Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Catalytic carbonyl hydrosilylations *via* a titanocene borohydride-PMHS reagent system

Godfred D. Fianu,[a] Kyle C. Schipper[a] and Robert A. Flowers II[a]

[a] *Department of Chemistry, Lehigh University, Bethlehem, PA 18015, USA*

Supporting Information

Table of Contents

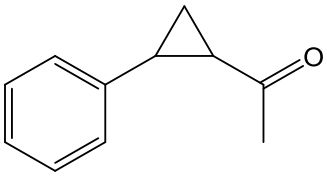
General Information

Unless otherwise stated, all reactions were carried out in the glove box under argon atmosphere. An Innovative Technology solvent purification system was used to purify all the solvents used for experiments. All reagents and chemicals, mostly argon or nitrogen flushed, were purchased from reputable chemical vendors (Alfa Aesar, Acros, Sigma Aldrich, Beantown Chemical, and TCI) and used without further purification. Chemicals not flushed with an inert gas were degassed with argon and used without any additional purification protocols. ^{1}H-NMR spectra were measured on either a Bruker 500MHz or a Bruker 400MHz spectrometer in deuterated chloroform ($CDCl_3$). ^{13}C-NMR spectra were measured at either 126 MHz or at 101 MHz in $CDCl_3$. GC-MS analyses were done with a Schimadzu GCMS-Q2010 series with a SHRX-5M (30m) column. Column chromatography was done using an automated CombiFlash® system from Teledyne Isco. Inc. Columns were prepacked with silica gel and product separations were performed with a gradient elution of hexanes and ethyl acetate. *In situ* IR experiments were done using Mettler-Toledo's ReactIR 15 fitted with DiComp probe and running iCIR software 4.3 SP1.

1. (GP 1) General procedure for carbonyl reduction with titanocene borohydride and PMHS

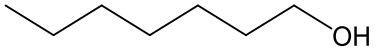
A 40 mL vial was charged with titanocene dichloride (Cp_2TiCl_2) (0.1 mmole, 25 mg) and sodium borohydride ($NaBH_4$) (0.2 mmole, 7.6 mg). To this was added 10 mL dimethoxyethane (DME) and left to stir till a violet colored solution was formed, which is indicative of the formation of titanocene borohydride (Cp_2TiBH_4). Polymethylhydrosiloxane (PMHS) (3 mmole, 195 mg) was added to the solution. 2.0 mmole of either the aldehyde or the ketone was added to the violet solution. The solution turned grey upon ketone addition then gradually turned to a dirty green color. The solution was left to stir for the appropriate time. Solution was taken out of the glovebox and exposed to air to quench the catalyst. About 10 mL of ether was added followed by dropwise addition of 10 mL 1 M NaOH solution to quench the excess PMHS. (Note: vigorous bubbling observed with NaOH addition). The mixture was stirred until bubbling stopped and clear layers were observed (Note: For good yields of alcohol products, the mixture was stirred overnight). Organic layer was separated and the aqueous layer was washed with 10 mL ether. Organic layers were combined and washed with 10 mL 1 M NaOH, followed by 10 mL brine solution then dried with $MgSO_4$. The solution was evaporated to dryness to obtain the isolated yield of clean product after NMR analysis.

(GP 2) General procedure for synthesizing 1-(2-phenylcyclopropyl) ethan-1-one (1-v)



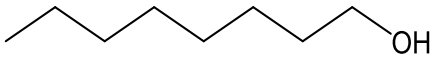
1-(2-phenylcyclopropyl) ethan-1-one **(1-v)** was synthesized using a variant of the Corey-Chaykovsky cyclopropanation reaction.[1] A 200 mL 3-necked round bottomed flask was charged with sodium hydride (NaH) (39.1 mmole, 1 g) under argon atmosphere. To this 20 mL of DMSO was added and stirred. Trimethylsulfoxonium iodide ($(CH_3)_3SOI$) (38 mmole, 8.3 g) was carefully and slowly added to the mixture. 40 mL of THF was added to the mixture and left to stir for about 30 minutes. Benzalacetone (34 mmole, 5 g) dissolved in 20 mL DMSO was added to the mixture followed by 40 mL THF. The mixture was left to stir overnight. Ice was added to the mixture to quench excess NaH and rotavaped to remove THF. Excess distilled water (approximately 100 mL) was added to the mixture followed by 100 mL hexanes. The aqueous layer was separated and washed three more times with about 100 mL hexanes. The organic layers were combined and washed one more time with distilled water. The solution was rotavaped and the compound was purified by flash chromatography (Hexanes: Ethyl acetate = 90:10) to obtain desired product **(1-v)**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.23 (dt, *J* = 9.2, 4.2 Hz, 1H), 7.11 (dd, *J* = 8.1, 0.9 Hz, 2H), 2.57 – 2.50 (m, 1H), 2.32 (s, 3H), 2.26 – 2.20 (m, 1H), 1.69 (ddd, *J* = 9.3, 5.2, 4.3 Hz, 1H), 1.40 (ddd, *J* = 8.1, 6.6, 4.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.35, 128.54, 126.56, 126.04, 77.37, 77.12, 76.86, 32.93, 30.90, 29.07, 19.19.

2. Reduction of aldehydes and ketones (1) to alcohol products (2)



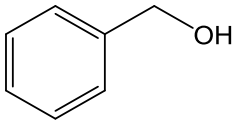
1-Heptanol (2-a)

1-heptanol (**2-a**) was prepared from heptanal (**1-a**) by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 60% isolated yield of alcohol product was obtained after complete workup and flash chromatography (Hex: EtOAc = 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (t, *J* = 6.8 Hz, 2H), 2.78 (s, 1H), 1.53 – 1.43 (m, 2H), 1.31 – 1.14 (m, 8H), 0.81 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 77.40, 77.09, 76.77, 62.70, 32.68, 31.83, 29.13, 25.72, 22.60, 14.03.



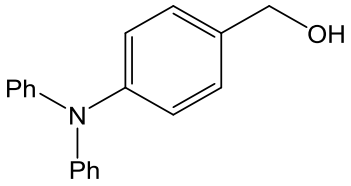
1-Octanol (2-b)

1-octanol (**2-b**) was prepared from octantal (**1-b**) by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 70% isolated yield of alcohol product was obtained after complete workup and flash chromatography (Hex: EtOAc = 70:30) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (t, *J* = 6.7 Hz, 2H), 2.57 (s, 1H), 1.50 (dq, *J* = 13.8, 6.7 Hz, 2H), 1.31 – 1.16 (m, 10H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 77.40, 77.08, 76.76, 62.77, 32.70, 31.83, 29.43, 29.30, 25.77, 22.65, 14.07.



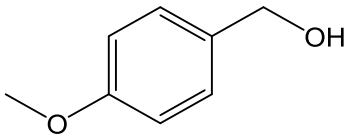
Phenyl methanol (2-c)

Phenyl methanol (**2-c**) was prepared from benzaldehyde (**1-c**) by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 86% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 4.59 (s, 2H), 2.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.92, 128.56, 127.60, 127.07, 77.52, 77.20, 76.88, 65.04.



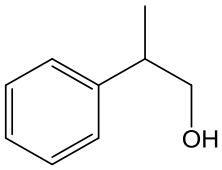
(4-(diphenylamino) phenyl) methanol (2-d)

(4-(diphenylamino) phenyl) methanol (**2-d**) was prepared from 4-(diphenylamino) benzaldehyde (**1-d**) by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 95% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (ddt, *J* = 7.2, 4.1, 2.1 Hz, 6H), 7.13 – 7.07 (m, 6H), 7.05 – 6.98 (m, 2H), 4.60 (s, 2H), 2.33 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.82, 147.47, 135.09, 129.34, 128.39, 124.28, 124.11, 122.88, 77.52, 77.20, 76.88, 64.97.



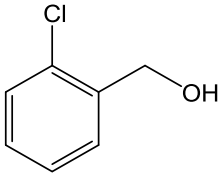
(4-methoxyphenyl) methanol (2-e)

(4-methoxyphenyl) methanol **(2-e)** was prepared from 4-methoxybenzaldehyde **(1-e)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 87% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 2H), 6.88 – 6.78 (m, 2H), 4.49 (s, 2H), 3.75 (s, 3H), 2.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.03, 133.22, 128.67, 113.87, 77.53, 77.22, 76.90, 64.63, 55.29.



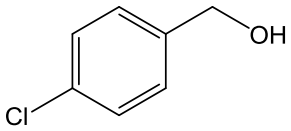
2-phenylpropan-1-ol (2-f)

2-phenylpropan-1-ol **(2-f)** was prepared from 2-phenylpropanal **(1-f)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 58% isolated yield of alcohol product was obtained after complete workup and flash chromatography (Hex: EtOAc = 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 3.71 – 3.59 (m, 2H), 2.98 – 2.86 (m, 1H), 2.04 (s, 1H), 1.27 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.88, 128.64, 127.57, 126.67, 77.52, 77.20, 76.88, 68.64, 42.45, 17.69.



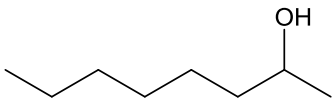
(2-chlorophenyl) methanol (2-g)

(2-chlorophenyl) methanol **(2-g)** was prepared from 2-chlorobenzaldehyde **(1-g)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 94% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (ddd, *J* = 7.1, 1.6, 0.5 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.25 – 7.13 (m, 2H), 4.68 (d, *J* = 5.2 Hz, 2H), 3.20 (t, *J* = 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.17, 132.58, 129.29, 128.74, 128.56, 127.01, 77.51, 77.19, 76.87, 62.49.



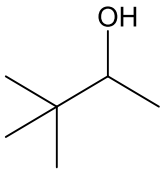
(4-chlorophenyl) methanol (2-h)

(4-chlorophenyl) methanol **(2-h)** was prepared from 4-chlorobenzaldehyde **(1-h)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 1 hour. 89% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (ddd, *J* = 8.7, 4.3, 1.2 Hz, 4H), 4.50 (s, 2H), 3.18 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.20, 133.26, 128.63, 128.29, 77.49, 77.17, 76.85, 64.20.



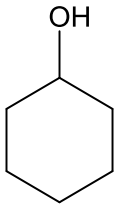
2-octanol (2-i)

2-octanol **(2-i)** was prepared from 2-octanone **(1-i)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 79% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.79 – 3.71 (m, 1H), 2.00 (s, 1H), 1.48 – 1.34 (m, 3H), 1.26 (s, 7H), 1.15 (d, *J* = 6.2 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 77.32, 77.06, 76.81, 68.02, 39.33, 31.83, 29.32, 25.73, 23.36, 22.59, 14.03.



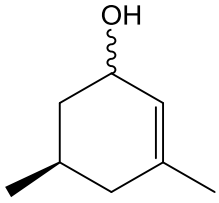
3,3-dimethylbutan-2-ol (2-j)

3,3-dimethylbutan-2-ol **(2-j)** was prepared from 3,3-dimethylbutan-2-one **(1-j)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 72% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (q, *J* = 6.4 Hz, 1H), 1.50 (s, 1H), 1.08 (d, *J* = 6.4 Hz, 3H), 0.85 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 77.38, 77.06, 76.74, 75.64, 34.90, 25.42, 17.87.



Cyclohexanol (2-k)

Cyclohexanol **(2-k)** was prepared from cyclohexanone **(1-k)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 43% isolated yield of alcohol product was obtained after complete workup. Note: Some of the product was lost during work up due to evaporation on the rotavap. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (dt, *J* = 9.1, 4.3 Hz, 1H), 1.93 – 1.81 (m, 3H), 1.72 (dd, *J* = 8.7, 4.1 Hz, 2H), 1.54 (d, *J* = 11.7 Hz, 1H), 1.32 – 1.20 (m, 4H), 1.17 (dd, *J* = 16.3, 7.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 77.31, 77.06, 76.81, 70.29, 35.52, 25.45, 24.15.



3,5-dimethylcyclohex-2-ene-1-ol (2-l)

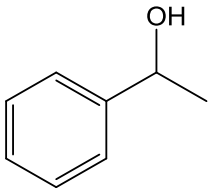
3,5-dimethylcyclohex-2-ene-1-ol **(2-l)** was prepared from 3,5-dimethylcyclohex-2-en-1-one **(1-l)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 84% combined isolated yield of alcohol product was obtained after complete workup.

Determining ratio for *cis* isomer using H11 (See NMR spectra for 2-l)

(1.00/(1.00+0.22))*100% = 82%

Ratio for *trans* isomer

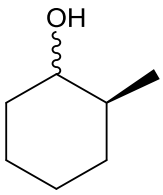
(0.22/(1.00+0.22)) *100% = 18%



1-phenylethan-1-ol (2-m)

1-phenylethan-1-ol **(2-m)** was prepared from acetophenone **(1-m)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 73% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 –

7.26 (m, 5H), 4.88 (q, *J* = 6.5 Hz, 1H), 2.42 (s, 1H), 1.50 (d, *J* = 6.5 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 145.90, 128.51, 127.45, 125.45, 77.39, 77.14, 76.88, 70.35, 25.18.



2-methylcyclohexanol (2-n)

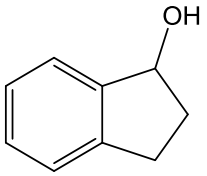
2-methylcyclohexanol **(2-n)** was prepared from 2-methylcyclohexanone **(1-n)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 85% combined isolated yield of alcohol product was obtained after complete workup.

Determining ratio for *cis* isomer using H9 (See NMR spectra for 2-n)

(1.00/(1.00+0.49))*100% = 67%

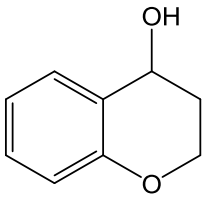
Ratio for *trans* isomer

(0.49/(1.00+0.49)) *100% = 33%



2,3-dihydro-1H-inden-1-ol (2-o)

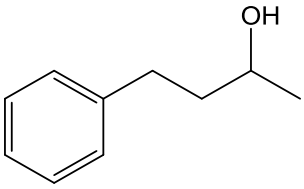
2,3-dihydro-1H-inden-1-ol **(2-o)** was prepared from 2,3-dihydro-1H-inden-1-one **(1-o)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 89% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.7 Hz, 1H), 7.30 – 7.19 (m, 3H), 5.16 (t, *J* = 6.1 Hz, 1H), 3.22 (s, 1H), 3.02 (ddd, *J* = 16.0, 8.6, 4.7 Hz, 1H), 2.83 – 2.73 (m, 1H), 2.46 – 2.36 (m, 1H), 1.89 (dddd, *J* = 13.2, 8.6, 6.8, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.09, 143.34, 128.22, 126.68, 124.88, 124.39, 77.60, 77.28, 76.96, 76.16, 35.74, 29.86.



Chroman-4-ol (2-p)

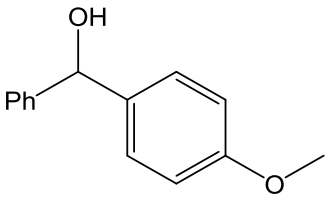
Chroman-4-ol **(2-p)** was prepared from chroman-4-one **(1-p)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 82% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* =

7.6, 1.7 Hz, 1H), 7.19 – 7.13 (m, 1H), 6.87 (td, *J* = 7.4, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.60 (d, *J* = 3.2 Hz, 1H), 4.20 – 4.07 (m, 2H), 3.35 (d, *J* = 3.2 Hz, 1H), 2.04 – 1.92 (m, 1H), 1.90 – 1.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.52, 129.91, 129.62, 124.31, 120.56, 116.97, 77.58, 77.26, 76.94, 62.98, 62.01, 30.83.



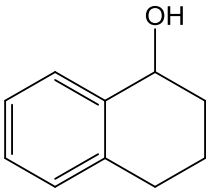
4-phenylbutan-2-ol (2-q)

4-phenylbutan-2-ol **(2-q)** was prepared from 4-phenylbutan-2-one **(1-q)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 97% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 3.83 (d, *J* = 5.7 Hz, 1H), 2.73 (dddd, *J* = 37.5, 13.8, 9.4, 6.5 Hz, 2H), 2.31 (d, *J* = 2.5 Hz, 1H), 1.87 – 1.70 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.21, 128.49, 128.47, 125.87, 77.54, 77.23, 76.91, 67.44, 40.91, 32.22, 23.61.



(4-methoxyphenyl) (phenyl) methanol (2-r)

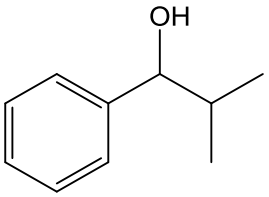
(4-methoxyphenyl) (phenyl) methanol **(2-r)** was prepared from (4-methoxyphenyl) (phenyl) methanone **(1-r)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 88% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 7H), 6.91 – 6.85 (m, 2H), 5.69 (d, *J* = 2.8 Hz, 1H), 3.77 (s, 3H), 3.37 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 144.30, 136.45, 128.50, 128.10, 127.43, 126.60, 113.91, 77.70, 77.38, 77.06, 75.67, 55.33.



1,2,3,4-tetrahydronaphthalen-1-ol (2-s)

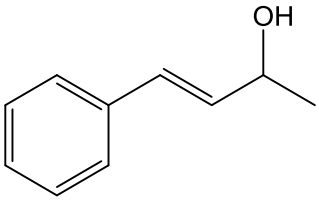
1,2,3,4-tetrahydronaphthalen-1-ol **(2-s)** was prepared from 3,4-dihydronaphthalen-1(2H)-one **(1-s)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 92% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, CDCl3) δ 7.45 – 7.39 (m, 1H), 7.24 – 7.18 (m, 2H), 7.14 – 7.08 (m, 1H),

4.74 – 4.69 (m, 1H), 2.83 (ddd, *J* = 16.9, 8.2, 4.1 Hz, 1H), 2.73 (ddd, *J* = 16.5, 8.0, 5.8 Hz, 2H), 2.03 – 1.91 (m, 2H), 1.91 – 1.82 (m, 1H), 1.82 – 1.70 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 138.93, 137.16, 129.00, 128.82, 127.52, 126.16, 77.60, 77.29, 76.97, 68.02, 32.29, 29.34, 18.98.



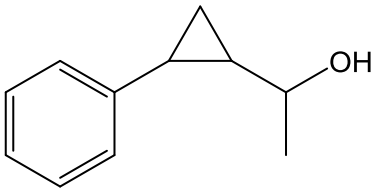
2-methyl-1-phenylpropan-1-ol (2-t)

2-methyl-1-phenylpropan-1-ol **(2-t)** was prepared from 2-methyl-1-phenylpropan-1-one **(1-t)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 2 hours. 99% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 3H), 4.27 (d, *J* = 6.9 Hz, 1H), 2.80 (s, 1H), 1.98 – 1.84 (m, *J* = 6.8 Hz, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.75, 128.15, 127.35, 126.74, 79.93, 77.58, 77.27, 76.95, 35.24, 19.01, 18.48.



4-phenylbut-3-en-2-ol (2-u)

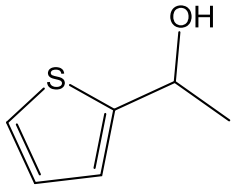
4-phenylbut-3-en-2-ol **(2-u)** was prepared from 4-phenylbut-3-en-2-one **(1-u)** by the procedure outlined in GP1. NMR analysis showed 66% conversion in 2 hours. Reaction did not proceed any further and 63% isolated yield of alcohol product was obtained after complete workup and flash chromatography (Hex: EtOAc = 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dt, *J* = 2.9, 1.9 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.47 (pd, *J* = 6.4, 1.2 Hz, 1H), 2.17 (s, 1H), 1.36 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.74, 133.63, 129.35, 128.64, 127.67, 126.50, 77.47, 77.15, 76.84, 68.92, 23.45.



1-(2-phenylcyclopropyl) ethan-1-ol (2-v)

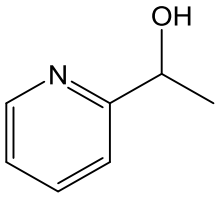
1-(2-phenylcyclopropyl) ethan-1-ol **(2-v)** was prepared from 1-(2-phenylcyclopropyl) ethan-1-one **(1-v)** by the procedure outlined in GP1. NMR analysis showed 100%

conversion in 3 hours. 73% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.21 – 7.15 (m, 1H), 7.12 – 7.06 (m, 2H), 3.40 – 3.31 (m, 1H), 2.67 (s, 1H), 1.95 – 1.75 (m, 1H), 1.52 – 1.46 (m, 1H), 1.34 (dd, *J* = 6.3, 2.3 Hz, 3H), 1.31 – 1.22 (m, 1H), 1.09 – 0.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.96, 128.43, 128.42, 125.99, 125.89, 125.69, 125.62, 77.61, 77.29, 76.97, 71.64, 71.57, 30.86, 30.79, 22.84, 22.53, 21.45, 20.78, 14.05, 13.51.



1-(thiophen-2-yl) ethan-1-ol (2-w)

1-(thiophen-2-yl) ethan-1-ol **(2-w)** was prepared from 1-(thiophen-2-yl) ethan-1-one **(1-w)** by the procedure outlined in GP1. NMR analysis showed 100% conversion in 3 hours. 89% isolated yield of alcohol product was obtained after complete workup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 5.1, 2.0 Hz, 1H), 6.96 – 6.88 (m, 2H), 5.05 (q, *J* = 6.3 Hz, 1H), 2.82 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.97, 126.68, 124.40, 123.23, 77.51, 77.20, 76.88, 66.14, 25.27.



1-(pyridin-2-yl) ethan-1-ol (2-x)

1-(pyridin-2-yl) ethan-1-ol **(2-x)** was prepared from 1-(pyridin-2-yl) ethan-1-one **(1-x)** by the procedure outlined in GP1. NMR analysis showed 92% conversion when left to stir overnight. Reaction did not proceed any further and 85% isolated yield of alcohol product was obtained after complete workup and flash chromatography (Hex: EtOAc = 70:30). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.29 – 7.22 (m, 1H), 7.11 (ddd, *J* = 7.5, 4.9, 0.9 Hz, 1H), 4.83 (q, *J* = 6.6 Hz, 1H), 4.69 (s, 1H), 1.43 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.39, 148.09, 136.88, 122.21, 119.81, 77.46, 77.14, 76.82, 69.09, 24.20.

3. Control and optimization experiments

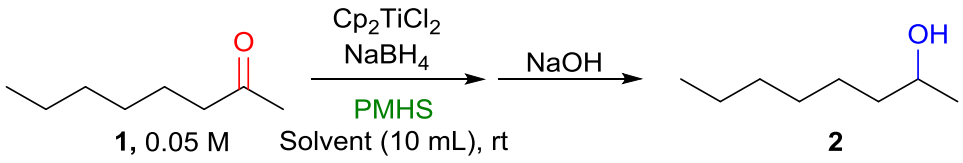
Procedure for reducing 2-octanone with titanocene borohydride (Table S1, Entries 1-5)

All the reactions were carried out in the glove box under argon atmosphere. To a 40-mL vial was charged with titanocene dichloride and sodium borohydride. To this was added 10 mL dimethoxyethane (DME) and left to stir till a violet colored solution was formed, which is indicative of the formation of titanocene borohydride. 2-octanone was added to the violet solution. The solution turned grey upon ketone addition. An aliquot (1 mL) was taken, exposed to air to quench the catalyst. 2 mL of ether was added followed by 2 mL H_2O to quench the excess $NaBH_4$. The organic layer was separated, biphenyl was then added and run through GCMS to evaluate progress of reaction and yield of product. For entries 6-8 the reaction was performed by following the procedure outlined in **GP 1**. An aliquot (approximately 1 mL) was taken, exposed to air to quench the catalyst. 2 mL of ether was added followed by dropwise addition of 2 mL 1 M NaOH solution to quench the excess PMHS. The organic layer was separated, biphenyl was added, and solution was run through the GCMS to evaluate progress of reaction. For entries 9-16, a 40-mL vial was charged with titanocene dichloride and $NaBHX_3$. To this was added 10 mL of solvent and left to stir till a color change was observed, which was either green (Cp_2TiCl_2 and NaH_3CN in THF/DME) or yellow (Cp_2TiCl_2 and $NaH(OAc)_3$ in THF/DME)(**Figure S1**). 2-octanone was added to the resulting solution and no color change was observed. The solution was left to stir for the indicated time. The solutions were exposed to air worked up and analyzed by GCMS.

Procedure for reducing 2-octanone with titanocene difluoride (Table S2)[2,3]

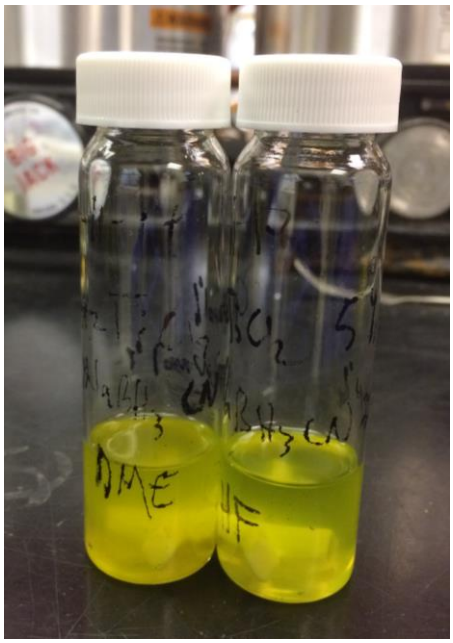
A 40-mL vial was charged with titanocene difluoride (0.025 mmole, 5.4 mg). To this was added 10 mL tetrahydrofuran (THF) and either PMHS (1 mmole, 65 µL) or $PhSiH_3$ (1 mmole, 123 µL). The solution was left to stir either under room temperature or under refluxing conditions until a green colored solution was formed. 2-octanone (0.5 mmole, 78 µL) was added to solution and left to stir for an hour. An aliquot (1 mL) was taken, exposed to air to quench the catalyst. 2 mL of ether was added followed by 2 mL 1M NaOH solution to quench the excess silane. The organic layer was separated, biphenyl was then added and run through GCMS to evaluate progress of reaction and yield of product.

Table 1: Results from control experiments



Entry	Cp_2TiCl_2 (mol%)	$NaBHX_3$	$NaBHX_3$ (mol%)	PMHS (mol%)	Solvent	Time (h)	Yield (%)[1]
1	20	$NaBH_4$	400	-	DME	1	100[2]
2	20	$NaBH_4$	200	-	DME	1	100[2]
3	10	$NaBH_4$	200	-	DME	4	95
4		$NaBH_4$	400	-	DME	96	41
5	5	$NaBH_4$	150	-	DME	4	57
6	5	$NaBH_4$	10	150	DME	1	100[2]
7	-	-	-	150	DME	24	-
8	-	$NaBH_4$	10	150	DME	24	13
9	-	$NaBH_3CN$	200	-	THF	24	-
10	5	$NaBH_3CN$	200	-	THF	6	-
11	-	$NaBH_3CN$	200	-	DME	24	-
12	5	$NaBH_3CN$	200	-	DME	6	-
13	-	$NaBH(OAc)_3$	200	-	THF	24	-
14	5	$NaBH(OAc)_3$	200	-	THF	6	-
15	-	$NaBH(OAc)_3$	200	-	DME	24	-
16	5	$NaBH(OAc)_3$	200	-	DME	6	-

[1]GC yields with biphenyl as internal standard. [2] Only product observed by GC.

a. 

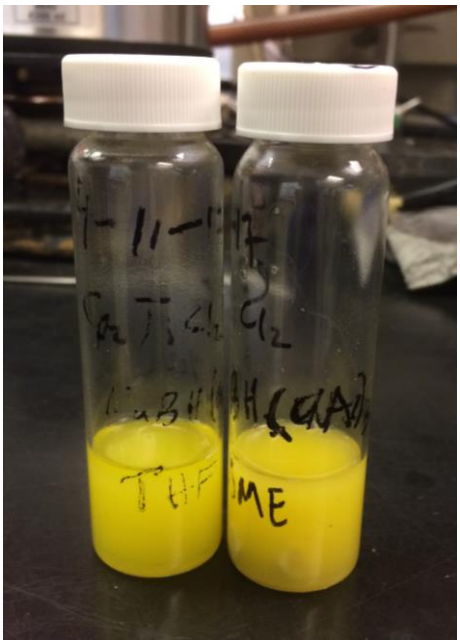
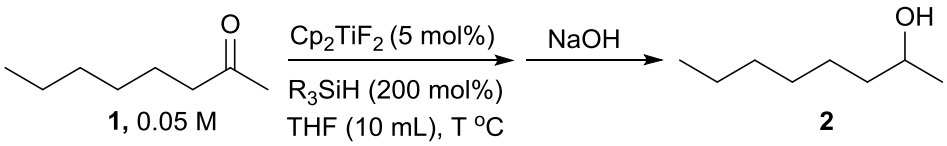
b. 

Figure S1: a. Solution of Cp_2TiCl_2, NaH_3CN, and **1** in THF and DME (Entries 10 & 12). **b.** Mixture of Cp_2TiCl_2, $NaH(OAc)_3$, and **1** in THF and DME (Entries 14 & 16).

Table S2 Reduction of **1** to **2** with Cp_2TiF_2



Entry	R_3SiH	T (°C)	Yield (%)[1]
1	$PhSiH_3$	r.t.	-
2	PMHS	r.t.	-
3	PMHS[2]	r.t	-
4	PMHS	60	45
5	PMHS[2]	60	91

[1]GC yields after 1 h with biphenyl as internal standard. [2] Active catalyst formed with 20 mol% $PhSiH_3$ under reflux.

Results in table S2 entries 3 & 5 were obtained from the same reaction. Active catalyst was generated under reflux with 20 mol% $PhSiH_3$, then cooled to room temperature before PMHS and **1** were added. Reaction was left to stir for an hour at room temperature. An aliquot was taken, worked up, and analyzed with GCMS. Only starting material was observed (Table S2, entry 3). The reaction was left to stir overnight at room temperature and still no product was observed. The reaction was then heated to 60 °C for an hour. An aliquot was taken, worked up, and analyzed with GCMS with biphenyl as internal standard to obtain 91% of **2**.

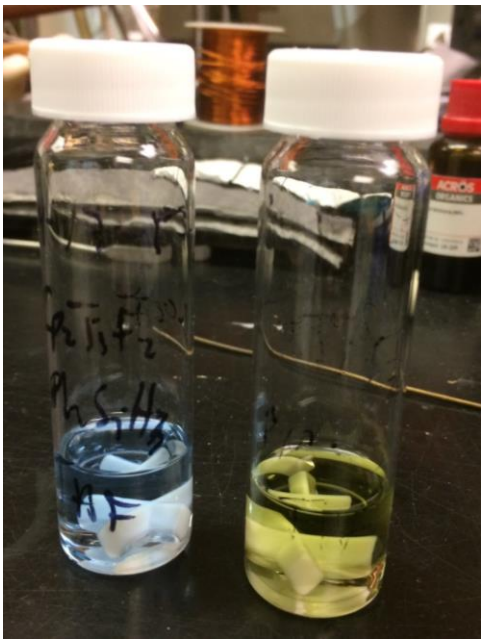


Figure S2 Solution of Cp_2TiF_2**,** $PhSiH_3$, and **1** in THF (**Table 2S**, Entry 1) (Left); Solution of Cp_2TiF_2**,** PMHS, and **1** in THF (**Table 2S**, Entry 2) (Right)

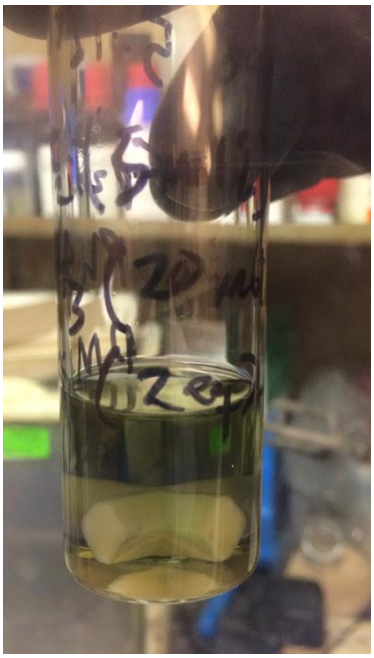
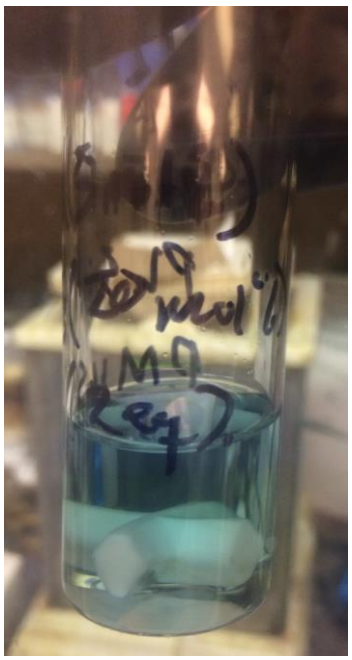
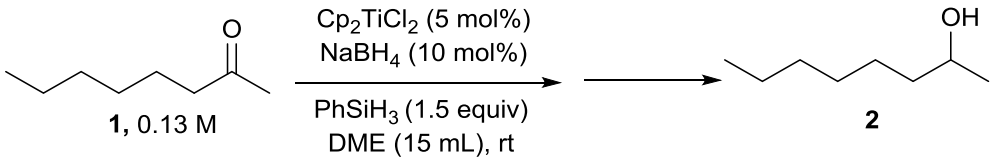
a.  b. 

Figure S3 a. Solution of Cp_2TiF_2**,** 20 mol% $PhSiH_3$, 2 equiv PMHS in THF; **b.** Solution of Cp_2TiF_2**,** 20 mol% $PhSiH_3$, 2 equiv PMHS and **1** in THF (**Table 2S**, Entries 3 & 5)

a.  b. 

Figure S4 a. Solution of Cp_2TiF_2**,** PMHS in THF at reflux; **b.** Solution of Cp_2TiF_2**,** PMHS, and **1** in THF at reflux (**Table 2S**, Entry 2) (**Table 2S**, Entry 4)

4. ReactIR studies



In situ IR experiments were done using Mettler-Toledo's ReactIR 15 fitted with DiComp probe and running iCIR software 4.3 SP1.

ReactIR Conditions

Reference Spectra **=** 00:01:53 (hh:mm:ss)

Background Replacement = Original

Baseline Correction = None

Spectrum Math = 2nd derivative (Subtle changes were observed when a 2nd derivative of the spectra was taken).

To a two-necked round bottom flask, sodium borohydride ($NaBH_4$) (0.2 mmole, 7.6 mg) was added and attached to a reflux condenser inside the glove box. This was taken out and fixed to the ReactIR probe and flushed with argon. An air background (256 scans) was obtained and 10 mL of DME was added to the round bottom flask through a rubber septum. The iCIR program was initiated to collect solvent background for 3 minutes (256 scans/minute). Titanocene dichloride (Cp_2TiCl_2) (0.1 mmole, 25 mg), dissolved in 2 mL DME, was added through the rubber septum, and rinsed with 0.5 mL DME. The mixture was left to stir until a violet solution was formed. The formation of Cp_2TiBH_4 was demonstrated by a shift in the C-H wag of the Cp ligand from 820 cm^{-1} to 809 cm^{-1} (Figure S5).

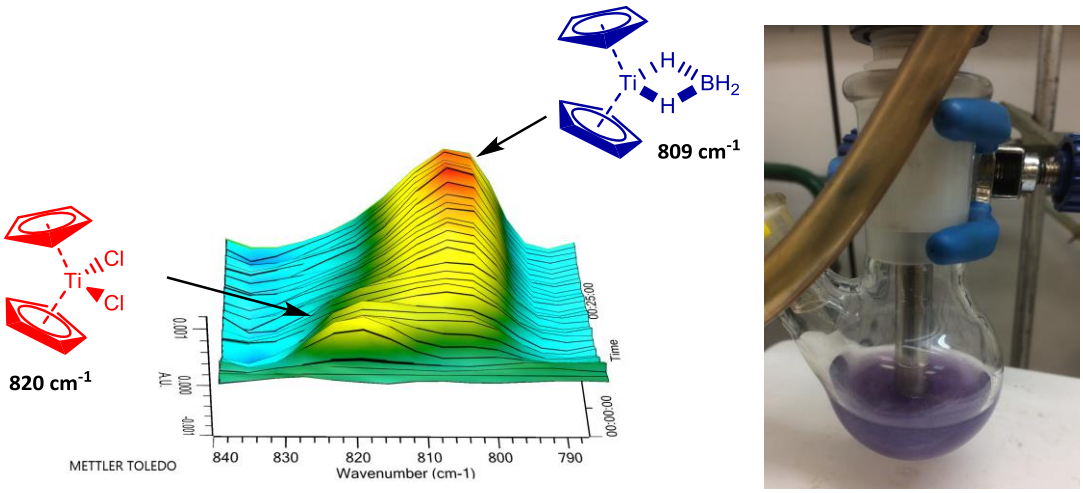


Figure S5: Formation of titanocene borohydride monitored by ReactIR.

To the violet solution, 2-octanone (2.0 mmole, 312 µL) dissolved in 1 mL DME was added and rinsed with 0.5 mL DME. The solution turned light blue upon ketone addition then gradually turned to a dirty green color. A shift in the C-H wag of the titanocene complex from 809 cm^{-1} to 799 cm^{-1} was also observed (Figure S6).

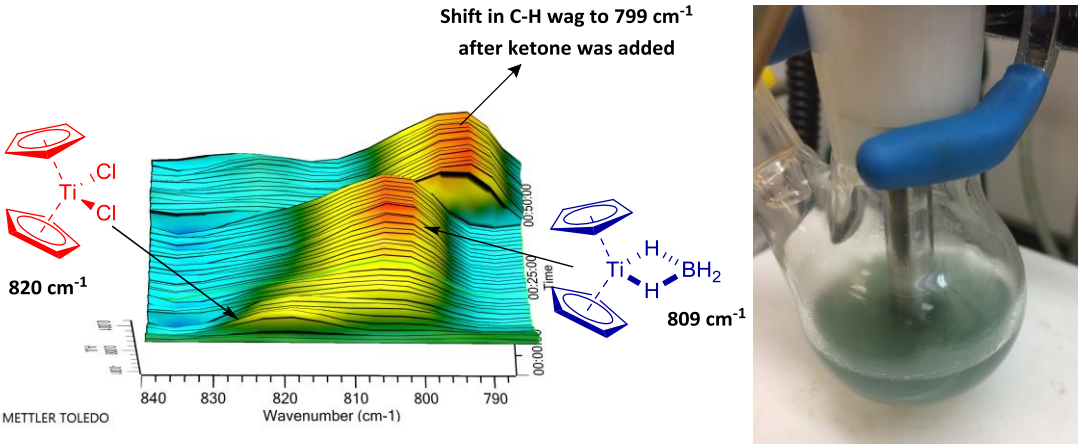


Figure S6: Shift in C-H wag upon ketone addition.

Reduction of 2-octanone could be observed by monitoring the decrease in absorption over time at 1719 cm^{-1}, which is a characteristic absorbance for most carbonyls. The minor drop in absorbance upon ketone addition is attributed to an initial reduction of ketone by titanocene borohydride with subsequent formation of a Ti(III)-O interaction (Figure S7).

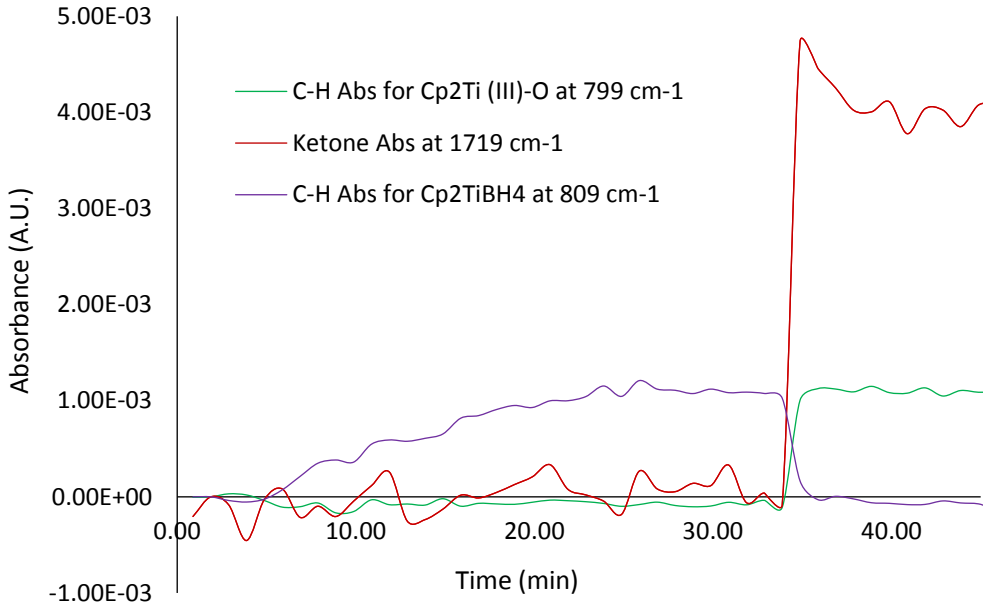


Figure S7: Trend observed on ReactIR for 2-octanone and catalyst.

After no further changes were observed, phenylsilane ($PhSiH_3$) (3.0 mmole, 195mg) in 1mL DME was added to the solution and was observed on the ReactIR by monitoring the Si-H absorbance at 705 cm^{-1} (Figure S8). The ketone is further reduced to completion which is demonstrated by the decay in the carbonyl absorbance. The absorbance of phenyl silane simultaneously decays with a concomitant growth in absorbance at 835 cm^{-1}, which is attributed to the development of sylilated product.

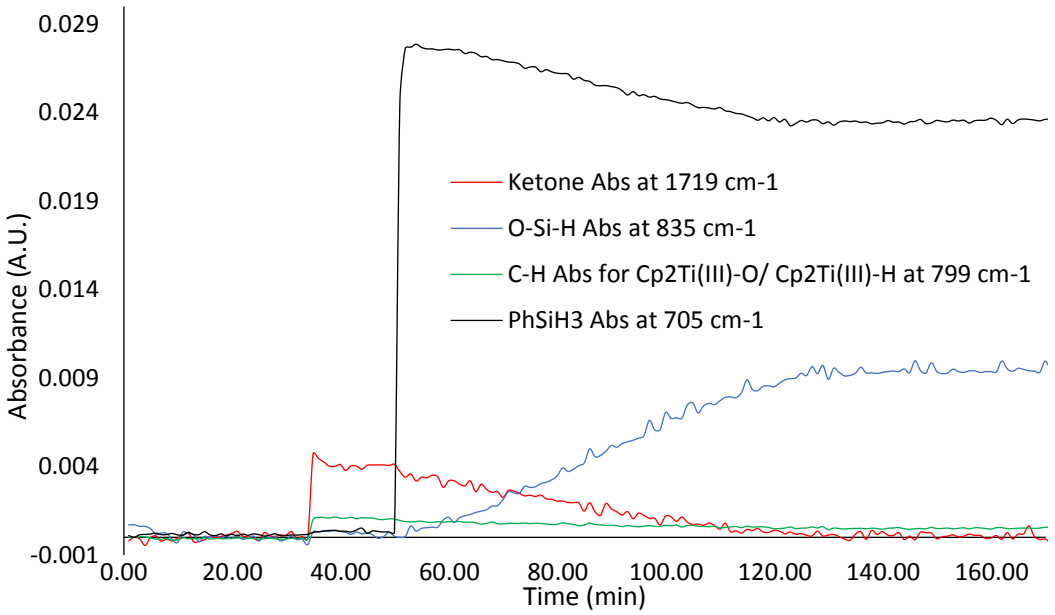


Figure S8: Monitoring the progress of the reaction after the addition of phenylsilane.

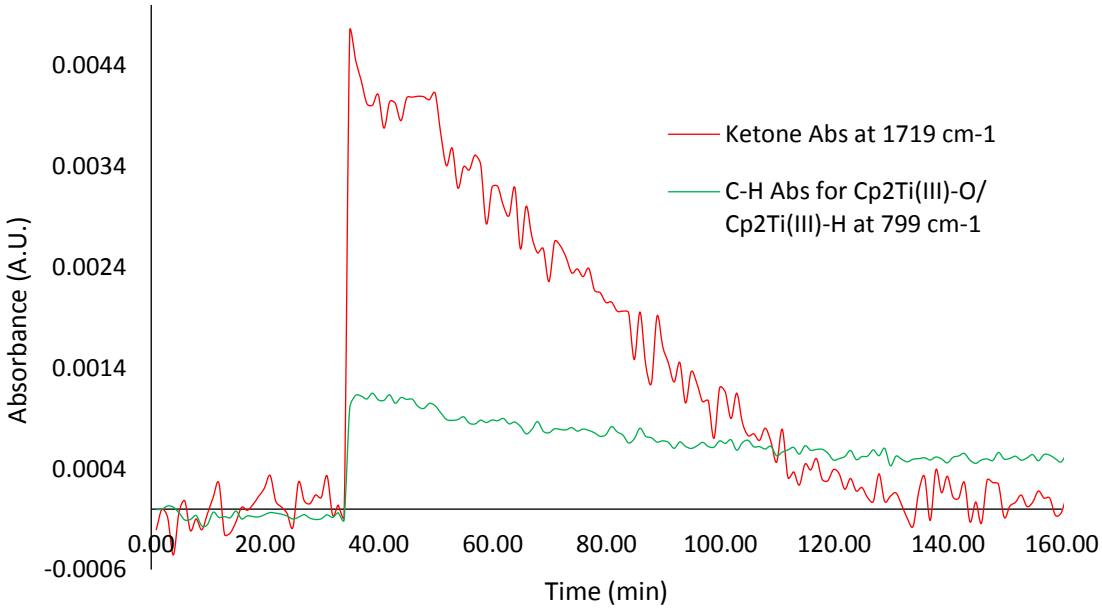


Figure S9: Persistence of the C-H wag absorbance at 799 cm^{-1} after complete ketone reduction.

As shown in figure S9**,** the C-H wag absorbance for the titanocene complex at 799 cm^{-1} persists after the reduction of ketone is complete. This indicates the presence of either a titanocene alkoxide intermediate or a titanocene hydride species formed in solution. To verify the intermediacy of a Ti(III) hydride, this complex was generated via a method outlined by Buchwald[3] and monitored by *in situ* IR spectroscopy. In this experiment, titanocene difluoride (0.1 mmole, 21.7 mg) was mixed with phenylsilane (0.6 mmole, 74 µL) in 15 mL of refluxing THF. The formation of the titanocene(III) hydride species was demonstrated by the shift in the C-H wag of the Cp ligand of titanocene from 813 cm^{-1} to 799 cm^{-1} and a change in color from yellow to green was observed (Figure S10). We could also observe the $PhSiF_2H$ vibrations at 858 cm^{-1} and 876 cm^{-1} (Figure S11). The C-H absorbance at 799 cm^{-1} upon titanocene(III) hydride formation suggests that Ti(III) hydride is formed as an intermediate in the reduction of ketones and aldehydes to alcohols with titanocene(III) borohydride and PMHS as the stoichiometric reductant.

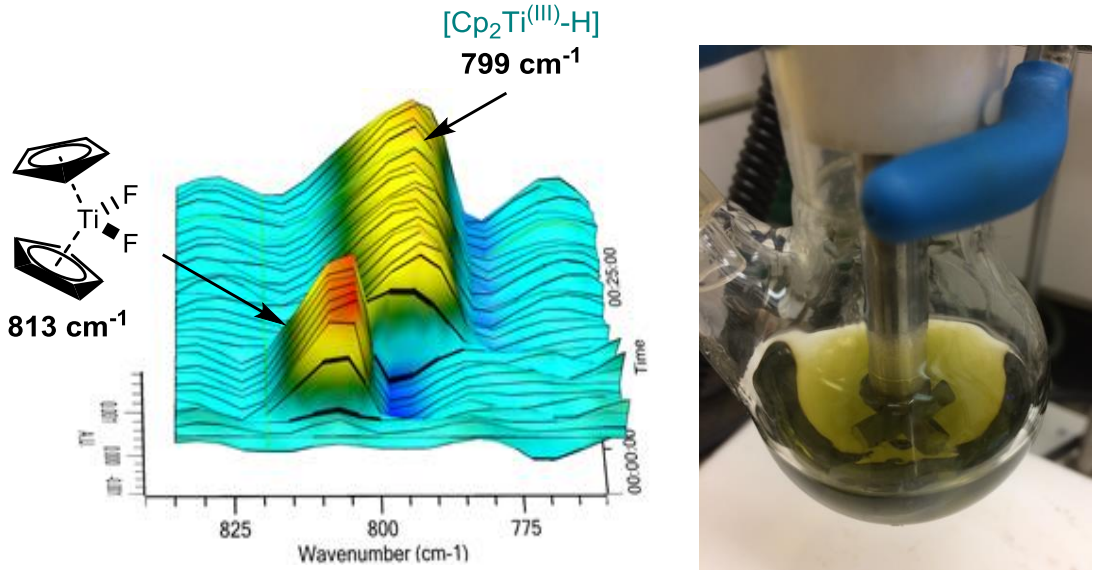


Figure S10: Formation of titanocene(III) hydride monitored by ReactIR.

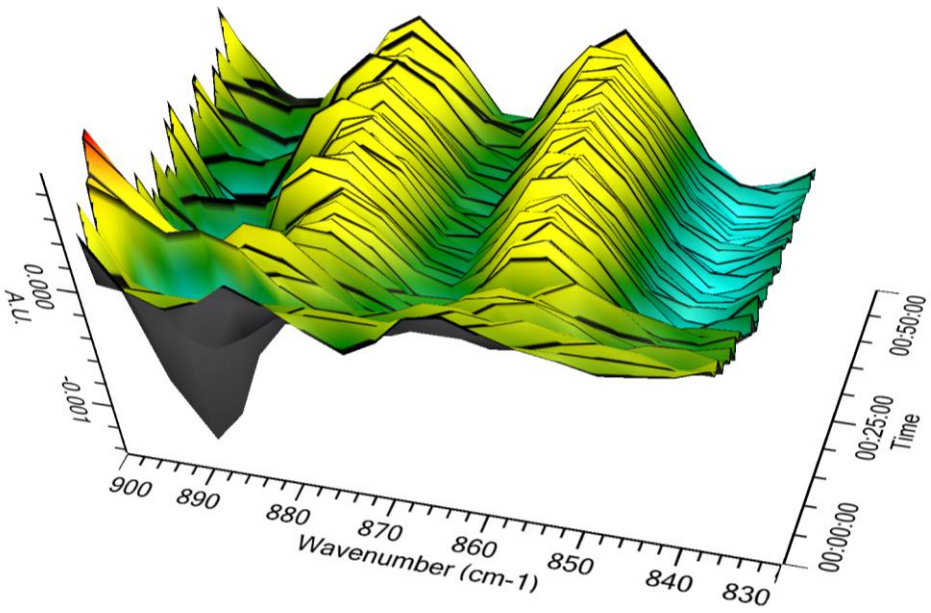
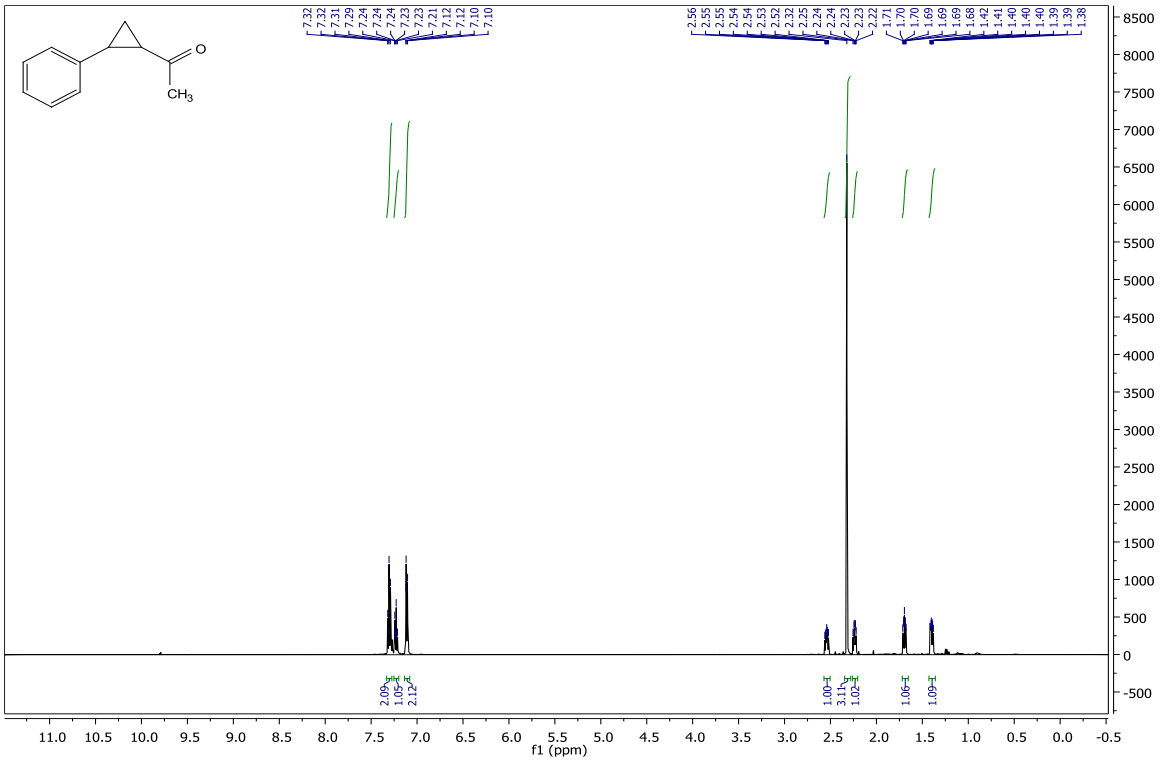


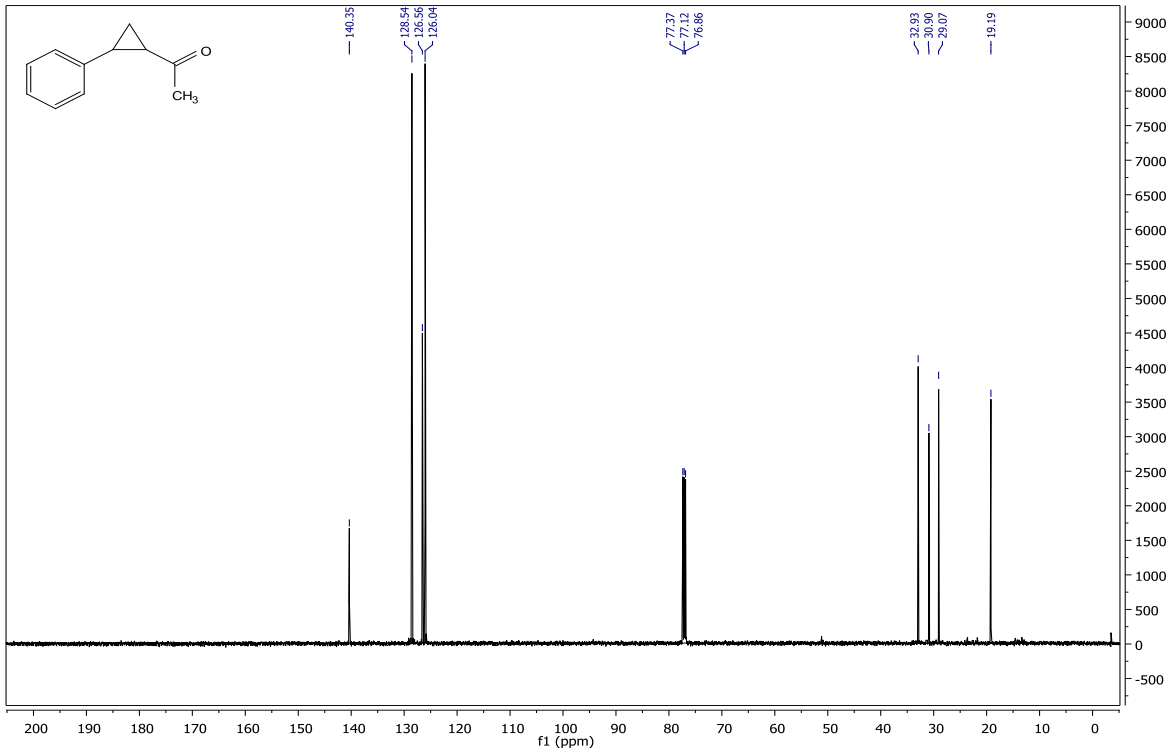
Figure S11. $PhSiF_2H$ vibrations at 876 cm^{-1} and 858 cm^{-1}

5. NMR spectra for compounds

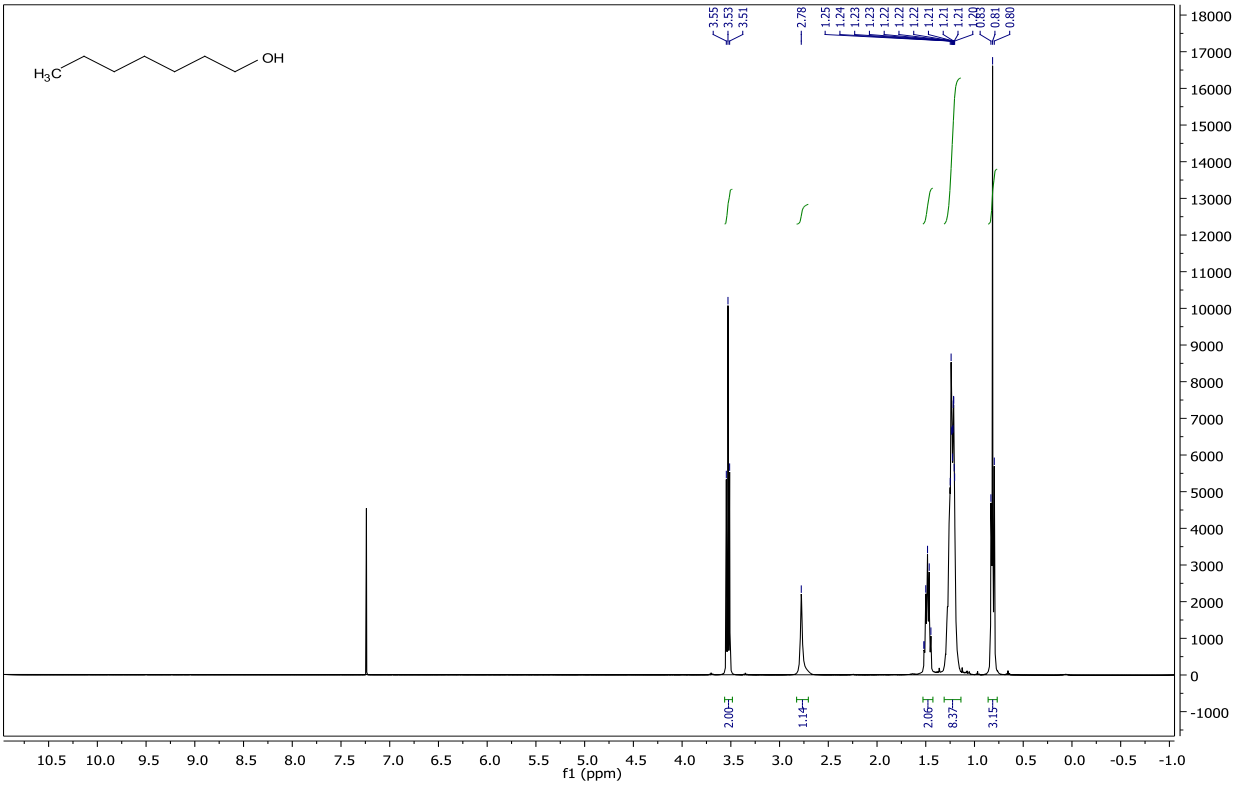
^{1}H NMR for 1-v



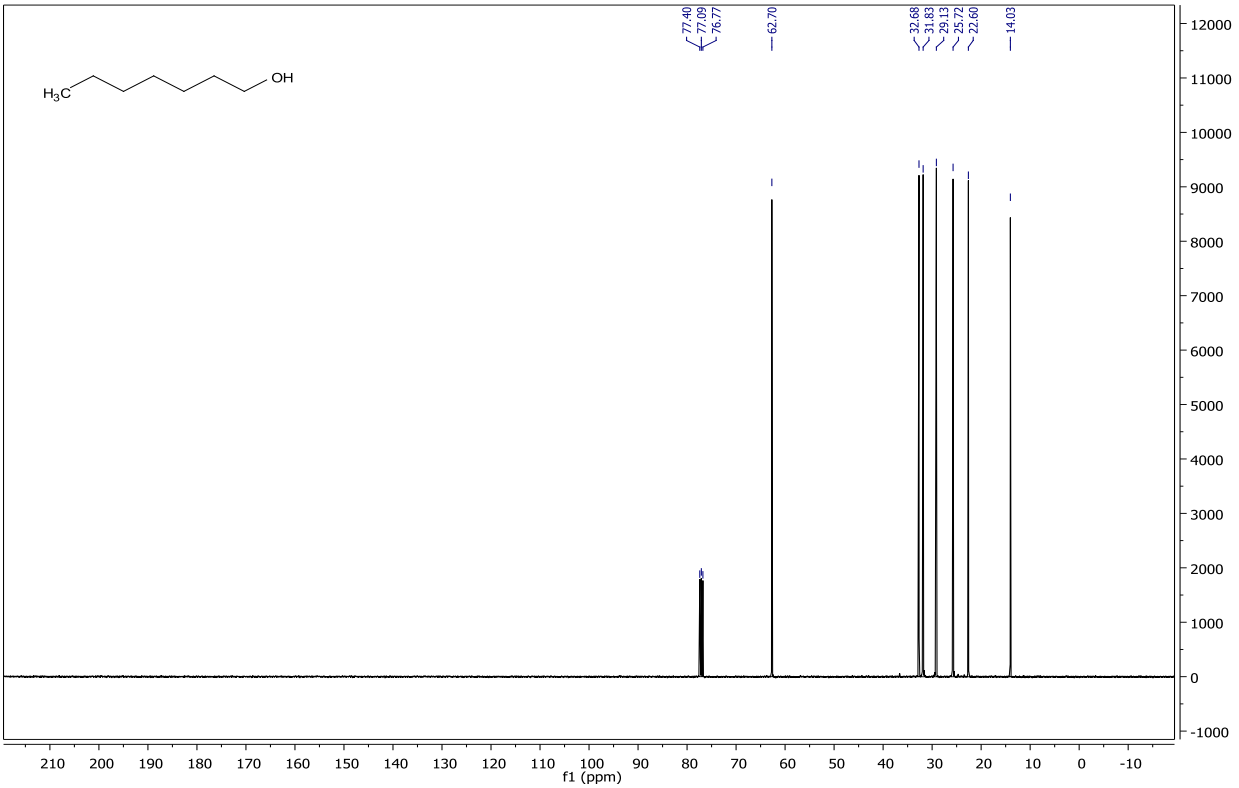
^{13}C NMR for 1-v



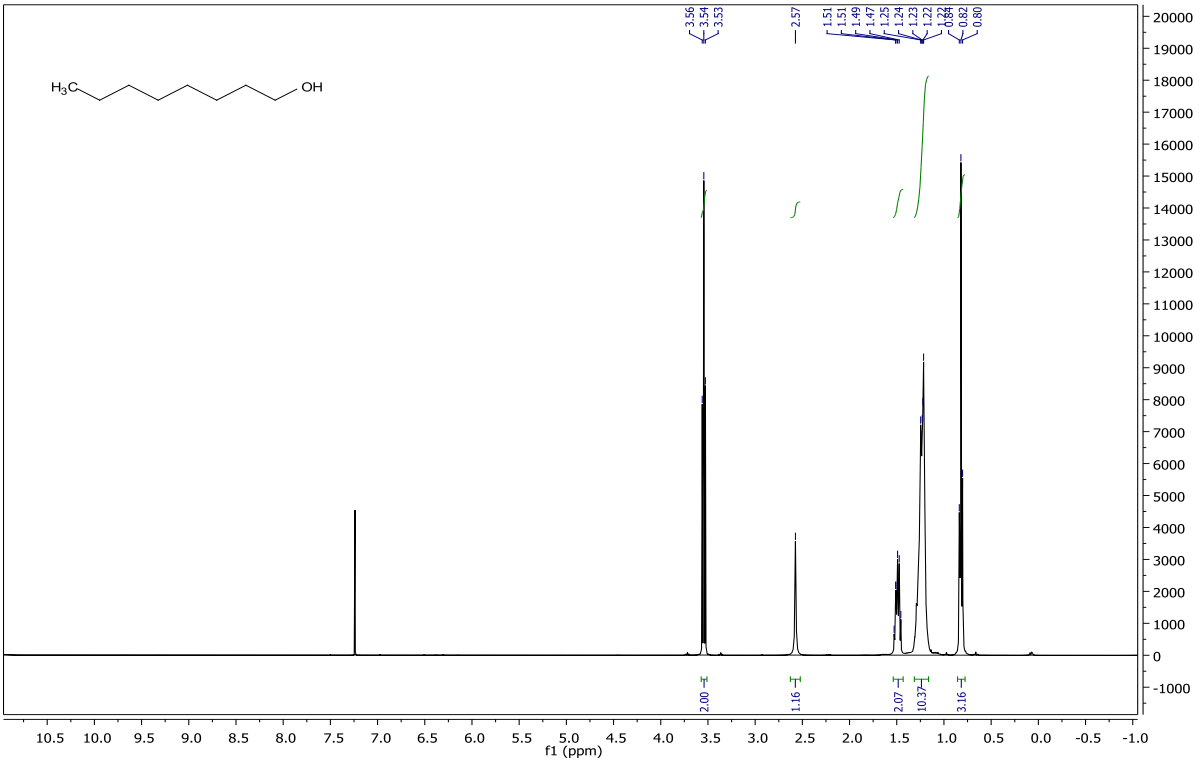
^{1}H NMR for 2-a



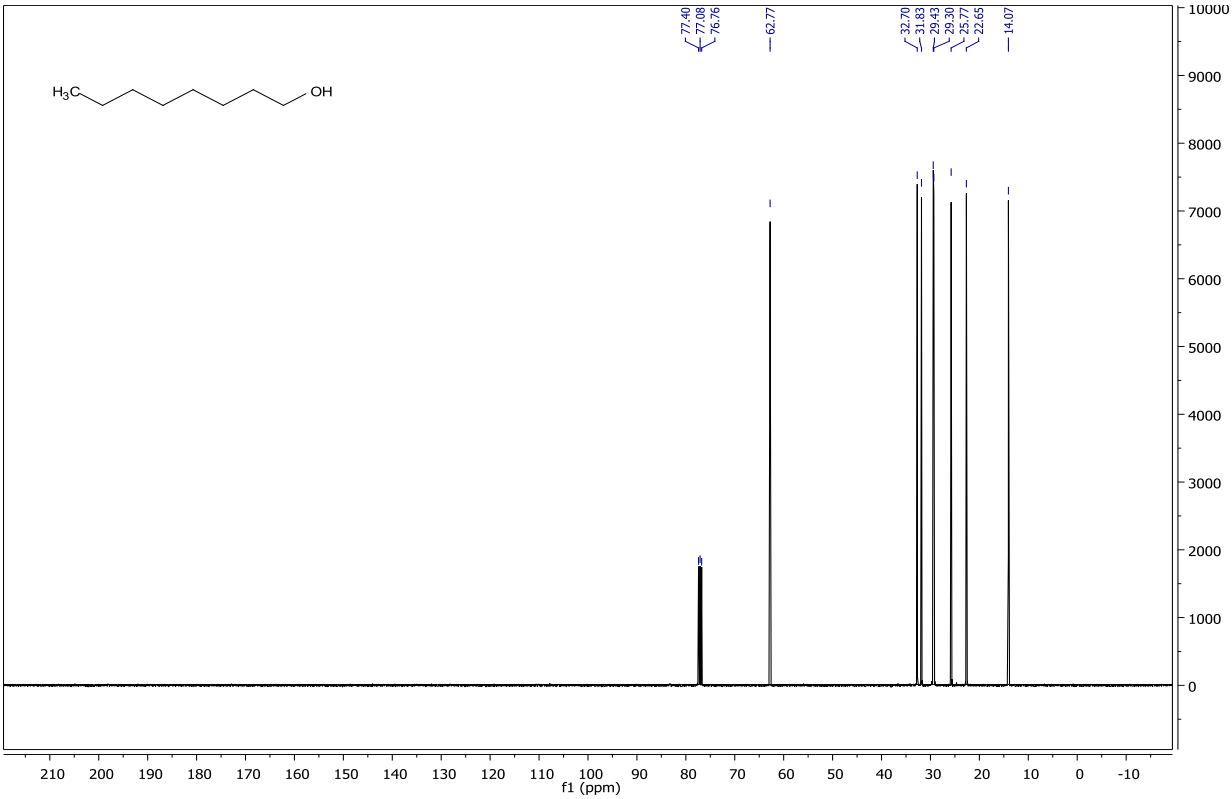
^{13}C NMR for 2-a



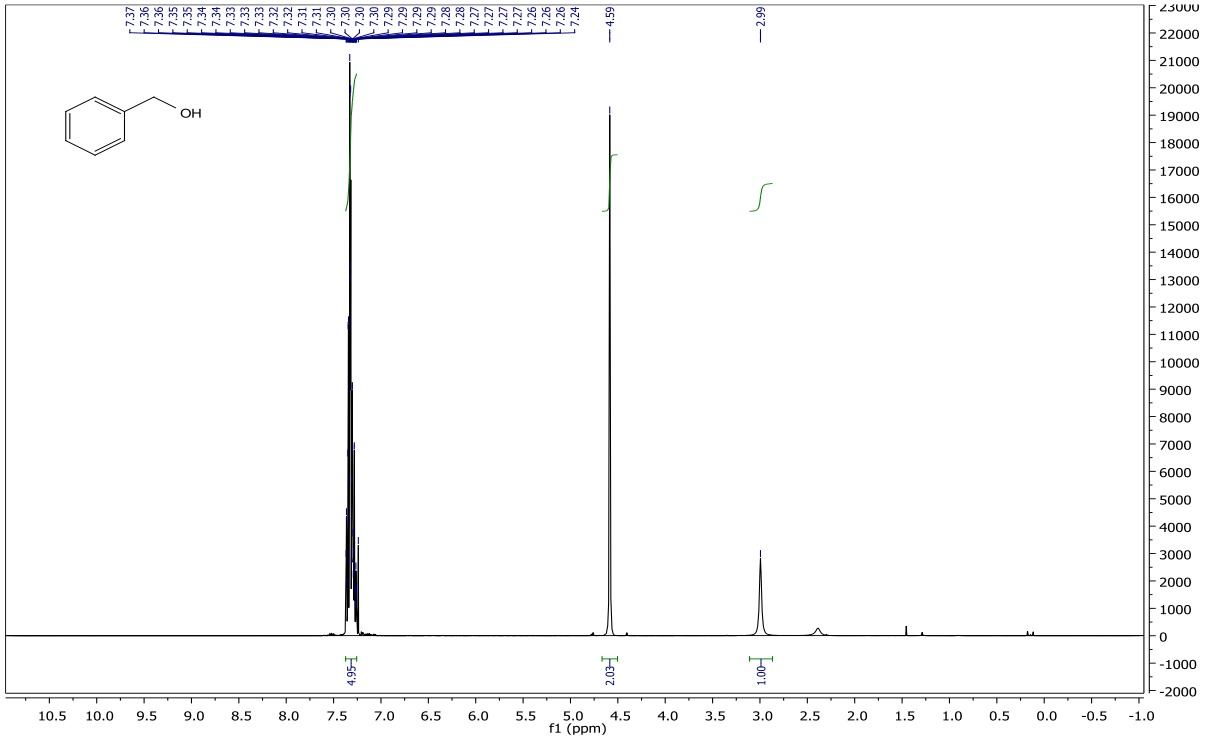
^{1}H NMR for 2-b



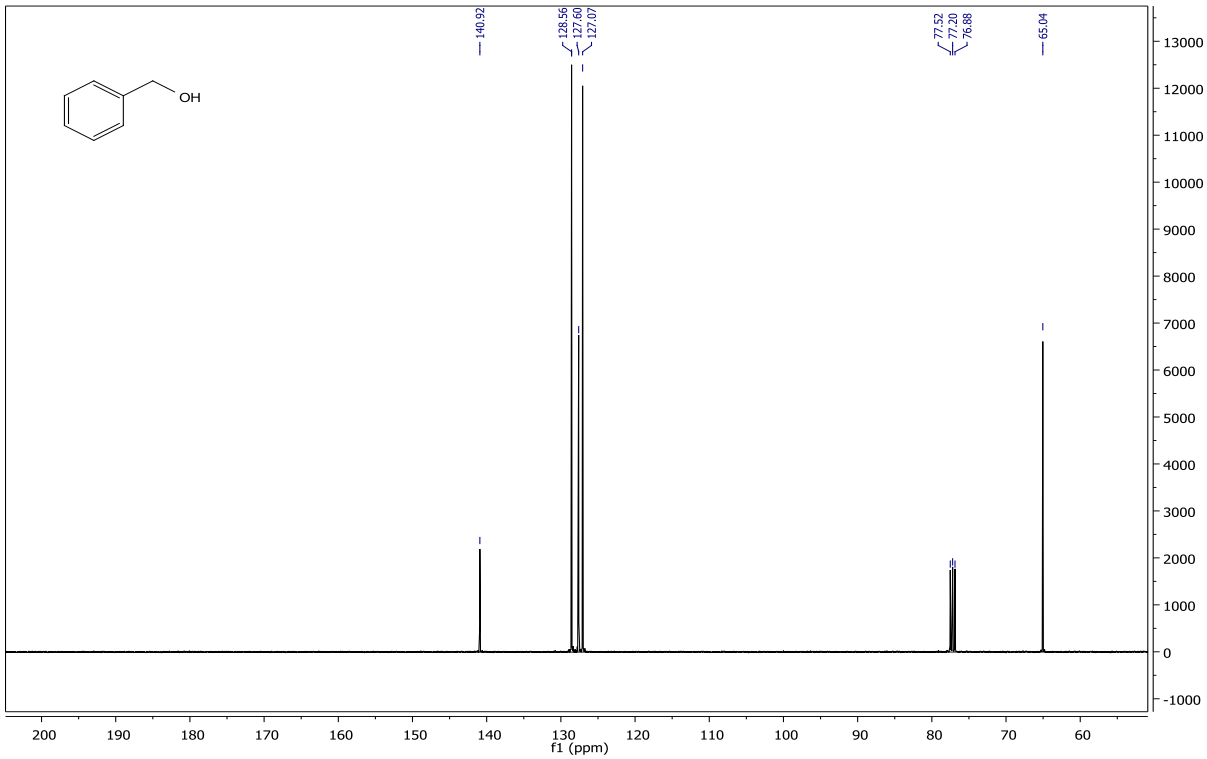
^{13}C NMR for 2-b



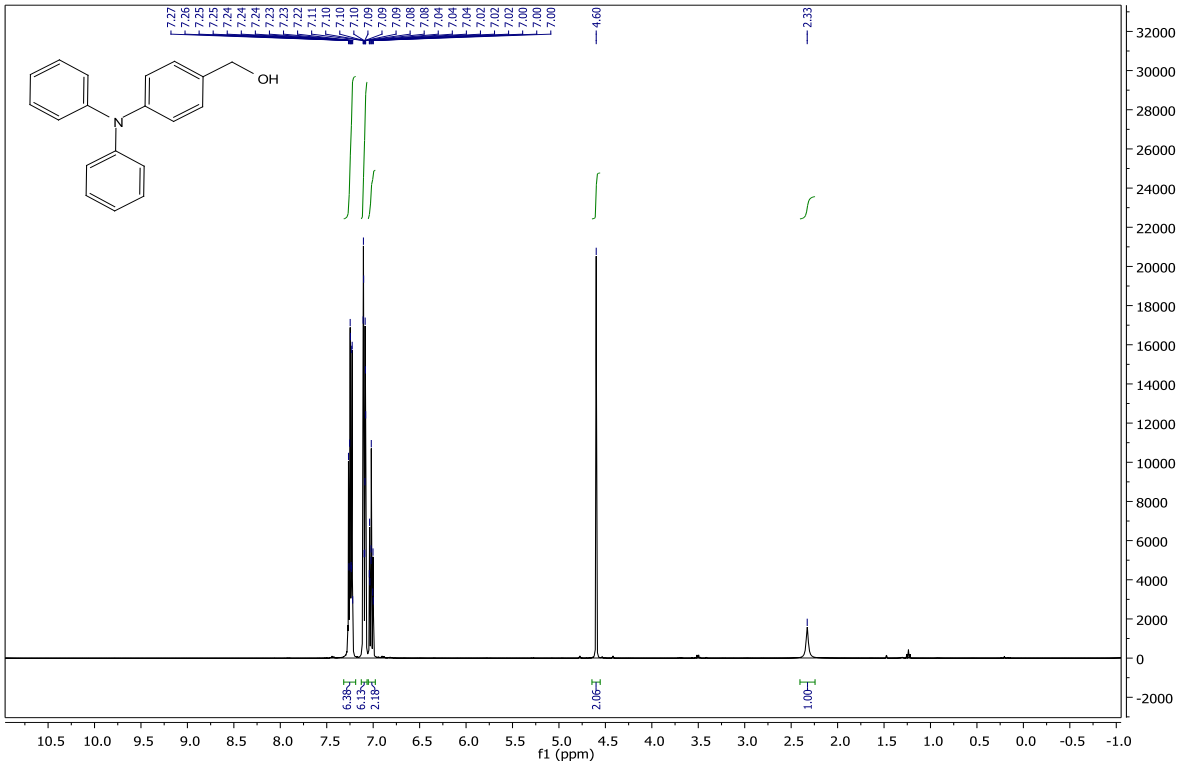
^{1}H NMR for 2-c



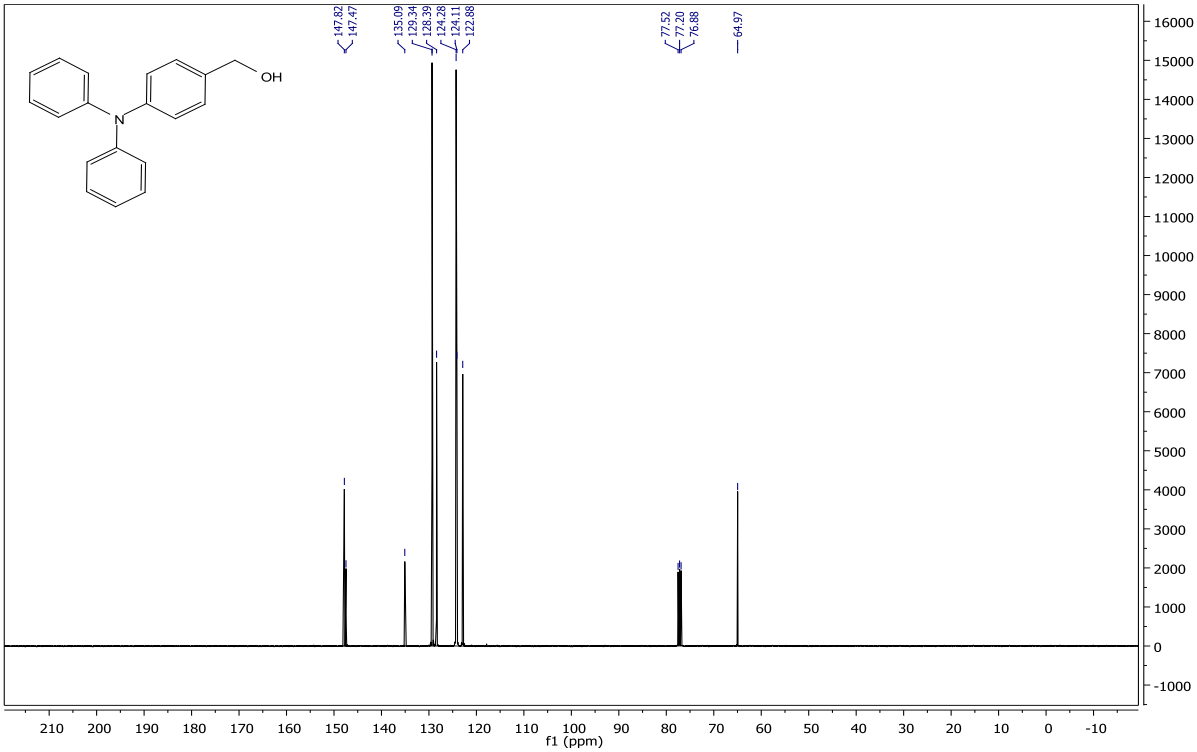
^{13}C NMR for 2-c



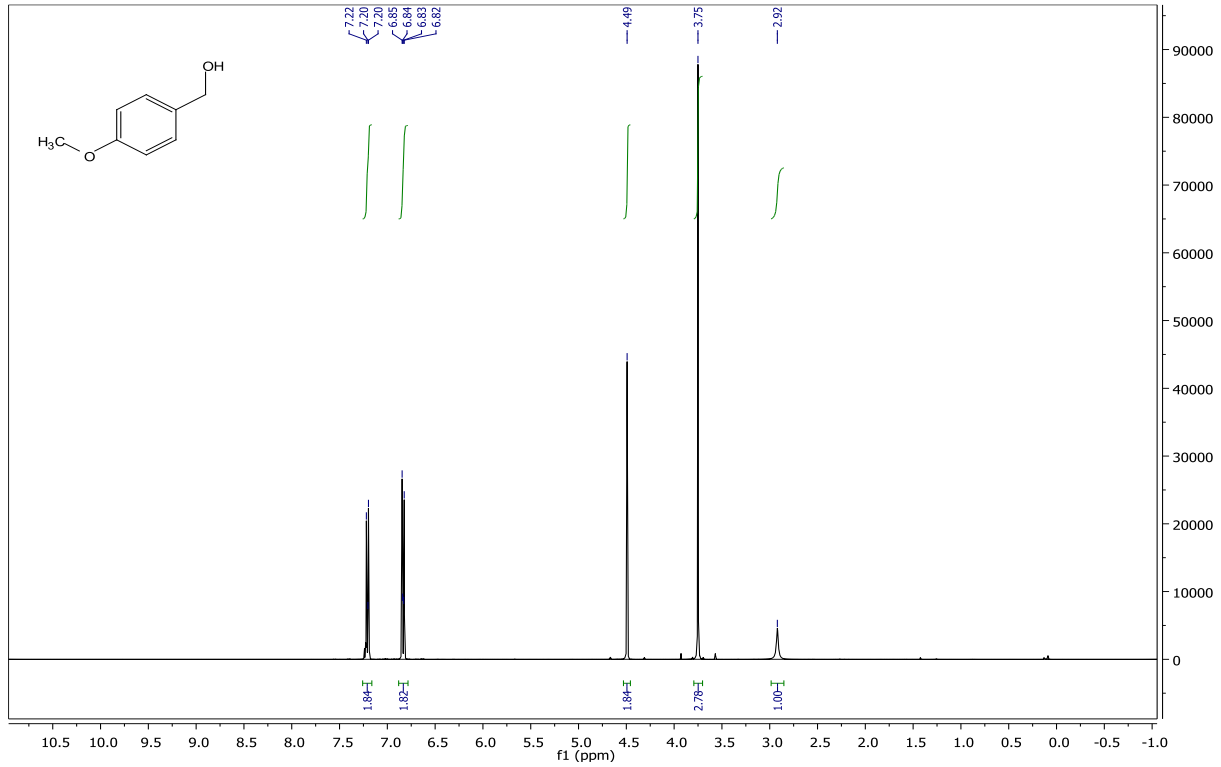
^{1}H NMR for 2-d



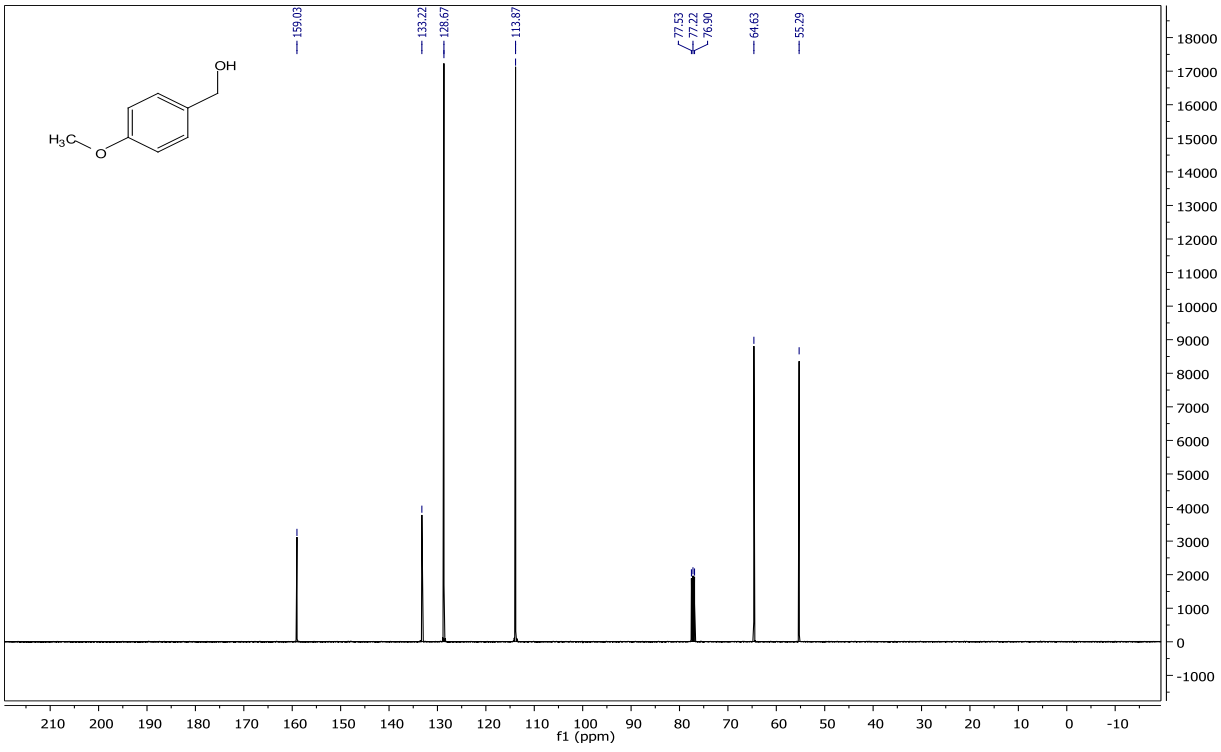
^{13}C NMR for 2-d



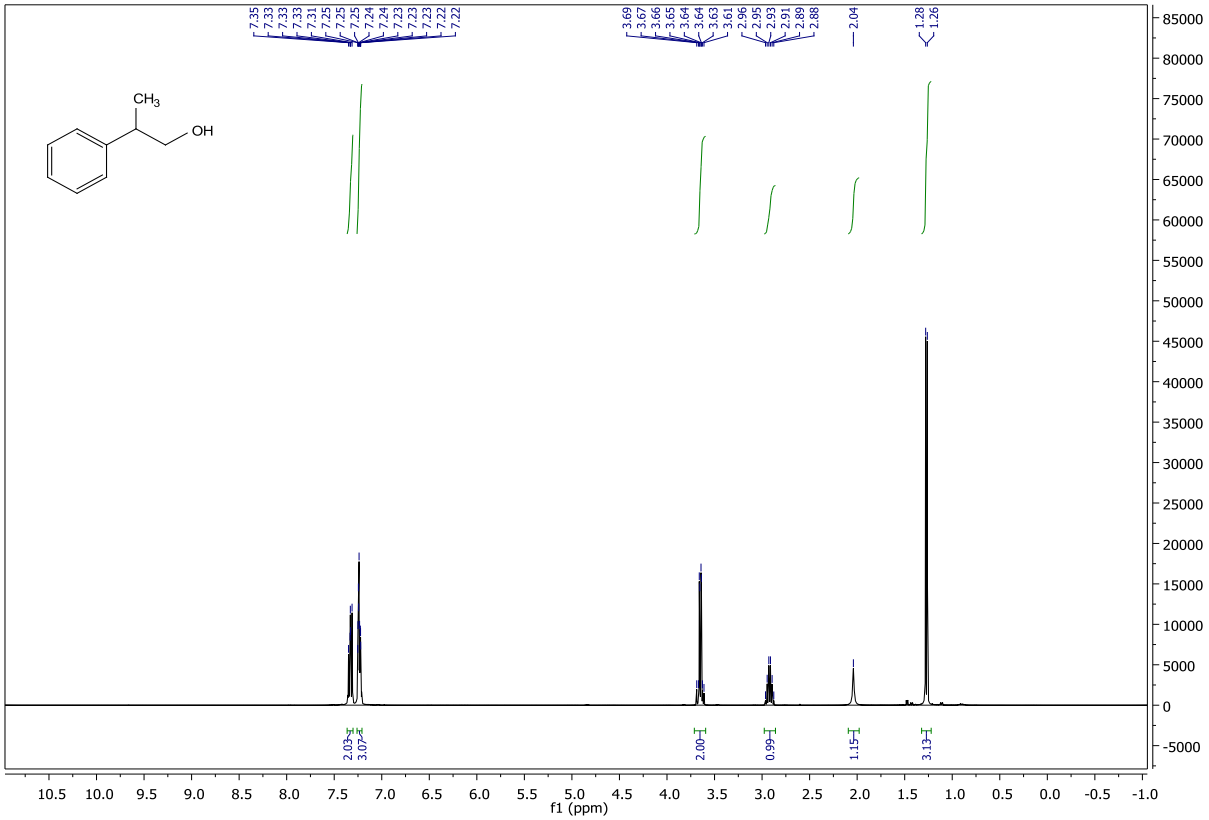
^{1}H NMR for 2-e



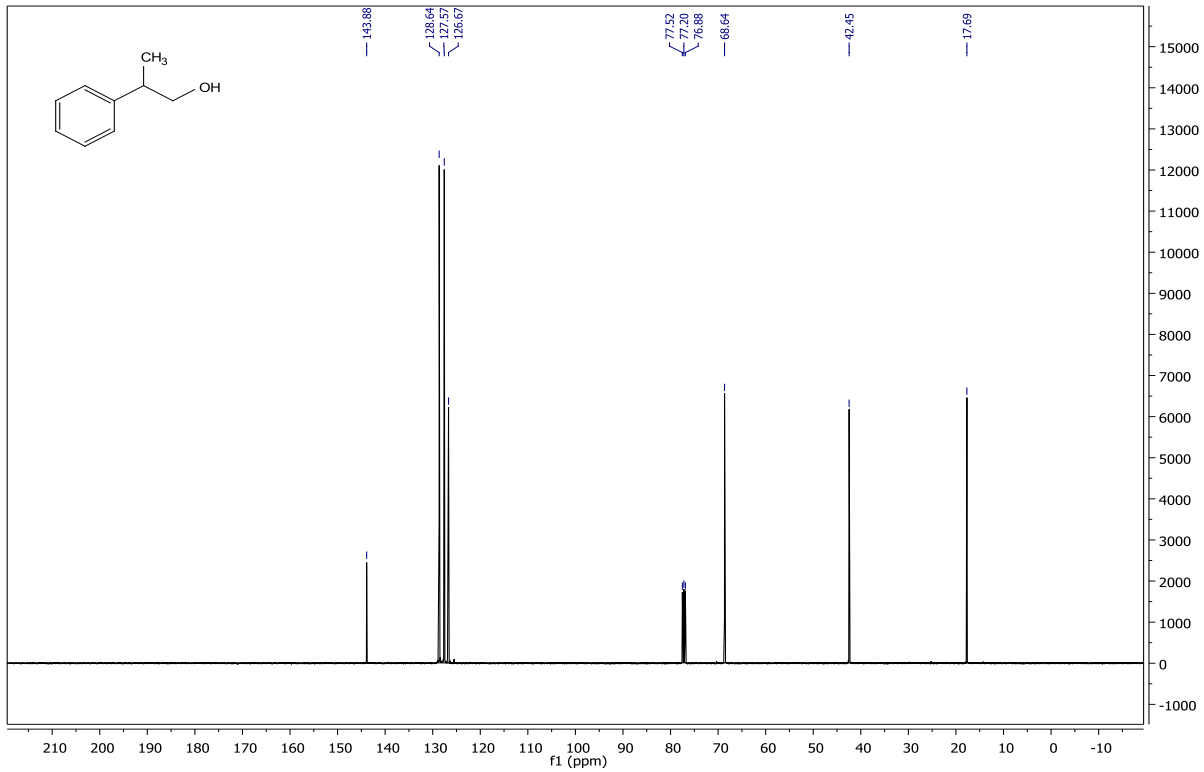
^{13}C NMR for 2-e



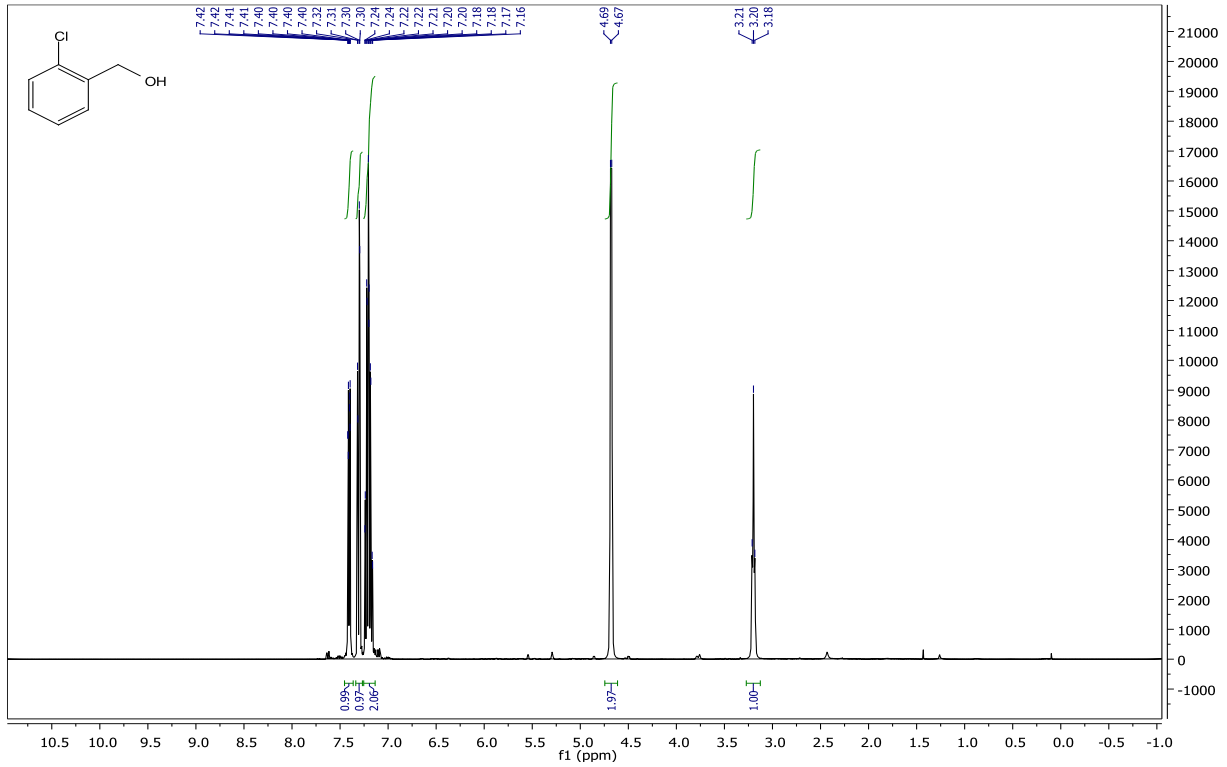
^{1}H NMR for 2-f



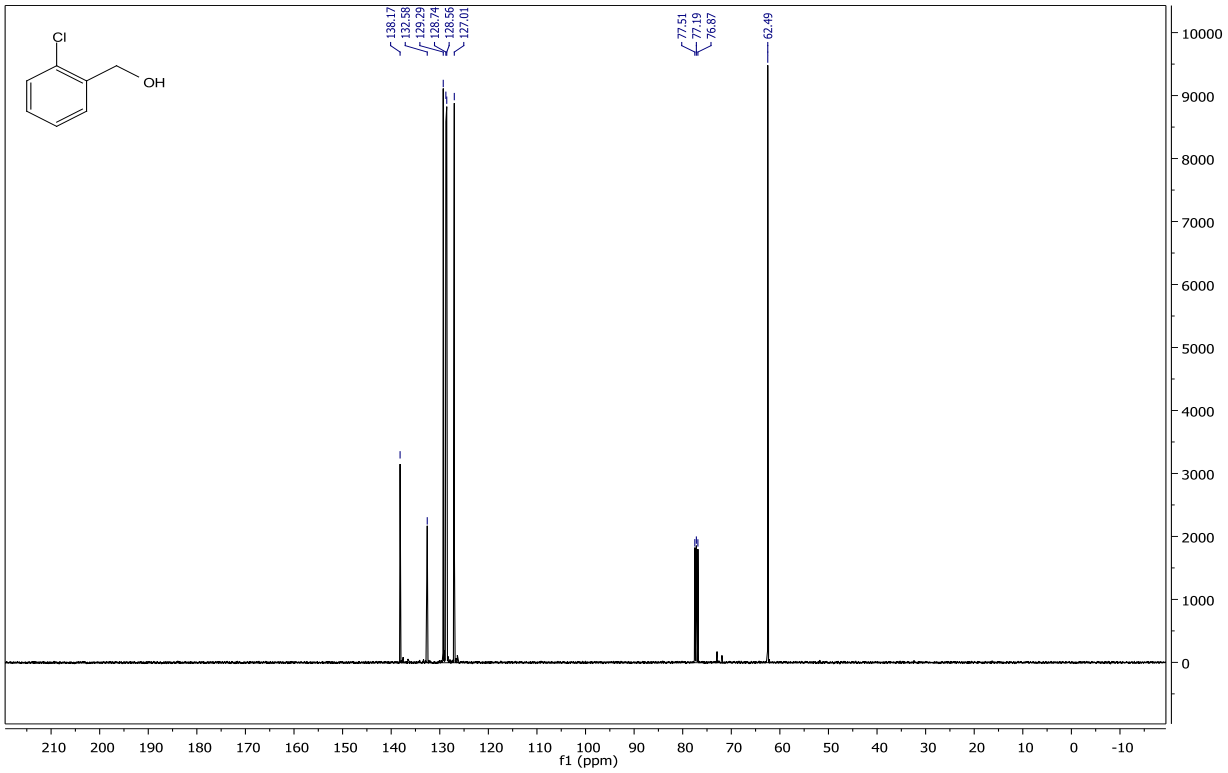
^{13}C NMR for 2-f



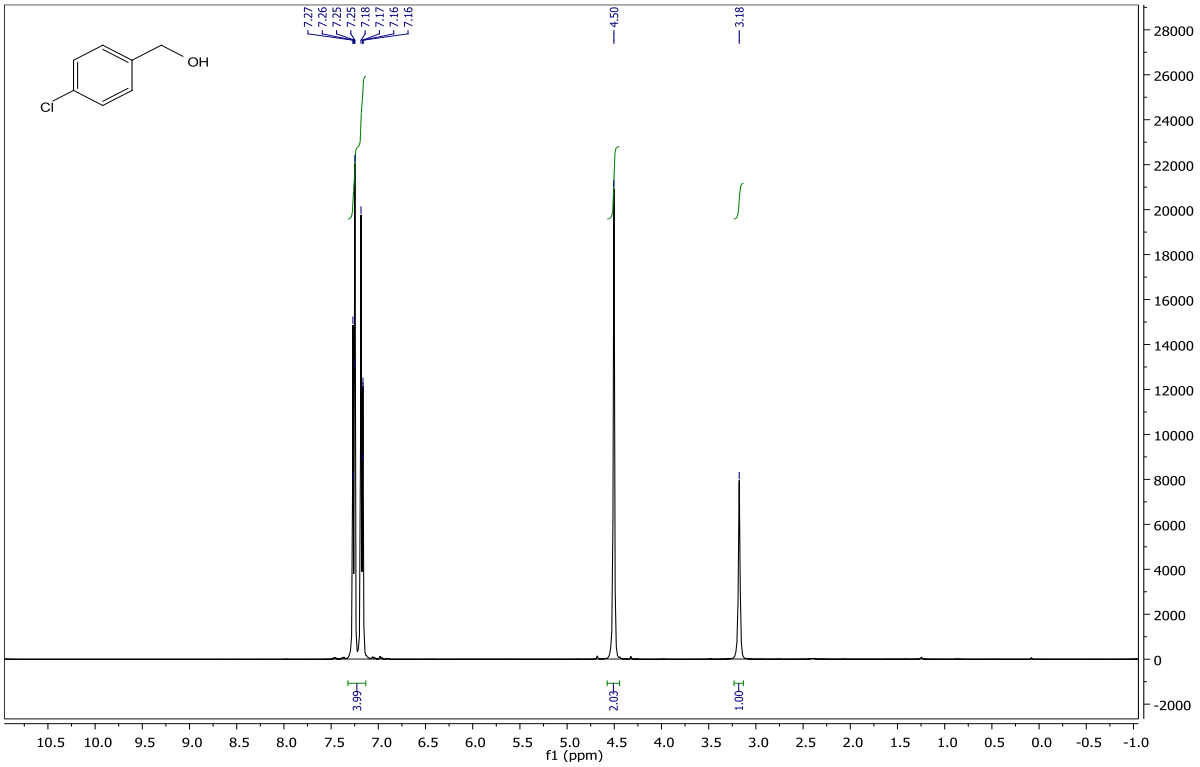
^{1}H NMR for 2-g



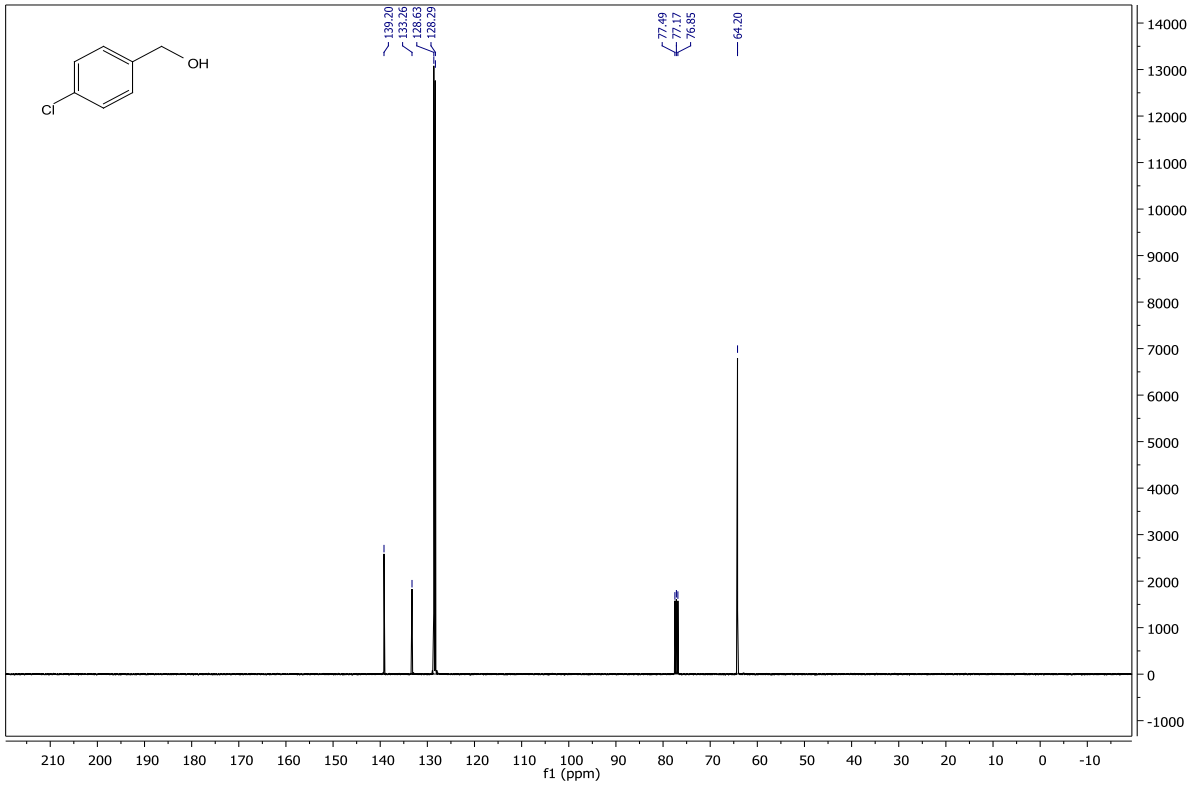
^{13}C NMR for 2-g



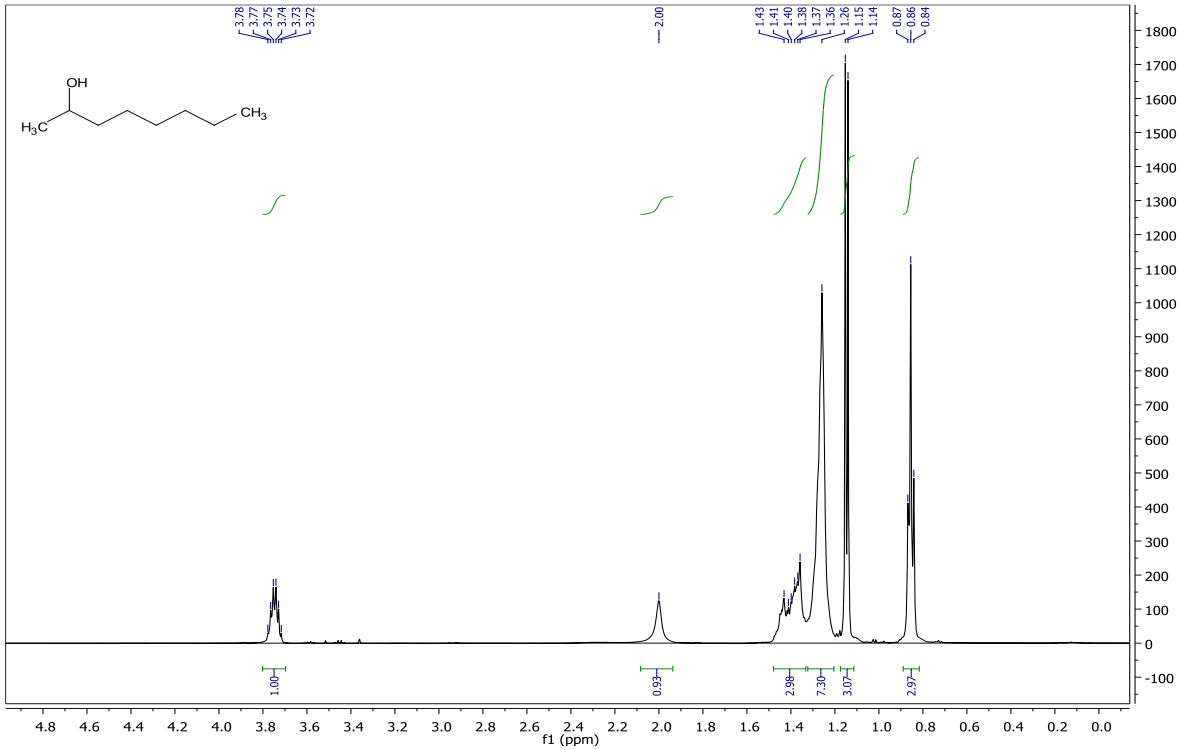
^{1}H NMR for 2-h



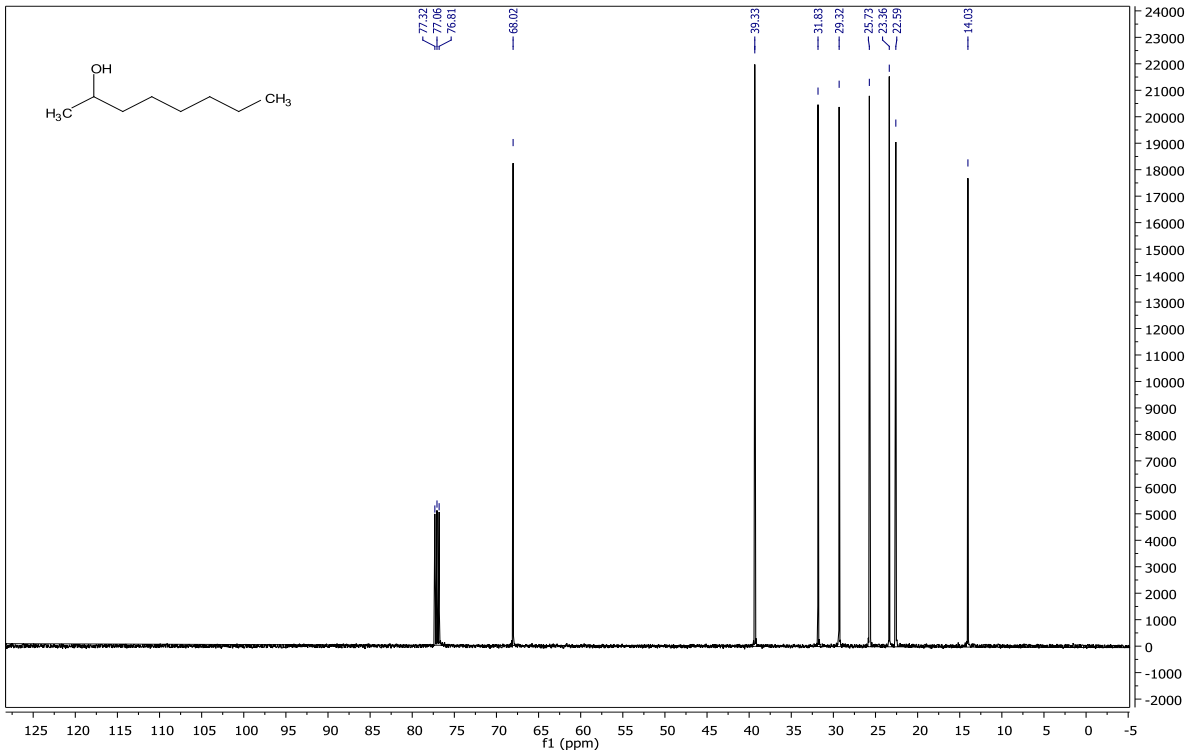
^{13}C NMR for 2-h



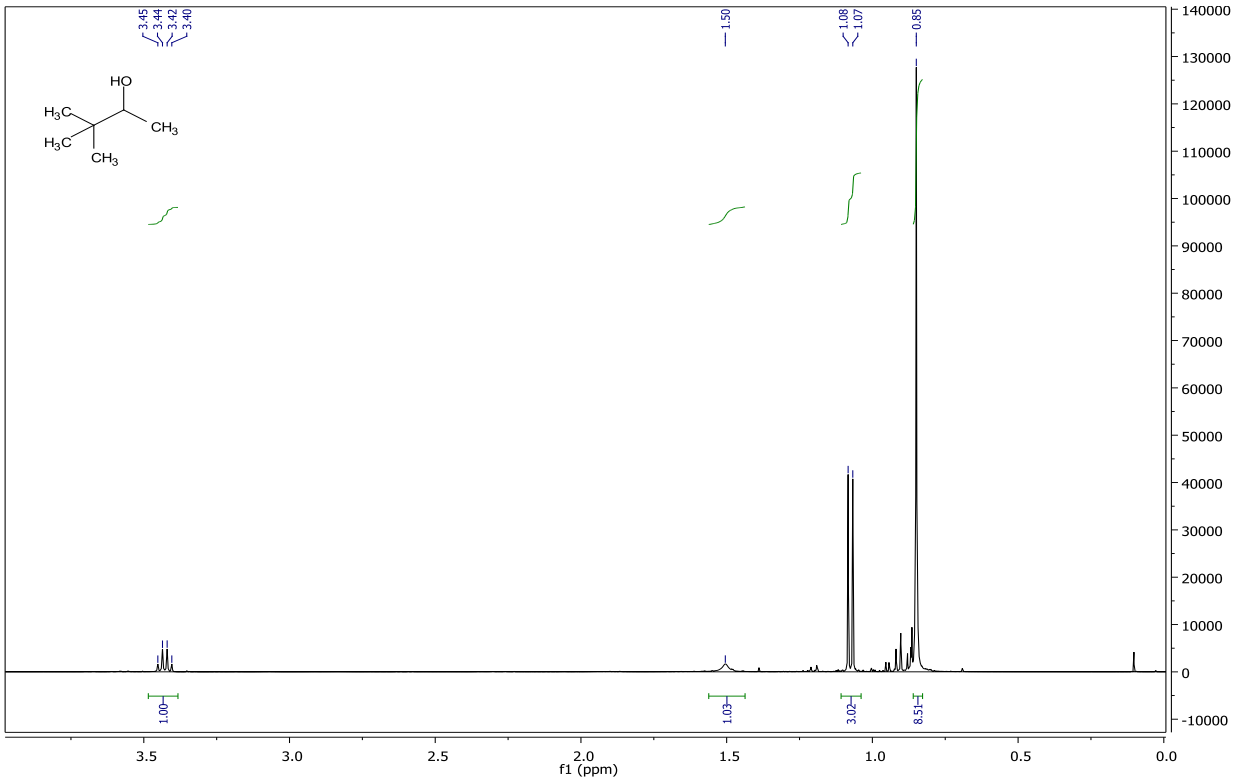
^{1}H NMR for 2-i



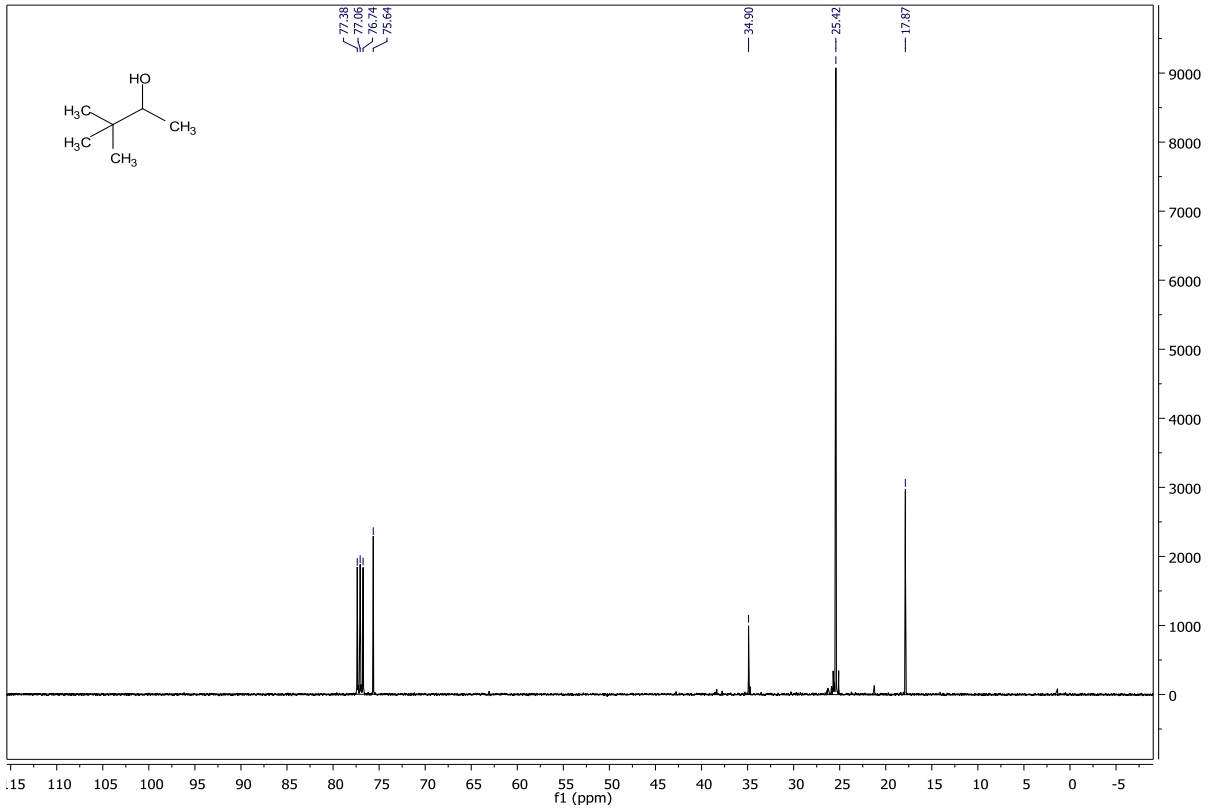
^{13}C NMR for 2-i



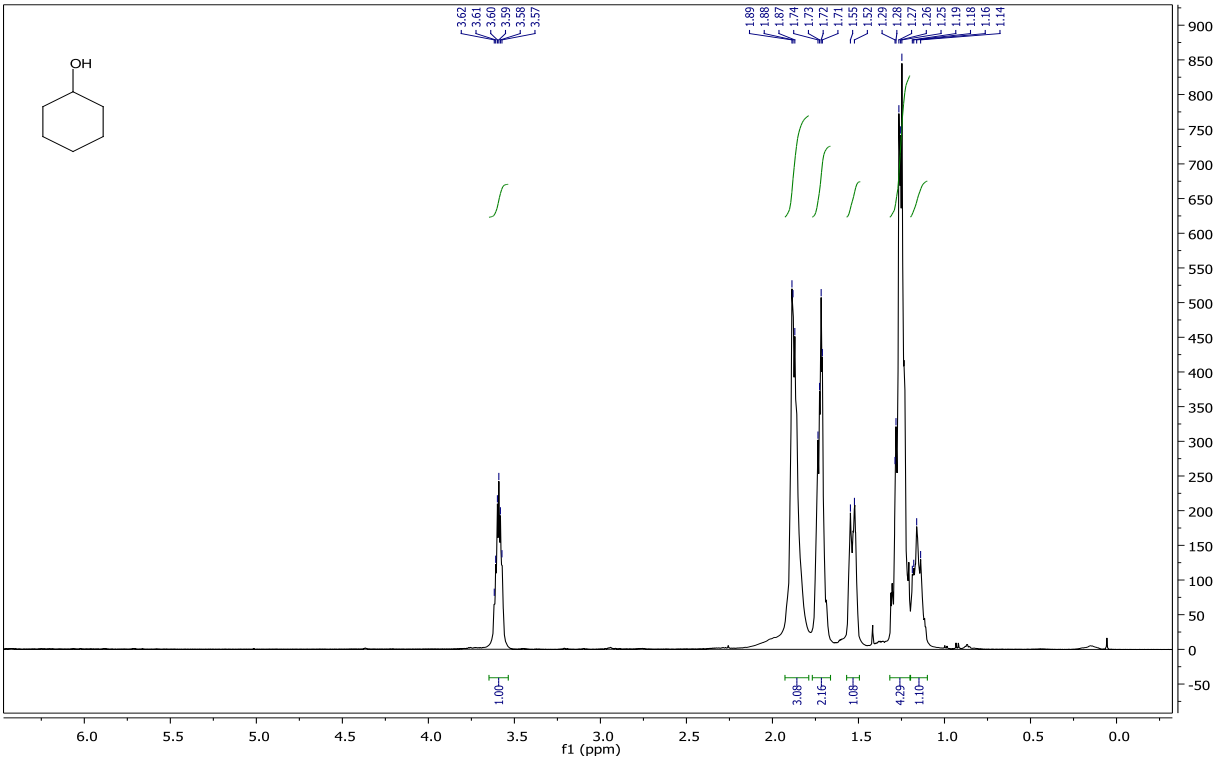
^{1}H NMR for 2-j



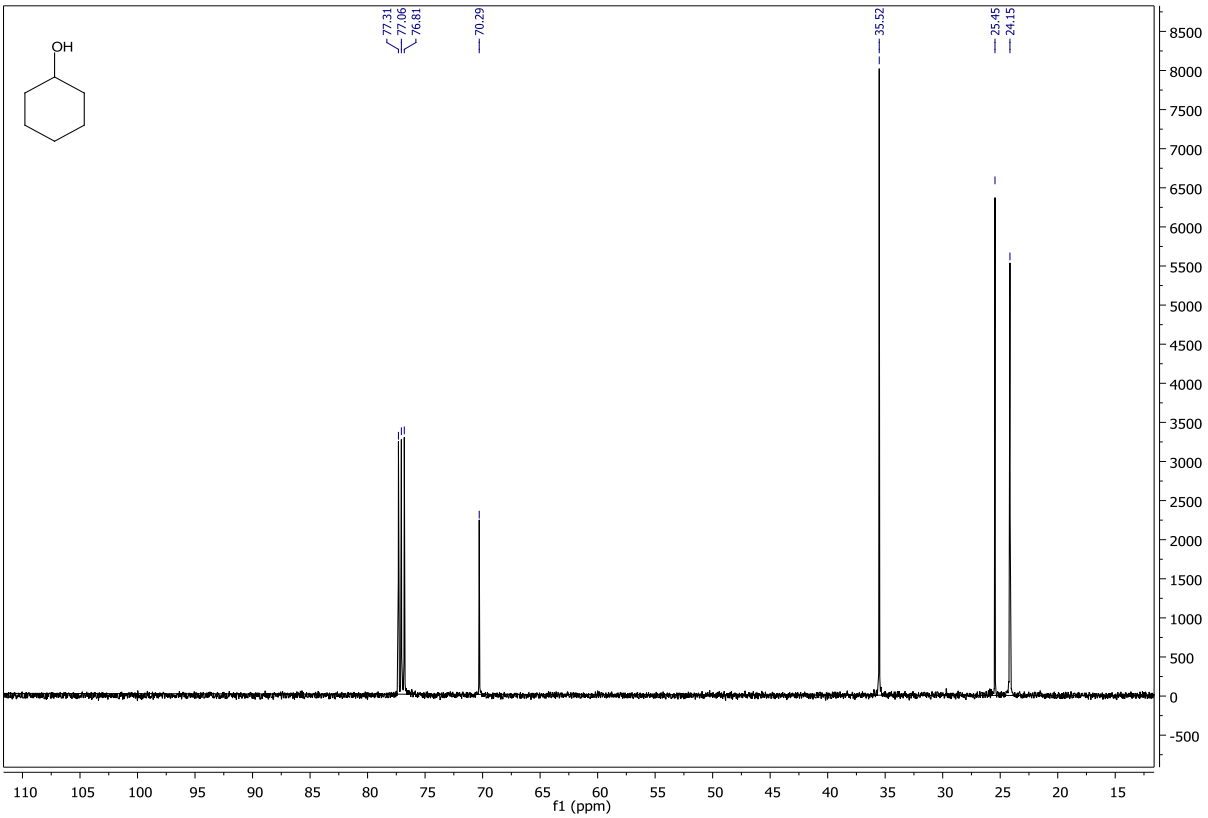
^{13}C NMR for 2-j



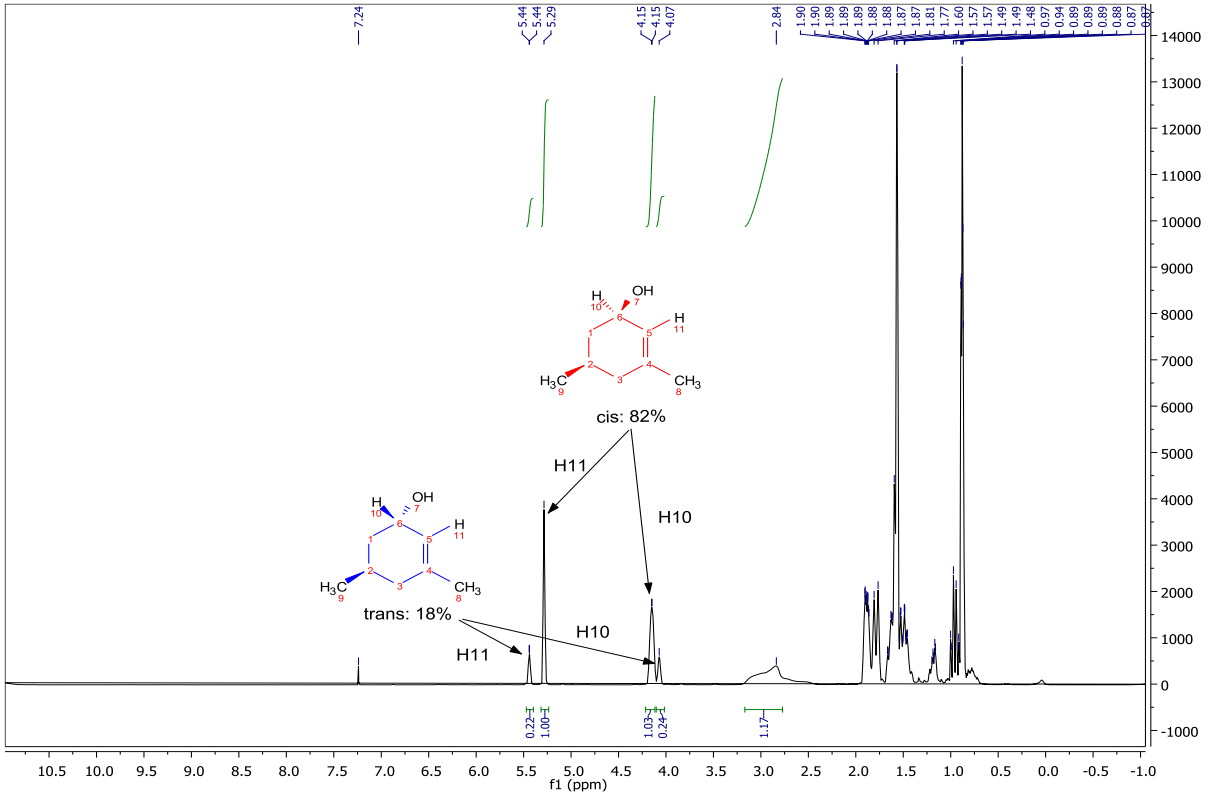
^{1}H NMR for 2-k



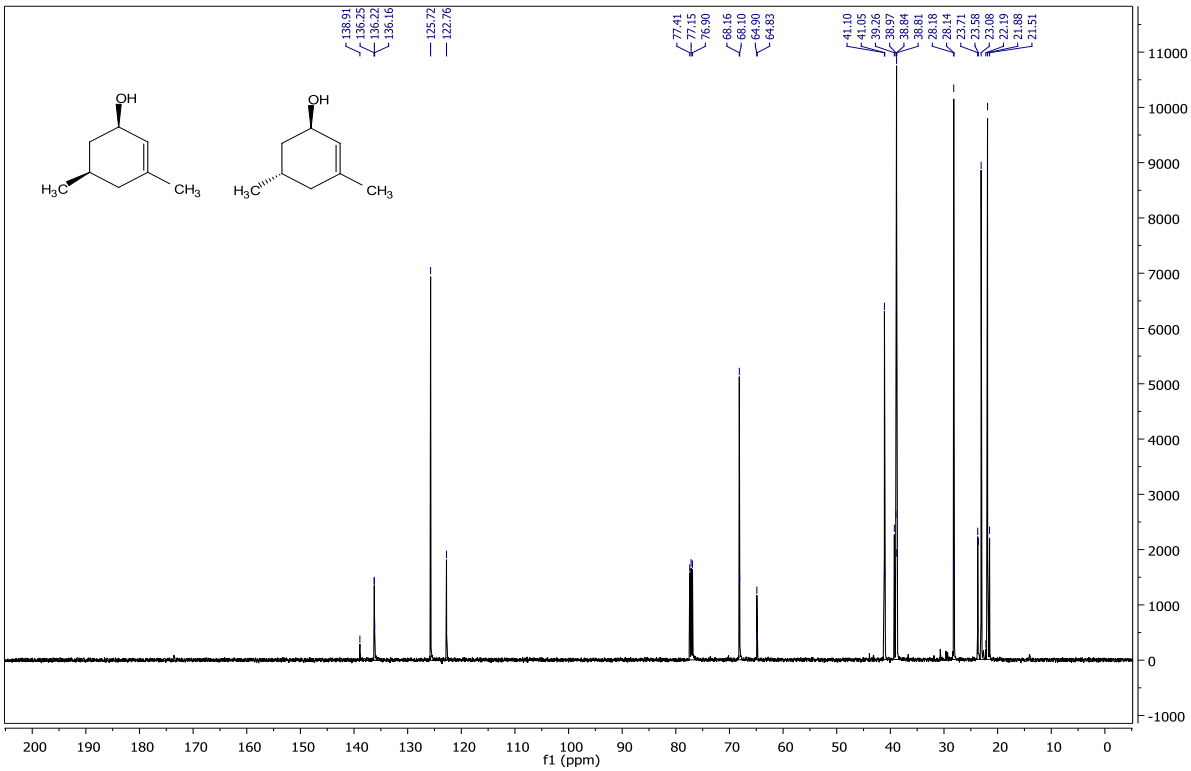
^{13}C NMR for 2-k



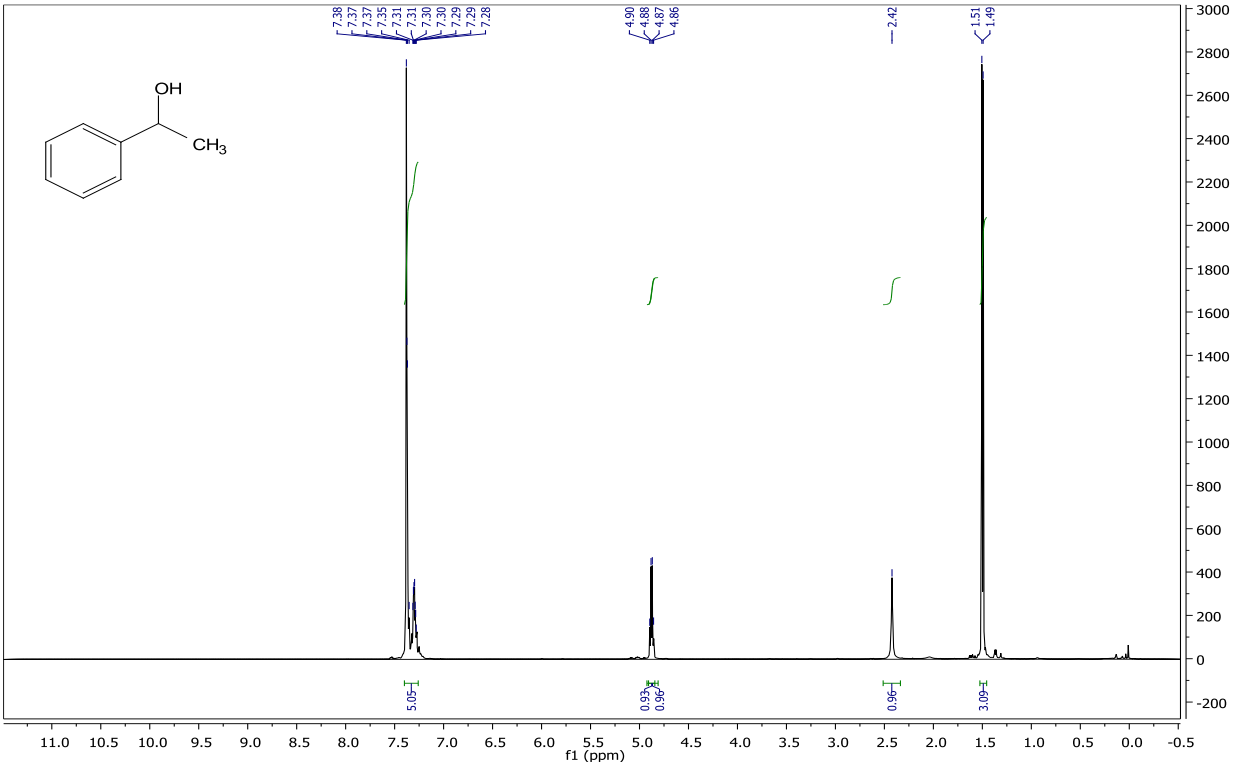
^{1}H NMR for 2-l and calculating ratio of cis vs. trans alcohol product



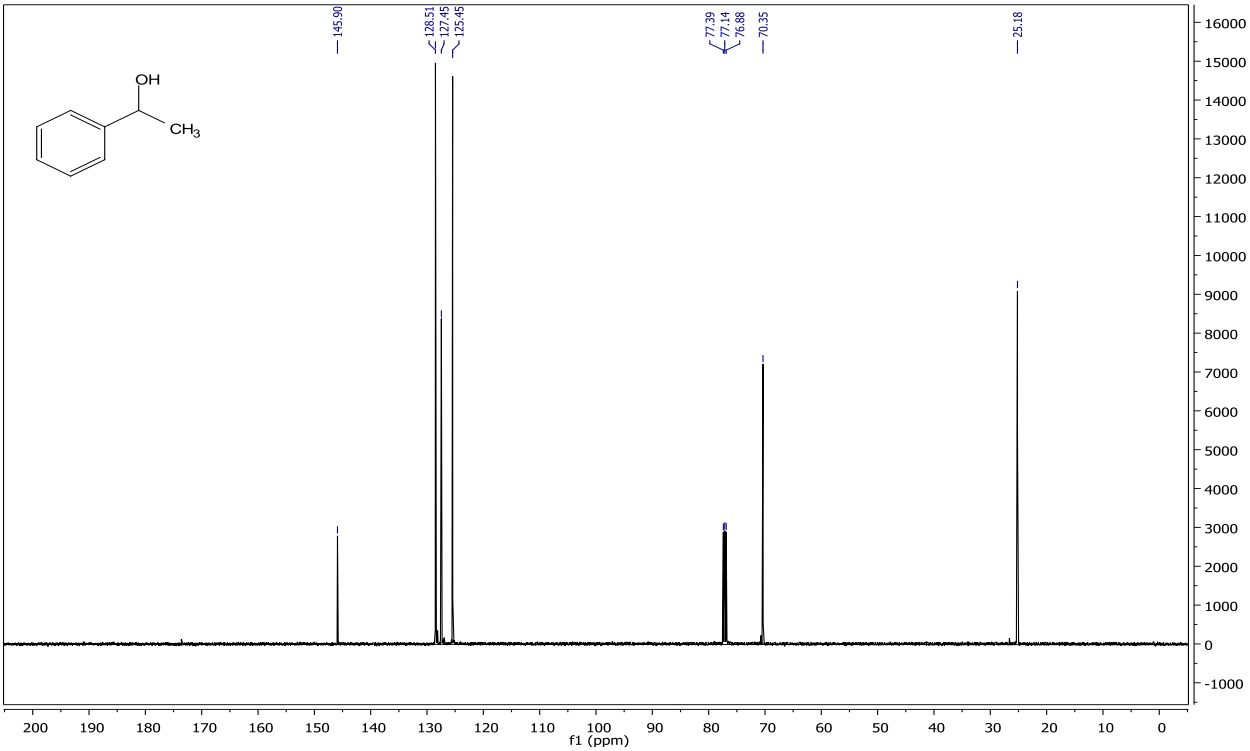
^{13}C NMR for 2-l (cis + trans alcohol products)



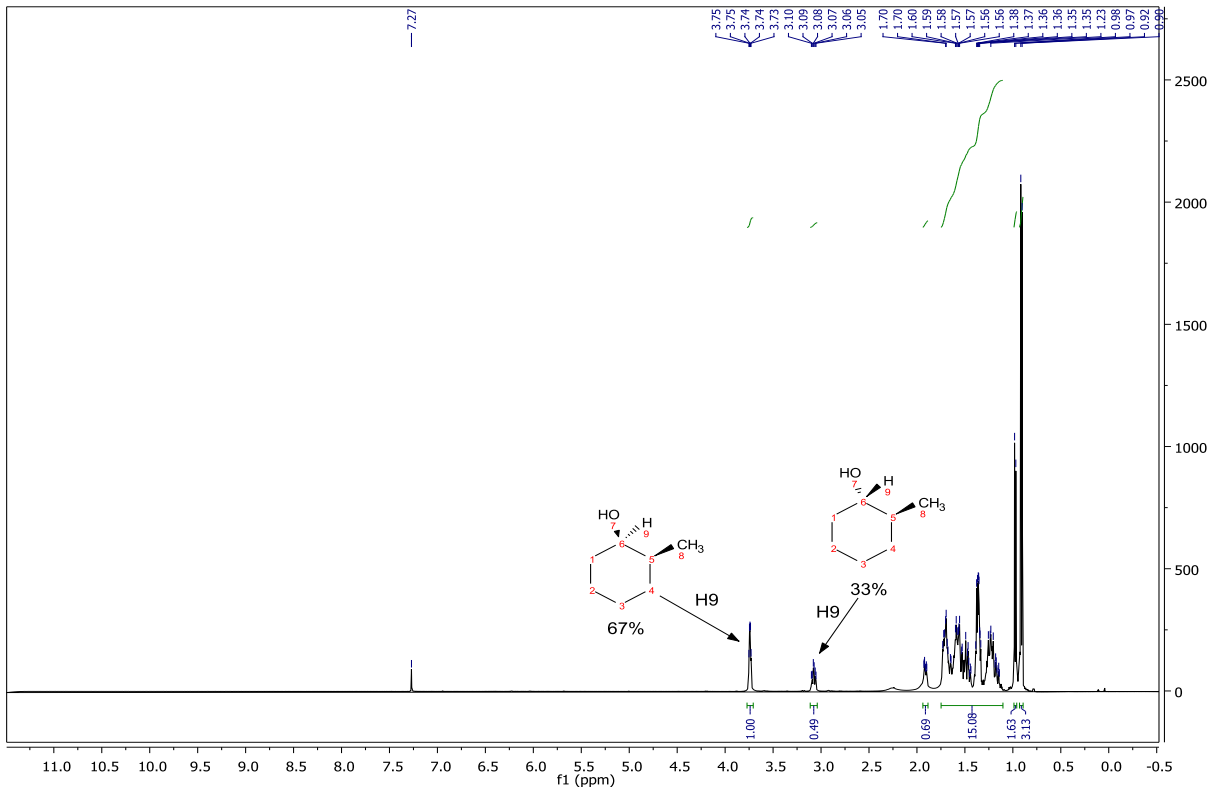
^{1}H NMR for 2-m



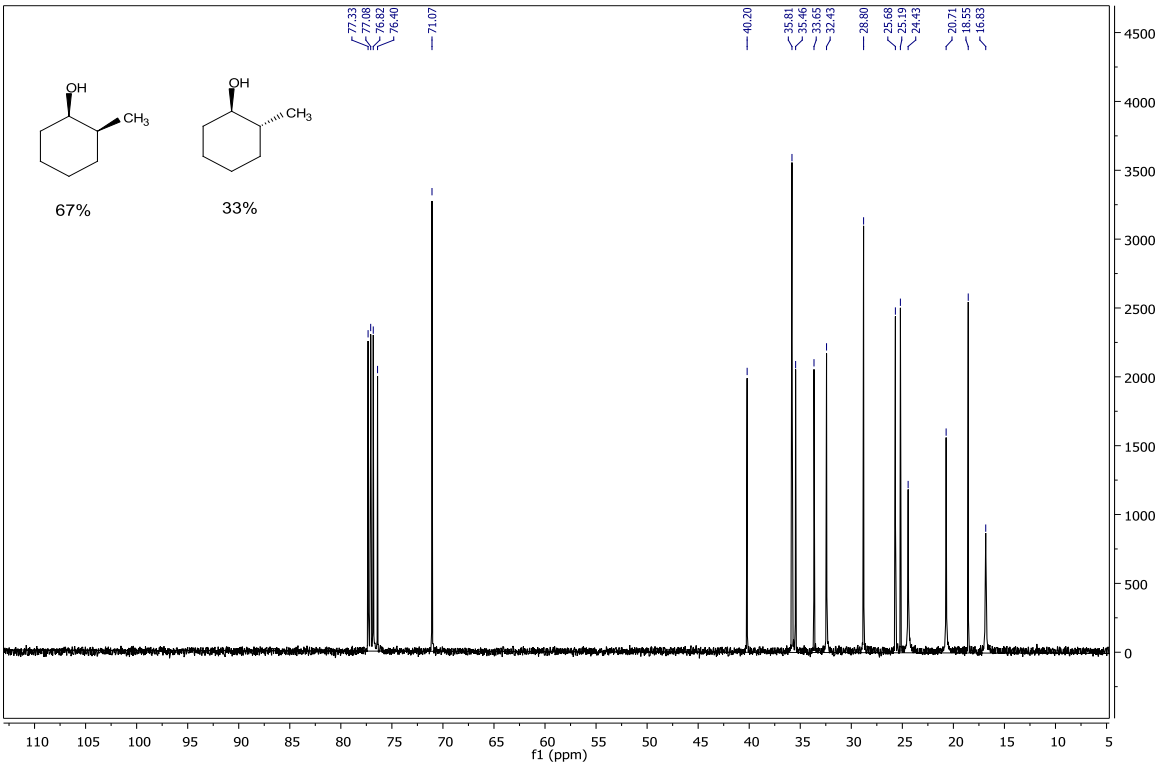
^{13}C NMR for 2-m



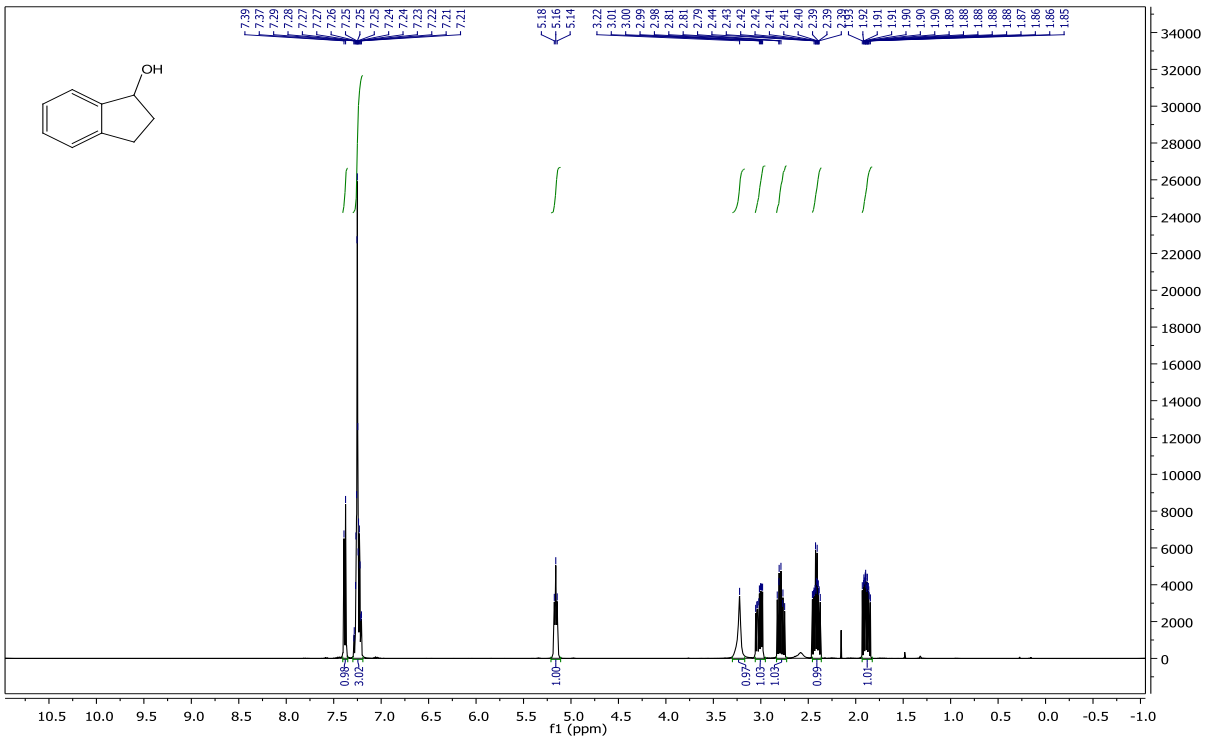
^{1}H NMR for 2-n and calculating ratio of cis vs. trans alcohol product



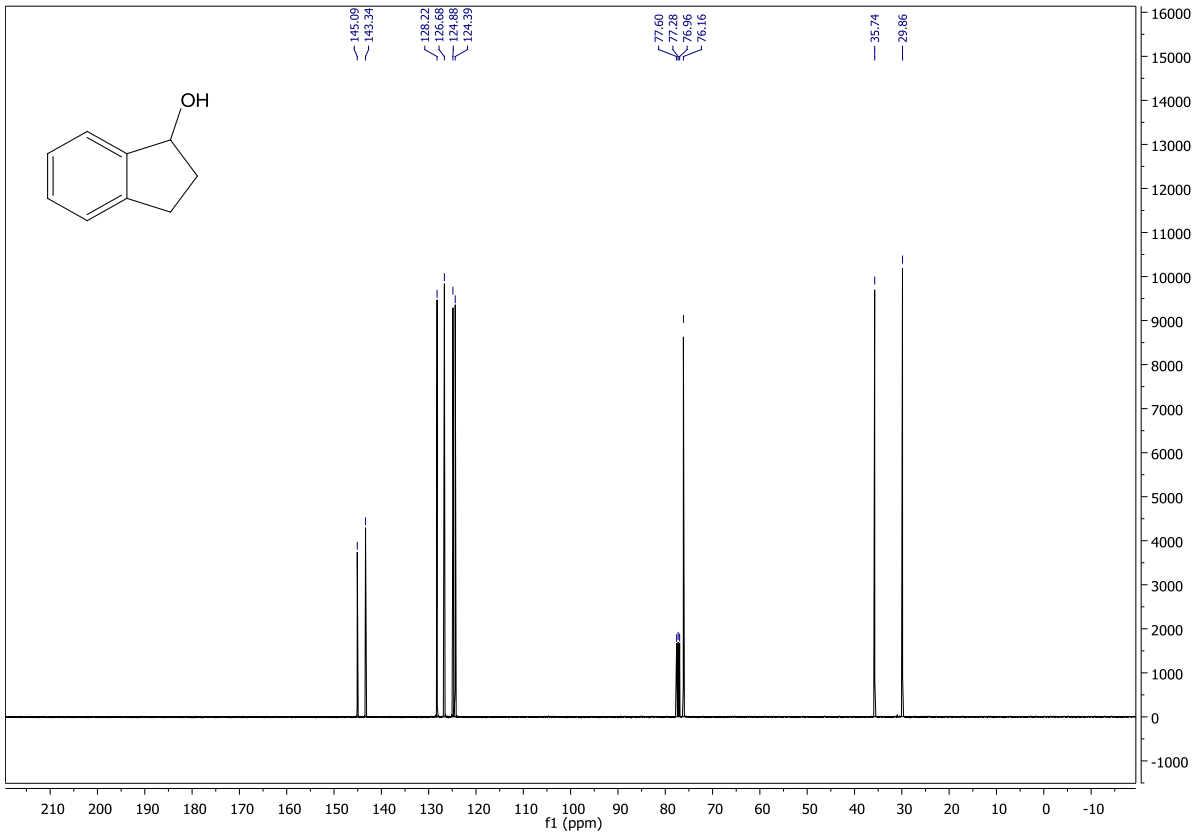
^{13}C NMR for 2-n (cis + trans alcohol products)



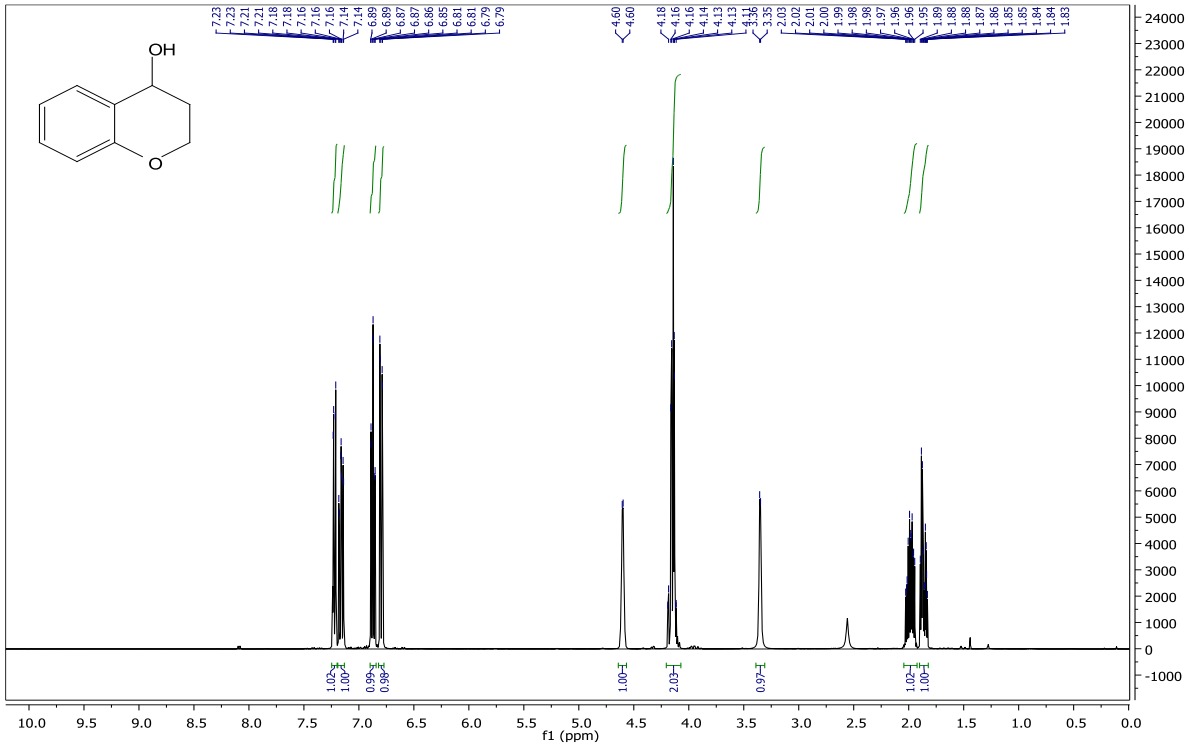
^{1}H NMR for 2-o



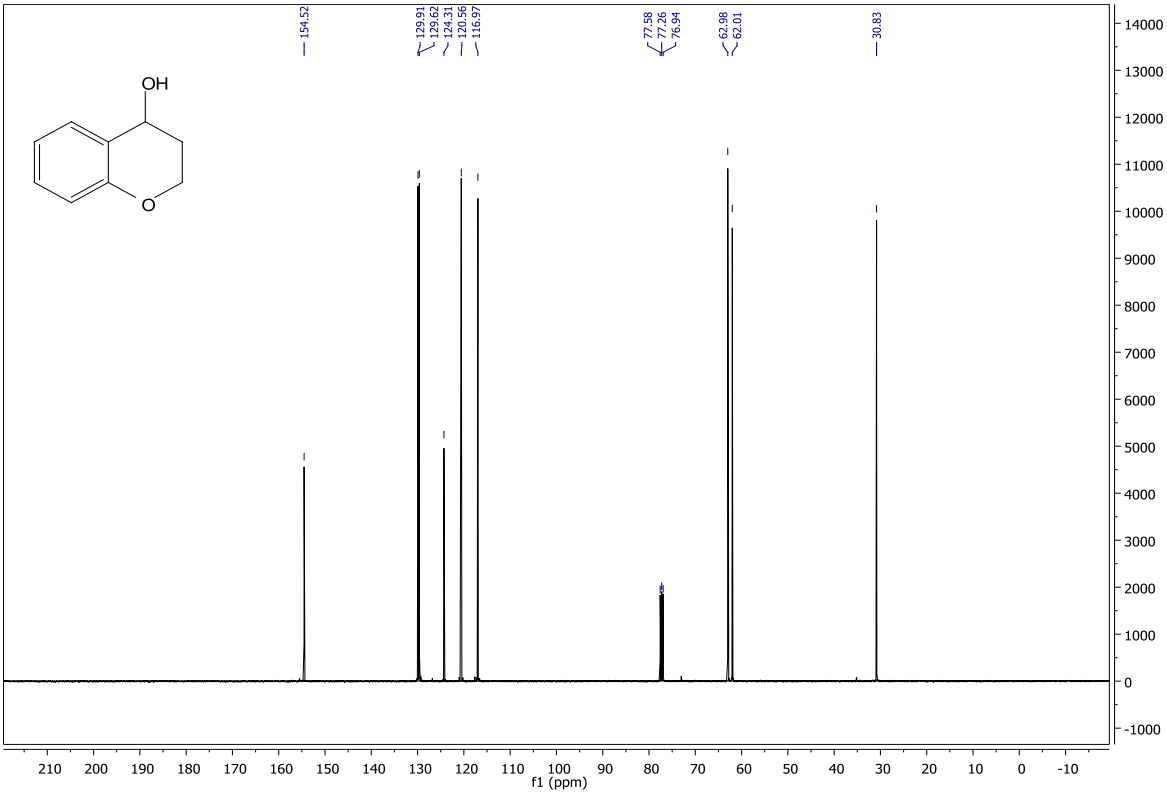
^{13}C NMR for 2-o



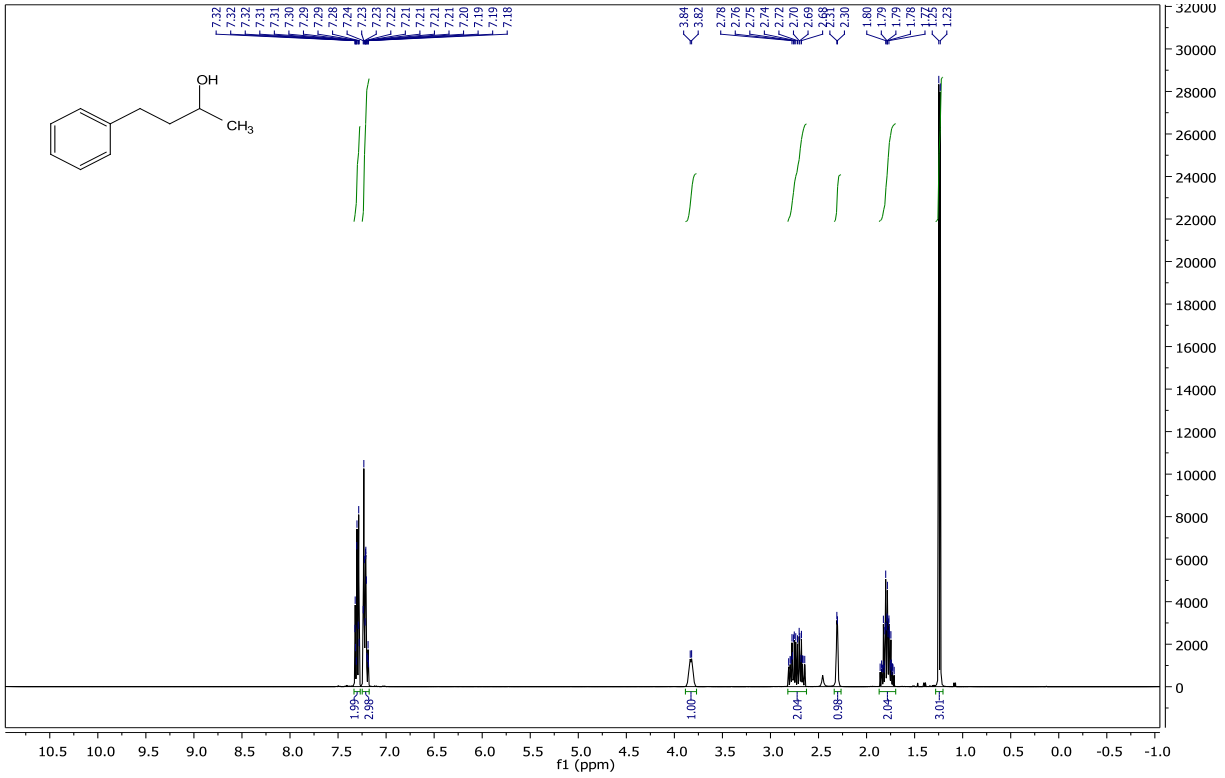
^{1}H NMR for 2-p



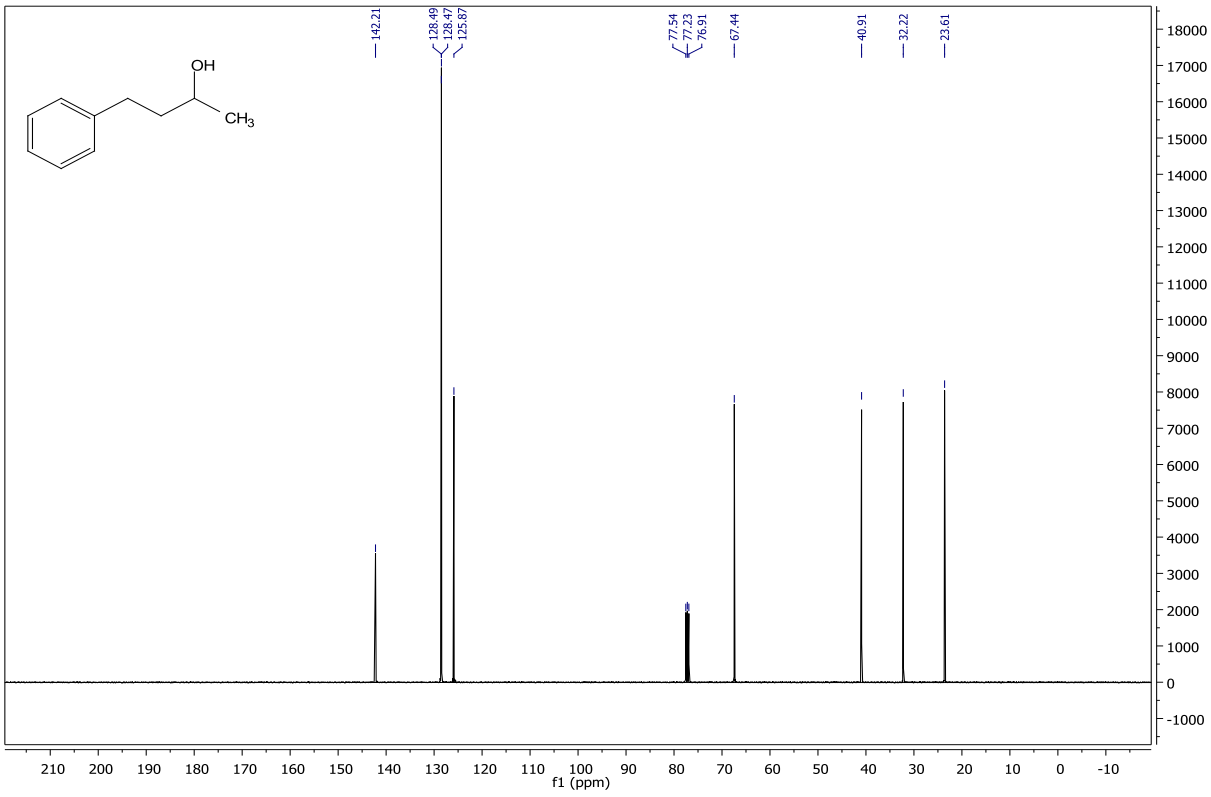
^{13}C NMR for 2-p



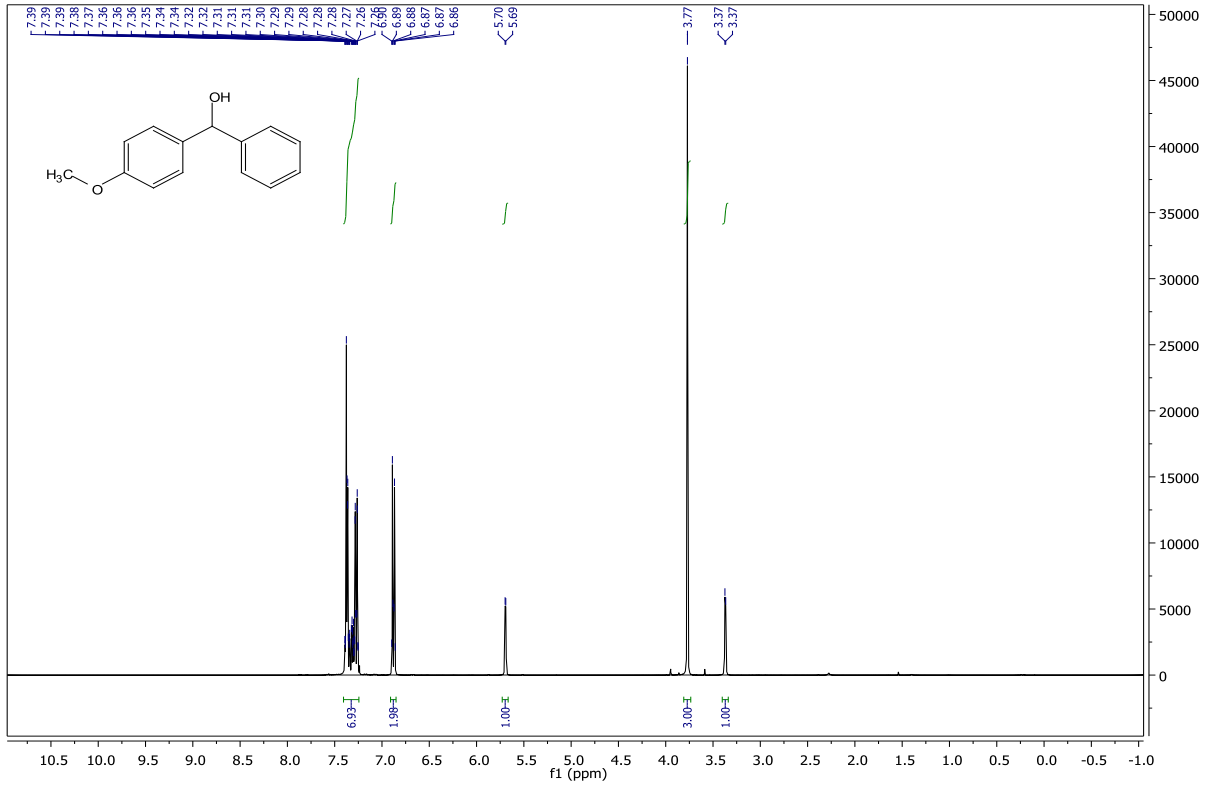
^{1}H NMR for 2-q



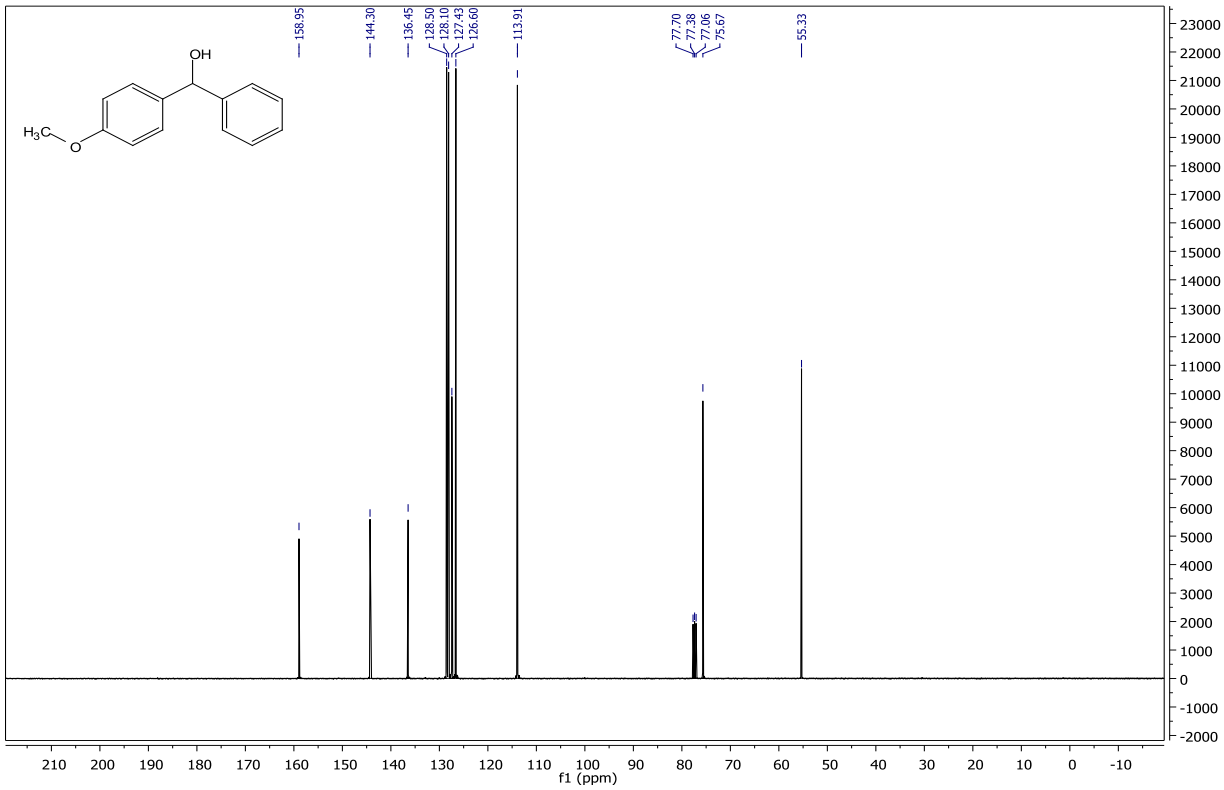
^{13}C NMR for 2-q



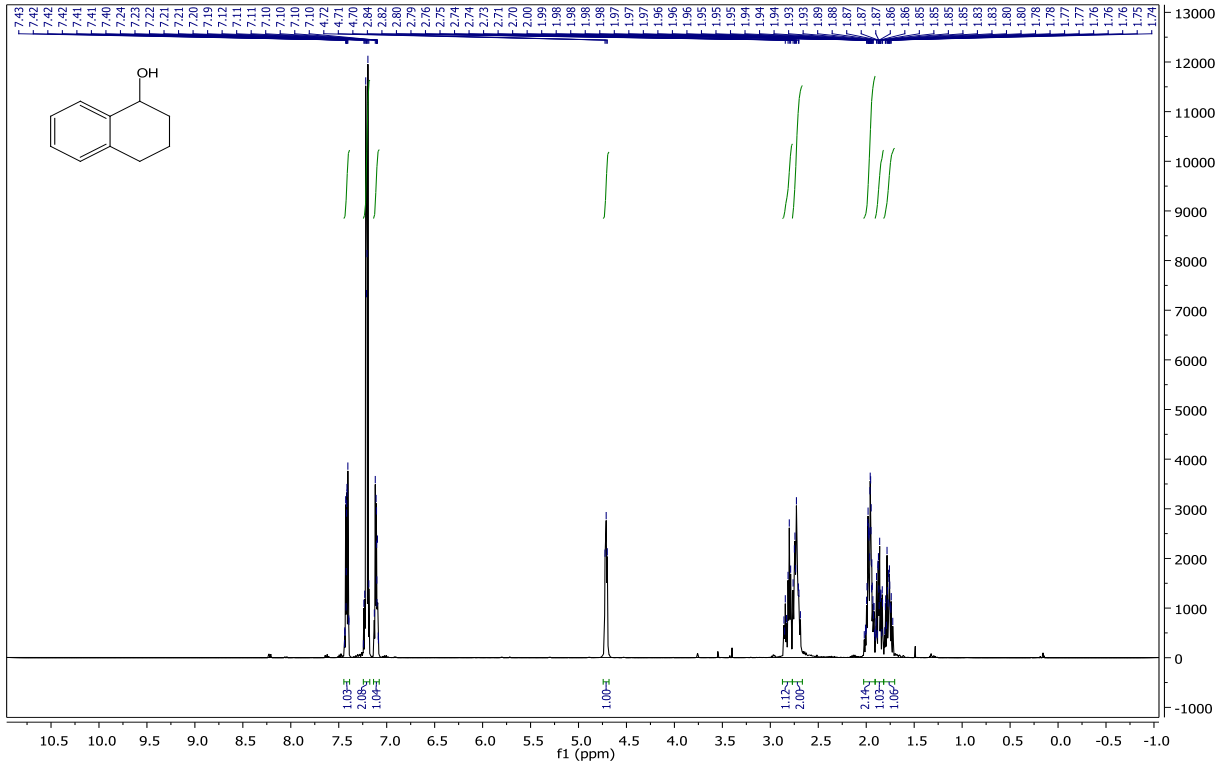
^{1}H NMR for 2-r



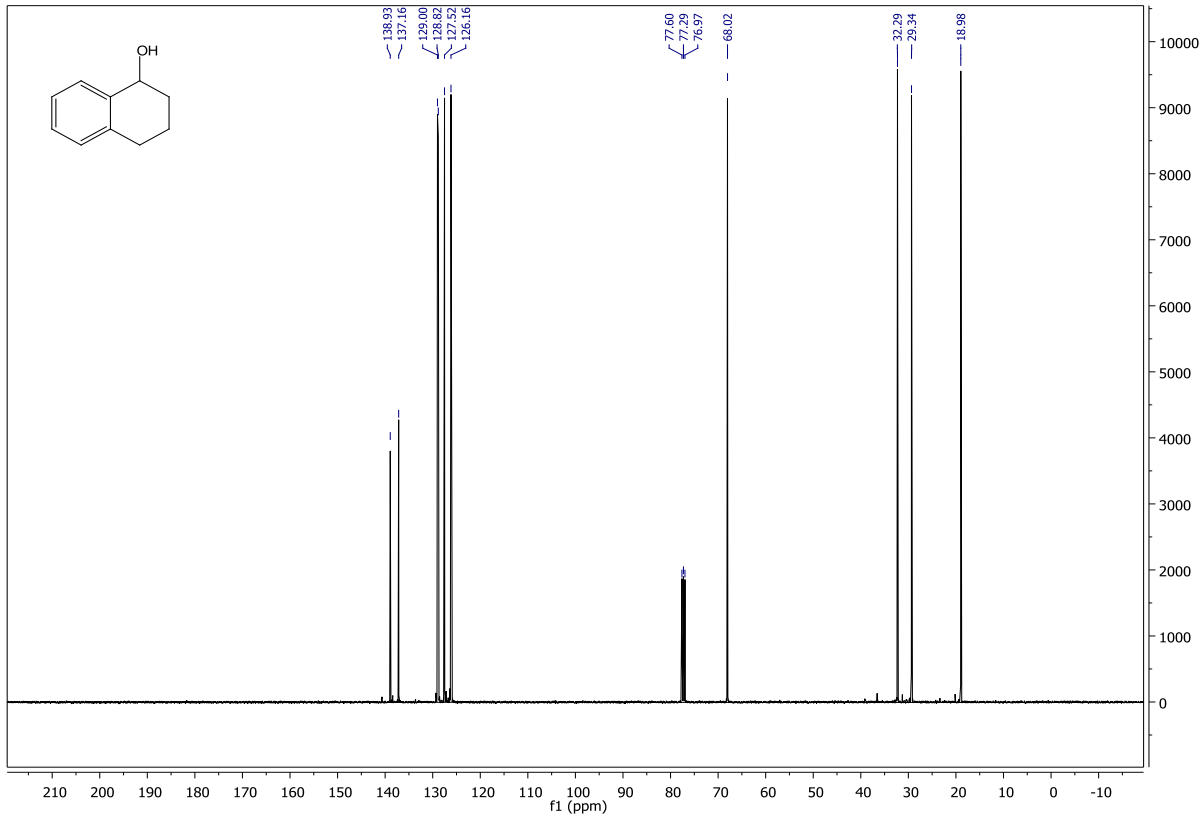
^{13}C NMR for 2-r



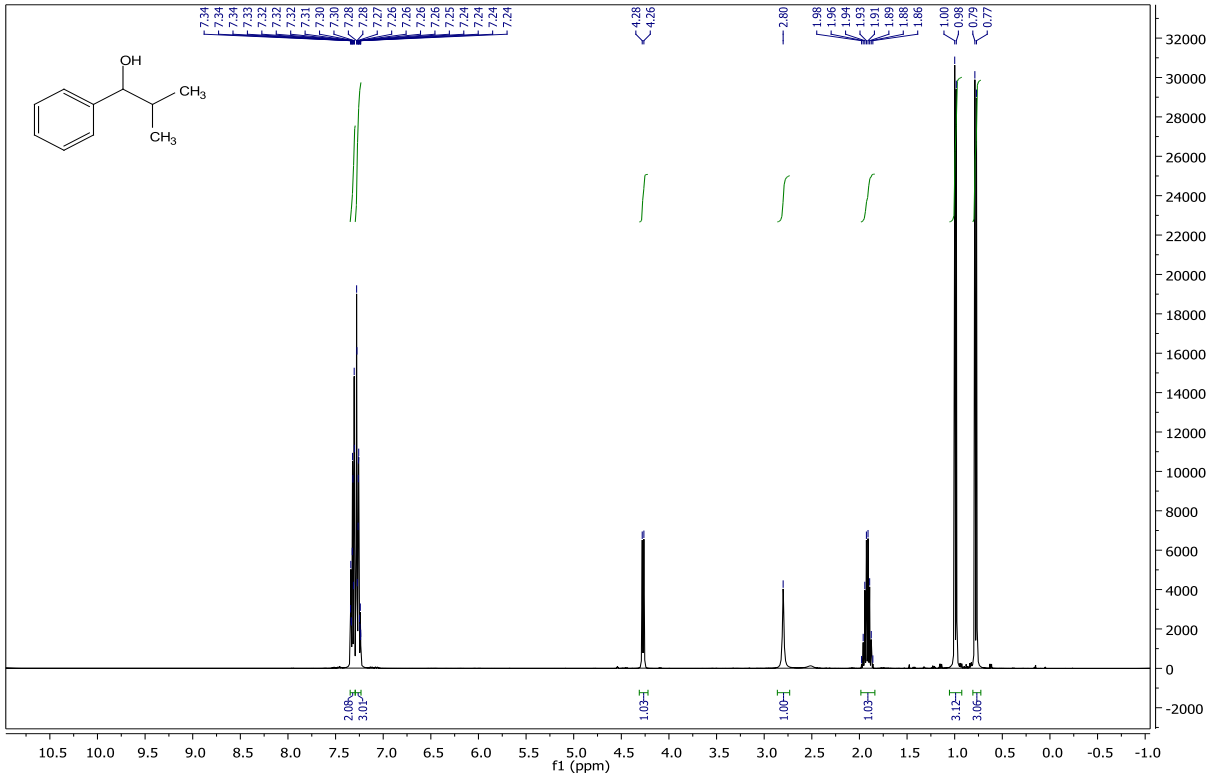
^{1}H NMR for 2-s



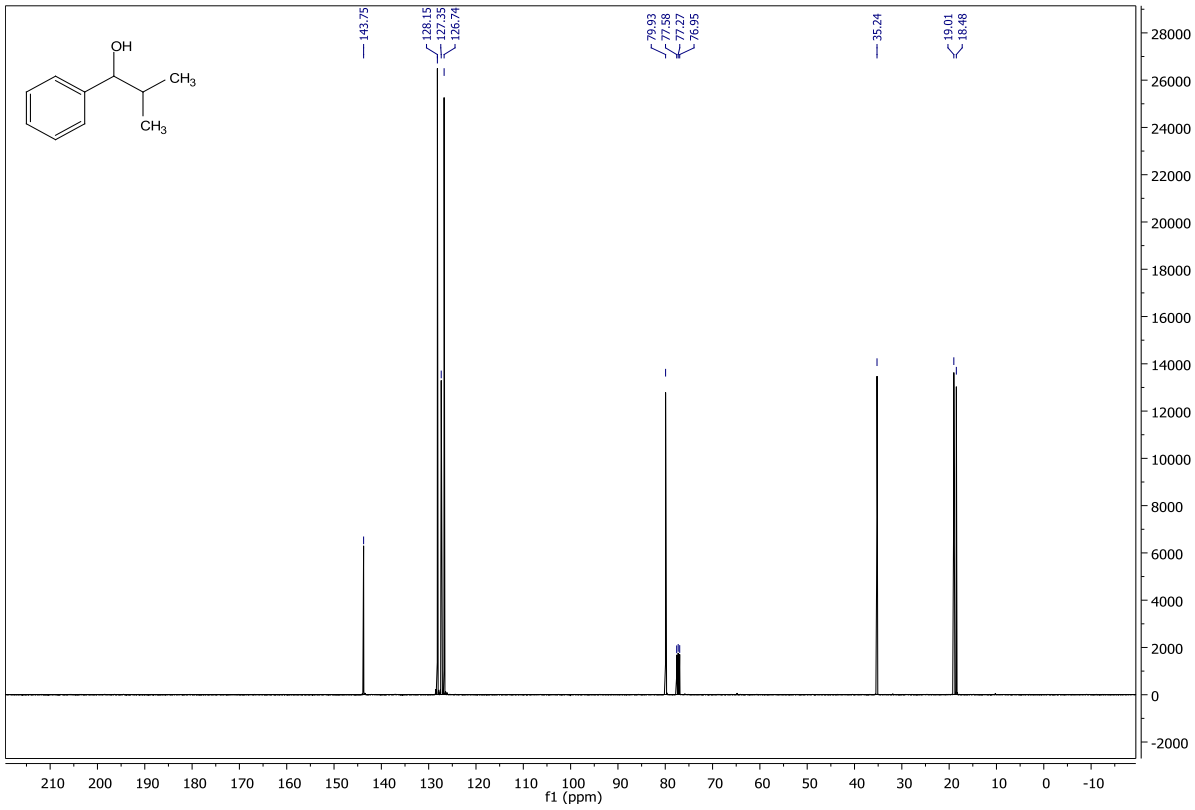
^{13}C NMR for 2-s



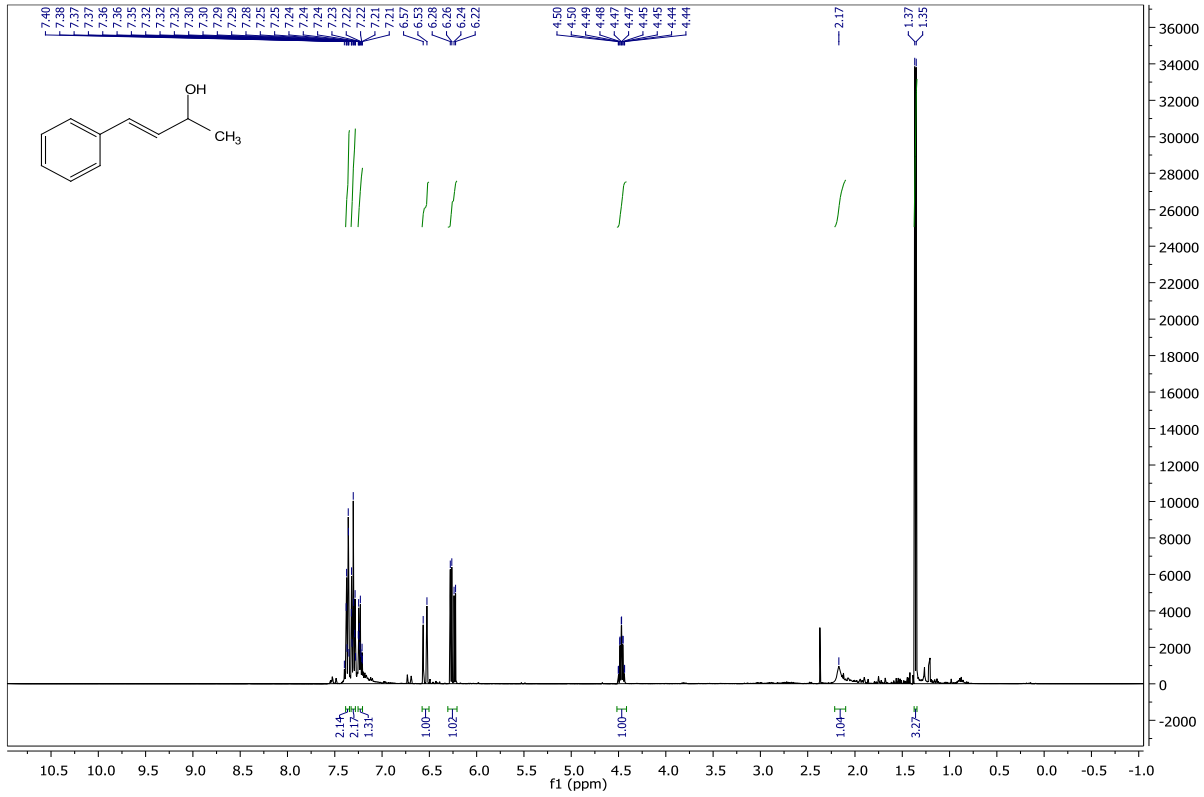
^{1}H NMR for 2-t



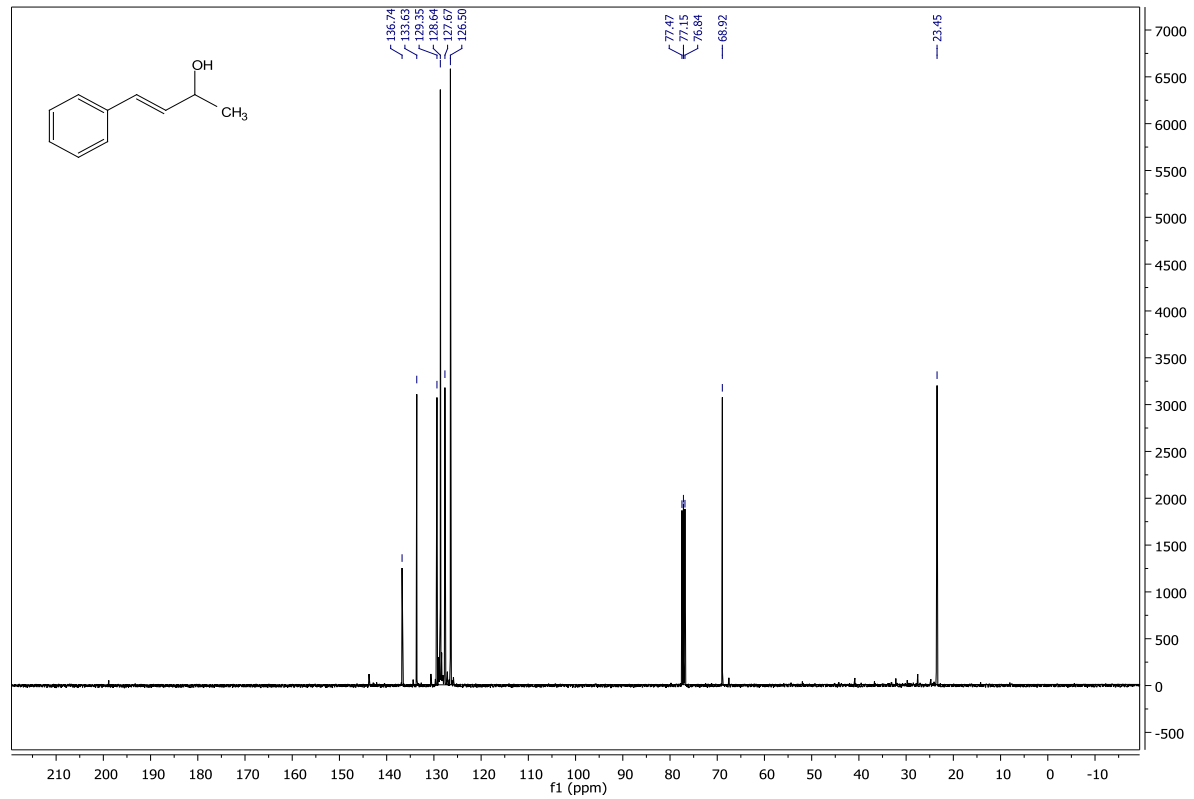
^{13}C NMR for 2-t



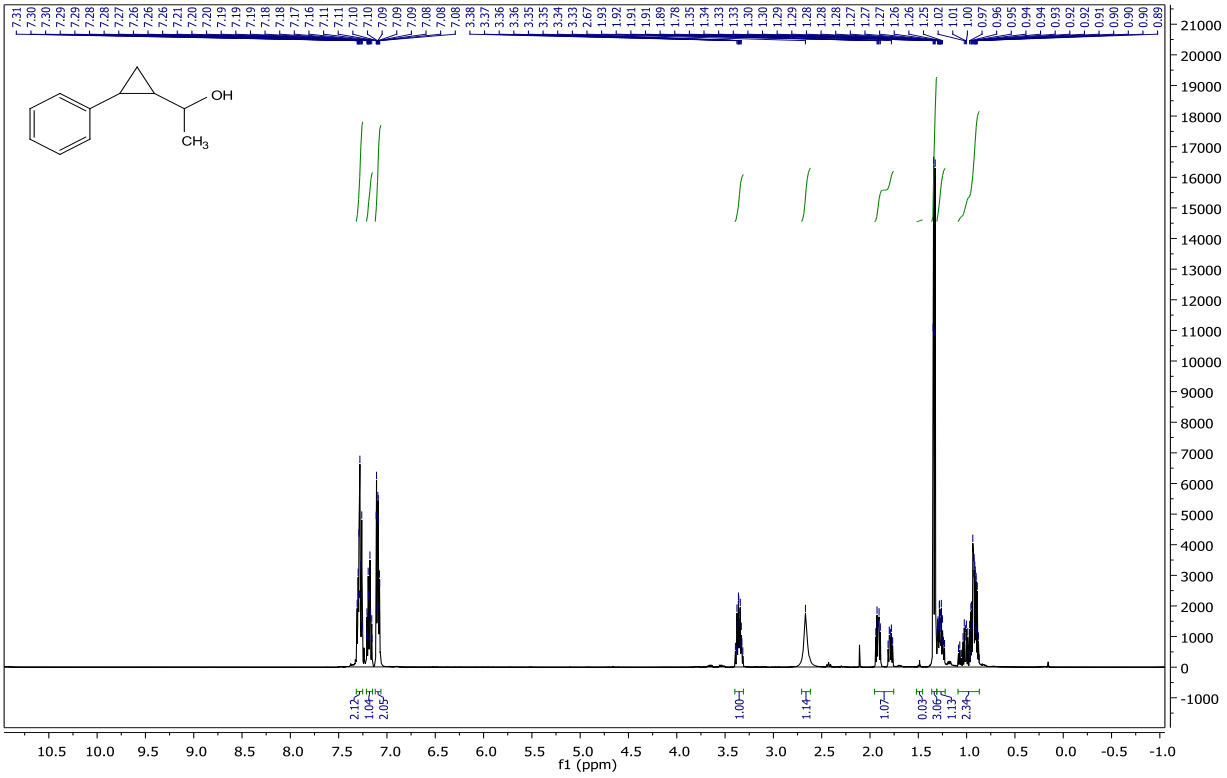
^{1}H NMR for 2-u



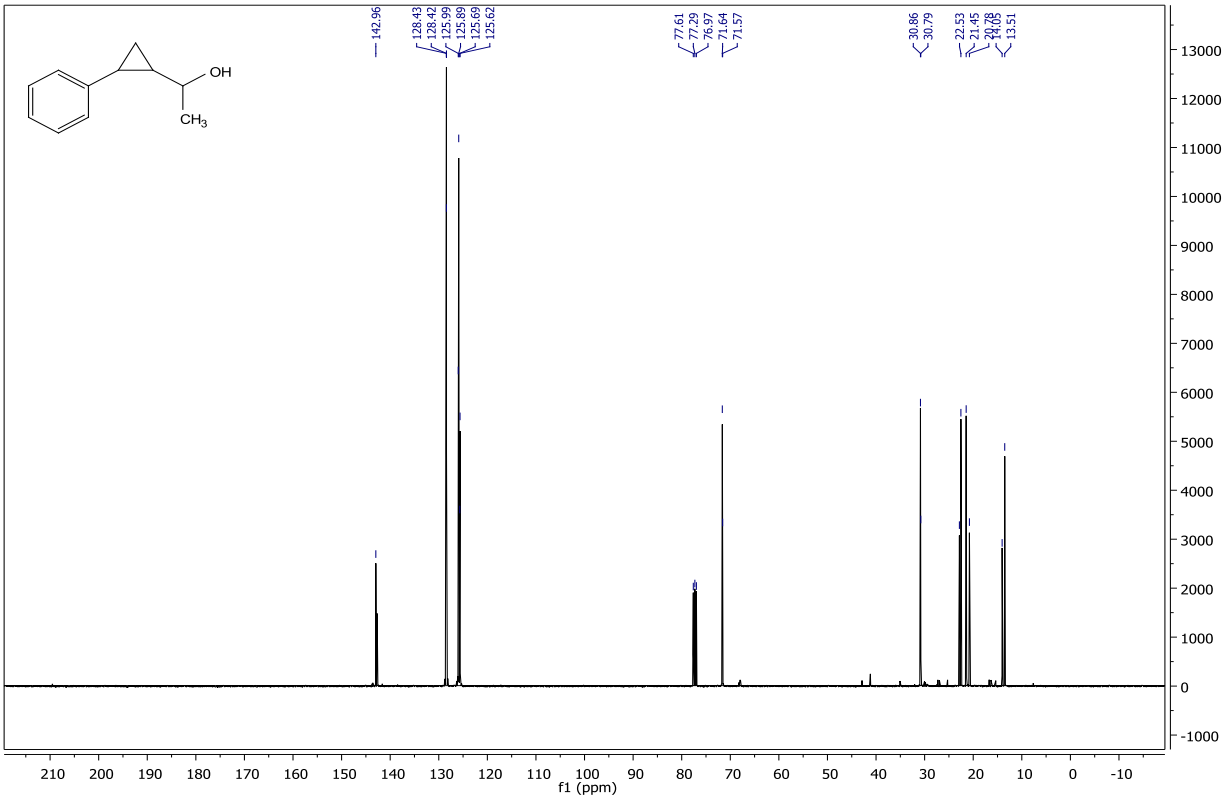
^{13}C NMR for 2-u



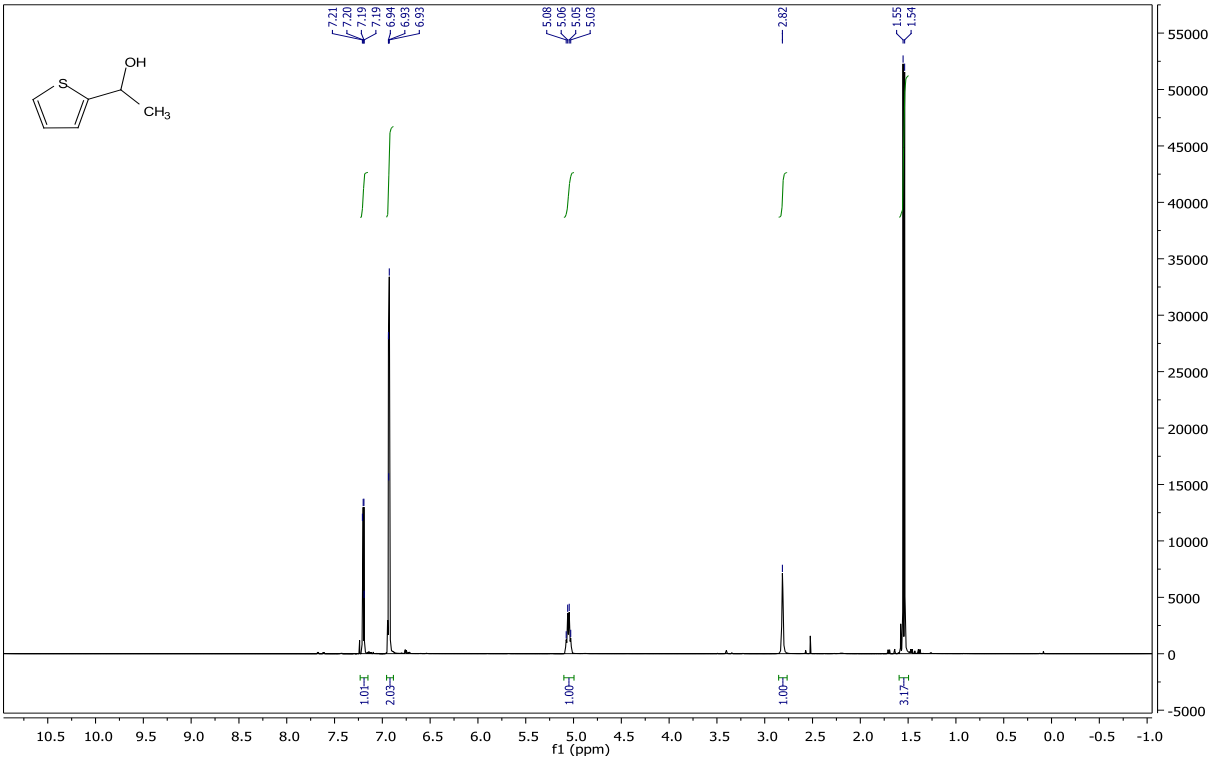
^{1}H NMR for 2-v



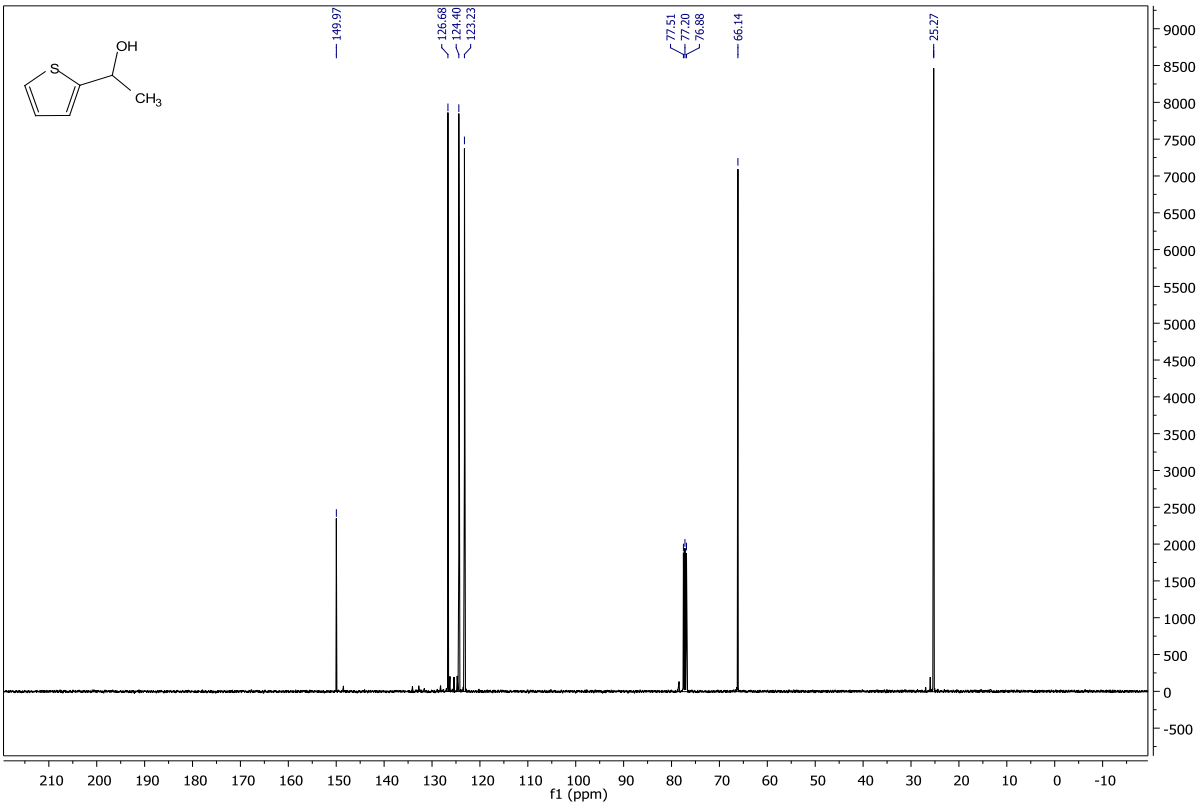
^{13}C NMR for 2-v



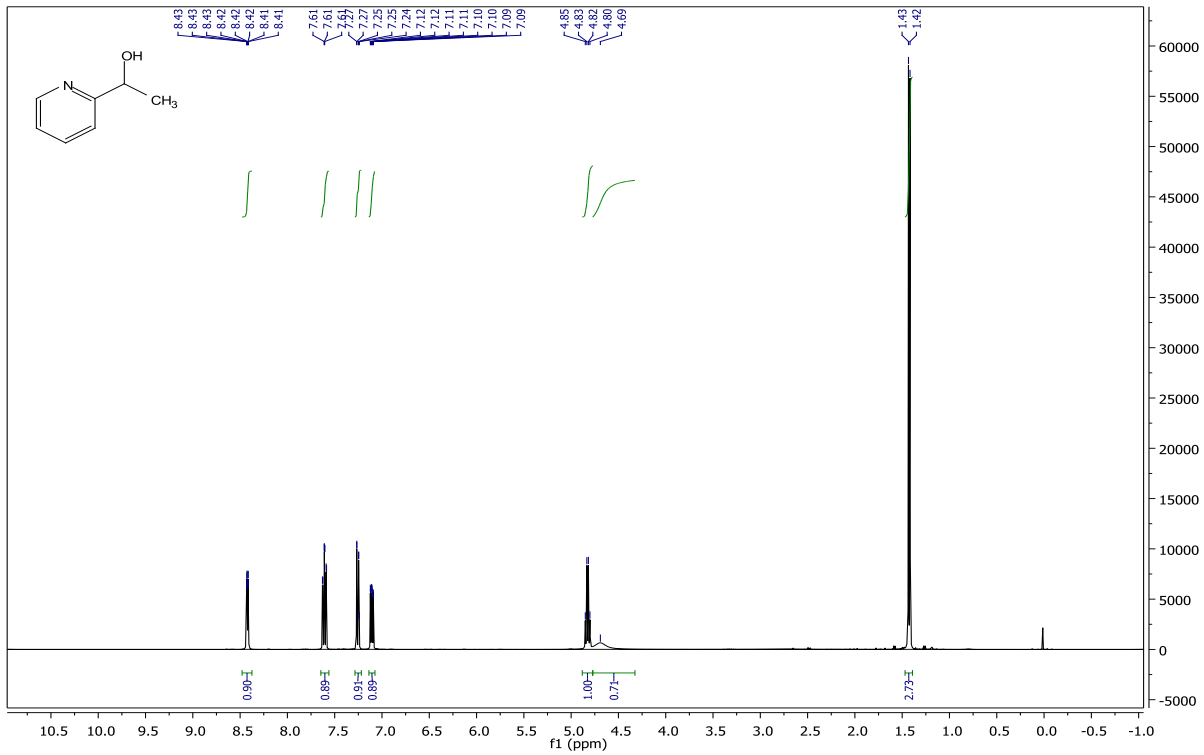
^{1}H NMR for 2-w



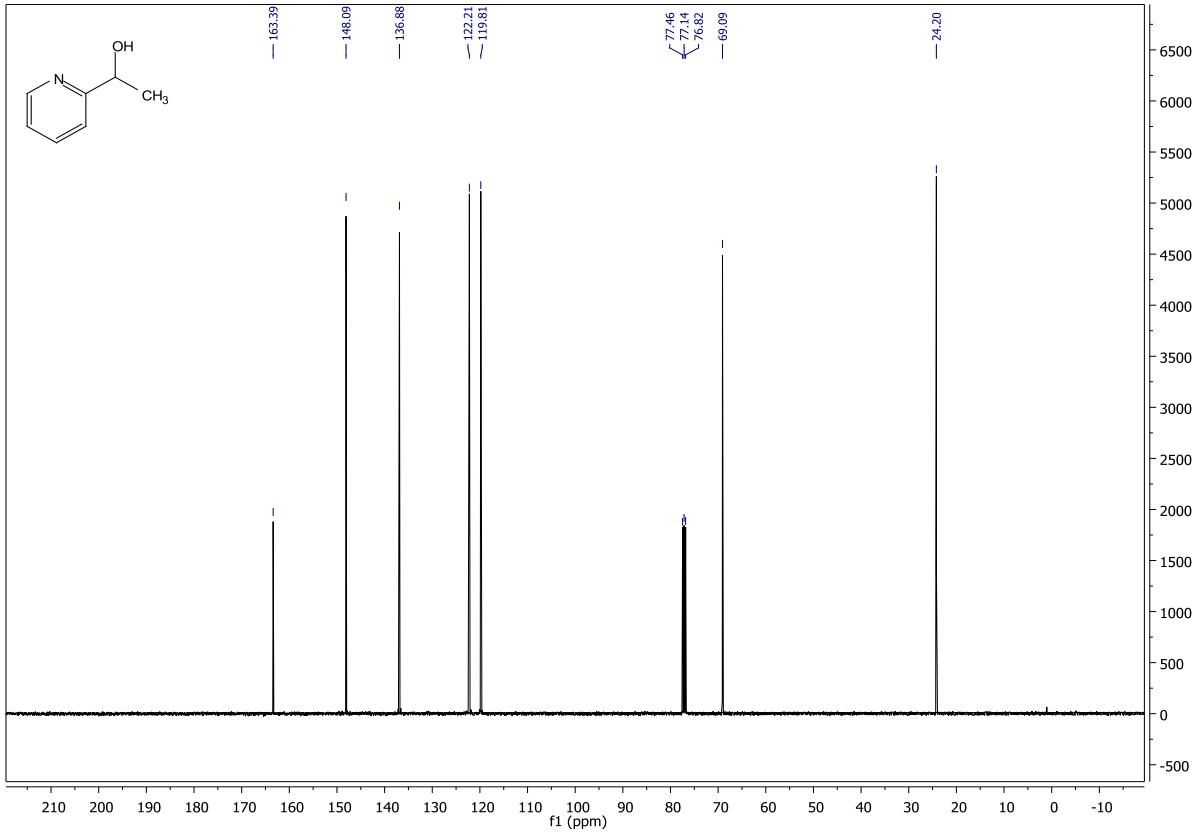
^{13}C NMR for 2-w



^{1}H NMR for 2-x



^{13}C NMR for 2-x



References

1 J. Corey, Elias and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353–1364.

2 J. Yun and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 5640–5644.

3 X. Verdaguer, M. C. Hansen, S. C. Berk and S. L. Buchwald, *J. Org. Chem.*, 1997, **62**, 8522–8528.