COBALT-CATALYZED ACCEPTORLESS DEHYDROGENATIVE HOMOCOUPLING OF PRIMARY ALCOHOLS TO ESTERS

by

Bedraj Pandey

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of

Master of Science in Chemistry

Middle Tennessee State University

August 2019

Thesis Committee:

Dr. Keying Ding, Chair

Dr. Scott Handy

Dr. Chengshan Wang

I dedicate this research work to my grandmother Kumari Pandey. Thank you so much for your contribution to my upbringing. Where ever you are, rest in peace. I will always miss you!

ABSTRACT

Esters are an important class of organic compounds widely used by human beings in their daily life. Currently existing industrial methods for esterification involve harmful starting compounds, toxic byproducts and high manufacturing costs. In this work, tripodal tetradentate $^{iPr}PPPN^{H}Py^{Me}$ cobalt complex is synthesized for use as a catalyst for the acceptorless dehydrogenative homocoupling of primary aliphatic and aromatic alcohols to esters. This method is economical, oxidant free and environmentally benign. $KO^{t}Bu$ is found as the best co-catalyst for the acceptorless dehydrogenative homocoupling. Primary aromatic alcohols with electron releasing or withdrawing groups at the ortho position are converted to esters with higher yields. Primary aliphatic alcohols also showed outstanding reactivity but slightly higher temperature and catalyst/co-catalyst loading are required. Lactones are also obtained in good yield from diol substrates. The mechanistic study suggests a two step reaction pathway. In the first step, cobalt complex catalyzes dehydrogenation of alcohol to intermediate aldehyde. In the second step, co-catalyst $KO^{t}Bu$ mediates Tishchenko-type condensation of intermediate aldehydes to esters.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION AND OBJECTIVES OF STUDY

1.1. Esters in Nature and Industry

Esters are an important class of organic compounds. They are widely distributed in nature and have widespread applications in the field of chemical, flavor, fragrance and textile industries.[1,2,3] Butyl acetate, isobutyl acetate, benzyl acetate, geranyl acetate, isoamyl acetate, isoamyl butyrate, 1,3-nonanediol diacetate, citronellyl acetate, benzyl propionate, 2-phenylethylphenyl acetate, vetiveryl acetate, isopentyl isovalerate, allyl hexanoate, decyl acetate and citronellyl formate are the most important flavor and perfume esters (Figure 1).[3]

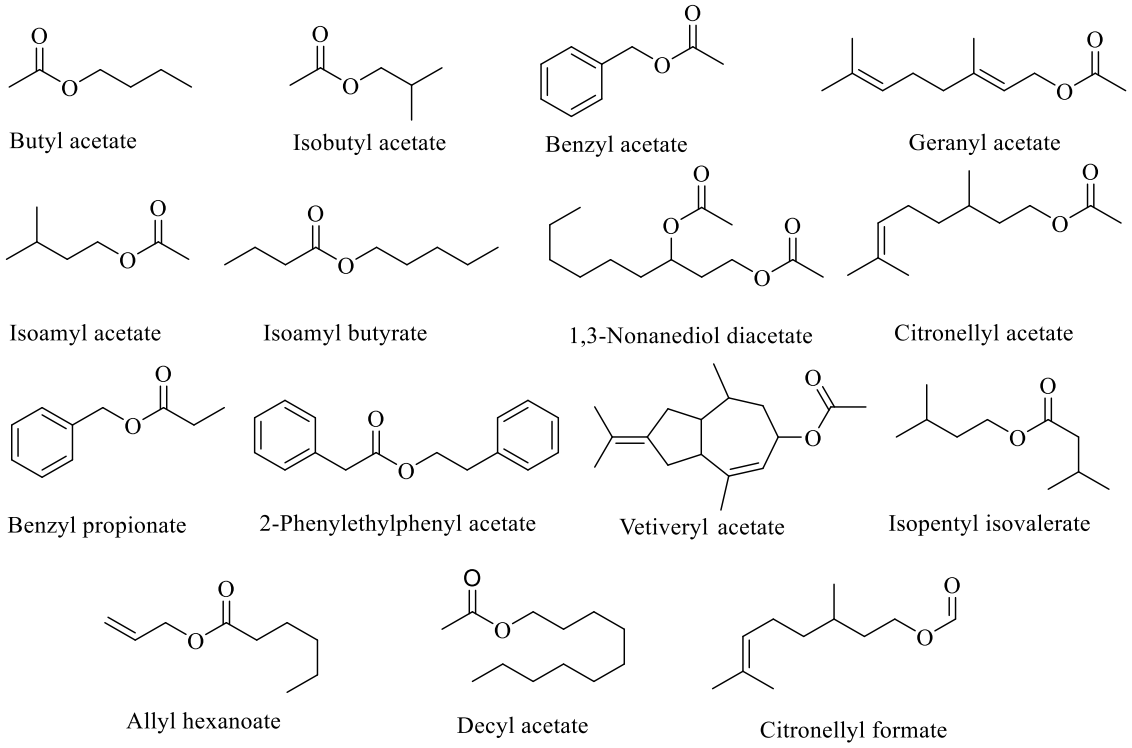


Figure 1. Widely used flavor and perfume esters[3]

Similarly, aspirin, benzocaine, phenyl salicylate (or salol) and methylphenidate are common medicines from the ester family of organic compounds (Figure 2).[3] Polyacrylates, polyethylene terephthalates, and polyvinyl acetate are also widely used esters. These polymers are commonly found in carpets, clothing, plastic bottles, etc. (Figure 3).[3] Lower ester members like methyl acetate, ethyl acetate, propyl acetate and butyl acetate are important solvents due to their low polarity, hydrophobic and lipophilic nature.[3]

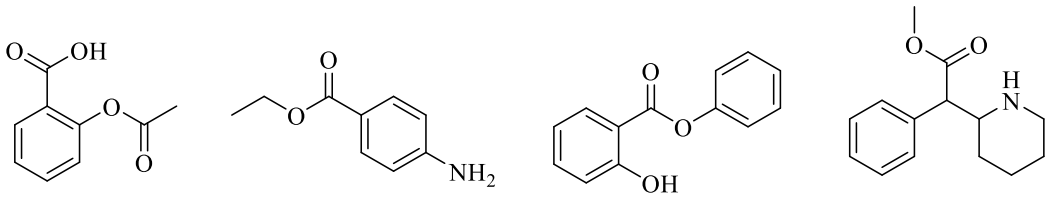


Figure 2. Common medicines from ester family[3]

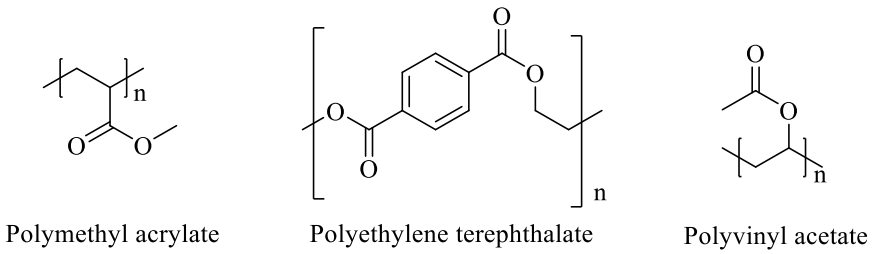
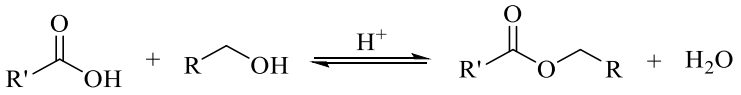


Figure 3. Widely used polymers from ester family[3]

1.2. Industrial Methods of Ester Synthesis

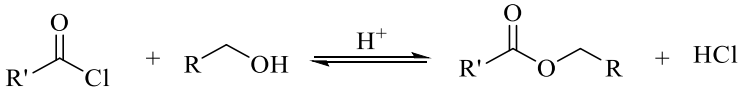
To fulfill daily needs of the ester products, there are many synthetic methods for their production in industry. Some of the important industrial methods for ester formation

Esterification of carboxylic acids



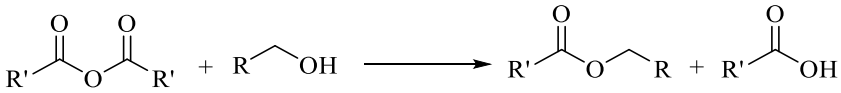
R', R = alkyl or aryl

Acylation of acyl halides



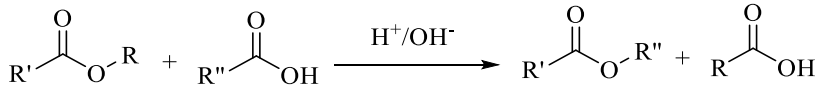
R', R = alkyl or aryl

Acylation of acid anhydrides



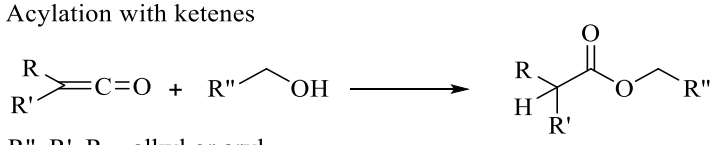
R', R = alkyl or aryl

Transesterification



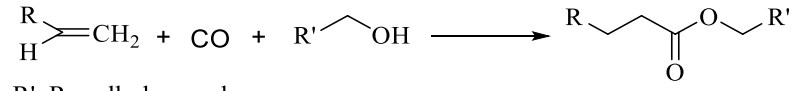
R", R', R = alkyl or aryl

Acylation with ketenes



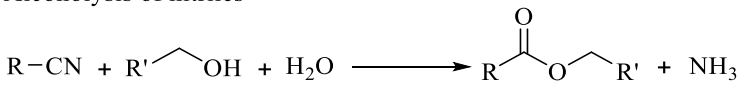
R", R', R = alkyl or aryl

Carbonylation of alkenes



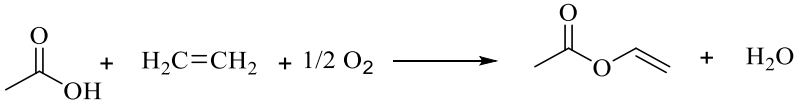
R', R = alkyl or aryl

Alcoholysis of nitriles



R', R = alkyl or aryl

Acylation of olefins

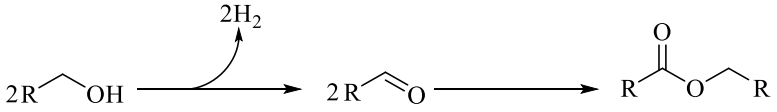


Scheme 1. Established industrial methods for ester synthesis[3]

include Fisher esterification, acylation of acyl halides, acylation of acid anhydrides, transesterification, acylation with ketenes, carbonylation of alkenes with alcohols, alcoholysis of nitriles, acylation of olefins, etc. (Scheme 1).[3]

1.3. Acceptorless Dehydrogenative Homocoupling of Alcohols to Esters

In addition to these deep-rooted methods, acceptor-less dehydrogenative coupling of alcohols to esters is a new approach towards ester synthesis. It uses primary alcohols which are relatively safe, easily available and inexpensive. Since, only hydrogen is produced as a byproduct, it is environmentally safe. Also, hydrogen can be used as an alternative source of an energy. It is also an atom economical and oxidant free method.[4-7] Use of inexpensive and easily available alcohols is one of the main advantages of this method (Scheme 2).



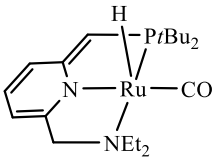
Scheme 2. Dehydrogenative homocoupling of primary alcohols to esters[4-7]

1.4. Precious Metal Catalysts in Dehydrogenative Homocoupling of Alcohols into Esters

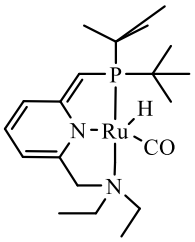
Over the last few decades, catalytic dehydrogenative method for esterification of alcohols to esters has been widely done using precious metal catalysts like Ru,[8-18] Os,[13, 19] and Ir[20-22] by various research groups (Figure 4). Milstein and co-workers developed Ru(II) hydride complexes which are based on electron rich Phosphorous Nitrogen Phosphorous (PNP) and Phosphorous Nitrogen Nitrogen (PNN) ligands and applied them for dehydrogenative homocoupling of aryl and alkyl primary alcohols to esters (Figure 4).[8]

Interestingly, Milstein and co-workers synthesized esters through acylation of secondary alcohols using non-activated symmetrical esters like ethyl acetate, under neutral conditions using dearomatized Ru pincer PNN complex with hydrogen as a byproduct (Figure 4).[9] Later, Milstein and co-workers applied a dearomatized bipy-PPN ruthenium metal pincer complex for cross-dehydrogenative coupling of primary alcohols with secondary alcohols under neutral conditions (Figure 4).[11] Beller and co-workers applied Ru and Ir based PNP pincer catalysts for the dehydrogenative homocoupling of ethanol into ethyl ethanoate (Figure 4).[12,22]

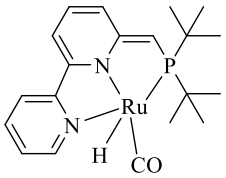
Gusev and co-workers developed a dimer $[MH(CO)(NNP{\it i}Pr)]_2$, (M = Os, *i*Pr = isopropyl), as a catalyst for the dehydrogenative homocoupling of alcohols to corresponding esters (Figure 4).[13] Vlugt and co-workers introduced $RuCl(CO)(H)(L^H)$, (L^H = 6-(di-tert-butylphosphinomethyl)-6′-hydroxy-2,2′-bipyridine) as a catalyst and performed dehydrogenative homocoupling of primary alcohols to esters (Figure 4).[14] Murahashi and co-workers applied $RuH_2(PPh_3)_4$ for the synthesis of esters from primary alcohols with hydrogen as byproduct. The group also recorded impressive results on lactone formation from 1,4- and 1,5-diols (Figure 4).[16] Gauvin and co-workers studied P*H*NP ruthenium complexes for acceptorless dehydrogenative homocoupling of primary alcohols into esters (Figure 4).[17] Madsen and co-workers investigated ruthenium N-heterocyclic carbene complexes which were found to have good catalytic activities towards direct condensation of primary alcohols into esters and lactones with the release of hydrogen gas (Figure 4).[18] Dalton and co-workers recorded $OsH_4[HN(C_2H_4PiPr_2)_2]$ (C_2H_4 = ethene) as an efficient catalyst for the dehydrogenative homocoupling of primary alcohols into esters (Figure 4).[19] Gelman and co-workers developed a bifunctional dibenzobarrelene based Phosphorous Carbon Phosphorous ($PC_{sp3}P$) iridium pincer ligand and applied it for dehydrogenative homocoupling of primary alcohols to esters (Figure 4).[20]



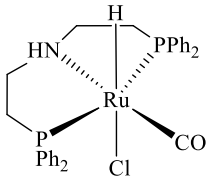
Milstein, D. *J. Am. Chem. Soc.* **2005**, *127* , 10840



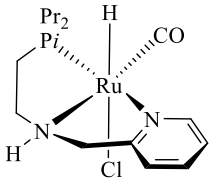
Milstein, D. *Adv. Synth. Catal.* **2010**, *352*, 3169



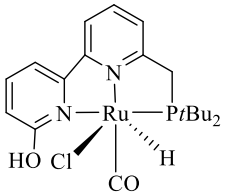
Milstein, D. *Adv. Synth. Catal.* **2012**, *354*, 2403



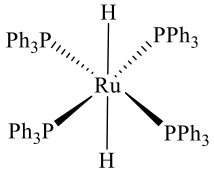
Beller, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 5711



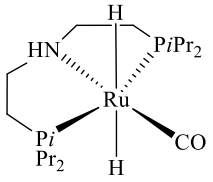
Gusev, D. G. *Angew. Chem. Int. Ed.* **2012**, *51*, 2772



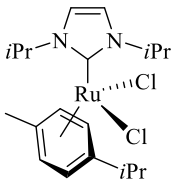
Vlugt, J. I. *Organometallics*, **2017**, *36*, 1541



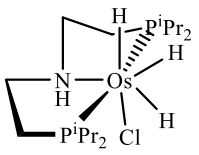
Murahashi, S. I. *J. Org. Chem.,* **1987**, *52*, 4319



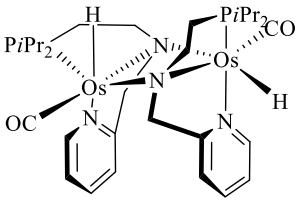
Gauvin, R. M. *ACS Catal*. **2018**, *8*, 4719



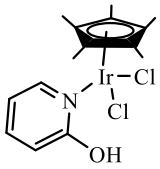
Madsen, R. *Organometallics*, **2011**, *30*, 6044



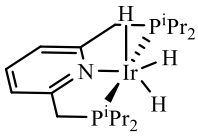
Moore, B. Dalton *Trans*. **2011**, *40*, 8941



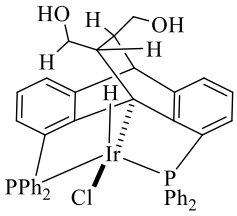
Gusev, D. G. *Angew. Chem. Int. Ed.* **2012**, *51*, 2772



Yemaguchi, R. *Org. Lett*. **2007**, *9*, 109



Beller, M. *Angew. Chem.* **2012**, *124*, 5809



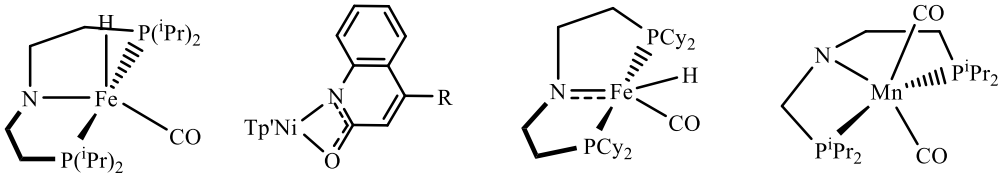
Gelman, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 3533

Figure 4. Precious metal-based catalysts for dehydrogenative homocoupling of alcohols to esters

1.5. Base Metal Catalysts in Dehydrogenative Homocoupling of Alcohols into Esters

With increasing concerns over health, environment and economic problems, replacement of precious, rare and toxic Ru, Ir, and Os metal catalysts with abundant, inexpensive and readily available less toxic base metals is necessary. However, dehydrogenative coupling supported by first row transition base metal catalyst is still challenging, and very few examples are found. Recently, there have been some developments in this direction.

Jones, Schneider and co-workers recorded catalytic PNP pincer ligand-supported iron complexes for dehydrogenation of primary alcohols to esters without any additives (Figure 5). Their group has recorded outstanding reactivity of benzyl alcohol with nearly full conversion to benzyl benzoate. They have proposed a probable mechanism where the intermediate aldehyde condenses with substrate alcohol resulting in a hemiacetal intermediate which undergoes dehydrogenation to yield an ester. The group has also recorded successful conversion of primary diols such as 1,2-benzenedimethanol and 1,5-pentanediol into their corresponding lactones.[23]



Jones, W. D. *ACS Catal.* **2014**, *4*, 3994

Jones W. D. *Organometallics* **2015**, *34*, 5203

Hazari, N. *ACS Catal.* **2015**, *5*, 2404

Gauvin, R. M. *ACS Catal.* **2017**, *7*, 2022

Figure 5. Base metal catalysts used for dehydrogenative homocoupling of alcohols to esters

A catalytic system based on TP'Ni(QR) (Tp' = tris(3,5-dimethylpyrazolyl) borate, Q = quinolinate, R = CF_3) was developed by Jones and co-workers and applied for

dehydrogenative homocoupling of benzyl alcohol to benzyl benzoate (Figure 5). The group has also recorded efficient conversion of 1,5-pentanediol into lactone.[24] Bernskoetter, Hazari, and co-workers developed a PNP pincer-stabilized iron complex and applied it for dehydrogenation of methanol to methyl formate (Figure 5).[25]

Recently, Gauvin and co-workers developed aliphatic PNP pincer-supported manganese(I) dicarbonyl complex and applied it for the acceptorless dehydrogenative coupling of various alcohols into their corresponding esters under base-free conditions (Figure 5). The reaction has been done under neat conditions, with modest catalyst loading (0.6 mol%) and releasing only hydrogen as a byproduct. The group has observed efficient conversion of alkyl and aryl alcohol substrates into their corresponding esters along with aliphatic diols into their corresponding lactones. They have also proposed a plausible mechanism where the intermediate aldehyde condenses with substrate alcohol resulting in a hemiacetal intermediate which undergoes dehydrogenation to give ester, similar to that reported by Jones, Schneider and co-workers.[26] All the esterification done above are based on sole catalytic activity of the metal complex. Use of co-catalyst for better yield at ordinary condition is still one of the new approaches in metal complex based esterification.

1.6. Objectives of Study

The objectives of the present study are:

1. To synthesize tripodal tetradentate $^{iPr}PPPN^{H}Py^{Me}$ ligand.
2. To develop cobalt complex using tripodal tetradentat ^{iPr}PPPNHPyMe ligand.
3. To use cobalt complex as an alternative to precious metal catalysts in acceptorless dehydrogenative homocoupling of primary alcohols to esters.
4. To perform mechanistic study of the esterification reaction.

CHAPTER II

EXPERIMENTAL METHODS

2.1. General Methods

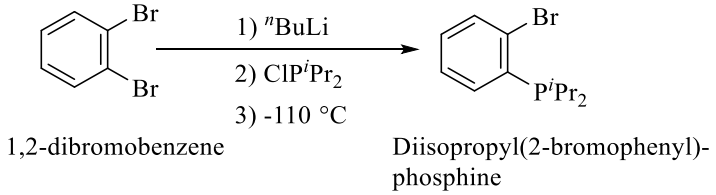
MBraun glovebox having N_2 atmosphere or standard Schlenk techniques with Ar atmosphere was used to carry out reactions. Deoxygenation of anhydrous solvents was done by sparging with dinitrogen. Drying of solvent was carried out by passing through a Pure Solv solvent purification system installed with activated alumina columns. Cambridge Isotope Lab was chosen as a vendor to buy $CDCl_3$. Molecular sieves (4 Å) were used to dry $CDCl_3$. Organic substrates were purchased from Oakwood Chemical or Fisher Scientific and used directly. Other required chemicals were bought from Sigma Aldrich and used directly. JEOL Unity 500 MHz spectrometer was used to record NMR spectra. Tetramethylsilane (0.00 ppm) was used as a reference and $CDCl_3$ as a solvent to record ^{1}H NMR spectra. Peak at 77.0 ppm due to $CDCl_3$ carbons was referenced for ^{13}C NMR. ^{19}F NMR spectra were referenced to fluorobenzene at –113.15 ppm. Hewlett-Packard 5890 GC (HP-5MS column, 30 m) with a flame ionization detector was used to analyze GC yield of products from catalytic experiments. Shimadzu QP2010S installed with auto sampler was used for gas chromatography mass spectral analysis. High resolution mass spectrometry analyses were performed on Waters GCT Premier orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer in positive EI method using MassLynx Software control.

2.2. Experimental Methods

2.2.1. Synthesis of Tripodal Tetradentate PPPN ligand and Cobalt Complexes

2.2.1.1. Synthesis of Diisopropyl(2-bromophenyl)phosphine

In a N_2 filled glovebox, a Schlenk flask (500 mL) was loaded with 1,2-dibromobenzene (4 g, 0.017 mol), diethyl ether (28.8 mL) and tetrahydrofurane (28.8 mL). The flask was taken out of glovebox and placed under Ar on a Schlenk line and cooled by an ethanol/liquid nitrogen bath at -110 °C. At maintained low bath temperature, n-butyl lithium (original 1.6 M solution in hexane, 10.6 mL, 0.017 mol) was added to the Schlenk flask dropwise for 15 min. The clear light yellow solution at the beginning was turned to a white slurry after around 30 minutes. Approximately, 5 minutes after the observation of white precipitate, chlorodiisopropyl phosphine (2.7 mL, 0.017 mol) was poured dropwisely over 15 minutes. The solution was turned into bright orange color, which was allowed to warm slowly to room temperature over 2 hours to obtain pale yellow slurry. Thus, obtained slurry was transferred to a 500 mL round bottom flask and volatiles were removed using rotavapor to obtain a sticky light-yellow solid. Pentane (25 mL) and silica gel (3 g) were added to the reaction mixture in the flask, which was stirred for 1 h, followed by filtration through celite. The celite plug was washed with pentane (8 mL) to minimize possible loss. A round bottom flask of 500 mL was used to collect the filtrate. Finally, the round bottom flask with filtrate was applied to rotavapor to obtain colorless thick oil as a product (3.94 g, yield = 85 %).[36]

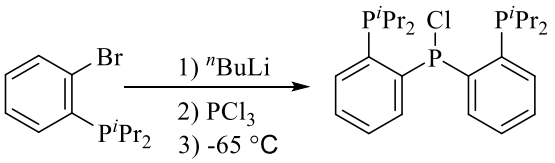


Scheme 3. Synthesis of Diisopropyl (2-bromophenyl)phosphine

2.2.1.2. Synthesis of Bis(2-diisopropylphosphinophenyl)chlorophosphine

In a N_2 filled glovebox, two 250 mL Erlenmeyer's flasks were taken and one was loaded with diisopropyl(2-bromophenyl)phosphine in diethyl ether (4 g, 0.015 mol, 28.8

mL diethyl ether) and other with trichlorophosphine in diethyl ether (642 µL, 0.007 mol + 8 mL diethyl ether). Both flasks were placed in a cool well at -65 °C set up inside the glovebox using dry ice and acetone. At maintained -65 °C temperature, n-butyl lithium (9.32 mL, 0.015 mol) was added to diisopropyl(2-bromophenyl)phosphine in diethyl ether dropwise with constant stirring for 15 minutes. The solution was changed into while slurry and the stirring was continued for at least 15 minutes. Eventually, the trichlorophosphine in diethyl ether on the other flask was transferred to the white slurry dropwise for 15 minutes, which converted white slurry to pale yellow solution. The resulted solution was taken out from the cold well and transferred into the umber bottle and stirred for a night at room temperature inside the glovebox. Next day, filtration was done through celite plug. The filtrate was sufficiently concentrated and kept inside the refrigerator for crystallization. The product was obtained in the form of light yellow crystals (2.58 g, yield = 76 %).[36]



Diisopropyl(2-bromophenyl)-phosphine

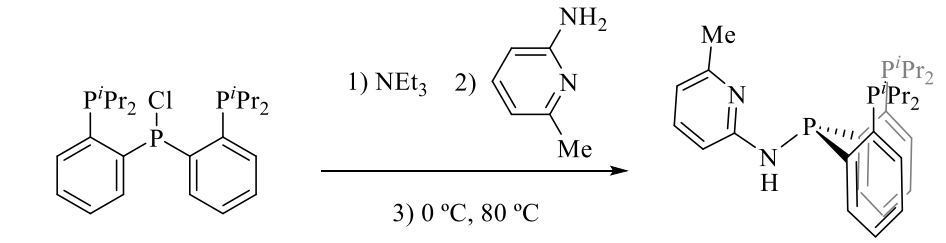
Bis(2-diisopropylphosphinophenyl)-chlorophosphine

Scheme 4. Synthesis of Bis(2-diisopropylphosphinophenyl)chlorophosphine

2.2.1.3. Synthesis of ^{iPr}PPPN^{H}Py^{Me} ligand

In a N_2 filled glovebox, a Schlenk flask (100 mL) was loaded with 2-amino-6-methyl pyridine (0.478 g, 0.004416 mol) and toluene (34 mL). NEt_3 (0.616 mL, 0.004416 mol) was added dropwise to the solution over 5 min. The flask was sealed with a rubber septum, taken out of glovebox and cooled at 0°C with ice bath. In the glovebox, bis(2-diisopropylphosphinophenyl)chlorophosphine (2 g, 0.004416 mol) was measured out and dissolved in toluene (15 mL). The solution was transferred into a 20 mL syringe and added

to the Schlenk flask under Ar flow dropwise over 15 min, and the mixture was warmed to room temperature. The rubber septum was replaced with a glass stopper and the reaction mixture was heated at 80 ºC for overnight. ^{31}PNMR was taken afterwards to confirm the completeness of the reaction. The mixture was filtered using Celite plug and the volatiles were removed by rotavap to a white solid. Colorless crystals were obtained through slow diffusion of pentane into diethyl ether solution of the crude product (1.85 g, yield 80%). The spectral data are in agreement with previously recorded.[36]



Bis(2-diisopropylphosphinophenyl)-chlorophosphine

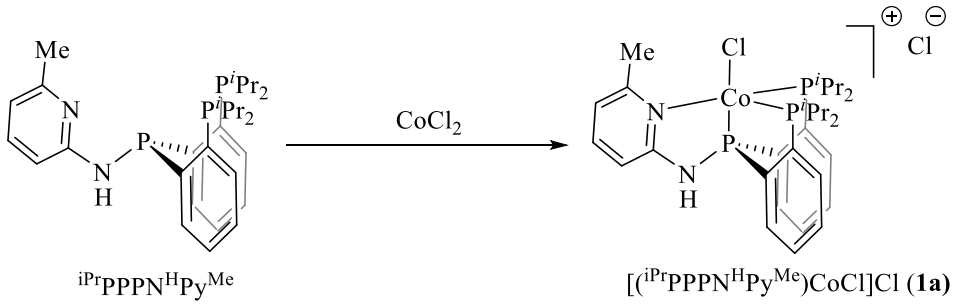
^{iPr}PPPN^{H}Py^{Me}

Scheme 5. Synthesis of ^{iPr}PPPN^{H}Py^{Me} ligand

2.2.1.4. Synthesis of [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a)**

In a N_2 filled glove box, $CoCl_2$ (0.248 g, 0.002 mol) was mixed with 20 mL tetrahydrofuran in Erlenmeyer's flask to make slurry. To the slurry of $CoCl_2$, solution of ^{iPr}PPPN^{H}Py^{Me} ligand (1 g, 0.002 mol) in tetrahydrofuran (20 mL) was added dropwise and the mixture was allowed to stirr for whole night at room temperature. To protect the loss of solvent, Erlenmeyer's flask was sealed with rubber cork. Next day, the reaction mixture was taken out from the glove box and the resulted red-orange slurry was poured into a 500 mL round bottom flask. Solvent was separated using rotavapor. The orange red solid settled at the bottom of round bottom flask was dissolved in methanol and filtered through celite plug to remove unreacted $CoCl_2$. The filtrate was concentrated to make saturated solution

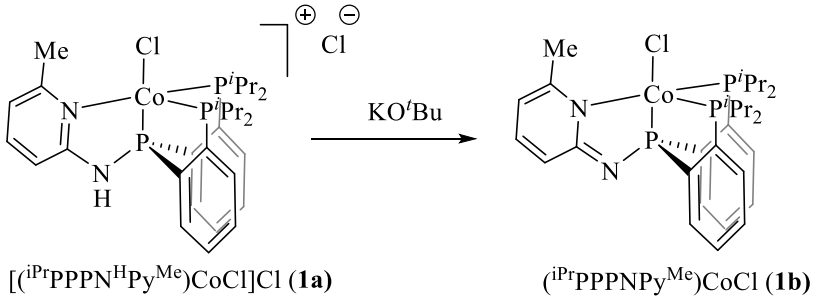
and crystals were grown using ether-methanol vapor diffusion method (1.110 g, yield 85%). The spectral data are in agreement with previously recorded.[36]



Scheme 6. Synthesis of [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a)**

2.2.1.5. Synthesis of ^{iPr}PPPNPy^{Me}CoCl (**1b)**

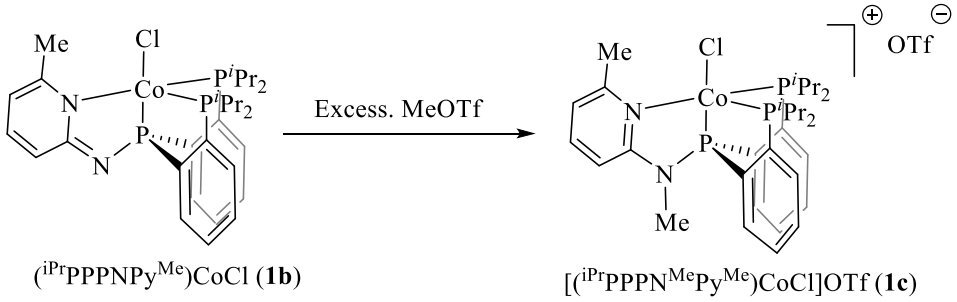
In a N_2 filled glovebox, 250 mL Erlenmeyer's flask was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (500 mg, 0.764 mmol), KO^{t}Bu (85.6 mg, 0.764 mmol) and 30 mL toluene. The resulted red slurry was stirred at room temperature for overnight. Next day, filtration was done using Celite plug and the filtrate was sufficiently concentrated under reduced pressure to grow crystals through pentane-toluene vapor diffusion method (382.43 mg, 81% yield). The spectral data are in agreement with previously recorded.[36]



Scheme 7. Synthesis of ^{iPr}PPPNPy^{Me}CoCl (**1b)**

2.2.1.6. Synthesis of [^{iPr}PPPN^{Me}Py^{Me}CoCl]OTf (**1c)**

In a N_2 filled glovebox, 250 mL Erlenmeyer's flask was loaded with ^{iPr}PPPNPy^{Me}CoCl (**1b**) (200 mg, 0.3245 mmol), THF (5 mL), and a solution of MeOTf (54.7 µL, 0.5 mmol) in THF (5 mL) was transferred dropwise with constantly stirring at maintained temperature of 0 °C. The resulted reaction mixture was further stirred at room temperature for overnight. Next day, the reaction mixture was concentrated enough under reduced pressure and crystals were grown using pentane-dichloromethane vapor diffusion method (173.7 mg, 71% yield). The spectral data are in good agreement with our previously reported results.[36]



(^{iPr}PPPNPy^{Me})CoCl (**1b**) [(^{iPr}PPPN^{Me}Py^{Me})CoCl]OTf (**1c**)

Scheme 8. Synthesis of [^{iPr}PPPN^{Me}Py^{Me}CoCl]OTf (**1c)**

2.2.2. Reaction Optimization taking Benzyl alcohol as a Model Substrate

2.2.2.1. General Considerations for optimization

Reaction set up was done inside the glove box with nitrogen environment. Different parameters like temperature, type of solvent, amount of solvent, amount of catalyst loading, amount of base loading, strength of base, duration of reaction time, and open or closed system for the reaction were considered.

2.2.2.2. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL Benzene, 105 °C Temperature and 100 mL Pressure Vessel

Inside a N_2 filled glovebox, an oven-dried 100 mL pressure vessel was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The vessel was sealed by a PTFE screw valve and taken out from the glove box. At 105°C, the reaction was heated for 24 h using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.3. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL Benzene, 105 °C Temperature and 15 ml Reaction tube with an Argon flow system

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 105°C, the reaction was heated for 24 h with an argon flow system using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.4. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon flow system

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon flow system using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.5. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.6. Dehydrogenative Homocoupling of Benzyl alcohol under 0.0 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.7. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 0.0 mol% KO^{t}Bu, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.8. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL Toluene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), toluene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.9. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL tetrahydrofuran, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), tetrahydrofuran (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.10. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KO^{t}Bu, 0.75 mL 1,4-dioxane, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), 1,4-dioxane (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.11. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% NaO^{t}Bu, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), NaO^{t}Bu (1.8 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.12. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% KOH, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KOH (1.1 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.2.13. Dehydrogenative Homocoupling of Benzyl alcohol under 1.25 mol % [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), 3.75 mol% K_2CO_3, 0.75 mL Benzene, 125 °C Temperature and 15 ml Reaction tube with an Argon filled balloon on top

Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), K_2CO_3 (2.6 mg, 3.75 mol %), benzene (0.75 mL) and benzyl alcohol (52 µL, 0.5 mmol). The tube was sealed by a screw cap with a PTFE septa and taken out from the glove box. At 125°C, the reaction was heated for 24 h with an argon filled balloon on top using oil bath inside the hood. At the end of the reaction, internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added by dissolving in diethyl ether. The resulted mixture was filtered through silica gel plug and solvent was evaporated under reduced pressure using rotavapor. A fraction of mixture was taken out and NMR analysis was done.

2.2.3. Study of Role of KO^{t}Bu and Plausible Mechanism for Dehydrogenative Homocoupling of Primary alcohols to Ester

2.2.3.1. Dehydrogenative Homocoupling of Benzyl Alcohol Catalyzed by ^{iPr}PPPNPy^{Me}CoCl (**1b**) and KO^{t}Bu

Inside a N_2 filled glovebox, an oven-dried 100 mL pressure vessel was loaded with cobalt complex ^{iPr}PPPNPy^{Me}CoCl (**1b**) (3.9 mg, 1.25 mol %), KO^{t}Bu (0 to 2.1 mg, 0 to 3.75 mol %), benzyl alcohol (0.5 mmol) and benzene (0.7 mL). The vessel was sealed with a PTFE screw valve and taken out from the glove box. At 125 °C, the reaction was heated for 24 h inside the hood. At the end of reaction, internal standard nitromethane (20 μL, 373 µmol) was added. A fraction of mixture was taken out, filtered through Celite, and NMR analysis was done.

2.2.3.2. Dehydrogenative Homocoupling of Benzyl Alcohol Catalyzed by [^{iPr}PPPN^{Me}Py^{Me}CoCl]OTf (**1c**) and KO^{t}Bu

Inside a N_2 filled glovebox, an oven-dried 100 mL pressure vessel was loaded with cobalt complex [^{iPr}PPPN^{Me}Py^{Me}CoCl]OTf (**1c)** (4.8 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), alcohol (0.5 mmol) and benzene (0.7 mL). The vessel was sealed with a PTFE valve and taken out from the glove box. At 125 °C, the reaction was heated for 24 h inside the hood. At the end of reaction, internal standard nitromethane (20 μL, 373 µmol) was added. A fraction of mixture was taken out, filtered through Celite, and NMR analysis was done.

2.2.3.3. KO^{t}Bu-Catalyzed Tishchenko Coupling of Benzaldehyde to Benzyl Benzoate

Inside a glovebox with nitrogen environment, a J-Young NMR tube was loaded with benzyl aldehyde (51 μL, 0.5 mmol), KO^{t}Bu (0.7 mg, 1.25 mol %), and benzene-d6 (0.5 mL). The tube was sealed by PTFE valve and taken out from the glove box. After 24 h at room temperature, it was subjected to NMR analysis.

2.2.3.4. KO^{t}Bu-Catalyzed Tishchenko Coupling of Benzaldehyde to Benzyl Benzoate in Presence of Benzyl Alcohol

Inside a N_2 filled glovebox, a 4 mL vial was loaded with KO^{t}Bu (0.7 mg, 1.25 mol %), benzene (0.4 mL), and benzyl alcohol (52 μL, 0.5 mmol). The mixture was stirred for 10 min, and benzaldehyde (51 μL, 0.5 mmol) was added. The reaction mixture was transferred to a 100 mL pressure vessel, and benzene (0.3 mL) was used to rinse the vial and combined to the mixture. The pressure vessel was sealed by a PTFE valve and taken out of the glove box. It was let to remain at room temperature for 24 h. After the reaction, nitromethane (20 μL, 373 µmol) was added. A fraction of mixture was taken out, filtered through Celite, and subjected to NMR analysis. The same reaction was repeated at 125 °C for 24 h.

2.2.3.5. [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a) /** KO^{t}Bu Catalyzed Dehydrogenative Homocoupling of Benzyl Alcohol in the Presence of Benzaldehyde

Inside a N_2 filled glovebox, a 4 mL vial was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.4 mL), and benzyl alcohol (52 μL, 0.5 mmol). The mixture was stirred for 10 min, and benzaldehyde (51 μL, 0.5 mmol) was added. The reaction mixture was transferred to a 100 mL pressure vessel, and benzene (0.3 mL) was used to rinse the vial and combined to the mixture. The pressure vessel was sealed by a PTFE valve and taken out of the glove box. At 125 °C, it was heated for 24 h inside the hood. After the reaction, nitromethane (20 μL, 373 µmol) was added. A

fraction of mixture was taken out, filtered through Celite, and subjected to NMR analysis. Yield of benzyl benzoate was calculated by treating both benzyl alcohol and benzyl aldehyde as substrates.

2.2.3.6. [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) / KO^{t}Bu Catalyzed Dehydrogenative Coupling of 4-Fluoro Benzyl Alcohol in the Presence of Benzaldehyde

Inside a N_2 filled glovebox, a 4 mL vial was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a)** (4.1 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzene (0.4 mL) and 4-fluoro benzyl alcohol (54 μL, 0.5 mmol). The mixture was stirred for 10 min, and benzaldehyde (51 μL, 0.5 mmol) was added. The reaction mixture was transferred to a 100 mL pressure vessel, and benzene (0.3 mL) was used to rinse the vial and combined to the mixture. The pressure vessel was sealed by a PTFE valve and taken out of the globe box. At 125 °C, it was heated for 24 h inside the hood. After the reaction, nitromethane (20 μL, 373 µmol) was added. A fraction of mixture was taken out, filtered through Celite, and subjected to NMR analysis.

2.2.3.7. Detection of H_2 as a Byproduct

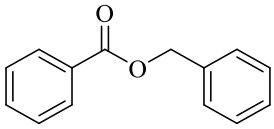
Inside a N_2 filled glovebox, an oven-dried 100 mL pressure vessel was loaded with cobalt complex [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 1.25 mol %), KOtBu (2.1 mg, 3.75 mol %), benzyl alcohol (0.5 mmol) and benzene (0.7 mL). The vessel was sealed by a PTFE valve and taken out of the glove box. At 125°C, it was heated for 24 h inside the hood. The headspace gas sample was taken by a needle syringe and detected by SRI 8610C Gas Chromatograph with a 5 Å molecular sieves column (Restek CP753415) with N2 carrier gas.

2.2.3.8. Homogeneity Test of the Reaction System

Inside a N_2 filled glovebox, a mixture of ^{iPr}PPPNPy^{Me}CoCl (**1b**) (3.9 mg, 1.25 mol %), KO^{t}Bu (2.1 mg, 3.75 mol %), benzyl alcohol (0.5 mmol) and benzene (0.7 mL) was loaded into a 100 mL pressure vessel and allowed to stir at room temperature. After 10 min., mercury (125 mg, 0.625 mmol) was added to the vessel, and sealed by a PTFE valve. The vessel was taken out of the globe box and heated for 24 hours at 125 °C inside the hood. After the reaction, nitromethane (20 μL, 373 µmol) was added to the reaction mixture. A fraction of mixture was taken out, filtered through Celite, and subjected to NMR analysis.

2.3. Synthetic Details and Characterization Data

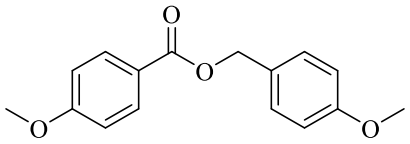
2.3.1. Synthesis of 1



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), benzyl alcohol (54.1 mg, 0.5 mmol), and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: >99%. The same reaction was repeated in 1 mmol substrate scale without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the

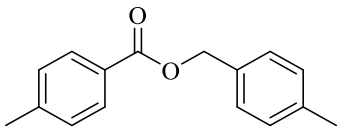
solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. Light yellow oil of 1 was isolated. Yield: 96.5 mg (91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.08 (d, *J* = 9.1 Hz, 2 H), 7.58–7.55 (t, *J* = 7.3 Hz, 1 H), 7.46–7.35 (m, 7 H), 5.38 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 136.2, 133.1, 130.2, 129.8, 128.7, 128.5, 128.3, 128.3, 66.8 ppm. The spectral data are in agreement with those previously recorded.[27]

2.3.2. Synthesis of 2



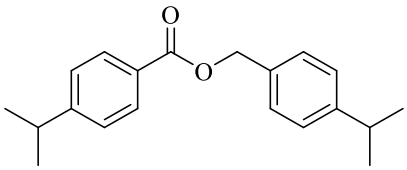
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), 4-methoxybenzyl alcohol (69.1 mg, 0.5 mmol), and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 81%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. Yellow oil of 2 was isolated. Yield: 49 mg (72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.9 Hz, 2 H), 7.38 (d, *J* = 8.9 Hz, 2 H), 6.89 – 6.92 (m, 4 H), 5.26 (s, 2 H), 3.85 (s, 3 H), 3.81 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 163.5, 159.7, 131.8, 130.1, 128.5, 122.8, 114.0, 113.7, 66.3, 55.5, 55.4 ppm. The spectral data are in agreement with those previously recorded.[27]

2.3.3. Synthesis of 3



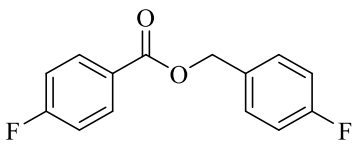
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), 4-methylbenzyl alcohol (61.1mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 79%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. Light yellow oil of 3 was isolated. Yield: 44.5 mg (74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 5.30 (s, 2 H), 2.40 (s, 3 H), 2.36 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 143.7, 138.1, 133.3, 129.8, 129.3, 129.1, 128.40, 127.6, 66.6, 21.8, 21.3 ppm. The spectral data are in agreement with those previously recorded.[27]

2.3.4. Synthesis of 4



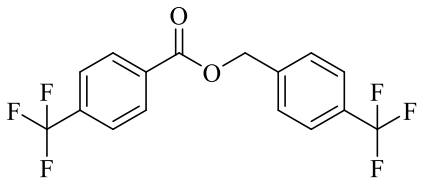
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), 4-isopropylbenzyl alcohol (75.1 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. An aliquot of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 92%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. Yellow oil of 4 was isolated. Yield: 57.8 mg (78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2 H), 7.38 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.24 (d, *J* = 8.1 Hz, 2 H), 5.33 (s, 2 H), 2.96 (sept, *J* = 7.0 Hz, 1 H), 2.92 (sept, *J* = 7.0 Hz, 1 H), 1.27 (d, *J* = 1.2 Hz, 6 H), 1.26 (d, *J* = 1.2 Hz, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 154.5, 149.0, 133.7, 130.0, 128.4, 127.9, 126.7, 126.5, 66.5, 34.3, 34.0, 24.1, 23.8 ppm. The spectral data are in agreement with those previously recorded.[28]

2.3.5. Synthesis of 5



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), 4-fluorobenzyl alcohol (63.1 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: >99%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate (1:10, v/v) as an eluent. Light yellow oil of 5 was isolated. Yield: 59.1 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10–8.06 (m, 2 H), 7.45–7.41 (m, 2 H), 7.13–7.05 (m, 4 H), 5.32 (s, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 165.5, 164.4 (d, *J* = 144.8 Hz), 161.8, 132.4 (d, *J* = 9.4 Hz), 131.8 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 8.3 Hz), 126.3, 115.7 (d, *J* = 21.8 Hz), 66.2 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ –105.18, –113.27 ppm. The spectral data are in agreement with those previously recorded.[27]

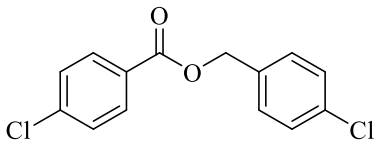
2.3.6. Synthesis of 6



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), 4-(trifluoromethyl) benzyl alcohol (88.1 mg, 0.5 mmol) and benzene (0.7

mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 95%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:15, v/v) as an eluent. White solid of 6 was isolated. Yield: 73.2 mg (84%). Melting point 57–58 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.56 (d, *J* = 8.2 Hz, 2 H), 5.45 (s, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 139.6, 134.9 (d, *J* = 31.5 Hz), 133.0, 130.1 (d, *J* = 31.5 Hz), 130.2, 128.4, 125.8 (q, *J* = 3.6 Hz), 125.6 (q, *J* = 3.6 Hz), 124.9 (d, *J* = 49.4 Hz), 122.7 (d, *J* = 49.4 Hz), 66.3 ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.51, –62.99 ppm. The spectral data are in agreement with those previously recorded.[27]

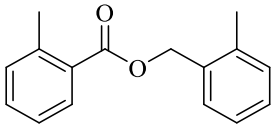
2.3.7. Synthesis of 7



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol %), 4-chlorobenzyl alcohol (71.3 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the

hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: >99%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:20, v/v) as an eluent. Greenish yellow solid of 7 was isolated. Yield: 64.7 mg (92%). Melting point 72–73 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 1 H), 7.39-7.35 (m, 4 H), 5.32 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) 165.6, 139.8, 134.4, 134.3, 131.2, 129.8, 129.0, 128.9, 128.4, 66.2 ppm. The spectral data are in agreement with those previously recorded.[27]

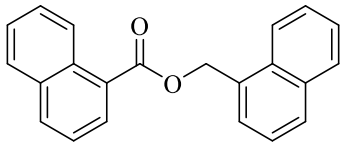
2.3.8. Synthesis of 8



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol %), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol %), 2-methyl benzyl alcohol (61.1 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. Light yellow oil of 8 was isolated. NMR yield: 52%. The same reaction was repeated, and 1,3,5-trimethoxy benzene (8.4 mg, 0.05 mmol) was added afterwards as an internal standard for GC analysis. GC yield 45%. GC-MS (m/z):

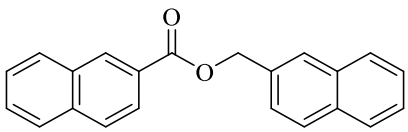
91($C_7H_7^+$), 105 ($C_8H_9^+$), 119 ($C_8H_7O^+$). The spectral data are in agreement with those previously recorded.[27]

2.3.9. Synthesis of 9



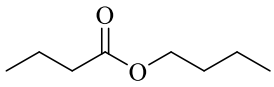
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol %), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol %), 1-naphthalenemethanol (79.1 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 19%. The same reaction was repeated, and 1,3,5-trimethoxy benzene (8.4 mg, 0.05 mmol) was added afterwards as an internal standard for GC analysis. GC yield 21%. GC-MS (m/z): 141($C_{11}H_9^+$), 155 ($C_{11}H_7O^+$), 312 ($C_{22}H_{16}O_2^+$). The spectral data are in agreement with those previously recorded.[27]

2.3.10. Synthesis of 10



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol %), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol %), 2-naphthalenemethanol (79.1 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 91%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:20, v/v) as an eluent. White solid of 10 was isolated. Yield: 69.5 mg (89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (apt. s, 1 H), 8.12 (apt dd, *J* = 8.1, 1.6 Hz, 1 H), 7.96 (s, 1H), 7.95 (s, 1H), 7.89 (m, 5H), 7.62 (m, 2H), 7.55 (m, 1H), 7.51 (m, 2H), 5.60 (s, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 135.7, 133.6, 133.4, 133.3, 132.6, 131.4, 129.5, 128.6, 128.4, 128.3, 128.1, 127.9, 127.9, 127.6, 127.5, 126.8, 126.5, 126.4, 126.1, 125.4, 67.2 ppm. The spectral data are in agreement with those previously recorded.[29]

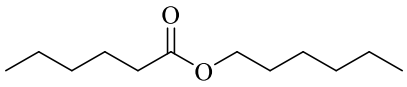
2.3.11. Synthesis of 11



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol%), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol%), 1-butanol (37.1 mg, 0.5 mmol) and THF (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was

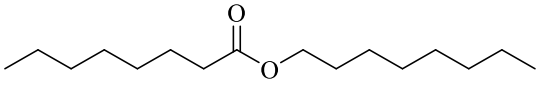
attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 62%. The same reaction was repeated, and 1,3,5-trimethoxy benzene (8.4 mg, 0.05 mmol) was added afterwards as an internal standard for GC analysis. GC yield 61%. GC-MS (m/z): 56 ($C_4H_8^+$), 71 ($C_4H_7O^+$), 89 ($C_4H_9O_2^+$). The spectral data are in agreement with those previously recorded.[32]

2.3.12. Synthesis of 12



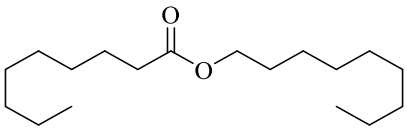
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol %), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol%), 1-hexanol (51.1 mg, 0.5 mmol) and toluene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top and heated at 140 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 81%. The same reaction was repeated, and 1,3,5-trimethoxy benzene (8.4 mg, 0.05 mmol) was added afterwards as an internal standard for GC analysis. GC yield 82%. GC-MS (m/z): 84 ($C_6H_{12}^+$), 99 ($C_6H_{11}O^+$), 117 ($C_6H_{13}O_2^+$). The spectral data are in agreement with those previously recorded.[31]

2.3.13. Synthesis of 13



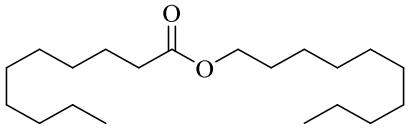
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol%), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol%), 1-octanol (65.1 mg, 0.5 mmol) and toluene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the box. An argon balloon was attached on the top and heated at 140 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 86%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of 13 was isolated. Yield: 50.6 mg (79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (t, 2 H), 2.26 (t, 2 H), 1.59 (m, 4H), 1.27 (m, 18H), 0.86 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 63.2, 33.2, 30.6, 30.5, 28.0, 27.9, 27.8, 27.5, 24.8, 23.9, 21.5, 21.4 ppm. The spectral data are in agreement with those previously recorded.[27]

2.3.14. Synthesis of 14



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol%), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol%), 1-nonanol (72.1 mg, 0.5 mmol) and toluene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the box. An argon balloon was attached on the top and heated at 140 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 83%. The same reaction was repeated, and 1,3,5-trimethoxy benzene (8.4 mg, 0.05 mmol) was added afterwards as an internal standard for GC analysis. GC-MS (m/z): 126 ($C_9H_{18}^+$), 141 ($C_9H_{17}O^+$), 159 ($C_9H_{19}O_2^+$). The spectral data are in agreement with those previously recorded.[33]

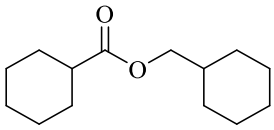
2.3.15. Synthesis of 15



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol%), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol%), 1-decanol (79.1 mg, 0.5 mmol) and toluene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the box. An argon balloon was attached on the top and heated at 140 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 80%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude

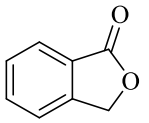
mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. Colorless oil of 15 was isolated. Yield: 56.2 mg (72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (t, 2 H), 2.26 (t, 2 H), 1.59 (m, 4H), 1.24 (m, 26H), 0.86 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 64.4, 34.5, 32.0, 31.9, 29.6, 29.5, 29.3, 29.2, 28.7, 26.0, 25.1, 22.7, 14.1 ppm. The spectral data are in agreement with those previously recorded.[32]

2.3.16. Synthesis of 16



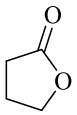
Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was charged with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol %), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol %), cyclohexylmethanol (57.1 mg, 0.5 mmol) and toluene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top and heated at 140 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 67%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:20, v/v) as an eluent. Light yellow oil of 16 was isolated. Yield: 64.4 mg (58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.87 (d, J = 6.5 Hz, 2H), 2.28 (m, J = 10.8, 3.6 Hz, 1H), 1.91 (m, J = 12.6 Hz, 2H), 1.80–1.60 (m, 9H), 1.50–1.38 (m, 2H), 1.34–1.33 (m, 6H), 0.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.3, 69.4, 43.4, 37.3, 29.8, 29.2, 26.5, 25.9, 25.8, 25.6 ppm. The spectral data are in agreement with those previously recorded.[27]

2.3.17. Synthesis of 17



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (4.1 mg, 6.25 µmol, 1.25 mol %), KO^{t}Bu (2.1 mg, 18.75 µmol, 3.75 mol%), benzene-1,2-dimethanol (69.1 mg, 0.5 mmol) and benzene (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: >99%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. White solid of 17 was isolated. Yield: 63.3 mg (93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.5 Hz, 1 H), 7.69 (apt. t, J = 7.5 Hz, 1 H), 7.49–7.56 (m, 2 H), 5.33 (s, 2 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 146.6, 134.1, 129.1, 125.9, 125.8, 122.2, 69.7 ppm. The spectral data are in agreement with those previously recorded.[34]

2.3.18. Synthesis of 18



Inside a N_2 filled glovebox, an oven-dried 15 mL reaction tube was loaded with cobalt complex [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) (8.2 mg, 12.5 µmol, 2.5 mol %), KO^{t}Bu (4.2 mg, 37.5 µmol, 7.5 mol %), 1,4-butanediol (45.1 mg, 0.5 mmol) and THF (0.7 mL). The tube was sealed by a screw cap fitted with a PTFE septa and taken out of the glove box. An argon balloon was attached on the top. The reaction was carried out at 125 °C for 24 h inside the hood. After 24 h, nitromethane (20 µL, 373 µmol) was added to the reaction mixture. A fraction of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 96%. The same reaction was repeated without adding an internal standard in order to obtain isolated yield. At the end of the reaction, the solvent was removed using rotavapor and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, v/v) as an eluent. Colorless oil of 18 was isolated. Yield: 36.2 mg (82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 (t, 2 H), 2.39 (t, 2 H), 2.18 (quint, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9, 68.6, 27.8, 22.2 ppm. The spectral data are in agreement with those previously recorded.[35]

CHAPTER III

RESULT AND DISCUSSION

3.1. Synthesis of Tripodal Tetradentate $^{iPr}PPPN^{H}Py^{Me}$ Ligand and Development of Cobalt Complexes

Ligand design is one of the crucial factors which determines the catalytic property of the metal complexes. Catalytic activity of base metal complexes for dehydrogenative coupling of primary alcohols to esters is rare and very few examples are available. Of these few cases, most of them are dominated by tripodal pincer type ligands (Figure 5). Also, those esterifications are solely based on catalytic activity of the metal complex. Reactions based on use of co-catalyst for better yield is not reported.

To develop a first row transition metal catalyst, tripodal tetradentate $^{iPr}PPPN^{H}Py^{Me}$ ligand was synthesized and applied for Co complex formation. This multidentate ligand is installed with strong field phosphine donors to stabilize low-spin metal centers. It can act as tetradentate or tridentate ligand due to flexible pendant arms which could regulate substrate accessibility to the active site and thereby control reactivity. Since the substituents on the phosphine and nitrogen donor can be varied, the electronic and steric properties of the ligands can be adjusted. Since, N-H spacer is installed between phosphine and nitrogen binding sites, it may cooperate with the metal to activate the substrate through Metal Ligand Cooperativity (MLC) (Scheme 5).[36]

The tripodal tetradentate $^{iPr}PPPN^{H}Py^{Me}$ ligand was synthesized through a three step process. Initially, 1,2-dibromobenzene was treated with 1 equiv. of n-butyllithium followed by diisopropylchlorophosphine to obtain diisopropyl(2-bromophenyl)phosphine in 85% yield (Scheme 3). In the second step, 2 equivalent of diisopropyl(2-

bromophenyl)phosphine was allowed to react with 1 equivalent of n-butyllithium followed by trichlorophosphine to obtain bis[2-(diisopropylphosphinophenyl)]chlorophosphine in 76% yield (Scheme 4). Eventually, in the final step, 2-amino-6-methylpyridine was treated with triethylamine and reacted with bis[2-(diisopropylphosphinophenyl]chlorophosphine to form $^{iPr}PPPN^{H}Py^{Me}$ in 80% yield (Scheme 5).[36]

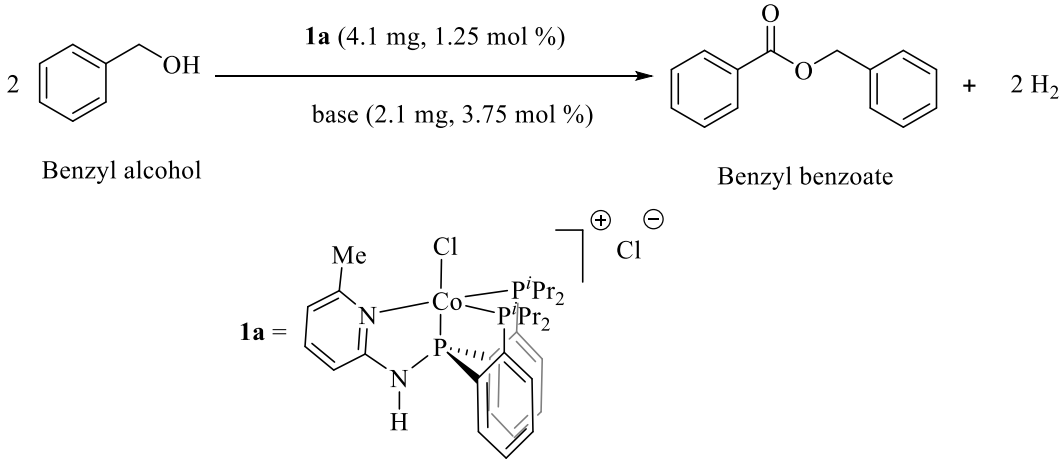
The metal complex [$^{iPr}PPPN^{H}Py^{Me}CoCl$]Cl (**1a**) was obtained by treating ligand $^{iPr}PPPN^{H}Py^{Me}$ with 1 equivalent of $CoCl_2$ in the presence of THF as solvent at room temperature. A red powder was obtained in 85% yield (Scheme 6). The reaction of [$^{iPr}PPPN^{H}Py^{Me}CoCl$]Cl (**1a**) with 1 equivalent of KO^{t}Bu in toluene at room temperature afforded $^{iPr}PPPN^{H}Py^{Me}CoCl$ (**1b**) with good yield of 81% (Scheme 7). The metal complex [$^{iPr}PPPN^{H}Py^{Me}CoCl$]OTf (**1c**) was obtained by treating $^{iPr}PPPN^{H}Py^{Me}CoCl$ (**1b**) with excess MeOTf at room temperature in a yield of 71% (Scheme 8).[36]

3.2. Reaction Optimization

Reaction optimization was carried out taking benzyl alcohol as a model substrate and [$^{iPr}PPPN^{H}Py^{Me}CoCl$]Cl (**1a**) as a catalyst for dehydrogenative homocoupling to benzyl benzoate (Scheme 9). To optimize a reaction, conditions like temperature, type of reaction vessel, and closed or open environment of reaction system are mainly considered. Optimization was started at 105°C in a closed 100 mL pressure vessel with nitrogen environment and only a 37% yield was recorded (Table 1, entry 1). When the reaction was repeated in a 15 mL reaction tube with an argon in and out flow system, a slightly better 46% yield was recorded (Table 1, entry 1). Eventually, a highly improved yield of 93% was obtained after increasing the temperature to 125 °C for 15 mL reaction tube with an argon in and out flow system, but some percentage of solvent was evaporated (Table 1, entry 2). As a midway, the reaction was repeated with an argon filled balloon on the top of

a 15 mL reaction tube, and an exciting almost quantitative esterification to benzyl benzoate was recorded (Table 1, entry 2).

Control reactions were carried out for further verification of the optimized reaction conditions. Without cobalt complex, esterification was not observed showing the need of cobalt complex for esterification (Table 1, entry 3). Since, no esterification was recorded without base, it also has a significant role for esterification (Table 1, entry 4). When the solvent benzene was replaced with toluene or THF or 1,4-dioxane, decreased yields (61%, 58%, and 42%, respectively) were recorded (Table 1, entries 5 to 7). Bases like KO^{t}Bu and NaO^{t}Bu were found to be more efficient bases for esterification than KOH and K_2CO_3 (Table 1, entries 8 to 10). Thus, an optimized condition of KO^{t}Bu or NaO^{t}Bu as a base, benzene as a solvent and 125 °C temperature was recorded. A 15 mL reaction tube with argon filled balloon on top was determined as a method of reaction for the best yield.



Scheme 9. Dehydrogenative homocoupling of benzyl alcohol to benzyl benzoate

Table 1. Optimization of reactions for dehydrogenative homocoupling of benzyl alcohol to benzyl benzoate[a]

Entry	Catalyst	Base	Solvent	Temperature (°C)	Yield (%)[b]
1	**1a**	KO^{t}Bu	Benzene	105	37[c], 46[d]
2	**1a**	KO^{t}Bu	Benzene	125	93[d], >99, 91[e]
3	…	KO^{t}Bu	Benzene	125	0
4	**1a**	…	Benzene	125	0
5	**1a**	KO^{t}Bu	Toluene	125	61
6	**1a**	KO^{t}Bu	THF	125	58
7	**1a**	KO^{t}Bu	1,4-dioxane	125	42
8	**1a**	NaO^{t}Bu	Benzene	125	92
9	**1a**	KOH	Benzene	125	44
10	**1a**	K_2CO_3	Benzene	125	0

[a]Reaction conditions: alcohol (0.5 mmol), **1a** (1.25 mol%), KO^{t}Bu (3.75 mol%), and solvent (0.7 mL) were heated in a 15 mL reaction tube with an argon balloon on the top for 24 h. [b]Yield was determined by ^{1}H NMR. [c]Reaction was run in a 100 mL pressure vessel. [d]Reaction was run in a 15 mL reaction tube under argon flow. [e]Isolated yield

3.3. Catalytic Dehydrogenative Homocoupling of Various Primary Alcohols to Esters

After having identified optimized conditions, various primary alcohol substrates were examined for dehydrogenative homocoupling to esters. At first, aromatic primary alcohols having electron releasing groups like −OMe,−Me, and −iPr at para position were carried out for esterification and a smooth reactivity with an isolated yield of 72% to 78% was recorded (Table 2, entry 2 to 4). In addition, primary aromatic alcohol substrates with an electron withdrawing group like −F, −Cl, and −CF_3 at para position also showed excellent reactivity and converted to their corresponding esters with an isolated yield of 84% to 95% (Table 2, entry 5 to 7). As expected, slightly lower yields were obtained from sterically hindered substrates like 2-methyl benzyl alcohol (NMR yield of 52%) and 1-naphthalenemethannol (NMR yield of 19%) (Table 2, entry 8 and 9). In contrast, a highly improved isolated yield of 89% was obtained from 2-naphthalenemethanol (Table 2, entry

10). Interestingly, significant yields were obtained from aliphatic primary alcohols (NMR yield of 62% to 80%) though slightly increased base/catalyst loading and temperature were required (Table 2, entry 11 to 16). Diols substrates like benzene-1,2-dimethanol and 1,4-butanediol also reacted well (isolated yields of 93% and 82% respectively) and converted to their corresponding lactones as expected (Table 2, entry 17 and 18).

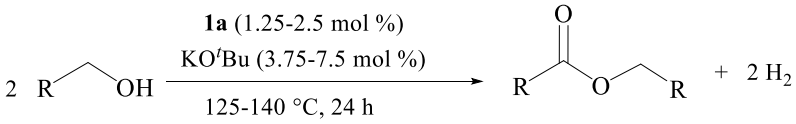
3.4. Mechanistic Study

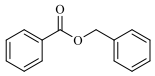
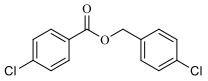
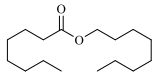
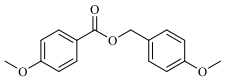
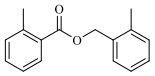
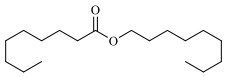
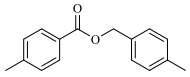
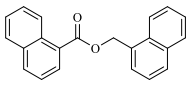
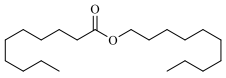
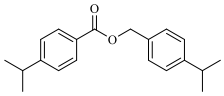
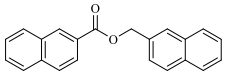
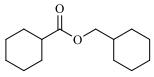
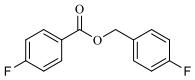
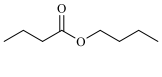
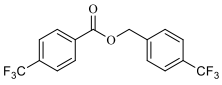
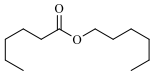
3.4.1. Roles of Base (KO^tBu) and Probable Mechanism in Esterification of Alcohols

The role of KO^tBu was studied by carrying out reactions loaded with various ratios of complex $^{iPr}PPPNPy^{Me}CoCl$ (**1b)** and KO^tBu (Table 3, entry 1 to 5). The complex **1b** was synthesized by treating $[^{iPr}PPPN^{H}Py^{Me}CoCl]Cl$ (**1a**) with 1 equivalent of KO^tBu at room temperature in presence of solvent THF (Scheme 7).

Without KO^tBu, esterification was not observed (Table 3, entry 1). An interesting observation of 4% yield was found when 1 equivalent of KO^tBu (1.25 mol%) was used for esterification (Table 3, entry 2). This observation is due to the presence of an amount of KO^tBu only sufficient to activate the Co precatalyst.[36] The activated Co precatalyst may not be sufficient to complete all necessary steps for esterification, thus only 4% yield was observed. The exciting result of 88% yield with 2.5 mol% KO^tBu (Table 3, entry 3) showed other important roles of base KO^tBu in addition to precatalytic activation.

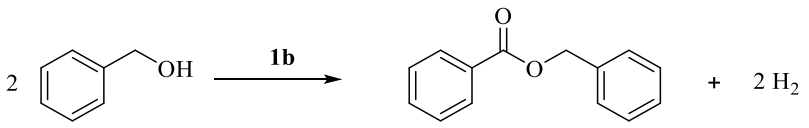
Table 2. Dehydrogenative homocoupling of primary alcohols catalyzed by cobalt complex and KO^{t}Bu[a,]



Entry	Product	Entry	Product	Entry	Product
1	 **1**, >99% (91%)	7	 **7**, >99% (92%)	13	 **13**^{e}, 86% (79%)
2	 **2**, 81% (72%)	8	 **8**^{d}, 52%, 45%^{c}	14	 **14**^{e}, 83%, 85%^{c}
3	 **3**, 79% (74%)	9	 **9**^{d}, 19%, 21%^{c}	15	 **15**^{e}, 80% (72%)
4	 **4**, 92% (78%)	10	 **10**^{d}, 91% (89%)	16	 **16**^{e}, 67% (58%)
5	 **5**, >99% (95%)	11	 **11**^{f}, 62%, 61%^{c}	17	 **17**, >99% (93%)
6	 **6**, 95% (84%)	12	 **12**^{e}, 81%, 82%^{c}	18	 **18**^{f}, 96% (82%)

[a]Reaction conditions: alcohol (0.5 mmol), **1a** (1.25 mol %), KOtBu (3.75 mol %), benzene (0.7 mL) were heated in 15 mL reaction tube with argon balloon on top at 125 °C for 24 h. [b]Yields were determined by ^{1}H NMR with nitromethane as internal standard. Isolated yields are in brackets. [c]Yield was determined by GC. [d]Reaction was run with **1a** (2.5 mol %) and KOtBu (7.5 mol %) at 125 °C for 24 h. [e]Reaction was run in toluene (0.7 mL) with **1a** (2.5 mol %) and KOtBu (7.5 mol %) at 140 °C for 24 h. [f]Reaction was run in THF (0.7 mL) with **1a** (2.5 mol %) and KOtBu (7.5 mol %) at 125 °C for 24 h.

Table 3. Effect of KO^{t}Bu loadings on dehydrogenative homocoupling of benzyl alcohol to benzyl benzoate[a,b]

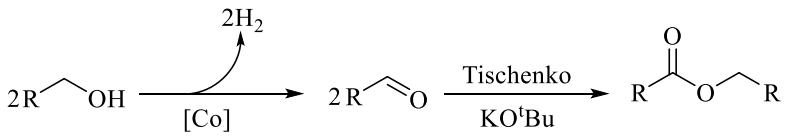


Entry	**1b**. (mol%)	KO^{t}Bu (mol%)	Yield[b] (%)
1	1.25	0	0
2	1.25	1.25	4
3	1.25	2.5	88
4	1.25	3.125	94
5	1.25	3.75	92

[a]Reaction conditions: benzyl alcohol (0.5 mmol), **1b** (1.25 mol%), KO^{t}Bu, benzene (0.70 mL) were heated in 100 mL pressure vessel, 125 °C, 24 h. [b]NMR yield using nitromethane as internal standard.

The esterification reactions were observed with small amounts of aldehydes as biproducts. It was observed that KO^{t}Bu itself can mediate Tishchenko coupling of aldehydes to esters at ordinary conditions (Section 2.2.3.3, NMR yield 84%), which was also observed by Berke and co-workers.[37] An interesting result of trace esterification was noted when a reaction was set up adding 1 equivalent of alcohol to aldehyde at room temperature, showing inverse effect of alcohol towards Tishchenko coupling (Section 2.2.3.4, Yield 3%). This observation contrasted with dehydrogenative coupling of alcohols catalyzed by Ru alkoxide system as reported by Gauvin et al. where alcohol is not detrimental to the yield, hence Tishchenko pathway is postulated.[17] However, as the reaction was set up at 125 °C, an improved yield of 67% was recorded showing the possibility of the Tishchenko pathway (Section 2.2.3.4).

In contrast, Beller et al. have observed a poisoning effect of aldehyde on the Ru catalyst system during esterification of ethanol and propose a mechanism with an intermediate hemiacetal which is eventually dehydrogenated by Ru complex to give ester.[12] However, a 61% yield of an ester was recorded using an equimolar mixture of benzyl alcohol and benzaldehyde in the Co/KO^{t}Bu catalytic system, showing less poisoning effects of aldehydes to the Co system (Section 2.2.3.5). This observation was further supported by a reaction where equimolar mixture of 4-fluoro benzyl alcohol and benzaldehyde gave four different esters from homo- and cross-couplings. In addition, benzyl alcohol was also recorded because of hydrogen transfer from the catalytic system (Section 2.2.3.6). Considering the above experimental evidence, a possible route where Co-catalyzed dehydrogenation of alcohol to intermediate aldehyde followed by condensation of aldehyde to ester by a Tishchenko pathway catalyzed by KO^{t}Bu can be proposed. However, a pathway where base might mediate the generation of a hemiacetal species,[12] followed by dehydrogenation assisted by Co catalyst to the final ester product cannot be completely ruled out.



Scheme 10. Probable pathway for dehydrogenative homocoupling of alcohols to esters

3.4.2. Study of Catalyst Activation Process

To study the catalyst activation process, complex ^{iPr}PPPNPy^{Me}CoCl (**1b**) was applied for dehydrogenative homocoupling of benzyl alcohol to benzyl benzoate in the presence of 2 equivalent of KO^{t}Bu (Table 3, entry 3), and comparable activity towards esterification as [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a)** was recorded. This observation showed that ^{iPr}PPPNPy^{Me}CoCl **(1b)** might be in the pathway for generation of actual catalyst.

3.4.3. Study of Metal Ligand Cooperativity (MLC)

The catalytic activity of the metal complex can be greatly affected through metal ligand cooperativity (MLC). Ligand can undergo reversible structural changes during substrate activation and product formation and can coordinate with the metal center which affects the catalytic activity.[38] To study possible metal ligand cooperativity due to the N-H linker present in [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**), a complex [(^{iPr}PPPN^{Me}Py^{Me})CoCl]OTf (**1c**) with N-Me was synthesized (Scheme 8), and applied for esterification of benzyl alcohol (Section 2.2.3.2). A high yield of 92% of the ester product was recorded which is close to those obtained from [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl (**1a**) and ^{iPr}PPPNPy^{Me}CoCl (**1b**). This result indicated that the N–H linker might not participate in the catalytic activity of the Co complex towards esterification.

3.4.4. Detection of H_2 as a Byproduct

To prove formation of a H_2 as byproduct, GC analysis of the head space gas after the reaction was carried out. A chromatogram peak with 1.235 retention time confirmed the generation of H_2 as a byproduct.

3.4.5. Homogeneity Test of the Reaction System

To test homogeneity of the reaction system, esterification of benzyl alcohol was carried out in presence of 100 equivalent mercury with respect to complex ^{iPr}PPPNPy^{Me}CoCl (**1b**) **(**Section 2.2.3.8).[39,40] The product analysis showed a yield of 93% suggesting no negative effect on the reactivity, indicating a homogeneous catalytic system.

CHAPTER IV

CONCLUSION

A catalytic system of Co supported by $^{iPr}PPPN^{H}Py^{Me}$ ligand and KO^{t}Bu was developed for efficient transformation of primary aliphatic and aromatic alcohols to esters. Aromatic primary alcohols with electron releasing groups at para position reacted well to convert into their corresponding esters. Aromatic substrates with electron withdrawing groups at para position presented outstanding reactivity and almost fully converted into their corresponding esters. The catalytic system was also successful for esterification of aliphatic primary alcohols with satisfactory yield. A conversion of diols into lactones was also recorded with very good yield. This method is economical, oxidant free, acceptor free, and environmentally benign compared to conventional methods.

The mechanistic study showed a two-step pathway for esterification. In the first step, Co assisted dehydrogenation of alcohols into intermediate aldehydes with the release of hydrogen gas as byproduct. In the second step, KO^{t}Bu mediates Tishchenko coupling of intermediate aldehydes to form esters. In addition, the base KO^{t}Bu was found to play a very important role in Co precatalyst activation.

It is expected that in the near future, this study will contribute to the development of green catalysis and advanced catalyst design with less toxic, inexpensive and earth-abundant transition metals.

REFERENCES:

1. Larock, R. C. *Comprehensive Organic Transformations*, VCH: New York, **1989**.
2. Ogliaruso, M. A.; Wolfe, J. F. *Synthesis of Carboxylic Acids, Esters and Their Derivatives*; John Wiley & Sons Ltd: Hoboken, NJ, **1991**.
3. Riemenschneider, W.; Bolt, H. M. *Esters, Organic Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH, Weinheim, **2005**.
4. Gunanathan, C.; Milstein, D. *Science* **2013**, *341*, 249−260.
5. Corma, A.; Nemeth, L. T.; Renz, M.; Valencia, S. *Nature* **2001**, *412*, 423−425.
6. Crabtree, R. H. *Chem. Rev*. **2017**, *117*, 9228−9246.
7. Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. *Chem. Soc. Rev*. **2018**, *47*, 1459−1483.
8. Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. J. *Am. Chem. Soc*. **2005**, *127*, 10840−10841.
9. Gnanaprakasam, B.; BenDavid, Y.; Milstein, D. *Adv. Synth. Catal.* **2010**, *352*, 3169−3173.
10. Blum, Y.; Shvo, Y. *J. Organomet. Chem*. **1985**, *282*, C7−C10.
11. Srimani, D.; Balaraman, E.; Gnanaprakasam, B.; Ben-David, Y.; Milstein, D. *Adv. Synth. Catal.* **2012**, *354*, 2403−2406.
12. Nielsen, M.; Junge, H.; Kammer, A.; Beller, M. *Angew. Chem., Int. Ed*. **2012**, *51*, 5711−5713.
13. Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem., Int. Ed*. **2012**, *51*, 2772−2775.
14. de Boer, S. Y.; Korstanje, T. J.; La Rooij, S. R.; Kox, R.; Reek, J. N. H.; van der Vlugt, J. I. *Organometallics*, **2017**, *36*, 1541−1549.
15. Sahoo, A. R.; Jiang, F.; Bruneau, C.; Sharma, G. V. M; Suresh, S.; Roisnel, T.; Dorcet, V.; Achard, M. *Catal. Sci. Technol*. **2017**, *7*, 3492−3498.
16. Murahashi, S.-I.; Naota, T.; Ito, K.; Maeda, Y.; Taki, H. *J. Org. Chem*. **1987**, *52*, 4319−4327.
17. Nguyen, D. H.; Trivelli, X.; Capet, F.; Swesi, Y.; Favre-Reguillon, A.; Vanoye, L.; Dumeignil, F.; Gauvin, R. M.́ *ACS Catal*. **2018**, *8*, 4719−4734.
18. Sølvhøj, A.; Madsen, R. *Organometallics*, **2011**, *30*, 6044−6048.

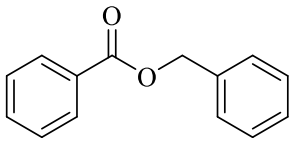
19. Bertoli, M.; Choualeb, A.; Gusev, D. G.; Lough, A. J.; Major, Q.; Moore, B. *Dalton Trans.* **2011**, *40*, 8941−8949.
20. Musa, S.; Shaposhnikov, I.; Cohen, S.; Gelman, D. *Angew. Chem., Int. Ed*. **2011**, *50*, 3533−3537.
21. Fijuta, K.; Tanino, N.; Yemaguchi, R. *Org. Lett*. **2007**, *9*, 109-111.
22. Nielsen, M.; Junke, H.; Beller, M. *Angew. Chem*. **2012**, *124*, 5809-5811.
23. Chakraborty, S.; Lagaditis, P. O.; Förster, M.; Bielinski, E. A.; Hazari, N.; Holthausen, M. C.; Jones, W. D.; Schneider S. *ACS Catal*. **2014**, *4*, 3994−4003.
24. Chakraborty, S.; Piszel, P. E.; Brennessel, W. W.; Jones, W. D. *Organometallics*, **2015**, *34*, 5203−5206.
25. Bielinski, E. A.; Förster, M.; Zhang, Y.; Bernskoetter, W. H.; Hazari, N.; Holthausen, M. C. *ACS Catal*. **2015**, *5*, 2404–2415.
26. Nguyen, D. H.; Trivelli, X.; Capet, F.; Paul, J. F.; Dumeignil, F.; Gauvin, R. M. *ACS Catal.* **2017**, *7*, 2022–2032.
27. Song, T.; Park, J. E.; Chung, Y. K. *J. Org. Chem*. **2018**, *83*, 4197–4203.
28. Zhu, Y.; Wei, Y. *Eur. J. Org. Chem*., **2013**, *21*, 4503–4508.
29. Doi, R.; Kikushima, K.; Ohashi, M.; Ogoshi, S. *J. Am. Chem. Soc*. **2015**, *137*, 3276–3282.
30. Ding, K.; Xu, S.; Alotaibi, R.; Paudel, K.; Reinheimer, E. W.; Weatherly, J. *J. Org. Chem*. **2017**, *82*, 4924–4929.
31. Gianetti, T. L.; Annen, S. P.; Santiso-Quinones, G.; Reiher, M.; Driess, M.; Grüetzmacher, H. *Angew. Chem. Int. Ed.* **2016**, *55*, 1854–1858.
32. Zhang, J.; Balaraman, E.; Leitus, G.; Milstein, D. *Organometallics* **2011**, *30*, 5716–5724.
33. Ortega, N.; Richter, C.; Glorius, F. *Org. Lett*. **2013**, *15*, 1776–1779.
34. Jaiswal, G.; Landge, V. G.; Jagadeesan, D.; Balaraman, E. *Nat. Commun*. **2017**, *8*, 1–13.
35. Miura, H.; Nakahara, K.; Kitajima, T.; Shishido, T. *ACS Omega* **2017**, *2*, 6167–6173.

36. Xu, S.; Alhthlol, L. M.; Paudel, K.; Reinheimer, E.; Tyer, D. L.; Taylor, D. K.; Smith, A. M.; Holzmann, J.; Lozano, E.; Ding, K. *Inorg. Chem.* **2018**, *57*, 2394−2397.
37. Rajesha, K.; Berke, H. *Adv. Synth. Catal*. **2013**, *355*, 901–906.
38. Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588−602.
39. Ananikov, V. P. *ACS Catal*. **2019**, *9*, 2984−2995.
40. Milstein, D., *ACS Catal*. **2018**, *8*, 7734−7741.

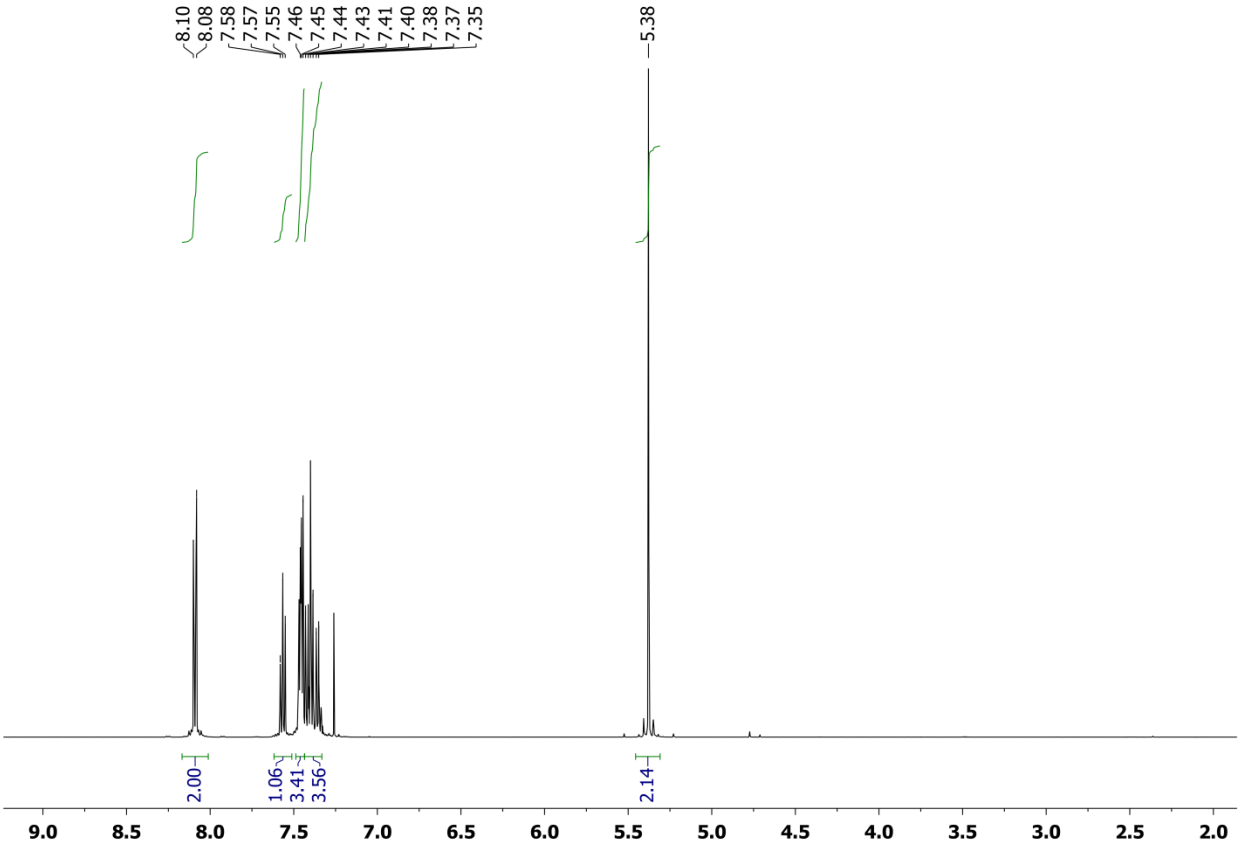
APPENDIX

Copies of NMR and GC Data

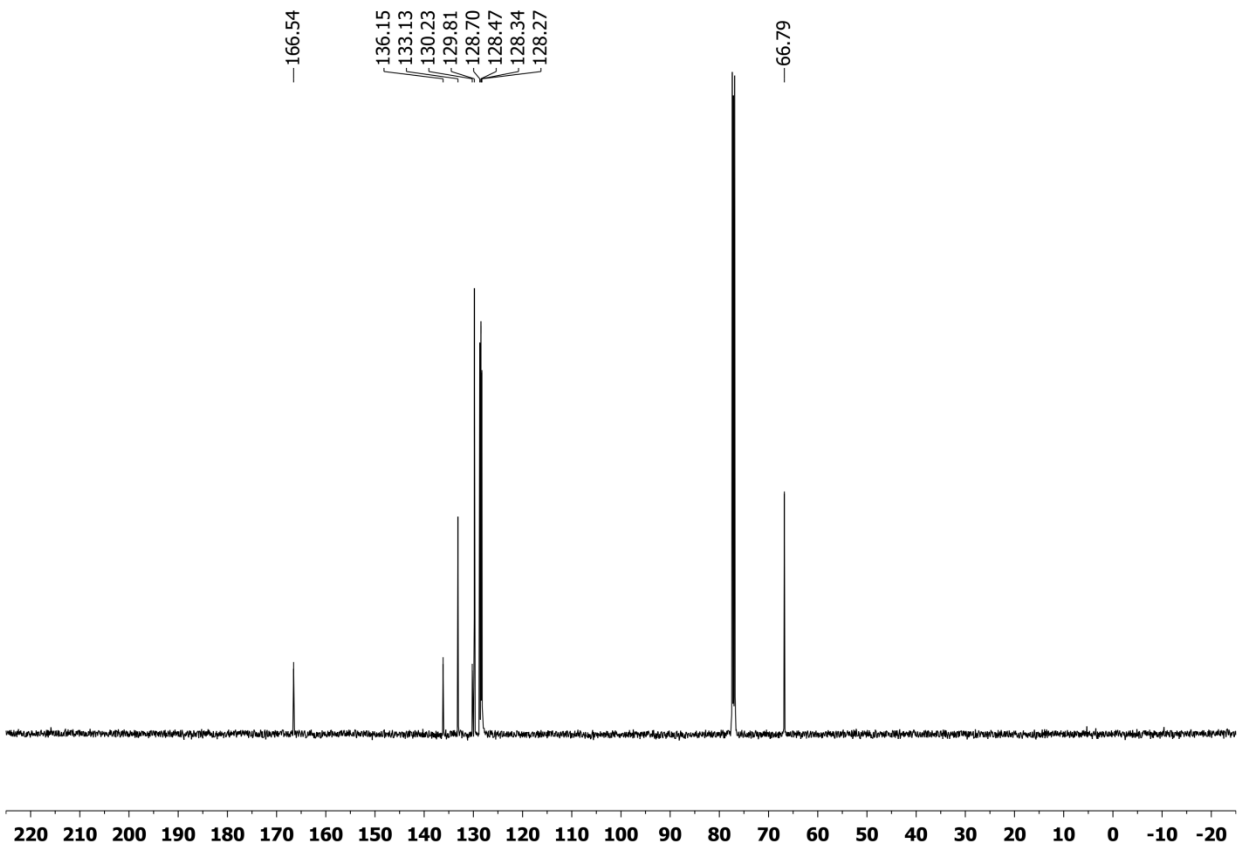
1.



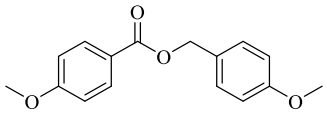
^{1}H NMR (500 MHz, $CDCl_3$):



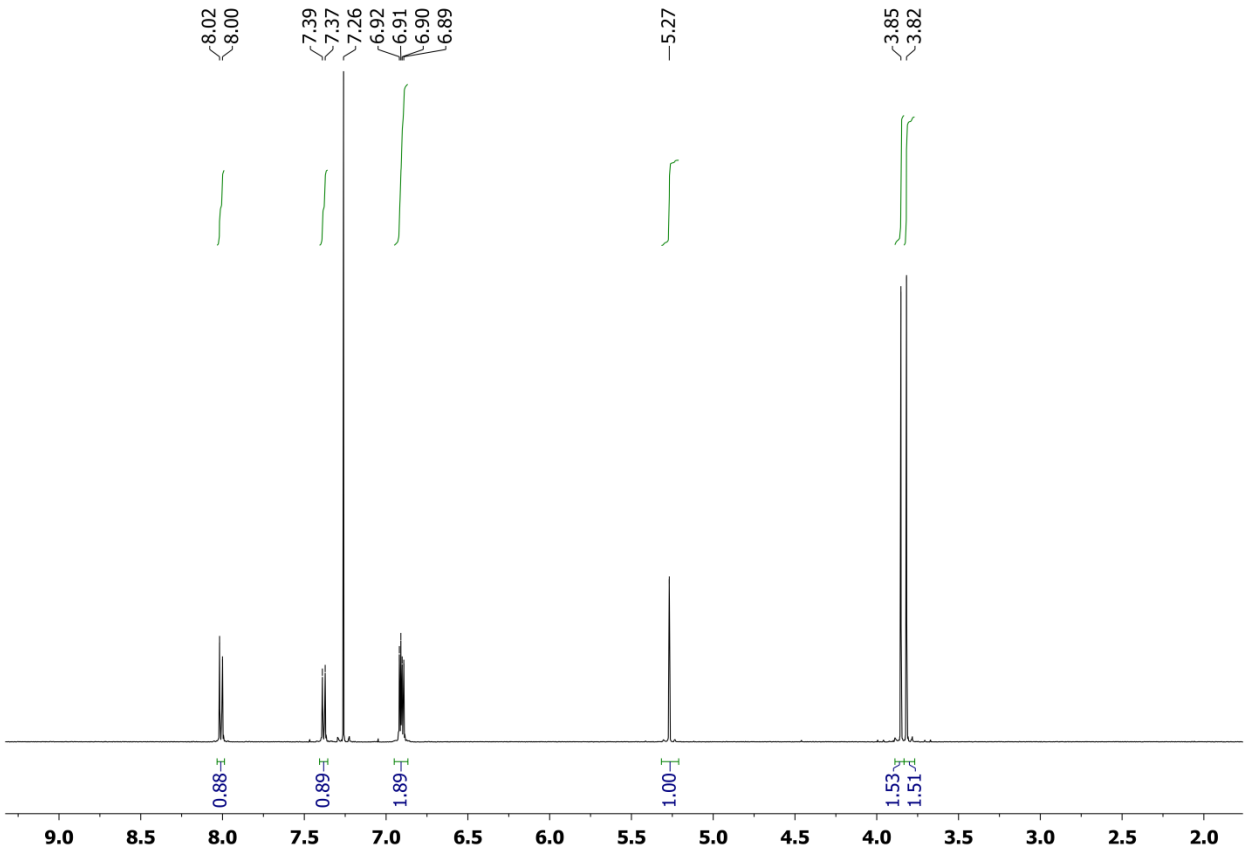
^{13}C NMR (125 MHz, $CDCl_3$):



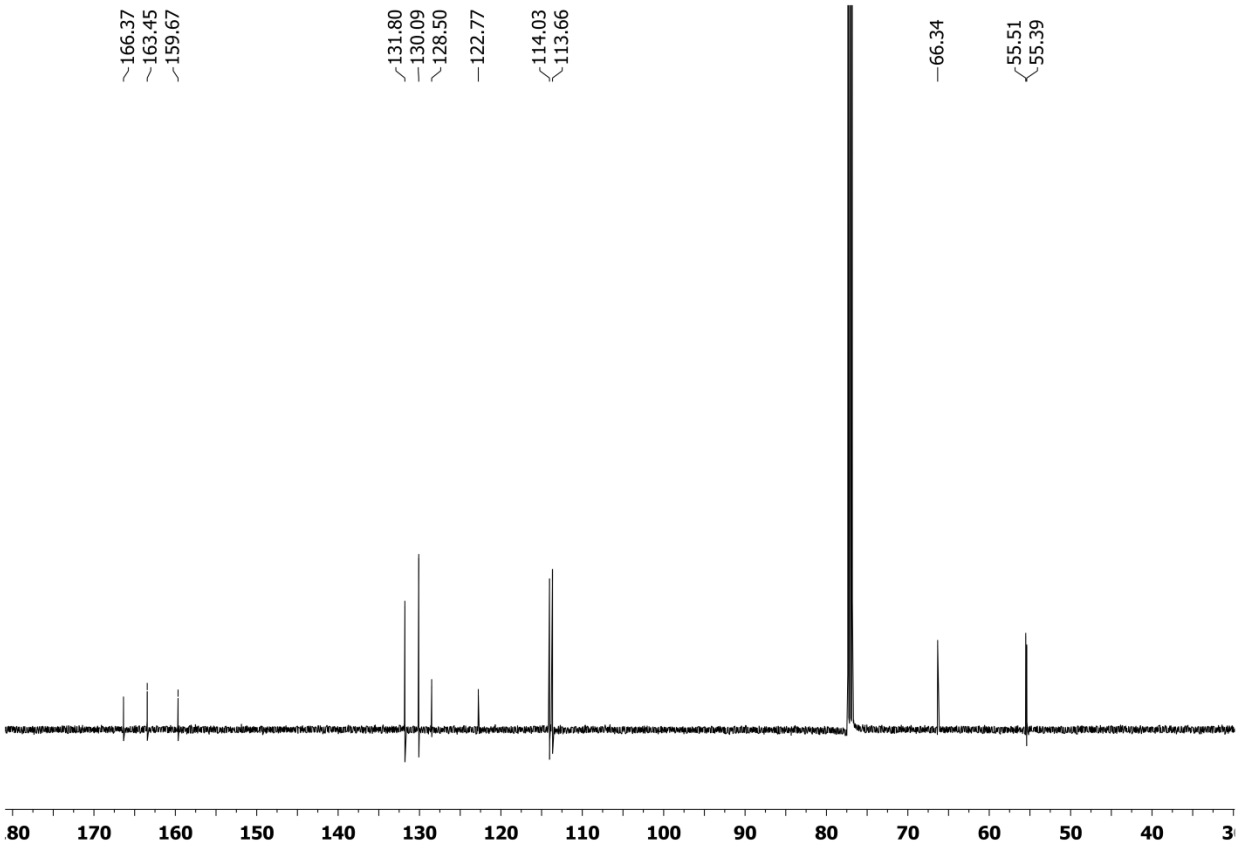
2.



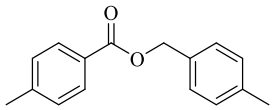
^{1}H NMR (500 MHz, $CDCl_3$):



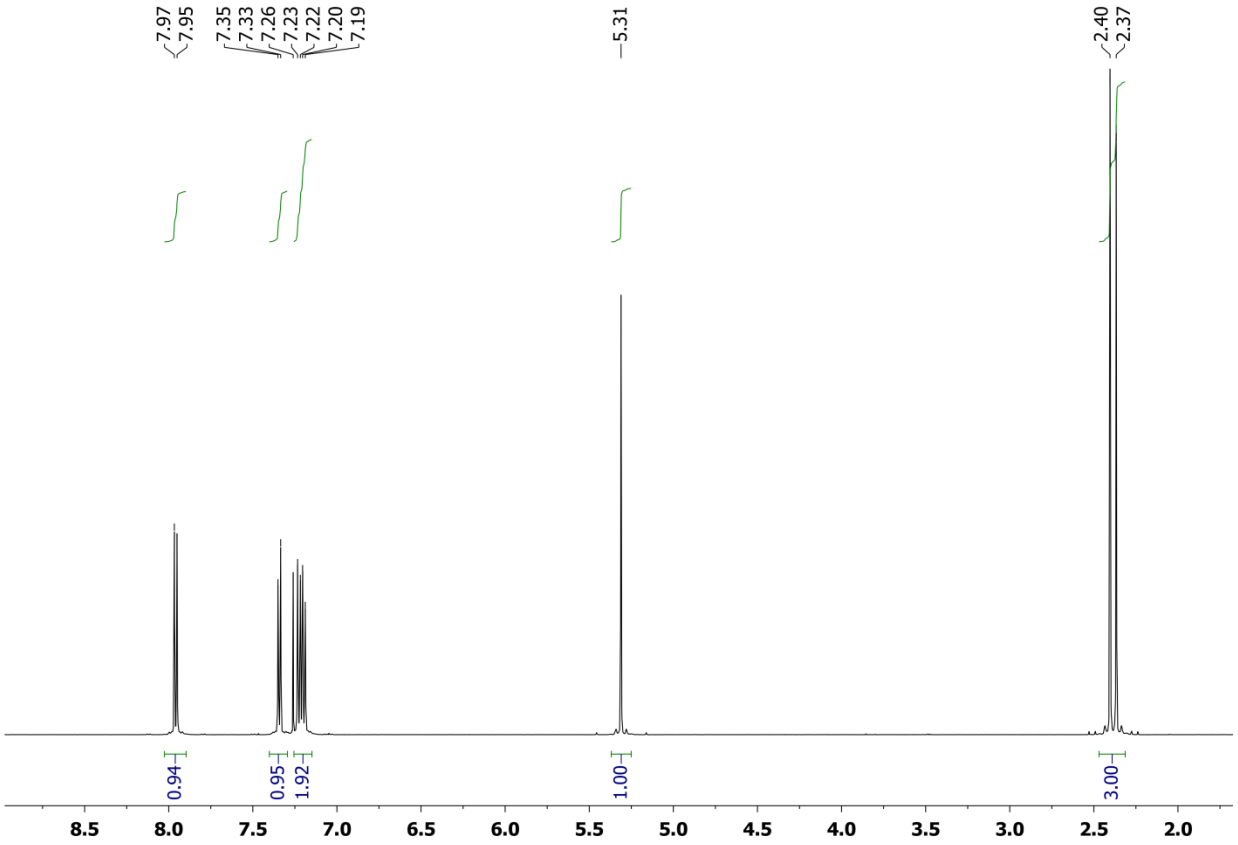
^{13}C NMR (125 MHz, $CDCl_3$):



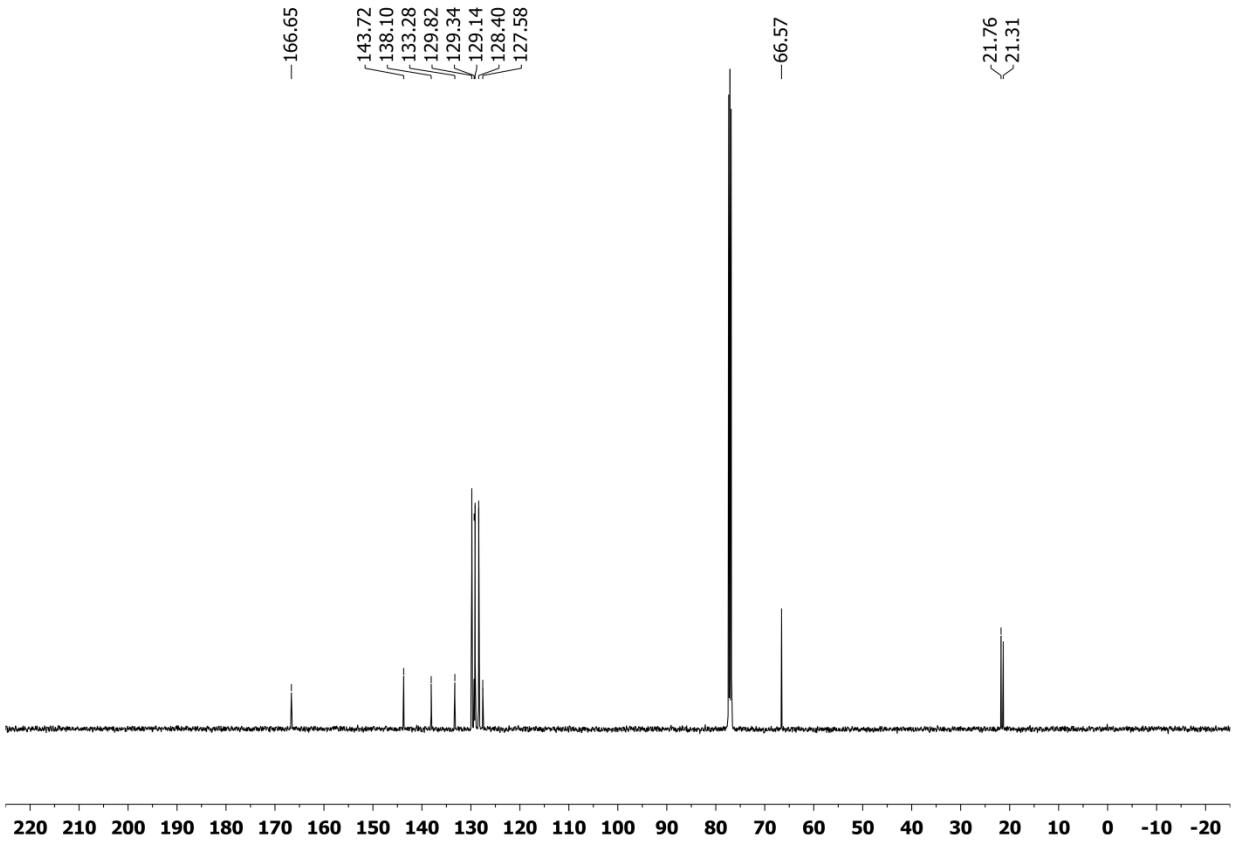
3.



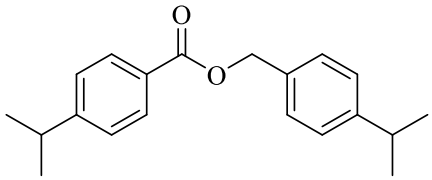
^{1}H NMR (500 MHz, $CDCl_3$):



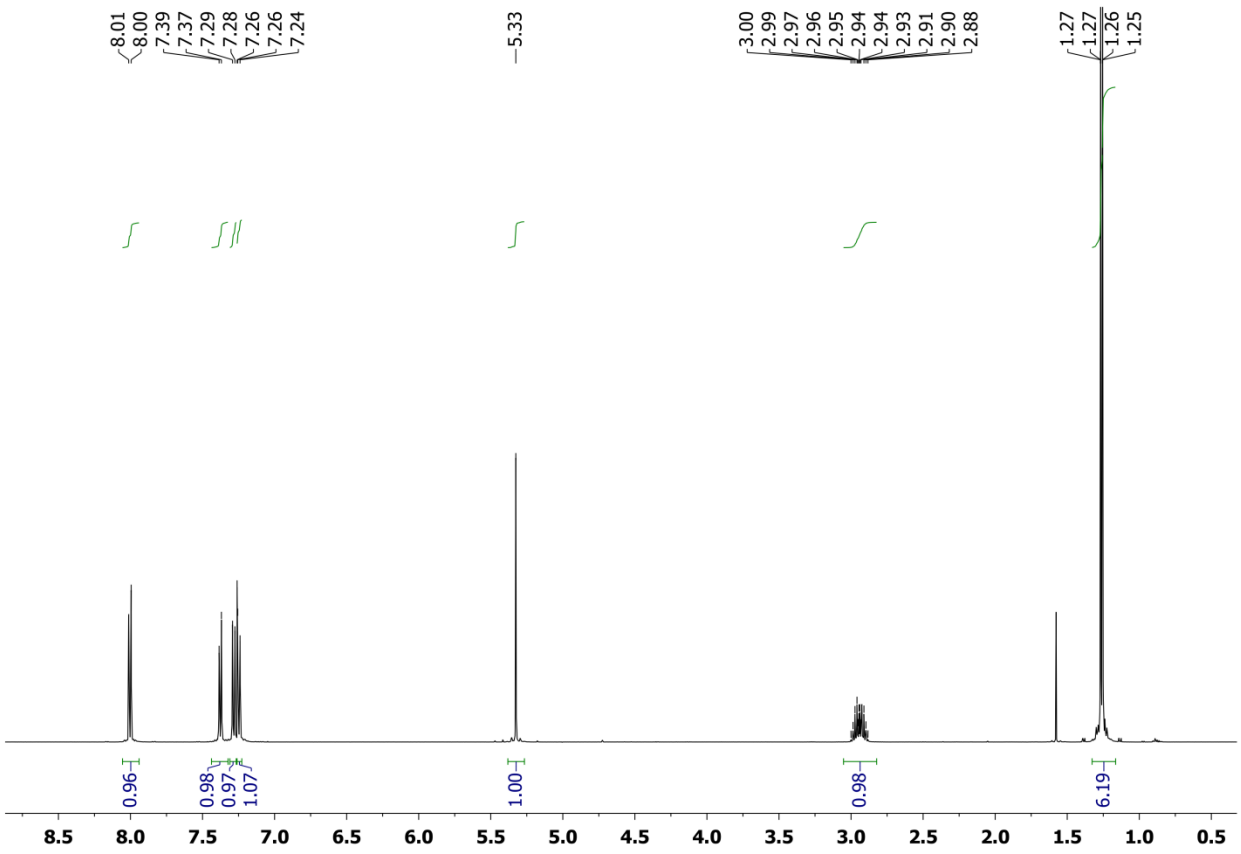
^{13}C NMR (125 MHz, $CDCl_3$):



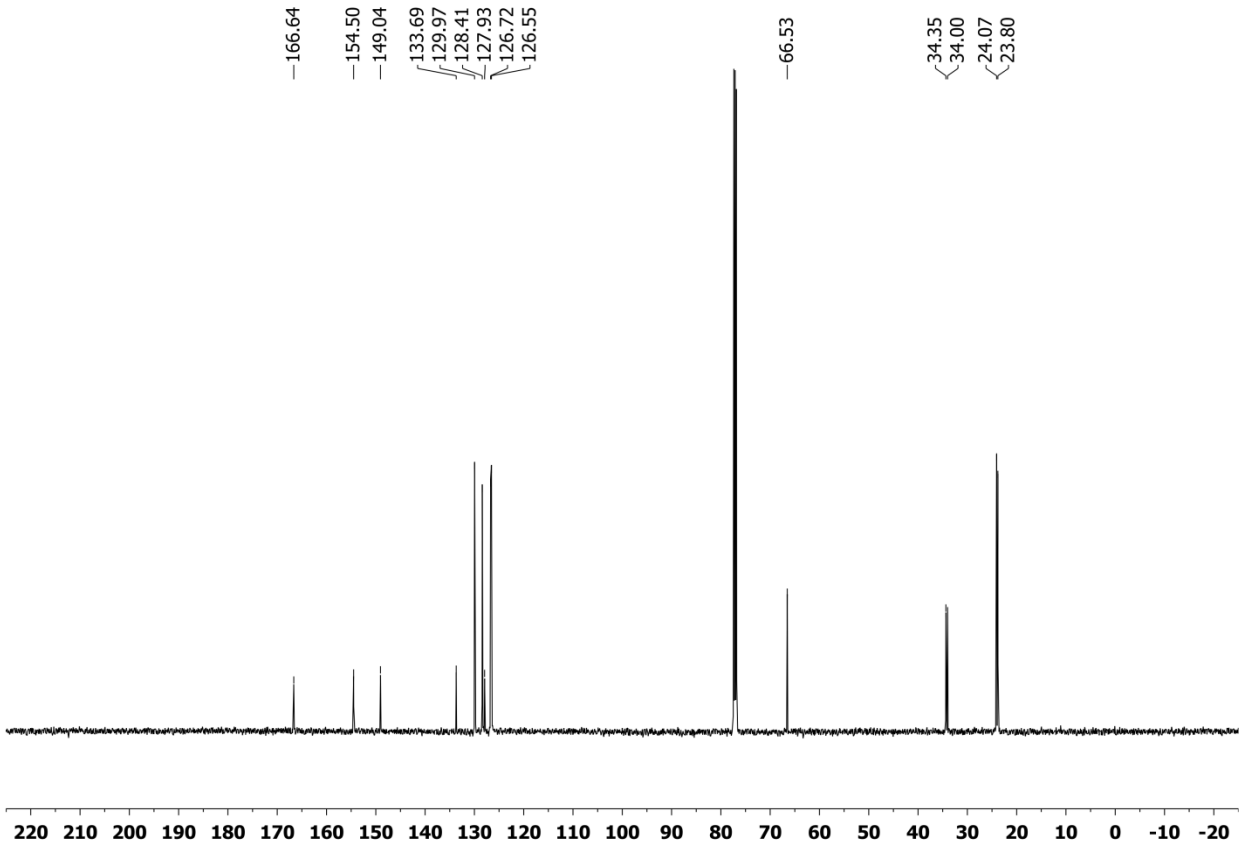
4.



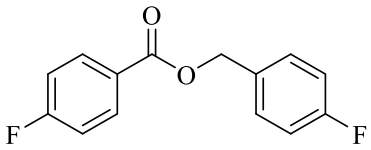
^{1}H NMR (500 MHz, $CDCl_3$):



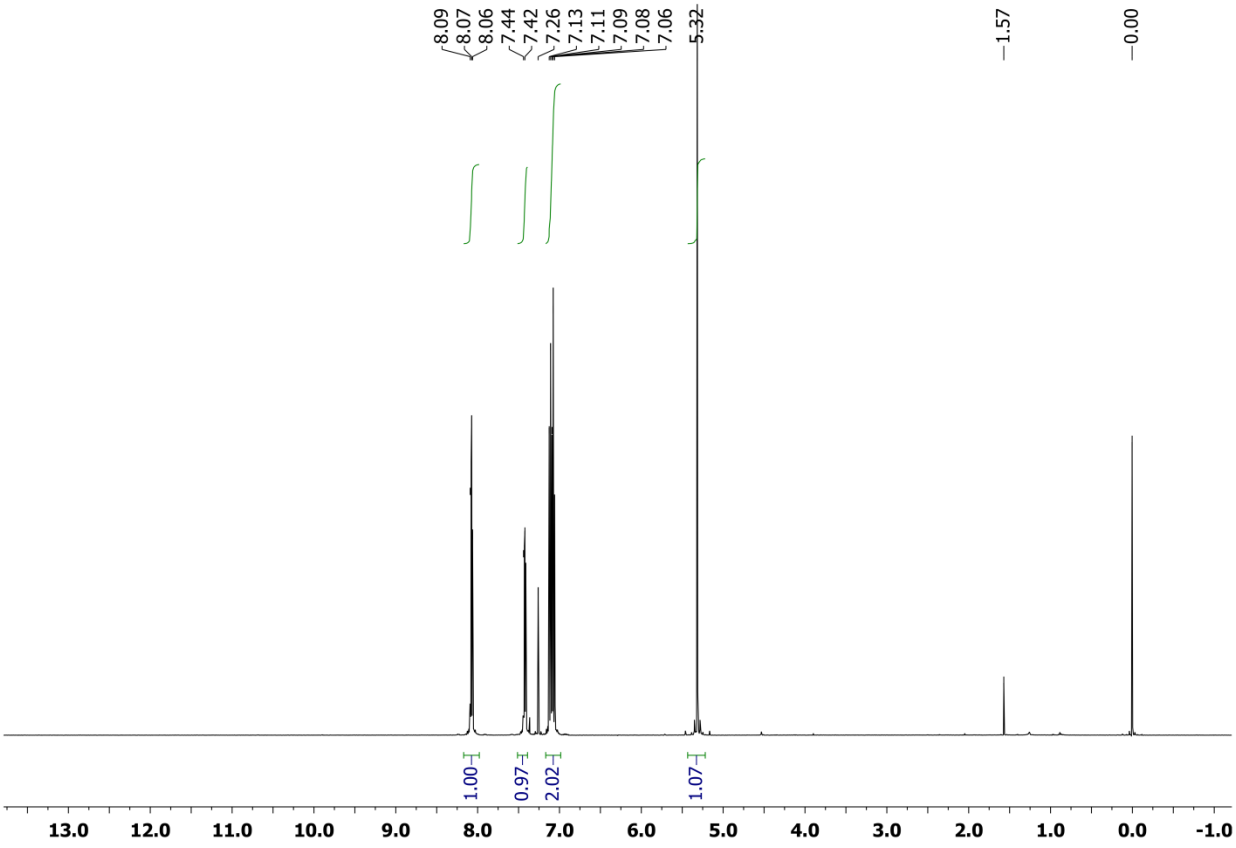
^{13}C NMR (125 MHz, $CDCl_3$):



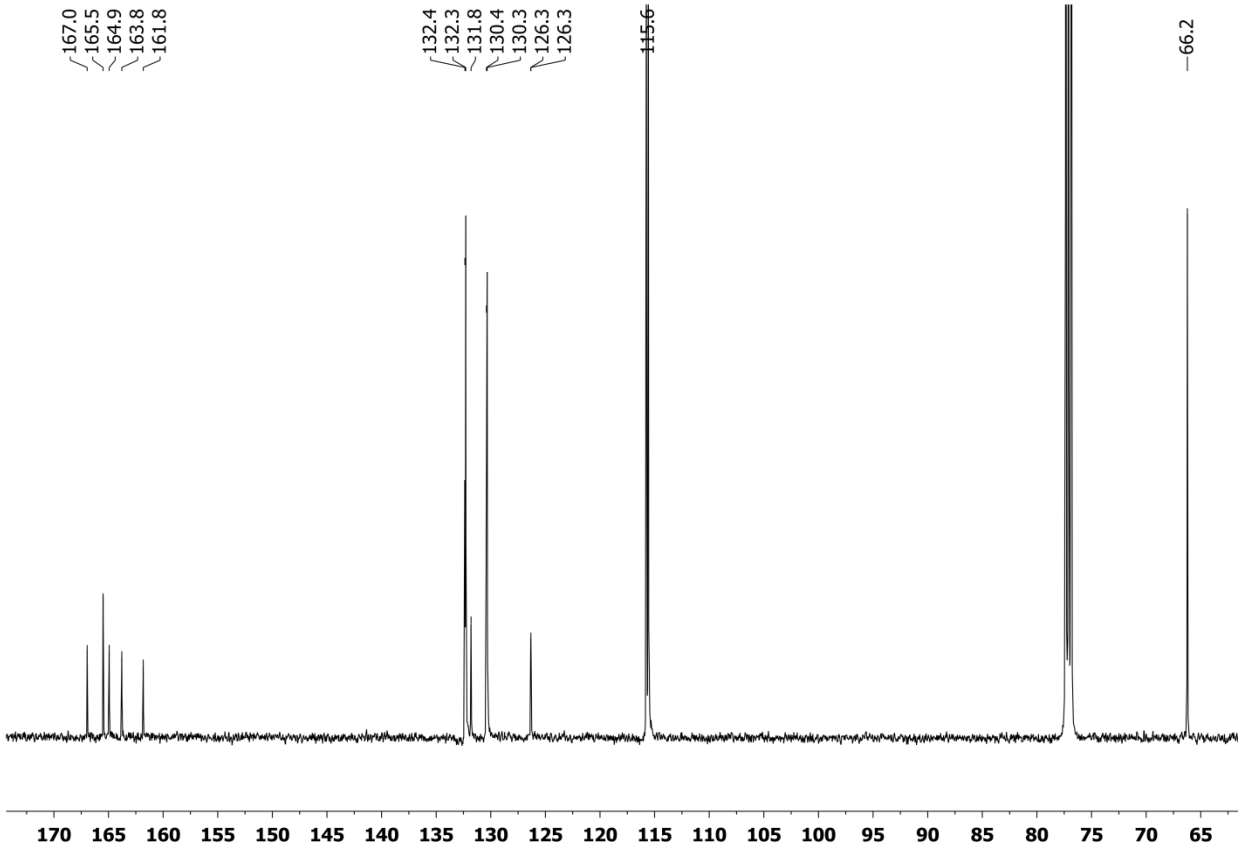
5.



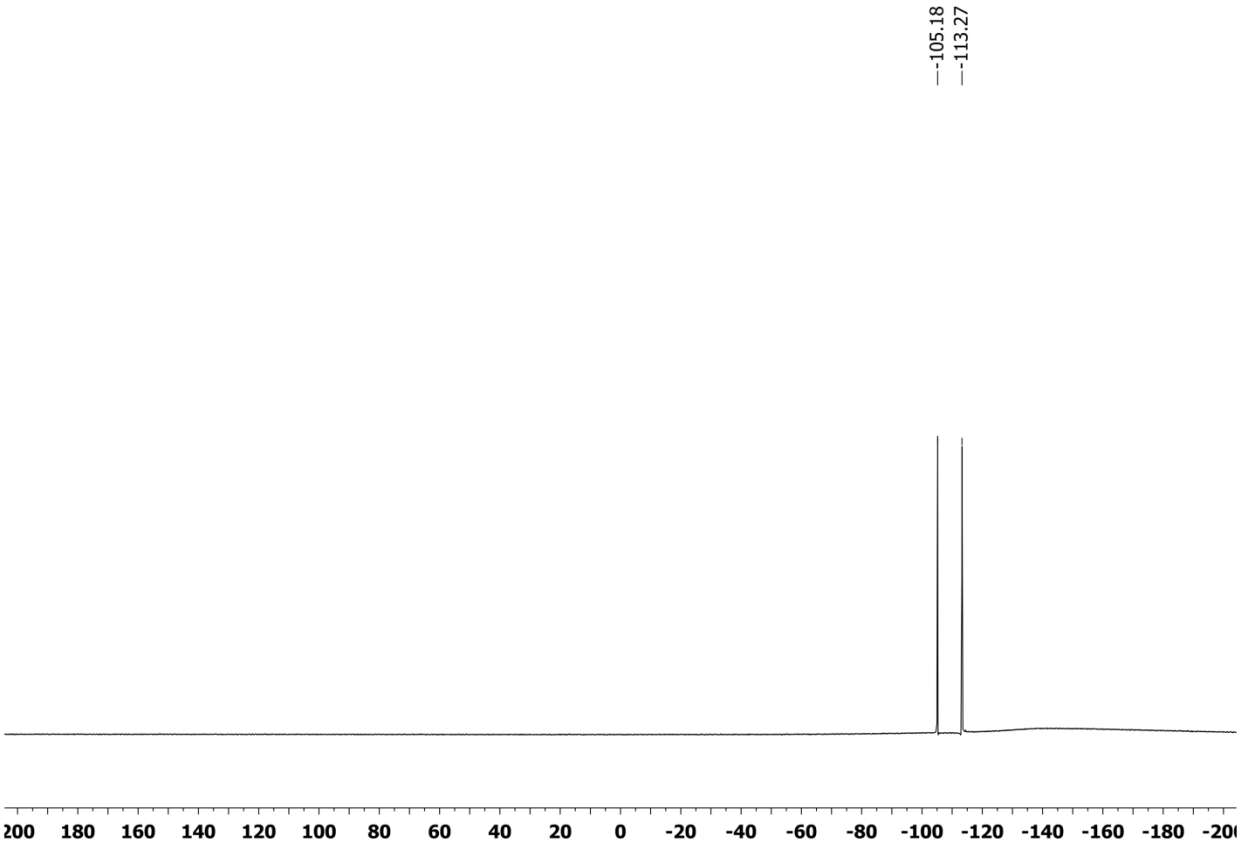
^{1}H NMR (500 MHz, $CDCl_3$):



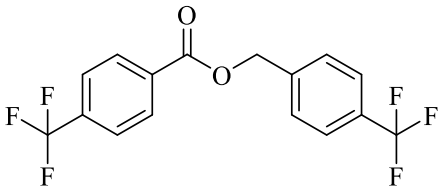
^{13}C NMR (125 MHz, $CDCl_3$):



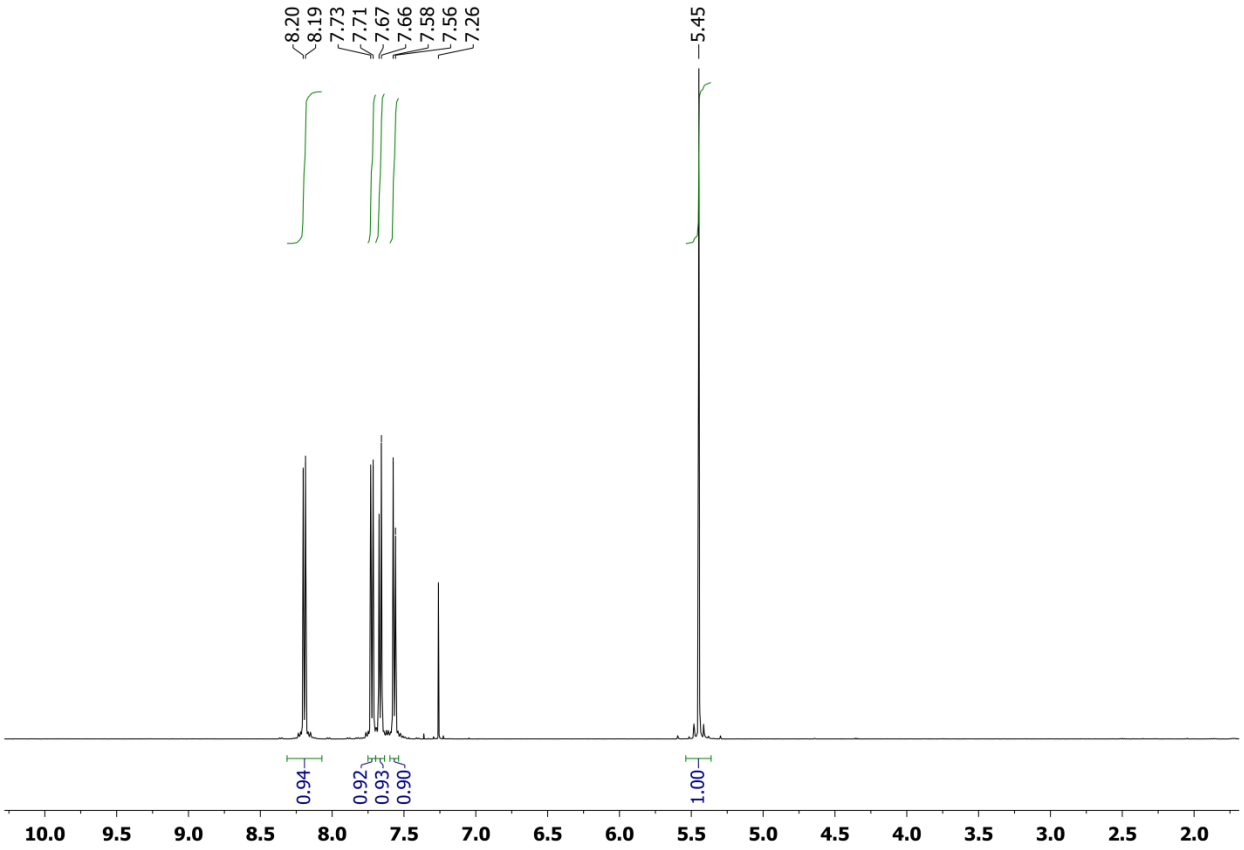
^{19}F NMR (471 MHz, $CDCl_3$):



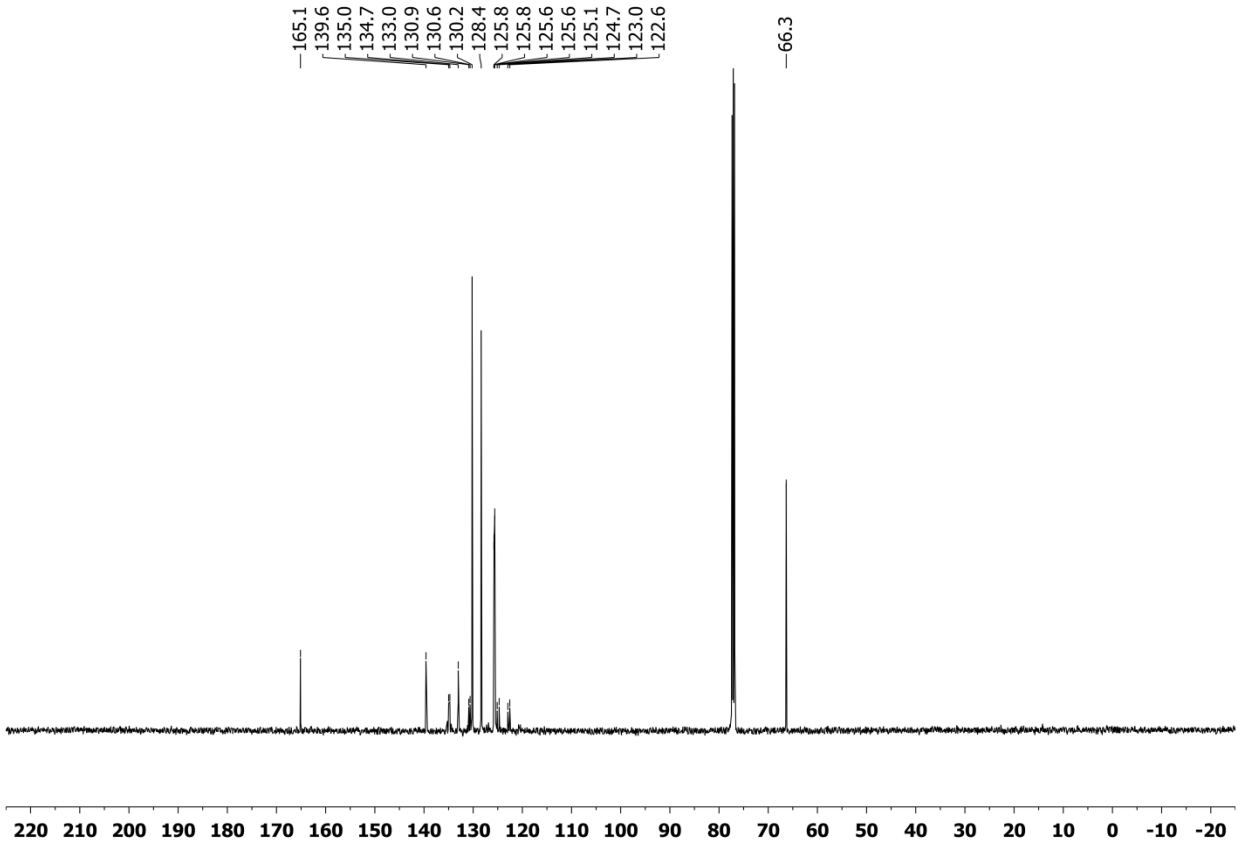
6.



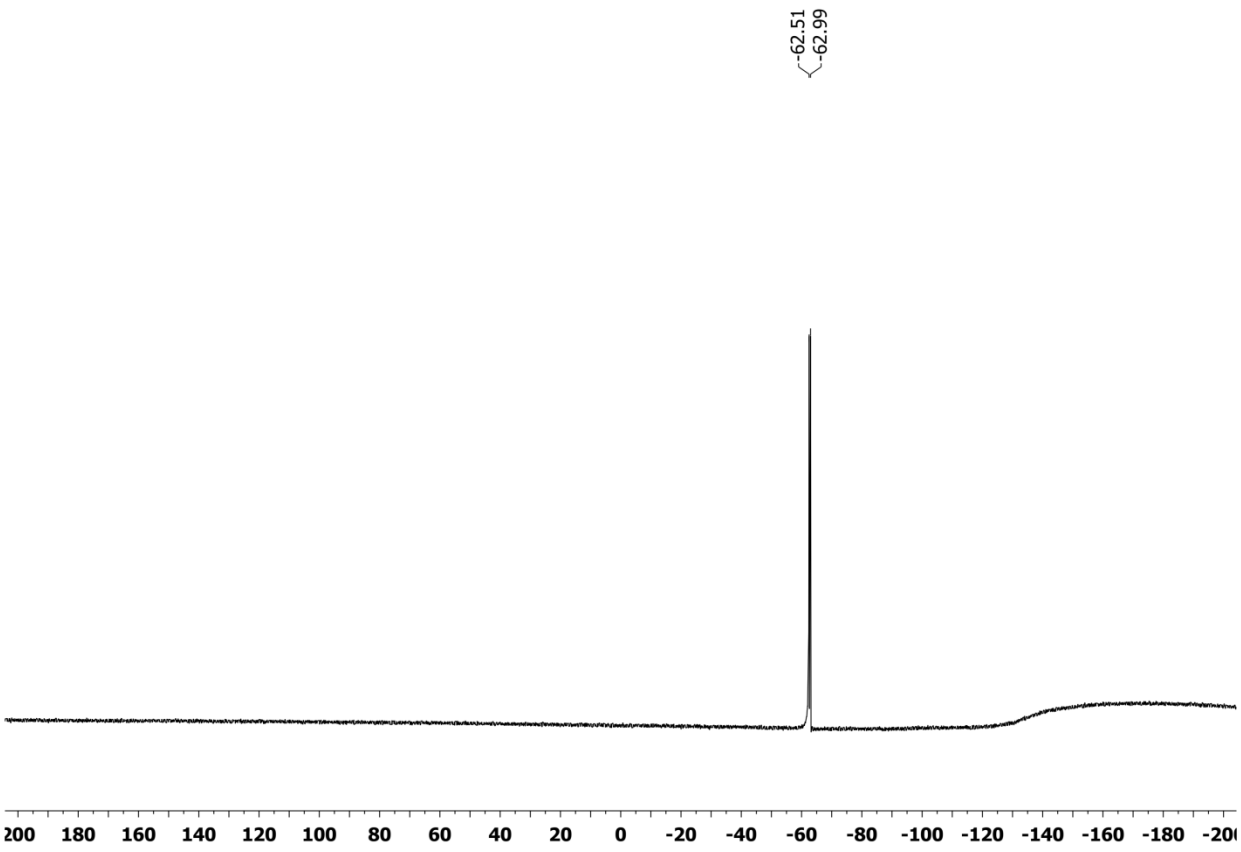
^{1}H NMR (500 MHz, $CDCl_3$):



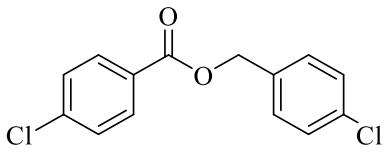
^{13}C NMR (125 MHz, $CDCl_3$):



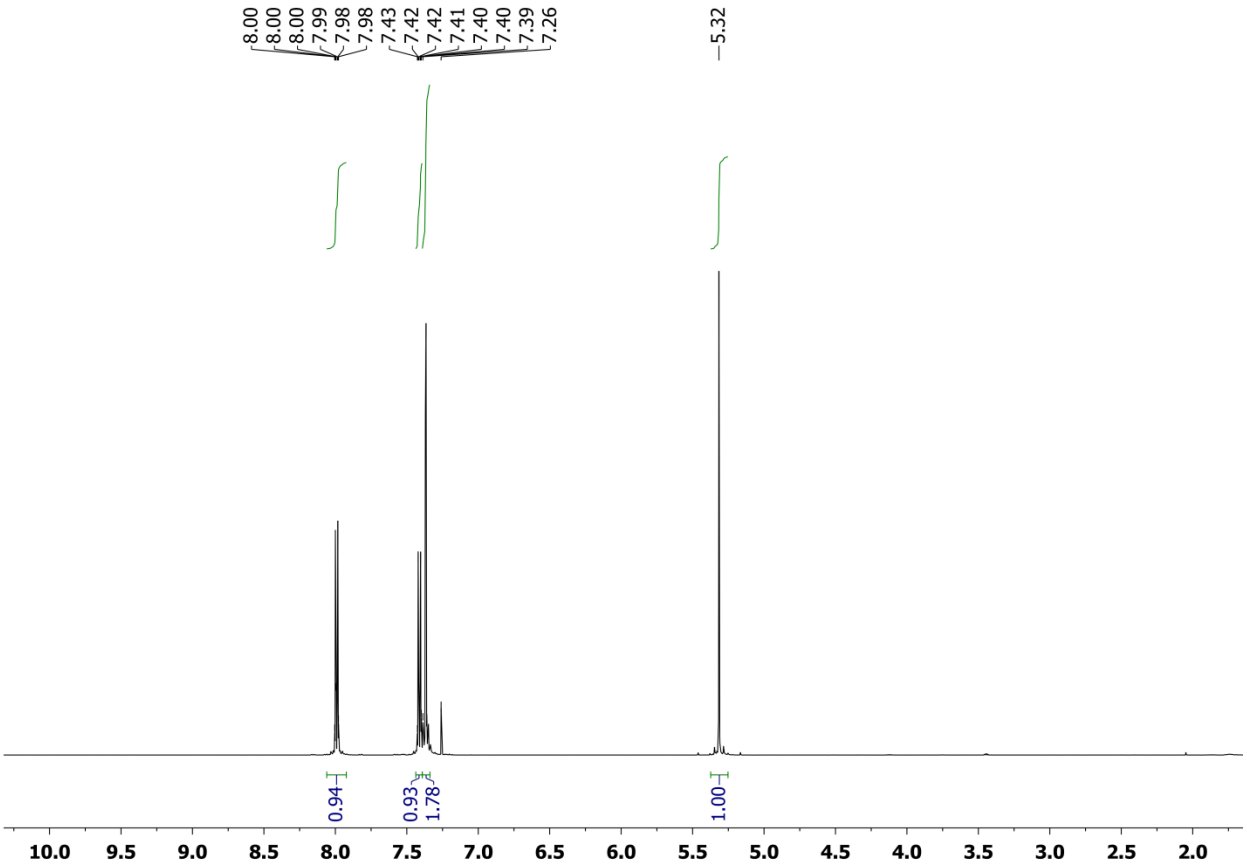
^{19}F NMR (471 MHz, $CDCl_3$):



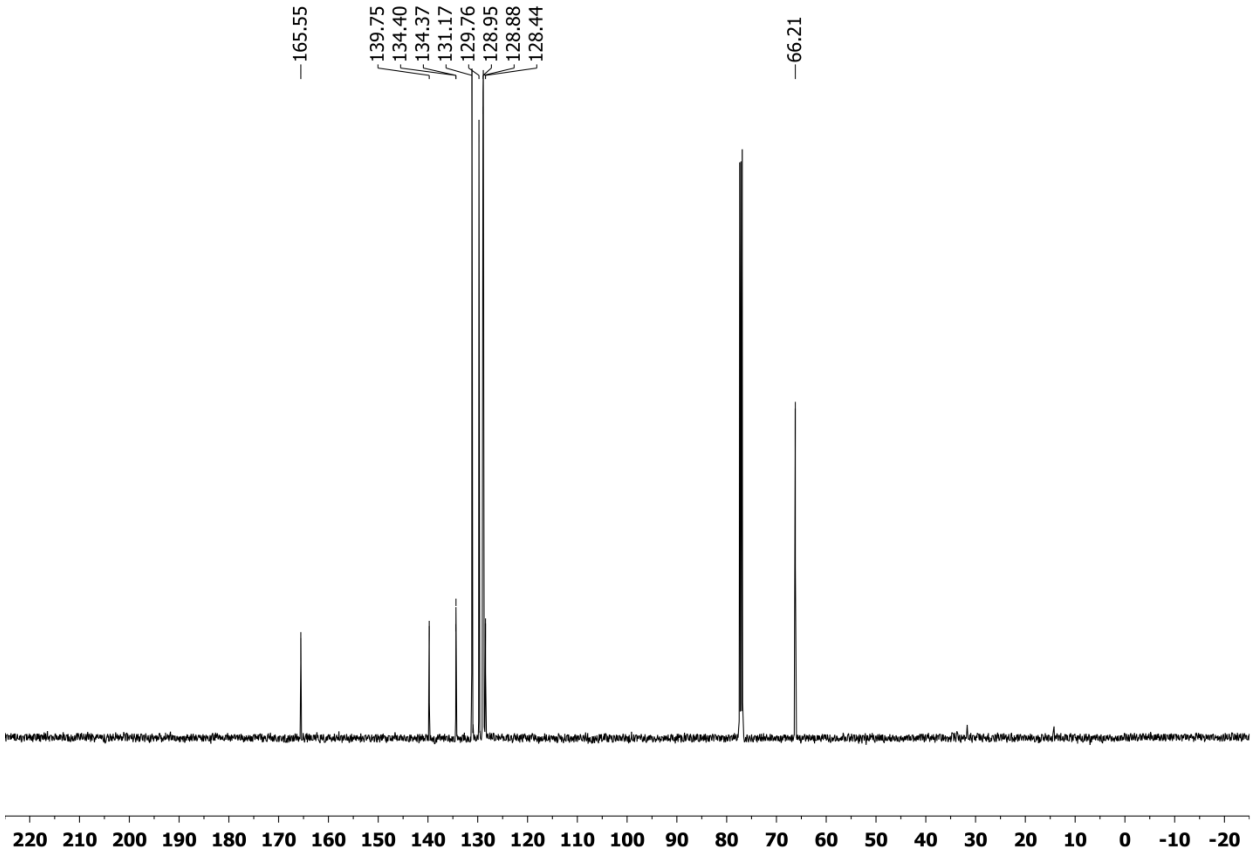
7.



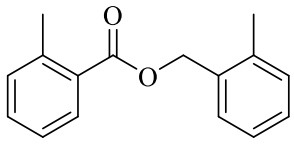
^{1}H NMR (500 MHz, $CDCl_3$):



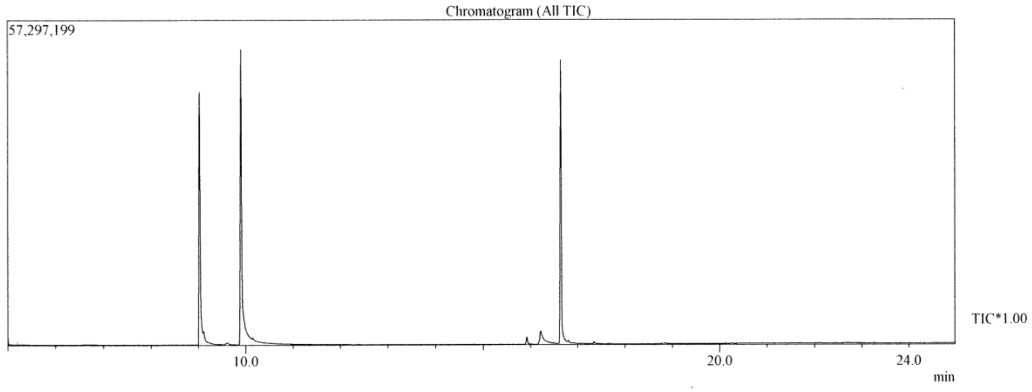
^{13}C NMR (125 MHz, $CDCl_3$):

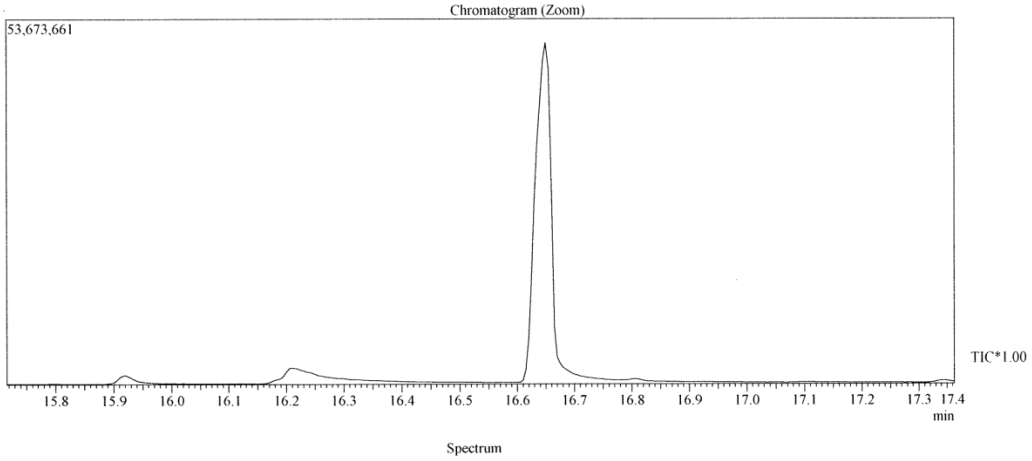


8.



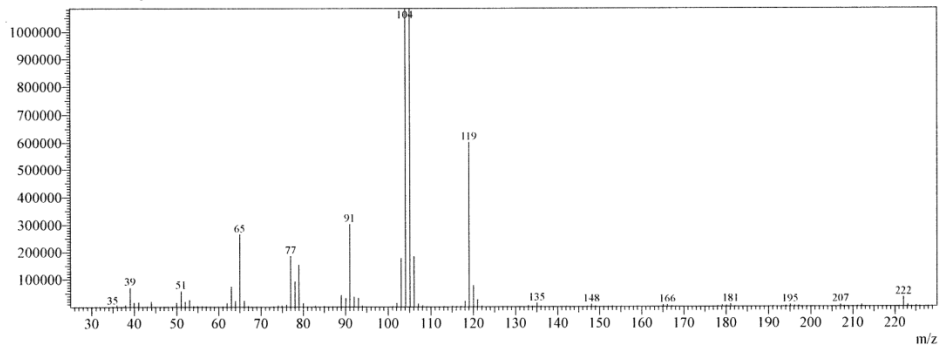
GCMS:



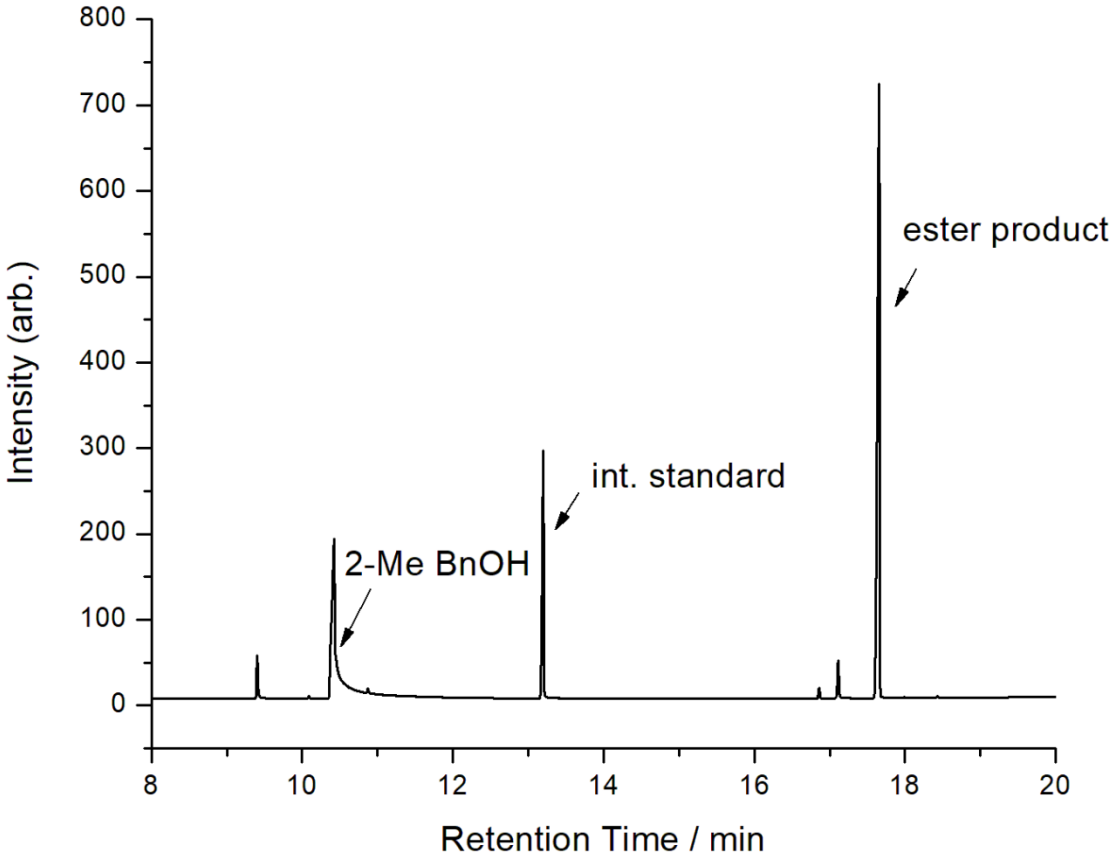


Spectrum

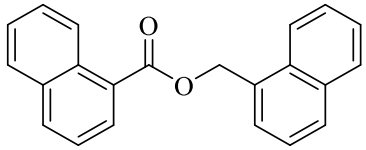
Line#:1 R.Time:16.620(Scan#:2325)
MassPeaks:415
RawMode:Single 16.620(2325) BasePeak:104.10(2038522)
BG Mode:None Group 1 - Event 1 Scan



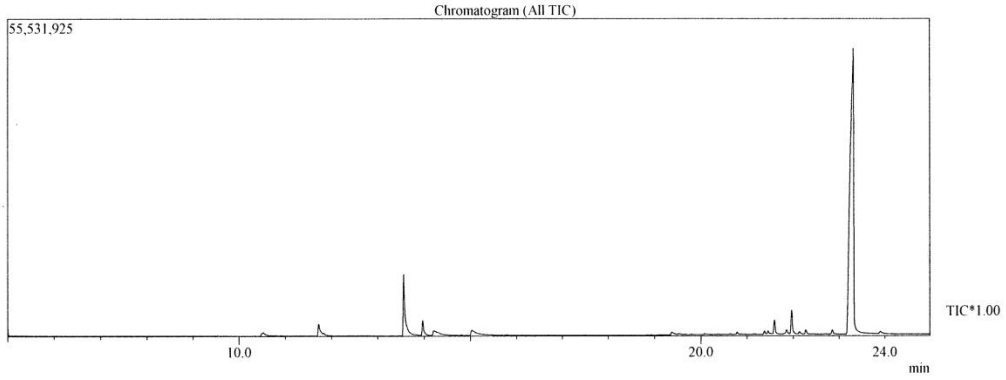
GC Chromatogram:

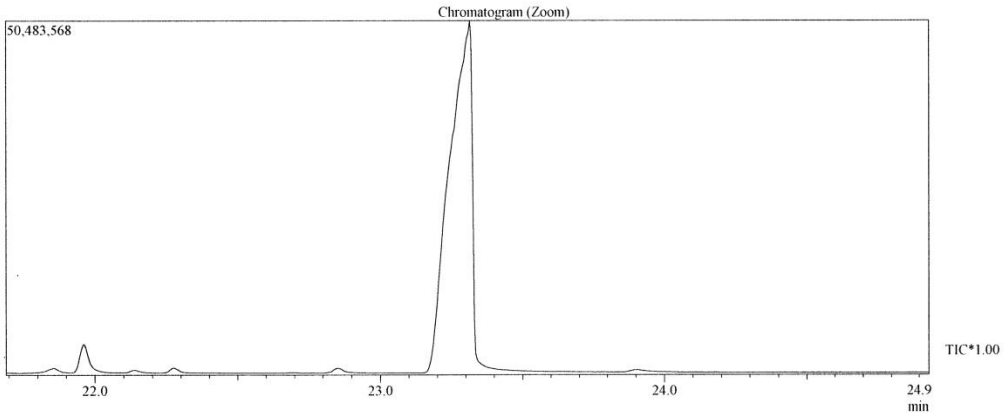


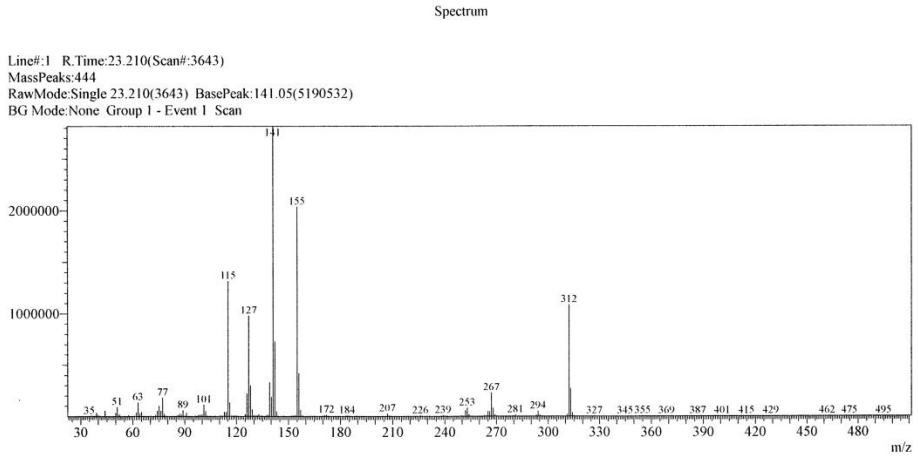
9.


O
O

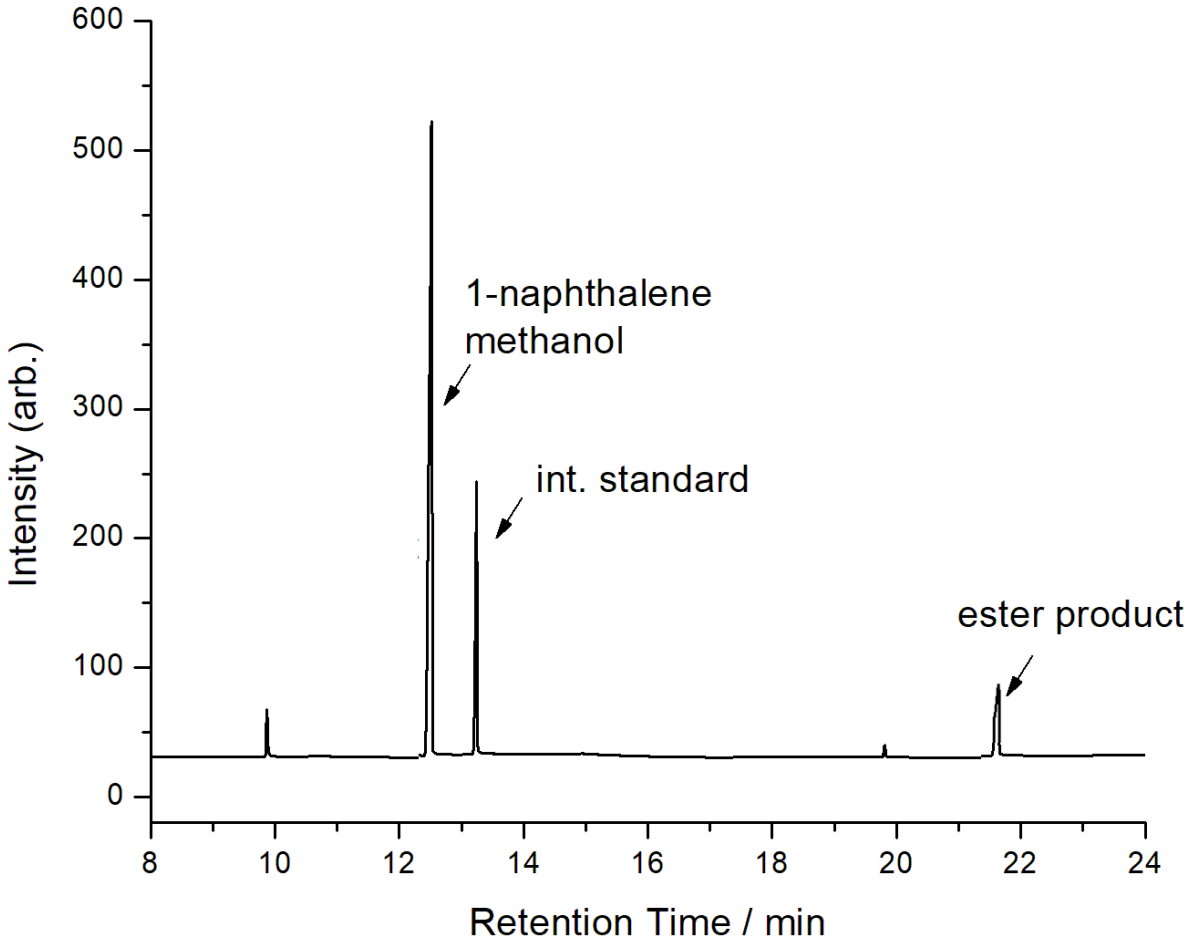
GCMS:


Chromatogram (All TIC)
55,531,925
TIC*1.00
10.0
20.0
24.0
min

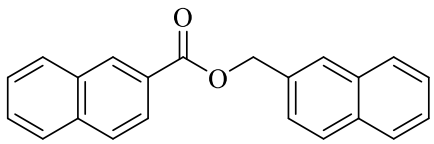

Chromatogram (Zoom)
50,483,568
TIC*1.00
22.0
23.0
24.0
24.9
min


Spectrum
Line#:1 R.Time:23.210(Scan#:3643)
MassPeaks:444
RawMode:Single 23.210(3643) BasePeak:141.05(5190532)
BG Mode:None Group 1 - Event 1 Scan
2000000
1000000
141
155
115
127
312
267
m/z

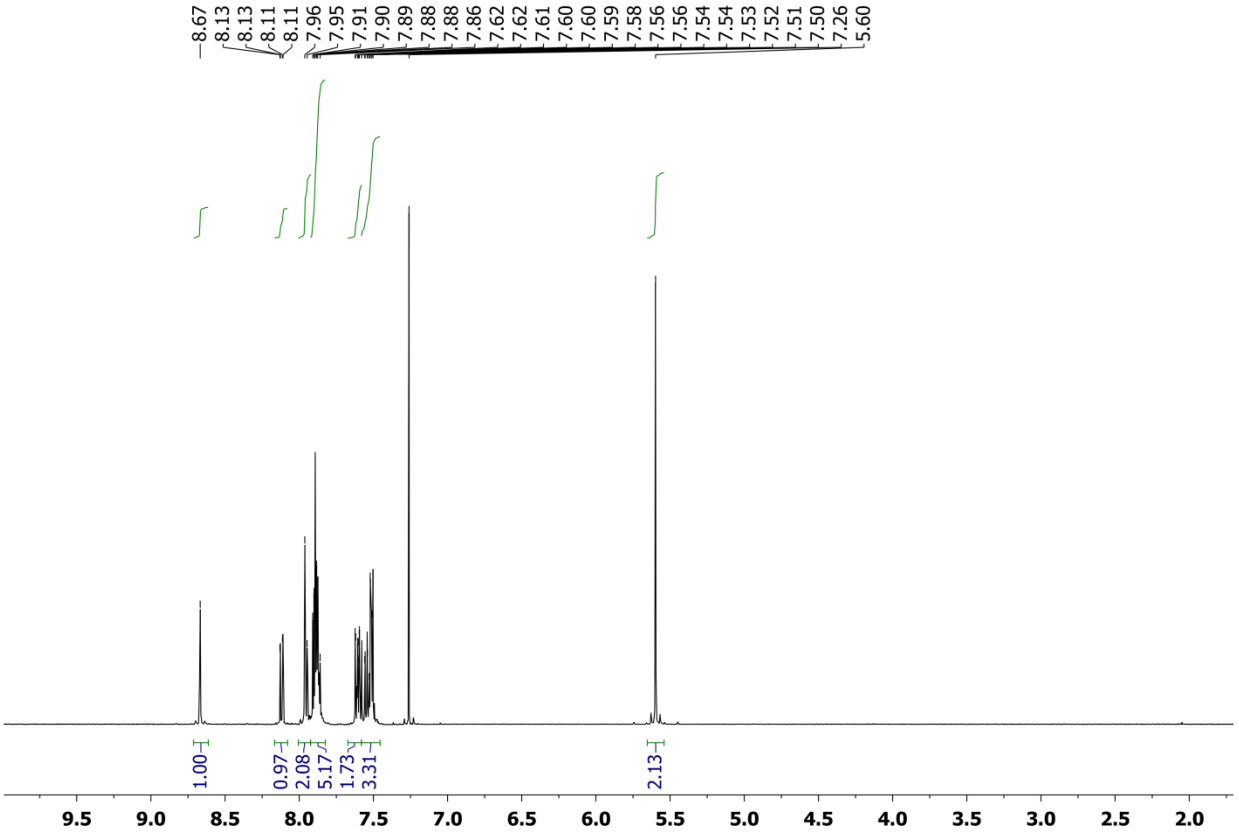
GC Chromatogram:



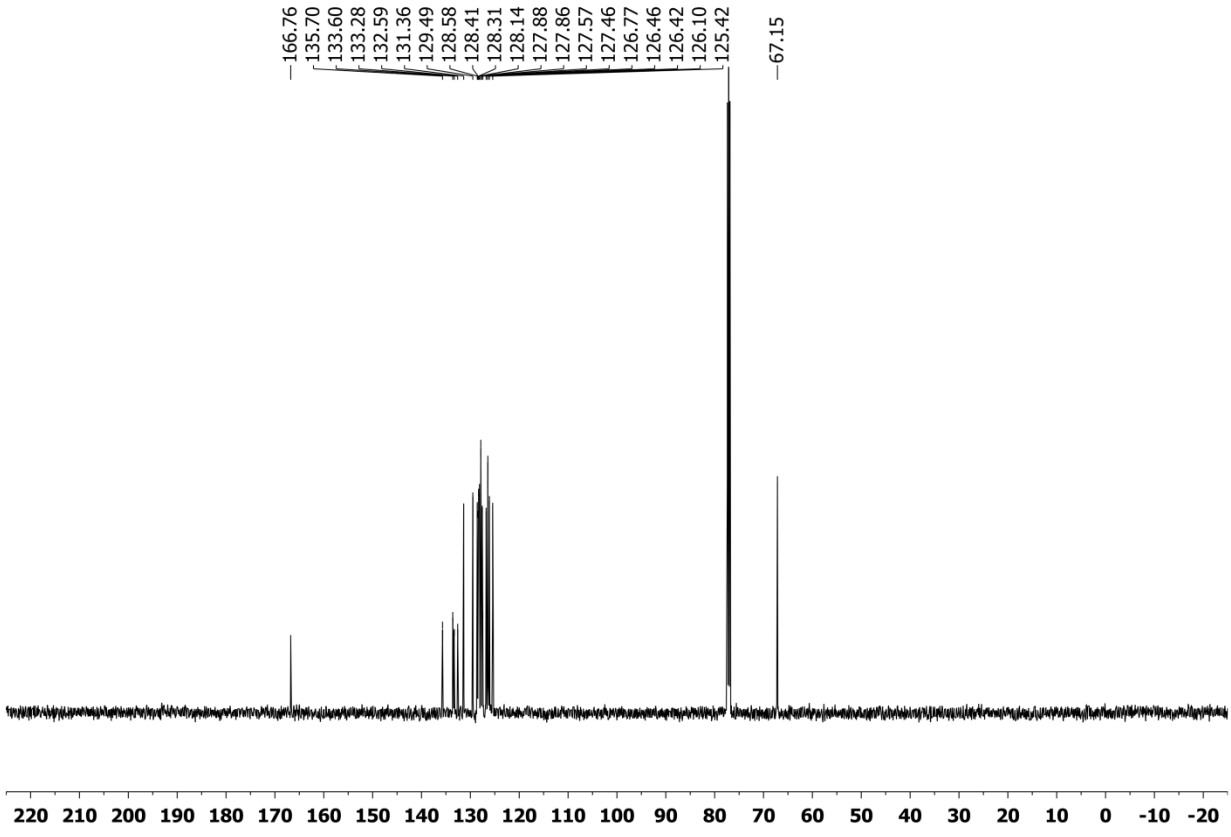
10.



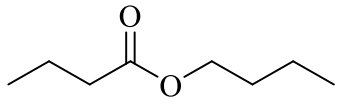
^{1}H NMR (500 MHz, $CDCl_3$):



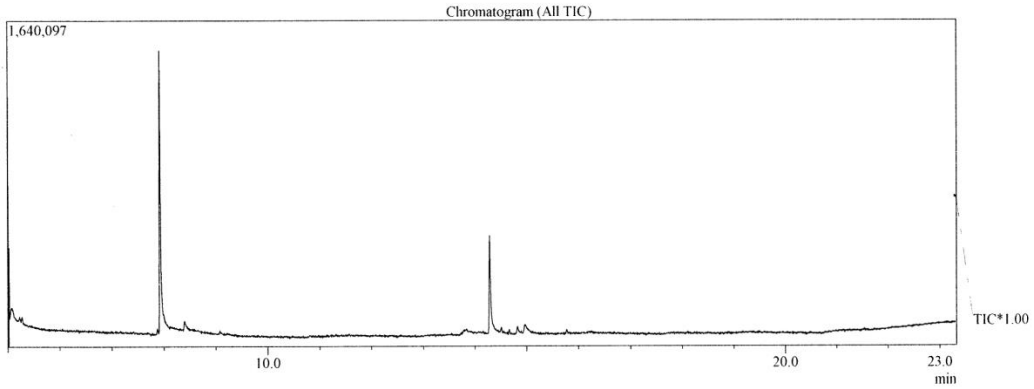
^{13}C NMR (125 MHz, $CDCl_3$):

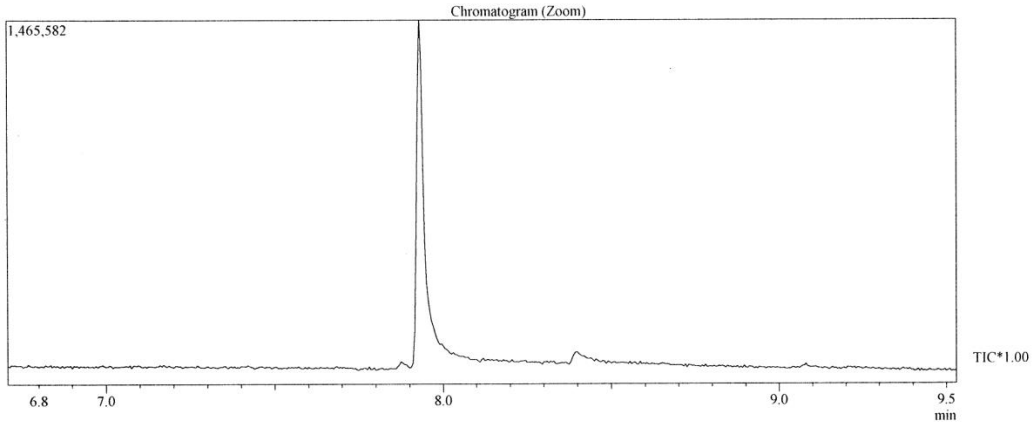


11.

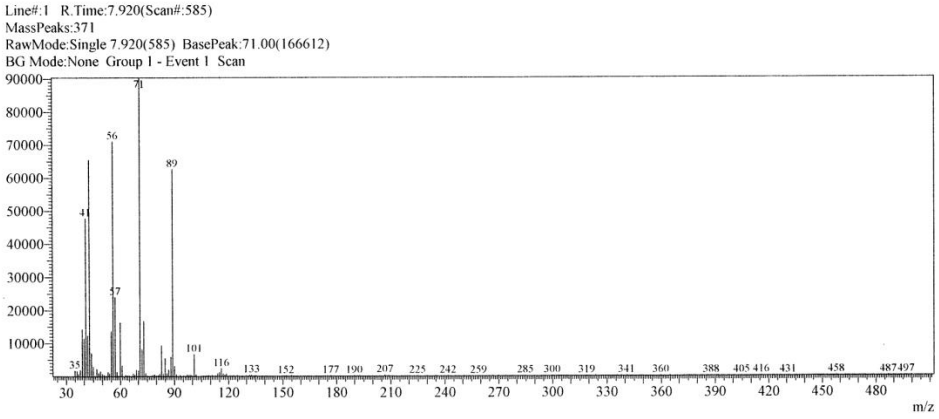


GCMS:

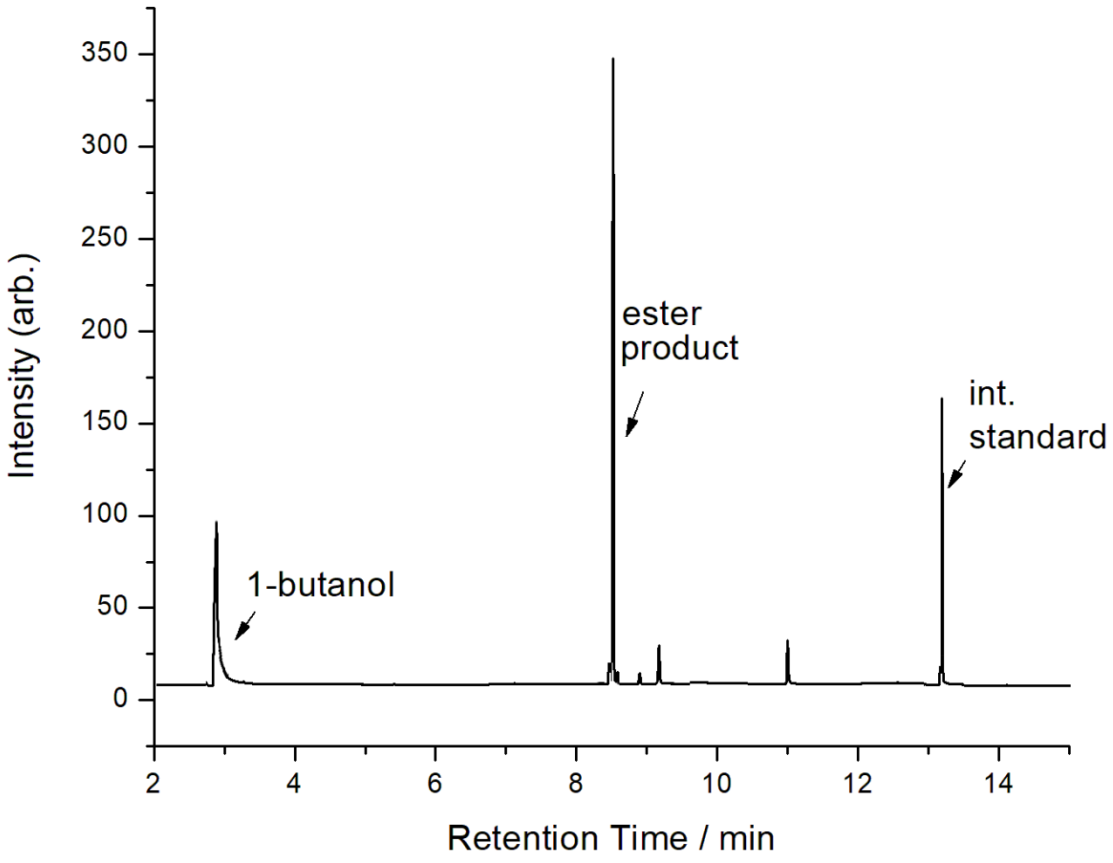




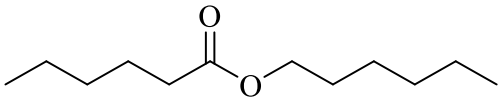
Spectrum



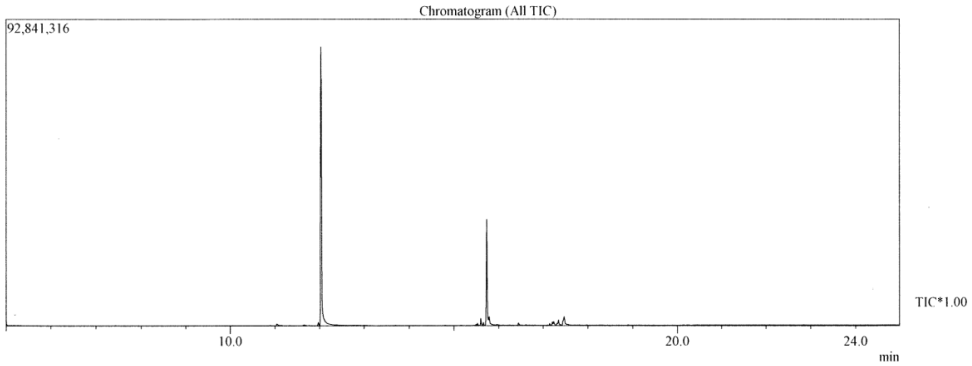
GC-FID Chromatogram:

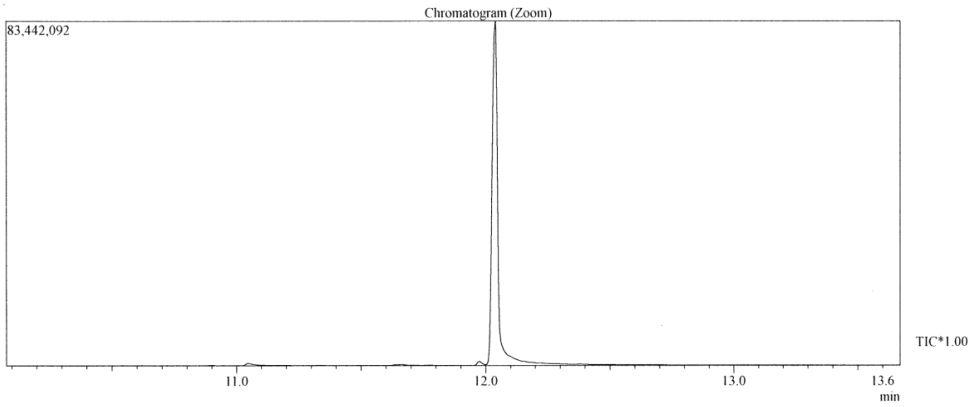


12.

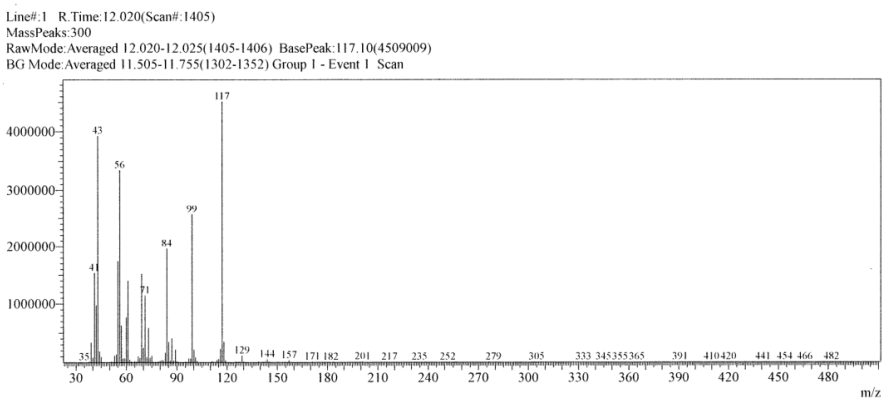


GCMS:

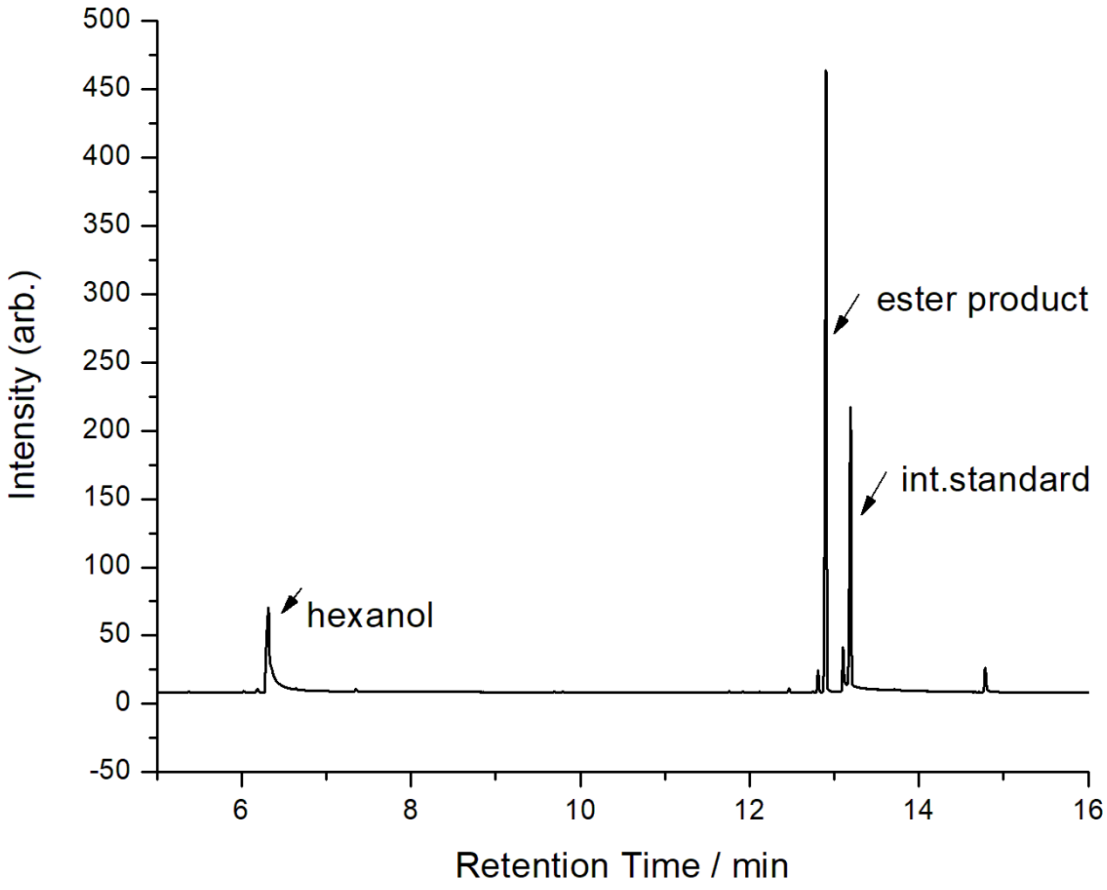




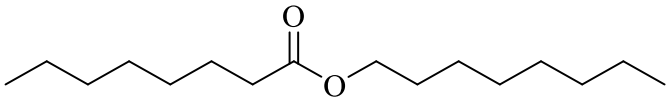
Spectrum



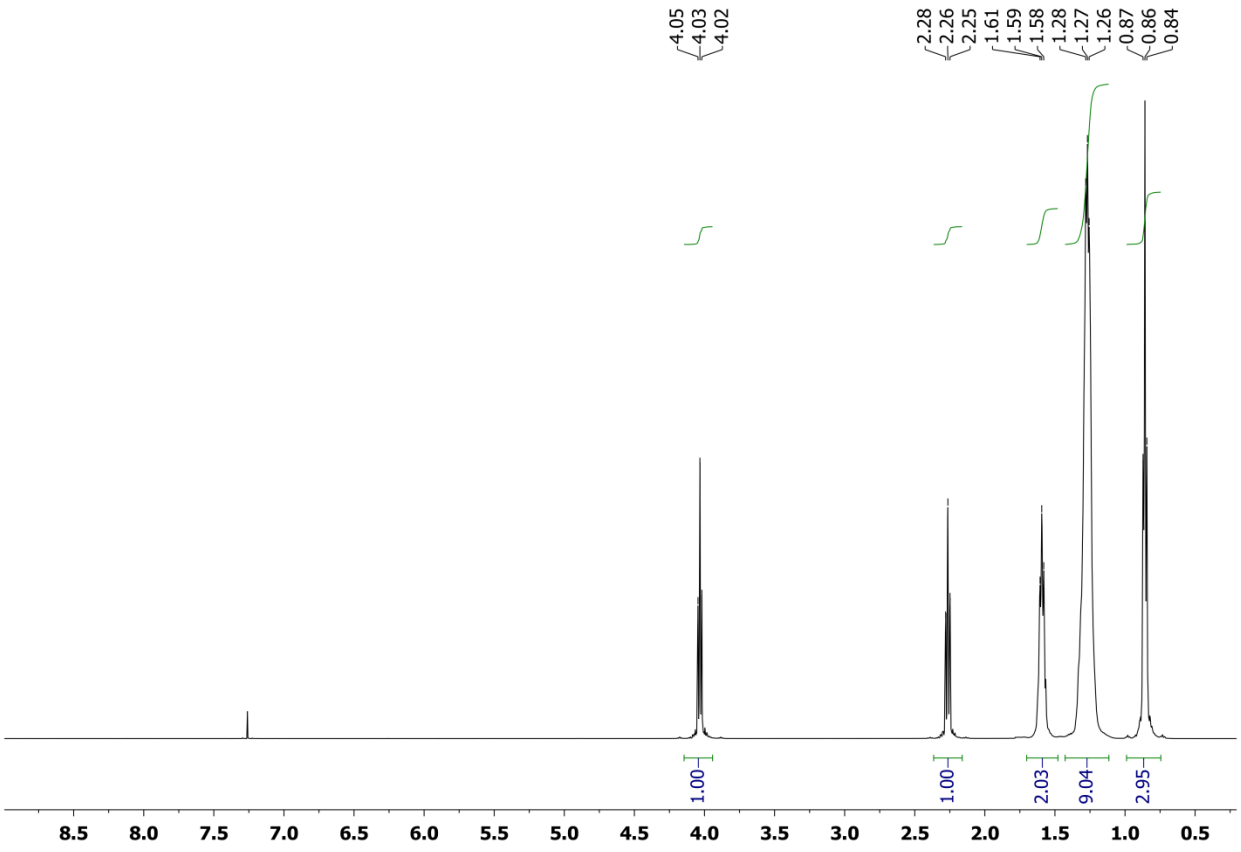
GC-FID Chromatogram:



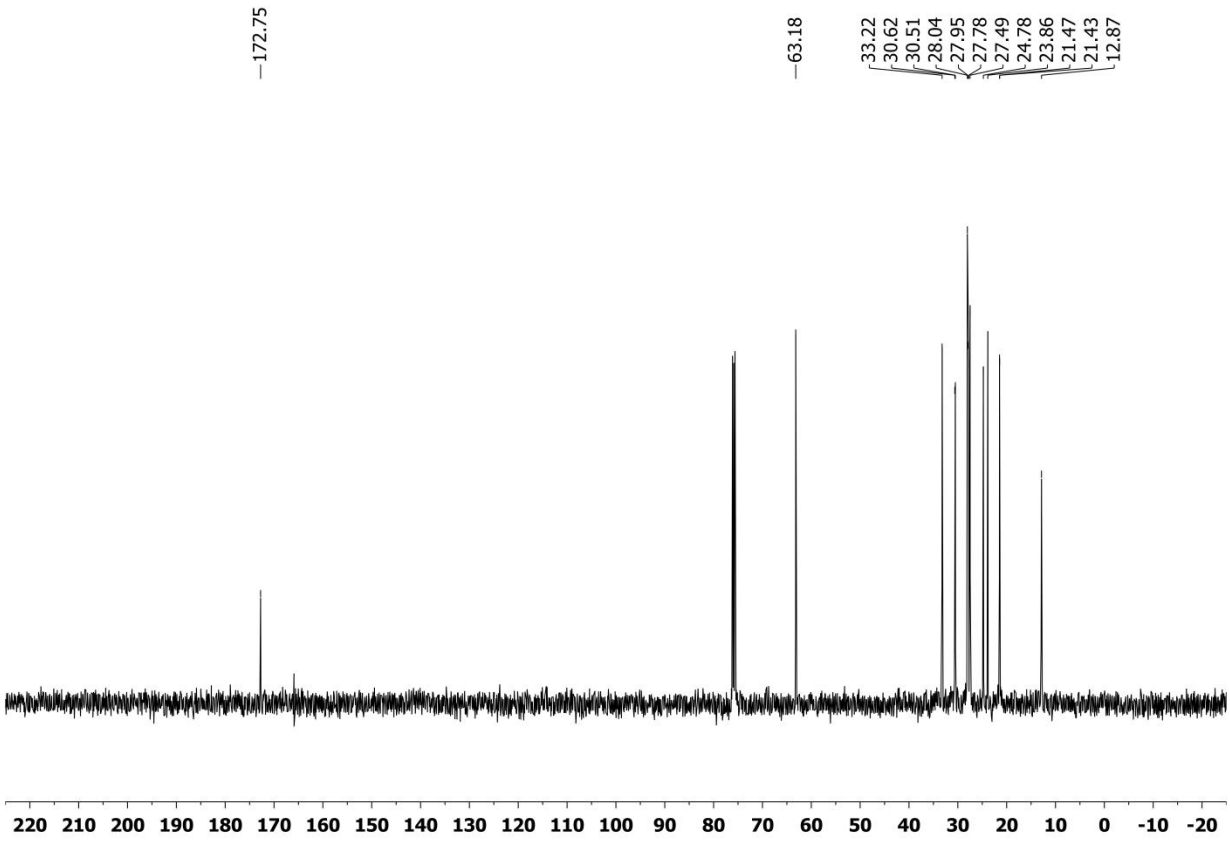
13.



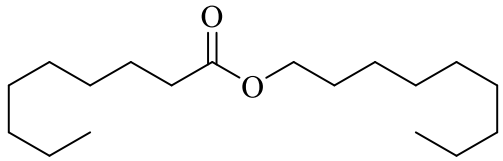
^{1}H NMR (500 MHz, $CDCl_3$):



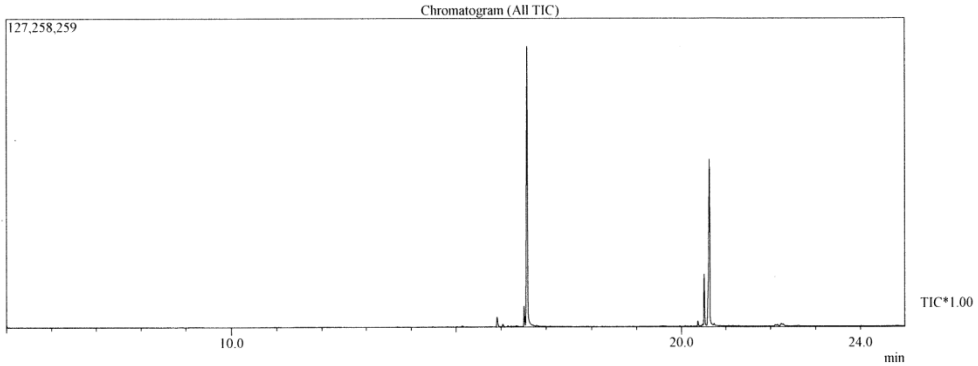
^{13}C NMR (125 MHz, $CDCl_3$):

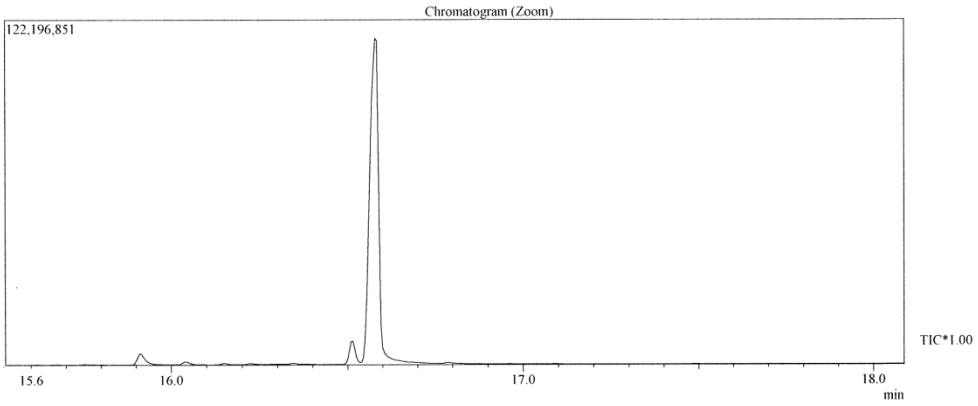


14.

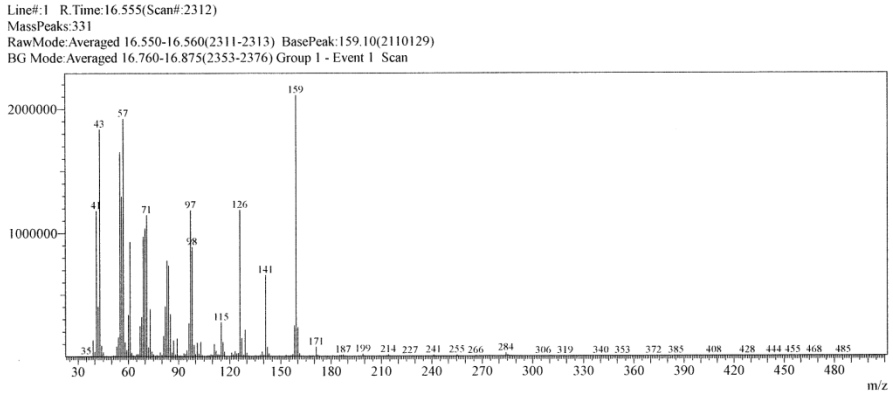


GCMS:

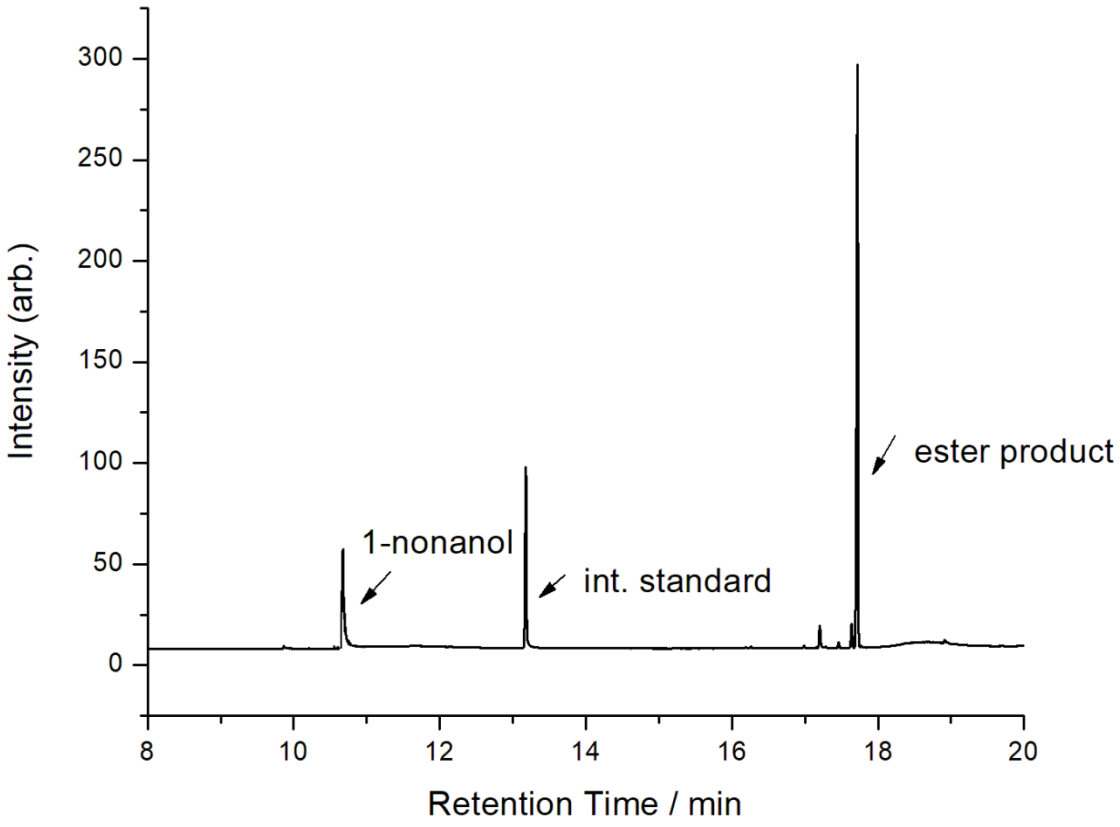




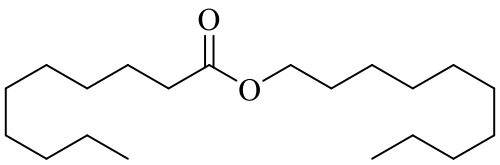
Spectrum



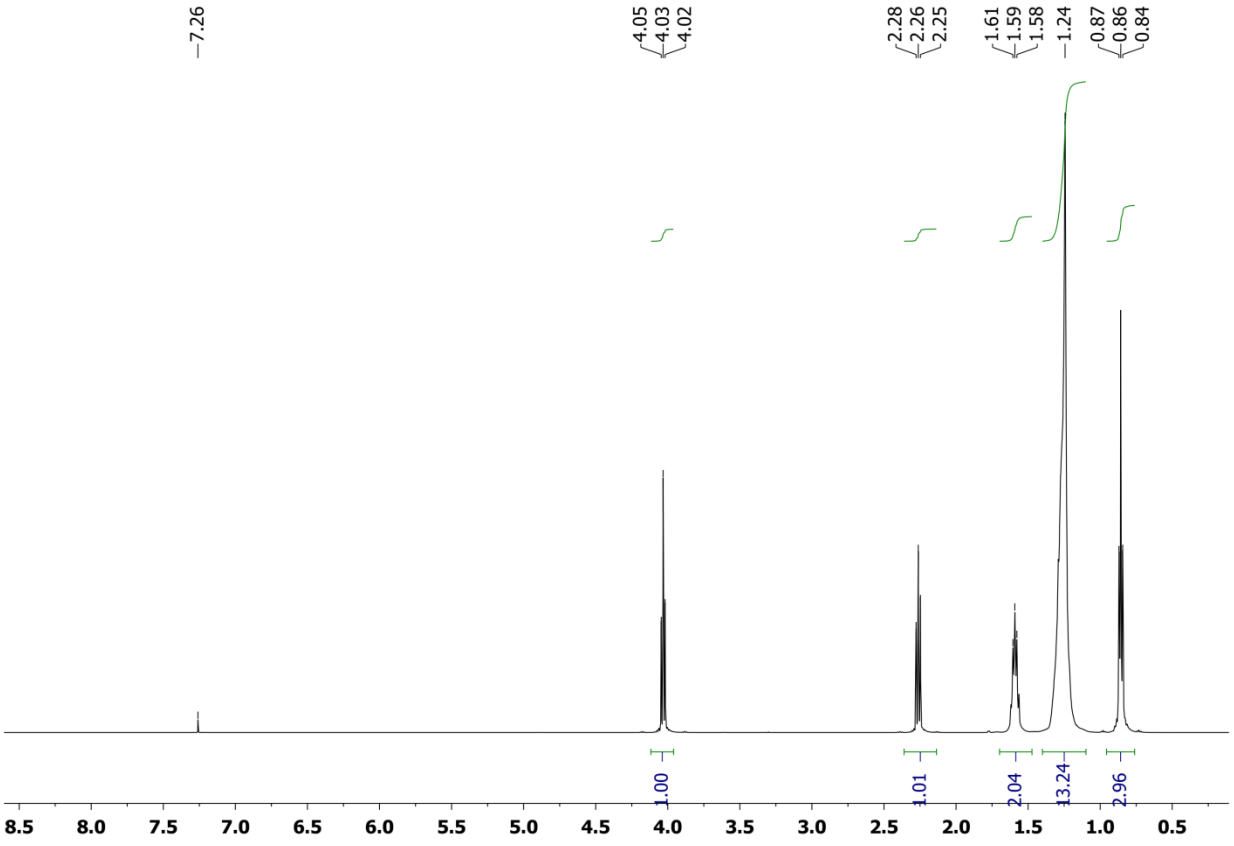
GC-FID Chromatogram:



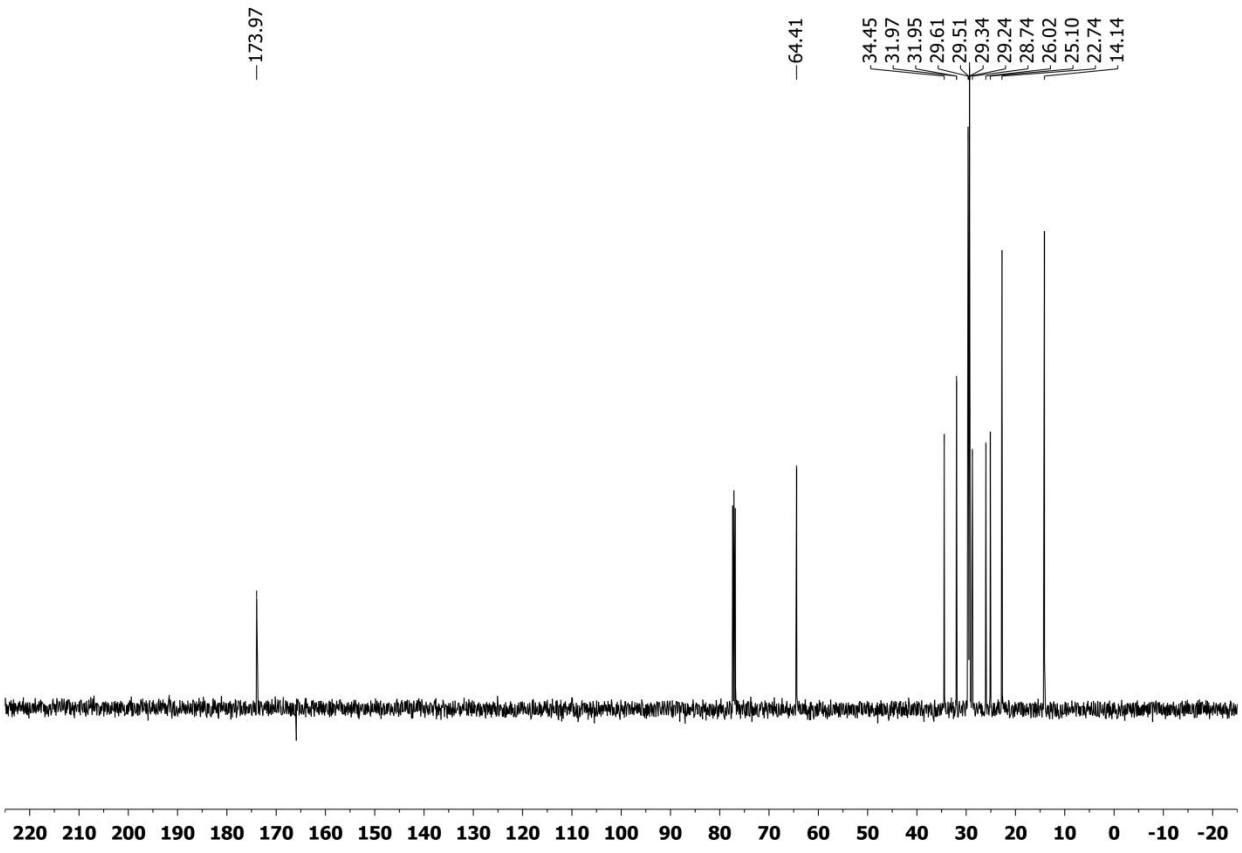
15.



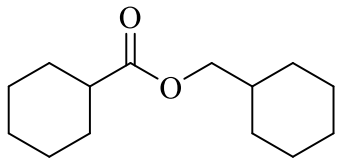
^{1}H NMR (500 MHz, $CDCl_3$):



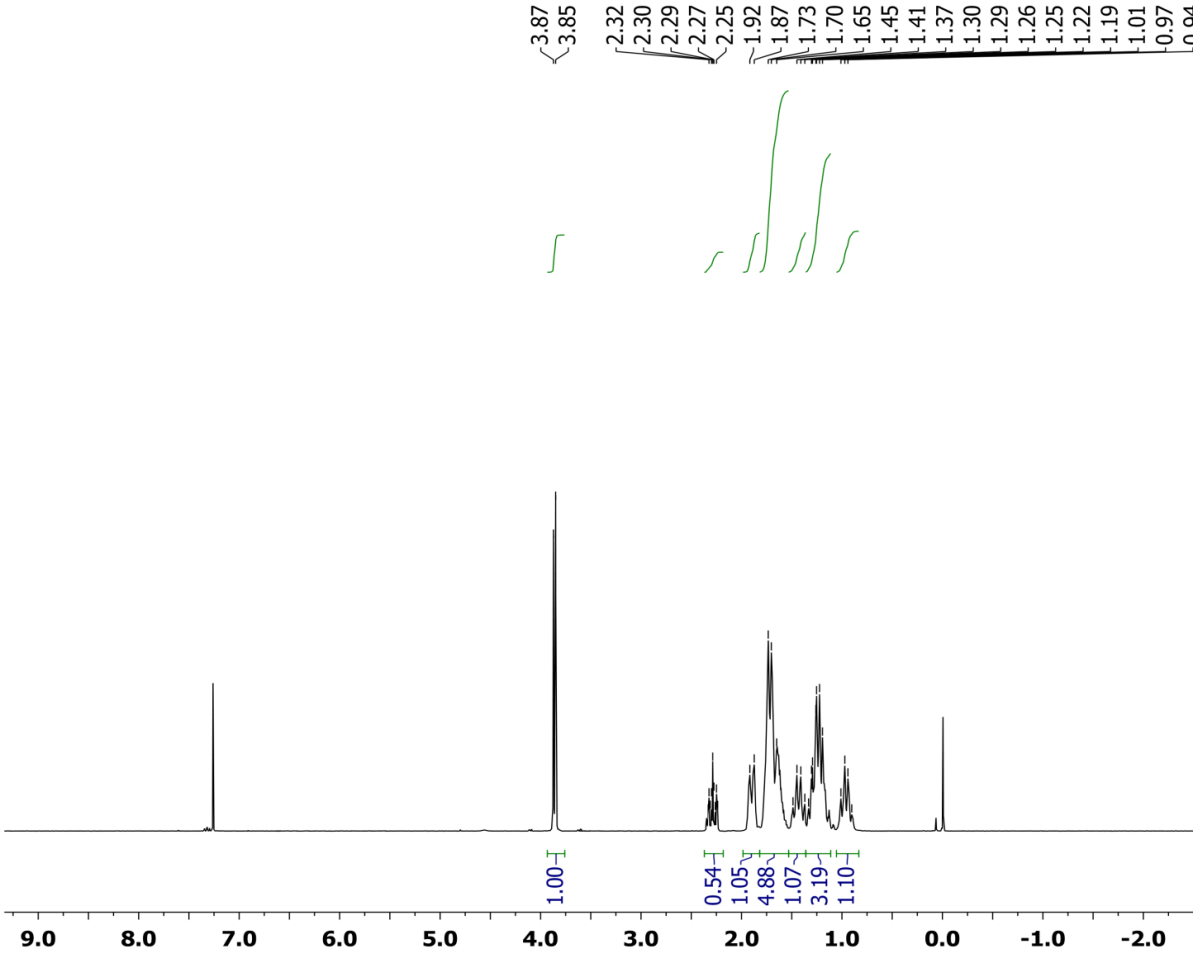
^{13}C NMR (125 MHz, $CDCl_3$):



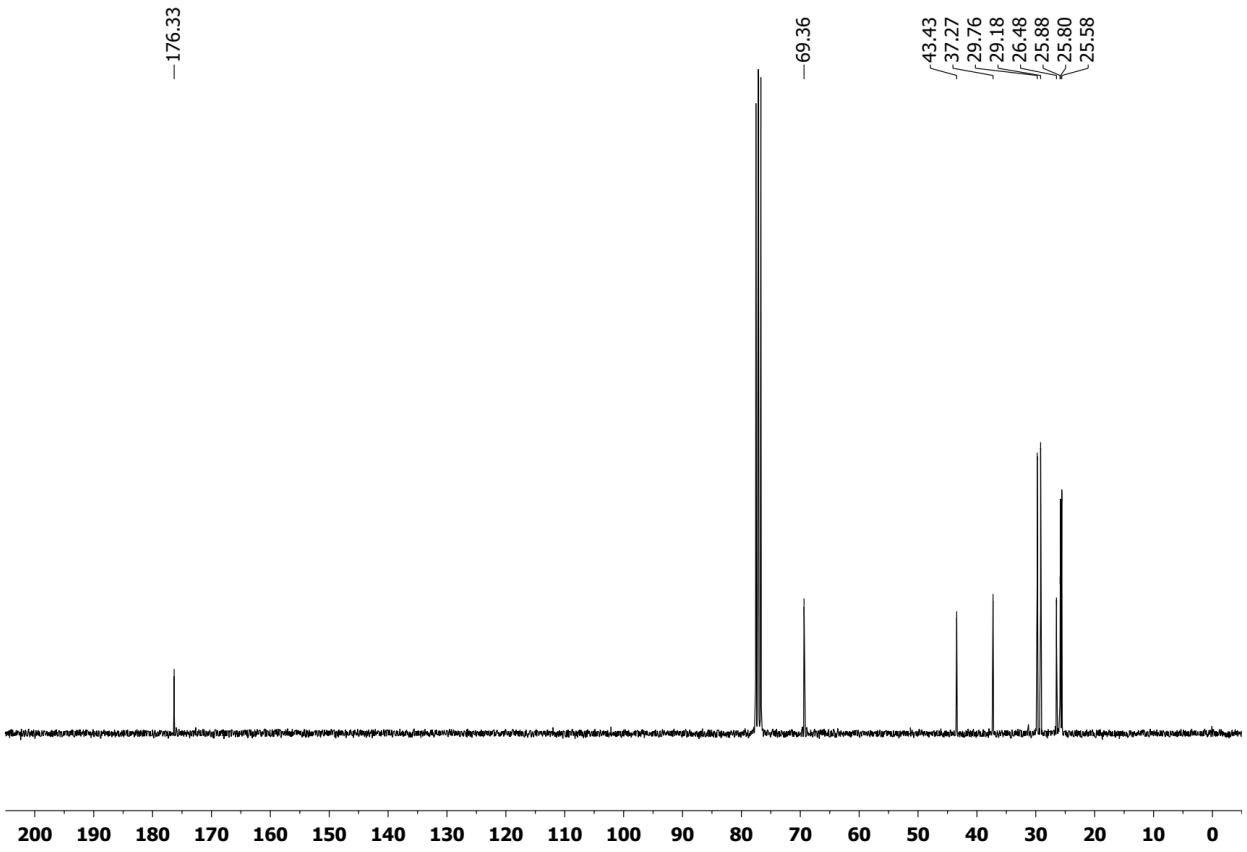
16.



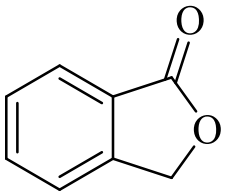
^{1}H NMR (300 MHz, $CDCl_3$):



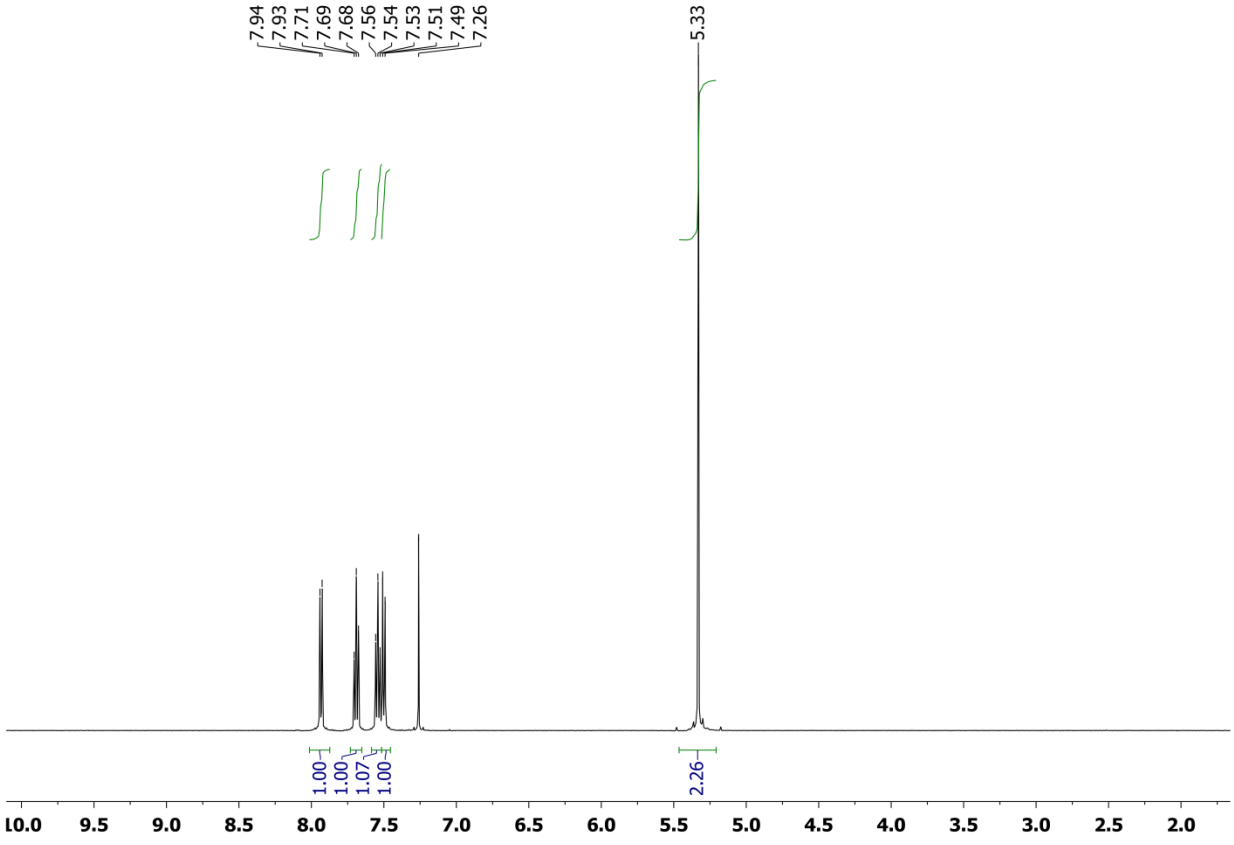
^{13}C NMR (75 MHz, $CDCl_3$):



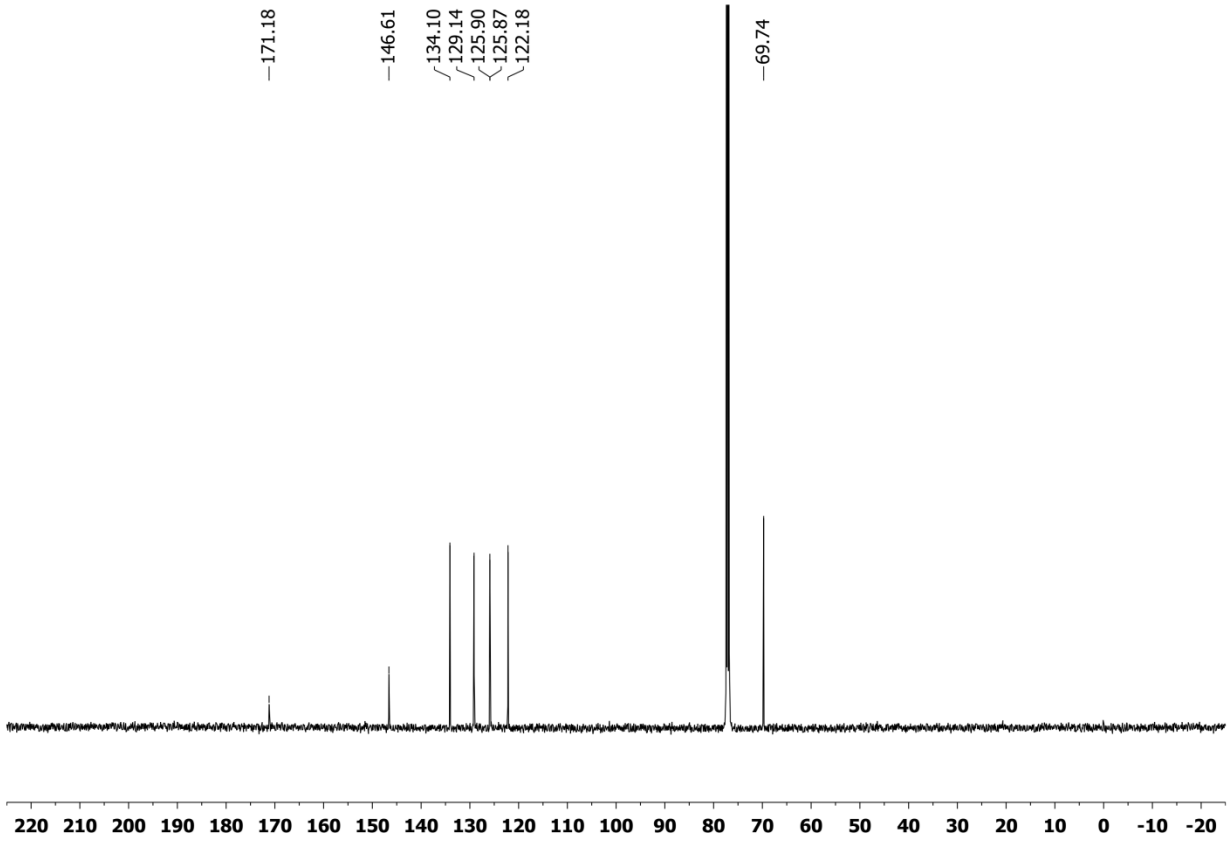
17.



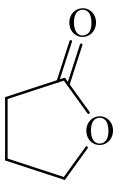
^{1}H NMR (500 MHz, $CDCl_3$):



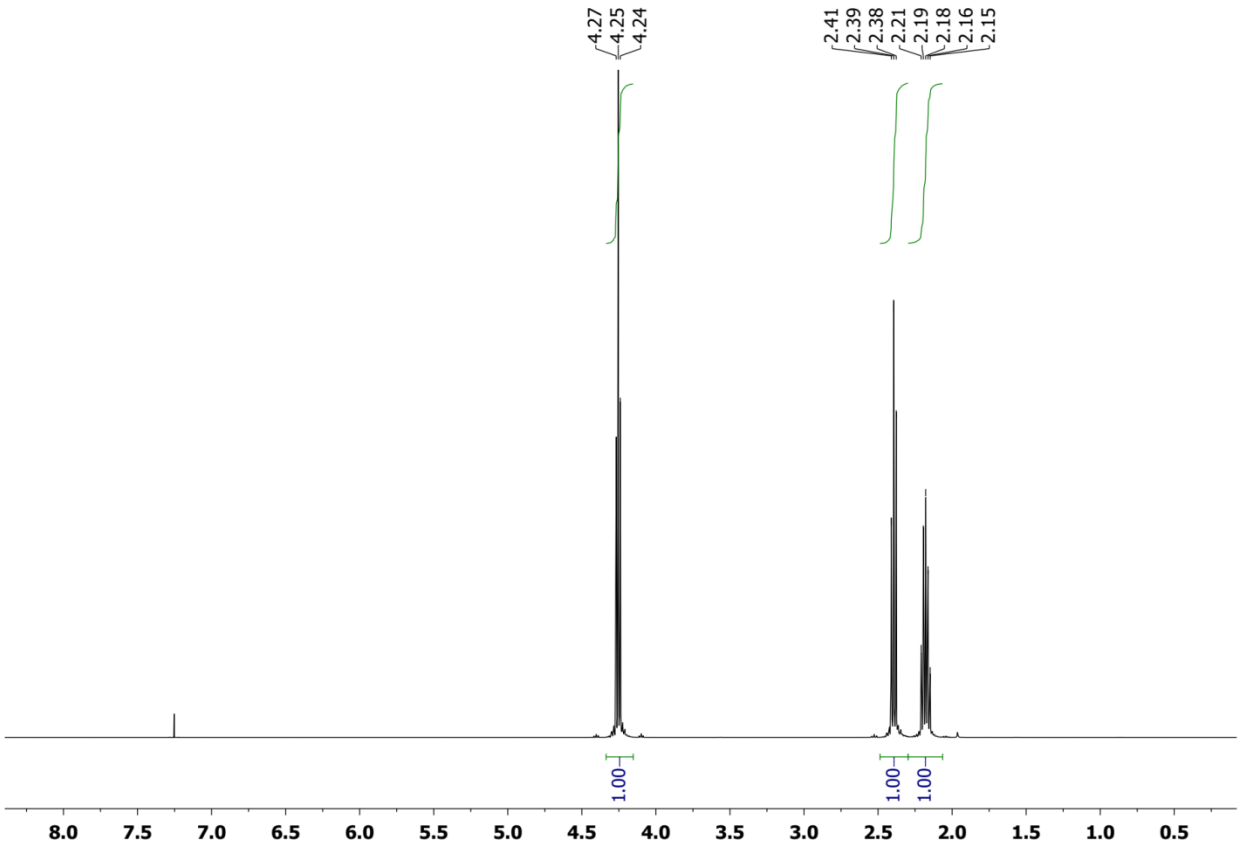
^{13}C NMR (125 MHz, $CDCl_3$):



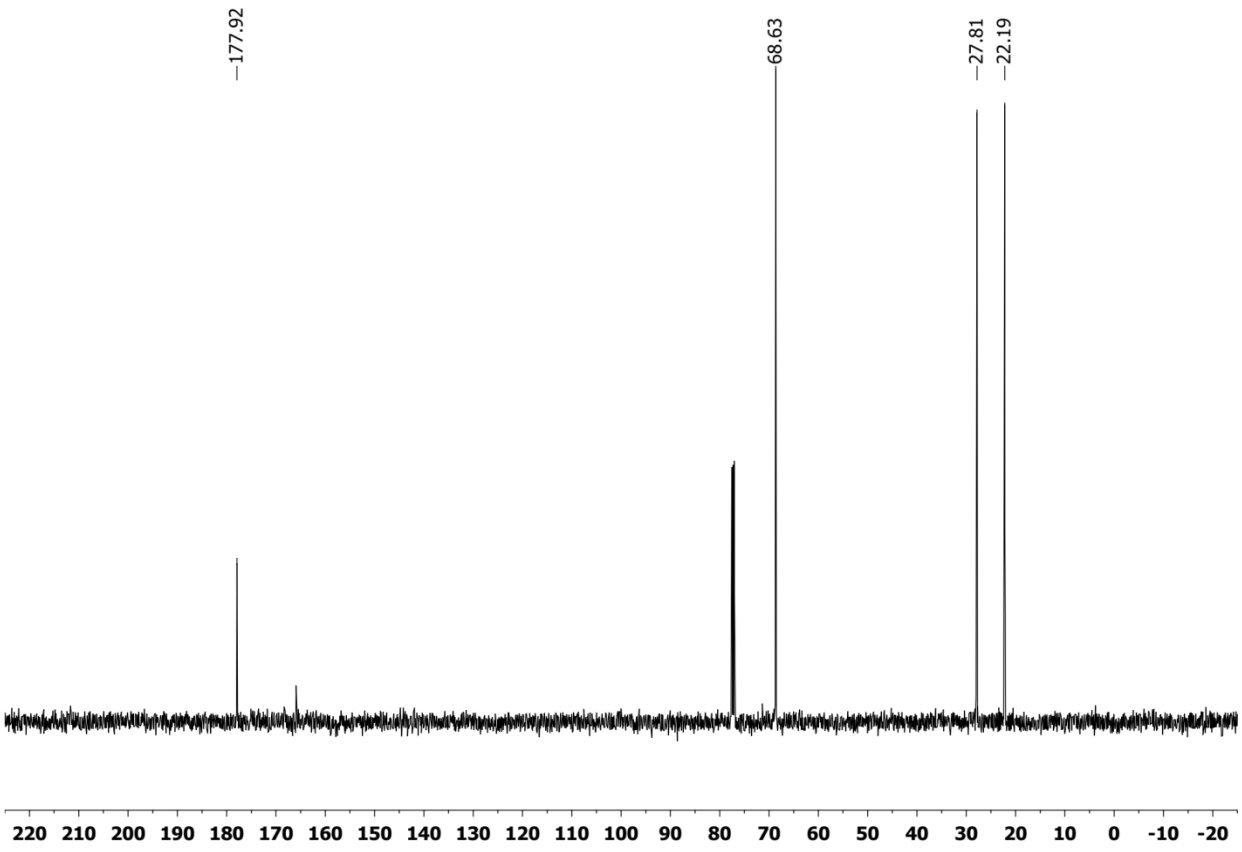
18.



^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (125 MHz, $CDCl_3$):



GC Chromatogram of H_2 as a Byproduct: