Master of Science Degree in Chemical Engineering

Exploring the reactivity of a new ruthenium complex as a hydrogenation catalyst in the reduction of aldehydes and ketones

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ABSTRACT

This work focuses on the study of newly discovered ruthenium complex ([Ru(H)(Cl)(^{t}Bu$_2$PH)(^{t}Bu$_2$Ppy)]), **1**, in the hydrogenation of aldehydes and ketones. We have demonstrated that catalyst 1 can completely convert a wide variety of aldehydes into their respective alcohols under mild conditions and it exhibits a moderate catalytic activity in the hydrogenation of ketones. We have also shown that there is selectivity between aldehydes and alkenes; we successfully reduced furfural to furfuryl alcohol and managed to reach a 96% selectivity when reducing cinnamaldehyde to cinnamyl alcohol.

1. Introduction

The catalytic hydrogenation of aldehydes and ketones with H_2 is one of the most important transformations in organic chemistry. The alcohols formed in these reduction reactions are used as a base to produce various derivatives such as esters, acetals or acids which are widely used in the chemical and pharmaceutical industries [1]. Historically, the reduction of aldehydes and ketones was carried out by stoichiometric means using alkali metal hydrides ($LiAlH_4$, Dibal-H, SMEAH) or borohydrides ($NaBH_4$, $NaCNBH_3$). But in addition to the time-consuming work-up processes and dangers associated with handling highly reactive hydride reagents, such methods of stoichiometric nature also cause a large amount of insoluble $Al(OH)_3$ effluents to be created during the process.

The Meerwin-Ponndorf-Verley reaction was the first homogeneous catalytic hydrogenation reported (1938). In this reaction, a ketone was reduced to alcohol by hydrogen transfer in the presence of an aluminium alkoxide and another alcohol that acted as a hydrogen donor [2]. Then in 1964, Wilkinson reported a catalyst ($[RhCl(PPh_3)_3]$) (fig.1.1) which was found to reduce olefins in the presence of H_2. The use of molecular hydrogen (H_2) as a reducer, an added advantage because it allows reaching an atomic efficiency of 100% [1]. Interest in ruthenium-based catalysts began in 1961 when it was discovered that one could catalytically hydrogenate alkynes and acids in a solution containing Ru(II) species in the presence of H_2 [3]. Ruthenium catalysts have many applications such as reducing not only aldehydes and simple ketones but also substrates more difficult like nitriles [3].

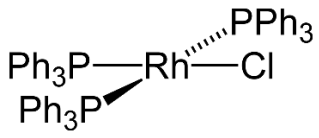


Figure 1.1- Wilkinson's catalyst

Another interesting application of ruthenium catalysts is the asymmetric hydrogenation of ketones. Noyori reported that Ru(II)-BINAP type complexes (fig.1.2) have a high catalytic activity and are highly stereoselective in the reduction of ketones, producing chiral alcohols that are of extreme importance in the pharmaceutical industry [3-5].

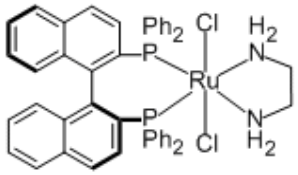


Figure 1.2- (S)BINAP/(S)diamine-Ru

Most catalysts used industrially for homogeneous catalytic hydrogenation use noble metals. These metals are expensive, often toxic, and not very abundant. For these reasons in recent years there has been more and more reports of the use complexes of the first transition series as hydrogenation catalysts since they are much more abundant and therefore cheaper. Among them, several iron complexes with pincer ligands have been reported to be able to reduce amides to alcohols and amines, an extremely difficult substrate to hydrogenate which until now only a few Ru complexes were able to do [6-9]. Iron catalysts are also capable of high selectivity in the hydrogenation of aldehydes [10] in relation to other types of substrates. There are also copper complexes that were reported to reduce esters to alcohols [11] and reduce carbon monoxide to formate [12]. Cobalt complexes have also demonstrated high stereoselectivity in the hydrogenation of alkenes [13] and can reduce various difficult substrates such as CO_2 [14], hindered alkenes [15] and carboxylic acids [16].

2. Results and Discussion

Complex **1** (fig. 2.2) was synthesised following a procedure developed in the lab [17] using the ligands **L1** and **L2** (fig. 2.1) which were also synthesised in the lab following the literature [18,19]

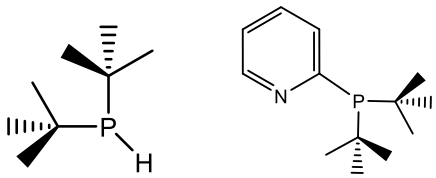


Figure 2.1- Ligands **L1** (left) and **L2** (right)

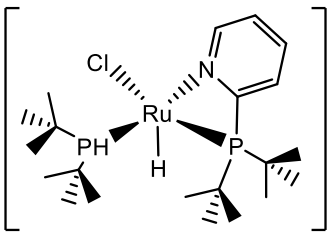


Figure 2.2- Complex **1**

2.1. Hydrogenation of aldehydes

In order to study the scope of complex **1** as a catalyst for the hydrogenation of aldehydes, it was first necessary to study the reduction of benzaldehyde. This was done by studying the effects of the H_2 pressure, the S/C (substrate/catalyst) ratio, the temperature, the reaction time, and the base as well as the solvent used. After these tests, we reached two optimal conditions which were named **A** and **B** (fig.2.3).

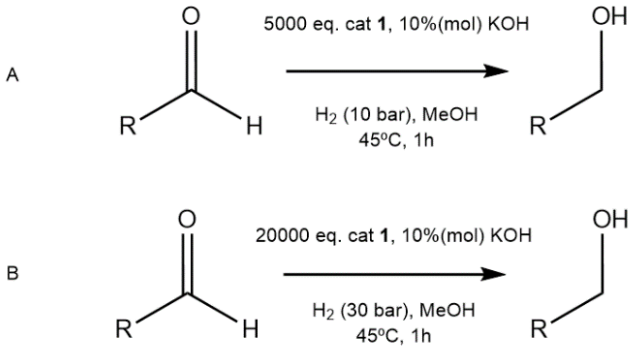
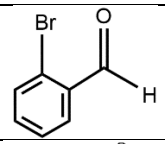
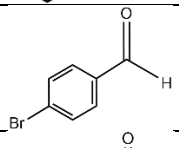
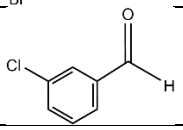
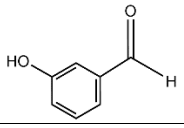
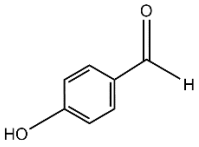
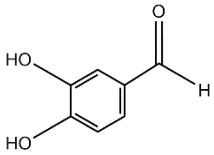
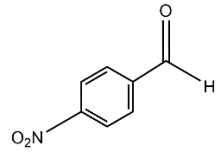
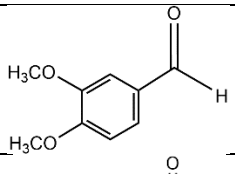
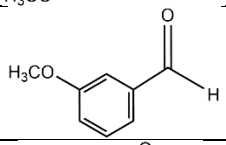
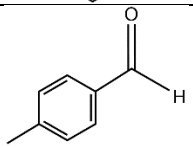
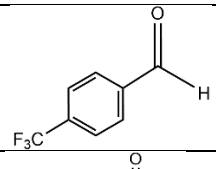
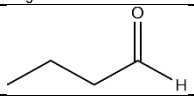


Figure 2.3- Catalytic reaction of aldehyde under conditions **A** and **B**

By analysing the data in Table 2.1, we concluded that the aldehydes with halogens as substituent groups (entries 1-6) were fully converted into the corresponding alcohols demonstrating that electronegative groups on the ring promote the catalytic reaction. This is supported by the aldehyde with the CF_3 group having also been fully converted into alcohol (entries 16 and 17). The methoxy group is electron withdrawing by induction but electron donating by resonance and, in the *para* position, the methoxy has a deactivating effect on the carbonyl. However, the aldehyde with two methoxy groups, one in the *meta* position and one in the *para* position (entries 11 and 12) converted more than the aldehyde with only one methoxy group in the *meta* position (entry 13). This may be due to the two methoxy groups, that together have a stronger induction effect than the resonance donor effect of the single methoxy group in the *para* position.

Table 2.1- Experimental results of catalytic reactions of aldehydes

Entry	Aldehyde	Conditions	Conversion [x]	conversion [y]	yield [y]	TON	TOF (h^{-1})
1		A	>99%	---	---	5000	5000
2		B	>99%	99%	90%	17902	17902
3		A	>99%	---	---	5000	5000
4		B	>99%	99%	89%	17873	17873
5		A	>99%	---	---	5000	5000
6		B	>99%	99%	83%	16637	16637
7		A	3%	---	---	167	167
8		A	0%	---	---	0	0
9		A	0%	---	---	0	0
10		A	8%	---	---	350	350
11		A	98%	---	---	4890	4890
12		B	>99%	87%	80%	15983	15983
13		A	72%	---	---	3600	3600
14		A	>99%	---	---	5000	5000
15		B	>99%	>99%	>99%	20000	20000
16		A	>99%	---	---	5000	5000
17		B	>99%	99%	87%	17463	17463
18		B	---	>99%	64%	12801	12801

x- Calculated from NMR ^{1}H spectra.
y- Calculated from GC.

Butyraldehyde (entry 18) was completely converted. Although sterically less hindered than the benzaldehyde derivatives, electronically it should be more challenging to reduce. It is important to highlight the low yield value which is due to the aldehyde being very volatile and therefore difficult to obtain an accurate measure of the amount of butyraldehyde that existed at the beginning of the reaction, and at the end, if any.

Hydroxyl and nitro substituted benzaldehydes show very little conversion. The presence of the hydroxyl group in the ring (entries 7-9) significatively hinders the catalytic reaction; only entry 7 shows some conversion. Increases in temperature and reaction time resulted in similar results, so the presence of the hydroxyl group somehow prevents the catalytic reaction. It was not possible however to determine if the hydroxyl group reacts directly with the catalyst. Another group that hinders the catalytic reaction is the nitro group (entry 10). Despite being an electron withdrawing group by induction and resonance, the nitro substituted aldehyde practically does not convert to alcohol. Literature reports other systems show that usually p-nitro benzaldehyde and halogen substituted benzaldehydes have similar conversions [20,21]. It is therefore reasonable to assume that the nitro group reacts with **1**. It is also reported that, for certain catalysts, the hydrogenation of the nitro group to NH_2 is more favourable than the reduction of the carbonyl group [22, 23], while in others the opposite happens [24]. Looking at the NMR spectrum of entry 10, it is concluded that the nitro group is not reduced because, if that were the case, the signals from the hydrogens of the aromatic ring would be much more shielded. Albeit low conversion, the reaction is selective for the aldehyde group.

2.2. Hydrogenation of ketones

Catalyst **1** was also tested in the hydrogenation of ketones which are a more difficult substrate to hydrogenate than aldehydes. For this study, the optimized reaction conditions of the hydrogenation of acetophenone were used (fig. 2.4) [17]. Under these conditions, the catalytic reaction

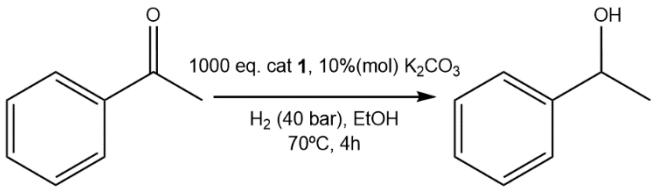
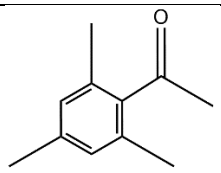
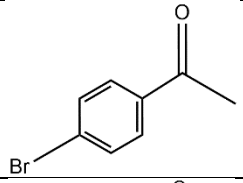
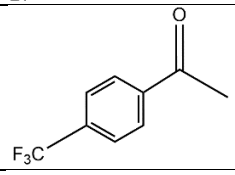
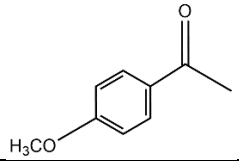


Figure 2.4- Optimal conditions of the reduction reaction of acetophenone [17]

Table 2.2- Experimental results of catalytic reactions of ketones

Entry	Ketone	conversion [x]	TON	TOF (h^{-1})
19		17%	170	42.5
20		75%	750	187.5
21		>99%	1000	250
22		59%	590	147.5

x- Calculated from NMR ^1H spectra.

was tested for a small array of ketones derived from acetophenone in order to study the scope of the catalyst. The conversions obtained are shown in table 2.2 as well as the TON and TOF.

Looking at the data in table 2.2, it is possible to notice once again that electron withdrawing groups favour the catalytic reaction. The ketone with the CF_3 group (entry 21) was completely converted to the corresponding alcohol while the ketone with several donor groups (entry 19) barely reacted. In addition to them being donor groups, the methyl groups at the ortho positions at entry 19 can also cause a steric hindrance which makes catalysis even more difficult to take place. Bromine is less electronegative than the CF_3 group which explains why the ketone with the bromine (entry 20) converted less than the one with the CF_3

group (entry 21). The ketone with the methoxy group (entry 22) converted less than the ketone with the bromine which makes sense since the methoxy group in the *para* position is a donor by resonance which deactivates the carbonyl group.

2.3. Selectivity competition

Selective hydrogenation plays an important role in the fine chemical industry [25]. Thus, it is of great interest to test whether catalyst **1** presents any selectivity in the hydrogenation between carbonyl and alkene groups.

2.3.1. Furfural

In an attempt to reduce only the aldehyde to furfuryl alcohol without reducing the double bonds in the ring, we tested the catalytic reaction for conditions **A**. Analyzing the ^{1}H NMR spectra, we concluded that only the carbonyl is completely hydrogenated under the given conditions producing exclusively furfuryl alcohol.

2.3.2. Cinnamaldehyde

Cinnamaldehyde was shown to be much more difficult to hydrogenate selectively than. The best entries as well as their conversions, yields and selectivity are shown in table 2.3.

Table 2.3- Experimental results of catalytic reactions of cinnamaldehyde

Entry	Conditions	Conversion [x]	Yield [x]	Selectivity [x]
23	**C**	52%	34%	66%
24	**D**	58%	52%	90%
25	**E**	87%	83%	96%

Reaction conditions: **C**- 10 bar H_2, 1000 equivalents (Substrate/Catalyst), 10%(mol) of K_2CO_3, room temperature, 1h in MeOH; **D**- 30 bar H_2, 5000 equivalents (Substrate/Catalyst), 100%(mol) of K_2CO_3, room temperature, 1h in MeOH; **E**- 30 bar H_2, 5000 equivalents (Substrate/Catalyst), 100%(mol) of K_2CO_3, room temperature, 3h in MeOH.
x- Calculated from NMR ^{1}H spectra.

By analyzing the data from table 2.3, we concluded that increasing the H_2 pressure as well as the Substrate/Catalyst and Base/Substrate ratios not only increases the conversion but also considerably increases the selectivity (entries 23 and 24). It is also noted that by increasing the reaction time, conversion and the selectivity increase (entries 24 and 25). Despite not achieving total selectivity, the conditions used in entry 25 are the most suitable for the selective reduction of the cinnamaldehyde's carbonyl group and could be used in the future as a basis to reach total selectivity.

3. Conclusions

From the results discussed above, it can be concluded that complex **1** is able to completely reduce a wide variety of aldehydes under very mild conditions. Conversion decreases for aldehydes with electrode donating groups. The presence of OH and NO_2 groups seams to inhibit catalyst activity. Complex **1** reduces ketones with lower TON and TOF values when compared to aldehydes. Catalyst **1** can selectively reduce aldehydes in the presence of double bonds, by tweaking reaction conditions. The study of this catalyst would benefit from a study of the reaction mechanism of the different catalytic reactions. This would allow the optimization of **1** and obtain better catalytic results. It would also be interesting to see if the OH and NO_2 groups reacts with the catalyst, deactivating it and how.

4. Experimental

All reactions and handling of air and/or moisture sensitive compounds were done using Schlenk and/or glove box techniques. All catalytic reactions were carried out in a Parr Reactor. All solvents used were previously dried and deoxygenated through the standard procedure: refluxing over a suitable drying agent (sodium/benzophenone for toluene; calcium hydride for n-hexane and dichloromethane; sodium for methanol) and distilled under a nitrogen atmosphere prior to use. All reagents were analyzed using nuclear magnetic resonance (NMR) spectroscopy, and, in case of impurities, they were purified according to the literature [26]. All liquid reagents were dried using 4Å molecular sieves, degassed by freeze-pump-thaw cycles and stored under nitrogen. NMR spectra were all obtained at room temperature on a Bruker Avance II at

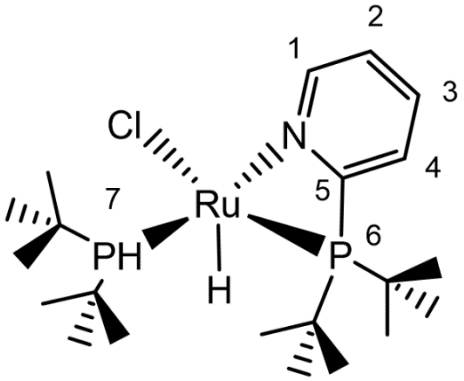
300 MHz or Bruker Avance II at 400 MHz. The deuterated solvents used in the NMR were dried using 4Å molecular sieves, degassed by freeze-vacuum-thaw cycles and stored under nitrogen. All chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. The multiplicities were abbreviated as follows: singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*), pseudo-triplet (*pseudo-t*), doublet of doublets (*dd*), doublet of triplets (*dt*) and multiplet (*m*). The spectra were referenced internally in relation to residual proton (^{1}H) or carbon (^{13}C) signals from the deuterated solvent or externally in the case of phosphor spectra (85% H_3PO_4) (^{31}P). Signals are reported relative to TMS (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P) at 0 ppm. NMR samples of air and/or moisture sensitive compounds were prepared inside the glove box in J. Young tubes. For non-sensitive compounds, NMR samples were prepared in standard NMR tubes with non-dry or degassed solvent.

GC (gas chromatography) analyzes were performed on an Agilent Technologies Series 7820A Gas Chromatograph (carrier gas: helium; detector: flame ionization; capillary column: BP20/SGE, 30 m × 0.22 mm × 0.25 µm).

4.1. Synthesis of the catalyst

The complex **1** was synthesised following a procedure developed in the lab [17] and using the ligands **L1** and **L2** which were also synthesised following the general route described in the literature [18,19].

A Parr reactor was charged with $\{Ru(COD)Cl_2\}_x$ (1.68 g, 6.0 mmol), $^{t}Bu_2PH$ (**L1**) (0.891 g, 6.1 mmol), $^{t}Bu_2Ppy$ (**L2**) (1.449 g, 6.1 mmol) and NEt_3 (0.84 mL, 6.0 mmol) in THF. The reactor was pressurized to 10 bars with H_2 and left to react for 70h at 80°C. After allowing to cool to room temperature and depressurizing the reactor, the mixture was filtered and the solid washed with MeOH to obtain 2.05 g (4.05 mmol, η = 67%) of a dark red solid.



^{1}H NMR (400 MHz, C_6D_6): δ = 9.19 (*d*, $^{3}J_{H1H2}$ = 4.2 Hz, 1H, *H*1), 6.72 (*br t*, $^{3}J_{HH}$ = 7.8 Hz, 1H, *H*3), 6.33-6.28 (*m*, 2H, *H*2+*H*4), 5.02 (*dd*, $^{1}J_{P7H}$ = 300.9 Hz, $^{3}J_{HH}$ = 7.4 Hz, 1H, P-*H*), 1.63 (*dd*, $^{3}J_{PH}$ = 26.0 Hz, $^{5}J_{PH}$ = 12.5 Hz, 18H, P7-(^{t}Bu)$_2$), 1.15 (*dd*, $^{3}J_{PH}$ = 39.0 Hz, $^{5}J_{PH}$ = 13.1 Hz, 18H, P6-(^{t}Bu)$_2$), -27.2 (*dd*, $^{2}J_{P6H}$ = 36.0 Hz, $^{2}J_{P7H}$ = 28.8 Hz, 1H, Ru-*H*).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ = 86.7 (*dd*, $^{2}J_{PH}$ = 29.9 Hz, $^{2}J_{PP}$ = 19.9 Hz, 1P, *P*7), 58.4 (*dd*, $^{2}J_{PH}$ = 39.6 Hz, $^{2}J_{PP}$ = 24.1 Hz, 1P, *P*6).

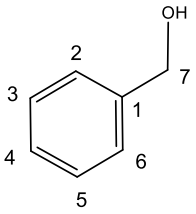
^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 173.8 (*d*, $^{1}J_{C5P6}$ = 33.8 Hz, 1C, *C*5), 148.8 (*d*, $^{3}J_{C1P6}$ = 10.3 Hz, 1C, *C*1), 133.7 (*d*, $^{3}J_{C3P6}$ = 2.1 Hz, 1C, *C*3), 124.1 (*pseudo-t*, J_{CP} = 2.1 Hz, 1C, *C*2 ou *C*4), 122.9 (*d*, J_{CP} = 2.2 Hz, 1C, *C*2 ou *C*4), 35.5 (*dd*, $^{1}J_{PC}$ = 120.0 Hz, $^{3}J_{CH}$ = 10.3 Hz, 2C, P6(*C*(CH3)$_3$)$_2$), 34.3 (*dd*, $^{1}J_{PC}$ = 17.9 Hz, $^{3}J_{CH}$ = 15.4 Hz, 2C, P7(*C*(CH3)$_3$)$_2$), 32.0 (*dd*, $^{2}J_{PC}$ = 94.9 Hz, $^{4}J_{CH}$ = 3.6 Hz, 6C, P7(C(*C*H3)$_3$)$_2$), 29.5 (*dd*, $^{2}J_{PC}$ = 36.0 Hz, $^{4}J_{CH}$ = 5.7 Hz, 6C, P6(C(*C*H3)$_3$)$_2$).

4.2. Catalysis

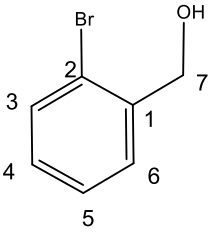
4.2.1. Hydrogenation of aldehydes

Aldehyde (986 mmol), catalyst **1** (0.1 mg, 1.97x10^{-4} mmol), KOH (5.5 mg, 98.6 mmol) and MeOH (1 ml) were mixed in the Parr reactor. The reactor was pressurized to 10 bar with H_2 and allowed to react for 1 h at 45ºC. The reactor was then depressurized and allowed to reach room temperature. This procedure was then repeated with a smaller amount of catalyst **1** (0.025 mg, 4.93*10−5 mmol) and at a higher H_2 pressure (30 bar).

The reaction mixture was then dried from solvent and dissolved into dichloromethane followed by silica gel filtration. The solvent was removed and an oil or solid was obtained which was then analyzed by NMR and/or GC.

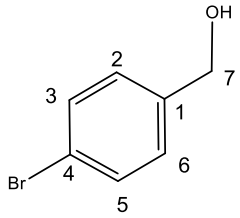


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (*d*, $^{3}J_{HH}$ = 8.7 Hz, 5H, *H*1+ *H*2+ *H*3+ *H*4+ *H*5), 4.60 (*s*, 2H, *H*7).

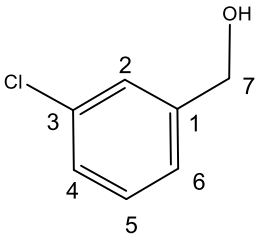


^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (*d*, $^{3}J_{H3H4}$ = 7.8 Hz, 1H, *H*3), 7.50 (*d*, $^{3}J_{H6H5}$ = 7.7 Hz, 1H, *H*6), 7.36 (*t*, $^{3}J_{HH}$ = 7.3 Hz, 1H, *H*5), 7.20 (*t*, $^{3}J_{HH}$ = 7.7 Hz, 1H, *H*4), 4.78 (*s*, 2H, *H*7).

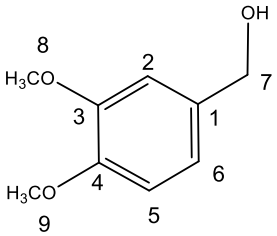
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 132.6 (*s*, 1C, *C*6), 129.2 (*s*, 1C, *C*4), 128.9 (*s*, 1C, *C*3), 127.7 (*s*, 1C, *C*5), 65.1 (*s*, 1C, *C*7).



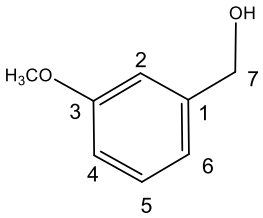
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (*d*, $^{3}J_{HH}$ = 8.3 Hz, 2H, *H*3+*H*5), 7.26 (*d*, $^{3}J_{HH}$ = 8.3 Hz, 2H, *H*2+*H*6), 4.67 (*s*, 2H, *H*7).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (*s*, 1H, *H*2), 7.23 (*s*, 2H, *H*4+*H*6), 7.17 (*s*, 1H, *H*5), 4.55 (*d*, $^{3}J_{HH}$ = 5.3 Hz, 2H, *H*7).

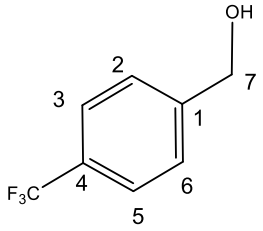


^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.95-6.85 (*m*, 3H, *H*2+*H*5+*H*6), 4.65 (*s*, 2H, *H*7), 3.92 (*s*, 3H, *H*9), 3.90 (*s*, 3H, *H*10).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (*d*, $^{3}J_{HH}$ = 8.4 Hz, 1H, *H*5), 6.96 (*d*, $^{3}J_{HH}$ = 7.6 Hz, 2H+*H*4+*H*6), 4.70 (*s*, 2H, *H*7), 3.84 (*s*, 3H, OCH_3).

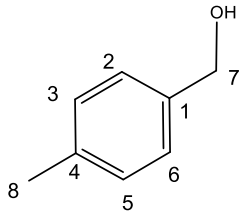
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 129.6 (*s*, 1C, *C*5), 119.1 (*s*, 1C, *C*6), 113.3 (*s*, 1C, *C*2), 112.2 (*s*, 1C, *C*4), 65.3 (*s*, 1C, *C*7), 55.2 (*s*, 1C, OCH_3).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (*d*, $^{3}J_{HH}$ = 8.2 Hz, 2H, *H*3+*H*5), 7.50 (*d*, $^{3}J_{HH}$ = 8.2 Hz, 2H, *H*2+*H*6), 4.80 (*s*, 2H, *H*7).

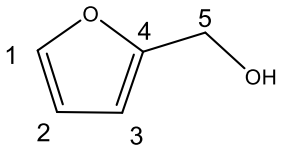
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 126.8 (*s*, 2C, *C*2+*C*6), 125.4 (*d*, $^{1}J_{HP}$ = 3.8 Hz, 2C, *C*3+*C*5), 64.5 (*s*, 1C, *C*7).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ = -62.5 (*s*).



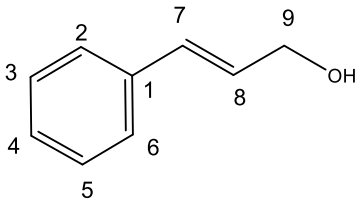
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (*d*, $^{3}J_{HH}$ = 8.4 Hz, 2H, *H*3+*H*5), 7.19 (*d*, $^{3}J_{HH}$ = 7.8 Hz, 2H, *H*2+*H*6), 4.67 (*s*, 2H, *H*7), 2.38 (*s*, 3H, *H*8).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 129.3 (*s*, 2C, *C*3+*C*5), 127.1 (*s*, 2C, *C*2+*C*6), 65.3 (*s*, 1C, *C*7), 21.2 (*s*, 1C, *C*8).



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (*s*, 1H, *H*1), 6.32 (*d*, $^{3}J_{HH}$ = 18.8 Hz, 2H, *H*2+*H*3), 4.64 (*s*, 2H, *H*5).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 142.6 (*s*, 1C, *C*1), 110.3 (*s*, 1C, *C*2), 107.8 (*s*, 1C, *C*3), 57.5 (*s*, 1C, *C*5).

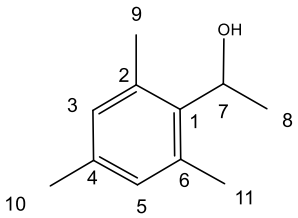


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.34 (*m*, 5H, *H*2+*H*3+*H*4+*H*5+*H*6), 6.45 (*d*, $^3J_{H7H8}$ = 16.1 Hz, 1H, *H*7), 6.19 (*dt*, $^3J_{H8H7}$ = 15.9 Hz, $^3J_{H8H9}$ = 5.6 Hz, 1H, *H*8), 4.11 (*d*, $^3J_{H9H8}$ = 4.9 Hz, 2H, *H*9).

4.2.2. Hydrogenation of ketones

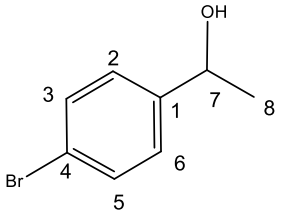
Ketone (986 mmol), catalyst **1** (0.5 mg, $9.86x10^{-4}$ mmol), K_2CO_3 (13.6 mg, 98.6 mmol) and EtOH (1 ml) were mixed in the Parr reactor. The reactor was pressurized to 40 bar with H_2 and allowed to react for 4 h at 70ºC. The reactor was then depressurized and allowed to reach room temperature.

The reaction mixture was then dried from solvent and dissolved into dichloromethane followed by silica gel filtration. The solvent was removed and an oil or solid was obtained which was analyzed by NMR.



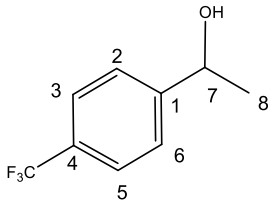
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (*s*, 2H, *H*3+*H*5), 5.39 (*q*, $^3J_{H7H8}$ = 6.7 Hz, 1H, *H*7), 2.30 (*s*, 6H, *H*9+*H*11) 2.27 (*s*, 3H, *H*10), 2.30 (*d*, $^3J_{H8H7}$ = 6.8 Hz, 3H, *H*8).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 128.5 (*s*, 2C, *C*3+*C*5), 32.3 (*s*, 1C, *C*7), 21.6 (*s*, 1C, *C*8), 21.0 (*s*, 1C, *C*9), 19.1 (*s*, 2C, *C*8+*C*10).



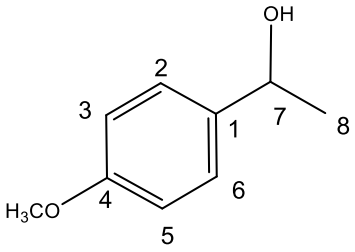
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (*d*, $^3J_{HH}$ = 7.9 Hz, 2H, *H*3+*H*5), 7.27 (*d*, $^3J_{HH}$ = 7.9 Hz, 2H, *H*2+*H*6), 4.89 (*q*, $^3J_{H7H8}$ = 6.4 Hz, 1H, *H*7), 1.49 (*d*, $^3J_{H8H7}$ = 6.3 Hz, 3H, *H*8).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 131.6 (*s*, 2C, *C*3+*C*5), 127.2 (*s*, 2C, *C*2+*C*6), 69.8 (*s*, 1C, *C*7), 25.3 (*s*, 1C, *C*8).



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (*d*, $^3J_{HH}$ = 7.9 Hz, 2H, *H*3+*H*5), 7.52 (*d*, $^3J_{HH}$ = 7.9 Hz, 2H, *H*2+*H*6), 4.99 (*q*, $^3J_{H7H8}$ = 6.3 Hz, 1H, *H*7), 1.53 (*d*, $^3J_{H8H7}$ = 6.5 Hz, 3H, *H*8).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 125.7 (*s*, 2C, *C*2+*C*6), 125.5 (*s*, 2C, *C*3+*C*5), 69.8 (*s*, 1C, *C*7), 25.4 (*s*, 1C, *C*8).



1H NMR (300 MHz, CDCl3): δ = 7.33 (*d*, 3*J*HH = 8.6 Hz, 2H, *H*2+*H*6), 6.91 (*d*, 3*J*HH = 8.6 Hz, 2H, *H*3+*H*5), 4.88 (*q*, 3*J*H7H8 = 6.3 Hz, 1H, *H*7), 3.83 (*s*, 3H, OC*H*3), 1.50 (*d*, 3*J*H8H7 = 6.4 Hz, 3H, *H*8).

13C{1H} NMR (75 MHz, CDCl3): δ = 126.7 (*s*, 2C, *C*2+*C*6), 113.9 (*s*, 2C, *C*3+*C*5), 70.0 (*s*, 1C, *C*7), 55.3 (*s*, 1C, O*C*H3), 25.0 (*s*, 1C, *C*8).

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