

ONO³⁻ AND OCO³⁻ TRIANIONIC Pincer AND Pincer TYPE LIGAND SYNTHESIS
AND APPLICATION TO NEW SULFIDE TUNGSTEN COMPLEX

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LIST OF ABBREVIATIONS

Bn	Benzyl
BOC	tert-butyloxycarbonyl
DMF	Dimethylformamide
CDCl ₃	Deuterated chloroform
Equiv	Equivalent
Et	Ethyl
GPC	Gel permeation chromatography
HMBC	Heteronuclear multiple bond coherence
HSQC	Heteronuclear single quantum correlation
ⁱ Pr	Isopropyl
IR	Infrared
Me	Methyl
MeOD	Deuterated Methanol
mg	Milligram
min	Minute
mL	Milliliter
mmol	Millimol
M _n	Number average molecular weight
M _w	Weight average molecular weight
NBS	N-Bromosuccinimide
NMR	Nuclear Magnetic Resonance
OCO ³⁻	Trianionic donor ligand with two oxygen donor atoms and one central carbon donor atom. For this thesis, [^t BuOCO] ³⁻ , or 3,3'-di-tert-butyl-1,1':3',1'-terphenyl-2,2'-dioxide
ONO ³⁻	Trianionic donor ligand with two oxygen donor atoms and one central nitrogen donor atom. For this thesis, [pyr-ONO] ³⁻ , or 6,6'-(1H-pyrrole-2,5-diyl)bis(2-(tert-butyl)phenoxy)
Ph	Phenyl
ppm	Part(s) per million
pyr	pyrrole
^t Bu	tert-butyl
THF	Tetrahydrofuran

ABSTRACT

Trianionic pincer ligands mark an important development in organometallic chemistry. Their relatively recent discovery has opened a number of possibilities related to their unique structure. The most notable advantage of these ligands is the catalytic ability and high kinetic stability attributed to their rigid tridentate conformation. Two specific examples of trianionic pincer and pincer-type ligands were synthesized and new reactions involving these ligands were explored. An ONO^{3-} trianionic pincer type ligand specific to the Veige group was synthesized according to existing methods and attempts were made to form several new metal complexes with IrCl_3 , FeCl_3 , and $\text{RuCl}_2(\text{PPh}_3)_3$. However, none of these attempts produced successful results. An OCO^{3-} pincer ligand was also synthesized and successfully formed a tungsten metal complex known as Sarkar's catalyst. This complex was used in a successful reaction with CS_2 , which led to a new complex with catalytic abilities. Upon heating, the formation of an addition sulfide complex through the loss of a CS fragment was detected. Analysis and characterization of these structures were performed via multidimensional NMR, IR, and mass spectroscopy. A crystal structure of the second sulfide complex was obtained via single crystal X-ray diffraction. The catalytic abilities of the sulfide complex prior to heating were explored through the catalyzed polymerization of norbornene. The resulting polymer was determined to be a highly *cis-syndiotactic* cyclic polynorbornene through ^1H NMR and GPC analysis.

CHAPTER 1

INTRODUCTION

The advancement and evolution of modern organometallic chemistry is largely influenced by the design of new ligands that manipulate the electronic and geometric structures of transition metal complexes.¹ Among the numerous variations of ligands, one of weighted significance is the pincer ligand. First appearing in the literature by Moulton and Shaw in 1976,² the pincer ligand is broadly defined as a ligand containing three donor atoms bound to adjacent coplanar sites in the meridional plane.³ Specific examples of these structures are referred to with the three donor atoms in their corresponding order such that the central donor atom takes the middle position in the name. For example, the pincer ligand in the complex depicted in **Figure 1** is referred to as a PCP pincer ligand. Ligands containing a heteroatom in the central position of the backbone are provided the label “pincer-type.”³

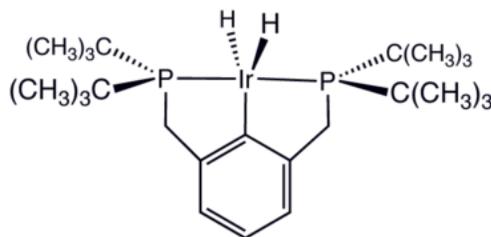


Figure 1. Iridium complex supported by monoanionic PCP pincer ligand.⁴

There are a number of advantages related to pincer ligands. Most pincer ligands hold a rigid conformation that provides structural control of the coordination sphere by retaining the donor groups in a predictable arrangement.⁵ This rigidity makes these structures ideal for asymmetric catalysis because the prevention of rotation in the wingtip groups allows specific substituents to be directed into the active site of the catalyst. Due to these same structural

reasons, pincer ligands, which involve tridentate coordination, allow the stable binding of ligands which otherwise might be labile. For example, groups such as an aryl or a pyridine which would easily be lost as monodentate ligands are able to form stable complexes, especially if bound to the central donor atom.⁵ The strong binding of pincer ligands to metal centers causes a further advantage of forming highly stable complexes that do not decompose until after being heated above 100°C, which is especially helpful in catalytic reactions performed at high temperatures.⁵ A major factor in this kinetic stability is the chelate effect associated with the ligand's structural arrangement.

A special type of pincer ligand, the trianionic pincer ligand, contains three anionic donors. This ligand was reported in the literature near the turn of the century, such as an NNN³⁻ by Shrock in 1996^{6,7}, even though the term 'trianionic pincer' was not found in literature prior to 2007.⁸ Previously, pincer and pincer-type ligands had been limited to complexes involving metal ions in low oxidation states. However, with the emergence of multi-anionic pincer ligands with electronically stabilizing properties, such as the trianionic one previously mentioned, applications involving metal ions in high oxidation states have begun to be explored.³

One application of trianionic pincer and pincer-type ligands is the possible improvement of tungsten catalyzed alkyne cross metathesis.⁹ This chemical process can be limited by the cycloaddition energy barrier associated with it, and thus improvements are possible if this energy barrier is able to be minimized. One method of achieving this outcome was explored by Jia and Lin whose theoretical calculations showed that a locked T-shaped geometry of ancillary ligands would lower the relative transition state barrier by ~24 kcal/mol.¹⁰ The rigid tridentate structure of trianionic pincer ligands helps to achieve this outcome by locking the supporting anionic

donors in the desired T-shaped geometry, thus lowering the required activation energy and providing easier access for the alkyne.⁹

This thesis focuses on two specific examples of trianionic pincer and pincer-type ligands, ONO^{3-} and OCO^{3-} , and their application to several reactions. Both ligands were originally synthesized and studied in the Veige laboratory for various applications, and this thesis expands upon this research. According to preceding literature,³ OCO^{3-} complexes have successfully been formed with a variety of different transition metals including titanium, zirconium, tantalum, chromium, and molybdenum. The research specific to this thesis focuses on OCO^{3-} tungsten complexes. ONO^{3-} ligands have also formed complexes with transition metals such as titanium, tantalum, and tungsten, to name a few.³ This thesis explores attempts to expand the selection of transition metal complexes made with the specific ONO^{3-} ligand studied in the Veige group.

CHAPTER 2

SYNTHESIS OF ONO^{3-} TRIANIONIC PINCER-TYPE LIGAND

Results and Discussion

The first compound that was synthesized was a pyrrolide-centered ONO^{3-} trianionic pincer-type ligand (2-2). This ligand was synthesized through a series of steps according to the literature⁹ and analysis was performed via ^1H NMR (**Figures A-1, A-2**). Synthesis began with a coupling reaction using a palladium catalyst to form compound 2-1, followed by the deprotection of the compound to produce 2-2 (**Figure 3-1**). Percent yields for the reactions involved (included in the experimental syntheses below) were lower than those found in the literature, but not by more than 11%. ^1H NMR spectral assignments were consistent with literature reports (**Figure A-2**).⁹

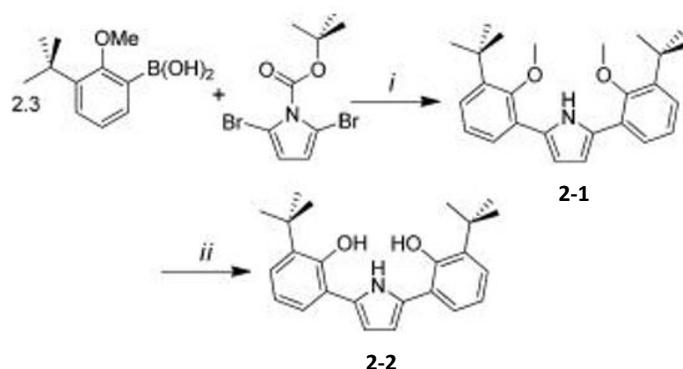


Figure 3-1. Synthesis of [pyr-ONO]Me₂ (2-1) and [pyr-ONO]H₃ (2-2).

Legend: (i) 10% Pd(PPh₃)₄, 8 Na₂CO₃, 3 KCl, toluene, EtOH, and H₂O, HCl/dioxane;

(ii) KOtBu, [HSCH₂CH₂NHMe₂]Cl, and DMF, HCl.

Following the synthesis of compound 2-2, several attempts were made to utilize it in the formation of new and unexplored metal complexes. According to literature, compound 2-2 had previously been combined with TiCl₄ and ZrBn₄ to successfully synthesize new titanium and zirconium metal complexes.¹¹ Using a similar method as described in the literature, attempts

were made to produce new complexes through the reaction of compound 2-2 with IrCl_3 , FeCl_3 , and $\text{RuCl}_2(\text{PPh}_3)_3$. The results were analyzed via ^1H NMR and ^{31}P NMR to monitor any changes in structure, however, none of these attempts produced new stable complexes (**Figures A-3 through A-6**). Factors such as the addition of heat or a base in the form of lutidine were explored without success. When combining 2-2 with IrCl_3 , for instance, the only change detected via NMR was the deuteration of the backbone of the pyrrole in the ligand, as seen in the disappearance of one of the resonance peaks (**Figure A-3**). The combination with FeCl_3 produced data that was equally inconclusive. The $\text{RuCl}_2(\text{PPh}_3)_3$ and 2-2 mixture was analyzed by ^1H NMR and ^{31}P NMR. The mixture was heated for 12 hr at 60°C in an attempt to induce change, but none occurred (**Figure A-5**).

Synthesis of 2,5-bis(3-(tert-butyl)-2-methoxyphenyl)-1H-pyrrole, [pyr-ONO]Me₂ (2-1).

Inside a nitrogen-filled glove box, a 50 mL toluene solution was prepared containing 3.799g (2.3 equiv.) (3-(tert-butyl)-2-methoxyphenyl)boronic acid, 0.916g (0.10 equiv.) tetrakis(triphenylphosphine)-palladium(0), 6.679g (7.9 equiv.) Na_2CO_3 , 1.773g (3 equiv.) KCl , and 2.579g (1 equiv.) tert-butyl -2,5-dibromo-1H-pyrrole-1-carboxylate. The reaction flask was then secured with a Liebig condenser and Y-adapter before it was removed from the glove box and attached to an argon Schlenk line. Under argon counter pressure, 50 mL of degassed ethanol-water (2:1) solution was added to the reaction flask. The mixture was heated at 96°C with stirring for about 20 h, during which the solution changed in color from yellow to an orange-red. After being allowed to cool, all volatiles were removed from the reaction mixture under reduced pressure. The oily residue that remained was dissolved in CH_2Cl_2 and washed with water and brine. The organic layer was then dried with MgSO_4 , and after gravity filtration, the solvent was removed under reduced pressure. 20 mL of hexanes was added to the residue to precipitate a

white solid and the mixture was stirred for 0.5 h before filtering off the white solid. Volatiles of the collected filtrate was removed under vacuum to yield an orange oil containing the BOC protected pyrrole. The BOC protecting group was removed by stirring the residue with 10 mL of 4 M HCl in 1,4-dioxane at 45 °C for 18 h. The solvent of the resulting solution was removed under reduced pressure. The residue was then dissolved in CH₂Cl₂, washed with a saturated solution of Na₂CO₃, and then washed again with water. The organic layer was dried with MgSO₄ before removing the solvent under reduced pressure. The resulting purple oily residue was dissolved in minimal 2-propanol (5 mL). The product, 2,5-bis(3-(tert-butyl)-2-methoxyphenyl)-1H-pyrrole, precipitated upon cooling the solution. (Yield = 0.971 g, 36.2%).

Synthesis of 6,6'-(1H-pyrrole-2,5-diyl)bis(2-(tert-butyl)phenol), [pyr-ONO]H₃ (2-2).

Inside a nitrogen-filled glove box, a 250 mL two-neck flask with a stir bar, condenser, and Y-adaptor was charged with 0.842g 2-(diethylamino)ethanethiol hydrochloride (2.4 equiv) and 1.199g NaOtBu (5.0 equiv). The apparatus was removed from the glovebox, then attached to a Schlenk line and cooled with an ice-water bath. Anhydrous DMF (10 mL) which had also been cooled in an ice-water bath was added to the reaction flask. Following 5 min of stirring, the reaction mixture was allowed to warm to room temperature. After stirring for additional 15 min, 0.971g of 2,5-bis(3-(tert-butyl)-2-ethoxyphenyl)-1H-pyrrole (1.0 equiv) was added under counter argon flow, and the reaction mixture was refluxed for 3 h. The reaction mixture was allowed to cool to ambient temperature and then placed in an ice water bath. Under counter argon flow, the mixture was neutralized by acidifying with 1 M HCl and then was diluted with water (25 mL). The aqueous phase was extracted with ethyl acetate (3 x 25 mL), then the combined organic extracts were washed with water (3 x 10 mL) and saturated brine solution (10 mL) and then dried

over MgSO_4 . All volatiles were removed under vacuum resulting in a brown oil.

Recrystallization in cold pentane produced a beige powder (Yield = 0.393 g, 42.85%).

Procedure for attempted synthesis of iridium complex

Inside a nitrogen-filled glove box, a J-Young NMR tube was charged with 0.015g of $[\text{pyr-ONO}]\text{H}_3$ (1 equiv) and deuterated methanol (MeOD) and frozen at -35°C . Then 0.01232g IrCl_3 (1 equiv) was dissolved in MeOD and the two solutions were combined. Two drops of lutidine were added to act as a base, and a precipitate formed. After this, the precipitate was filtered off. Results were analyzed via ^1H NMR. No changes in the complex structure were detected.

In a second attempt in the glove box, a J-Young NMR tube was charged with 0.015g of $[\text{pyr-ONO}]\text{H}_3$ (1 equiv) and CDCl_3 and frozen at -35°C . Then 0.0207g of Lithium bis(trimethylsilyl)amide (3 equiv) in CDCl_3 was added. The mixture was then taken out of the glove box where 0.01232g iridium (III) chloride hydrate was added. When this occurred, the reaction turned green for a couple seconds and then turned into a brown slurry.

Procedure for attempted synthesis of iron complex

Inside a nitrogen-filled glove box, a J-Young NMR tube was charged with 0.015g of $[\text{pyr-ONO}]\text{H}_3$ (1 equiv) and THF. After being frozen at -35°C , 0.0207g of Lithium bis(trimethylsilyl)amide (3 equiv) in THF was added to make a green solution. Then, 0.0074 g of FeCl_3 (1 equiv) was added at -35°C , making a dark purple solution.

Procedure for attempted synthesis of ruthenium complex

Inside a nitrogen-filled glove box, a J-Young NMR tube was charged with 0.01181g of $[\text{pyr-ONO}]\text{H}_3$ (1 equiv) and THF and frozen at -35°C . 0.031g $\text{RuCl}_2(\text{PPh}_3)_3$ (1 equiv) was dissolved in THF and the two solutions were combined.

CHAPTER 3
SYNTHESIS OF OCO^{3-} TRIANIONIC LIGAND AND COMPLEX

Results and Discussion

Another focus of the trianionic pincer ligand research covered in this thesis involves OCO^{3-} ligand (3-4) synthesis and its application to forming a tungsten complex (3-6) with catalytic abilities. Synthesis of the OCO^{3-} ligand and its corresponding tungsten complex, referred to as Sarkar's catalyst was performed according to the literature.¹² The synthetic process was initiated with a bromination reaction using NBS to form complex 3-1, which was then given a protecting group to form 3-2 (**Figures 3-1, B-1**). This was followed with a palladium-catalyzed coupling with 1,3 dibromobenzene to form 3-3. The desired OCO^{3-} ligand (3-4) was then obtained after the deprotection of 3-3 (**Figures 3-2, B-2**). The trianionic ligand $[\text{tBuOCO}]_3\text{H}_3$ (3-4) that was synthesized was utilized in the formation of a tungsten metal complex (3-6) with the compound known as Shrock's catalyst 3-5 (**Figures B-3, 3-3**). The complex 3-6 was determined to be successfully synthesized through the comparison of experimental ^1H NMR spectra to the literature (**Figures B-4**). This tungsten complex was then used to explore reactions with CS_2 (See Chapter 4) and the resultant complex's ability to catalyze norbornene polymerization (See Chapter 5).

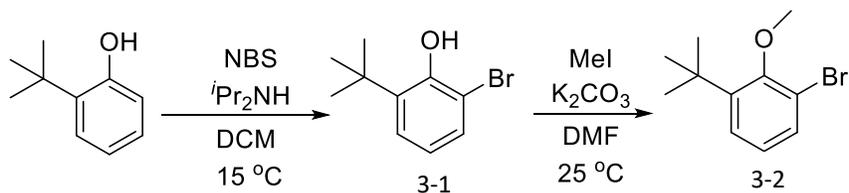


Figure 3-1. Synthesis of 2-bromo-6-tert-butylphenol (3-1) and 2-bromomethoxyphenol (3-2).

Synthesis of 2-bromo-6-tert-butylphenol (3-1).

In a 500mL round bottom flask attached to an argon Schlenk line, 20.1 mL 2-tert-butylphenol (1 equiv.) and 1.8 mL diisopropylamine (1 equiv.) were added to 150 mL oxygen-free CH_2Cl_2 under an argon counter pressure. In the fume-hood, 23.304 g N-bromosuccinimide (1 equiv.) was slowly added to the solution in four portions while stirring. After stirring overnight, the mixture was acidified through the addition of 1 M HCl. The organic phase of the reaction mixture was then washed two times with water and then dried with MgSO_4 . The solvent was then evaporated under reduced pressure to obtain a yellow oil. (Yield = 27.3 g, 91.05%)

Synthesis of 2-bromomethoxyphenol (3-2).

In a 500 mL round bottom flask, 150 mL of dry DMF was added to 27.3g 2-bromo-6-tert-butylphenol (3-1) (1 equiv.) while stirring. Then 24.67g K_2CO_3 (1.5 equiv.) was added to produce a green solution. 11.154g MeI (1.5 equiv.) was directly added to the flask via syringe and then the reaction mixture was placed under argon and left to stir overnight. 100 mL water was added to the reaction mixture and which was then extracted with Et_2O and washed with water and saturated brine solution. The organic layer was then dried with MgSO_4 before removing all volatiles under reduced pressure, resulting in a yellow oil. Crystallization in cold isopropanol formed white crystals of the product 2-bromomethoxyphenol. (Yield 8.56g, 29.56%)

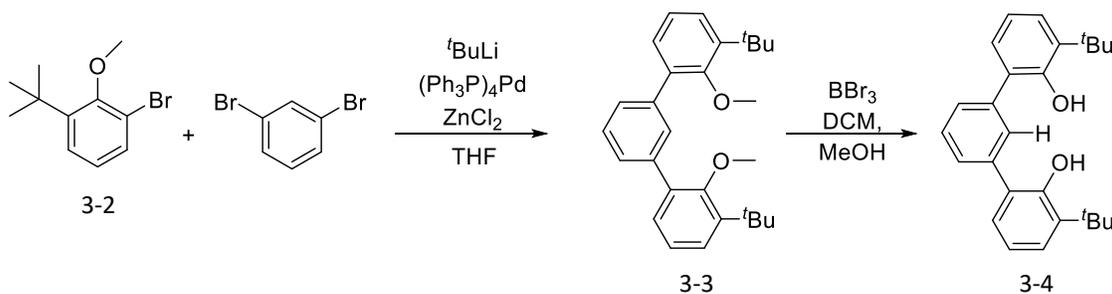


Figure 3-2. Synthesis of $[\text{tBuOCO}](\text{CH}_3)_2$ (3-3) and $[\text{tBuOCO}]\text{H}_3$ (3-4).

Synthesis of [^tBuOCO](CH₃)₂ (3-3).

In a nitrogen filled glove box, 8.56g 2-bromomethoxyphenol (3-2) (1 equiv.) was dissolved in a minimal amount of THF and frozen in a cold well using liquid nitrogen. 44.56 mL of tert-butyl lithium (2.15 equiv.) was added dropwise in 15 mL increments while freezing the solution for 10-20 minutes in between each addition. After the addition was complete, the solution was allowed to warm to room temperature and stirred for 1 hour as a whitish yellow solution. 3.36g of solid ZnCl₂ (0.7 equiv.) was added before adding some additional THF to the mixture. The reaction mixture was allowed to stir for 30 min before 0.407g (Ph₃P)₄Pd (0.01 equiv.) was added. After the addition of 1.87 mL 1,3 dibromobezene (0.44 equiv.), which resulted in the solution turning a darker color of yellow, the reaction mixture was taken out of the glove box with a condenser and y-adapter securely attached to it and was refluxed overnight. The mixture was then quenched under argon with water and the solvent was evaporated under reduced pressure. Water was then added before extracting with Et₂O and then washing with water and concentrated brine solution. The organic layer was then dried with MgSO₄ and then all volatiles were removed under reduced pressure to leave a yellow oil. This was then crystallized with cold isopropanol to obtain a white powder of the product. (Yield 2.816 g, 19.86%)

Synthesis of [^tBuOCO]H₃ (3-4).

In a three-neck flask with two septa attached, 2.816g of [^tBuOCO](CH₃)₂ (3-3) (1 equiv.) was dissolved in 100mL of dry CH₂Cl₂ under counter argon flow. After chilling in an ice bath, 3.32 mL BBr₃ (5 equiv.) was added via syringe through one septum. The reaction mixture was stirred for 5.5 hours and then was quenched with cold methanol. The solvent was then evaporated under reduced pressure. The residue was dissolved in hexanes, filtered, then an orange oil was removed from the bottom layer of the filtrate. The solvent was evaporated under

reduced pressure, re-dissolved in hexanes and cooled to induce precipitation. The precipitate was then collected as the product. (Yield not measured)

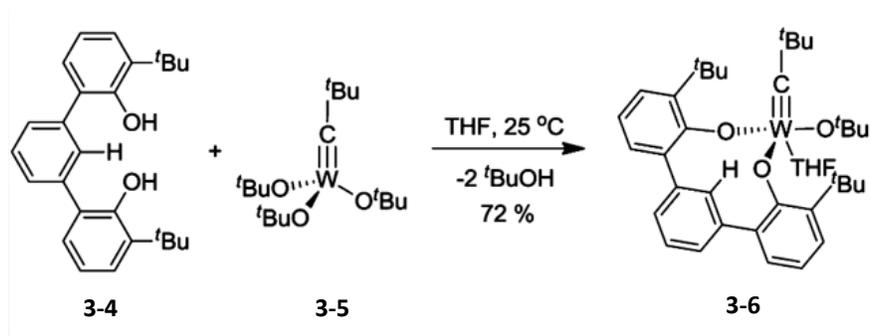


Figure 3-3. Synthesis of $[t\text{BuOCHO}]W\equiv\text{CC}(\text{CH}_3)_3(\text{O}t\text{Bu})(\text{THF})$ (3-6).

Synthesis of $[t\text{BuOCHO}]W\equiv\text{CC}(\text{CH}_3)_3(\text{O}t\text{Bu})(\text{THF})$ (3-6).

In a nitrogen-filled glove box, 291.2 mg $[t\text{BuOCO}]H_3$ (3-4) (1 equiv) in 1 mL THF was added to a glass vial and cooled to $-35\text{ }^\circ\text{C}$. In another vial 416 mg $(t\text{BuO})_3W\equiv\text{CC}(\text{CH}_3)_3$ (3-5) (1.14 equiv) was dissolved in THF (1 mL) and added dropwise to the first solution while stirring. As the dark brown solution was allowed to warm to room temperature a color change to dark yellow was observed, and the solution was allowed to stir for 30 additional minutes at room temperature. A dark tannish yellow tacky material was obtained after removing all volatiles under reduced pressure. The solid was triturated with pentane three times before a final volume of 4 mL of pentane was added and the solution was cooled overnight at $-35\text{ }^\circ\text{C}$. The product formed as a tan precipitate. (Yield = 174 mg, 29.3%)

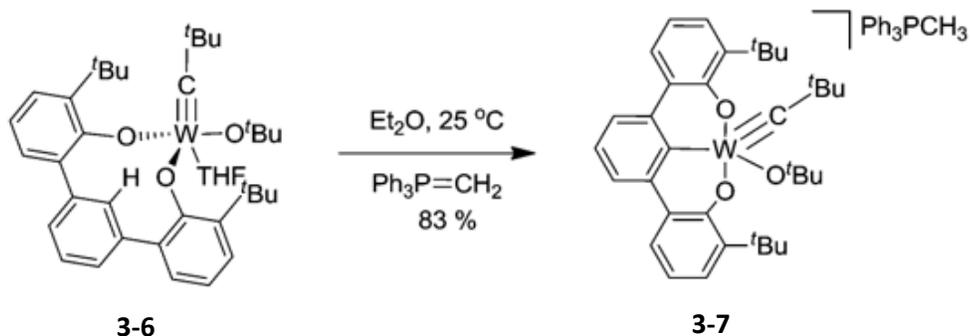


Figure 3-4. Synthesis of $\{[{}^t\text{BuOCO}]\text{W}\equiv\text{CC}(\text{CH}_3)_3(\text{O}'\text{Bu})\}\{\text{Ph}_3\text{PCH}_3\}$ (3-7).

Synthesis of $\{[{}^t\text{BuOCO}]\text{W}\equiv\text{CC}(\text{CH}_3)_3(\text{O}'\text{Bu})\}\{\text{Ph}_3\text{PCH}_3\}$ (3-7).

In a glass vial 174 mg $[{}^t\text{BuOCHO}]\text{W}\equiv\text{CC}(\text{CH}_3)_3(\text{O}'\text{Bu})(\text{THF})$ (3-6) (0.225 mmol, 1 equiv.) was dissolved in 1 mL Et_2O and then cooled to $-35\text{ }^\circ\text{C}$. 62.5 mg $\text{Ph}_3\text{P}=\text{CH}_2$ (0.225 mmol, 1 equiv.) was dissolved in 0.5 mL Et_2O and was then added to the cold solution of 3-6. The resulting mixture was warmed to $25\text{ }^\circ\text{C}$ and the solution brightened to a more yellow color. The solution was stirred for 45 min at room temperature and during that time a yellow solid precipitated out of solution. The yellow product was collected by filtration and then washed with pentanes (3 x 1 mL). (Yield = 158 mg, 72.01%)

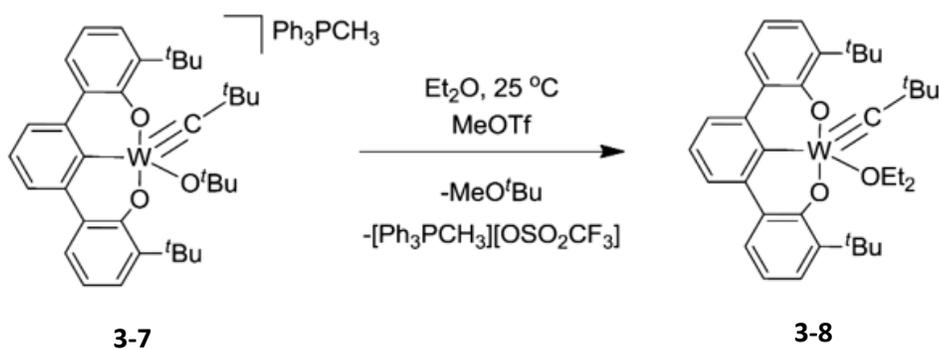


Figure 3-5. Synthesis of $[{}^t\text{BuOCO}]\text{W}\equiv\text{CC}(\text{CH}_3)_3(\text{Et}_2\text{O})$ (3-8).

Synthesis of [^tBuOCO]W≡CC(CH₃)₃(Et₂O) (3-8).

A glass vial was charged with 158 mg {[^tBuOCO]W≡CC(CH₃)₃(O^tBu)}{Ph₃PCH₃} (3-7) (0.162 mmol, 1 equiv.) and 1 mL Et₂O and then cooled to -35 °C. 17.541 μL MeOTf (0.162 mmol, 1 equiv.) was dissolved in 0.5 mL Et₂O and was then added dropwise to the cold suspension of 3-7. The resulting mixture was warmed to 25 °C and stirred for 1 hour. While stirring, the solution changed in color from yellow to dark orange. Phosphonium triflate ([Ph₃PCH₃][OSO₂CF₃]) was formed as a white solid precipitate which was removed via filtration. All volatiles were removed under reduced pressure and the resulting orange solid was triturated with pentane. Crystals were obtained by cooling a dilute diethyl ether solution of the product at -35 °C for 3 d. (Yield = 67 mg, 58.97%)

CHAPTER 4
REACTION OF OCO^{3-} TUNGSTEN COMPLEX WITH CS_2

Results and Discussion

After the successful synthesis of 4-1 as seen in Chapter 3, several avenues in the application of this tungsten complex with regard to chemical reactions were explored. Following the precedent set by Gonsales with the successful reaction of 4-1 with CO_2 to form a new metal complex,¹ an attempt was made to form a new molecule through the reaction of 4-1 with CS_2 . The experiment was performed on a small scale using similar methods to the previously successful reaction using CO_2 .¹ ^1H NMR analysis on the reaction solution in reference to the initial reactants indicated the success of the reaction and the formation of a new metal complex (**Figure C-1**).

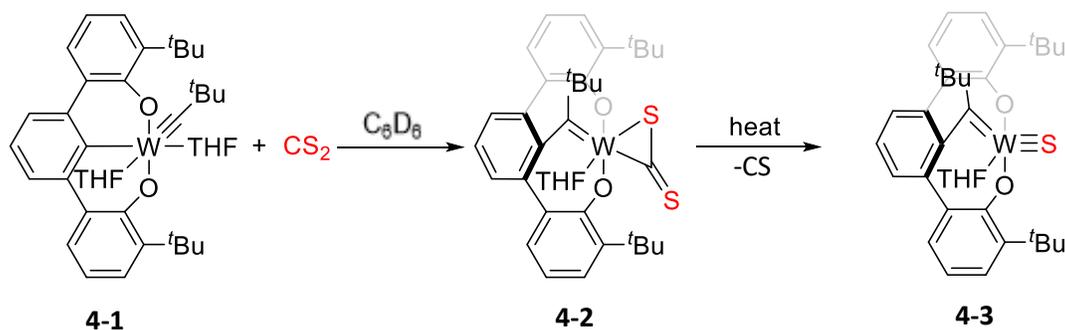


Figure 4-1. Synthesis of complexes 4-2 and 4-3.

Initial attempts to isolate the resulting complex (4-2) were unsuccessful due to decomposition with the removal of solvents. However, subsequent experiments performed by Vineet Jakhar revealed the crystal structure of 4-2 as seen in **Figure 4-1**. The reaction product was able to be characterized by multidimensional NMR (**Figures C-4, C-5**), IR (**Figure C-3**), and mass spectroscopy in THF (**Figures C-6, C-7**). In the IR spectrum, unreacted CS_2 was detected along with a resonance that may be associated with the $\text{C}=\text{S}$ bond, though its close

approximation with other strong resonances required further confirmation (**Figure C-3**). The $W\equiv S$ bond was out of the spectral range and thus was not present in the obtained IR spectrum. Heating of 4-2 in solution for 18 h at 95°C lead to the formation of a darker solution of 4-3 through the loss of a CS fragment (**Figure 4-1**). Unlike 4-2, the 4-3 complex did not decompose with the removal of volatiles. Crystals of 4-3 were obtained from a concentrated Et_2O solution and were used to obtain a crystal structure via single crystal X-ray diffraction (**Figure 4-2**).

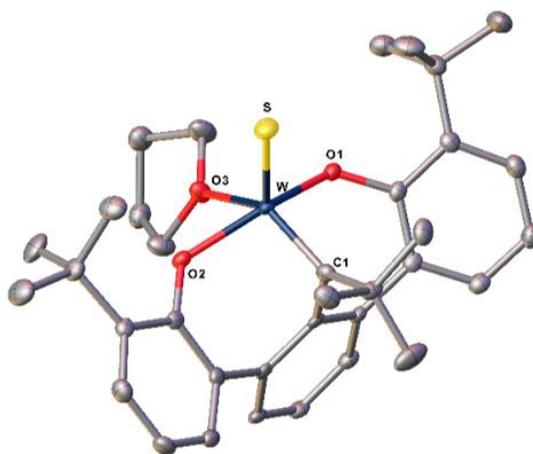


Figure 4-2. Crystal structure of 4-3

Synthesis of Compounds 4-2 and 4-3

A J-Young NMR tube was charged with tungsten alkylidyne $[OCO]W\equiv CC(CH_3)_3(THF)_2$ (4-1) (0.100 g, 0.130 mmol, 1 equiv.) in C_6D_6 . After cooling the solution in the tube to $-35^\circ C$, CS_2 (11.8 μL , 0.195 mol, 1.5 equiv.) was then added to it. The resulting solution, which darkened in color to a black-brown, was allowed to warm to room temperature. At this point, the compound 4-2 was characterized in situ and then was heated at $95^\circ C$ for 18 hours. All volatiles were removed in vacuo and the resulting residue was triturated with pentane (3 x 2 mL) and then taken up in a minimal amount of Et_2O and filtered. The remaining volatiles of the filtrate was then removed in vacuo. Single crystals were obtained from a concentrated Et_2O solution of 4-3.

CHAPTER 5

POLYMERIZATION OF NORBORNENE

Results and Discussion

The successful formation of a tungsten pincer complex with CS₂ that was the focus of Chapter 4 led to experimentation on the new complex's potential applications. It was noted in the study by Gonsales that the tungsten pincer complex incorporating CO₂ was the first complex to promote the ring expansion metathesis polymerization (REMP) of norbornene to give highly *cis-syndiotactic* cyclic polynorbornene.¹ Due to the similarities to the compound synthesized by Gonsales, the initial complex formed with CS₂ prior to heating (5-1) was added to norbornene to determine its efficiency in acting as a polymerization catalyst. The result was analyzed via ¹H NMR at different intervals to monitor the reaction progression (**Figure D-1**). Over time, the NMR resonances corresponding to the *cis* conformation (5.36 and 2.92 ppm) grew in intensity while those of the *trans* conformation (5.95 and 2.73 ppm) decreased in relative intensity resulting in a 96% of the structure in the *cis* conformation (**Figure D-3**). Thus, the synthesized catalyst was determined to give a highly *cis-syndiotactic* polymer similar to the catalyst studied by Gonsales.¹ Gel Permeation Chromatography (GPC) was also used to analyze the resultant polynorbornene to provide evidence toward the cyclic nature of the polymer (**Figure D-4**). Due to their smaller hydrodynamic radii, cyclic polymers have shorter elution times for a given molecular weight than their linear counterparts.¹³ Comparison with literature results of cyclic polynorbornene confirmed the cyclic nature of the polymer. Catalysis of polymerization with complex 5-3 was not attempted and remains to be explored in future research.

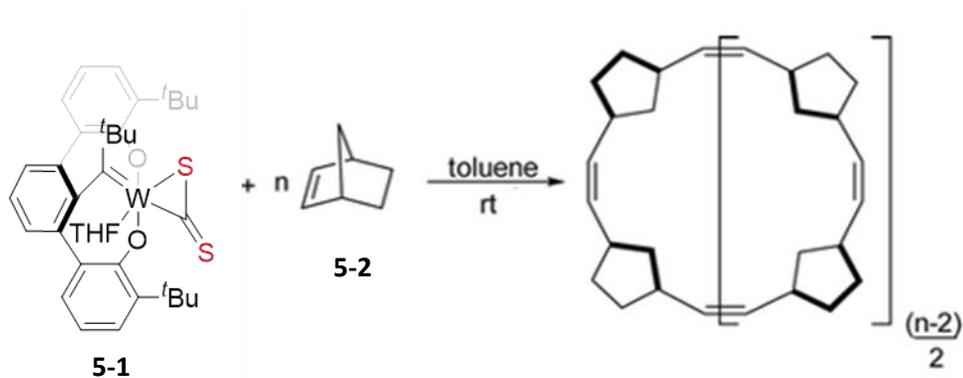


Figure 5-1. Catalysis of the polymerization of norbornene by 5-1.

Procedure for catalytic polymerization of Norbornene

In a nitrogen-filled glove box, a J-Young NMR tube was charged with 19 mg of norbornene (0.2018 mmol) dissolved in 1 mL of C_6D_6 . To this solution was added 2 drops of a 1 mL solution of 5-1 in C_6D_6 , as prepared in Chapter 4 with 30 mg and 1.1 equiv. of CS_2 . The mixture was monitored with 1H NMR at intervals before leaving it overnight. The mixture was then dissolved in a small amount of toluene (3 mL) and added dropwise to a stirring methanol solution. The polymer was then recovered by filtration.

CHAPTER 6

CONCLUSION

The synthesis of an ONO^{3-} trianionic pincer type ligand specific to the Veige group was successfully achieved. Confirmation of the structure was made via ^1H NMR in reference to pre-established literature. Following ligand synthesis, complexation with IrCl_3 , FeCl_3 , and $\text{RuCl}_2(\text{PPh}_3)_3$ was attempted. The addition of heat or lutidine base were explored as contributing factors. Results were monitored via ^1H NMR and ^{31}P NMR, and all attempts were deemed unsuccessful. An OCO^{3-} trianionic pincer ligand and the associated tungsten metal complex known as Sarkar's catalyst was also synthesized according to the literature. It was then used in the formation of a new complex through the reaction of CS_2 . This complex was characterized by multidimensional NMR, IR, and mass spectroscopy. Despite decomposition under reduced pressure, the sulfide complex became a new stable complex upon heating through the loss of a CS fragment. Single crystals of this more stable sulfide complex were obtained and used for the determination of its crystal structure using single crystal X-ray diffraction. The catalytic abilities of the original sulfide complex prior to heating were evaluated with its catalysis of the polymerization of norbornene. Through ^1H NMR and GPC analysis, the resultant polymer was determined to be a highly *cis-syndiotactic* cyclic polynorbornene.

ACKNOWLEDGMENTS

I would like to thank Dr. Adam Veige for his patience and support and for allowing me to do research as an undergraduate in his research lab in the inorganic division of the Department of Chemistry at the University of Florida. I would also like to acknowledge Dr. Soufiane Nadif for training me in the necessary lab techniques as well as for his guidance and support throughout my research. Finally, I would like to thank the members of the lab for providing a friendly and supportive environment, especially Stella Gonsales, Chris Beto, Chris Roland, Sud Venkatramani, and Vineet Jakhar.

APPENDIX A

SUPPORTING INFORMATION FOR CHAPTER 2

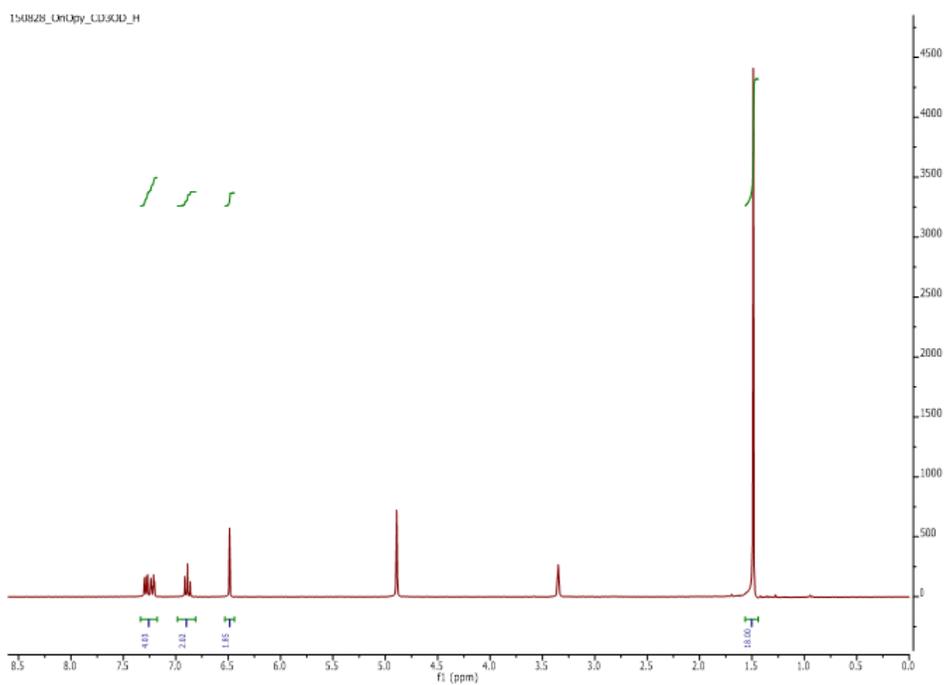


Figure A-1. ^1H NMR spectrum of 2-2 in MeOD.

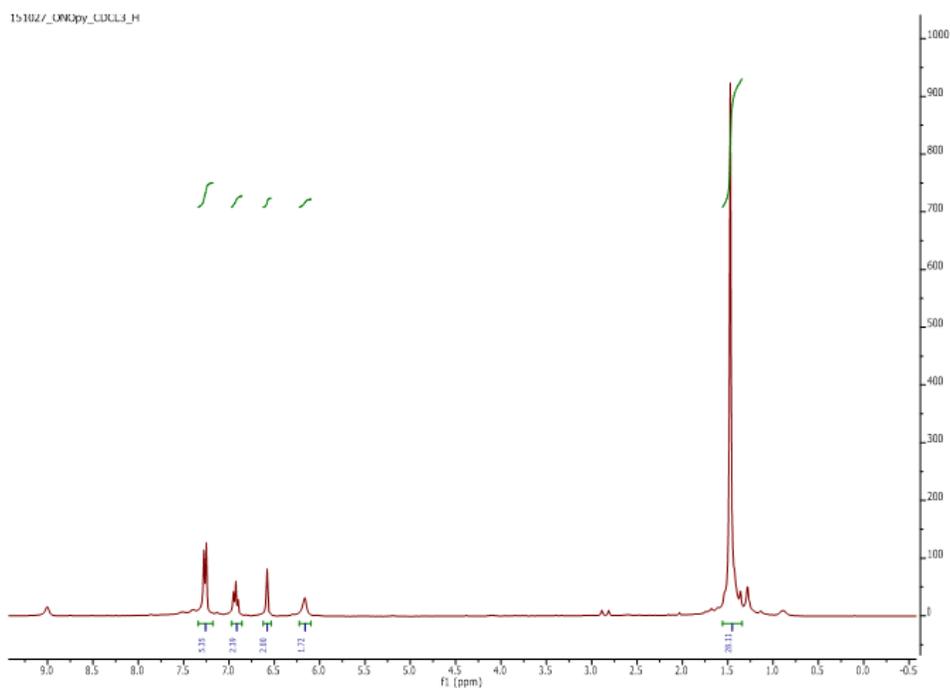


Figure A-2. ^1H NMR spectrum of 2-2 in CDCl_3 .

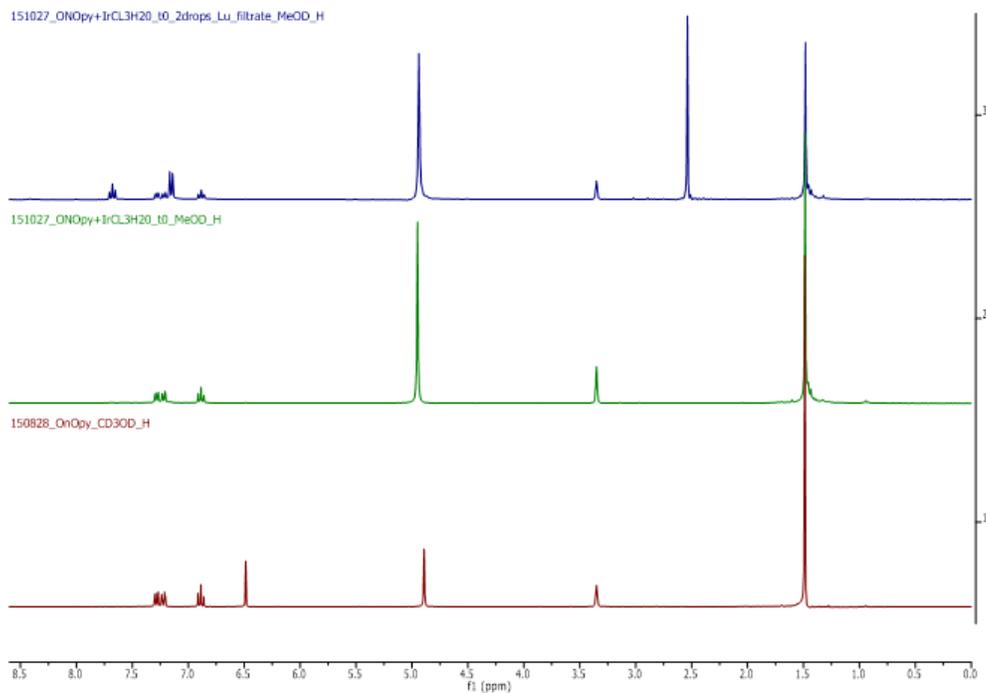


Figure A-3. ^1H NMR spectra of 2-2 before (bottom) and after (middle) adding IrCl_3 in MeOD, and the filtrate after lutidine was added (top).

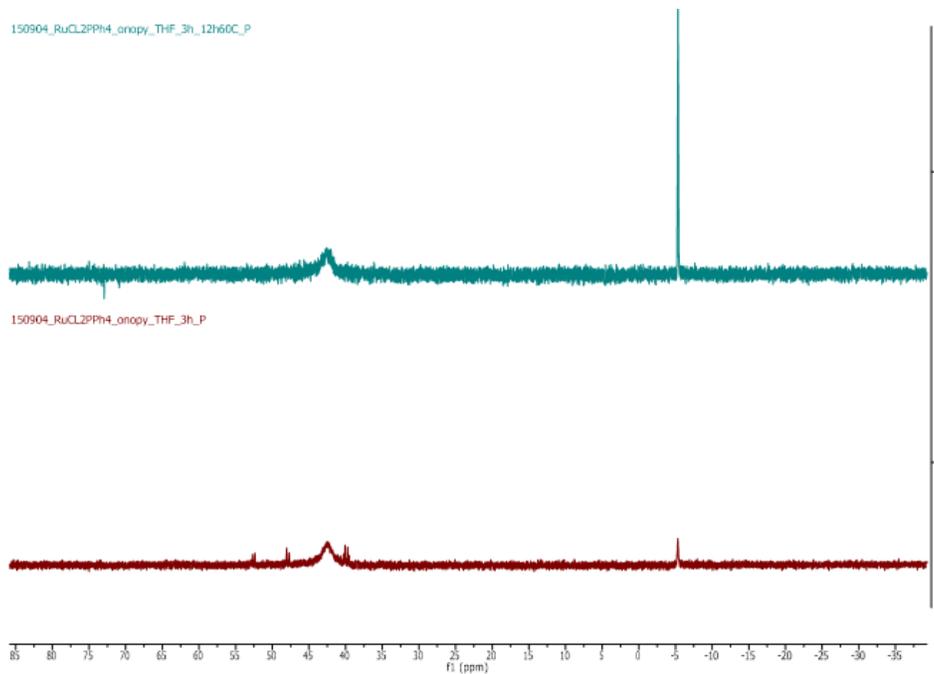


Figure A-4. ^{31}P NMR spectra of 2-2 with $\text{RuCl}_2(\text{PPh}_3)_3$ in THF before (bottom) and after (top) heating for 12 hr at 60°C .

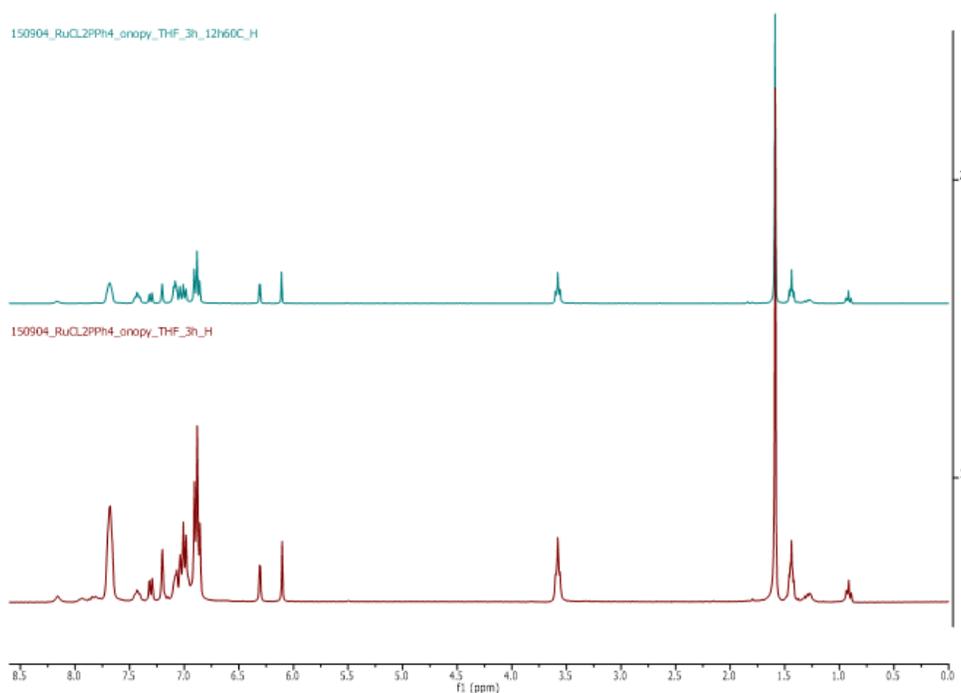


Figure A-5. ^1H NMR spectra of 2-2 with $\text{RuCl}_2(\text{PPh}_3)_3$ in THF before (bottom) and after (top) heating for 12 hr at 60°C .

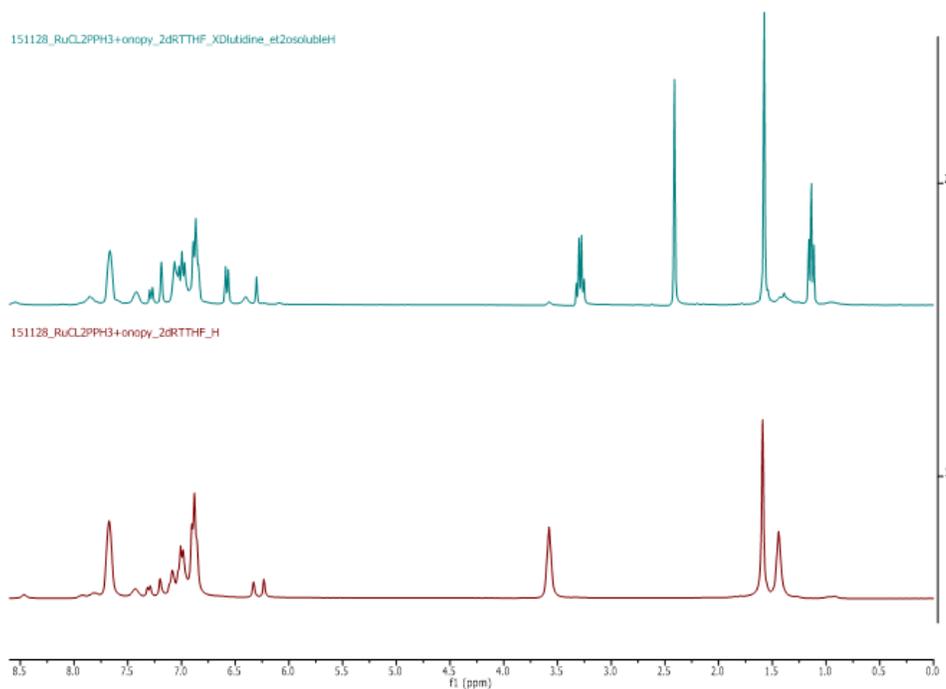


Figure A-6. ^1H NMR spectra of 2-2 with $\text{RuCl}_2(\text{PPh}_3)_3$ in THF before (bottom) and after (top) adding lutidine base.

APPENDIX B

SUPPORTING INFORMATION FOR CHAPTER 3

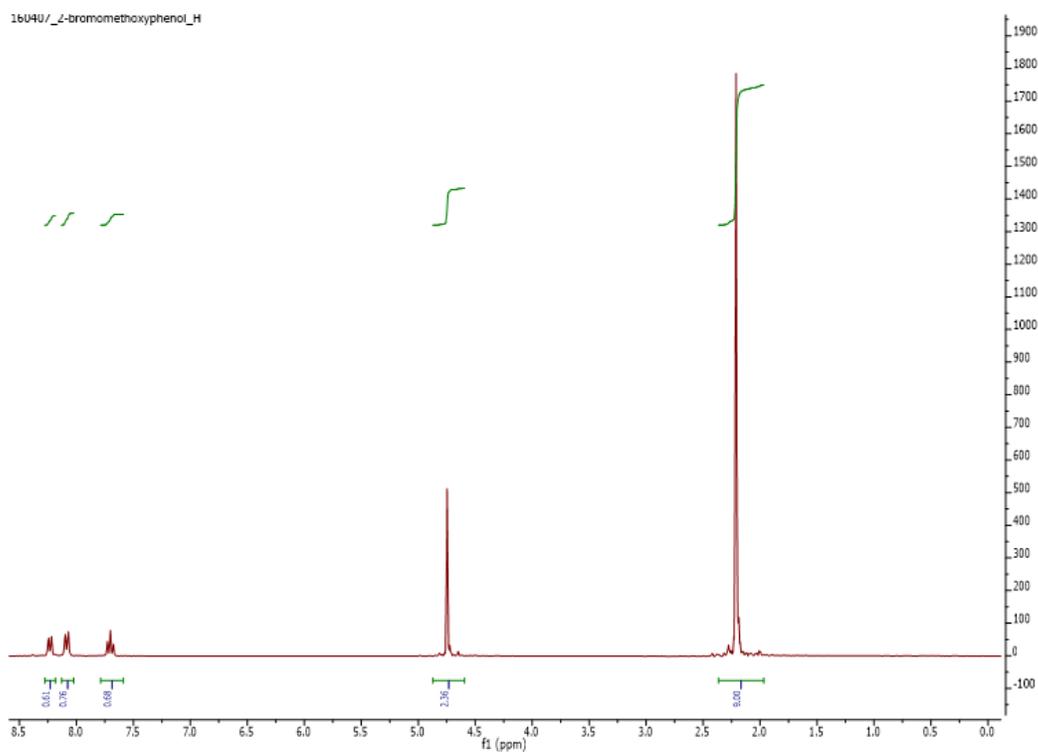


Figure B-1. ^1H NMR spectrum of 2-bromomethoxyphenol (3-2).

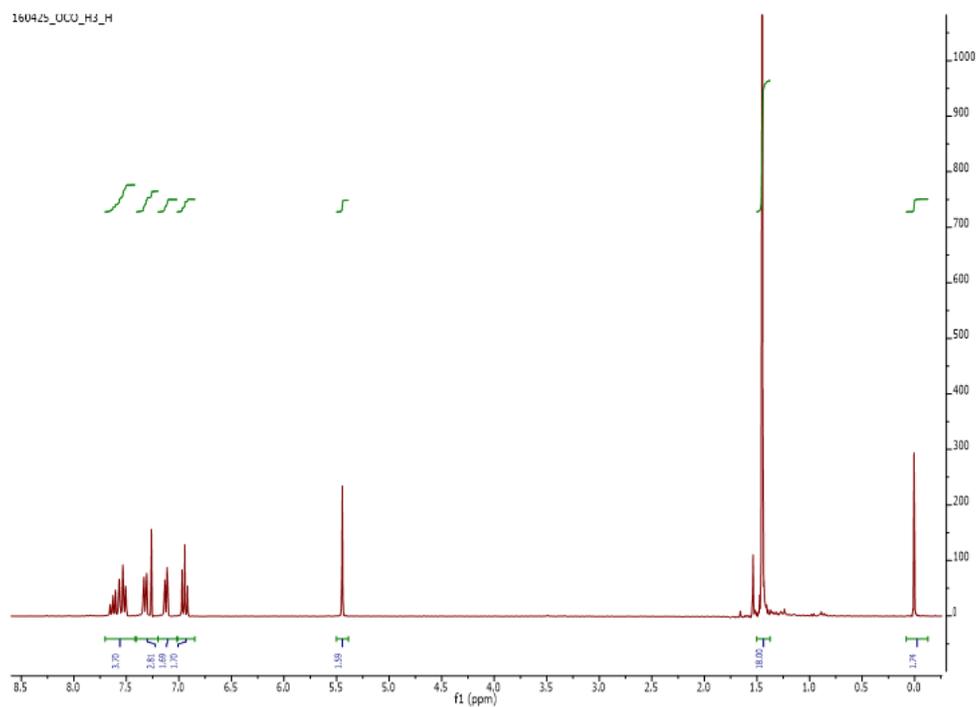


Figure B-2. ^1H NMR spectrum of [tBuOCO] H_3 (3-4)

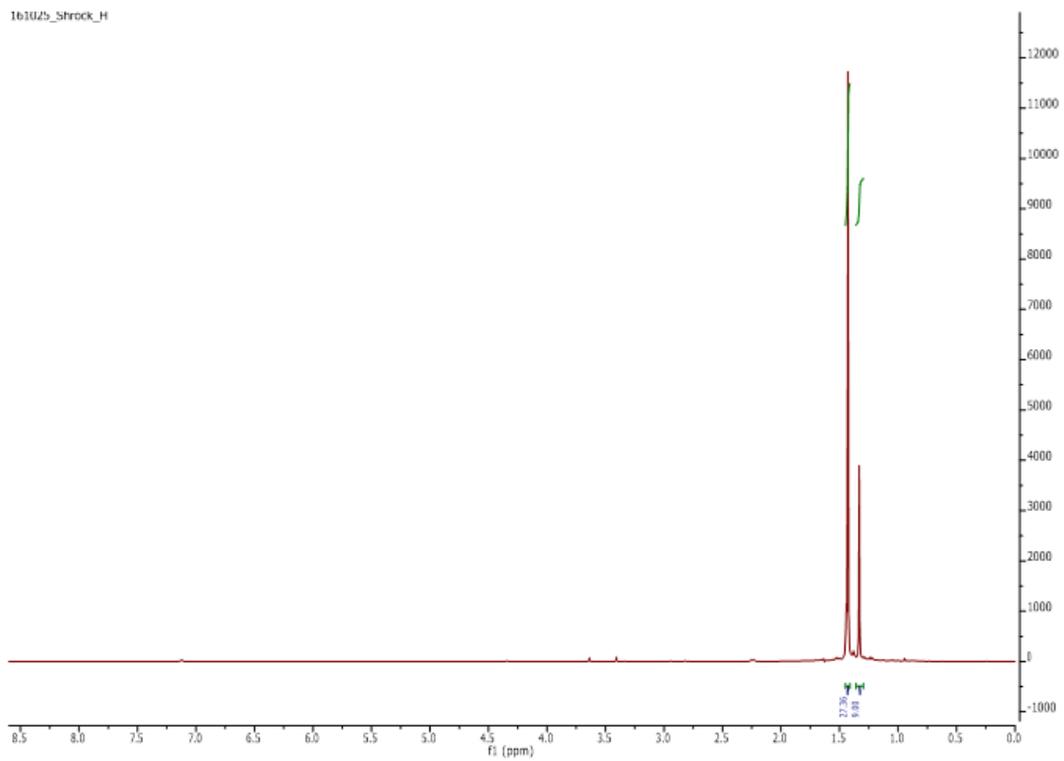


Figure B-3. ^1H NMR spectrum of 3-5.

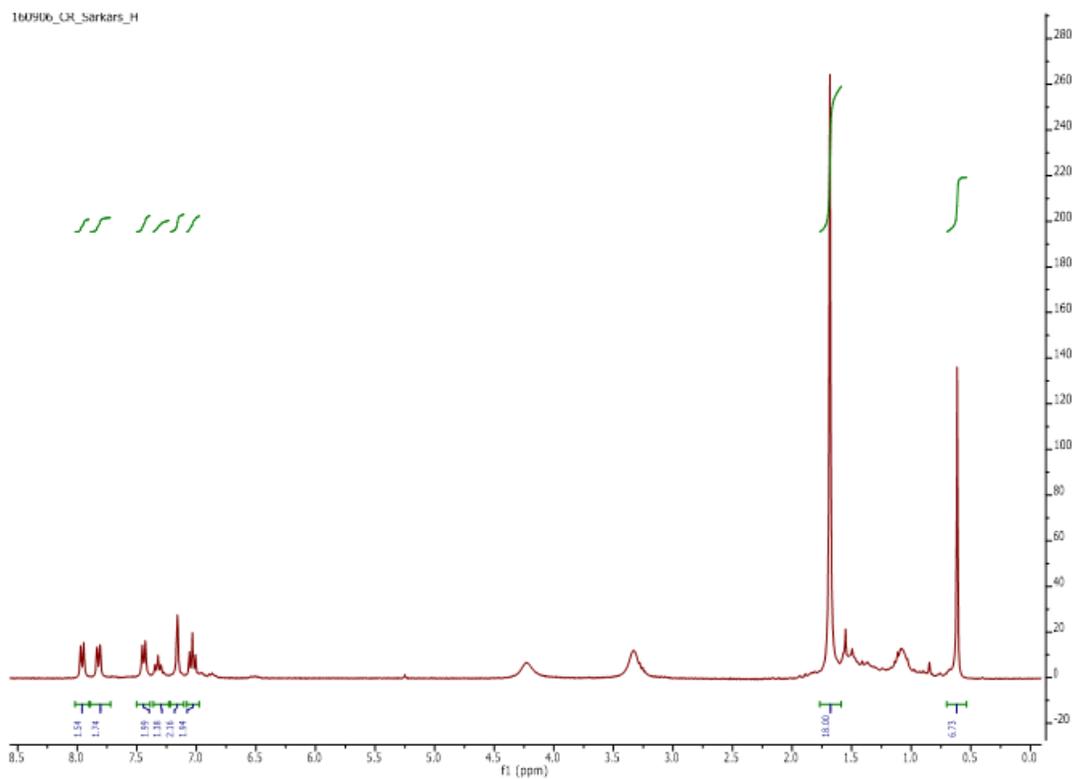


Figure B-4. ^1H NMR spectrum of Sarkar's catalyst (3-6).

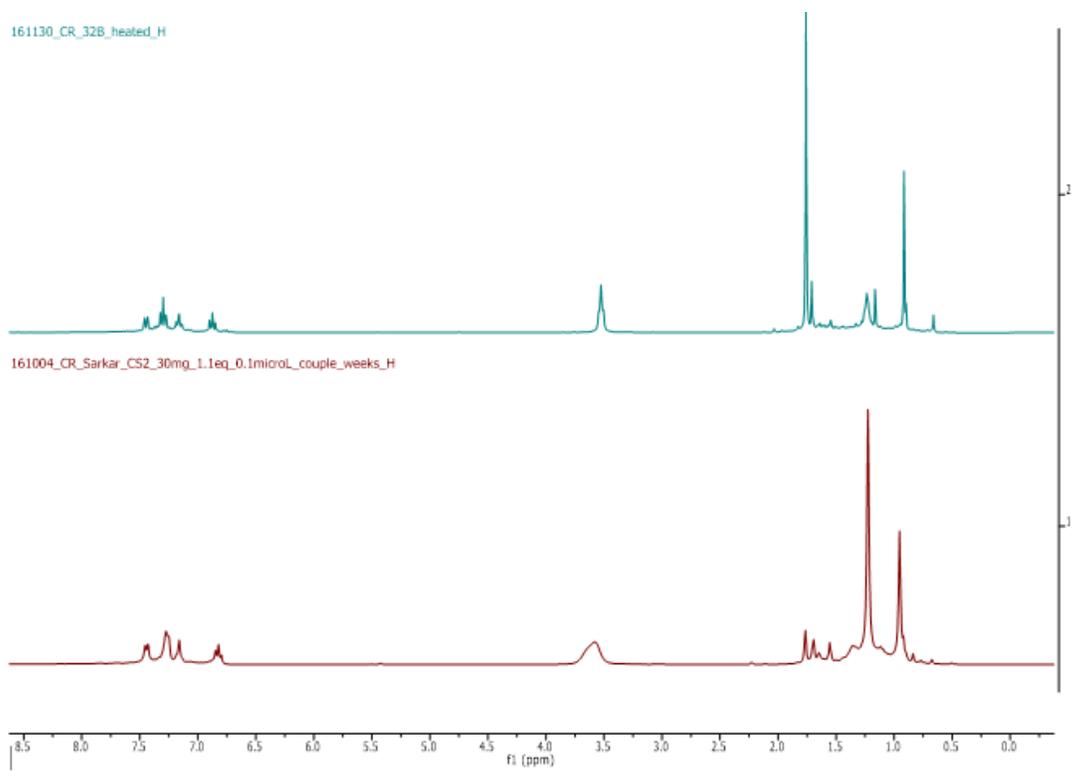


Figure C-2. ^1H NMR spectrum of the emergence of 4-3 after heating 4-2 (top) compared to before heating was induced (bottom).

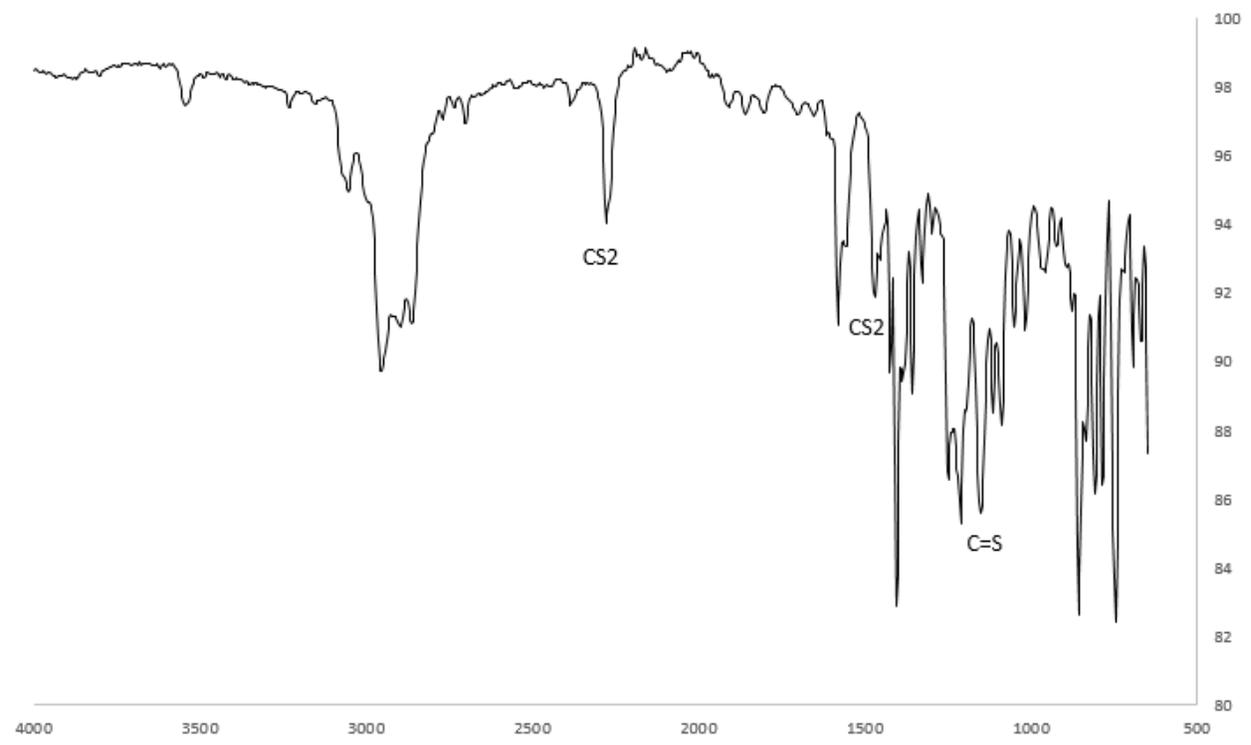


Figure C-3. IR spectrum of 4-2 with significant peaks labeled.

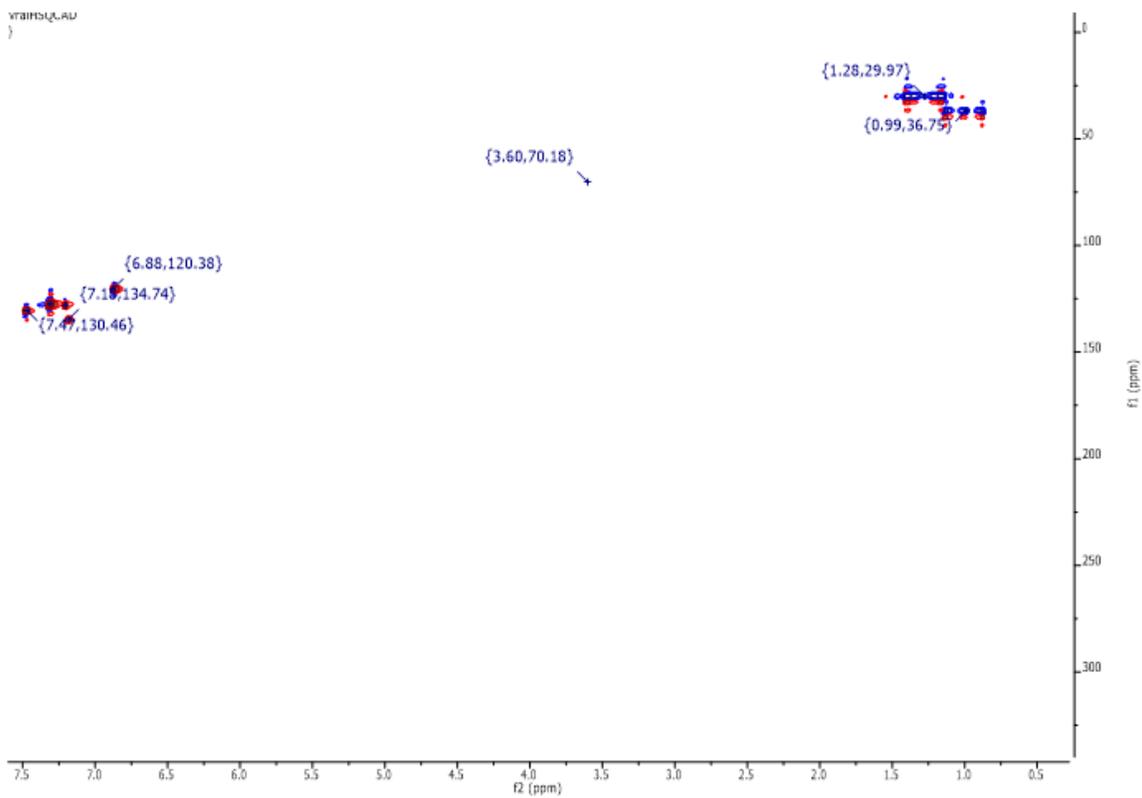


Figure C-4. ^1H - ^{13}C HSQC NMR spectrum of 4-2.

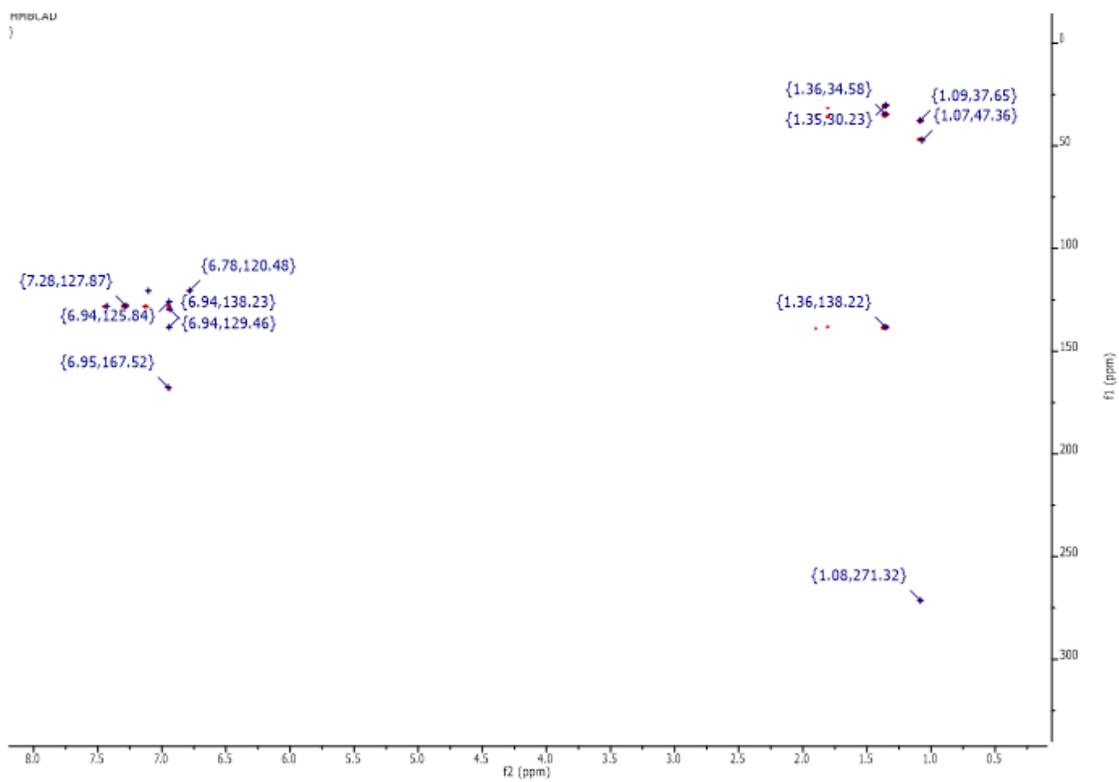


Figure C-5. ^1H - ^{13}C HMBC NMR spectrum of 4-2.

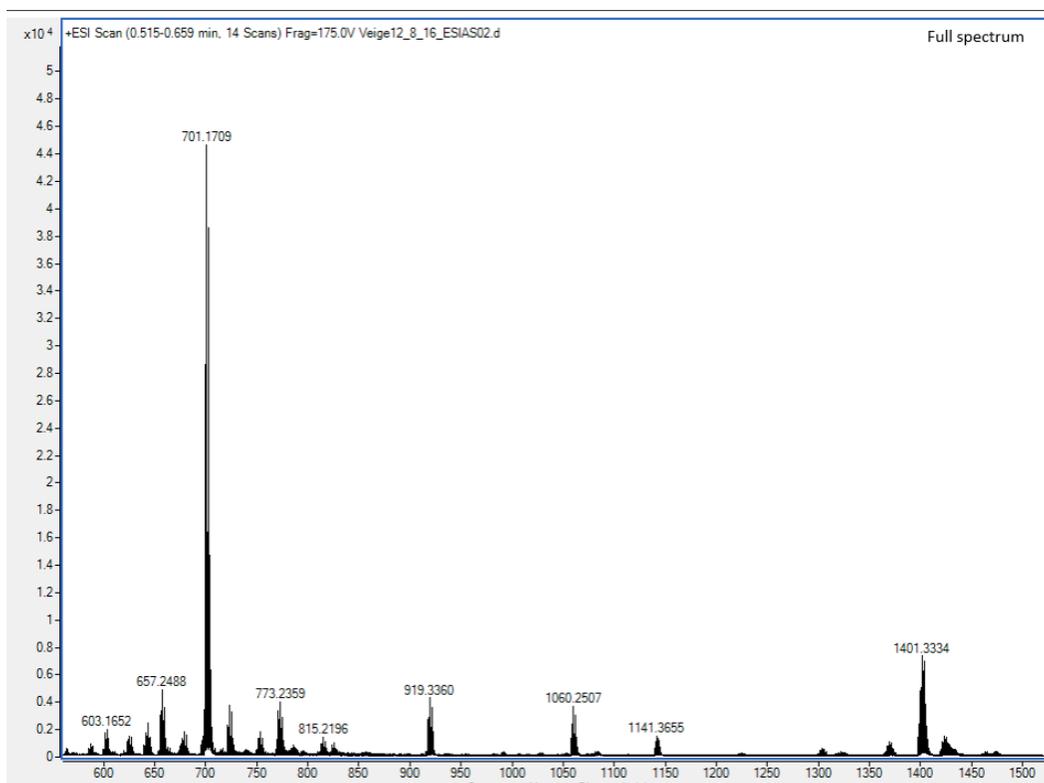


Figure C-6. ESI-MS Spectrum of 4-2.

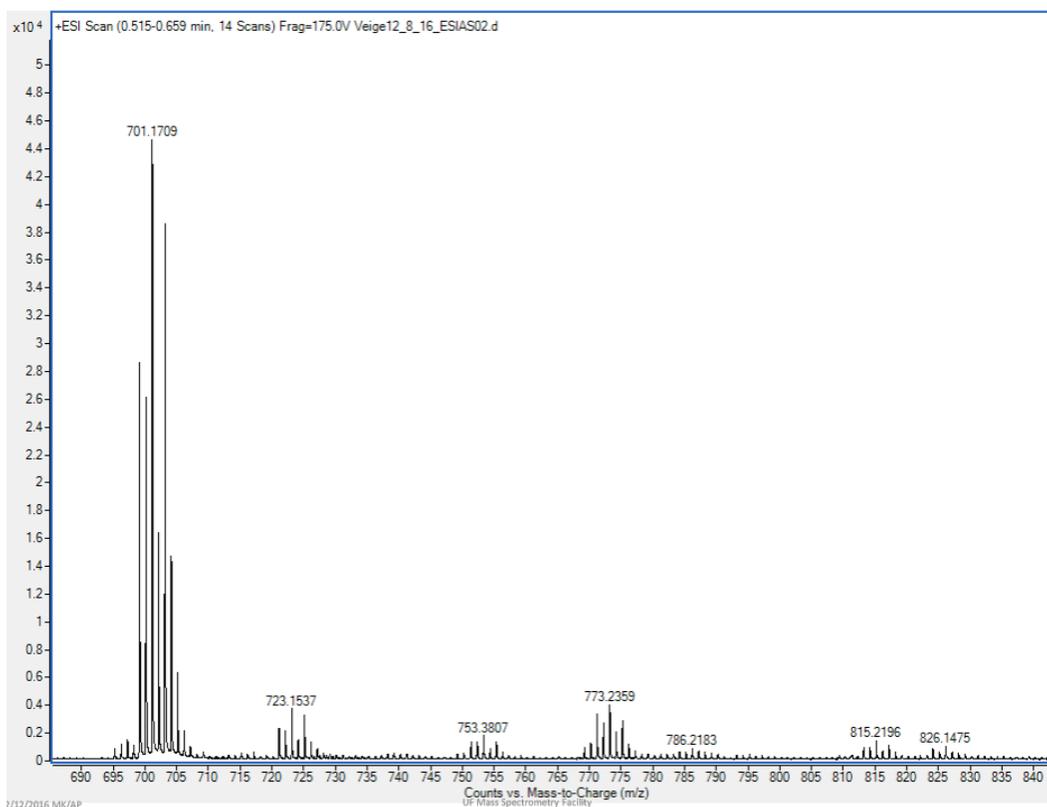


Figure C-7. ESI-MS Spectrum of 4-2.

APPENDIX D

SUPPORTING INFORMATION FOR CHAPTER 5

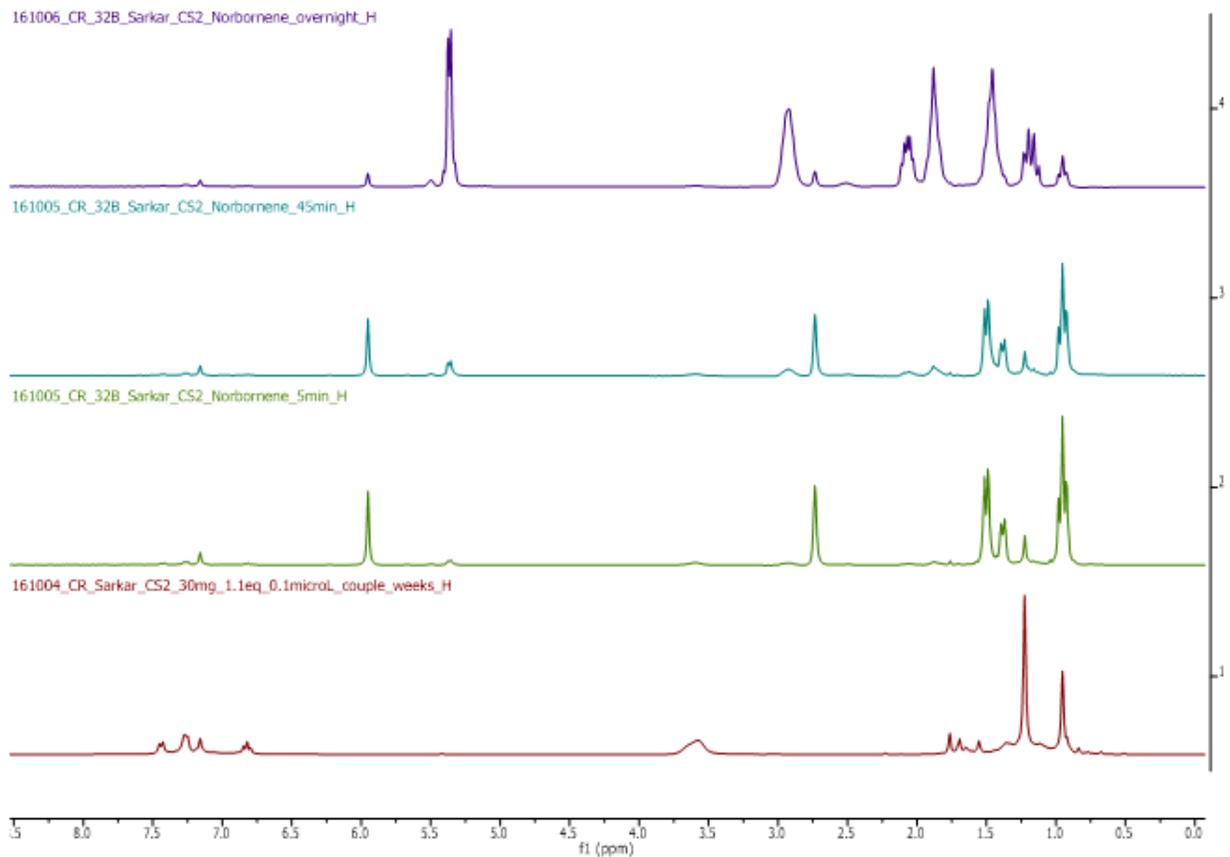


Figure D-1. ^1H NMR spectra of polymerization of norbornene catalyzed by 5-1 over time. From bottom to top: catalyst 5-1 alone, polymerization reaction after 5 min, polymerization reaction after 45 min, and polymerization after being left overnight.

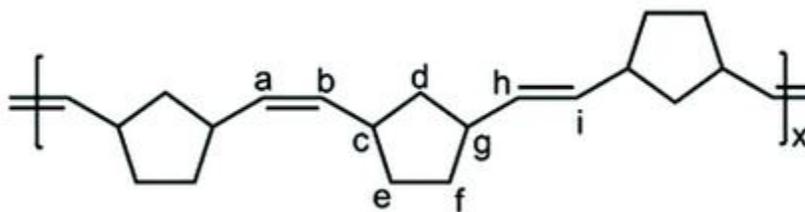


Figure D-2. Labeled structure of polynorbornene.

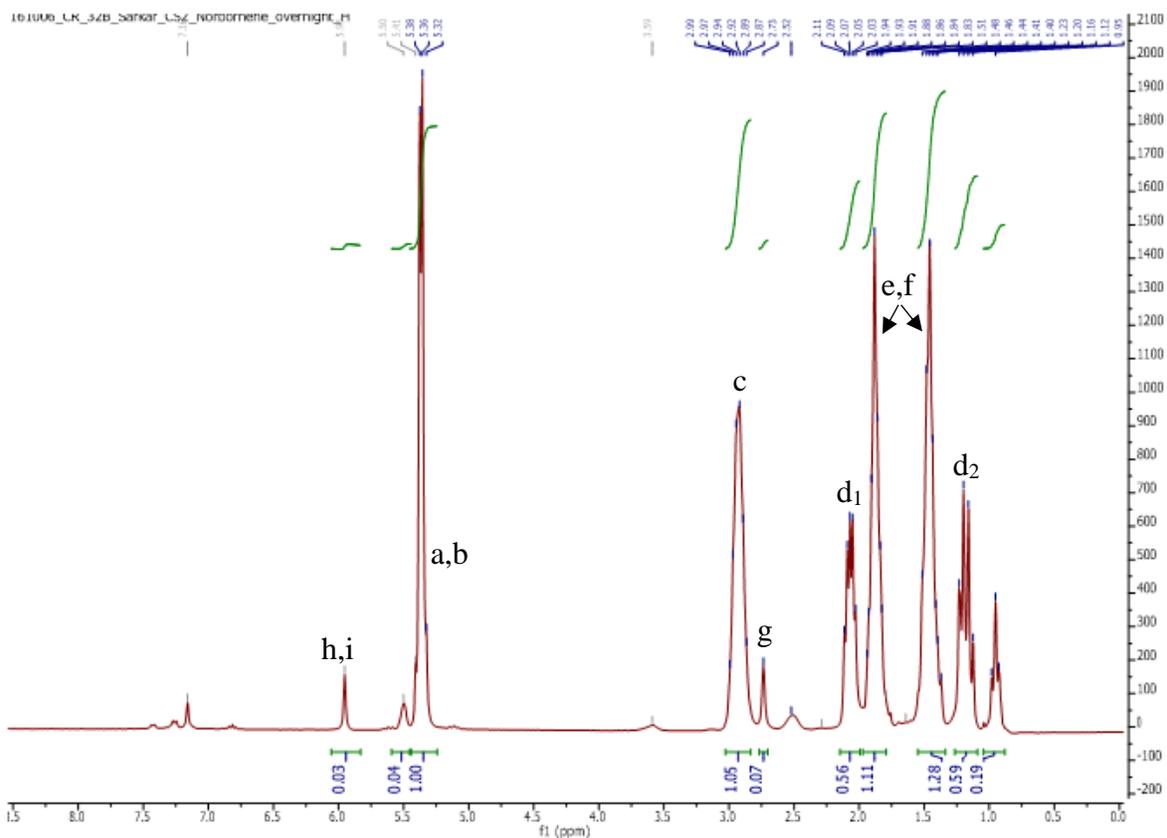


Figure D-3. Labelled ^1H NMR spectrum of polymerized norbornene as catalyzed by 5-1 (corresponding to structure in Figure D-2).

	M_n (g/mol)	M_w/M_n
CR33	1,558,000	1.380

GPC Traces

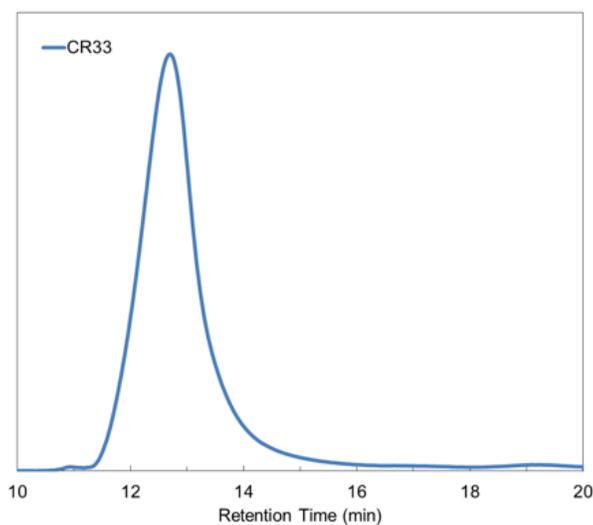


Figure D-4. Gel Permeation Chromatography (GPC) data of norbornene polymerized by 5-1.

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