CATALYTIC UPGRADING OF BIOFUEL

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Catalytic Upgrading of Biofuel

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

June, 2017

CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

Lee Hang Wai

June, 2017

Abstract

Abstract of thesis entitled “Catalytic Upgrading of Biofuel”

In view of depletion of fossil fuel sources, it is in urgency to explore and develop renewable energy for substitution. In the past decade vast efforts have been devoted to the exploration of biomass derived energy sources, vegetable oils were found to be potential renewable energy sources however its application as transportation fuel was retarded due to its incompatibility with current engine design. Therefore biofuel upgrading processes such as cracking, transesterification and deoxygenation reactions (decarboxylation/decarbonylation/hydrodeoxygenation) were in great interest. Since biomass derived hydrocarbon could be compatible to our current engine thus deoxygenation reactions drew much attention and were interested by industrial sector. Extensive studies were focused on the development of heterogeneous catalytic system towards deoxygenation reactions however there was drawback that drastic conditions (>300^{o}C) were often required. Therefore it was in great interest to develop homogenous catalyst to catalyze deoxygenation reactions under mild reactions.

Numerous studies were done on exploration of homogenous catalyst such as palladium, rhodium, iridium and iron were found to be active towards decarbonylation of carboxylic acids. Palladium catalyst gave superior results however only biaryl ether phosphine ligand (DPEPhos, XantPhos) work well towards decarbonylation reactions. Thus in my study I would like to explore if there is another catalytic system towards decarbonylation of biomass derived compounds, in particularly fatty acids. During my exploration of feasible catalytic system for decarbonylation of carboxylic acids, indolylbisphosphine ligand was firstly reported for decarbonylation of long chain fatty acids. By employing 1mol% palladium-indolylbisphosphine catalyst, various carboxylic acids were converted to

their corresponding alpha olefins in satisfied yields and selectivity.

It was in doubt that whether monophosphine could be employed to catalyze decarbonylation leading to alpha olefins in good yield and selectivity. Therefore two sets of new developed monophosphine with quinolinyl and naphthyl scaffold were synthesized and employed to test for their catalytic activity. After optimizing reaction conditions, employing 1-3mol% palladium-monophosphine ligand could catalyze decarbonylation of various carboxylic acids into alpha olefins in good and selectivity.

Glycerol, which is the by-product from biofuel refinery process, could be utilized as solvent and hydrogen source for catalytic transfer hydrogenation. During my study inexpensive commercial available 2-aminobenzyl alcohol was combined with $[Ru(p\text{-cymene})Cl_2]_2$ as catalyst to catalyze transfer hydrogenation of ketones. Various kinds of aryl ketones, heteroaryl ketones, diaryl ketones as well as cyclic ketones were smoothly converted into alcohol in good yields by our catalytic system under mild condition (120^oC) within 6-18 hours.

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Abbreviations

δ	Chemical shift (NMR)
m/z	Mass-to-charge ratio
s	Singlet
d	Doublet
t	Triplet
q	Quartet
m	Multiplet
GC	Gas chromatography
HRMS	High resolution mass spectroscopy
MS	Mass spectrometry
IR	Infra-red
NMR	Nuclear magnetic resonance spectroscopy
equiv.	Equivalent
h	Hour
min	minute
rt	Room temperature
L	Generalized ligand
THF	Tetrahydrofuran
MeOH	Methanol
EtOH	Ethanol
Et_2O	Diethyl ether
EA	Ethyl acetate
DMF	*N*,*N*-Dimethyl formamide
DMAc	*N*,*N*-Dimethyl acetamide
DCM	Dichloromethane

DME	1,2-Dimethoxyethane
t-BuOH	*tert*-Butanol
t-AmOH	*tert*-Amyl alcohol
$ClPPh_2$	Chlorodiphenylphosphine
$ClPCy_2$	Chlorodicyclohexylphosphine
dba	dibenzylideneacetone
n-BuLi	*n*-Butyllithium
R	Generalized alkyl group
Me	Methyl
Et	Ethyl
n-Bu	*n*-butyl
i-Pr	*iso*-propyl
t-Bu	*tert*-butyl
Ar	Aryl
Ph	Phenyl
Bn	Benzyl
Cy	Cyclohexyl
Ac	Acetyl
Ad	Adamantyl
Tol	Toluene
NHC	*N*-Heterocyclic Carbene

Chapter 1 Introduction

1.1 Introduction to the development of Biofuel

There are growing demands on energy with the emerging economies, burning of fossil fuels such as charcoal and crude oil is the major sources of energy in the past few decades. However burning of fossil fuels led to serious environmental pollution problems such as acid rain and global warming. Meanwhile declining of fossil fuels reserves have aroused our concerns on the sustainability of fossil fuels in future. To encounter the shortage of fossil fuels and reduce the environmental impacts, it is a matter of urgency to search for an alternative energy sources and they should be sustainable and green.

Development in biofuel drew much attention and extensive studies were done on modifying the biofuel to substitute the conventional fossil fuels. Biofuel is referred to as solid (bio-char), liquid (bioethanol, vegetable oil and biodiesel) or gaseous (biogas, biosyngas and biohydrogen).[1] In view of ease of transportation, liquid biofuel is preferable as fossil fuel substitute. Therefore modifications and technology advancements on liquid biofuel would be described in this article.

1.1.1 Classification of biofuel

The classification on biofuel are based on their production technology and they are divided into first generation biofuels (FGBs), second generation biofuels (SGBs),

third generation biofuels (TGBs) and fourth generation biofuels.[2] First generation biofuels refer to biofuels made from food crops[3] such as sugar, starch, vegetable oils or animal fats using conventional techniques. Bioethanol, edible vegetable oils and biodiesel are examples of FGBs. Nowadays bioethanol is produced mainly in Brazil, US, Germany and Malaysia and there are expected strong growth to meet the increasing demands on bioethanol in coming future.[4]

Since FGBs are mainly produced from food crops hence there will be competition on the land and resource for food crops agricultures. According to a report[5] there are almost 870 million people suffered from chronically undernourished. Therefore European Commission released a proposal[6] in October 2012 and stated *10% of all energy used in transportation is to originate from renewable fuels by 2020 and the amount of FGBs should be limited to a maximum 5% of renewable fuels* and thus second generation biofuels are developed for substitution.

SGBs are mainly produced from lignocellulosic materials included cereal straw, forest residues, bagasse hence the production of SGBs would not compete with food. Besides algae oil was found to be sources of biofuel in recent decades, so called third generation biofuels and fourth generation biofuels are those converted from vegetable oil and biodiesel using advanced technology.[7]

1.1.2 Advantages of biofuel

In view of economic benefits biofuels can be produced from easily available biomass such as vegetable oils and waste fat hence it helps to reduce the dependence on fossil fuels. Besides biofuels are sustainable and renewable energy sources which can solve the energy crisis in future. In view of environmental benefits the burning of biofuels emits less air pollutants such as SO_2 and N_2O than fossil fuels.[1] Furthermore emission of carbon monoxide, particulate matter and hydrocarbon were found to be reduced by using neat biofuel or blend biodiesel with diesel fuel (Table 1.1).

Emission type	B100 biodiesel	B20 biodiesel
Total unburned hydrocarbons (HC)	-67%	-20%
Carbon monoxide	-48%	-12%
Particulate matter	-47%	-12%
NOx	+10%	+2%
Sulfates	-100%	-20%
Polycyclic aromatic hydrocarbons[a]	-80%	-13%
Ozone potential of speciated hydrocarbons	-50%	-10%

a Average reduction across all compound measured

Table 1.1: Average biodiesel emissions (%) compared to conventional diesel[8]

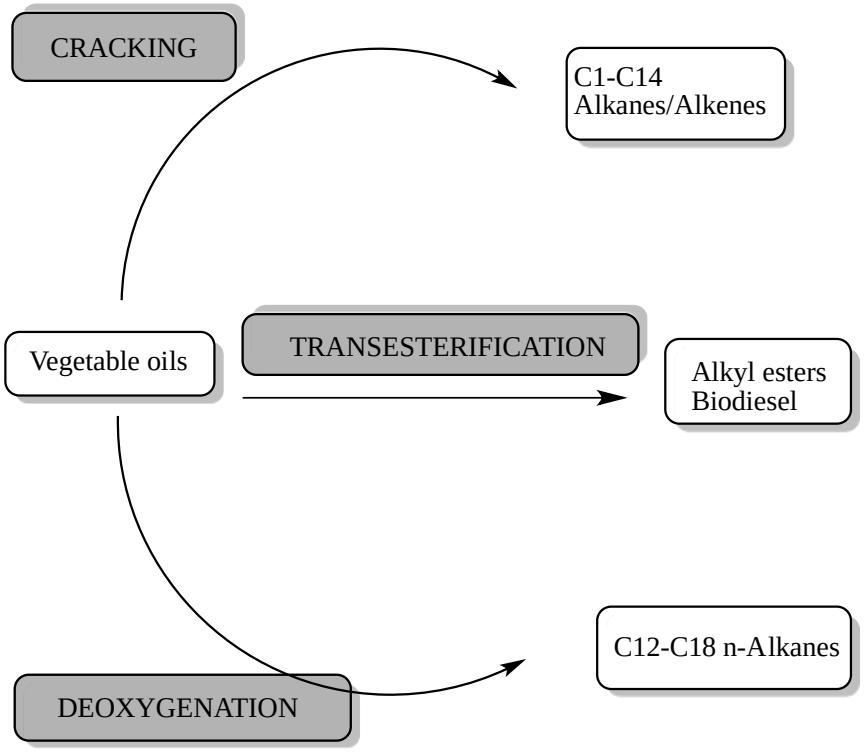
1.1.3 Disadvantages of biofuel

Although there are numerous benefits of using biofuels as alternative to fossil fuels, there are many barriers to prohibit the application of biofuel thus nowadays we still depend on fossil fuels for the major energy source.

First generation biofuels (FGBs) from vegetable oils is not a newly develop technology. In fact there was a diesel engine running on peanut oils exhibited at the 1900 World Fair in Paris[9] however vegetable oils would cause injector coking, carbon deposition that led to thickening of engine lubricant[10] and these problems would reduce the combustion efficiency of engine and may harm the engine and special design of engine is needed for burning vegetable oils. In addition to physical and chemical properties of vegetable oils (high viscosity and low volatility) that posed barrier to their application as fuels, the competition of land for food agriculture is another barrier that retards the development and application of FGBs. Therefore upgrading processes on biofuels and new biomass sources are extensively studied in recent decades.

1.2 Introduction to biofuel upgrading reactions

Several upgrading processes have been developed to produce biofuels that suit for the modern engine design and are mainly divided into: (1) Cracking, (2) Transesterification and (3) Deoxygenation (Scheme 1.1).



Scheme.1.1: Biofuels (vegetable oils) upgrading process

1.2.1 Cracking

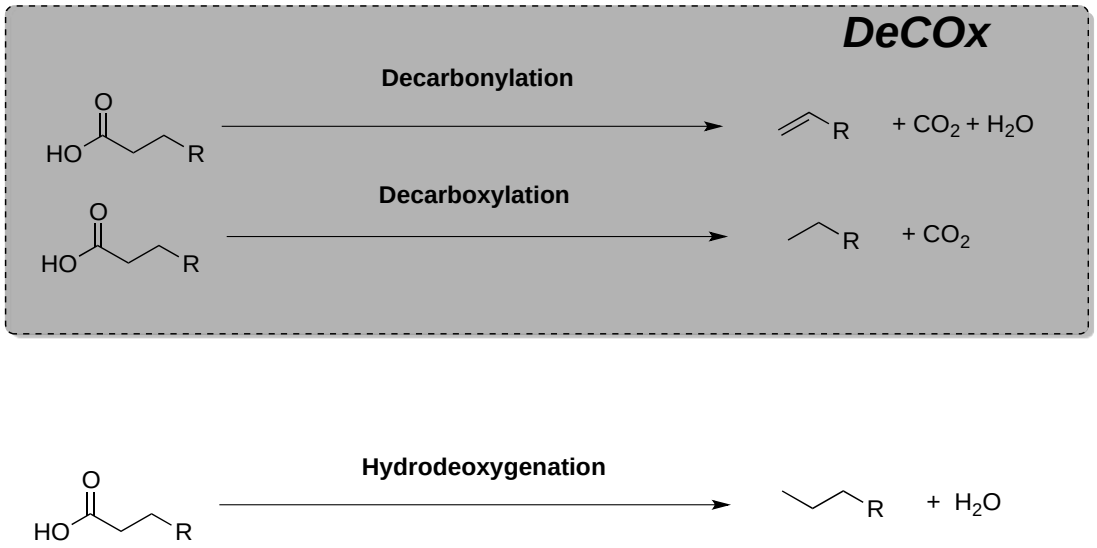
Cracking involves the thermal or catalytic decomposition of triglycerides into alkanes, alkenes and fatty acids.[11] Conventional cracking catalysts in petrol-chemical industry such as zeolites and mesoporous aluminosilicates were found to be applied in cracking of vegetable oils as well. However the process is highly unselective and results in producing large range of hydrocarbons and fatty acids.[11]

1.2.2 Transesterification

Transesterification is currently the major process to produce biodiesels from vegetable oils or waste fats. Fatty acids in the vegetable oils are methylated or ethylated to produce their corresponding fatty acid methyl or ethyl ester (FAMEs/FAEEs). Though the process is highly selective than cracking process, there are still several drawbacks for the transesterification. (1) The high oxygen content of FAMEs (normally range from 10% to 45%) lower their combustion efficiency so that the biodiesel could not compatible with conventional diesel engine, new design engine or biodiesel blend with petrol is needed[12] for the application of biodiesel (FAMEs). (2) The poor cold-flow properties of FAMEs are another disadvantage that retard its globalized application. (3) The high catalyst loading and high downstream processing cost also restrain the application of transesterification on biofuel upgrading process.[13] The poor storage stability of FAMEs makes it not an ideal transportation fuel. To increase the applicability of FAMEs as ideal renewable fuel, processes to lower its oxygen content is in great interest. Therefore extensive studies were done on developing deoxygenation to produce hydrocarbons from vegetable oils.

1.2.3 Deoxygenation

The deoxygenation process could be divided into three reactions: (1) decarbonylation, (2) decarboxylation and (3) hydrodeoxygenation. (Scheme 1.2)



Scheme 1.2: Possible reactions sued in deoxygenation process.

Among the mentioned reactions, hydrodeoxygenation has been currently industrialized (Neste Oil's NEXBTL™, UOP/Eni's Ecofining™) to produce commercial "green" diesel from vegetable oils and animal fats. However drawbacks for hydrodeoxygenation are the use of sulfide catalyst and high pressure of hydrogen needed. The former problem would lead to environmental pollution and high treatment cost meanwhile the latter problem would limit the location of hydrodeoxygenation factory where centralized hydrogen supply is available.[14]

Decarbonylation/decarboxylation provides alternative tools to upgrade vegetable oils into hydrocarbons. In fact it is believed that parts of petroleum were formed through decarboxylation reactions of fatty acids in plants or animals catalyzed by natural clay.[13] Nowadays biofuel upgrading processes by decarbonylation/decarboxylation

can be catalyzed by homogenous and heterogenous catalysts and it is believed that they would be in great interests in future due to the use of simple catalyst and require less hydrogen during the process.[15]

1.3 Recent advancements on heterogeneous catalytic deoxygenation reactions (deCOx)

Advancements (includes feed, catalyst, reactor and reaction condition) on the decarbonylation and decarboxylation reactions on biofuel upgrading would be discussed herein.

1.3.1 Feed

As mentioned vegetable oils such as peanut oil was found to be fuel and applied in diesel engine however due to the competition with agriculture of food for land, another biomass sources have to be considered. Nowadays the attention has moved towards the uses of inedible oil, waste fat (includes tall oil fatty acids[16] and ultra-high yield biomass feedstock such as algae,[17] via deCOx reactions to yield hydrocarbons. Inedible oils tend to be more saturated then edible feedstock hence less hydrogen is required to convert them into fuels.[18]

1.3.2 Substrate scope

Biomass feedstock is matrix of fatty acids and their derivatives such as triglyceride and FAMEs hence different products would be yielded by using various kinds of catalysts. For instance, Pd/C catalyst would catalyze decarbonylation and decarboxylation of fatty acids and their esters to form hydrocarbons.[10] Although fatty acids would give higher reactivity and selectivity over than esters,[19] catalyst

deactivation was observed.[20]

By using Pd/SiO_2 and Ni/Al_2O_3 catalysts, aromatic carboxylic acids would give superior results to aliphatic acids[21] and it was attributed to the electron-withdrawing substitutions weaken the bond between carboxylic carbon and the α-carbon to facilitate decarboxylation.[22]

In addition to the difference of reactivity between acids and esters towards deoxygenation (deCOx) reactions, the degree of unsaturation of fatty acids would also affect their reactivity towards deoxygenation (deCOx), an increase in the degree of unsaturation of fatty acids was found to increase catalyst deactivation hence resulted in lower catalyst reactivity as well as the selectivity of reaction[16b]. There are several explanations suggested: (1) The unsaturated fatty acids are suggested to be more probe to coking reactions.[23] (2) Immer *et al.* speculated the adsorption of unsaturated fatty acids or its unsaturated products on the catalyst via C=C bond interaction and it may occupy the vacant site on the catalyst result to inhibit the deoxygenation reactions.[24] And the formation of oligomers and aromatics from the unsaturated substrates were observed.[25] (3) Formation of carbon monoxide during the deoxygenation reactions of unsaturated fatty acids would poison the catalyst and decrease it catalytic activity.

1.3.3 Catalyst

Poor yields were reported by thermal decarboxylation of fatty acids and esters at moderate temperature (<400ºC) thus catalytic decarbonylation /decarboxylation are of great interest. In 2006 Snåre *et al.*[23a] have screened a number of metals (Pd, Pt, Ru, Mo, Ni, Rh, Ir and Os) supported catalysts, they found out carbonaceous supported catalysts gave higher reactivity and they suggested it may due to the solid support (a) promote the reaction through amphoteric properties and surface functionalities and (b) reduce the coke-induced deactivation of catalyst. Furthermore they concluded the deoxygenation ability of metals as Pd>Pt>Ni>Rh>Ir>Ru>Os.[23a,26] (Table 1.2).

Catalyst	Feed[a]	Temp (oC)	Pressure (atm)[b]	Atmosphere	Reaction time (h)	Conversion (%)	Selectivity (%) heptadecane : heptadecene : total C17
60% Ni/SiO_2	Stearic acid	300	6	He	6	18.1	19 : 30 : 58
5% Ru/C	Stearic acid	300	6	He	6	13.2	24 : 27 : 65
5% Pd/C	Stearic acid	300	6	He	6	100	95 : 0 : 99
5% Pt/C	Stearic acid	300	6	He	6	86	87 : 1 : 95
1% Ir/SiO_2	Stearic acid	300	6	He	6	4.6	14 : 29 : 69
5% Os/C	Stearic acid	300	6	He	6	6.9	29 : 15 : 53
1% Rh/C	Stearic acid	300	6	He	6	19.9	18 : 13 : 85

1% Pt/C	Tristearin[c]	350	6.8	N2	4	42	C8- C17
5% Pd/C	Tristearin[c]	350	6.8	N2	4	29	C8- C17
20% Ni/C	Tristearin[c]	350	6.8	N2	4	85	C8- C17

[a] Reactions were run using dodecane as solvent

[b] Values reported correspond to the operating pressure during reactions

[c] Solventless reactions

Table 1.2: Performance of representative catalysts on the deoxygenation of stearic acid and tristearin via deCOx reactions

Solid support also plays another important role in catalytic deCOx reactions, a series of Pd/C catalysts with varying acidity were screened and the most alkaline catalyst was found to have superior results on decarboxylation of ethyl stearate.[10] Moreover mesoporous silica was found to offer additional advantage over carbon support by enabling easily characterization that is impractical done on carbon support.[27] Although Pd and Pt were found to be most active catalyst for deCOx reactions, attentions have moved to find out the others cheaper metals for catalysis. Influence of different reaction condition parameters were investigated and would be briefly discussed.

1.3.4 Reactions atmosphere

DeCOx reactions of fatty acids and their derivatives were found to be active under inert gas and hydrogen atmosphere. Although it is suggested presence of hydrogen could promote the deCOx, its effect is not monotonic, when hydrogen

partial pressure exceed certain level that it would inhibit the deCOx and lower hydrocarbon yields. A limited amount of hydrogen would lead to hydrogenation of fatty acids and leads to increasing yield of saturated hydrocarbons meanwhile it hydrogenates the reactants and prevent the deactivation of catalysts by the unsaturated reactants.[10, 28] However the drops of deCOx activity with continual increasing hydrogen partial pressure is still remain unclear. It is speculated that increasing hydrogen partial pressure promote decarbonylation while inhibit decaroxylation.[15b,29]

1.3.5 Temperature

Deoxygenation can proceed through hydrodeoxygenation and deCOx pathways and it is observed that deCOx reaction pathways is favored at high temperature[16a,20,30] however side reactions such as cracking, aromatization and isomerization also be enhanced at high temperature.

1.3.6 Solvent

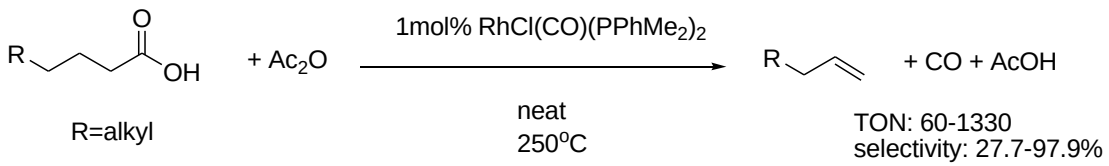
Low-boiling point solvents lead to better catalytic activity towards deCOx were observed and Immer and Lamb tried to conclude that the solvent effect is due to the influence of solvent vapor pressure generated on the partial pressure of hydrogen.[24] They speculated the low solvent vapor pressure would cause hydrogen partial pressure increased, the higher hydrogen partial pressure may inhibit decarboxylation that would unfavor deCOx reaction.

1.4 Recent advancement on homogenous catalytic decarbonylation reactions of carboxylic acids

There was drawback on heterogeneous catalytic deoxygenation of carboxylic acids that drastic condition including high temperature (>300^{o}C) and narrow ranges of substrate scopes reported. Therefore development of homogenous catalytic deoxygenation is in great interest. Herein I would like to highlight the development of homogeneous catalytic decarbonylation of carboxylic acids. Several palladium,[31] nickel,[32] iridium,[33] rhodium[31b] and iron[34] were found to convert various carboxylic acids into alkenes.

1.4.1 Rhodium-catalyzed decarbonylation reactions

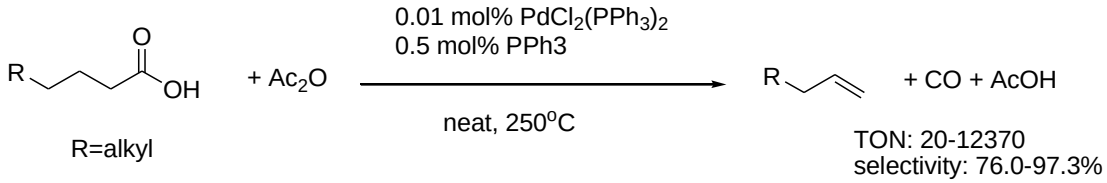
In 1976 Fogila and Barr[31a] has reported using Rh-based catalyst to convert stearic acid into 1-heptadecene with poor selectivity. To produce high selective alpha-alkene, Miller *et al.* employed 1mol% Rh(CO)Cl(PPhMe$_2$) to convert various kinds of long chain carboxylic acids into alkenes with good selectivity (up to 97.9%α-selectivity) in 1993 (Scheme 1.3).[31b]



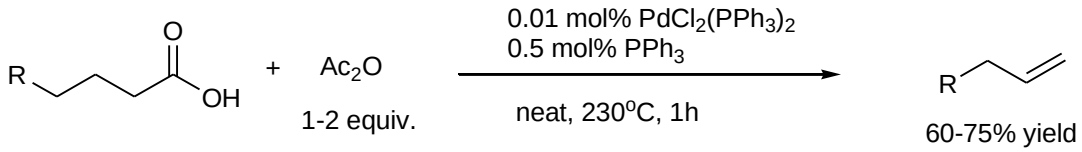
Scheme 1.3: Rh-catalyzed decarbonylation reaction reported by Miller *et al*.

1.4.2 Palladium-catalyzed decarbonylation reactions

In addition to Rh-catalyzed decarbonylation, Miller *et al.*[31b] also employed 0.01mol% $PdCl_2(PPh_3)_2$ to convert carboxylic acids into alpha alkenes with excellent selectivity (up to 97.3% α-selectivity) and good yield (TON = 12370) (Scheme 1.4).



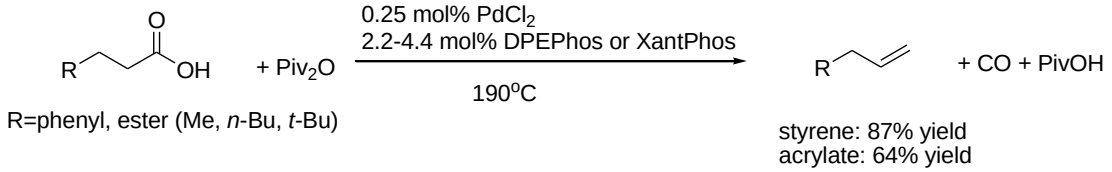
Scheme 1.4: Pd-catalyzed decarbonylation reaction reported by Miller *et al.*



Scheme 1.5: Pd-catalyzed decarbonylation reaction reported by Kraus *et al.*

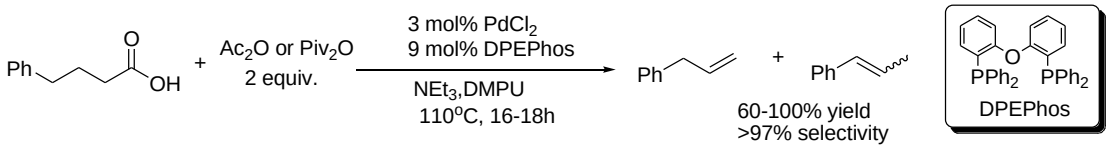
Kraus *et al.* employed the lowest Pd-catalyst loading (0.01mol% $Pd(PPh_3)_4$ with 0.5ml% PPh_3) to catalyze decarbonylation of long chain carboxylic acids into alkenes with moderate conversion under elevated temperature (230°C) (Scheme 1.5).[31e] Karus *et al.* extended the substrate scope to produce allylbenzene, styrene, cyclohexene as well as diene. Although Miller and Kraus reported the lowest catalyst loading for decarbonylation of carboxylic acids, the drastic reaction condition was concerned. To develop mild catalytic protocol and improve the applicability of Pd-catalyzed decarbonylation of carboxylic acids, Hillmyer and Tolman employed 0.25mol% $PdCl_2$ with large excess of phosphine ligands (2.2mol% to 4.4mo%) and addition of pivalic

anhydride to convert bio-derived hydrocinnamic acid into alkenes.[31f] Furthermore they extended the scope to mono-alkyl succinate to produce corresponding alkyl acrylate (Scheme 1.6).



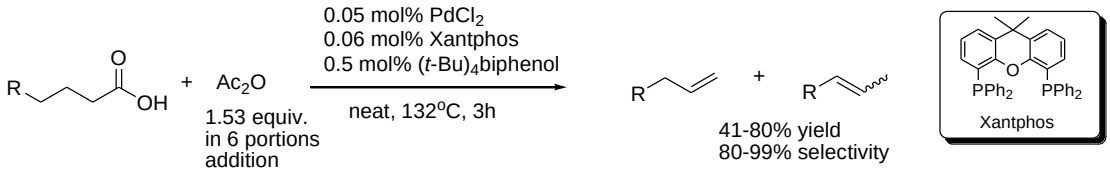
Scheme 1.6: Pd-catalyzed decarbonylation of carboxylic acids and alkyl succinate.

Gooβen[31c] and Scott[Error! Bookmark not defined.31d] catalyzed decarbonylation reaction under milder condition (110°C) albeit higher catalyst loading (3mol% Pd-DPEphos) and an expensive high-boiling point solvent (DMPU) was used (Scheme 1.7).



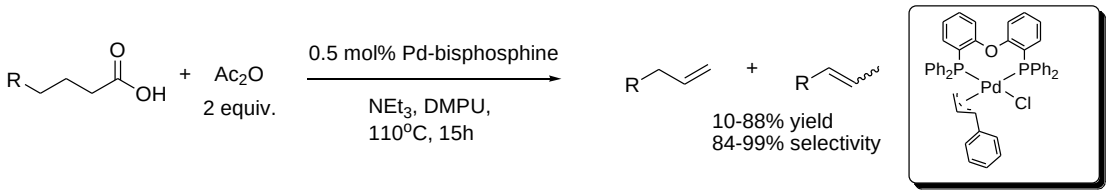
Scheme 1.7: Palladium-bisphosphine catalyzed decarbonylation of carboxylic acids under mild reaction condition.

Recently Grubbs and Stoltz [31g] reported another example of low catalyst loading protocol (0.05mol% $PdCl_2(PPh_3)_2$-Xantphos) to convert broad ranges of carboxylic acids into alpha alkenes in good yield and selectivity however the protocol required stepwise addition of acetic anhydride (Scheme 1.8).



Scheme 1.8: Stepwise addition of acetic anhydride protocol reported by Grubbs and Stoltz.

The aforementioned literatures reported *in situ* generated palladium catalysts using large excess of phosphine ligands. To minimize waste produced from reaction, Jensen[31i] developed a well-defined palladium pre-catalyst and applied 0.5mol% palladium-bisphosphine pre-catalyst to catalyze decarbonylation reaction (Scheme 1.9), high product yield and α-selectivity are achieved. Moreover substrates with aliphatic alcohol and amine functional group were found to be tolerating to the reaction and converted to desired alkenes.

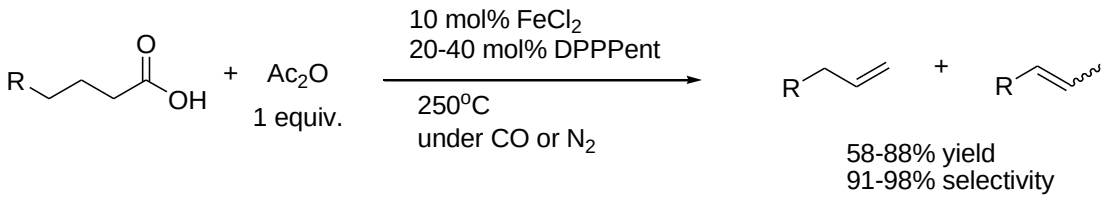


Scheme 1.9: Pd-DPEphos pre-catalyst catalyzed decarbonylation reaction reported by Jensen *et al*.

1.4.3 Iron-catalyzed decarbonylation reactions

It is in great interest to develop inexpensive catalytic decarbonylation protocol thus catalytic decarbonylation of bio-derived carboxylic acids could be applied to industrial uses. Fukuyama and Ryu have demonstrated iron-catalyzed decarbonylation

reaction of aliphatic carboxylic acids to produce alpha olefins[34] with moderate yields and high α-selectivity (Scheme 1.10). However reaction condition was found to be drastic as 10 mol% $FeCl_2$, 1 equivalent of KI, high pressure (20 psi) of carbon monoxide atmosphere and high reaction temperature (250°C) were required.



Scheme 1.10: Iron-catalyzed decarbonylation reaction report by Fukuyama and Ryu.

1.4.4 Nickel-catalyzed decarbonylation reactions

Inspired by Fukuyama and Ryu's works, the inexpensive first-row transition metals were desirable to be applied on catalytic decarbonylation reactions. Nickel has been proven to be active species to decarbonylate 2-pyridyl thioates[35] and thioethers.[32a] Therefore Tolman *et al.* screened wide ranges of first-row transition metals as well as different ligands to investigate the feasibility of first-row metal catalyzed decarbonylation reactions using hydrocinnamic acids as model substrate (Figure 1.1 and Figure 1.2).

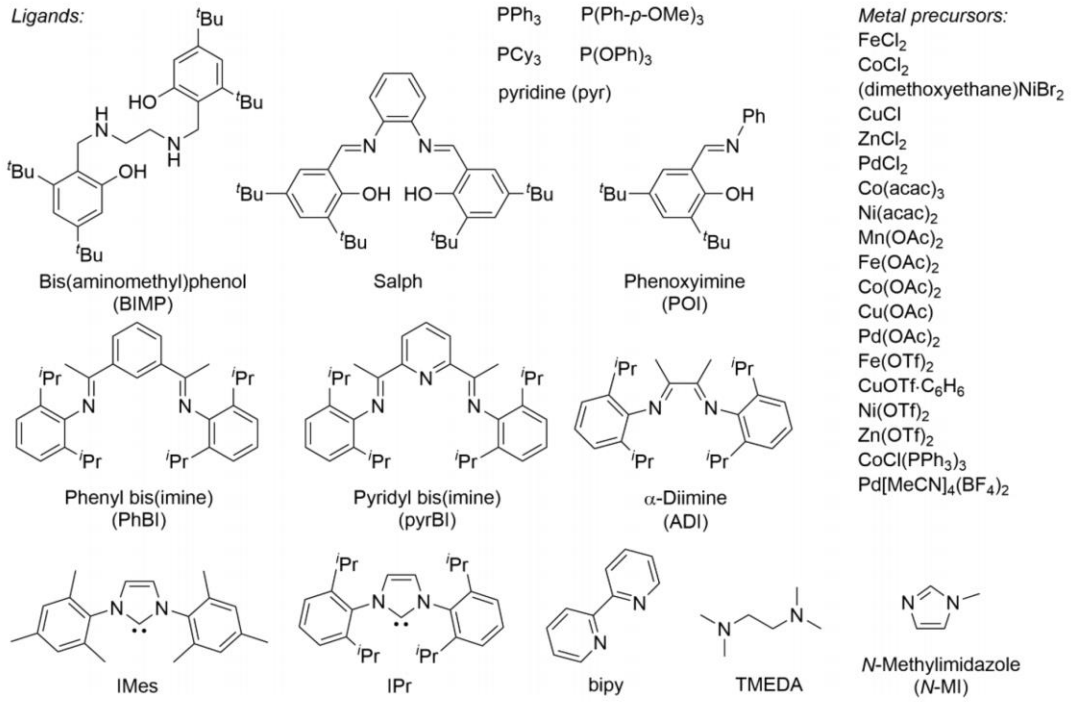


Figure 1.1: First set of high throughput screening on metals and ligands

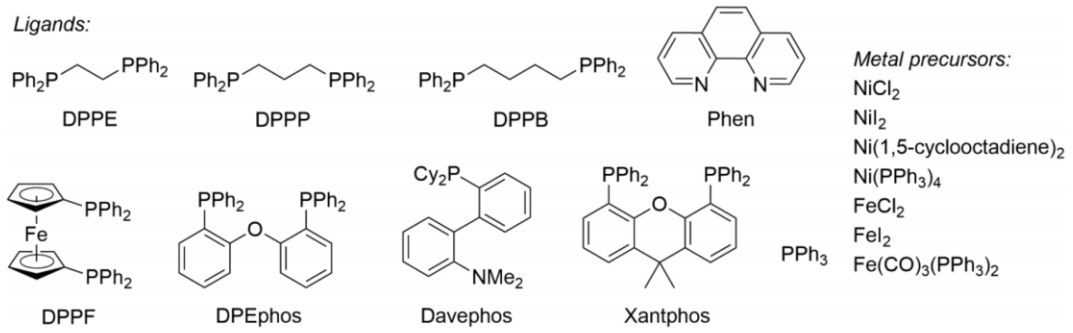
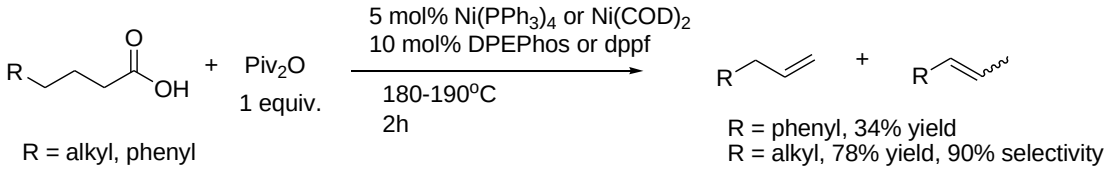


Figure 1.2: Second set of high throughput screening on Nickel and iron.

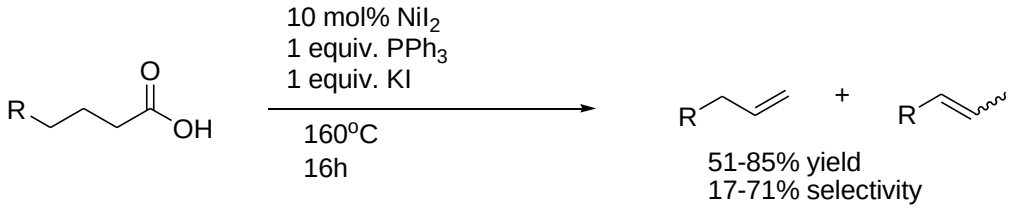
By using 5mol% $Ni(PPh_3)_4$ in conjunction with DPEphos, styrene could be obtained via decarbonylation of hydrocinnamic acid, the substrate scope could be extended to aliphatic carboxylic acids, with the use of 5mol% $Ni(COD)_2$ with dppf, 78% of octene with 90% α-selectivity was obtained via decarbonylation of nonanoic

acid (Scheme 1.11).[32b]



Scheme 1.11: Ni-catalyzed decarbonylation reaction reported by Tolman *et al*.

Afterwards the same research group demonstrated another catalytic protocol for nickel-catalyzed decarbonylation of carboxylic acids without the uses of anhydride as additive. By using 10mol% NiI_2 or $Ni(OAc)_2$ and 1 equivalent of phosphine ligands (PPh_3) under 160°C, several aliphatic carboxylic acids and one example of cyclohexane were decarbonylated to corresponding alkenes in moderate to good yield and selectivity (Scheme 1.12). [32c]

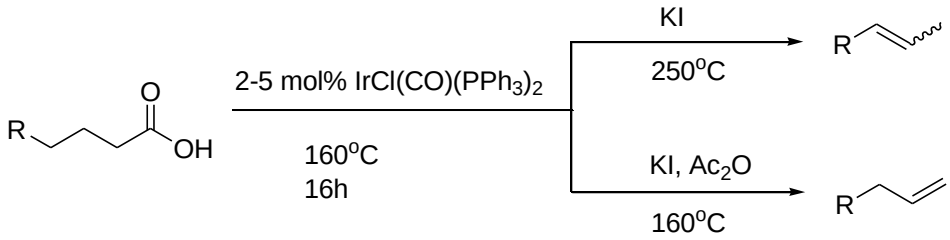


Scheme 1.12: Ni-catalyzed decarbonylation of carboxylic acids without activation of anhydride.

1.4.5 Iridium-catalyzed decarbonylation reactions

In effort to explore another catalytic system for decarbonylation reactions, Fukuyama and Ryu reported iridium-catalyzed synthesis of terminal or internal alkenes via decarbonylation of aliphatic carboxylic acids (scheme 1.13).[33a] With the uses of acetic anhydride and catalyzed the reaction under lower temperature (160°C),

high selective terminal alkenes were formed meanwhile without addition of anhydride and catalyzed the reaction under higher temperature (250^{o}C), internal alkenes were obtained.



Scheme 1.13: Synthesis of high selective terminal or internal alkenes by applying different reaction conditions.

Recently Hapiot employed 2.5mol% $[Ir(COD)Cl]_2$ with PPh_3 to decarbonylate various kinds of carboxylic acids to desired alkenes in good yield and selectivity with the aid of KI. Unlike the Pd-catalytic system, they found that bidentate phosphine ligands such as dppb and DPEphos were ineffective in conjunction with Ir-metal. Besides that their Ir-catalyst could decarbonylate carboxylic acids without adding anhydride to activate the substrate, albeit using large excess of phosphine (15mol% PPh_3) and under drastic condition (240^{o}C). Furthermore their catalytic system was proven to be stable under distillation at high temperature thus the catalytic system could be recycled to use. [33b]

1.5 Conclusion

With the depletion of fossil fuel and growing demand on energy worldwide, it is a matter of urgency to explore alternative sustainable energy. Unlike wind, solar and hydropower, there is no geographic limitation on the production of biofuel so that it would be one of the potential alternatives for fossil fuel in future. However its application is retarded by several factors: (1) Competition of agricultural land for biomass. (2) Poor combustion properties of biofuel. (3) Ineffective biofuel upgrading process.

To tackle the problems and overcome technical barriers for the practical uses of biofuel. With the advancement of technologies, biofuel no longer depends on food crops. To date biofuel could be produced from algae, jatropha and lignocellulosic biomass compounds. Furthermore vast effort were put on the development of effective biofuel upgrading technologies, transesterification and deoxygenation were extensively studied however heterogeneous catalytic reactions took the lead in the past. There are drawbacks concerning high catalyst loading, high reaction temperature and narrow scopes of reaction. Therefore it is in great interest to develop effective homogeneous catalytic biofuel upgrading reactions.

1.6 References

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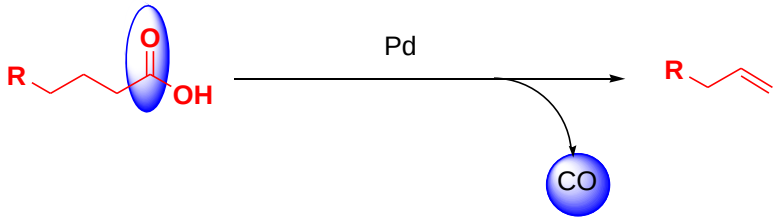
Chapter 2 Palladium-Indolylbisphosphine Catalyzed Decarbonylation of fatty acids

2.1 Introduction



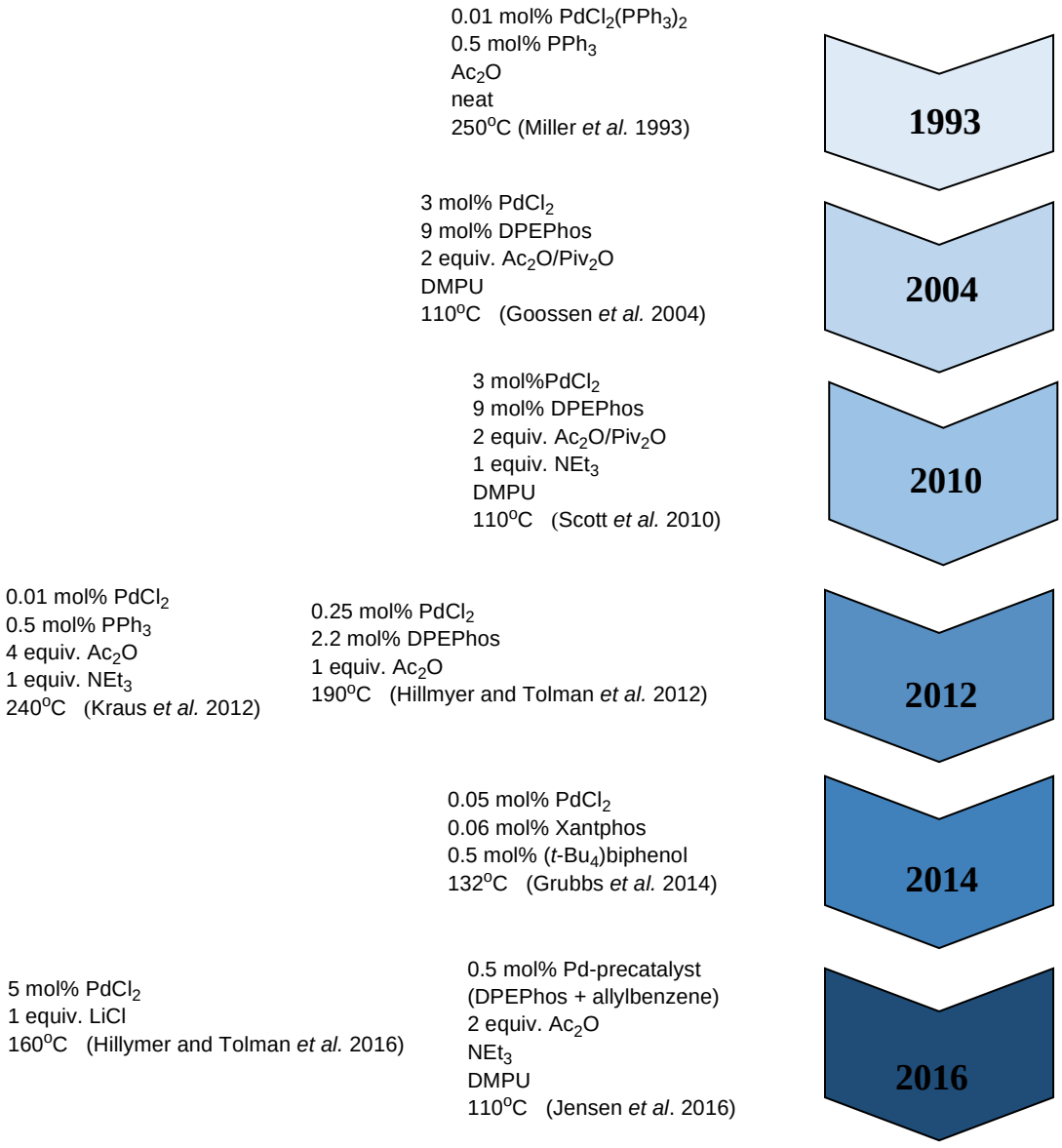
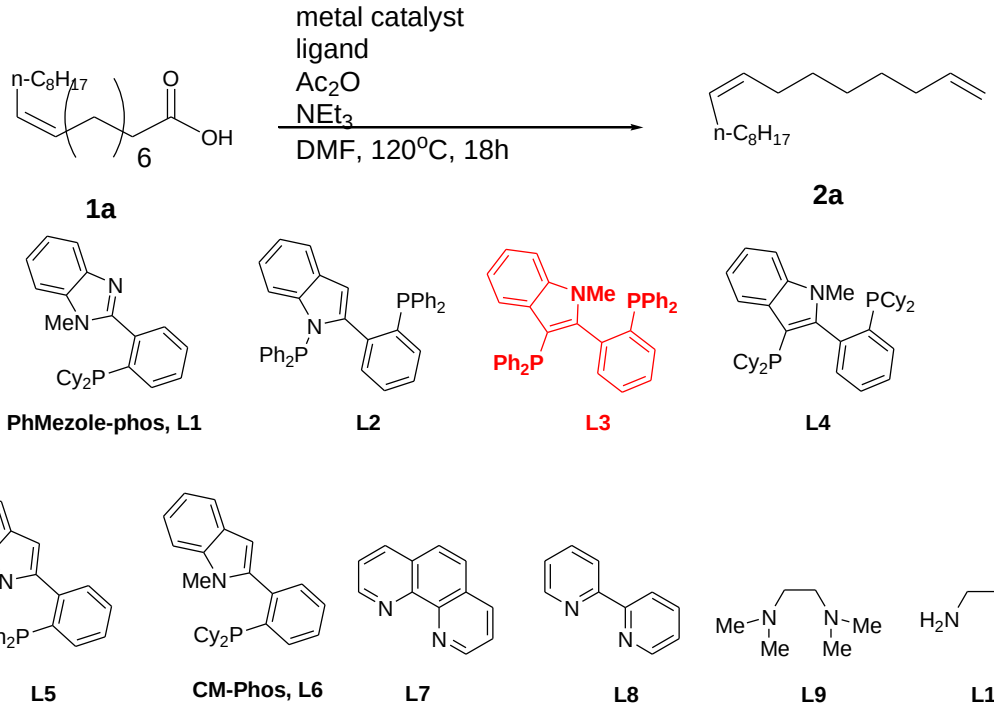


Figure 2.1: Recent development on Pd-catalyzed decarbonylation reaction

As mentioned in the first chapter, to meet the fast growing demand on biofuel, several biofuel grading processes were developed to improve the physical properties of biofuel so as to enhance its real application. Among those reported processes, decarboxylation/decarbonylation was in great interest as highly selective alkenes could be obtained. Those alkenes not only served as fuel but also act as valuable fine chemicals in polymer industry.[36] Numerous studies were done on the exploration of different homogenous catalytic systems on decarbonylation of long chain carboxylic acids, and palladium catalyst has been proven to give superior result than others metals such as iron,[37] rhodium,[38] nickel[39] and iridium.[40] However most of the reported palladium catalytic systems are based on palladium-bisphosphine,[41] in particularly biaryl ether ligands (DPEphos, and Xantphos), with the addition of anhydride[38,41a,b,c,e] to activate carboxylic acids for decarbonylation. Therefore I would like to investigate if there are others effective catalysts to catalyze decarbonylation of bio-derived carboxylic acids.

2.2 Results and discussion

2.2.1 Preliminary evaluation of palladium-indolylbisphosphine catalyzed decarbonylation of fatty acids



Entry	Metal Catalyst (mol%)	Ligand (mol%)	GC yield,%[b]
1	$PdCl_2$ (3)	L1 (9)	n.r.[c]
2	$PdCl_2$ (3)	L2 (9)	18
3	$PdCl_2$ (3)	L3 (9)	58
4	$PdCl_2$ (3)	L4 (9)	23
5	$PdCl_2$ (3)	L5 (9)	n.r.
6	$PdCl_2$ (3)	CM-Phos, L6 (9)	n.r.
7	$PdCl_2$ (3)	1,10 phenanthroline, L7 (9)	n.r.
8	$PdCl_2$ (3)	2,2'-Bipyridyl , L8 (9)	n.r.
9	$PdCl_2$ (3)	*N,N,N',N'*-tetramethylethylene diamine , L9 (9)	n.r.
10	$PdCl_2$ (3)	N,N'-dimethylethylene diamine , L10 (9)	n.r.
11	$PdCl_2$ (1)	L3 (3)	55

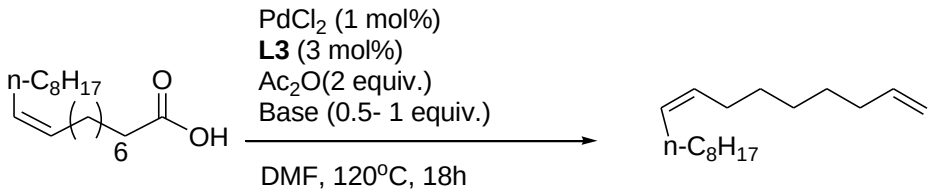
[a]Oleic acid (1mmol), Ac_2O (2mmol), $PdCl_2$ (1-3mol%), Ligand (3-9mol%), NEt_3 (1equiv.), DMF (2mL), 120°C, 18hours.

[b] Calibrated GC yield
[c] n.r. = no reaction

Table 2.1: Ligand screening for palladium-indolylbisphosphine catalyzed decarbonylation of fatty acids

Inspired by Gooβen's works of palladium-imidazoylphosphine catalyzed decarbonylative cross-coupling reactions.[42] We envisaged the combination of palladium with imidazole or indole scaffold ligands could be active catalyst towards decarbonylation of long chain carboxylic acids. Therefore palladium-imidazoylphosphine ligand, PhMezole-phos (**L1**) was chosen to catalyze the decarbonylation of oleic acids (C18-chain mono-unsaturated fatty acids that commonly found in vegetable oils) however no desired olefin was detected. Thus we attempted to employ indolylbisphosphine ligand (**L2)** in conjunction with $PdCl_2$ to catalyze decarbonylation reaction. By employing 3mol% $PdCl_2$-indolylbisphosphine ligand (**L2**), 18% desired olefin was obtained (Table 2.1, entry 2) hence several others classes of indolylbisphosphine ligands (**L3**-**L6**) were tested, indolylbisphosphine with PPh_2 moiety found to give moderate yield of desired heptadecene (58%) (Table 2.1, entry 3). Changing the same ligand scaffold to PCy_2 moiety diminished the product yield to 23% apparently (Table 2.1, entry 4). In addition to indolylbisphosphine ligands, indolylmonophosphine (**L5**) and CM-Phos (**L6**) were also tested however no desired products observed (Table 2.1, entry 5 and 6). Then we lowered the catalyst loading to 1mol% Pd and no detrimental effects on the product yield observed (Table

2.1, entry 11). In addition to N,P ligands, different commercial available diamines were also examined to probe their feasibility in catalyzing decarbonylation of fatty acids. However no desired product was obtained by using diamine ligands (Table 2.1, entries 7-10).



1a **2a**

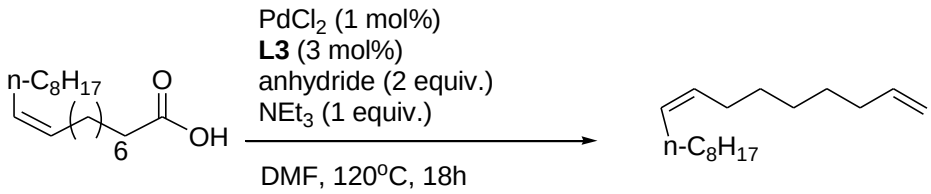
Entry	Base (equiv.)	GC yield ,%[b]
1	NEt_3 (0.5)	45
2	NEt_3 (1)	52
3	NEt_3 (3)	42
4	piperidine (1)	24
5	pyridine (1)	30
6	K_2CO_3 (1)	n.r.[c]

[a] Oleic acid (1 mmol), Ac_2O (2 mmol), $PdCl_2$ (1 mol%), Ligand (3 mol%), NEt_3 (1 equiv.), DMF (2 mL), 120°C, 18 hours.
[b] Calibrated GC yield
[c] n.r. =no reaction

Table 2.2: Amine/base screening for palladium-indolylbisphosphine catalyzed decarbonylation of fatty acids

With the promising results obtained, we then further optimized the reaction conditions to improve the product yields. Amine was believed to activate the Pd-catalyst and to enhance α-selectivity of olefins thus different amines as well as inorganic salt were tested, when potassium carbonate was added into the reaction, no desired product observed (Table 2.2, entry 5). Various amines were screened and triethylamine gave better yield than aromatic amines such as pyridine and piperidine

(Table 2.2, entry 2-4). Decreasing the amount of amines to 0.5 equivalent to substrate would lightly decrease the product yield (Tale 2.2, entry 1 versus entry 2).



1a **2a**

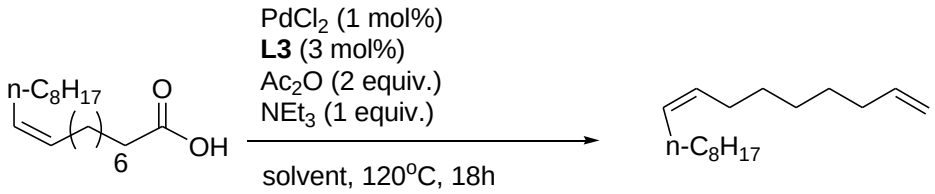
Entry	Anhydride (equiv.)	GC yield, %[b]
1	Acetic anhydride (1)	43
2	Acetic anhydride (2)	53
	Acetic anhydride (3)	55
4	Pivalic anhydride (2)	34
5	Benzoic anhydride (2)	26
6	Hexanoic anhydride (2)	trace
7	Methanesulfonic anhydride (2)	n.r.[c]

[a] Oleic acid (1 mmol), Ac_2O (2 mmol), $PdCl_2$ (1 mol%), Ligand (3 mol%), NEt_3 (1 equiv.), DMF (2 mL), 120°C, 18 hours.
[b] Calibrated GC yield
[c] n.r. = no reaction

Table 2.3: Anhydride screening for palladium-indolylbisphosphine catalyzed decarbonylation of fatty acids

The role of anhydride is crucial in palladium-catalyzed decarbonylation of carboxylic acids as it would react with the substrate to form mixed anhydride so that the substrate is activated and allows undergoing oxidative addition by palladium-catalyst. Therefore several anhydrides sources were tested. Acetic anhydride gave best results over screened sources (Table 2.3, entry 1). 2 equivalent of acetic anhydride was sufficient to activate the decarbonylation and to give moderate

yields of desired product (Table 2.3, entries 1-3). Pivalic anhydride that commonly reported as activator towards Pd-catalyzed decarbonylation, did not have apparent enhancement to the product yield in our catalytic system (Table 2.3, entry 4). Changing the anhydride sources to benzoic anhydride and hexanoic anhydride would drastic decrease the product yield (Table 2.3, entries 5 and 6). No product was observed when methanesulfonic anhydride was used (Table 2,3, entry 7) and it may due to the inability to form mixed anhydride for decarbonylation.



1a **2a**

Entry	Solvent	GC yield,%[b]
1	Toluene	trace
2	*tert*-amyl alcohol	trace
3	1,4 Dioxane	38
4	DMF	53
5	DMAc	54[c]
6	DMPU	52

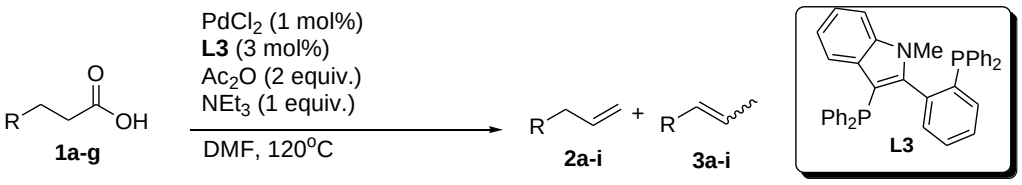
[a]Oleic acid (1 mmol), Ac_2O (2 mmol), $PdCl_2$ (1 mol%), Ligand (3 mol%), NEt_3 (1 equiv.), DMF (2 mL), 120°C, 18 hours.
[b] Calibrated GC yield
[c] Reaction temperature = 140°C

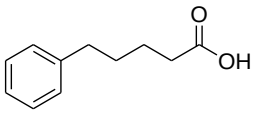
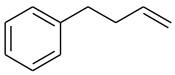
Table 2.4: Solvent screening for palladium-indolylbisphosphine catalyzed decarbonylation of fatty acids

A high boiling point polar solvent, *N,N'*-Dimethylpropyleneurea (DMPU) is often used for decarbonylation of carboxylic acid. Since it is an expensive solvent

(USD$ 630 for 1L, listed price from Sigma-Aldrich) thus we would like to look for alternative with lower cost. Solvents with different polarity was screened and *N*,*N*-Dimethylformamide (DMF) and *N*,*N*-Dimethylacetamide (DMAc) were found to decarbonylate oleic acid smoothly into heptadecane in moderate yield (Table 2.4, entry 4 and 5).

2.2.2 Scope of palladium-indolylbisphosphine catalyzed decarbonylation of fatty acids



Entry	carboxylic acid		alkene		yield/%[b]	selectivity/%[c]
1	$C_{17}H_{33}COOH$	**1a**	$C_{15}H_{29}$	**2a**	52	88
2	$C_{13}H_{27}COOH$	**1b**	$C_{11}H_{23}$	**2b**	43	90
3	$C_{15}H_{31}COOH$	**1c**	$C_{13}H_{27}$	**2c**	38	90
4	$C_{17}H_{35}COOH$	**1d**	$C_{15}H_{31}$	**2d**	63	89
5		**1e**		**2e**	57	91
6	$H_2N(CH_2)_7CH_2CH_2COOH$	**1f**	$H_2N(CH_2)_7CH=CH_2$	**2f**	trace	
7	$HO(CH_2)_7CH_2CH_2COOH$	**1g**	$HO(CH_2)_7CH=CH_2$	**2g**	trace	

[a] Oleic acid (1 mmol), Ac_2O (2 mmol), $PdCl_2$ (1 mol%), Ligand (3 mol%), NEt_3 (1 equiv.), DMF (2 mL), 120°C, 18 hours.

[b] Calibrated GC yield.

[c] Alpha-selectivity (selectivity to produce alpha-olefin) determined by ^1H NMR.

Table 2.5: Palladium-indolylbisphosphine (L3) catalyzed decarbonylation of fatty acids

With the optimal reaction conditions obtained we further extend our substrate scopes. By applying our catalytic system, unsaturated long chain carboxylic acid, oleic acid (C18:1) could be decarbonylated to desired alkenes with moderate product yields (52%, table 2.5, entry 1) and it is comparative to previous reports under Gooßen's reaction protocol.[41a] (3mol% $PdCl_2$, 9mol% DPEphos, 69%) Not only unsaturated long chain carboxylic acids could be converted to alkenes. Various long chain saturated fatty acids could be converted to terminal alkenes in moderate to good yield (45-63%) and selectivity (88-91%) (Table 2.5, entries 2-4). This protocol provided alternative synthetic pathway to prepare valuable odd-numbered alkenes.[43] Our catalytic system could be further extended to decarbonylate 5-phenylvaleric acid into corresponding alkenes in good yield (57%) (Table 2.5, entry 5). However functional groups such as amine or hydroxyl could not tolerate to our catalytic system (Table 2.5, entries 6 and 7).

2.3 Conclusion

In addition to biaryl ether ligands (DPEphos and Xantphos) that commonly used in conjunction with palladium metal for decarbonylation of carboxylic acids. We have explored other classes of indolylbisphosphine ligand to catalyze decarbonylation of carboxylic acids. By employing 1mol% Pd-indolylbisphosphine ligand (**L3**), various kinds of alpha olefins were produced in good yield and selectivity.

2.4 Experimental section

2.4.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All deoxygenation reactions were performed in resealable screw cap Schlenk tube (approx. 15 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4 mm 10 mm). Toluene and 1,4-dioxane were distillated from sodium and sodium benzophenone ketyl under nitrogen, respectively.

Ligands L2 – L5 were synthesized according to literature procedures. Ligands L1, L6 – L10 were purchased from commercial suppliers. New bottle of *n*-butyllithium was used (Note: since the concentration of *n*-BuLi may vary, we recommend performing a titration prior to use). Thin layer chromatography was performed on pre-coated silica gel 60 F254 plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. NMR spectra were recorded on a Brüker spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P). Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). ^{31}P NMR spectra were referenced to 85% H_3PO_4

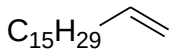
externally. Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FTICR mass spectrometer (ESI-MS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. X-ray crystal structure was determined by Bruker D8 Venture. All yields reported refer to isolated yield of compounds estimated to be greater than 95% purity as determined by capillary gas chromatography (GC) or ^{1}H NMR. Compounds described in the literature were characterized by comparison of their ^{1}H and/or ^{13}CNMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables.

2.4.2 General procedure for Pd-indolylbisphosphine (L3) catalyzed decarbonylation of carboxylic acids

An array of Schlenk tubes were charged with magnetic stirrer bar (4 mm x 10 mm) and were evacuated and backfilled with nitrogen (3 cycles). The Schlenk tubes were charged with $PdCl_2$ (1mol%, 0.0018g), ligand **L3** (9mol%, 0.017g) and 2mL DMF was added by syringe then again evacuated and backfilled with nitrogen (3 cycles) and stirred for 1 minute. The Schlenk tubes were then added with carboxylic acids substrates (1 mmol), acetic anhydride (2 mmol,, 0.188 mL) and triethylamine (1 mmol, 0.15 mL). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 120 ^{o}C oil bath for 18 h. The reactions were allowed to reach room temperature. Ethyl acetate (~4 mL), dodecane (113 μL, internal standard) and water (~2 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane calibration curve.

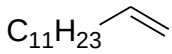
2.4.3 Characterization data of alpha olefins

(*Z*)-Heptadeca-1,8-diene (Table2.5, **2a**)



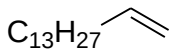
Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*= 6.6Hz, 3H), 1.26 (m, 18H), 2.02 (m, 6H), 4.92-5.01 (m, 2H), 5,35 (m, 2H), 5.80 (m, 1H).

1-Tridecene (Table 2.5, **2b**)



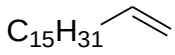
Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*= 7.1Hz, 3H), 1.27 (s, 18H), 2.05 (q, *J*= 6.9Hz, 3H), 4.93 (d, *J*= 11.1Hz, 1H), 5.00 (dd, *J*= 1.4Hz, 17.0Hz, 1H), 5.77-5.87 (m, 1H).

1-Pentadecene (Table 2.5, **2c**)



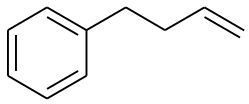
Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*= 6.9Hz, 3H), 1.26 (s, 22H), 2.04 (q, *J*= 7.2Hz, 3H), 4.93 (d, *J*= 10.1Hz, 1H), 5.00 (dd, *J*= 1.5Hz, 17.2Hz, 1H), 5.76-5.86 (m, 1H).

1-Heptadecene (Table 2.5, **2d**)



Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J*= 6.9Hz, 3H), 1.26 (s, 24H), 2.05 (q, *J*= 6.9Hz, 3H), 4.92 (d, *J*= 10.0Hz, 1H), 5.01 (dd, *J*= 1.5Hz, 17.1Hz, 1H), 5.76-5.86 (m, 1H).

4-Phenyl-1-butene (Table 2.5, **2e**)



Eluents (Hexane, R_f= 0.6) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (q, *J*= 7.6Hz, 2H), 2.73 (t, *J*= 7.6Hz, 2H), 4.99 (d, *J*= 10.2Hz, 1H), 5.06 (dd, *J*= 1.8Hz, 17.3Hz, 1H), 5.83-5.93 (m, 1H), 7.20-7.22 (m, 3H), 7.28-7.32 (m, 2H).

2.5 References

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Chapter 3 Palladium-Naphthylphosphine Catalyzed Decarbonylation of Carboxylic Acids into Alpha Olefins

3.1 Introduction

Owing to the depletion of fossil fuels, there is growing demand on exploring alternative renewable energy sources.[44] Biomass-derived hydrocarbons were believed to be good alternative for fossil fuels since they could be readily obtained by cracking or decarbonylation/decarboxylation. Cracking of vegetable oils results in producing broad ranges of hydrocarbons with different carbon-chain numbers. Compared to cracking, decarbonylation/decarboxylation of biomass-derived carboxylic acids are particularly attractive since substrates are inexpensive, readily available from various natural sources[44a] and highly selective alkenes could be obtained. In former chapter we have discussed the recent advancement of palladium-catalyzed decarbonylation reactions and palladium-bisphosphine catalyst (particularly biaryl ether ligands, DPEphos and Xantphos) to serve as active species in decarbonylation reactions to afford alkenes with good selectivity. Recently Cramer[45] *et al.* investigated the palladium-catalyzed decarbonylation of biomass-derived hydrocinnamic acid to styrene by computational study and suggested monophosphine acyl complexes could

be stable reaction intermediates during decarbonylation reaction (Figure 3.1). Moreover their computational study proposed mechanism involved deliberation of phosphine ligands for provision of reaction vacant site (TS3-5) and re-coordination of phosphine ligands for stabilization of intermediates (TS7-trans-4).

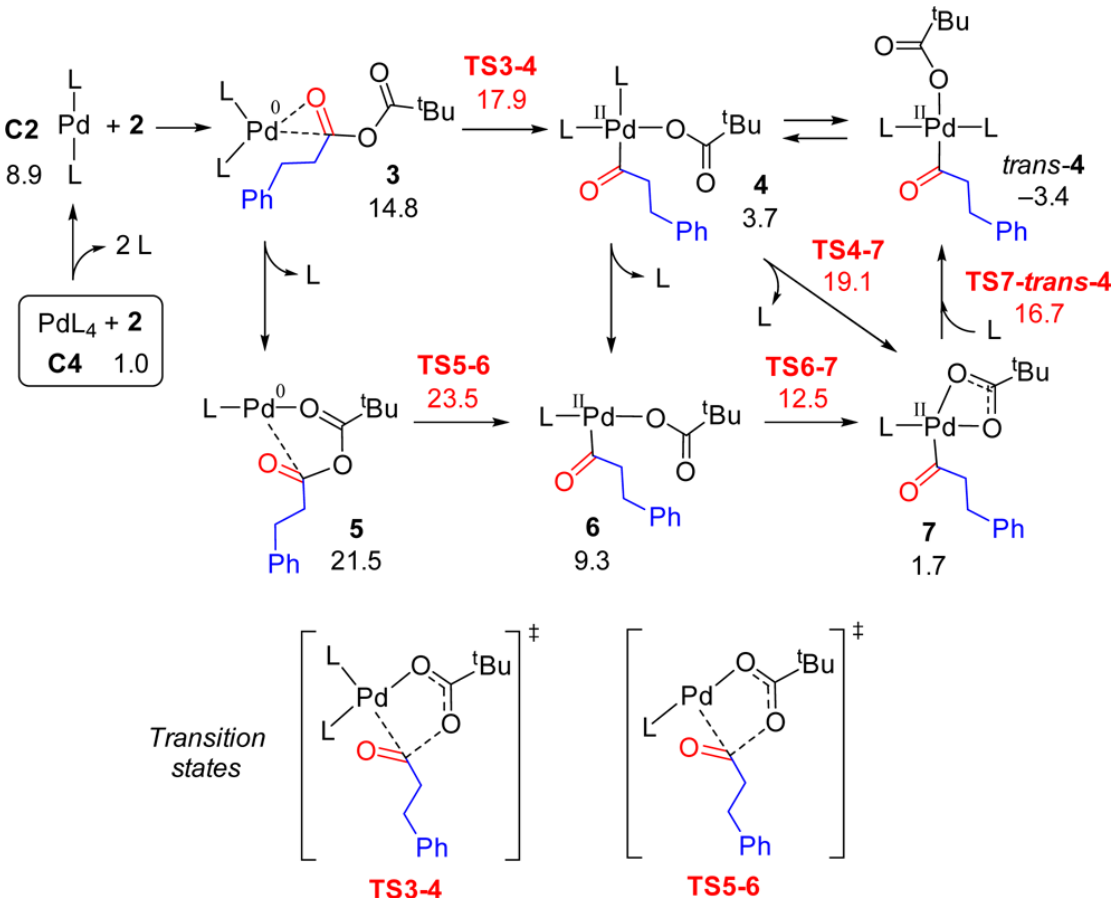


Figure 3.1: Proposed oxidative addition step during Pd-catalyzed decarbonylation of carboxylic acid.

Therefore we postulated monophosphine ligand with hemilabile atoms may be favorable for the decarbonylation reaction. Hemilability of N-P ligand are believed to offer "on and off" function during catalytic cycle, the labile donor N-atom could chelate to the metal center and stabilize catalyst meanwhile it could leave and provide vacant site for reaction.[46] In order to examine the postulation, new monophosphine

ligands with quinolinyl scaffold (NP-1 and NP-2)[47] and naphthyl scaffold (CP-1 and CP-2) were synthesized (Figure 3.2).

(Figure 3.2)

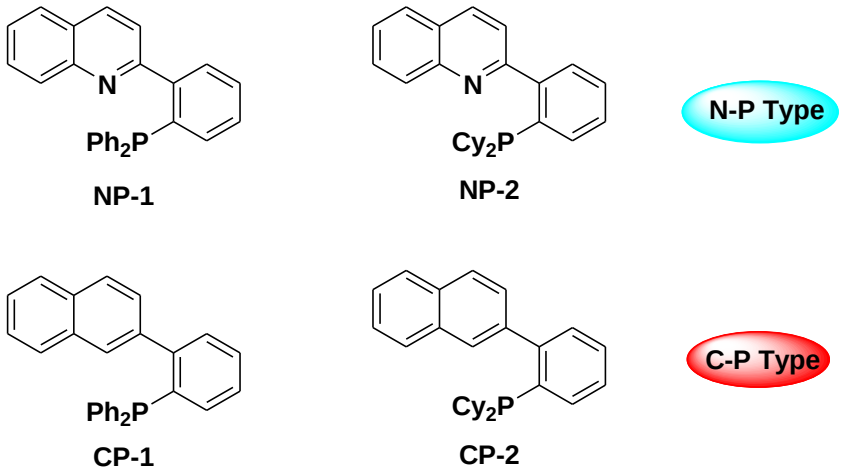
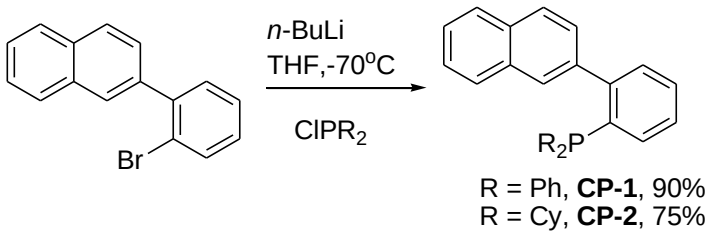


Figure 3.2: Monophosphine with naphthyl scaffold (C-P type) and quinolinyl scaffold (N-P type)

3.2 Results and discussion

3.2.1 Synthesis of Monophosphine ligands (C-P type and N-P type)

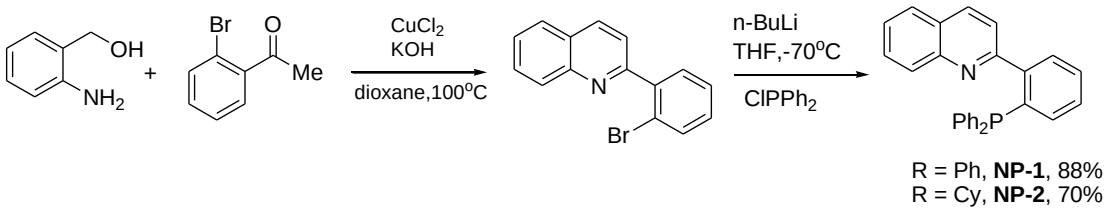
3.2.1.1 Synthesis of Monophosphine ligand with naphthyl scaffold (C-P type)



Scheme 3.1: Synthetic pathway of C-P type ligand

For the synthesis of C-P type naphthyl phosphine ligand, 2-(2-Bromophenyl)naphthalene was reacted with *n*-BuLi for lithium/bromide exchange, followed by trapping with $ClPR_2$ to afford corresponding phosphine in moderate to good yield (Scheme 3.1).

3.2.2.2 Synthesis of Monophosphine with quinolinyl scaffold (N-P type)

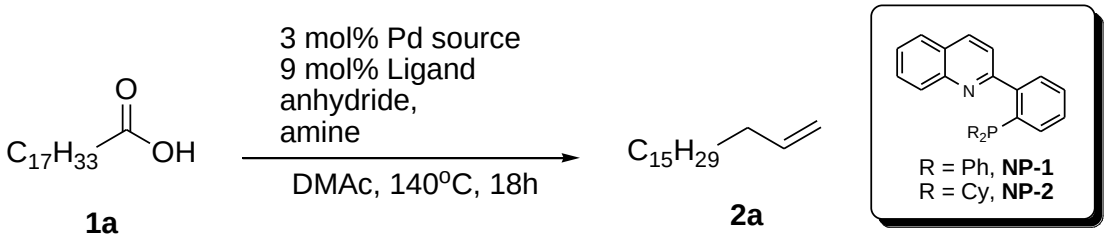


Scheme 3.2: Synthetic pathway of N-P type ligand

For the synthesis of N-P type quinolinyl phosphine ligand, 2-(2-Bromophenyl)quinoline were synthesized via Friedländer quinoline reaction between 2-Aminobenzyl alcohol and acetophenones. Then 2-(2-Bromophenyl)quinoline was reacted with *n*-BuLi for lithium/bromide exchange,

followed by trapping with $ClPR_2$ to afford corresponding phosphine in moderate to good yield (Scheme 3.2).

3.2.2 Preliminary evaluation of palladium-naphthylphosphine catalyzed decarbonylation of carboxylic acids into alpha olefins



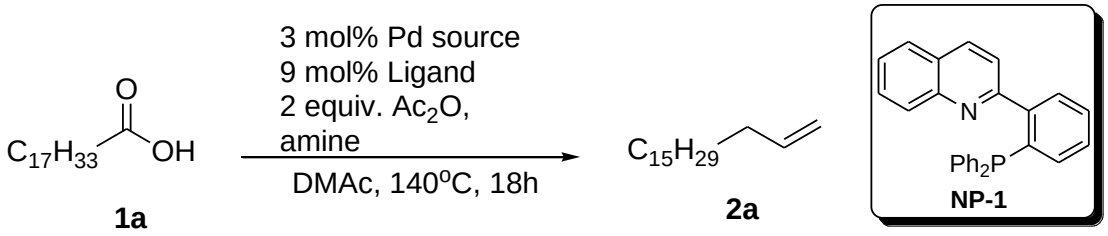
Entry	Pd source (mol%)	Ligand (mol%)	Additive (equiv.)	Amine (equiv.)	Yield,%[b]
1	$PdCl_2$ (3)	NP-2 (9)	Ac_2O (2)	NEt_3 (1)	n.r.[c]
2	$PdCl_2$ (3)	NP-1 (9)	Ac_2O (2)	NEt_3 (1)	11
3	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (2)	NEt_3 (1)	30
4	$Pd(OAc)_2$ (3)	NP-1 (9)	Ac_2O (2)	NEt_3 (1)	n.r.
5	$Pd(TFA)_2$ (3)	NP-1 (9)	Ac_2O (2)	NEt_3 (1)	n.r.
6	$[Pd(cinnamyl)Cl]_2$ (1.5)	NP-1 (9)	Ac_2O (2)	NEt_3 (1)	n.r.

[a] Reaction conditions: 3mol% $Pd(COD)Cl_2$, 9mol% Ligand, 2-6 equiv. anhydride, 1-3 equiv. amine, 1mL *N*,*N*-Dimethylacetamide (DMAc), 140°C, 18h.
[b] Calibrated GC yield % by GC-FID.
[c] n.r. = no reaction

Table 3.1: Pd sources screening for palladium-monophosphine catalyzed decarbonylation of carboxylic acids

Oleic acid which is a major component presented in various kinds of vegetable oil[48] such as peanut oil (up to 71.1%), almond oil (up to 67.2%), was chosen as model substrate to optimize reaction conditions. By applying standard

palladium-bisphosphine catalytic system ($PdCl_2$, metal to ligand ratio 1:3, using acetic anhydride and triethylamine as additives). When quinolinyl scaffold ligand with PCy_2 moiety (**NP-2**) was employed, no decarbonylation reaction occurred (Table 3.1, entry1). Changing to the ligand with PPh_2 moiety (**NP-1**), 11% desired alkenes were obtained (Table 3.1, entry 2). Besides $PdCl_2$, others commercial available Pd sources were screened (Table 3.1, entry 3-6) and $Pd(COD)Cl_2$ was found to give best results in conjunction with ligand **NP-1** towards decarbonylation of oleic acid.



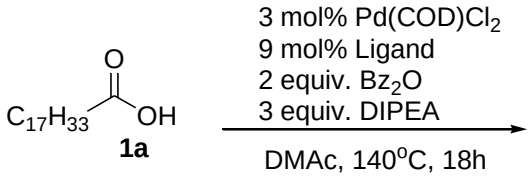
Entry	Pd source (mol%)	Ligand (mol%)	Additive (equiv.)	Amine (equiv.)	Yield,%[b]
1	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (2)	NEt_3 (1)	30
2	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (4)	NEt_3 (1)	28.3
3	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (6)	NEt_3 (1)	23.8
4	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (2)	NPr_3 (1)	32.8
5	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (2)	NPr_3 (2)	35.4
6	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (2)	NPr_3 (3)	40.5
7	$Pd(COD)Cl_2$ (3)	NP-1 (9)	Ac_2O (2)	DIPEA (3)	46.5

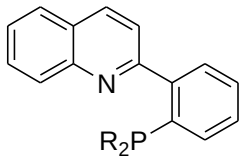
[a] Reaction conditions: 3mol% $Pd(COD)Cl_2$, 9mol% Ligand, 2-6 equiv. anhydride, 1-3 equiv. amine, 1mL *N*,*N*-Dimethylacetamide (DMAc), 140°C, 18h.
[b] Calibrated GC yield % by GC-FID.

Table 3.2: Amine screening for palladium-monophosphine catalyzed decarbonylation of carboxylic acids

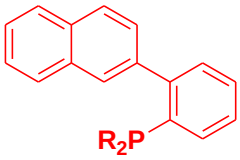
Amine was known to be crucial to stabilize palladium active specie and helps to enhance selectivity of the reaction[49] and hence different amines (triethylamine, tributylamine as well as *N*,*N*-diisopropylethylamine) were tested (Table 3.2, entries

1-7). 3 equivalents of *N,N*-diisopropylethylamine (DIPEA) was found to enhance yields of alkenes (46.5%: table 3.2, entry 7).

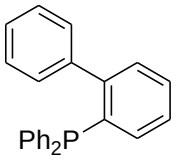




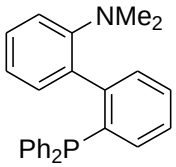
L1: R = Ph, **NP-1**: 46.5%[b]
L2: R = Cy, **NP-2**: n.r. [b]



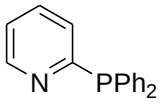
L3: R = Ph, CP-1: 70%,67.5%[d], 36%[e], 47.2%[f]
L4: R = Cy, **CP-2**: n.r.



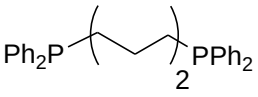
L5: 63%



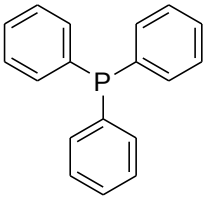
L6: PhDavePhos
56%



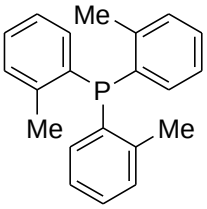
L7: 38%



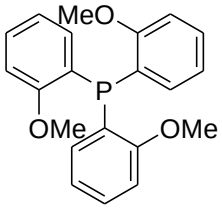
L8: 29%



L9: 42.3%



L10: n.r.[c]



L11: n.r.[c]

[a] Reaction conditions: 3mol% $Pd(COD)Cl_2$, 9mol% Ligand, 2 equiv. Benzoic anhydride, 3 equiv. diisopropylethylamine, 1mL *N*,*N*-Dimethylacetamide (DMAc), 140°C, 6-18h.

[b] Acetic anhydride used instead of benzoic anhydride.

[c] n.r. = no reaction

[d] Reaction time = 6 hours

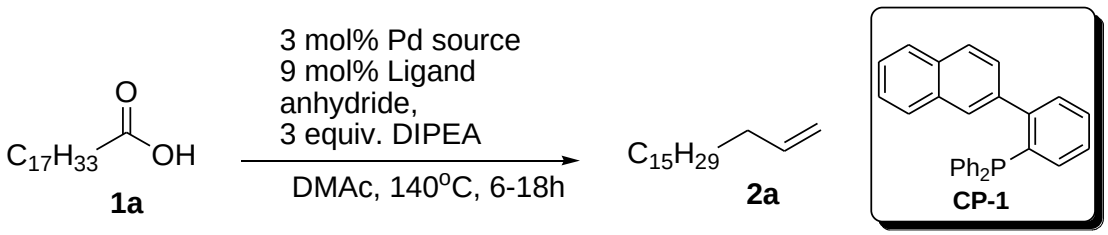
[e] metal to liagnd ratio = 1:1

[f] metal to ligand ratio = 1:2

Table 3.3: Ligand screening for palladium-monophosphine catalyzed decarbonylation of carboxylic acids

With promising results in hands we then compared the catalytic activity of N-P type monophosphines with C-P type monophosphines (**L1-L4**) as well as others

commercially available monophosphine ligands (**L5-L11**) (Table 2). $Pd(COD)Cl_2$ with **CP-1** (**L3**) gave the best catalytic activity among the screened ligands. We observed that with the presence of the N- donor atom on our monophosphine, the product yield diminished. (Table 3.3: **L1**:46.5% versus **L3**:68.9%). This might be due to chelation of NP ligand to metal center[46] during the reaction that retards decarbonylation of substrates. Lowered the amount of ligand would decrease product yields (9mol% = 70%; 6mol% = 47.2%; 3mol% = 36%). Furthermore reaction time could be shortened from 18 hours to 6 hours without diminishing product yields (18h: 70%; 6h: 67.5%).



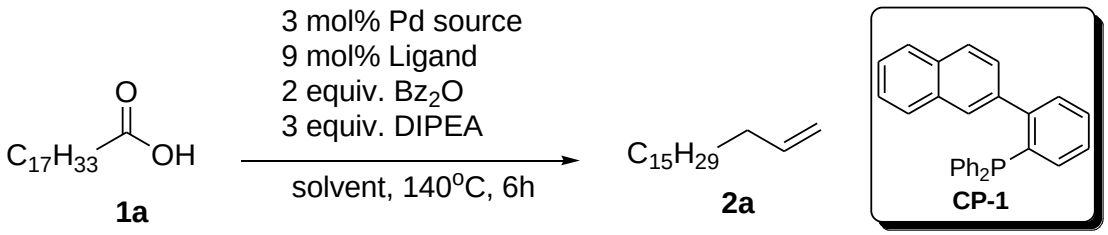
Entry	Pd source (mol%)	Ligand (mol%)	Additive (equiv.)	Amine (equiv.)	Yield,%[b]
1	$Pd(COD)Cl_2$ (3)	CP-1 (9)	Ac_2O (2)	DIPEA (3)	68.9
2	$Pd(COD)Cl_2$ (3)	CP-1 (9)	Piv_2O (2)[e]	DIPEA (3)	57
3	$Pd(COD)Cl_2$ (3)	CP-1 (9)	Bz_2O(2)[e]	DIPEA (3)	70, 67.5[d]
4	$Pd(COD)Cl_2$ (3)	CP-1 (9)	--	DIPEA (3)	n.r.
5	$Pd(COD)Cl_2$ (3)	CP-1 (9)	Bz_2O(2)	---	43

[a] Reaction conditions: 3mol% $Pd(COD)Cl_2$, 9mol% Ligand, 2 equiv. benzoic anhydride, 3 equiv. diisopropylethylamine, 1mL *N*,*N*-Dimethylacetamide (DMAc), 140°C, 18h.
[b] Calibrated GC yield % by GC-FID.
[c] n.r. = no reaction
[d] Reaction time = 6 hours

Table 3.4: Anhydride screening for palladium-naphthylphosphine (CP-1) catalyzed decarbonylation of carboxylic acids

Without the addition of anhydrides, no desired alkenes were obtained (table 3.4, entry 4) and thus various kinds of acid anhydrides were tested (Table 3.4), benzoic anhydride was found to give superior result (70%: table 3.4, entry 3). In addition, the reaction time could be shorten to 6 hours without diminishing product yield (70%,

18h versus 67.5%, 6h). It is noteworthy that product yield was significantly decreased without addition of amine (Table 3.4, entry 5).



Entry	Pd source (mol%)	Ligand (mol%)	Solvent	Yield, %[b]
1	$Pd(COD)Cl_2$ (3)	CP-1 (9)	Toluene	53
2	$Pd(COD)Cl_2$ (3)	CP-1 (9)	CPME	55.2
3	$Pd(COD)Cl_2$ (3)	CP-1 (9)	γ-butyrolactone	27.5
4	$Pd(COD)Cl_2$ (3)	CP-1 (9)	2-MeTHF	43
5	$Pd(COD)Cl_2$ (3)	CP-1 (9)	DMPU	54.3

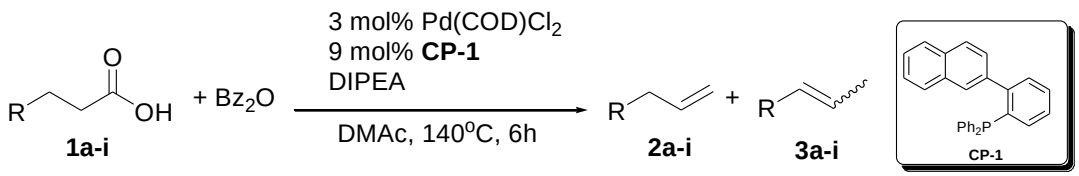
[a] Reaction conditions: 3mol% $Pd(COD)Cl_2$, 9mol% Ligand, 2 equiv. benzoic anhydride, 3 equiv. diisopropylethylamine, 1mL *N*,*N*-Dimethylacetamide (DMAc), 140°C, 6-h.
[b] Calibrated GC yield % by GC-FID.

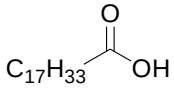
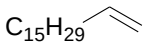
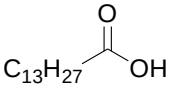
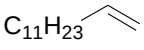
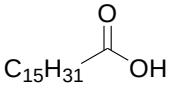
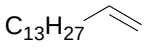
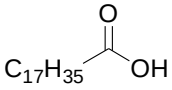
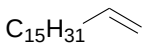
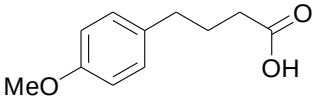
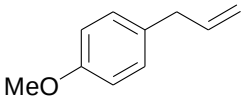
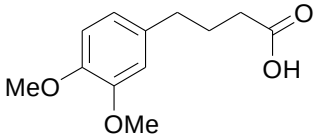
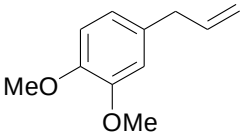
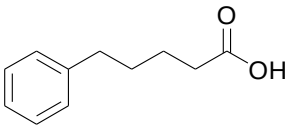
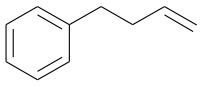
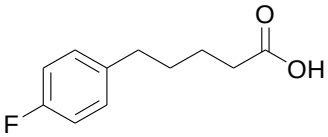
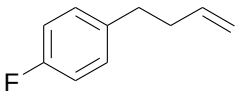
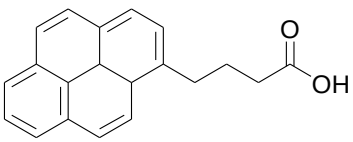
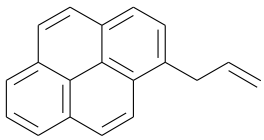
Table 3.5: Solvent screening for palladium-naphthylphosphine (CP-1) catalyzed decarbonylation of carboxylic acids

As mentioned in part of introduction, it is in great interest to develop efficient and inexpensive catalytic protocol for decarbonylation reaction of carboxylic acid to produce high selective alpha olefin, DMPU which is an expensive solvent that often employed in Pd-catalyzed decarbonylation, worth to search for its alternative hence different solvents were tested. Different solvents with polarity were tested, toluene and DMPU gave moderate yields meanwhile several green solvents

(cyclopentylmethylether CMPE, 2-methyltetrahydrofuran 2MeTHF and γ-butyrolactone were tested however their results were inferior than *N*,*N*-Dimethylacetamide (DMAc).

3.2.3 Scope of palladium-naphthylphosphine catalyzed decarbonylation of carboxylic acids into alpha olefins



Entry	carboxylic acid		alkene		yield,%[b]	selectivity,%[c]
1		**1a**		**2a**	70	88
2		**1b**		**2b**	66, 52[d]	97
3		**1c**		**2c**	78, 58[d]	98
4		**1d**		**2d**	80, 63[d]	97
5		**1e**		**2e**	60	82
6		**1f**		**2f**	65	79
7		**1g**		**2g**	53	85
8		**1h**		**2h**	58	96
9		**1i**		**2i**	60	90

[

[a] Reaction conditions: 3mol% Pd(COD)Cl_2, 9mol% Ligand, 2 equiv. benzoic anhydride, 3 equiv. DIPEA, 1mL *N*,*N*-Dimethylacetamide (DMAc), 140^{o}C, 6h.
[b] Isolated yield.
[c] Alpha-selectivity (selectivity to produce alpha-alkene) is determined by ^{1}H NMR.
[d] 1mol% Pd-naphthylphosphine employed.

Table 3.6: Pd-naphthylphosphine (CP-1) catalyzed decarbonylation of carboxylic acids

Odd-numbered alkenes which are valuable building blocks for various fine chemicals[50] but they are largely inaccessible and expensive. Even-numbered long chain fatty acids could be easily accessed from vegetable oils. Therefore it is in great interest if we could convert inexpensive even-numbered saturated fatty acids into value added odd-numbered alkenes.[51] By applying our catalytic system, various even-numbered long chain fatty acids could be converted to odd-numbered alkenes in good yields and selectivity. When the catalyst loading was lowered to 1mol% Pd, even-numbered long chain fatty acids could be still smoothly converted into their corresponding odd-numbered alkenes. (Table 3.6, entries 2-4). In addition to the saturated long chain fatty acid, 5-phenylvaleric acid and 5-(4-Flurophenyl)valeric acid were also be converted to corresponding alkenes smoothly (Table 3.6, entries 7 and 8). Estragole (60%: table 3.6, entry 5) and its derivatives (65%: table 3.6, entry 6) which served as precursors for fungicide and fragrance,[52] could be readily obtained by deoxygenating 4-(4-methoxyphenyl)butyric acid and 4-(3,4-Dimethoxyphenyl)butyric acid respectively. Noteworthy that it is the first example of synthesis of allylpyrene via decarbonylation of pyrenecarboxylic acid (60%: table 3.6, entry 9).

3.3 Conclusion

In conclusion we have developed new monophosphine ligands with quinolinyl (**L1-L2)** and naphthyl **(L3-L4)** scaffold and demonstrated that 1-3mol% palladium-naphthylphosphine catalyst (**Pd-CP-1**) could be employed to convert various carboxylic acids into alkenes in good yield and selectivity under mild condition. And the protocol is simple without distillation of olefins, stepwise addition of anhydride as well as pre-complexation.

3.4 Experimental section

3.4.1 General considerations

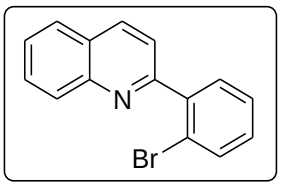
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All deoxygenation reactions were performed in resealable screw cap Schlenk tube (approx. 15 mL volume) in the presence of Teflon-coated magnetic stirrer bar (4 mm 10 mm). Toluene was distillated from sodium and sodium benzophenone ketyl under nitrogen, respectively.

2-(2-Bromophenyl)naphthalene and Ligands **L5** – **L11** were purchased from commercial suppliers. New bottle of *n*-butyllithium was used (Note: since the concentration of *n*-BuLi may vary, we recommend performing a titration prior to use). Thin layer chromatography was performed on pre-coated silica gel 60 F254 plates. Silica gel (Merck, 70-230 and 230-400 mesh) was used for column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. NMR spectra were recorded on a Brüker spectrometer (400 MHz for 1H, 100 MHz for 13C and 162 MHz for 31P). Spectra were referenced internally to the residual proton resonance in CDCl3 (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. 13C NMR spectra were referenced to CDCl3 (δ 77.0 ppm, the middle peak). 31P NMR spectra were referenced to 85% H3PO4 externally. Coupling constants (J) were

reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FTICR mass spectrometer (ESI-MS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. X-ray crystal structure was determined by Bruker D8 Venture. All yields reported refer to isolated yield of compounds estimated to be greater than 95% purity as determined by capillary gas chromatography (GC) or 1H NMR. Compounds described in the literature were characterized by comparison of their 1H and/or 13CNMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables.

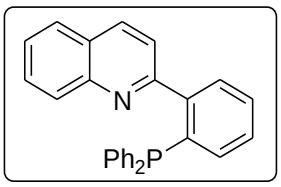
3.4.2 Characterizations of N-P type and C-P type ligands

2-(2-Bromophenyl)quinoline



Synthesis of 2-(2-Bromophenyl)quinoline was according to literature procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, *J*= 1.6Hz, 7.6Hz, 1H), 7.45 (t, *J*= 7.5Hz, 1H), 7.58 (t, *J*= 7.5Hz, 1H), 7.65 (dd, *J*= 1.5Hz, 7.6Hz, 1H), 7.71 (d, *J*= 8.8Hz, 2H), 7.75 (t, *J*= 7.6Hz, 1H), 7.87 (d, *J*= 8.2Hz, 1H) 8.21 (t, *J*= 8.3Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.8, 126.4, 126.8, 127.1, 127.5, 127.7, 129.5, 129.7, 130.0, 131.6, 133.2, 135.7, 141.5, 147.8, 158.6; MS (EI): *m/z* (relative intensity) 283.1 (M^+, 50), 204.2 (100), 176.2 (25), 102.1 (32)

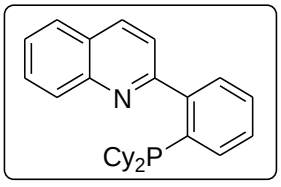
(2-(Quinoline-2-yl)phenyl)diphenylphosphine, **NP-1**



2-(2-Bromophenyl)quinoline (0.849g, 3.0mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was

added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodiphenylphosphine (0.66 mL, 3.3 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. Pale yellow solid of (2-(Quinoline-2-yl)phenyl)diphenylphosphine **NP-1** (1.03 g, 88%) were obtained. Melting point. 162.6-163.3 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.21 (dd, *J*= 3.4Hz, 7.9Hz, 1H), 7.31-7.42 (m, 11H), 7.55 (t, *J*= 8.0Hz, 2H), 7.59-7.67 (m, 2H), 7.76 (d, *J*= 8.3Hz, 1H), 7.83-7.88 (m, 2H), 8.21 (d, *J*= 8.3Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ121.3, 126.4, 126.6, 127.4, 128.1 (d, *J*= 4.0Hz), 128.2, 128.5, 128.6, 128.9, 129.3 (d, *J*= 4.0Hz), 129.4, 133.8 (d, *J*= 19.8Hz), 135.4, 135.9, 137.1 (d, *J*= 18.8Hz), 139.4 (d, *J*= 11.1Hz), 145.7 (d, *J*= 23.3Hz), 146.9, 158.3; ^{31}P NMR (162 MHz, CD_2Cl_2) δ -10.86; MS (EI): *m/z* (relative intensity) 389.3 (M^+, 23), 312.2 (100), 235.2 (35), 194.7 (7); HRMS: calcd. for C27H21NP+: 390.1412, found 390.1403.

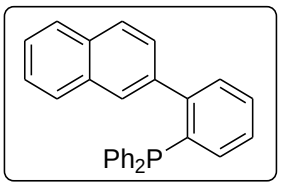
(2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine, **NP-2**



2-(2-Bromophenyl)quinoline (0.849g, 3.0mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodicyclohexylphosphine (0.72mL, 3.3 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. White solid of (2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine **NP-2** (0.84 g, 70%) were obtained. Melting point. 136.6-137.2 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.09-1.32 (m, 10H), 1.63-1.76 (m, 10H), 1.99 (td, *J*= 3.0Hz, 12.0Hz, 2H), 7.48-7.52 (m, 2H), 7.56-7.62 (m, 3H), 7.70-7.73 (m, 1H), 7.76 (td, *J*= 1.3Hz, 7.2Hz, 1H), 7.91 (d, *J*= 8.2Hz, 1H), 8.12 (d, *J*= 8.2Hz, 1H), 8.18 (d, *J*= 8.2Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 26.4, 27.1 (d, *J*= 7.0Hz), 27.2 (d, *J*= 4.3Hz), 29.7 (d, *J*= 10.5Hz), 30.3 (d, *J*= 17.5Hz), 34.5 (d, *J*= 13.4Hz), 124.3 (d, *J*= 6.6Hz), 126.2, 126.7, 127.5 (d, *J*= 2.7Hz), 128.3, 129.3 (d, *J*= 16.6Hz), 129.8 (d, *J*= 5.0Hz), 132.9 (d, *J*= 2.0Hz), 134.2, 134.7 (d, *J*= 23.6Hz), 147.6, 149.3 (d, *J*= 27.3Hz), 161.0 (d, *J*= 4.9Hz); ^{31}P NMR (162 MHz, CD_2Cl_2) δ -11.01; MS (EI): *m/z* (relative intensity) 401.4 (M^+, 2), 318.3 (100), 235.2 (43).

HRMS: calcd. for C27H33NP+: 402.2351, found 402.2342.

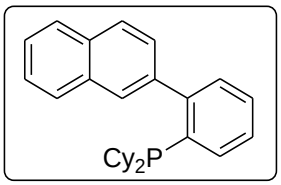
(2-(Naphthalene-2-yl)phenyl)diphenylphosphine, **CP-1**



2-(2-Bromophenyl)naphthalene (0.849g, 3.0mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to -78 °C in dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodiphenylphosphine (0.66 mL, 3.3 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. White solid of (2-(Naphthalene-2-yl)phenyl)diphenylphosphine **CP-1** (1.05g, 90%) were obtained. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.14 (dd, *J*= 3.8Hz, 7.6Hz, 1H), 7.22-7.26 (m, 4H), 7.32-7.34 (m, 7H), 7.4-7.51 (m, 5H), 7.57 (s, 1H), 7.63 (d, *J*= 7.6Hz, 1H), 7.78 (d, *J*= 8.2Hz, 1H), 7.86 (d, *J*= 8.2Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 125.8 (d, *J*= 10.0Hz), 126.8, 127.3, 127.4, 127.8, 127.9 (d, *J*= 2.3Hz), 128.2, 128.3, 128.4, 128.6,

130 (d, *J*= 5.0Hz), 132.5 (d, *J*= 29.0Hz), 133.6, 133.8, 134.1, 137.6, 137.7, 139.2, 148.1 (d, *J*= 27.0Hz); ^{31}P NMR (162 MHz, CD_2Cl_2) δ -13.70; MS (EI): *m/z* (relative intensity) 387.3 (M^+, 100), 309.2 (5), 233.2 (16).

(2-(Naphthalene-2-yl)phenyl)dicyclohexylphosphine, **CP-2**

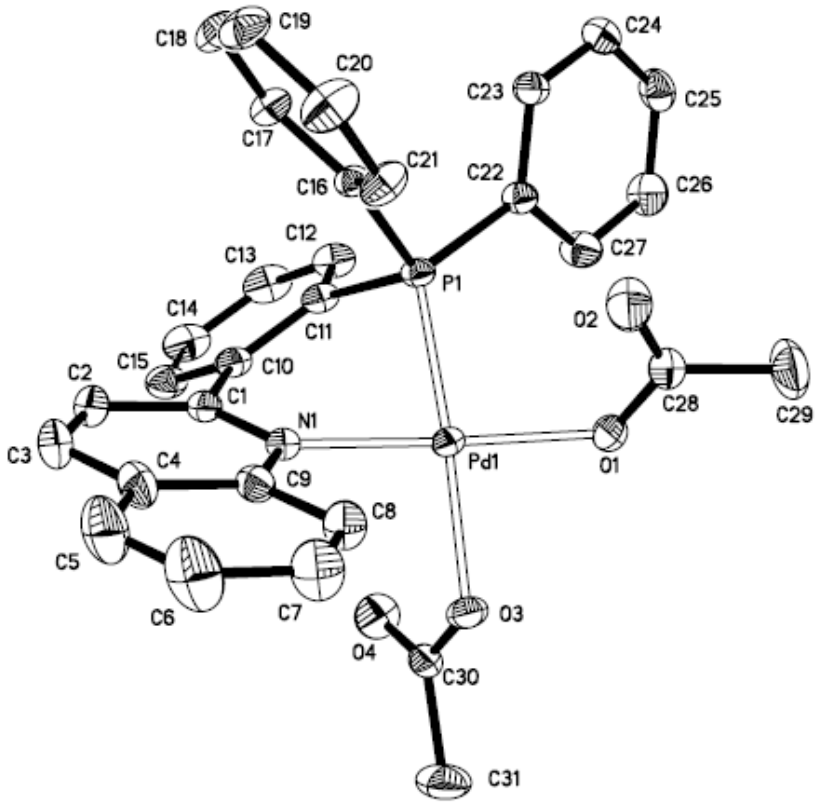


2-(2-Bromophenyl)naphthalene (0.849g, 3.0mmol) was dissolved in freshly distilled THF (20 mL) at room temperature under a nitrogen atmosphere. The solution was cooled to -78°C in dry ice/acetone bath. Titrated *n*-BuLi (3.3 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 min at -78 °C, chlorodicyclohexylphosphine (0.72mL, 3.3 mmol) in THF (5 mL) was added. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washed with cold MeOH/EtOH mixture. The product was then dried under vacuum. White solid of (2-(Naphthalene-2-yl)phenyl)dicyclohexylphosphine **CP-2** (0.90g, 75%) were obtained. Melting point. 128.6-129.8 °C;^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.07-1.34 (m, 10H), 1.56-1.72 (m, 10H), 1.90 (t, *J*= 11.4Hz, 2H), 7.39-7.46 (m, 3H), 7,49-7.55 (m, 3H), 7.69-7.71 (m, 1H), 7.76 (s, 1H), 7.86-7.93 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 26.4, 27.1 (d, *J*= 4.0Hz), 27.2, 29.4 (d, *J*= 9.3Hz), 30.6 (d, *J*= 17.5Hz), 34.9 (d, *J*= 17.4Hz), 125.8 (d, *J*= 21.9Hz), 126.2, 126.6, 127.7 (d, *J*= 33.0Hz), 128.2, 129.0

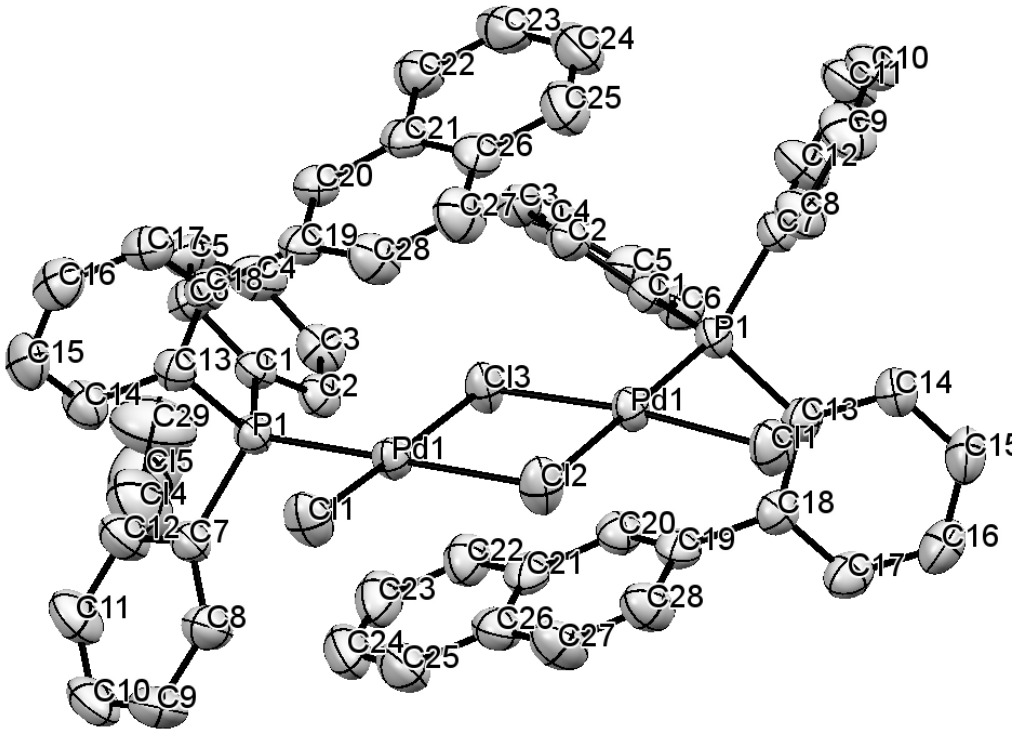
(d, *J*= 3.0Hz), 129.6 (d, *J*= 4.9Hz), 130.2 (d, *J*= 4.9Hz), 132.1, 132.9, 133.0 (d, *J*= 4.0Hz), 134.5 (d, *J*= 22.9Hz), 140.8 (d, *J*= 7.1Hz), 150.4 (d, *J*= 30.3Hz); ^{31}P NMR (162 MHz, CD_2Cl_2) δ -13.08; MS (EI): *m/z* (relative intensity) 399.4 (M^+, 100), 317.3 (60), 233.2 (87), 202.2 (16). HRMS: calcd. for C28H34P+: 401.2398, found 401.2395.

3.4.3 Crystalline structure of Pd-monophsophine complex

3.4.3.1 Crsyalline structure of Pd-quinolinylphosphine (NP-1)



3.4.3.2 Crystalline structure of Pd-nahthylphosphine (CP-1)

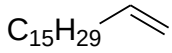


*3.4.4 General procedure for the Pd-naphthalylphosphine (**CP-1**) catalyzed decarbonylation of carboxylic acids*

An array of Schlenk tubes were charged with magnetic stirrer bar (4 mm x 10 mm) and were evacuated and backfilled with nitrogen (3 cycles). The Schlenk tubes were charged with $Pd(COD)Cl_2$ (3 mol%, 0.0043g), **CP-1** (9 mol%, 0.017g) and evacuated and backfilled with nitrogen (3 cycles). 1mL DMAc was added by syringe and then allowed to stirr for 1 minute. The Schlenk tubes were then added with carboxylic acids substrates (0.5 mmol), benzoic anhydride (1 mmol) and DIPEA (0.5 mmol). This batch of Schlenk tube was resealed and magnetically stirred in a preheated 140 ^oC oil bath for 6 h. The reactions were allowed to reach room temperature. Ethyl acetate (~4 mL), dodecane (113 μL, internal standard) and water (~2 mL) were added. The organic layer was subjected to GC analysis. The GC yield was previously calibrated by authentic sample/dodecane. .

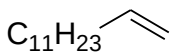
3.4.4 Characterization data of alpha olefins

(*Z*)-Heptadeca-1,8-diene (Table 3.6, **2a**)



Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*= 7.9Hz, 3H), 1.28-1.39 (m, 18H), 2.03-2.06 (m, 6H), 4.92-5.02 (m, 2H), 5,34-5.37 (m, 2H), 5.76-5.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 27.1, 27.2, 28.7, 28.8, 29.3, 29.5, 29.6, 29.7, 31.9, 32.4, 33.7, 114.1, 129.7, 129.9, 139.0; MS (EI): *m/z* (relative intensity) 236.4 (M^+, 20), 138.2 (11), 124.2 (22), 109.2 (36), 96.2 (96), 81.2 (100), 67.2 (97), 55.2 (98).

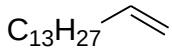
1-Tridecene (Table 3.6, **2b**)



Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*= 7.9Hz, 3H), 1.27 (s, 18H), 2.05 (q, *J*= 7.9Hz, 3H), 4.93 (d, *J*= 10.7Hz, 1H), 5.00 (dd, *J*= 1.8Hz, 17.6Hz, 1H), 5.77-5.87 (m, 1H); ^{13}C NMR (100

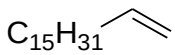
MHz, $CDCl_3$) δ 14.1, 22.7, 28.9, 29.2, 29.3, 29.5, 29.66, 29.68, 29.7, 31.9, 33.8, 114.0, 139.2; MS (EI): *m/z* (relative intensity) 182.4 (M^+, 9), 125.3 (10), 111.3 (35), 97.2 (80), 83.2 (96), 69.2 (95), 55.2 (100).

1-Pentadecene (Table 3.6, **2c**)



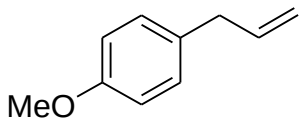
Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*= 7.0Hz, 3H), 1.27 (s, 22H), 2.05 (q, *J*= 7.4Hz, 3H), 4.92 (d, *J*= 10.0Hz, 1H), 5.01 (dd, *J*= 1.9Hz, 17.7Hz, 1H), 5.78-5.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9, 33.8, 114.0, 139.2; MS (EI): *m/z* (relative intensity) 210.4 (M^+, 7), 182.4 (5), 140.3 (7), 125.3 (17), 111.3 (46), 97.2 (95), 83.2 (100), 69.2 (87), 55.2 (93).

1-Heptadecene (Table 3.6, **2d**)



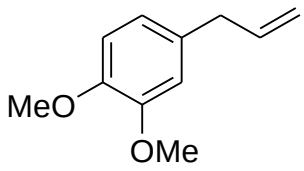
Eluents (Hexane, R_f= 0.7) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J*= 7.2Hz, 3H), 1.27 (s, 24H), 2.05 (q, *J*= 7.0Hz, 3H), 4.93 (d, *J*= 10.0Hz, 1H), 5.01 (dd, *J*= 1.9Hz, 17.1Hz, 1H), 5.77-5.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9, 33.8, 114.0, 139.2; MS (EI): *m/z* (relative intensity) 238.5 (M^+, 7), 210.4 (5), 125.3 (28), 111.3 (57), 97.2 (100), 83.2 (98), 69.2 (78), 55.2 (85).

1-Allyl-4-methoxybenzene (Table 3.6, **2e**)



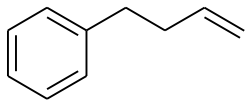
Eluents (Hexane: ethyl acetate 10:1, R_f= 0.6) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (d, *J*= 6.6Hz, 2H), 3.79 (s, 4H), 5.04-5.0 (m, 2H), 5.91-6.01 (m, 1H), 6.85 (d, *J*= 8.6Hz, 2H), 7.11 (d, *J*= 8.5Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.3, 55.2, 113.8, 115.3, 129.4, 132.0, 137.8, 157.9; MS (EI): *m/z* (relative intensity) 148.2 (M^+, 100), 133.1 (23), 121.1 (38), 105.1 (21), 91.1 (21), 77.1 (23).

1-Allyl-3,4-dimethoxybenzene (Table 3.6, **2f**)



Eluents (Hexane: ethyl acetate 10:1, R_f= 0.3) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (d, *J*= 6.6Hz, 2H), 3.85 (s, 3H), 3.86 (s, 3H), 5.05-5.10 (m, 2H), 5.91-5.99 (m, 1H), 6.72 (d, *J*= 7.6Hz, 2H), 6.78-6.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.7, 55.7, 55.8, 111.2, 111.8, 115.5, 120.3, 134.4, 137.6, 147.3, 148.8; MS (EI): *m/z* (relative intensity) 178.2 (M^+, 100), 163.1 (30), 147.1 (30), 103.1 (25), 91.1 (25), 77.1 (20).

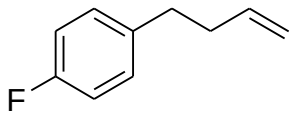
4-Phenyl-1-butene (Table 3.6, **2g**)



Eluents (Hexane, R_f= 0.6) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (q, *J*= 7.6Hz, 2H), 2.73 (t, *J*= 7.6Hz, 2H), 4.99 (d, *J*= 10.2Hz, 1H), 5.06 (dd, *J*= 1.8Hz, 17.3Hz, 1H), 5.83-5.93 (m, 1H), 7.20-7.22 (m, 3H),

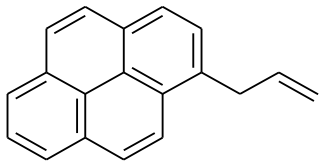
7.28-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3, 35.4, 114.8, 125.7, 128.2, 128.4, 138.0, 141.8; MS (EI): *m/z* (relative intensity) 132.1 (M^+, 20), 91.1 (100).

4-(4-Fluorophenyl)-1-butene (Table 3.6, **2h**)



Eluents (Hexane, R_f= 0.5) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (q, *J*= 7.4Hz, 2H), 2.68 (t, *J*= 7.7Hz, 2H), 4.97-5.05 (m, 2H), 5.78-5.88 (m, 1H), 6.96 (t, *J*= 8.6Hz, 2H), 7.11-7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.5, 35.5, 114.8, 115.0 (d, J= 4.3Hz), 129.6 (d, *J*= 7.9Hz), 137.3 (d, *J*= 3.0Hz), 137.7, 161.2 (d, *J*= 243.0Hz); MS (EI): *m/z* (relative intensity) 150.2 (M^+, 14), 109.2 (100), 83.2 (7).

1-Allyl-pyrene (Table 3.6, **2i**)



Eluents (Hexane, R_f= 0.5) was used for flash column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (d, *J*= 6.6Hz, 2H) 5.17-5.27 (m, 2H), 6.26-6.36 (m, 1H), 7.92 (d, *J*= 7.5Hz, 1H), 8.03-8.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.5, 116.0, 123.4, 124.7, 124.8, 124.9, 125.6, 126.6, 127.1, 127.2, 127.35, 127.38, 128.8, 129.9, 130.7, 131.2, 133.7, 137.2; MS (EI): *m/z* (relative intensity) 242.2 (M^+, 100), 227.2(29), 215.2 (33), 119.9 (20).

3.5 References

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[48] Jana O.; Ladislava M.; Jarmila V. A.; Robert V.; Jiri M. *Int. J. Mol. Sci.* **2015**, *16*, 12871-12890.

[49] Le Nôtre J.; Scott E. L.; Franssen M. C. R.; Sanders J. P. M. *Tetrahedron Lett.* **2010**, *51*, 3712−3715.

[50] Franke R.; Selent D.; Börner A. *Chem. Rev.* **2012**, *112*, 5675-5732.

[51] Listed prices for odd-numbered alkenes from Sigma-Aldrich: 1-Tridecene, USD$146.50 for T57703-5G, ≥96%; 1-Pentadecene, USD$127.00 for 222887-5ML, ≥98%; 1-Hexadecene, USD$292.00 for H2131-100ML, ≥99%.

[52] Koeduka T. *Plant Biotechnol* **2014**, *31*, 401-407.

Chapter 4 Ruthenium-(2-aminobenzyl alcohol) Catalyzed Transfer Hydrogenation of Ketones using Glycerol as H_2 Surrogate

4.1 Introduction

Transfer hydrogenation (TH) [53] continues to be a key reaction of interest for the fine chemical and pharmaceutical industries since it provides a safe and milder alternative tool to hydrogenate multiple bonds using flammable hydrogen gas (H_2) and low infrastructure cost as high-pressure reactors is needed for classic hydrogenation. Thus, extensive studies have been done on finding H_2 surrogate, ruthenium (Ru)[54], osmium (Os)[55], rhodium (Rh)[56], iridium (Ir)[57] and iron (Fe)[58] were reported to catalyze transfer hydrogenation of various bonds such as C=O, C=N, N=O and C=C bonds using isopropanol and formic acid as hydrogen source. Different ruthenium(II) complexes with diamines[59], amino alcohols[60] as well as N,P ligands[61] were synthesized and explored their application. In terms of good product yield and selectivity, ruthenium(II) complexes with diphosphines/diamines, amino alcohol ligands have drawn much attention for the catalytic transfer hydrogenation (TH). (Figure4.1)

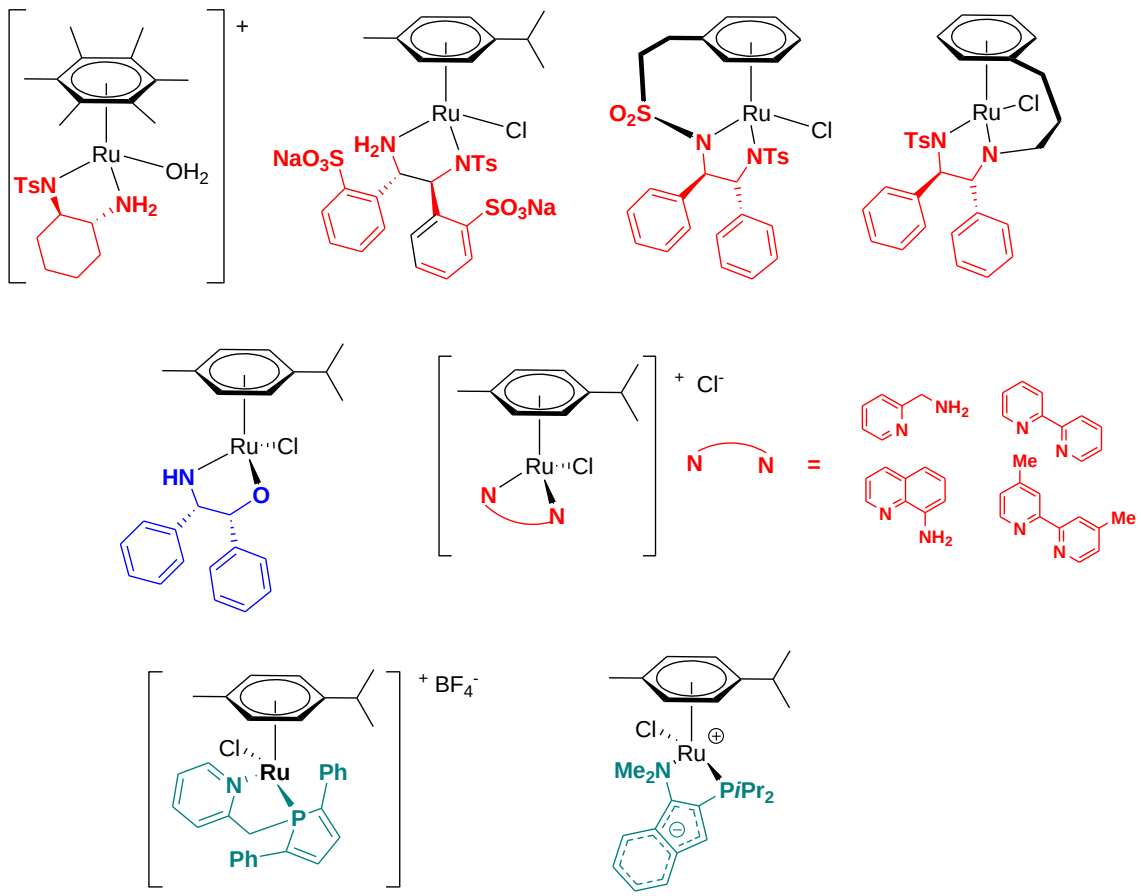
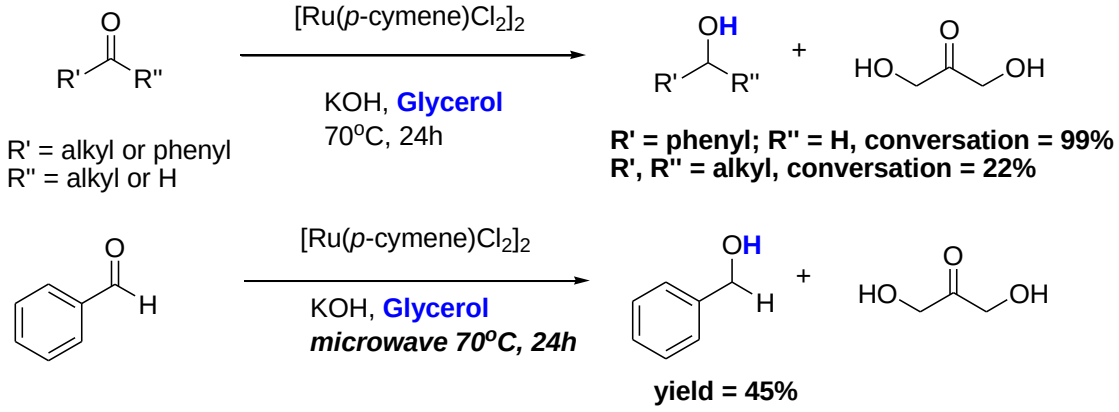


Figure 4.1: Selected examples of ruthenium(II) complexes for the catalytic transfer hydrogenation reactions.

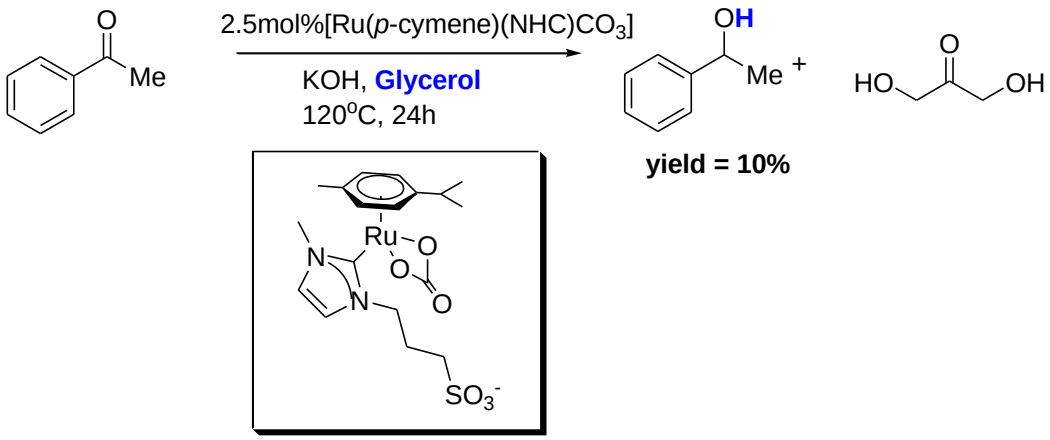
In recent decade frontiers of TH catalysis has been expended to renewable and inexpensive hydrogen source. To meet criterion of green solvent as well as the role of hydrogen source, glycerol is a promising candidate due to (1) its low cost and easily accessible as byproduct from biodiesel production and (2) its physical and solvation properties (high dielectric constant, high boiling point and good solvation to metal complexes).[62] Furthermore glycerol is non-toxic and biodegradable that makes it as attractive H_2 surrogate for industrial application. Several catalytic systems have been

reported on the catalytic transfer hydrogenation using glycerol as hydrogen source.[2e, 6c, 63] In 2009, Wolfson first demonstrated using glycerol as solvent and hydrogen source for the transfer hydrogenation of benzaldehyde and 2-Octanone. With the use of ~1.3mol% [Ru(*p*-cymene)Cl_2]$_2$ and addition of KOH as base, 99% conversion of benzaldehyde was achieved. Later they reported microwave assisted ruthenium-catalyzed transfer hydrogenation of benzaldehyde in glycerol and 48% yield of benzyl alcohol obtained. (Scheme 4.1)



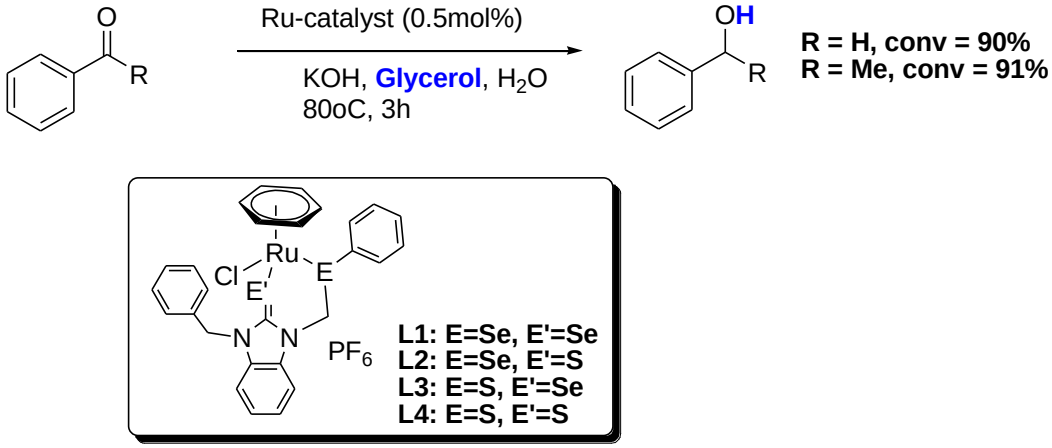
Scheme 4.1: Catalytic transfer hydrogenation of aldehydes and ketones reported by Wolfson *et al*.

Inspiring by pioneer works of Wolfson, different ruthenium catalysts were developed to enhance the productivity of transfer hydrogenation reactions using glycerol as hydrogen source. Peris *et al.* employed ruthenium-carbene catalyst [Ru(*p*-cymene)(NHC)CO_3] to catalyze transfer hydrogenation of acetophenone in glycerol however very low yield (10% after 24hours) of 1-phenylethanol was observed. (Scheme 4.2)



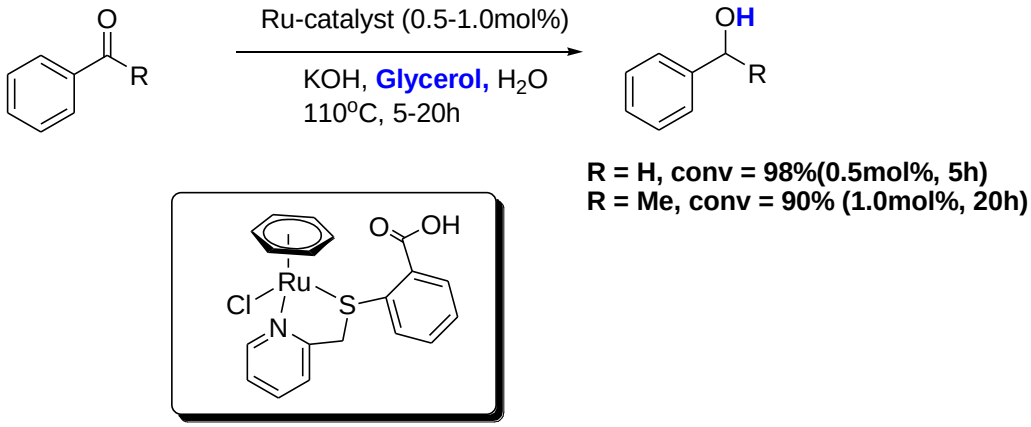
Scheme 4.2: Ru(*p*-cymene)(NHC)CO_3 catalyzed transfer hydrogenation of acetophenone reported by Peris *et al*.

In 2014 Singh *et al.* reported two Ru-catalysts that could be employed to highly converted benzaldehyde and acetophenone. (Scheme 4.3)



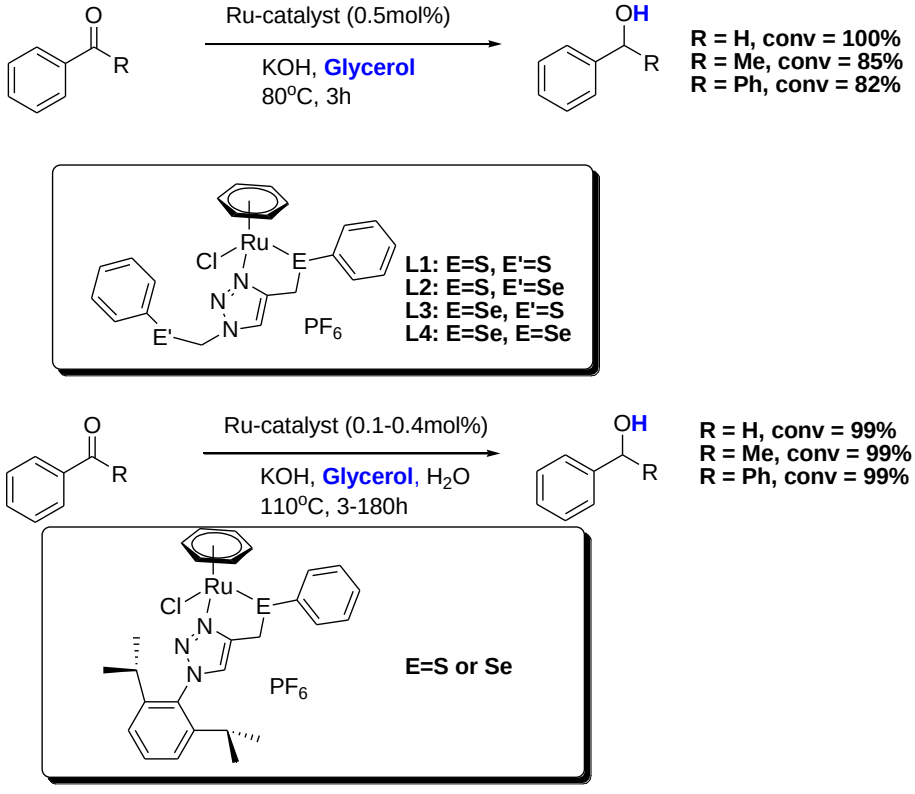
Scheme 4.3: Ruthenium (II)-chalcogen complexes catalyzed transfer hydrogenation of benaldehyde and acetophenone reported by Singh *et al*.

With the use of 0.5mol% ruthenium(II)-bidentate chalcogen complex, 90% benzaldehyde and 91% acetophenone were converted to benzyl alcohol and 1-phenylehtanol respectively. Besides, 0.5mol% ruthenium-(phenylthio)methyl-2-pyridine catalyst was reported by Singh *et al.* to catalyze the transfer hydrogenation of aldehydes and ketones using glycerol in water with good conversion. (Scheme 4.4)



Scheme 4.4: Ruthenium-(phenylthio)methyl-2-pyridine complex catalyzed transfer hydrogenation of benzaldehyde and acetophenone reported by Singh *et al*.

To improve the conversion and shorten reaction time, Singh's research group developed ruthenium (II) complexes with 1,2,3-triazole based organosulfur/selenium ligands to catalyze transfer hydrogenation of aldehydes and ketones and up to ~100% conversion was reported. (Scheme 4.5)



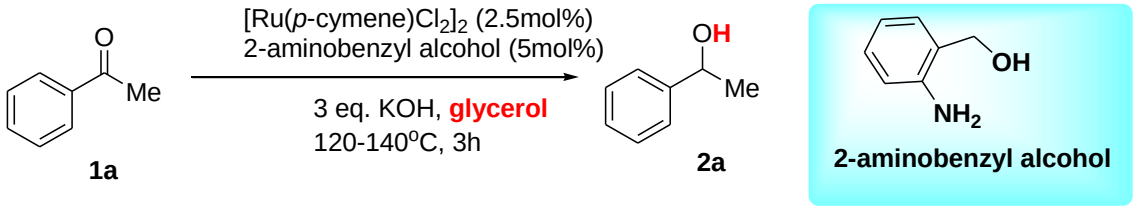
Scheme 4.5: Ruthenium(II)-1,2,3-triazole based organosulfur/selenium

complexes catalyzed transfer hydrogenation of aldehydes and ketones reported by Singh *et al*.

In recent decades extensive studies were done on exploring Ru-catalysts to catalyze transfer hydrogenation of aldehydes and ketones however tailor-made N,N, N,S, N,Se S,S as well as S,Se ligands were reported and those ligands often involve tedious synthetic steps thus retards their real industrial application .Hence combination of inexpensive ruthenium metals with commercial available ligands to catalyze transfer hydrogenation reactions is in great interests. While commercial diamine ligands were extensive studied and applied towards catalytic transfer hydrogenation, amino alcohols were rare studied comparatively.[64] Therefore I would like to explore the uses of inexpensive commercial available amino alcohol as ligand towards catalytic transfer hydrogenation reactions.

4.2 Results and discussion

4.2.1 Preliminary evaluation of ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of ketones



Entry	Solvent (mL)	Co-solvent (mL)	Temp,°C	GC yield, %[b]	Conversion, %[c]
1	Glycerol (0.5)	--	120	n.r.[d]	
2	Glycerol (0.5)	--	120	40	62
3	Glycerol (1)	--	120	35	63
4	Glycerol (0.5)	--	120[e]	52	91
5	Glycerol (0.5)	--	140	53	95
6	Glycerol (0.5)	--	80[f]	7	9
7	Glycerol (0.1)	NMP (0.5)	120	25	95
8	Glycerol (0.5)	NMP (0.5)	120	37	93
9	Glycerol (1)	NMP (0.5)	120	39	91
10	Glycerol (0.5)	Diglyme[g]	120	26	65
11	Glycerol (0.5)	CPME[g]	120	32	64
12	Glycerol (0.5)	1-Butanol (0.5)	120	37	61
13	Glycerol (0.5)	H_2O (0.5)	120	n.r.	
14	Glycerol (0.5)	NMP:H_2O,1:1 (0.5)	120	n.r.	
15	NMP[g] (0.5)	--	120	n.r.	

[a] Reaction conditions: Acetophenone (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%), 2-aminobenzyl alcohol (5mol%), KOH (3mmol), glycerol (0.1-1mL), co-solvent (0.5mL), 120-140°C, 3hours.
[b] GC yield calculated using anisole as internal standard.
[c] Conversion determined by GC-FID.
[d] n.r. = no reaction.
[e] Reaction time = 6hours.
[f] Reaction time = 18hours.
[g] Diglyme = Bis(2-methoxyethyl) ether; CPME = Cyclopentyl methyl ether; NMP = *N*-Methyl-2-pyrrolidone.

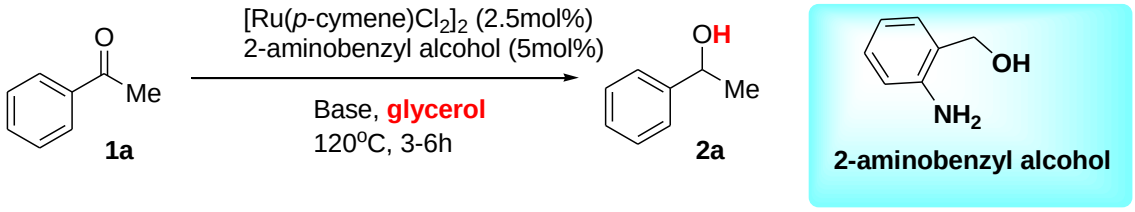
Table 4.1: Solvent screening for ruthenium-(2-aminobenzyl alcohol) catalyzed

transfer hydrogenation of acetophenone

With the use of 2.5mol% [Ru(*p*-cymene)Cl_2]$_2$, 5mol% 2-aminobenzyl alcohol together with 3 equivalent of potassium hydroxide as base, 40% 1-phenylethanol was obtained within 3hours. (Table 4.1, entry2) Without Ru-catalyst, no 1-phenylethanol was detected. (Table 4.1, entry1) Increasing the amount of glycerol could not enhance the product yield apparently (35% yield, 63% conversion). (Table 4.1, entry 3) Trace amount of product was obtained when reaction temperature was lowered to 80^{o}C (7% yield, 9% conversion). (Table 4.1, entry 5) Increasing the reaction temperature to 140^{o}C could fasten the reaction rate (53% yield, 95% conversion) however similar product yield could be obtained by prolonging reaction time to 6 hours (52% yield, 91% conversion). (Table 4.1, entries 4 and 5)

To study co-solvent effect of the reaction, different solvents were added as co-solvent, *N*-Methyl-2-pyrrolidone was found to be best co-solvent in terms of conversion however the co-solvent could not enhance the product yield of 1-phenylethanol. (Table 4.1, entries 7-9) Furthermore green solvents such as cyclopentyl methyl ether (CPME) and 1-butanol were also screened however no improvement of product yields were observed. (Table 4.1, entries 10-12) Meanwhile our catalytic system could not work in aqueous medium. (Table 4.1, entries 13 and 14) Therefore the catalytic transfer hydrogenation was performed under neat condition

onwards. Without the addition of glycerol, no transfer hydrogenated product was observed and it suggested that glycerol is the hydrogen source for the transfer hydrogenation reaction. (Table 4.1, entry 15)



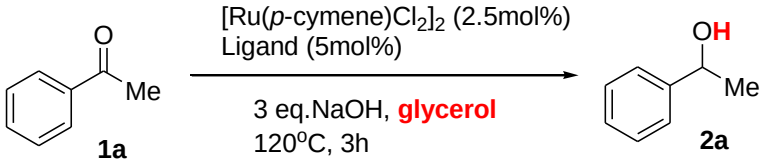
Entry	Base (equiv.)	Time, hrs	GC yield, %[b]	Conversion, %[c]
1	--	3	n.r.	
2	KOH (0.5)	3	24	46
3	KOH (1)	3	31	65
4	KOH (3)	3	48	70
5	KOH (5)	3	28	69
6	NaOH (3)	3	43	60
7	NaO*t*Bu (3)	3	26	55
8	KO*t*Bu (3)	3	24	46
9	KOH (3)	6	52	91
10	NaOH (3)	6	64	88

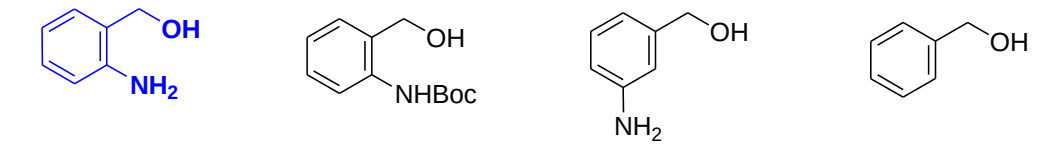
[a] Reaction conditions: Acetophenone (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%), 2-aminobenzyl alcohol (5mol%), Base (0.5-3mmol), glycerol (0.5mL), 120^{o}C, 3-18hours.
[b] GC yield calculated using anisole as internal standard.
[c] Conversion determined by GC-FID.

Table 4.2: Base screening for ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of acetophenone

After solvent screening, different amount of base were tested to investigate its effect on the transfer hydrogenation reaction. No hydrogenated product was obtained without the addition of potassium hydroxide. (Table 4.2, entry 1) And 3 equivalent of

base was found to be sufficient to give 48% 1-phenylethanol in 3 hours. (Table 4.2, entries 2-5) Then different kinds of bases were screened and sodium hydroxide and potassium hydroxide gave superior result over others. And highest yield of 1-phenylethanol was obtained (64% yield, 88% conversion) by adding 3 equivalent of sodium hydroxide and prolonged reaction time to 6 hours. (Table 4.2, entry 11)



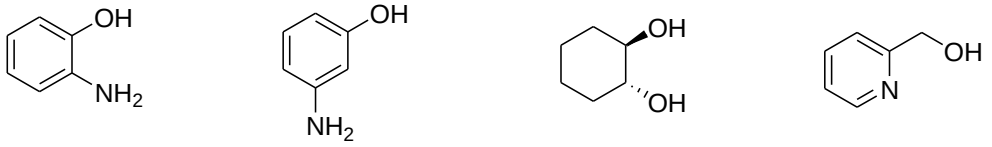


L1
50% (68%)
40% (59%)[d]

L2
31% (47%)

L3
30% (35%)

L4
7% (8%)



L5
41% (53%)

L6
38% (83%)

L7
23% (28%)

L8
30% (32%)

[a] Reaction conditions: Acetophenone (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%), 2-aminobenzyl alcohol (5mol%), NaOH (3mmol), glycerol (0.5mL), 120°C, 3hours.
[b] GC yield calculated using anisole as internal standard.
[c] Conversion reported in parenthesis, determined by GC-FID.
[d] 1.25mol% [Ru(*p*-cymene)Cl_2]$_2$ employed.

Table 4.3: Ligand screening for ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of acetophenone

Then we examined different commercial available amino alcohol to investigate their effect on the transfer hydrogenation. (**L1-L8**) The catalytic activities of

aminobenzyl alcohol (**L1-L3**), aminophenol (**L5, L6**) and cyclohexandiol (**L7**) were compared and 2-aminobenzyl alcohol (**L1**) gave superior results (50% yield, 68% conversion). Free NH_2 moiety on the ligand scaffold was suggested to be crucial in the catalytic transfer hydrogenation[65] thus we compared the catalytic activities of 2-aminobenzyl alcohol (**L1**), *N*-Boc-2-aminobenzyl alcohol (**L2**), 2-pyridyl carbinol (**L8**) and benzyl alcohol (**L4**). Without the presence of NH_2 group, trace amount of product were obtained by employing benzyl alcohol (**L2)** (7% yield, 8% conversion) and 2-pyridyl carbinol **(L8)** as ligands (30% yield, 32% conversion) respectively. With *N*-Boc group substituted on the ligand, lower catalytic activity was observed compared to aminobenzyl alcohol **(L1: 50% yield, 68% conversion** vs **L2: 31% yield, 47% conversion**). The presence of free NH_2 moiety on the ligand may imply that our catalytic transfer hydrogenation may not follow the conventional mechanism (Figure4.2)

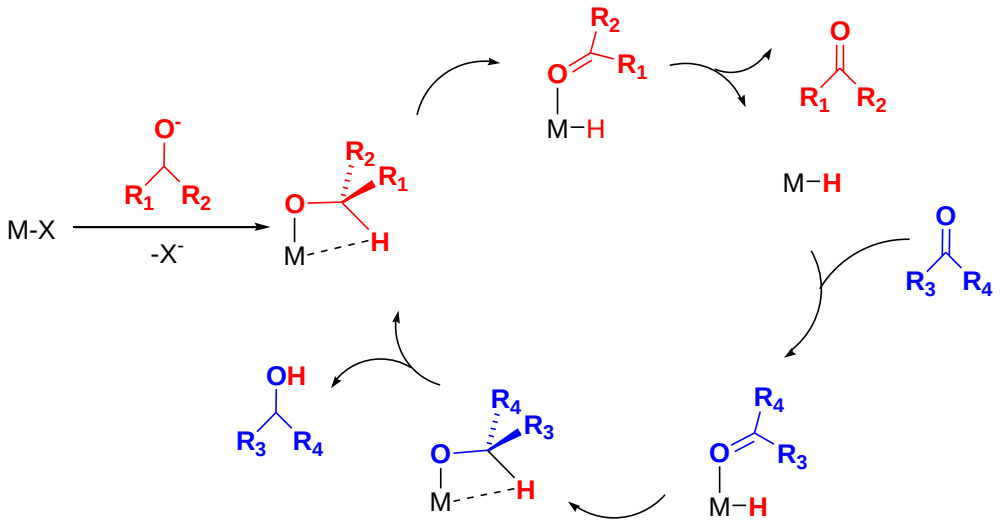


Figure 4.2: Conventional transfer hydrogenation reaction mechanism

and non-classic metal-ligand bi-functional mechanism (N-H effect) may take place instead. (Figure 4.3)

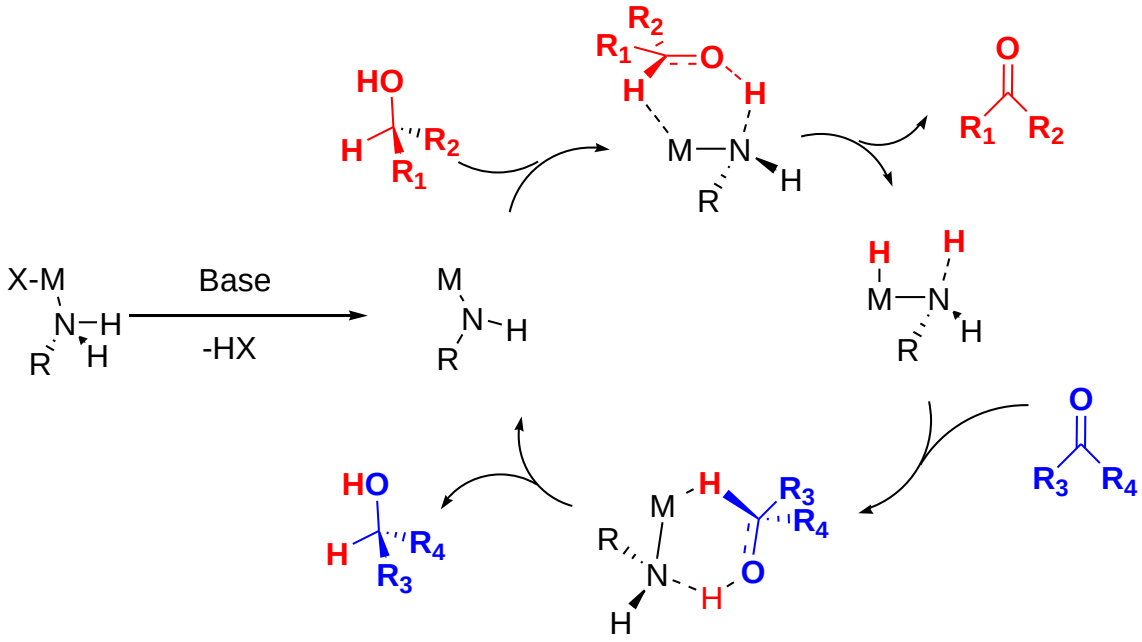
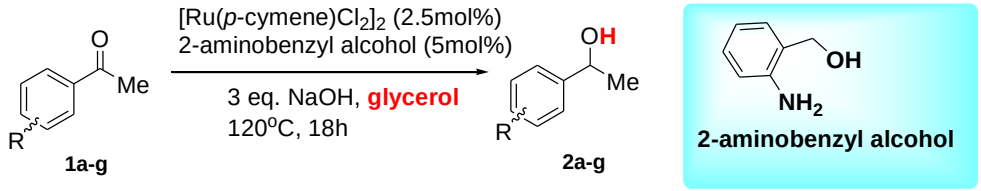
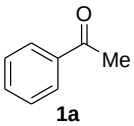
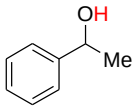
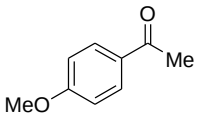
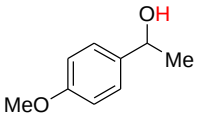
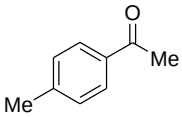
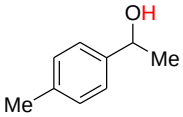
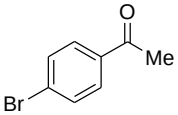
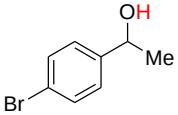
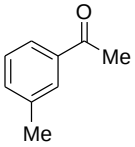
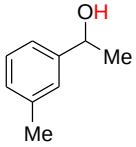
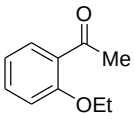
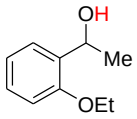
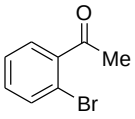
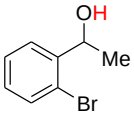


Figure 4.3: Metal-ligand bi-functional (N-H effect) transfer hydrogenation mechanism.

In addition, the position of NH_2 would affect the coordination of ligand towards metal so as to affect its catalytic activity (**L1: 50% yield, 68% conversion** vs **L3: 30% yield, 35% conversion**). Similar results were observed when we compared the catalytic activities of 2-aminophenol with 3-aminophenol (**L5: 41% yield, 53% conversion** vs **L6: 38% yield, 83% conversion**). Lower the catalyst loading showed decrease in the product yield. (1.25mol% Ru-catalyst gave 40% yield, 59% conversion in 3 hours)

4.2..2 Scope of ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of ketones



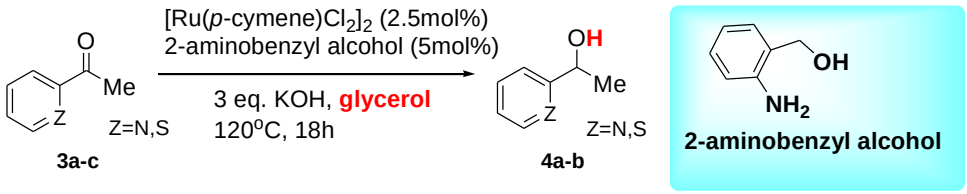
Entry	Substrate	Product	Isolated yield,%	Convresion.%[b]
1	 **1a**	 **2a**	69	89
2	 **1b**	 **2b**	70	78
3	 **1c**	 **2c**	60	68
4	 **1d**	 **2d**	35	46
5	 **1e**	 **2e**	69	82
6	 **1f**	 **2f**	78	82
7	 **1g**	 **2g**	trace	trace

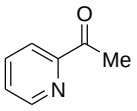
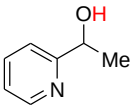
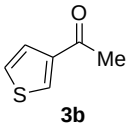
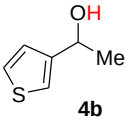
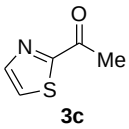
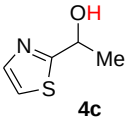
[a] Reaction conditions: Substrate (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%),

2-aminobenzyl alcohol (5mol%), NaOH (3mmol), glycerol (0.5mL), 120^{o}C, 18hours.
[b] Conversion determined by GC-FID.

Table 4.4: Ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of aryl ketones

With the optimal reaction conditions in hands, we then investigate the substrate scopes of the catalytic transfer hydrogenation reaction. Electronic effects of the substituted groups on acetophenone were studied however no apparent electronic effect on the product yield was observed and various substituted acetophenone (**1a-1e**) could be converted to corresponding substituted benzyl alcohol (**2a-2e**) smoothly in moderate yields. (Table 4.4, entries 1-5) Steric effects of the substituted acetophenone were also studied, *ortho*- substituted acetophenone (2'-ethoxyacetophenone **1f** and 2'-bromoacetophenone **1g**) were subjected to the reaction. 2'-ethoxyacetophenone could be hydrogenated to 2-ethoxybenzyl alcohol **2f** in good yield. (78% yield, 82% conversion) However trace mount of 2'-bromobenzyl alcohol **2g** obtained and it may due to the significant steric effect as bulkiness of the *ortho*-substituted group increased.

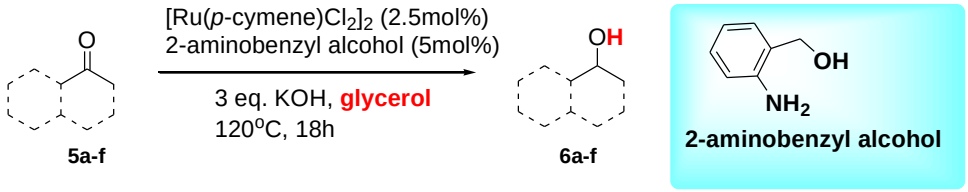


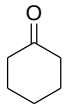
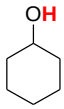
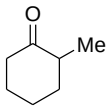
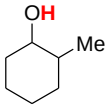
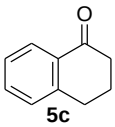
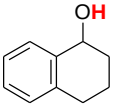
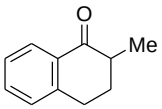
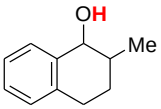
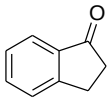
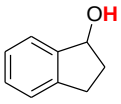
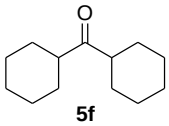
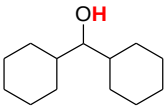
Entry	Substrate	Product	Isolated yield,%	conversion,%[b]
1	 **3a**	 **4a**	48	94
2	 **3b**	 **4b**	40	75
3	 **3c**	 **4c**	trace	trace

[a] Reaction conditions: Substrate (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%), 2-aminobenzyl alcohol (5mol%), NaOH (3mmol), glycerol (0.5mL), 120^{o}C, 18hours.
[b] Conversion determined by GC-FID.

Table 4.5: Ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of heteroaryl ketones.

We then extended the scopes to heteroaryl ketones. 2-acetylpyridine **3a**, 3-acetylthiophene **3b** and 2-acetylthiazole **3c** were subjected to the reaction. 2-acetylpyridine and 3-acetylthiophene were hydrogenated to give products in moderate yields. (Table 4.5, entries 1 and 2) However 2-acetylthiazole **3c** could not hydrogenated by our catalytic system.



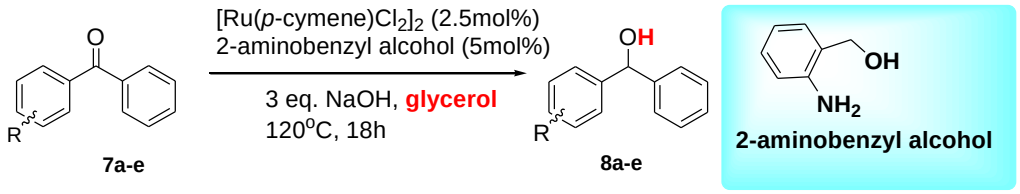
Entry	Substrate	Product	Isolated yield,%	Convresion.%[b]
1	 5a	 6a	55	90
2	 5b	 6b	48	87
3	 5c	 6c	trace	25
4	 5d	 6d	trace	trace
5	 5e	 6e	trace	56
6	 5f	 6f	trace	trace

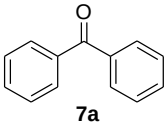
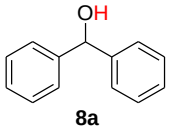
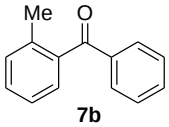
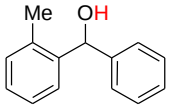
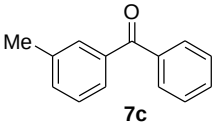
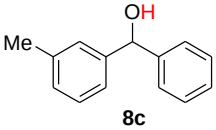
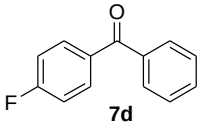
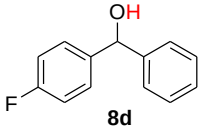
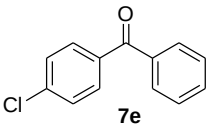
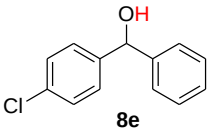
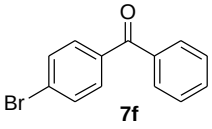
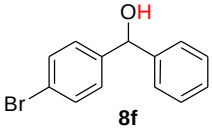
[a] Reaction conditions: Substrate (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%), 2-aminobenzyl alcohol (5mol%), NaOH (3mmol), glycerol (0.5mL), 120^{o}C, 18hours.
[b] Conversion determined by GC-FID.

Table 4.6: Ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of cyclic ketones.

Various cyclic ketones were subjected to the reaction, cyclohexanone **5a** and 2-methylcyclohexanone **5b** could be hydrogenated to cyclohexanol **6a** (55% yield, 90% conversion) and 2-methylcyclohexanol **6b** (48% yield, 87% conversion) in

moderate yields respectively. (Table 4.6, entries 1 and 2) Meanwhile 1-tetralone **5c** and 2-methyl-1-tetalone **5d** could not be hydrogenated to desired products. (Table 4.6, entries 3 and 4) and 1-indanone was converted to 1-indanol in trace amount. (Table 4.6, entry 5) Dicyclohexanyl ketone could not converted to desired products by our catalytic system. (Table 4.6, entry 6)



Entry	Substrate	Product	Isolated yield,%	Convresion.%[b]
1	 7a	 8a	70	80
2	 7b	 8b	46	51
3	 7c	 8c	65	70
4	 7d	 8d	50	77
5	 7e	 8e	63	79
6	 7f	 8f	55	71

[a] Reaction conditions: Substrate (1mmol), [Ru(*p*-cymene)Cl_2]$_2$ (2.5mol%), 2-aminobenzyl alcohol (5mol%), NaOH (3mmol), glycerol (0.5mL), 120^{o}C, 18hours.
[b] Conversion determined by GC-FID.

Table 4.7: Ruthenium-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of diaryl ketones.

Apart from acetophenone we further extend the scopes to catalyze transfer hydrogenation of benzophenone. No significant electronic effect was observed and various kinds of benzophenones with different electronic properties substituted groups **7a**, **7c**-**7f**) were converted to corresponding substituted benzhydrols in moderate to good yields. (Table 4.7, entries 1, 3-6) However steric effect was observed on 2-methylbenzophenone **7b**, with its *ortho*-position substituted by methyl group, both conversion and product yield dropped (46% yield, 51% conversion) when compared to benzophenone. (Table 4.7, entry 2)

4.3 Conclusion

In conclusion we have demonstrated inexpensive commercial available 2-aminobenzyl alcohol could be ligand to catalyze transfer hydrogenation of ketones using glycerol as solvent and hydrogen source. By using 2.5mol% $[Ru(p\text{-cymene})Cl_2]_2$ and 2-aminobenzyl alcohol (**L1**) (metal:ligand = 1:2), various kinds of aryl ketones, heteroaryl ketones, cyclic ketones and diaryl ketones were converted to desired alcohols in moderate to good yields. It is noteworthy that heteroaryl ketones, 2-caetylpyridine and 3-acetylthiophene were firstly reported to be hydrogenated by using glycerol as hydrogen source. This exploration of inexpensive ruthenium-amino alcohol catalytic system increased the feasibility of real industrial application of catalytic transfer hydrogenation of ketones by using glycerol that is an inexpensive by-product from bio-refinery process.

4.4 Experimental section

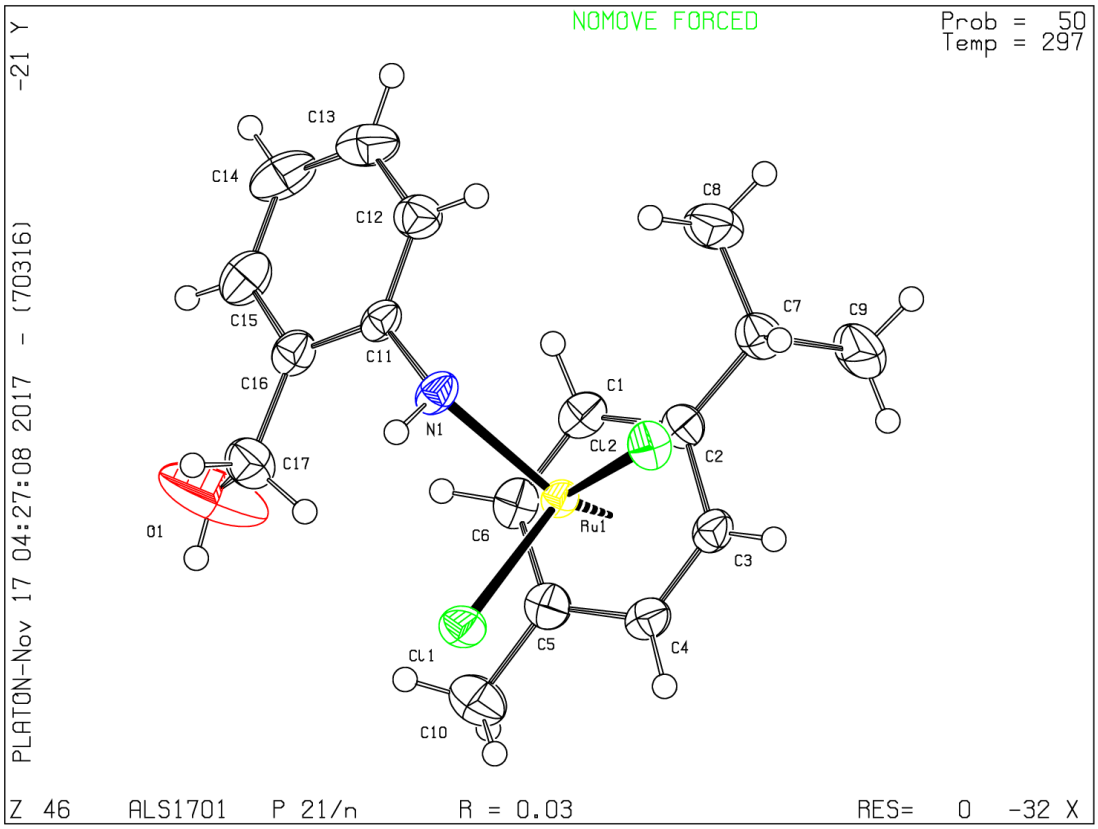
4.4.1 General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. All transfer hydrogenation reactions were performed in 8mL glass vials in the presence of Teflon-coated magnetic stirrer bar (4 mm 10 mm). . Aminobenzyl alcohol and its derivatives, benzyl alcohol, aminophenol and its derivatives, cyclohexanol and 2-pyridyl carbinol **L1**-**L8** were purchased from commercial suppliers. NMR spectra were recorded on a Brüker spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P). Spectra were referenced internally to the residual proton resonance in CDCl3 (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Mass spectra (EI-MS and ES-MS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FTICR mass spectrometer (ESI-MS). GC-MS analysis was conducted on a HP 5973 GCD system using a HP5MS column (30 m × 0.25 mm). The products described in GC yield were accorded to the authentic samples/dodecane calibration standard from HP 6890 GC-FID system. X-ray crystal structure was determined by Bruker D8 Venture.

Compounds described in the literature were characterized by comparison of their ^{1}H and/or ^{13}C NMR spectra to the previously reported data. The procedures in this section are representative, and thus the yields may differ from those reported in tables.

4.4.2 Crystalline structure of Ruthenium-(2-aminobenzyl alcohol) complex

$C_{17}H_{22}Cl_2NORu$

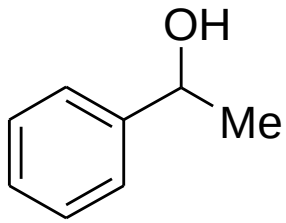


4.4.3 General procedure for the Ru-(2-aminobenzyl alcohol) catalyzed transfer hydrogenation of ketones

A batch of 8mL glass vials were charged with magnetic stirrer bar (4 mm x 10 mm) and [Ru(*p*-cymene)Cl_2]$_2$ (2.5 mol%, 0.015g), 2-aminobenzyl alcohol **L1** (5 mol%, 0.006g), NaOH (3mmol, 0.12g), 0.5mL glycerol and substrate (1mmol) were to the vials. This batch of vials was resealed and magnetically stirred in a preheated 120 ^oC oil bath for 6-18 h. The reactions were allowed to reach room temperature. During the optimization of reaction conditions, diethyl ether (~4 mL), anisole (100 μL, internal standard) and water (~2 mL) were added after reaction mixture was cooled to room temperature. And the organic layer was subjected to GC analysis, the GC yield was previously calibrated by authentic sample/anisole. After completion of the reaction, the reaction mixture was cooled to room temperature. The mixture was extracted with diethyl ether (3 × 4mL), and the solvent was removed on a rotary evaporator. The resulting semisolid extract was passed through a short column (~8 cm in length) of silica gel. The column was washed with ~50 mL of diethyl ether. All the eluates from the column were collected and the solvent from the mixture was evaporated off on a rotary evaporator. The resulting residue was subjected to 1H NMR. The final conversions are reported as an average of two runs of each catalytic reaction.

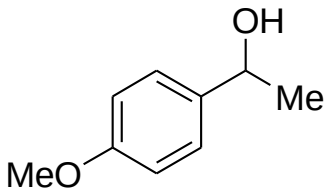
4.4.4 Characterization data of alcohols

1-phenylethanol (Table 4.4, **2a**)



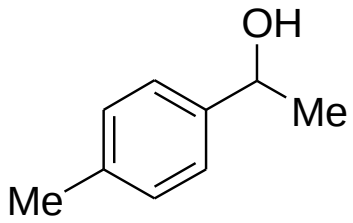
^{1}H NMR (400 MHz, $CDCl_3$ *J*= Hz) δ: 1.50 (d, *J* = 6.5 Hz, 3 H), 4.90 (q, *J* = 6.5 Hz, 1 H), 7.25–7.37 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): d = 25.0, 70.2, 125.3, 127.3, 128.4, 145.7.

1-(4-Methoxyphenyl)ethanol (Table 4.4, **2b**)



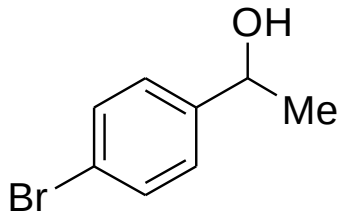
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.45 (d, *J* = 6.5 Hz, 3 H), 3.78 (s, 3 H), 4.82 (q, *J* = 6.3 Hz, 1 H), 6.86 (d, *J*= 8.6 Hz, 2 H), 7.27 (d, *J*= 8.7, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.0, 55.2, 69.8, 113.8, 126.6, 138.0, 158.9.

1-(4-Methylphenyl)ethanol e (Table 4.4, **2c**)



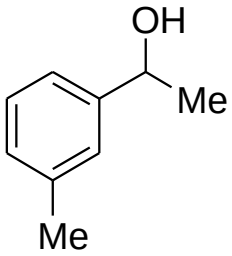
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.48 (d, *J* = 6.8 Hz, 3 H), 2.34 (s, 3 H), 4.87 (q, *J* = 6.4 Hz, 1 H), 7.15 (d, *J*= 7.7 Hz, 2 H), 7.26 (d, *J*= 7.7 Hz,2 H); ^{13}C NMR (100 MHz, CDCl3) δ: 21.0, 25.0, 70.2, 125.3, 129.1, 137.0, 142.9.

1-(4-Bromophenyl)ethanol (Table 4.4, **2d**)



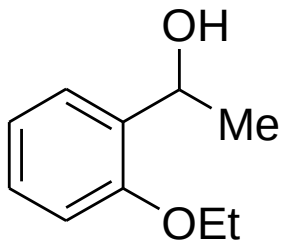
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.44 (d, *J* = 6.2 Hz, 3 H), 4.83 (q, *J* = 6.34 Hz, 1 H), 7.23 (d, *J*= 8.3 Hz, 2 H), 7.43 (d, *J*= 8.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.1, 69.5, 127.0, 131.4, 135.6, 144.7.

1-(3-Methylphenyl)ethanol (Table 4.4, **2e**)



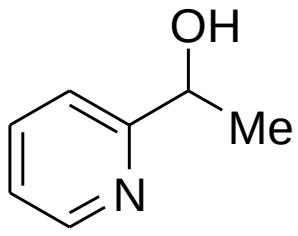
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.48 (d, *J* = 6.3 Hz, 3 H), 4.85 (q, *J* = 6.4 Hz, 1 H), 7.09 (d, *J* =7.3 Hz, 1 H), 7.15-7.19 (m, 2H), 7.22-7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.3, 25.0, 70.3, 122.3, 126.0, 128.1,128.3, 138.0, 145.7.

1-(2-Ethoxyphenyl)ethanol (Table 4.4, **2f**)



^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.43 (t, *J* = 6.8 Hz, 3 H), 1.51 (d, *J*= 6.4 Hz, 3H), 4.07 (q, *J*= 6.8 Hz, 2H), 5.09 (q, *J*= 6.4 Hz, 1 H), 6.85 (d, *J*= 8.1 Hz, 1 H), 6.94 (t, *J*= 7.9 Hz, 1H), 7.21 (dt, *J*= 1.5 Hz, 7.6 Hz, 1H), 7.32 (dd, *J*= 1.1 Hz, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.8, 22.8, 63.4, 66.6, 111.2, 120.6, 126.0, 128.1, 130.3, 155.8.

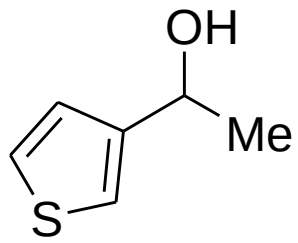
1-(pyridine-2-yl)ethanol (Table 4.5, **4a**)



^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ:1.50 (d, *J*= 6.6 Hz, 3H), 4.87 (q, *J*= 6.6 Hz, 1H), 7.18 (dd, *J*= 1.8 Hz, 7.0 Hz, 1H), 7.27 (d, *J*= 8.1 Hz, 1H), 7.68 (dt, *J*= 1.5 Hz, 7.7 Hz,

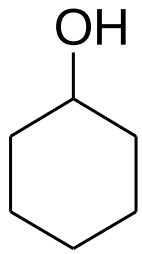
1H), 8.53 (d, *J*= 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.2, 68.8, 119.8, 122.2, 136.8, 148.1, 163.0.

1-(Thiophen-3-yl)ethanol (Table 4.5, **4b**)



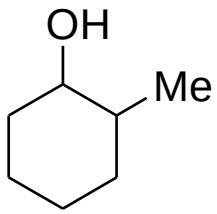
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.52 (1H, *J*= 6.5 Hz, 1H), 2.52 (s, 1H), 4.96 (q, *J*= 6.6 Hz, 1H), 7.09-7.10 (m, 1H), 7.182-7.188 (m, 1H), 7.25-7.31 (m, 1H), 7.18-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.4, 66.5, 120.1, 125.6, 126.1, 147.2.

Cyclohexanol (Table 4.6, **6a**)



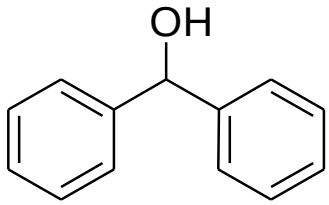
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.25 (m, 4H), 1.52 (m, 1H), 1.72 (m, 2H), 1.89 (m, 2H), 3.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.0, 25.4, 35.5, 70.3.

2-Methylcyclohexanol (Table 4.6, **6b**)



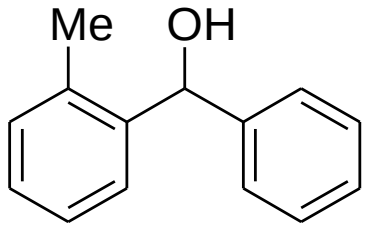
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 1.52 (d, 1H, *J*=6.5 Hz), 2.52 (s, 1H), 4.96 (q, 1H, *J*=6.6 Hz), 7.09-7.10 (m, 1H), 7.182-7.188 (m, 1H), 7.25-7.31 (m, 1H), 7.18-7.20 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 66.5, 120.1, 125.6, 126.1, 147.2

Benzhydrol (Table 4.7, **8a**)



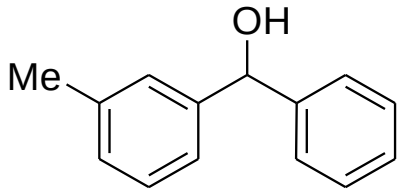
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 2.82 (brs,1H), 5.80 (s, 1H), 7.25-7.31 (m, 2H), 7.32-7.36 (m, 3H), 7.38-7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 75.9, 126.4, 127.3, 128.3, 143.7.

2-Methylphenyl(phenyl)methanol (Table 4.7, **8b**)



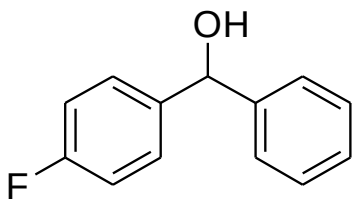
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 2.26 (s, 3H), 5.98 (s, 1H), 7.15-7.31 (m, 5H), 7.40-7.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.2, 73.1, 125.9, 126.2, 127.0, 127.32, 127.35, 128.2, 128.3, 130.0, 135.2, 141.4, 142.8..

3-Methylphenyl(phenyl)methanol (Table 4.7, **8c**)



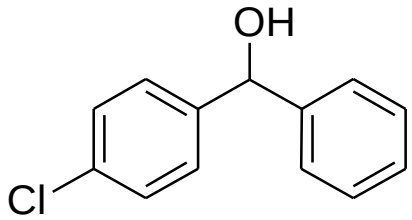
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 2.25 (s, 3H), 6.00 (s, 1H), 7.14-7.33 (m, 7H), 7.38-7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.3, 73.3, 126.0, 126.2, 127.0, 127.4, 128.4, 130.0, 133.0, 135.3, 141.4, 142.8.

4-Fluorophenyl(phenyl)methanol (Table 4.7, **8d**)



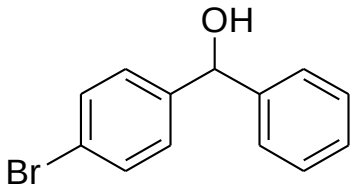
^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 5.82 (s, 1H), 6.87-7.04 (m, 5H), 7.11-7.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 75.8, 115.2 (d, J_{CF} = 21.4, -C-CF), 126.4, 127.7, 128.2 (d, J_{CF} = 8.5, -C-C-CF), 128.5, 129.7 (d, J_{CF} = 4.5, -C-C-C-CF), 143.6, 162.1 (d, J_{CF} = 284, -CF); ^{19}F NMR (376 MHz) δ -115.0.

4-Chlorophenyl(phenyl)methanol (Table 4.7, **8e**)



^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 5.74 (s, 1H), 7.28-7.45 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 75.4, 126.4, 127.6, 127.8, 128.4, 128.5, 129.8, 130.0 131.4, 132.6, 133.0, 142.1, 143.3.

4-bromophenyl)(phenyl)methanol (Table 4.7, **8f**)



^{1}H NMR (400 MHz, $CDCl_3$, *J*= Hz) δ: 7.24-7.50 (m, 5H), 7.57-7.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 75.5, 126.53, 126.55, 127.5, 127.7, 128.2, 129.9, 130.0, 132.4, 132.7, 142.9, 143.5, 143.9.

4.5 References

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Chapter 5 Conclusion

Due to the depletion of fossil fuel, we have to look for renewable energy resources that can be alternative to the fossil fuel. Regardless of the geographic limitation, biofuel (in particular biodiesel) generated from non-edible biomass such as vegetable oils would be an ideal alternative however its application is retarded by poor cold-flow properties. With the efforts paid on the exploration of different kinds of biofuel upgrading process, decarbonylation is particular attractive as high selective alpha-olefins could be produced.

To further improve the decarbonylation reactions of carboxylic acids, we have successfully introduced the first example of palladium-indolylbisphosphine catalyzed decarbonylation to produce alpha olefins in good yield and alpha-selectivity.

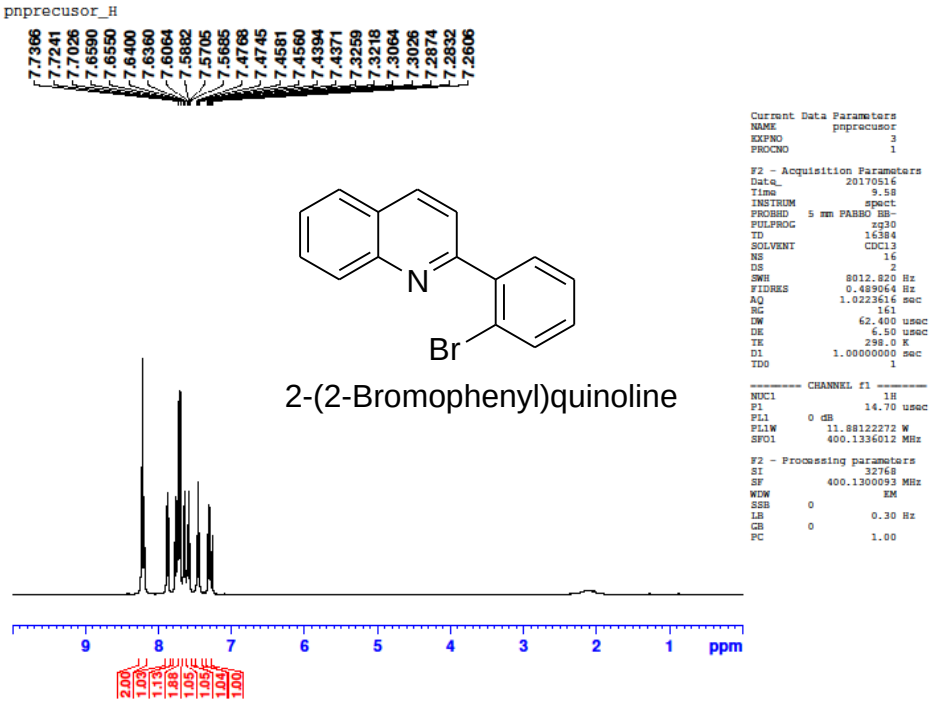
Furthermore we have also investigated the feasibility of monophosphine ligand in conjunction with palladium to act as active catalyst towards decarbonylation of carboxylic acids. By employing palladium-naphthylphosphine to catalyze the decarbonylation reaction, various kinds of high alpha-selective olefins were obtained and noteworthy allylpyrene is firstly prepared by decarbonylation of pyrenecarboxylic acid.

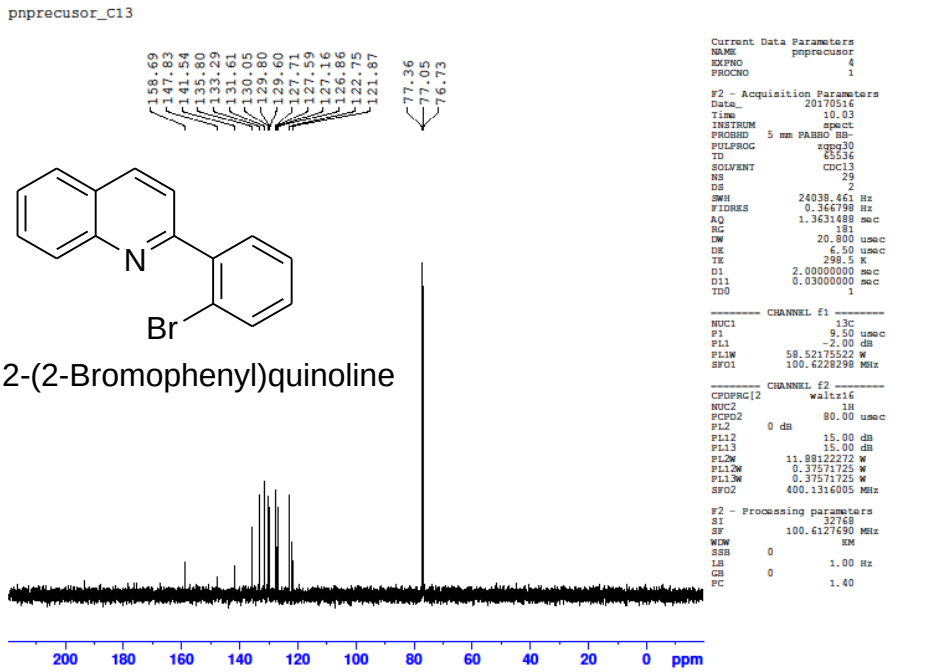
Glycerol which is byproduct from the biofuel upgrading process, usually discarded as waste in the past however it is found to be green solvent and could be applied as hydrogen sources for the transfer hydrogenation process. We demonstrated that

ruthenium metal could be combined with inexpensive, commercial available 2-aminobenzyl alcohol to be active catalyst in catalytic transfer hydrogenation of ketones. A broad range of ketones including aryl ketones, heteroaryl ketones, cyclic ketones and diketones were converted to their corresponding desired alcohols in good yields. It could explore a field for the application of glycerol and reduce the wastage problem of biofuel upgrading process.

Appendix

^{1}H, ^{13}C, ^{31}P NMR, MS and HRMS spectra





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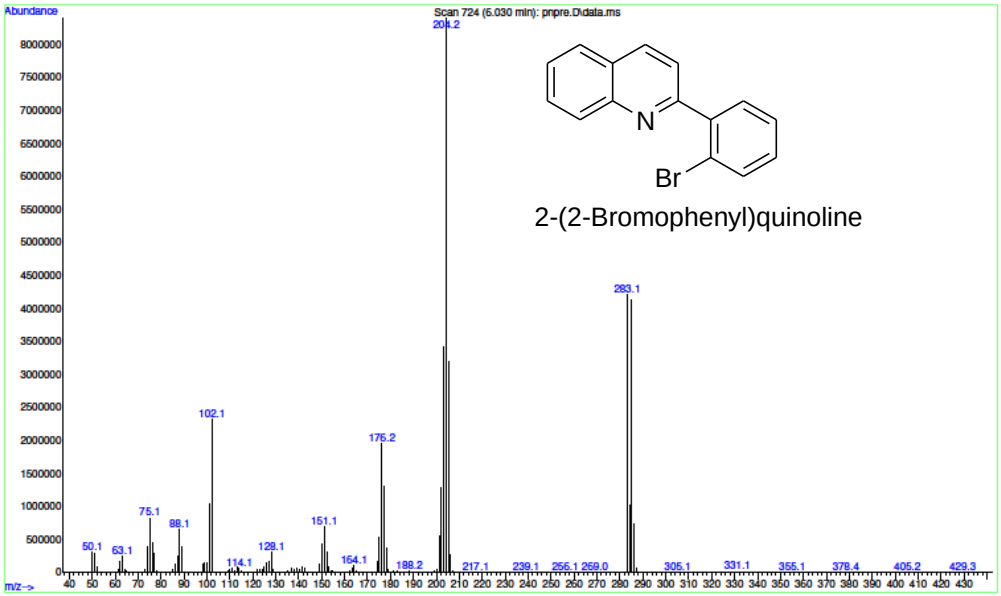

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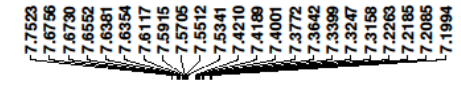
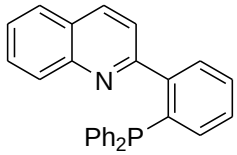
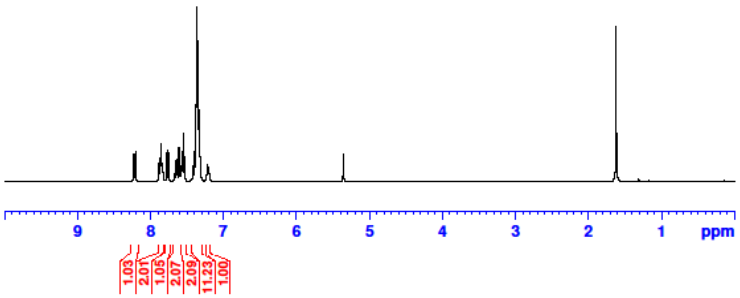




(2-(Quinoline-2-yl)phenyl)diphenylphosphine, **PN-1**

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DS                         2
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FIDRES             0.244532 Hz
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RG                       181
DW                  62.400 usec
DE                   6.50 usec
TE                  295.7 K
D1                 1.00000000 sec
TD0                        1

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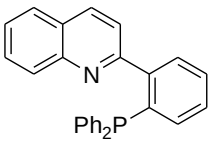

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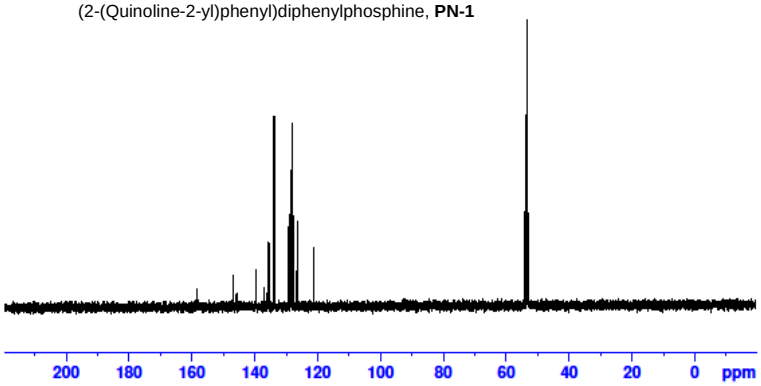


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TD0                        1

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PCPD2                  80.00 usec
PL2          0 dB
PL12                  15.00 dB
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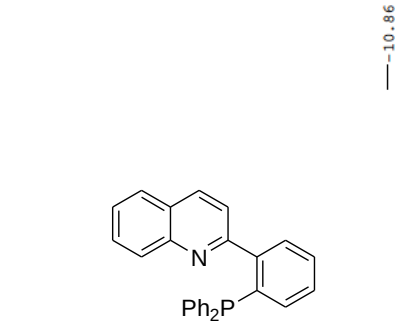
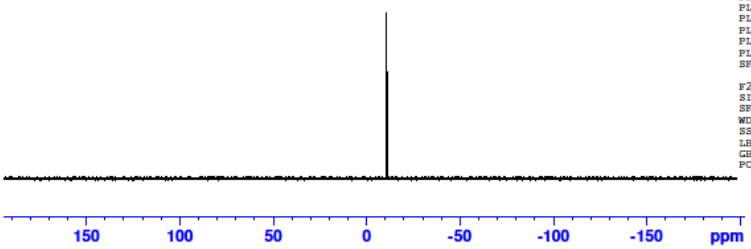
FSyn14P



(2-(Quinoline-2-yl)phenyl)diphenylphosphine, **PN-1**

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PL12                15.00 dB
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PL12W             0.37571725 W
PL13W             0.37571725 W
SFO2            400.1316005 MHz

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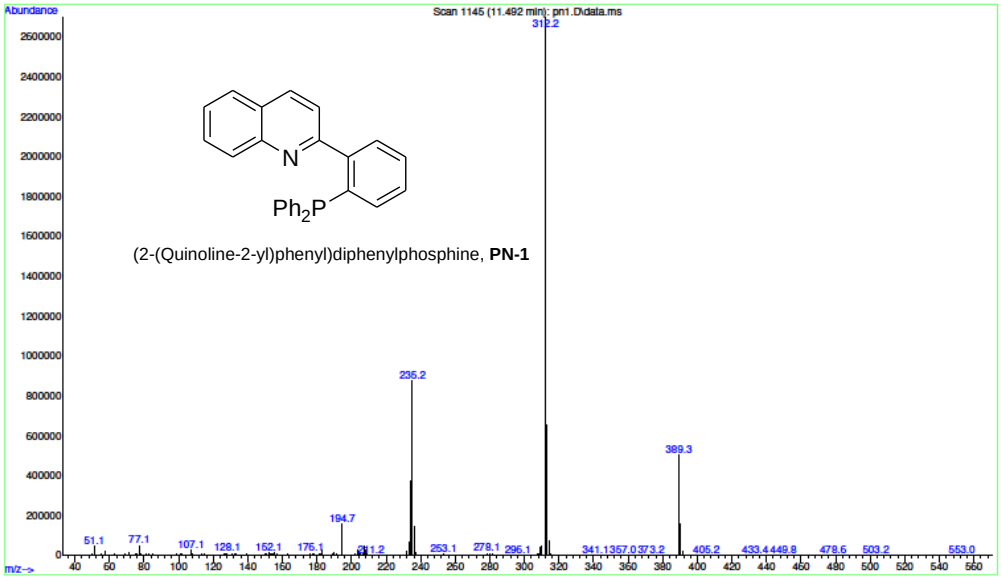
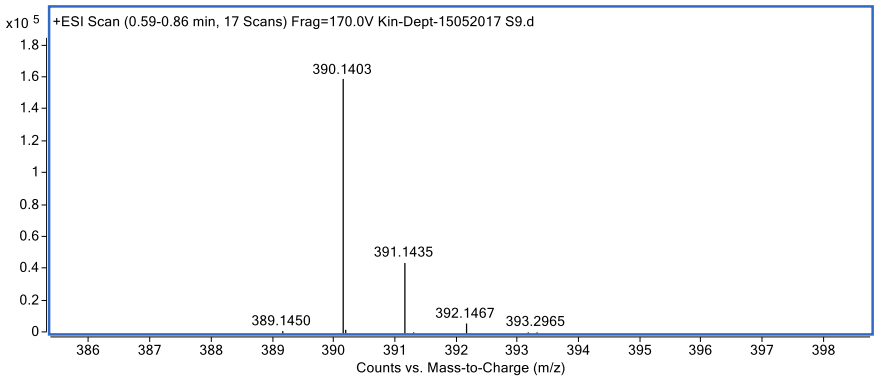
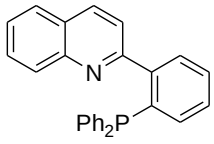
Vial Number: 7
```



(2-(Quinoline-2-yl)phenyl)diphenylphosphine, **PN-1**

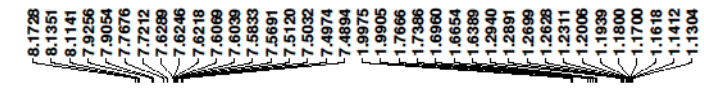


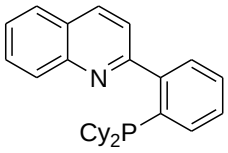


(2-(Quinoline-2-yl)phenyl)diphenylphosphine, **PN-1**

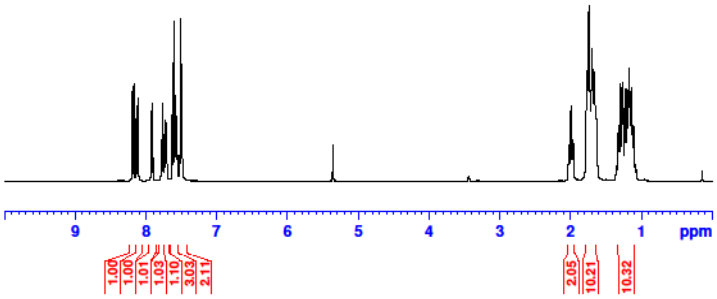
Mass	Calc. Mass	mDa	PPM	Formula
390.1403	390.1412	-0.9	-2.2	C27 H21 N P

Fsyn32aH





(2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine, **PN-2**



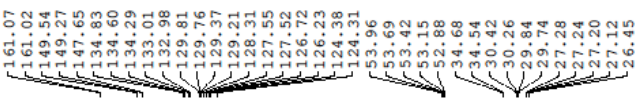

```
Current Data Parameters
NAME                  Fsyn32a
EXPNO                       2
PROCNO                      1

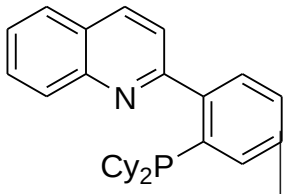
F2 - Acquisition Parameters
Date_               20151006
Time                   19.02
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                     32768
SOLVENT                CD2Cl2
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.244532 Hz
AQ                  2.0447233 sec
RG                       25.4
DW                  62.400 usec
DE                   6.50 usec
TE                   297.2 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1             0 dB
PL1W               11.88122272 W
SFO1               400.1324008 MHz

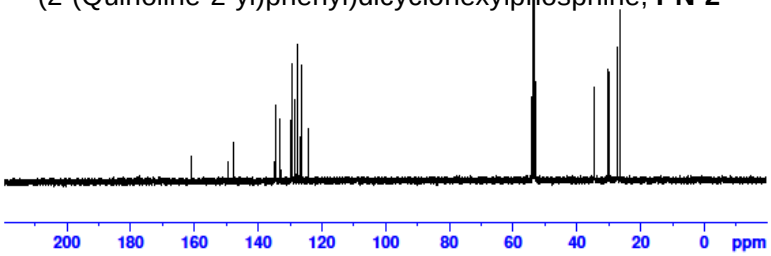
F2 - Processing parameters
SI                         32768
SF                  400.1300000 MHz
WDW                           EM
SSB             0
LB                       0.30 Hz
GB              0
PC                         1.00
```

Fsyn32aC





(2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine, **PN-2**




```
Current Data Parameters
NAME                  Fsyn32a
EXPNO                       3
PROCNO                      1

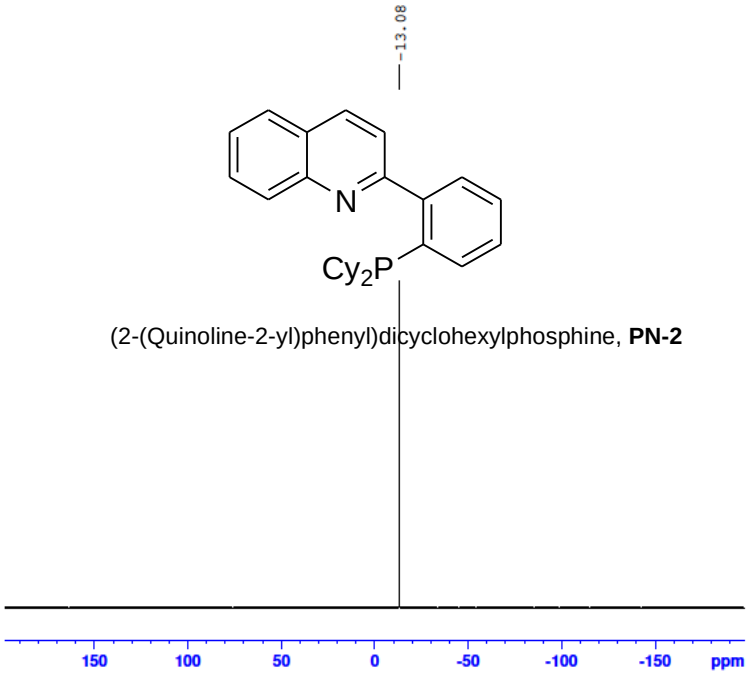
F2 - Acquisition Parameters
Date_               20151006
Time                   19.09
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CD2Cl2
NS                       220
DS                          2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                        203
DW                  20.800 usec
DE                   6.50 usec
TE                   297.9 K
D1                  1.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       9.50 usec
PL1                     -2.00 dB
PL1W               58.52175522 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2             0 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W               11.88122272 W
PL12W               0.37571725 W
PL13W               0.37571725 W
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127690 MHz
WDW                           EM
SSB             0
LB                       1.00 Hz
GB              0
PC                         1.40
```

Fsyn120P



(2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine, **PN-2**

```
Current Data Parameters
NAME                  Fsyn120
EXPNO                       3
PROCNO                      1

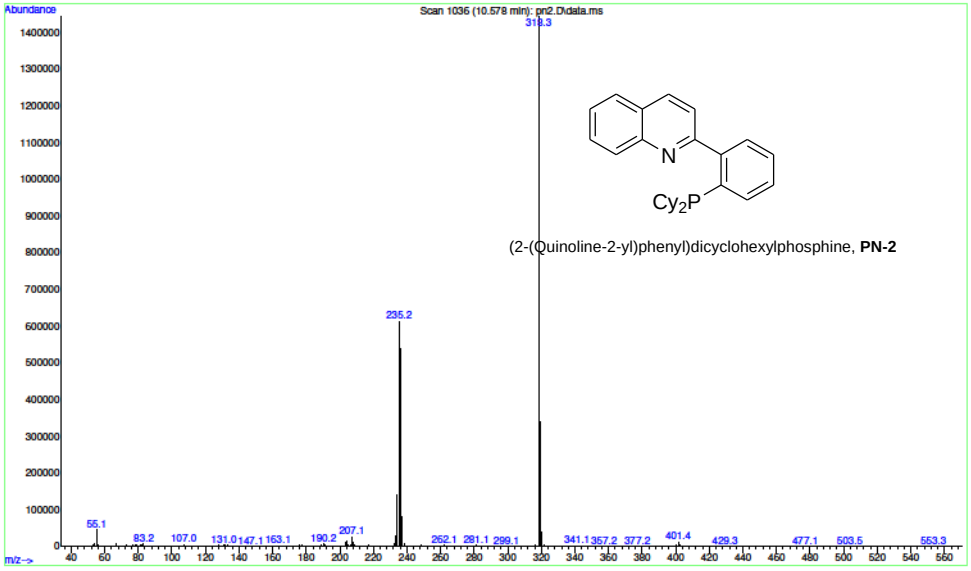
F2 - Acquisition Parameters
Date_              20170208
Time                  11.37
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CD2Cl2
NS                       46
DS                        4
SWH               64102.562 Hz
FIDRES            0.978127 Hz
AQ                0.5111808 sec
RG                     2050
DW                  7.800 usec
DE                  6.50 usec
TE                  298.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                    31P
P1                   14.70 usec
PL1                   3.00 dB
PL1W             12.96693134 W
SFO1            161.9755930 MHz

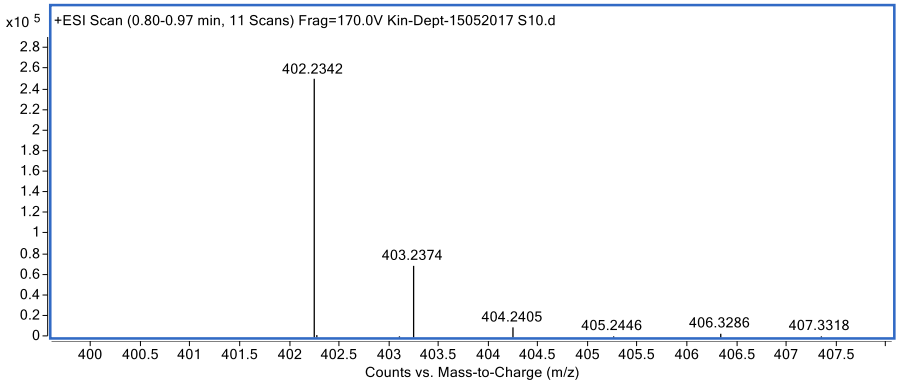
======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2          0 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W             11.88122272 W
PL12W             0.37571725 W
PL13W             0.37571725 W
SFO2            400.1316005 MHz

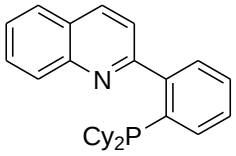
F2 - Processing parameters
SI                       32768
SF              161.9755930 MHz
WDW                         EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

```
File       :D:\MassHunter\GCMS\1\data\alston\pn2.D
Operator   : duan
Acquired   : 12 May 2017  11:32     using AcqMethod M3.M
Instrument :    5977
Sample Name: pn2
Misc Info  :
Vial Number: 8
```



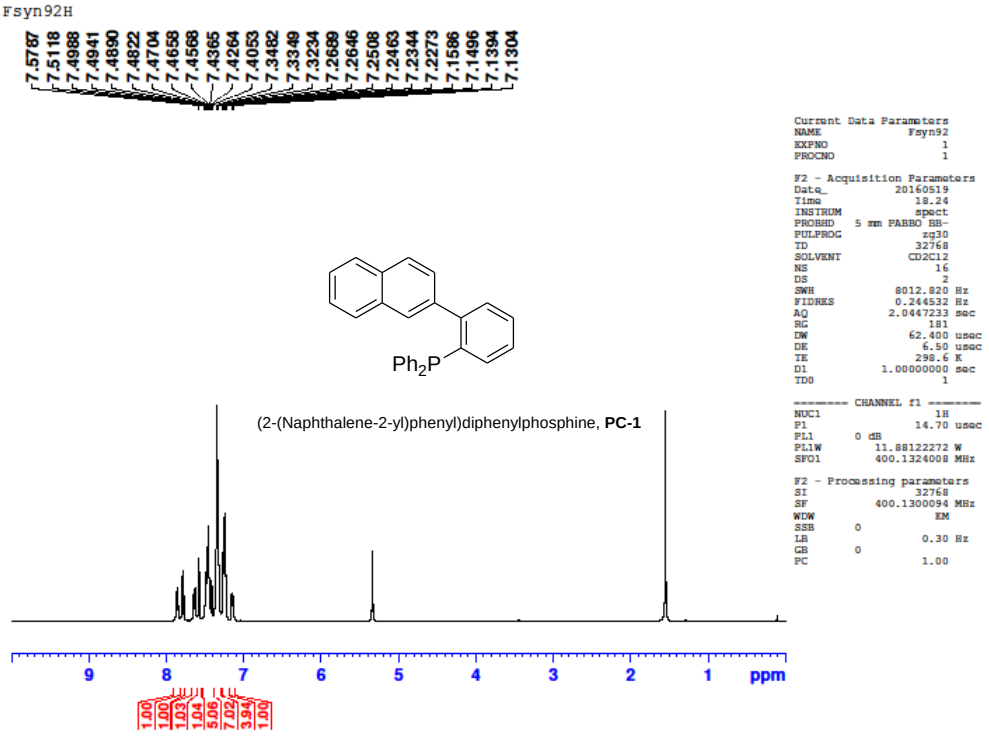
(2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine, **PN-2**



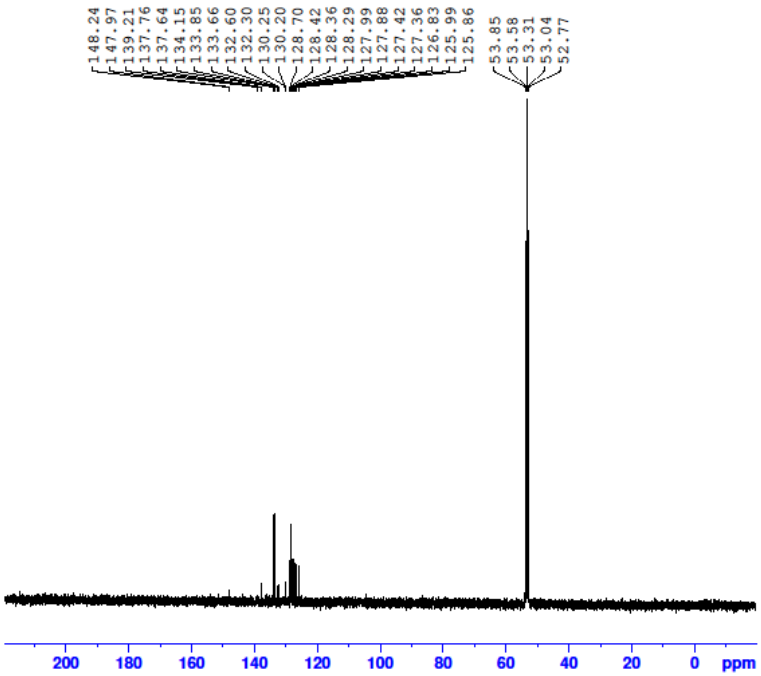


(2-(Quinoline-2-yl)phenyl)dicyclohexylphosphine, **PN-2**

Mass	Calc. Mass	mDa	PPM	Formula
402.2342	402.2351	-0.9	-2.1	C27 H33 N P



Fsyn92C




```
Current Data Parameters
NAME                 Fsyn92
EXPNO                     2
PROCNO                    1

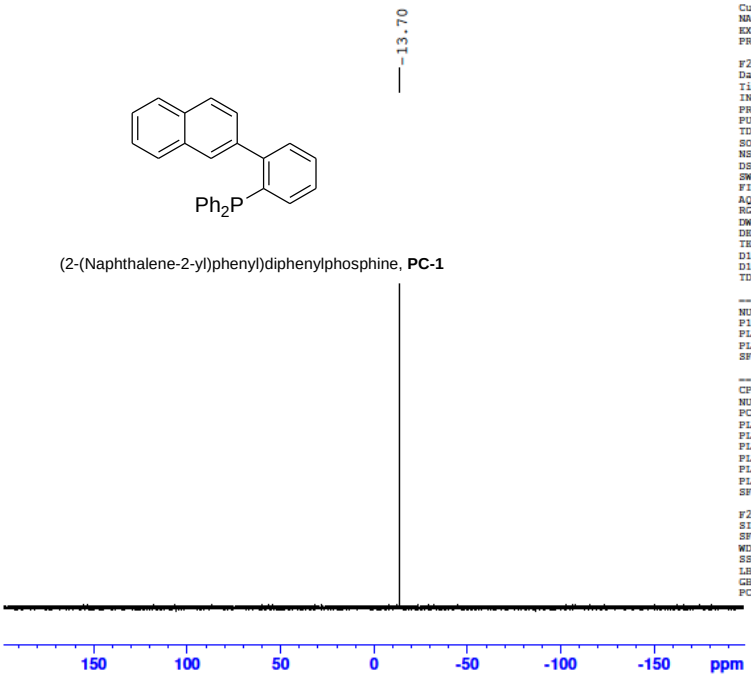
F2 - Acquisition Parameters
Date_               20160519
Time                   18.26
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT               CD2Cl2
NS                       201
DS                         2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                       144
DW                    20.800 usec
DE                     6.50 usec
TE                    299.4 K
D1                  1.00000000 sec
D11                 0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     9.50 usec
PL1                   -2.00 dB
PL1W           58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2          0 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            100.6127769 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

Fsyn92P



(2-(Naphthalene-2-yl)phenyl)diphenylphosphine, **PC-1**

```
Current Data Parameters
NAME                 Fsyn92
EXPNO                     3
PROCNO                    1

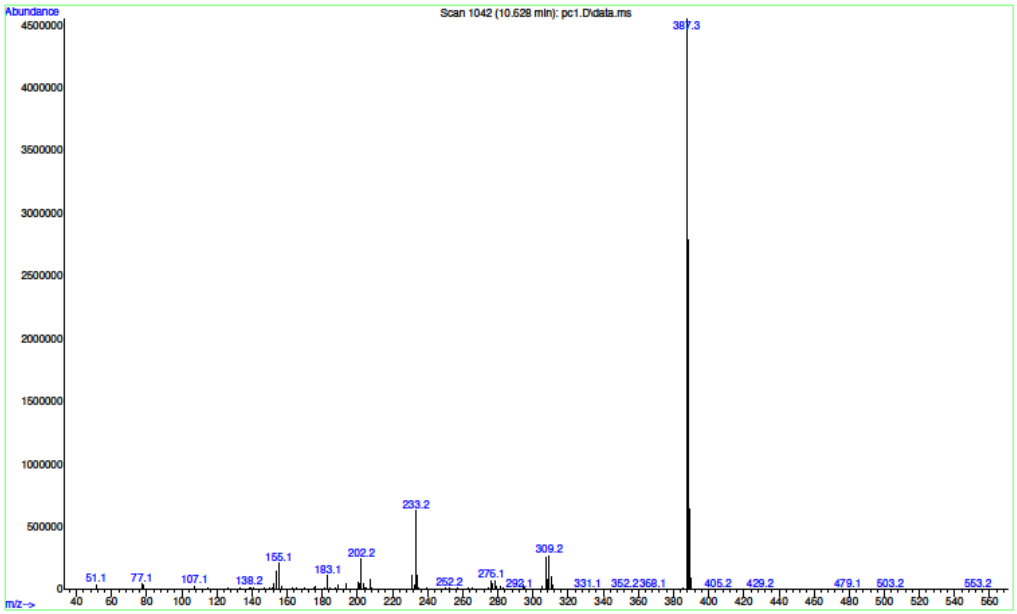
F2 - Acquisition Parameters
Date_               20160519
Time                   18.36
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
TD                     65536
SOLVENT               CD2Cl2
NS                        23
DS                         4
SWH                64102.562 Hz
FIDRES              0.978127 Hz
AQ                  0.5111808 sec
RG                       203
DW                    7.800 usec
DE                     6.50 usec
TE                    299.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                        1

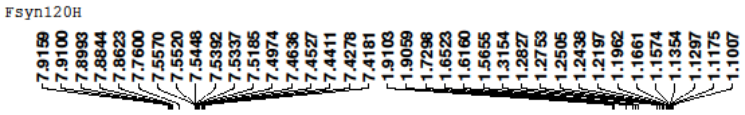
======== CHANNEL f1 ========
NUC1                     31P
P1                    14.70 usec
PL1                    3.00 dB
PL1W           12.96693134 W
SFO1          161.9755930 MHz

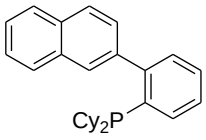
======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2          0 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF            161.9755930 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

```
File      :D:\MassHunter\GCMS\1\data\alston\pc1.D
Operator  : duan
Acquired  : 12 May 2017  11:55     using AcqMethod M3.M
Instrument :   5977
Sample Name: pc1
Misc Info  :
Vial Number: 9
```







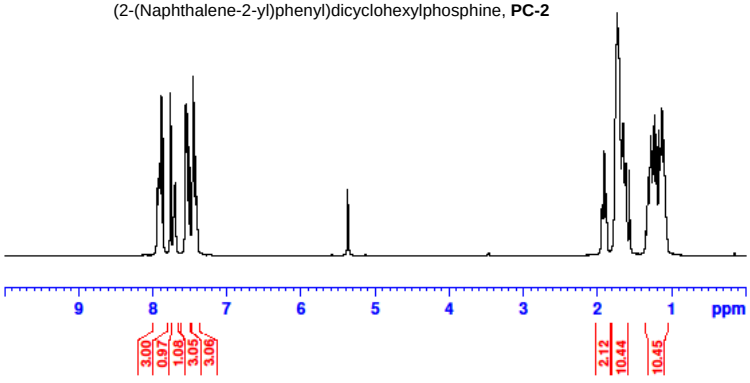
(2-(Naphthalene-2-yl)phenyl)dicyclohexylphosphine, **PC-2**

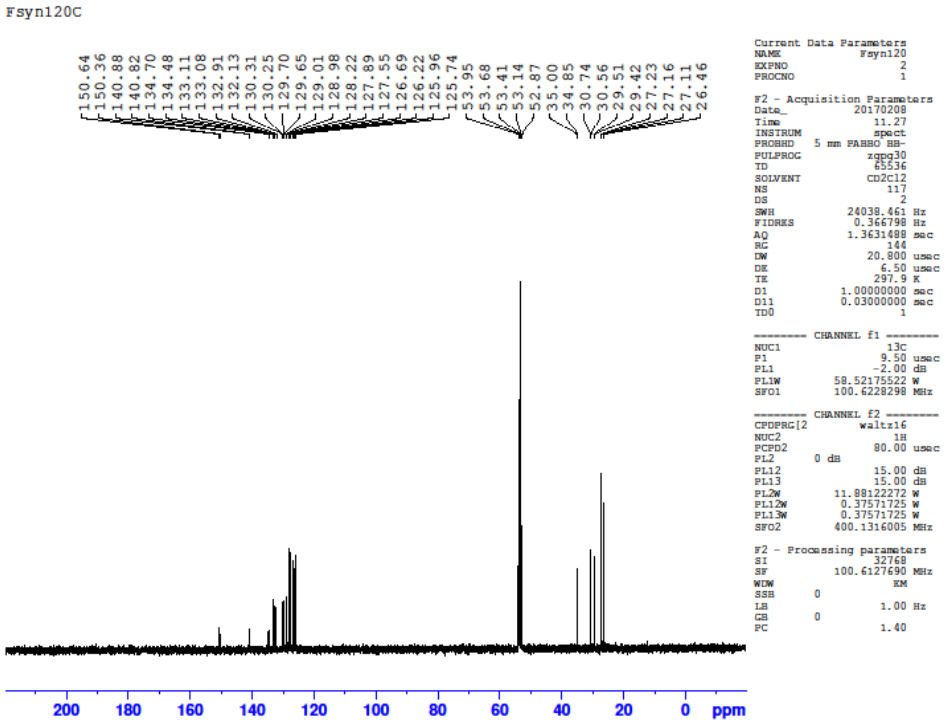
```
Current Data Parameters
NAME              Fsyn120
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20170208
Time              11.25
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT           CD2Cl2
NS                    12
DS                     2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ             2.0447233 sec
RG                    57
DW               62.400 usec
DE                6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

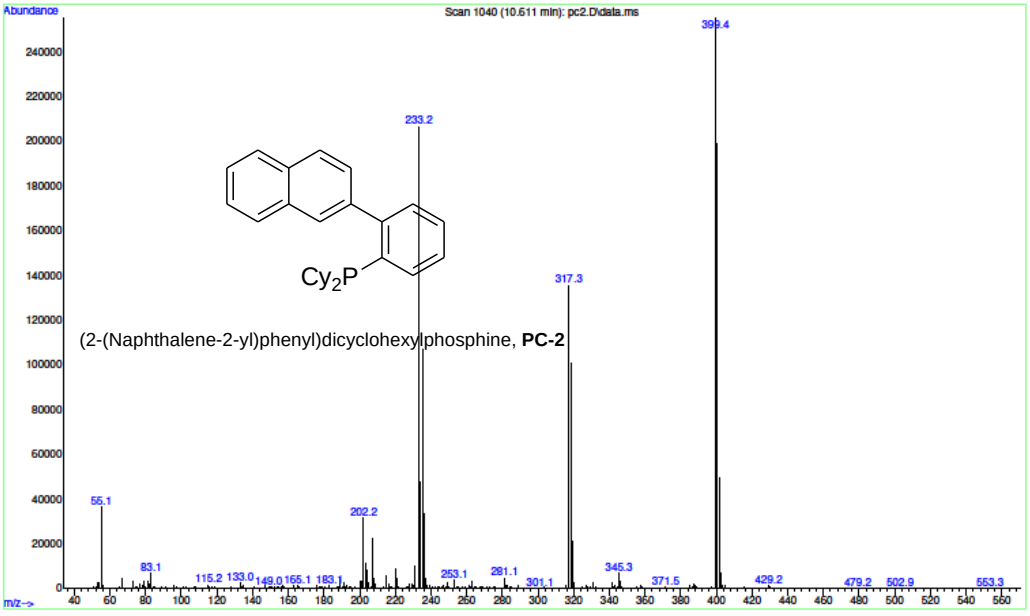
======== CHANNEL f1 ========
NUC1                  1H
P1                14.70 usec
PL1        0 dB
PL1W        11.88122272 W
SFO1        400.1324008 MHz

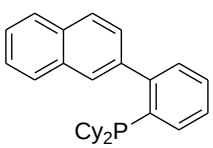
F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB        0
LB                 0.30 Hz
GB         0
PC                 1.00
```

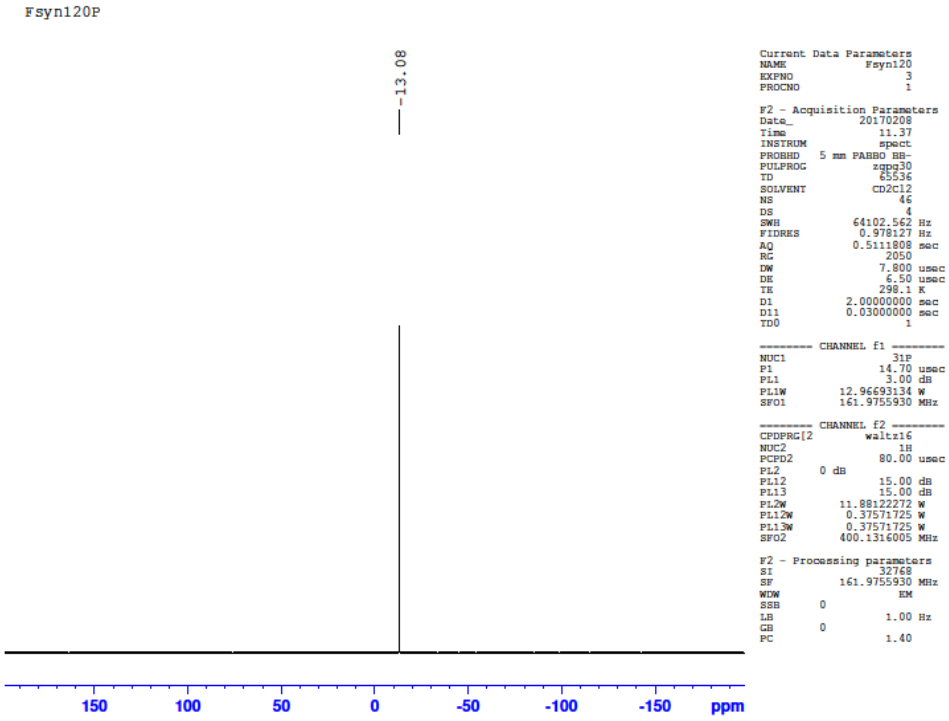


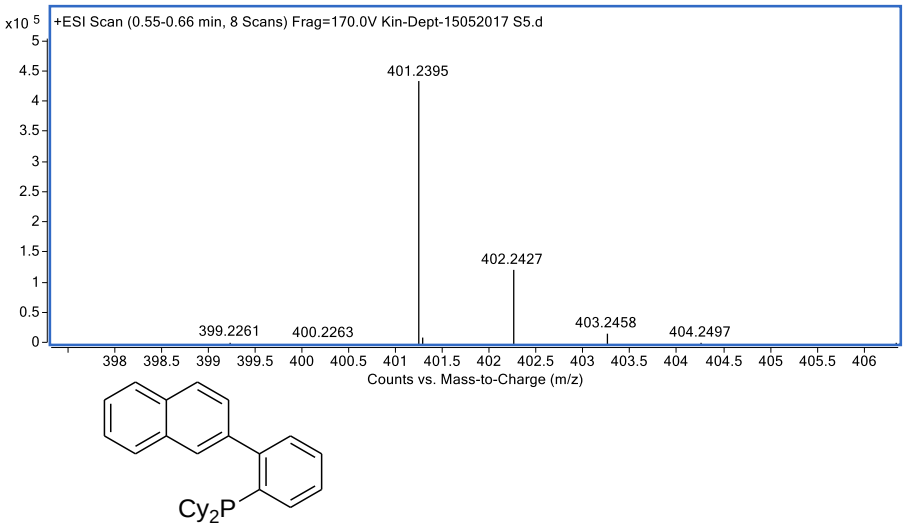



```
File       :D:\MassHunter\GCMS\1\data\alston\pc2.D
Operator   : duan
Acquired   : 12 May 2017  12:19     using AcqMethod M3.M
Instrument :   5977
Sample Name: pc2
Misc Info  :
Vial Number: 10
```





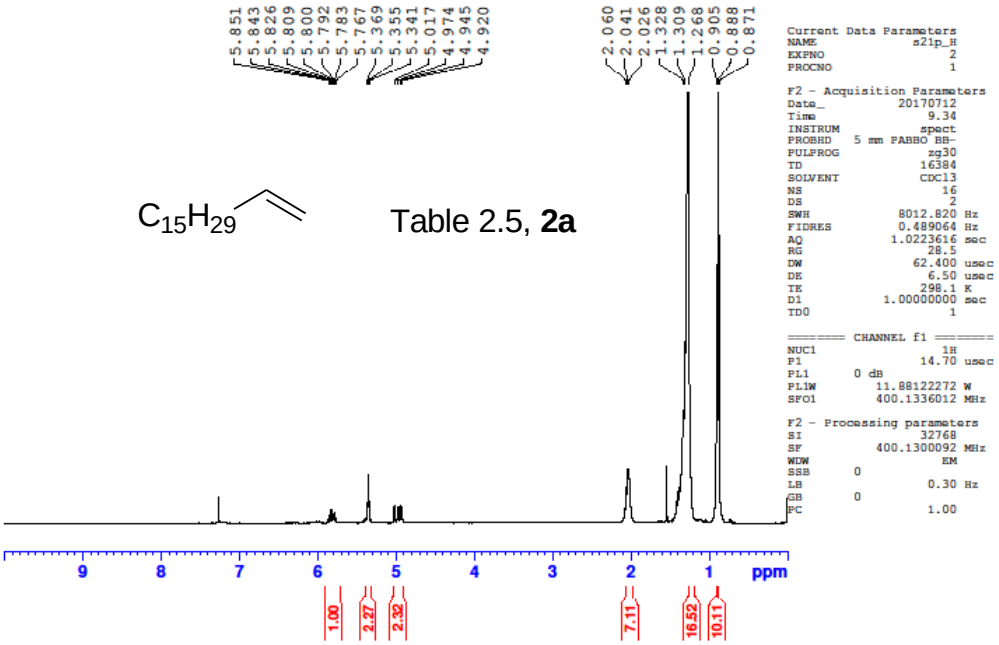




(2-(Naphthalene-2-yl)phenyl)dicyclohexylphosphine, **PC-2**

Mass	Calc. Mass	mDa	PPM	Formula
401.2395	401.2398	-0.3	-0.7	C28 H34 P

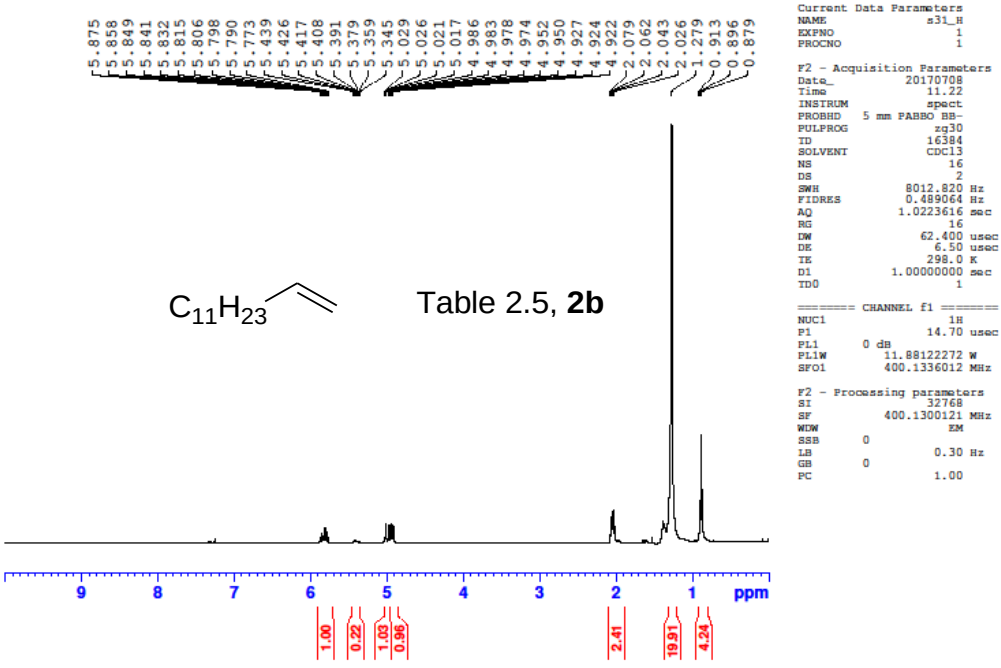
s21p_H (1,9-heptadecene)



$C_{15}H_{29}$

Table 2.5, **2a**

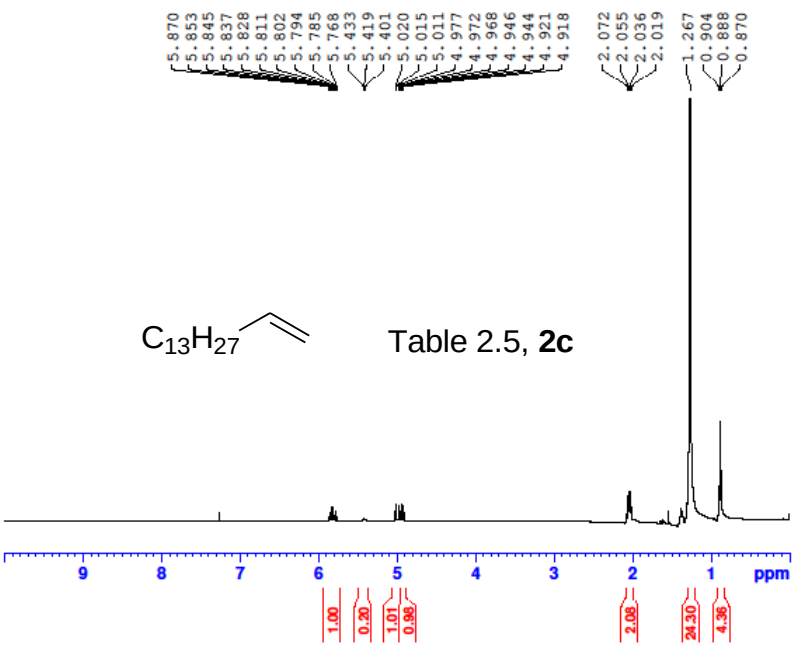
s31_H



$C_{11}H_{23}$

Table 2.5, **2b**

s32p_H (1-pentadecene)



$C_{13}H_{27}$

Table 2.5, **2c**

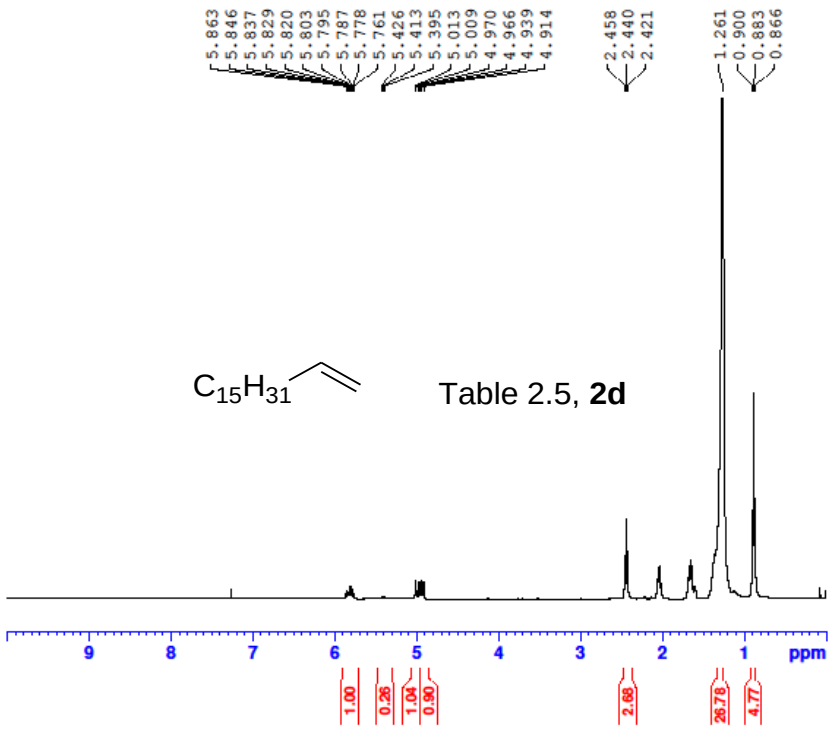
```
Current Data Parameters
NAME                  s32p_H
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170712
Time                   9.46
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                1.0223616 sec
RG                      28.5
DW                    62.400 usec
DE                     6.50 usec
TE                    298.3 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 =======
NUC1                      1H
P1                     14.70 usec
PL1          0 dB
PL1W          11.88122272 W
SFO1         400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF               400.1300092 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

s33p_H (1-heptadecene)



$C_{15}H_{31}$

Table 2.5, **2d**

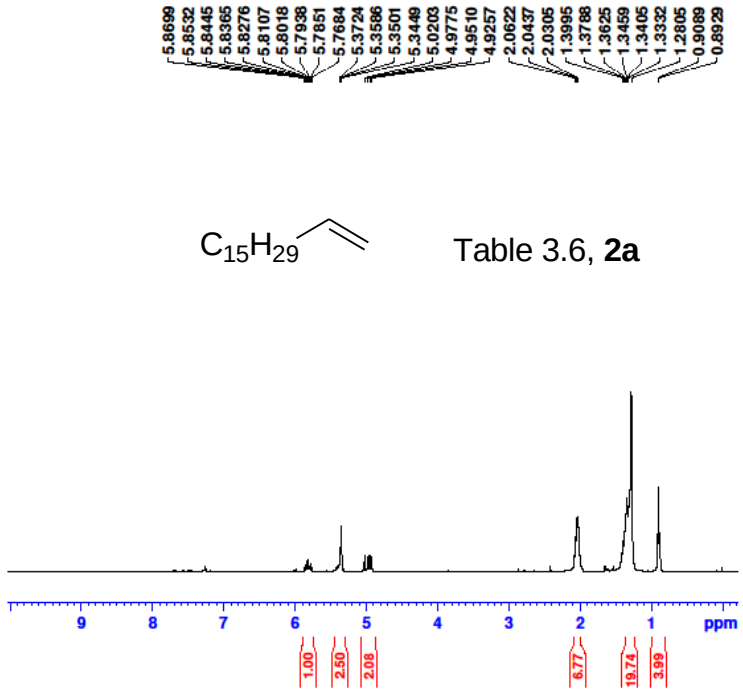
```
Current Data Parameters
NAME                  s33p_H
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20170711
Time                  17.32
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                1.0223616 sec
RG                        16
DW                    62.400 usec
DE                     6.50 usec
TE                     298.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 =======
NUC1                      1H
P1                     14.70 usec
PL1          0 dB
PL1W          11.88122272 W
SFO1         400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF               400.1300092 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

als175a_H



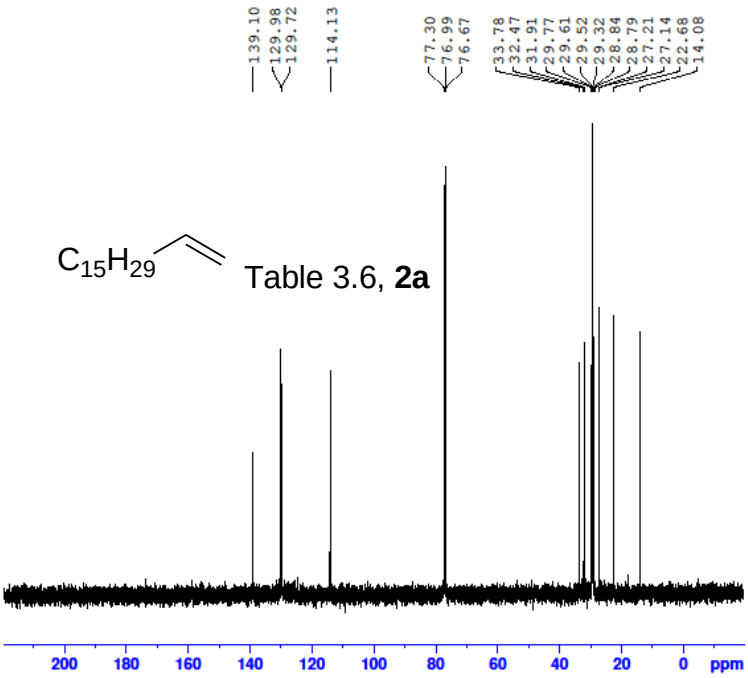

```
Current Data Parameters
NAME                  als175a
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20170210
Time                    9.35
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      20.2
DW                    62.400 usec
DE                     6.50 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1            0 dB
PL1W              11.88122272 W
SFO1              400.1336012 MHz

F2 - Processing parameters
SI                         32768
SF                400.1300110 MHz
WDW                           EM
SSB            0
LB                      0.30 Hz
GB             0
PC                         1.00
```

als175a_C13




```
Current Data Parameters
NAME                  als175a
EXPNO                       2
PROCNO                      1

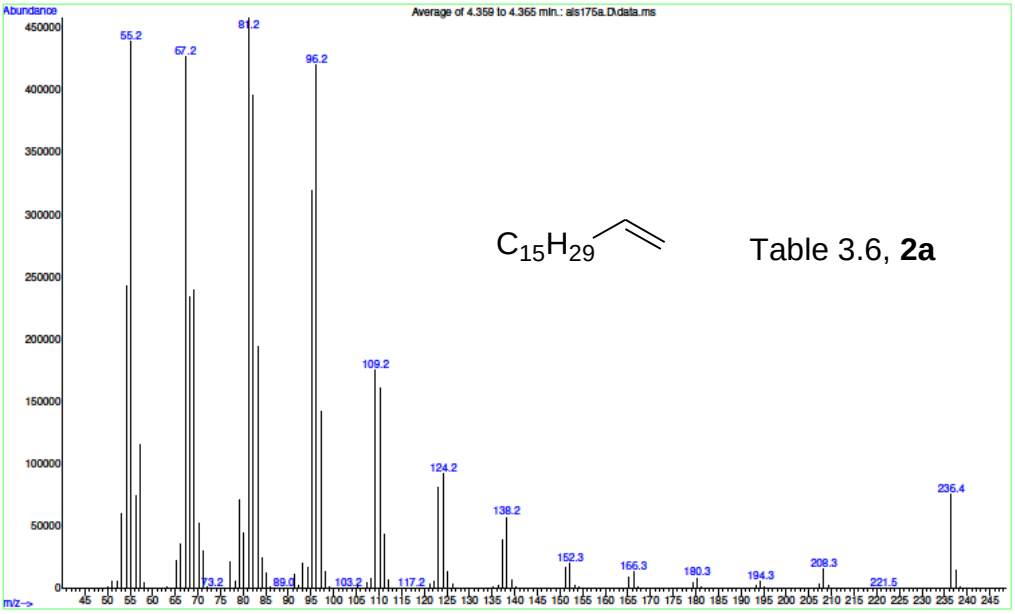
F2 - Acquisition Parameters
Date_               20170210
Time                    9.39
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        40
DS                         2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                        181
DW                    20.800 usec
DE                     6.50 usec
TE                    298.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2            0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                100.6127712 MHz
WDW                           EM
SSB            0
LB                      1.00 Hz
GB             0
PC                         1.40
```

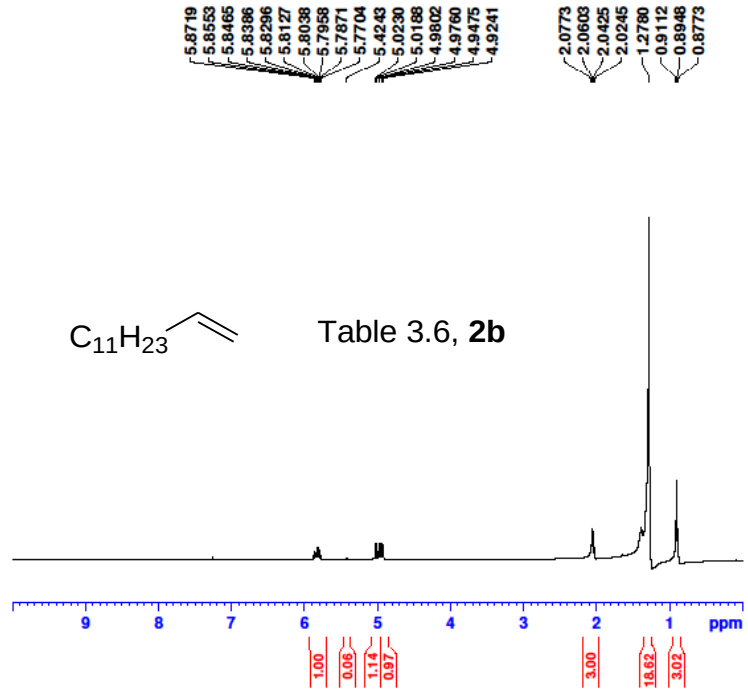
```
File       :D:\MassHunter\GCMS\1\data\alston\als175a.D
Operator   : duan
Acquired   : 07 Feb 2017  14:50     using AcqMethod M1.M
Instrument :   5977
Sample Name: als175a
Misc Info  :
Vial Number: 146
```



$C_{15}H_{29}$

Table 3.6, **2a**

als174H_H



$C_{11}H_{23}$

Table 3.6, **2b**

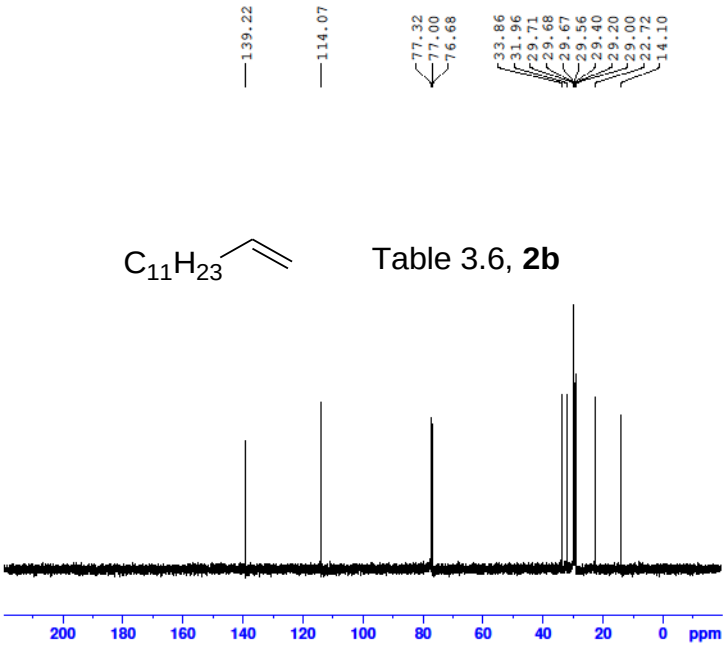
```
Current Data Parameters
NAME                  als174H_H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_               20161208
Time                     14.03
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      16384
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                 8012.820 Hz
FIDRES              0.489064 Hz
AQ                  1.0223616 sec
RG                         18
DW                     62.400 usec
DE                      6.50 usec
TE                     298.6 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1                0 dB
PL1W               11.88122272 W
SFO1               400.1336012 MHz

F2 - Processing parameters
SI                         32768
SF                  400.1300099 MHz
WDW                           EM
SSB                0
LB                      0.30 Hz
GB                 0
PC                      1.00
```

als174H_c13



$C_{11}H_{23}$

Table 3.6, **2b**

```
Current Data Parameters
NAME                 als174H_c13
EXPNO                         1
PROCNO                        1

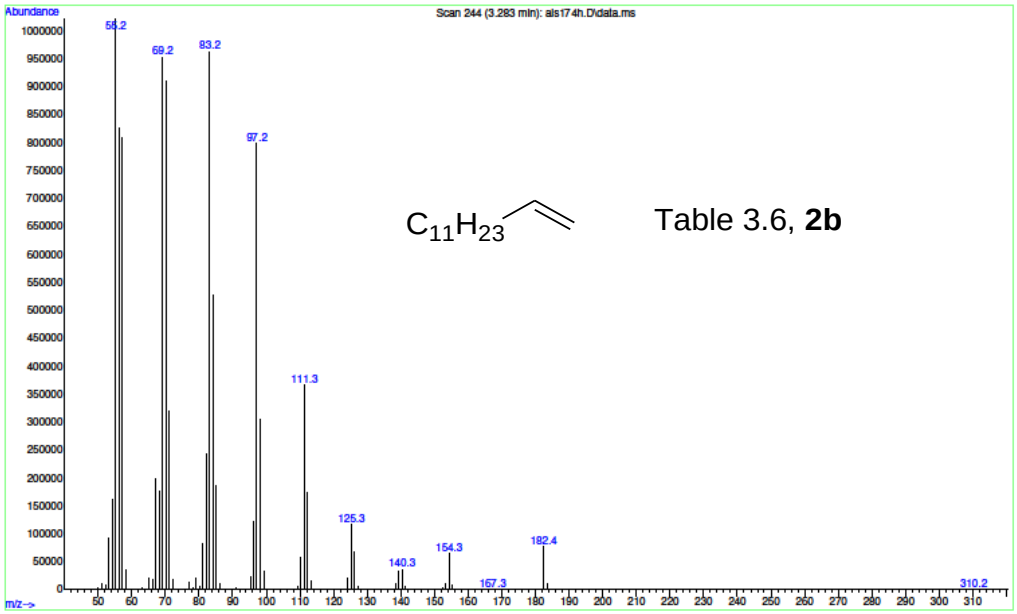
F2 - Acquisition Parameters
Date_               20161208
Time                     14.05
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         31
DS                          2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                        228
DW                     20.800 usec
DE                      6.50 usec
TE                     299.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W               58.52175522 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W               11.88122272 W
PL12W               0.37571725 W
PL13W               0.37571725 W
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127675 MHz
WDW                           EM
SSB                0
LB                      1.00 Hz
GB                 0
PC                      1.40
```

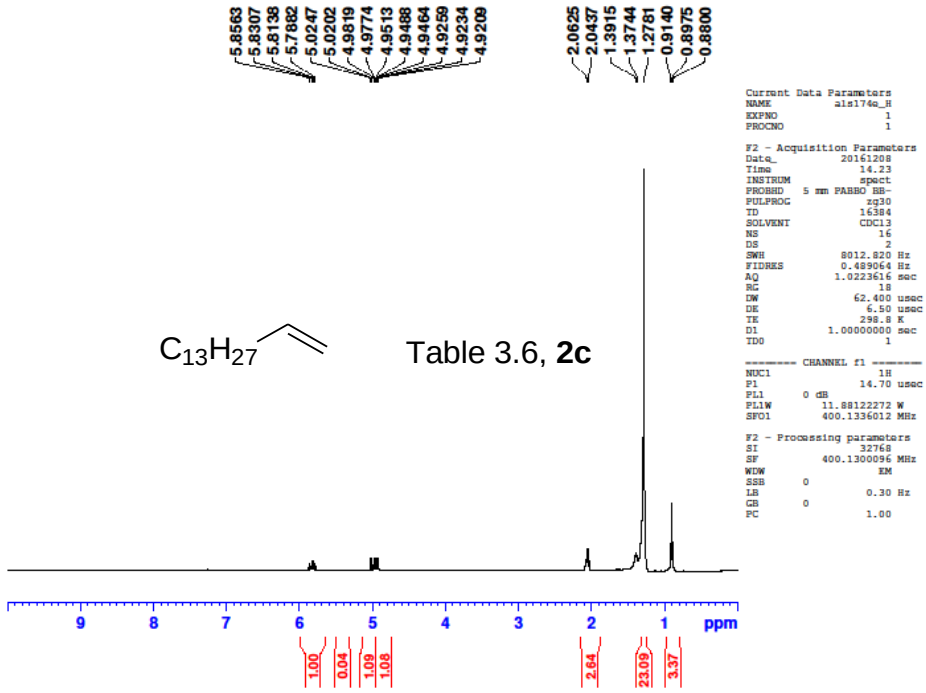
```
File       :D:\MassHunter\GCMS\1\data\alston\als174h.D
Operator   : duan
Acquired   : 02 Dec 2016  11:31     using AcqMethod M1.M
Instrument :   5977
Sample Name: als174h
Misc Info  :
Vial Number: 8
```



$C_{11}H_{23}$

Table 3.6, **2b**

als174e_H



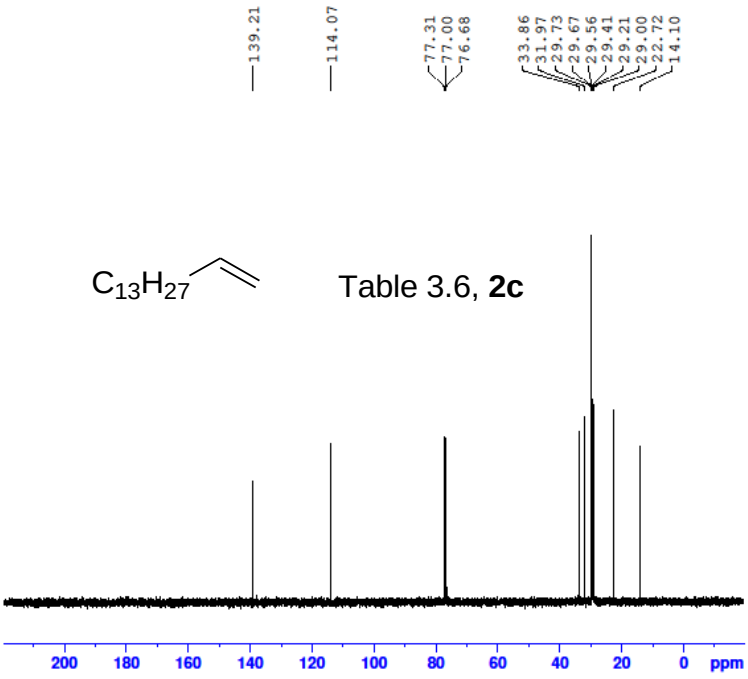

```
Current Data Parameters
NAME                  als174e_H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20161208
Time                      14.23
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       16384
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8012.820 Hz
FIDRES                0.489064 Hz
AQ                    1.0223616 sec
RG                          18
DW                       62.400 usec
DE                        6.50 usec
TE                       298.8 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                       14.70 usec
PL1                  0 dB
PL1W                 11.88122272 W
SFO1                 400.1336012 MHz

F2 - Processing parameters
SI                           32768
SF                   400.1300096 MHz
WDW                             EM
SSB                  0
LB                            0.30 Hz
GB                   0
PC                            1.00
```

als174e_c13




```
Current Data Parameters
NAME                 als174e_c13
EXPNO                         1
PROCNO                        1

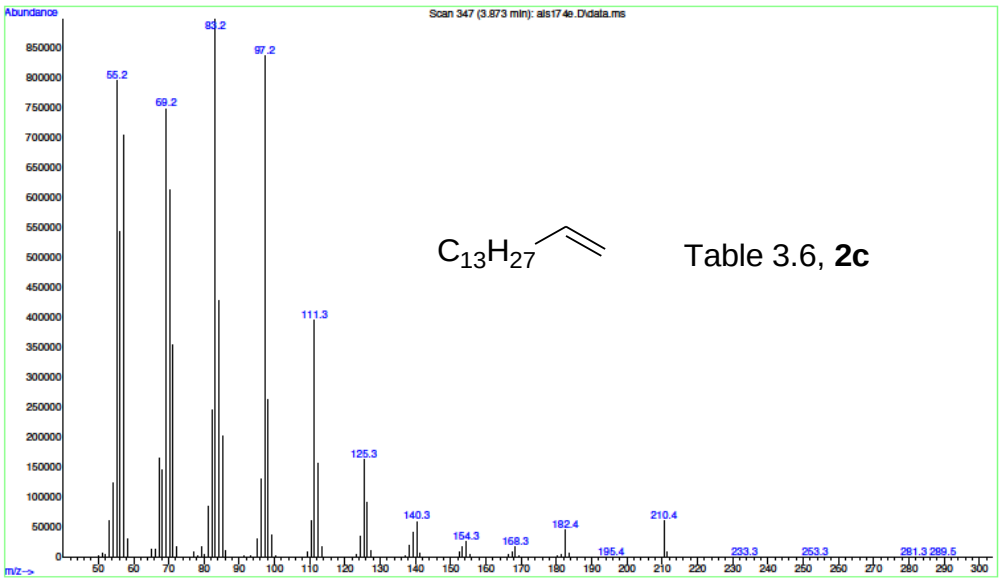
F2 - Acquisition Parameters
Date_                  20161208
Time                      14.24
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                          35
DS                           2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                          228
DW                       20.800 usec
DE                        6.50 usec
TE                       298.8 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         13C
P1                        9.50 usec
PL1                      -2.00 dB
PL1W                 58.52175522 W
SFO1                 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                         1H
PCPD2                    80.00 usec
PL2                  0 dB
PL12                     15.00 dB
PL13                     15.00 dB
PL2W                 11.88122272 W
PL12W                 0.37571725 W
PL13W                 0.37571725 W
SFO2                 400.1316005 MHz

F2 - Processing parameters
SI                           32768
SF                   100.6127670 MHz
WDW                             EM
SSB                  0
LB                            1.00 Hz
GB                   0
PC                            1.40
```

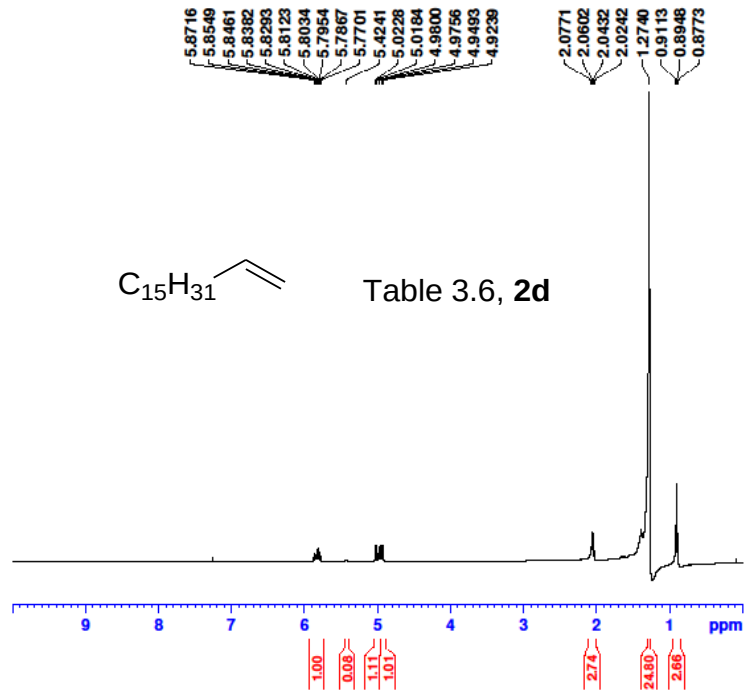
```
File       :D:\MassHunter\GCMS\1\data\alston\als174e.D
Operator   : duan
Acquired   : 02 Dec 2016  11:06     using AcqMethod M1.M
Instrument :   5977
Sample Name: als174e
Misc Info  :
Vial Number: 6
```



$C_{13}H_{27}$

Table 3.6, **2c**

als174f_H



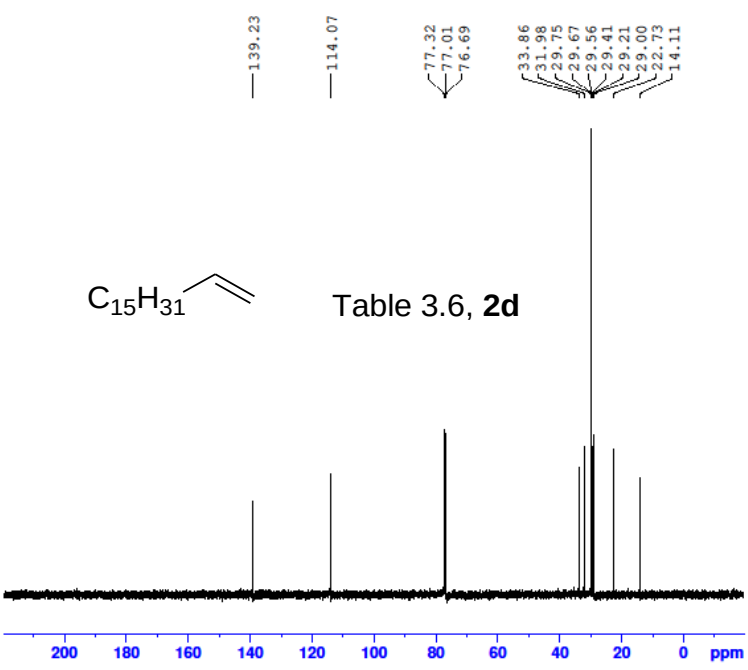
Current Data Parameters
NAME als174f_H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161208
Time 14.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 1.0223616 sec
RG 18
DW 62.400 usec
DE 6.50 usec
TE 298.7 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.70 usec
PL1 0 dB
PL1W 11.88122272 W
SFO1 400.1336012 MHz

F2 - Processing parameters
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

als174f_c13



Current Data Parameters
NAME als174f_c13
EXPNO 1
PROCNO 1

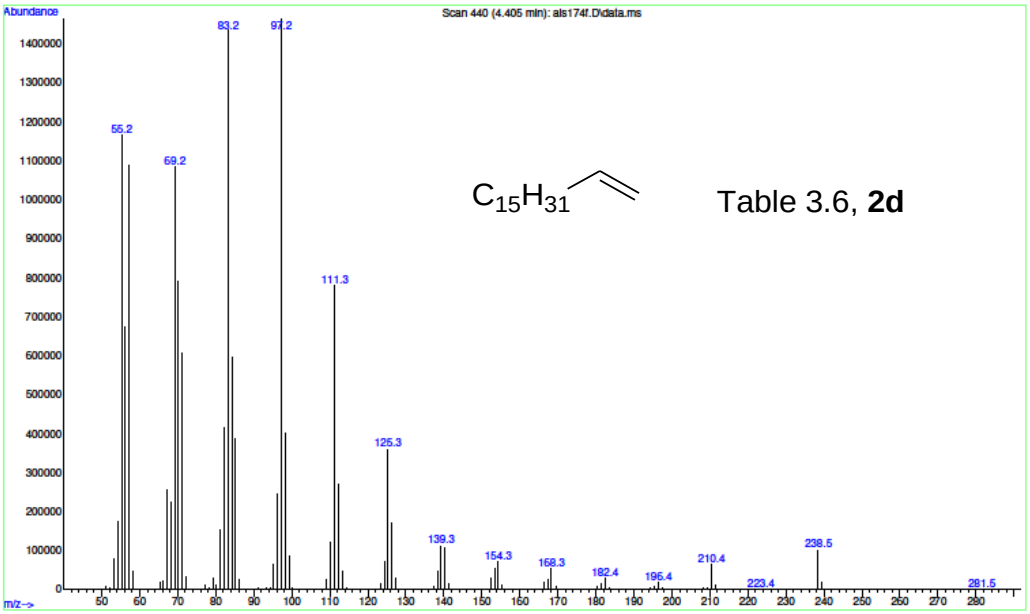
F2 - Acquisition Parameters
Date_ 20161208
Time 14.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 47
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 228
DW 20.800 usec
DE 6.50 usec
TE 299.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127671 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

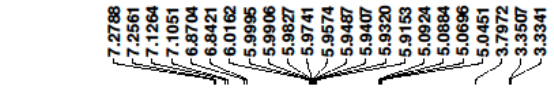
```
File      :D:\MassHunter\GCMS\1\data\alston\als174f.D
Operator  : duan
Acquired  : 02 Dec 2016  11:19     using AcqMethod M1.M
Instrument :  5977
Sample Name: als174f
Misc Info  :
Vial Number: 7
```



$C_{15}H_{31}$

Table 3.6, **2d**

als184e_H



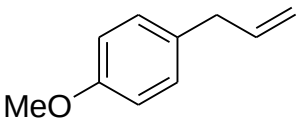
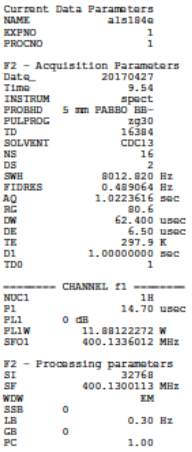
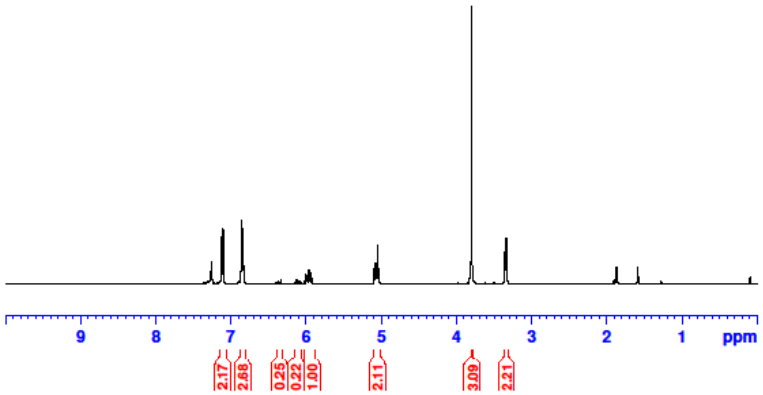


Table 3.6, **2e**





als184e_13C

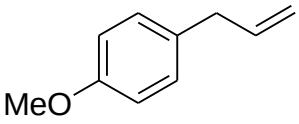
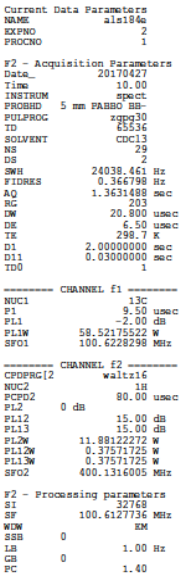
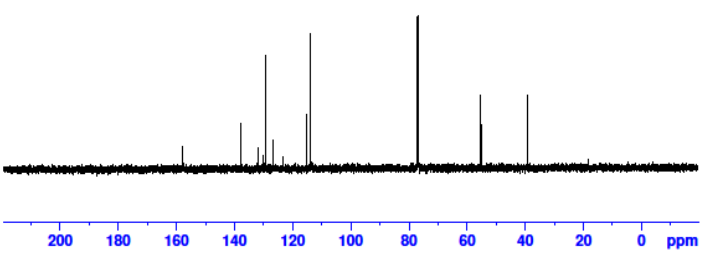


Table 3.6, **2e**





```
File       :D:\MassHunter\GCMS\1\data\alston\als184et2.D
Operator   : duan
Acquired   : 26 Apr 2017  15:37     using AcqMethod M1.M
Instrument :   5977
Sample Name: als184et2
Misc Info  :
Vial Number: 2
```

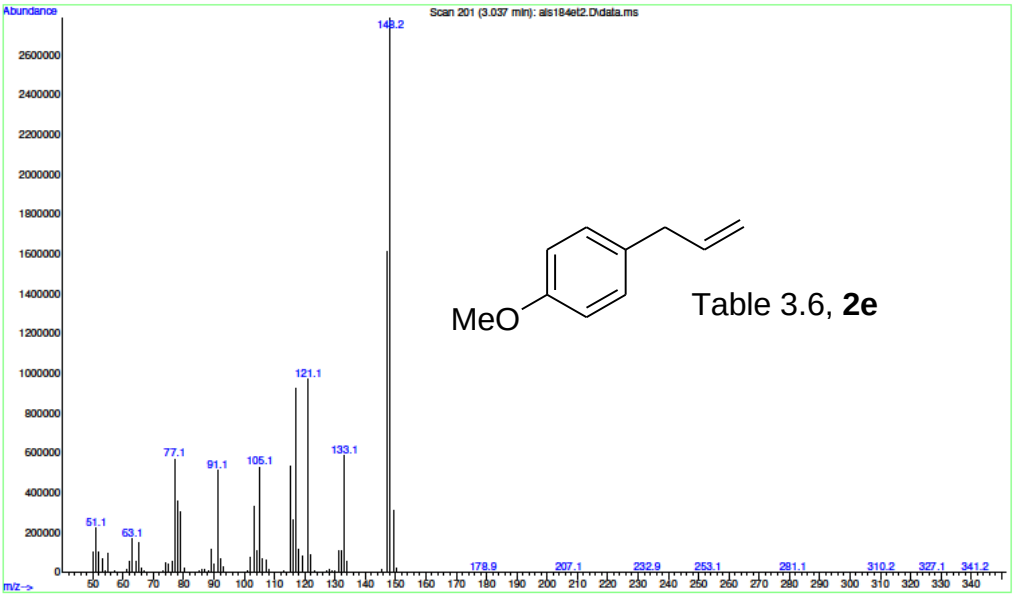
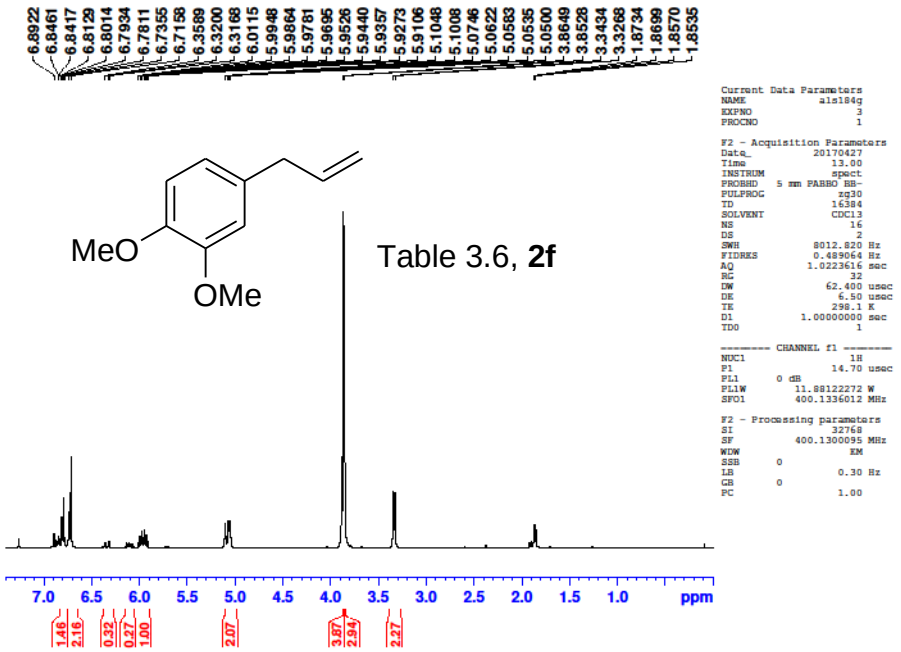


Table 3.6, **2e**

als184g_H



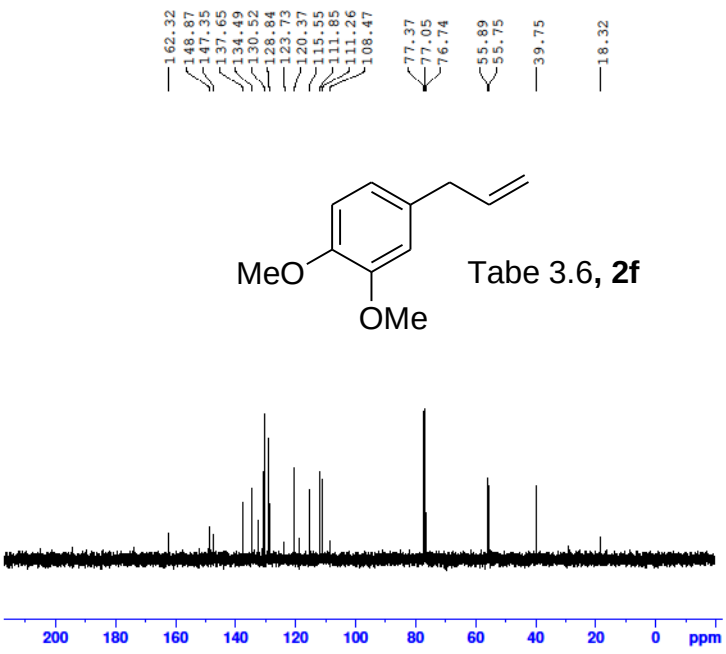

```
Current Data Parameters
NAME                  als184g
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_               20170427
Time                   13.00
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                       32
DW                   62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    14.70 usec
PL1            0 dB
PL1W              11.88122272 W
SFO1             400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300095 MHz
WDW                       EM
SSB            0
LB                     0.30 Hz
GB             0
PC                     1.00
```

als184gc13




```
Current Data Parameters
NAME                  als184g
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_               20170427
Time                   13.06
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       8
DS                       2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                     228
DW                   20.800 usec
DE                    6.50 usec
TE                   298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.50 usec
PL1                   -2.00 dB
PL1W              58.52175522 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2            0 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127741 MHz
WDW                       EM
SSB            0
LB                     1.00 Hz
GB             0
PC                     1.40
```

```
File      :D:\MassHunter\GCMS\1\data\alston\als184g.D
Operator  : duan
Acquired  : 26 Apr 2017  12:17     using AcqMethod M1.M
Instrument :   5977
Sample Name: als184g
Misc Info  :
Vial Number: 4
```

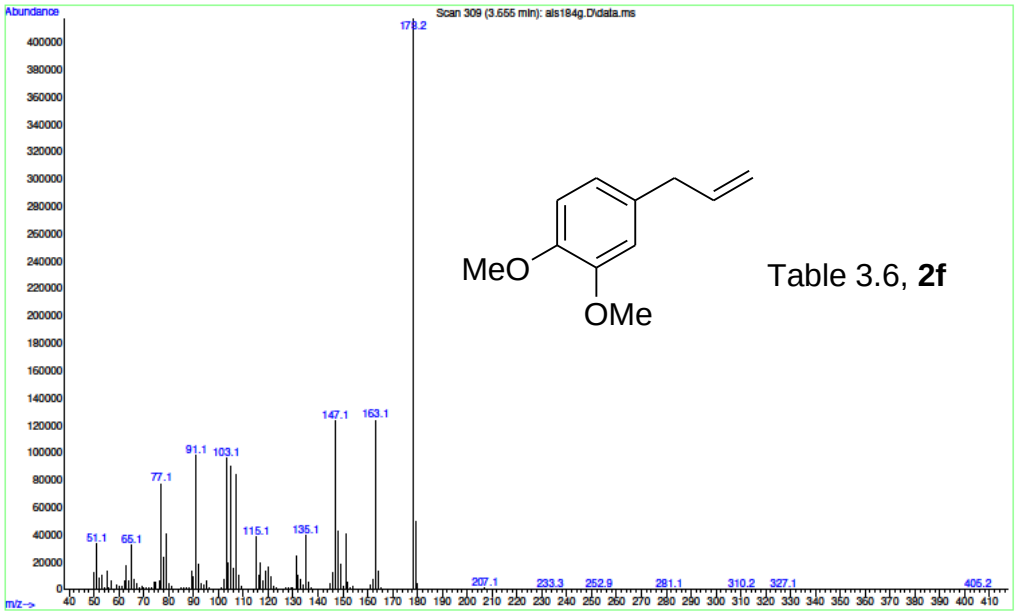


Table 3.6, **2f**

als169H_H

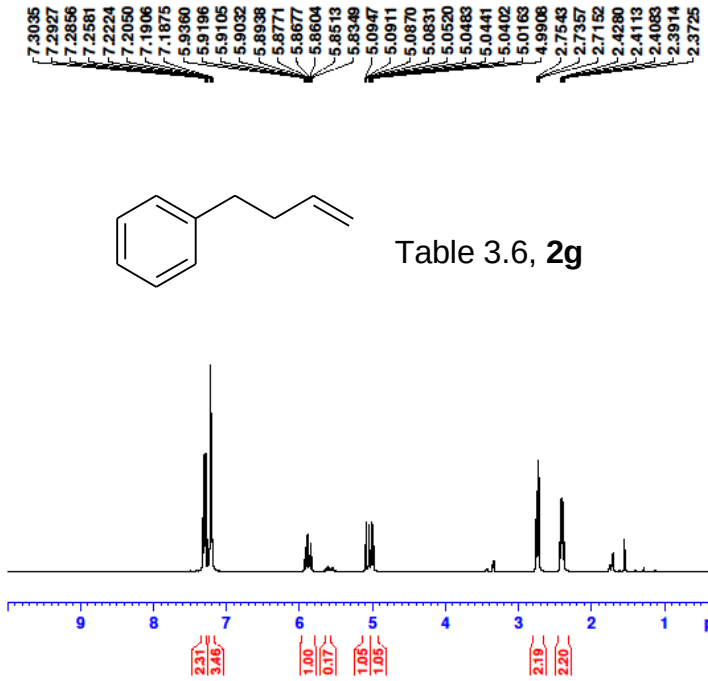


Table 3.6, **2g**

```
Current Data Parameters
NAME                  als169H_H
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20160915
Time                      15.38
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       16384
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8012.820 Hz
FIDRES                0.489064 Hz
AQ                    1.0223616 sec
RG                         80.6
DW                       62.400 usec
DE                        6.50 usec
TE                       297.7 K
D1                    1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        14.70 usec
PL1                  0 dB
PL1W                 11.88122272 W
SFO1                 400.1336012 MHz

F2 - Processing parameters
SI                           32768
SF                    400.1300104 MHz
WDW                             EM
SSB                  0
LB                            0.30 Hz
GB                   0
PC                            1.00
```

als169H_13C

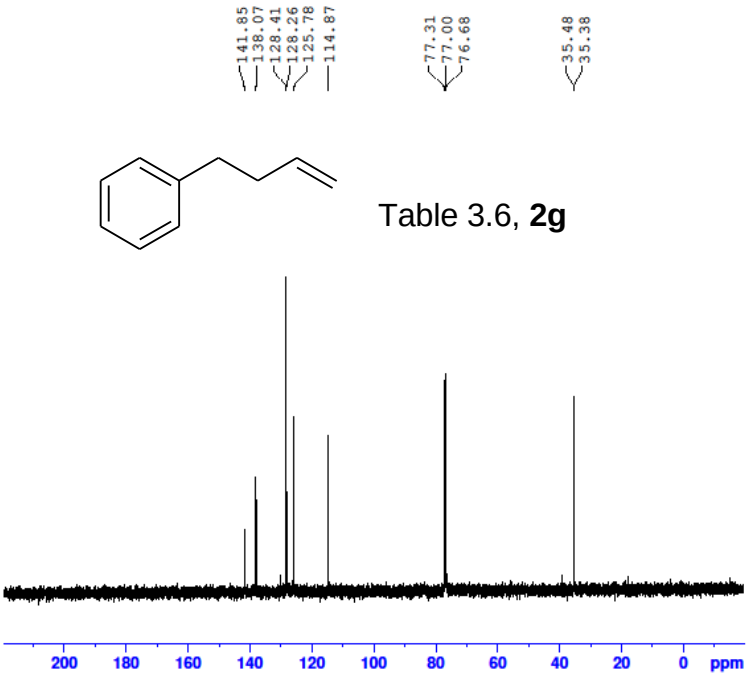


Table 3.6, **2g**

```
Current Data Parameters
NAME                  als169H_13C
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20160919
Time                      10.35
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         108
DS                           2
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                         203
DW                       20.800 usec
DE                        6.50 usec
TE                       299.8 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         13C
P1                         9.50 usec
PL1                       -2.00 dB
PL1W                 58.52175522 W
SFO1                 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                  0 dB
PL12                      15.00 dB
PL13                      15.00 dB
PL2W                 11.88122272 W
PL12W                 0.37571725 W
PL13W                 0.37571725 W
SFO2                 400.1316005 MHz

F2 - Processing parameters
SI                           32768
SF                    100.6127741 MHz
WDW                             EM
SSB                  0
LB                            1.00 Hz
GB                   0
PC                            1.40
```

```
File       :D:\MassHunter\GCMS\1\data\alston\als169H_P.D
Operator   : duan
Acquired   : 14 Sep 2016  15:28     using AcqMethod M1.M
Instrument :   5977
Sample Name: als169H_P
Misc Info  :
Vial Number: 20
```

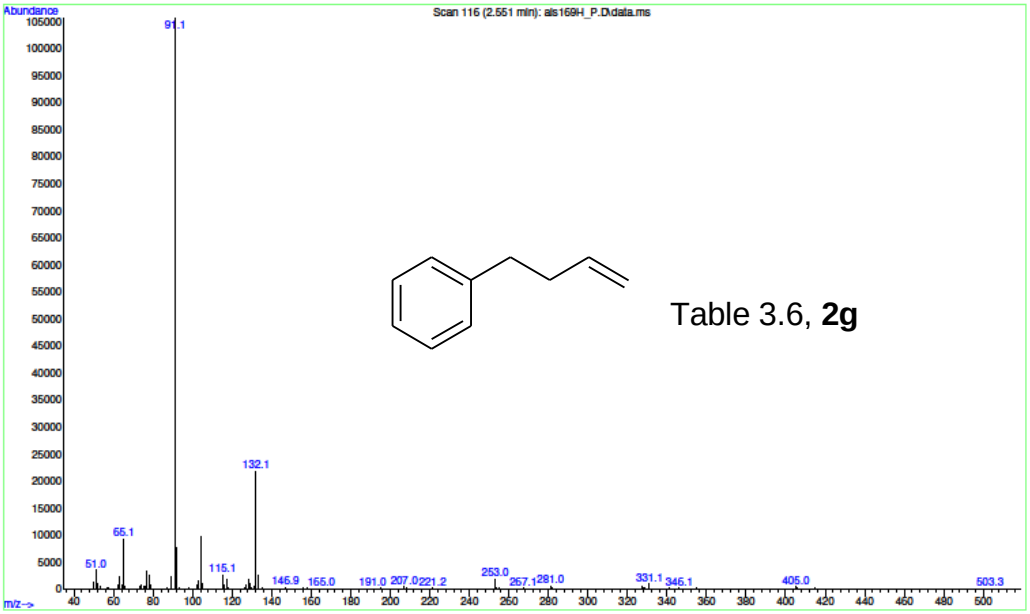
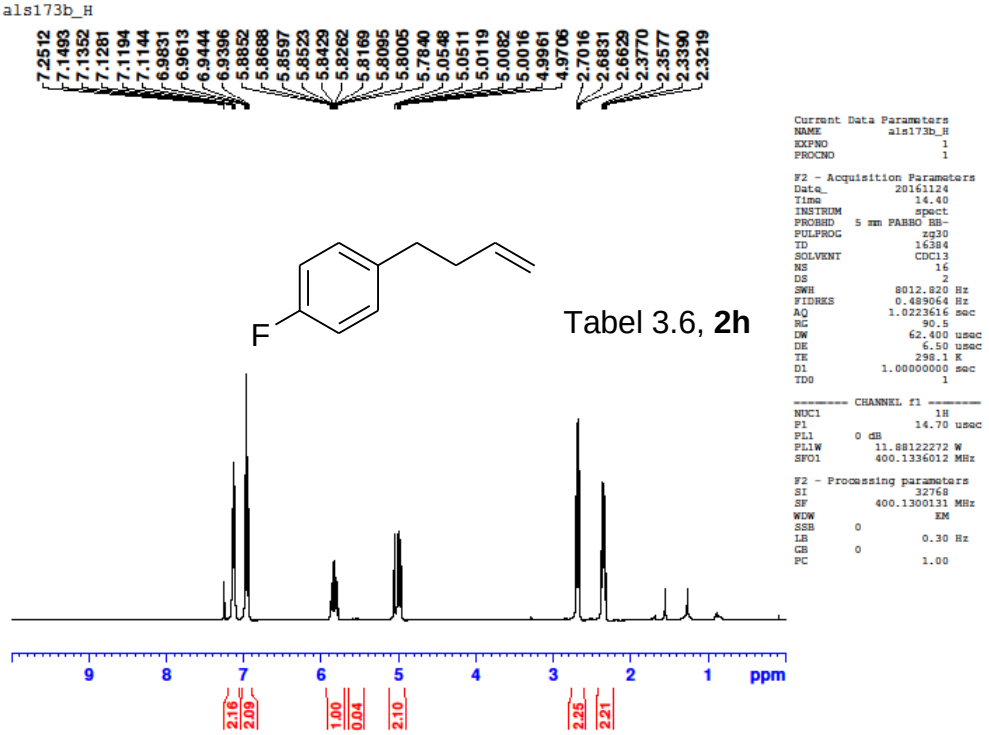
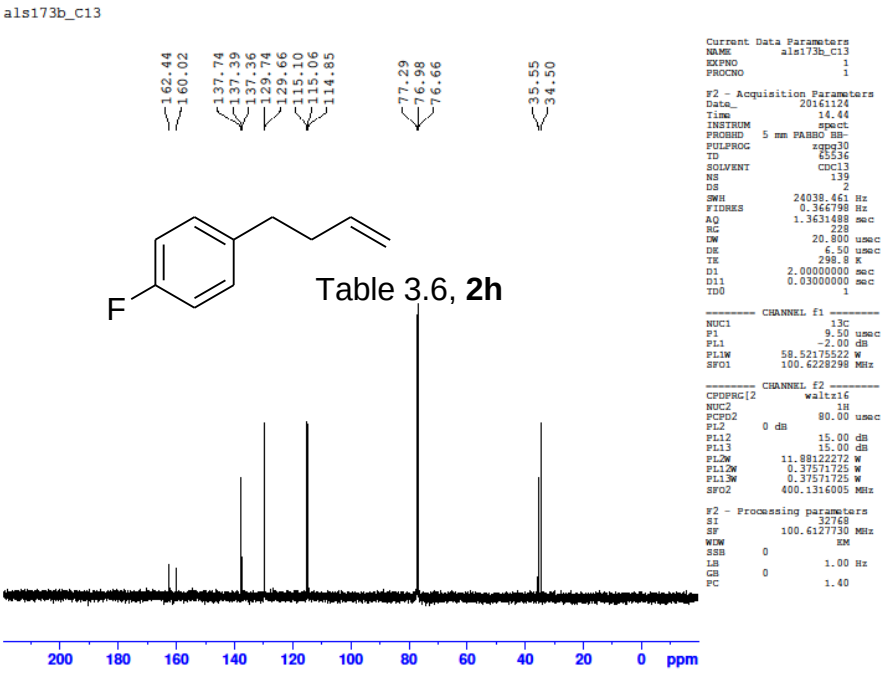


Table 3.6, **2g**


als173b_H
7.2512
7.1493
7.1352
7.1281
7.1194
7.1144
6.9831
6.9613
6.9444
6.9396
5.8852
5.8688
5.8597
5.8523
5.8429
5.8262
5.8169
5.8095
5.8005
5.7840
5.0548
5.0511
5.0119
5.0082
5.0016
4.9961
4.9706
2.7016
2.6831
2.6629
2.3770
2.3577
2.3390
2.3219
F
Tabel 3.6, 2h
Current Data Parameters
NAME als173b_H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Data_ 20161124
Time 14.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 1.0223616 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.70 usec
PL1 0 dB
PL1W 11.88122272 W
SFO1 400.1336012 MHz
F2 - Processing parameters
SI 32768
SF 400.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.16
2.09
1.00
0.04
2.10
2.25
2.21


als173b_C13
162.44
160.02
137.74
137.39
137.36
129.74
129.66
115.10
115.06
114.85
77.29
76.98
76.66
35.55
34.50
F
Table 3.6, 2h
Current Data Parameters
NAME als173b_C13
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Data_ 20161124
Time 14.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 139
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 228
DW 20.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.50 usec
PL1 -2.00 dB
PL1W 58.52175522 W
SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0 dB
PL12 15.00 dB
PL13 15.00 dB
PL2W 11.88122272 W
PL12W 0.37571725 W
PL13W 0.37571725 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127730 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

```
File      :D:\MassHunter\GCMS\1\data\alston\ALS173B.D
Operator  : duan
Acquired  : 11 Nov 2016  14:58     using AcqMethod M1.M
Instrument :
   5977
Sample Name: ALS173B
Misc Info  :
Vial Number: 2
```

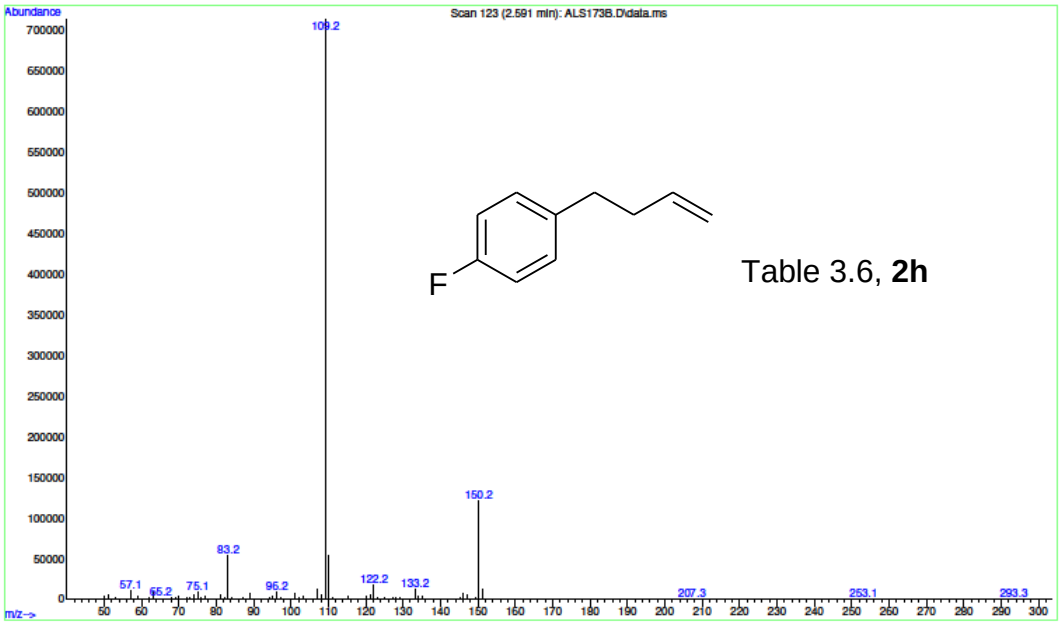
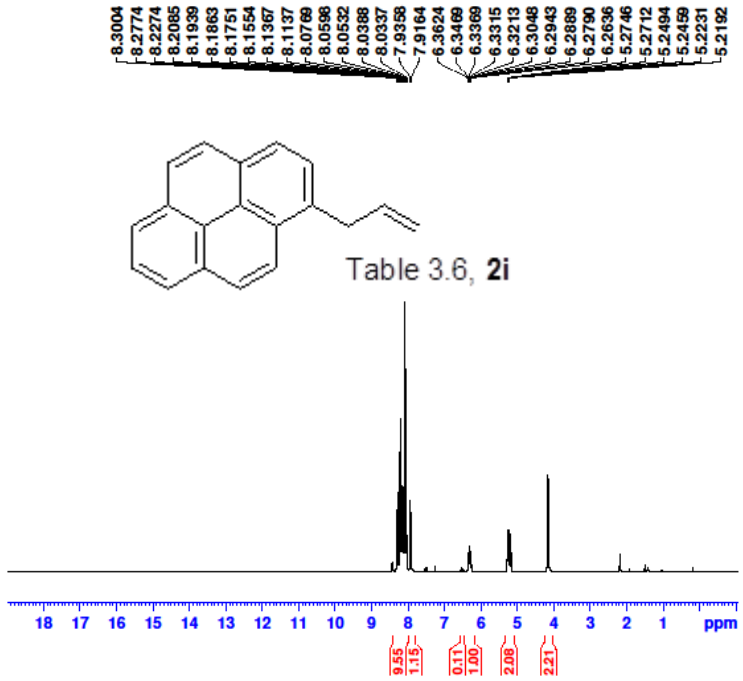


Table 3.6, **2h**

als175e_H




```
Current Data Parameters
NAME                  als175e
EXPNO                       1
PROCNO                      1

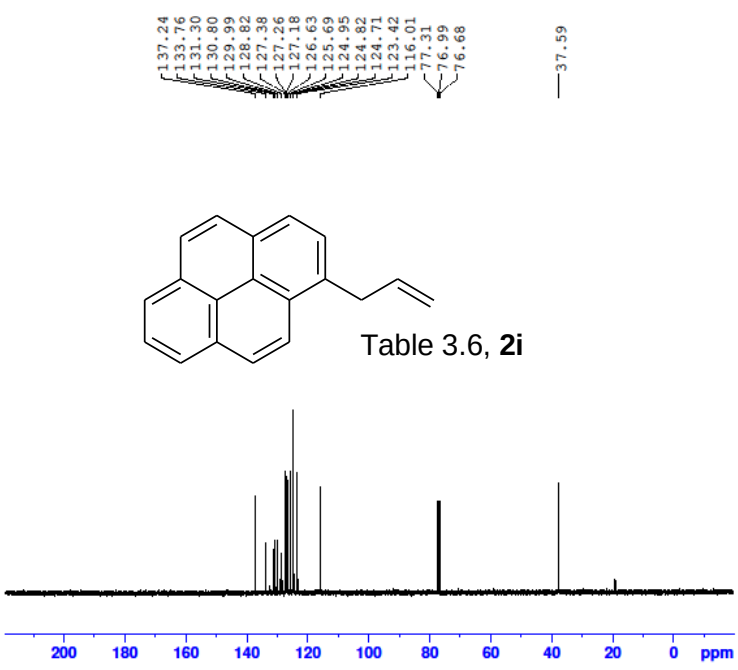
F2 - Acquisition Parameters
Date_               20170210
Time                    9.22
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      22.6
DW                    62.400 usec
DE                     6.50 usec
TE                    297.9 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1                0 dB
PL1W              11.88122272 W
SFO1             400.1336012 MHz

F2 - Processing parameters
SI                         32768
SF                400.1300103 MHz
WDW                           EM
SSB                0
LB                         0.30 Hz
GB                 0
PC                         1.00
```

Table 3.6, **2i**

als175e_C13




```
Current Data Parameters
NAME                  als175e
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20170210
Time                    9.28
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        43
DS                         2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                        144
DW                    20.800 usec
DE                     6.50 usec
TE                    298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                100.6127909 MHz
WDW                           EM
SSB                0
LB                         1.00 Hz
GB                 0
PC                         1.40
```

```
File       :D:\MassHunter\GCMS\1\data\alston\als175e.D
Operator   : duan
Acquired   : 07 Feb 2017  15:39     using AcqMethod M1.M
Instrument :    5977
Sample Name: als175e
Misc Info  :
Vial Number: 150
```

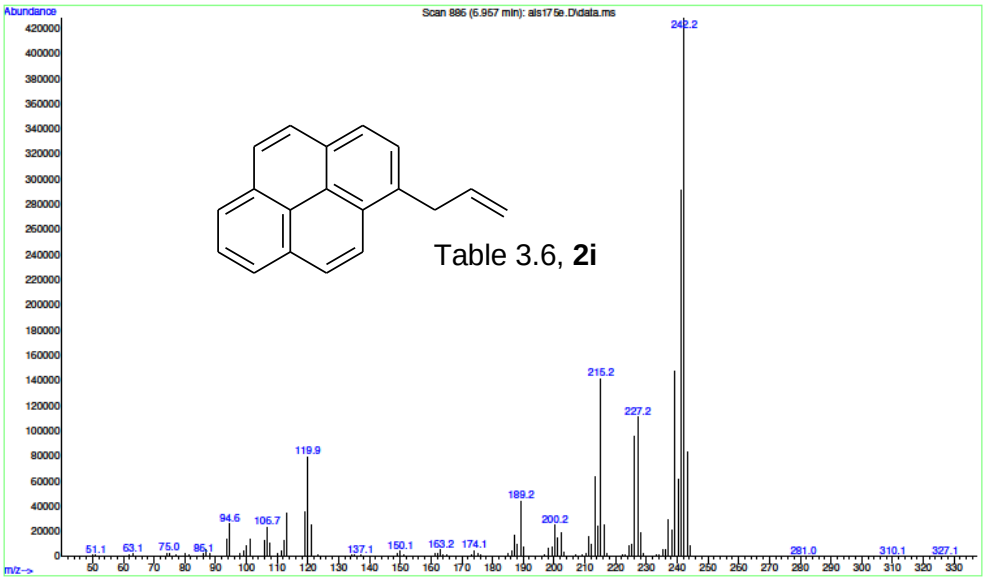


Table 3.6, **2i**

acth25a_H

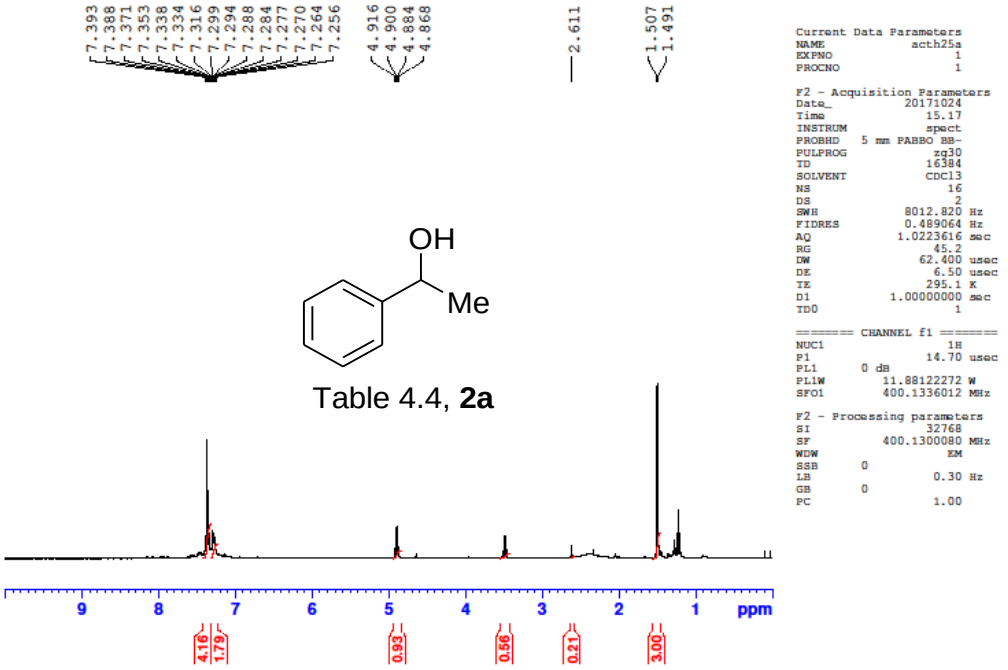


Table 4.4, **2a**

```
Current Data Parameters
NAME                  acth25a
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171024
Time                   15.17
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      45.2
DW                    62.400 usec
DE                     6.50 usec
TE                    295.1 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1            0 dB
PL1W              11.88122272 W
SFO1              400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300080 MHz
WDW                          EM
SSB            0
LB                         0.30 Hz
GB             0
PC                         1.00
```

acth25a_c13

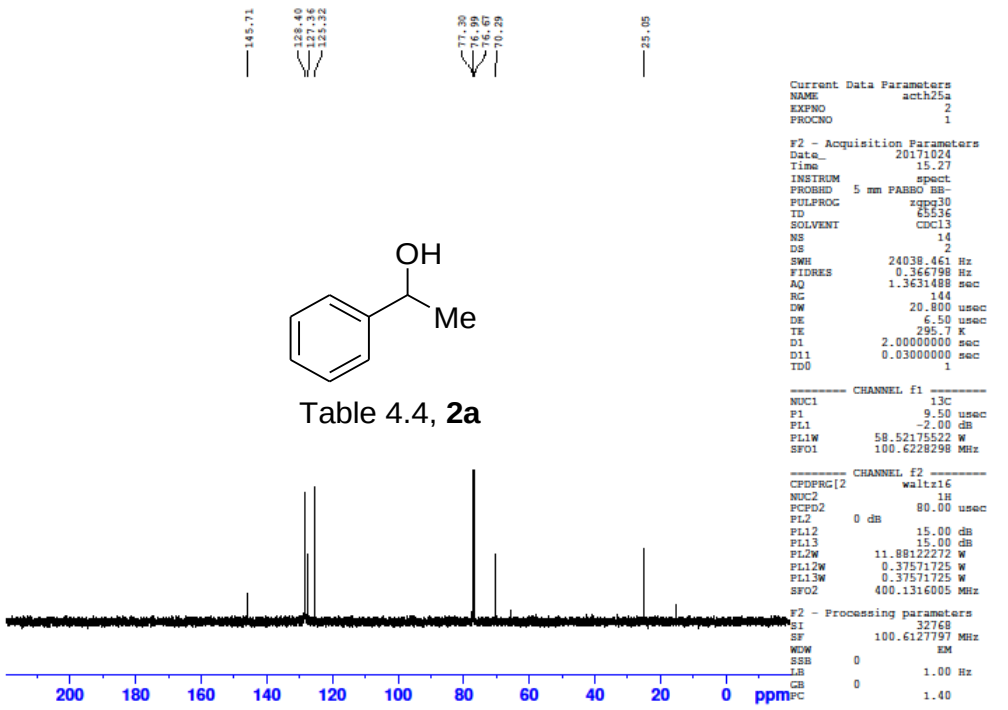


Table 4.4, **2a**

```
Current Data Parameters
NAME                  acth25a
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171024
Time                   15.27
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       14
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      144
DW                    20.800 usec
DE                     6.50 usec
TE                    295.7 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2            0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127797 MHz
WDW                          EM
SSB            0
LB                         1.00 Hz
GB             0
PC                         1.40
```

acth33H2_H

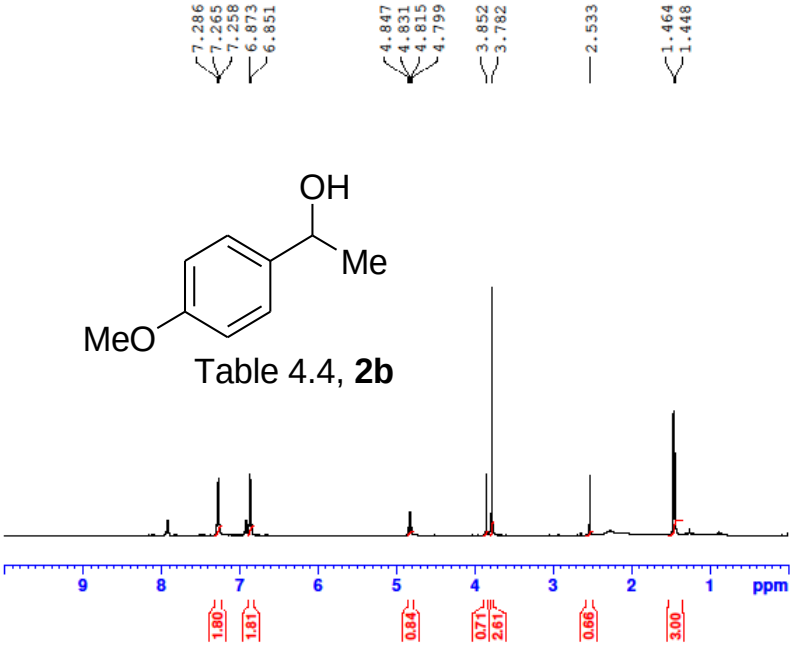


Table 4.4, **2b**

```
Current Data Parameters
NAME            acth33H2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171116
Time               16.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                16384
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.489064 Hz
AQ             1.0223616 sec
RG                   36
DW                62.400 usec
DE                 6.50 usec
TE                298.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1        0 dB
PL1W       11.88122272 W
SFO1       400.1336012 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300102 MHz
WDW                   EM
SSB        0
LB                 0.30 Hz
GB         0
PC                 1.00
```

acth33H2_C13

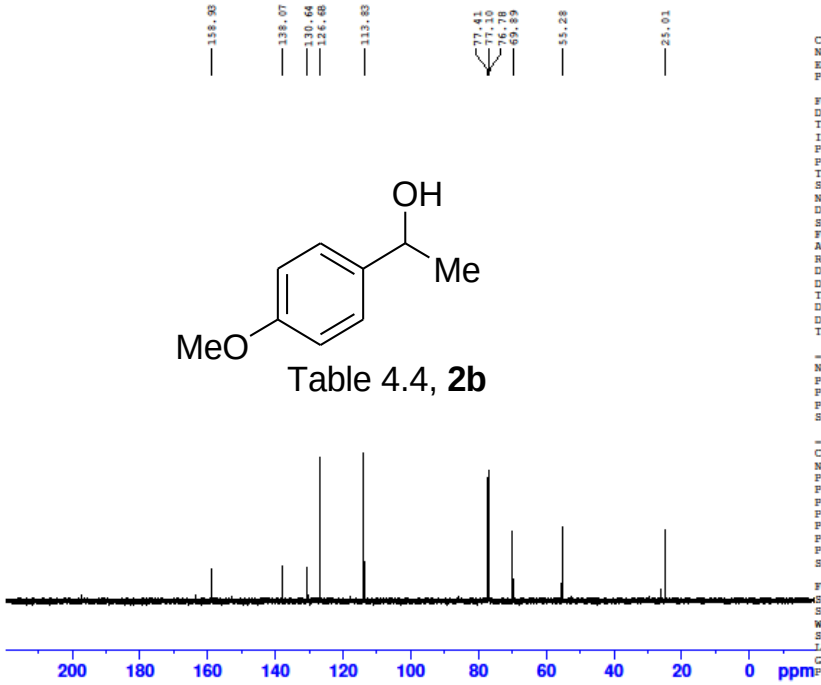


Table 4.4, **2b**

```
Current Data Parameters
NAME            acth33H2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171116
Time               16.07
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   27
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                  228
DW                20.800 usec
DE                 6.50 usec
TE                298.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.50 usec
PL1               -2.00 dB
PL1W       58.52175522 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2        0 dB
PL12              15.00 dB
PL13              15.00 dB
PL2W       11.88122272 W
PL12W       0.37571725 W
PL13W       0.37571725 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB        0
LB                 1.00 Hz
GB         0
PC                 1.40
```

acth33I2_H

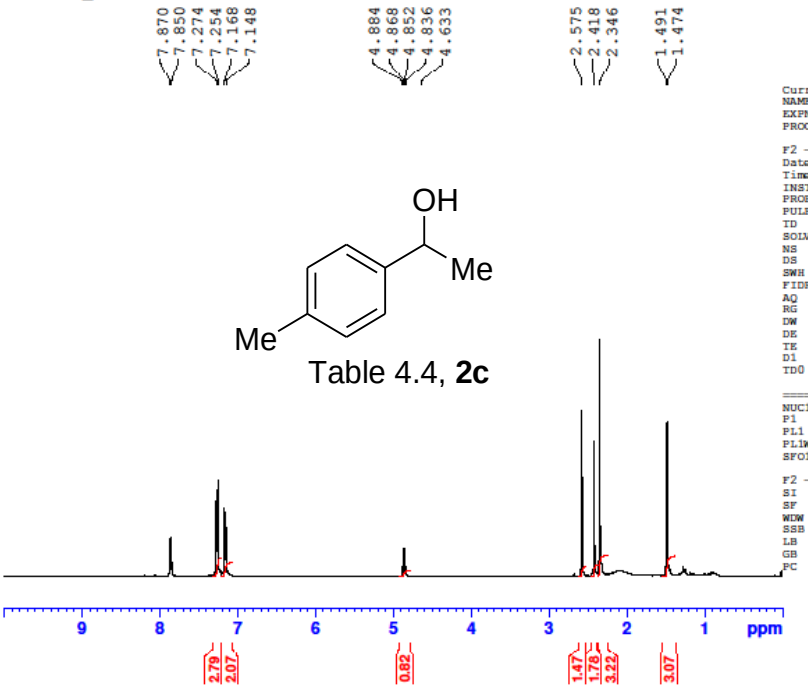


Table 4.4, **2c**

```
Current Data Parameters
NAME                  acth33I2
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_               20171116
Time                   18.16
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                       32
DW                    62.400 usec
DE                     6.50 usec
TE                   298.3 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.70 usec
PL1          0 dB
PL1W            11.88122272 W
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                       32768
SF                 400.1300093 MHz
WDW                         EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

acth33I2_c13

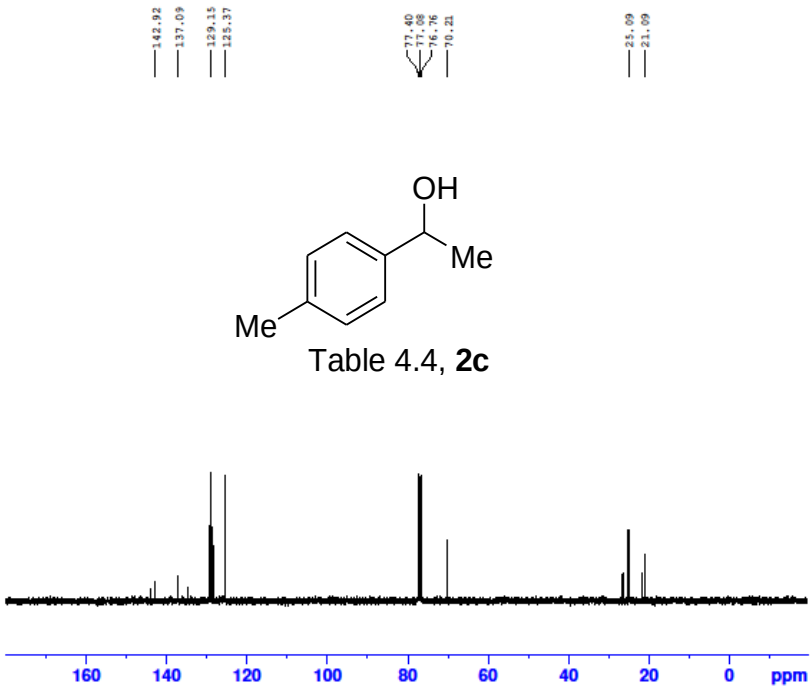


Table 4.4, **2c**

```
Current Data Parameters
NAME                  acth33I2
EXPNO                        3
PROCNO                       1

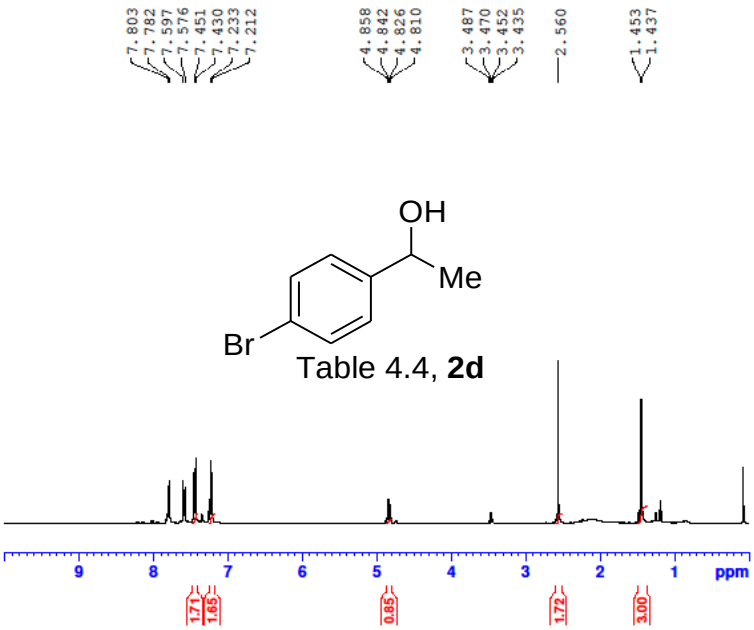
F2 - Acquisition Parameters
Date_               20171116
Time                   18.23
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       20
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                       64
DW                    20.800 usec
DE                     6.50 usec
TE                   298.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                     13C
P1                     9.50 usec
PL1                   -2.00 dB
PL1W            58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2          0 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W            11.88122272 W
PL12W            0.37571725 W
PL13W            0.37571725 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF                 100.6127690 MHz
WDW                         EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

acth33k_H



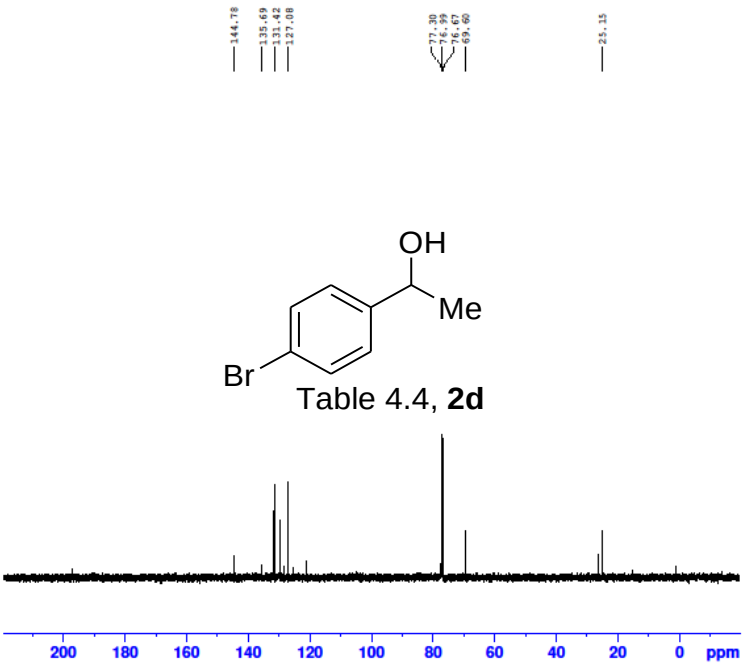

```
Current Data Parameters
NAME                  acth33k
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171114
Time                   16.18
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                       36
DW                    62.400 usec
DE                     6.50 usec
TE                   298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 =======
NUC1                       1H
P1                      14.70 usec
PL1          0 dB
PL1W            11.88122272 W
SFO1            400.1336012 MHz

F2 - Processing parameters
SI                      32768
SF              400.1300095 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

acth33k_c13




```
Current Data Parameters
NAME                  acth33k
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171114
Time                   16.22
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       18
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      228
DW                    20.800 usec
DE                     6.50 usec
TE                   298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W            58.52175522 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2          0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W            11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF              100.6127785 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

acth33o_H

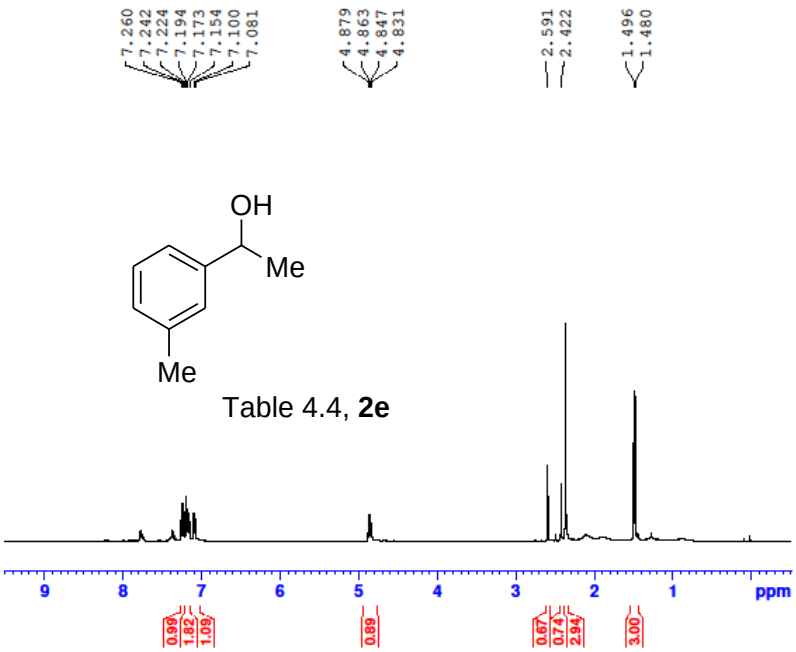


Table 4.4, **2e**

```
Current Data Parameters
NAME                  acth33o
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Data_                20171114
Time                    16.27
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.489064 Hz
AQ                1.0223616 sec
RG                        36
DW                    62.400 usec
DE                     6.50 usec
TE                    298.1 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.70 usec
PL1          0 dB
PL1W           11.88122272 W
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                     32768
SF                400.1300099 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```

acth33o_C13

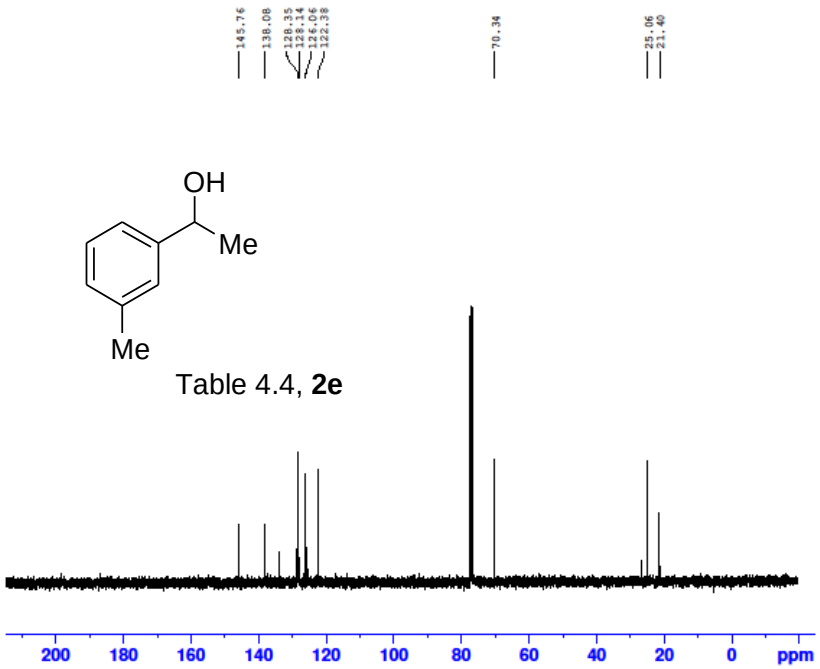


Table 4.4, **2e**

```
Current Data Parameters
NAME                  acth33o
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Data_                20171114
Time                    17.11
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        42
DS                         2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                1.3631488 sec
RG                       256
DW                    20.800 usec
DE                     6.50 usec
TE                    298.6 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     9.50 usec
PL1                   -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2          0 dB
PL12                  15.00 dB
PL13                  15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                     32768
SF                100.6127750 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```

acth33q_H

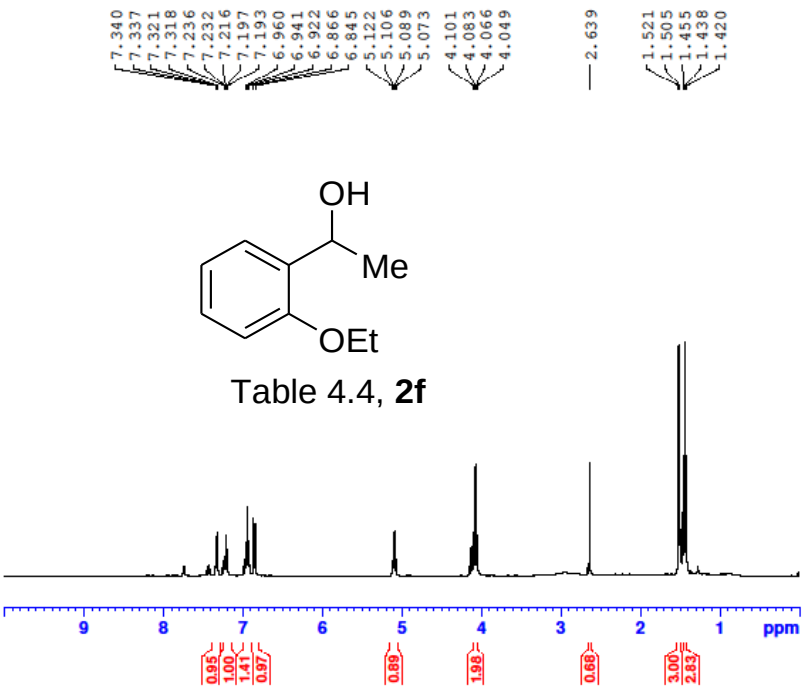


Table 4.4, **2f**

```
Current Data Parameters
NAME                  acth33q
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171116
Time                   16.24
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      25.4
DW                    62.400 usec
DE                     6.50 usec
TE                    298.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1            0 dB
PL1W              11.88122272 W
SFO1             400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300093 MHz
WDW                          EM
SSB            0
LB                         0.30 Hz
GB             0
PC                         1.00
```

acth33q_C13

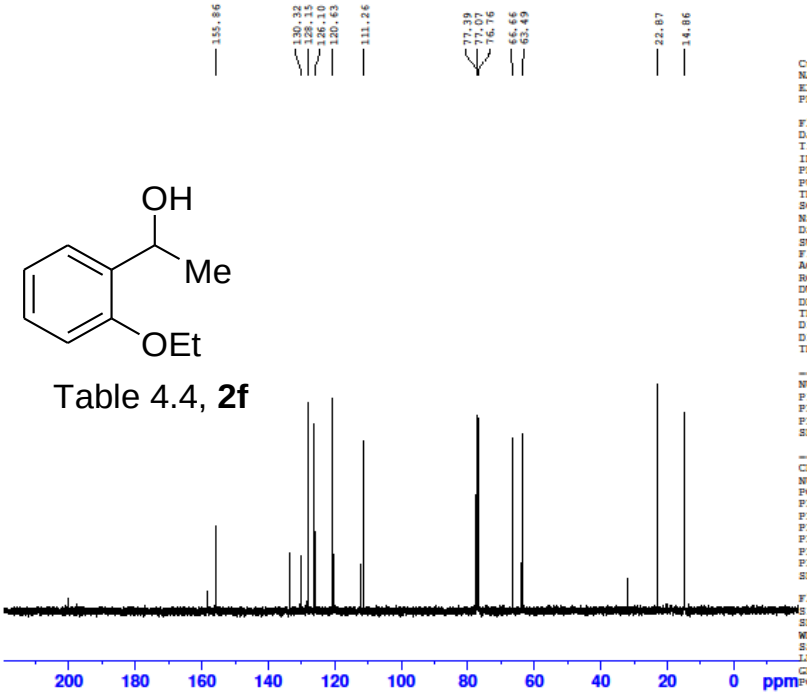


Table 4.4, **2f**

```
Current Data Parameters
NAME                  acth33q
EXPNO                       2
PROCNO                      1

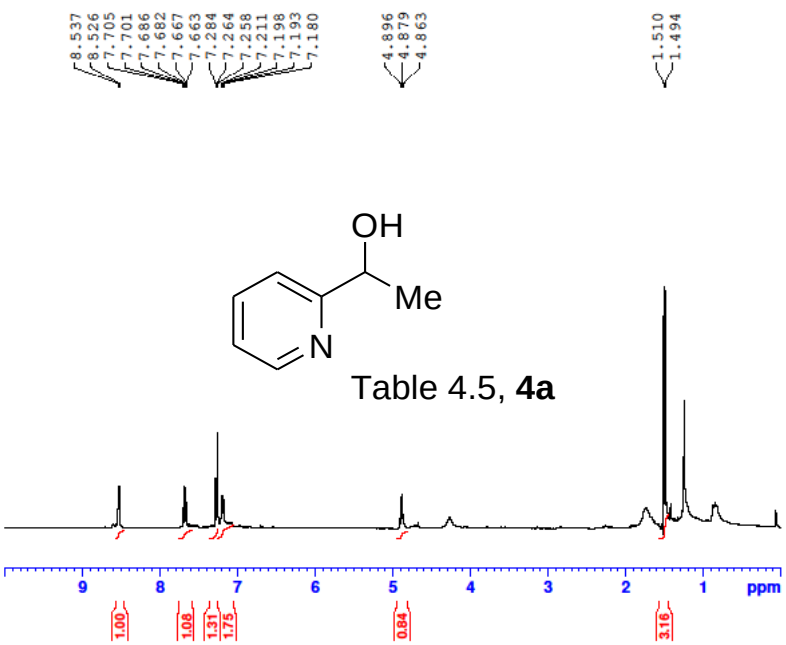
F2 - Acquisition Parameters
Date_               20171116
Time                   18.09
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       40
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      228
DW                    20.800 usec
DE                     6.50 usec
TE                    298.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2            0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127741 MHz
WDW                          EM
SSB            0
LB                         1.00 Hz
GB             0
PC                         1.40
```

acth33a_H



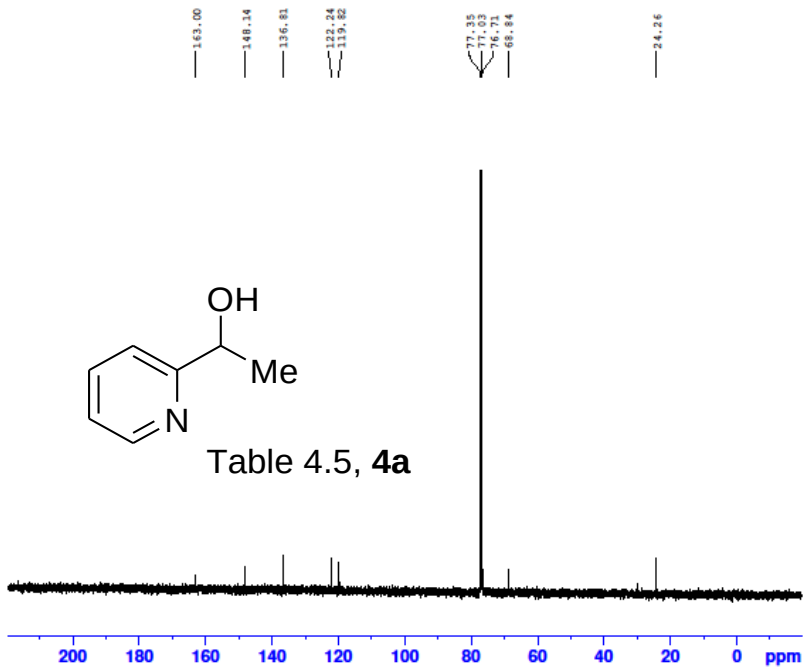

```
Current Data Parameters
NAME                  acth33a
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171109
Time                    9.43
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      128
DW                   62.400 usec
DE                    6.50 usec
TE                   297.9 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1             0 dB
PL1W           11.88122272 W
SFO1          400.1336012 MHz

F2 - Processing parameters
SI                      32768
SF                400.1300106 MHz
WDW                        EM
SSB             0
LB                      0.30 Hz
GB              0
PC                      1.00
```

acth33a_13C




```
Current Data Parameters
NAME                  acth33a
EXPNO                       2
PROCNO                      1

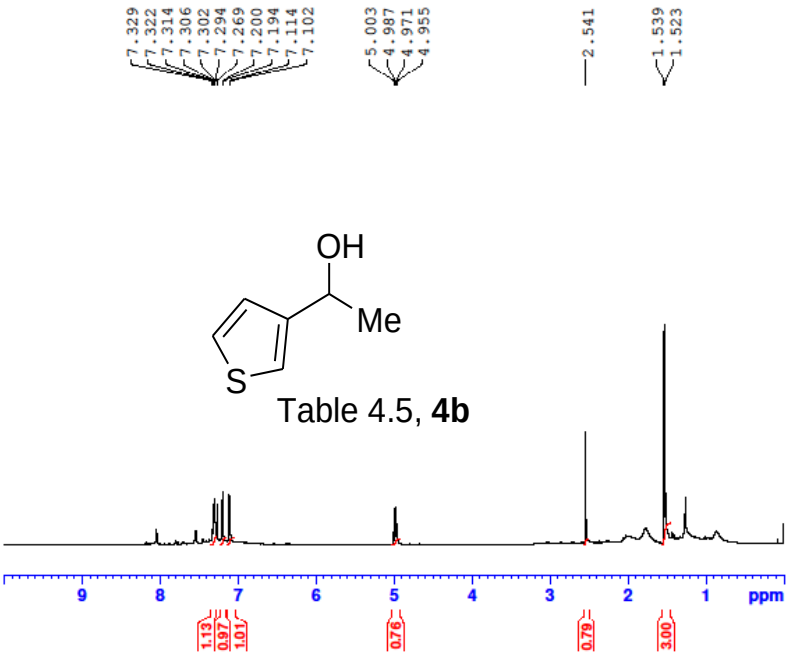
F2 - Acquisition Parameters
Date_               20171109
Time                   10.52
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      145
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      203
DW                   20.800 usec
DE                    6.50 usec
TE                   298.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -2.00 dB
PL1W           58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2             0 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF                100.6127678 MHz
WDW                        EM
SSB             0
LB                      1.00 Hz
GB              0
PC                      1.40
```

acth33d_H



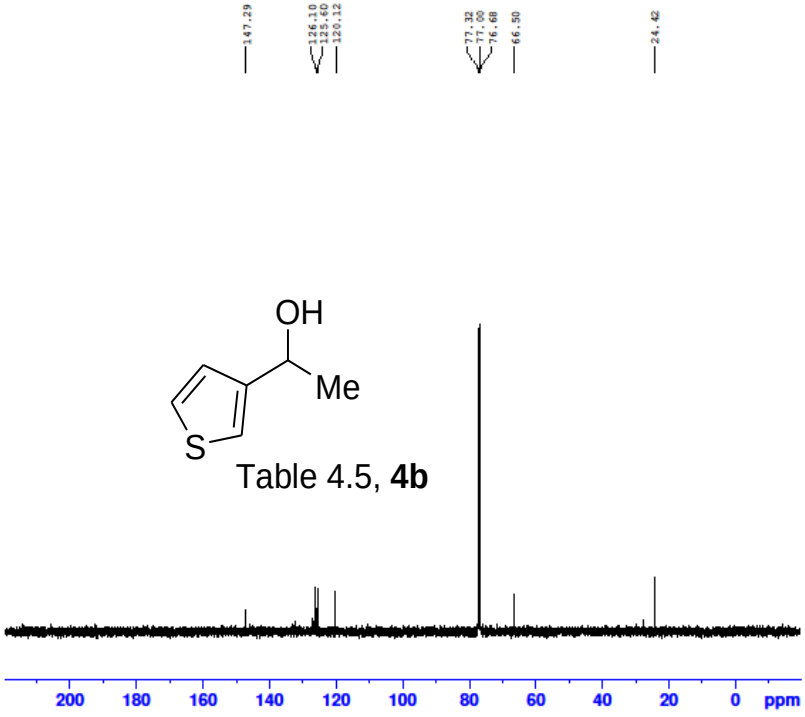

```
Current Data Parameters
NAME                  acth33d
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20171114
Time                   16.05
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      101
DW                   62.400 usec
DE                    6.50 usec
TE                   298.2 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1          0 dB
PL1W            11.88122272 W
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300059 MHz
WDW                          EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

acth33d_ac13




```
Current Data Parameters
NAME                  acth33d
EXPNO                       2
PROCNO                      1

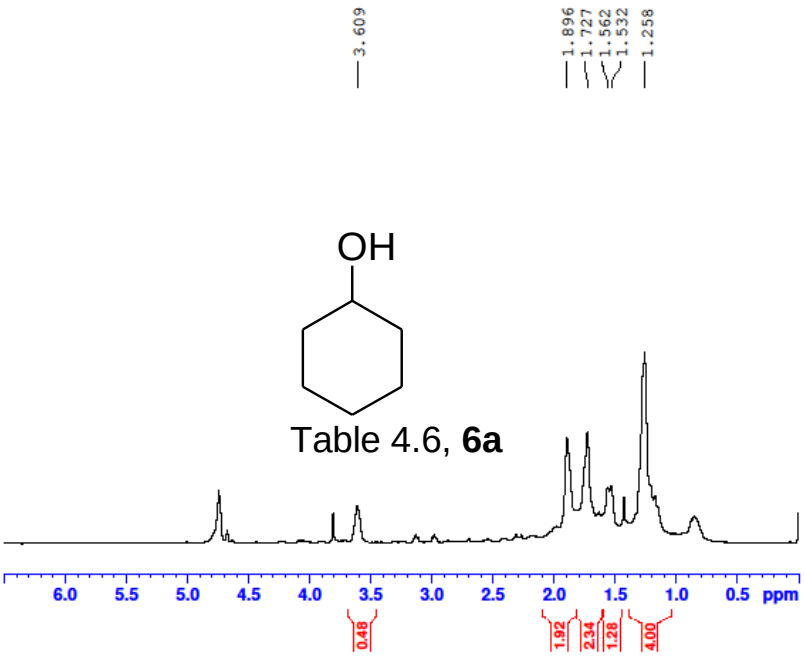
F2 - Acquisition Parameters
Date_              20171114
Time                   16.11
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       59
DS                        2
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      228
DW                   20.800 usec
DE                    6.50 usec
TE                   298.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -2.00 dB
PL1W            58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2          0 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W            11.88122272 W
PL12W            0.37571725 W
PL13W            0.37571725 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127736 MHz
WDW                          EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.40
```

acth35a_H



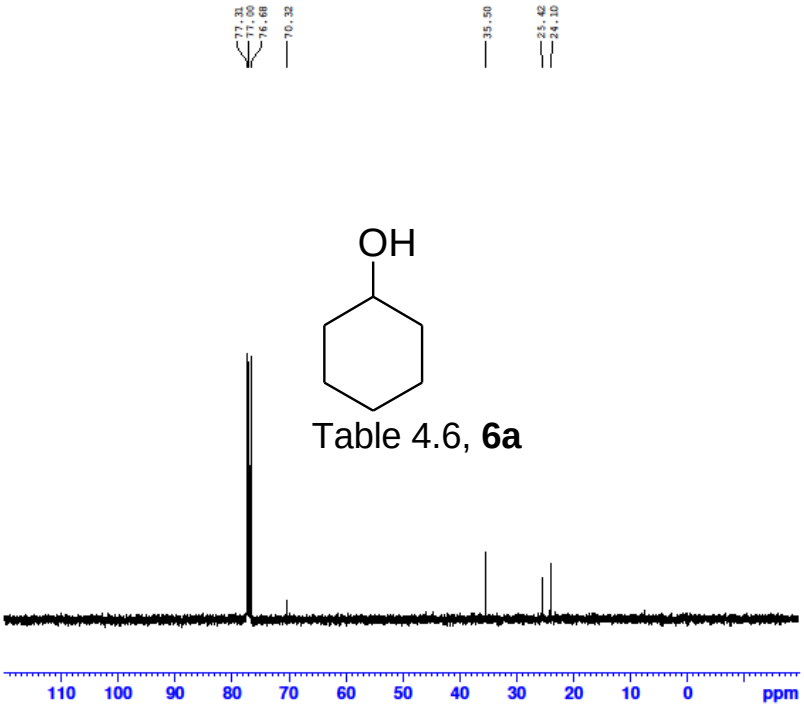

```
Current Data Parameters
NAME                  acth35a
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171214
Time                   12.00
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      90.5
DW                    62.400 usec
DE                     6.50 usec
TE                    297.9 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1            0 dB
PL1W            11.88122272 W
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300080 MHz
WDW                          EM
SSB            0
LB                      0.30 Hz
GB             0
PC                        1.00
```

acth35a_13C




```
Current Data Parameters
NAME                  acth35a
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171214
Time                   12.05
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       67
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      256
DW                    20.800 usec
DE                     6.50 usec
TE                    298.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2            0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W            11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127722 MHz
WDW                          EM
SSB            0
LB                      1.00 Hz
GB             0
PC                        1.40
```

acth35b_H

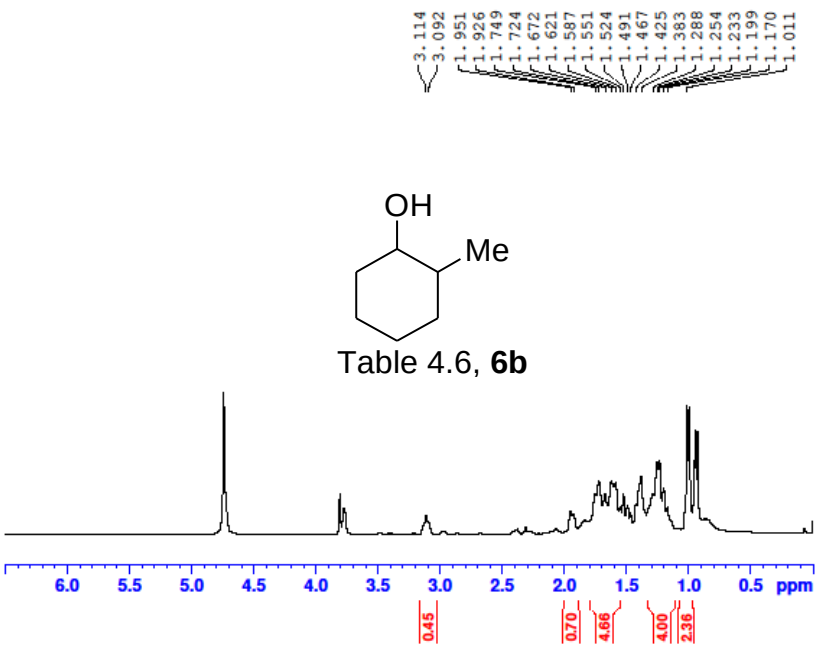


Table 4.6, **6b**

```
Current Data Parameters
NAME                  acth35b
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171214
Time                   12.13
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.489064 Hz
AQ                  1.0223616 sec
RG                      50.8
DW                    62.400 usec
DE                     6.50 usec
TE                    297.8 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1          0 dB
PL1W          11.88122272 W
SFO1          400.1336012 MHz

F2 - Processing parameters
SI                      32768
SF            400.1300069 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

acth35b_c13

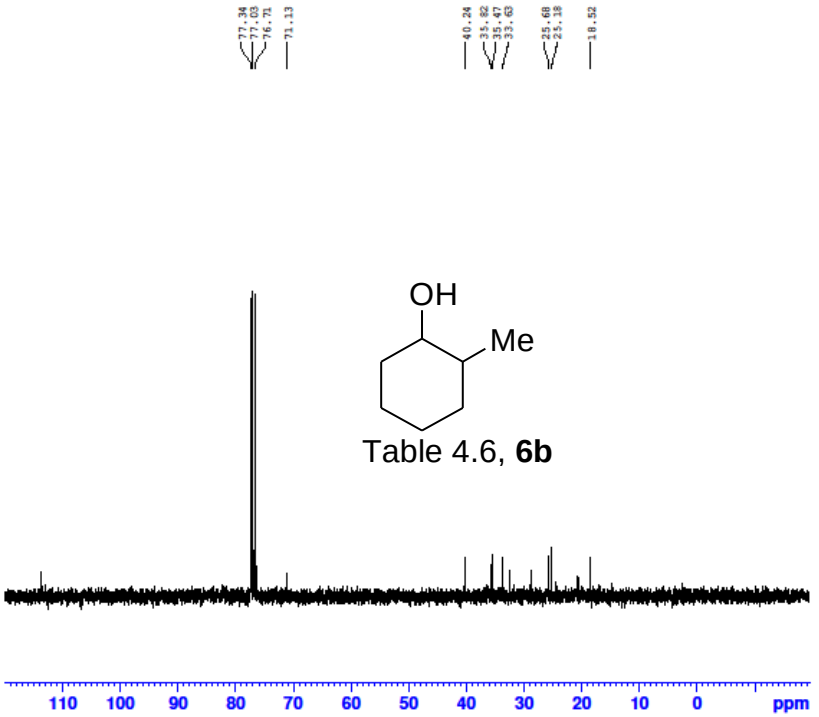


Table 4.6, **6b**

```
Current Data Parameters
NAME                  acth35b
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171214
Time                   12.17
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        34
DS                         2
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631488 sec
RG                        203
DW                    20.800 usec
DE                     6.50 usec
TE                    298.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W          58.52175522 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2          0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W          11.88122272 W
PL12W          0.37571725 W
PL13W          0.37571725 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF            100.6127702 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

acth33g_H

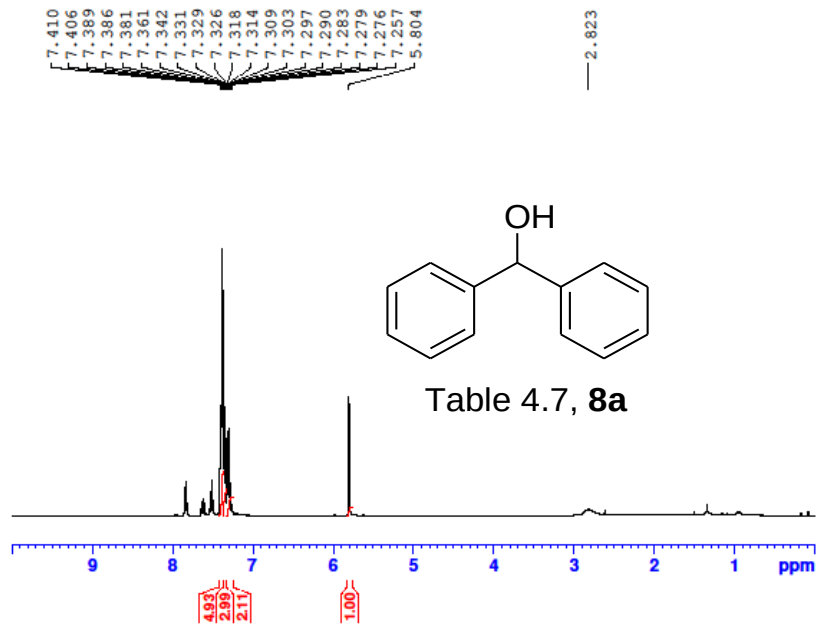


Table 4.7, **8a**

```
Current Data Parameters
NAME                  acth33g
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171109
Time                   10.40
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      25.4
DW                    62.400 usec
DE                     6.50 usec
TE                   298.1 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1             0 dB
PL1W              11.88122272 W
SFO1             400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                 400.1300106 MHz
WDW                          EM
SSB             0
LB                       0.30 Hz
GB              0
PC                       1.00
```

acth33g_13C

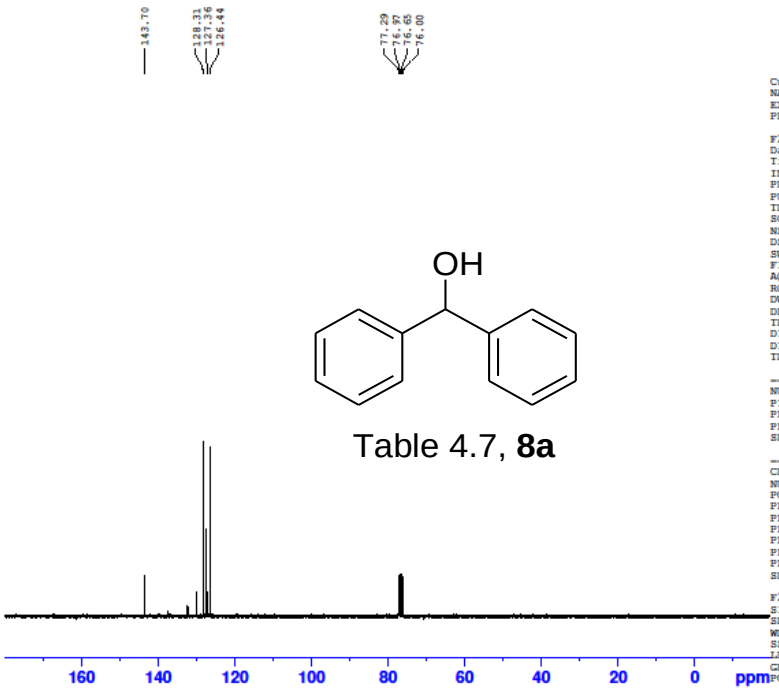


Table 4.7, **8a**

```
Current Data Parameters
NAME                  acth33g
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171109
Time                   10.46
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      203
DW                   20.800 usec
DE                     6.50 usec
TE                   298.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2             0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                 100.6127909 MHz
WDW                          EM
SSB             0
LB                       1.00 Hz
GB              0
PC                       1.40
```

acth34a_H

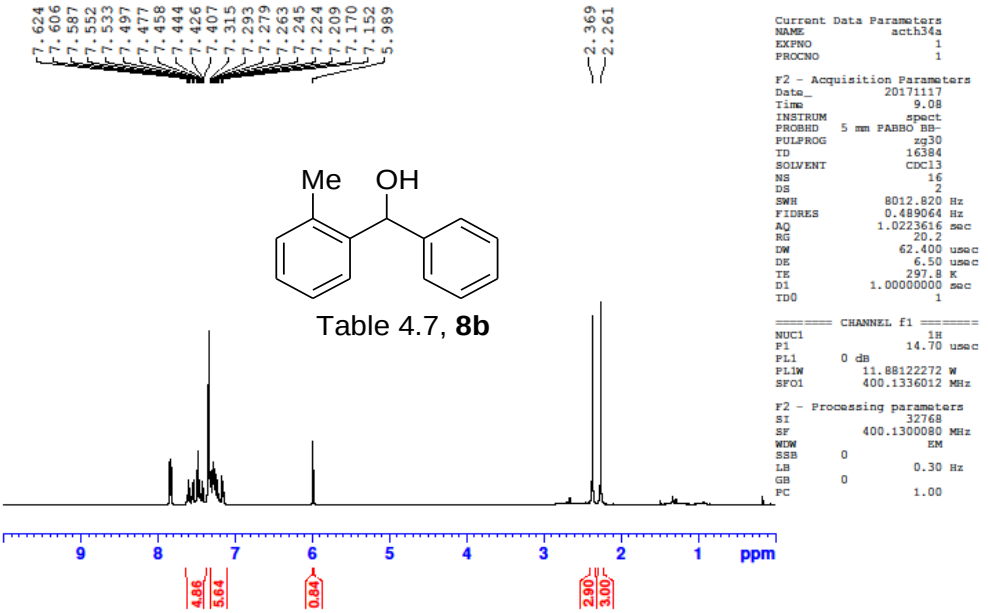


Table 4.7, **8b**

```
Current Data Parameters
NAME                  acth34a
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                    9.08
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      20.2
DW                    62.400 usec
DE                     6.50 usec
TE                   297.8 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1             0 dB
PL1W              11.88122272 W
SFO1              400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                  400.1300080 MHz
WDW                        EM
SSB             0
LB                       0.30 Hz
GB              0
PC                       1.00
```

acth34a_C13

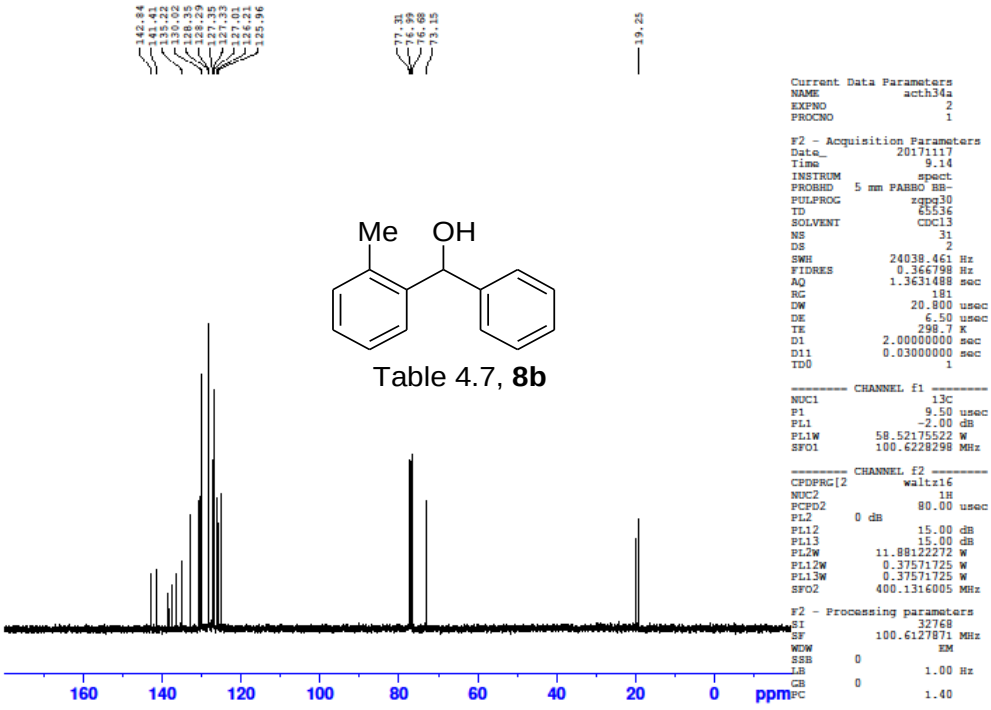


Table 4.7, **8b**

```
Current Data Parameters
NAME                  acth34a
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                    9.14
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       31
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      181
DW                    20.800 usec
DE                     6.50 usec
TE                   298.7 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.50 usec
PL1                     -2.00 dB
PL1W              58.52175522 W
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2             0 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127871 MHz
WDW                        EM
SSB             0
LB                       1.00 Hz
GB              0
PC                       1.40
```

acth34f_H

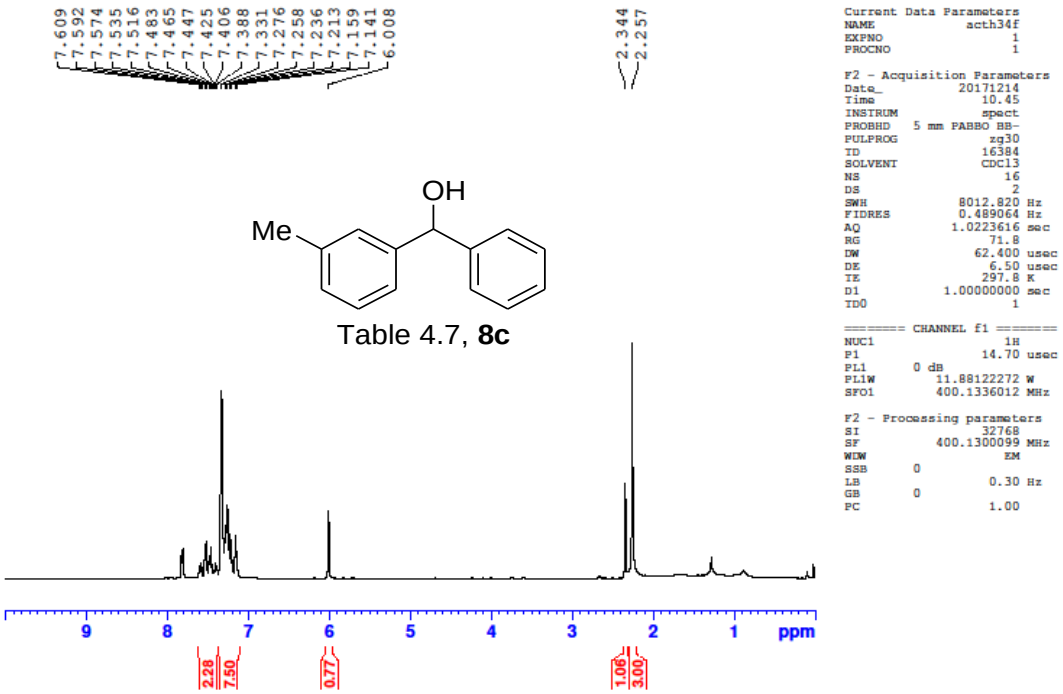


Table 4.7, **8c**

```
Current Data Parameters
NAME                  acth34f
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171214
Time                   10.45
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDC13
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      71.8
DW                    62.400 usec
DE                     6.50 usec
TE                    297.8 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 =======
NUC1                       1H
P1                      14.70 usec
PL1            0 dB
PL1W            11.88122272 W
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                      32768
SF                 400.1300099 MHz
WDW                        EM
SSB            0
LB                      0.30 Hz
GB             0
PC                      1.00
```

acth34f_c13

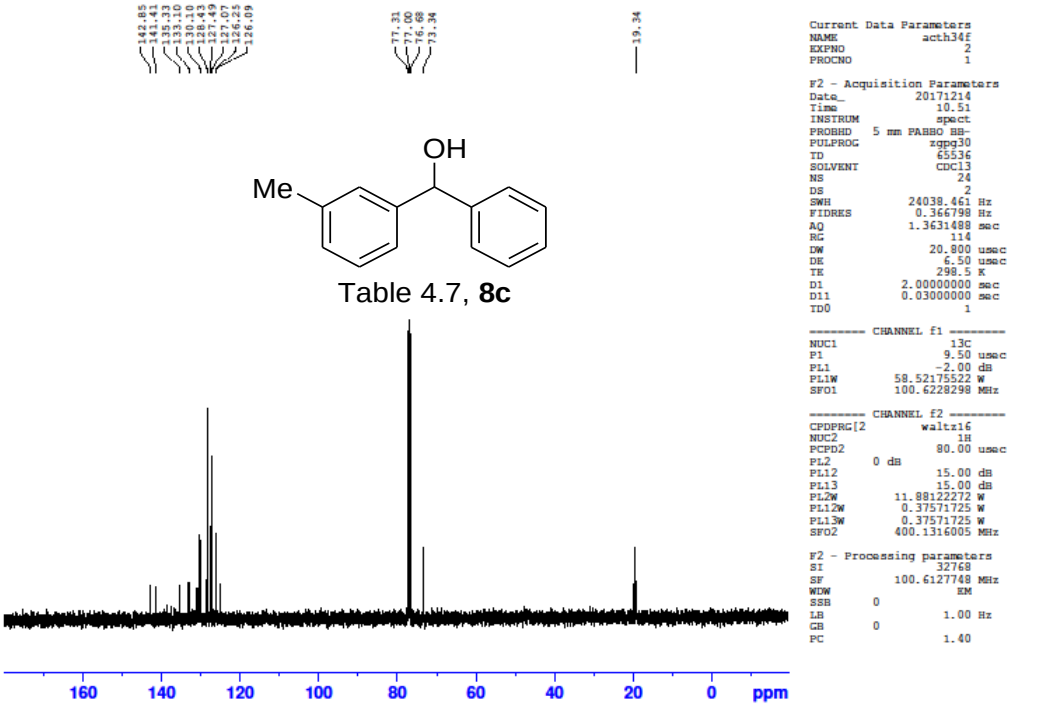


Table 4.7, **8c**

```
Current Data Parameters
NAME                  acth34f
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171214
Time                   10.51
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDC13
NS                       24
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      114
DW                    20.800 usec
DE                     6.50 usec
TE                    298.5 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W            58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2            0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W            11.88122272 W
PL12W            0.37571725 W
PL13W            0.37571725 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF                 100.6127748 MHz
WDW                        EM
SSB            0
LB                      1.00 Hz
GB             0
PC                      1.40
```

ACTH34D_H

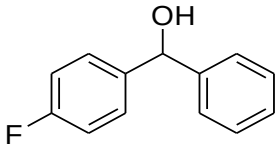
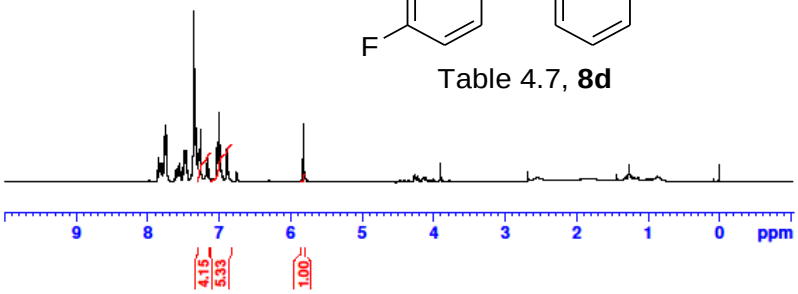


Table 4.7, **8d**



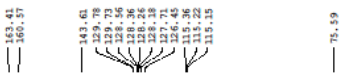

```
Current Data Parameters
NAME                  ACTH34D
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                   14.04
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      80.6
DW                    62.400 usec
DE                     6.50 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1             0 dB
PL1W              11.88122272 W
SFO1             400.1336012 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300097 MHz
WDW                        EM
SSB             0
LB                      0.30 Hz
GB              0
PC                      1.00
```

acth34d_13C



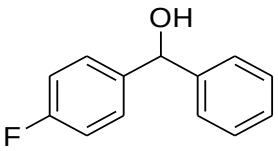
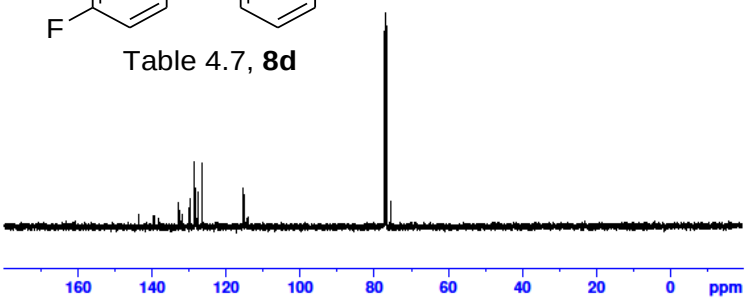


Table 4.7, **8d**




```
Current Data Parameters
NAME                  ACTH34D
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                   14.07
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       81
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      203
DW                    20.800 usec
DE                     6.50 usec
TE                    298.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W              58.52175522 W
SFO1             100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2             0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
PL13W              0.37571725 W
SFO2             400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127726 MHz
WDW                        EM
SSB             0
LB                      1.00 Hz
GB              0
PC                      1.40
```

acth34d_19F

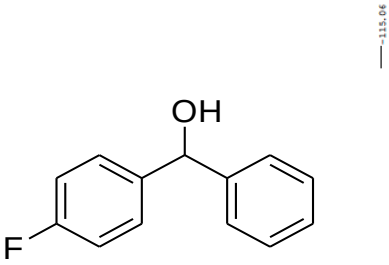


Table 4.7, **8d**


```
Current Data Parameters
NAME                 ACTH34D
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20171117
Time                   14.17
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG            zgfhigqn
TD                    131072
SOLVENT                CDCl3
NS                        16
DS                         4
SWH                89285.711 Hz
FIDRES             0.681196 Hz
AQ                 0.7340032 sec
RG                      2050
DW                     5.600 usec
DE                     6.50 usec
TE                     297.8 K
D1                 1.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     19F
P1                     14.20 usec
PL1                    -3.00 dB
PL1W              18.69428444 W
SFO1              376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                     1H
PCPD2                  80.00 usec
PL2        0 dB
PL12                   15.00 dB
PL2W              11.88122272 W
PL12W              0.37571725 W
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                       65536
SF                376.4983660 MHz
WDW                         EM
SSB        0
LB                      0.30 Hz
GB         0
PC                      1.00
```

acth34e_H

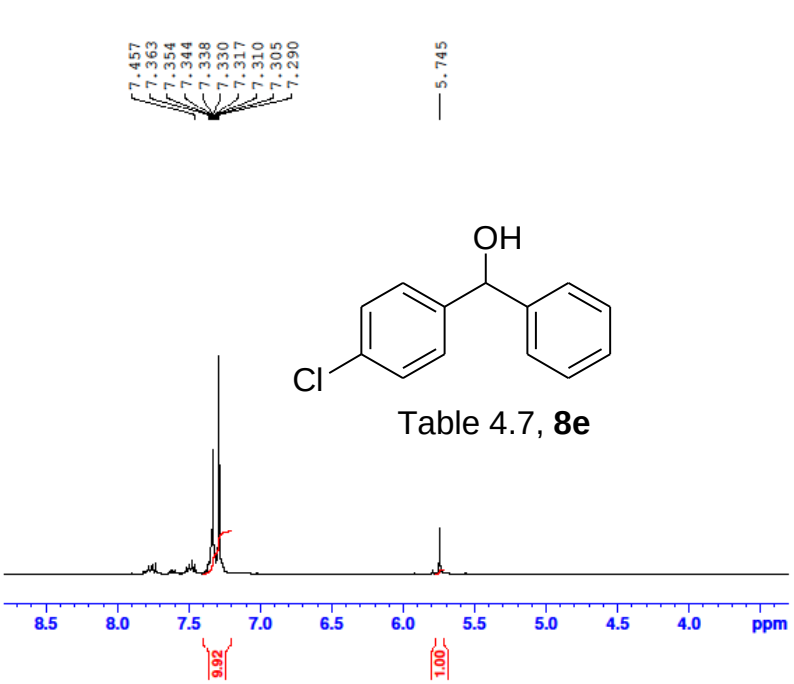


Table 4.7, **8e**

```
Current Data Parameters
NAME                  acth34e
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                   14.21
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      28.5
DW                    62.400 usec
DE                     6.50 usec
TE                   298.1 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1          0 dB
PL1W            11.88122272 W
SFO1            400.1336012 MHz

F2 - Processing parameters
SI                      32768
SF                400.1300099 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

acth34e_c13

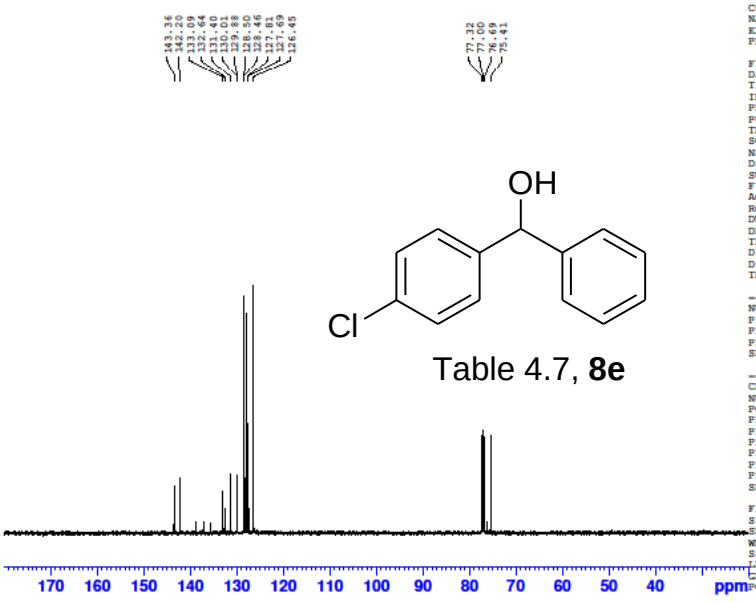


Table 4.7, **8e**

```
Current Data Parameters
NAME                  acth34e
EXPNO                       2
PROCNO                      1

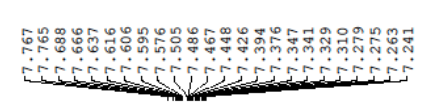
F2 - Acquisition Parameters
Date_               20171117
Time                   14.30
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       65
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      228
DW                    20.800 usec
DE                     6.50 usec
TE                   298.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      9.50 usec
PL1                    -2.00 dB
PL1W            58.52175522 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2          0 dB
PL12                   15.00 dB
PL13                   15.00 dB
PL2W            11.88122272 W
PL12W            0.37571725 W
PL13W            0.37571725 W
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                      32768
SF                100.6127828 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

acth34c_H



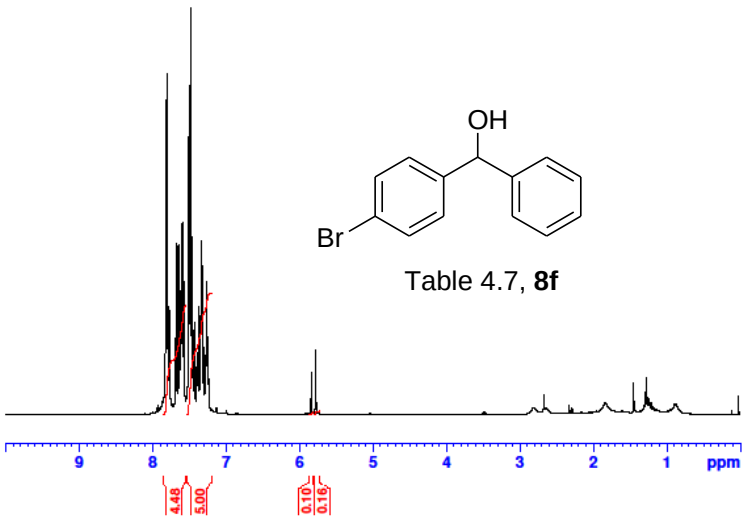


Table 4.7, **8f**

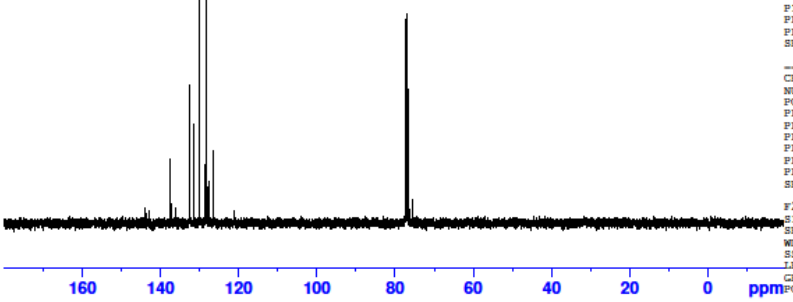
```
Current Data Parameters
NAME                  acth34c
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                    9.18
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    16384
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                      40.3
DW                   62.400 usec
DE                    6.50 usec
TE                   298.1 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1          0 dB
PL1W           11.88122272 W
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                      32768
SF                400.1300080 MHz
WDW                        EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
```

acth34c_C13



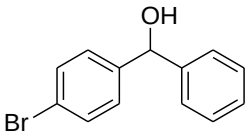


Table 4.7, **8f**

```
Current Data Parameters
NAME                  acth34c
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171117
Time                    9.22
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       17
DS                        2
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                      181
DW                   20.800 usec
DE                    6.50 usec
TE                   298.4 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       9.50 usec
PL1                     -2.00 dB
PL1W           58.52175522 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2          0 dB
PL12                    15.00 dB
PL13                    15.00 dB
PL2W           11.88122272 W
PL12W           0.37571725 W
PL13W           0.37571725 W
SFO2           400.1316005 MHz

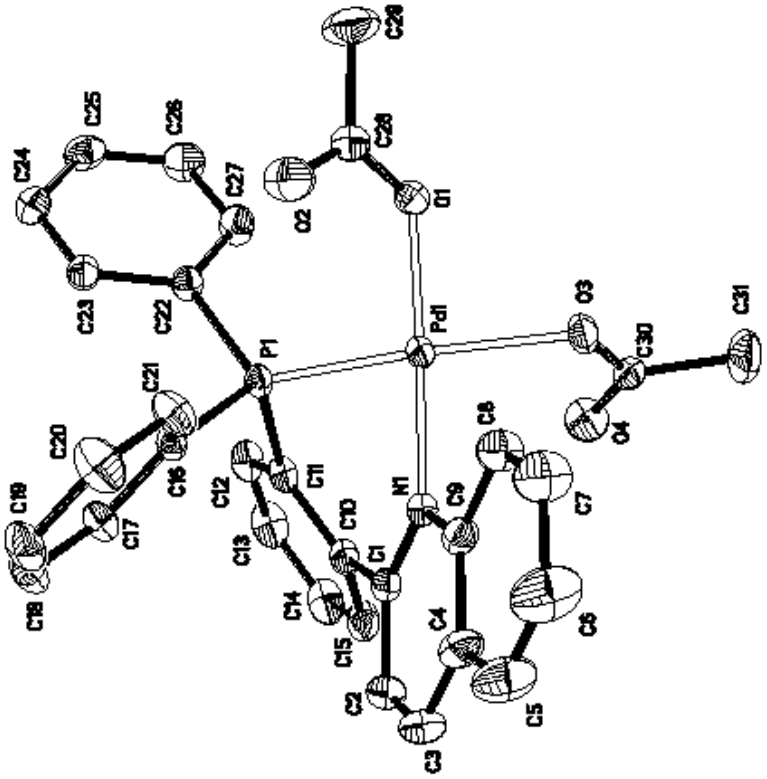
F2 - Processing parameters
SI                      32768
SF                100.6127712 MHz
WDW                        EM
SSB          0
LB                      1.00 Hz
GB           0
PC                      1.40
```

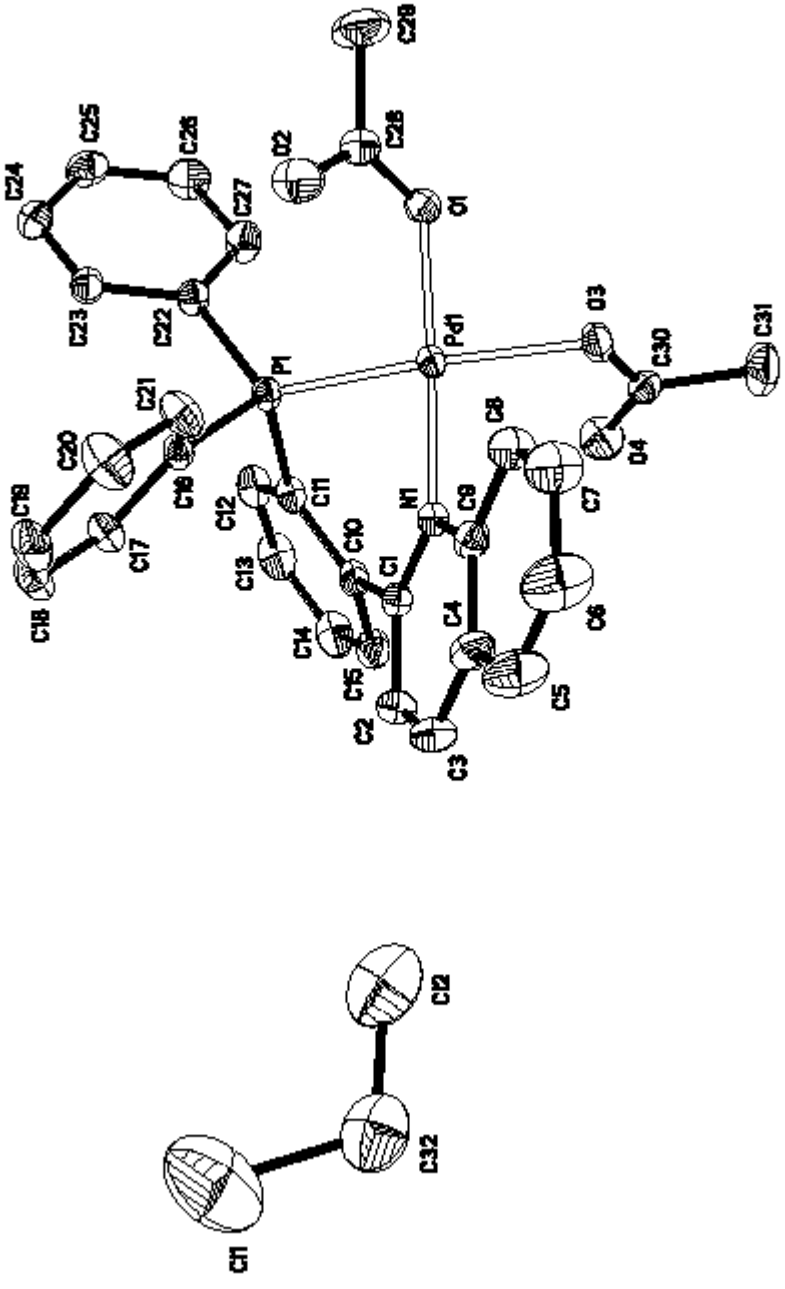
Crystal structure data of Pd-quinolinylphosphine complex (Pd-NP-1)

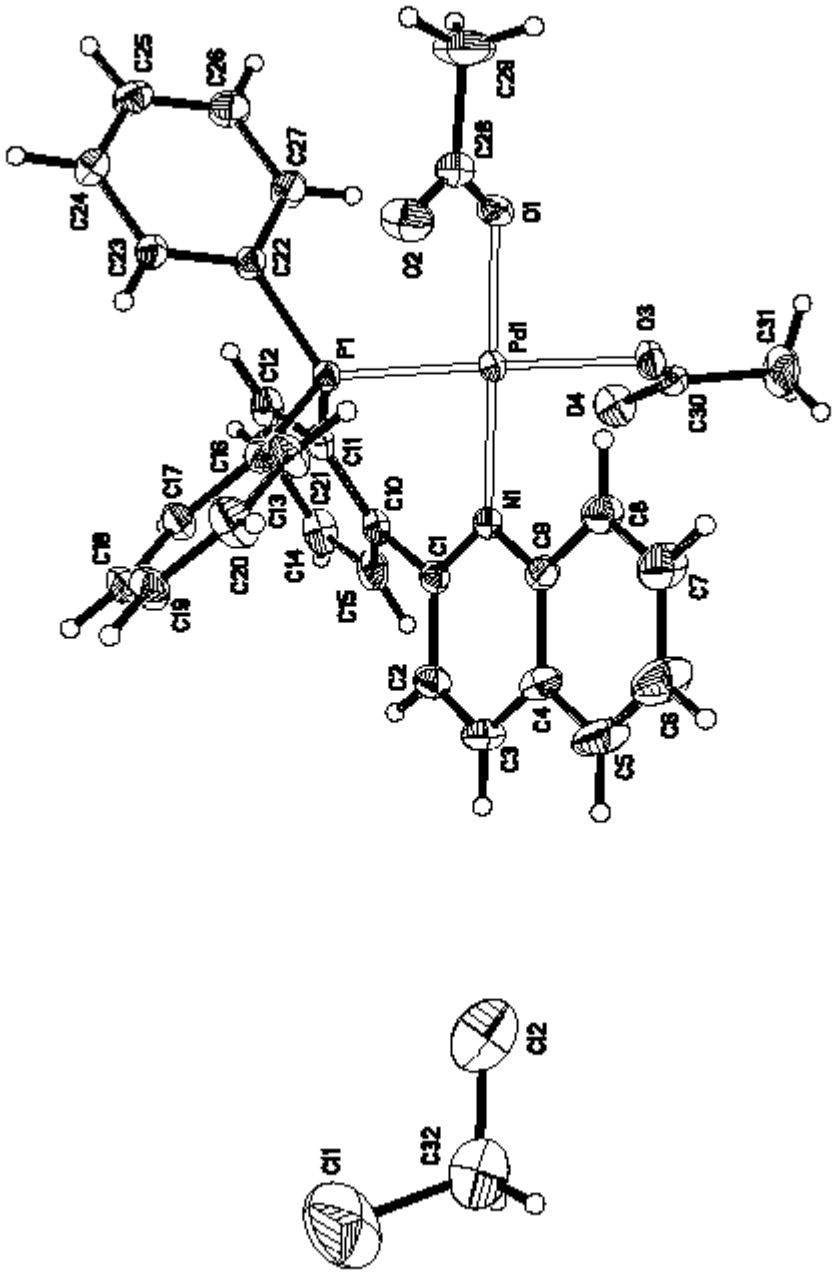
$Pd(C_{27}H_{20}NP)(CH_3CO_2)_2 \cdot CH_2Cl_2$

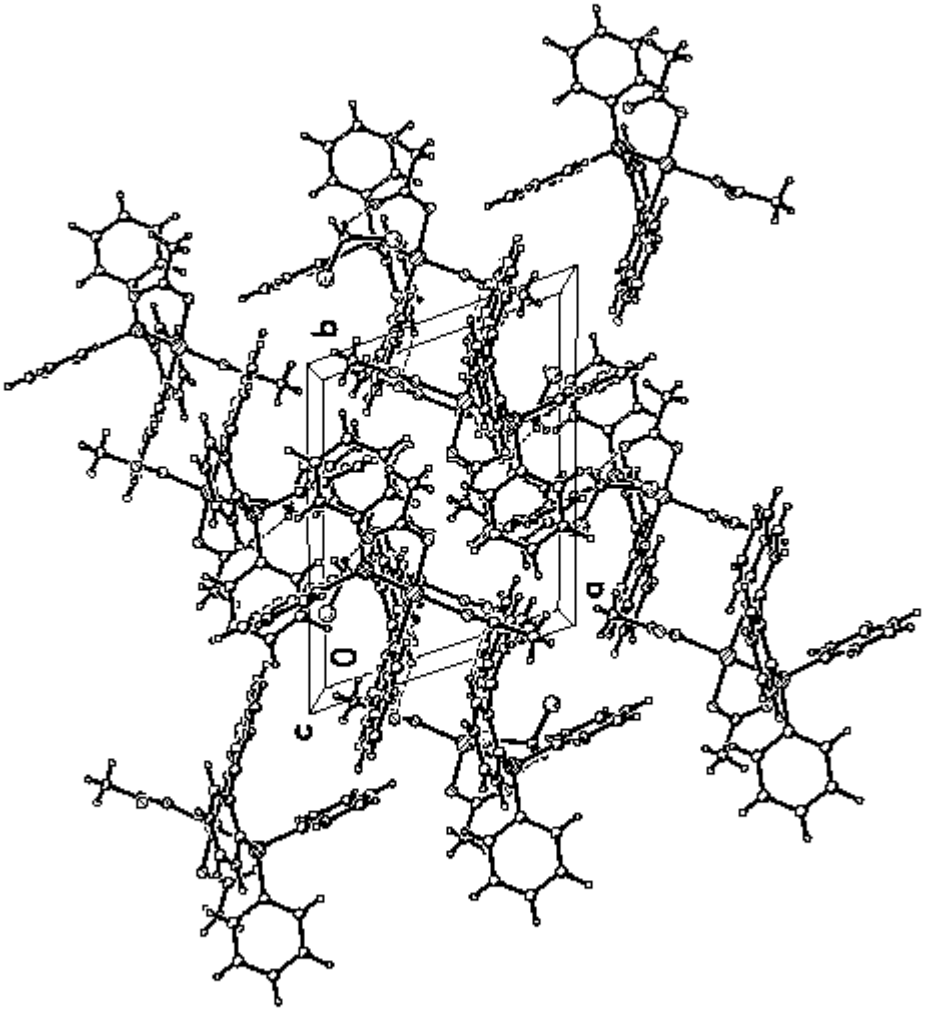
Table 1. Crystal data and structure refinement for BCYOY6 (6 Apr 2016).

Identification code	yoy6	
Empirical formula	$Pd(C_{27}H_{20}NP)(CH_3CO_2)_2 \cdot CH_2Cl_2$	
Formula weight	698.82	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0468(5) Å	• = 81.570(2)°.
	b = 12.3263(7) Å	• = 75.746(2)°.
	c = 13.6449(8) Å	• = 69.269(2)°.
Volume	1528.42(15) $Å^3$	
Z	2	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	0.872 mm^{-1}	
F(000)	708	
Crystal size	0.12 x 0.06 x 0.04 mm^3	
Theta range for data collection	2.22 to 30.61°.	
Index ranges	-14<=h<=14, -17<=k<=17, -19<=l<=19	
Reflections collected	135040	
Independent reflections	9404 [R(int) = 0.0355]	
Completeness to theta = 30.61°	99.7 %	
Absorption correction	None	
Max. and min. transmission	0.7461 and 0.7084	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9404 / 0 / 386	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.1031	
R indices (all data)	R1 = 0.0498, wR2 = 0.1175	
Largest diff. peak and hole	1.080 and -0.961 e.$Å^{-3}$	


C28
C25
C26
C24
C27
C29
O1
C23
C22
O3
C31
P1
Pd1
C30
O4
C21
C6
C20
C12
C11
N1
C9
C7
C19
C16
C17
C10
C13
C1
C14
C4
C8
C15
C2
C5
C18
C3


C29
C25
C26
O2
C28
C24
C27
O1
C23
C22
O3
Pd1
C31
P1
C30
C21
C20
C8
O4
C19
C12
C11
N1
C9
C7
C16
C10
C1
C13
C6
C17
C4
C14
C5
C15
C2
C18
C3
C12
C32
Cl1


C25
C26
C27
C24
C23
C22
C28
C29
O1
O2
P1
Pd1
O3
C31
C12
O4
C30
C18
C11
C17
C21
C10
C13
Ni
C1
C8
C6
C16
C20
C14
C15
C7
C19
C2
C4
C5
C3
C32
Cl2
Cl1


b
c
O
a

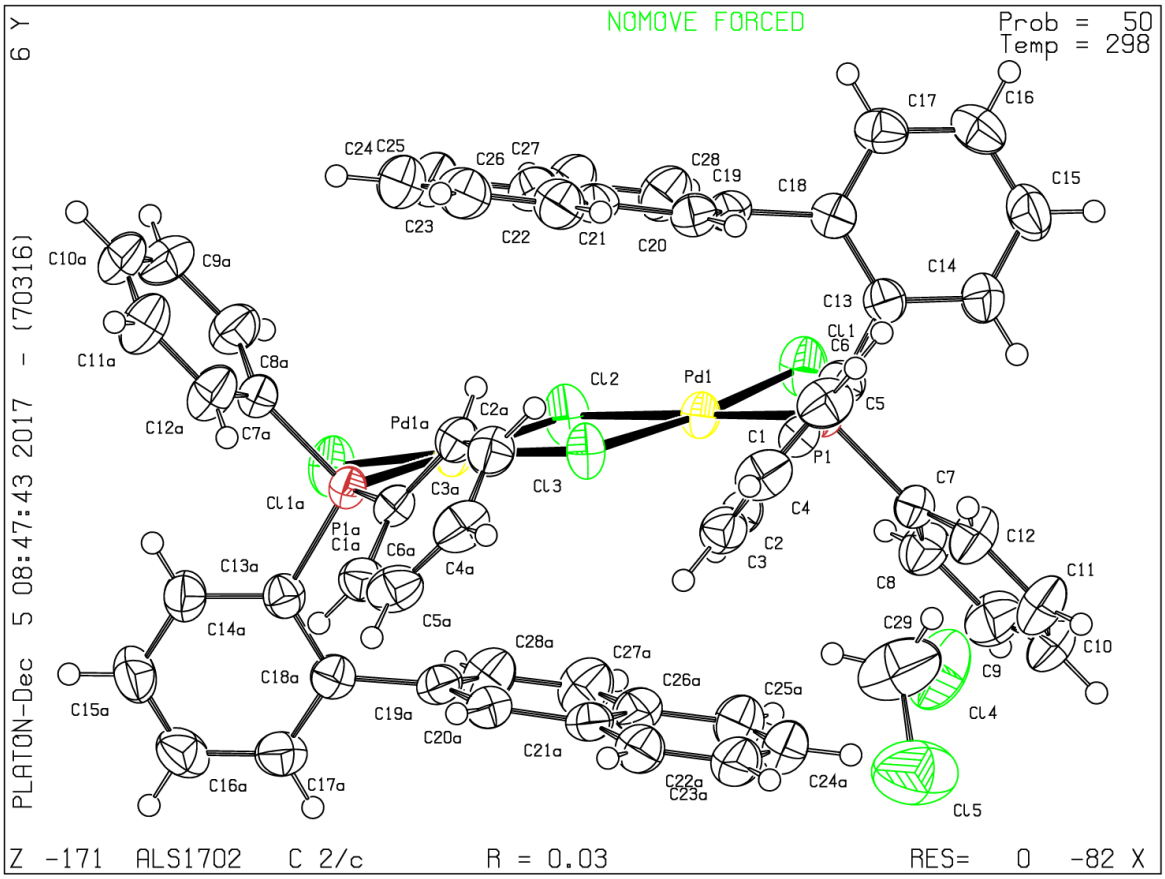
Crystal structure data of Pd- naphthalylphosphine complex (Pd-CP-1)

C58H46Cl8P2Pd2

Table 1. Crystal data and structure refinement for ALS1702.

Identification code	ALS1702
Empirical formula	C58 H46 Cl8 P2 Pd2
Formula weight	1301.29
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 26.9421(86) A alpha = 90 deg. b = 11.1527(33) A beta = 114.7781(86) deg. c = 19.7203(59) A gamma = 90 deg.
Volume	5380(3) A^3
Z, Calculated density	4, 1.607 Mg/m^3
Absorption coefficient	1.164 mm^-1
F(000)	2608
Crystal size	0.16 x 0.10 x 0.08 mm
Theta range for data collection	2.76 to 27.51 deg.
Limiting indices	-34<=h<=34, -14<=k<=14, -25<=l<=25

Reflections collected / unique	60625 / 6168 [R(int) = 0.0426]
Completeness to theta = 27.51	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9126 and 0.8356
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6168 / 0 / 317
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0774
R indices (all data)	R1 = 0.0515, wR2 = 0.0850
Largest diff. peak and hole	0.675 and -0.910 e.A^-3


NOMOVE FORCED
Prob = 50
Temp = 298
6 Y
PLATON-Dec 5 08:47:43 2017 - (70316)
Z -171 ALS1702 C 2/c R = 0.03 RES= 0 -82 X
C17
C16
C24
C25
C26
C27
C28
C19
C18
C15
C23
C22
C21
C20
C14
C10a
C9a
C13
Cl1
C6
C11a
C8a
Cl2
Pd1
C2a
C5
C12a
C7a
Pd1a
C1
P1
Cl3
C7
Cl1a
C3a
C4
P1a
C1a
C2
C12
C6a
C3
C13a
C4a
C8
C11
C14a
C5a
C29
C28a
C27a
C10
C18a
C26a
C9
C25a
C15a
C19a
Cl4
C20a
C21a
C22a
C24a
C16a
C17a
C23a
Cl5

Crystal structure data of Ru-(2-aminobenzyl alcohol) complex

C17H22Cl2NORu

Table 1. Crystal data and structure refinement for ALS1701.

Identification code	ALS1701
Empirical formula	C17 H22 Cl2 N O Ru
Formula weight	428.33
Temperature	297(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 8.5254(6) A alpha = 90 deg. b = 8.1427(6) A beta = 93.2099(21) deg. c = 25.0351(19) A gamma = 90 deg.
Volume	1735.2(2) A^3
Z, Calculated density	4, 1.640 Mg/m^3
Absorption coefficient	1.212 mm^-1
F(000)	868
Crystal size	0.26 x 0.12 x 0.06 mm
Theta range for data collection	2.48 to 27.52 deg.
Limiting indices	-11<=h<=11, -10<=k<=10, -32<=l<=32
Reflections collected / unique	42578 / 3995 [R(int) = 0.0482]

Completeness to theta = 27.52	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9308 and 0.7435
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3995 / 2 / 208
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0677
R indices (all data)	R1 = 0.0386, wR2 = 0.0710
Largest diff. peak and hole	1.154 and -0.659 e.A^-3

PLATON version of 09/11/2017; check.def file version of 08/11/2017

Datablock ALS1701 - ellipsoid plot