

CATALYTIC VINYLIDENE INSERTION AND TRANSFER REACTIONS

by

Annah E. Kalb

A Dissertation

Submitted to the Faculty of Purdue University

In Partial Fulfillment of the Requirements for the degree of

Doctor of Philosophy



Department of Chemistry

West Lafayette, Indiana

May 2022

THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Dr. Christopher Uyeda, Chair

Department of Chemistry

Dr. Mingji Dai

Department of Chemistry

Dr. Suzanne Bart

Department of Chemistry

Dr. Elizabeth Parkinson

Department of Chemistry

Approved by:

Dr. Christine Hrycyna

Ad Majorem Dei Gloriam

TABLE OF CONTENTS

LIST OF TABLES	6
LIST OF FIGURES	7
ABSTRACT.....	9
CHAPTER 1. DINICKEL CATALYZED VINYLIDENE OLEFIN CYCLIZATION REACTIONS 	10
1.1 Abstract	10
1.2 Introduction.....	10
1.3 Results and Discussion	12
1.3.1 Catalytic Intramolecular Vinylidene Additions to Alkenes.....	12
1.3.2 Substrate Scope Studies	13
1.3.3 Evidence in Support of a Stepwise Ni ₂ (vinylidene) Addition Mechanism	15
1.4 Electrocatalytic Reductive Cyclizations and the Role of Zn	16
1.5 Stoichiometric Reductive Cyclization Reactions.....	17
1.6 DFT Calculations	20
1.7 Conclusions.....	22
1.8 Acknowledgements.....	23
1.9 References.....	23
CHAPTER 2. A DINICKEL-CATALYZED THREE-COMPONENT CYCLOADDITION OF VINYLIDENES	27
2.1 Abstract	27
2.2 Introduction.....	27
2.3 Results and Discussion	29
2.3.1 Reaction Development.....	29
2.3.2 Substrate Scope.....	31
2.3.3 Mechanistic Studies	33
2.3.4 DFT Modeling Studies	34
2.4 Conclusions.....	36
2.5 Acknowledgements.....	37
2.6 References.....	37

CHAPTER 3. A DINICKEL CATALYZED CYCLOPROPANATION WITHOUT THE FORMATION OF A METAL CARBENE INTERMEDIATE	40
3.1 Introduction.....	40
3.2 DFT Models for the Ni ₂ -Catalyzed Cyclopropanation	41
APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 1	44
APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 2	133
APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 3	232

LIST OF TABLES

Table 1.1. Effects of Reaction Parameters on the Reductive Vinylidene Cyclization.	13
Table 2.1 Effect of Reaction Parameters	30

LIST OF FIGURES

Figure 1.1. (a) Exo and endo cyclization modes of 1,6-enynes. (b) Reductive activation of 1,1-dichloroalkenes enable selective vinylidene–alkene cyclization reactions. 11

Figure 1.2. Substrate scope studies. Isolated yields were determined following purification and were averaged over two runs. Standard reaction conditions: substrate (0.2 mmol), *i*-PrNDI (**4**) (5–10 mol%), Ni(dme)Cl₂ (10–20 mol%), Zn (3.0 equiv), NMP (1.6 mL), THF (6.4 mL), rt or 50 °C, 24h. ^asubstrate (0.2 mmol), ^{c-pent}NDI (**7**), (10 mol%), Ni(dme)Cl₂ (20 mol%), Zn (3.0 equiv), NMP (0.8 mL), THF (7.2 mL), rt, 24h. 14

Figure 1.3. Experiments supporting a stepwise vinylidene addition mechanism. 16

Figure 1.4. (a) Controlled potential electrolysis experiments for the catalytic conversion of **1** to **2**. (b) Experimental setup (CE = counter electrode; RE = reference electrode; WE = working electrode) and a proposed one-electron catalytic cycle. (c) Cyclic voltammetry data for complex **5** in the presence and absence of **1** (0.3 M [*n*-BuN₄]PF₆ in NMP; 100 mV/s scan rate). All cyclic voltammograms were internally referenced to the Cp₂Fe/Cp₂Fe⁺ couple. 17

Figure 1.5. Experiments probing the stoichiometric activation of 1,1-dichloroalkene substrates with (*i*-PrNDI)Ni₂(C₆H₆) complex **6**. (a) Stoichiometric reductive cyclization of **1** using complex **6**. (b) Stoichiometric reaction between complex **6** and substrate **25** to form metallacycle **38**. (c) XRD structure of metallacycle **38**. Selected bond metrics: Ni1–Ni2: 2.743(1) Å; Ni1–C1: 2.000(6) Å; Ni1–C3: 1.967(4) Å; Ni2–C1: 1.954(5) Å; Ni2–Cl: 2.243(2) Å. (d) Frozen solution EPR spectrum for **38** (105 K; toluene). Simulated parameters: *g* = [2.378, 2.226, 2.093]. * corresponds to a *S* = 1/2 impurity. (e) UM06-L spin density plot for **38**. 18

Figure 1.6. Comparison of rates and yields for stoichiometric cyclizations to form **26** as a function of oxidation state. 19

Figure 1.7. (a) DFT-calculated reaction pathways for the cyclization of **25** to give complex **38**. Relative Gibbs free energies are shown in kcal/mol. Isopropyl groups were modeled as methyl groups. (b) 3D representations of key transition-state structures. Spin states are given in parenthesis. Hydrogens are removed for clarity. Distances are reported in Å. 21

Figure 1.8. DFT-calculated reaction pathways for conversion of **38** to **44/46** as a function of oxidation state. Relative Gibbs free energies are shown in kcal/mol. 22

Figure 2.1. (a) A mechanism of the Pauson–Khand reaction initiated by a dinuclear oxidative coupling of the alkene and the alkyne. (b) A proposed vinylidene [2 + 2 + 1]-cycloaddition process involving a metallacycle derived from the migratory insertion of a 2π-component into a Ni₂(vinylidene). (c) A dinickel-catalyzed [2 + 2 + 1]-cycloaddition of two aldehydes and a vinylidene to generate methylenedioxolanes and synthetic applications to the synthesis of α-hydroxy ketones. 29

Figure 2.2. Substrate scope studies. Isolated yields were determined following purification and were averaged over two runs. Standard reaction conditions: dichloroalkene (0.2 mmol, 1.0 equiv), aldehyde (2.0 equiv), (*i*-PrNDI)Ni₂Cl₂ (**6**) (10 mol%), Zn (4.0 equiv), DMA (0.2 mL), Et₂O (0.8

mL), rt, 24 h; then TFA, 0 °C to rt, 2 h. ^aSynthesized using 2-(4-((trimethylsilyl)oxy)phenyl)acetaldehyde..... 32

Figure 2.3 Mechanistic Studies. (a) Competing β -hydride elimination and aldehyde migratory pathways. Concentration dependence of β -hydride elimination vs. aldehyde migratory insertion under (b) catalytic and (c) stoichiometric conditions. (d) Deuterium labelling experiment tracking the hydrogen undergoing β -hydride elimination. (e) Experiment assessing the intermediacy of enone 41 in the cycloaddition. 34

Figure 2.4. DFT modeling studies. All stationary points are fully optimized at the BP86/6-311g(d,p) level of theory and verified by frequency analysis. *i*-Pr groups on the catalyst were truncated to Me groups. Relative ΔG values at 298 K are shown in kcal/mol. The major pathway leading to the [2 + 2 + 1]-cycloaddition product is shown in blue. Competing pathways to form the E-isomer of the product and the enone product are shown in green..... 35

Figure 3.1. Metal carbenes are key intermediates in several catalytic cyclopropanation reactions using diazoalkanes. Dinickel complexes catalyze regioselective cyclopropanations of 1,3-dienes without generating a Ni₂(μ -CR₂) intermediate. 41

Figure 3.2. Calculated reaction pathway for the (^{*i*}-PrNDI)Ni₂ catalyzed cyclopropanation to form **8** (BP86/6-311g(d,p) level of DFT). Relative free energies are shown in kcal/mol. Unless otherwise indicated, all structures correspond to *S* = 0 spin states. S7, S8, and S8' were modelled as open-shell singlets with a C-centered α -TMS radical and the other unpaired electron delocalized in the NDI π -system. Transition states leading to the alternative regioisomer and diastereomer are shown. 43

ABSTRACT

Metal-stabilized carbenes, most commonly formed through the decomposition of diazoacetates, are extensively employed in organic synthesis. However, several classes of carbenes, such as vinylidenes, are challenging to utilize in transition metal catalysis due to the instability of the required diazo precursors. To overcome this challenge, most transition metal-catalyzed vinylidene transfer and insertion methods rely on alkynes as vinylidene precursors. Only catalysts that form stable $M=C$ multiple bonds and weak $M(\pi-C\equiv C)$ interactions can promote this alkyne isomerization, and the resultant metal(vinylidene) species is often less reactive compared to free vinylidenes. The discovery of 1,1-dihaloalkenes as precursors to transition metal vinylidene complexes has significantly expanded the scope of vinylidene transfer and insertion reactions. Dinuclear catalysts were found to promote the reductive cyclization of 1,1-dichloroalkenes containing pendant alkenes to form methylenecycloalkenes, and mechanistic studies are consistent with the formation of a $Ni_2(\text{vinylidene})$ species. Furthermore, these catalysts promote reductive three-component cycloaddition reactions with 1,1-dichloroalkenes and aldehydes to generate methylenedioxolanes, which upon treatment with aqueous acid provides access in one step to new, unsymmetrical aliphatic α -hydroxy ketones that would be difficult to access with existing methods. Under dilute conditions, an enone byproduct is formed and a DFT model is presented that accounts for concentration-based reaction selectivity.

CHAPTER 1. DINICKEL CATALYZED VINYLIDENE OLEFIN CYCLIZATION REACTIONS

Reprinted with permission from Steiman, T. J.; Kalb, A. E.; Coombs, J. C.; Kirkland, J. K.; Torres, H. Ess, D. H.; and Uyeda C. *ACS Catalysis*. 2021, 11, 23, 14408-14416. Copyright 2021 American Chemical Society.

1.1 Abstract

A dinickel catalyst promotes reductive cyclization reactions of 1,1-dichloroalkenes containing pendant olefins. The reactions can be conducted with a Zn reductant or electrocatalytically using a carbon working electrode. Mechanistic studies are consistent with the intermediacy of a $\text{Ni}_2(\text{vinylidene})$ species, which adds to the alkene and generates a metallacyclic intermediate. β -Hydride elimination followed by C–H reductive elimination forms the cyclization product. The proposed dinickel metallacycle is structurally characterized and its stoichiometric conversion to product is demonstrated. Spin polarized, unrestricted DFT calculations are used to further examine the cyclization mechanism. These computational models reveal that both nickel centers function cooperatively to mediate the key oxidative addition, migratory insertion, β -hydride elimination, and reductive elimination steps.

1.2 Introduction

Catalytic 1,6-enyne cycloisomerizations are valuable transformations that yield cyclic unsaturated building blocks from acyclic precursors.¹ A notable feature of these reactions is the diversity of products that can be generated from a single starting material (Figure 1.1a). There are various mechanisms by which transition metal catalysts can engage enyne substrates: oxidative ene–yne coupling to form a metallacycle, attack of an alkene on an electrophilic $\text{M}(\text{alkyne})$ species, and addition of a M–H to an alkyne followed by migratory insertion of an alkene. A majority of these processes favor the formation of five-membered ring exocyclization products, with the position of substituents dictated by the specific catalyst/substrate combination being used.

There is a less common type of enyne cycloisomerization that generates endocyclization products.² For example, Wilkinson’s catalyst converts 1,6-enynes into conjugated methylenecyclohexenes.³ On the basis of isotopic labelling experiments, Lee proposed that the

reaction is initiated by the isomerization of a Rh(alkyne) complex to a Rh(vinylidene).^{4,5} It stands to reason that this pathway is disfavored for most other catalysts, because alkynes are approximately 43 kcal/mol more stable than their corresponding vinylidene isomers.⁶ Consequently, only catalysts that form stable M=C multiple bonds and weak M(π -C \equiv C) interactions can carry out this step.⁷

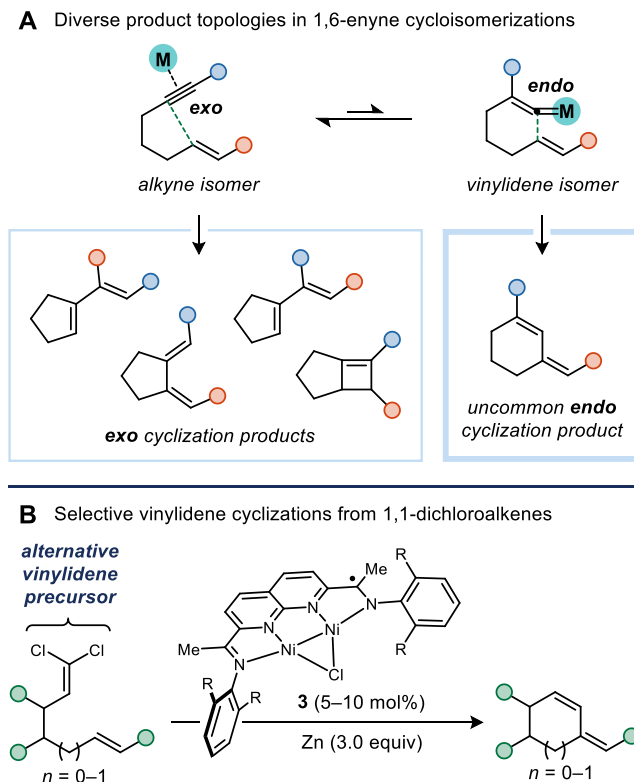


Figure 1.1. (a) Exo and endo cyclization modes of 1,6-enynes. (b) Reductive activation of 1,1-dichloroalkenes enable selective vinylidene–alkene cyclization reactions.

If generation of the key $M=C=CR_2$ intermediate did not rely on an isomerization of an alkyne, it may be possible to develop a more general strategy for catalytic vinylidene transfer. In this context, it was striking to us that the hypothetical reaction of 1,1-dichloroethylene⁸ and Zn to form vinylidene⁹ and $ZnCl_2$ is near thermoneutral. Thus, reactive $M=C=CR_2$ species should be thermodynamically accessible from these starting materials. Based on this hypothesis, we discovered that dinickel catalysts could successfully promote intermolecular [2 + 1]-cycloadditions of vinylidenes generated reductively from various substituted 1,1-dichloroalkenes.¹⁰ Here, we present the intramolecular variant of this process, which generates the

product of a formal vinylidene insertion into a C(sp²)–H bond (Figure 1.1b). This approach to vinylidene generation addresses some of the previous limitations of enyne endo-cycloisomerizations. For example, internal alkenes are tolerated, and five-membered ring formations are demonstrated. A dinickel metallacycle derived from the addition of a vinylidene to an alkene is structurally characterized, and its role in the mechanism of catalysis is discussed. DFT calculations reveal that catalysis occurs through a series of intermediates and transition states where both Ni centers cooperatively direct bonding changes.

1.3 Results and Discussion

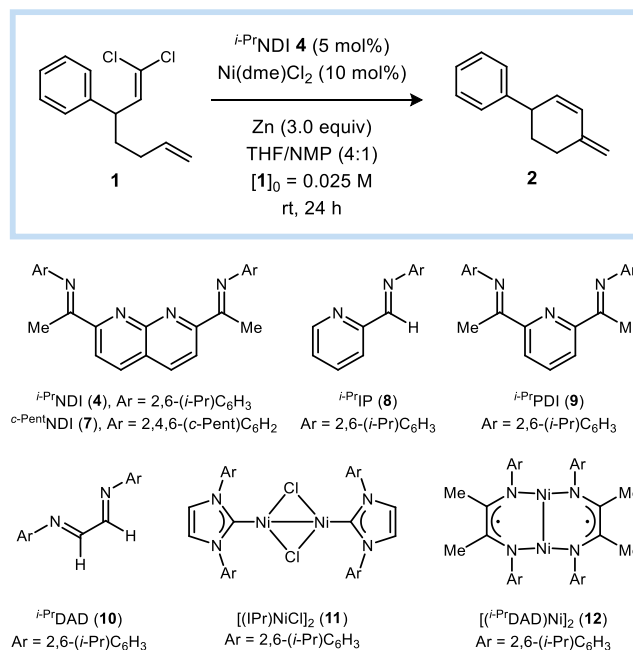
1.3.1 Catalytic Intramolecular Vinylidene Additions to Alkenes

Following reaction optimization studies, we identified a set of conditions that induces the reductive cyclization of model substrate **1** to form methylenecyclohexene **2** in 92% yield (Table 1.1, entry 1). The active (*i*-PrNDI)Ni₂Cl (**3**) catalyst was generated *in situ* by stirring *i*-PrNDI (**4**) (5 mol%) and Ni(dme)Cl₂ (10 mol%) over Zn powder (3.0 equiv) for 20 min prior to the addition of **1**. Formation of **3** is indicated by the appearance of a deep violet colored reaction solution.¹¹ Premetallated complexes, such as (*i*-PrNDI)Ni₂Cl₂ (**5**) and (*i*-PrNDI)Ni₂(C₆H₆) (**6**), provided comparable yields of product **2**, 91% and 90%, respectively (entries 4 and 5). The NDI variant containing ortho *c*-Pent substituents (**7**) was equally effective in the reaction (entry 6).

A low initial concentration of substrate **1** was beneficial for yield, presumably due to the suppression of competing bimolecular processes. For example, a two-fold increase in concentration to 0.05 M resulted in an 11% decrease in yield (entry 7). In our survey of reductants, Mn provided a similar yield to that obtained with Zn (entry 8).

As a point of comparison, we also tested mononickel catalysts containing various combinations of pyridine and imine donors. In all cases, only trace quantities of **2** were produced (<10% yield, entry 9). Likewise, other Ni(I) dimers **11**¹² and **12**¹³ also proved to be ineffective as catalysts (entry 10). Collectively, these results suggest that the constrained dinuclear active site of the (NDI)Ni₂ system is a requirement for efficient catalysis.

Table 1.1. Effects of Reaction Parameters on the Reductive Vinylidene Cyclization.



entry	deviation from standard conditions ^a	yield (2)
1	none	92%
2	no 4	0%
3	no 4 and no Ni(dme)Cl ₂	0%
4	(<i>i</i> -PrNDI)Ni ₂ Cl ₂ (5) instead of 4 /Ni(dme)Cl ₂	91%
5	(<i>i</i> -PrNDI)Ni ₂ (C ₆ H ₆) (6) instead of 4 /Ni(dme)Cl ₂	90%
6	<i>c</i> -PentNDI (7) instead of 4	90%
7	0.05 M instead of 0.025 M	81%
8	Mn instead of Zn	88%
9	Ligands 8–10 (5 mol%) instead of 4 ^b	<10%
10	11 or 12 (5 mol%) instead of 4 /Ni(dme)Cl ₂	<1%

^aStandard reaction conditions: **1** (0.10 mmol, 1.0 equiv), *i*-PrNDI (5 mol%), Ni(dme)Cl₂ (10 mol%), Zn (0.3 mmol, 3.0 equiv), NMP (0.8 mL), THF (3.2 mL), 24 h, rt. All yields were determined by ¹H NMR using mesitylene (1.0 equiv) as an internal standard. ^b5 mol% of Ni(dme)Cl₂.

1.3.2 Substrate Scope Studies

With optimized reaction conditions in hand, we next examined how structural changes to the substrate influence the yield of cyclization (Figure 1.2). A variety of synthetic routes were used to prepare the requisite 1,1-dichloroalkene substrates. For example, diastereoselective conjugate

allylation using an oxazolidinone chiral auxiliary yielded **13**.¹⁴ Conversion of **13** to aldehyde **14** was carried out with DIBAL-H, and one-carbon homologation using CCl₄ (2.0 equiv) and Ph₃P (4.0 equiv) yielded 1,1-dichloroalkene **15**. The catalytic reductive cyclization was carried out under standard conditions and provided **16** in 81% yield.

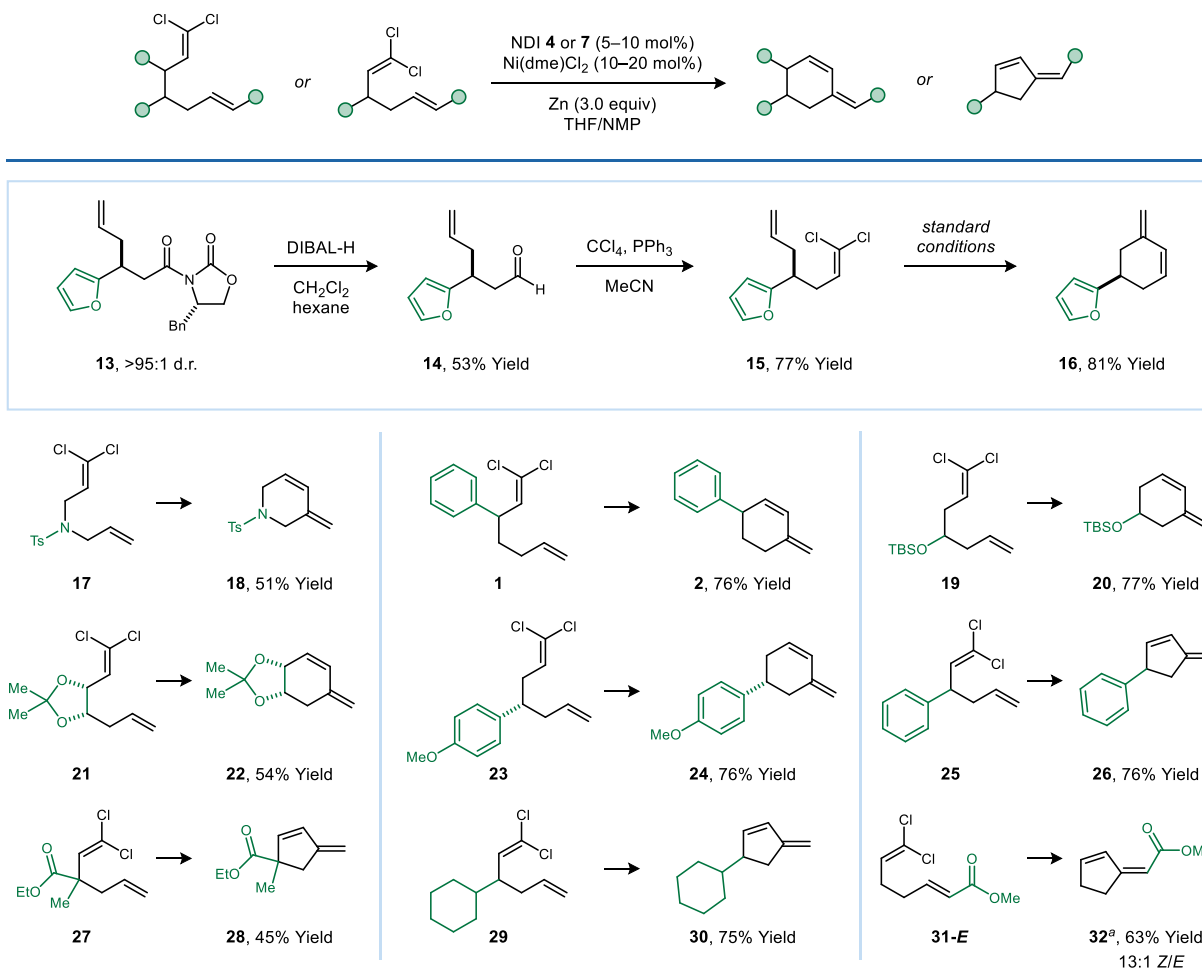


Figure 1.2. Substrate scope studies. Isolated yields were determined following purification and were averaged over two runs. Standard reaction conditions: substrate (0.2 mmol), i-PrNDI (**4**) (5–10 mol%), Ni(dme)Cl₂ (10–20 mol%), Zn (3.0 equiv), NMP (1.6 mL), THF (6.4 mL), rt or 50 °C, 24h. ^asubstrate (0.2 mmol), *c*-pentNDI (**7**), (10 mol%), Ni(dme)Cl₂ (20 mol%), Zn (3.0 equiv), NMP (0.8 mL), THF (7.2 mL), rt, 24h.

Variation of the substrate tether length grants access to five-membered ring products, requiring only slight modifications to the reaction conditions: increased catalyst loading (10 mol%) and heating at 50 °C. In addition to forming methylenecyclohexenes and methylenecyclopentenes, this method is also amendable to the formation of unsaturated heterocycles (product **18**). However,

an attempted cyclization to form a seven-membered ring did not yield any product. Common functional groups are tolerated, including protected alcohols, acetals, and esters. Steric hindrance adjacent to the 1,1-dichloroalkene is well-tolerated (products **26**, **28**, and **30**). However, substituting the position next to the terminal alkene results in no yield of cyclized product.

Upon further evaluation of the reaction conditions, we found that a limited scope of products containing substituted exocyclic alkenes are accessible when the *c*-Pent substituted NDI ligand **7** was used in the place of the *i*-Pr ligand **4**. For example, ester substituted methylenecyclopentene **32** is formed in 63% yield (13:1 *Z/E* mixture) from **31-E**. On the other hand, a substrate containing a Ph substituent on the alkene proved to be unreactive (see Supporting Information for a summary of the reaction limitations).

1.3.3 Evidence in Support of a Stepwise Ni₂(vinylidene) Addition Mechanism

The proposed mechanism for Rh-catalyzed 1,6-enyne cycloisomerization reactions involves an initial [2 + 2]-cycloaddition of a Rh vinylidene and the pendant alkene.⁴ The metallacyclic intermediate then undergoes β -hydride elimination followed by C–H reductive elimination to form the product. There is evidence to support a similar mechanism for the Ni₂-catalyzed reductive cyclization, as opposed to a direct C–H insertion mechanism as would be typical for free vinylidene 1,5-insertions into C(sp³)–H bonds (Figure 1.3).¹⁵

A substrate containing a methyl substituent on the alkene was prepared and tested in the reductive cyclization. The putative metallacycle that would be generated from this substrate would have two potential pathways for β -hydride elimination. Indeed, **33** reacts under standard catalytic conditions to yield a 1:4 mixture of two isomeric products (**34** and **35**) in a combined yield of 84%.

Substrates **36-E** and **36-Z** react in a stereoconvergent fashion to provide the same product with *Z* stereochemistry at the exocyclic alkene. One possible explanation for this observation is that the alkene stereochemistry scrambles through a reversible β -hydride elimination/migratory insertion process. This result is inconsistent with a direct C–H insertion mechanism, which would preserve the alkene stereochemistry.

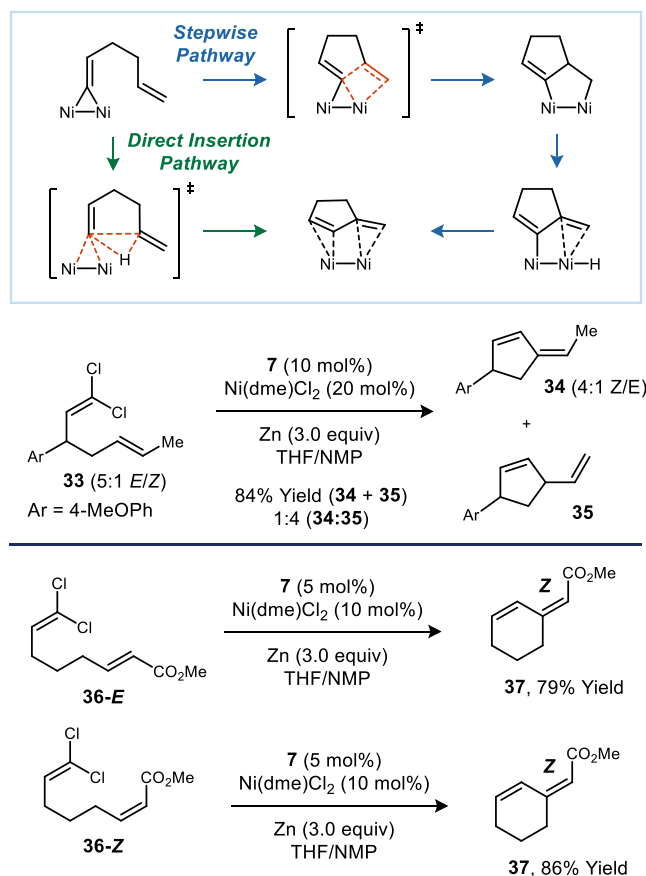


Figure 1.3. Experiments supporting a stepwise vinylidene addition mechanism.

1.4 Electrocatalytic Reductive Cyclizations and the Role of Zn

By cyclic voltammetry (CV), (*i*-PrNDI)Ni₂Cl₂ (**5**) possesses two reduction waves at -1.14 V and -1.34 V vs. Cp₂Fe/Cp₂Fe⁺ and one return oxidation at -1.05 V (Figure 4c). We attribute the presence of two reductive events to partial dissociation of chloride in the polar NMP solvent.¹⁷ When the CV of **5** was obtained in THF, only the more cathodic wave at -1.34 V was observed.¹⁷ There is a second reversible reduction at $E_{1/2} = -1.64$ V. When (*i*-PrNDI)Ni₂Cl₂ complex **5** is stirred over excess Zn powder, it undergoes a one-electron reduction to the violet (*i*-PrNDI)Ni₂Cl complex **3**, and no further reduction is observed. This result suggests that the mechanism of catalysis does not require accessing the two-electron reduced state of the Ni₂ complex. When CV experiments were conducted using solutions of complex **5** containing substrate **1**, the reduction events for **5** became irreversible, indicating that activation of the 1,1-dichloroalkene by the reduced catalyst is rapid on the CV timescale.

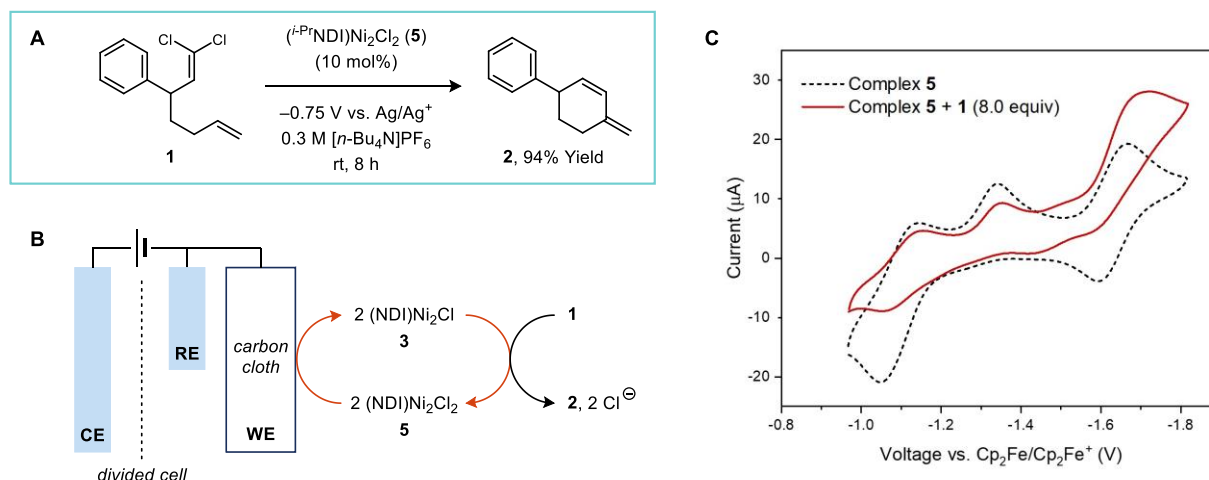


Figure 1.4. (a) Controlled potential electrolysis experiments for the catalytic conversion of **1** to **2**. (b) Experimental setup (CE = counter electrode; RE = reference electrode; WE = working electrode) and a proposed one-electron catalytic cycle. (c) Cyclic voltammetry data for complex **5** in the presence and absence of **1** (0.3 M $[n\text{-Bu}_4\text{N}]\text{PF}_6$ in NMP; 100 mV/s scan rate). All cyclic voltammograms were internally referenced to the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple.

Based on these data, bulk electrolysis experiments were carried out at constant potential (-0.75 V vs. a Ag/Ag^+ reference electrode; approximately -1.35 V vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$) using substrate **1** in a divided H-cell (Figure 1.4a and 1.4b). In order to ensure high mass transport, a large surface area carbon cloth working electrode was used, and the reaction was stirred vigorously at 900 rpm. After 8 h of electrolysis, an aliquot of the reaction mixture was removed. Analysis by ^1H NMR spectroscopy indicated that product **2** was formed in 94% yield, and 20.6 C of charge (2.27 F/mol of product) were passed during the 8 h reaction period, corresponding to a Faradaic efficiency of 88%.

1.5 Stoichiometric Reductive Cyclization Reactions

Having established that Zn is only involved in catalyst turnover, we next examined a series of stoichiometric reactions using $(i\text{-PrNDI})\text{Ni}_2(\text{C}_6\text{H}_6)$ (**6**). A reaction between **6** (1.0 equiv) and substrate **1** was carried out in C_6D_6 and monitored by ^1H NMR spectroscopy (Figure 1.5a). Over the course of 24 h, cyclized product **2** was generated (90% yield), concomitant with the formation of $(i\text{-PrNDI})\text{Ni}_2\text{Cl}_2$ (**5**). When the same experiment was repeated using substrate **25**, some amount of $(i\text{-PrNDI})\text{Ni}_2\text{Cl}_2$ (**5**) was still generated, but the expected cyclized product **26** could not be detected, and no other diagnostic peaks were observed in the ^1H NMR spectrum, even after 24 h.

(Figure 1.5b). A frozen-solution EPR spectrum of the product mixture showed a prominent rhombic signal, indicating the presence of an $S = 1/2$ Ni₂ complex (Figure 1.5d).

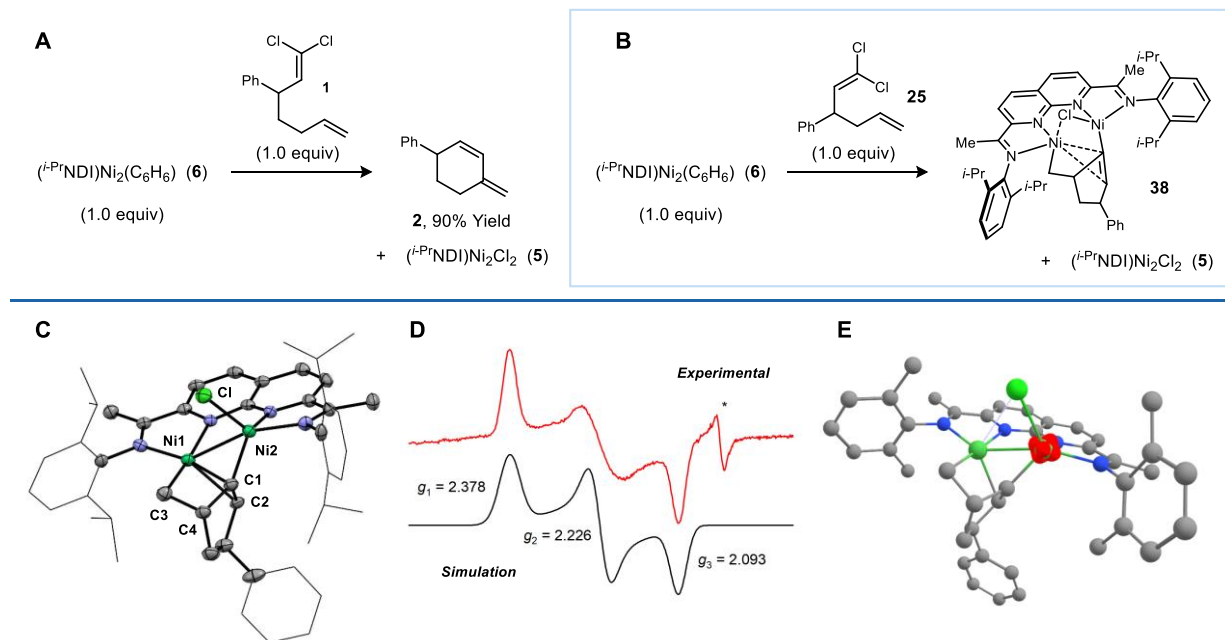


Figure 1.5. Experiments probing the stoichiometric activation of 1,1-dichloroalkene substrates with (*i*-PrNDI)Ni₂(C₆H₆) complex **6**. (a) Stoichiometric reductive cyclization of **1** using complex **6**. (b) Stoichiometric reaction between complex **6** and substrate **25** to form metallacycle **38**. (c) XRD structure of metallacycle **38**. Selected bond metrics: Ni1–Ni2: 2.743(1) Å; Ni1–C1: 2.000(6) Å; Ni1–C3: 1.967(4) Å; Ni2–C1: 1.954(5) Å; Ni2–Cl: 2.243(2) Å. (d) Frozen solution EPR spectrum for **38** (105 K; toluene). Simulated parameters: $g = [2.378, 2.226, 2.093]$. * corresponds to a $S = 1/2$ impurity. (e) UM06-L spin density plot for **38**.

After removing the (*i*-PrNDI)Ni₂Cl₂ byproduct (**5**) from this crude mixture, the EPR active complex was successfully isolated, and single crystals were obtained from a pentane/THF solution. XRD analysis revealed that the unknown Ni₂ species (**38**) is a metallacycle, resulting from the addition of a vinylidene to the pendant alkene (Figure 1.5c). The two Ni atoms, the alkene, and the vinylidene form a five-membered ring, and Ni1 is engaged in a secondary π -interaction with the C1–C2 double bond. Only one chloride is present in the structure, consistent with **38** being in a non-integer spin system. Therefore, the balanced equation for this reaction involves 1.5 equiv of (*i*-PrNDI)Ni₂(C₆H₆) (**6**) reacting with 1.0 equiv of substrate **25** to form 0.5 equiv of (*i*-PrNDI)Ni₂Cl₂ (**5**) and 1.0 equiv of **38**.

Complex **38** is best described as a mixed valent Ni(II)/Ni(I) species, with the NDI ligand having a neutral charge. The neutral charge of the ligand is supported by analysis of the ligand C–C and C–N bond metrics in the XRD structure. The Ni1–Ni2 distance is 2.743 Å, which is considerably longer than the Ni(I)–Ni(I) single bond in complex **6**, suggesting that there is minimal covalent bonding between the two Ni atoms. The spin density plot shows that the unpaired electron is localized on Ni2, which is in a pseudo-tetrahedral geometry ($\tau_4 = 0.85$) (Figure 1.5e). Ni1 is pseudo-square planar ($\tau_4 = 0.14$) and is calculated to be in a low-spin configuration.

Metallacycle **38** is sufficiently stable at room temperature to allow for its isolation. However, upon extended heating at 50 °C in NMP/THF, the optimal solvent mixture for the catalytic cyclization, it reacts to form cyclized product **26** in 64% yield after 9 h (Figure 1.6). Given the relatively slow rate of this stoichiometric process and the modest yield of **26**, we wondered whether the catalytic cyclization may require reduction of metallacycle **38**. Indeed, metallacycle **38** possesses a reversible one-electron reduction at -1.59 V vs. $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$, which would be accessible using Zn (see Supporting Information).

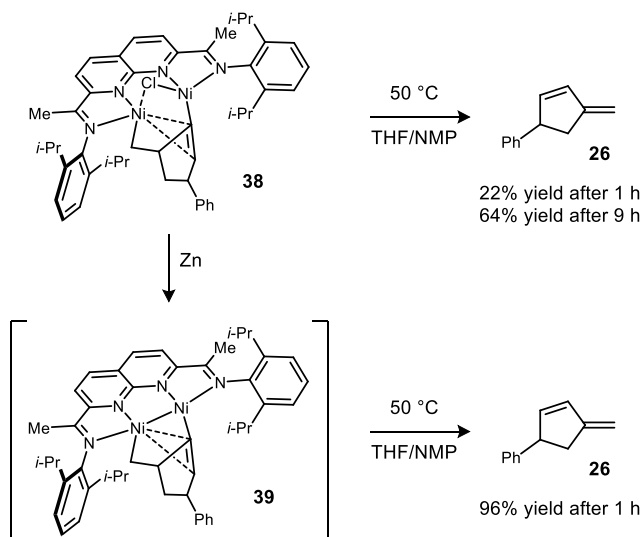


Figure 1.6. Comparison of rates and yields for stoichiometric cyclizations to form **26** as a function of oxidation state.

When **38** was stirred over Zn (3.0 equiv) in NMP/THF at 50 °C, product **26** was obtained in 96% yield after only 1 h. Given the fast rate of product formation, we were unable to isolate the reduced metallacycle **39**. However, when metallacycle **38** was dissolved in C_6D_6 and reduced over

KC₈ (1.2 equiv), a new set of diamagnetic signals was observed in the ¹H NMR spectrum. These signals decay over the course of 3 h at 50 °C to provide product **26** in 58% yield and the (*i*-Pr₃NDI)Ni₂(C₆D₆) complex **6** in 61% yield.

1.6 DFT Calculations

We used unrestricted DFT (UM06-L)^{18,19,20} to calculate the thermodynamics, barriers, and spin crossovers (MECPro program)²¹ of reaction pathways that convert **40** to **38** and then to **44** (Figures 1.7 and 1.8). From previous benchmarking studies of DFT methods, the M06-L functional was identified as producing relative energies of different spin states for (NDI)Ni₂ complexes that matched experimental data.²² Five major pathways were explored for the conversion of **40** to **38**, each having oxidative addition, migratory insertion, and reduction steps in different orders. Figure 1.7 displays only the lowest energy pathway.

The initial π -complex **40** favors a triplet ground state, but the singlet is only 3 kcal/mol higher in energy, suggesting that it may have some multireference character. Oxidative addition of the C–Cl bond (TS40) has a low barrier on both the singlet and triplet surfaces. Both Ni centers are directly involved in the oxidative addition, such that the resulting vinyl and chloride fragments in **41** are situated in bridging positions. Vinyl complex **41** has a quintet ground state, and an energy-degenerate spin crossover structure (minimum energy crossing point; MECP) between the triplet and quintet surfaces was identified.

From **41**, reduction with Zn coupled to chloride loss is endothermic by 4 kcal/mol. The thermodynamics of this first reduction was calculated as the conversion of Zn₂ to linear Zn₂Cl. Later, the second reduction was calculated as the conversion of Zn₂Cl to ZnCl₂ and Zn. This reduction step provides a low barrier pathway for activation of the second C–Cl bond through TS41. Similar to TS40, both Ni centers participate in C–Cl oxidative addition. This transition state leads to bridging vinylidene complex **42**, which features a secondary interaction between the vinylidene π -bond and one of the Ni centers (Figure 1.7). The isolable complex **38** can be accessed through a low energy migratory insertion pathway with a barrier of <2 kcal/mol on the quartet surface (TS42). In progressing from **42** to **38**, the Ni–Ni distance elongates from 2.60 to 2.69 Å to accommodate the incoming alkene.

As an alternative mechanism for the formation of **38**, a non-reductive second C–Cl oxidative addition step from **41** was considered but found to be higher in energy. Furthermore, without

formation of vinylidene **42**, migratory insertion of the pendant alkene into the Ni(vinyl) bond of **41** was calculated to be prohibitive in energy (activation barrier: 28 kcal/mol).

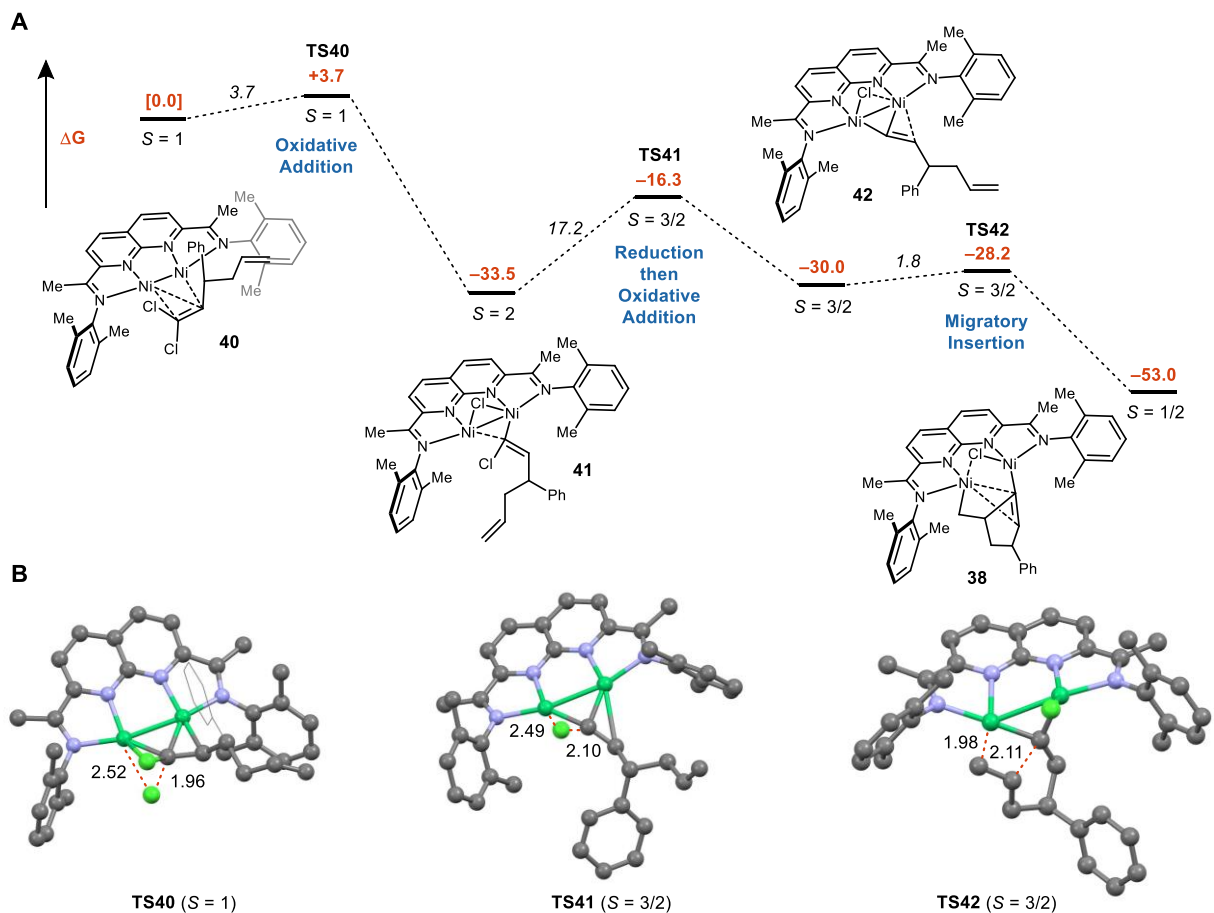


Figure 1.7. (a) DFT-calculated reaction pathways for the cyclization of **25** to give complex **38**. Relative Gibbs free energies are shown in kcal/mol. Isopropyl groups were modeled as methyl groups. (b) 3D representations of key transition-state structures. Spin states are given in parenthesis. Hydrogens are removed for clarity. Distances are reported in Å.

Finally, we examined pathways for the conversion of metallacycle **38** to the cyclized product. The fact that complex **38** can be isolated indicates that the subsequent β -hydride elimination must have a relatively high barrier (Figure 1.8). Our DFT calculations corroborate this finding, and the calculated barrier for β -hydride elimination is 29 kcal/mol. Reduction of **38** and loss of chloride lowers the migratory insertion barrier to 26 kcal/mol, which is also consistent with experimental findings (Figure 1.8). β -Hydride elimination gives hydride **43**. Reductive elimination

occurs at a single Ni center and has a barrier of 3 kcal/mol, yielding the product complex **44**, where the conjugated diene is η^4 -coordinated to both Ni centers.

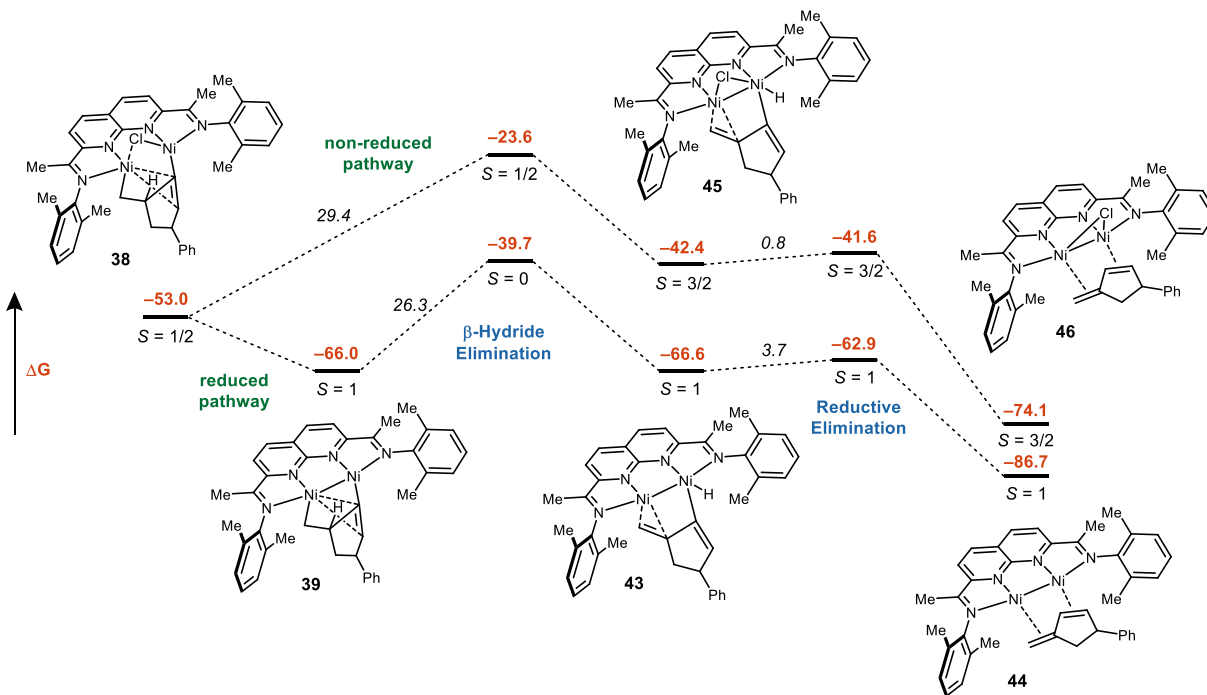


Figure 1.8. DFT-calculated reaction pathways for conversion of **38** to **44/46** as a function of oxidation state. Relative Gibbs free energies are shown in kcal/mol.

1.7 Conclusions

In summary, dinickel catalysts promote the reductive cyclization of 1,1-dichloroalkenes containing pendant alkenes through a Ni_2 -bound bridging vinylidene intermediate. Previous approaches to carrying out such cyclizations relied on a metal-induced alkyne-to-vinylidene isomerization. However, there is a limited scope of catalysts that can carry out this step, and endo cycloisomerizations are significantly less common than exo cycloisomerizations that proceed through metal(alkyne) intermediates. This reductive strategy may therefore prove useful in other transformations where alkynes are not viable as metal(vinylidene) precursors.

Mechanistic studies are consistent with a putative $\text{Ni}_2(\text{vinylidene})$ undergoing migratory insertion to generate a metallacyclic intermediate. Product formation would then proceed by β -hydride elimination followed by C–H reductive elimination. In the case of a five-membered ring-forming reaction, the key metallacyclic intermediate proved to be an isolable complex, and

reduction with Zn resulted in high-yielding conversion to product. DFT models reveal that the canonical organometallic steps—oxidative addition, migratory insertion, β -hydride elimination, and reductive elimination—involve the direct participation of both Ni centers, with the Ni–Ni interaction responding as needed to accommodate various reactive intermediates.

1.8 Acknowledgements

This research was supported by the NIH (R35 GM124791). C.U. acknowledges support from a Camille Dreyfus Teacher–Scholar award and a Lilly Grantee award. D.H.E. thanks the NSF Chemical Catalysis Program for support (CHE-1764194). Funding for Hector Torres was provided by the NSF Chemistry and Biochemistry REU Site to Prepare Students for Graduate School and an Industrial Career under award CHE-1757627. We thank Dr. Matthias Zeller for assistance with X-ray crystallography. D.H.E. thanks Brigham Young University (BYU) and the Fulton Supercomputing Lab (FSL).

1.9 References

- (1) (a) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. "Transition Metal-Catalyzed Carbocyclizations in Organic Synthesis" *Chem. Rev.* **1996**, 96, 635-662; (b) Aubert, C.; Buisine, O.; Malacria, M. "The Behavior of 1,n-Enynes in the Presence of Transition Metals" *Chem. Rev.* **2002**, 102, 813-834; (c) Lloyd-Jones, G. C. "Mechanistic aspects of transition metal catalysed 1,6-diene and 1,6-enyne cycloisomerisation reactions" *Org. Biomol. Chem.* **2003**, 1, 215-236; (d) Echavarren, A. M.; Nevado, C. "Non-stabilized transition metal carbenes as intermediates in intramolecular reactions of alkynes with alkenes" *Chem. Soc. Rev.* **2004**, 33, 431-436; (e) Zhang, L.; Sun, J.; Kozmin, S. A. "Gold and Platinum Catalysis of Enyne Cycloisomerization" *Adv. Synth. Catal.* **2006**, 348, 2271-2296; (f) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. "Cycloisomerization of 1,n-Enynes: Challenging Metal-Catalyzed Rearrangements and Mechanistic Insights" *Angew. Chem., Int. Ed.* **2008**, 47, 4268-4315.
- (2) (a) Nuñez-Zarur, F.; Solans-Monfort, X.; Rodríguez-Santiago, L.; Sodupe, M. "Exo/endo Selectivity of the Ring-Closing Enyne Methathesis Catalyzed by Second Generation Ru-Based Catalysts. Influence of Reactant Substituents" *ACS Catal.* **2013**, 3, 206-218; (b) Lee, O. S.; Kim, K. H.; Kim, J.; Kwon, K.; Ok, T.; Ihee, H.; Lee, H.-Y.; Sohn, J.-H. "Correlation between Functionality Preference of Ru Carbenes and exo/endo Product Selectivity for Clarifying the Mechanism of Ring-Closing Enyne Metathesis" *J. Org. Chem.* **2013**, 78, 8242-8249.
- (3) Grigg, R.; Stevenson, P.; Worakun, T. "Rhodium (I) catalysed regiospecific cyclisation of 1,6-enynes to methylenecyclohex-2-enes" *Tetrahedron* **1988**, 44, 4967-4972.

- (4) Kim, H.; Lee, C. "Cycloisomerization of Enynes via Rhodium Vinylidene-Mediated Catalysis" *J. Am. Chem. Soc.* **2005**, *127*, 10180-10181.
- (5) (a) Bruneau, C.; Dixneuf, P. H. "Metal Vinylidenes and Allenylidenes in Catalysis: Applications in Anti-Markovnikov Additions to Terminal Alkynes and Alkene Metathesis" *Angew. Chem., Int. Ed.* **2006**, *45*, 2176-2203; (b) Bruneau, C.; Dixneuf, P. *Metal vinylidenes and allenylidenes in catalysis: from reactivity to applications in synthesis*; John Wiley & Sons, 2008; (c) Trost, B. M.; McClory, A. "Metal Vinylidenes as Catalytic Species in Organic Reactions" *Chem. Asian J.* **2008**, *3*, 164-194; (d) Roh, S. W.; Choi, K.; Lee, C. "Transition Metal Vinylidene- and Allenylidene-Mediated Catalysis in Organic Synthesis" *Chem. Rev.* **2019**, *119*, 4293-4356.
- (6) Chang, N.-Y.; Shen, M.-Y.; Yu, C.-H. "Extended ab initio studies of the vinylidene-acetylene rearrangement" *J. Chem. Phys.* **1997**, *106*, 3237-3242.
- (7) Bruce, M. I. "Organometallic chemistry of vinylidene and related unsaturated carbenes" *Chem. Rev.* **1991**, *91*, 197-257.
- (8) Manion, J. A. "Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 Chlorinated Hydrocarbons" *J. Phys. Chem. Ref. Data* **2002**, *31*, 123-172.
- (9) Lee, H.; Baraban, J. H.; Field, R. W.; Stanton, J. F. "High-Accuracy Estimates for the Vinylidene-Acetylene Isomerization Energy and the Ground State Rotational Constants of :C=CH₂" *J. Phys. Chem. A* **2013**, *117*, 11679-11683.
- (10) (a) Pal, S.; Zhou, Y.-Y.; Uyeda, C. "Catalytic Reductive Vinylidene Transfer Reactions" *J. Am. Chem. Soc.* **2017**, *139*, 11686-11689; (b) Zhou, Y.-Y.; Uyeda, C. "Catalytic reductive [4 + 1]-cycloadditions of vinylidenes and dienes" *Science* **2019**, *363*, 857-862.
- (11) Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. "Dinuclear Nickel Complexes in Five States of Oxidation Using a Redox-Active Ligand" *Inorg. Chem.* **2014**, *53*, 11770-11777.
- (12) Dible, B. R.; Sigman, M. S.; Arif, A. M. "Oxygen-Induced Ligand Dehydrogenation of a Planar Bis- μ -Chloronickel(I) Dimer Featuring an NHC Ligand" *Inorg. Chem.* **2005**, *44*, 3774-3776.
- (13) Dong, Q.; Yang, X.-J.; Gong, S.; Luo, Q.; Li, Q.-S.; Su, J.-H.; Zhao, Y.; Wu, B. "Distinct Stepwise Reduction of a Nickel-Nickel-Bonded Compound Containing an α -Diimine Ligand: From Perpendicular to Coaxial Structures" *Chem. Eur. J.* **2013**, *19*, 15240-15247.
- (14) Smith, A. B.; Cantin, L.-D.; Pasternak, A.; Guise-Zawacki, L.; Yao, W.; Charnley, A. K.; Barbosa, J.; Sprengeler, P. A.; Hirschmann, R.; Munshi, S.; Olsen, D. B.; Schleif, W. A.; Kuo, L. C. "Design, Synthesis, and Biological Evaluation of Monopyrrolinone-Based HIV-1 Protease Inhibitors" *J. Med. Chem.* **2003**, *46*, 1831-1844.

- (15) Knorr, R. "Alkylidenecarbenes, Alkylidenecarbenoids, and Competing Species: Which Is Responsible for Vinylic Nucleophilic Substitution, [1 + 2] Cycloadditions, 1,5-CH Insertions, and the Fritsch–Buttenberg–Wiechell Rearrangement?" *Chem. Rev.* **2004**, *104*, 3795-3850.
- (16) (a) Perkins, R. J.; Pedro, D. J.; Hansen, E. C. "Electrochemical Nickel Catalysis for sp^2 - sp^3 Cross-Electrophile Coupling Reactions of Unactivated Alkyl Halides" *Org. Lett.* **2017**, *19*, 3755-3758; (b) Perkins, R. J.; Hughes, A. J.; Weix, D. J.; Hansen, E. C. "Metal-Reductant-Free Electrochemical Nickel-Catalyzed Couplings of Aryl and Alkyl Bromides in Acetonitrile" *Org. Process Res. Dev.* **2019**, *23*, 1746-1751; (c) DeLano, T. J.; Reisman, S. E. "Enantioselective Electroreductive Coupling of Alkenyl and Benzyl Halides via Nickel Catalysis" *ACS Catal.* **2019**, *9*, 6751-6754; (d) Jiao, K.-J.; Liu, D.; Ma, H.-X.; Qiu, H.; Fang, P.; Mei, T.-S. "Nickel-Catalyzed Electrochemical Reductive Relay Cross-Coupling of Alkyl Halides to Aryl Halides" *Angew. Chem., Int. Ed.* **2020**, *59*, 6520-6524; (e) Truesdell, B. L.; Hamby, T. B.; Sevov, C. S. "General $C(sp^2)$ - $C(sp^3)$ Cross-Electrophile Coupling Reactions Enabled by Overcharge Protection of Homogeneous Electrocatalysts" *J. Am. Chem. Soc.* **2020**, *142*, 5884-5893.
- (17) Zhou, Y.-Y.; Uyeda, C. "Reductive Cyclopropanations Catalyzed by Dinuclear Nickel Complexes" *Angew. Chem., Int. Ed.* **2016**, *55*, 3171-3175.
- (18) Stationary points were optimized in Gaussian 16 using unrestricted M06-L. All singlet structures refer to open-shell singlets that have spin contamination. All structures were verified as minima or transition-state structures using normal-mode vibrational frequency analysis. All Gibbs energies include standard thermochemical enthalpy and entropy corrections at 298 K.
- (19) Zhao, Y.; Truhlar, D. G. "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals" *Theo. Chem. Acc.* **2008**, *120*, 215-241.
- (20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, revision B.01; Gaussian, Inc., Wallingford CT, 2016.

- (21) MECPro Version 1.0.6. Minimum Energy Crossing Program (2020) Justin D. Snyder, Lily-Anne Hamill, Kavika E. Faleumu, Allen R. Schultz and Daniel H. Ess.
- (22) Kwon, D.-H.; Proctor, M.; Mendoza, S.; Uyeda, C.; Ess, D. H. "Catalytic Dinuclear Nickel Spin Crossover Mechanism and Selectivity for Alkyne Cyclotrimerization" *ACS Catal.* **2017**, 7, 4796-4804.

CHAPTER 2. A DINICKEL-CATALYZED THREE-COMPONENT CYCLOADDITION OF VINYLIDENES

Abstract

A dinickel catalyst promotes the [2 + 2 + 1]-cycloaddition of two aldehyde equivalents and a vinylidene. The resulting methylenedioxolane products can be deprotected in one pot under acidic conditions to reveal α -hydroxy ketones. This method provides convenient access to unsymmetrical alkyl-substituted α -hydroxy ketones, which are challenging to synthesize selectively using cross-benzoin reactions. Mechanistic studies are consistent with an initial migratory insertion of the aldehyde into a dinickel bridging vinylidene. Insertion of the second aldehyde followed by C–O reductive elimination furnishes the cycloadduct. Under dilute conditions, an enone side product is generated due to a competing β -hydride elimination from the proposed metallacyclic intermediate. A DFT model consistent with the concentration-dependent formation of the methylenedioxolane and enone is presented.

2.1 Introduction

[2 + 2 + 1]-Cycloadditions provide some of the most direct routes to five-membered rings and feature in numerous total syntheses of polycyclic natural products.¹ The Pauson–Khand reaction is the prototypical example in this class of cycloadditions and uses $\text{Co}_2(\text{CO})_8$ to mediate the coupling of an alkyne, an alkene, and CO (Figure 2.1a).² In the half century since its discovery, other transition metal catalysts have been found to promote Pauson–Khand reactions,³ and variants where the alkene is replaced with a hetero- π -system, such as an imine⁴ or an aldehyde,⁵ have been developed. In most cases, CO is required to serve as the one-atom partner, though in some cases isonitriles can also be used.⁶ Mechanistically, Pauson–Khand reactions are initiated by the oxidative cyclization of the alkene and the alkyne.⁷ CO is then incorporated by migratory insertion followed by C–C reductive elimination.

It would be synthetically valuable to expand the scope of [2 + 2 + 1]-cycloadditions to include more reactive classes of carbenes.⁸ To that end, we became interested in a mechanistic pathway that would effectively reverse the typical sequence of events in the Pauson–Khand reaction. First, a metal carbene ($\text{M}=\text{CR}_2$), generated from an appropriate precursor, would react

with a 2π -component to form a four-membered metallacycle.⁹ If reductive elimination were sufficiently slow, then it may be possible to intercept this intermediate with a second 2π -component to yield a five-membered cycloadduct. The principal challenge in this scheme is avoiding direct $[2 + 1]$ -additions of the metal carbene, which would lead to the formation three-membered ring products. Indeed, many of the most common carbene transfer catalysts, such as $\text{Rh}_2(\text{CO}_2\text{R})_4$ ¹⁰ and Cu(I) complexes,¹¹ carry out cyclopropanation reactions by this concerted pathway, making them unsuitable for the development of three-component cycloadditions.

Dinickel catalysts promote methylenecyclopropanation reactions using vinylidenes derived from 1,1-dichloroalkenes (Figure 2.1b).¹² Mechanistic studies suggest that, rather than a concerted $[2 + 1]$ -cycloaddition, these reactions proceed in a stepwise manner. The primary evidence came from experiments probing stereospecificity. When a geometrically pure alkene was used, the cyclopropane was formed as a cis/trans mixture. This observation, supported by DFT modelling studies, led us to propose a mechanism in which the alkene first undergoes migratory insertion into a $\text{Ni}_2(\text{vinylidene})$ to form an intermediate with the general structure **1**. Then, C–C reductive elimination generates the cyclopropane product. We were recently successful in arresting this process and obtaining direct experimental support for metallacycle **1**.¹³ By using a substrate in which the 1,1-dichloroalkene is tethered to the alkene, the final C–C reductive elimination is precluded by the high ring-strain of the hypothetical bicyclic methylenecyclopropane product.

Based on this stepwise mechanism, we wondered whether metallacycles such as **1** could be intercepted with a third reaction partner to form rings larger than cyclopropanes. Here, we provide an example of such a transformation in the context of a $[2 + 2 + 1]$ -cycloaddition of two aldehyde equivalents and a vinylidene (Figure 2.1c). Key to the realization of this reaction is the fact that competing $[2 + 1]$ -cycloadditions would produce methylene epoxides, which are sufficiently unstable to disfavor reductive elimination.¹⁴ The $[2 + 2 + 1]$ -cycloaddition products are methylenedioxolanes and can be deprotected under acidic conditions to reveal α -hydroxy ketones.

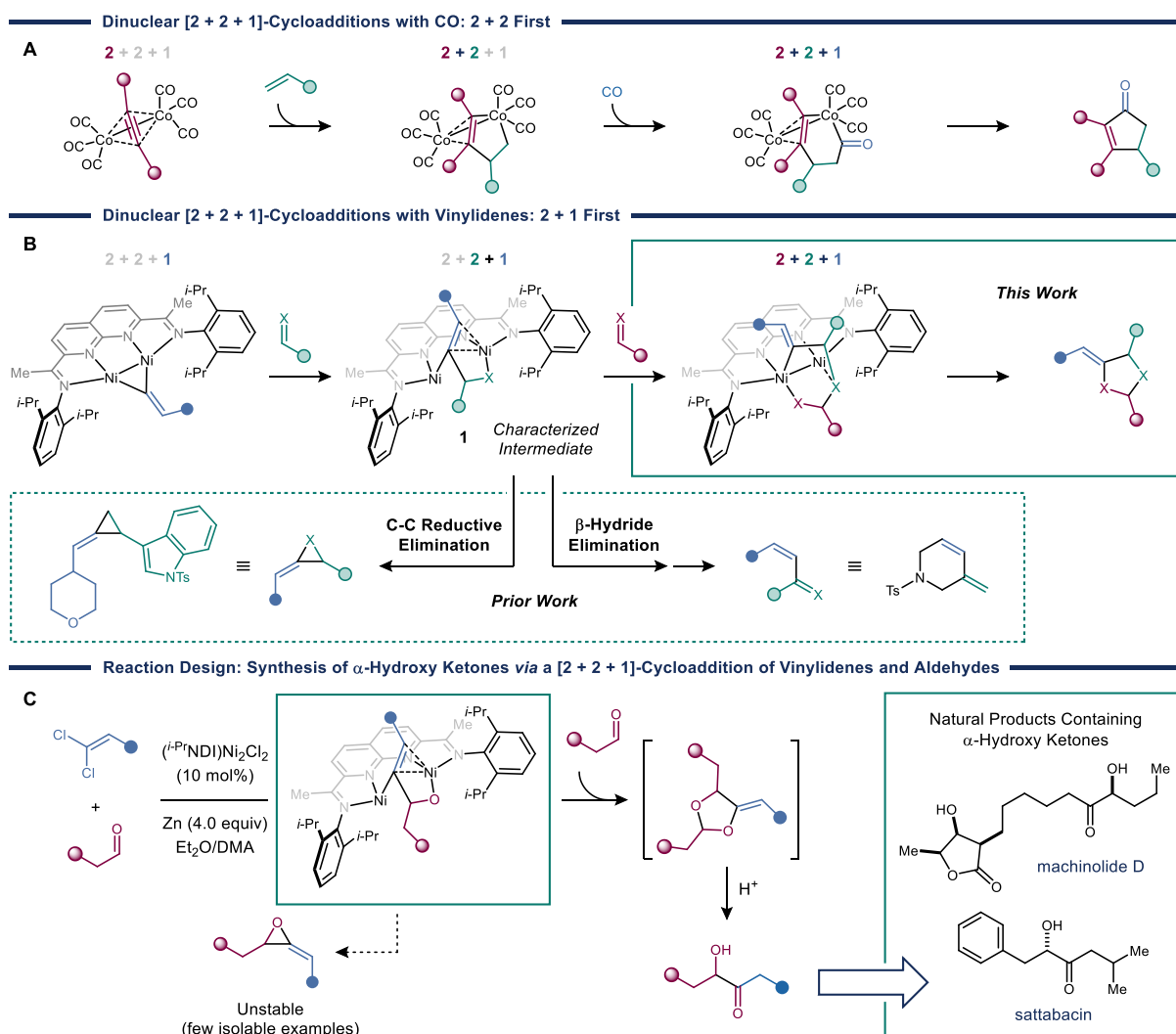


Figure 2.1. (a) A mechanism of the Pauson–Khand reaction initiated by a dinuclear oxidative coupling of the alkene and the alkyne. (b) A proposed vinylidene [2 + 2 + 1]-cycloaddition process involving a metallacycle derived from the migratory insertion of a 2π -component into a $\text{Ni}_2(\text{vinylidene})$. (c) A dinickel-catalyzed [2 + 2 + 1]-cycloaddition of two aldehydes and a vinylidene to generate methylenedioxolanes and synthetic applications to the synthesis of α -hydroxy ketones.

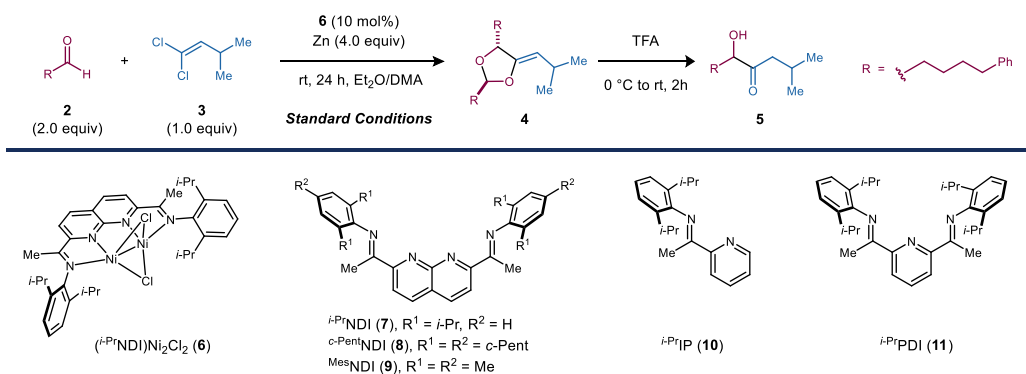
2.2 Results and Discussion

2.2.1 Reaction Development

Reaction optimization studies were carried out using aldehyde **2** (2.0 equiv) and 1,1-dichloroalkene **3** (1.0 equiv) as model substrates. Under conditions similar to those previously employed in [2 + 1]-cycloaddition reactions, dinickel catalyst **6** affords methylenedioxolane **4** in 89% yield as an 8:1 mixture of diastereomers and with exclusively *Z* stereochemistry at the

exocyclic alkene (Table 2.1, entry 1). Mn provided similar yields to those obtained with Zn (entry 2). Interestingly, the homogeneous reductant Cp₂Co also produced **4** but in significantly lower yields (entry 3). The observation that Zn can be replaced with Cp₂Co indicates that the reaction does not require the formation of an organozinc intermediate.

Table 2.1 Effect of Reaction Parameters



entry	deviations from Standard Conditions	yield (%) (4)	anti:syn (4)	Z/E (4)
1	none	89	8:1	>20:1
2	Mn instead of Zn	81	14:1	>20:1
3	Cp ₂ Co instead of Zn	58	1:4	>20:1
4	no Et ₂ O	47	4:1	>20:1
5	<i>i</i> -PrNDI (7) (10 mol%) + Ni(dme)Cl ₂ (20 mol%) instead of 6	85	6:1	>20:1
6	<i>c</i> -PentNDI (8) (10 mol%) + Ni(dme)Cl ₂ (20 mol%) instead of 6	46	3:1	>20:1
7	MesNDI (9) (10 mol%) + Ni(dme)Cl ₂ (20 mol%) instead of 6	<5	—	—
8	<i>i</i> -PrIP (10) (10 mol%) + Ni(dme)Cl ₂ (10 mol%) instead of 6	0	—	—
9	<i>i</i> -PrPDI (11) (10 mol%) + Ni(dme)Cl ₂ (10 mol%) instead of 6	0	—	—
10	Ni(dme)Cl ₂ (10 mol%) instead of 6	0	—	—

^aStandard reaction conditions: **2** (2.0 equiv), **3** (0.1 mmol, 1.0 equiv), (*i*-PrNDI)Ni₂Cl₂ (**6**) (10 mol%), Zn (4.0 equiv), DMA (0.1 mL), Et₂O (0.4 mL), 24 h, rt. All yields and selectivities were determined by ¹H NMR integration using mesitylene as an internal standard.

During reaction development, we found that the inclusion of a nonpolar cosolvent such as Et₂O was critical for reaction efficiency. With DMA alone, the yield of **4** decreased to 47% (entry 4). Both the identity of the reductant and the solvent appeared to have a significant effect on d.r. but did not impact the high Z selectivity at the exocyclic alkene. Under standard conditions, a premetallated dinickel catalyst was used (**6**). However, the active catalyst could also be assembled *in situ* by stirring free ⁱ-PrNDI (**7**) and Ni(dme)Cl₂ over Zn, and there was no significant change in reaction outcome (entry 5). Increasing (entry 6) or decreasing (entry 7) the steric profile of the NDI ligand decreased the yield of **4**. Finally, Ni(dme)Cl₂ alone or other mononickel catalysts bearing imine and/or pyridine donors analogous to those found in **6** proved to be ineffective in the reaction (entries 8, 9, and 10).

Following the [2 + 2 + 1]-cycloaddition, methylenedioxolane **4** was deprotected using TFA to form α-hydroxy ketone **5**. This two-step sequence can be carried out in a single pot without the need to isolate the intermediate dioxolane (62% yield over the two steps). α-Hydroxy ketones are found in many biologically active natural products (Figure 2.1c).¹⁵ The benzoin reaction, which involves the umpolung coupling of two aldehydes *via* an acyl anion intermediate, is one of the most common C–C coupling strategies used to form α-hydroxy ketones. In certain cases, it is possible to carry out selective cross-benzoin reactions by exploiting differences in the steric or electronic properties of the two partners.¹⁶ However, in cases where the two aldehydes are relatively unbiased, catalytic cross-coupling is generally not feasible. In these cases, a pregenerated acyl anion equivalent, such as a dithiane¹⁷ or a cyanohydrin,¹⁸ is required. The drawbacks of this approach are the need for additional synthetic steps and the use of a strong base (for example, an organolithium or metal amide) to generate the requisite anion.

2.2.2 Substrate Scope

To demonstrate the synthetic utility of this α-hydroxy ketone synthesis, we explored the substrate scope of the one-pot [2 + 2 + 1]-cycloaddition and deprotection sequence (Figure 2.2). The reaction proceeds in high yield with a variety of alkyl and aryl substituted 1,1-dichloroalkenes. Aliphatic aldehydes are effective reaction partners, whereas aromatic aldehydes and hindered aliphatic aldehydes containing α-branching are current limitations of the method. A variety of common functional groups and electron-rich heterocycles are compatible with the reaction conditions. Aryl bromides are tolerated (product **15**), demonstrating that 1,1-dichloroalkenes

undergo activation by the dinickel catalyst at faster rates than C(Ar)–Br bonds. Both a dichloroalkene and an aldehyde containing a pendant alkene proved to be efficient coupling partners (products **23** and **36**), and no competing cyclopropanation was observed. Other carbonyl functional groups, such as esters (products **24** and **30**), ketones (product **34**), and carbamates (product **22**), are left untouched in the cycloaddition.

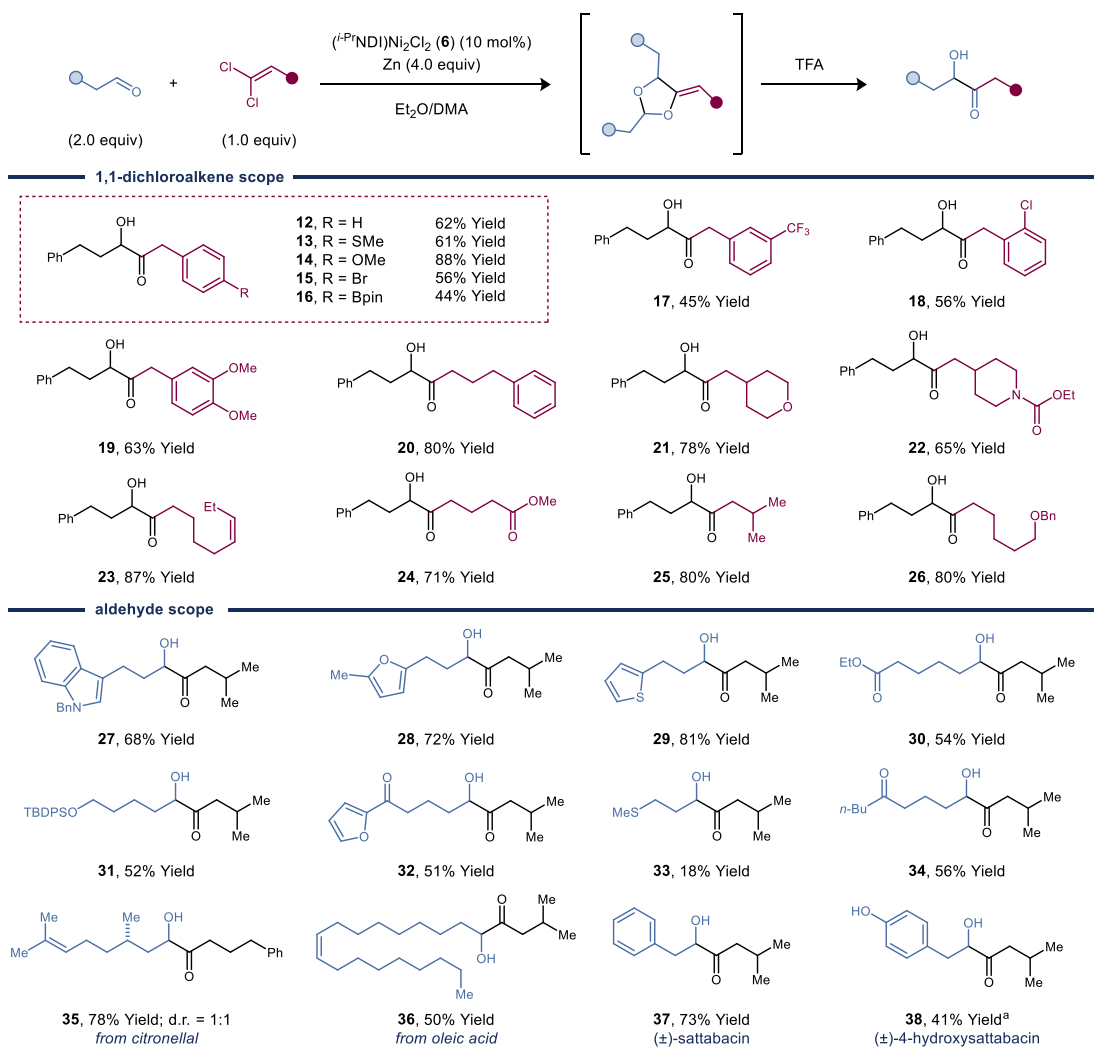


Figure 2.2. Substrate scope studies. Isolated yields were determined following purification and were averaged over two runs. Standard reaction conditions: dichloroalkene (0.2 mmol, 1.0 equiv), aldehyde (2.0 equiv), $(i\text{-PrNDI})\text{Ni}_2\text{Cl}_2$ (**6**) (10 mol%), Zn (4.0 equiv), DMA (0.2 mL), Et_2O (0.8 mL), rt, 24 h; then TFA, 0 °C to rt, 2 h. ^aSynthesized using 2-(4-((trimethylsilyl)oxy)phenyl)acetaldehyde.

As a synthetic application of this method, two acyloin-containing natural products were prepared.¹⁹ Phenylacetaldehyde is an effective substrate, forming (±)-sattabacin (**37**) in 73% yield. Although free phenols are not tolerated, (±)-4-hydroxysattabacin (**38**) could also be synthesized in 41% yield by utilizing a TMS protecting group. The TMS group is conveniently removed under the same TFA conditions used to deprotect the dioxolane.

2.2.3 Mechanistic Studies

There is evidence supporting a metallacyclic intermediate in the [2 + 2 + 1]-cycloaddition similar to that proposed in the dinickel-catalyzed vinylidene–alkene cyclization reaction (Figure 2.3a). When the cycloaddition between 1,1-dichloroalkene **39** and aldehyde **40** was carried out at four-fold dilution relative to the standard conditions, the [2 + 2 + 1]-cycloaddition product was formed in a decreased 61% yield, and a minor enone byproduct was generated in 13% yield (Figure 2.3b). Presumably, enone formation is due to a competing β-hydride elimination from an intermediate of the general structure **1**. The same product profile was observed in experiments carried out under single turnover conditions (Figure 2.3c). Reactions between 1,1-dichloroalkene **39**, aldehyde **40**, and the isolable low-valent form of the catalyst, (*i*-PrNDI)Ni₂Cl (**43**), were carried out at two different concentrations. The dioxolane was the exclusive product at higher concentrations, whereas the enone was the exclusive product at lower concentrations.

When deuterium-labelled aldehyde **40-*d*₁** was used, the enone product was labelled exclusively at the α-carbon (>99% deuterium incorporation), confirming the fate of the hydrogen undergoing β-hydride elimination (Figure 2.3d). Finally, when enone **41** was subjected to the standard catalytic conditions with an additional equivalent of aldehyde **40**, it was not converted to dioxolane **43**, indicating that enone **41** is not an intermediate in the [2 + 2 + 1]-cycloaddition (Figure 2.3e).

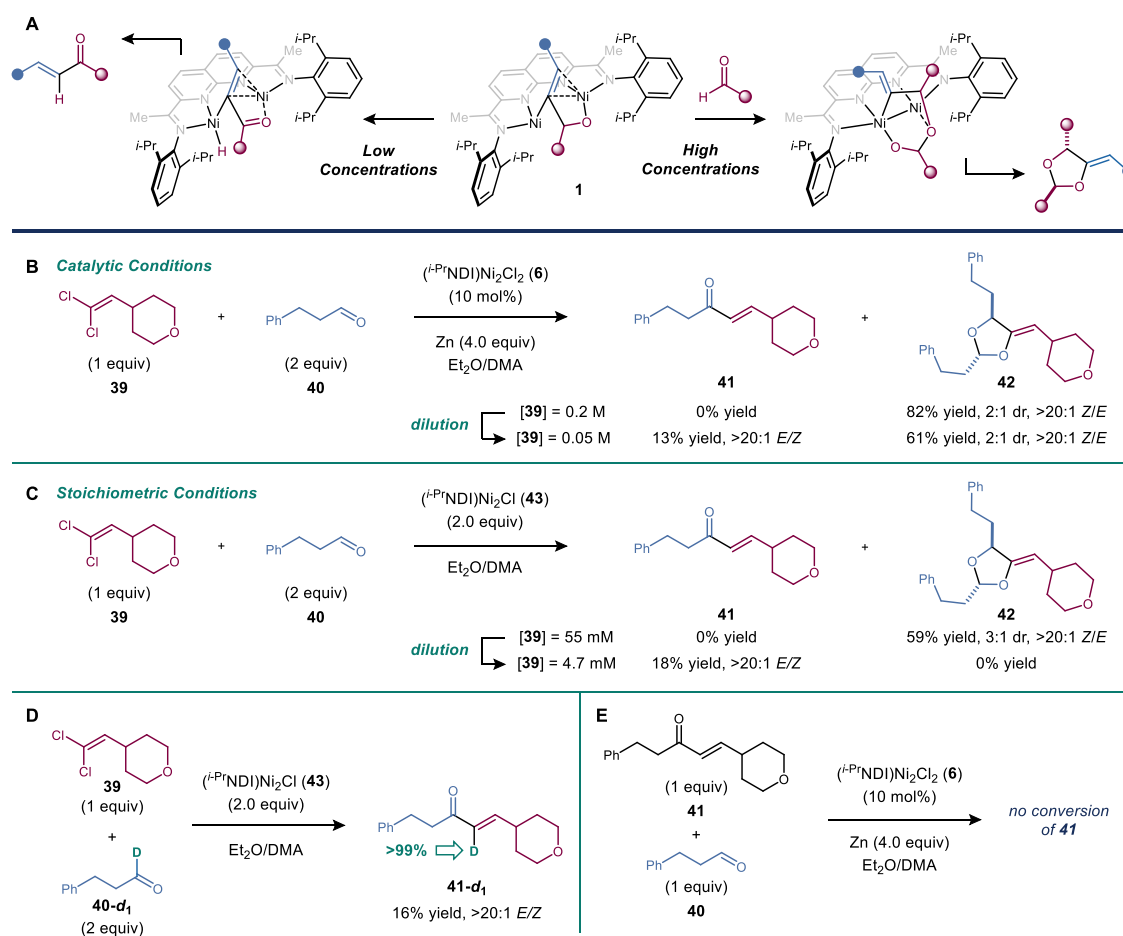
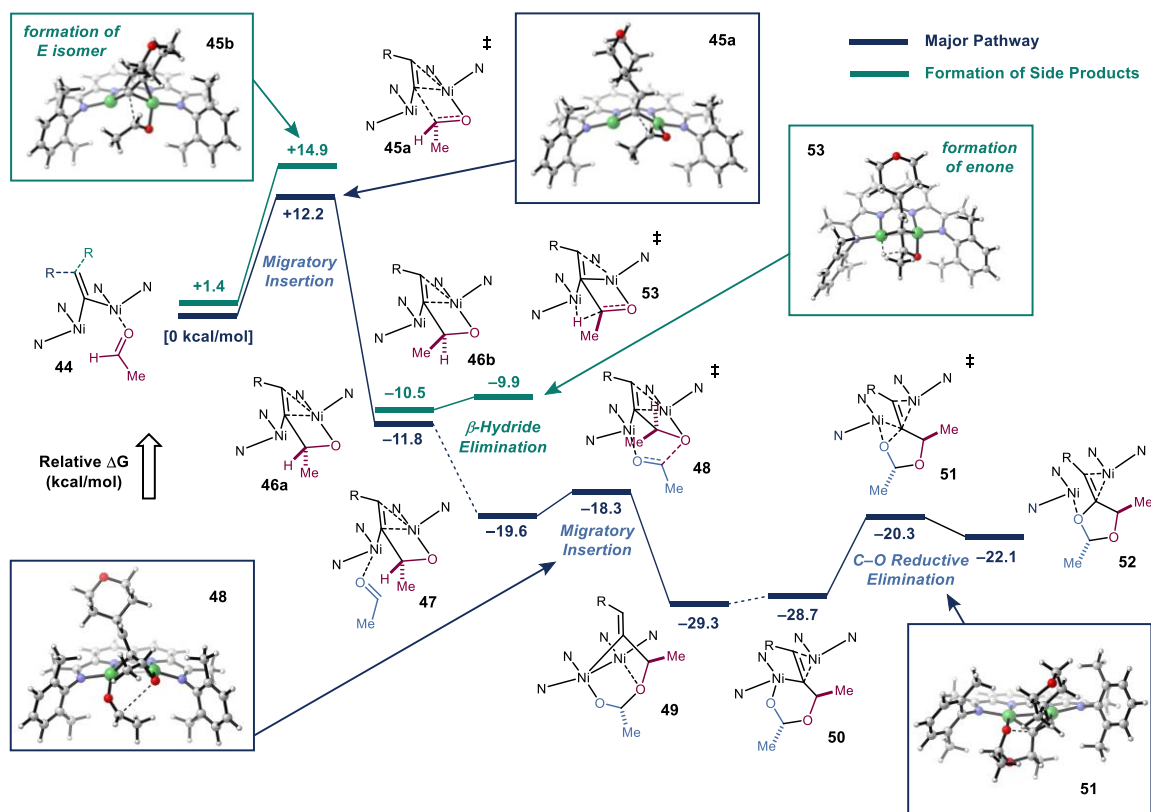


Figure 2.3 Mechanistic Studies. (a) Competing β -hydride elimination and aldehyde migratory pathways. Concentration dependence of β -hydride elimination vs. aldehyde migratory insertion under (b) catalytic and (c) stoichiometric conditions. (d) Deuterium labelling experiment tracking the hydrogen undergoing β -hydride elimination. (e) Experiment assessing the intermediacy of enone 41 in the cycloaddition.

2.2.4 DFT Modeling Studies

With these mechanistic insights in hand, we carried out a series of DFT calculations to further examine the $[2 + 2 + 1]$ -cycloaddition pathway (Figure 2.4). As part of these studies, we sought to calculate the competing β -hydride elimination process and explain the origin of the high Z selectivity at the exocyclic alkene, which was observed universally across all reaction conditions and substrates that were tested. Stationary points were optimized at the BP86/6-311g(d,p) level of theory, which had previously produced stationary points that corresponded closely to X-ray structures.²⁰

Our model commences with complex **44** ($S = 1$), which is the aldehyde adduct of the putative $\text{Ni}_2(\mu\text{-vinylidene})$ intermediate. There are four possible migratory insertion transition states, differing in the orientation of the vinylidene and aldehyde substituents. The most favorable pathway has a barrier of 12.2 kcal/mol and generates Ni_2 metallacycle **46a** (see Supporting Information for a description of the higher energy pathways). The calculated structure of **46a** is analogous to the metallacycle that we experimentally characterized from the intramolecular addition of a vinylidene to an alkene.¹³



Binding of the second aldehyde to form **47** is exothermic by 7.8 kcal/mol, and the second migratory insertion to form **49** has a low activation barrier of 1.3 kcal/mol. Metallacycle **49** has a relatively short Ni–Ni distance of 2.5 Å, and NBO analysis suggests that there may be weak Ni–

Ni covalent bonding (Wiberg bond index = 0.05). Reductive elimination transition states from metallacycle **49** are prohibitively high in energy. However, dissociation of the ether oxygen and association of the C=C π -bond to one of the Ni atoms would form to an isomeric metallacycle (**50**) that is nearly identical in energy (+0.6 kcal/mol). Metallacycle **50** has an elongated Ni–Ni distance of 2.9 Å but a notably shortened distance between the C and O undergoing reductive elimination (2.5 Å vs. 2.7 Å in **49**). Accordingly, C–O reductive elimination from **50** has a barrier of only 8.4 kcal/mol, and this step yields the product adduct **52**. Key to this overall process is the ability of the dinuclear active site to form and break weak Ni–Ni interactions in order to traverse different intermediates in the catalytic cycle.

According to the calculated mechanism, the migratory insertion of the first aldehyde is rate-limiting and irreversible. Thus, the *E/Z* selectivity of the reaction should be determined in this step. Consistent with the high *Z* selectivity observed experimentally, the migratory insertion transition state that would lead to the *E* product is 2.7 kcal/mol higher in energy.

To model the enone formation under dilute reaction conditions, we searched for β -hydride elimination transition states from intermediate **46**. Isomer **46a** cannot undergo β -hydride elimination, because the β -H is positioned away from Ni. However, isomer **46b**, where the Me and H substituents of the aldehyde are swapped, is poised to undergo a nearly barrierless β -hydride elimination. The reason that the enone is only formed as a minor byproduct under dilute conditions may be due to the migratory insertion step forming metallacycle isomer **46b** being disfavored by 1.1 kcal/mol.

2.3 Conclusions

In summary, a dinickel catalyst promotes [2 + 2 + 1]-cycloadditions of two aldehyde equivalents and a vinylidene to form methylenedioxolane products. Unlike the Pauson–Khand reaction, these cycloadditions involve an initial coupling of a vinylidene, which is the C1 component, and an aldehyde to form a metallacyclic intermediate. By avoiding competing reductive elimination and β -hydride elimination processes, it is possible to intercept this intermediate with a second aldehyde and achieve a net three-component cycloaddition. In principle, this mechanism should be compatible with other classes of 2π -systems, and future studies will focus on expanding the scope of partners that can be used.

2.4 Acknowledgements

This research was supported by the NIH (R35 GM124791). C.U. acknowledges support from a Camille Dreyfus Teacher-Scholar award and a Lilly Grantee award.

2.5 References

- (1) (a) Chen, S.; Jiang, C.; Zheng, N.; Yang, Z.; Shi, L. "Evolution of Pauson-Khand Reaction: Strategic Applications in Total Syntheses of Architecturally Complex Natural Products (2016–2020)" *Catalysts* **2020**, *10*, 1199; (b) Yang, Z. "Navigating the Pauson-Khand Reaction in Total Syntheses of Complex Natural Products" *Acc. Chem. Res.* **2021**, *54*, 556-568; (c) Heravi, M. M.; Mohammadi, L. "Application of Pauson-Khand reaction in the total synthesis of terpenes" *RSC Adv.* **2021**, *11*, 38325-38373.
- (2) (a) Pauson, P. L. "The khand reaction : A convenient and general route to a wide range of cyclopentenone derivatives" *Tetrahedron* **1985**, *41*, 5855-5860; (b) Brummond, K. M.; Kent, J. L. "Recent Advances in the Pauson-Khand Reaction and Related [2+2+1] Cycloadditions" *Tetrahedron* **2000**, *56*, 3263-3283; (c) Schore, N. E. The Pauson-Khand Cycloaddition Reaction for Synthesis of Cyclopentenones. *Org. React.* **1991**, *40*, 1–90.
- (3) (a) Geis, O.; Schmalz, H.-G. "New Developments in the Pauson-Khand Reaction" *Angew. Chem., Int. Ed.* **1998**, *37*, 911-914; (b) Gibson, S. E.; Stevenazzi, A. "The Pauson-Khand Reaction: the Catalytic Age Is Here!" *Angew. Chem., Int. Ed.* **2003**, *42*, 1800-1810; (c) Shibata, T. "Recent Advances in the Catalytic Pauson-Khand-Type Reaction" *Adv. Synth. Catal.* **2006**, *348*, 2328-2336.
- (4) Hoshimoto, Y.; Ohata, T.; Sasaoka, Y.; Ohashi, M.; Ogoshi, S. "Nickel(0)-Catalyzed [2 + 2 + 1] Carbonylative Cycloaddition of Imines and Alkynes or Norbornene Leading to γ -Lactams" *J. Am. Chem. Soc.* **2014**, *136*, 15877-15880.
- (5) (a) Kablaoui, N. M.; Hicks, F. A.; Buchwald, S. L. "Diastereoselective Synthesis of γ -Butyrolactones from Enones Mediated or Catalyzed by a Titanocene Complex" *J. Am. Chem. Soc.* **1996**, *118*, 5818-5819; (b) Chatani, N.; Morimoto, T.; Fukumoto, Y.; Murai, S. "Ru₃(CO)₁₂-Catalyzed Cyclocarbonylation of Yne-Aldehydes to Bicyclic α,β -Unsaturated γ -Butyrolactones" *J. Am. Chem. Soc.* **1998**, *120*, 5335-5336; (c) Adrio, J.; Carretero, J. C. "Butenolide Synthesis by Molybdenum-Mediated Hetero-Pauson-Khand Reaction of Alkynyl Aldehydes" *J. Am. Chem. Soc.* **2007**, *129*, 778-779.
- (6) (a) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. "Titanocene-catalyzed conversion of enynes to bicyclic cyclopentenones" *J. Am. Chem. Soc.* **1993**, *115*, 4912-4913; (b) Berk, S. C.; Grossman, R. B.; Buchwald, S. L. "Development of a Titanocene-Catalyzed Enyne Cyclization/Isocyanide Insertion Reaction" *J. Am. Chem. Soc.* **1994**, *116*, 8593-8601.

- (7) (a) Magnus, P.; Principe, L. M. "Origins of 1,2- and 1,3-stereoselectivity in dicobaltoctacarbonyl alkene-alkyne cyclizations for the synthesis of substituted bicyclo[3.3.0]octenones" *Tetrahedron Lett.* **1985**, 26, 4851-4854; (b) Banide, E. V.; Müller-Bunz, H.; Manning, A. R.; Evans, P.; McGlinchey, M. J. "X-ray Crystal Structure of an Alkene–Pentacarbonyldicobalt–Alkyne Complex: Isolation of a Stable Magnus-Type Pauson–Khand Reaction Intermediate" *Angew. Chem., Int. Ed.* **2007**, 46, 2907-2910; (c) Lesage, D.; Milet, A.; Memboeuf, A.; Blu, J.; Greene, A. E.; Tabet, J.-C.; Gimbert, Y. "The Pauson–Khand Mechanism Revisited: Origin of CO in the Final Product" *Angew. Chem., Int. Ed.* **2014**, 53, 1939-1942; (d) Hartline, D. R.; Zeller, M.; Uyeda, C. "Well-Defined Models for the Elusive Dinuclear Intermediates of the Pauson–Khand Reaction" *Angew. Chem., Int. Ed.* **2016**, 55, 6084-6087.
- (8) (a) Sierra, M. A.; Soderberg, B.; Lander, P. A.; Hegedus, L. S. "Formal [2 + 2 + 1] and [4 + 1] cycloadditions of electron poor alkenes to pentacarbonyl[(N,N-dimethylamino)methylene]chromium" *Organometallics* **1993**, 12, 3769-3771; (b) Fernández-Rodríguez, M. Á.; García-García, P.; Aguilar, E. "Multi-component reactions involving group 6 Fischer carbene complexes: a source of inspiration for future catalytic transformations" *Chem. Commun.* **2010**, 46, 7670-7687.
- (9) (a) Grubbs, R. H.; Miyashita, A. "Carbon-carbon bond cleavage reactions in the decomposition of metallacycles" *J. Am. Chem. Soc.* **1978**, 100, 7418-7420; (b) Waterman, R.; Hillhouse, G. L. "Group Transfer from Nickel Imido, Phosphinidene, and Carbene Complexes to Ethylene with Formation of Aziridine, Phosphirane, and Cyclopropane Products" *J. Am. Chem. Soc.* **2003**, 125, 13350-13351.
- (10) Hansen, J.; Autschbach, J.; Davies, H. M. L. "Computational Study on the Selectivity of Donor/Acceptor-Substituted Rhodium Carbenoids" *J. Org. Chem.* **2009**, 74, 6555-6563.
- (11) (a) Fraile, J. M.; García, J. I.; Martínez-Merino, V.; Mayoral, J. A.; Salvatella, L. "Theoretical (DFT) Insights into the Mechanism of Copper-Catalyzed Cyclopropanation Reactions. Implications for Enantioselective Catalysis" *J. Am. Chem. Soc.* **2001**, 123, 7616-7625; (b) Rasmussen, T.; Jensen, J. F.; Østergaard, N.; Tanner, D.; Ziegler, T.; Norrby, P.-O. "On the Mechanism of the Copper-Catalyzed Cyclopropanation Reaction" *Chem.-Eur. J.* **2002**, 8, 177-184.
- (12) Pal, S.; Zhou, Y.-Y.; Uyeda, C. "Catalytic Reductive Vinylidene Transfer Reactions" *J. Am. Chem. Soc.* **2017**, 139, 11686-11689.
- (13) Steiman, T. J.; Kalb, A. E.; Coombs, J. C.; Kirkland, J. K.; Torres, H.; Ess, D. H.; Uyeda, C. "Dinickel-Catalyzed Vinylidene–Alkene Cyclization Reactions" *ACS Catal.* **2021**, 14408-14416.
- (14) (a) Camp, R. L.; Greene, F. D. "1,3-Di-tert-butylallene oxide. Isolation and isomerization to trans-2,3-di-tert-butylcyclopropanone" *J. Am. Chem. Soc.* **1968**, 90, 7349-7349; (b) Hess, B. A.; Eckart, U.; Fabian, J. "Rearrangements of Allene Oxide, Oxyallyl, and Cyclopropanone" *J. Am. Chem. Soc.* **1998**, 120, 12310-12315.

- (15) (a) Lin, Z.; Marett, L.; Huguen, R. W.; Flores, M.; Forteza, I.; Ammon, M. A.; Concepcion, G. P.; Espino, S.; Olivera, B. M.; Rosenberg, G.; Haygood, M. G.; Light, A. R.; Schmidt, E. W. "Neuroactive diol and acyloin metabolites from cone snail-associated bacteria" *Bioorg. Med. Chem. Lett.* **2013**, 23, 4867-4869; (b) Park, J.-S.; Kagaya, N.; Hashimoto, J.; Izumikawa, M.; Yabe, S.; Shin-ya, K.; Nishiyama, M.; Kuzuyama, T. "Identification and Biosynthesis of New Acyloins from the Thermophilic Bacterium *Thermosporothrix hazakensis* SK20-1T" *ChemBioChem* **2014**, 15, 527-532; (c) Schieferdecker, S.; Shabuer, G.; Letzel, A.-C.; Urbansky, B.; Ishida-Ito, M.; Ishida, K.; Cyrulies, M.; Dahse, H.-M.; Pidot, S.; Hertweck, C. "Biosynthesis of Diverse Antimicrobial and Antiproliferative Acyloins in Anaerobic Bacteria" *ACS Chem. Biol.* **2019**, 14, 1490-1497.
- (16) Gaggero, N.; Pandini, S. "Advances in chemoselective intermolecular cross-benzoin-type condensation reactions" *Org. Biomol. Chem.* **2017**, 15, 6867-6887.
- (17) Corey, E. J.; Seebach, D. "Carbanions of 1,3-Dithianes. Reagents for C-C Bond Formation by Nucleophilic Displacement and Carbonyl Addition" *Angew. Chem., Int. Ed.* **1965**, 4, 1075-1077.
- (18) Albright, J. D. "Reactions of acyl anion equivalents derived from cyanohydrins, protected cyanohydrins and α -dialkylaminonitriles" *Tetrahedron* **1983**, 39, 3207-3233.
- (19) Lampis, G.; Deidda, D.; Maullu, C.; Madeddu, M. A.; Pompei, R.; Delle Monache, F.; Satta, G. "Sattabacins and sattazolins: new biologically active compounds with antiviral properties extracted from a *Bacillus* sp" *J. Antibiot.* **1995**, 48, 967-972.
- (20) Zhou, Y.-Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. "Dinuclear Nickel Complexes in Five States of Oxidation Using a Redox-Active Ligand" *Inorg. Chem.* **2014**, 53, 11770-11777.

CHAPTER 3. A DINICKEL CATALYZED CYCLOPROPANATION WITHOUT THE FORMATION OF A METAL CARBENE INTERMEDIATE

Reprinted with permission from Maity, A. K.; Kalb, A. E.; Zeller, M.; and Uyeda C. *Angewandte Chemie International Edition*. 2021, 60, 1897-1902. Copyright 2021 Wiley.

3.1 Introduction

Most transition metal catalyzed cyclopropanation reactions use diazoalkanes as carbene precursors.^[1] Mechanistic proposals for these reactions generally invoke the formation of a metal carbene complex by catalyst-induced N₂ extrusion (Figure 3.1). It should be noted however that for a majority of catalysts, the key M=CR₂ intermediate cannot be directly observed, let alone structurally characterized.^[2] Therefore, alternative cyclopropanation pathways that do not involve M=CR₂ species warrant consideration. Additionally, identifying such pathways may provide new avenues to develop cyclopropanation reactions with substrate scopes or selectivity properties that are complementary to existing methods.

Catalytic cyclopropanations are mechanistically related to oxygen-atom transfer reactions. For example, the active oxidant in a cytochrome P450 catalyzed oxidation is a ferryl porphyrin radical cation (compound I), generated from the activation of O₂.^[3] Abiological variants of this process have also been developed, often using iodosylarenes or peroxycarboxylic acids as O-atom sources.^[4] Collman and Brauman demonstrated that the selectivities observed in (TPP)Mn catalyzed alkane C–H hydroxylations are dependent on the identity of the oxidant.^[5] This observation indicates that the O-atom donor is present in the selectivity-determining step, effectively ruling out a common M=O intermediate. In related work, Nam investigated a (TMC)Fe catalyzed epoxidation and observed that chiral peroxycarboxylic acid and iodosylarene reagents can induce high levels of enantioselectivity.^[6] Taken together, these and several other studies^[7] show that high-valent M=O species may not always be true catalytic intermediates, even in cases where they have been synthesized and characterized. Similar observations have been made for nitrene transfer reactions using organoazides and iminoiodinanes.^[8]

Here, we present a diazoalkane-based cyclopropanation reaction that does not involve the formation of a metal-bound carbene intermediate (Figure 1). The reaction being investigated is a

(NDI)Ni₂ catalyzed (NDI = naphthyridine–diimine) cyclopropanation of 1,3-dienes using (Me₃Si)CHN₂. The putative (NDI)Ni₂(CHSiMe₃) intermediate in this reaction is an isolable molecule but is unreactive toward 1,3-dienes. On the basis of DFT modeling studies, we instead propose a mechanism in which the Ni₂(diazalkane) adduct reacts with the 1,3-diene to generate a metallacycle. Subsequent N₂ elimination and diradical cyclization yields the cyclopropane product.

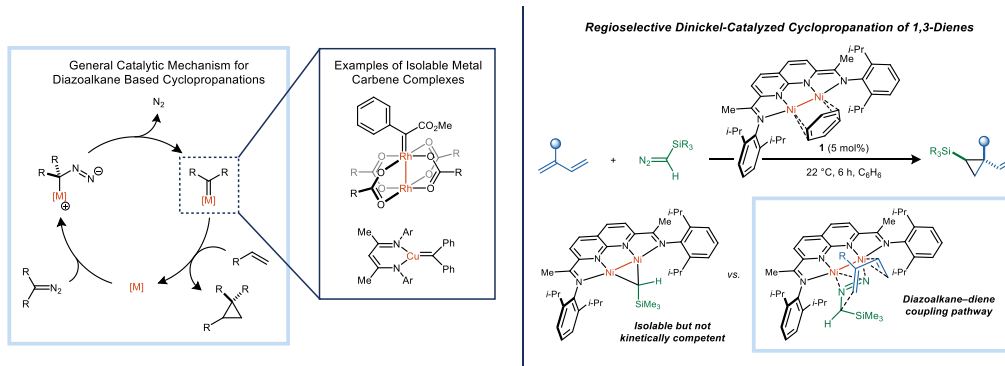


Figure 3.1. Metal carbenes are key intermediates in several catalytic cyclopropanation reactions using diazoalkanes. Dinickel complexes catalyze regioselective cyclopropanations of 1,3-dienes without generating a Ni₂(μ-CR₂) intermediate.

3.2 DFT Models for the Ni₂-Catalyzed Cyclopropanation

Experimental results performed by Arnab Maity indicate that there is a viable cyclopropanation mechanism that proceeds from the diazoalkane and does not involve the formation of a Ni₂ carbene complex. To identify such a mechanism, DFT calculations were carried out with the constraint that any reasonable model would need to rationalize the unusual regioselectivity observed in the reaction. First, the diazoalkane and diene adducts were calculated at the BP86/6-311G(d,p) level of theory (Figure 6). The optimized structures (**S1** and **S2**) were found to closely reproduce the structures observed experimentally by XRD. Additionally, the calculations accurately determined an *S* = 1 ground state for the diazoalkane complex and an *S* = 0 ground state for the diene complex.

A (NDI)Ni₂ complex containing both the diazoalkane and the diene bound to the active site was located (**S3**). The diazoalkane lies in the (NDI)Ni₂ plane and maintains its μ-η²:η¹ coordination mode. The diene binds in an η²-fashion through the less hindered double bond. The Ni–Ni distance is significantly elongated to 3.103 Å, suggesting the absence of a direct metal-to-metal covalent

bond. The 1-position of the diene is located in close proximity to the diazoalkane carbon, and a transition state (**S4**) for the coupling could be successfully optimized with an activation barrier of +16.3 kcal/mol.^[17] The resulting metallacycle (**S5**) is nearly isoenergetic with **S3**.

From here, we explored several possible concerted pathways for cyclopropanation where C–C bond-formation occurs in concert with N₂ expulsion. While several such transition states could be located, they were all found to be prohibitively high in energy. Instead, an energetically viable stepwise mechanism was identified. Homolytic cleavage of the C–N bond (**S6**) has a calculated activation barrier of +18.0 kcal/mol. The resulting diradical intermediate (**S7**) was modeled as an open-shell singlet with a C-centered α -TMS radical. The other unpaired electron (anti-parallel spin) is delocalized in the π -system of the NDI ligand. The triplet spin state for **S7** was also considered and found to be 0.6 kcal/mol lower in energy. Given this small energy difference, any barrier to spin flipping would likely make the open-shell singlet pathway more favorable. From **S7**, the final cyclopropane product is generated from a low-barrier attack of the C-centered radical on the Ni-bound allyl ligand (+1.0 kcal/mol).

In the calculated reaction pathway, the initial coupling step (**S4**) is reversible, and the N₂ expulsion step (**S6**) is rate-determining and irreversible. Therefore, the regioselectivity of the cyclopropanation is determined by the relative energies of the **S6** transition states. Gratifyingly, the transition state leading to the alternative regioisomer (**S6'**) is 5.9 kcal/mol higher in energy. In **S6'**, the metallacycle is rotated in order to alleviate an unfavorable steric interaction between the benzyl group and an *i*-Pr substituent of the catalyst (Figure 6).

Because C–N bond cleavage in **S6** forms of a planar radical intermediate, the diastereoselectivity of the cyclopropanation is not determined in this step but rather in the later recombination step **S8**. From **S7**, single bond rotation would allow for the C–C bond formation to occur on either face of the radical. The transition state leading to the alternative diastereomer was calculated to be 1.1 kcal/mol higher in energy, which is consistent with the dr determined experimentally for this substrate combination (6:1 dr; $\Delta\Delta G^\ddagger = +1.1$ kcal/mol).

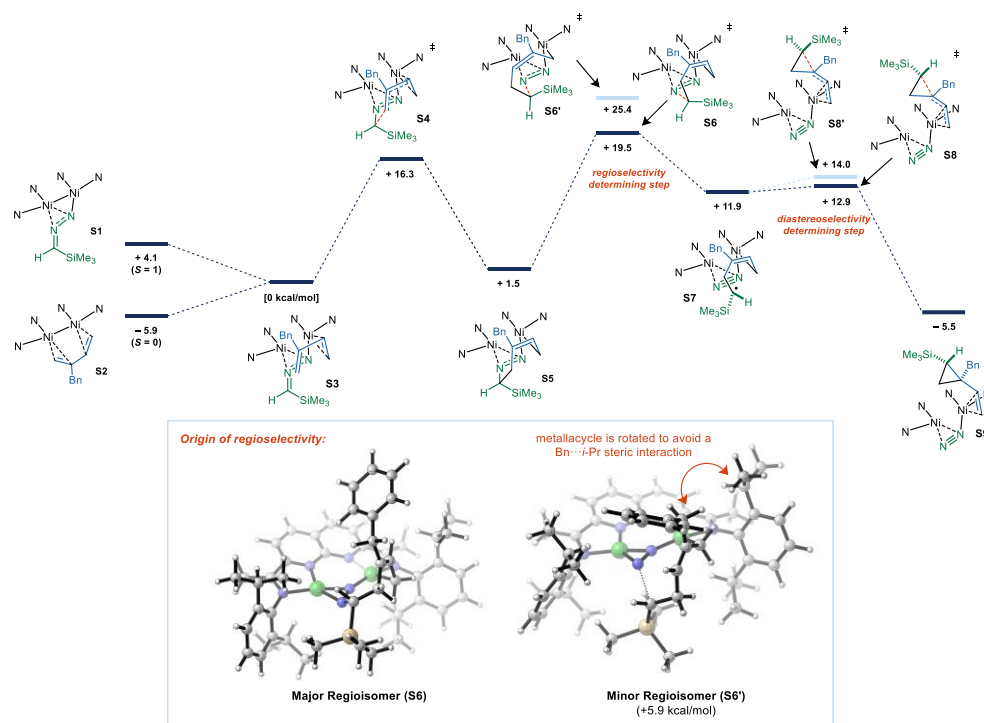


Figure 3.2. Calculated reaction pathway for the (*i*-PrNDI)Ni₂ catalyzed cyclopropanation to form **8** (BP86/6-311g(d,p) level of DFT). Relative free energies are shown in kcal/mol. Unless otherwise indicated, all structures correspond to *S* = 0 spin states. S7, S8, and S8' were modelled as open-shell singlets with a C-centered α -TMS radical and the other unpaired electron delocalized in the NDI π -system. Transition states leading to the alternative regioisomer and diastereomer are shown.

APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 1

. General Information

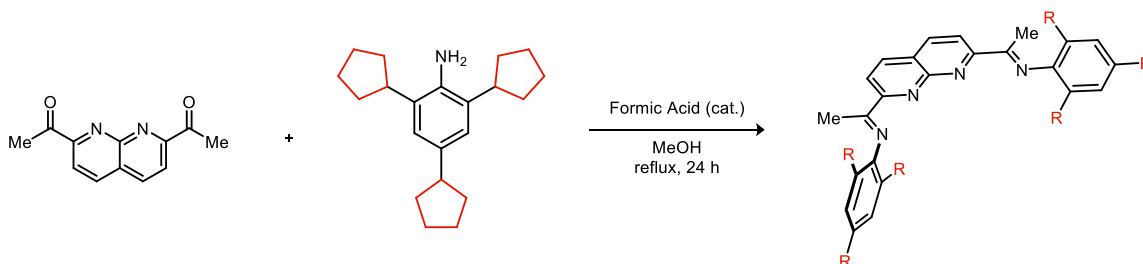
General considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an N₂ atmosphere. Solvents were dried and degassed by passing through a column of activated alumina and sparging with Ar gas. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. C₆D₆ was degassed using the freeze-pump-thaw method and stored over activated 3 Å molecular sieves prior to use. All reagents were purchased from commercial vendors and used without further purification unless otherwise noted. Zn powder (325 mesh, 99.9%), Ni(dme)Cl₂ and Ni(cod)₂ were purchased from Strem Chemicals, stored under inert atmosphere, and used without further purification. Liquid reagents were degassed using the freeze-pump-thaw method and stored over activated 3 Å molecular sieves prior to use in the glovebox. All catalytic reactions were run in the glovebox unless otherwise noted. The *i*-PrNDI ligand¹ (**4**), (*i*-PrNDI)Ni₂(C₆H₆)¹ (**6**) and (*i*-PrNDI)Ni₂Cl₂² (**3**) are prepared according to previously reported procedures.

Physical Methods. ¹H NMR, ¹³C{¹H} NMR, COSY NMR and NOESY NMR spectra were collected at room temperature on a Varian Inova300 with a 5mm 4-nucleus/BB Z-gradient probe, Varian Mercury300 with a 5mm 4-nucleus/BB probe, Bruker AV400 with a 5mm BBFO Z-gradient SmartProbe, a Bruker DRX500 with a 5 mm BBFO Z-gradient ATM probe, or AV800 with a QCI cryoprobe. ¹H NMR and ¹³C{¹H} NMR spectra were reported in parts per million relative to tetramethylsilane, using the referenced residual solvent resonances as an internal standard (¹H NMR: CDCl₃ = 7.26 ppm, C₆D₆ = 7.16 ppm and ¹³C{¹H} NMR: CDCl₃ = 77.16 ppm). High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer. Gas chromatography data were obtained on a Shimadzu GC-2010 equipped with an Agilent DB-5MS column. X-Band EPR spectra were recorded on a Bruker EMX EPR spectrometer and simulated using the Easyspin program³. Cyclic voltammetry (CV) was performed using a Gamry Interface 1000 Potentiostat. CV experiments were run under an N₂ atmosphere in a 0.3 M *n*-Bu₄NPF₆ electrolyte solution in THF or NMP that was stored over 3 Å molecular sieves for at least 3 days. A standard three-electrode configuration consisted of a glassy carbon working electrode (3 mm

diameter disk), a platinum counter electrode and silver wire reference electrode. The potentials were internally referenced to the reversible $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple.

X-ray crystallography. Single-crystal X-ray diffraction studies were carried out at the Purdue X-ray crystallography facility using a Bruker AXS D8 Quest CMOS diffractometer. Single crystals of were coated with NVH oil and quickly transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, an I- μ -S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon2 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 100 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.⁴ Structure Solution and Refinement. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs⁵ and refined by full matrix least squares against F^2 with all reflections using Shelxl201⁶ using the graphical interface Shelxle.⁷ If not specified otherwise H atoms attached to carbon and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 \AA for and aromatic C-H, 1.00, 0.99 and 0.98 \AA for aliphatic C-H, CH_2 and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Uiso(H) values were set to a multiple of Ueq(C) with 1.5 for CH_3 , and 1.2 for C-H units, respectively. Additional data collection and refinement details, including description of disorder and/or twinning (where present) can be found in the CIF file.

2. Synthesis of *c*-Pent^tNDI ligand (7)



1,1'-(1,8-naphthyridine-2,7-diyl)bis(*N*-(2,4,6-tricyclopentylphenyl)ethan-1-imine) (*c*-Pent^tNDI) (7). A flask equipped with a stir bar was charged with 2,6-diacetylnaphthyridine (200 mg,

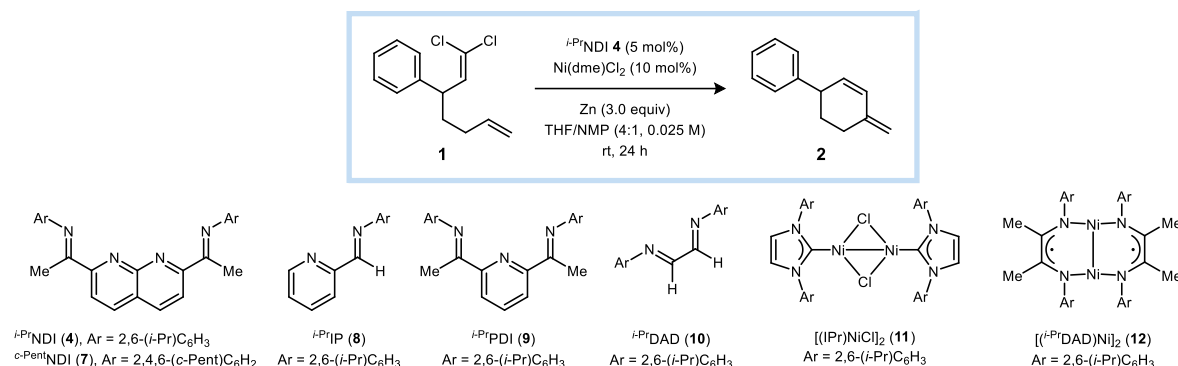
0.9 mmol, 1.0 equiv) and MeOH (5 mL). 2,4,6-Tricyclopentylaniline⁸ (555 mg, 1.9 mmol, 2.0 equiv) and formic acid (10 μ L) were added. The reaction mixture was refluxed for 24 h under an N₂ atmosphere, causing a yellow precipitate to form. The mixture was cooled in the freezer at – 30 °C for 1 h then filtered. The precipitate was washed with cold EtOH to give 530 mg (76% yield) of *c*-PentNDI (**7**) as a yellow powder.

¹H NMR (800 MHz, CDCl₃) δ 8.70 (d, *J* = 8.5 Hz, 2H), 8.35 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 4H), 2.98 (sext, *J* = 8.0 Hz, 2H), 2.79 (sext, 8.0 Hz, 4H), 2.46 (s, 6H), 2.12 – 2.06 (m, 4H), 2.02 – 1.95 (m, 4H), 1.87 – 1.78 (m, 8H), 1.77 – 1.66 (m, 14H), 1.66 – 1.43 (m, 24 h).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 167.8, 159.9, 155.1, 146.0, 141.5, 137.3, 133.0, 124.4, 122.4, 120.8, 46.2, 40.7, 35.0, 34.0, 25.8, 25.7, 17.8.

HRMS (ESI) *m/z*: [M+H] Calcd for C₅₄H₆₉N₄ 773.5517; found 773.5511.

3. Reaction Optimization Studies

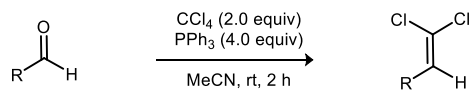


entry	deviation from standard conditions	yield (2)
1	none	92%
2	no 4	0%
3	no 4 and no Ni(dme)Cl ₂	0%
4	(<i>i</i> -Pr ^t NDI)Ni ₂ Cl ₂ (5) instead of 4 /Ni(dme)Cl ₂	91%
5	(<i>i</i> -Pr ^t NDI)Ni ₂ (C ₆ H ₆) (6) instead of 4 /Ni(dme)Cl ₂	90%
6	<i>c</i> -Pent ^t NDI (7) instead of 4	90%
7	0.05 M instead of 0.025 M	81%
8	Mn instead of Zn	88%
9	Cr(C ₆ H ₆) ₂ instead of Zn	15%
10	Ligands 8–10 (5 mol%) instead of 4	<10%
11	11 or 12 (5 mol%) instead of 4 /Ni(dme)Cl ₂	<1%

Procedure for entries 1-3 and 6-10: A 2-dram vial equipped with a stir bar was charged with ligand (0.005 mmol, 5 mol%), Ni(dme)Cl₂ (2.2 mg, 0.01 mmol, 10 mol%), reductant (3.0 equiv), and N-methyl-2-pyrrolidone (0.8 mL). The mixture was stirred at 600 rpm for approximately 20 minutes, during which time the solution turned violet in color. The reaction mixture was diluted with THF (3.6 mL), and 80 μ L of a 1.24 M stock solution containing (1,1-dichlorohepta-1,6-dien-3-yl)benzene (1.0 equiv) and mesitylene (1.0 equiv) in THF was added. Stirring was continued at 600 rpm for 24 h at room temperature. After 24 h, the reaction was exposed to air and an aliquot of the reaction solution was filtered through a 5 cm silica plug, eluting with CDCl₃. Yields of **2** were determined by ¹H NMR integration against mesitylene.

Procedure for entries 4-6 and 11: A 2-dram vial equipped with a stir bar was charged with catalyst (0.005 mmol, 5 mol%), Zn (3.0 equiv) and N-methyl-2-pyrrolidone (0.8 mL). The reaction mixture was diluted with THF (3.6 mL), and 80 μ L of a 1.24 M stock solution containing (1,1-dichlorohepta-1,6-dien-3-yl)benzene (1.0 equiv) and mesitylene (1.0 equiv) in THF was added. Stirring was continued at 600 rpm for 24 h at room temperature. After 24 h, the reaction was exposed to air and an aliquot of the reaction solution was filtered through a 5 cm silica plug, eluting with CDCl_3 . Yields of **2** were determined by ^1H NMR integration against mesitylene.

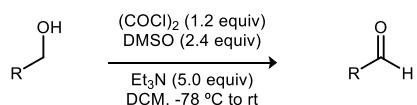
4. Synthesis of 1,1-Dichloroalkenes



General Procedure A: Synthesis of 1,1-Dichloroalkenes from Aldehydes

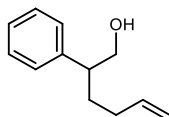
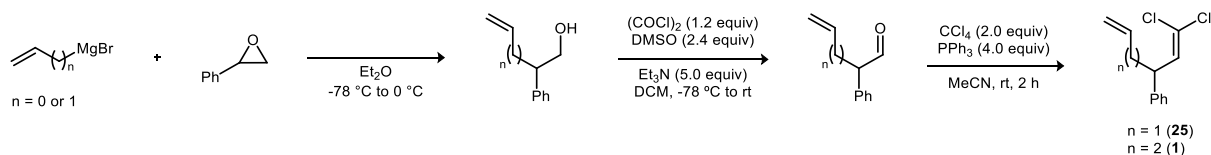
A flame-dried flask equipped with a stir bar was charged with PPh₃ (4.0 equiv). The flask was placed under an N₂ atmosphere, and MeCN (0.5 M) was added to create a slurry. In a separate flask, the aldehyde (1.0 equiv) and CCl₄ (2.0 equiv) were dissolved in MeCN (2.0 M solution). The aldehyde/CCl₄ solution was added dropwise to the slurry over 5 min, and the reaction was stirred for 2 h. The reaction mixture was quenched with Et₂O, washed with H₂O (x2) then brine. The organic phase was dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The crude product was suspended in Et₂O and triphenylphosphine was filtered off. The filtrate was concentrated to dryness under vacuum and was purified by flash column chromatography.

Note: reactions larger than 20 mmol were cooled to 0 °C and addition of the aldehyde solution was done over 30 min. After the addition, the reaction was stirred at room temperature for 2 h.



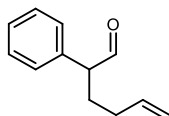
General Procedure B: Swern Oxidation

A flame-dried flask under an N₂ atmosphere equipped with a stir bar was charged with oxalyl chloride (1.2 equiv) and CH₂Cl₂ ([alcohol] = 0.1 M). The solution was cooled to -78 °C. A 5.0 M solution of DMSO in CH₂Cl₂ (2.4 equiv) was added, and the reaction was stirred for 20 min. A 0.5 M solution of the alcohol (1.0 equiv) in CH₂Cl₂ was added, and the reaction was stirred for 45 min at -78 °C. Et₃N (5.0 equiv) was added, and the mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. NH₄Cl (aq), and the product was extracted with Et₂O (x3). The combined organic phases were washed with water then brine, dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum.



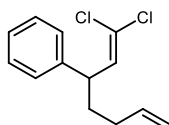
Step 1: 2-Phenylhex-5-en-1-ol (177037-77-3)

Under an N_2 atmosphere, a flame-dried flask equipped with a stir bar was charged with styrene oxide (4.6 mL, 40 mmol, 1.0 equiv) and Et_2O (200 mL). The solution was cooled to $-78^\circ C$, and a freshly prepared 15 M but-3-en-1-ylmagnesium bromide solution (6.1 mL, 60 mmol, 1.5 equiv) in Et_2O was slowly added via syringe over 10 min. The reaction mixture was warmed to $0^\circ C$ then stirred for 2 h. The reaction was quenched with sat. NH_4Cl (aq), and the organic phase was washed with water, dried over Na_2SO_4 , and filtered. The filtrate was concentrated to dryness under vacuum, and the crude product was purified by flash column chromatography (SiO_2 , 10% to 20% $EtOAc$ in hexanes) to provide 3.02 g (43% yield) of product as a colorless oil. 1H NMR data match the previously reported spectrum.⁹



Step 2: 2-Phenylhex-5-enal (53847-17-9)

The reaction was conducted according to General Procedure B with oxalyl chloride (1.8 mL, 20.4 mmol, 1.2 equiv) in CH_2Cl_2 (170 mL), DMSO (2.9 mL, 41 mmol, 2.4 equiv) in CH_2Cl_2 (8 mL), 2-phenylhex-5-en-1-ol (3.03 g, 17.0 mmol, 1.00 equiv) in CH_2Cl_2 (35 mL), and Et_3N (11.8 mL, 85.0 mmol, 5.00 equiv). The product was used without further purification. 1H NMR data match the previously reported spectrum.¹⁰



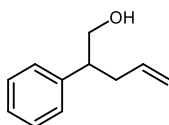
Step 3: (1,1-dichlorohepta-1,6-dien-3-yl)benzene (1)

The reaction was conducted according to General Procedure A using PPh₃ (17.5 g, 66.0 mmol, 4.0 equiv) dissolved in MeCN (35 mL), CCl₄ (3.2 mL, 33 mmol, 2.0 equiv), and 2-phenylhex-5-enal (2.91 g, 16.7 mmol, 1.0 equiv) dissolved in MeCN (8 mL). Addition of the aldehyde was done at 0 °C due to the large scale. The product was purified by flash column chromatography (SiO₂, hexanes) to provide 2.27 g (57% yield) of product as a pale yellow oil.

¹H NMR (800 MHz, CDCl₃) δ 7.32 (t, *J* = 7.7 Hz, 2H), 7.24 (t, 8.0 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.01 (d, *J* = 9.9 Hz, 1H), 5.84 – 5.77 (m, 1H), 5.05 – 4.96 (m, 2H), 3.69 (q, *J* = 9.6 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.89 – 1.78 (m, 2H).

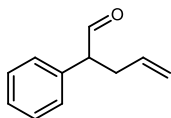
¹³C{¹H} NMR (201 MHz, CDCl₃) δ 142.3, 137.9, 133.3, 128.9, 127.5, 127.0, 120.6, 115.4, 45.8, 35.0, 31.5.

HRMS (APCI) *m/z*: [M+H] Calcd for C₁₃H₁₄Cl₂ 240.0473; found 240.0480.



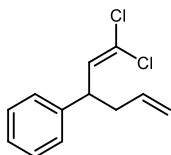
Step 1: 2-Phenylpent-4-en-1-ol (16014-71-4)

Under an N₂ atmosphere, a flame-dried flask equipped with a stir bar was charged with styrene oxide (3.5 mL, 31 mmol, 1.0 equiv) and Et₂O (250 mL). The solution was cooled to –78 °C, and a 1.0 M allylmagnesium bromide solution in Et₂O (40 mL, 40 mmol, 1.3 equiv) was slowly added via syringe over 10 min. The reaction mixture was warmed to 0 °C and stirred for 2 h. The reaction was quenched with sat. NH₄Cl (aq). The organic phase was washed with water, dried over Na₂SO₄, and filtered. The filtrate was concentrated to dryness under reduced pressure, and the crude material was purified by flash column chromatography (SiO₂, 15% EtOAc in hexanes) to provide 3.78 g (76% yield) of product as a colorless oil. ¹H NMR data matched the previously reported spectrum.¹¹



Step 2: 2-Phenylpent-4-enal (24401-36-3)

The reaction was conducted according to General Procedure B with oxalyl chloride (2.8 mL, 32 mmol, 1.2 equiv) in CH₂Cl₂ (270 mL), DMSO (4.6 mL, 64 mmol, 2.4 equiv) in CH₂Cl₂ (13 mL), 2-phenylpent-4-en-ol (4.4 g, 27 mmol, 1.0 equiv) in CH₂Cl₂ (50 mL), and Et₃N (19 mL, 135 mmol, 5.0 equiv). The product was used without further purification. ¹H NMR data matched the previously reported spectrum.¹²



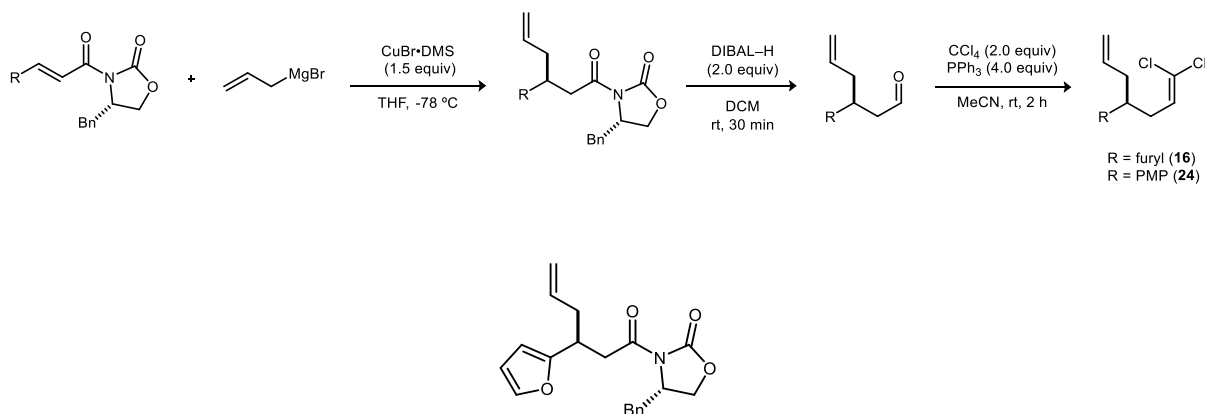
Step 3: (1,1-dichlorohexa-1,5-dien-3-yl)benzene (25)

The reaction was conducted according to General Procedure A using PPh₃ (27 g, 0.10 mol, 4.0 equiv) dissolved in MeCN (50 mL), CCl₄ (5.1 mL, 53 mmol, 2.0 equiv), and 2-phenylpent-4-enal (4.3 g, 26 mmol, 1.0 equiv) dissolved in MeCN (13 mL). Addition of the aldehyde was done at 0 °C due to the large scale. The product was purified by flash column chromatography (SiO₂, hexanes) to provide 2.5 g (42% yield) of product as a yellow oil.

¹H NMR (800 MHz, CDCl₃) δ 7.35 – 7.31 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.21 (m, 2H), 6.04 (d, *J* = 9.8 Hz, 1H), 5.74 – 5.68 (m, 1H), 5.08 (dq, *J* = 17.0, 1.5 Hz, 1H), 5.05 – 5.02 (m, 1H), 3.78 (q, *J* = 8.0 Hz, 1H), 2.57 – 2.45 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 141.9, 135.3, 132.7, 128.9, 127.5, 127.0, 120.8, 117.3, 46.1, 40.1.

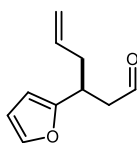
HRMS (APCI) *m/z*: [M-H] Calcd for C₁₂H₁₁Cl₂ 225.0232; found 225.0230.



Step 1. (S)-4-benzyl-3-((S)-3-(furan-2-yl)hex-5-enoyl)oxazolidin-2-one (**13**)

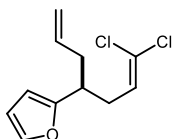
The reaction was conducted according to a procedure reported by Hoveyda.¹³ Under an N₂ atmosphere a flame dried flask wrapped in aluminum foil and equipped with a stir bar was charged with CuBr·SMe₂ (2.3 g, 11 mmol, 1.5 equiv) and THF (28 mL, 0.4 M). The solution was cooled to -78 °C, and a 1.0 M solution of allylmagnesium bromide (20 mL, 20 mmol, 2.7 equiv) was added dropwise over 30 min. The reaction mixture was stirred at -78 °C for 1.5 h. A 1.0 M solution of (S)-4-benzyl-3-(3-(furan-2-yl)acryloyl)oxazolidin-2-one (2.2 g, 7.4 mmol, 1.0 equiv) in THF was added, and stirring was continued for 2.5 h. The reaction was quenched at -78 °C with sat. NH₄Cl (aq), and the product was extracted with EtOAc (x3). The combined organic phases were dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The crude material was purified by flash column chromatography (SiO₂, 10% to 20% EtOAc in hexanes) to provide 1.0 g (40% yield) of product as a pale yellow solid.

¹H NMR (300 MHz, CDCl₃) δ 7.39 – 7.17 (m, 6H), 6.28 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.08 (d, *J* = 3.1 Hz, 1H), 5.75 (ddt, *J* = 17.1, 10.3, 7.0 Hz, 1H), 5.15 – 4.99 (m, 2H), 4.68 – 4.56 (m, 1H), 4.24 – 4.09 (m, 2H), 3.53 (q, *J* = 6.9 Hz, 1H), 3.41 – 3.28 (m, 1H), 3.33 – 3.17 (m, 2H), 2.72 (dd, *J* = 13.3, 9.8 Hz, 1H), 2.50 (dtd, *J* = 20.9, 14.0, 7.0 Hz, 2H).



Step 2. (S)-3-(furan-2-yl)hex-5-enal (**14**)

Under an N₂ atmosphere, a flame dried flask equipped with a stir bar was charged with (*S*)-4-benzyl-3-((*S*)-3-(furan-2-yl)hex-5-enoyl)oxazolidin-2-one (1.01 g, 3.00 mmol, 1.00 equiv) and CH₂Cl₂ (30 mL). The solution was cooled to –78 °C, and a 1.0 M solution of DIBAL–H (6.0 mL, 6.0 mmol, 2.0 equiv) in hexane was added over 20 min. The reaction was stirred at –78 °C for 30 min then quenched at that temperature with sat. sodium potassium tartrate (aq). Et₂O (75 mL) was added, and the mixture was vigorously stirred for 2 h at room temperature. The product was extracted with Et₂O (x3), and the combined organic phases were washed with brine, dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (SiO₂, 5% EtOAc in hexanes) to provide 260 mg (53% yield) of product as a colorless oil. ¹H NMR data matched the previously reported spectrum.¹⁴



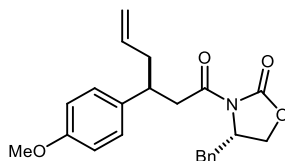
Step 3. (*S*)-2-(1,1-dichlorohepta-1,6-dien-4-yl)furan (15)

The reaction was conducted according to General Procedure A using PPh₃ (1.7 g, 6.3 mmol, 4.0 equiv) dissolved in MeCN (2 mL), CCl₄ (0.31 mL, 3.2 mmol, 2.0 equiv), and (*S*)-3-(furan-2-yl)hex-5-enal (260 mg, 1.6 mmol, 1.0 equiv) dissolved in MeCN (1 mL). The product was purified by flash column chromatography (SiO₂, hexanes) to provide 282 mg (77% yield) of product as a pale yellow oil.

¹H NMR (800 MHz, CDCl₃) δ 7.33 (d, *J* = 2.3 Hz, 1H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 5.78 (t, *J* = 7.3 Hz, 1H), 5.74 – 5.67 (m, 1H), 5.05 (dq, *J* = 17.1, 1H), 5.05 – 5.00 (m, 1H), 2.92 (sext, *J* = 13.6, 6.4 Hz, 1H), 2.56 – 2.41 (m, 3H), 2.38 – 2.32 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 156.9, 141.4, 135.7, 127.6, 121.1, 117.1, 110.1, 105.7, 38.0, 37.8, 33.5.

HRMS (APCI) *m/z*: [M–H] Calcd for C₁₁H₁₁Cl₂O 229.0182; found 229.0186.



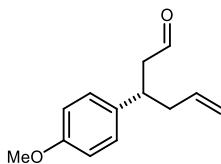
Step 1. (S)-4-benzyl-3-((S)-3-(4-methoxyphenyl)hex-5-enoyl)oxazolidin-2-one

Under an N₂ atmosphere, a flame dried flask wrapped with aluminum foil and equipped with a stir bar was charged with CuBr·SMe₂ (1.48 g, 7.20 mmol, 1.50 equiv) and THF (18 mL, 0.4 M). The solution was cooled to –78 °C, and a 1.0 M solution of allylmagnesium bromide (12.9 mL, 12.9 mmol, 2.7 equiv) was added dropwise over 30 min then stirred at –78 °C for 1.5 h. A 1.0 M solution of (S)-4-benzyl-3-(3-(4-methoxyphenyl)acryloyl)oxazolidin-2-one (1.63 g, 4.87 mmol, 1.00 equiv) in THF was added, and stirring was continued for 2.5 h. The reaction was quenched at –78 °C with sat. NH₄Cl (aq), and the product was extracted with EtOAc (x3). The combined organic phases were dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The crude material was purified by flash column chromatography (SiO₂, 10% to 15% EtOAc in hexanes) to provide 810 mg (44% yield) of product as a pale yellow solid.

¹H NMR (800 MHz, CDCl₃) δ 7.34 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.19 – 7.14 (m, 4H), 6.87 – 6.81 (m, 2H), 5.70 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.01 – 4.96 (m, 1H), 4.51 (dddd, *J* = 10.1, 7.8, 3.5, 2.5 Hz, 1H), 4.07 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.01 (ddd, *J* = 8.9, 7.8, 0.8 Hz, 1H), 3.77 (s, 3H), 3.37 (dd, *J* = 16.0, 9.2 Hz, 1H), 3.35 – 3.29 (m, 1H), 3.24 – 3.18 (m, 2H), 2.65 (dd, *J* = 13.5, 9.9 Hz, 1H), 2.47 – 2.37 (m, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 172.0, 158.2, 153.4, 136.2, 135.7, 135.3, 129.4, 128.9, 128.6, 127.3, 116.9, 113.8, 77.2, 77.0, 76.9, 66.1, 55.2, 53.4, 41.3, 41.1, 40.6, 37.8.

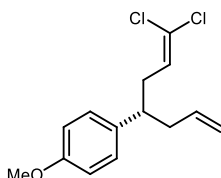
HRMS (APCI) *m/z*: [M+H] Calcd for C₂₃H₂₆NO₄ 380.1856; found 380.1854.



Step 2. (S)-3-(4-methoxyphenyl)hex-5-enal

Under an N₂ atmosphere, a flame dried flask equipped with a stir bar was charged with (S)-4-benzyl-3-((S)-3-(4-methoxyphenyl)hex-5-enoyl)oxazolidin-2-one (810 mg, 2.1 mmol, 1.0 equiv)

and CH₂Cl₂ (20 mL, 0.1 M). The solution was cooled to –78 °C, and a 1.0 M solution of DIBAL–H (4.3 mL, 4.3 mmol, 2.0 equiv) in hexane was added over 20 min. The reaction was stirred at –78 °C for 30 min then quenched at that temperature with sat. sodium potassium tartrate (aq). Et₂O (75 mL) was added, and the solution was vigorously stirred for 2 h at room temperature. The product was extracted with Et₂O (x3). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The crude product was purified by flash chromatography (SiO₂, 5% to 10% EtOAc in hexanes) to provide 258 mg (60% yield) of product as a colorless oil. ¹H NMR matched the previously reported spectrum.¹⁵



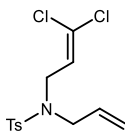
Step 3. (S)-1-(1,1-dichlorohepta-1,6-dien-4-yl)-4-methoxybenzene (23)

The reaction was conducted according to General Procedure A using PPh₃ (1.3 g, 5.0 mmol, 4.0 equiv) dissolved in MeCN (2 mL), CCl₄ (0.24 mL, 2.5 mmol, 2.0 equiv), and (S)-3-(4-methoxyphenyl)hex-5-enal (258 mg, 1.3 mmol, 1.0 equiv) dissolved in MeCN (1 mL). The product was purified by flash column chromatography (SiO₂, 5% EtOAc in hexanes) to provide 177 mg (52% yield) of product as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.70 (t, *J* = 8.0 Hz, 1H), 5.69 – 5.62 (m, 1H), 5.00 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.98 – 4.95 (m, 1H), 3.80 (s, 3H), 2.72 (sext, 7.2 Hz, 1H), 2.58 – 2.52 (m, 1H), 2.41 – 2.35 (m, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 158.3, 136.4, 135.7, 128.6, 128.4, 120.6, 116.7, 114.0, 55.4, 44.1, 40.8, 36.2.

HRMS (ESI) *m/z*: [M–H] Calcd for C₁₄H₁₅Cl₂O 269.0495; found 269.0493.



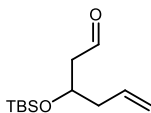
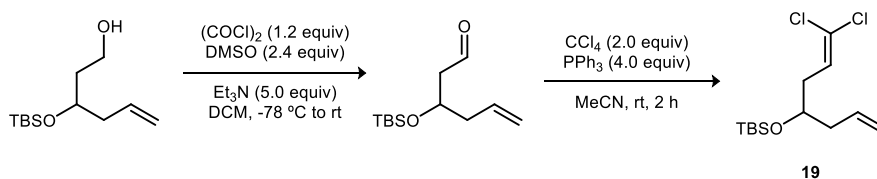
N-allyl-N-(3,3-dichloroallyl)-4-methylbenzenesulfonamide (17)

The aldehyde was synthesized according to a previously reported procedure.¹⁶ The reaction was conducted according to General Procedure A using PPh₃ (7.3 g, 28 mmol, 4.0 equiv) dissolved in MeCN (15 mL), CCl₄ (1.3 mL, 14 mmol, 2.0 equiv), and *N*-allyl-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (1.8 g, 7.0 mmol, 1.0 equiv) dissolved in MeCN (3.5 mL). The product was purified by flash column chromatography (SiO₂, 5% EtOAc in hexanes) to provide 1.39 g (62% yield) of product as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.80 (t, *J* = 6.7 Hz, 1H), 5.70 – 5.62 (m, 1H), 5.22 – 5.17 (m, 2H), 3.89 (d, *J* = 6.8 Hz, 2H), 3.78 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H).

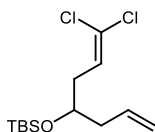
¹³C{¹H} NMR (201 MHz, CDCl₃) δ 143.8, 136.8, 132.5, 123.0, 127.3, 125.4, 123.6, 119.6, 50.8, 45.8, 21.7.

HRMS (APCI) *m/z*: [M+H] Calcd for C₁₃H₁₆Cl₂NO₂S 320.0273; found 320.0278.



Step 1: 3-((*tert*-butyldimethylsilyl)oxy)hex-5-enal

The alcohol was synthesized as the racemate according to a previously reported procedure.¹⁷ The reaction was conducted according to General Procedure B with oxalyl chloride (1.1 mL, 13 mmol, 1.2 equiv) in CH₂Cl₂ (110 mL), DMSO (1.9 mL, 27 mmol, 2.4 equiv) in CH₂Cl₂ (5 mL), 3-((*tert*-butyldimethylsilyl)oxy)hex-5-en-1-ol (2.6 g, 11 mmol, 1.0 equiv) in CH₂Cl₂ (525 mL), and Et₃N (7.7 mL, 56 mmol, 5.0 equiv). The product was purified by flash column chromatography (SiO₂, 2% to 5% EtOAc in hexanes). ¹H NMR matched previously reported spectra.¹⁸



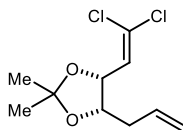
Step 2: *tert*-Butyl((1,1-dichlorohepta-1,6-dien-4-yl)oxy)dimethylsilane (19)

The reaction was conducted according to General Procedure A using PPh₃ (2.5 g, 9.6 mmol, 4.0 equiv) dissolved in MeCN (5 mL), CCl₄ (0.47 mL, 4.8 mmol, 2.0 equiv), and 3-((*tert*-butyldimethylsilyl)oxy)hex-5-enal (551 mg, 2.40 mmol, 1.00 equiv) dissolved in MeCN (1.5 mL). The product was purified by flash column chromatography (SiO₂, hexanes) to provide 373 mg (52% yield) as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 5.92 (t, *J* = 7.5 Hz, 1H), 5.83 – 5.75 (m, 1H), 5.11 – 5.03 (m, 2H), 3.80 (quint, *J* = 5.6 Hz, 1H), 2.32 (t, *J* = 5.6 Hz, 2H), 2.22 (t, *J* = 6.6 Hz, 2H), 0.89 (s, 9H), 0.06 (s, 6H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 134.6, 126.9, 121.1, 117.6, 70.8, 42.0, 37.2, 25.9, 18.2, -4.4, -4.6.

HRMS (APCI) *m/z*: [M+H] Calcd for C₁₃H₂₅Cl₂SiO₂ 295.1046; found 295.1049.



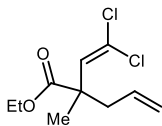
(4*S*,5*R*)-4-allyl-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane (21)

The aldehyde was synthesized according to a previously reported procedure.¹⁹ The reaction was conducted according to General Procedure A using PPh₃ (19.7 g, 75 mmol, 4.0 equiv) dissolved in MeCN (38 mL), CCl₄ (3.7 mL, 36 mmol, 2.0 equiv), and (4*S*,5*S*)-5-allyl-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (3.23 g, 18.7 mmol, 1.00 equiv) dissolved in MeCN (10 mL). The product was purified by flash chromatography (SiO₂, 1.5% to 2% to 2.5% EtOAc in hexanes) to provide 1.9 g (43% yield) of product as a pale yellow oil.

¹H NMR (800 MHz, CDCl₃) δ 5.94 (d, *J* = 8.9 Hz, 1H), 5.83 – 5.76 (m, 1H), 5.18 – 5.10 (m, 2H), 4.87 (dd, *J* = 8.9, 6.0 Hz, 1H), 4.31 – 4.26 (m, 1H), 2.36 – 2.30 (m, 1H), 2.25 – 2.20 (m, 1H), 1.48 (s, 3H), 1.37 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 133.8, 126.9, 124.2, 117.9, 109.2, 77.5, 76.1, 34.6, 28.3, 25.7.

HRMS (APCI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_{10}\text{H}_{15}\text{Cl}_2\text{O}_2$ 237.0449; found 237.0452



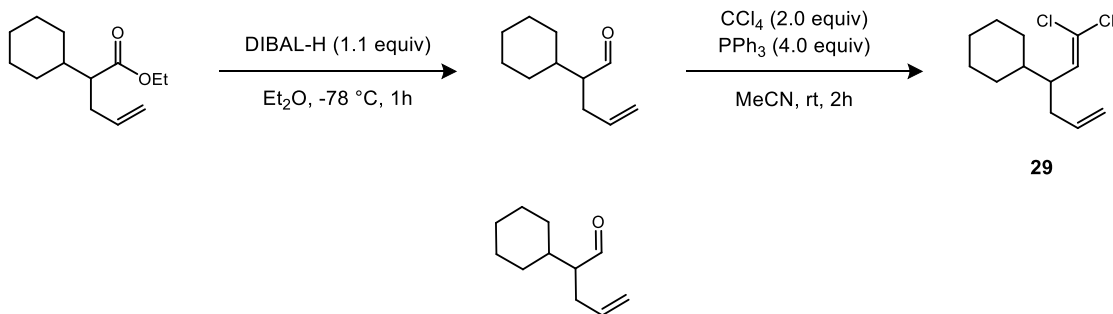
Ethyl 2-(2,2-dichlorovinyl)-2-methylpent-4-enoate (27)

The aldehyde was synthesized from a previously reported procedure.²⁰ The reaction was conducted according to General Procedure A using PPh_3 (4.0 g, 15.2 mmol, 4.0 equiv) dissolved in MeCN (8 mL), CCl_4 (0.74 mL, 7.6 mmol, 2.0 equiv), and ethyl 2-formyl-2-methylpent-4-enoate (646 mg, 3.8 mmol, 1.0 equiv) dissolved in MeCN (2 mL). The product was purified by flash column chromatography (SiO_2 5% EtOAc in hexanes) to provide 470 mg (52% yield) as a colorless oil.

^1H NMR (800 MHz, CDCl_3) δ 6.02 (s, 1H), 5.74 – 5.66 (m, 1H), 5.14 – 5.09 (m, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 2.54 – 2.46 (m, 2H), 1.38 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H).

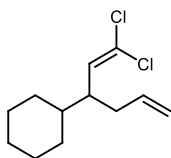
$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 174.1, 132.8, 132.7, 121.9, 119.4, 61.4, 47.9, 43.4, 21.9, 14.3.

HRMS (APCI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_8\text{H}_{11}\text{Cl}_2\text{O}_2$ 209.0136; found 209.0143.



Step 1: 2-cyclohexylpent-4-enal

2-Cyclohexylpent-4-enoate was synthesized from a previously reported procedure.²¹ Under an N₂ atmosphere, a flame dried flask equipped with a stir bar was charged ethyl 2-cyclohexylpent-4-enoate (0.927 g, 4.4 mmol, 1.0 equiv) and CH₂Cl₂ (22 mL, 0.2 M). The solution was cooled to −78 °C, and a 1.0 M solution of DIBAL–H (4.9 mL, 4.9 mmol, 1.1 equiv) in hexane was added slowly. The reaction was stirred for 1 h at −78 °C. The solution was quenched with sat. sodium potassium tartrate (aq) at −78 °C and vigorously stirred for 2 h at room temperature. The product was extracted with CH₂Cl₂ (x3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The product was purified by flash column chromatography (SiO₂, 2.5% EtOAc in hexanes) to provide 268 mg (37% yield) of product as a clear oil. ¹H NMR matched the previously reported spectrum.²²



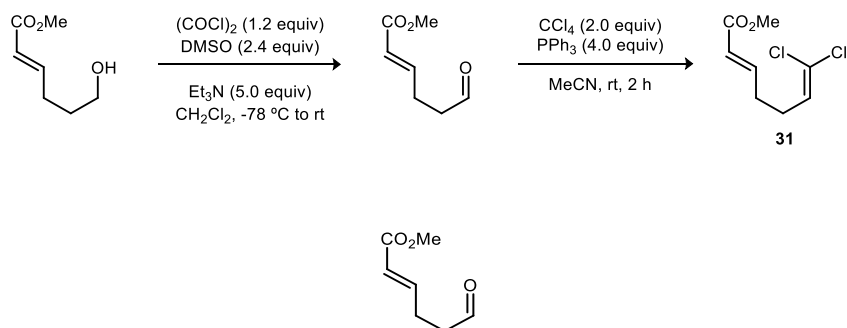
Step 2. (1,1-dichlorohexa-1,5-dien-3-yl)cyclohexane (29)

The reaction was conducted according to General Procedure A using PPh₃ (3.0 g, 11 mmol, 4.0 equiv) dissolved in MeCN (6 mL), CCl₄ (0.56 mL, 5.8 mmol, 2.0 equiv), and 2-cyclohexylpent-4-enal (490 mg, 2.9 mmol, 1.0 equiv) dissolved in MeCN (1.5 mL). The product was purified by flash column chromatography (SiO₂, hexanes) to provide 405 mg (60% yield) of product as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 5.75 – 5.69 (m, 1H), 5.67 (d, *J* = 10.4 Hz, 1H), 5.05 – 4.98 (m, 2H), 2.40 (dddd, *J* = 10.4, 8.9, 6.4, 4.9 Hz, 1H), 2.26 (dddt, *J* = 14.4, 6.4, 4.9, 1.4 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.76 – 1.70 (m, 3H), 1.73 – 1.66 (m, 1H), 1.69 – 1.62 (m, 1H), 1.34 (tdt, *J* = 11.7, 6.4, 3.2 Hz, 1H), 1.27 – 1.15 (m, 2H), 1.13 (qt, *J* = 12.8, 3.4 Hz, 1H), 1.04 – 0.91 (m, 2H).

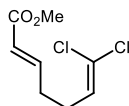
¹³C NMR (201 MHz, CDCl₃) δ 136.2, 132.9, 119.9, 116.5, 46.0, 41.4, 36.1, 31.2, 29.7, 26.6, 26.6.

HRMS (APCI) *m/z*: [M-H] Calcd for C₁₂H₁₇Cl₂ = 231.0702; found 231.0698.



Step 1: Methyl-6-oxohex-2-enoate

Methyl-6-hydroxyhex-2-enoate was synthesized according to a previously known procedure.²³ The reaction was conducted according to General Procedure B using oxalyl chloride (0.71 mL, 8.3 mmol, 1.2 equiv) in CH₂Cl₂ (70 mL), DMSO (1.18 mL, 16.6 mmol, 2.40 equiv) in CH₂Cl₂ (4 mL), methyl-6-hydroxyhex-2-enoate (1.0 g, 6.9 mmol, 1.0 equiv) in CH₂Cl₂ (14 mL), and Et₃N (4.8 mL, 35.0 mmol, 5.00 equiv). The product was used without any further purification. ¹H NMR matched previously reported spectrum.⁸



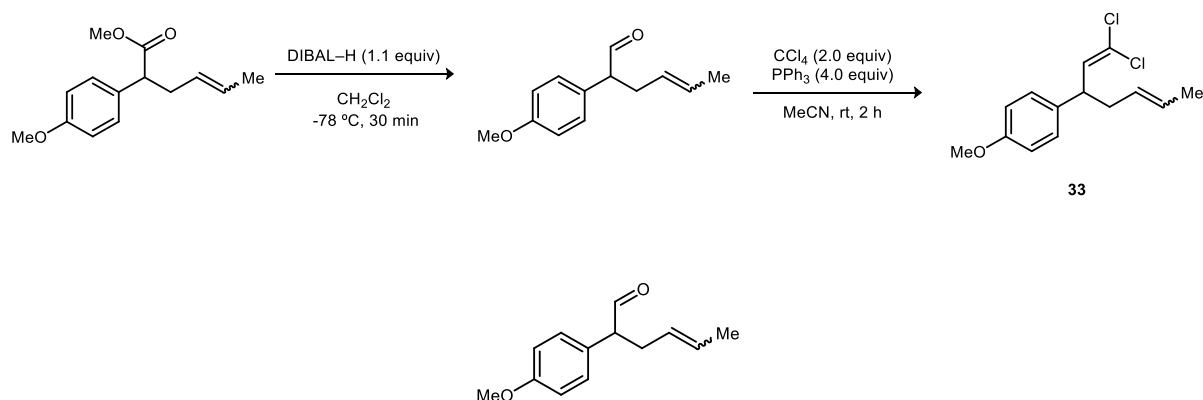
Step 2: Methyl (*E*)-7,7-dichlorohepta-2,6-dienoate (31)

The reaction was conducted according General Procedure A using PPh₃ (5.9 g, 22 mmol, 4.0 equiv) dissolved in MeCN (12 mL), CCl₄ (1.1 mL, 11 mmol, 2.0 equiv), and methyl-6-oxohex-2-enoate (795 mg, 5.60 mmol, 1.00 equiv) dissolved in MeCN (3 mL). The product was purified by flash column chromatography (SiO₂, 5% EtOAc in hexanes) to provide 180 mg (15% yield) of the *E* isomer as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 6.93 (dt, *J* = 15.6, 6.5 Hz, 1H), 5.88 – 5.82 (m, 2H), 3.74 (s, 2H), 2.37 – 2.30 (m, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 166.9, 147.2, 128.1, 122.2, 121.5, 51.7, 30.7, 28.2.

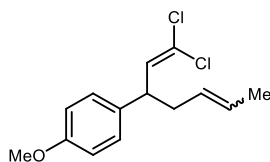
HRMS (APCI) *m/z*: [M+H] Calcd for C₁₀H₁₅Cl₂O₂ 237.0444; found 237.0446.



Step 1: 2-(4-methoxyphenyl)hex-4-enal

Methyl 2-(4-methoxyphenyl)hex-4-enoate was synthesized according to a previously reported procedure.²⁴ Under an N₂ atmosphere, a flame dried flask equipped with a stir bar was charged with methyl 2-(4-methoxyphenyl)hex-4-enoate (1.3 g, 5.5 mmol, 1.0 equiv) and CH₂Cl₂ (28 mL). The solution was cooled to −78 °C, and a 1.0 M solution of DIBAL–H (6.1 mL, 6.1 mmol, 1.1 equiv) in hexane was added slowly. The reaction was stirred for 30 min at −78 °C. The reaction mixture was quenched with sat. sodium potassium tartrate (aq) at −78 °C and vigorously stirred for 1 h at room temperature. The product was extracted with CH₂Cl₂ (x3). The combined organic phases were washed with brine, dried over Na₂SO₄, filtered, and concentrated to dryness under vacuum. The crude product was used without further purification.

Crude ¹H NMR (300 MHz, CDCl₃) *E* isomer: δ 9.65 (d, *J* = 2.0 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.98 – 6.86 (m, 2H), 5.77 – 5.37 (m, 2H), 3.60 – 3.42 (m, 2H), 2.79 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.64 (dq, *J* = 6.3, 1.3 Hz, 3H).



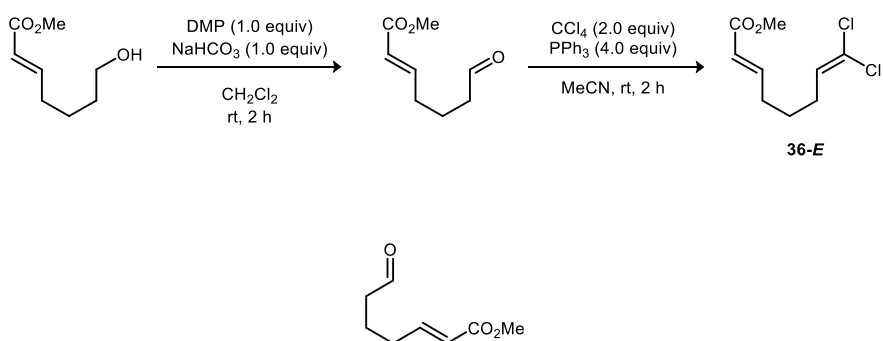
Step 2: 1-(1,1-dichlorohepta-1,5-dien-3-yl)-4-methoxybenzene (33)

The reaction was conducted according to General Procedure A using PPh₃ (5.77 g, 22.0 mmol, 4.00 equiv) dissolved in MeCN (11 mL), CCl₄ (1.1 mL, 11 mmol, 2.0 equiv), and 2-(4-

methoxyphenyl)hex-4-enal (1.12 g, 5.48 mmol, 1.00 equiv) dissolved in MeCN (3 mL). The product was purified by flash column chromatography (SiO₂, 5% CH₂Cl₂ in hexanes) to provide 270 mg (18% yield) of a 4.5:1 E/Z mixture as a colorless oil.

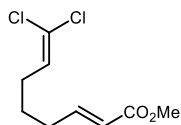
¹H NMR (500 MHz, CDCl₃) *E isomer*: δ 7.17 – 7.08 (m, 2H), 6.92 – 6.79 (m, 2H), 5.98 (dd, *J* = 9.7, 0.7 Hz, 1H), 5.50 – 5.39 (m, 1H), 5.31 (dtd, *J* = 15.6, 7.0, 1.8 Hz, 1H), 3.80 (d, *J* = 0.8 Hz, 3H), 3.67 (ddt, *J* = 14.6, 9.6, 7.4 Hz, 1H), 2.41 – 2.31 (m, 2H), 1.71 – 1.53 (m, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 158.5, 134.3, 133.3, 128.5, 127.8, 127.8, 120.2, 114.2, 55.4, 45.7, 39.0, 18.1.



Step 1: Methyl-7-oxohept-2-enoate

Methyl-7-hydroxyhept-2-enoate was synthesized according to a previously reported procedure.²⁵ A flask equipped with a stir bar was charged with methyl-7-hydroxyhept-2-enoate (867 mg, 5.48 mmol, 1.00 equiv) and CH₂Cl₂ (20 mL). Dess–Martin periodinane (2.3 g, 5.4 mmol, 1.0 equiv) and NaHCO₃ (460 mg, 5.4 mmol, 1.0 equiv) were added, and the reaction was stirred at room temperature for 2 h. The reaction was quenched with a 20% Na₂S₂O₃ (aq) and sat. NaHCO₃ (aq), and the product was extracted with CH₂Cl₂ (x3). The combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated to dryness under vacuum. The crude solid was redissolved in a minimal amount of Et₂O, filtered through a plug of silica gel, and concentrated to dryness under vacuum. The crude product was used without further purification. ¹H NMR data match the previously reported spectrum.²⁶



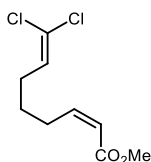
Step 2: Methyl (*E*)-8,8-dichloroocta-2,7-dienoate (**36-E**)

The reaction was conducted according to General Procedure A using PPh₃ (4.7 g, 18 mmol, 4.0 equiv) dissolved in MeCN (10 mL), CCl₄ (0.87 mL, 9.0 mmol, 2.0 equiv), and methyl (*E*)-7-oxohept-2-enoate (700 mg, 4.5 mmol, 1.0 equiv) dissolved in MeCN (3 mL). The product was purified by flash column chromatography (SiO₂, 5% EtOAc in hexanes) to provide 300 mg (30% yield) of the *E* isomer as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 6.94 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.87 – 5.81 (m, 2H), 3.73 (s, 3H), 2.26 – 2.17 (m, 4H), 1.59 (p, *J* = 7.5 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 167.1, 148.4, 129.1, 121.7, 120.9, 51.6, 31.6, 29.1, 26.7.

HRMS (APCI) *m/z*: [M+H] Calcd for C₉H₁₃Cl₂O₂ 223.0287; found 223.0289.



Methyl (*Z*)-8,8-dichloroocta-2,7-dienoate (**36-Z**)

The reaction was conducted according to General Procedure A using PPh₃ (5.37 g, 20.5 mmol, 4.00 equiv) dissolved in MeCN (10 mL), CCl₄ (1.00 mL, 10.8 mmol, 2.10 equiv), and methyl (*Z*)-7-oxohept-2-enoate²⁷ (800 mg, 5.10 mmol, 1.00 equiv) dissolved in MeCN (2.5 mL). The product was purified by flash chromatography (SiO₂, 5% EtOAc in hexanes) to provide 204 mg (18% yield) of the *Z* isomer as a colorless oil.

¹H NMR (800 MHz, CDCl₃) δ 6.23 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.89 (t, *J* = 7.4 Hz, 1H), 5.83 (dt, *J* = 11.4, 1.7 Hz, 1H), 3.74 (s, 3H), 2.71 (qd, *J* = 7.5, 1.7 Hz, 2H), 2.24 (q, *J* = 7.5 Hz, 2H), 1.60 (p, *J* = 7.5 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 166.7, 149.4, 129.3, 120.4, 120.0, 77.2, 77.0, 76.9, 51.1, 29.2, 28.3, 27.5.

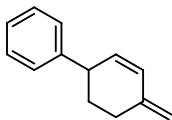
HRMS (ESI) m/z : $[M+H]$ Calcd for $C_9H_{13}Cl_2O_2$ 223.0287; found 223.0290.

5. Catalytic Reductive Cyclization Reactions with NDI

General Procedure C: A scintillation vial was charged with i-PrNDI (**4**) (0.01-0.02 mmol, 5-10 mol%), $Ni(dme)Cl_2$ (0.02-0.04 mmol, 10-20 mol%), Zn (40 mg, 0.60 mmol, 3.0 equiv), and NMP (1.6 mL). The solution was stirred at 600 rpm for 20 min, during which time the solution turned violet in color (during metallation of the catalyst, the vial was tilted at a 45° angle). The 1,1-dichloroalkene substrate (0.20 mmol, 1.0 equiv) dissolved in THF (6.4 mL) was added to the catalyst mixture. Stirring was continued at 600 rpm for 24 h. The reaction was diluted with Et_2O (2 mL), and the organic phase was washed with water (5 mL) and brine (5 mL). The organic phase was dried over Na_2SO_4 , filtered, and concentrated to dryness under vacuum. The products were purified by flash chromatography.

Note: reactions forming 6-membered ring products were run at room temperature, and reactions forming 5-membered ring products were run at 50 °C.

General Procedure D: A scintillation vial was charged with c -PentNDI (**7**) (0.01-0.02 mmol, 5-10 mol%), $Ni(dme)Cl_2$ (0.02-0.04 mmol, 10-20 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), and NMP (0.8 mL). The solution was stirred at 600 rpm for 20 min, during which time the solution turned violet in color (during metallation of the catalyst, the vial was tilted at a 45° angle). The 1,1-dichloroalkene substrate (0.2 mmol, 1.0 equiv) dissolved in THF (7.2 mL) was added to the catalyst mixture. Stirring was continued at a 45° angle at 600 rpm for 24 h. The reaction was diluted with Et_2O (2 mL), and the organic phase was washed with water (5 mL) and brine (5 mL). The organic phase was dried over Na_2SO_4 , filtered, and concentrated to dryness under vacuum. The products were purified by flash chromatography.



4-methylene-1,2,3,4-tetrahydro-1,1'-biphenyl (2**)**

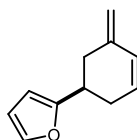
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (5.3 mg, 0.010 mmol, 5.0 mol%), Ni(dme)Cl₂ (4.4 mg, 0.02 mmol, 10 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), (1,1-dichlorohepta-1,6-dien-3-yl)benzene (**1**) (48 mg, 0.20 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at room temperature. The product was purified by flash chromatography (SiO₂, pentane) to provide the product as a colorless oil.

Run 1: 26 mg (76% yield) Run 2: 26 mg (76% yield)

¹H NMR (800 MHz, CDCl₃) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 3H), 6.33 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.88 – 5.85 (m, 1H), 4.88 (s, 1H), 4.84 (s, 1H), 3.54 – 3.50 (m, 1H), 2.48 – 2.43 (m, 1H), 2.42 – 2.37 (m, 1H), 2.12 – 2.07 (m, 1H), 1.71 – 1.65 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 145.7, 142.9, 133.2, 130.4, 128.6, 127.9, 126.4, 111.3, 42.3, 32.9, 29.5.

HRMS (APCI) *m/z*: [M+H] Calcd for C₁₃H₁₅ 171.1168; found 171.1166.



(R)-2-(5-methylenecyclohex-3-en-1-yl)furan (16**)**

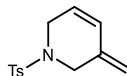
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (5.3 mg, 0.010 mmol, 5.0 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 10 mol%), Zn (40 mg, 0.60 mmol, 3.0 equiv), (*S*)-2-(1,1-dichlorohepta-1,6-dien-4-yl)furan (**15**) (48 mg, 0.20 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at room temperature. The product was purified by flash chromatography (SiO₂, pentane) to provide the product as a colorless oil.

Run 1: 27 mg (84% yield) Run 2: 25 mg (78% yield)

¹H NMR (800 MHz, CDCl₃) δ 7.33 – 7.20 (m, 1H), 6.31 – 6.29 (m, 1H), 6.20 (d, *J* = 11.2 Hz, 1H), 6.04 – 6.02 (m, 1H), 5.88 – 5.85 (m, 1H), 4.87 (s, 1H), 4.84 (s, 1H), 3.08 – 3.01 (m, 1H), 2.73 (d, *J* = 16.0 Hz, 1H), 2.52 – 2.44 (m, 2H), 2.35 – 2.28 (m, 1H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 159.2, 142.3, 141.0, 129.6, 128.7, 111.9, 110.1, 103.7, 35.6, 33.8, 30.4.

HRMS (ESI) *m/z*: [M+H] Calcd for C₁₁H₁₃O 161.0961; found 161.0959.

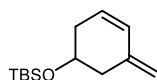


3-methylene-1-tosyl-1,2,3,6-tetrahydropyridine (**18**)

The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (10.6 mg, 0.020 mmol, 10 mol%), Ni(dme)Cl₂ (8.8 mg, 0.040 mmol, 20 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), *N*-allyl-*N*-(3,3-dichloroallyl)-4-methylbenzenesulfonamide (**17**) (64 mg, 0.2 mmol, 1.0 equiv), THF (6.4 mL), NMP (1.6 mL) at room temperature. The product was purified by flash chromatography (SiO₂, 5% to 10% Et₂O in pentane) to provide the product as an off-white solid.

Run 1: 24 mg (48% yield) Run 2: 27 mg (53% yield)

Spectra match those previously reported in the literature.²⁷



tert-Butyldimethyl((5-methylenecyclohex-3-en-1-yl)oxy)silane (**20**)

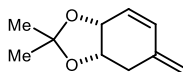
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (5.3 mg, 0.010 mmol, 5 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 10 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), *tert*-butyl((1,1-dichlorohepta-1,6-dien-4-yl)oxy)dimethylsilane (**21**) (59 mg, 0.20 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at room temperature. The product was purified by flash chromatography (SiO₂, pentane) to provide the product as a colorless oil.

Run 1: 37 mg (82% yield). Run 2: 32 mg (71% yield)

¹H NMR (800 MHz, CDCl₃) δ 6.12 – 6.08 (m, 1H), 5.72 – 5.68 (m, 1H), 4.85 (s, 1H), 4.78 (s, 1H), 3.94 – 3.88 (m, 1H), 2.52 (dd, *J* = 14.4, 4.1 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.15 – 2.08 (m, 1H), 0.91 – 0.88 (m, 9H), 0.07 (dd, *J* = 5.4, 1.2 Hz, 6H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 142.9, 129.6, 127.8, 112.0, 68.2, 40.8, 35.5, 26.0, 18.3, -4.5.

HRMS (ESI) *m/z*: [M+H] Calcd for C₁₃H₂₅OSi 225.1669; found 225.1672.



(3a*S*,*R*-2,2-dimethyl-5-methylene-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole (22)

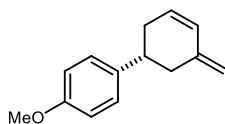
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (5.3 mg, 0.010 mmol, 5 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 10 mol%), Zn (40 mg, 0.60 mmol, 3.0 equiv), (4*S*,5*R*)-4-allyl-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane (**23**) (47 mg, 0.20 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at room temperature. The product was purified by flash chromatography (SiO₂, 1% to 1.5% to 2% Et₂O in pentane) to provide the product as a colorless oil.

Run 1: 17 mg (52% yield). Run 2: 19 mg (56% yield)

¹H NMR (800 MHz, CDCl₃) δ 6.25 (d, *J* = 10.0 Hz, 1H), 5.67 (d, *J* = 8.8 Hz, 1H), 5.03 (s, 1H), 4.98 (s, 1H), 4.54 (t, *J* = 5.6 Hz, 1H), 4.38 (q, *J* = 2.4, 1H), 2.69 (dd, *J* = 15.7, 4.9 Hz, 1H), 2.63 – 2.58 (m, 1H), 1.41 (s, 3H), 1.38 (s, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) δ 138.2, 131.2, 126.9, 115.3, 109.3, 73.0, 71.8, 32.6, 28.3, 26.9.

HRMS (ESI) *m/z*: [M+H] Calcd for C₁₀H₁₅O₂ 167.1067; found 167.1065.



(*R*)-4'-methoxy-3-methylene-1,2,3,6-tetrahydro-1,1'-biphenyl (24)

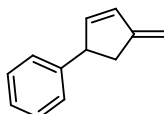
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (5.3 mg, 0.01 mmol, 5 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 10 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), (*S*)-1-(1,1-dichlorohepta-1,6-dien-4-yl)-4-methoxybenzene (**19**) (54 mg, 0.20 mmol, 1.00 equiv), THF (6.4 mL), and NMP (1.6 mL) at room temperature. The product was purified by flash chromatography (SiO₂, 2.5% Et₂O in pentane) to provide the product as a colorless oil.

Run 1: 31 mg (77% yield) Run 2: 30 mg (75% yield)

¹H NMR (800 MHz, CDCl₃) δ 7.17 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.23 (d, *J* = 9.8 Hz, 1H), 5.91 (t, *J* = 6.4 Hz, 1H), 4.87 (s, 1H), 4.80 (s, 1H), 3.81 (s, 3H), 2.91 – 2.85 (m, 1H), 2.60 – 2.55 (m, 1H), 2.53 – 2.48 (m, 1H), 2.36 (dt, *J* = 18.3, 5.5 Hz, 1H), 2.29 – 2.22 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 158.2, 143.7, 138.4, 129.9, 129.4, 127.9, 114.0, 111.3, 55.4, 39.9, 38.5, 33.8.

HRMS (ESI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_{14}\text{H}_{17}\text{O}$ 201.1274; found 201.1277.



(4-methylenecyclopent-2-en-1-yl)benzene (**26**)

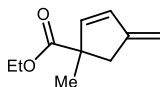
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (10.6 mg, 0.020 mmol, 10 mol%), $\text{Ni}(\text{dme})\text{Cl}_2$ (8.8 mg, 0.040 mmol, 20 mol%), Zn (40 mg, 0.60 mmol, 3.0 equiv), (1,1-dichlorohexa-1,5-dien-3-yl)benzene (**25**) (45 mg, 0.2 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at 50 °C. The product was purified by flash chromatography (SiO_2 , pentane) to provide the product as a colorless oil.

Run 1: 24 mg (77% yield) Run 2: 23 mg (74% yield)

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 6.33 (dd, $J = 5.5$, 2.7 Hz, 1H), 6.17 – 6.13 (m, 1H), 4.95 (s, 1H), 4.83 (s, 1H), 4.09 – 4.00 (m, 1H), 3.08 (ddt, $J = 16.8$, 8.3, 2.2 Hz, 1H), 2.52 – 2.43 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.1, 145.5, 142.4, 134.9, 128.7, 127.3, 126.5, 103.5, 50.8, 39.8.

HRMS (APCI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_{12}\text{H}_{13}$ 157.1012; found 157.1010.



ethyl 1-methyl-4-methylenecyclopent-2-ene-1-carboxylate (**28**)

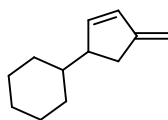
The reaction was conducted according to General Procedure C with *i*-PrNDI (**4**) (10.6 mg, 0.020 mmol, 10 mol%), $\text{Ni}(\text{dme})\text{Cl}_2$ (8.8 mg, 0.04 mmol, 20 mol%), Zn (40 mg, 0.60 mmol, 3.0 equiv), ethyl 2-(2,2-dichlorovinyl)-2-methylpent-4-enoate (**27**) (47 mg, 0.20 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at 50 °C. The product was purified by flash chromatography (SiO_2 , 2% Et_2O in pentane) to provide the product as a colorless oil.

Run 1: 15 mg (45% yield) Run 2: 15 mg (45% yield)

^1H NMR (800 MHz, CDCl_3) δ 6.15 (d, $J = 5.4$ Hz, 1H), 6.06 (d, $J = 5.5$ Hz, 1H), 4.92 (s, 1H), 4.84 (s, 1H), 4.14 (d, $J = 7.1$ Hz, 2H), 3.13 (dt, $J = 16.7, 2.4$ Hz, 1H), 2.41 – 2.36 (m, 1H), 1.35 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 176.1, 152.1, 142.3, 134.0, 104.9, 61.0, 55.3, 41.1, 25.5, 14.3.

HRMS (APCI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2$ 167.1067; found 167.1064.



(4-methylenecyclopent-2-en-1-yl)cyclohexane (30)

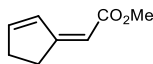
The reaction was conducted according to General Procedure C with $i\text{-Pr}$ NDI (**4**) (10.6 mg, 0.02 mmol, 10 mol%), $\text{Ni}(\text{dme})\text{Cl}_2$ (8.8 mg, 0.040 mmol, 20 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), (1,1-dichlorohexa-1,5-dien-3-yl)cyclohexane (**29**) (47 mg, 0.20 mmol, 1.0 equiv), THF (6.4 mL), and NMP (1.6 mL) at 50 °C. The product was purified by flash chromatography (SiO_2 , pentane) to provide the product as a colorless oil.

Run 1: 24 mg (75% yield) Run 2: 24 mg (75% yield)

^1H NMR (800 MHz, CDCl_3) δ 5.75 – 5.69 (m, 1H), 5.67 (d, $J = 10.4$ Hz, 1H), 5.05 – 4.98 (m, 2H), 2.40 (dddd, $J = 10.4, 8.9, 6.4, 4.9$ Hz, 1H), 2.26 (dddt, $J = 14.4, 6.4, 4.9, 1.4$ Hz, 1H), 2.09 – 2.02 (m, 1H), 1.76 – 1.70 (m, 3H), 1.73 – 1.66 (m, 1H), 1.69 – 1.62 (m, 1H), 1.34 (tdt, $J = 11.7, 6.4, 3.2$ Hz, 1H), 1.27 – 1.15 (m, 2H), 1.13 (qt, $J = 12.8, 3.4$ Hz, 1H), 1.04 – 0.91 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 136.2, 132.9, 119.9, 116.5, 46.0, 41.4, 36.1, 31.2, 29.7, 26.6, 26.6.

HRMS (APCI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_{12}\text{H}_{19}$ 163.1481; found 163.1480.



Methyl (Z)-2-(cyclopent-2-en-1-ylidene)acetate (32)

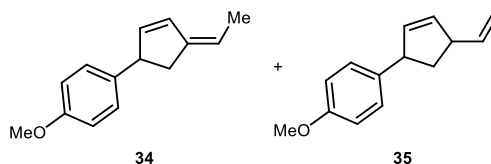
The reaction was conducted according to procedure D with *c*-Pent^tNDI (**7**) (15.4 mg, 0.0200 mmol, 10 mol%), Ni(dme)Cl₂ (8.8 mg, 0.040 mmol, 20 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), methyl (*E*)-7,7-dichlorohepta-2,6-dienoate (**31**) (42 mg, 0.20 mmol, 1.0 equiv), THF (7.2 mL), and NMP (0.8 mL) at room temperature. The product was purified by flash chromatography (SiO₂, 2% Et₂O in pentane) to provide the product as a colorless oil. The major isomer was assigned by analysis of COSY and NOESY NMR spectra.

Run 1: 18 mg (64% yield); 14 : 1 *Z*/*E* Run 2: 17 mg (61% yield); 12 : 1 *Z*/*E*

¹H NMR (400 MHz, CDCl₃) **32-Z** δ 7.38 (dtd, *J* = 5.6, 2.3, 0.9 Hz, 1H), 6.66 (dtd, *J* = 5.6, 2.7, 1.6 Hz, 1H), 5.62 (tt, *J* = 2.0, 1.0 Hz, 1H), 3.70 (s, 3H), 2.67 (dt, *J* = 7.1, 2.1 Hz, 2H), 2.54 (dddd, *J* = 6.9, 4.3, 2.4, 1.3 Hz, 2H).

¹H NMR (400 MHz, CDCl₃) **32-E** δ 6.65 – 6.59 (m, 1H), 6.30 (dt, *J* = 5.4, 2.1 Hz, 1H), 5.77 (t, *J* = 2.6 Hz, 1H), 3.68 (s, 3H), 3.02 (dt, *J* = 7.4, 2.5 Hz, 2H), 2.72 – 2.58 (m, 3H), 2.54 (dddd, *J* = 6.9, 4.3, 2.4, 1.3 Hz, 2H).

¹³C{¹H} NMR (201 MHz, CDCl₃) **32-Z** δ 167.5, 166.4, 149.1, 132.2, 106.9, 51.0, 31.4, 31.2.



Major product: 1-methoxy-4-((4*S*)-4-vinylcyclopent-2-en-1-yl)benzene (**35**)

Minor Product: 1-(4-ethylidenecyclopent-2-en-1-yl)-4-methoxybenzene (34**)**

The reaction was conducted according to procedure D with *c*-Pent^tNDI (**7**) (15.4 mg, 0.020 mmol, 10 mol%), Ni(dme)Cl₂ (8.8 mg, 0.040 mmol, 20 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), methyl (*E*)-7,7-dichlorohepta-2,6-dienoate (**33**) (42 mg, 0.20 mmol, 1.0 equiv), THF (7.2 mL), and NMP (0.8 mL) at room temperature. The product was purified by flash chromatography (SiO₂, 2% Et₂O in pentane) to provide products **34** and **35** as a clear oil. Products were identified through analysis of COSY and NOESY NMR spectra.

Run 1: 32 mg (81% combined yield) **35**:**34** = 3.5 : 1; **35-cis**:**35-trans** = 1.3 : 1; **34-Z**:**34-E** = 3:1

Run 2: 35 mg (87% combined yield) **35:34** = 3.4 : 1; **35-cis:35-trans** = 1.6 : 1; **34-Z:34-E** = 5:1

¹H NMR (800 MHz, CDCl₃) **35-cis**: δ 7.14 – 7.06 (m, 2H), 6.87 – 6.81 (m, 2H), 5.86 – 5.76 (m, 2H), 5.08 – 5.03 (m, 1H), 4.97 – 4.93 (m, 1H), 3.85 (td, *J* = 8.3, 2.3 Hz, 1H), 3.79 (s, 3H), 3.39 (q, *J* = 9.0, 8.1 Hz, 2H), 2.62 (dt, *J* = 13.0, 8.1 Hz, 1H), 1.43 (dt, *J* = 13.0, 8.4 Hz, 2H).

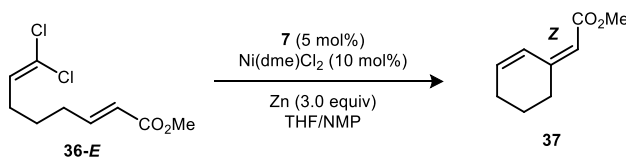
¹H NMR (800 MHz, CDCl₃) **35-trans**: δ 7.14 – 7.06 (m, 2H), 6.87 – 6.81 (m, 2H), 5.86 – 5.76 (m, 2H), 5.08 – 5.03 (m, 1H), 4.97 – 4.93 (m, 1H), 3.96 – 3.91 (m, 1H), 3.79 (s, 3H), 3.52 – 3.47 (m, 1H), 2.14 (ddd, *J* = 13.4, 8.7, 4.9 Hz, 1H), 1.99 (ddd, *J* = 13.1, 8.5, 5.7 Hz, 1H).

¹H NMR (800 MHz, CDCl₃) **34-Z**: δ 7.14 – 7.03 (m, 2H), 6.87 – 6.79 (m, 2H), 6.54 (ddd, *J* = 5.6, 2.2, 1.0 Hz, 1H), 6.09 – 6.06 (m, 1H), 5.23 (q, *J* = 7.6 Hz, 1H), 3.96 – 3.91 (m, 1H), 3.79 (s, 3H), 3.00 (ddt, *J* = 16.2, 8.5, 1.9 Hz, 1H), 2.39 (ddt, *J* = 16.2, 4.2, 2.2 Hz, 1H), 1.76 (d, *J* = 7.0 Hz, 3H).

¹H NMR (800 MHz, CDCl₃) **34-E**: δ 7.14 – 7.03 (m, 2H), 6.87 – 6.79 (m, 2H), 6.24 (dd, *J* = 5.5, 2.1 Hz, 1H), 5.97 – 5.93 (m, 1H), 5.46 – 5.39 (m, 1H), 4.00 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H), 3.00 (ddt, *J* = 16.2, 8.5, 1.9 Hz, 1H), 2.33 (d, *J* = 16.8 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 3H).

¹³C{¹H} NMR (201 MHz, CDCl₃) **34 & 35**: δ 158.2, 142.5, 141.9, 140.9, 138.3, 138.0, 135.4, 135.3, 134.8, 134.5, 130.0, 129.6, 128.5, 128.4, 128.2, 114.0, 114.0, 114.0, 113.5, 113.2, 55.4, 50.9, 50.0, 49.9, 49.4, 49.1, 41.6, 40.9, 40.3, 14.8.

HRMS (APCI) *m/z*: [M+H] Calcd for C₁₄H₁₇O 201.1274; found 201.1276.



Methyl (Z)-2-(cyclohex-2-en-1-ylidene)acetate (**37**)

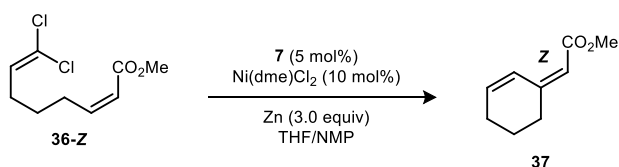
The reaction was conducted according to procedure D with *c*-PentNDI (**7**) (7.7 mg, 0.020 mmol, 5 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 10 mol%), Zn (40 mg, 0.6 mmol, 3.0 equiv), methyl (E)-8,8-dichloroocta-2,7-dienoate (**36-E**) (45 mg, 0.20 mmol, 1.0 equiv), THF (7.2 mL), and NMP (0.8 mL) at room temperature. The product was purified by flash chromatography (SiO₂, 2% Et₂O in pentane) to provide the product as a colorless oil.

Run 1: 23 mg (77% yield) Run 2: 24 mg (80% yield)

^1H NMR (800 MHz, CDCl_3) δ 7.47 (dtd, $J = 10.2, 2.1, 0.9$ Hz, 1H), 6.24 (dtd, $J = 10.1, 4.1, 1.6$ Hz, 1H), 5.50 – 5.47 (m, 1H), 3.69 (s, 3H), 2.41 – 2.37 (m, 2H), 2.23 (td, $J = 6.1, 4.1, 2.2, 0.9$ Hz, 2H), 1.81 – 1.76 (m, 2H).

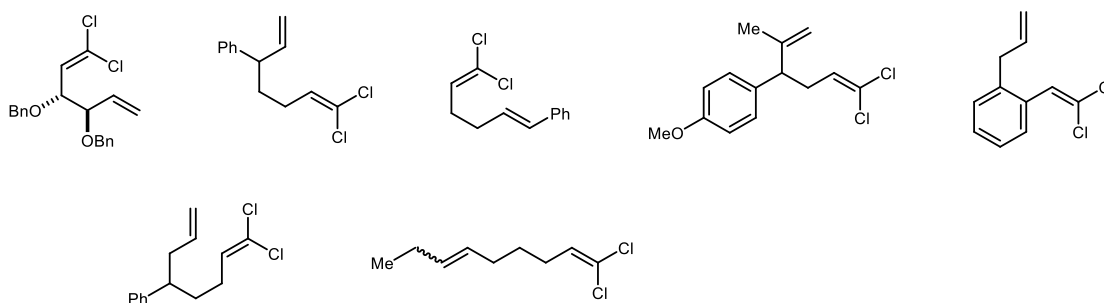
$^{13}\text{C}\{^1\text{H}\}$ NMR (201 MHz, CDCl_3) δ 167.1, 152.9, 138.6, 125.3, 112.7, 51.1, 32.7, 26.3, 22.8.

HRMS (APCI) m/z : $[\text{M}+\text{H}]$ Calcd for $\text{C}_9\text{H}_{18}\text{O}_2$ 153.0910; found 153.0909.



The reaction was conducted with slight modification to procedure D with *c*-PentNDI (3.9 mg, 0.010 mmol, 5 mol%), Ni(dme)Cl_2 (2.2 mg, 0.02 mmol, 10 mol%), Zn (20 mg, 0.3 mmol, 3.0 equiv), methyl (Z)-8,8-dichloroocta-2,7-dienoate (21 mg, 0.1 mmol, 1.0 equiv), THF (3.6 mL), and NMP (0.4 mL). After 24 h, an aliquot of the reaction solution was filtered through a 5 cm silica plug, eluting with CDCl_3 to provide **37-Z** (86% ^1H NMR yield by integrating against mesitylene).

Substrates that were ineffective in the cyclization



6. Electrocatalytic Reductive Cyclization Reactions

Construction of Electrocatalytic Cell:

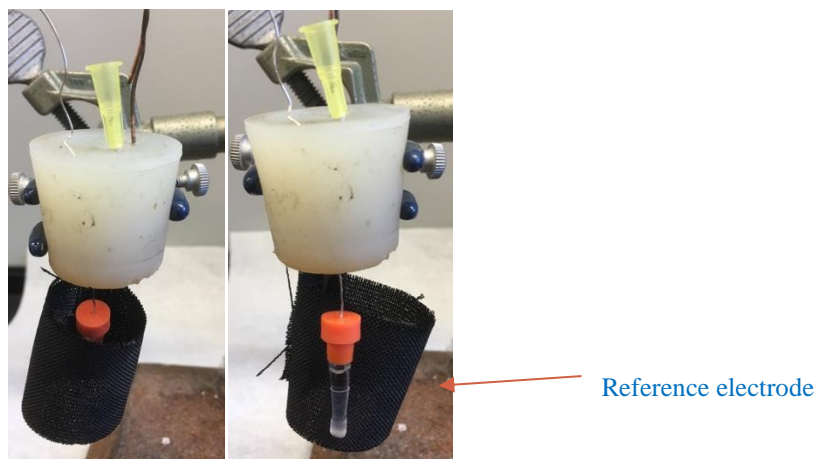
Electrocatalytic reactions were performed in an H-cell purchased from James Glass Inc. The two sides of the cell were divided by a porous glass frit. The cell also contained a luer port which was not used and was sealed with a NMR septum.



Figure S1. H-cell divided by a porous glass frit

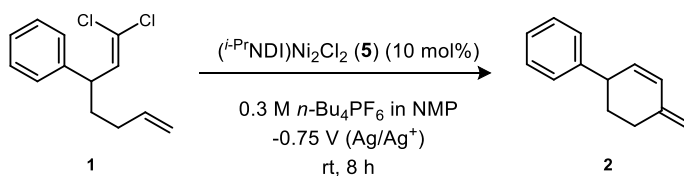
Carbon cloth purchased from Fuel Cell Earth was used for the both the cathode and anode. Each side was fitted with a 9.5 cm x 3.2 cm carbon cloth electrode, with each end sewn together in a cylindrical shape, using copper wire, to fit the inner diameter of the cell. Silver wire was used as the reference electrode.

The cell was closed using silicon stoppers purchased from Fisher (09-704-1L). Both the copper wire attached to the electrode and silver wire were pushed through the top of the septa. Needles were also added as vents to the septa to equalize pressure when sealing the cell.



Setting Up Electrocatalytic Reactions:

General Considerations. Electrocatalytic reactions were set up and run in a glovebox under a N₂ atmosphere. Experiments were carried out using a Gamry Interface 1000 Potentiostat. *n*-Bu₄NPF₆ was purchased from Fisher and crystallized from hot EtOH prior to use. Electrolyte solutions were prepared and stored over molecular sieves for at least 3 days prior to use.



Procedure for constant potential electrolysis. The working electrode compartment of the H-cell was equipped with a stirbar and charged with (*i*-PrNDI)Ni₂Cl₂ (**5**) (7.2 mg, 0.010 mmol, 10

mol%), (1,1-dichlorohepta-1,6-dien-3-yl)benzene (**1**) (24 mg, 0.10 mmol, 1.0 equiv), and mesitylene (14 μ L, 0.10 mmol, 1.0 equiv). An electrolyte solution composed of 0.3 M *n*-Bu₄NPF₆ in NMP (6.6 mL, 0.15 M) was added to both sides of the H-cell. The reaction was run at a constant potential of -0.75 V (Ag/Ag⁺), stirring at 900 rpm, until the charge passed reached a plateau (approximately 8 h). An aliquot of the reaction solution was filtered through a 5 cm silica plug, eluting with CDCl₃. The yield of **2** was determined by ¹H NMR integration against mesitylene.

Run 1: 88% yield. Run 2: 99% yield. 94% Faradaic efficiency.

Procedure for constant current electrolysis. The working electrode compartment of the H-cell was equipped with a stirbar and charged with (*i*-PrNDI)Ni₂Cl₂ (**5**) (7.2 mg, 0.010 mmol, 10 mol%), (1,1-dichlorohepta-1,6-dien-3-yl)benzene (**1**) (24 mg, 0.10 mmol, 1.0 equiv), and mesitylene (14 μ L, 0.10 mmol, 1.0 equiv). An electrolyte solution composed of 0.3 M *n*-Bu₄NPF₆ in NMP (6.6 mL, 0.15 M) was added to both sides of the H-cell. The reaction was run at a constant current of -0.7 mA with stirring at 300 rpm. An aliquot of the reaction solution was filtered through a 5 cm silica plug, eluting with CDCl₃. The yield of **2** was determined by ¹H NMR integration against mesitylene.

40 min reaction time: 20% conversion of **1**; 2% yield of **2**

5.5 h reaction time: 73% conversion of **1**; 41% yield of **2**

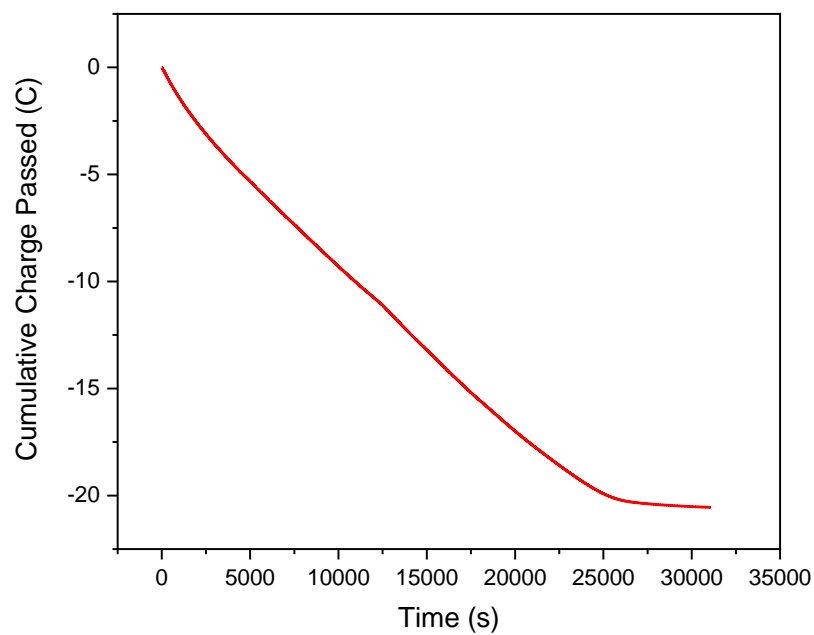


Figure A1.2. Plot of charge passed vs. time for constant potential bulk electrolysis.

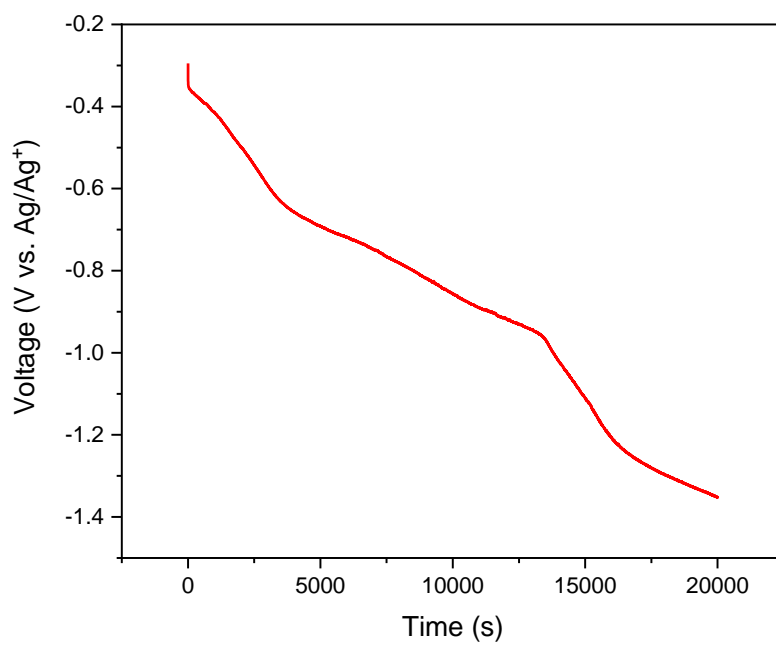


Figure A1.3. Plot of voltage vs. time for constant current bulk electrolysis.

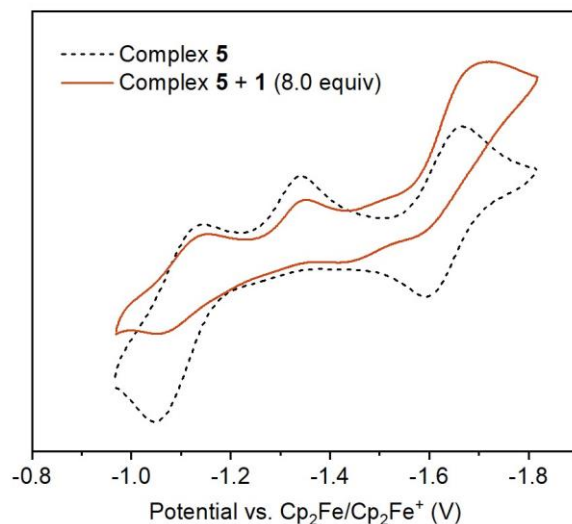


Figure A1.4. Cyclic voltammogram of ($i\text{Pr}$ NDI) Ni_2Cl_2 (**5**) (1.9 mM) in 0.3 M $n\text{-Bu}_4\text{NPF}_6$ in NMP (black dashed line). Cyclic voltammogram of ($i\text{Pr}$ NDI) Ni_2Cl_2 (**5**) (1.9 mM), **1** (15 mM) in 0.3 M $n\text{-Bu}_4\text{NPF}_6$ in NMP (red solid line).

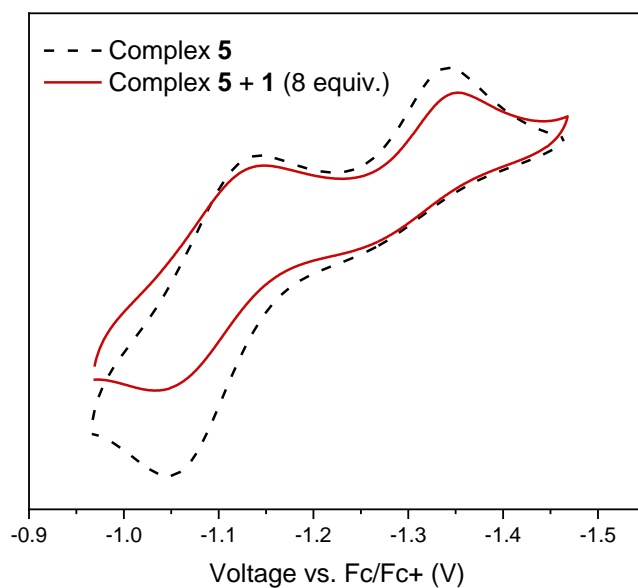


Figure A1.5. Cyclic voltammogram of ($i\text{Pr}$ NDI) Ni_2Cl_2 (**5**) (1.9 mM) in 0.3 M $n\text{-Bu}_4\text{NPF}_6$ in NMP (black dashed line). Cyclic voltammogram of ($i\text{Pr}$ NDI) Ni_2Cl_2 (**5**) (1.9 mM), **1** (15 mM) in 0.3 M $n\text{-Bu}_4\text{NPF}_6$ in NMP (red solid line).

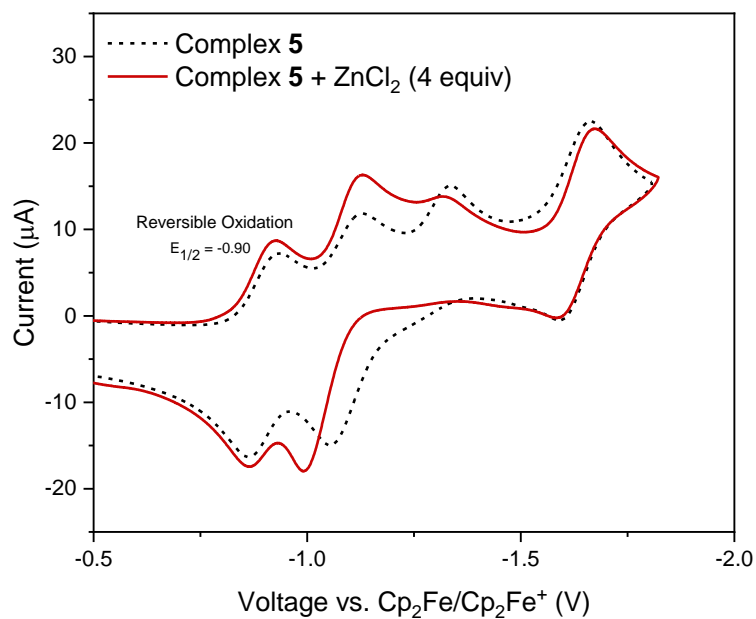
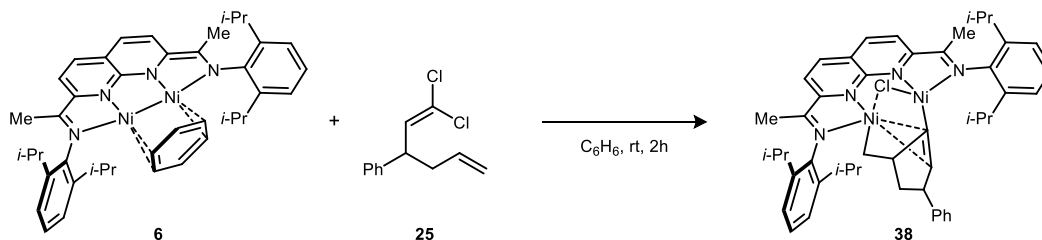


Figure A1.6. Cyclic voltammogram of (ⁱPrNDI)Ni₂Cl₂ (**5**) (1.9 mM) in 0.3 M *n*-Bu₄NPF₆ in NMP (black dashed line). Cyclic voltammogram of (ⁱPrNDI)Ni₂Cl₂ (**5**) (1.9 mM), ZnCl₂ (7.6 mM) in 0.3 M *n*-Bu₄NPF₆ in NMP (red solid line).

7. Synthesis and Characterization of Organometallic Complex 38



Synthesis of Organometallic Complex 38

A scintillation vial was charged with (*i*-PrNDI)Ni₂(C₆H₆) (**6**) (40 mg, 0.054 mmol, 1.0 equiv), (1,1-dichlorohexa-1,5-dien-3-yl)benzene (**26**) (12 mg, 0.054 mmol, 1.0 equiv), and C₆H₆ (5 mL). The solution was stirred at room temperature for 2 h then placed in the freezer (−30 °C). Once frozen, the solid mixture was thawed, and the mixture was filtered through a glass fiber pad to remove insoluble (*i*-PrNDI)Ni₂Cl₂ (**5**). The filtrate was concentrated under vacuum. This freeze-thaw-filter process was repeated two more times. The isolated solid was washed with pentane (2 mL x 3). The greenish-brown powder was crystallized by diffusion of pentane vapor into a saturated THF solution to yield 9.8 mg (22% yield) of green-brown crystals.

¹H NMR (400 MHz, C₆D₆) δ 17.07 (br), 13.37, 10.10, 9.50, 8.06, 7.41, 4.37, 3.57, 1.00, 0.81, 0.03, -7.60 (br), -13.56 (br), -23.56 (br).

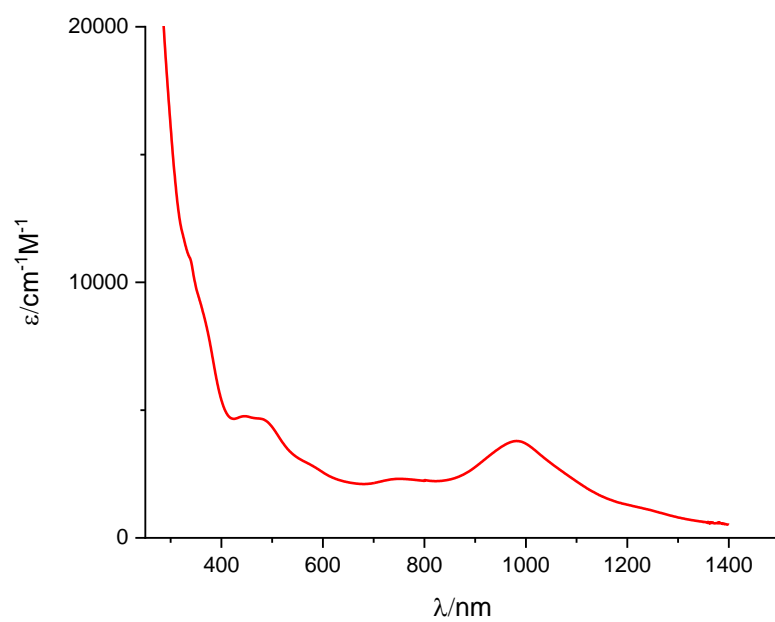


Figure A1.7. Room temperature UV-Vis spectrum of complex **38** in THF (0.075 mM).

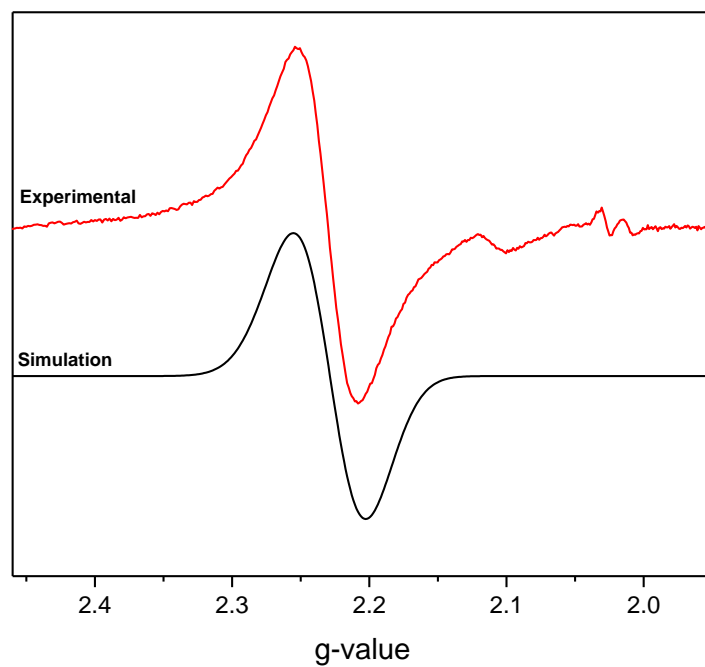


Figure A1.8. X-Band EPR spectrum of complex **38** at room temperature in toluene. Simulated parameters $g = 2.228$

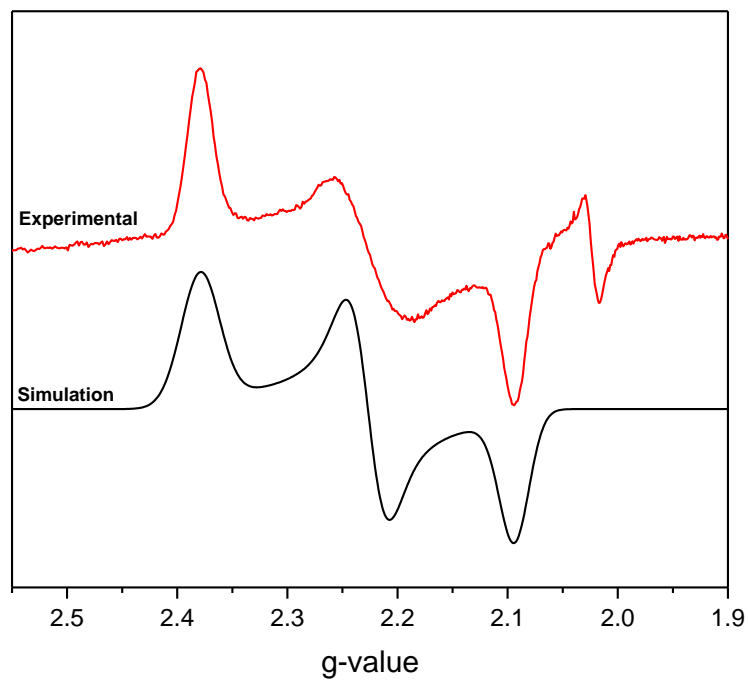


Figure A1.9. X-Band EPR spectrum of complex **38** at 105 K in toluene. Simulated parameters $g_1 = 2.378$, $g_2 = 2.226$ and $g_3 = 2.093$.

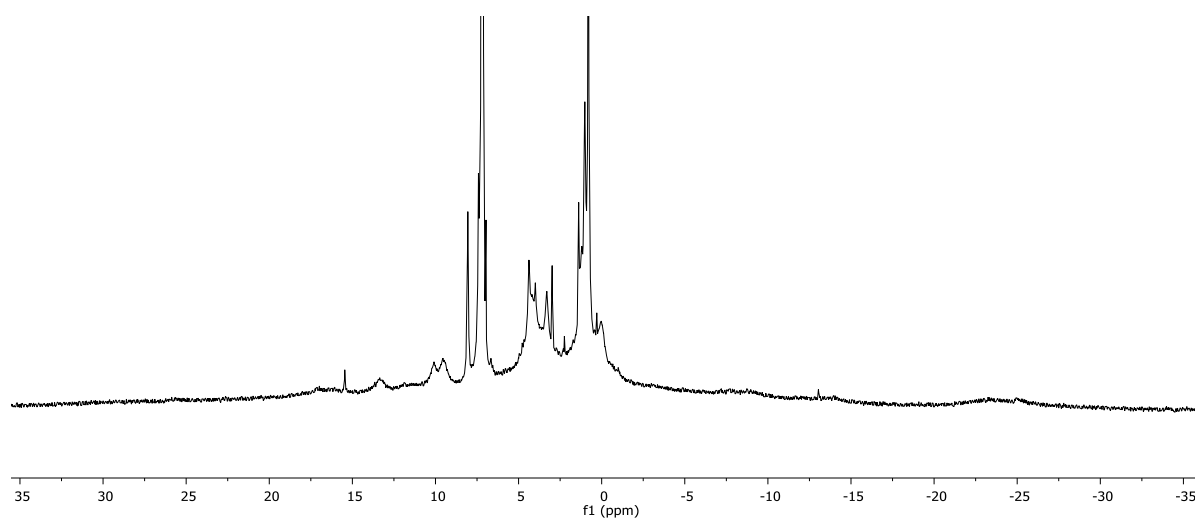


Figure A1.10. ^1H NMR spectrum of complex **38** at room temperature in C_6D_6

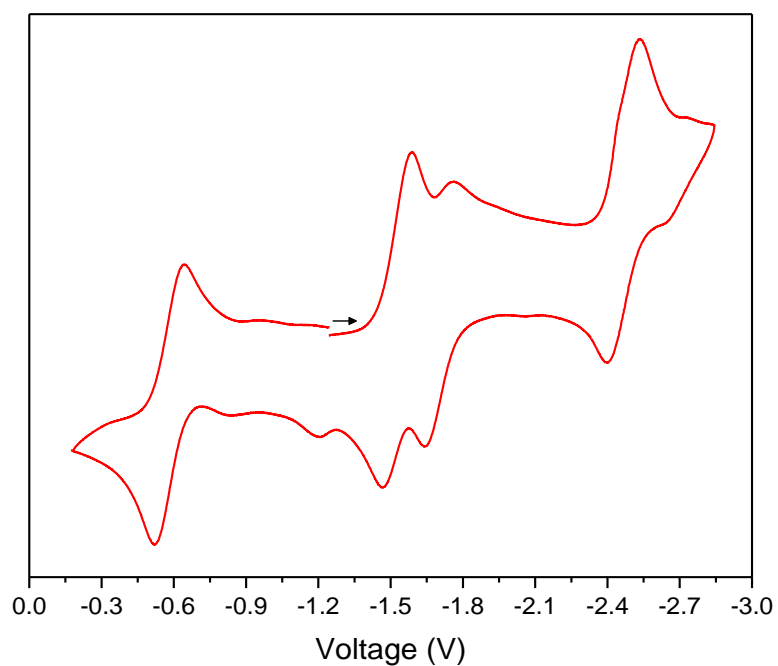
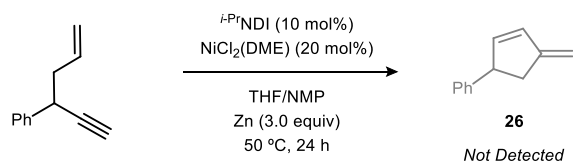


Figure A1.11. Cyclic voltammogram of complex **38** (0.3 M n-Bu₄NPF₆ in THF; glassy carbon working electrode; 100 mV/s scan rate). Scans begin at the open circuit potential and proceed in the indicated direction. The cyclic voltammogram is referenced to the Cp₂Fe/Cp₂Fe⁺ couple.

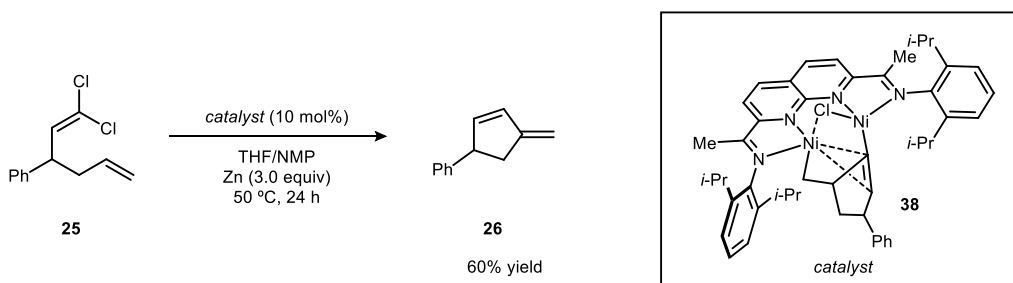
8. Mechanistic Experiments

Attempted Catalytic C–H Insertion with Hex-5-en-1-yn-3-ylbenzene



A 2 dram vial equipped with a stir bar was charged with $i\text{-PrNDI}$ ligand (**4**) (5.3 mg, 0.010 mmol, 10 mol%), $\text{Ni}(\text{dme})\text{Cl}_2$ (4.4 mg, 0.020 mmol, 20 mol%), Zn (20 mg, 0.3 mmol, 3 equiv), and NMP (0.8 mL). The mixture was stirred at room temperature at 600 rpm for approximately 20 minutes until a violet color developed. A solution of hex-5-en-1-yn-3-ylbenzene²⁸ (16 mg, 0.1 mmol, 1.0 equiv) and mesitylene (14 μL , 0.1 mmol, 1.0 equiv) in THF (3.2 mL) was added to the catalyst solution. The reaction mixture was stirred at 600 rpm for 24 h at 50 °C. An aliquot of the reaction solution was filtered through a 5 cm silica plug eluting with CDCl_3 . (4-methylenecyclopent-2-en-1-yl)benzene (**26**) was not observed by ^1H NMR.

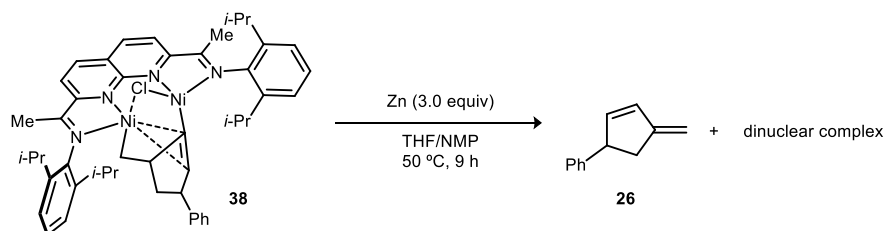
Complex **38** as a viable catalyst for vinylidene olefin cyclization



A 2 dram vial equipped with a stir bar was charged with **38** (4.2 mg, 0.0050 mmol, 10 mol%), Zn (10 mg, 0.15 mmol, 3.0 equiv), and NMP (0.4 mL). A solution of (1,1-dichlorohexa-1,5-dien-3-yl)benzene (**25**) (11 mg, 0.05 mmol, 1.0 equiv) and mesitylene (7 μL , 0.05 mmol, 1.0 equiv) in THF (1.6 mL) was added to the catalyst solution. The reaction mixture was stirred at 600 rpm for 24 h at 50 °C. An aliquot of the reaction solution was filtered through a 5 cm silica plug

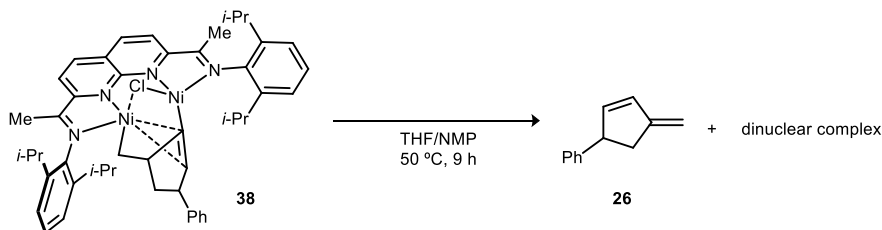
eluting with CDCl₃. The yield of product **26** (60% yield) was determined by ¹H NMR against mesitylene.

Stoichiometric Reactions with Complex **38**



A 1.5 dram vial equipped with a stir bar was charged with **38** (3.0 mg, 0.0036 mmol, 1 equiv), Zn (0.7 mg, 0.01 mmol, 3.0 equiv), mesitylene (1.3 mg, 0.011 mmol, 3.0 equiv), NMP (30 μ L), and THF (110 μ L). The reaction mixture was heated at 50 $^{\circ}$ C, stirring at 600 rpm. The yield of product **26** was determined by GC over the course of 9 h. Within 20 min, the solution color changes from green-brown to purple and remains that color over the 9 h reaction time.

Time	Yield of 26
1 h	96%
3 h	92%
9 h	99%

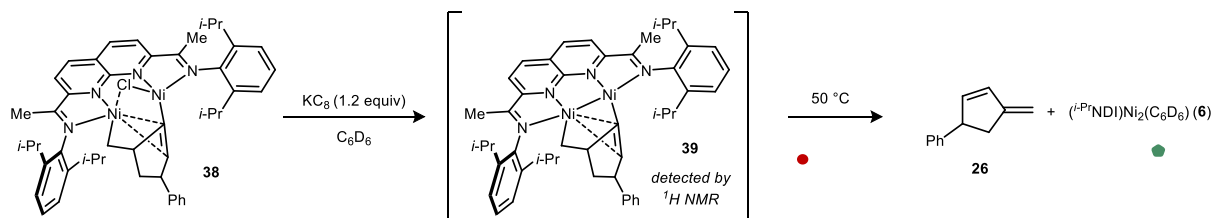


A 1.5 dram vial equipped with a stir bar was charged with **38** (3 mg, 0.004 mmol, 1.0 equiv), mesitylene (1.4 mg, 0.012 mmol, 3.3 equiv), NMP (30 μ L), and THF (110 μ L). The

solution was heated at 50 °C, stirring at 600 rpm. The yield of product **26** was determined by GC over the course of 9 h. The solution color remained green-brown over the 9 h reaction time.

Time	Yield of 26
1 h	22%
3 h	24%
9 h	64%

Reduction of Complex **38** with KC_8 and Heating at 50 °C



A J-Young NMR tube was charged with complex **38** (3.0 mg, 0.004 mmol, 1.0 equiv), KC_8 (0.6 mg, 0.004, 1.2 equiv), mesitylene (0.6 mg, 0.005, 1.4 equiv), and C_6D_6 (0.6 mL). Within 10 min the solution color changed from green-brown to brown. The solution was left to react at room temperature for 1 h then heated to 50 °C for an additional 4 h. Prior to heating, a new diamagnetic complex is present which disappears upon heating to form **26** and $(i\text{-PrNDI})\text{Ni}_2(\text{C}_6\text{H}_6)$ (**6**). Time points were taken after 1 h of heating and ^1H NMR yields are based off of integration against mesitylene.

Time	Yield of 26	Complex 38	$(i\text{-PrNDI})\text{Ni}_2(\text{C}_6\text{D}_6)$ (6)
1 h	30%	22%	36%
3 h	58%	3%	61%
4 h	59%	<1%	65%

Figure A1.12. ^1H NMR of the reduction of **38** with KC_8 after heating at 50 °C for 1h. (room

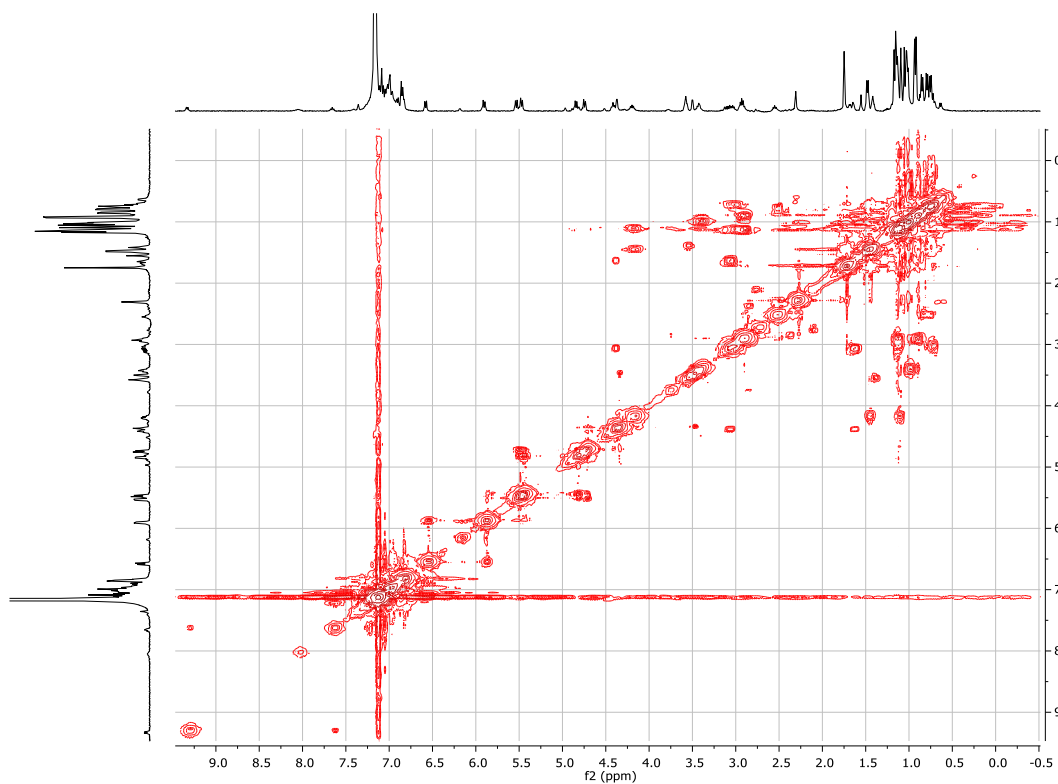
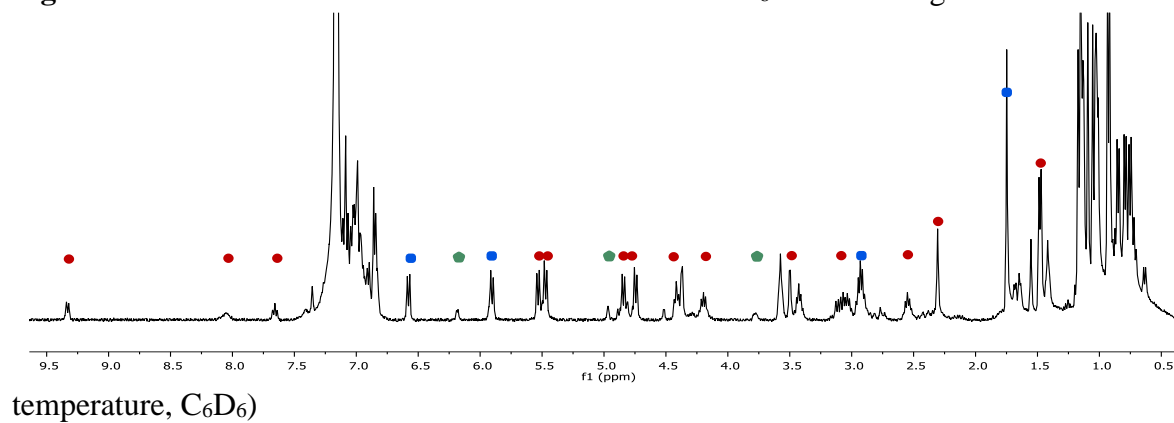
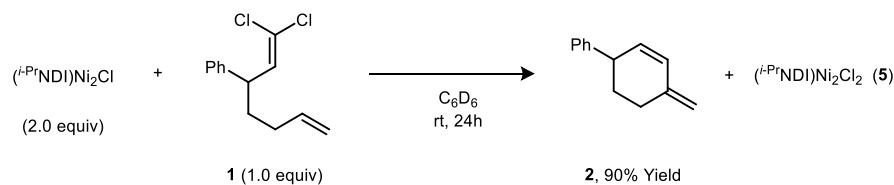


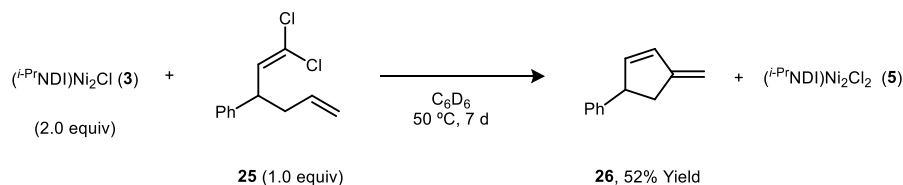
Figure A1.13. COSY NMR of the reduction of **38** with KC_8 after 1h. (room temperature, C_6D_6)

Stoichiometric Reactions with **1** and (*i*-PrNDI) Ni_2Cl (**3**)



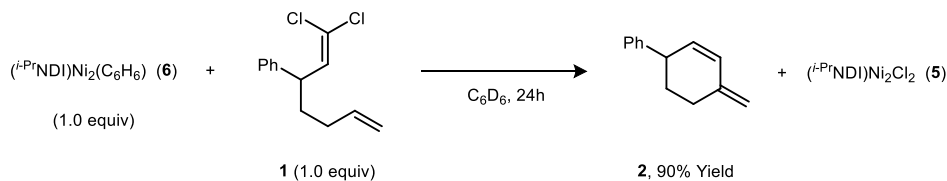
A J-Young NMR tube was charged with $(i\text{-PrNDI})\text{Ni}_2\text{Cl}$ (**3**) (4.1 mg, 0.0057 mmol, 2.0 equiv) and C_6D_6 (0.6 mL). A 0.17 M stock solution of mesitylene (1.0 equiv) and (1,1-dichlorohepta-1,6-dien-3-yl)benzene (18 μL , 0.0030 mmol, 1.0 equiv) in C_6D_6 was added to the J-Young tube. The reaction was monitored over 24 h at room temperature. $(i\text{-PrNDI})\text{Ni}_2\text{Cl}_2$ (**5**) was filtered off, and the yield of 4-methylene-1,2,3,4-tetrahydro-1,1'-biphenyl (**26**) (90% yield) was determined by ^1H NMR integration against mesitylene.

Stoichiometric Reactions with **25** and $(i\text{-PrNDI})\text{Ni}_2\text{Cl}$ (**3**)



A J-Young NMR tube was charged with $(i\text{-PrNDI})\text{Ni}_2\text{Cl}$ (**3**) (4.1 mg, 0.0057 mmol, 2.0 equiv) and C_6D_6 (0.6 mL). A 0.22 M stock solution of mesitylene (1.0 equiv) and (1,1-dichlorohexa-1,5-dien-3-yl)benzene (**25**) (14 μL , 0.0030 mmol, 1.0 equiv) in C_6D_6 was added to the J-Young tube. The reaction was heated at 50 $^\circ\text{C}$ and monitored over 7 d. $(i\text{-PrNDI})\text{Ni}_2\text{Cl}_2$ (**5**) was filtered off, and the yield of 4-methylene-1,2,3,4-tetrahydro-1,1'-biphenyl (**26**) (52% yield) was determined by ^1H NMR integration against mesitylene.

Stoichiometric Reactions with **1** and $(i\text{-PrNDI})\text{Ni}_2(\text{C}_6\text{H}_6)$ (**6**)



A J-Young NMR tube was charged with (*i*-PrNDI)Ni₂(C₆H₆) (**6**) (5.0 mg, 0.007 mmol, 1.0 equiv) and C₆D₆ (0.6 mL). A 0.17 M stock solution of trimethoxybenzene (1.0 equiv) and (1,1-dichlorohepta-1,6-dien-3-yl)benzene (**1**) (40 μL, 0.007 mmol, 1.0 equiv) in C₆D₆ was added to the J-Young tube. The reaction was monitored over 24 h at room temperature. (*i*-PrNDI)Ni₂Cl₂ (**5**) was filtered off, and the yield of 4-methylene-1,2,3,4-tetrahydro-1,1'-biphenyl (**2**) (90% yield) was determined by ¹H NMR integration against trimethoxybenzene.

9. NMR Spectral Data

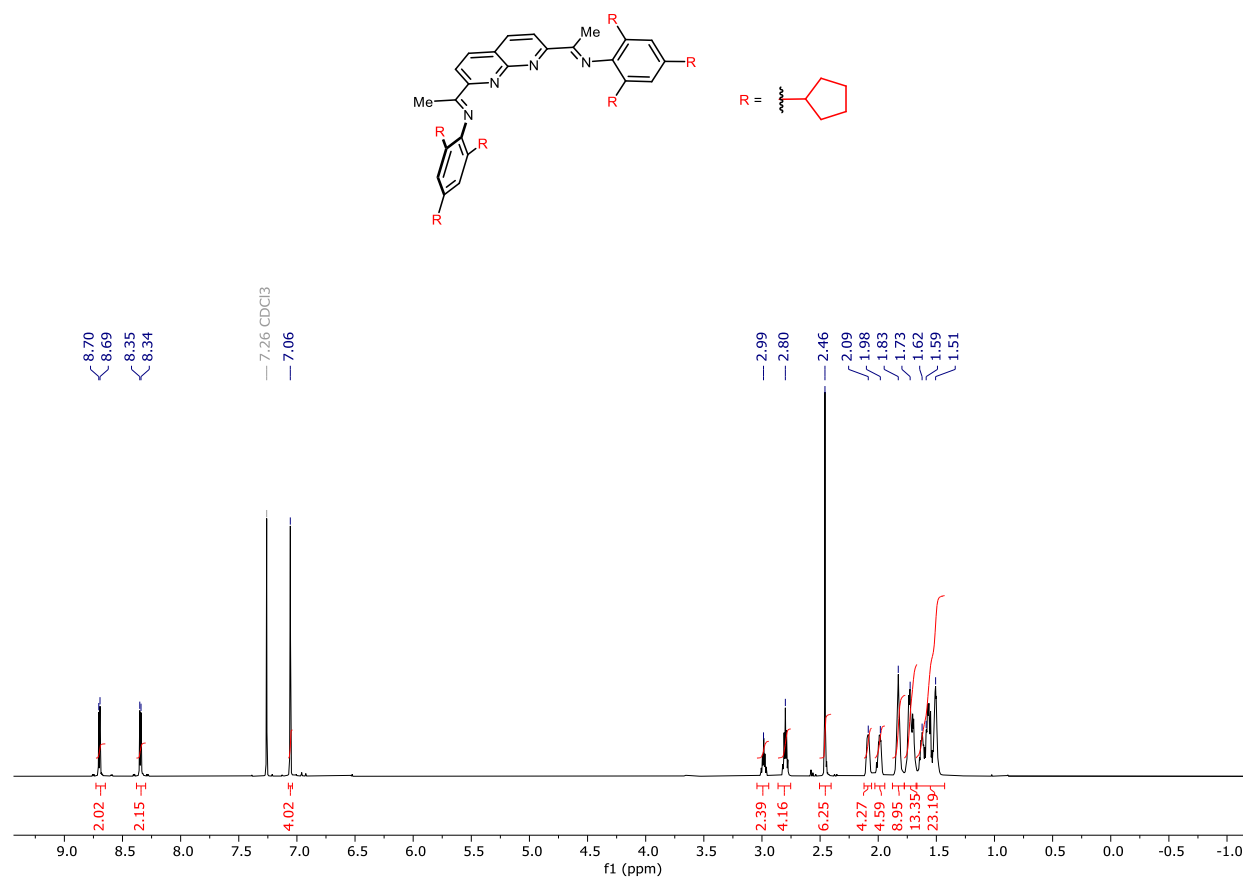


Figure A1.14. 800 MHz ¹H NMR of *c*-PentNDI (7) in CDCl₃ at room temperature.

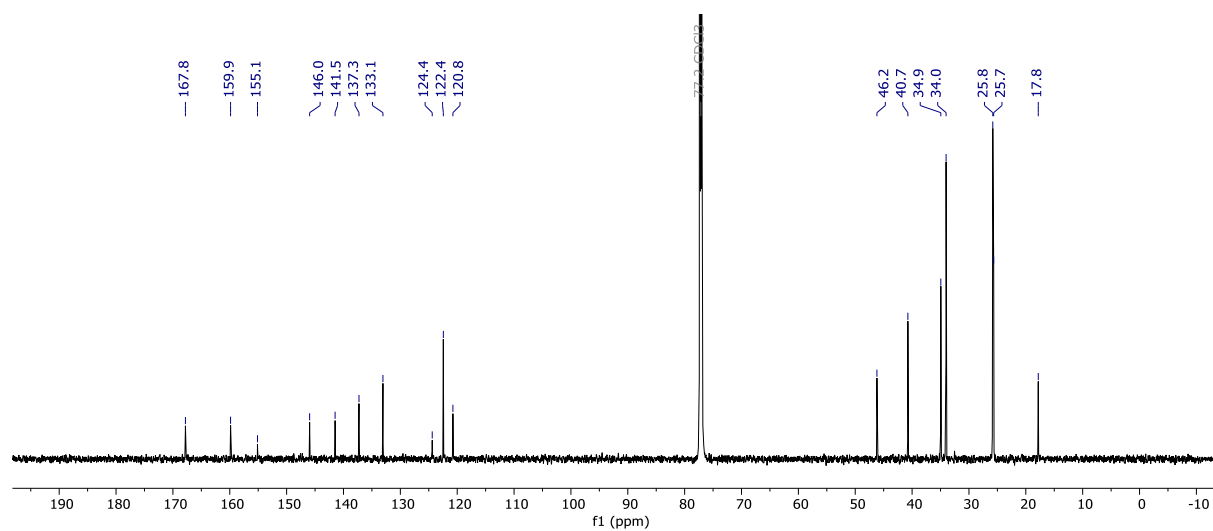


Figure A1.15. 201 MHz ¹³C{¹H} NMR of *c*-PentNDI (7) in CDCl₃ at room temperature.

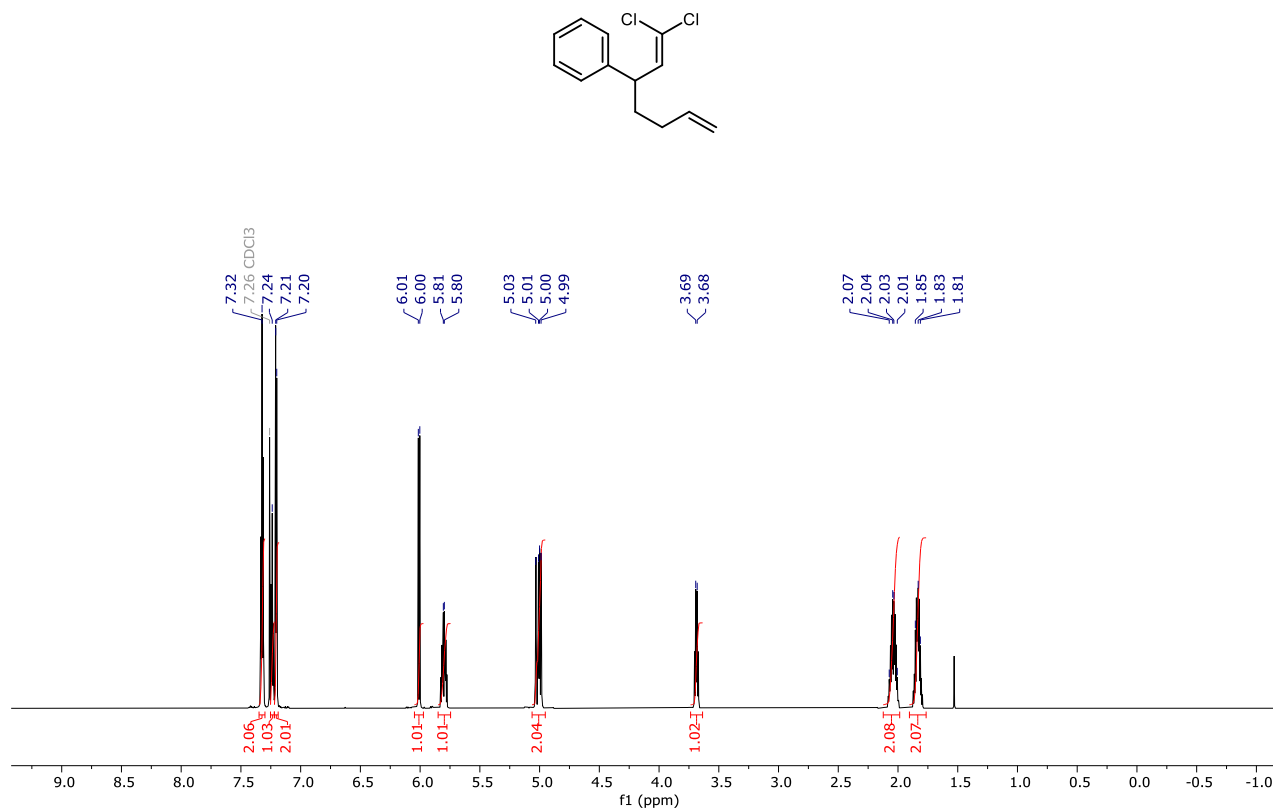


Figure A1.16. 800 MHz ¹H NMR of (1,1-dichlorohepta-1,6-dien-3-yl)benzene (**1**) in CDCl₃ at room temperature.

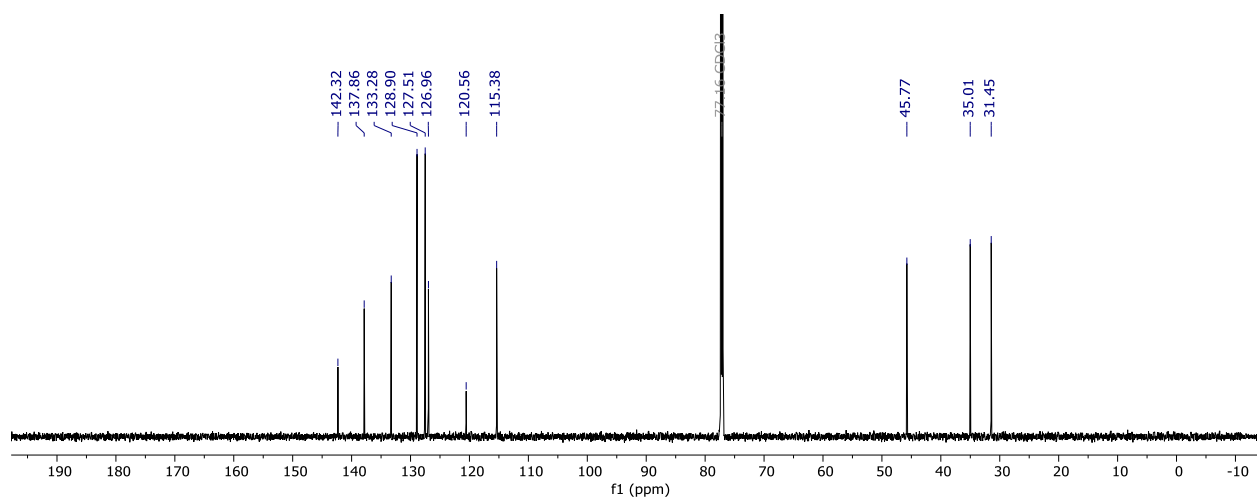


Figure A1.17. 201 MHz ¹³C{¹H} NMR of (1,1-dichlorohepta-1,6-dien-3-yl)benzene (**1**) in CDCl₃ at room temperature.

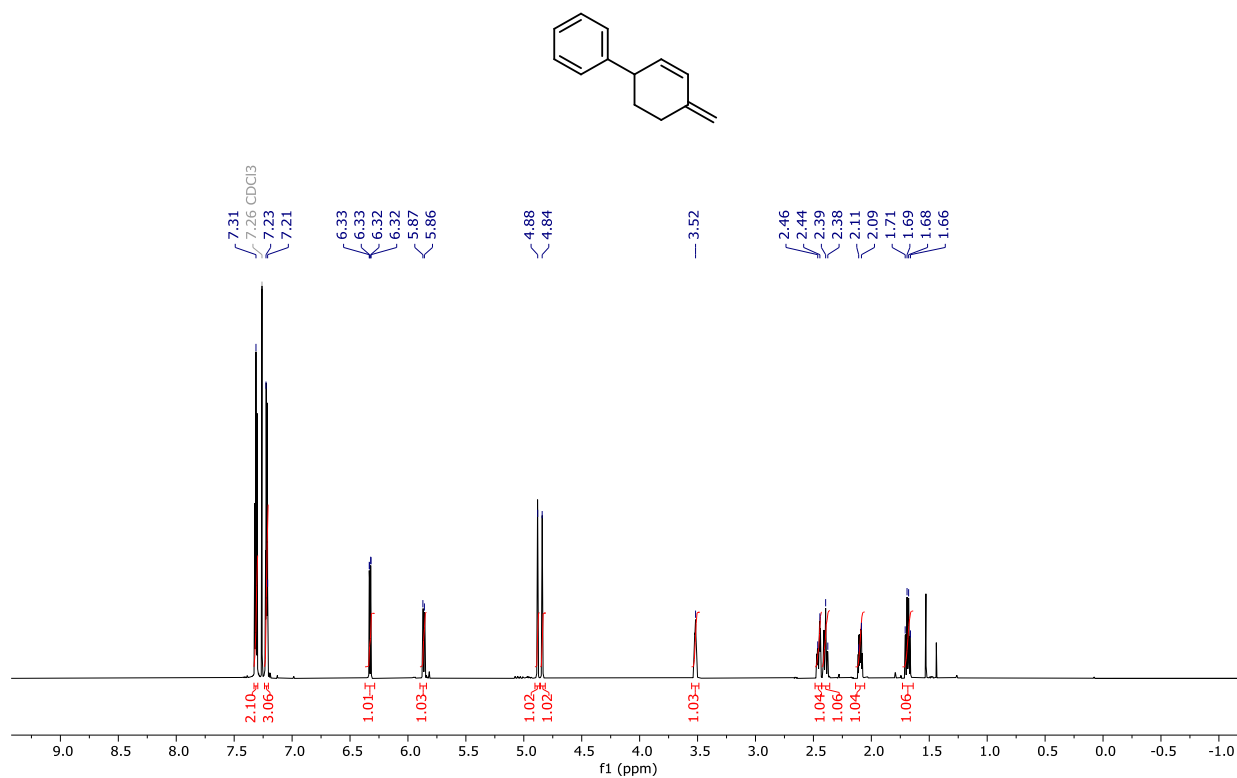


Figure A1.18. 800 MHz ¹H NMR of 4-methylene-1,2,3,4-tetrahydro-1,1'-biphenyl (**2**) in CDCl₃ at room temperature.

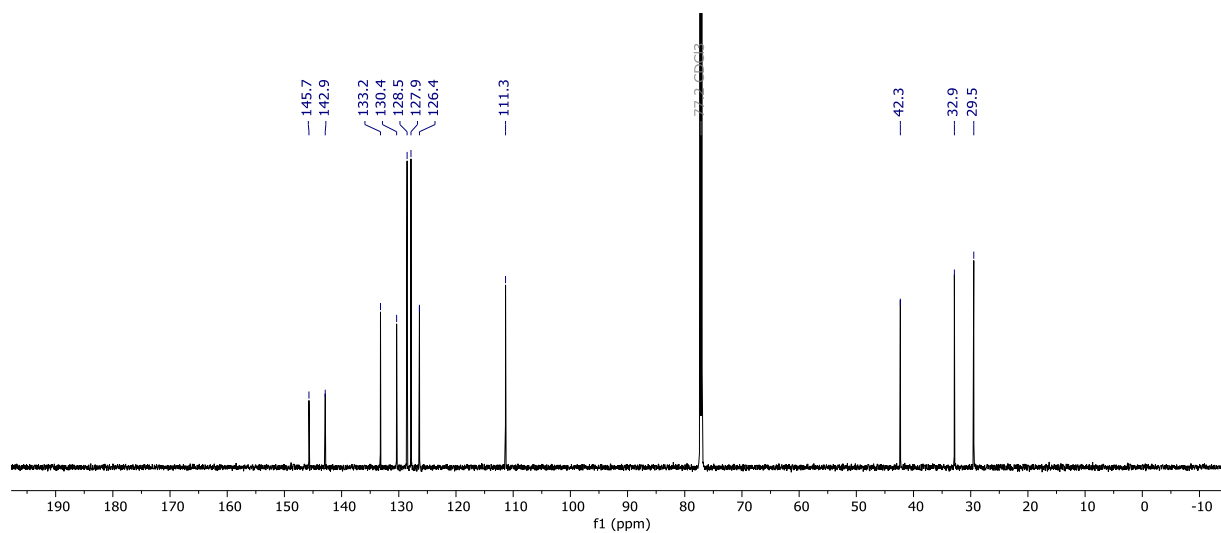


Figure A1.19. 201 MHz ¹³C{¹H} NMR of 4-methylene-1,2,3,4-tetrahydro-1,1'-biphenyl (**2**) in CDCl₃ at room temperature.

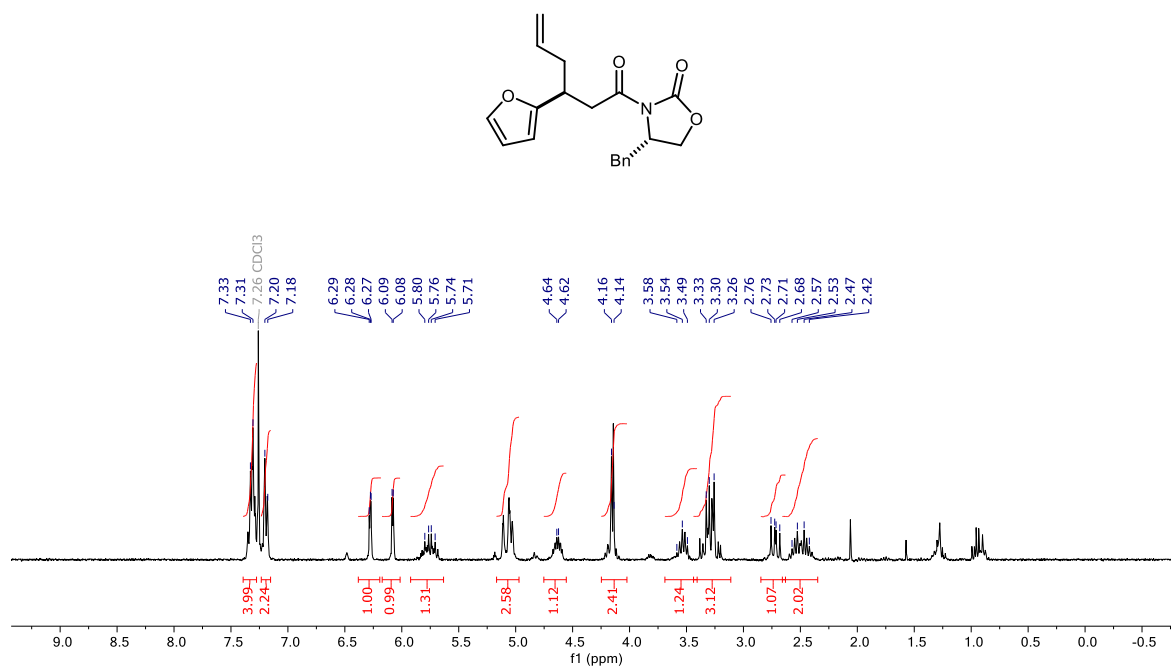


Figure A1.20. 300 MHz ¹H NMR of (S)-4-benzyl-3-((S)-3-(furan-2-yl)hex-5-enoyl)oxazolidin-2-one (13) in CDCl₃ at room temperature.

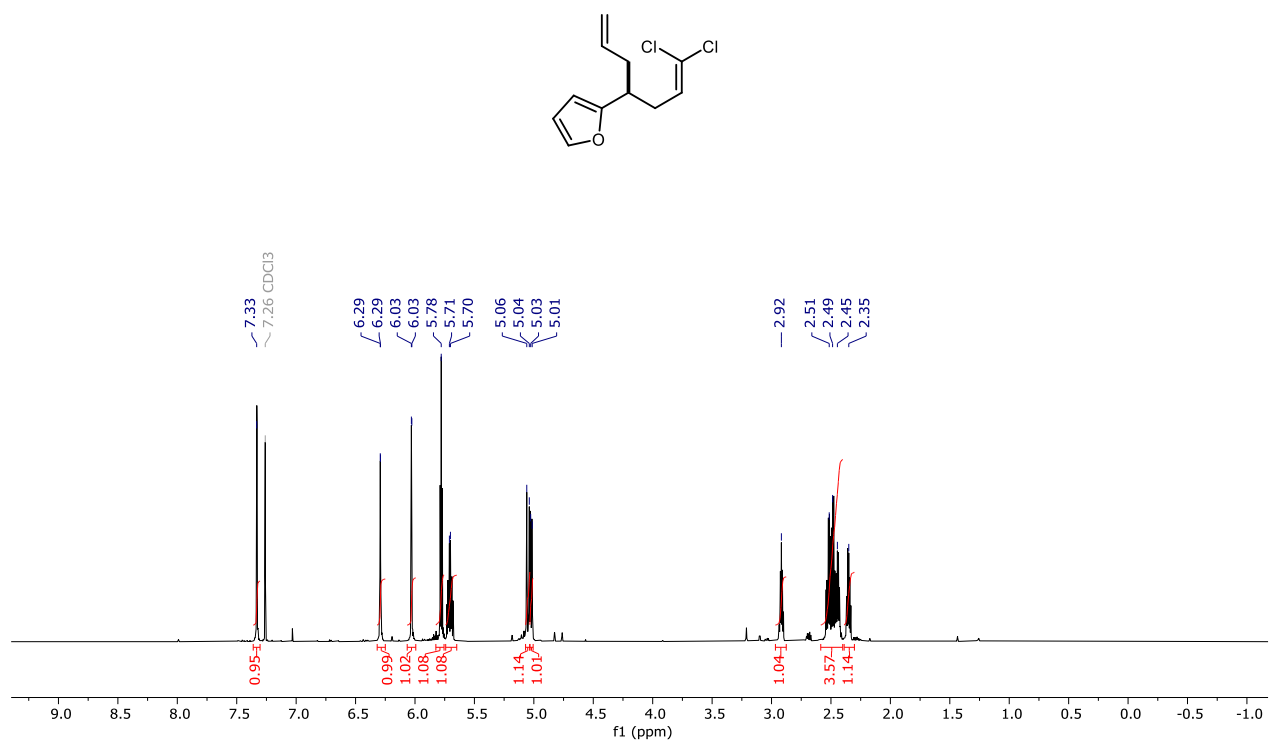


Figure A1.21. 800 MHz ¹H NMR of (*S*)-2-(1,1-dichlorohepta-1,6-dien-4-yl)furan (**15**) in CDCl₃ at room temperature.

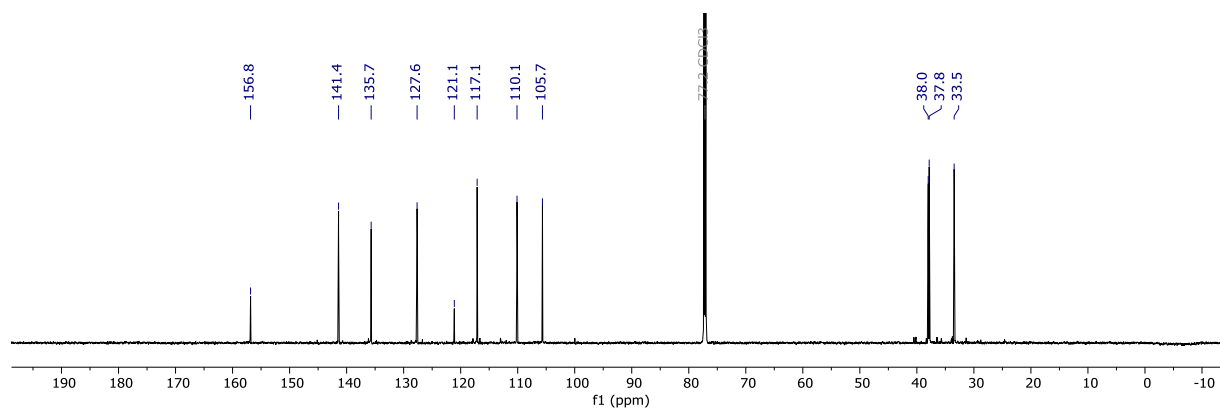


Figure A1.22. 201 MHz ¹³C{¹H} NMR of (*S*)-2-(1,1-dichlorohepta-1,6-dien-4-yl)furan (**15**) in CDCl₃ at room temperature.

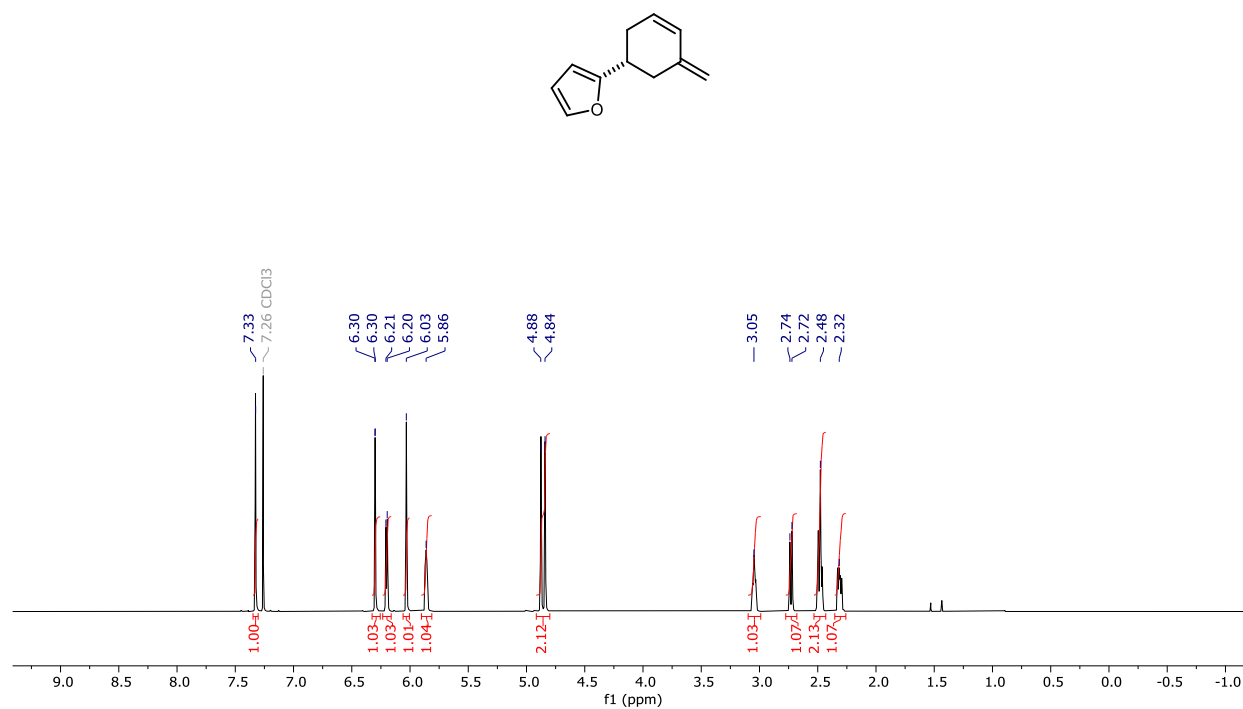


Figure A1.23. 800 MHz ¹H NMR of (*R*)-2-(5-methylenecyclohex-3-en-1-yl)furan (**16**) in CDCl₃ at room temperature.

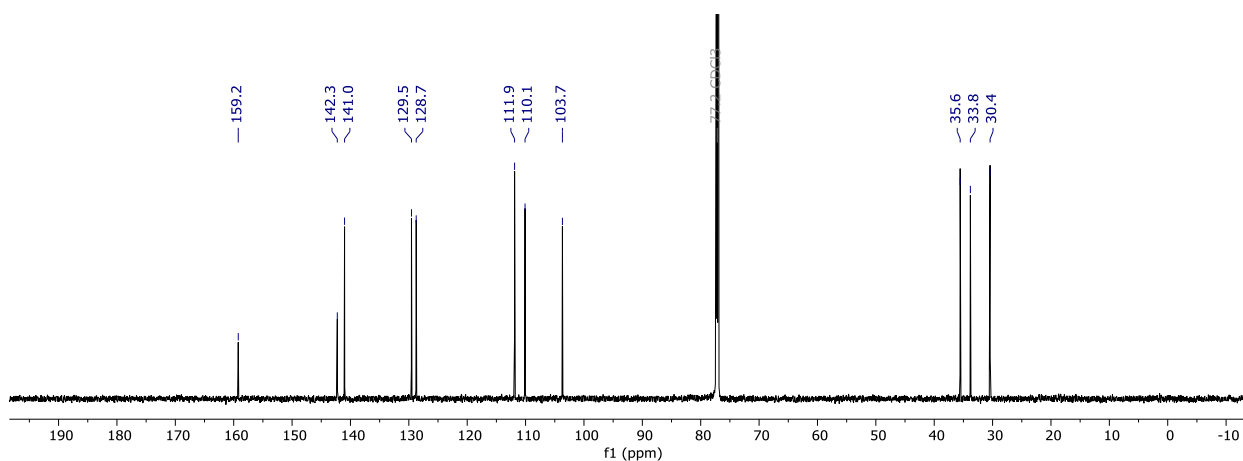


Figure A1.24. 201 MHz ¹³C{¹H} NMR of (*R*)-2-(5-methylenecyclohex-3-en-1-yl)furan (**16**) in CDCl₃ at room temperature.

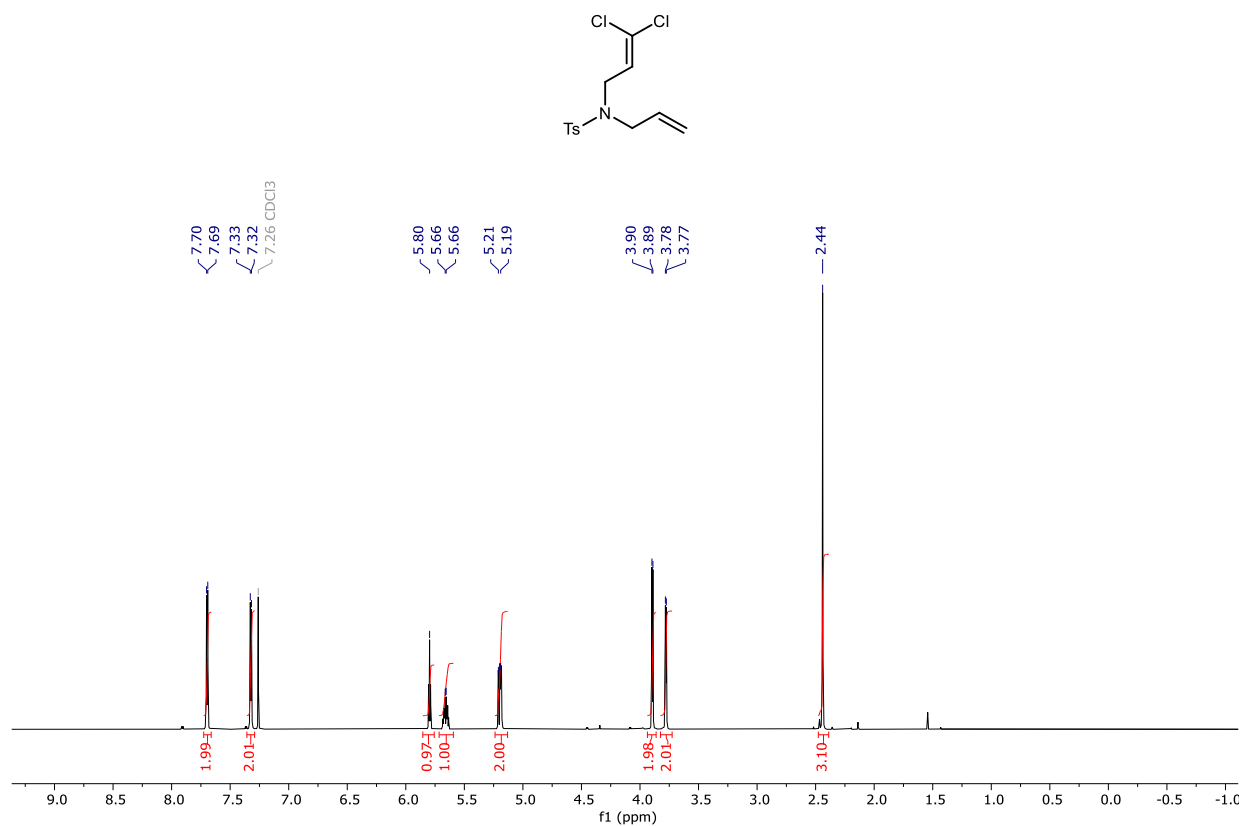


Figure A1.25. 800 MHz ¹H NMR of *N*-allyl-*N*-(3,3-dichloroallyl)-4-methylbenzenesulfonamide (**17**) in CDCl₃ at room temperature.

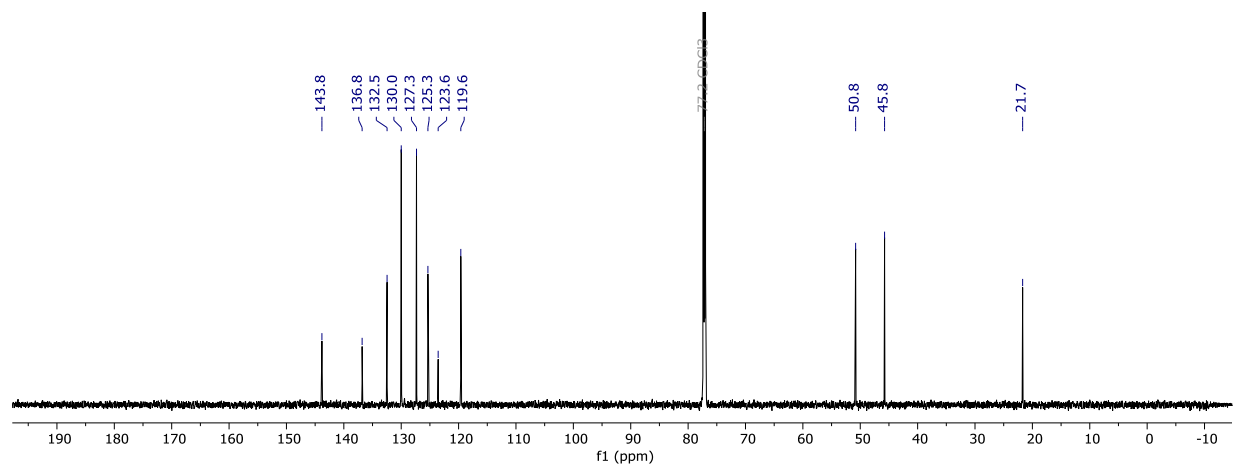


Figure A1.26. 201 MHz ¹³C{¹H} NMR of *N*-allyl-*N*-(3,3-dichloroallyl)-4-methylbenzenesulfonamide (**17**) in CDCl₃ at room temperature

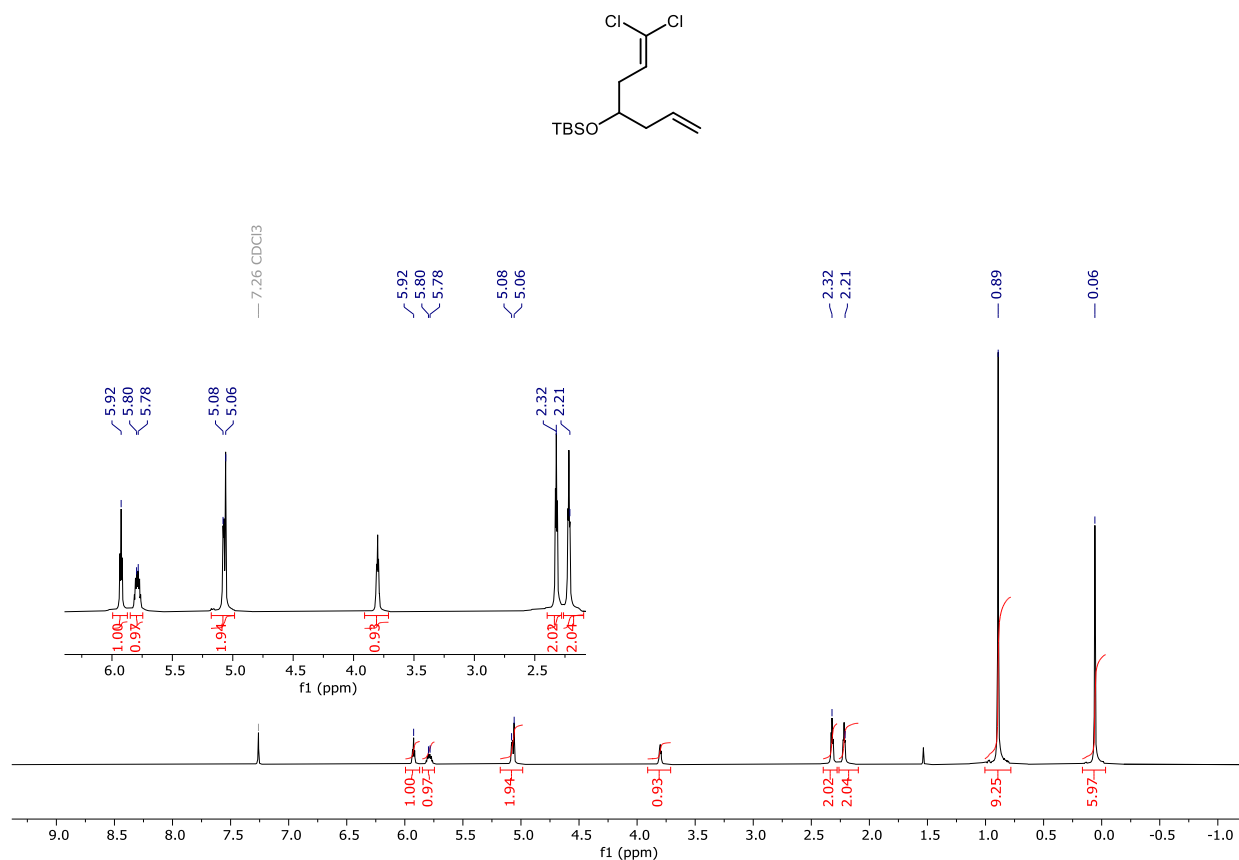


Figure A1.27. 800 MHz ¹H NMR of *tert*-butyl((1,1-dichlorohepta-1,6-dien-4-yl)oxy)dimethylsilane (**19**) in CDCl₃ at room temperature.

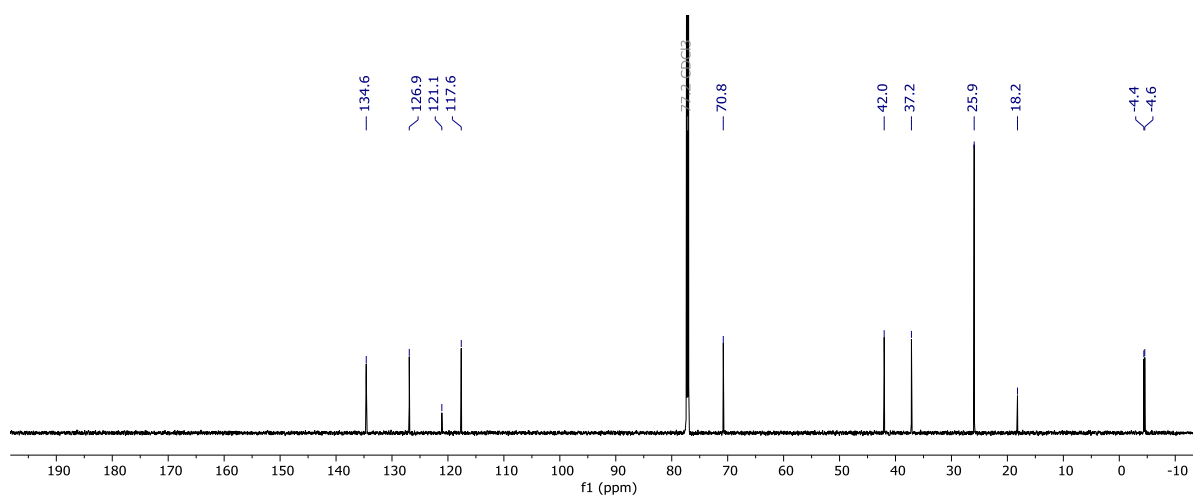


Figure A1.28. 201 MHz ¹³C{¹H} NMR of *tert*-butyl((1,1-dichlorohepta-1,6-dien-4-yl)oxy)dimethylsilane (**19**) in CDCl₃ at room temperature.

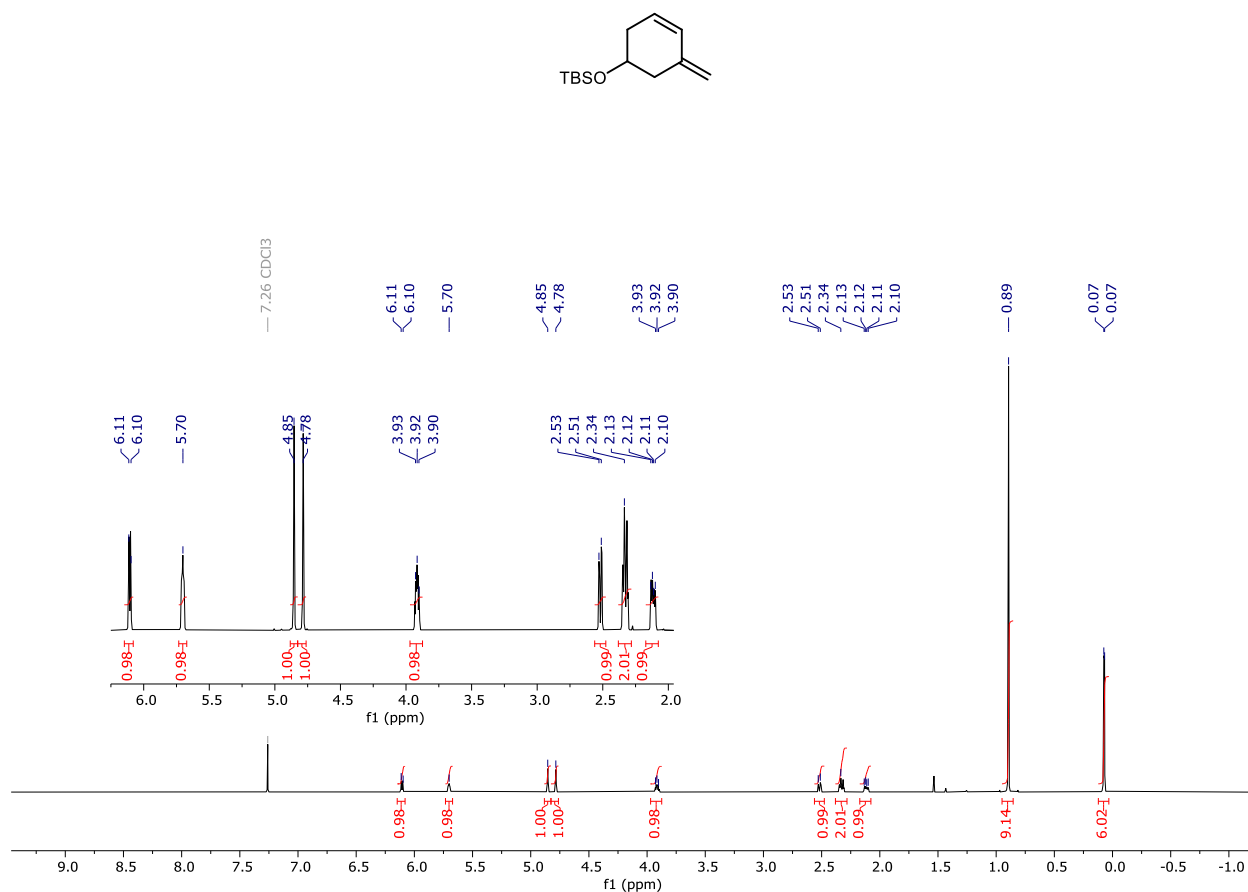


Figure A1.29. 800 MHz ¹H NMR of *tert*-butyldimethyl((5-methylenecyclohex-3-en-1-yl)oxy)silane (**20**) in CDCl₃ at room temperature.

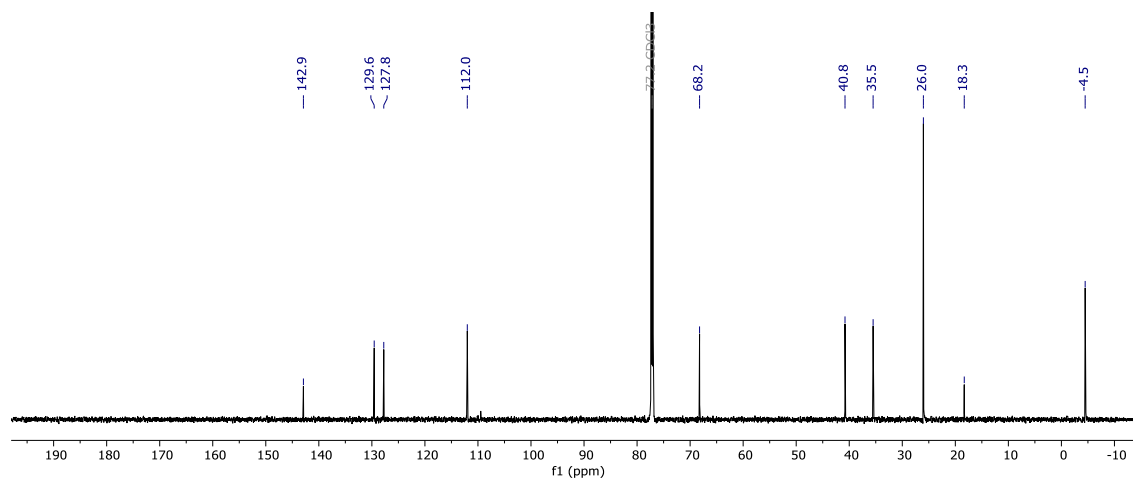


Figure A1.30. 201 MHz ¹³C{¹H} NMR of *tert*-butyldimethyl((5-methylenecyclohex-3-en-1-yl)oxy)silane (**20**) in CDCl₃ at room temperature.

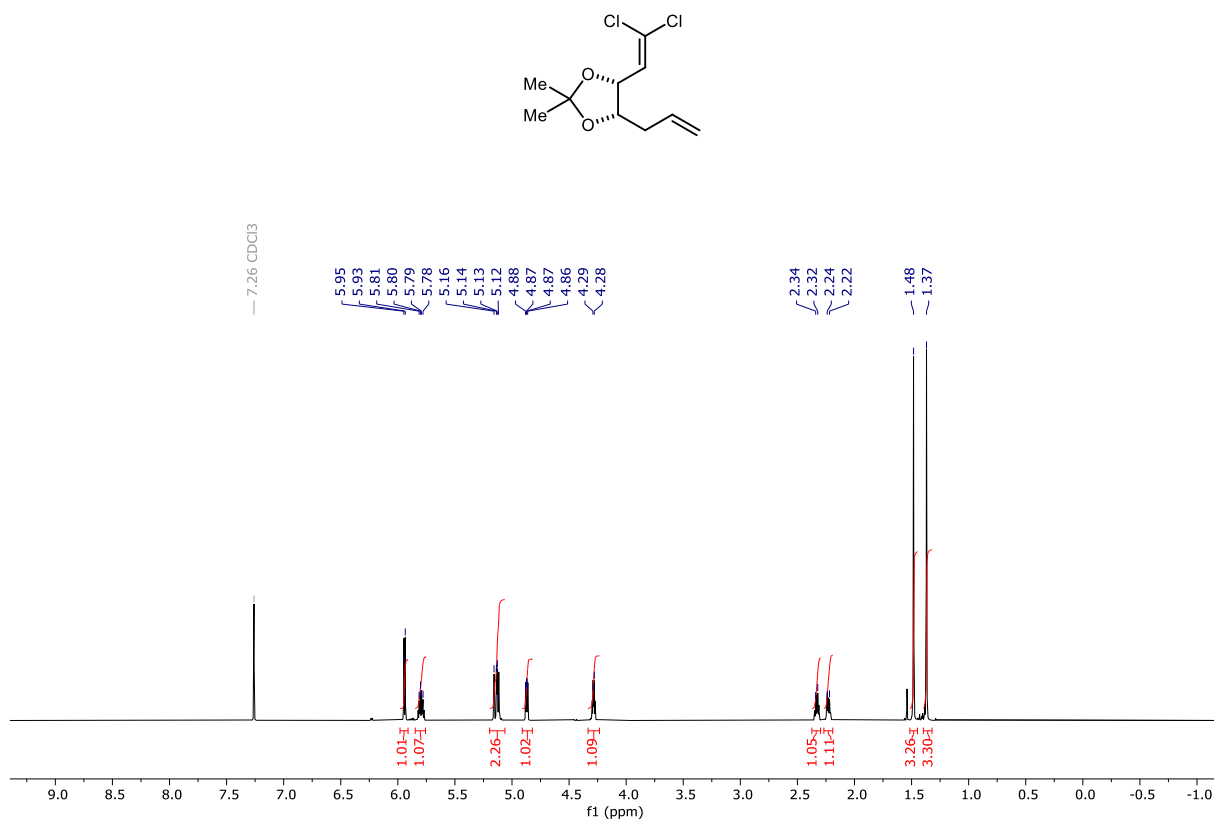


Figure A1.31. 800 MHz ¹H NMR of (4*S*,5*R*)-4-allyl-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane (**21**) in CDCl₃ at room temperature.

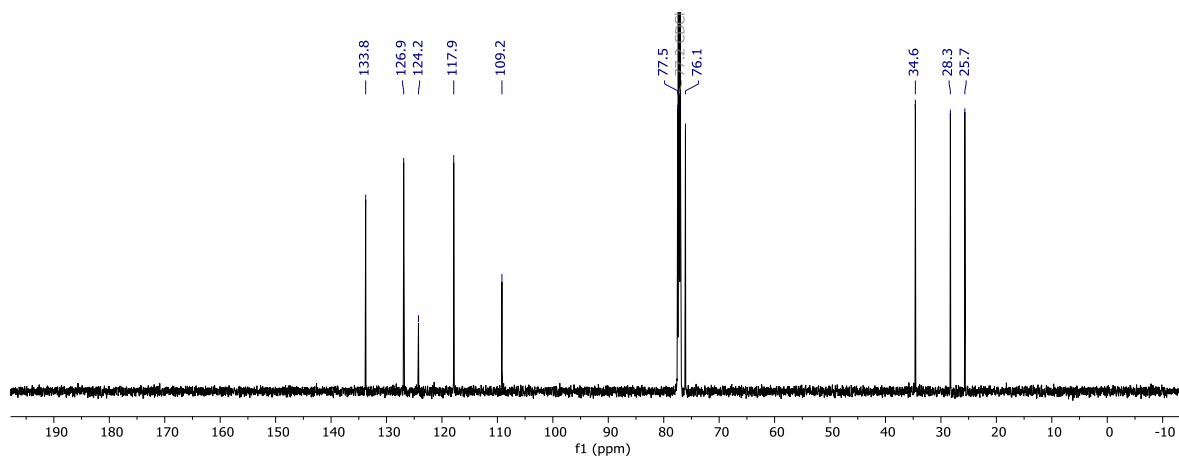


Figure A1.32. 201 MHz ¹³C{¹H} NMR of (4*S*,5*R*)-4-allyl-5-(2,2-dichlorovinyl)-2,2-dimethyl-1,3-dioxolane (**21**) in CDCl₃ at room temperature.

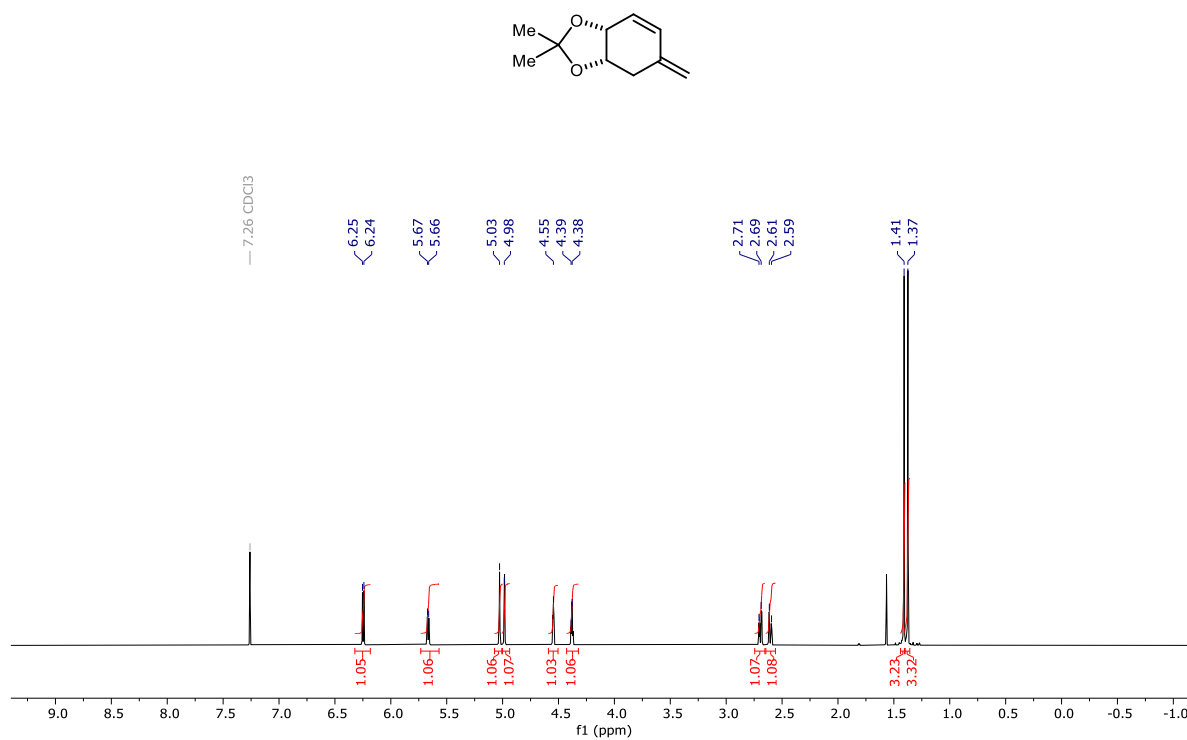


Figure A1.33. 800 MHz ¹H NMR of (3a*S*,7a*R*)-2,2-dimethyl-5-methylene-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole (**22**) in CDCl₃ at room temperature.

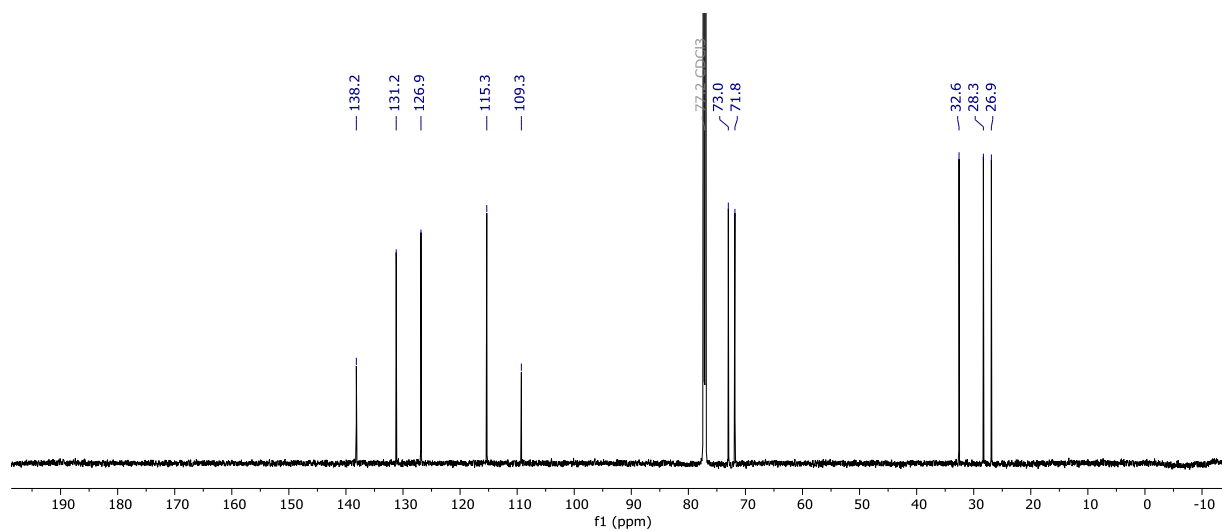


Figure A1.34. 201 MHz ¹³C{¹H} NMR of (3a*S*,7a*R*)-2,2-dimethyl-5-methylene-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole (**22**) in CDCl₃ at room temperature.

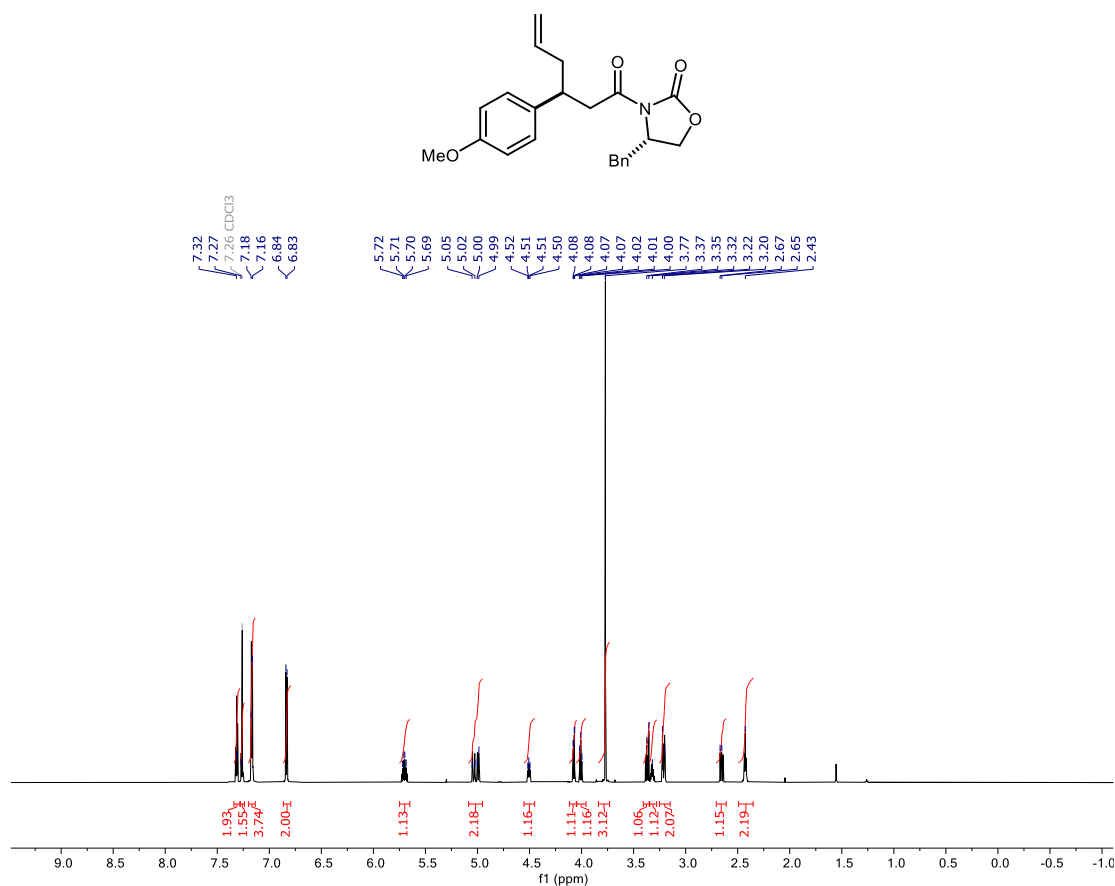


Figure A1.35. 800 MHz ¹H NMR of (S)-4-benzyl-3-((S)-3-(4-methoxyphenyl)hex-5-enoyl)oxazolidin-2-one in CDCl₃ at room temperature.

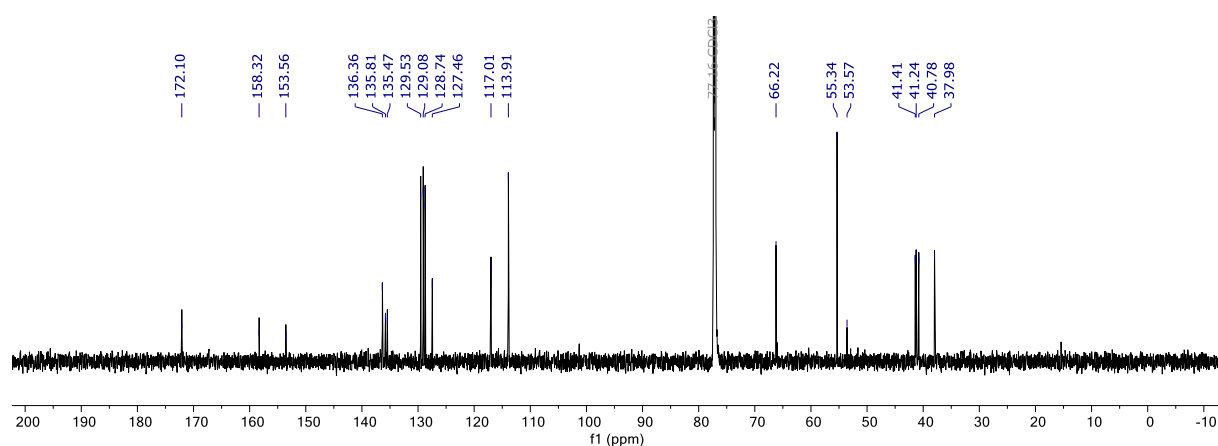


Figure A1.36. 201 MHz ¹³C{¹H} NMR of (S)-4-benzyl-3-((S)-3-(4-methoxyphenyl)hex-5-enoyl)oxazolidin-2-one in CDCl₃ at room temperature.

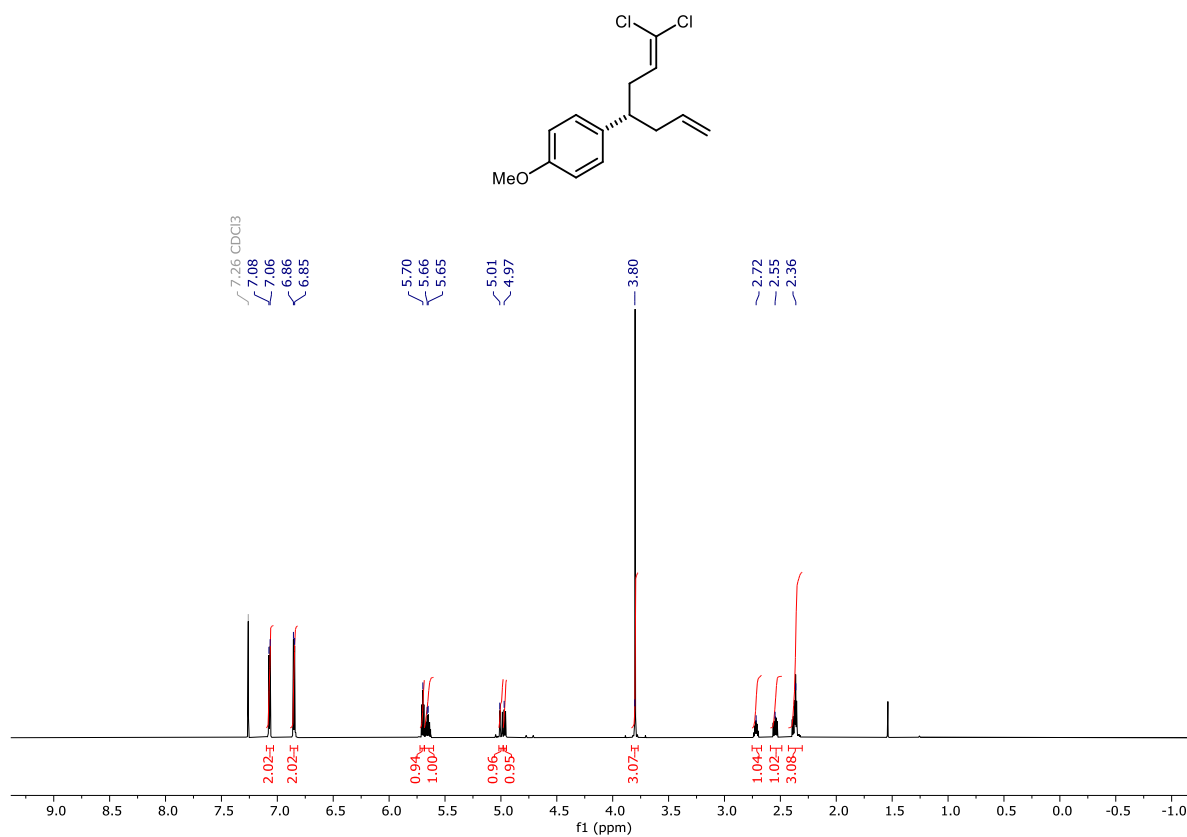


Figure A1.37. 800 MHz ¹H NMR of (S)-1-(1,1-dichlorohepta-1,6-dien-4-yl)-4-methoxybenzene (**23**) in CDCl₃ at room temperature.

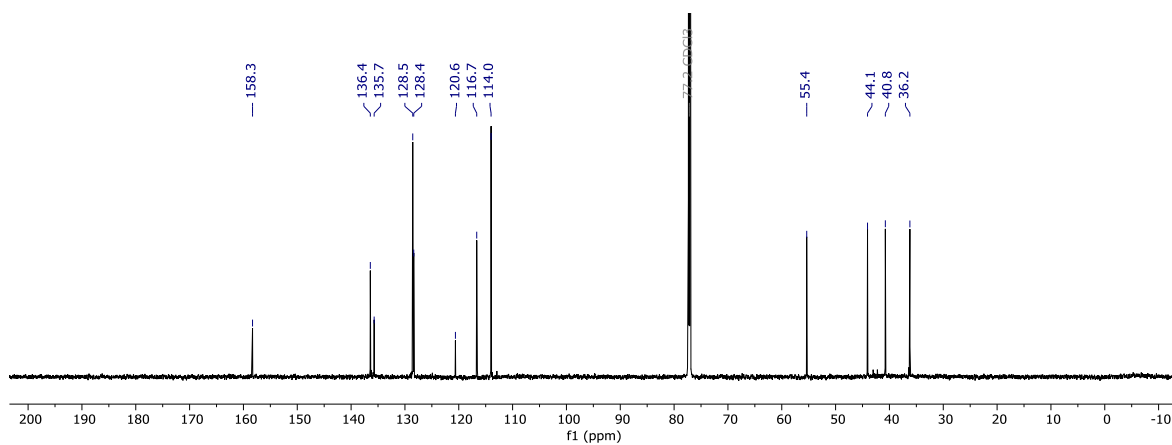


Figure A1.38. 201 MHz ¹³C{¹H} NMR of (S)-1-(1,1-dichlorohepta-1,6-dien-4-yl)-4-methoxybenzene (**23**) in CDCl₃ at room temperature.

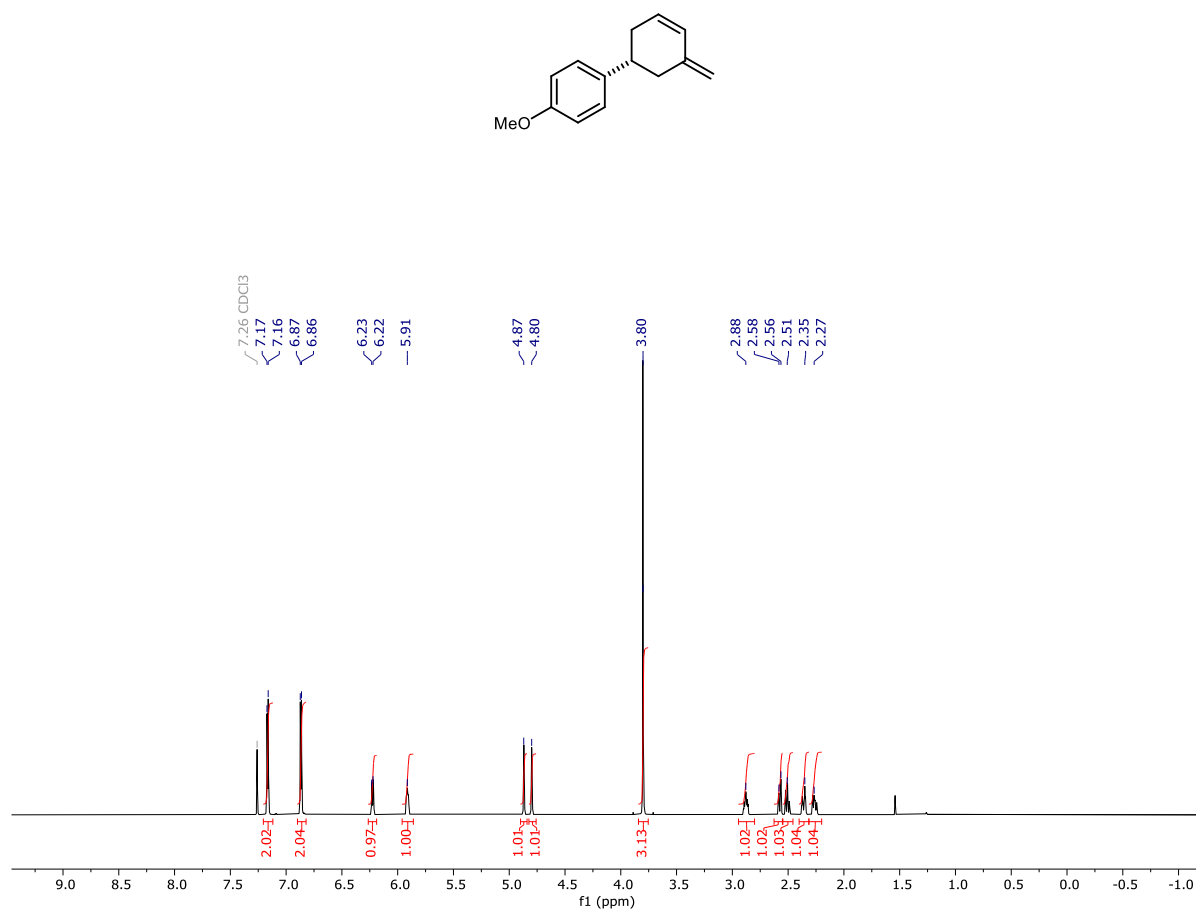


Figure A1.39. 800 MHz ¹H NMR of (*R*)-4'-methoxy-3-methylene-1,2,3,6-tetrahydro-1,1'-biphenyl (**24**) in CDCl₃ at room temperature.

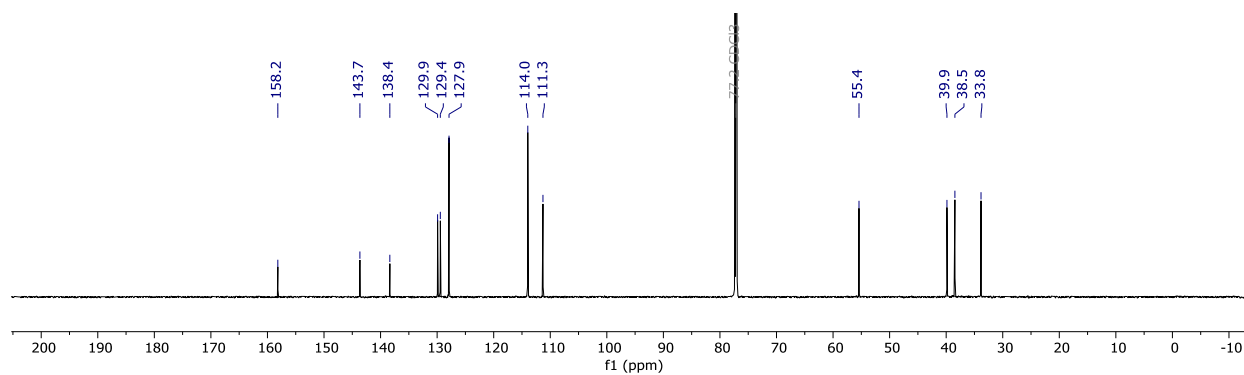


Figure A1.40. 201 MHz ¹³C{¹H} NMR of (*R*)-4'-methoxy-3-methylene-1,2,3,6-tetrahydro-1,1'-biphenyl (**24**) in CDCl₃ at room temperature.

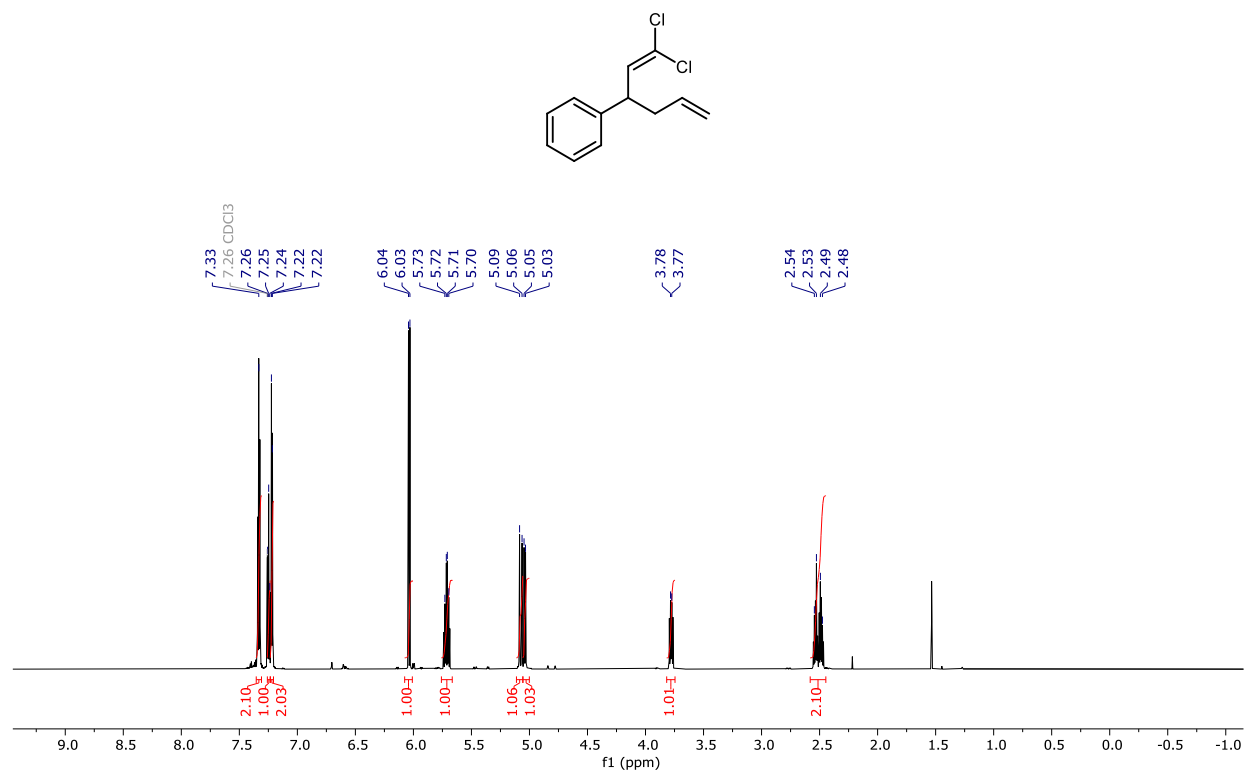


Figure A1.41. 800 MHz ¹H NMR of (1,1-dichlorohexa-1,5-dien-3-yl)benzene (**25**) in CDCl₃ at room temperature.

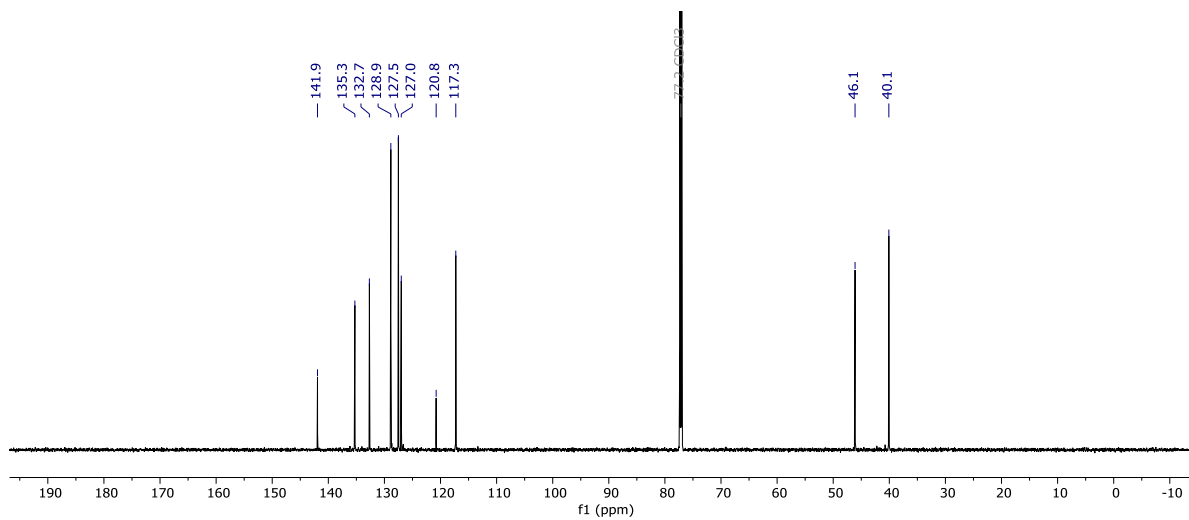


Figure A1.42. 201 MHz ¹³C{¹H} NMR of (1,1-dichlorohexa-1,5-dien-3-yl)benzene (**25**) in CDCl₃ at room temperature.

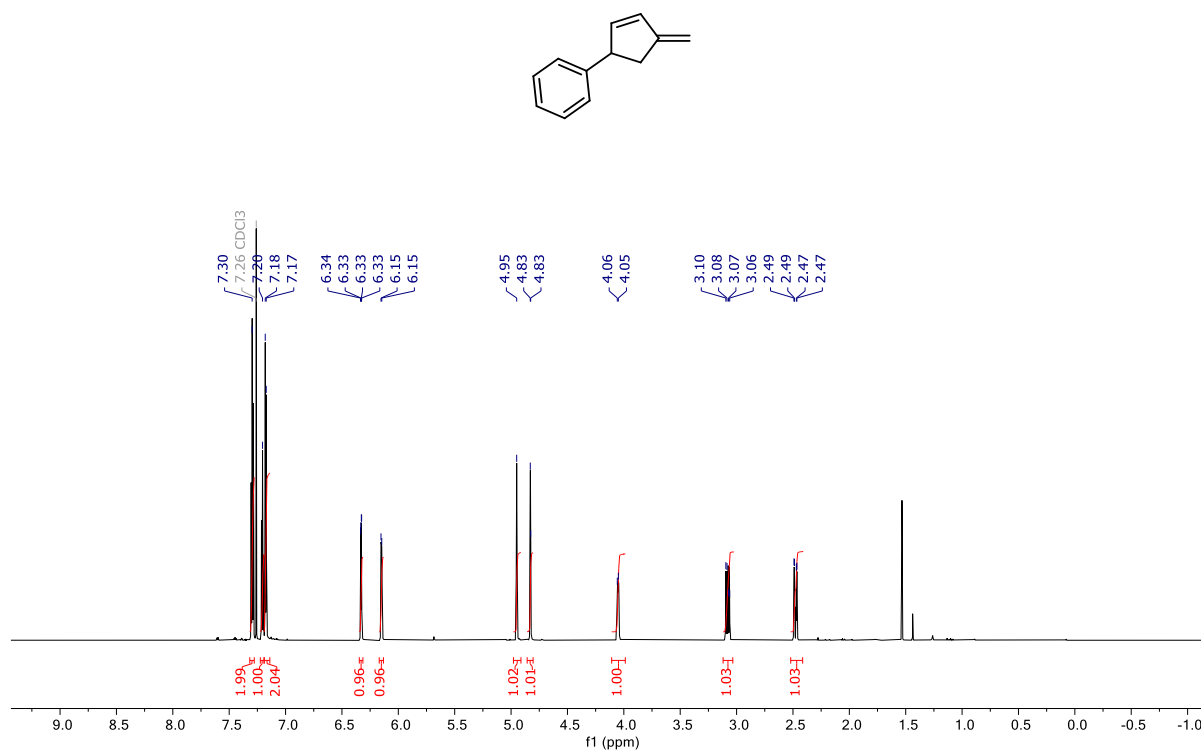


Figure A1.43. 800 MHz ¹H NMR of (4-methylenecyclopent-2-en-1-yl)benzene (**26**) in CDCl₃ at room temperature.

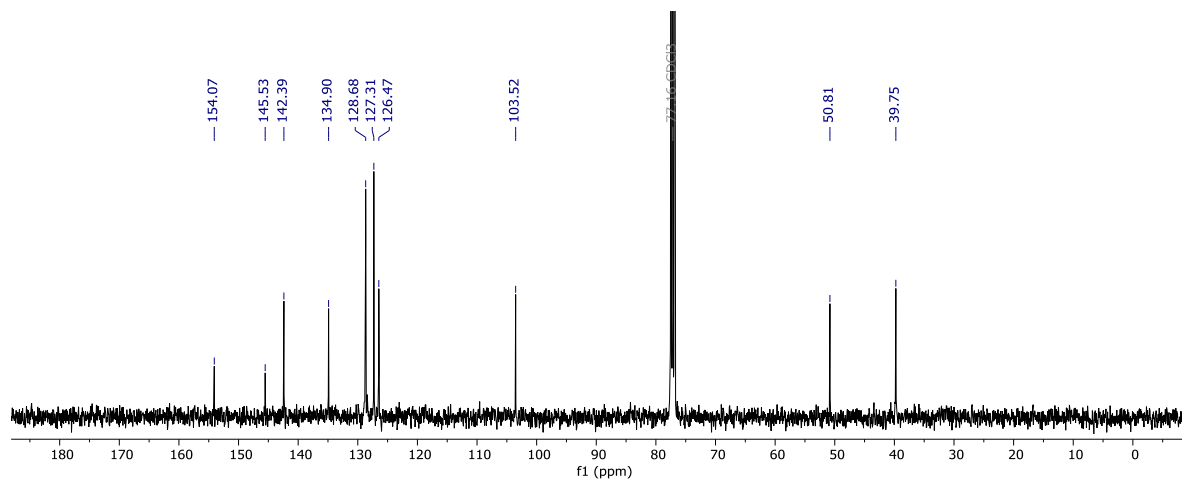


Figure A1.44. 101 MHz ¹³C{¹H} NMR of (4-methylenecyclopent-2-en-1-yl)benzene (**26**) in CDCl₃ at room temperature

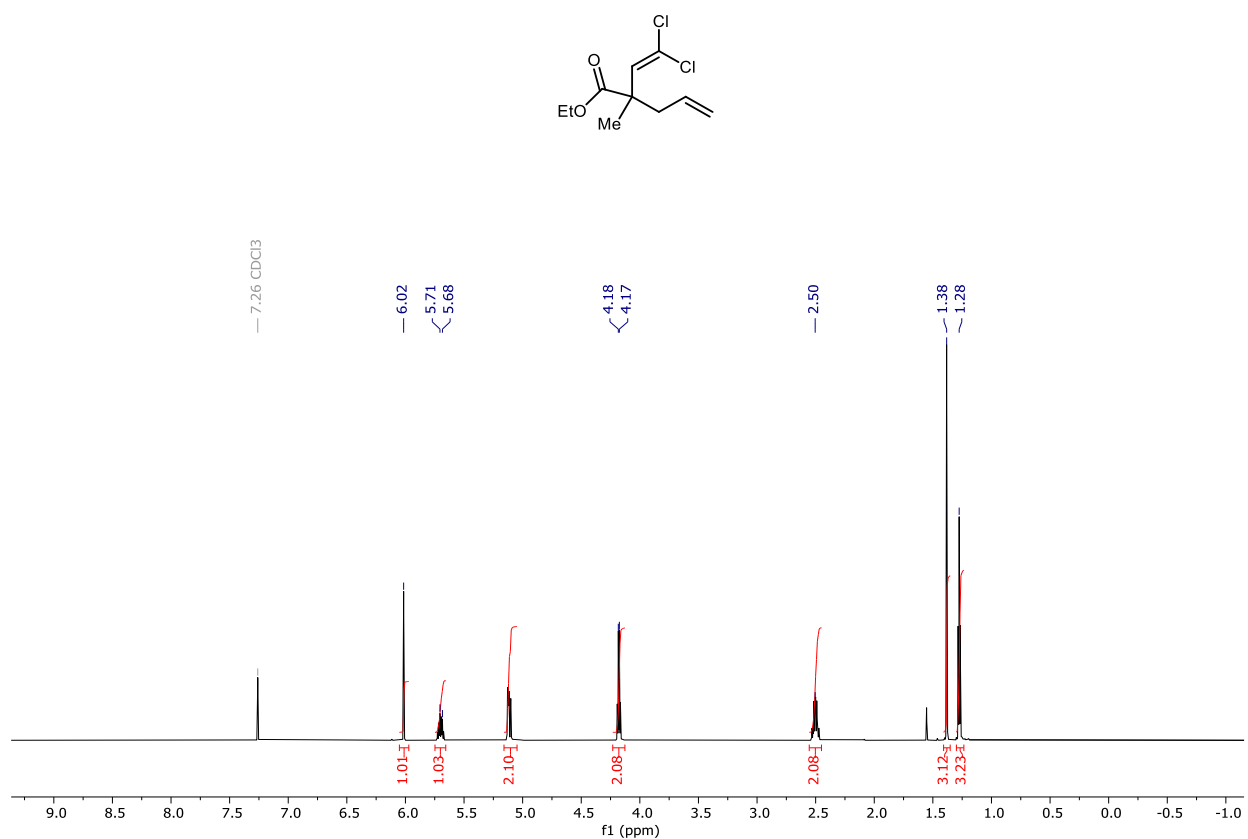


Figure A1.45. 800 MHz ¹H NMR of Ethyl 2-(2,2-dichlorovinyl)-2-methylpent-4-enoate (**27**) in CDCl₃ at room temperature.

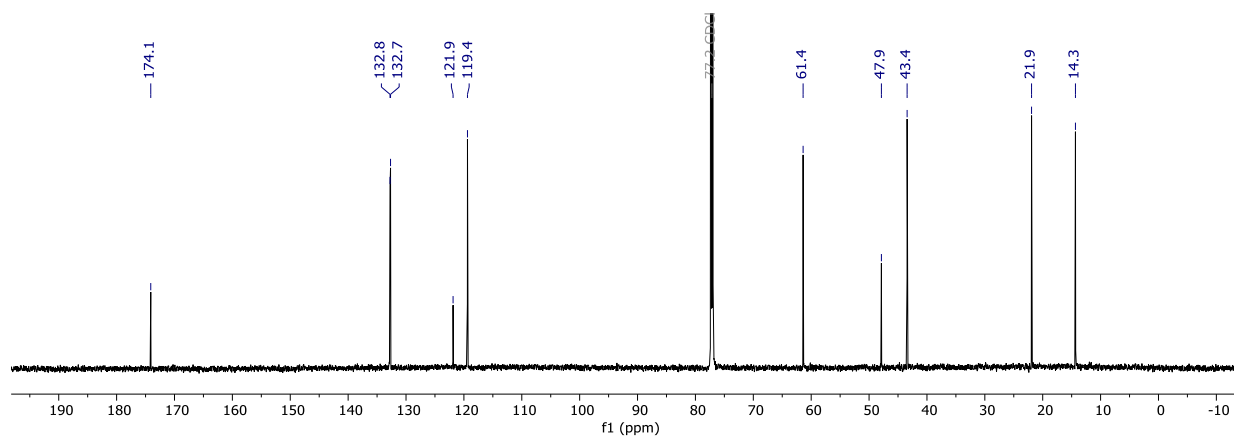


Figure A1.46. 201 MHz ¹³C{¹H} NMR of Ethyl 2-(2,2-dichlorovinyl)-2-methylpent-4-enoate (**27**) in CDCl₃ at room temperature.

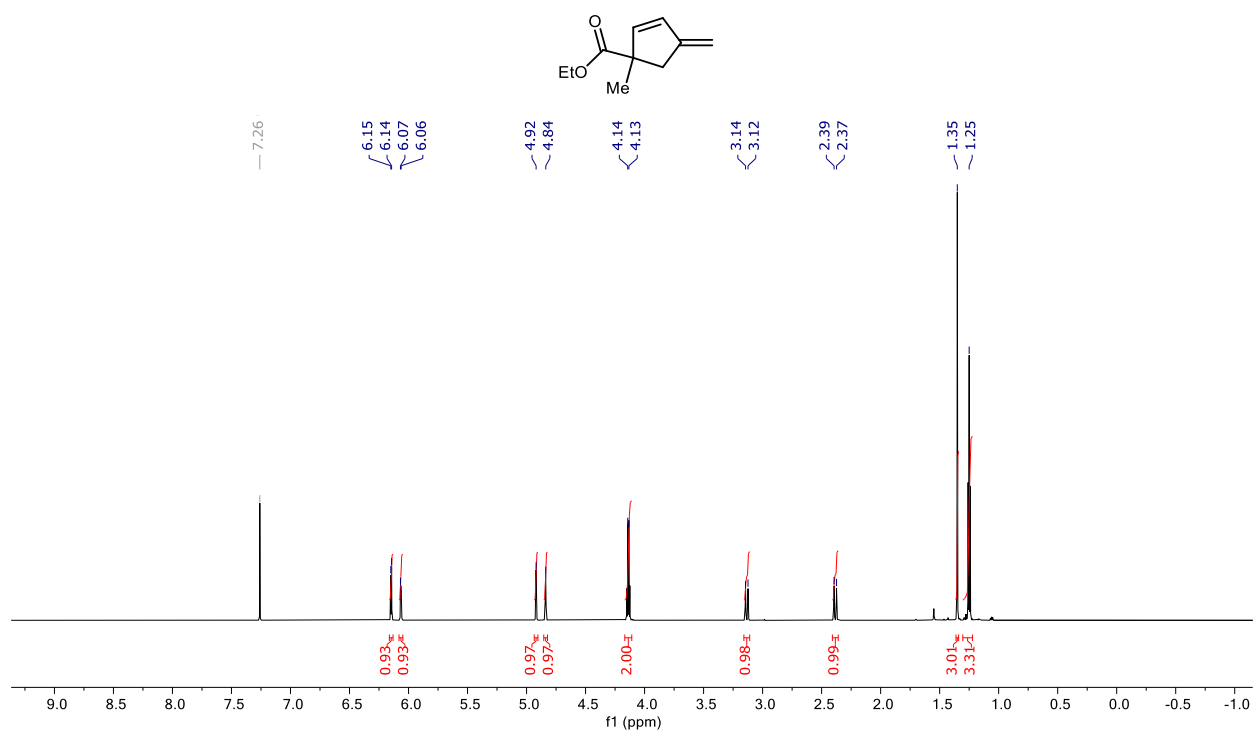


Figure A1.47. 800 MHz ¹H NMR of ethyl 1-methyl-4-methylenecyclopent-2-ene-1-carboxylate (**28**) in CDCl₃ at room temperature.

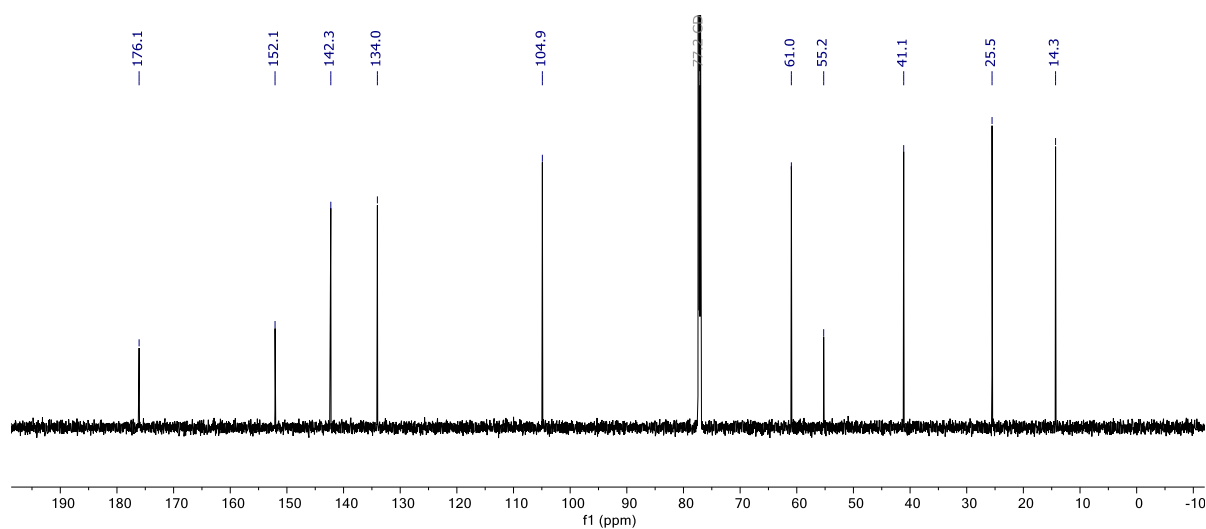


Figure A1.48. 201 MHz ¹³C{¹H} NMR of ethyl 1-methyl-4-methylenecyclopent-2-ene-1-carboxylate (**28**) in CDCl₃ at room temperature.

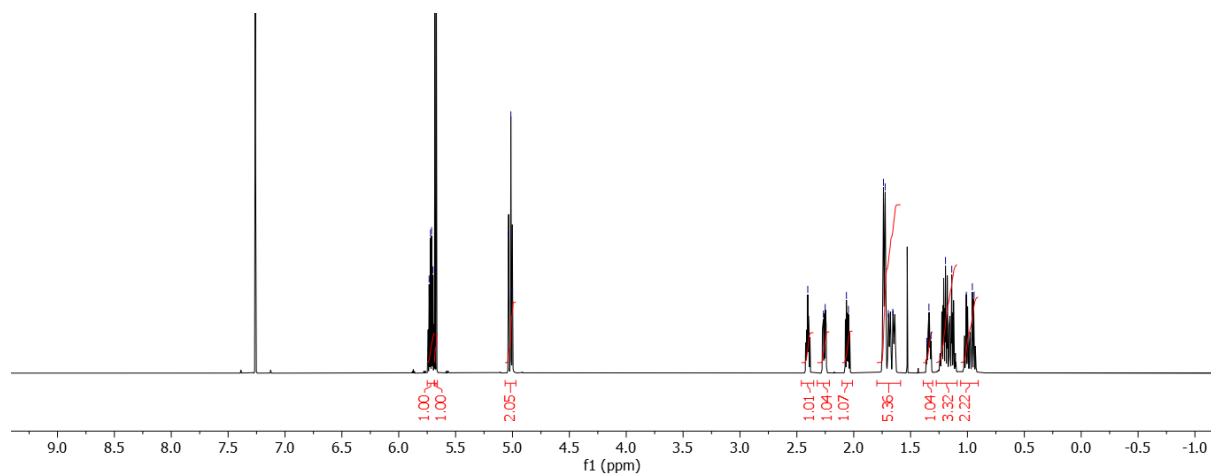
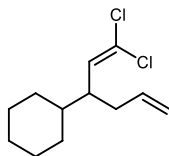


Figure A1.49. 800 MHz ^1H NMR of (1,1-dichlorohexa-1,5-dien-3-yl)cyclohexane (**29**) in CDCl_3 at room temperature.

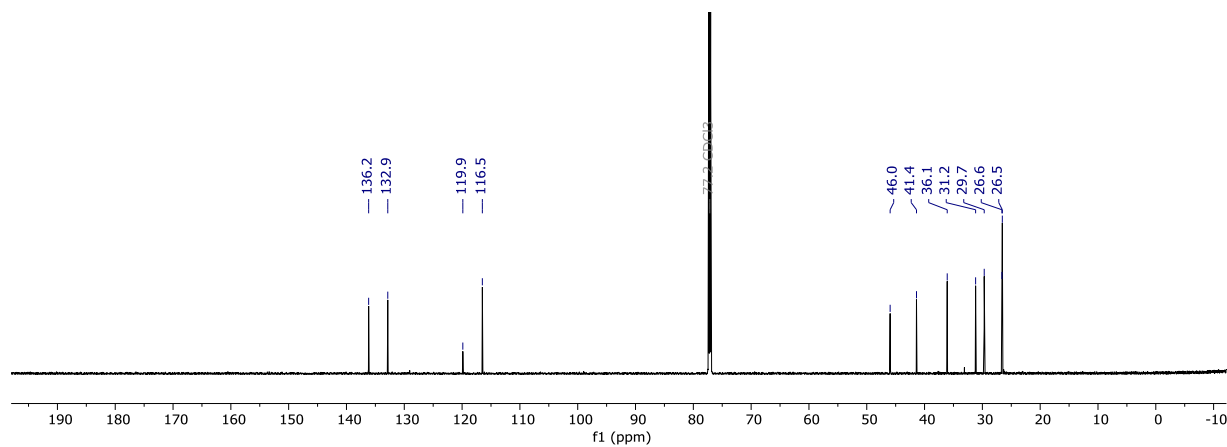


Figure A1.50. 201 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR of (1,1-dichlorohexa-1,5-dien-3-yl)cyclohexane (**29**) in CDCl_3 at room temperature.

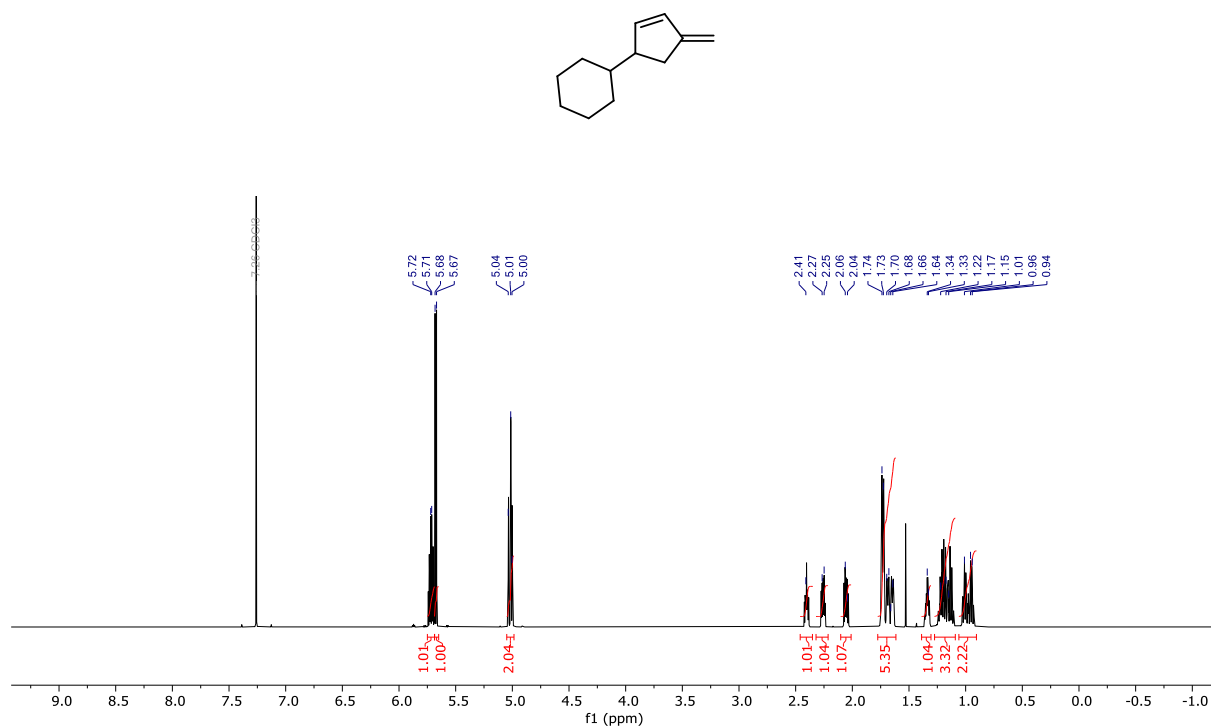


Figure A1.51. 800 MHz ¹H NMR of (4-methylenecyclopent-2-en-1-yl)cyclohexane (**30**) in CDCl₃ at room temperature.

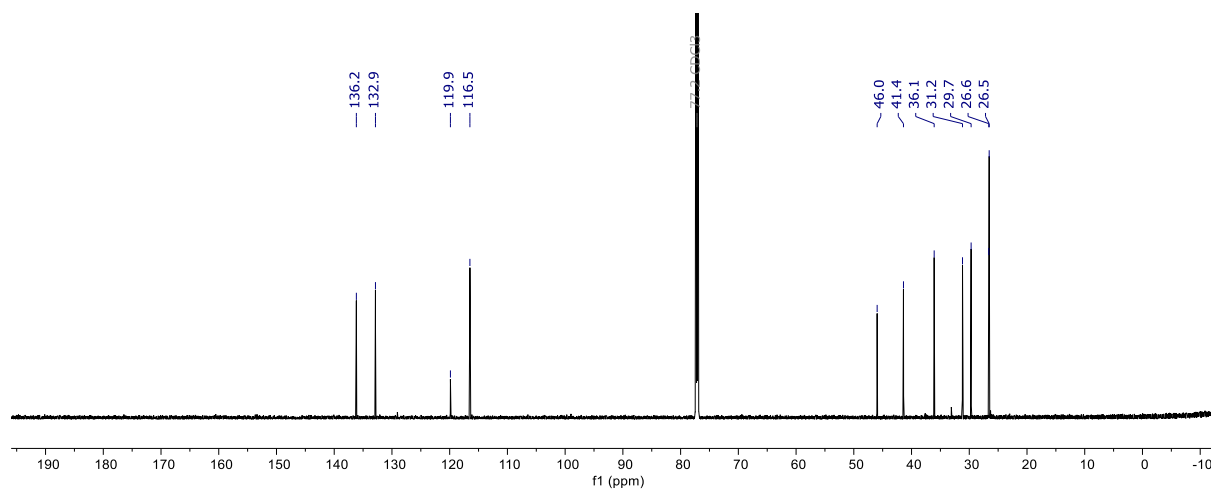


Figure A1.52. 201 MHz ¹³C{¹H} NMR of (4-methylenecyclopent-2-en-1-yl)cyclohexane (**30**) in CDCl₃ at room temperature.

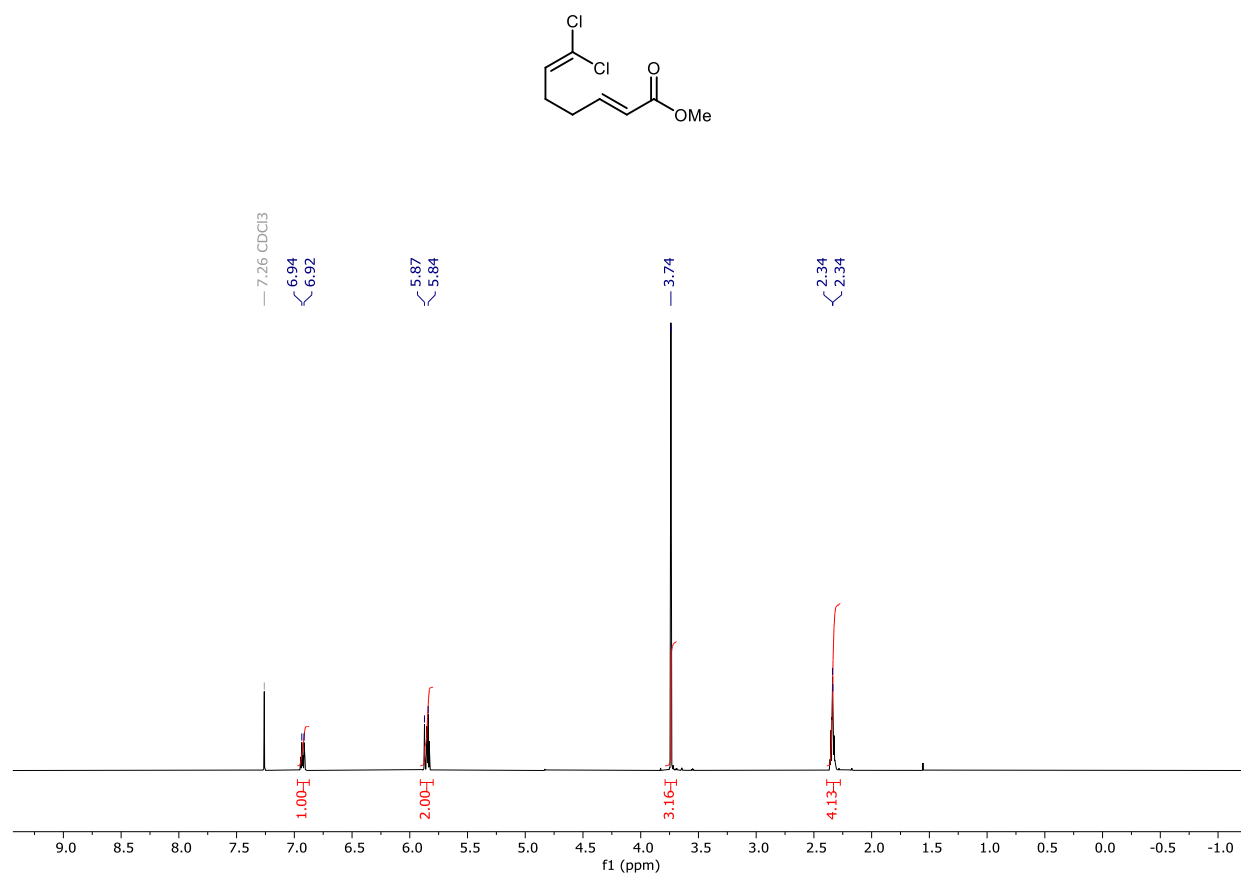


Figure A1.53. 800 MHz ¹H NMR of methyl (*E*)-7,7-dichlorohepta-2,6-dienoate (**31**) in CDCl₃ at room temperature.

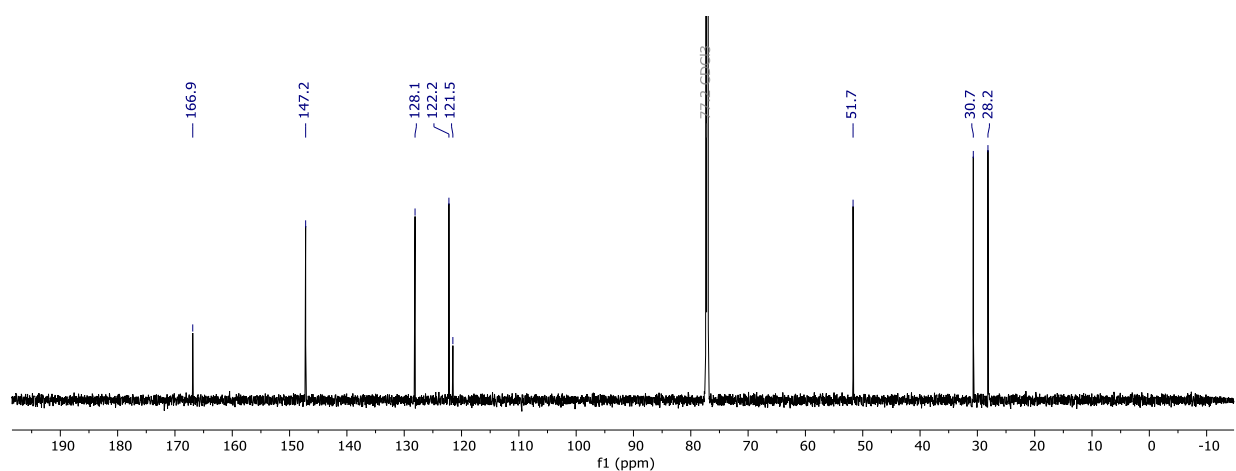


Figure A1.54. 201 MHz ¹³C{¹H} NMR of methyl (*E*)-7,7-dichlorohepta-2,6-dienoate (**31**) in CDCl₃ at room temperature.

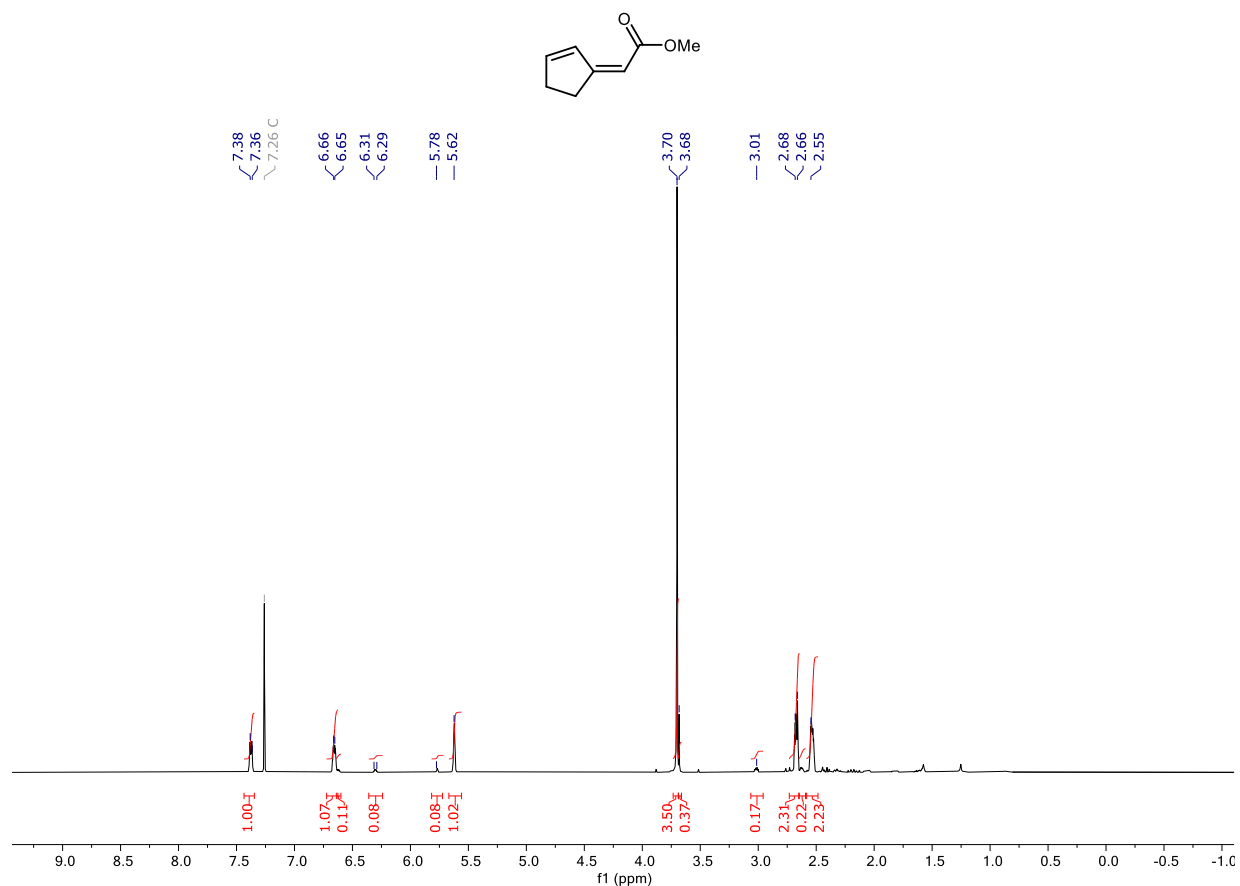


Figure A1.55. 400 MHz ^1H NMR of methyl (Z)-2-(cyclopent-2-en-1-ylidene)acetate (**32**) in CDCl_3 at room temperature.

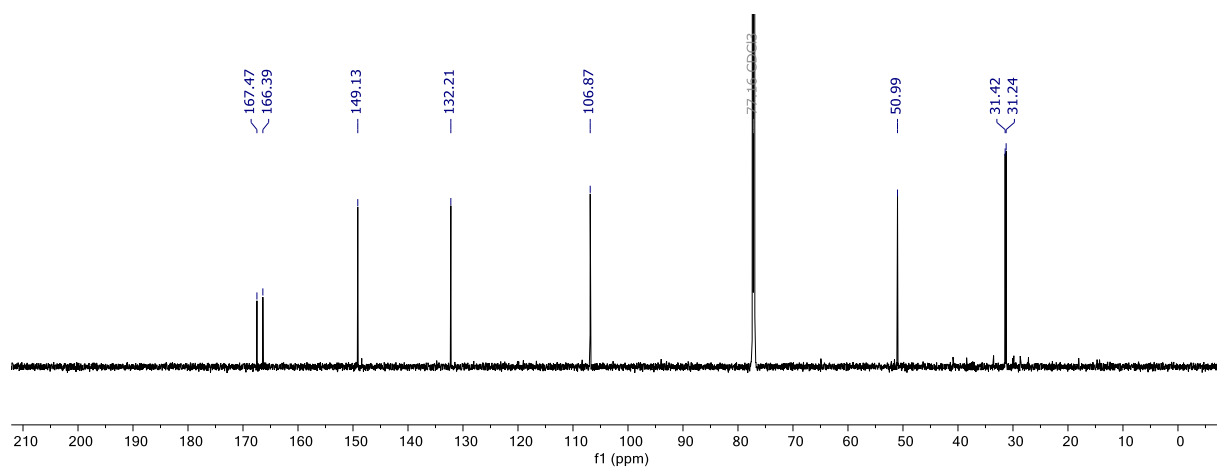


Figure A1.56. 101 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR of methyl (Z)-2-(cyclopent-2-en-1-ylidene)acetate (**32**) in CDCl_3 at room temperature.

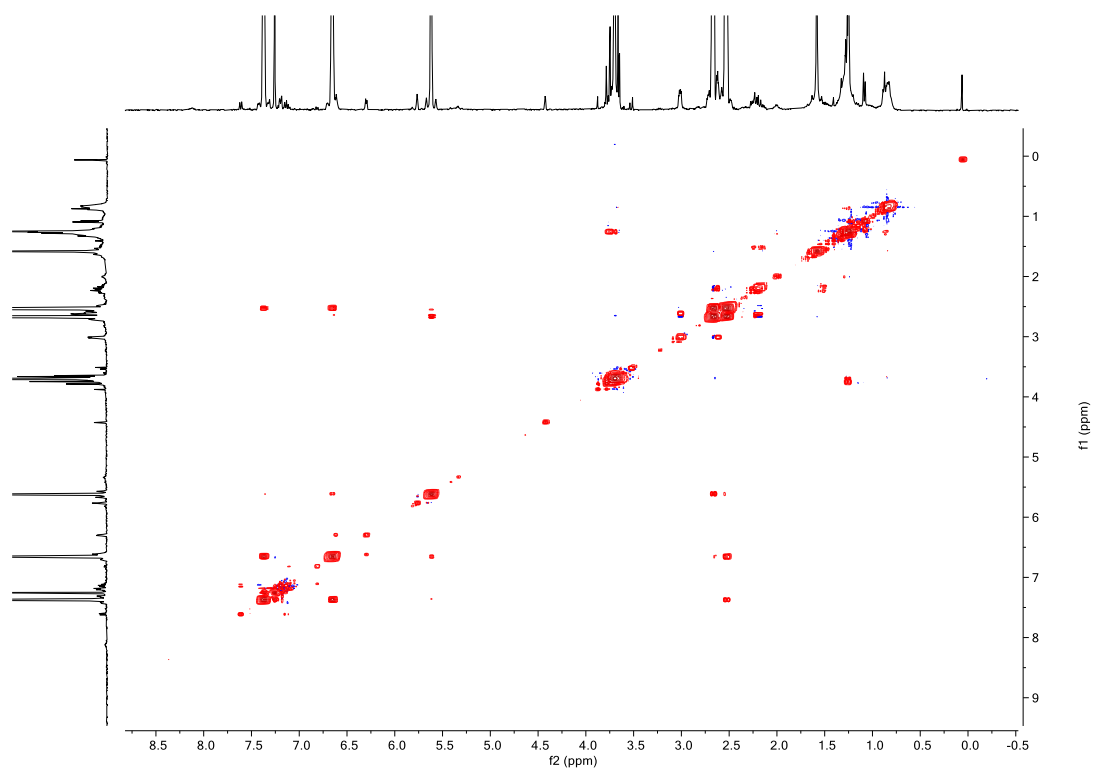


Figure A1.57. COSY NMR of **32** in CDCl_3 at room temperature.

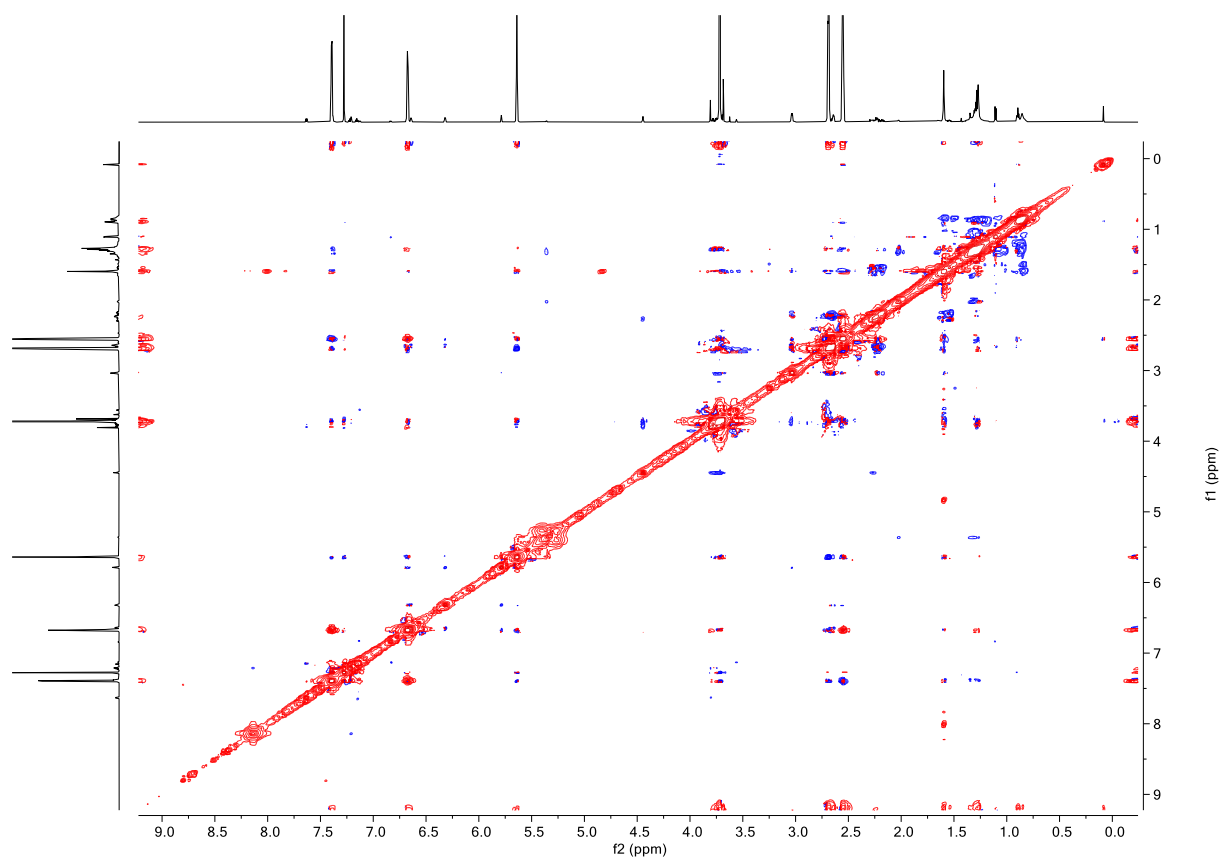


Figure A1.58. NOESY NMR of **32** in CDCl_3 at room temperature.

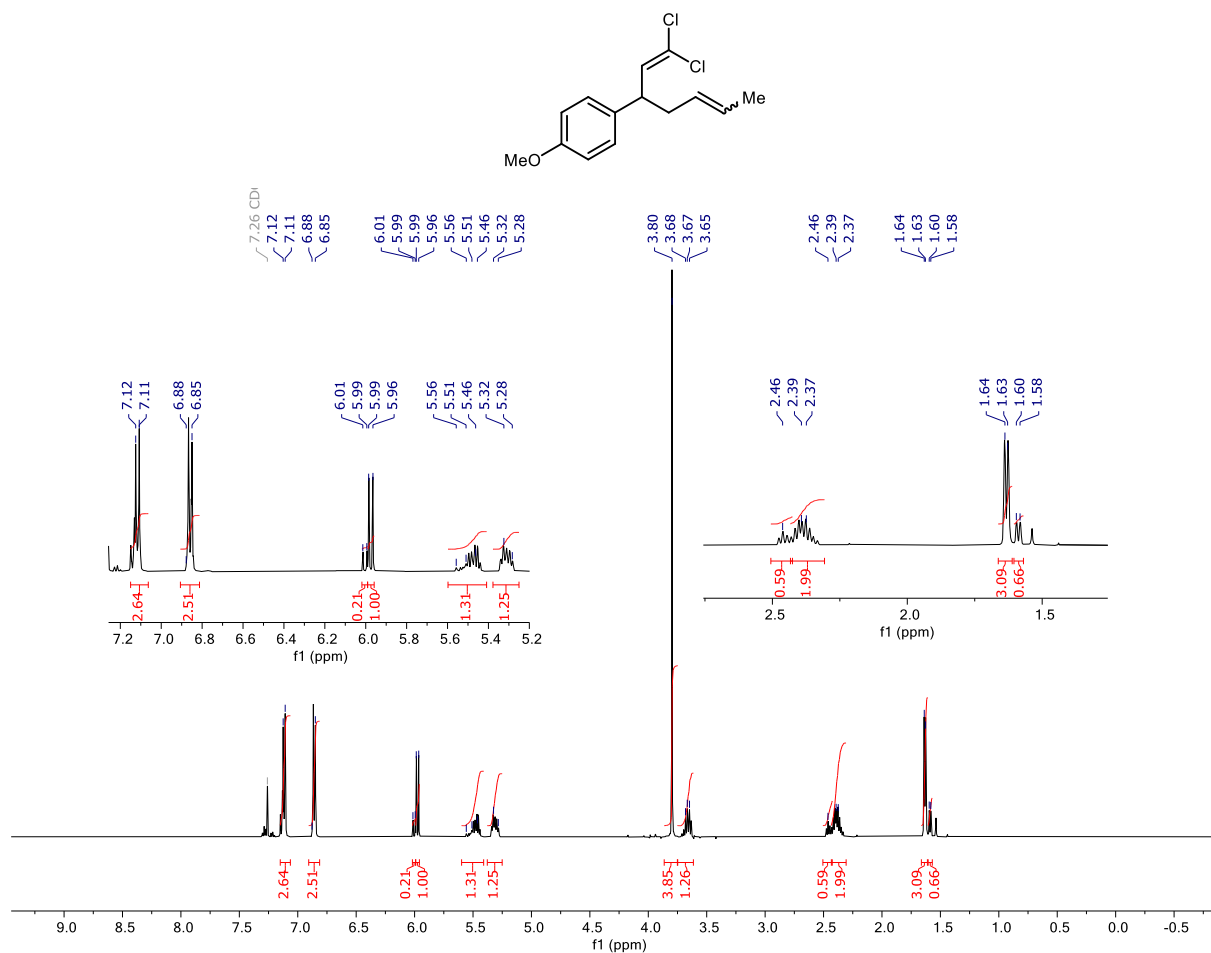


Figure A1.59. 500 MHz ¹H NMR of 1-(1,1-dichlorohepta-1,5-dien-3-yl)-4-methoxybenzene (**33**) in CDCl₃ at room temperature.

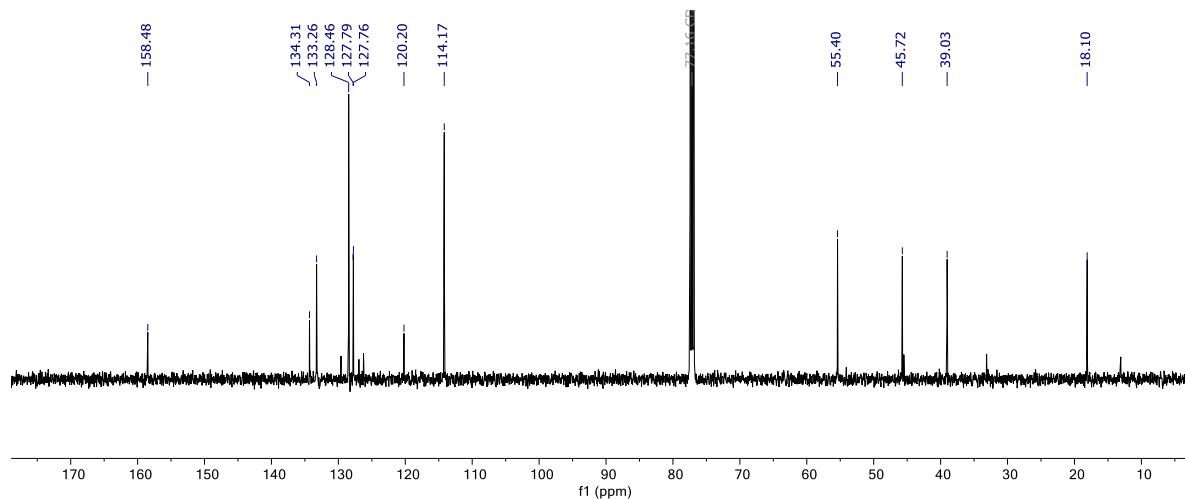


Figure A1.60. 126 MHz ¹³C{¹H} NMR of methyl 1-(1,1-dichlorohepta-1,5-dien-3-yl)-4-methoxybenzene (**33**) in CDCl₃ at room temperature.

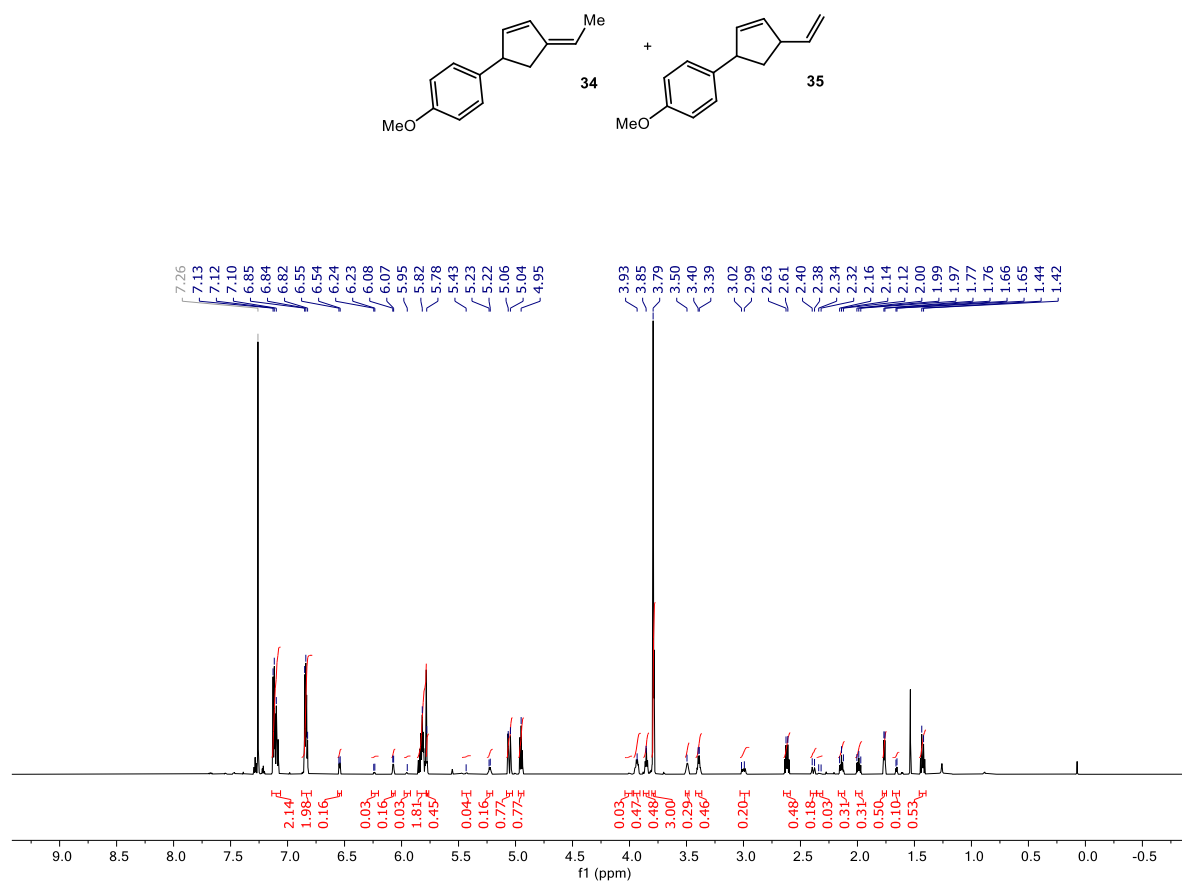


Figure A1.61. 800 MHz ^1H NMR of **34** and **35** in CDCl_3 at room temperature.

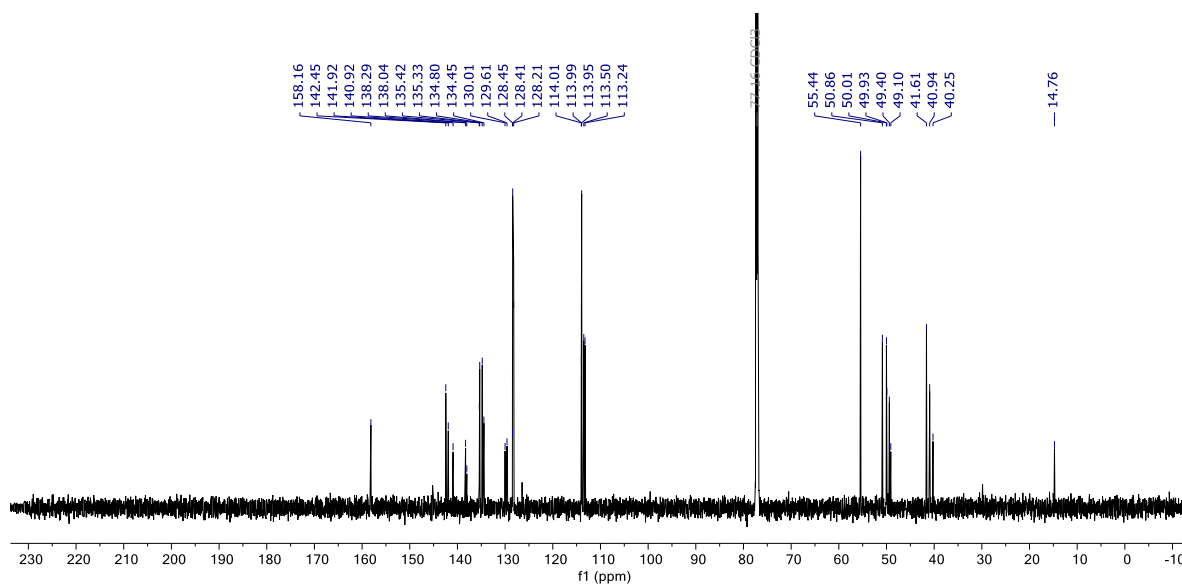


Figure A1.62. 126 MHz $^1\text{H}\{^{13}\text{C}\}$ NMR of **34** and **35** in CDCl_3 at room temperature.

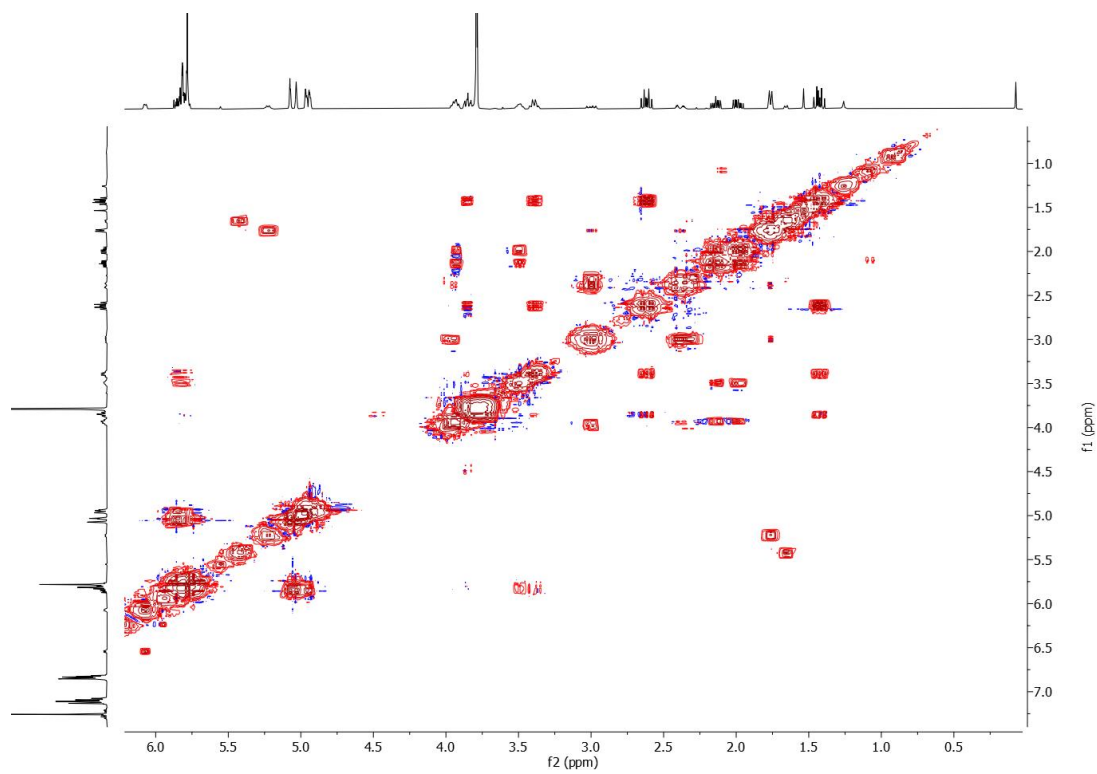


Figure A1.63. 800 MHz COSY NMR of **34** and **35** in CDCl_3 at room temperature.

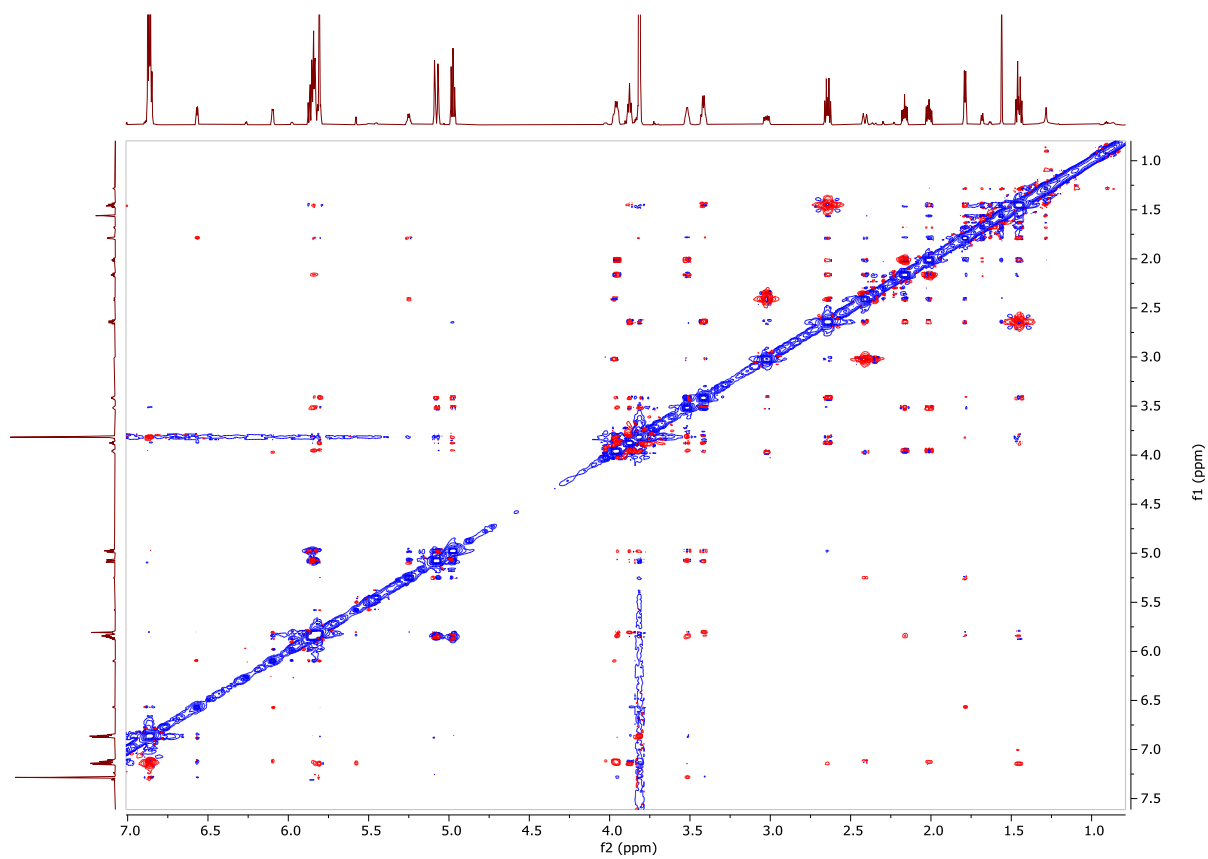


Figure A1.64. 800 MHz NOESY NMR of **34** and **35** in CDCl_3 at room temperature.

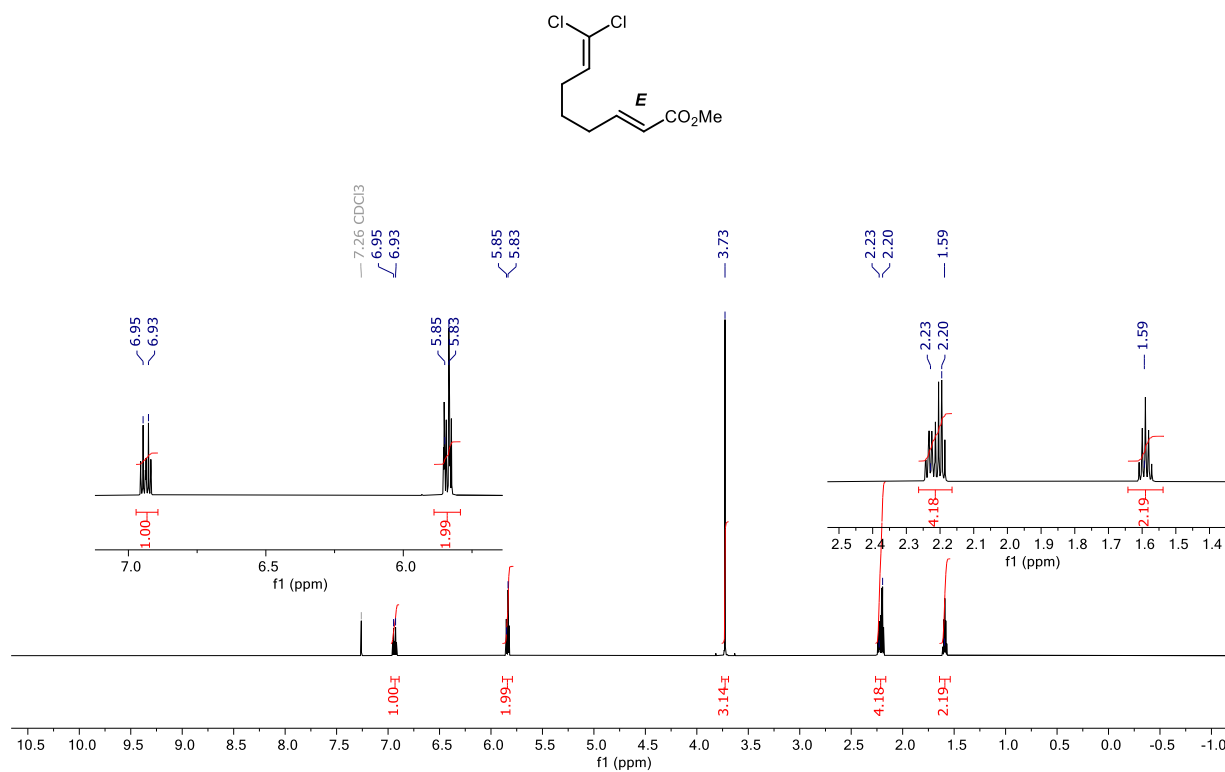


Figure A1.65. 800 MHz ¹H NMR of methyl (*E*)-8,8-dichloroocta-2,7-dienoate (**36-E**) in CDCl₃ at room temperature.

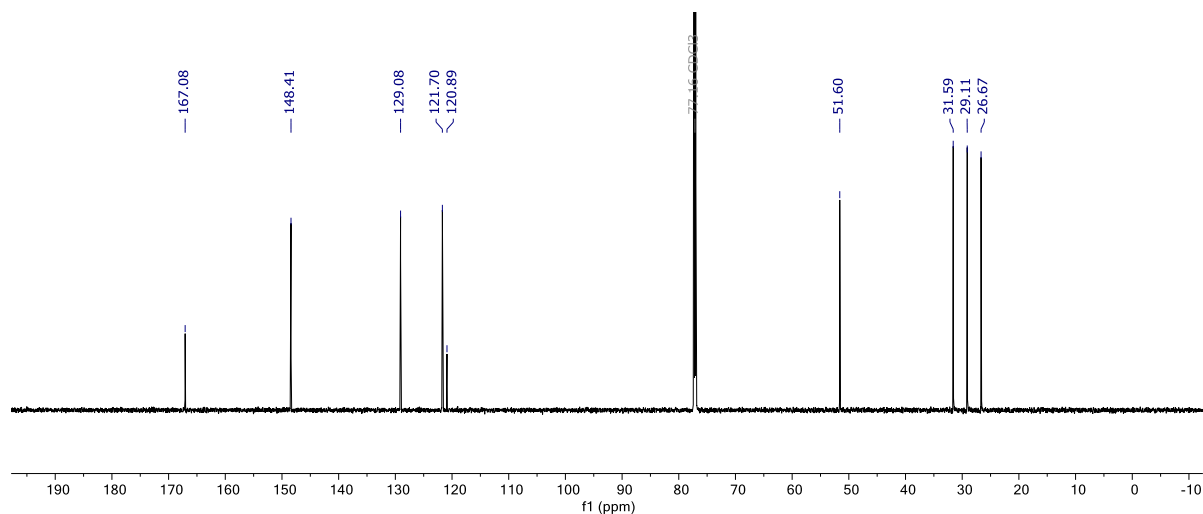


Figure A1.66. 201 MHz ¹³C{¹H} NMR of methyl (*E*)-7,7-dichlorohepta-2,6-dienoate (**36-E**) in CDCl₃ at room temperature.

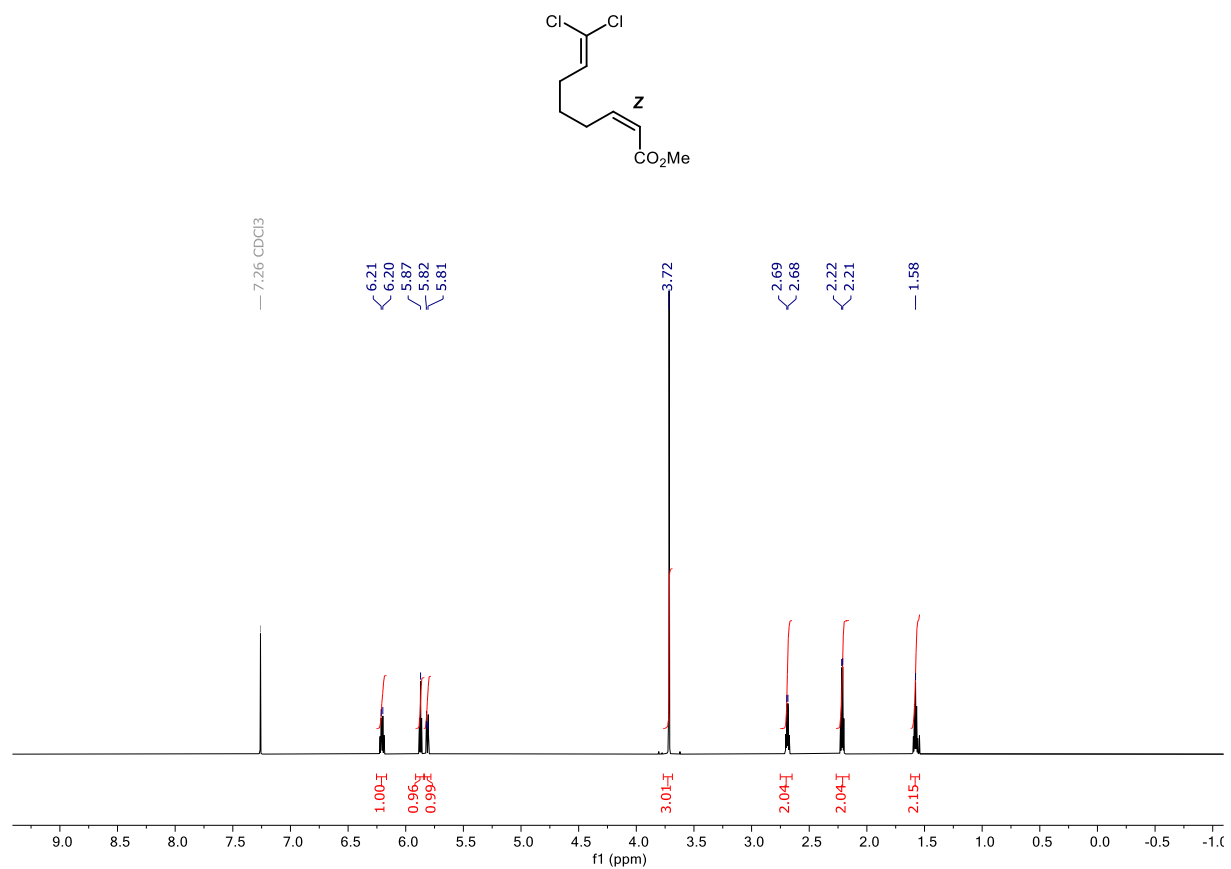


Figure A1.67. 800 MHz ¹H NMR of methyl (Z)-8,8-dichloroocta-2,7-dienoate (**36-Z**) in CDCl₃ at room temperature.

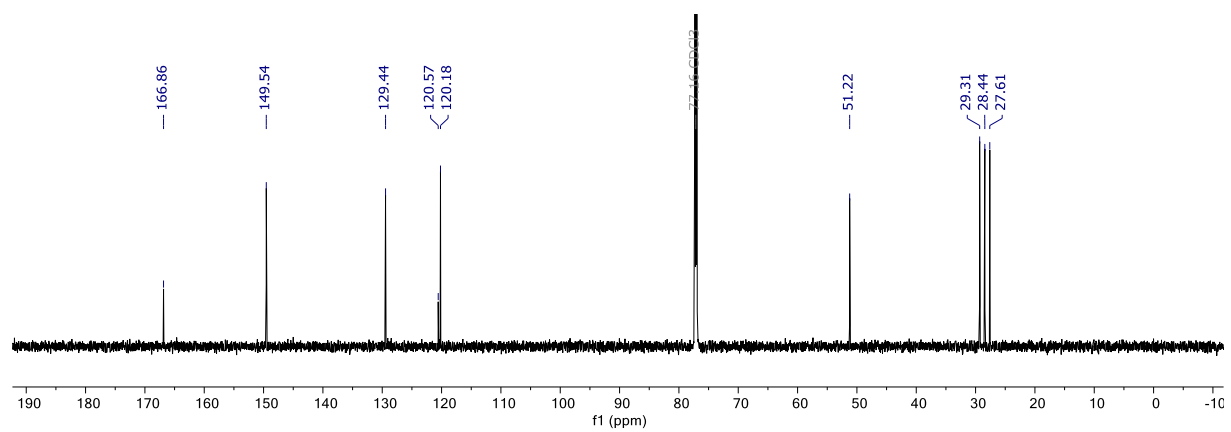


Figure A1.68. 201 MHz ¹³C{¹H} NMR of methyl (Z)-7,7-dichlorohepta-2,6-dienoate (**36-Z**) in CDCl₃ at room temperature.

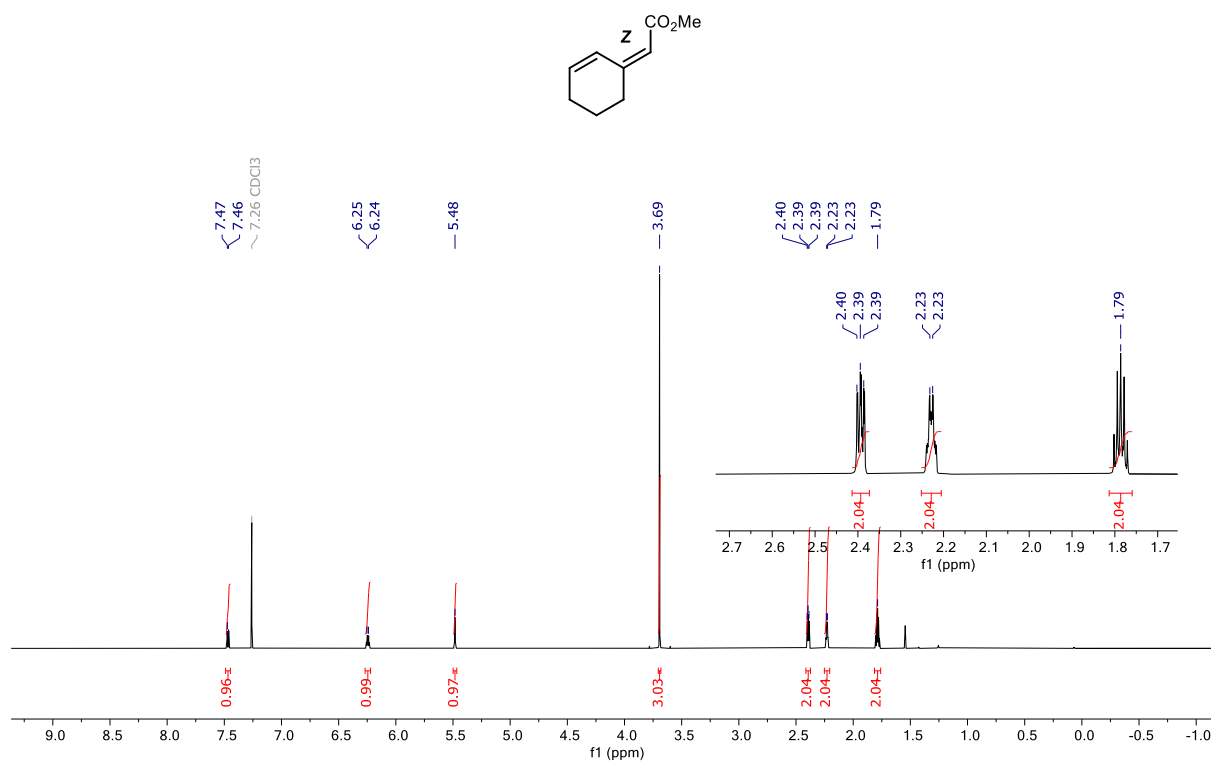


Figure A1.69. 800 MHz ¹H NMR of methyl (Z)-2-(cyclohex-2-en-1-ylidene)acetate (**37-Z**) in CDCl₃ at room temperature.

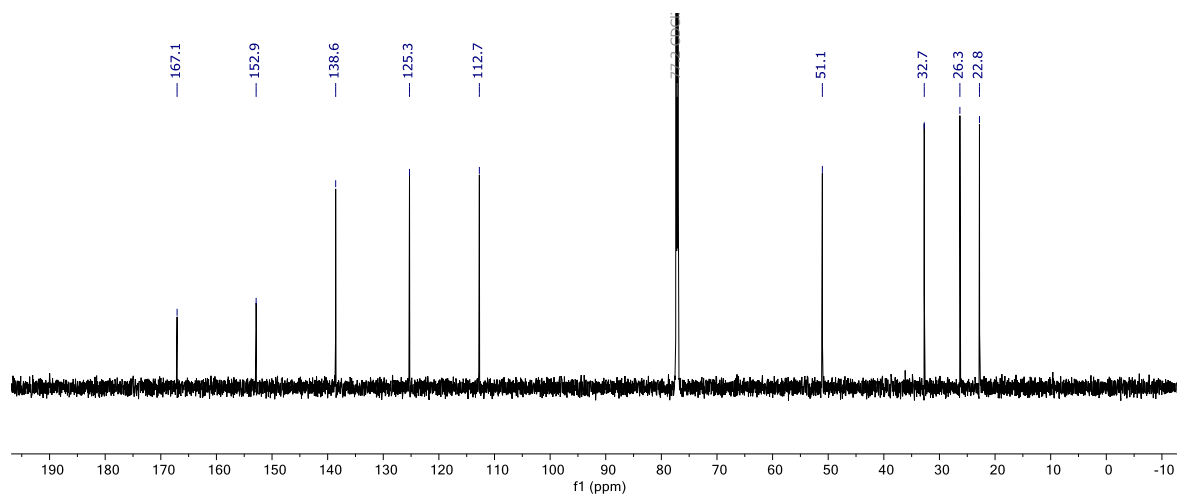


Figure A1.70. 201 MHz ¹³C{¹H} NMR of methyl (Z)-2-(cyclohex-2-en-1-ylidene)acetate (**37-Z**) in CDCl₃ at room temperature.

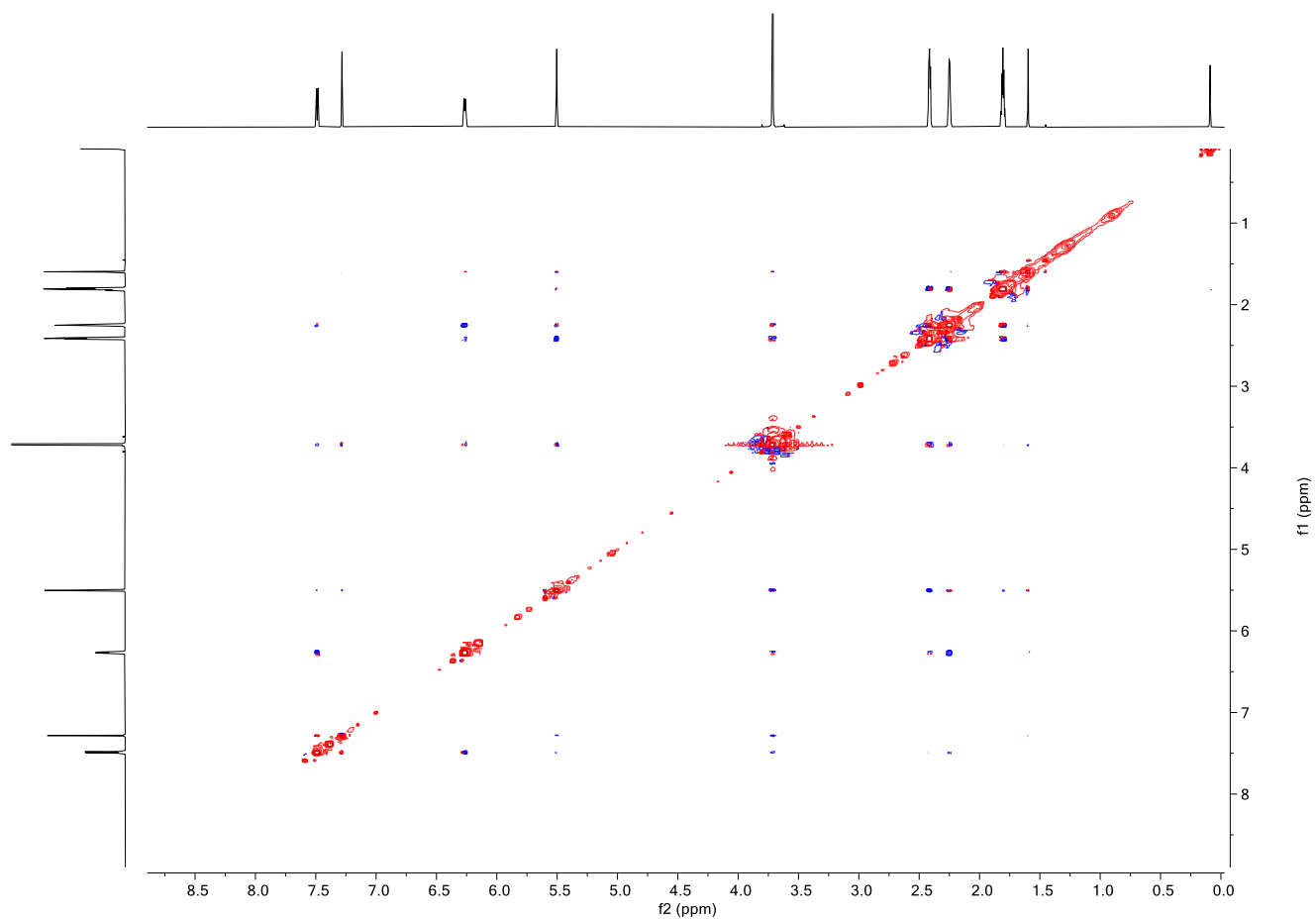
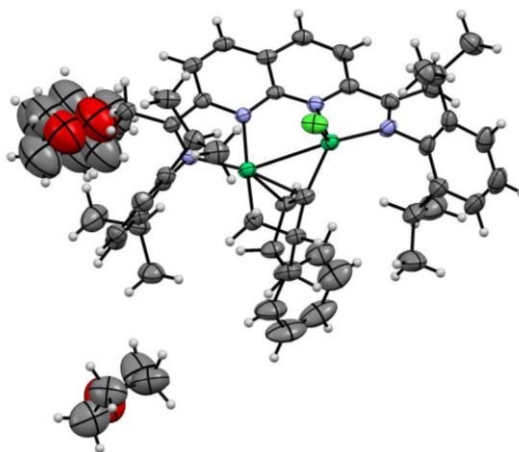


Figure A1.71. 800 MHz NOESY of **37-Z** in CDCl₃ at room temperature.

10. X-Ray Diffraction Data



	Complex 38
Crystal data	
Chemical formula	$\text{C}_{48}\text{H}_{56}\text{ClN}_4\text{Ni}_2 \cdot 2(\text{C}_4\text{H}_8\text{O})$
M_r	986.04
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (Å)	11.7896 (7), 14.2794 (10), 15.3833 (10)
α, β, γ (°)	85.562 (5), 79.370 (3), 81.396 (4)
V (Å ³)	2513.4 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	1.76
Crystal size (mm)	$0.10 \times 0.04 \times 0.03$
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl.

	Cryst. 48 (2015) 3-10
T_{\min}, T_{\max}	0.633, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22220, 9724, 5798
R_{int}	0.089
$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.079, 0.235, 0.98
No. of reflections	9724
No. of parameters	643
No. of restraints	250
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e \AA^{-3})	1.83, -0.75

Computer programs: Apex3 v2016.9-0 (Bruker, 2016), SAINT V8.37A (Bruker, 2016), SHELXS97 (Sheldrick, 2008), SHELXL2016/6 (Sheldrick, 2015, 2016), SHELXLE Rev714 (Hübschle *et al.*, 2011).

11. DFT Calculations

All structures were optimized using the unrestricted M06-L functional (UM06-L)²⁹ using the LANL2DZ basis set (and its associated electron core potential)^{30,31} for the two nickel atoms and the 6-31G(d,p) Pople basis set³² for all other atoms using the Gaussian 16 software package.³³ Final Gibbs free energies are reported by using the SCF energy from single point calculations using the UM06-L/def2-TZVP^{34,35} functional/basis set combination for each atom and applying the thermal corrections from the UM06-L/6-31G(d,p)/LANL2DZ[Ni] calculations at 298 K.

The reduction steps were performed using the following methodology: the first reduction step involved the conversion of dimeric Zn_2 to Zn_2Cl . The second reduction step involved the Zn_2Cl from the previous reduction step forming ZnCl_2 and atomic zinc.

Note about spin states:

The M06-L functional is generally accurate for relative spin states of first-row transition metal complexes. In prior work this functional accurately captured the correct ground spin state of the (NDI) Ni_2 (benzene) complex and related structures (*ACS Catal.* **2017**, 7, 4796). For this vinylidene-olefin cyclization reaction there are many DFT optimized structures with spin state energies within only a few kcal/mol. These structures should be interpreted as close-lying spin states rather than a prediction of a specific ground spin state. These close lying spin states also suggest multireference character. As examples, for structure **40** the singlet state is only 3 kcal/mol higher than the triplet state and for structure **38** the doublet and quartet states are nearly identical in energy. Despite the very good prediction of ground spin states in our previous work, M06-L predicts a slightly lower energy triplet than singlet for structure **39**, which is generated after reduction of **38** and the ^1H NMR spectrum of **39** suggests that this complex is diamagnetic. All DFT methods (used with unrestricted orbitals) show a lower energy triplet energy than singlet energy for **39**. Functionals tested include: B3LYP*, BLYP, BP86, OPBE, PBE, TPSS, TPSSH, MN15-L, and $\omega\text{B97X-D}$. The triplet energy was lower than the singlet for the complete ligand with iPr groups rather than Me groups as well as gas and solution phases.

Table A1.1. Structure energies, relative to Int40 triplet ground state, for the cyclization of a vinylidene-olefin (kcal/mol). Absolute energies in parentheses (Hartree). Relative SCF energies (ΔE_{SCF}), ZPE-corrected (ΔE_{ZPE}), enthalpy (ΔH), Gibbs free energy (ΔG) at UM06-L/6-31G(d,p)/LANL2DZ[Ni].

Structure	ΔE_{SCF}	ΔE_{ZPE}	ΔH	ΔG
UM06-L/6-31G(d,p)[LANL2DZ(Ni)]				
Int38 (S=1/2)	-56.2 (-2566.285322)	-55.5 (-2565.583709)	-56.4 (-2565.537312)	-51.8 (-2565.664616)
Int38 (S=3/2)	-52.5 (-2566.279466)	-51.6 (-2565.577647)	-52.7 (-2565.531378)	-48.5 (-2565.659353)
Int39 (S=0)	-55.5 (-2106.037157)	-55.8 (-2105.33772)	-56.0 (-2105.293084)	-60.3 (-2105.415939)
Int39 (S=1)	-57.9 (-2106.041042)	-58.1 (-2105.341427)	-58.4 (-2105.296835)	-63.4 (-2105.420827)
Int39 (S=2)	-47.0 (-2106.023555)	-47.7 (-2105.324874)	-47.9 (-2105.280111)	-52.9 (-2105.404033)
Int40 (S=0)	1.8 (-3026.421758)	1.6 (-3025.720318)	1.7 (-3025.671761)	2.1 (-3025.801082)
Int40 (S=1)	0.0 (-3026.424647)	0.0 (-3025.722933)	0.0 (-3025.674452)	0.0 (-3025.804485)
Int41 (S=0)	-21.2 (-3026.458422)	-20.0 (-3025.754852)	-20.0 (-3025.706347)	-20.5 (-3025.837232)
Int41 (S=1)	-25.2 (-3026.464748)	-25.0 (-3025.762852)	-24.6 (-3025.713617)	-27.3 (-3025.847976)
Int41 (S=2)	-27.4 (-3026.468323)	-27.9 (-3025.767417)	-27.0 (-3025.717508)	-32.3 (-3025.855881)
Int42 (S=1/2)	-27.5 (-2566.239596)	-28.6 (-2565.540848)	-28.4 (-2565.492687)	-26.4 (-2565.624095)
Int42 (S=3/2)	-26.6 (-2566.238233)	-27.9 (-2565.53976)	-27.7 (-2565.491439)	-26.6 (-2565.624357)
Int43 (S=0)	-55.8 (-2106.037612)	-58.2 (-2105.341599)	-58.6 (-2105.297207)	-61.4 (-2105.417591)
Int43 (S=1)	-57.5 (-2106.040289)	-59.7 (-2105.343996)	-60.2 (-2105.299663)	-63.3 (-2105.420675)
Int44 (S=0)	-82.3 (-2106.07986)	-81.5 (-2105.378702)	-82.2 (-2105.334697)	-85.1 (-2105.455487)
Int44 (S=1)	-83.4 (-2106.081649)	-83.1 (-2105.381331)	-83.7 (-2105.33713)	-86.8 (-2105.458118)
Int44 (S=2)	-62.4 (-2106.048098)	-63.3 (-2105.349674)	-63.3 (-2105.304606)	-69.4 (-2105.430325)
Int45 (S=1/2)	-41.9 (-2566.262563)	-43.3 (-2565.564285)	-44.2 (-2565.517759)	-39.1 (-2565.644347)
Int45 (S=3/2)	-41.7 (-2566.262338)	-43.4 (-2565.564562)	-44.1 (-2565.517709)	-40.6 (-2565.646693)
Int46 (S=1/2)	-81.1 (-2566.325014)	-80.0 (-2565.622844)	-81.1 (-2565.576655)	-75.6 (-2565.702461)
Int46 (S=3/2)	-81.4 (-2566.32556)	-80.9 (-2565.624241)	-81.8 (-2565.577634)	-77.1 (-2565.704854)
TS38 (S=1/2)	-23.3 (-2566.232981)	-25.3 (-2565.535606)	-26.5 (-2565.489655)	-21.6 (-2565.61648)
TS38 (S=3/2)	-22.6 (-2566.23182)	-24.9 (-2565.535011)	-26.3 (-2565.489209)	-20.6 (-2565.614876)
TS39 (S=0)	-27.8 (-2105.993054)	-31.0 (-2105.298195)	-31.5 (-2105.254031)	-34.8 (-2105.375187)
TS39 (S=1)	-24.2 (-2105.98731)	-28.1 (-2105.293591)	-28.4 (-2105.249053)	-33.5 (-2105.373124)

TS40 (S=0)	7.0 (-3026.413561)	6.5 (-3025.712654)	6.5 (-3025.664072)	6.2 (-3025.794566)
TS40 (S=1)	5.5 (-3026.415918)	5.2 (-3025.714655)	5.2 (-3025.666222)	4.4 (-3025.797484)
TS41 (S=1/2)	-15.0 (-2566.219667)	-16.7 (-2565.521934)	-16.8 (-2565.474195)	-14.5 (-2565.605114)
TS41 (S=3/2)	-17.1 (-2566.223147)	-18.4 (-2565.524703)	-18.7 (-2565.477216)	-16.0 (-2565.607549)
TS42 (S=1/2)	-23.8 (-2566.233689)	-25.4 (-2565.535758)	-26.0 (-2565.488855)	-21.2 (-2565.615836)
TS42 (S=3/2)	-31.9 (-2566.246686)	-32.4 (-2565.54701)	-33.5 (-2565.500668)	-28.0 (-2565.626584)
TS43 (S=0)	-50.6 (-2106.029304)	-54.3 (-2105.335315)	-54.4 (-2105.290519)	-59.5 (-2105.414623)
TS43 (S=1)	-52.3 (-2106.032113)	-55.3 (-2105.337002)	-55.8 (-2105.292634)	-59.8 (-2105.415071)
TS43 (S=2)	-25.5 (-2105.989312)	-29.9 (-2105.296419)	-30.0 (-2105.251566)	-35.2 (-2105.375833)
TS45 (S=1/2)	-41.5 (-2566.261941)	-44.2 (-2565.565834)	-45.1 (-2565.519171)	-40.7 (-2565.646892)
TS45 (S=3/2)	-40.8 (-2566.260841)	-43.6 (-2565.564822)	-44.4 (-2565.518116)	-40.8 (-2565.646969)
MECP-Int41 (S=1/2)	-26.2 (-3026.466476)	-26.9 (-3025.76584)	-26.9 (-3025.716609)	-29.5 (-3025.851471)

Table A1.2. Structure energies, relative to Int40 triplet ground state, for the cyclization of a vinylidene-olefin (kcal/mol). Absolute energies in parentheses (Hartree). Relative SCF energies (ΔE_{SCF}), at UM06-L/def2-TZVP.

Structure	ΔE_{SCF}
UM06-L/def2-TZVP	
Int38 (S=1/2)	-57.3 (-5244.763667)
Int38 (S=3/2)	-54.8 (-5244.75961538)
Int39 (S=0)	-56.7 (-4784.4809)
Int39 (S=1)	-60.6 (-4784.4871)
Int39 (S=2)	-49.3 (-4784.39184)
Int40 (S=0)	+2.2 (-5704.927508)
Int40 (S=1)	0.0 (-5704.931059)
Int41 (S=0)	-23.9 (-5704.969138)
Int41 (S=1)	-27.3 (-5704.974621)
Int41 (S=2)	-29.5 (-5704.978045)
Int42 (S=1/2)	-31.1 (-5244.721856)
Int42 (S=3/2)	-29.9 (-5244.720008)
Int43 (S=0)	-58.5 (-4784.483795)

Int43 (S=1)	-60.7 (-4784.487362)
Int44 (S=0)	-83.6 (-4784.523866)
Int44 (S=1)	-83.3 (-4784.523364)
Int44 (S=2)	-64.6 (-4784.49352)
Int45 (S=1/2)	-42.4 (-5244.739887)
Int45 (S=3/2)	-43.6 (-5244.741742)
Int46 (S=1/2)	-77.8 (-5244.796331)
Int46 (S=3/2)	-78.4 (-5244.79726)
TS38 (S=1/2)	-25.3 (-5244.71254)
TS38 (S=3/2)	-25.2 (-5244.712406)
TS39 (S=0)	-16.4 (-4784.416706)
TS39 (S=1)	-19.9 (-4784.422346)
TS40 (S=0)	+6.7 (-5704.920321)
TS40 (S=1)	+4.8 (-5704.923458)
TS41 (S=1/2)	-14.8 (-5244.69589)
TS41 (S=3/2)	-17.4 (-5244.700008)
TS42 (S=1/2)	-24.0 (-5244.71047)
TS42 (S=3/2)	-32.2 (-5244.723561)
TS43 (S=0)	-53.3 (-4784.475554)
TS43 (S=1)	-55.4 (-4784.478932)
TS43 (S=2)	-30.8 (-4784.439761)
TS45 (S=1/2)	-41.4 (-5244.738288)
TS45 (S=3/2)	-41.6 (-5244.738654)
MECP-Int41 (S=1/2)	-27.9 (-5704.975532)

Table A1.3. Structure energies for the cyclization of a vinylidene-olefin (kcal/mol). Absolute energies in parentheses (Hartree). Relative SCF energies (ΔE_{SCF}), ZPE-corrected (ΔE_{ZPE}), enthalpy (ΔH), Gibbs free energy (ΔG) at UM06-L/6-31G(d,p)/LANL2DZ[Ni].

Structure	ΔE_{SCF}	ΔE_{ZPE}	ΔH	ΔG
UM06-L/6-31G(d,p)[LANL2DZ(Ni)]				
Zn	-65.11021637	-65.110216	-65.107856	-65.126094
ZnCl	-525.3213191	-525.34502	-2239.580273	-2239.604
Zn₂	-130.2187784	-130.218693	-130.214527	-130.24461
Zn₂Cl	-590.4475945	-590.446285	-590.441624	-590.46707
ZnCl₂	-985.5844767	-985.582574	-985.577358	-985.60321

References

- ¹ Zhou, Y-Y.; Hartline, D.R.; Steiman, T. J.; Fanwick, P. E.; Uyeda, C. Dinuclear Nickel Complexes in Five States of oxidation Using a Redox-Active Ligand *Inorg. Chem.* **2014**, *53*, 11770–11777.
- ² Zhou, Y-Y.; Uyeda, C. Reductive Cyclopropanations Catalyzed by Dinuclear Nickel Complexes *Angew. Chem. Int. Ed.* **2016**, *55*, 3171–3175.
- ³ Stoll, S.; Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* **2006**, *178*, 42–55.
- ⁴ Bruker (2016). Apex3 v2016.9-0, Saint V8.34A, SAINT V8.37A, Bruker AXS Inc.: Madison (WI), USA, 2013/2014.
- ⁵ a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA) b) Sheldrick GM. A short history of SHELX. *Acta Crystallogr A.* **2008**, *64*(1), 112–122.
- ⁶ Sheldrick G. M. University of Göttingen, Germany, 2018. b) Sheldrick GM. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem.* **2015**, *71*(1), 3–8.
- ⁷ Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44*(6), 1281–1284.
- ⁸ Schmidt, V. A.; Hoyt, J. M.; Margulieux, G. W.; Chirik, P. J. Cobalt-Catalyzed $[2\pi + 2\pi]$ Cycloadditions of Alkenes: Scope, Mechanism, and Elucidation of Electronic Structure of Catalytic Intermediates. *J. Am. Chem. Soc.* **2015**, *137*, 7903–7914.
- ⁹ Hennessy E. T.; Betley, T. A. Complex N-Heterocycle Synthesis via Iron-Catalyzed, Direct C–H Bond Amination *Science*, **2013**, *340*, 591–595.

-
- ¹⁰ Schmidt, Y.; Lam, J.K.; Pham, H. V.; Houk, K. N.; Vanderwal, C. D. Studies on the Himbert Intramolecular Arene/Allene Diels–Alder Cycloaddition. Mechanistic Studies and Expansion of Scope to All-Carbon Tethers *J. Am. Chem. Soc.* **2013**, *135*, 7339 – 7348.
- ¹¹ Chen, Y. L.; Hoppe, D. 1-(N,N-Diisopropylcarbamoyloxy)-1-tosyl-1-alkenes— a^2d^1 Synthons via Tandem Umpolung *J. Org. Chem.* **2009**, *74*, 4188–4194.
- ¹² Zhao, X.; Liu, D.; Guo, H.; Liu, Y.; Zhang W. C–N Bond Cleavage of Allylic Amines via Hydrogen Bond Activation with Alcohol Solvents in Pd-Catalyzed Allylic Alkylation of Carbonyl Compounds *J. Am. Chem. Soc.* **2011**, *133*, 19354–19357.
- ¹³ Hoveyda A.; Zoute, L.; Lenoir, F. Novel compounds, method for use them and pharmaceutical composition containing them. WO2011151436A2, 2011.
- ¹⁴ Allin, S. M.; Horro-Pita, C.; Essat, M.; Aspinall, I.; & Shah, P. Utilizing the Asymmetric Amino-Cope Rearrangement as a Novel Approach to Enantiomerically Enriched 3-Substituted Aldehydes. *Synth. Comm.*, **2010**, *40*, 2696–2711.
- ¹⁵ Kawajiri, T.; Ohta, R.; Fujioka, H.; Sajiki, H.; & Sawama, Y. Aromatic aldehyde-selective aldol addition with aldehyde-derived silyl enol ethers. *Chem. Comm.*, **2018**, *54*, 374–377
- ¹⁶ Clavette, C.; Vincent Rocan, J.-F.; & Beauchemin, A. M. Diversity-Oriented Synthesis of Hydrazine-Derived Compounds from Amino Isocyanates Generated In Situ. *Angew. Chem. Int. Ed.*, **2013**, *52*, 12705–12708.
- ¹⁷ Smith, A. B.; Minbirole, K. P.; Verhoest, P. R.; Schelhaas, M. Total Synthesis of (+)-Phorboxazole A Exploiting the Petasis–Ferrier Rearrangement. *J. Am. Chem. Soc.*, **2001**, *123*, 10942–10953.
- ¹⁸ Li, J.; Ahmed, T. S.; Xu, C.; Stoltz, B. M.; Grubbs, R. H. Concise Synthesis of Δ^{12} -Prostaglandin J Natural Products via Stereoretentive Metathesis. *J. Am. Chem. Soc.* **2019**, *141*(1), 154–158.
- ¹⁹ Moretti, J. D.; Wang, X.; Curran, D. P. Minimal Fluorous Tagging Strategy that Enables the Synthesis of the Complete Stereoisomer Library of SCH725674 Macrolactones. *J. Am. Chem. Soc.* **2012**, *134*(18), 7963–7970.
- ²⁰ Xing, X.; O'Connor, N. R.; Stoltz, B. M. Palladium(II)-Catalyzed Allylic C–H Oxidation of Hindered Substrates Featuring Tunable Selectivity Over Extent of Oxidation *Angew. Chem. Int. Ed.*, **2015**, *54*, 11186–11190
- ²¹ Yip, S. Y. Y.; Aïssa, C. Isomerization of Olefins Triggered by Rhodium-Catalyzed C–H Bond Activation: Control of Endocyclic β -Hydrogen Elimination., *Angew. Chem. Int. Ed.* **2015**, *54*, 6870–6873.
- ²² Peng, B.; Geerdink, D.; Maulide, N. Electrophilic Rearrangements of Chiral Amides: A Traceless Asymmetric α -Allylation *J. Am. Chem. Soc.*, **2013**, *135*, 14968–14971.

-
- ²³ Watanabe, K.; Suzuki, Y.; Aoki, K.; Sakakura, A.; Suenaga, K.; Kigoshi, H. Formal Synthesis of Optically Active Ingenol via Ring-Closing Olefin Metathesis. *J. Org. Chem.*, **2004**, *69*, 7802–7808.
- ²⁴ Bloome, K. S.; Alexanian, E. J. Palladium-Catalyzed Carbonylative Heck-Type Reactions of Alkyl Iodides. *J. Am. Chem. Soc.*, **2010**, *132*, 12823–12825.
- ²⁵ Petrignet, J.; Boudhar, A.; Blond, G.; Suffert, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3285–3289.
- ²⁶ Kumpulainen, E. T. T.; Koskinen, A. M. P.; Rissanen, K. Total Synthesis of Amaminol A: Establishment of the Absolute Stereochemistry. *Org. Lett.*, **2007**, *9*, 5043–5045.
- ²⁷ Kim, H.; Lee, C. Cycloisomerization of Enynes via Rhodium Vinylidene-Mediated Catalysis, *J. Am. Chem. Soc.* **2005**, *127*, 10180–10181.
- ²⁸ Bohan, P. T.; Toste, F. D. Well-Defined Chiral Gold(III) Complex Catalyzed Direct Enantioconvergent Kinetic Resolution of 1,5-Enynes. *J. Am. Chem. Soc.*, **2017**, *139*, 11016–11019.
- ²⁹ Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125* (19), 194101.
- ³⁰ Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for the Transition Metal Atoms Sc to Hg. *J. Chem. Phys.* **1985**, *82* (1), 270–283.
- ³¹ Wadt, W. R.; Hay, P. J. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for Main Group Elements Na to Bi. *J. Chem. Phys.* **1985**, *82* (1), 284–298..
- ³² Dunning, T. H.; Hay, P. J. Gaussian Basis Sets for Molecular Calculations. In *Methods of Electronic Structure Theory*; Springer US, 1977; pp 1–27.
- ³³ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision, C.01. 2016.

-
- ³⁴ Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7 (18), 3297.
- ³⁵ Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, 8 (9), 1057–1065.

APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 2

1. General Information

General considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of N₂. Solvents were dried and degassed by passage through a column of activated alumina and sparging with Ar gas. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. C₆D₆ was degassed using the freeze-pump-thaw method and stored over activated 3 Å molecular sieves prior to use in the glovebox. CDCl₃ was stored over activated 3 Å molecular sieves prior to use. Zn powder (325 mesh, 99.9%), Ni(dme)Cl₂ and Ni(COD)₂ were purchased from Strem Chemicals, stored under inert atmosphere and used without further purification. Dimethylacetamide (DMA) was stored over 3 Å molecular sieves prior to use. Commercial aldehydes were distilled prior to use. All aldehydes were stored without molecular sieves in the glovebox freezer (−30 °C). All catalytic reactions were run in the glovebox unless otherwise noted. The *i*-PrNDI ligand (**7**),¹ *c*-PentNDI (**8**),² MesNDI (**9**),³ (*i*-PrNDI)Ni₂Cl₂ (**6**)⁴ and (*i*-PrNDI)Ni₂Cl (**43**)³ were prepared according to previously reported procedures. All other reagents and starting materials were purchased from commercial vendors and used without further purification unless otherwise noted.

Physical methods. ¹H NMR, ¹³C{¹H} NMR, ¹⁹F NMR, COSY NMR and NOESY NMR spectra were collected at room temperature on a Varian Inova300 with a 5mm 4-nucleus/BB Z-gradient probe, Varian Mercury300 with a 5mm 4-nucleus/BB probe, Bruker AV400 with a 5mm BBFO Z-gradient SmartProbe, a Bruker DRX500 with a 5 mm BBFO Z-gradient ATM probe, or AV800 with a QCI cryoprobe. ¹H NMR and ¹³C{¹H} NMR spectra were reported in parts per million relative to tetramethylsilane, using the referenced residual solvent resonances as an internal standard (¹H NMR: CDCl₃ = 7.26 ppm, C₆D₆ = 7.16 ppm and ¹³C{¹H} NMR: CDCl₃ = 77.16 ppm). High-resolution mass data were obtained using a Thermo Scientific LTQ Orbitrap XL mass spectrometer or a Thermo Electron Corporation MAT 95XP-Trap mass spectrometer. IR data were obtained on a Thermo Nicolet Nexus FT-IR spectrometer with an MCT* detector and a KBr beam splitter with a range of 800 – 4500 cm^{−1}.

Computational Methods. DFT calculations were performed with the Gaussian 16 software package. All geometries were fully optimized at the BP86/6-311G(d,p) level of DFT. All stationary points were verified by frequency analysis.

2. Reaction Optimization Studies

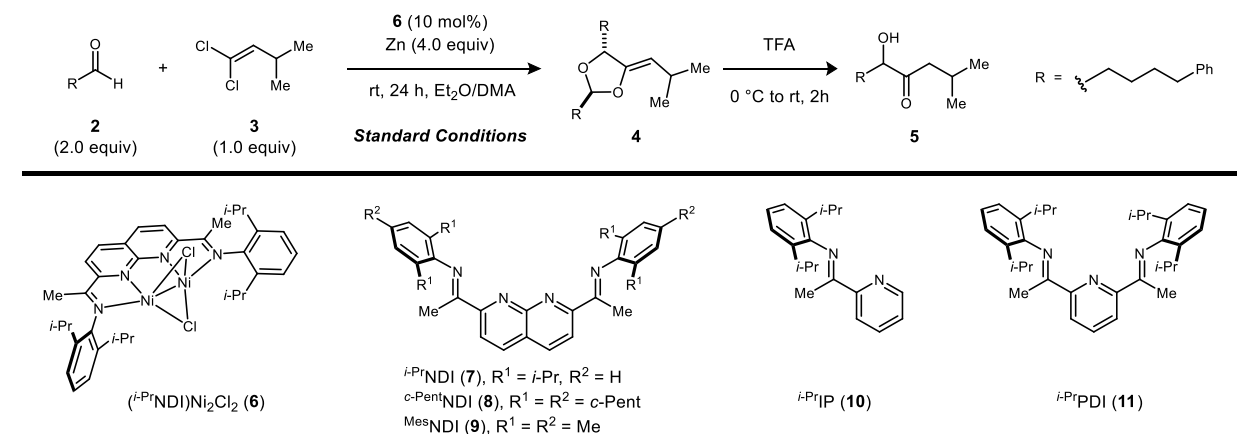
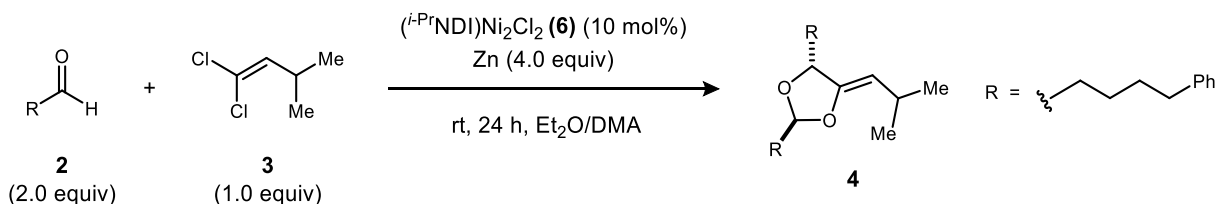


Table A2.1: Effect of Reaction Parameters

entry	Deviations from Standard Conditions	yield (%) (4)	anti:syn (4)	Z/E (4)
1	none	89	8:1	>20:1
2	Mn instead of Zn	81	14:1	>20:1
3	Cp ₂ Co instead of Zn	58	1:4	>20:1
4	no Et ₂ O	47	4:1	>20:1
5	<i>i</i> -Pr ^t NDI (7) (10 mol%) + Ni(dme)Cl ₂ (20 mol%) instead of 6	85	6:1	>20:1
6	<i>c</i> -Pent ^t NDI (8) (10 mol%) + Ni(dme)Cl ₂ (20 mol%) instead of 6	46	3:1	>20:1
7	Mes ^t NDI (9) (10 mol%) + Ni(dme)Cl ₂ (20 mol%) instead of 6	<5	–	–
8	<i>i</i> -PrIP (10) (10 mol%) + Ni(dme)Cl ₂ (10 mol%) instead of 6	0	–	–
9	<i>i</i> -PrPDI (11) (10 mol%) + Ni(dme)Cl ₂ (10 mol%) instead of 6	0	–	–
10	Ni(dme)Cl ₂ (10 mol%) instead of 6	0	–	–

General procedure for entries 1-4. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, (*i*-PrNDI)Ni₂Cl₂ (7.2 mg, 0.010 mmol, 10 mol%) and reductant (0.4 mmol, 4.0 equiv). A stock solution of 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (0.1 mmol, 1.0 equiv), 5-phenylpentanal (36884-28-3) (0.2 mmol, 2.0 equiv), mesitylene (0.1 mmol, 1.0 equiv) and DMA (0.1 mL) was added to the catalyst. Et₂O or DMA (entry 5) (0.4 mL) was added, the vial was sealed, and the reaction mixture was stirred (600 rpm) at room temperature. After 24 h, the reaction vial was removed from the glovebox and exposed to air. An aliquot was filtered through a pad of silica (approx. 1 cm) with C₆D₆ and analyzed by ¹H NMR spectroscopy. The yield of the product was determined by ¹H NMR integration against mesitylene.

General procedure for entries 5-10. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, ligand (0.010 mmol, 10 mol%), Ni(dme)Cl₂ (2.2 mg or 4.4 mg, 0.020 mmol or 0.020 mmol, 10 or 20 mol%) and Zn powder (26.2 mg, 0.4 mmol, 4.0 equiv). A stock solution of 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (0.1 mmol, 1.0 equiv), 5-phenylpentanal (36884-28-3) (0.2 mmol, 2.0 equiv), mesitylene (0.1 mmol, 1.0 equiv) and DMA (0.1 mL) was added to the catalyst. Et₂O (0.4 mL) was added, the vial was sealed, and the reaction mixture was stirred (600 rpm) at room temperature. After 24 h, the reaction vial was removed from the glovebox and exposed to air. An aliquot was filtered through a pad of silica (approx. 1 cm) with C₆D₆ and analyzed by ¹H NMR spectroscopy. The yield of the product was determined by ¹H NMR integration against mesitylene.



Isolation and Stereochemical Analysis of 4. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, (*i*-PrNDI)Ni₂Cl₂ (14.4 mg, 0.02 mmol, 10 mol%), and Zn powder (52.3 mg, 0.8 mmol, 4.0 equiv). DMA (0.2 mL) was added. A solution of 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (0.3 mmol, 1.5 equiv), 5-phenylpentanal (36884-28-3) (0.4 mmol, 2.0 equiv) and Et₂O (0.8 mL) was added. The vial was sealed, and the reaction mixture was stirred

(600 rpm) at room temperature. After 24 h, the reaction vial was opened to air and concentrated under a stream of N₂. The remaining residue was loaded directly onto SiO₂ column for purification. Bond connectivity and stereochemistry were determined through analysis of COSY and NOESY NMR.

Purification: SiO₂ column; 1% Et₂O in pentane

TLC: R_f = 0.17 (1% Et₂O in pentane)

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 4H), 7.23 – 7.16 (m, 6H), **4-anti** – 5.30 (t, *J* = 4.8 Hz, 1H), **4-syn** – 5.15 (t, *J* = 4.6 Hz, 1H), 4.49 **4-anti** – (ddd, *J* = 8.3, 4.1, 1.4 Hz, 1H), **4-syn** – 4.41 – 4.34 (m, 1H), **4-anti** – 4.02 (dd, *J* = 8.7, 1.4 Hz, 1H), **4-syn** – 3.98 (dd, *J* = 8.7, 1.7 Hz, 1H), 2.72 – 2.61 (m, 5H), 1.81 – 1.41 (m, 12H), 1.03 – 0.97 (m, 6H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 150.7, 142.7, 128.5, 128.4, 125.8, 104.9, 102.7, 77.3, 36.0, 34.3, 31.4, 25.4, 25.2, 23.7, 23.5, 23.4.

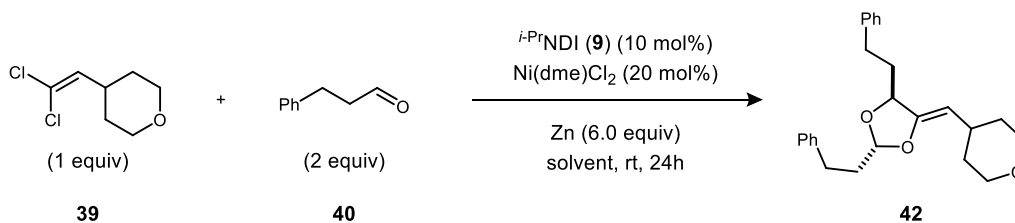


Table A2.2: Effect of Solvent

entry	Solvent	yield (%) (42)	d.r. (anti:syn)	Z/E
1	Et ₂ O/DMA (4:1)	94	5:1	>99 : 1
2	C ₆ H ₆ /DMA (4:1)	74	5:1	>99 : 1
3	THF/DMA (4:1)	84	5:1	>99 : 1
4	MeCN/DMA (4:1)	n.d.	--	--
5	NMP	56	1:3	>99 : 1
6	DMA	43	1:1	>99 : 1
7	Et ₂ O/DMA (2:3)	60	3:1	>99 : 1

Effect of Solvent. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, *i*-PrNDI (**9**) (5.3 mg, 0.010 mmol, 10 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 20mol%), and Zn (39 mg, 0.6 mmol, 6.0 equiv). A stock solution of dichloroalkene **39**⁵ (0.1 mmol, 1.0 equiv),

aldehyde **40** (104-53-0) (0.2 mmol, 2.0 equiv), mesitylene (0.1 mmol, 1.0 equiv) and DMA (0.1 mL) was added to the same vial. Additional solvent was added (total of 0.5 mL including DMA stock solution), the vial was sealed, and the reaction mixture was stirred (600 rpm) at room temperature. After 24 h, the reaction vial was removed from the glovebox and exposed to air. An aliquot was filtered through a pad of silica (approx. 1 cm) with CDCl₃ and analyzed by ¹H NMR spectroscopy. The yield and d.r. of the product was determined by ¹H NMR integration against mesitylene.

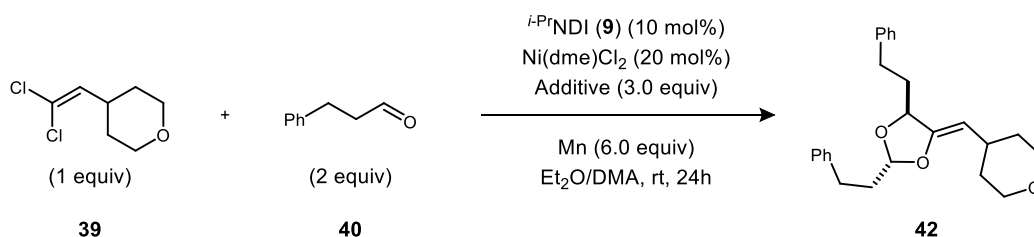


Table A2.3: Effect of Additives

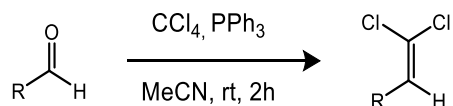
entry	additive	yield (%) (42)	d.r. (anti:syn)	Z/E
1	none	85	6:1	>99 : 1
2	<i>n</i> Bu ₄ I	70	1:1	>99 : 1
3	<i>n</i> Bu ₄ Br	95	1:3	>99 : 1
4	<i>n</i> Bu ₄ Cl	8	--	>99 : 1
5	LiBr	33	1:4	>99 : 1
6	LiCl	48	1:3	>99 : 1
7	NaBr	99	6:1	>99 : 1
8	NaCl	72	9:1	>99 : 1
9	KBr	100	6:1	>99 : 1

Effect of Additives. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, *i*-PrNDI (**9**) (5.3 mg, 0.010 mmol, 10 mol%), Ni(dme)Cl₂ (4.4 mg, 0.020 mmol, 20 mol%), additive (0.3 mmol, 3.0 equiv) and Mn (33 mg, 0.6 mmol, 6.0 equiv). A stock solution of dichloroalkene **39**⁵ (0.1 mmol, 1.0 equiv), aldehyde **40** (104-53-0) (0.2 mmol, 2.0 equiv), mesitylene (0.1 mmol, 1.0 equiv) and DMA (0.1 mL) was added to the same vial. Et₂O was added

(0.4 mL), the vial was sealed, and the reaction mixture was stirred (600 rpm) at room temperature. After 24 h, the reaction vial was removed from the glovebox and exposed to air. An aliquot was filtered through a pad of silica (approx. 1 cm) with CDCl_3 and analyzed by ^1H NMR spectroscopy. The yield and d.r. of the product was determined by ^1H NMR integration against mesitylene.

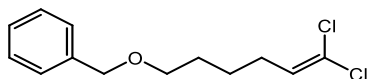
4. Synthesis and Characterization of Novel Dichloroalkenes and Aldehydes

General Procedure A. Synthesis of 1,1-Dichloroalkenes from Aldehydes



A flame-dried flask, equipped with a stir bar, was charged with PPh₃ (4.0 equiv). The flask was placed under an N₂ atmosphere, and MeCN (0.5 M) was added to create a slurry. In a separate flask was added aldehyde (1.0 equiv) and CCl₄ (2.0 equiv). The aldehyde/CCl₄ solution was added dropwise to the slurry over 5 min and the reaction was stirred for 2 h. Upon completion, the solution was diluted with Et₂O, washed with H₂O (x2) then brine. The organic layer was dried with Na₂SO₄ and concentrated to dryness. Triphenylphosphine oxide was filtered off and washed with Et₂O. The crude material was purified by flash chromatography.

Note: reactions larger than 20 mmol were cooled to 0 °C, and addition of the aldehyde solution was done over 30 min.



(((6,6-dichlorohex-5-en-1-yl)oxy)methyl)benzene (S1). The reaction was conducted with 5-(benzyloxy)pentanal⁶ (1.24 g, 6.4 mmol), CCl₄ (1.24 mL, 12.8 mmol), and PPh₃ (6.7g, 25.6mmol) in MeCN (13 mL) without modification from general procedure A to provide **S1** as a clear, colorless oil.

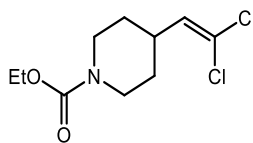
Purification: SiO₂ column; 5% EtOAc/Hexanes

557mg, 33% Yield.

¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.25 (m, 5H), 5.86 (td, *J* = 7.4, 1.7 Hz, 1H), 4.51 (s, 2H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.70 – 1.58 (m, 2H), 1.58 – 1.48 (m, 2H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 138.7, 129.9, 128.5, 127.8, 127.7, 120.2, 73.1, 70.0, 29.5, 29.3, 25.0.

HRMS (APCI) [M+H]⁺ calc. for C₁₃H₁₇Cl₂O: *m/z*=259.0651, found: *m/z*=259.0645



ethyl 4-(2,2-dichlorovinyl)piperidine-1-carboxylate (S2). The reaction was conducted with ethyl 4-formylpiperidine-1-carboxylate⁷ (99658-58-9) (5.09 g, 27.5 mmol), CCl₄ (5.3 mL, 55.0 mmol), and PPh₃ (29.1 g, 110.0 mmol) in MeCN (13 mL) without modification from general procedure A to provide **S2** as a clear, colorless oil that solidified upon standing.

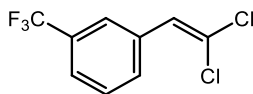
Purification: SiO₂ column; 10% EtOAc in Hexanes

3.578 g, 14% Yield

¹H NMR (500 MHz, CDCl₃) δ 5.69 (dd, *J* = 9.0, 1.2 Hz, 1H), 4.18 – 4.05 (m, 4H), 2.82 (t, *J* = 12.7 Hz, 2H), 2.60 – 2.48 (m, 1H), 1.74 – 1.67 (m, 2H), 1.37 – 1.27 (m, 2H), 1.25 (td, *J* = 7.1, 1.3 Hz, 3H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 155.6, 133.0, 120.4, 61.5, 43.5, 37.4, 30.6, 14.8.

HRMS (APCI) [M+H] calc. for C₁₀H₁₆Cl₂NO₂: *m/z*=252.0553, found: *m/z*=252.0555



1-(2,2-dichlorovinyl)-3-(trifluoromethyl)benzene (S3). The reaction was conducted with 3-(trifluoromethyl)benzaldehyde (454-89-7) (1.00 g, 5.74 mmol), CCl₄ (1.11 mL, 11.5 mmol), and PPh₃ (6.02 g, 23.0 mmol) in MeCN (12 mL) without modification from general procedure A to provide **S3** as a clear, colorless oil.

Purification: SiO₂ column; 100% Hexanes

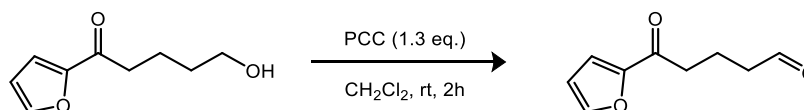
390 mg, 28% Yield

¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.71 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 6.89 (s, 1H).

¹⁹F NMR (470 MHz, CDCl₃) δ -64.39.

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 134.3, 131.9, 131.2 (q, ²*J*_{CF} = 32.4 Hz), 129.2, 127.4, 125.6 (q, ³*J*_{CF} = 4.0 Hz), 125.2 (q, ³*J*_{CF} = 3.7 Hz), 124.0 (q, ¹*J*_{CF} = 272.4 Hz), 123.3.

HRMS (APCI) [M-] calc. for C₉H₅Cl₂F₃: *m/z*=239.9715, found: *m/z*=239.9710



5-(furan-2-yl)-5-oxopentanal (S4). 1-(furan-2-yl)-5-hydroxypentan-1-one⁸ (1.40 g, 8.30 mmol, 1 equiv) was dissolved in dry CH₂Cl₂ (14 mL, 0.6 M), in a flame-dried round bottom flask containing a stir bar. PCC (2.35 g, 10.9 mmol, 1.3 equiv) and celite (800 mg) were added to the round bottom flask containing the alcohol. The reaction was stirred at rt under N₂ for 2 h. Et₂O (15 mL) was added to the reaction mixture, and the mixture was filtered through celite. The filtrate was evaporated under reduced pressure. The crude product was purified using column chromatography to provide **S4** as an off-white solid. (Note: the aldehyde decomposes rapidly under air at ambient conditions. Once purified, the aldehyde was stored in a glovebox freezer.)

Purification: SiO₂, 20% EtOAc in pentane

118 mg, 8.5% Yield.

MP: 43-45 °C

¹H NMR (500 MHz, CDCl₃) δ 9.78 (s, 1H), 7.56 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.56 (td, *J* = 7.1, 1.3 Hz, 2H), 2.04 (p, *J* = 7.1 Hz, 2H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 201.9, 188.6, 152.7, 146.5, 117.2, 112.4, 43.1, 37.2, 16.6.

HRMS (APCI) [M+H] calc. for C₉H₁₁O₃: m/z=167.0708, found: m/z=167.0702

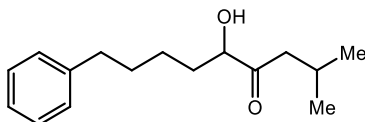
4. One Pot [2 + 2 + 1]-Cycloadditions/Deprotection and Characterization

General Procedure B (reactions with alkyl-substituted dichloroalkenes). In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, (*i*-PrNDI)Ni₂Cl₂ (**6**) (14.4 mg, 0.02 mmol, 10 mol%), and Zn powder (52.3 mg, 0.8 mmol, 4.0 equiv). DMA (0.2 mL, 2.0 M) was added. Immediately following DMA addition, a solution of 1,1-dichloroalkene (0.2 mmol, 1.0 equiv), aldehyde (0.4 mmol, 2.0 equiv) and Et₂O (0.8 mL, 0.25 M) was added. The vial was sealed with a Teflon cap, and the reaction mixture was stirred (600 rpm) at room temperature. After 24 h, the reaction vial was removed from the glovebox and opened to air.

The vial was placed in an ice bath, and a 33 vol% solution of trifluoroacetic acid (156 µL, 2.0 mmol, 10 equiv) in water was added slowly to the reaction mixture. The reaction was warmed to room temperature and stirred for 2 h. The aqueous layer was removed, and the organic layer was diluted with Et₂O (2 mL). The organic layer was washed with sat. NaHCO₃ (2 x 4 mL), washed with brine (1 x 4 mL), dried over Na₂SO₄, and concentrated to dryness. The crude product was redissolved in a minimal amount of CH₂Cl₂ and loaded onto a SiO₂ column for purification.

General Procedure C (reactions with aryl-substituted dichloroalkenes). In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, (*i*-PrNDI)Ni₂Cl₂ (**6**) (14.4 mg, 0.02 mmol, 10 mol%), and Zn powder (52.3 mg, 0.8 mmol, 4.0 equiv). DMA (0.2 mL, 2.0 M) was added. Immediately following DMA addition, a solution of 1,1-dichloroalkene (0.2 mmol, 1.0 equiv), aldehyde (0.4 mmol, 2.0 equiv) and Et₂O (0.8 mL, 0.25 M) was added. The vial was sealed with a Teflon cap, and the reaction mixture was stirred (600 rpm) at room temperature. After 24 h, the reaction vial was removed from the glovebox and opened to air.

The vial was placed in an ice bath and trifluoroacetic acid (780 µL, 10.0 mmol, 50 equiv) was added slowly to the reaction mixture. The reaction was warmed to room temperature and stirred for 2 h. The reaction was diluted with Et₂O (2 mL) and washed with H₂O (1 x 4 mL). The organic layer was washed with sat. NaHCO₃ (2 x 4mL), washed with brine (1 x 4 mL), dried over Na₂SO₄, and concentrated to dryness. The crude product was redissolved in a minimal amount of CH₂Cl₂ and loaded onto a SiO₂ column for purification.



5-hydroxy-2-methyl-9-phenylnonan-4-one (5). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 5-phenylpentanal (36884-28-3) (65.0 mg, 0.4 mmol) without modification from general procedure B to provide **5** as a light yellow oil.

Purification: SiO₂ column; 15% Et₂O in pentane

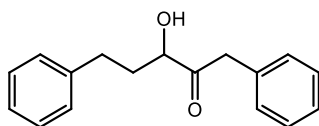
30.9 mg, 62% Yield.

TLC: R_f = 0.12 (15% Et₂O in pentane)

¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 4.12 (dt, *J* = 7.9, 4.4 Hz, 1H), 3.50 (d, *J* = 4.9 Hz, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.31 (d, *J* = 6.9 Hz, 2H), 2.19 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.84 (ddt, *J* = 11.2, 8.1, 3.7 Hz, 1H), 1.76 – 1.57 (m, 2H), 1.57 – 1.46 (m, 2H), 1.49 – 1.37 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 6H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 212.1, 142.5, 128.5, 128.5, 125.9, 76.7, 46.9, 35.9, 33.6, 31.4, 24.7, 24.7, 22.7, 22.7.

HRMS (APCI) [M-H] calc. for C₁₆H₂₃O₂: m/z = 247.1698, found: m/z = 247.17053



3-hydroxy-1,5-diphenylpentan-2-one (12). The reaction was conducted with (2,2-dichlorovinyl)benzene⁹ (698-88-4) (34.6 mg, 0.200 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **12** as a light yellow oil.

Run 1: 33.7 mg, 66% Yield. Run 2: 28.9 mg, 57% Yield

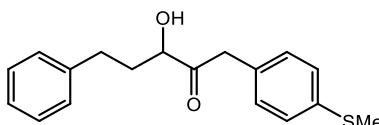
Purification: SiO₂ column; 20% Et₂O in pentane

TLC: R_f = 0.12 (25% Et₂O in pentane)

^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.27 (m, 5H), 7.25 – 7.12 (m, 5H), 4.28 (ddd, J = 8.3, 5.0, 3.5 Hz, 1H), 3.74 (s, 2H), 3.42 (d, J = 5.1 Hz, 1H), 2.86 – 2.64 (m, 2H), 2.19 (dddd, J = 13.8, 9.6, 7.1, 3.5 Hz, 1H), 1.87 (dddd, J = 13.6, 9.4, 8.1, 5.2 Hz, 1H).

^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 209.7, 141.2, 133.0, 129.5, 129.0, 128.8, 128.7, 127.5, 126.3, 75.4, 45.0, 35.6, 31.2.

HRMS (APCI) $[\text{M}-\text{H}]$ calc. for $\text{C}_{17}\text{H}_{17}\text{O}_2$: m/z =253.1223, found: m/z =253.1226



3-hydroxy-1-(4-(methylthio)phenyl)-5-phenylpentan-2-one (13). The reaction was conducted with (4-(2,2-dichlorovinyl)phenyl)(methyl)sulfane³ (43.8 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **13** as a light yellow oil.

Run 1: 40.1 mg, 67% Yield. Run 2: 32.4 mg, 54% Yield

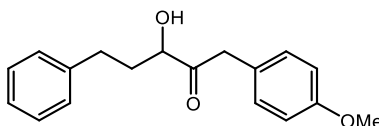
Purification: SiO_2 column; 30% Et_2O in pentane

TLC: R_f = 0.15 (40% Et_2O in pentane)

^1H NMR (500 MHz, CDCl_3) δ 7.30 (t, J = 7.5 Hz, 2H), 7.24 – 7.15 (m, 5H), 7.06 (d, J = 8.2 Hz, 2H), 4.26 (dd, J = 8.1, 3.5 Hz, 1H), 3.69 (d, J = 1.8 Hz, 2H), 3.40 (s, 1H), 2.83 – 2.62 (m, 2H), 2.47 (s, 1H), 2.18 (dddd, J = 13.4, 10.1, 7.1, 3.5 Hz, 1H), 1.86 (dtd, J = 13.8, 8.7, 5.1 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 209.7, 141.1, 137.8, 130.0, 129.7, 128.8, 128.7, 127.1, 126.3, 75.4, 44.4, 35.5, 31.2, 16.0.

HRMS (APCI) $[\text{M}-\text{H}]$ calc. for $\text{C}_{18}\text{H}_{19}\text{O}_2\text{S}$: m/z =299.1100, found: m/z =299.1101



3-hydroxy-1-(4-methoxyphenyl)-5-phenylpentan-2-one (14). The reaction was conducted with 1-(2,2-dichlorovinyl)-4-methoxybenzene⁹ (40.4 mg, 0.2 mmol) and

hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **14** as a light yellow oil.

Run 1: 46.0 mg, 81% Yield. Run 2: 51.5 mg, 94%

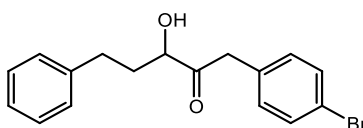
Purification: SiO₂ column; 35% Et₂O in pentane

TLC: R_f = 0.19 (40% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.14 (m, 6H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.26 (dd, *J* = 8.1, 3.5 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 2H), 2.83 – 2.60 (m, 2H), 2.18 (dddd, *J* = 13.4, 9.6, 7.1, 3.5 Hz, 1H), 1.93 – 1.79 (m, 1H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 210.1, 159.0, 141.2, 130.6, 128.8, 128.7, 126.3, 125.0, 114.4, 75.2, 55.4, 44.2, 35.6, 31.2.

HRMS (APCI) [M-H] calc. for C₁₈H₁₉O₃: m/z=283.1329, found: m/z=283.1330



1-(4-bromophenyl)-3-hydroxy-5-phenylpentan-2-one (15). The reaction was conducted with 1-bromo-4-(2,2-dichlorovinyl)benzene⁹ (50.4 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **15** as a light yellow oil.

Run 1: 36.3 mg, 54% Yield. Run 2: 37.7 mg, 57% Yield.

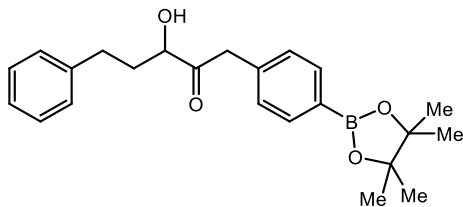
Purification: SiO₂ column; 25% Et₂O in pentane

TLC: R_f = 0.08 (25% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.25 – 7.14 (m, 3H), 7.01 (d, *J* = 8.3 Hz, 2H), 4.25 (d, *J* = 8.2 Hz, 1H), 3.68 (s, 2H), 3.39 (s, 1H), 2.86 – 2.66 (m, 2H), 2.18 (dddd, *J* = 13.9, 9.2, 7.3, 3.5 Hz, 1H), 1.95 – 1.80 (m, 1H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 209.2, 141.0, 132.0, 131.9, 131.3, 128.8, 128.7, 126.4, 121.6, 75.5, 44.2, 35.5, 31.2.

HRMS (APCI) [M-H] calc. for C₁₇H₁₆BrO₂: m/z=331.0328, found: m/z=331.0329



3-hydroxy-5-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pentan-2-one (16). The reaction was conducted with 2-(4-(2,2-dichlorovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane³ (59.8 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **16** as a light yellow oil.

Run 1: 36.0 mg, 47% Yield. Run 2: 31.5 mg, 41% Yield.

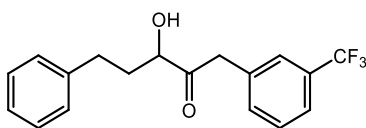
Purification: SiO₂ column: 25-30% Et₂O in pentane

TLC: R_f = 0.10 (25% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.73 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.11 (m, 5H), 4.25 (ddd, *J* = 8.3, 4.9, 3.5 Hz, 1H), 3.74 (s, 2H), 3.40 (d, *J* = 5.0 Hz, 1H), 2.83 – 2.63 (m, 2H), 2.17 (dddd, *J* = 13.9, 9.6, 7.2, 3.5 Hz, 1H), 1.93 – 1.78 (m, 1H), 1.34 (s, 12H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 209.5, 141.1, 136.1, 135.4, 128.9, 128.8, 128.7, 126.3, 84.0, 75.4, 45.3, 35.5, 31.2, 25.0.

HRMS (APCI) [M+H]⁺ calc. for C₂₃H₃₀B¹⁰O₄: m/z=380.2268, found: m/z=280.2259



3-hydroxy-5-phenyl-1-(3-(trifluoromethyl)phenyl)pentan-2-one (17). The reaction was conducted with 1-(2,2-dichlorovinyl)-3-(trifluoromethyl)benzene **S3** (48.2 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **17** as a light yellow oil.

Run 1: 29.3 mg, 45% Yield. Run 2: 29.3 mg, 45% Yield

Purification: SiO₂ column; 25% Et₂O in pentane

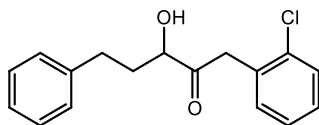
TLC: R_f = 0.09 (25% Et₂O in pentane)

^1H NMR (800 MHz, CDCl_3) δ 7.54 (d, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 7.9$, 2.6 Hz, 1H), 7.40 (s, 1H), 7.35 – 7.27 (m, 3H), 7.27 – 7.18 (m, 3H), 4.28 (ddd, $J = 8.3$, 5.0, 3.4 Hz, 1H), 3.78 (s, 2H), 3.36 (dd, $J = 5.0$, 1.7 Hz, 1H), 2.84 – 2.78 (m, 1H), 2.78 – 2.71 (m, 1H), 2.21 (dddt, $J = 13.9$, 9.0, 7.1, 3.3 Hz, 1H), 1.91 (dtd, $J = 14.0$, 8.6, 5.3 Hz, 1H).

^{19}F NMR (376 MHz, CDCl_3) δ -64.17.

^{13}C NMR (201 MHz, CDCl_3) δ 208.9, 140.9, 133.9, 133.0, 131.2 (q, $^2J_{\text{CF}} = 32.2$ Hz), 129.3, 128.8, 128.8, 126.5, 126.4 (q, $^3J_{\text{CF}} = 3.7$ Hz), 124.4 (q, $^3J_{\text{CF}} = 3.8$ Hz), 124.1 (q, $^1J_{\text{CF}} = 272.4$ Hz), 75.7, 44.4, 35.5, 31.2.

HRMS (ESI) $[\text{M}+\text{Na}]$ calc. for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{O}_2\text{Na}$: $m/z=345.1073$, found: $m/z=345.1077$



1-(2-chlorophenyl)-3-hydroxy-5-phenylpentan-2-one (18). The reaction was conducted with 1-chloro-2-(2,2-dichlorovinyl)benzene³ (41.5 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **18** as an off-white solid.

Run 1: 33.7 mg, 58% Yield. Run 2: 31.4 mg, 54% Yield

Purification: SiO_2 column; 25% Et_2O in pentane

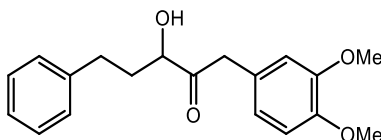
TLC: $R_f = 0.10$ (25% Et_2O in pentane)

MP: 55-57 $^\circ\text{C}$

^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 7.27 – 7.07 (m, 6H), 4.33 (ddd, $J = 8.4$, 5.0, 3.5 Hz, 1H), 3.99 – 3.80 (m, 2H), 3.40 (d, $J = 5.0$ Hz, 1H), 2.89 – 2.69 (m, 2H), 2.25 (dddd, $J = 13.9$, 9.1, 7.7, 3.5 Hz, 1H), 1.93 (dtd, $J = 14.3$, 8.4, 6.1 Hz, 1H).

^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 208.6, 141.2, 134.4, 131.9, 131.7, 129.7, 129.1, 128.8, 128.7, 127.2, 126.3, 75.7, 42.9, 35.7, 31.3.

HRMS (APCI) $[\text{M}-\text{H}]$ calc. for $\text{C}_{17}\text{H}_{16}\text{ClO}_2$: $m/z=287.0833$, found: $m/z=287.0838$



1-(3,4-dimethoxyphenyl)-3-hydroxy-5-phenylpentan-2-one (19). The reaction was conducted with 4-(2,2-dichlorovinyl)-1,2-dimethoxybenzene³ (60561-55-9) (46.6 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure C to provide **19** as a light-yellow oil.

Run 1: 38.8 mg, 62% Yield. Run 2: 39.7 mg, 63% Yield

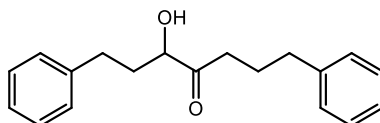
Purification: SiO₂ column; 45% Et₂O in pentane

TLC: R_f = 0.12 in 45% Et₂O in pentane

¹H NMR (500 MHz, CDCl₃) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.71 – 6.64 (m, 2H), 4.27 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.67 (s, 2H), 3.40 (s, 1H), 2.83 – 2.74 (m, 1H), 2.74 – 2.65 (m, 1H), 2.18 (dddd, *J* = 13.4, 10.4, 7.1, 3.5 Hz, 1H), 1.91 – 1.80 (m, 1H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 210.1, 149.2, 148.5, 141.1, 128.7, 128.7, 126.3, 125.4, 121.7, 112.5, 111.5, 75.2, 56.0, 44.6, 35.6, 31.2.

HRMS (APCI) [M-H] calc. for C₁₉H₂₁O₄: m/z=313.1434, found: m/z=313.1430



3-hydroxy-1,7-diphenylheptan-4-one (20). The reaction was conducted with (4,4-dichlorobut-3-en-1-yl)benzene⁹ (40.2 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **20** as a light-yellow oil.

Run 1: 45.6 mg, 81% Yield. Run 2: 44.6 mg, 79% Yield.

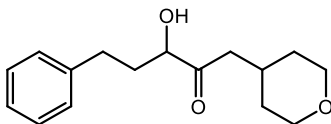
Purification: SiO₂ column; 20% Et₂O in pentane

TLC: R_f = 0.15 (25% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.26 (m, 4H), 7.24 – 7.12 (m, 6H), 4.12 (d, *J* = 8.1 Hz, 1H), 3.54 (s, 1H), 2.83 – 2.65 (m, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.52 – 2.32 (m, 2H), 2.09 (dddd, *J* = 13.8, 9.7, 7.1, 3.5 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.77 (dddd, *J* = 13.7, 9.4, 8.4, 5.2 Hz, 1H).

^{13}C { ^1H } NMR (101 MHz, CDCl_3) δ 212.0, 141.2, 128.7, 128.7, 128.6, 128.6, 126.3, 75.8, 37.0, 35.7, 35.1, 31.3, 25.1.

HRMS (APCI) $[\text{M}+\text{H}]$ calc. for $\text{C}_{19}\text{H}_{23}\text{O}_2$: $m/z=283.1693$, found: $m/z=283.1686$



3-hydroxy-5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentan-2-one (21). The reaction was conducted with 4-(2,2-dichlorovinyl)tetrahydro-2H-pyran⁵ (36.2 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **21** as a light yellow oil.

Run 1: 45.6 mg, 87% Yield; Run 2: 36.1 mg, 69% Yield

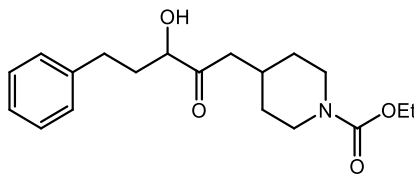
Purification: SiO_2 column; 50% Et_2O in pentane

TLC: $R_f = 0.11$ (50% Et_2O in pentane)

^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.11 (ddd, $J = 8.3$, 4.8, 3.4 Hz, 1H), 3.97 – 3.88 (m, 2H), 3.51 (d, $J = 4.9$ Hz, 1H), 3.40 (td, $J = 11.8$, 2.2 Hz, 2H), 2.86 – 2.66 (m, 2H), 2.43 – 2.27 (m, 2H), 2.19 – 2.03 (m, 1H), 1.79 (dtd, $J = 14.1$, 8.8, 5.4 Hz, 1H), 1.62 – 1.52 (m, 2H), 1.36 – 1.19 (m, 2H).

^{13}C { ^1H } NMR (101 MHz, CDCl_3) δ 211.2, 141.2, 128.7, 128.7, 126.4, 76.2, 67.8, 44.9, 35.7, 33.0, 32.9, 31.4, 30.9.

HRMS (APCI) $[\text{M}+\text{Na}]$ calc. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}$: $m/z=285.1461$, found: $m/z=285.1464$



ethyl 4-(3-hydroxy-2-oxo-5-phenylpentyl)piperidine-1-carboxylate (22). The reaction was conducted with ethyl 4-(2,2-dichlorovinyl)piperidine-1-carboxylatediene **S2** (50.4 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **22** as a light yellow oil.

Run 1: 38.3 mg, 57% Yield. Run 2: 48.7 mg, 73% Yield

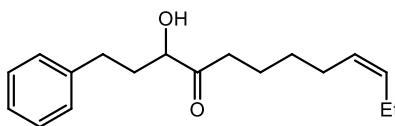
Purification: SiO₂ column; 10% Et₂O in CH₂Cl₂

TLC: R_f = 0.18 (10% Et₂O in CH₂Cl₂)

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.25 (m, 2H), 7.25 – 7.14 (m, 3H), 4.11 (q, *J* = 6.8 Hz, 5H), 3.49 (d, *J* = 4.9 Hz, 1H), 2.85 – 2.68 (m, 4H), 2.42 – 2.25 (m, 2H), 2.17 – 1.95 (m, 2H), 1.77 (dtd, *J* = 14.1, 8.8, 5.5 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.18 – 1.00 (m, 2H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 211.2, 155.6, 141.1, 128.7, 128.7, 126.4, 76.1, 61.4, 44.5, 43.9, 35.7, 32.1, 31.9, 31.8, 31.3, 14.8.

HRMS (APCI) [M+H] calc. for C₁₉H₂₈NO₄: m/z=334.2013, found: m/z=334.2011



(Z)-3-hydroxy-1-phenyldodec-9-en-4-one (23). The reaction was conducted with (Z)-1,1-dichloronona-1,6-diene³ (38.6 mg, 0.2 mmol) hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **23** as a light yellow oil.

Run 1: 49.1 mg, 89% Yield. Run 2: 45.9 mg, 84% Yield.

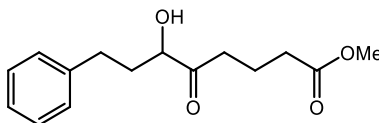
Purification: SiO₂ column; 15% Et₂O in pentane

TLC: R_f = 0.21 (25% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.25 (m, 2H), 7.25 – 7.16 (m, 3H), 5.43 – 5.33 (m, 1H), 5.33 – 5.22 (m, 1H), 4.15 (dt, *J* = 8.2, 4.0 Hz, 1H), 3.56 (d, *J* = 4.7 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.51 – 2.33 (m, 2H), 2.21 – 2.07 (m, 1H), 2.07 – 1.93 (m, 4H), 1.80 (dddd, *J* = 13.8, 9.3, 8.4, 5.3 Hz, 1H), 1.60 (dt, *J* = 15.3, 7.5 Hz, 2H), 1.39 – 1.23 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 212.3, 141.3, 132.4, 128.7, 128.7, 128.5, 126.3, 75.8, 37.9, 35.8, 31.3, 29.4, 26.9, 23.3, 20.7, 14.5.

HRMS (APCI) [M+H] calc. for C₁₈H₂₇O₂: m/z=275.2006, found: m/z=275.2009



methyl 6-hydroxy-5-oxo-8-phenyloctanoate (24). The reaction was conducted with methyl 5,5-dichloropent-4-enoate¹⁰ (36.6 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **24** as a light yellow oil.

Run 1: 36.9 mg, 70% Yield. Run 2: 37.7 mg, 71% Yield.

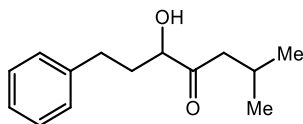
Purification: SiO₂ column; 40% Et₂O in pentane

TLC: R_f = 0.11 (40% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 4.15 (dd, *J* = 8.4, 3.5 Hz, 1H), 3.66 (s, 3H), 2.85 – 2.67 (m, 2H), 2.61 – 2.38 (m, 2H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.13 (m, 1H), 1.92 (p, *J* = 7.1 Hz, 2H), 1.81 (m, 1H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 211.5, 173.4, 141.2, 128.8, 128.7, 126.3, 75.8, 51.8, 36.8, 35.7, 33.0, 31.3, 18.8.

HRMS (APCI) [M+H] calc. for C₁₅H₂₁O₄: m/z=265.1434, found: m/z=265.1440



3-hydroxy-6-methyl-1-phenylheptan-4-one (25). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **25** as a light yellow oil.

Run 1: 36.1 mg, 82% Yield. Run 2: 34.4 mg, 78% Yield

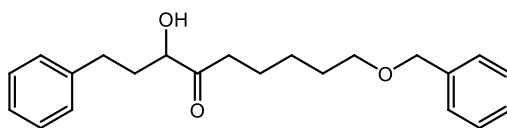
Purification: SiO₂ column; 20% Et₂O in pentane

TLC: R_f = 0.27 (25% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 2H), 7.24 – 7.15 (m, 3H), 4.12 (ddd, *J* = 8.3, 4.7, 3.4 Hz, 1H), 3.60 (d, *J* = 4.8 Hz, 1H), 2.86 – 2.66 (m, 2H), 2.34 – 2.28 (m, 1H), 2.27 – 2.06 (m, 2H), 1.78 (dddd, *J* = 13.8, 9.4, 8.4, 5.3 Hz, 1H), 0.92 (dd, *J* = 6.6, 4.4 Hz, 6H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 211.9, 141.3, 128.7, 128.6, 126.3, 76.1, 46.9, 35.7, 31.4, 24.6, 22.8, 22.6.

HRMS (APCI) [M+Na] calc. for C₁₄H₂₀O₂Na: m/z=243.1353, found: m/z=243.1357



9-(benzyloxy)-3-hydroxy-1-phenylnonan-4-one (26).

The reaction was conducted with (((6,6-dichlorohex-5-en-1-yl)oxy)methyl)benzene **S1** (51.8 mg, 0.2 mmol) and hydrocinnamaldehyde (104-53-0) (53.7 mg, 0.4 mmol) without modification from general procedure B to provide **26** as a light yellow oil.

Run 1: 51.5 mg, 76% Yield. Run 2: 56.2 mg, 83% Yield.

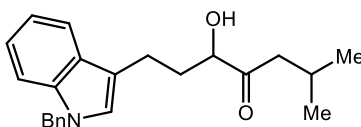
Purification: SiO₂ column; 30% Et₂O in pentane

TLC: R_f = 0.22 (40% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.26 (m, 7H), 7.24 – 7.16 (m, 3H), 4.49 (s, 2H), 4.14 (dd, *J* = 8.4, 3.4 Hz, 1H), 3.45 (t, *J* = 6.5 Hz, 2H), 2.85 – 2.67 (m, 2H), 2.52 – 2.33 (m, 2H), 2.19 – 2.06 (m, 1H), 1.79 (dddd, *J* = 13.8, 9.3, 8.4, 5.3 Hz, 1H), 1.67 – 1.55 (m, 4H), 1.47 – 1.30 (m, 2H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 212.2, 141.3, 138.7, 128.7, 128.7, 128., 127.8, 127.7, 126.3, 75.8, 73.1, 70.1, 37.9, 35.7, 31.3, 29.6, 26.0, 23.5.

HRMS (APCI) [M+H] calc. for C₂₂H₂₉O₃: m/z=341.2111, found: m/z=341.2116



1-(1-benzyl-1H-indol-2-yl)-3-hydroxy-6-methylheptan-4-one (27). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 3-(1-benzyl-1H-indol-2-yl)propanal ¹¹ (105.3 mg, 0.4 mmol) without modification from general procedure B to provide **27** as a cream colored solid.

Run 1: 46.2 mg, 66% Yield. Run 2: 50.4 mg, 70% Yield

Purification: SiO₂ column; 20% Et₂O in pentane

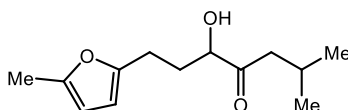
TLC: R_f = 0.10 (25% Et₂O in pentane)

MP: 44-47 °C

^1H NMR (400 MHz, CDCl_3) δ 7.63 (dt, $J = 7.7, 1.1$ Hz, 1H), 7.34 – 7.07 (m, 8H), 6.95 (s, 1H), 5.28 (s, 2H), 4.21 – 4.12 (m, 1H), 3.61 (d, $J = 4.8$ Hz, 1H), 3.02 – 2.85 (m, 2H), 2.30 – 2.07 (m, 4H), 1.86 (dtd, $J = 14.0, 8.4, 5.7$ Hz, 1H), 0.88 (dd, $J = 6.6, 1.8$ Hz, 6H).

^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 212.7, 137.8, 136.9, 128.9, 128.2, 127.7, 126.9, 126.1, 122.0, 120.2, 119.2, 114.5, 109.9, 76.3, 50.0, 46.8, 34.5, 24.7, 22.8, 22.6, 20.8.

HRMS (APCI) $[\text{M}+\text{H}]$ calc. for $\text{C}_{13}\text{H}_{19}\text{NO}_2$: $m/z=350.2115$, found: $m/z=350.2110$



3-hydroxy-6-methyl-1-(5-methylfuran-2-yl)heptan-4-one (28). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and ethyl 3-(5-methylfuran-2-yl)propanal (34756-16-6) (55.3 mg, 0.4 mmol) without modification from general procedure B to provide **28** as a light yellow oil.

Run 1: 33.9 mg, 76% Yield. Run 2: 30.7 mg, 68% Yield.

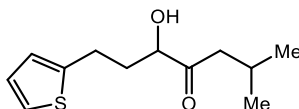
Purification: SiO_2 column; 10% Et_2O in pentane

TLC: $R_f = 0.18$ (15% Et_2O in pentane)

^1H NMR (400 MHz, CDCl_3) δ 5.91 – 5.81 (m, 2H), 4.12 (ddd, $J = 8.3, 4.5, 3.4$ Hz, 1H), 3.56 (d, $J = 4.8$ Hz, 1H), 2.82 – 2.64 (m, 2H), 2.35 – 2.29 (m, 2H), 2.26 (s, 3H), 2.24 – 2.11 (m, 2H), 1.76 (dtd, $J = 14.0, 8.5, 5.6$ Hz, 1H), 0.92 (dd, $J = 6.6, 3.9$ Hz, 6H).

^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 211.8, 153.0, 150.8, 106.5, 106.1, 76.0, 46.8, 32.4, 24.7, 23.8, 22.8, 22.7, 13.7.

HRMS (APCI) $[\text{M}+\text{H}]$ calc. for $\text{C}_{13}\text{H}_{21}\text{O}_3$: $m/z=225.1485$, found: $m/z=225.1483$



3-hydroxy-6-methyl-1-(thiophen-2-yl)heptan-4-one (29). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 3-(thiophen-2-

yl)propanal¹² (26359-21-7)(50.5mg, 0.4 mmol) without modification from general procedure B to provide **29** as a light yellow oil.

Run 1: 36.8 mg, 81% Yield. Run 2: 36.0 mg, 80% Yield.

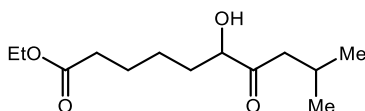
Purification: SiO₂ column; 10% Et₂O in pentane

TLC: R_f = 0.18 (15% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.83 (dq, *J* = 3.3, 1.0 Hz, 1H), 4.14 (ddd, *J* = 8.5, 4.8, 3.3 Hz, 1H), 3.57 (d, *J* = 4.9 Hz, 1H), 3.11 – 2.86 (m, 2H), 2.36 – 2.29 (m, 2H), 2.28 – 2.12 (m, 2H), 1.81 (dtd, *J* = 13.8, 8.9, 5.0 Hz, 1H), 0.92 (dd, *J* = 6.6, 4.3 Hz, 6H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 211.8, 143.9, 127.1, 125.1, 123.6, 75.8, 46.9, 35.9, 25.6, 24.7, 22.8, 22.7.

HRMS (APCI) [M+H] calc. for C₁₂H₁₉O₂S: m/z=227.1100, found: m/z=227.1103



ethyl 6-hydroxy-9-methyl-7-oxodecanoate (30). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and ethyl 6-oxohexanoate¹³ (63.3 mg, 0.4 mmol) without modification from general procedure B to provide **30** as a light yellow oil.

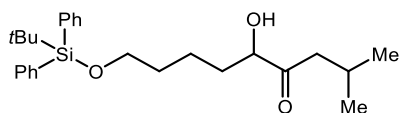
Run 1: 31.4 mg, 64% Yield. Run 2: 21.2 mg, 43% Yield.

Purification: SiO₂ column; 30% Et₂O in pentane

¹H NMR (500 MHz, CDCl₃) δ 4.23 – 4.10 (m, 3H), 3.55 (d, *J* = 4.9 Hz, 1H), 2.45 – 2.33 (m, 4H), 2.26 (dp, *J* = 13.5, 6.7 Hz, 1H), 1.96 – 1.82 (m, 1H), 1.80 – 1.64 (m, 2H), 1.62 – 1.48 (m, 2H), 1.50 – 1.37 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.99 (dd, *J* = 6.6, 4.1 Hz, 6H).

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 212.0, 173.6, 76.6, 60.4, 46.9, 34.2, 33.4, 24.8, 24.7, 24.6, 22.7, 22.7, 14.4.

HRMS (APCI) [M+H] calc. for C₁₃H₂₅O₄: m/z=245.17526, found: m/z=245.17353



9-((tert-butyldiphenylsilyl)oxy)-5-hydroxy-2-methylnonan-4-one (31). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 5-((tert-butyldiphenylsilyl)oxy)pentanal¹⁴ (136.2 mg, 0.4 mmol) without modification from general procedure B to provide **31** as a light yellow oil.

Run 1: 53.2 mg, 62% Yield. Run 2: 34.7 mg, 41% Yield.

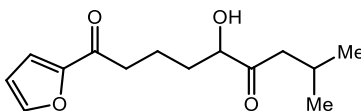
Purification: 15% Et₂O in pentane

TLC: R_f = 0.17 (15% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.62 (m, 4H), 7.47 – 7.33 (m, 6H), 4.15 – 4.06 (m, 1H), 3.66 (t, *J* = 6.1 Hz, 2H), 3.49 (d, *J* = 4.9 Hz, 1H), 2.32 (d, *J* = 6.9 Hz, 2H), 2.20 (ddd, *J* = 12.9, 7.3, 6.4 Hz, 1H), 1.85 – 1.74 (m, 1H), 1.69 – 1.34 (m, 5H), 1.04 (s, 9H), 0.93 (dd, *J* = 6.6, 1.9 Hz, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 212.1, 135.7, 134.1, 129.7, 127.8, 63.7, 46.9, 33.5, 32.4, 27.0, 24.7, 22.8, 22.7, 21.4, 19.4.

HRMS (APCI) [M+H]⁺ calc. for C₂₆H₃₉O₃Si: *m/z* = 427.2663, found: *m/z* = 427.2666



1-(furan-2-yl)-5-hydroxy-8-methylnonane-1,6-dione (32). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 5-(furan-2-yl)-5-oxopentanal (**S4**) (66.5 mg, 0.4 mmol) without modification from general procedure B to provide **32** as a light yellow oil.

Run 1: 25.2 mg, 50% Yield. Run 2: 25.6 mg, 51% Yield

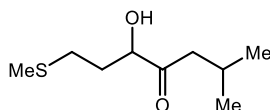
Purification: SiO₂ column; 5% Et₂O in CH₂Cl₂

TLC: R_f = 0.19 (5% Et₂O in CH₂Cl₂)

¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.18 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.15 (ddd, *J* = 8.1, 4.9, 3.4 Hz, 1H), 3.56 (d, *J* = 4.8 Hz, 1H), 2.89 (td, *J* = 6.9, 2.0 Hz, 2H), 2.45 – 2.29 (m, 2H), 2.20 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.98 – 1.72 (m, 3H), 1.66 – 1.50 (m, 1H), 0.93 (dd, *J* = 6.6, 4.7 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 212.0, 189.2, 146.5, 117.1, 112.4, 76.6, 46.9, 37.8, 32.9, 24.7, 22.8, 22.7, 19.6.

HRMS (APCI) $[\text{M}+\text{Na}]$ calc. for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{Na}$: $m/z=275.1254$, found: $m/z=275.1255$



3-hydroxy-6-methyl-1-(methylthio)heptan-4-one (33). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 3-(methylthio)propionaldehyde (3268-49-3) (41.7 mg, 0.4 mmol) without modification from general procedure B to provide **33** as a light yellow oil.

Run 1: 8.1 mg, 23% Yield. Run 2: 5.0 mg, 13% Yield.

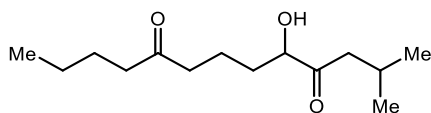
Purification: SiO_2 column; 20% Et_2O in pentane

TLC: $R_f = 0.18$ (25% Et_2O in pentane)

^1H NMR (400 MHz, CDCl_3) δ 4.25 (ddd, $J = 8.4, 4.9, 3.3$ Hz, 1H), 3.55 (d, $J = 4.9$ Hz, 1H), 2.75 – 2.53 (m, 2H), 2.37 (dd, $J = 7.0, 2.0$ Hz, 2H), 2.29 – 2.14 (m, 1H), 2.13 (s, 3H), 2.14 – 2.02 (m, 1H), 1.74 (dtd, $J = 13.8, 8.3, 5.2$ Hz, 1H), 0.94 (dd, $J = 6.7, 2.8$ Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 211.6, 75.7, 47.0, 33.4, 30.2, 24.8, 22.8, 22.7, 15.9.

HRMS (APCI) $[\text{M}+\text{H}]$ calc. for $\text{C}_9\text{H}_{19}\text{O}_2\text{S}$: $m/z=191.1100$, found: $m/z=191.1102$



5-hydroxy-2-methyltridecane-4,9-dione (34). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 5-oxononanal¹⁵ (62.5 mg, 0.4 mmol) without modification from general procedure B to provide **34** as a light yellow oil.

Run 1: 22.8 mg, 47% Yield. Run 2: 31.4 mg, 65% Yield.

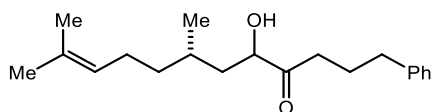
Purification: SiO_2 column; 25% Et_2O in pentane

TLC: $R_f = 0.07$ (25% Et_2O in pentane)

^1H NMR (400 MHz, CDCl_3) δ 4.09 (dt, $J = 7.8, 3.9$ Hz, 1H), 3.55 (d, $J = 4.8$ Hz, 1H), 2.50 – 2.32 (m, 6H), 2.18 (dp, $J = 13.4, 6.7$ Hz, 1H), 1.93 – 1.42 (m, 6H), 1.35 – 1.21 (m, 2H), 0.96 – 0.82 (m, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 211.9, 211.1, 76.6, 46.8, 42.7, 42.1, 32.9, 26.1, 24.6, 22.7, 22.6, 22.5, 19.2, 14.0.

HRMS (APCI) $[\text{M}-\text{H}]$ calc. for $\text{C}_{14}\text{H}_{25}\text{O}_3$: $m/z=241.1798$, found: $m/z=241.1801$



(7S)-5-hydroxy-7,11-dimethyl-1-phenyldodec-10-en-4-one (35). The reaction was conducted with (4,4-dichlorobut-3-en-1-yl)benzene (40.2 mg, 0.2 mmol) and (*S*)-citronellal (5949-05-3) (61.7 mg, 0.4 mmol) without modification from general procedure B to provide **35** as a light yellow oil.

Run 1: 47.6 mg, 79% Yield. Run 2: 45.7 mg, 76% Yield. 1:1 d.r.

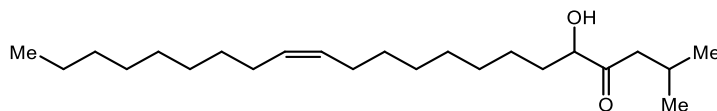
Purification: SiO_2 column; 10% Et_2O in pentane

TLC: $R_f = 0.21$ (15% Et_2O in pentane)

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.25 (m, 2H), 7.25 – 7.13 (m, 3H), 5.10 (dtp, $J = 9.9, 7.1, 1.4$ Hz, 1H), 4.20 – 4.11 (m, 1H), 3.37 (t, $J = 4.9$ Hz, 1H), 2.64 (td, $J = 7.6, 1.6$ Hz, 2H), 2.58 – 2.34 (m, 2H), 2.05 – 1.87 (m, 2H), 1.87 – 1.72 (m, 1H), 1.75 – 1.56 (m, 7H), 1.58 – 1.47 (m, 1H), 1.51 – 1.37 (m, 1H), 1.41 – 1.27 (m, 1H), 1.27 (ddd, $J = 7.9, 4.5, 1.9$ Hz, 1H), 1.26 – 1.06 (m, 1H), 0.95 (dd, $J = 15.1, 6.7$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 212.7, 141.3, 131.5, 128.6, 128.6, 126.2, 124.7, 124.6, 75.3, 74.9, 41.5, 41.3, 38.1, 37.1, 37.0, 35.8, 35.1, 29.5, 29.2, 25.9, 25.6, 25.4, 25.2, 20.5, 18.7, 17.8.

HRMS (APCI) $[\text{M}+\text{H}]$ calc. for $\text{C}_{20}\text{H}_{31}\text{O}_2$: $m/z=303.2319$, found: $m/z=303.2321$



(Z)-5-hydroxy-2-methyldocos-13-en-4-one (36). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and olealdehyde¹⁶ (106.6 mg, 0.4 mmol) without modification from general procedure B to provide **36** as a light yellow oil.

Run 1: 35.1 mg, 50% Yield. Run 2: 35.0 mg, 50% Yield

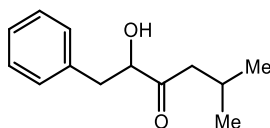
Purification: 5% Et₂O in pentane

TLC: R_f = 0.08 (5% Et₂O in pentane)

¹H NMR (500 MHz, CDCl₃) δ 5.40 – 5.29 (m, 2H), 4.15 – 4.09 (m, 1H), 3.48 (d, *J* = 5.0 Hz, 1H), 2.38 – 2.32 (m, 2H), 2.21 (dp, *J* = 13.4, 6.7 Hz, 1H), 2.09 – 1.97 (m, 4H), 1.86 – 1.76 (m, 1H), 1.53 – 1.42 (m, 1H), 1.37 – 1.32 (m, 2H), 1.35 – 1.24 (m, 22H), 0.94 (dd, *J* = 6.6, 4.6 Hz, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).

¹³C{¹H} NMR (126 MHz, C₆D₆) δ 211.5, 130.3, 130.2, 76.8, 46.5, 34.1, 32.3, 30.3, 30.2, 30.0, 29.9, 29.9, 29.8, 29.8, 29.7, 27.7, 27.7, 25.4, 24.5, 23.1, 22.6, 22.5, 14.4.

HRMS (APCI) [M-H] calc. for C₂₃H₄₃O₂: m/z=351.3263; found: m/z=351.3276



2-hydroxy-5-methyl-1-phenylhexan-3-one (37). The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 2-phenylacetaldehyde (122-78-1) (48.0 mg, 0.4 mmol) without modification from general procedure B to provide **37** as a light yellow oil.

Run 1: 30.2 mg, 73% Yield. Run 2: 30.3 mg, 73% Yield.

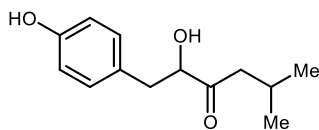
Purification: SiO₂ column; 10% Et₂O in pentane

TLC: R_f = 0.15 (15% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.27 (m, 2H), 7.31 – 7.20 (m, 3H), 4.37 (dt, *J* = 7.5, 4.8 Hz, 1H), 3.43 (d, *J* = 5.4 Hz, 1H), 3.13 (dd, *J* = 14.1, 4.5 Hz, 1H), 2.83 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.37 (d, *J* = 6.9 Hz, 2H), 2.18 (dp, *J* = 13.5, 6.7 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 6H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 211.3, 136.8, 129.4, 128.7, 127.0, 77.6, 47.6, 40.2, 29.8, 24.7, 22.8, 22.7.

HRMS (APCI) [M+H] calc. for C₁₃H₁₉O₂: m/z=207.1380, found: m/z=207.1378



2-hydroxy-1-(4-hydroxyphenyl)-5-methylhexan-3-one [(±) 4-hydroxysattabacin] (38).

The reaction was conducted with 1,1-dichloro-3-methylbut-1-ene (32363-91-0) (27.8 mg, 0.2 mmol) and 2-(4-((trimethylsilyl)oxy)phenyl)acetaldehyde ¹⁷ (83.3 mg, 0.4 mmol) without modification from general procedure B to provide **38** as a light yellow oil.

Run 1: 17.8 mg, 40% Yield. Run 2: 18.6 mg, 42% Yield

Purification: 40% Et₂O in pentane

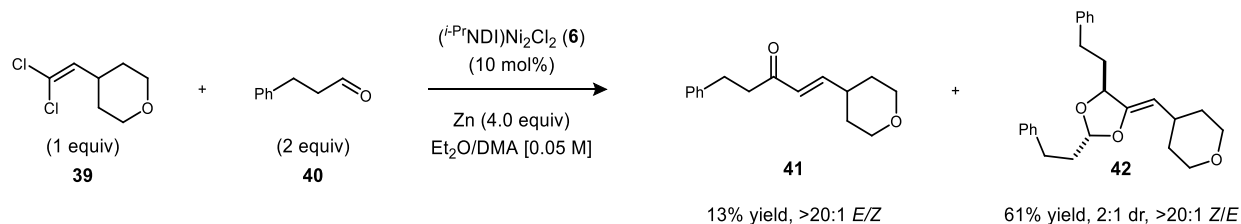
TLC: R_f = 0.13 (40% Et₂O in pentane)

¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.92 (s, 1H), 4.34 (dt, *J* = 7.3, 4.8 Hz, 1H), 3.45 (d, *J* = 5.4 Hz, 1H), 3.07 (dd, *J* = 14.3, 4.5 Hz, 1H), 2.76 (dd, *J* = 14.3, 7.4 Hz, 1H), 2.37 (d, *J* = 6.9 Hz, 2H), 2.27 – 2.09 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 5H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 211.5, 154.7, 130.6, 128.7, 115.6, 77.7, 47.6, 39.3, 24.8, 22.8, 22.7.

HRMS (APCI) [M+H] calc. for C₁₃H₁₉O₃=223. 1329; found m/z=223.1335

5. Mechanistic Studies



Catalytic C(sp²)-H bond insertion vs. [2 + 2 + 1]-cycloaddition under dilute conditions. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, (*i*-PrNDI)Ni₂Cl₂ (**6**) (7.2 mg, 0.01 mmol, 10 mol%), and Zn powder (26.1 mg, 0.4 mmol, 4.0 equiv). DMA (0.4 mL) was added. A stock solution of 1,1-dichloroalkene **39**⁵ (9.0 mg, 0.10 mmol, 1.0 equiv), aldehyde **40** (104-53-0) (13.4 mg, 0.2 mmol, 2.0 equiv), mesitylene (12 mg, 0.10 mmol, 1.0 equiv), and Et₂O (0.4 mL) was added. The reaction was diluted with additional Et₂O (1.2 mL). The vial was sealed,

and the reaction mixture was stirred (600 rpm) at room temperature for 24 h. The reaction was removed from the glovebox and exposed to air. An aliquot was removed, filtered through a small pad of silica (approx. 1 cm) eluting with CDCl₃, and analyzed by ¹H NMR spectroscopy. The product yields were determined by ¹H NMR integration against mesitylene. The products were isolated via column chromatography (10 to 25% Et₂O in pentane). COSY and NOESY were used to determine stereochemistry of **42**.

(E)-5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pent-1-en-3-one (41).

13 % NMR Yield

TLC: R_f = 0.19 (20% EtOAc in hexanes)

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 4H), 6.72 (dd, *J* = 16.0, 6.6 Hz, 1H), 6.07 (dd, *J* = 16.0, 1.4 Hz, 1H), 3.99 (ddd, *J* = 11.6, 4.6, 2.0 Hz, 2H), 3.43 (td, *J* = 11.8, 2.2 Hz, 2H), 3.02 – 2.79 (m, 4H), 2.44 – 2.28 (m, 1H), 1.65 (ddd, *J* = 13.2, 4.1, 2.1 Hz, 2H), 1.56 – 1.39 (m, 2H).

¹³C{¹H} NMR (126 MHz, CDCl₃) δ 199.8, 150.2, 141.4, 128.6, 128.6, 128.5, 126.3, 67.5, 42.0, 38.0, 31.5, 30.2.

HRMS (APCI) [M-H] calc. for C₁₆H₁₉O₂=243.1385. found *m/z*=243.1395

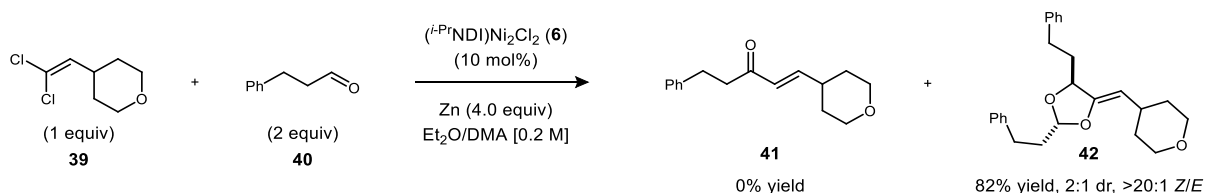
(Z)-4-((2,5-diphenethyl-1,3-dioxolan-4-ylidene)methyl)tetrahydro-2H-pyran (42).

61% NMR Yield; 2:1 d.r.; >20:1 *Z/E*

TLC: R_f = 0.62 (20% EtOAc in hexanes)

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.17 (m, 10H), **42-anti** – 5.39 (t, *J* = 4.8 Hz, 1H), **42-syn** – 5.21 (t, *J* = 4.5 Hz, 1H), **42-anti** – 4.56 (ddd, *J* = 8.5, 4.2, 1.4 Hz, 1H), **42-syn** – 4.43 (dt, *J* = 8.1, 2.5 Hz, 1H), 4.07 (dd, *J* = 8.5, 1.4 Hz, 1H), **42-syn** – 4.03 (dd, *J* = 8.5, 1.7 Hz, 2H), **42-anti** – 3.93 (ddd, *J* = 11.6, 4.3, 2.3 Hz, 2H), 3.46 (tt, *J* = 11.6, 2.2 Hz, 2H), 2.88 – 2.68 (m, 4H), 2.64 – 2.53 (m, 1H), **42-syn** – 2.15 – 2.08 (m, 1H), 2.08 – 1.99 (m, 2H), 1.97 – 1.81 (m, 2H), 1.67 – 1.57 (m, 2H), 1.48 – 1.35 (m, 2H).

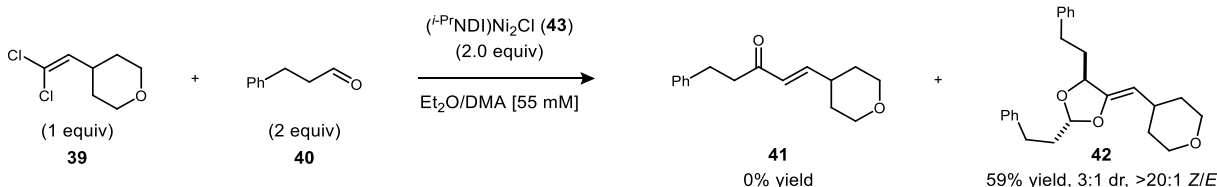
¹³C{¹H} NMR (126 MHz, CDCl₃) δ 151.7, 141.6, 141.4, 128.6, 128.6, 128.6, 126.1, 104.6, 99.6, 76.7, 68.0, 36.2, 36.0, 33.5, 33.2, 32.1, 31.7, 29.9.



Catalytic C(sp²)–H bond insertion vs. [2 + 2 + 1]-cycloaddition under concentrated conditions. In an N₂-filled glovebox, a 2-dram vial was charged with a magnetic stir bar, (*i*-Pr₃NDI)Ni₂Cl₂ (**6**) (7.2 mg, 0.01 mmol, 10 mol%), and Zn powder (26.1 mg, 0.4 mmol, 4.0 equiv). DMA (0.1 mL) was added. A stock solution of 1,1-dichloroalkene **39** (18.1 mg, 0.1 mmol, 1.0 equiv), aldehyde **40** (13.4 mg, 0.2 mmol, 2.0 equiv), mesitylene (12 mg, 0.10 mmol, 1.0 equiv) and Et₂O (0.4 mL) was added. The vial was sealed, and the reaction mixture was stirred (600 rpm) at room temperature for 24 h. The reaction was removed from the glovebox and exposed to air. An aliquot was removed, filtered through a small pad of silica (approx. 1 cm) eluting with CDCl₃, and analyzed by ¹H NMR spectroscopy. The product yields were determined by ¹H NMR integration against mesitylene.

30: 81% Yield; 2:1 d.r.; >20:1 Z/E

31: 0 % Yield

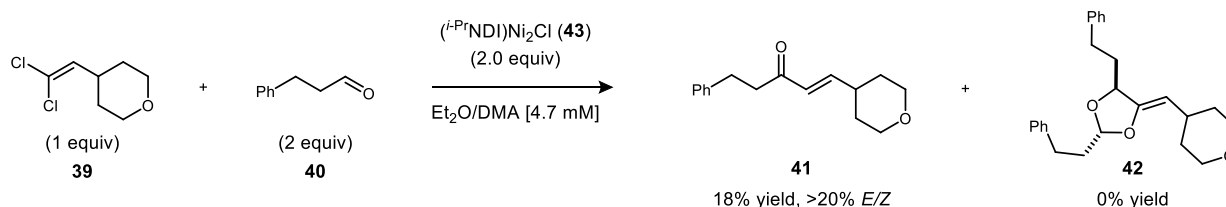


Stoichiometric [2 + 2 + 1]-cycloaddition using an isolable low-valent (NDI)Ni₂Cl complex with concentrated conditions. In an N₂ filled glovebox, a 2-dram vial was charged with a magnetic stir bar and (*i*-Pr₃NDI)Ni₂Cl (**43**) (15.0 mg, 22.0 μmol, 2.00 equiv). DMA (40 μL) was added to the vial, forming a dark purple solution. A solution of 1,1-dichloroalkene **39** (2.0 mg, 11 μmol, 1.0 equiv), hydrocinnamaldehyde (**40**) (3.0 mg, 11 μmol, 2.0 equiv), and mesitylene (2.6 mg, 22 μmol, 2.0 equiv) in Et₂O (160 μL) was added to the purple solution. The reaction was stirred (600 rpm) at room temperature for 1.5 h. The reaction was removed from the glovebox and exposed to air. An aliquot was removed, filtered through a small pad of silica (approx. 1 cm)

eluting with CDCl_3 , and analyzed by ^1H NMR spectroscopy. The yield of dioxolane was determined by ^1H NMR integration against mesitylene.

41: 0% Yield.

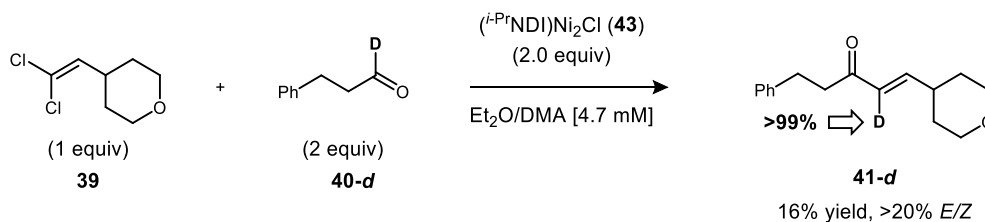
42: 59% Yield. 3:1 d.r. (anti:syn). >20:1 Z/E



Stoichiometric [2 + 2 + 1]-cycloaddition using an isolable low-valent (NDI) Ni_2Cl complex with dilute conditions. In an N_2 filled glovebox, a 2-dram vial was charged with a magnetic stir bar and $(i\text{-PrNDI})\text{Ni}_2\text{Cl}$ (**43**) (22.7 mg, 33.1 μmol , 2.00 equiv). DMA (700 μL) was added to the vial, forming a dark purple solution. A 0.5 M stock solution (32 μL) of 1,1-dichloroalkene **39** (2.9 mg, 17 μmol , 1.0 equiv), hydrocinnamaldehyde (**40**) (4.6 mg, 34 μmol , 2.0 equiv), and trimethoxybenzene (5.7 mg, 34 μmol , 2.0 equiv) in Et_2O was added to the purple solution. An addition portion of Et_2O (2.8 mL) was added. The reaction was stirred (600 rpm) at room temperature for 24 h. The reaction was removed from the glovebox and exposed to air. An aliquot was removed, filtered through a small pad of silica (approx. 1 cm) eluting with CDCl_3 , and analyzed by ^1H NMR spectroscopy. The yield of **41** and **42** were determined by ^1H NMR integration against trimethoxybenzene.

41: 18% Yield. >20:1 E/Z

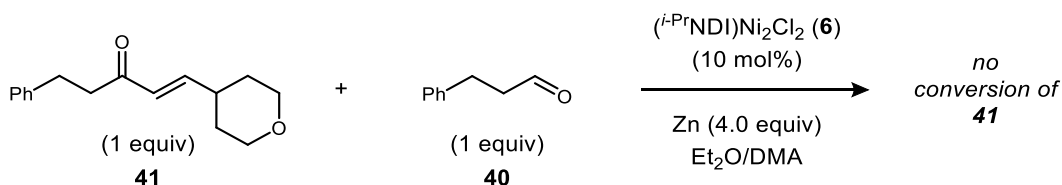
42: 0% Yield.



Stoichiometric bond insertion reaction with deuterium labeled substrate. In an N_2 filled glovebox, a 2-dram vial was charged with a magnetic stir bar and $(i\text{-PrNDI})\text{Ni}_2\text{Cl}$ (**43**) (22.7 mg,

33.1 μmol , 2.00 equiv). DMA (700 μL) was added to the vial, forming a dark purple solution. A 0.5 M stock solution (32 μL) of 1,1-dichloroalkene **39** (2.9 mg, 17 μmol , 1.0 equiv), aldehyde **40-d**¹⁸ (4.6 mg, 34 μmol , 2.0 equiv), and trimethoxybenzene (5.7 mg, 34 μmol , 2.0 equiv) in Et_2O was added to the purple solution. An additional portion of Et_2O (2.8 mL) was added. The reaction was stirred (600 rpm) at room temperature for 24 h. The reaction was removed from the glovebox and exposed to air. An aliquot was removed, filtered through a small pad of silica (approx. 1 cm) eluting with CDCl_3 , and analyzed by ^1H NMR spectroscopy. The yield and deuterium incorporation of **41-d** were determined from ^1H NMR integration against trimethoxybenzene.

41-d: 16% Yield. >20:1 E/Z



Resubjection of enone to catalytic conditions. In an N_2 -filled glovebox, a 2-dram vial was charged with a magnetic stir bar, $(i\text{-PrNDI})\text{Ni}_2\text{Cl}_2$ (3.4 mg, 4.8 μmol , 10 mol%), and Zn powder (12.4 mg, 190 μmol , 4.00 equiv). DMA (50 μL) was added. A solution of (*E*)-5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pent-1-en-3-one (11.6 mg, 47.5 μmol , 1.00 equiv), hydrocinnamaldehyde (6.37 mg, 47.5 μmol , 1.00 equiv), mesitylene (5.7 mg, 47.5 μmol , 1.00 equiv), and Et_2O (190 μL) was added. The vial was sealed, and the reaction mixture was stirred (600 rpm) at room temperature for 24 h. The reaction was removed from the glovebox and exposed to air. An aliquot was removed, filtered through a small pad of silica (approx. 1 cm) eluting with CDCl_3 , and analyzed by ^1H NMR spectroscopy. Conversion of **41** was determined by ^1H NMR integration against mesitylene.

6. NMR Spectral Data

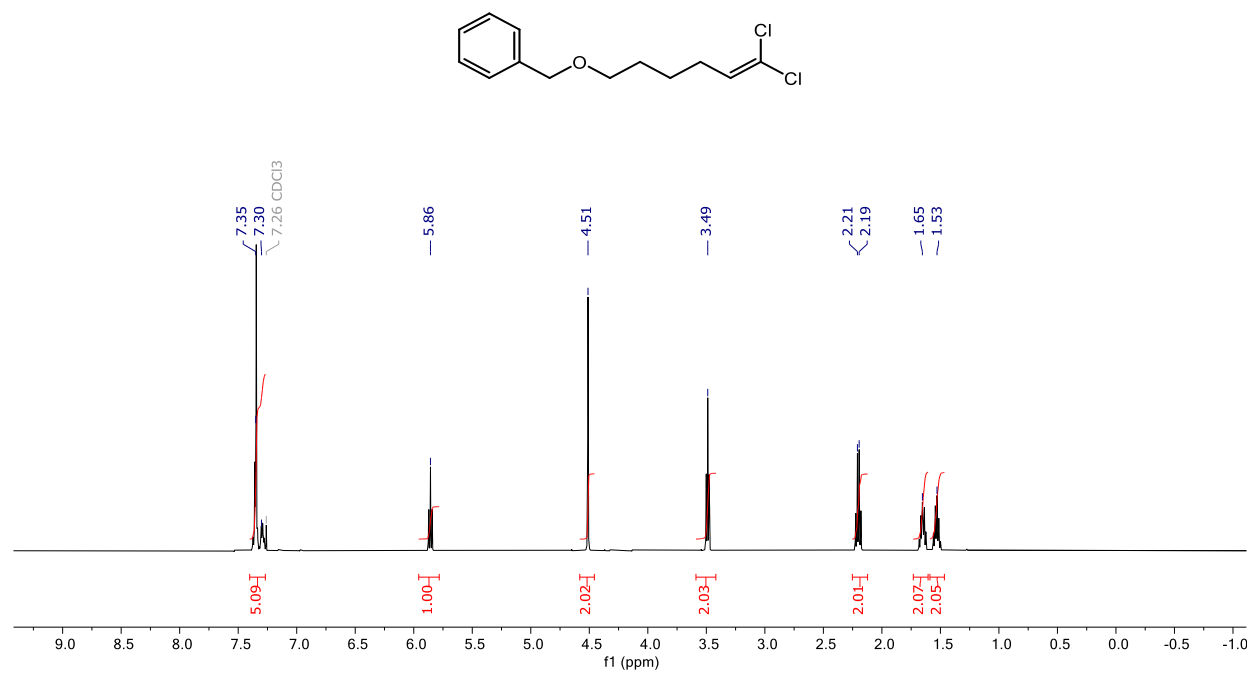


Figure A2.1. ¹H NMR spectrum for **S1** (500 MHz, CDCl₃, room temperature).

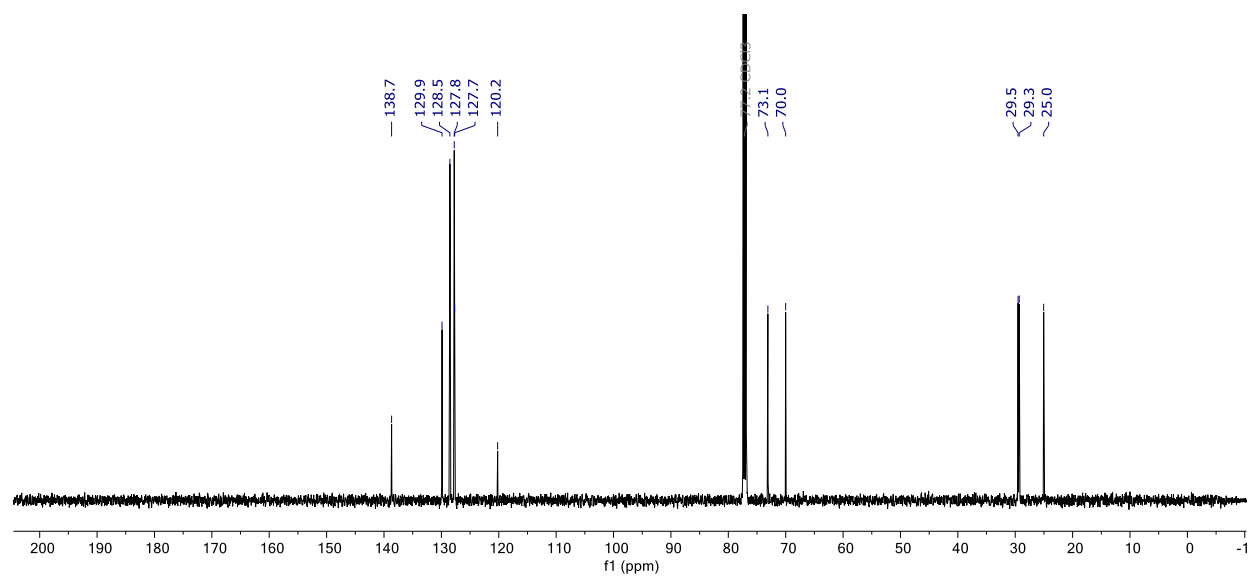


Figure A2.2. ¹³C{¹H} NMR spectrum for **S1** (126 MHz, CDCl₃, room temperature).

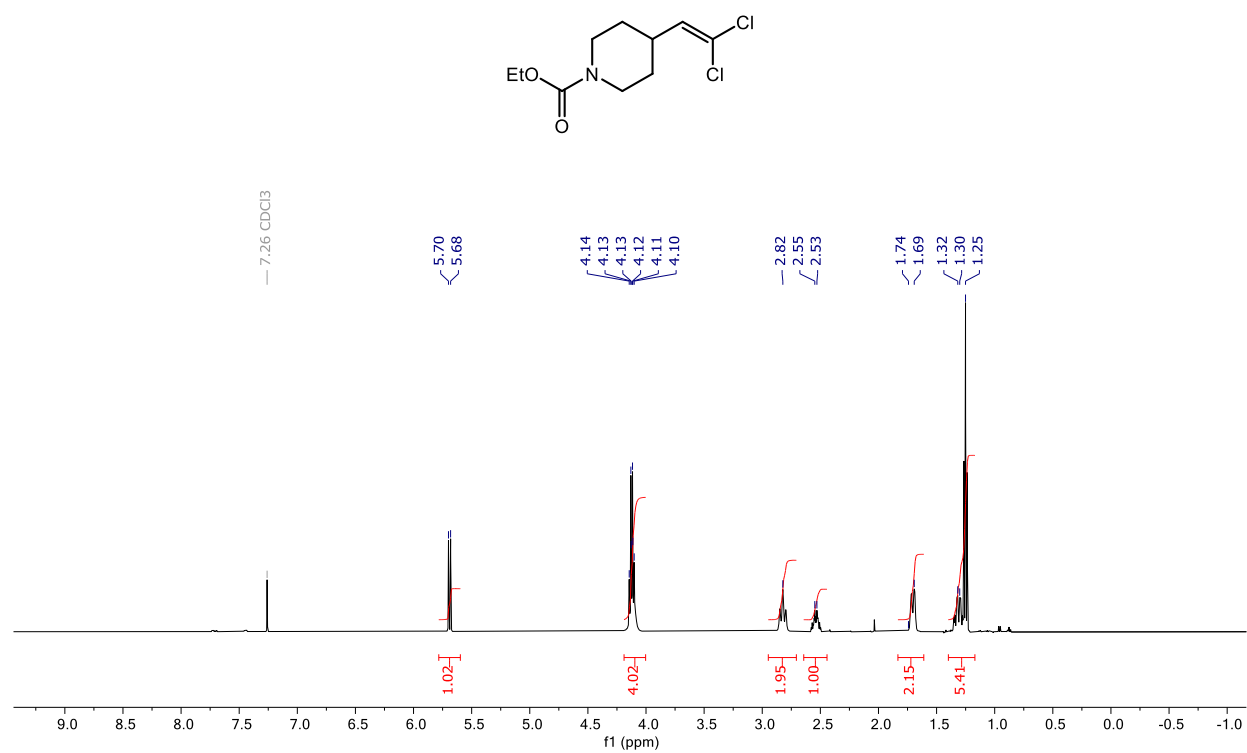


Figure A2.3. ¹H NMR spectrum for S2 (500 MHz, CDCl₃, room temperature).

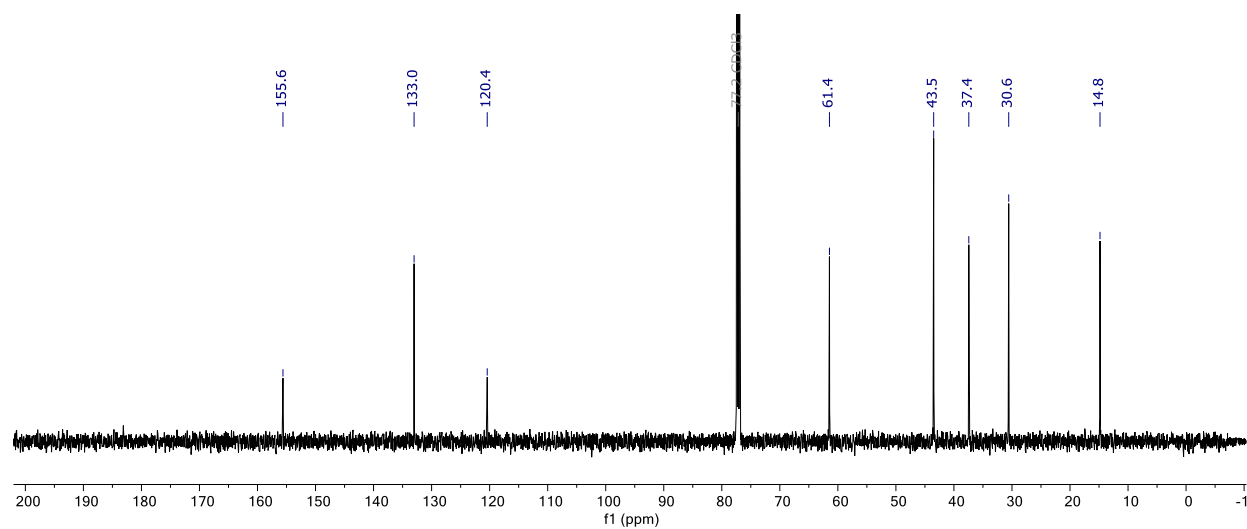


Figure A2.4. ¹³C{¹H} NMR spectrum for S2 (126 MHz, CDCl₃, room temperature).

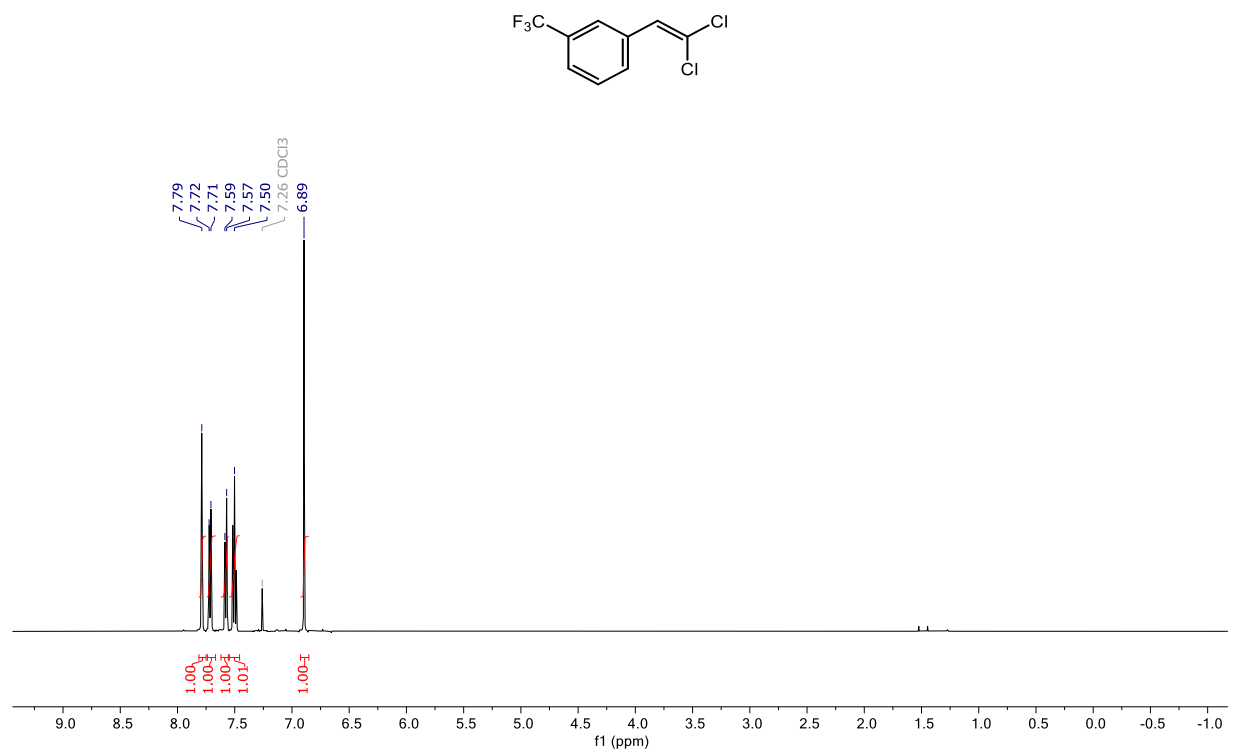


Figure A2.5. ^1H NMR spectrum for **S3** (500 MHz, CDCl_3 , room temperature).

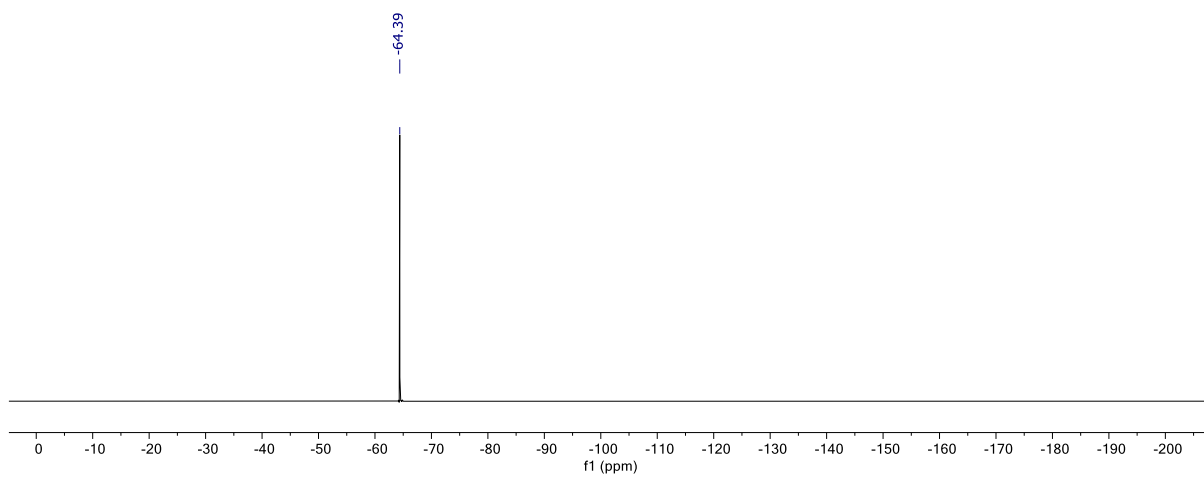


Figure A2.6. ^{19}F NMR spectrum for **S3** (470 MHz, CDCl_3 , room temperature).

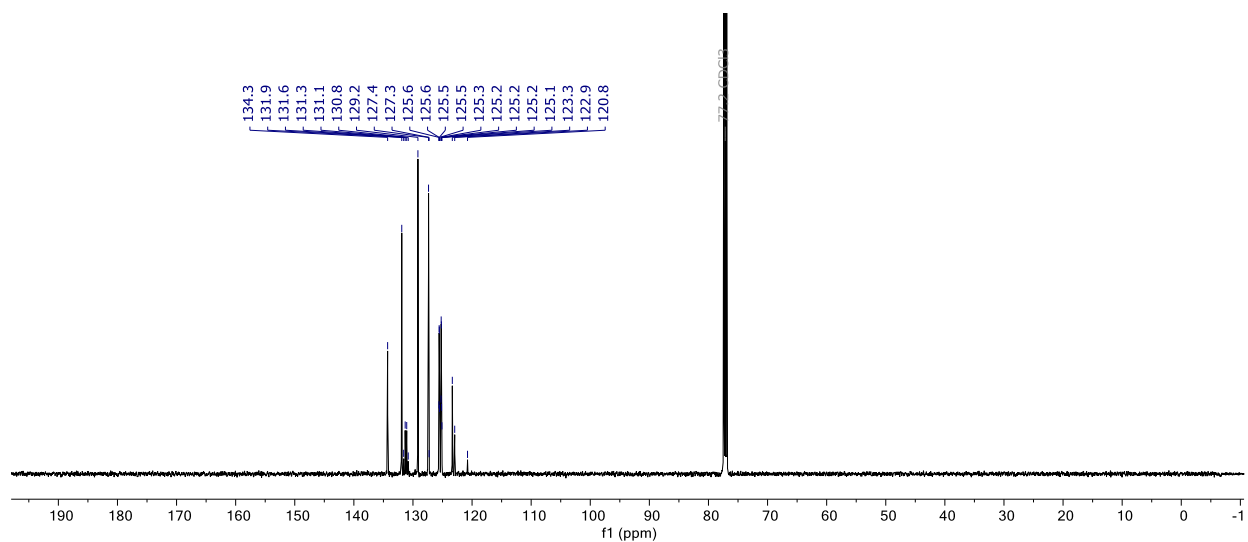


Figure A2.7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **S3** (126 MHz, CDCl_3 , room temperature).

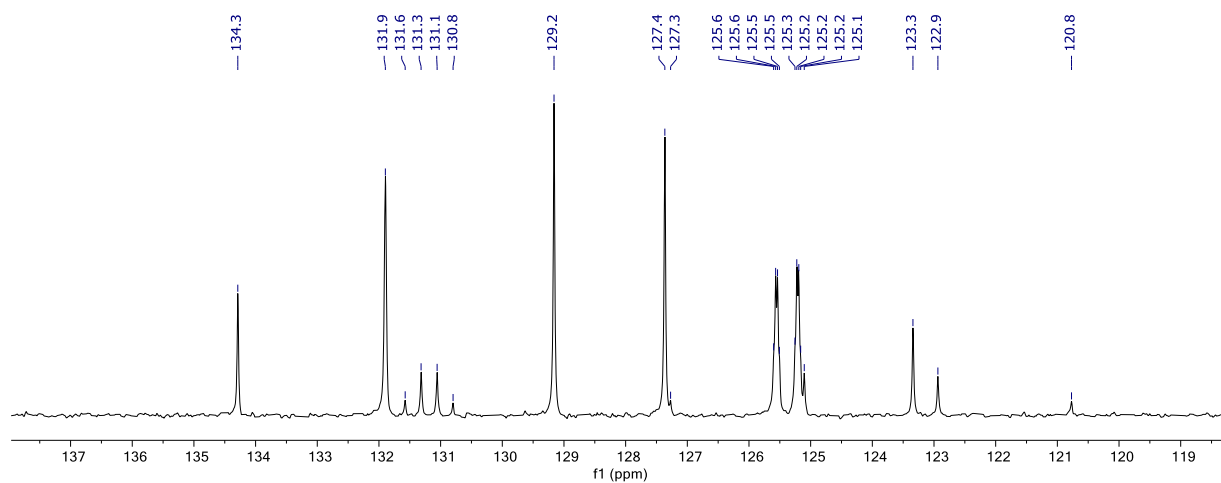


Figure A2.8. Expansion of $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **S3** (126 MHz, CDCl_3 , room temperature).

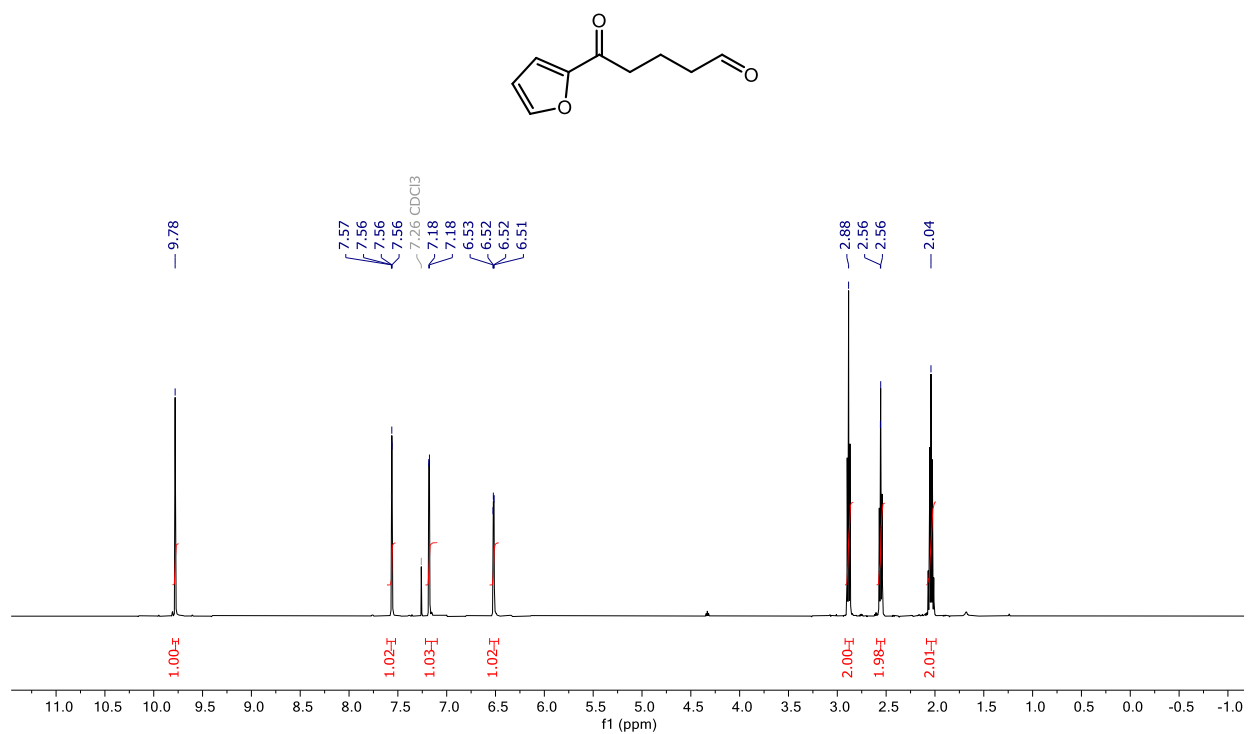


Figure A2.9. ¹H NMR spectrum for **S4** (500 MHz, CDCl₃, room temperature).

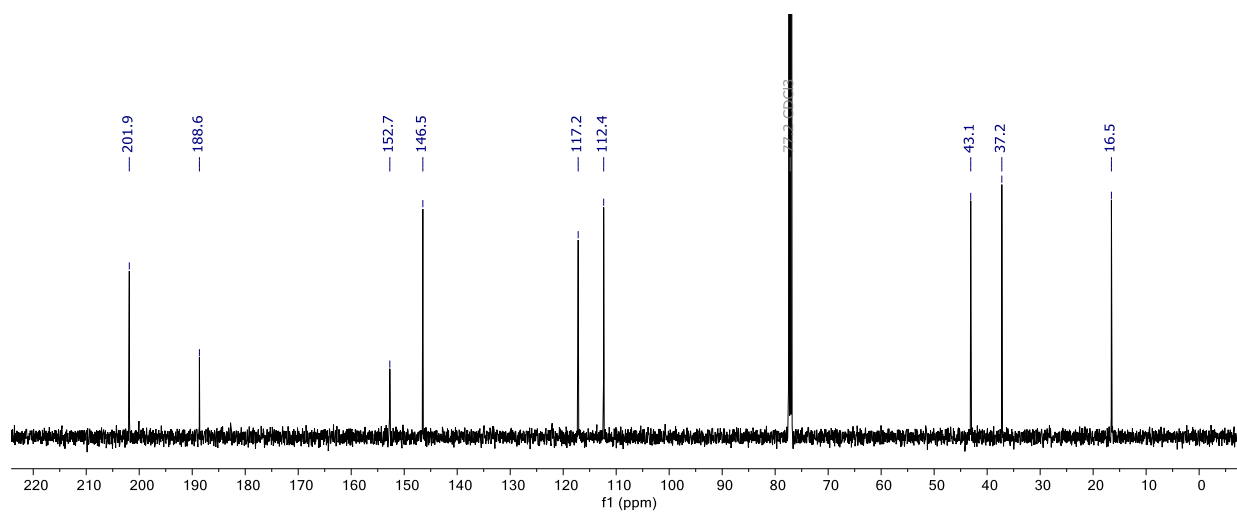


Figure A2.10. ¹³C{¹H} NMR spectrum for **S4** (126 MHz, CDCl₃, room temperature).

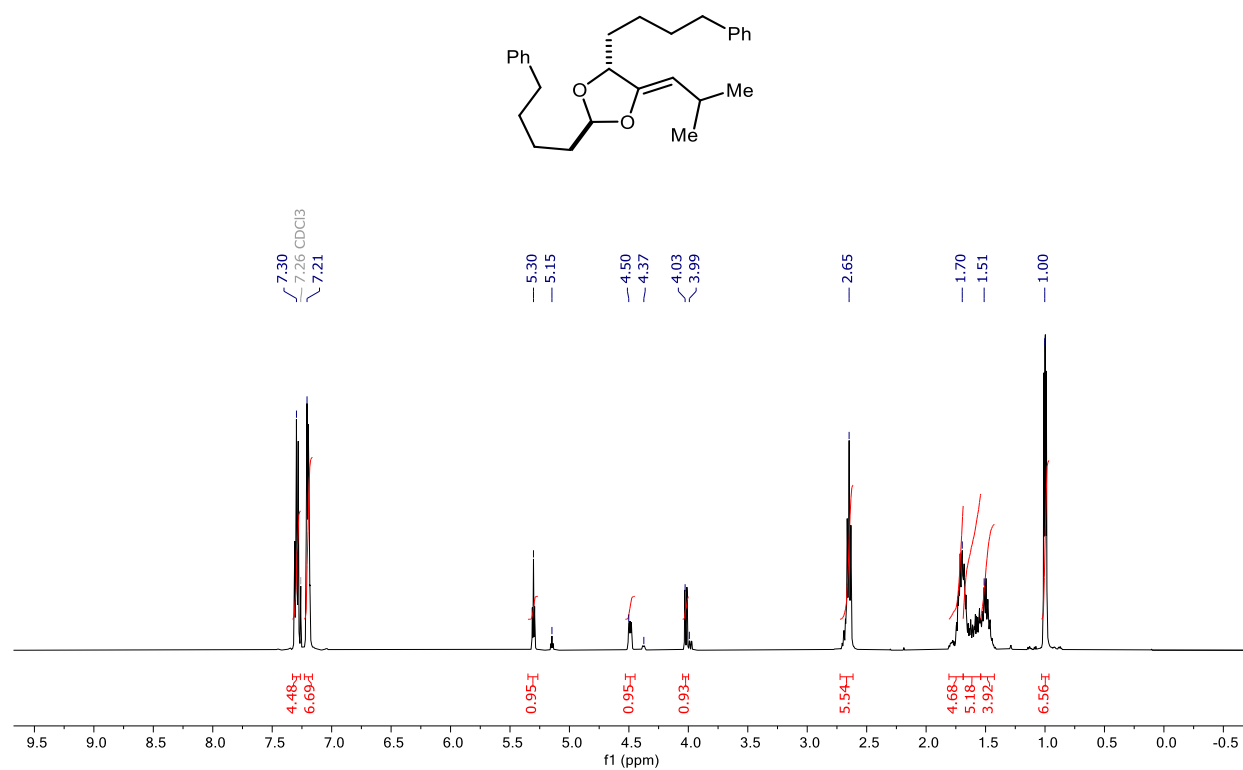


Figure A2.11. ^1H NMR spectrum for **4** (500 MHz, CDCl_3 , room temperature).

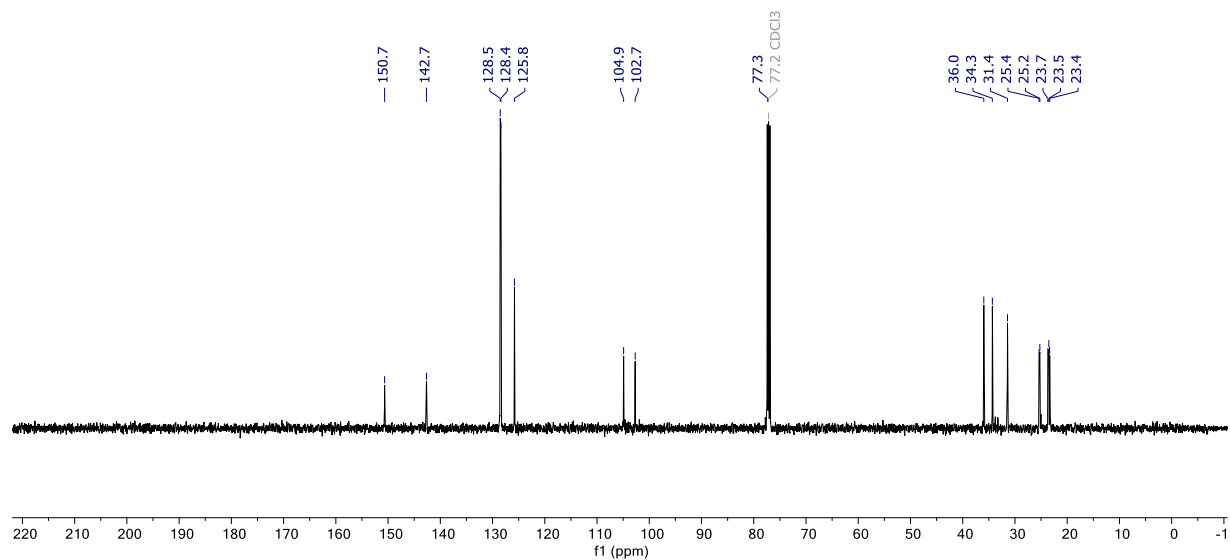


Figure A2.12. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **4** (126 MHz, CDCl_3 , room temperature).

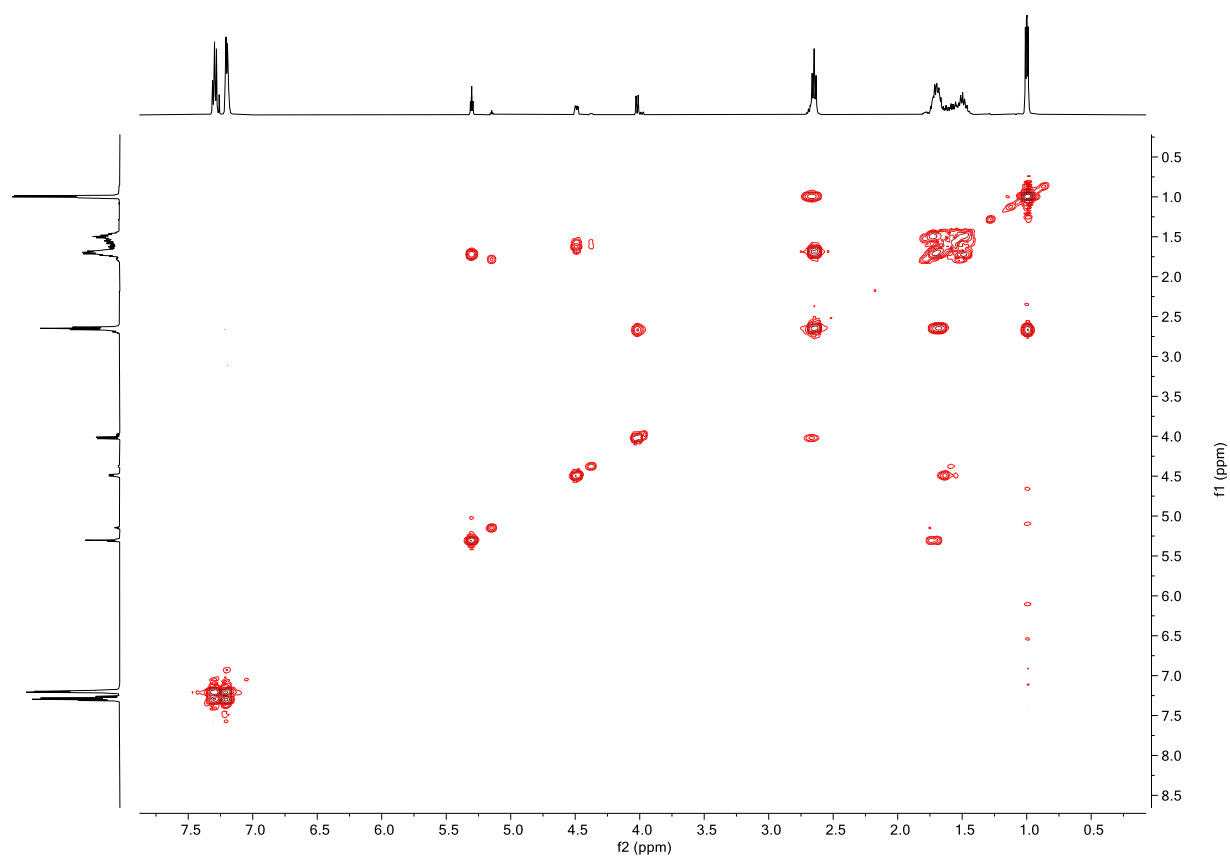


Figure A2.13. COSY NMR spectrum for **4** (500 MHz, CDCl_3 , room temperature).

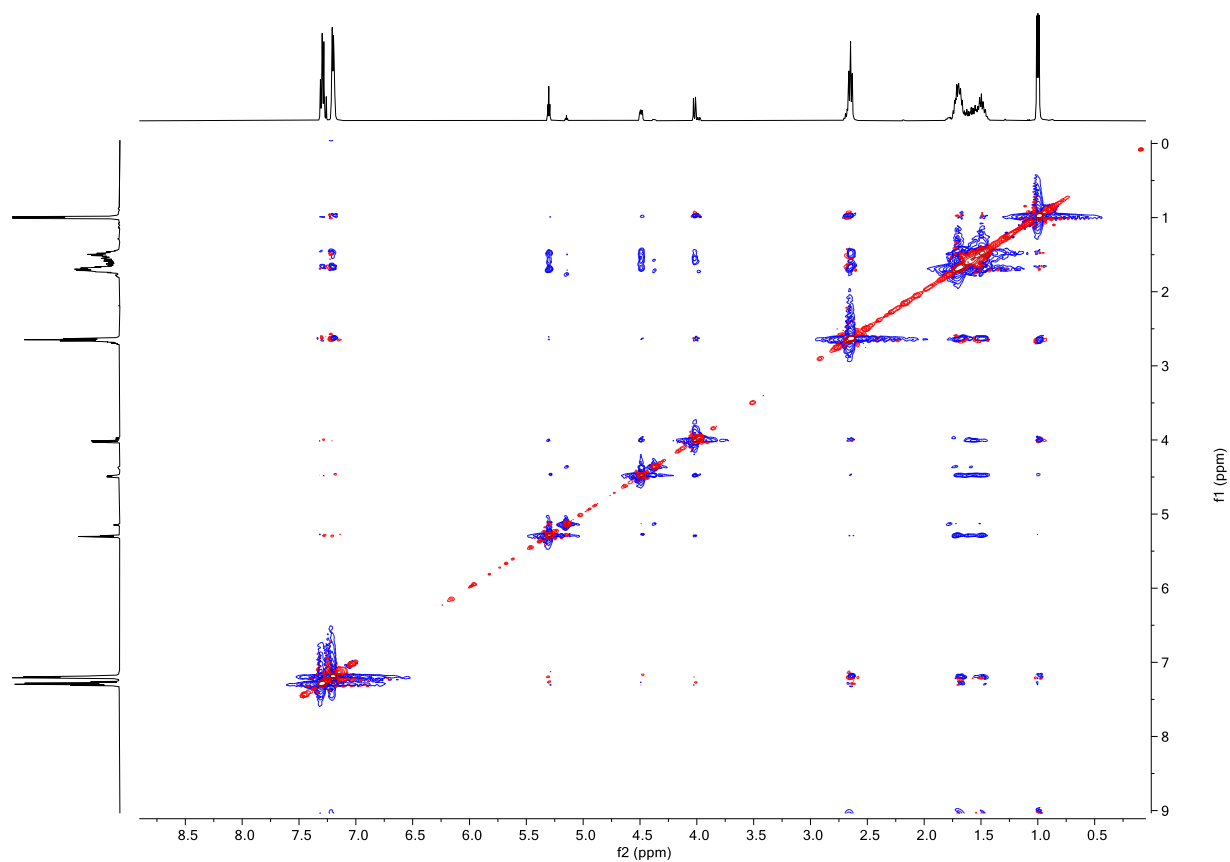


Figure A2.14. NOESY NMR spectrum for **4** (500 MHz, CDCl₃, room temperature).

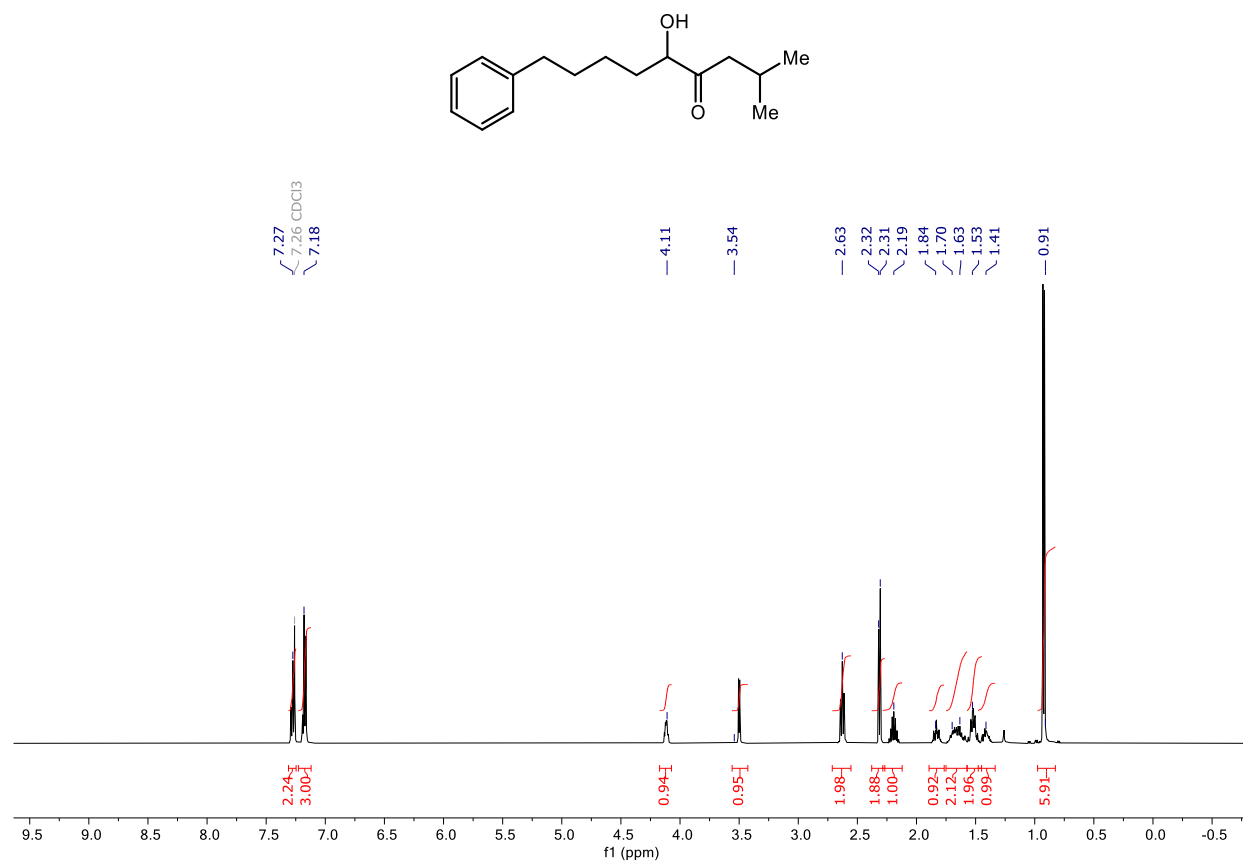


Figure A2.15. ^1H NMR spectrum for **5** (500 MHz, CDCl_3 , room temperature).

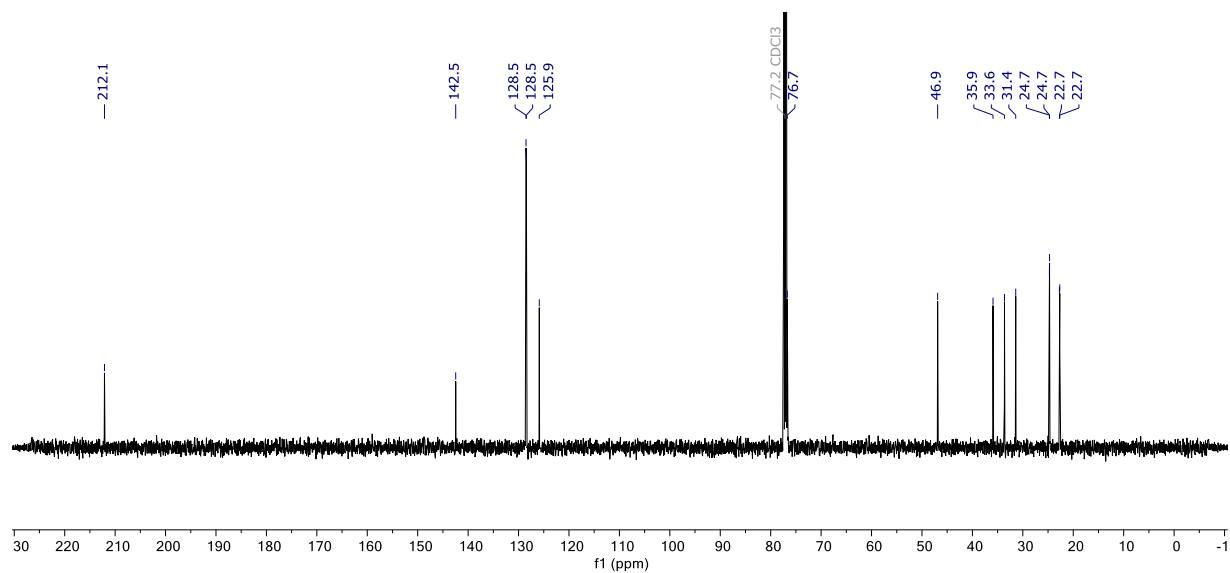


Figure A2.16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **5** (126 MHz, CDCl_3 , room temperature).

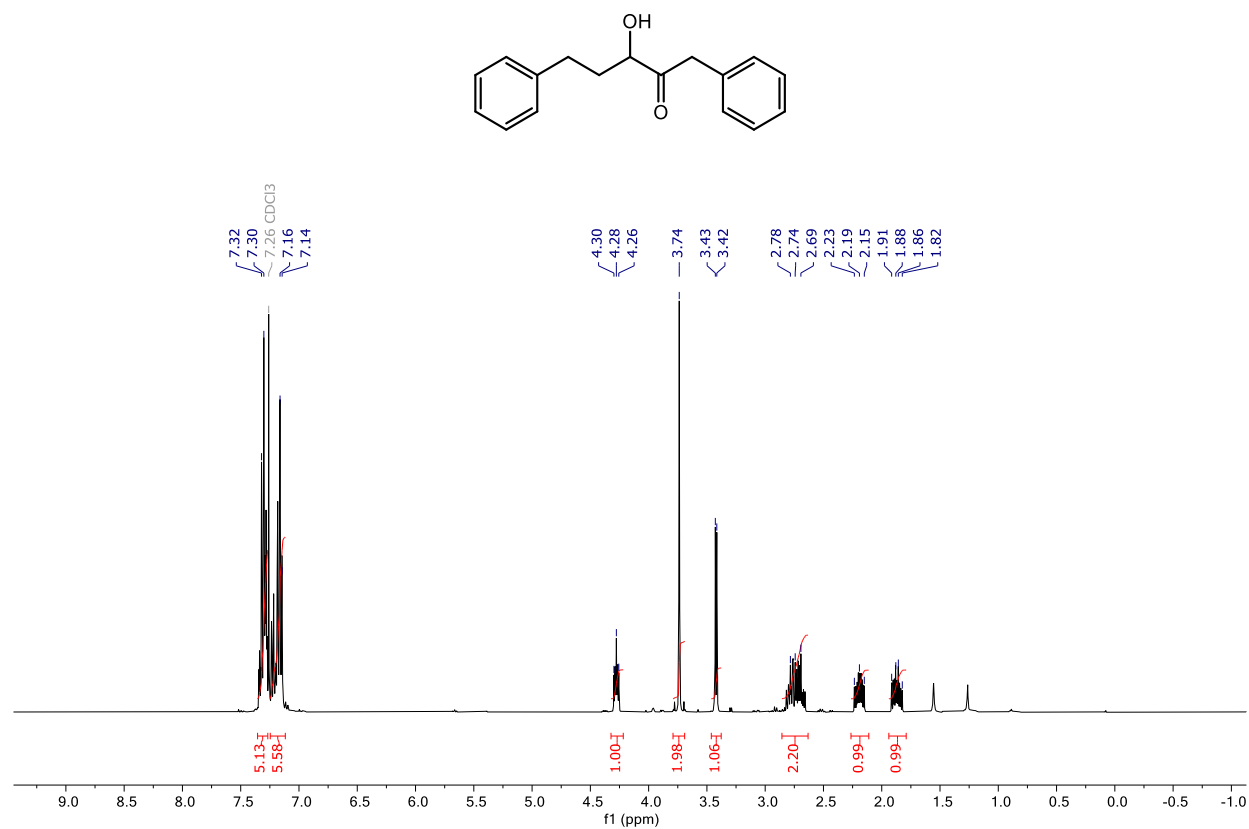


Figure A2.17. ¹H NMR spectrum for **12** (400 MHz, CDCl₃, room temperature).

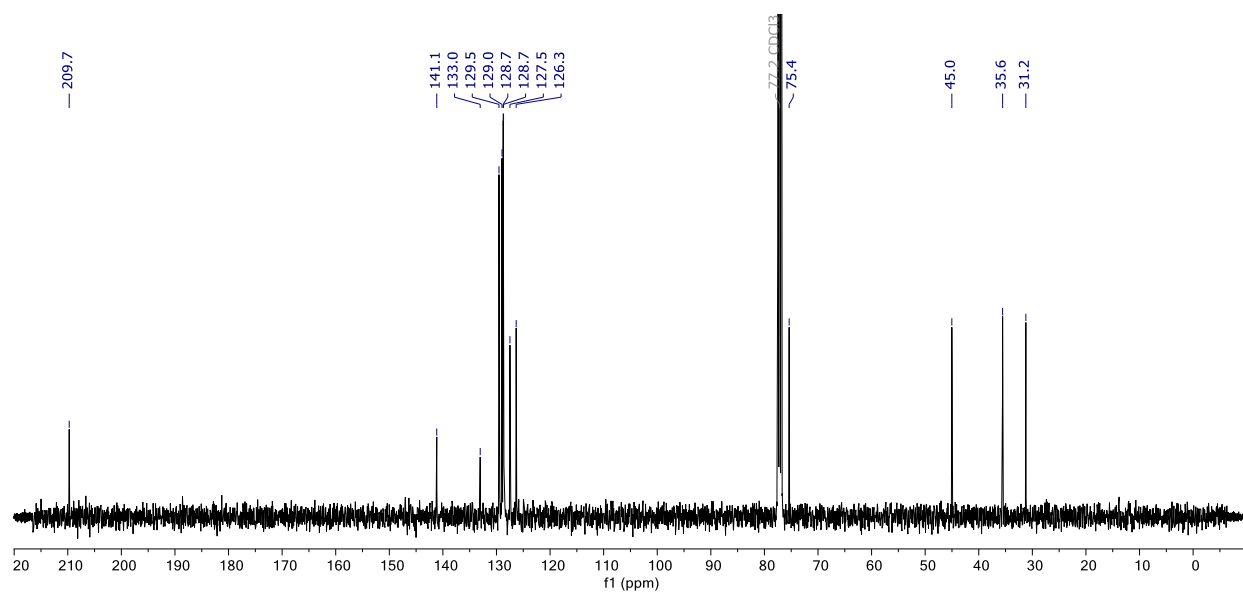


Figure A2.18. ¹³C{¹H} NMR spectrum for **12** (101 MHz, CDCl₃, room temperature).

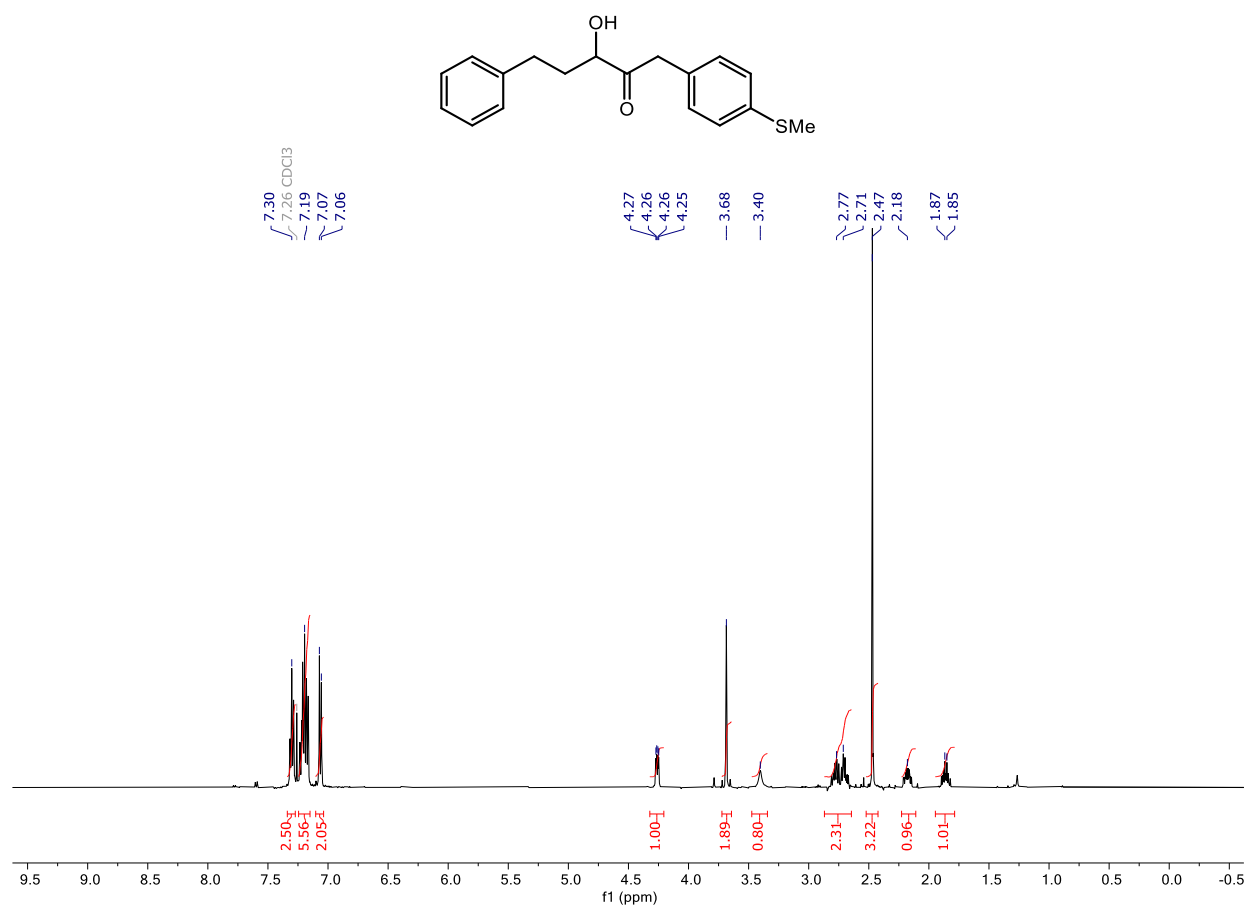


Figure A2.19. ¹H NMR spectrum for **13** (500 MHz, CDCl₃, room temperature).

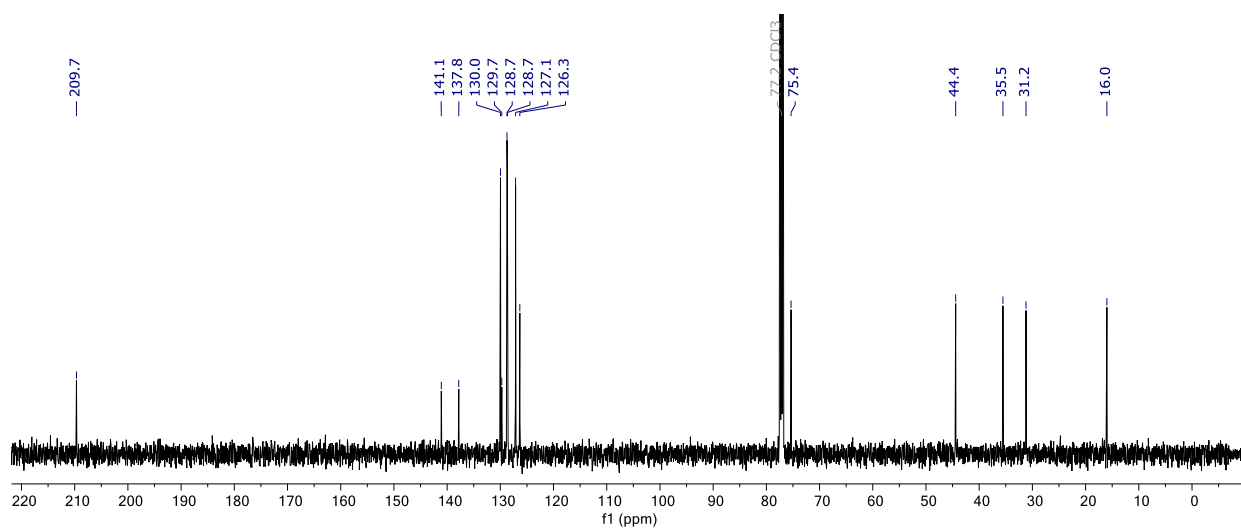


Figure A2.20. ¹³C{¹H} NMR spectrum for **13** (126 MHz, CDCl₃, room temperature).

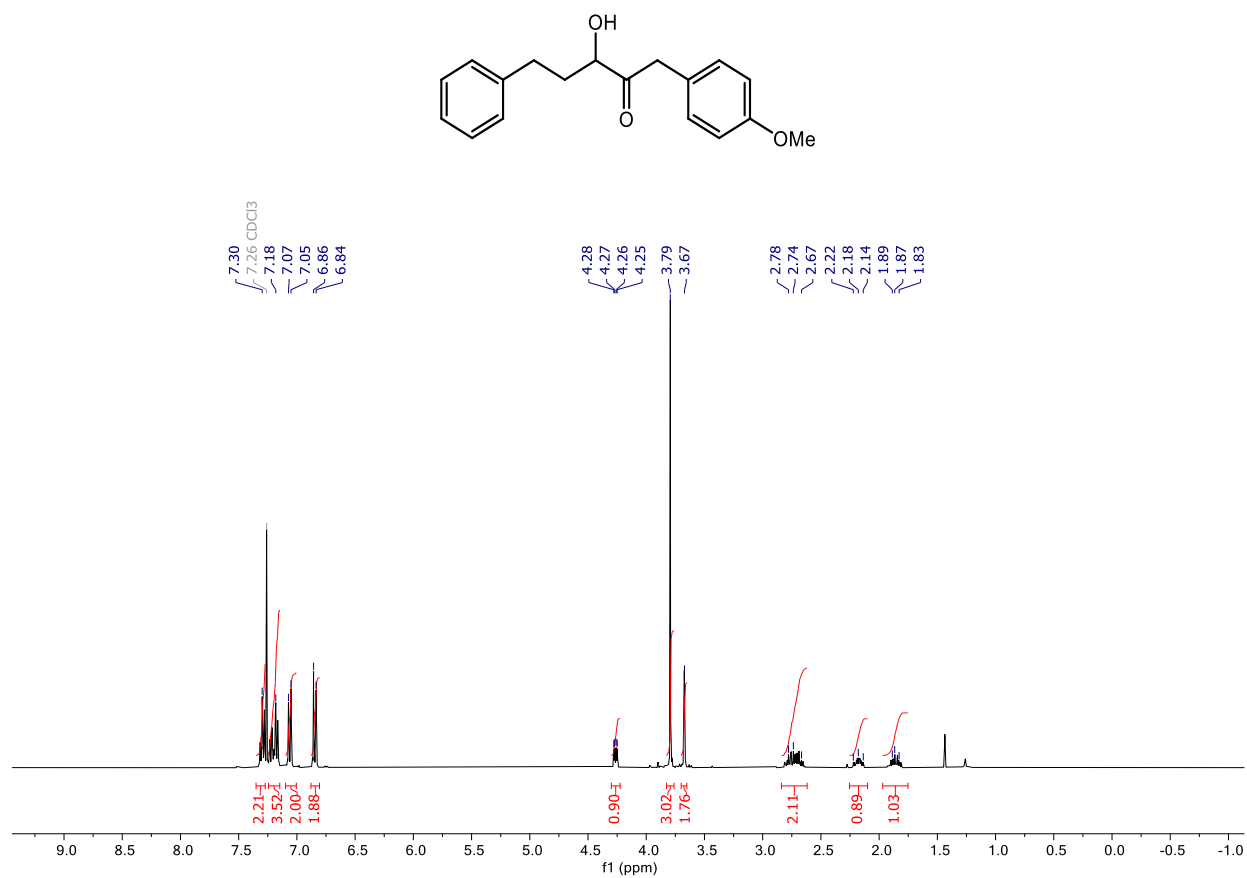


Figure A2.21. ¹H NMR spectrum for **14** (400 MHz, CDCl₃, room temperature).

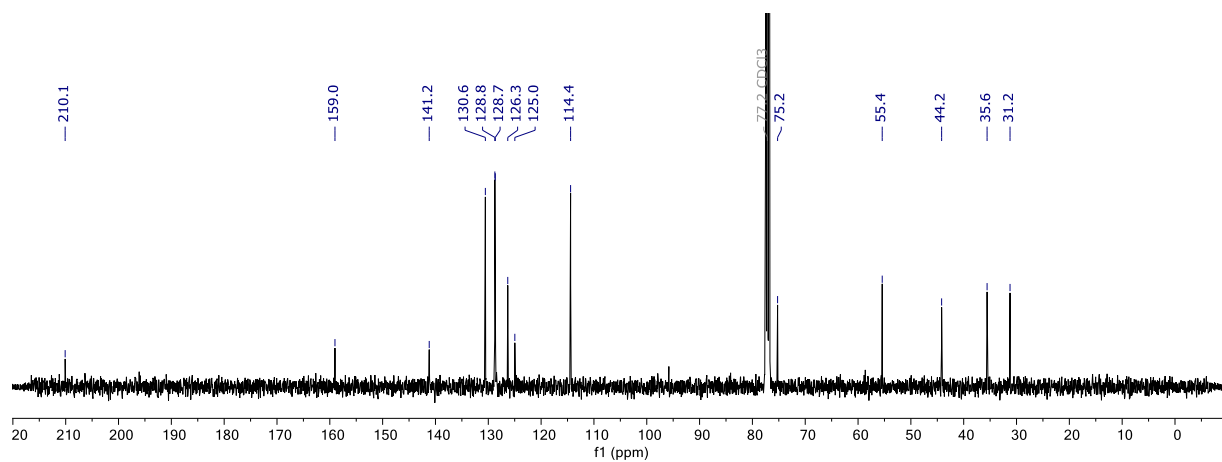


Figure A2.22. ¹³C{¹H} NMR spectrum for **14** (101 MHz, CDCl₃, room temperature).

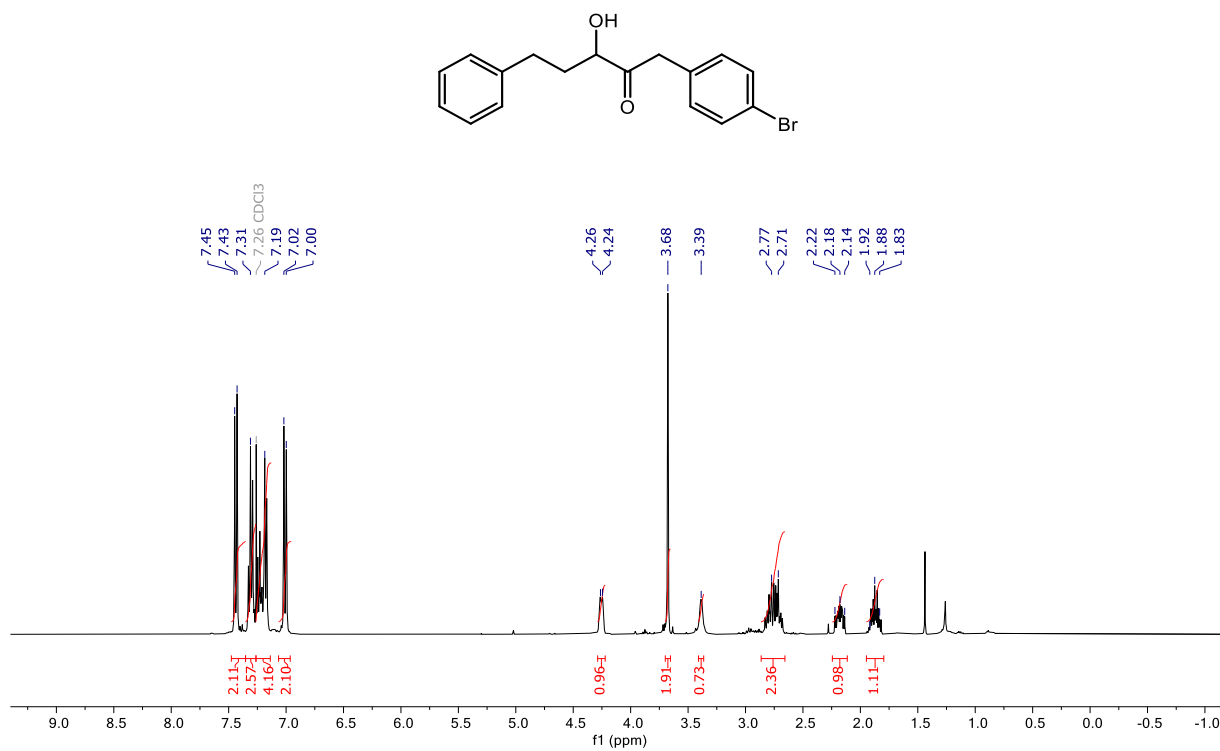


Figure A2.23. ¹H NMR spectrum for **15** (400 MHz, CDCl₃, room temperature).

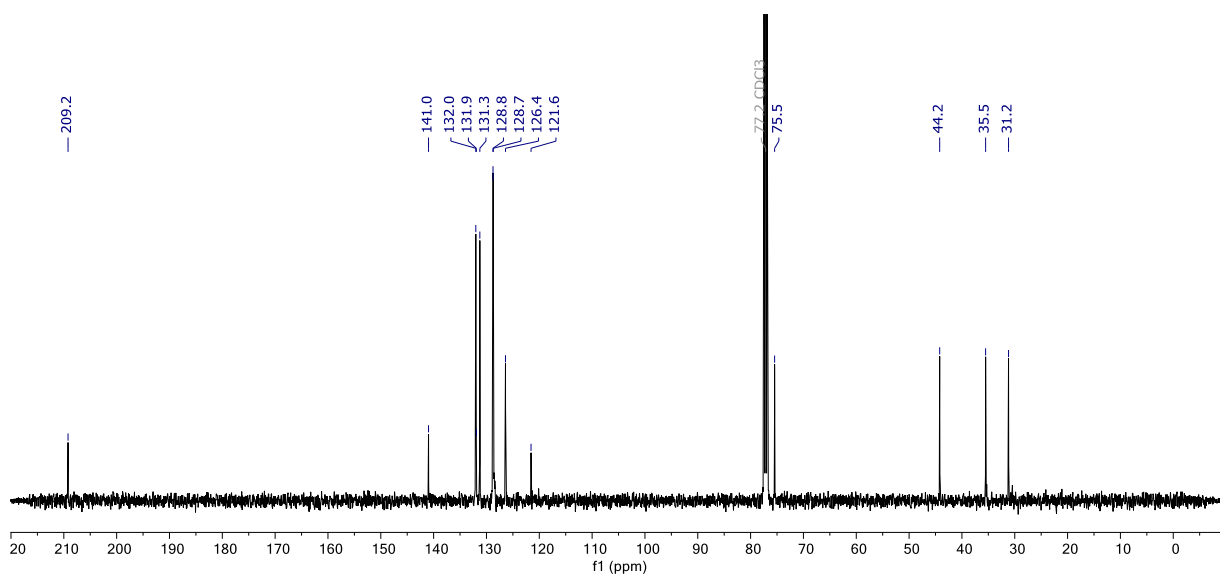


Figure A2.24. ¹³C{¹H} NMR spectrum for **15** (101 MHz, CDCl₃, room temperature).

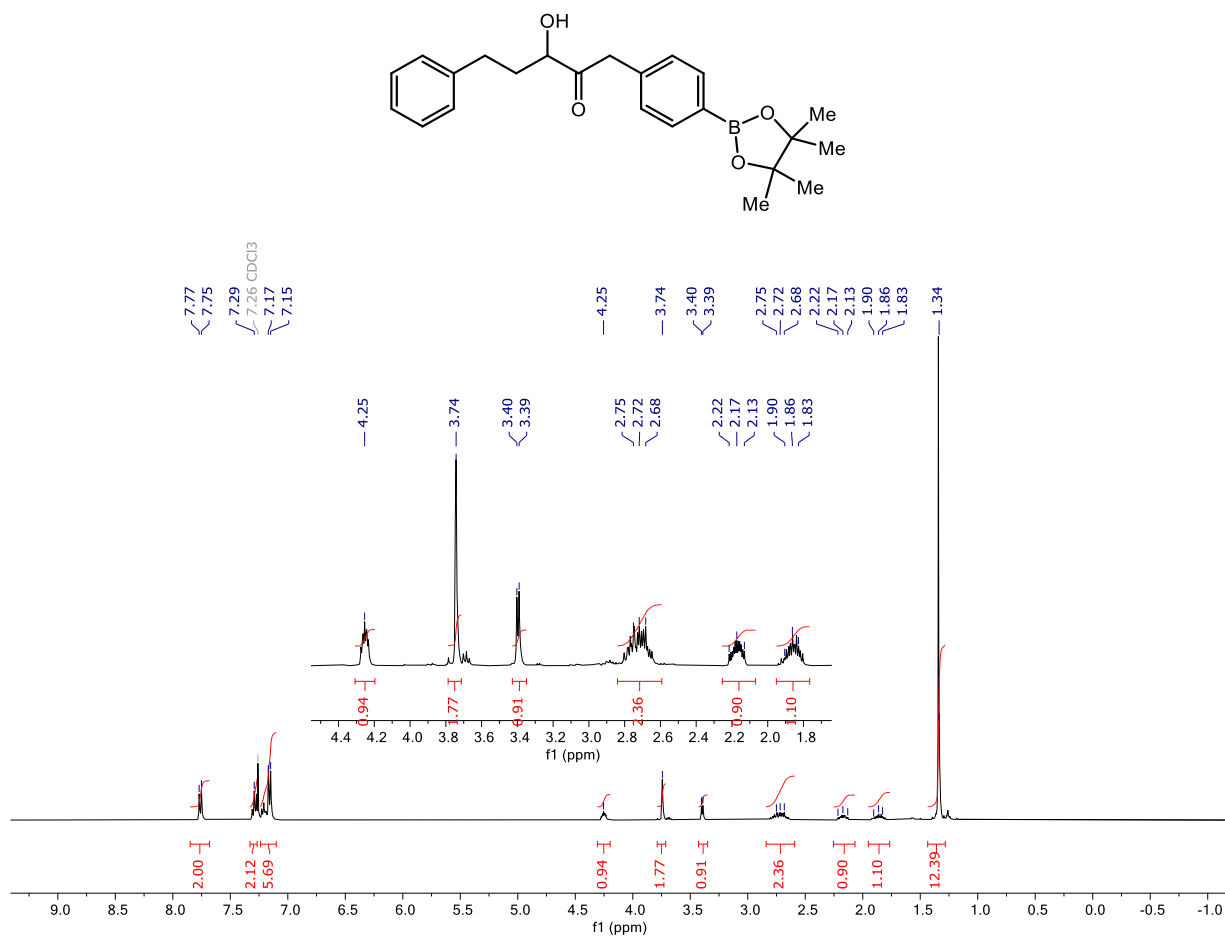


Figure A2.25. ¹H NMR spectrum for **16** (400 MHz, CDCl₃, room temperature).

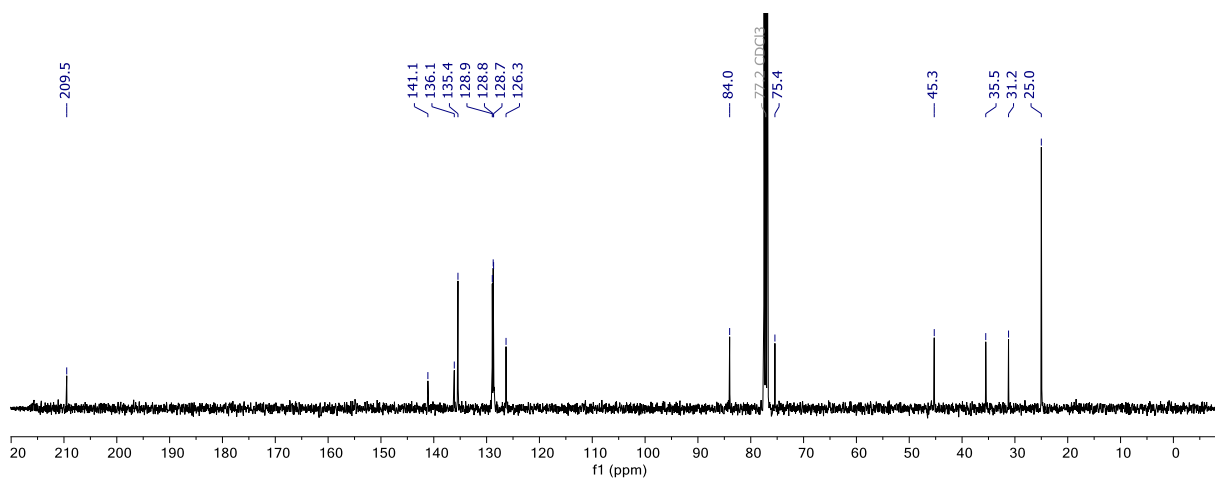


Figure A2.26. ¹³C{¹H} NMR spectrum for **16** (101 MHz, CDCl₃, room temperature).

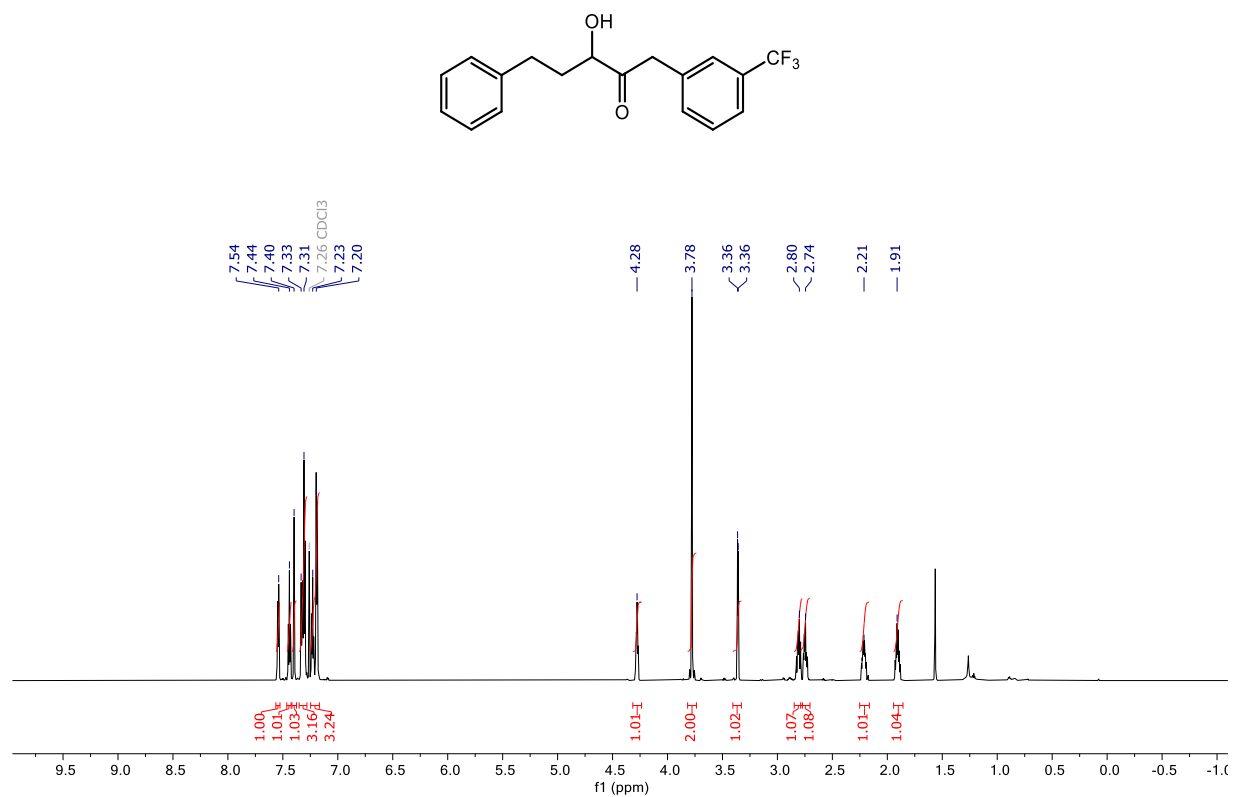


Figure A2.27. ¹H NMR spectrum for **17** (800 MHz, CDCl₃, room temperature).

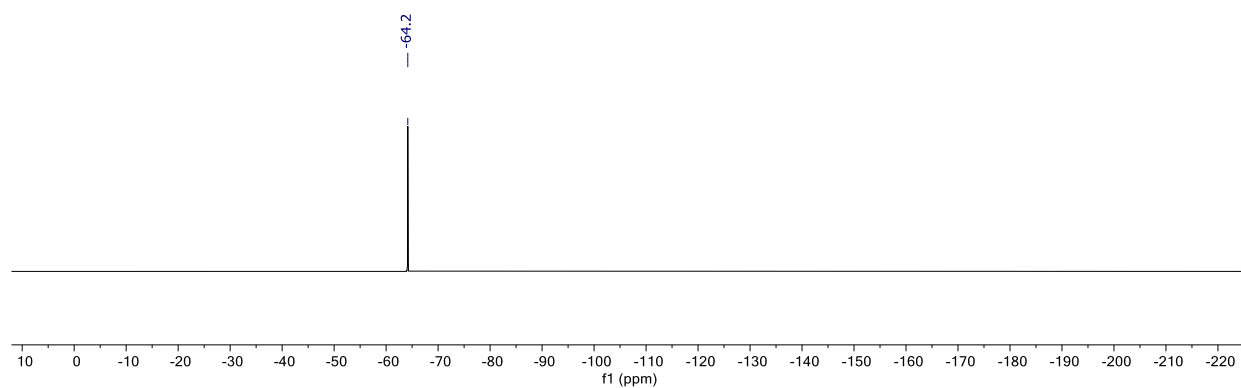


Figure A2.28. ¹⁹F NMR spectrum for **17** (376 MHz, CDCl₃, room temperature).

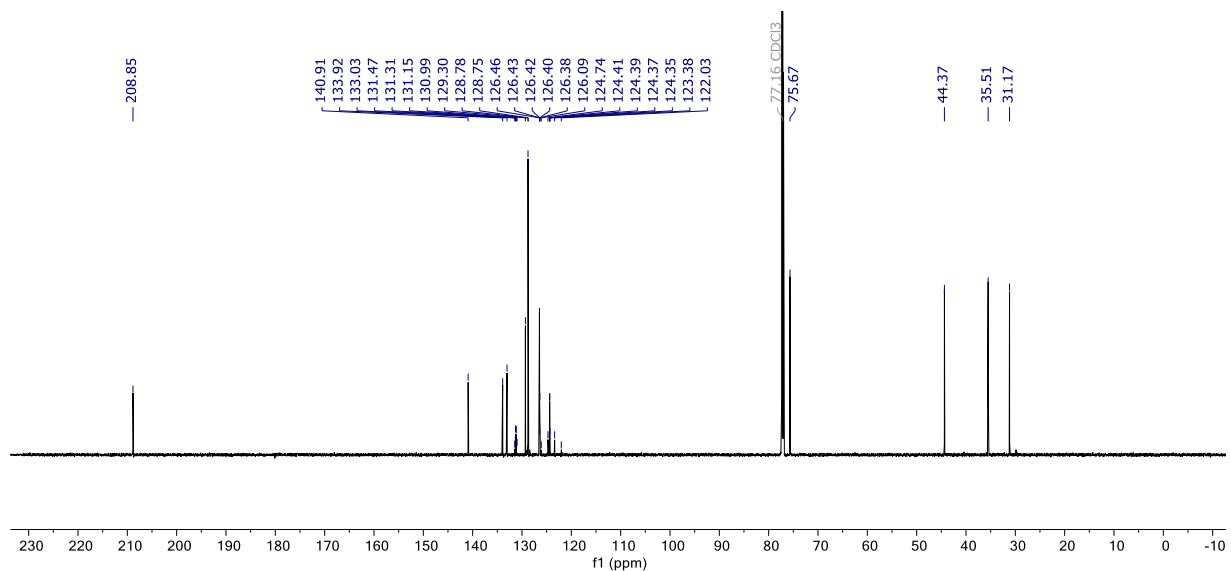


Figure A2.29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **17** (201 MHz, CDCl_3 , room temperature).

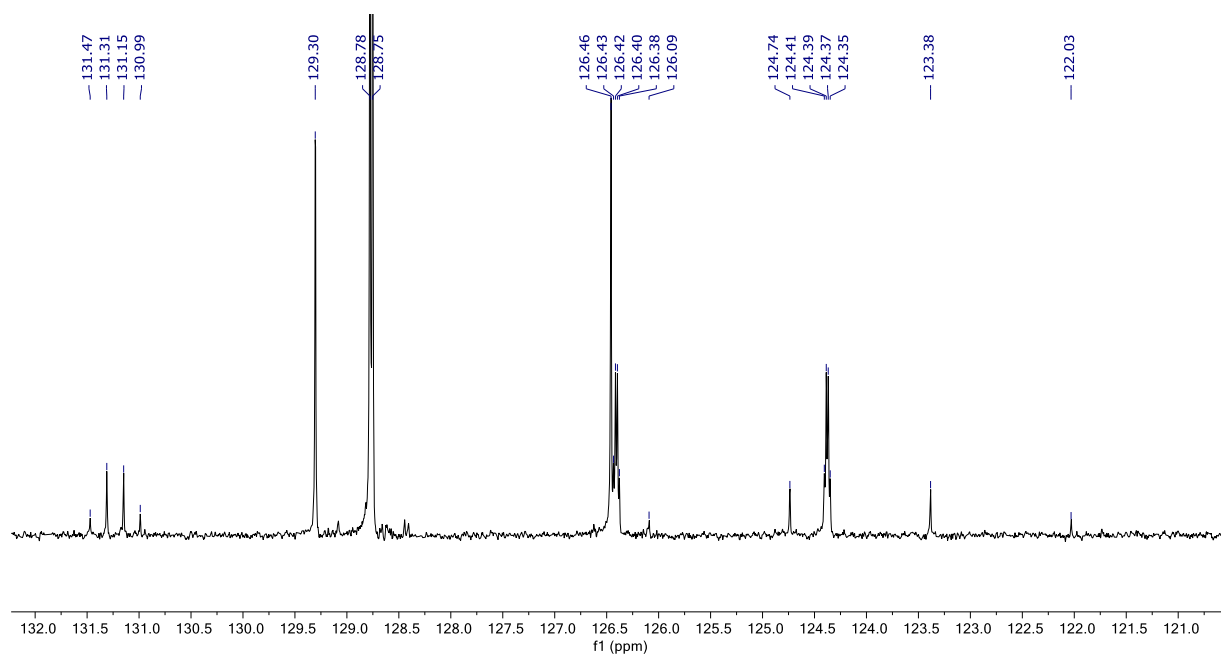


Figure A2.30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **17** (201 MHz, CDCl_3 , room temperature).

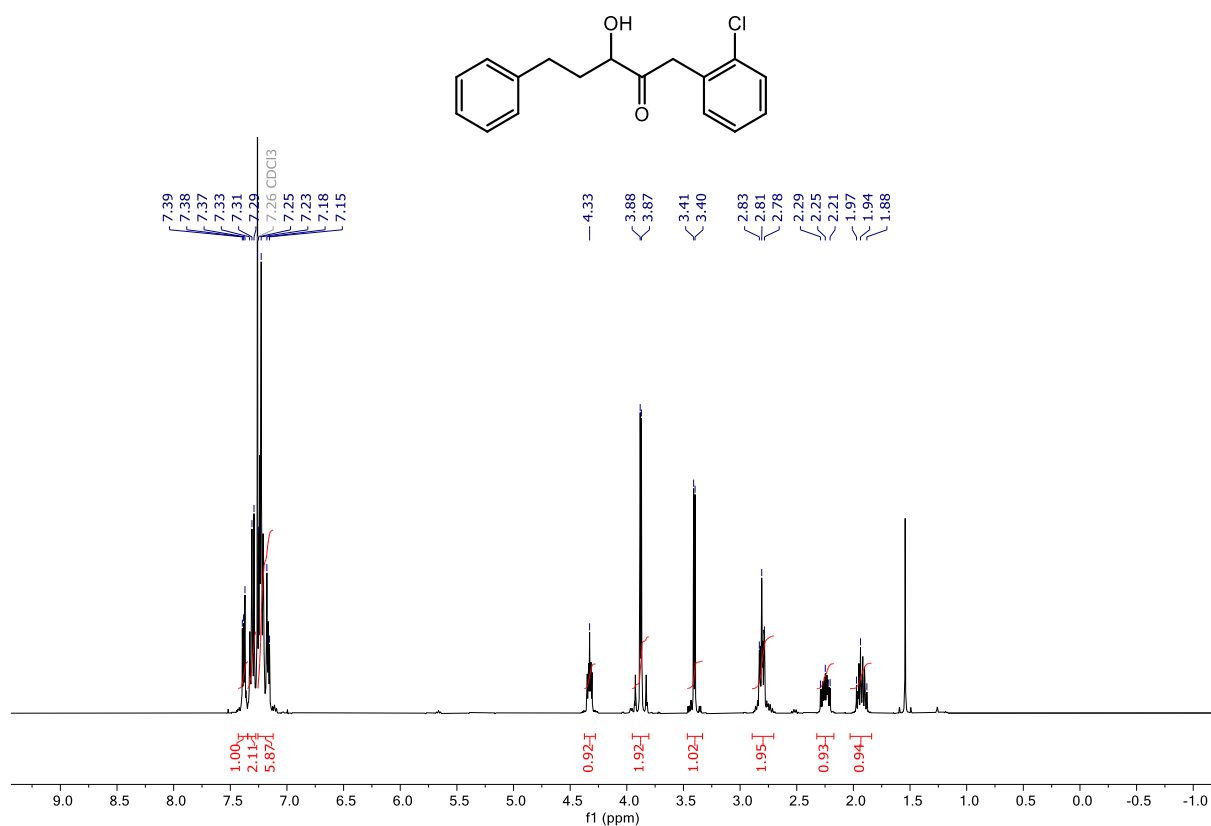


Figure A2.31. ¹H NMR spectrum for **18** (400 MHz, CDCl₃, room temperature).

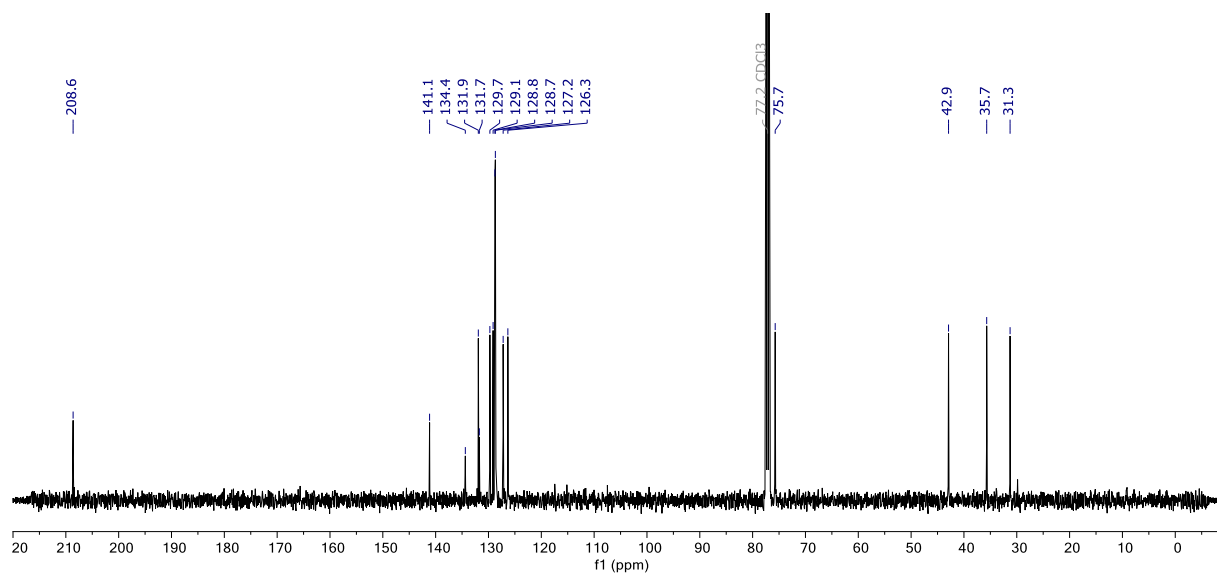


Figure A2.32. ¹³C{¹H} NMR spectrum for **18** (101 MHz, CDCl₃, room temperature).

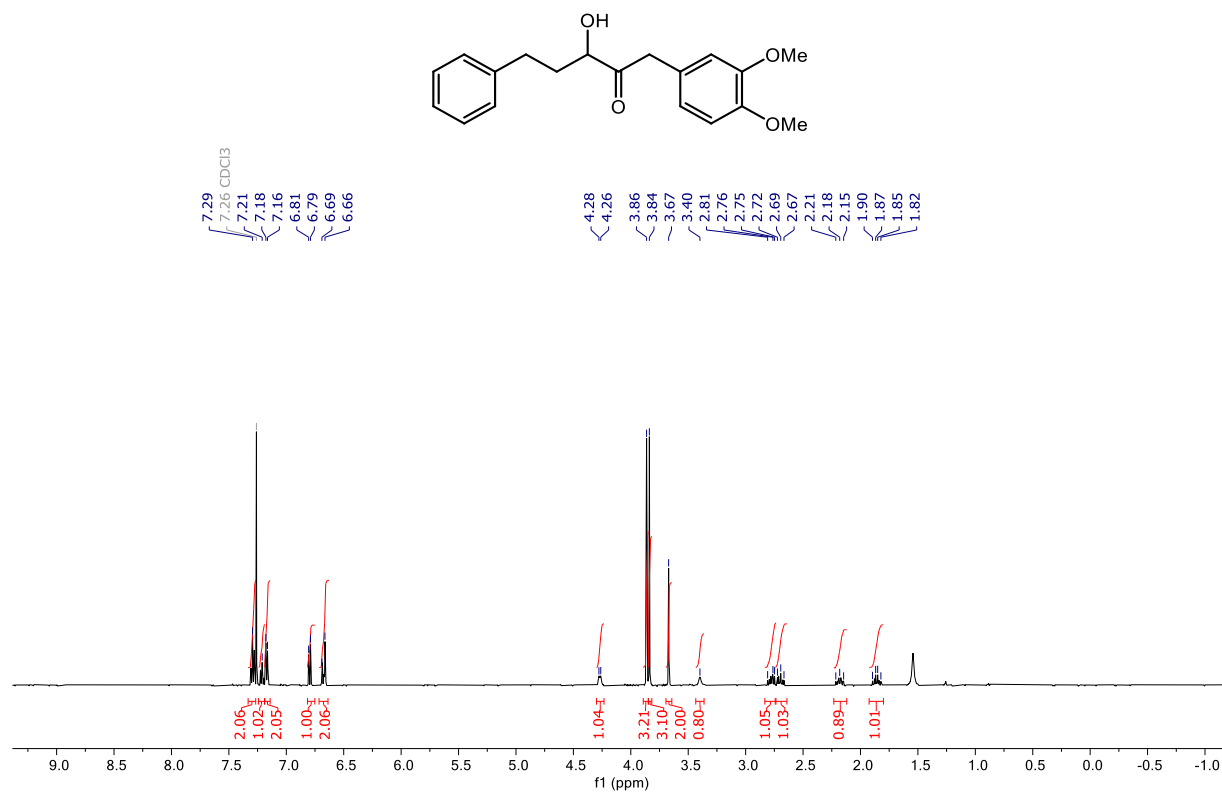


Figure A2.33. ¹H NMR spectrum for **19** (500 MHz, CDCl₃, room temperature).

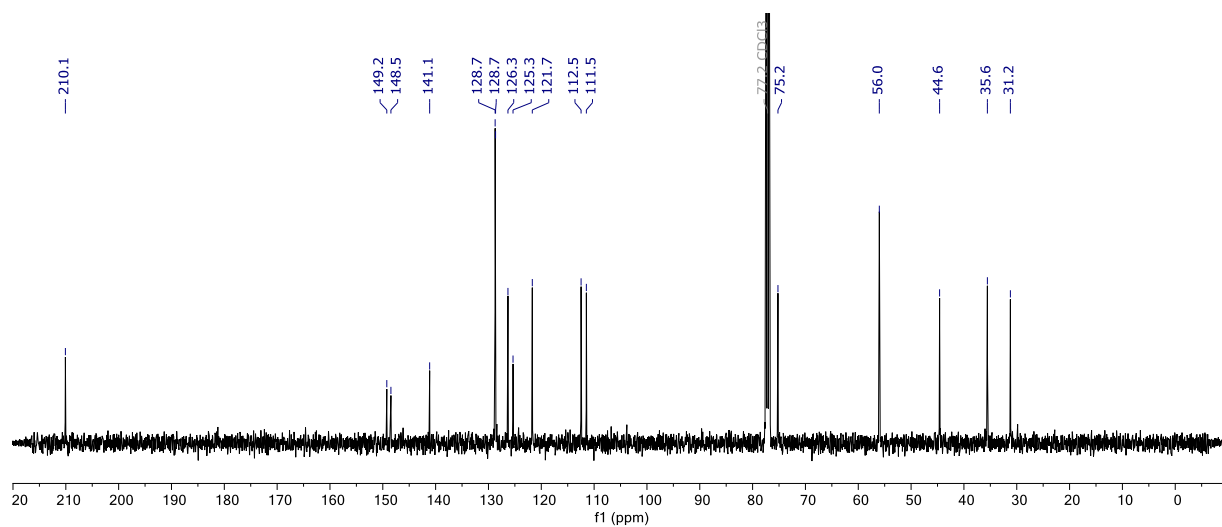


Figure A2.34. ¹³C{¹H} NMR spectrum for **19** (101 MHz, CDCl₃, room temperature).

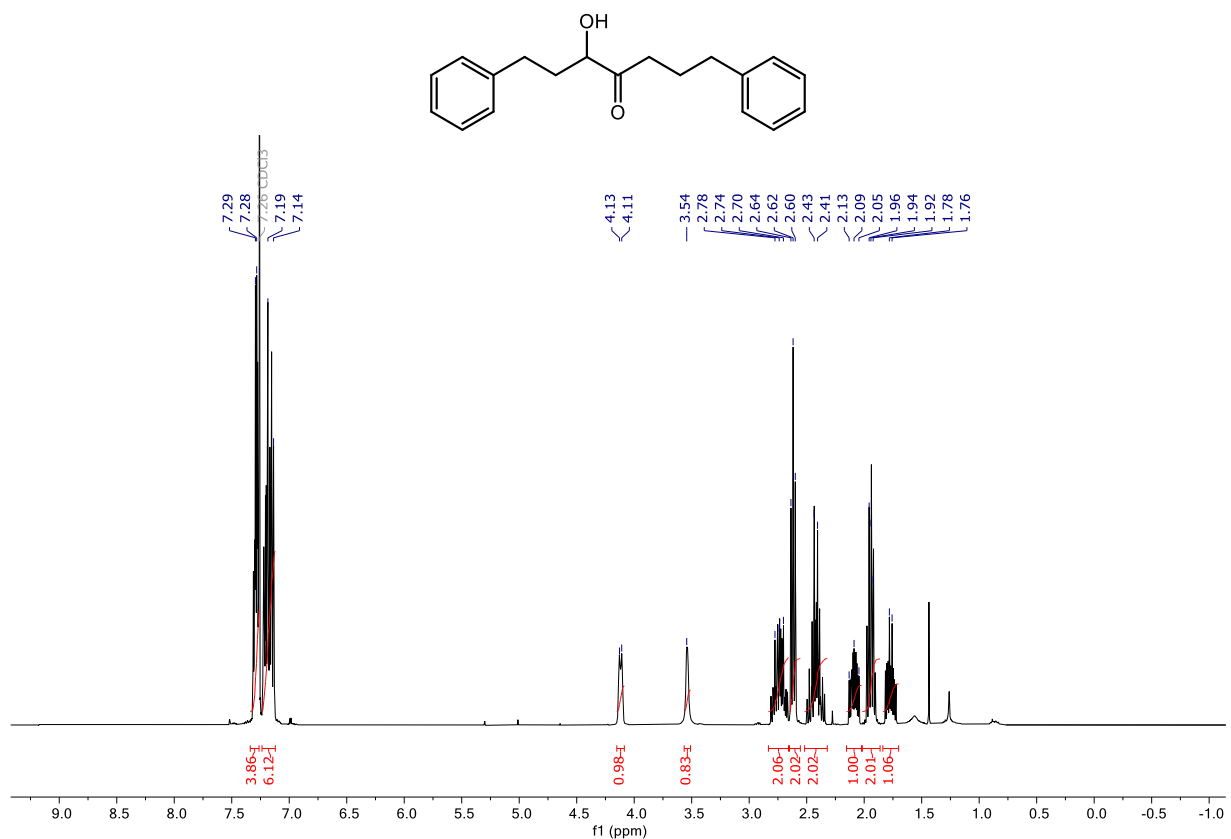


Figure A2.35. ¹H NMR spectrum for **20** (400 MHz, CDCl₃, room temperature).

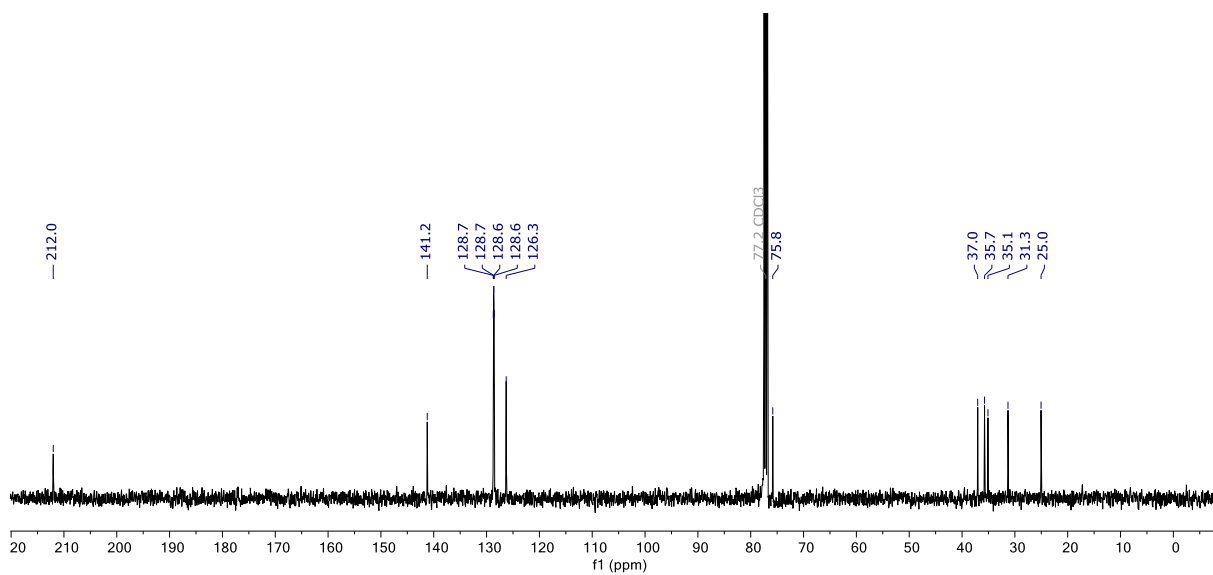


Figure A2.36. ¹³C{¹H} NMR spectrum for **20** (101 MHz, CDCl₃, room temperature).

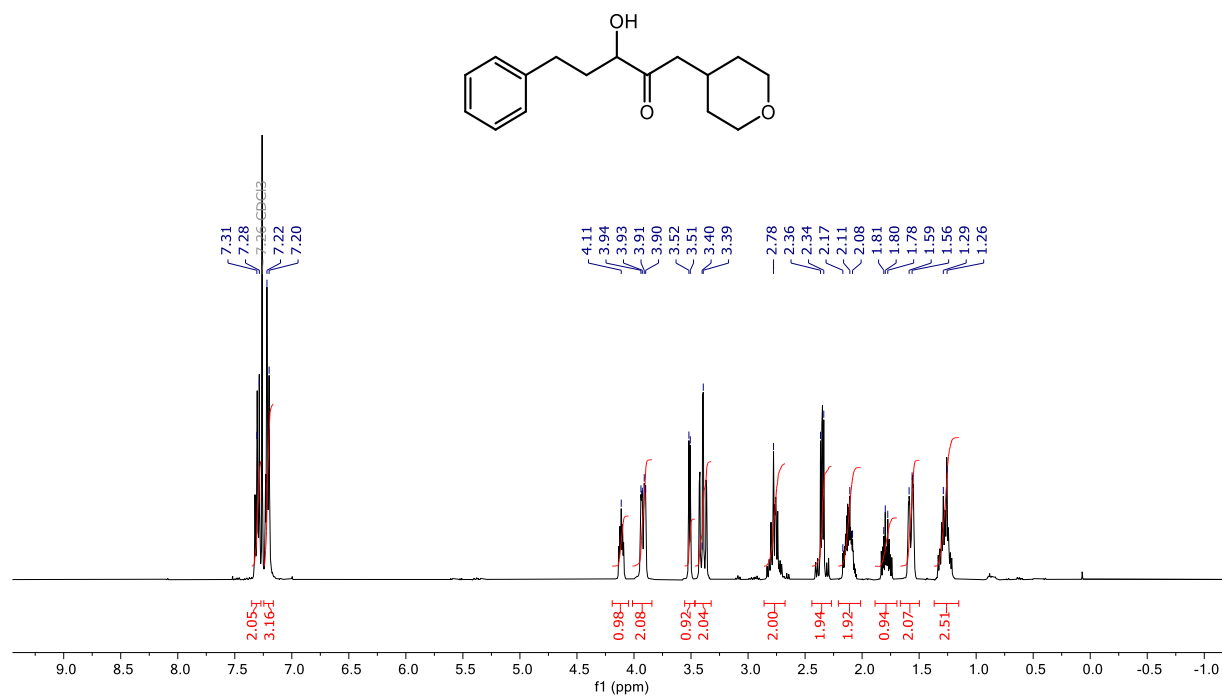


Figure A2.37. ¹H NMR spectrum for **21** (400 MHz, CDCl₃, room temperature).

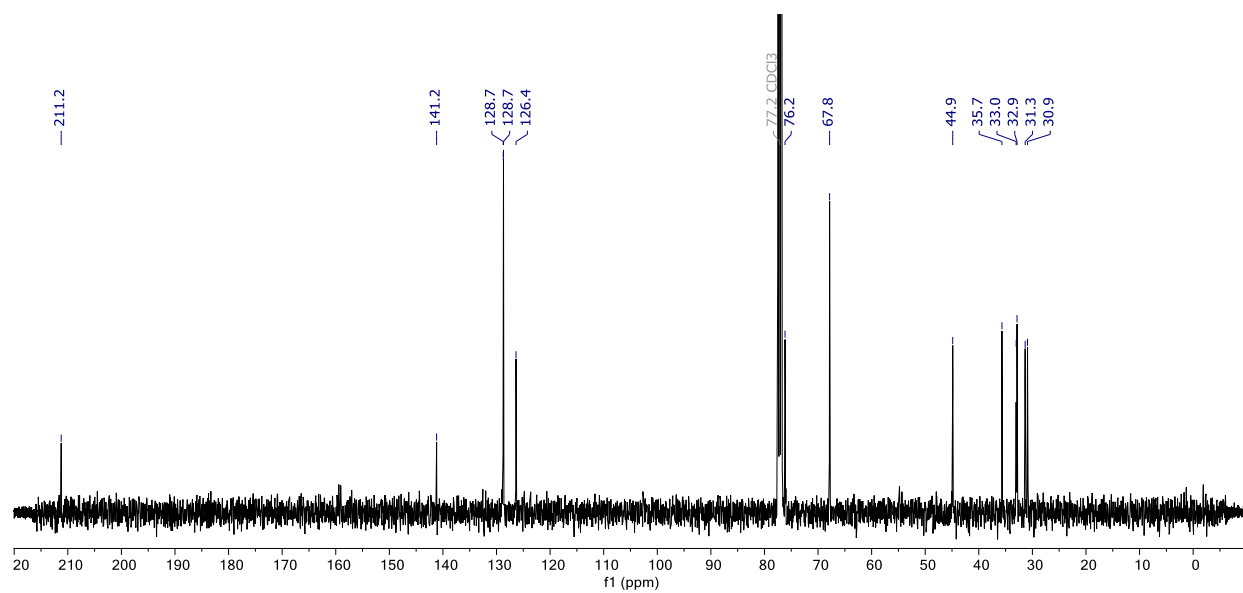


Figure A2.38. ¹³C{¹H} NMR spectrum for **21** (101 MHz, CDCl₃, room temperature).

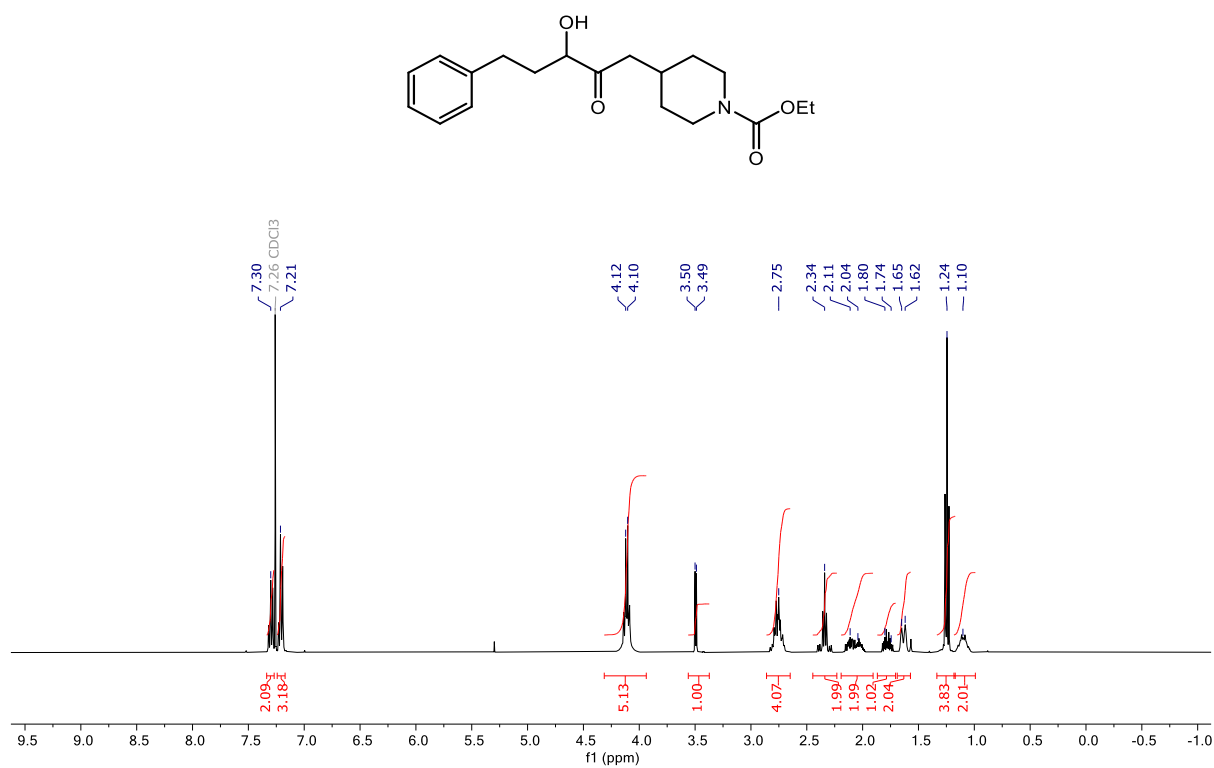


Figure A2.39. ¹H NMR spectrum for **22** (400 MHz, CDCl₃, room temperature).

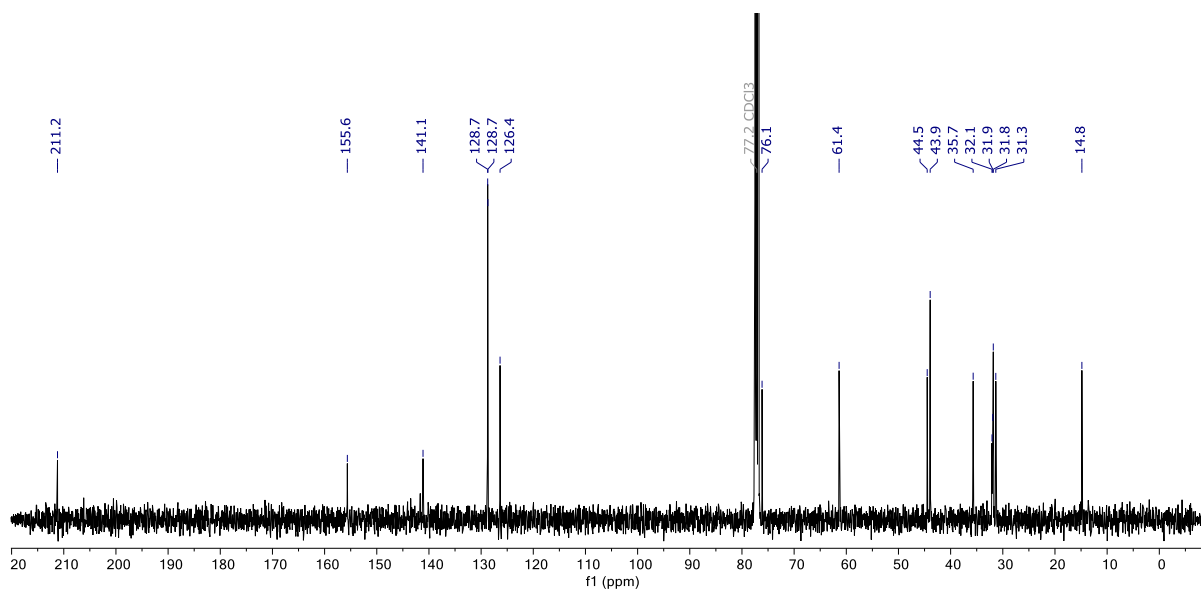


Figure A2.40. ¹³C{¹H} NMR spectrum for **22** (101 MHz, CDCl₃, room temperature).

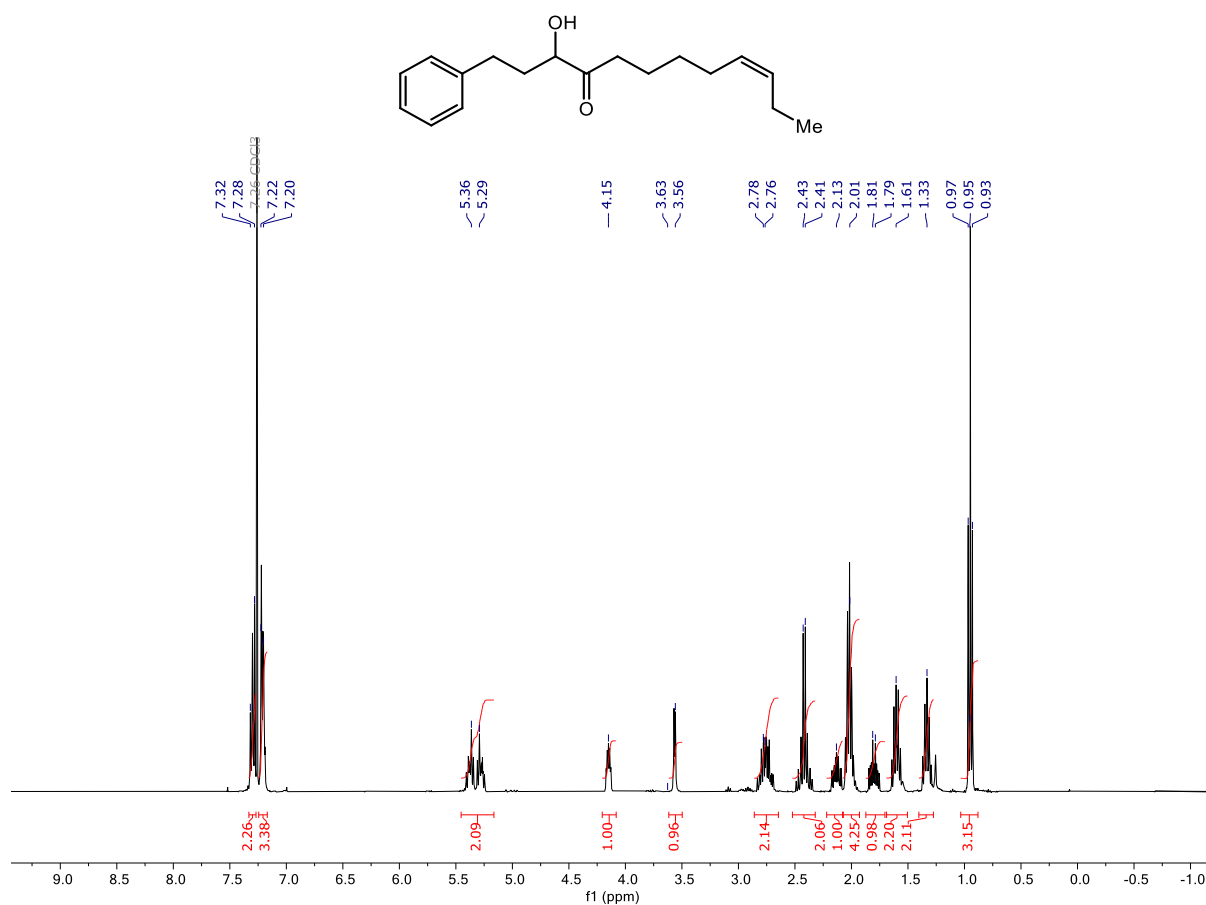


Figure A2.41. ¹H NMR spectrum for **23** (400 MHz, CDCl₃, room temperature).

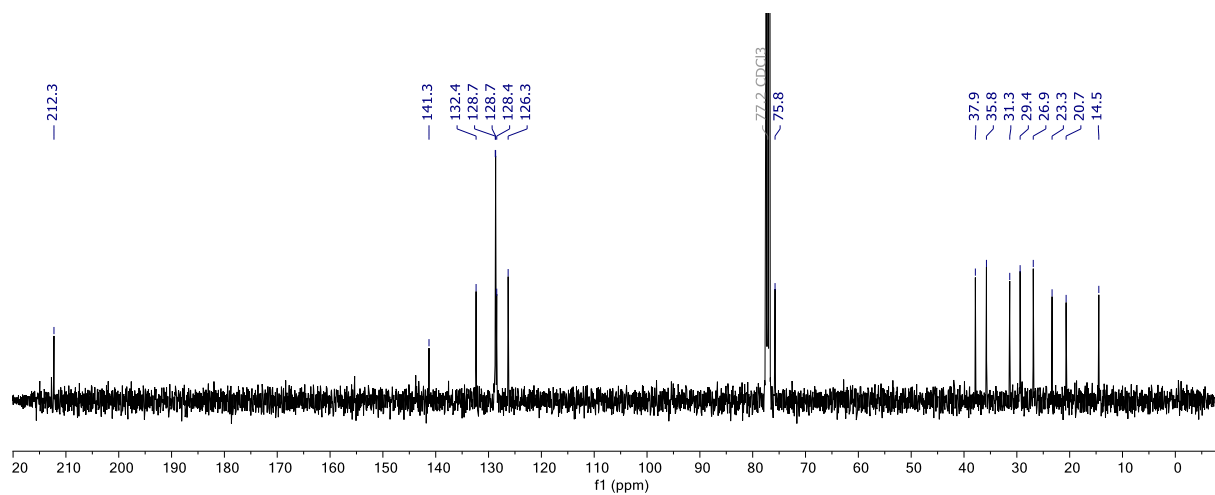


Figure A2.42. ¹³C{¹H} NMR spectrum for **23** (101 MHz, CDCl₃, room temperature).

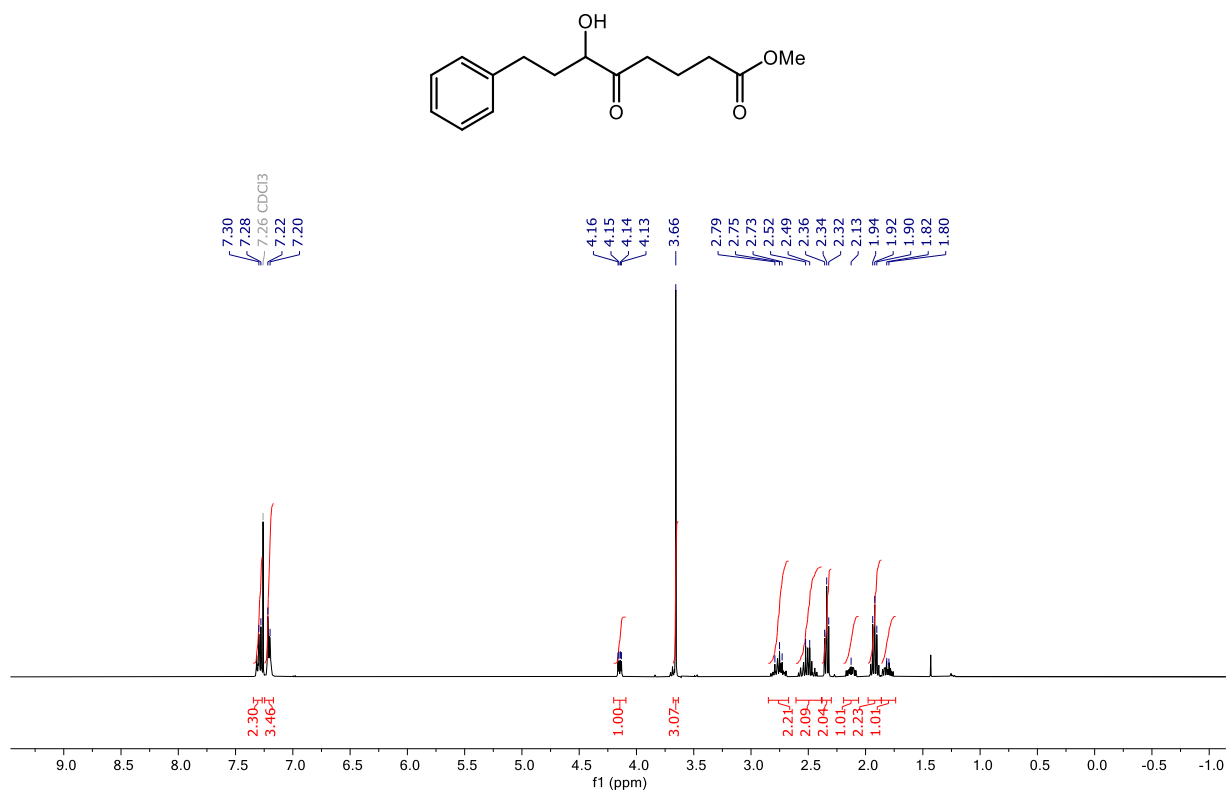


Figure A2.43. ¹H NMR spectrum for **24** (400 MHz, CDCl₃, room temperature).

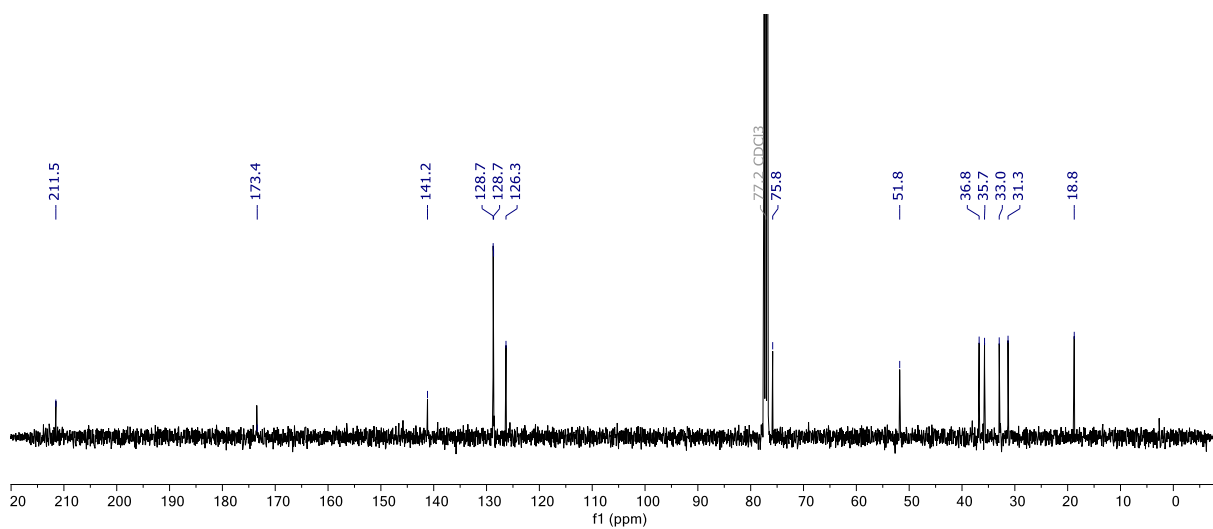


Figure A2.44. ¹³C{¹H} NMR spectrum for **24** (101 MHz, CDCl₃, room temperature).

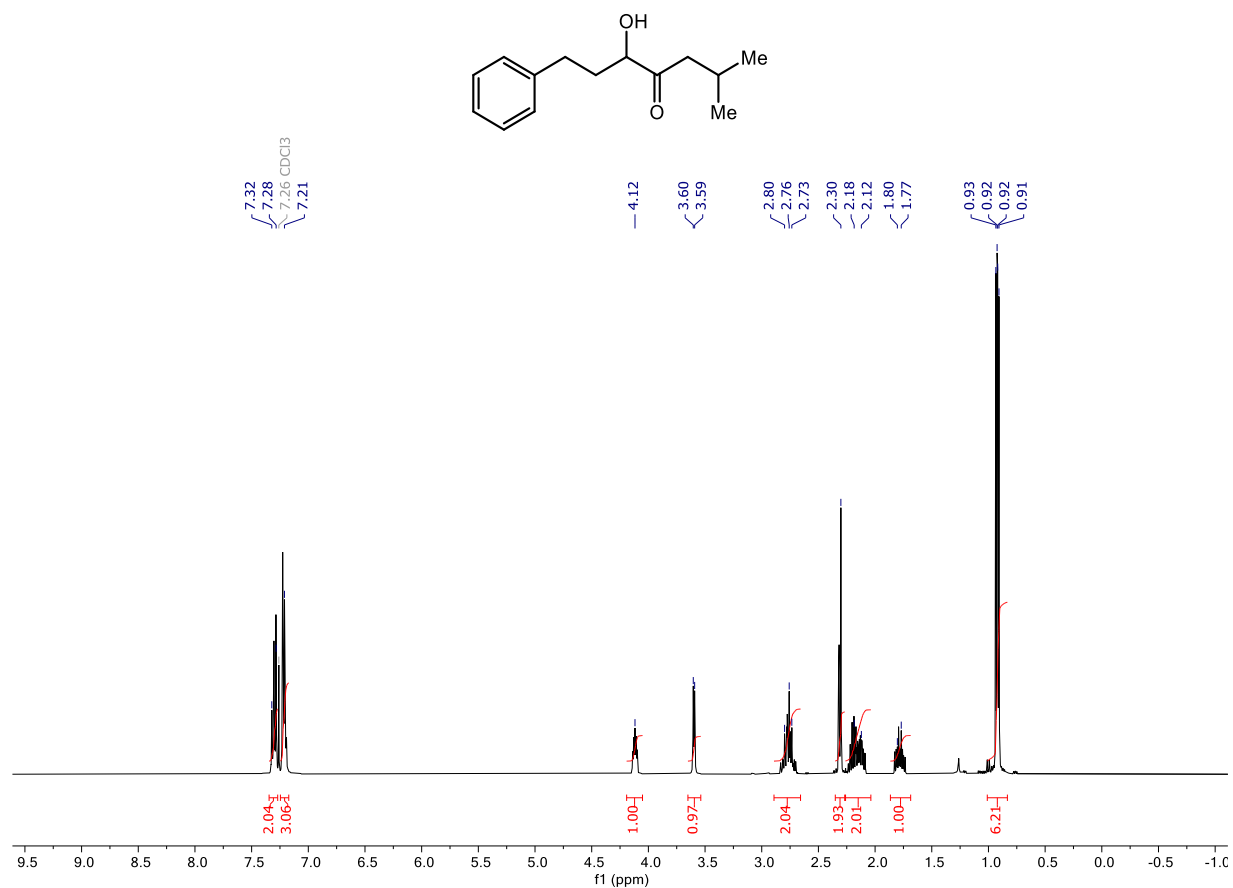


Figure A2.45. ^1H NMR spectrum for **25** (400 MHz, CDCl_3 , room temperature).

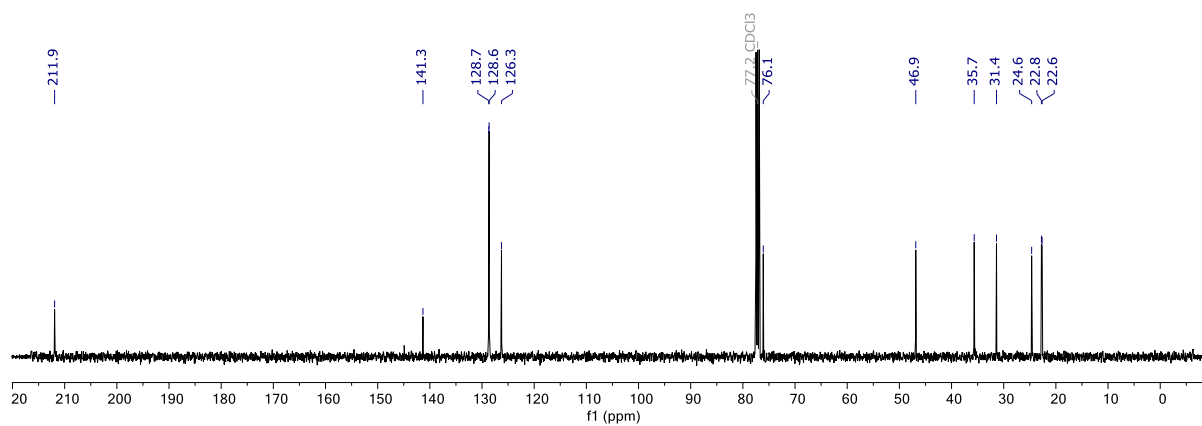


Figure A2.46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for **25** (101 MHz, CDCl_3 , room temperature).

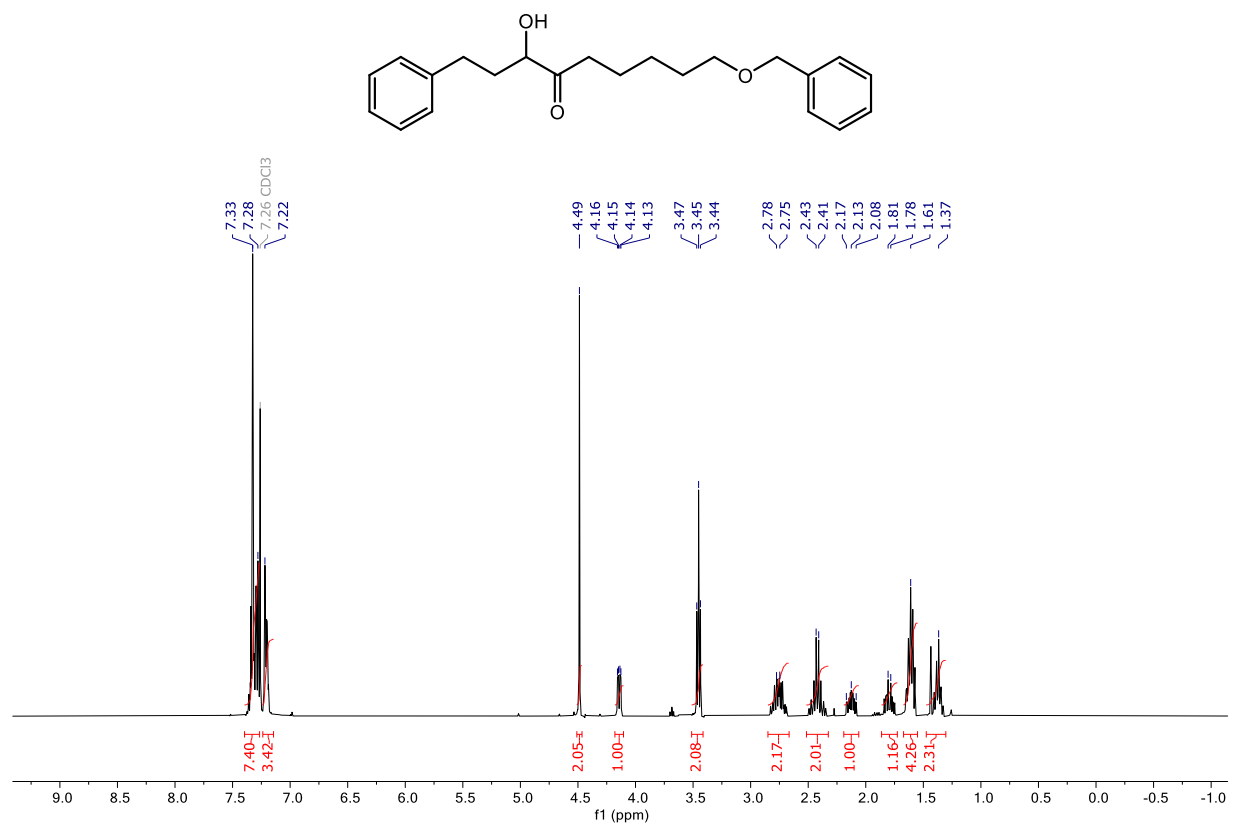


Figure A2.47. ¹H NMR spectrum for **26** (400 MHz, CDCl₃, room temperature).

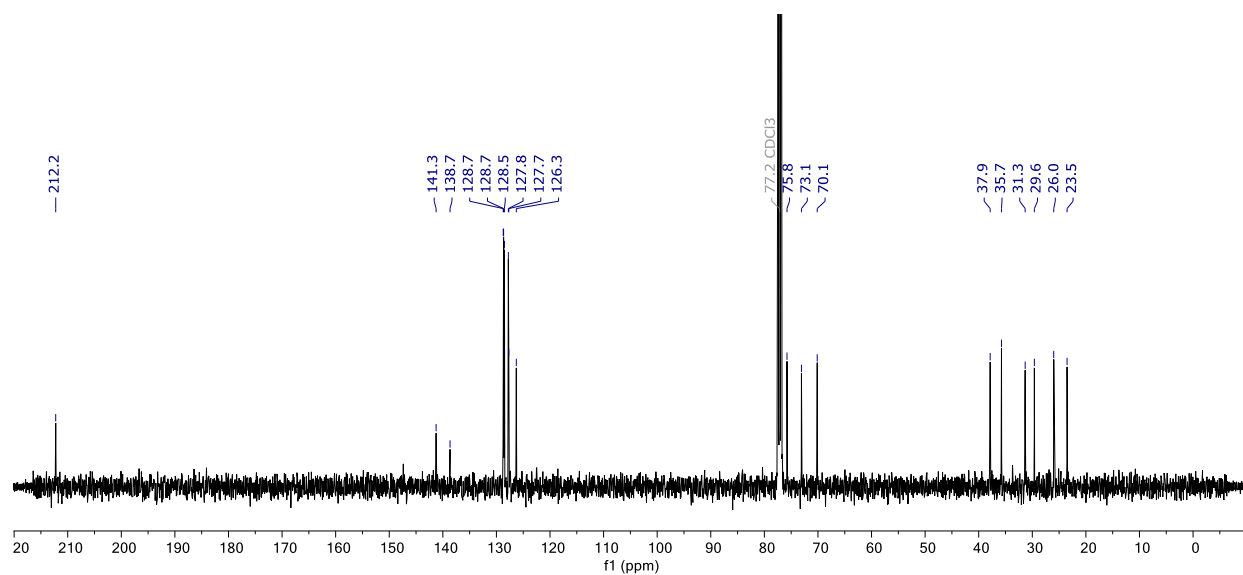


Figure A2.48. ¹³C{¹H} NMR spectrum for **26** (101 MHz, CDCl₃, room temperature).

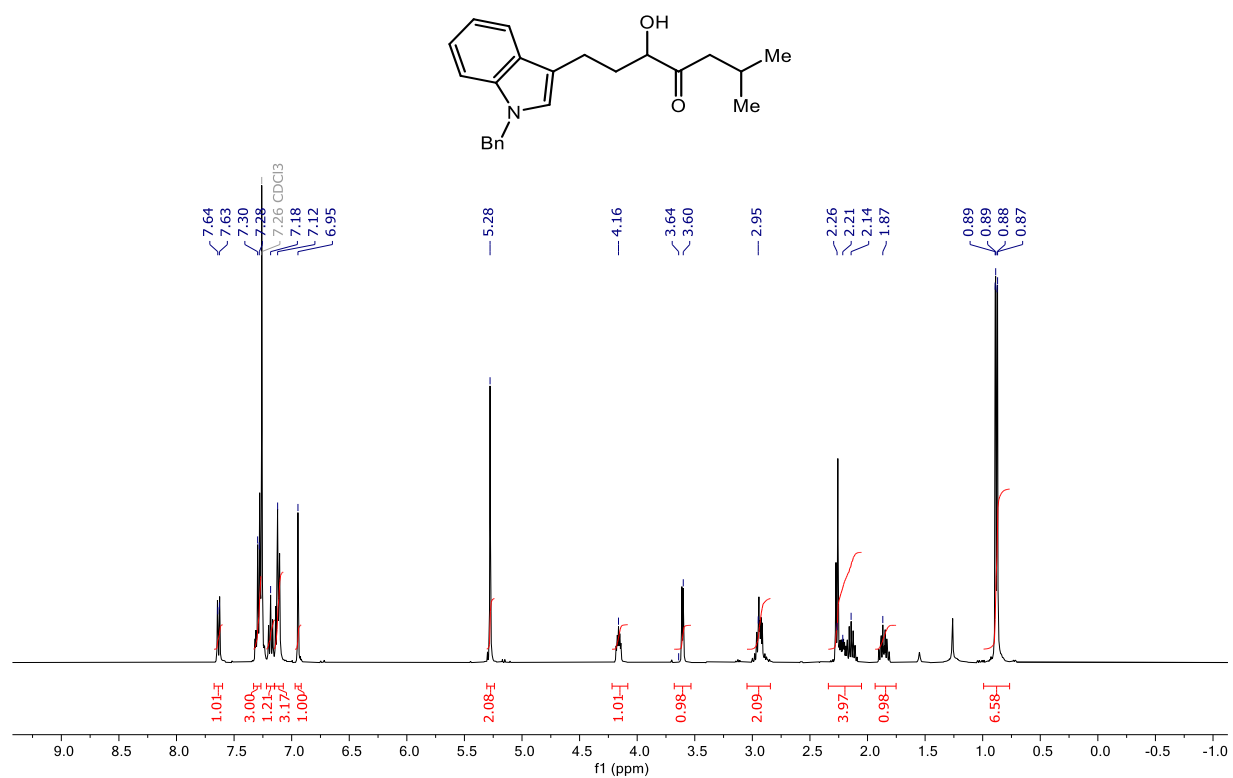


Figure A2.49. ¹H NMR spectrum for **27** (400 MHz, CDCl₃, room temperature).

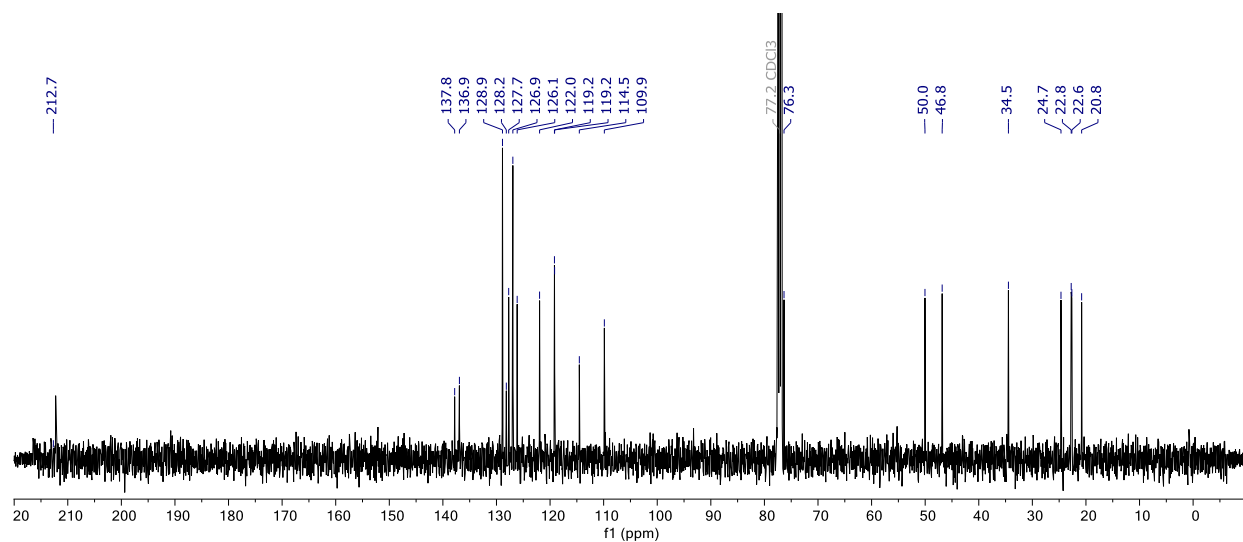


Figure A2.50. ¹³C{¹H} NMR spectrum for **27** (101 MHz, CDCl₃, room temperature).

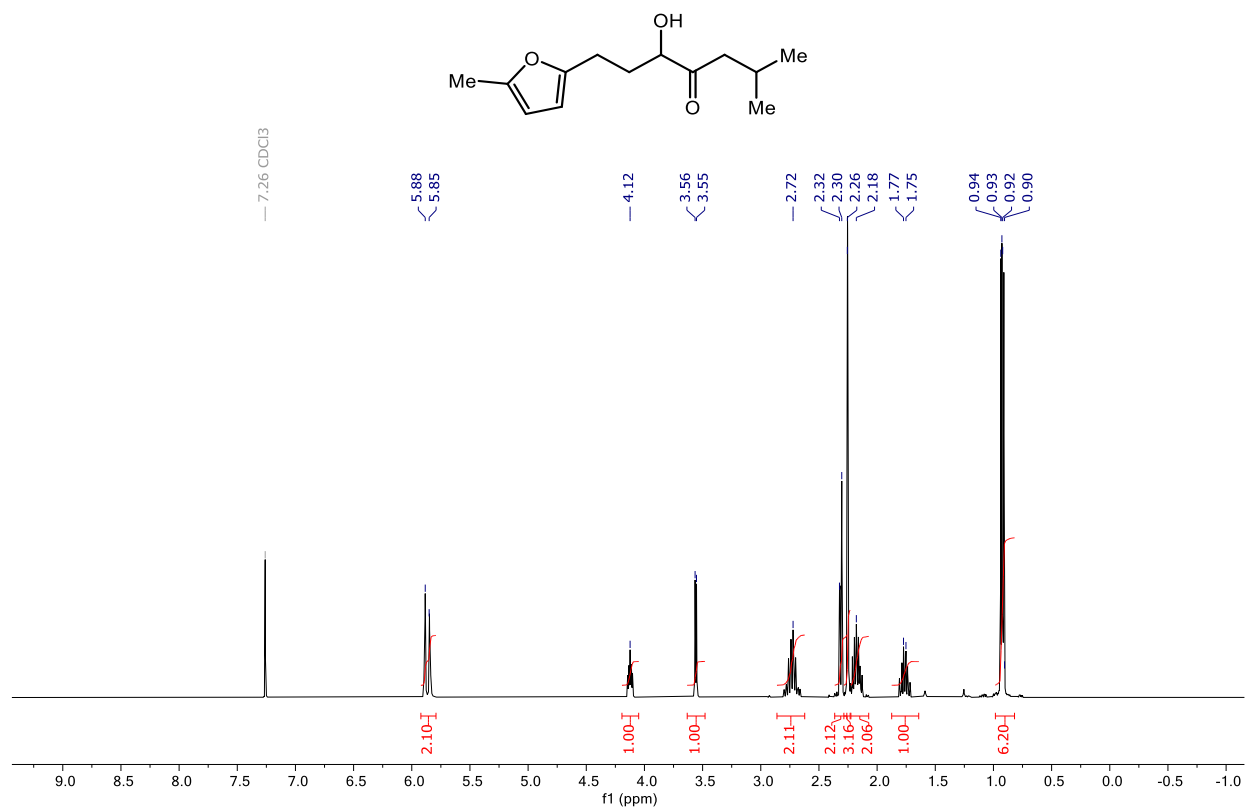


Figure A2.51. ¹H NMR spectrum for **28** (400 MHz, CDCl₃, room temperature).

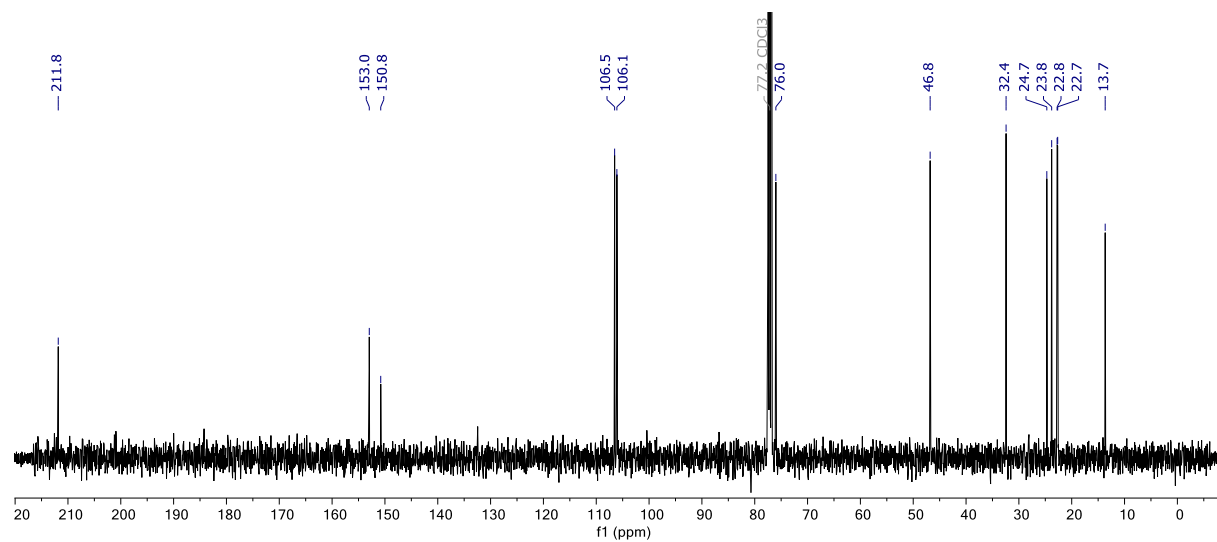


Figure A2.52. ¹³C{¹H} NMR spectrum for **28** (101 MHz, CDCl₃, room temperature).

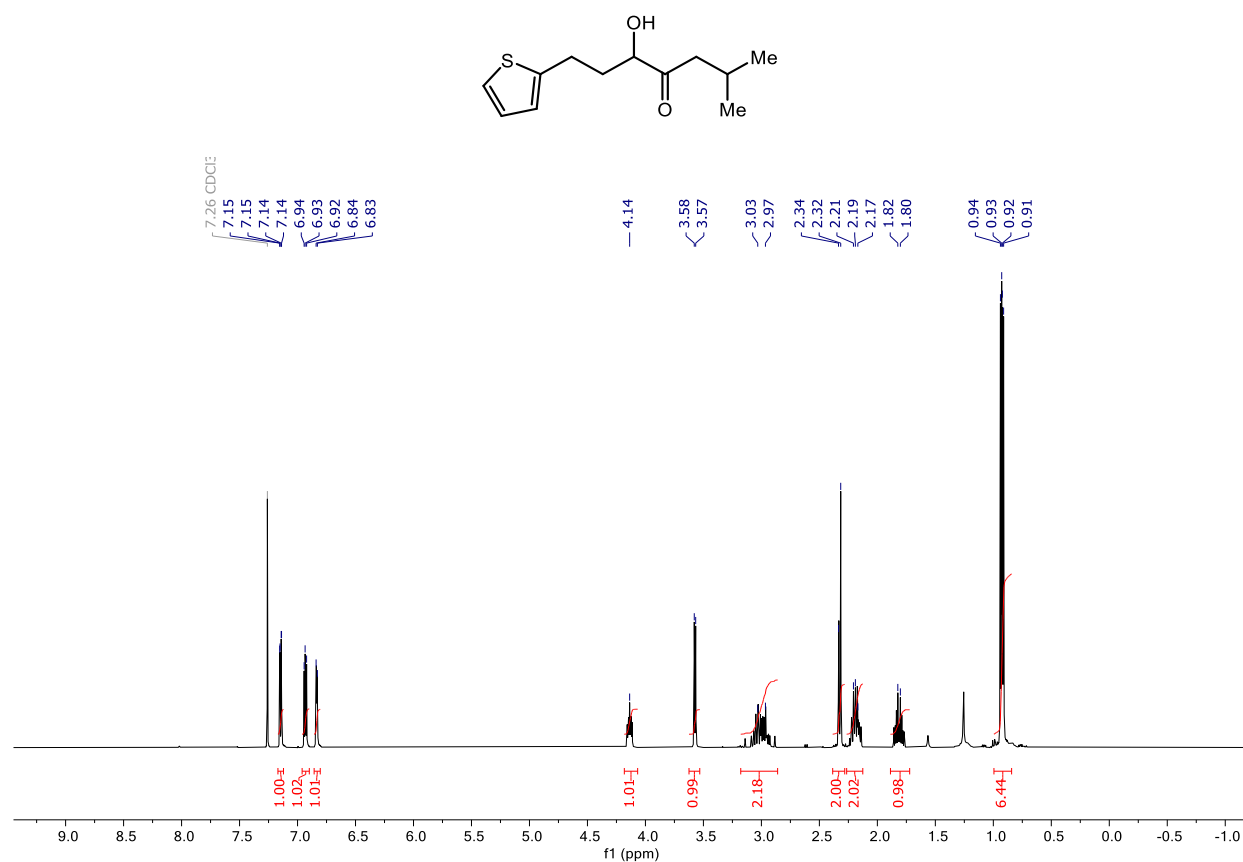


Figure A2.53. ¹H NMR spectrum for **29** (400 MHz, CDCl₃, room temperature).

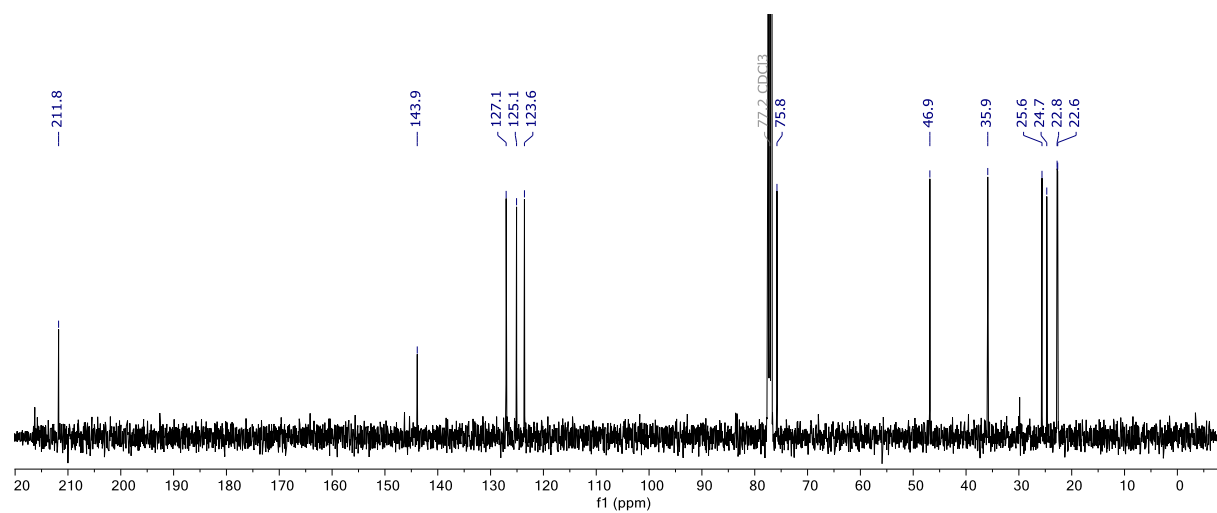


Figure A2.54. ¹³C{¹H} NMR spectrum for **29** (101 MHz, CDCl₃, room temperature).

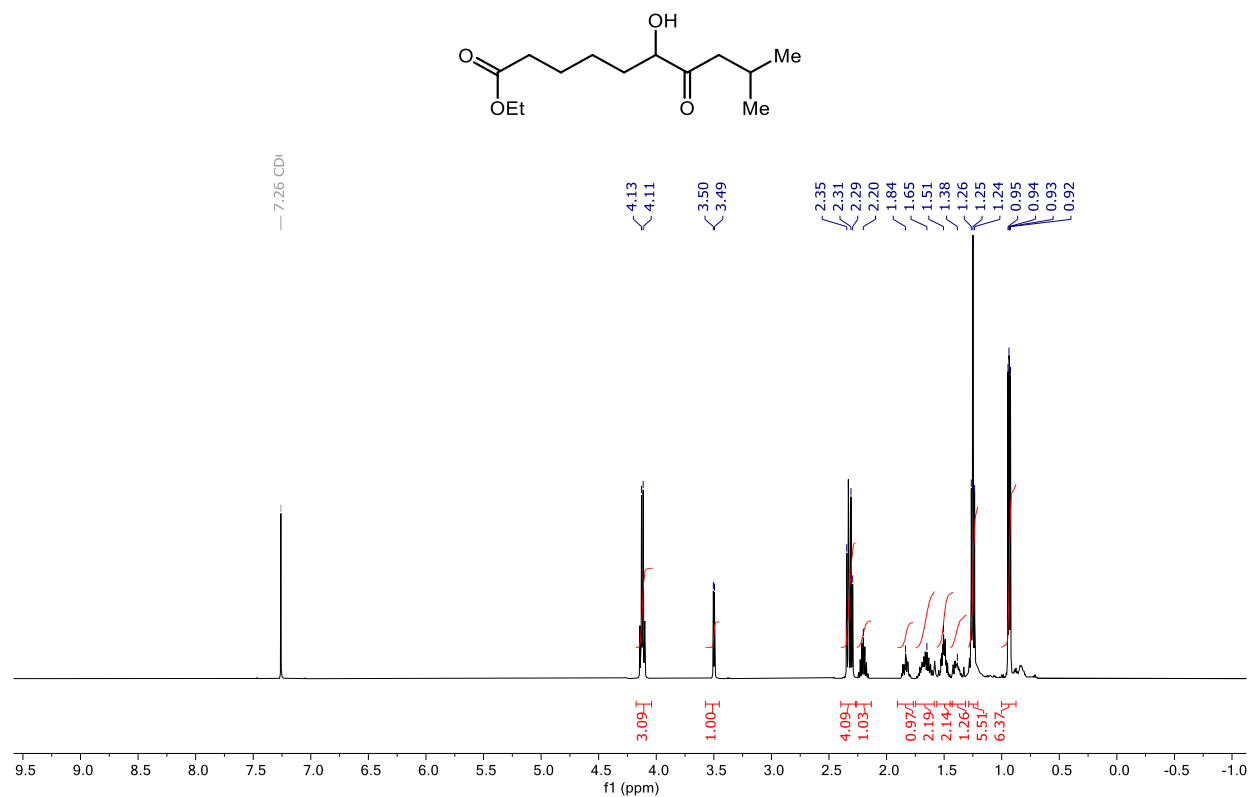


Figure A2.55. ¹H NMR spectrum for **30** (500 MHz, CDCl₃, room temperature).

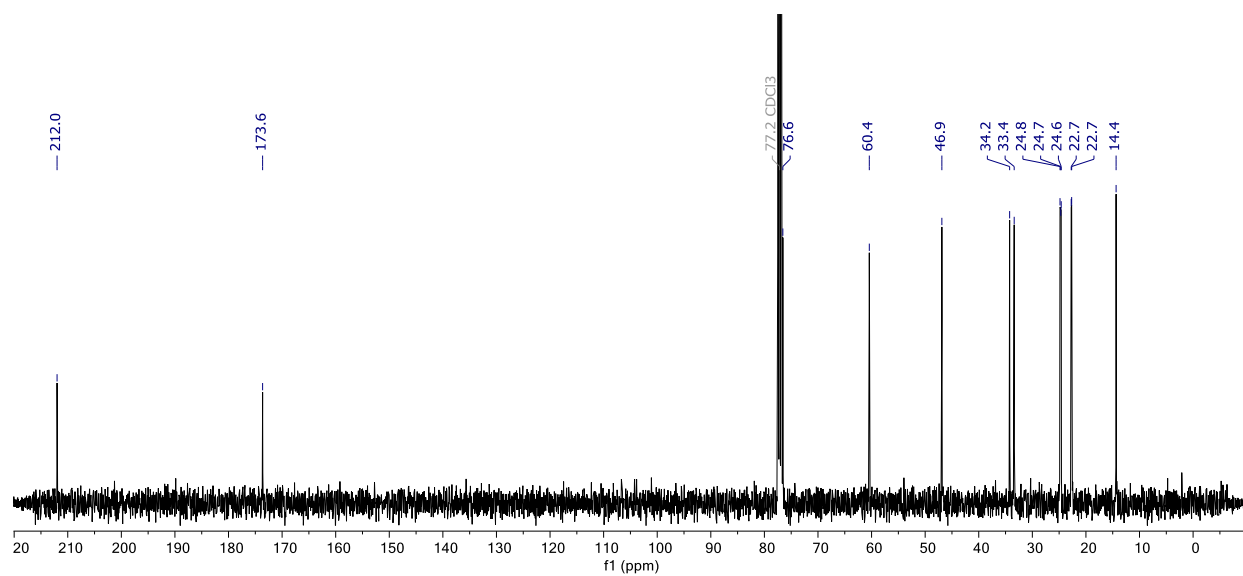


Figure A2.56. ¹³C{¹H} NMR spectrum for **30** (101 MHz, CDCl₃, room temperature).

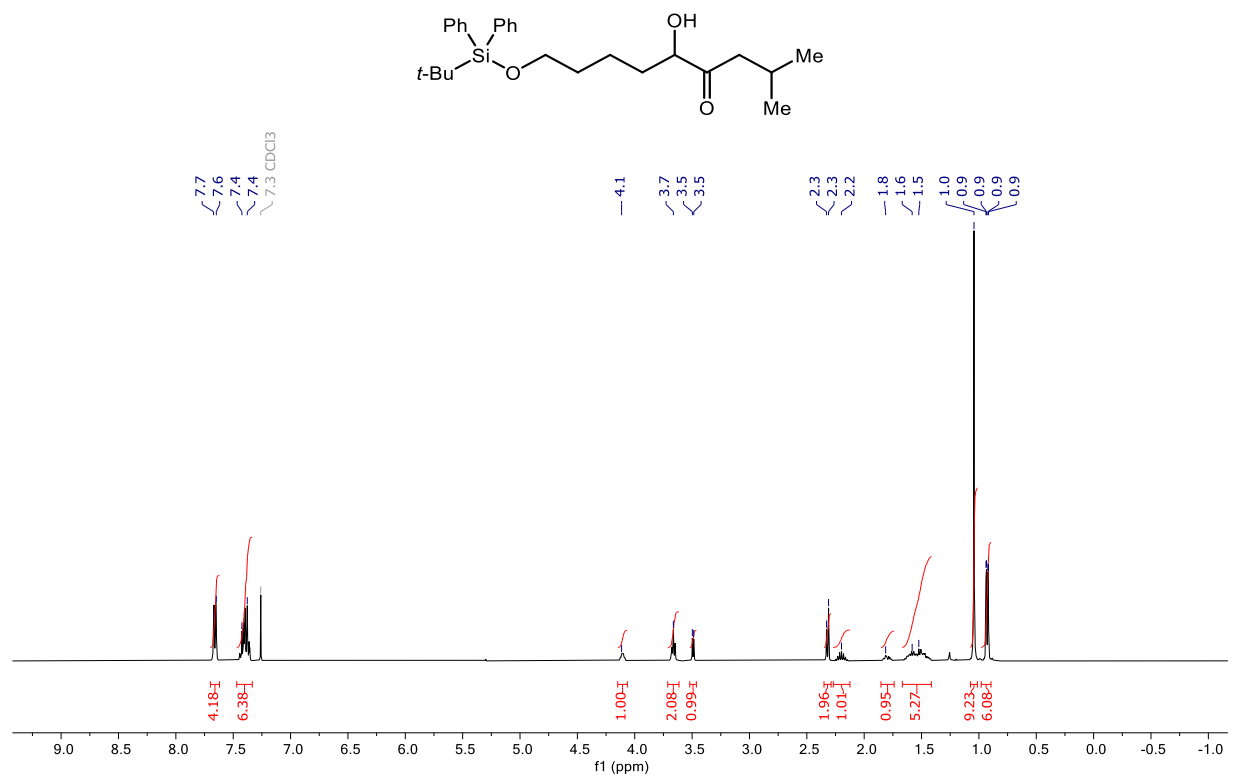


Figure A2.57. ¹H NMR spectrum for **31** (400 MHz, CDCl₃, room temperature).

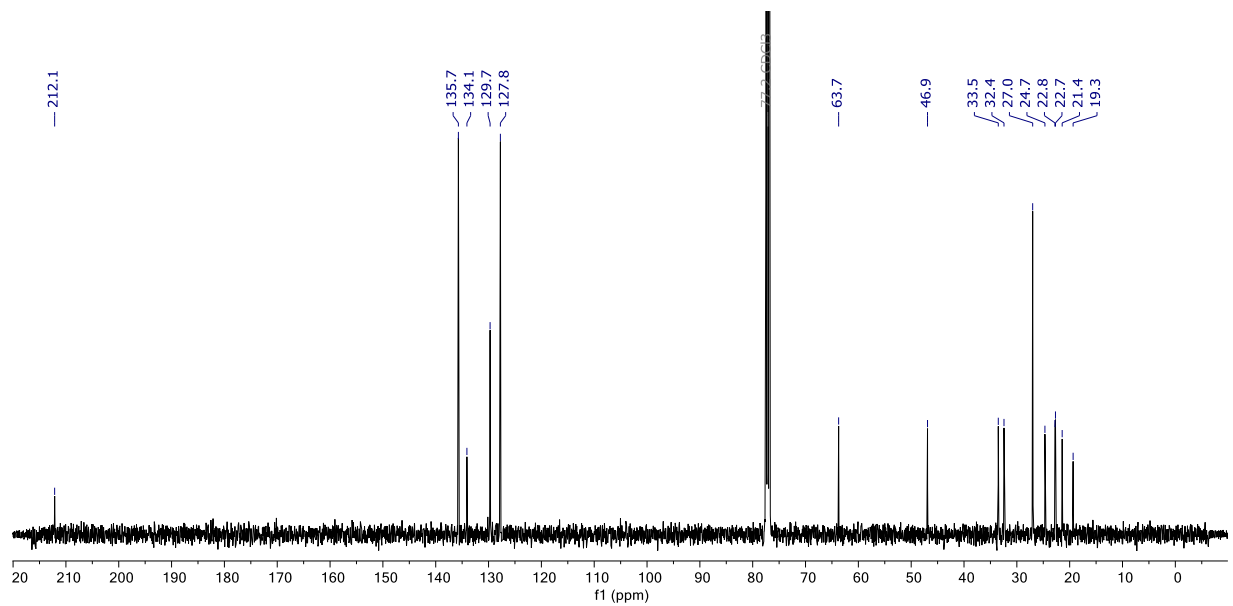


Figure A2.58. ¹³C{¹H} NMR spectrum for **31** (101 MHz, CDCl₃, room temperature).

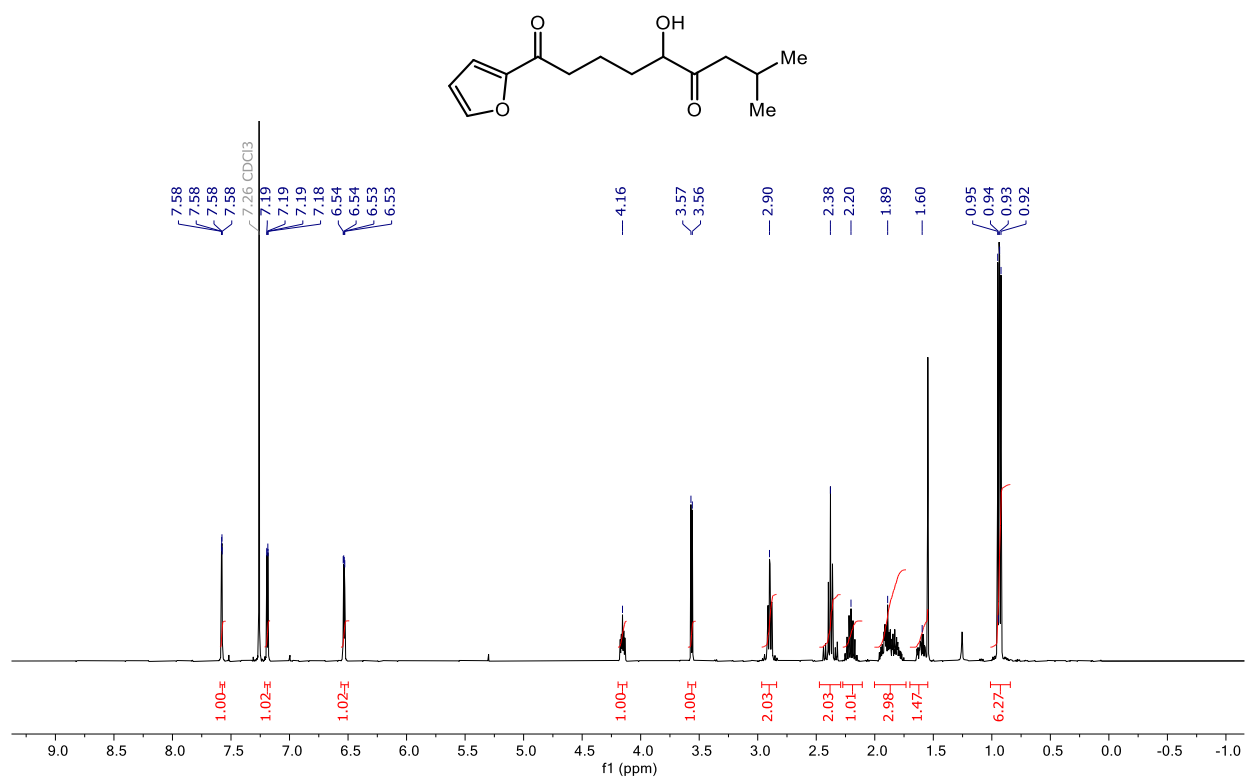


Figure A2.59. ¹H NMR spectrum for **32** (400 MHz, CDCl₃, room temperature).

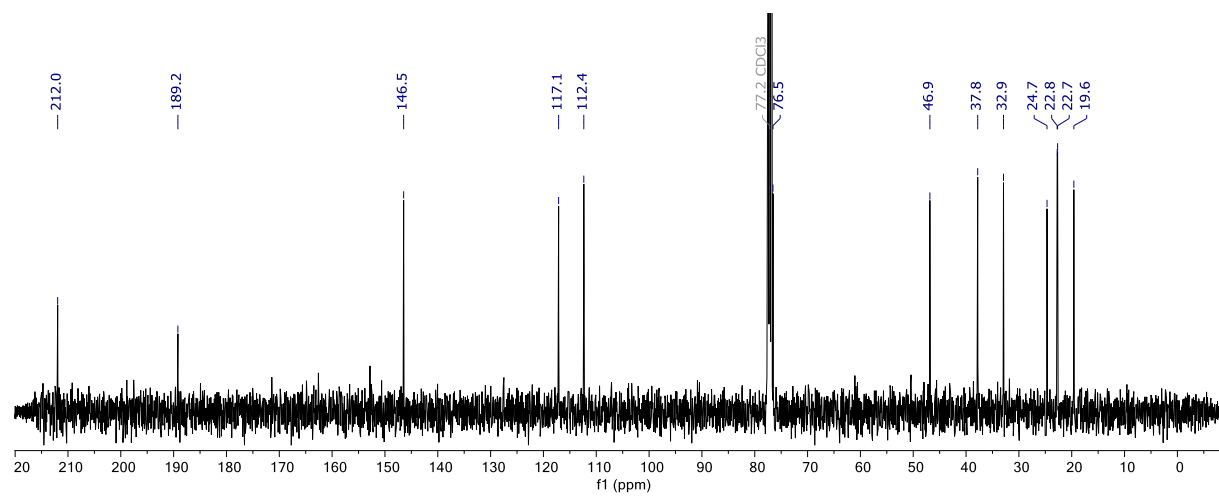


Figure A2.60. ¹³C{¹H} NMR spectrum for **32** (101 MHz, CDCl₃, room temperature).

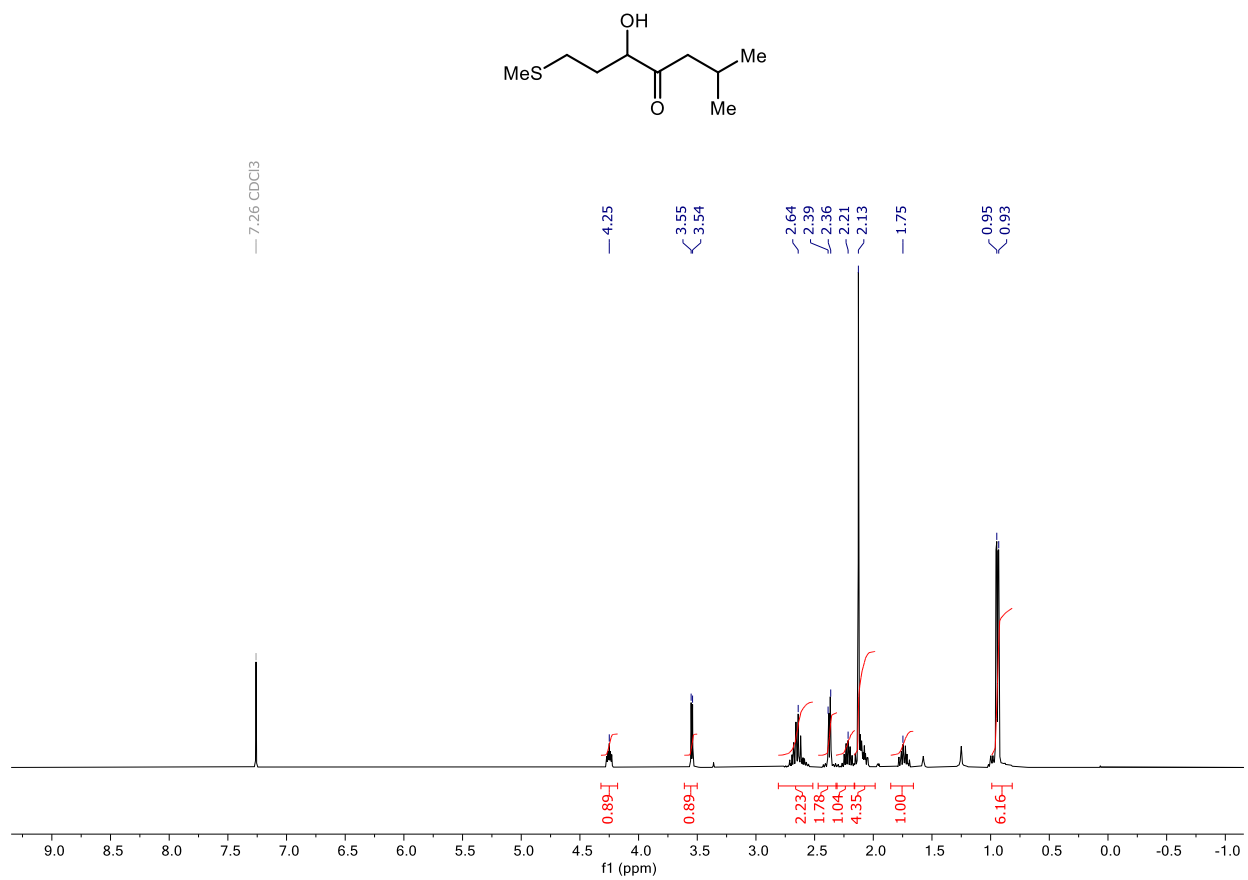


Figure A2.61. ^1H NMR spectrum for **33** (400 MHz, CDCl_3 , room temperature).

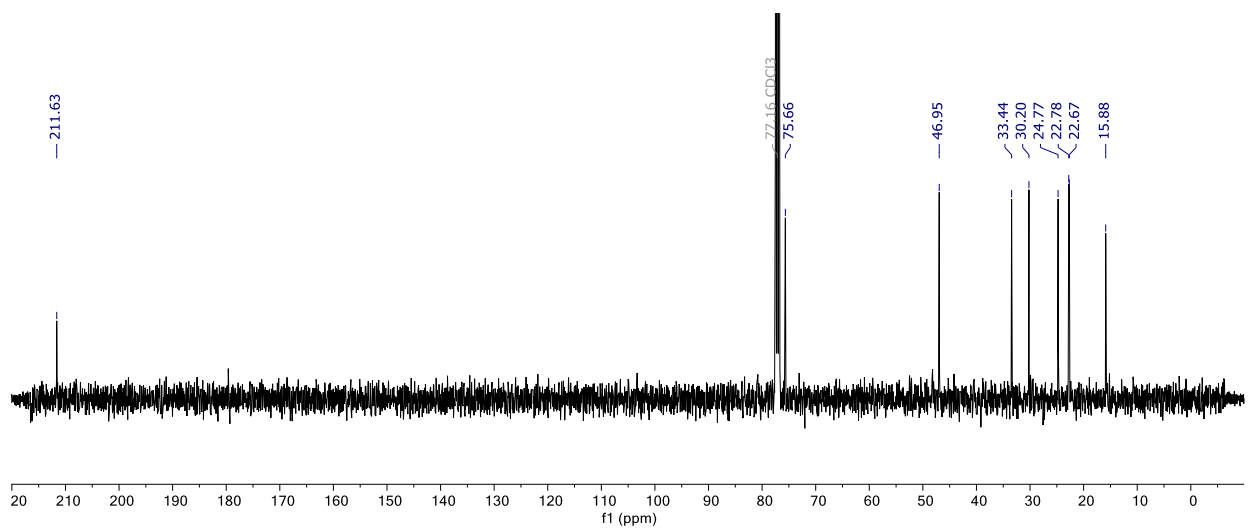


Figure A2.62. ^{13}C NMR spectrum for **33** (400 MHz, CDCl_3 , room temperature).

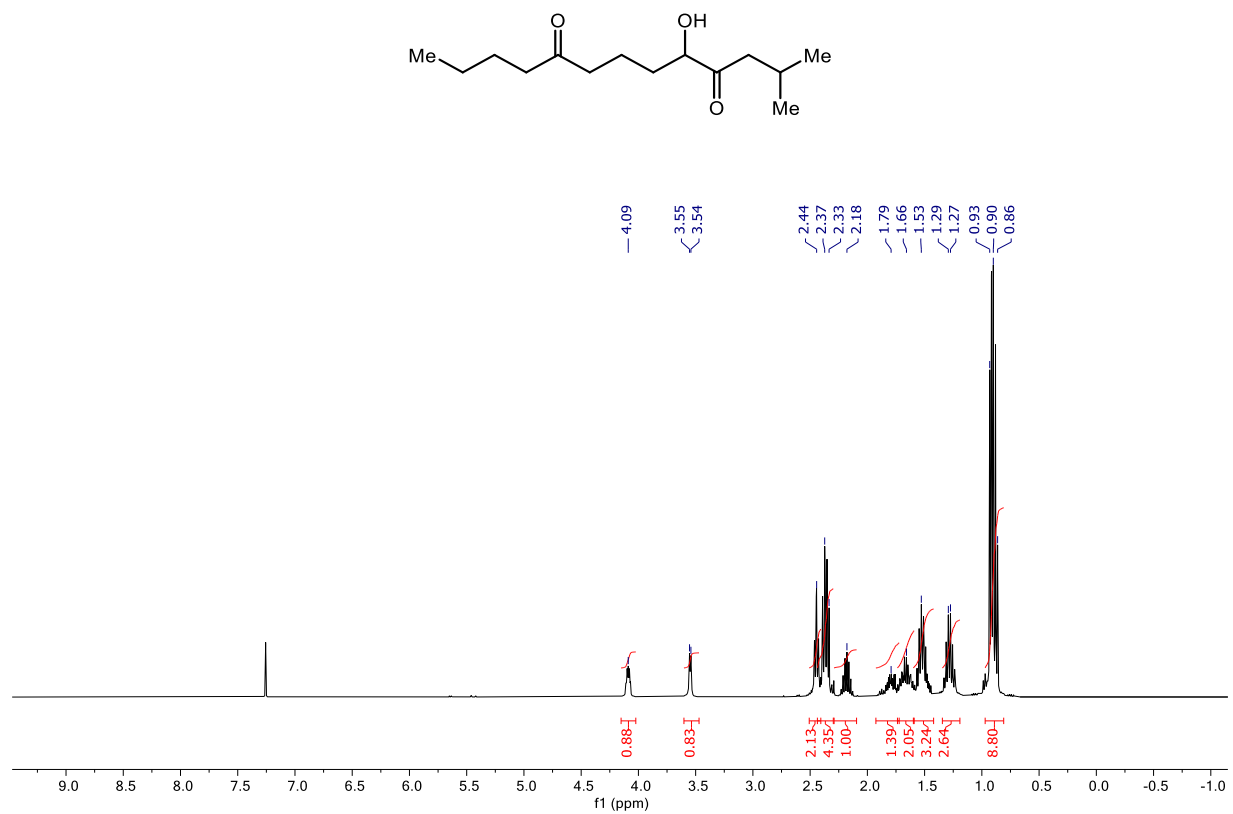


Figure 63. ¹H NMR A2.ppectrum for **34** (400 MHz, CDCl₃, room temperature).

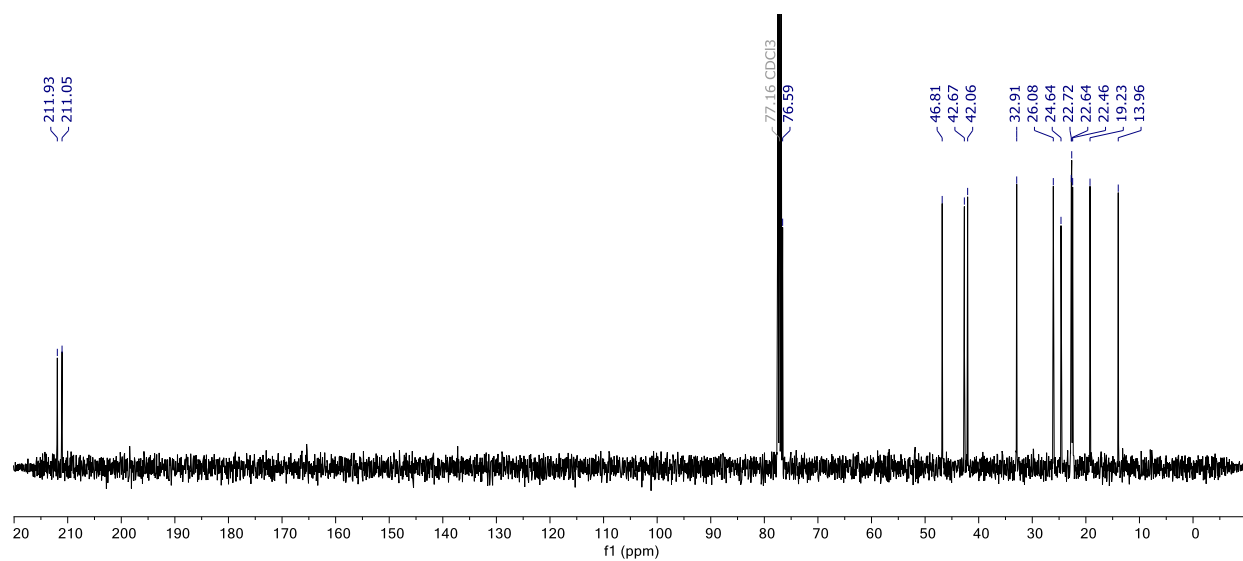


Figure S64. ¹³C{¹H} NMR A2.ppectrum for **34** (101 MHz, CDCl₃, room temperature).

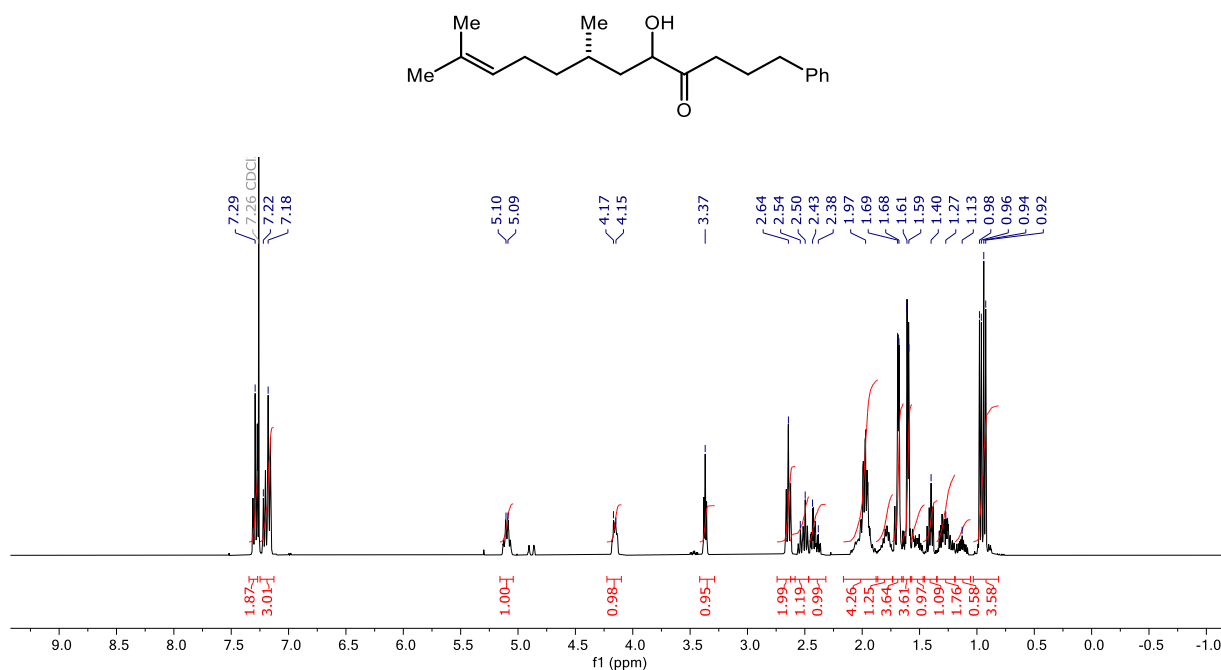


Figure A2.65. ¹H NMR spectrum for **35** (400 MHz, CDCl₃, room temperature).

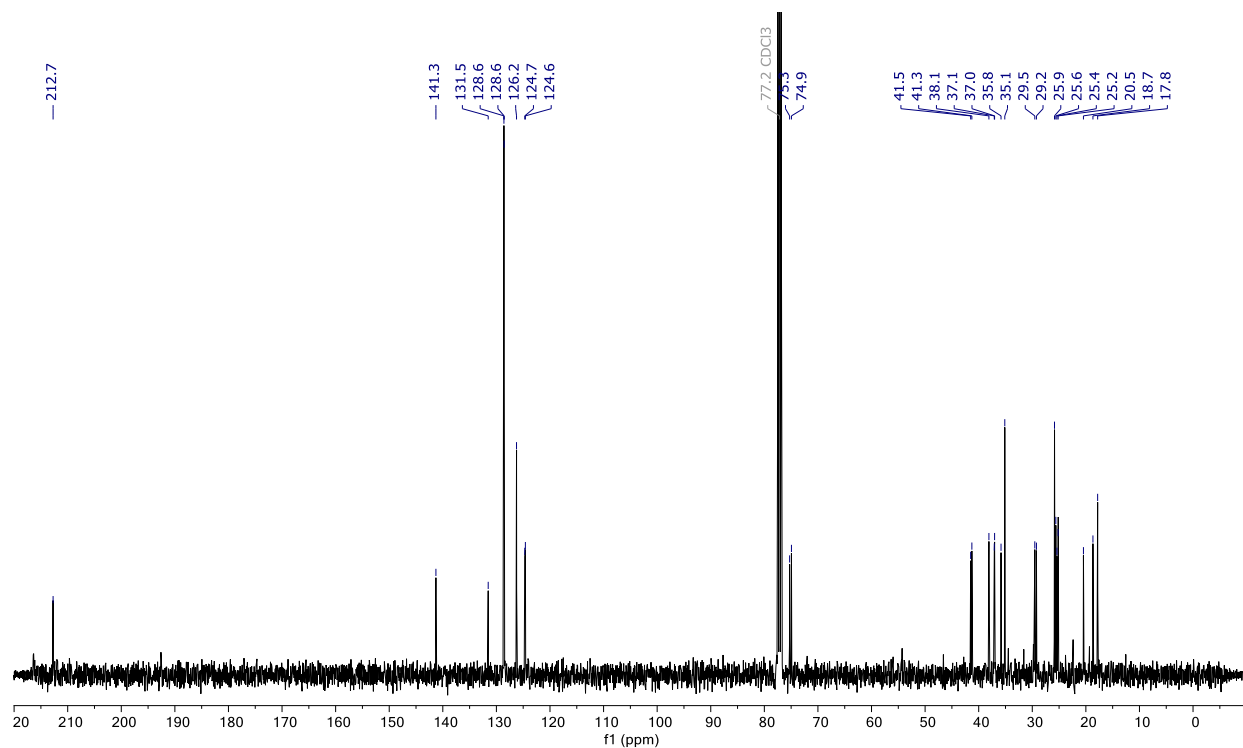


Figure A2.66. ¹³C{¹H} NMR spectrum for **35** (101 MHz, CDCl₃, room temperature).

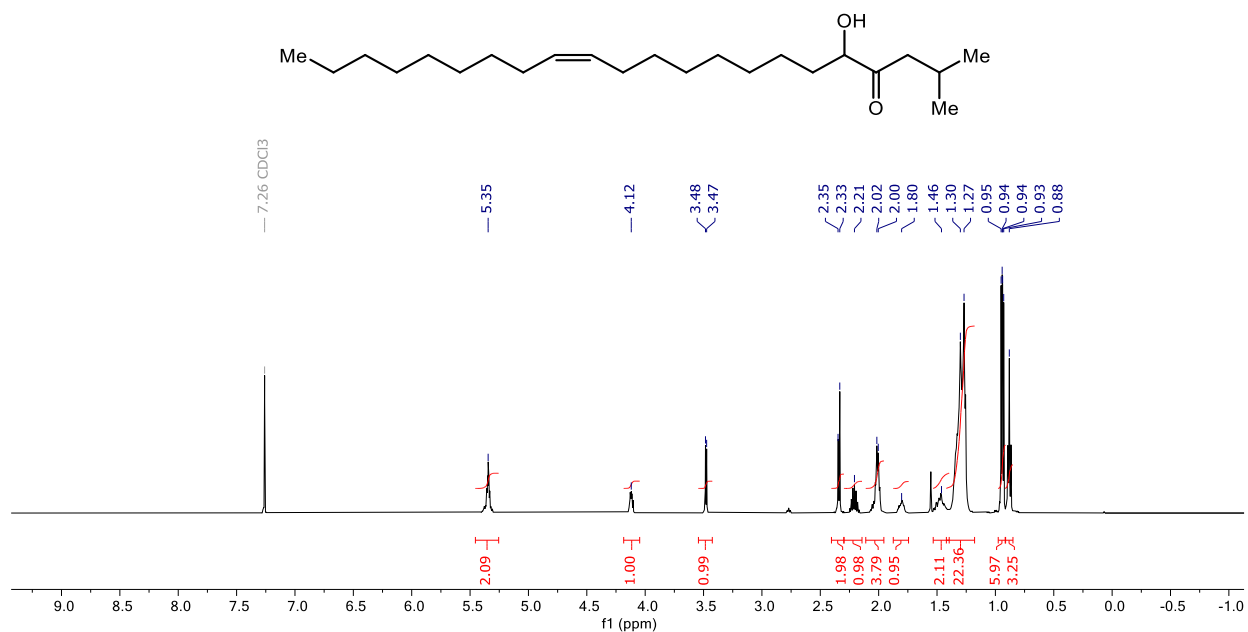


Figure A2.67. ¹H NMR spectrum for **36** (500 MHz, CDCl₃, room temperature).

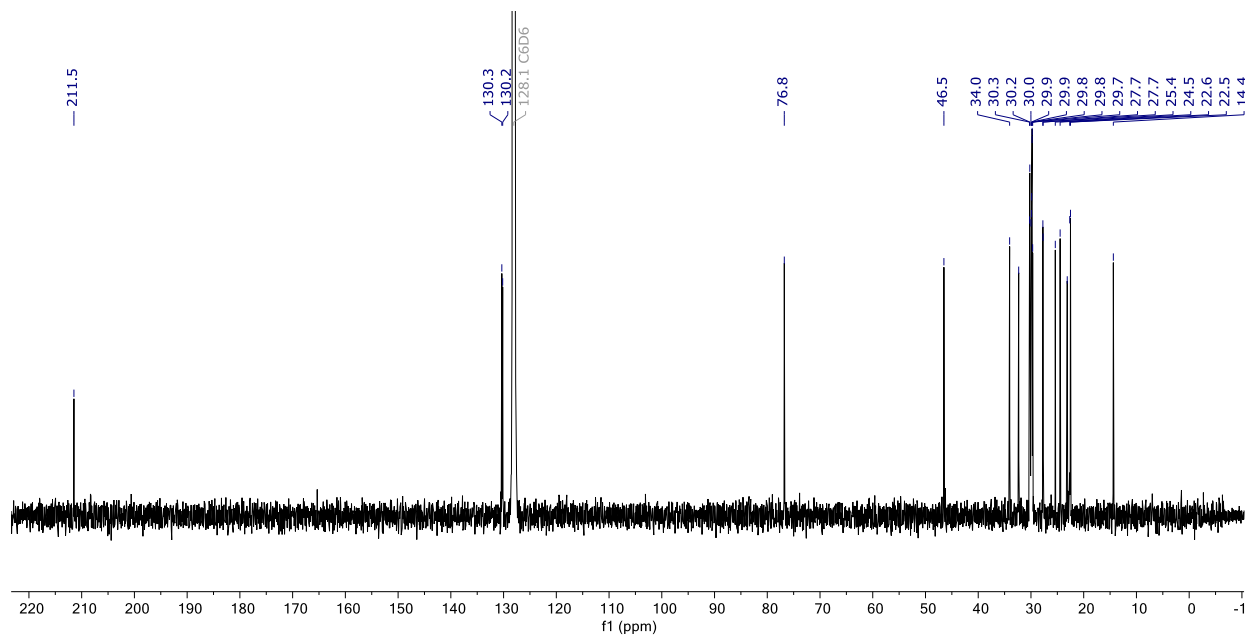


Figure A2.68. ¹³C{¹H} NMR spectrum for **36** (126 MHz, C₆D₆, room temperature).

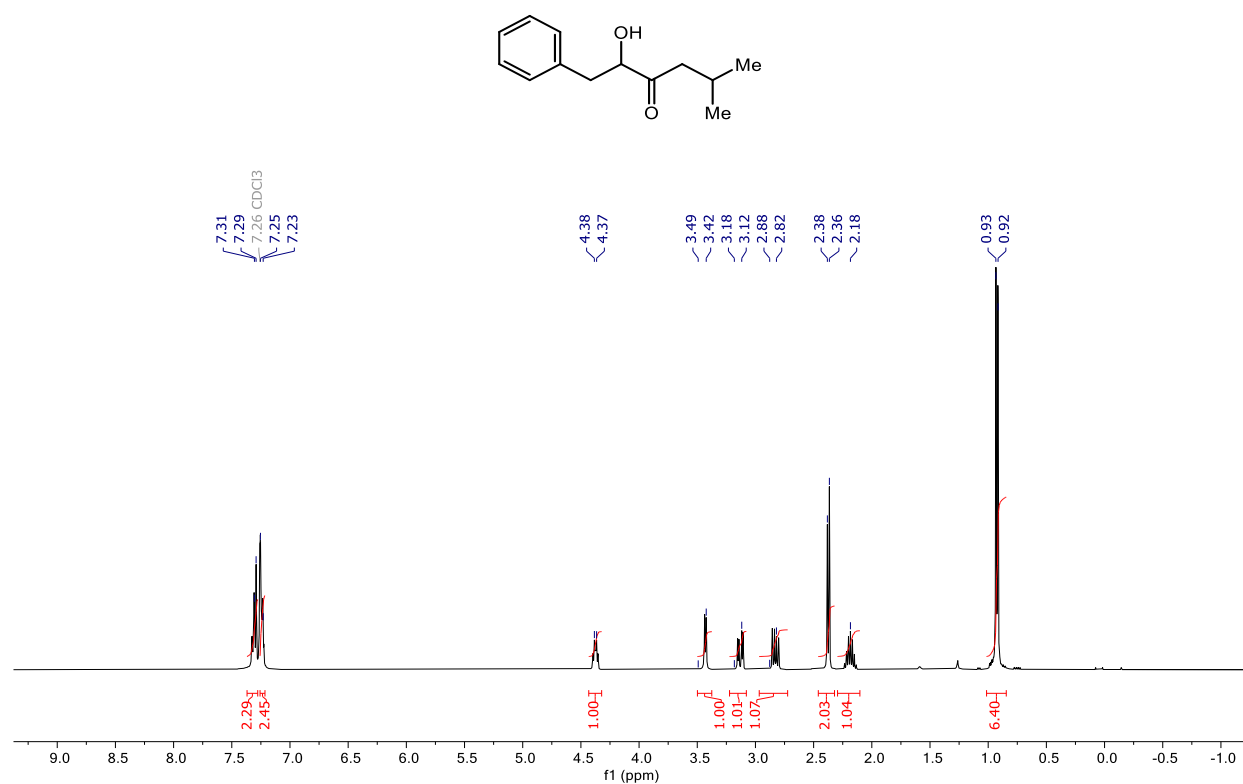


Figure A2.69. ¹H NMR spectrum for **37** (400 MHz, CDCl₃, room temperature).

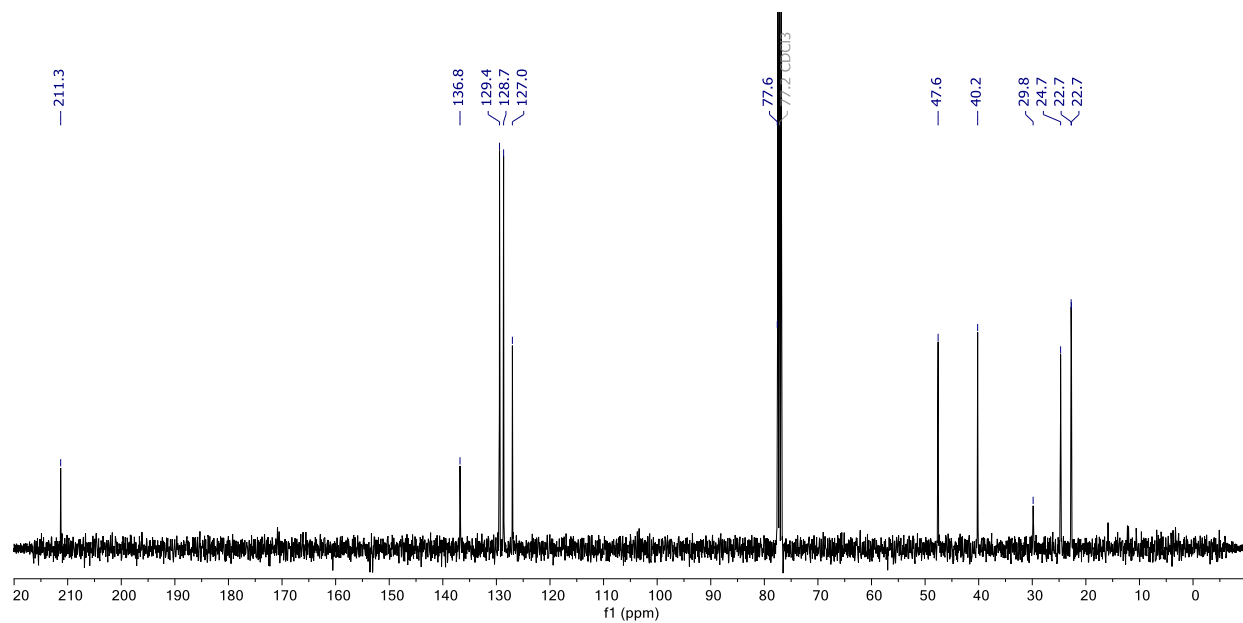


Figure A2.70. ¹³C{¹H} NMR spectrum for **37** (101 MHz, CDCl₃, room temperature)

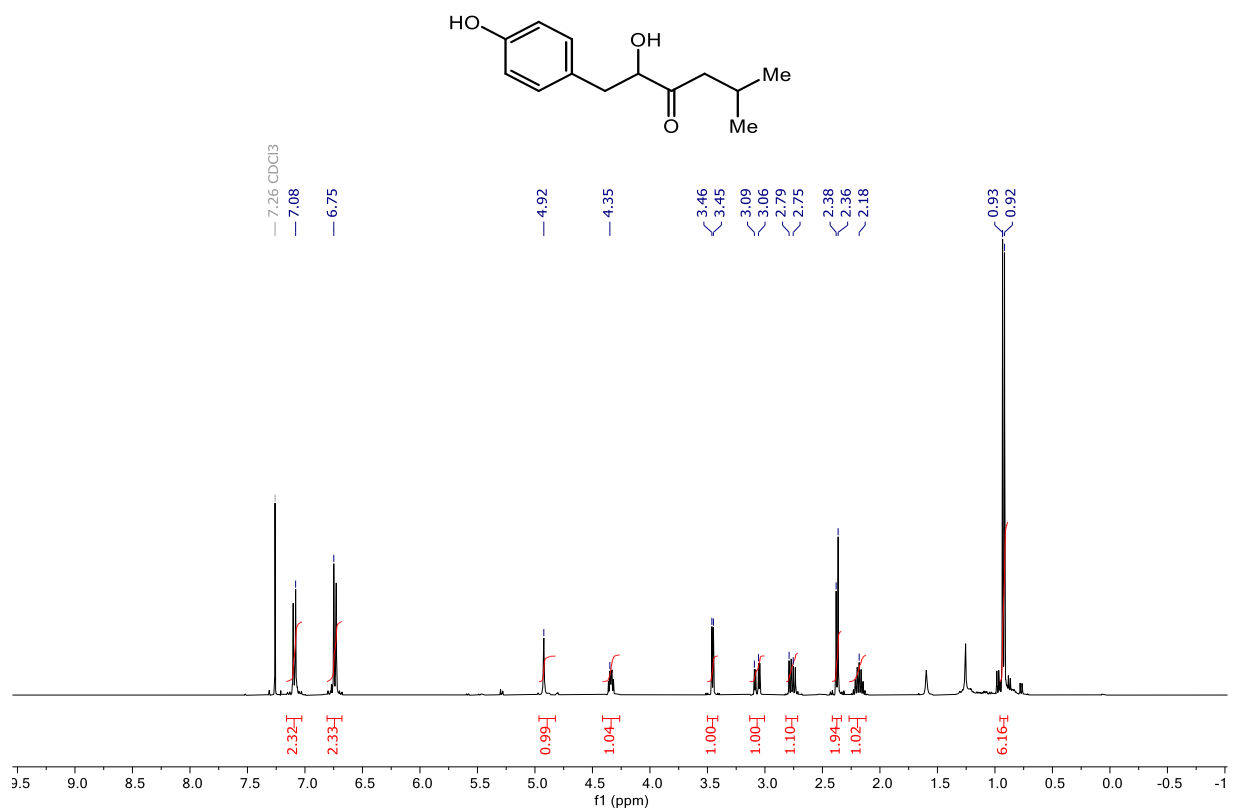


Figure A2.71. ¹H NMR spectrum for **38** (400 MHz, CDCl₃, room temperature).

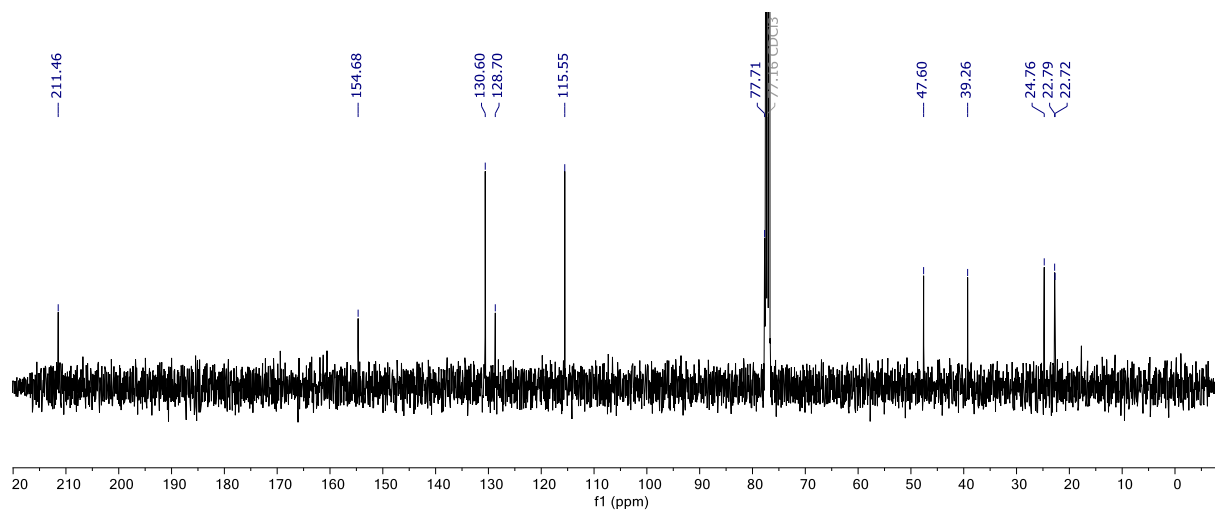


Figure A2.72. ¹³C{¹H} NMR spectrum for **38** (101 MHz, CDCl₃, room temperature)

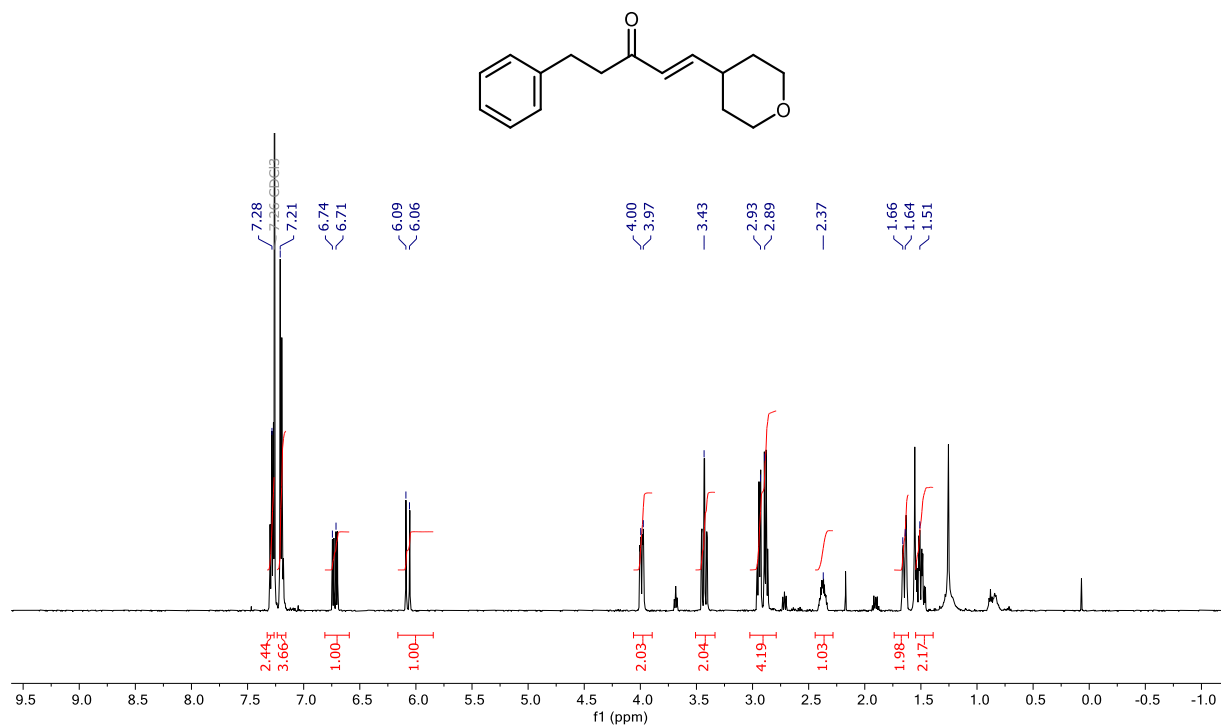


Figure A2.73. ¹H NMR spectrum for **41** (500 MHz, CDCl₃, room temperature).

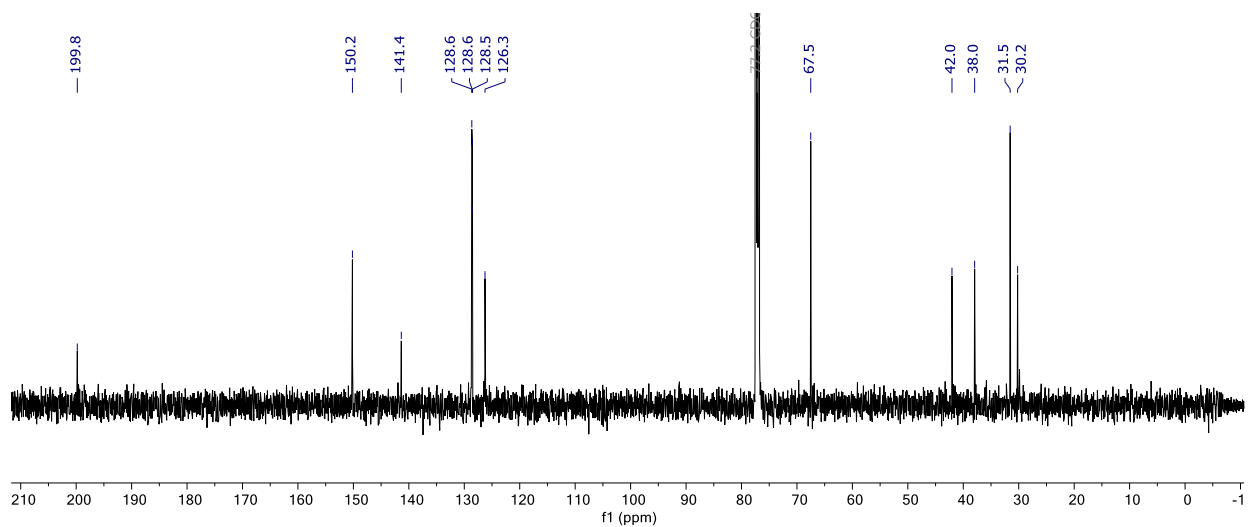


Figure A2.74. ¹³C{¹H} NMR spectrum for **41** (126 MHz, CDCl₃, room temperature).

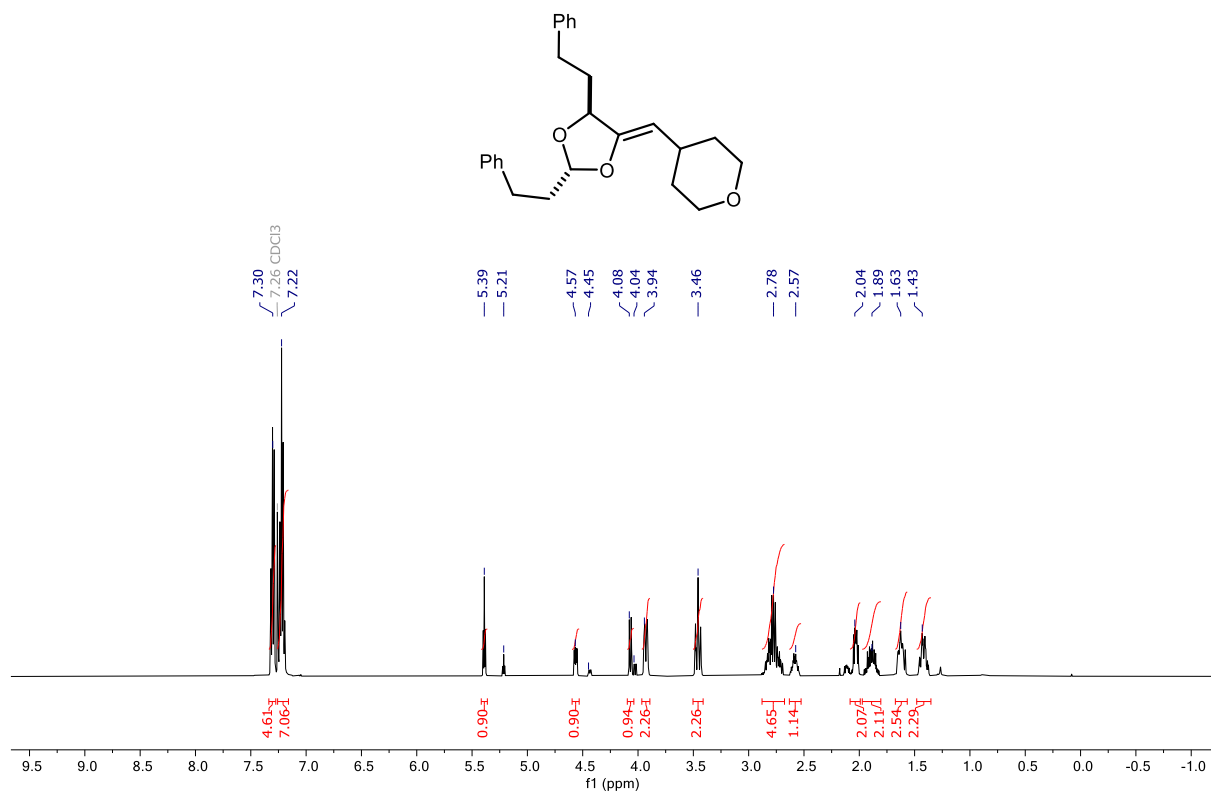


Figure A2.75. ¹H NMR spectrum for **42** (500 MHz, CDCl₃, room temperature).

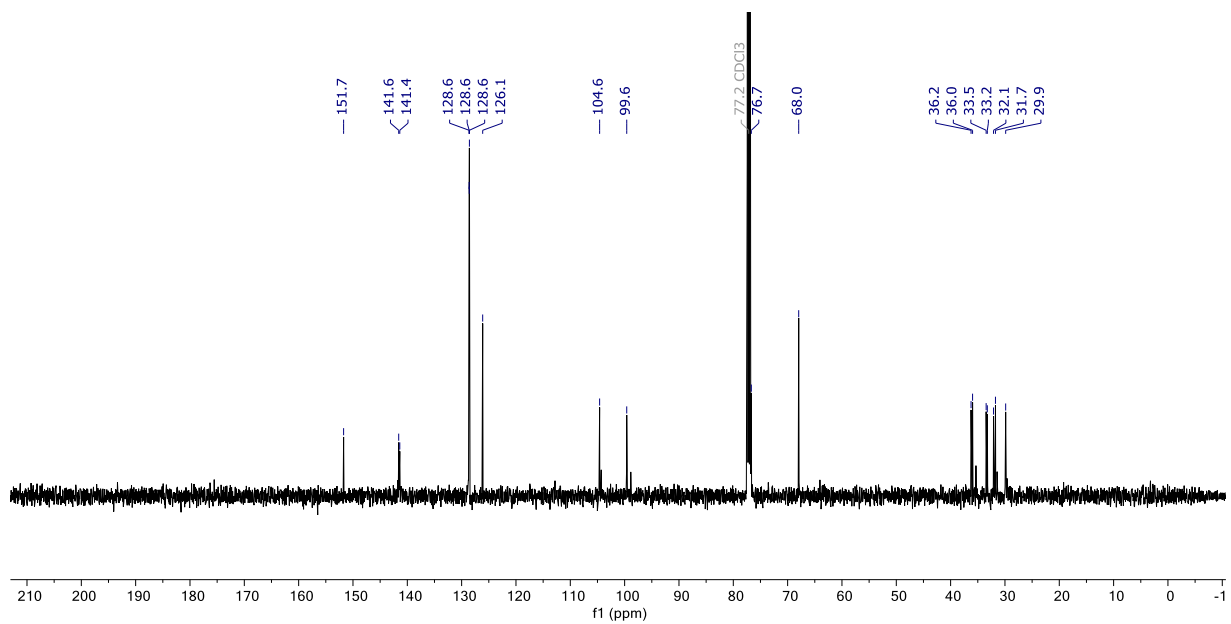


Figure A2.76. ¹³C {¹H} NMR spectrum for **42** (126 MHz, CDCl₃, room temperature)

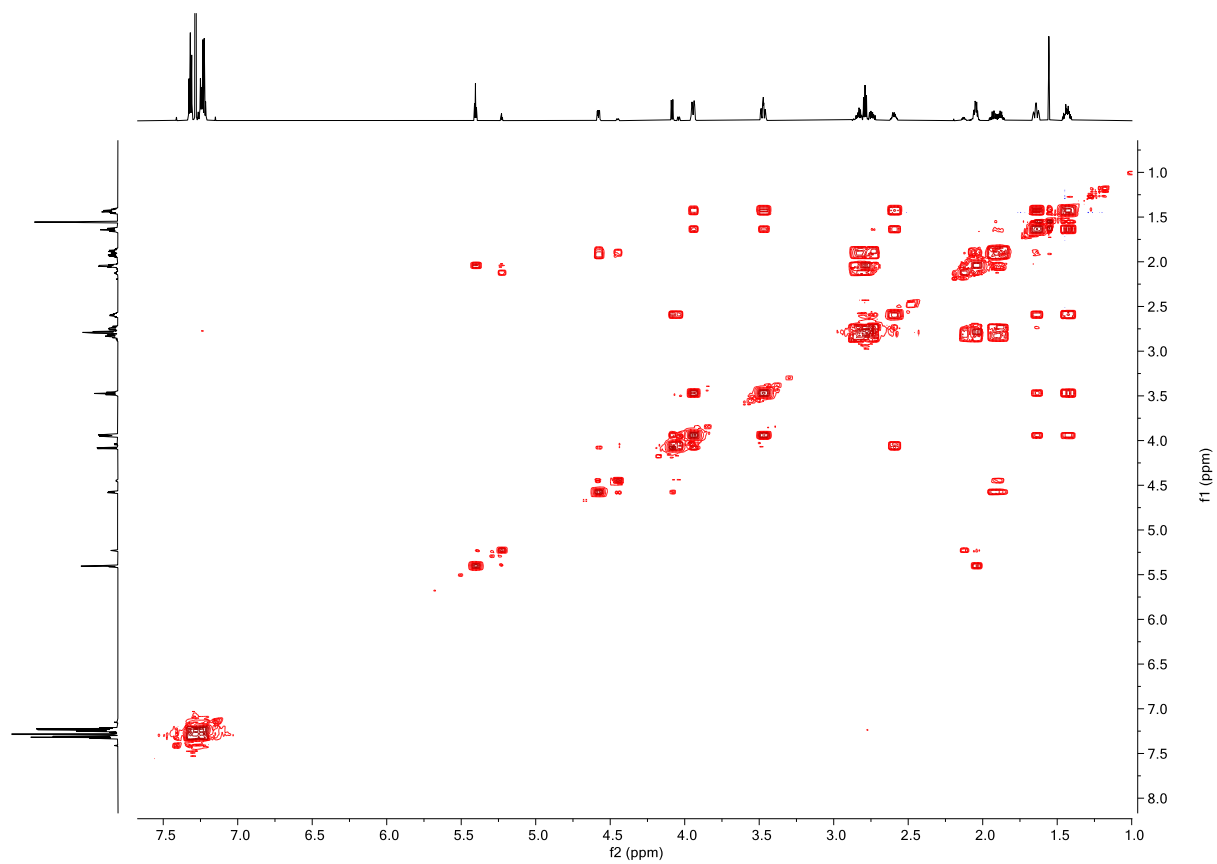


Figure A2.77. COSY NMR spectrum for **42** (800 MHz, CDCl₃, room temperature)

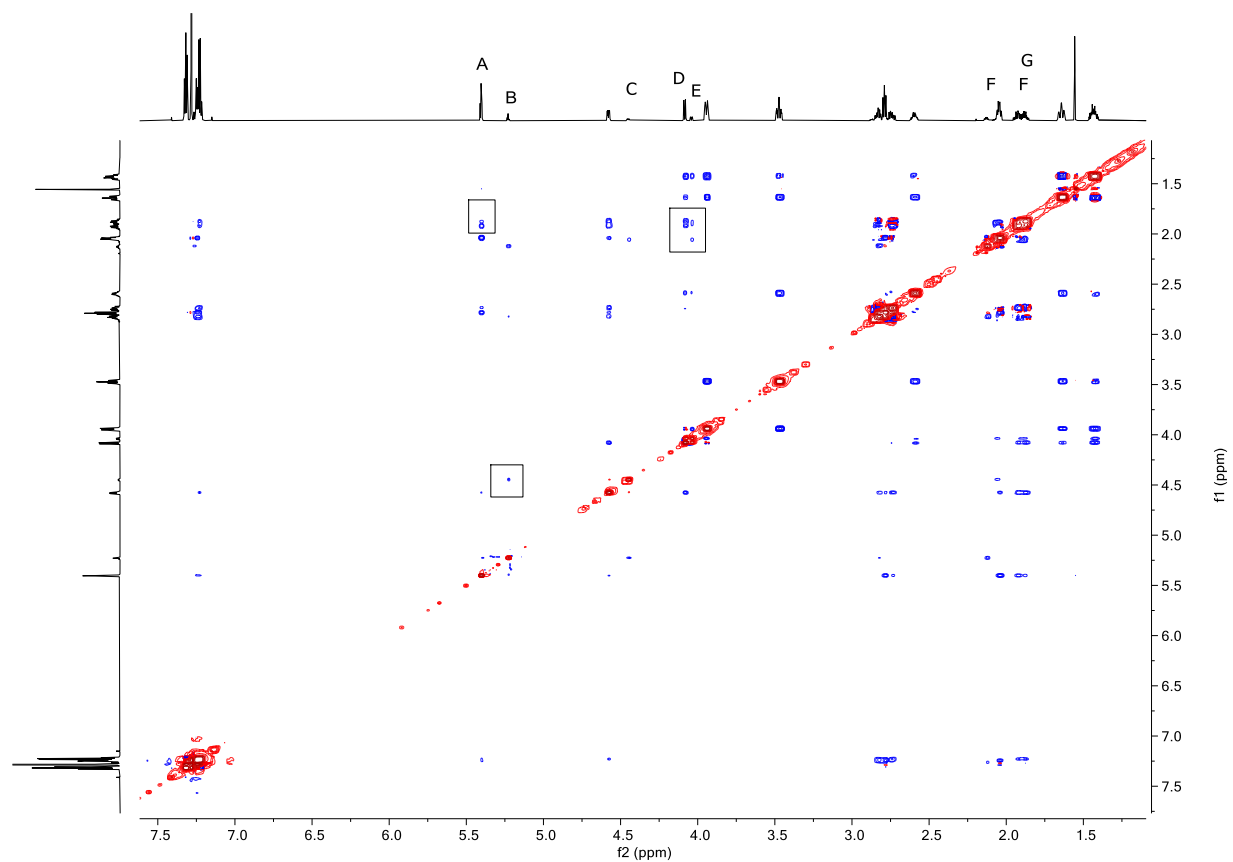
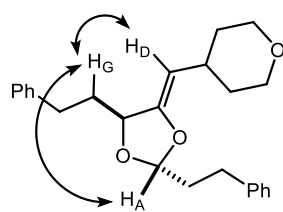
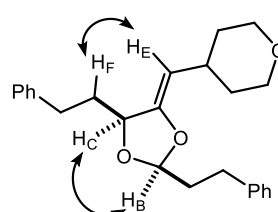


Figure A2.78. NOESY NMR spectrum for **42** (800 MHz, CDCl_3 , room temperature)



MAJOR
(Z)-anti



MINOR
(Z)-syn

6. FT-IR Data

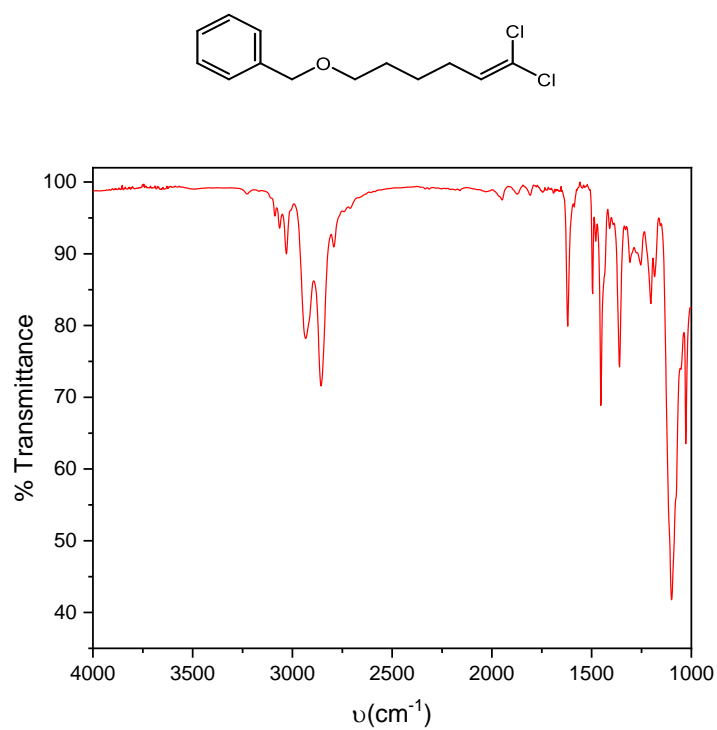


Figure A2.79. FT-IR spectrum for **S1**.

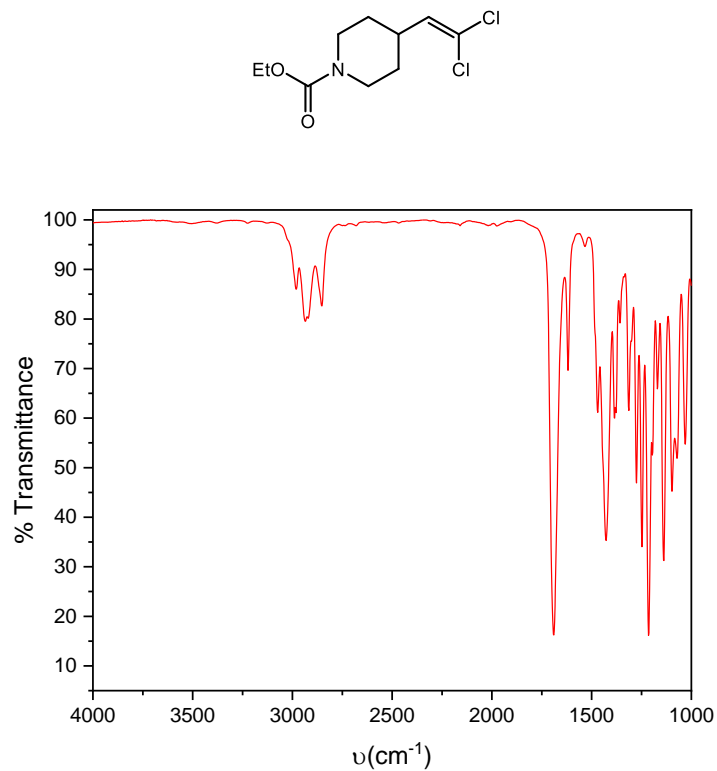


Figure A2.80. FT-IR spectrum for **S2**.

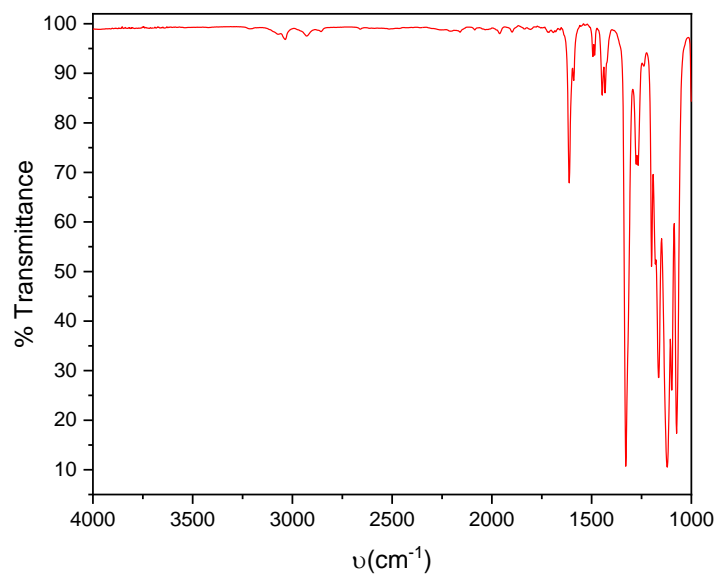
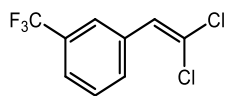


Figure A2.81. FT-IR spectrum for **S3**.

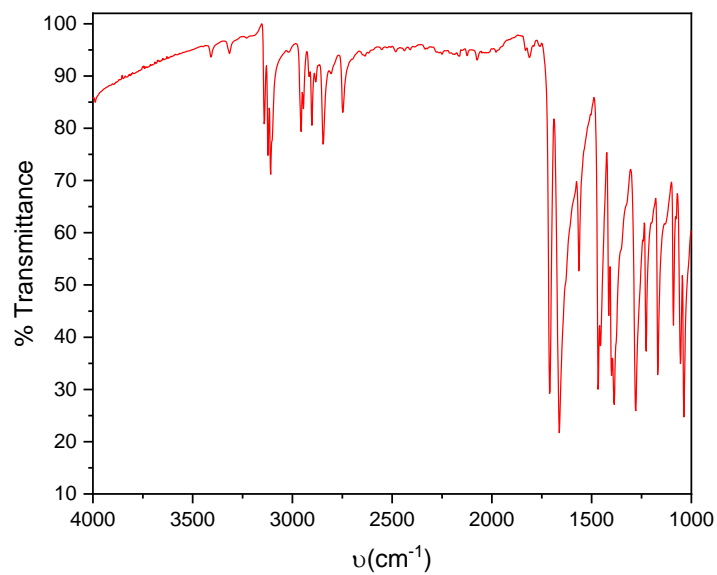
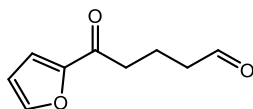


Figure A2.82. FT-IR spectrum for **S4**.

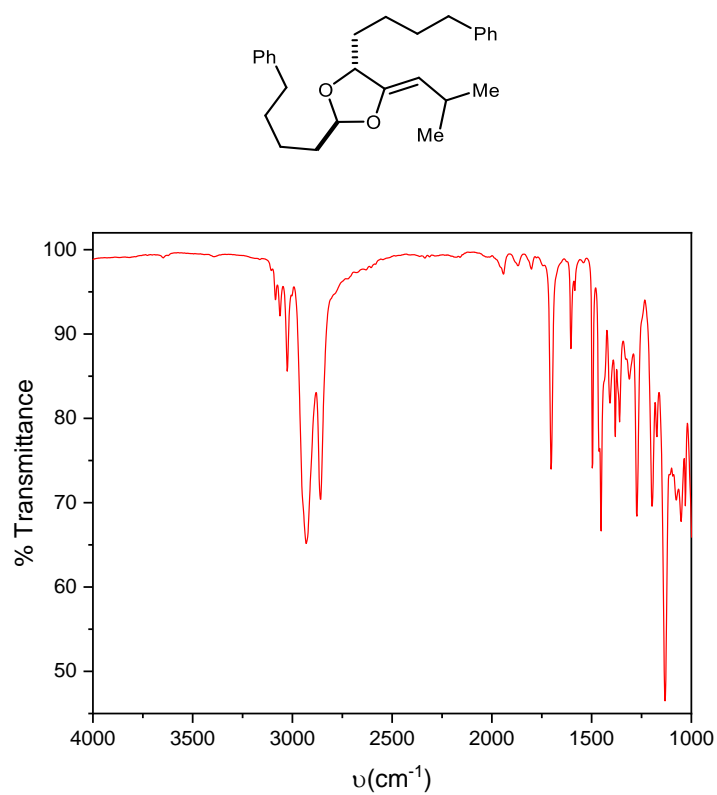


Figure A2.83. FT-IR spectrum for **4**.

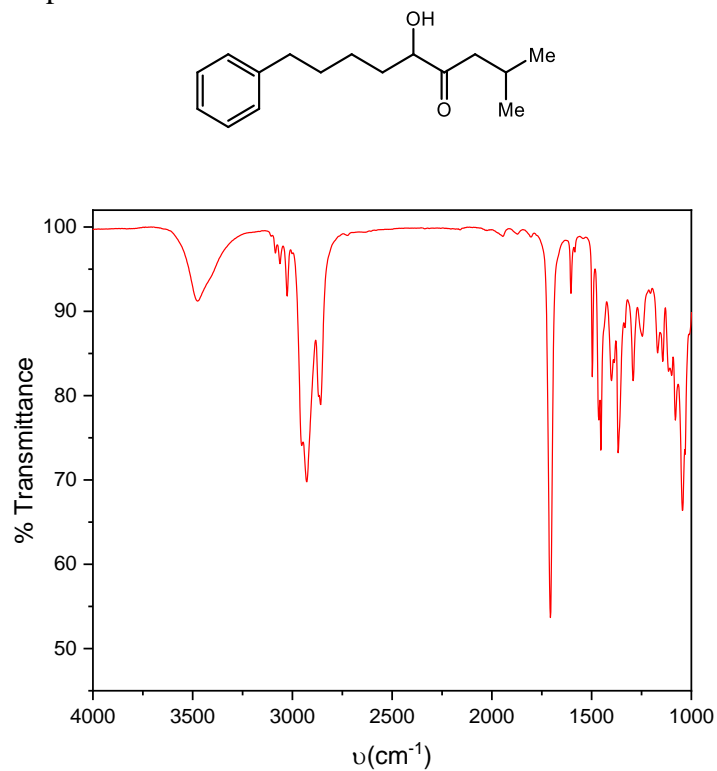


Figure A2.84. FT-IR spectrum for **5**.

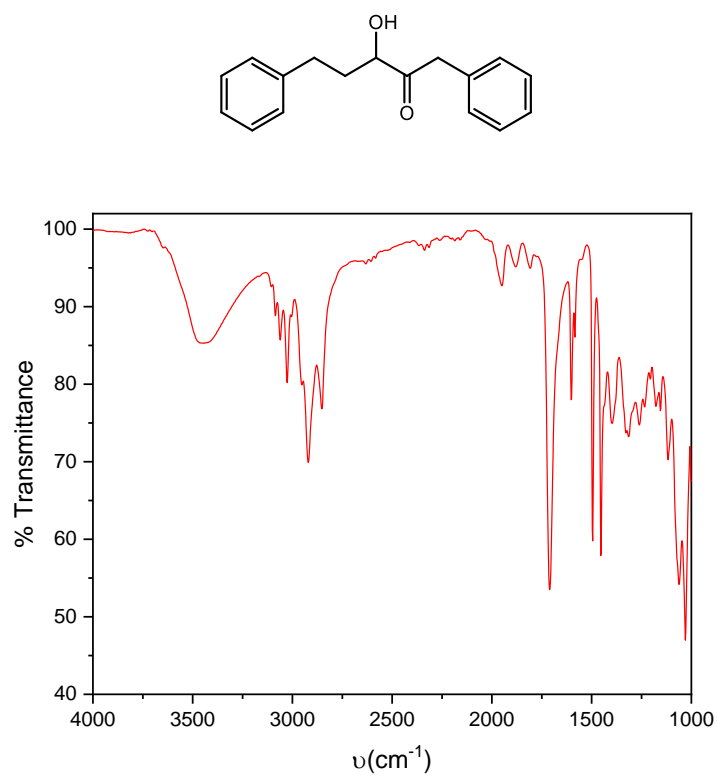


Figure A2.85. FT-IR spectrum for **12**.

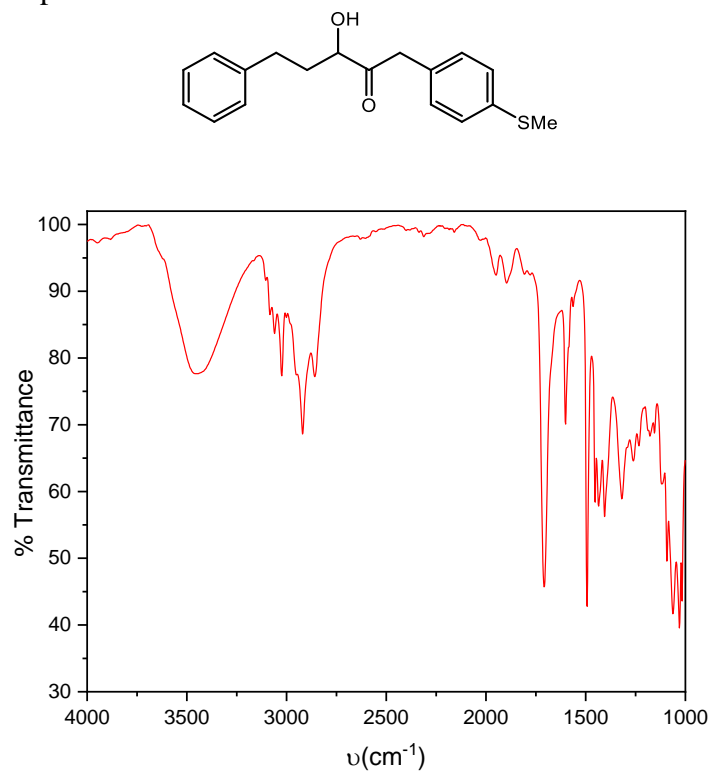


Figure A2.86. FT-IR spectrum for **13**.

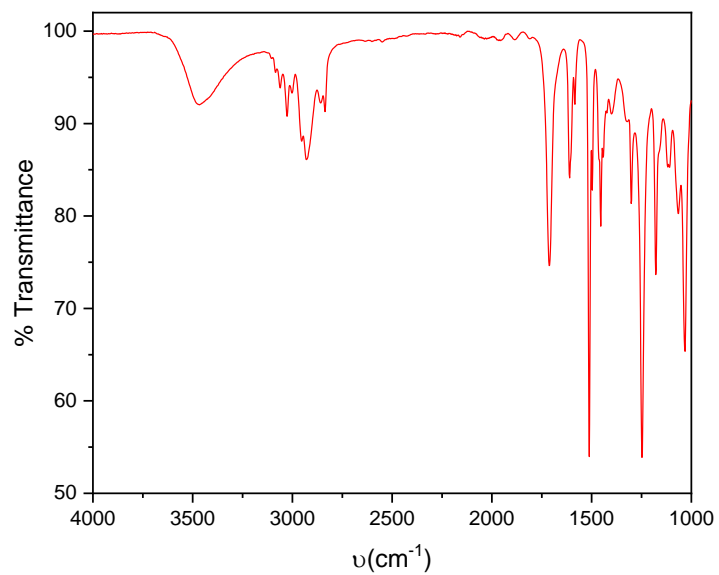
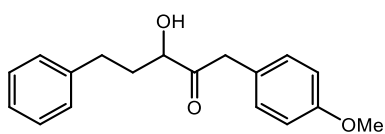


Figure A2.87. FT-IR spectrum for **14**.

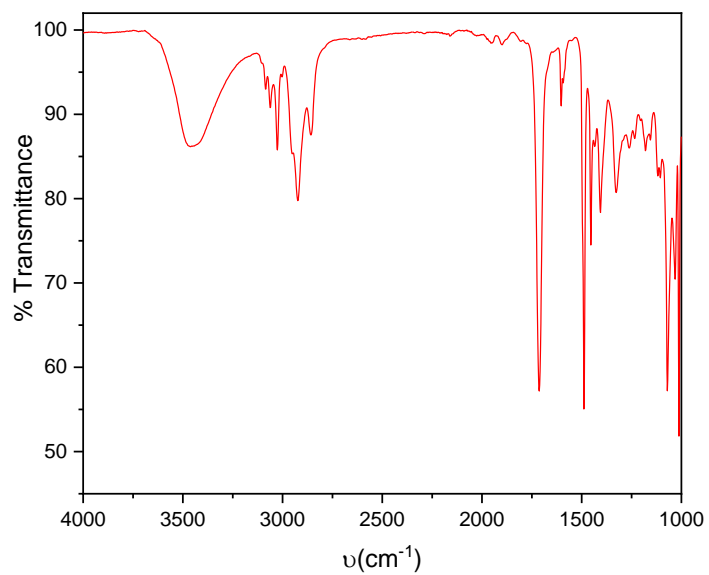
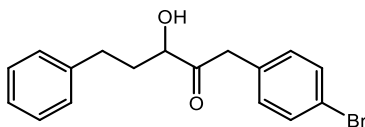


Figure A2.88. FT-IR spectrum for **15**.

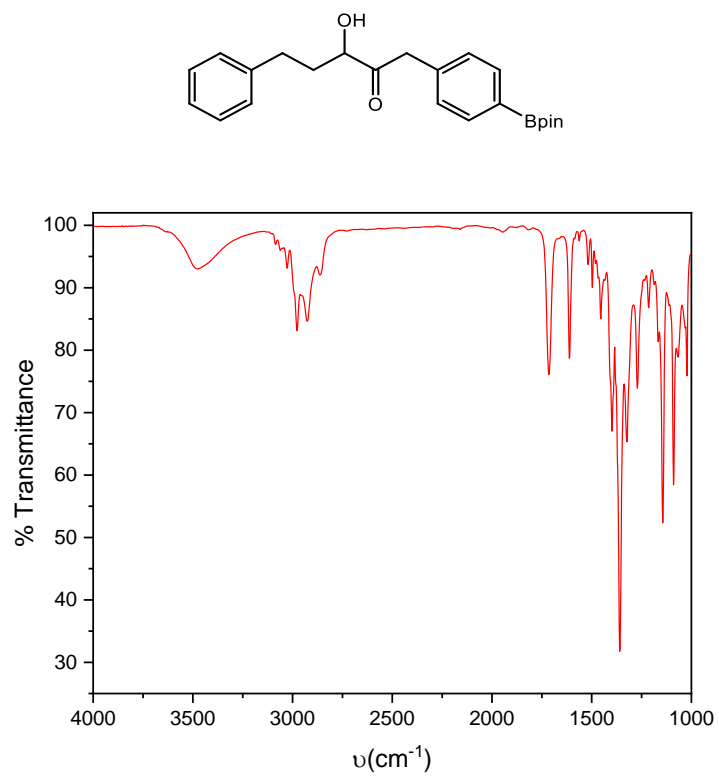


Figure A2.89. FT-IR spectrum for **16**.

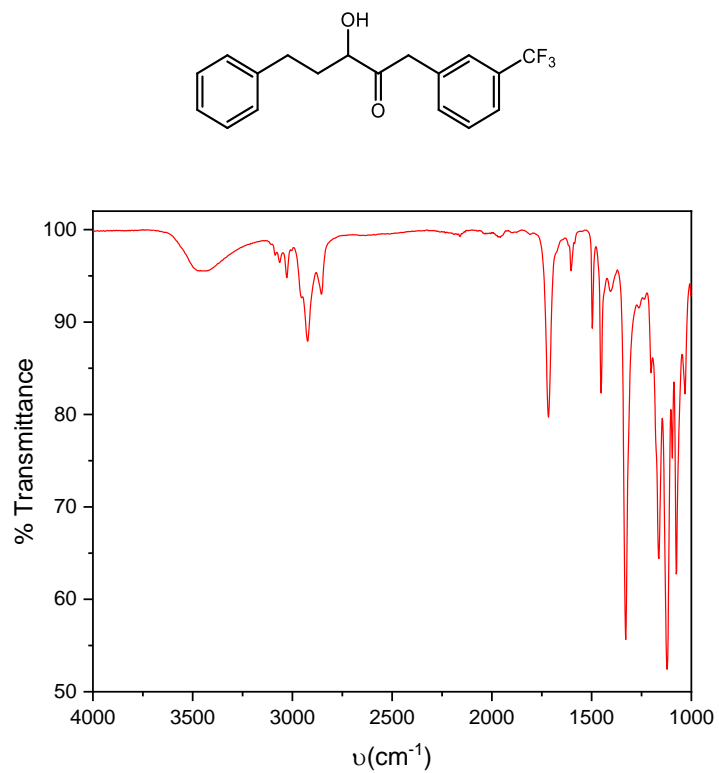


Figure A2.90. FT-IR spectrum for **17**.

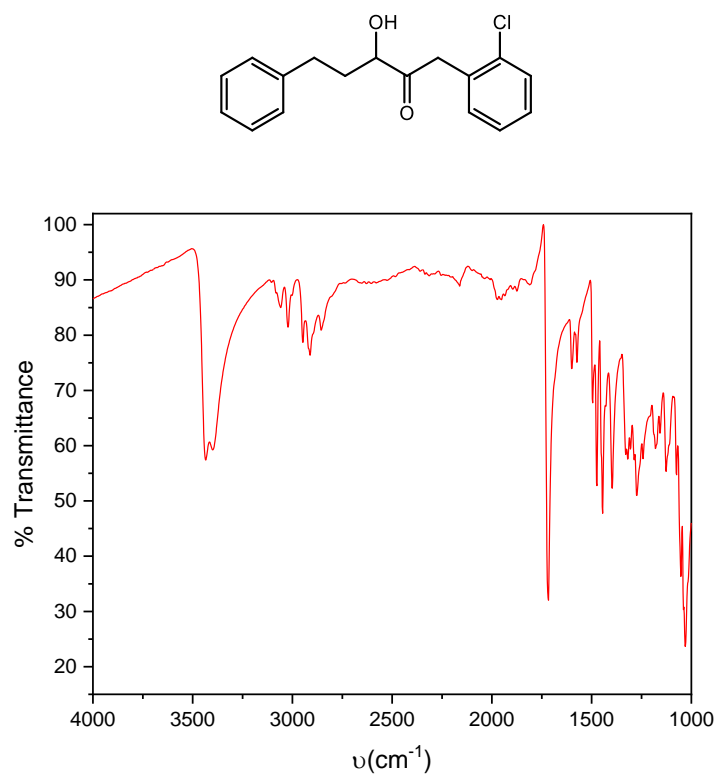


Figure A2.91. FT-IR spectrum for **18**.

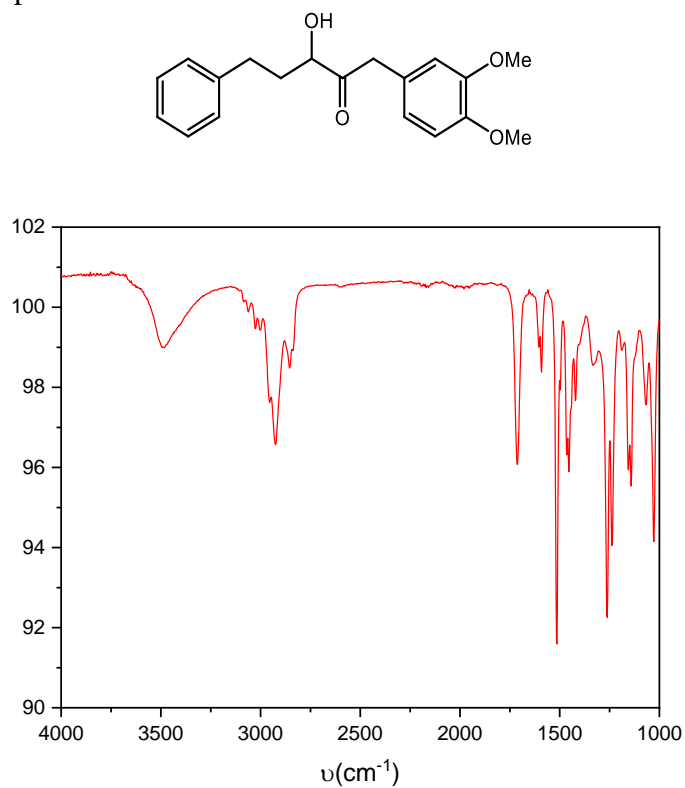


Figure A2.92. FT-IR spectrum for **19**.

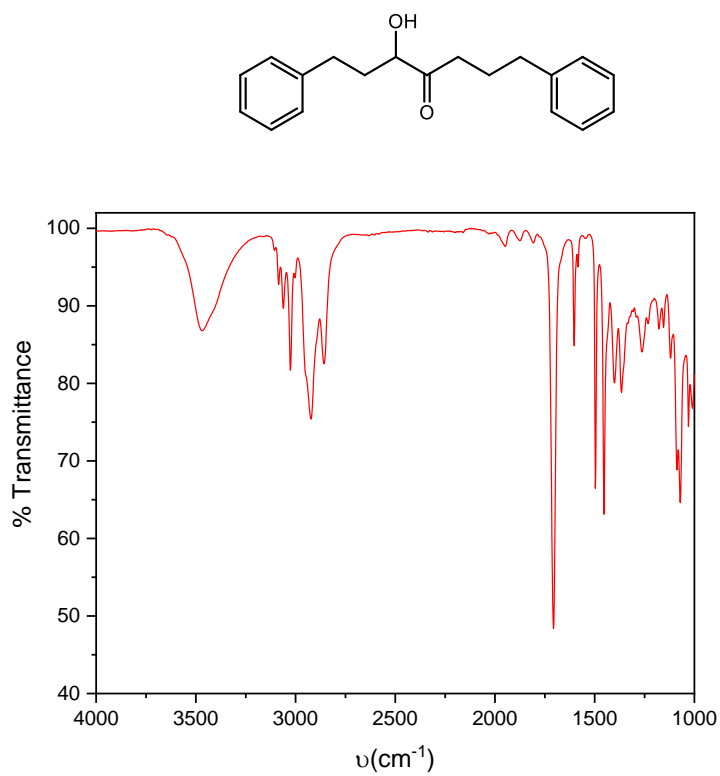


Figure A2.93. FT-IR spectrum for **20**.

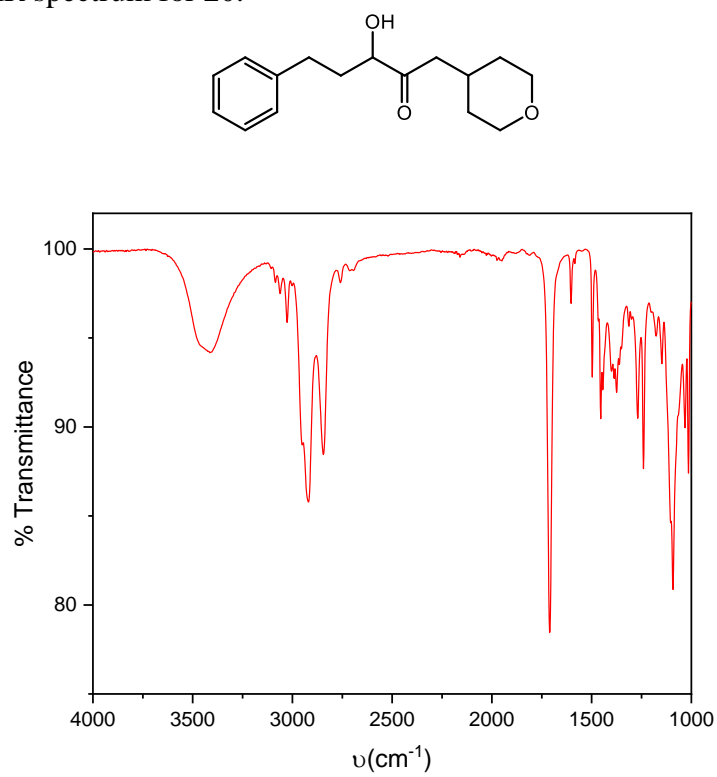


Figure A2.94. FT-IR spectrum for **21**.

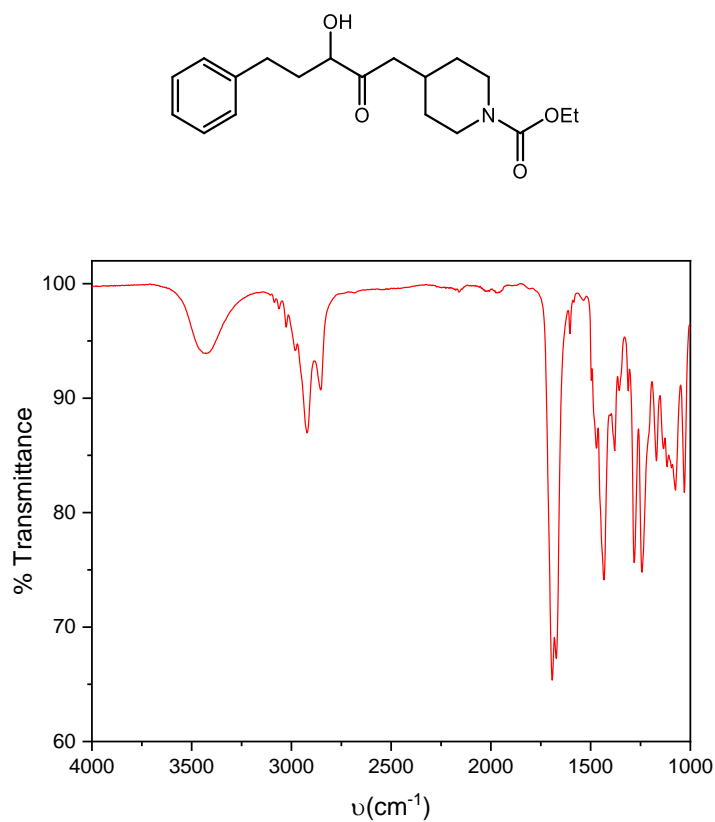


Figure A2.95. FT-IR spectrum for **22**.

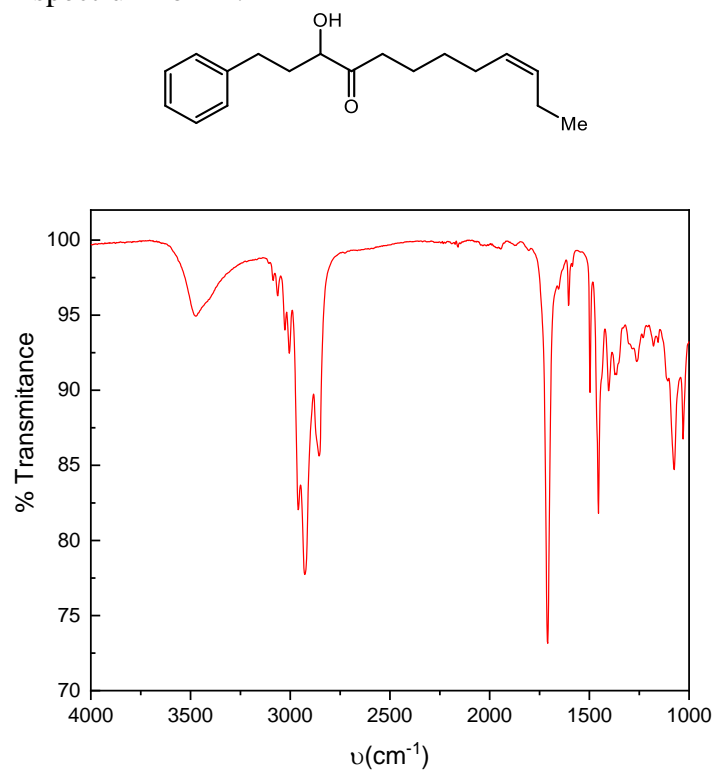


Figure A2.96. FT-IR spectrum for **23**.

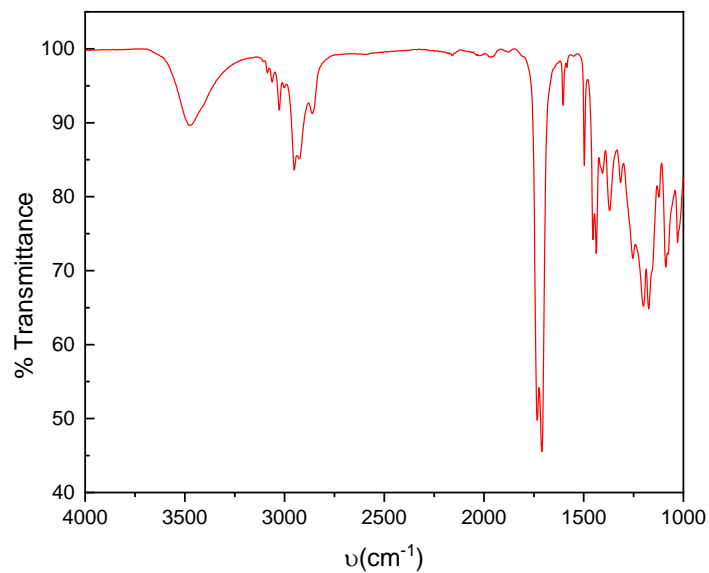
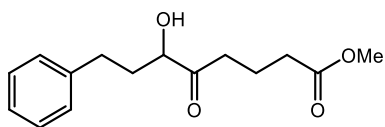


Figure A2.97. FT-IR spectrum for **24**.

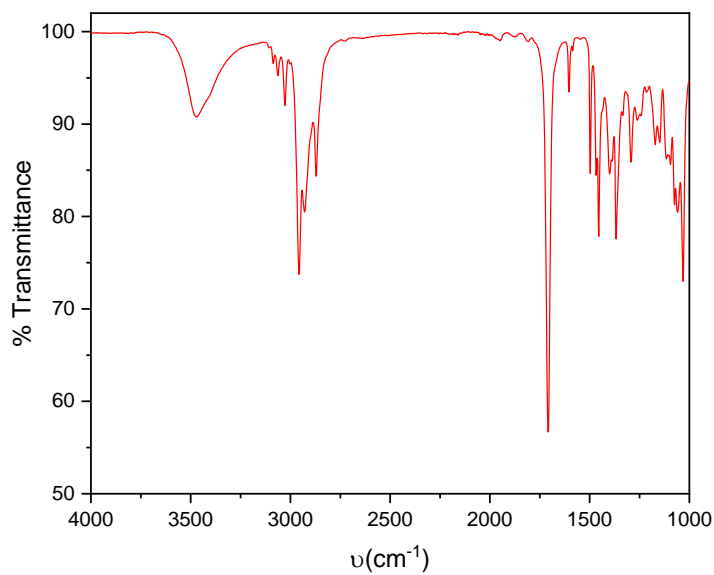
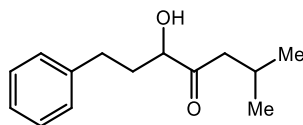


Figure A2.98. FT-IR spectrum for **25**.

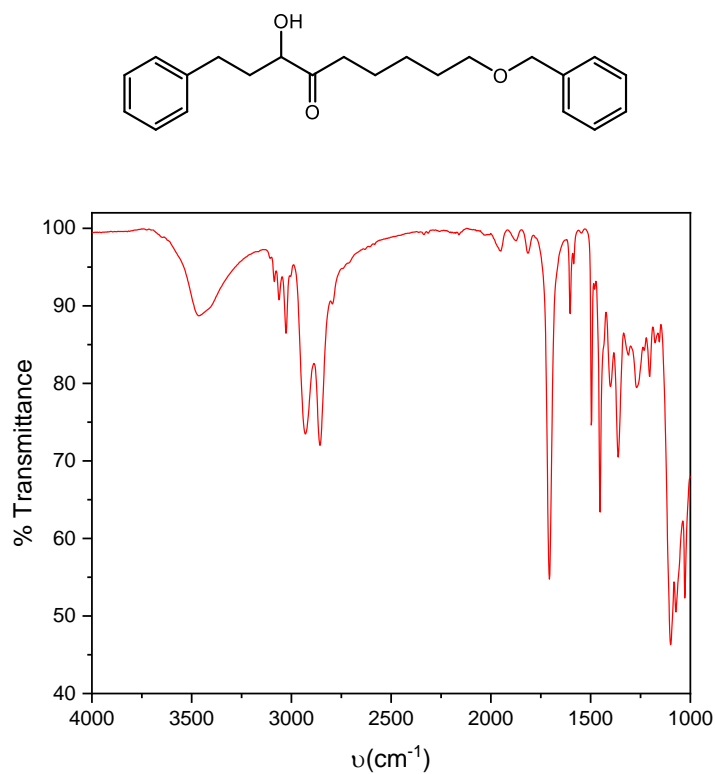


Figure A2.99. FT-IR spectrum for **26**.

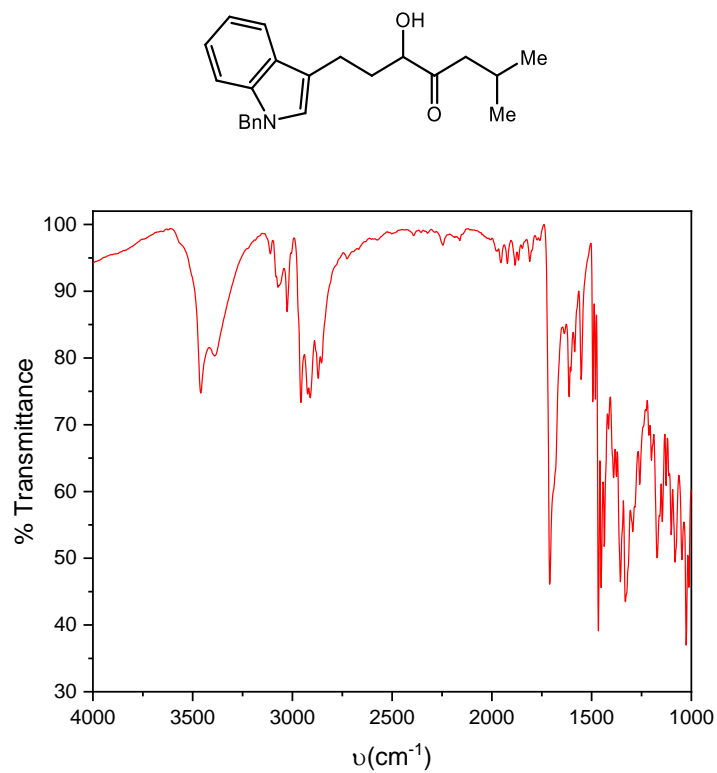


Figure A2.100. FT-IR spectrum for **27**.

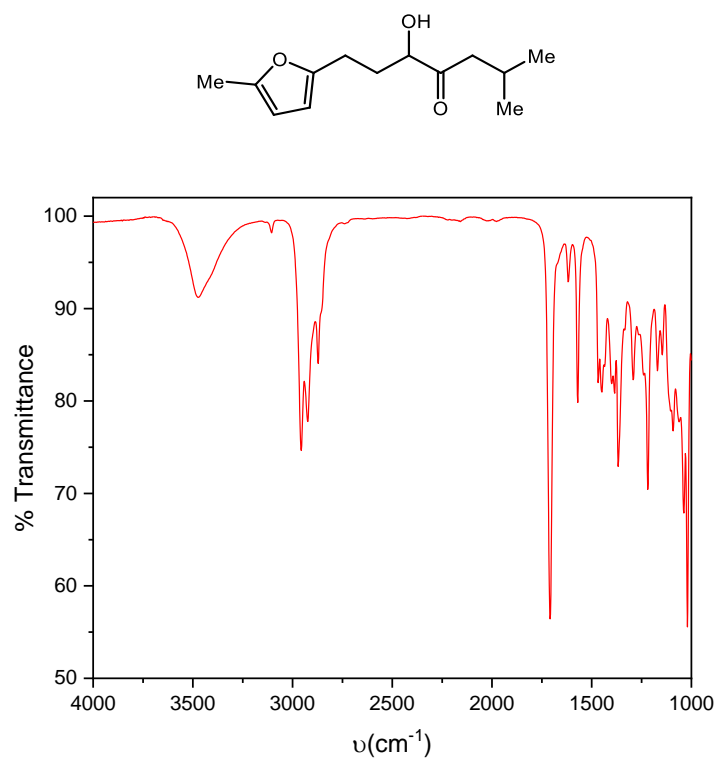


Figure A2.101. FT-IR spectrum for **28**.

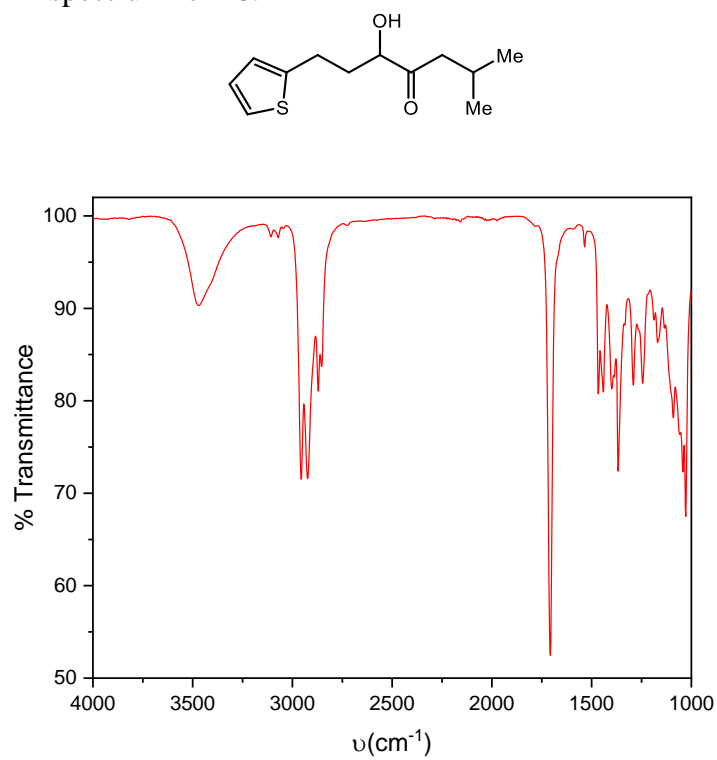


Figure A2.102. FT-IR spectrum for **29**.

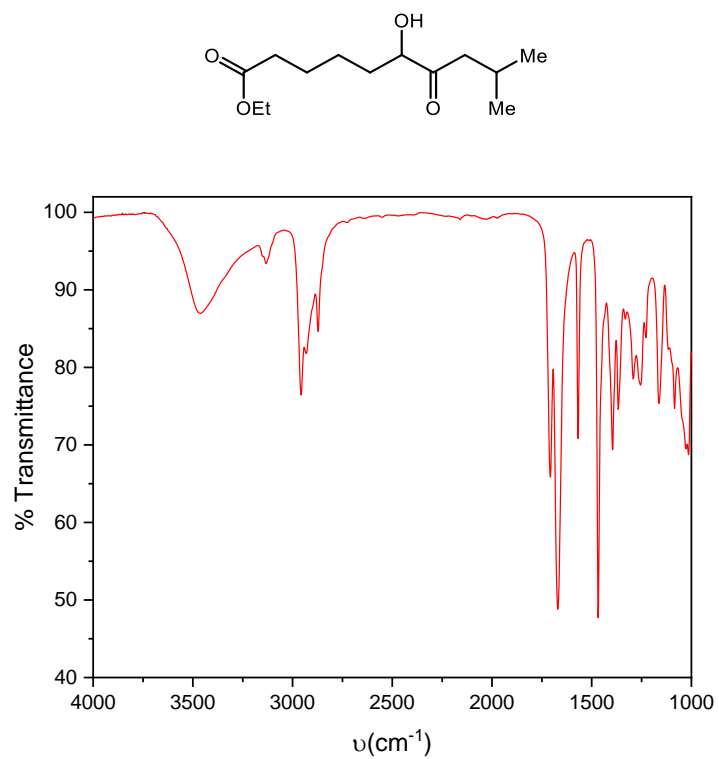


Figure A2.103. FT-IR spectrum for **30**.

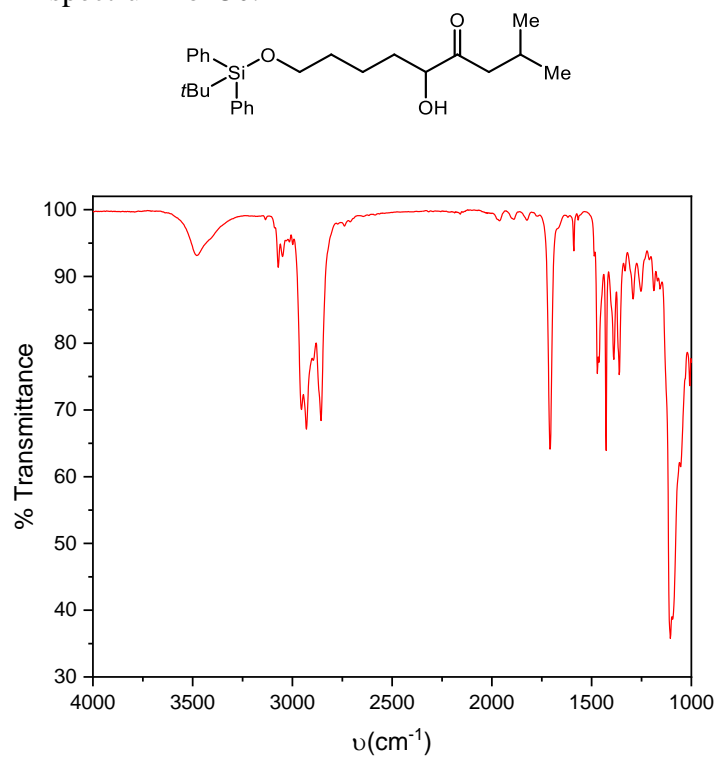


Figure A2.104. FT-IR spectrum for **31**.

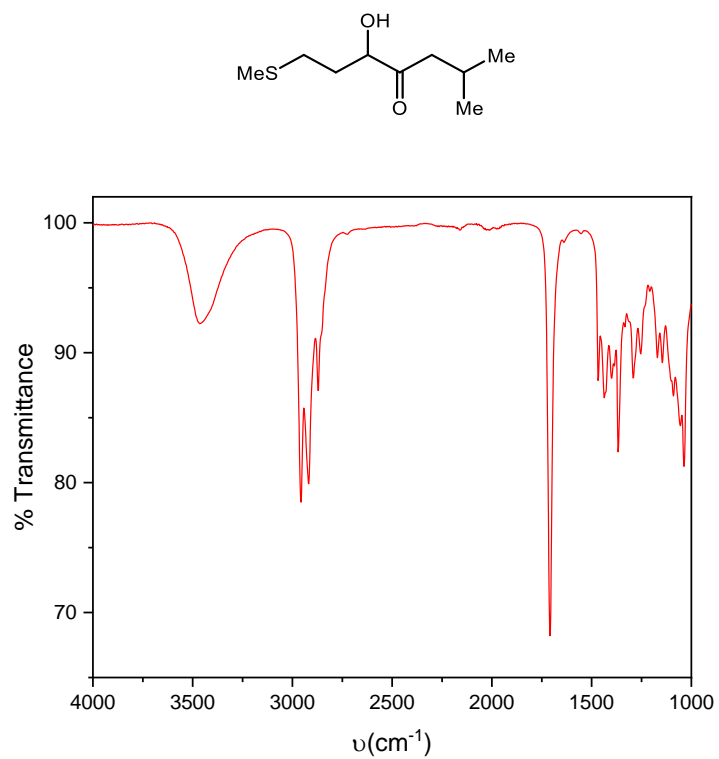


Figure A2.105. FT-IR spectrum for **33**.

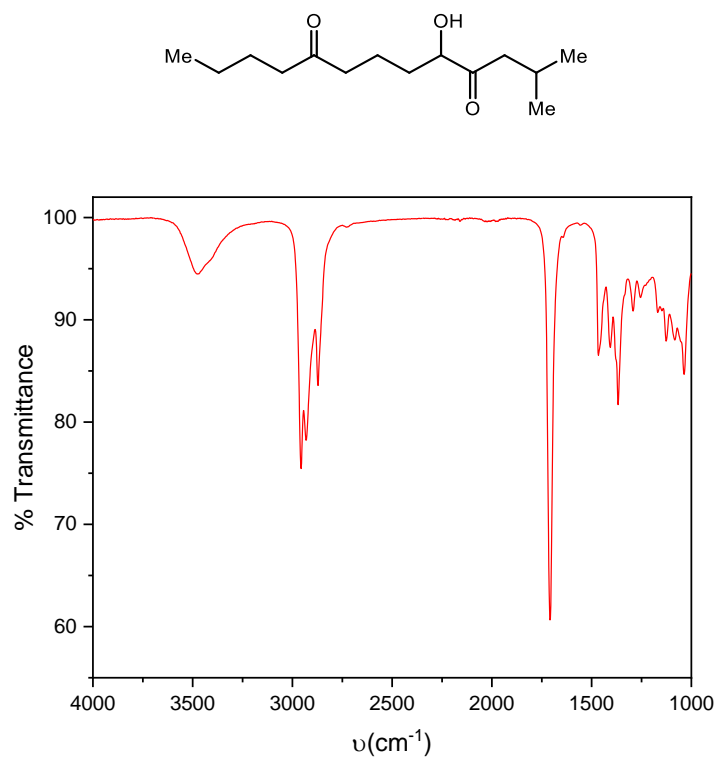


Figure A2.106. FT-IR spectrum for **34**.

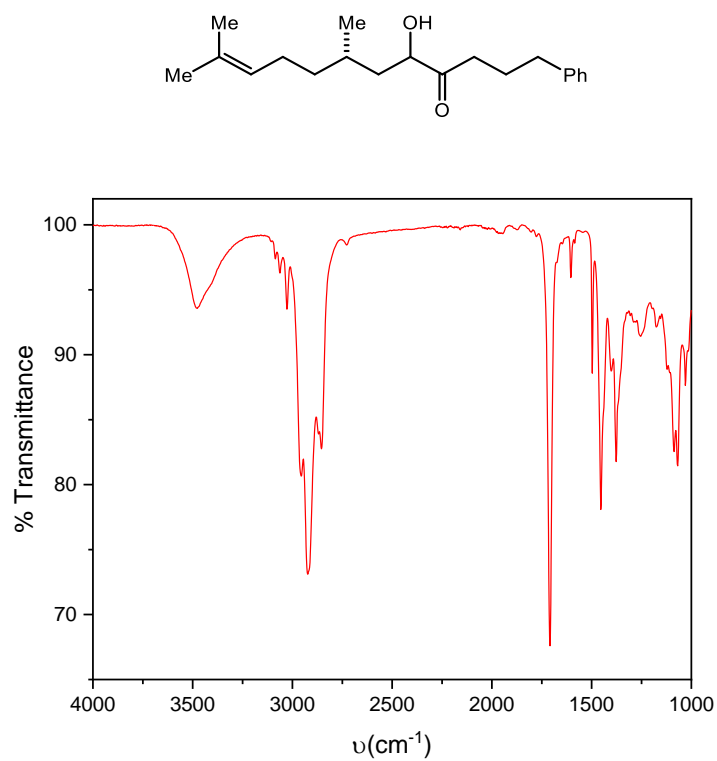


Figure A2.107. FT-IR spectrum for **35**.

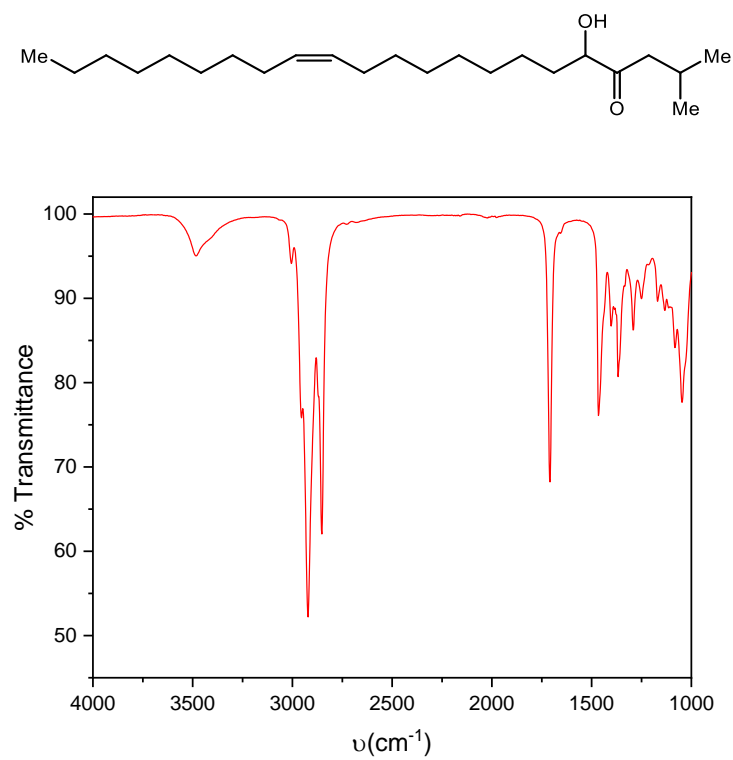


Figure A2.108. FT-IR spectrum for **36**.

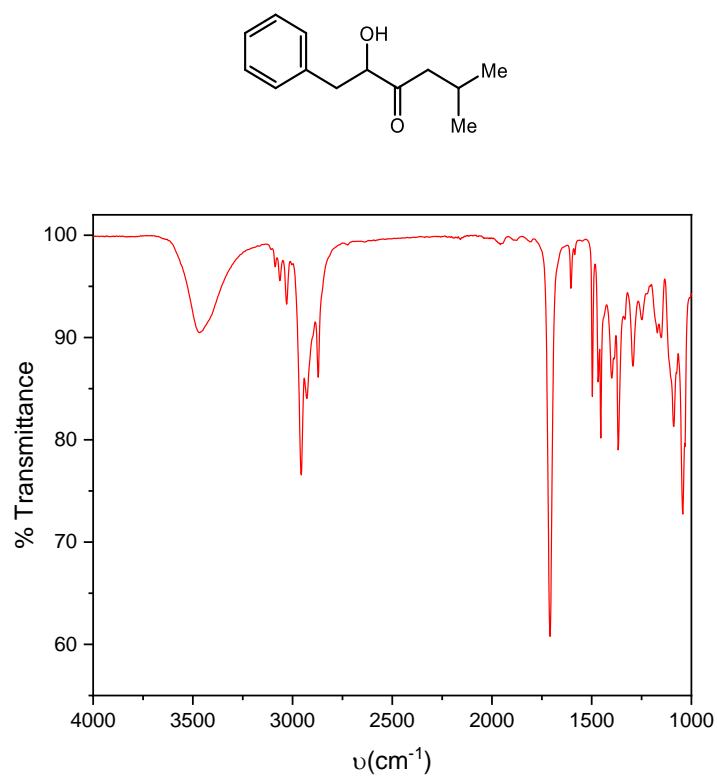


Figure A2.109. FT-IR spectrum for **37**.

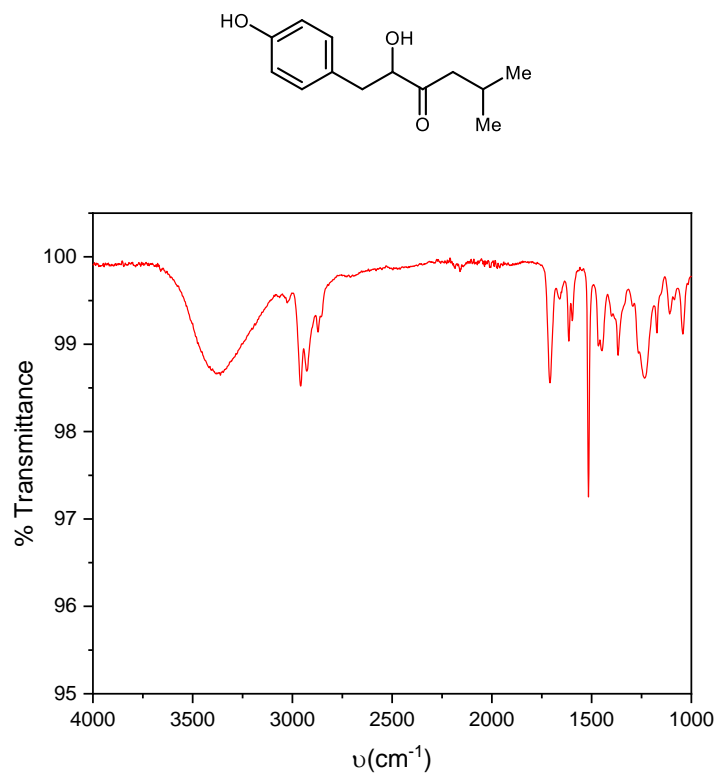


Figure A2.110. FT-IR spectrum for **38**.

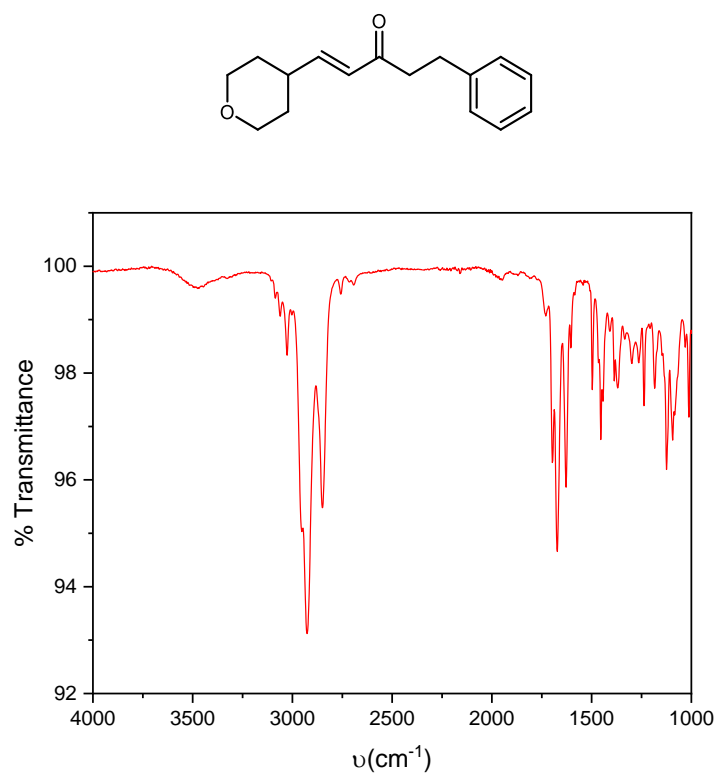


Figure A2.111. FT-IR spectrum for **41**.

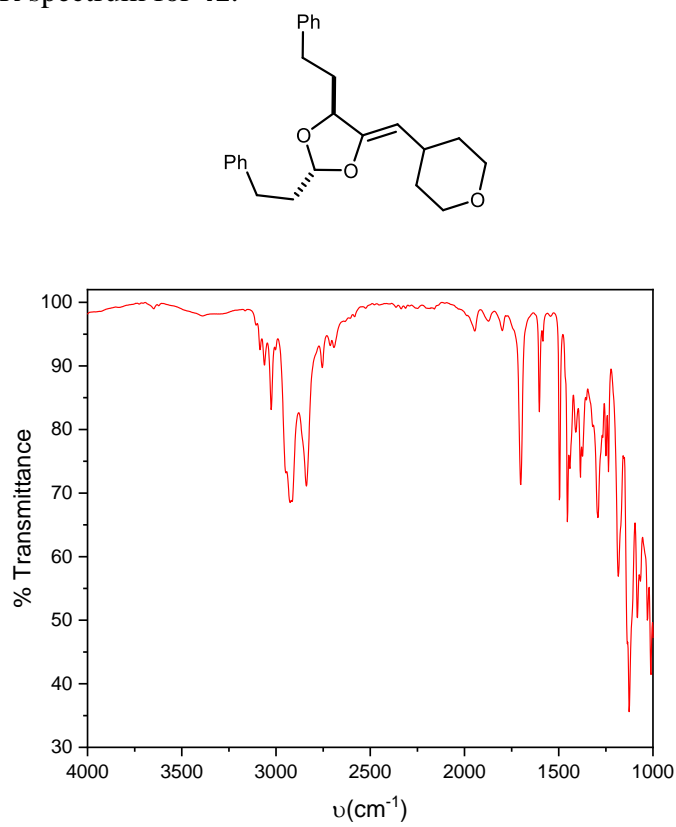


Figure A2.112. FT-IR spectrum for **42**.

6. DFT Calculations

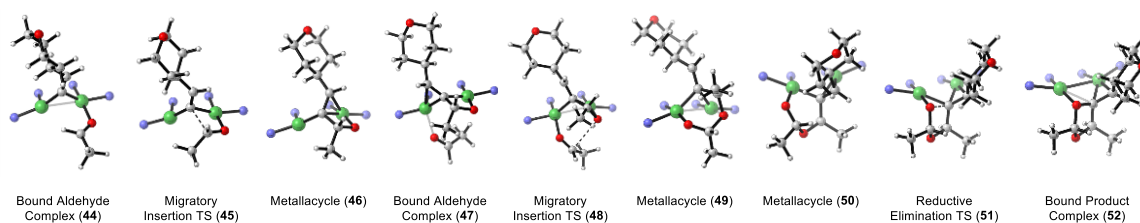
Computational Methods. Geometry optimizations were performed with Gaussian16/A.03 software package¹⁹ using the BP86 functional and the 6-311G(d,p) basis set. Stationary points were confirmed by frequency analysis. Geometries are reported as Cartesian coordinates. All energies are reported in kcal/mol and are the sum of electronic energies and thermal enthalpy corrections at 298 K. All energy values are normalized to the energy of bound aldehyde complex **44a** in the triplet spin state.

Reaction Mechanism. The first intermediate modeled in the reaction mechanism is aldehyde complex (**44**). Initial C–C bond formation occurs through migratory insertion (**45**), forming a metallacycle (**46**). At this point, there are two pathways to form the dioxolane and enone products.

A second aldehyde can bind to the metallacycle to form another bound aldehyde complex (**47**). Migratory insertion occurs (**48**); subsequently, a larger metallacycle (**49**) is formed. Upon rearrangement of the metallacycle (**50**), the final C–O bond is formed upon reductive elimination (**51**), forming a bound dioxolane complex (**52**).

Alternatively, the other isomer of **46** can undergo β -hydride elimination (**53**), forming nickel–hydride complex (**54**). Upon reductive elimination (**55**), the bound product is formed (**56**).

Dioxolane Formation



Enone Formation

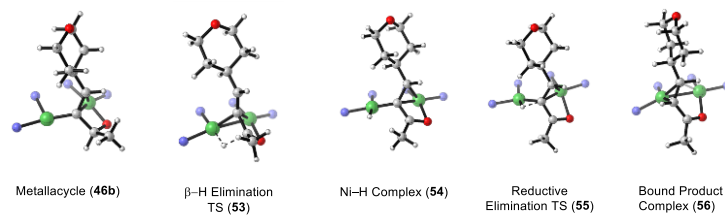


Figure A2.113. Optimized structures of intermediates and transition states.

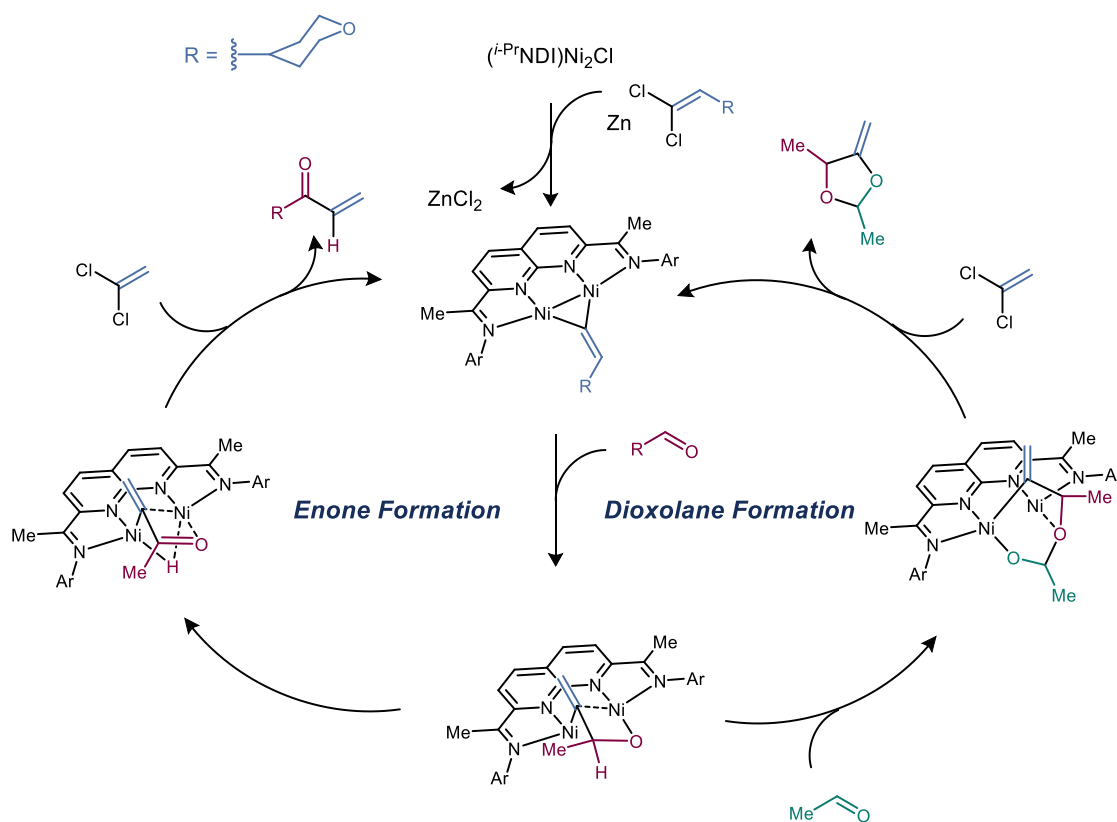


Figure A2.114. An overview of the proposed catalytic cycle.

[2 + 2 + 1] Reaction Selectivity: *E/Z* Selectivity Determining Step. There are two possible orientations of the vinylidene, as well as two orientations of each aldehyde, leading to eight total pathways to four possible products. The first step of the reaction is selectivity-determining and irreversible. Therefore, only the first migratory insertion transition state was calculated for the (*E*)-*anti* and (*E*)-*syn* products, which are not experimentally observed.

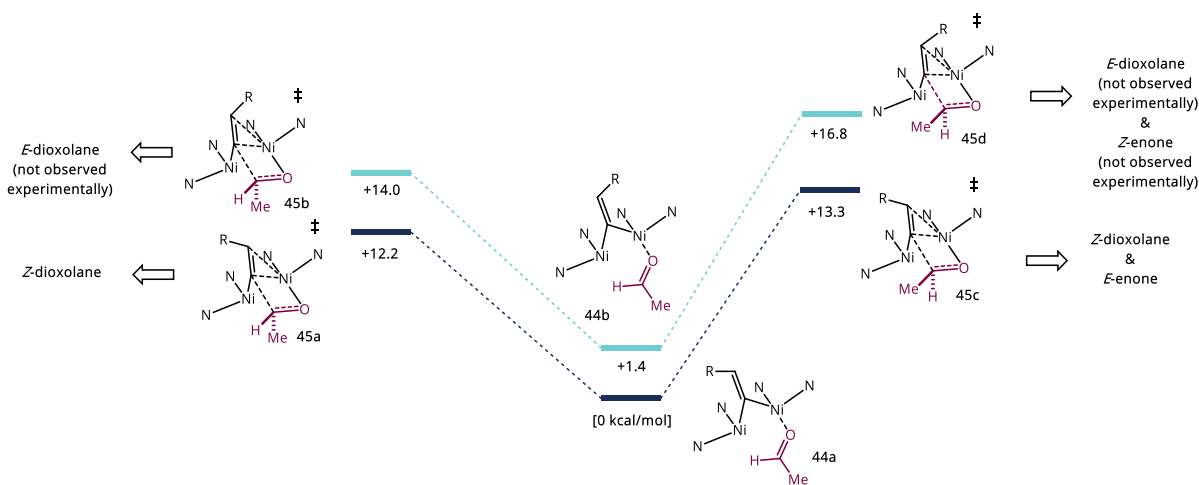


Figure A2.115. Energy diagram for *E/Z* Selectivity Determining Step

Anti:Syn Selectivity. Due to the dependence of the anti/syn selectivity on reductant and solvent, we did not attempt to explain the experimentally observed diastereoselectivity computationally. By varying the orientation of each aldehyde, there are four potential pathways, with two pathways leading to the (*Z*)-*anti* and the other two leading to the (*Z*)-*syn* products. Only the lowest energy pathway leading to the (*Z*)-*anti* and (*Z*)-*syn* dioxolane are presented here.

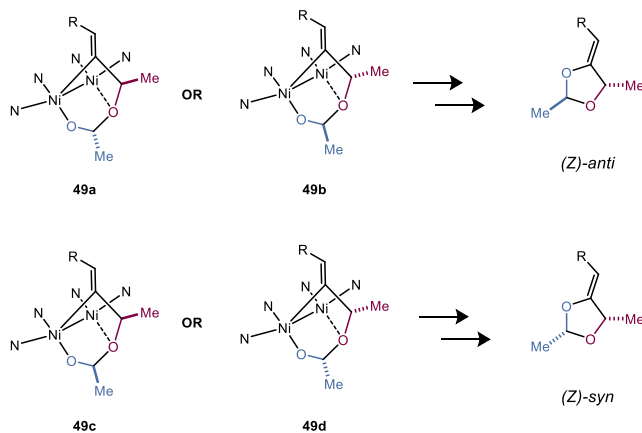


Figure A2.116. Metallacycles leading to (*Z*)-dioxolanes.

Catalyst Oxidation State. The first step of the reaction can occur with either one or no chlorines bound to the catalyst. However, complex **49** is not viable without reduction of a chlorine from the catalyst. Previous studies have demonstrated the competency of zinc to reduce metalacyclic intermediates such as **46**. Therefore, reduction could potentially happen before or after formation of metallacycle **46**.

Calculated Reaction Coordinate Diagrams. The reaction coordinate diagrams are shown below. All energies are normalized to the energy of the triplet (*Z*) bound aldehyde complex (**44a**). There are four possible reaction coordinate diagrams leading to the *Z* isomers of the dioxolane that are shown below.

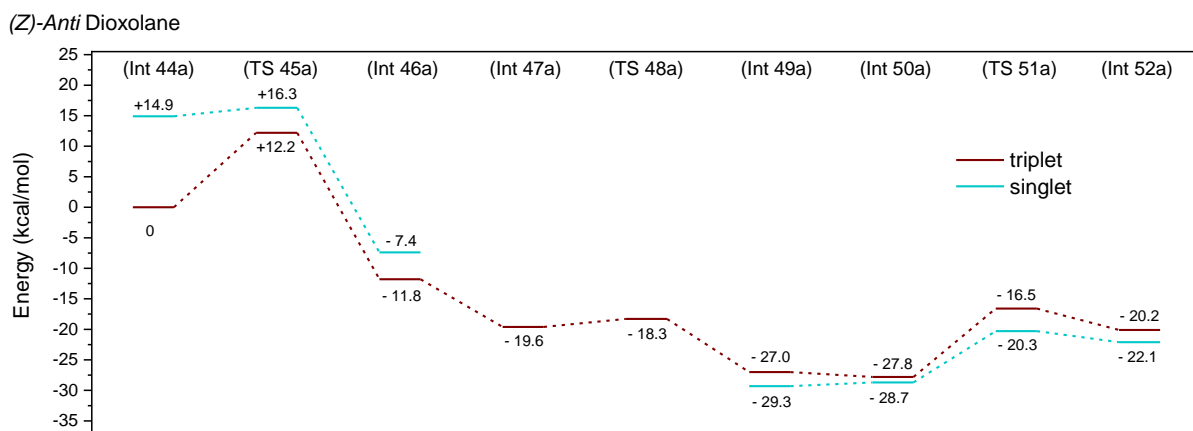


Figure A2.116. Energy diagram for the lowest energy formation of (*Z*)-*anti* dioxolane.

(Z)-Syn Dioxolane

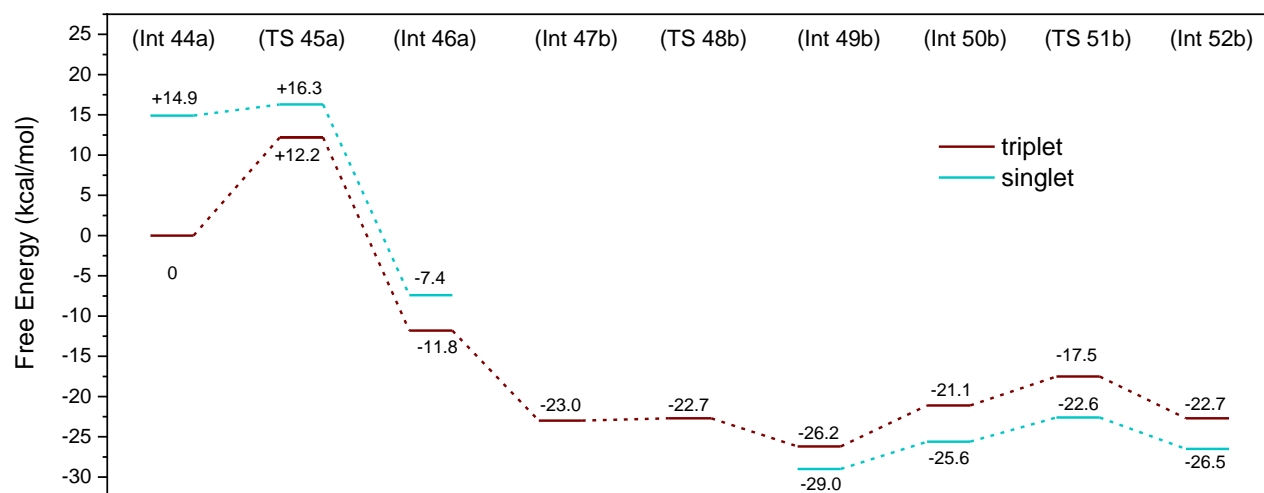


Figure A2.117. Energy diagram for the lowest energy formation of (Z)-syn dioxolane.

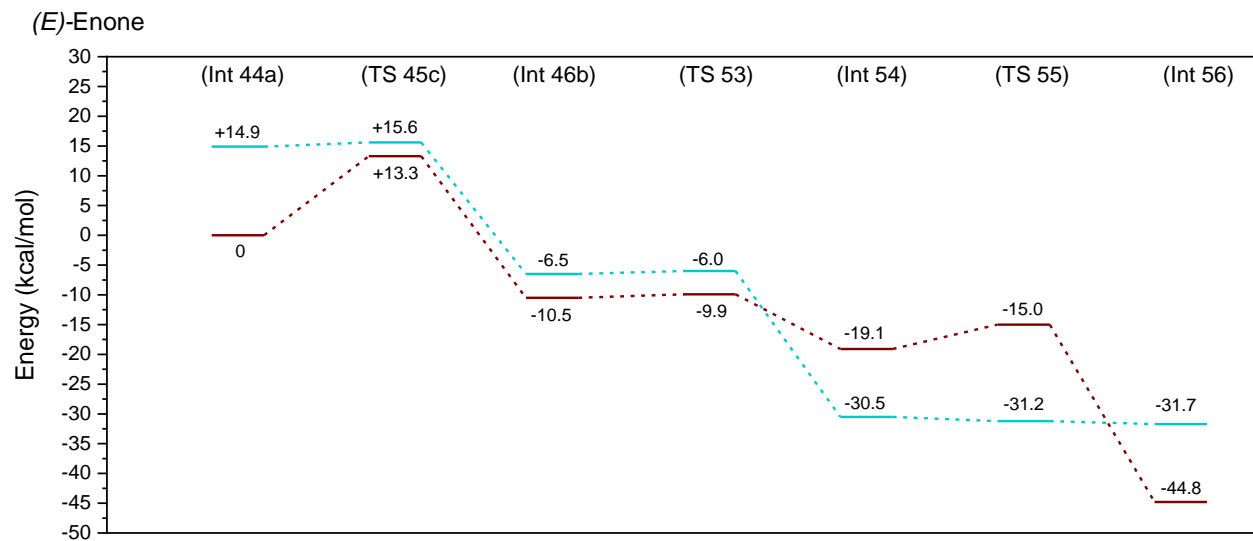


Figure A2.118. Energy diagram for (E)-enone

Table A2.4: Structure energies, relative to the triplet bound aldehyde complex **44a** (kcal/mol). Absolute energies in parentheses (Hartree).

Structure BP86/6-311g(d,p)	EE + Thermal Free Enthalpy Correction	Charge	Number of Imaginary Frequencies
44a (S=0)	14.9 (-4821.444971)	0	0
44a (S=1)	0 (-4821.468764)	0	0
44b (S=1)	1.4 (-4821.466552)	0	0
45a (S=0)	16.3 (-4821.442772)	0	1
45a (S=1)	12.2 (-4821.44927)	0	1
45b (S=0)	17.9 (-4821.440309)	0	1
45b (S=1)	14.1 (-4821.446342)	0	1
45c (S=0)	15.6 (-4821.443918)	0	1
45c (S=1)	13.3 (-4821.447559)	0	1
45d (S=0)	19.7 (-4821.437405)	0	1
45d (S=1)	16.8 (-4821.441977)	0	1
46a (S=0)	-7.4 (-4821.480528)	0	0
46a (S=1)	-11.8 (-4821.487497)	0	0
46b (S=0)	-6.5 (-4821.479102)	0	0
46b (S=1)	-10.5 (-4821.485537)	0	0
47a (S=1)	-19.6 (-4975.315169)	0	0
47b (S=1)	-23.0 (-4975.320494)	0	0
48a (S=1)	-18.3 (-4975.312953)	0	1
48b (S=1)	-22.7 (-4975.31999)	0	1
49a (S=0)	-29.3 (-4975.330531)	0	0
49a (S=1)	-27.0 (-4975.326864)	0	0
49b (S=0)	-29.0 (-4975.330068)	0	0
49b (S=1)	-26.2 (-4975.325652)	0	0
50a (S=0)	-28.7 (-4975.329674)	0	0
50a (S=1)	-27.8	0	0

	(-4975.328095)		
50b (S=0)	-25.6	0	0
	(-4975.324695)		
50b (S=1)	-21.1	0	0
	(-4975.31742)		
51a (S=0)	-20.3	0	1
	(-4975.316201)		
51a (S=1)	-16.5	0	1
	(-4975.310239)		
51b (S=0)	-22.6	0	1
	(-4975.319868)		
51b (S=1)	-17.5	0	1
	(-4975.31174)		
52a (S=0)	-22.1	0	0
	(-4975.319053)		
52a (S=1)	-20.2	0	0
	(-4975.315986)		
52b (S=0)	-26.5	0	0
	(-4975.325701)		
52b (S=1)	-22.7	0	0
	(-4975.32012)		
53 (S=0)	-6.0	0	1
	(-4821.478355)		
53 (S=1)	-9.9	0	1
	(-4821.484467)		
54 (S=0)	-30.5	0	0
	(-4821.517384)		
54 (S=1)	-19.1	0	0
	(-4821.499236)		
55 (S=0)	-31.2	0	1
	(-4821.518471)		
55 (S=1)	-15.0	0	1
	(-4821.492645)		
56 (S=0)	-31.7	0	0
	(-4821.519305)		
56 (S=1)	-44.8	0	0
	(-4821.540165)		

9. References

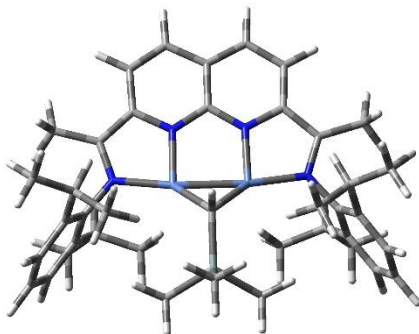
- ¹ Zhou, Y.Y.; Hartline, D. R.; Steiman, T. J.; Fanwick, P. E., and Uyeda, C. "Dinuclear Nickel Complexes in Five States of Oxidation Using a Redox-Active Ligand" *Inor. Chem.*, **2014**, 53 (21), 11770-11777
- ² Steiman, T. J.; Kalb, A. E.; Coombs, J. C.; Kirkland, J. K.; Torres, H.; Ess, D. H.; Uyeda, C. "Dinickel-Catalyzed Vinylidene-Alkene Cyclization Reactions" *ACS Catal.*, **2021**, 14408-14416.
- ³ Zhou, Y.-Y., and Uyeda, C. "Catalytic Reductive [4+1-Cycloadditions of Vinylidenes and Dienes." *Science*, **2019**, 363(6429), 857-862.

-
- ⁴ Zhou, Y.-Y.; Uyeda, C. "Reductive Cyclopropanations Catalyzed by Dinuclear Nickel Complexes." *Angew. Chem., Int. Ed.*, **2016**, 128 (9), 3223-3227.
- ⁵ Pal, S., Zhou, Y.-Y., and Uyeda C. "Catalytic Reductive Vinylidene Transfer Reactions" *J. Am. Chem. Soc.*, **2017** 139 (34), 11686-11689.
- ⁶ Spallarossa, M., Wang, Q. Riva, R., and Zhu, J. "Synthesis of Vinyl Isocyanides and Development of a Convertible Isonitrile" *Org. Lett.*, **2016** 18 (7), 1622-1625
- ⁷ Makings, L. R.; Garcia-Guzman Blanco, M.; Hurley, D. J.; Drutu, I.; Raffai, G.; Bergeron, D. M.; Nakatani, A.; Termin, A. P.; Silina, A. "Preparation of benzo-fused spiropiperidine compounds as modulators of muscarinic receptors" WO 2007076070, 2007
- ⁸ Murphy S. K., and Dong V. M. "Enantioselective Ketone Hydroacylation Using Noyori's Transfer Hydrogenation Catalyst" *J. Am. Chem. Soc.*, **2013**, *135*(15), 5553-5556
- ⁹ Tu, Y.; Zeng, X.; Wang, H.; Zhao, J. "A Robust One-Step Approach to Enamides" *Org. Lett.*, **2018**, 20(1), 280-283.
- ¹⁰ Taylor, W. G. "Synthesis of 5,5-Dichloro-4-pentenoic Acid by the Wittig Reaction with Bromotrichloromethane and Triphenylphosphine" *J. Org. Chem.*, **1981**, 46, 4292-4294.
- ¹¹ Friden-Saxin, M.; Pemberton, N.; Andersson, K. S.; Dyrager, C.; Friberg, A.; Grotli, M.; Luthman, K. "Synthesis of 2-Alkyl-Substituted Chromone Derivatives Using Microwave Irradiation" *J. Org. Chem.*, **2009**, 74(7), 2755-2759.
- ¹² Jui, N. T.; Lee, Esther C. Y.; MacMillan, D. W. C. "Enantioselective Organo-SOMO Cascade Cycloadditions: A Rapid Approach to Molecular Complexity from Simple Aldehydes and Olefins" *J. Am. Chem. Soc.*, **2010**, 132(29), 10015-10017.
- ¹³ a) Alcohol synthesis: Vulovic, B.; Trmcic, M.; Matovic, R.; Saicic, R. N. "Cyclization Reactions of Oxyallyl Cation. A Method for Cyclopentane Ring Formation" *Org. Lett.* **2019**, 21, (23), 9618-9621. b) Aldehyde synthesis: Dachavaram, S. S.; Kalyankar, K. B.; Das, S. "First stereoselective total synthesis of Neocosmosin A: a facile approach" *Tet. Lett.* **2014**, 55(41), 5629-5631.
- ¹⁴ Fraser, A. L.; Menzies, S. K.; King, E. F. B.; Tulloch, L. B.; Gould, E. R.; Zacharova, M. K.; Smith, T. K.; Florence, G. J. "Design and Synthesis of Broad Spectrum Trypanosomatid Selective Inhibitors" *ACS Infect. Dis.*, **2018**, 4(4), 560-567.
- ¹⁵ Takeoka, G. R.; Buttery, R. G.; and Perrino, C. T. Jr. "Synthesis and Occurrence of Oxoaldehydes in Used Frying Oils" *J. Agric. Food Chem.*, **1995**, 43(1), 22-26.
- ¹⁶ Matuszewska, I., Leniewski, A., Roszkowski P., Czarnocki, Z. "Synthesis of a Novel Class of Fatty Acids-Derived Isoquinolines" *Chem. Phys. Lipids*, **2005**, 135, 131-145.

-
- ¹⁷ Buhler, H.; Effenberger, F.; Forster, S.; Roos, J.; Wajant, H. "Enzyme-catalyzed reactions, part 47. Substrate specificity of mutants of the hydroxynitrile lyase from *Manihot esculenta*" *ChemBioChem* **2003**, 4, (2-3), 211-216
- ¹⁸ Davies, A. T.; Taylor, J. E.; Douglas, J. Collett, C. J.; Morrill, L. C.; Fallan, C.; Slawin, A. M. C.; Churchill, C. and Smith, A. D. "Stereospecific Asymmetric N-Heterocyclic Carbene (NHC)-Catalyzed Redox Synthesis of Trifluoromethyl Dihydropyranones and Mechanistic Insights" *J. Org. Chem.* **2013**, 78, 18, 9243–9257.
- ¹⁹ Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 3

Computational Methods. Geometry optimizations were performed using the Gaussian16 software package.^[1] All geometries were fully optimized at the BP86/6-311G(d,p) level of DFT. Stationary points were verified by frequency analysis.



19

Charge: 0

Multiplicity: 3

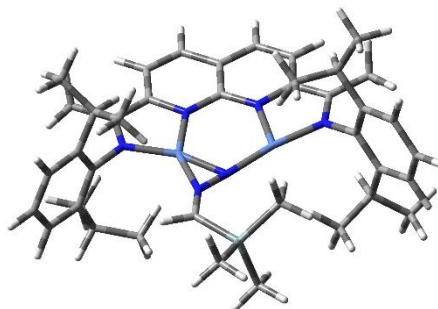
Imaginary Frequencies: 0

Sum of Electronic and Thermal Free Energies: -5082.144455

N	3.06587400	0.59489600	-0.00354400
N	1.14413500	2.15012000	-0.35736500
N	-1.14392900	2.15020600	-0.35694700
N	-3.06566600	0.59501300	-0.00291900
C	4.90507700	2.27522200	-0.23878700
H	5.49371700	1.69823300	0.48990000
H	5.02022900	3.34486500	-0.01488300
H	5.35077100	2.08900400	-1.23225000
C	3.46022400	1.85960300	-0.21127800
C	2.37265800	2.78446700	-0.40484000
C	2.43930300	4.17759700	-0.59262400
H	3.41052000	4.67318000	-0.65361100
C	1.26860500	4.92983500	-0.69784300
H	1.31895700	6.01264500	-0.83749400
C	0.00013100	4.29572000	-0.61539200
C	0.00012100	2.86488100	-0.44356700
C	-1.26832800	4.92993600	-0.69721100
H	-1.31865700	6.01276000	-0.83676100
C	-2.43904500	4.17777800	-0.59155000
H	-3.41025100	4.67343900	-0.65204400

C	-2.37240700	2.78463000	-0.40393600
C	-3.45998900	1.85975600	-0.21037000
C	-4.90482300	2.27544800	-0.23786600
H	-5.49368500	1.69784500	0.49014500
H	-5.35024700	2.09016700	-1.23162900
H	-5.01997000	3.34489900	-0.01304100
C	4.01469500	-0.43044100	0.29385100
C	4.29883900	-0.71216000	1.66024800
C	5.16736100	-1.77586300	1.94816000
H	5.39868800	-2.01438600	2.98880900
C	5.75093500	-2.53356100	0.92642900
H	6.41915800	-3.36261500	1.17401800
C	5.48765100	-2.22053300	-0.40876500
H	5.96069800	-2.80634700	-1.20186400
C	4.63071800	-1.16105200	-0.75398700
C	3.65563400	0.12206100	2.77017600
H	3.60001000	1.16202500	2.40196300
C	4.46637300	0.14478300	4.07847200
H	4.01947200	0.86476200	4.78281400
H	5.51372300	0.44112200	3.90656900
H	4.46811000	-0.83801200	4.57876100
C	2.20369400	-0.33214000	3.03869400
H	2.18109200	-1.36746900	3.41681600
H	1.60000200	-0.28712600	2.11399600
H	1.72292100	0.31997600	3.78639100
C	4.34623800	-0.84383800	-2.22123600
H	3.84646100	0.13814500	-2.25576100
C	5.63072200	-0.74454400	-3.06901500
H	6.14363200	-1.71700800	-3.15096300
H	6.34657300	-0.02480800	-2.63998500
H	5.38647700	-0.41668300	-4.09280300
C	3.35966400	-1.86912600	-2.81856700
H	3.78749000	-2.88563000	-2.80265500
H	3.11589400	-1.61520200	-3.86364600
H	2.42262200	-1.87760000	-2.24101800
C	-4.01460300	-0.43045900	0.29369300
C	-4.29925600	-0.71284500	1.65985700
C	-5.16802000	-1.77656400	1.94692100
H	-5.39976000	-2.01557900	2.98736800
C	-5.75133000	-2.53368700	0.92460200
H	-6.41975600	-3.36276600	1.17156000
C	-5.48748600	-2.22006600	-0.41033000
H	-5.96027600	-2.80544500	-1.20390500
C	-4.63028100	-1.16051900	-0.75471900
C	-3.65623700	0.12064600	2.77043700
H	-3.60009700	1.16076400	2.40275000

C	-4.46750100	0.14302500	4.07840900
H	-4.46983300	-0.84001200	4.57821200
H	-5.51466400	0.43984600	3.90619400
H	-4.02063000	0.86248200	4.78330400
C	-2.20457600	-0.33424300	3.03925800
H	-2.18252100	-1.36964700	3.41722400
H	-1.72365400	0.31752900	3.78715100
H	-1.60067200	-0.28937500	2.11469300
C	-4.34529600	-0.84266800	-2.22173000
H	-3.84456500	0.13884700	-2.25560200
C	-3.35970200	-1.86852900	-2.81971100
H	-2.42258500	-1.87817200	-2.24231200
H	-3.11586400	-1.61424500	-3.86468700
H	-3.78842500	-2.88466400	-2.80432200
C	-5.62964700	-0.74161700	-3.06953300
H	-6.14344700	-1.71356200	-3.15210900
H	-5.38504700	-0.41332700	-4.09309900
H	-6.34485900	-0.02150300	-2.64007600
Ni	1.18534900	0.24893800	-0.26183000
Ni	-1.18514400	0.24903600	-0.26129400
C	-0.00015200	-1.00224800	-1.01064900
H	-0.00043100	-0.95085500	-2.11948400
Si	-0.00015500	-2.81735700	-0.47993600
C	-1.52283100	-3.29390600	0.55176400
H	-1.53507300	-2.77026900	1.52037200
H	-1.50459900	-4.37819800	0.75885000
H	-2.46892800	-3.06444300	0.03758200
C	0.00086800	-3.93004700	-2.02677900
H	0.89127200	-3.75764600	-2.65245900
H	-0.88885900	-3.75780600	-2.65347900
H	0.00078100	-4.99287700	-1.72947500
C	1.52156500	-3.29320200	0.55347900
H	1.50369300	-4.37751400	0.76050200
H	1.53240500	-2.76960300	1.52212700
H	2.46813000	-3.06321900	0.04037100



S1

Charge: 0

Multiplicity: 3

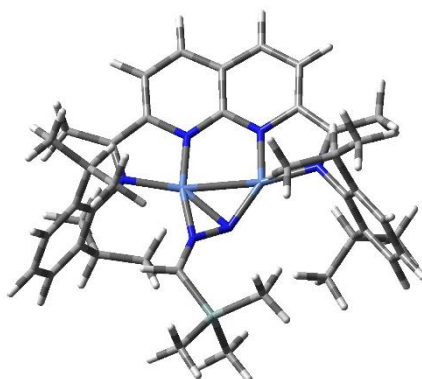
Imaginary Frequencies: 0

Sum of Electronic and Thermal Free Energies: -5191.685509

C	-5.08653700	2.47001700	0.14392500
H	-5.82637000	1.65929000	0.16962400
H	-5.36395200	3.16247700	-0.66758100
H	-5.15764900	3.03056100	1.09215400
N	-3.40342200	0.61736700	-0.05250700
Ni	-1.58985900	0.22263300	-0.25432200
C	-3.69879000	1.91804300	-0.04807000
N	-1.33069100	2.10613100	-0.27738000
Ni	1.55410600	0.22563100	-0.25950400
N	1.04572000	2.16474000	-0.28721200
C	-2.54772600	2.77890700	-0.19480900
N	3.28754100	0.85328300	-0.07662900
C	-2.63227900	4.18138200	-0.23916200
H	-3.60699200	4.66826800	-0.18174900
C	-1.47039700	4.92401400	-0.35630400
H	-1.50028600	6.01574800	-0.40394100
C	-0.21296200	4.27174400	-0.38948100
C	-0.15934400	2.82286100	-0.32360000
C	1.00159600	5.00040100	-0.46710600
H	0.96347200	6.09042800	-0.53911800
C	2.20577800	4.32669600	-0.42429800
H	3.15021100	4.87155300	-0.46602000
C	2.21896200	2.92155100	-0.31132300
C	3.44404000	2.18131100	-0.16942100
C	4.78846000	2.86196700	-0.12151600
H	4.85720500	3.57497000	0.71759800
H	4.98069500	3.42898700	-1.04842200
H	5.59123200	2.12159600	-0.00537400
C	-4.40503500	-0.39472200	0.10257800
C	-4.72313100	-0.83248500	1.41556000

C	-5.68686800	-1.84274800	1.57336500
H	-5.93858200	-2.18726000	2.58061200
C	-6.32346700	-2.41246500	0.46971200
H	-7.07373600	-3.19551400	0.60754200
C	-5.98209700	-1.98409000	-0.81616800
H	-6.46721500	-2.44056800	-1.68466300
C	-5.02301500	-0.97913900	-1.03812400
C	-4.00885600	-0.26864100	2.64343000
H	-3.34056800	0.53602200	2.29893400
C	-3.11947200	-1.34605900	3.30232500
H	-3.72380700	-2.18899500	3.67760500
H	-2.56541200	-0.92099200	4.15572300
H	-2.38767900	-1.74603100	2.58329300
C	-4.99358300	0.34056400	3.66339600
H	-5.66803300	-0.42486200	4.08230400
H	-5.62003100	1.12136500	3.20360300
H	-4.44392300	0.79435400	4.50454800
C	-4.70665900	-0.61688700	-2.49473300
H	-5.29941800	-1.33492700	-3.09099900
C	-5.18742500	0.78945800	-2.91512200
H	-6.23512500	0.96351900	-2.62211000
H	-5.12017700	0.89415600	-4.01091800
H	-4.56323700	1.57942200	-2.47117700
C	-3.23112300	-0.83492200	-2.88545000
H	-2.56562300	-0.11638000	-2.37748100
H	-3.10619100	-0.70225500	-3.97308200
H	-2.89123500	-1.84706900	-2.61857700
C	4.38798700	-0.01779400	0.20861200
C	4.78677000	-0.20898000	1.56155800
C	5.82052100	-1.12378000	1.81843000
H	6.14614900	-1.29069900	2.84755100
C	6.44999400	-1.82052900	0.78130500
H	7.25394000	-2.52640800	1.00664600
C	6.05678200	-1.60631700	-0.54201200
H	6.56300500	-2.14467000	-1.34726200
C	5.02784200	-0.70292400	-0.85655400
C	4.08175200	0.54034000	2.69483500
H	3.89301700	1.56852400	2.33819400
C	4.91774800	0.65364500	3.98181400
H	4.40505200	1.31097000	4.70224700
H	5.91724900	1.07523000	3.78746200
H	5.04910700	-0.32456300	4.47393400
C	2.70120800	-0.08679200	2.99388800
H	2.80979700	-1.12735500	3.34061900
H	2.07239600	-0.08558500	2.08467900
H	2.17116700	0.48706400	3.77181200

C	4.56680200	-0.49859800	-2.29820100
H	4.10669200	0.50239600	-2.35417200
C	5.71137100	-0.54308300	-3.32718900
H	6.51883600	0.16014100	-3.06754900
H	5.33043200	-0.27290800	-4.32542100
H	6.15262000	-1.55007000	-3.41143700
C	3.46391800	-1.52243200	-2.64538400
H	3.85434300	-2.55243400	-2.60074800
H	3.05990200	-1.34452300	-3.65559400
H	2.63083400	-1.43869400	-1.92663000
N	-0.02167200	-0.63296300	-0.51424300
N	-0.94009000	-1.49161000	-0.23568000
C	-1.04572700	-2.80329200	-0.09837500
H	-2.07201000	-3.12737500	0.10507500
C	-0.14810700	-5.63216100	0.57119200
H	0.64889100	-6.39089300	0.50136700
H	-1.04448800	-6.04582900	0.08017100
H	-0.38406500	-5.48785900	1.63780400
C	1.89184700	-3.26368700	0.64453500
H	1.98953500	-2.19563400	0.37745500
H	1.76941700	-3.31260400	1.73822800
H	2.83694300	-3.76303700	0.37944300
C	0.80565200	-4.32719000	-2.06772200
H	1.66438000	-5.01278900	-2.16701800
H	-0.05220400	-4.77822100	-2.59241600
H	1.05991700	-3.38828300	-2.58395900
Si	0.39231000	-4.00720500	-0.24301000



S1

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

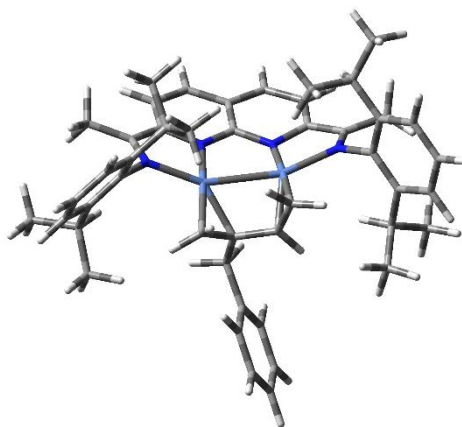
Sum of Electronic and Thermal Free Energies: -5191.682578

C	-5.08653700	2.47001700	0.14392500
---	-------------	------------	------------

H	-5.82637000	1.65929000	0.16962400
H	-5.36395200	3.16247700	-0.66758100
H	-5.15764900	3.03056100	1.09215400
N	-3.40342200	0.61736700	-0.05250700
Ni	-1.58985900	0.22263300	-0.25432200
C	-3.69879000	1.91804300	-0.04807000
N	-1.33069100	2.10613100	-0.27738000
Ni	1.55410600	0.22563100	-0.25950400
N	1.04572000	2.16474000	-0.28721200
C	-2.54772600	2.77890700	-0.19480900
N	3.28754100	0.85328300	-0.07662900
C	-2.63227900	4.18138200	-0.23916200
H	-3.60699200	4.66826800	-0.18174900
C	-1.47039700	4.92401400	-0.35630400
H	-1.50028600	6.01574800	-0.40394100
C	-0.21296200	4.27174400	-0.38948100
C	-0.15934400	2.82286100	-0.32360000
C	1.00159600	5.00040100	-0.46710600
H	0.96347200	6.09042800	-0.53911800
C	2.20577800	4.32669600	-0.42429800
H	3.15021100	4.87155300	-0.46602000
C	2.21896200	2.92155100	-0.31132300
C	3.44404000	2.18131100	-0.16942100
C	4.78846000	2.86196700	-0.12151600
H	4.85720500	3.57497000	0.71759800
H	4.98069500	3.42898700	-1.04842200
H	5.59123200	2.12159600	-0.00537400
C	-4.40503500	-0.39472200	0.10257800
C	-4.72313100	-0.83248500	1.41556000
C	-5.68686800	-1.84274800	1.57336500
H	-5.93858200	-2.18726000	2.58061200
C	-6.32346700	-2.41246500	0.46971200
H	-7.07373600	-3.19551400	0.60754200
C	-5.98209700	-1.98409000	-0.81616800
H	-6.46721500	-2.44056800	-1.68466300
C	-5.02301500	-0.97913900	-1.03812400
C	-4.00885600	-0.26864100	2.64343000
H	-3.34056800	0.53602200	2.29893400
C	-3.11947200	-1.34605900	3.30232500
H	-3.72380700	-2.18899500	3.67760500
H	-2.56541200	-0.92099200	4.15572300
H	-2.38767900	-1.74603100	2.58329300
C	-4.99358300	0.34056400	3.66339600
H	-5.66803300	-0.42486200	4.08230400
H	-5.62003100	1.12136500	3.20360300
H	-4.44392300	0.79435400	4.50454800

C	-4.70665900	-0.61688700	-2.49473300
H	-5.29941800	-1.33492700	-3.09099900
C	-5.18742500	0.78945800	-2.91512200
H	-6.23512500	0.96351900	-2.62211000
H	-5.12017700	0.89415600	-4.01091800
H	-4.56323700	1.57942200	-2.47117700
C	-3.23112300	-0.83492200	-2.88545000
H	-2.56562300	-0.11638000	-2.37748100
H	-3.10619100	-0.70225500	-3.97308200
H	-2.89123500	-1.84706900	-2.61857700
C	4.38798700	-0.01779400	0.20861200
C	4.78677000	-0.20898000	1.56155800
C	5.82052100	-1.12378000	1.81843000
H	6.14614900	-1.29069900	2.84755100
C	6.44999400	-1.82052900	0.78130500
H	7.25394000	-2.52640800	1.00664600
C	6.05678200	-1.60631700	-0.54201200
H	6.56300500	-2.14467000	-1.34726200
C	5.02784200	-0.70292400	-0.85655400
C	4.08175200	0.54034000	2.69483500
H	3.89301700	1.56852400	2.33819400
C	4.91774800	0.65364500	3.98181400
H	4.40505200	1.31097000	4.70224700
H	5.91724900	1.07523000	3.78746200
H	5.04910700	-0.32456300	4.47393400
C	2.70120800	-0.08679200	2.99388800
H	2.80979700	-1.12735500	3.34061900
H	2.07239600	-0.08558500	2.08467900
H	2.17116700	0.48706400	3.77181200
C	4.56680200	-0.49859800	-2.29820100
H	4.10669200	0.50239600	-2.35417200
C	5.71137100	-0.54308300	-3.32718900
H	6.51883600	0.16014100	-3.06754900
H	5.33043200	-0.27290800	-4.32542100
H	6.15262000	-1.55007000	-3.41143700
C	3.46391800	-1.52243200	-2.64538400
H	3.85434300	-2.55243400	-2.60074800
H	3.05990200	-1.34452300	-3.65559400
H	2.63083400	-1.43869400	-1.92663000
N	-0.02167200	-0.63296300	-0.51424300
N	-0.94009000	-1.49161000	-0.23568000
C	-1.04572700	-2.80329200	-0.09837500
H	-2.07201000	-3.12737500	0.10507500
C	-0.14810700	-5.63216100	0.57119200
H	0.64889100	-6.39089300	0.50136700
H	-1.04448800	-6.04582900	0.08017100

H	-0.38406500	-5.48785900	1.63780400
C	1.89184700	-3.26368700	0.64453500
H	1.98953500	-2.19563400	0.37745500
H	1.76941700	-3.31260400	1.73822800
H	2.83694300	-3.76303700	0.37944300
C	0.80565200	-4.32719000	-2.06772200
H	1.66438000	-5.01278900	-2.16701800
H	-0.05220400	-4.77822100	-2.59241600
H	1.05991700	-3.38828300	-2.58395900
Si	0.39231000	-4.00720500	-0.24301000



S2

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

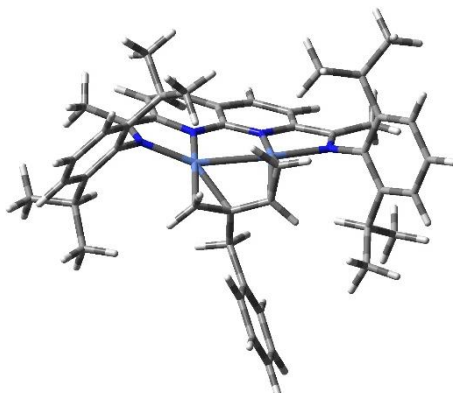
Sum of Electronic and Thermal Free Energies: -5060.551983

Ni	-1.31620500	-0.07404900	0.15472600
Ni	1.26629300	-0.09843800	0.15205100
N	3.11776300	-0.68307800	0.28726500
N	1.16208600	-0.77348600	1.91213100
N	-1.11667700	-1.04479200	1.77820600
N	-3.05537200	-0.93655900	0.11598400
C	4.90941300	-1.26107100	1.95804500
H	5.61775400	-0.76387300	1.28276200
H	5.12951600	-2.34298100	1.91454800
H	5.10503400	-0.92249300	2.98619700
C	3.48386800	-0.98656600	1.55047600
C	2.39314000	-1.15350800	2.45549500
C	2.45770600	-1.76756600	3.71611900
H	3.43176000	-1.99553300	4.15427200
C	1.28864500	-2.14220700	4.37455100
H	1.33060700	-2.65524800	5.33844200

C	0.03374500	-1.95565700	3.73879000
C	0.02148600	-1.25676200	2.47333600
C	-1.20624000	-2.44046600	4.22391000
H	-1.23804700	-2.97092700	5.17894600
C	-2.35525300	-2.30250500	3.44928200
H	-3.30394000	-2.71566300	3.79743600
C	-2.29850400	-1.63936100	2.21247400
C	-3.37687300	-1.54039600	1.26898700
C	-4.71850900	-2.16739200	1.55141300
H	-5.29065800	-1.59196000	2.29853800
H	-4.59018100	-3.18577500	1.95067000
H	-5.32245000	-2.23023500	0.63654200
C	4.12090600	-0.59765100	-0.73220600
C	4.79295000	0.62144300	-1.01491700
C	5.73969000	0.63521000	-2.05637600
H	6.26790000	1.56564600	-2.28384900
C	6.02099500	-0.51160100	-2.79925200
H	6.76065000	-0.47811700	-3.60368600
C	5.35335600	-1.70671500	-2.50858600
H	5.58359800	-2.60232500	-3.09040400
C	4.39976000	-1.77706800	-1.48203400
C	4.53760900	1.90125100	-0.21743800
H	3.67246200	1.71276600	0.43970300
C	4.19167100	3.09803400	-1.13043600
H	3.90615400	3.97314300	-0.52429900
H	3.35755600	2.86768700	-1.81041900
H	5.05497600	3.39405400	-1.74945700
C	5.74091200	2.26105200	0.68404800
H	5.52621000	3.17231000	1.26662700
H	6.64293300	2.45245200	0.07890100
H	5.97845600	1.45480800	1.39446200
C	3.64784400	-3.07624600	-1.18735800
H	3.47175400	-3.11245800	-0.09849600
C	4.42367800	-4.34905200	-1.57087800
H	5.43358400	-4.36182400	-1.13009300
H	4.52788800	-4.45605600	-2.66361900
H	3.88309300	-5.23903900	-1.21027000
C	2.25746100	-3.05681500	-1.86166500
H	1.67957000	-2.18329000	-1.51995400
H	1.68855300	-3.96711000	-1.60955600
H	2.35584600	-3.00095700	-2.95866400
C	-4.00683800	-0.78309900	-0.94099900
C	-5.13018800	0.08414400	-0.84036700
C	-5.98571800	0.19371000	-1.95256100
H	-6.85270400	0.85804900	-1.89165100
C	-5.75311200	-0.51893900	-3.12913800

H	-6.43703400	-0.41987200	-3.97632600
C	-4.63133600	-1.34951800	-3.22344200
H	-4.44260700	-1.89314200	-4.15236700
C	-3.74100400	-1.49005900	-2.14960900
C	-5.42754100	0.93409000	0.39820300
H	-4.68087400	0.68643300	1.16996600
C	-6.83178900	0.64702100	0.97777400
H	-6.97985000	1.20124300	1.91943100
H	-6.98543000	-0.42310700	1.18152900
H	-7.62195900	0.96780700	0.27893600
C	-5.29569500	2.44463500	0.09673600
H	-6.02996000	2.76311600	-0.66157200
H	-4.29491300	2.70228800	-0.28070800
H	-5.47670600	3.03661500	1.00926000
C	-2.51421300	-2.39233900	-2.24814900
H	-1.75093600	-1.94094100	-1.58453500
C	-2.81700400	-3.80433900	-1.69846700
H	-3.16766200	-3.76264900	-0.65602300
H	-1.91266300	-4.43472900	-1.72585000
H	-3.59757800	-4.29834300	-2.30174300
C	-1.92073000	-2.47676900	-3.66526800
H	-2.58082800	-3.02401300	-4.35947400
H	-0.96091200	-3.01711100	-3.63838100
H	-1.73723800	-1.47674000	-4.08920400
C	1.27122100	0.60515100	-1.68586800
H	2.25850100	0.69359200	-2.14570300
H	0.53555200	0.05174600	-2.28087600
C	0.84260300	1.58496300	-0.76310500
H	1.54198800	2.35718300	-0.42106400
C	-0.54472100	1.69634400	-0.29353300
C	-1.62403800	1.31238600	-1.15560400
H	-1.41309300	1.03474600	-2.19472900
H	-2.60522700	1.77403500	-1.00813900
C	-0.77329000	2.68311400	0.84643200
H	-0.18164800	2.36034900	1.71995400
H	-1.83194100	2.63106700	1.15804800
C	-0.42522100	4.13042800	0.51648700
C	0.18505700	4.94979700	1.48355600
C	-0.72521100	4.68977300	-0.73953900
C	0.47461600	6.29372000	1.21292400
H	0.43197200	4.52592800	2.46238000
C	-0.43567500	6.03209300	-1.01405800
H	-1.18554200	4.06261100	-1.50784100
C	0.16372400	6.84071300	-0.03871300
H	0.94789800	6.91291400	1.98020500
H	-0.67701500	6.44834800	-1.99620500

H	0.39065600	7.88816900	-0.25430100
---	------------	------------	-------------



S2

Charge: 0

Multiplicity: 3

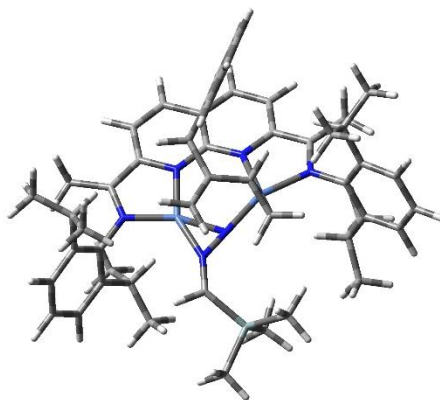
Imaginary Frequencies: 0

Sum of Electronic and Thermal Free Energies: -5060.541842

Ni	-1.43834700	-0.08607300	0.12986400
Ni	1.13894300	-0.38115000	-0.00007700
N	3.11493400	-0.77413800	0.26740500
N	1.01580600	-1.45608800	1.57472300
N	-1.28316900	-1.40254000	1.51581400
N	-3.26188300	-0.71694200	0.06918300
C	4.75195100	-1.94613900	1.77859200
H	5.51192300	-1.59855100	1.06658600
H	4.81122200	-3.04621900	1.83735200
H	5.01044400	-1.55490400	2.77732700
C	3.37462200	-1.48775300	1.36497900
C	2.21646500	-1.83816800	2.14797500
C	2.23571600	-2.56298000	3.35900100
H	3.19150700	-2.81295200	3.82362100
C	1.04391300	-2.96732500	3.94549300
H	1.04646400	-3.55000000	4.87045000
C	-0.19780600	-2.64980900	3.32682800
C	-0.15718100	-1.82096700	2.15047800
C	-1.46752900	-3.10275300	3.76684300
H	-1.53388800	-3.74406600	4.64949600
C	-2.60688600	-2.76185800	3.04647100
H	-3.58490200	-3.14003900	3.34950400
C	-2.50383500	-1.91946800	1.92100500
C	-3.60336500	-1.53361700	1.06977900
C	-4.98894700	-2.08120500	1.29173400
H	-5.45706800	-1.64693100	2.19200200
H	-4.95655700	-3.17315000	1.43599600

H	-5.63820900	-1.86445800	0.43317700
C	4.13642500	-0.51586200	-0.69578800
C	4.72854300	0.77413900	-0.76127500
C	5.65619800	1.03466500	-1.78504200
H	6.12001100	2.02253300	-1.84678500
C	5.99661600	0.05667200	-2.72072900
H	6.71486600	0.28034800	-3.51404500
C	5.42266300	-1.21631300	-2.63327000
H	5.71025800	-1.98014200	-3.35913400
C	4.49654900	-1.53608900	-1.62784000
C	4.42235600	1.83930300	0.29065700
H	3.45401300	1.57114400	0.74734900
C	4.30069900	3.25999900	-0.29560000
H	3.91579800	3.95565500	0.46658500
H	3.61385400	3.29239500	-1.15573900
H	5.27725400	3.64700400	-0.63205500
C	5.48115100	1.81941600	1.41788300
H	5.23598300	2.56476700	2.19289300
H	6.48037400	2.06053900	1.01740400
H	5.54228900	0.83270300	1.90143200
C	3.88453600	-2.93806800	-1.53836600
H	3.82973100	-3.20172000	-0.46759400
C	4.72521000	-4.03078500	-2.22309100
H	5.77063200	-4.02650100	-1.87452400
H	4.73034300	-3.91858100	-3.32023000
H	4.29646400	-5.02161400	-2.00258400
C	2.43467300	-2.95288700	-2.06823700
H	1.82573700	-2.21462200	-1.51976700
H	1.97907700	-3.94803600	-1.93507500
H	2.40524700	-2.69692000	-3.14039200
C	-4.21676800	-0.28505300	-0.90502700
C	-5.22514200	0.66824600	-0.59950300
C	-6.09731300	1.06286100	-1.63103600
H	-6.87913600	1.79653600	-1.41345600
C	-5.98545200	0.54574700	-2.92232200
H	-6.67923000	0.86527300	-3.70448600
C	-4.97093800	-0.37257300	-3.21380200
H	-4.87528900	-0.76304400	-4.23006800
C	-4.07037300	-0.79588900	-2.22587700
C	-5.37256600	1.31122400	0.78146200
H	-4.62558400	0.85378200	1.45030200
C	-6.77284900	1.07120000	1.38980200
H	-6.82203500	1.47563900	2.41443400
H	-7.02732900	0.00142000	1.43122300
H	-7.55469400	1.57534100	0.79790600
C	-5.07899600	2.82786000	0.73214000

H	-5.80839100	3.35308100	0.09350100
H	-4.07549700	3.03444800	0.33114900
H	-5.13984800	3.26585700	1.74230400
C	-2.96267600	-1.79952000	-2.53494100
H	-2.15257600	-1.59327700	-1.80807600
C	-3.43896400	-3.24811700	-2.28621200
H	-3.79414900	-3.38265100	-1.25297200
H	-2.61683500	-3.96293100	-2.45701900
H	-4.26741500	-3.50889900	-2.96662600
C	-2.37717300	-1.65456000	-3.95077200
H	-3.09950200	-1.95038700	-4.73027800
H	-1.49617200	-2.30703900	-4.06213600
H	-2.06305600	-0.61890500	-4.15590200
C	1.06202400	0.30439900	-1.93431200
H	1.97549500	0.22919200	-2.52886700
H	0.16603400	-0.13902000	-2.38144100
C	0.96532900	1.31001400	-0.96350100
H	1.82871500	1.95538300	-0.76706500
C	-0.26848500	1.56017000	-0.18973700
C	-1.54280700	1.54168300	-0.86238000
H	-1.56073700	1.40812700	-1.95169000
H	-2.34472600	2.18253400	-0.47725300
C	-0.11295200	2.42360300	1.06149600
H	0.58595700	1.94006000	1.76571900
H	-1.08583800	2.45299400	1.58580600
C	0.34669000	3.85811000	0.81987100
C	1.05006000	4.54333600	1.82893400
C	0.05833300	4.54486500	-0.37305900
C	1.44446200	5.87628100	1.65938800
H	1.28692300	4.02136500	2.76205100
C	0.45528100	5.87742700	-0.54819800
H	-0.47859000	4.02682700	-1.17186700
C	1.14787800	6.55001600	0.46665700
H	1.98816600	6.38845200	2.45835100
H	0.22246500	6.39211900	-1.48470500
H	1.45742200	7.58935900	0.32867500



S3

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

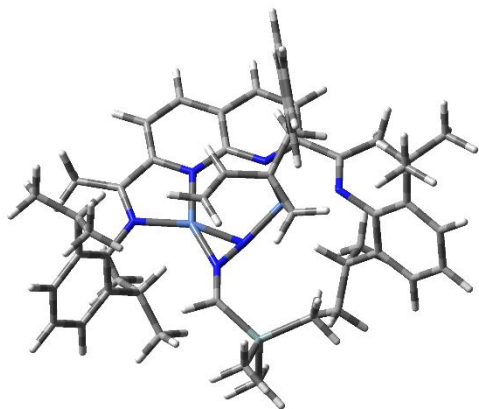
Sum of Electronic and Thermal Free Energies: -5617.988529

Ni	-1.77699700	0.04897900	0.41358600
Ni	1.29577800	0.38263700	0.13427400
N	-3.52137300	-0.65967100	0.54269900
N	-1.29882000	-1.26761200	1.67178400
N	1.03256600	-0.82015700	1.75464600
N	3.13188200	0.47902800	0.81396200
C	-4.95396700	-2.27757100	1.82867400
H	-5.11819500	-2.25115100	2.91796500
H	-4.97513600	-3.33728300	1.52138300
H	-5.79505100	-1.76538000	1.34313100
C	-3.64543100	-1.62796500	1.45809600
C	-2.41445300	-1.98220900	2.11479400
C	-2.32637200	-2.91175400	3.16040300
H	-3.21388700	-3.46510200	3.47204900
C	-1.11307800	-3.09671000	3.80341800
H	-1.02101600	-3.78722600	4.64565800
C	0.03013600	-2.37388800	3.38477900
C	-0.07297100	-1.46382700	2.25562900
C	1.28002000	-2.51045200	4.03643900
H	1.36118200	-3.17135000	4.90318900
C	2.36799300	-1.80016400	3.57060300
H	3.33517600	-1.88796800	4.06681400
C	2.24299100	-0.97754200	2.43343100
C	3.37419300	-0.28500700	1.88607500
C	4.73698200	-0.41167000	2.53056700
H	5.44776700	0.29482600	2.08396300
H	5.14769600	-1.42852000	2.41490500

H	4.68341600	-0.20136900	3.61094300
C	-4.66526000	-0.07586000	-0.09350400
C	-5.27757200	-0.68806600	-1.21669000
C	-6.40893500	-0.06837500	-1.77805500
H	-6.89663600	-0.53176100	-2.64067600
C	-6.91875600	1.12376700	-1.26100100
H	-7.80264600	1.58445900	-1.71021900
C	-6.28217100	1.73466000	-0.17574300
H	-6.67250900	2.67802200	0.21509100
C	-5.15135800	1.15837000	0.42300900
C	4.21047100	1.20165100	0.19921700
C	4.28515500	2.60603000	0.43768800
C	5.32037000	3.33490800	-0.16790600
H	5.39343300	4.41001500	0.01042700
C	6.25696600	2.71540100	-1.00128300
H	7.05250700	3.30325000	-1.46697100
C	6.16330100	1.34508700	-1.24016000
H	6.89194300	0.86334200	-1.89851300
C	5.15378600	0.56081800	-0.65140100
C	1.45479000	-0.62805700	-1.59068800
H	2.33672200	-1.25787400	-1.42740900
C	0.27259600	-1.38501100	-2.03838800
C	0.05533000	-2.74471600	-1.38745200
H	-0.08617300	-2.59706800	-0.30457300
H	-0.88265400	-3.17906200	-1.77502800
C	3.27867800	3.29770600	1.35668100
H	2.31884400	2.76567100	1.22562600
C	5.12343800	-0.93707900	-0.96081500
H	4.26824100	-1.37840300	-0.42333900
C	-4.72831700	-1.96478000	-1.85091400
H	-3.80842500	-2.23453900	-1.30635900
C	-4.46279100	1.82741900	1.61062500
H	-3.43138500	1.42999000	1.63368000
C	1.64787100	0.76889300	-1.76791100
H	0.85240900	1.35276300	-2.23852900
H	2.65784700	1.16854400	-1.90079800
C	4.92440300	-1.20499000	-2.47029900
H	5.79450800	-0.85552800	-3.05107300
H	4.80699500	-2.28516800	-2.65465800
H	4.03235400	-0.69405200	-2.86122700
C	6.40441900	-1.65247400	-0.47295100
H	7.29062400	-1.29682700	-1.02454700
H	6.59044700	-1.48333100	0.59818500
H	6.32109500	-2.73875400	-0.64028100
C	3.05403500	4.78159400	1.01442600
H	2.21896100	5.18058600	1.61124600

H	3.94033200	5.39554400	1.24821700
H	2.80981600	4.92504500	-0.04951800
C	3.68228200	3.16180600	2.84313200
H	3.76000200	2.10921600	3.15014400
H	4.65641400	3.64610900	3.02684000
H	2.93254500	3.64577400	3.49095900
C	-4.34462500	-1.72594500	-3.32771600
H	-3.86743600	-2.62435500	-3.75373100
H	-5.23277600	-1.50057400	-3.94115900
H	-3.64542000	-0.88201700	-3.42521300
C	-5.71854300	-3.14502300	-1.74094100
H	-5.99659400	-3.35099800	-0.69633000
H	-6.64724400	-2.93554400	-2.29778200
H	-5.27560400	-4.06217300	-2.16344400
C	-4.36532500	3.35736900	1.47050800
H	-3.74667700	3.76949300	2.28403900
H	-3.90165200	3.64015600	0.51289900
H	-5.35314800	3.84436500	1.53290800
C	-5.14291300	1.44430000	2.94315100
H	-6.18529800	1.80529600	2.96821100
H	-5.16061500	0.35359600	3.08963400
H	-4.60537500	1.89160400	3.79571100
C	1.19351400	-3.72987300	-1.61425200
C	1.88017500	-4.30566300	-0.53108000
C	1.56896500	-4.10223900	-2.91927500
C	2.90868200	-5.23533200	-0.74235100
H	1.60133700	-4.02267800	0.48834900
C	2.59423800	-5.03020200	-3.13447200
H	1.05193900	-3.65053800	-3.77144000
C	3.26825500	-5.60215600	-2.04515800
H	3.42770600	-5.67463800	0.11418300
H	2.86853100	-5.31016500	-4.15549400
H	4.06749600	-6.32915400	-2.21252100
C	-0.55999200	-0.94254800	-3.00787500
H	-1.41990400	-1.53672900	-3.32461200
H	-0.39989400	0.01199400	-3.51343000
N	-1.35515000	1.46595900	-0.64655400
C	-1.65960100	2.46171600	-1.45824200
H	-2.66059300	2.33690900	-1.89141100
N	-0.37551700	1.14715700	0.15976100
Si	-0.81393900	4.14293600	-1.65215300
C	-2.04947700	5.18039400	-2.64996800
H	-3.03207100	5.23056800	-2.15346200
H	-1.68297900	6.21308200	-2.77154500
H	-2.20254500	4.76120600	-3.65818800
C	0.84201200	4.13234700	-2.57298200

H	1.16982900	5.17214000	-2.74496300
H	1.63116900	3.62086500	-2.00219400
H	0.76100500	3.64128900	-3.55589900
C	-0.57923900	4.87540800	0.07926100
H	-0.01373000	4.17859800	0.71775900
H	-0.02984600	5.83036200	0.03981900
H	-1.55240100	5.05835400	0.56180900



S3'

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

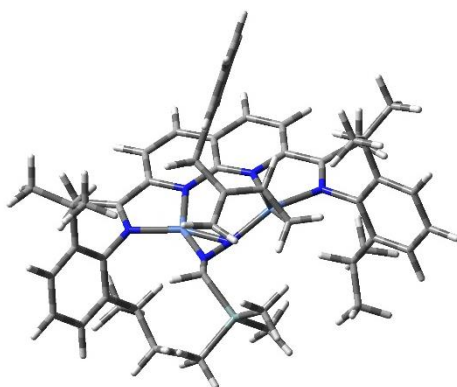
Sum of Electronic and Thermal Free Energies: -5617.981705

Ni	1.81061200	-0.01785400	0.40730100
Ni	-1.27004600	-0.11098200	0.16801100
N	3.59362200	0.54880600	0.66610400
N	1.41539400	1.05538900	1.91845600
N	-0.91328600	0.64663000	2.01774300
N	-2.98792100	-0.60599300	1.00217800
C	5.11987300	1.81577700	2.21170700
H	5.26493100	1.59404800	3.28124200
H	5.22185100	2.90771300	2.08764500
H	5.92925100	1.33318100	1.64813500
C	3.77431600	1.33450600	1.73306000
C	2.56131500	1.65307900	2.44237500
C	2.52057700	2.43903600	3.60444900
H	3.43357200	2.91153300	3.97102700
C	1.32384400	2.58550500	4.28813000
H	1.27113900	3.16283800	5.21479800
C	0.15190900	1.95626500	3.80313800
C	0.21068500	1.20801700	2.55993200

C	-1.08313200	2.01971400	4.49582500
H	-1.13979600	2.57672100	5.43466200
C	-2.18354100	1.35528100	3.99003700
H	-3.13336700	1.37343000	4.52647400
C	-2.09055600	0.67190100	2.75963000
C	-3.20226400	-0.05304500	2.20022600
C	-4.49421200	-0.20314300	2.96999200
H	-5.10716100	-1.00572800	2.53859700
H	-5.08849900	0.72676400	2.94246900
H	-4.30938200	-0.44462700	4.02799800
C	4.69928200	-0.00515600	-0.05866000
C	5.38721300	0.74465800	-1.04689000
C	6.47404100	0.13920100	-1.70387400
H	7.01890200	0.70664400	-2.46402300
C	6.86822000	-1.16724400	-1.40991500
H	7.71999000	-1.61464400	-1.92914200
C	6.15617100	-1.90648600	-0.45983000
H	6.45470100	-2.93601800	-0.24498900
C	5.06493100	-1.35118200	0.22550100
C	-3.91460800	-1.55526500	0.45160600
C	-3.57535200	-2.93521200	0.60302500
C	-4.40937800	-3.90085200	0.02081700
H	-4.15831800	-4.95878300	0.13096100
C	-5.55172500	-3.53792400	-0.69975100
H	-6.18227200	-4.30533500	-1.15663800
C	-5.88551400	-2.18959200	-0.82078900
H	-6.79046900	-1.90823700	-1.36737100
C	-5.09619500	-1.17740900	-0.24279000
C	-1.30821100	1.48412200	-1.05567700
C	0.02984500	2.07348300	-1.25195000
C	-2.36369800	-3.35702900	1.43473700
H	-1.64378000	-2.52214200	1.40042000
C	-5.57499300	0.27038400	-0.35845200
H	-4.84257400	0.90704000	0.16444700
C	4.96245200	2.15706300	-1.44603100
H	4.06636100	2.41248300	-0.85663900
C	4.29392400	-2.16344800	1.26374600
H	3.31147200	-1.66873700	1.37660700
C	-1.70702500	0.27812600	-1.70704300
H	-1.00716800	-0.20015200	-2.39829300
H	-2.76510300	0.09785500	-1.92061700
C	-5.66204200	0.74803900	-1.82426300
H	-6.41354900	0.16742500	-2.38454000
H	-5.95521300	1.80942300	-1.86938300
H	-4.70109000	0.64132000	-2.34902100
C	-6.94380300	0.47235600	0.33299100

H	-7.73478600	-0.09707100	-0.18237200
H	-6.92786300	0.14256600	1.38257100
H	-7.23173200	1.53654600	0.31115900
C	-1.65126400	-4.61183700	0.89808100
H	-0.71081200	-4.77060800	1.44991200
H	-2.26088500	-5.52233900	1.02696700
H	-1.40724500	-4.51379400	-0.17013400
C	-2.76067000	-3.56971400	2.91443200
H	-3.20911200	-2.66507200	3.35104000
H	-3.49328800	-4.38957300	3.00769200
H	-1.87526600	-3.83182000	3.51742900
C	4.57272800	2.21300800	-2.93996100
H	4.18641600	3.21190900	-3.20287300
H	5.44267100	2.01284800	-3.58724800
H	3.79816600	1.46875000	-3.17889400
C	6.05439200	3.20585900	-1.14052100
H	6.34209900	3.20074800	-0.07833400
H	6.96466600	3.01450900	-1.73306000
H	5.69876300	4.21848400	-1.39330100
C	4.02814800	-3.61327000	0.81970500
H	3.37100200	-4.11460900	1.54867600
H	3.53184400	-3.64446800	-0.16224000
H	4.95650900	-4.20557000	0.75609000
C	4.99805300	-2.12807800	2.63741600
H	5.99328900	-2.60111300	2.58004200
H	5.13660900	-1.09577800	2.99422600
H	4.40473300	-2.67071800	3.39200900
C	0.81033200	1.92879900	-2.34025800
H	1.78091900	2.42289400	-2.40676900
H	0.50097700	1.32520700	-3.19725000
N	1.31027100	-1.09115600	-0.97963400
C	1.55043900	-1.77001700	-2.08526700
H	2.57108200	-1.59252900	-2.45152100
N	0.35487800	-0.95761100	-0.10341900
Si	0.55740000	-3.12664000	-2.95167300
C	1.05064500	-3.04108200	-4.78179100
H	2.14183800	-3.13274500	-4.91018900
H	0.57961800	-3.86002900	-5.35070500
H	0.73677500	-2.08923100	-5.23966100
C	-1.31540800	-2.96371300	-2.76323800
H	-1.80487500	-3.92271800	-3.00141500
H	-1.60241700	-2.67714200	-1.73987600
H	-1.72555600	-2.20313600	-3.44559400
C	1.12818900	-4.80062700	-2.25515300
H	0.90078800	-4.88835500	-1.18122700
H	0.62282500	-5.63067700	-2.77815300

H	2.21465600	-4.93510700	-2.38173300
H	0.37072400	2.73722600	-0.44720700
C	-2.34333500	2.47181300	-0.52021500
H	-3.28811000	1.93283200	-0.34285600
H	-2.01788700	2.84999400	0.46444700
C	-2.61738400	3.66673000	-1.42853600
C	-2.73872200	3.51927000	-2.82240500
C	-2.78534000	4.95006700	-0.87852000
C	-3.03295100	4.61822700	-3.63836500
H	-2.59055000	2.53298900	-3.27039100
C	-3.08065900	6.05295900	-1.69079100
H	-2.68308900	5.08488200	0.20328600
C	-3.20723600	5.89030800	-3.07603400
H	-3.12188300	4.48180800	-4.71986600
H	-3.20616600	7.04172600	-1.24050300
H	-3.43386500	6.74883000	-3.71383200



S4

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 1

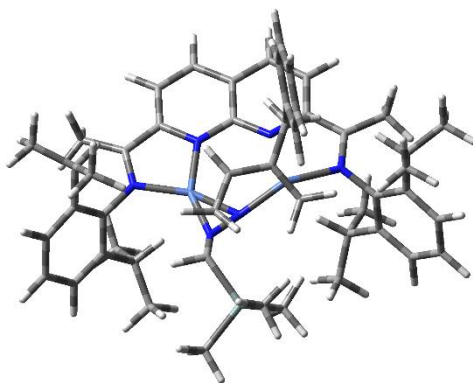
Sum of Electronic and Thermal Free Energies: -5617.962574

Ni	1.72980100	-0.07599800	0.62416700
Ni	-1.45409000	-0.29335800	0.22274300
N	3.52259800	0.46290300	0.82287900
N	1.30767500	1.28576600	1.83547500
N	-1.07114100	1.10297600	1.71817600
N	-3.26658000	-0.16730300	0.90012300
C	5.03769400	1.96226400	2.15143600
H	5.10847100	2.05980900	3.24575700
H	5.23295700	2.95931300	1.71940500
H	5.83807400	1.28968300	1.81326800
C	3.68788000	1.43470500	1.73622400
C	2.46992400	1.92606100	2.30303600

C	2.40356500	2.94513900	3.25904700
H	3.31895500	3.42658700	3.60793200
C	1.16698200	3.32666900	3.75242900
H	1.08070100	4.10168600	4.51836000
C	-0.01745200	2.71535100	3.27257400
C	0.06511100	1.67233400	2.25397900
C	-1.28573200	3.09168500	3.76874400
H	-1.35161700	3.87013900	4.53299900
C	-2.41121600	2.44254000	3.30202000
H	-3.39470100	2.69912700	3.69656800
C	-2.30285600	1.45945900	2.30381700
C	-3.46275200	0.77603700	1.83784600
C	-4.82503400	1.07458100	2.42804000
H	-5.56664300	0.33765400	2.09621700
H	-5.18517300	2.07478600	2.13399300
H	-4.79382800	1.04780500	3.52854000
C	4.62127200	-0.21208200	0.20872300
C	5.34265700	0.38202300	-0.86015300
C	6.40253500	-0.34222900	-1.43555500
H	6.96808600	0.10429600	-2.25887600
C	6.74514700	-1.61676400	-0.98031200
H	7.57642100	-2.15938400	-1.43855200
C	6.01191300	-2.20061300	0.05848600
H	6.27671700	-3.20295400	0.40529700
C	4.94433400	-1.52195600	0.66548800
C	-4.38224000	-0.95374000	0.45226800
C	-4.48539000	-2.28739400	0.94366800
C	-5.55788500	-3.08252700	0.51082900
H	-5.65194200	-4.10500000	0.88467500
C	-6.50614100	-2.59330400	-0.39346800
H	-7.33300500	-3.22952800	-0.72064400
C	-6.38678500	-1.29142400	-0.88009400
H	-7.12593000	-0.91419600	-1.59297400
C	-5.33580100	-0.44771600	-0.47416500
C	-1.52936900	0.33112700	-1.75440400
H	-2.20490300	1.18788900	-1.64576500
C	-0.24909200	0.59150200	-2.34679300
C	0.41974800	1.93740000	-2.08960800
H	0.74772300	1.97852300	-1.03551000
H	1.33172100	2.00820200	-2.70577600
C	-3.46453400	-2.82626700	1.94449100
H	-2.51388300	-2.30469900	1.73199800
C	-5.26488000	0.96841400	-1.05084900
H	-4.39152200	1.47059100	-0.60318500
C	4.97067200	1.75030100	-1.42962300
H	4.15639400	2.15957100	-0.81043900

C	4.15299200	-2.15215600	1.80881900
H	3.16149300	-1.66170400	1.80021700
C	-2.03130800	-0.98797600	-1.53399100
H	-1.43556200	-1.83207000	-1.88512900
H	-3.10591400	-1.17693500	-1.53136900
C	-5.06972200	0.95627500	-2.58433100
H	-5.93494700	0.49512500	-3.08947800
H	-4.96806800	1.98576700	-2.96480900
H	-4.16984900	0.39649200	-2.87770000
C	-6.52149200	1.79710900	-0.69756100
H	-7.42021400	1.37901700	-1.18091800
H	-6.70842900	1.82301900	0.38612000
H	-6.40672200	2.83498200	-1.05110100
C	-3.21802200	-4.34067000	1.81720300
H	-2.36099700	-4.63418200	2.44434200
H	-4.08616200	-4.92949400	2.15911700
H	-2.99501400	-4.63340300	0.77971100
C	-3.86376200	-2.47375300	3.39572400
H	-3.95668500	-1.38724700	3.53726300
H	-4.82978300	-2.93814300	3.65751800
H	-3.10358000	-2.84156400	4.10483300
C	4.43065600	1.61427800	-2.87059300
H	4.10945000	2.59449000	-3.26054000
H	5.20288500	1.21689100	-3.55035500
H	3.56818500	0.93040200	-2.90495200
C	6.14962200	2.74623800	-1.38806100
H	6.55190800	2.85724500	-0.36933900
H	6.97707700	2.41751500	-2.03875500
H	5.82673800	3.74029500	-1.73905500
C	3.92578500	-3.66418100	1.63754300
H	3.24069100	-4.03244300	2.41830100
H	3.47977100	-3.89366800	0.65718000
H	4.86254100	-4.23950500	1.72903300
C	4.80832200	-1.84908500	3.17403700
H	5.81498100	-2.29710400	3.23292300
H	4.90946200	-0.76583900	3.34007200
H	4.20079200	-2.26172600	3.99662600
C	-0.47377700	3.13443000	-2.37571500
C	-0.98081800	3.92379600	-1.32904100
C	-0.81449800	3.47351000	-3.69905300
C	-1.80345500	5.02788400	-1.59591900
H	-0.72626600	3.66783000	-0.29638500
C	-1.63238700	4.57639700	-3.96931300
H	-0.43316200	2.86243800	-4.52322600
C	-2.13030000	5.35868500	-2.91664200
H	-2.18588500	5.63119400	-0.76799700

H	-1.88061000	4.82930500	-5.00396500
H	-2.76739000	6.22192800	-3.12699000
C	0.42171300	-0.42229300	-3.06226400
H	1.31841300	-0.12795700	-3.61748900
H	-0.19947000	-1.16009400	-3.57274600
N	1.22026000	-1.31732300	-0.58524000
C	1.32400200	-1.84560900	-1.84495400
H	2.37527900	-1.75748300	-2.16112200
N	0.23913600	-0.99174600	0.17715100
Si	0.67764700	-3.62595000	-2.21031800
C	2.23474500	-4.64963700	-2.56615400
H	2.93880300	-4.62450300	-1.71927200
H	1.97252400	-5.70397100	-2.75623300
H	2.76793200	-4.27406100	-3.45529900
C	-0.43006200	-3.74195200	-3.74745800
H	-0.64874000	-4.80626600	-3.94028300
H	-1.39576900	-3.22472700	-3.63827200
H	0.07203800	-3.34499500	-4.64487600
C	-0.20986500	-4.29391000	-0.68378200
H	-1.00069500	-3.61163300	-0.33764200
H	-0.66632100	-5.27388000	-0.90009000
H	0.49774500	-4.42463100	0.15018400



S4'

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 1

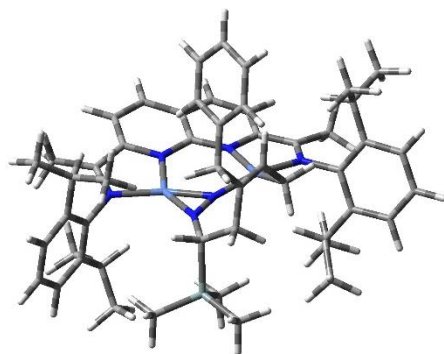
Sum of Electronic and Thermal Free Energies: -5617.958250

Ni	1.87644300	-0.26591600	0.51022500
Ni	-1.30286500	-0.23845200	0.20540700
N	3.67739400	0.15709800	0.86702400
N	1.51236800	0.41282100	2.22181900
N	-0.85696900	0.20776500	2.17510600
N	-3.02934900	-0.70111800	0.96425300

C	5.25467300	0.92870300	2.66342600
H	5.37558600	0.50237600	3.67147700
H	5.43199200	2.01545000	2.74257500
H	6.03709500	0.50927600	2.01607900
C	3.88676300	0.62651300	2.10647600
C	2.69243400	0.79925200	2.87849000
C	2.67387500	1.29276100	4.18847200
H	3.60771500	1.58715600	4.67089800
C	1.46589900	1.39154400	4.86008900
H	1.42265100	1.74667300	5.89294900
C	0.26105200	1.01606400	4.21820000
C	0.29660900	0.53252300	2.84320700
C	-0.98535900	1.08673200	4.88397600
H	-1.02041500	1.45605500	5.91209500
C	-2.12585600	0.65191700	4.23743100
H	-3.08887300	0.66979900	4.74924700
C	-2.05621400	0.20134300	2.90649500
C	-3.21030800	-0.31152800	2.23660100
C	-4.53114200	-0.45612200	2.95858100
H	-5.20128200	-1.12744700	2.40590000
H	-5.04004400	0.51740000	3.06699900
H	-4.39582900	-0.87088800	3.96893000
C	4.73768900	-0.10307200	-0.05211900
C	5.41732400	0.95841300	-0.70775600
C	6.42591500	0.63312000	-1.63268300
H	6.95598100	1.43919700	-2.14850600
C	6.76264300	-0.69377700	-1.90757300
H	7.55404100	-0.92230300	-2.62650500
C	6.07654600	-1.72960100	-1.26431800
H	6.33905400	-2.76715000	-1.48677100
C	5.05893600	-1.46090100	-0.33673600
C	-4.01012100	-1.51661300	0.30063500
C	-3.77148300	-2.92578400	0.31101500
C	-4.67718400	-3.76944300	-0.34927500
H	-4.50177000	-4.84814600	-0.34661000
C	-5.79735500	-3.25788900	-1.01136200
H	-6.48849500	-3.93091900	-1.52600800
C	-6.02946400	-1.88320500	-1.00430000
H	-6.91420600	-1.48690700	-1.51100500
C	-5.16075400	-0.98877300	-0.35000100
C	-1.29975300	1.46323500	-0.97737100
C	0.02766300	1.79574700	-1.42647900
C	-2.58148400	-3.51469900	1.07001200
H	-1.80334800	-2.73269700	1.10020100
C	-5.53078500	0.49704100	-0.34180100
H	-4.70965700	1.04278400	0.15218600

C	5.04508100	2.42447100	-0.48561000
H	4.33080800	2.46790100	0.35158800
C	4.32388400	-2.58831500	0.38324200
H	3.33914300	-2.17515900	0.67368600
C	-1.99848500	0.34051000	-1.53415400
H	-1.55320400	-0.18314600	-2.38366400
H	-3.08904600	0.33027800	-1.52751400
C	-5.70538100	1.07605700	-1.76451700
H	-6.57688200	0.62753200	-2.26963600
H	-5.87119300	2.16429400	-1.71689400
H	-4.82549800	0.89584200	-2.39976200
C	-6.82570900	0.75632600	0.46443000
H	-7.68914300	0.26852800	-0.01772600
H	-6.75932400	0.37345200	1.49262300
H	-7.03690900	1.83747200	0.51349300
C	-1.97768500	-4.76282300	0.39979600
H	-1.03554200	-5.03574700	0.90214400
H	-2.64840700	-5.63574900	0.47414500
H	-1.75890100	-4.58901200	-0.66408200
C	-2.96506400	-3.84064400	2.53239200
H	-3.32526500	-2.95069500	3.06834400
H	-3.76106900	-4.60418000	2.56476200
H	-2.09214000	-4.23265800	3.08040200
C	4.32452300	2.99745500	-1.72602800
H	4.01350700	4.04080300	-1.55124900
H	4.98237000	2.98188900	-2.61104600
H	3.42519600	2.40800800	-1.96192300
C	6.26346100	3.29595300	-0.11384900
H	6.79563700	2.89697500	0.76376300
H	6.98718600	3.35619300	-0.94350800
H	5.94265500	4.32491900	0.11814100
C	4.06895400	-3.82042800	-0.50186100
H	3.42391600	-4.53855100	0.02980100
H	3.56572900	-3.54135900	-1.44069500
H	5.00230500	-4.34961400	-0.75843100
C	5.05877500	-2.98697400	1.68182700
H	6.06080600	-3.39039600	1.45672000
H	5.18445100	-2.12365100	2.35315200
H	4.49253000	-3.76017600	2.22737000
C	0.58894200	1.32015500	-2.62284900
H	1.51840900	1.79122400	-2.95505700
H	-0.09913200	1.07137600	-3.43330900
N	1.31019300	-0.81823900	-1.12371200
C	1.34102700	-0.60138600	-2.47509300
N	0.36418600	-0.89551900	-0.26371700
H	0.62678400	2.44680100	-0.78070500

C	-2.02137000	2.51441700	-0.13874700
H	-2.94717400	2.07886600	0.27479400
H	-1.39788600	2.76864800	0.73518700
C	-2.36517300	3.80295900	-0.88115300
C	-2.39234700	5.02487200	-0.18422100
C	-2.69464900	3.80929900	-2.24826800
C	-2.74833700	6.21669700	-0.82804900
H	-2.12882900	5.03989700	0.87837500
C	-3.05062200	4.99907600	-2.89648100
H	-2.66533100	2.87234700	-2.81059800
C	-3.08047000	6.20811500	-2.18908400
H	-2.75976900	7.15504000	-0.26641500
H	-3.30194200	4.98182300	-3.96076700
H	-3.35487400	7.13716200	-2.69570500
H	2.38576400	-0.42196700	-2.77215600
Si	0.48240400	-1.81969100	-3.69575800
C	1.89589100	-2.74457700	-4.56031500
H	1.49755300	-3.48598400	-5.27329300
H	2.54454800	-2.05453400	-5.12493000
H	2.52883600	-3.28132000	-3.83567600
C	-0.60083600	-3.03545700	-2.74359900
H	0.02463500	-3.69718600	-2.12392500
H	-1.30507700	-2.52206600	-2.07178300
H	-1.18008900	-3.66493800	-3.43917500
C	-0.51477900	-0.92706400	-5.04186400
H	0.09363000	-0.18014500	-5.57759900
H	-0.84994000	-1.67070300	-5.78488800
H	-1.41496100	-0.42290100	-4.65665400



S5

Charge: 0

Multiplicity: 1

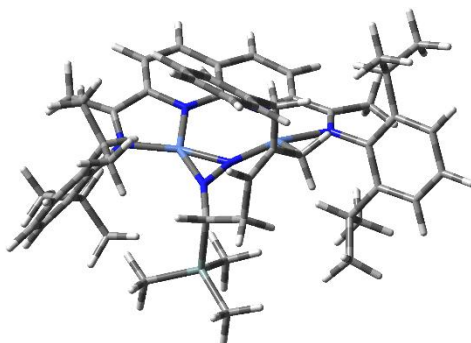
Imaginary Frequencies: 0

Sum of Electronic and Thermal Free Energies: -5617.986184

Ni	-1.57113900	-0.38255800	-0.46683900
Ni	1.67273400	-0.36882100	-0.10807700
N	-3.39152600	-0.47073000	-1.01803000
N	-1.15361700	-1.05882600	-2.15211400
N	1.19560500	-1.37780900	-1.83305700
N	3.40321300	-1.06999600	-0.40819100
C	-4.83634000	-0.72766100	-3.04959500
H	-4.92064800	-1.55101000	-3.77368200
H	-4.96035800	0.21704500	-3.60871900
H	-5.67239900	-0.80331700	-2.34087800
C	-3.51317700	-0.75204800	-2.32561900
C	-2.28734100	-1.07609700	-2.98687400
C	-2.20637000	-1.48179900	-4.32177100
H	-3.09152900	-1.44850900	-4.95886400
C	-0.99811700	-1.95714100	-4.80867300
H	-0.91116500	-2.33110000	-5.83202200
C	0.13858300	-2.00934700	-3.96965400
C	0.07163300	-1.46297000	-2.61566600
C	1.34562600	-2.60406800	-4.40930000
H	1.38799400	-3.04795800	-5.40702600
C	2.43681300	-2.62343000	-3.56556000
H	3.37108500	-3.08674000	-3.88537900
C	2.37210700	-1.99086400	-2.31192700
C	3.52720700	-1.85788100	-1.50125100
C	4.82027500	-2.56082600	-1.84985300
H	5.47389900	-2.63859600	-0.97124100
H	5.38265100	-2.02094600	-2.63137300
H	4.62910400	-3.57776700	-2.22304500
C	-4.54219100	-0.34654900	-0.17984700
C	-5.22558000	0.89304500	-0.06380300
C	-6.34387000	0.96206400	0.78471800
H	-6.88182700	1.90803900	0.88743900
C	-6.79213600	-0.15997000	1.48728300
H	-7.66984200	-0.08645100	2.13507800
C	-6.11544600	-1.37650400	1.35851000
H	-6.47226400	-2.25030200	1.90990800
C	-4.98433500	-1.49593500	0.53342500
C	4.53849600	-0.91040600	0.45582700
C	4.56292500	-1.63148000	1.68217200
C	5.67273200	-1.47888500	2.52855300
H	5.71202500	-2.03380900	3.46931200
C	6.72830800	-0.62492000	2.19335600
H	7.58345200	-0.51878000	2.86647400
C	6.67856900	0.10008700	1.00188300
H	7.49812300	0.78028900	0.75190400

C	5.59405200	-0.02179900	0.11431900
C	1.66214700	2.24999000	0.95991300
H	2.03184600	2.86021700	0.12733300
C	0.61875600	2.73114600	1.67869600
C	-0.07270800	4.05687000	1.40147300
H	-1.15968800	3.87094300	1.29024500
H	0.01845700	4.69955300	2.29970800
C	3.41356600	-2.56786100	2.05116100
H	2.51419400	-2.16357500	1.54825500
C	5.57550000	0.82199500	-1.16214800
H	4.68884200	0.52574500	-1.74506900
C	-4.73612800	2.13145000	-0.81279300
H	-4.17223200	1.78110500	-1.69290600
C	-4.25861500	-2.83261700	0.37707700
H	-3.22223400	-2.58956000	0.08080200
C	2.34380000	0.96100000	1.17073000
H	2.23262400	0.53871100	2.18237600
H	3.41161500	1.05280200	0.94217000
C	5.43765700	2.32763100	-0.84037400
H	6.30194600	2.68928600	-0.25834200
H	5.38710800	2.91680900	-1.77098700
H	4.52897400	2.53823600	-0.25697100
C	6.82698400	0.58499300	-2.03637500
H	7.74036800	0.94689900	-1.53529700
H	6.97431600	-0.48201300	-2.26329700
H	6.73626200	1.12937500	-2.99081100
C	3.13678200	-2.62285600	3.56469300
H	2.22093900	-3.20353000	3.76058400
H	3.95376700	-3.11796300	4.11631400
H	3.00443200	-1.61574100	3.99164600
C	3.64617100	-3.99133000	1.49685400
H	3.75577300	-3.98441300	0.40240200
H	4.55831800	-4.43592500	1.93031500
H	2.79467800	-4.64684600	1.74501400
C	-3.74397200	2.92573600	0.06443900
H	-3.35706700	3.80611500	-0.47494800
H	-4.23240400	3.27634300	0.98937200
H	-2.88936900	2.28768100	0.33947600
C	-5.87374300	3.03811400	-1.31930300
H	-6.60902600	2.47311000	-1.91410000
H	-6.41292000	3.52725400	-0.49116300
H	-5.46256000	3.83931600	-1.95453600
C	-4.20515800	-3.65986200	1.67541300
H	-3.55575500	-4.53872500	1.53279400
H	-3.80670300	-3.07557800	2.51853200
H	-5.20067800	-4.03694600	1.96446600

C	-4.87754300	-3.67771000	-0.75955700
H	-5.93062700	-3.91926800	-0.53578000
H	-4.84680800	-3.14883300	-1.72297900
H	-4.32677600	-4.62547100	-0.87873300
C	0.41793800	4.82176100	0.18993000
C	0.01450100	4.44708800	-1.10600400
C	1.29436500	5.91182200	0.32801700
C	0.46787400	5.14748600	-2.23013600
H	-0.65466600	3.59024300	-1.23021000
C	1.75035400	6.61668400	-0.79446700
H	1.62107500	6.21212000	1.32861900
C	1.33695900	6.23709900	-2.07755300
H	0.14226200	4.84175800	-3.22818500
H	2.42859900	7.46467100	-0.66540800
H	1.68955100	6.78647000	-2.95447100
C	0.05243400	1.90788900	2.81366300
H	-0.35249400	2.56580300	3.60419200
H	0.85972200	1.32440800	3.28192200
N	-0.97515100	0.32855400	1.08668500
C	-1.11150900	0.96716100	2.39931100
H	-2.03928200	1.55707200	2.29692300
N	-0.00188700	-0.08917200	0.40109500
Si	-1.53454700	-0.39571500	3.74953800
C	-3.41143900	-0.43596500	3.95407700
H	-3.93270300	-0.60781700	2.99917000
H	-3.71597300	-1.23224700	4.65375400
H	-3.77716500	0.52015000	4.36471300
C	-0.75128400	0.09653200	5.40484700
H	-1.03729700	-0.64271900	6.17234500
H	0.34866300	0.12026100	5.36199700
H	-1.10039300	1.08247600	5.75150200
C	-0.83663200	-2.05266700	3.17657100
H	0.24595900	-1.98044300	2.98570600
H	-0.99448000	-2.82691300	3.94545900
H	-1.31363500	-2.39318700	2.24473300



S5'

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

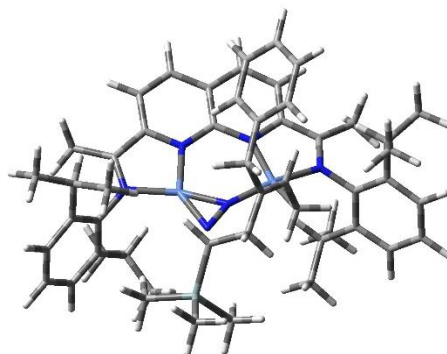
Sum of Electronic and Thermal Free Energies: -5617.987562

Ni	-1.54840800	-0.50066200	-0.36578300
Ni	1.69237800	-0.38482800	-0.07299900
N	-3.37086200	-0.74121600	-0.85685800
N	-1.14510200	-1.70962200	-1.72058800
N	1.18962800	-1.96819100	-1.26985500
N	3.42792600	-1.14068700	-0.13025500
C	-4.82032700	-1.66419900	-2.68522900
H	-5.21342400	-2.68125900	-2.51504500
H	-4.71280400	-1.53171900	-3.77285100
H	-5.57310500	-0.95224200	-2.32009400
C	-3.50023200	-1.45055100	-1.98818600
C	-2.28489800	-2.02843000	-2.47776200
C	-2.23193100	-2.94504600	-3.53070500
H	-3.12491700	-3.14983500	-4.12377200
C	-1.04789100	-3.63148300	-3.76304700
H	-0.98560000	-4.39920700	-4.53855000
C	0.09029300	-3.38488800	-2.96170200
C	0.05683800	-2.32550200	-1.95614500
C	1.26740600	-4.16181600	-3.09667600
H	1.28123800	-4.98715300	-3.81285900
C	2.36757800	-3.86518800	-2.31922600
H	3.28075100	-4.45516400	-2.41012900
C	2.34279300	-2.75907900	-1.45101600
C	3.51652400	-2.32059800	-0.79003700
C	4.78594400	-3.14286600	-0.82126800
H	5.49437000	-2.80323100	-0.05494100
H	5.29563600	-3.07548000	-1.79751500
H	4.56880500	-4.20633200	-0.63742900
C	-4.50644600	-0.27885300	-0.12931500
C	-4.77386700	1.11851200	-0.07532800

C	-5.87248300	1.56418100	0.67584000
H	-6.09212400	2.63372200	0.72107000
C	-6.69539000	0.66446400	1.36129000
H	-7.54805800	1.03051300	1.93946400
C	-6.41830100	-0.70317500	1.30857600
H	-7.05732100	-1.40098300	1.85715400
C	-5.33149400	-1.20495200	0.57071500
C	4.59476000	-0.63043700	0.53184100
C	4.67789300	-0.73948300	1.94885700
C	5.81799600	-0.23821200	2.59697300
H	5.90028500	-0.32404900	3.68336100
C	6.85094100	0.37269900	1.87947700
H	7.73022700	0.75808600	2.40281000
C	6.74883800	0.49471900	0.49337000
H	7.55412600	0.98271900	-0.06363400
C	5.63190400	0.00318700	-0.20664500
C	1.56712900	2.54253200	0.24453900
C	0.61914300	3.03623700	1.07493500
C	3.56449000	-1.42140500	2.74239600
H	2.63777900	-1.28598800	2.15281500
C	5.57534300	0.17824800	-1.72593500
H	4.64655000	-0.29500200	-2.08265700
C	-3.89965900	2.09576000	-0.85625800
H	-2.88578100	1.65610500	-0.87626100
C	-5.03679300	-2.70688100	0.59575600
H	-4.28485700	-2.91941300	-0.17942700
C	2.38952400	1.34485400	0.56040200
H	2.57719300	1.22401700	1.63891000
H	3.35936400	1.41476100	0.04758900
C	5.52180200	1.67017200	-2.12306300
H	6.43693200	2.19929800	-1.80867100
H	5.43170100	1.77509400	-3.21701400
H	4.66367300	2.18036400	-1.66145300
C	6.76873200	-0.50294300	-2.43347800
H	7.71959100	-0.00705100	-2.17584600
H	6.86291600	-1.56341800	-2.15595500
H	6.65024600	-0.44391800	-3.52806000
C	3.34499300	-0.80209200	4.13518400
H	2.45064000	-1.23927700	4.60822300
H	4.19232700	-0.99900300	4.81333900
H	3.20649200	0.28970100	4.07882500
C	3.81222200	-2.94172600	2.86386100
H	3.88291800	-3.41769300	1.87482300
H	4.75009900	-3.14305900	3.40907400
H	2.98703400	-3.42617100	3.41221100
C	-3.79858300	3.49071200	-0.21420200

H	-3.02306100	4.08396400	-0.72366100
H	-4.74582000	4.05095200	-0.29404400
H	-3.53272800	3.43188100	0.85362300
C	-4.37624600	2.21459700	-2.32169200
H	-4.36900200	1.23863000	-2.82953600
H	-5.40275700	2.61641000	-2.36617800
H	-3.71825400	2.89468900	-2.88751800
C	-4.41320000	-3.12564600	1.94576300
H	-4.17805400	-4.20306000	1.94578800
H	-3.47999500	-2.57454500	2.13806600
H	-5.10432200	-2.92681200	2.78186000
C	-6.28348600	-3.56204200	0.28546500
H	-7.04338200	-3.48007900	1.08019100
H	-6.75863500	-3.26043000	-0.66136400
H	-6.00610200	-4.62602000	0.20671900
C	0.21223300	2.34456400	2.34691900
H	-0.06229000	3.07730000	3.12567200
H	1.04462000	1.74774600	2.75293700
N	-0.93568200	0.59859500	0.93431500
C	-1.02496000	1.43951800	2.12922600
N	0.02942900	0.02223600	0.36383400
H	0.05114600	3.92637300	0.78585000
C	1.88957800	3.20475800	-1.09423700
H	1.83617600	2.42193600	-1.87383400
H	2.94986500	3.52063500	-1.06737800
C	1.03455100	4.38261800	-1.50585500
C	-0.08544800	4.20690500	-2.33876600
C	1.34298300	5.68470700	-1.06936400
C	-0.87188400	5.29931000	-2.72877600
H	-0.33503700	3.20126200	-2.69106400
C	0.55690700	6.77923600	-1.45181900
H	2.21321200	5.83868900	-0.42363800
C	-0.55389200	6.59007600	-2.28492100
H	-1.72924900	5.14388400	-3.38957600
H	0.81685100	7.78329900	-1.10516500
H	-1.16379800	7.44377000	-2.59202200
H	-1.91320900	2.06945900	1.94237700
Si	-1.49594100	0.31305400	3.66266800
C	-0.86932700	1.15374900	5.24209200
H	0.22682100	1.25709800	5.25467500
H	-1.30846900	2.15583200	5.37497700
H	-1.15749700	0.54911100	6.11876100
C	-0.67624900	-1.37553700	3.45238300
H	-1.02134200	-1.88365100	2.53807100
H	0.41920100	-1.28302300	3.38143900
H	-0.90600800	-2.02653700	4.31216700

C	-3.37756000	0.18288000	3.73268500
H	-3.80844800	-0.14533600	2.77403200
H	-3.69472100	-0.53412900	4.50795700
H	-3.82671900	1.15914100	3.97934500



S6

Charge: 0

Multiplicity: 1 (open shell)

Imaginary Frequencies: 1

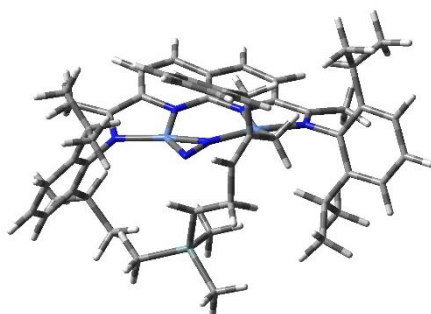
Sum of Electronic and Thermal Free Energies: -5617.957388

Ni	1.64679000	0.38598700	-0.47683300
Ni	-1.57044400	0.42478700	0.03131600
N	3.42947100	0.49445200	-1.14029900
N	1.11560000	0.79256300	-2.25171900
N	-1.22661200	1.04534200	-1.89870200
N	-3.30220900	1.12799800	-0.27229200
C	4.77189200	0.81341600	-3.23727000
H	4.77758800	1.76898000	-3.78679100
H	4.89316200	0.00879000	-3.98247500
H	5.64200000	0.79360700	-2.56844100
C	3.49043500	0.64765300	-2.46060300
C	2.20411700	0.71955900	-3.11885300
C	2.06205000	0.80083900	-4.51001700
H	2.93846400	0.71876700	-5.15487300
C	0.80072300	1.01033600	-5.04514500
H	0.65258500	1.10511100	-6.12390600
C	-0.31721100	1.14063800	-4.18886500
C	-0.15008400	0.97511800	-2.75223400
C	-1.60303900	1.44693200	-4.70177500
H	-1.73454800	1.56112200	-5.78065400
C	-2.65301600	1.62085100	-3.82517200
H	-3.64505100	1.88582100	-4.19349100
C	-2.45927500	1.41244200	-2.44618600
C	-3.53997800	1.56027700	-1.51824300

C	-4.83674600	2.21065000	-1.93825600
H	-5.43609800	2.48947800	-1.06239900
H	-5.44626900	1.52869700	-2.55649200
H	-4.65000600	3.11751000	-2.53350800
C	4.60962200	0.56428700	-0.33305100
C	5.47737800	-0.55860500	-0.23299900
C	6.61473300	-0.44101600	0.58133800
H	7.29951800	-1.28743800	0.67092200
C	6.89460100	0.74068500	1.27701900
H	7.78905200	0.80851900	1.90184600
C	6.02523900	1.82796800	1.17463300
H	6.24499900	2.74921100	1.72203400
C	4.87233200	1.76463200	0.37371200
C	-4.25970600	1.40973600	0.76487900
C	-3.98738200	2.50145400	1.63313200
C	-4.91009800	2.79150200	2.65054500
H	-4.72089600	3.63548200	3.31970500
C	-6.06326300	2.02026600	2.82469200
H	-6.76998600	2.26119000	3.62336700
C	-6.30182900	0.93376900	1.98116500
H	-7.19646700	0.32262100	2.13181700
C	-5.41365500	0.60215000	0.94149900
C	-1.89643000	-1.98035800	1.08602800
H	-2.51505900	-2.28161900	0.23093300
C	-0.99674300	-2.88751100	1.54375200
C	-0.75937700	-4.24039200	0.89083200
H	0.33164100	-4.34985700	0.72325800
H	-1.01430200	-5.03620000	1.61912500
C	-2.73548800	3.35875500	1.45384200
H	-2.06067900	2.80296500	0.77871400
C	-5.70713000	-0.61735400	0.06611700
H	-4.90259000	-0.69193100	-0.68375700
C	5.14335500	-1.86738800	-0.95027200
H	4.68673900	-1.60875900	-1.92080400
C	3.93524100	2.96685500	0.27190700
H	3.07007300	2.65427700	-0.33707500
C	-2.10387800	-0.61321000	1.59529300
H	-1.49369600	-0.35354800	2.47145800
H	-3.15753800	-0.37255200	1.78564300
C	-5.69522800	-1.92266600	0.89349900
H	-6.49748000	-1.91977300	1.65037000
H	-5.85537300	-2.79307600	0.23629500
H	-4.73725500	-2.06377500	1.41528400
C	-7.05122700	-0.48218800	-0.68431400
H	-7.89993800	-0.46829700	0.01974500
H	-7.09998400	0.44151200	-1.28072600

H	-7.19831600	-1.33751200	-1.36423000
C	-1.97856300	3.58455600	2.77673700
H	-1.03740800	4.12567000	2.58652700
H	-2.56499600	4.18625300	3.49120200
H	-1.72883900	2.62858700	3.26194100
C	-3.07554800	4.70289200	0.77357500
H	-3.56622400	4.54885600	-0.20032900
H	-3.75592800	5.30311300	1.40151800
H	-2.16015400	5.29346700	0.60273900
C	4.07809500	-2.65202000	-0.15199500
H	3.74750000	-3.54424800	-0.70924600
H	4.48717700	-2.98195100	0.81731000
H	3.19954000	-2.01773000	0.04481400
C	6.36661800	-2.75240100	-1.24708400
H	7.15013100	-2.20052400	-1.79097600
H	6.81400700	-3.15860300	-0.32471700
H	6.06462700	-3.61343200	-1.86486600
C	3.39034900	3.38906300	1.65149500
H	2.68792000	4.23198200	1.54333200
H	2.85387100	2.55774000	2.13392300
H	4.19855500	3.71193900	2.32863400
C	4.61370800	4.15204000	-0.44760200
H	5.48210900	4.52205600	0.12322400
H	4.97094400	3.86349300	-1.44888500
H	3.90638000	4.98964600	-0.56558700
C	-1.48352000	-4.50033700	-0.41279900
C	-1.02669900	-3.92563200	-1.61444100
C	-2.62874500	-5.31432300	-0.45521300
C	-1.69222900	-4.16249200	-2.82279700
H	-0.14403100	-3.27909600	-1.59610600
C	-3.29803100	-5.55575000	-1.66329700
H	-2.99729000	-5.76711200	0.47066000
C	-2.83062700	-4.98086100	-2.85162400
H	-1.32079600	-3.70778000	-3.74515600
H	-4.18337500	-6.19759800	-1.67556800
H	-3.34850300	-5.16997900	-3.79572400
C	-0.15288700	-2.62363500	2.78010600
H	0.02397300	-3.59769700	3.29399900
H	-0.73082000	-2.02300800	3.50384300
N	1.05412800	-0.12909600	1.24175900
C	1.19388400	-1.99510200	2.53418300
H	1.77114800	-2.43266900	1.71047000
N	0.13795300	0.14973700	0.48524000
Si	2.12092000	-1.13939400	3.92980800
C	3.79175000	-0.51961600	3.30956700
H	3.67577200	0.05689800	2.37918000

H	4.28133000	0.12812500	4.05507000
H	4.47684500	-1.35598600	3.09701000
C	2.39371300	-2.39159700	5.34270900
H	2.93194100	-1.91693100	6.18111900
H	1.43799300	-2.77493400	5.73668500
H	2.99104400	-3.25541700	5.00783900
C	1.07919400	0.29246500	4.60956400
H	0.10298100	-0.05418300	4.98696400
H	1.59782100	0.79161600	5.44512800
H	0.89317400	1.03899300	3.82210600



S6'

Charge: 0

Multiplicity: 1 (open shell)

Imaginary Frequencies: 1

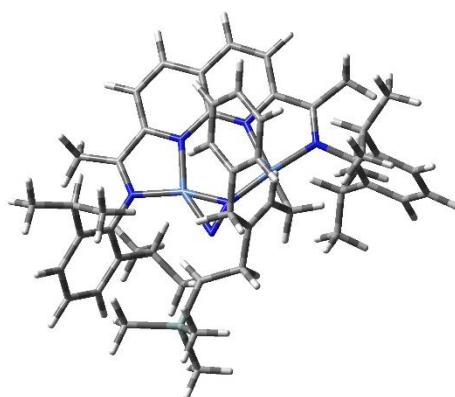
Sum of Electronic and Thermal Free Energies: -5617.948025

Ni	-1.62220300	-0.44931900	-0.51229400
Ni	1.61066500	-0.44442500	-0.21010500
N	-3.46859600	-0.76533300	-0.84248300
N	-1.31699900	-2.01885900	-1.49875000
N	1.00964700	-2.25541500	-1.05675700
N	3.30997100	-1.34393000	-0.08053100
C	-4.99818800	-2.00738200	-2.40428500
H	-5.34857200	-3.01580400	-2.12609700
H	-4.93961300	-1.97406100	-3.50457700
H	-5.75666000	-1.28413000	-2.07663600
C	-3.65712500	-1.68853000	-1.79414500
C	-2.46372500	-2.38499200	-2.20151700
C	-2.45362400	-3.42976300	-3.14105000
H	-3.35836500	-3.66949300	-3.70219600
C	-1.29665900	-4.16864600	-3.30841400
H	-1.26225700	-5.01741800	-3.99619400
C	-0.13309400	-3.84773100	-2.56220000
C	-0.13656800	-2.67890300	-1.69721300

C	1.03119800	-4.64618200	-2.62998800
H	1.03247500	-5.54262800	-3.25512900
C	2.14369400	-4.27448100	-1.90021800
H	3.05009400	-4.87945100	-1.92850100
C	2.12879400	-3.07484400	-1.16325300
C	3.33097200	-2.60006400	-0.53089500
C	4.53489700	-3.50628600	-0.41349900
H	5.29208700	-3.07578100	0.25253500
H	5.00782100	-3.67131500	-1.39644900
H	4.24380400	-4.49349200	-0.02182600
C	-4.57580100	-0.18480200	-0.15133900
C	-4.83394300	1.20480500	-0.31484000
C	-5.90057300	1.77650700	0.39537200
H	-6.11303400	2.84164600	0.27535300
C	-6.69423100	1.00943700	1.25366000
H	-7.51930500	1.47329600	1.80073400
C	-6.42061100	-0.35001700	1.41733100
H	-7.03299300	-0.94090100	2.10431800
C	-5.37113600	-0.97815900	0.72454900
C	4.50884300	-0.81898300	0.52308600
C	4.60312100	-0.78360400	1.94041400
C	5.77781200	-0.27531700	2.51849200
H	5.87117600	-0.24851300	3.60692100
C	6.82733800	0.20233600	1.72844100
H	7.73306900	0.59520000	2.19802500
C	6.70813300	0.18596700	0.33811500
H	7.52587800	0.57361200	-0.27631800
C	5.55673400	-0.31737700	-0.29372500
C	1.76513600	2.57576300	0.04023000
C	0.99813500	3.19249100	0.96860300
C	3.46963800	-1.31526400	2.81677100
H	2.54572000	-1.24806400	2.21299300
C	5.47986100	-0.30211000	-1.82232700
H	4.49955500	-0.71272000	-2.11352700
C	-3.98788700	2.03528700	-1.27381400
H	-2.99868900	1.54657400	-1.31051000
C	-5.08361400	-2.45799000	0.99087300
H	-4.34641100	-2.80337900	0.25000300
C	2.44560900	1.27775000	0.26102100
H	2.73227000	1.12937300	1.31433600
H	3.35549600	1.22643100	-0.35679900
C	5.56792200	1.13399200	-2.38466500
H	6.54298100	1.59500300	-2.15554100
H	5.45107600	1.12479100	-3.48085200
H	4.78371100	1.78151600	-1.96475900
C	6.57917100	-1.17987200	-2.46291700

H	7.58226000	-0.77036700	-2.25737200
H	6.55914700	-2.21164500	-2.08110600
H	6.45246100	-1.21685500	-3.55746300
C	3.25949400	-0.48649500	4.09830200
H	2.34591500	-0.81846800	4.61689500
H	4.09501000	-0.60641500	4.80802900
H	3.15688500	0.58751200	3.87649900
C	3.68032700	-2.80406800	3.17318100
H	3.74750200	-3.43260500	2.27301600
H	4.60961200	-2.93929500	3.75212900
H	2.84053000	-3.17705300	3.78235700
C	-3.77311700	3.48409700	-0.80366900
H	-3.03031500	3.98336500	-1.44531200
H	-4.70105400	4.07910500	-0.85290600
H	-3.39686500	3.51841400	0.23000800
C	-4.57896200	2.00293200	-2.70120900
H	-4.67008800	0.97220100	-3.07766100
H	-5.58263800	2.46083100	-2.72035900
H	-3.93560300	2.56240700	-3.40082400
C	-4.44076500	-2.65448600	2.38168900
H	-4.21229200	-3.71964800	2.55421100
H	-3.50333500	-2.08552800	2.46783800
H	-5.11851400	-2.31651100	3.18318800
C	-6.34182700	-3.34023500	0.84439200
H	-7.08767100	-3.11736200	1.62513600
H	-6.83039300	-3.19659300	-0.13224200
H	-6.07454600	-4.40538200	0.94166500
C	0.63268900	2.60274600	2.30771900
H	0.70897500	3.39286800	3.08801900
H	1.35128900	1.82062800	2.60514400
N	-0.85218200	1.08355800	0.29885800
C	-0.77871000	2.05780800	2.33407500
N	-0.03724300	0.25572500	-0.07737600
H	0.53269200	4.15292000	0.72207700
C	1.97535300	3.17109100	-1.35259900
H	1.59109800	2.43732700	-2.08701900
H	3.06473100	3.22998900	-1.54001400
C	1.35922400	4.52520100	-1.62611300
C	0.12022100	4.64059800	-2.28113700
C	2.01702900	5.70598800	-1.23261100
C	-0.44472000	5.89660500	-2.54078400
H	-0.40259100	3.73133300	-2.59280700
C	1.45555600	6.96352200	-1.48649200
H	2.98176700	5.63359800	-0.72077200
C	0.22143200	7.06323300	-2.14343700
H	-1.40512100	5.96450100	-3.05940200

H	1.98506000	7.86850600	-1.17558300
H	-0.21616100	8.04406800	-2.34757600
H	-1.53188600	2.75342100	1.94374100
Si	-1.37364400	0.76146200	3.55564500
C	-0.69796400	1.17388900	5.29051300
H	0.40360900	1.20796700	5.30210200
H	-1.06815100	2.15176400	5.63922900
H	-1.01717400	0.41217800	6.02251600
C	-0.74514500	-0.97088800	3.09283300
H	-1.10312900	-1.28204400	2.09737500
H	0.35644700	-0.99563500	3.05972600
H	-1.07593200	-1.72022100	3.83140000
C	-3.26397800	0.80428800	3.61572600
H	-3.71386300	0.61416500	2.62859500
H	-3.65947200	0.05102800	4.31679800
H	-3.61579900	1.79222700	3.95663000



S7

Charge: 0

Multiplicity: 1 (open shell)

Imaginary Frequencies: 0

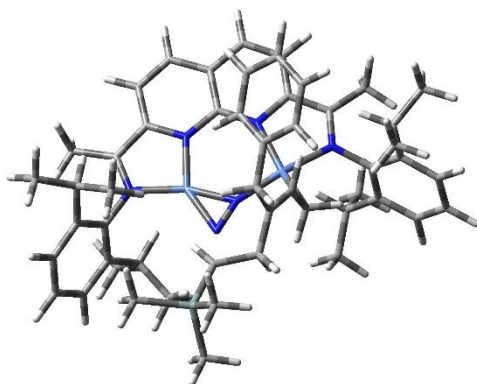
Sum of Electronic and Thermal Free Energies: -5617.969537

Ni	1.53226700	-1.20096500	-0.00528800
Ni	-1.59265700	-0.51617600	-0.35320400
N	3.27617800	-1.81134300	0.40627300
N	0.93673000	-2.49698500	1.22310800
N	-1.40137000	-2.17103000	0.92171500
N	-3.42919200	-1.01312000	-0.34681200
C	4.56050700	-3.46979100	1.78237700
H	4.48736600	-4.55972300	1.63418500
H	4.74210000	-3.29673700	2.85686300
H	5.43267900	-3.10200900	1.22611300
C	3.30445200	-2.78101100	1.31564600

C	1.99801400	-3.16814000	1.81630500
C	1.80467800	-4.13848700	2.81043400
H	2.66316800	-4.63977700	3.26061300
C	0.51282800	-4.44235600	3.20894900
H	0.32173400	-5.18971900	3.98322000
C	-0.58958300	-3.79652600	2.59699400
C	-0.35647800	-2.79638500	1.56901800
C	-1.92289900	-4.11456000	2.95391300
H	-2.10692100	-4.84635400	3.74449000
C	-2.96169700	-3.51503300	2.27166500
H	-3.99614600	-3.76177100	2.51334200
C	-2.69030800	-2.57142000	1.26129700
C	-3.76192100	-2.00383000	0.48069900
C	-5.15418100	-2.58269800	0.56804900
H	-5.79919200	-2.17585900	-0.21989100
H	-5.61969800	-2.34902100	1.54095800
H	-5.13264300	-3.67929900	0.46935500
C	4.46572100	-1.28695900	-0.18927900
C	5.30793200	-0.40930900	0.54911900
C	6.45286700	0.09550900	-0.08794200
H	7.11538000	0.77085700	0.45838400
C	6.76448700	-0.24853500	-1.40801400
H	7.66627000	0.15106900	-1.87938900
C	5.91216300	-1.09202700	-2.12332800
H	6.14989700	-1.34772500	-3.15999000
C	4.75109000	-1.62179100	-1.53622900
C	-4.38953500	-0.56102500	-1.32238600
C	-4.27754200	-1.07794600	-2.64078800
C	-5.21236700	-0.65992200	-3.60129700
H	-5.14786900	-1.05786300	-4.61796000
C	-6.21988800	0.25504400	-3.28212700
H	-6.94008200	0.56704400	-4.04318300
C	-6.29216400	0.78059500	-1.99070800
H	-7.06854300	1.51270700	-1.75081400
C	-5.38300700	0.39492600	-0.98858100
C	-1.59901400	2.18920300	-0.05040400
H	-2.21712200	2.06103900	0.84777500
C	-0.69040900	3.19829000	-0.00738200
C	-0.49980700	4.07786300	1.22449200
H	0.58502500	4.09577600	1.44992500
H	-0.74850200	5.12244800	0.95155000
C	-3.17989400	-2.07306800	-3.01583200
H	-2.47313100	-2.11206800	-2.16841200
C	-5.47993800	1.03123100	0.39843600
H	-4.65907600	0.62391000	1.01140600
C	4.91933100	0.05195200	1.95407700

H	4.39079400	-0.77880400	2.45045100
C	3.81621400	-2.51568800	-2.34715200
H	2.95495400	-2.75517300	-1.70123000
C	-1.87947400	1.24524700	-1.15260700
H	-1.23384800	1.37623600	-2.03312900
H	-2.93449100	1.26163700	-1.46098400
C	-5.29319600	2.56340100	0.32788400
H	-6.11378200	3.03857200	-0.23541600
H	-5.28691100	2.99358000	1.34245300
H	-4.34464900	2.83355400	-0.15918200
C	-6.81471400	0.69374900	1.10021200
H	-7.66996100	1.12107100	0.55044000
H	-6.97867400	-0.39178500	1.17767600
H	-6.82924900	1.11536200	2.11868400
C	-2.38171900	-1.61818500	-4.25409000
H	-1.55106000	-2.31632500	-4.44780100
H	-3.00956100	-1.59061200	-5.16024600
H	-1.95458800	-0.61466400	-4.10548200
C	-3.75410100	-3.49236400	-3.21570000
H	-4.28387700	-3.84392200	-2.31622100
H	-4.46877200	-3.51670000	-4.05584000
H	-2.94630300	-4.20945000	-3.43693900
C	3.91800500	1.22629500	1.85496400
H	3.54413800	1.51007300	2.85280500
H	4.40119600	2.10812800	1.40358400
H	3.05622500	0.95436400	1.22509500
C	6.11623600	0.42450500	2.84733400
H	6.85855800	-0.38840600	2.89691700
H	6.62940200	1.33268900	2.49055000
H	5.76881000	0.63316100	3.87210300
C	3.26722900	-1.77524100	-3.58441600
H	2.55615700	-2.41684800	-4.13113200
H	2.74250700	-0.85445900	-3.28718700
H	4.07507800	-1.50066700	-4.28315200
C	4.49404300	-3.84526600	-2.73976500
H	5.36212000	-3.67353000	-3.39828400
H	4.85125800	-4.39248900	-1.85272100
H	3.78658300	-4.49563700	-3.28060500
C	-1.26176500	3.69082400	2.47223700
C	-0.85069300	2.59167500	3.25204900
C	-2.38982400	4.41814100	2.89146400
C	-1.54357800	2.23386600	4.41429500
H	0.02091800	2.01062600	2.93616900
C	-3.08612400	4.06528700	4.05626800
H	-2.72219000	5.27608400	2.29857600
C	-2.66473200	2.97110600	4.82212500

H	-1.20544200	1.37904600	5.00662400
H	-3.95579100	4.65058400	4.36809500
H	-3.20300200	2.69619100	5.73318900
C	0.17247600	3.61700800	-1.19101800
H	-0.17263600	4.61541300	-1.52983600
H	-0.02748300	2.92751100	-2.03484200
N	1.11399400	0.21232100	-1.19492800
C	1.65649100	3.63510200	-0.93380100
H	2.05038800	2.70369900	-0.50496700
N	0.15641600	-0.28530100	-0.65004900
Si	2.83450000	4.95863400	-1.52453200
C	4.52789100	4.71951000	-0.70392600
H	4.93847000	3.72137400	-0.92749400
H	5.25253500	5.46832400	-1.06495700
H	4.45981300	4.81984200	0.39156800
C	2.15595800	6.68421900	-1.09864900
H	2.82845000	7.47177100	-1.47860300
H	1.16367800	6.85356100	-1.54844700
H	2.05839700	6.82051900	-0.00949200
C	3.04511500	4.86158700	-3.41580800
H	2.08001800	4.99153200	-3.93238600
H	3.72929200	5.64836000	-3.77724000
H	3.45740400	3.88555800	-3.71810000



S7

Charge: 0

Multiplicity: 3

Imaginary Frequencies: 0

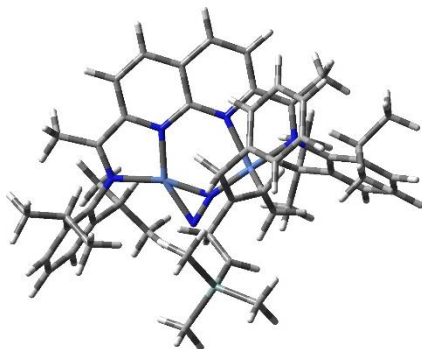
Sum of Electronic and Thermal Free Energies: -5617.970576

Ni	1.53235200	-1.20075800	-0.00560700
Ni	-1.59253800	-0.51579400	-0.35350000
N	3.27623400	-1.81098600	0.40641400
N	0.93675100	-2.49590100	1.22374300

N	-1.40133000	-2.16986600	0.92227400
N	-3.42891900	-1.01298700	-0.34743200
C	4.56043600	-3.46863400	1.78360200
H	4.48707600	-4.55867100	1.63631100
H	4.74218700	-3.29474000	2.85792800
H	5.43261300	-3.10145800	1.22694600
C	3.30445200	-2.77999500	1.31647100
C	1.99798400	-3.16663900	1.81746700
C	1.80460700	-4.13635700	2.81219500
H	2.66307500	-4.63730700	3.26279000
C	0.51271500	-4.44016300	3.21064000
H	0.32157100	-5.18719400	3.98522100
C	-0.58965100	-3.79479300	2.59815000
C	-0.35648500	-2.79507600	1.56977700
C	-1.92300900	-4.11291400	2.95488600
H	-2.10709000	-4.84440200	3.74573200
C	-2.96173500	-3.51388500	2.27212500
H	-3.99619500	-3.76078100	2.51359800
C	-2.69029900	-2.57045500	1.26157500
C	-3.76182500	-2.00314100	0.48073100
C	-5.15419600	-2.58169300	0.56841600
H	-5.79901600	-2.17543200	-0.21998400
H	-5.61984600	-2.34710100	1.54104100
H	-5.13284000	-3.67837900	0.47063900
C	4.46581600	-1.28729700	-0.18969600
C	5.30826500	-0.40921300	0.54790300
C	6.45322900	0.09487500	-0.08969100
H	7.11592700	0.77053800	0.45601800
C	6.76466100	-0.25032200	-1.40950400
H	7.66647100	0.14872300	-1.88129900
C	5.91211700	-1.09426000	-2.12403400
H	6.14971300	-1.35087400	-3.16050200
C	4.75099000	-1.62330100	-1.53639700
C	-4.38926000	-0.56100200	-1.32303300
C	-4.27727800	-1.07821400	-2.64132800
C	-5.21205800	-0.66035400	-3.60195000
H	-5.14756100	-1.05853000	-4.61852100
C	-6.21953500	0.25474300	-3.28301200
H	-6.93968600	0.56662000	-4.04415900
C	-6.29183700	0.78055100	-1.99170300
H	-7.06820400	1.51273100	-1.75197900
C	-5.38274500	0.39503600	-0.98945400
C	-1.59866800	2.18861600	-0.05055600
H	-2.21657300	2.05978800	0.84768100
C	-0.69018600	3.19785600	-0.00706100
C	-0.49918300	4.07632300	1.22559600

H	0.58556800	4.09361800	1.45125200
H	-0.74748600	5.12121800	0.95348600
C	-3.17972000	-2.07353200	-3.01611000
H	-2.47292000	-2.11226200	-2.16871700
C	-5.47981300	1.03161800	0.39743200
H	-4.65918300	0.62423300	1.01066800
C	4.91993300	0.05319300	1.95256800
H	4.39174500	-0.77726000	2.44982000
C	3.81586000	-2.51767700	-2.34649500
H	2.95462400	-2.75650000	-1.70029400
C	-1.87927000	1.24544100	-1.15333400
H	-1.23340700	1.37643000	-2.03365700
H	-2.93425800	1.26196500	-1.46178400
C	-5.29272100	2.56374000	0.32662700
H	-6.11305900	3.03895300	-0.23700000
H	-5.28662800	2.99411800	1.34111400
H	-4.34399000	2.83361000	-0.16022900
C	-6.81482000	0.69461000	1.09899200
H	-7.66984400	1.12213300	0.54903100
H	-6.97912500	-0.39086500	1.17653800
H	-6.82941200	1.11633700	2.11741500
C	-2.38161500	-1.61914900	-4.25459200
H	-1.55100200	-2.31739900	-4.44810100
H	-3.00951300	-1.59188000	-5.16072000
H	-1.95442000	-0.61559600	-4.10638700
C	-3.75405900	-3.49285600	-3.21541100
H	-4.28376400	-3.84404100	-2.31574300
H	-4.46882100	-3.51744200	-4.05546600
H	-2.94633900	-4.21008300	-3.43647400
C	3.91828400	1.22718500	1.85271500
H	3.54465800	1.51176500	2.85041800
H	4.40110400	2.10873100	1.40038300
H	3.05637200	0.95447100	1.22336800
C	6.11698700	0.42680900	2.84518400
H	6.85954600	-0.38585600	2.89523100
H	6.62979600	1.33484300	2.48750700
H	5.76978500	0.63621500	3.86987500
C	3.26687800	-1.77809700	-3.58428900
H	2.55559900	-2.41999200	-4.13039700
H	2.74239700	-0.85695400	-3.28775100
H	4.07471400	-1.50427700	-4.28333900
C	4.49336900	-3.84769100	-2.73815800
H	5.36139300	-3.67665000	-3.39692600
H	4.85058700	-4.39430000	-1.85073700
H	3.78570700	-4.49833600	-3.27840400
C	-1.26143900	3.68857300	2.47295400

C	-0.85074000	2.58880900	3.25210000
C	-2.38941400	4.41585000	2.89246900
C	-1.54390200	2.23038200	4.41399000
H	0.02078600	2.00775900	2.93598800
C	-3.08598000	4.06238400	4.05693100
H	-2.72149800	5.27425100	2.30008700
C	-2.66495500	2.96760400	4.82213100
H	-1.20606100	1.37508500	5.00579800
H	-3.95556700	4.64766800	4.36900700
H	-3.20343500	2.69220500	5.73292500
C	0.17181700	3.61764900	-1.19093000
H	-0.17339500	4.61647200	-1.52840300
H	-0.02905800	2.92912700	-2.03534200
N	1.11421600	0.21169700	-1.19622800
C	1.65593500	3.63516500	-0.93459500
H	2.05000200	2.70310300	-0.50735600
N	0.15658800	-0.28548900	-0.65105300
Si	2.83364300	4.95990200	-1.52323300
C	4.52740300	4.71951900	-0.70374600
H	4.93796000	3.72179400	-0.92917400
H	5.25181500	5.46899300	-1.06388300
H	4.45985200	4.81802600	0.39194300
C	2.15518200	6.68470100	-1.09405100
H	2.82760200	7.47292700	-1.47273200
H	1.16279800	6.85490000	-1.54329600
H	2.05790000	6.81901900	-0.00462100
C	3.04371100	4.86620600	-3.41474400
H	2.07851100	4.99703300	-3.93090400
H	3.72780500	5.65362000	-3.77493900
H	3.45597200	3.89072200	-3.71883600



S8

Charge: 0

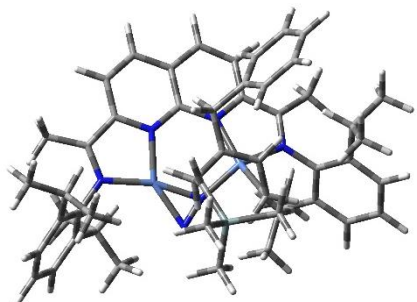
Multiplicity: 1 (open shell)

Imaginary Frequencies: 1**Sum of Electronic and Thermal Free Energies: -5617.968009**

Ni	2.05877000	-0.78582500	-0.02977400
Ni	-1.12751800	-0.80245400	-0.39052800
N	3.85543900	-0.72170700	0.56520500
N	1.63502500	-1.28193100	1.74330100
N	-0.70009800	-1.62629800	1.44500100
N	-2.79448000	-1.72219100	-0.15700100
C	5.33422800	-1.06143200	2.56299800
H	5.45119100	-2.01914900	3.09524800
H	5.43501800	-0.25564900	3.31044800
H	6.15771800	-0.96114100	1.84371000
C	4.00403700	-0.99580700	1.85859100
C	2.76435300	-1.28248700	2.55607400
C	2.69678400	-1.59345800	3.92164500
H	3.59896000	-1.56157000	4.53497500
C	1.47763300	-1.96224600	4.47014300
H	1.39385800	-2.23760800	5.52455800
C	0.32160100	-2.02083400	3.65464300
C	0.41202800	-1.62751800	2.25907400
C	-0.92423200	-2.47308200	4.15896500
H	-1.00266500	-2.76230900	5.21004000
C	-2.00106400	-2.57931200	3.30147300
H	-2.95719100	-2.96471000	3.65828900
C	-1.87987100	-2.16047500	1.96159200
C	-2.97690800	-2.28694700	1.03739800
C	-4.20543200	-3.08463700	1.40318500
H	-4.80817200	-3.29809100	0.51116600
H	-4.84356600	-2.53540400	2.11674200
H	-3.93056000	-4.04168400	1.87287900
C	4.96348600	-0.45684400	-0.29759000
C	5.66280500	0.77792000	-0.22724400
C	6.73011400	0.98621500	-1.11740100
H	7.27546700	1.93347700	-1.08327600
C	7.10561700	0.01302500	-2.04711900
H	7.94575300	0.19392600	-2.72275300
C	6.38797300	-1.18405000	-2.12079300
H	6.67012300	-1.93768200	-2.86171600
C	5.30690800	-1.43920200	-1.26316600
C	-3.72191200	-1.95915600	-1.22941100
C	-3.32252700	-2.88391500	-2.23522400
C	-4.19829700	-3.12865500	-3.30379500
H	-3.90909200	-3.84616400	-4.07678800
C	-5.42886300	-2.47185800	-3.39924600
H	-6.09652100	-2.67369600	-4.24110800

C	-5.79530200	-1.54944100	-2.41831800
H	-6.75260700	-1.02716600	-2.50319100
C	-4.96119200	-1.27134300	-1.31916300
C	-1.86807300	1.28372900	-0.50185500
H	-2.77798300	1.17441000	0.09760200
C	-0.95709100	2.23999000	-0.06633600
C	-1.05672900	2.86586200	1.31569400
H	-0.30843800	2.36207400	1.96063600
H	-0.72738600	3.91641900	1.24918000
C	-1.98677600	-3.62109700	-2.15350300
H	-1.39785000	-3.13431000	-1.35759700
C	-5.41381700	-0.23215200	-0.29248800
H	-4.64094500	-0.16873400	0.49133300
C	5.21623600	1.90628800	0.70197300
H	4.52407000	1.48122700	1.44613400
C	4.51220100	-2.73661400	-1.38705200
H	3.65838300	-2.65773800	-0.69187200
C	-1.76424200	0.48004500	-1.70731600
H	-1.00406900	0.76047600	-2.44389300
H	-2.69837000	0.13544800	-2.16317400
C	-5.54939700	1.16896900	-0.93057300
H	-6.34647400	1.18082000	-1.69275200
H	-5.80272400	1.91550300	-0.16063800
H	-4.61440500	1.48621200	-1.41554700
C	-6.74393900	-0.62888300	0.38713700
H	-7.57290200	-0.64338200	-0.33987100
H	-6.69007400	-1.62639100	0.84900000
H	-7.00252500	0.09981400	1.17256600
C	-1.17268800	-3.50376300	-3.45686900
H	-0.18842000	-3.98366400	-3.33298900
H	-1.67722900	-3.99610100	-4.30497600
H	-1.00241800	-2.44983000	-3.72447500
C	-2.19083800	-5.09829200	-1.75291100
H	-2.73001100	-5.18555600	-0.79623600
H	-2.77357600	-5.64077700	-2.51676300
H	-1.21875900	-5.60701600	-1.64314800
C	4.42121500	2.96111800	-0.10135300
H	4.04129700	3.75430700	0.56448200
H	5.05876000	3.43395000	-0.86680000
H	3.56564600	2.49719100	-0.61610100
C	6.38208900	2.55901600	1.47142700
H	6.96456500	1.81307200	2.03523900
H	7.07629100	3.08346200	0.79450400
H	5.99782800	3.30522400	2.18621900
C	3.92957000	-2.90902800	-2.80433900
H	3.31649400	-3.82413300	-2.85699800

H	3.29209000	-2.05164900	-3.06932300
H	4.72390800	-2.99585100	-3.56433900
C	5.35127600	-3.96092300	-0.96578400
H	6.22224900	-4.09576800	-1.62927600
H	5.72907800	-3.85438700	0.06367400
H	4.74587100	-4.88138500	-1.01386100
C	-2.40860900	2.81067600	1.99913400
C	-2.68192100	1.85810300	2.99652000
C	-3.41963200	3.72732500	1.65367500
C	-3.92797800	1.82584900	3.63891600
H	-1.90725100	1.13745900	3.27552200
C	-4.66377400	3.70133300	2.29467400
H	-3.22288300	4.46807500	0.87273100
C	-4.92208800	2.74954400	3.29218100
H	-4.11766400	1.08219700	4.41775600
H	-5.43194800	4.43005200	2.02119400
H	-5.89061900	2.73300000	3.79904300
C	0.18106400	2.73417200	-0.93524700
H	0.60264100	1.94151500	-1.57823000
H	1.00293600	3.12953300	-0.31538900
N	1.44680600	-0.27690800	-1.74817800
C	-0.52752200	3.81142300	-1.71578200
N	0.57434000	-0.65245500	-0.99699100
H	-1.26263300	3.41536000	-2.42877400
Si	-0.23465300	5.65484800	-1.69386300
C	-1.77590900	6.54022800	-2.35938800
H	-2.03478700	6.17828600	-3.36820100
H	-2.65081100	6.37262300	-1.71072400
H	-1.61106700	7.62835300	-2.42922500
C	1.24037300	6.07321300	-2.82654800
H	2.16228100	5.57791500	-2.48145200
H	1.05262200	5.74396700	-3.86116500
H	1.42536700	7.16120300	-2.84373900
C	0.17793500	6.30621100	0.04475200
H	-0.67832200	6.22370100	0.73345800
H	1.02938900	5.76969000	0.49488100
H	0.45650500	7.37227500	-0.00996600



S8'

Charge: 0

Multiplicity: 1 (open shell)

Imaginary Frequencies: 1

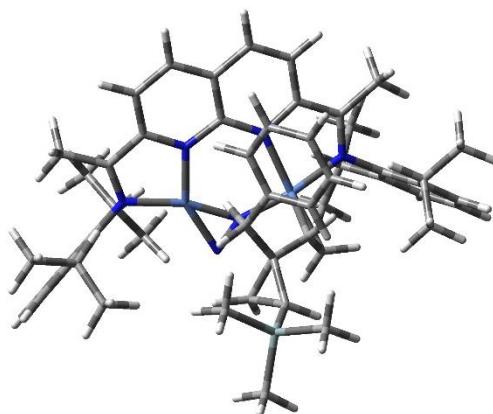
Sum of Electronic and Thermal Free Energies: -5617.966173

Ni	1.96224200	-0.78392600	-0.02907900
Ni	-1.18543900	-0.50532600	-0.29551800
N	3.73999800	-0.61162500	0.62211200
N	1.47381100	-0.96320300	1.80473300
N	-0.85077100	-1.32325500	1.49871500
N	-2.86695600	-1.49140600	-0.16782700
C	5.15277600	-0.67067300	2.69583800
H	5.25331600	-1.55728900	3.34253500
H	5.23072200	0.21896000	3.34405500
H	5.99870400	-0.65670100	1.99609100
C	3.84467200	-0.69602300	1.94757500
C	2.58715400	-0.89695300	2.63975900
C	2.48614100	-1.11743300	4.02156100
H	3.36871500	-1.01680500	4.65584400
C	1.26956300	-1.51196900	4.56145500
H	1.17292900	-1.73750500	5.62648500
C	0.14049200	-1.67162500	3.72102200
C	0.25410000	-1.30927000	2.32015000
C	-1.09240300	-2.19217400	4.19132100
H	-1.18532900	-2.47942600	5.24176800
C	-2.13751900	-2.37368800	3.30253100
H	-3.07275000	-2.82894600	3.63194500
C	-2.01263800	-1.93458700	1.97056800
C	-3.07583500	-2.07750100	1.01061300
C	-4.29971200	-2.90109200	1.33216400
H	-4.89076700	-3.08727000	0.42621100
H	-4.95027600	-2.38820600	2.06091800
H	-4.01696500	-3.87228800	1.76778900
C	4.87638400	-0.48082900	-0.23410900
C	5.60702600	0.73581600	-0.31066200

C	6.69926800	0.79934100	-1.19341700
H	7.26736500	1.73090900	-1.27000600
C	7.07094600	-0.29566800	-1.97667000
H	7.93047600	-0.22490000	-2.64843700
C	6.32420100	-1.47573700	-1.90971500
H	6.60423900	-2.32728300	-2.53631700
C	5.21809300	-1.59012100	-1.05475900
C	-3.79518900	-1.65717600	-1.24885500
C	-3.42996800	-2.55179600	-2.29393900
C	-4.30582700	-2.70619700	-3.37934900
H	-4.04156700	-3.40007800	-4.18234900
C	-5.50530600	-1.99182300	-3.45287400
H	-6.17356200	-2.12401900	-4.30794100
C	-5.84072900	-1.10285200	-2.43029600
H	-6.77506600	-0.53771800	-2.49524400
C	-5.00497500	-0.91323100	-1.31423500
C	-1.79934900	1.43528500	-0.43555200
H	-2.76488300	1.51010600	0.07216200
C	-0.65660300	1.86102600	0.26430300
C	-0.73392900	2.20707600	1.74803400
H	-0.29888700	1.36346100	2.31405100
H	-0.06427500	3.06350700	1.93958100
C	-2.13409400	-3.35818700	-2.23338100
H	-1.54088300	-2.95544100	-1.39739800
C	-5.42474900	0.08970100	-0.23839100
H	-4.64483200	0.09963100	0.54073100
C	5.18741800	1.99026100	0.45586900
H	4.40867500	1.70226500	1.18018700
C	4.40205300	-2.87954600	-1.01235400
H	3.49349500	-2.66004500	-0.42302100
C	-1.72459000	0.75680400	-1.70069600
H	-0.88779800	0.95369400	-2.37638300
H	-2.66069300	0.50510000	-2.20718400
C	-5.53586700	1.52187000	-0.80875300
H	-6.34857100	1.59120000	-1.55097000
H	-5.75270300	2.23990500	-0.00132900
H	-4.60544800	1.83758700	-1.30414800
C	-6.75839400	-0.30852100	0.43378500
H	-7.59140000	-0.27614100	-0.28804500
H	-6.72130900	-1.32579400	0.85187500
H	-6.99815100	0.39066700	1.25153200
C	-1.28470300	-3.19820700	-3.50983200
H	-0.33374500	-3.74438800	-3.40270900
H	-1.79921000	-3.59634100	-4.40046500
H	-1.04312300	-2.14088200	-3.69543300
C	-2.42146500	-4.84667000	-1.93753100

H	-2.99033800	-4.96963800	-1.00211100
H	-3.00884500	-5.30790600	-2.74958500
H	-1.47876500	-5.41012900	-1.83946300
C	4.55424100	3.01843000	-0.50895000
H	4.19043500	3.90098100	0.04312600
H	5.29011200	3.36269200	-1.25469800
H	3.70420900	2.57943100	-1.05297600
C	6.34890700	2.62649400	1.24782900
H	6.81506700	1.90527400	1.93745800
H	7.13806700	3.00423200	0.57699700
H	5.98560200	3.48209700	1.84082000
C	3.93720200	-3.31754300	-2.41466500
H	3.30199600	-4.21594100	-2.34098800
H	3.35015900	-2.52096200	-2.89655400
H	4.78745200	-3.56670400	-3.07126700
C	5.16898000	-4.00783300	-0.29122000
H	6.09153100	-4.27164300	-0.83585200
H	5.45747700	-3.70954300	0.72934800
H	4.54736900	-4.91590500	-0.21854300
C	-2.10777800	2.52495000	2.30628000
C	-2.77917500	1.61955600	3.14615500
C	-2.73136700	3.75167700	2.00704300
C	-4.03909100	1.93146800	3.67772900
H	-2.30611300	0.66387600	3.39071200
C	-3.98781700	4.06695500	2.53648100
H	-2.22078100	4.46294200	1.35048200
C	-4.64698800	3.15629900	3.37567800
H	-4.54178400	1.21763600	4.33613100
H	-4.45247400	5.02796100	2.29922200
H	-5.62579900	3.40408600	3.79487900
C	0.63591800	2.27347900	-0.42301500
H	0.78774400	1.73948300	-1.37063100
H	1.49838000	2.03165900	0.22634900
N	1.40062300	-0.64585100	-1.84038100
C	0.47289800	3.75498500	-0.64783900
N	0.49963400	-0.83699100	-1.06176600
H	0.56322900	4.37768300	0.25346800
Si	0.05039200	4.60908100	-2.25794700
C	-1.82885300	4.78391100	-2.50575800
H	-2.05024600	5.29260200	-3.45974600
H	-2.31935200	3.79790900	-2.52218300
H	-2.28616400	5.37279600	-1.69428400
C	0.77007400	3.64344100	-3.72368200
H	0.34716300	2.62852900	-3.79883500
H	0.54881400	4.16188400	-4.67170600
H	1.86423000	3.54269400	-3.64260100

C	0.80730000	6.35086600	-2.19732000
H	0.56232000	6.91799600	-3.11094700
H	0.42236900	6.92420300	-1.33756000
H	1.90481300	6.30980300	-2.10951700



S9

Charge: 0

Multiplicity: 1

Imaginary Frequencies: 0

Sum of Electronic and Thermal Free Energies: -5617.997323

Ni	1.83038900	-0.95522900	-0.07034800
Ni	-1.35351700	-0.79817000	-0.37912600
N	3.65586600	-0.83754000	0.44905400
N	1.45218000	-0.91512100	1.78472000
N	-0.92224000	-1.05695900	1.63503800
N	-3.07172100	-1.46604400	0.16127500
C	5.18504200	-0.86801700	2.43586400
H	5.22806400	-1.69044300	3.16807200
H	5.39423000	0.06801900	2.98187100
H	5.98322600	-1.01622100	1.69684500
C	3.83897700	-0.81941400	1.76232300
C	2.60873600	-0.80317600	2.54164500
C	2.58402200	-0.75704700	3.94238900
H	3.51300300	-0.65026800	4.50473700
C	1.36658500	-0.88981200	4.59411600
H	1.31132100	-0.90873000	5.68570800
C	0.17575800	-1.04342400	3.84874300
C	0.22483400	-0.99692200	2.39855900
C	-1.07508900	-1.26022100	4.48469100
H	-1.12469000	-1.28589200	5.57609400
C	-2.19019200	-1.46637600	3.70834900

H	-3.15430100	-1.67647900	4.17264400
C	-2.10909900	-1.36916700	2.29898000
C	-3.26623600	-1.58760000	1.48274000
C	-4.57746400	-2.02199700	2.09639500
H	-5.28680300	-2.32687600	1.31657800
H	-5.04532800	-1.21541400	2.68574400
H	-4.42950400	-2.88063000	2.77103600
C	4.74536700	-0.92411900	-0.47493900
C	5.58060900	0.19665300	-0.72620800
C	6.62025700	0.05097200	-1.66113900
H	7.26959200	0.90565600	-1.87144000
C	6.83758600	-1.15589500	-2.32966800
H	7.65846300	-1.24775600	-3.04568100
C	5.98623600	-2.23890200	-2.09151800
H	6.14537800	-3.17806500	-2.62879100
C	4.92675100	-2.14587200	-1.17658200
C	-4.13619000	-1.75423400	-0.75799900
C	-4.03245900	-2.96051500	-1.50710900
C	-5.03529500	-3.26000900	-2.44223300
H	-4.96833800	-4.18904500	-3.01584200
C	-6.11126600	-2.39445000	-2.65646800
H	-6.88023900	-2.64227000	-3.39300800
C	-6.19367700	-1.20726200	-1.92693100
H	-7.03263600	-0.52758400	-2.10232200
C	-5.22429000	-0.86119800	-0.96763100
C	-1.64745900	1.11106700	-1.00271100
H	-2.49486500	1.42690400	-0.38123300
C	-0.50992000	2.09151700	-0.98930900
C	0.08937800	2.36282300	0.39039600
H	0.53954200	1.41392700	0.73594400
H	0.93229800	3.06759300	0.27874800
C	-2.86980800	-3.93193700	-1.30922700
H	-2.18956900	-3.47982100	-0.57043900
C	-5.37907300	0.46211200	-0.21410600
H	-4.53649900	0.55349900	0.49106300
C	5.32657000	1.56323700	-0.08997600
H	4.55735500	1.43959800	0.68891600
C	3.99568600	-3.33356100	-0.94573200
H	3.14882000	-2.96101400	-0.34070000
C	-1.91185100	0.16839400	-2.02583300
H	-1.19802300	0.03700700	-2.84421900
H	-2.94050300	-0.11562300	-2.26411400
C	-5.32316200	1.67313300	-1.17322300
H	-6.16881900	1.65713300	-1.88078800
H	-5.38192200	2.61513800	-0.60342600
H	-4.39296300	1.68492800	-1.75981900

C	-6.69026700	0.51028300	0.60384600
H	-7.57126900	0.49693500	-0.05913300
H	-6.77985600	-0.34291500	1.29239800
H	-6.73629600	1.43711100	1.19905800
C	-2.06634200	-4.12893700	-2.61135100
H	-1.21181600	-4.80291300	-2.43591100
H	-2.68521100	-4.57207300	-3.40945700
H	-1.67004300	-3.16983900	-2.97813700
C	-3.35322700	-5.28313300	-0.73988300
H	-3.89753900	-5.14831100	0.20837400
H	-4.02867200	-5.79880400	-1.44325300
H	-2.49557700	-5.94941600	-0.54921700
C	4.75325400	2.54014800	-1.14146200
H	4.50769500	3.51074400	-0.67887900
H	5.48097800	2.72320500	-1.94940400
H	3.84005200	2.13041600	-1.60000400
C	6.58318300	2.15649000	0.58069600
H	7.00760000	1.46979800	1.32994300
H	7.37266600	2.37290700	-0.15772500
H	6.33719300	3.10506200	1.08589500
C	3.40424600	-3.87093800	-2.26319600
H	2.69621100	-4.69011800	-2.05503500
H	2.86132700	-3.07669900	-2.79772900
H	4.18460300	-4.26946300	-2.93270100
C	4.69494100	-4.44903700	-0.14074500
H	5.55205400	-4.86275000	-0.69872500
H	5.07429400	-4.07355000	0.82311000
H	3.99510300	-5.27562500	0.06655900
C	-0.83291400	2.89165200	1.47813600
C	-0.48983800	2.68875400	2.82916200
C	-2.00265400	3.62151700	1.19818300
C	-1.27686100	3.20654500	3.86411200
H	0.40956100	2.11317000	3.06913200
C	-2.79754800	4.13814500	2.23199200
H	-2.29539000	3.78446900	0.15865100
C	-2.43686400	3.93627200	3.56966400
H	-0.98653500	3.03456800	4.90429600
H	-3.70244400	4.70216000	1.98817700
H	-3.05535700	4.33980200	4.37580600
C	0.44366900	2.14200500	-2.15826100
H	0.36176600	1.40041800	-2.95380700
H	1.47794700	2.41135300	-1.92451800
N	1.21079100	-0.96421000	-1.83581900
C	-0.61628000	3.23307700	-2.04914200
N	0.32023900	-1.11411100	-1.02706200
H	-1.46049200	3.05264900	-2.73040600

Si	-0.19080100	5.07808100	-2.00107300
C	-1.75403600	6.11414300	-1.70242500
H	-2.56477200	5.82622100	-2.39216300
H	-2.12939900	6.00594400	-0.67271200
H	-1.54406100	7.18433500	-1.86775900
C	0.48070400	5.50271200	-3.72712300
H	1.39438500	4.92922000	-3.95296000
H	-0.25853200	5.27130900	-4.51175100
H	0.72691000	6.57501000	-3.80594600
C	1.11737100	5.54882300	-0.71019800
H	0.75119900	5.40915900	0.31914700
H	2.04820500	4.97081000	-0.82932500
H	1.37779300	6.61456600	-0.82815000

Reference

¹Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.