COBALT-CATALYZED ACCEPTORLESS DEHYDROGENATIVE HOMOCOUPLING OF SECONDARY ALCOHOLS TO KETONES

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ABSTRACT

The replacement of rare and expensive transition metals such as Ru, Rh, Pt, Pd, and Ir with earth abundant transition metals is an appealing target in the field of catalysis. A cobalt complex bearing a novel tetradentate tripodal ligand has been synthesized and utilized for the homo-coupling of secondary alcohols to form ketones. Along with the cobalt complex, a strong base is introduced into the coupling reaction in order to activate the catalyst. A wide variety of both aliphatic and aromatic secondary alcohol substrates have been investigated to determine the effects of different substituents on reactivity. All reactions were performed under an inert atmosphere using either argon flow or nitrogen filled pressure vessels. Coupled products are assessed using NMR with an internal standard to determine yield as well as GCMS to confirm structure. These reactions provide high yields of coupled ketone products using cobalt-catalyst loadings as low as 3.5 mol%. Acceptorless dehydrogenative coupling is an eco-friendly method for ketone production, generating only H_2 gas and water as byproducts.

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CHAPTER 1

INTRODUCTION

1.1. Ketones in Nature, Industry, and Synthesis

Since the dawn of modern organic chemistry, ketones have been among the most studied naturally forming chemical compounds. They are found in abundance in nature, and play important roles in many natural processes. Industrially, many naturally occurring ketones are used in perfumes, fragrances, and flavorings (Figure 1). In nature, they are found in and used in our bodies as hormones and sugars (Figure 2). Acetone, one of the most widely used solvents in chemistry and industry, and several other common solvents are ketone based (Figure 3).

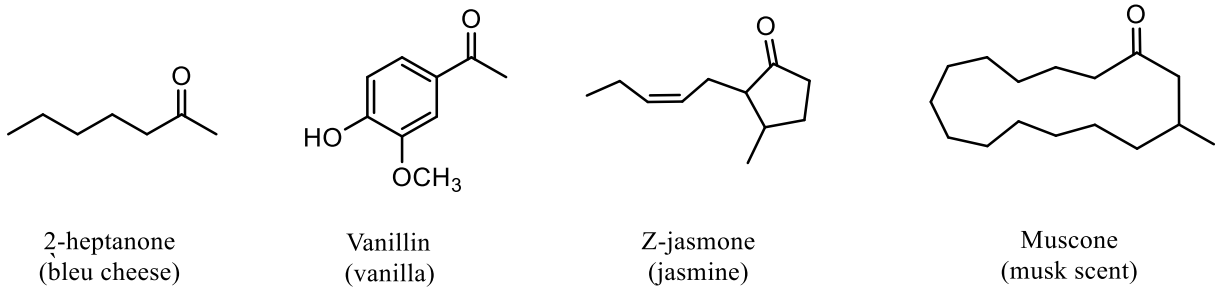


Figure 1. Examples of naturally occurring ketones that are used in perfumes, fragrances and flavorings.

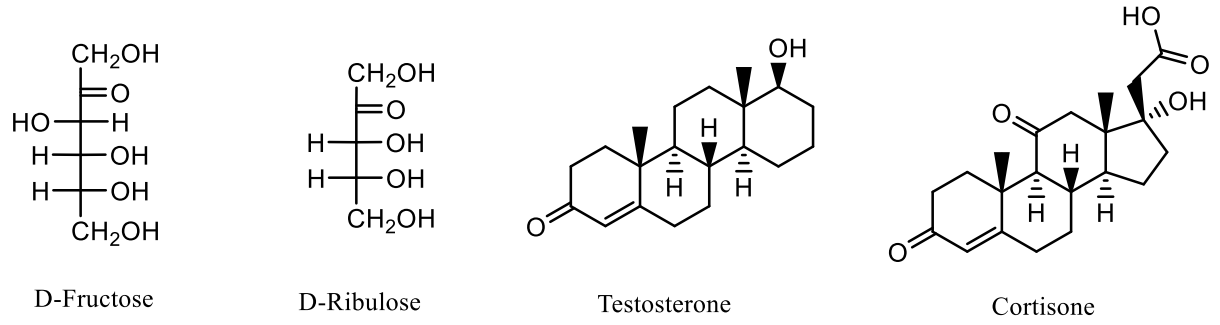
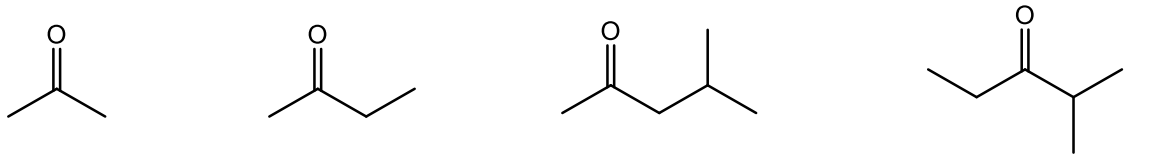


Figure 2. Examples of naturally occurring ketones that are used as sugars (ketoses) and hormones within the body.

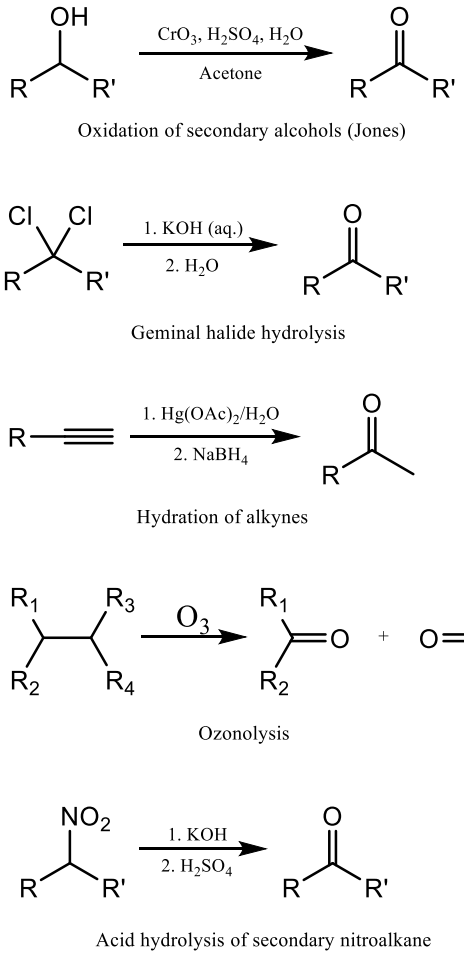


Acetone | Butanone (Methyl ethyl ketone) | Methyl isobutyl ketone | Ethyl isopropyl ketone

Figure 3. Ketones commonly used as solvents.

1.2. Traditional Synthesis Methods for Ketone Production

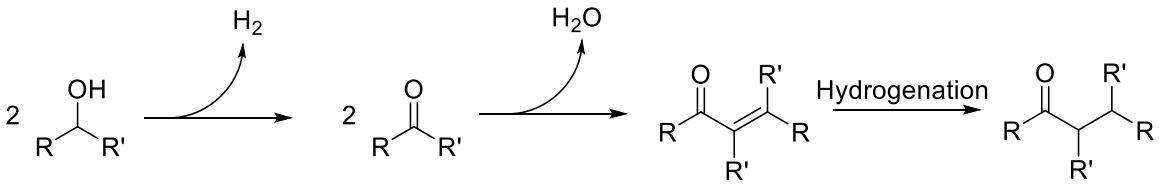
Many different methods are available for the large scale production of ketones for both synthetic and industrial purposes. Some of the most common methods are listed below (Scheme 1). Unfortunately, there are several drawbacks to many of these methods. Besides the use of expensive, rare transition metals in many cases, these reactions require a hydrogen acceptor or generate undesirable by-products.



Scheme 1. Traditional methods for ketone production.

1.3. Catalytic Acceptorless Dehydrogenation for Homocoupling of Secondary Alcohols to Ketones

In the past twenty years, a new catalytic method to produce ketones has grown in popularity. This method, known as "catalytic acceptorless dehydrogenation," uses environmentally benign secondary alcohol substrates along with an organometallic catalyst to produce coupled ketone products with only hydrogen gas and water as byproducts. Because the byproducts of this reaction are not harmful to the environment, catalytic acceptorless dehydrogenation is a sustainable alternative to many other methods of ketone production. There has even been some interest in using acceptorless dehydrogenation of alcohols as a source of hydrogen gas for alternative fuel production.[1] There are two primary mechanisms by which this reaction takes place that have been identified. The first, commonly referred to as the "borrowing hydrogen" method or "hydrogen autotransfer" method, allows the catalyst to utilize the hydrogen gas produced in the initial dehydrogenation step to then hydrogenate the olefin formed in the subsequent steps.[2] In the second proposed mechanism, the hydrogen gas produced in the initial dehydrogenation is not the hydrogen source for the final hydrogenation. Instead, an alternative hydrogen source such as the hydrogen of excess alcohol must be used. Regardless of the mechanism used by the catalyst, secondary alcohol homocoupling takes place in three primary steps: dehydrogenation, β-alkylation, and hydrogenation (Scheme 2).



Scheme 2. Catalytic acceptorless dehydrogenation and subsequent homocoupling of secondary alcohols to ketones

1.4. 2nd and 3rd Row Transition Metals for Coupling Catalysts

Since 2004, catalysts being used for ketone production via a catalytic acceptorless dehydrogenation pathway have primarily used rare and expensive 2nd and 3rd row transition metals such as Ru, Rh, Pd, Os, Ir, and Pt. In 2004, Dr. David Milstein and co-workers published one of the first works on a homogenous acceptorless dehydrogenation catalyst that does not require the presence of an acid as a hydride acceptor.[3] This was a tremendous advancement for the field of coupling catalysis. However, the initial Ru(II) hydride catalysts synthesized and used by Milstein were not particularly efficient. They produced low ketone yields, had poor turnover numbers (TON), and required a large amount of base (sodium isopropoxide) for the dehydrogenation reactions to occur. The catalysts used in this early work were only successful in dehydrogenating secondary alcohols to ketones, with no dehydrogenation taking place when primary alcohols were used, and no overall coupling reaction occurring. The following year, in 2005, the Milstein group published another paper in which much higher yields were achieved after some minor ligand adjustments were made.[4] The original paper used Ru(II) hydride catalysts bearing tridentate PNP (phosphorous-nitrogen-phosphorous) pincer ligands (Figure 4). These highly electron rich ligands were an important steppingstone in the development of a new series of pincer ligands, one of the most significant being a Ru(II) hydride bearing a PNN (phosphorous-nitrogen-nitrogen) pincer ligand (Figure 4). Using this new Ru(II) PNN catalyst, the group was able to perform acceptorless dehydrogenation of primary alcohols achieving ester yields greater than 95%. Importantly, the group was able to determine the only role of base in these reactions was for catalyst activation. Once the catalyst was activated using KOH, they were able to isolate the active catalyst. Coupling reactions were then run using the active catalyst with primary alcohol substrates, and the difference

in yield between the catalyst plus base reactions and the active catalyst without base reactions were negligible.

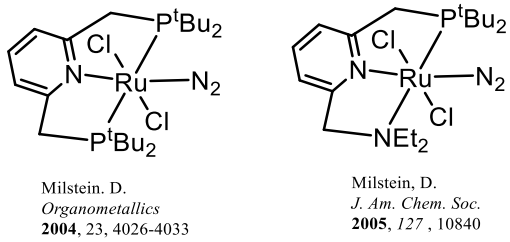


Figure 4. Early Ru(II) pincer catalysts developed by Milstein and co-workers.

Following the publication of these studies, coupling via catalytic acceptorless dehydrogenation became a more mainstream research focus. Numerous groups began working with 2nd and 3rd row transition metal catalysts for alcohol coupling. For the most part, groups have had success with the homocoupling of primary alcohols to esters, cross-coupling of primary alcohols to esters, alkylation of alcohols with amines, and β-alkylation of secondary alcohols with primary alcohols to produce ketones. Through the development of new ligands, along with the expansion to metals other than ruthenium, many improvements have been made in the past 15 years as the understanding of acceptorless dehydrogenation has improved. Beller and co-workers synthesized and worked with several ruthenium and iridium catalysts capable of homocoupling 1-ethanol to develop a new means of ethyl acetate production.[5] NHC-Ru catalysts have been used by groups such as Peris and co-workers as well as Sanchez and co-workers for esterification of alcohols.[6,7] Yamaguchi and co-workers and Pullarkat and co-workers both developed iridium catalysts bearing cyclopentadiene ligands.[8,9] The catalyst developed by the Yamaguchi group was one of the earliest examples of an iridium catalyst being used for dehydrogenation of secondary alcohols. However, their experiments only went so far as to produce the initial ketone product of dehydrogenation, and no coupled ketone products were ever identified. The Pullarkat catalyst was used for β-alkylation

of primary alcohols with secondary alcohols, forming coupled ketone products. Baratta and co-workers synthesized a ruthenium complex bearing a unique CNN ligand for hydrogen transfer reduction of ketones.[10] Gelman and co-workers synthesized a PCP-Ir catalyst for acceptorless dehydrogenation.[11] Nozaki and co-workers also used an Ir complex bearing a PNP pincer ligand for hydrogenation of carbon dioxide.[12] Gusev and co-workers developed an Os catalyst for acceptorless dehydrogenation of primary alcohols to esters.[13]

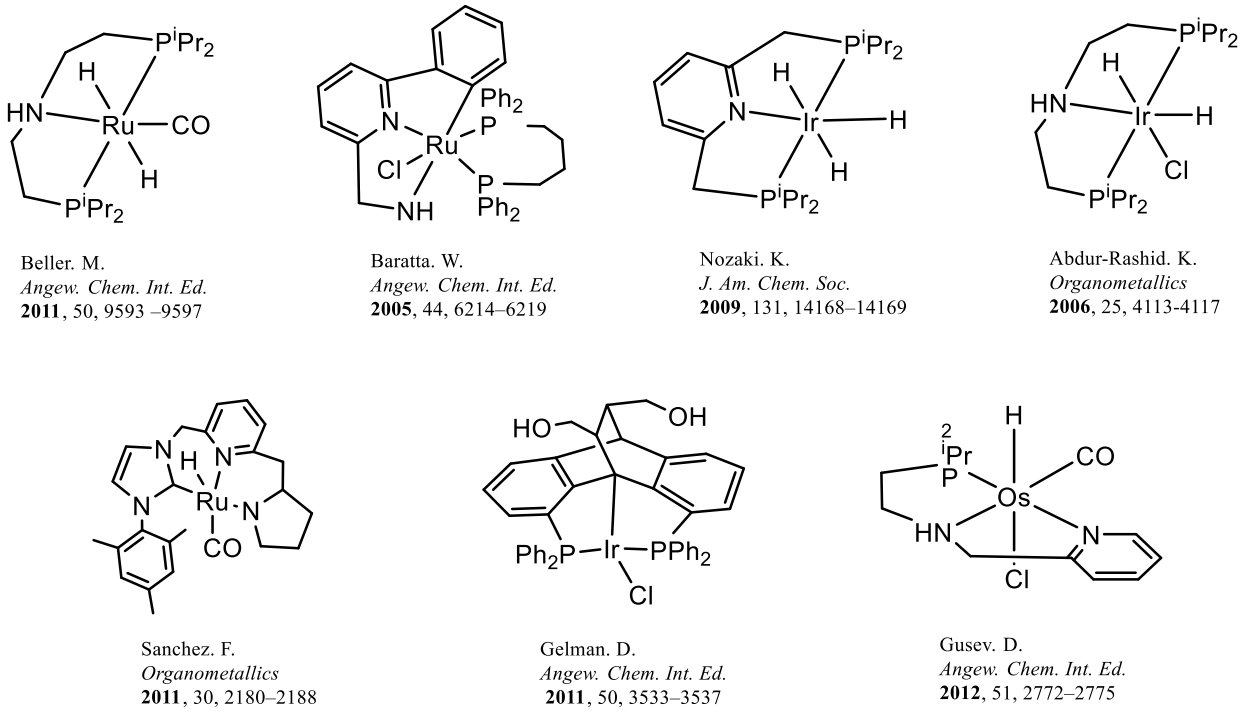
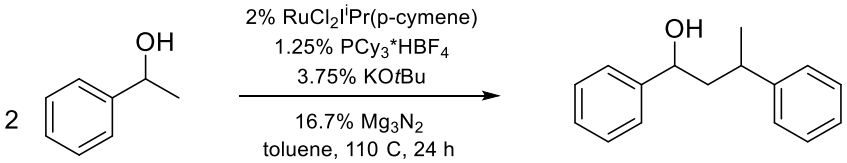


Figure 5. 2nd and 3rd row acceptorless dehydrogenation catalysts

It was not until the work of Makarov and Madsen was published in 2013 that homocoupling of secondary alcohols to ketones using catalytic acceptorless dehydrogenation was a realistic means for ketone production.[14] The group exploited a Ru(II) chloride complex bearing a symmetrical NHC and p-cymene ligand for the coupling reaction. This reaction was discovered incidentally while attempting a cross-coupling esterification reaction between 2-phenylethanol and 1-

phenylethanol. Rather than producing the cross-coupled ester, the 2-phenylethanol homocoupled to form its symmetrical ester, and 2-phenylethanol formed acetophenone. No cross-coupling occurred. After this reaction, a new experiment was run without the presence of the primary alcohol, and to their surprise, the dimeric ketone product of acetophenone was formed at a yield greater than 95% (Scheme 3). To date, the results of this study remain the benchmark for secondary alcohol coupling using a catalytic acceptorless dehydrogenation pathway.



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Scheme 3. Madsen secondary alcohol homocoupling via catalytic acceptorless dehydrogenation

1.5. First Row Transition Metals for Coupling Catalysts

In recent years, many research groups have been attempting to move away from the 2nd and 3rd row transition metals in favor of base transition metals such as Fe, Co, and Mn. While the afore mentioned metals are useful due to their electronic structure, several groups have had comparable results using base transition metals. The more desirable base transition metals are earth-abundant, and significantly less expensive, making them a practical alternative. On top of abundance and price, noble metals like ruthenium, iridium and osmium are more toxic than base transition metals, and the expense of large scale removal through purification to acceptable levels can be expensive, decreasing sustainability.[15]

Over the past 5 years, new base transition metals catalysts have been developed for acceptorless dehydrogenative coupling reactions (Figure 6). In 2015, Wills and co-workers published an article in which an iron catalyst bearing a cyclopentadiene ligand for alkylation between alcohols and

amines was synthesized.[16] This was one of the first published works using an iron catalyst for alkylation of aromatic amines and benzyl alcohol substrates. In a similar work, Barta and co-workers developed an iron catalyst bearing cyclopentadiene ligand for the amination of benzyl alcohols with secondary amines.[17] In 2013, Hanson and Zhang reported their findings on a cobalt catalyst bearing a PNP pincer ligand for acceptorless dehydrogenation of alcohols with amines to selectively form coupled imines.[18] Synthetic formation of imines has long been considered a challenging task for chemists. Using their cobalt complex, Hanson and Zhang were able to selectively produce imines in yields greater than or comparable to those made by groups using noble transition metals. In 2015, Kempe and co-workers published a work using a cobalt catalyst for acceptorless dehydrogenation.[2] The Kempe group was able to synthesize a cobalt complex stabilized by a PN_5P ligand including a triazine backbone. Catalysts bearing PN_5P ligands with triazine backbones were previously shown possess high activity for the hydrogenation of carbonyl groups. Similar to the Wills group, Kempe and co-workers also used their cobalt complex to catalyze amine/alcohol alkylation reactions. Recently, Madsen and co-workers published a work using manganese porphyrin complexes to catalyze amine/alcohol alkylation reactions.[19] No porphyrin complexes have been previously reported for the dehydrogenation and subsequent hydrogen release in a coupling reaction. Interestingly, while aromatic amines and benzyl alcohols had a tendency to provide high yields of coupled imines, reactions using aliphatic alcohols were unable to produce yields >50%. To date, to my knowledge no published work on a base metal acceptorless dehydrogenation coupling catalyst for secondary alcohol homocoupling to ketones exists.

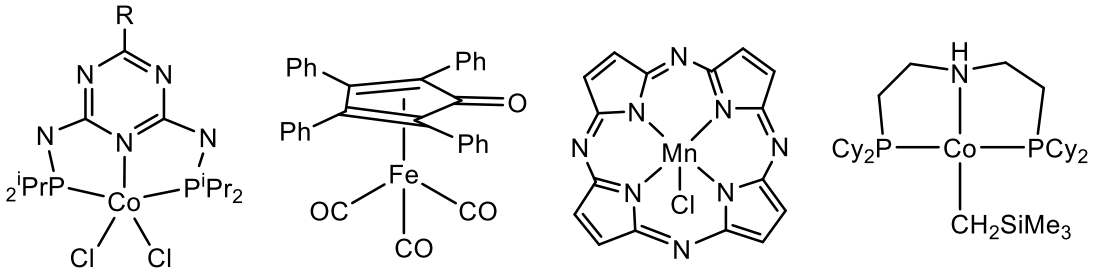

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Figure 6. Examples of base transition metal catalysts for acceptorless dehydrogenation

1.6. Objectives of Study

1. Synthesis of a tripodal ligand consisting of three strong field phosphine donors, a pyridine pendant arm, and an N-H linker allowing for a flexible binding site.

2. Synthesis of a cobalt complex bearing a tetradentate ligand with tripodal geometry for the homocoupling of secondary alcohols via a catalytic acceptorless dehydrogenation pathway.

3. Optimization of secondary alcohol homocoupling through the tuning of catalyst loading, base loading, time, temperature, and reaction vessel.

4. Efficient production of both aliphatic and aromatic coupled ketones using a cobalt catalyst.

5. Mechanistic studies of acceptorless dehydrogentation pathway for secondary alcohol homocoupling.

CHAPTER 2

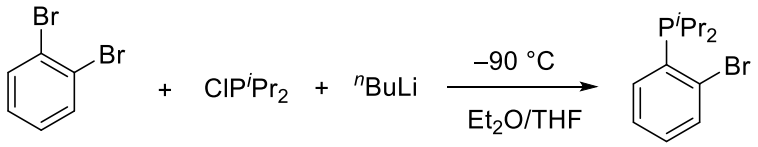
EXPERIMENTAL METHODS

2.1. Synthesis of Tripodal $^{iPr}PPPN^{H}Py^{Me}$ Ligand

2.1.1 Synthesis of 2-(diisopropylphosphino)-phenyl bromide

After drying in an oven for 24 hrs, a 500 mL round bottom Schlenk flask was brought into an N_2 filled glovebox. The flask was loaded with 1,2-dibromobenzene (0.017 mol), 28.8 mL of ethyl ether, and 28.8 mL of tetrahydrofuran. A rubber septum was then placed on the flask. The flask was removed from the glove box and placed in a large dewar containing a mixture of liquid nitrogen and ethanol. The liquid nitrogen/ethanol bath generated a temperature of -110 ^{o}C. As the flask cooled, the bath was stirred, and liquid nitrogen was added periodically to maintain an evenly cooled surface on the flask. The flask was left to cool while stirring until the solution reached -110 ^{o}C. While the flask was cooling, a syringe with a reusable stainless steel needle was brought into the glove box. In the box, the syringe was loaded with n-butyl lithium (0.017 mol). A rubber stopper was placed on the tip of the needle to maintain the inert atmosphere within, and the syringe was removed from the glove box. After removing the stopper, the needle of the syringe was used to pierce the septum of the Schlenk flask. With the needle inside of the flask, the n-butyl lithium was dispensed into the flask dropwise over 15 min. As the n-butyl lithium was added, the solution became pale yellow in color. Once all of the n-butyl lithium was added, the solution was left to stir until white precipitate began forming in solution. Approximately 5 min. after the first appearance of white precipitate, a syringe under inert atmosphere was used to add of chlorodiisopropyl phosphine (0.017 mol) dropwise to the flask. As the chlorodiisopropyl

phosphine was added, the solution began to turn orange in color. The flask was then removed from the bath, and allowed to come to room temperature. As the flask warmed, the orange color faded resulting in a pale yellow slurry. Once at room temperature, the contents of the flask were transferred to a 500 mL round bottom flask, and volatile solvents were removed using a rotavapor. The resulting product was a viscous yellow material. 25 mL of pentane and 3 g of silica gel were added to the flask, and the solution was left to stir for 1 h. After stirring the precipitate was removed through a celite filtration. The celite plug was further washed with pentane to maximize yield. The filtrate was collected in a 500 mL flask, and placed on a rotavapor. The resulting product was 3.94 g (85% yield) of a pale yellow oil.

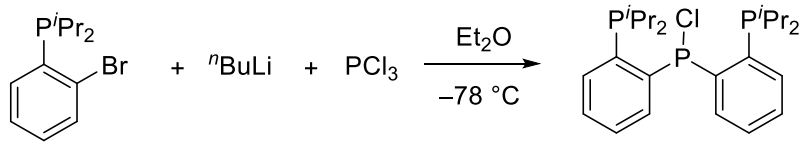


Scheme 4. Ligand synthesis step 1

2.1.2 Synthesis of bis[2-(diisopropylphosphinophenyl)]-chlorophosphine

Two oven-dried 250 mL Erlenmeyer flasks were brought into an N_2filled glove box. To one of the flasks, 2-(diisopropylphosphino)-phenyl bromide (0.015 mol) in 28.8mL of diethyl ether was added. In the second flask, trichlorophosphine (0.007 mol) in 8 mL of diethyl ether was added. A cooling well was set up in the glove box using a mixture of acetone and dry ice to generate a constant temperature of −65 °C. Acetone and dry ice were added periodically to maintain the temperature. The two Erlenmeyer flasks were then placed in the cooling well, and left to cool while stirring. Once the temperature in the flasks reached −65 °C, n-butyl lithium (0.015 mol) was added

to the flask containing 2-(diisopropylphosphino)-phenyl bromide dropwise over the course of 15 min. As n-butyl lithium was added, a white precipitate began forming. After all of the n-butyl lithium was added, the solution was left in the cooling well for an additional 15 min. to allow additional product to form. The contents of the flask containing trichlorophosphine was then slowly poured into the flask containing white precipitate. The resulting product was a faint yellow color. The flask was left to stir in the cool well for 15 min. The solution was then removed from the cooling well and transferred into an amber bottle. It was left in the glove box at room temperature stirring for 24 hrs. The bottle was then removed from the glove box and filtered through a celite plug. The filtrate was rotavaped and placed into a refrigerator for crystallization. The resulting product was obtained as 2.58 g (76% yield) of yellow crystals.

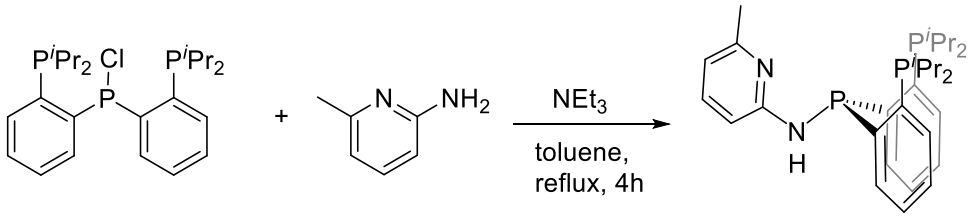


Scheme 5. Ligand synthesis step 2

2.1.3 Synthesis of ^{iPr}PPPN^{H}Py^{Me}

After drying in an oven for over 24 hrs, a 100 mL Schlenk flask was brought into a N_2 filled glove box. Inside of the box, the flask was loaded with 2-amino-6-methyl pyridine (0.004416 mol) and 34 mL of toluene. Next, NEt_3 was added to the solution dropwise over a 5 min period. A rubber septum was placed over the top of the Schlenk flask, and the flask was removed from the glove box. The flask was then placed on a Schlenk line under Ar in a previously prepared ice bath with

a temperature of 0 °C. In the glove box, bis(2diisopropylphosphinophenyl) chlorophosphine (0.004416 mol) was dissolved in 15 mL of toluene. This solution was then placed in a 20 mL syringe with a reusable stainless steel needle. A stopper was placed on the tip of the needle, and the syringe was removed from the glove box. Once the solution in the Schlenk flask had cooled to 0 °C, the stopper was removed from the syringe, and the bis(2diisopropylphosphinophenyl) chlorophosphine solution was added dropwise under Ar flow. After the addition was complete, the flask was removed from the ice bath and allowed to come to room temperature. The rubber septum was removed from the top of the Schlenk flask, replaced with a glass stopper, and placed in an oven at 80 °C for 24 h. After 24 h, a ^{31}PNMR was taken of to ensure the reaction had gone to completion. The reaction was then filtered through celite, and the filtrate was collected in a 100 mL round bottom flask. The solution was rotavaped to remove volatiles. The resulting product was a white powder. For further purification, recrystallization was performed through slow diffusion of pentane and diethyl ether. 1.85 g (80%) of crystals were obtained.

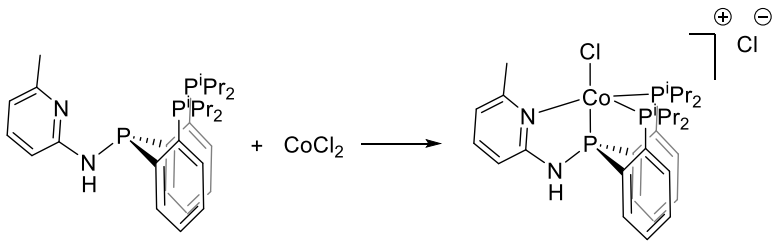


Scheme 6. Ligand synthesis step 3

2.2 Synthesis of Tripodal Cobalt Catalyst

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

An oven dried Erlenmeyer flask was brought into an N_2 filled glove box. $CoCl_2$ (0.002 mol) was placed in the flask along with 20 mL of tetrahydrofuran, producing a red slurry. To the slurry, the $^{iPr}PPPN^{H}Py^{Me}$ (0.002 mol) ligand in solution (20 mL tetrahydrofuran) was added dropwise. The flask was stoppered and the mixture was stirred for 24 h. The resulting product was red-orange in color. After 24 h, the flask was removed from the glove box and transferred into a 500 mL round bottom flask. Tetrahydrofuran was removed using a rotavapor. The remaining red-orange powder remained in the flask. Methanol was added to the round bottom flask to dissolve the red-orange product, leaving unreacted $CoCl_2$ undissolved. The excess $CoCl_2$ was removed from solution using a Celite filtration. The filtrate was again collected in a round bottom flask, and placed on a rotavapor for concentration. The product was then crystallized through vapor diffusion of ether and methanol, resulting in a 1.110 g (85% yield) of purified product.



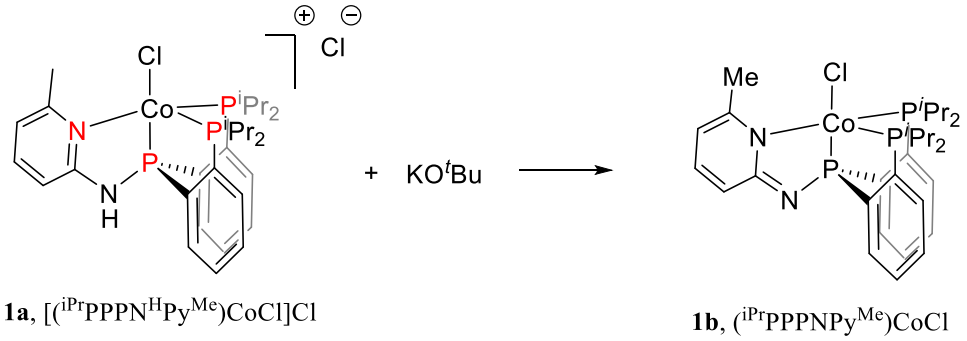
L^{A}, $^{iPr}PPPN^{H}Py^{Me}$ **1a**, [($^{iPr}PPPN^{H}Py^{Me}$)CoCl]Cl

Scheme 7. Synthesis of cobalt complex **1a**

2.2.2 Synthesis of $^{iPr}PPPNPy^{Me}CoCl$ (**1b**)

An oven dried 250 mL Erlenmeyer flask was brought into a N_2 filled glove box. [$^{iPr}PPPN^{H}Py^{Me}CoCl$]Cl (0.764 mol) was added to the flask along with KO^{t}Bu (0.764 mol) and

30mL of toluene. The resulting solution became a red slurry. The slurry was stoppered and left to stir in the glove box for 24 h. After 24 h the solution was removed from the glove box and filtered through a Celite plug. The filtrate was collected in a round bottom flask and concentrated on a rotavapor. The resulting viscous material was then crystallized for purification through slow vapor diffusion of pentane and toluene. 382.43 mg (81% yield) of crystals were obtained.



1a, [(^{iPr}PPPN^{H}Py^{Me})CoCl]Cl

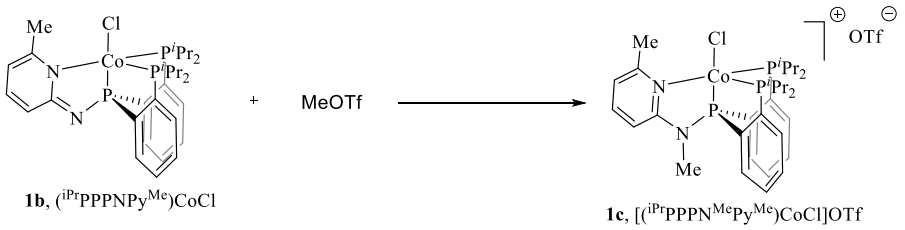
1b, (^{iPr}PPPNPy^{Me})CoCl

Scheme 8. Synthesis of cobalt complex **1b**

2.2.3 Synthesis of [^{iPr}PPPNPy^{Me}CoCl]OTf (**1c**)

An oven dried, 250 mL Erlenmeyer flask was brought into a N_2 filled glove box. The flask was loaded with 200 mg of ^{iPr}PPPNPy^{Me}CoCl, 5 mL of tetrahydrofuran. It was then placed in an ice bath with stirring and allowed to cool to 0°C. To the flask, MeOTf (0.5 mmol) was dissolved in an additional 5 mL of THF, and added dropwise over 15 min. After the addition was complete, the flask was removed from the ice bath and allowed to stir at room temperature for 24 h. After 24 h,

the solution was concentrated under reduced pressure. Crystallization was performed using vapor diffusion of pentane and dichloromethane, resulting in 173.7 mg (71% yield) of purified product.



1b, (^{iPr}PPPNPy^{Me})CoCl

1c, [(^{iPr}PPPN^{Me}Py^{Me})CoCl]OTf

Scheme 9. Synthesis of cobalt complex **1c**

2.3 Coupling Reaction Optimization Using 2-Octanol as an Analogue for Aliphatic Secondary Alcohols

2.3.1 Homocoupling of 2-octanol Using 2.5 mol% **1a** and 15 mol% NaO^{t}Bu in a 100 mL Pressure Vessel at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (2.5 mol%) and NaO^{t}Bu (15 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 °C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction

solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.2. Homocoupling of 2-octanol Using 2.5 mol % **1a** and 30 mol % NaO^{t}Bu in a 100 mL Pressure Vessel at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (2.5 mol%) and NaO^{t}Bu (30 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 $^\circ$C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0,05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.3. Homocoupling of 2-octanol Using 2.5 mol % **1a** and 15 mol % KO^{t}Bu in a 100 mL Pressure Vessel at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (2.5 mol%) and 4.2 mg (15 mol%) of KO^{t}Bu were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.4. Homocoupling of 2-octanol Using 2.5 mol % **1a** and 30 mol % NaO^{t}Bu in a 100 mL Pressure Vessel at 105 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (2.5 mol%) and KO^{t}Bu (30 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 105 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room

temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.5. Homocoupling of 2-octanol Using 2.5 mol % **1a** and 30 mol % NaO^{t}Bu in a 100 mL Pressure Vessel at 85 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a (**2.5 mol%) and KO^{t}Bu (30 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 85 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.6. Homocoupling of 2-octanol Using 3.5 mol % **1a** and 60 mol % NaO^{t}Bu in a 15mL sealed reaction tube at 125 ^{o}C

An oven dried 15mL sealed reaction tube was brought into an N_2 filled glove box. The tube was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the tube using 1.5 mL of toluene. A stir bar was added, and the tube was sealed using a screw cap. The sealed tube was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the tube. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.7. Homocoupling of 2-octanol Using 3.5 mol % **1a** and 60 mol % NaO^{t}Bu in a 100 mL Pressure Vessel at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed

pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.8. Homocoupling of 2-octanol Using 3.5 mol % **1a** and 30 mol % KHMDS in a 100 mL Pressure Vessel at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and KHMDS (30 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.9. Homocoupling of 2-octanol Using 3.5 mol % **1a** and 90 mol % NaO^{t}Bu in a 100 mL Pressure Vessel at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (90 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.3.10. Homocoupling of 2-octanol Using 3.5 mol % **1a** and 60 mol % NaO^{t}Bu in a 15mL reaction tube with argon flow at 125 ^{o}C

An oven dried 15mL reaction tube was brought into an N_2 filled glove box. The tube was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%)

were placed in a scintillation vial, and quantitatively transferred to the tube using 1.5 mL of toluene. A stir bar was added, and the vessel was sealed using screw cap with a rubber septum disc. The sealed tube was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring. A needle connected to an argon source was inserted through the septum. The argon flow was turned on. A needle to allow flow out of the tube was inserted through the septum. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.4. Coupling Reaction Optimization Using 1-(4-methoxyphenyl)ethanol as an Analogue for Aromatic Secondary Alcohols

2.4.1. Homocoupling of 1-(4-methoxyphenyl)ethanol Using 3.5 mol % **1a** and 20 mol % NaO^{t}Bu in a 100 mL Pressure Vessel in Benzene at 105 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (20 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of benzene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil

bath set to 105 °C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.4.2 Homocoupling of 1-(4-methoxyphenyl)ethanol Using 3.5 mol % **1a** and 50 mol % NaO^{t}Bu in a 100 mL Pressure Vessel in Benzene at 105 °C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (50 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of benzene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 105 °C with stirring for 24 h . After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on

a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.4.3. Homocoupling of 1-(4-methoxyphenyl)ethanol Using 3.5 mol % **1a** and 50 mol % NaO^{t}Bu in a 100 mL Pressure Vessel in Benzene at 115 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (50 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of benzene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 115 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.4.4. Homocoupling of 1-(4-methoxyphenyl)ethanol Using 1.75 mol % **1a** and 30 mol % NaO^{t}Bu in a 100 mL Pressure Vessel in Toluene at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (30 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of benzene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug dwas washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

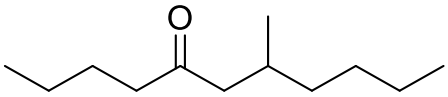
2.4.5. Homocoupling of 1-(4-methoxyphenyl)ethanol Using 1.75 mol % **1a** and 60 mol % NaO^{t}Bu in a 100 mL Pressure Vessel in Toluene at 125 ^{o}C

An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and

allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether, and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

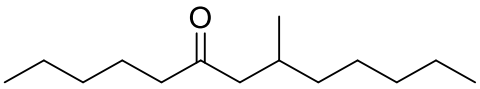
2.5 Synthesis of Ketone Products

2.5.1. Synthesis of 1



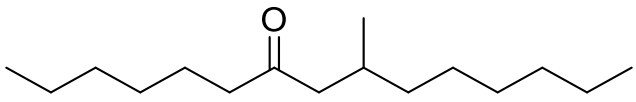
An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-hexanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.2. Synthesis of 2



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-heptanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

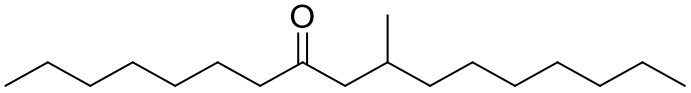
2.5.3. Synthesis of 3



An oven dried 15mL reaction tube was brought into an N_2 filled glove box. The tube was loaded with 2-octanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the tube using 2 mL of toluene. A stir bar was added, and the tube was sealed using a screw cap with a rubber septum disc. The

sealed tube was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction tube was removed from the oil bath and allowed to come to room temperature with the screw cap removed 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the tube. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

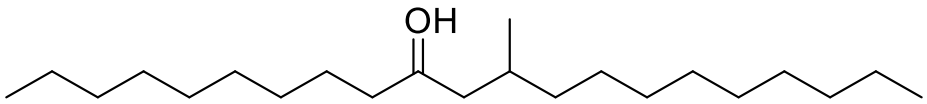
2.5.4. Synthesis of 4



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-nonanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and

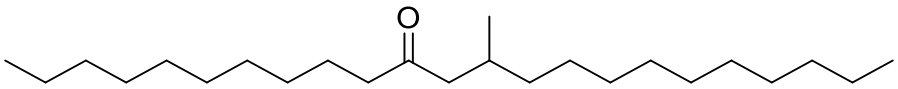
placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.5. Synthesis of 5



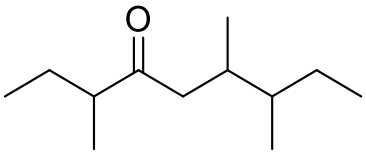
An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-undecanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.6. Synthesis of 6



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 2-dodecanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

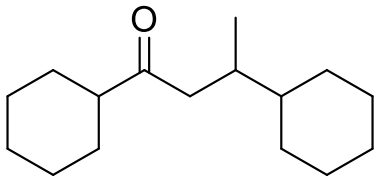
2.5.7. Synthesis of 7



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 3-methylpentan-2-ol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and

NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

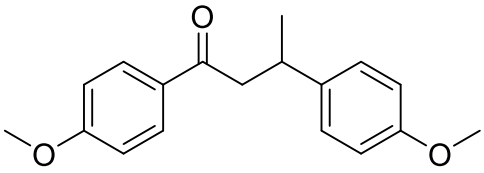
2.5.8. Synthesis of 8



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-cyclohexylethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (3.5 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol),

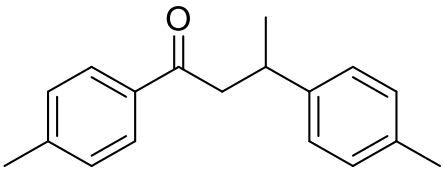
used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.9. Synthesis of 9



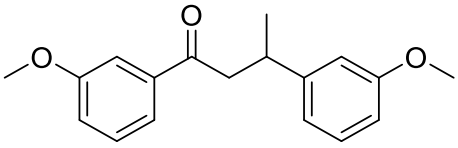
An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.10. Synthesis of 10



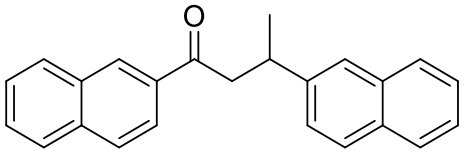
An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(4-methylphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.11. Synthesis of 11



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with 1-(3-methoxyphenyl)ethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

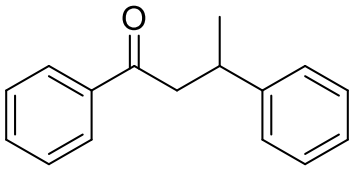
2.5.12. Synthesis of 12



An oven dried 100 mL pressure vessel was brought into an N_2 filled glove box. The vessel was loaded with α-methyl-2-naphthalenemethanol (0.25 mmol) dissolved in toluene using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (60 mol%) were placed in a scintillation vial, and quantitatively transferred to the pressure vessel using 2 mL of toluene. A stir bar was added, and the vessel was sealed using a PTFE screw. The sealed pressure vessel was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring for 24 h. After 24 h, the reaction vessel

was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the pressure vessel. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

2.5.13. Synthesis of 13



An oven dried 15mL reaction tube was brought into an N_2 filled glove box. The tube was loaded with 1-phenylethanol (0.25 mmol) using a 50 µL gastight syringe. **1a** (1.75 mol%) and NaO^{t}Bu (30 mol%) were placed in a scintillation vial, and quantitatively transferred to the tube using 2 mL of toluene. A stir bar was added, and the tube was sealed using a screw cap with a rubber septum disc. The sealed tube was removed from the glove box and placed in an oil bath set to 125 ^{o}C with stirring. A needle connected to an argon source was inserted through the septum. The argon flow was turned on. A needle to allow flow out of the tube was inserted through the septum. After 24 h, the reaction tube was removed from the oil bath and allowed to come to room temperature with the screw cap removed. 1,3,5-trimethoxybenzene (0.05 mmol), used as an internal standard, was dissolved in diethyl ether and added to the tube. The reaction solution was then filtered through a plug of celite and silica gel. The plug was washed with excess diethyl ether. The filtrate was

collected in a round bottom flask and placed on a rotavapor to remove volatile solvents. NMR spectroscopy was used for analysis of the remaining contents.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Synthesis of Tripodal Tetradentate Ligand and Subsequent Cobalt Complexes

Ligand design is of critical importance with regard to the functionality of a first-row transition metal catalyst. There are several reasons for developing a tripodal tetradentate ligand for the acceptorless dehydrogenative homocoupling of secondary alcohols. The first proposed advantage of a tetradentate ligand is that the increased coordination may provide stability to the transition state during the coupling reaction. The second proposed advantage is that the unique geometry of a tripodal ligand may provide a coordination environment that has otherwise not yet been studied with the use of tridentate pincer ligands which have historically dominated the field.

The ligand used in this work features an isopropyl-substituted tris(phosphino)pyridine ligand with an N-H linker tethering the pyridine and phosphino moieties allowing for pendant arm flexibility. The ligand was designed with maximal stability in mind. The three phosphine groups serve as strong field donors to stabilize the low-spin Co metal center. Substituents on the phosphine groups may be substituted to adjust and tune reactivity. Due to the flexible pendant arm, the ligand can

act as either tridentate or tetradentate in the transition state making the activation site more accessible.

The tetradentate ligand ^{iPr}PPPN^{H}Py^{Me} is produced using a three-step synthetic pathway. In the first step, 1,2-dibromobenzene was activated with 1 equiv. of n-BuLi via lithium-halogen exchange and then quenched with diisopropylchlorophosphine to give phosphinophenyl bromide (68% yield). Afterward, 2 equiv. of 2-diisopropylphosphinophenyl bromide reacted with 1 equiv of ^{n}BuLi. Phosphorus trichloride was then added to afford bis(2-diisopropylphosphinophenyl)chlorophosphine (52% yield). Lastly, 1 equiv. of 2-amino-6-methylpyridine was activated by triethylamine and reacted with 1 equiv. of chlorophosphine to form ^{iPr}PPPN^{H}Py^{Me} (81% yield).

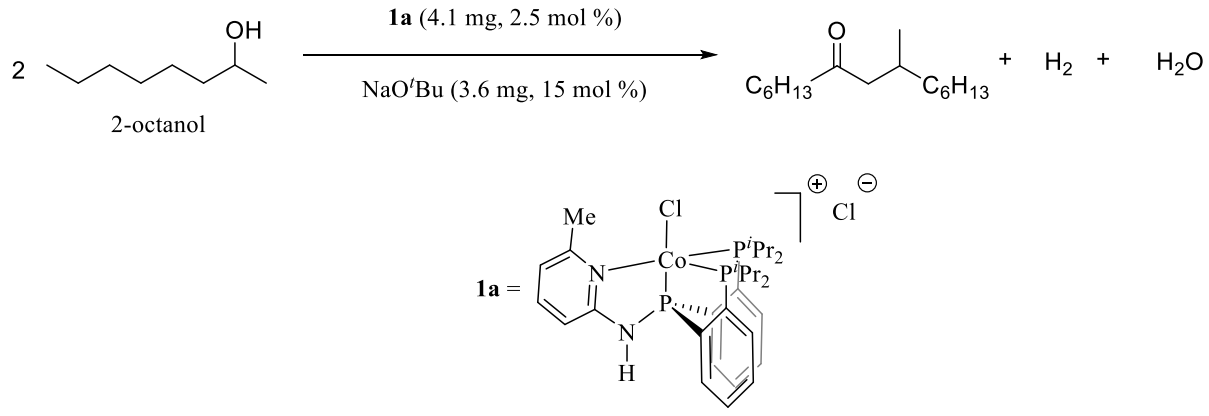
Several cobalt complexes bearing the tripodal tetradentate ^{iPr}PPPN^{H}Py^{Me} were synthesized. The [^{iPr}PPPN^{H}Py^{Me}CoCl]Cl, which was the primary complex used for coupling reactions, was synthesized by reacting the ligand ^{iPr}PPPN^{H}Py^{Me} with 1 equiv. of $CoCl_2$ in THF at room temperature. The reaction generated the product in the form of a red powder (86% yield). The addition of 1 equiv. of KO^{t}Bu caused the precipitation of KCl, deionizing the complex and producing ^{iPr}PPPN^{H}Py^{Me}CoCl (81% yield). The anionic triflate complex was then produced by reacting ^{iPr}PPPN^{H}Py^{Me}Co with an excess of MeOTf at room temperature to generate [^{iPr}PPPN^{H}Py^{Me}CoCl]OTf (71% yield).

3.2. Reaction Optimization

3.2.1. Aliphatic Alcohols

Part of the reaction optimization was performed using 2-octanol as an analogue for aliphatic secondary alcohols. In every optimization reaction, **1a** was used as the catalyst for the dehydrogenative homocoupling reactions of the substrate. A variety of conditions including base, catalyst loading, base loading, temperature, solvent, and in some cases vessel type and conditions were systematically altered until the best yield was reproducibly achieved. In all reactions listed below, toluene was used as the solvent during the coupling process. Initially, reactions were run in 100 mL pressure vessels under inert atmosphere at 125 °C. Catalyst **1a** was loaded at 2.5 mol%, and the base, NaO^{t}Bu was loaded at 15 mol%. The resulting coupled ketone product was found to have a yield of 51% (Table 1,Entry 1). Next, the base loading was increased to 30 mol%. Using more base, the coupled ketone product was formed at a yield of 71% (Table 1, Entry 2). Before continuing to adjust catalyst and base loadings, another base, KO^{t}Bu, was tested. KO^{t}Bu was loaded at 15 mol% under the same conditions. The resulting coupled ketone product was found to have a yield of 48% (Table 1, Entry 3), suggesting NaO^{t}Bu was the superior base for the reaction. The next variable that was adjusted was temperature. The reaction was run once again using NaO^{t}Bu loaded at 30 mol%, **1a** loaded at 2.5 mol%, and the temperature was set to 105 C. Using the lower temperature, the coupled ketone product yield was decreased to 46% (Table 1, Entry 4). The reaction was repeated using a lower temperature, 85 ^{o}C, and the coupled ketone product yield decreased further to 21% (Table 1, Entry 5). The preferred temperature was accepted to be 125 C. The next variable to be adjusted was the catalyst **1a** loading. The reaction was re-run in a 15 mL pressure vessel at 125 ^{o}C using 3.5 mol% catalyst loading. With the higher **1a** loading, the coupled ketone product was obtained at a yield of 66% (Table 1, Entry 6). From that point on, a catalyst **1a** loading of 3.5 mol% was used. An identical reaction was then re-run in a 100 mL pressure vessel. The coupled product was obtained at a greatly improved yield of 90% (Table 1, Entry 7).

From that point on, the larger vessel was used for coupling reactions. Another base, KHMDS, was tested in the following optimization reaction. The reaction was run using KHMDS at a base loading of 30 mol%, producing a coupled ketone yield of 44% (Table 1, Entry 8), reaffirming that NaO^{t}Bu was the superior base for the reaction. Next, the NaO^{t}Bu loading was once again increased to 90 mol%. At the higher base loading, the coupled product was obtained at a yield of 78% (Table 1, Entry 9). Lastly, the vessel type was once again adjusted. Rather than using a pressure vessel, the reaction was set up using a 15 mL tube with a rubber septum which allowed for constant argon flow in order to vent the hydrogen produced through the reaction. Using the argon flow set up, the coupled ketone product was produced with a yield of 95% (Table 1 , Entry 10). Unfortunately, the argon flow design was significantly more difficult to set up, and was inconsistent relative to the pressure vessel method. Over time, depending on the flow rate, solvent would evaporate, and air could leak into the tube causing catalyst oxidation and deactivation. Because comparable results were obtained using the 100 mL pressure vessel set-up, the Ar flow method was not utilized for future dehydrogenative coupling reactions.



Scheme 10. Aliphatic alcohol optimization using 2-octanol as an analogue

Entry	Catalyst	Base	Cat. Load. (mol %)	Base Load. (mol %)	Temperature (^{o}C)	Yield (%)
1	**1a**	NaO^{t}Bu	2.5	15	125	51
2	**1a**	NaO^{t}Bu	2.5	30	125	71
3	**1a**	KO^{t}Bu	2.5	15	125	48
4	**1a**	NaO^{t}Bu	2.5	30	105	46
5	**1a**	NaO^{t}Bu	2.5	30	85	21
6[a]	**1a**	NaO^{t}Bu	3.5	60	125	66
7[b]	**1a**	NaO^{t}Bu	3.5	60	125	90
8	**1a**	KHMDS	3.5	30	125	44
9	**1a**	NaO^{t}Bu	3.5	90	125	78
10[c]	**1a**	NaO^{t}Bu	3.5	60	125	95

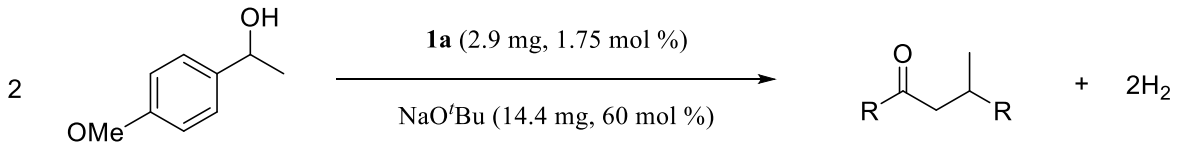
[a] Run in a 15 mL pressure vessel. [b] Run in a 100 mL pressure vessel. [c] Run in a 15 mL tube under Ar flow.

Table 1. Optimization reactions for secondary aliphatic alcohol homocoupling

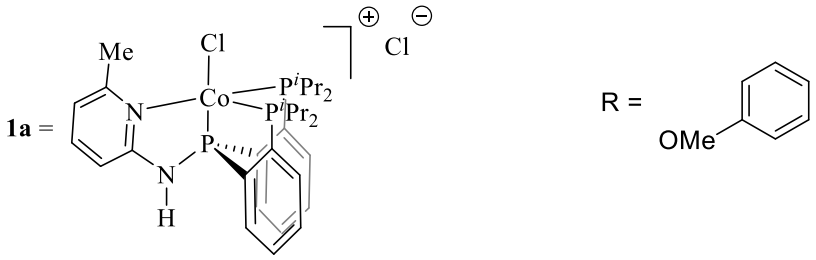
3.2.2 Aromatic Alcohols

Following the optimization of the coupling reaction using 2-octanol, 1-(4-methoxyphenyl)ethanol was used as an analogue for the coupling of aromatic secondary alcohols to ketones. Initially, conditions minimizing required energy and excess catalyst/base were selected. The first successful optimization reaction was run at 105 ^{o}C in a 100 mL pressure vessel with 3.5 mol% catalyst **1a** and 20 mol% NaO^{t}Bu. The reaction produced the coupled ketone product in a yield of 35% (Table 2, Entry 1). The same reaction was then repeated with a higher base loading of 50 mol% Using the higher base loading, a ketone yield of 41% (Table 2, Entry 2) was obtained. As with the aliphatic alcohols, the larger base loading resulted in higher yields of coupled ketone product. Next, the

temperature was adjusted. The previous reactions (base loading: 50 mol%, catalyst loading: 3.5 mol%) was repeated at 115 ^{o}C. At the higher temperature, the coupled ketone product was produced with a 77% yield (Table 2, Entry 3). The catalyst **1a** loading was then decreased to 1.75 mol%, and the base loading to 30 mol%. At the lowered loadings, the coupled ketone product was obtained at a slightly decreased yield of 70% (Table 2, Entry 4). In the final optimization reaction, the catalyst **1a** loading was left at 1.75 mol%, but the base loading was increased to 60 mol%. Using the decreased catalyst loading with the higher base loading, the coupled ketone product was obtained at 85% (Table 2, Entry 5).



4-methoxy-a-methylbenzyl alcohol



Scheme 11. Aromatic alcohol optimization using 1-(4-methoxyphenyl)ethanol as an analogue

Entry	Catalyst	Base	Cat. Load. (mol %)	Base Load. (mol %)	Temperature (^{o}C)	Yield (%)
1	**1a**	NaO^{t}Bu	3.5	20	105	35
2	**1a**	NaO^{t}Bu	3.5	50	105	41
3	**1a**	NaO^{t}Bu	3.5	50	115	77
4	**1a**	NaO^{t}Bu	1.75	30	125	70
5	**1a**	NaO^{t}Bu	1.75	60	125	85

Table 2. Optimization reactions for secondary aromatic alcohol homocoupling

3.3. Catalytic Homocoupling of Secondary Alcohols

Following the optimization of conditions for both aliphatic and aromatic secondary alcohols, multiple substrates of each form were assessed for acceptorless dehydrogenative homocoupling to ketones.

3.3.1. Homocoupling of Aliphatic Secondary Alcohols

As in the optimization, aliphatic alcohols were tested first. Aliphatic alcohols with hydrocarbon chains of various lengths were examined to evaluate the effect of longer chains. The shortest chain aliphatic alcohol tested was 2-hexanol, and the longest chain aliphatic alcohol tested was 2-dodecanol. The coupled ketone products of all unbranched aliphatic alcohols with chain lengths greater than 6C were obtained in yields >95%. 2-hexanol was obtained with a yield of 86%, likely due to the lower boiling point causing some loss of product during work-up. Three other non-aromatic/aliphatic alcohols were examined. The branched secondary alcohol 3-methyl-2-pentanol was tested and afforded a coupled ketone product yield of 66%. Similar to 2-hexanol, 3-methyl-2-pentanol has a lower boiling point that could cause some loss of product during the work-up process. Besides being a smaller substrate, the β-methyl group could also lead to some steric hindrance in the reaction mechanism, making the transition state less accessible, and provoking a less substantial yield. Two cyclic non-aromatic secondary alcohols, 1-cyclohexylethanol and cycloheptanol, were examined for coupling reactivity. The coupled ketone product of 1-cyclohexylethanol was obtained at a yield of 79%. The coupled ketone product of cycloheptanol

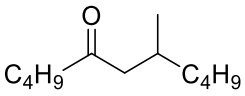
was obtained at a yield of 54%. Decreased yield is likely due to increased steric hindrance brought on by the bulky, non-aromatic rings.

3.3.2. Homocoupling of Aromatic Secondary Alcohols

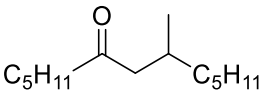
Following the optimization for aromatic secondary alcohols, a variety of aromatic substrates were selected for examination of their dehydrogenative homocoupling properties using catalyst **1a**. 1-(4-methoxyphenyl)ethanol was used as an aromatic analogue for the optimization of aromatic alcohols. The electron donating –OMe group was expected to assist in the transition by shifting electron density in order to overcome the larger steric hindrance the bulky benzyl ring establishes. The coupled ketone product of the methoxy substrate was obtained with a yield of 85%. Following the successful optimization, the same conditions were used with 1-(3-methoxyphenyl)ethanol. The coupled ketone product of 1-(3-methoxyphenyl)ethanol was obtained at a yield of 71%. The decrease in yield is likely due to the meta positioning of the methoxy group altering the electronics and sterics of the molecule with regards to their interactions with the catalyst. Next, 1-(4-methylphenyl)ethanol was examined for homocoupling properties to determine the effect of a weaker electron donating group on an aromatic secondary alcohol substrate. The coupled ketone product was obtained in a yield of 78%. Comparing the ketone product yields of 1-(4-methoxyphenyl)ethanol (85%) 1-(4-methylphenyl)ethanol (78%), a possible conclusion is that stronger electron donating groups lead to better homocoupled ketone production. In order to assess the homocoupling properties of a larger aromatic secondary alcohol, the reaction was repeated using α-methyl-2-naphthalenemethanol. Unsurprisingly, following the trend of other bulky and steric hindering substrates, α-methyl-2-naphthalenemethanol produced a yield of only 64% homocoupled ketone product. The final aromatic secondary alcohol substrate to be tested was 1-

phenylethanol. The homocoupling of 1-phenylethanol resulted in a yield of 87% coupled ketone product. Having no electron donating groups on the phenyl ring, and no extra steric hindering substituents, it makes sense that the product would be generated in a lower yield than 1-(4-methoxyphenyl)ethanol, and a higher yield than α-methyl-2-naphthalenemethanol.

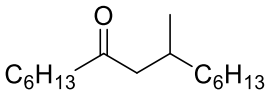
Table 3. HOMOCOUPLED KETONE PRODUCTS



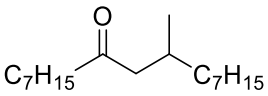
1, 86%



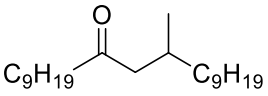
2, 98%



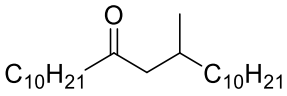
3, 96%



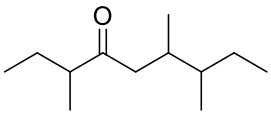
4, >99%



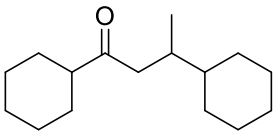
5, 98%



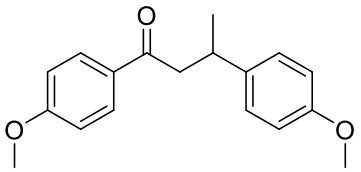
6, >99%



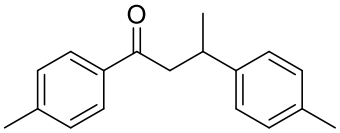
7, 66%



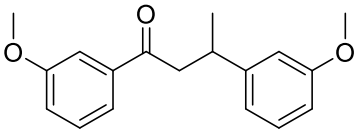
8, 79%



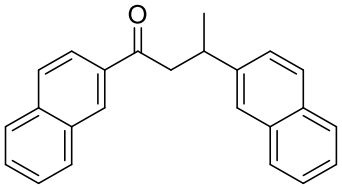
9, 85%



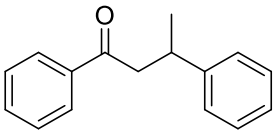
10, 78%



11, 70%



12, 64%



13, 87%

CHAPTER FOUR

CONCLUSION

A unique catalytic system consisting of novel cobalt catalyst **1a**, bearing a tetradentate catalyst with tripodal geometry, and co-catalyst NaO^{t}Bu was employed for the homocoupling of a variety of secondary alcohol substrates to ketones. Secondary alcohol substrates were optimized using 2-octanol and 1-(4-methoxyphenyl)ethanol as analogues for aliphatic and aromatic alcohols independently. Optimal conditions were then used to couple aliphatic and aromatic secondary alcohols substrates into ketones. Amongst aliphatic alcohols, there seemed to be a positive correlation between chain length and coupled ketone product yield. Larger chains likely decreased the possibility for polymerization or side product generation. Substrates with additional substituents near the reaction site performed poorly, likely due to increased steric hindrance in the transition state. Amongst aromatic alcohols, substrates bearing electron donating groups had a tendency to produce higher yields of ketone product than those without. Similar to the aliphatic alcohols, aromatic alcohols with bulky groups near the homocoupling reaction site had a tendency to product ketone product in lower yields. The use of catalyst **1a** along with NaO^{t}Bu for the homocoupling of secondary alcohols is an atom economical and environmentally friendly process, producing only H_2 as a byproduct.

In the future, further studies on acceptorless dehydrogenative homocoupling for the production of ketones as a viable method for industrial scale ketone generation should be examined. It is an oxidant free, atom economical, environmentally benign method, that should be exploited for its advantages. More secondary alcohol substrates should be tested to further determine the effects of

various substituents. Hetercoupling of these substrates should also be performed. The use of base transition metals in coupling catalysis is expected to contribute to the pursuit of sustainable practices in the field of catalytic chemistry.

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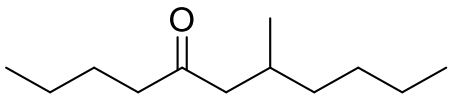
APPENDIX

NMR Spectroscopy

1. 

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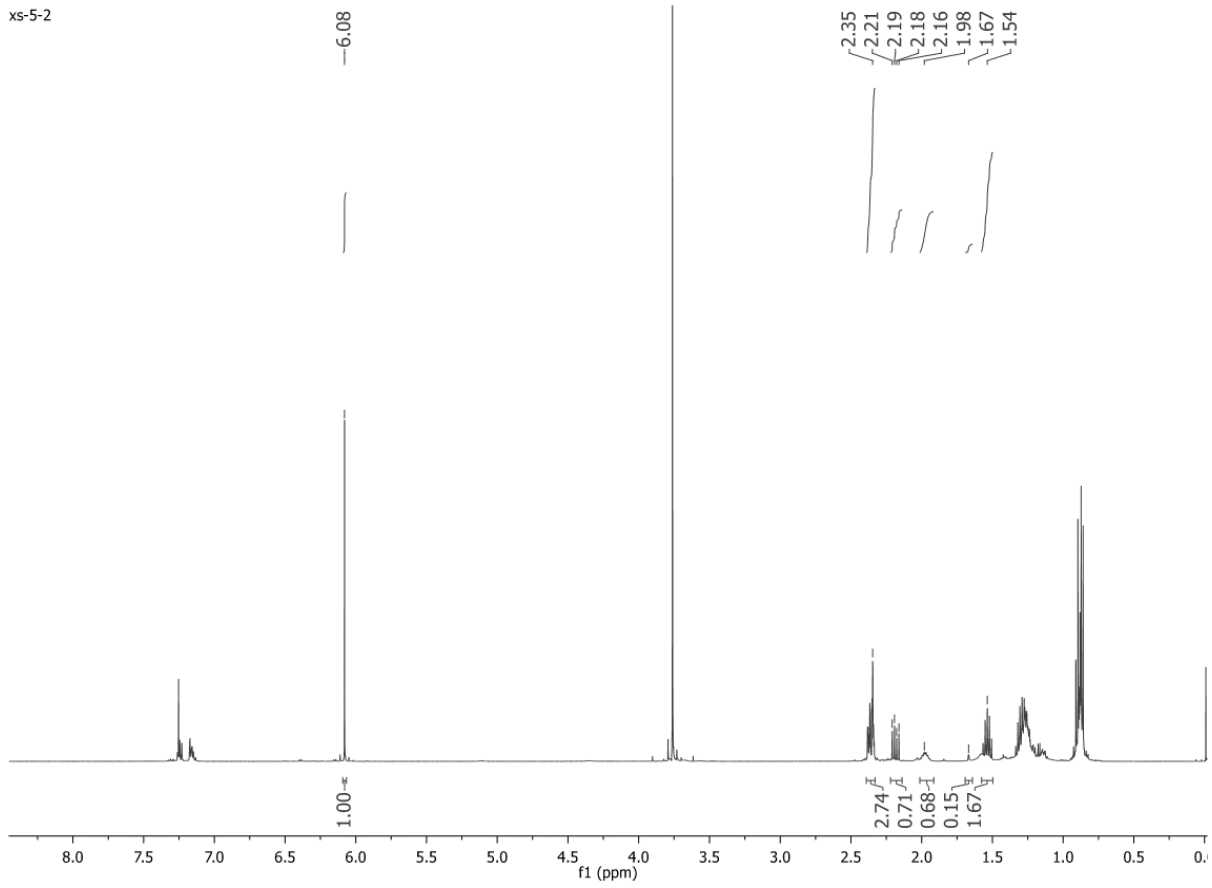
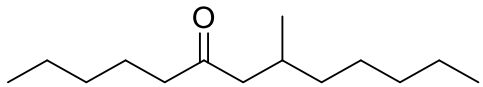


2. 

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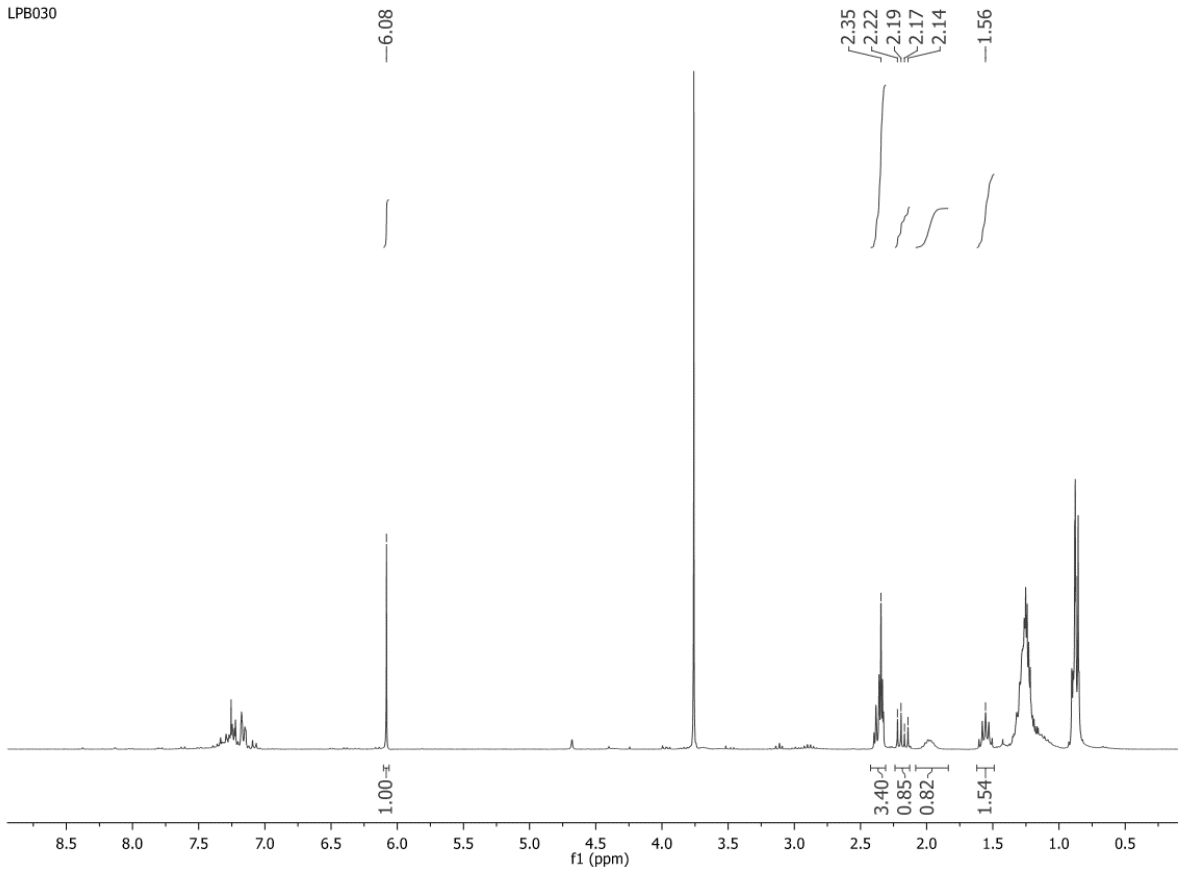
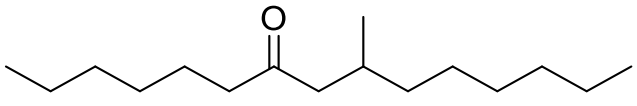


3. 

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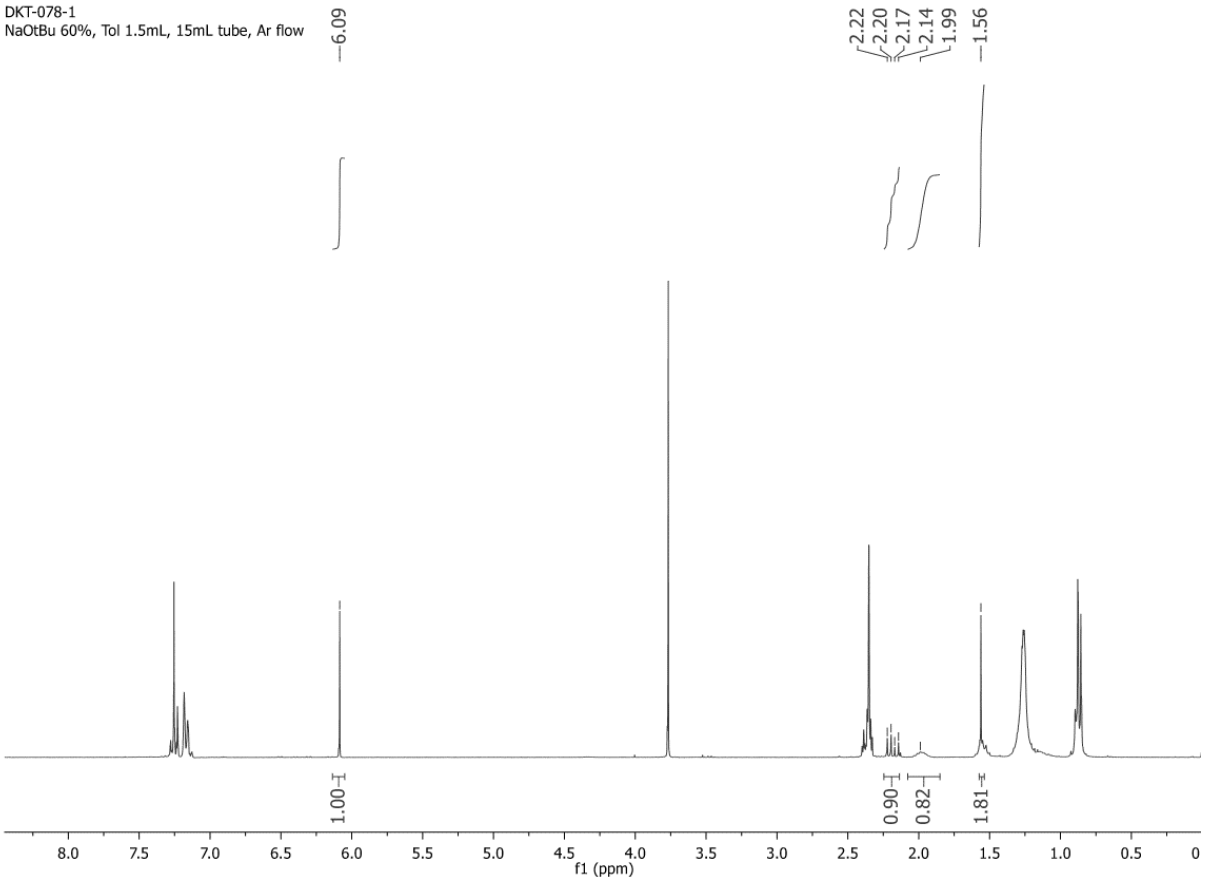
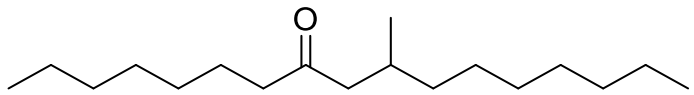


4. 

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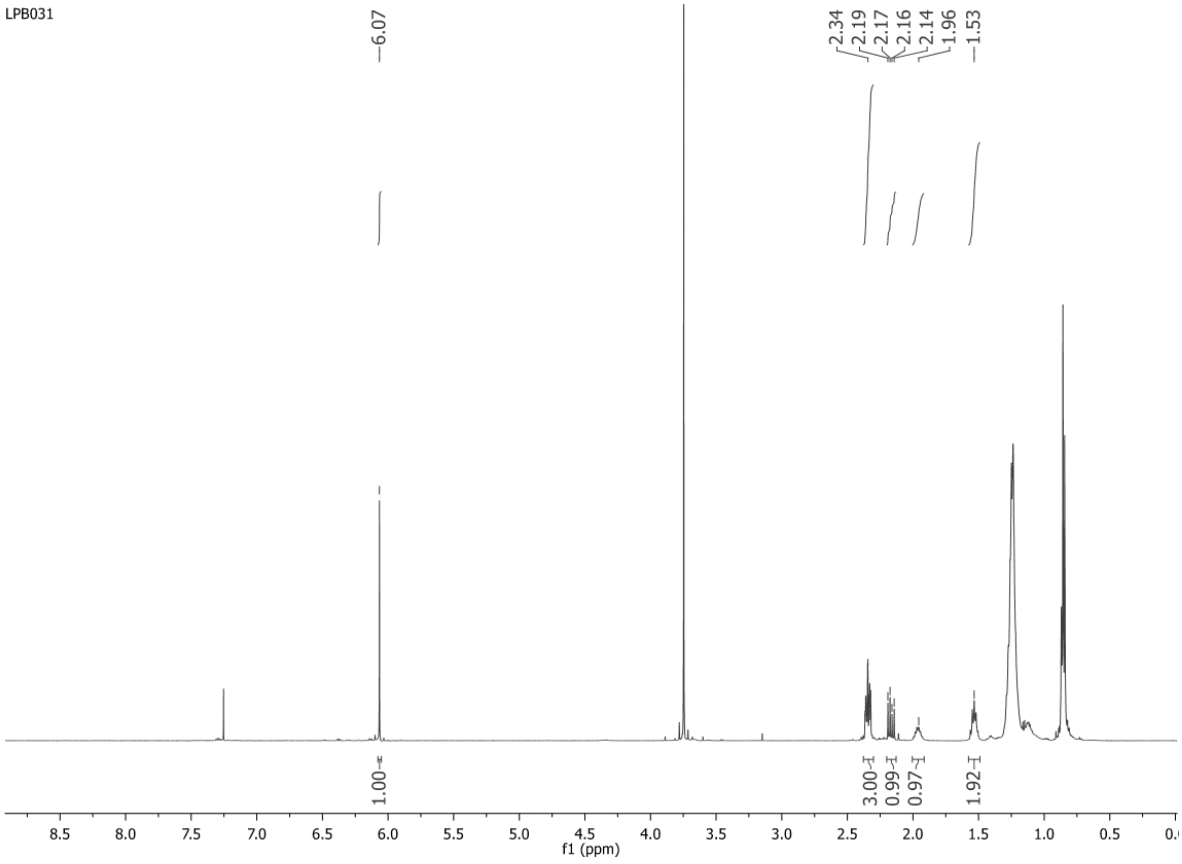
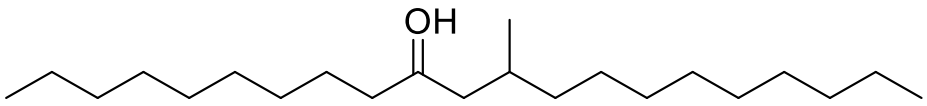


5. 

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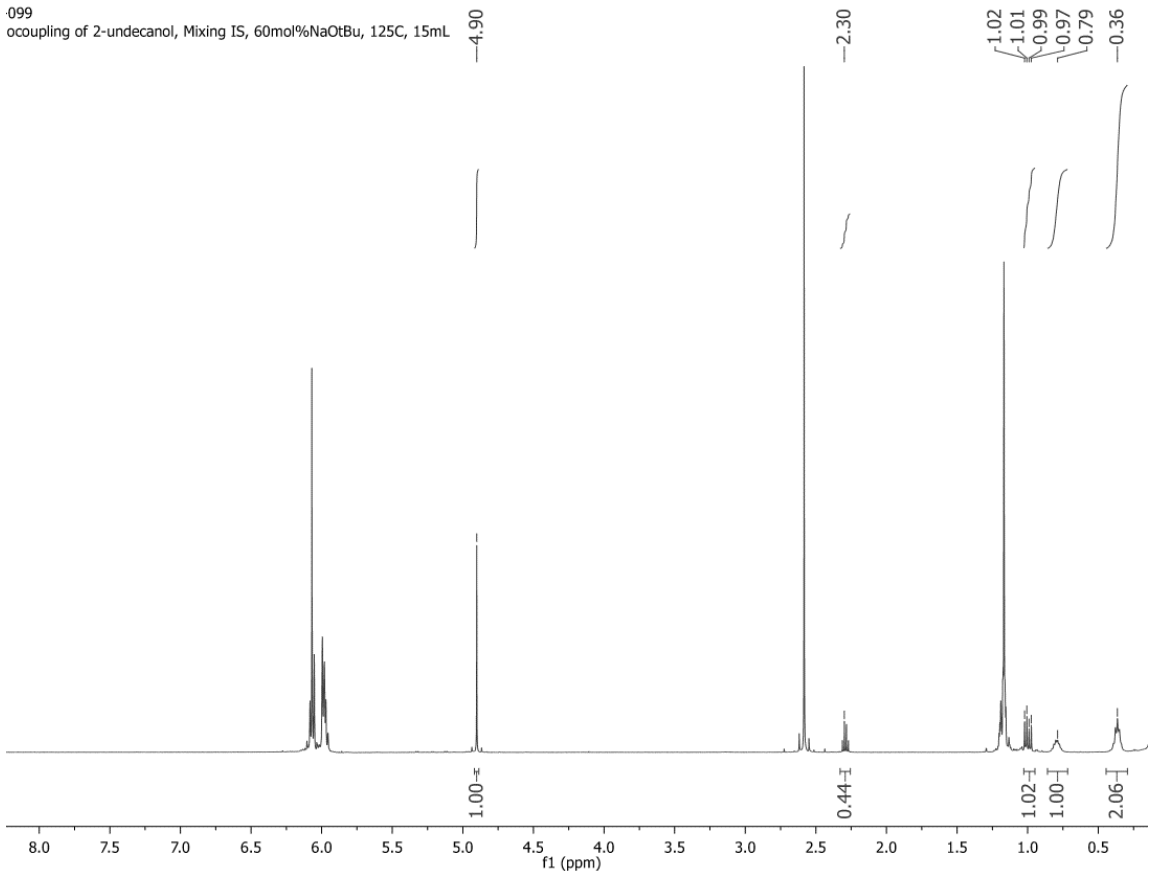
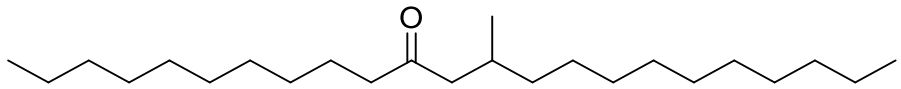


6. 

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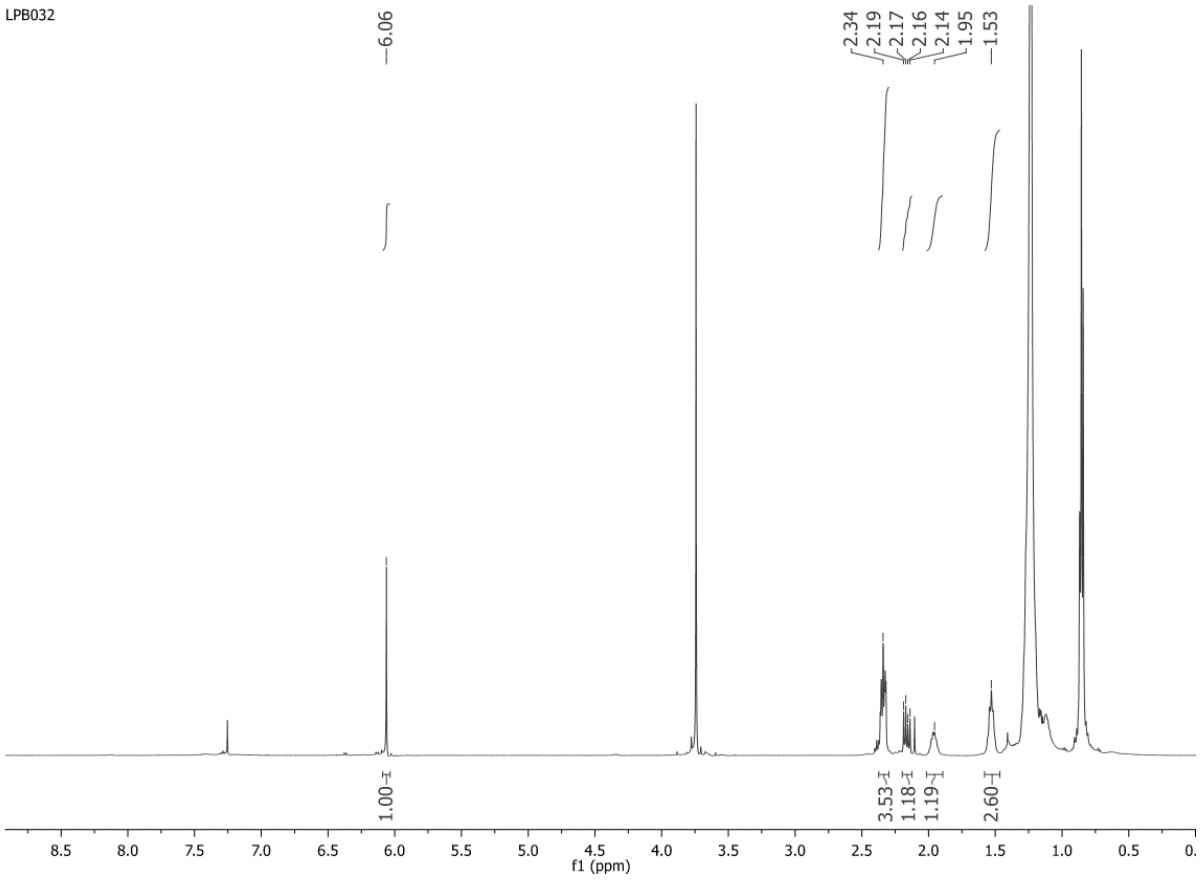
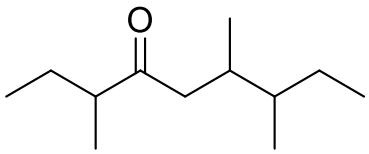


7. 

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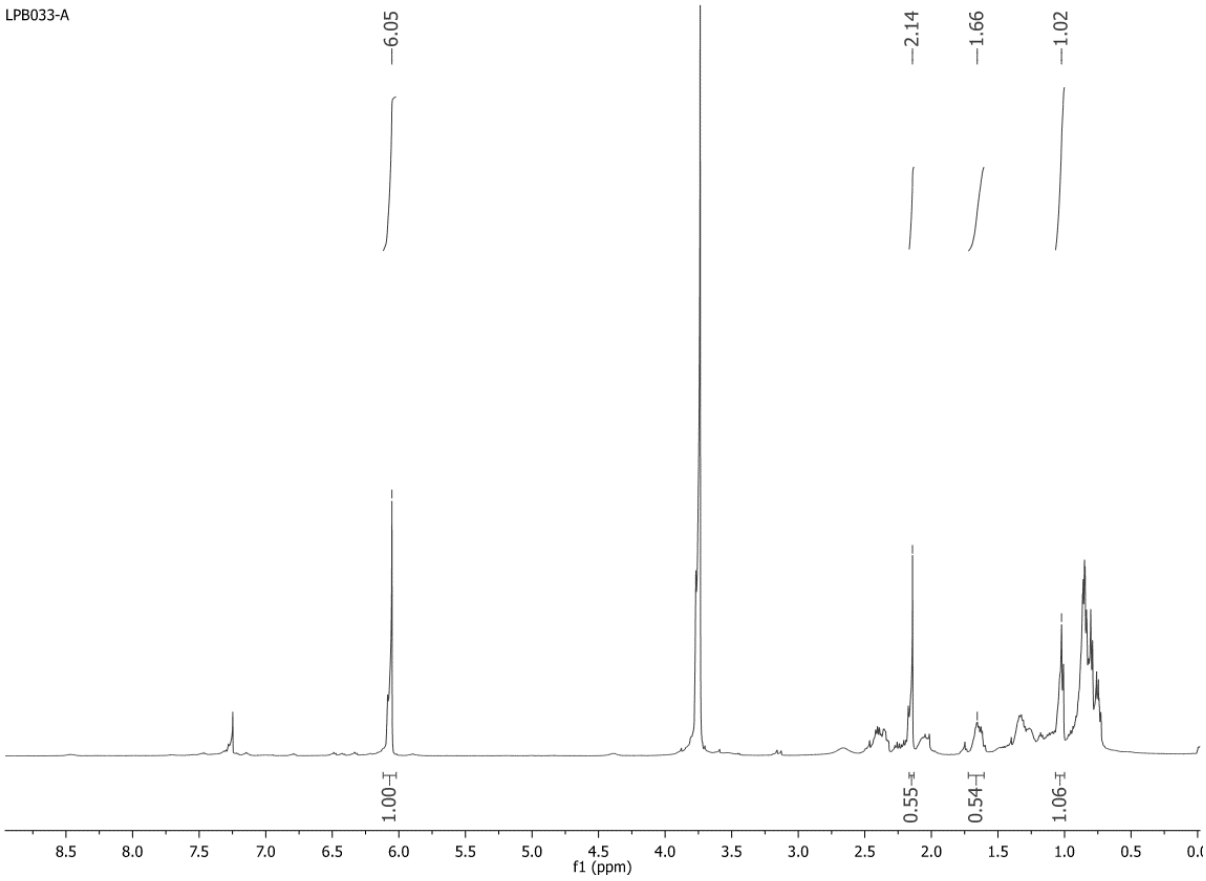
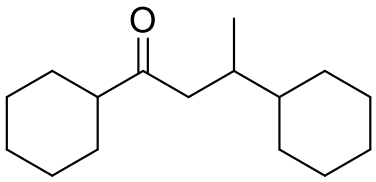


8. 

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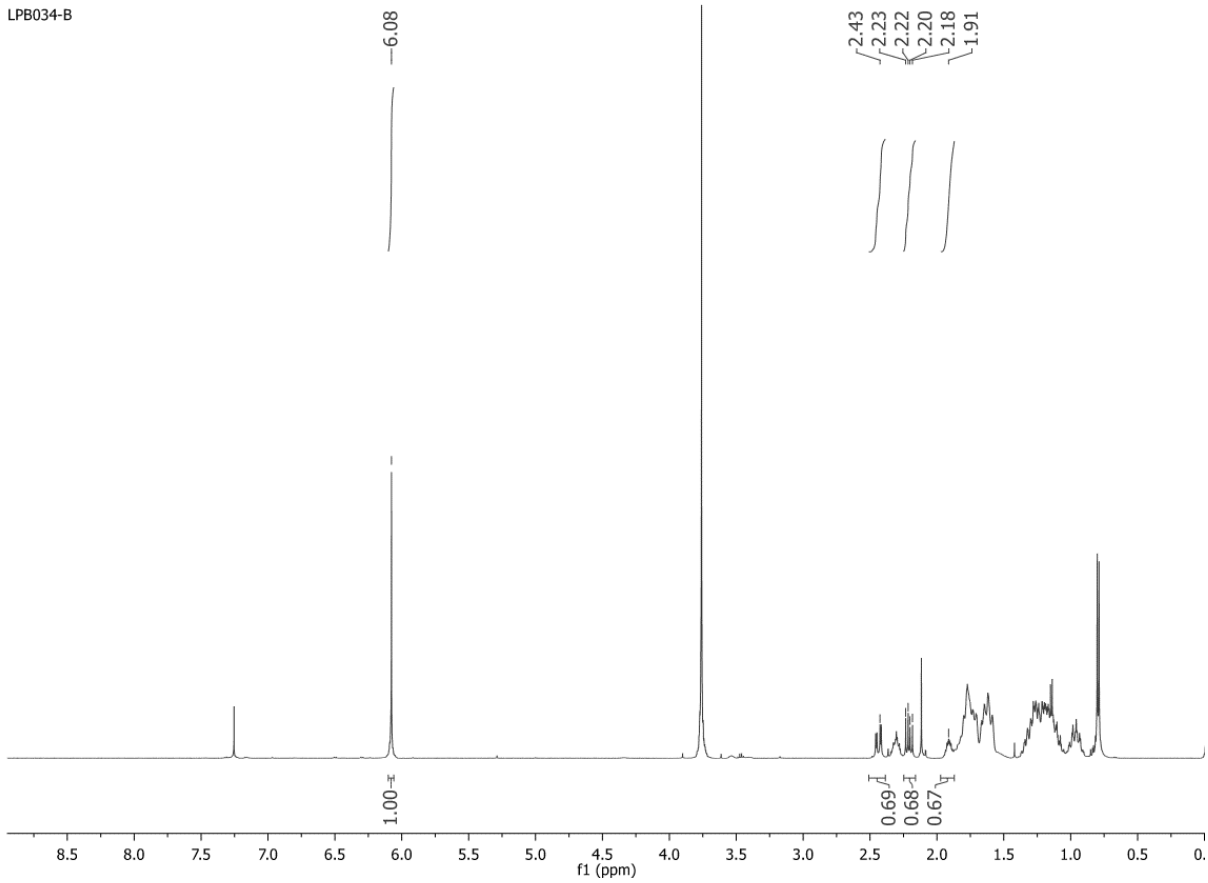
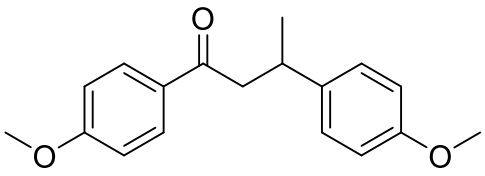


9. 

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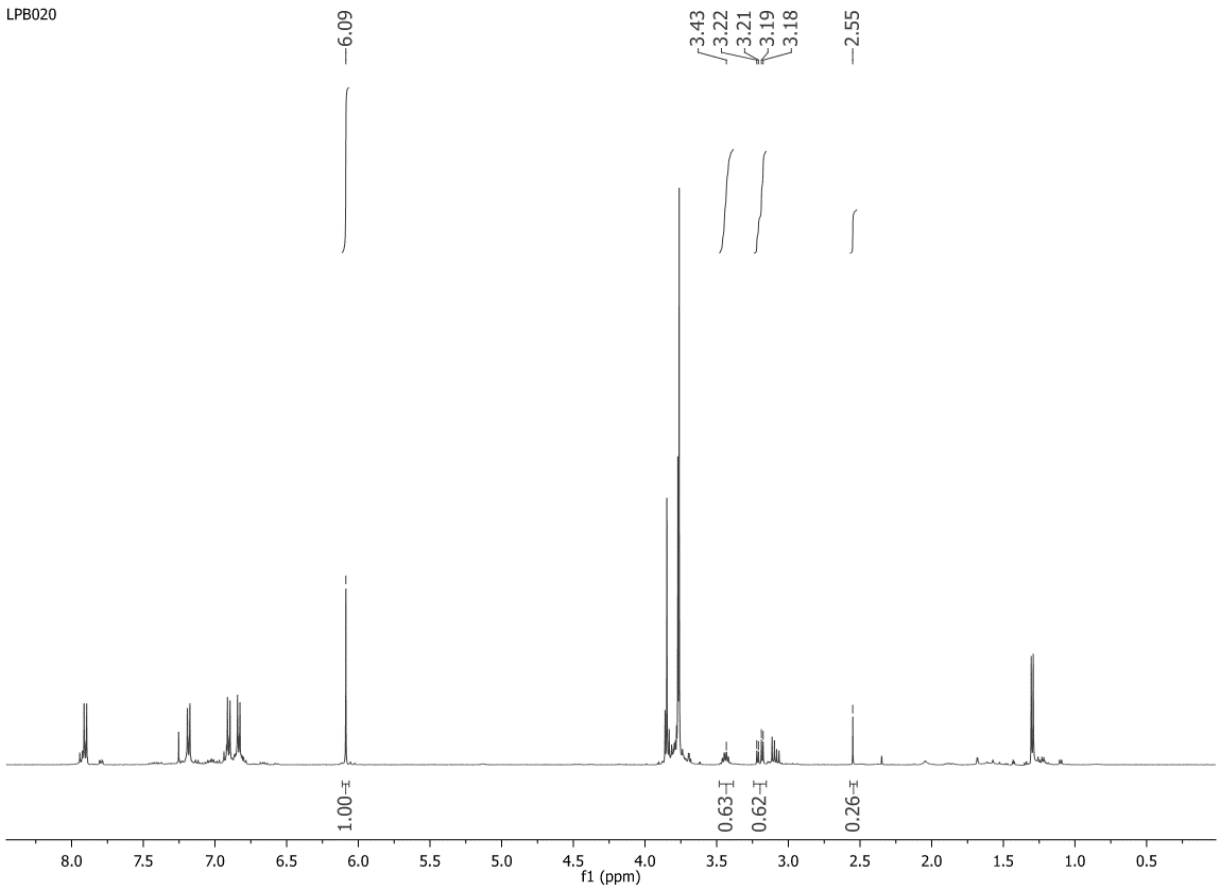
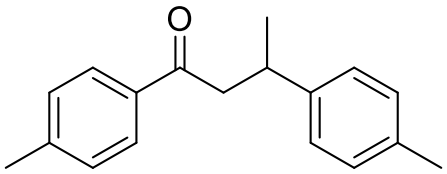


10. 

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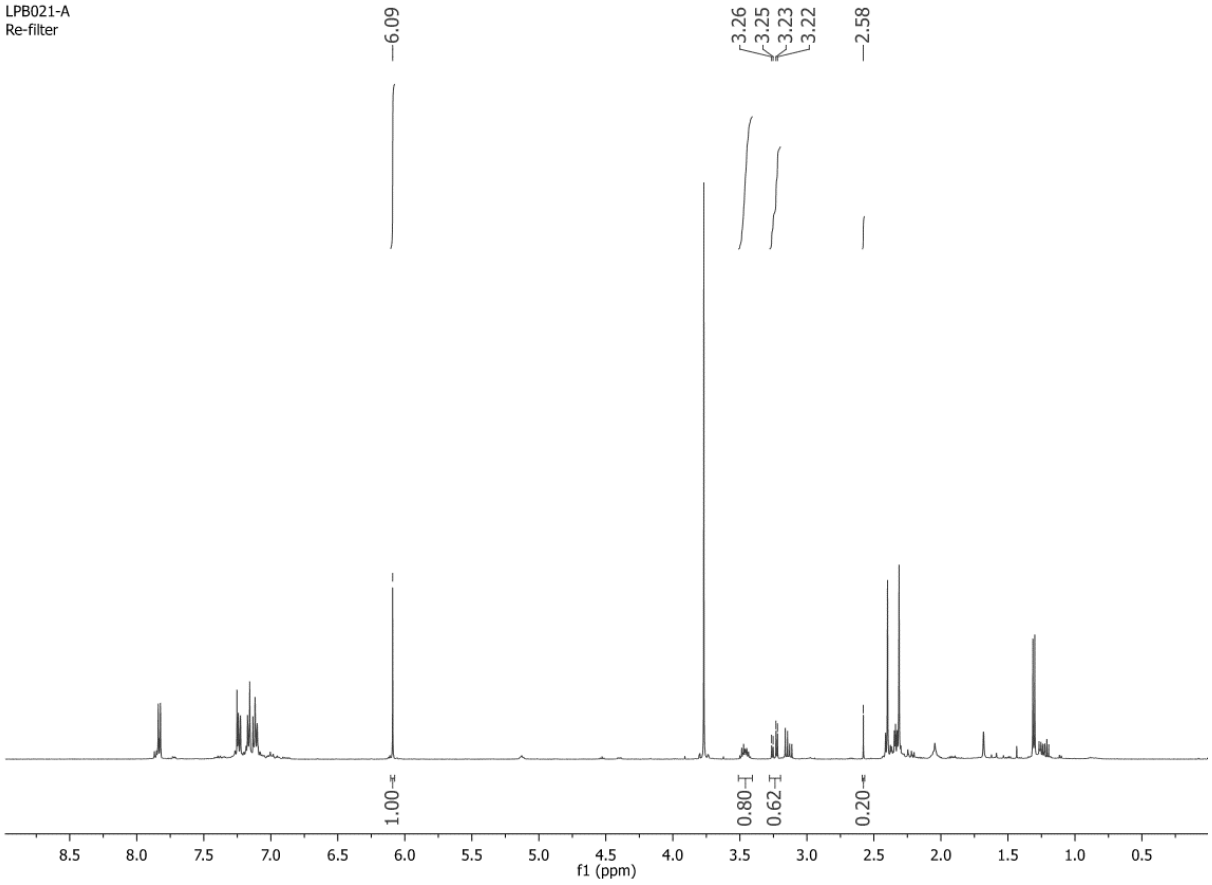
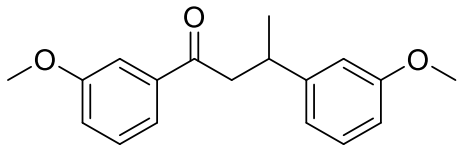


11. 

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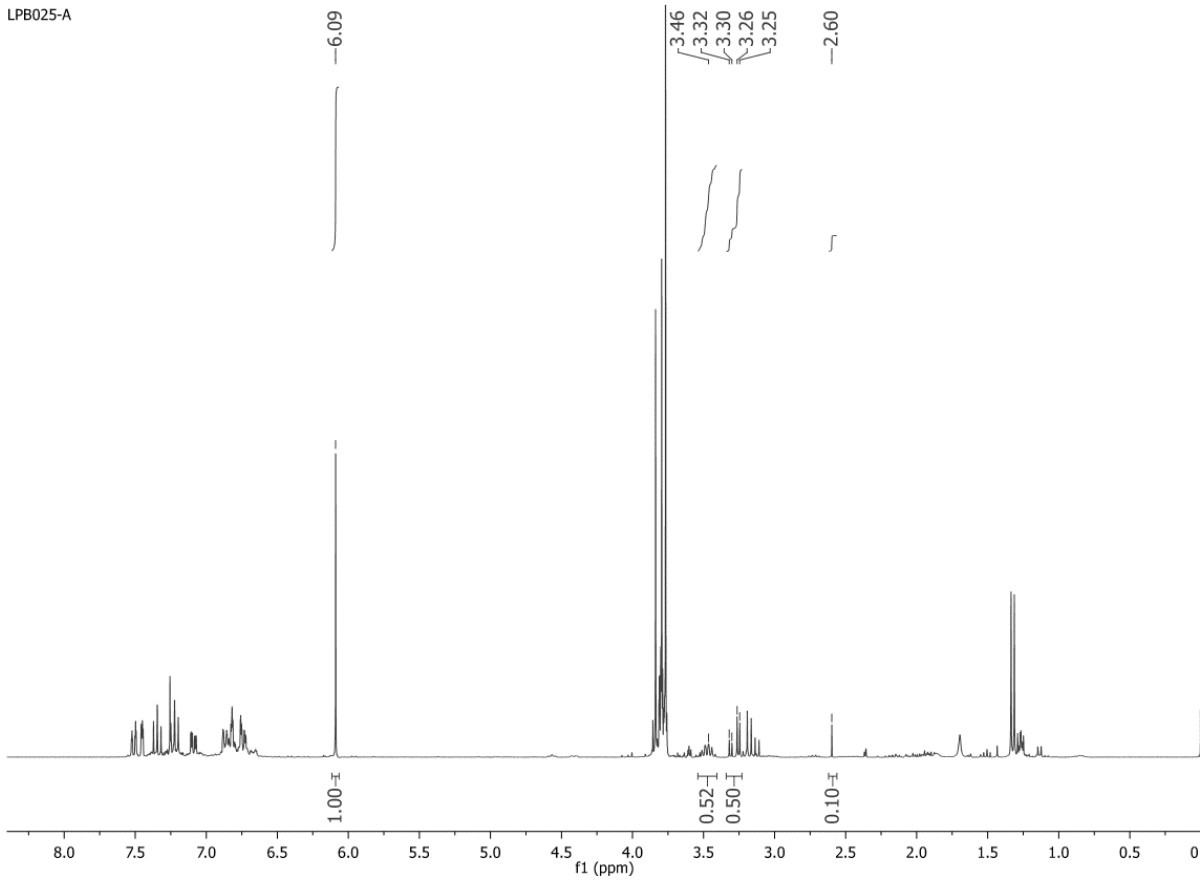
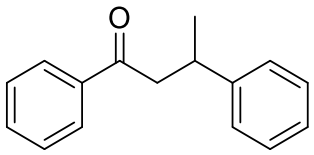


12. 

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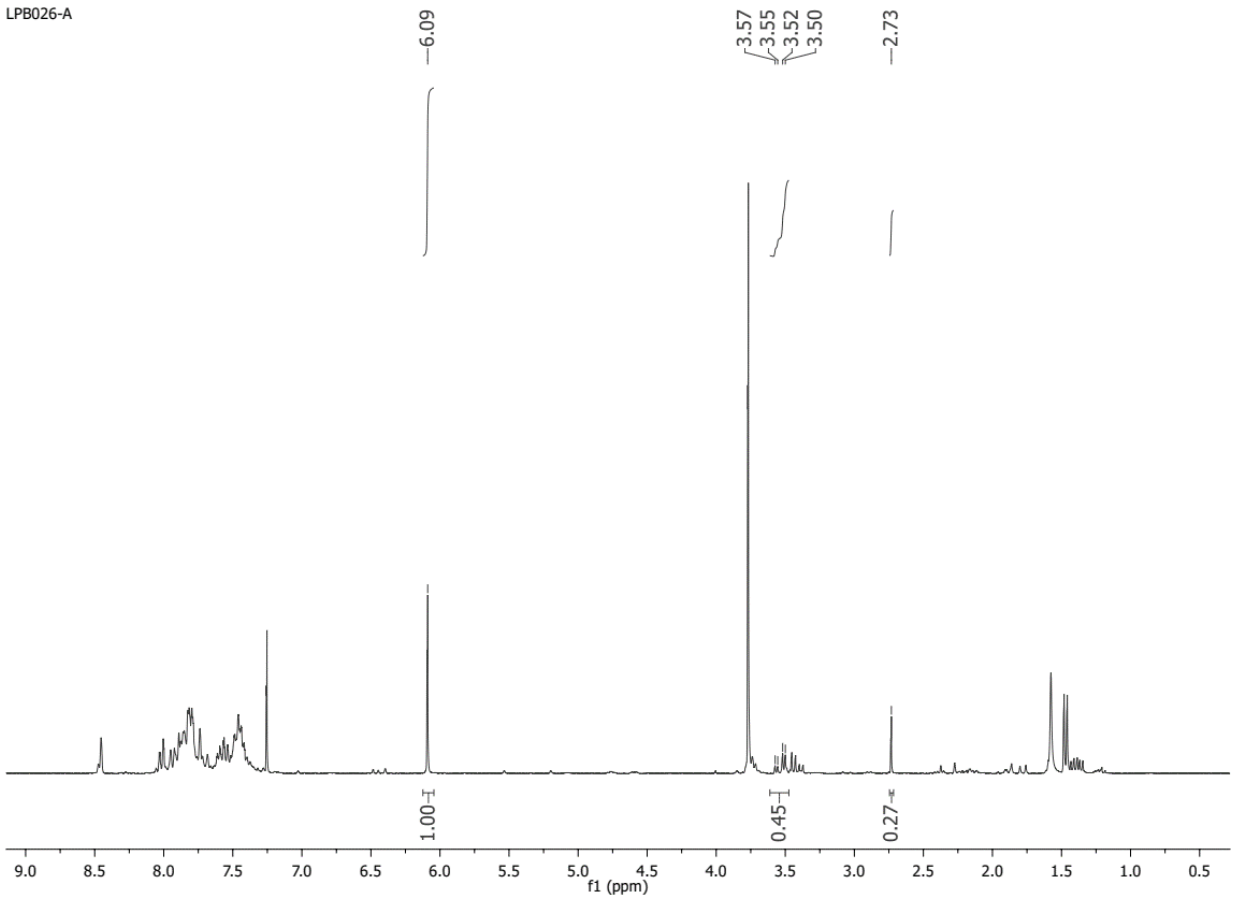
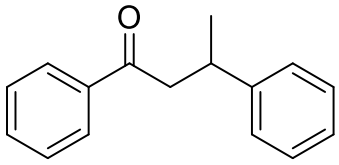


13. 

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