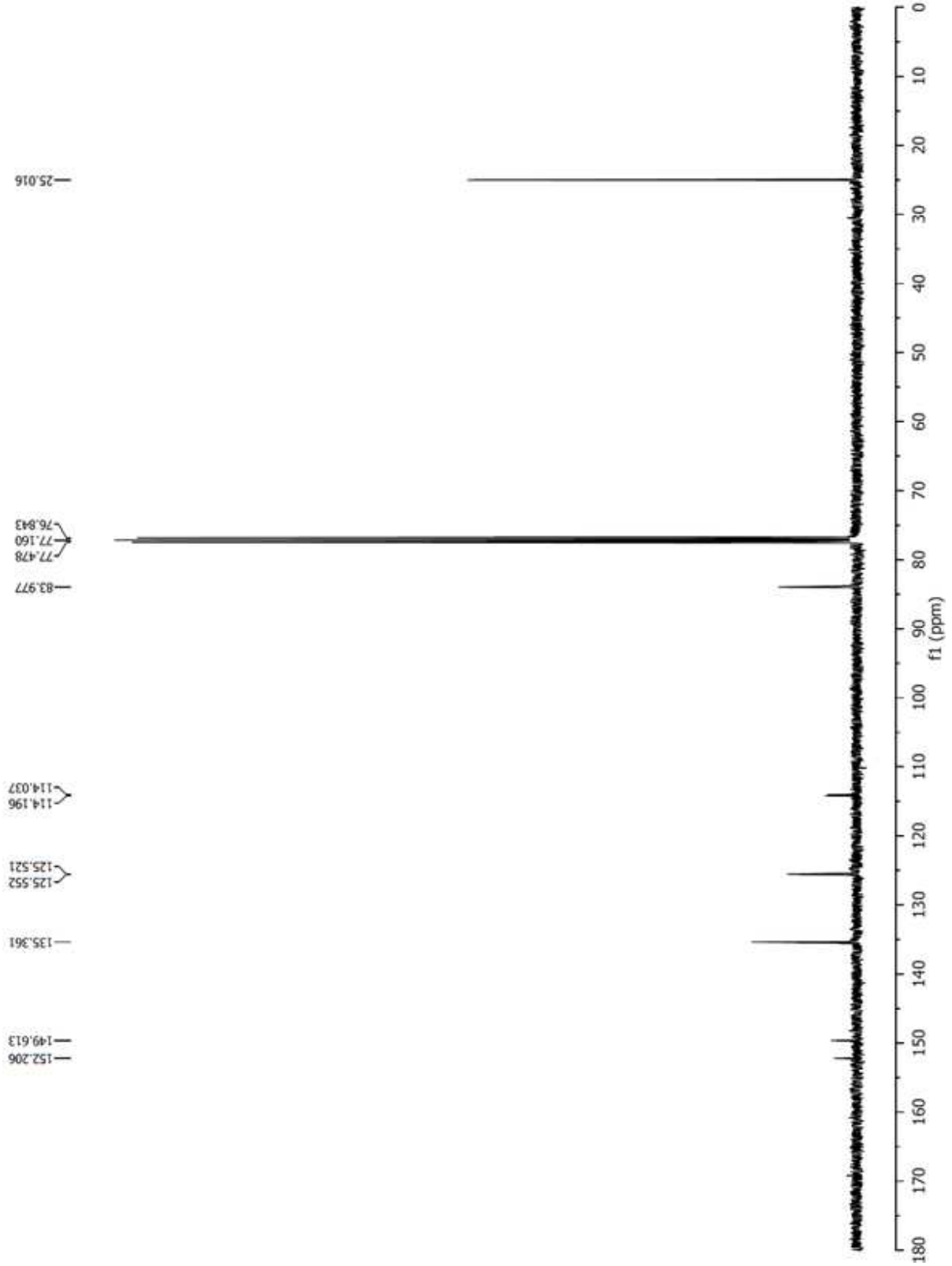
^{19}F NMR spectrum of 2.109



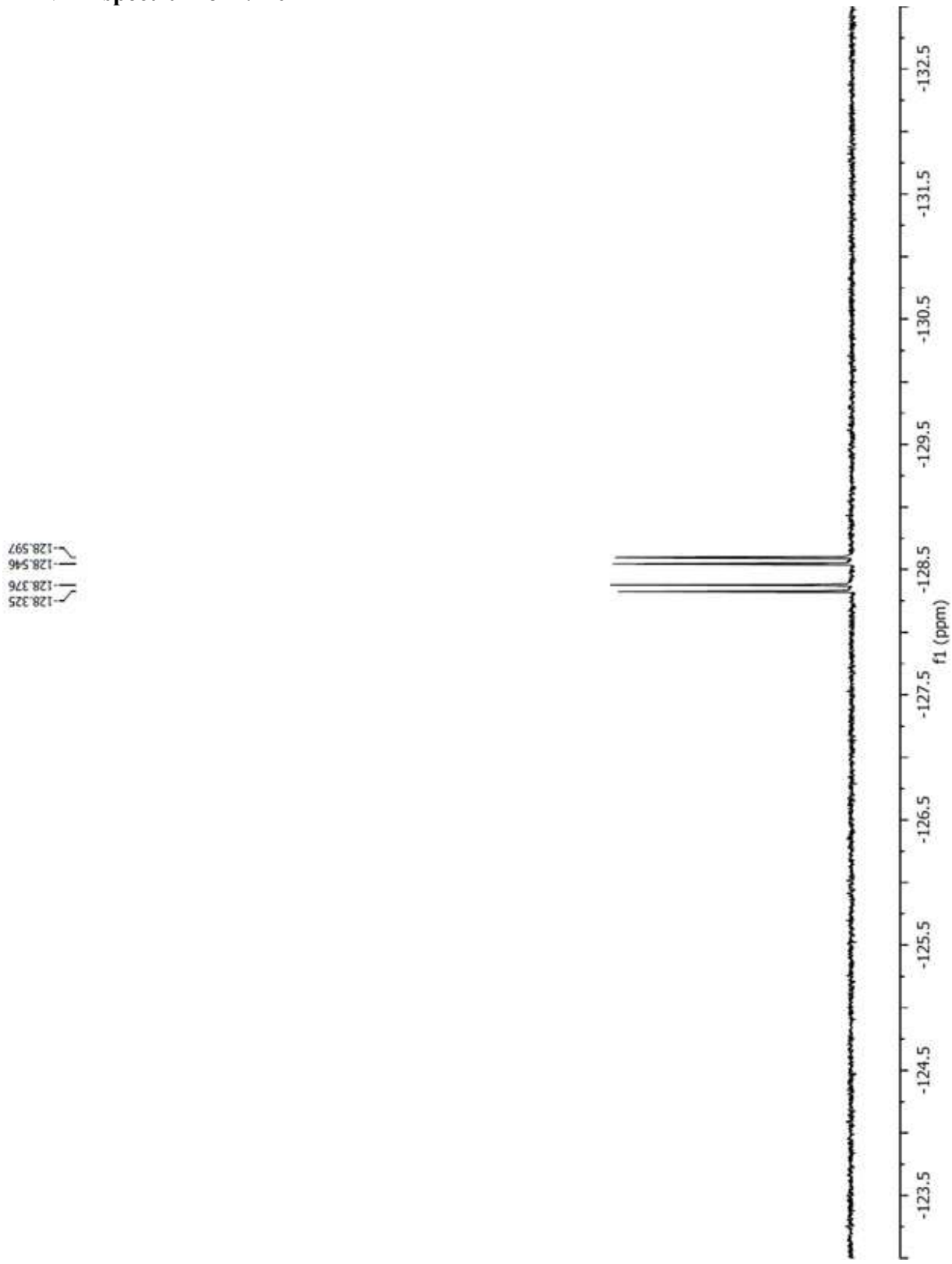
^{1}H NMR spectrum of 2.110



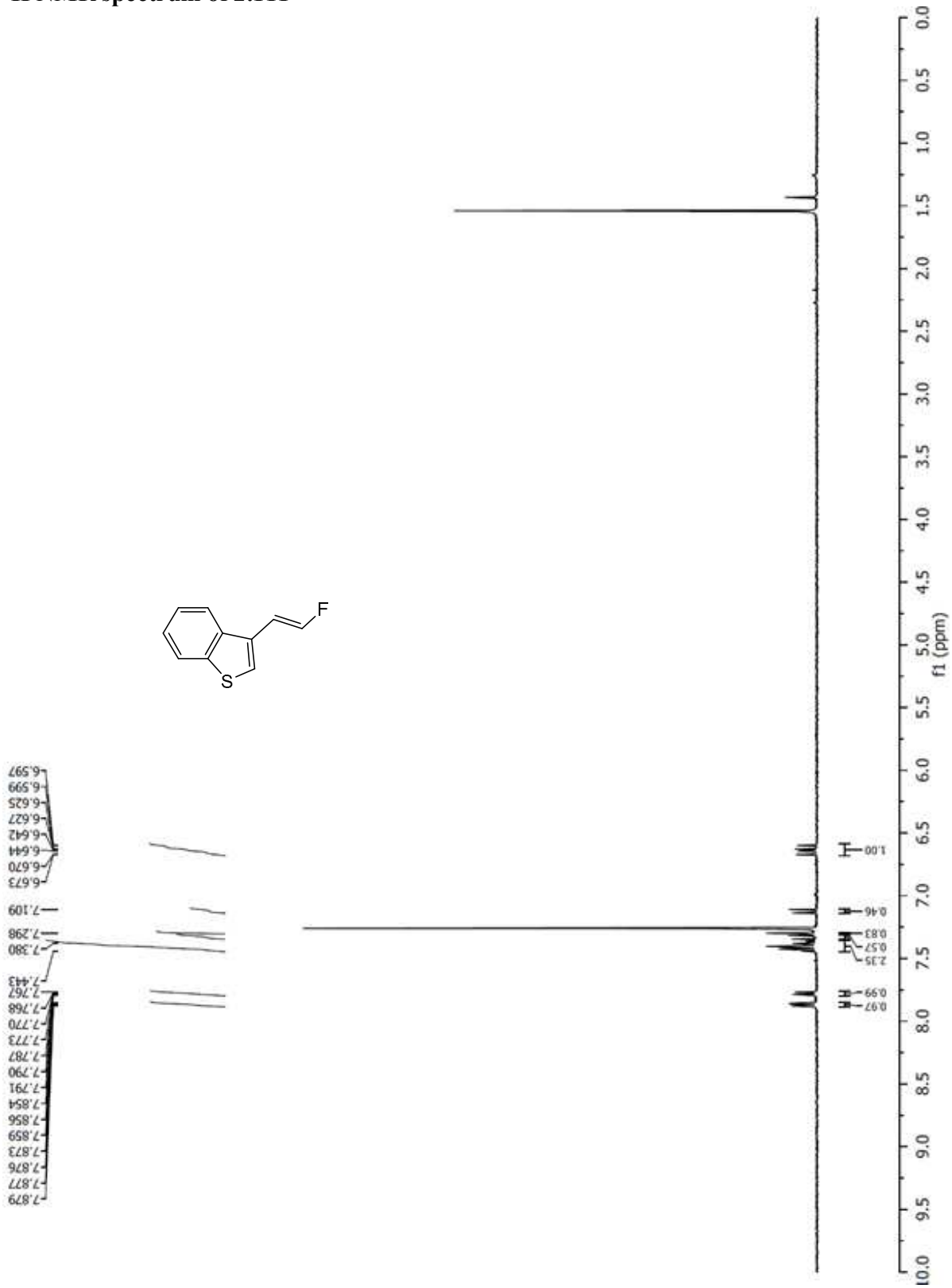
^{13}C NMR spectrum of 2.110



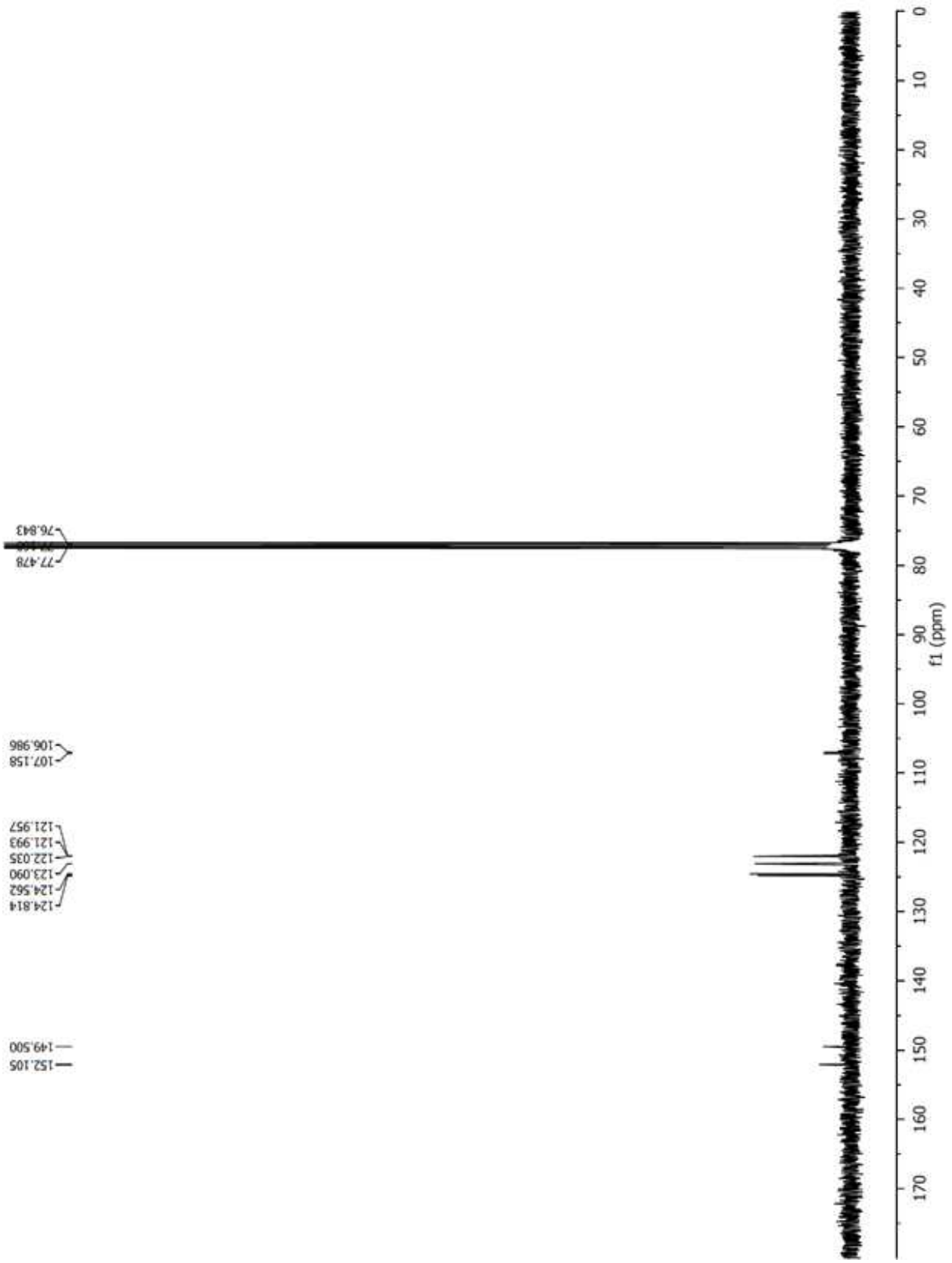
^{19}F NMR spectrum of 2.110



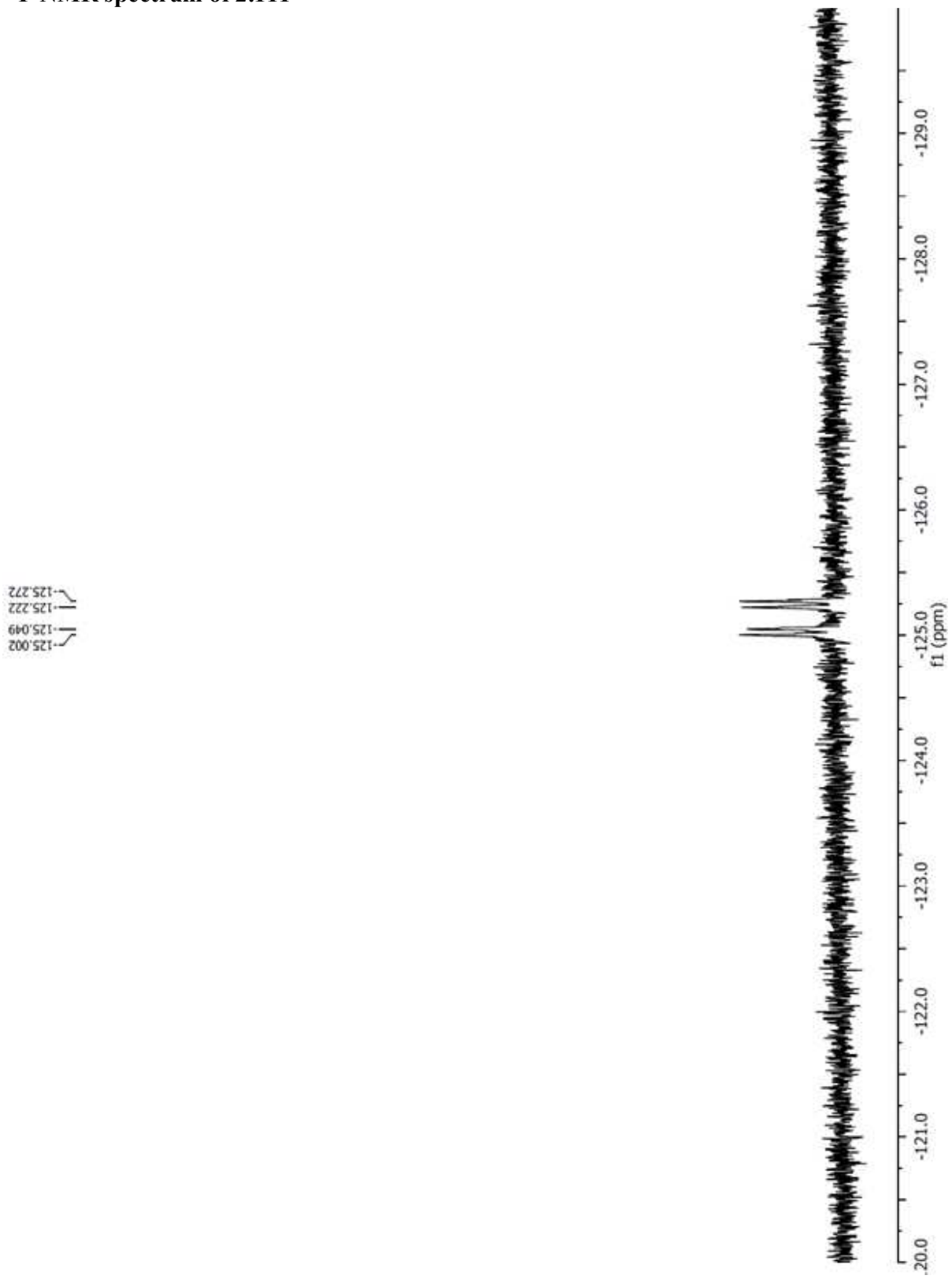
^{1}H NMR spectrum of 2.111



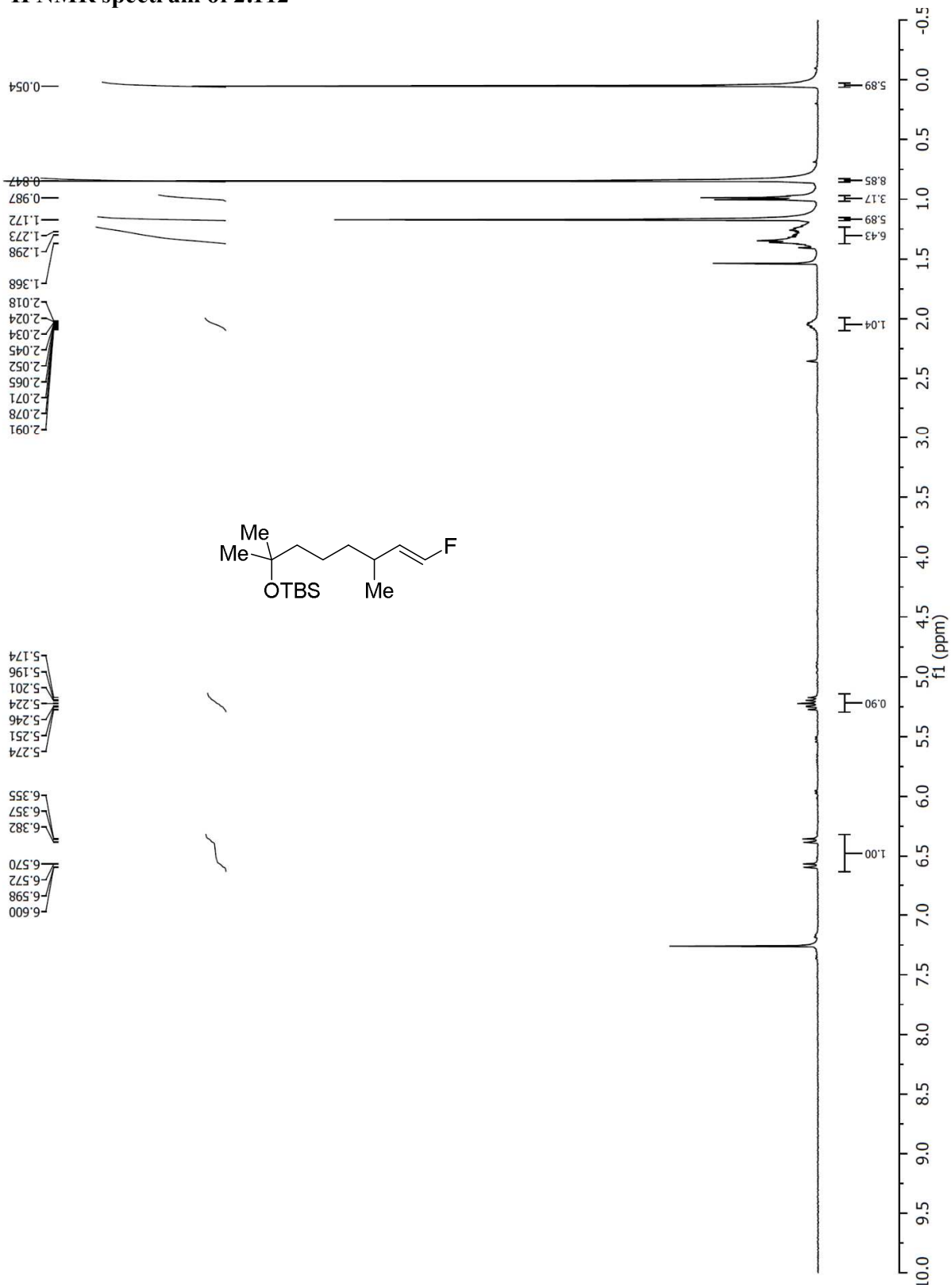
^{13}C NMR spectrum of 2.111



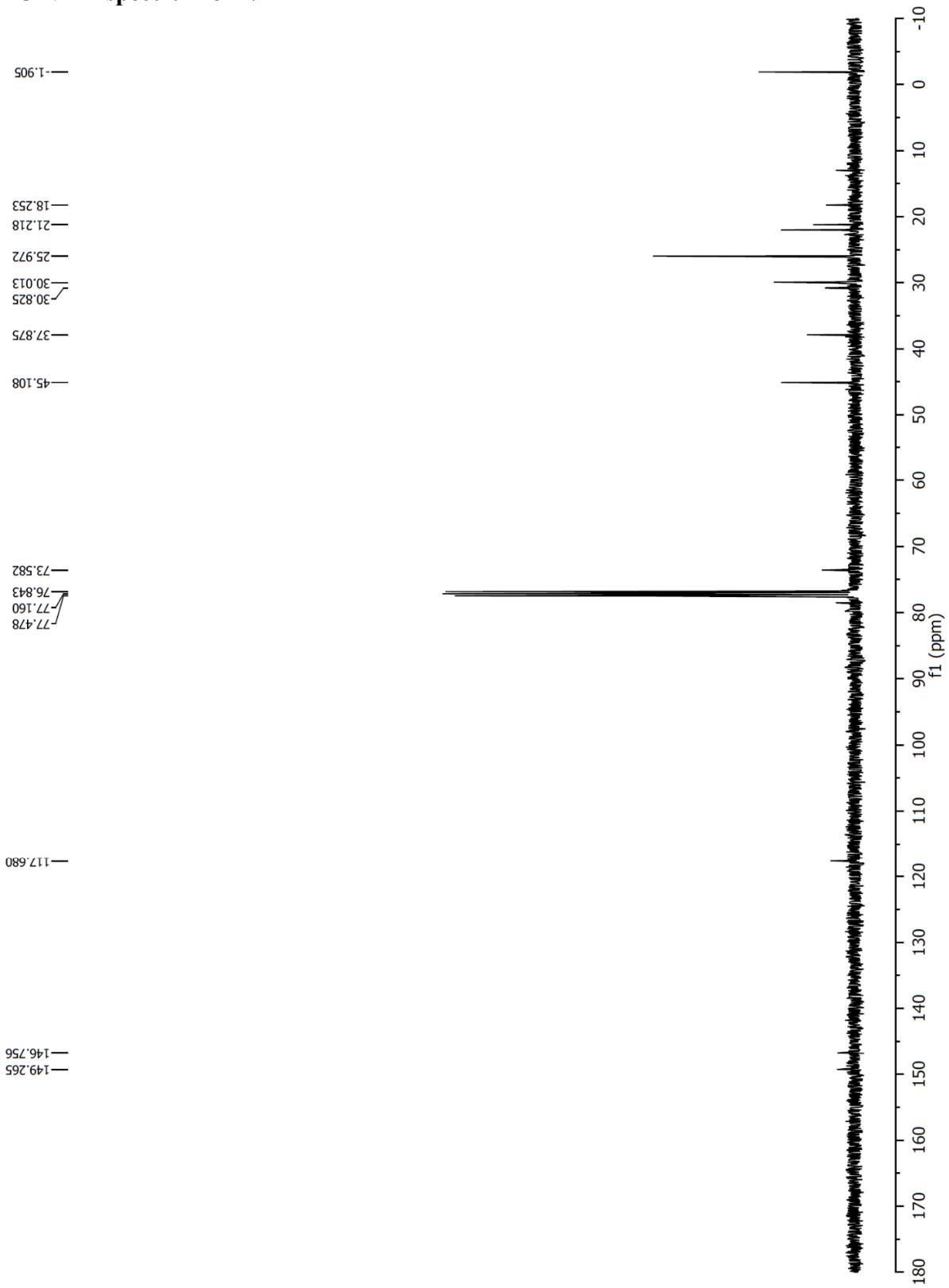
^{19}F NMR spectrum of 2.111



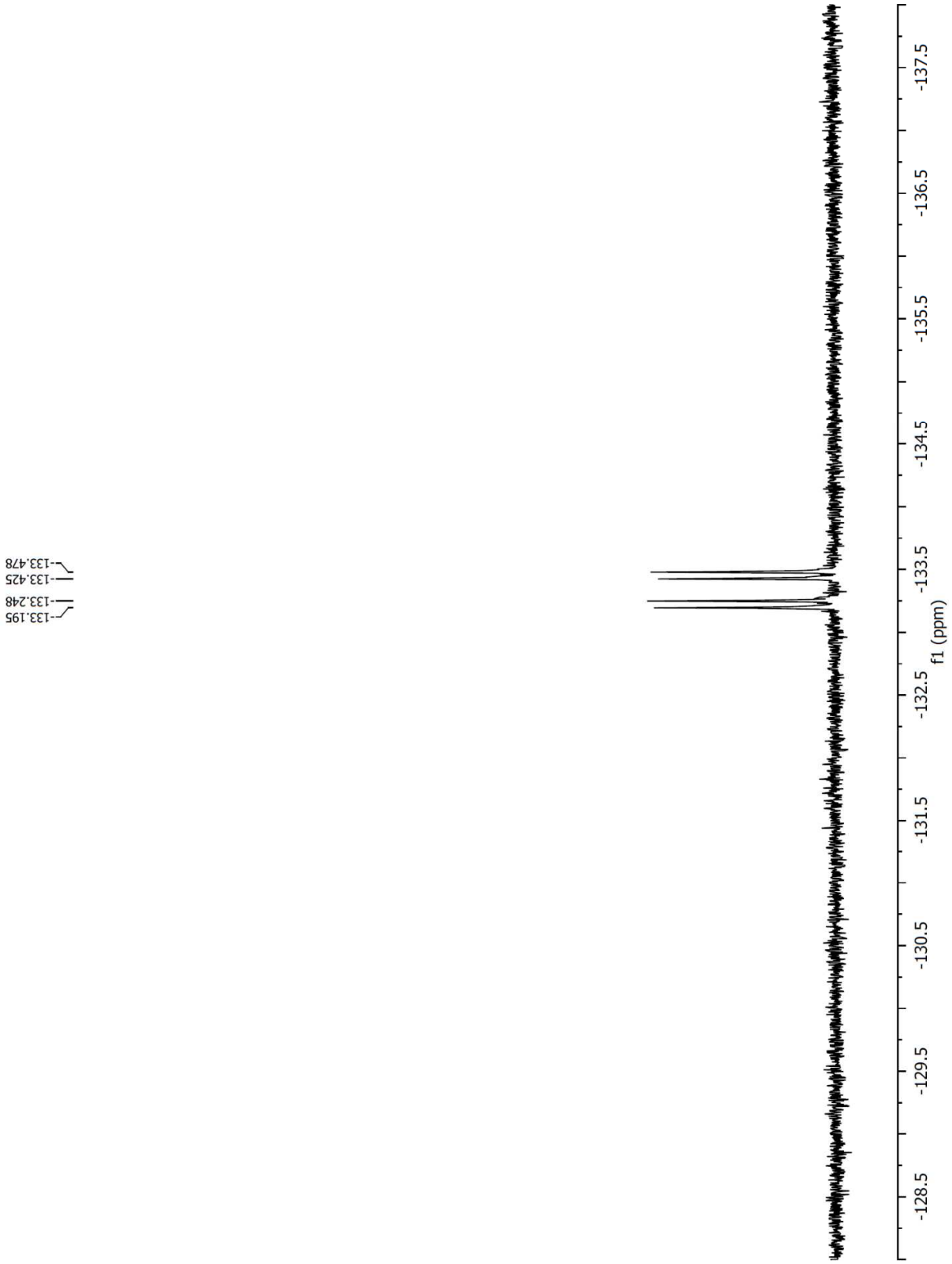
^{1}H NMR spectrum of 2.112



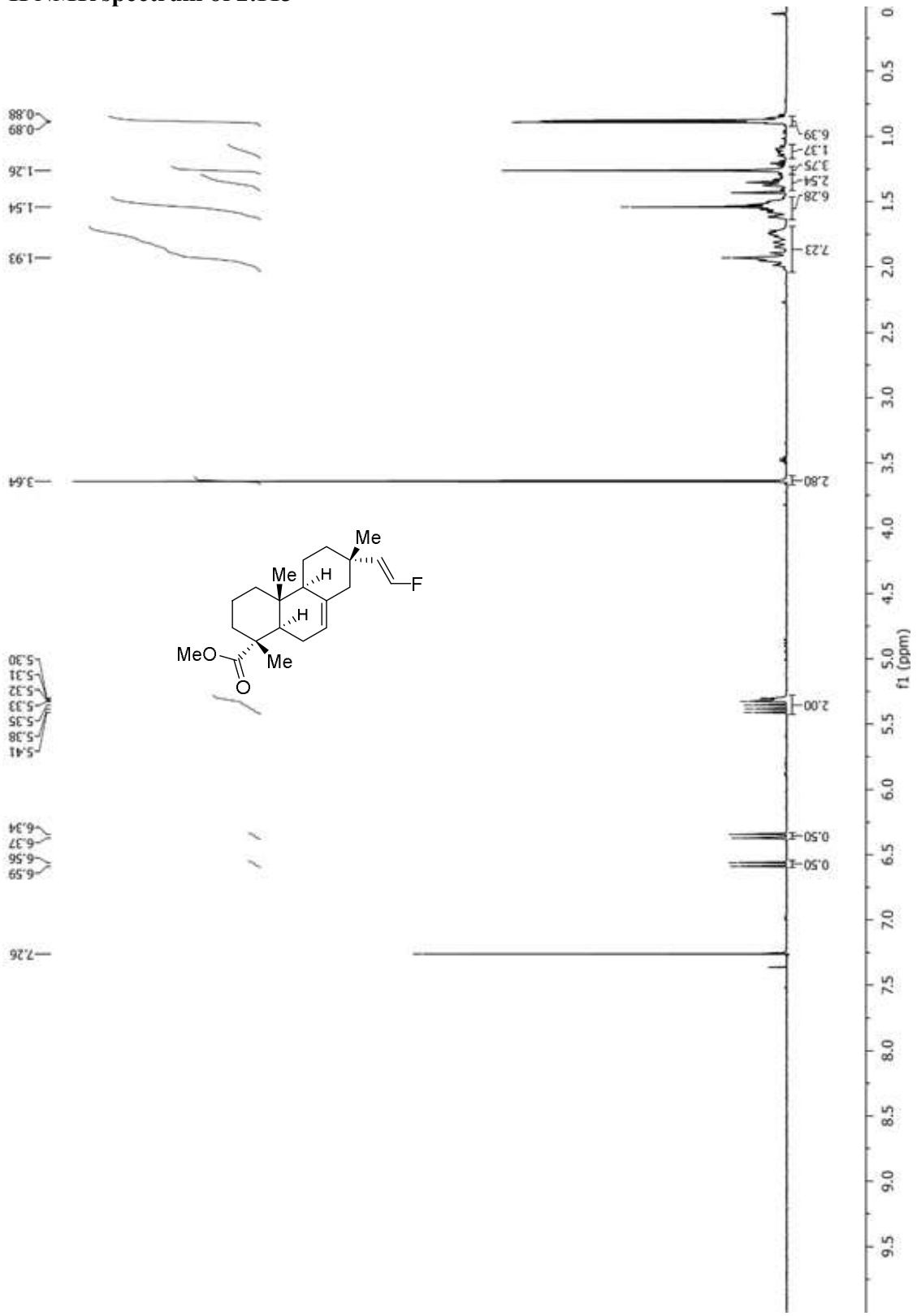
^{13}C NMR spectrum of 2.112



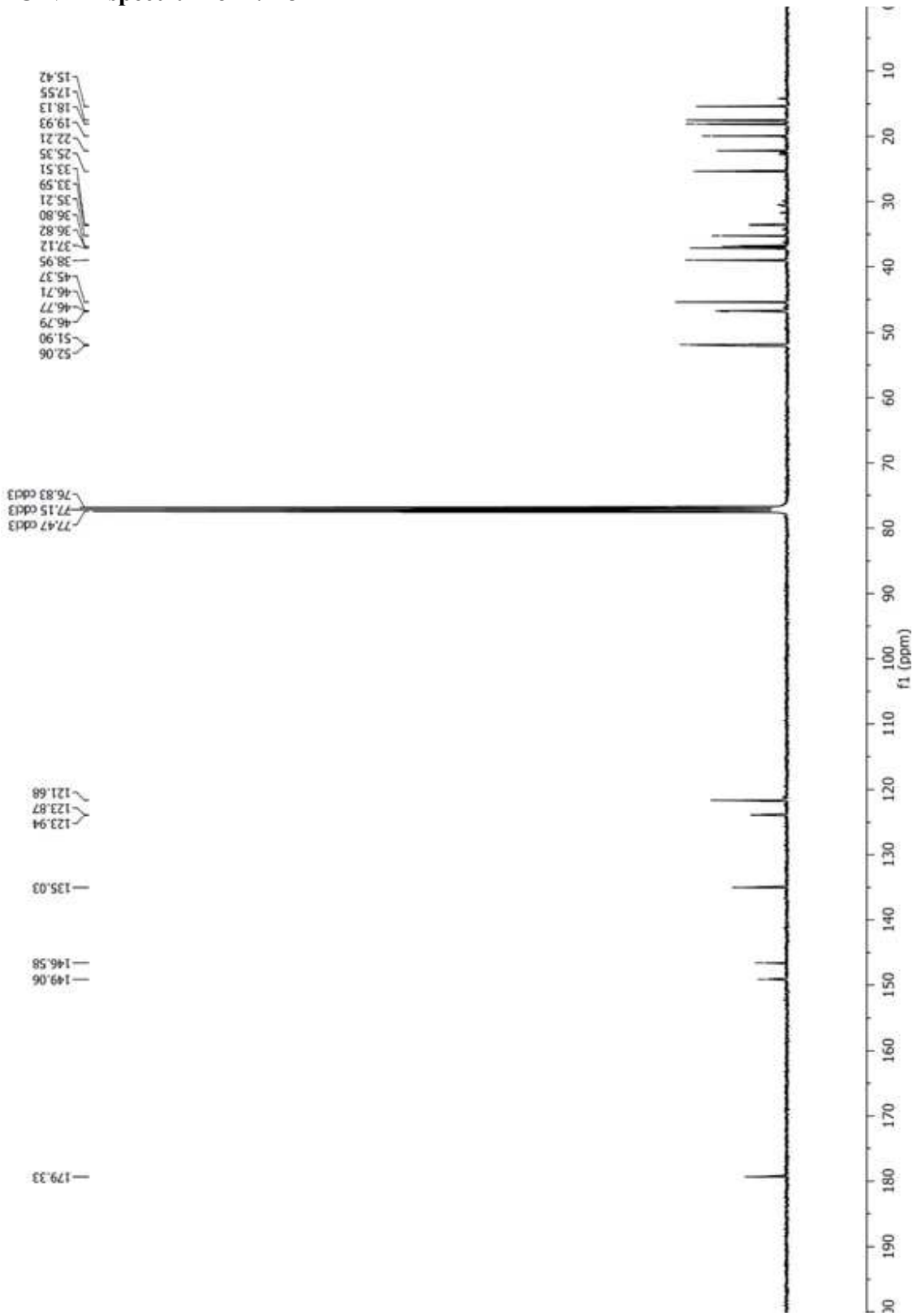
^{19}F NMR spectrum of 2.112



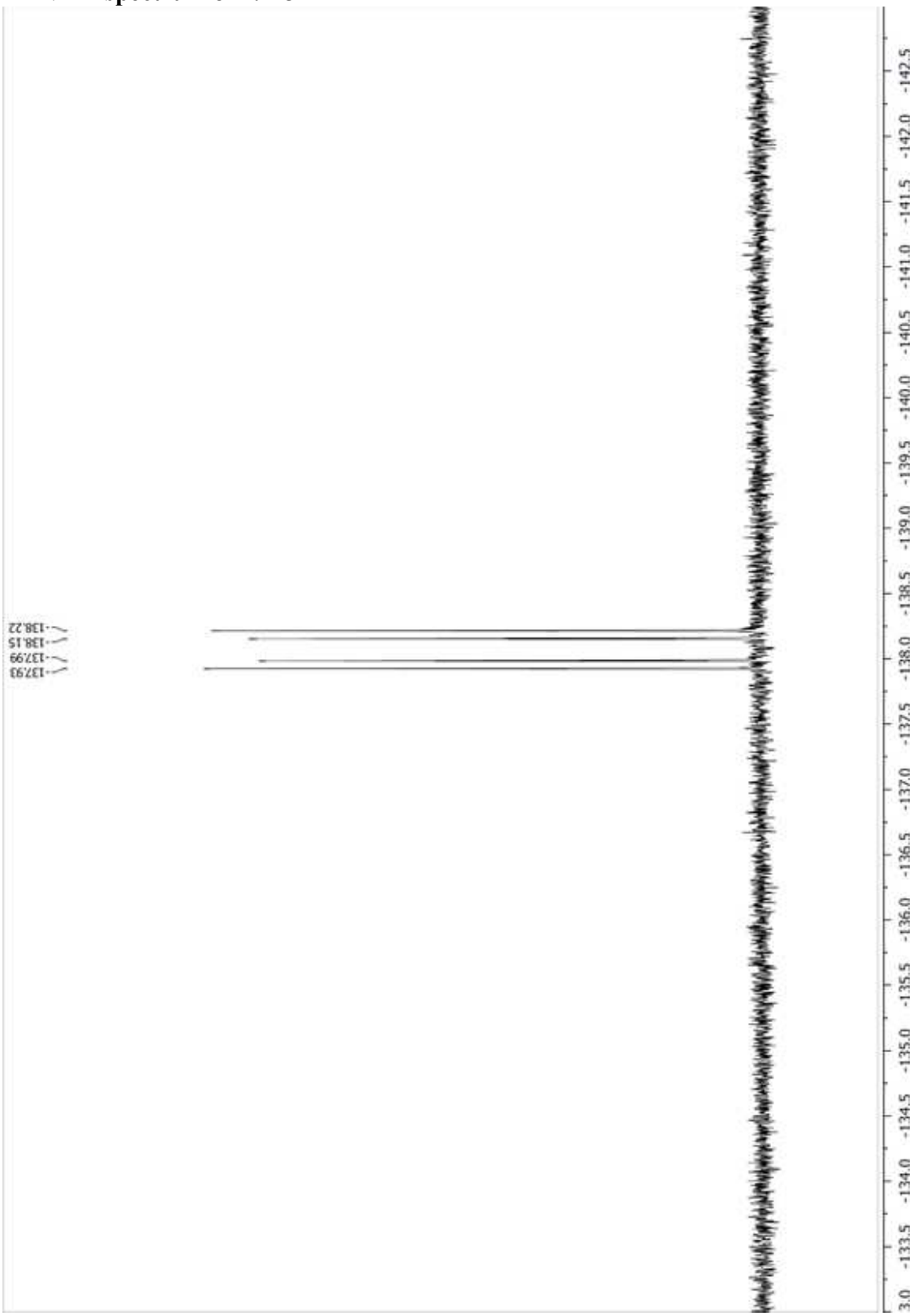
^{1}H NMR spectrum of 2.113



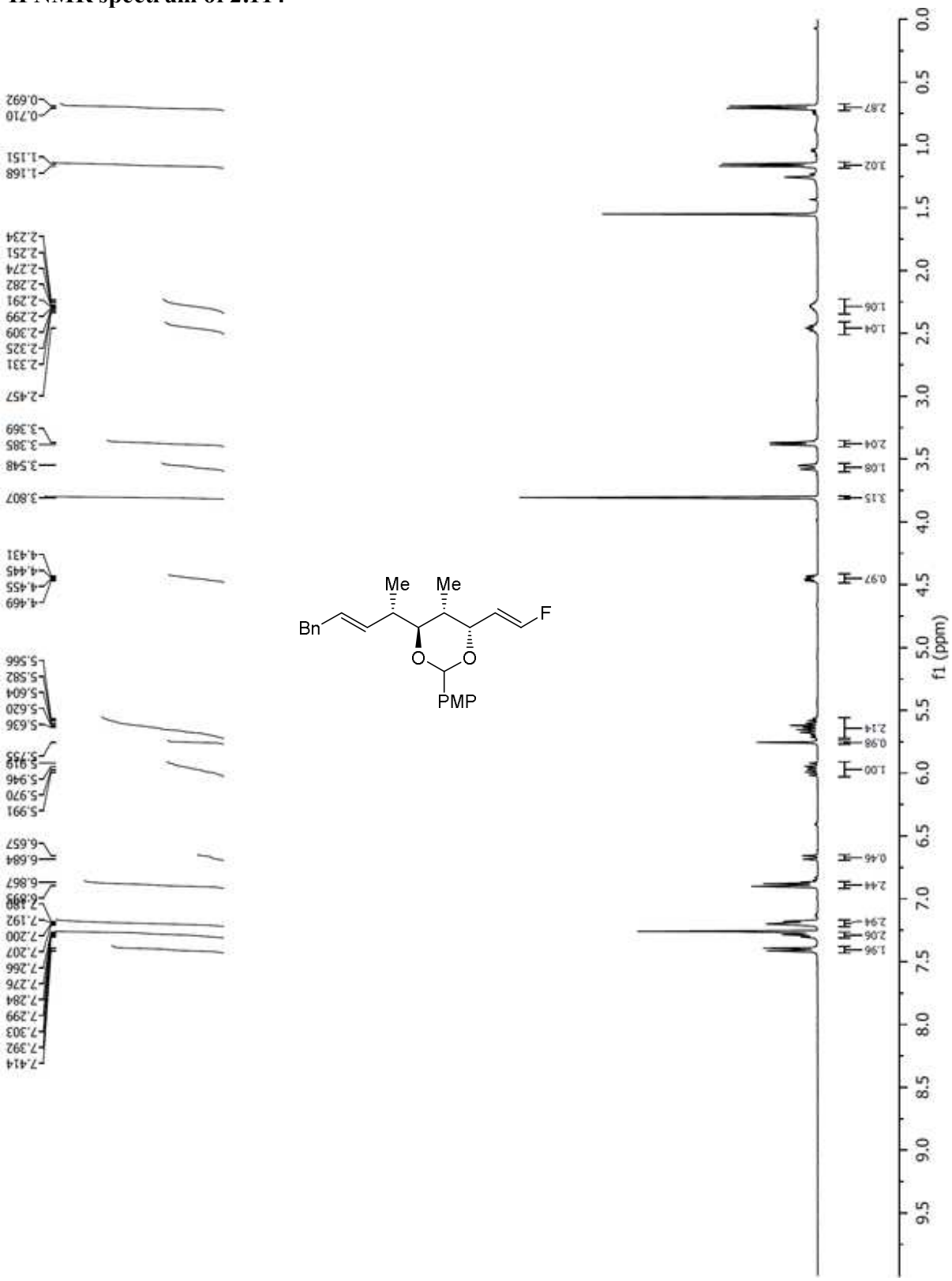
^{13}C NMR spectrum of 2.113



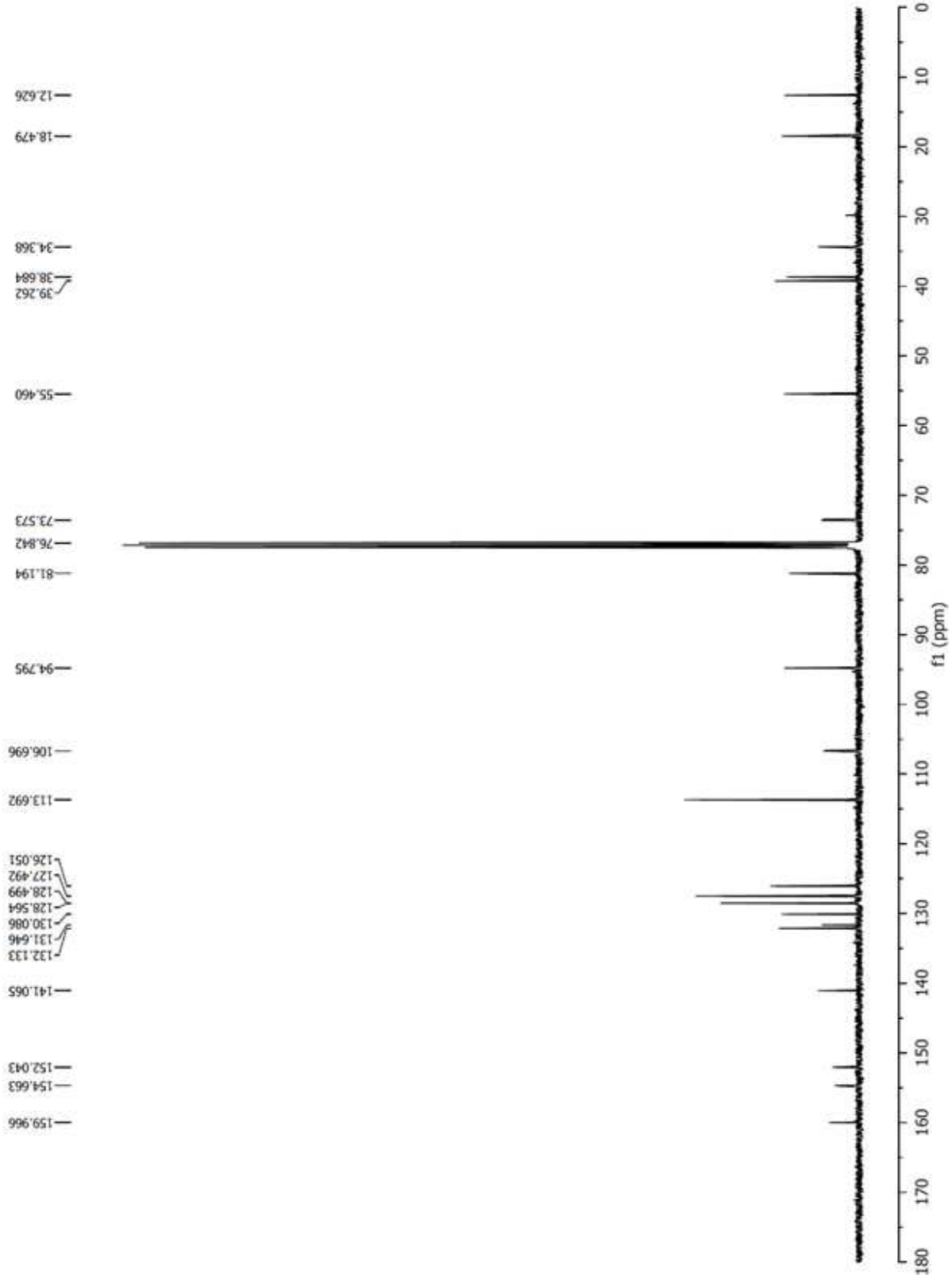
^{19}F NMR spectrum of 2.113



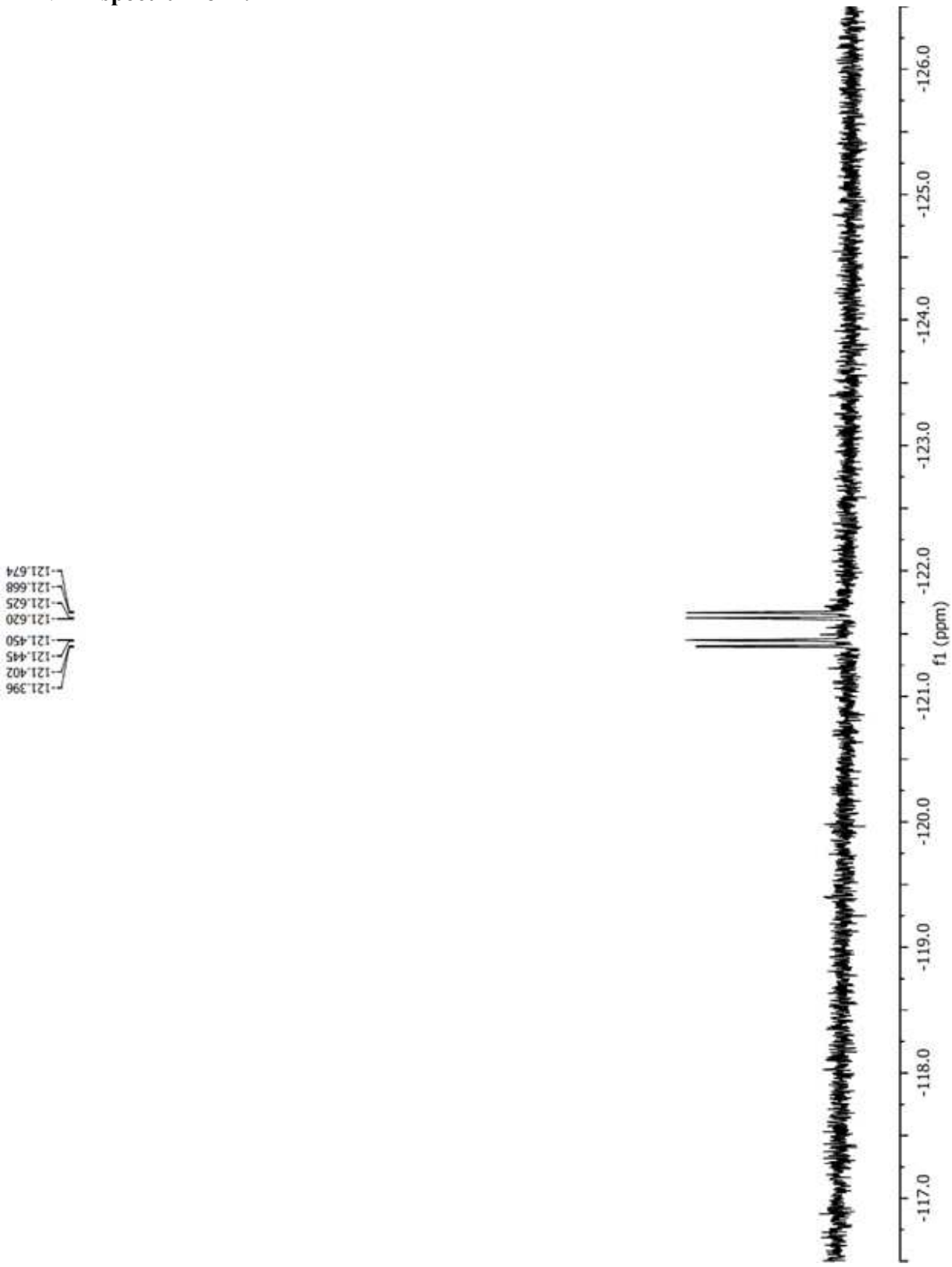
^{1}H NMR spectrum of 2.114



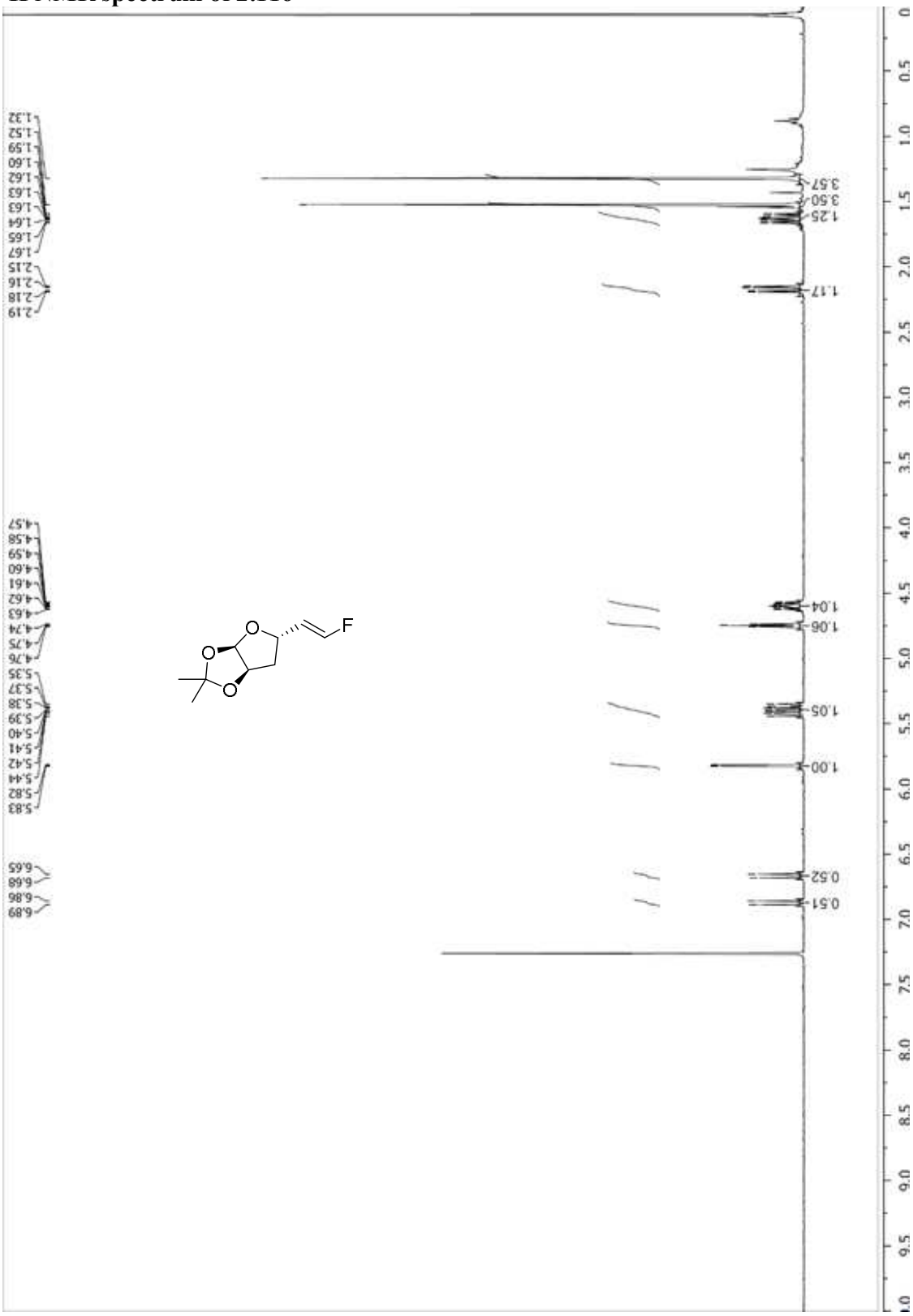
^{13}C NMR spectrum of 2.114



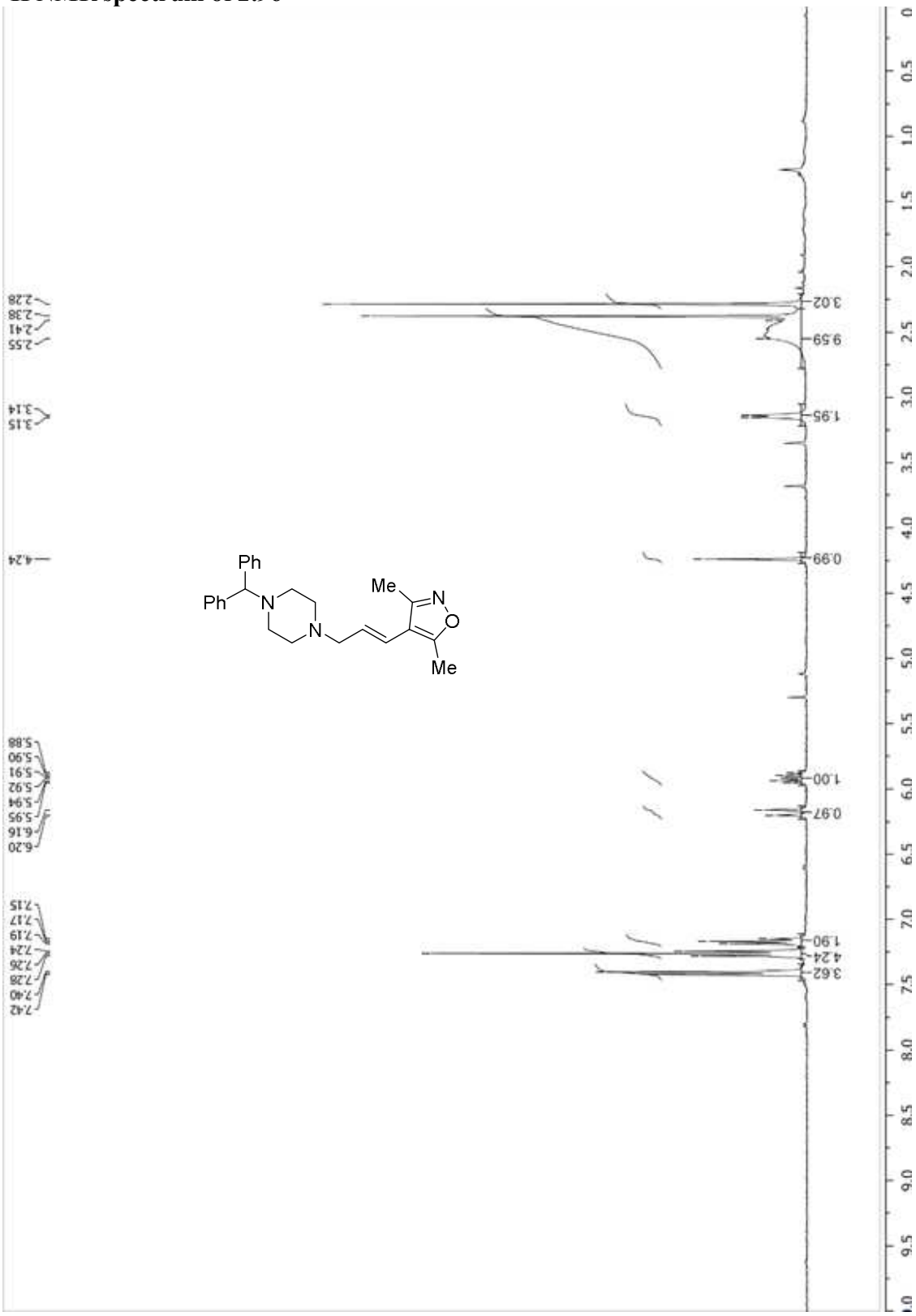
^{19}F NMR spectrum of 2.114



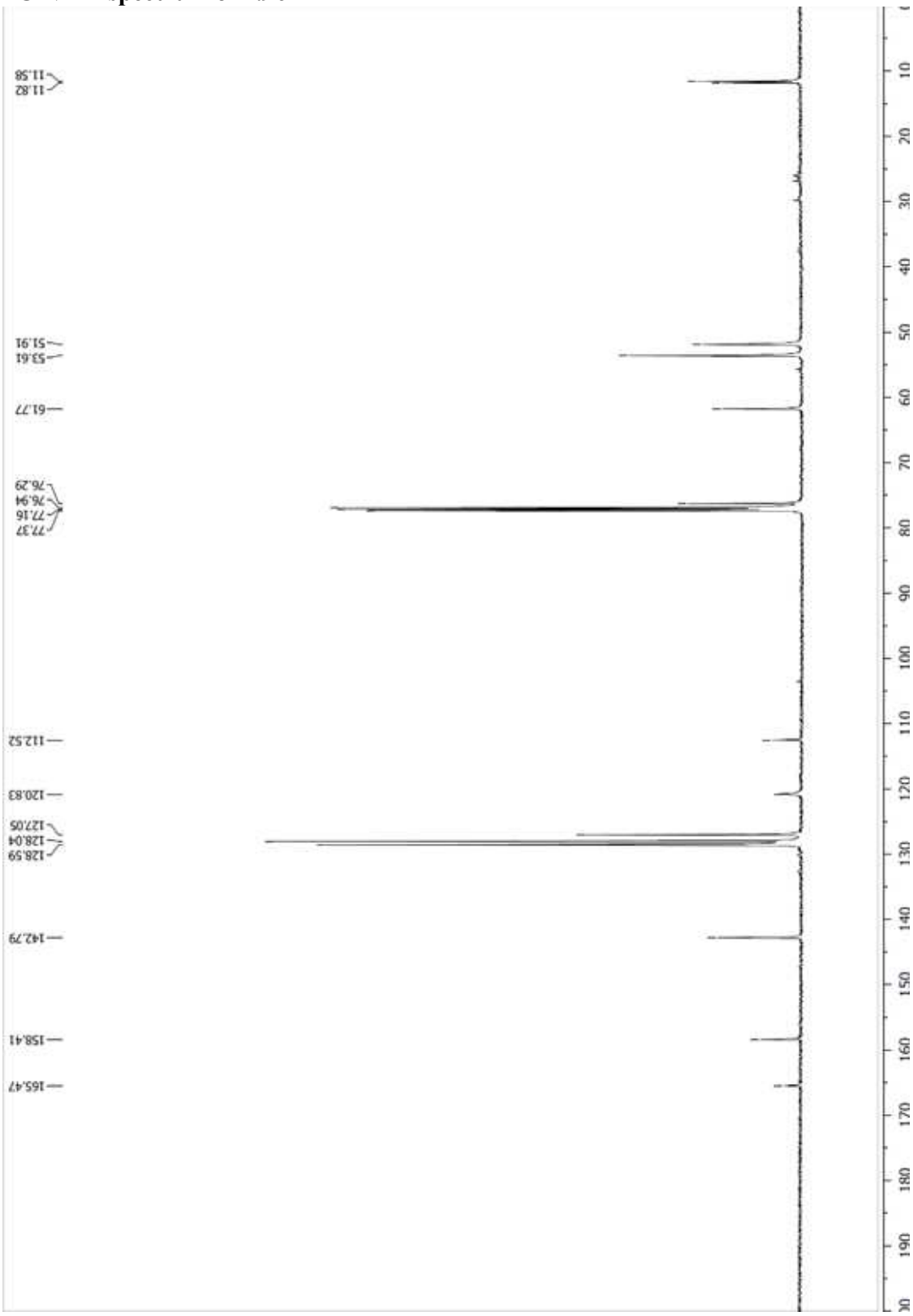
^{1}H NMR spectrum of 2.116



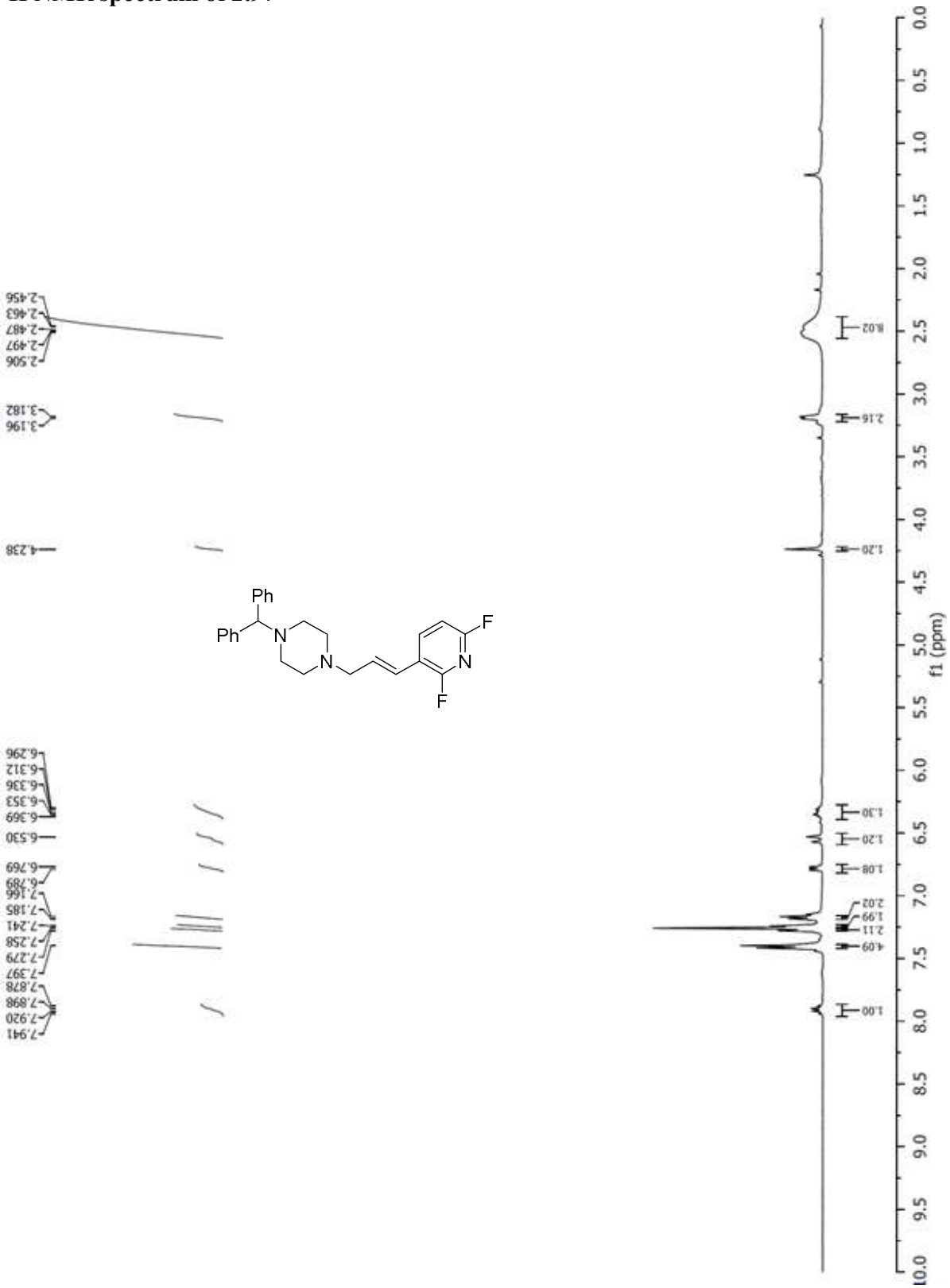
^{1}H NMR spectrum of 2.96



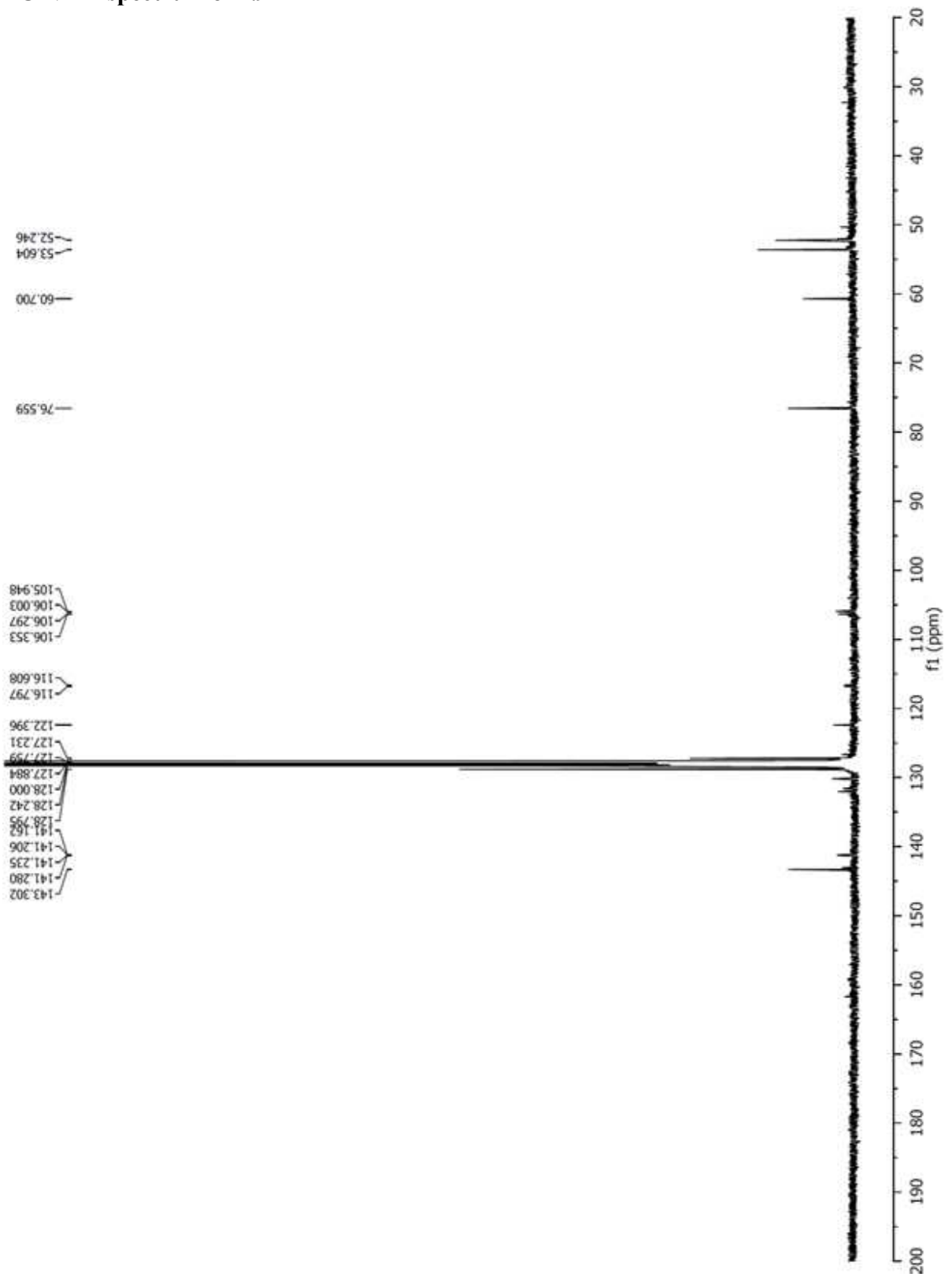
^{13}C NMR spectrum of 2.96



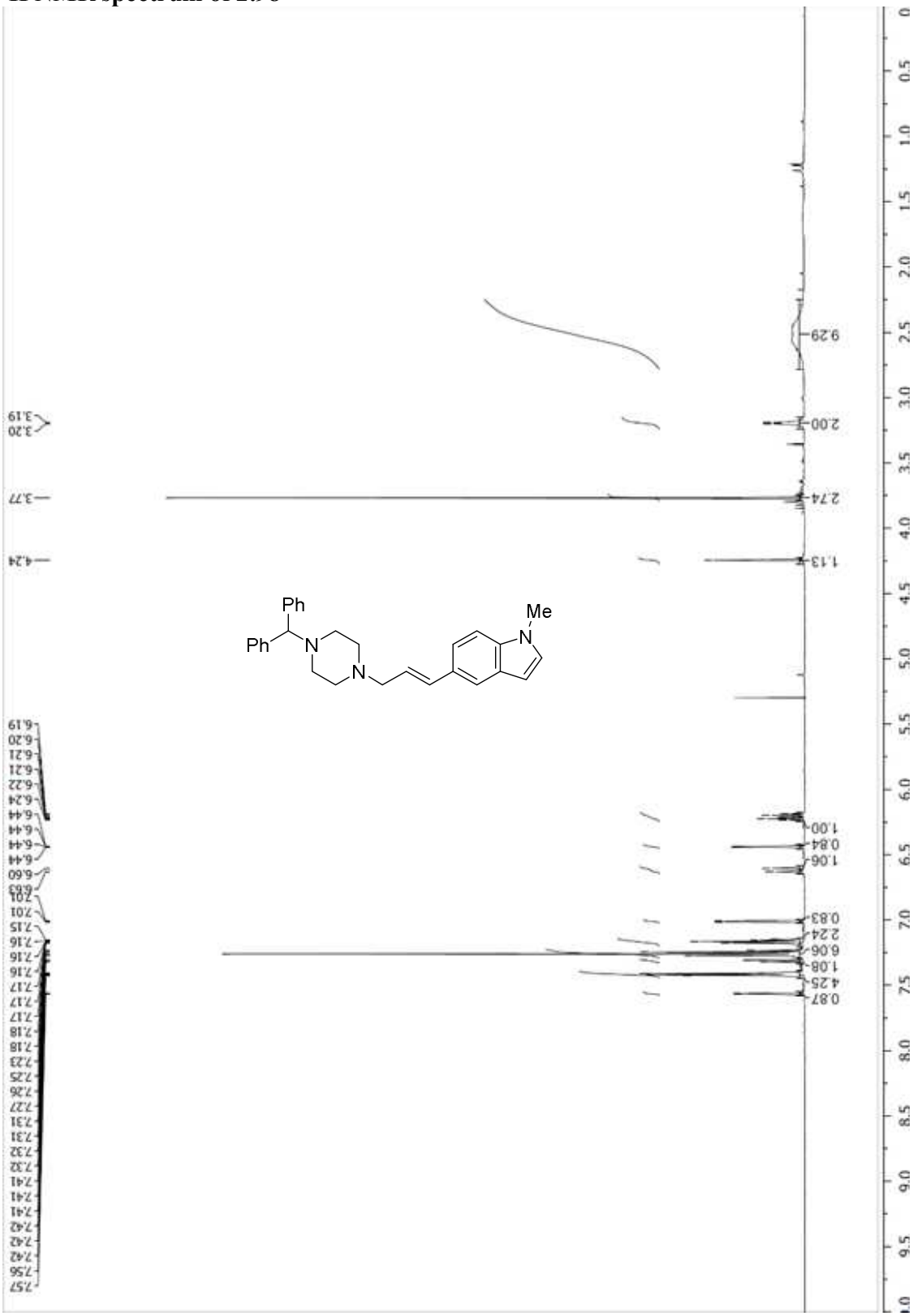
^{1}H NMR spectrum of 2.97



^{13}C NMR spectrum of 2.97



^{1}H NMR spectrum of 2.98



^{13}C NMR spectrum of 2.98

2.6.14. X-ray Crystallographic Data

X-ray Crystal Structure for 2.22

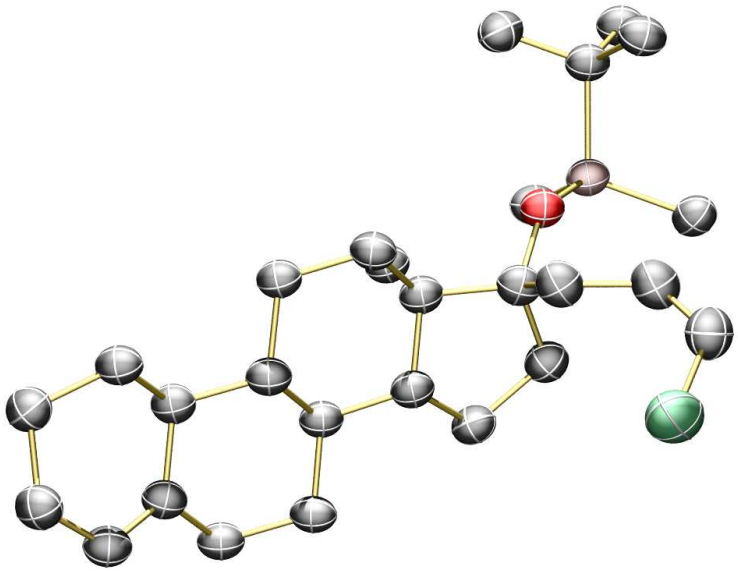


Table 1. Crystal data and structure refinement for 2.22

Identification code	$C_{27}H_{45}ClOSi$	
Empirical formula	C_{27} H_{45} Cl O Si	
Formula weight	449.17	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.0979(7) Å	α= 90°.
	b = 7.5039(5) Å	β= 90.799(3)°.
	c = 17.1057(11) Å	γ = 90°.
Volume	1296.03(15) $Å^3$	
Z	2	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	1.847 mm^{-1}	
F(000)	492	
Crystal size	0.250 x 0.100 x 0.060 mm^3	
Theta range for data collection	2.583 to 66.833°.	
Index ranges	-12<=h<=12, 0<=k<=8, 0<=l<=20	

Reflections collected	2478
Independent reflections	2478 [R(int) = 0.0760]
Completeness to theta = 67.679°	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.4574
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2478 / 1 / 278
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1830
R indices (all data)	R1 = 0.0778, wR2 = 0.1864
Absolute structure parameter	0.03(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.517 and -0.538 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^{2x}$ 10^3) for 2.22. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Cl(1)	5202(2)	5392(3)	-140(1)	88(1)
Si(1)	-360(1)	5714(2)	1733(1)	42(1)
O(1)	1224(3)	6080(4)	1893(2)	45(1)
C(1)	3527(5)	5996(8)	-151(3)	62(1)
C(2)	2844(5)	6276(8)	483(3)	56(1)
C(3)	3327(4)	6208(8)	1310(3)	51(1)
C(4)	2447(4)	5127(7)	1863(3)	45(1)
C(5)	2287(4)	3155(7)	1594(3)	49(1)
C(6)	3213(5)	1998(7)	2125(3)	48(1)
C(7)	4021(4)	3381(6)	2577(2)	42(1)
C(8)	4750(4)	2799(6)	3324(2)	41(1)
C(9)	5676(4)	1232(6)	3191(3)	43(1)
C(10)	6386(4)	705(6)	3955(2)	44(1)
C(11)	7097(4)	2249(6)	4324(2)	42(1)
C(12)	8363(5)	2099(7)	4560(3)	49(1)
C(13)	9103(4)	3527(7)	4999(3)	50(1)
C(14)	8151(4)	4897(7)	5334(3)	49(1)
C(15)	7147(4)	5483(6)	4709(3)	44(1)
C(16)	6298(4)	3925(6)	4419(2)	42(1)
C(17)	5533(4)	4403(6)	3656(3)	42(1)
C(18)	4658(4)	6062(6)	3755(2)	42(1)
C(19)	3881(4)	6542(6)	3006(3)	44(1)
C(20)	3085(4)	4944(6)	2702(2)	43(1)
C(21)	1978(4)	4485(7)	3289(3)	45(1)
C(22)	-1109(5)	4053(7)	2405(3)	52(1)
C(23)	-716(4)	4981(8)	703(3)	51(1)
C(24)	-1109(4)	7990(7)	1920(3)	45(1)
C(25)	-724(5)	8651(8)	2738(3)	55(1)
C(26)	-2631(4)	7862(8)	1863(3)	54(1)
C(27)	-617(5)	9314(7)	1310(3)	52(1)

Table 3. Bond lengths [Å]and angles [°] for 2.22

Cl(1)-C(1)	1.751(6)
Si(1)-O(1)	1.641(3)
Si(1)-C(22)	1.864(5)
Si(1)-C(23)	1.875(5)
Si(1)-C(24)	1.897(5)
O(1)-C(4)	1.429(5)
C(1)-C(2)	1.310(7)
C(2)-C(3)	1.491(7)
C(3)-C(4)	1.537(6)
C(4)-C(5)	1.558(7)
C(4)-C(20)	1.571(6)
C(5)-C(6)	1.559(6)
C(6)-C(7)	1.524(6)
C(7)-C(20)	1.523(6)
C(7)-C(8)	1.530(6)
C(8)-C(9)	1.521(6)
C(8)-C(17)	1.544(6)
C(9)-C(10)	1.534(6)
C(10)-C(11)	1.498(6)
C(11)-C(12)	1.340(6)
C(11)-C(16)	1.504(6)
C(12)-C(13)	1.502(7)
C(13)-C(14)	1.525(7)
C(14)-C(15)	1.528(6)
C(15)-C(16)	1.529(6)
C(16)-C(17)	1.549(6)
C(17)-C(18)	1.537(6)
C(18)-C(19)	1.537(6)
C(19)-C(20)	1.530(6)
C(20)-C(21)	1.552(6)
C(24)-C(27)	1.528(7)
C(24)-C(25)	1.530(6)
C(24)-C(26)	1.542(6)

O(1)-Si(1)-C(22)	114.32(19)
O(1)-Si(1)-C(23)	112.30(18)
C(22)-Si(1)-C(23)	108.0(2)
O(1)-Si(1)-C(24)	102.18(19)
C(22)-Si(1)-C(24)	109.4(2)
C(23)-Si(1)-C(24)	110.6(2)
C(4)-O(1)-Si(1)	138.7(3)
C(2)-C(1)-Cl(1)	123.5(4)
C(1)-C(2)-C(3)	127.7(5)
C(2)-C(3)-C(4)	114.7(4)
O(1)-C(4)-C(3)	105.4(4)
O(1)-C(4)-C(5)	113.6(4)
C(3)-C(4)-C(5)	112.2(4)
O(1)-C(4)-C(20)	110.7(3)
C(3)-C(4)-C(20)	112.0(3)
C(5)-C(4)-C(20)	103.1(4)
C(4)-C(5)-C(6)	107.3(4)
C(7)-C(6)-C(5)	103.2(4)
C(20)-C(7)-C(6)	105.5(3)
C(20)-C(7)-C(8)	113.2(3)
C(6)-C(7)-C(8)	118.5(4)
C(9)-C(8)-C(7)	112.7(3)
C(9)-C(8)-C(17)	110.2(3)
C(7)-C(8)-C(17)	108.8(4)
C(8)-C(9)-C(10)	110.7(4)
C(11)-C(10)-C(9)	112.0(4)
C(12)-C(11)-C(10)	120.8(4)
C(12)-C(11)-C(16)	123.3(4)
C(10)-C(11)-C(16)	115.9(3)
C(11)-C(12)-C(13)	123.8(4)
C(12)-C(13)-C(14)	111.0(4)
C(13)-C(14)-C(15)	110.3(4)
C(14)-C(15)-C(16)	111.8(4)
C(11)-C(16)-C(15)	112.1(3)
C(11)-C(16)-C(17)	111.4(4)
C(15)-C(16)-C(17)	111.6(4)

C(18)-C(17)-C(8)	112.3(3)
C(18)-C(17)-C(16)	112.0(4)
C(8)-C(17)-C(16)	112.1(4)
C(19)-C(18)-C(17)	112.7(3)
C(20)-C(19)-C(18)	111.0(4)
C(7)-C(20)-C(19)	109.1(3)
C(7)-C(20)-C(21)	112.0(4)
C(19)-C(20)-C(21)	109.5(4)
C(7)-C(20)-C(4)	100.7(3)
C(19)-C(20)-C(4)	116.6(4)
C(21)-C(20)-C(4)	108.7(3)
C(27)-C(24)-C(25)	109.5(4)
C(27)-C(24)-C(26)	109.3(4)
C(25)-C(24)-C(26)	108.6(4)
C(27)-C(24)-Si(1)	109.6(3)
C(25)-C(24)-Si(1)	110.4(3)
C(26)-C(24)-Si(1)	109.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2.22. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	82(1)	112(2)	71(1)	4(1)	25(1)	32(1)
Si(1)	35(1)	43(1)	49(1)	-1(1)	9(1)	-1(1)
O(1)	38(2)	47(2)	50(2)	0(1)	10(1)	2(1)
C(1)	63(3)	67(4)	56(2)	4(2)	3(2)	-5(3)
C(2)	43(2)	67(3)	60(2)	10(2)	4(2)	-5(2)
C(3)	35(2)	61(3)	56(2)	6(2)	7(2)	-3(2)
C(4)	32(2)	52(3)	51(2)	1(2)	9(2)	0(2)
C(5)	43(2)	53(3)	51(2)	-4(2)	6(2)	-1(2)
C(6)	45(2)	47(2)	53(2)	-7(2)	5(2)	0(2)
C(7)	36(2)	44(2)	47(2)	-2(2)	9(2)	1(2)
C(8)	37(2)	40(2)	47(2)	0(2)	9(2)	1(2)
C(9)	34(2)	40(2)	56(2)	-1(2)	7(2)	0(2)
C(10)	37(2)	40(2)	54(2)	0(2)	11(2)	-1(2)
C(11)	35(2)	44(2)	48(2)	2(2)	8(2)	0(2)
C(12)	45(2)	46(2)	55(2)	1(2)	7(2)	2(2)
C(13)	40(2)	55(3)	57(2)	-1(2)	2(2)	0(2)
C(14)	42(2)	52(2)	53(2)	-4(2)	3(2)	-3(2)
C(15)	36(2)	43(2)	54(2)	-3(2)	6(2)	0(2)
C(16)	32(2)	46(2)	48(2)	0(2)	8(2)	-2(2)
C(17)	35(2)	41(2)	50(2)	0(2)	8(2)	0(2)
C(18)	35(2)	41(2)	50(2)	-3(2)	6(2)	-1(2)
C(19)	38(2)	41(2)	55(2)	0(2)	4(2)	2(2)
C(20)	38(2)	44(2)	47(2)	-1(2)	8(2)	0(2)
C(21)	36(2)	48(2)	52(2)	-3(2)	8(2)	1(2)
C(22)	46(2)	46(3)	65(3)	4(2)	15(2)	-4(2)
C(23)	37(2)	60(3)	55(2)	-9(2)	4(2)	1(2)
C(24)	38(2)	47(2)	51(2)	-1(2)	10(2)	4(2)
C(25)	61(3)	51(3)	55(2)	-4(2)	6(2)	2(2)
C(26)	37(2)	59(3)	66(3)	-1(2)	11(2)	4(2)
C(27)	45(2)	49(2)	61(3)	4(2)	9(2)	4(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 2.22

	x	y	z	U(eq)
H(1)	3090	6127	-643	74
H(2)	1934	6557	407	68
H(3A)	3398	7441	1512	61
H(3B)	4228	5686	1321	61
H(5A)	2538	3030	1039	59
H(5B)	1355	2768	1647	59
H(6A)	2694	1244	2483	58
H(6B)	3792	1226	1808	58
H(7)	4716	3814	2212	51
H(8)	4077	2436	3716	49
H(9A)	6339	1558	2795	52
H(9B)	5161	203	2989	52
H(10A)	5729	233	4326	52
H(10B)	7030	-255	3847	52
H(12)	8820	1027	4442	59
H(13A)	9725	4129	4643	61
H(13B)	9627	2980	5430	61
H(14A)	8655	5945	5525	59
H(14B)	7680	4372	5783	59
H(15A)	7623	6009	4263	53
H(15B)	6565	6414	4928	53
H(16)	5624	3683	4828	50
H(17)	6213	4716	3259	50
H(18A)	4026	5845	4182	51
H(18B)	5223	7084	3910	51
H(19A)	3271	7542	3114	53
H(19B)	4505	6936	2599	53
H(21A)	1492	3431	3105	68
H(21B)	1367	5494	3329	68
H(21C)	2375	4238	3803	68

H(22A)	-681	2894	2334	79
H(22B)	-2059	3945	2288	79
H(22C)	-982	4447	2948	79
H(23A)	-394	5885	339	76
H(23B)	-1673	4827	628	76
H(23C)	-266	3847	605	76
H(25A)	236	8839	2769	83
H(25B)	-981	7761	3127	83
H(25C)	-1180	9777	2844	83
H(26A)	-3016	9051	1927	81
H(26B)	-2954	7073	2275	81
H(26C)	-2890	7382	1351	81
H(27A)	-1016	10484	1403	78
H(27B)	-870	8895	786	78
H(27C)	349	9410	1350	78

Table 6. Torsion angles [°] for 2.22

C(22)-Si(1)-O(1)-C(4)	64.1(5)
C(23)-Si(1)-O(1)-C(4)	-59.4(5)
C(24)-Si(1)-O(1)-C(4)	-177.9(4)
Cl(1)-C(1)-C(2)-C(3)	2.1(10)
C(1)-C(2)-C(3)-C(4)	-132.3(6)
Si(1)-O(1)-C(4)-C(3)	124.0(4)
Si(1)-O(1)-C(4)-C(5)	0.8(6)
Si(1)-O(1)-C(4)-C(20)	-114.7(4)
C(2)-C(3)-C(4)-O(1)	-65.4(6)
C(2)-C(3)-C(4)-C(5)	58.7(6)
C(2)-C(3)-C(4)-C(20)	174.1(4)
O(1)-C(4)-C(5)-C(6)	-138.0(4)
C(3)-C(4)-C(5)-C(6)	102.6(4)
C(20)-C(4)-C(5)-C(6)	-18.1(5)
C(4)-C(5)-C(6)-C(7)	-9.0(5)
C(5)-C(6)-C(7)-C(20)	34.2(4)
C(5)-C(6)-C(7)-C(8)	162.2(4)
C(20)-C(7)-C(8)-C(9)	179.7(3)
C(6)-C(7)-C(8)-C(9)	55.4(5)
C(20)-C(7)-C(8)-C(17)	-57.8(4)
C(6)-C(7)-C(8)-C(17)	177.9(3)
C(7)-C(8)-C(9)-C(10)	179.8(3)
C(17)-C(8)-C(9)-C(10)	58.0(4)
C(8)-C(9)-C(10)-C(11)	-54.7(4)
C(9)-C(10)-C(11)-C(12)	-130.7(4)
C(9)-C(10)-C(11)-C(16)	50.3(5)
C(10)-C(11)-C(12)-C(13)	-174.2(4)
C(16)-C(11)-C(12)-C(13)	4.8(7)
C(11)-C(12)-C(13)-C(14)	15.9(7)
C(12)-C(13)-C(14)-C(15)	-47.7(5)
C(13)-C(14)-C(15)-C(16)	61.7(5)
C(12)-C(11)-C(16)-C(15)	7.7(6)
C(10)-C(11)-C(16)-C(15)	-173.3(3)
C(12)-C(11)-C(16)-C(17)	133.5(4)

C(10)-C(11)-C(16)-C(17)	-47.5(5)
C(14)-C(15)-C(16)-C(11)	-40.3(5)
C(14)-C(15)-C(16)-C(17)	-166.0(3)
C(9)-C(8)-C(17)-C(18)	176.6(3)
C(7)-C(8)-C(17)-C(18)	52.6(4)
C(9)-C(8)-C(17)-C(16)	-56.2(4)
C(7)-C(8)-C(17)-C(16)	179.8(3)
C(11)-C(16)-C(17)-C(18)	177.2(3)
C(15)-C(16)-C(17)-C(18)	-56.7(5)
C(11)-C(16)-C(17)-C(8)	49.9(4)
C(15)-C(16)-C(17)-C(8)	175.9(3)
C(8)-C(17)-C(18)-C(19)	-52.2(5)
C(16)-C(17)-C(18)-C(19)	-179.4(3)
C(17)-C(18)-C(19)-C(20)	53.7(4)
C(6)-C(7)-C(20)-C(19)	-168.8(3)
C(8)-C(7)-C(20)-C(19)	60.1(5)
C(6)-C(7)-C(20)-C(21)	69.8(4)
C(8)-C(7)-C(20)-C(21)	-61.3(5)
C(6)-C(7)-C(20)-C(4)	-45.6(4)
C(8)-C(7)-C(20)-C(4)	-176.7(3)
C(18)-C(19)-C(20)-C(7)	-56.2(5)
C(18)-C(19)-C(20)-C(21)	66.7(4)
C(18)-C(19)-C(20)-C(4)	-169.3(3)
O(1)-C(4)-C(20)-C(7)	159.9(3)
C(3)-C(4)-C(20)-C(7)	-82.7(4)
C(5)-C(4)-C(20)-C(7)	38.1(4)
O(1)-C(4)-C(20)-C(19)	-82.2(5)
C(3)-C(4)-C(20)-C(19)	35.1(5)
C(5)-C(4)-C(20)-C(19)	156.0(4)
O(1)-C(4)-C(20)-C(21)	42.1(5)
C(3)-C(4)-C(20)-C(21)	159.5(4)
C(5)-C(4)-C(20)-C(21)	-79.7(4)
O(1)-Si(1)-C(24)-C(27)	64.9(3)
C(22)-Si(1)-C(24)-C(27)	-173.6(3)
C(23)-Si(1)-C(24)-C(27)	-54.8(4)
O(1)-Si(1)-C(24)-C(25)	-55.8(4)

C(22)-Si(1)-C(24)-C(25)	65.7(4)
C(23)-Si(1)-C(24)-C(25)	-175.5(3)
O(1)-Si(1)-C(24)-C(26)	-175.3(3)
C(22)-Si(1)-C(24)-C(26)	-53.8(4)
C(23)-Si(1)-C(24)-C(26)	65.0(4)

Symmetry transformations used to generate equivalent atoms:

X-ray Crystal Structure for 2.59

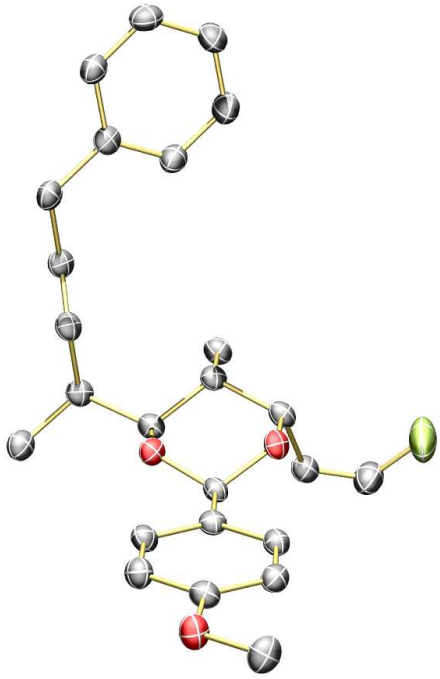


Table 7. Crystal data and structure refinement for 2.59

Identification code	$C_{25}H_{29}FO_3$	
Empirical formula	$C_{25}H_{29}FO_3$	
Formula weight	396.48	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 5.0411(3) Å	α= 90°.
	b = 21.2212(12) Å	β= 93.887(4)°.
	c = 20.2570(11) Å	γ = 90°.
Volume	2162.1(2) $Å^3$	
Z	4	
Density (calculated)	1.218 Mg/m^3	
Absorption coefficient	0.680 mm^{-1}	
F(000)	848	
Crystal size	0.300 x 0.140 x 0.060 mm^3	
Theta range for data collection	4.166 to 66.765°.	
Index ranges	-5<=h<=5, -24<=k<=24, -24<=l<=23	

Reflections collected	12247
Independent reflections	3469 [R(int) = 0.0668]
Completeness to theta = 66.750°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.5939
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3469 / 2 / 265
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1168
R indices (all data)	R1 = 0.0609, wR2 = 0.1232
Extinction coefficient	na
Largest diff. peak and hole	0.183 and -0.213 e.Å^{-3}

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 2.59. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
F(1)	8152(7)	8444(2)	7239(2)	76(1)
O(1)	5997(5)	7365(1)	5951(1)	26(1)
O(2)	7566(5)	6920(1)	5001(1)	25(1)
O(3)	572(5)	4679(2)	5875(1)	32(1)
C(1)	10204(10)	8105(3)	7010(2)	43(1)
C(2)	10083(8)	7856(2)	6421(2)	28(1)
C(3)	7714(7)	7909(2)	5925(2)	26(1)
C(4)	8468(7)	8017(2)	5211(2)	24(1)
C(5)	9513(7)	7411(2)	4924(2)	24(1)
C(6)	10046(7)	7439(2)	4189(2)	26(1)
C(7)	7634(8)	7657(2)	3767(2)	27(1)
C(8)	7491(8)	8182(2)	3418(2)	27(1)
C(9)	5094(8)	8400(2)	2998(2)	29(1)
C(10)	3937(7)	9025(2)	3206(2)	27(1)
C(11)	2253(8)	9357(2)	2763(2)	30(1)
C(12)	1031(8)	9909(2)	2943(2)	36(1)
C(13)	1517(8)	10144(2)	3576(2)	37(1)
C(14)	3210(9)	9819(2)	4022(2)	39(1)
C(15)	4409(8)	9263(2)	3835(2)	32(1)
C(16)	10381(8)	8570(2)	5173(2)	29(1)
C(17)	7144(7)	6825(2)	5671(2)	22(1)
C(18)	5292(7)	6275(2)	5731(2)	23(1)
C(19)	3812(7)	6203(2)	6275(2)	24(1)
C(20)	2189(7)	5677(2)	6346(2)	26(1)
C(21)	2058(7)	5213(2)	5858(2)	26(1)
C(22)	3525(8)	5286(2)	5304(2)	29(1)
C(23)	5142(8)	5807(2)	5248(2)	26(1)
C(24)	-1017(8)	4602(2)	6434(2)	34(1)
C(25)	11004(8)	6803(2)	3952(2)	32(1)

Table 9. Bond lengths [Å] and angles [°] for 2.59

F(1)-C(1)	1.368(6)
O(1)-C(17)	1.418(5)
O(1)-C(3)	1.447(5)
O(2)-C(17)	1.402(5)
O(2)-C(5)	1.447(5)
O(3)-C(21)	1.360(5)
O(3)-C(24)	1.440(5)
C(1)-C(2)	1.302(7)
C(1)-H(1)	0.9500
C(2)-C(3)	1.512(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.537(5)
C(3)-H(3)	1.0000
C(4)-C(5)	1.520(5)
C(4)-C(16)	1.524(5)
C(4)-H(4)	1.0000
C(5)-C(6)	1.532(5)
C(5)-H(5)	1.0000
C(6)-C(7)	1.512(5)
C(6)-C(25)	1.521(6)
C(6)-H(6)	1.0000
C(7)-C(8)	1.318(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.502(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.520(6)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(15)	1.377(6)
C(10)-C(11)	1.385(6)
C(11)-C(12)	1.384(6)
C(11)-H(11)	0.9500
C(12)-C(13)	1.381(7)
C(12)-H(12)	0.9500

C(13)-C(14)	1.385(7)
C(13)-H(13)	0.9500
C(14)-C(15)	1.390(6)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.505(5)
C(17)-H(17)	1.0000
C(18)-C(19)	1.381(6)
C(18)-C(23)	1.393(6)
C(19)-C(20)	1.397(6)
C(19)-H(19)	0.9500
C(20)-C(21)	1.393(6)
C(20)-H(20)	0.9500
C(21)-C(22)	1.394(6)
C(22)-C(23)	1.383(6)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800

C(17)-O(1)-C(3)	111.7(3)
C(17)-O(2)-C(5)	110.8(3)
C(21)-O(3)-C(24)	116.8(3)
C(2)-C(1)-F(1)	122.3(4)
C(2)-C(1)-H(1)	118.8
F(1)-C(1)-H(1)	118.8
C(1)-C(2)-C(3)	124.4(4)
C(1)-C(2)-H(2)	117.8
C(3)-C(2)-H(2)	117.8

O(1)-C(3)-C(2)	111.3(3)
O(1)-C(3)-C(4)	109.8(3)
C(2)-C(3)-C(4)	113.7(3)
O(1)-C(3)-H(3)	107.2
C(2)-C(3)-H(3)	107.2
C(4)-C(3)-H(3)	107.2
C(5)-C(4)-C(16)	113.3(3)
C(5)-C(4)-C(3)	110.4(3)
C(16)-C(4)-C(3)	111.0(3)
C(5)-C(4)-H(4)	107.3
C(16)-C(4)-H(4)	107.3
C(3)-C(4)-H(4)	107.3
O(2)-C(5)-C(4)	108.3(3)
O(2)-C(5)-C(6)	107.3(3)
C(4)-C(5)-C(6)	115.2(3)
O(2)-C(5)-H(5)	108.6
C(4)-C(5)-H(5)	108.6
C(6)-C(5)-H(5)	108.6
C(7)-C(6)-C(25)	110.7(3)
C(7)-C(6)-C(5)	112.0(3)
C(25)-C(6)-C(5)	110.7(3)
C(7)-C(6)-H(6)	107.8
C(25)-C(6)-H(6)	107.8
C(5)-C(6)-H(6)	107.8
C(8)-C(7)-C(6)	125.2(4)
C(8)-C(7)-H(7)	117.4
C(6)-C(7)-H(7)	117.4
C(7)-C(8)-C(9)	125.2(4)
C(7)-C(8)-H(8)	117.4
C(9)-C(8)-H(8)	117.4
C(8)-C(9)-C(10)	114.9(4)
C(8)-C(9)-H(9A)	108.5
C(10)-C(9)-H(9A)	108.5
C(8)-C(9)-H(9B)	108.5
C(10)-C(9)-H(9B)	108.5
H(9A)-C(9)-H(9B)	107.5

C(15)-C(10)-C(11)	118.2(4)
C(15)-C(10)-C(9)	122.1(4)
C(11)-C(10)-C(9)	119.6(4)
C(12)-C(11)-C(10)	121.6(4)
C(12)-C(11)-H(11)	119.2
C(10)-C(11)-H(11)	119.2
C(13)-C(12)-C(11)	119.7(4)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(12)-C(13)-C(14)	119.3(4)
C(12)-C(13)-H(13)	120.4
C(14)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	120.3(4)
C(13)-C(14)-H(14)	119.8
C(15)-C(14)-H(14)	119.8
C(10)-C(15)-C(14)	120.9(4)
C(10)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(4)-C(16)-H(16A)	109.5
C(4)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(4)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
O(2)-C(17)-O(1)	111.4(3)
O(2)-C(17)-C(18)	108.9(3)
O(1)-C(17)-C(18)	108.8(3)
O(2)-C(17)-H(17)	109.3
O(1)-C(17)-H(17)	109.3
C(18)-C(17)-H(17)	109.3
C(19)-C(18)-C(23)	118.3(4)
C(19)-C(18)-C(17)	121.5(4)
C(23)-C(18)-C(17)	120.1(3)
C(18)-C(19)-C(20)	121.6(4)
C(18)-C(19)-H(19)	119.2
C(20)-C(19)-H(19)	119.2

C(21)-C(20)-C(19)	119.4(4)
C(21)-C(20)-H(20)	120.3
C(19)-C(20)-H(20)	120.3
O(3)-C(21)-C(20)	124.8(4)
O(3)-C(21)-C(22)	115.8(4)
C(20)-C(21)-C(22)	119.4(4)
C(23)-C(22)-C(21)	120.1(4)
C(23)-C(22)-H(22)	119.9
C(21)-C(22)-H(22)	119.9
C(22)-C(23)-C(18)	121.2(4)
C(22)-C(23)-H(23)	119.4
C(18)-C(23)-H(23)	119.4
O(3)-C(24)-H(24A)	109.5
O(3)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
O(3)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(6)-C(25)-H(25A)	109.5
C(6)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(6)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters ($Å^2$ x 10^3) for 2.59. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	70(2)	118(3)	40(2)	-20(2)	6(2)	39(2)
O(1)	18(1)	30(2)	29(1)	-2(1)	7(1)	-1(1)
O(2)	21(1)	27(2)	26(1)	1(1)	5(1)	-2(1)
O(3)	30(1)	32(2)	34(2)	-4(1)	8(1)	-6(1)
C(1)	40(3)	57(3)	33(2)	0(2)	1(2)	6(2)
C(2)	23(2)	29(2)	34(2)	1(2)	5(2)	-1(2)
C(3)	21(2)	23(2)	34(2)	-1(2)	5(2)	0(2)
C(4)	17(2)	27(2)	28(2)	1(2)	2(1)	1(2)
C(5)	20(2)	24(2)	30(2)	-1(2)	2(1)	-2(2)
C(6)	18(2)	30(2)	31(2)	3(2)	6(2)	-2(2)
C(7)	19(2)	32(2)	31(2)	-2(2)	6(2)	-1(2)
C(8)	22(2)	33(2)	29(2)	1(2)	8(2)	-1(2)
C(9)	30(2)	35(3)	24(2)	1(2)	6(2)	-1(2)
C(10)	17(2)	34(2)	29(2)	2(2)	6(1)	-3(2)
C(11)	27(2)	39(3)	25(2)	1(2)	3(2)	-1(2)
C(12)	29(2)	43(3)	36(2)	8(2)	-2(2)	5(2)
C(13)	32(2)	41(3)	38(2)	-3(2)	4(2)	9(2)
C(14)	39(2)	47(3)	30(2)	-6(2)	-1(2)	6(2)
C(15)	25(2)	44(3)	27(2)	1(2)	2(2)	5(2)
C(16)	27(2)	26(2)	35(2)	-1(2)	4(2)	-1(2)
C(17)	18(2)	22(2)	26(2)	-3(1)	0(1)	2(2)
C(18)	17(2)	26(2)	27(2)	2(2)	0(1)	1(2)
C(19)	20(2)	26(2)	26(2)	-1(2)	1(1)	1(2)
C(20)	21(2)	31(2)	26(2)	2(2)	2(2)	0(2)
C(21)	20(2)	25(2)	32(2)	1(2)	1(2)	-1(2)
C(22)	28(2)	31(2)	29(2)	-3(2)	3(2)	-2(2)
C(23)	25(2)	26(2)	29(2)	0(2)	6(2)	3(2)
C(24)	28(2)	41(3)	34(2)	1(2)	5(2)	-10(2)
C(25)	26(2)	40(3)	30(2)	0(2)	5(2)	0(2)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 2.59

	x	y	z	U(eq)
H(1)	11773	8048	7291	52
H(2)	11583	7626	6295	34
H(3)	6660	8284	6053	31
H(4)	6801	8131	4942	29
H(5)	11198	7291	5183	29
H(6)	11501	7751	4138	31
H(7)	6101	7396	3752	33
H(8)	9024	8443	3433	33
H(9A)	3697	8073	3009	35
H(9B)	5586	8437	2535	35
H(11)	1929	9202	2325	36
H(12)	-138	10125	2633	43
H(13)	699	10524	3703	44
H(14)	3554	9977	4458	47
H(15)	5569	9045	4146	39
H(16A)	12142	8446	5364	44
H(16B)	9725	8927	5422	44
H(16C)	10505	8692	4710	44
H(17)	8881	6730	5919	27
H(19)	3900	6518	6609	29
H(20)	1185	5635	6724	31
H(22)	3414	4977	4964	35
H(23)	6169	5846	4874	32
H(24A)	139	4604	6843	51
H(24B)	-1975	4200	6395	51
H(24C)	-2297	4949	6444	51
H(25A)	9601	6488	3991	47
H(25B)	12594	6675	4225	47
H(25C)	11434	6837	3489	47

Table 12. Torsion angles [°] for 2.59

F(1)-C(1)-C(2)-C(3)	0.0(8)
C(17)-O(1)-C(3)-C(2)	-73.0(4)
C(17)-O(1)-C(3)-C(4)	53.9(4)
C(1)-C(2)-C(3)-O(1)	-95.7(5)
C(1)-C(2)-C(3)-C(4)	139.7(5)
O(1)-C(3)-C(4)-C(5)	-50.8(4)
C(2)-C(3)-C(4)-C(5)	74.6(4)
O(1)-C(3)-C(4)-C(16)	-177.4(3)
C(2)-C(3)-C(4)-C(16)	-51.9(4)
C(17)-O(2)-C(5)-C(4)	-60.4(4)
C(17)-O(2)-C(5)-C(6)	174.7(3)
C(16)-C(4)-C(5)-O(2)	178.7(3)
C(3)-C(4)-C(5)-O(2)	53.5(4)
C(16)-C(4)-C(5)-C(6)	-61.2(4)
C(3)-C(4)-C(5)-C(6)	173.6(3)
O(2)-C(5)-C(6)-C(7)	66.4(4)
C(4)-C(5)-C(6)-C(7)	-54.3(4)
O(2)-C(5)-C(6)-C(25)	-57.7(4)
C(4)-C(5)-C(6)-C(25)	-178.3(3)
C(25)-C(6)-C(7)-C(8)	-120.1(5)
C(5)-C(6)-C(7)-C(8)	115.9(5)
C(6)-C(7)-C(8)-C(9)	-180.0(4)
C(7)-C(8)-C(9)-C(10)	118.6(5)
C(8)-C(9)-C(10)-C(15)	-21.2(6)
C(8)-C(9)-C(10)-C(11)	161.8(4)
C(15)-C(10)-C(11)-C(12)	-1.0(6)
C(9)-C(10)-C(11)-C(12)	176.2(4)
C(10)-C(11)-C(12)-C(13)	1.0(7)
C(11)-C(12)-C(13)-C(14)	-0.5(7)
C(12)-C(13)-C(14)-C(15)	0.1(7)
C(11)-C(10)-C(15)-C(14)	0.5(6)
C(9)-C(10)-C(15)-C(14)	-176.5(4)
C(13)-C(14)-C(15)-C(10)	-0.1(7)
C(5)-O(2)-C(17)-O(1)	64.9(3)

C(5)-O(2)-C(17)-C(18)	-175.2(3)
C(3)-O(1)-C(17)-O(2)	-61.4(3)
C(3)-O(1)-C(17)-C(18)	178.6(3)
O(2)-C(17)-C(18)-C(19)	-157.4(3)
O(1)-C(17)-C(18)-C(19)	-35.9(5)
O(2)-C(17)-C(18)-C(23)	26.0(5)
O(1)-C(17)-C(18)-C(23)	147.6(3)
C(23)-C(18)-C(19)-C(20)	-0.2(5)
C(17)-C(18)-C(19)-C(20)	-176.9(3)
C(18)-C(19)-C(20)-C(21)	0.1(5)
C(24)-O(3)-C(21)-C(20)	1.6(5)
C(24)-O(3)-C(21)-C(22)	-178.4(3)
C(19)-C(20)-C(21)-O(3)	179.4(3)
C(19)-C(20)-C(21)-C(22)	-0.7(5)
O(3)-C(21)-C(22)-C(23)	-178.6(3)
C(20)-C(21)-C(22)-C(23)	1.5(6)
C(21)-C(22)-C(23)-C(18)	-1.6(6)
C(19)-C(18)-C(23)-C(22)	1.0(6)
C(17)-C(18)-C(23)-C(22)	177.7(3)

Symmetry transformations used to generate equivalent atoms:

Chapter Three

Molybdenum-Based Chloride Catalysts for Z-Selective Olefin Metathesis

3.1. Introduction

High-oxidation-state (Mo/W) MAP alkylidenes were first prepared through substitution of a pyrrolide ligand within a bispyrrolyl imido alkylidene complex with an appropriate alcohol.[1] These unique species were shown to be capable of promoting efficient and stereoselective OM[2] including *Z*-selective CM transformations that employ electron-deficient alkene cross-partners such as vinylboronic acid pinacol ester,[3] acrylates[4] and 1,2-dihaloethenes,[5] as well as kinetically *E*-selective CM reactions.[6] Nonetheless, crucial limitations still persist, especially in processes that involve halogen-containing olefin reagents.

3.2. Shortcomings in Olefin Metathesis with Mo-Based MAP Alkylidenes

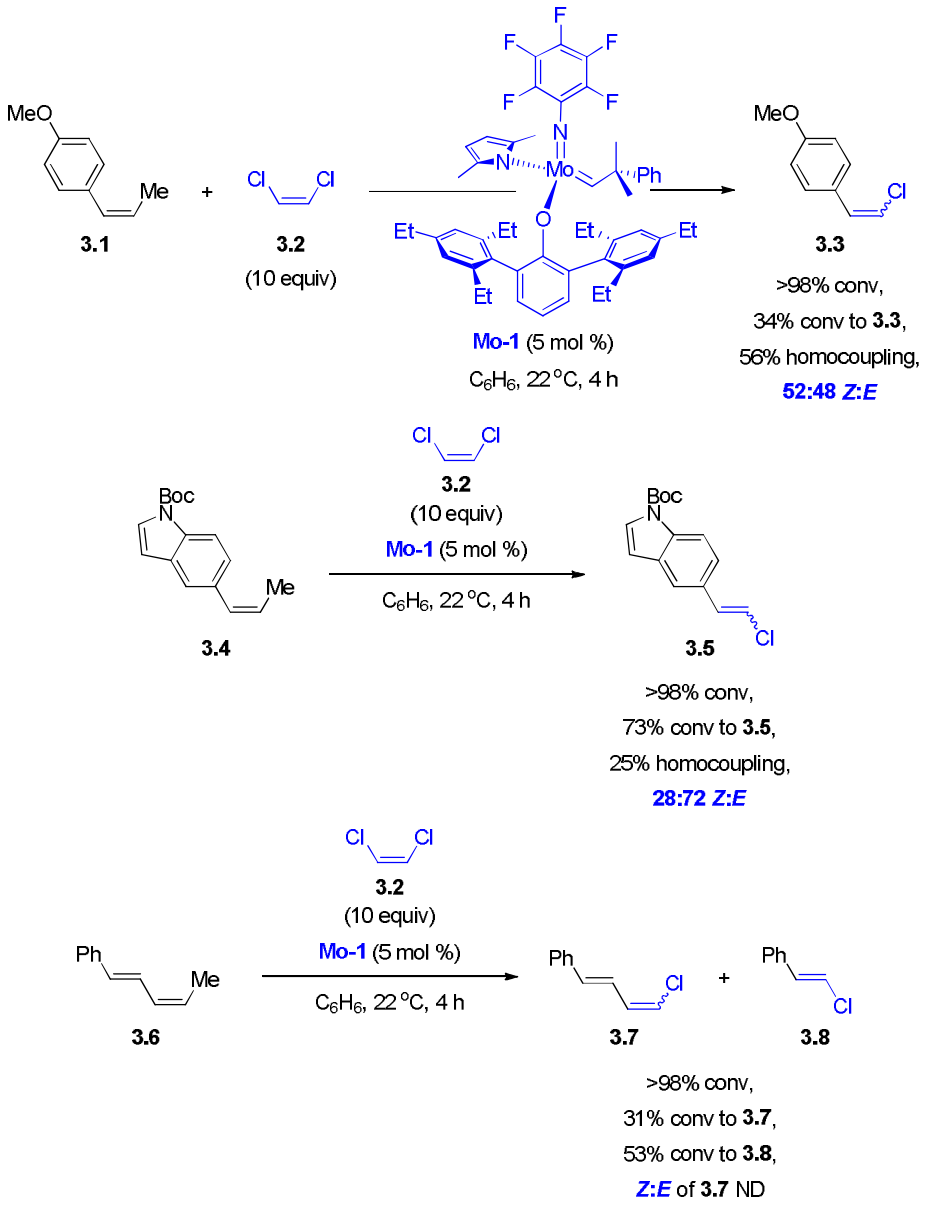
3.2.1. CM of Aryl Olefins and 1,3-Dienes with Z-1,2-Dichloroethene

We have demonstrated that pentafluorophenylimido MAP complex **Mo-1** catalyzes efficient and *Z*-selective CM of *Z*-1,2-dichloroethene **3.2** with a broad variety of mono-substituted alkyl olefins including sterically congested α-branched aliphatic alkenes.[5] However, aryl olefins were not effective substrates due to rapid homocoupling

(1) Singh, R.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654–12655.
(2) Hoveyda, A. H. *J. Org. Chem.* **2014**, *79*, 4763–4792.
(3) Kiesewetter, E. T.; O'Brien, R. V.; Yu, E. C.; Meek, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2013**, *135*, 6026–6029.
(4) Yu, E. C.; Johnson, B. M.; Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **201 6**, *55*, 13210–13214.
(5) Koh, M. J.; Nguyen, T. T.; Zhang, H.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2016**, *531*, 459–465.
(6) Nguyen, T. T.; Koh, M. J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. *Science* **2016**, *352*, 569–575.

to give stilbenes that do not re-enter the catalytic cycle easily (cf. Chapter 2, Section 2.3.2).

Scheme 3.1. Challenges in CM of Aryl Olefins & 1,3-Dienes with *Z*-1,2-Dichloroethene.

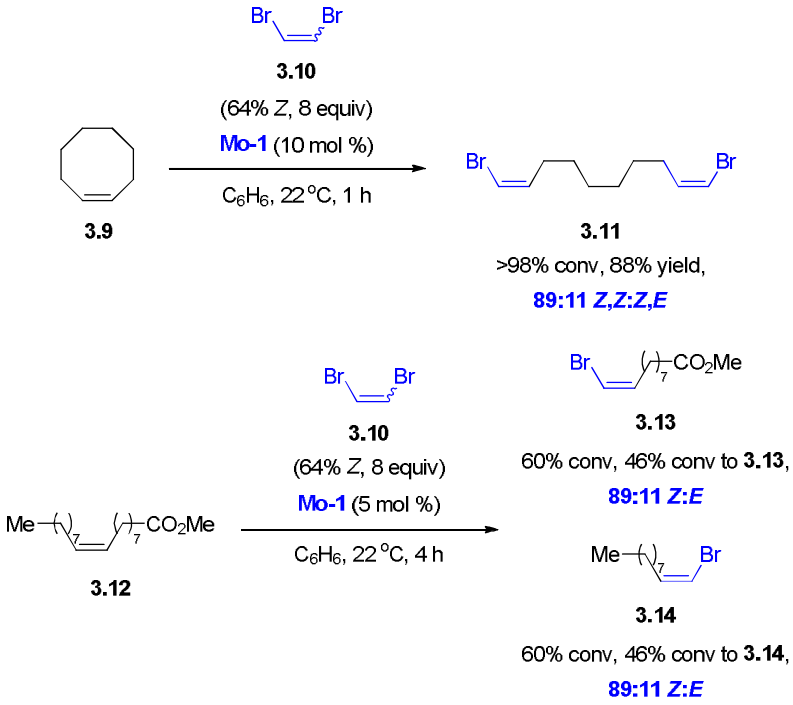


Representative examples are presented in Scheme 3.1. CM of *Z*-β-methyl styrene **3.1** with excess **3.2** in the presence of 5 mol % **Mo-1** delivered alkenyl chloride **3.3** in poor efficiency (34% conversion, 56% conversion to homocoupling products) and

stereoselectivity (52:48 *Z*:*E*). The low selectivity observed is presumably a consequence of facile *Z*-to-*E* isomerization of **3.1** through self-metathesis, which would react with **3.2** to give isomeric mixtures of **3.3**. The situation improved slightly with heteroaryl olefin **3.4**, which gave 73% conversion to chloro-alkene **3.5** as a 28:72 *Z*:*E* mixture. Reactions with 1,3-dienes pose a new complication in chemoselectivity. As highlighted by CM involving *Z*,*E*-diene **3.6**, there was 31% conversion to desired **3.7** but 53% conversion to **3.8** was also detected, which suggested reaction at the styrenyl site as well.

3.2.2. CM and ROCM with 1,2-Dibromoethene

Scheme 3.2. Limitations in *Z*-Selective CM & ROCM with 1,2-Dibromoethene.



Another drawback with MAP alkylidenes relates to *Z*-selective synthesis of alkenyl bromides (cf. Chapter 2, Scheme 2.7). ROCM of cyclooctene **3.9** with commercially available 1,2-dibromoethene **3.10** (64:36 *Z*:*E* mixture) using **Mo-1** as catalyst afforded **3.11** in 88% yield, albeit as a 89:11 *Z*,*Z*:*Z*,*E* mixture (Scheme 3.2). In

another instance, CM of **3.10** with acyclic 1,2-disubstituted olefins exemplified by *Z*-methyl oleate **3.12** was only moderately efficient (46% conversion to alkenyl bromides **3.13** and **3.14**). Analogous to the ROCM case, stereoselectivity was incomplete (89:11 *Z*:*E* ratio). As already rationalized in Chapter 2, Section 2.3.5, the sizeable **3.10** probably slows down the rate of CM, causing homocoupling to be more competitive. Adventitious *Z*-to-*E* isomerization of self-metathesis byproducts coupled with the ability of **Mo-1** to engage with *trans*-1,2-disubstituted alkenes probably give rise to the lower stereoselectivity levels detected. Evidently, the same problems of chemoselectivity (CM vs. homocoupling; reaction with *Z*-alkenes vs. *E*-alkenes) seem to plague these transformations.

3.2.3. Significance of Z-CF_3-Olefins and Attempted Synthesis by CM

One of our goals in *Z*-selective OM was to develop practical and reliable processes that allow access to functionalized CF_3-substituted alkenes. *Z*-trifluoromethylated alkenes represent a valuable set of fluorine-containing motifs that are potentially useful in medicinal chemistry,[7] agrochemicals[8] and materials research.[9] In addition, the incorporation of a CF_3 moiety into organic molecules may alter their properties. For example, the substitution of CF_3 for a methyl group can lead to different chemical/stereochemical outcomes which may be significantly magnified in a metabolic cascade of chemical reactions, resulting in changes in the biological activity of a compound.[10] Similar effects have also been documented in polymeric systems.[11] In this

(7) (a) Gillis, E. P.; Eastman, K. J.; Hill, M. D.; Donnelly, D. J.; Meanwell, N. A. *J. Med. Chem.* **2015**, *58*, 8315–8359. For an example of a bioactive *Z*-CF3-alkene, see: (b) Innocenti, P.; Chueng, K..-M. J.; Solanki, S.; Mas-Droux, C.; Rowan, F.; Yeoh, S.; Boxall, K.; Westlake, M.; Pickard, L.; Hardy, T.; Baxter, J. E.; Ahe rne, G. W.; Bayliss, R.; Fry, A. M.; Hoelder, S. *J. Med. Chem.* **2012**, *55*, 3228–3241.
(8) Fujiwara, T.; O'Hagan, D. *J. Fluorine Chem.* **2014**, *167*, 16–29.
(9) Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. *Chem. Soc. Rev.* **2011**, *40*, 3496–3508.
(10) For a representative example, see: Diana, G. D.; Rudewicz, P.; Pevear, D. C.; Nitz, T. J.; Aldous, S. C.;

context, we envisioned that CM could serve as an economical and convenient method to introduce CF_3 groups site- and stereoselectively into biologically relevant molecules.

However, the only disclosed CM protocol that afford CF_3-alkenes involved dichloro-Ru carbenes using gaseous 3,3,3-trifluoropropene; thermodynamically favored *E*-CF_3-alkenes are exclusively generated albeit with a limited scope.[12] Other strategies that furnish trifluoromethylated olefins are either minimally stereoselective[13] or afford the more stable *E*-isomers predominantly.[14] A small number of methods for preparing *Z*-CF_3-olefins employ expensive materials and produce varying *Z*:*E* mixtures,[15] entail multi-step sequences[16] or involve partial hydrogenation of CF_3-substituted alkynes wherein over-reduction can be an issue.[17]

Taking advantage of the principle of stereoretentive *Z*-selective CM (cf. Chapters 1 & 2), we conceived a CM protocol between a readily accessible olefin substrate such as **3.12** and commercially available *Z*-1,1,1,4,4,4-hexafluoro-2-butene **3.15** (Scheme 3.3). **3.15** is an environmentally benign hydrofluoroolefin that is industrially used as a foam-blowing agent; among its numerous attractive properties include zero ozone depleting potential (ODP) and low global warming potential (GWP) values.[18] Furthermore, **3.15** is a non-flammable liquid at ambient conditions (boiling point = 33 ^{o}C), rendering it more convenient to use than 3,3,3-trifluoropropene (boiling point = -22 ^{o}C). Prior to our

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Aldous, D. J.; Robinson, D. T.; Draper, T.; Dutko, F. J.; Aldi, C.; Gendron, G.; Oglesby, R. C.; Volkots, D. L.; Reurnan, M.; Bailey, T. R.; Czerniak, R.; Block, T.; Roland, R.; Oppermann, J. *J. Med. Chem.* **1995**, *38*, 1355–1371.

(11) For a representative example, see: Lee, J.-R.; Jin, F.-L.; Park, S.-J. *J. Appl. Polym. Sci.* **2005**, *98*, 1860–1864.

(12) Imhof, S.; Randl, S.; Blechert, S. *Chem. Commun.* **2001**, 1692–1693.

(13) (a) Hafner, A.; Fischer, T. S.; Bräse, S. *Eur. J. Org. Chem.* **2013**, 7996–8003. (b) Choi, S.; Kim, Y. J.; Kim, S. M.; Yang, J. W.; Kim, S. W.; Cho, E. J. *Nature Commun.* **2014**, *5*, 4881.

(14) Choi, W. J.; Choi, S.; Ohkubo, K.; Fukuzumi, S.; Cho, E. J.; You, Y. *Chem. Sci.* **2015**, *6*, 1454–1464.

(15) Lin, Q.-Y.; Xu, X.-H.; Qing, F.-L. *J. Org. Chem.* **2014**, *79*, 10434–10446.

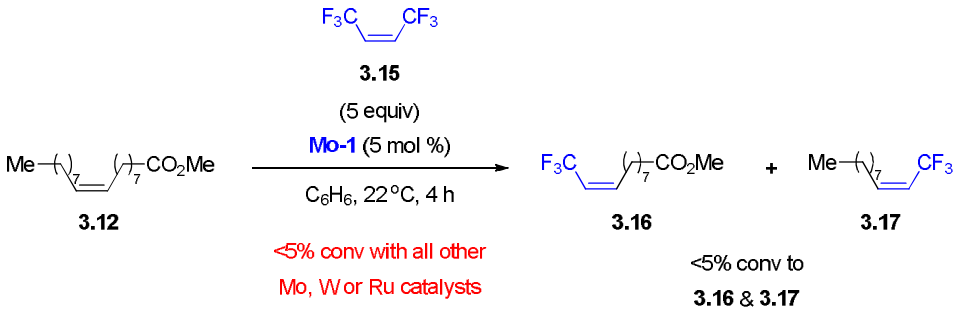
(16) Ramachandran, P. V.; Mitsubishi, W. *Org. Lett.* **2015**, *17*, 1252–1255.

(17) Ichikawa, T.; Kawasaki-Takasuka, T.; Yamada, S.; Yamazaki, T. *J. Fluorine Chem.*. **2013**, *152*, 38–45.

(18) Baasandorj, M.; Ravishankara, A. R.;Burkholder, J. B. *J. Phys. Chem. A* **2011**, *115*, 10539–10549.

investigations, **3.15** has not been used in organic chemistry, presumably due to its inert nature as a result of steric bulkiness and high electron-deficiency. As represented by the reaction in Scheme 3.3, initial efforts to employ **3.15** in CM with known Mo-, W- or Ru-based complexes were unsuccessful (self-metathesis of **3.12** was mostly observed). We surmised that more active forms of OM catalysts which are capable of reacting with **3.15** would have to be developed.

Scheme 3.3. Poor Efficiency in CM with *Z*-1,1,1,4,4,4-Hexafluoro-2-butene.



3.3. Monoaryloxide Chloride (MAC) Complexes as Potential OM Catalysts

3.3.1. Initial Hypothesis

Previously reported bispyrrolyl imido alkylidenes have been shown to be less active in OM compared to the corresponding MAP complexes,[1] presumably due to the strong σ-donating properties of the pyrrolide ligand. We reasoned that replacing the pyrrolide with an electron-withdrawing unit such as a chloride (electron-withdrawing chlorides are better σ-acceptors) could potentially increase Lewis acidity at the Mo center, thus giving rise to a more polarized alkylidene species (Scheme 3.4). The pressing question then was whether the net result of this substitution would lead to a Mo complex with enhanced reactivity. If so, how would that affect the catalyst lifetime and whether we can achieve high reaction efficiency without sacrificing stereoselectivity.

Scheme 3.4. MAC Complexes as Potentially More Active Catalysts than MAP Complexes.

Mo monoaryloxide pyrrolide (MAP)

pyrrolide:

strong σ–donor

weak π-donor

Mo monoaryloxide chloride (MAC)

chloride:

stronger σ–acceptor

stronger π-donor

1. Increased Lewis acidity at Mo-center?

2. More polarized Mo=C bond?

3. Enhanced reactivity?

4. Stereoselectivity?

3.3.2. General Synthesis of MAC Alkylidene Complexes

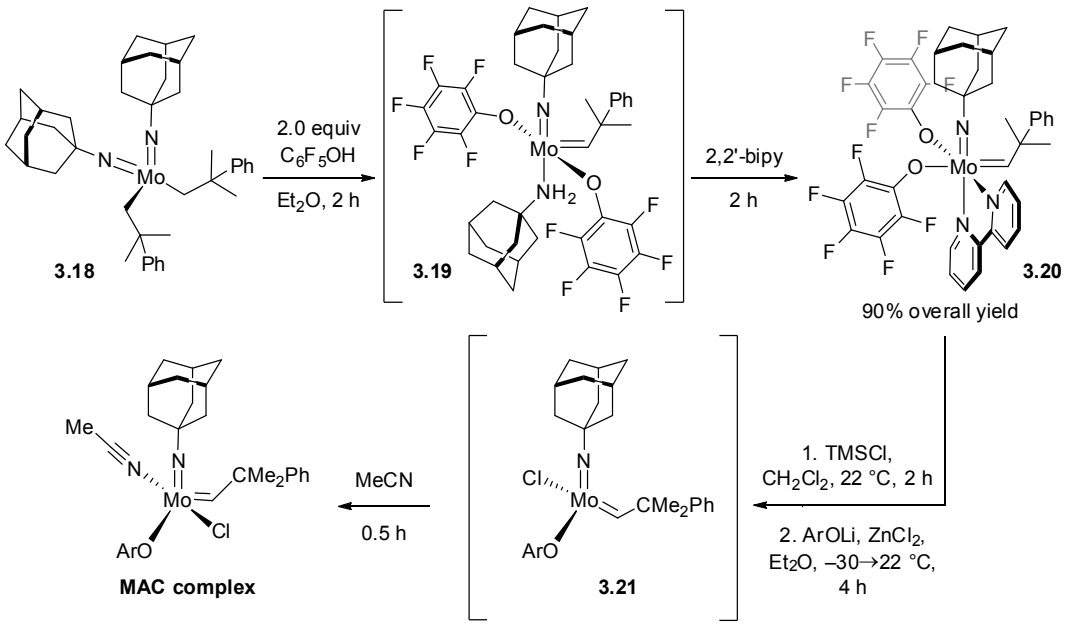
As part of a mechanistic initiative to prepare halo-substituted Mo alkylidenes, required intermediates in stereoselective CM reactions that furnish alkenyl halides,[5,6] a reliable synthesis route to alkylimido MAC alkylidenes,[19] isolated as 5-coordinate acetonitrile or pyridine adducts, from readily accessible materials was developed (Scheme 3.5). The X-ray structure of a representative complex (**Mo-2**) shows that coordination of 3-bromopyridine is *trans* to the chloride, suggesting that an olefin substrate would likely bind in a similar fashion which is reminiscent of MAP systems (olefin *trans* to pyrrolide).[20] The pyridine complexes were found to be much slower in ROCM studies compared to the acetonitrile analogues,[19] a consequence of the stronger binding of pyridine to the catalytically active 14-electron species (represented by **3.21**). Hence, we decided to focus our attention on examining the nitrile adducts, which have been shown to dissociate readily in solution to give 14-electron species.[19]

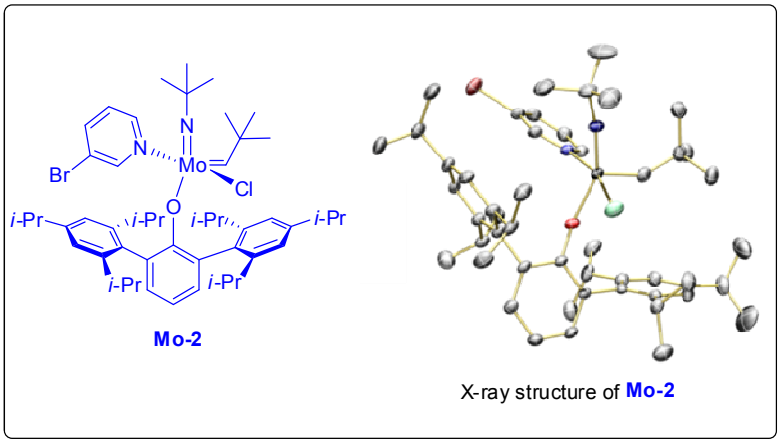
---

(19) MAC alkylidenes were initially thought to be viable intermediates in OM reactions that furnish alkenyl chlorides, see: Lam, J. K.; Zhu, C.; Bukhryakov, K. V.; Müller, P.; Hoveyda, A. H.; Schrock, R. R. *J. Am. C hem. Soc.* **2016**, *138*, 15774–15783.

(20) (a) Poater, A.; Solans-Monfort, X.; Clot, E.; Copéret, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129*, 8207–8216. (b) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H *J. Am. Chem. Soc.* **2009**, *131*, 58–5 9.

Scheme 3.5. Representative Synthesis Route to Access Mo MAC Complexes.





3.4. Comparison of MAP and MAC Complexes in OM with 1,2-Dihaloethenes[21]

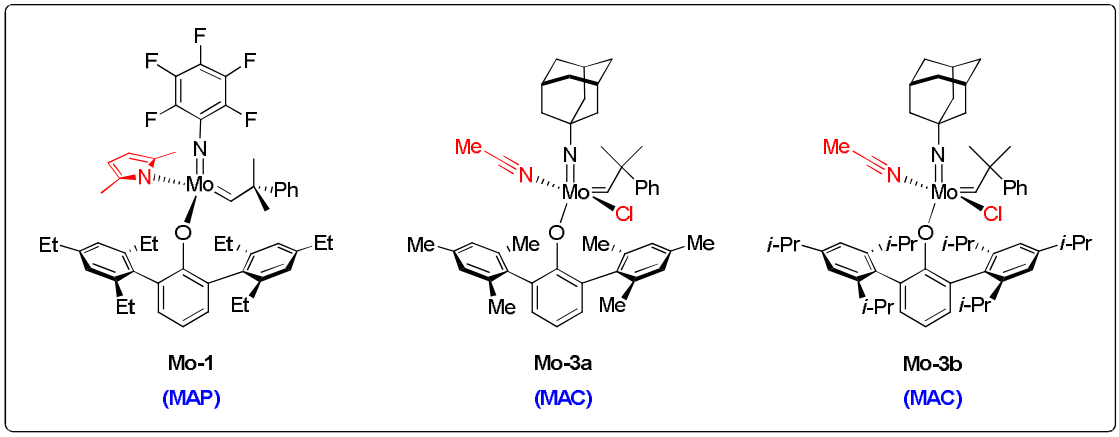
3.4.1. CM with Z-1,2-Dichloroethene

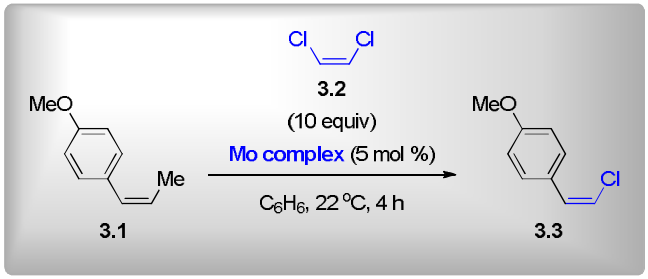
With the MAC complexes in hand, we proceeded to evaluate their performance in OM reactions that proved challenging with MAP systems (cf. Section 3.2). Whereas CM of *Z*-β-methyl styrene **3.1** with excess **3.2** in the presence of 5 mol % **Mo-1** was non-

(21) Koh, M. J.; Nguyen, T. T.; Lam, J. K.; Torker, S.; Hyvl, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2017**, *542*, 80–85.

stereoselective (52:48 *Z*:*E*), the analogous reaction with **Mo-3a** delivered **3.3** in >98% *Z* selectivity, albeit with diminished efficiency (Scheme 3.6). With a longer-living catalyst containing a more bulky aryloxide ligand (**Mo-3b**), **3.3** could be obtained in 80% yield as a single stereoisomer (minimal homocoupling was observed). It merits mention that alkylimido MAP alkylidenes are not optimal catalysts for reactions that afford alkenyl halides, and that the more active pentafluorophenylimido variants are necessary for efficient CM (cf. Chapter 2, Schemes 2.4.1–2). On the contrary, an alkylimido MAC system already suffices to promote highly efficient and *Z*-selective transformations.

Scheme 3.6. Comparison of MAC & MAP Complexes in CM of **3.1** with *Z*-1,2-Dichloroethene.





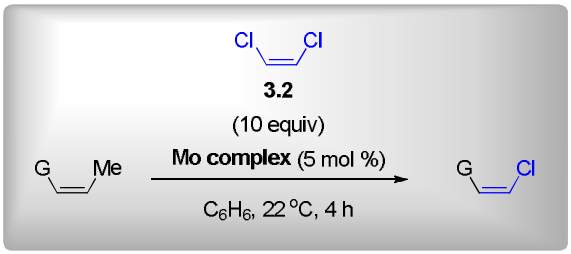
with Mo-1,
>98% conv,
34% conv to **3.3**,
56% homocoupling,
52:48 *Z*:*E*

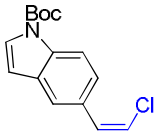
with Mo-3a,
40% conv,
23% conv to **3.3**,
17% homocoupling,
>98:2 *Z*:*E*

with Mo-3b,
>98% conv, 80% yield,
>98:2 *Z*:*E*

CM with **Mo-3b** can be extended to heteroaryl olefins and 1,3-dienes as delineated in Scheme 3.7. Both alkenyl chlorides **3.5** and **3.7** were furnished in 83% yield and >98:2 *Z*:*E* ratio. In contrast, CM with **Mo-1** was less stereoselective (28:72 *Z*:*E* for **3.5**) and/or less chemoselective (31% conversion to **3.7** with 53% conversion to β-chlorostyrene **3.8**, cf. Scheme 3.1).

Scheme 3.7. Additional Comparison Studies in CM with *Z*-1,2-Dichloroethene.

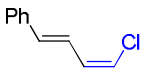




3.5

with **Mo-1**,
>98% conv, 73% conv to **3.5**,
28:72 *Z*:*E*

with **Mo-3b**,
>98% conv, 83% yield,
>98:2 *Z*:*E*



3.7

with **Mo-1**,
>98% conv, 31% conv to **3.7**,
Z*:*E of **3.7** ND

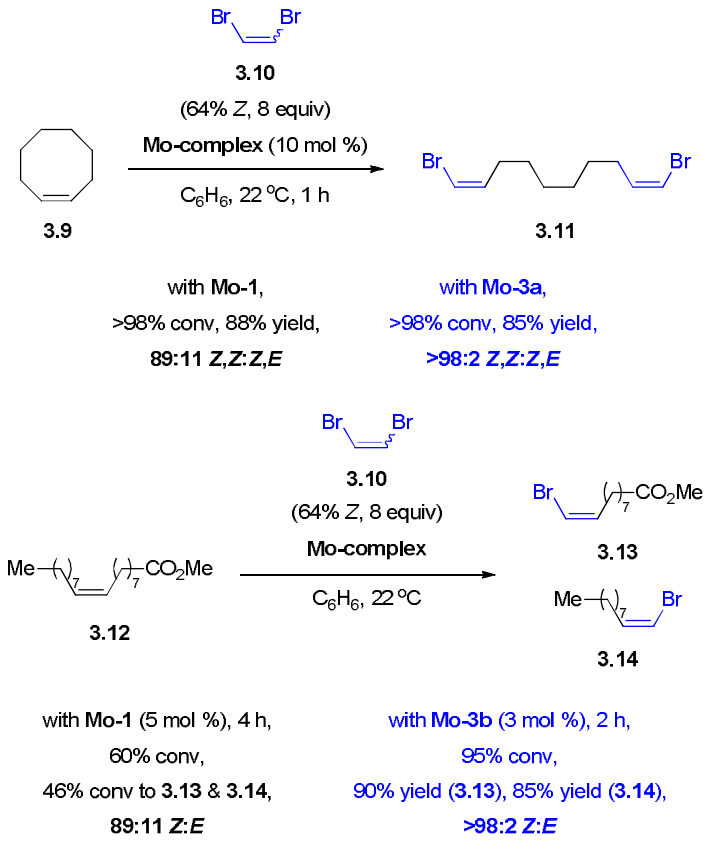
with **Mo-3b**,
>98% conv, 83% yield,
>98:2 *Z*:*E*

3.4.2. CM and ROCM with 1,2-Dibromoethene

Next, we examined CM and ROCM transformations with the more sizeable 1,2-dibromoethene **3.10** (Scheme 3.8). With **Mo-1**, ROCM of cyclooctene **3.9** and **3.10** afforded bis-alkenyl bromide **3.11** in 88% yield as a 89:11 *Z*,*Z*:*Z*,*E* mixture. With **Mo-3b**, the reaction was similarly efficient (**3.11** obtained in 85% yield) but completely stereoselective (>98:2 *Z*,*Z*:*Z*,*E*). Similarly, CM of *Z*-methyl oleate **3.12** with **3.10** was more efficient and *Z*-selective in the presence of **Mo-3b** as catalyst. Control experiments

indicated that the MAC complex reacts preferentially with the *Z*-isomer of **3.10**, which is supported by the diminished *Z*:*E* ratio (41:59) of recovered reagent after reaction of **3.12** with 2.3 equivalents of **3.10** (~1.5 equivalents of *Z*-isomer) and 5 mol % **Mo-3b** (four hours).

Scheme 3.8. Comparison of MAC & MAP Complexes in CM & ROCM with 1,2-Dibromoethene.



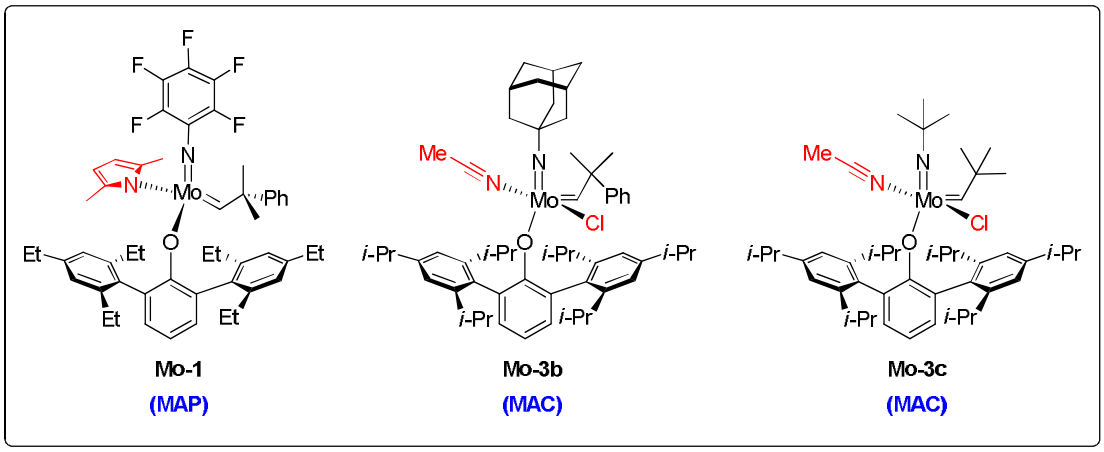
The higher *Z* selectivity and chemoselectivity (CM vs. homocoupling) displayed by MAC complexes in reactions with 1,2-dihaloethenes were somewhat surprising initially since these systems are presumably more active and can potentially give rise to *Z*-to-*E* post-metathesis isomerization issues (see Section 3.8 for further discussion).

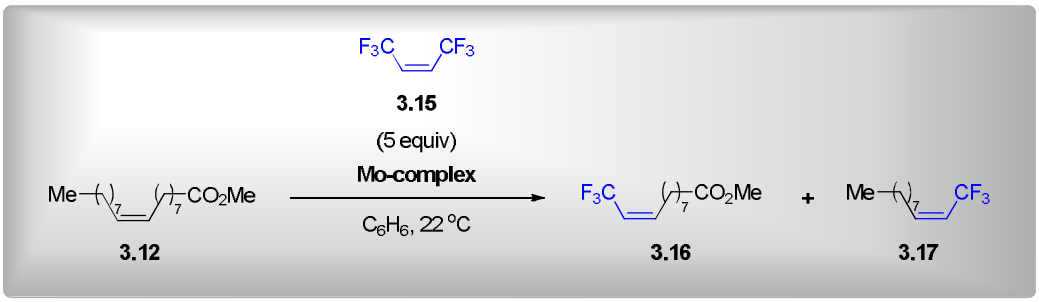
3.5. CM to Access Functionalized Z-Trifluoromethylated Alkenes

3.5.1. Identification of an Effective Catalyst for CM

As illustrated in Scheme 3.3, no reported OM catalyst, including MAP species **Mo-1**, was capable of promoting CM between **3.12** and *Z*-1,1,1,4,4,4-hexafluoro-2-butene **3.15** in our hands. In contrast, there was >98% conversion in the presence of just 2 mol % **Mo-3b**, affording the expected CM products **3.16** and **3.17** in 92% and 62% yield, respectively, as single stereoisomers (>98% *Z* selectivity) within 15 minutes (Scheme 3.9). Slightly higher yields were obtained with *tert*-butylimido MAC complex **Mo-3c**. In both cases, **3.17** was obtained in lower yields due to its volatility. These results provide additional testament to the superior activity and selectivity exhibited by MAC catalysts.

Scheme 3.9. Identification of an Effective Catalyst for CM with *Z*-1,1,1,4,4,4-Hexafluoro-2-butene.





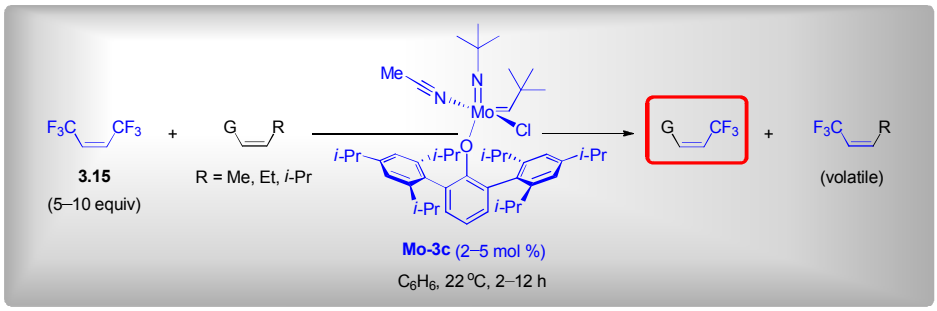
with **Mo-1** (5 mol %), 4 h, <5% conv to **3.16** & **3.17**

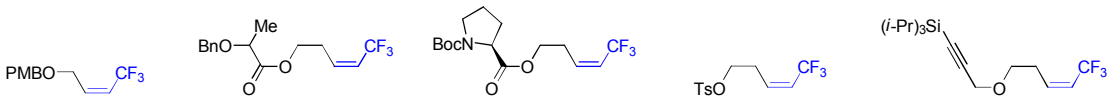
with **Mo-3b** (2 mol %), 15 min, >98% conv, 92% yield (**3.16**), 62% yield (**3.17**), **>98:2 *Z*:*E***

with **Mo-3c** (2 mol %), 15 min, >98% conv, 95% yield (**3.16**), 67% yield (**3.17**), **>98:2 *Z*:*E***

3.5.2. Substrate Scope Analysis

Scheme 3.10. The range of *Z*-CF_3-Alkenes Obtained by *Z*-Selective CM with **Mo-3c**.





3.22

R = Et,
87% conv, 77% yield
>98:2 *Z*:*E*

3.23

R = Et,
73% conv, 70% yield
>98:2 *Z*:*E*

3.24

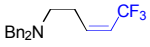
R = Et,
>98% conv, 80% yield
>98:2 *Z*:*E*

3.25

R = Et,
82%% conv, 77% yield
>98:2 *Z*:*E*

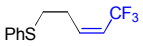
3.26

R = Et,
>98% conv, 82% yield
>98:2 *Z*:*E*



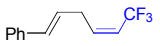
3.27

R = Et,
>98% conv, 92% yield
>98:2 *Z*:*E*



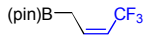
3.28

R = Et,
>98% conv, 69% yield
95:5 *Z*:*E*



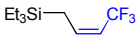
3.29

R = Me,
92% conv, 62% yield
97:3 *Z*:*E*



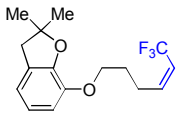
3.30

R = Me,
>98% conv, 70% yield
97:3 *Z*:*E*



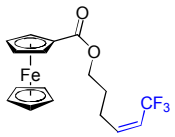
3.31

R = Me,
>98% conv, 62% yield
94:6 *Z*:*E*



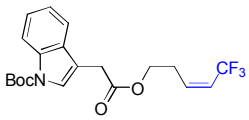
3.32

R = Me,
>98% conv, 86% yield
>98:2 *Z*:*E*



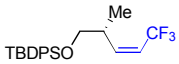
3.33

R = Me,
>98% conv, 98% yield
>98:2 *Z*:*E*



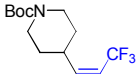
3.34

R = Et,
>98% conv, 88% yield
>98:2 *Z*:*E*



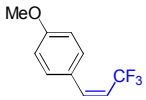
3.35

R = Me,
>98% conv, 85% yield
>98:2 *Z*:*E*



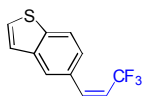
3.36

R = Me,
>98% conv, 88% yield
>98:2 *Z*:*E*



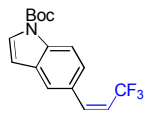
3.37

R = *i*-Pr,
89% conv, 59% yield,
>98:2 *Z*:*E*



3.38

R = *i*-Pr,
90% conv, 61% yield,
>98:2 *Z*:*E*



3.39

R = *i*-Pr,
92% conv, 64% yield,
>98:2 *Z*:*E*

Even though *Z*-1,2-disubstituted alkenes such as **3.12** are effective substrates for the CM protocol, reactions with terminal alkenes were found to be inefficient (<10% conversion), the reasons for which remain to be determined. Nevertheless, we focused

our efforts on utilizing *Z*-1,2-disubstituted alkene substrates, many of which are either commercially available, readily derived from naturally occurring *Z*-olefins (for example, *Z*-3-hexen-1-ol) or easily prepared by catalytic cross-coupling (from commercially available *Z*-1-bromo-1-propene). The present approach of converting easily accessible *Z*-olefins to higher-value *Z*-CF_3-alkenes that are more challenging to prepare offers a compelling solution to a longstanding problem.

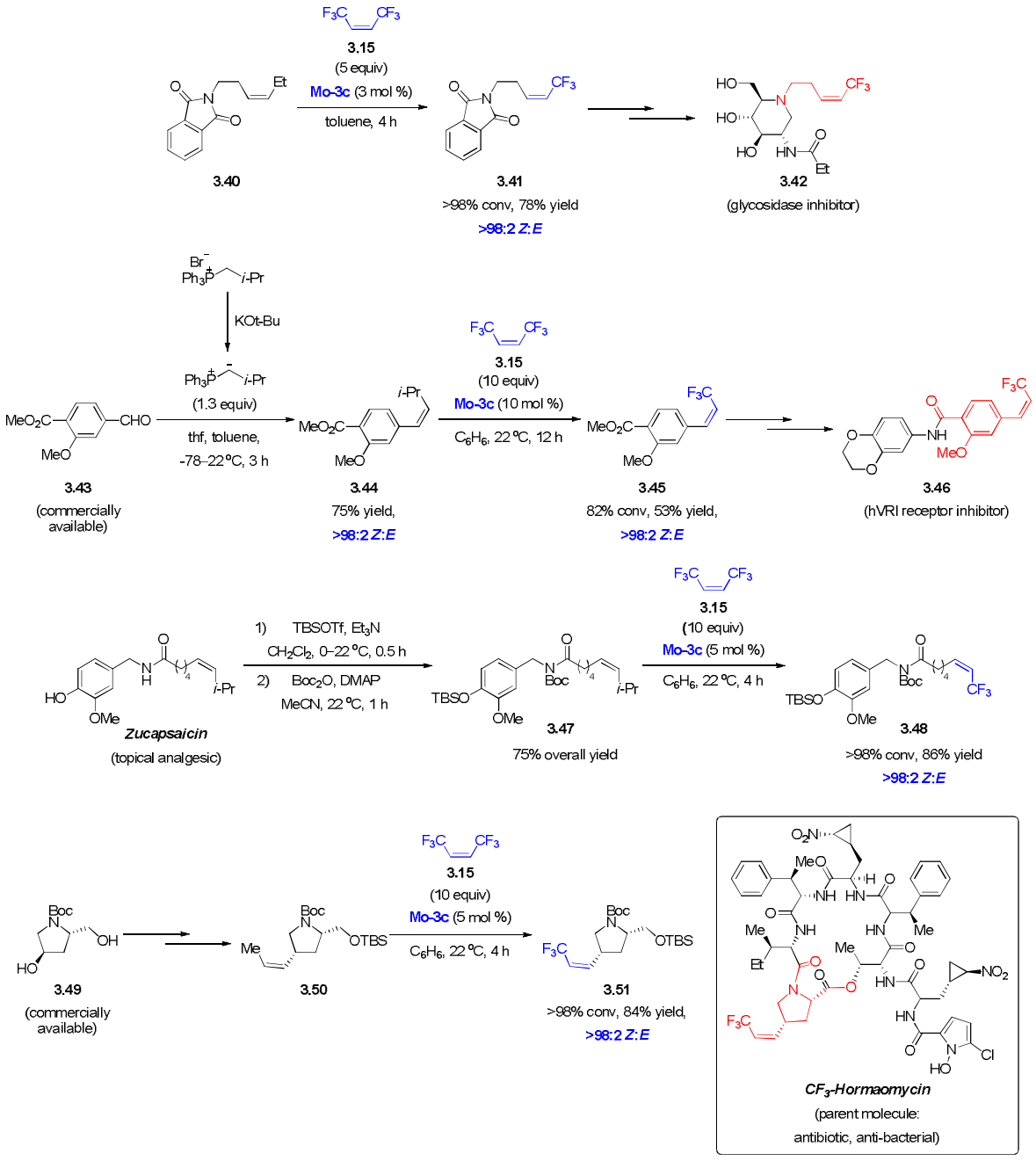
As depicted in Scheme 3.10, a myriad of trifluromethylated olefins were obtained in 59–98% yield and ≥94:6 *Z*:*E* ratio. These include products containing an allylic ether (**3.22**), an α-alkoxy ester capable of coordinating to the Mo center (**3.23**), a carbamate (**3.24**), an electrophilic tosylate (**3.25**), an alkyne (**3.26**), a tertiary amine (**3.27**), a sulfide (**3.28**) or a 1,4-diene (**3.29**). Similarly, a crotyl-B(pin) (**3.30**) and a crotylsilane (**3.31**) were suitable substrates for CM; **3.30**[22] and **3.31** represent potential allylating agents for C–C bond forming reactions. Alkenes bearing a cyclic ether (**3.32**), a ferrocenyl moiety (**3.33**) or a Boc-indole (**3.34**) were also tolerated under the CM conditions. Reactions with sterically congested α-branched 1,2-disubstituted aliphatic olefins (**3.35**–**3.36**) and β-substituted styrenes (**3.37**–**3.39**) also proceeded successfully. It merits mention that transformations with aryl olefins entail the use of *Z*-β-isopropyl styrenyl substrates (prepared in a single step from the corresponding aldehydes, cf. **3.44** in Scheme 3.11 below) so that homocoupling is less competitive. The MAC complexes may be delivered in the form of air- and moisture-resistant paraffin tablets, allowing reactions to be performed in the fume hood without a glove box.[23] For example, CM performed with a

(22) Compound **3.30** is used in ongoing studies involving catalytic enantioselective additions to aldehydes, see: van der Mei, F. W.; Hoveyda, A. H. *unpublished results*.
(23) Ondi, L.; Nagy, G. M.; Czirok, J. B.; Bucsai, A.; Frater, G. E. *Org. Process Res. Dev.* **2016**, *20*, 1709–1

tablet containing **Mo-3c** (3 mol %, toluene, 35 °C, 2 h) allows access to **3.24** in 74% yield and >98:2 *Z*:*E* ratio.

3.5.3. Synthesis of Bioactive Compounds and CF_3-Analogues

Scheme 3.11. Synthesis of Bioactive Compounds & CF_3-Derivatives through Z-Selective CM.



Given the importance of the trifluoromethyl motif in chemical synthesis (cf. Section 3.2.3), we proceeded to evaluate the plausibility of preparing CF_3-containing therapeutic agents and their derivatives through catalytic CM (Scheme 3.11). **3.41**, generated in 78% yield with complete *Z* selectivity from **3.40**, has been converted to glycosidase inhibitor **3.42**.[24] A *Z*-selective Wittig reaction involving commercially available aldehyde **3.43** followed by CM allows access to sterically hindered *Z*-CF_3-olefin **3.45**, a precursor en route to hvRI receptor inhibitor,[25] in 40% overall yield as a single stereoisomer. **3.45** was previously synthesized by a Wittig reaction with **3.43** and 2,2,2-trifluoroethyl diphenylphosphine oxide, affording a mixture of *E*/*Z* isomers (exact yield and selectivity not reported[25]).

Two representative cases underscore utility of our CM protocol in preparing trifluoromethyl analogues of biologically relevant molecules. Reaction of **3.47**, derived from analgesic zucapsaicin,[26] with excess **3.15** delivered **3.48** in 86% yield and >98:2 *Z*:*E* ratio. In another example, **3.50**, previously synthesized in 5 steps and 27% overall yield from commercially available **3.49**, was transformed to **3.51** in 84% yield and >98% *Z* selectivity, potentially facilitating preparation of a CF_3-derivative of antibiotic and anti-bacterial hormaomycin.[27]

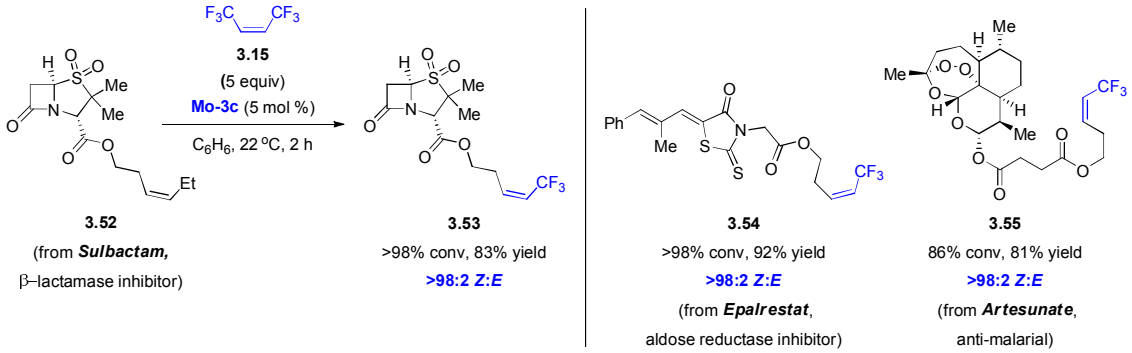
3.5.4. Demonstration of Functional Group Compatibility with Complex Molecules

The exceptional functional group tolerance exhibited by MAC complex **Mo-3c** towards sensitive polar and Lewis basic groups commonly found in therapeutic molecules is further highlighted in Scheme 3.12. The synthesis of *Z*-CF_3-olefins **3.53**,

(24) Mceachern, E. J.; Vocaldo, D. J.; Zhou, Y.; Selnick, H. G. Patent WO 2014/032187 A1 (2014).
(25) Kelly, M.; Kincaid, J.; Duncton, M.; Sahasrabudhe, K.; Janagani, S.; Upasani, R. B.; Wu, G.; Fang, Y.; Wei, Z.-L.; Kaub, C. Patent WO 2006/093832 A2 (2006).
(26) Hua, X.-Y.; Chen, P.; Hwang, J.; Yaksh, T. L. *Pain* **1997**, *71*, 313–322.
(27) Zlatopolskiy, B. D.; Kroll, H.-P.; Melotto, E.; de Meijere, A. *Eur. J. Org. Chem.* **2004**, 4492–4502.

3.54 and **3.55** from derivatives of biologically active sulbactam,[28] epalrestat[29] and artesunate[30] under mild reactions conditions demonstrates the benefits of CM as a reliable strategy in complex molecule systems.

Scheme 3.12. *Z*-Selective CM with Complex Molecules.



3.6. Elucidation of Superior Reactivity and Selectivity Levels of MAC Catalysts through DFT Calculations

DFT calculations were performed to shed light on the origins regarding the superior reactivity and selectivity profiles of MAC complexes (Scheme 3.13). We investigated the transformations between *Z*-2-butene (**A**; homocoupling pathway) and *Z*-1,2-dichloroethene (**B**; CM pathway) with **Mo-4** (MAP species) as well as **Mo-5** (MAC species). The results suggest that the improved efficiency and *Z* selectivity in forming alkenyl halides with MAC complexes arise from differences in chemoselectivity (vs. MAP systems). These discrepancies are indicated by the larger gap in energy needed to overcome the activation barrier for metallacyclobutane formation (**ts1**) in reactions of **Mo-4** with *Z*-2-butene (17.3 kcal mol^{-1}) and *Z*-1,2-dichloroethene (23.0 kcal mol^{-1}),

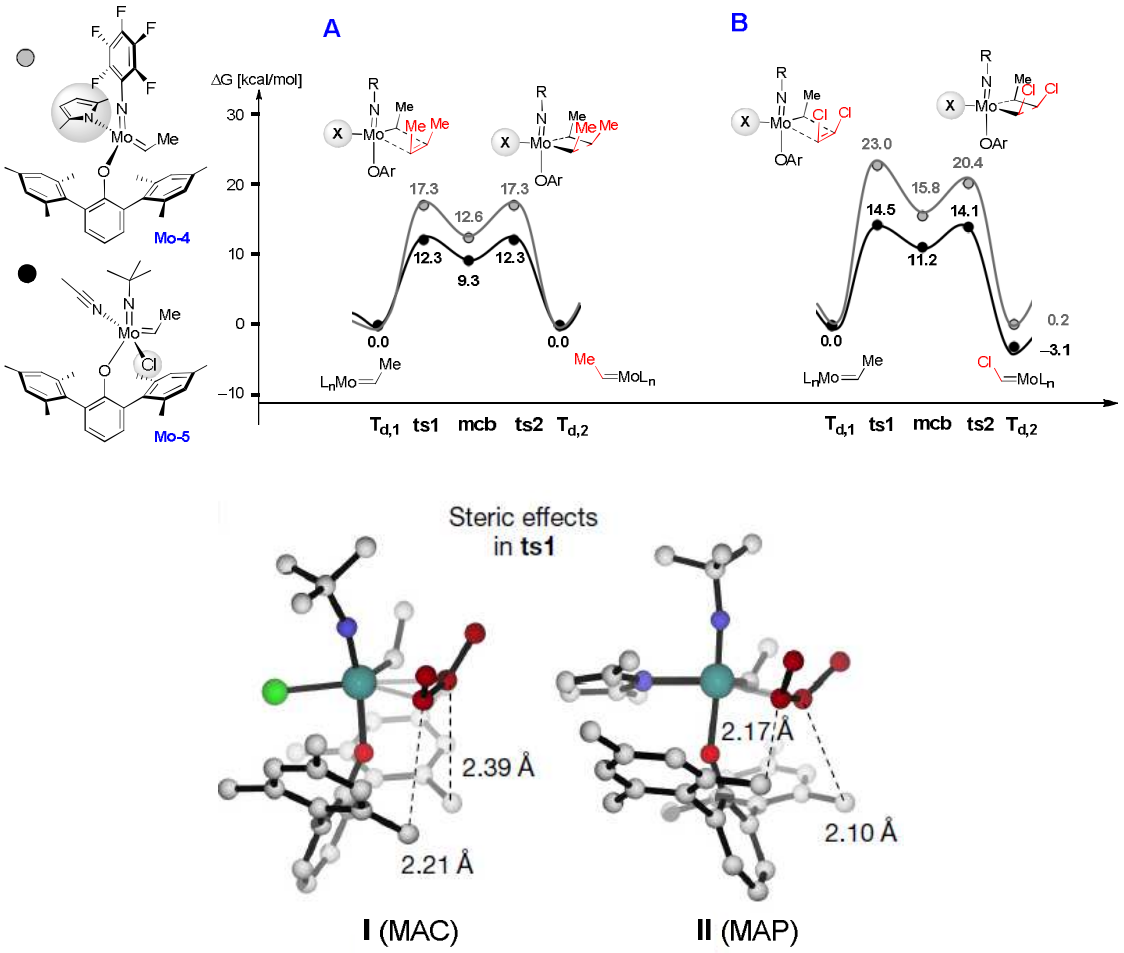
(28) English, A. R.; Girard, D.; Jasys, V. J.; Martingano, R. J.; Kellogg, M. S. *J. Med. Chem.* **1990**, *33*, 344–347.
(29) Ramirez, M. A.; Borja, N. L. *Pharmacotherapy* **2008**, *28*, 646–655.
(30) Luo, X.-D.; Shen, C.-C. *Med. Res. Rev.* **1987**, *7*, 29–52.

compared to those for **Mo-5** (12.3 kcal mol^{-1} for *Z*-2-butene and 14.5 kcal mol^{-1} for *Z*-1,2-dichloroethene). Thus, an alkyl-substituted MAP alkylidene tends to react with another aliphatic alkene (rather than the more electron-deficient *Z*-1,2-dichloroethene) to furnish homocoupling products. With excess dihaloethene reagent, homocoupling becomes less competitive and the desired CM may become favorable (however, for certain substrates such as aryl olefins and 1,3-dienes (cf. Scheme 3.1), homocoupling is still a major competing pathway). In contrast, with a MAC system that is capable of reacting with either *Z*-2-butene or *Z*-1,2-dichloroethene at comparable rates, adventitious homocoupling/*Z*-to-*E* post-metathesis isomerization is minimal, particularly when excess dihaloethene is employed (control experiments indicate that isomerization of *Z*-1,2-dichloroethene is slow). Consequently, under the reaction conditions for CM, the desired alkenyl chlorides can be obtained efficiently and *Z*-selectively. Similar arguments may be applied to transformations that deliver alkenyl bromides and trifluoromethylated olefins.

Further DFT calculations revealed that MAC complexes possess enhanced Lewis acidity compared to the MAP alkylidenes (see Experimental section for further details on the electronic effects of the anionic ligand in Mo-based alkylidenes). In addition, as illustrated by the transition state structures for metallacyclobutane formation (**ts1**) between methylimido alkylidene complexes and *Z*-2-butene (Scheme 3.13, bottom), the aryloxy group tilts towards the chloride as the incoming olefin coordinates to the Mo center in MAC complex **I** (C–H···H–C distances of 2.21 Å and 2.39 Å). On the other hand, the aryloxide and the alkene are forced into closer contact (2.10 Å and 2.17 Å) in MAP system **II** due to the larger dimethylpyrrolide ligand. The greater steric pressure in **II** partly accounts for the generally higher activation barriers leading to **ts1** with MAP

complexes (Scheme 3.13, top). Overall, the greater Lewis acidity coupled with diminution in steric repulsion within metallacyclobutane intermediates may help rationalize the superior reactivity of MAC catalysts (vs. MAP).

Scheme 3.13. Comparison of the Reactivity & Selectivity of MAP & MAC Systems with *Z*-2-Butene & *Z*-1,2-Dichloroethene.



3.7. Conclusions

Through substitution of the pyrrolide ligand with a chloride within a MAP system, a new class of Mo-based MAC complexes was developed. These highly active complexes were found to be effective catalysts for promoting efficient and stereoretentive CM between *Z*-1,2-disubstituted alkene substrates and sterically hindered, electron-poor *Z*-1,1,1,4,4,4-hexafluoro-2-butene **3.15** to furnish a wide assortment of

trifluoromethylated olefins with exceptional *Z* selectivity. The results were unprecedented given that no other reported OM catalyst was capable of accomplishing these transformations. Intriguingly, the higher reactivity observed did not come at the expense of stereoselectivity and functional group tolerance as numerous Lewis basic motifs commonly found in biologically active molecules were shown to be compatible under the CM conditions. Furthermore, otherwise inefficient and poorly-selective MAP-catalyzed CM reactions with *Z*-1,2-dichloroethene **3.2** (for example, with aryl olefins and 1,3-dienes as substrates) and 1,2-dibromoethene **3.10** can be effected with appreciably improved efficiency and *Z* selectivity by employing the MAC variants, thereby expanding the scope of these catalytic protocols.

DFT calculations showed that the origins of the superior activity and selectivity levels are likely rooted in differences in chemoselectivity exhibited by MAC (vs. MAP) systems, owing to enhanced Lewis acidity and diminution in steric repulsion within the metallacyclobutane intermediate. A MAP species is more prone to engage with an olefin substrate (vs. the more electron-deficient **3.2**, **3.10** or **3.15**) to promote homocoupling. Consequently, *Z*-to-*E* isomerization of these self-metathesis products followed by CM results in diminished levels of *Z* selectivity. With a MAC system, the energy gap between the rate-limiting barriers for homocoupling and CM is smaller, such that employing a large excess of the halogen-containing reagent causes the desired CM pathway to become more favorable.

A caveat of these MAC-catalyzed CM transformations is that stereodefined *Z*-1,2-disubstituted alkenes have to be employed as substrates; many of these compounds are commercially available or readily prepared by a number of reported methods. Reactions

with mono-substituted terminal alkenes are inefficient, for reasons that remain to be determined through ongoing mechanistic and computational investigations. Nonetheless, the advent of these readily accessible and highly active complexes is likely to inspire development of new catalyst systems and catalytic methods to address other existing challenges (for example, stereoselective OM to access trisubstituted alkenes) in the field of OM.

3.8. Experimentals

3.8.1. General

Unless otherwise noted, transformations were performed with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum line techniques. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz), 500 (500 MHz) or 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.16 ppm, CD_2Cl_2: δ 5.32 ppm, CD_3OD: δ 3.31 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz), 500 (125 MHz), or 600 (150 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm, C_6D_6: δ 128.00 ppm, CD_2Cl_2: δ 54.00 ppm, CD_3OD: δ 49.00 ppm). ^{19}F NMR spectra were recorded on a Varian Unity INOVA 400 (376 MHz) spectrometer without proton decoupling. High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS and JEOL Accu TOF Dart (positive mode) at the Boston College Mass Spectrometry Facility. Melting points were determined using a Thomas Hoover Uni-melt capillary melting point apparatus. Values for *Z*:*E* ratios of products were determined by ^1H NMR analysis of unpurified mixtures.

Solvents:

Solvents (CH_2Cl_2, pentane, benzene and toluene) were purified under a positive pressure of dry argon gas by a modified Innovative Technologies purification system. Tetrahydrofuran was distilled from Na/benzophenone. Methanol was distilled over Mg. Acetone was used as received. All purification procedures of CM products were carried out with reagent grade solvents (purchased from Fisher) under bench-top conditions.

Reagents:

Chlorotrimethylsilane (Alfa Aesar) was degassed by freeze-pump-thaw method prior to use. Lithium aryloxides (LiOAr) were prepared by addition of one equivalent of *n*-butyllithium to a cold pentane or Et_2O solution of ArOH, and the solid was collected on a glass frit, washed with pentane, and dried *in vacuo*.

(*Z*)-Methyl oleate (Aldrich), (*Z*)-cyclooctene (Aldrich) and (*Z*)-crotylboronic acid pinacol ester (Frontier Scientific) were either distilled (from CaH_2 or $CaCl_2$) under vacuum or dried by azeotropic distillation (with anhydrous benzene) prior to use.

(*Z*)-1-Methoxy-4-(prop-1-enyl)benzene (from 4-methoxyphenylboronic acid (Combi-blocks) and (*Z*)-1-bromo-1-propene (Aldrich)), (*Z*)-*t*-butyl 5-(prop-1-enyl)-1*H*-indole-1-carboxylate (from 1-Boc-indole-5-boronic acid pinacol ester (Combi-blocks) and (*Z*)-1-bromo-1-propene (Aldrich)) and (1*E*,3*Z*)-penta-1,3-dienylbenzene (from (*E*)-phenylethenylboronic acid (Combi-blocks) and (*Z*)-1-bromo-1-propene (Aldrich)) were prepared by cross-coupling in analogy to a reported procedure.[31]

(31) Fristrup, P.; Tanner, D.; Norrby, P.-O. *Chirality* **2003**, *15*, 360–368.

(*Z*)-1-Methoxy-4-((pent-2-enyloxy)methyl)benzene, [32] (*Z*)-3-hexenyl 4-methylbenzenesulfonate,[33] (*R*,*Z*)-*t*-butyl(2-methylpent-3-enyloxy)diphenylsilane,[34] (*Z*)-2-(3-hexenyl)isoindoline-1,3-dione, [35] (*Z*)-*N*,*N*-dibenzylhex-3-en-1-amine, [36] (*Z*)-hex-3-enyl(phenyl)sulfane, [37] (1*E*,4*Z*)-1,4-hexadienylbenzene [38] and (2*S*,4*R*)-*t*-butyl 2-((*t*-butyldimethylsilyloxy)methyl)-4-((*Z*)-prop-1-enyl)pyrrolidine-1-carboxylate[27] were prepared according to reported procedures.

(*Z*)-7-(Hex-4-enyloxy)-2,2-dimethyl-2,3-dihydrobenzofuran[7b] (from 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran (TCI) and (*Z*)-4-hexen-1-ol (Alfa Aesar)), (*Z*)-3-hexenyl 2-(benzyloxy)propanoate [39] (from (*Z*)-3-hexenyl lactate (Aldrich)), (*Z*)-(3-(hex-3-enyloxy)prop-1-ynyl)triisopropylsilane[40] (from 3-bromo-1-(triisopropylsilyl)-1-propyne[41] and (*Z*)-3-hexen-1-ol (TCI)), (*Z*)-*t*-butyl 4-(prop-1-enyl)piperidine-1-carboxylate[42] (from 1-Boc-4-piperidinecarboxaldehyde (Combi-blocks)), (*Z*)-but-2-en-1-yltriethylsilane[43] and (*Z*)-*t*-butyl 4-(*t*-butyldimethylsilyloxy)-3-methoxybenzyl(8-methylnon-6-enoyl)carbamate[44] (from zucapsaicin (AstaTech)) were prepared in analogy to reported procedures.

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(*Z*)-*t*-Butyl 3-(2-(3-hexenyloxy)-2-oxoethyl)-1*H*-indole-1-carboxylate (from 1-Boc-3-carboxymethylindole (AstaTech) and (*Z*)-3-hexen-1-ol (TCI)), (*S*,*Z*)-1-*t*-butyl 2-hex-3-enyl pyrrolidine-1,2-dicarboxylate (from *N*-(*t*-butoxycarbonyl)-L-proline (Advanced Chemtech) and (*Z*)-3-hexen-1-ol (TCI)), (*Z*)-4-hexenyl ferrocenecarboxylate (from ferrocenecarboxylic acid (Aldrich) and (*Z*)-4-hexen-1-ol (Alfa Aesar)), (*Z*)-hex-3-enyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (from sulbactam (TCI) and (*Z*)-3-hexen-1-ol (TCI)), (*Z*)-pent-3-en-1-yl 2-((*Z*)-5-((*E*)-2-methyl-3-phenylallylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetate (from epalrestat (TCI) and (*Z*)-3-hexen-1-ol (TCI)) and artesunate (*Z*)-hex-3-enyl ester (from artesunate (TCI) and (*Z*)-3-hexen-1-ol (TCI)) were prepared by esterification in analogy to a reported procedure.[45]

(*Z*)-1-Methoxy-4-(3-methylbut-1-enyl)benzene (from *p*-anisaldehyde (Aldrich)), (*Z*)-5-(3-methylbut-1-enyl)benzo[*b*]thiophene (from 1-benzothiophene-5-carboxaldehyde (Maybridge)), *t*-butyl (*Z*)-5-(3-methylbut-1-en-1-yl)-1*H*-indole-1-carboxylate (*t*-butyl 5-formyl-1*H*-indole-1-carboxylate (Matrix)) and (*Z*)-methyl 2-methoxy-4-(3-methylbut-1-enyl)benzoate (from methyl 4-formyl-3-methoxybenzoate (AstaTech)) were prepared by Wittig reaction in analogy to a reported procedure.[46]

Pentafluorophenol (Oakwood), 2,6-dibromophenol (Oakwood), palladium(II) acetylacetonate (Strem), (*Z*)-1,1,1,4,4,4-hexafluoro-2-butene (Synquest), (*Z*)-1,2-dichloroethene (Aldrich) and 1,2-dibromoethene (TCI) were used as received.

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Organometallic Complexes:

Mo monoaryloxide pyrrolide (MAP) complex **Mo-1a** was prepared according to a previously reported procedure.[5] Mo complexes were manipulated under an atmosphere of N_2 in a glove box. Paraffin pellets were received from XiMo, AG.

3.6.2. Synthesis of 2,6-bis(2,4,6-triisopropylphenyl)phenol

A solution of 2,6-dibromophenol (1.00 g, 3.97 mmol, 1.00 equiv) in anhydrous THF (5 mL) was added dropwise to a suspension of NaH (60% wt in mineral oil, 192 mg, 4.80 mmol, 1.20 equiv) in anhydrous THF (10 mL) chilled in an ice/water bath. The resulting mixture was allowed to warm to 22 ^{o}C and stir for 10 min, then treated with $Pd(acac)_2$ (123 mg, 0.401 mmol, 10 mol %) followed by a solution of 2,4,6-triisopropylphenylmagnesium bromide (0.5 M in THF, 20.0 mL, 10.0 mmol, 2.50 equiv) and the mixture was heated under reflux for 12 h. Upon cooling to 0 ^{o}C, water was carefully added to quench the excess Grignard reagent and NaH. An aqueous 1.0 M solution of HCl (20 mL) was added followed by Celite with vigorous stirring. The mixture was filtered through a pad of Celite and the separated aqueous phase was extracted with Et_2O (3 x 25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (100% hexanes then 5% EtOAc in hexanes) to obtain 2,6-bis(2,4,6-triisopropylphenyl)phenol (1.14 g, 2.28 mmol, 57% yield) as beige solid. The spectral data for this compound were identical to those reported previously.[47]

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3.6.3. Synthesis of Mo Monoaryloxide Halide Complexes

Complex 3.20: Compound **3.18** was prepared according to a previously reported procedure.[48] This compound (2.00 g, 3.02 mmol) was first dissolved in Et_2O (50 mL). This solution was then allowed to cool to –25 °C and treated with a pre-chilled solution of pentafluorophenol (1.17 g, 6.34 mmol) in Et_2O (10 mL). The orange mixture was allowed to stir at 22 °C for 2 h. At this time, solid bipyridine was added in a single portion (0.48 g, 3.02 mmol) and the mixture was allowed to stir at 22 °C for 2 h, during which time a yellow precipitate was formed. The solution was allowed to cool to –25 °C and the precipitate was collected by filtration and washed with a solution of cold Et_2O, affording **3.20** (2.44 g, 2.72 mmol, 90% yield) as yellow solid, which was recrystallized from CH_2Cl_2/pentane. **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ 13.87 (1H, s), 9.31 (1H, d, J = 5.7 Hz), 8.06 (1H, ddd, J = 10.0, 10.0, 2.1 Hz), 7.98 (2H, dd, J = 10.2, 10.2 Hz), 7.87 (1H, ddd, J = 9.7, 9.7, 2.0 Hz), 7.65 (1H, m), 7.55–7.47 (3H, m), 7.34 (2H, m), 7.22 (1H, m), 6.90 (1H, m), 2.07 (3H, s), 1.81 (3H, brs), 1.57–1.33 (15H, m); **^{13}C NMR (100 MHz, CD_2Cl_2)**: (overlapping resonances due to F coupling are omitted) δ 311.1, 158.6, 253.8, 151.6, 149.6, 140.2, 140.1, 128.7, 126.7, 126.6, 126.2, 125.4, 122.34, 121.6, 72.0, 53.8, 51.1, 42.8, 36.0, 31.4, 30.8, 29.5; **^{19}F NMR (282 MHz, CD_2Cl_2)**: δ –160.1 (d, J = 22 Hz), –162.6 (d, J = 21 Hz), –169.5 (d, J = 21 Hz), –170.1 (d, J = 21 Hz), –178.1 (m), –180.2 (m). Anal Calcd for $C_{44}H_{51}F_{10}MoN_3O_2$: C, 56.07; H, 3.92; N, 4.67. Found: C, 55.36; H, 3.90; N, 4.28.

Complex Mo-3a: Compound **3.20** (415 mg, 0.461 mmol) was dissolved in CH_2Cl_2 (10 mL) and then subjected to Me_3SiCl (660 mg, 6.08 mmol). The solution was allowed to

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stir at 22 °C for 10 h after which the volatiles were removed in vacuo. The resulting solid was allowed to stir in Et_2O (10 mL) and the yellow residue was collected by filtration to afford Mo(N-adamantyl)($CHCMe_2Ph$)Cl_2(bipy) (bipy, 2,2'-bipyridine; 242 mg, 0.401 mmol, 87% yield) as yellow solid. **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ (major isomer, 60%; selected resolved peaks only) 14.35 (1H, s), 9.58 (2H, d, J = 5.8 Hz) 1.99 (3H, s); **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ (minor isomer, 40%; selected resolved peaks only) 12.98 (1H, s), 8.90 (1H, brs); **^{13}C NMR (100 MHz, CD_2Cl_2)**: δ (resonances reported for the mixture of isomers) 316.8, 313.9, 158.5, 154.4, 149.7, 140.8, 140.0 139.9, 139.6, 128.6, 128.2, 126.9, 126.6, 126.1, 125.9, 123.8, 123.0, 122.8, 75.7, 73.5, 54.2, 52.3, 52.1, 42.7, 42.2, 36.1, 35.7, 41.6, 30.6, 30.2, 29.7, 29.2.

Mo(N-adamantyl)($CHCMe_2Ph$)Cl_2(bipy) (bipy, 2,2'-bipyridine; 250 mg, 0.538 mmol) was suspended in Et_2O (50 mL) and allowed to cool to –25 °C. The solution was then slowly charged with a suspension of lithium 2,6-bis(2,4,6-trimethylphenyl)phenoxide (196 mg, 0.522 mmol) in Et_2O (5 mL), followed by a solution of $ZnCl_2$ (73 mg, 0.522 mmol) in Et_2O (5 mL). After the mixture was allowed to stir at 22 °C for 2 h, it was filtered through Celite and the volatiles were removed in vacuo to afford red-brown foam, which was then washed with pentane (30 mL) and filtered through Celite to give a dark brown solution. Acetonitrile (2 mL) was added to this pentane solution, and the resulting pink slurry was concentrated to dryness in vacuo, affording dark-colored heterogeneous material that was triturated with pentane (5 mL). The solution was then allowed to cool to –25 °C and kept at this temperature for 16 h. The off-white solid was collected by filtration, washed with cold pentane (~1 mL) and cold MeCN (~1 mL) to afford **Mo-3a** (167 mg, 0.213 mmol, 41% yield) as off-white solid. **^{1}H NMR (500 MHz, C_6D_6)**: δ

12.07 (1H, brs, J_{C-H} = 127 Hz), 7.28–7.26 (2H, m), 7.20–7.14 (4H, m), 7.05 (1H, m), 7.00 (1H, dd), 6.87 (2H, brs), 6.85 (2H, brs), 2.38 (6H, s), 2.36 (6H, s), 2.15 (6H, s), 1.84 (3H, m), 1.70–1.67 (6H, m), 1.65 (3H, s), 1.57 (3H, s), 1.47–1.39 (6H, m), 0.59 (3H, brs); **^{13}C NMR (100 MHz, C_6D_6)**: δ 307.1, 161.0, 150.2, 137.7, 137.6, 135.7, 131.5, 129.8, 128.9, 128.5, 128.4, 126.8, 126.0, 121.9, 119.6, 72.3, 51.1, 43.5, 36.2, 31.8, 29.8, 21.5, 21.2, 0.6. Anal Calcd for $C_{46}H_{55}ClMoN_2O$ (with 0.67 equiv. of toluene, based on ^{1}H NMR): C, 72.04; H, 7.20; N, 3.32. Found: C, 72.00; H, 7.51; N, 3.07.

Complex Mo-3b: Mo(N-adamantyl)(CHCMe$_2$Ph)Cl$_2$(bipy) (bipy, 2,2'-bipyridine; 334 mg, 0.719 mmol) was suspended in Et$_2$O (50 mL) and allowed to cool to –25 °C. The resulting suspension was treated slowly with a suspension of lithium 2,6-bis(2,4,6-triisopropylphenyl)phenoxide (416 mg, 0.719 mmol) and $ZnCl_2$ (98 mg, 0.719 mmol) in THF (10 mL). After the mixture was allowed to stir at 22 °C for 6 h, it was filtered through Celite and concentrated to give brown foam, which was washed with pentane (30 mL) and filtered through Celite to give a pale brown solution containing Mo(N-adamantyl)(CHCMe$_2$Ph)(OHIPT)(Cl) (OHIPT, 2,6-(2,4,6-triisopropylphenyl)phenoxide) and unidentified alkylidyne by-products. Acetonitrile (0.1 mL) was then added and the mixture was allowed to stir for 1 h. The slurry was concentrated to dryness *in vacuo*, affording a dark-colored heterogeneous material that was triturated with pentane (~2 mL). The solution was then allowed to cool to –25 °C and kept at this temperature for 16 h. The resulting off-white solid was collected by filtration and washed with cold pentane (~1 mL) to give **Mo-3b** (398 mg, 0.417 mmol, 58% yield) as off-white solid. **^{1}H NMR (500 MHz, C_6D_6)**: δ 12.43 (1H, s), 7.31 (2H, d, J = 7.5 Hz), 7.25 (4H, m), 7.21–7.11 (4H, m), 7.02–6.97 (2H, m), 3.43 (4H, m), 2.88 (2H, sep, J = 6.9 Hz), 1.89 (3H, brs),

1.78–1.65 (9H, m), 1.48–1.39 (21H, m), 1.69 (12H, m), 1.24 (12H, m), 0.67 (3H, s); **^{13}C NMR (100 MHz, C_6D_6)**: δ 307.1, 161.3, 149.5, 148.1, 147.2, 136.4, 131.2, 127.0, 125.8, 120.9, 120.8, 119.1, 72.6, 51.1, 43.4, 36.1, 34.5, 31.4, 31.1, 30.92, 30.90, 29.7, 26.2, 24.60, 24.57, 24.20, 24.17, 0.9. Anal Calcd for $C_{58}H_{79}ClMoN_2$: C, 73.20; H, 8.37; N, 2.94. Found: C, 73.19; H, 8.48; N, 2.92.

Complex 3.56: Compound **3.56** was synthesized in a similar manner as **3.20**. Mo(N-*t*-Bu)(CH-*t*-Bu)(OC_6F_5)$_2$(H_2N-*t*-Bu) was prepared according to a reported procedure[49], or generated *in situ* by treating dialkyl Mo complex Mo(N-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ with 2.05 equivalents of C_6F_5OH in toluene. Mo(N-*t*-Bu)(CH-*t*-Bu)(OC_6F_5)$_2$(H_2N-*t*-Bu) (3.07 g, 4.53 mmol) was suspended in toluene (50 mL) and treated with solid bipyridine (0.73 g, 4.67 mmol). The brown solution was allowed to stir at 22 °C for 4 h causing a yellow precipitate to form. The suspension was then allowed to cool to –25 °C and the precipitate was collected by filtration and washed with cold Et_2O to furnish **3.56** (2.74 g, 3.62 mmol, 80% yield) as yellow solid, which was used directly in the next step without further purification. **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ (major isomer, ~95%) 13.89 (1H, s), 9.28 (1H, d, J = 5.0 Hz), 8.70 (1H, d, J = 5.5 Hz), 8.13–8.01 (4H, m), 7.67 (1H， ddd, J = 6.9, 5.3, 1.5 Hz), 7.41 (1H, ddd, J = 7.1, 5.5, 1.5 Hz), 1.24 (9H, s), 0.93 (9H, s); **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ (minor isomer, ~5% ; selected resolved peaks only) 13.84 (1H, s), 9.09 (1H, d, J = 5.4 Hz), 8.82 (1H, d, J = 5.3 Hz), 8.13–8.01 (4H, m), 7.67 (1H, ddd, J = 6.9, 5.3, 1.5 Hz), 7.41 (1H, ddd, J = 7.1, 5.5, 1.5 Hz), 1.19 (9H, s). ^{13}C NMR, ^{19}F NMR and elemental analysis data were not obtained for this compound.

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Complex Mo-2: Compound **Mo-2** was synthesized in a similar manner as **Mo-3a**. Complex **3.56** (2.74 g, 3.61 mmol) was suspended in CH_2Cl_2 (50 mL) and the resulting mixture was treated with Me_3SiCl (3.7 mL, 28.89 mmol). The solution was allowed to stir at 22 °C for 10 h after which the volatiles were removed *in vacuo*. The resulting solid was allowed to stir in Et_2O (10 mL) and the yellow residue was collected by filtration to afford Mo(N-*t*-Bu)(CH-*t*-Bu)Cl_2(bipy) (bipy, 2,2'-bipyridine; 1.49 g, 3.21 mmol, 89% yield) as pale yellow solid. **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ (major isomer, ~80%) 14.40 (1H, s), 9.55 (1H, d, J = 2.8 Hz), 8.73 (1H, d, J = 3.8 Hz), 8.29 (2H, d, J = 13.7 Hz), 8.21 (2H, d, J = 13.6 Hz) 1.99 (3H, s), 8.16–8.04 (2H, m), 7.63 (1H, m), 7.47 (1H, m), 1.42 (9H, s), 1.00 (9H, s); **^{1}H NMR (500 MHz, CD_2Cl_2)**: δ (minor isomer, ~20%; selected resolved peaks only) 13.00 (1H, brs), 9.60 (1H, m), 9.00 (1H, m).

Mo(N-*t*-Bu)(CH-*t*-Bu)Cl_2(bipy) (bipy, 2,2'-bipyridine; 445 mg, 0.958 mmol) was suspended in Et_2O (50 mL) and then allowed to cool to –25 °C. The resulting suspension was treated slowly with a solution of lithium 2,6-bis(2,4,6-triisopropylphenyl)phenoxide (555 mg, 0.958 mmol) and $ZnCl_2$ (131 mg, 0.958 mmol) in THF (10 mL). After the mixture was allowed to stir at 22 °C for 4 h, it was passed through Celite and the volatiles were removed *in vacuo*, affording brown foam, which was washed with pentane (30 mL) and filtered through Celite to give a brown solution containing Mo(N-*t*-Bu)(CH-*t*-Bu)(OHIPT)(Cl) (OHIPT, 2,6-(2,4,6-triisopropylphenyl)phenoxide) and an unidentified alkylidyne by-products. 3-Bromopyridine (48 μL, 0.500 mmol) was added to this pentane solution and the mixture was allowed to stir for 1 h. The resulting slurry was concentrated to dryness *in vacuo*, affording a dark-colored heterogeneous material that was triturated with pentane (~2 mL). The solution was then allowed to cool to –25 °C and kept at this

temperature for 16 h. The resulting pale-green solid was collected by filtration and washed with cold pentane (~1 mL) to give **Mo-2** (661 mg, 0.709 mmol, 74% yield) as pale green solid. **^{1}H NMR (500 MHz, C_6D_6)**: δ 12.42 (1H, s), 8.30 (1H, d, J = 1.5 Hz) 7.42–7.34 (4H, m), 7.25 (1H, d, J = 5.0 Hz), 7.17–7.13 (2H, m), 7.02 (1H, dd, J = 7.4 Hz), 6.90 (1H, bd, J = 8.1 Hz), 6.49 (1H, dd, J = 8.0, 5.5 Hz), 3.97 (1H, m), 3.80 (1H, m), 3.19 (1H, m), 2.92 (2H, m), 2.81 (1H, m), 1.72 (3H, d, J = 6.4 Hz), 1.60 (3H, d, J = 6.3 Hz), 1.39–1.19 (21H, m), 1.15 (9H, s), 1.13 (2H, m), 1.02 (1H, d, J = 6.9 Hz), 1.01 (9H, s), 0.91 (3H, d, J = 6.4 Hz), 0.81 (3H, d, J = 6.5 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: δ 309.2, 162.4, 154.9, 150.6, 150.5, 149.5, 149.4, 147.9, 147.5, 147.2, 140.6, 137.7, 137.6, 132.5, 132.4, 131.5, 130.9, 130.7, 126.02, 125.98, 122.9, 122.8, 121.01, 120.95, 120.2, 119.9, 119.8, 118.4, 70.2, 45.5, 35.0, 34.5, 31.1, 31.0, 30.5, 30.3, 30.14, 30.10, 27.6, 27.5, 26.22, 26.16, 25.4, 25.2, 24.6, 24.3, 22.8, 22.6. Anal Calcd for $C_{50}H_{72}BrClMoN_2O$: C, 64.68; H, 7.82; N, 3.02. Found: C, 64.74; H, 7.80; N, 2.95.

Complex Mo-3c: Mo(N-*t*-Bu)(CH-*t*-Bu)Cl_2(bipy) (bipy, 2,2'-bipyridine; 425 mg, 0.915 mmol) was suspended in Et_2O (50 mL) and allowed to cool to –25 °C. The resulting suspension was treated slowly with a suspension of lithium 2,6-bis(2,4,6-triisopropylphenyl)phenoxide (529 mg, 0.915 mmol) and $ZnCl_2$ (124 mg, 0.915 mmol) in THF (10 mL). After the mixture was allowed to stir at 22 °C for 6 h, it was filtered through Celite and concentrated to give brown foam. This material was washed with pentane (30 mL) and filtered through Celite to give a pale brown solution containing Mo(N-*t*-Bu)(CH-*t*-Bu)(OHIPT)(Cl) (OHIPT, 2,6-(2,4,6-triisopropylphenyl)phenoxide) and unidentified alkylidyne byproducts. Acetonitrile (0.1 mL) was then added and the mixture was allowed to stir for 1 h. The resulting pink slurry was then concentrated to

dryness in vacuo, affording dark-colored heterogeneous material that was triturated with pentane (~2 mL). The solution was then allowed to cool to –25 °C and kept at this temperature for 16 h. The resulting off-white solid was collected by filtration and washed with cold pentane (~1 mL) to give **Mo-3c** (377 mg, 0.467 mmol, 51% yield) as off-white solid. **^{1}H NMR (500 MHz, C_6D_6)**: δ 12.28 (1H, s) 7.30 (2H, d, J = 7.5 Hz), 7.29–7.23 (4H, m), 6.99 (1H, dd, J = 7.4 Hz), 3.39 (4H, m), 2,93 (2H, sep, J = 6.9 Hz), 1.44 (6H, bd, J = 4.5 Hz), 1.40 (6H, bd, J = 6.7 Hz), 1.35 (12H, d, J = 6.9 Hz), 1.25 (6H, d, J = 6.9 Hz), 1.23 (6H, d, J = 6.9 Hz), 1.15 (9H, s), 1.10 (9H, s), 0.67 (3H, s); **^{13}C NMR (100 MHz, C_6D_6)**: δ 309.7, 161.2, 148.2, 148.0, 147.4, 136.3, 131.4, 131.4, 131.2, 121.0, 120.9, 119.2, 71.2, 44.8, 34.8, 31.0, 30.9, 30.5, 30.4, 26.12, 26.05, 24.63, 24.55, 24.3, 24.14, 24.05, 0.8. Anal Calcd for $C_{47}H_{71}ClMoN_2O$: C, 69.56; H, 8.82; N, 3.45. Found: C, 69.38; H, 8.82; N, 3.38.

3.6.4. Z-Selective Cross-Metathesis (CM) Reactions

General Procedure: In a N_2-filled glove box, an oven-dried 8 mL vial equipped with a magnetic stir bar was charged with alkene substrate and the corresponding organohalogen reagent (*Z*-1,1,1,4,4,4-hexafluoro-2-butene, *Z*-1,2-dichloroethene or 1,2-dibromoethene). A solution of **Mo-3a**, **Mo-3b** or **Mo-3c** in benzene was then added. The resulting mixture was allowed to stir for 15 min–12 h at 22 °C, after which the reaction was quenched by the addition of wet (undistilled) $CDCl_3$ (percent conversion was determined by ^{1}H NMR analysis of the unpurified mixture). Purification was performed through silica gel chromatography, preparative thin layer chromatography and/or Kugelrohr distillation.

(*Z*)-1-(2-Chlorovinyl)-4-methoxybenzene (3.3): Based on the general procedure, a solution of **Mo-3b** in benzene (0.1 M, 50 μL, 5.0 μmol) was transferred by syringe to an

oven-dried vial containing *Z*-1,2-dichloroethene (96.9 mg, 1.00 mmol) and *Z*-1-methoxy-4-(prop-1-enyl)benzene (14.8 mg, 0.100 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *Z*-1-methoxy-4-(prop-1-enyl)benzene. The resulting green oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **3.3** (13.5 mg, 0.0801 mmol, 80% yield) in >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those reported previously.[50]

(*Z*)-*t*-Butyl 5-(2-chlorovinyl)-1*H*-indole-1-carboxylate (3.5): Based on the general procedure, a solution of **Mo-3b** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (48.5 mg, 0.500 mmol) and (Z)-*t*-butyl 5-(prop-1-enyl)-1*H*-indole-1-carboxylate (12.9 mg, 0.0500 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was then quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-*t*-butyl 5-(prop-1-enyl)-1*H*-indole-1-carboxylate. The resulting green oil was purified by silica gel chromatography (1% EtOAc/hexanes to 2% EtOAc/hexanes) to afford **3.5** (11.5 mg, 0.0414 mmol, 83% yield) in >98:2 *Z*:*E* ratio as pale yellow oil. **IR (CH_2Cl_2)**: 2932 (w), 1731 (s), 1464 (m), 1368 (s), 1344 (s), 1327 (s), 1253 (s), 1160 (s), 1123 (s), 1081 (s), 1022 (s), 713 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 8.11 (1H, d, J = 8.6 Hz), 7.95 (1H, s), 7.62–7.56 (2H, m), 6.73 (1H, d, J = 8.2 Hz), 6.58 (1H, d, J = 3.7 Hz), 6.24 (1H, d, J = 8.1 Hz), 1.68 (9H, s); **^{13}C NMR**

(50) Lebrun, M.-V.; Marquand, P. L.; Berthelette, C. *J. Org. Chem.* **2006**, *71*, 2009–2013.

(100 MHz, $CDCl_3$): δ 148.7, 129.7, 128.9, 128.9, 126.7, 126.0, 121.9, 116.4, 115.0, 110.2, 107.7, 28.4; **HRMS [M+H]$^+$** calcd for $C_{15}H_{17}ClNO_2$: 278.0948, found: 278.0957

(1*E*,3*Z*)-4-Chlorobuta-1,3-dienyl)benzene (3.7): Based on the general procedure, a solution of **Mo-3b** in benzene (0.1 M, 50 μL, 5.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (96.9 mg, 1.00 mmol) and (1*E*,3*Z*)-penta-1,3-dienylbenzene (14.4 mg, 0.100 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet (undistilled) $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (1*E*,3*Z*)-penta-1,3-dienylbenzene. The resulting green oil was purified by silica gel chromatography (100% hexanes) to afford **3.7** (13.7 mg, 0.0832 mmol, 83% yield) in >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those reported previously.[50]

(1*Z*,9*Z*)-1,10-Dibromodeca-1,9-diene (3.11): In a N_2-filled glove box, a solution of **Mo-3a** in benzene (0.1 M, 100 μL, 10.0 μmol, 10 mol %) was transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (148.7 mg, 0.800 mmol) and *Z*-cyclooctene (11.0 mg, 0.100 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *Z*-cyclooctene. The resulting green oil was purified by silica gel chromatography (100% hexanes) to afford **3.11** (25.2 mg, 0.0851 mmol, 85% yield) in >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those reported previously.[51]

(*Z*)-Methyl 10-bromodec-9-enoate (3.13) & (*Z*)-1-bromodec-1-ene (3.14): Based on the general procedure, a solution of **Mo-3b** in benzene (0.1 M, 12 μL, 1.2 μmol) was

(51) López, S.; Fernández-Trillo, F.; Midón, P.; Castedo, L.; Saá, C. *J. Org. Chem.* **2005**, *70*, 6346–6352.

transferred by syringe to an oven-dried vial containing 1,2-dibromoethene (59.5 mg, 0.320 mmol) and *Z*-methyl oleate (11.9 mg, 0.0400 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 95% consumption of *Z*-methyl oleate. The resulting green oil was purified by silica gel chromatography (100% hexanes to 4% Et_2O/hexanes) to afford **3.13** (10.0 mg, 0.0380 mmol, 95% yield) in >98:2 *Z*:*E* ratio as colorless oil and **3.14** (7.5 mg, 0.0342 mmol, 85% yield) in >98:2 *Z*:*E* ratio as colorless oil. Spectral data for **3.13**: **IR (CH_2Cl_2)**: 2928 (m), 2856 (w), 1736 (s), 1436 (w), 1264 (m), 1170 (m), 732 (s); **^{1}H NMR (500 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.14 (1H, d, *J* = 6.9 Hz), 6.08 (1H, q, *J* = 6.9 Hz), 3.67 (3H, s), 2.30 (2H, t, *J* = 7.5 Hz), 2.18 (2H, dt, *J* = 7.6, 4.0 Hz), 1.61 (2H, dd, *J* = 14.2, 7.1 Hz), 1.43–1.38 (2H, m), 1.32 (6H, brs); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 174.4, 135.1, 107.8, 51.6, 34.2, 29.8, 29.2, 29.2, 29.0, 28.2, 25.1; **HRMS $[M+H]^+$** calcd for $C_{11}H_{20}BrO_2$: 263.0647, found: 263.0647. The spectral data for **3.14** were identical to those reported previously.[52]

(*Z*)-Methyl 11,11,11-trifluoro-9-undecenoate (3.16) & (*Z*)-1,1,1-trifluoro-2-undecene (3.17): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 8 μL, 0.8 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.8 mg, 0.200 mmol) and *Z*-methyl oleate (11.9 mg, 0.0400 mmol). The resulting solution was allowed to stir for 15 min at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *Z*-methyl oleate. The resulting green oil was purified by silica gel chromatography (100% pentane to 4% Et_2O/pentane) to afford **3.16** (9.6 mg, 0.0381

(52) Millar, J. G.; Underhill, E. W. *J. Org. Chem.* **1986**, *51*, 4726–4728.

mmol, 95% yield) in >98:2 *Z*:*E* ratio as colorless oil and **3.17** (5.6 mg, 0.0269 mmol, 67% yield) in >98:2 *Z*:*E* ratio as colorless oil. Spectral data for **3.16**: **IR (CH_2Cl_2)**: 2931 (w), 2859 (w), 1738 (m), 1669 (w), 1418 (w), 1162 (m), 1116 (s), 1092 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z*-isomer (major): δ 5.97 (1H, dt, J = 11.5, 7.9 Hz), 5.64–5.51 (1H, m), 3.67 (3H, s), 2.33–2.26 (4H, m), 1.67–1.58 (2H, m), 1.45–1.37 (2H, m), 1.34–1.29 (6H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 174.4, 143.2 (q, $J_{C\text{-}F}$ = 5.4 Hz), 123.5 (q, $J_{C\text{-}F}$ = 271.7 Hz), 118.5 (q, $J_{C\text{-}F}$ = 33.2 Hz), 51.6, 34.2, 29.1, 29.1, 29.0, 28.9, 28.4, 25.0; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.10 (3F, dt, J = 8.6, 2.3 Hz); **HRMS $[M+H]^+$** calcd for $C_{12}H_{20}F_3O_2$: 253.1415, found: 253.1412. The spectral data for **3.17** were identical to those reported previously.[53]

(*Z*)-1-Methoxy-4-((4,4,4-trifluorobut-2-enyloxy)methyl)benzene (3.22): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (41.0 mg, 0.250 mmol) and (*Z*)-1-methoxy-4-((pent-2-enyloxy)methyl)benzene (10.3 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 87% consumption of (*Z*)-1-methoxy-4-((pent-2-enyloxy)methyl)benzene. The resulting green oil was purified by silica gel chromatography (5% Et_2O/pentane to 10% Et_2O/pentane) to afford **3.22** (9.5 mg, 0.0386 mmol, 77% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 3004 (w), 2938 (w), 2839 (w), 1613 (m), 1513 (s), 1247 (s), 1117 (s), 1089 (s), 1035 (s), 820 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.27 (2H, d, J = 8.6 Hz), 6.89 (2H, d, J = 8.6 Hz), 6.17 (1H, dt, J = 11.8, 5.7 Hz),

(53) Fuchikami, T.; Urata, H. Jpn. Kokai Tokkyo Koho, JP 03218325, A 19910925, 1991.

5.75–5.61 (1H, m), 4.46 (2H, s), 4.29 (2H, td, J = 5.2, 2.5 Hz), 3.81 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.6, 140.2 (q, $J_{C\text{-}F}$ = 5.1 Hz), 129.6, 129.5, 125.7 (q, $J_{C\text{-}F}$ = 270.2 Hz), 118.8 (q, $J_{C\text{-}F}$ = 34.6 Hz), 114.0, 72.7, 65.9, 55.4; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –59.23 (3F, dt, J = 8.7, 2.6 Hz); **HRMS $[M-H]^+$** calcd for $C_{12}H_{12}F_3O_2$: 245.0789, found: 245.0804.

(*Z*)-5,5,5-Trifluoro-3-pentenyl 2-(benzyloxy)propanoate (3.23): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 8 μL, 0.8 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.8 mg, 0.200 mmol) and (*Z*)-3-hexenyl 2-(benzyloxy)propanoate (10.5 mg, 0.0400 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 73% consumption of (*Z*)-3-hexenyl 2-(benzyloxy)propanoate. The resulting green oil was purified by silica gel chromatography (4% Et_2O/pentane to 12% Et_2O/pentane) to afford **3.23** (8.5 mg, 0.0281 mmol, 70% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2919 (w), 1748 (m), 1672 (w), 1194 (m), 1118 (s), 1075 (m), 738 (w), 698 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.39–7.27 (5H, m), 6.01 (1H, dt, J = 11.6, 7.7 Hz), 5.79–5.67 (1H, m), 4.69 (1H, d, J = 11.6 Hz), 4.45 (1H, d, J = 11.7 Hz), 4.31–4.22 (2H, m), 4.06 (1H, q, J = 6.9 Hz), 2.74–2.65 (2H, m), 1.43 (3H, d, J = 6.9 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.43 (3F, dd, J = 8.5, 2.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.2, 138.0 (q, $J_{C\text{-}F}$ = 4.9 Hz), 137.6, 128.6, 128.1, 128.0, 125.8 (q, $J_{C\text{-}F}$ = 271.9 Hz), 121.1 (q, $J_{C\text{-}F}$ = 33.6 Hz), 74.1, 72.2, 63.0, 28.1, 18.8; **HRMS $[M+H]^+$** calcd for $C_{15}H_{18}F_3O_3$: 303.1208, found: 303.1200.

(*S*,*Z*)-1-*t*-Butyl 2-(5,5,5-trifluoropent-3-enyl) pyrrolidine-1,2-dicarboxylate (3.24): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 9 μL, 0.9 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (24.6 mg, 0.150 mmol) and **(*S*,*Z*)-1-*t*-butyl 2-hex-3-enyl pyrrolidine-1,2-dicarboxylate** (8.9 mg, 0.0299 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of **(*S*,*Z*)-1-*t*-butyl 2-hex-3-enyl pyrrolidine-1,2-dicarboxylate**. The resulting green oil was purified by silica gel chromatography (4% Et_2O/pentane to 20% Et_2O/pentane) to afford **3.24** (8.1 mg, 0.0240 mmol, 80% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2977 (w), 2931 (w), 1747 (m), 1694 (s), 1148 (s), 1118 (s), 735 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.02 (1H, ddd, J = 17.3, 13.9, 7.5 Hz), 5.79–5.64 (1H, m), 4.34–4.13 (3H, m), 3.59–3.33 (2H, m), 2.67 (2H, brs), 2.27–2.14 (1H, m), 2.01–1.81 (3H, m), 1.46 (3H, s), 1.41 (6H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.49 (3F, dd, J = 25.0, 8.4 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: mixture of two rotational isomers: δ 172.9, 172.7, 154.3, 153.5, 138.9 (q, $J_{C\text{-}F}$ = 5.5 Hz), 138.3 (q, $J_{C\text{-}F}$ = 5.1 Hz), 123.7 (q, $J_{C\text{-}F}$ = 271.2 Hz), 123.6 (q, $J_{C\text{-}F}$ = 270.3 Hz), 120.4 (q, $J_{C\text{-}F}$ = 33.3 Hz), 119.9 (q, $J_{C\text{-}F}$ = 33.2 Hz), 79.3, 79.3, 62.7, 62.6, 59.2, 59.2, 46.7, 46.6, 30.9, 29.8, 29.5, 28.4, 28.1, 28.0, 24.4, 23.5; **HRMS $[M+H]^+$** calcd for $C_{15}H_{23}F_3NO_4$: 338.1579, found: 338.1573.

(*Z*)-5,5,5-Trifluoro-3-pentenyl 4-methylbenzenesulfonate (3.25): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 8 μL, 0.8 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.9 mg, 0.201 mmol) and (*Z*)-3-hexenyl 4-methylbenzenesulfonate (10.2 mg, 0.0401 mmol). The

resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 82% consumption of (*Z*)-3-hexenyl 4-methylbenzenesulfonate. The resulting green oil was purified by silica gel chromatography (5% Et_2O/hexanes) to afford **3.25** (9.1 mg, 0.0309 mmol, 77% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 1672 (w), 1598 (w), 1360 (m), 1175 (s), 1117 (s), 913 (m), 661 (s), 552 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.79 (2H, d, J = 8.3 Hz), 7.36 (2H, d, J = 8.5 Hz), 5.96 (1H, dt, J = 11.7, 7.5 Hz), 5.75–5.64 (1H, m), 4.10 (2H, t, J = 6.3 Hz), 2.69–2.60 (2H, m), 2.46 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.2, 136.5 (q, $J_{C\text{-}F}$ = 5.4 Hz), 133.0, 130.1, 128.1, 123.0 (q, $J_{C\text{-}F}$ = 271.8 Hz), 121.5 (q, $J_{C\text{-}F}$ = 33.7 Hz), 68.5, 28.0, 21.8; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.73 (3F, d, J = 8.3 Hz); **HRMS $[M+NH_4]^+$** calcd for $C_{12}H_{17}F_3NO_3S$: 312.0881, found: 312.0887.

(*Z*)-Triisopropyl(3-(5,5,5-trifluoropent-3-enyloxy)prop-1-ynyl)silane (3.26): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 20 μL, 2.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.9 mg, 0.200 mmol) and (*Z*)-(3-(hex-3-enyloxy)prop-1-ynyl)triisopropylsilane (11.8 mg, 0.0401 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-(3-(hex-3-enyloxy)prop-1-ynyl)triisopropylsilane. The resulting green oil was purified by silica gel chromatography (1% Et_2O/hexanes to 2% Et_2O/hexanes) to afford **3.26** (11.0 mg, 0.0329 mmol, 82% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2944 (m), 2866 (m), 1670 (w), 1265 (m), 1123 (s), 1102 (s), 1071 (m), 882 (m), 736 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.10

(1H, dt, J = 11.5, 7.4 Hz), 5.72–5.60 (1H, m), 4.19 (2H, d, J = 0.6 Hz), 3.64 (2H, t, J = 6.3 Hz), 2.64–2.57 (2H, m), 1.07 (21H, brs); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.48 (3F, d, J = 21.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.6 (q, $J_{C\text{-}F}$ = 5.4 Hz), 126.1 (q, $J_{C\text{-}F}$ = 271.8 Hz), 119.9 (q, $J_{C\text{-}F}$ = 33.4 Hz), 103.2, 88.0, 68.0, 59.0, 28.9, 18.7, 11.3; **HRMS $[M+NH_4]^+$** calcd for $C_{17}H_{33}F_3NOSi$: 352.2284, found: 352.2285.

(*Z*)-*N*,*N*-Dibenzyl-5,5,5-trifluoropent-3-en-1-amine (3.27): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 12 μL, 1.2 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.9 mg, 0.200 mmol) and (*Z*)-*N*,*N*-dibenzylhex-3-en-1-amine (11.2 mg, 0.0401 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-*N*,*N*-dibenzylhex-3-en-1-amine. The resulting green oil was purified by silica gel chromatography (5% EtOAc/hexanes) to afford **3.27** (11.8 mg, 0.0369 mmol, 92% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 3028 (w), 2800 (w), 1669 (w), 1216 (m), 1113 (s), 743 (m), 697 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.44–7.17 (10H, m), 5.96 (1H, dt, J = 12.8, 6.4 Hz), 5.67–5.53 (1H, m), 3.57 (4H, s), 2.62–2.43 (4H, m); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.29 (3F, d, J = 8.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.4 (q, $J_{C\text{-}F}$ = 5.4 Hz), 139.6, 128.9, 128.4, 127.1, 123.5 (q, $J_{C\text{-}F}$ = 271.7 Hz), 118.9 (q, $J_{C\text{-}F}$ = 33.3 Hz), 58.2, 52.1, 26.1; **HRMS $[M+H]^+$** calcd for $C_{19}H_{21}F_3N$: 320.1626, found: 320.1638.

(*Z*)-Phenyl(5,5,5-trifluoropent-3-enyl)sulfane (3.28): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 18 μL, 1.9 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (49.0 mg, 0.299 mmol) and

(*Z*)-hex-3-enyl(phenyl)sulfane (11.5 mg, 0.0598 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-hex-3-enyl(phenyl)sulfane. The resulting green oil was purified by silica gel chromatography (100% pentane to 2% Et_2O/pentane) to afford **3.28** (9.6 mg, 0.0413 mmol, 69% yield) in 95:5 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 3059 (w), 2926 (w), 1671 (w), 1416 (w), 1241 (m), 1114 (s), 736 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.36 (2H, d, J = 7.9 Hz), 7.30 (2H, t, J = 7.6 Hz), 7.36 (1H, t, J = 7.2 Hz), 6.09 (1H, dt, J = 11.7, 7.6 Hz), 5.72–5.59 (1H, m), 3.00 (2H, t, J = 7.2 Hz), 2.67–2.58 (2H, m); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.46 (3F, dd, J = 8.6, 2.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.2 (q, $J_{C\text{-}F}$ = 5.4 Hz), 135.5, 130.0, 129.2, 125.4 (q, $J_{C\text{-}F}$ = 271.3 Hz), 126.7, 120.0 (q, $J_{C\text{-}F}$ = 33.6 Hz), 33.1, 27.9; **HRMS $[M+H]^+$** calcd for $C_{11}H_{12}F_3S$: 233.0612, found: 233.0613.

((1*E*,4*Z*)-6,6,6-Trifluoro-1,4-hexadienyl)benzene (3.29): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 19 μL, 1.9 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (51.8 mg, 0.316 mmol) and (1*E*,4*Z*)-1,4-hexadienylbenzene (10.0 mg, 0.0632 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 92% consumption of (1*E*,4*Z*)-1,4-hexadienylbenzene. The resulting green oil was purified by silica gel chromatography (100% pentane) to afford **3.29** (8.3 mg, 0.0391 mmol, 62% yield) in 97:3 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 3029 (w), 2960 (w), 1669 (w), 1415 (w), 1230 (m), 1197 (m), 1078 (s), 964 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.37–7.27 (4H, m), 7.25–7.21 (1H, m), 6.45 (1H, d, J = 15.8 Hz), 6.16 (1H, dt, J = 15.7, 6.7 Hz), 6.08 (1H,

dt, J = 11.6, 7.9 Hz), 5.76–5.63 (1H, m), 3.26–3.17 (2H, m); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.11 (3F, d, J = 8.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 140.1 (q, $J_{C\text{-}F}$ = 5.4 Hz), 137.2, 132.1, 128.7,127.6, 126.3, 126.1 (q, $J_{C\text{-}F}$ = 271.6 Hz), 125.9, 119.2 (q, $J_{C\text{-}F}$ = 33.5 Hz), 31.9; **HRMS $[M+H]^+$** calcd for $C_{12}H_{12}F_3$: 213.0891, found: 213.0885.

(*Z*)-4,4,5,5-Tetramethyl-2-(4,4,4-trifluoro-2-butenyl)-1,3,2-dioxaborolane (3.30): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 50 μL, 5.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (82.0 mg, 0.500 mmol) and *Z*-crotylboronic acid pinacol ester (18.2 mg, 0.100 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of *Z*-crotylboronic acid pinacol ester. The resulting green oil was purified by Kugelrohr distillation (50 °C, 1 torr, 15 min) to afford **3.30** (16.6 mg, 0.0703 mmol, 70% yield) in 97:3 *Z*:*E* ratio as colorless oil. **IR (in CH_2Cl_2)**: 2982 (m), 1666 (m), 1372 (m), 1328 (s), 1272 (m), 1242 (m), 1142 (s), 1110 (s), 965 (m), 846 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.16 (1H, dt, J = 11.5, 8.9 Hz), 5.63–5.50 (1H, m), 1.98 (2H, d, J = 8.2 Hz), 1.25 (12H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.32 (3F, dt, J = 8.4, 2.5 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.9 (d, $J_{C\text{-}F}$ = 5.6 Hz), 117.9 (q, $J_{C\text{-}F}$ = 33.0 Hz), 83.9, 24.8.

(*Z*)-Triethyl(4,4,4-trifluorobut-2-en-1-yl)silane (3.31): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (40.5 mg, 0.250 mmol) and (*Z*)-but-2-en-1-yltriethylsilane (8.5 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and

analysis of the unpurified mixture revealed >98% consumption of (*Z*)-but-2-en-1-yltriethylsilane. The resulting green oil was purified by silica gel chromatography (100% pentane) to afford an inseparable mixture of **3.31** and (*Z*)-1,4-bis(triethylsilyl)but-2-ene (8.6 mg, 82% wt, 0.0314 mmol, 62% yield) in 94:6 *Z*:*E* ratio as colorless oil. **IR (in $CDCl_3$)**: 2954 (w), 2877 (w), 1653 (w), 1416 (w), 1245 (m), 1185 (m), 1141 (m), 1116 (s), 1103 (s), 1012 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.04 (1H, dt, J = 11.6, 9.6 Hz), 5.49–5.35 (1H, m), 1.90–1.81 (2H, m), 1.00–0.89 (9H, m), 0.59 (6H, t, J = 8.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –57.58 (3F, dt, J = 8.7, 2.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.5 (q, $J_{C\text{-}F}$ = 5.8 Hz), 123.2, 115.1 (q, $J_{C\text{-}F}$ = 32.7 Hz), 16.7, 12.7, 7.6, 7.3, 3.5, 3.3.

(*Z*)-2,2-Dimethyl-7-(6,6,6-trifluorohex-4-enyloxy)-2,3-dihydrobenzofuran (3.32): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (41.0 mg, 0.250 mmol) and (*Z*)-7-(hex-4-enyloxy)-2,2-dimethyl-2,3-dihydrobenzofuran (12.3 mg, 0.0499 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-7-(hex-4-enyloxy)-2,2-dimethyl-2,3-dihydrobenzofuran. The resulting green oil was purified by silica gel chromatography (2% Et_2O/hexanes) to afford **3.32** (12.9 mg, 0.0430 mmol, 86% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2973 (w), 2930 (w), 1669 (w), 1593 (w), 1460 (w), 1241 (m), 1116 (s), 1077 (s), 876 (m), 756 (m), 721 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 6.82–6.69 (3H, m), 6.05 (1H, dtd, J = 11.6, 7.9, 0.9 Hz), 5.62 (1H, dddd, J = 11.6, 10.2, 8.5, 7.1 Hz), 4.12–4.03 (2H, m), 3.06–2.98 (2H, m), 2.54–2.43 (2H, m), 2.00–1.87 (2H,

m), 1.50 (6H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 148.0, 143.7, 142.2 (q, $J_{C\text{-}F}$ = 5.4 Hz), 128.7, 123.4 (q, $J_{C\text{-}F}$ = 271.7 Hz), 120.4, 119.1 (q, $J_{C\text{-}F}$ = 33.4 Hz), 117.9, 113.4, 87.4, 68.4, 43.5, 28.6, 28.4, 25.2; **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.18 (3F, dt, J = 8.5, 2.1 Hz); **HRMS $[M+NH_4]^+$** calcd for $C_{16}H_{20}F_3O_2$: 301.1415, found: 301.1423.

(*Z*)-6,6,6-Trifluoro-4-hexenyl ferrocenecarboxylate (3.33): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 12 μL, 1.2 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.8 mg, 0.200 mmol) and (*Z*)-4-hexenyl ferrocenecarboxylate (12.5 mg, 0.0400 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-4-hexenyl ferrocenecarboxylate. The resulting reddish-brown oil was purified by silica gel chromatography (2% EtOAc/hexanes to 5% EtOAc/hexanes) to afford **3.33** (14.4 mg, 0.0393 mmol, 98% yield) in >98:2 *Z*:*E* ratio as red oil. **IR (CH_2Cl_2)**: 2955 (w), 2923 (w), 1707 (s), 1670 (w), 1458 (m), 1277 (s), 1116 (s), 1085 (s), 821 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.06 (1H, dt, J = 11.5, 7.9 Hz), 5.74–5.62 (1H, m), 4.84–4.77 (2H, m), 4.43–4.37 (2H, m), 4.24 (2H, t, J = 6.4 Hz), 4.22–4.17 (5H, m), 2.54–2.45 (2H, m), 1.93–1.83 (2H, m); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.13 (3F, d, J = 8.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.8, 141.7 (q, $J_{C\text{-}F}$ = 5.4 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.1 Hz), 119.5 (q, $J_{C\text{-}F}$ = 33.5 Hz), 71.5, 70.2, 69.9, 63.3, 28.4, 25.3; **HRMS $[M+H]^+$** calcd for $C_{17}H_{18}F_3FeO_2$: 367.0608, found: 367.0618.

(*Z*)-*t*-Butyl 3-(2-oxo-2-(5,5,5-trifluoro-3-pentenyloxy)ethyl)-1*H*-indole-1-carboxylate (3.34): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 9 μL, 0.9 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-

hexafluoro-2-butene (24.6 mg, 0.150 mmol) and (*Z*)-*t*-butyl 3-(2-(3-hexenyloxy)-2-oxoethyl)-1*H*-indole-1-carboxylate (10.7 mg, 0.0299 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-*t*-butyl 3-(2-(3-hexenyloxy)-2-oxoethyl)-1*H*-indole-1-carboxylate. The resulting green oil was purified by silica gel chromatography (10% Et_2O/hexanes to 15% Et_2O/hexanes) to afford **3.34** (10.5 mg, 0.0264 mmol, 88% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2979 (w), 2932 (w), 1730 (s), 1452 (m), 1366 (s), 1254 (s), 1117 (s), 1077 (s), 1016 (s), 744 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 8.14 (1H, d, J = 7.1 Hz), 7.56 (1H, s), 7.52 (1H, J = 7.8 Hz), 7.33 (1H, ddd, J = 8.4, 7.3, 1.3 Hz), 7.27–7.23 (1H, m), 5.93 (1H, dt, J = 11.7, 7.7 Hz), 5.71–5.59 (1H, m), 4.21 (2H, t, J = 6.3 Hz), 3.72 (2H, d, J = 1.0 Hz), 2.69–2.60 (2H, m), 1.67 (9H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.45 (3F, d, J = 8.3 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.0, 149.7, 138.0 (q, $J_{C\text{-}F}$ = 5.4 Hz), 130.2, 120.9 (q, $J_{C\text{-}F}$ = 33.6 Hz), 124.7, 124.6, 124.5, 122.8, 121.8, 119.1, 115.4, 113.0, 83.8, 63.2, 31.2, 28.3, 28.0; **HRMS $[M+NH_4]^+$** calcd for $C_{20}H_{26}F_3N_2O_4$: 415.1845, found: 415.1838.

(*R*,*Z*)-*t*-Butyldiphenyl(5,5,5-trifluoro-2-methylpent-3-enyloxy)silane (3.35): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 20 μL, 2.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (65.4 mg, 0.399 mmol) and (*R*,*Z*)-*t*-butyl(2-methylpent-3-enyloxy)diphenylsilane (13.5 mg, 0.0399 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*R*,*Z*)-*t*-butyl(2-methylpent-3-enyloxy)diphenylsilane.

The resulting green oil was purified by preparative thin layer chromatography (100% hexanes) to afford **3.35** (13.3 mg, 0.0339 mmol, 85% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2932 (w), 2859 (w), 1670 (w), 1428 (w), 1224 (w), 1166 (m), 1112 (s), 1081 (s), 701 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.68–7.62 (4H, m), 7.46–7.35 (6H, m), 5.98 (1H, dd, J = 11.6, 10.9 Hz), 5.60 (1H, dq, J = 11.6, 8.8 Hz), 3.61–3.50 (2H, m), 3.06–2.95 (1H, m), 1.05 (12H, brs); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –57.89 (3F, dd, J = 8.4, 1.2 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.8 (q, $J_{C\text{-}F}$ = 5.4 Hz), 135.8, 135.7, 133.7, 129.8, 127.8, 118.3 (q, $J_{C\text{-}F}$ = 33.7 Hz), 67.9, 36.1, 26.9, 19.4, 16.9; **HRMS $[M+H]^+$** calcd for $C_{22}H_{28}F_3OSi$: 393.1862, found: 393.1853.

(*Z*)-*t*-Butyl 4-(3,3,3-trifluoroprop-1-enyl)piperidine-1-carboxylate (3.36): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 20 μL, 2.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (65.5 mg, 0.399 mmol) and (*Z*)-*t*-butyl 4-(prop-1-enyl)piperidine-1-carboxylate (9.0 mg, 0.0399 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-*t*-butyl 4-(prop-1-enyl)piperidine-1-carboxylate. The resulting green oil was purified by silica gel chromatography (1.5% Et_2O/hexanes) to afford **3.36** (9.8 mg, 0.0351 mmol, 88% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2935 (w), 2856 (w), 1690 (s), 1422 (m), 1168 (s), 1108 (s), 962 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 5.78 (1H, dd, J = 11.5, 10.5 Hz), 5.62–5.51 (1H, m), 4.21–4.04 (2H, m), 2.82–2.65 (3H, m), 1.68–1.60 (2H, m), 1.46 (9H, s), 1.35–1.24 (2H, m); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –57.97 (3F, d, J = 8.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 154.9, 146.1 (q, $J_{C\text{-}F}$ = 5.3 Hz), 123.4 (q, $J_{C\text{-}F}$ = 272.0 Hz), 117.9 (q, $J_{C\text{-}F}$ = 33.7

Hz), 79.7, 36.1, 31.4, 28.6, 28.6; **HRMS [M+H]$^+$** calcd for $C_{13}H_{21}F_3NO_2$: 280.1524, found: 280.1522.

(*Z*)-1-Methoxy-4-(3,3,3-trifluoroprop-1-enyl)benzene (3.37): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (81.9 mg, 0.499 mmol) and (*Z*)-1-methoxy-4-(3-methylbut-1-enyl)benzene (8.8 mg, 0.0499 mmol). The resulting solution was allowed to stir for 12 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 89% consumption of (*Z*)-1-methoxy-4-(3-methylbut-1-enyl)benzene. The resulting green oil was purified by preparative thin layer chromatography (5% EtOAc/hexanes) to afford **3.37** (6.0 mg, 0.0297 mmol, 59% yield) in >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those reported previously.[54]

(*Z*)-5-(3,3,3-Trifluoroprop-1-enyl)benzo[*b*]thiophene (3.38): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (81.9 mg, 0.499 mmol) and (*Z*)-5-(3-methylbut-1-enyl)benzo[*b*]thiophene (10.1 mg, 0.0499 mmol). The resulting solution was allowed to stir for 12 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 90% consumption of (*Z*)-5-(3-methylbut-1-enyl)benzo[*b*]thiophene. The resulting green oil was purified by preparative thin layer chromatography (100% hexanes) to afford **3.38** (7.0 mg, 0.0307 mmol, 61% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2924 (w), 2851 (w), 1650 (w), 1438 (w), 1202 (m), 1145 (m), 1113 (s), 740 (m), 694 (s); **^{1}H**

(54) Zhang, X.-G.; Chen, M.-W.; Zhong, P.; Hu, M.-L. *J. Fluorine Chem.* **2008**, *129*, 335–342.

NMR (400 MHz, $CDCl_3$): *Z* isomer (major): δ 7.89–7.86 (2H, m), 7.48 (1H, d, J = 5.5 Hz), 7.39 (1H, d, J = 8.4 Hz), 7.36 (1H, d, J = 5.5 Hz), 7.05 (1H, d, J = 12.6 Hz), 5.80 (1H, dq, J = 12.9, 9.1 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –57.44 (3F, d, J = 9.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.9 (q, $J_{C\text{-}F}$ = 5.7 Hz), 139.7, 130.0, 127.5, 125.8 (q, $J_{C\text{-}F}$ = 272.1 Hz), 125.0 (q, $J_{C\text{-}F}$ = 2.7 Hz), 124.5 (dd, $J_{C\text{-}F}$ = 5.1, 2.6 Hz), 124.2, 122.5, 117.9 (q, $J_{C\text{-}F}$ = 34.9 Hz), 100.6; **HRMS [M+H]$^+$** calcd for $C_{11}H_8F_3S$: 229.0299, found: 229.0303.

***t*-Butyl (*Z*)-5-(3,3,3-trifluoroprop-1-en-1-yl)-1*H*-indole-1-carboxylate (3.39):** Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 20 μL, 2.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (65.6 mg, 0.400 mmol) and *t*-butyl (*Z*)-5-(3-methylbut-1-en-1-yl)-1*H*-indole-1-carboxylate (11.4 mg, 0.0400 mmol). The resulting solution was allowed to stir for 12 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 92% consumption of *t*-butyl (*Z*)-5-(3-methylbut-1-en-1-yl)-1*H*-indole-1-carboxylate. The resulting green oil was purified by preparative thin layer chromatography (5% EtOAc/hexanes) to afford **3.39** (8.0 mg, 0.0257 mmol, 64% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2981 (w), 1733 (s), 1649 (m), 1471 (m), 1368 (m), 1334 (m), 1136 (s), 1109 (s), 1082 (s), 1022 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 8.12 (1H, d, J = 8.7 Hz), 7.64 (1H, s), 7.62 (1H, d, J = 3.7 Hz), 7.39–7.34 (1H, m), 7.02 (1H, d, J = 12.6 Hz), 6.59 (1H, dt, J = 3.7, 0.9 Hz), 5.74 (1H, dqd, J = 12.6, 9.2, 0.8 Hz), 1.68 (9H, s); **^{19}F NMR (376 MHz, $CDCl_3$)** δ –57.40 (3F, d, J = 9.2 Hz); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 149.7, 140.3 (q, $J_{C\text{-}F}$ = 5.8 Hz), 135.5, 130.7, 128.3, 126.9, 125.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 124.1, 122.3, 122.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 116.9

(q, $J_{C\text{-}F}$ = 34.9 Hz), 115.1, 84.2, 28.3; **HRMS [M+H]$^+$** calcd for $C_{16}H_{17}F_3NO_2$: 312.1211, found: 312.1208.

(*Z*)-2-(5,5,5-Trifluoro-3-pentenyl)isoindoline-1,3-dione (3.41): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 12 μL, 1.2 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.9 mg, 0.201 mmol), (*Z*)-2-(3-hexenyl)isoindoline-1,3-dione (9.2 mg, 0.0401 mmol) and toluene (80 μL). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-2-(3-hexenyl)isoindoline-1,3-dione. The resulting green oil was purified by silica gel chromatography (5% EtOAc/hexanes) to afford **3.41** (8.4 mg, 0.0312 mmol, 78% yield) in >98:2 *Z*:*E* ratio as colorless oil. The spectral data for this compound were identical to those reported previously.[55]

(*Z*)-Methyl 2-methoxy-4-(3,3,3-trifluoroprop-1-enyl)benzoate (3.45): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 30 μL, 3.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (49.0 mg, 0.299 mmol) and (*Z*)-methyl 2-methoxy-4-(3-methylbut-1-enyl)benzoate (7.0 mg, 0.0299 mmol). The resulting solution was allowed to stir for 12 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 82% consumption of (*Z*)-methyl 2-methoxy-4-(3-methylbut-1-enyl)benzoate. The resulting green oil was purified by silica gel chromatography (5% EtOAc/hexanes to 10% EtOAc/hexanes) to afford **3.45** (4.1 mg, 0.0158 mmol, 53% yield) in >98:2 *Z*:*E* ratio

(55) Mizuta, S.; Verhoog, S.; Engle, K. M.; Khotavivattana, T.; O'Duill, M.; Wheelhouse, K.; Rassias, G.; Médebielle, M.; Gouverneur, V. *J. Am. Chem. Soc.* **2013**, *135*, 2505–2508.

as colorless oil. **IR (CH_2Cl_2)**: 2923 (w), 2852 (w), 1729 (m), 1609 (w), 1410 (w), 1254 (m), 1216 (m), 1113 (s), 1083 (s), 1033 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.79 (1H, d, J = 8.0 Hz), 7.01 (1H, s), 6.98 (1H, d, J = 8.1 Hz), 6.94 (1H, d, J = 12.7 Hz), 5.93–5.80 (1H, m), 3.92 (3H, s), 3.90 (3H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –57.45 (3F, d, J = 8.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.3, 159.0, 138.9, 138.8 (q, $J_{C\text{-}F}$ = 5.4 Hz), 120.8 (q, $J_{C\text{-}F}$ = 2.1 Hz), 120.5, 120.0 (q, $J_{C\text{-}F}$ = 35.0 Hz), 119.8 (q, $J_{C\text{-}F}$ = 279.4 Hz), 112.4 (q, $J_{C\text{-}F}$ = 2.9 Hz), 56.2, 52.3; **HRMS [M+H]$^+$** calcd for $C_{12}H_{12}F_3O_3$: 261.0739, found: 261.0736.

(*Z*)-*t*-Butyl 4-(*t*-butyldimethylsilyloxy)-3-methoxybenzyl(8,8,8-trifluorooct-6-enoyl)carbamate (3.48): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (49.2 mg, 0.300 mmol) and (*Z*)-*t*-butyl 4-(*t*-butyldimethylsilyloxy)-3-methoxybenzyl(8-methylnon-6-enoyl)carbamate (15.6 mg, 0.0300 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-*t*-butyl 4-(*t*-butyldimethylsilyloxy)-3-methoxybenzyl(8-methylnon-6-enoyl)carbamate. The resulting green oil was purified by silica gel chromatography (2% EtOAc/hexanes to 4% EtOAc/hexanes) to afford **3.48** (14.1 mg, 0.0258 mmol, 86% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2932 (w), 2858 (w), 1733 (m), 1693 (m), 1513 (m), 1368 (m), 1274 (m), 1234 (m), 1147 (s), 1119 (s), 898 (m), 839 (m), 781 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.76 (2H, d, J = 8.1 Hz), 6.73–6.66 (1H, m), 5.98 (1H, dt, J = 11.5, 7.8 Hz), 5.66–5.50 (1H, m), 4.79 (2H, s), 3.76 (3H, s), 2.90 (2H, t, J = 7.3 Hz), 2.36–2.27 (2H, m), 1.75–1.64

(2H, m), 1.52–1.44 (2H, m), 1.42 (9H, s), 0.98 (9H, s), 0.13 (6H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.12 (3F, dt, J = 8.5, 2.1 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: δ 176.0, 153.3, 150.9, 144.3, 142.8 (q, $J_{C\text{-}F}$ = 5.1 Hz), 132.0, 120.7, 120.4, 118.9, 118.6, 112.0, 83.2, 55.6, 47.3, 38.1, 28.6, 28.3, 28.1, 25.9, 24.8, 18.6, –4.5; **HRMS $[M+H]^+$** calcd for $C_{27}H_{43}F_3NO_5Si$: 546.2863, found: 546.2891.

(2*S*,4*R*)-*t*-Butyl 2-((*t*-butyldimethylsilyloxy)methyl)-4-((*Z*)-3,3,3-trifluoroprop-1-enyl)pyrrolidine-1-carboxylate (3.51): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 15 μL, 1.5 μmol,) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (49.4 mg, 0.301 mmol) and (2*S*,4*R*)-*t*-butyl 2-((*t*-butyldimethylsilyloxy)methyl)-4-((*Z*)-prop-1-enyl)pyrrolidine-1-carboxylate (10.7 mg, 0.0301 mmol). The resulting solution was allowed to stir for 4 hours at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (2*S*,4*R*)-*t*-butyl 2-((*t*-butyldimethylsilyloxy)methyl)-4-((*Z*)-prop-1-enyl)pyrrolidine-1-carboxylate. The resulting green oil was purified by silica gel chromatography (1% EtOAc/hexanes to 4% EtOAc/hexanes) to afford **3.51** (10.4 mg, 0.0254 mmol, 84% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2929 (w), 2858 (w), 1733 (m), 1399 (m), 1252 (m), 1152 (m), 1120 (s), 1089 (m), 836 (m), 737 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 5.88 (1H, dd, J = 11.5, 10.3 Hz), 5.65 (1H, dq, J = 11.9, 8.4 Hz), 4.01–3.60 (4H, m), 3.22 (1H, dd, J = 18.1, 9.3 Hz), 2.92 (1H, t, J = 10.3 Hz), 2.29–2.12 (1H, m), 1.96–1.80 (1H, m), 1.46 (9H, s), 0.88 (9H, s), 0.04 (6H, d, J = 3.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –57.04 (3F, d, J = 8.3 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: δ 153.8, 143.2, 121.0 (q, $J_{C\text{-}F}$ =

271.6 Hz), 119.2 (q, $J_{C\text{-}F}$ = 32.3 Hz), 79.0, 63.1, 58.9, 53.0, 37.1, 34.4, 30.2, 28.5, 26.1, 18.4, –5.2, –5.3; **HRMS [M+H]$^+$** calcd for $C_{19}H_{35}F_3NO_3Si$: 410.2338, found: 410.2340.

(*Z*)-5,5,5-Trifluoropent-3-enyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (3.53): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 20 μL, 2.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (32.8 mg, 0.200 mmol) and (*Z*)-hex-3-enyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide (12.6 mg, 0.0400 mmol). The resulting solution was allowed to stir for 2 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 86% consumption of (*Z*)-hex-3-enyl (2*S*,5*R*)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide. The resulting green oil was purified by silica gel chromatography (20% EtOAc/hexanes to 30% EtOAc/hexanes) to afford **3.53** (11.8 mg, 0.0332 mmol, 83% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 1793 (m), 1754 (m), 1672 (w), 1320 (m), 1188 (m), 1149 (m), 1115 (s), 1075 (m), 732 (m), 550 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.99 (1H, dt, J = 11.7, 7.7 Hz), 5.85–5.72 (1H, m), 4.60 (1H, dd, J = 4.0, 2.3 Hz), 4.38 (1H, s), 4.31 (2H, t, J = 6.3 Hz), 3.47 (2H, dd, J = 5.0, 3.2 Hz), 2.78–2.67 (2H, m), 1.60 (3H, s), 1.41 (3H, s); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.49 (3F, dt, J = 8.3, 1.9 Hz); **^{13}C NMR (100 MHz, C_6D_6)**: δ 170.8, 167.0, 137.2 (q, $J_{C\text{-}F}$ = 5.3 Hz), 124.3, 121.8 (q, $J_{C\text{-}F}$ = 33.7 Hz), 64.7, 63.4, 62.8, 61.2, 38.5, 27.8, 20.5, 18.7; **HRMS [M+H]$^+$** found for $C_{13}H_{17}F_3NO_5S$: 356.0789.

(*Z*)-5,5,5-Trifluoropent-3-en-1-yl 2-((*Z*)-5-((*E*)-2-methyl-3-phenylallylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetate (3.54): Based on the general procedure, a solution of **Mo-**

3c in benzene (0.1 M, 10 μL, 1.0 μmol, 5 mol %) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (16.2 mg, 0.100 mmol) and (*Z*)-pent-3-en-1-yl 2-((*Z*)-5-((*E*)-2-methyl-3-phenylallylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetate (8.0 mg, 0.0200 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-pent-3-en-1-yl 2-((*Z*)-5-((*E*)-2-methyl-3-phenylallylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetate. The resulting green oil was purified by silica gel chromatography (10% Et_2O/pentane to 20% Et_2O/pentane) to afford **3.54** (8.1 mg, 0.0183 mmol, 92% yield) in >98:2 *Z*:*E* ratio as yellow oil. **IR (in CH_2Cl_2)**: 2964 (w), 2930 (w), 1751 (m), 1726 (m), 1327 (s), 1194 (s), 1148 (s), 1119 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.57 (1H, d, J = 1.0 Hz), 7.45–7.32 (5H, m), 7.09 (1H, s), 6.00 (1H, dt, J = 11.7, 7.6 Hz), 5.74 (1H, dtdd, J = 11.7, 8.4, 6.7, 1.8 Hz), 4.86 (2H, s), 4.27 (2H, t, J = 6.3 Hz), 2.68 (2H dtq, J = 10.4, 6.3, 2.1 Hz), 2.26 (3H, d, J = 1.3 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ –58.41 (3F, d, J = 8.2 Hz); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 193.3, 167.3, 166.0, 144.4, 142.4, 140.3, 137.6, 136.1, 133.4, 129.8, 129.7, 128.9, 128.8, 128.7, 121.3 (q, $J_{C\text{-}F}$ = 33.5 Hz), 64.1, 44.8, 27.8, 16.3; **HRMS $[M+H]^+$** calcd for $C_{20}H_{19}F_3NO_3S_2$: 442.0758, found: 442.0757.

Artesunate (*Z*)-5,5,5-trifluoropent-3-enyl ester (3.55): Based on the general procedure, a solution of **Mo-3c** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,1,1,4,4,4-hexafluoro-2-butene (49.2 mg, 0.150 mmol), artesunate (*Z*)-hex-3-enyl ester (14.0 mg, 0.0300 mmol) and toluene (45 μL). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 86% consumption

of artesunate (*Z*)-hex-3-enyl ester. The resulting green oil was purified by silica gel chromatography (10% EtOAc/hexanes to 20% EtOAc/hexanes) to afford **3.55** (12.3 mg, 0.0243 mmol, 81% yield) in >98:2 *Z*:*E* ratio as colorless oil. **IR (CH_2Cl_2)**: 2928 (w), 2876 (w), 1738 (s), 1217 (m), 1145 (s), 1119 (s), 1009 (s), 876 (m), 734 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 6.03 (1H, dt, J = 11.7, 7.7 Hz), 5.79 (1H, d, J = 9.9 Hz), 5.77–5.67 (1H, m), 5.43 (1H, s), 4.18 (2H, t, J = 6.4 Hz), 2.76–2.53 (8H, m), 2.38 (1H, ddd, J = 14.5, 13.4, 4.0 Hz), 2.03 (1H, ddd, J = 14.7, 4.6, 3.0 Hz), 1.93–1.85 (1H, m), 1.80–1.69 (2H, m), 1.62 (1H, dt, J = 13.9, 4.4 Hz), 1.43 (3H, s), 1.39–1.25 (4H, m), 0.96 (3H, d, J = 6.0 Hz), 0.85 (3H, d, J = 7.1 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ –58.46 (3F, dt, J = 8.5, 1.8 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 172.1, 171.2, 138.1 (q, $J_{C\text{-}F}$ = 5.2 Hz), 124.5, 120.9 (q, $J_{C\text{-}F}$ = 33.5 Hz), 104.6, 92.4, 91.7, 80.3, 63.0, 51.7, 45.4, 37.4, 36.4, 34.2, 32.0, 29.3, 29.0, 27.9, 26.1, 24.7, 22.2, 20.4, 12.2; **HRMS $[M+NH_4]^+$** calcd for $C_{24}H_{37}F_3NO_8$: 524.2471, found: 524.2476.

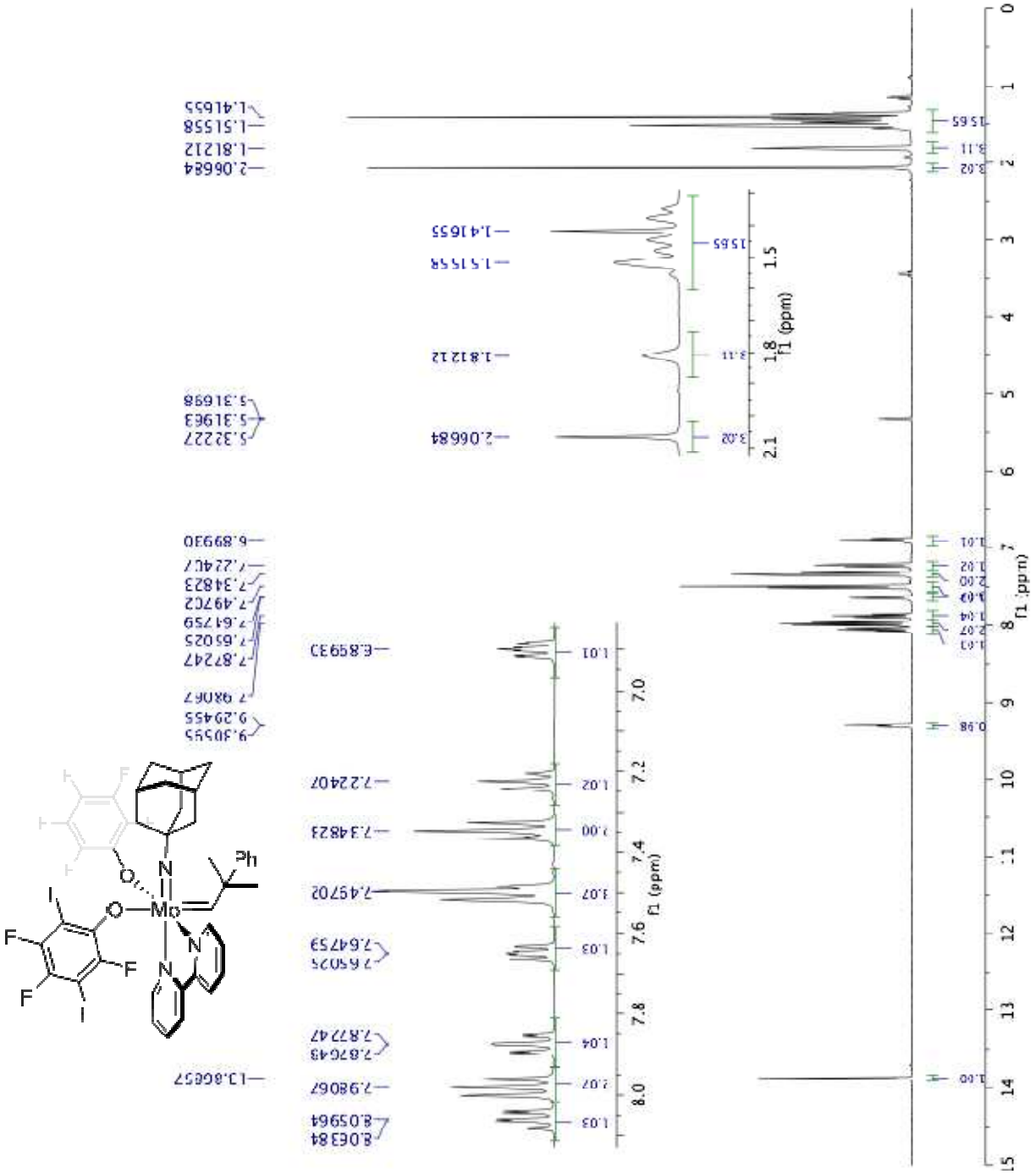
3.6.5. Z-Selective CM with Air- and Moisture-Resistant Paraffin Tablets

Representative Procedure: An oven-dried 8 mL vial equipped with a magnetic stir bar was charged with a paraffin tablet (9 wt% in **Mo-3c**, 20.0 mg, 2.2 μmol) and (*S*,*Z*)-1-*t*-butyl 2-hex-3-enyl pyrrolidine-1,2-dicarboxylate (22.0 mg, 0.0740 mmol). The vial was sealed with a septum, then evacuated and back-filled with N_2 three times to remove oxygen. *Z*-1,1,1,4,4,4-Hexafluoro-2-butene (43 μL, 0.370 mmol) and toluene (74 μL) were added by syringe and the resulting mixture was allowed to stir at 35 °C for 2 h under N_2. The reaction was quenched by addition of MeCN (1.5 mL) and the mixture was allowed to stir at 22 °C for 10 min. The slurry was filtered through a short plug of silica gel and eluted with MeCN (2 mL). The filtrate was concentrated and analysis of the

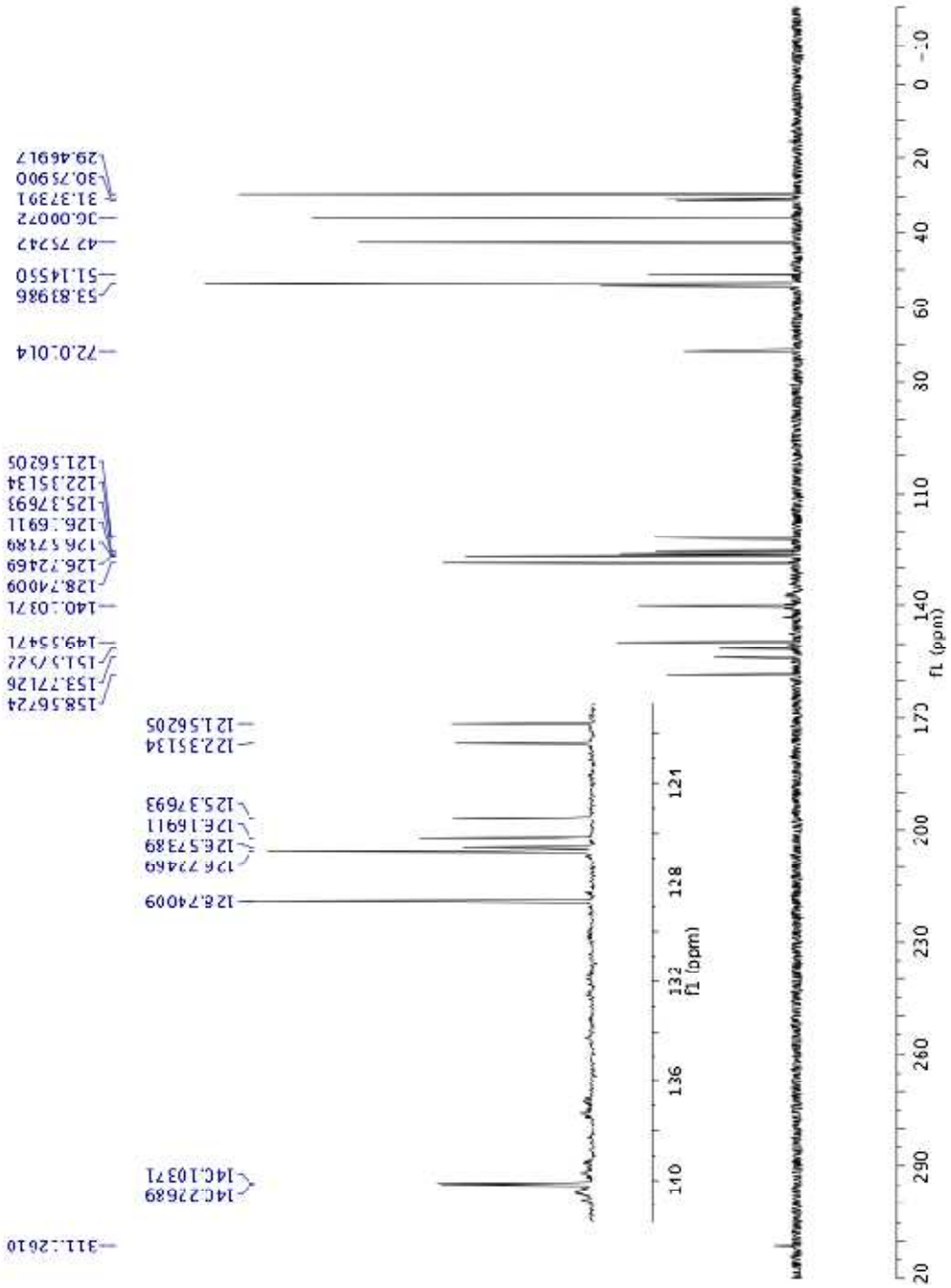
unpurified mixture revealed 98% consumption of (*S*,*Z*)-1-*t*-butyl 2-hex-3-enyl pyrrolidine-1,2-dicarboxylate. The resulting green oil was purified by silica gel chromatography (4% Et_2O/pentane to 20% Et_2O/pentane) to afford **3.24** (18.5 mg, 0.0548 mmol, 74% yield) in >98:2 *Z*:*E* ratio as colorless oil.

3.6.6. NMR Spectra

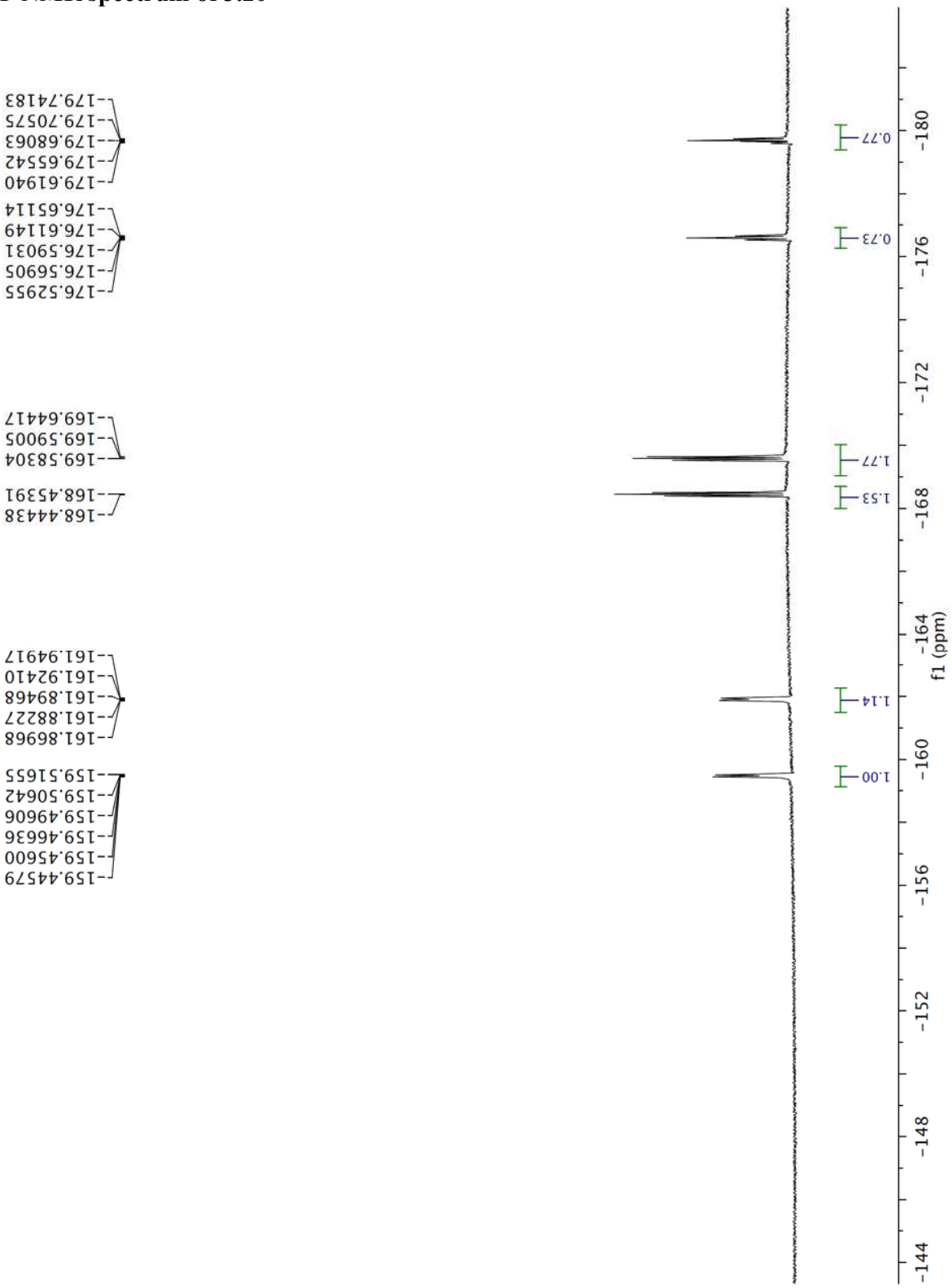
^{1}H NMR spectrum of 3.20



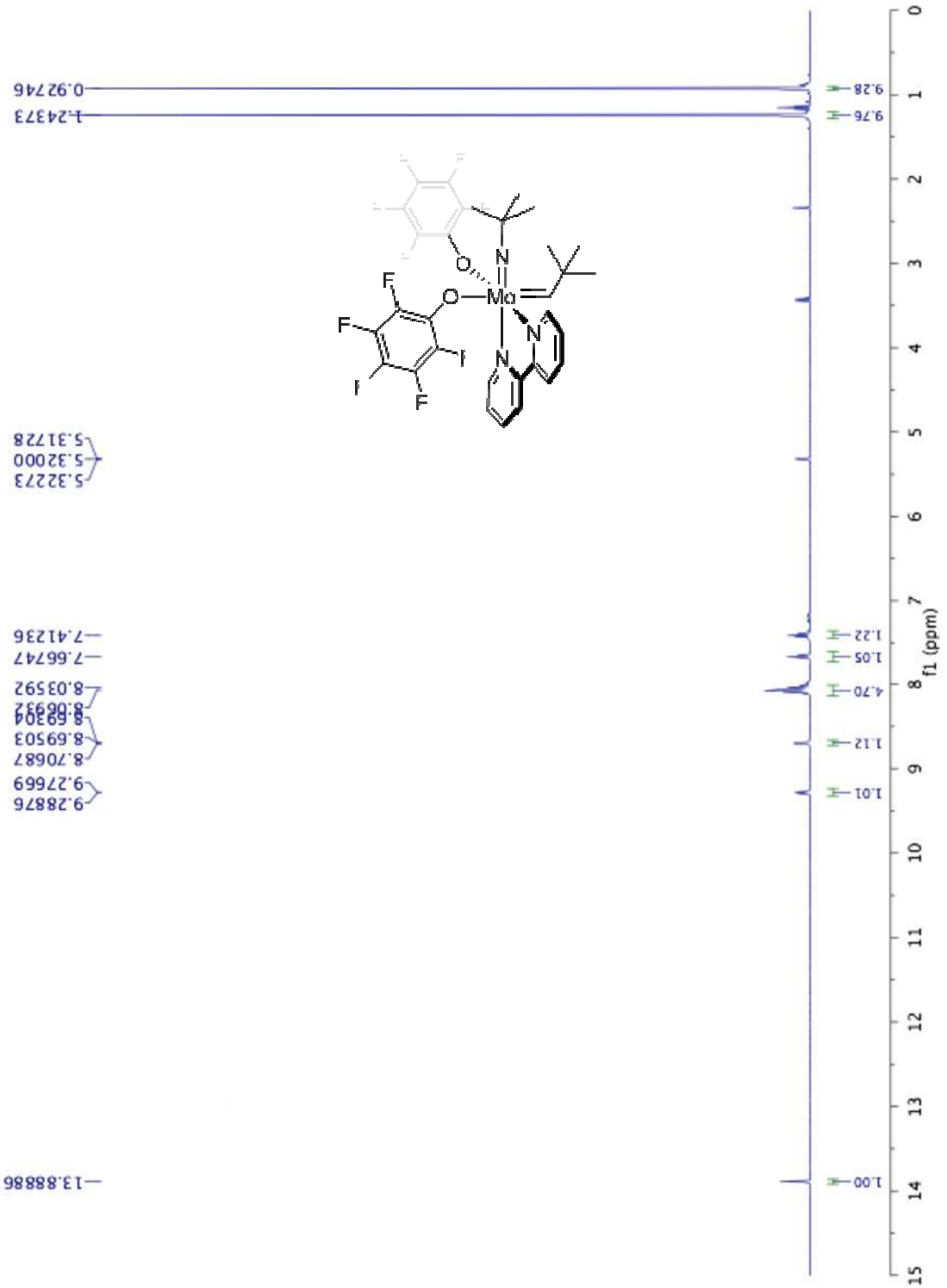
^{13}C NMR spectrum of 3.20



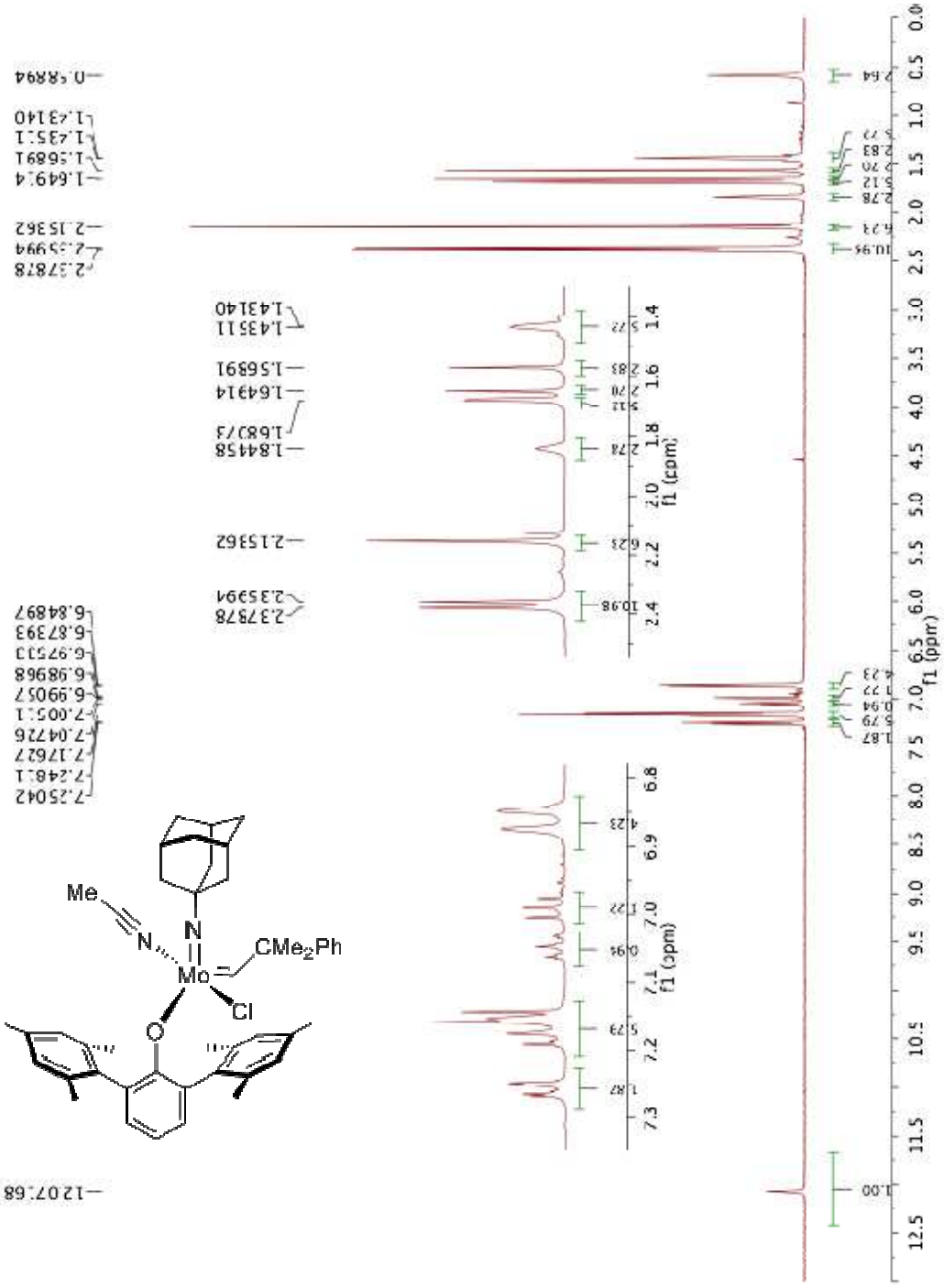
^{19}F NMR spectrum of 3.20



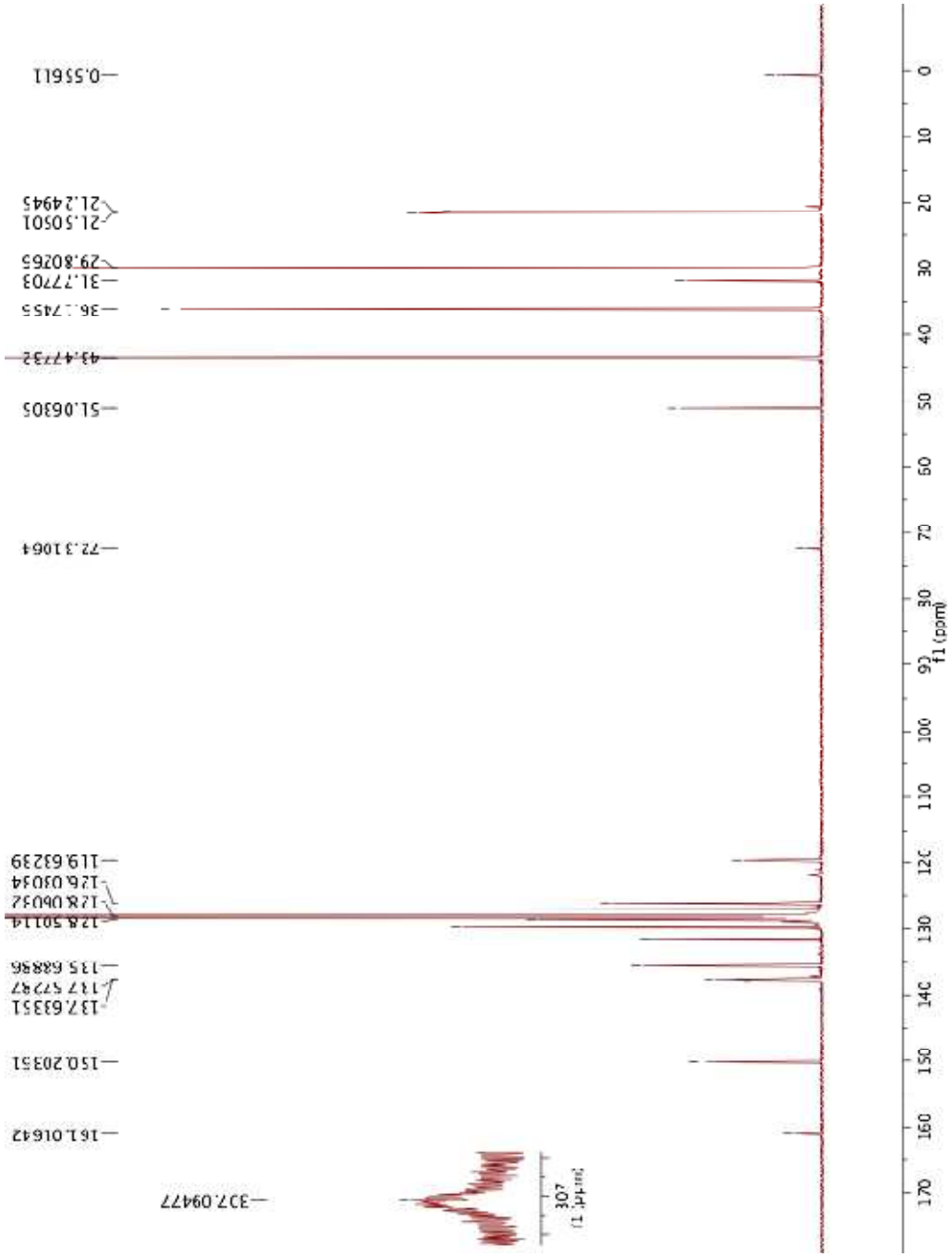
^{1}H NMR spectrum of 3.56



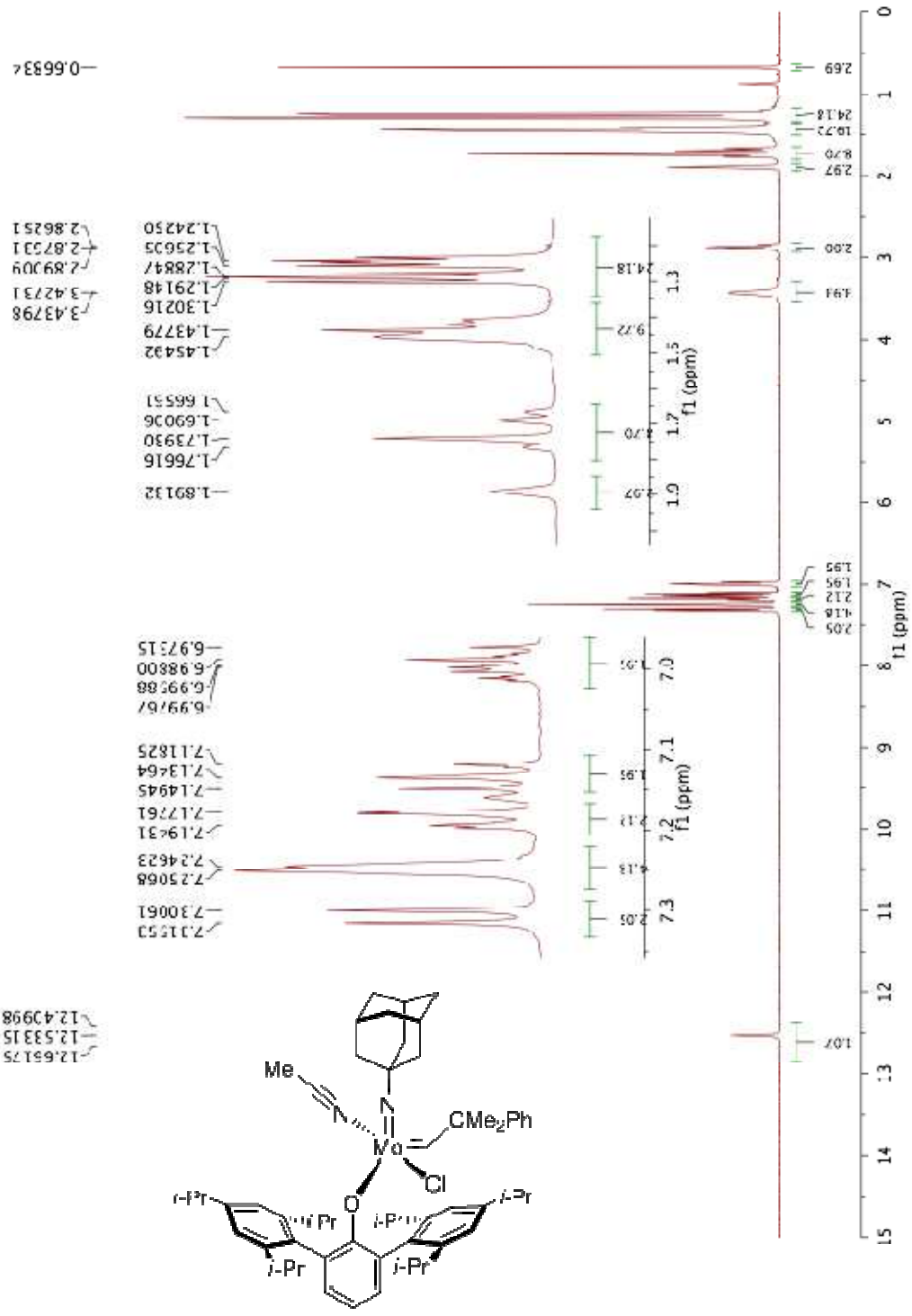
^{1}H NMR spectrum of Mo-3a



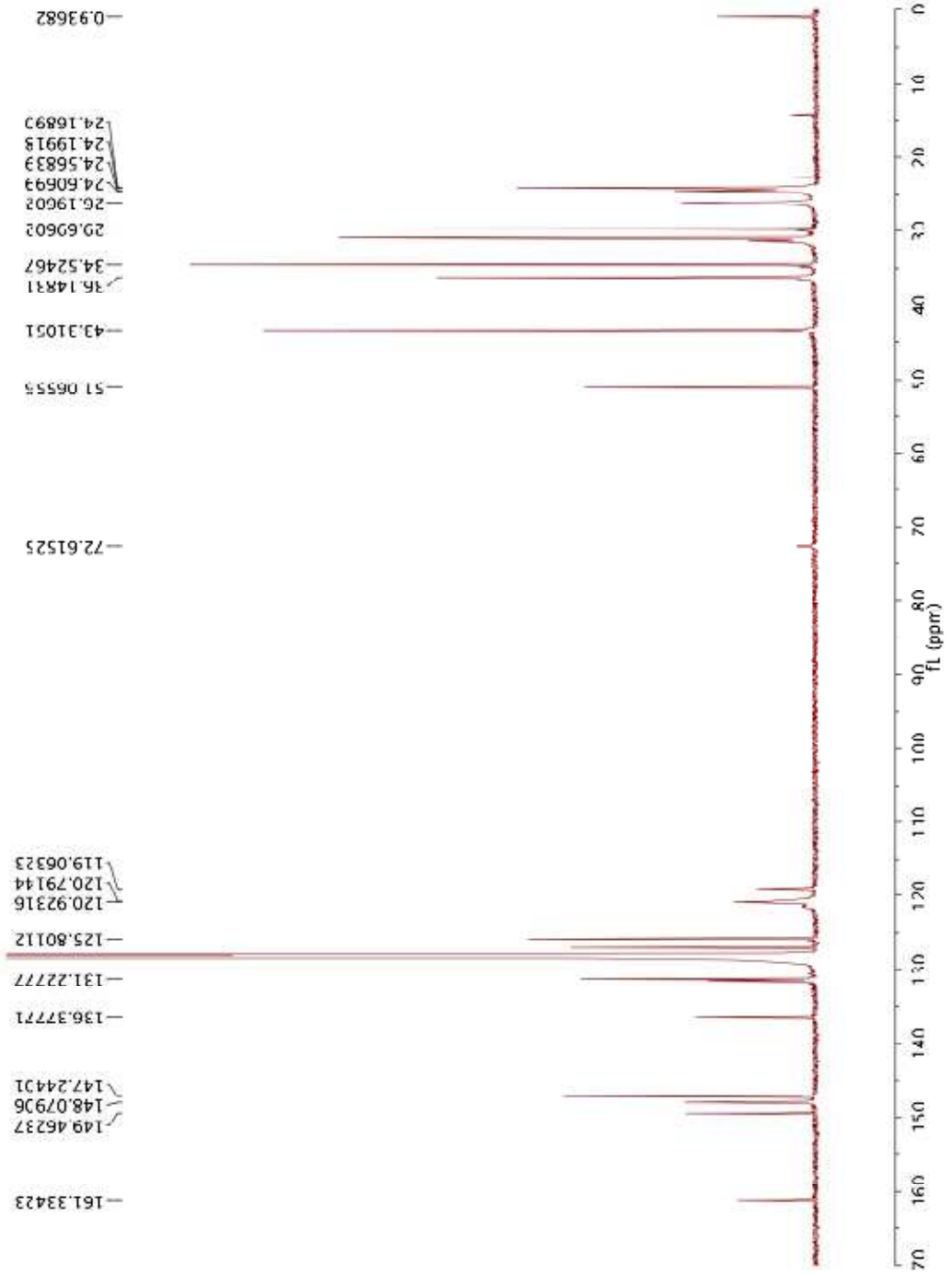
^{13}C NMR spectrum of Mo-3a



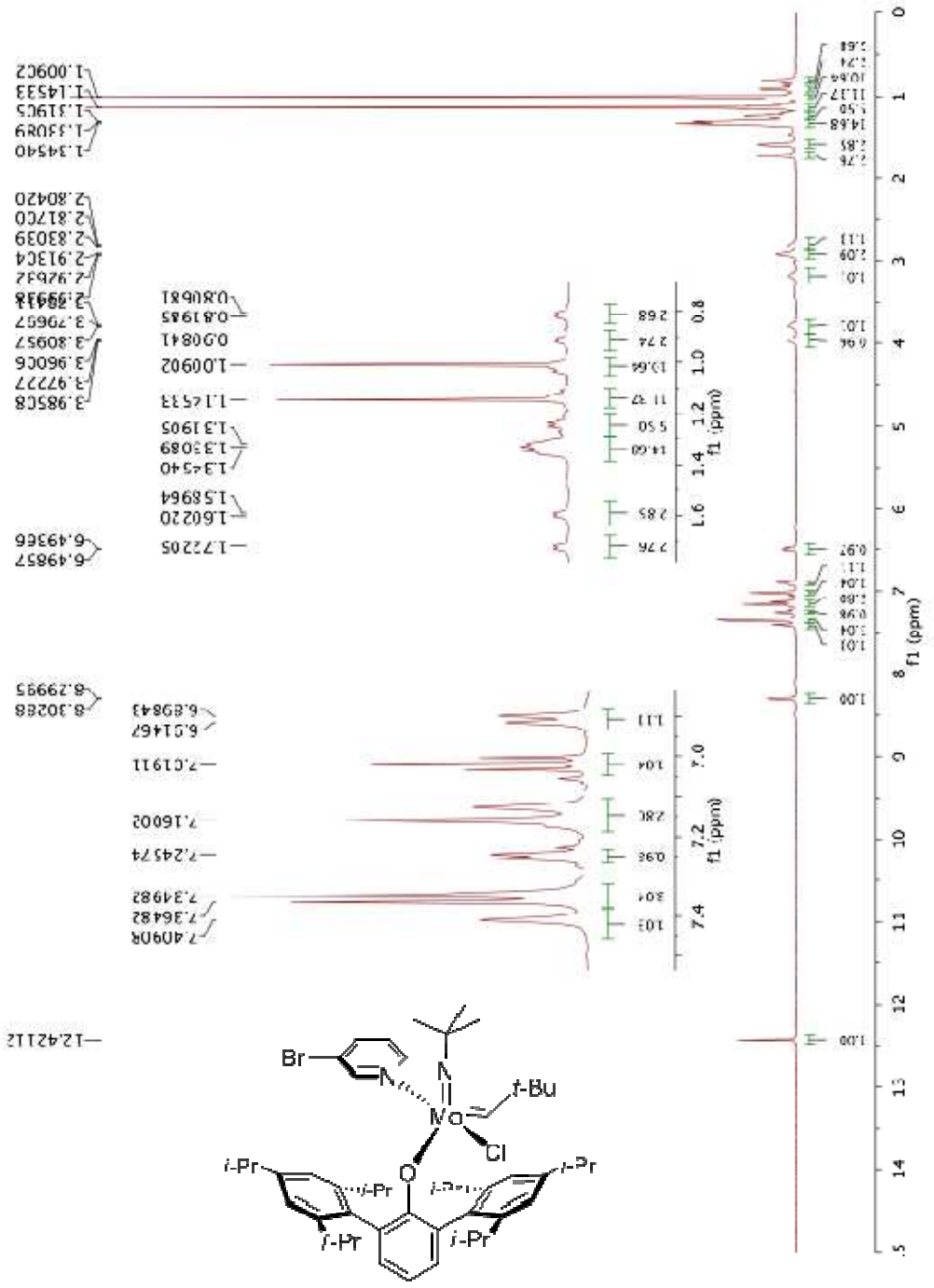
^{1}H NMR spectrum of Mo-3b



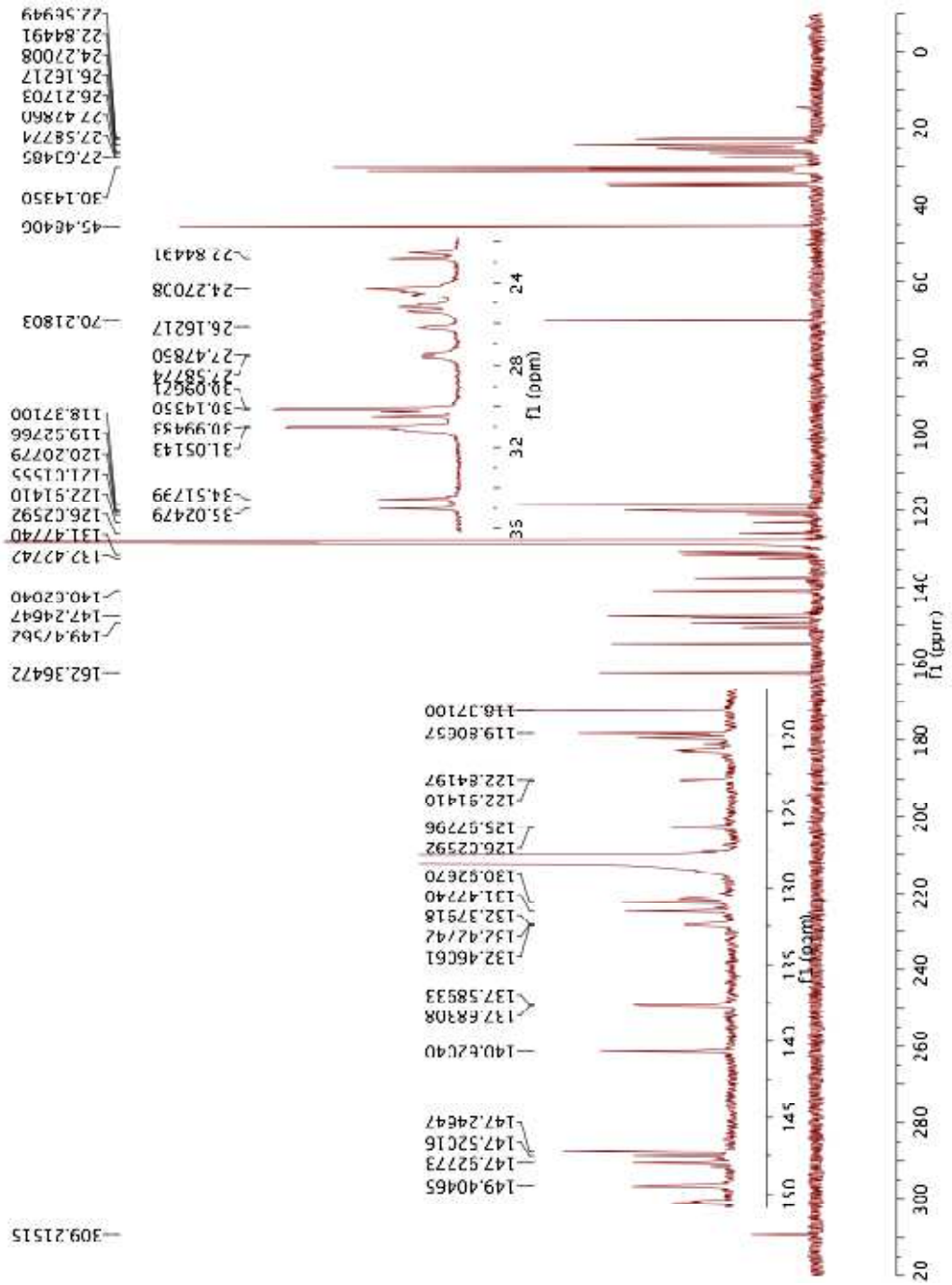
^{13}C NMR spectrum of Mo-3b



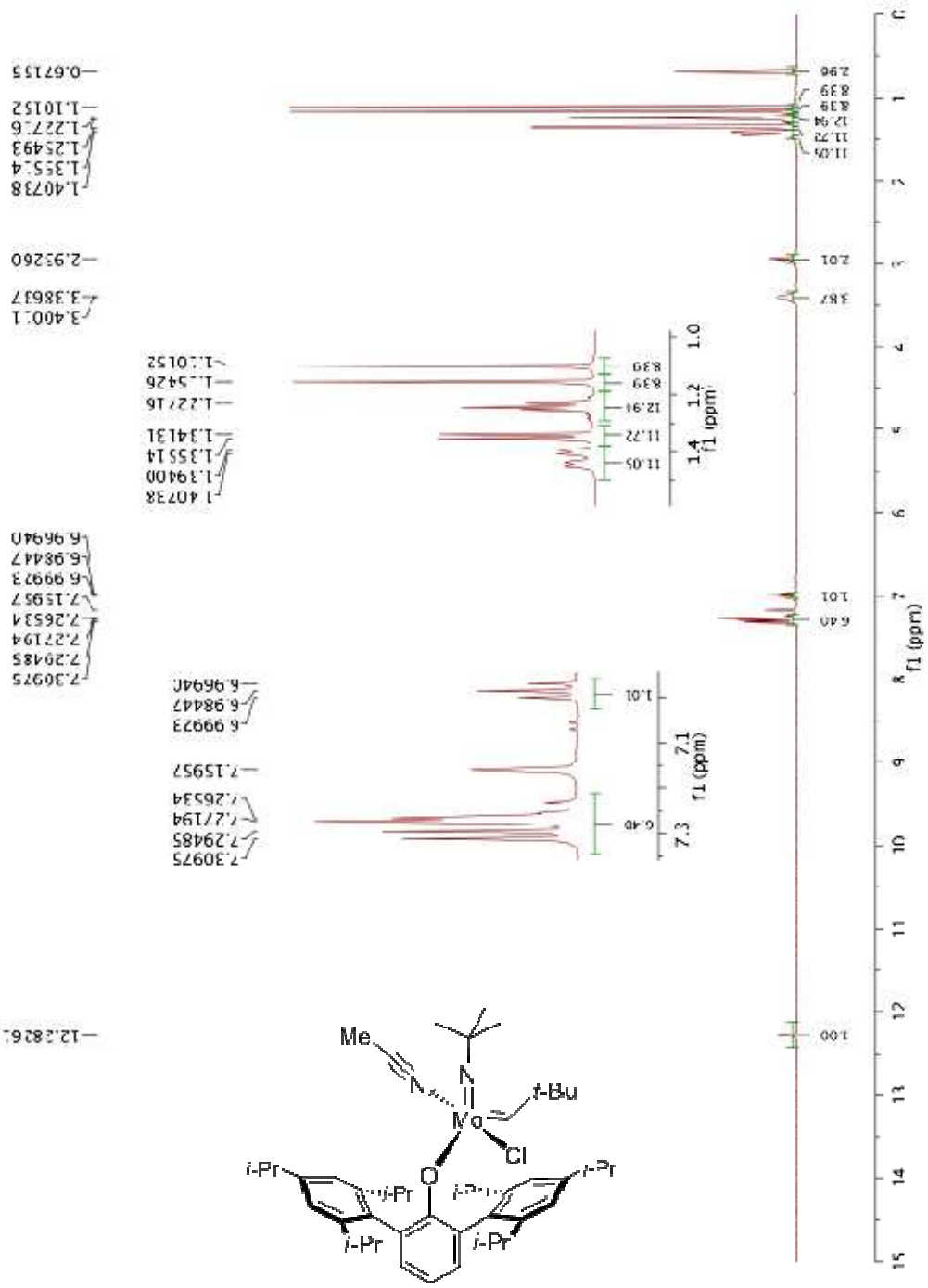
^{1}H NMR spectrum of Mo-2



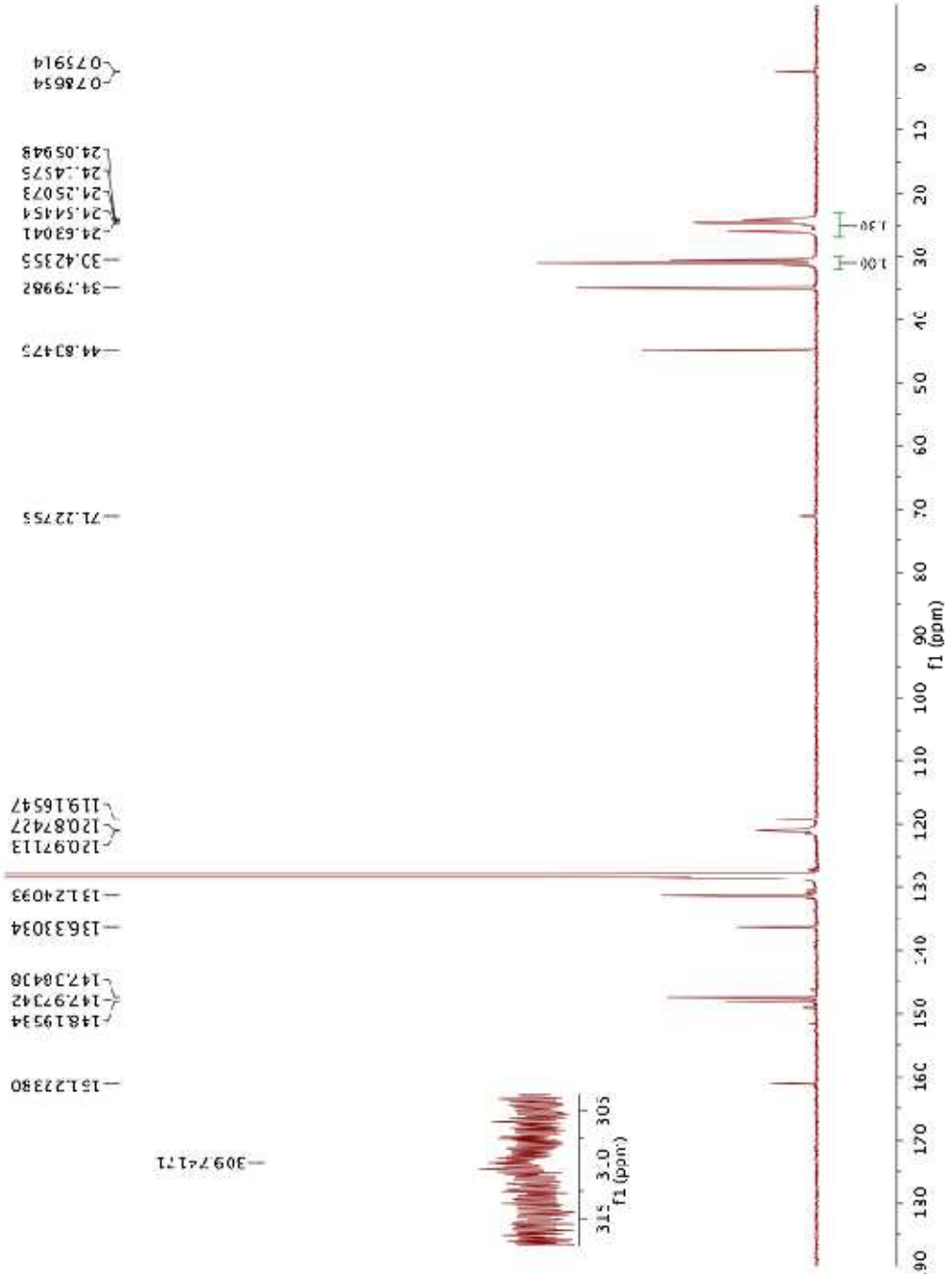
^{13}C NMR spectrum of Mo-2



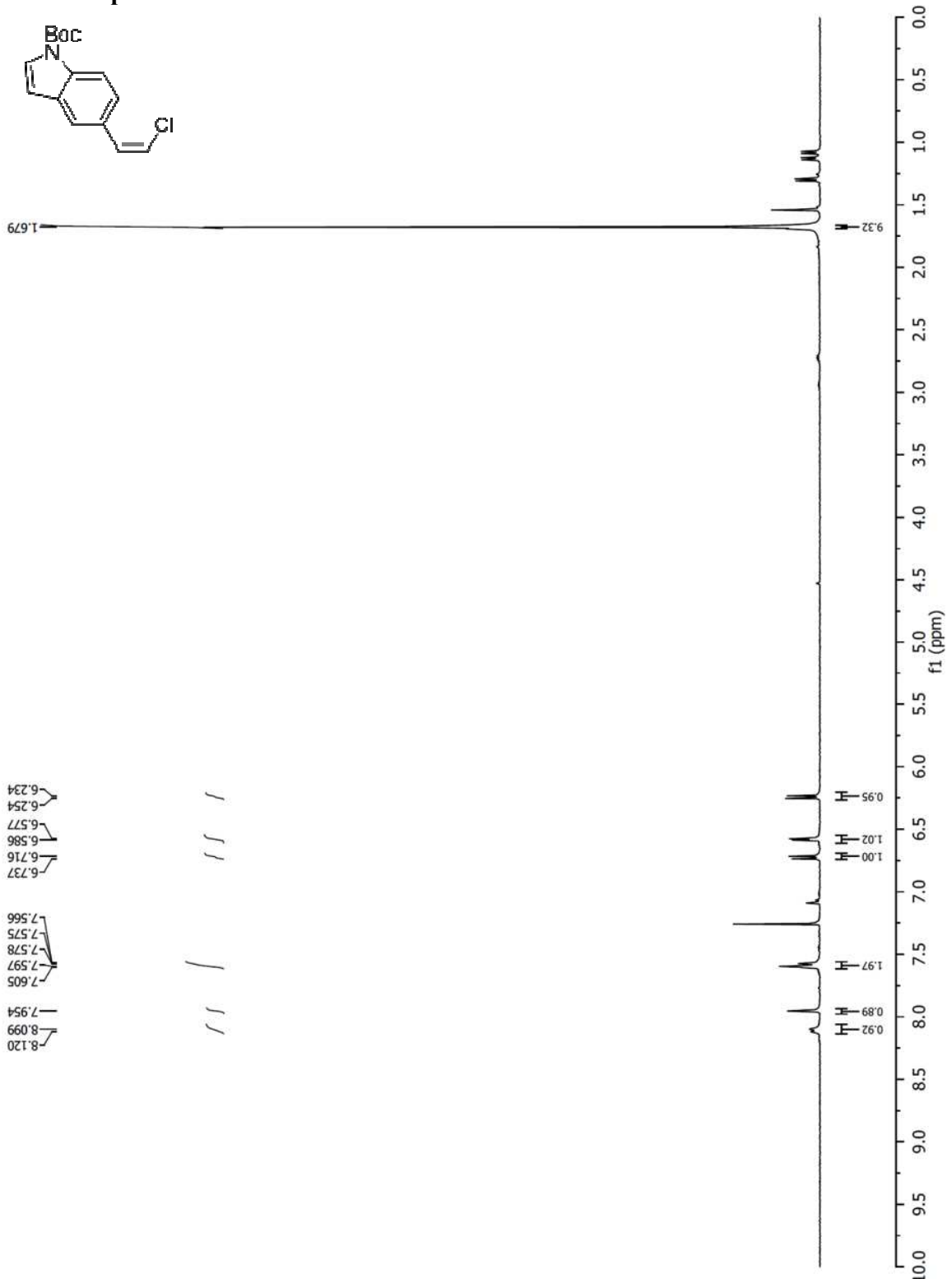
^{1}H NMR spectrum of Mo-3c



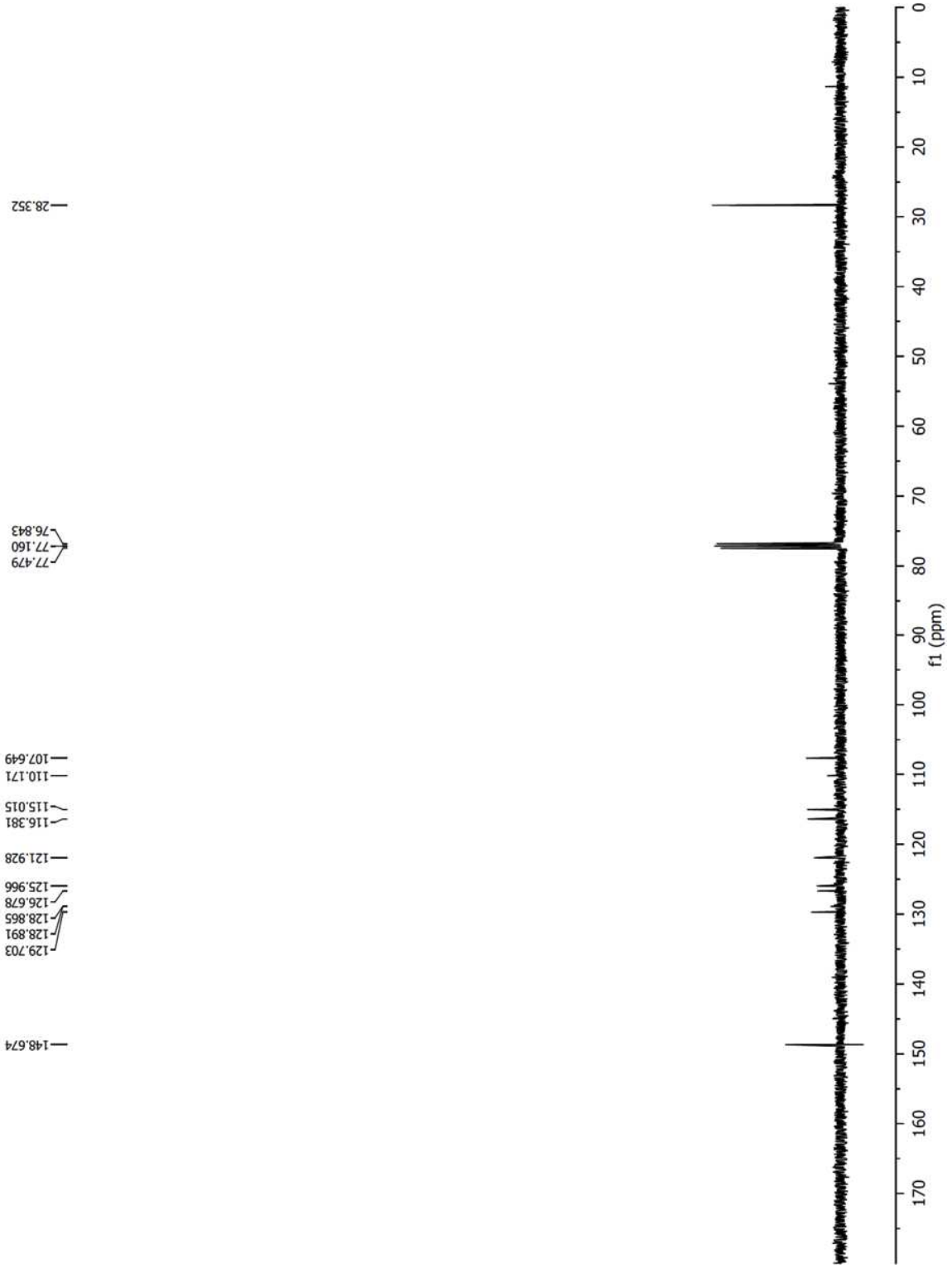
^{13}C NMR spectrum of Mo-3c



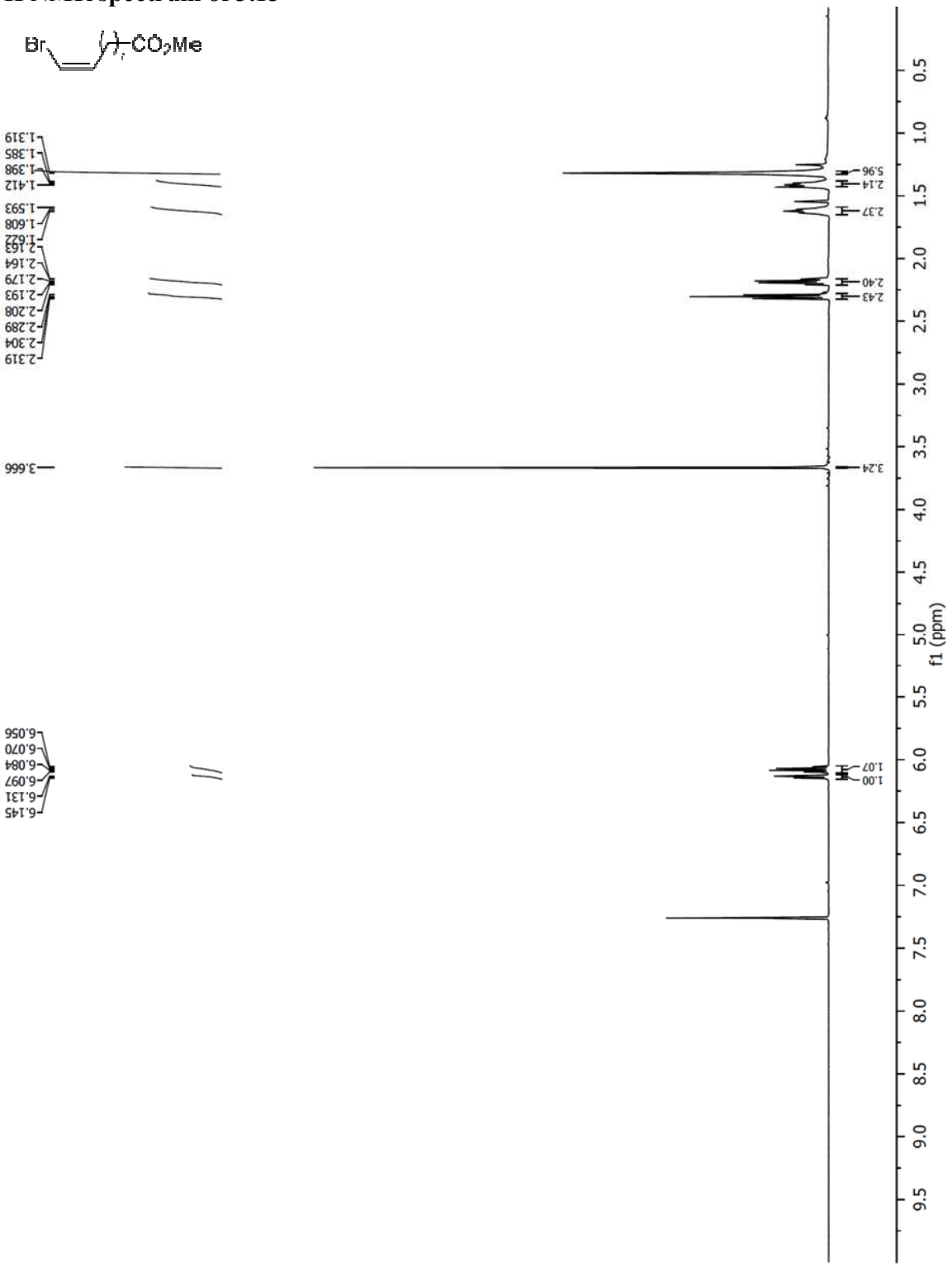
^{1}H NMR spectrum of 3.5



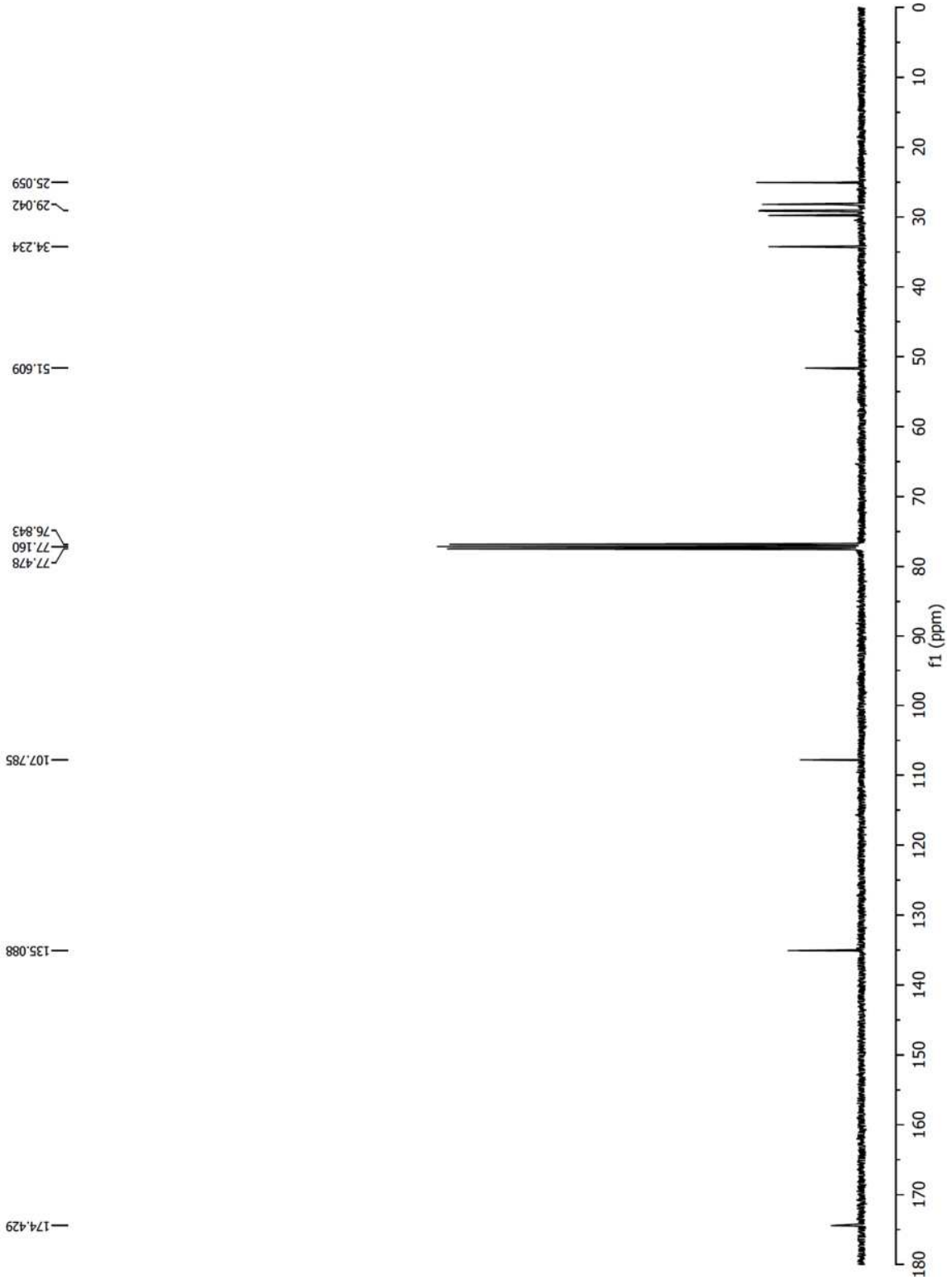
^{13}C NMR spectrum of 3.5



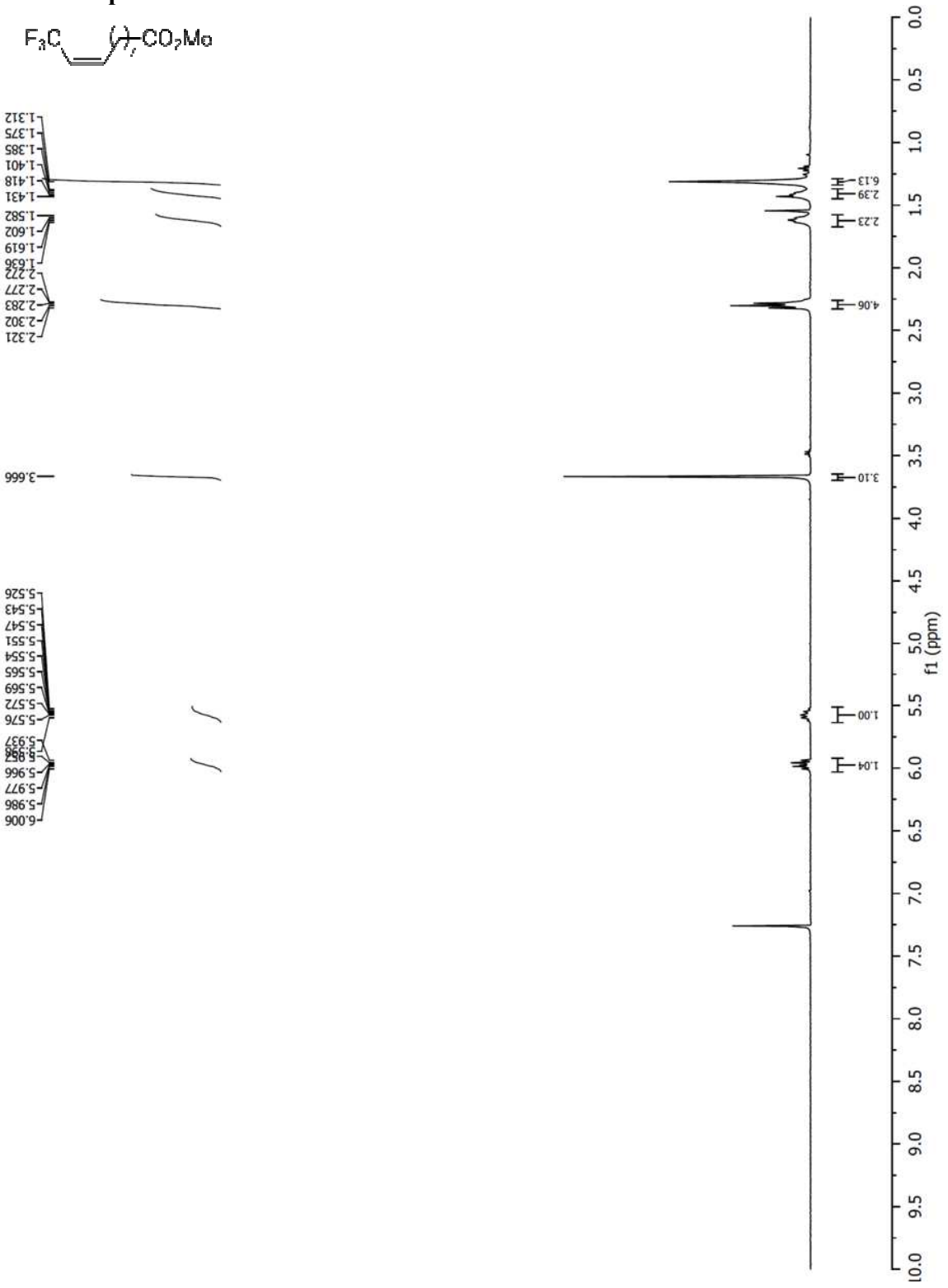
^{1}H NMR spectrum of 3.13



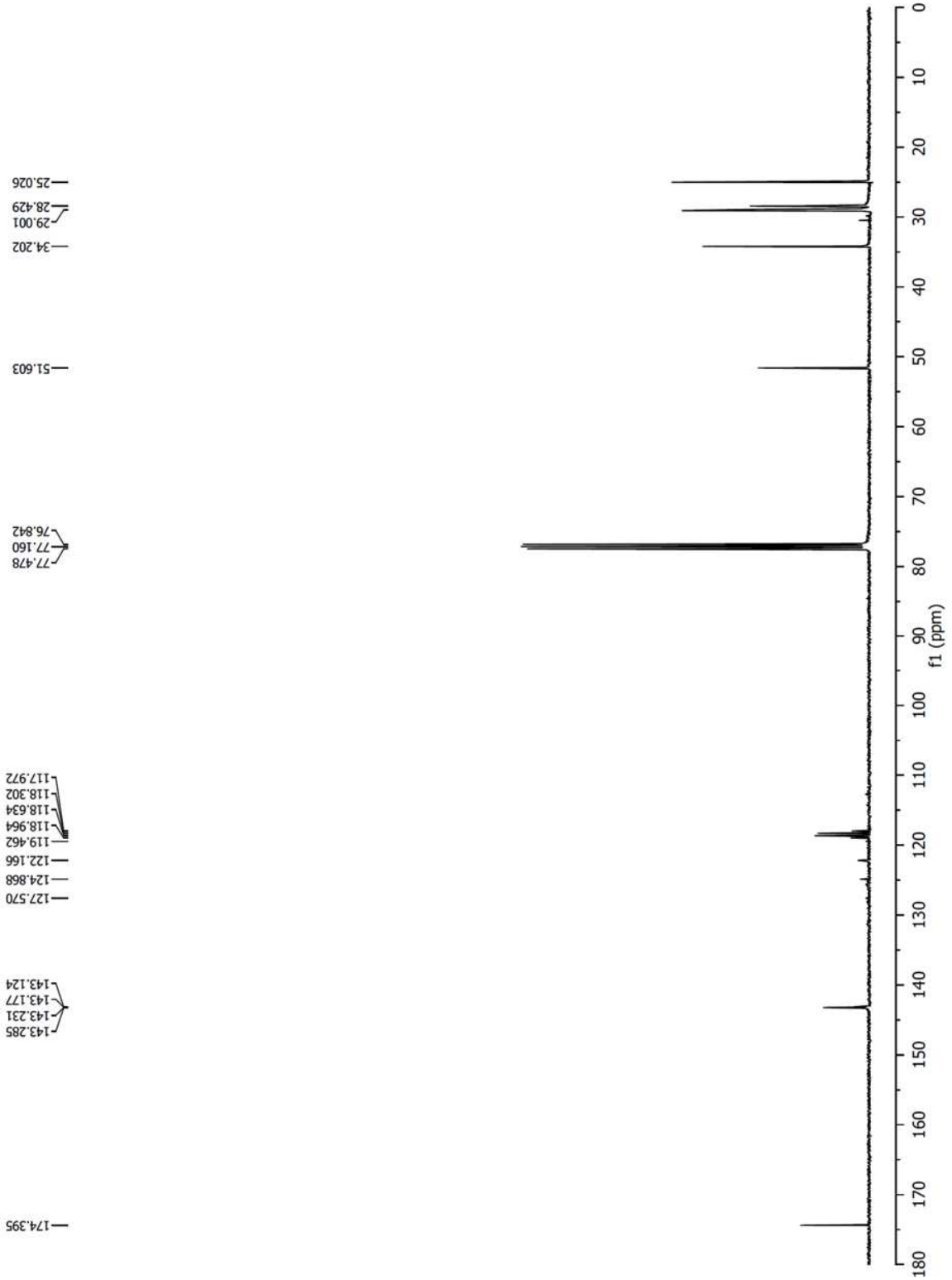
^{13}C NMR spectrum of 3.13



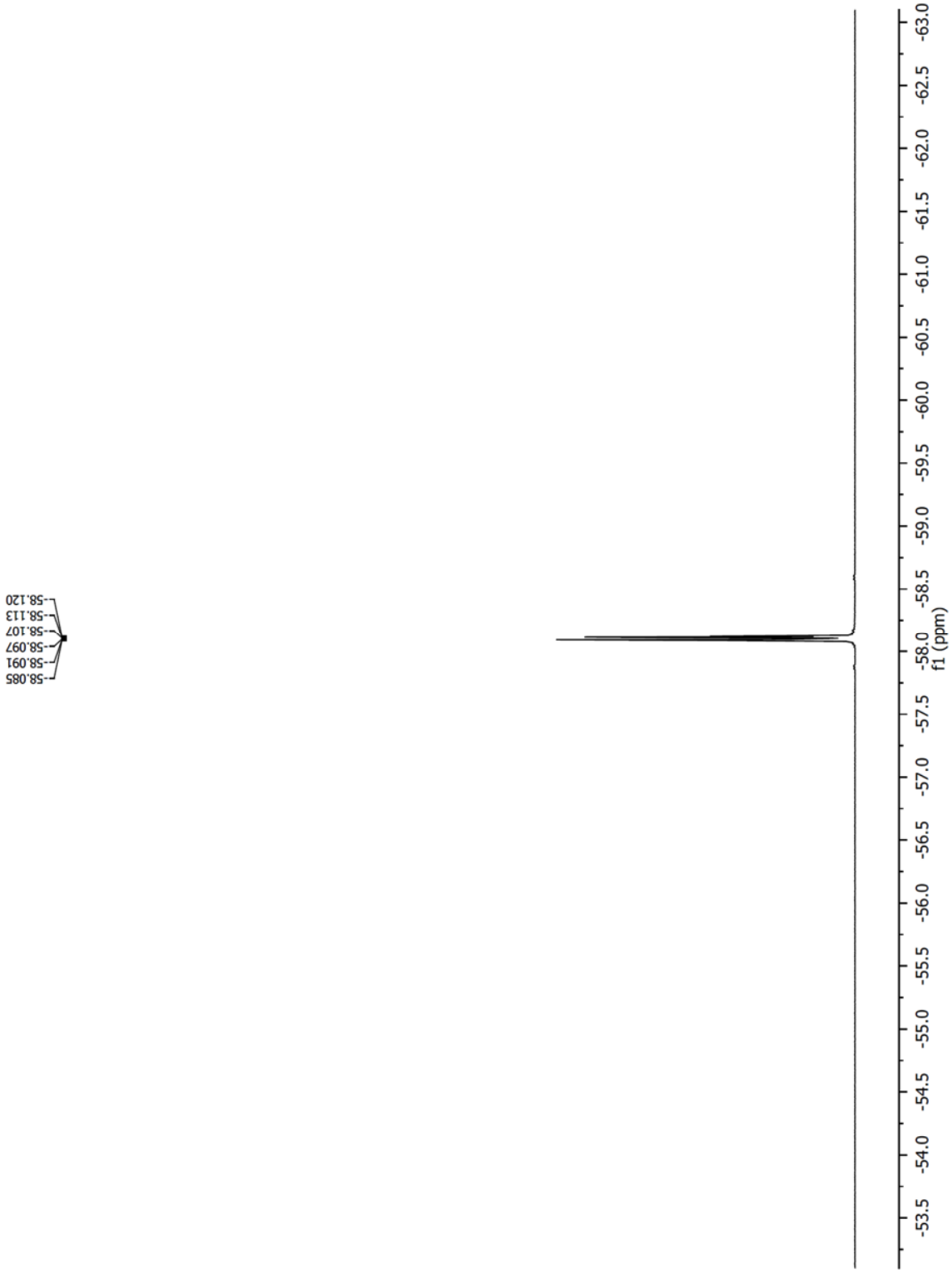
^{1}H NMR spectrum of 3.16



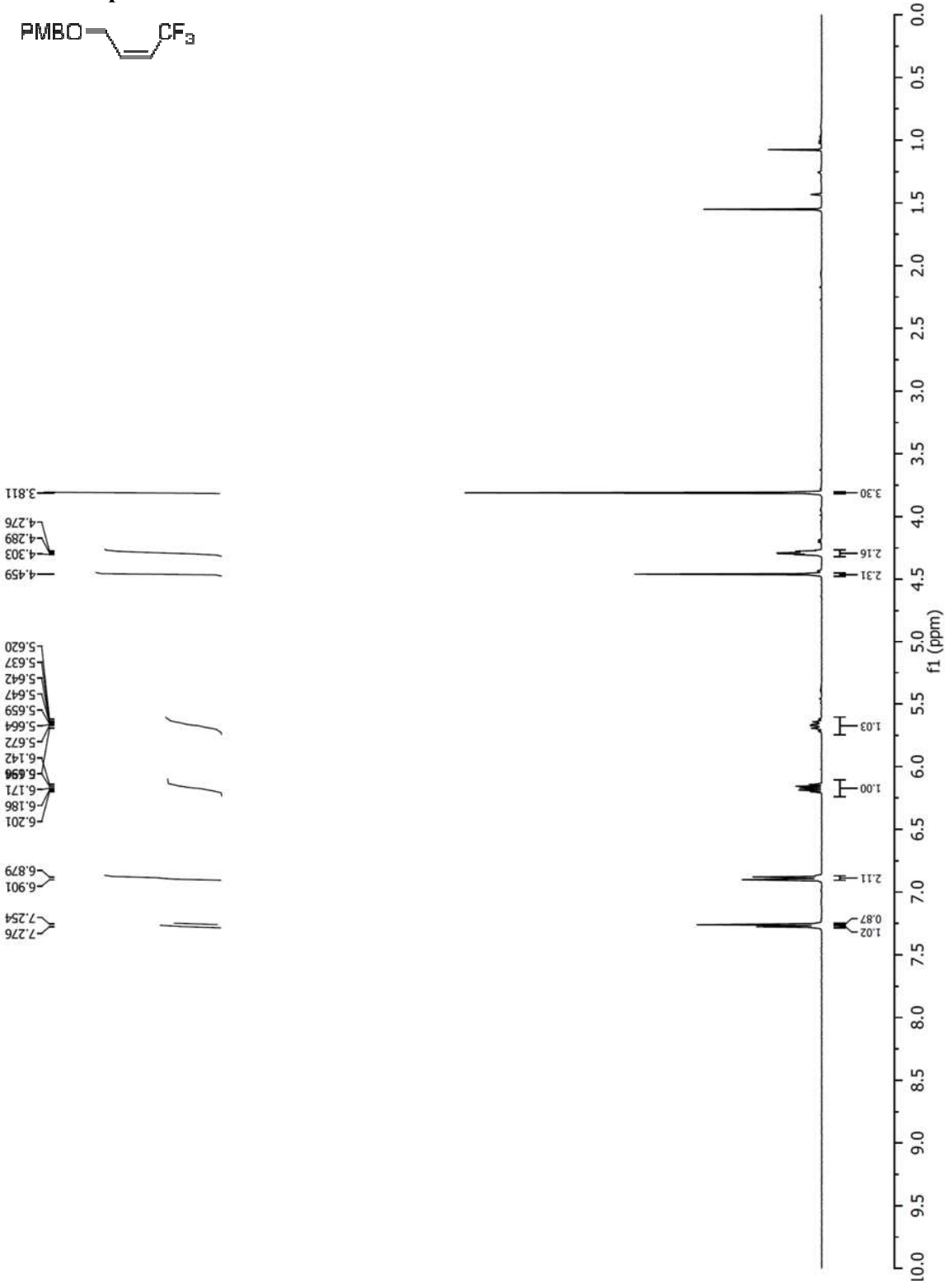
^{13}C NMR spectrum of 3.16



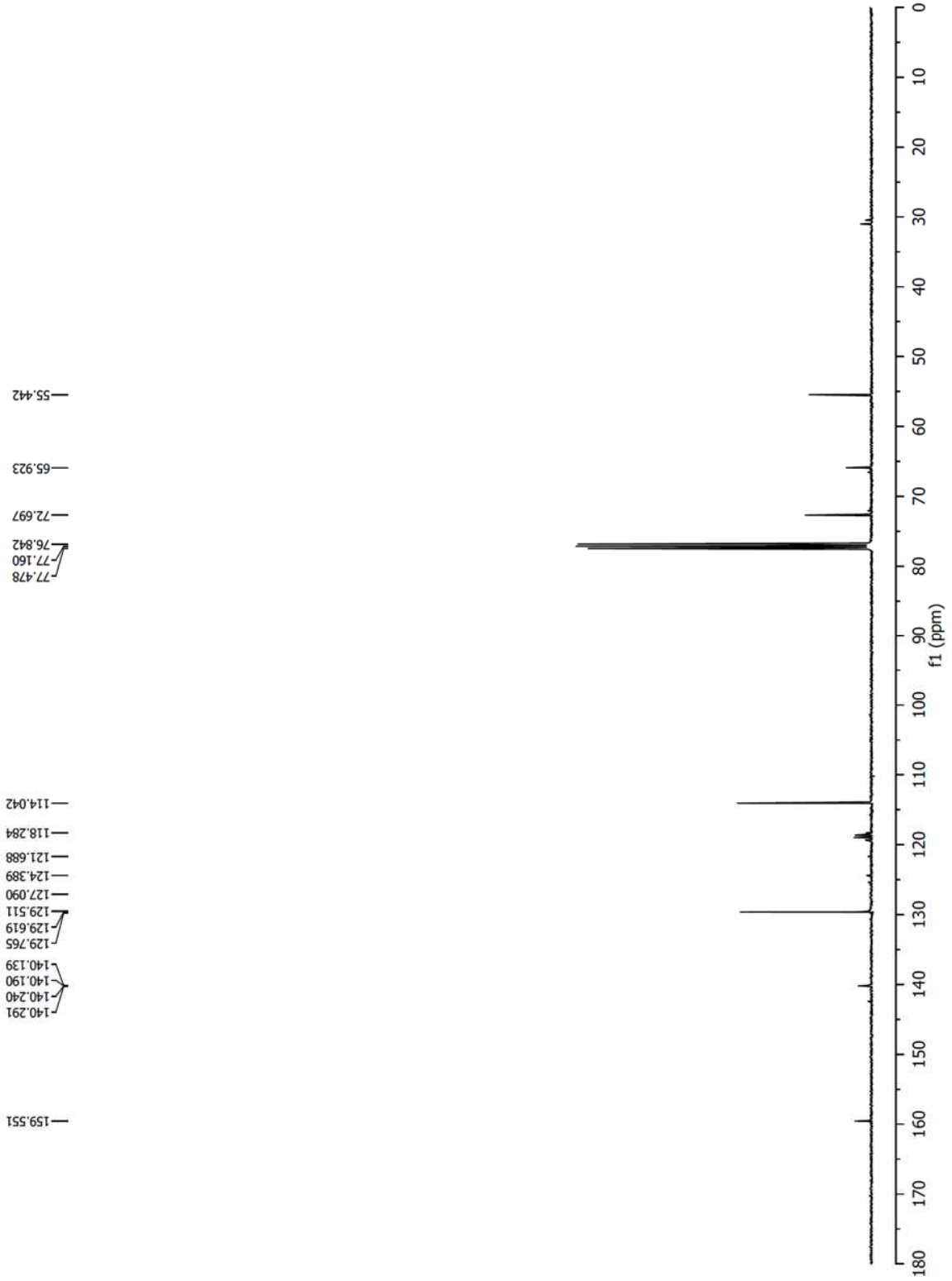
^{19}F NMR spectrum of 3.16



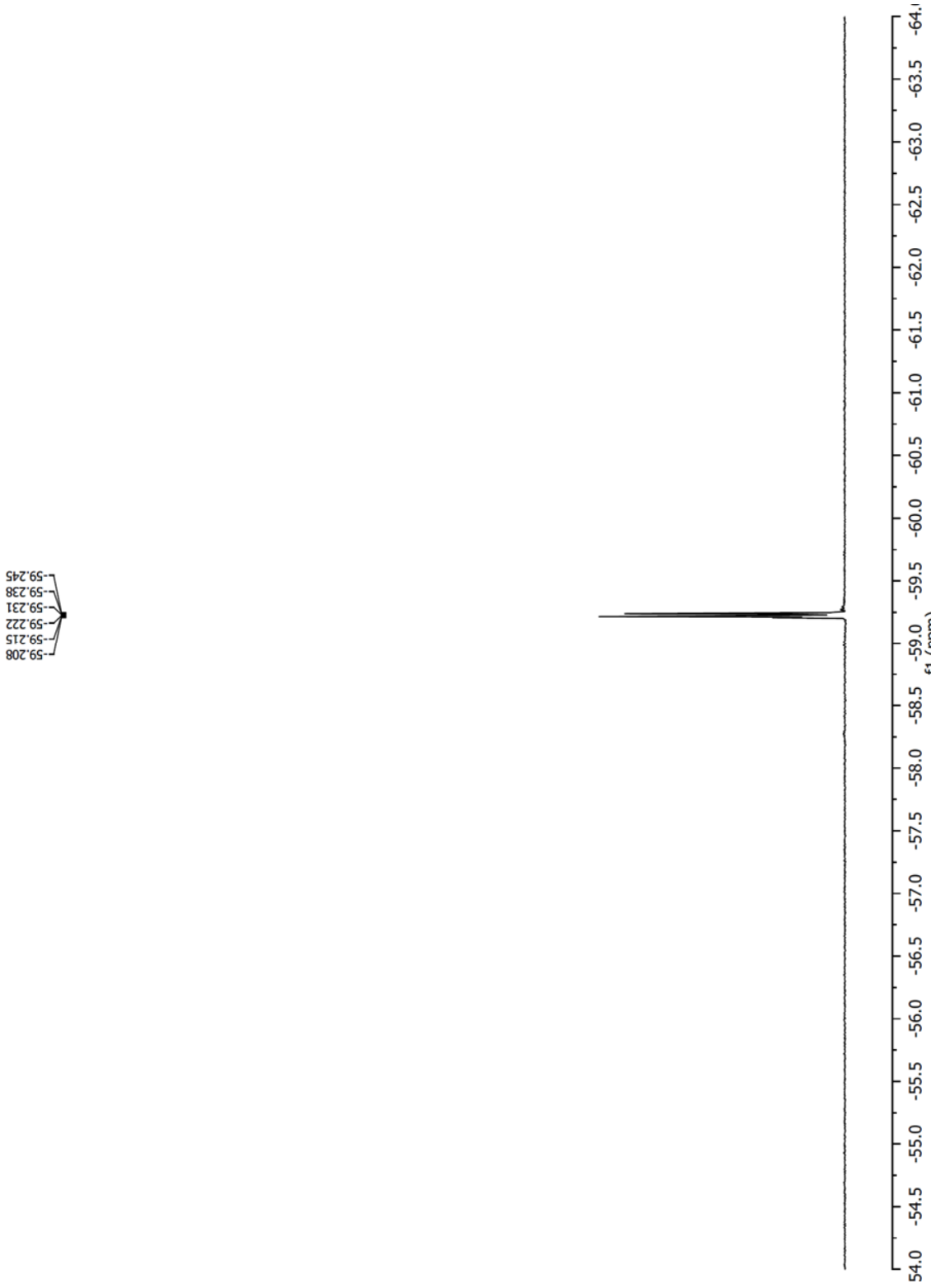
^{1}H NMR spectrum of 3.22



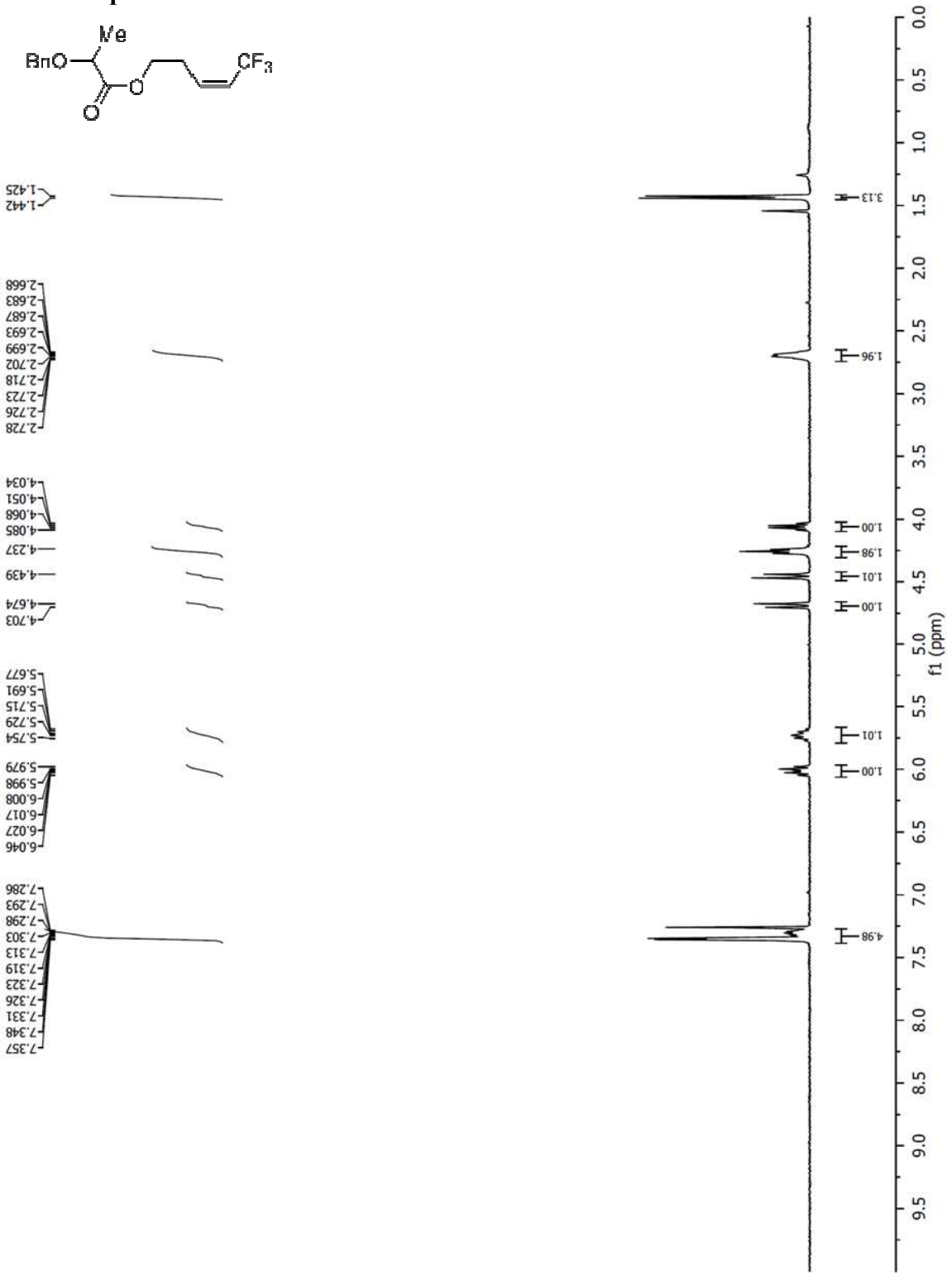
^{13}C NMR spectrum of 3.22



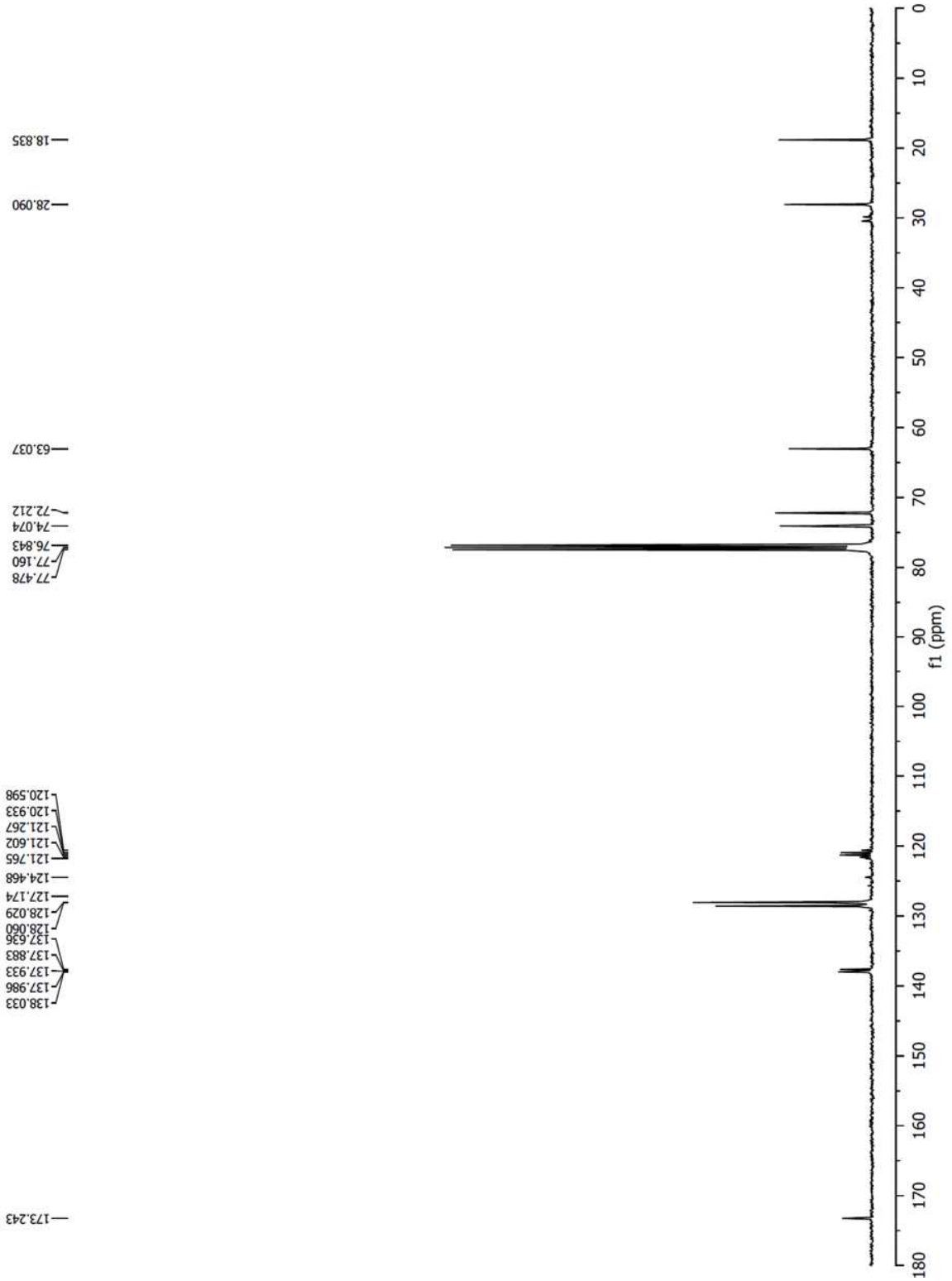
^{19}F NMR spectrum of 3.22



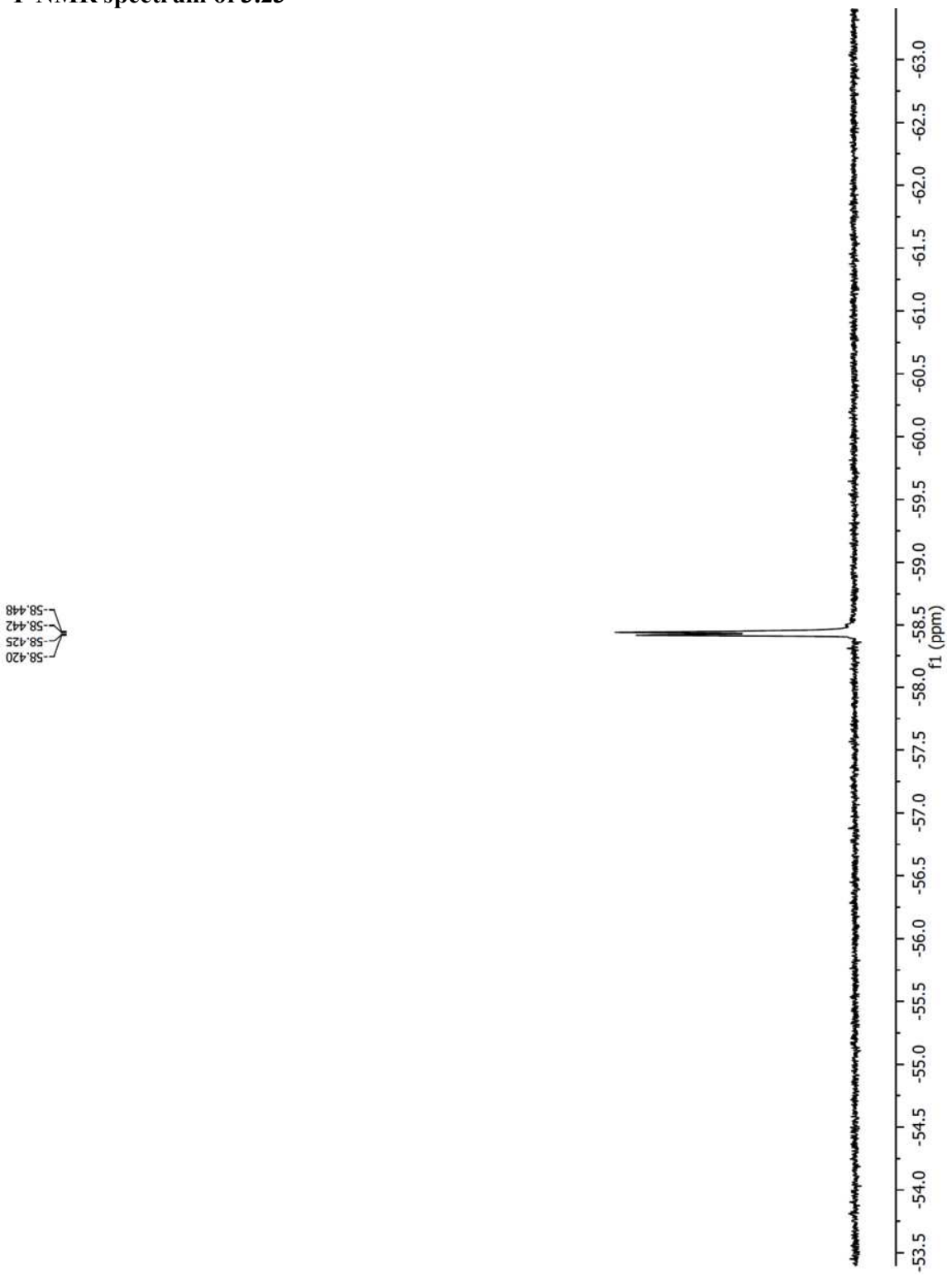
^{1}H NMR spectrum of 3.23



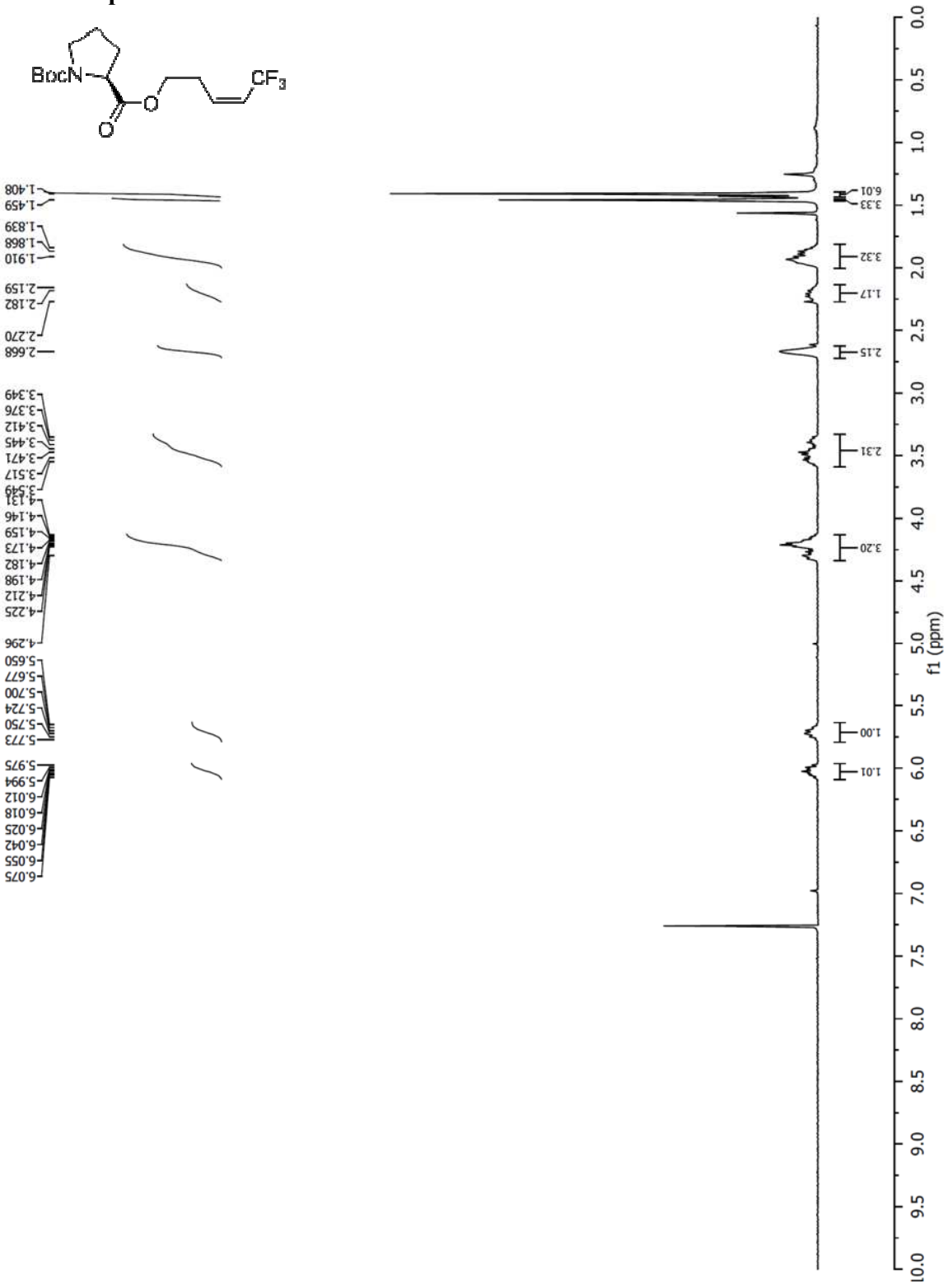
^{13}C NMR spectrum of 3.23



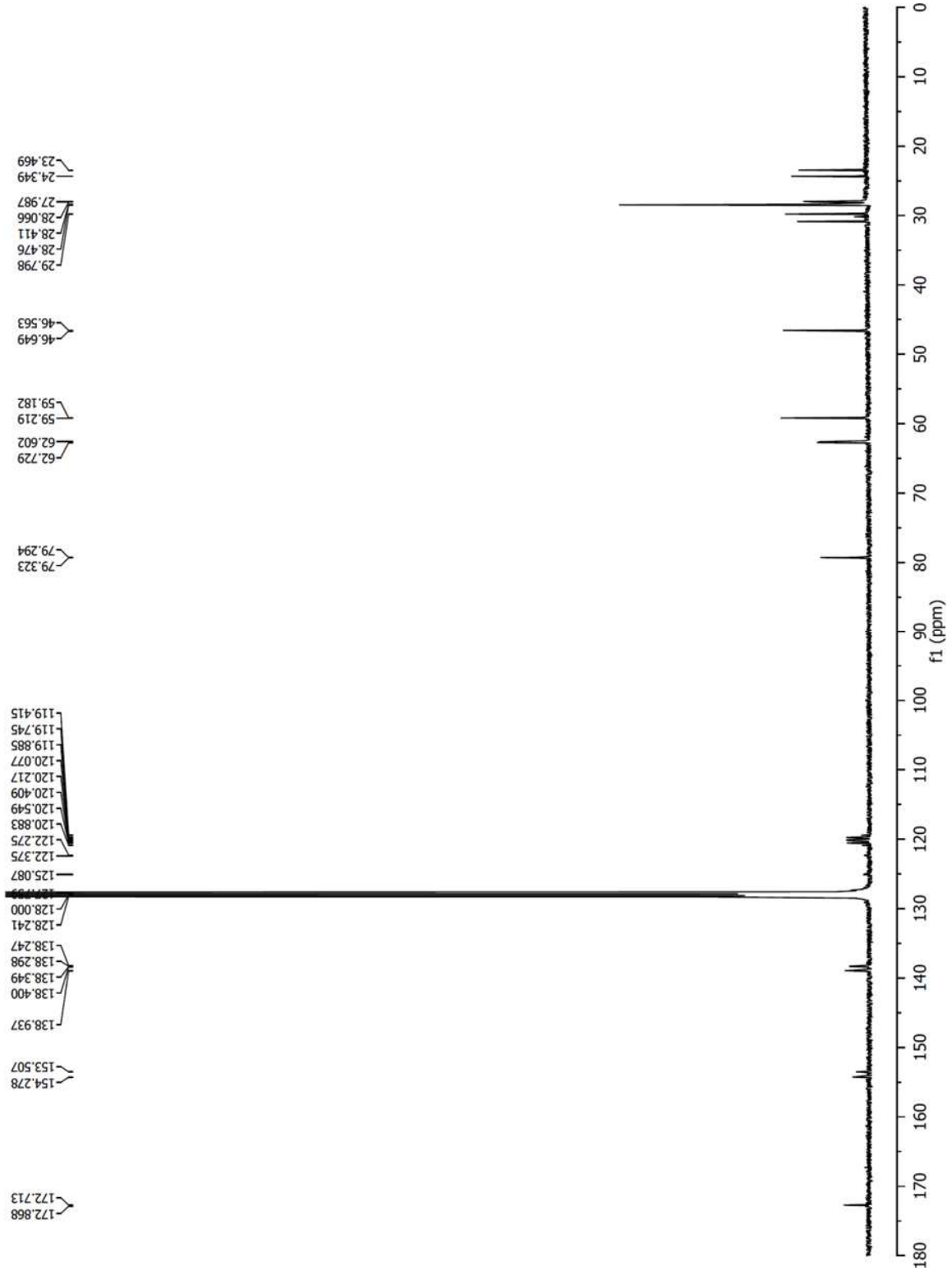
^{19}F NMR spectrum of 3.23



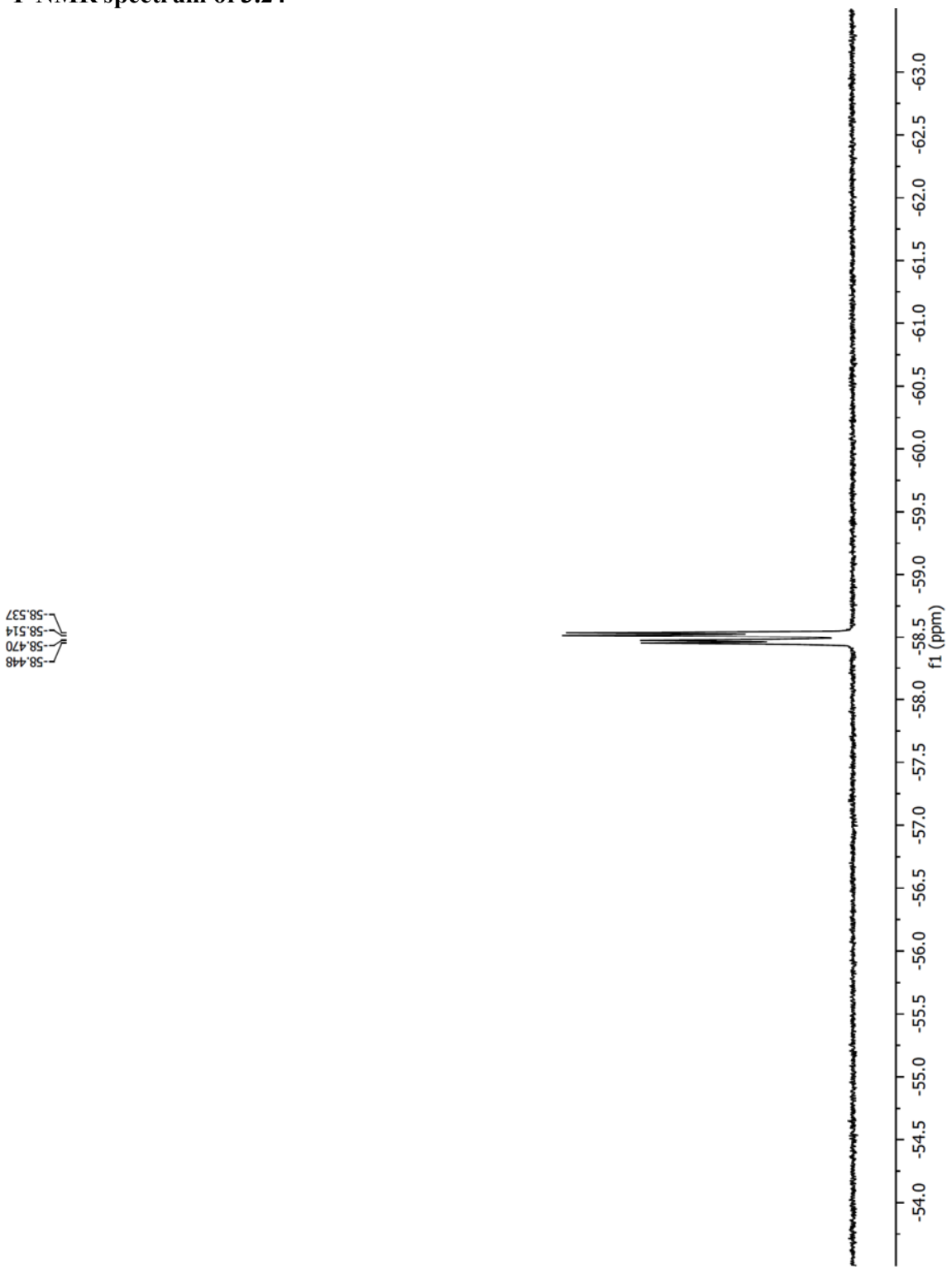
^{1}H NMR spectrum of 3.24



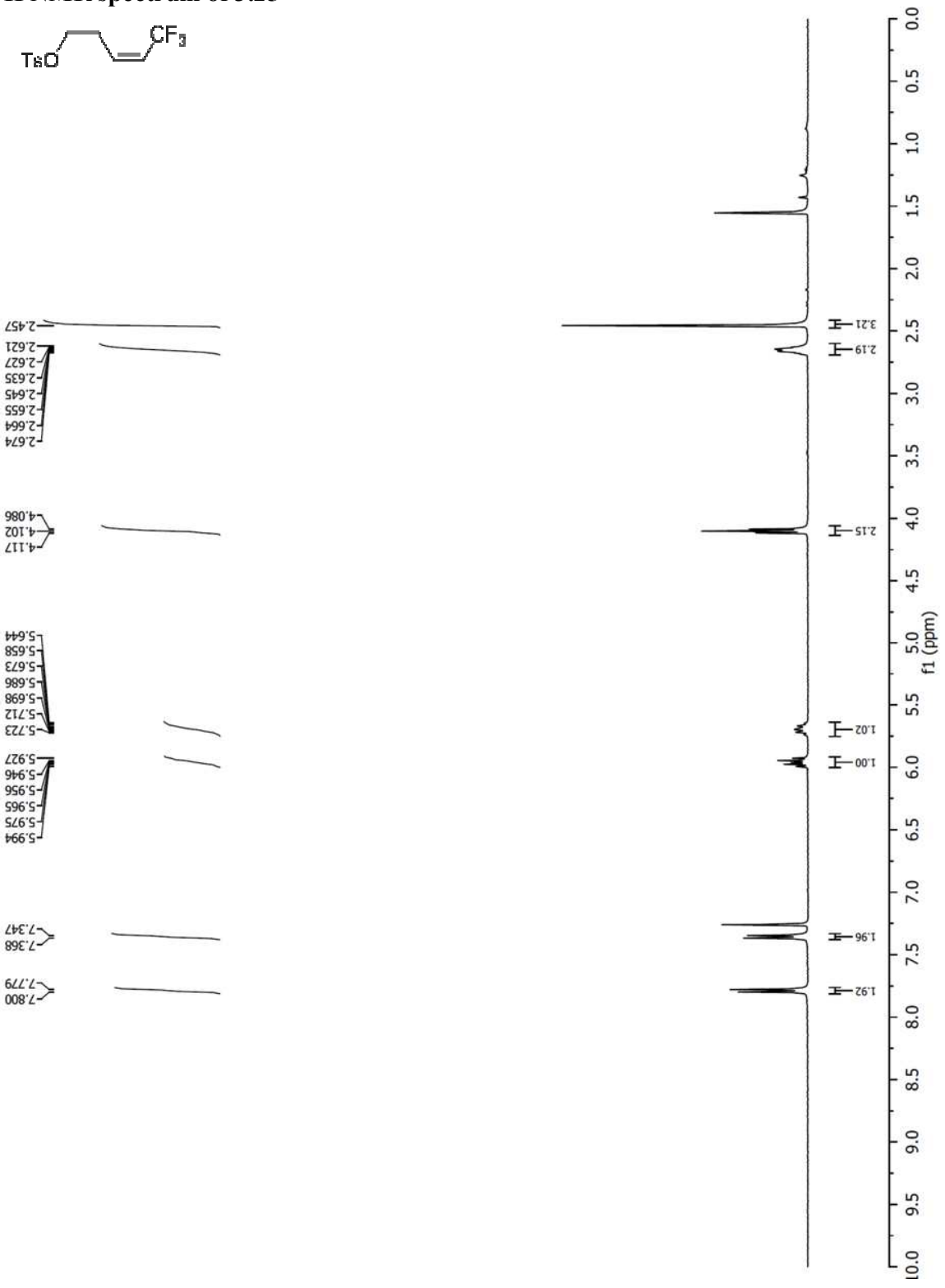
^{13}C NMR spectrum of 3.24



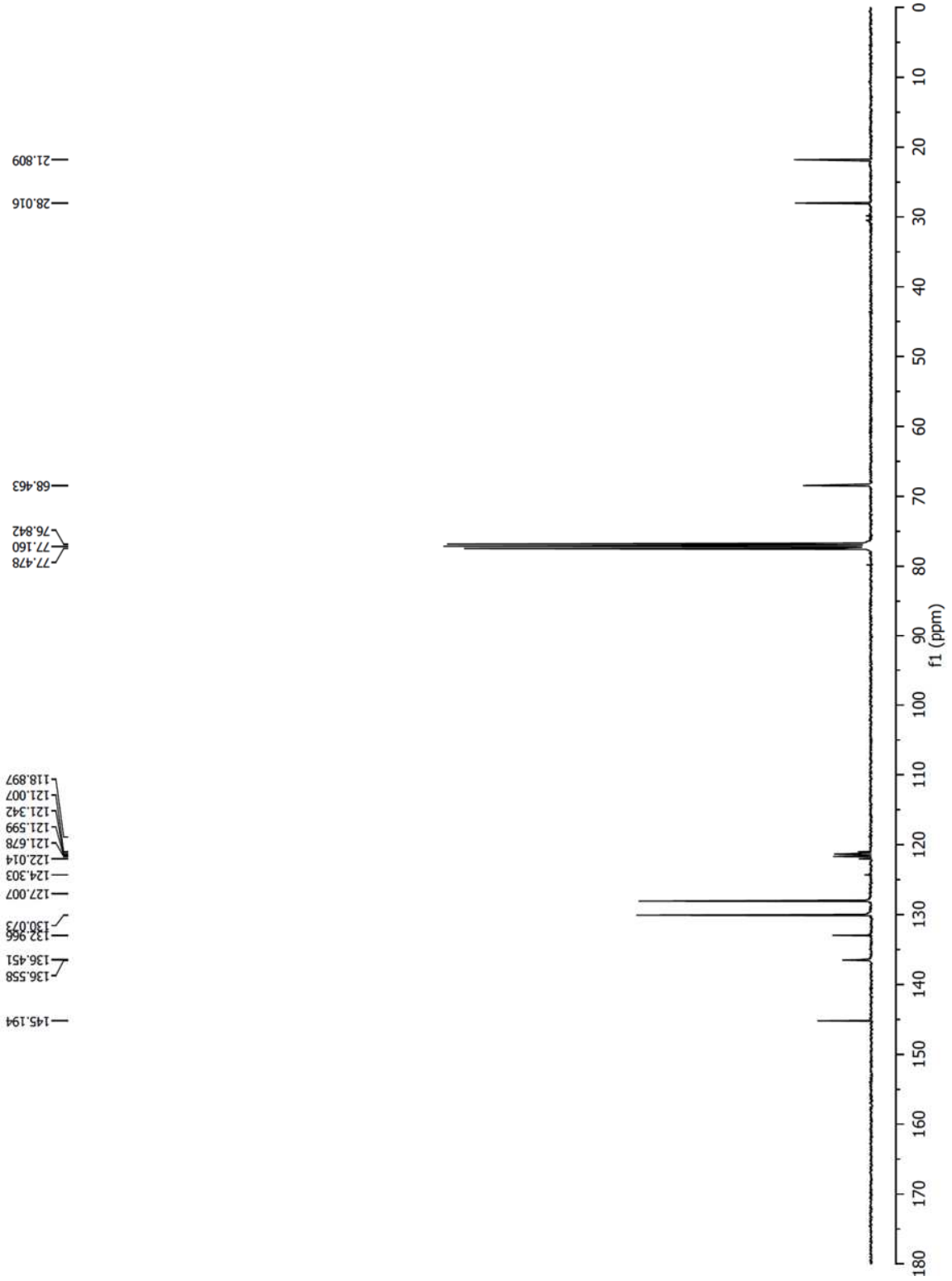
^{19}F NMR spectrum of 3.24



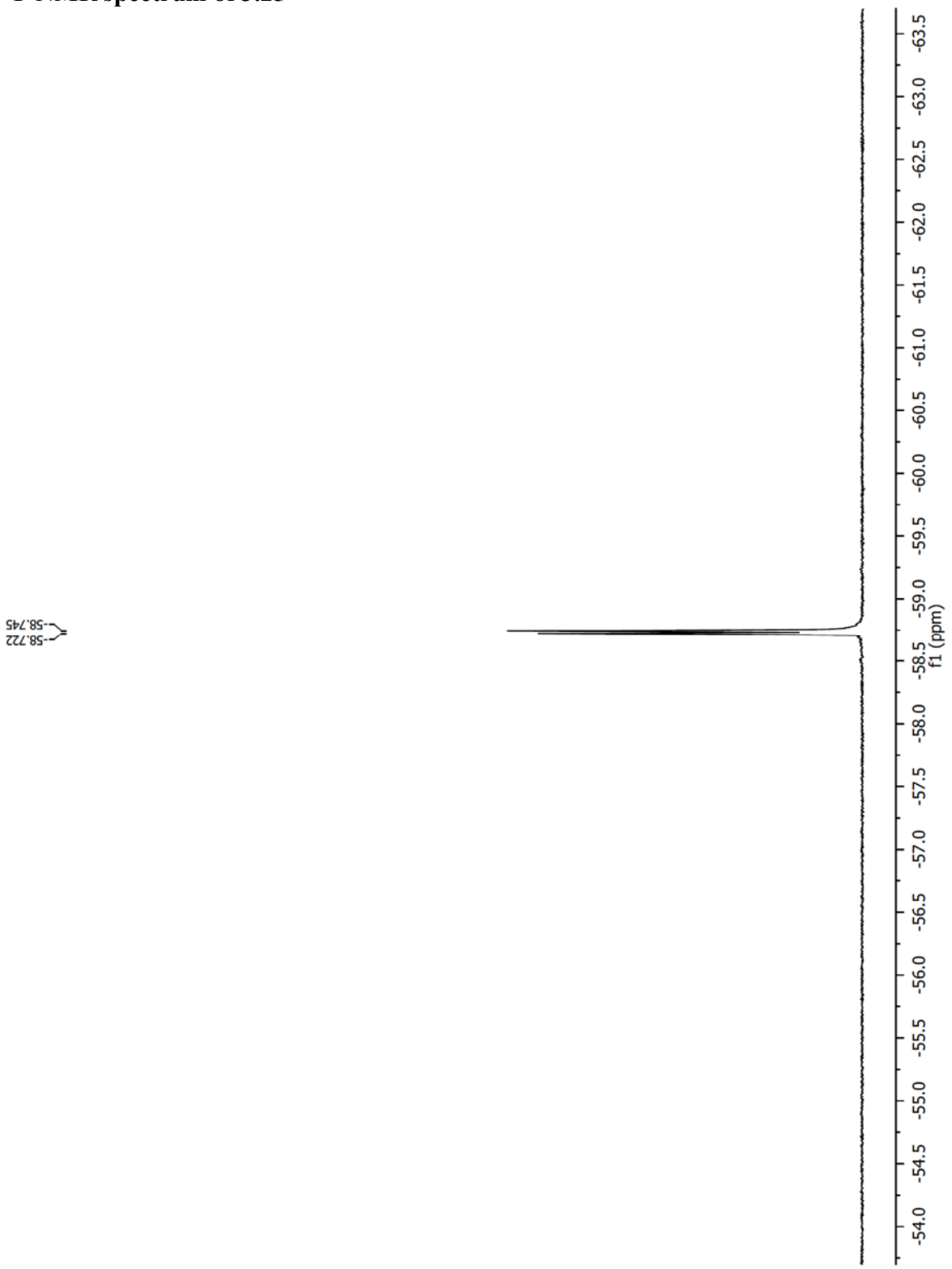
^{1}H NMR spectrum of 3.25



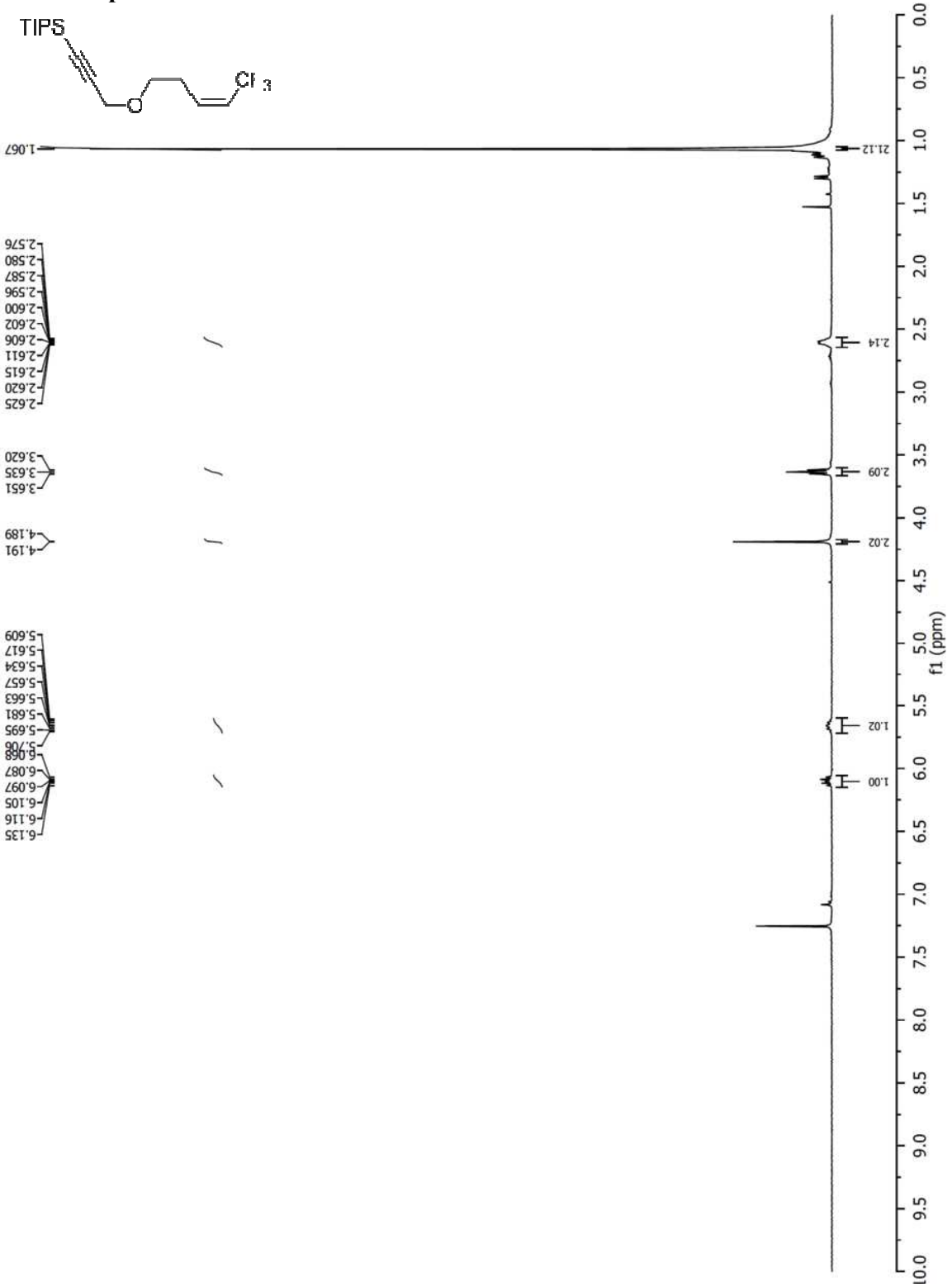
^{13}C NMR spectrum of 3.25



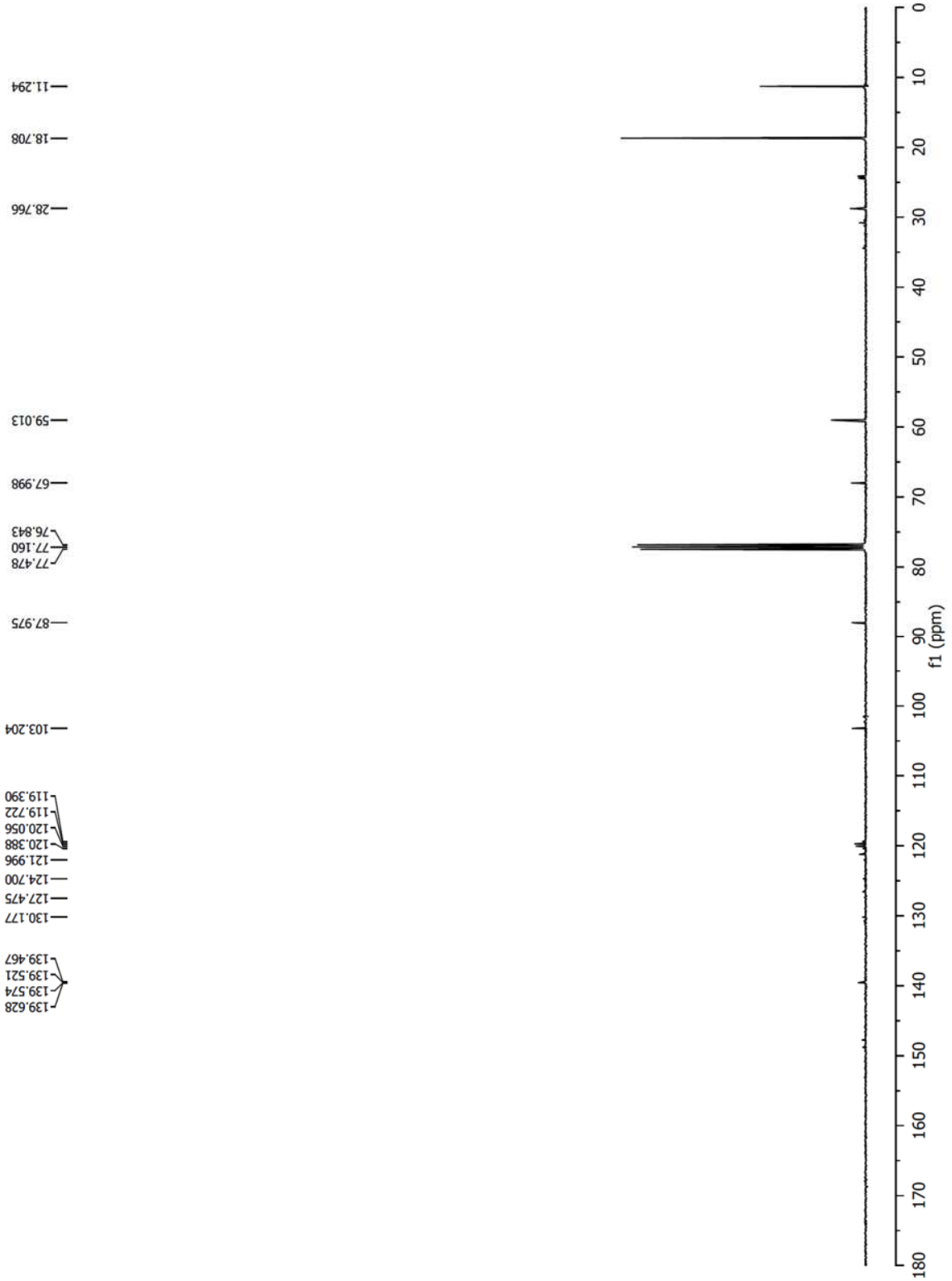
^{19}F NMR spectrum of 3.25



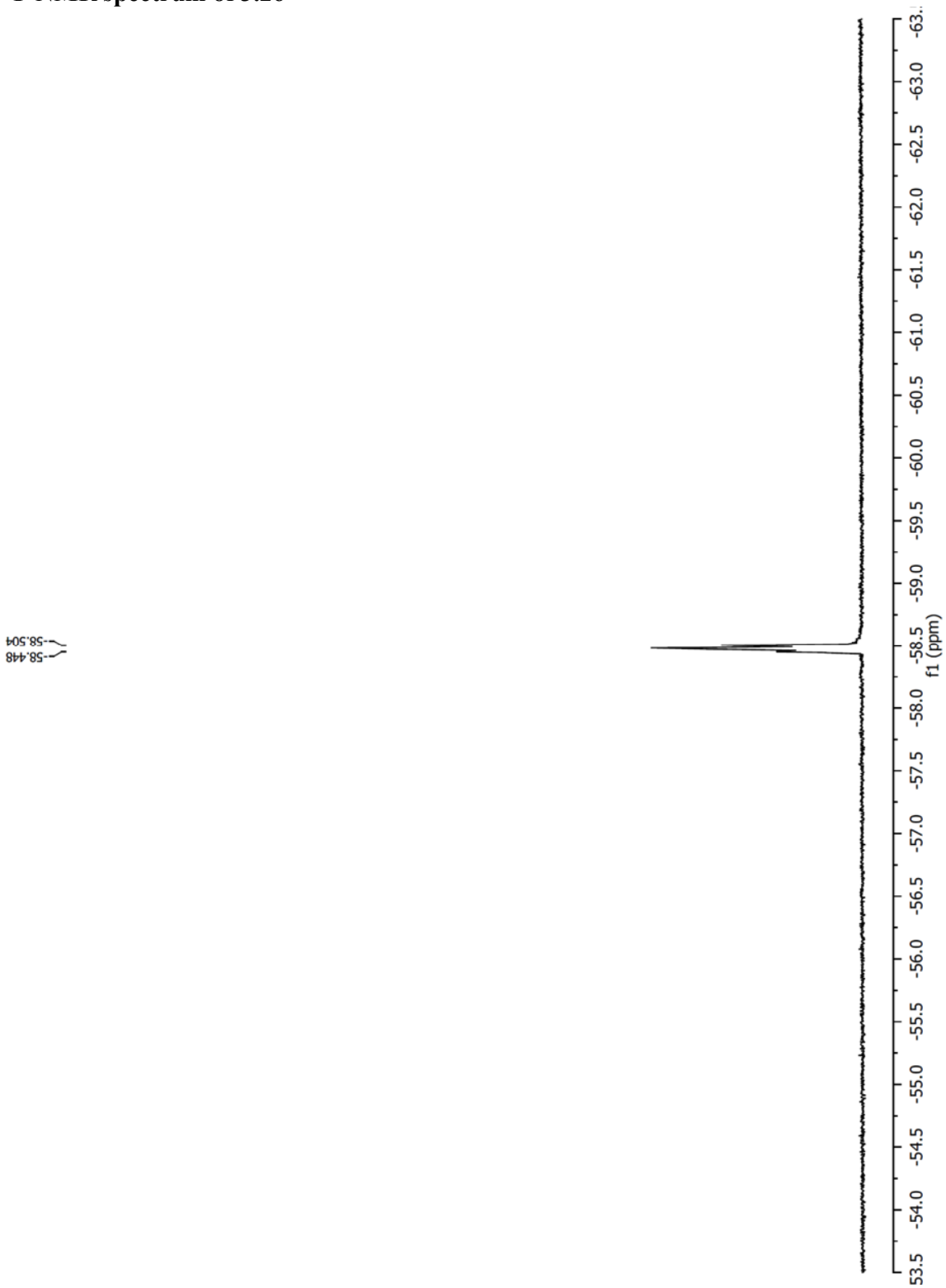
^{1}H NMR spectrum of 3.26



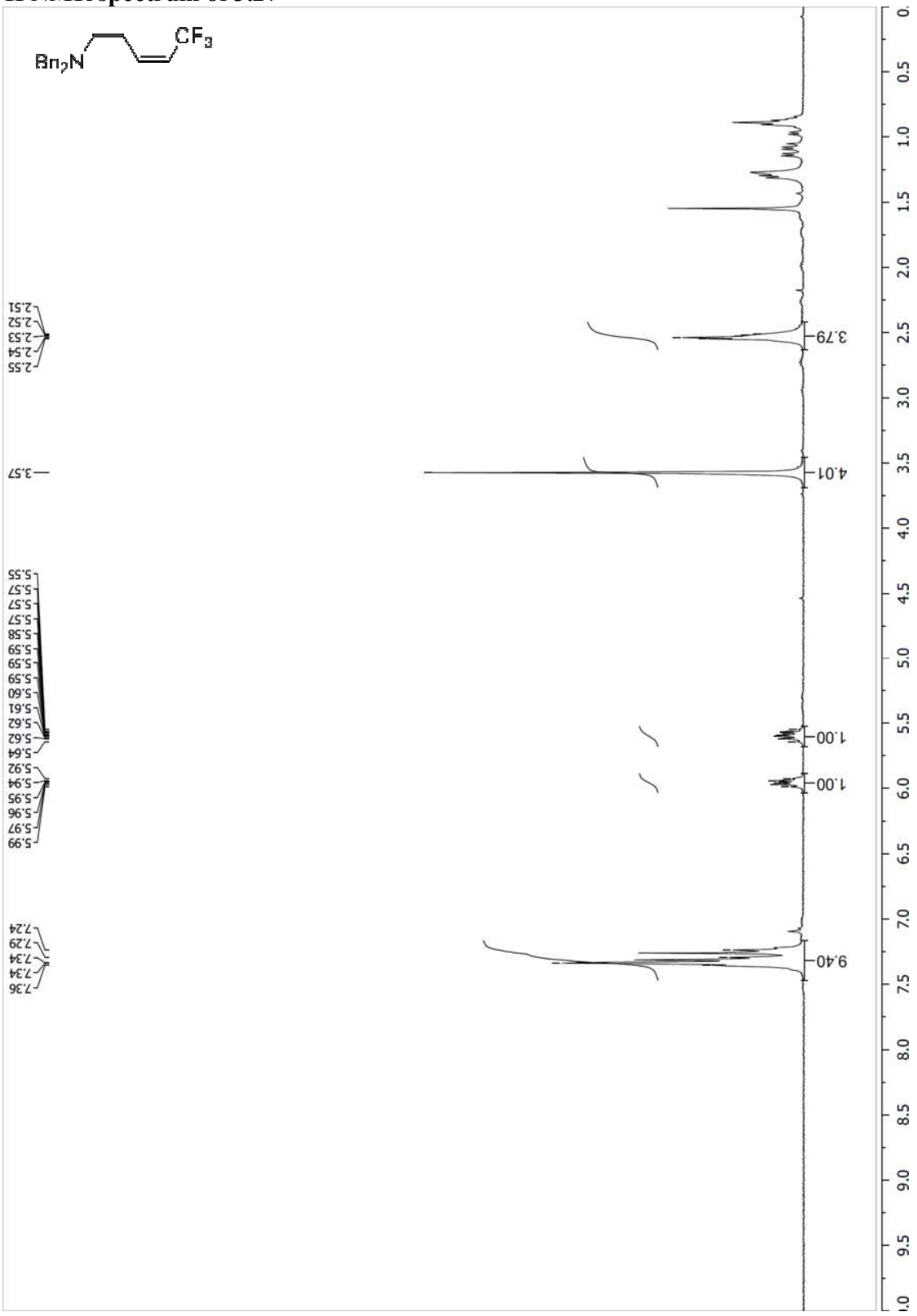
^{13}C NMR spectrum of 3.26



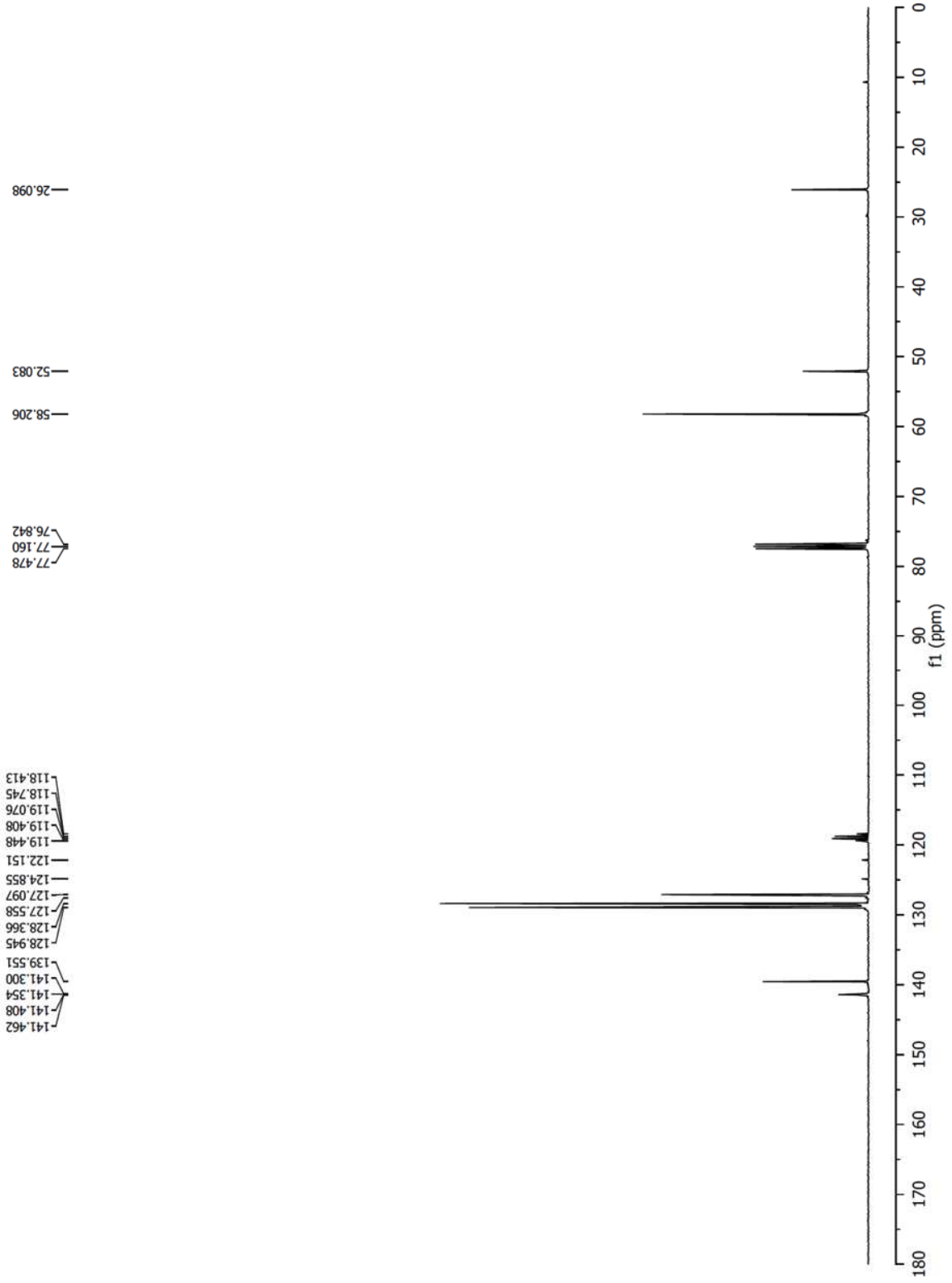
^{19}F NMR spectrum of 3.26



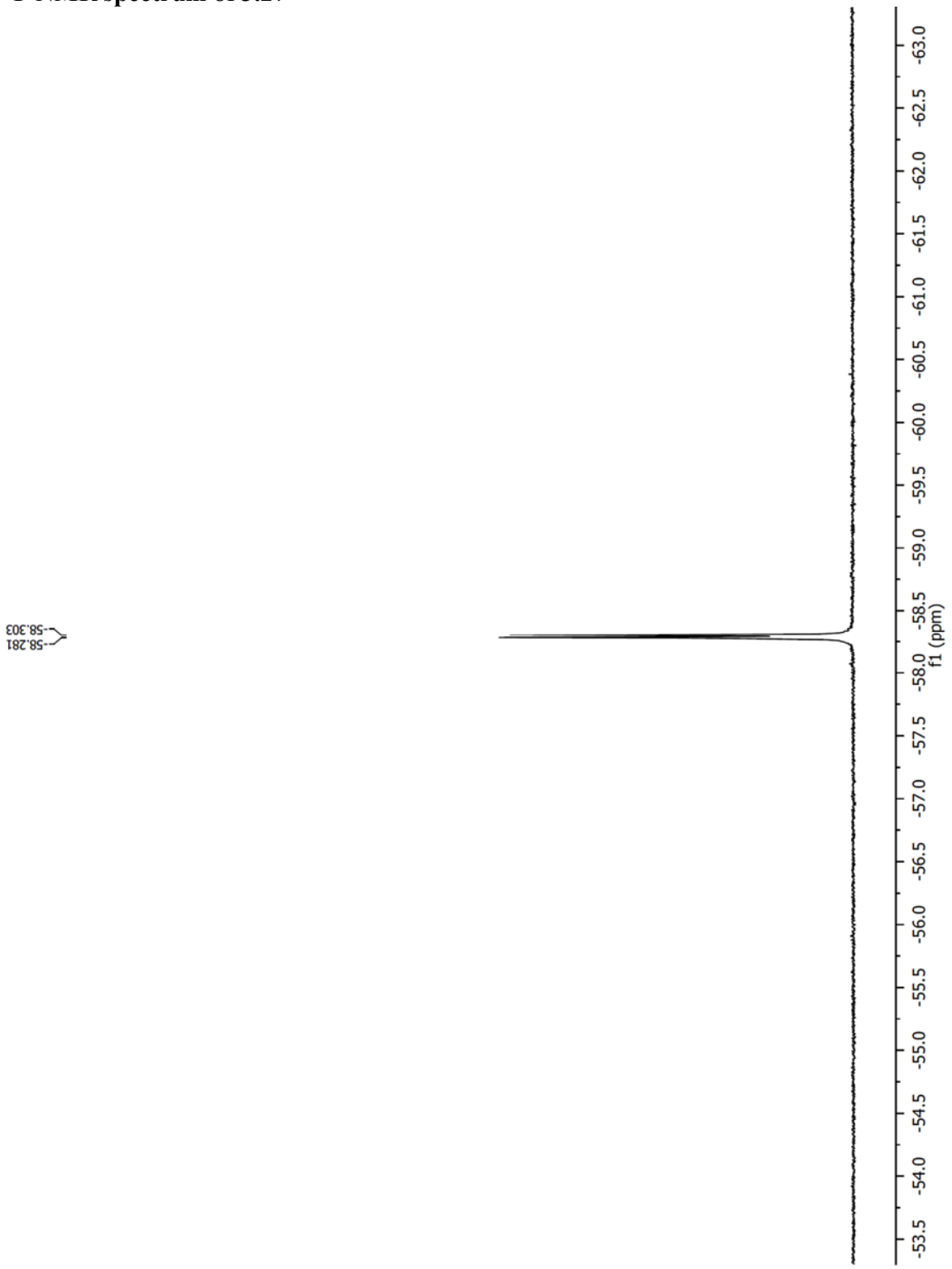
^{1}H NMR spectrum of 3.27



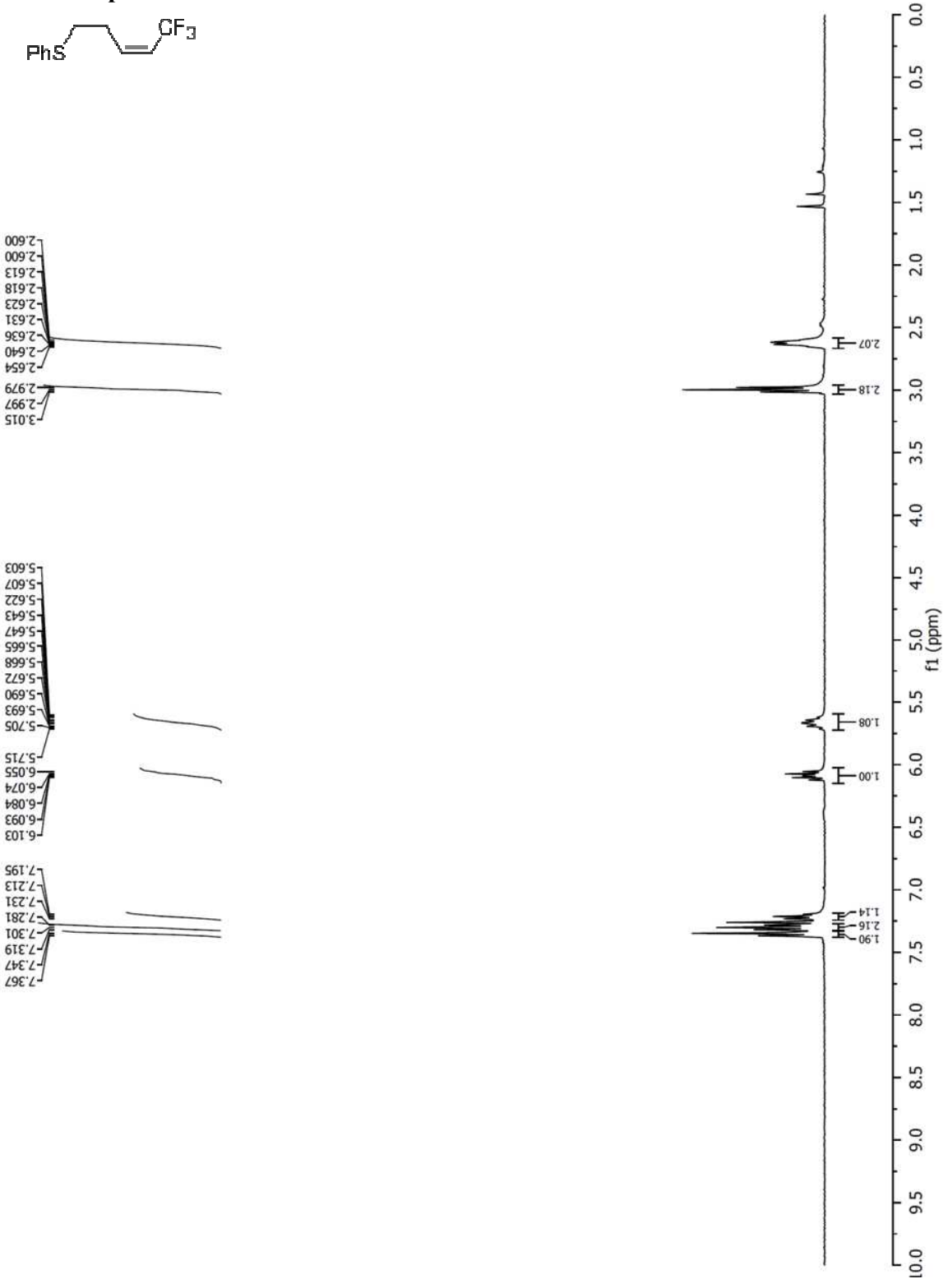
^{13}C NMR spectrum of 3.27



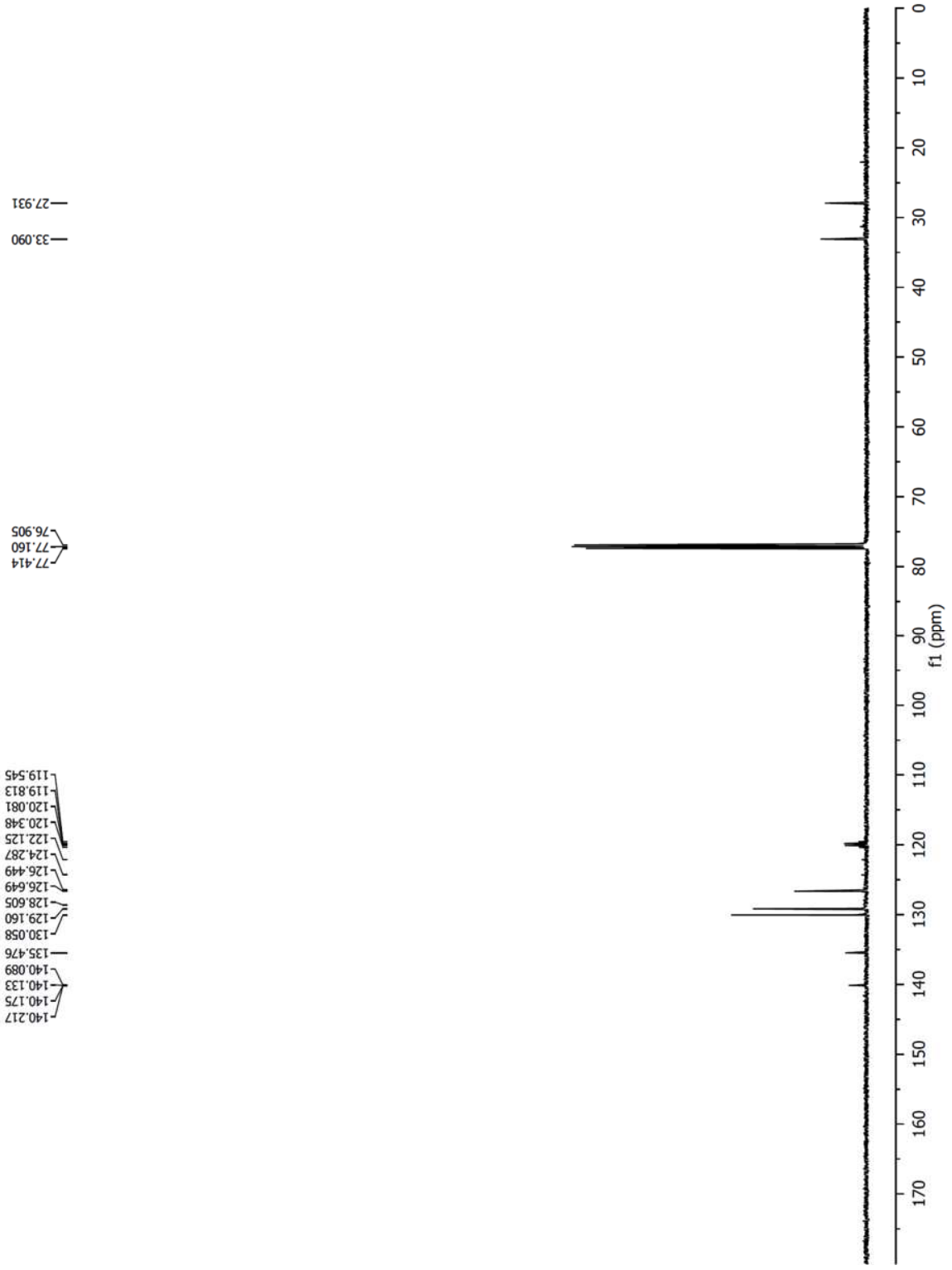
^{19}F NMR spectrum of 3.27



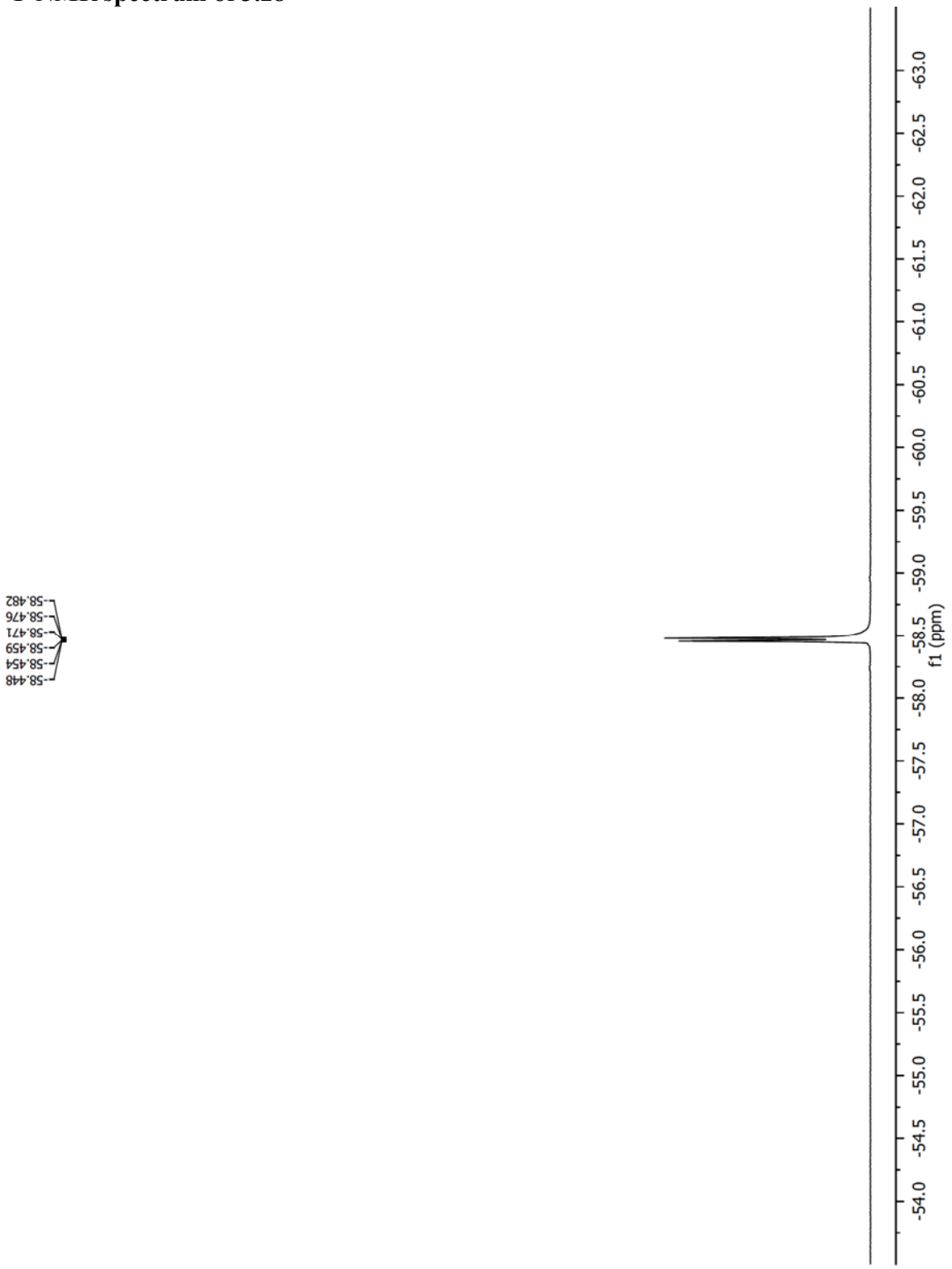
^{1}H NMR spectrum of 3.28



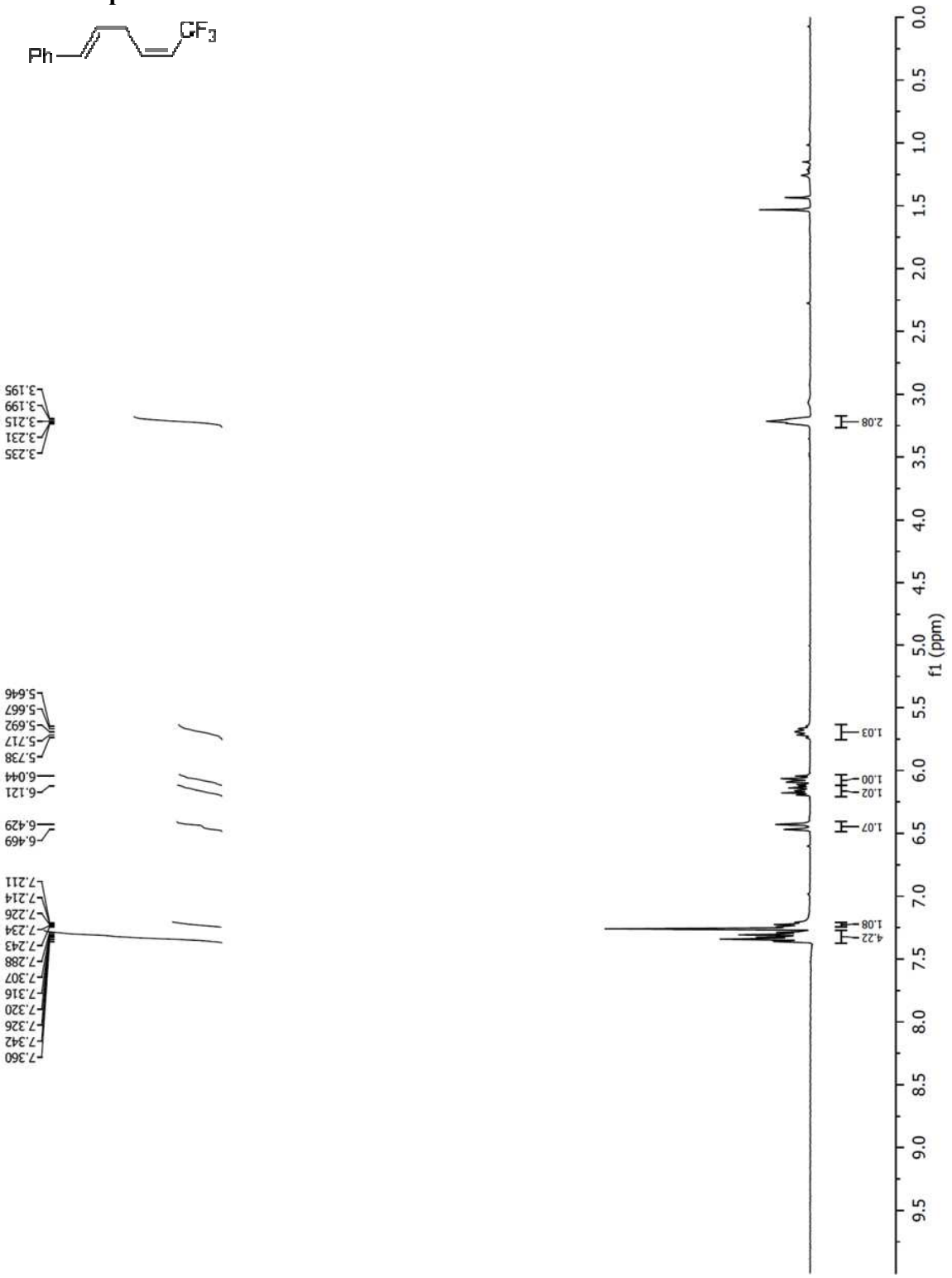
^{13}C NMR spectrum of 3.28



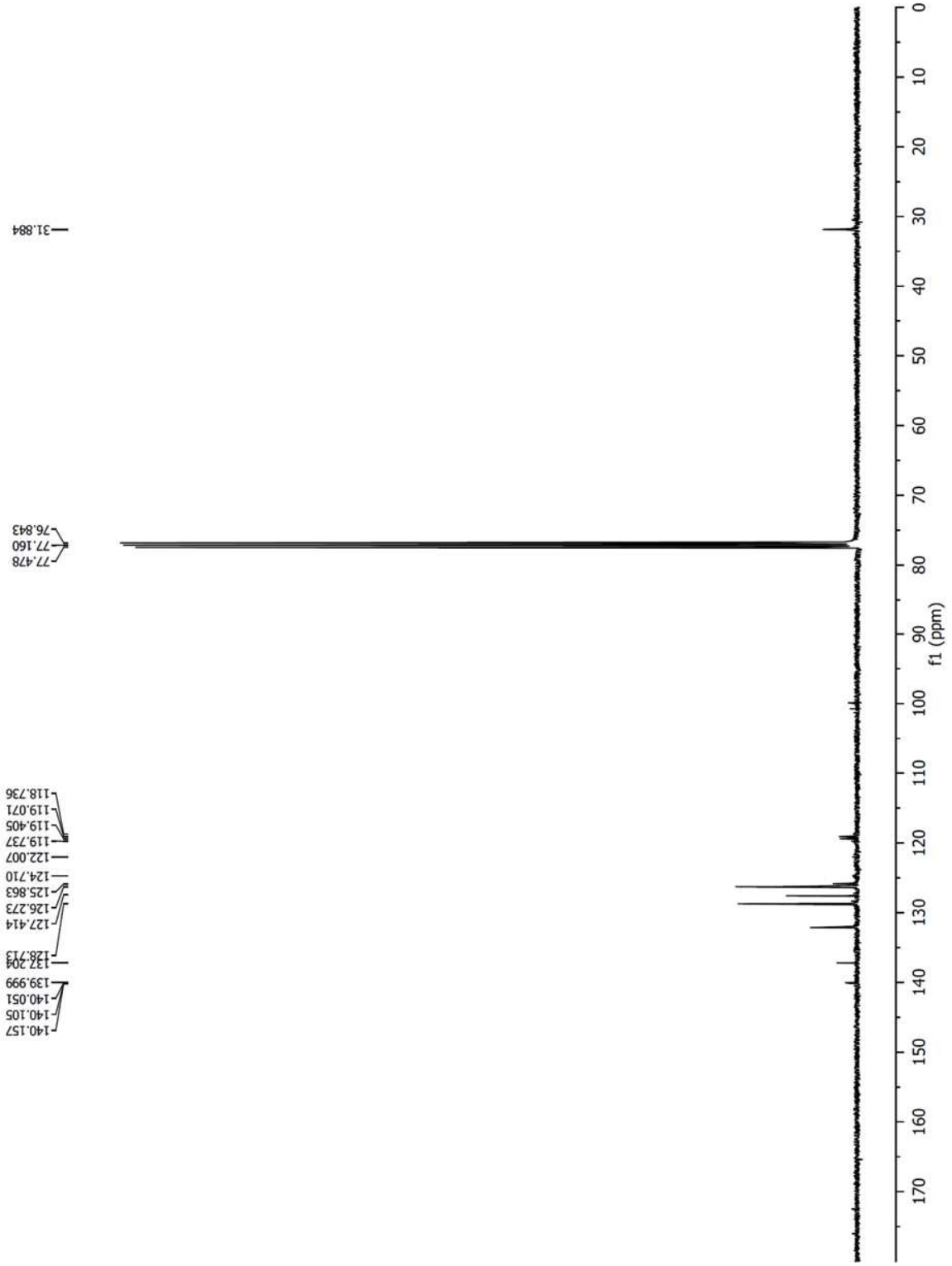
^{19}F NMR spectrum of 3.28



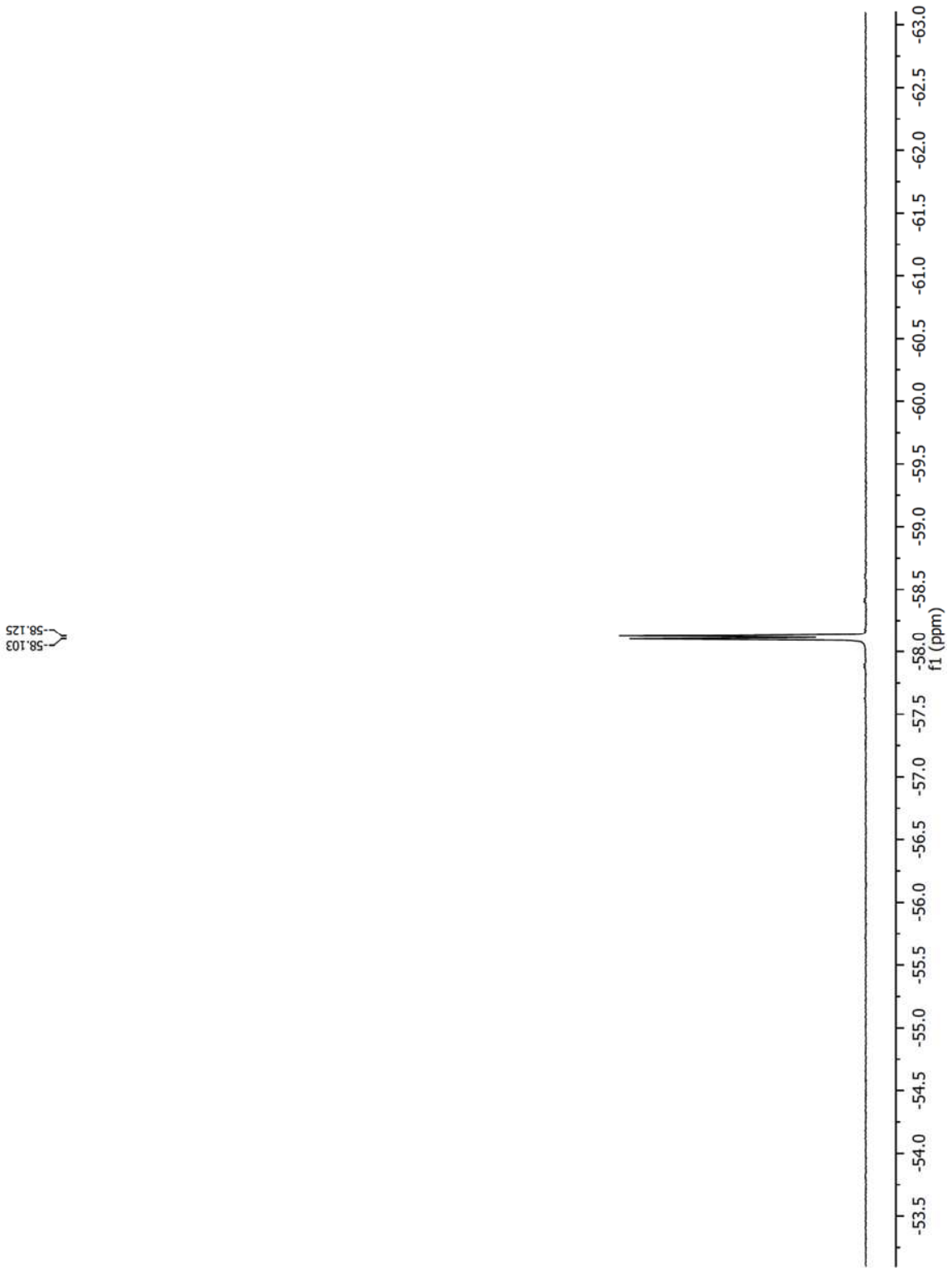
^{1}H NMR spectrum of 3.29



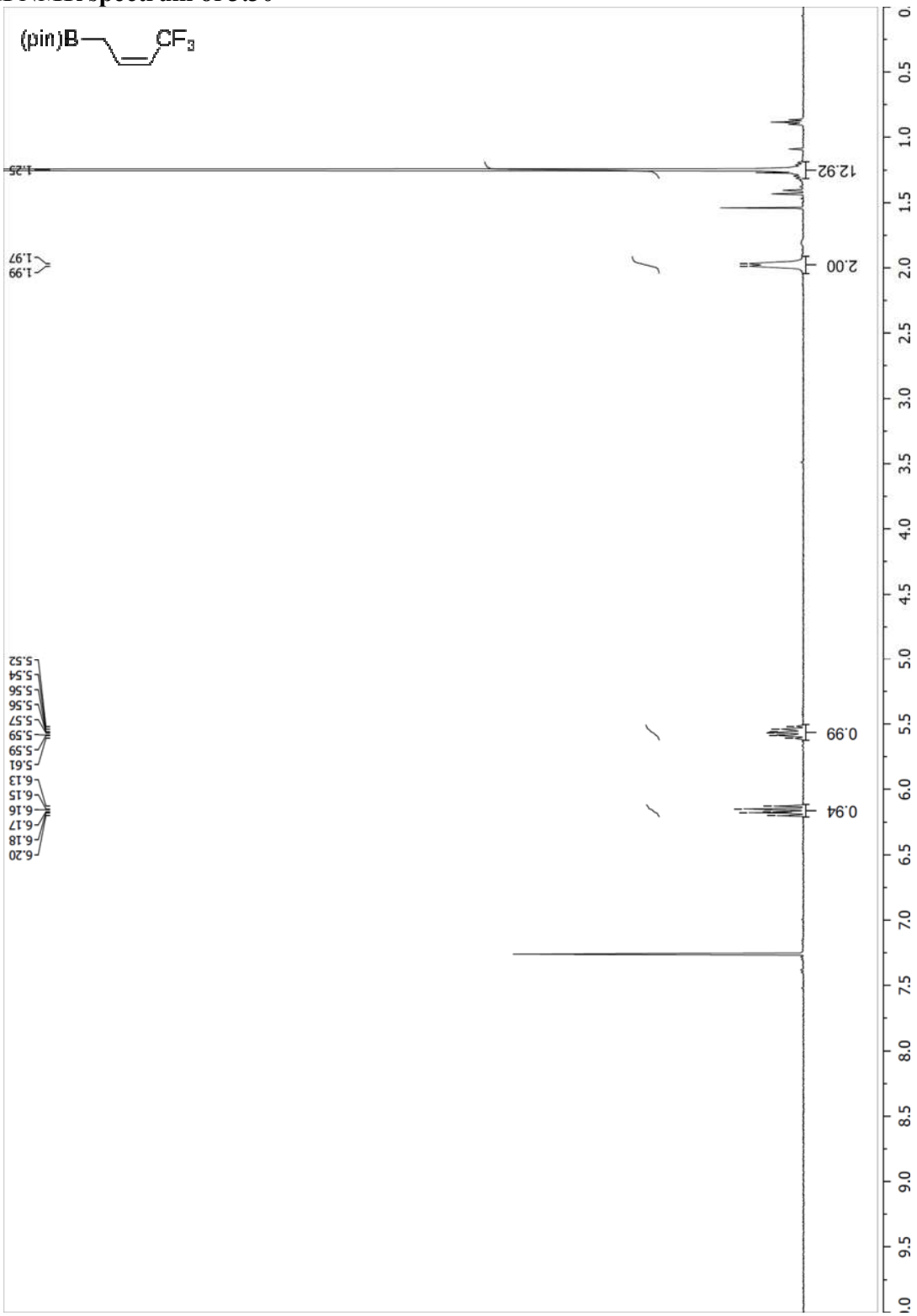
^{13}C NMR spectrum of 3.29



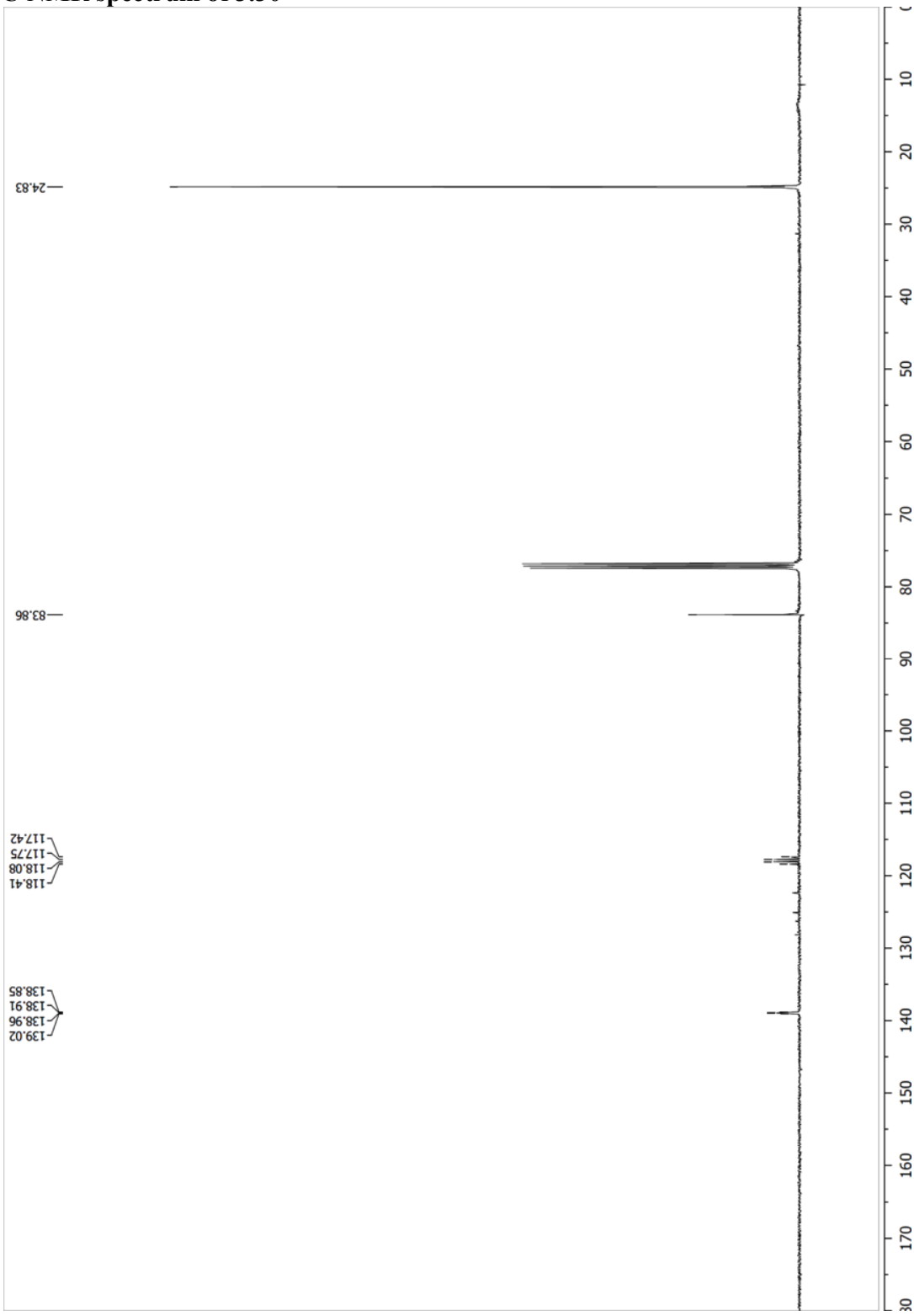
^{19}F NMR spectrum of 3.29



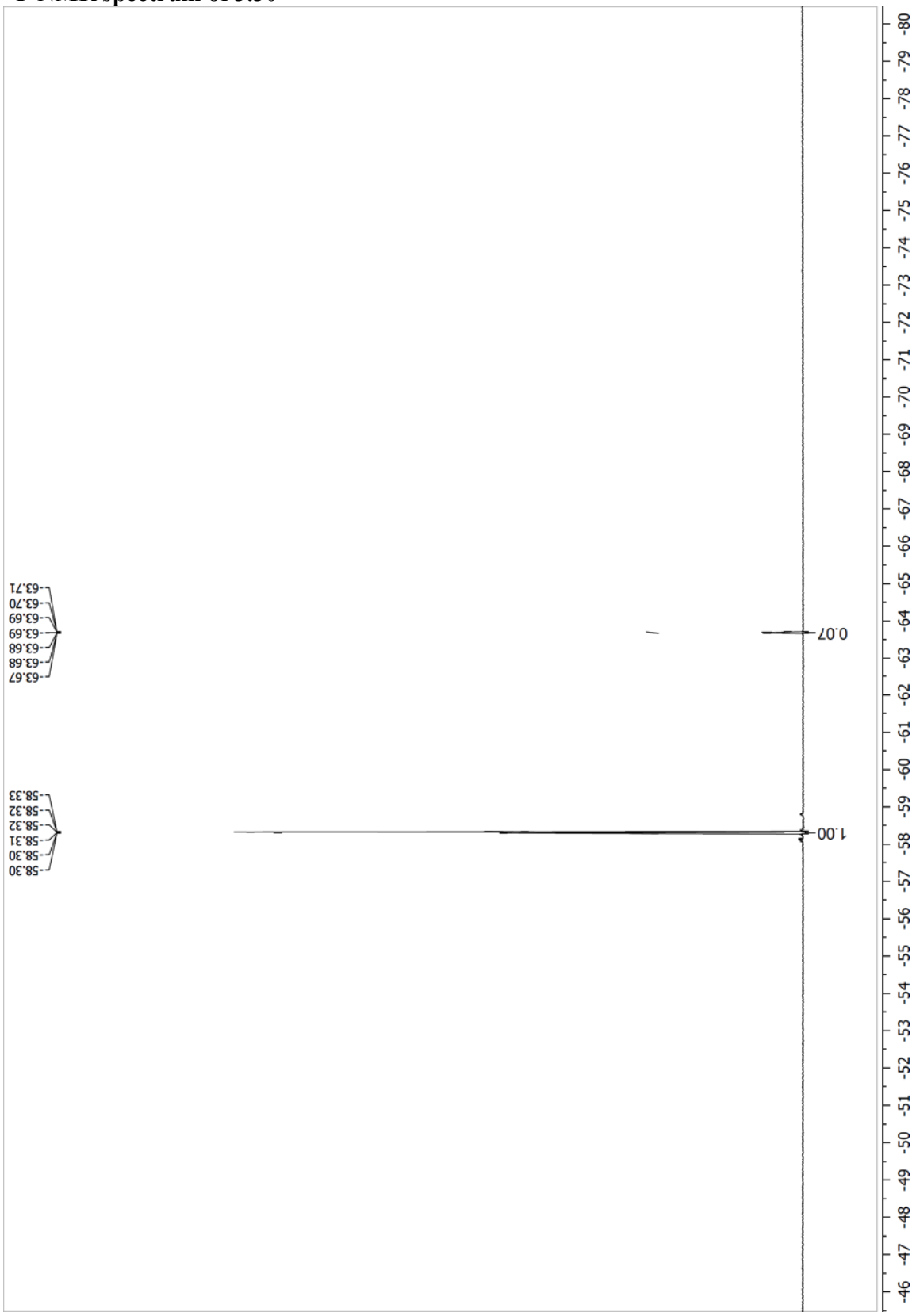
^{1}H NMR spectrum of 3.30



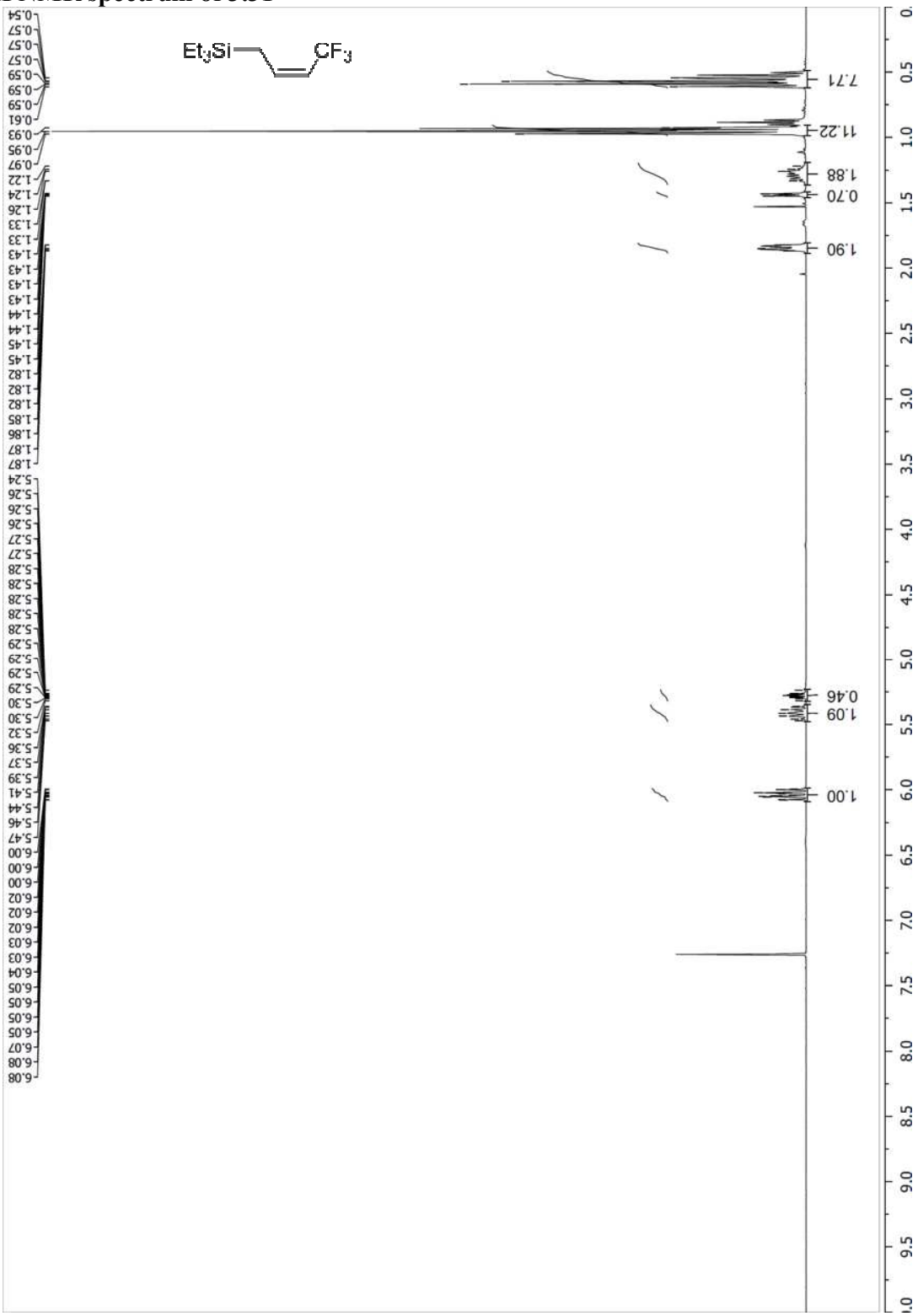
^{13}C NMR spectrum of 3.30



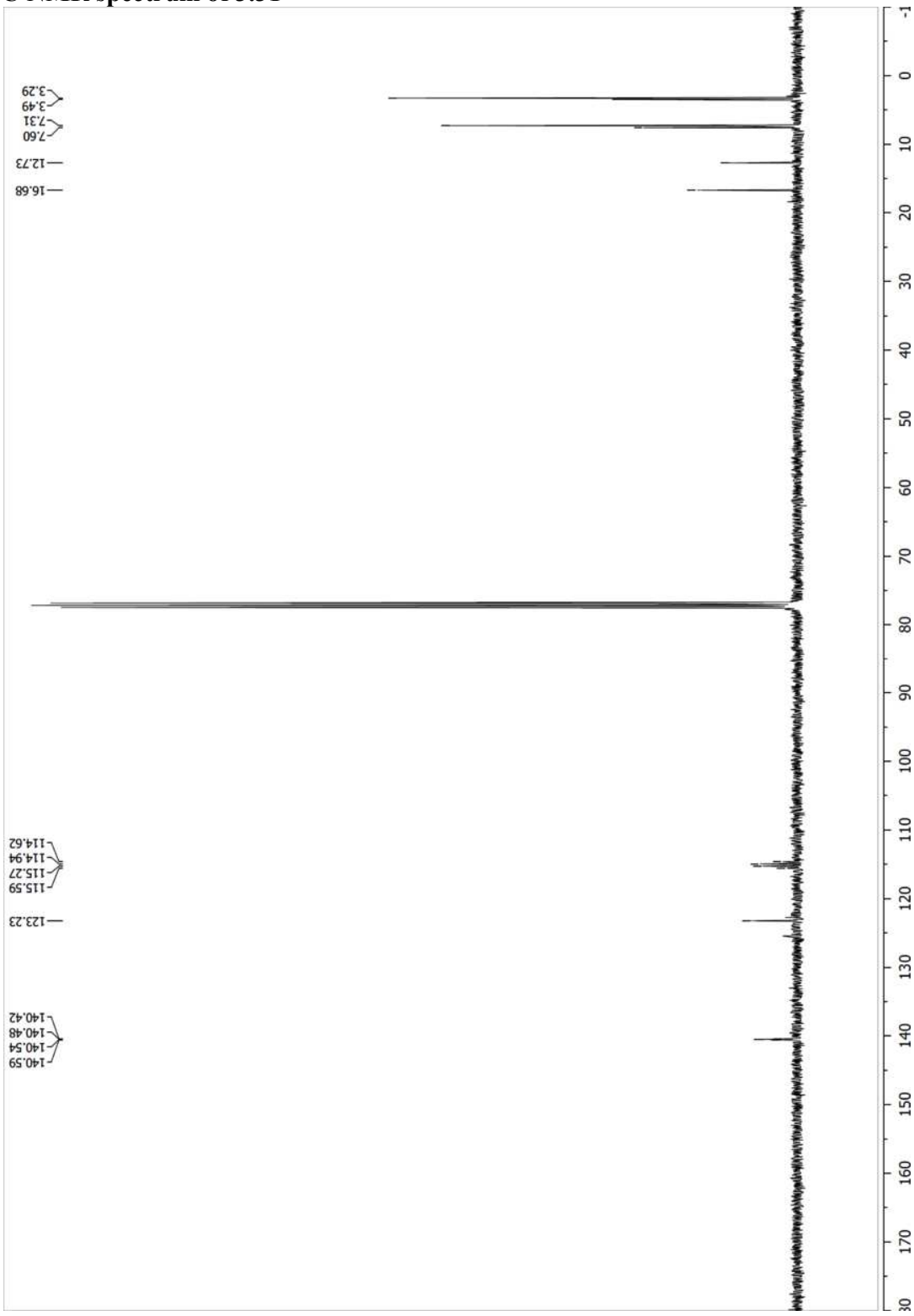
^{19}F NMR spectrum of 3.30



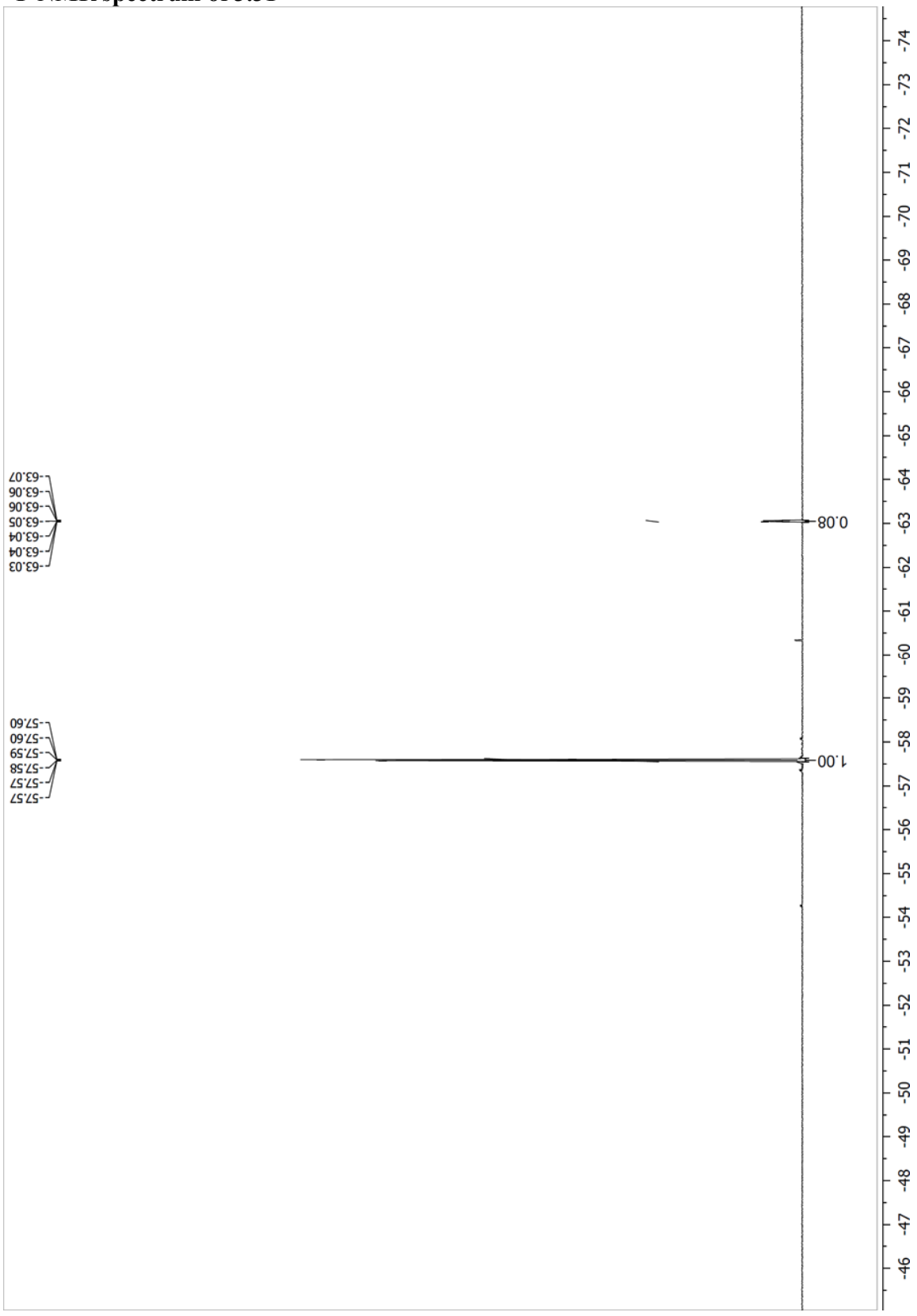
^{1}H NMR spectrum of 3.31



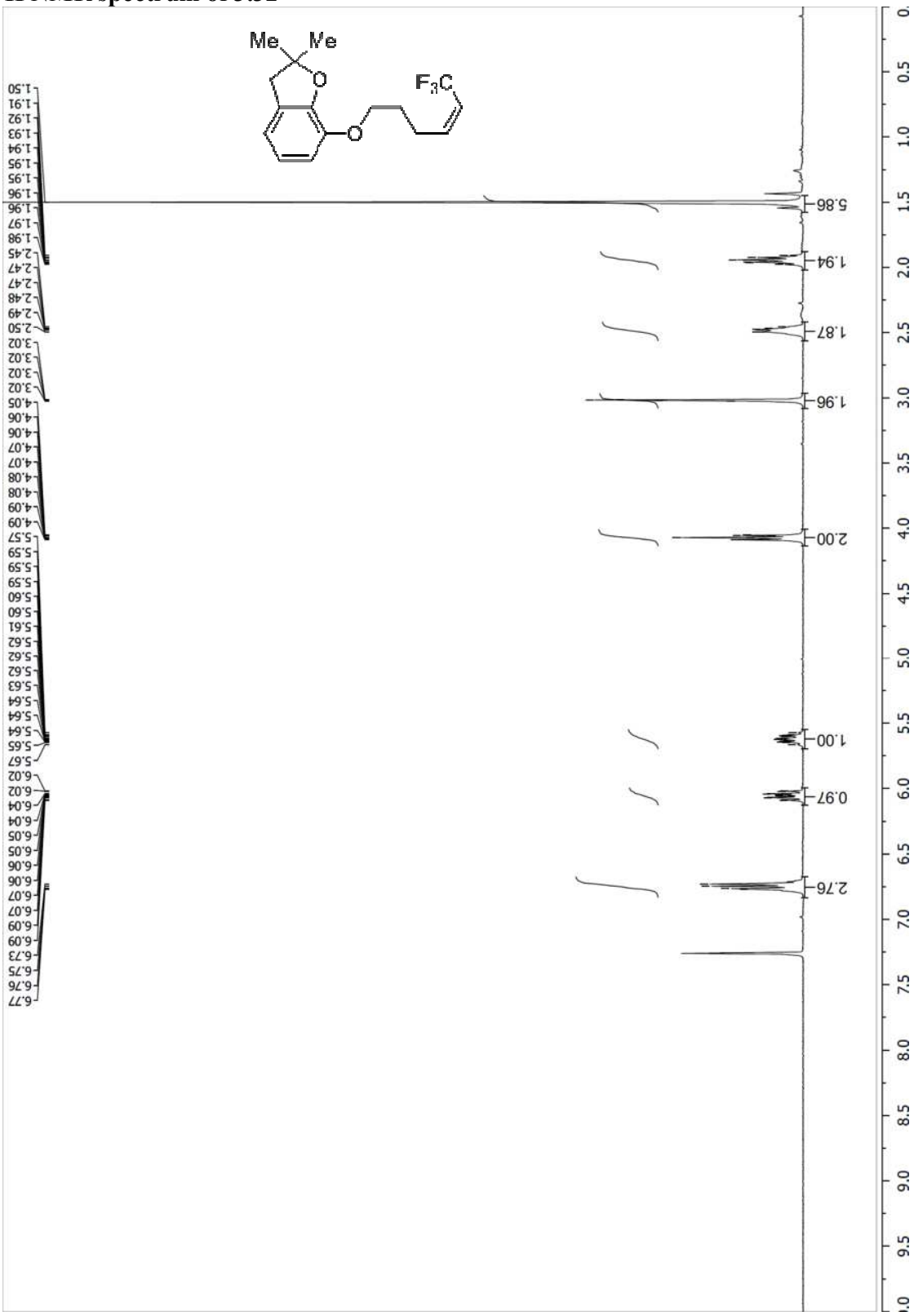
^{13}C NMR spectrum of 3.31



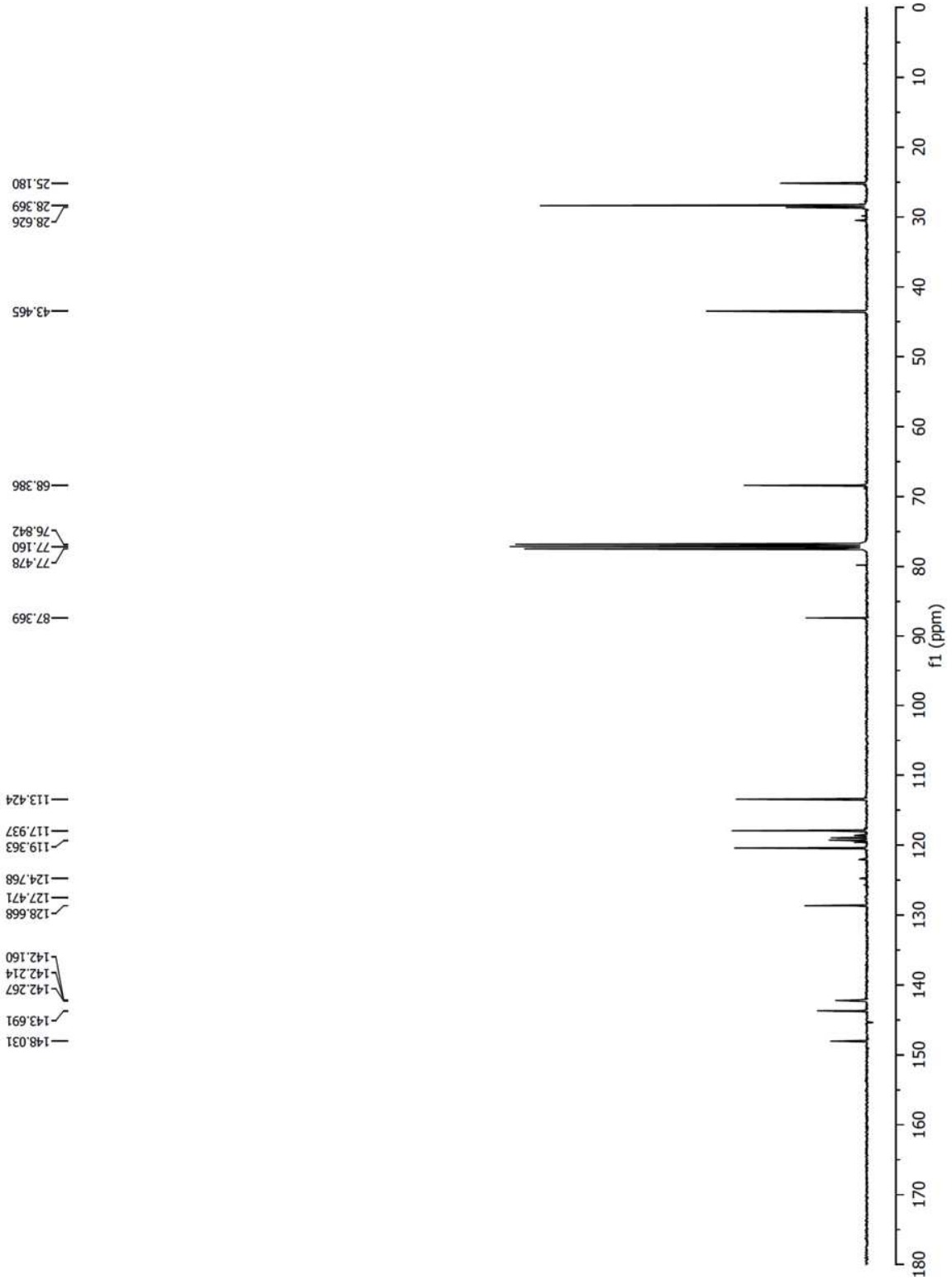
^{19}F NMR spectrum of 3.31



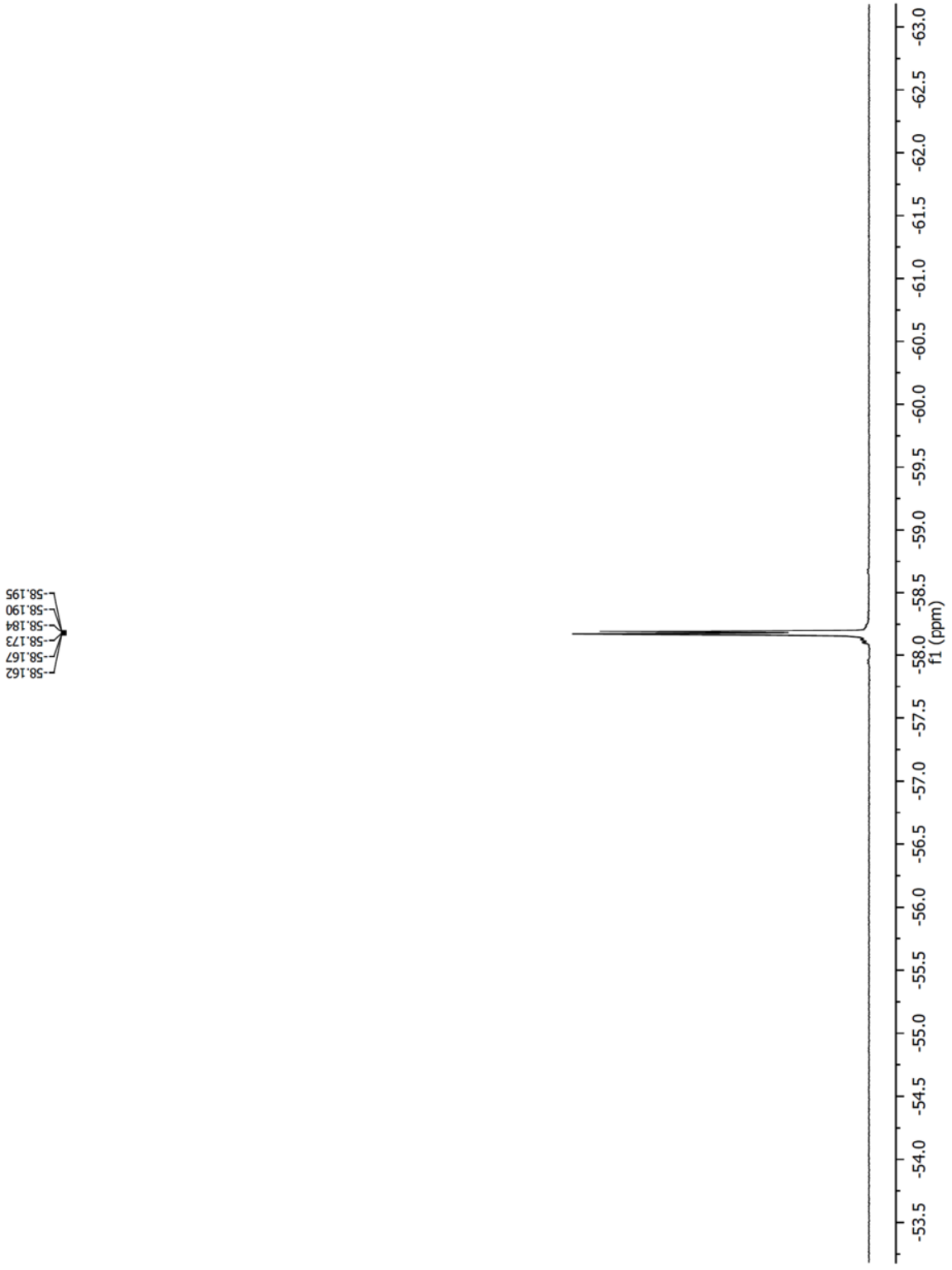
^{1}H NMR spectrum of 3.32



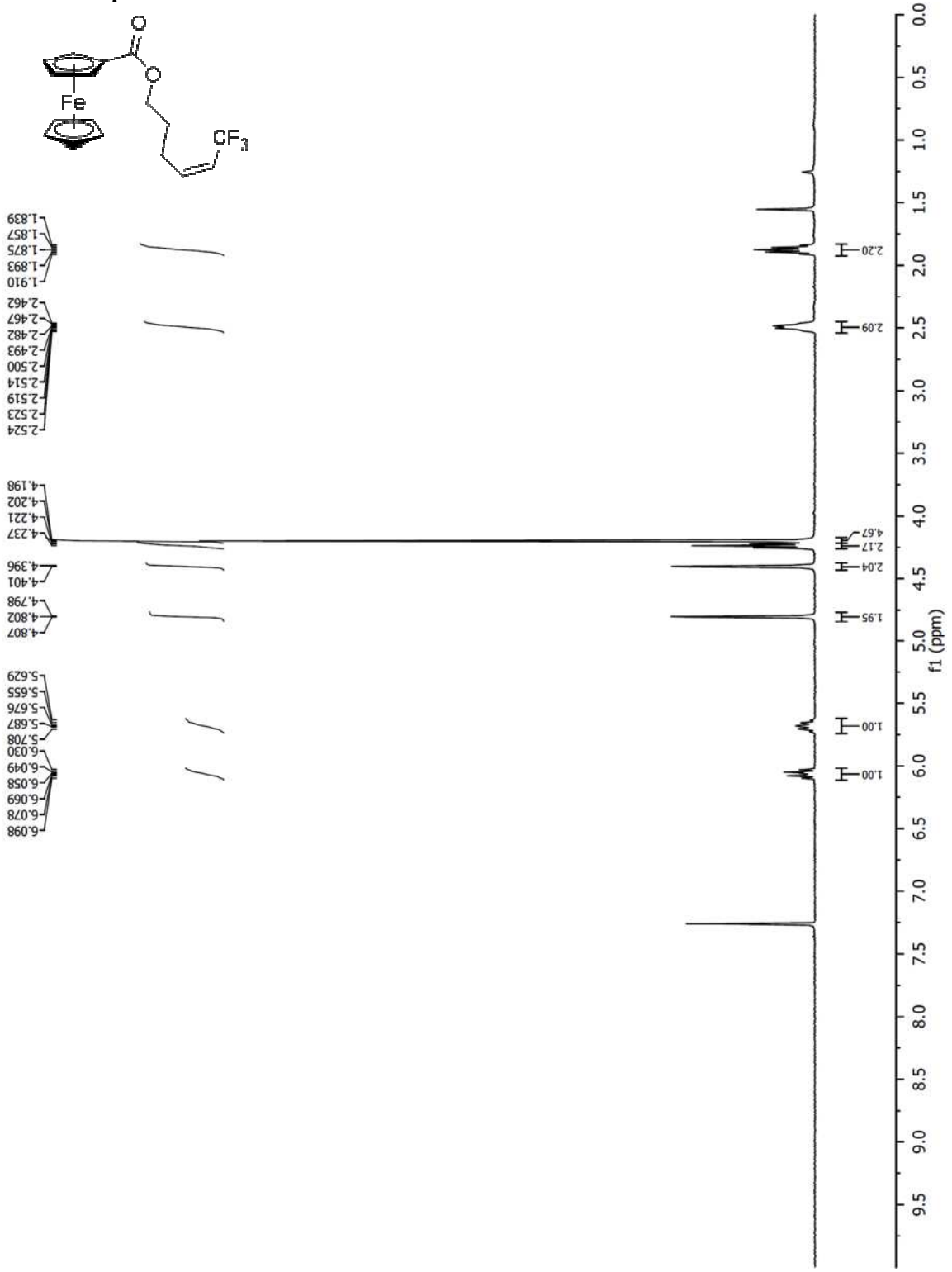
^{13}C NMR spectrum of 3.32



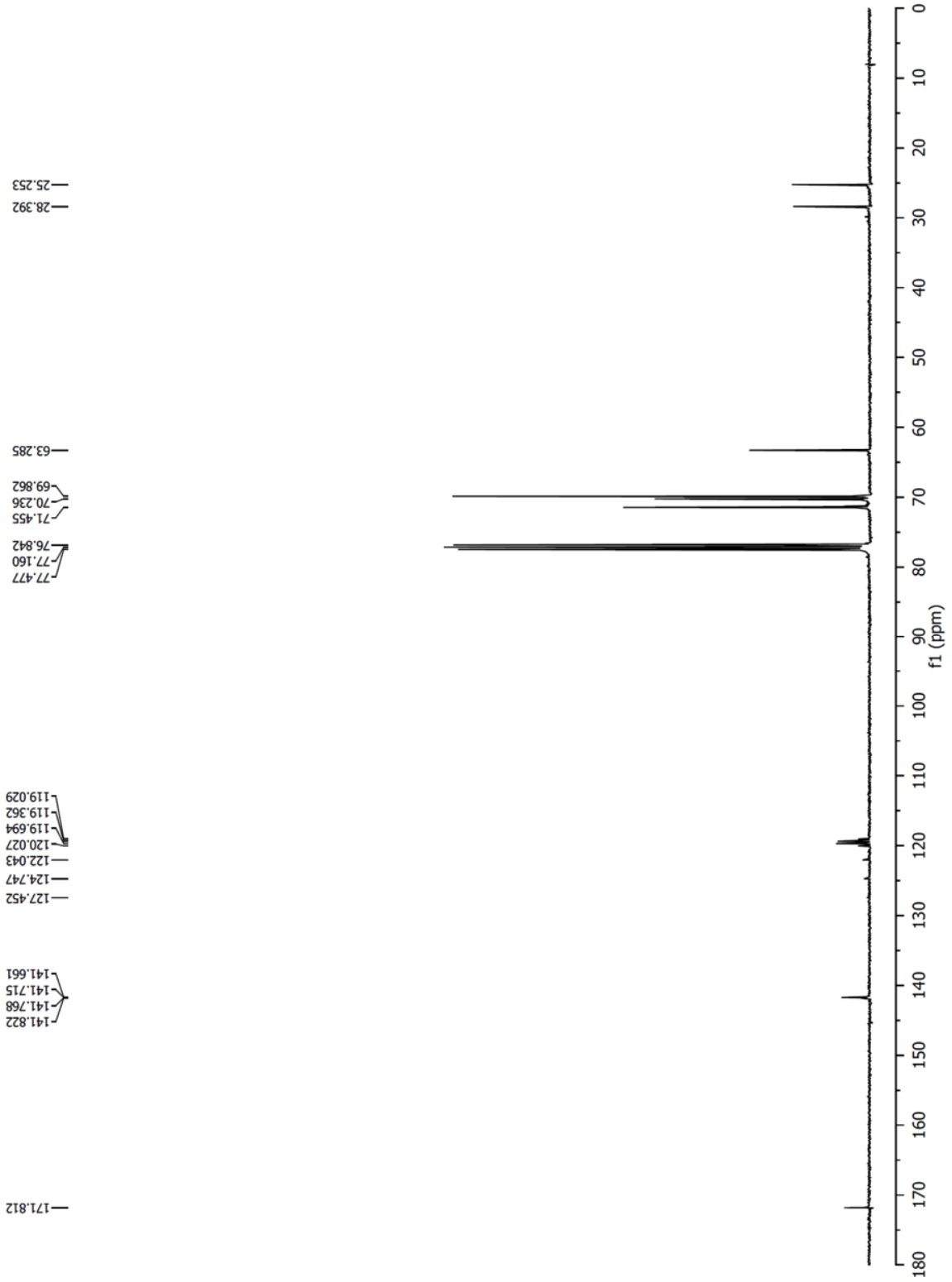
^{19}F NMR spectrum of 3.32



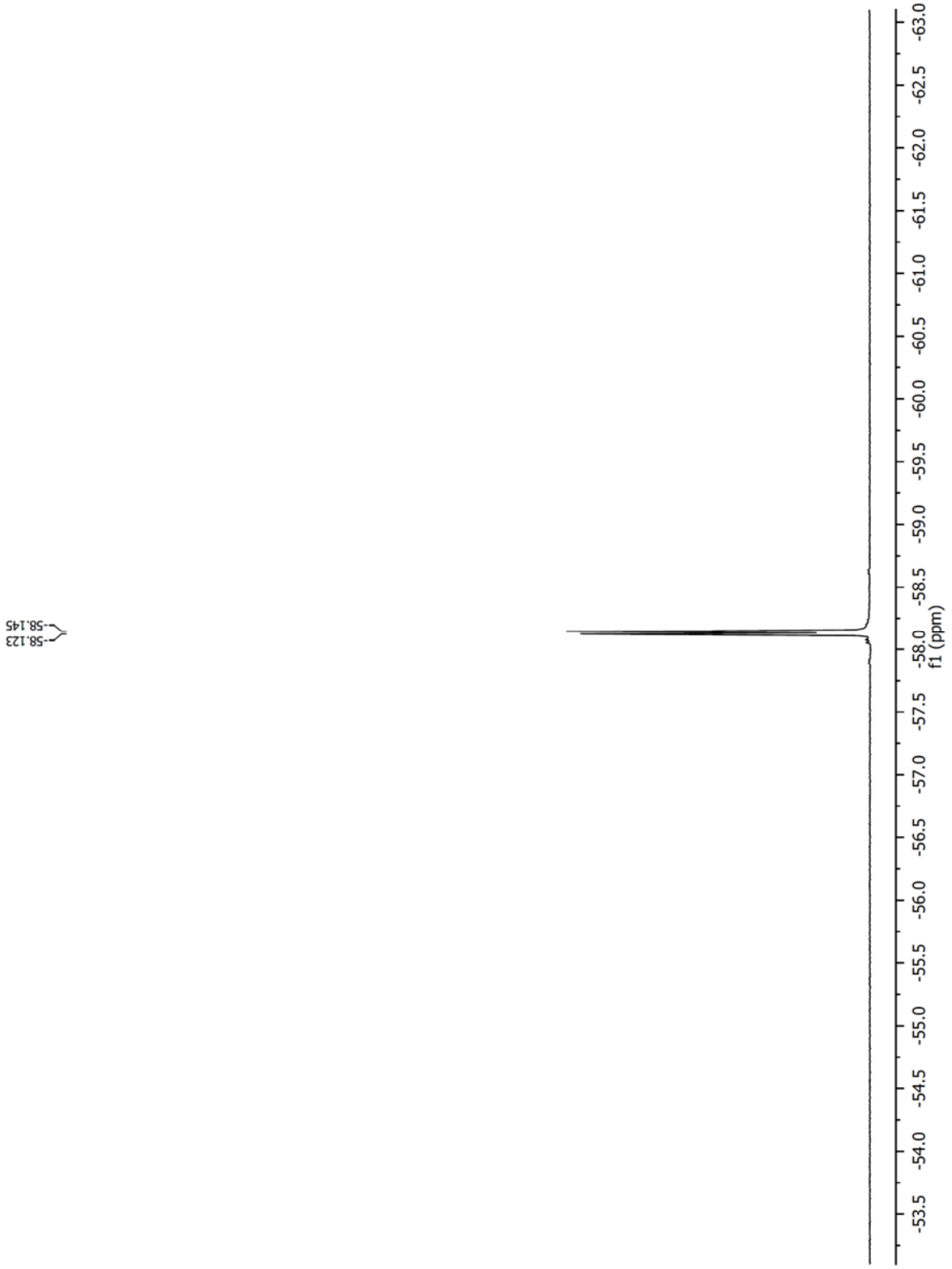
^{1}H NMR spectrum of 3.33



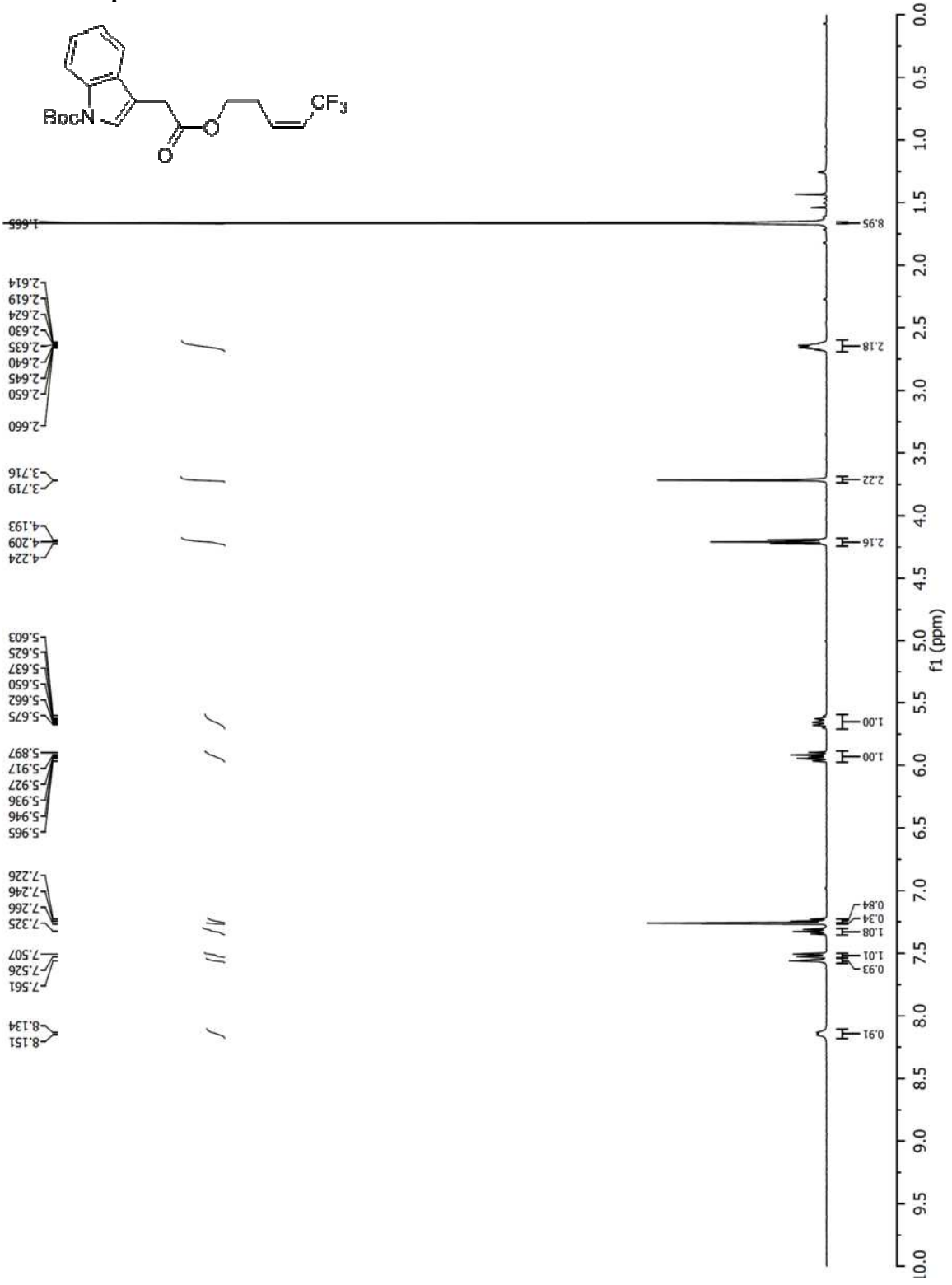
^{13}C NMR spectrum of 3.33



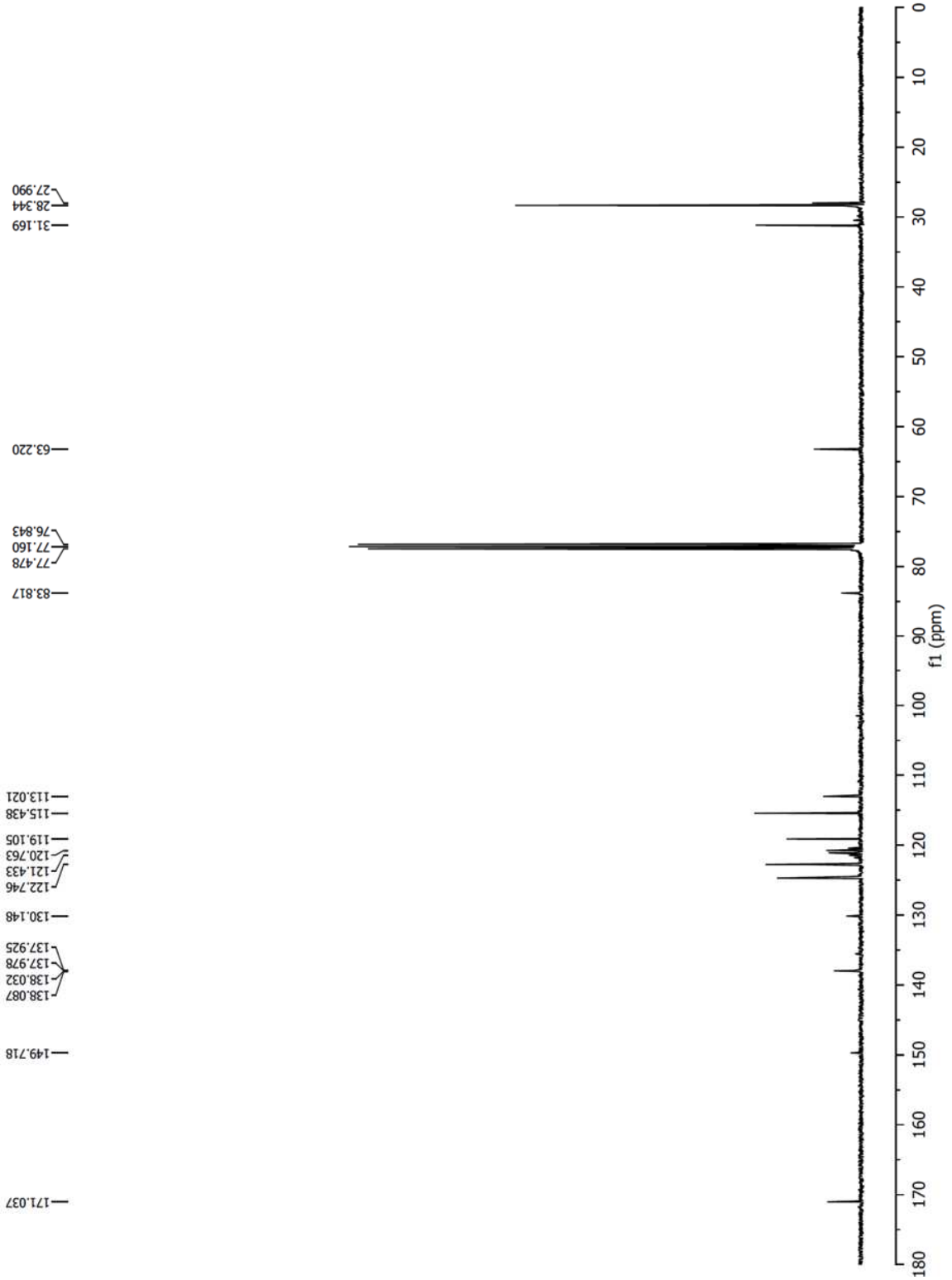
^{19}F NMR spectrum of 3.33



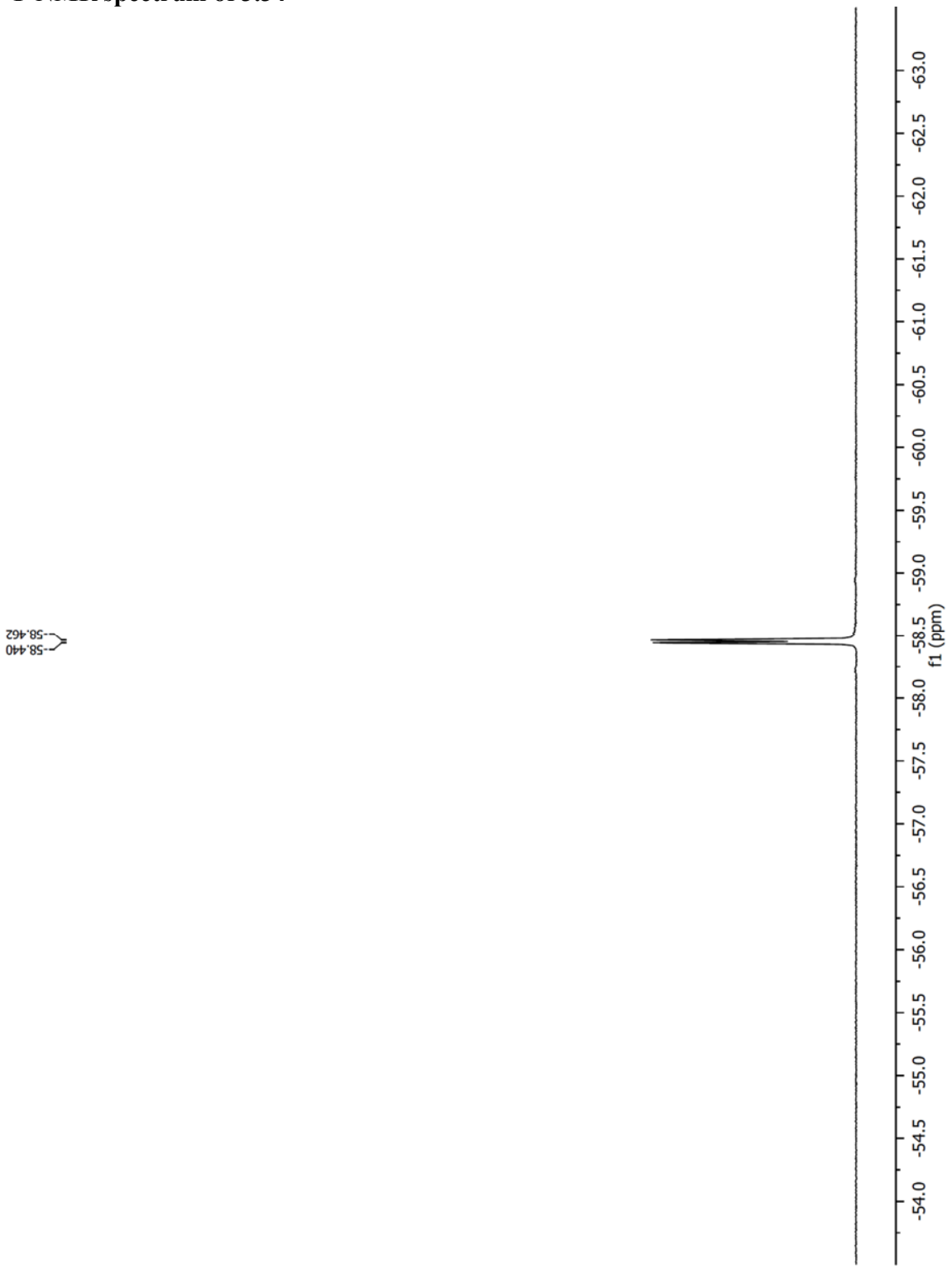
^{1}H NMR spectrum of 3.34



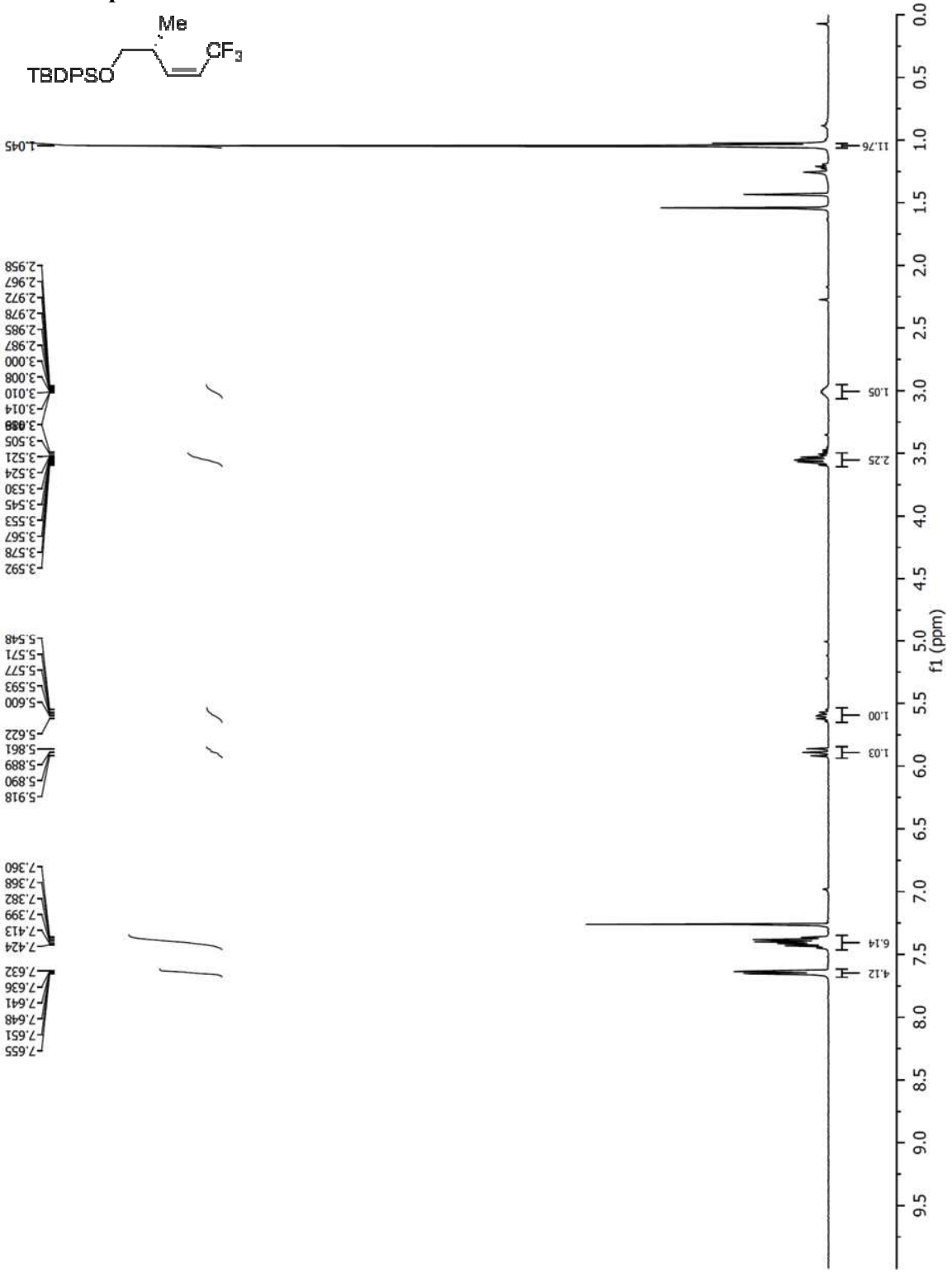
^{13}C NMR spectrum of 3.34



^{19}F NMR spectrum of 3.34



^{1}H NMR spectrum of 3.35



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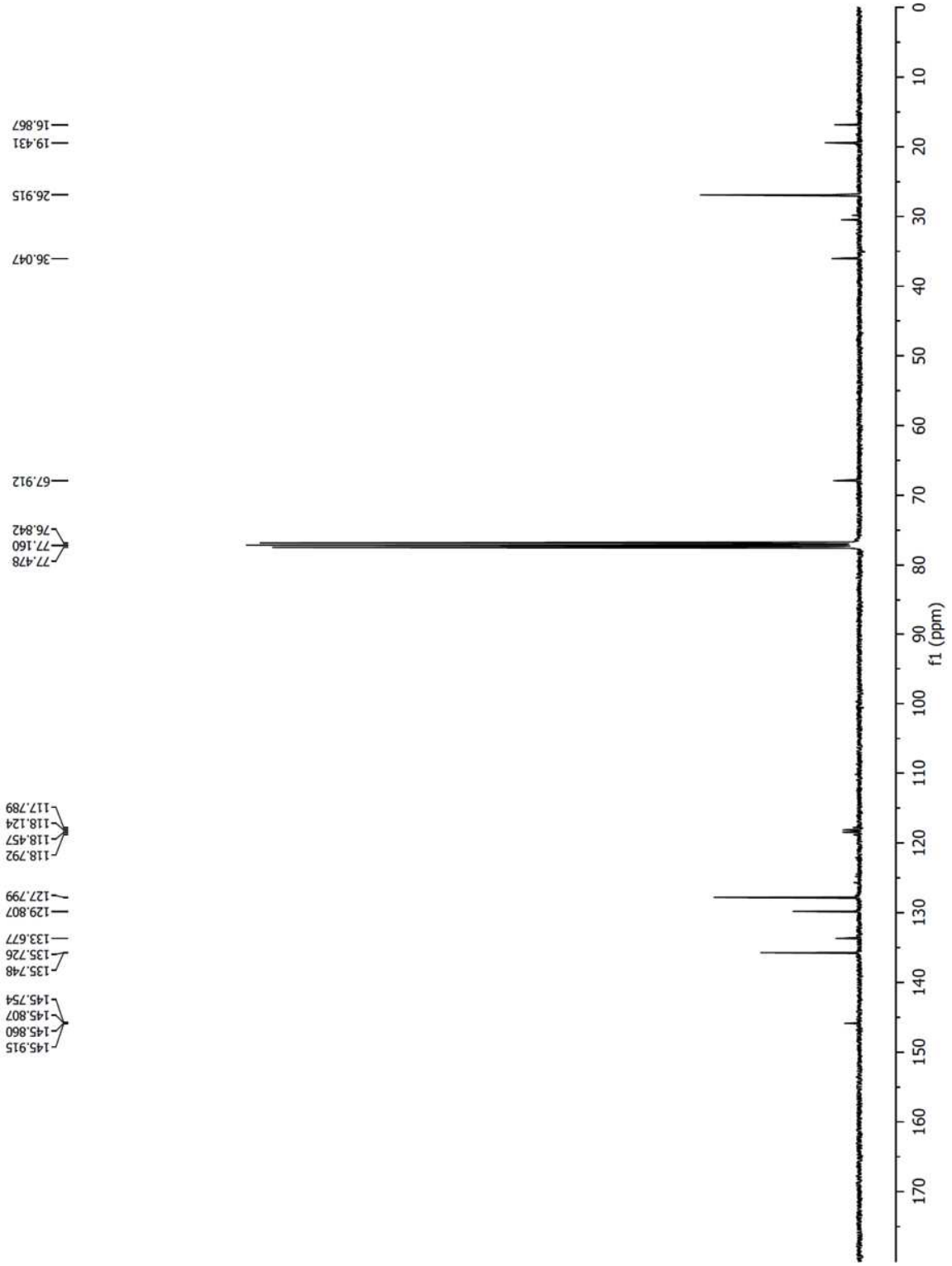
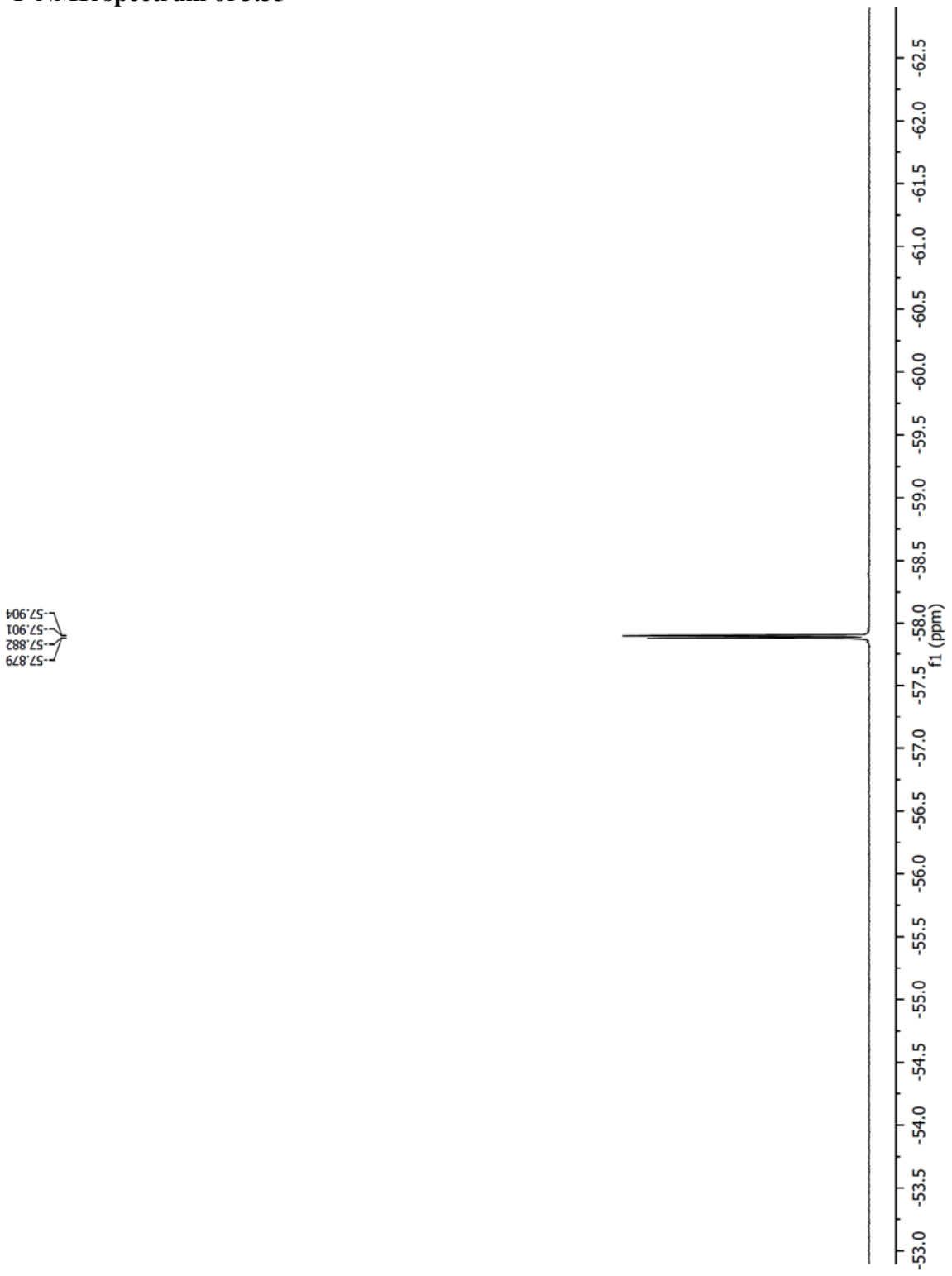


^{19}F NMR spectrum of 3.35



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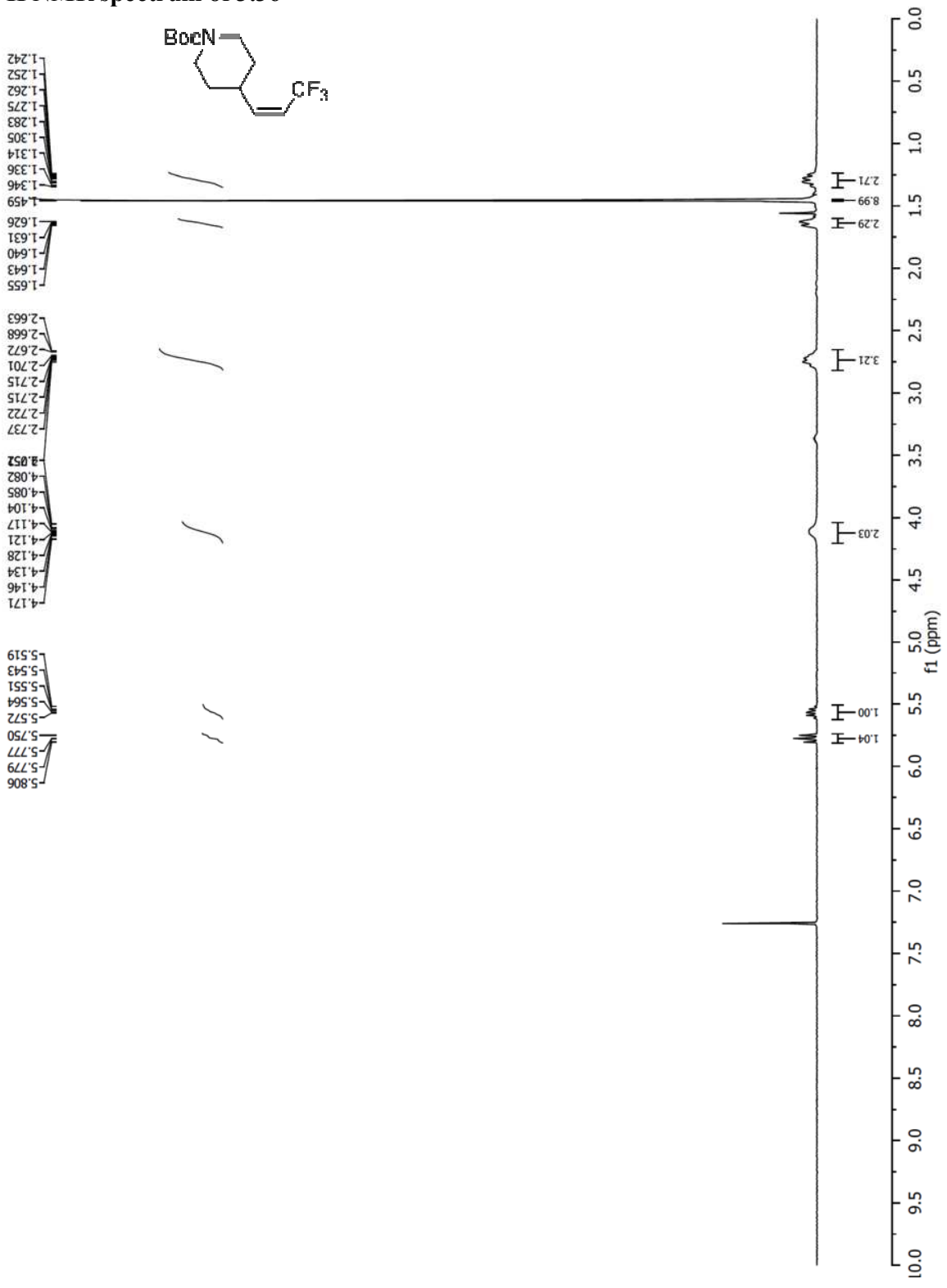
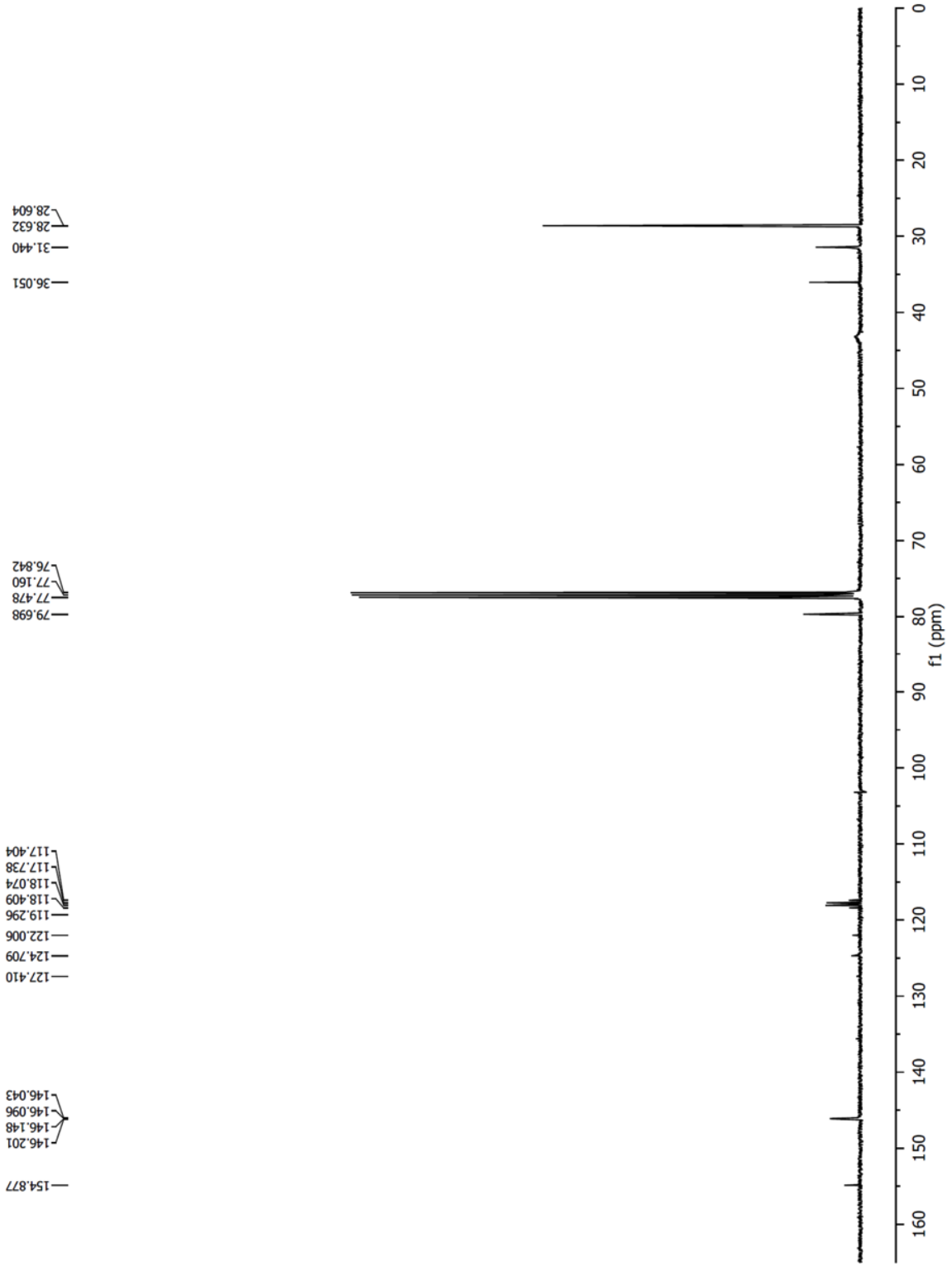


^{13}C NMR spectrum of 3.36



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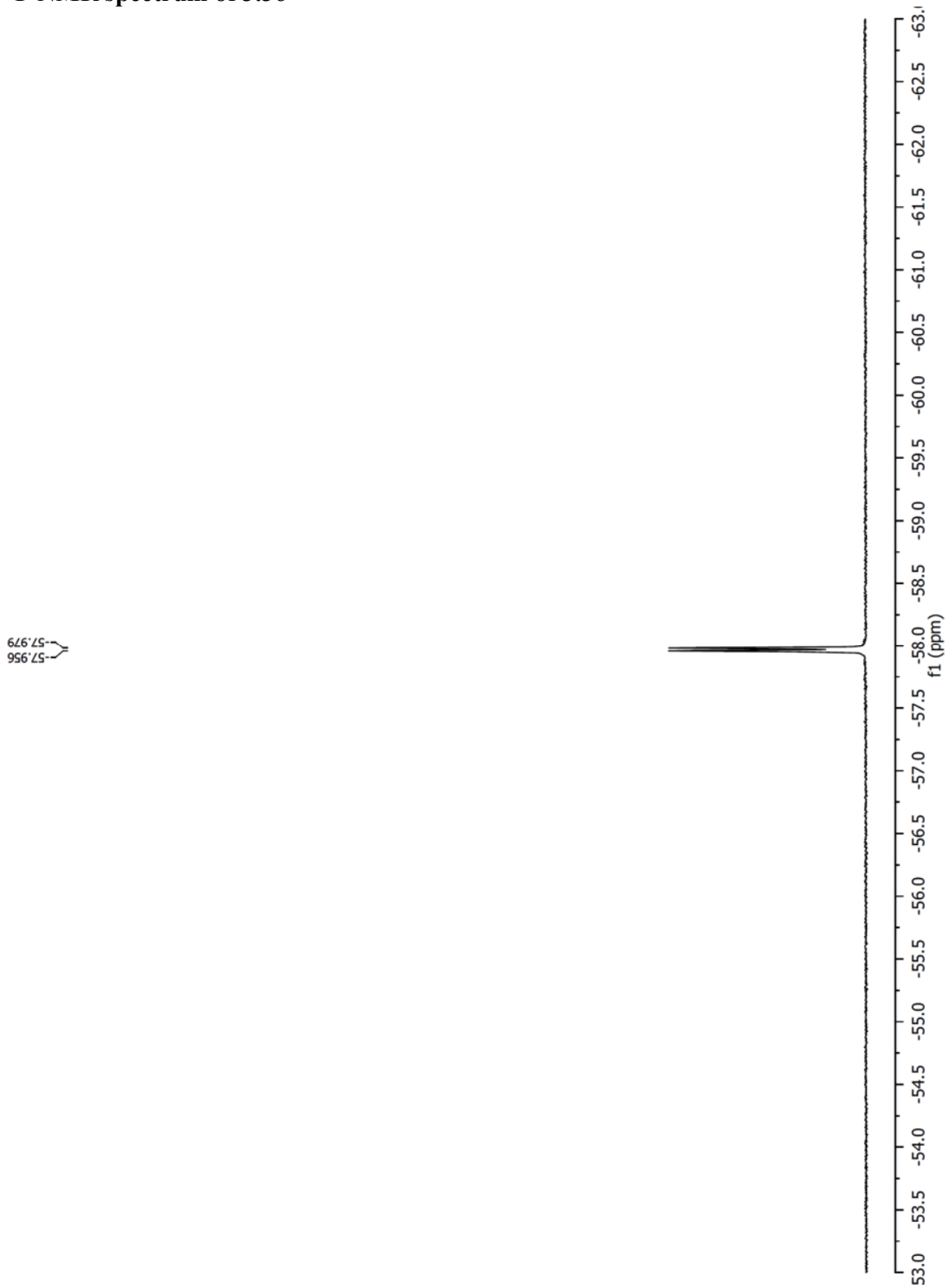
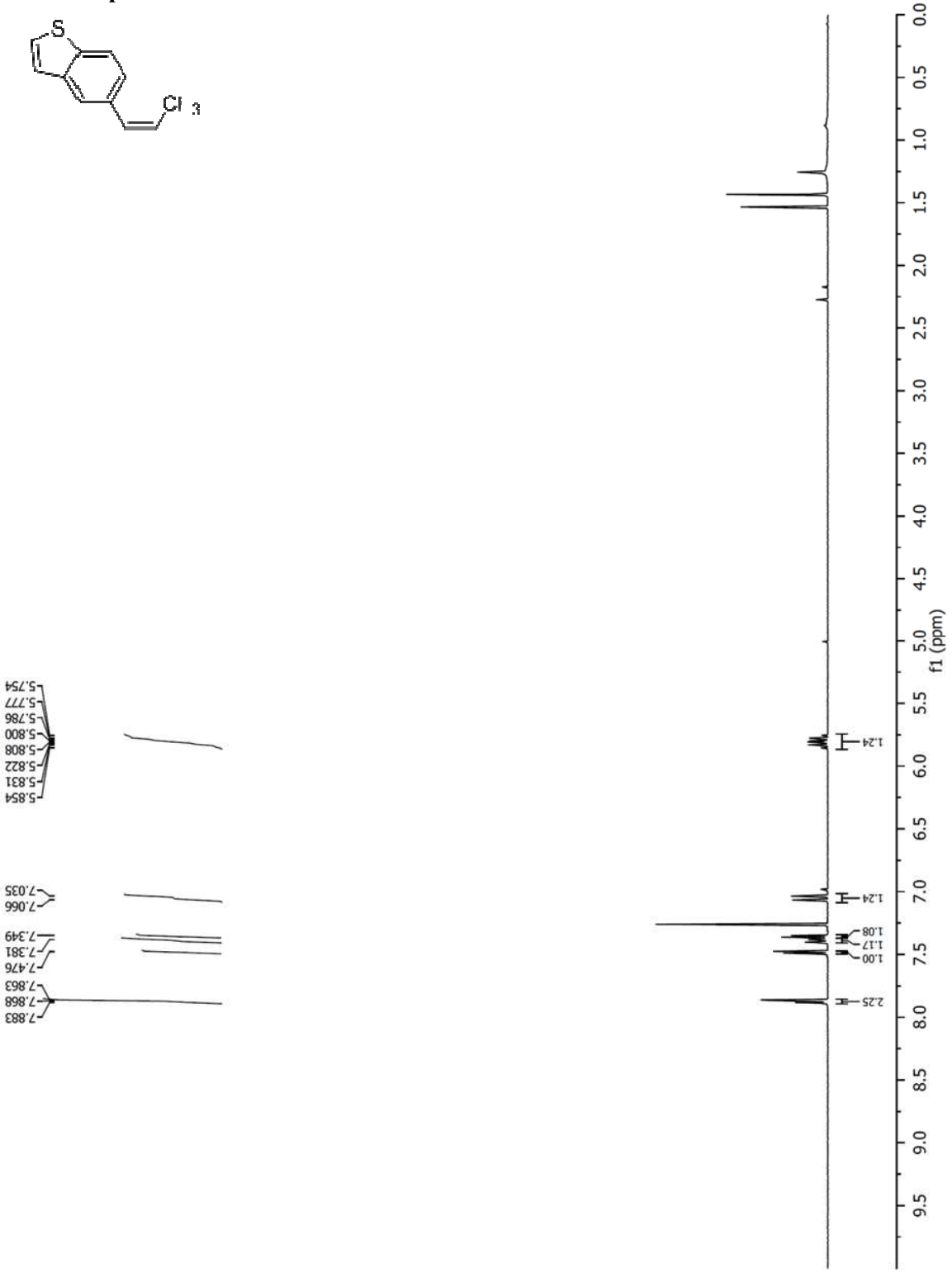
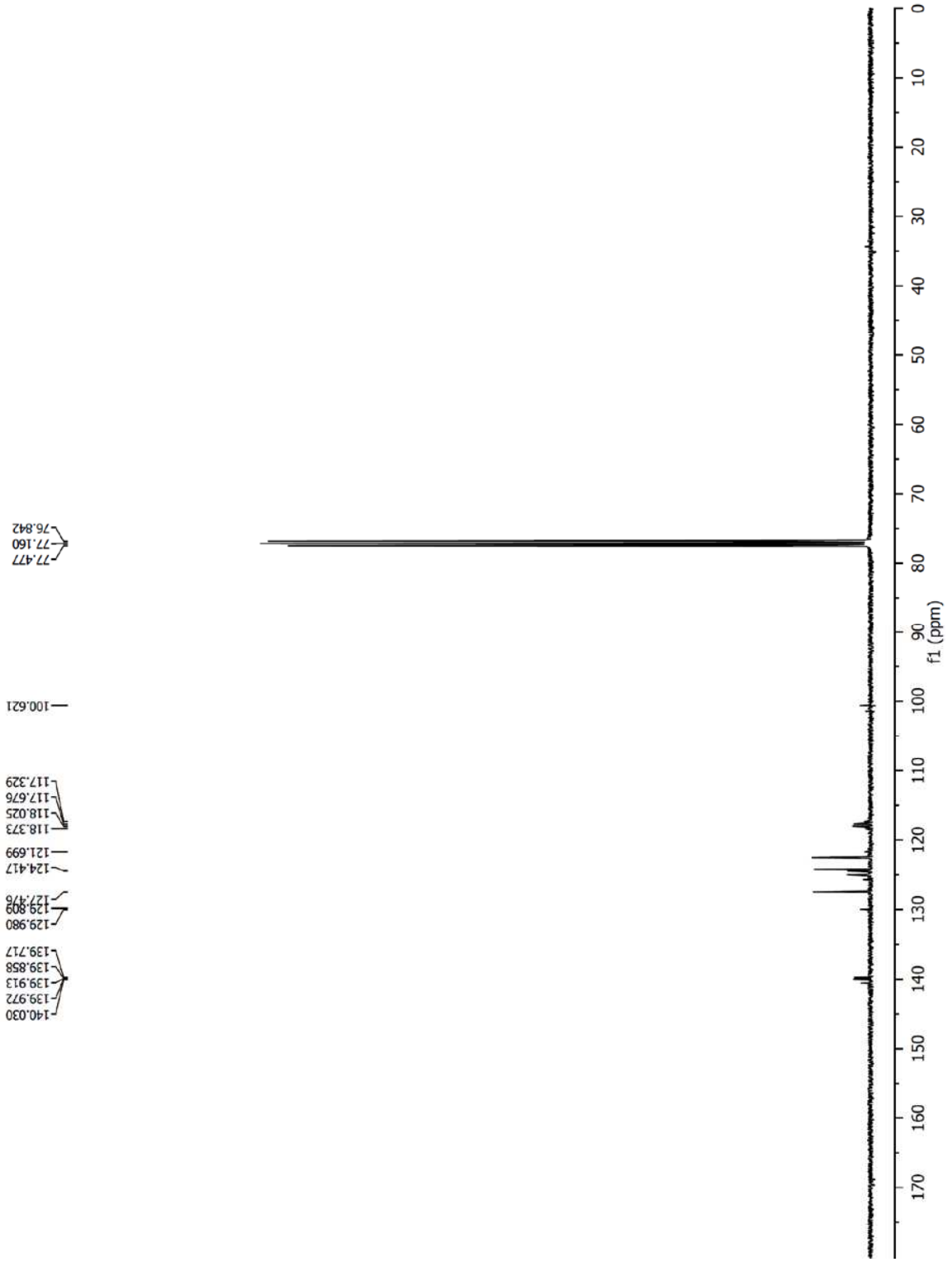


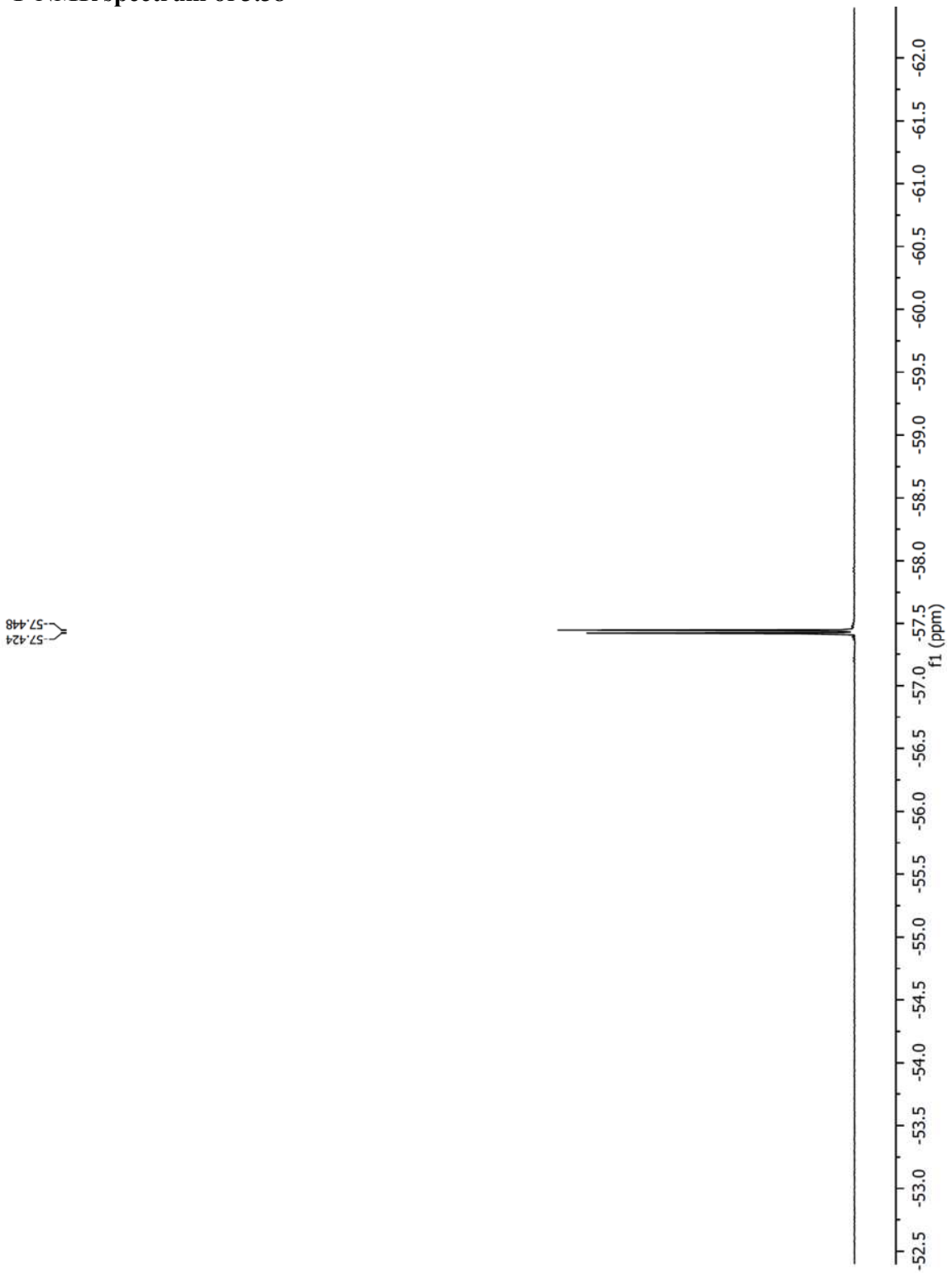
^{1}H NMR spectrum of 3.38



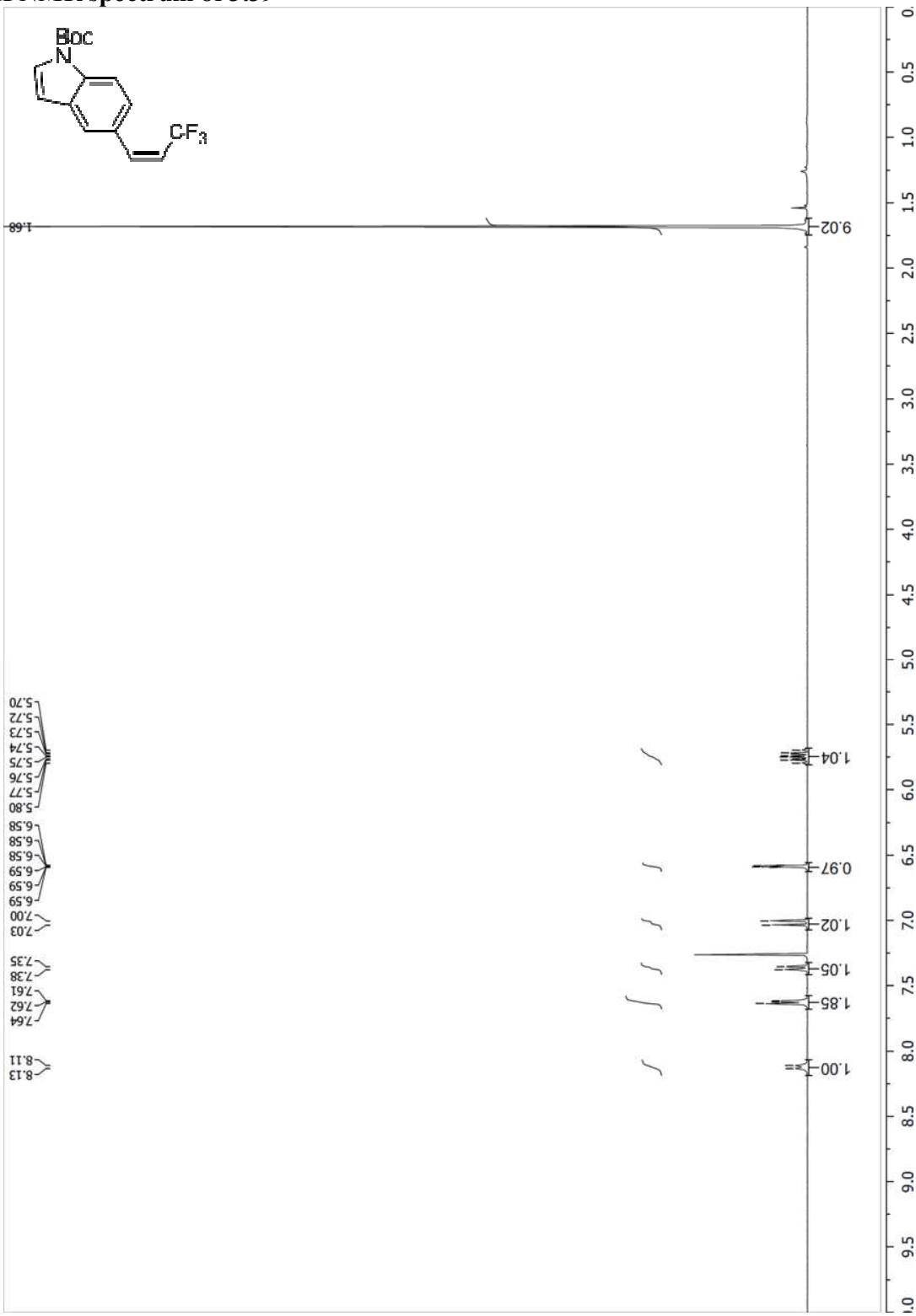
^{13}C NMR spectrum of 3.38



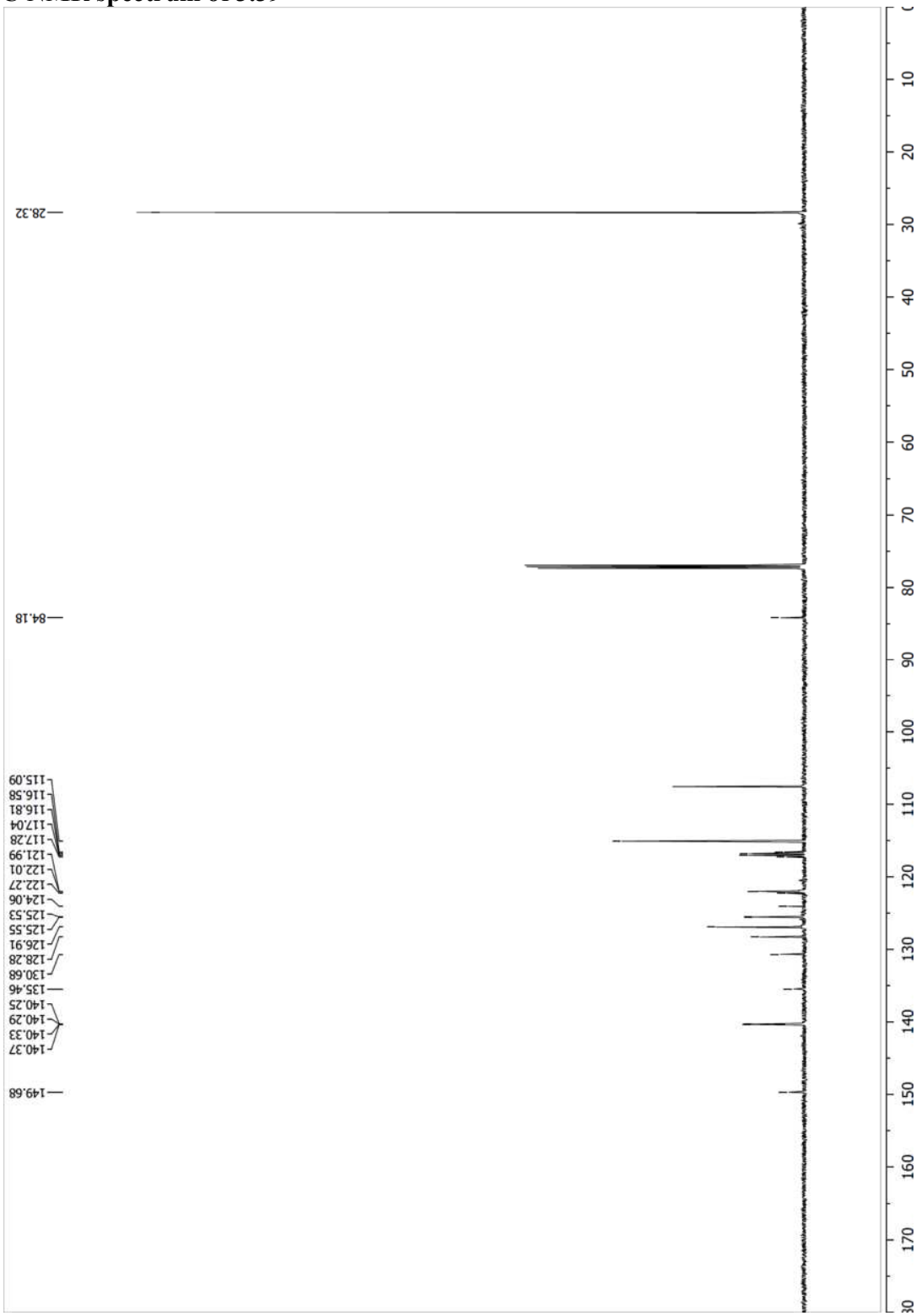
^{19}F NMR spectrum of 3.38



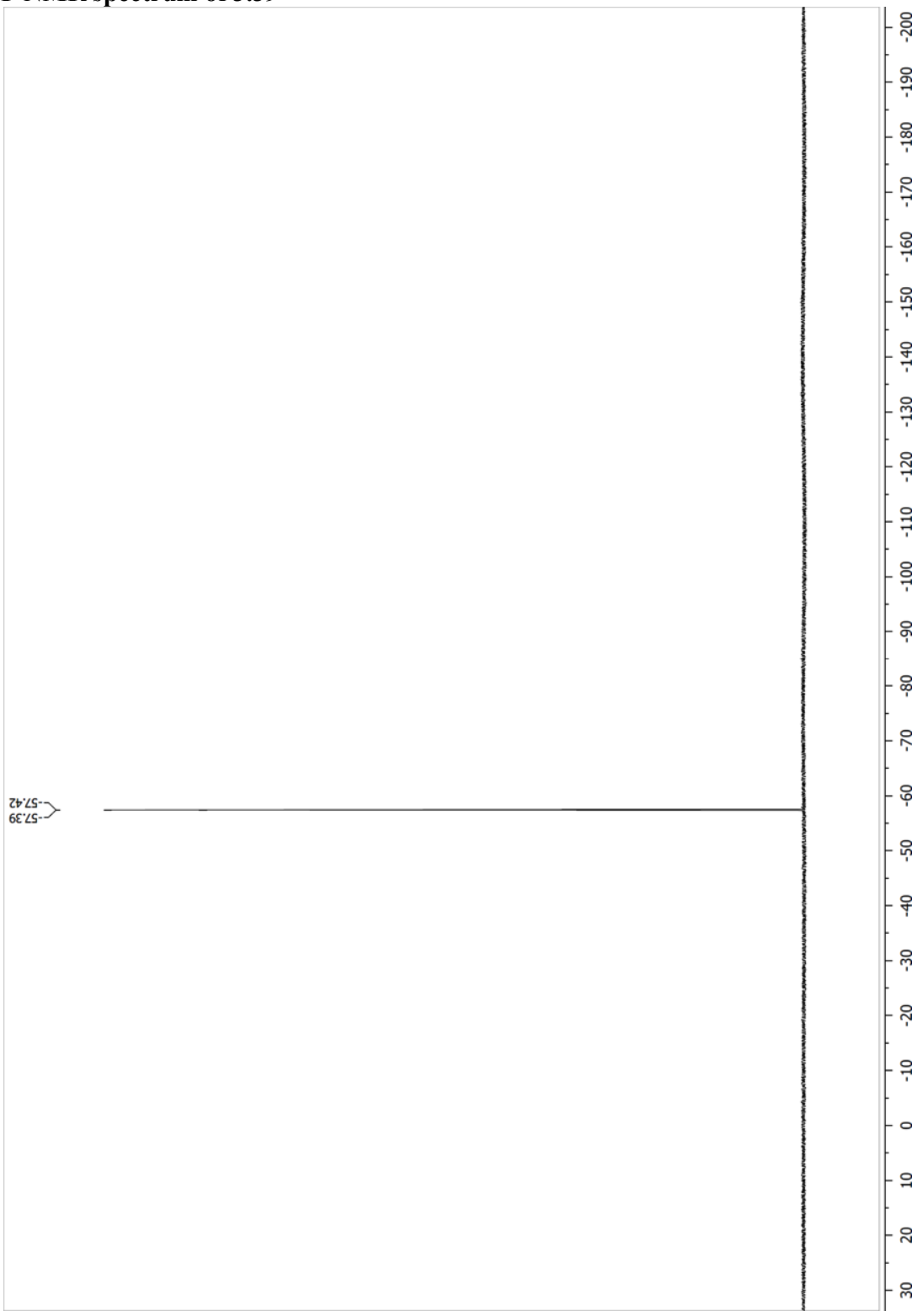
^{1}H NMR spectrum of 3.39



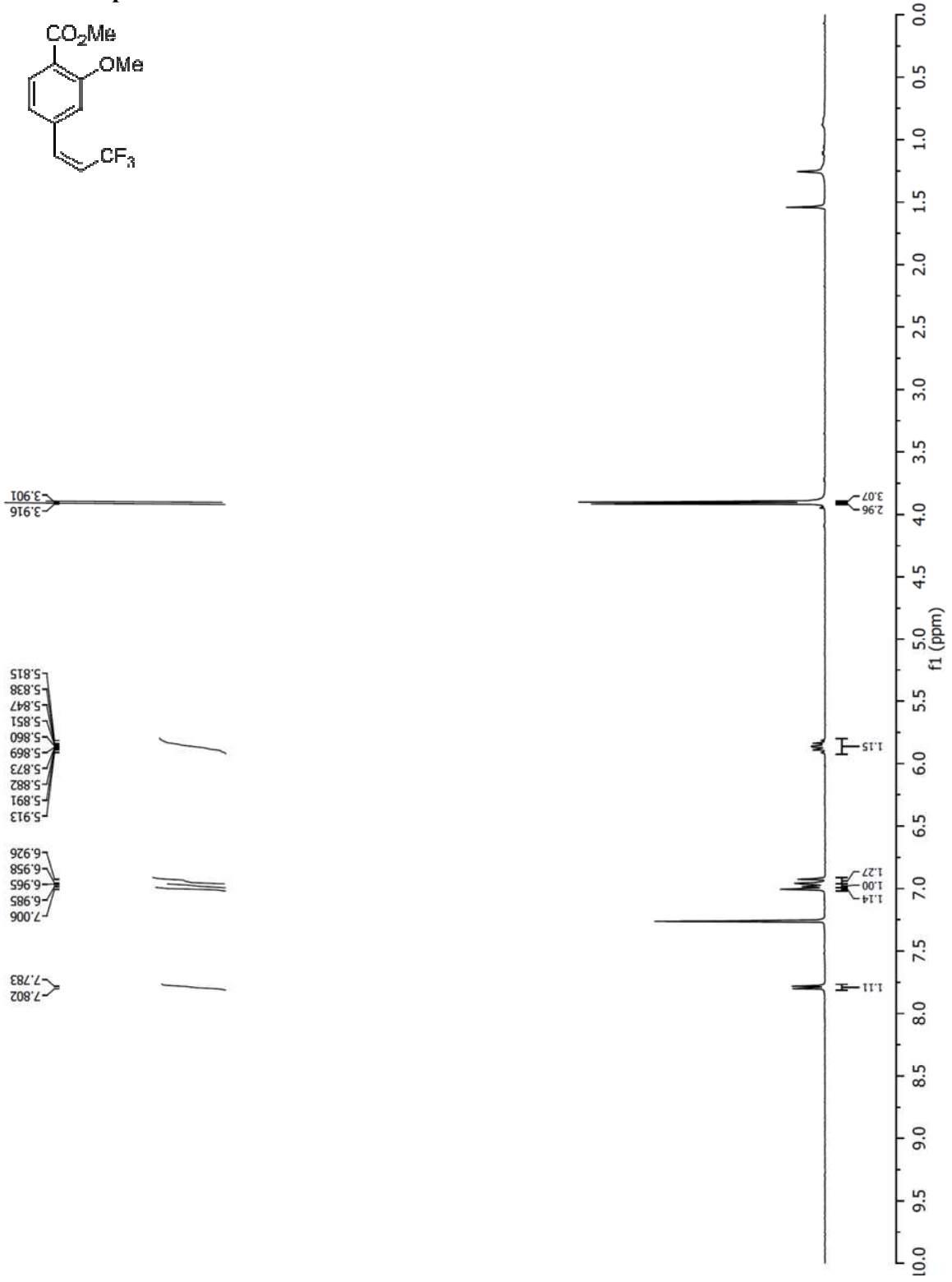
^{13}C NMR spectrum of 3.39



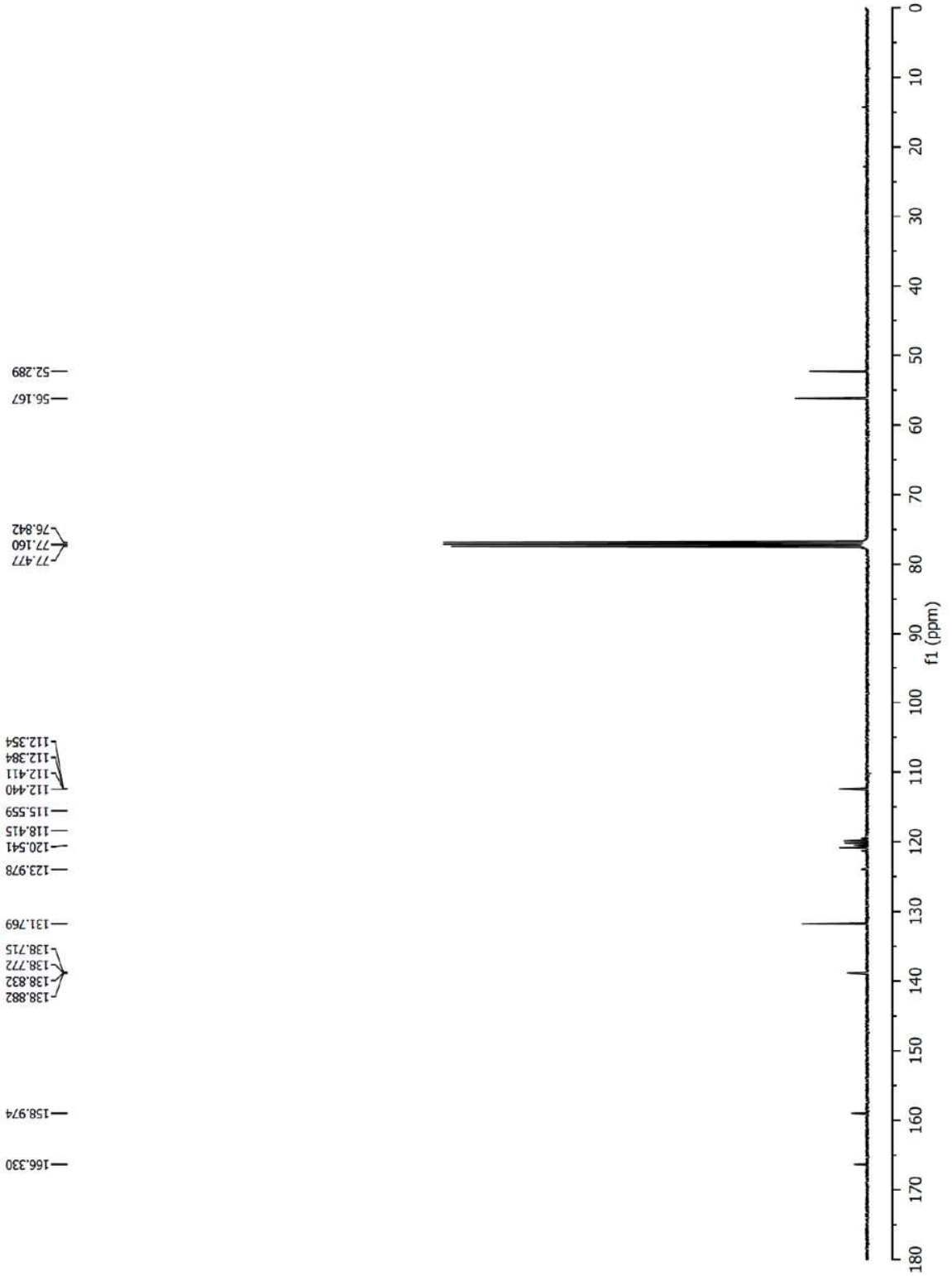
^{19}F NMR spectrum of 3.39



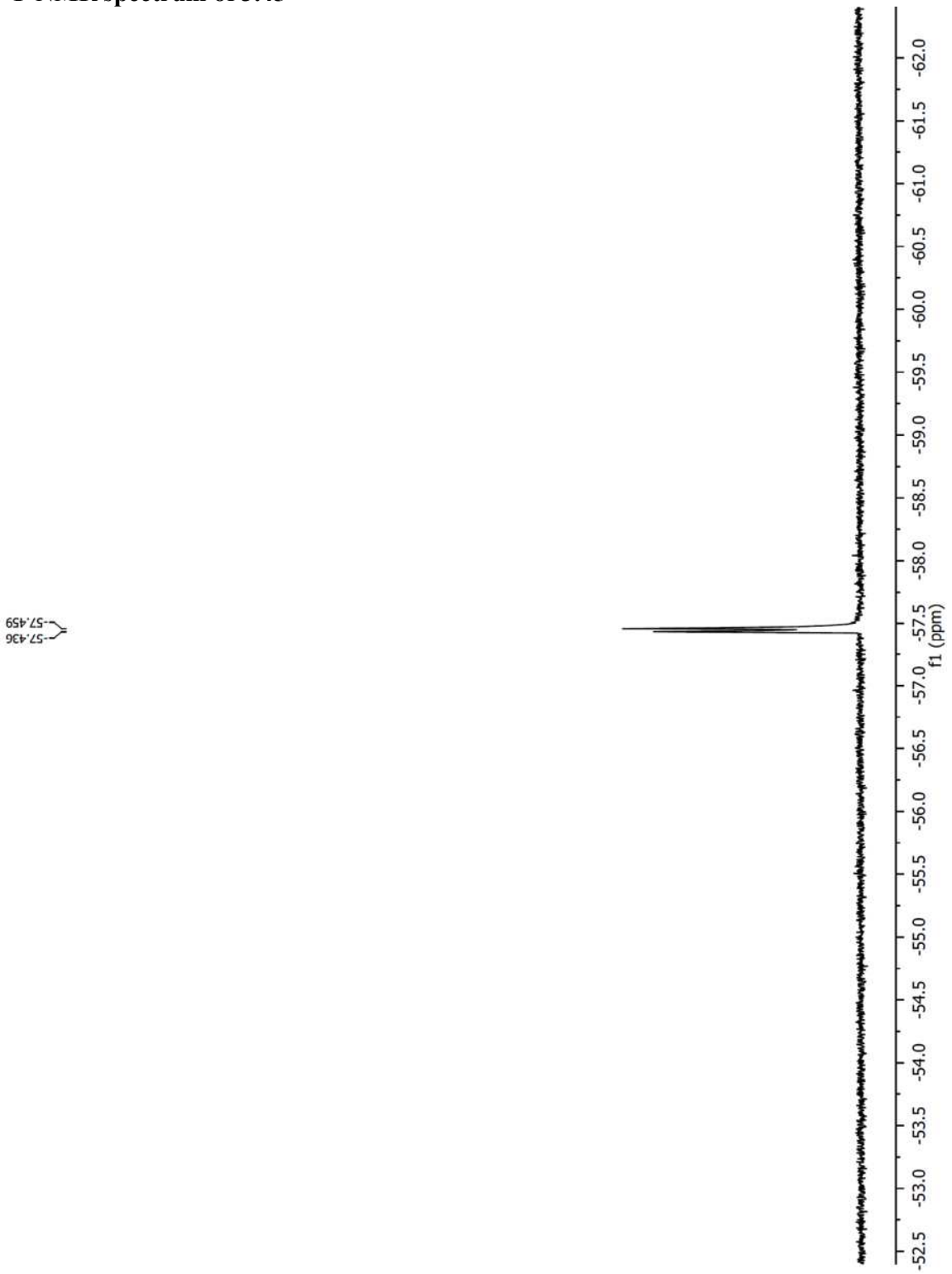
^{1}H NMR spectrum of 3.45



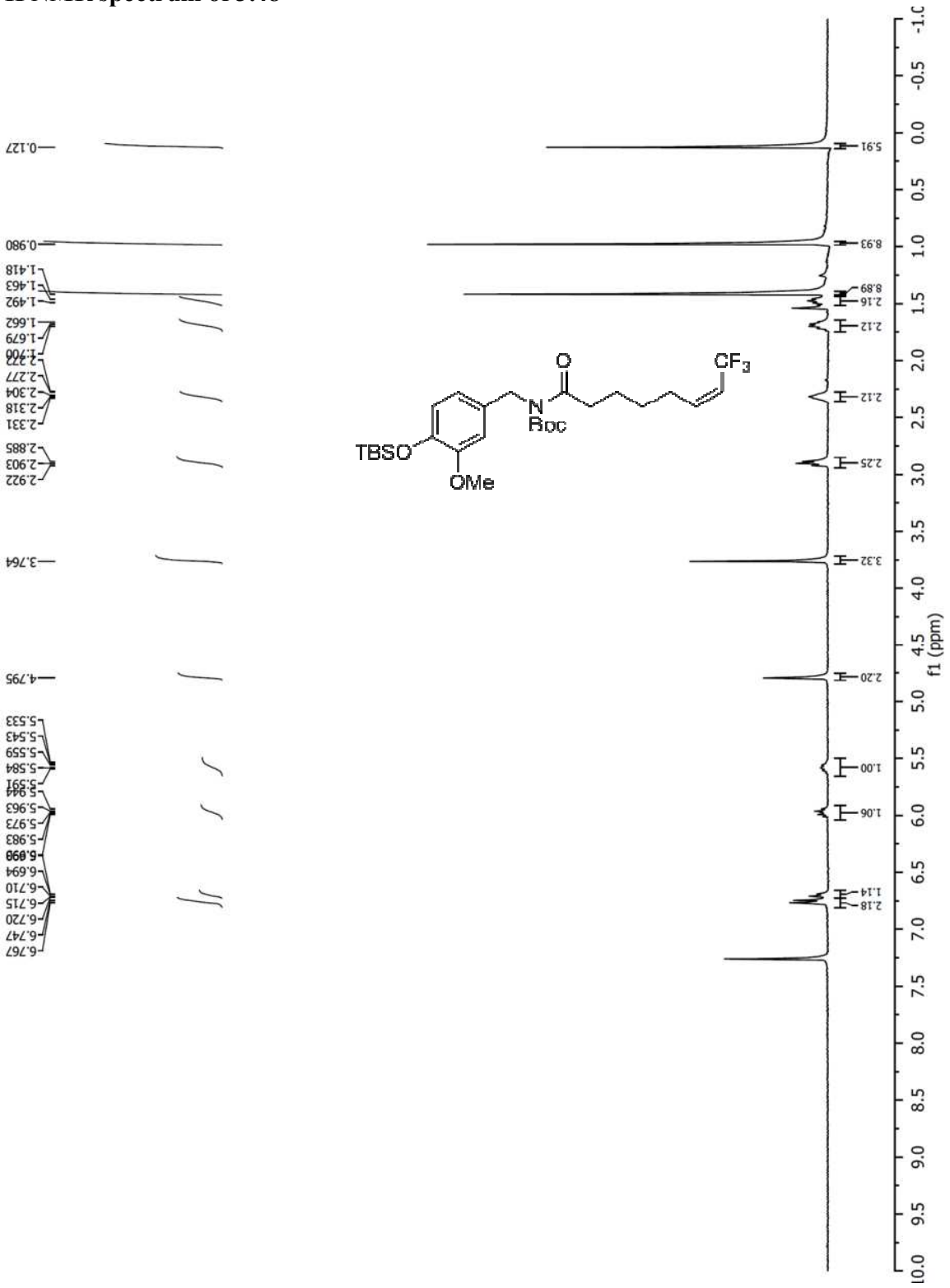
^{13}C NMR spectrum of 3.45



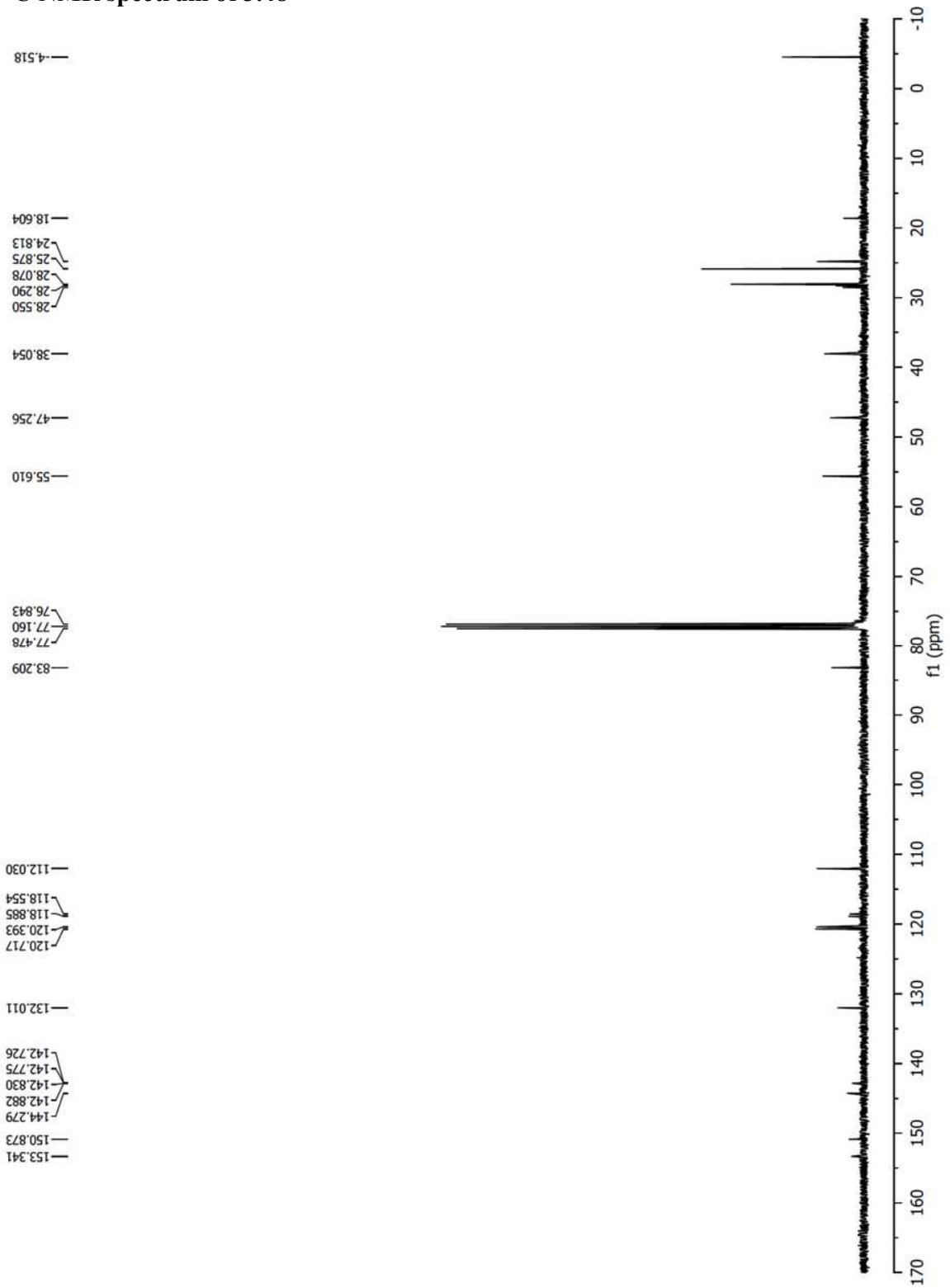
^{19}F NMR spectrum of 3.45



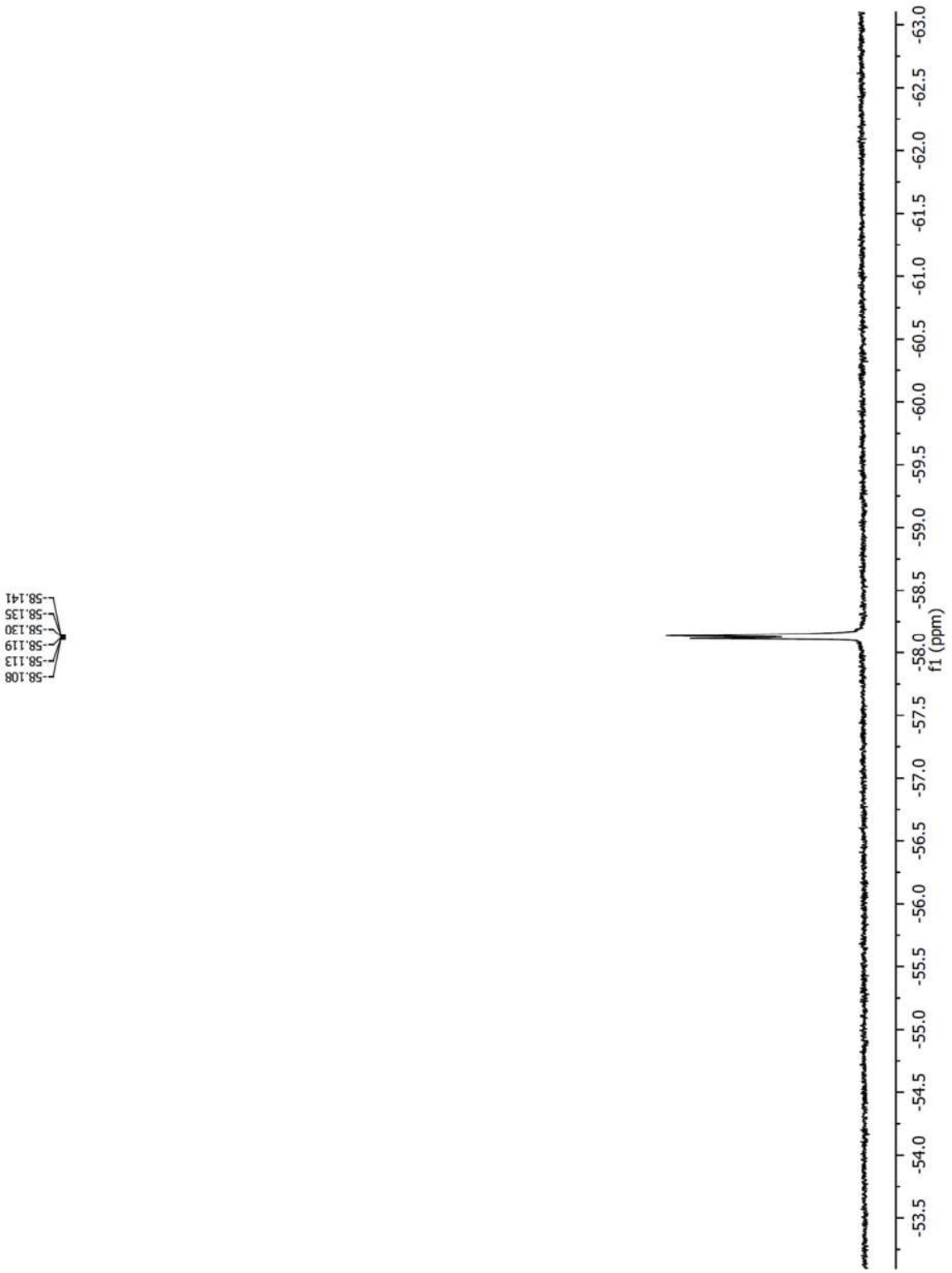
^{1}H NMR spectrum of 3.48



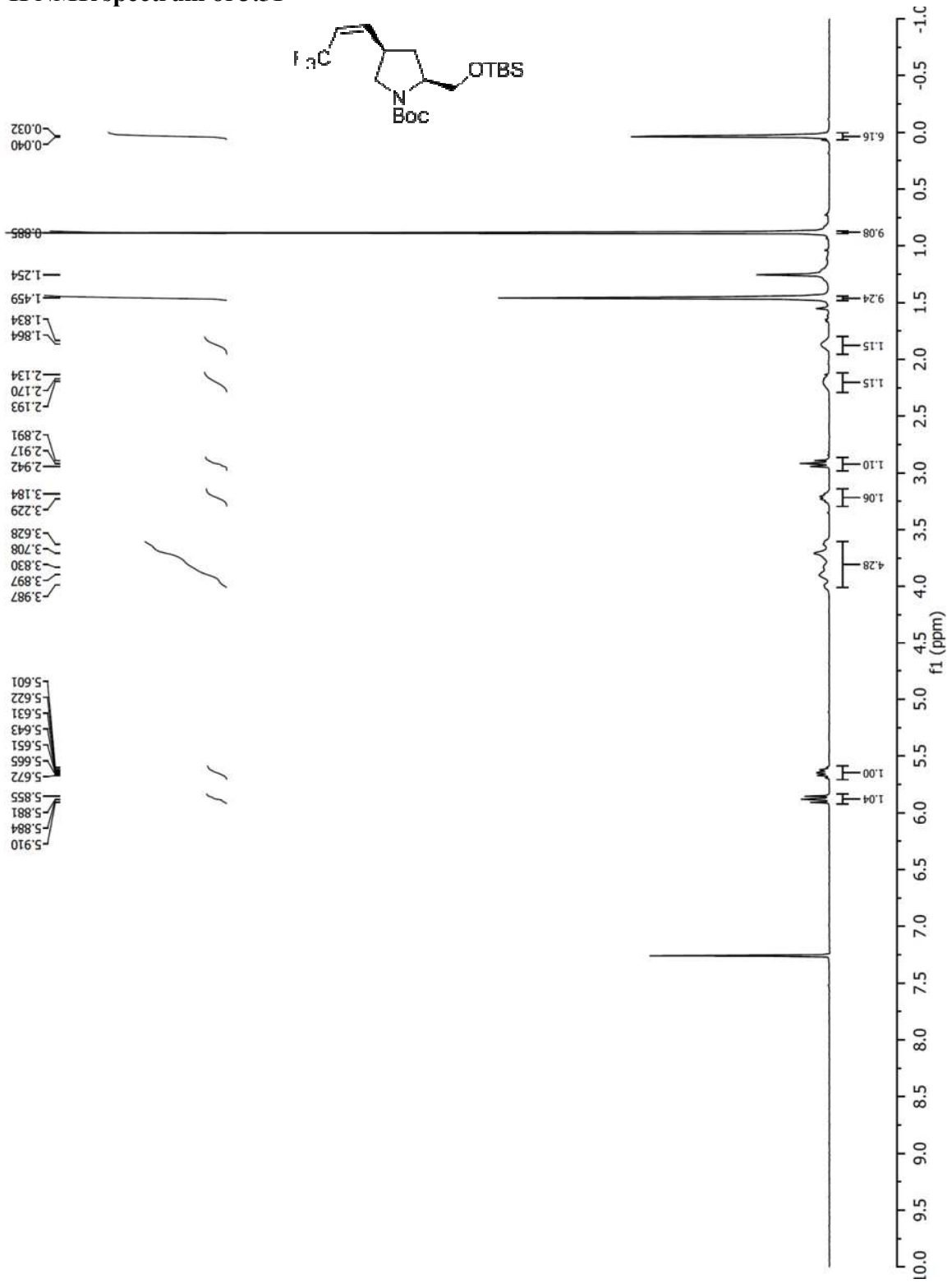
^{13}C NMR spectrum of 3.48



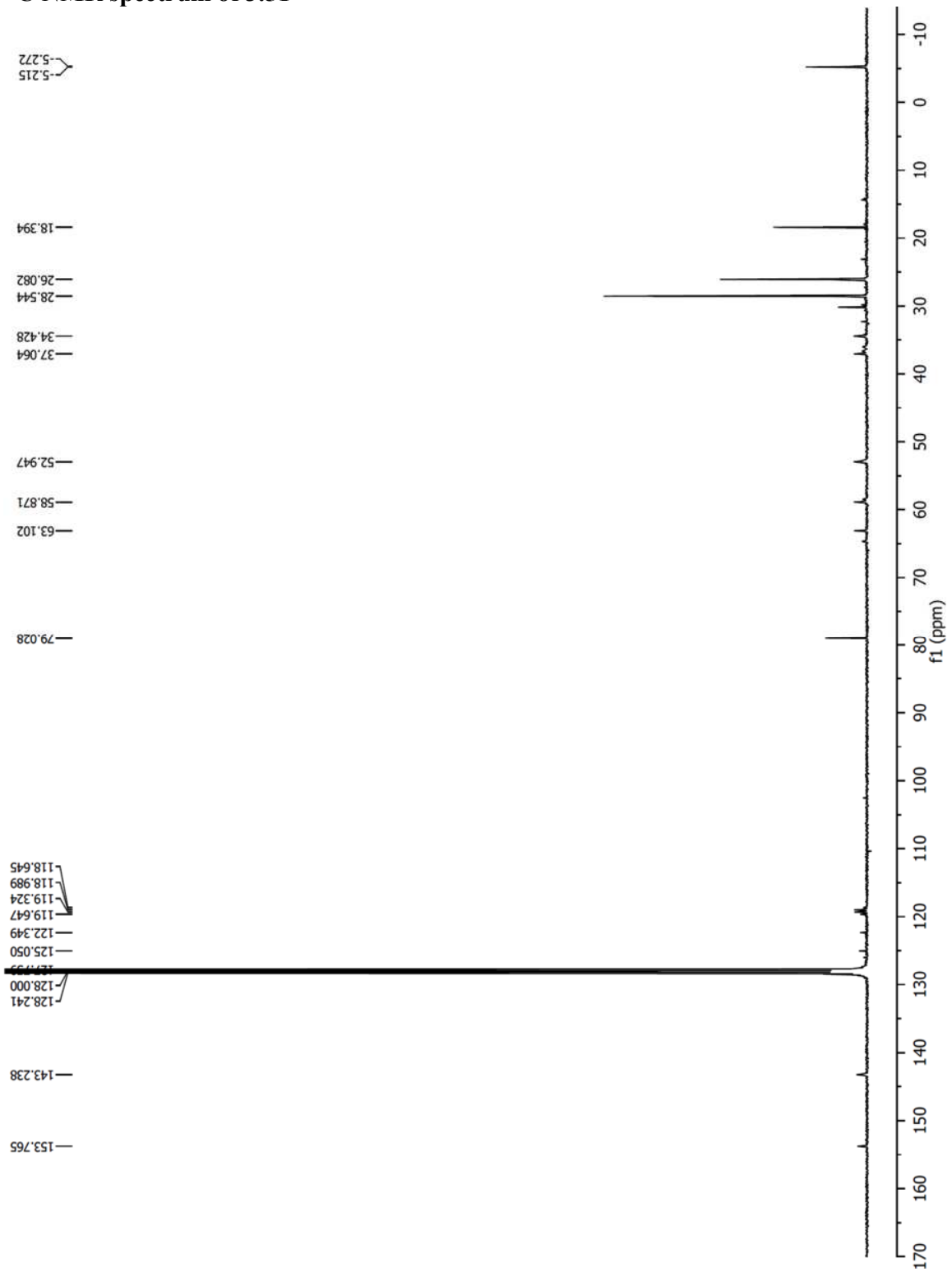
^{19}F NMR spectrum of 3.48



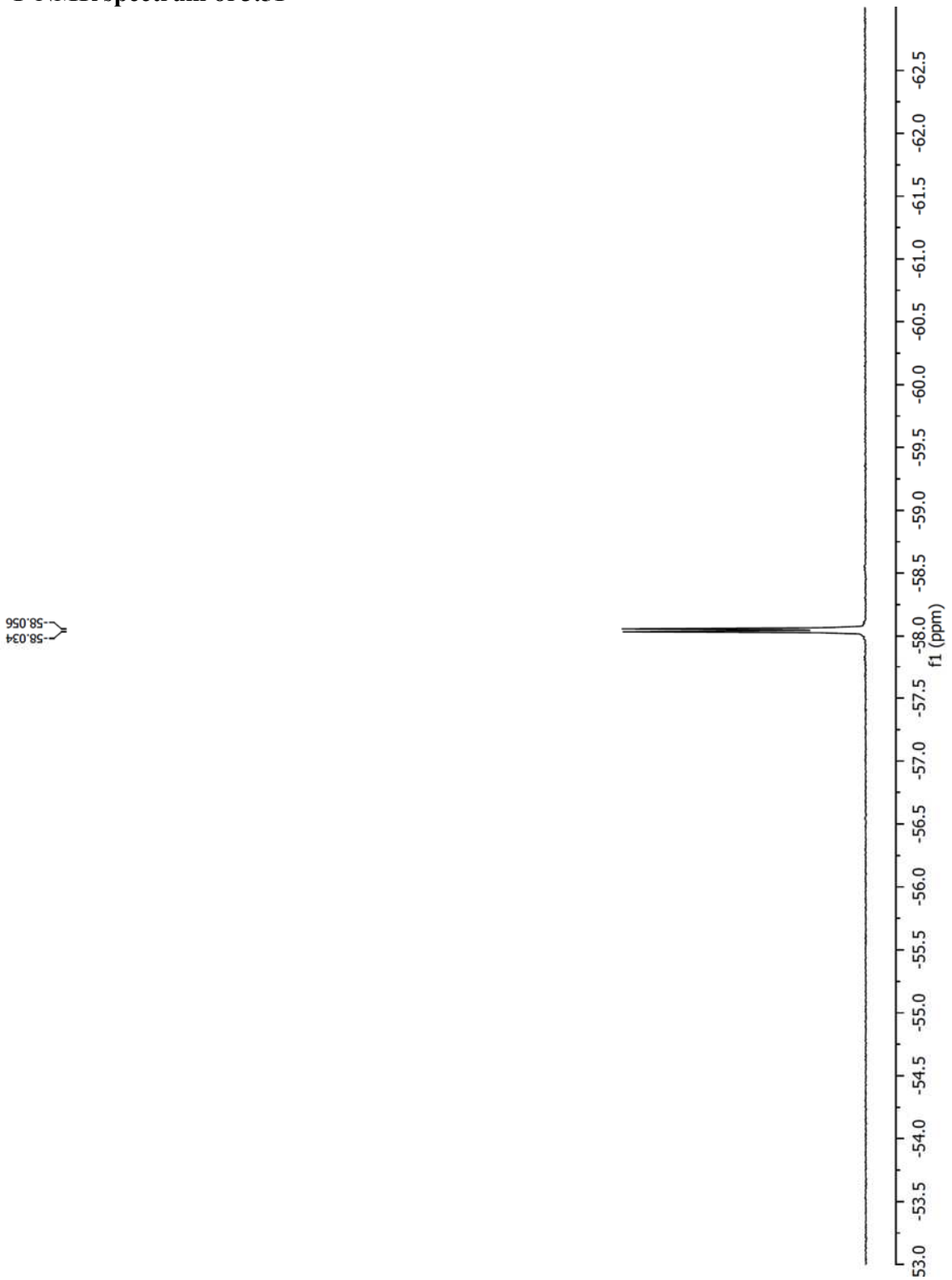
^{1}H NMR spectrum of 3.51



^{13}C NMR spectrum of 3.51



^{19}F NMR spectrum of 3.51



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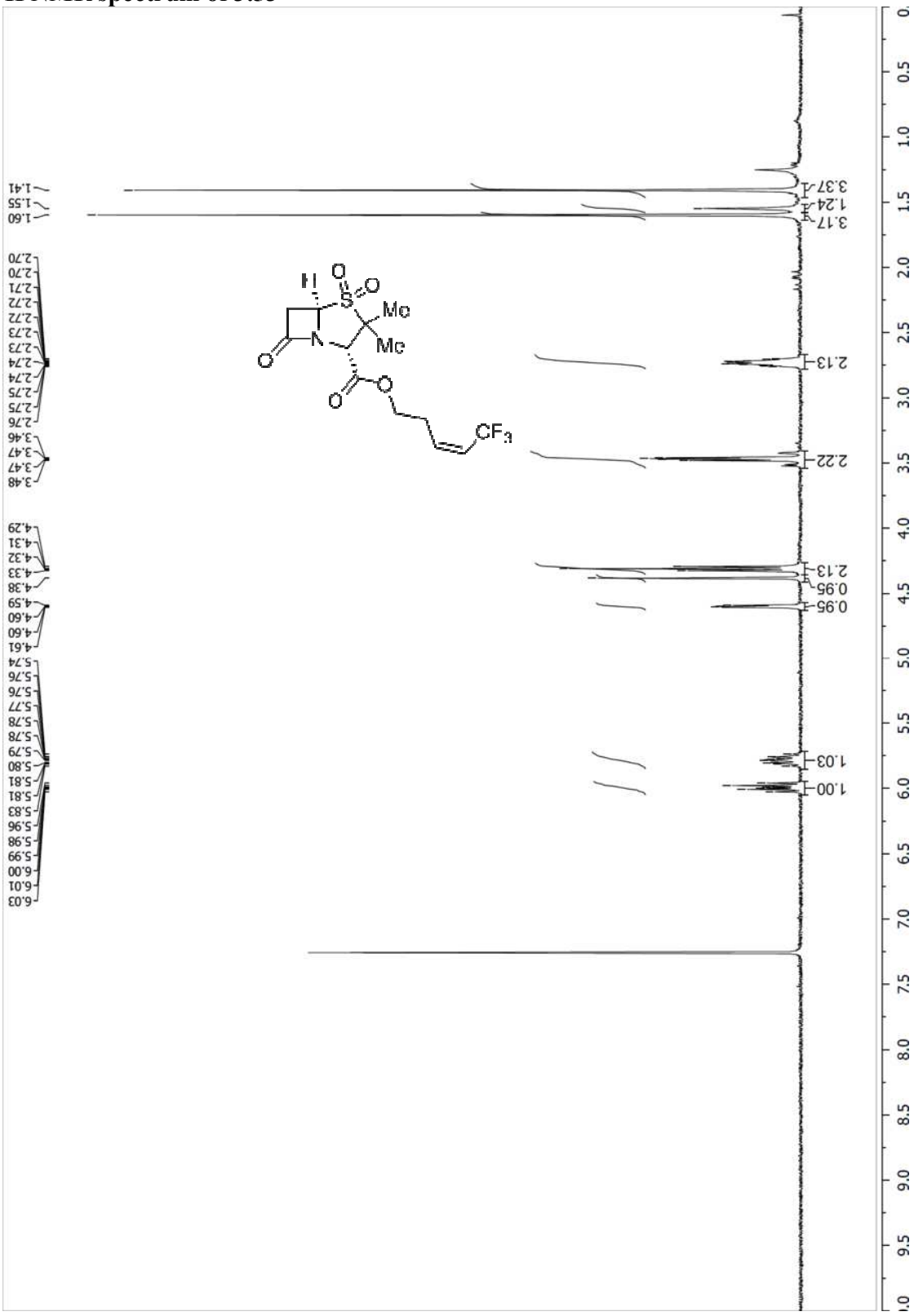
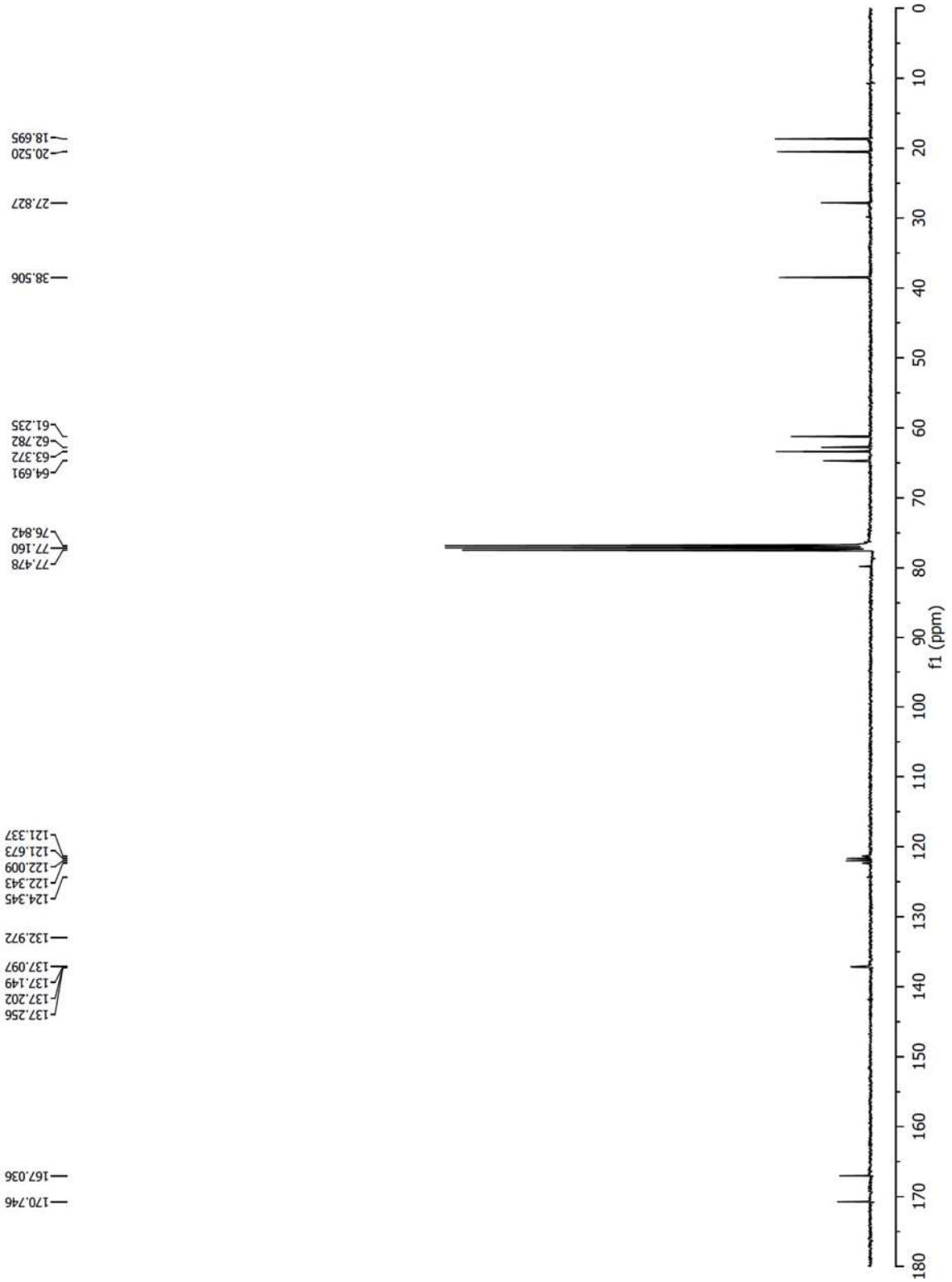


^{13}C NMR spectrum of 3.53



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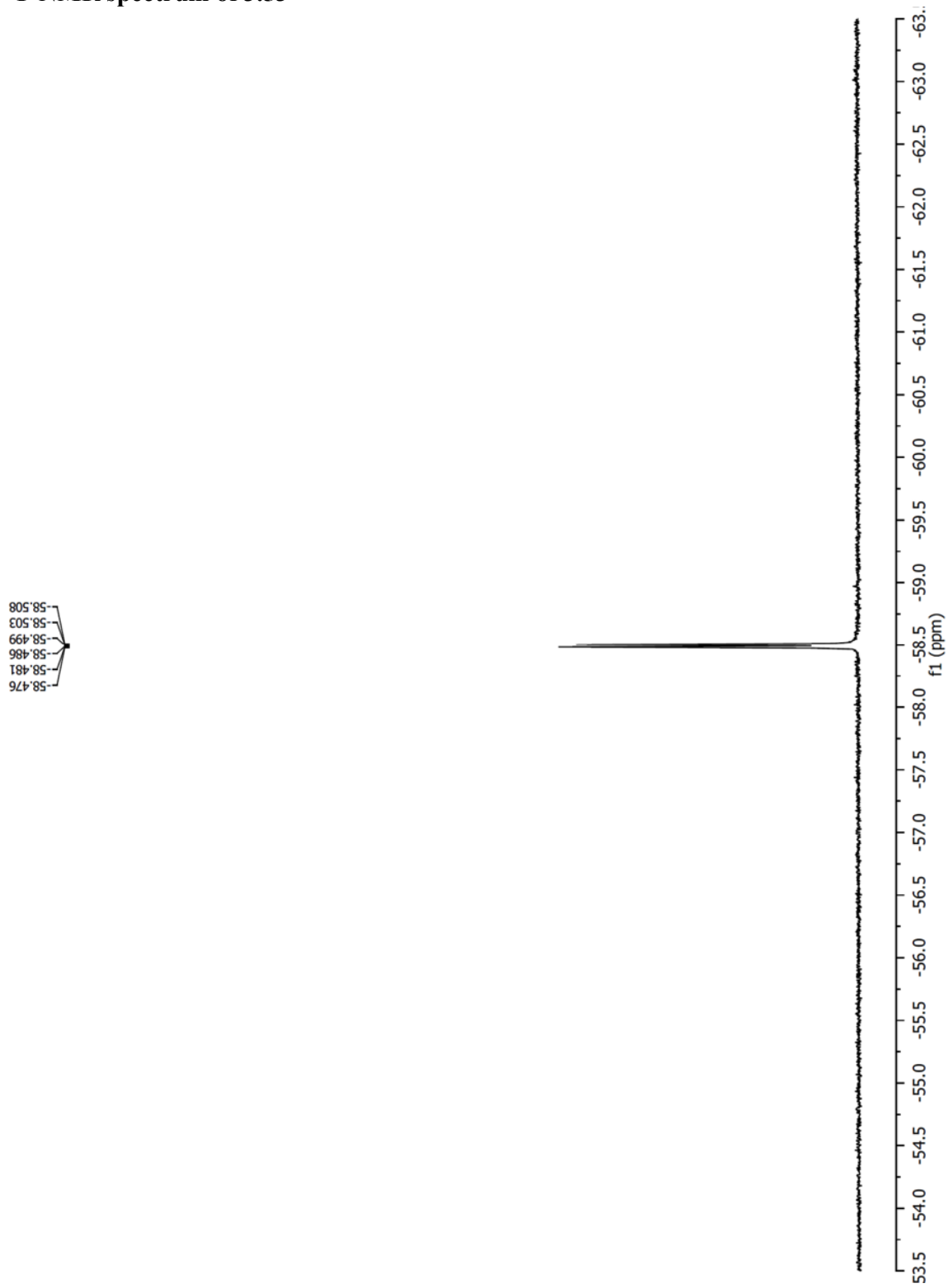

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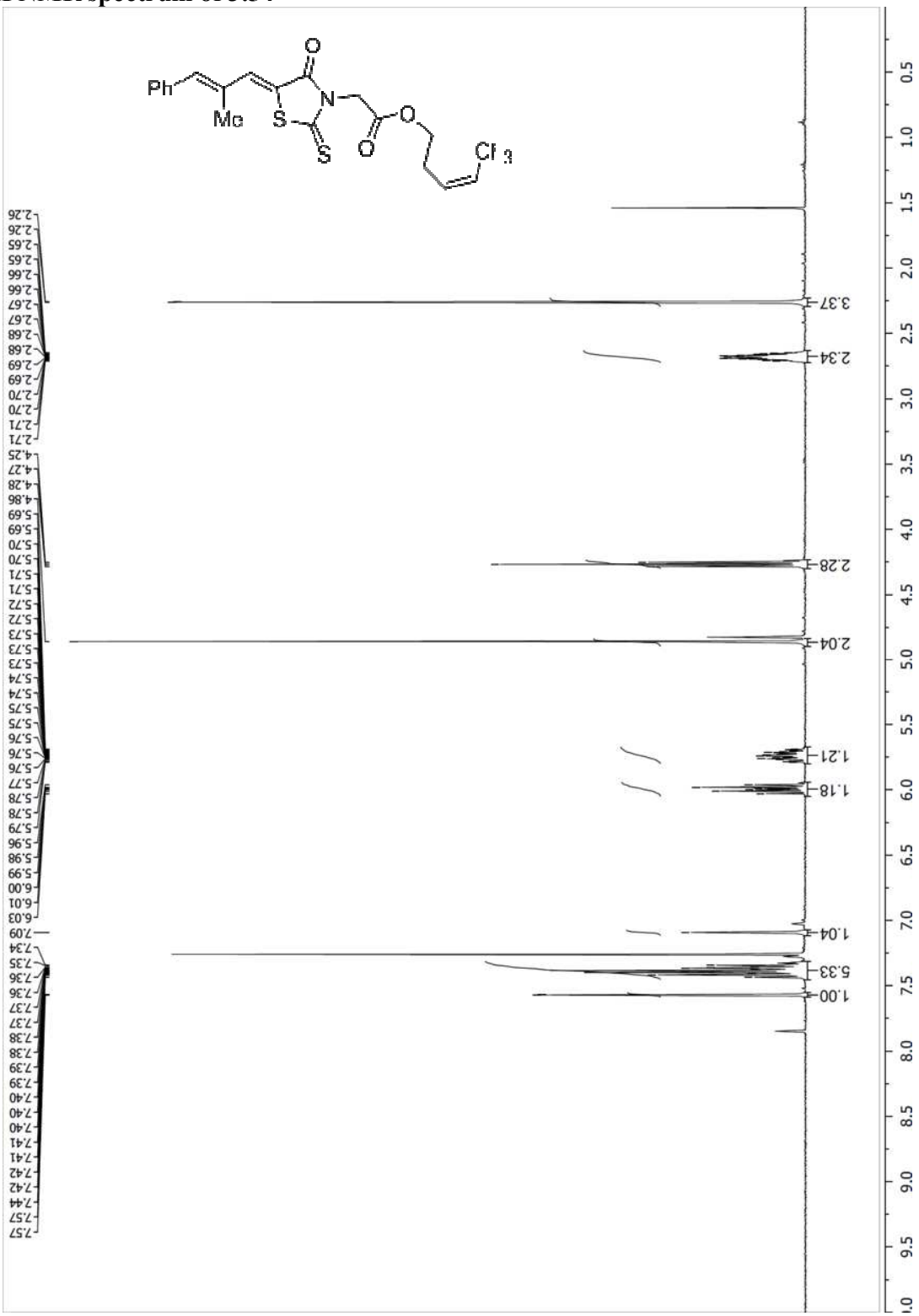

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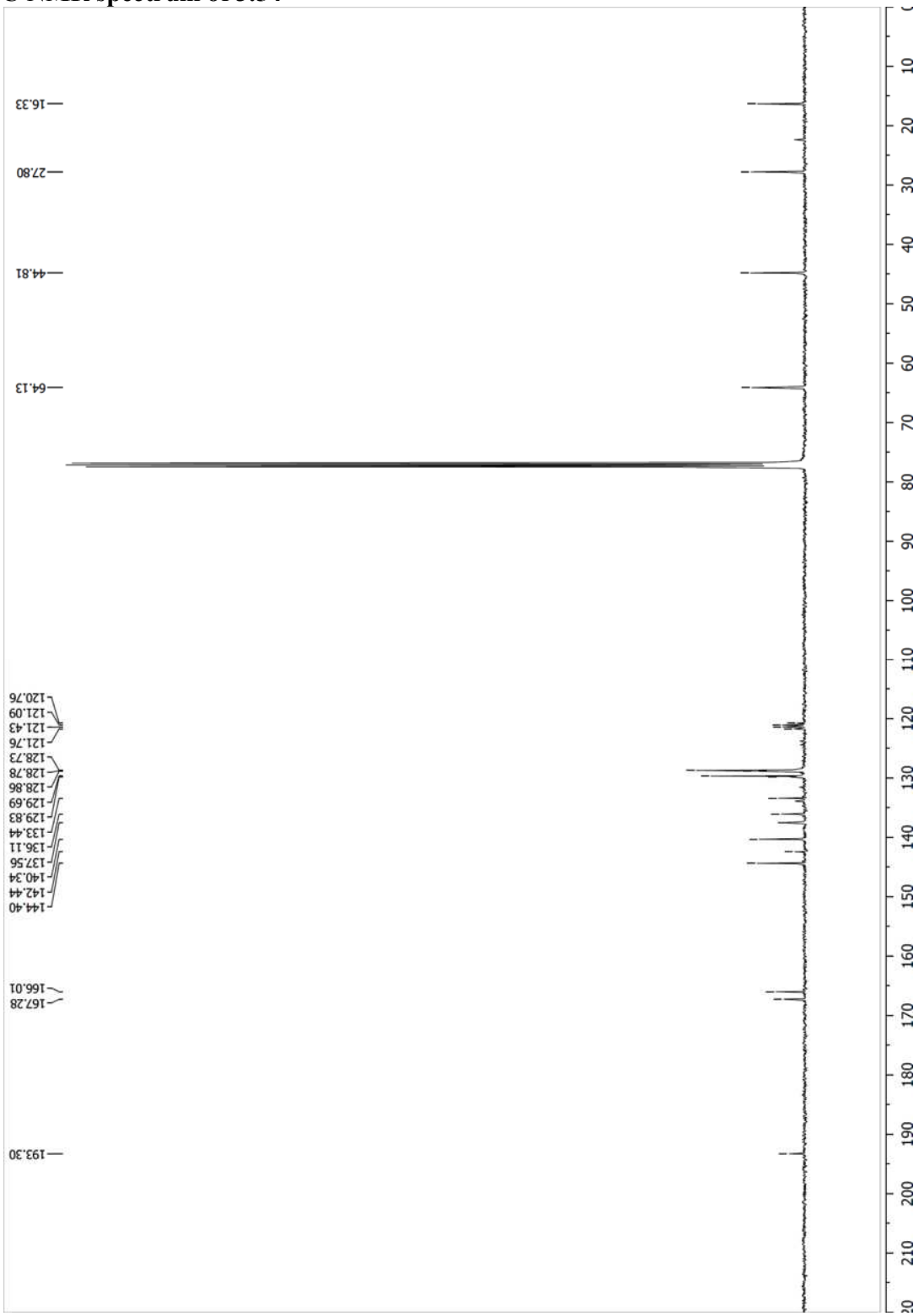
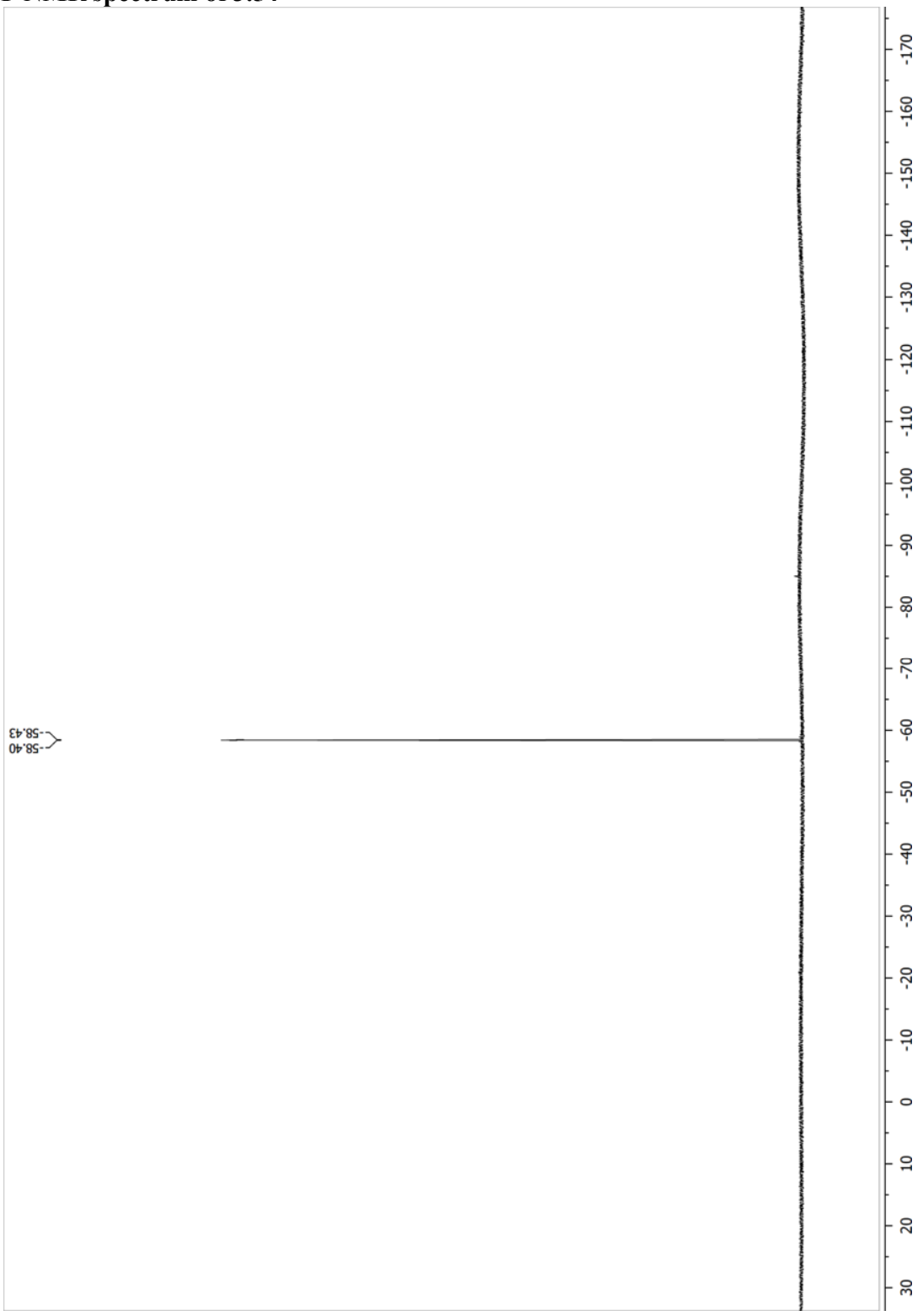


^{19}F NMR spectrum of 3.54



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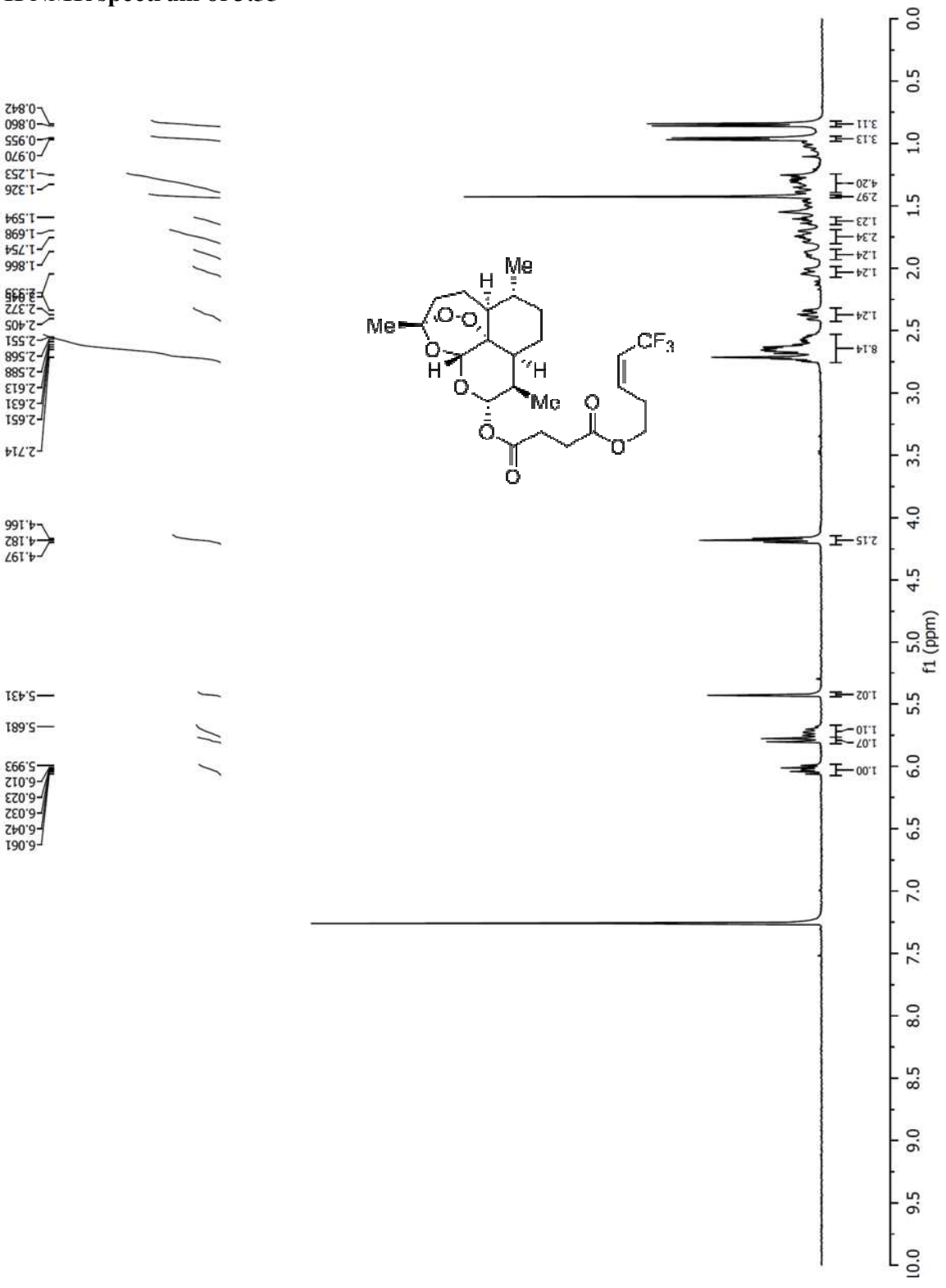
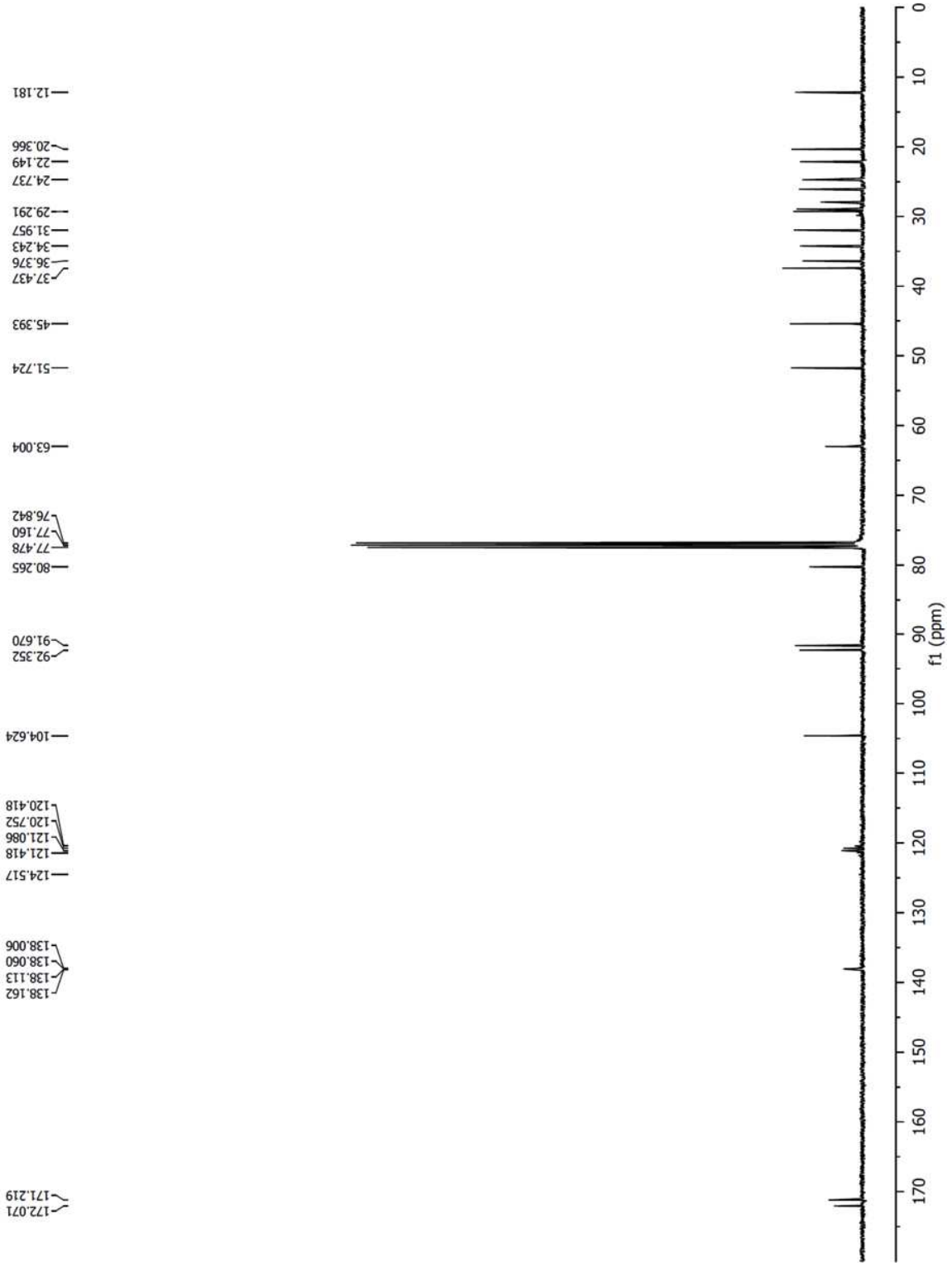
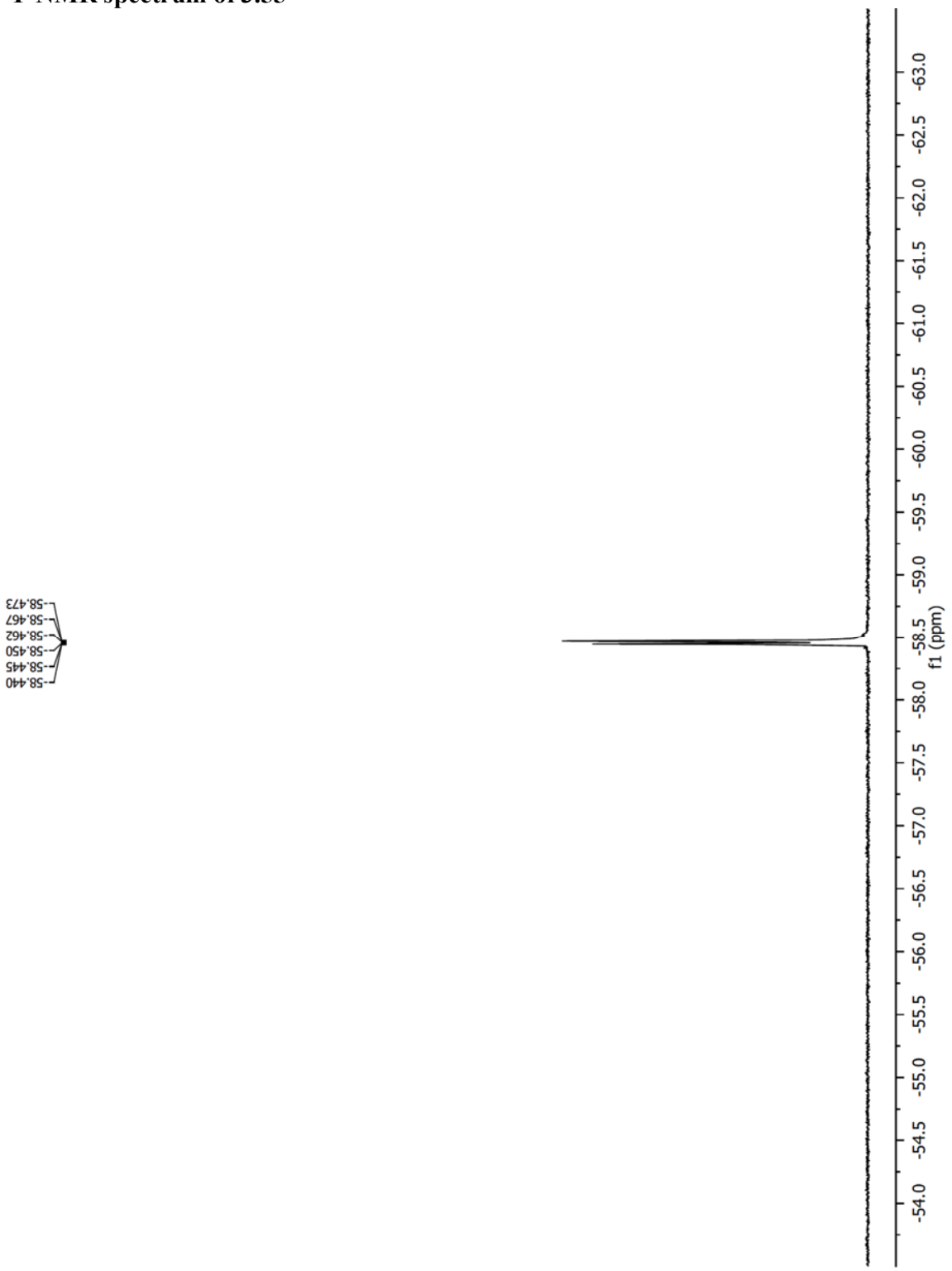


^{13}C NMR spectrum of 3.55



^{19}F NMR spectrum of 3.55



3.6.7. Density Functional Theory (DFT) Calculations

DFT computations[56] were performed with the Gaussian 09 suite of programs[57]. Geometries were optimized by application of the ωB97XD[58] functional. The Def2SVP basis set[59] was used for all atoms and the effect of a polar medium (benzene) was modeled using the SMD solvation model[60]. Stationary points were probed through vibrational analysis and Gibbs free energy corrections were performed under standard conditions (298.15 K, 1.0 atm). The ground states on either side of the transition state have been obtained through intrinsic reaction coordinate (IRC) calculations employing the L(ocal) Q(uadratic) A(approximation) method and subsequent geometry optimization[61]. Single point energy calculations at the geometries optimized at the ωB97XD/Def2SVP$_{benzene(SMD)}$ level have been performed with a range of density functionals that account for dispersion[62] and the larger Def2TZVPP[59] basis set in benzene (SMD). Since the correct density functional is not known we tested several state of the art approaches that have been developed over the past decade[56]: ωB97XD[58] and M06[63], MN12SX[64], MN12L[64], M06L[63], BP86-D3BJ[65,56b] and PBE0-D3BJ[66,56b]. Figures S3-1,

(56) For reviews on the application of DFT calculations to transition metal chemistry, see: (a) Cramer, C. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10757–10816. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem*. **2011**, *32*, 1456–1465. (c) Peverati, R.; Truhlar, D. G. *Phil. Trans. R. Soc. A* 372:20120476 (2014).

(57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr.; J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision* ***D.01,*** Gaussian, Inc., Wallingford CT (2009).

(58) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

(59) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(60) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

(61) (a) Page, M.; McIver Jr.; J. W. *J. Chem. Phys.* **1988**, *88*, 922–935. (b) Page, M.; Doubleday Jr.; C.; McIver Jr.; J. W. *J. Chem. Phys.* **1990**, *93*, 5634–5642.

(62) For selected examples highlighting the importance of including treatment of dispersion interactions in modeling olefin metathesis reactions promoted by Ru carbene complexes, see: (a) Torker, S.; Merki, D.; Chen, P. *J. Am. Chem. Soc.* **2008**, *130*, 4808–4814. (b) Minenkov, Y.; Occhipinti, G.; Singstad, A.; Jensen, V. R. *Dalton Trans.* **2012**, *41*, 5526–5541. (c) Minenkov, Y.; Occhipinti, G.; Jensen, V. R. *Organometallics* **2013**, *32*, 2099–2111. (d) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2014**, *136*, 14337–14340. (e) Torker, S.; Koh, M. J.; Khan, R. K. M.; Hoveyda, A. H. *Organometallics* **2016**, *35*, 543–562.

(63) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.

(64) Peverati, R.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16187–16191.

(65) (a) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988***, 38*, 3098–3100. (b) Perdew, J. P.; Yue, W. *Phys. Rev. B* **1986***, 33*, 8800–8802.

S3-3, S7-1 and S8-1 show the Gibbs free energy surfaces according to the MN12SX/Def2TZVPP$_{benzene(SMD)}$// ωB97XD/Def2SVP$_{benzene(PCM)}$ level of theory for model systems **Mo-4**, **Mo-5** and **Mo-6**. This level is also used in the discussion on the following pages. Gibbs free energies with all other investigated density functionals, which yield qualitatively comparable trends, are provided in Figures S3-2, S3-4, S7-2 and S8-2 and, furthermore, in Tables S1–S4. A file for convenient viewing of computed geometries with the program Mercury 3.3 is appended as separate "coordinates.xyz" file in Section 10[67]. For geometries and energies of computed structures in gas-phase, refer to supplementary information in reference 21.

Introduction

Previous studies by Eisenstein et al.[68] have put forth a model for the reactivity of high oxidation state d^0 olefin metathesis catalysts that is largely based on two factors: (i) the opening of an empty coordination site for the incoming olefin *trans* to a suitable anionic ligand and (ii) the stability of the metallacyclobutane intermediate. Point (i) is proposed to be favored by a dissymmetric ligand environment [i.e.; a good σ-donor (e.g., alkyl) in combination with a weak σ-donor (e.g., alkoxide/aryloxide)], whereas (ii) is increased by the nature of the metal [Mo (4d) vs W (5d)] and the number of O-based ligands (vs. alkyl)[68b]. The scope investigated within this study was limited to alkyl, alkoxide/siloxide and pyrrolide anions and, furthermore, monomethyl-substituted metallacyclobutane intermediates. Additionally, discussions have largely been based on the electronic energy surface. The latter two factors overestimate the stability of transition states for metallacyclobutane formation (**ts1**) relative to transition states for olefin association/dissociation (**ts$_{assoc}$**/**ts$_{dissoc}$**) since they ignore the significantly decreased entropy in the more tightly associated [2+2]-cycloaddition structures (**ts1**). In order to explain the increased performance of newly discovered MonoAryloxideChloride (MAC) complexes over MonoAryloxidePyrrolide (MAP) complexes in reactions with (*Z*)-1,1,1,4,4,4-hexafluoro-2-butene, we hence performed studies with a range of σ- and π-donating as well as π-accepting anionic ligands (X = Pyr, PyrMe$_2$, Me, Cl, CN, OMe). The high experimentally observed reactivity of the MAC complex seems to contradict the mechanistic rationales provided by Eisenstein et al. (i.e., OM pathway likely occurs *trans* to a fairly weak halide donor). Furthermore, we focused on sterically more demanding

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(66) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**,*110*, 6158–6169.
(67) *Organometallics* **2014**, *33*, 835−835. The "coordinates.xyz" file can be generated by copying all the coordinates in Section 10 into a text file without empty lines and changing the extension to ".xyz".
(68) For an early theoretical study regarding the influence of anionic ligands in Mo, W and Re systems on the barrier of olefin coordination and metallacyclobutane stability, see: (a) Solans-Monfort, X.; Clot, E.; Coperet, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2005**, *127*, 14015−14025. (b) Poater, A.; Solans-Monfort, X.; Clot, E.; Coperet, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2007**, *129*, 8207−8216. (c) Solans-Monfort, X.; Coperet, C.; Eisenstein, O. *J. Am. Chem. Soc.* **2010**, *132*, 7750−7757.

tri-substituted metallacyclobutane intermediates. The latter are relevant in recently developed and highly efficient stereoretentive (*E*- and *Z*-selective) OM processes, which circumvent the formation of relatively unstable methylidene species[5,6].

Correlating the computed energy values for acetonitrile binding to experimental results

Experimental data provide insight into the relative binding energies of acetonitrile to Mo complexes, which we use as test to validate the computational approaches. For example, acetonitrile complexes have been isolated for MAC (current report) and MAP complexes containing electron-deficient aryloxides[69]. Other examples show that there are equilibria between **ac** (= acetonitrile adduct) and $\mathbf{T_d}$ (= tetrahedral ground state), furthermore underscoring that **ac** and $\mathbf{T_d}$ are presumably fairly close in free energy under experimental conditions[4]. The fact that the free energies for **ac** are comparable to the free energy values for **Td** suggests that the correct relative order may be subject to errors associated with the density functional or the free energy correction (ΔG_{corr}), which has been estimated in gas-phase and is likely overestimated (please compare to the negative ΔE values of –10.2 and –9.4 kcal/mol for $\mathbf{ac_{Cl}}$ and $\mathbf{ac_{PyrMe2}}$, respectively; cf. Table S2). These arguments suggest that the low (and positive) computed free energy value in a model system containing a methoxide ligand (Figure S3-1) for $\mathbf{ac_{Cl}}$ (2.5 kcal/mol) or $\mathbf{ac_{PyrMe2}}$ (1.8 kcal/mol) is in reasonable agreement with the experimental observations. In the real system containing the larger aryloxide, $\mathbf{ac_{Cl}}$ is 2.0 kcal/mol above $\mathbf{T_d}$, which is an absolute error of > 2.0 kcal/mol, but reproduces the correct relative order with respect to $\mathbf{ac_{PyrMe2}}$ (6.7 kcal/mol; see Figure S7-1).

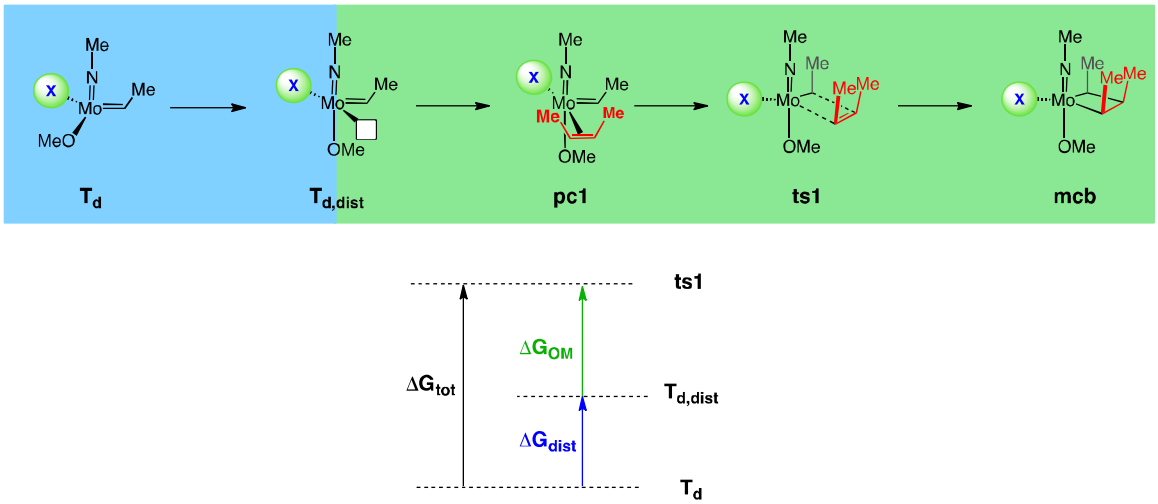


Figure S2. Dissecting the overall OM barrier into two energetic contributions: (a) Energy required

(69) Yuan, J.; Schrock, R. R.; Gerber, L. C. H.; Müller, P.; Smith, S. *Organometallics* **2013**, *32*, 2983–2992.

for distortion of the tetrahedral ground state geometry ($\Delta\mathbf{G_{dist}}$: $\mathbf{T_d \rightarrow T_{d,dist}}$) and (b) the energy component relevant for the C−C bond formation process ($\Delta\mathbf{G_{OM}}$: $\mathbf{T_{d,dist} \rightarrow ts1}$).

Energetic analysis

In order to reveal the ability of the anionic ligands to generate an open coordination site, as well as their influence on the C=C bond forming process, we dissected the overall OM barrier (ΔG_{tot}) into two energetic contributions (Figure S2). (i) $\mathbf{\Delta G_{dist}}$ is the energy required to distort the tetrahedral complex to open an empty ligation site ($\mathbf{T_d \rightarrow T_{d,dist}}$; the N–Mo–$C^{alkylidene}$–O dihedral angle in $\mathbf{T_{d,dist}}$ was constrained to 175 º) and (ii) $\mathbf{\Delta G_{OM}}$ is the energy associated with C=C bond formation ($\mathbf{T_{d,dist} \rightarrow ts1}$).

Electronic effects: reaction of model system (Mo-6) with *Z*-MeCH=CHMe

Comparison of the free energy barriers for reaction of model MAX-ethylidene complexes (Figure S3-1; X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) reveals the highest OM barriers ($\mathbf{\Delta G_{tot}}$, cf. Figure S2) for strongly σ- (18.9 kcal/mol for X = Me) and strongly π-donating ligands (18.3 kcal/mol for X = OMe). This is in stark contrast to the study by Eisenstein et al., which suggests the catalyst with X = Me to be superior relative to the bis-methoxy version (X = OMe)[68]. Complexes with weaker σ-donating (Pyr, $PyrMe_2$ and Cl) or π-accepting (CN) X-ligands display lower overall barriers in a narrow 12.5–14.1 kcal/mol range.

Energy required for distortion ($\mathbf{T_d \rightarrow T_{d,dist}}$)

Detailed analysis of the free energy surfaces (Figure S3-1) suggests that the main reason for the high overall barrier with X = OMe is the fairly large energy (12.2 kcal/mol) required to distort the tetrahedral complex ($\mathbf{T_d \rightarrow T_{d,dist}}$), whereas the complex with X = Me undergoes distortion relatively easily (3.4 kcal/mol). Complexes with pyrrolide ligands (X = Pyr, $PyrMe_2$) and chloride have similar and modest distortion energies (8.2–8.9 kcal/mol), and the complex with the CN ligand exhibits the lowest value among all investigated anions (2.4 kcal/mol). The observed trend agrees well with the general *trans effect* series of ligands: π-donors (p → d donation; e.g. X = OMe) disfavor distortion of the second OMe ligand trans to the amido group, as they make the corresponding d-orbital on Mo less accepting, whereas σ-donors and π-acceptors (e.g. X = CN) cause the opposite.

Energy required for C=C bond formation ($\mathbf{T_{d,dist} \rightarrow}$ mcb)

Removing the penalty for distortion (i.e.; using $\mathbf{T_{d,dist}}$ as a reference point) suggests that C=C bond formation is least favored with strongly σ-donating and π-accecpting ligands (X = Me and CN), with barriers of 15.4 and 10.9 kcal/mol, respectively (Figure S3-3). The weaker σ-donating ligands (Pyr, Me_2Pyr, Cl and OMe)

exhibit significantly lower barriers for **ts1** (3.6–6.1 kcal/mol), with the chloride complex having the lowest barrier (3.6 kcal/mol).

Correlation of the reaction barriers for OM with Mo-6 with electronic parameters

Structural analysis of the π-complexes (**pc1**) reveals a possible explanation for the observed trend in ability to promote C=C bond formation. The C2=C3 bond lengths in the corresponding π-complexes **pc1** (Figure S4) provide a measure of the double bond activation and can be correlated fairly well with the OM barriers when distortion is excluded (**pc1** → **ts1**; Figure S5-1a). For the qualitatively comparable correlation of $\mathbf{T_{d,dist}}$ → **ts1** vs the C2=C3 bond lengths, see Figure S5-7a'. To gain better understanding of the factors that are the basis for C=C bond activation, we correlated the **pc1** → **ts1** barrier (MN12SX/Def2TZVPP$_{benzene(SMD)}$) with the LUMO of $\mathbf{T_{d,dist}}$ assessed with two density functionals [ω–B97XD/Def2TZVPP$_{benzene(SMD)}$; Figure S5-1b and (MN12SX/Def2TZVPP$_{benzene(SMD)}$; Figure S5-1c] as well as the HOMO of $\mathbf{T_{d,dist}}$ obtained at the ω–B97XD/Def2TZVPP$_{benzene(SMD)}$ level Figure S5-1d. Furthermore, correlation with the natural charge on the alkylidene carbon C1 in $\mathbf{T_{d,dist}}$ assessed with two density functionals [ω–B97XD/Def2TZVPP$_{benzene(SMD)}$; Figure S5-2e and MN12SX/Def2TZVPP$_{benzene(SMD)}$; Figure S5-2f] is provided. These two factors (i.e., LUMO and HOMO/natural charge) are hypothesized to have a positive influence on the reaction barrier. The LUMO is likely responsible for activation through π(C=C) → Mo σ-donation, whereas the greater nucleophilicity of the alkylidene, as expressed by the natural charge on the alkylidene carbon C1, is likely responsible for back-donation into the C=C π*-orbital of the olefin. We observe an overall positive influence of the Lewis acidity (i.e., low LUMO) on the reaction barrier (Figure S5-1b; R^2 = 0.47), particularly when strongly π-donating or π-accepting ligands are excluded (R^2 = 0.94). In other words, the CN-ligand, despite having a low LUMO (–0.00560 hartree), has a reasonably high barrier (6.7 kcal/mol for **pc1** → **ts1**), whereas the complex with the OMe-ligand has a fairly low barrier (4.8 kcal/mol for **pc1** → **ts1**) compared to its relatively high LUMO (0.01083 hartree). A similar qualitative trend is obtained with the LUMO at the MN12SX/Def2TZVPP$_{benzene(SMD)}$ level (Figure S5-1c). On the other hand, there is an overall negative influence of a high HOMO on the reaction barrier, although the correlation is rather poor (Figure S5-1d). Furthermore, there is a similarly negative impact of the natural charge on C1 on the **pc1** → **ts1** barrier, with a fairly good correlation when strongly π-donating or π-accepting ligands are excluded (R^2 = 0.99; Figure S5-2e). These data suggest that the CN complex might be strongly deactivated through π(Mo=C) → π*(C≡N) hyperconjugation, depleting the natural charge on C1 (–0.208 e). In contrast, the complex with X = OMe appears to be significantly activated through competitive π-donation with the alkylidene p-orbital into the same Mo d-orbital,

raising the natural charge on C1 (–0.333). The importance of high electrophilicity for high activity is furthermore reflected when the **pc1** → **ts1** barrier is plotted against the acetonitrile affinity ($\mathbf{T_{d,dist}} \rightarrow$ **ac**; Figure S5-2g) or the *Z*-butene affinity ($\mathbf{T_{d,dist}} \rightarrow$ **pc1**; Figure S5-2h). Consistent with the π-donating or π-accepting properties outlined above, while the complexes with X = OMe and X = CN have similar acetonitrile affinities (-4.5 and –3.7 kcal/mol, respectively), the methoxy version of $\mathbf{T_{d,dist}}$ binds *Z*-butene significantly more efficiently (1.3 vs 4.1 kcal/mol for X = CN).

Correlation of the reaction barriers for OM with Mo-6 with structural parameters

The data outlined above support a dual activation mode of the olefin (i.e., *Z*-MeCH=CHMe), although with a dominance of the Lewis acidity (LUMO) over the nucleophilicity (i.e., NPA charge on the alkylidene C1). In other words, the low electrophilicity when X = Me effectively counteracts the highly nucleophilic character of the alkylidene, leading to a significantly raised $\mathbf{T_{d,dist}} \rightarrow$ **ts1** barrier. The overall energetic picture is furthermore reflected in the structural changes of the Mo–X bond length during the transition from $\mathbf{T_{d,dist}} \rightarrow$ **mcb** (Figure S6). In case of X = CN, this reaction sequence ($\mathbf{T_{d,dist}} \rightarrow$ **mcb**) requires significant elongation of the Mo–CN bond (by 0.070 Å), likely attributable to the loss of the π(Mo=C1) → π*(C≡N) hyperconjugative stabilization present in $\mathbf{T_{d,dist}}$ and to a large degree also in **pc1**. Alternatively, the Mo–OMe bond length remains constant in **mcb** (vs $\mathbf{T_{d,dist}}$) when X = OMe, likely because it is already elongated in $\mathbf{T_{d,dist}}$ as a result of p(OMe) ↔ π(Mo=C1) repulsion. Furthermore, the Mo–C1 bond lengthens significantly for X = Me and X = OMe in the corresponding **mcb**, whereas its length increases the least for X = CN (Figure S6). Particularly, the strongly electron-donating Me group destabilizes the Mo–C1 and Mo–C3 bonds in the mcb (by raising the energy of Mo d-orbitals and making them less accepting), whereas the elongation of the Mo–C1 and Mo–C3 bonds in case of X = OMe [as a result of p(OMe) → σ*(Mo–C1) hyperconjugation] is likely compensated by significant C1–C2 and C2–C3 → Mo agostic interactions. The latter is also reflected in significantly shorter Mo•••••C2 distances (2.377 vs 2.401 Å for X = OMe and Me, respectively; cf. Figure S4). The shortest Mo•••••C2 distances are observed for the most Lewis acidic complexes with the lowest LUMOs [X = CN (2.350 Å) and X = Cl (2.337 Å)].

Steric effects: reaction of real system (Mo-5) with *Z*-MeCH=CHMe

In summary, the above data suggest that there are two important barrier-determining factors in a degenerate OM reaction: (i) Weakly σ-donating X-ligands favor the binding of the reacting olefin to Mo not only in the π-complex **pc1**, but also in **ts1** (small trans influence; cf. Figure 54-1a) and (ii) π-donating or π-accepting properties of the X-ligands are responsible for the activation or deactivation of the alkylidene carbon

(NPA charge; cf. Figure S5-2e). Although this analysis on a model system (**Mo-6**) provides fairly detailed insight into the electronic aspects of OM promoted by Mo alkylidene complexes, steric factors might certainly alter the overall effect an anionic ligand might have (Figure S7-1). From changes of the energetics upon a change of the small methylamido and methoxide ligands in Figure S3-1 for the larger *t*-butylimido and hexamethylterphenoxide (**Mo-5**; Figure S7-1) it can be read that steric factors cannot be neglected. While electronic factors overall disfavor OM with X = Me and OMe when distortion ($\mathbf{T_d \rightarrow T_{d,dist}}$) is included (Figure S5-1), the sterically more demanding Pyr and $PyrMe_2$ ligands raise the barriers in the real system and are now similarly deactivating compared to X = Me and OMe (Figure S7-1), which are significantly smaller. It hence appears that a reasonable balance between electronic as well as steric factors is crucial for a highly active OM catalyst.

Reaction of real systems (Mo-4, Mo-5$_{Cl}$ and Mo-5$_{PyrMe2}$) with *Z*-MeCH=CHMe, *Z*-CF_3CH=CHCF_3, *Z*-ClCH=CHCl and *E*-ClCH=CHCl

After analysis of general steric and electronic trends the reactivities of the actual catalyst systems (**Mo-4** vs **Mo-5$_{Cl}$**) toward electron-poor olefins are assessed (Figure S8-1). We find that chloride complex **Mo-5$_{Cl}$** is in general at least 5 kcal/mol more reactive compared to pyrrolide catalyst **Mo-4**. In agreement with the experimentally observed trend, the rate-limiting barrier for reaction of **Mo-4** with (*Z*)-1,1,1,4,4,4-hexafluoro-2-butene (26.1 kcal/mol for **ts2**) is higher relative to the corresponding barrier for reaction with *Z*-1,2-dichloroethene (23.0 kcal/mol for **ts1**). Comparison of the free energy surfaces for reaction with *Z*- and *E*-1,2-dichloroethene, on the other hand, suggests that the reason for the improved *Z* selectivity of **Mo-5$_{Cl}$** (over **Mo-4**) is likely not rooted in different kinetic selectivities (energy differences of ~3 kcal/mol for both catalysts; 14.5 vs 17.4 kcal/mol and 23.0 vs 26.0 kcal/mol, respectively). Additionally, comparison of the free energy surfaces for pyrrolide complexes **Mo-4** and **Mo-5$_{PyrMe2}$** suggests that electron repulsion between the F atoms on the pentafluorophenylamido moiety and the CF_3 or Cl substituents on the reacting olefin likely raises the barrier in reactions with (*Z*)-1,1,1,4,4,4-hexafluoro-2-butene (25.7 vs 26.1 kcal/mol) and *Z*- (23.4 vs 23.0 kcal/mol) and *E*-1,2-dichloroethene (26.2 vs 26.0 kcal/mol) as opposed to reaction with *Z*-2-butene (20.4 vs 17.3 kcal/mol).

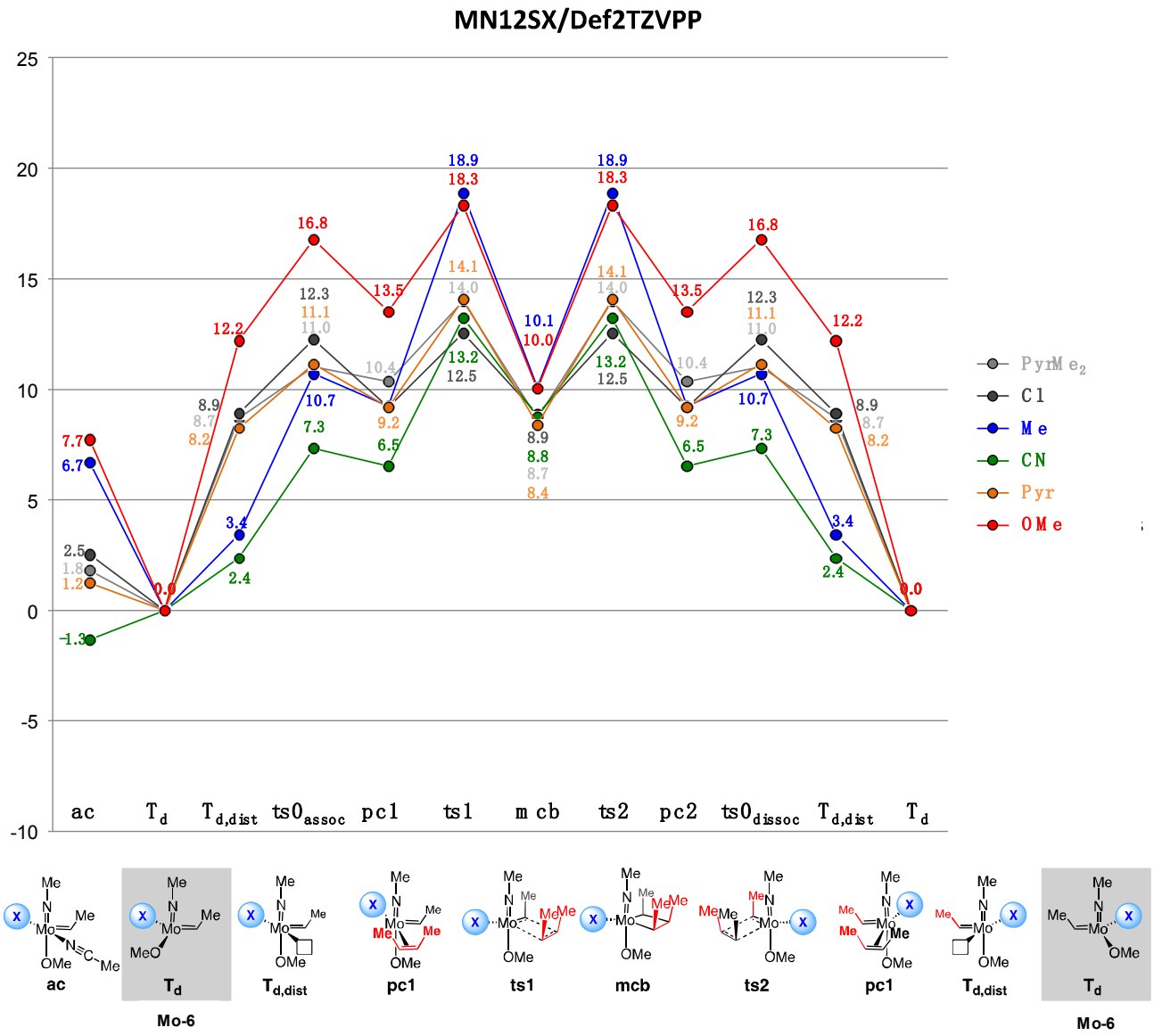


Figure S3-1. Free energy surfaces (ΔG in kcal/mol) for reaction of model MAX-ethylidene complexes **Mo-6** (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene at the MN12SX/Def2TZVPP$_{benzene(SMD)}$//ω–B97XD/ Def2SVP$_{benzene(SMD)}$ level relative to the 4-coordinate tetrahedral complex (**T_d**).

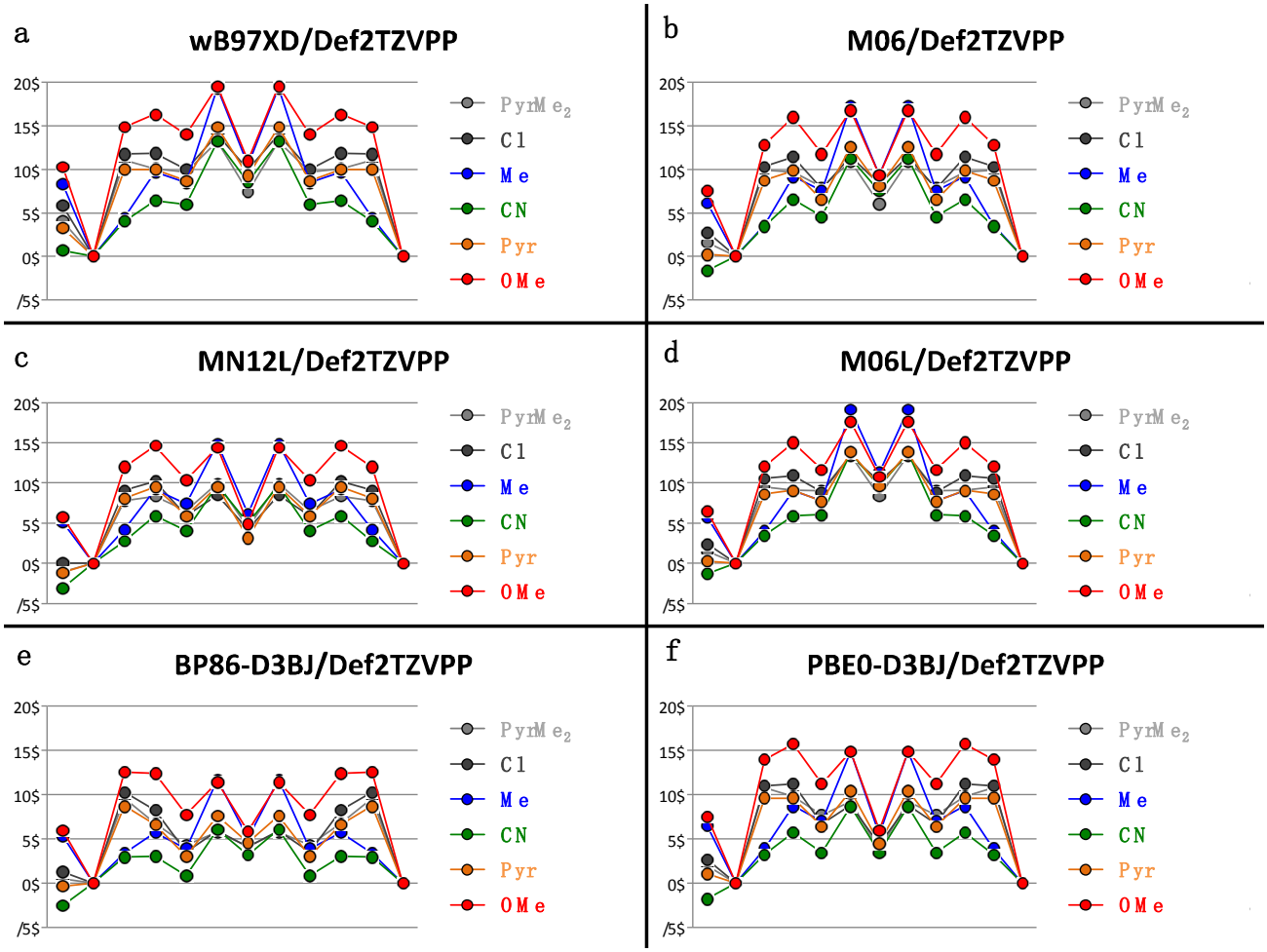


Figure S3-2. Free energy surfaces (ΔG in kcal/mol) for reaction of model MAX-ethylidene complexes **Mo-6** (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene with various levels of theory (density functional/$Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$) relative to the 4-coordinate tetrahedral complex ($\mathbf{T_d}$).

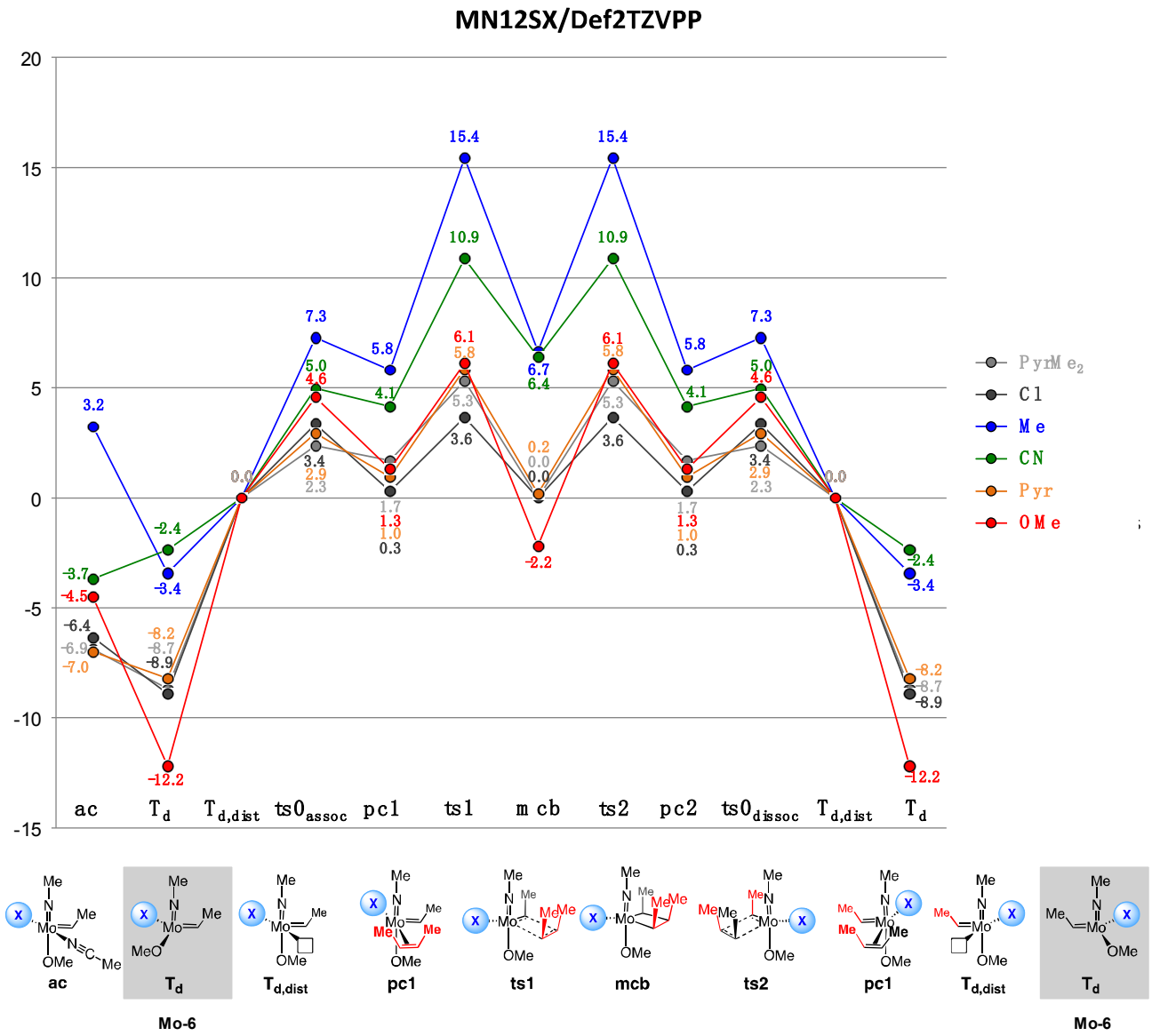


Figure S3-3. Free energy surfaces (ΔG in kcal/mol) for reaction of model MAX-ethylidene complexes **Mo-6** (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene at the $MN12SX/Def2TZVPP_{benzene(SMD)}//\omega$–B97XD/ $Def2SVP_{benzene(SMD)}$ level relative to the distorted 4-coordinate tetrahedral complex ($\mathbf{T_{d,dist}}$).

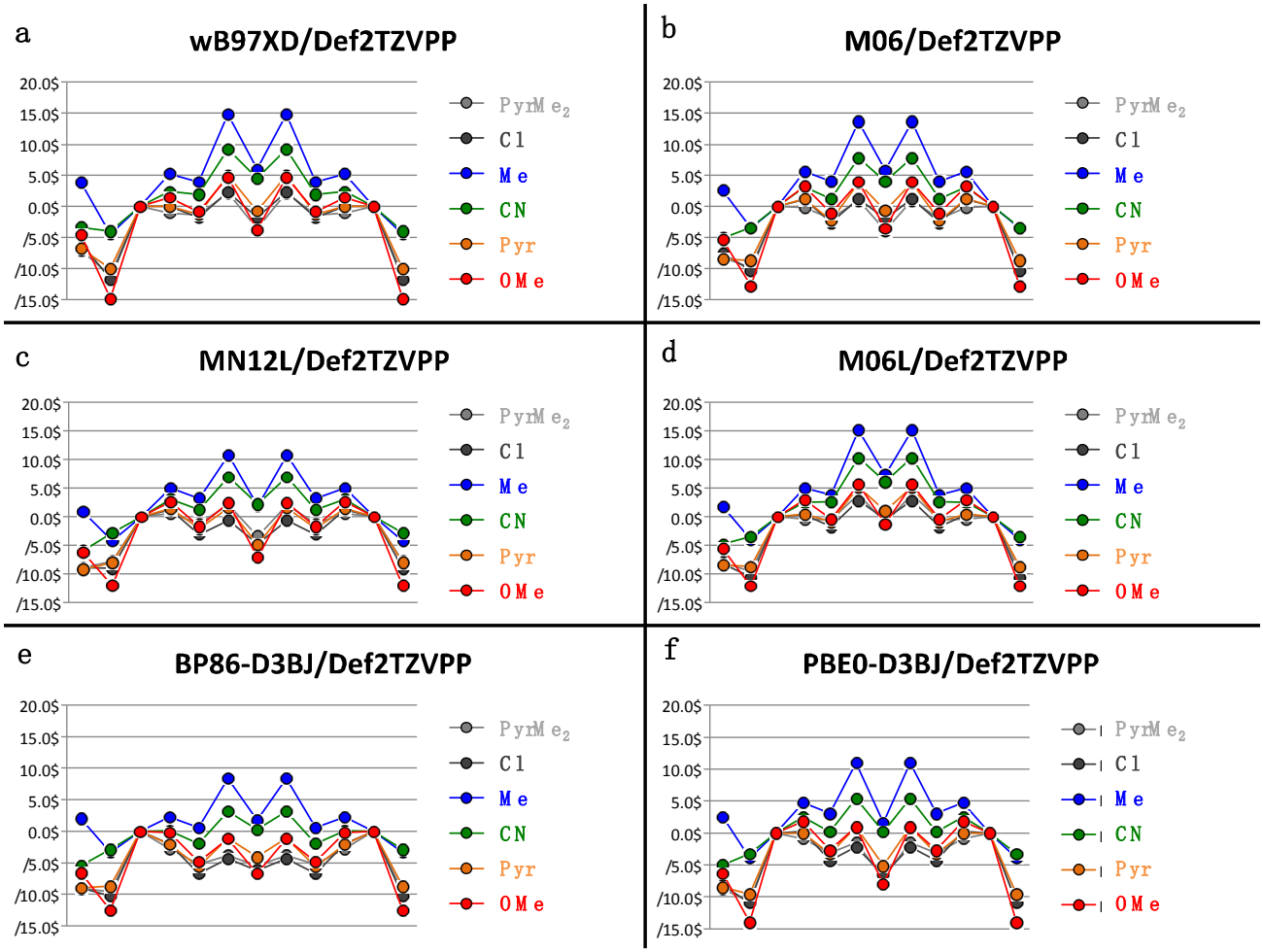


Figure S3-4. Free energy surfaces (ΔG in kcal/mol) for reaction of model MAX-ethylidene complexes **Mo-6** (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene with various levels of theory (density functional/$Def2TZVPP_{benzene(SMD)}$//ω–$B97XD/Def2SVP_{benzene(SMD)}$) relative to the distorted 4-coordinate tetrahedral complex ($\mathbf{T_{d,dist}}$).

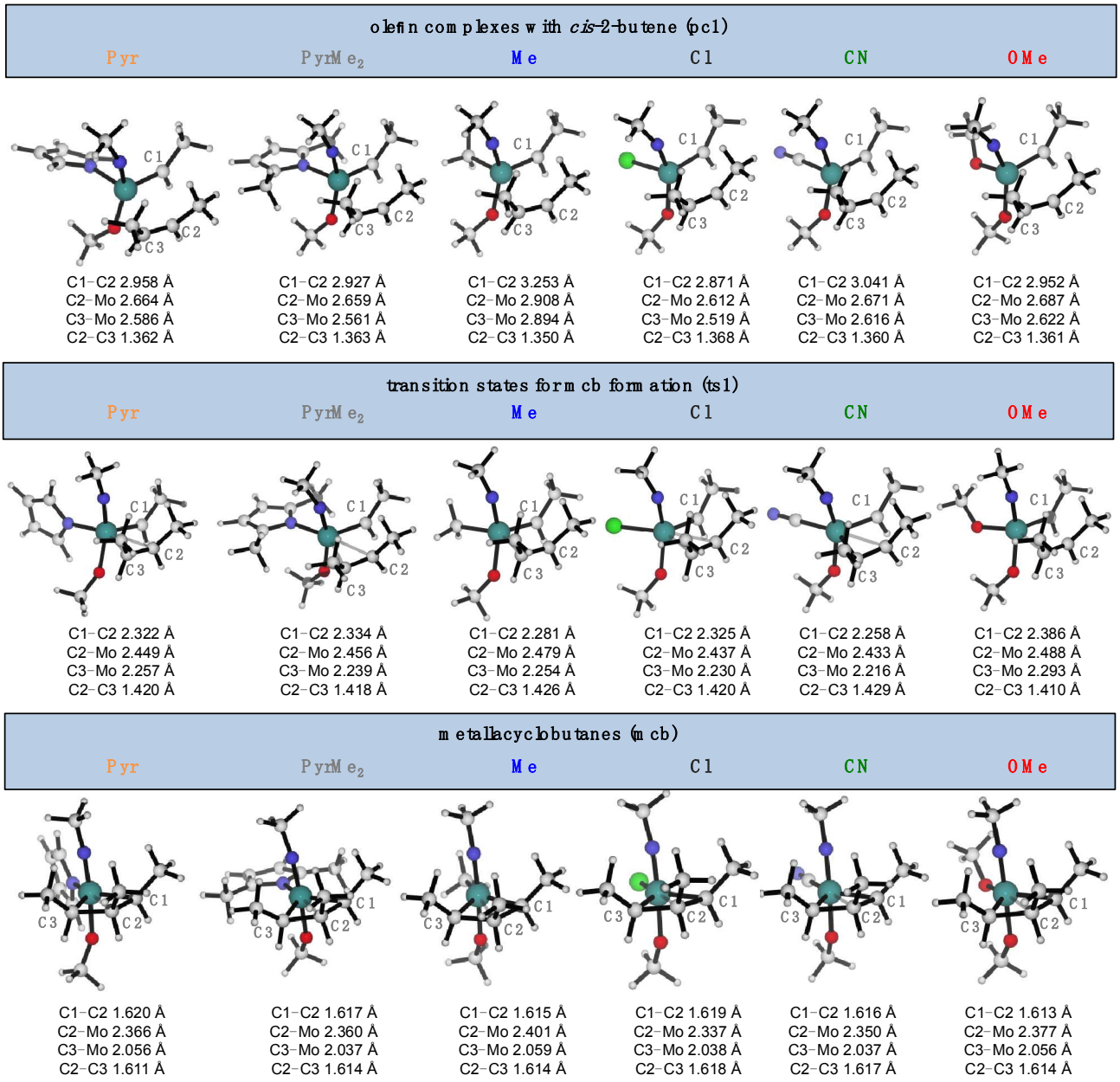


Figure S4. Computed structures for olefin complexes (**pc1**), transition states for mcb formation (**ts1**) and metallacyclobutanes (**mcb**) during reaction of model MAX-ethylidene complexes **Mo-6** after optimization with ω–B97XD/Def2SVP$_{\text{benzene(SMD)}}$.

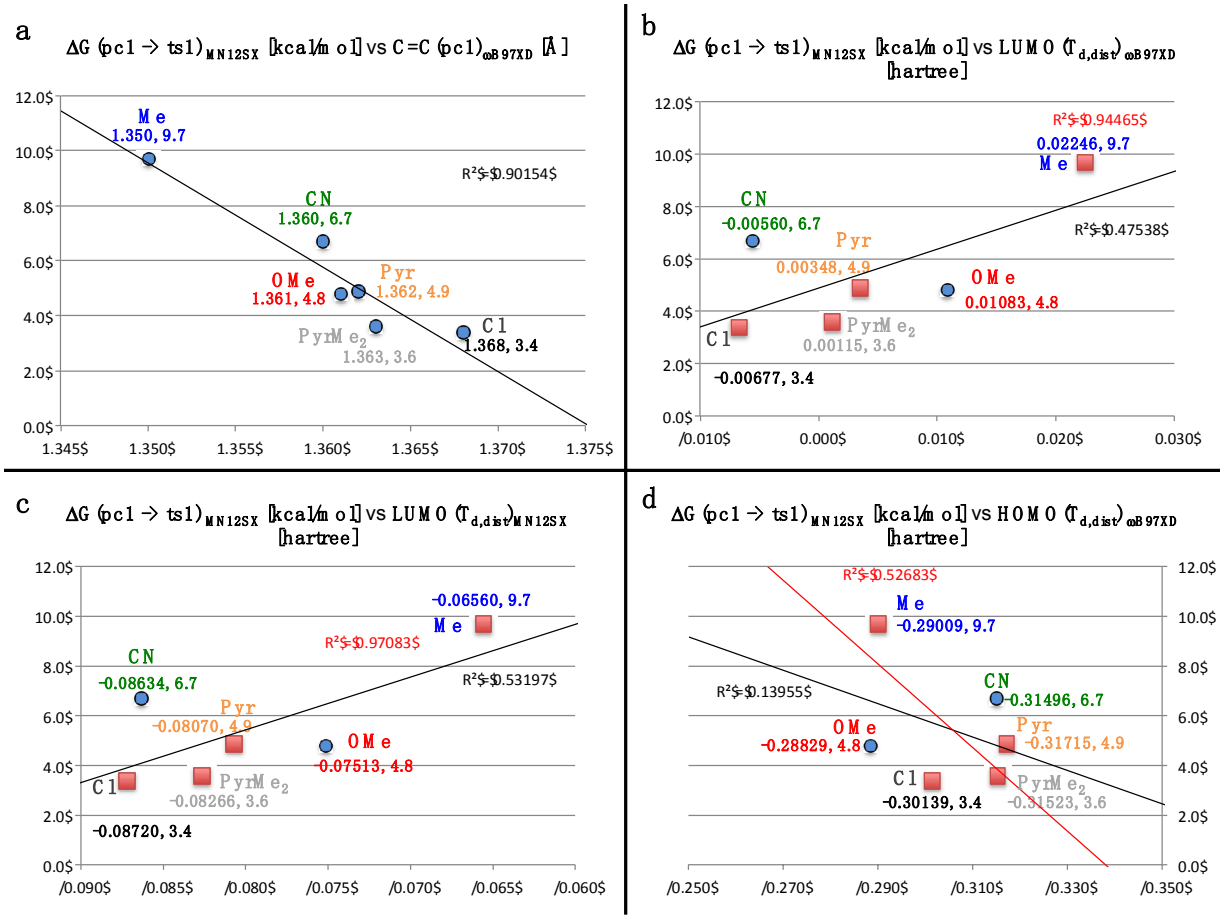


Figure S5-1. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) optimized at the MN12SX/ $Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$ level with various parameters: (**a**) correlation with the C2=C3 double bond length [Å] in **pc1**; (**b**) correlation with the LUMO of $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**c**) correlation with the LUMO of $\mathbf{T_{d,dist}}$ at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**d**) correlation with the HOMO or HOMO-2 (corresponding to the Mo=C1 π bond) of $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level.

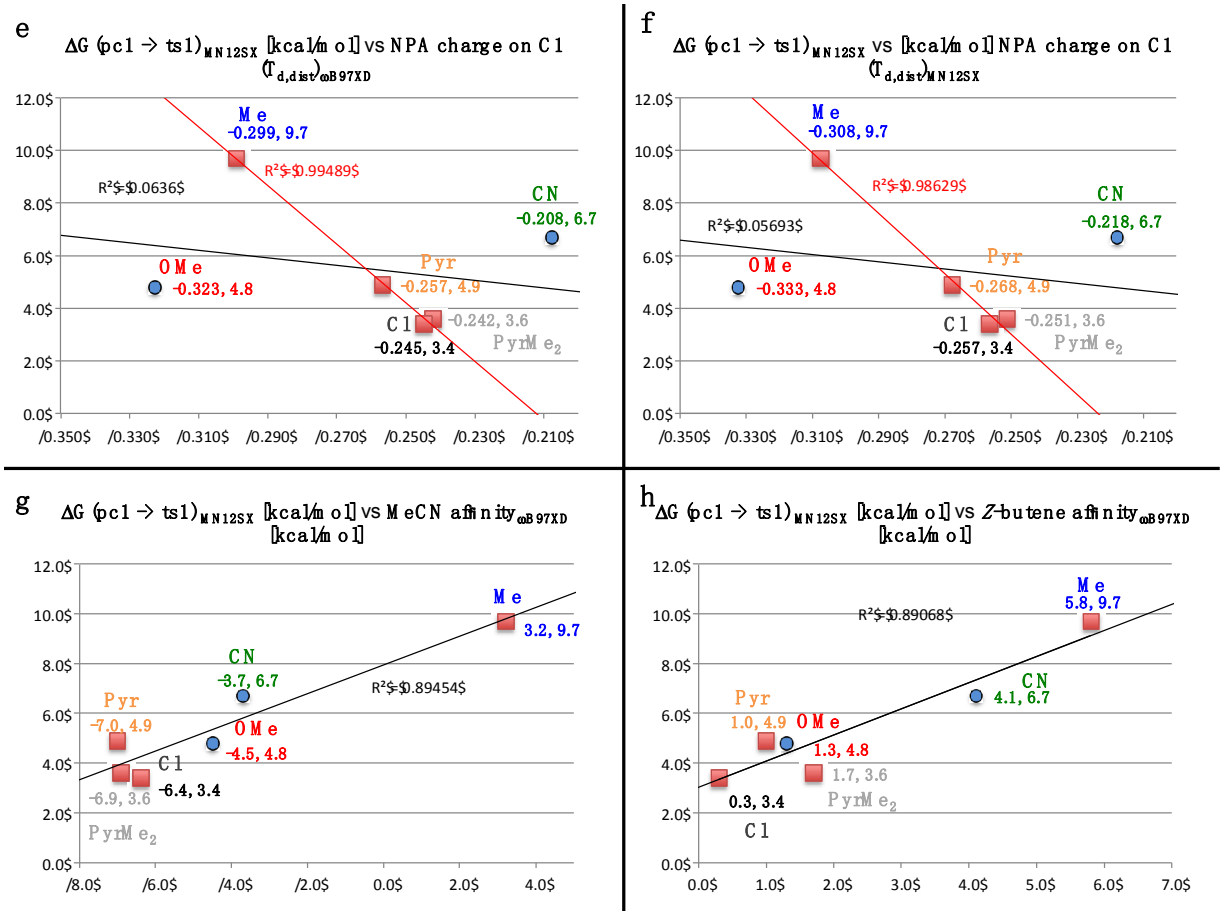


Figure S5-2. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) optimized at the MN12SX/ $Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$ level with various parameters: (**e**) correlation with the NPA charge on the alkylidene carbon in $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**f**) correlation with the NPA charge on the alkylidene carbon in $\mathbf{T_{d,dist}}$ at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**g**) correlation with the acetonitrile affinity ($\mathbf{T_{d,dist}}$ → **ac** in kcal/mol) at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**h**) correlation with the *(Z)*-2-butene affinity ($\mathbf{T_{d,dist}}$ → **pc1** in kcal/mol) at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level.

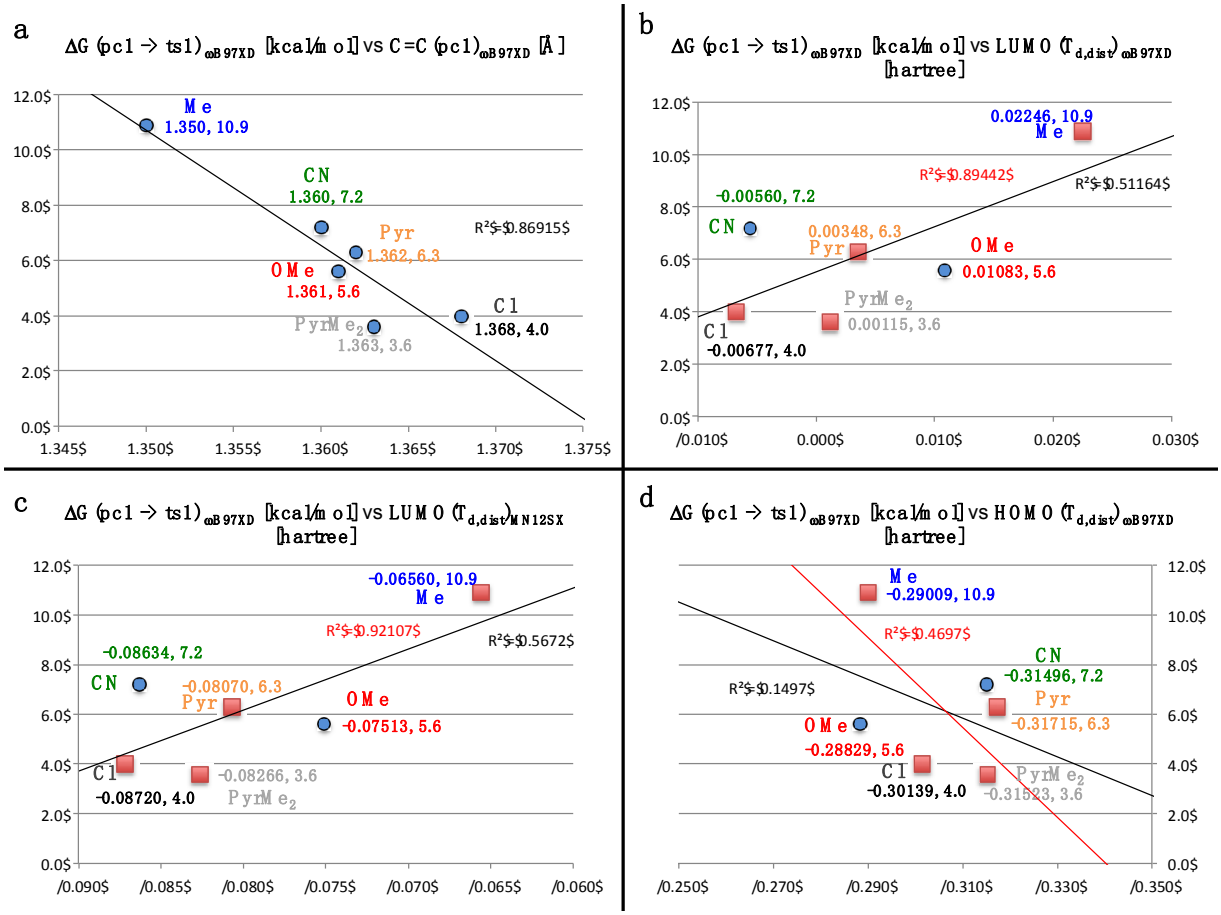


Figure S5-3. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) optimized at the ω–B97XD/ $Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$ level with various parameters: (**a**) correlation with the C2=C3 double bond length [Å] in **pc1**; (**b**) correlation with the LUMO of $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**c**) correlation with the LUMO of $\mathbf{T_{d,dist}}$ at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**d**) correlation with the HOMO or HOMO-2 (corresponding to the Mo=C1 π bond) of $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level.

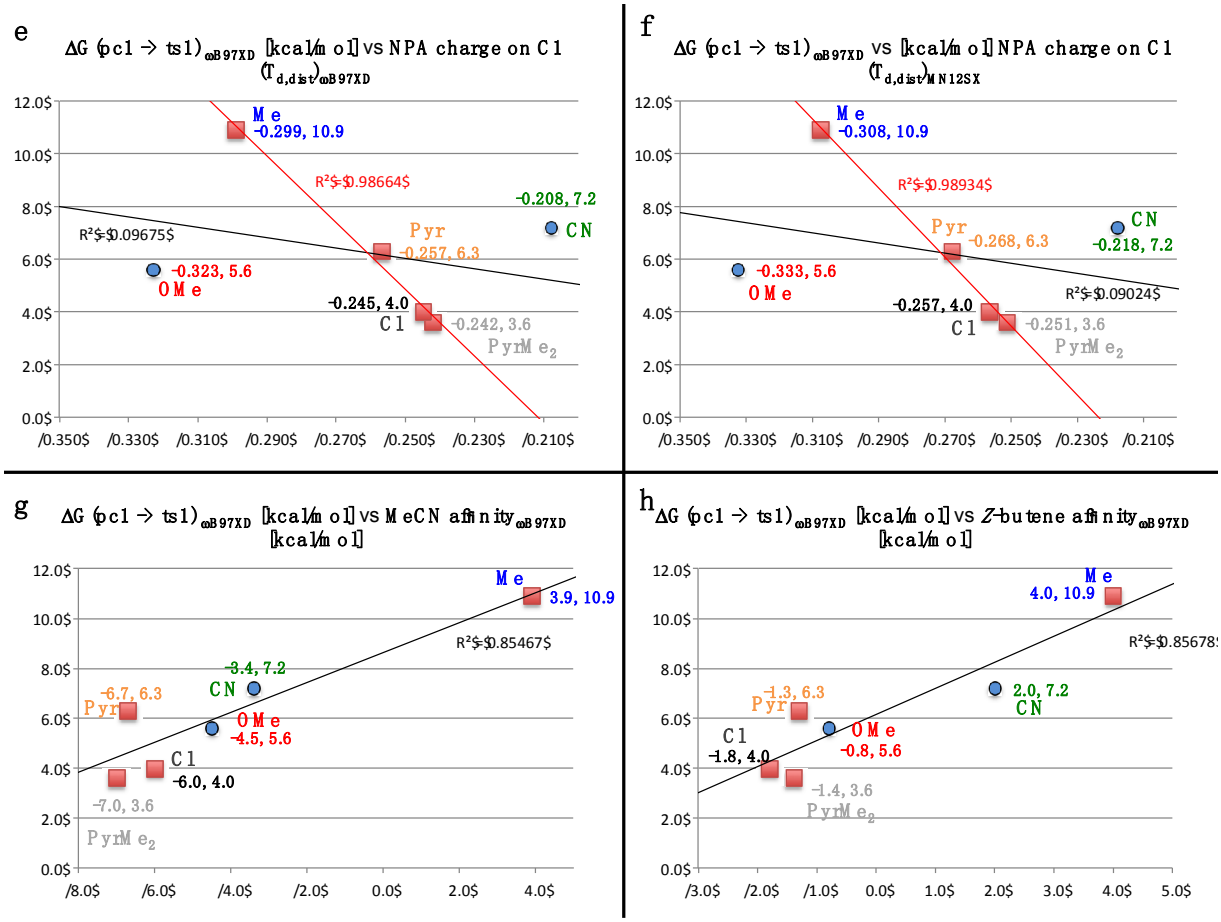


Figure S5-4. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) optimized at the ω–B97XD/ $Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$ level with various parameters: (**e**) correlation with the NPA charge on the alkylidene carbon in $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**f**) correlation with the NPA charge on the alkylidene carbon in $\mathbf{T_{d,dist}}$ at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**g**) correlation with the acetonitrile affinity ($\mathbf{T_{d,dist}}$ → **ac** in kcal/mol) at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**h**) correlation with the *(Z)*-2-butene affinity ($\mathbf{T_{d,dist}}$ → **pc1** in kcal/mol) at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level.

Figure S5-5. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) optimized at the M06/ $Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$ level with various parameters: (**a**) correlation with the C2=C3 double bond length [Å] in **pc1**; (**b**) correlation with the LUMO of $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**c**) correlation with the LUMO of $\mathbf{T_{d,dist}}$ at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**d**) correlation with the HOMO or HOMO-2 (corresponding to the Mo=C1 π bond) of $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level.

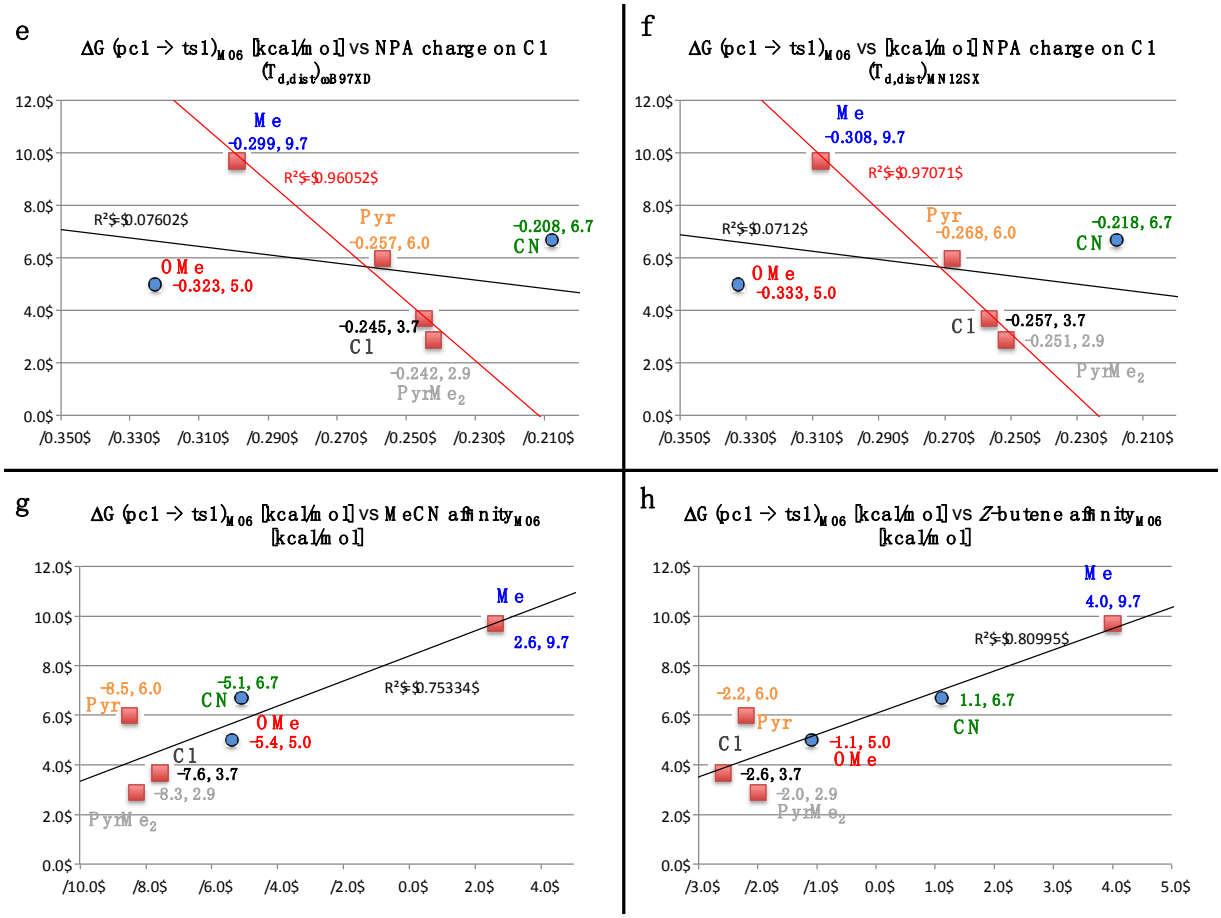


Figure S5-6. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) optimized at the M06/ $Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$ level with various parameters: (**e**) correlation with the NPA charge on the alkylidene carbon in $\mathbf{T_{d,dist}}$ at the ω–B97XD/$Def2TZVPP_{benzene(SMD)}$ level; (**f**) correlation with the NPA charge on the alkylidene carbon in $\mathbf{T_{d,dist}}$ at the MN12SX/$Def2TZVPP_{benzene(SMD)}$ level; (**g**) correlation with the acetonitrile affinity ($\mathbf{T_{d,dist}}$ → **ac** in kcal/mol) at the M06/$Def2TZVPP_{benzene(SMD)}$ level; (**h**) correlation with the *(Z)*-2-butene affinity ($\mathbf{T_{d,dist}}$ → **pc1** in kcal/mol) at the M06/$Def2TZVPP_{benzene(SMD)}$ level.

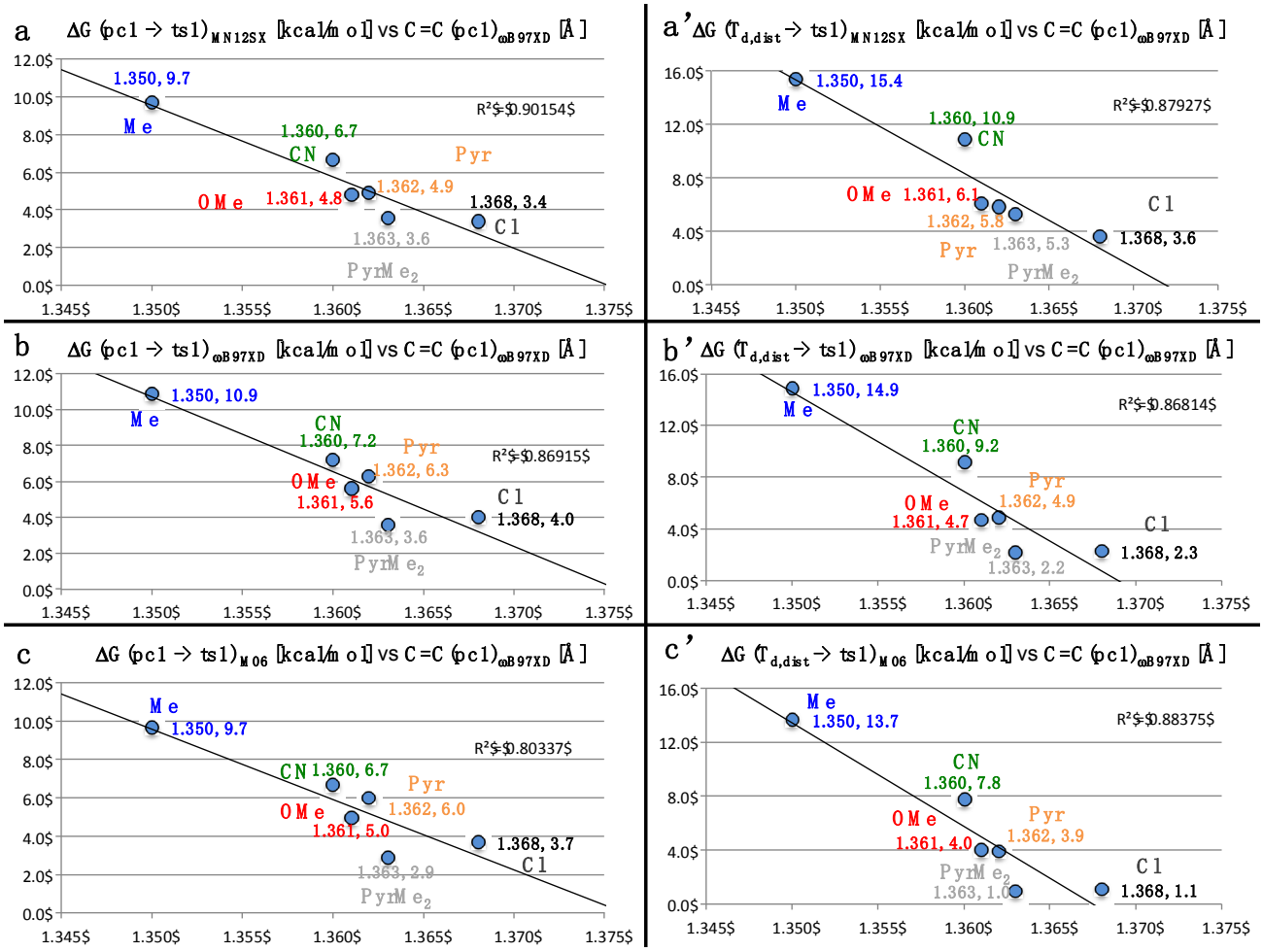


Figure S5-7. Correlation of free energy barriers (ΔG for **pc1** → **ts1**) and (ΔG for $\mathbf{T_{d,dist}}$ → **ts1**) for reaction of model MAX-ethylidene complexes **Mo-6** and *(Z)*-2-butene (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) obtained with three density functionals [MN12SX/Def2TZVPP$_{benzene(SMD)}$ (**a** and **a'**), ω–B97XD/Def2TZVPP$_{benzene(SMD)}$ (**b** and **b'**) and M06/Def2TZVPP$_{benzene(SMD)}$ (**c** and **c'**)] with the C2=C3 double bond length [Å] in **pc1** after optimization with ω–B97XD/Def2SVP$_{benzene(SMD)}$.

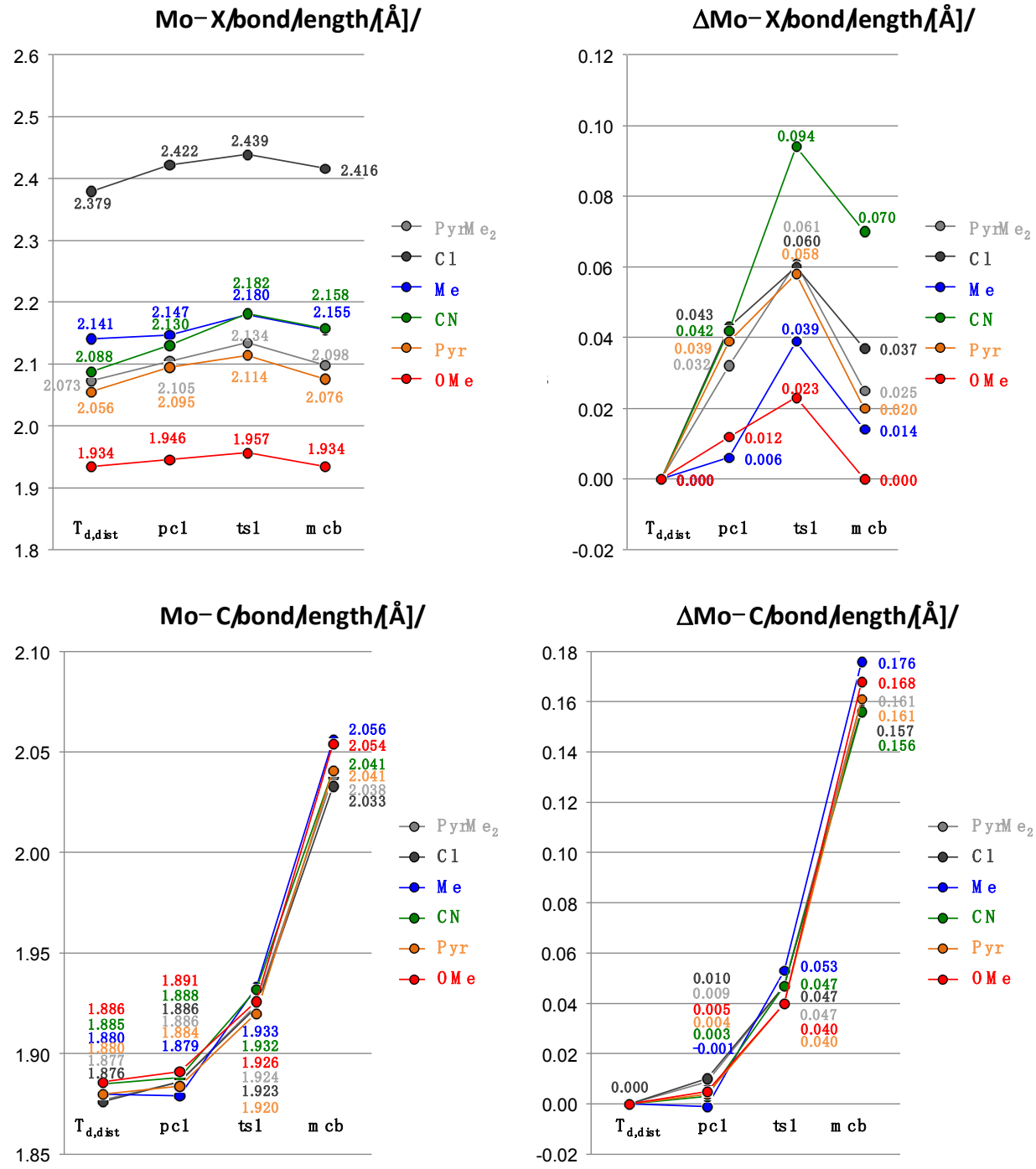


Figure S6. Structural parameters and changes in structural parameters (Mo–X and Mo–$C_{alkylidene}$ bond lengths) for reaction of MAX-ethylidene complexes **Mo-6** (model system; X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene as a function of the reaction coordinate optimized at the ω–B97XD/Def2SVP$_{benzene(SMD)}$ level relative to the distorted 4-coordinate tetrahedral complex (**$T_{d,dist}$**).

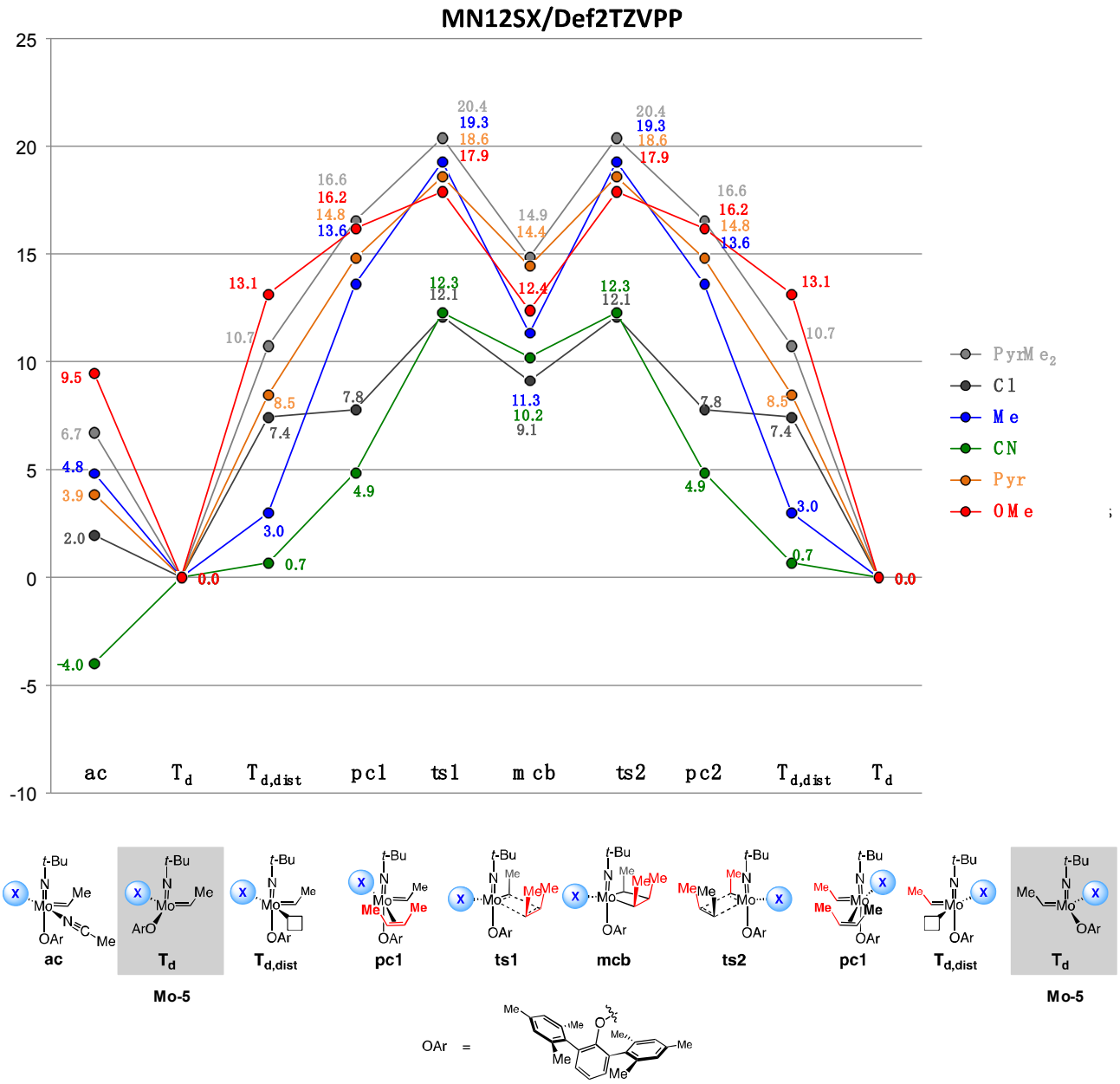


Figure S7-1. Free energy surfaces (ΔG in kcal/mol) for reaction of MAX-ethylidene complexes **Mo-5** (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene at the $MN12SX/Def2TZVPP_{benzene(SMD)}//\omega$–B97XD/ $Def2SVP_{benzene(SMD)}$ level relative to the 4-coordinate tetrahedral complex ($\mathbf{T_d}$).

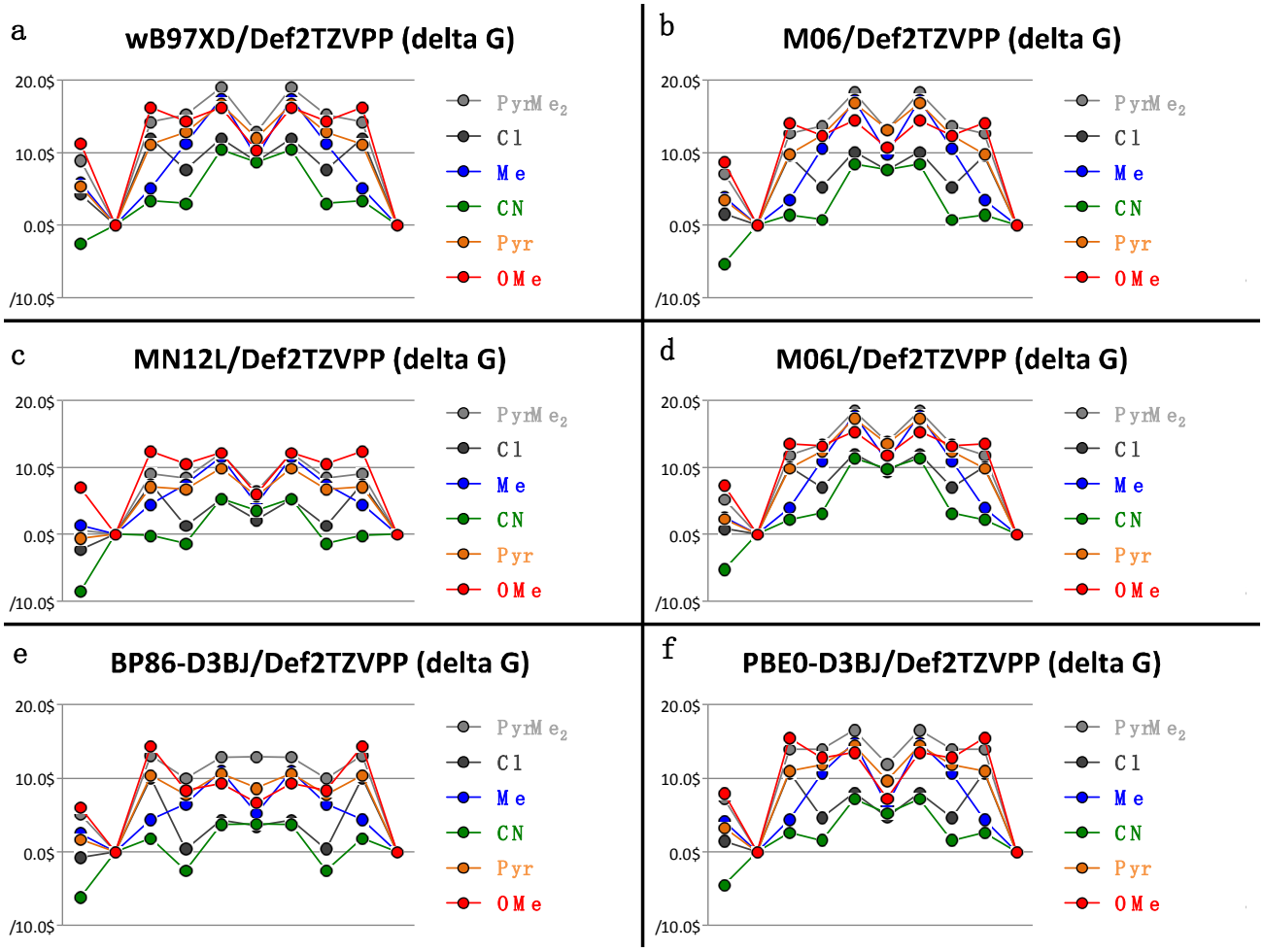


Figure S7-2. Free energy surfaces (ΔG in kcal/mol) for reaction of MAX-ethylidene complexes **Mo-5** (X = Pyr, $PyrMe_2$, Me, Cl, CN, OMe) with *(Z)*-2-butene with various levels of theory (density functional/$Def2TZVPP_{benzene(SMD)}$//ω–B97XD/$Def2SVP_{benzene(SMD)}$) relative to the 4-coordinate tetrahedral complex ($\mathbf{T_d}$).

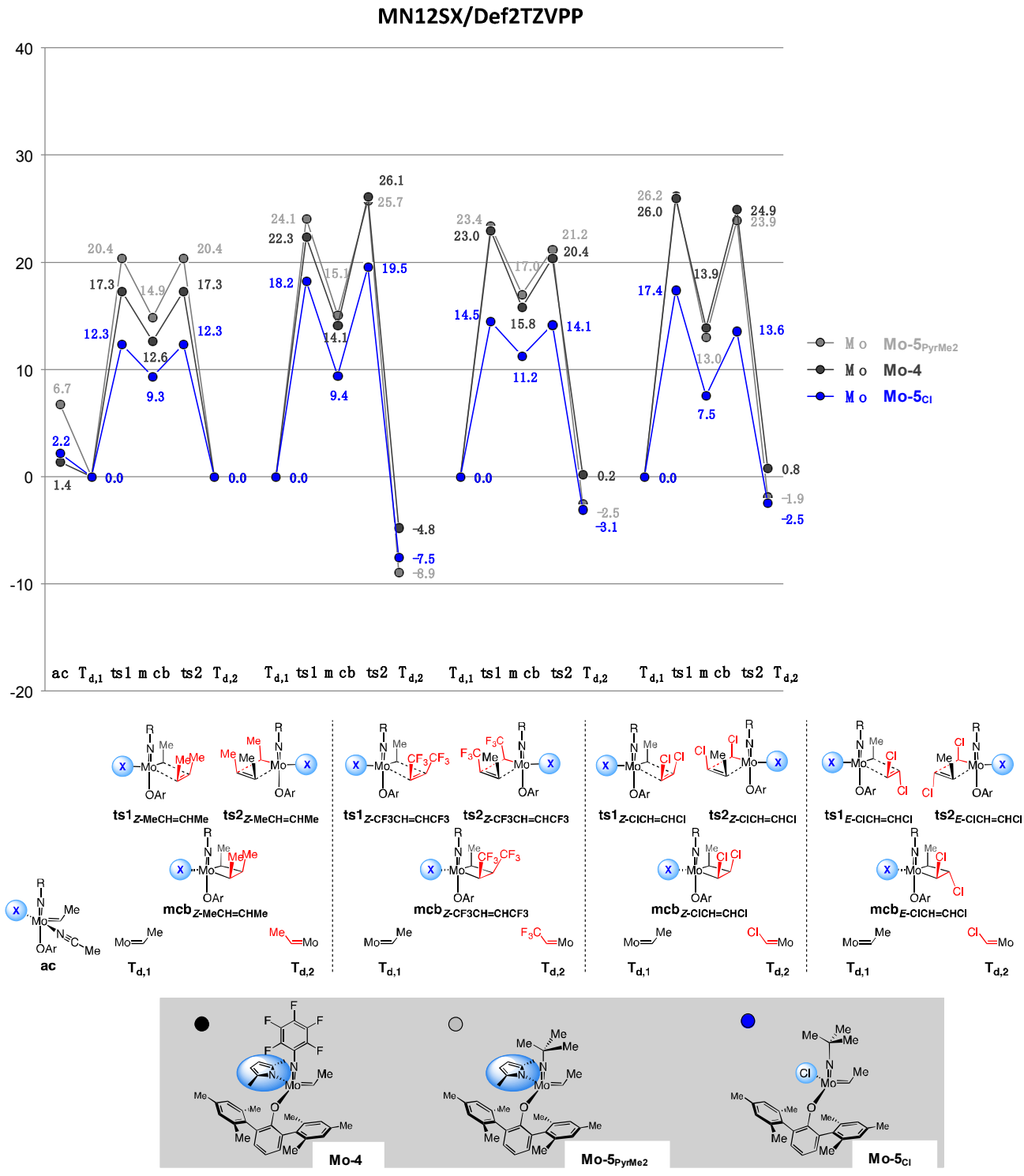


Figure S8-1. Free energy surfaces (ΔG in kcal/mol) for reaction of ethylidene complexes **Mo-4**, **Mo-5$_{PyrMe2}$** and **Mo-5$_{Cl}$** with various internal olefins [*Z*-MeCH=CHMe, *Z*-CF_3CH=CHCF_3, *Z*-ClCH=CHCl and *E*-ClCH=CHCl] at the

MN12SX/Def2TZVPP$_{benzene(SMD)}$//ω–B97XD/Def2SVP$_{benzene(SMD)}$ level relative to the 4-coordinate tetrahedral complex (**T$_d$**).

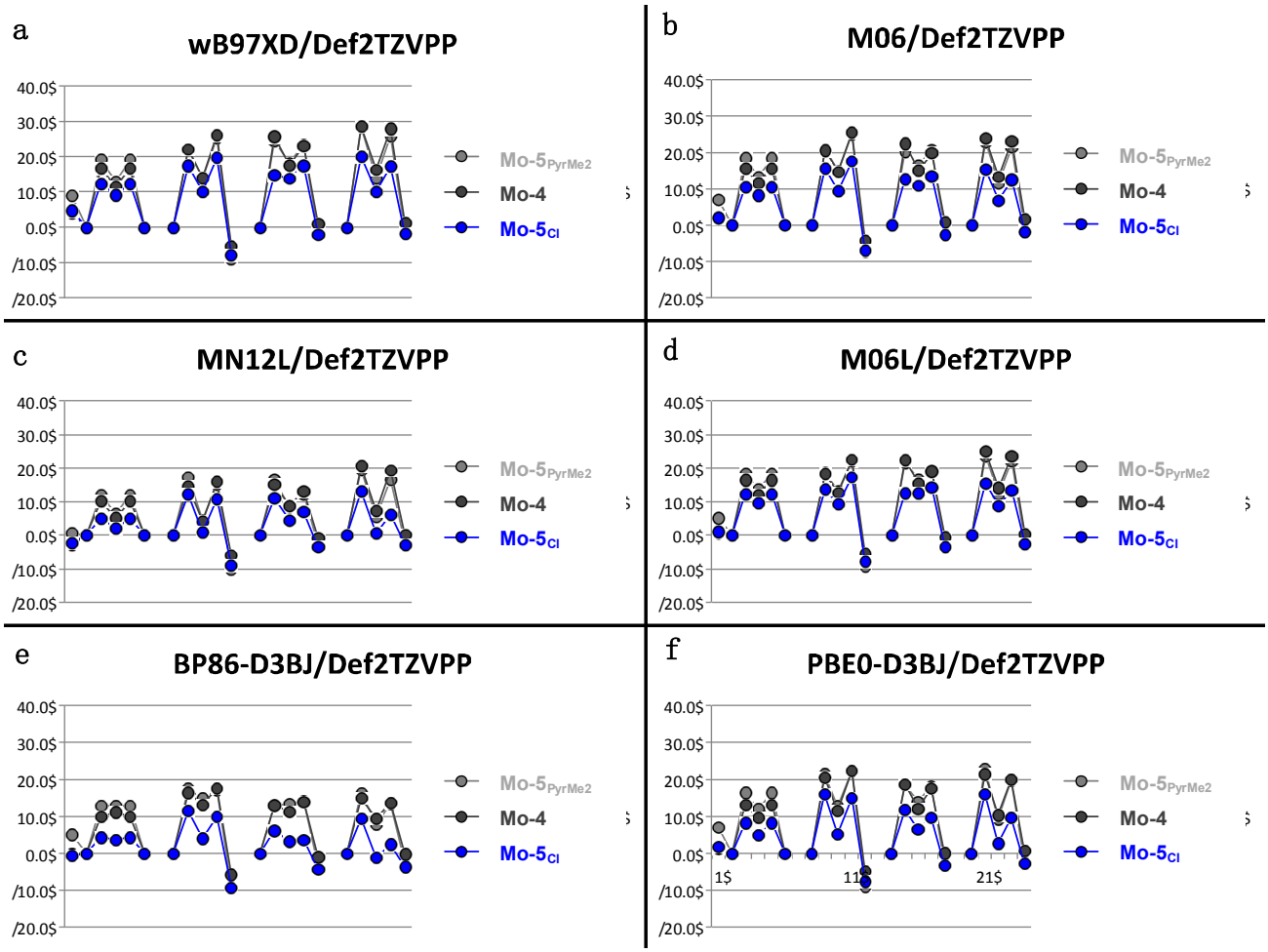
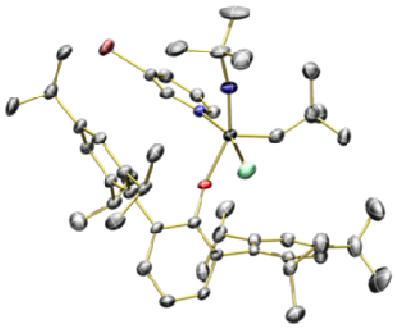


Figure S8-2. Free energy surfaces (ΔG in kcal/mol) for reaction of ethylidene complexes **Mo-4**, **Mo-5$_{PyrMe2}$** and **Mo-5$_{Cl}$** with various internal olefins [*Z*-MeCH=CHMe, *Z*-CF_3CH=$CHCF_3$, *Z*-ClCH=CHCl and *E*-ClCH=CHCl] at various levels of theory (density functional/Def2TZVPP$_{benzene(SMD)}$//ω–B97XD/Def2SVP$_{benzene(SMD)}$) relative to the 4-coordinate tetrahedral complex (**T$_d$**).

3.6.8. X-ray Crystallographic Data

X-ray Crystal Structure for Mo-2



Crystal data and structure refinement for Mo-2.

Identification code	X16032_t5	
Empirical formula	C52 H77 Br Cl Mo N2 O1.50	
Formula weight	965.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.371(3) Å	a= 98.450(5)°.
	b = 18.923(5) Å	b= 102.087(5)°.
	c = 23.926(6) Å	g = 106.193(4)°.
Volume	5132(2) $Å^3$	
Z	4	
Density (calculated)	1.249 Mg/m^3	
Absorption coefficient	1.123 mm^{-1}	
F(000)	2036	
Crystal size	0.30 x 0.12 x 0.07 mm^3	
Theta range for data collection	1.148 to 28.945°.	
Index ranges	-16<=h<=16, -25<=k<=25, 0<=l<=32	
Reflections collected	24296	
Independent reflections	24296 [R(int) = 0.0657]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745685 and 0.555157	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24296 / 1937 / 1143	

Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.1181
R indices (all data)	R1 = 0.0786, wR2 = 0.1278
Extinction coefficient	n/a
Largest diff. peak and hole	1.072 and -1.154 e.$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Mo-2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	784(1)	5698(1)	1521(1)	32(1)
Mo(1)	-72(1)	4585(1)	1846(1)	20(1)
C(1)	-141(4)	3857(3)	1206(2)	28(1)
C(2)	-873(4)	3366(3)	621(2)	33(1)
C(3)	-880(5)	2553(3)	605(2)	40(1)
C(4)	-2137(4)	3369(3)	503(2)	38(1)
C(5)	-345(5)	3686(3)	147(2)	36(1)
N(1)	-1440(3)	4685(2)	1695(2)	28(1)
C(6)	-2431(4)	4975(3)	1666(2)	35(1)
C(7)	-2392(5)	5355(4)	2278(3)	51(1)
C(8)	-3564(5)	4330(4)	1415(4)	66(2)
C(9)	-2294(5)	5542(4)	1267(3)	51(2)
O(1)	1483(2)	4789(2)	2392(1)	22(1)
C(11)	2571(3)	5280(2)	2615(2)	19(1)
C(12)	3477(3)	5211(2)	2360(2)	20(1)
C(13)	4595(4)	5714(2)	2625(2)	26(1)
C(14)	4846(4)	6270(3)	3126(2)	28(1)
C(15)	3944(4)	6312(2)	3384(2)	27(1)
C(16)	2805(3)	5828(2)	3130(2)	21(1)
C(17)	3291(3)	4598(2)	1841(2)	20(1)
C(18)	3155(4)	3855(2)	1920(2)	26(1)
C(19)	3073(4)	3302(2)	1442(2)	28(1)
C(20)	3128(4)	3456(3)	894(2)	31(1)
C(21)	3241(4)	4186(2)	830(2)	28(1)
C(22)	3316(4)	4759(2)	1287(2)	21(1)
C(23)	3132(4)	3660(3)	2514(2)	32(1)
C(24)	4376(5)	3873(3)	2911(2)	40(1)
C(25)	2469(5)	2833(3)	2480(3)	42(1)
C(26)	3060(5)	2839(3)	388(2)	40(1)
C(27)	1861(6)	2524(4)	-27(3)	68(2)

C(28)	3958(7)	3083(4)	60(4)	84(3)
C(29)	3437(4)	5546(2)	1177(2)	25(1)
C(30)	2589(5)	5535(3)	614(2)	35(1)
C(31)	4693(4)	5969(3)	1175(3)	40(1)
C(32)	1864(4)	5843(2)	3434(2)	22(1)
C(33)	1654(4)	5361(2)	3820(2)	22(1)
C(34)	764(4)	5366(2)	4096(2)	24(1)
C(35)	105(4)	5841(2)	4012(2)	26(1)
C(36)	326(4)	6316(2)	3628(2)	25(1)
C(37)	1201(4)	6329(2)	3336(2)	23(1)
C(38)	2401(4)	4856(2)	3964(2)	26(1)
C(39)	1686(4)	4025(2)	3799(2)	32(1)
C(40)	3093(5)	5094(3)	4611(2)	41(1)
C(41)	-795(4)	5872(3)	4356(2)	31(1)
C(42)	-1942(4)	5891(3)	3982(2)	38(1)
C(43)	-276(5)	6541(3)	4877(2)	39(1)
C(44)	1510(4)	6911(2)	2968(2)	27(1)
C(45)	2415(4)	7633(2)	3355(2)	33(1)
C(46)	466(4)	7095(3)	2625(2)	34(1)
N(2)	-593(3)	3766(2)	2402(2)	22(1)
C(51)	-1030(4)	3979(2)	2841(2)	24(1)
C(52)	-1499(4)	3470(2)	3158(2)	25(1)
C(53)	-1486(4)	2738(2)	3042(2)	28(1)
C(54)	-995(4)	2537(2)	2604(2)	29(1)
C(55)	-562(4)	3058(2)	2291(2)	23(1)
Br(1)	-2183(1)	3785(1)	3743(1)	38(1)
Cl(2)	6376(1)	11267(1)	3267(1)	34(1)
Mo(2)	5295(1)	9945(1)	2941(1)	20(1)
C(101)	5957(4)	9561(3)	3554(2)	31(1)
C(102)	5849(4)	9303(3)	4112(2)	31(1)
C(103)	5802(5)	8467(3)	4017(3)	43(1)
C(104)	6932(5)	9788(4)	4599(2)	48(1)
C(105)	4762(5)	9374(3)	4289(2)	42(1)
N(3)	4060(3)	10067(2)	3126(2)	29(1)
C(106)	3051(4)	10302(3)	3176(2)	30(1)
C(107)	1938(4)	9636(3)	2937(3)	48(1)

C(108)	3190(5)	10584(4)	3826(2)	52(2)
C(109)	3025(5)	10925(4)	2854(3)	54(2)
O(2)	6264(3)	9887(2)	2378(1)	23(1)
C(111)	7075(3)	10211(2)	2120(2)	18(1)
C(112)	8242(3)	10245(2)	2338(2)	18(1)
C(113)	9077(4)	10561(2)	2051(2)	24(1)
C(114)	8763(4)	10833(3)	1553(2)	27(1)
C(115)	7608(4)	10777(2)	1329(2)	25(1)
C(116)	6751(3)	10477(2)	1611(2)	20(1)
C(117)	8605(4)	9900(2)	2849(2)	21(1)
C(118)	8412(4)	9113(2)	2751(2)	26(1)
C(119)	8786(4)	8801(2)	3220(2)	29(1)
C(120)	9357(4)	9245(3)	3779(2)	30(1)
C(121)	9538(4)	10015(2)	3862(2)	27(1)
C(122)	9162(4)	10347(2)	3408(2)	22(1)
C(123)	7855(4)	8615(2)	2139(2)	31(1)
C(124)	7163(5)	7800(3)	2136(3)	46(1)
C(125)	8791(5)	8607(3)	1807(2)	50(2)
C(126)	9786(5)	8896(3)	4286(2)	36(1)
C(127)	10784(5)	8629(4)	4215(2)	46(1)
C(128)	8814(5)	8284(4)	4381(4)	75(2)
C(129)	9355(4)	11195(2)	3538(2)	26(1)
C(130)	9098(5)	11469(3)	4114(2)	40(1)
C(131)	10606(4)	11642(3)	3547(3)	41(1)
C(132)	5491(3)	10388(2)	1350(2)	19(1)
C(133)	4766(4)	9711(2)	963(2)	22(1)
C(134)	3587(4)	9626(2)	745(2)	26(1)
C(135)	3119(4)	10190(2)	892(2)	25(1)
C(136)	3867(3)	10866(2)	1262(2)	23(1)
C(137)	5048(3)	10980(2)	1496(2)	20(1)
C(138)	5251(4)	9088(2)	758(2)	25(1)
C(139)	4772(6)	8377(3)	966(3)	47(2)
C(140)	5002(6)	8905(3)	88(2)	50(2)
C(141)	1839(4)	10093(3)	631(2)	37(1)
C(142)	1228(5)	10244(4)	1110(3)	69(2)
C(143)	1735(6)	10572(4)	180(3)	76(2)

C(144)	5854(4)	11745(2)	1859(2)	24(1)
C(145)	5273(4)	12188(3)	2223(2)	33(1)
C(146)	6378(4)	12233(3)	1460(2)	33(1)
N(4)	4210(3)	8822(2)	2370(2)	25(1)
C(151)	3250(4)	8786(2)	1976(2)	27(1)
C(152)	2460(4)	8109(3)	1645(2)	35(1)
C(153)	2678(5)	7437(3)	1707(2)	41(1)
C(154)	3686(5)	7482(3)	2099(2)	43(1)
C(155)	4443(5)	8177(2)	2429(2)	32(1)
Br(2)	1087(1)	8111(1)	1126(1)	52(1)
C(2S)	3124(19)	7570(20)	5127(10)	48(5)
C(1S)	4063(17)	7306(16)	5446(10)	37(3)
O(1S)	4938(13)	7362(13)	5130(8)	34(3)
C(3S)	5801(14)	7039(13)	5374(8)	35(3)
C(4S)	6484(17)	6897(12)	4942(10)	50(4)
C(2T)	3010(30)	7520(30)	4971(15)	50(6)
C(1T)	4050(20)	7430(20)	5371(13)	43(5)
O(1T)	4764(16)	7194(18)	5020(10)	42(5)
C(3T)	5830(20)	7210(20)	5414(11)	47(6)
C(4T)	6731(17)	7196(16)	5089(11)	44(5)

Bond lengths [Å] and angles [°] for Mo-2.

Cl(1)-Mo(1)	2.3961(12)
Mo(1)-N(1)	1.724(4)
Mo(1)-C(1)	1.872(4)
Mo(1)-O(1)	1.985(3)
Mo(1)-N(2)	2.237(3)
C(1)-C(2)	1.502(6)
C(1)-H(1)	0.895(19)
C(2)-C(3)	1.530(6)
C(2)-C(4)	1.532(7)
C(2)-C(5)	1.540(6)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
N(1)-C(6)	1.471(5)
C(6)-C(8)	1.515(7)
C(6)-C(7)	1.517(7)
C(6)-C(9)	1.536(7)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
O(1)-C(11)	1.347(5)
C(11)-C(16)	1.409(5)

C(11)-C(12)	1.410(5)
C(12)-C(13)	1.393(6)
C(12)-C(17)	1.500(5)
C(13)-C(14)	1.390(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.400(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.397(6)
C(15)-H(15)	0.9500
C(16)-C(32)	1.501(5)
C(17)-C(22)	1.408(5)
C(17)-C(18)	1.414(5)
C(18)-C(19)	1.396(6)
C(18)-C(23)	1.525(6)
C(19)-C(20)	1.395(6)
C(19)-H(19)	0.9500
C(20)-C(21)	1.383(6)
C(20)-C(26)	1.527(6)
C(21)-C(22)	1.391(6)
C(21)-H(21)	0.9500
C(22)-C(29)	1.522(5)
C(23)-C(25)	1.533(7)
C(23)-C(24)	1.537(7)
C(23)-H(23)	1.0000
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(28)	1.499(8)
C(26)-C(27)	1.502(8)
C(26)-H(26)	1.0000
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800

C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-C(30)	1.518(6)
C(29)-C(31)	1.537(6)
C(29)-H(29)	1.0000
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-C(33)	1.403(5)
C(32)-C(37)	1.404(6)
C(33)-C(34)	1.399(5)
C(33)-C(38)	1.530(6)
C(34)-C(35)	1.379(6)
C(34)-H(34)	0.9500
C(35)-C(36)	1.394(6)
C(35)-C(41)	1.524(5)
C(36)-C(37)	1.403(5)
C(36)-H(36)	0.9500
C(37)-C(44)	1.526(5)
C(38)-C(39)	1.520(6)
C(38)-C(40)	1.536(6)
C(38)-H(38)	1.0000
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(43)	1.522(7)
C(41)-C(42)	1.523(7)
C(41)-H(41)	1.0000
C(42)-H(42A)	0.9800

C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-C(45)	1.522(6)
C(44)-C(46)	1.534(6)
C(44)-H(44)	1.0000
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
N(2)-C(55)	1.339(5)
N(2)-C(51)	1.339(5)
C(51)-C(52)	1.386(5)
C(51)-H(51)	0.9500
C(52)-C(53)	1.377(6)
C(52)-Br(1)	1.888(4)
C(53)-C(54)	1.377(6)
C(53)-H(53)	0.9500
C(54)-C(55)	1.381(6)
C(54)-H(54)	0.9500
C(55)-H(55)	0.9500
Cl(2)-Mo(2)	2.4042(13)
Mo(2)-N(3)	1.741(4)
Mo(2)-C(101)	1.870(5)
Mo(2)-O(2)	1.992(3)
Mo(2)-N(4)	2.230(4)
C(101)-C(102)	1.506(6)
C(101)-H(101)	0.908(19)
C(102)-C(105)	1.526(6)
C(102)-C(104)	1.530(7)
C(102)-C(103)	1.547(7)
C(103)-H(10A)	0.9800

C(103)-H(10B)	0.9800
C(103)-H(10C)	0.9800
C(104)-H(10D)	0.9800
C(104)-H(10E)	0.9800
C(104)-H(10F)	0.9800
C(105)-H(10G)	0.9800
C(105)-H(10H)	0.9800
C(105)-H(10I)	0.9800
N(3)-C(106)	1.459(5)
C(106)-C(109)	1.504(7)
C(106)-C(107)	1.518(7)
C(106)-C(108)	1.525(7)
C(107)-H(10J)	0.9800
C(107)-H(10K)	0.9800
C(107)-H(10L)	0.9800
C(108)-H(10M)	0.9800
C(108)-H(10N)	0.9800
C(108)-H(10O)	0.9800
C(109)-H(10P)	0.9800
C(109)-H(10Q)	0.9800
C(109)-H(10R)	0.9800
O(2)-C(111)	1.338(4)
C(111)-C(116)	1.409(5)
C(111)-C(112)	1.409(5)
C(112)-C(113)	1.404(5)
C(112)-C(117)	1.513(5)
C(113)-C(114)	1.391(6)
C(113)-H(113)	0.9500
C(114)-C(115)	1.386(6)
C(114)-H(114)	0.9500
C(115)-C(116)	1.407(5)
C(115)-H(115)	0.9500
C(116)-C(132)	1.504(5)
C(117)-C(122)	1.391(6)
C(117)-C(118)	1.416(5)
C(118)-C(119)	1.396(6)

C(118)-C(123)	1.522(6)
C(119)-C(120)	1.392(6)
C(119)-H(119)	0.9500
C(120)-C(121)	1.389(6)
C(120)-C(126)	1.534(6)
C(121)-C(122)	1.394(6)
C(121)-H(121)	0.9500
C(122)-C(129)	1.528(6)
C(123)-C(125)	1.537(7)
C(123)-C(124)	1.539(7)
C(123)-H(123)	1.0000
C(124)-H(12A)	0.9800
C(124)-H(12B)	0.9800
C(124)-H(12C)	0.9800
C(125)-H(12D)	0.9800
C(125)-H(12E)	0.9800
C(125)-H(12F)	0.9800
C(126)-C(127)	1.489(7)
C(126)-C(128)	1.500(7)
C(126)-H(126)	1.0000
C(127)-H(12G)	0.9800
C(127)-H(12H)	0.9800
C(127)-H(12I)	0.9800
C(128)-H(12J)	0.9800
C(128)-H(12K)	0.9800
C(128)-H(12L)	0.9800
C(129)-C(130)	1.527(6)
C(129)-C(131)	1.537(6)
C(129)-H(129)	1.0000
C(130)-H(13A)	0.9800
C(130)-H(13B)	0.9800
C(130)-H(13C)	0.9800
C(131)-H(13D)	0.9800
C(131)-H(13E)	0.9800
C(131)-H(13F)	0.9800
C(132)-C(133)	1.402(6)

C(132)-C(137)	1.408(5)
C(133)-C(134)	1.397(6)
C(133)-C(138)	1.529(5)
C(134)-C(135)	1.384(6)
C(134)-H(134)	0.9500
C(135)-C(136)	1.392(6)
C(135)-C(141)	1.524(6)
C(136)-C(137)	1.394(5)
C(136)-H(136)	0.9500
C(137)-C(144)	1.520(6)
C(138)-C(139)	1.511(6)
C(138)-C(140)	1.536(6)
C(138)-H(138)	1.0000
C(139)-H(13G)	0.9800
C(139)-H(13H)	0.9800
C(139)-H(13I)	0.9800
C(140)-H(14A)	0.9800
C(140)-H(14B)	0.9800
C(140)-H(14C)	0.9800
C(141)-C(143)	1.516(8)
C(141)-C(142)	1.534(8)
C(141)-H(141)	1.0000
C(142)-H(14D)	0.9800
C(142)-H(14E)	0.9800
C(142)-H(14F)	0.9800
C(143)-H(14G)	0.9800
C(143)-H(14H)	0.9800
C(143)-H(14I)	0.9800
C(144)-C(145)	1.536(6)
C(144)-C(146)	1.539(6)
C(144)-H(144)	1.0000
C(145)-H(14J)	0.9800
C(145)-H(14K)	0.9800
C(145)-H(14L)	0.9800
C(146)-H(14M)	0.9800
C(146)-H(14N)	0.9800

C(146)-H(14O)	0.9800
N(4)-C(151)	1.331(6)
N(4)-C(155)	1.349(5)
C(151)-C(152)	1.381(6)
C(151)-H(151)	0.9500
C(152)-C(153)	1.393(7)
C(152)-Br(2)	1.883(5)
C(153)-C(154)	1.369(8)
C(153)-H(153)	0.9500
C(154)-C(155)	1.388(7)
C(154)-H(154)	0.9500
C(155)-H(155)	0.9500
C(2S)-C(1S)	1.505(12)
C(2S)-H(2S1)	0.9800
C(2S)-H(2S2)	0.9800
C(2S)-H(2S3)	0.9800
C(1S)-O(1S)	1.435(12)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
O(1S)-C(3S)	1.437(12)
C(3S)-C(4S)	1.504(11)
C(3S)-H(3S1)	0.9900
C(3S)-H(3S2)	0.9900
C(4S)-H(4S1)	0.9800
C(4S)-H(4S2)	0.9800
C(4S)-H(4S3)	0.9800
C(2T)-C(1T)	1.504(14)
C(2T)-H(2T1)	0.9800
C(2T)-H(2T2)	0.9800
C(2T)-H(2T3)	0.9800
C(1T)-O(1T)	1.446(14)
C(1T)-H(1T1)	0.9900
C(1T)-H(1T2)	0.9900
O(1T)-C(3T)	1.443(15)
C(3T)-C(4T)	1.486(13)
C(3T)-H(3T1)	0.9900

C(3T)-H(3T2)	0.9900
C(4T)-H(4T1)	0.9800
C(4T)-H(4T2)	0.9800
C(4T)-H(4T3)	0.9800

N(1)-Mo(1)-C(1)	104.1(2)
N(1)-Mo(1)-O(1)	150.47(16)
C(1)-Mo(1)-O(1)	105.01(17)
N(1)-Mo(1)-N(2)	91.10(15)
C(1)-Mo(1)-N(2)	95.44(16)
O(1)-Mo(1)-N(2)	81.39(12)
N(1)-Mo(1)-Cl(1)	93.28(12)
C(1)-Mo(1)-Cl(1)	99.04(14)
O(1)-Mo(1)-Cl(1)	86.94(9)
N(2)-Mo(1)-Cl(1)	163.35(10)
C(2)-C(1)-Mo(1)	145.6(4)
C(2)-C(1)-H(1)	105(3)
Mo(1)-C(1)-H(1)	109(3)
C(1)-C(2)-C(3)	109.6(4)
C(1)-C(2)-C(4)	111.7(4)
C(3)-C(2)-C(4)	108.2(4)
C(1)-C(2)-C(5)	107.6(4)
C(3)-C(2)-C(5)	111.5(4)
C(4)-C(2)-C(5)	108.3(4)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5

C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(6)-N(1)-Mo(1)	164.4(3)
N(1)-C(6)-C(8)	109.6(4)
N(1)-C(6)-C(7)	109.3(4)
C(8)-C(6)-C(7)	109.4(5)
N(1)-C(6)-C(9)	106.3(4)
C(8)-C(6)-C(9)	110.9(5)
C(7)-C(6)-C(9)	111.1(5)
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(6)-C(9)-H(9A)	109.5
C(6)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-O(1)-Mo(1)	145.8(3)
O(1)-C(11)-C(16)	118.8(3)
O(1)-C(11)-C(12)	120.4(4)
C(16)-C(11)-C(12)	120.6(4)
C(13)-C(12)-C(11)	117.9(4)

C(13)-C(12)-C(17)	119.5(3)
C(11)-C(12)-C(17)	122.5(3)
C(14)-C(13)-C(12)	122.8(4)
C(14)-C(13)-H(13)	118.6
C(12)-C(13)-H(13)	118.6
C(13)-C(14)-C(15)	118.5(4)
C(13)-C(14)-H(14)	120.7
C(15)-C(14)-H(14)	120.7
C(16)-C(15)-C(14)	120.8(4)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(11)	119.4(4)
C(15)-C(16)-C(32)	120.1(4)
C(11)-C(16)-C(32)	120.2(4)
C(22)-C(17)-C(18)	119.7(4)
C(22)-C(17)-C(12)	121.0(3)
C(18)-C(17)-C(12)	119.2(4)
C(19)-C(18)-C(17)	118.5(4)
C(19)-C(18)-C(23)	120.3(4)
C(17)-C(18)-C(23)	121.2(4)
C(20)-C(19)-C(18)	122.6(4)
C(20)-C(19)-H(19)	118.7
C(18)-C(19)-H(19)	118.7
C(21)-C(20)-C(19)	117.5(4)
C(21)-C(20)-C(26)	121.6(4)
C(19)-C(20)-C(26)	120.9(4)
C(20)-C(21)-C(22)	122.6(4)
C(20)-C(21)-H(21)	118.7
C(22)-C(21)-H(21)	118.7
C(21)-C(22)-C(17)	119.1(4)
C(21)-C(22)-C(29)	119.1(4)
C(17)-C(22)-C(29)	121.8(4)
C(18)-C(23)-C(25)	114.1(4)
C(18)-C(23)-C(24)	110.8(4)
C(25)-C(23)-C(24)	109.7(4)
C(18)-C(23)-H(23)	107.3

C(25)-C(23)-H(23)	107.3
C(24)-C(23)-H(23)	107.3
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(28)-C(26)-C(27)	110.4(6)
C(28)-C(26)-C(20)	113.4(5)
C(27)-C(26)-C(20)	111.9(4)
C(28)-C(26)-H(26)	106.9
C(27)-C(26)-H(26)	106.9
C(20)-C(26)-H(26)	106.9
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(30)-C(29)-C(22)	112.5(4)
C(30)-C(29)-C(31)	110.1(4)
C(22)-C(29)-C(31)	111.7(4)
C(30)-C(29)-H(29)	107.4

C(22)-C(29)-H(29)	107.4
C(31)-C(29)-H(29)	107.4
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(33)-C(32)-C(37)	120.3(4)
C(33)-C(32)-C(16)	118.7(4)
C(37)-C(32)-C(16)	121.1(3)
C(34)-C(33)-C(32)	118.8(4)
C(34)-C(33)-C(38)	119.4(4)
C(32)-C(33)-C(38)	121.8(3)
C(35)-C(34)-C(33)	122.3(4)
C(35)-C(34)-H(34)	118.8
C(33)-C(34)-H(34)	118.8
C(34)-C(35)-C(36)	118.2(4)
C(34)-C(35)-C(41)	120.8(4)
C(36)-C(35)-C(41)	120.9(4)
C(35)-C(36)-C(37)	121.7(4)
C(35)-C(36)-H(36)	119.1
C(37)-C(36)-H(36)	119.1
C(36)-C(37)-C(32)	118.7(4)
C(36)-C(37)-C(44)	120.6(4)
C(32)-C(37)-C(44)	120.4(3)
C(39)-C(38)-C(33)	112.4(4)
C(39)-C(38)-C(40)	111.3(4)
C(33)-C(38)-C(40)	111.0(4)
C(39)-C(38)-H(38)	107.3

C(33)-C(38)-H(38)	107.3
C(40)-C(38)-H(38)	107.3
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(43)-C(41)-C(42)	111.1(4)
C(43)-C(41)-C(35)	109.8(4)
C(42)-C(41)-C(35)	113.4(4)
C(43)-C(41)-H(41)	107.4
C(42)-C(41)-H(41)	107.4
C(35)-C(41)-H(41)	107.4
C(41)-C(42)-H(42A)	109.5
C(41)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(41)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(45)-C(44)-C(37)	109.8(4)
C(45)-C(44)-C(46)	109.7(4)
C(37)-C(44)-C(46)	114.7(4)
C(45)-C(44)-H(44)	107.4

C(37)-C(44)-H(44)	107.4
C(46)-C(44)-H(44)	107.4
C(44)-C(45)-H(45A)	109.5
C(44)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
C(44)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(44)-C(46)-H(46A)	109.5
C(44)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(44)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(55)-N(2)-C(51)	118.7(3)
C(55)-N(2)-Mo(1)	122.9(3)
C(51)-N(2)-Mo(1)	118.2(3)
N(2)-C(51)-C(52)	121.0(4)
N(2)-C(51)-H(51)	119.5
C(52)-C(51)-H(51)	119.5
C(53)-C(52)-C(51)	120.7(4)
C(53)-C(52)-Br(1)	120.0(3)
C(51)-C(52)-Br(1)	119.3(3)
C(54)-C(53)-C(52)	117.4(4)
C(54)-C(53)-H(53)	121.3
C(52)-C(53)-H(53)	121.3
C(53)-C(54)-C(55)	119.9(4)
C(53)-C(54)-H(54)	120.1
C(55)-C(54)-H(54)	120.1
N(2)-C(55)-C(54)	122.2(4)
N(2)-C(55)-H(55)	118.9
C(54)-C(55)-H(55)	118.9
N(3)-Mo(2)-C(101)	103.2(2)
N(3)-Mo(2)-O(2)	152.10(16)
C(101)-Mo(2)-O(2)	104.04(17)
N(3)-Mo(2)-N(4)	89.90(16)

C(101)-Mo(2)-N(4)	95.31(18)
O(2)-Mo(2)-N(4)	81.54(12)
N(3)-Mo(2)-Cl(2)	92.80(13)
C(101)-Mo(2)-Cl(2)	101.29(15)
O(2)-Mo(2)-Cl(2)	87.91(9)
N(4)-Mo(2)-Cl(2)	162.10(10)
C(102)-C(101)-Mo(2)	146.5(4)
C(102)-C(101)-H(101)	106(3)
Mo(2)-C(101)-H(101)	108(3)
C(101)-C(102)-C(105)	112.9(4)
C(101)-C(102)-C(104)	107.9(4)
C(105)-C(102)-C(104)	109.0(4)
C(101)-C(102)-C(103)	107.8(4)
C(105)-C(102)-C(103)	109.2(4)
C(104)-C(102)-C(103)	110.0(4)
C(102)-C(103)-H(10A)	109.5
C(102)-C(103)-H(10B)	109.5
H(10A)-C(103)-H(10B)	109.5
C(102)-C(103)-H(10C)	109.5
H(10A)-C(103)-H(10C)	109.5
H(10B)-C(103)-H(10C)	109.5
C(102)-C(104)-H(10D)	109.5
C(102)-C(104)-H(10E)	109.5
H(10D)-C(104)-H(10E)	109.5
C(102)-C(104)-H(10F)	109.5
H(10D)-C(104)-H(10F)	109.5
H(10E)-C(104)-H(10F)	109.5
C(102)-C(105)-H(10G)	109.5
C(102)-C(105)-H(10H)	109.5
H(10G)-C(105)-H(10H)	109.5
C(102)-C(105)-H(10I)	109.5
H(10G)-C(105)-H(10I)	109.5
H(10H)-C(105)-H(10I)	109.5
C(106)-N(3)-Mo(2)	165.0(3)
N(3)-C(106)-C(109)	109.1(4)
N(3)-C(106)-C(107)	110.2(4)

C(109)-C(106)-C(107)	111.2(5)
N(3)-C(106)-C(108)	107.4(4)
C(109)-C(106)-C(108)	110.3(5)
C(107)-C(106)-C(108)	108.5(4)
C(106)-C(107)-H(10J)	109.5
C(106)-C(107)-H(10K)	109.5
H(10J)-C(107)-H(10K)	109.5
C(106)-C(107)-H(10L)	109.5
H(10J)-C(107)-H(10L)	109.5
H(10K)-C(107)-H(10L)	109.5
C(106)-C(108)-H(10M)	109.5
C(106)-C(108)-H(10N)	109.5
H(10M)-C(108)-H(10N)	109.5
C(106)-C(108)-H(10O)	109.5
H(10M)-C(108)-H(10O)	109.5
H(10N)-C(108)-H(10O)	109.5
C(106)-C(109)-H(10P)	109.5
C(106)-C(109)-H(10Q)	109.5
H(10P)-C(109)-H(10Q)	109.5
C(106)-C(109)-H(10R)	109.5
H(10P)-C(109)-H(10R)	109.5
H(10Q)-C(109)-H(10R)	109.5
C(111)-O(2)-Mo(2)	151.4(3)
O(2)-C(111)-C(116)	120.1(3)
O(2)-C(111)-C(112)	119.7(3)
C(116)-C(111)-C(112)	120.0(3)
C(113)-C(112)-C(111)	119.2(4)
C(113)-C(112)-C(117)	118.9(4)
C(111)-C(112)-C(117)	121.8(3)
C(114)-C(113)-C(112)	120.9(4)
C(114)-C(113)-H(113)	119.6
C(112)-C(113)-H(113)	119.6
C(115)-C(114)-C(113)	119.7(4)
C(115)-C(114)-H(114)	120.2
C(113)-C(114)-H(114)	120.2
C(114)-C(115)-C(116)	121.0(4)

C(114)-C(115)-H(115)	119.5
C(116)-C(115)-H(115)	119.5
C(115)-C(116)-C(111)	119.1(4)
C(115)-C(116)-C(132)	120.6(4)
C(111)-C(116)-C(132)	120.2(3)
C(122)-C(117)-C(118)	119.6(4)
C(122)-C(117)-C(112)	121.0(3)
C(118)-C(117)-C(112)	119.3(4)
C(119)-C(118)-C(117)	119.1(4)
C(119)-C(118)-C(123)	120.1(4)
C(117)-C(118)-C(123)	120.7(4)
C(120)-C(119)-C(118)	121.8(4)
C(120)-C(119)-H(119)	119.1
C(118)-C(119)-H(119)	119.1
C(121)-C(120)-C(119)	117.9(4)
C(121)-C(120)-C(126)	121.0(4)
C(119)-C(120)-C(126)	121.1(4)
C(120)-C(121)-C(122)	122.1(4)
C(120)-C(121)-H(121)	119.0
C(122)-C(121)-H(121)	119.0
C(117)-C(122)-C(121)	119.5(4)
C(117)-C(122)-C(129)	121.4(4)
C(121)-C(122)-C(129)	119.0(4)
C(118)-C(123)-C(125)	110.2(4)
C(118)-C(123)-C(124)	113.5(4)
C(125)-C(123)-C(124)	109.5(4)
C(118)-C(123)-H(123)	107.8
C(125)-C(123)-H(123)	107.8
C(124)-C(123)-H(123)	107.8
C(123)-C(124)-H(12A)	109.5
C(123)-C(124)-H(12B)	109.5
H(12A)-C(124)-H(12B)	109.5
C(123)-C(124)-H(12C)	109.5
H(12A)-C(124)-H(12C)	109.5
H(12B)-C(124)-H(12C)	109.5
C(123)-C(125)-H(12D)	109.5

C(123)-C(125)-H(12E)	109.5
H(12D)-C(125)-H(12E)	109.5
C(123)-C(125)-H(12F)	109.5
H(12D)-C(125)-H(12F)	109.5
H(12E)-C(125)-H(12F)	109.5
C(127)-C(126)-C(128)	111.6(5)
C(127)-C(126)-C(120)	112.2(4)
C(128)-C(126)-C(120)	111.9(4)
C(127)-C(126)-H(126)	106.9
C(128)-C(126)-H(126)	106.9
C(120)-C(126)-H(126)	106.9
C(126)-C(127)-H(12G)	109.5
C(126)-C(127)-H(12H)	109.5
H(12G)-C(127)-H(12H)	109.5
C(126)-C(127)-H(12I)	109.5
H(12G)-C(127)-H(12I)	109.5
H(12H)-C(127)-H(12I)	109.5
C(126)-C(128)-H(12J)	109.5
C(126)-C(128)-H(12K)	109.5
H(12J)-C(128)-H(12K)	109.5
C(126)-C(128)-H(12L)	109.5
H(12J)-C(128)-H(12L)	109.5
H(12K)-C(128)-H(12L)	109.5
C(130)-C(129)-C(122)	112.6(4)
C(130)-C(129)-C(131)	109.7(4)
C(122)-C(129)-C(131)	111.0(4)
C(130)-C(129)-H(129)	107.8
C(122)-C(129)-H(129)	107.8
C(131)-C(129)-H(129)	107.8
C(129)-C(130)-H(13A)	109.5
C(129)-C(130)-H(13B)	109.5
H(13A)-C(130)-H(13B)	109.5
C(129)-C(130)-H(13C)	109.5
H(13A)-C(130)-H(13C)	109.5
H(13B)-C(130)-H(13C)	109.5
C(129)-C(131)-H(13D)	109.5

C(129)-C(131)-H(13E)	109.5
H(13D)-C(131)-H(13E)	109.5
C(129)-C(131)-H(13F)	109.5
H(13D)-C(131)-H(13F)	109.5
H(13E)-C(131)-H(13F)	109.5
C(133)-C(132)-C(137)	120.6(4)
C(133)-C(132)-C(116)	119.3(3)
C(137)-C(132)-C(116)	120.1(4)
C(134)-C(133)-C(132)	118.5(4)
C(134)-C(133)-C(138)	120.1(4)
C(132)-C(133)-C(138)	121.4(4)
C(135)-C(134)-C(133)	122.3(4)
C(135)-C(134)-H(134)	118.9
C(133)-C(134)-H(134)	118.9
C(134)-C(135)-C(136)	118.0(4)
C(134)-C(135)-C(141)	121.2(4)
C(136)-C(135)-C(141)	120.7(4)
C(135)-C(136)-C(137)	122.2(4)
C(135)-C(136)-H(136)	118.9
C(137)-C(136)-H(136)	118.9
C(136)-C(137)-C(132)	118.4(4)
C(136)-C(137)-C(144)	120.6(4)
C(132)-C(137)-C(144)	120.9(3)
C(139)-C(138)-C(133)	112.5(3)
C(139)-C(138)-C(140)	109.7(4)
C(133)-C(138)-C(140)	110.7(4)
C(139)-C(138)-H(138)	107.9
C(133)-C(138)-H(138)	107.9
C(140)-C(138)-H(138)	107.9
C(138)-C(139)-H(13G)	109.5
C(138)-C(139)-H(13H)	109.5
H(13G)-C(139)-H(13H)	109.5
C(138)-C(139)-H(13I)	109.5
H(13G)-C(139)-H(13I)	109.5
H(13H)-C(139)-H(13I)	109.5
C(138)-C(140)-H(14A)	109.5

C(138)-C(140)-H(14B)	109.5
H(14A)-C(140)-H(14B)	109.5
C(138)-C(140)-H(14C)	109.5
H(14A)-C(140)-H(14C)	109.5
H(14B)-C(140)-H(14C)	109.5
C(143)-C(141)-C(135)	109.8(4)
C(143)-C(141)-C(142)	113.5(5)
C(135)-C(141)-C(142)	111.5(4)
C(143)-C(141)-H(141)	107.2
C(135)-C(141)-H(141)	107.2
C(142)-C(141)-H(141)	107.2
C(141)-C(142)-H(14D)	109.5
C(141)-C(142)-H(14E)	109.5
H(14D)-C(142)-H(14E)	109.5
C(141)-C(142)-H(14F)	109.5
H(14D)-C(142)-H(14F)	109.5
H(14E)-C(142)-H(14F)	109.5
C(141)-C(143)-H(14G)	109.5
C(141)-C(143)-H(14H)	109.5
H(14G)-C(143)-H(14H)	109.5
C(141)-C(143)-H(14I)	109.5
H(14G)-C(143)-H(14I)	109.5
H(14H)-C(143)-H(14I)	109.5
C(137)-C(144)-C(145)	114.5(3)
C(137)-C(144)-C(146)	110.0(4)
C(145)-C(144)-C(146)	108.5(4)
C(137)-C(144)-H(144)	107.9
C(145)-C(144)-H(144)	107.9
C(146)-C(144)-H(144)	107.9
C(144)-C(145)-H(14J)	109.5
C(144)-C(145)-H(14K)	109.5
H(14J)-C(145)-H(14K)	109.5
C(144)-C(145)-H(14L)	109.5
H(14J)-C(145)-H(14L)	109.5
H(14K)-C(145)-H(14L)	109.5
C(144)-C(146)-H(14M)	109.5

C(144)-C(146)-H(14N)	109.5
H(14M)-C(146)-H(14N)	109.5
C(144)-C(146)-H(14O)	109.5
H(14M)-C(146)-H(14O)	109.5
H(14N)-C(146)-H(14O)	109.5
C(151)-N(4)-C(155)	118.9(4)
C(151)-N(4)-Mo(2)	117.7(3)
C(155)-N(4)-Mo(2)	123.3(3)
N(4)-C(151)-C(152)	122.1(4)
N(4)-C(151)-H(151)	119.0
C(152)-C(151)-H(151)	119.0
C(151)-C(152)-C(153)	119.7(5)
C(151)-C(152)-Br(2)	119.1(4)
C(153)-C(152)-Br(2)	121.2(4)
C(154)-C(153)-C(152)	117.7(5)
C(154)-C(153)-H(153)	121.1
C(152)-C(153)-H(153)	121.1
C(153)-C(154)-C(155)	120.3(5)
C(153)-C(154)-H(154)	119.9
C(155)-C(154)-H(154)	119.9
N(4)-C(155)-C(154)	121.3(5)
N(4)-C(155)-H(155)	119.4
C(154)-C(155)-H(155)	119.4
C(1S)-C(2S)-H(2S1)	109.5
C(1S)-C(2S)-H(2S2)	109.5
H(2S1)-C(2S)-H(2S2)	109.5
C(1S)-C(2S)-H(2S3)	109.5
H(2S1)-C(2S)-H(2S3)	109.5
H(2S2)-C(2S)-H(2S3)	109.5
O(1S)-C(1S)-C(2S)	108.5(11)
O(1S)-C(1S)-H(1S1)	110.0
C(2S)-C(1S)-H(1S1)	110.0
O(1S)-C(1S)-H(1S2)	110.0
C(2S)-C(1S)-H(1S2)	110.0
H(1S1)-C(1S)-H(1S2)	108.4
C(1S)-O(1S)-C(3S)	111.7(12)

O(1S)-C(3S)-C(4S)	110.2(11)
O(1S)-C(3S)-H(3S1)	109.6
C(4S)-C(3S)-H(3S1)	109.6
O(1S)-C(3S)-H(3S2)	109.6
C(4S)-C(3S)-H(3S2)	109.6
H(3S1)-C(3S)-H(3S2)	108.1
C(3S)-C(4S)-H(4S1)	109.5
C(3S)-C(4S)-H(4S2)	109.5
H(4S1)-C(4S)-H(4S2)	109.5
C(3S)-C(4S)-H(4S3)	109.5
H(4S1)-C(4S)-H(4S3)	109.5
H(4S2)-C(4S)-H(4S3)	109.5
C(1T)-C(2T)-H(2T1)	109.5
C(1T)-C(2T)-H(2T2)	109.5
H(2T1)-C(2T)-H(2T2)	109.5
C(1T)-C(2T)-H(2T3)	109.5
H(2T1)-C(2T)-H(2T3)	109.5
H(2T2)-C(2T)-H(2T3)	109.5
O(1T)-C(1T)-C(2T)	108.8(16)
O(1T)-C(1T)-H(1T1)	109.9
C(2T)-C(1T)-H(1T1)	109.9
O(1T)-C(1T)-H(1T2)	109.9
C(2T)-C(1T)-H(1T2)	109.9
H(1T1)-C(1T)-H(1T2)	108.3
C(3T)-O(1T)-C(1T)	107.8(16)
O(1T)-C(3T)-C(4T)	110.3(16)
O(1T)-C(3T)-H(3T1)	109.6
C(4T)-C(3T)-H(3T1)	109.6
O(1T)-C(3T)-H(3T2)	109.6
C(4T)-C(3T)-H(3T2)	109.6
H(3T1)-C(3T)-H(3T2)	108.1
C(3T)-C(4T)-H(4T1)	109.5
C(3T)-C(4T)-H(4T2)	109.5
H(4T1)-C(4T)-H(4T2)	109.5
C(3T)-C(4T)-H(4T3)	109.5
H(4T1)-C(4T)-H(4T3)	109.5

H(4T2)-C(4T)-H(4T3)	109.5

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Mo-2.
The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	30(1)	26(1)	48(1)	17(1)	19(1)	8(1)
Mo(1)	17(1)	19(1)	25(1)	6(1)	9(1)	5(1)
C(1)	28(2)	29(2)	33(2)	12(2)	15(2)	8(2)
C(2)	37(3)	33(2)	31(2)	8(2)	13(2)	10(2)
C(3)	50(3)	28(2)	39(3)	7(2)	12(2)	8(2)
C(4)	34(3)	40(3)	36(3)	11(2)	7(2)	5(2)
C(5)	43(3)	37(3)	28(2)	8(2)	15(2)	11(2)
N(1)	17(2)	32(2)	35(2)	12(2)	9(2)	5(2)
C(6)	22(2)	40(3)	51(3)	17(2)	14(2)	16(2)
C(7)	33(3)	69(4)	62(3)	18(3)	22(3)	24(3)
C(8)	23(3)	52(3)	123(6)	11(3)	13(3)	19(2)
C(9)	48(3)	64(4)	60(4)	28(3)	20(3)	36(3)
O(1)	15(1)	18(1)	33(2)	7(1)	10(1)	3(1)
C(11)	16(2)	21(2)	24(2)	7(2)	9(2)	6(2)
C(12)	16(2)	24(2)	21(2)	7(2)	8(2)	6(2)
C(13)	19(2)	31(2)	28(2)	6(2)	12(2)	7(2)
C(14)	18(2)	32(2)	31(2)	5(2)	9(2)	2(2)
C(15)	26(2)	25(2)	31(2)	5(2)	13(2)	6(2)
C(16)	21(2)	23(2)	25(2)	12(2)	13(2)	8(2)
C(17)	14(2)	22(2)	22(2)	3(2)	5(2)	6(2)
C(18)	25(2)	28(2)	28(2)	8(2)	9(2)	12(2)
C(19)	32(2)	22(2)	32(2)	4(2)	10(2)	9(2)
C(20)	30(2)	32(2)	28(2)	1(2)	5(2)	12(2)
C(21)	29(2)	31(2)	25(2)	5(2)	7(2)	11(2)
C(22)	18(2)	22(2)	22(2)	3(2)	6(2)	6(2)
C(23)	45(3)	31(2)	33(2)	14(2)	20(2)	21(2)
C(24)	58(3)	36(3)	29(2)	9(2)	7(2)	22(2)
C(25)	51(3)	37(3)	58(3)	26(2)	32(3)	23(2)
C(26)	56(3)	37(3)	31(2)	0(2)	10(2)	25(2)
C(27)	60(4)	76(5)	53(4)	-24(3)	1(3)	28(3)

C(28)	95(5)	70(5)	90(5)	-19(4)	57(5)	24(4)
C(29)	30(2)	22(2)	27(2)	7(2)	14(2)	11(2)
C(30)	45(3)	38(3)	29(2)	12(2)	9(2)	22(2)
C(31)	35(3)	42(3)	52(3)	20(3)	20(2)	13(2)
C(32)	19(2)	22(2)	26(2)	5(2)	12(2)	4(2)
C(33)	22(2)	21(2)	27(2)	7(2)	12(2)	6(2)
C(34)	25(2)	25(2)	23(2)	11(2)	12(2)	4(2)
C(35)	26(2)	27(2)	26(2)	3(2)	15(2)	6(2)
C(36)	21(2)	25(2)	35(2)	7(2)	14(2)	9(2)
C(37)	21(2)	22(2)	30(2)	9(2)	12(2)	6(2)
C(38)	25(2)	30(2)	31(2)	13(2)	14(2)	11(2)
C(39)	35(3)	27(2)	38(3)	14(2)	14(2)	12(2)
C(40)	40(3)	42(3)	42(3)	8(2)	5(2)	18(2)
C(41)	34(2)	31(2)	33(2)	11(2)	21(2)	11(2)
C(42)	32(2)	46(3)	41(3)	6(2)	22(2)	14(2)
C(43)	43(3)	47(3)	32(2)	5(2)	23(2)	15(2)
C(44)	29(2)	26(2)	36(2)	13(2)	21(2)	12(2)
C(45)	33(2)	22(2)	50(3)	13(2)	21(2)	8(2)
C(46)	39(3)	37(3)	39(3)	17(2)	22(2)	19(2)
N(2)	17(2)	24(2)	26(2)	8(1)	7(1)	4(1)
C(51)	19(2)	21(2)	30(2)	7(2)	9(2)	4(2)
C(52)	19(2)	26(2)	29(2)	10(2)	10(2)	3(2)
C(53)	25(2)	24(2)	32(2)	14(2)	7(2)	1(2)
C(54)	32(2)	21(2)	33(2)	10(2)	8(2)	7(2)
C(55)	21(2)	24(2)	28(2)	9(2)	7(2)	9(2)
Br(1)	41(1)	40(1)	44(1)	15(1)	29(1)	12(1)
Cl(2)	33(1)	24(1)	41(1)	3(1)	16(1)	-1(1)
Mo(2)	20(1)	21(1)	21(1)	6(1)	11(1)	5(1)
C(101)	31(2)	29(2)	30(2)	6(2)	9(2)	4(2)
C(102)	30(2)	36(2)	28(2)	12(2)	9(2)	7(2)
C(103)	44(3)	44(3)	51(3)	22(2)	19(3)	20(2)
C(104)	42(3)	62(4)	33(3)	10(2)	10(2)	5(3)
C(105)	43(3)	48(3)	41(3)	10(2)	24(2)	12(2)
N(3)	24(2)	26(2)	36(2)	4(2)	13(2)	3(2)
C(106)	22(2)	36(2)	37(2)	6(2)	16(2)	12(2)
C(107)	26(2)	54(3)	67(4)	10(3)	25(3)	8(2)

C(108)	52(4)	68(4)	43(3)	9(3)	17(3)	29(3)
C(109)	46(3)	66(4)	73(4)	36(3)	35(3)	31(3)
O(2)	22(2)	26(2)	27(2)	10(1)	14(1)	8(1)
C(111)	19(2)	17(2)	19(2)	1(2)	10(2)	4(2)
C(112)	20(2)	19(2)	21(2)	5(2)	9(2)	9(2)
C(113)	19(2)	26(2)	31(2)	5(2)	14(2)	7(2)
C(114)	25(2)	32(2)	31(2)	11(2)	20(2)	8(2)
C(115)	22(2)	21(2)	32(2)	7(2)	12(2)	4(2)
C(116)	18(2)	20(2)	22(2)	4(2)	9(2)	5(2)
C(117)	22(2)	22(2)	24(2)	9(2)	12(2)	7(2)
C(118)	21(2)	23(2)	36(2)	7(2)	12(2)	8(2)
C(119)	32(2)	22(2)	40(2)	13(2)	17(2)	12(2)
C(120)	34(2)	29(2)	35(2)	15(2)	14(2)	16(2)
C(121)	29(2)	27(2)	27(2)	8(2)	12(2)	9(2)
C(122)	21(2)	24(2)	26(2)	8(2)	12(2)	8(2)
C(123)	34(2)	20(2)	37(2)	3(2)	4(2)	12(2)
C(124)	36(3)	25(2)	68(4)	1(2)	8(3)	6(2)
C(125)	54(3)	48(3)	39(3)	-8(3)	21(3)	6(3)
C(126)	48(3)	39(3)	34(2)	19(2)	18(2)	21(2)
C(127)	35(3)	71(4)	39(3)	26(3)	10(2)	22(3)
C(128)	36(3)	94(5)	110(6)	81(5)	15(3)	16(3)
C(129)	29(2)	23(2)	27(2)	4(2)	6(2)	10(2)
C(130)	58(3)	37(3)	29(2)	5(2)	10(2)	27(3)
C(131)	31(3)	23(2)	65(4)	10(2)	10(2)	6(2)
C(132)	16(2)	21(2)	21(2)	7(2)	10(2)	3(2)
C(133)	25(2)	23(2)	21(2)	6(2)	11(2)	8(2)
C(134)	22(2)	24(2)	27(2)	3(2)	6(2)	4(2)
C(135)	20(2)	27(2)	27(2)	7(2)	7(2)	5(2)
C(136)	18(2)	24(2)	29(2)	6(2)	9(2)	9(2)
C(137)	17(2)	20(2)	23(2)	6(2)	10(2)	4(2)
C(138)	22(2)	22(2)	30(2)	3(2)	12(2)	5(2)
C(139)	78(4)	33(3)	58(3)	22(2)	51(3)	32(3)
C(140)	83(4)	56(3)	38(3)	21(2)	36(3)	45(3)
C(141)	20(2)	33(3)	50(3)	-2(2)	-2(2)	8(2)
C(142)	25(3)	90(5)	77(4)	-17(4)	5(3)	20(3)
C(143)	42(4)	59(4)	100(5)	29(4)	-24(3)	-2(3)

C(144)	19(2)	22(2)	30(2)	4(2)	9(2)	6(2)
C(145)	27(2)	31(2)	37(3)	-5(2)	10(2)	8(2)
C(146)	28(2)	26(2)	43(3)	8(2)	14(2)	3(2)
N(4)	29(2)	23(2)	27(2)	7(1)	17(2)	8(2)
C(151)	28(2)	26(2)	26(2)	2(2)	13(2)	6(2)
C(152)	30(2)	38(2)	26(2)	-5(2)	18(2)	-6(2)
C(153)	54(3)	30(2)	31(2)	0(2)	25(2)	-5(2)
C(154)	68(3)	23(2)	38(3)	5(2)	26(2)	7(2)
C(155)	45(3)	23(2)	34(2)	8(2)	20(2)	14(2)
Br(2)	29(1)	74(1)	37(1)	-12(1)	8(1)	2(1)
C(2S)	43(7)	82(12)	35(10)	18(9)	23(6)	31(8)
C(1S)	37(5)	49(8)	38(6)	21(5)	22(4)	18(5)
O(1S)	34(5)	43(8)	42(6)	24(5)	27(4)	18(5)
C(3S)	34(5)	33(8)	44(6)	14(6)	14(4)	14(5)
C(4S)	54(8)	42(9)	70(9)	19(7)	35(7)	24(7)
C(2T)	49(8)	64(12)	43(14)	13(11)	16(7)	22(8)
C(1T)	43(7)	54(12)	40(9)	17(7)	20(6)	17(7)
O(1T)	33(5)	43(10)	52(7)	12(6)	19(4)	10(6)
C(3T)	42(6)	42(13)	54(7)	-4(7)	11(5)	16(7)
C(4T)	42(7)	48(13)	54(10)	18(9)	15(7)	28(8)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Mo-2.

	x	y	z	U(eq)
H(1)	570(20)	3810(30)	1240(20)	34
H(3A)	-76	2544	709	60
H(3B)	-1285	2245	211	60
H(3C)	-1285	2351	887	60
H(4A)	-2489	3165	800	57
H(4B)	-2581	3057	114	57
H(4C)	-2150	3887	520	57
H(5A)	-364	4203	165	54
H(5B)	-800	3372	-240	54
H(5C)	464	3686	215	54
H(7A)	-2561	4973	2511	76
H(7B)	-2976	5616	2253	76
H(7C)	-1615	5720	2463	76
H(8A)	-3601	4095	1015	100
H(8B)	-4224	4523	1408	100
H(8C)	-3602	3955	1659	100
H(9A)	-1525	5929	1419	77
H(9B)	-2903	5781	1257	77
H(9C)	-2365	5278	870	77
H(13)	5212	5675	2456	31
H(14)	5614	6614	3289	34
H(15)	4107	6675	3736	32
H(19)	2976	2802	1492	34
H(21)	3268	4300	458	34
H(23)	2724	3974	2705	38
H(24A)	4341	3738	3288	60
H(24B)	4762	4417	2975	60
H(24C)	4818	3600	2723	60
H(25A)	2927	2516	2365	63
H(25B)	1714	2680	2188	63

H(25C)	2344	2772	2863	63
H(26)	3220	2417	561	48
H(27A)	1683	2916	-219	102
H(27B)	1286	2353	192	102
H(27C)	1831	2097	-323	102
H(28A)	3912	2652	-238	126
H(28B)	4737	3271	333	126
H(28C)	3812	3484	-131	126
H(29)	3249	5835	1507	30
H(30A)	2818	5318	277	53
H(30B)	2602	6052	596	53
H(30C)	1800	5230	605	53
H(31A)	5233	5972	1540	60
H(31B)	4758	6489	1143	60
H(31C)	4888	5715	841	60
H(34)	609	5032	4350	29
H(36)	-128	6641	3562	30
H(38)	2980	4931	3724	32
H(39A)	1107	3931	4027	48
H(39B)	2203	3723	3884	48
H(39C)	1285	3884	3380	48
H(40A)	3553	5629	4703	62
H(40B)	3616	4793	4684	62
H(40C)	2551	5010	4858	62
H(41)	-970	5404	4514	37
H(42A)	-1809	6360	3841	57
H(42B)	-2505	5864	4218	57
H(42C)	-2250	5459	3647	57
H(43A)	417	6489	5131	58
H(43B)	-855	6556	5099	58
H(43C)	-57	7009	4738	58
H(44)	1877	6703	2677	32
H(45A)	2080	7852	3646	50
H(45B)	2646	7993	3113	50
H(45C)	3101	7517	3555	50
H(46A)	140	7353	2899	51

H(46B)	-132	6626	2392	51
H(46C)	724	7422	2364	51
H(51)	-1020	4486	2937	28
H(53)	-1805	2385	3257	33
H(54)	-953	2040	2516	34
H(55)	-232	2910	1987	28
H(101)	6620(30)	9490(30)	3490(20)	37
H(10A)	5070	8155	3731	64
H(10B)	5842	8306	4390	64
H(10C)	6463	8412	3871	64
H(10D)	7633	9734	4493	73
H(10E)	6892	9623	4966	73
H(10F)	6964	10318	4651	73
H(10G)	4826	9908	4389	64
H(10H)	4692	9151	4630	64
H(10I)	4070	9108	3963	64
H(10J)	1830	9453	2517	73
H(10K)	1272	9794	2995	73
H(10L)	1993	9231	3143	73
H(10M)	3174	10168	4028	78
H(10N)	2550	10777	3874	78
H(10O)	3936	10989	3995	78
H(10P)	3740	11354	3028	80
H(10Q)	2346	11084	2885	80
H(10R)	2971	10743	2441	80
H(113)	9866	10589	2199	29
H(114)	9339	11055	1367	32
H(115)	7391	10945	980	30
H(119)	8647	8272	3156	34
H(121)	9931	10326	4241	32
H(123)	7300	8840	1923	37
H(12A)	6718	7535	1735	69
H(12B)	6625	7806	2383	69
H(12C)	7705	7540	2289	69
H(12D)	9157	9118	1761	74
H(12E)	8429	8268	1421	74

H(12F)	9386	8431	2029	74
H(126)	10080	9305	4650	43
H(12G)	11045	8426	4554	69
H(12H)	11427	9052	4188	69
H(12I)	10535	8233	3858	69
H(12J)	8489	7876	4030	113
H(12K)	8202	8490	4459	113
H(12L)	9117	8089	4716	113
H(129)	8808	11302	3215	31
H(13A)	8302	11180	4108	59
H(13B)	9173	12005	4162	59
H(13C)	9653	11397	4441	59
H(13D)	10705	12183	3624	61
H(13E)	10749	11491	3167	61
H(13F)	11162	11539	3855	61
H(134)	3089	9166	488	31
H(136)	3561	11262	1358	27
H(138)	6117	9277	926	30
H(13G)	4922	8497	1393	70
H(13H)	5155	8010	852	70
H(13I)	3930	8162	787	70
H(14A)	4160	8679	-87	75
H(14B)	5398	8550	-32	75
H(14C)	5290	9370	-47	75
H(141)	1450	9554	420	45
H(14D)	1386	9952	1406	104
H(14E)	385	10094	936	104
H(14F)	1523	10783	1295	104
H(14G)	2181	11101	364	114
H(14H)	913	10524	26	114
H(14I)	2044	10401	-141	114
H(144)	6511	11662	2136	28
H(14J)	4671	12316	1959	49
H(14K)	5862	12652	2469	49
H(14L)	4915	11878	2471	49
H(14M)	6789	11969	1241	49

H(14N)	6928	12715	1700	49
H(14O)	5752	12326	1185	49
H(151)	3104	9242	1922	32
H(153)	2145	6964	1484	49
H(154)	3869	7035	2147	52
H(155)	5138	8199	2701	38
H(2S1)	2519	7539	5339	73
H(2S2)	3463	8100	5105	73
H(2S3)	2777	7260	4731	73
H(1S1)	4414	7619	5849	44
H(1S2)	3726	6776	5473	44
H(3S1)	5415	6558	5473	42
H(3S2)	6337	7387	5738	42
H(4S1)	7070	6677	5113	75
H(4S2)	5953	6547	4584	75
H(4S3)	6874	7374	4849	75
H(2T1)	2526	7682	5204	75
H(2T2)	3282	7907	4752	75
H(2T3)	2560	7043	4696	75
H(1T1)	4514	7911	5652	52
H(1T2)	3790	7044	5595	52
H(3T1)	5686	6776	5601	56
H(3T2)	6125	7679	5726	56
H(4T1)	7453	7209	5361	66
H(4T2)	6447	6732	4783	66
H(4T3)	6884	7633	4909	66

Chapter Four

Stereoselective Synthesis of Z- and E-Trisubstituted Alkenes by Merging Cross-Coupling with Cross-Metathesis

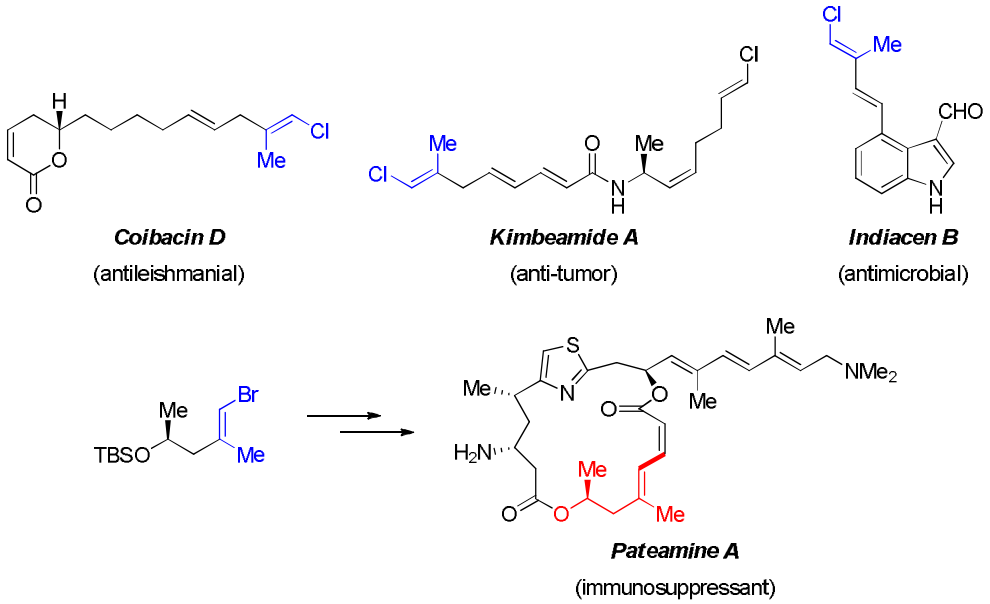
4.1. Introduction

Stereochemically defined acyclic dissymmetrical trisubstituted alkenes are ubiquitous in Nature and are commonly employed in chemical synthesis,[1] including catalytic enantioselective transformations such as hydrogenation,[2] dihydroxylation,[3] allylic substitution[4] and conjugation addition.[5] Given the preponderance of trisubstituted alkenes, numerous synthetic approaches have been developed for the preparation of these moieties, but crucial shortcomings limiting their general utility exist. For example, ketones and phosphonium salts may be utilized in Wittig reactions,[6] but these are poorly stereoselective unless an α-alkoxy ketone is involved,[7] or if the substituents are sterically differentiated.[8] The Schlosser variant of the Wittig transformation allows aldehydes and phosphonium salts to be coupled followed by trapping with an electrophile to generate certain trisubstituted olefins such as allylic alcohols[9] and allylic esters.[10] However, these

(1) (a) Negishi, E.; Huang, Z.; Wang, G.; Mohan, S.; Wang, C.; Hattori, H. *Acct. Chem. Res.* **2008**, *41*, 1474–1485. (b) Siau, W.-Y.; Zhang, Y.; Zhao, Y. *Top. Curr. Chem.* **2012**, *327*, 33–58.
(2) Shang, G.; Li, W.; Zhang, X. in *Catalytic Asymmetric Synthesis* (ed Ojima, I.) 344–436 (Wiley, 2010).
(3) Noe, M. C.; Letavic, M. A.; Snow, S. L. in *Organic Reactions* (ed Denmark, S. E.) 109–625 (John Wiley & Sons, 2005).
(4) Baslé, O.; Denicourt-Nowicki, A.; Crévisy, C.; Mauduit, M. in *Copper-Catalyzed Asymmetric Synthesis* (eds Alexakis, A.; Krause, N.; Woodward, S.) 85–119 (VCH–Wiley, 2014).
(5) Alexakis, A.; Krause, N.; Woodward, S. in *Copper-Catalyzed Asymmetric Synthesis* (eds Alexakis, A.; Krause, N.; Woodward, S.) 33–68 (VCH–Wiley, 2014).
(6) (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863–927. (b) Taber, D. F.; Meagley, R. P.; Doren, D. J. *J. Org. Chem.* **1996**, *61*, 5723–5728.
(7) Sreekumar, C.; Darst, K. P.; Still, W. C. *J. Org. Chem.* **1980**, *45*, 4260–4262.
(8) Schlosser, M.; Christmann, K.-F. *Synthesis* **1969**, 38–39.
(9) Corey, E. J.; Yamamoto, H. *J. Am. Chem. Soc.* **1970**, *92*, 226–228.
(10) Hodgson, D. M.; Arif, T. *Org. Lett.* **2010**, *12*, 4204–4207.

processes typically employ strongly basic and cryogenic conditions that may pose complications with sensitive functionalities. Other strategies for converting an alkyne[11] or a carbonyl compound[12] to trisubstituted alkenes have been reported (see Experimental section for extended bibliography), but notable problems such as the need for multi-step sequences, employment of harsh reaction conditions, applicability to synthesis of only one stereoisomer and/or limited substrate scope remain to be addressed.

Scheme 4.1. Trisubstituted *E*- and *Z*-Alkenyl Halides in Natural Products & Precursors.



Trisubstituted alkenyl chlorides and bromides (halogen situated at the terminal position) represent a desirable class of compounds because these motifs are prevalent in natural products[13] (Scheme 4.1). Many of these compounds originate from marine microorganisms which produce various halogen-containing metabolites by incorporating

(11) For representative examples, see: (a) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc. Perkin Trans 1* **1981**, 2527–2532. (b) Trost, B. M.; Balls, Z. T. *Synthesis* **2005**, 853–887. (c) Wang, C.; Tobrman, T.; Xu, Z.; Negishi, E.-i. *Org. Lett.* **2009**, *11*, 4092–4095. (d) Mun, B.; Kim, S.; Yoon, H.; Kim, K. H.; Lee, Y. *J. Org. Chem.* **2017**, *82*, 6349–6357.
(12) For a representative example, see: Minato, A.; Suzuki, K. *J. Am. Chem.* Soc. **1987**, *109*, 1257–1258.
(13) Gribble, G. W. *Mar. Drugs* **2015**, *13*, 4044–4136.

halide ions from seawater.[14] Furthermore, by converting the C–halogen bond to another C–C bond through commonly used reactions such as catalytic cross-coupling,[15] access to numerous other olefins can be achieved (cf. pateamine A in Scheme 4.1).

Methods that deliver stereoisomerically pure trisubstituted halo-alkenes have been reported. One of the most common protocols involves zirconocene-catalyzed alkylaluminum additions to terminal alkynes followed by treatment of the resulting alkenylaluminum intermediates with an electrophilic halogen source (for example, bromine or *N*-chlorosuccinimide) afford *E*-trisubstituted alkenyl halides with excellent stereoselectivity.[16] However, the need for excess pyrophoric trialkylaluminum reagents poses issues with scalability as well as functional group compatibility with certain organic units (for example, epoxides and carboxylic esters). Furthermore, a directing allylic or homoallylic hydroxyl group has to be present in order to obtain the corresponding *Z*-isomers by zirconocene-catalyzed alkylaluminum[17] or copper-catalyzed alkylmagnesium additions.[18] To the best of our knowledge, efficient and broadly applicable catalytic methods that furnish linear trisubstituted alkenes, especially alkenyl halides, in either stereoisomeric form selectively under mild reaction conditions have not been disclosed. This provided us the opportunity to develop catalytic CM as a possible solution to address the aforementioned challenge.

4.2. Challenges with Efficient and Stereoselective Synthesis of Trisubstituted Alkenes through OM

(14) Nunnery, J. K.; Engene, N.; Byrum, T.; Cao, Z.; Jabba, S. V.; Pereira, A. R.; Matainaho, T.; Murray, T. F.; Gerwick, W. H. *J. Org. Chem.* **2012**, *77*, 4198–4208.
(15) Johansson Seechurn, C. C. C.; Kitching, M. O.; Colacot, T. J.; Sniekus, V. *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085.
(16) Negishi, E.-i.; Van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639–6647.
(17) Ma, S.; Negishi, E.-i. *J. Org. Chem.* **1996**, *62*, 784–785.
(18) Lu, Z.; Ma, S. *J. Org. Chem.* **2006**, *71*, 2655–2660.

4.2.1. Advances in CM to Access Trisubstituted Olefins

In addition to offering a distinct synthesis approach for the preparation of trisubstituted olefins that would be complementary to the aforementioned methods in Section 4.1, catalytic CM utilizes olefin substrates that are generally more abundant, robust and less costly (compared to alkynes, for example). Consequently, synthesis routes involving alkenes are often more concise.[19] Furthermore, transformations can be performed under mild conditions with reliable control of stereochemistry.[20] Studies related to formation of trisubstituted alkenes by CM only involved Ru-based carbenes and are scarce and limited in scope.[21] In cases that lead to dissymmetrical olefins, stereoselectivity arises presumably from substrate control and hence, reactions are either poorly stereoselective or give the *E*-isomer predominantly.[21a,c,d]

4.2.2. Challenges in Kinetically Controlled CM for Trisubstituted Alkenes

Several challenges have to be overcome in the development of kinetically controlled *E*- or *Z*-selective synthesis of trisubstituted alkenes. One difficulty stems from the steric factors involved during the course of forming a more hindered trisubstituted olefin (vs. disubstituted), which may decelerate the reaction and/or lead to poor stereoselectivity. Another problem pertains to the inherently smaller energy difference between the *E*- and *Z*-isomers of a trisubstituted alkene (vs. disubstituted).[22] Thus, a

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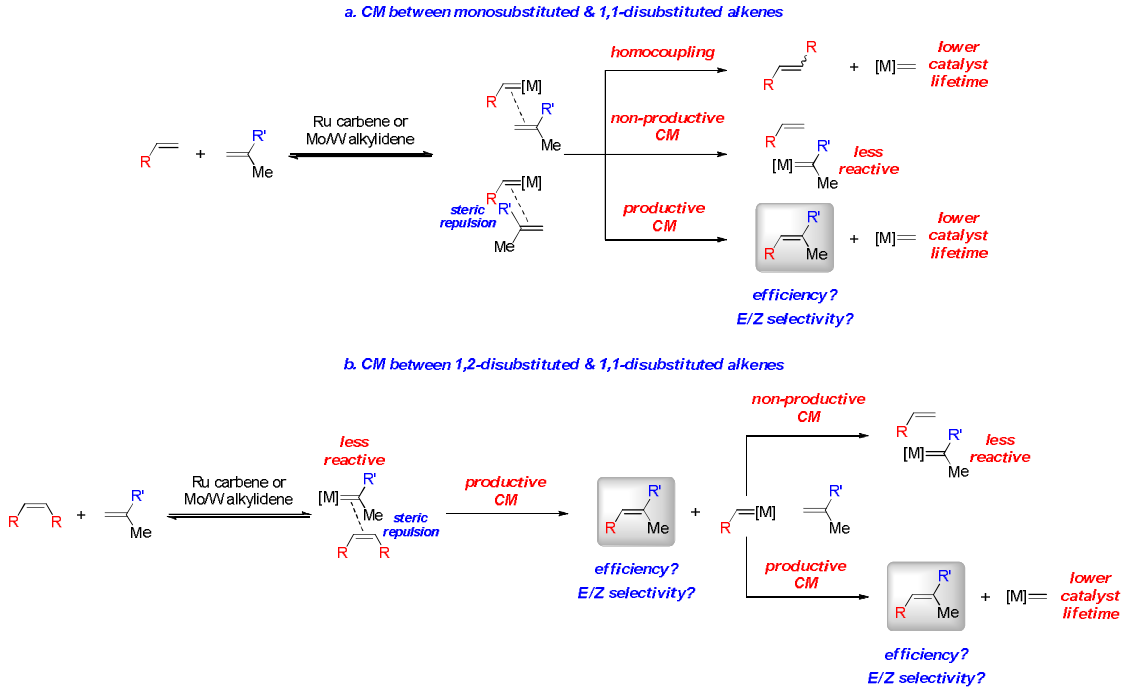
(19) Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88–93.
(20) (a) Hoveyda, A. H.; Khan, R. K. M.; Torker, S.; Malcolmson, S. J. in *Handbook of Metathesis* (eds Grubbs, R. H.; Wenzel, A. G.; O'Leary, D. J.; Khosravi, E.) 503–562 (Wiley–VCH, 2014). (b) Hoveyda, A. H. *J. Org. Chem.* **2014**, *79*, 4763–4792.
(21) (a) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751–1753. (b) Chatterjee, A. K.; Sanders, D. P.; Grubbs, R. H. *Org. Lett.* **2002**, *4*, 1939–1942. (c) Morrill, C. M.; Funk, T. W.; Grubbs, R. H. *Tetrahedron Lett.* **2004**, *45*, 7733–7736. (d) Wang, Z. J.; Jackson, W. R.; Robinson, A. J. *Org. Lett.* **2003**, *15*, 3006–3009.
(22) Cuvigny, T.; du Penhoat, H.; Julia, M. *Tetrahedron Lett.* **1980**, *21*, 1331–1334.

process whereby stereoselectivity is subjected to substrate control tends to result in *E*/*Z* isomeric mixtures that are difficult to separate in many instances.

Scheme 4.2. Challenges in Catalyst-Controlled Stereoselective CM to Access Trisubstituted Alkenes.



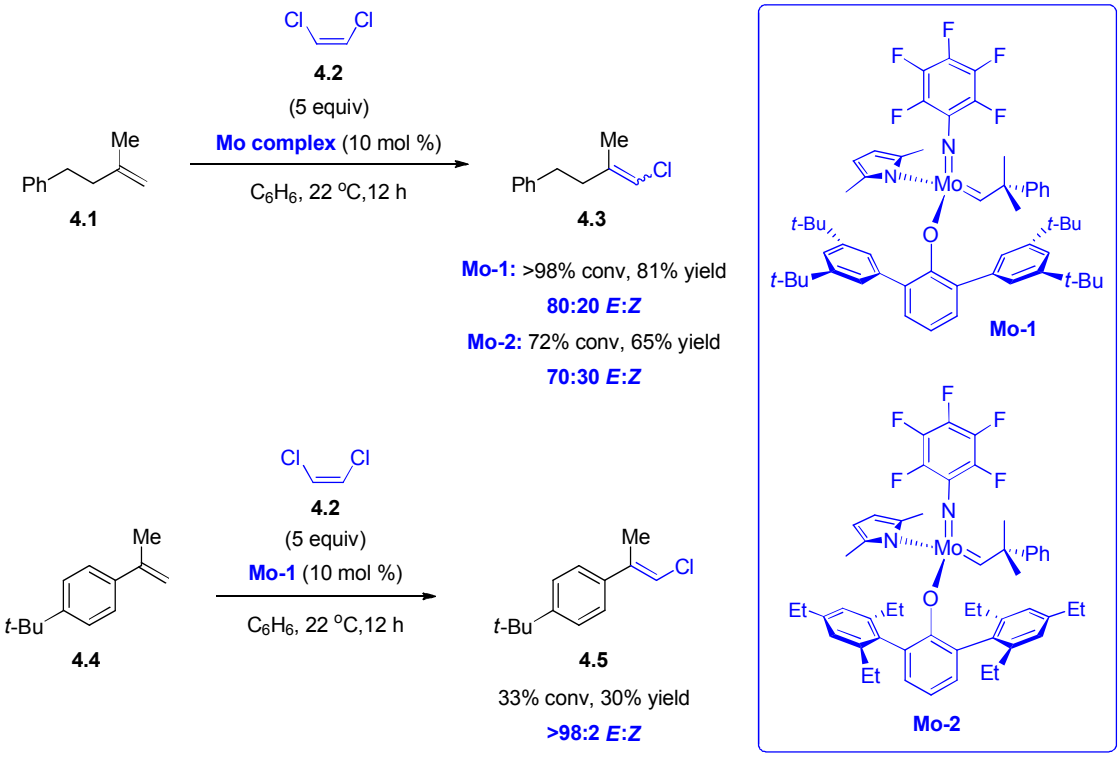
In designing a catalyst-controlled CM transformation to access trisubstituted alkenes, a number of issues have to be considered (Scheme 4.2). Unlike processes that lead to 1,2-disubstituted olefin products, in a CM reaction that affords a trisubstituted olefin, one substrate can be a monosubstituted alkene whereas the other cross-partner has to contain additional substituent(s) (typically a 1,1-disubstituted alkene). In the event, CM is likely to be less efficient and homocoupling of the more reactive (sterically less hindered) monosubstituted olefin predominates.[21d] As a consequence, ethylene and relatively unstable methylidene complexes[23] are generated leading to diminished catalyst lifetime and efficiency. The problem may be addressed to a certain extent when a more hindered (for example, α-branched) monosubstituted or 1,2-disubstituted alkene is

(23) (a) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633. (b) Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 7961−7968.

employed. However, self-metathesis of the less hindered cross-partner resulting in methylidene formation may still occur, and adventitious generation of the congested and less reactive 1,1-disubstituted alkylidene[23a] coupled with increased steric pressure within the metallacyclobutane intermediates may slow down the rate of CM. Added to these complications is the need for a reliable catalyst platform to achieve kinetically controlled stereoselectivity.

4.2.3. Trisubstituted Alkenyl Halide CM with 1,1-Disubstituted Alkenes as Substrates

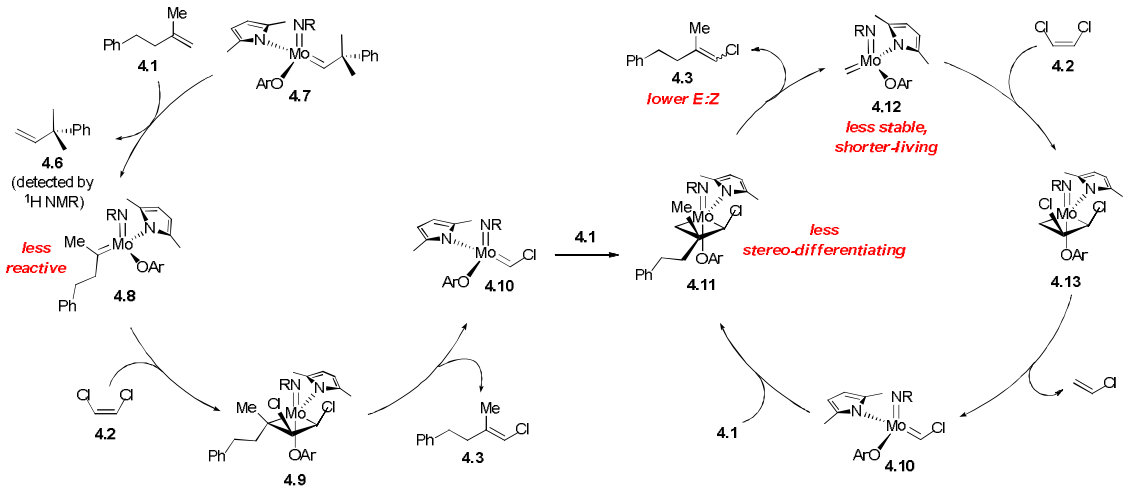
Scheme 4.3. CM of 1,1-Disubstituted Alkenes with *Z*-1,2-Dichloroethene.



As shown in Scheme 4.3, we began our preliminary investigations in CM using 1,1-disubstiuted alkenes **4.1** and **4.4** with *Z*-1,2-dichloroethene **4.2** as reagent to deliver trisubstituted alkenyl chlorides **4.3** and **4.5**, respectively (OM with alkenyl halides lies in the purview of high-oxidation-state alkylidene catalysis, cf. Chapter 2). Reaction of **4.1** with **4.2** required 10 mol % of either **Mo-1** or **Mo-2** to furnish the desired products in

81% and 65% yield with moderate stereoselectivity (80:20 and 70:30 *E*:*Z*, respectively). It merits mention that the corresponding CM with *E*-1,2-dichloroethene as reagent gave similar stereoselectivities. The transformation leading to **4.5** was less efficient (30% yield) but more selective, presumably due to more effective substrate control. Control experiments indicated that post-metathesis isomerization of the products was minimal in these reactions.

Scheme 4.4. Proposed Catalytic Cycle for CM between a 1,1-Disubstituted Alkene and *Z*-1,2-Dichloroethene.



Based on ^{1}H NMR analysis of the aforementioned crude reaction mixtures, we detected the presence of monosubstituted alkene **4.6** (~10 mol %), which implied that initiation of the neophylidene complex **4.7** entails reaction between **4.7** and the 1,1-disubstituted olefin substrate (for example, **4.1**) to give 1,1-disubstituted alkylidene **4.8** (Scheme 4.4). Reaction of **4.8** with **4.2** may give rise to chloro-substituted alkylidene **4.10**[24] and alkenyl chloride **4.3** via the all-*syn* metallacyclobutane **4.9**. **4.10** may then react with **4.1** via metallacyclobutane **4.11** to afford methylidene **4.12** and more of **4.3** (instead of forming **4.8** and vinyl chloride because the quaternary carbon center is

(24) Lam, J. K.; Zhu, C.; Bukhryakov, K. V.; Müller, P.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2016**, *138*, 15774–15783.

situated at the sterically less demanding C_β[25] in **4.11**.) Subsequent reaction of **4.12** with **4.2** should regenerate **4.10** and release vinyl chloride as byproduct.

The proposed catalytic pathway in Scheme 4.4 may offer a possible rationale for the poor efficiency and moderate stereoselectivity observed in CM with 1,1-disubstituted olefins (Scheme 4.3). The need for high catalyst loading (10 mol %) and an extended reaction time (12 hours) may be rooted in the low reactivity of the 1,1-disubstituted alkylidene **4.8**,[23a] particularly when a sterically more encumbered aryl olefin is involved (for example, **4.4**). Another reason may be due to generation of the relatively less stable methylidene species **4.12**, which can lead to shorter catalyst lifetime.[23a] The energy difference between the transition states leading to metallacyclobutane **4.11** and its corresponding isomer (wherein stereochemistry at C_β is inverted) is probably insufficient for high selectivity to be obtained unless one substituent is considerably larger (i.e. aryl vs. methyl in **4.4** (>98% *E*) compared to $(CH_2)_2Ph$ vs. methyl in **4.1** (70–80% *E*)).

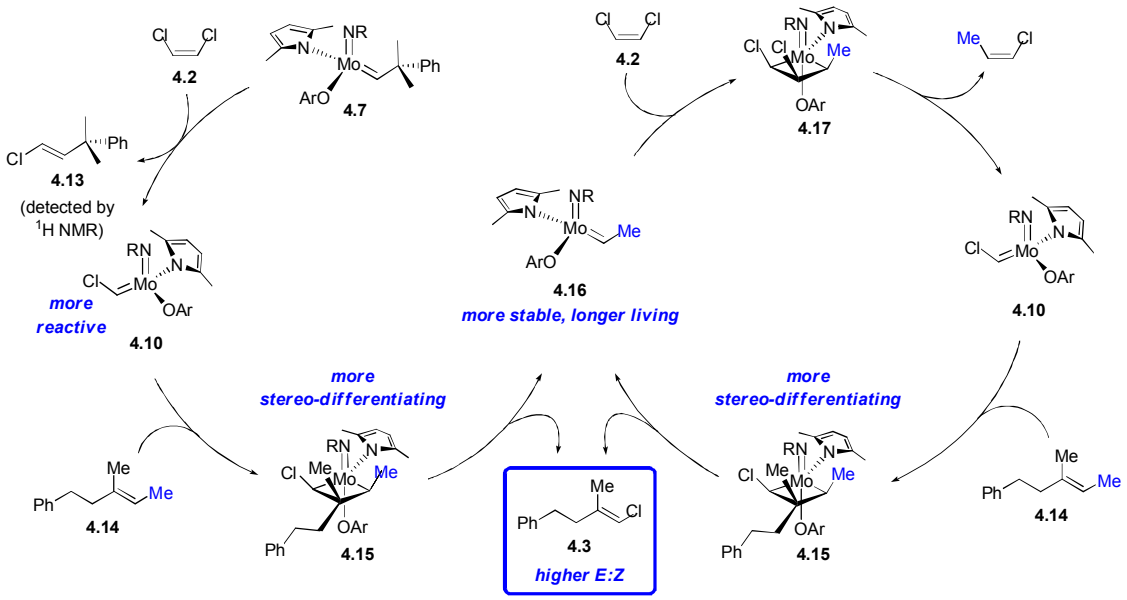
4.2.4. Higher Efficiency and Selectivity with Trisubstituted Alkenes as Substrates

In order to address the aforementioned problems in efficiency and selectivity, we surmised that a trisubstituted olefin such as **4.14** should serve as a more effective substrate (vs. 1,1-disubstituted alkene) in CM (Scheme 4.5). Initial experiments showed that subjection of a mixture of **4.14** and **4.2** to **Mo-1** or **Mo-2** afforded alkenyl chloride **4.13** exclusively (detected by ^{1}H NMR analysis). Thus, in contrast to the case with 1,1-disubstituted alkenes, neophylidene complex **4.7** first engages with the less hindered **4.2** to generate chloro-substituted alkylidene **4.10**, a species that is presumably more reactive than 1,1-disubstituted alkylidene **4.8**. Reaction of **4.10** with **4.14** may proceed through

(25) Nguyen, T. T.; Koh, M. J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. *Science* **2016**, *352*, 569–575.

metallacyclobutane **4.15** to furnish ethylidene **4.16** and the desired alkenyl chloride **4.3**. We speculated that reaction via **4.15** (vs. the less substituted **4.11** in Scheme 4.4) should be more stereoselective because the competing mode of addition would give rise to a higher-energy metallacycle wherein a substituent at C_α will be oriented towards the sizeable aryloxide ligand resulting in severe steric repulsion.[25] Formation of the presumably more stable ethylidene species **4.16** (vs. methylidene **4.12**) should translate to increased catalyst longevity and overall reaction efficiency. **4.16** may subsequently engage with **4.2** to regenerate **4.10** and discharge 1-chloro-1-propene as byproduct.

Scheme 4.5. Proposed Catalytic Cycle for CM between a *E*-Trisubstituted Alkene and *Z*-1,2-Dichloroethene.

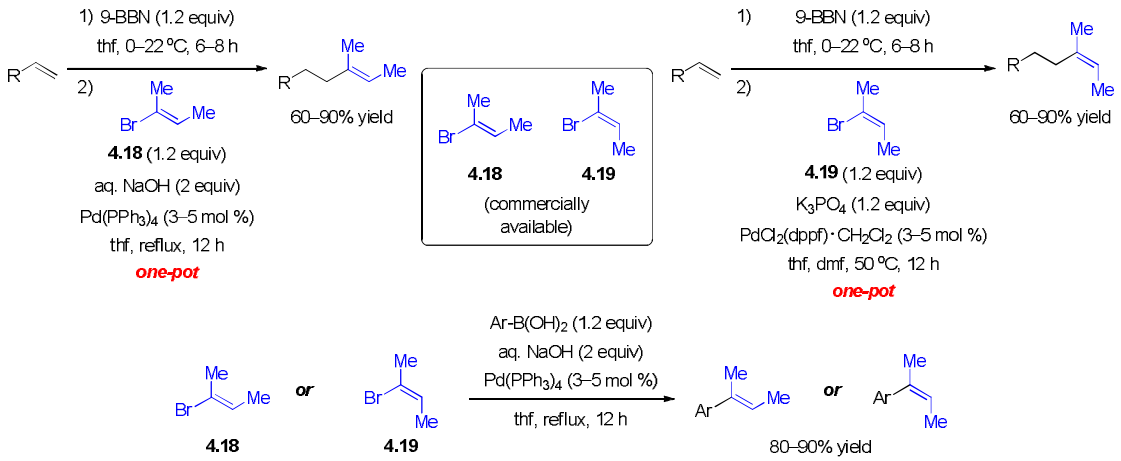


The successful implementation of the above strategy should offer a general solution to efficient and stereoselective synthesis of trisubstituted alkenes by CM. However, it remains to be seen if trisubstituted alkenes like **4.14** are sufficiently reactive to participate in CM, and whether the aforementioned principles would give rise to improved efficiency and selectivity.

4.3. Stereoselective Synthesis of Trisubstituted Alkenyl Chlorides

4.3.1. Representative Methods to Prepare Trisubstituted Olefin Substrates

Scheme 4.6. Facile Synthesis of Trisubstituted Aliphatic & Aryl Olefins by Catalytic Cross-Coupling.



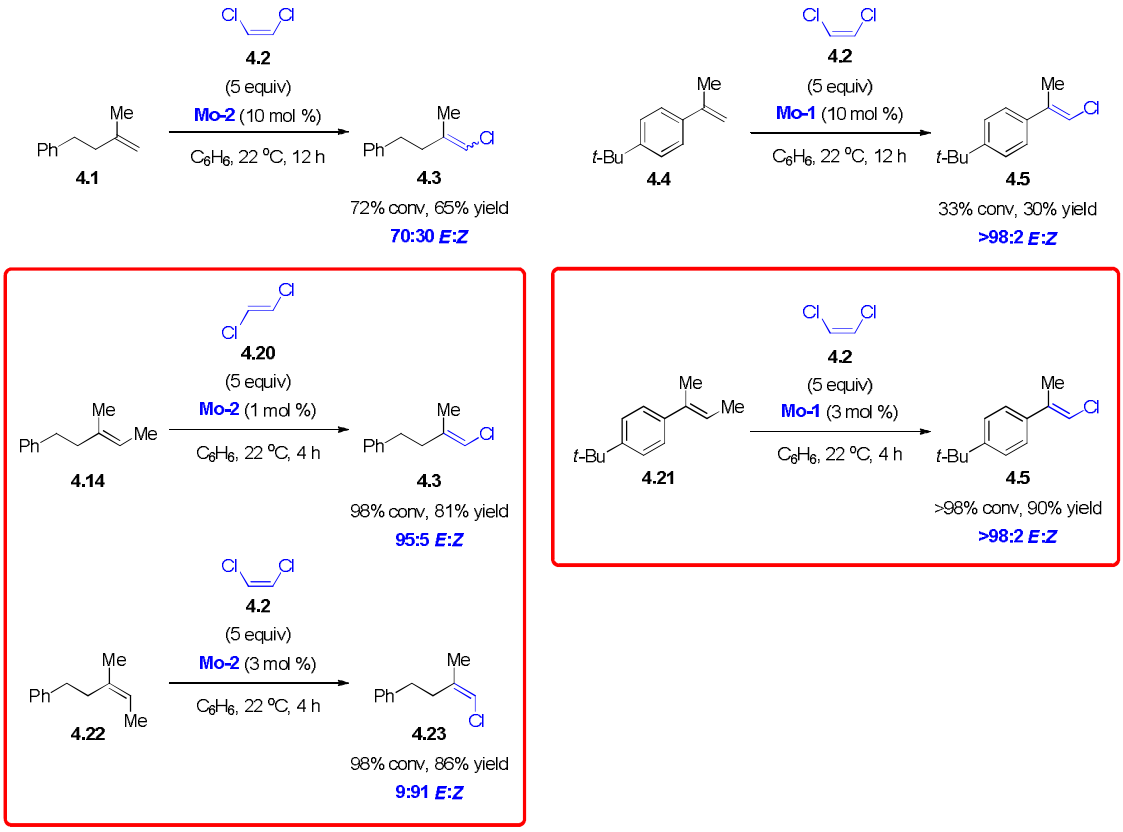
The use of a more hindered trisubstituted olefin[21d] to achieve both greater efficiency and stereoselectivity in CM to deliver another trisubstituted alkene may appear to be counter-intuitive and impractical. However, we found that many aliphatic and aryl *E*- and *Z*-trisubstituted alkenes can be efficiently accessed either by a one-pot procedure involving hydroboration of readily available monosubstituted olefins followed by catalytic cross-coupling with commercially available, inexpensive and stereoisomerically pure *E*- or *Z*-2-bromo-2-butene **4.18** or **4.19**, respectively,[26] or through direct cross-coupling between **4.18** or **4.19** and commercially available aryl boronic acids[27] (Scheme 4.6). Hence, the tenable solution to the problem of efficient and stereoselective synthesis of valuable and more difficult-to-prepare trisubstituted alkenes (such as alkenyl halides) may be to convert easily accessible stereodefined trisubstituted olefin substrates (obtained by catalytic cross-coupling) by stereoretentive CM[28] to give the desired products.

---

(26) Chemler, S. R.; Trauner, D.; Danishefsky, S. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4544–4568.
(27) Fristrup, P.; Tanner, D.; Norrby, P.-O. *Chirality* **2003**, *15*, 360–368.
(28) For a recent review, see: Montgomery, T. P.; Ahmed, T. S.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 11024–11036.

4.3.2. Comparison of Trisubstituted and 1,1-Disubstituted Alkenes in CM

Scheme 4.7. Comparison of Trisubstituted vs. 1,1-Disubstituted Alkenes in CM with *Z*-1,2-Dichloroethene.

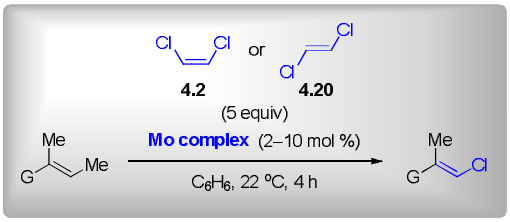


With the trisubstituted olefin substrates in hand, we proceeded to examine their reactivity in CM to access alkenyl chlorides (Scheme 4.7). In the presence of just 1 mol % **Mo-2**, CM between **4.14** and excess *E*-1,2-dichloroethene **4.20** delivered **4.3** in 81% yield and 95:5 *E*:*Z* ratio within four hours (vs. 65% yield, 70:30 *E*:*Z* using 10 mol % **Mo-2**, 12 hours with 1,1-disubstituted **4.1**). The analogous reaction with *Z*-1,2-dichloroethene **4.2** was similarly stereoselective but less efficient (50% yield). Since the same chloro-substituted alkylidene **4.10**[24] is formed by the use of **4.2** or **4.20** (both commercially available), either isomer of the reagent may be used depending on the olefin substrate employed. Treatment of **4.21** and **4.2** with 3 mol% **Mo-1** furnished *E*-alkenyl chloride **4.5**

as a single stereoisomer in 90% yield within four hours (vs. 30% yield, 12 hours with 1,1-disubstituted **4.4**). The above comparison studies lend credence to the postulations described in Section 4.2.4 that greater efficiency and selectivity can be accomplished in CM with more hindered trisubstituted alkenes as starting materials. The stereoretentive transformations are also applicable to *Z*-trisubstituted olefins, as exemplified by CM between **4.22** and **4.2** to give *Z*-alkenyl chloride **4.23** in 86% yield and 91:9 *Z*:*E* ratio.

4.3.3. CM to Access Functionalized E- and Z-Alkenyl Chlorides

Scheme 4.8. Synthesis of Trisubstituted *E*- & *Z*-Alkenyl Chlorides by CM.



4.24
with 5 mol % **Mo-2**, 83% conv, 56% yield
94:6 *E*:*Z*

4.25
with 5 mol % **Mo-1**, >98% conv, 91% yield
93:7 *E*:*Z*

4.26
with 5 mol % **Mo-2**, 85% conv, 65% yield,
96:4 *E*:*Z*

4.27
with 10 mol % **Mo-2**, 96% conv, 86% yield,
95:5 *E*:*Z*

4.28
with 5 mol % **Mo-1**, 90% conv, 87% yield
>98:2 *E*:*Z*

4.29
with 10 mol % **Mo-1**, >98% conv, 91% yield
>98:2 *E*:*Z*

4.30
with 5 mol % **Mo-1**, 89% conv, 65% yield
21:79 *E*:*Z*

4.31
with 3 mol % **Mo-2**, 94% conv, 89% yield
12:88 *E*:*Z*

4.32
with 3 mol % **Mo-2**, 96% conv, 94% yield
12:88 *E*:*Z*

4.33
with 5 mol % **Mo-2**, >98% conv, 83% yield
5:95 *E*:*Z*

4.34
with 5 mol % **Mo-2**, >98% conv, 89% yield
14:86 *E*:*Z*

4.35
with 2 mol % **Mo-2**, 82% conv, 78% yield
13:87 *E*:*Z*

A variety of trisubstituted *E*- and *Z*-alkenyl chlorides could be prepared as outlined in Scheme 4.8. In general, *E*-alkenyl chlorides **4.24**–**4.29** were obtained in 56–91% yield and 93:7 to >98:2 *E*:*Z* ratio, whereas *Z*-alkenyl chlorides **4.30**–**4.35** were isolated in 65–94% yield but with somewhat lower selectivity (21:79 to 5:95 *E*:*Z* ratio, see Section 4.3.4 for further discussion). Lewis basic groups such as an amine (**4.34**) as

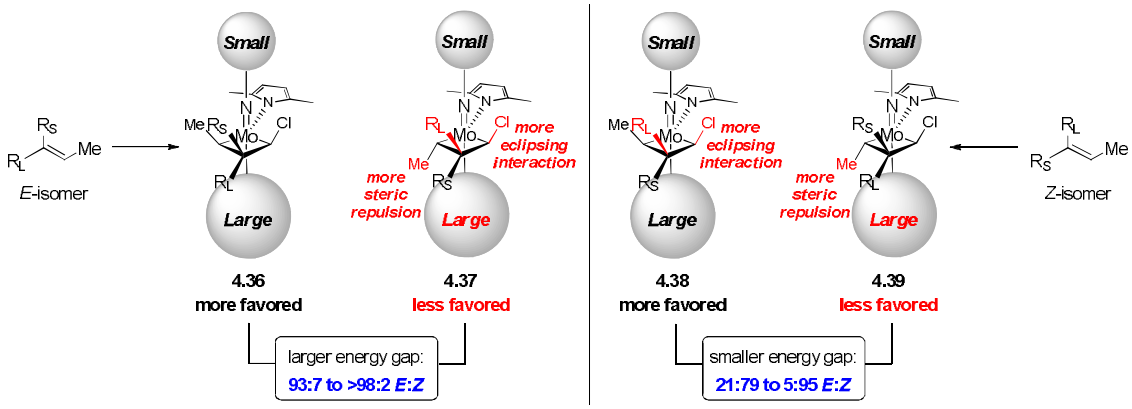
well as functionalities that are incompatible with the aforementioned zirconocene-catalyzed carbometallation approach such as an epoxide (**4.24**),[29] a carboxylic ester (**4.26**, **4.31** and **4.34**), a boronate (**4.27** and **4.33**) or a Boc-indole (**4.29** and **4.35**)[30] are tolerated under the CM conditions. As previously noted, carbometallation strategies cannot be used to access *Z*-isomers of trisubstituted alkenyl halides unless a directing hydroxyl group is present.[17,18] CM with diene substrates occurred chemoselectively with the more hindered trisubstituted olefin (vs. the less substituted but more electron-deficient enoate or alkenyl-B(pin)) to furnish **4.26** and **4.27**. Transformations with *E*-isomers of sterically congested aryl and heteroaryl olefins also proceeded efficiently to give **4.28** and **4.29** in ≥87% yield and complete *E* selectivity, but lower selectivity was observed for the corresponding *Z*-selective process (**4.30** obtained in 65% yield and 79% *Z* selectivity).

4.3.4. Rationale for Lower Stereoselectivity with Z-Alkenyl Chlorides

CM transformations that deliver *E*-alkenyl chlorides generally exhibit a higher level of stereoretention than those that afford *Z*-isomers. This can be rationalized by considering the difference in steric strain within competitive metallacyclobutanes generated in the catalytic process (Scheme 4.9).

(29) Miyazawa, M.; Ishibashi, N.; Ohnuma, S.; Miyashita, M. *Tetrahedron Lett.* **1997**, *38*, 3419–3422.
(30) Anantoju, K. K.; Mohd, B. S.; Maringanti, T. C. *Tetrahedron Lett.* **2017**, *58*, 1499–1500.

Scheme 4.9. Plausible Explanation for Lower *E*/*Z* Selectivity with *Z*-Alkenyl Chlorides vs. *E*-Alkenyl Chlorides.



For reactions leading to the *E*-alkenyl chlorides, formation of metallacycle **4.37** should be favored over **4.36** due to the greater steric strain inherent in the latter, presumably as a consequence of steric repulsion between a C_α substituent and the sizeable aryloxide (C_α groups are closer to the aryloxide and thus experience greater steric repulsion than C_β groups[25]) as well as eclipsing interaction between the larger olefin substituent (R_L) and the adjacent chlorine. In the analogous CM processes that afford *Z*-isomers, metallacycle **4.38** should be generated preferentially but the energy difference between the transition states leading to **4.38** and its competitive isomer **4.39** is probably smaller (vs. **4.36** and **4.37**). This is because of a destabilizing eclipsing interaction between R_L and chlorine that now exists in **4.38**, which is exacerbated when R_L is larger (for example, aryl group in **4.30**).

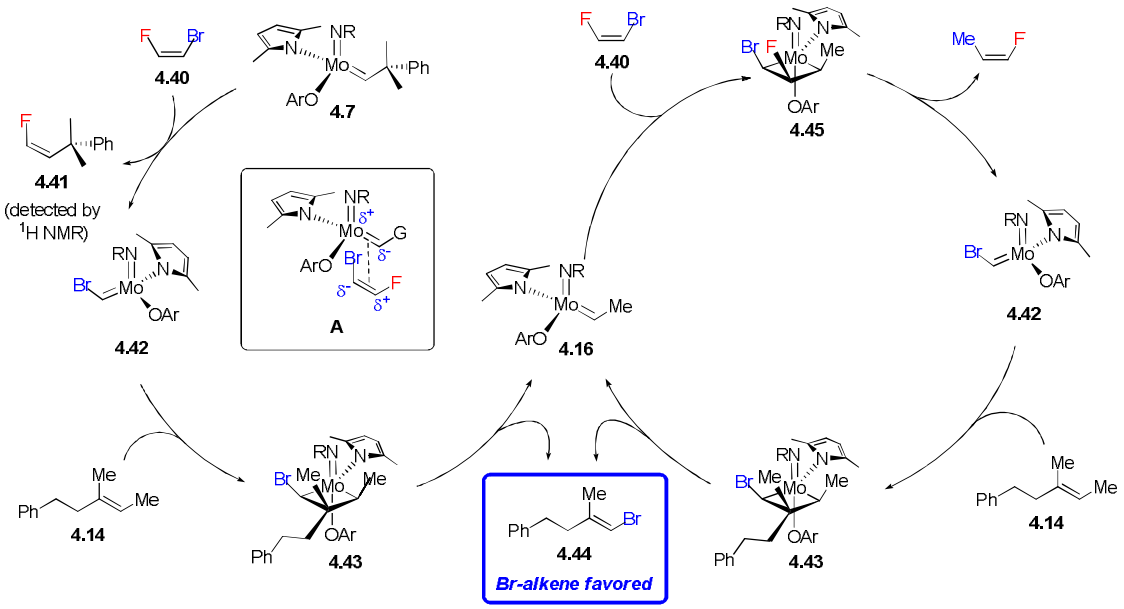
4.4. Stereoselective Synthesis of Trisubstituted Alkenyl Bromides

4.4.1. Design of Stereoselective CM that Afford Trisubstituted Alkenyl Bromides

CM to access trisubstituted alkenyl bromides entails the use of a suitable bromine-containing reagent such as 1,2-dibromoethene (available as a mixture of 64:36 *Z*:*E* isomers, cf. Section 2.3.4 in Chapter 2). However, preliminary experiments indicated that

reactions between trisubstituted olefins and the sizeable 1,2-dibromoethene are considerably inefficient, which led us to consider dissymmetrical bromo-alkene reagents such as *Z*-1-bromo-2-fluoroethene **4.41**. The same principles that govern CM involving trisubstituted alkenes (Scheme 4.5) and the previously established steric and electronic factors[31] (cf. Section 2.3.6 in Chapter 2) imply that reaction between Mo complex **4.7** and **4.41** should favor formation of bromo-substituted alkylidene **4.43** via **A** with concomitant release of an alkenyl fluoride byproduct (Scheme 4.10). This was substantiated when **Mo-1** or **Mo-2** was treated with a mixture of trisubstituted olefin **4.14** and **4.41** to afford fluoro-alkene **4.42** (detected by ^{1}H NMR analysis). **4.43** may then react with **4.14** via the expected metallacyclobutane **4.44** to afford alkenyl bromide **4.45** as the predominant product (in contrast to CM between **4.43** and mono- or 1,2-disubstituted olefins that delivers alkenyl fluorides as the major product).[25,31]

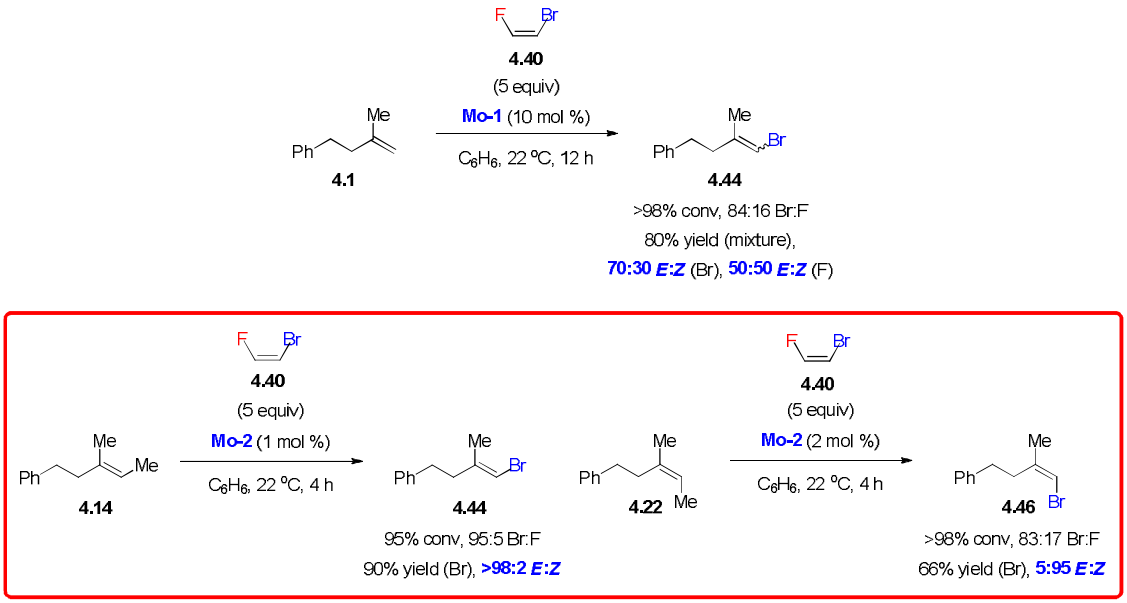
Scheme 4.10. Proposed Catalytic Cycle for CM between a *E*-Trisubstituted Alkene and *Z*-1-Bromo-2-fluoroethene.



(31) Koh, M. J.; Nguyen, T. T.; Zhang, H.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2016**, *531*, 459–465.

As illustrated in Scheme 4.11, reaction of 1,1-disubstituted alkene **4.1** with **4.40** in the presence of 10 mol % **Mo-1** generated alkenyl bromide **4.44** within 12 hours as the major product albeit as a mixture of 70:30 *E*:*Z* isomers, analogous to the cases that afford alkenyl chlorides (cf. Scheme 4.3). By comparison, CM between trisubstituted *E*-alkene **4.14** and **4.40** with 1 mol % **Mo-2** furnished **4.44** in 80% yield and 95:5 Br:F selectivity with complete retention of stereochemistry (>98% *E*) within four hours (**Mo-2** gave better Br:F ratio compared to **Mo-1**). The transformation involving trisubstituted *Z*-alkene **4.22** and **4.40** led to **4.46** in 66% yield and 5:95 *E*:*Z* ratio with somewhat diminished Br:F selectivity (see Section 4.4.3 for further discussion).

Scheme 4.11. Comparison of Trisubstituted vs. 1,1-Disubstituted Alkenes in CM with *Z*-1-Bromo-2-fluoroethene.

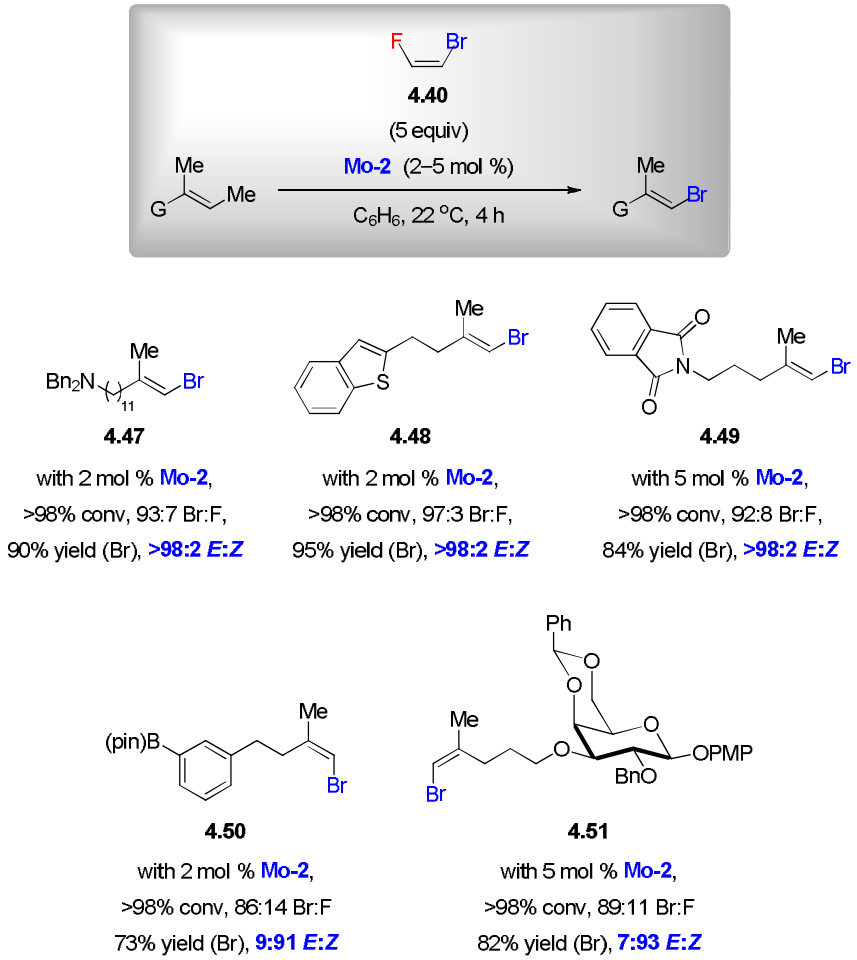


4.4.2. CM to Access Functionalized E- and Z-Alkenyl Bromides

Further analysis of the substrate scope is highlighted in Scheme 4.12. In practice, alkenyl bromides **4.47**–**4.51** were generated in 73–95% yield and ≥91% stereoselectivity. These include products that bear a Lewis basic amine (**4.47**) or phthalimide (**4.49**) as well

as acetals (**4.51**), motifs that are sensitive to trialkylaluminum compounds using the carbometallation approach.[32] **4.50** represents a difunctional compound containing an alkenyl bromide and a B(pin) that offers the opportunity of orthogonal functionalization.

Scheme 4.12. Synthesis of Trisubstituted *E*- & *Z*-Alkenyl Bromides by CM.



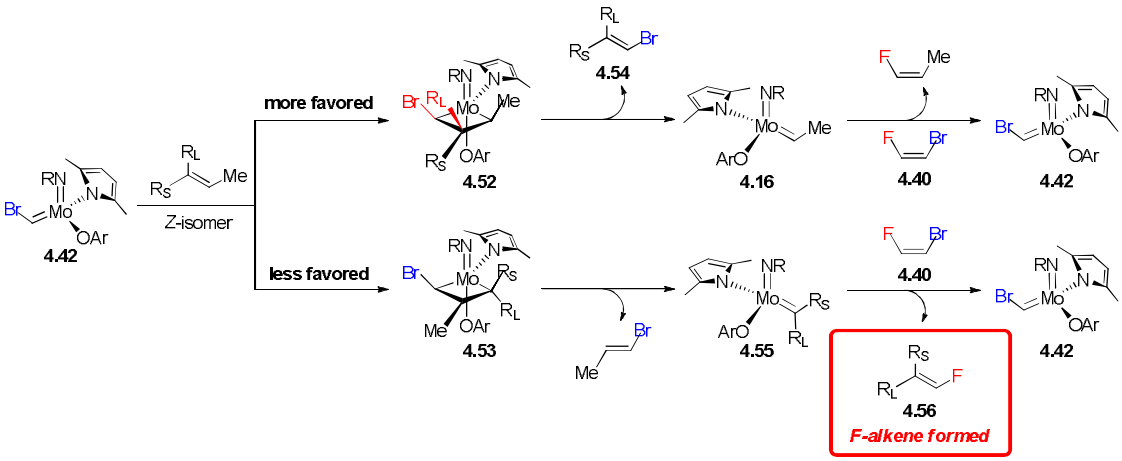
4.4.3. Rationale for Lower Br:F Selectivity with Z-Alkenyl Bromides

In CM reactions with **4.40**, the preference for the bromo-alkene product is typically lower for *Z*-alkenyl bromides compared to the *E*-isomers (83:17–89:11 vs. 92:8–97:3 Br:F ratio, respectively). This may be explained by considering the mechanistic rationale as depicted in Scheme 4.13. Reaction of bromo-substituted

(32) Mori, A.; Fujiwara, J.; Maruoka, K.; Yamamoto, H. *J. Organomet. Chem.* **1985**, *285*, 83–94.

alkylidene **4.42** with the *Z*-olefin substrate generally proceeds through the preferred metallacyclobutane **4.52** based on the arguments delineated in Scheme 4.9. However, as a consequence of an inherent destabilizing eclipsing interaction between R_L and bromine **4.52** (presumably more severe compared to that between R_L and the smaller chlorine (cf. **4.38** in Scheme 4.9)), formation of alternative undesired metallacyclobutanes such as **4.53** becomes even more competitive. Collapse of **4.53** then leads to the 1,1-disubstituted alklylidene **4.55** with concomitant release of 1-bromo-1-propene as byproduct. The ensuing reaction between **4.55** and **4.40** will regenerate **4.42** and inevitably form alkenyl fluoride **4.56**, giving rise to the erosion of Br:F selectivity.

Scheme 4.13. Plausible Explanation for Lower Br:F Selectivity with *Z*-Alkenyl Bromides.



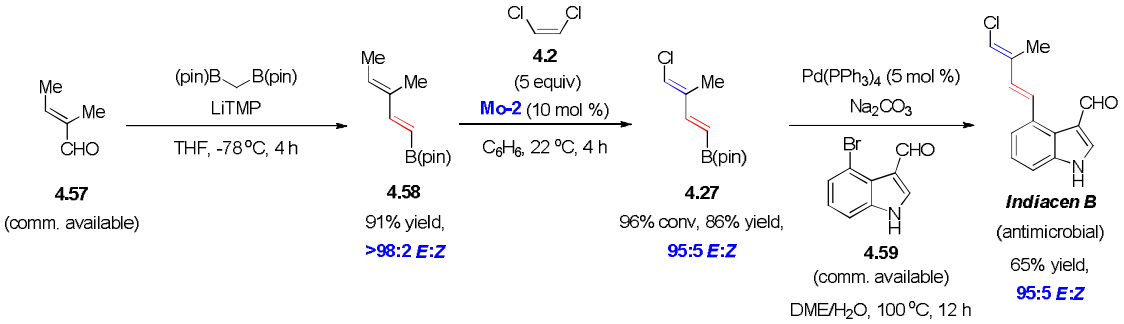
4.5. Application to Synthesis of Biologically Active Compounds

4.5.1. Synthesis of Indiacen B

To demonstrate utility of our developed catalytic protocol, representative applications to concise and stereoselective synthesis of biologically active targets are performed. A common strategy in these synthesis routes involves the synergistic combination of catalytic cross-coupling and CM to rapidly assemble key fragments. The

first instance relates to the total synthesis of antimicrobial indiacen B[30,33] (Scheme 4.14). *E*,*E*-Diene **4.58** was obtained by a boron-Wittig transformation from commercially available enal **4.57** and bis[(pinacolato)boryl]methane in 91% yield as a single stereoisomer. The ensuing chemoselective CM with excess **4.2** and 10 mol % **Mo-2** delivered **4.27** in 86% yield and 95:5 *E*:*Z* selectivity. Subsequent Suzuki coupling with **4.59** furnished the final target in 65% yield. Overall, indiacen B was secured in 51% yield over three steps, which compares favorably to a previously reported seven-step route generating the product in 16% overall yield.[30]

Scheme 4.14. Total Synthesis of Antimicrobial Indiacen B.



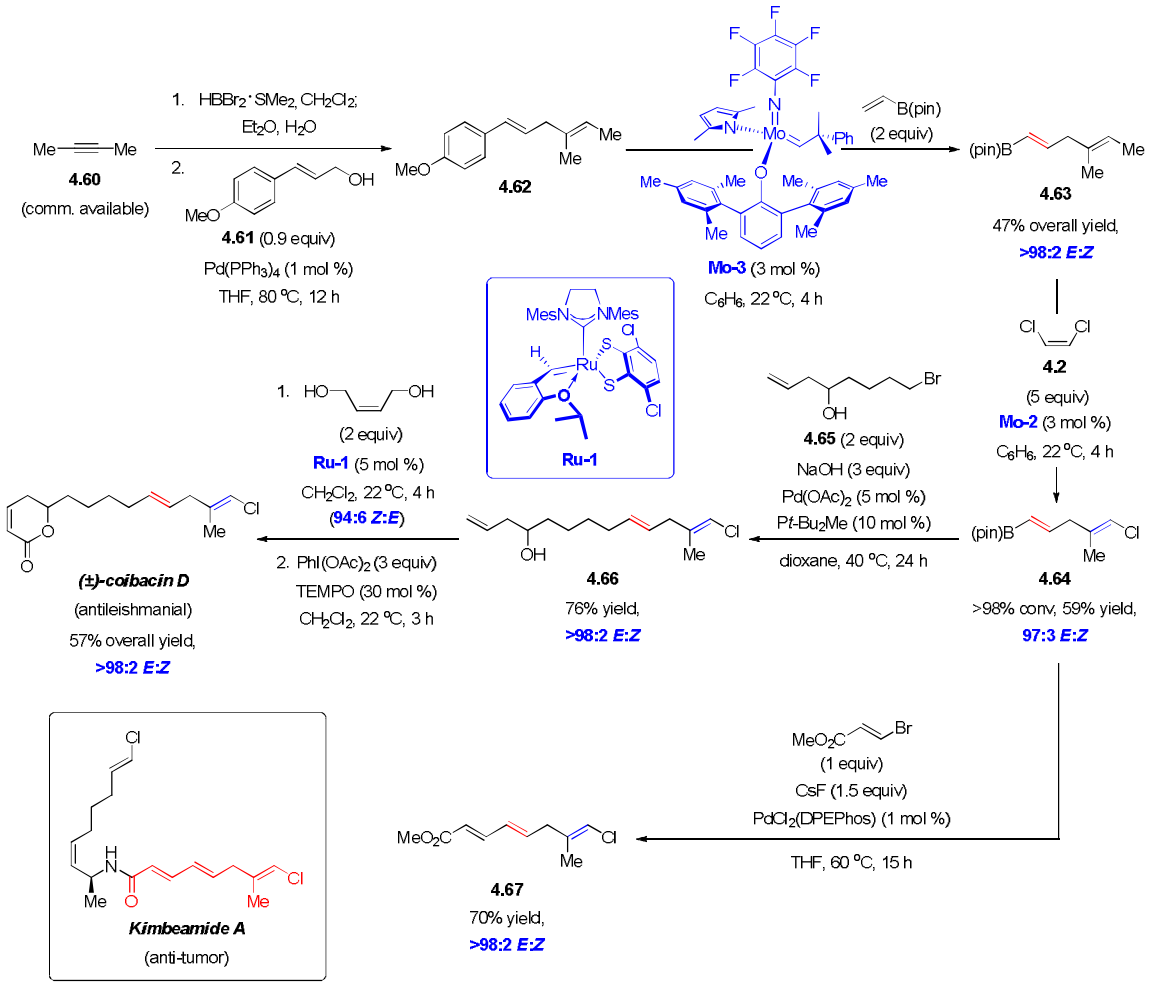
4.5.2. Synthesis of Coibacin D and Kimbeamide A

The next cases focus on the synthesis of antileishmanial and anti-inflammatory coibacin D[34] and anti-tumor kimbeamide A.[14] *E*,*E*-Diene **4.62** was prepared by a two-step procedure involving hydroboration/hydrolysis of commercially available 2-butyne and cross-coupling of the resulting alkenyl boronic acid with *E*-allylic alcohol **4.61**.[35] Subsequent CM of **4.62** with 3 mol % of the optimal **Mo-3** and vinyl-B(pin) proceeded

(33) (a) Steinmetz, H.; Mohr, K. I.; Zander, W.; Jansen, R.; Gerth, K.; Müller, R. *J. Nat. Prod.* **2012**, *75*, 1803–1805. (b) Marsch, N.; Jones, P. G.; Lindel, T. *Beilstein J. Org. Chem.* **2015**, *11*, 1700–1706.
(34) Balunas, M. J.; Grosso, M. F.; Villa, F. A.; Engene, N.; McPhail, K. L.; Tidgewell, K.; Pineda, L. M.; Gerwick, L.; Spadafora, C.; Kyle, D. E.; Gerwick, W. H. *Org. Lett.* **2012**, *14*, 3878–3881.
(35) Tsukamoto, H.; Uchiyama, T.; Suzuki, T.; Kondo, Y. *Org. Biomol. Chem.* **2008**, *6*, 3005–3013.

chemoselectively at the less hindered styrenyl site to give **4.63** in 47% overall yield as a single stereoisomer.

Scheme 4.15. Synthesis of Antileishmanial Coibacin D & Anti-tumor Kimeamide A Side Chain.



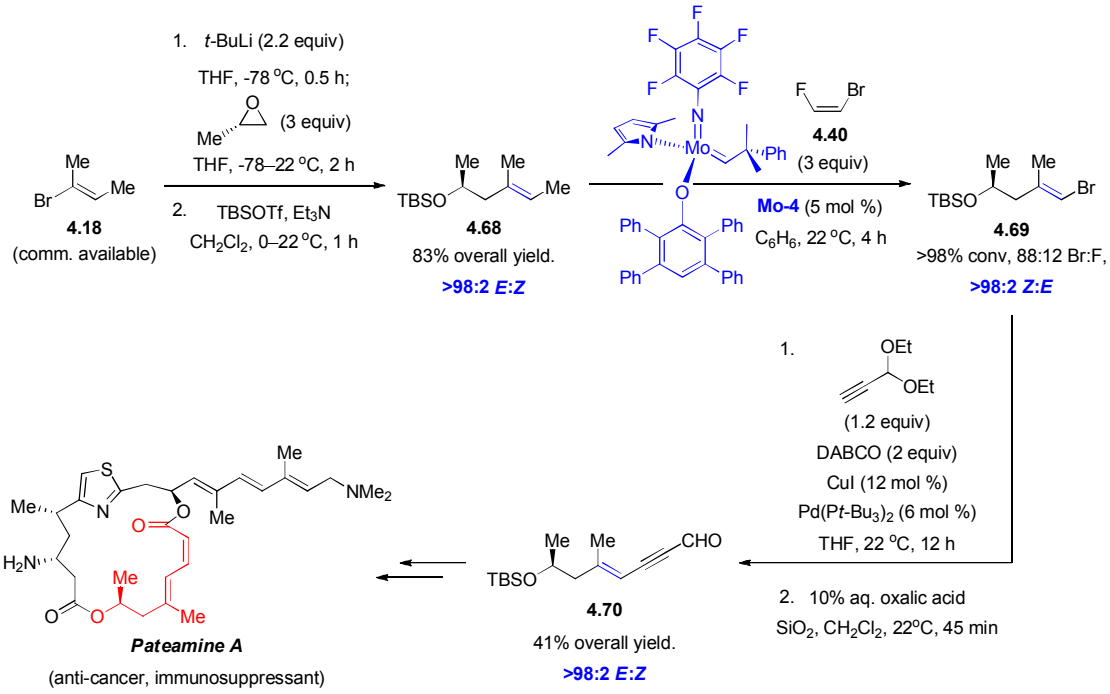
A second chemoselective CM with 3 mol % **Mo-2** and **4.2** delivered **4.64** in 59% yield and 97% *E* selectivity; the more electron-rich trisubstituted olefin reacted preferentially vs. the less substituted but more electron-deficient alkenyl-B(pin) motif. This was followed by catalytic cross-coupling between **4.64** and **4.65** to give homoallylic alcohol **4.66** in 76% yield. A third chemoselective CM with *Z*-2-butene-1,4-diol and 5 mol % **Ru-1** generated the desired *Z*-allylic alcohol intermediate in 94:6 *Z*:*E* ratio, which

was subjected to oxidative cyclization conditions to furnish racemic coibacin D in 57% overall yield (>98% *E*,*E* at the acyclic olefin sites). Overall, the target was secured in seven steps and 12% yield (longest linear sequence) as a single olefin isomer, compared to 4% overall yield and 75:25 mixture of alkene isomers after six steps in the previously disclosed route.[36]

Dienyl chloride **4.64** also serves as a common precursor en route to kimbeamide A. Suzuki coupling between **4.64** and *E*-methyl 3-bromoacrylate led to dienoate **4.67** (70% yield, >98% *E*), an intermediate that may be applied to the preparation of the aforementioned target molecule. The amine fragment required for the synthesis has been synthesized by kinetically *E*-selective CM[25] (cf. Scheme 2.17 in Chapter 2).

4.5.3. Synthesis of Pateamine A

Scheme 4.16. Formal Synthesis of Anti-cancer & Immunosuppressant Pateamine A.



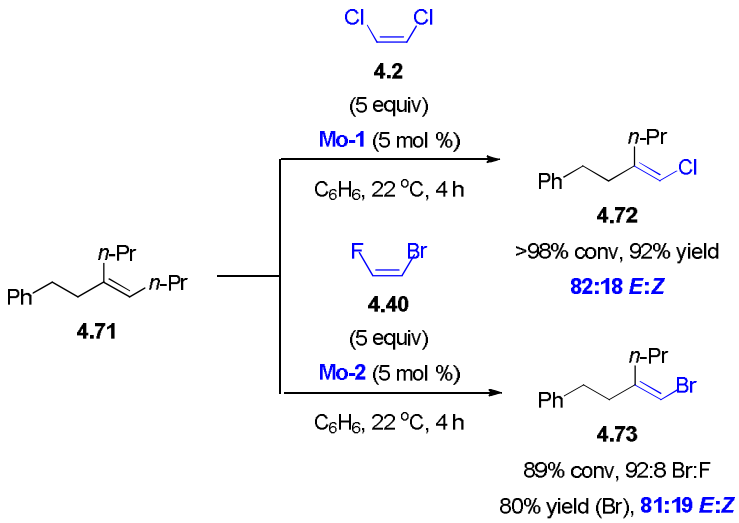
(36) Kolská, K.; Ghavre, M.; Pour, M.; Hybelbauerová, S.; Kotora, M. *Asian J. Org. Chem.* **2016**, *5*, 646–651.

The final application involves synthesis of a trisubstituted *E*-alkenyl bromide as a key intermediate for the preparation of anti-cancer and immunosuppressant pateamine A.[37] *E*-2-Bromo-2-butene **4.18** was converted to homoallylic silyl ether **4.68** in 83% overall yield and >98:2 *E*:*Z* ratio through lithium-halogen exchange followed by trapping with commercially available and enantiomerically pure (*S*)-propylene oxide and subsequent silylation of the resulting alcohol. The ensuing CM with **4.40** and 5 mol % of the optimal **Mo-4** afforded *E*-alkenyl bromide **4.69** in 88:12 Br:F selectivity as a single alkene isomer. Following Sonogashira coupling with 3,3-diethoxy-1-propyne and acetal deprotection, *E*-enyne **4.70** was obtained in 41% yield over three steps. This fragment has been employed in the total synthesis of pateamine A.[37b] Overall, our approach enables access to **4.70** in 34% overall yield within six steps (vs. 33% yield in 8 steps).

4.6. Stereoselective Synthesis of Other Classes of Trisubstituted Alkenes

4.6.1. Preliminary Results with Alkenyl Halides Bearing Larger Substituents (vs. Me)

Scheme 4.17. CM to Access Trisubstituted Alkenyl Halides Bearing Larger Groups (vs. Me).



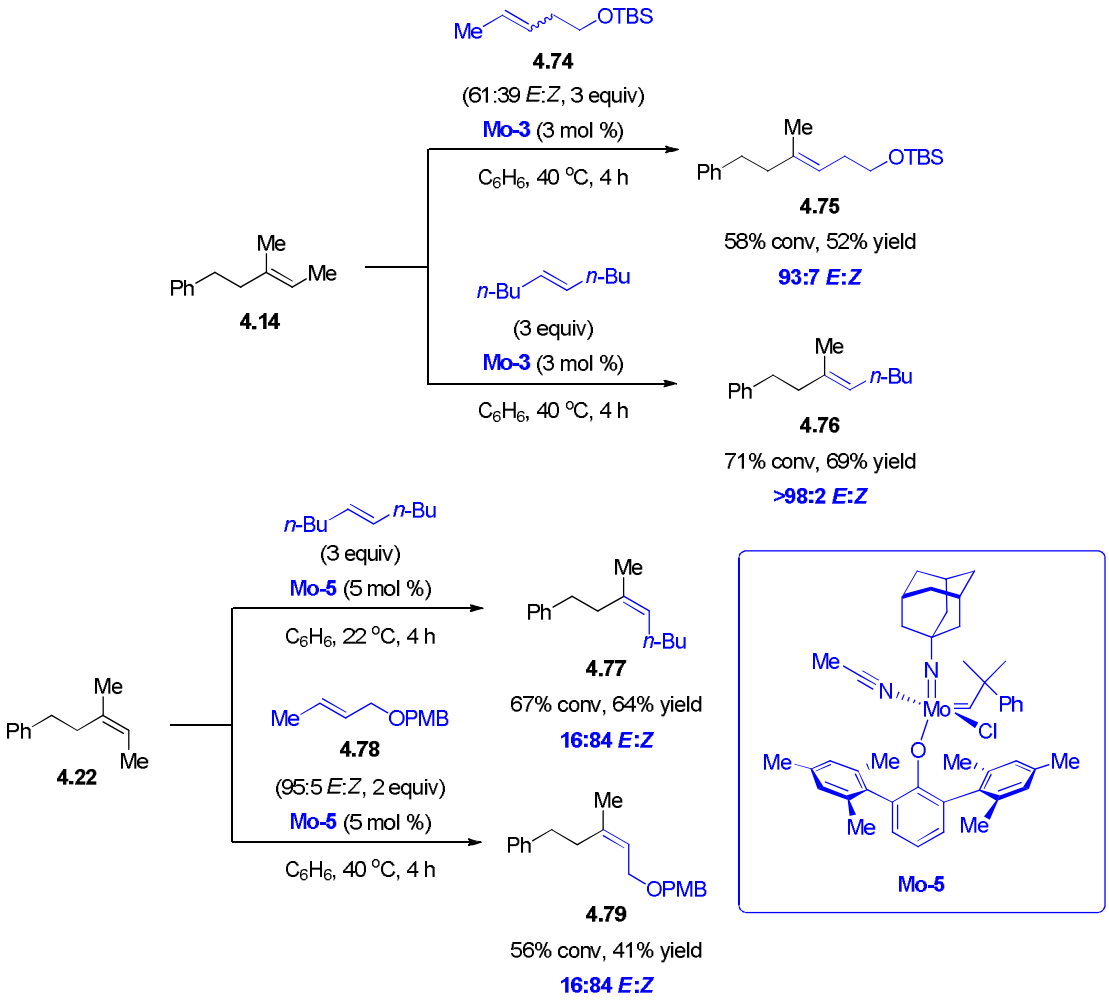
(37) (a) Northcote, P. T.; Blunt, J. W.; Munro, M. H. G. *Tetrahedron Lett.* **1991**, *32*, 6411–6414. (b) Romo, D.; Rzasa, R. M.; Shea, H. A.; Park, K.; Langenhan, J. M.; Sun, L.; Akhiezer, A.; Liu, J. O. *J. Am. Chem. Soc.* **1998**, *120*, 12237–12254.

Preliminary results demonstrate that trisubstituted alkenyl halides containing longer alkyl chains (other than a methyl unit) may be synthesized by CM using **4.2** or **4.40** as reagent (Scheme 4.17). Alkenyl chloride **4.72** and alkenyl bromide **4.73** were obtained in 92% and 80% yield with 82:18 and 81:19 *E*:*Z* ratios, respectively. The diminished level of stereoretention is probably due to the smaller size differentiation between the two alkyl groups (*n*-Pr and $(CH_2)_2Ph$) at C_β of the intermediate metallacyclobutane (cf. **4.36** and **4.37** in Scheme 4.9). Nonetheless, alternative carbometallation approaches using higher-order trialkylaluminum compounds (not as readily available as Me_3Al)[16] are comparatively less practical than CM. Efforts are ongoing to develop catalyst systems that provide higher degrees of stereo-differentiation to improve *E*/*Z* selectivity.

4.6.2. Preliminary Results with Aliphatic Alkenes

The stereoretentive CM reactions may be extended to non-halogenated trisubstituted olefins (Scheme 4.18). Treatment of **4.14** with 1,2-disubstituted homoallylic ether **4.74** (61:39 *E*:*Z* mixture) and 5 mol % **Mo-3** furnished **4.75** in 52% yield and 93:7 *E*:*Z* ratio within four hours at 40 °C. Similarly, CM between **4.14** and commercially available *E*-5-decene gave **4.76** in 69% yield and complete *E* selectivity. Elevated temperatures and use of a Mo complex bearing a sterically less encumbered aryloxide (**Mo-3** vs. **Mo-2**) are necessary to accommodate the larger 1,2-disubstituted alkyl olefin cross-partner (vs. 1,2-dihaloethene) for higher reaction efficiency. As discussed in Section 4.3.2, since the catalyst is capable of reacting with isomer of the 1,2-disubstituted alkene reagent to generate the same alkylidene species, the cross-partner used does not need to be stereoisomerically pure.

Scheme 4.18. CM to Access Trisubstituted Aliphatic Olefins.



Trisubstituted *Z*-alkenes **4.77** and **4.79** were also obtained by CM in 41–64% yield and 84% *Z* selectivity. Since these transformations occur through the intermediacy of more congested metallacyclobutanes (cf. **4.38** and **4.39** vs. **4.36** and **4.37** in Scheme 4.9), use of the more active Mo-based monoaryloxide chloride (MAC)[38] complex **Mo-5** is needed for improved efficiency. It merits mention that MAC catalysts are inefficient in promoting CM for trisubstituted alkenyl halides, likely because the putative halo-substituted metallacyclobutane generated by reaction of neophylidene complex **4.7** with

(38) Koh, M. J.; Nguyen, T. T.; Lam, J. K.; Torker, S.; Hyvl, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2017**, *542*, 80–85.

1,2-dihaloethene during initiation (cf. Schemes 4.5 and 4.10) is susceptible to decomposition.[38]

4.7. Conclusions

A general, reliable and broadly applicable solution for efficient and kinetically controlled stereoselective synthesis of acyclic *E*- and *Z*-trisubstituted alkenes, previously a challenging and unsolved problem in OM, was conceived by a sequence of catalytic cross-coupling between commercially available *E*- or *Z*-2-bromo-2-butene and an organoboron compound (purchasable or easily accessible from alkene hydroboration) followed by stereoretentive CM with an appropriate Mo alkylidene complex. This strategy was developed in light of the fundamental complications plaguing conventional processes that employ 1,1-disubstituted olefins as substrates for CM. Reactions between a 1,1-disubstituted alkene and a monosubstituted or 1,2-disubstituted olefin may suffer from two complicating issues: (1) Inevitable homocoupling of the less hindered olefin resulting in ethylene and methylidene formation translates to decreased catalyst longevity. (2) Adventitious generation of the presumably less reactive 1,1-disubstituted alkylidene and increased steric pressure within the requisite metallacyclobutane intermediates slow down CM. We have demonstrated that these limitations can be circumvented by replacing 1,1-disubstituted olefins with stereodefined trisubstituted alkenes in combination with a 1,2-disubstituted olefin reagent that does not need to be stereoisomerically pure.

The successful implementation of our strategy hinges on the ease with which many aliphatic and aryl trisubstituted *E*- and *Z*-alkenes can be reliably prepared in stereoisomerically pure forms through catalytic cross-coupling, as well as the availability

of appropriately reactive Mo-based catalysts that are capable of promoting CM between a wide array of tri- and 1,2-disubstituted alkenes, particularly the electron-deficient 1,2-dihaloethenes with high stereochemical control. In short, easily accessible trisubstituted olefin substrates may be converted to more valuable and challenging-to-prepare trisubstituted alkene products (for example, alkenyl halides).

Utility of our strategy for trisubstituted alkenyl halides is showcased through concise and stereoselective preparation of biologically active compounds, all of which rely on sequences of cross-coupling and CM transformations to construct the desired target molecule. Hence, by adopting the proper combination of these two important catalytic C–C bond forming reactions, a critical limitation in trisubstituted alkene synthesis has been resolved. The present protocol is anticipated to facilitate preparation of diverse organic compounds and efforts are underway to expand the scope to other classes of desirable trisubstituted alkenes (for example, alkenyl nitriles). In addition, the underlying principles for stereoretentive CM may be extended to other OM transformations such as macrocyclic RCM to access trisubstituted macrocyclic ring systems[39] for applications in natural product synthesis.

(39) Wang, C.; Haeffner, F.; Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2013**, *52*, 1939–1943.

4.8. Experimentals

4.8.1. Representative References for Stereoselective Synthesis of Acyclic Trisubstiuted Alkenes

a. Regio- and Stereoselective 1,2-Additions to Alkynes:

a) Wang, K. K.; Wang, Z.; Tarli, A.; Gannett, P. *J. Am. Chem. Soc.* **1996**, *118*, 10783–10791.

b) Tarli, A.; Wang, K. K. *J. Org. Chem.* **1997**, *62*, 8841–8847.

c) Ohmura, T.; Oshima, K.; Suginome, M. *Chem. Commun*. **2008**, 1416–1418.

d) Xu, Z.; Negishi, E.-i. *Org. Lett.* **2008**, *10*, 4311–4314.

e) Negishi, E.-i.; Tobrman, T.; Rao, H.; Xu, S.; Lee, C.-T. *Isr. J. Chem.* **2010**, *50*, 696–701.

f) Xu, S.; Lee, C.-T.; Rao, H.; Negishi, E.-i. *Adv. Synth. Catal.* **2011**, *353*, 2981–2987.

g) Valot, G.; Mailhol, D.; Regens, C. S.; O'Malley, D. P.; Godineau, E.; Takikawa, H.; Philipps, P.; Fürstner, A. *Chem. Eur. J.* **2015**, *21*, 2398–2408.

h) Huwyler, N.; Radkowski, K.; Rummelt, S. M.; Fürstner, A. *Chem. Eur. J.* **2017**, *23*, 12412–12419.

b. Stereoselective Alder-Ene and Carbonyl-Ene Reactions:

a) Trost, B. M.; Shen, H. C.; Pinkerton, A. B. A *Chem. Eur. J.* **2002**, *8*, 2341–2349.

b) Hutson, G. E.; Dave, A. H. & Rawal, V. H. *Org. Lett*. **2007**, *9*, 3869−3872.

c) Hilt, G.; Erver, F. & Harms, K. *Org. Lett*. **2011**, *13*, 304−307.

d) Erver, F. & Hilt, G. *J. Org. Chem.* **2012**, *77*, 5215–5219.

e) Trost, B. M.; Koester, D. C. & Herron, A. N. *Angew. Chem. Int. Ed.* **2015**, *54*, 15863–15866.

c. Stereoselective Synthesis of Trisubstituted Alkenes by Shapiro Reactions:

a) Corey, E. J.; Lee, J.; Roberts, B. E. *Tetrahedron Lett.* **1997***, 38*, 8915−8918.

b) Corey, E.J.; Roberts, B. E. *Tetrahedron Lett.* **1997***, 38*, 8919−8920.

d. Additional Examples of Stereoselective Synthesis of Trisubstituted Alkenes:

a) Tan, Z.; Negishi, E.-i. *Angew. Chem. Int. Ed.* **2006**, *45*, 762–765.

b) Hodgson, D. M.; Arif, T. *J. Am. Chem. Soc.* **2008**, *130*, 16500–16501.

4.8.2. General

Unless otherwise noted, transformations were performed with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum line techniques. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR Mode) spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), or weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz), 500 (500 MHz), or 600 (600MHz_ spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard ($CDCl_3$: δ 7.26 ppm, C_6D_6: δ 7.16 ppm, CD_2Cl_2: δ 5.32 ppm, CD_3OD: δ 3.31 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz), 500 (125 MHz), or 600 (150 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm, C_6D_6: δ 128.00 ppm, CD_2Cl_2: δ 54.00 ppm, CD_3OD: δ 49.00 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS and JEOL Accu TOF Dart (positive mode) at the Boston College Mass Spectrometry Facility.

Melting points were determined using a Thomas Hoover Uni-melt capillary melting point apparatus. Values for *E*:*Z* ratios of products were determined by ^{1}H NMR analysis of unpurified mixtures.

Solvents:

Solvents (CH_2Cl_2, Et_2O, pentane, benzene and toluene) were purified under a positive pressure of dry argon gas by a modified Innovative Technologies purification system. Tetrahydrofuran was distilled from Na/benzophenone. Methanol was distilled over Mg. Acetone, *N*,*N*-dimethylformamide (anhydrous), 1,2-dimethoxyethane (anhydrous) and 1,4-dioxane (anhydrous) were used as received. All purification procedures of CM products were carried out with reagent grade solvents (purchased from Fisher) under bench-top conditions.

Reagents:

(*E*)-5-Decene (Aldrich) and vinylboronic acid pinacol ester (Aldrich) were either distilled (from CaH_2 or $CaCl_2$) under vacuum or dried by azeotropic distillation (with anhydrous benzene) prior to use.

(*E*)-(5-Propylnon-5-en-1-yl)benzene was prepared by hydroboration of 4-octyne (Aldrich) followed by cross-coupling with 1-bromo-4-phenylbutane (Aldrich) in analogy to reported procedures.[40]

(3-Methylbut-3-en-1-yl)benzene (from 4-phenyl-2-butanone (Aldrich)) and 1-(*tert*-butyl)-4-(prop-1-en-2-yl)benzene (from 4'-*tert*-butylacetophenone (Aldrich)) were prepared by Wittig reaction in analogy to a reported procedure.[41]

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(40) (a) Brown, H. C.; Bhat, N. G.; Rajagopalan, S. *Synthesis* **1986**, 480–482. (b) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662–13663.
(41) Pine, S. H.; Shen, G. S.; Hoang, H. *Synthesis* **1991**, 165–167.

(*E*)-1-(But-2-en-2-yl)-4-(*tert*-butyl)benzene (from 4-*tert*-butylphenyl boronic acid (Combi-Blocks) and (*E*)-2-bromo-2-butene (Aldrich)), (*Z*)-1-(but-2-en-2-yl)-4-(*tert*-butyl)benzene (from 4-*tert*-butylphenyl boronic acid (Combi-Blocks) and (*Z*)-2-bromo-2-butene (Aldrich)), (*E*)-1-(but-2-en-2-yl)-3-methoxybenzene (from 3-methoxyphenyl boronic acid (Combi-Blocks) and (*E*)-2-bromo-2-butene (Aldrich)) and (*E*)-*tert*-butyl 5-(but-2-en-2-yl)-1*H*-indole-1-carboxylate (from 1-Boc-indole-5-boronic acid pinacol ester (Combi-Blocks) and (*E*)-2-bromo-2-butene (Aldrich)) were prepared by cross-coupling in analogy to a reported procedure.[27]

(*E*)-(3-Methylpent-3-en-1-yl)benzene (from styrene (Aldrich)), (*E*)-2-(9-methylundec-9-en-1-yl)oxirane (from 1,2-epoxy-9-decene (Aldrich)), (*E*)-2-(3-methylpent-3-en-1-yl)benzo[*b*]thiophene (from 2-vinylbenzo[*b*]thiophene [42]), (*E*)-*N*,*N*-dibenzyl-12-methyltetradec-12-en-1-amine (from *N*,*N*-dibenzyl-10-undecen-1-amine[31]) and (*E*)-2-(4-methylhex-4-en-1-yl)isoindoline-1,3-dione (from 2-allylisoindoline-1,3-dione (Ark Pharm)) were prepared by hydroboration with 9-BBN dimer (Alfa Aesar) followed by cross-coupling with (*E*)-2-bromo-2-butene (Aldrich) in analogy to a reported procedure.[27]

(*Z*)-(3-Methylpent-3-en-1-yl)benzene (from styrene (Aldrich)), (*Z*)-(3-methylpent-3-en-1-yl)ferrocene (from vinylferrocene (Alfa Aesar)), (*Z*)-methyl 7-methylnon-7-enoate (from methyl oct-7-enoate[43]), (*Z*)-benzyl 2-(dibenzylamino)-6-methyloct-6-enoate (from benzyl 2-(dibenzylamino)pent-4-enoate [44]), (*Z*)-4,4,5,5-tetramethyl-2-(3-(3-methylpent-3-en-1-yl)phenyl)-1,3,2-dioxaborolane (from 2-(3-ethenylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Combi-Blocks)), (*Z*)-*tert*-butyl 5-(3-methylpent-3-en-1-yl)-1*H*-indole-1-

(42) Falk, A.; Cavalieri, A.; Nichol, G. S.; Vogt, D.; Schmalz, H. *Adv. Synth. Catal.* **2015**, *357*, 3317–3320.
(43) Yun, J. I.; Kim, H. R.; Kim, S. K.; Kim, D.; Lee, J. *Tetrahedron* **2012**, *68*, 1177–1184.
(44) Rodriquez, M.; Bruno, I.; Cini, E.; Marchetti, M.; Taddei, M.; Gomez-Paloma, L. *J. Org. Chem.* **2006**, *71*, 103–107.

carboxylate (*tert*-butyl 5-vinyl-1*H*-indole-1-carboxylate[45]) and (2*S*,4a*R*,6*S*,7*R*,8*S*,8a*S*)-7-(benzyloxy)-6-(4-methoxyphenoxy)-8-(((*Z*)-4-methylhex-4-en-1-yl)oxy)-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxine (from 4-methoxyphenyl 3-*O*-allyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (TCI America)) were prepared by hydroboration with 9-BBN dimer (Alfa Aesar) followed by cross-coupling with (*Z*)-2-bromo-2-butene (Aldrich) in analogy to a reported procedure.[46]

(*E*)-1-Methoxy-4-(((2-methylbut-2-en-1-yl)oxy)methyl)benzene (from (*E*)-2-methylbut-2-en-1-ol[47]) was prepared in analogy to a reported procedure.[48]

(2*E*,6*E*)-Ethyl 6-methylocta-2,6-dienoate was prepared in analogy to reported procedures.[49]

(*E*)-4-Methoxycinnamyl alcohol was prepared according to a reported procedure.[50]

methyl (*E*)-3-bromopropenoate was prepared according to a reported procedure.[51]

(*Z*)-4,4,5,5-tetramethyl-2-(2-methylhept-2-en-1-yl)-1,3,2-dioxaborolane was prepared as a 93:7 mixture of 1,4- and 1,2-addition product in analogy to a reported procedure.[52]

1-((but-2-en-1-yloxy)methyl)-4-methoxybenzene (95:5 *E*:*Z*) was prepared from crotyl alcohol (95:5 *E*:*Z*, Aldrich) in analogy to a reported procedure.[53]

(*Z*)-but-2-en-2-ylboronic acid was prepared according to a reported procedure.[54]

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(45) Duan, J.; Field, S.; Kobayashi, S. Patent WO2004/063336 A2 (2004).
(46) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314–321.
(47) Hazelden, I. R.; Ma, X.; Langer, T.; Bower, J. F. *Angew. Chem. Int. Ed.* **2016**, *55*, 11198–11202.
(48) Helliwell, M.; Karim, S.; Parmee, E. R.; Thomas, E. J. *Org. Biomol. Chem.* **2005**, *3*, 3636–3653.
(49) (a) Kobayashi, Y.; Yoshida, S.; Nakayama, Y. *Eur. J. Org. Chem.* **2001**, 1873–1881. (b) Gemma, S.; Martí, F.; Gabellieri, E.; Campiani, G.; Novellino, E.; Butini, S. *Tetrahedron Lett.* **2009**, *50*, 5719–5722.
(50) Maeda, H.; Matsuda, S.; Mizuno, K. *J. Org. Chem.* **2016**, *81*, 8544–8551.
(51) Crombie, L.; Horsham, M. A.; Jarret, S. R. M. *J. Chem. Soc. Perkin Trans. 1* **1991**, 1511−1524.
(52) Ely, R. J.; Morken, J. P. *Org. Synth.* **2011**, *88*, 342−352.
(53) Bourque, L. E.; Haile, P. A.; Loy, J. M. N.; Woerpel, K. A. *Tetrahedron* **2009**, *65*, 5608–5613.
(54) Patil, A. S.; Mo, D.; Wang, H.; Mueller, D. S.; Anderson, L. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 7799 – 7803.

(*Z*)-1,2-Dichloroethene (Aldrich), (*E*)-1,2-dichloroethene, (*Z*)-1-bromo-2-fluoroethene (Synquest), (*Z*)-2-butene-1,4-diol (Aldrich), methyl 5-bromovalerate (Aldrich), allylboronic acid pinacol ester (Frontier Scientific), diisobutylaluminum hydride solution (1.0 M in cyclohexane) (Aldrich), 4-bromoindole-3-carboxyaldehyde (Ark-Pharm), 1-propenylmagnesium bromide 0.5 M solution in THF (Aldrich), ethylene oxide 2.5−3.3 M solution in THF (Aldrich), tetrakis(triphenylphosphine)palladium(0) (Strem), dichloro 1,1'-bis(diphenylphosphino)ferrocene palladium (II) dichloromethane (Strem), bis[(pinacolato)boryl]methane (Aldrich), lithium 2,2,6,6-tetramethylpiperidide (Aldrich), dibromoborane dimethyl sulfide complex solution (1.0 M in dichloromethane) (Aldrich), palladium (II) acetate (Strem), di-*tert*-butylmethylphosphine (Aldrich), TEMPO (Aldrich), (diacetoxyiodo)benzene (Oakwood), *tert*-butyllithium solution (1.7 M in pentane) (Aldrich), cesium fluoride (Aldrich), dichloro[bis(2-(diphenylphosphino)phenyl)ether]palladium(II) (Aldrich), (*S*)-propylene oxide (Aldrich), *tert*-butyldimethylsilyl trifluoromethanesulfonate (Aldrich), triethylamine (Aldrich), bis(tri-*tert*-butylphosphine)palladium(0) (Aldrich), copper (I) iodide (Aldrich), 1,4-diazabicyclo[2.2.2]octane (Aldrich), 3,3-diethoxy-1-propyne (Aldrich) and oxalic acid dihydrate (Fisher) were used as received.

4.8.3. Preparation of Organometallic Complexes

Mo-1[25], **Mo-2**[31], **Mo-3**[55] and **Mo-5**[38] were prepared according to previously reported procedures. Mo complexes were manipulated under an atmosphere of N_2 in a glove box. **Ru-1**[56] was prepared according to a previously reported procedure.

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General procedure for *in situ* preparation of Mo-4 for spectroscopic analysis: In a N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with pentafluorophenylimido Mo bispyrrolide complex[57] (16.7 mg, 0.0280 mmol), 4',5'-diphenyl-[1,1':2',1"-terphenyl]-3'-ol[58] (11.2 mg, 0.0280 mmol) and C_6D_6 (1 mL), resulting in a dark red solution. The vial was capped and the mixture was allowed to stir for 2 h at 22 °C, at which time it was transferred to a screw cap NMR tube by a pipette. The NMR tube was capped and sealed with Teflon tape. For *in situ* generated complexes, only the diagnostic α proton signal of the *syn*-alkylidene of **Mo-4** is reported: **^{1}H NMR (500 MHz, C_6D_6)**: δ 12.38 (1H, s).

General procedure for *in situ* preparation of Mo-4 for use in reactions: In a N_2-filled glove box, an oven-dried 4 mL vial equipped with a magnetic stir bar was charged with pentafluorophenylimido Mo bispyrrolide complex (59.8 mg, 0.100 mmol), 4',5'-diphenyl-[1,1':2',1"-terphenyl]-3'-ol (39.9 mg, 0.100 mmol) and C_6H_6 (1 mL), resulting in a dark red solution. The vial was capped and the mixture was allowed to stir for 2 h at 22 °C, after which the catalyst solution was transferred to the reaction mixture by syringe (dried at 65 °C).

4.8.4. Cross-Metathesis (CM) Reactions

General Procedure: In a N_2-filled glove box, an oven-dried 8 mL vial equipped with a magnetic stir bar was charged with trisubstituted alkene substrate and the corresponding disubstituted alkene substrate (*Z*-1,2-dichloroethene, *E*-1,2-dichloroethene, *Z*-1-bromo-2-fluoroethene, (*E*)-5-decene, *tert*-butyldimethyl(pent-3-en-1-yloxy)silane) or (*E*)-1-((but-

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2-en-1-yloxy)methyl)-4-methoxybenzene). A solution of **Mo-1**, **Mo-2**, **Mo-3**, **Mo-4** or **Mo-5** in benzene was then added. The resulting mixture was allowed to stir for 4 h at 22 °C, after which the reaction was quenched by the addition of wet (undistilled) $CDCl_3$ (percent conversion was determined by ^1H NMR analysis of the unpurified mixture). Purification was performed through silica gel chromatography and/or preparative thin layer chromatography.

(*E*)-(4-Chloro-3-methylbut-3-en-1-yl)benzene (4.3): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 10 μL, 1.0 μmol) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (48.5 mg, 0.500 mmol) and (*E*)-(3-methylpent-3-en-1-yl)benzene (16.0 mg, 0.100 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 98% consumption of (*E*)-(3-methylpent-3-en-1-yl)benzene. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **4.3** (14.6 mg, 0.0808 mmol, 81% yield) in 95:5 *E*:*Z* ratio as colorless oil. **IR (neat)**: 3064 (w), 2926 (w), 2855 (w), 1641 (w), 1602 (w), 1454 (m), 1030 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.32–7.26 (2H, m), 7.23–7.18 (1H, m), 7.18–7.14 (2H, m), 5.81–5.78 (1H, m), 2.77–2.71 (2H, m), 2.40–2.34 (2H, m), 1.83 (3H, d, J = 1.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.4, 138.2, 128.6, 128.5, 126.2, 112.8, 39.2, 34.4, 16.8; **HRMS $[M+H]^+$** calcd for $C_{11}H_{14}Cl$: 181.0784, found: 181.0785.

(*E*)-1-(*tert*-Butyl)-4-(1-chloroprop-1-en-2-yl)benzene (4.5): Following the general procedure, a solution of **Mo-1** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*E*)-1-(but-2-en-2-yl)-4-(*tert*-butyl)benzene (9.4 mg, 0.0499 mmol). The resulting

solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*E*)-1-(but-2-en-2-yl)-4-(*tert*-butyl)benzene. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **4.5** (9.4 mg, 0.0450 mmol, 90% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 3034 (w), 2962 (m), 2867 (w), 1620 (w), 1363 (m), 1245 (m), 1114 (m), 985 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.38–7.34 (2H, m), 7.30–7.26 (2H, m), 6.32–6.30 (1H, m), 2.20–2.19 (3H, m), 1.33 (9H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 151.0, 138.4, 137.5, 125.7, 125.6, 115.3, 34.7, 31.4, 16.9; **HRMS [M+H]$^+$** calcd for $C_{13}H_{18}Cl$: 209.1097, found: 209.1102.

(*Z*)-(4-Chloro-3-methylbut-3-en-1-yl)benzene (4.23): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.3 mg, 0.500 mmol) and (*Z*)-(3-methylpent-3-en-1-yl)benzene (8.0 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 98% consumption of (*Z*)-(3-methylpent-3-en-1-yl)benzene. The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **4.23** (7.8 mg, 0.0432 mmol, 86% yield) in 91:9 *Z*:*E* ratio as colorless oil. **IR (neat)**: 3027 (w), 2929 (w), 2859 (w), 1603 (w), 1494 (m), 1433 (m), 1031 (m), 741 (s), 700 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *E*-isomer (major): δ 7.34 –7.14 (5H, m), 5.80 (1H, dt, J = 1.5, 0.7 Hz), 2.79 – 2.68 (2H, m), 2.55 – 2.46 (2H, m), 1.74 (3H, d, J = 1.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.7, 138.2, 128.5, 128.5, 126.1, 112.3, 34.0, 33.2, 21.2.

(*E*)-2-(10-Chloro-9-methyldec-9-en-1-yl)oxirane (4.24): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.3 mg, 0.251 mmol) and (*E*)-2-(9-methylundec-9-en-1-yl)oxirane (10.5 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 83% consumption of starting material. The resulting red oil was purified by silica gel chromatography (1% Et_2O in pentane) to afford **4.24** (6.5 mg, 0.0282 mmol, 56% yield) in 94:6 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2925 (s), 2854 (m), 1460 (w), 771 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.78 (1H, h, J = 1.3 Hz), 2.90 (1H, tdd, J = 5.3, 4.0, 2.7 Hz), 2.75 (1H, dd, J = 5.1, 4.0 Hz), 2.46 (1H, dd, J = 5.1, 2.7 Hz), 2.05 (2H, td, J = 7.4, 1.3 Hz), 1.76 (3H, d, J = 1.3 Hz), 1.59–1.14 (14H, m); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.1, 111.8, 52.5, 47.3, 37.2, 32.6, 29.6, 29.5, 29.4, 29.2, 27.6, 26.1, 16.5; **HRMS $[M+H]^+$** calcd for $C_{14}H_{24}ClO$: 231.1516, found: 231.1514.

(*E*)-1-(((3-Chloro-2-methylallyl)oxy)methyl)-4-methoxybenzene (4.25): Following the general procedure, a solution of **Mo-1** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*E*)-1-methoxy-4-(((2-methylbut-2-en-1-yl)oxy)methyl)benzene (10.3 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting trisubstituted alkene. The resulting orange oil was purified by silica gel chromatography (1% to 2% EtOAc in hexanes) to afford **4.25** (10.3 mg, 0.0454 mmol, 91% yield) in 93:7 *E*:*Z* ratio as pale yellow oil. **IR (neat)**: 3000 (w),

2917 (w), 2853 (w), 1612 (m), 1512 (s), 1245 (s), 1077 (s), 1033 (s), 818 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.25 (2H, d, J = 7.3 Hz), 6.88 (2H, d, J = 8.6 Hz), 6.12–6.09 (1H, m), 3.93 (2H, s), 3.81 (3H, s), 1.82 (3H, d, J = 1.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 136.0, 130.1, 129.5, 115.9, 114.0, 101.2, 72.7, 71.7, 55.4, 14.6.

(2*E*,6*E*)-Ethyl 7-chloro-6-methylhepta-2,6-dienoate (4.26): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (2*E*,6*E*)-ethyl 6-methylocta-2,6-dienoate (9.1 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 85% consumption of (2*E*,6*E*)-ethyl 6-methylocta-2,6-dienoate. The resulting orange oil was purified by silica gel chromatography (2% Et_2O in pentane) to afford **4.26** (6.6 mg, 0.0326 mmol, 65% yield) in 96:4 *E*:*Z* ratio as pale yellow oil. **IR (neat)**: 2917 (w), 2850 (w), 1716 (s), 1654 (m), 1265 (s), 1152 (s), 1041 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 6.90 (1H, dt, J = 15.6, 6.8 Hz), δ 5.86–5.80 (2H, m), 4.19 (2H, q, J = 7.1 Hz), 2.38–2.30 (2H, m), 2.26–2.19 (2H, m), 1.78 (3H, d, J = 1.3 Hz), 1.29 (3H, t, J = 7.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.6, 147.5, 137.3, 122.2, 113.3, 60.4, 35.6, 30.4, 16.6, 14.4; **HRMS $[M+H]^+$** calcd for $C_{10}H_{16}ClO_2$: 203.0839, found: 203.0830.

2-((1*E*,3*E*)-4-Chloro-3-methylbuta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.27): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 500 μL, 50.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (242 mg, 2.50 mmol) and **4.58** (104 mg, 0.500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of

wet $CDCl_3$ and analysis of the unpurified mixture revealed 96% consumption of **19**. The resulting red oil was purified by silica gel chromatography (5% Et_2O in pentane) to afford a mixture of **4.58**, (1'r,3'r)-2,2",4,4",6,6"-hexaethyl-[1,1':3',1"-terphenyl]-2'-ol (protonated aryloxide ligand from Mo-2) and **4.27** (80% by weight accounting for the mass of unreacted **4.58** and terphenol, 133 mg, 0.466 mmol, 93% yield) in 95:5 *E*:*Z* ratio as wet orange solid. **IR (neat)**: 2978 (m), 2929 (w), 1615 (m), 1380 (m), 1340 (s), 1324 (s), 1270 (w), 1200 (w), 1142 (s), 989 (m), 969 (m), 89 (m), 789 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *E*-isomer (major): δ 6.98 (1H, d, J = 18.1 Hz), 6.35 – 6.30 (m, 1H), 5.61 (1H, dd, J = 18.1, 0.7 Hz), 1.89 (3H, d, J = 1.3 Hz), 1.27 (12H, s); *Z*-isomer (resolved signals only): δ 7.57 (1H, d, J = 18.2 Hz), 6.10 – 6.05 (1H, m), 5.74 (1H, dd, J = 18.2, 0.8 Hz), 1.85 (3H, d, J = 1.5 Hz); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.6, 138.4, 123.6, 83.5, 24.9, 12.2; **HRMS [M+H]$^+$** calcd for $C_{11}H_{19}BClO_2$: 229.1167, found: 229.1166.

(*E*)-1-(1-Chloroprop-1-en-2-yl)-3-methoxybenzene (4.28): Following the general procedure, a solution of **Mo-1** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*E*)-1-(but-2-en-2-yl)-3-methoxybenzene (8.1 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 90% consumption of (*E*)-1-(but-2-en-2-yl)-3-methoxybenzene. The resulting orange oil was purified by silica gel chromatography (100% hexanes to 1% EtOAc in hexanes) to afford **4.28** (7.9 mg, 0.0433 mmol, 87% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2953 (m), 2926 (s), 2855 (m), 1601 (m), 1577 (m), 1457 (m), 1263 (s), 1048 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.26–7.26(1H, m), 6.95–6.90 (1H, m), 6.88–6.82 (2H, m), 6.35–6.31(1H, m), 3.82 (3H,

s), 2.19 (3H, d, J = 1.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.6, 129.6, 118.6, 116.1, 113.2, 112.1, 101.2, 55.4, 31.1; **HRMS [M]$^+$** calcd for $C_{10}H_{11}ClO$: 182.0498, found: 182.0495.

***tert*-Butyl (*E*)-5-(1-chloroprop-1-en-2-yl)-1H-indole-1-carboxylate (4.29):** Following the general procedure, a solution of **Mo-1** in benzene (0.1 M, 50 μL, 5.0 μmol) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (24.3 mg, 0.251 mmol) and *tert*-butyl (*E*)-5-(but-2-en-2-yl)-1H-indole-1-carboxylate (13.6 mg, 0.0501 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 91% consumption of *tert*-butyl (*E*)-5-(but-2-en-2-yl)-1H-indole-1-carboxylate. The resulting red oil was purified by preparative thin layer chromatography (2% Et_2O in pentane) to afford **4.29** (13.3 mg, 0.0456 mmol, 91% yield) in >98:2 *E*:*Z* ratio as clear colorless oil. **IR (neat)**: 2977 (w), 2931 (w), 1731 (s), 1486 (m), 1364 (s), 1334 (s), 1231 (s), 1135 (s), 1083 (s), 1022 (s), 782 (m), 764 (m), 724 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *E* isomer (major): δ 8.09 (1H, d, J = 8.7 Hz), 7.60 (1H, d, J = 3.7 Hz), 7.52 (1H, dd, J = 1.9, 0.6 Hz), 7.30 (1H, dd, J = 8.7, 1.9 Hz), 6.56 (1H, dd, J = 3.7, 0.8 Hz), 6.33 (1H, d, J = 1.4 Hz), 2.26 (3H, d, J = 1.4 Hz), 1.68 (9H, s); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.9, 135.2, 130.8, 126.7, 122.5, 118.4, 115.2, 115.1, 107.5, 84.0; **HRMS [M+H]$^+$** calcd for $C_{16}H_{19}ClNO_2$: 292.1104, found: 292.1103.

(*Z*)-1-(*tert*-Butyl)-4-(1-chloroprop-1-en-2-yl)benzene (4.30): Following the general procedure, a solution of **Mo-1** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.3 mg, 0.251 mmol) and (*Z*)-1-(*tert*-butyl)-4-(1-chloroprop-1-en-2-yl)benzene (9.4 mg, 0.0500 mmol). The

resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 86% consumption of starting material. The resulting red oil was purified by silica chromatography (100% hexanes) to afford **4.30** (6.8 mg, 0.0326 mmol, 65% yield) in >98:2 *Z*:*E* ratio as clear colorless oil. **IR (neat)**: 2962 (m), 2868 (w), 1509 (m), 1463 (w), 1438 (w), 1400 (w), 1363 (m), 1269 (m), 1114 (m), 1014 (m), 838 (s), 788 (m), 587 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.42–7.38 (2H, m), 7.36–7.32 (2H, m), 6.10 (1H, q, J = 1.6 Hz), 2.09 (3H, d, J = 1.6 Hz), 1.34 (9H, s); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.7, 137.8, 135.7, 127.7, 125.2, 112.3, 34.8, 31.5, 23.5; **HRMS $[M+H]^+$** calcd for $C_{13}H_{18}Cl$: 209.1097, found: 209.1099.

(*Z*)-Methyl 8-chloro-7-methyloct-7-enoate (4.31): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*Z*)-methyl 7-methylnon-7-enoate (9.2 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 94% consumption of (*Z*)-methyl 7-methylnon-7-enoate. The resulting orange oil was purified by silica gel chromatography (1.5% to 3% EtOAc in hexanes) to afford **4.31** (9.1 mg, 0.0445 mmol, 89% yield) in 88:12 *Z*:*E* ratio as colorless oil. **IR (neat)**: 2936 (m), 2860 (w), 1736 (s), 1436 (m), 1196 (m), 1170 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 5.77 (1H, s), 3.67 (3H, s), 2.32 (2H, t, J = 7.5 Hz), 2.24–2.17 (2H, m), 1.72 (3H, d, J = 1.5 Hz), 1.68–1.61 (2H, m), 1.49–1.39 (2H, m), 1.39–1.29 (2H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 174.3, 138.7, 111.7, 51.6, 34.2,

31.7, 28.9, 26.5, 24.9, 20.9; **HRMS [M+H]$^+$** calcd for $C_{10}H_{18}ClO_2$: 205.0995, found: 205.0985.

(*Z*)-(4-Chloro-3-methylbut-3-en-1-yl)ferrocene (4.32): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 15 μL, 1.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*Z*)-(3-methylpent-3-en-1-yl)ferrocene (13.4 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 96% consumption of (*Z*)-(3-methylpent-3-en-1-yl)ferrocene. The resulting red oil was purified by silica gel chromatography (100% hexanes to 1% EtOAc in hexanes) to afford **4.32** (13.6 mg, 0.0471 mmol, 94% yield) in 88:12 *Z*:*E* ratio as orange oil. **IR (neat)**: 3093 (w), 2926 (w), 2854 (w), 1639 (w), 1444 (w), 1105 (m), 1000 (m), 816 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 5.80 (1H, q, *J* = 1.5 Hz), 4.13 (5H, s), 4.10 (2H, dd, *J* = 3.6, 2.5 Hz), 4.06 (2H, dd, *J* = 3.5, 1.7 Hz), 2.45 (4H, brs), 1.75 (3H, d, *J* = 1.6 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.6, 111.8, 88.7, 68.7, 68.0, 67.3, 33.4, 26.8, 21.3; **HRMS [M+H]$^+$** calcd for $C_{15}H_{18}ClFe$: 289.0446, found: 289.0451.

(*Z*)-2-(3-Chloro-2-methylallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.33): Following the general procedure, a solution of **Mo-1** in benzene (0.1 M, 50 μL, 5.0 μmol) was transferred by syringe to an oven-dried vial containing *E*-1,2-dichloroethene (48.5 mg, 0.500 mmol) and (*Z*)-4,4,5,5-tetramethyl-2-(2-methylhept-2-en-1-yl)-1,3,2-dioxaborolane (93% wt, 25.6 mg, 0.100 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of starting trisubstituted alkene. The

resulting red oil was purified by silica gel chromatography (2% Et_2O in pentane with silica gel dried at 140 °C for 12 h) to afford **4.33** (18.0 mg, 0.0831 mmol, 83% yield) in 95:5 *Z*:*E* ratio as clear colorless oil. **IR (neat)**: 2978 (m), 2931 (w), 1324 (s), 1142 (s), 967 (m), 846 (m), 770 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.75 (1H, qt, *J* = 1.6, 0.9 Hz), 1.86 (2H, s), 1.79 (3H, d, *J* = 1.6 Hz), 1.25 (12H, s); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.3, 110.5, 83.6, 24.8, 23.1; **HRMS $[M+NH_4]^+$** calcd for $C_{10}H_{22}BClO_2N$: 234.1432, found: 234.1421.

(*Z*)-Benzyl 7-chloro-2-(dibenzylamino)-6-methylhept-6-enoate (4.34): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*Z*)-benzyl 2-(dibenzylamino)-6-methyloct-6-enoate (22.1 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-benzyl 2-(dibenzylamino)-6-methyloct-6-enoate. The resulting orange oil was purified by preparative thin layer chromatography (5% EtOAc in hexanes) to afford **4.34** (20.6 mg, 0.0446 mmol, 89% yield) in 86:14 *Z*:*E* ratio as colorless oil. **IR (neat)**: 3030 (w), 2922 (w), 2851 (w), 1728 (m), 1453 (w), 1143 (m), 964 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.44–7.34 (5H, m), 7.33–7.26 (8H, m), 7.25–7.19 (2H, m), 5.77–5.71 (1H, m), 5.26 (1H, d, *J* = 12.3 Hz), 5.16 (1H, d, *J* = 12.3 Hz), 3.91 (2H, d, *J* = 13.9 Hz), 3.52 (2H, d, *J* = 13.9 Hz), 3.40–3.35 (1H, m), 2.16–2.01 (2H, m), 1.80–1.70 (2H, m), 1.64 (3H, d, *J* = 1.5 Hz), 1.61–1.53 (1H, m), 1.39–1.30 (1H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.0, 139.7, 138.4, 136.3, 129.0, 128.7, 128.6,

128.4, 128.4, 127.1, 112.0, 66.1, 60.9, 54.7, 31.5, 29.2, 23.5, 20.9; **HRMS [M+H]$^+$** calcd for $C_{29}H_{33}ClNO_2$: 462.2200, found: 462.2203.

***tert*-Butyl (*Z*)-5-(4-chloro-3-methylbut-3-en-1-yl)-1*H*-indole-1-carboxylate (4.35):** Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 10 μL, 1.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.3 mg, 0.251 mmol) and *tert*-butyl (*Z*)-5-(3-methylpent-3-en-1-yl)-1H-indole-1-carboxylate (15.0 mg, 0.0501 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 82% consumption of *tert*-butyl (*Z*)-5-(3-methylpent-3-en-1-yl)-1H-indole-1-carboxylate. The resulting red oil was purified by preparative thin layer chromatography (2% Et_2O in pentane) to afford **4.35** (12.5 mg, 0.0391 mmol, 78% yield) in 87:13 *Z*:*E* ratio as clear colorless oil. **IR (neat)**: 2976 (w), 2931 (w), 1708 (s), 1610 (m), 1439 (m), 1369 (m), 1341 (m), 1288 (m), 1251 (m), 1146 (s), 764 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 8.06 (1H, s), 7.54 (1H, d, J = 3.8 Hz), 7.47 (1H, dd, J = 8.0, 0.6 Hz), 7.12 (1H, dd, J = 8.0, 1.5 Hz), 6.53 (1H, dd, J = 3.8, 0.8 Hz), 5.85–5.76 (1H, m), 2.90–2.80 (2H, m), 2.62–2.50 (2H, m), 1.77 (3H, d, J = 1.5 Hz), 1.68 (9H, s); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.4, 138.2, 128.9, 125.7, 123.6, 120.8, 115.0, 112.2, 107.3, 83.7, 34.7, 33.8, 28.4, 21.3; **HRMS [M+H]$^+$** calcd for $C_{18}H_{23}ClNO_2$: 320.1417, found: 320.1416.

(*E*)-(4-Bromo-3-methylbut-3-en-1-yl)benzene (4.44): Following the general procedure, a solution of Mo-2 in benzene (0.1 M, 10 μL, 1.0 μmol) was transferred by syringe to an oven-dried vial containing Z-1-bromo-2-fluoroethene (62.5 mg, 0.500 mmol) and (*E*)-(3-methylpent-3-en-1-yl)benzene (16.0 mg, 0.100 mmol). The resulting solution was

allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet CDCl3 and analysis of the unpurified mixture revealed 95% consumption of (E)-(3-methylpent-3-en-1-yl)benzene that resulted in the formation of a mixture of Br- and F-alkenes (95:5 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (100% pentane) to afford **4.44** (20.3 mg, 0.0902 mmol, 90% yield) in >98:2 E:Z ratio as colorless oil. The spectral data for this compound were consistent with those reported in the literature.[59]

(*Z*)-(4-bromo-3-methylbut-3-en-1-yl)benzene (4.46): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.2 mg, 0.250 mmol) and (*Z*)-(3-methylpent-3-en-1-yl)benzene (8.0 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-(3-methylpent-3-en-1-yl)benzene that resulted in the formation of a mixture of Br- and F-alkenes (83:17 bromo:fluoro). The resulting red oil was purified by silica gel chromatography (1% Et_2O in pentane) to afford **4.46** (7.5 mg, 0.0.333 mmol, 66% yield) in 95:5 *Z*:*E* ratio as clear colorless oil. The spectral data for this compound were consistent with those reported in the literature.[60]

(*E*)-*N*,*N*-Dibenzyl-13-bromo-12-methyltridec-12-en-1-amine (4.47): Based on the general procedure, a solution of Mo-2 in benzene (0.1 M, 10 μL, 1.0 μmol) was transferred by syringe to an oven-dried vial containing Z-1-bromo-2-fluoroethene (31.2 mg, 0.250 mmol) and (E)-N,N-dibenzyl-12-methyltetradec-12-en-1-amine (20.3 mg,

(59) Stoermer, M. J.; Pinhey, J. T. *Molecules* **1998**, *3*, M58.
(60) Stoermer, M. J.; Pinhey, J. T. *Molecules* **1998**, *3*, M57.

0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*E*)-*N*,*N*-dibenzyl-12-methyltetradec-12-en-1-amine that resulted in the formation of a mixture of Br- and F-alkenes (93:7 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (100% hexanes to 1% EtOAc in hexanes) to afford **4.47** (21.2 mg, 0.0451 mmol, 90% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2924 (m), 2852 (w), 1452 (w), 1264 (m), 1028 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.38–7.35 (4H, m), 7.32–7.28 (4H, m), 7.25–7.20 (2H, m), 5.88 (1H, dd, J = 2.5, 1.2 Hz), 3.55 (4H, s), 2.42–2.38 (2H, m), 2.12–2.07 (2H, m), 1.78 (3H, d, J = 1.2 Hz), 1.55–1.46 (2H, m), 1.45–1.37 (2H, m), 1.28–1.20 (14H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 142.2, 140.3, 128.9, 128.2, 126.8, 101.0, 58.4, 53.6, 38.5, 29.8, 29.7, 29.7, 29.6, 29.6, 29.2, 27.7, 27.4, 27.2, 19.2; **HRMS [M+H]$^+$** calcd for $C_{28}H_{41}BrN$: 470.2422, found: 470.2445.

(*E*)-2-(4-Bromo-3-methylbut-3-en-1-yl)benzo[*b*]thiophene (4.48): Based on the general procedure, a solution of **Mo-2** in benzene (0.1 M, 10 μL, 1.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.2 mg, 0.250 mmol) and (*E*)-2-(3-methylpent-3-en-1-yl)benzo[*b*]thiophene (10.8 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*E*)-2-(3-methylpent-3-en-1-yl)benzo[*b*]thiophene that resulted in the formation of a mixture of Br- and F-alkenes (97:3 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (100% hexanes to 0.5% EtOAc/hexanes) to afford **4.48** (13.4 mg, 0.0477 mmol, 95% yield) in >98:2 *E*:*Z* ratio as white solid. M.p.

76–78 °C; **IR (neat)**: 3058 (w), 2922 (w), 2850 (w), 1632 (w), 1436 (m), 1264 (w), 822 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.76 (1H, d, J = 7.8 Hz), 7.67 (1H, d, J = 7.6 Hz), 7.33–7.26 (2H, m), 7.00 (1H, s), 6.02–5.95 (1H, m), 3.07–3.01 (2H, m), 2.59–2.52 (2H, m), 1.87 (3H, d, J = 1.2 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.9, 140.4, 140.2, 139.5, 124.3, 123.8, 123.0, 122.3, 121.1, 102.8, 39.8, 29.2, 19.3; **HRMS $[M+H]^+$** calcd for $C_{13}H_{14}BrS$: 281.0000, found: 280.9999.

(*E*)-2-(5-Bromo-4-methylpent-4-en-1-yl)isoindoline-1,3-dione (4.49): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.3 mg, 0.251 mmol), (*E*)-2-(4-methylhex-4-en-1-yl)isoindoline-1,3-dione (12.2 mg, 0.0501 mmol) and toluene (75 μL). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*E*)-2-(4-methylhex-4-en-1-yl)isoindoline-1,3-dione that resulted in the formation of a mixture of Br- and F-alkenes (92:8 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (1.5% to 5% EtOAc in hexanes) to afford **4.49** (12.9 mg, 0.0419 mmol, 84% yield) in >98:2 *E*:*Z* ratio as pale yellow solid. M.p. 78–80 °C; **IR (neat)**: 2928 (w), 2853 (w), 1771 (w), 1705 (s), 1395 (m), 1369 (w), 1083 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.85 (2H, dd, J = 5.4, 3.1 Hz), 7.72 (2H, dd, J = 5.5, 3.0 Hz), 5.96 (1H, d, J = 1.2 Hz), 3.70–3.64 (2H, m), 2.18 (2H, t, J = 7.6 Hz), 1.87–1.81 (2H, m), 1.79 (3H, d, J = 1.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 168.5, 140.5, 134.1, 132.2, 123.4, 102.2, 37.6, 35.7, 26.4, 19.1; **HRMS $[M+H]^+$** calcd for $C_{14}H_{15}BrNO_2$: 308.0286, found: 308.0283.

(*Z*)-2-(3-(4-Bromo-3-methylbut-3-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.50): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 10 μL, 1.0 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.2 mg, 0.250 mmol) and (*Z*)-4,4,5,5-tetramethyl-2-(3-(3-methylpent-3-en-1-yl)phenyl)-1,3,2-dioxaborolane (14.3 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*Z*)-4,4,5,5-tetramethyl-2-(3-(3-methylpent-3-en-1-yl)phenyl)-1,3,2-dioxaborolane that resulted in the formation of a mixture of Br- and F-alkenes (86:14 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (100% hexanes to 1% EtOAc in hexanes) to afford **4.50** (12.8 mg, 0.0365 mmol, 73% yield) in 91:9 *Z*:*E* ratio as colorless oil. **IR (neat)**: 2977 (w), 2928 (w), 2859 (w), 1426 (w), 1359 (s), 1320 (m), 1144 (s), 1078 (w); **^{1}H NMR (400 MHz, $CDCl_3$)**: *E* isomer (major):δ 7.69–7.63 (2H, m), 7.36–7.28 (2H, m), 5.90 (1H, s), 2.74 (2H, dd, J = 9.8, 6.7 Hz), 2.51 (2H, dd, J = 9.9, 6.5 Hz), 1.79 (3H, dd, J = 1.5, 0.8 Hz), 1.35 (12H, s); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.2, 140.9, 134.8, 132.7, 131.5, 128.0, 101.4, 83.9, 36.6, 33.1, 25.0, 22.5; **HRMS [M+H]$^+$** calcd for $C_{17}H_{25}BBrO_2$: 351.1131, found: 351.1140.

(2*S*,4a*R*,6*S*,7*R*,8*S*,8a*S*)-7-(Benzyloxy)-8-(((*Z*)-5-bromo-4-methylpent-4-en-1-yl)oxy)-6-(4-methoxyphenoxy)-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxine (4.51): Based on the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.2 mg, 0.250 mmol), (2*S*,4a*R*,6*S*,7*R*,8*S*,8a*S*)-7-(benzyloxy)-6-(4-methoxyphenoxy)-8-(((*Z*)-4-methylhex-4-en-1-yl)oxy)-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxine (28.0 mg,

0.0499 mmol) and benzene (175 μL). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (2*S*,4a*R*,6*S*,7*R*,8*S*,8a*S*)-7-(benzyloxy)-6-(4-methoxyphenoxy)-8-(((*Z*)-4-methylhex-4-en-1-yl)oxy)-2-phenylhexahydropyrano[3,2-*d*][1,3]dioxine that resulted in the formation of a mixture of Br- and F-alkenes (89:11 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (10% to 20% EtOAc in hexanes) to afford **4.51** (25.6 mg, 0.0409 mmol, 82% yield) in 93:7 *Z*:*E* ratio as white solid. M.p. 140–142 °C; **IR (neat)**: 2922 (w), 2856 (w), 1509 (s), 1226 (s), 1078 (s), 1064 (s), 1028 (s), 1007 (s), 823 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: *E* isomer (major):*δ* 7.57 (2H, dd, *J* = 7.6, 1.7 Hz), 7.41–7.26 (8H, m), 7.07 (2H, d, *J* = 9.0 Hz), 6.82 (2H, d, *J* = 9.0 Hz), 5.85 (1H, s), 5.58 (1H, s), 4.97 (1H, d, *J* = 10.9 Hz), 4.90 (1H, dd, *J* = 7.8, 1.4 Hz), 4.85 (1H, d, *J* = 11.0 Hz), 4.37 (1H, d, *J* = 12.3 Hz), 4.32 (1H, d, *J* = 3.1 Hz), 4.09 (1H, dd, *J* = 12.3, 1.6 Hz), 4.02 (1H, dd, *J* = 9.6, 7.9 Hz), 3.78 (3H, s), 3.76–3.68 (1H, m), 3.68–3.60 (1H, m), 3.57–3.50 (1H, m), 3.48 (1H, s), 2.29–2.22 (2H, m), 1.83–1.76 (2H, m), 1.75 (3H, d, *J* = 1.4 Hz); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 155.5, 151.8, 141.4, 138.9, 138.0, 129.1, 128.4, 128.3, 128.2, 127.7, 127.0, 119.2, 114.6, 103.4, 101.5, 101.1, 80.4, 78.1, 75.5, 73.8, 70.1, 69.4, 66.8, 55.8, 31.2, 27.4, 22.3; **HRMS [M+Na]$^+$** calcd for $C_{33}H_{37}BrO_7Na$: 647.1620, found: 647.1640.

2-((1*E*,4*E*)-5-Chloro-4-methylpenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.64): Following the general procedure, a solution of **Mo-2** in benzene (0.1 M, 75 μL, 7.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (73 mg, 0.75 mmol) and **4.63** (55.5 mg, 0.250 mmol). The resulting

solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 98% consumption of **4.63**. The resulting red oil was purified by SiO_2 gel chromatography (5% Et_2O in pentane) to afford **4.64** (35.7 mg, 0.147 mmol, 59% yield) in 97:3 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2978 (m), 1636 (m), 1358 (s), 1321 (s), 1142 (s), 970 (m), 846 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 6.53 (1H, dt, J = 17.9, 6.5 Hz), 5.84 (1H, q, J = 1.3 Hz), 5.48 (1H, dt, J = 17.9, 1.5 Hz), 2.88 (2H, dt, J = 6.5, 1.5 Hz), 1.77 (3H, d, J = 1.4 Hz), 1.26 (12H, s); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.8, 136.4, 113.8, 83.4, 43.3, 24.9, 16.9; **HRMS [M+H]$^+$** calcd for $C_{12}H_{21}BClO_2$: 243.1323, found: 243.1324.

(*E*)-(5-(Chloromethylene)octyl)benzene (4.72): Based on the general procedure, a solution of **Mo-1** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1,2-dichloroethene (24.2 mg, 0.250 mmol) and (*E*)-(5-propylnon-5-en-1-yl)benzene (12.2 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed >98% consumption of (*E*)-(5-propylnon-5-en-1-yl)benzene. The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **4.72** (10.8 mg, 0.0456 mmol, 91% yield) in 82:18 *E*:*Z* ratio as colorless oil. **IR (neat)**: 3053 (w), 2932 (w), 2860 (w), 1454 (w), 1264 (m), 909 (w); **^{1}H NMR (600 MHz, $CDCl_3$)**: *E* isomer (major):δ 7.28 (2H, t, J = 7.5 Hz), 7.19 (1H, d, J = 7.3 Hz), 7.17 (2H, d, J = 7.4 Hz), 5.78 (1H, s), 2.63–2.59 (2H, m), 2.19–2.15 (2H, m), 2.08 (2H, t, J = 7.6 Hz), 1.61 (2H, dt, J = 15.4, 7.7 Hz), 1.48–1.41 (4H, m), 0.92 (3H, t, J = 7.4 Hz); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 142.7, 142.5, 128.5, 128.4, 125.9, 112.2,

35.9, 34.8, 32.2, 31.2, 27.4, 20.5, 14.1; **HRMS [M+H]$^+$** calcd for $C_{15}H_{22}Cl$: 237.1410, found: 237.1422.

(*E*)-(5-(Bromomethylene)octyl)benzene (4.73): Based on the general procedure, a solution of **Mo-2** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing *Z*-1-bromo-2-fluoroethene (31.2 mg, 0.250 mmol) and (*E*)-(5-propylnon-5-en-1-yl)benzene (12.2 mg, 0.0499 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 89% consumption of (*E*)-(5-propylnon-5-en-1-yl)benzene that resulted in the formation of a mixture of Br- and F-alkenes (92:8 bromo:fluoro). The resulting orange oil was purified by silica gel chromatography (100% hexanes) to afford **4.73** (11.2 mg, 0.0398 mmol, 80% yield) in 81:19 *E*:*Z* ratio as colorless oil. **IR (neat)**: 3026 (w), 2958 (w), 2930 (m), 2858 (w), 1454 (m), 1230 (w), 909 (w); **^{1}H NMR (500 MHz, $CDCl_3$)**: *E* isomer (major): δ 7.28 (2H, t, J = 7.4 Hz), 7.19 (1H, d, J = 7.5 Hz), 7.17 (2H, d, J = 7.4 Hz), 5.87 (1H, s), 2.61 (2H, t, J = 7.7 Hz), 2.20–2.14 (2H, m), 2.12 (2H, t, J = 7.6 Hz), 1.61 (2H, dt, J = 15.4, 7.6 Hz), 1.51–1.40 (4H, m), 0.93 (3H, t, J = 7.4 Hz); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 145.6, 142.5, 128.5, 128.4, 125.9, 101.4, 36.0, 35.9, 34.6, 31.1, 27.4, 20.5, 14.1; **HRMS [M+H]$^+$** calcd for $C_{15}H_{22}Br$: 281.0905, found: 281.0913.

***tert*-Butyldimethyl(pent-3-en-1-yloxy)silane (4.74)**: A solution of 1-propenylmagnesium bromide in THF (0.5 M, 12 mL, 6.00 mmol) was added slowly to a solution of ethylene oxide in THF (2.5−3.3 M, 2.0 mL) at 0 °C. The resulting solution was allowed to stir for 2 h at 22 °C, after which the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (2.0 mL). The aqueous layer was

washed with Et_2O (3 x 5 mL), the combined organic layers were dried over $MgSO_4$ and volatiles were removed by rotary evaporator in an ice bath at 60 torr to obtain crude pent-3-en-1-ol. The resulting yellow oil was sufficiently clean and used in the next step without further purification.

TBSCl (0.90 g, 5.97 mmol) was added in one portion to a solution of pent-3-en-1-ol from above and imidazole (0.45 g, 6.61) in 6 mL of CH_2Cl_2 at 0 °C. The resulting mixture was allowed to stir for 1 h at 22 °C. The reaction mixture was diluted with pentane (10 mL) then filtered through a pad of celite, and volatiles were removed in vacuo. The resulting slightly yellow oil was purified by silica gel chromatography (5% Et_2O in hexanes) to afford **4.74** (595 mg, 2.97, 60% yield over 2 steps) in 61:39 *E*:*Z* ratio as colorless oil. The spectral data for this compound were consistent with those reported previously.[61]

(*E*)-*tert*-Butyldimethyl((4-methyl-6-phenylhex-3-en-1-yl)oxy)silane (4.75): Following the general procedure, a solution of **Mo-3** in benzene (0.1 M, 15 μL, 1.5 μmol)was transferred by syringe to an oven-dried vial containing *tert*-butyldimethyl(pent-3-en-1-yloxy)silane (61:39 *E*:*Z* mixture, 30.0 mg, 0.150 mmol) and (*E*)-(3-methylpent-3-en-1-yl)benzene (8.0 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 40 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 58% consumption of (*E*)-(3-methylpent-3-en-1-yl)benzene. The resulting red oil was purified by silica gel chromatography (1% to 2% Et_2O in hexanes) to afford **4.75** (7.9 mg, 0.0259 mmol, 52% yield) in 93:7 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2926 (s), 2855 (s), 1462 (m), 1381 (m), 1252 (s), 1090 (s), 833 (s), 774 (s), 734 (s), 697 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.31–7.23 (2H, m), 7.21–7.14 (3H, m),

(61) Wang, Y.; Qin, C.; Jia, X.; Leng, X.; Huang, Z. *Angew. Chem. Int. Ed.* **2017**, *56*, 1614 –1618.

5.14 (1H, ddd, J = 8.7, 5.9, 1.4 Hz), 3.55 (2H, t, J = 7.2 Hz), 2.75–2.63 (2H, m), 2.33–2.17 (4H, m), 1.67 (3H, s), 0.90 (9H, s), 0.06 (6H, s); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.6, 136.7, 128.5, 128.4, 125.8, 121.0, 63.2, 41.9, 34.9, 32.0, 30.0, 26.1, 18.6, 16.4, -5.1; **HRMS $[M+NH_4]^+$** calcd for $C_{19}H_{36}ONSi$: 322.2566, found: 322.2555.

(*E*)-(3-Methyloct-3-en-1-yl)benzene (4.76): Following the general procedure, a solution of **Mo-3** in benzene (0.1 M, 30 μL, 3.0 μmol) was transferred by syringe to an oven-dried vial containing (*E*)-5-decene (42.1 mg, 0.300 mmol) and (*E*)-(3-methylpent-3-en-1-yl)benzene (16.0 mg, 0.100 mmol). The resulting solution was allowed to stir for 4 h at 40 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 71% consumption of (*E*)-(3-methylpent-3-en-1-yl)benzene. The resulting red oil was purified by silica gel chromatography (100% hexanes) to afford **4.76** (14.0 mg, 0.0692 mmol, 69% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 3026 (w), 2955 (s), 2924 (s), 2855 (m), 1602 (w), 1494 (m), 1426 (m), 1378 (w), 741 (m), 696 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.31–7.15 (5H, m), 5.15 (1H, tq, J = 7.2, 1.4 Hz), 2.84–2.51 (2H, m), 2.34–2.12 (2H, m), 1.99 (2H, q, J = 6.8 Hz), 1.66 (3H, s), 1.33–1.25 (4H, m), 0.97–0.78 (3H, m); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.7, 134.4, 128.5, 128.3, 125.7, 125.5, 41.8, 34.9, 32.1, 27.8, 22.5, 16.2, 14.2; **HRMS $[M+H]^+$** calcd for $C_{15}H_{23}$: 203.1800, found: 203.1796.

(*Z*)-(3-Methyloct-3-en-1-yl)benzene (4.77): Following the general procedure, a solution of **Mo-5** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing (*E*)-5-decene (21.0 mg, 0.150 mmol) and (*Z*)-(3-methylpent-3-en-1-yl)benzene (8.0 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the

unpurified mixture revealed 65% consumption of (*Z*)-(3-methylpent-3-en-1-yl)benzene. The resulting red oil was purified by silica gel chromatography (100% hexanes) to afford **4.77** (6.5 mg, 0.0321 mmol, 64% yield) in 84:16 *Z*:*E* ratio as colorless oil. **IR (neat):** 2957 (s), 2925 (s), 2857 (s), 1494 (m), 1453 (m), 1376 (w), 966 (m), 741 (m), 696 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.35–7.09 (5H, m), 5.24–5.05 (1H, m), 2.67 (2H, dd, *J* = 9.3, 6.8 Hz), 2.32 (2H, dd, *J* = 9.3, 6.9 Hz), 1.90 (2H, q, *J* = 7.2 Hz), 1.79–1.70 (3H, m), 1.37–1.14 (4H, m), 0.87 (3H, t, *J* = 7.0 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.6, 134.3, 128.5, 128.4, 126.4, 125.9, 34.7, 34.2, 32.3, 27.6, 23.6, 22.6, 14.2; **HRMS [M+H]$^+$** calcd for $C_{15}H_{23}$: 203.1800, found: 203.1804.

(*Z*)-1-Methoxy-4-(((3-methyl-5-phenylpent-2-en-1-yl)oxy)methyl)benzene (4.79): Following the general procedure, a solution of **Mo-5** in benzene (0.1 M, 25 μL, 2.5 μmol) was transferred by syringe to an oven-dried vial containing 1-((but-2-en-1-yloxy)methyl)-4-methoxybenzene (95:5 *E*:*Z* mixture, 19.2 mg, 0.100 mmol) and (*Z*)-(3-methylpent-3-en-1-yl)benzene (8.0 mg, 0.0500 mmol). The resulting solution was allowed to stir for 4 h at 40 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 56% consumption of (*Z*)-(3-methylpent-3-en-1-yl)benzene. The resulting red oil was purified by silica gel chromatography (2% to 5% EtOAc in hexanes) to afford **4.79** (6.1 mg, 0.0206 mmol, 41% yield) in 84:16 *Z*:*E* ratio as colorless oil. **IR (neat):** 2931 (w), 2854 (w), 1611 (m), 1511 (s), 1452 (m), 1301 (m), 1245 (s), 1172 (m), 1033 (s), 817 (s), 744 (s), 698 (s); **^{1}H NMR (500 MHz, $CDCl_3$)**: *Z* isomer (major): δ 7.31–7.08 (7H, m), 6.91–6.83 (2H, m), 5.45–5.38 (1H, m), 4.37 (2H, s), 3.85–3.77 (5H, m), 2.71–2.63 (2H, m), 2.33 (2H, dd, *J* = 9.1, 6.9 Hz), 1.80 (3H, q, *J* = 1.1 Hz); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.3, 142.0, 139.9, 130.9, 129.6, 128.5, 128.4, 126.0,

122.6, 113.9, 71.9, 66.0, 55.4, 34.7, 34.5, 23.7; **HRMS [M+NH$_4$]$^+$** calcd for $C_{20}H_{28}O_2N$: 314.2120, found: 314.2111.

4.8.5. Synthesis of Indiacen B

4,4,5,5-Tetramethyl-2-((1*E*,3*E*)-3-methylpenta-1,3-dien-1-yl)-1,3,2-dioxaborolane (4.58): In analogy to a previously reported procedure[28], **4.58**was prepared by a boron-Wittig reaction with LiTMP (347 mg, 2.36 mmol), bis[(pinacolato)boryl]methane (600 mg, 2.36 mmol, 1.20 equiv) and trans-2-methyl-2-butenal (0.19 mL, 1.97 mmol) and 10 mL THF. The resulting yellow oil was purified by silica gel chromatography (5% EtOAc in hexanes) to obtain **4.58** (384 mg, 1.85 mmol, 89% yield) in >98:2 *E*:*Z* ratio as clear colorless oil. The spectral data for this compound were consistent with those reported previously.[62]

Indiacen B: An oven-dried 2-dram vial was charged with **4.27** (80% wt, 24.3 mg, 0.110 mmol), 4-bromoindole-3-carboxyaldehyde (22.4 mg, 0.100 mmol), Pd(PPh$_3$)$_4$ (5.8 mg, 0.00502 mmol), an aqueous solution of Na_2CO_3 (2.0 M, 0.15 mL, 0.300 mmol) and 2.0 mL of DME. The vial was sealed with a Teflon-lined screw cap and the resulting mixture was allowed to stir at 10 °C for 12 h, filtered through a short plug of celite, and concentrated *in vacuo*. The resulting yellow oil was purified by preparative thin layer chromatography (50% EtOAc in hexanes) to obtain a mixture of pinacol and indiacen B (90% by weight accounting for the mass of pinacol, 17.7 mg, 0.0647 mmol, 65% yield) in 96:4 *E*:*Z* ratio at the chloro-alkene site. The spectral data for this compound were consistent with those reported before.[30]

4.8.6. Synthesis of (±)-Coibacin D

(62) Coombs, J. R.; Zhang, L.; Morken, J. P. *Org. Lett.* **2015**, *11*, 1708–1711.

1-Methoxy-4-((1*E*,4*E*)-4-methylhexa-1,4-dien-1-yl)benzene (4.62): In analogy to a previously reported procedure[35], an oven-dried 6-dram vial was charged with (*E*)-4-methoxycinnamyl alcohol (493 mg, 3.00 mmol), (*Z*)-but-2-en-2-ylboronic acid (360 mg, 3.60 mmol), $Pd(PPh_3)_4$ (35 mg, 0.0303 mmol) and 9.0 mL of THF. The vial was sealed with a Teflon-lined screw cap and the resulting mixture was allowed to stir at 80 °C for 12 h, filtered through a short plug of celite rising with Et_2O, and concentrated *in vacuo*. The resulting clear brown oil was purified by silica chromatography (5% EtOAc in hexanes) to obtain **4.62** (532 mg, 2.63 mmol, 88% yield) as a single stereoisomer. **IR (neat):** 2912 (w), 2834 (w), 1607 (m), 1509 (s), 1294 (m), 1243 (s), 1173 (m), 1035 (m), 964 (m), 827 (m); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.33–7.26 (2H, m), 6.87–6.79 (2H, m), 6.33 (1H, dt, J = 15.7, 1.5 Hz), 6.05 (1H, dt, J = 15.7, 7.1 Hz), 5.30 (1H, dddq, J = 7.8, 6.5, 5.2, 1.3 Hz), 3.80 (3H, s), 2.84 (2H, dq, J = 7.1, 1.3 Hz), 1.66–1.58 (6H, m); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.8, 134.8, 130.7, 130.4, 127.2, 127.0, 119.6, 114.0, 55.4, 43.3, 16.0, 13.6; **HRMS $[M+H]^+$** calcd for $C_{14}H_{19}O$: 203.1436, found: 203.1438.

4,4,5,5-Tetramethyl-2-((1*E*,4*E*)-4-methylhexa-1,4-dien-1-yl)-1,3,2-dioxaborolane (4.63): A solution of **Mo-3** in benzene (0.1 M, 30 μL, 3.0 μmol was transferred by syringe to an oven-dried vial containing vinylboronic acid pinacol ester (30.8 mg, 0.200 mmol) and **4.62** (20.2 mg, 0.100 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet $CDCl_3$ and analysis of the unpurified mixture revealed 82% consumption of **4.62**. The resulting red oil was purified by silica gel chromatography (1% Et_2O in pentane) to afford **4.63** (14.5 mg, 0.0653 mmol, 65% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2977 (m), 2928 (w), 1635 (m), 1356 (s), 1316 (s), 1143 (s), 970 (m), 849 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ

6.59 (1H, dt, J = 17.9, 6.6 Hz), 5.43 (1H, dt, J = 17.9, 1.6 Hz), 5.24 (1H, dddd, J = 7.9, 6.6, 5.4, 1.3 Hz), 2.80 (2H, dq, J = 6.6, 1.3 Hz), 1.61–1.53 (6H, m), 1.26 (12H, s); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 152.59, 133.43, 120.45, 83.15, 46.29, 24.93, 16.00, 13.57; **HRMS $[M+H]^+$** calcd for $C_{13}H_{24}BO_2$: 223.1869, found: 223.1879.

8-Bromooct-1-en-4-ol (4.65): An oven-dried round-bottom flask equipped with a magnetic stir bar was charged with methyl 5-bromovalerate (0.956 g, 4.90 mmol) and Et_2O (24.5 mL) and the solution was cooled to −78 °C. Diisobutylaluminum hydride solution (1.0 M in cyclohexane, 5.4 mL, 5.39 mmol) was added dropwise over 10 min. The resulting solution was allowed to stir for 2 h at −78 °C under N_2, after which CH_3OH (1.5 mL) and then a saturated solution of Rochelle salt (16 mL) were added. The mixture was allowed to stir for 2 h at 22 °C to obtain two layers. The organic layer was separated and the aqueous layer was washed with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to afford crude aldehyde (0.638 g, 3.86 mmol, 79% yield) as yellow oil.

The unpurified aldehyde was re-dissolved in toluene (7.7 mL) and allylboronic acid pinacol ester (0.87 mL, 4.64 mmol) was added. The solution was allowed to stir for 12 h at 22 °C, after which the reaction was quenched by the addition of 1M HCl (15 mL). The aqueous layer was then washed with Et_2O (3 x 10 mL) and the combined organic layers were washed with brine (10 mL), then dried over $MgSO_4$ and concentrated *in vacuo* to afford yellow oil, which was purified by silica gel chromatography (2.5% to 7% EtOAc in hexanes) to afford **4.65** (0.609, 2.94 mmol, 76% yield) as pale yellow oil. **IR (neat)**: 3347 (br), 2935 (m), 2864 (w), 1640 (w), 1433 (m), 1237 (m), 1052 (m), 994 (s), 914 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.89–5.74 (1H, m), 5.17–5.09 (2H, m), 3.65 (1H, dt, J =

11.7, 5.7 Hz), 3.44–3.37 (2H, m), 2.36–2.25 (1H, m), 2.19–2.08 (1H, m), 1.94–1.82 (2H, m), 1.66 (1H, brs), 1.63–1.43 (4H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 134.7, 118.5, 70.4, 42.1, 35.9, 33.9, 32.8, 24.5; **HRMS $[M+H-H_2O]^+$** calcd for $C_8H_{14}Br$: 189.0279, found: 189.0273.

(9*E*,12*E*)-13-Chloro-12-methyltrideca-1,9,12-trien-4-ol (4.66): Prepared in analogy to a previously reported procedure.[63] In a N_2-filled glove box, an oven-dried vial equipped with a magnetic stir bar was charged with di-*tert*-butylmethylphosphine (1.9 mg, 12 μmol), palladium (II) acetate (1.3 mg, 6.0 μmol), powdered NaOH (14.4 mg, 0.360 mmol), **4.64** (29.1 mg, 0.120 mmol), **4.65** (49.7 mg, 0.240 mmol) and anhydrous 1,4-dioxane (0.6 mL). The vial was sealed and removed from the glove box. The mixture was allowed to stir for 24 h at 40 °C, after which it was allowed to cool to room temperature. The mixture was passed through a short plug of silica gel eluting with EtOAc (3 x 1 mL). The filtrate was concentrated *in vacuo* to afford brown oil, which was purified by silica gel chromatography (2% to 6% EtOAc in hexanes) to afford **4.66** (24.9 mg, 0.913 mmol, 76% yield) as pale yellow oil. **IR (neat)**: 2928 (w), 2855 (w), 1640 (w), 1435 (w), 1264 (m), 911 (m); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.89–5.77 (2H, m), 5.52–5.42 (1H, m), 5.39–5.29 (1H, m), 5.20–5.09 (2H, m), 3.70–3.59 (1H, m), 2.72 (2H, d, J = 6.5 Hz), 2.35–2.26 (1H, m), 2.19–2.09 (1H, m), 2.05–1.99 (2H, m), 1.75 (3H, s), 1.71–1.67 (1H, m), 1.48–1.45 (2H, m), 1.41–1.32 (4H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.1, 135.0, 133.3, 126.5, 118.3, 112.7, 70.7, 42.1, 20.4, 36.8, 32.5, 29.5, 25.3, 16.7; **HRMS $[M-H]^+$** calcd for $C_{14}H_{22}ClO$: 241.1359, found: 241.1351.

(63) Tonogaki, K.; Soga, K.; Itami, K.; Yoshida, J.-i. *Synlett* **2005**, *11*, 1802–1804.

(2*Z*,10*E*,13*E*)-14-Chloro-13-methyltetradeca-2,10,13-triene-1,5-diol (4.80; not shown in text): In a N_2-filled glove box, a solution of **Ru-1** (3.1 mg, 4.0 μmol) in CH_2Cl_2 (160 μL) was transferred by syringe to an oven-dried vial containing *Z*-2-butene-1,4-diol (14.1 mg, 0.160 mmol) and **4.66** (19.4 mg, 0.0799 mmol). The resulting solution was allowed to stir for 4 h at 22 °C. The reaction was quenched by addition of wet CH_3CN and concentrated *in vacuo*. Analysis of the unpurified mixture revealed 85% consumption of **4.66**. The resulting brown oil was purified by silica gel chromatography (10% to 40% EtOAc in hexanes) to afford **4.80** (15.3 mg, 0.0561 mmol, 70% yield) in 94:6 *Z*:*E* ratio as pale yellow oil. **IR (neat)**: 3347 (br), 2923 (s), 2854 (m), 1638 (w), 1435 (m), 1083 (m), 1010 (s), 969 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.89 (1H, dtt, *J* = 12.4, 6.8, 1.3 Hz), 5.81 (1H, dd, *J* = 2.7, 1.4 Hz), 5.70–5.61 (1H, m), 5.52–5.43 (1H, m), 5.34 (1H, dddd, *J* = 14.0, 7.3, 2.8, 1.5 Hz), 4.21 (1H, dd, *J* = 11.8, 7.7 Hz), 4.12 (1H, dd, *J* = 12.6, 6.5 Hz), 3.69–3.61 (1H, m), 2.72 (2H, d, *J* = 6.7 Hz), 2.32–2.24 (2H, m), 2.06–1.99 (2H, m), 1.95 (1H, brs), 1.75 (3H, d, *J* = 1.4 Hz), 1.50–1.34 (7H, m); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.1, 133.2, 131.7, 129.6, 126.6, 112.7, 70.8, 58.0, 40.4, 37.1, 35.3, 32.5, 29.5, 25.4, 16.8; **HRMS $[M+H]^+$** calcd for $C_{15}H_{26}ClO_2$: 273.1621, found: 273.1624.

(±)-Coibacin D: Prepared in analogy to a previously reported procedure.[64] An oven-dried round-bottom flask equipped with a magnetic stir bar was charged with **4.80** (13.6 mg, 0.0499 mmol), (diacetoxyiodo)benzene (48.2 mg, 0.150 mmol), TEMPO (2.3 mg, 0.0147 mmol) and CH_2Cl_2 (0.5 mL). The solution was allowed to stir for 3 h at 22 °C under N_2, after which the reaction was quenched by the addition of a saturated solution of $Na_2S_2O_3$. The aqueous layer was then extracted with CH_2Cl_2 (3 x 1 mL) and the

(64) Oliveira, J. M.; Freitas, J. C. R.; Comasseto, J. V.; Menezes, P. H. *Tetrahedron* **2011**, *67*, 3003–3009.

combined organic layers were washed successively with saturated $NaHCO_3$ (2 mL), saturated NH_4Cl (2 mL), and brine (2 x 2 mL), then dried over $MgSO_4$ and concentrated *in vacuo* to afford yellow oil, which was purified by silica gel chromatography (5% to 15% EtOAc in hexanes) to afford **(±)-**coibacin D (11.0 mg, 0.0409 mmol, 82% yield) as pale yellow oil. The spectral data for this compound were identical to those reported previously.[36]

4.8.7. Synthesis of Dienoate* 4.67 *en route to Kimbeamide A

Methyl (2*E*,4*E*,7*E*)-8-chloro-7-methylocta-2,4,7-trienoate (4.67): An oven-dried 2-dram vial was charged with **4.64** (24.3 mg, 0.100 mmol), methyl (*E*)-3-bromopropenoate (16.5 mg, 0.100 mmol), $PdCl_2$(dpephos) (0.7 mg, 0.00098 mmol), CsF (22.8 mg, 0.150 mmol). The mixture was degassed by evacuation and back-fill with N_2 three times before 1 mL of anhydrous THF was added. The resulting mixture was allowed to stir at 60 ^oC for 15 h, filtered through a short plug of celite, and concentrated *in vacuo*. The crude product mixture was purified by silica gel chromatography (2% to 5% Et_2O in pentane) to obtain **4.67** as colorless oil in >98:2 stereoisomeric purity. **IR (neat)**: 2950 (w), 1716 (s), 1644 (m), 1615 (m), 1434 (m), 1303 (m), 1265 (m), 1246 (s), 1203 (m), 1162 (m), 1133 (s), 998 (s); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 (1H, dd, J = 15.3, 10.9 Hz), 6.25–6.16 (1H, m), 6.04 (1H, dtt, J = 15.3, 7.0, 0.7 Hz), 5.89–5.80 (2H, m), 3.75 (3H, s), 2.91 (2H, d, J = 7.0 Hz), 1.77 (3H, d, J = 1.4 Hz); **^{13}C NMR (150 MHz, $CDCl_3$):** δ 167.6, 144.4, 139.6, 136.2, 130.6, 120.3, 114.2, 51.7, 40.4, 16.8; **HRMS $[M+H]^+$** calcd for $C_{10}H_{14}ClO_2$: 201.0682, found: 201.0690.

4.8.8. Synthesis of Enyne* 4.70 *en route to Pateamine A

(*E*)-*tert*-Butyldimethyl((4-methylhex-4-en-2-yl)oxy)silane (4.68): In analogy to a previously reported procedure[65], *t*-BuLi (12.5 mL, 1.7M in pentane, 21.3 mmol) was added dropwise to a stirred solution of (*E*)-2-bromobut-2-ene (1.00 mL, 9.85 mmol) in 25 mL of THF at –78 °C. The resulting solution was allowed to stir at −78 °C for 30 min then *S*-propylene oxide (1.04 mL, 14.9 mmol) was added in one portion. The reaction mixture was allowed to stir at –78 °C for 1 h and then warm to 22 °C and stir at for an addition 1 h. At this point, the reaction was quenched by the addition of a saturated solution of NH_4Cl (10 mL) at 0 °C. The separated aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic layers were washed with de-ionized water (25 mL), brine (25 mL), dried over $MgSO_4$, and concentrated *in vacuo* to obtain (*E*)-4-methylhex-4-en-2-ol (1.05 g, 9.19 mmol, 93% yield). The resulting clear colorless oil was sufficiently clean and used in the next step without further purification.

TBSOTf (0.85 mL, 3.69 mmol) was added in a dropwise manner to a solution of (*E*)-4-methylhex-4-en-2-ol and Et_3N (1.0 mL, 7.21 mmol) in 15 mL of CH_2Cl_2 at 0 °C. The solution was allowed to warm to 22 °C and stir for 3 h. Volatiles were removed *in vacuo* and the resulting slightly yellow oil was purified by silica gel chromatography (10% Et_2O in pentane) to afford **4.68** (0.753 g, 3.28 mmol, 89% yield) in >98:2 *E*:*Z* ratio as colorless oil. **IR (neat)**: 2956 (m), 2928 (m), 2892 (m), 2857 (m), 1472 (m), 1462 (m), 1374 (m), 1361 (m), 1252 (m), 1128 (m), 1093 (m), 1068 (m), 1027 (m), 831 (s), 805 (m), 772 (s); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 5.22 (1H, q, J = 6.4 Hz), 3.90 (1H, h, J = 6.1 Hz), 2.16 (1H, dd, J = 13.1, 6.6 Hz), 2.01 (1H, dd, J = 13.1, 6.2 Hz), 1.61–1.54 (5H, m), 1.09 (3H, d, J = 6.1 Hz), 0.88 (9H, s), 0.04 (3H, s), 0.02 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$):** δ

(65) Wuts, P. G. M.; Thompson, P. A.; Callen, G. R. *J. Org. Chem.* **1983**, *48*, 5398–5400.

132.9, 121.1, 67.4, 50.1, 25.8, 23.6, 18.1, 16.2, 13.3, -4.6, -4.9; **HRMS [M + H]$^+$** calcd for $C_{13}H_{29}OSi$: 229.1988, found: 229.1995.

(*S*,*E*)-*tert*-Butyl((8,8-diethoxy-4-methyloct-4-en-6-yn-2-yl)oxy)dimethylsilane (4.81, not shown in text): In the glovebox, 4.0 mL anhydrous THF was added to a mixture of **4.69** (81% wt of bromo-alkene, 412 mg, 1.14 mmol), Pd[(*t*-Bu$_3$)P]$_2$ (35 mg, 0.0685 mmol), CuI (26 mg, 0.136 mmol), DABCO (254 mg, 2.26 mmol), and 3,3-diethoxy-1-propyne (175 mg, 1.36 mmol) in an oven-dried 2-dram vial. The vial was sealed with a Teflon-lined screw cap and the mixture was allowed to stir at 22 °C for 12 h. The reaction mixture was filtered through a pad of celite and the filtrate was concentrated *in vacuo*. The crude product mixture was purified by silica gel chromatography (2–5% Et_2O in pentane) to obtain **4.81** (286 mg, 0.738 mmol, 74% yield). **IR (neat)**: 2973 (m), 2955 (m), 2929 (m), 2884 (m), 2857 (m), 2215 (w), 1472 (w), 1462 (w), 1444 (w), 1354 (m), 1327 (m), 1254 (m), 1171 (m), 1124 (m), 1106 (m), 1087 (s), 1051 (s), 1026 (s), 1002 (s), 833 (s), 773 (s); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.41 (1H, d, J = 1.5 Hz), 5.32 (1H, dt, J = 2.3, 1.1 Hz), 3.94 (1H, h, J = 6.1 Hz), 3.76 (2H, dq, J = 9.5, 7.1 Hz), 3.61 (2H, dq, J = 9.5, 7.1 Hz), 2.25 (1H, ddd, J = 13.2, 6.6, 1.0 Hz), 2.13 (1H, ddd, J = 13.2, 5.9, 1.0 Hz), 1.90 (3H, d, J = 1.2 Hz), 1.24 (6H, t, J = 7.1 Hz), 1.10 (3H, d, J = 6.1 Hz), 0.87 (9H, s), 0.04 (3H, s), 0.03 (3H, s); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.0, 106.4, 92.1, 87.2, 83.5, 67.3, 60.9, 60.8, 49.0, 26.0, 23.8, 20.3, 18.2, 15.3, -4.4, -4.7; **HRMS [M+H-EtOH]$^+$** calcd for $C_{17}H_{31}O_2Si$: 295.2093, found: 295.2090.

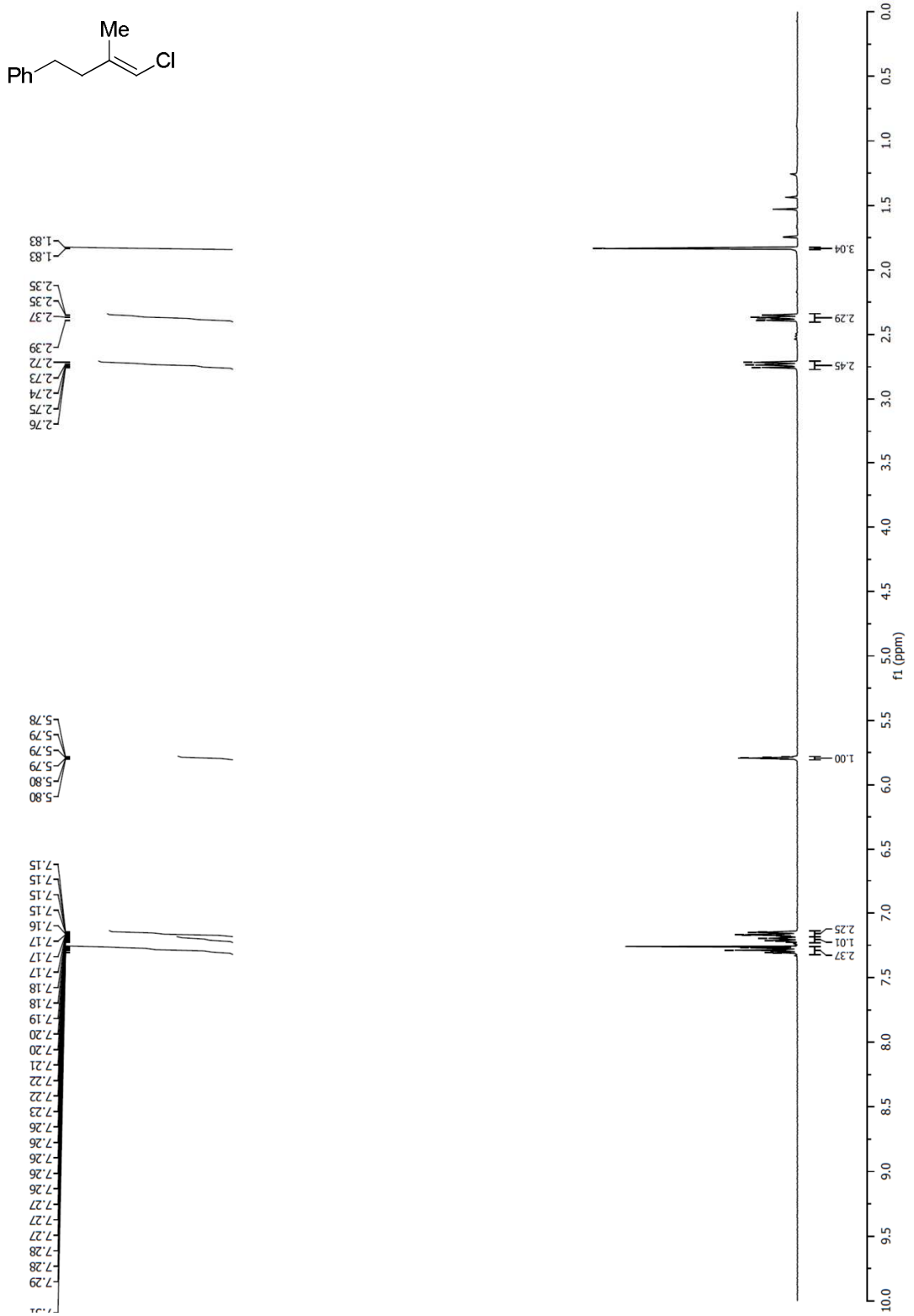
(*S*,*E*)-7-((*tert*-Butyldimethylsilyl)oxy)-5-methyloct-4-en-2-ynal (4.70): In analogy to a previously reported procedure[66], a mixture of **4.81** (34.0 mg, 0.100 mmol) and SiO_2 (0.60 g, 60–200 mesh) in 1.0 mL of CH_2Cl_2 was treated with a solution of oxalic acid (10%

(66) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63−65.

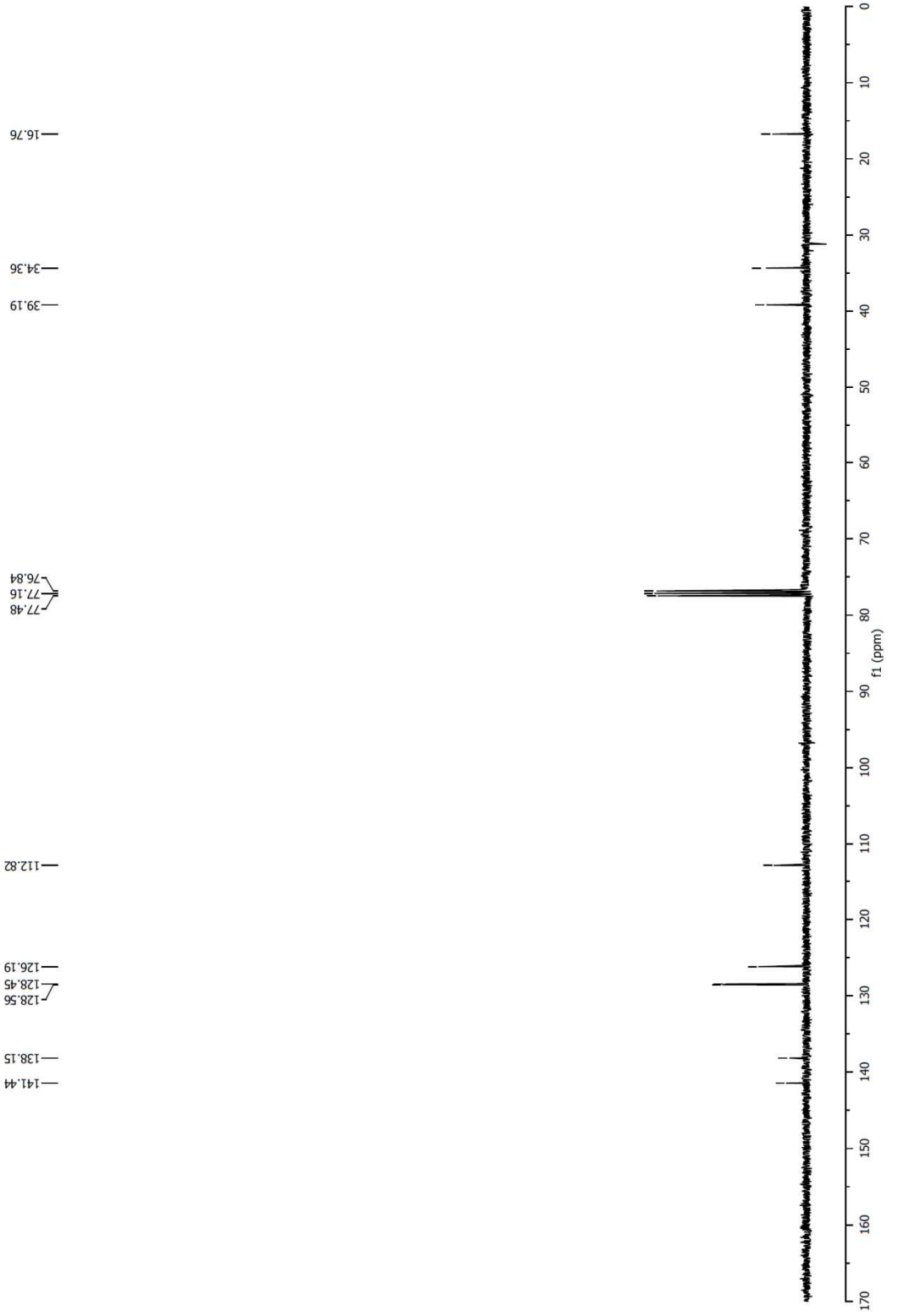
w/w in H_2O, 60 μL). The resulting mixture was allowed to stir at 22 ^oC for 45 min, then filtered through a plug of celite, and concentrated *in vacuo*. The resulting yellow oil was purified by silica gel chromatography (5% Et_2O in pentane) to obtain **4.70** as slight yellow oil (25.2 mg, 0.0946 mmol, 95% yield). The spectral data for this compound were consistent with those reported previously.[37b]

4.8.9. NMR Spectra

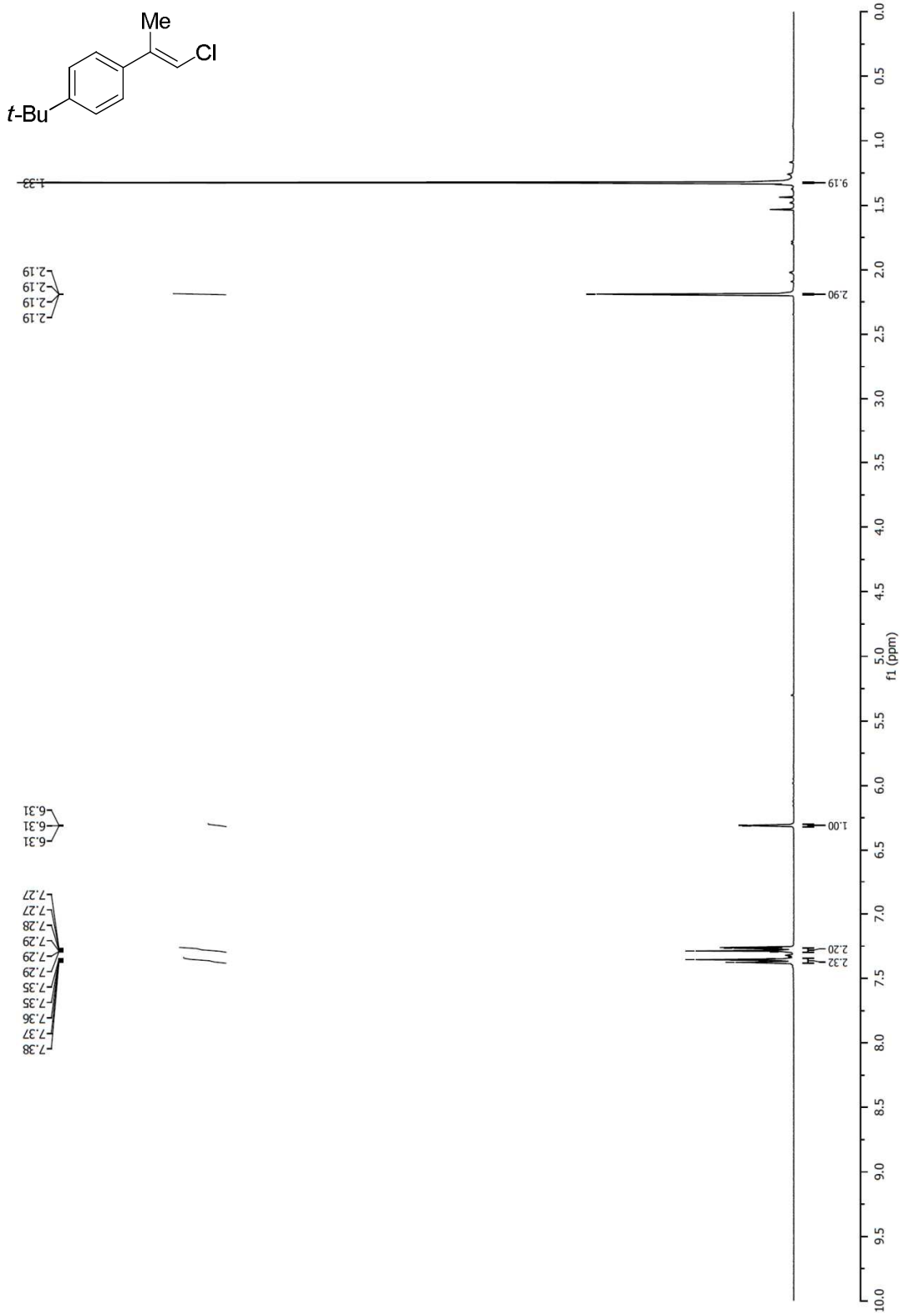
^{1}H NMR spectrum of 4.3



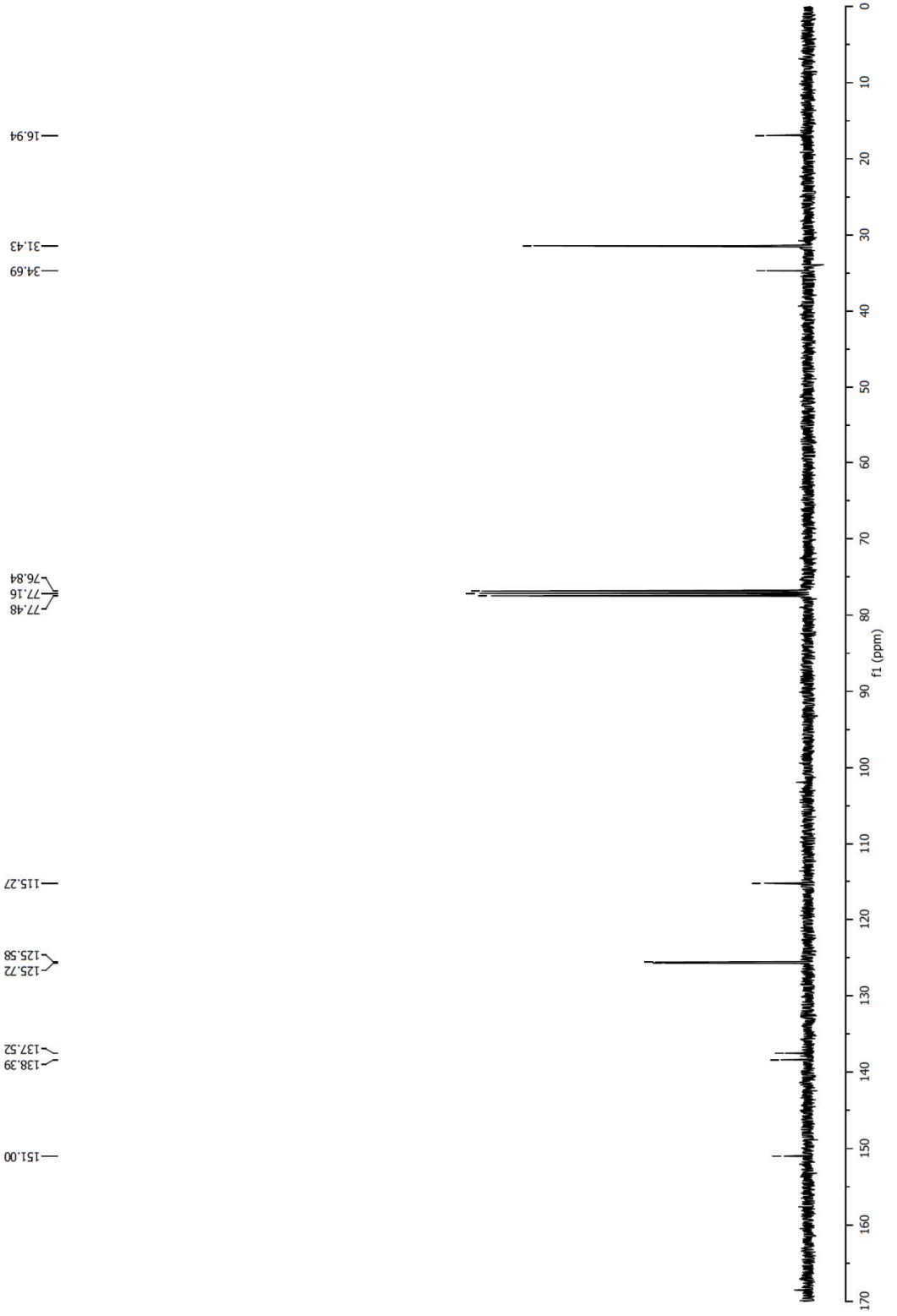
^{13}C NMR spectrum of 4.3



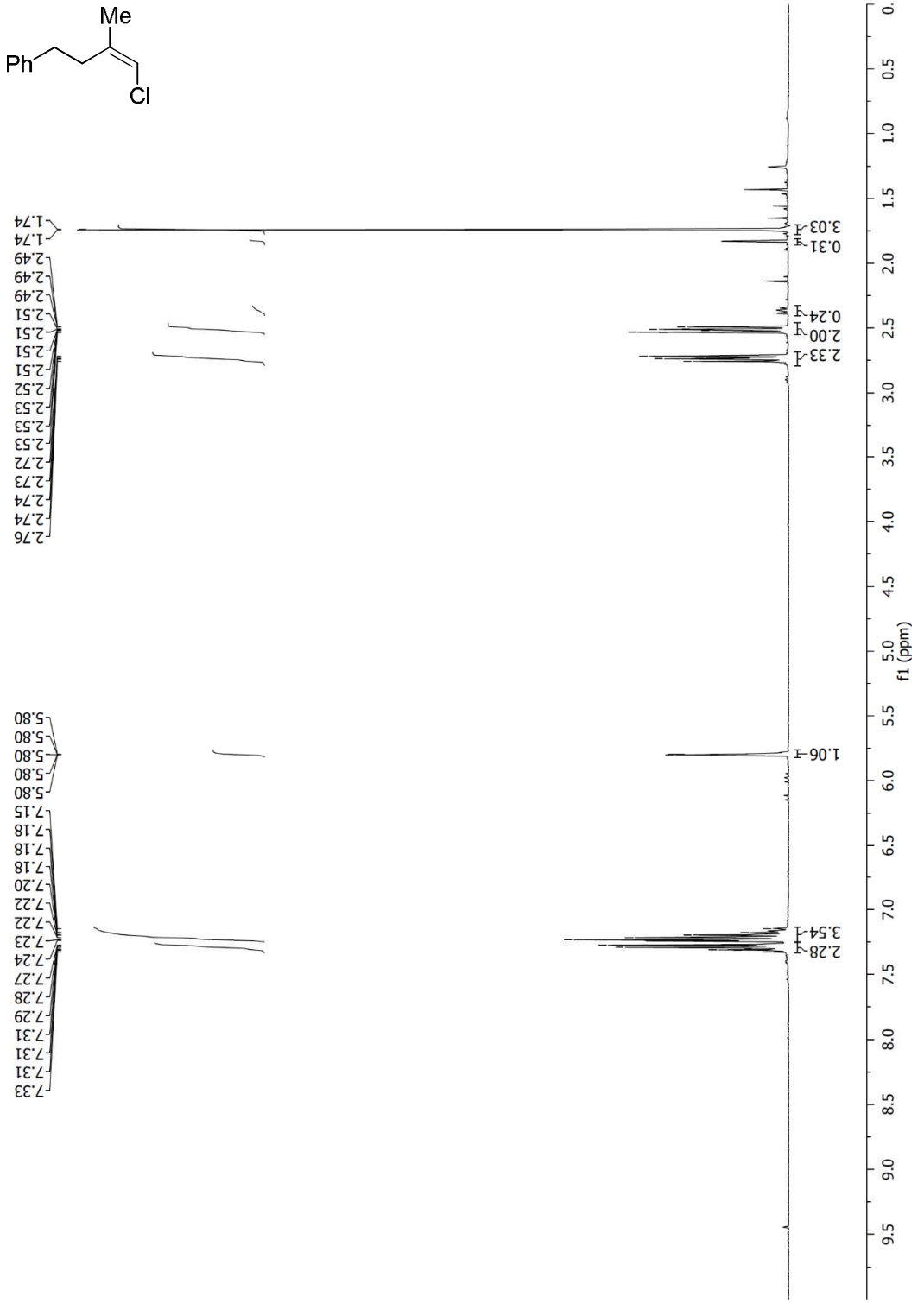
^{1}H NMR spectrum of 4.5



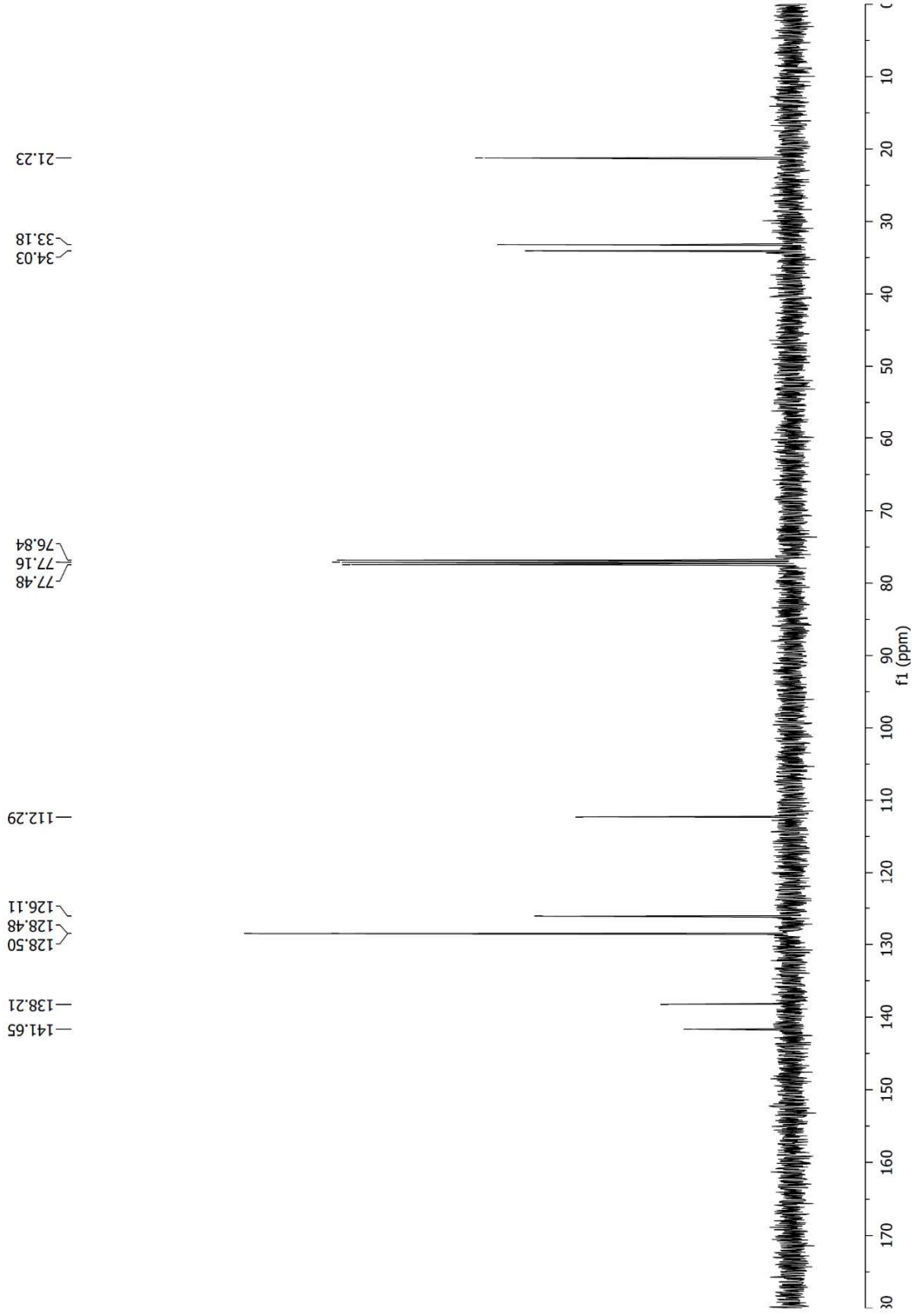
^{13}C NMR spectrum of 4.5



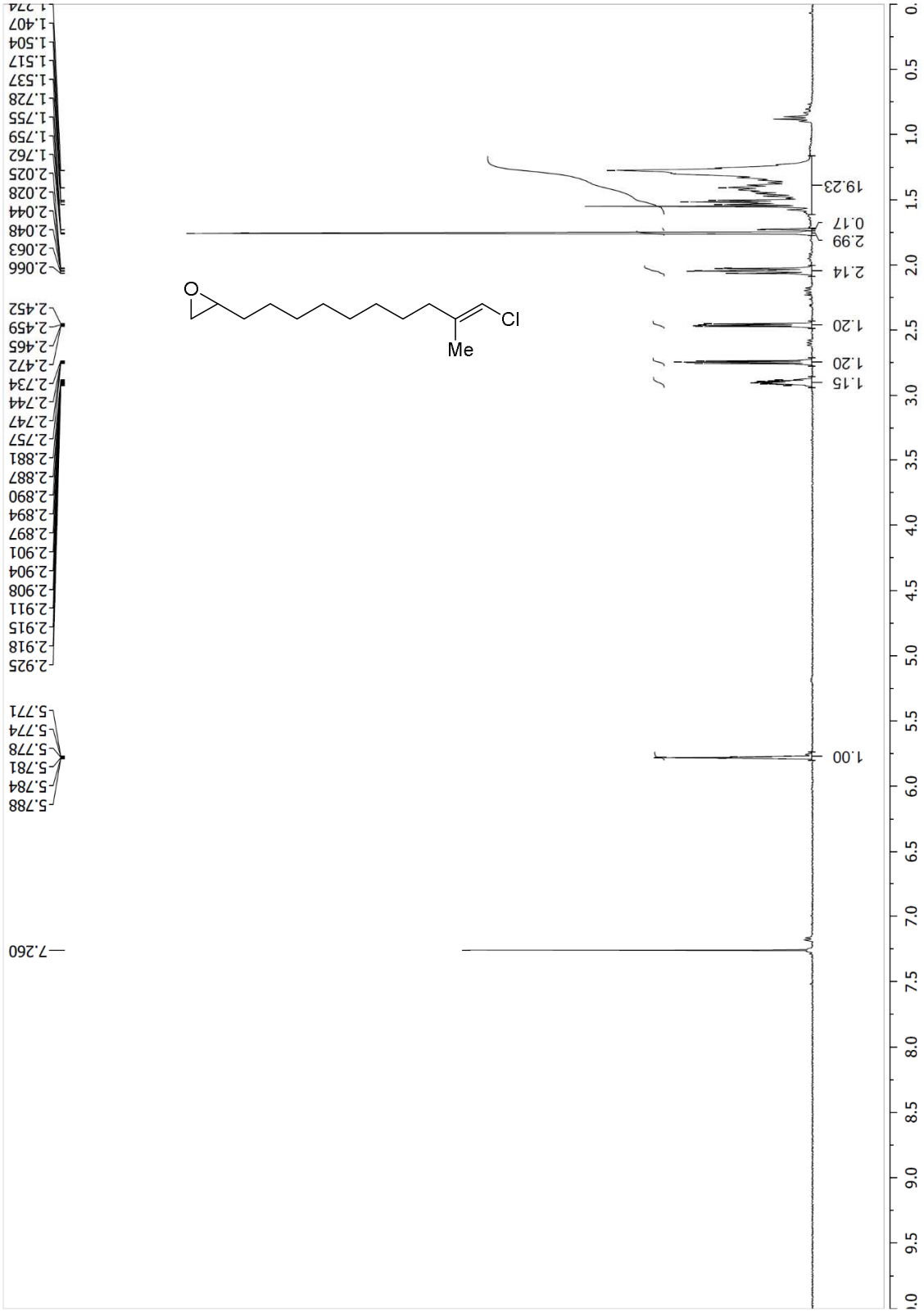
^{1}H NMR spectrum of 4.23



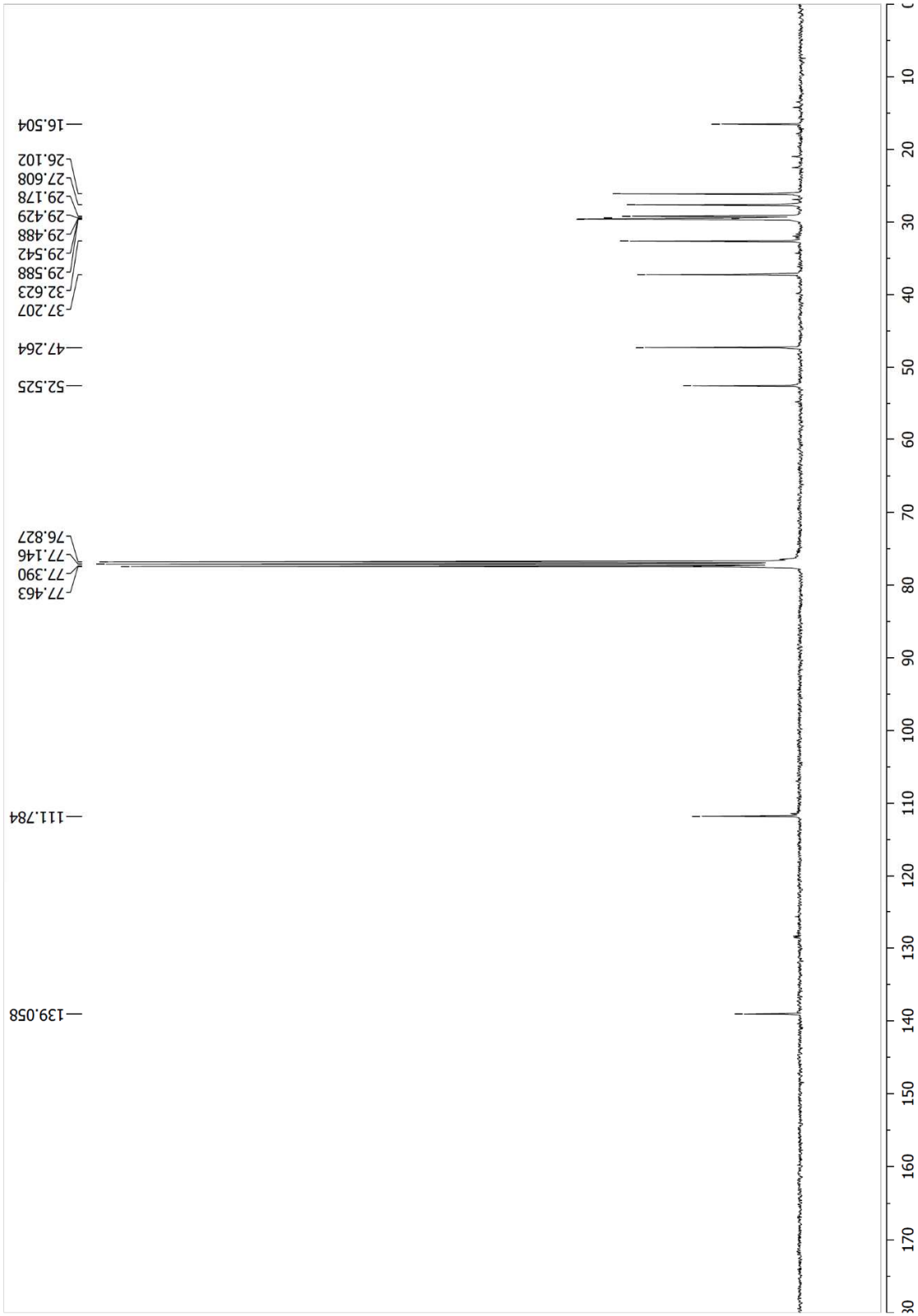
^{13}C NMR spectrum of 4.23



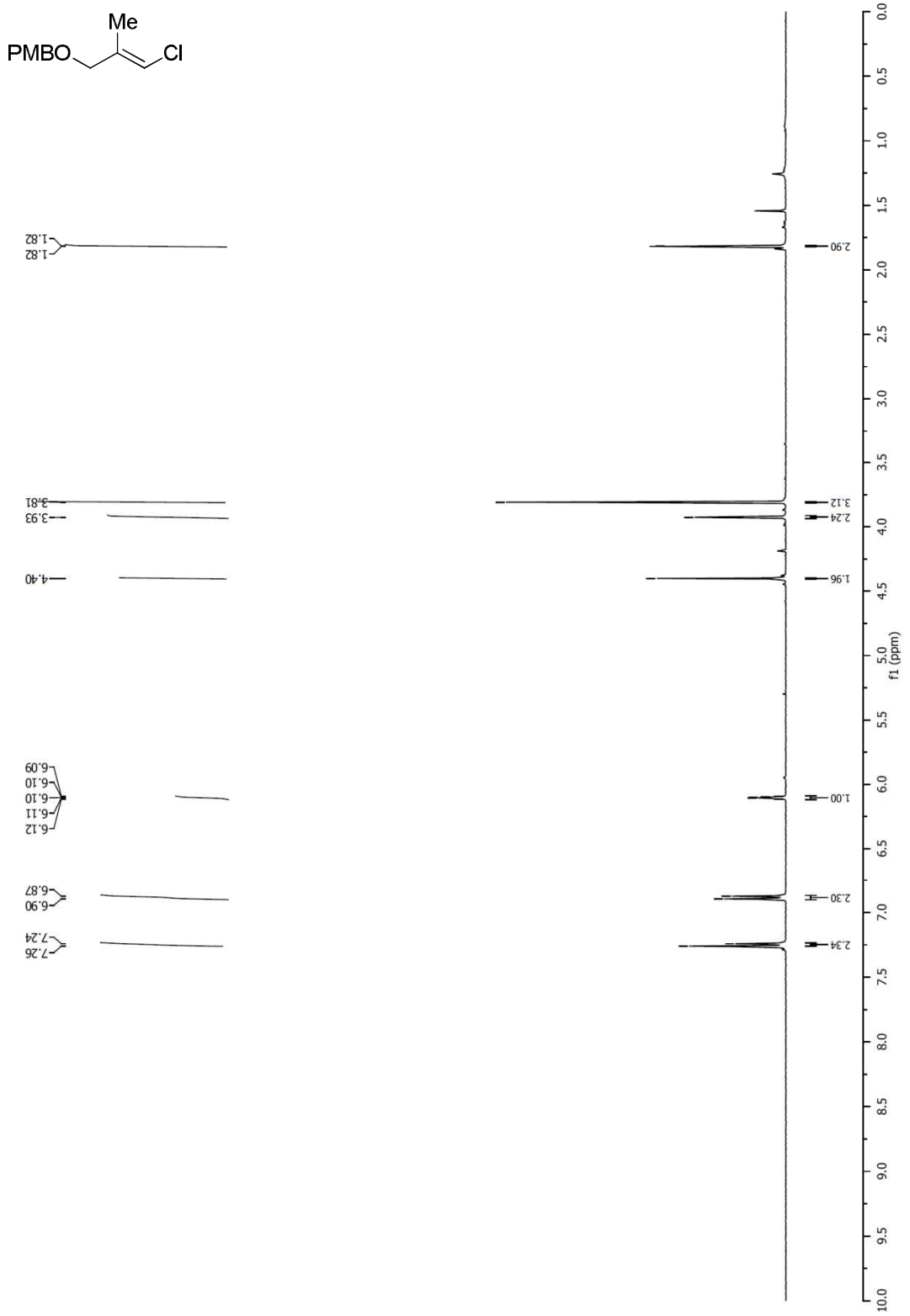
^{1}H NMR spectrum of 4.24



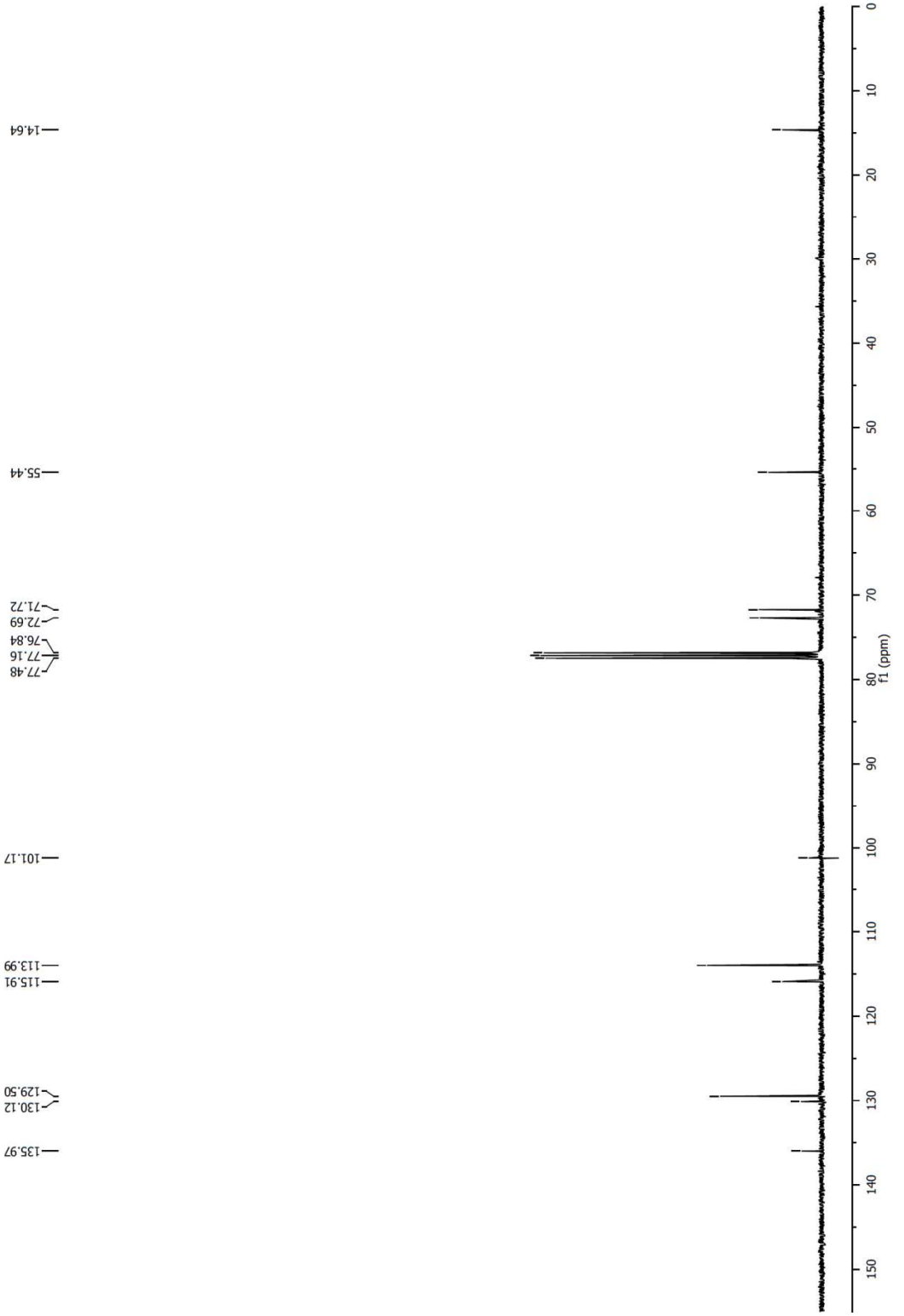
^{13}C NMR spectrum of 4.24



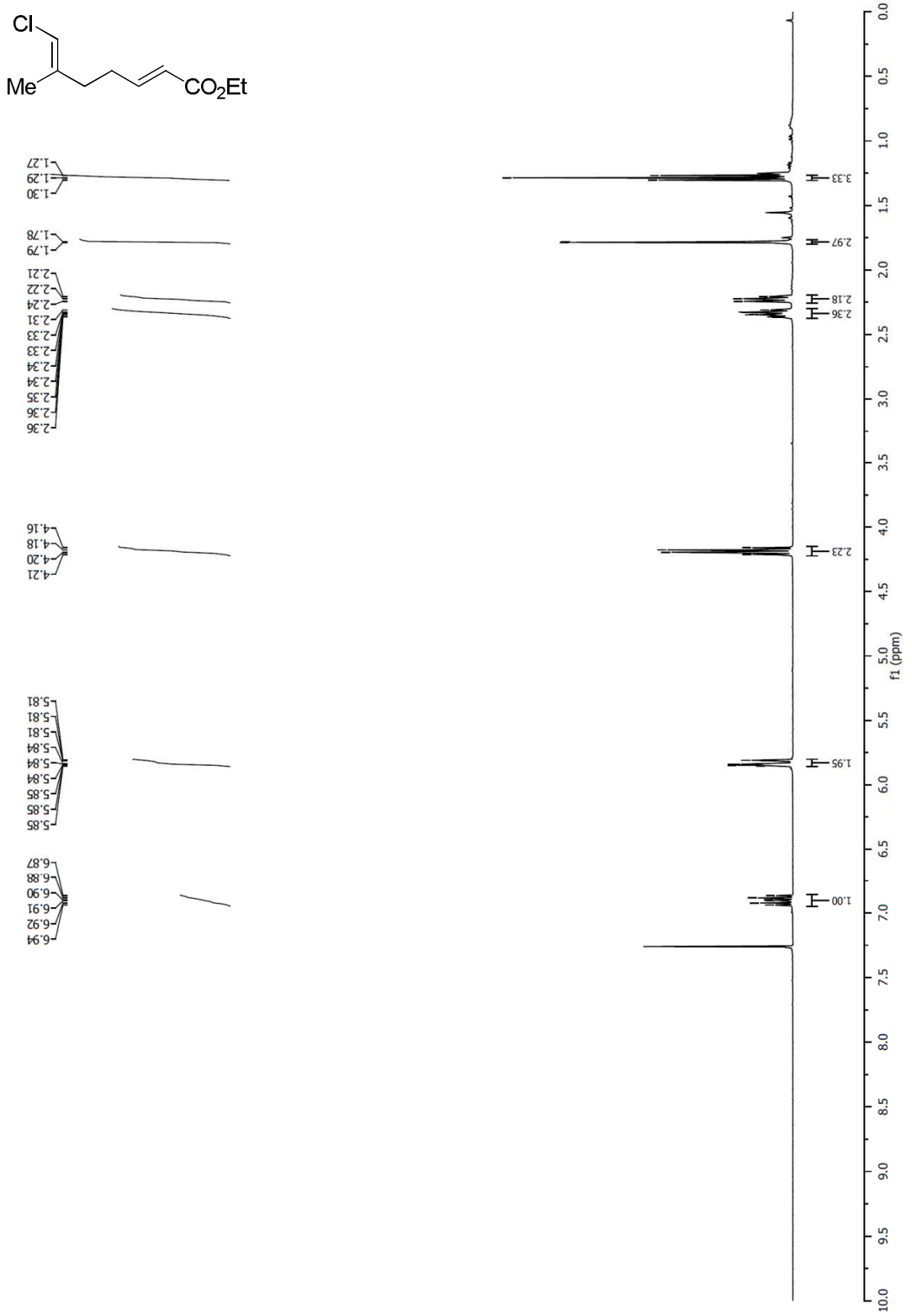
^{1}H NMR spectrum of 4.25



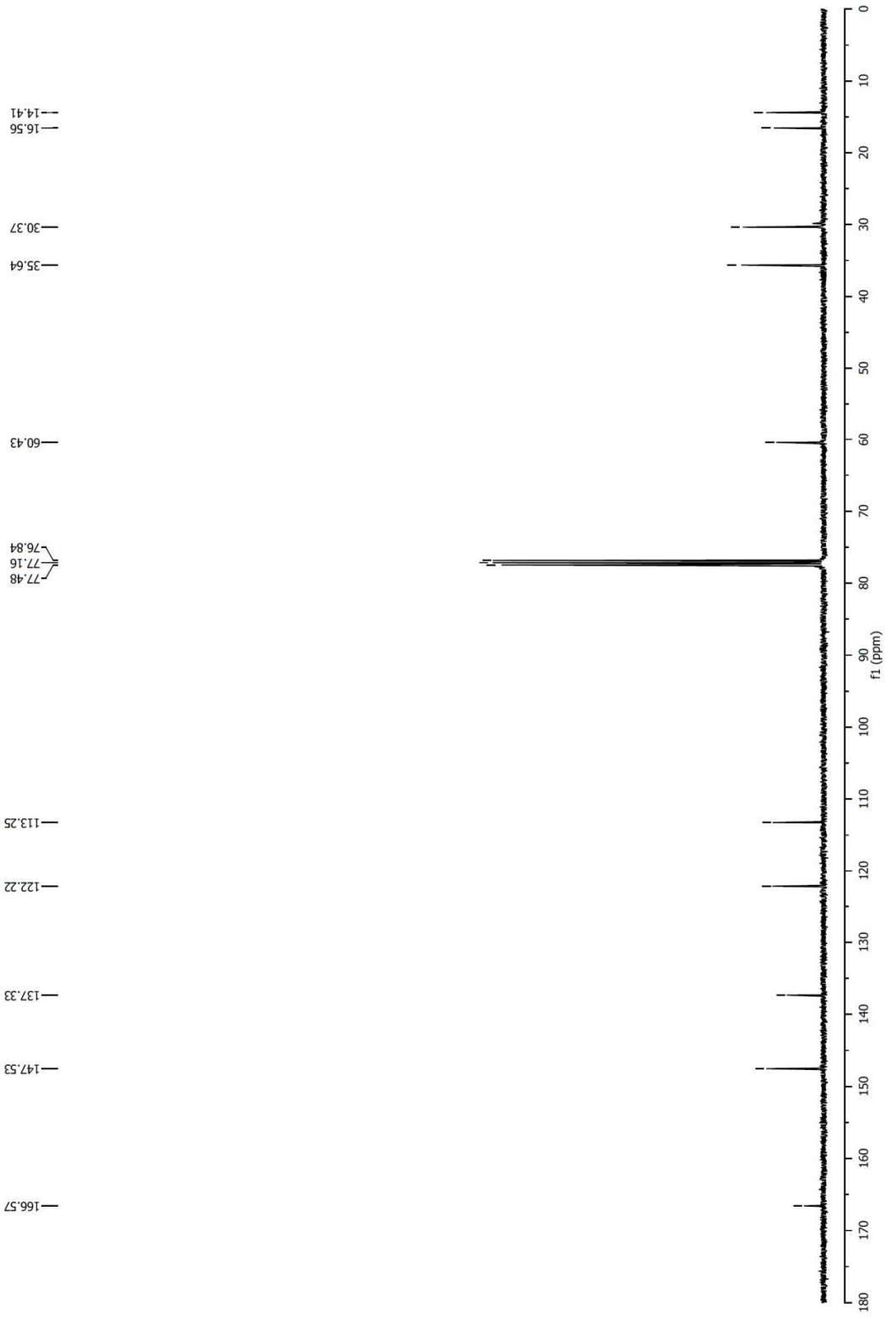
^{13}C NMR spectrum of 4.25



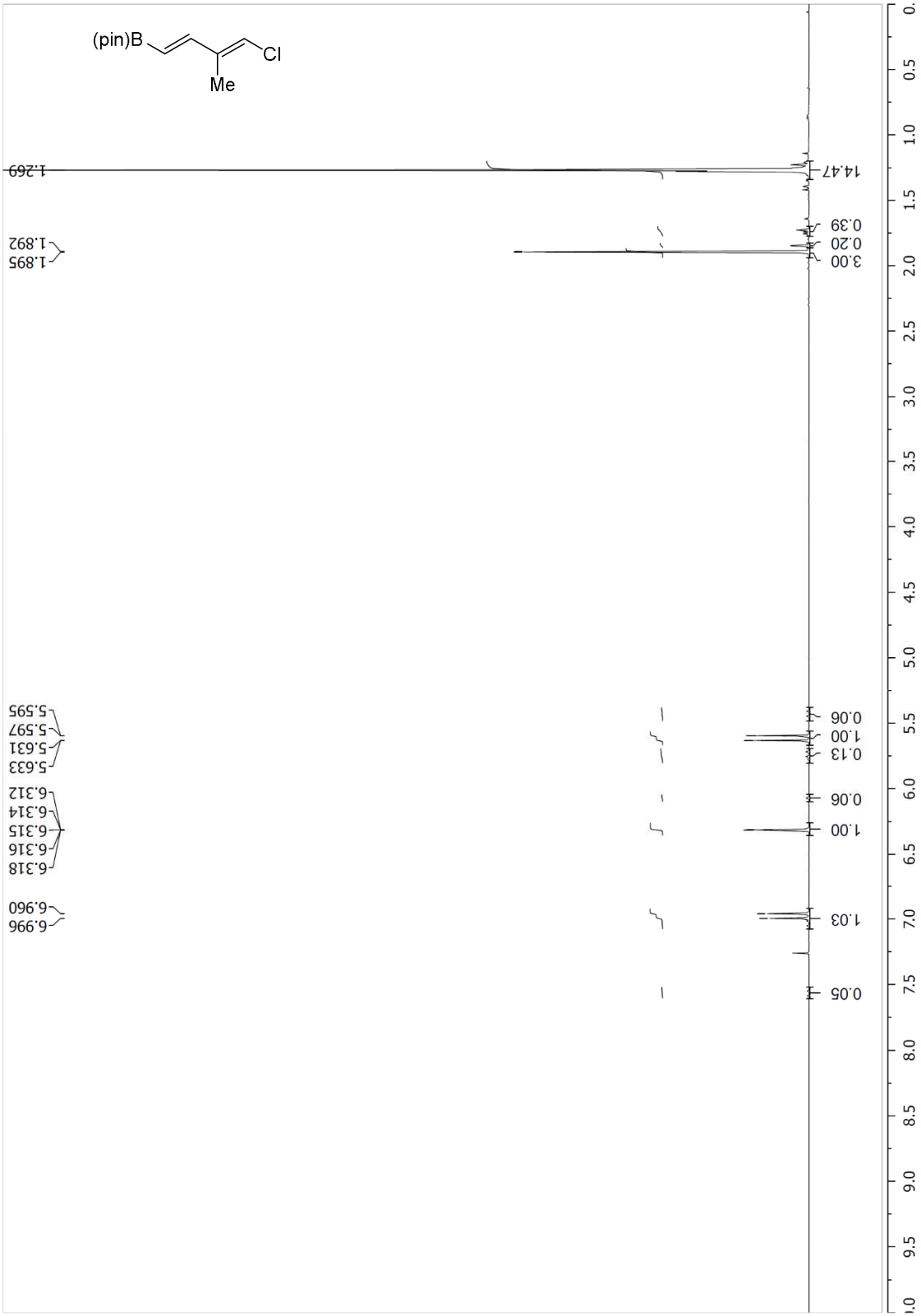
^{1}H NMR spectrum of 4.26



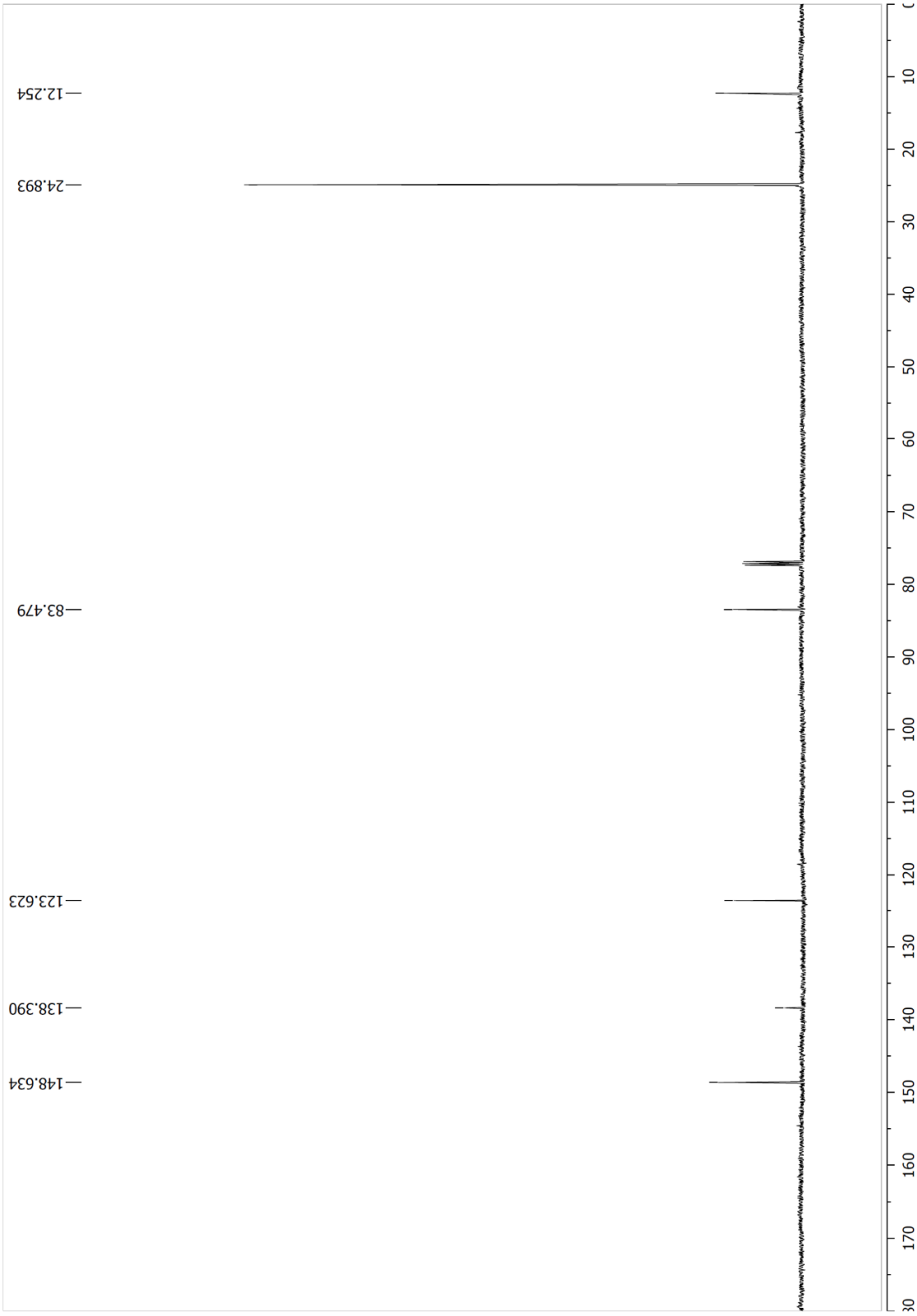
^{13}C NMR spectrum of 4.26



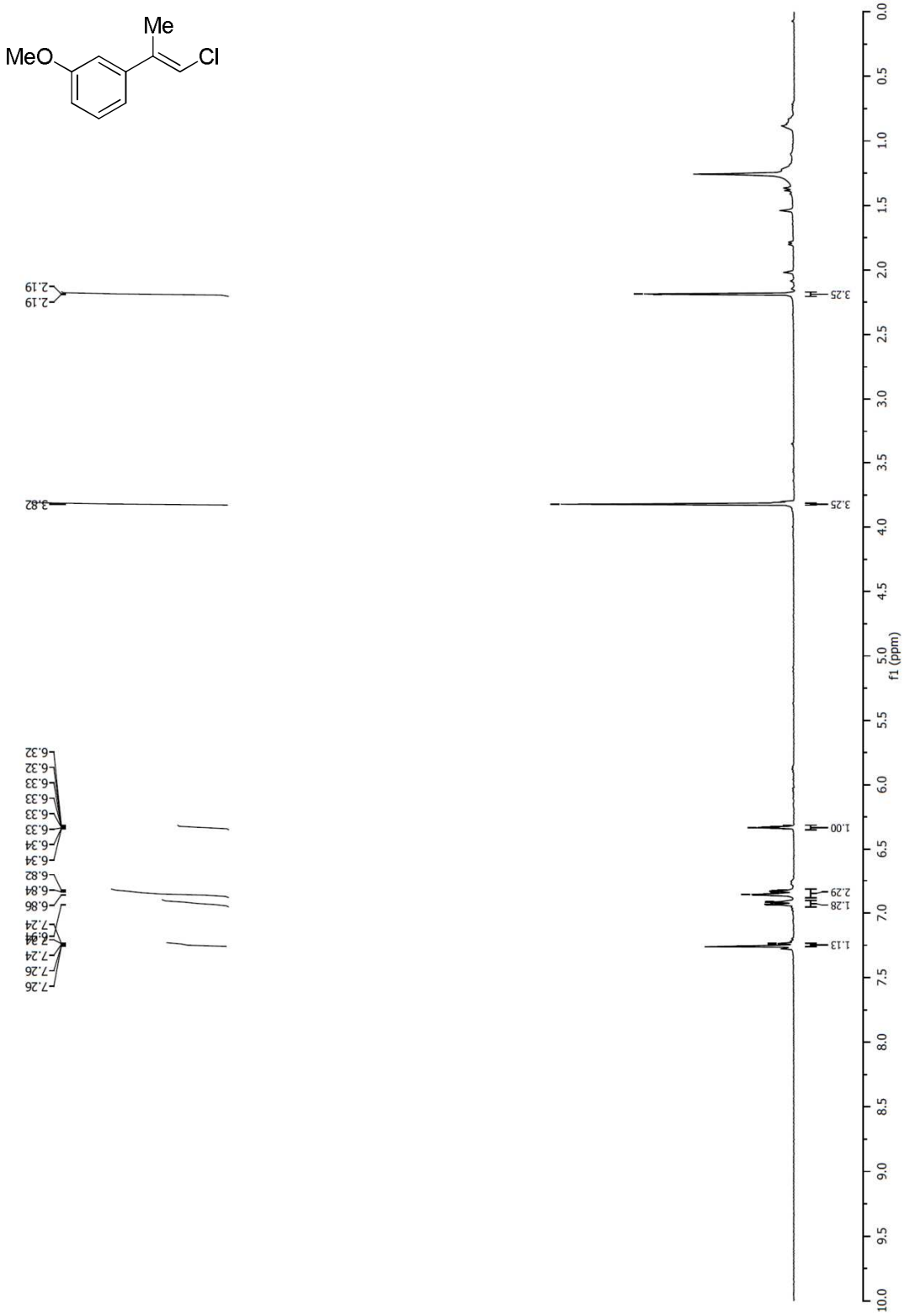
^{1}H NMR spectrum of 4.27



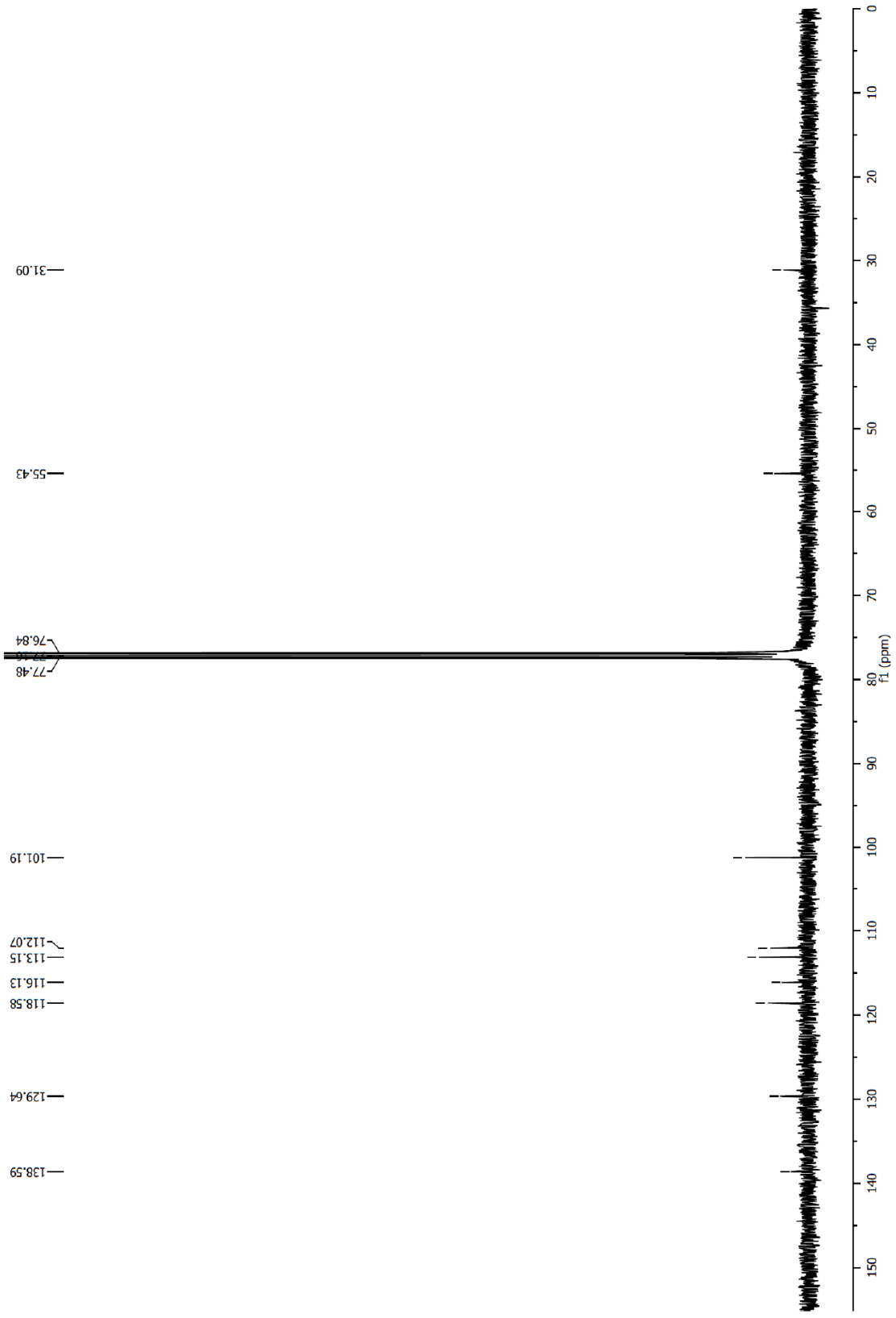
^{13}C NMR spectrum of 4.27



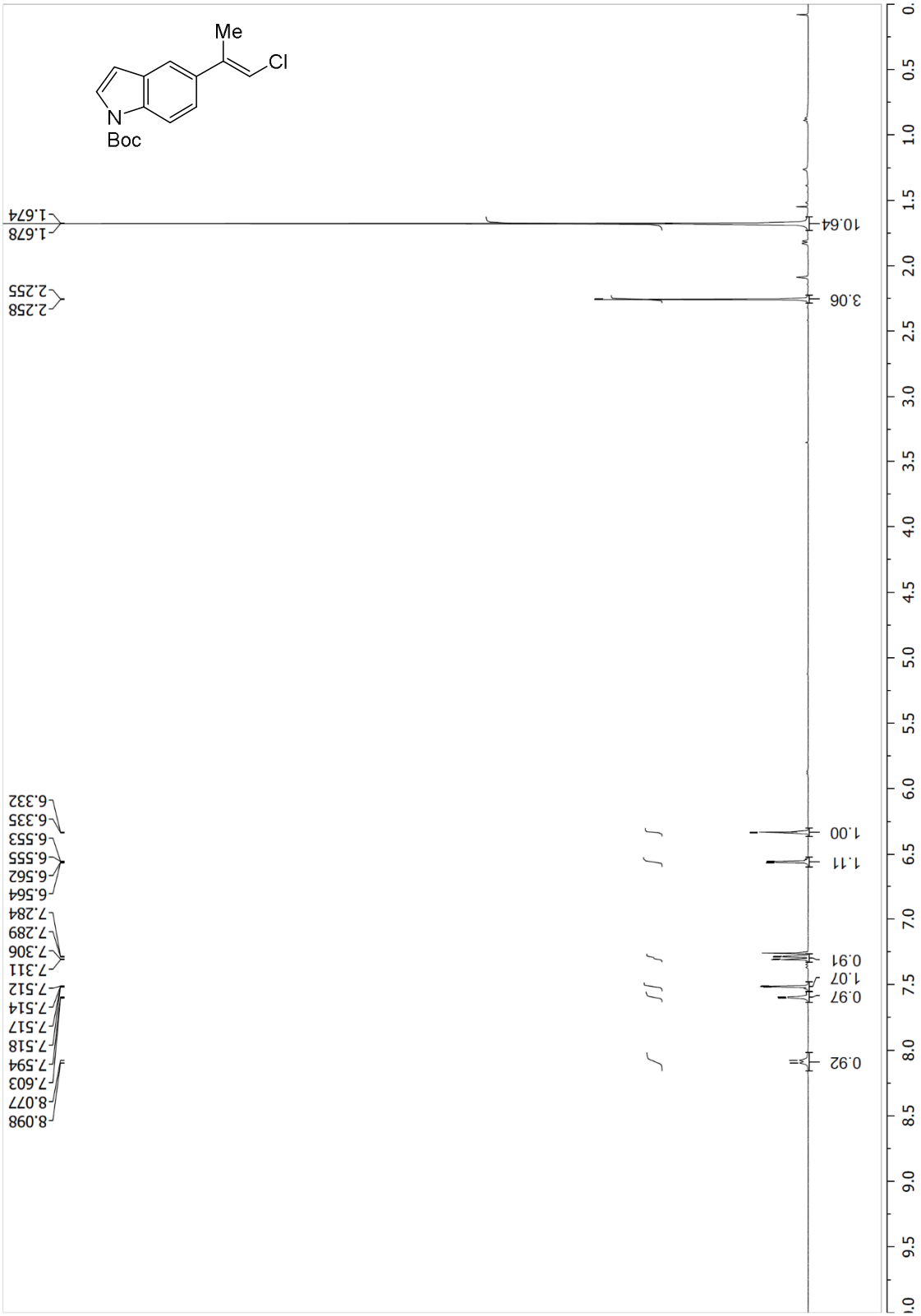
^{1}H NMR spectrum of 4.28



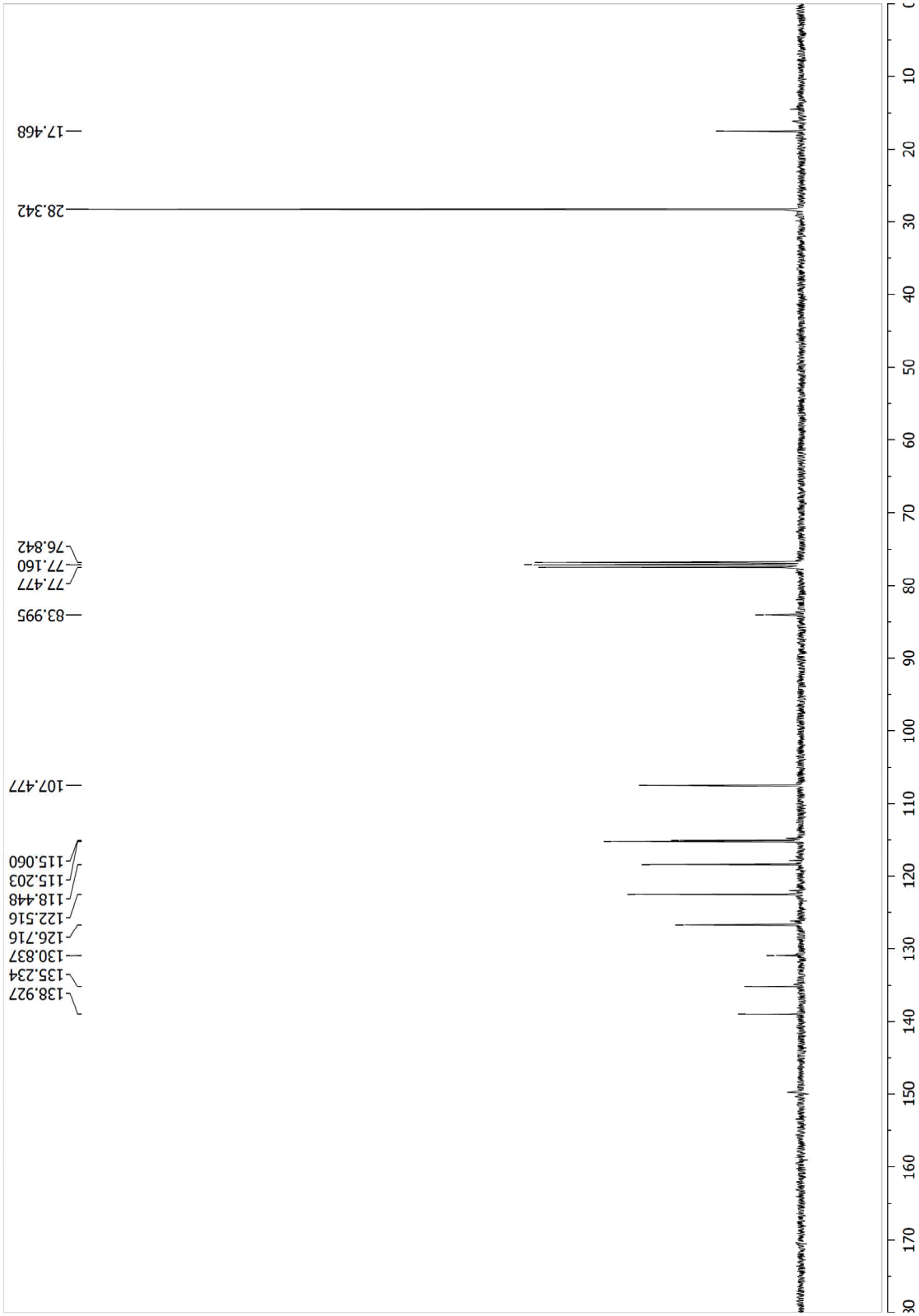
^{13}C NMR spectrum of 4.28



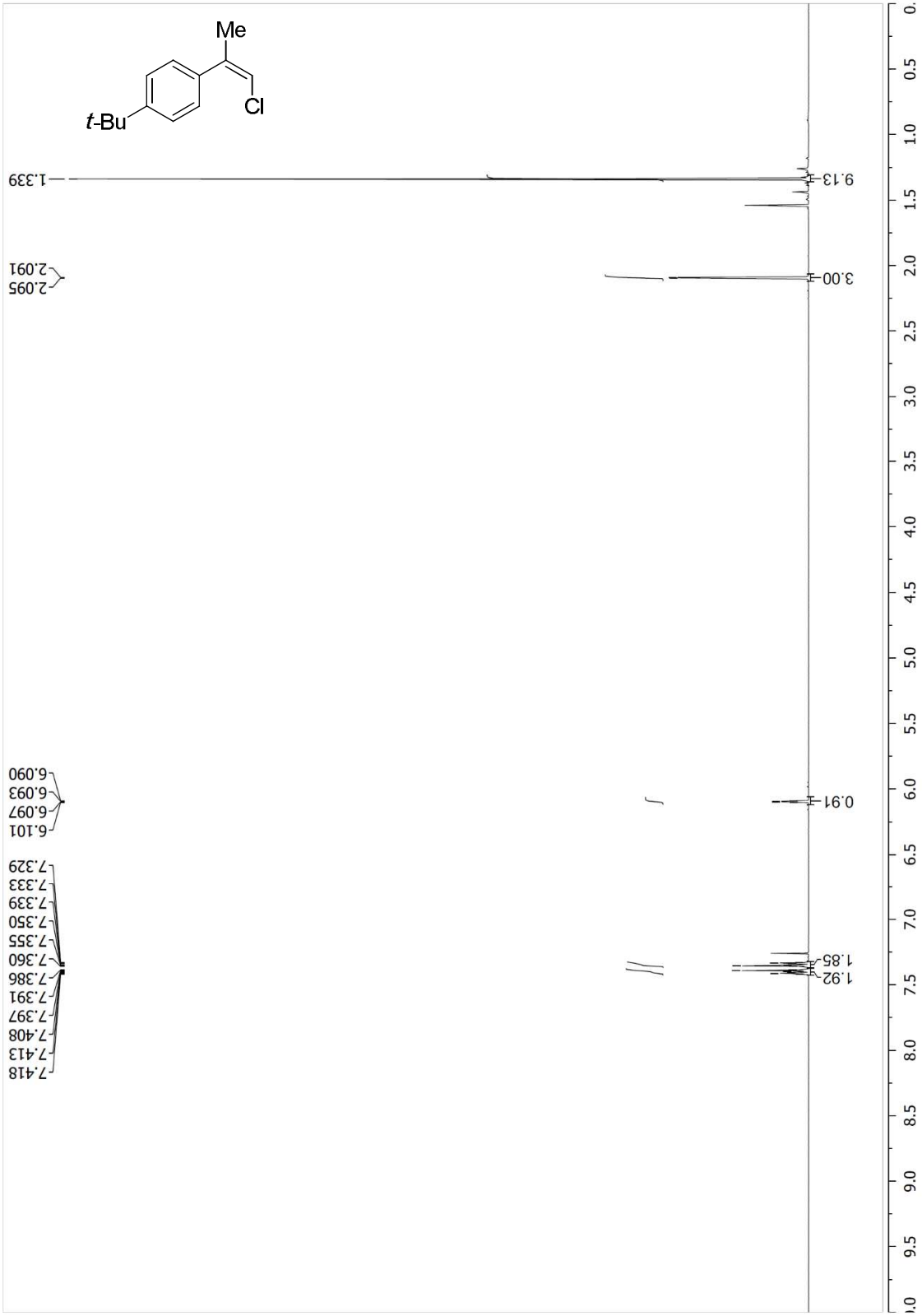
^{1}H NMR spectrum of 4.29



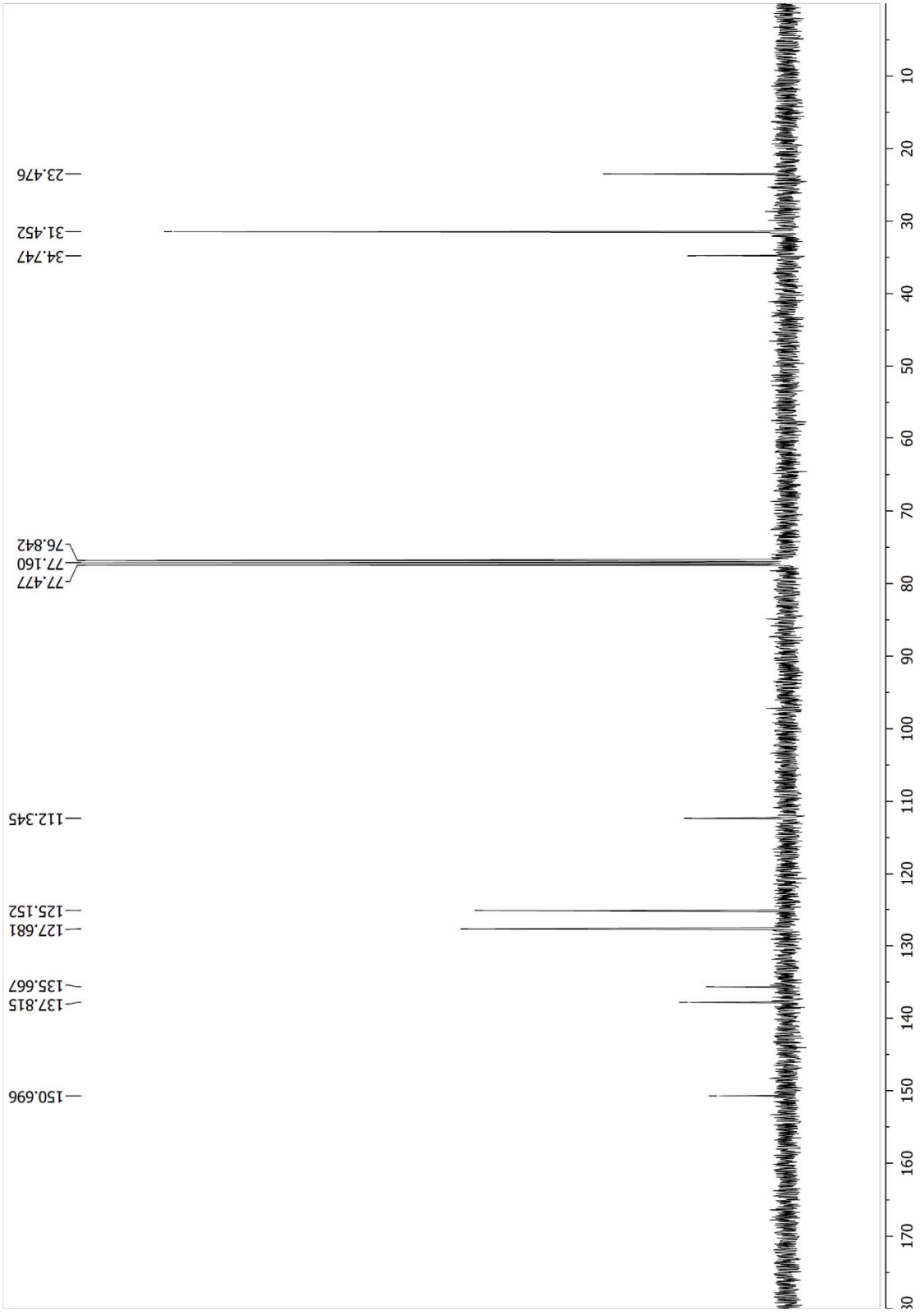
^{13}C NMR spectrum of 4.29



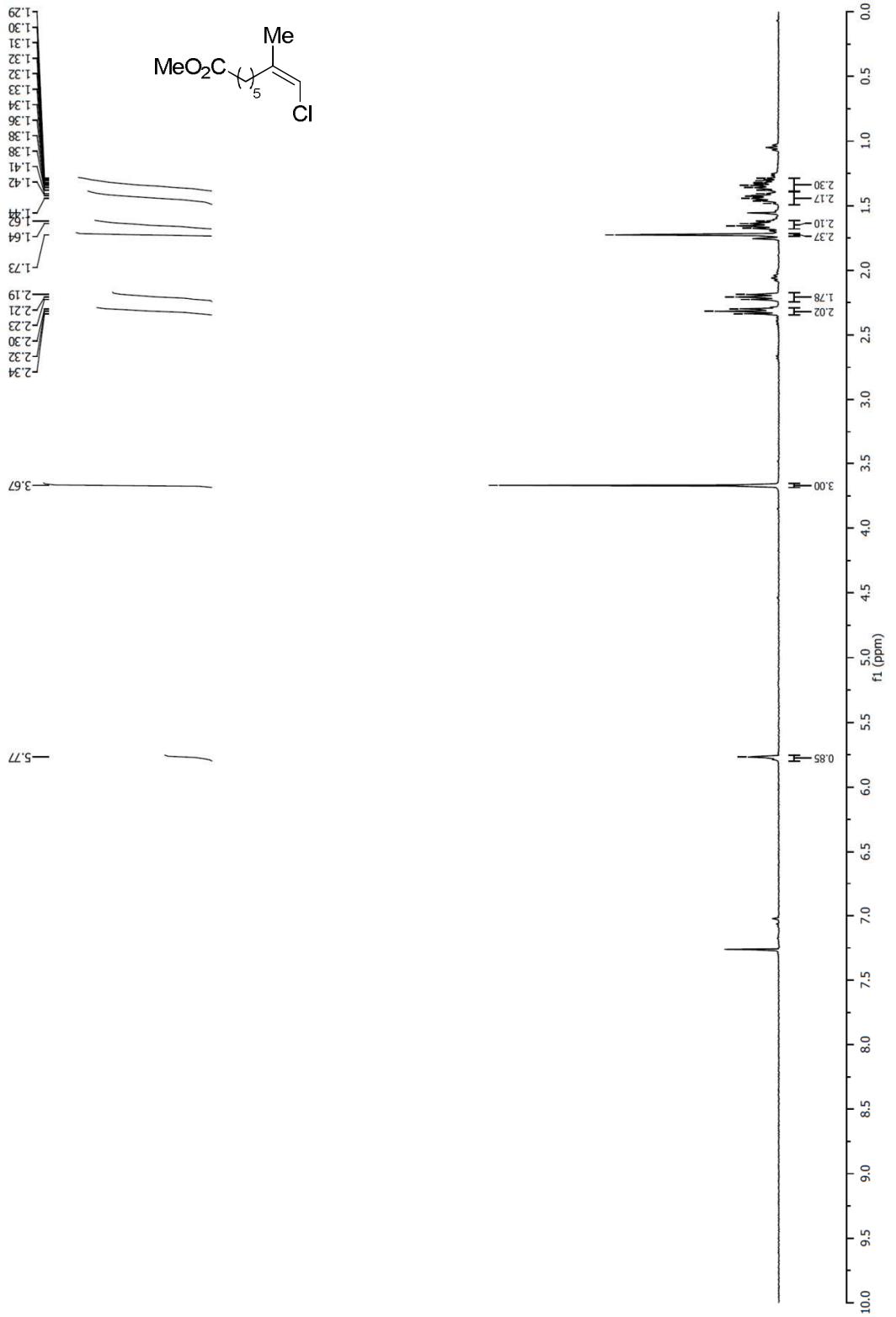
^{1}H NMR spectrum of 4.30



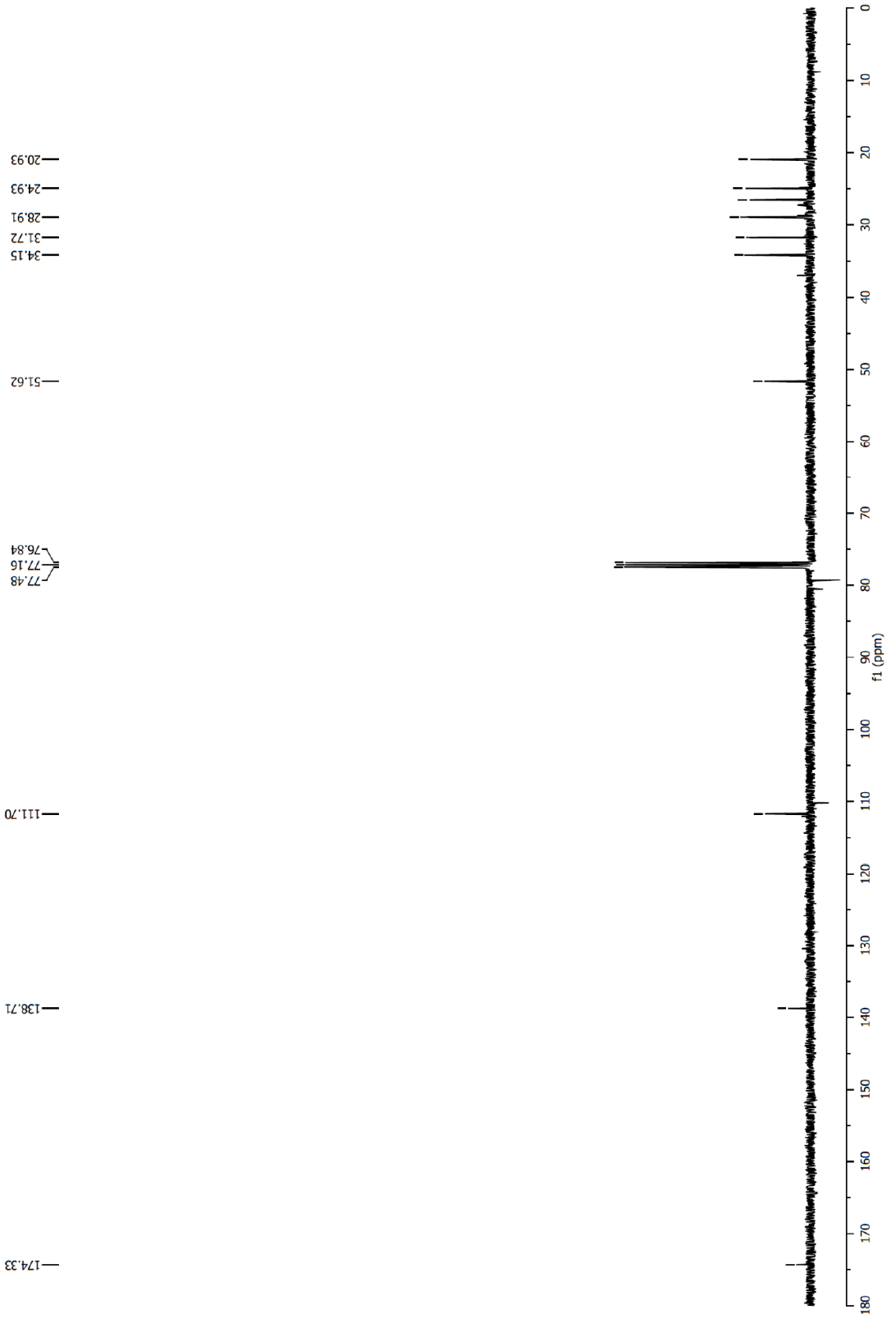
^{13}C NMR spectrum of 4.30



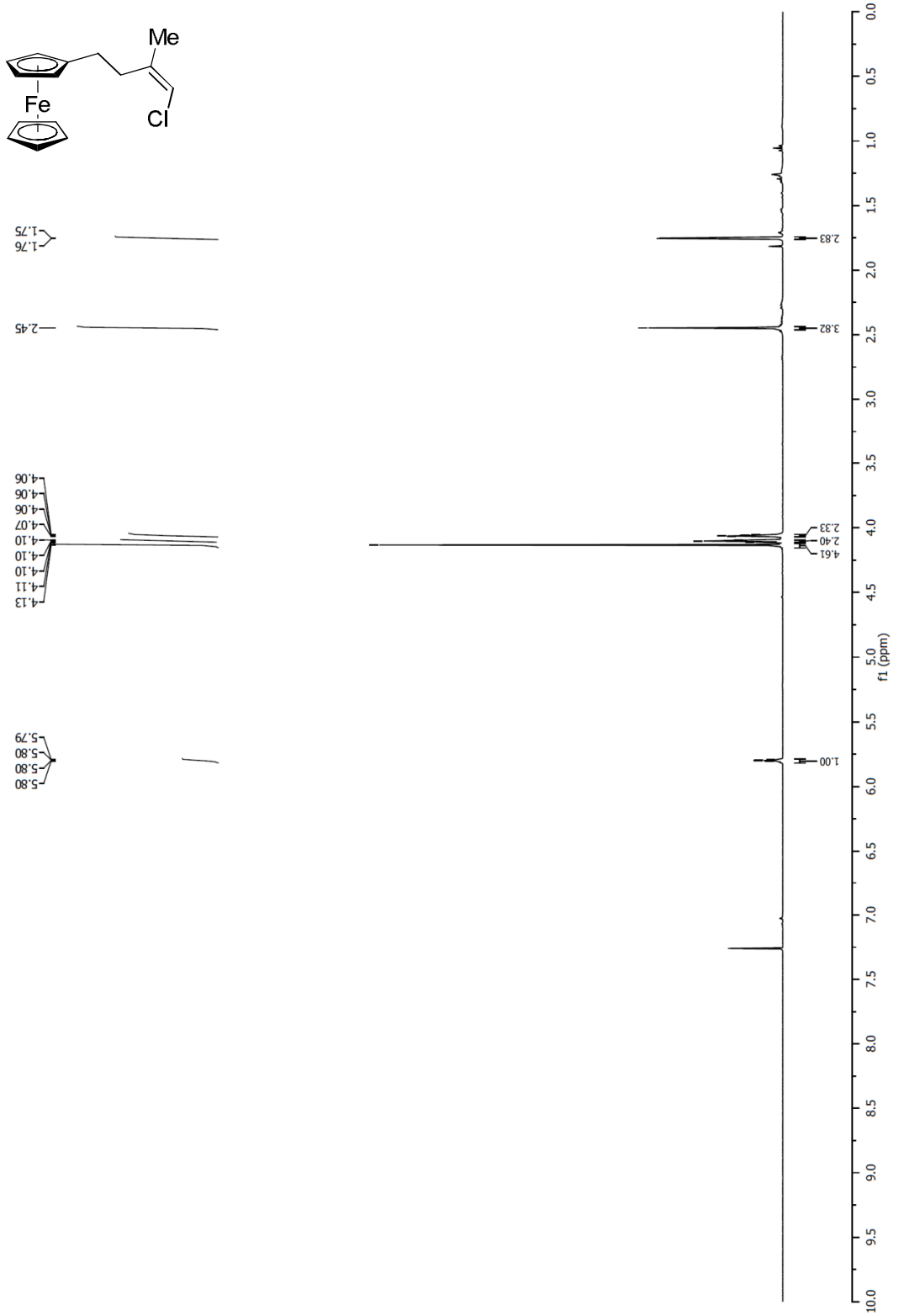
^{1}H NMR spectrum of 4.31



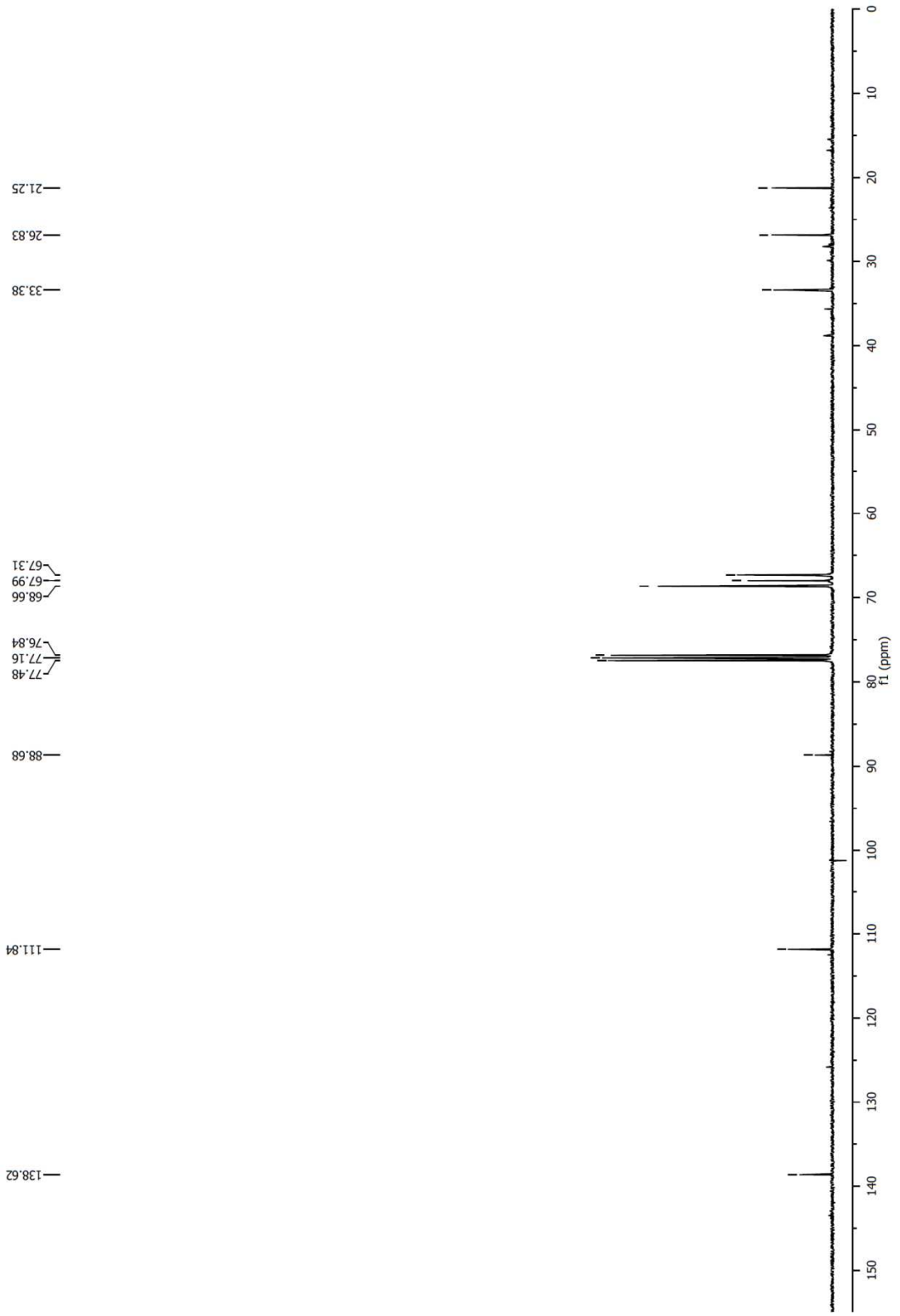
^{13}C NMR spectrum of 4.31



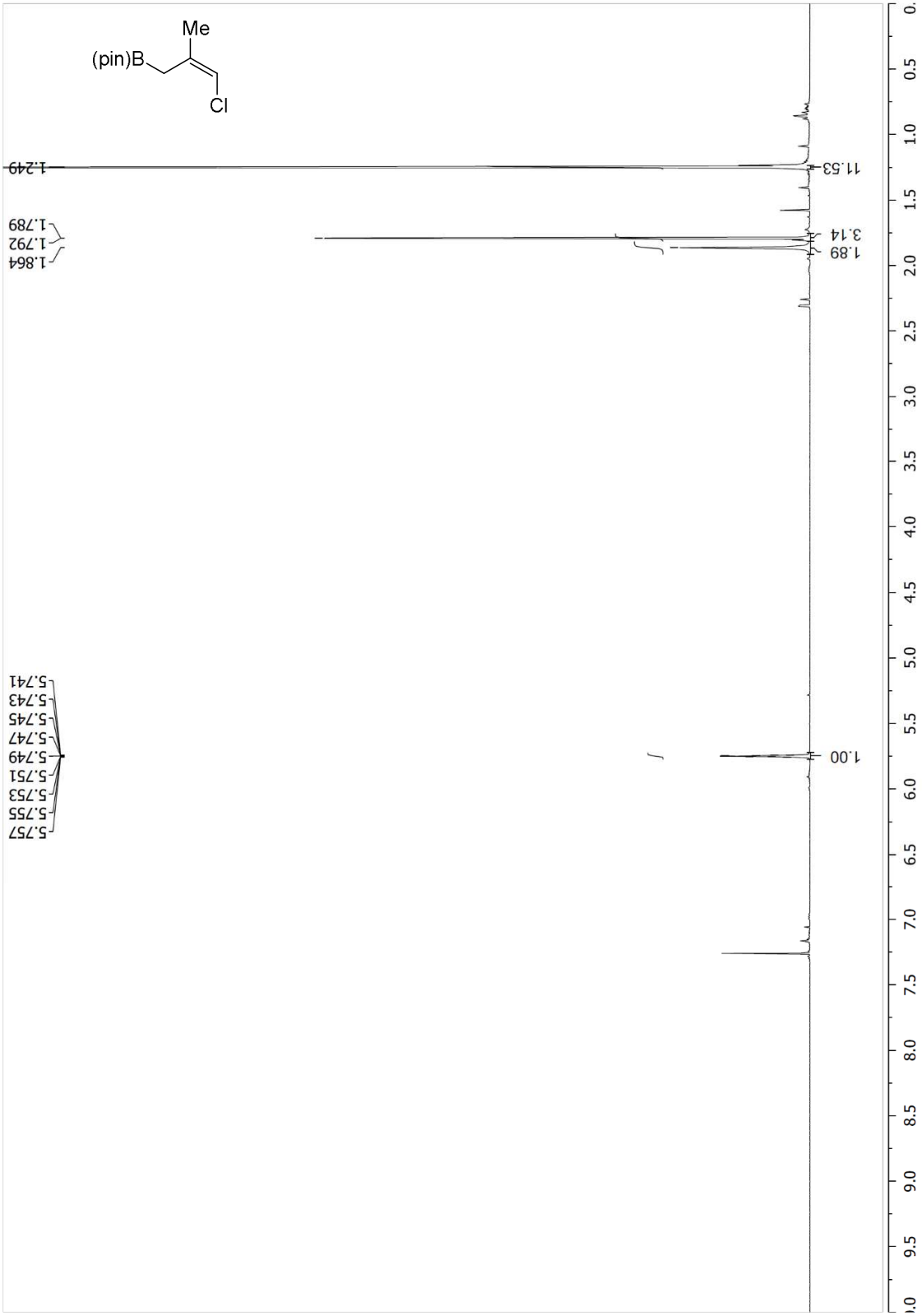
^{1}H NMR spectrum of 4.32



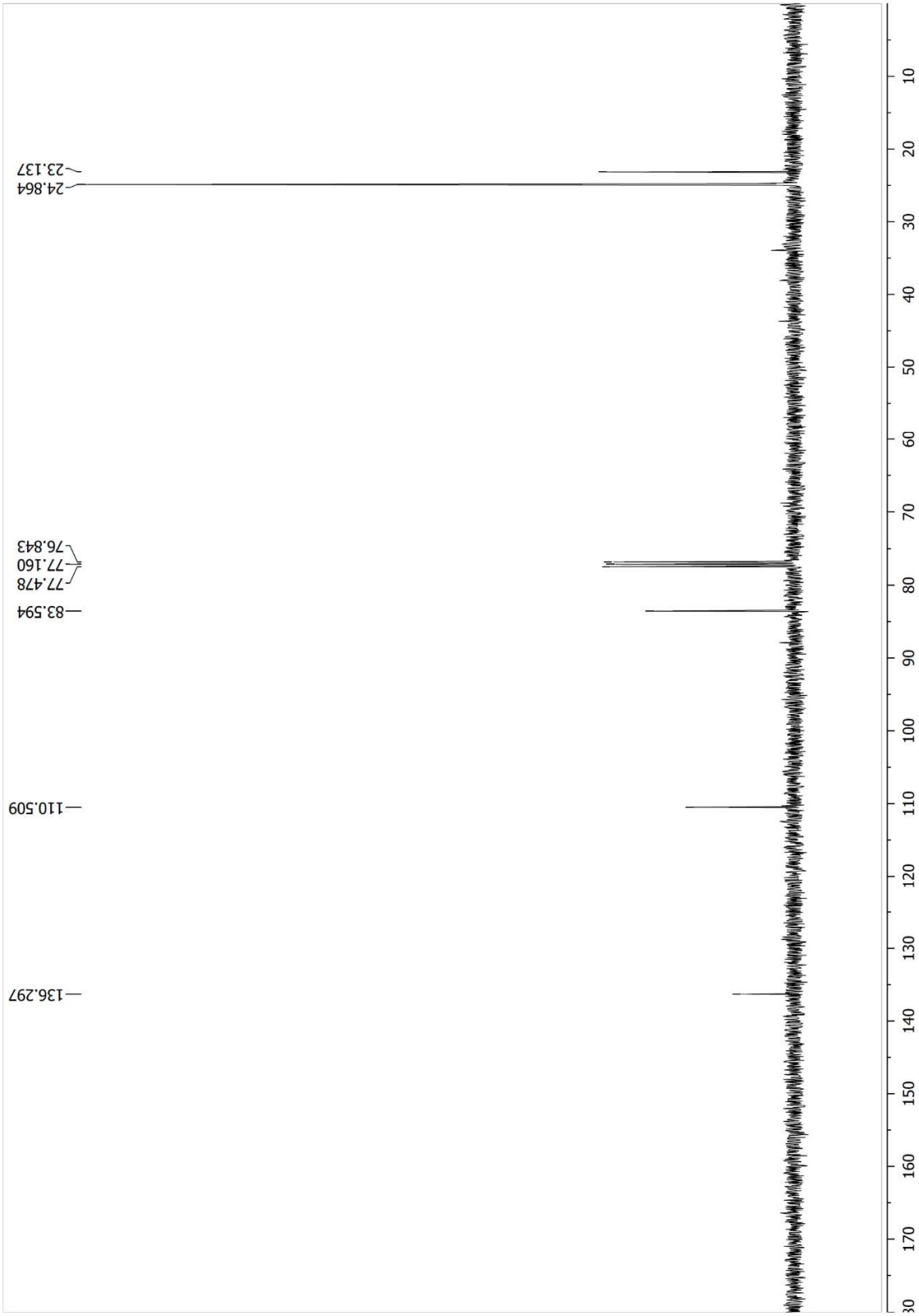
^{13}C NMR spectrum of 4.32



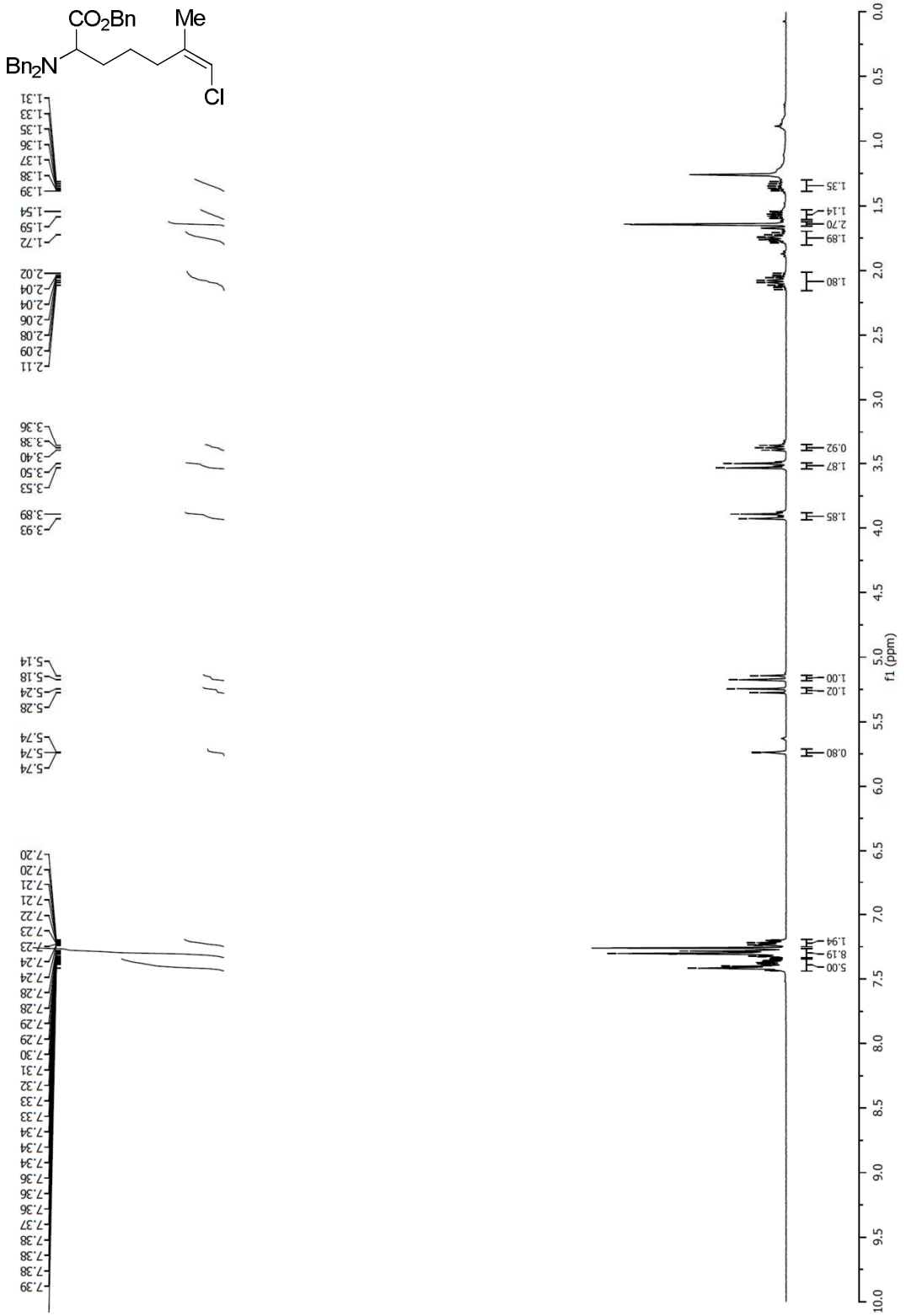
^{1}H NMR spectrum of 4.33



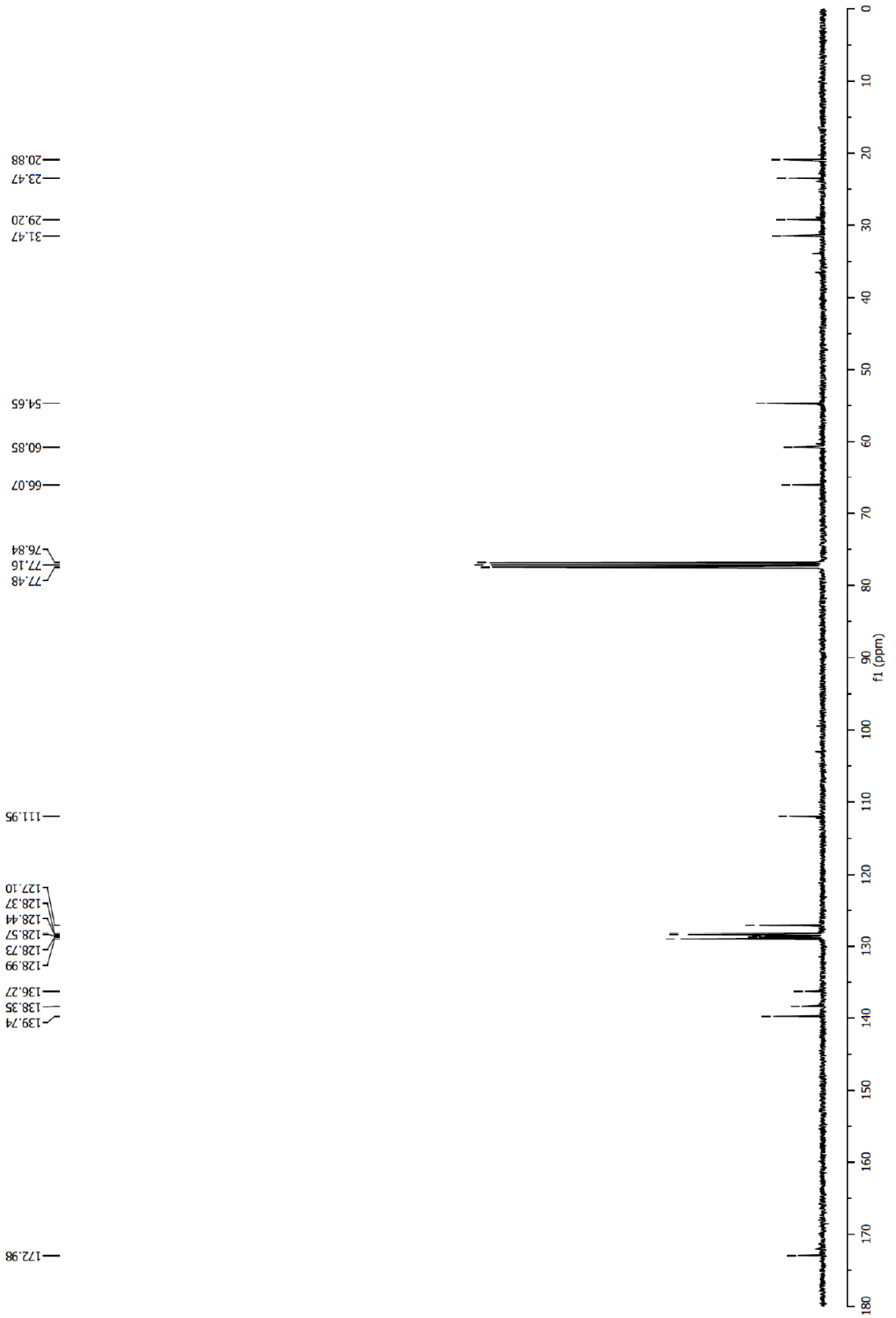
^{13}C NMR spectrum of 4.33



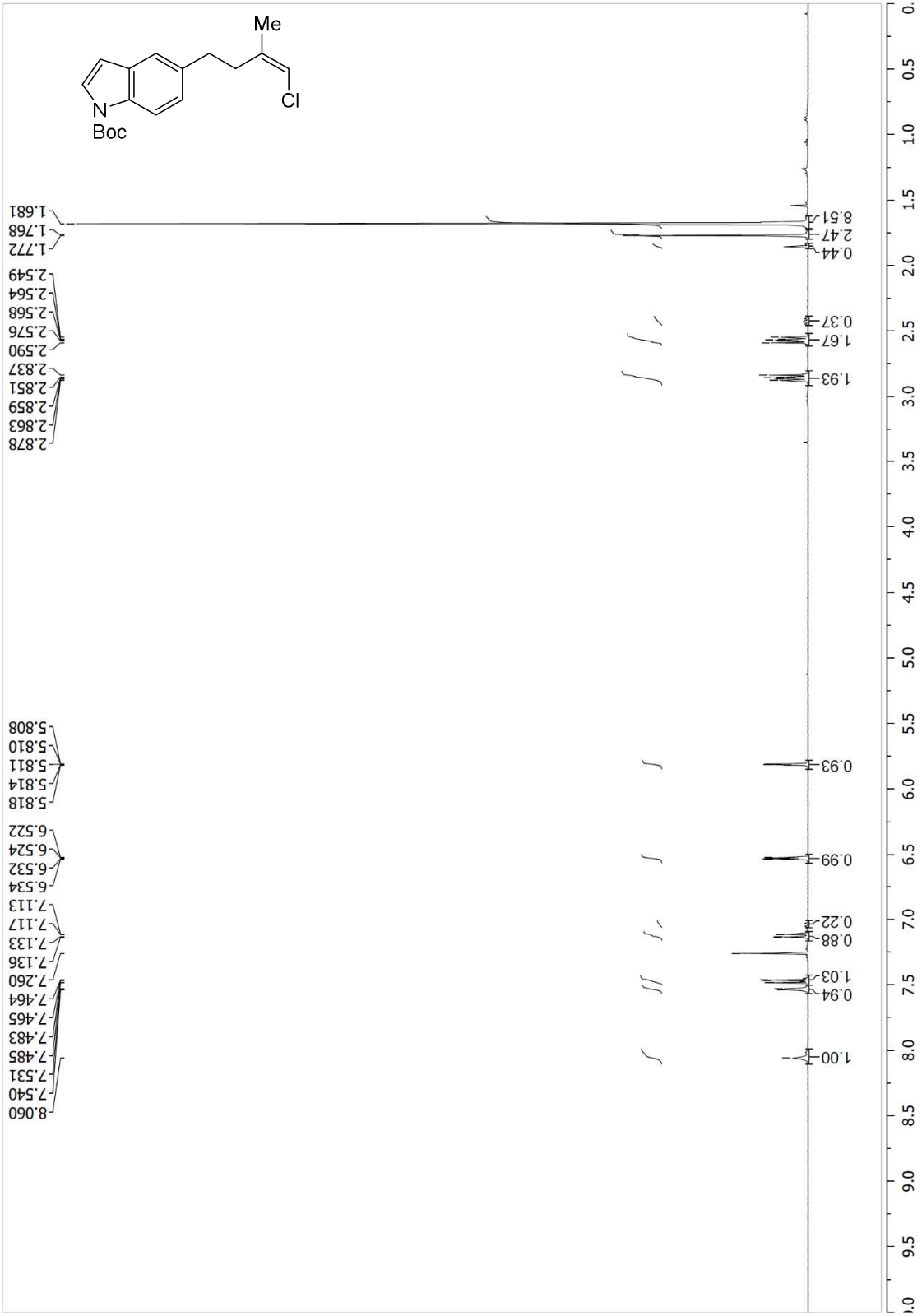
^{1}H NMR spectrum of 4.34



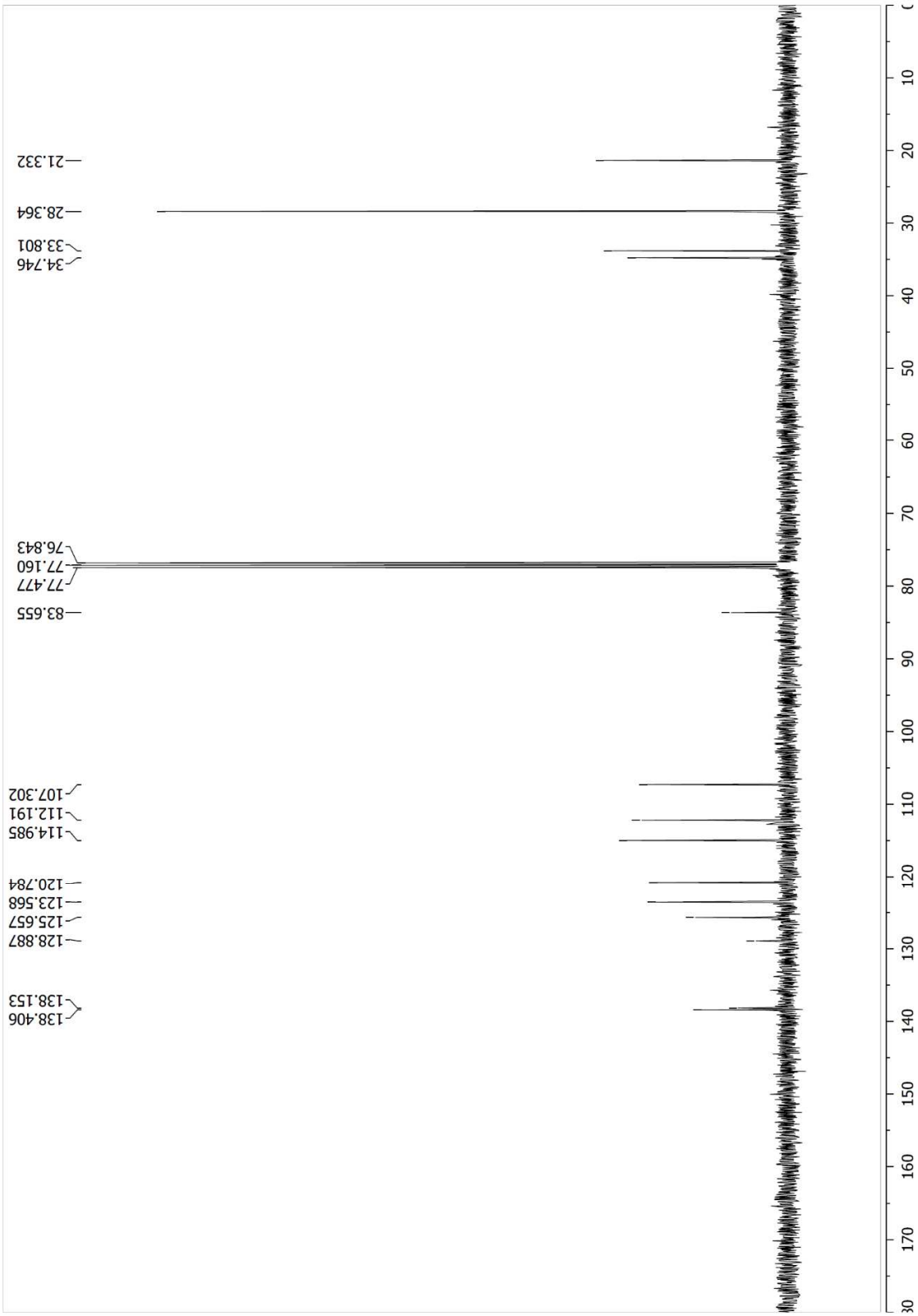
^{13}C NMR spectrum of 4.34



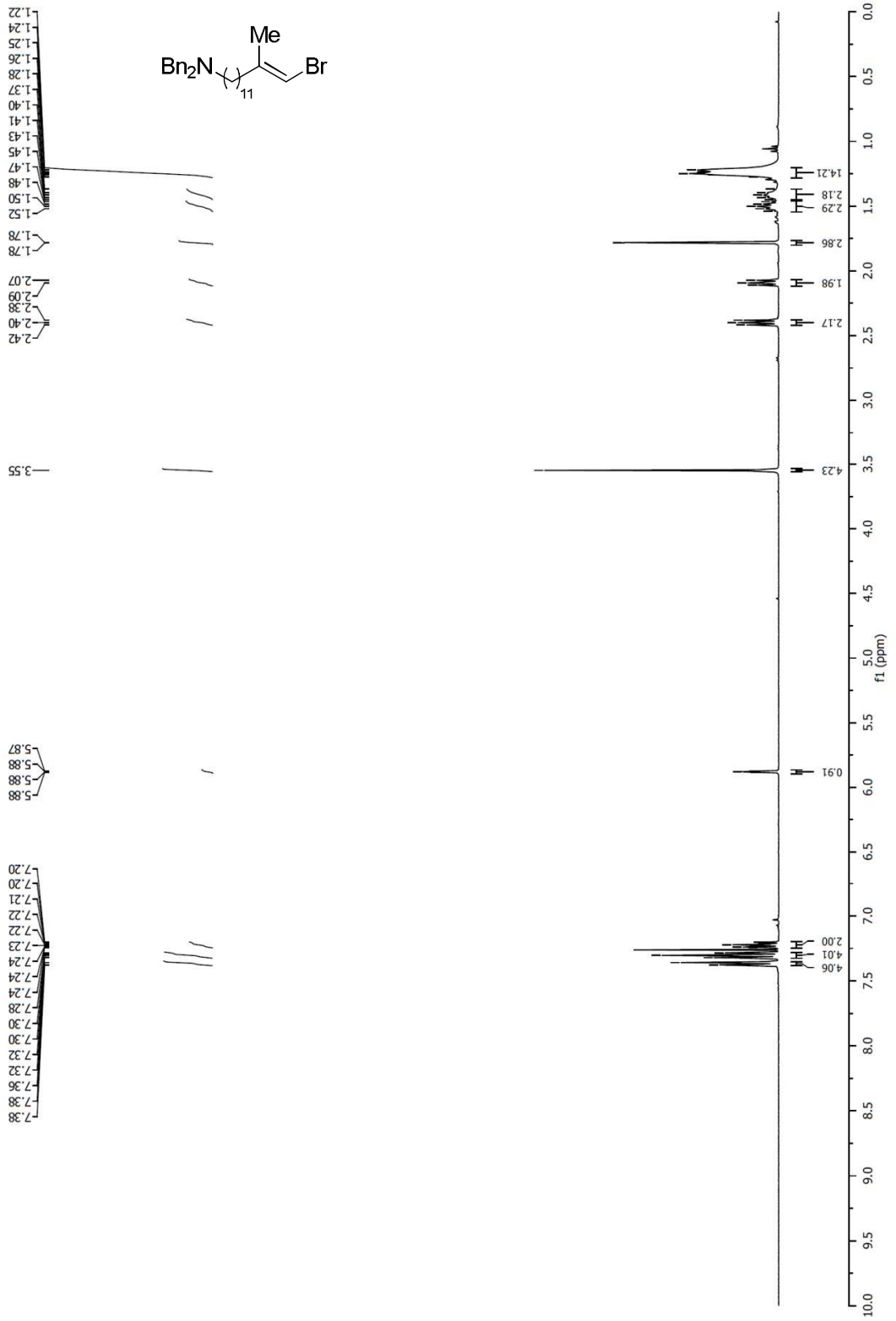
^{1}H NMR spectrum of 4.35



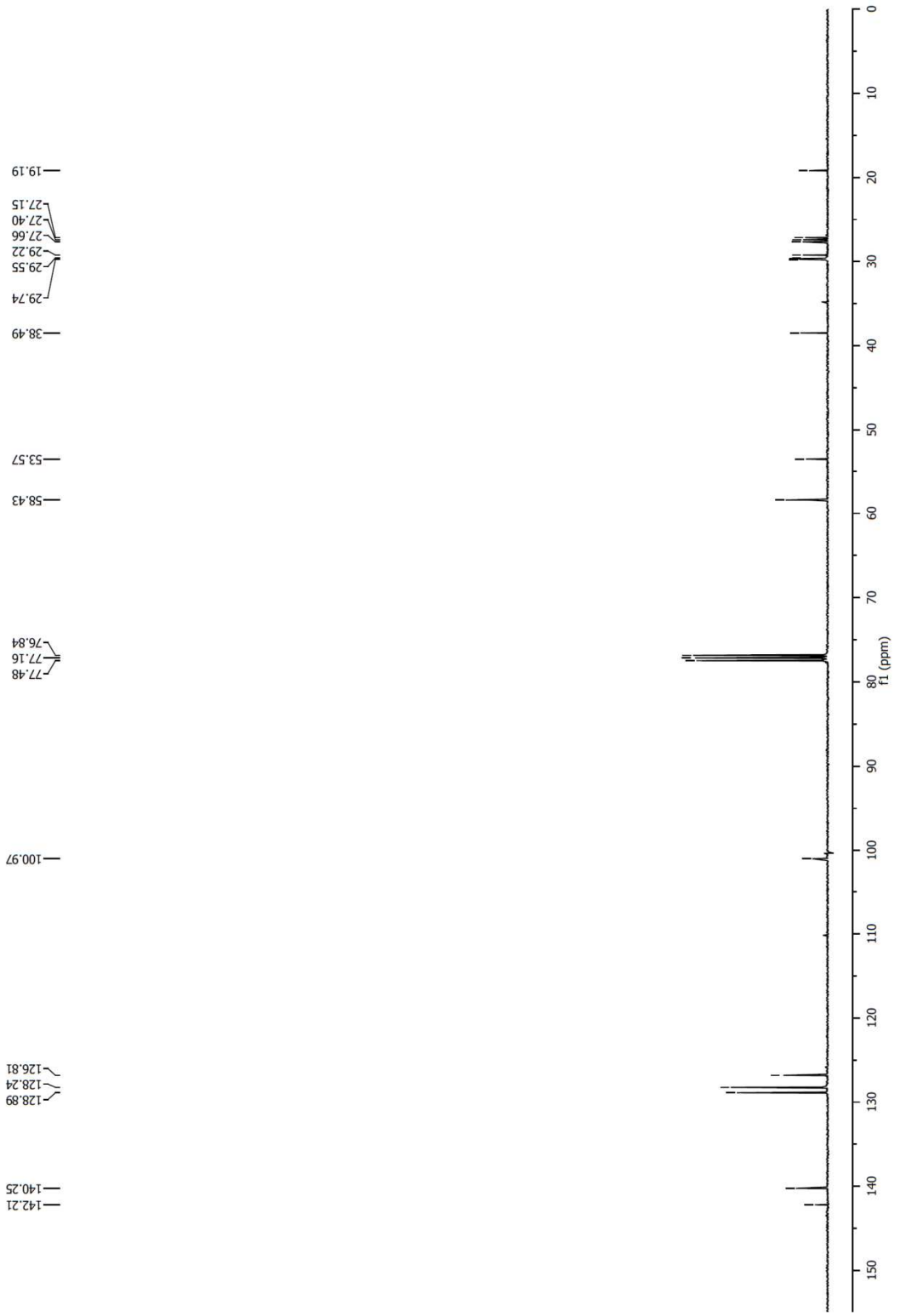
^{13}C NMR spectrum of 4.35



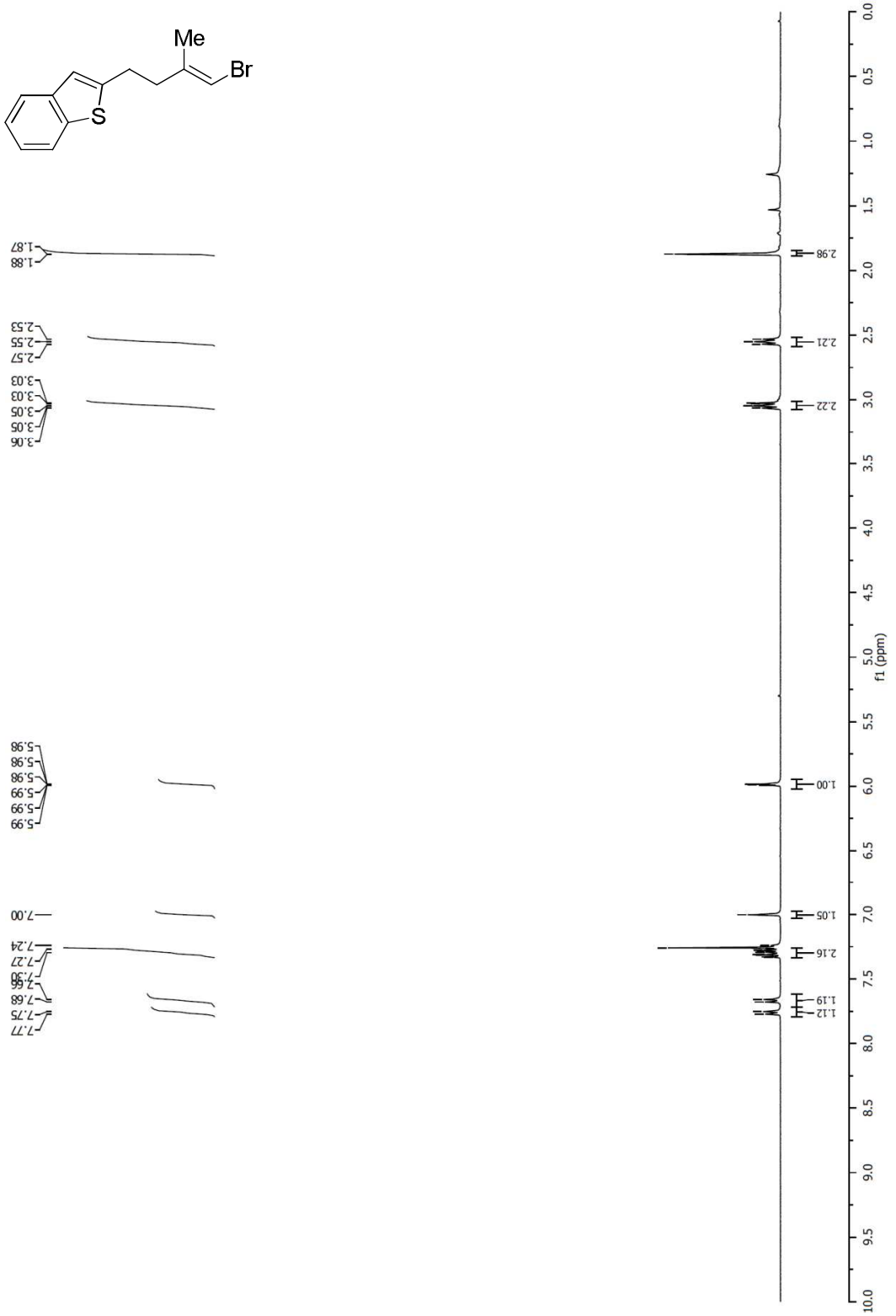
^{1}H NMR spectrum of 4.47



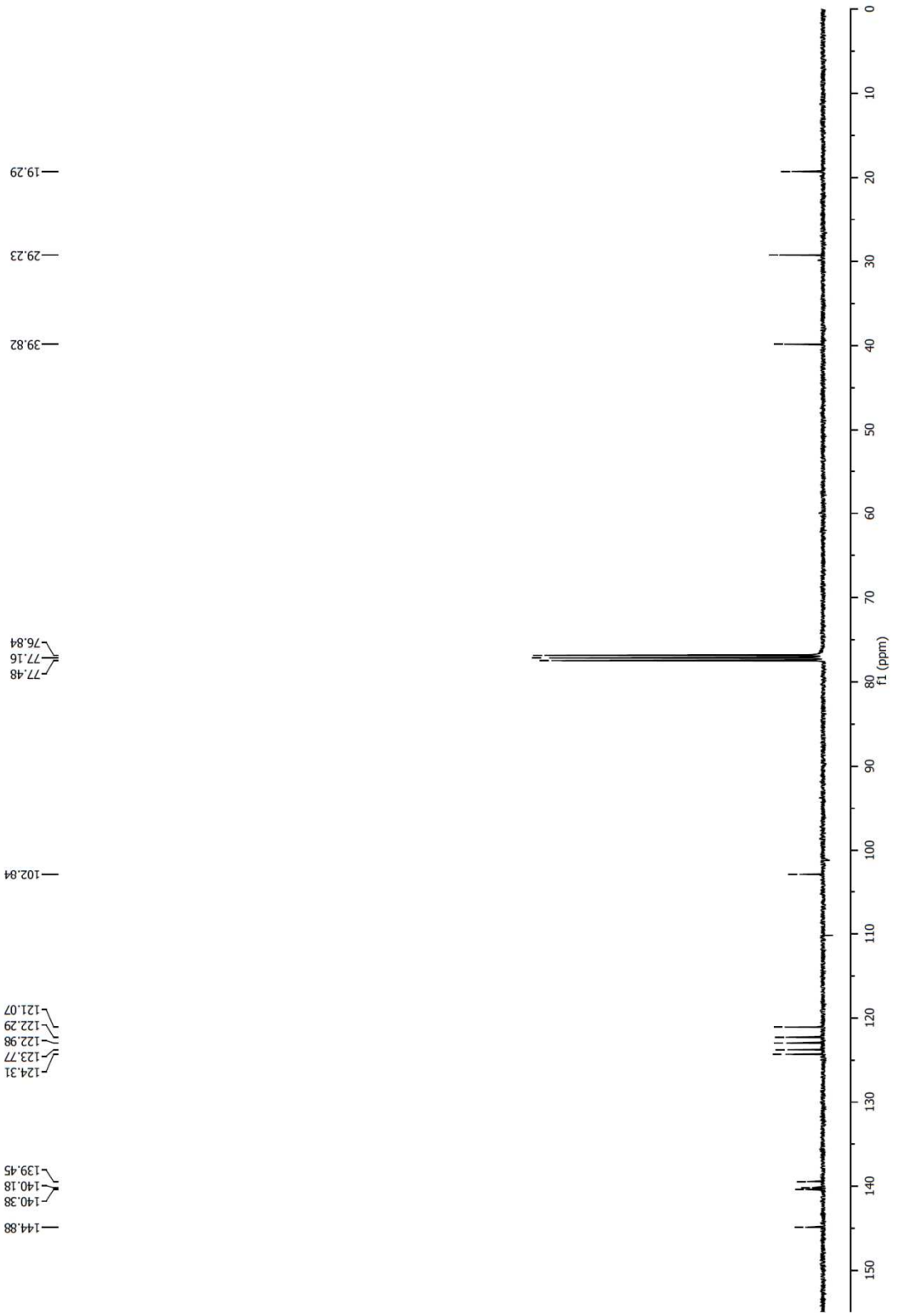
^{13}C NMR spectrum of 4.47



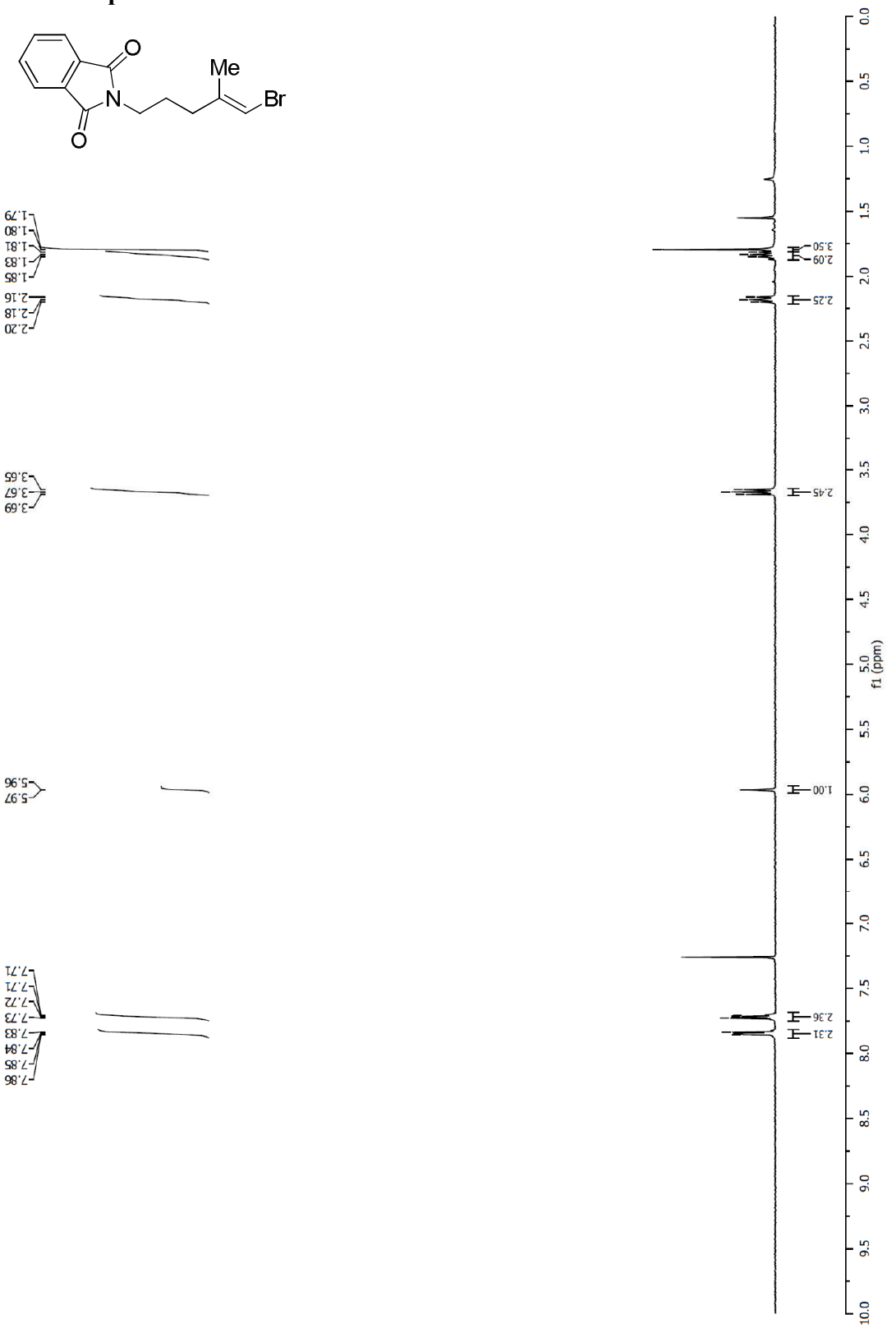
^{1}H NMR spectrum of 4.48



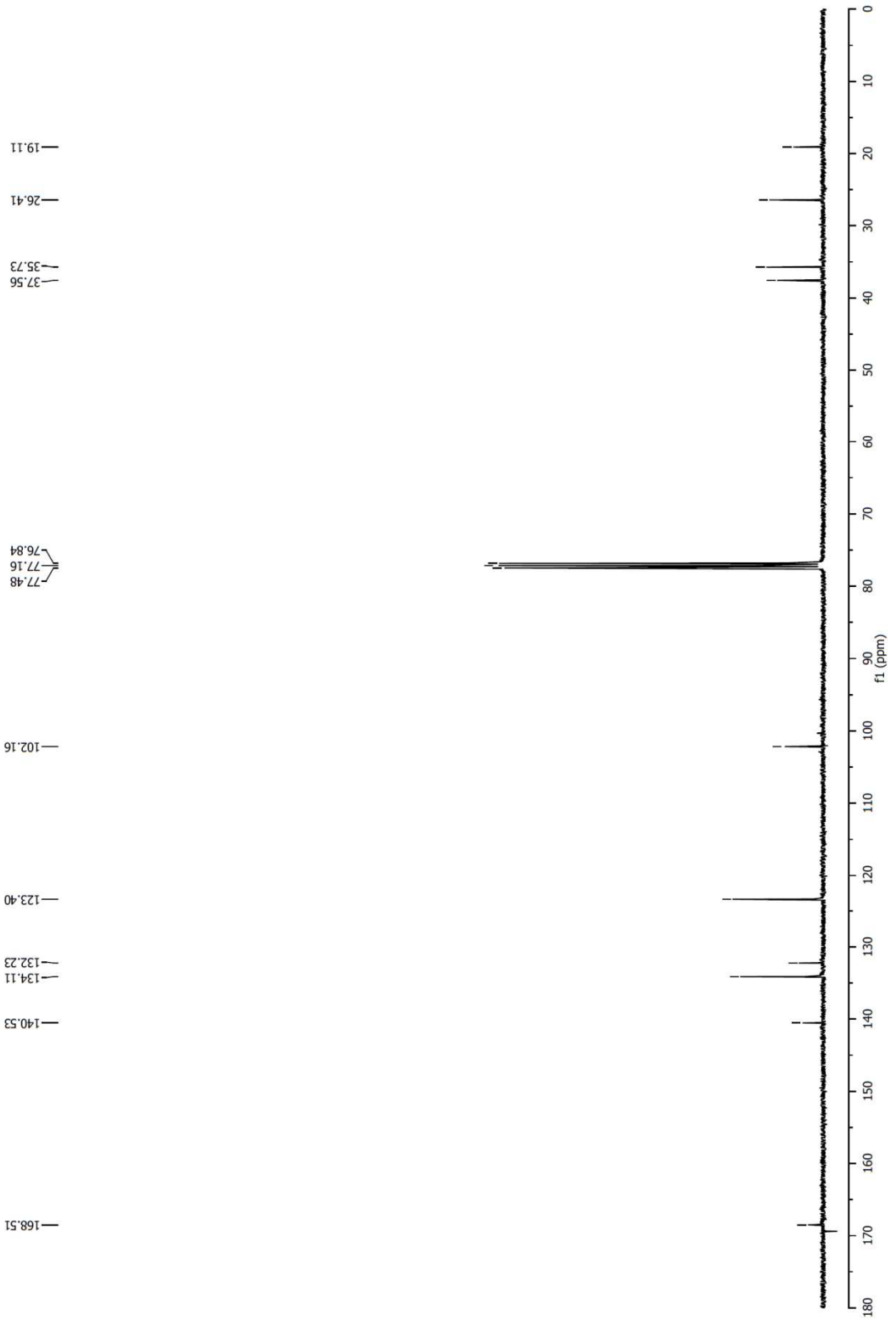
^{13}C NMR spectrum of 4.48



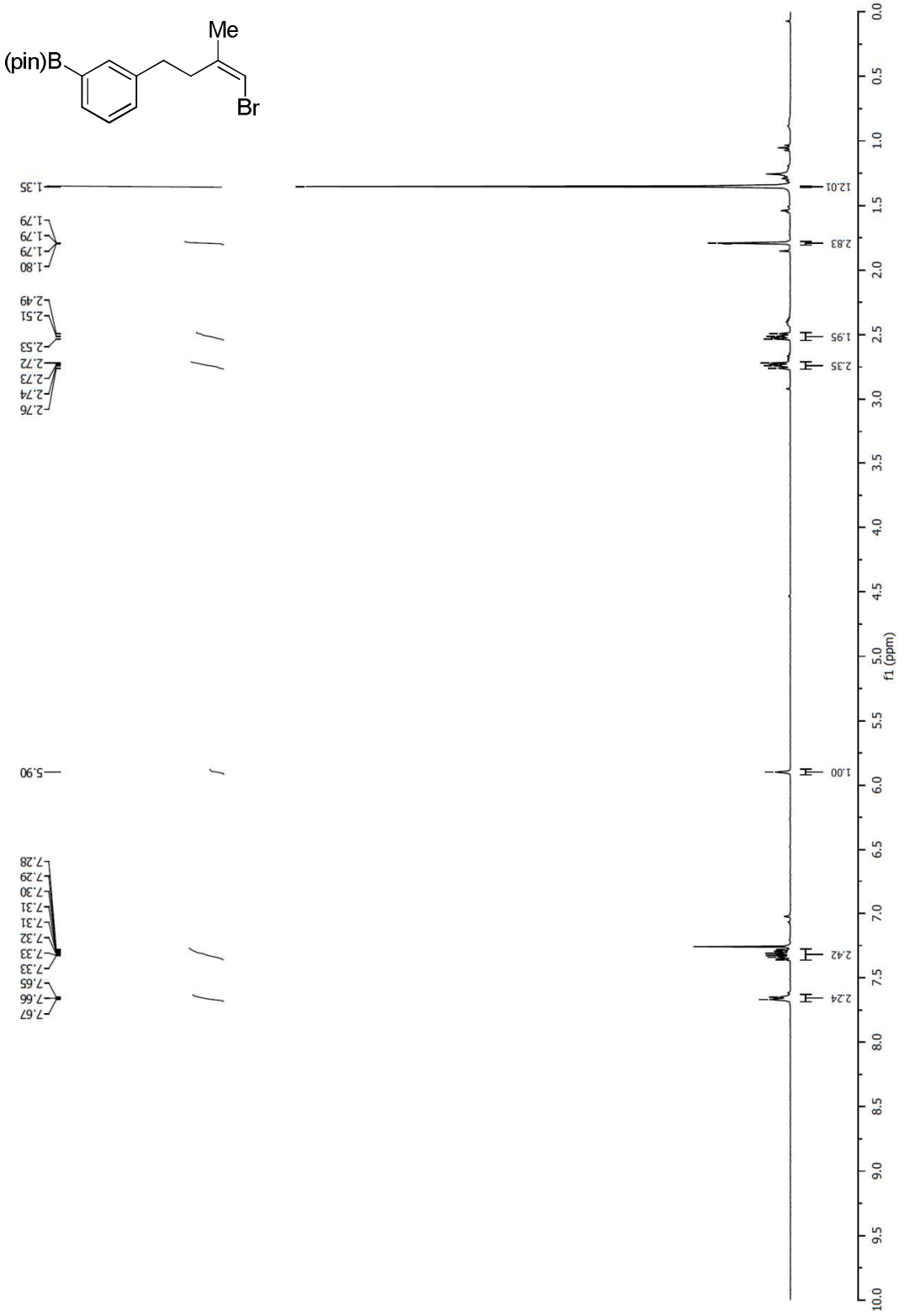
^{1}H NMR spectrum of 4.49



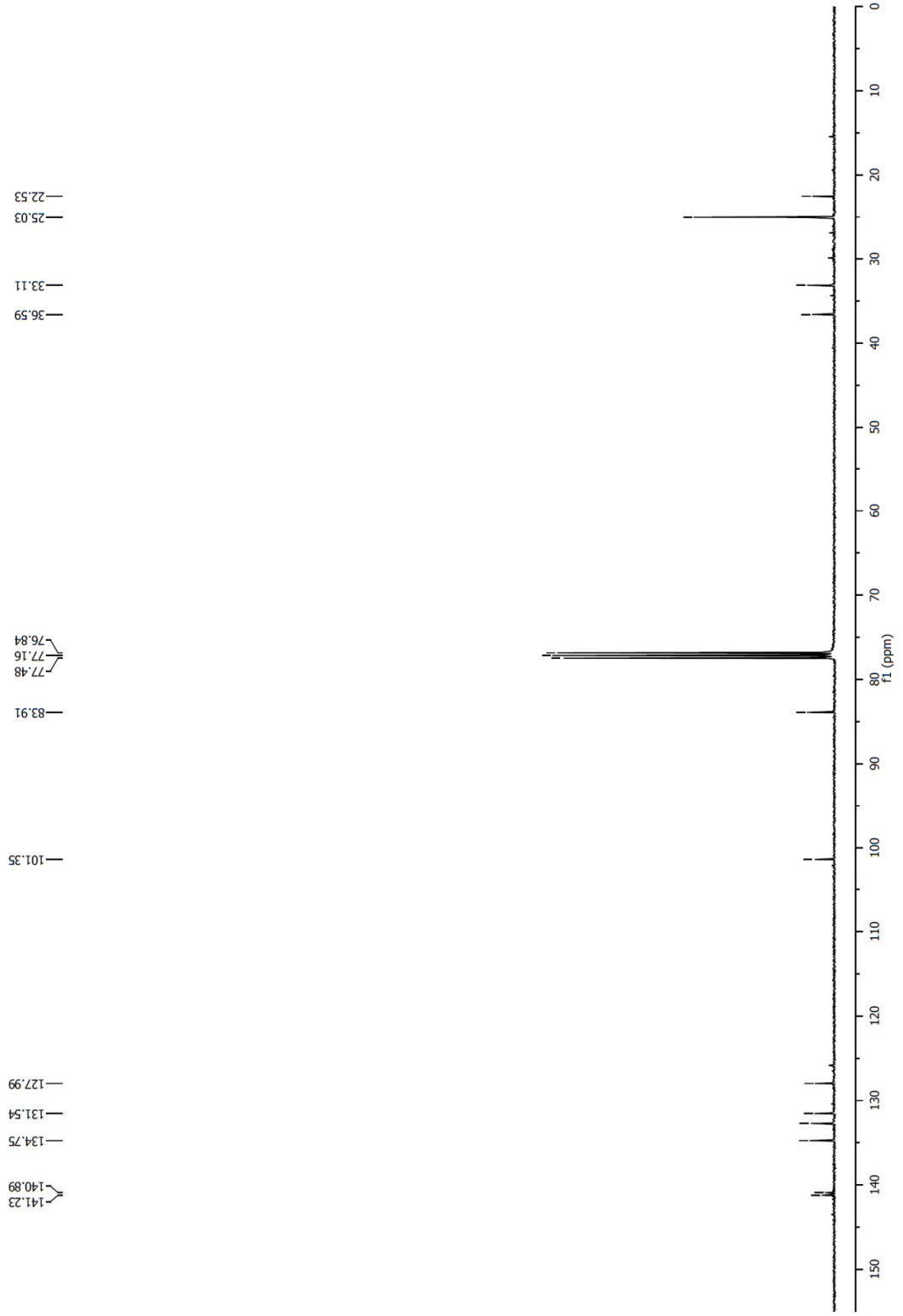
^{13}C NMR spectrum of 4.49



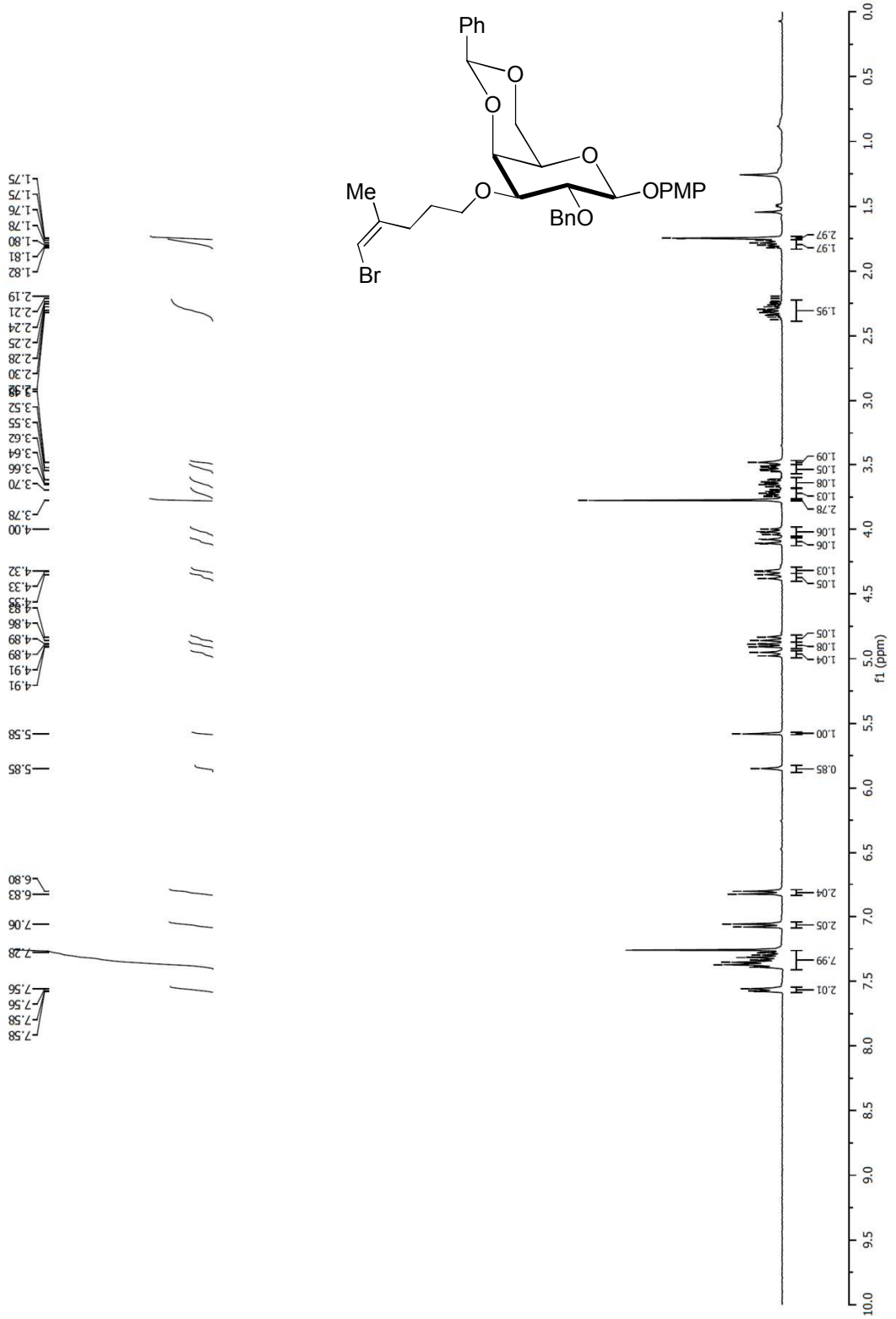
^{1}H NMR spectrum of 4.50



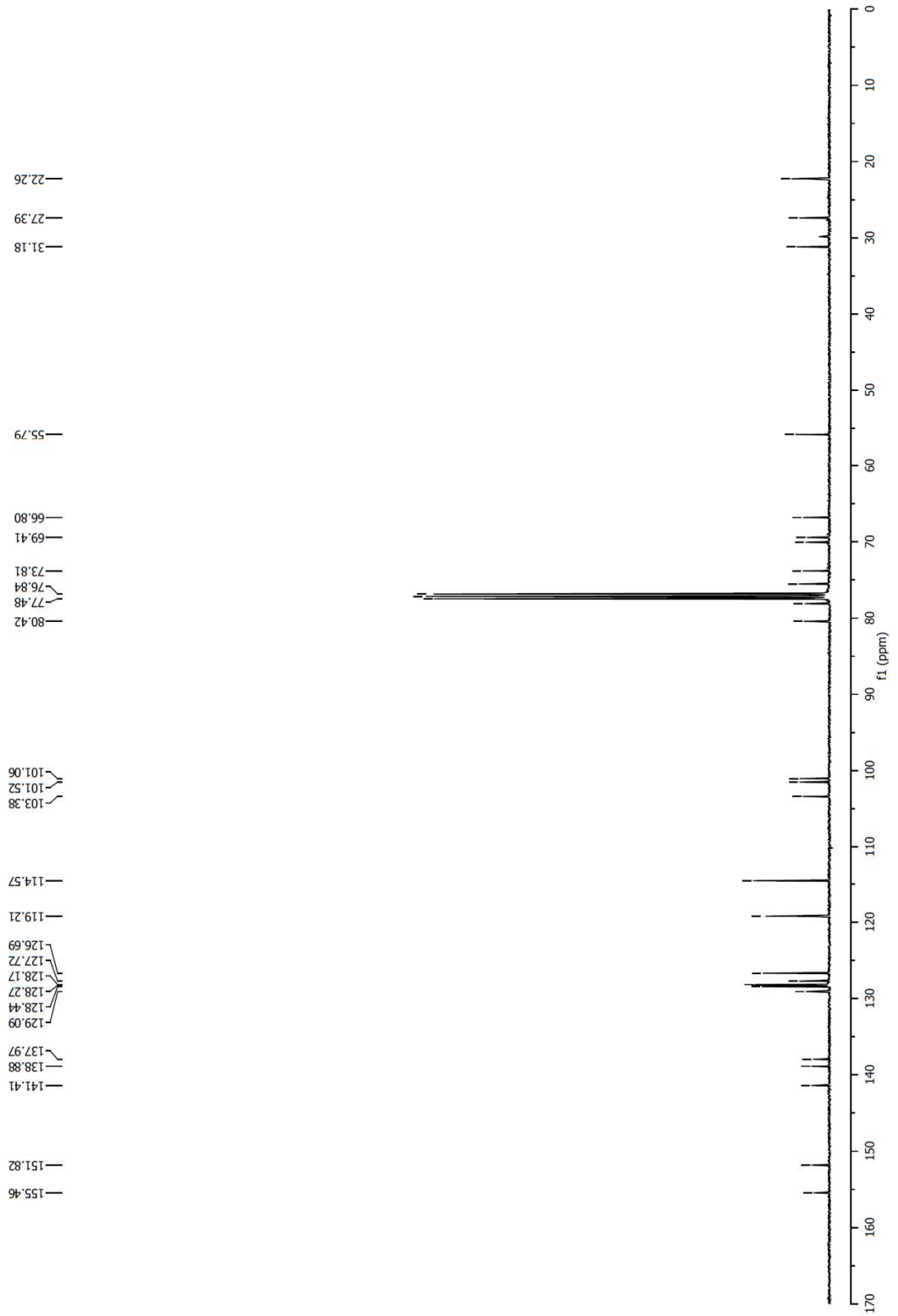
^{13}C NMR spectrum of 4.50



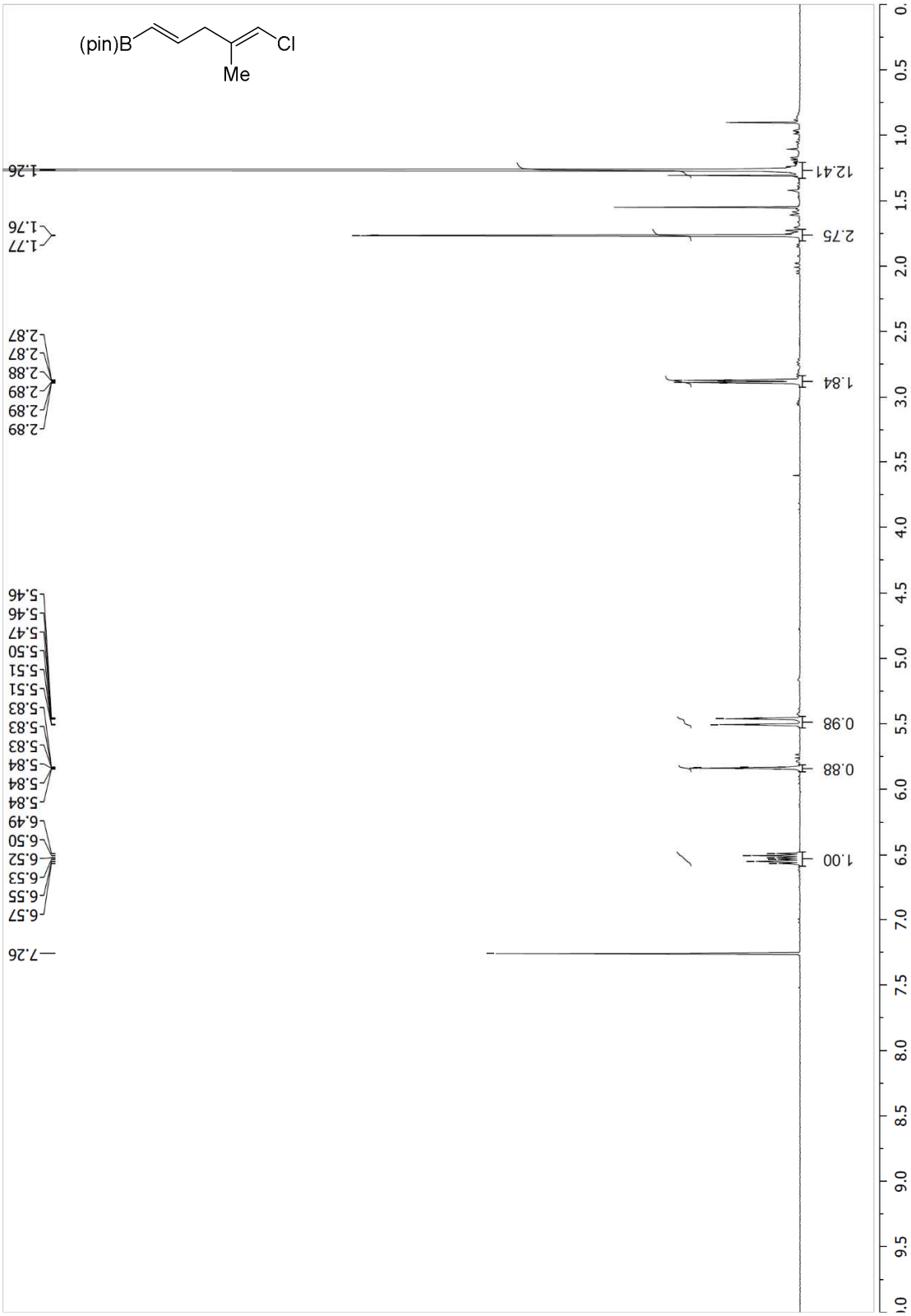
^{1}H NMR spectrum of 4.51



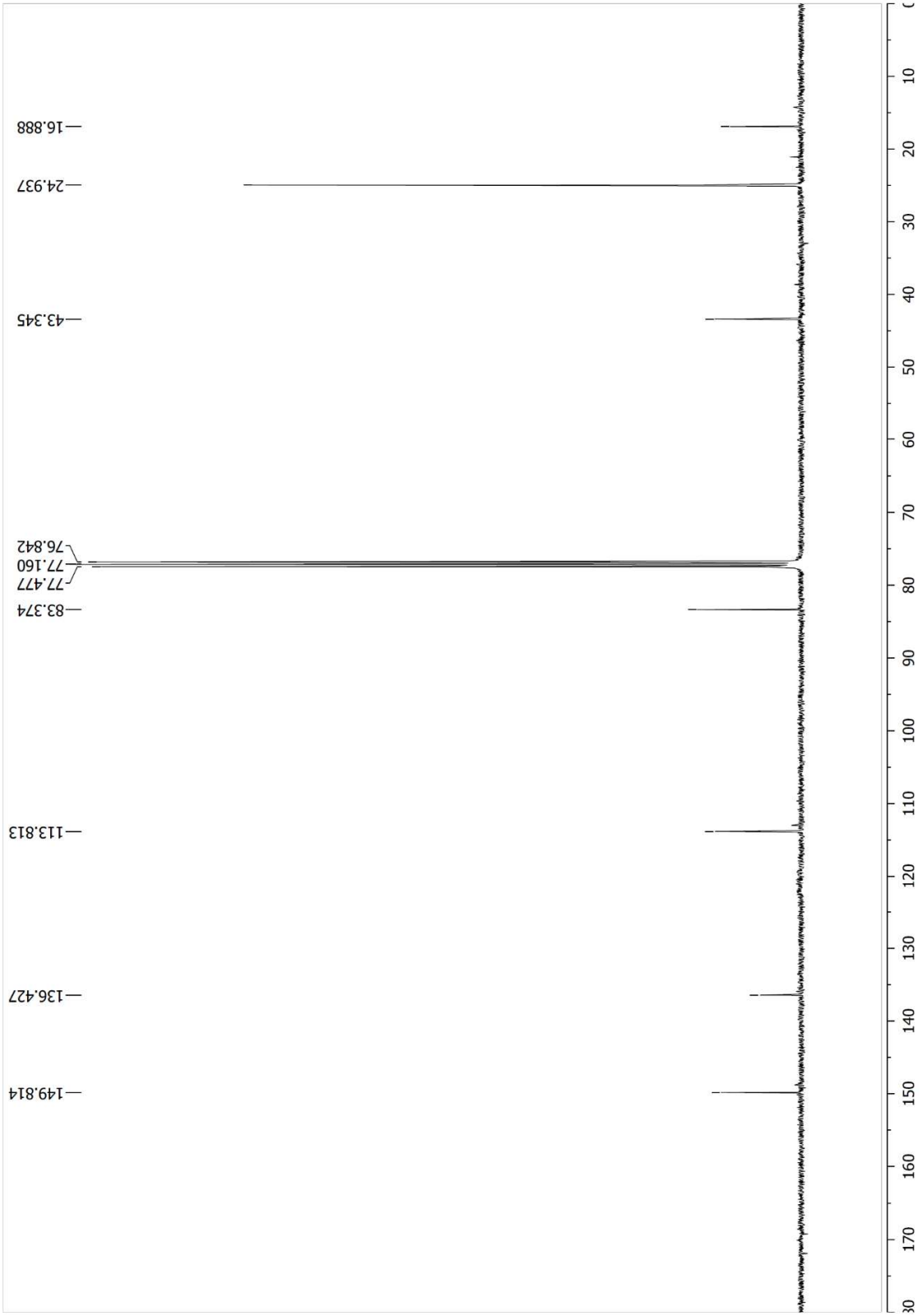
^{13}C NMR spectrum of 4.51



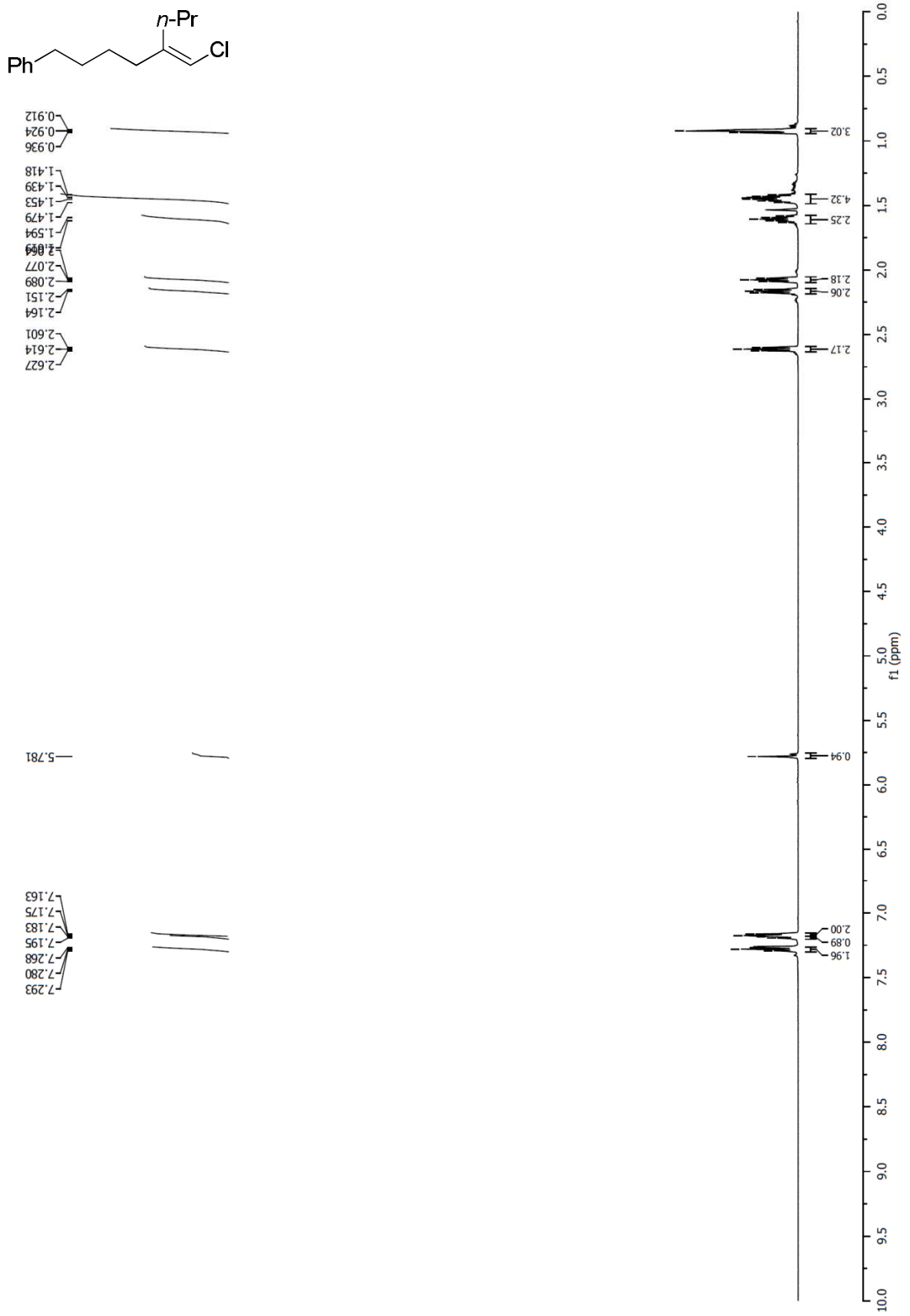
^{1}H NMR spectrum of 4.64



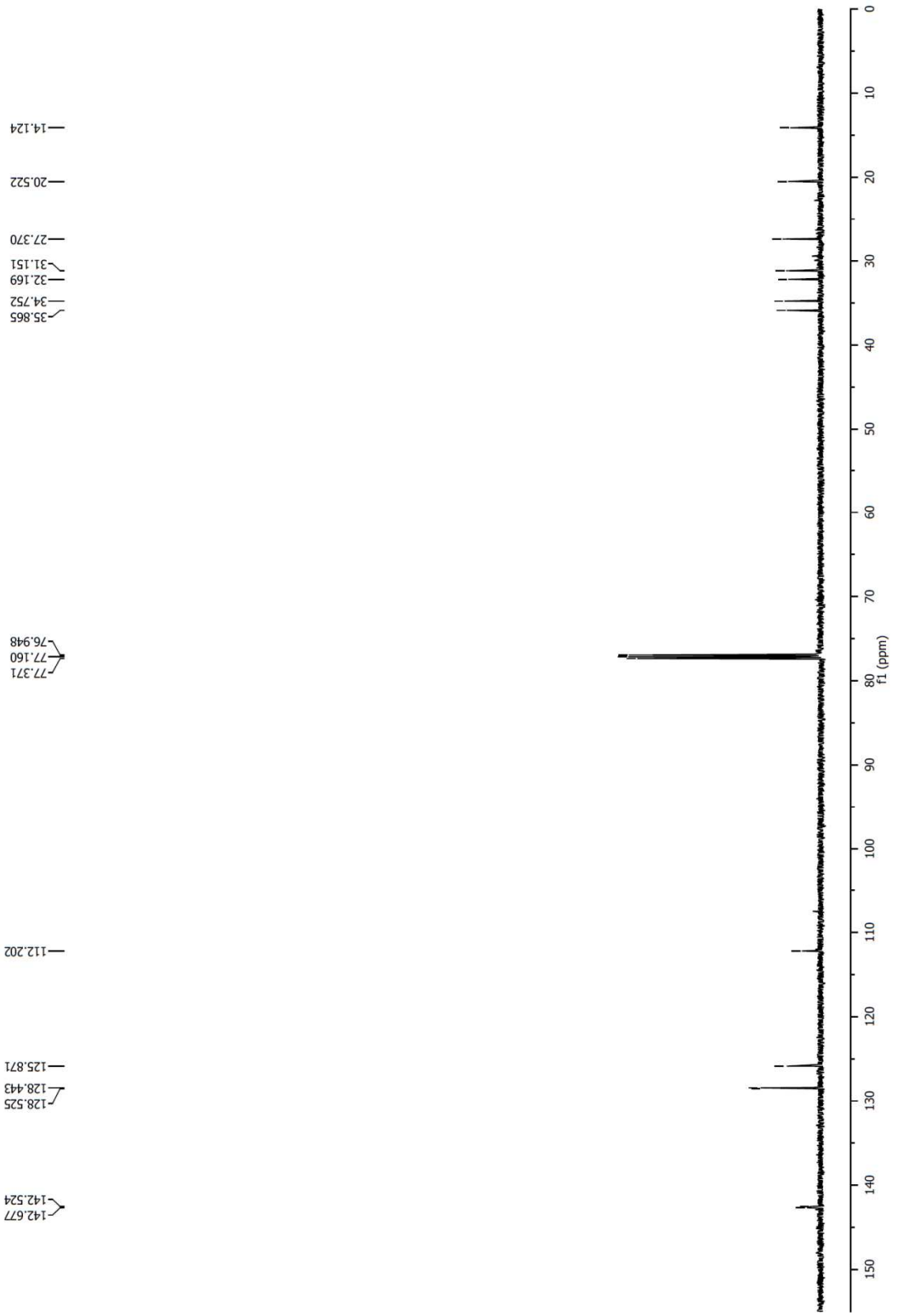
^{13}C NMR spectrum of 4.64



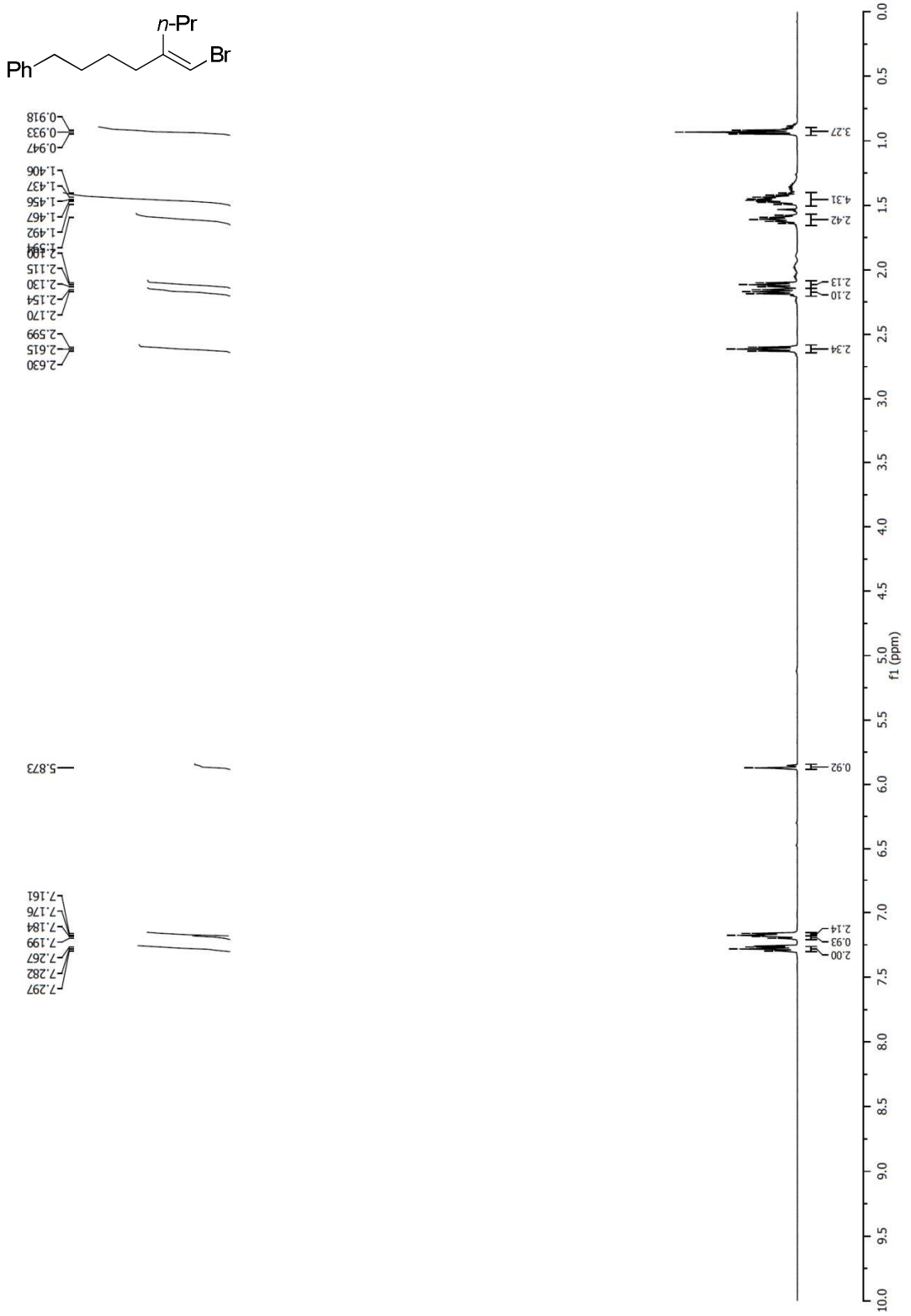
^{1}H NMR spectrum of 4.72



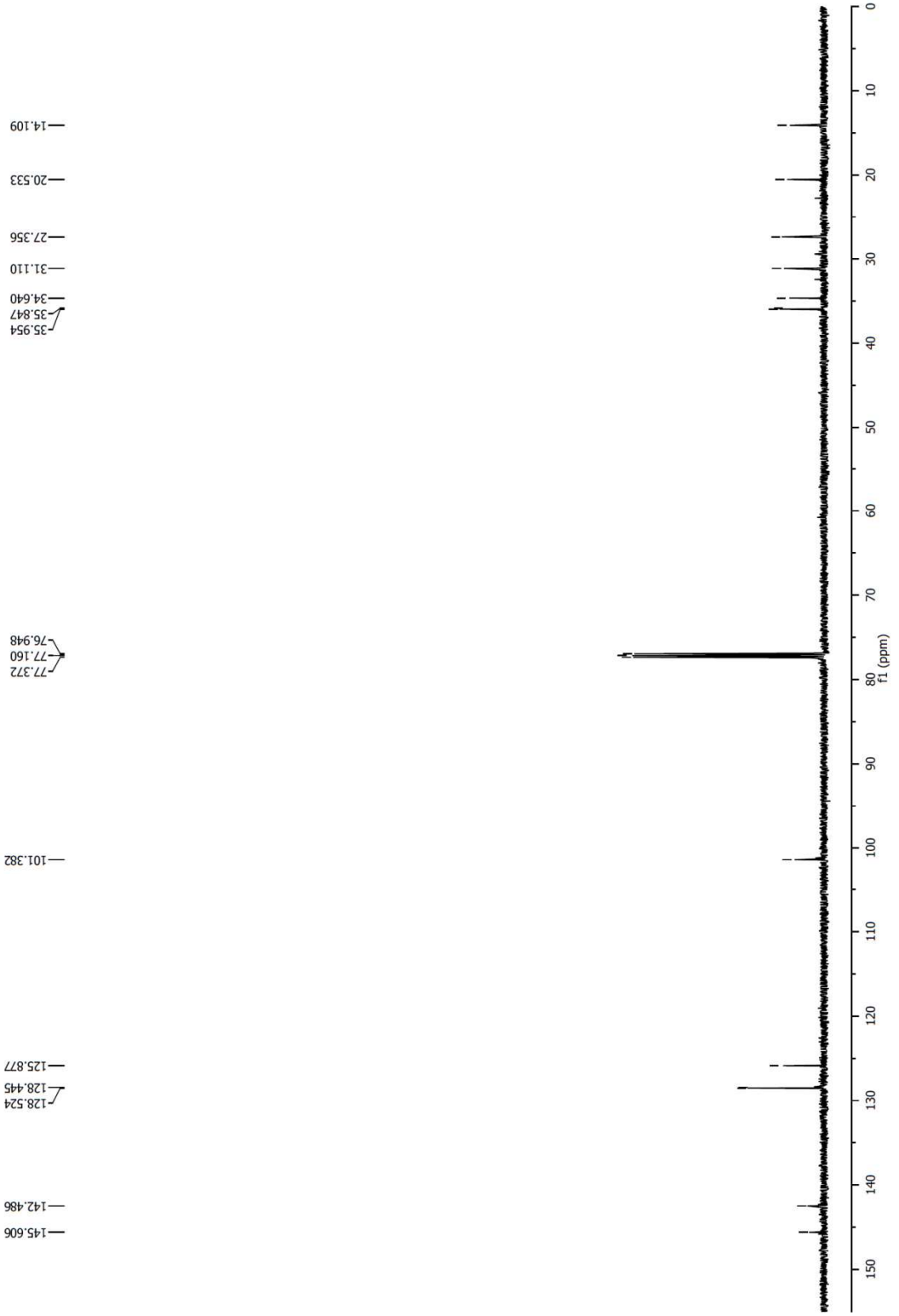
^{13}C NMR spectrum of 4.72



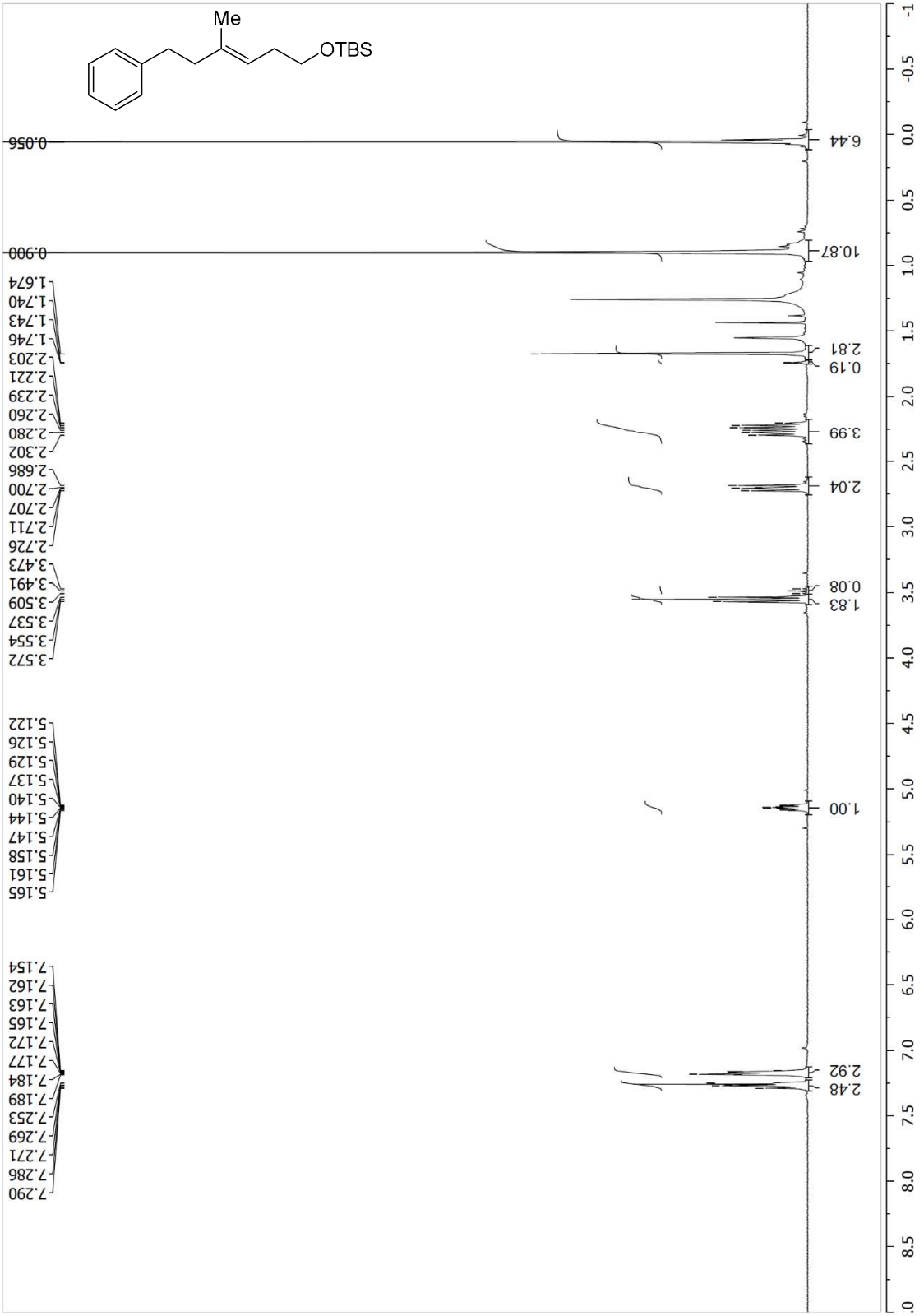
^{1}H NMR spectrum of 4.73



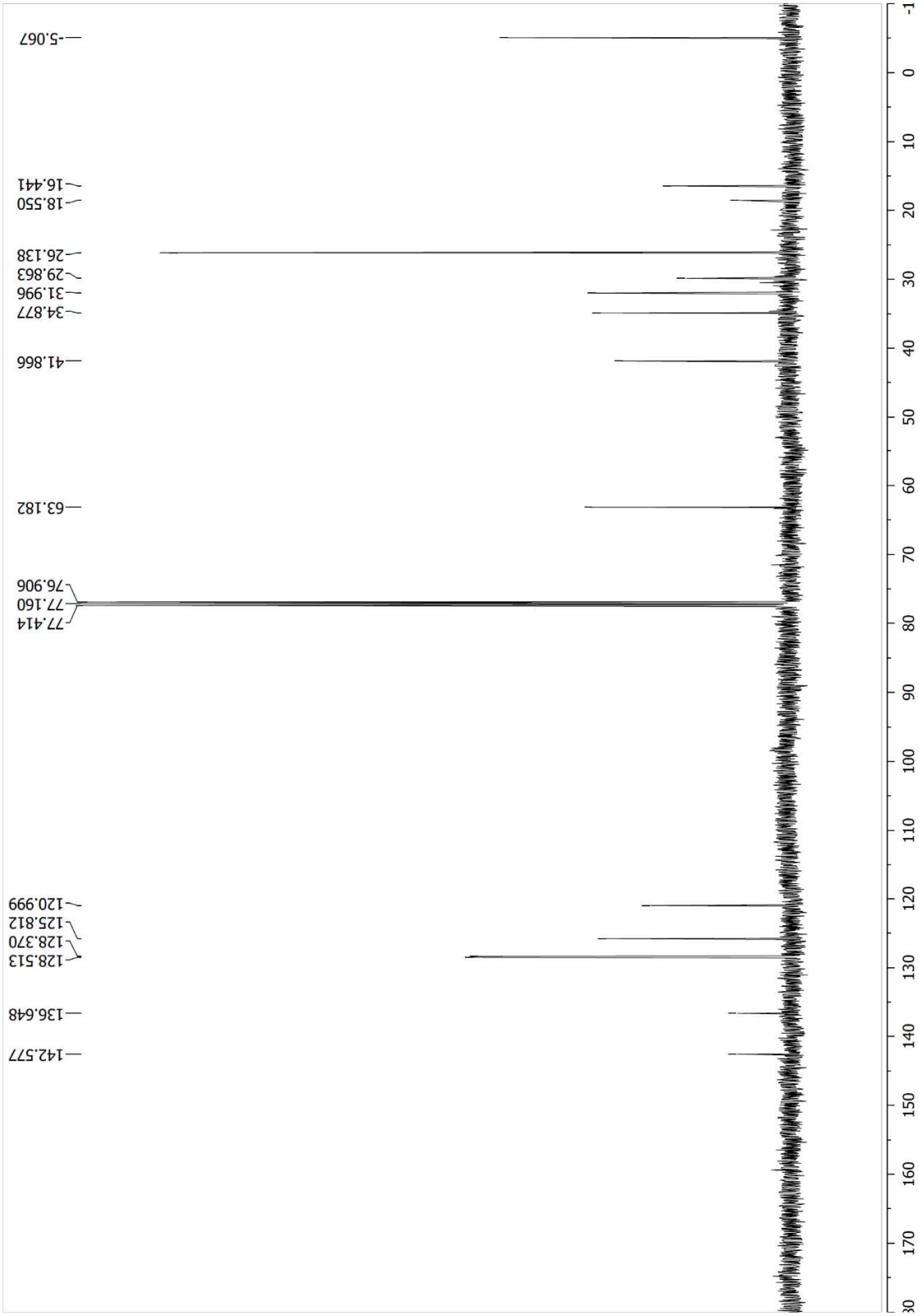
^{13}C NMR spectrum of 4.73



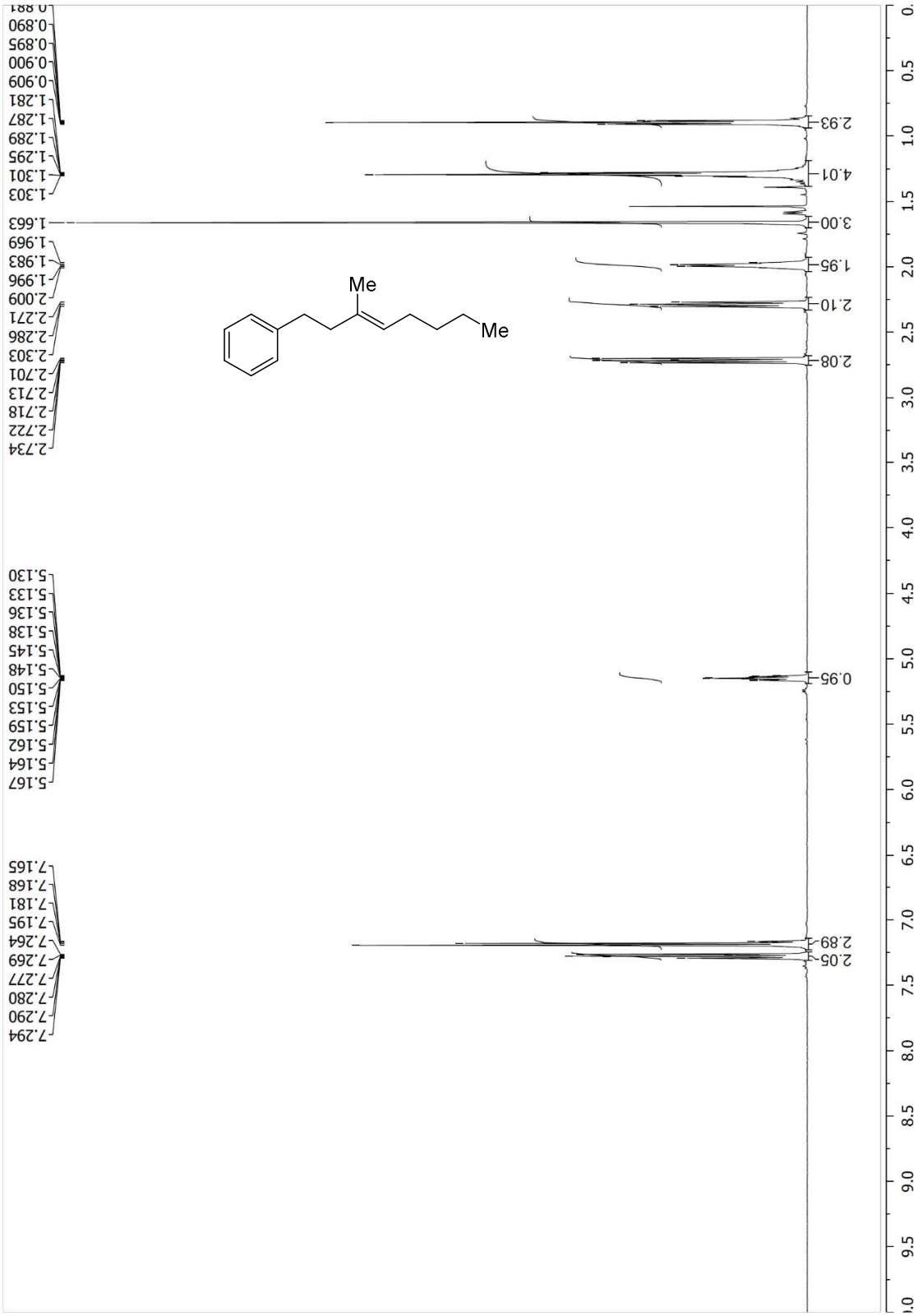
^{1}H NMR spectrum of 4.75



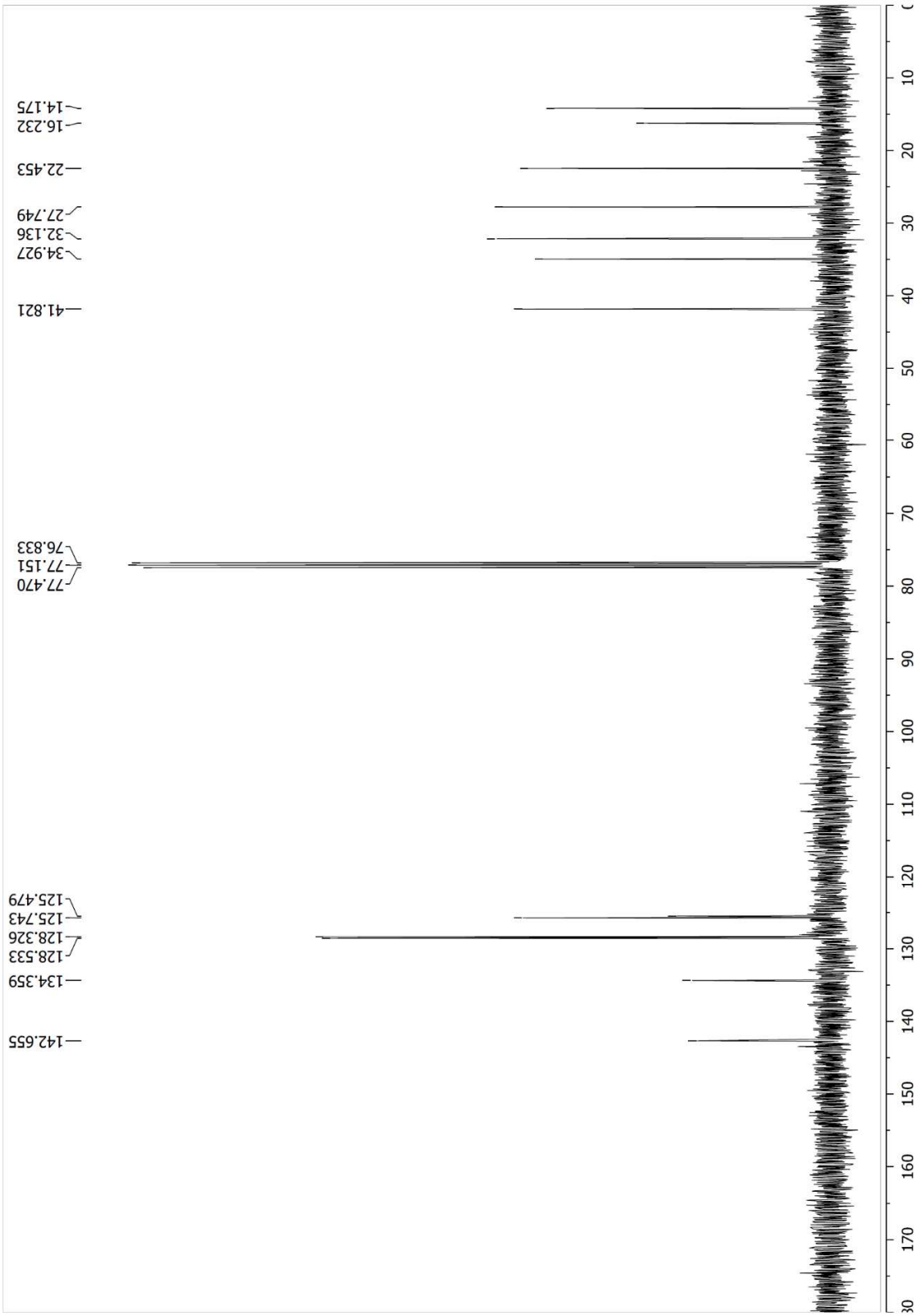
^{13}C NMR spectrum of 4.75



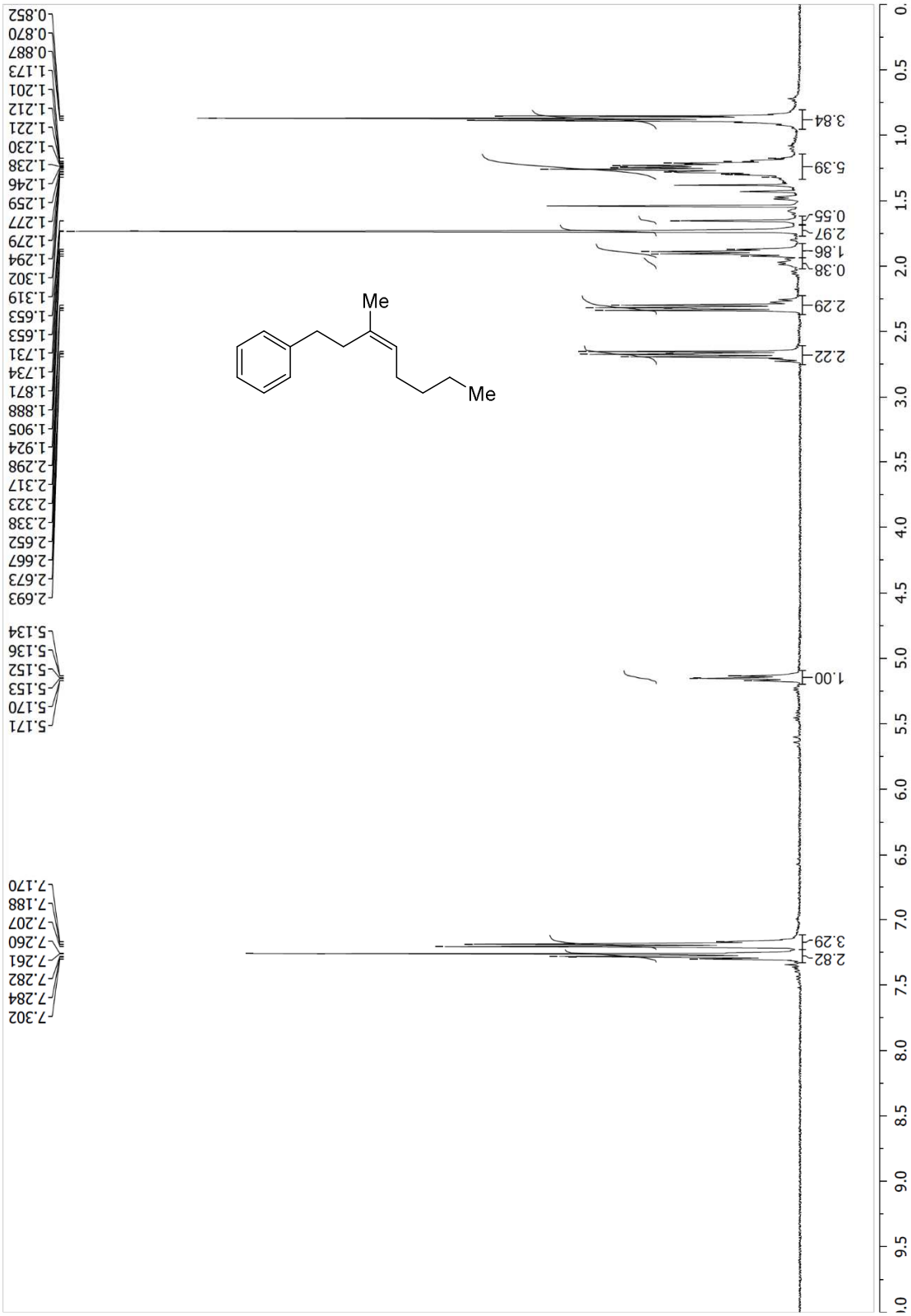
^{1}H NMR spectrum of 4.76



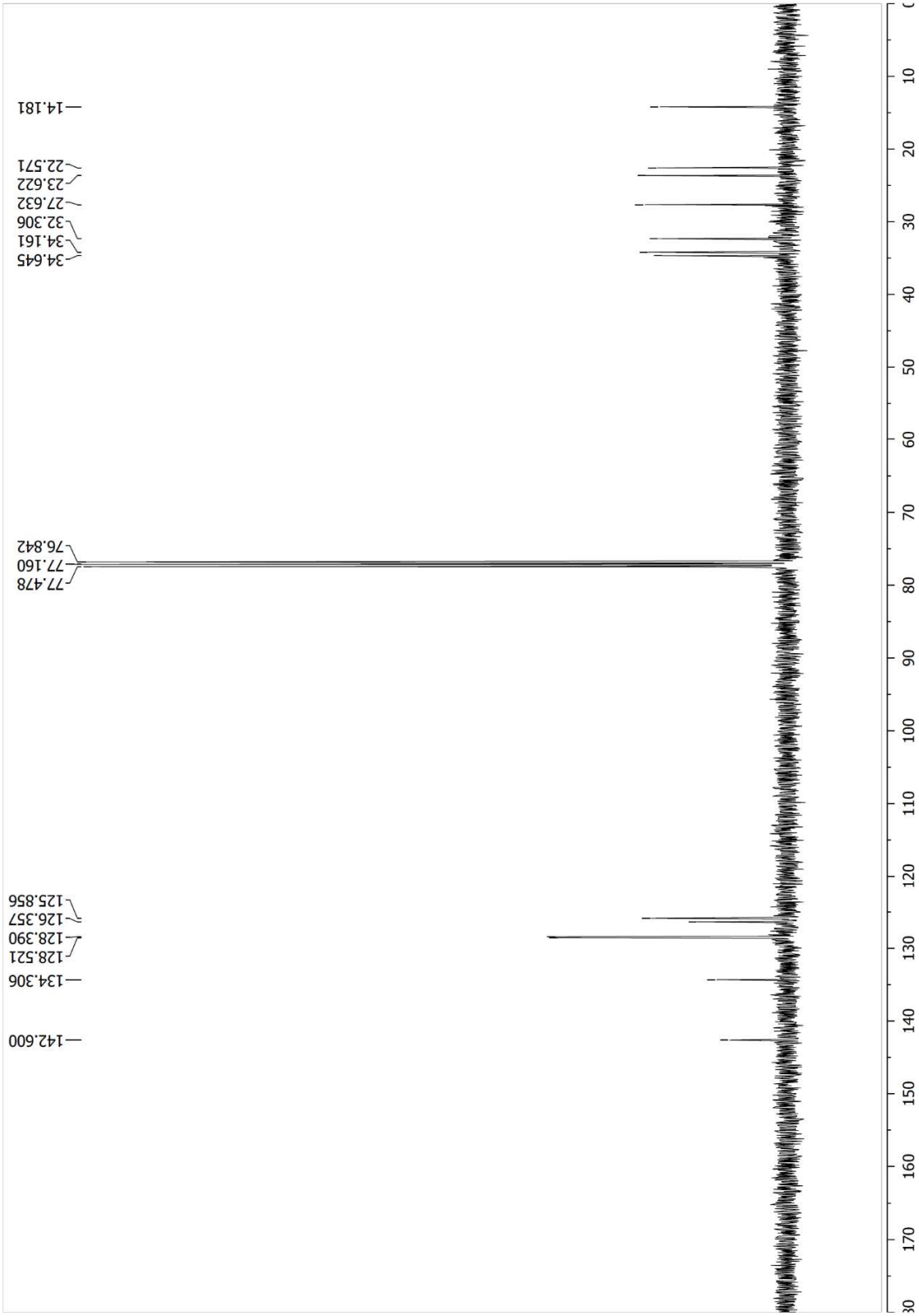
^{13}C NMR spectrum of 4.76



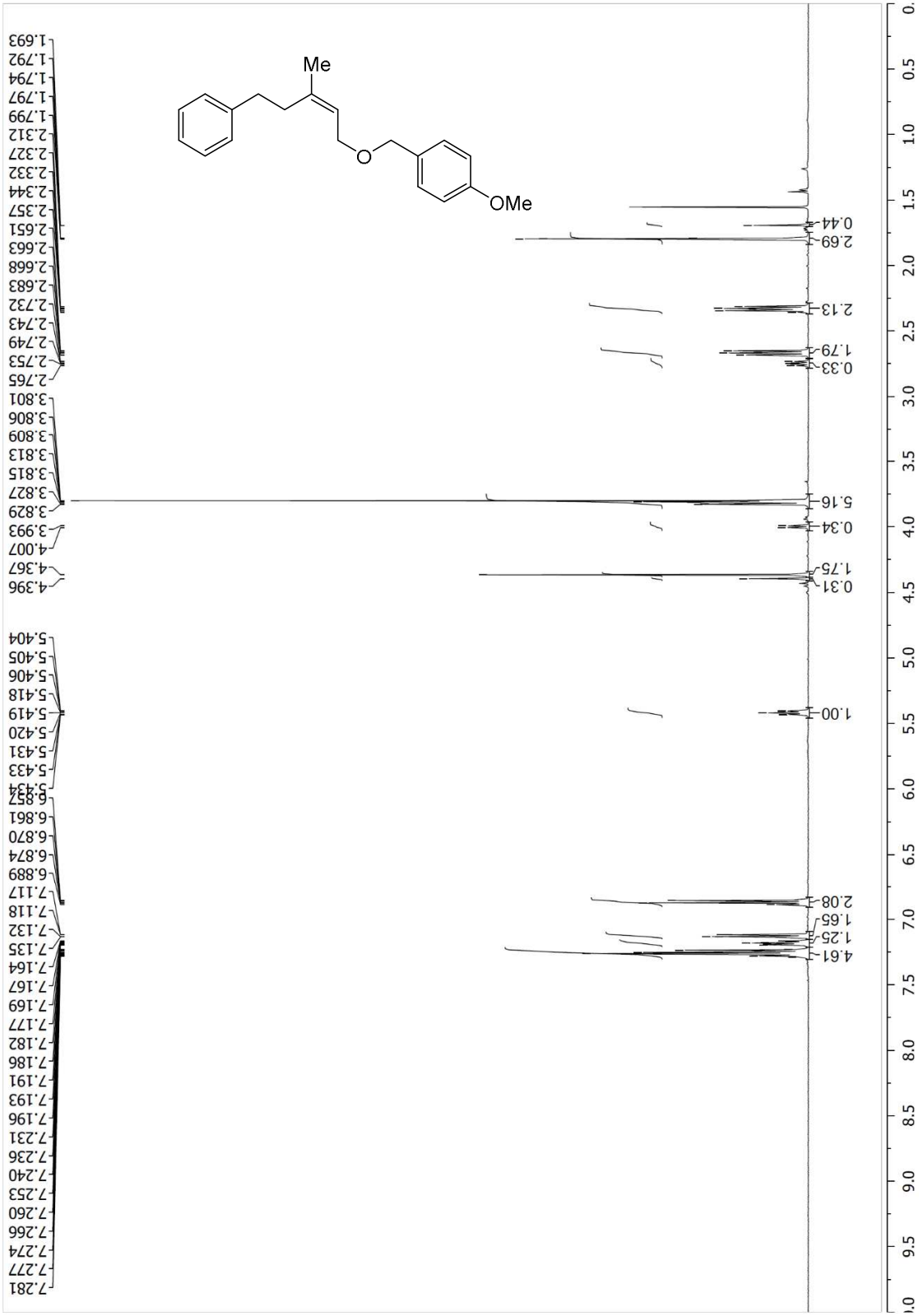
^{1}H NMR spectrum of 4.77



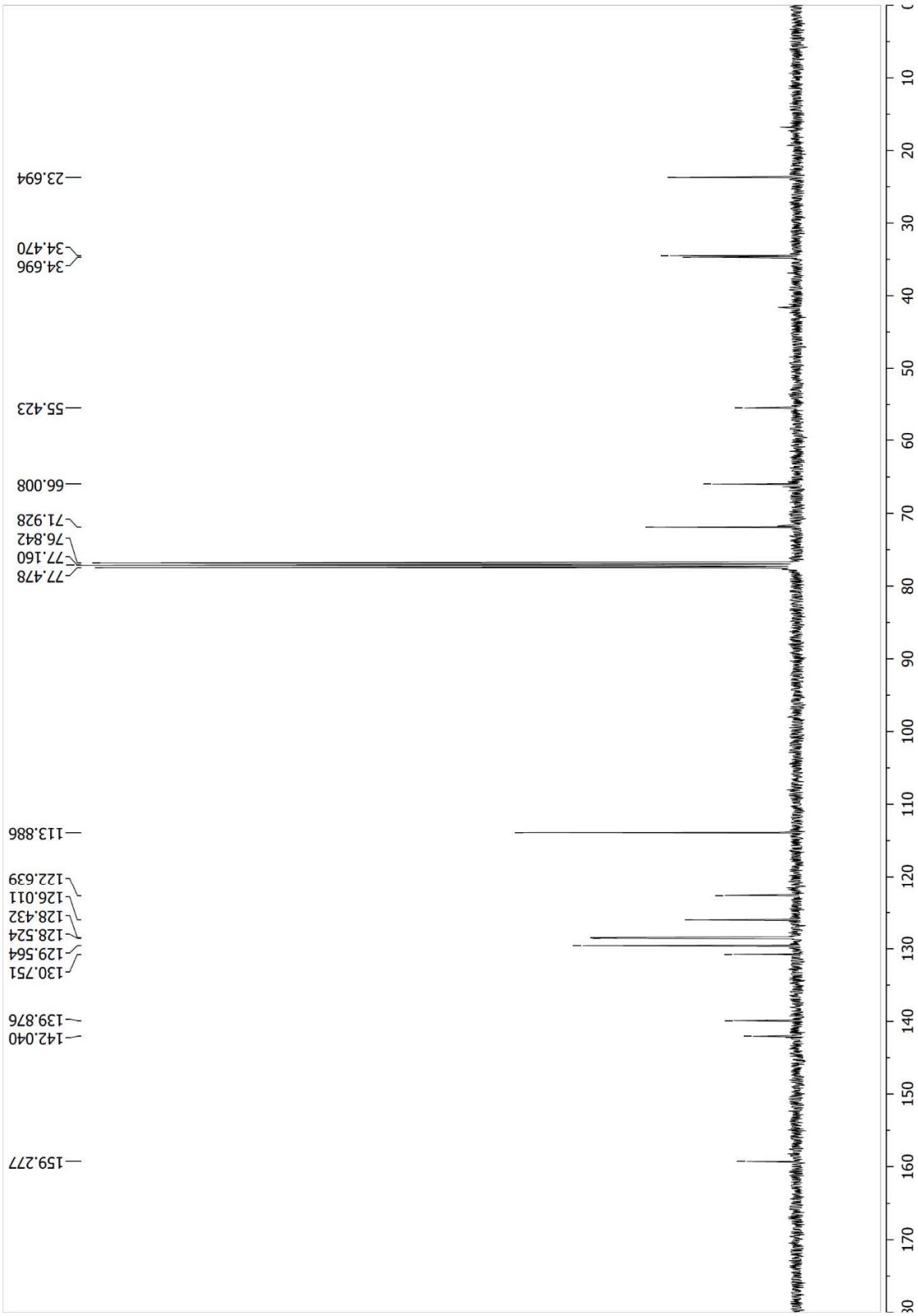
^{13}C NMR spectrum of 4.77



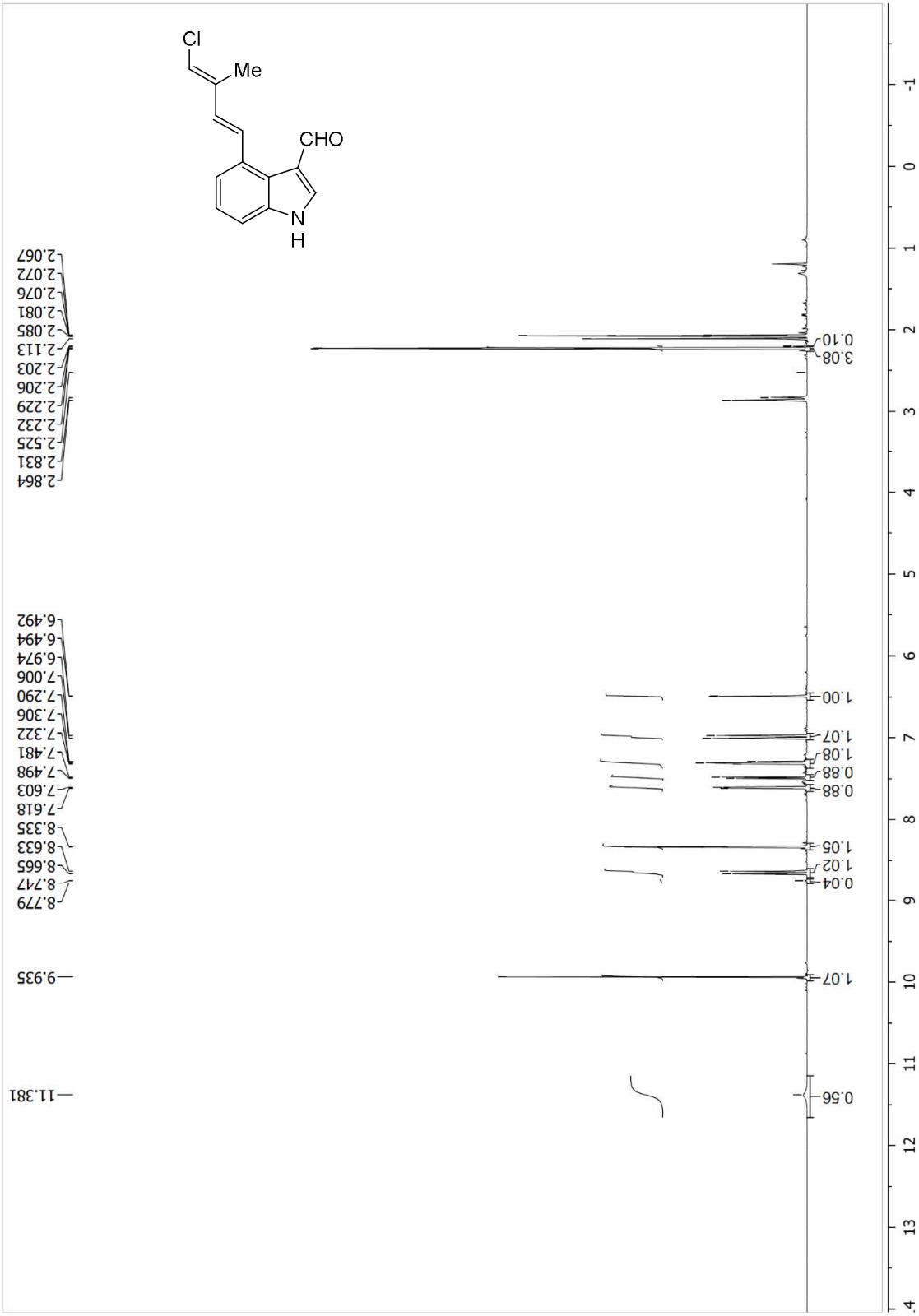
^{1}H NMR spectrum of 4.78



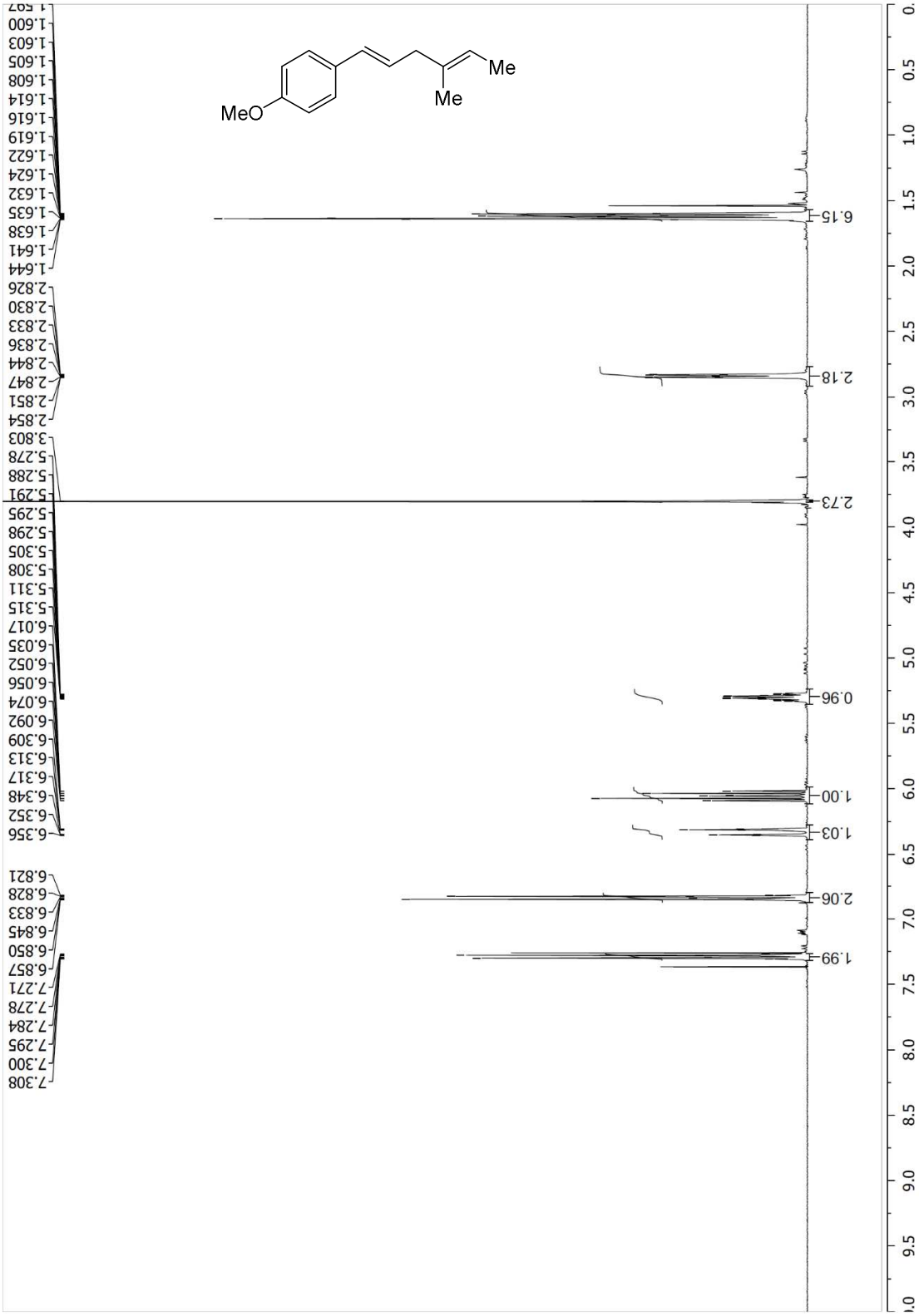
^{13}C NMR spectrum of 4.78



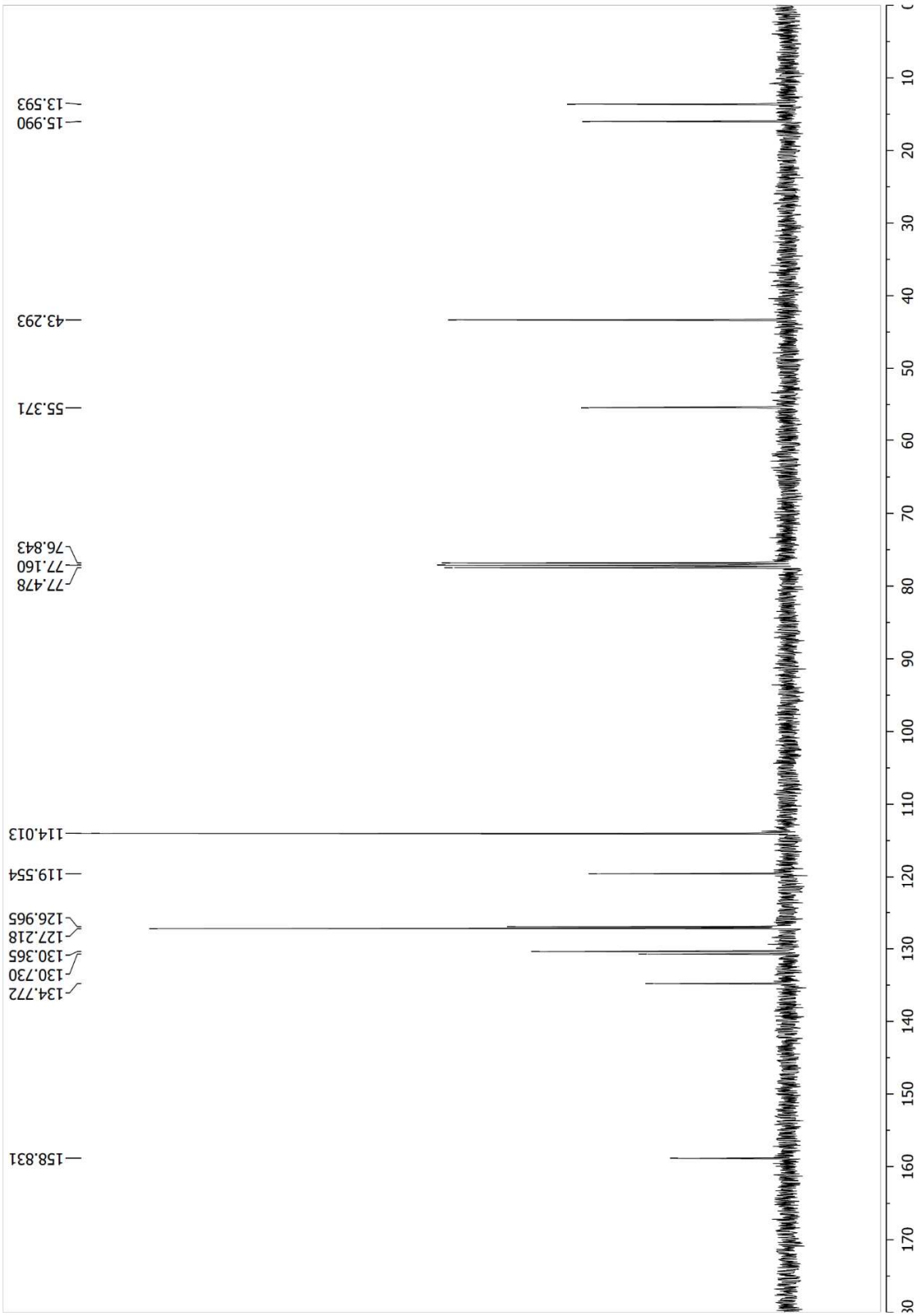
^{1}H NMR spectrum of Indiacen B



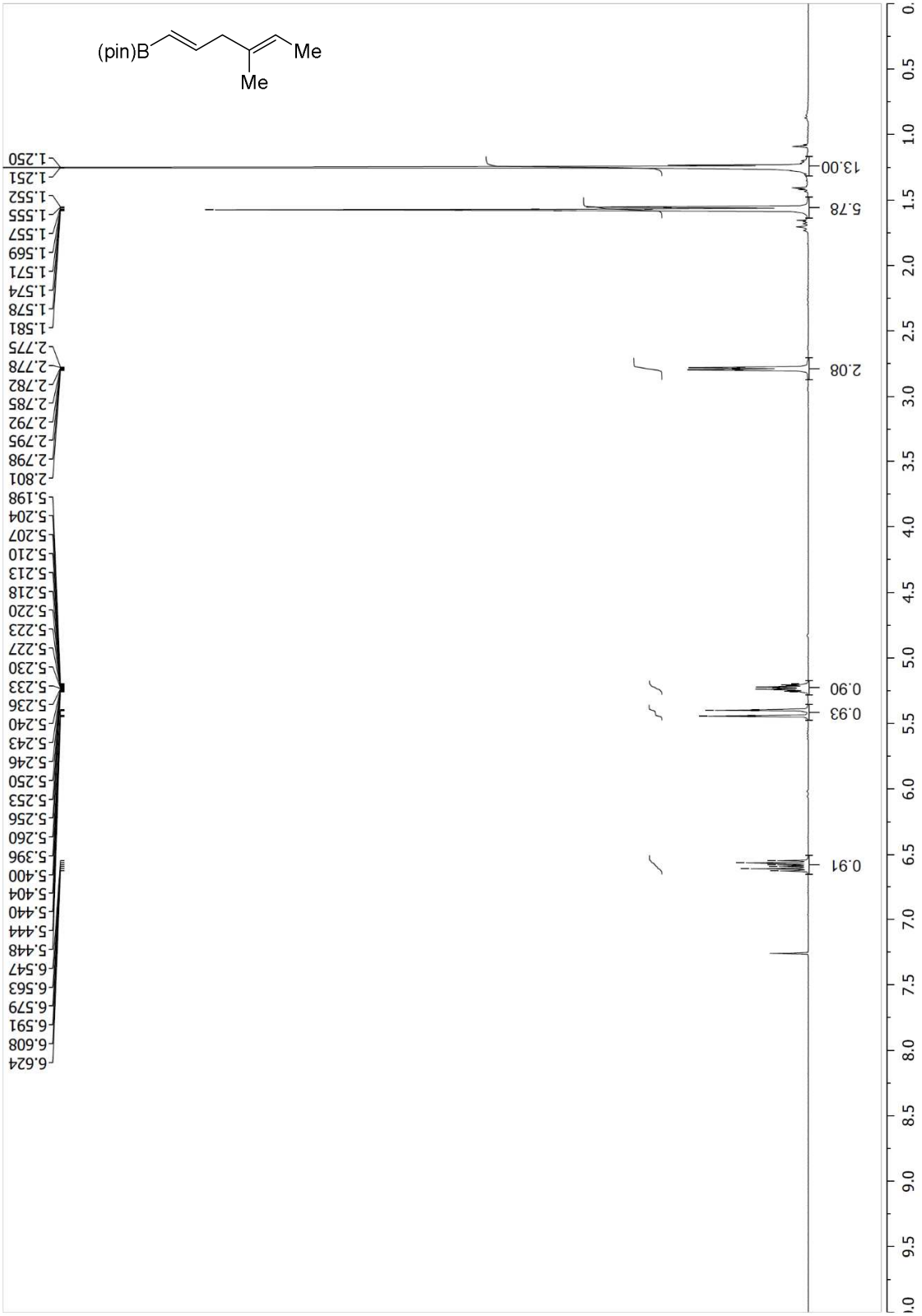
^{1}H NMR spectrum of 4.62



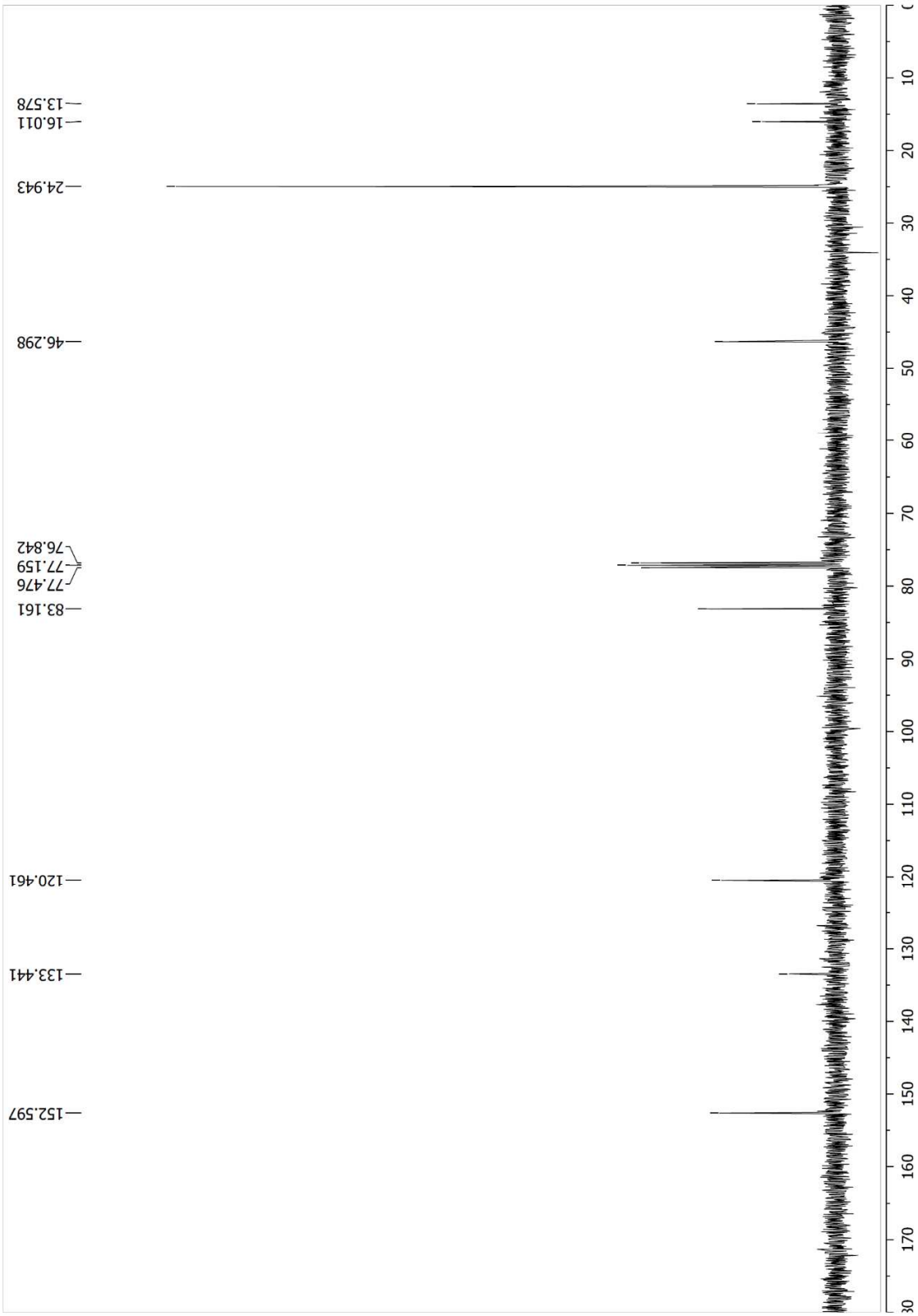
^{13}C NMR spectrum of 4.62



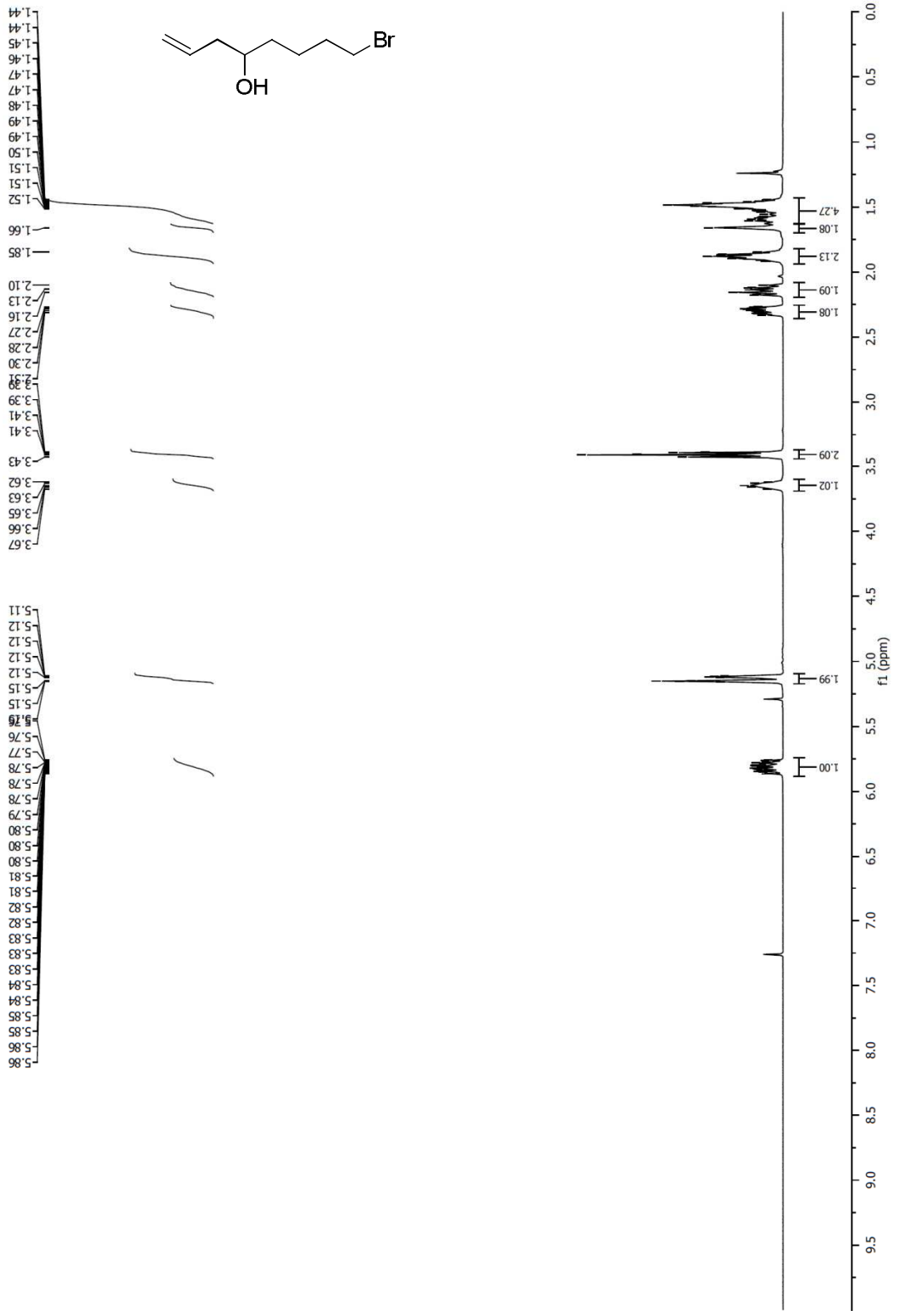
^{1}H NMR spectrum of 4.63



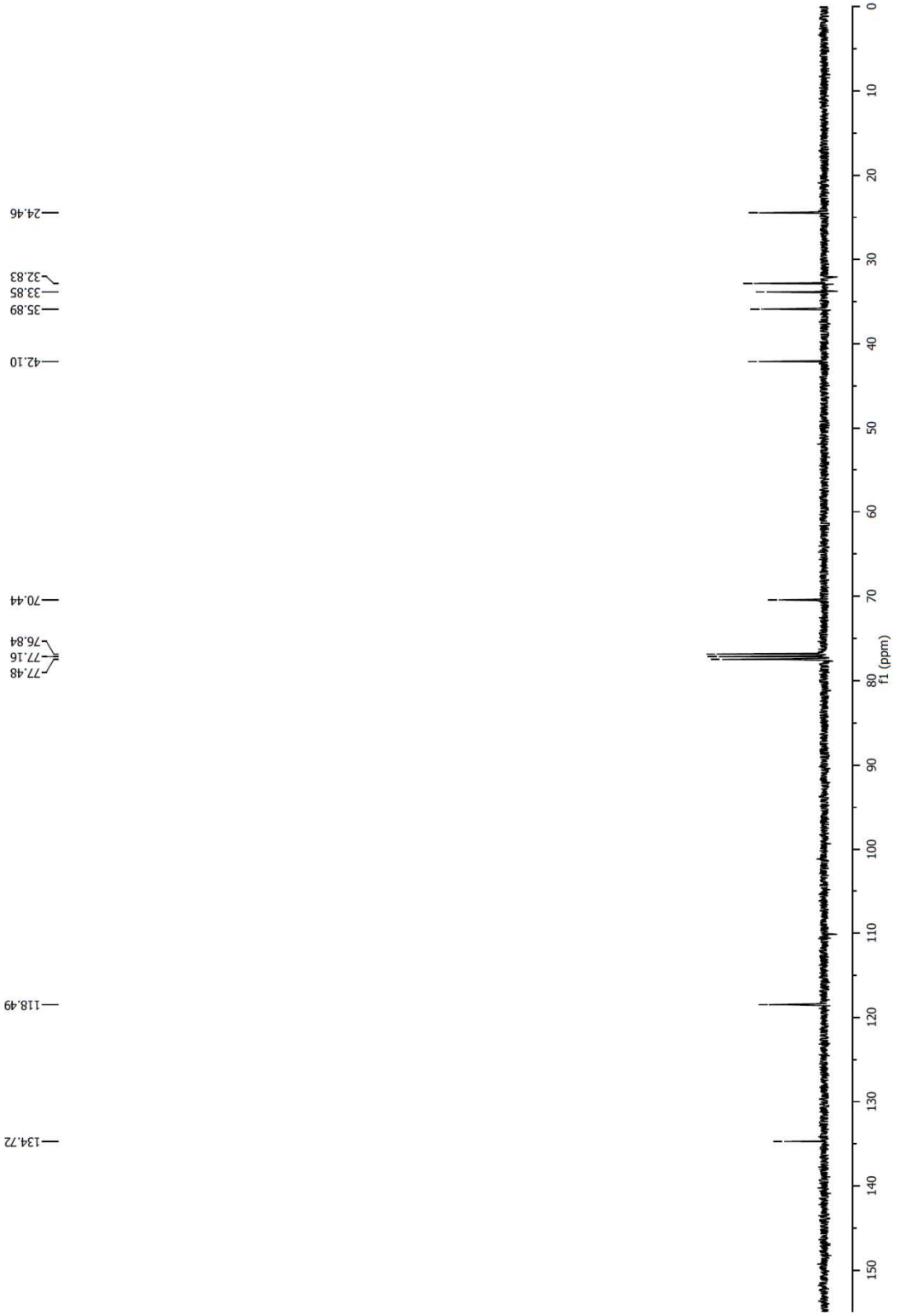
^{13}C NMR spectrum of 4.63



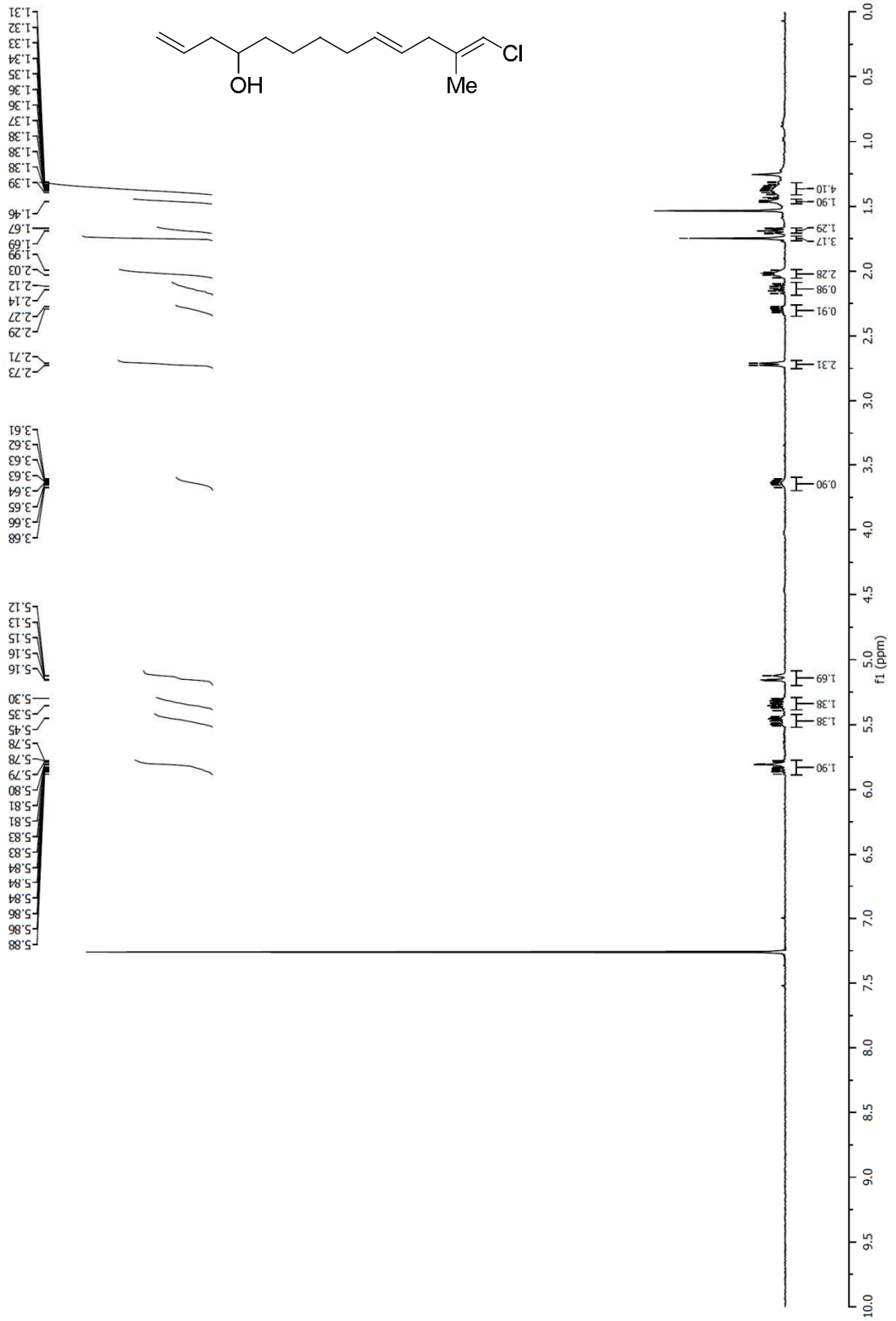
^{1}H NMR spectrum of 4.65



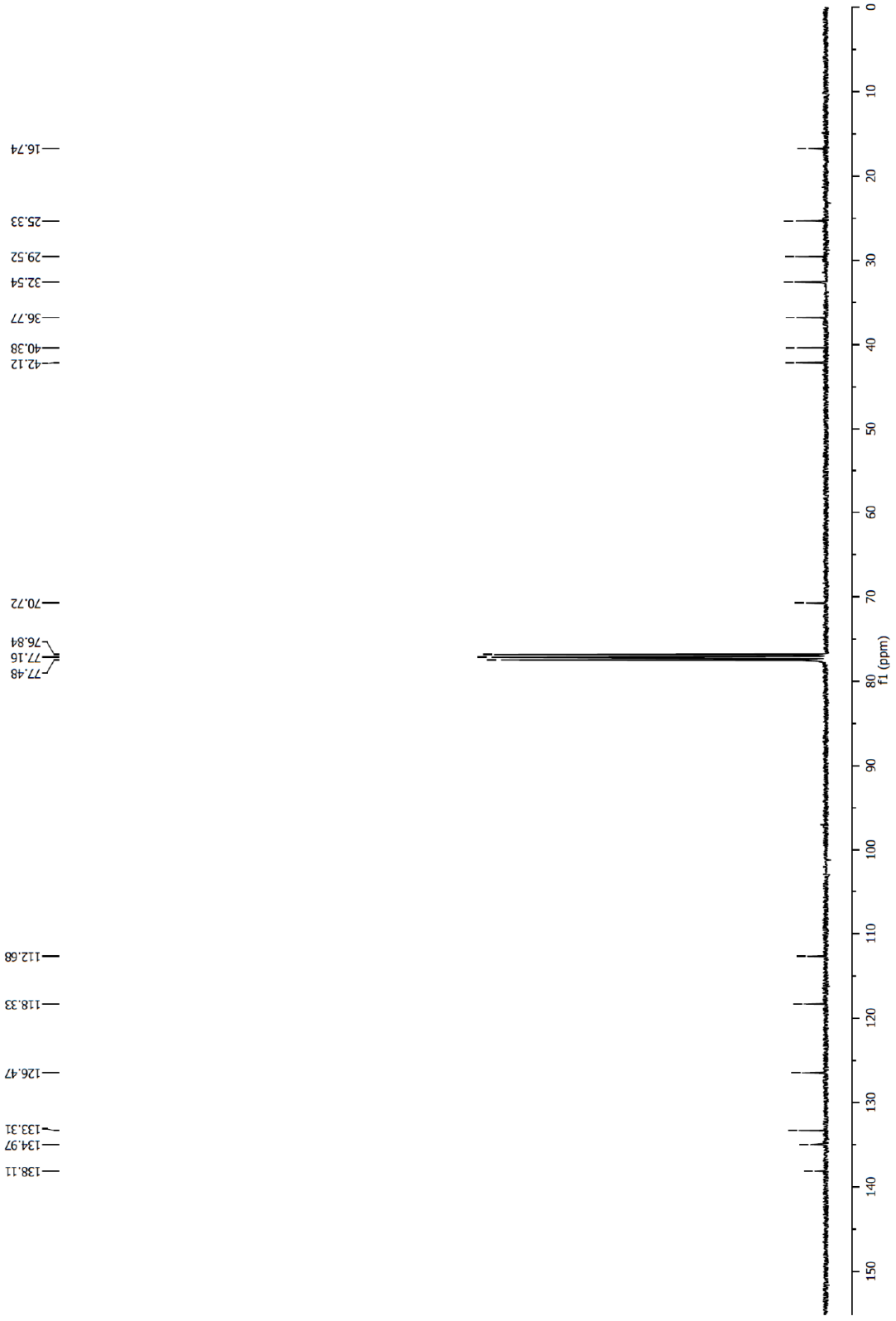
^{13}C NMR spectrum of 4.65



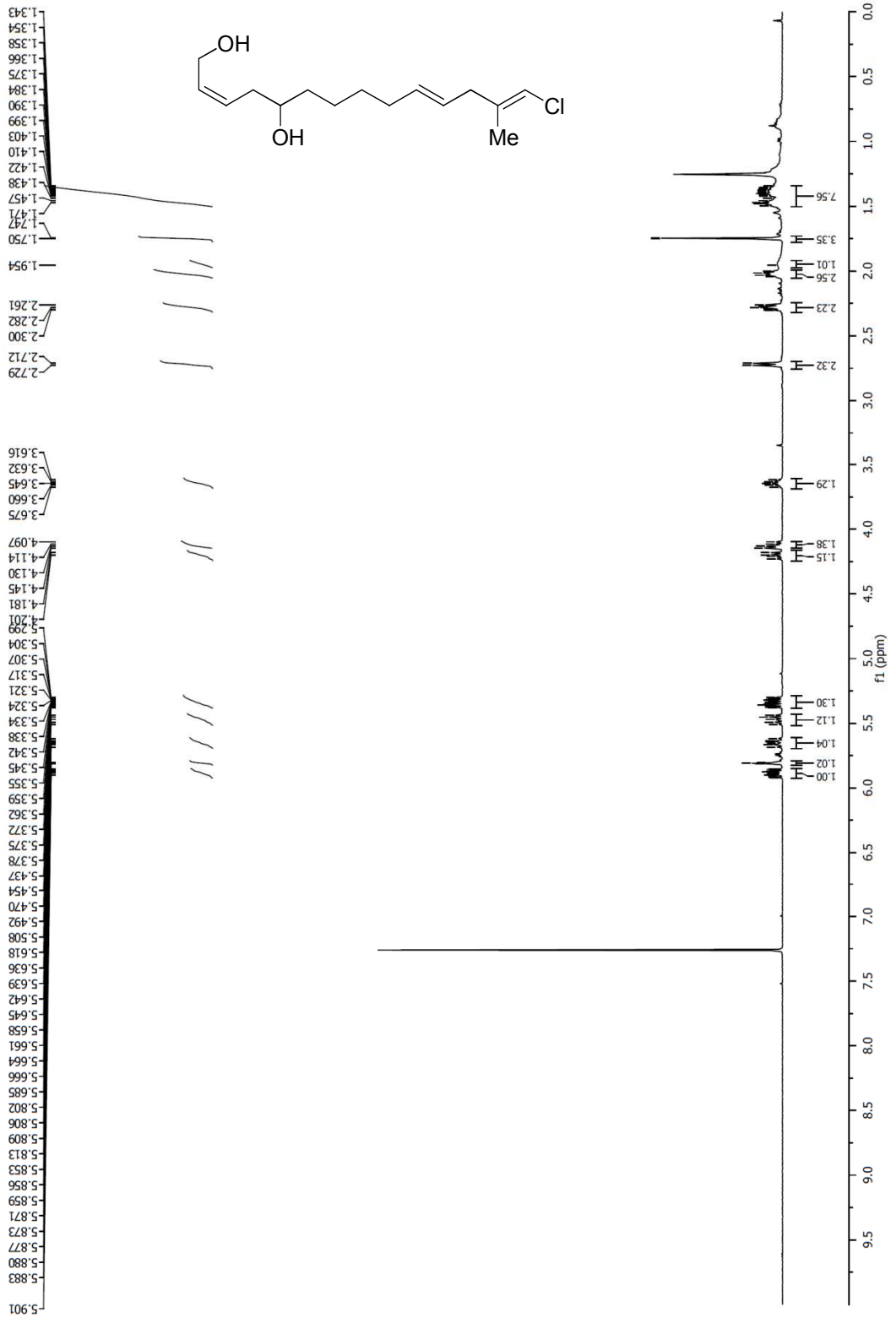
^{1}H NMR spectrum of 4.66



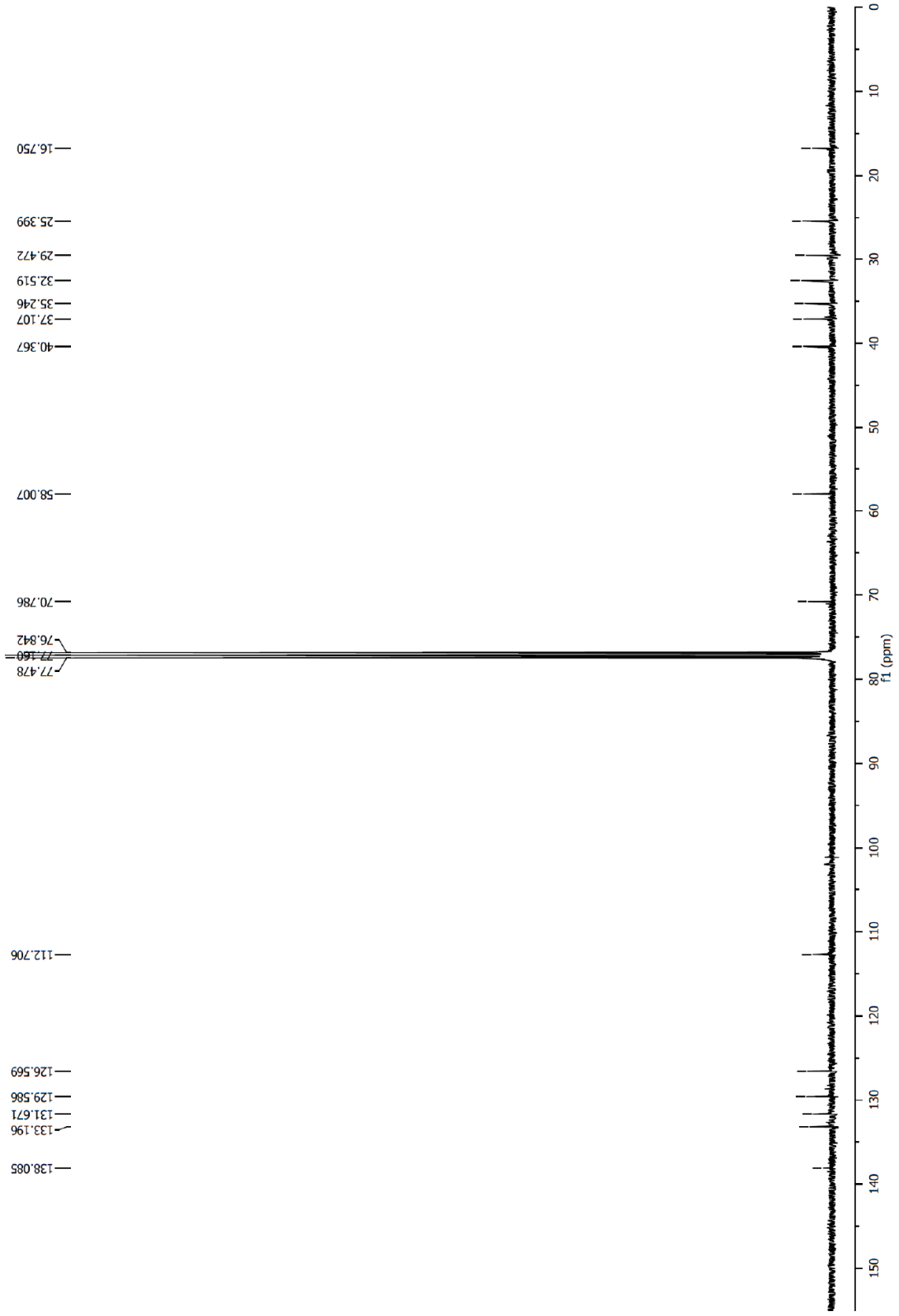
^{13}C NMR spectrum of 4.66



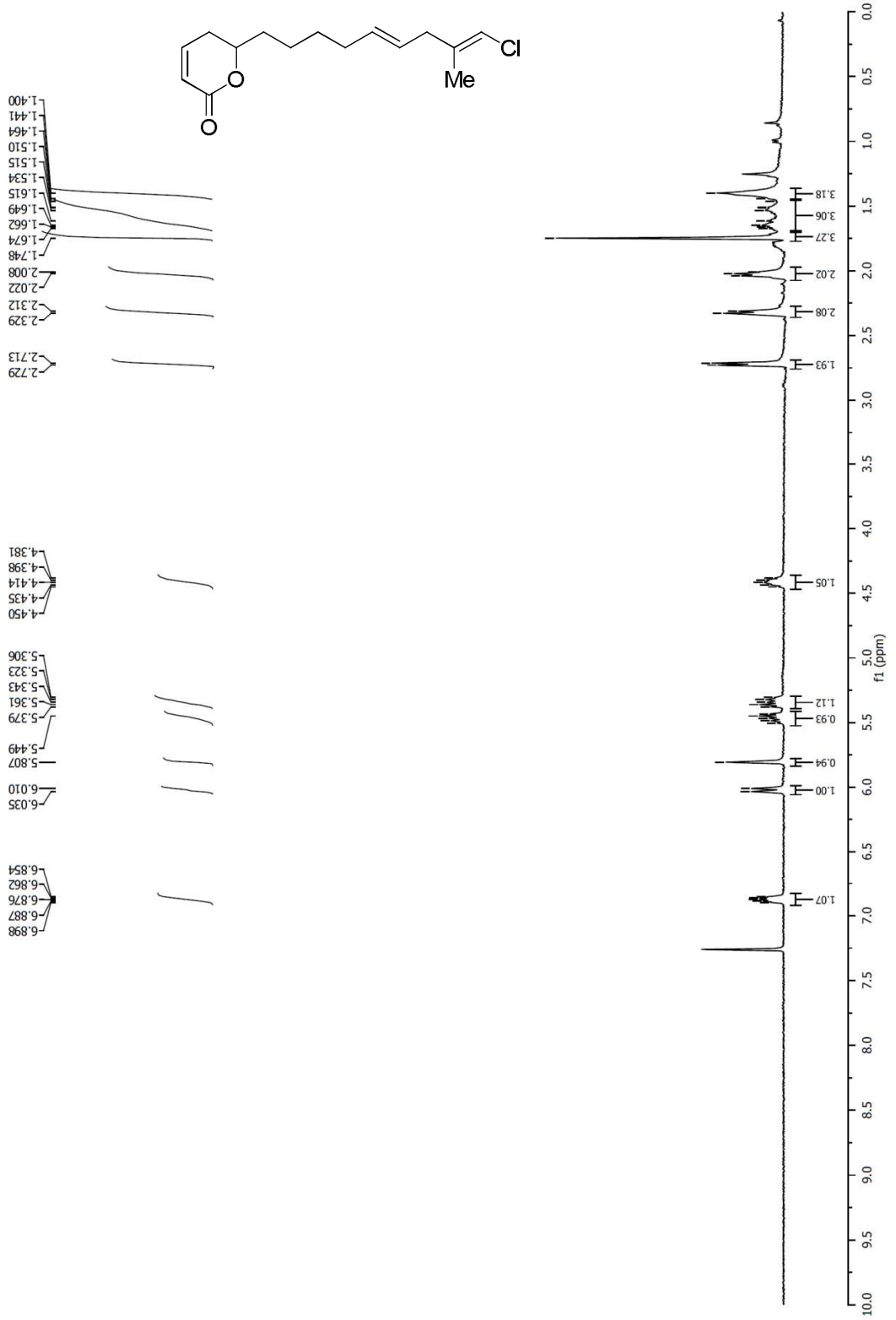
^{1}H NMR spectrum of 4.80



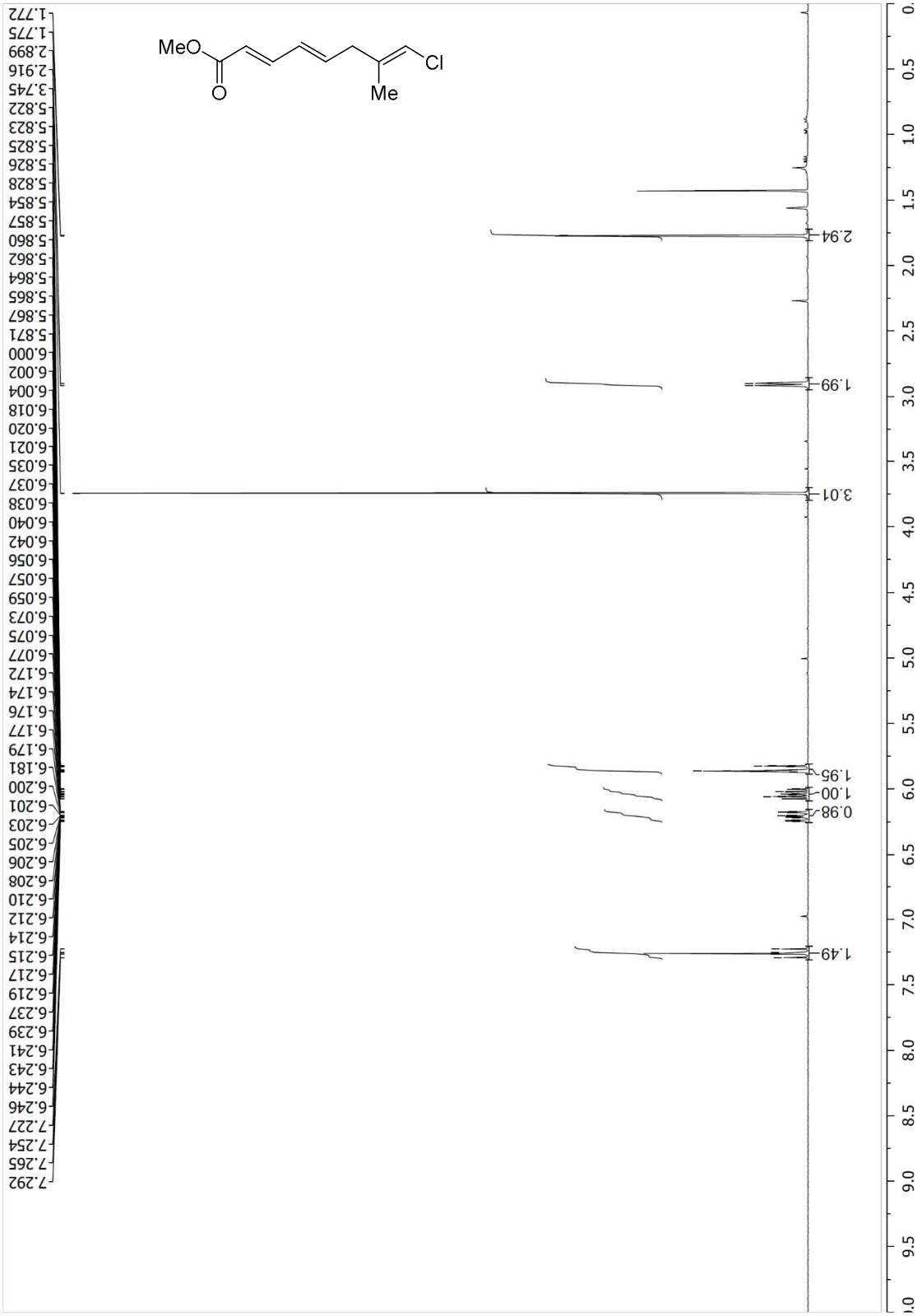
^{13}C NMR spectrum of 4.80



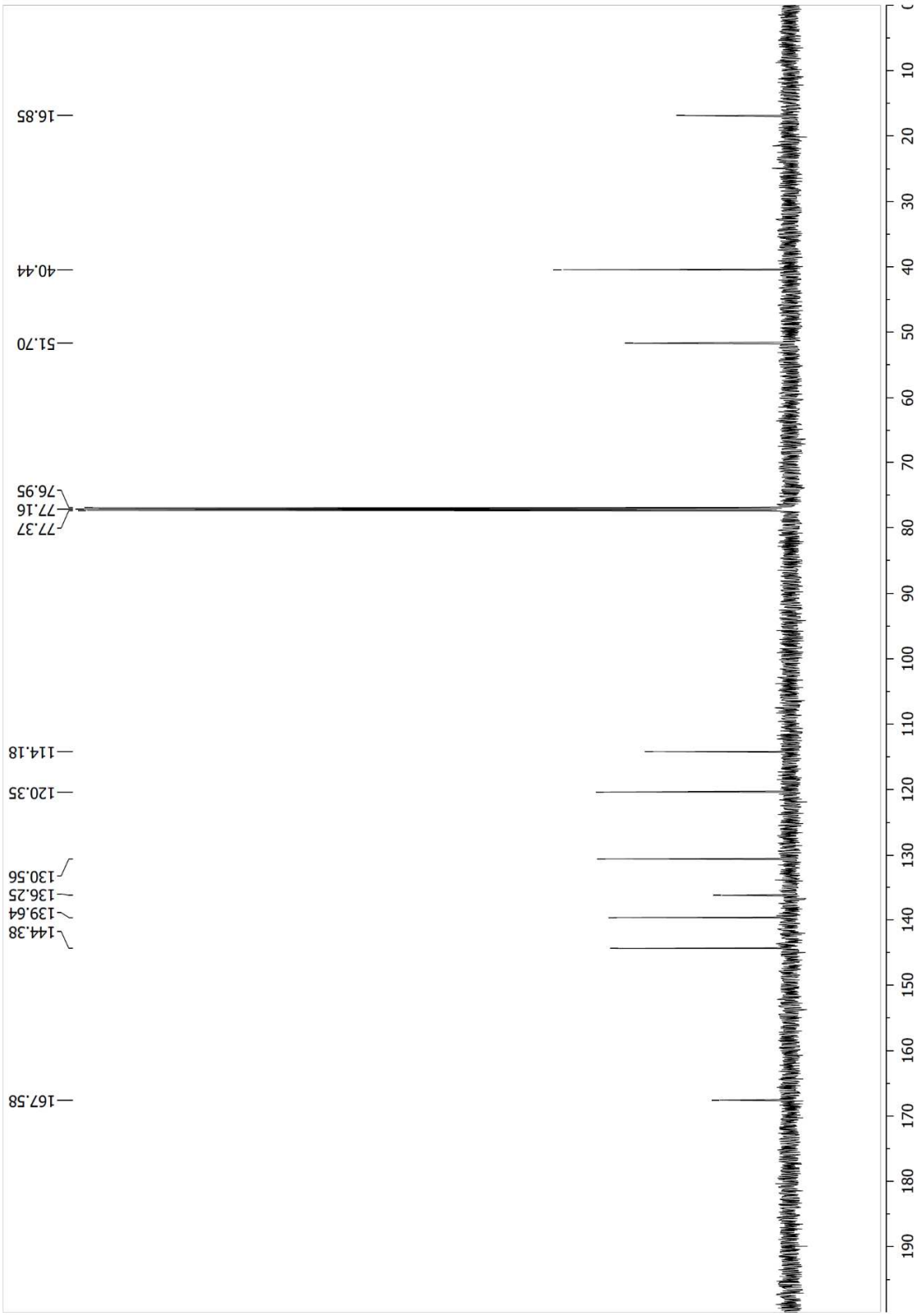
^{1}H NMR spectrum of (±)-Coibacin D



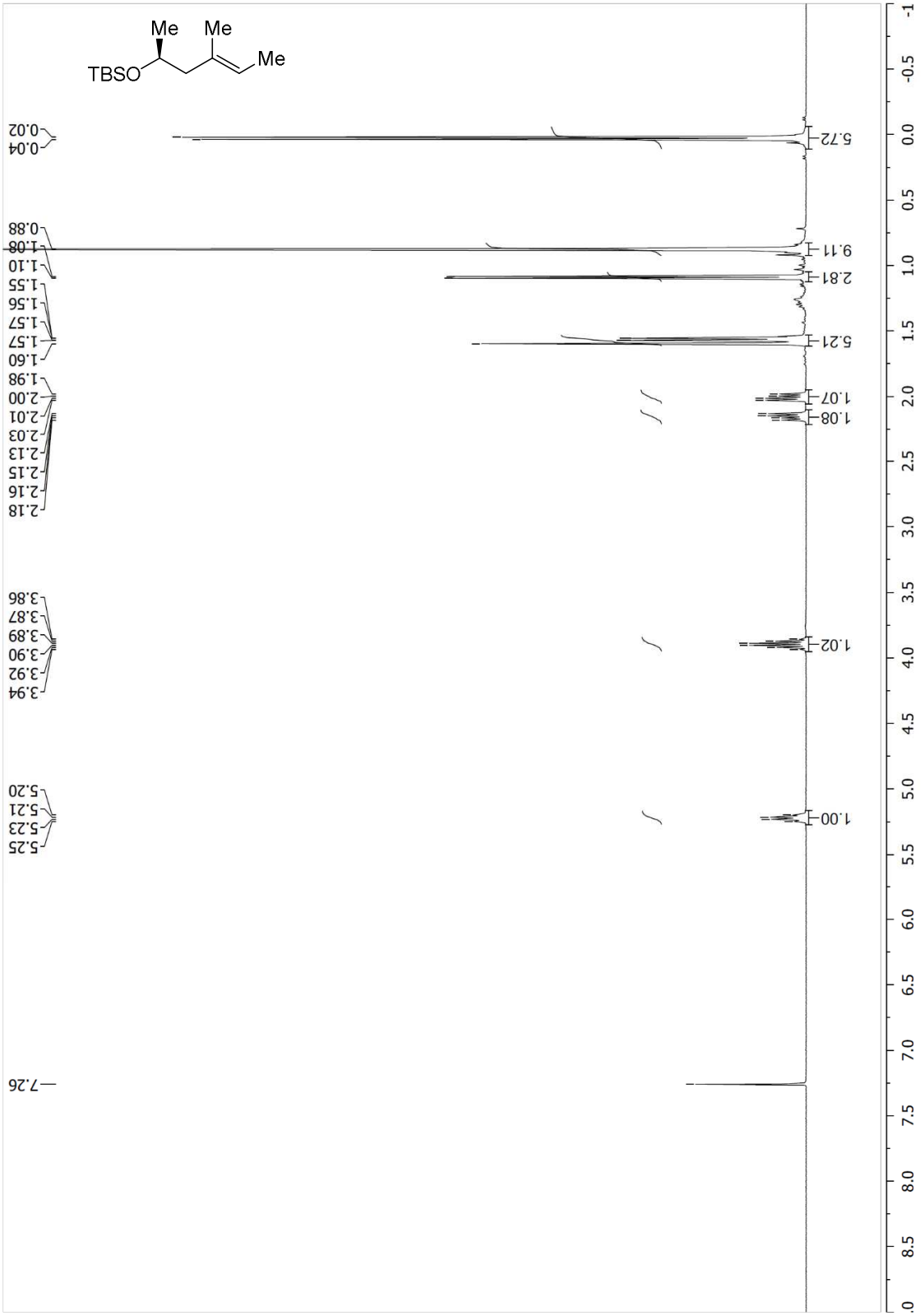
^{1}H NMR spectrum of 4.67



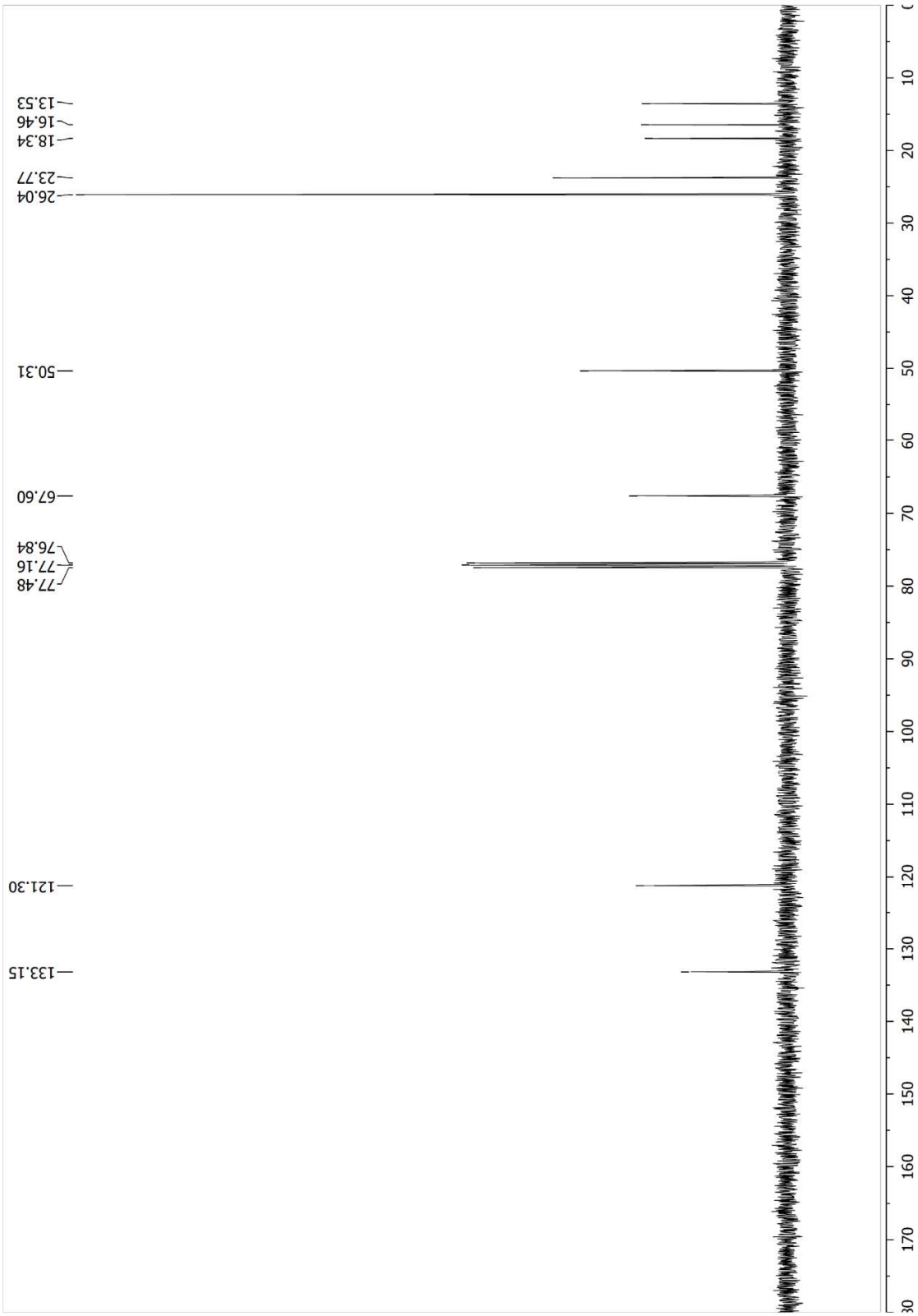
^{13}C NMR spectrum of 4.67



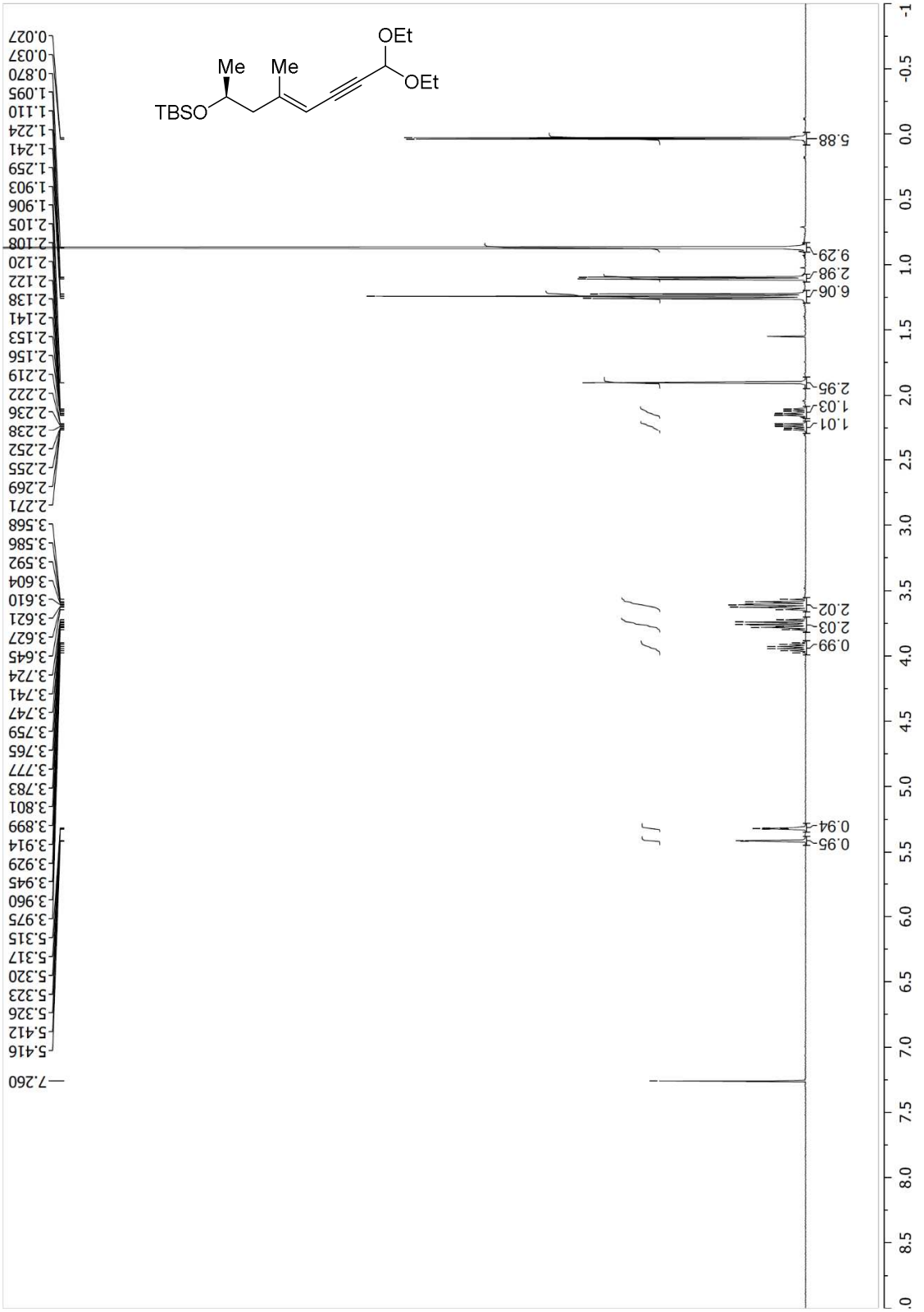
^{1}H NMR spectrum of 4.68



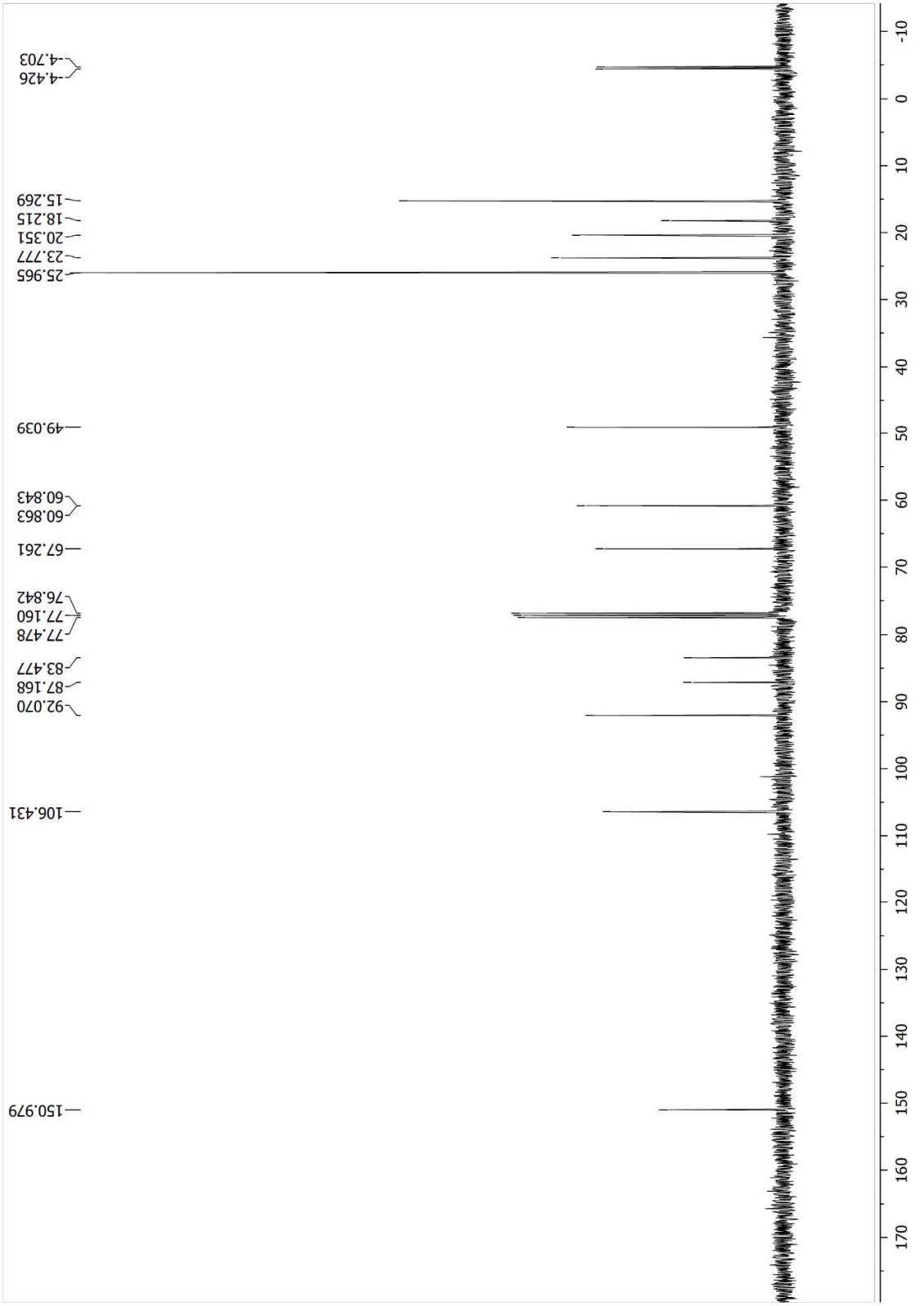
^{13}C NMR spectrum of 4.68



^{1}H NMR spectrum of 4.81



^{13}C NMR spectrum of 4.81



^{1}H NMR spectrum of 4.70