SUPPORTING INFORMATION

Efficient and chemoselective hydrogenation of aldehydes catalyzed by well-defined PN^3 pincer manganese (II) catalyst precursors: an application in furfural conversion

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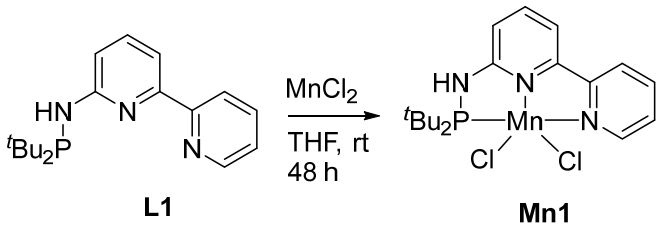
I. General Information

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or in an argon gas glovebox. Hydrogen (99.999% purity) was purchased from Abdullah Hashim Industrial Gases and Equipment Center (AHG) and used as received. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4Å molecular sieves. All aldehyde substrates were obtained from commercial sources and purified by distillation before use when it is necessary. $MnCl_2$ and $MnBr_2$ were purchased from Aldrich. Furfural was purchased from Aldrich. 2-Formyl furfural was purchased from Tokyo Chemical Industry (TCI). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AVANCE- 400, and 500 MHz spectrometers. ^1H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents, and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, s = sextet, h = heptet, m = multiplet, br = broad), coupling constants (Hz) and integration. Gas chromatography was performed on Agilent 5975C GC inert XL EI/CI MSD with Triple-Axis MS Detector. The X-ray diffraction data were collected using Bruker-AXS KAPPA-APEXII CCD diffractometer (CuKα, λ= 1.54178 Å). Indexing was performed using APEX2 (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01. Absorption correction was performed by multi-scan method implemented in SADABS. Space groups were determined using XPREP implemented in APEX2. Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full matrix least-squares on F2). Elemental analyses were conducted by Flash 2000-Thermo Scientific CHNO Analyzer.

II. The procedure for the preparation of PN^3 manganese (II) pincer complexes:

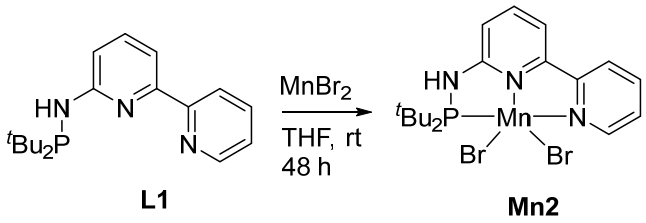
1. Synthesis of PN^3 pincer manganese complex Mn1



L1 **Mn1**

To a suspension of $^tBu_2PNH$-BPy (**L1**) (400 mg, 1.26 mmol) in THF (6.0 mL) was added $MnCl_2$ (156 mg, 1.34 mmol) under an argon atmosphere and the mixture was stirred at room temperature for 48 h. The solution was filtered and the solid was washed with pentane (3×3.0 mL), The yellow solid was dried under vacuum afforded **Mn1** (458 mg, 87%). Crystals of **Mn1** were obtained by slow evaporation of its methanol solution and confirmed by X-Ray crystallography. Elemental analysis (%) for $C_{18}H_{26}Cl_2MnN_3P$: Calculated: C, 49.00; H, 5.94; N, 9.52; Found: C, 49.04; H, 5.97; N, 9.49.

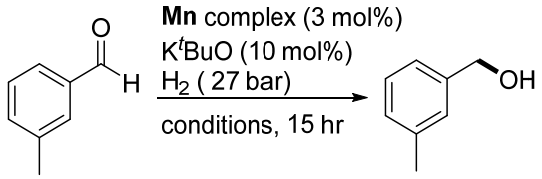
2. Synthesis of PN^3 pincer manganese complex Mn2



L1 **Mn2**

To a suspension of $^tBu_2PNH$-BPy (**L1**) (400 mg, 1.26 mmol) in THF (6.0 mL) was added $MnBr_2$ (272 mg, 1.26 mmol) under an argon atmosphere and the mixture was stirred at room temperature for 48 h. The solution was filtered and the solid was washed with pentane (3×3.0 mL), the yellow solid was dried under vacuum afforded **Mn2** (458 mg, 87%). Crystals of **Mn2** were obtained by slow evaporation of its methanol solution and confirmed by X-Ray crystallography. Elemental analysis (%) for $C_{18}H_{26}Br_2MnN_3P$: Calculated: C, 40.78; H, 4.94; N, 7.93; Found: C, 40.80; H, 4.90; N, 7.96.

III. Table S1: Optimization of the reaction condition for the hydrogenation of 3-methyl benzaldehyde

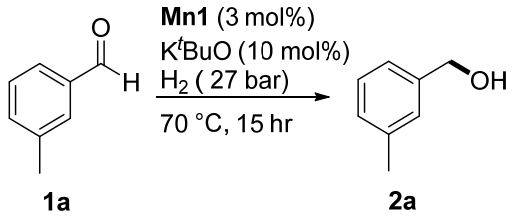


1a **2a**

Entry	Mn cat	Solvent	T(°C)	Conversion (%)	Yield[b]
1	**Mn1**	toluene	130	75	71
2	**Mn1**	MeOH	130	100	98
3	**Mn1**	THF	130	70	64
4	**Mn2**	toluene	130	70	62
5	**Mn2**	THF	130	70	59
6	**Mn2**	MeOH	130	90	90
7	**Mn1**	MeOH	110	100	97
8	**Mn1**	MeOH	100	100	98
9	**Mn1**	MeOH	90	100	98
10	**Mn1**	MeOH	70	100	98
11	**Mn1**	MeOH	70	60	55[c]
12	**Mn1**	MeOH	70	70	65[d]

[a]For the reaction, 3-methylbenzladheyde (0.83 mmol), Mn cat (3 mol%, 0.024), K^{t}BuO (0.083 mmol), H_2 (27 bar). [b]Yield is calculated based on staring material conversion. [c]10 h. [d]6 h.

IV. A typical procedure for the hydrogenation of 3-methylbenzaldehyde



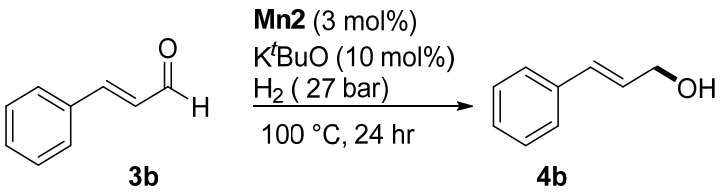
In a typical experiment, the high-pressure autoclave reactor was charged with 3-methylbenzaldehyde (100 mg, 0.83 mmol), **Mn1**(11.0 mg, 0.024 mmol), K^{t}BuO (9.3 mg, 0.083 mmol) in methanol (2.0 mL) inside the glovebox. Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (27 bar). The reactor was heated at 70 °C with stirring for 15 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. The solvent was removed under vacuum and the reaction mixture dissolve in DCM and filtered through a short plug of silica gel. After solvent removal under vacuum to afford 3-methyl benzyl alcohol as a pure product (99 mg, 98% yield).

3-Methyl benzyl alcohol: ^{1}H NMR (500 MHz $CDCl_3$): δ (ppm) 7.20-7.27 (m, 2H); 7.22 (s, 1H); 7.18-7.13 (m, 1H); 4.69 (brs, 1H); 2.39 (s, 3H); ^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) 140.8, 138.3, 128.5, 127.8, 124.1, 65.5, 21.4.

Characterization of the products was compared with the reported one.[4]

All the hydrogenation of aldehyde was carried out according to the typical procedure (**III**) and characterization of all alcohol products was compared with the reported one.[3,4]

V. A typical procedure for the hydrogenation of cinnamaldehyde (*α,β*-unsaturated substrate)



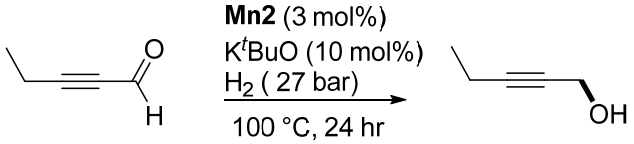
In a typical experiment, the high-pressure autoclave reactor was charged with cinnamaldehyde (100 mg, 0.75 mmol), **Mn2** (11.9 mg, 0.022 mmol), K^{t}BuO (8.4 mg, 0.075 mmol) in methanol (2.0 mL) under an inert atmosphere. Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (27 bar). The reactor was heated at 100 °C with stirring for 24 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. The solvent was removed under vacuum and the reaction mixture dissolve in DCM and

filtered through a short plug of silica gel. After solvent removal under vacuum to afford (*E*)-3-Phenylprop-2-en-1-ol as a pure product (81 mg, 80% yield).

Cinnamyl alcohol: ^{1}H NMR (500 MHz $CDCl_3$): δ (ppm) 7.42-7.41 (m, 2H); 7.36-7.33 (m, 2H); 7.28-7.26 (m, 1H); 6.66 (d, *J* = 15.0 Hz 2H); 6.45-6.37 (m, 2H); 4.35 (d, *J* = 5.0 Hz, 2H); ^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) 136.8, 131.2, 128.7, 128.6, 127.8, 126.6, 63.8.

Characterization of the product was compared with the reported one.[3]

VI. A typical procedure for the hydrogenation of pent-2-ynal

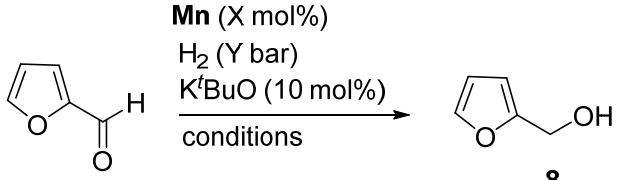


5a **6a**

In a typical experiment, the high-pressure autoclave reactor was charged with cinnamaldehyde (100 mg, 1.22 mmol), **Mn2** (16.1 mg, 0.037 mmol), K^{t}BuO (13.7 mg, 0.122 mmol) in methanol (2.0 mL) under an inert atmosphere. Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (27 bar). The reactor was heated at 100 °C with stirring for 24 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. The solvent was removed under vacuum and the reaction mixture dissolve in DCM and filtered through a short plug of silica gel. After solvent removal under vacuum to afford 2-pentyn-1-ol as a pure product (82 mg, 80% yield).

Pent-2-yn-1-ol: ^{1}H NMR (500 MHz $CDCl_3$): δ (ppm) 4.22 (s, 2H); 2.23-2.19 (m, 2H); 1.2 (t, *J* =7.2 Hz, 3H); ^{13}C NMR (126 MHz $CDCl_3$): δ (ppm) 87.9, 51.4, 13.9, 12.5.

VII. Table S2: Optimization of the reaction condition for the hydrogenation of furfural (FAL) to furfuryl alcohol (FOL)

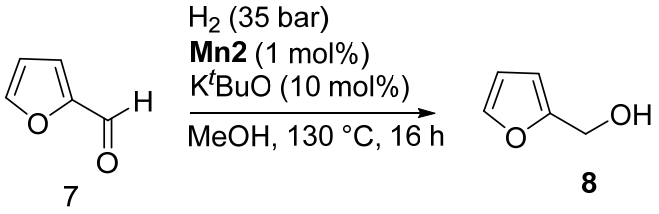


7 **8**

entry	**Mn**	(X mol%)	Y (bar)	temp (°C)	conversion (%)	yield (%)[b]
1	**Mn1**	0.5	20	160	90	70
2	**Mn1**	1	20	160	90	80
3	**Mn1**	1	35	130	92	85
4	**Mn2**	0.5	20	150	85	81
5	**Mn2**	1	20	130	83	80
6	**Mn2**	1	35	120	85	83
7	**Mn2**	1	35	100	95	92
8	**Mn2**	2	35	130	100	99

Reaction condition: [a]Furfural (1.04 mmol), **Mn2** (5.5 mg, 0.010 mmol), K^{t}BuO (11.6 mg, 0.103 mmol) in MeOH for 16 hr. [b]Isolated yield.

VIII. A typical procedure for the hydrogenation of furfural (FAL) to furfuryl alcohol (FOL



7 **8**

In a typical experiment, the high-pressure autoclave reactor was charged with furfural (100 mg, 1.04 mmol), **Mn2** (5.5 mg, 0.010 mmol), K^{t}BuO (11.6 mg, 0.103 mmol) in methanol. Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (35 bar). The reactor was heated at 130 °C with stirring for 48 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. The solvent was removed under vacuum and the reaction mixture dissolve in DCM and filtered through a short plug of silica gel. After solvent removal under vacuum to afford furfuryl alcohol as a pure product (101 mg, 99% yield).

Furfuryl alcohol: ^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) 7.45 (d, J = 1.8Hz, 1H); 6.36-6.15 (m, 1H); 6.29 (d, *J* =3.2 Hz, 3H); 4.89 (s, 1H); 4.50 (s, 2H); ^{13}C NMR (101 MHz $CDCl_3$): δ (ppm) 155.9, 111.2, 108.3, 57.3.

The characterization of the product was compared with the reported one.[4,5]

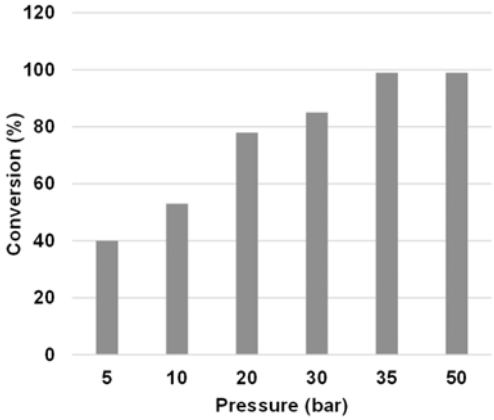
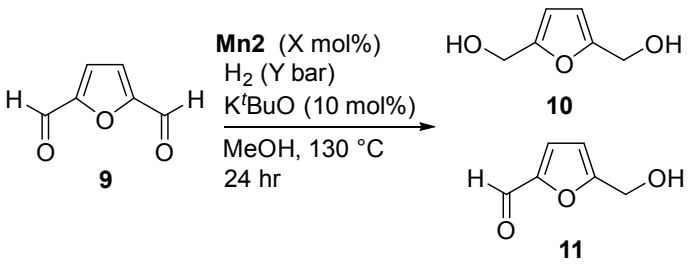


Figure S1: Effect of the pressure of H_2 (bar) on FAL to FOL conversion.

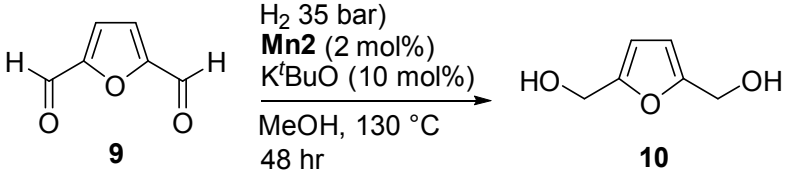
IX. Table S3: Optimization of the reaction condition for the hydrogenation of 5-formylfurfural (FFAL) to 5-(hydroxymethyl)furfuryl alcohol (HMFOL)



Entry	**Mn2** (X mol%)	H_2 (bar)	Conv. (%)	Yield of **10**, **11** (%)[b]	Selectivity of **10** (%)
1	1.0	20	75	70, 5	93
2	2.0	30	85	82, 3	96
3[c]	2.0	30	89	88, -	99
4[c]	2.0	35	100	99, -	99

Reaction conditions: [a]5-formylfurfural (0.80 mmol), **Mn2** (8.5 mg, 0.016 mmol), K^{t}BuO (9.0 mg, 0.080 mmol) in MeOH for 24 h. [b]Isolated yield. [c]48h.

X. A typical procedure for the hydrogenation of 5-formylfurfural (FFAL) to 5-(hydroxymethyl) furfuryl alcohol (HMFOL)

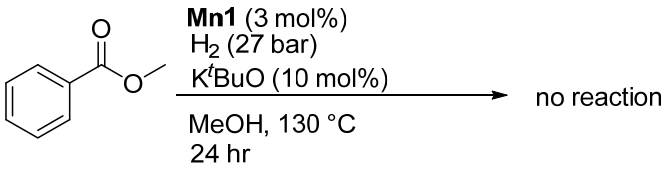


In an autoclave reactor, the solution was prepared inside a glovebox by mixing the 5-formylfurfural (100 mg, 0.80 mmol), **Mn2** (8.5 mg, 0.016 mmol) and K^{t}BuO (9.0 mg, 0.080 mmol). Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (35 bar). The reactor was heated at 130 °C with stirring for 48 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. The solvent was removed under vacuum and the reaction mixture dissolve in DCM and filtered through a short plug of silica gel. After solvent removal under vacuum to afford 5-(hydroxymethyl)furfuryl alcohol as a pure product (102 mg, 99%). The characterization of the product was compared with the reported one.[4]

5-(hydroxymethyl)furfuryl alcohol: ^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) 6.23 (s, 2H); 4.89 (s, 2H); 4.48 (s, 4H); ^{13}C NMR (101 MHz $CDCl_3$): δ (ppm) 155.7, 109.0, 57.3.

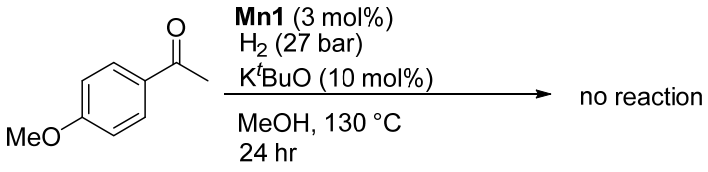
The characterization of the product was compared with the reported one.[4,5]

XI. Attempt of the hydrogenation of Methyl benzoate



In an autoclave reactor, the solution was prepared inside a glovebox by mixing the methylbenzoate (100 mg, 0.73 mmol), **Mn1** (9.7 mg, 0.020 mmol) and K^{t}BuO (8.2 mg, 0.073 mmol). Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (35 bar). The reactor was heated at 130 °C with stirring for 48 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. No product formation was observed.

XII. Attempt of the hydrogenation of 4- methoxyacetophenone



In an autoclave reactor, the solution was prepared inside a glovebox by mixing the 4-methoxyacetophenone (100 mg, 0.66 mmol), **Mn1** (8.8 mg, 0.019 mmol) and K^{t}BuO (5.8 mg, 0.052 mmol). Then, the autoclave reactor was removed from the glove box and purged three times with H_2 and then finally pressurized with H_2 (35 bar). The reactor was heated at 130 °C with stirring for 48 h. After completion of the reaction, the autoclave reactor was cooled down to room temperature and cooled in an ice bath for 20 minutes before release the H_2 pressure. No product formation was observed.

XIII. Crystal Structure Determination of Mn1 and Mn2

X-ray quality crystals were immersed in cryo-oil, mounted in a Nylon loop, and measured at 130/120 K. Intensity data were collected using a Bruker D8 Venture SMART CCD diffractometer with graphite monochromated Mo−Kα (λ = 0.71073 Å) radiation. Cell parameters were retrieved using Bruker SMART software[1] and refined using Bruker SAINT[1] on all the observed reflections. Data were corrected for absorption effects using the multi-scan method (SADABS).[6] The Structures were solved by direct methods by using the SHELXS-2016 package[7] and refined with SHELXL-2016. All other hydrogen atoms in the compound were inserted on geometrically calculated positions with fixed thermal parameters. All the hydrogen atoms, either located or inserted, were refined isotropically, while all the nonhydrogen atoms were refined anisotropically. The final least-squares refinements (R_1) based on $I > 2\sigma(I)$ converged to 0.0427 / 0.0521 for catalysts **Mn1** and **Mn2** respectively.

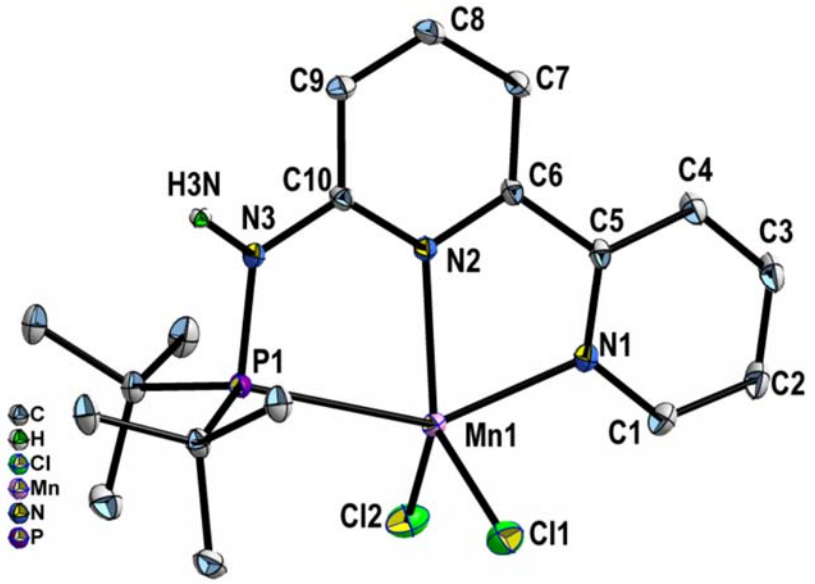


Figure S2: Crystal structure of **Mn1**. All atoms have been shown with 30% probability ellipsoids, All hydrogen atoms except N-H have been omitted for clarity. Selected bond distances (Å) and angles (°) : Cl1 Mn1 2.3719(6); Cl2 Mn1 2.3829(6); Mn1 N1 2.2099(16); Mn1 N2 2.2642(15); Mn1 P1 2.6340(6); N3 H3N 0.89(3); N1 Mn1 N2 72.44(6); N2 Mn1 Cl1 122.52(4); N2 Mn1 Cl2 127.15(4).

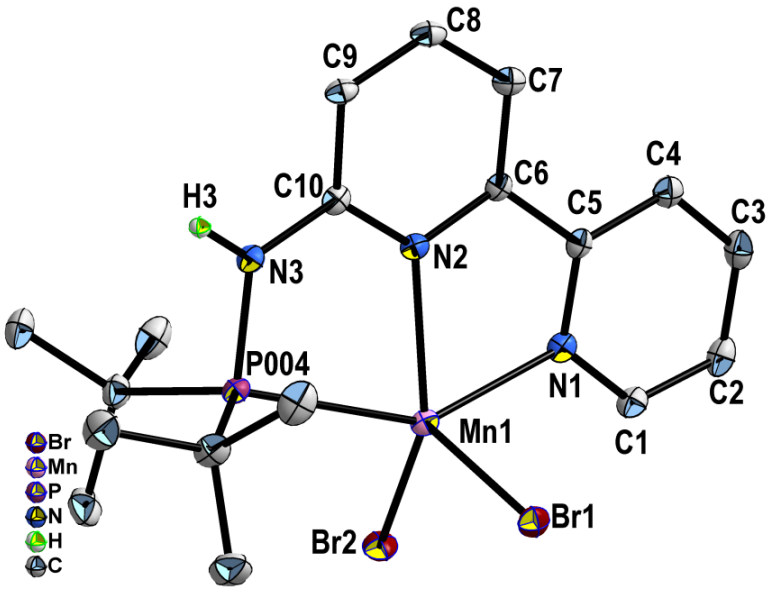


Figure S3: Crystal structure of **Mn2**. All atoms have been shown with 30% probability ellipsoids, All hydrogen atoms except of N-H have been omitted for clarity. Selected bond distances (Å): Mn1−N2 2.216(3), Mn1−N3 2.251(2), Mn1 P004 2.6609(9); Br2 Mn1 2.5108(6); Br1 Mn1 2.5155(6). Br2 Mn1 Br1 109.03(2); Br2 Mn1 P004 103.05(3); Br1 Mn1 P004 104.90(3).

Table S4: Crystallographic information for Mn1 and Mn2

	Mn1	**Mn2**
empirical formula	$C_{18}H_{26}Cl_2MnN_3P$	$C_{21}H_{33}Br_2MnN_4OP$
fw	441.23	603.24
crystal system	Monoclinic	Triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	12.9997(16)	8.8591(13)
b (Å)	12.4522(13)	10.2949(15)
c (Å)	14.3781(18)	14.571(2)
α (deg)	90.00	96.607(5)
β (deg)	109.245(5)	97.226(5)
γ (deg)	90.00	94.321(5)
V (Å^3)	2197.4(5)	1304.2(3)
Z	4	2
T (K)	150(2)	130(2)
2ϑ (deg)	3.66–66.30	4.60 – 65.87
μ (mm^{-1})	0.923	3.650
ρ_{calcd} (g cm^{-3})	1.334	1.536

$F(000)$	916	610
Index ranges	$-18 \leq h \leq 18$	$-13 \leq h \leq 13$
	$-19 \leq k \leq 20$	$-15 \leq k \leq 15$
	$-22 \leq l \leq 22$	$-22 \leq l \leq 22$
R_{int}	0.0718	0.1135
R_1^a/ wR_2^b [I > 2σ(I)]	0.0427/ 0.1227	0.0521 / 0.1274
R_1^a/ wR_2^b [for all F_o^2]	0.0699/ 0.1588	0.0935 / 0.1462
GOF on F^2	1.055	1.005

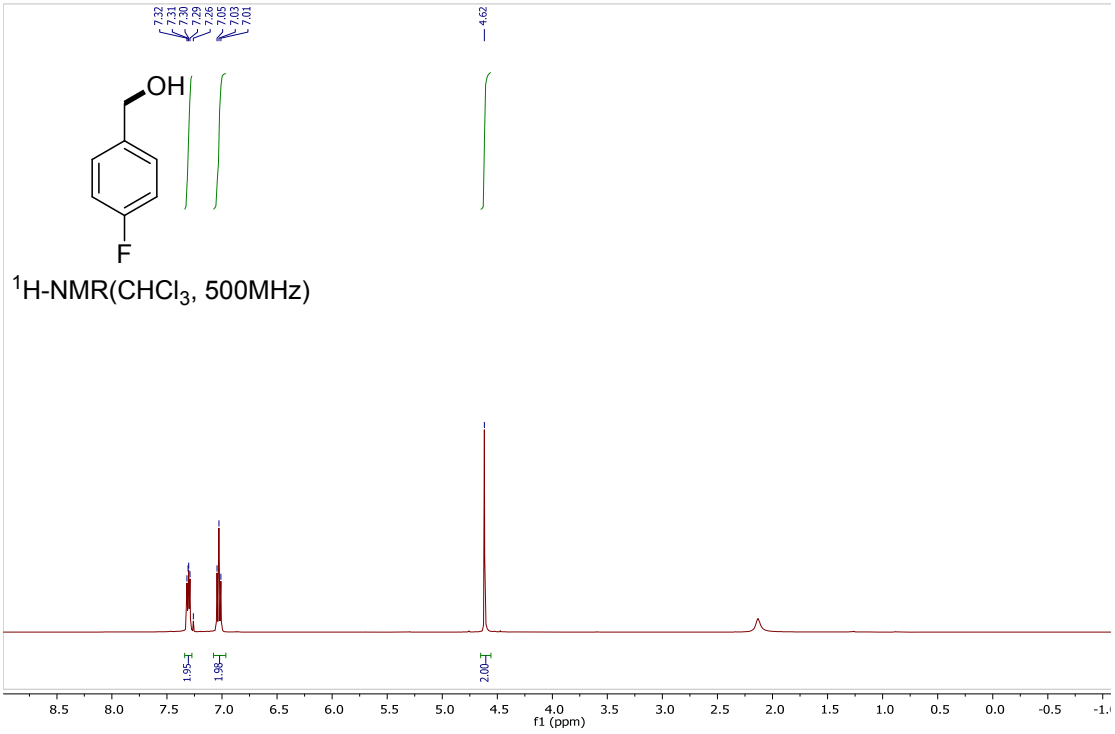
XIV. Table S5: Comparison of selected metric parameters for Mn1 and Mn2.

Parameters	**Mn1**	**Mn2**
Mn-N(pyridine)	2.2099(16), 2.2642(15)	2.216(3), 2.251(2)
Mn-P	2.6340(6)	2.6609(9)
Mn-X(Cl/Br)	2.3719(6), 2.3829(6)	2.5108(6), 2.5155(6)
C-NH	1.379(2)	1.363(4)
N-H	0.89(3)	0.8800

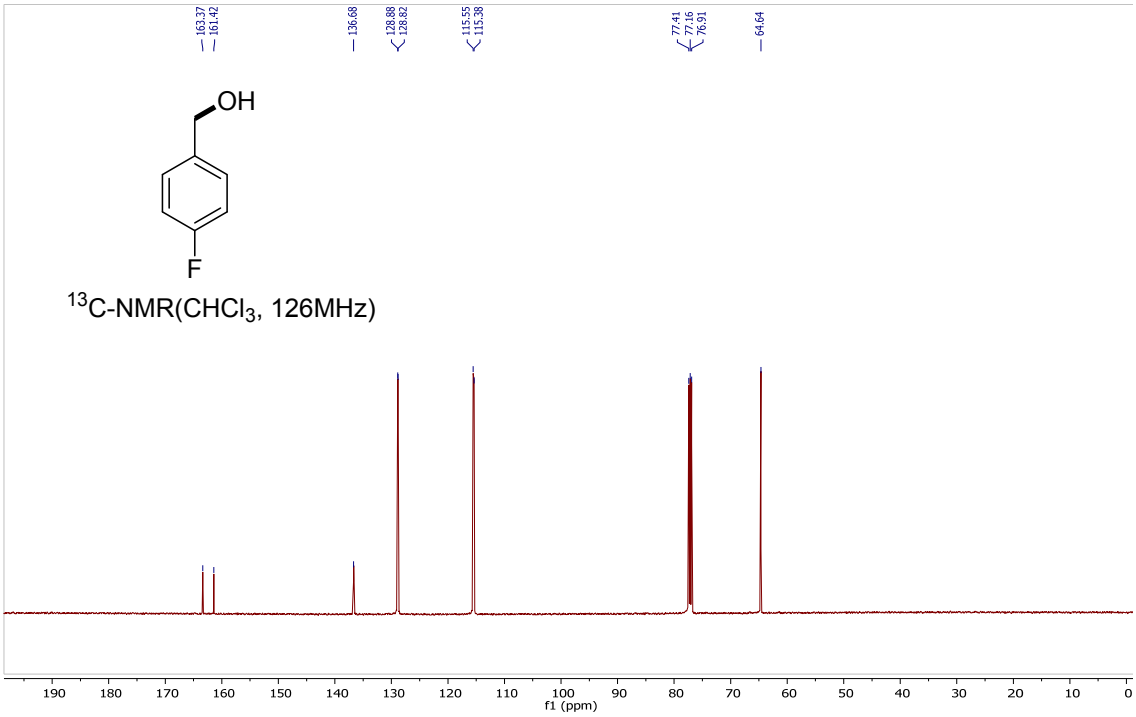
XV. References

1. APEX2, SMART, SAINT & SADABS; Bruker, AXS Inc.: Madison, Wisconsin, USA, **2012**.
2. G. M. Sheldrick, *Acta Crystallogr*. *Sect*. *C*: *Struct. Chem.* **2015**, *71*, 3−8.
3. S. Chakraborty, H. Dai, P. Bhattacharya, N. T. Fairweather, M. S. Gibson, J. A. Krause, H. Guan, *J. Am. Chem. Soc.*, 2014, **136**, 7869-7872.
4. Y. Liu, S. He, Z. Quan, H. Cai, Y. Zhao, B. Wang, *Green Chem.*, 2020, **21**, 830-838.
5. S. Paganelli; O. Piccolo; P. Pontini; R. Tassini; V. Rathod, *Catal. Today* **2015**, *247*, 64-69.
6. R. Padilla, S. Koranchalil, M. Nielsen, *Green Chem.*, 2020, **22**, 6767-6772.
7. F. Huang, W. Li, Q. Lu, X. Zhu, *Chem. Eng. Technol.* **2010**, *33*, 2082-2088.

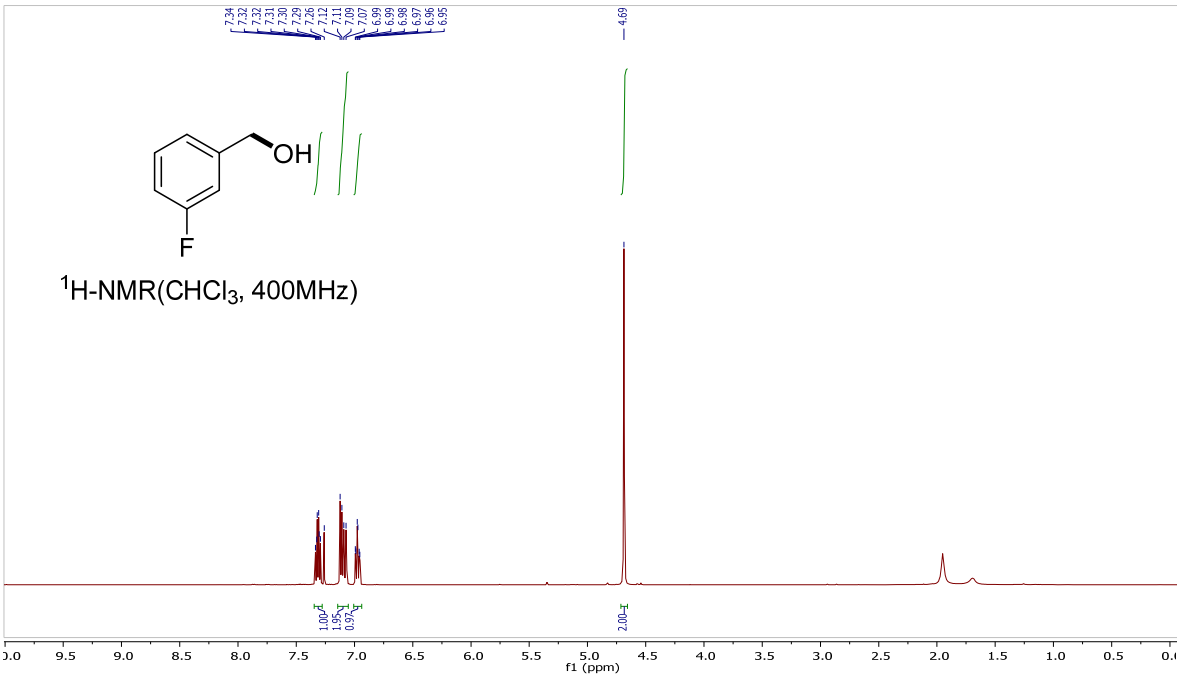
Spectral data of isolated alcohol products:

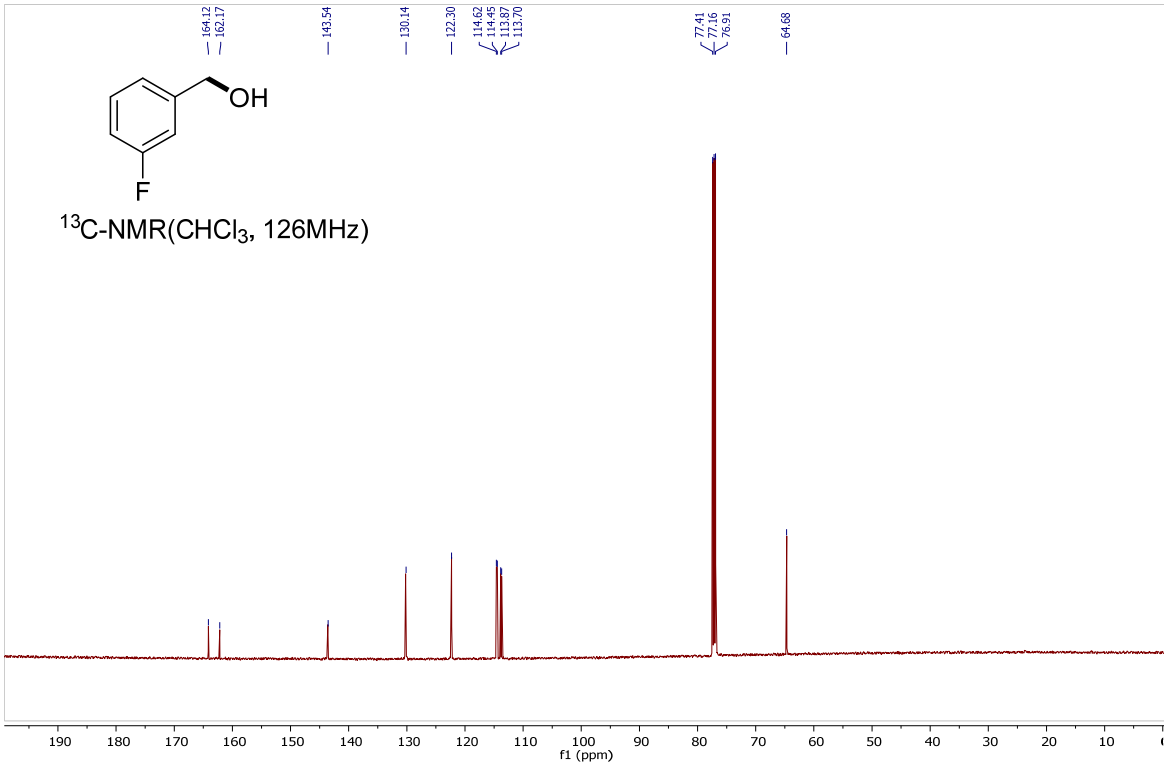


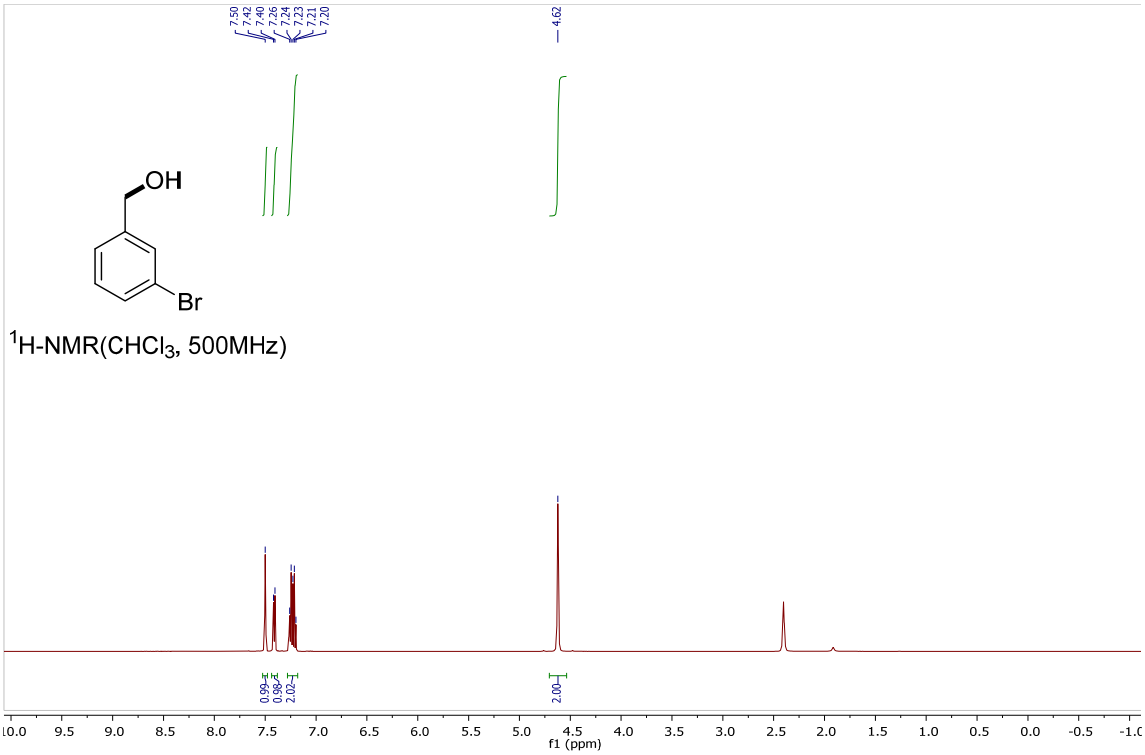
^{1}H-NMR($CHCl_3$, 500MHz)



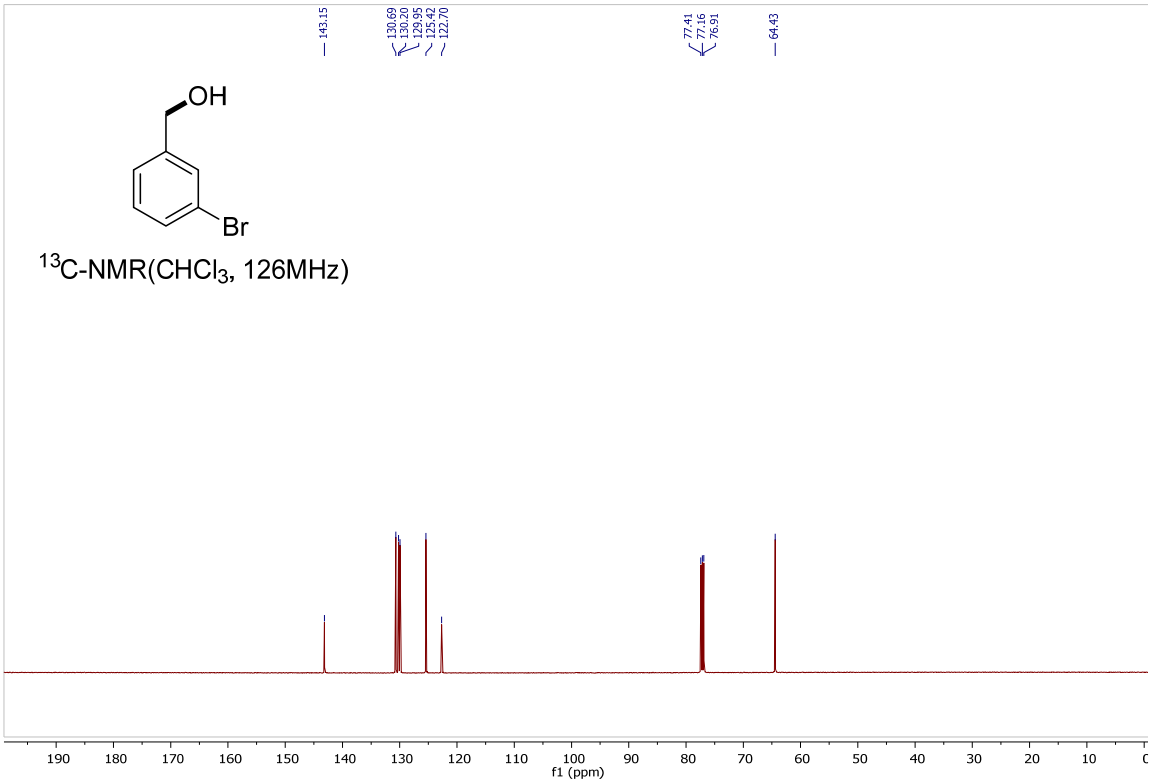
^{13}C-NMR($CHCl_3$, 126MHz)


OH
F
^{1}H-NMR($CHCl_3$, 400MHz)
f1 (ppm)

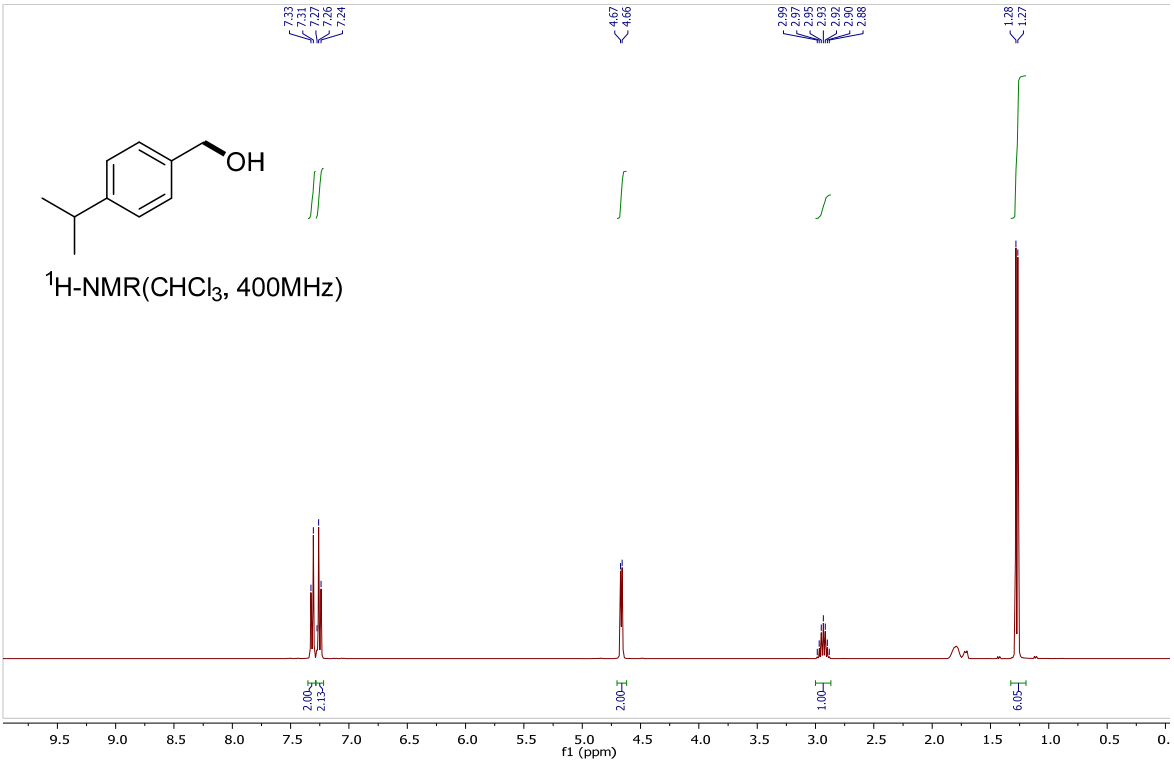

OH
F
^{13}C-NMR($CHCl_3$, 126MHz)
f1 (ppm)

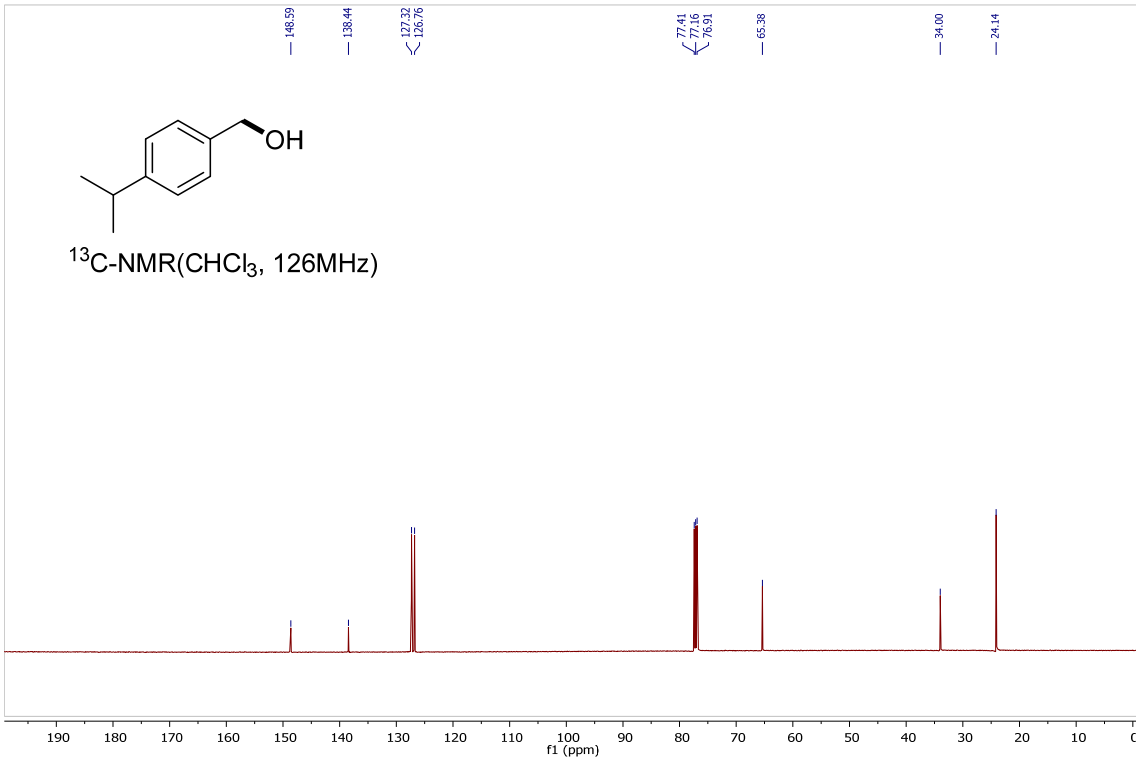


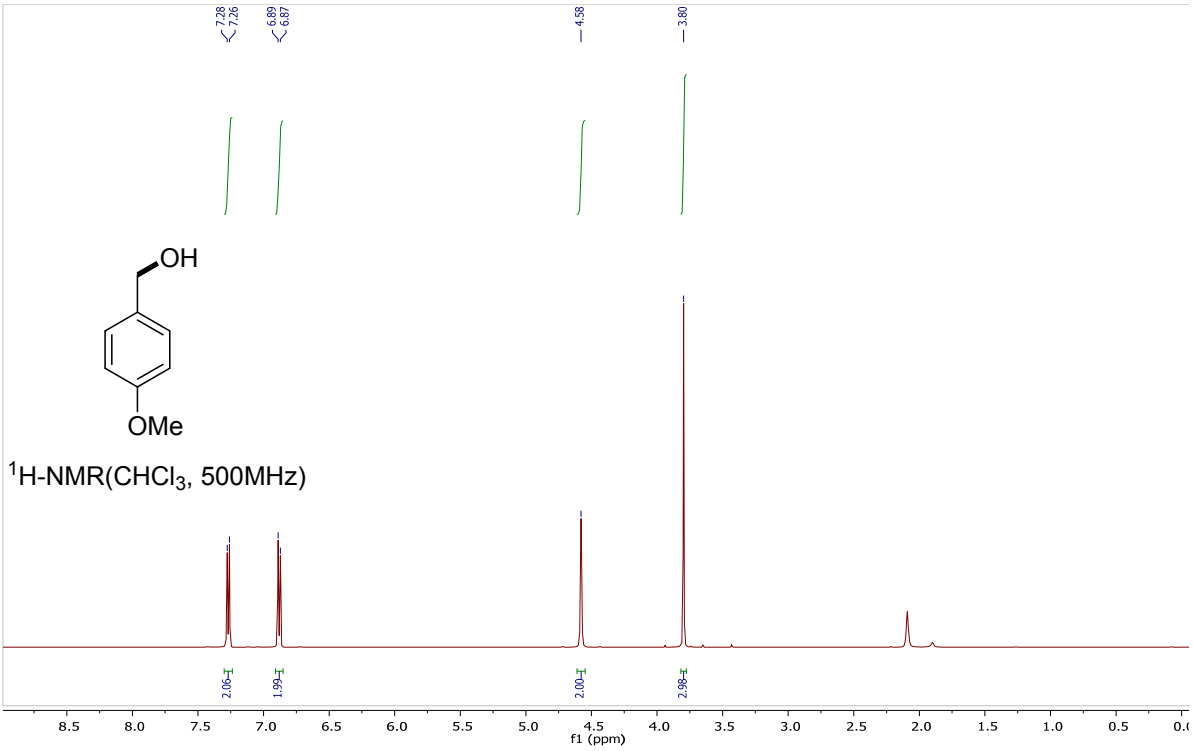
^{1}H-NMR($CHCl_3$, 500MHz)



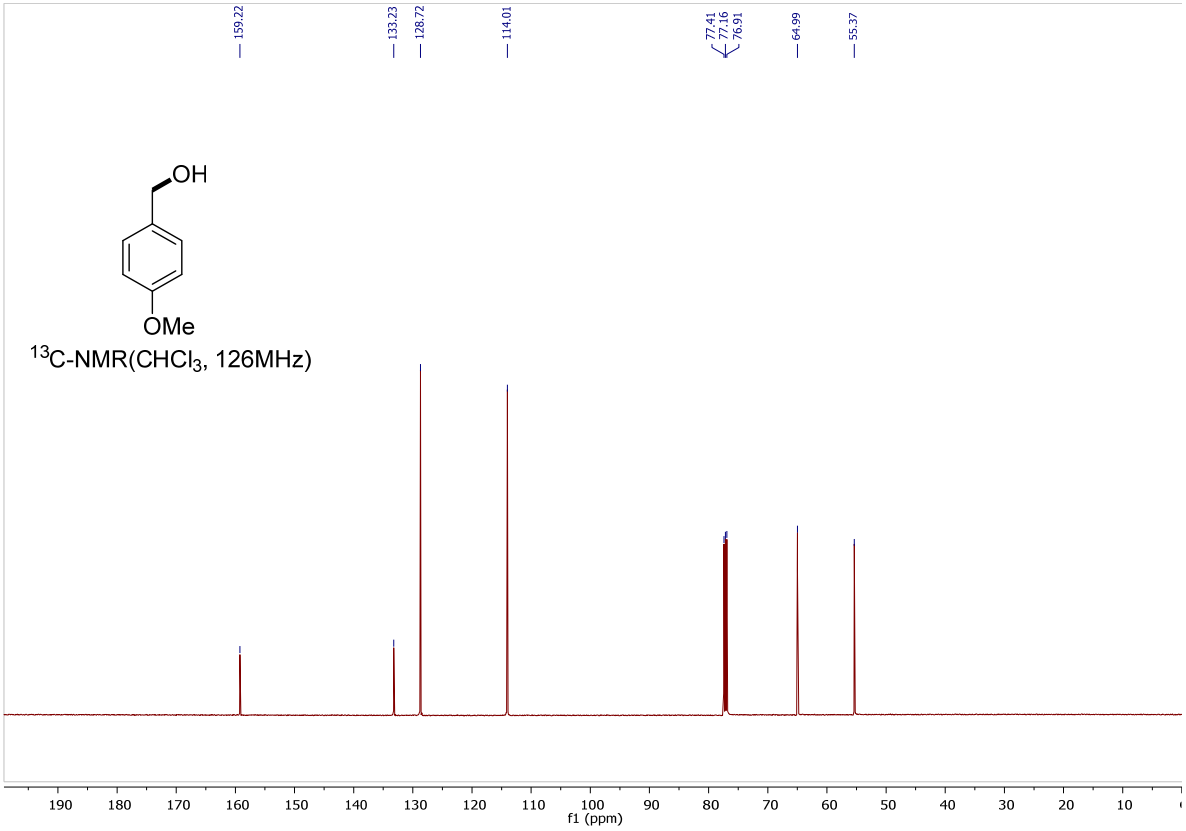
^{13}C-NMR($CHCl_3$, 126MHz)


OH
1H-NMR(CHCl3, 400MHz)
f1 (ppm)

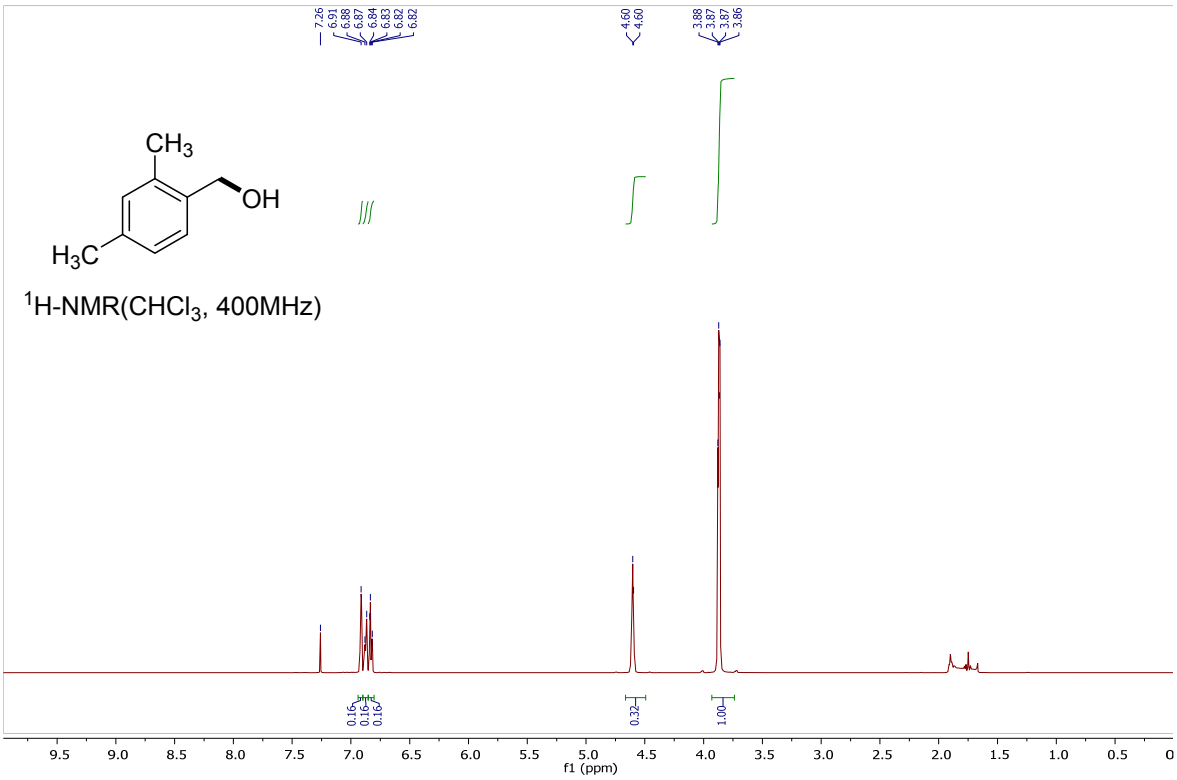

OH
13C-NMR(CHCl3, 126MHz)
f1 (ppm)



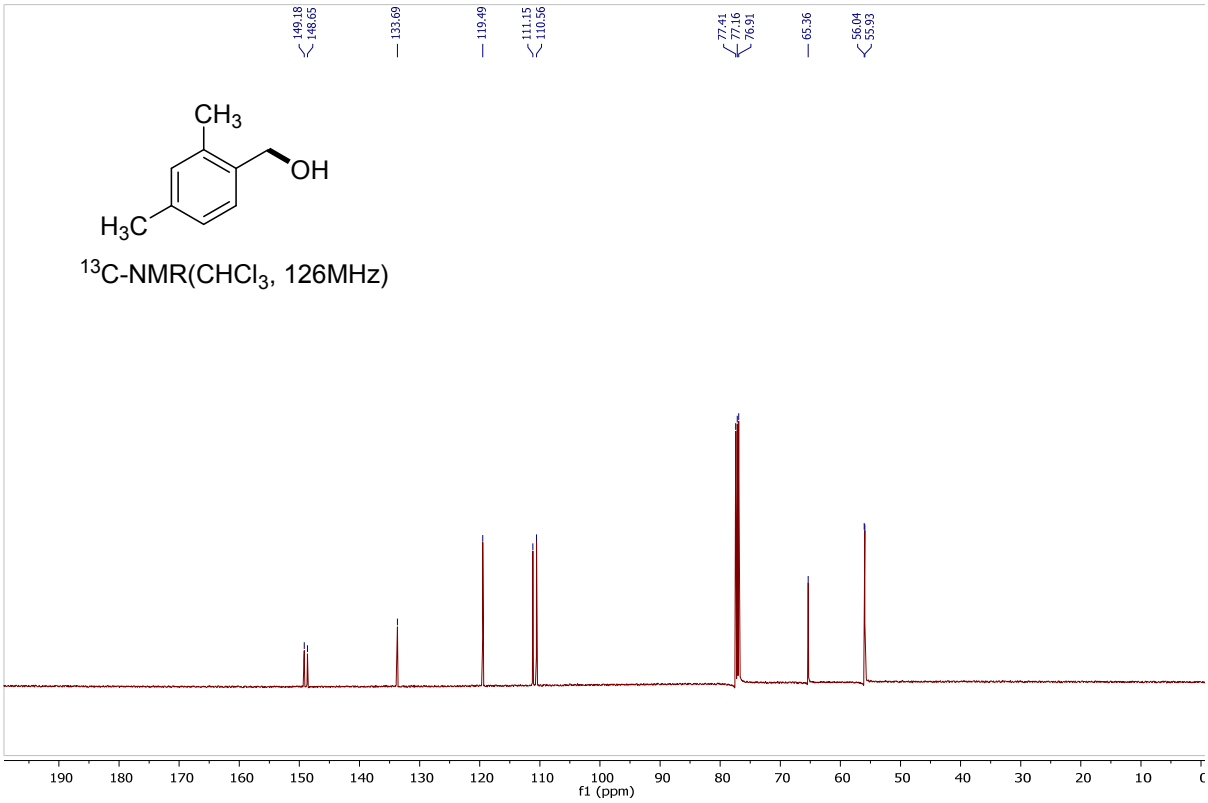
^{1}H-NMR($CHCl_3$, 500MHz)



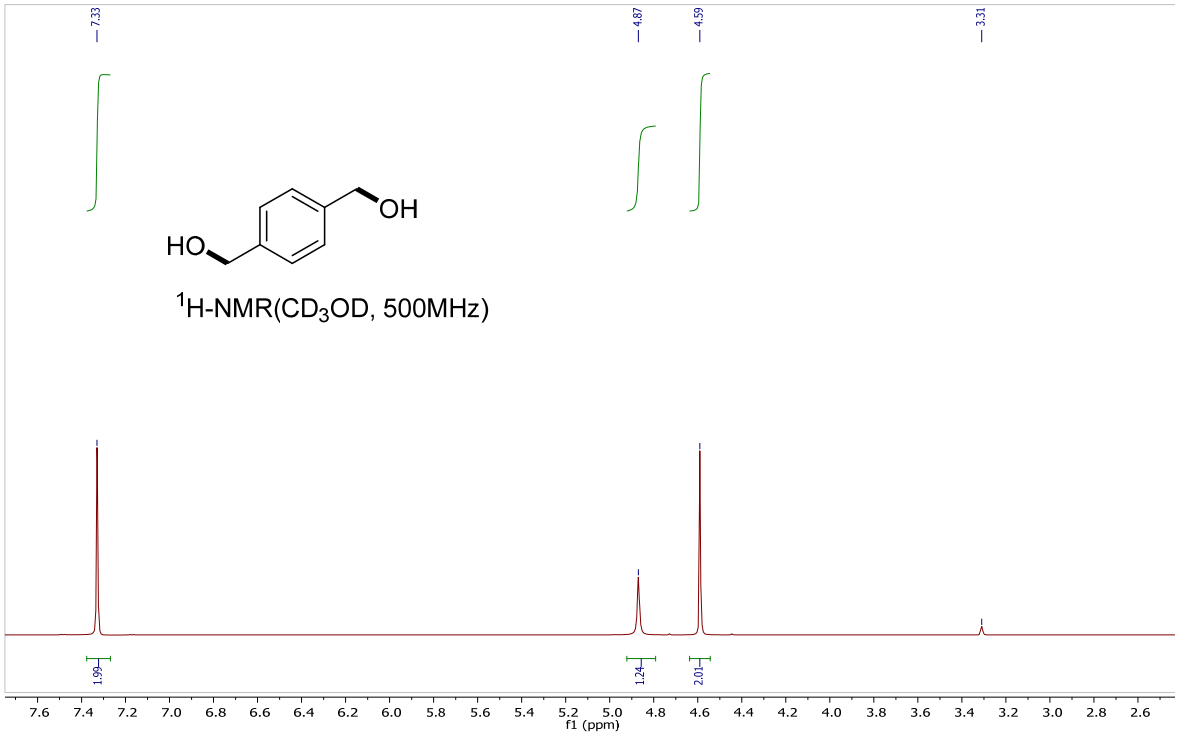
^{13}C-NMR($CHCl_3$, 126MHz)

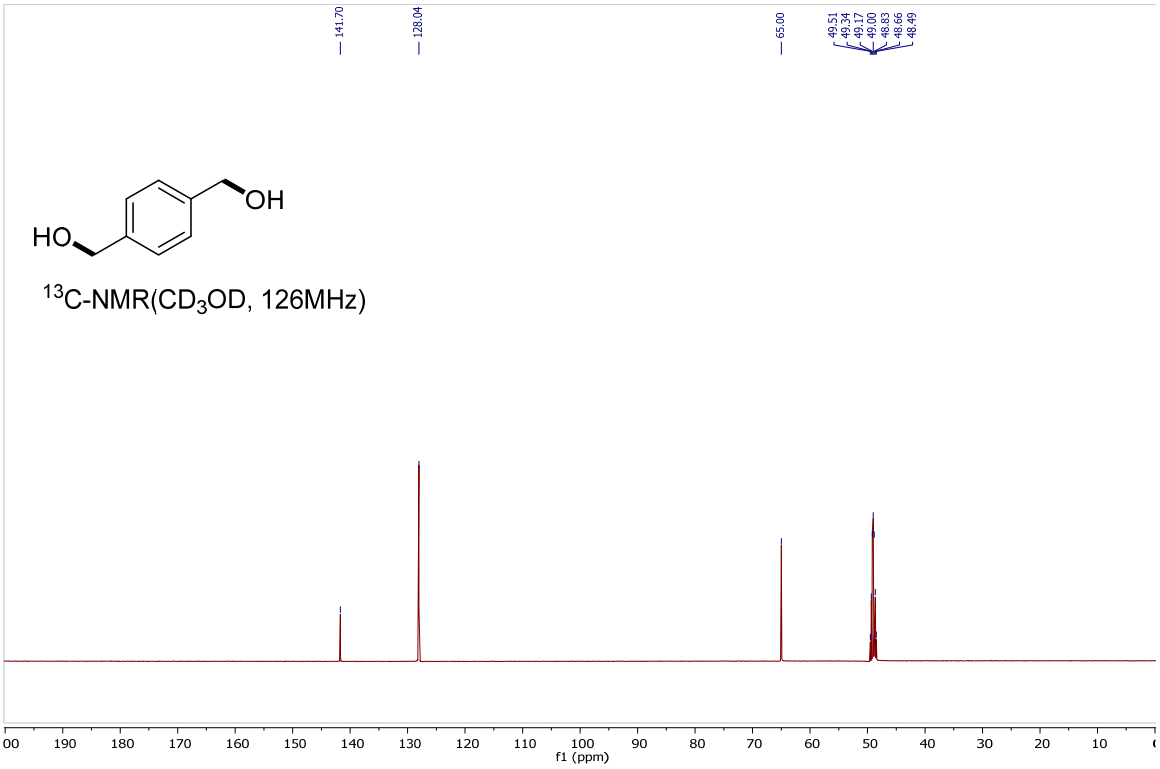


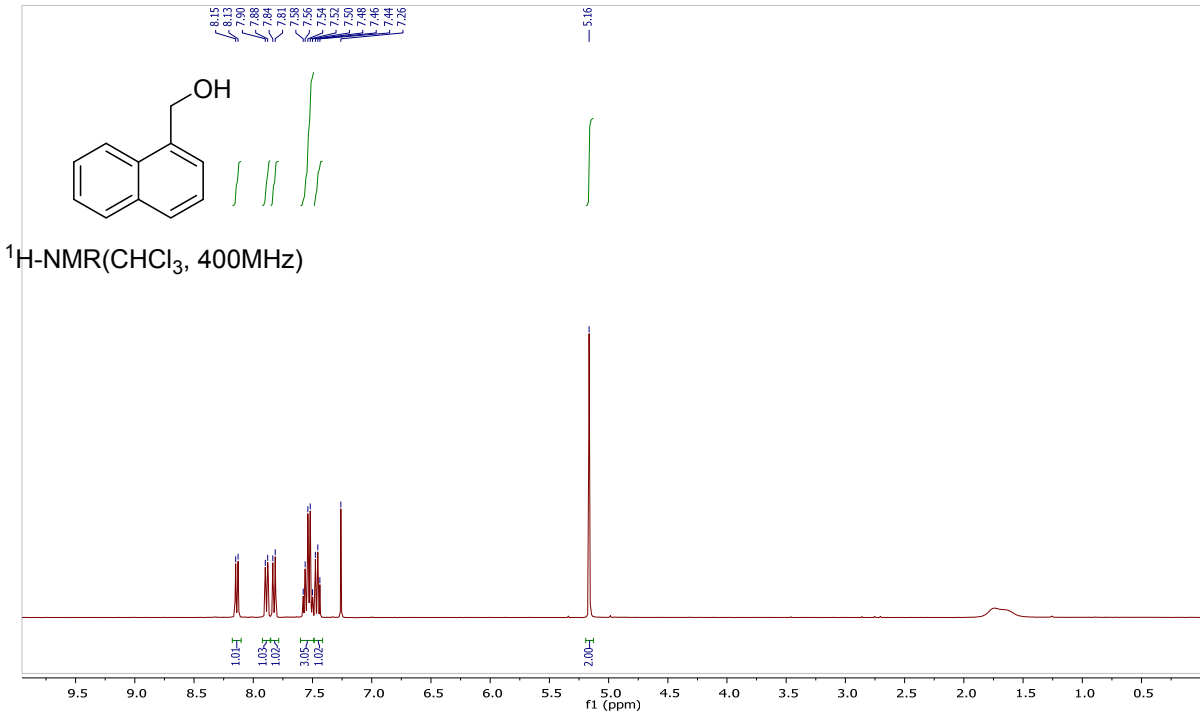
^{1}H-NMR($CHCl_3$, 400MHz)



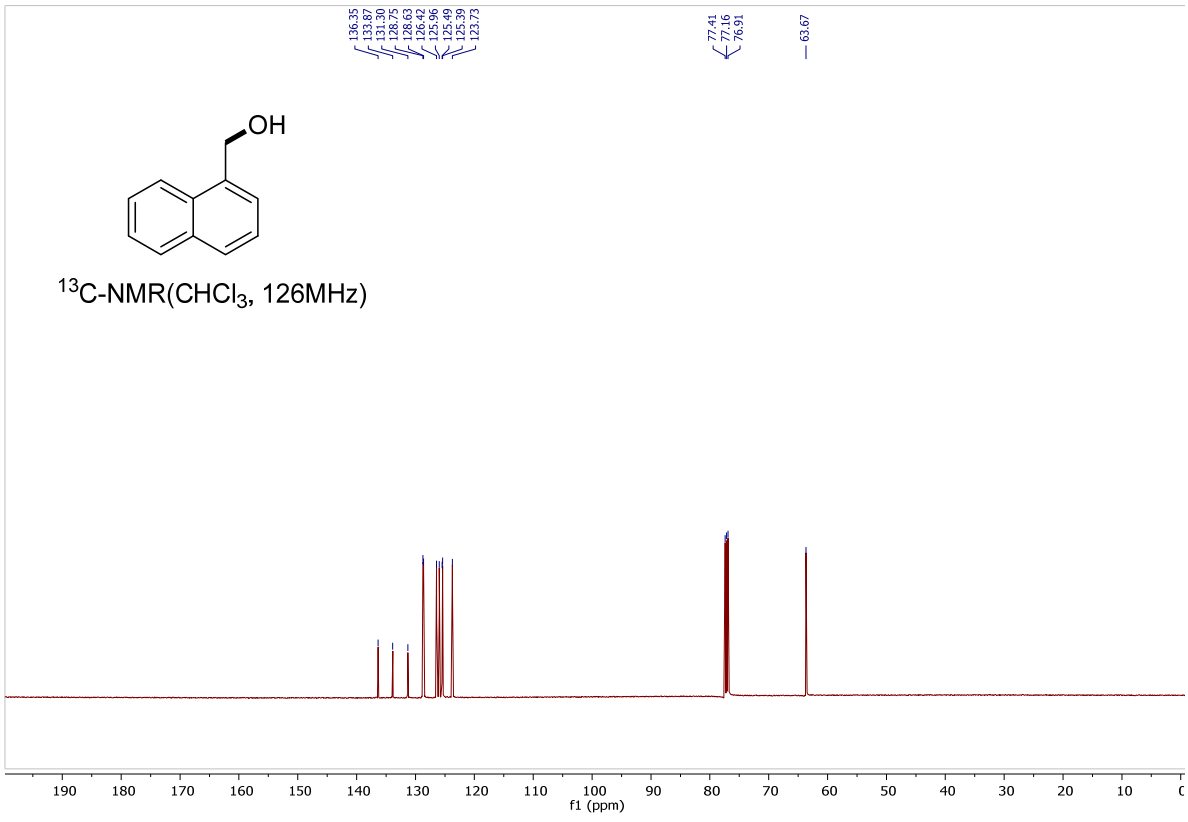
^{13}C-NMR($CHCl_3$, 126MHz)


7.33
4.87
4.59
3.31
OH
HO
1H-NMR(CD3OD, 500MHz)
1.99
1.24
2.01
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6
f1 (ppm)

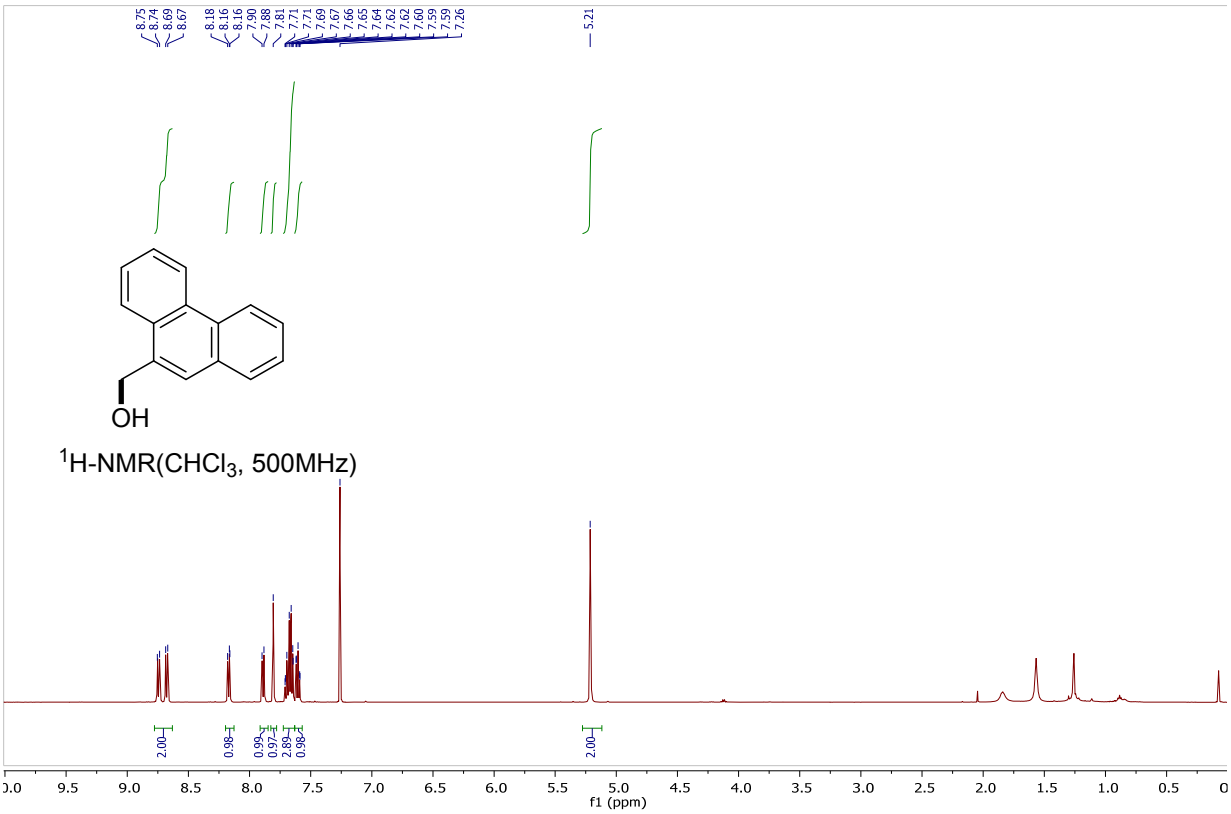

141.70
128.04
65.00
49.51
49.34
49.17
49.00
48.83
48.66
48.49
OH
HO
13C-NMR(CD3OD, 126MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

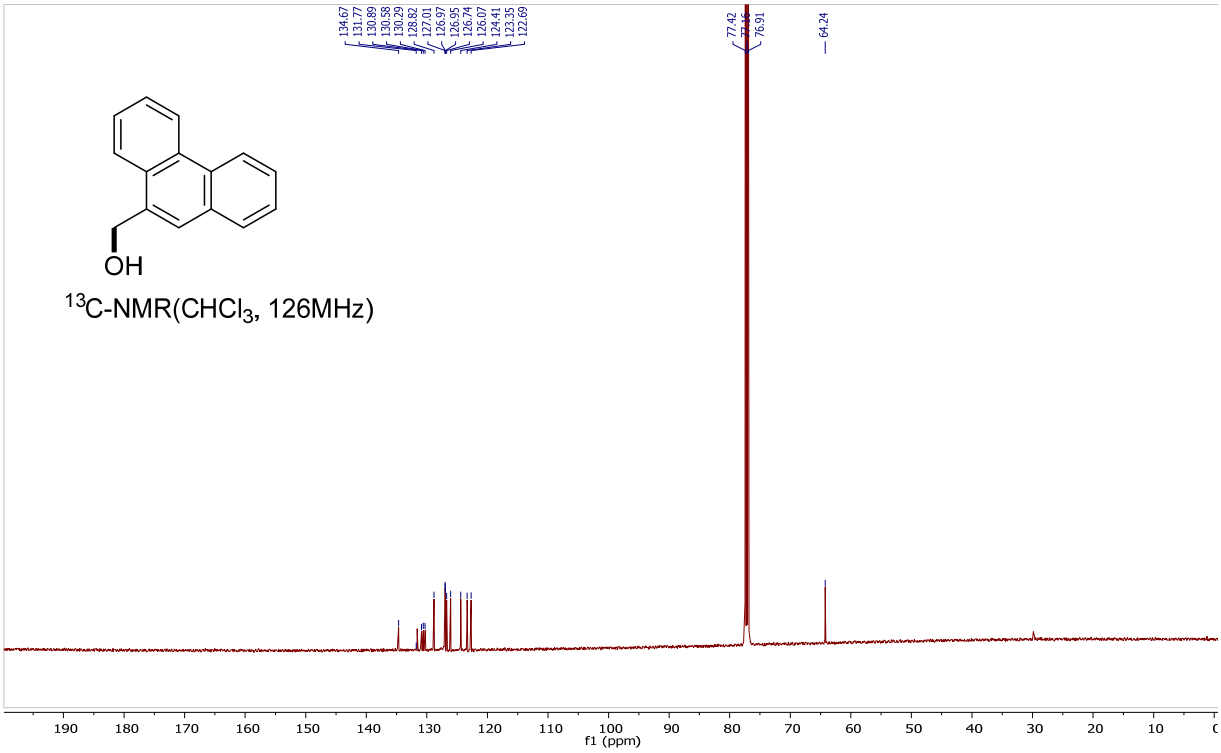


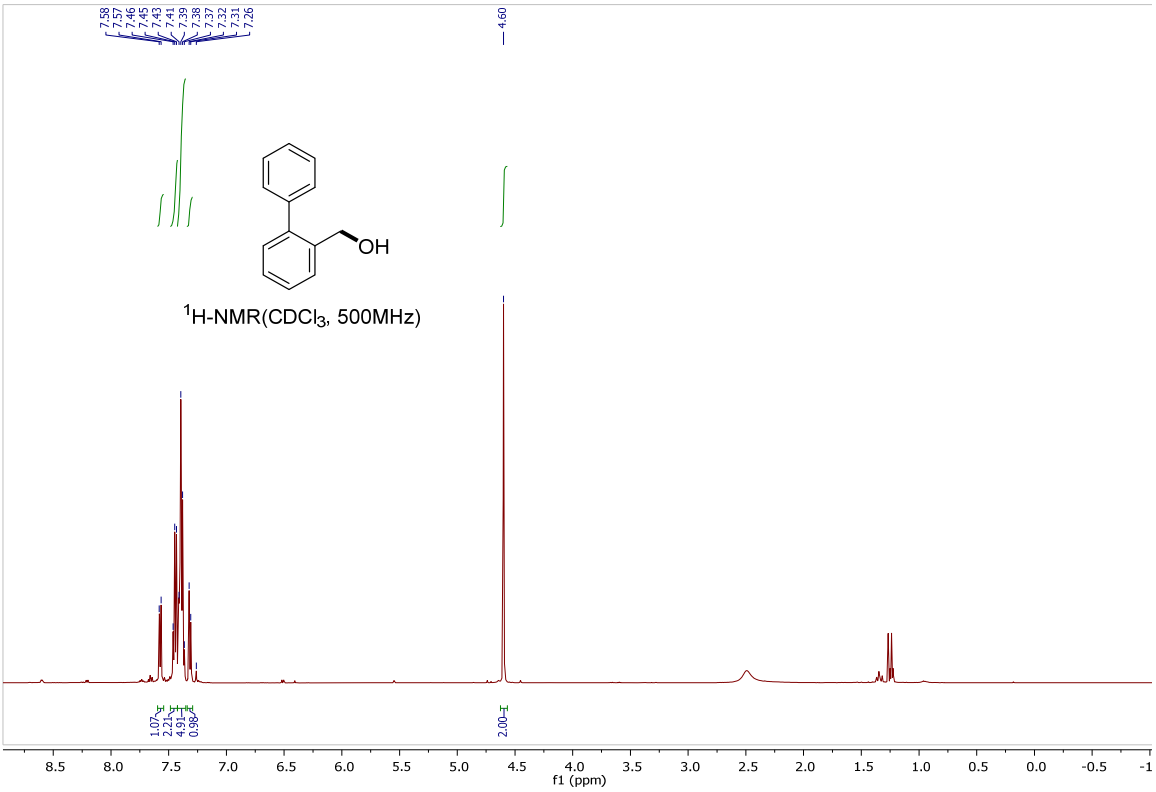
^{1}H-NMR($CHCl_3$, 400MHz)



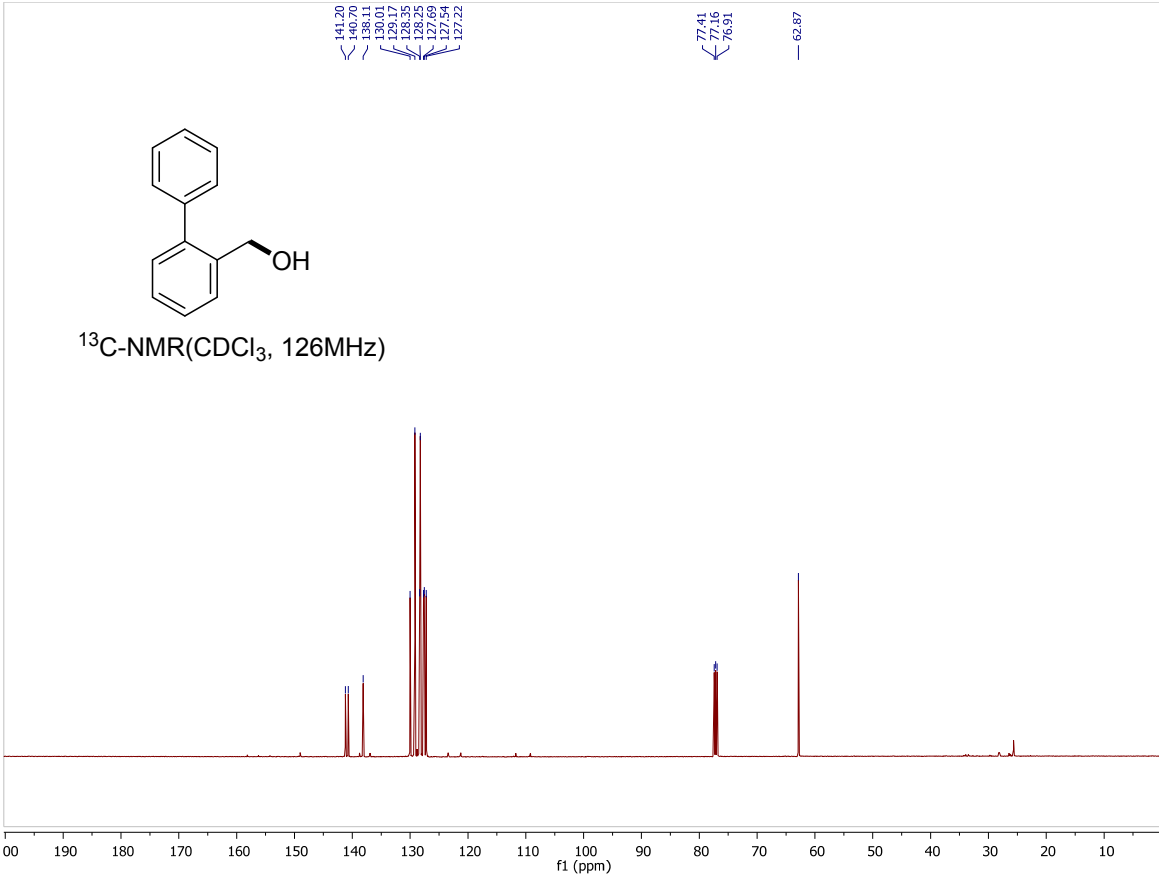
^{13}C-NMR($CHCl_3$, 126MHz)


8.75
8.74
8.69
8.67
8.18
8.16
8.16
8.00
7.88
7.81
7.71
7.71
7.69
7.67
7.66
7.65
7.64
7.62
7.62
7.60
7.59
7.59
7.26
5.21
OH
^{1}H-NMR(CHCl$_3$, 500MHz)
2.00
0.98
0.99
0.97
2.89
0.98
2.00
f1 (ppm)

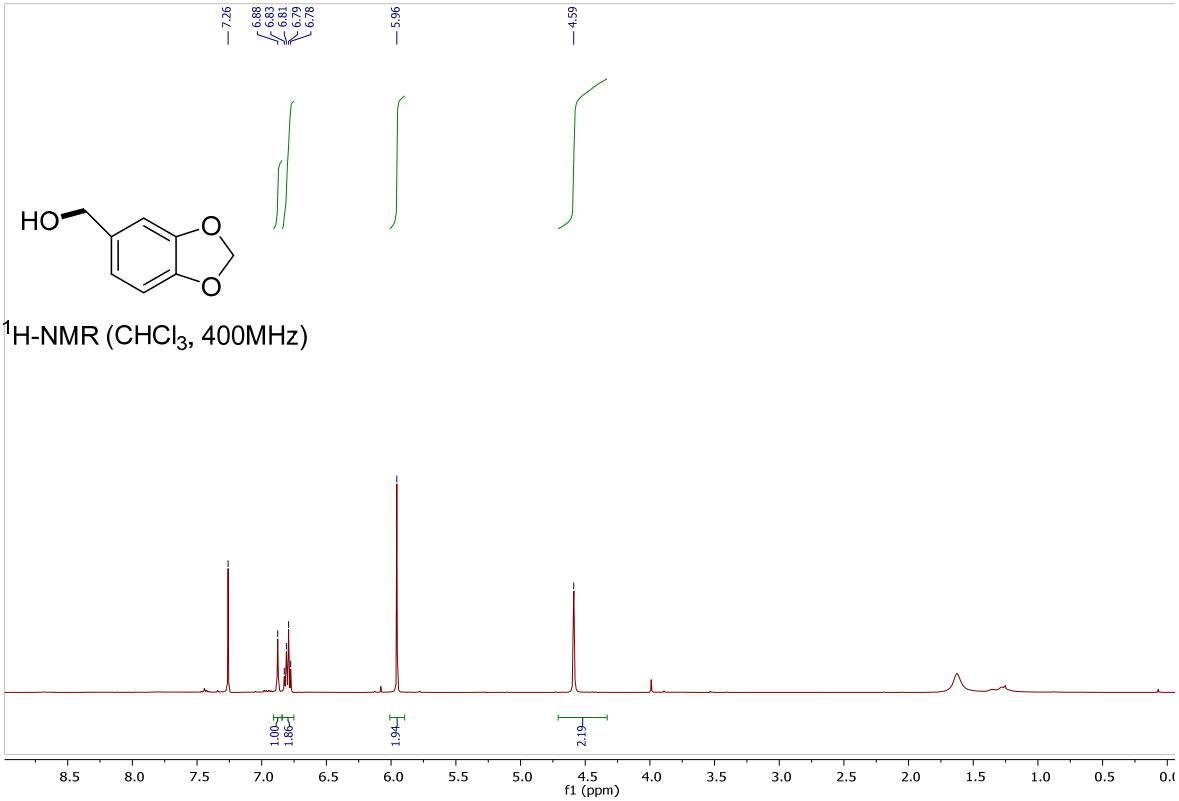

134.67
131.77
130.89
130.58
130.29
128.82
127.01
126.97
126.95
126.74
126.07
124.41
123.35
122.69
77.42
77.16
76.91
64.24
OH
^{13}C-NMR(CHCl$_3$, 126MHz)
f1 (ppm)



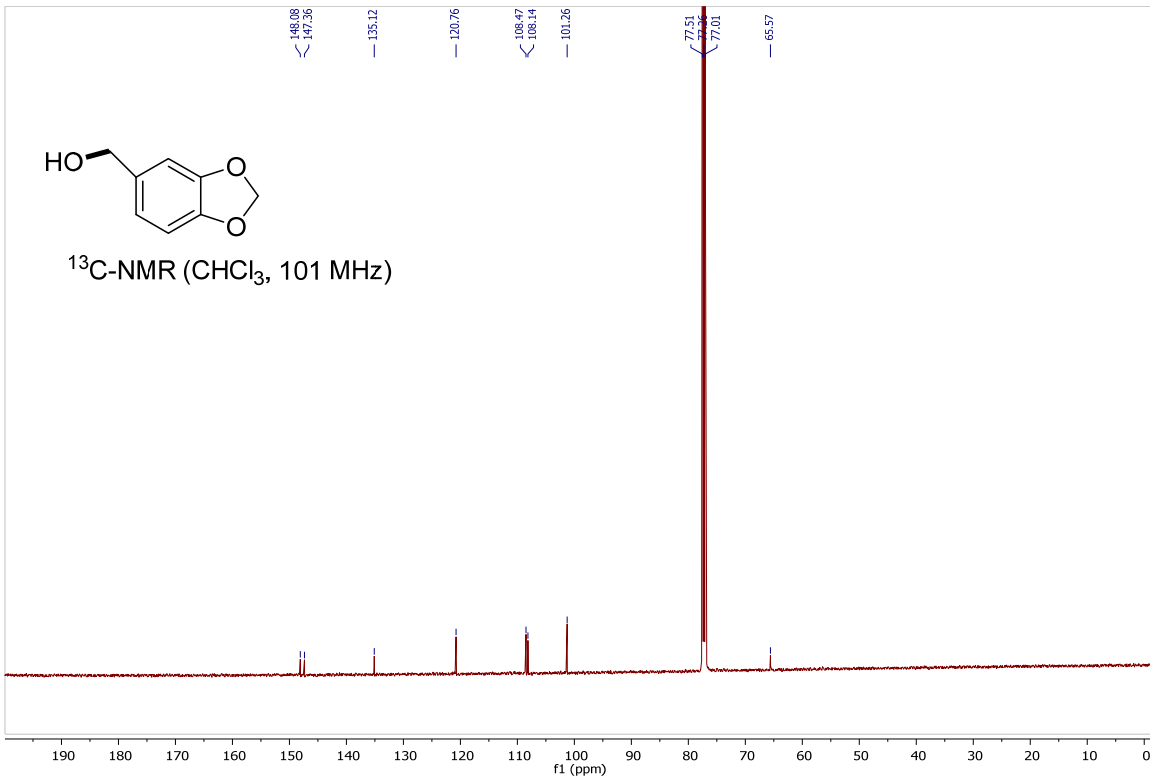
^{1}H-NMR($CDCl_3$, 500MHz)



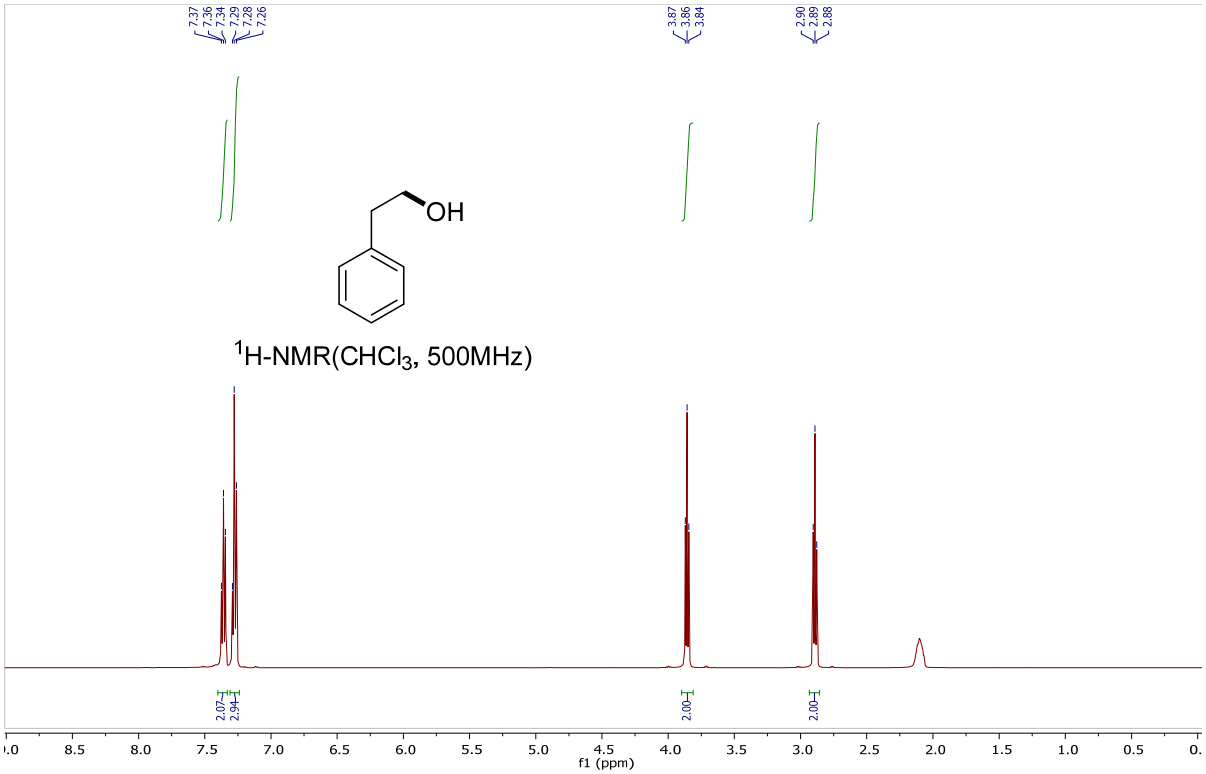
^{13}C-NMR($CDCl_3$, 126MHz)



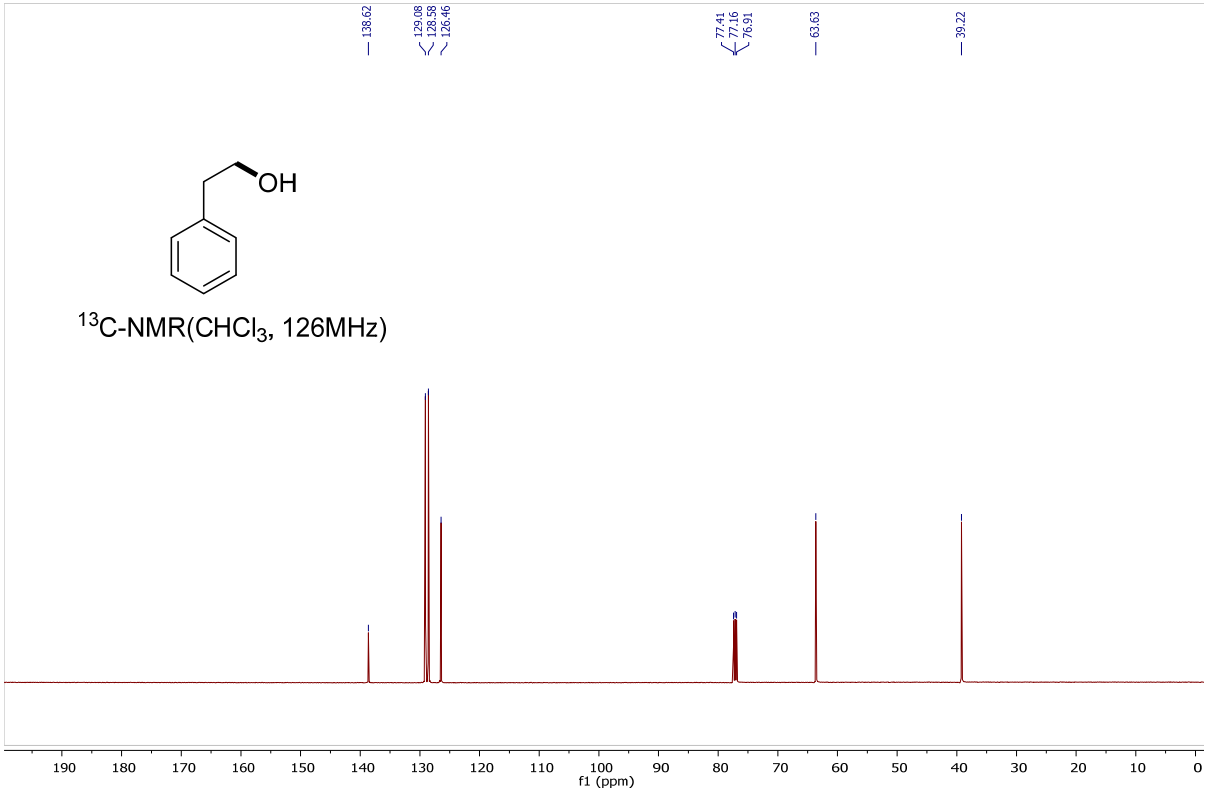
^{1}H-NMR ($CHCl_3$, 400MHz)



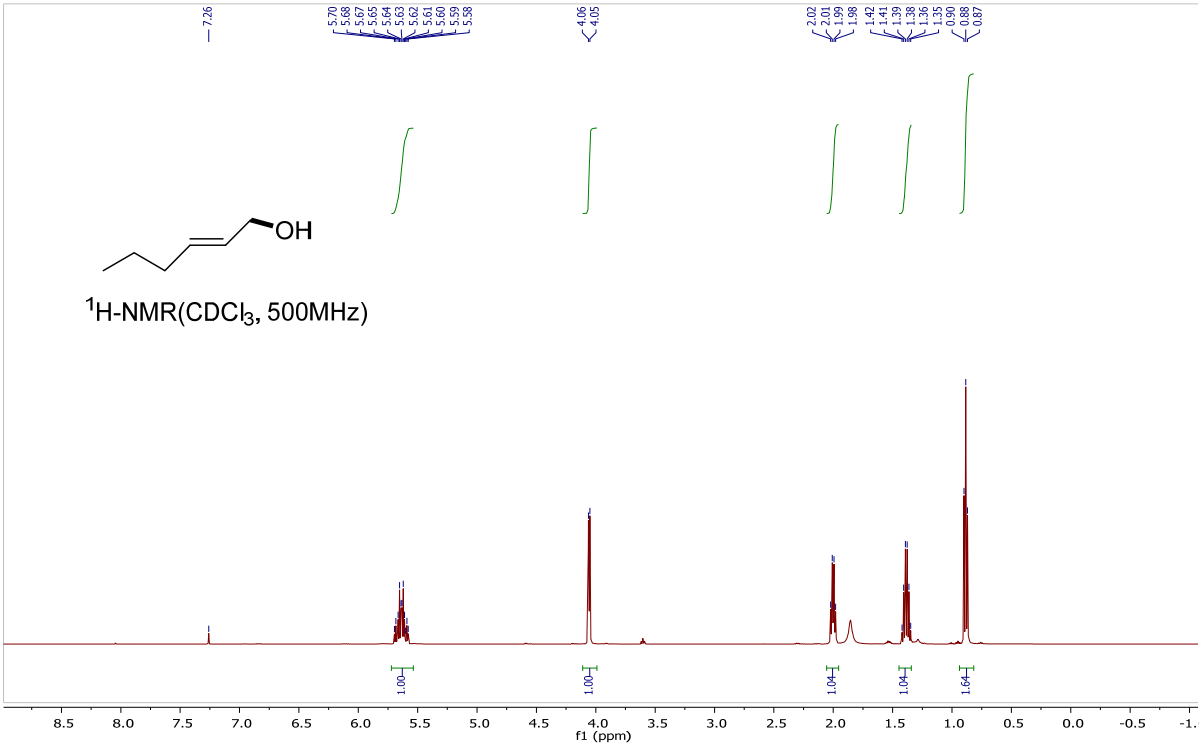
^{13}C-NMR ($CHCl_3$, 101 MHz)



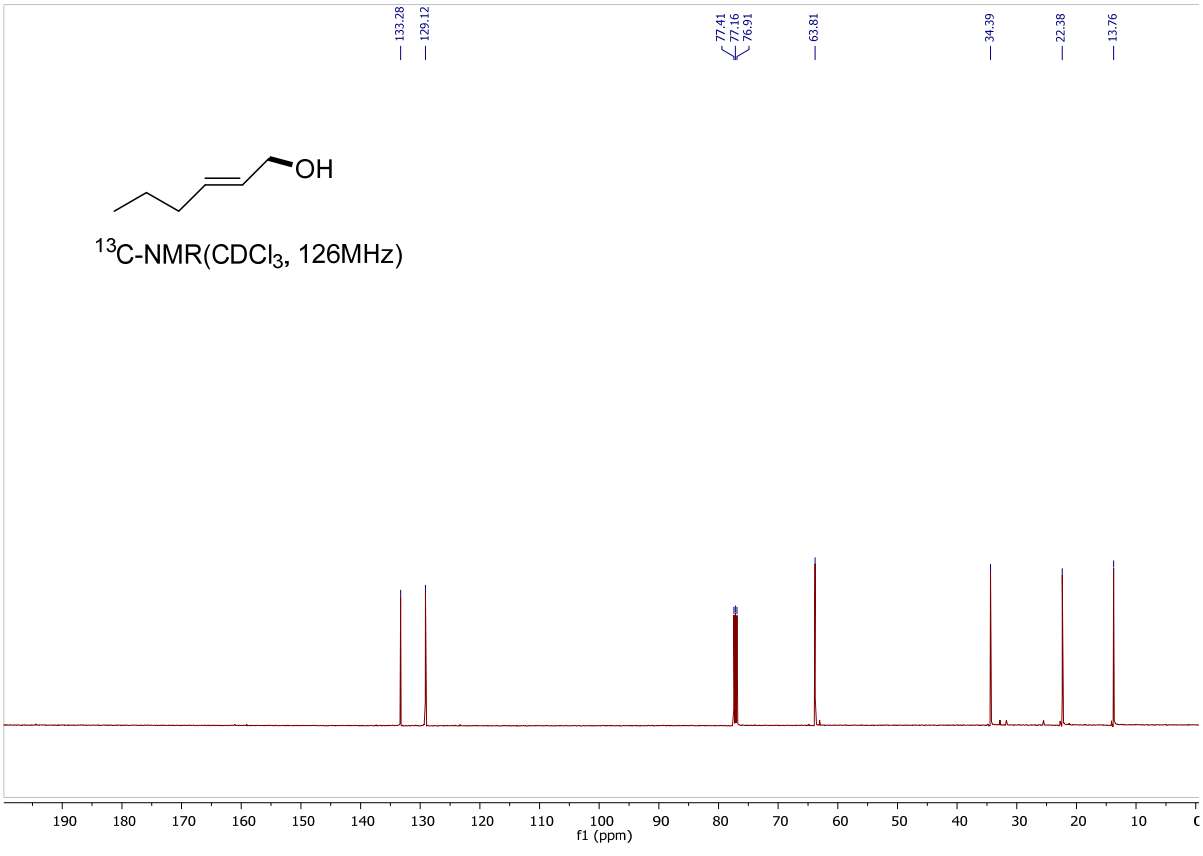
^{1}H-NMR($CHCl_3$, 500MHz)



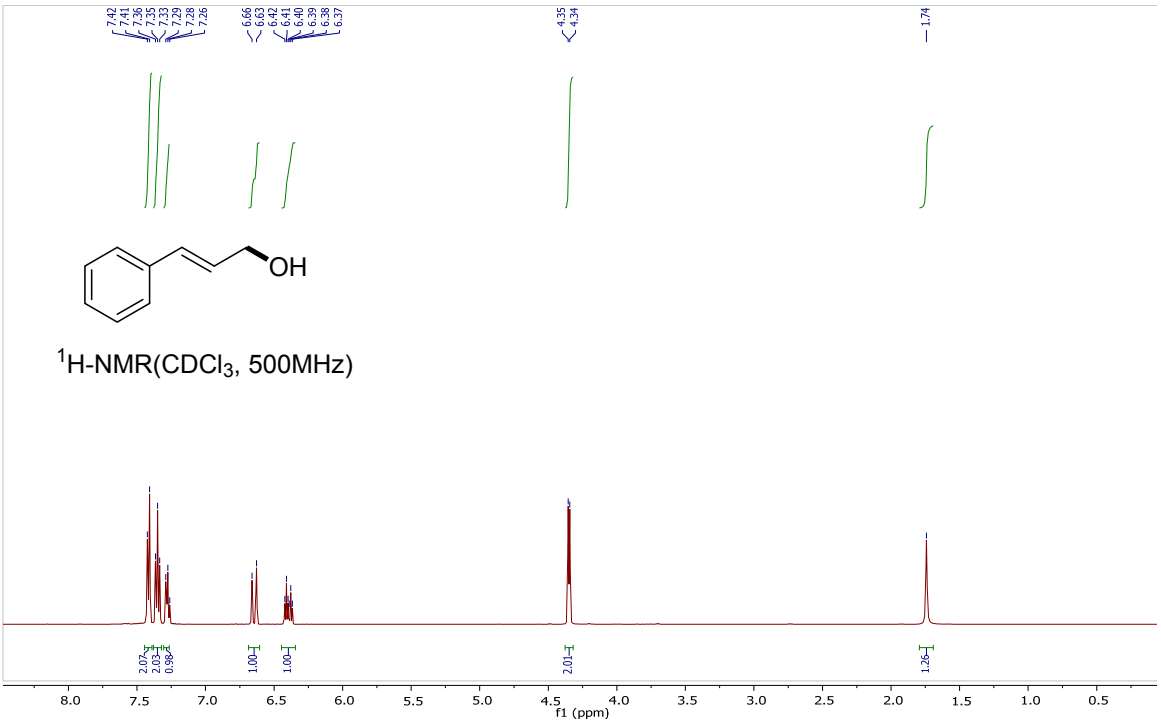
^{13}C-NMR($CHCl_3$, 126MHz)



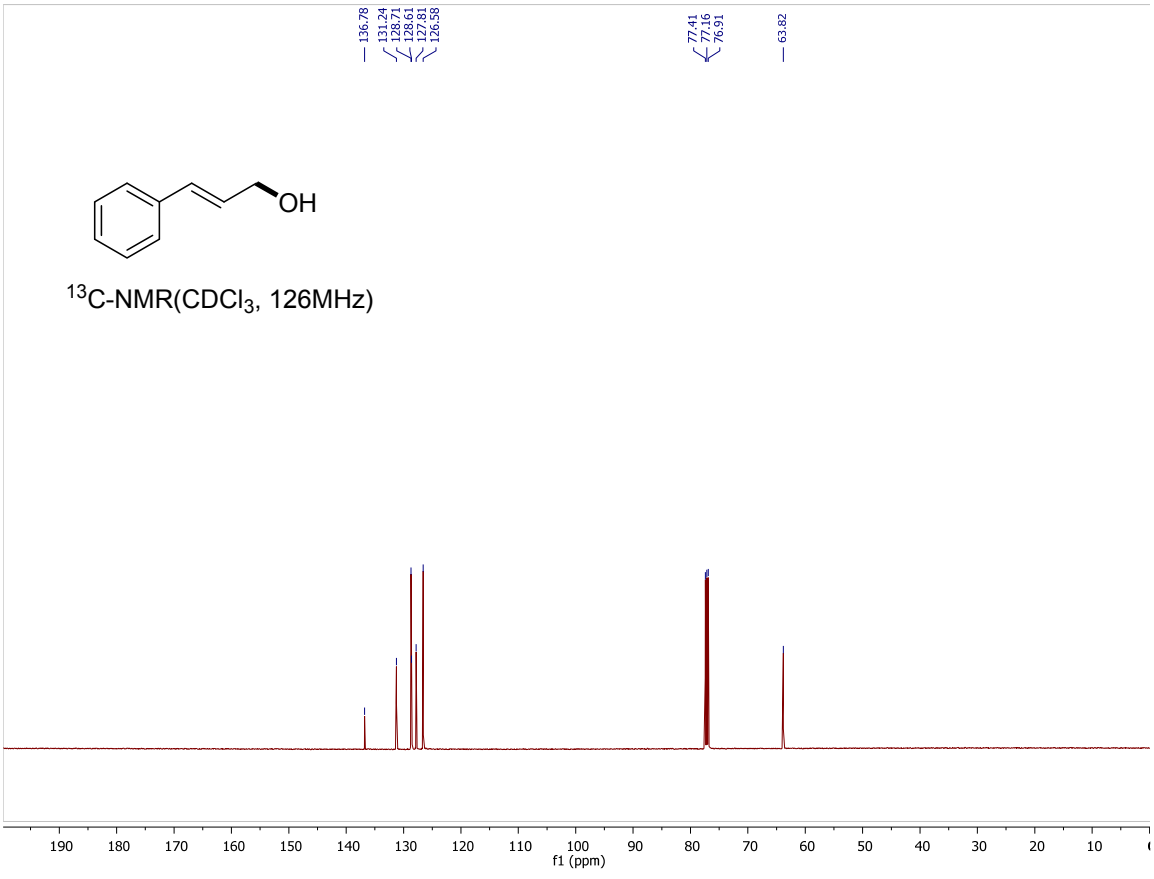
^{1}H-NMR($CDCl_3$, 500MHz)



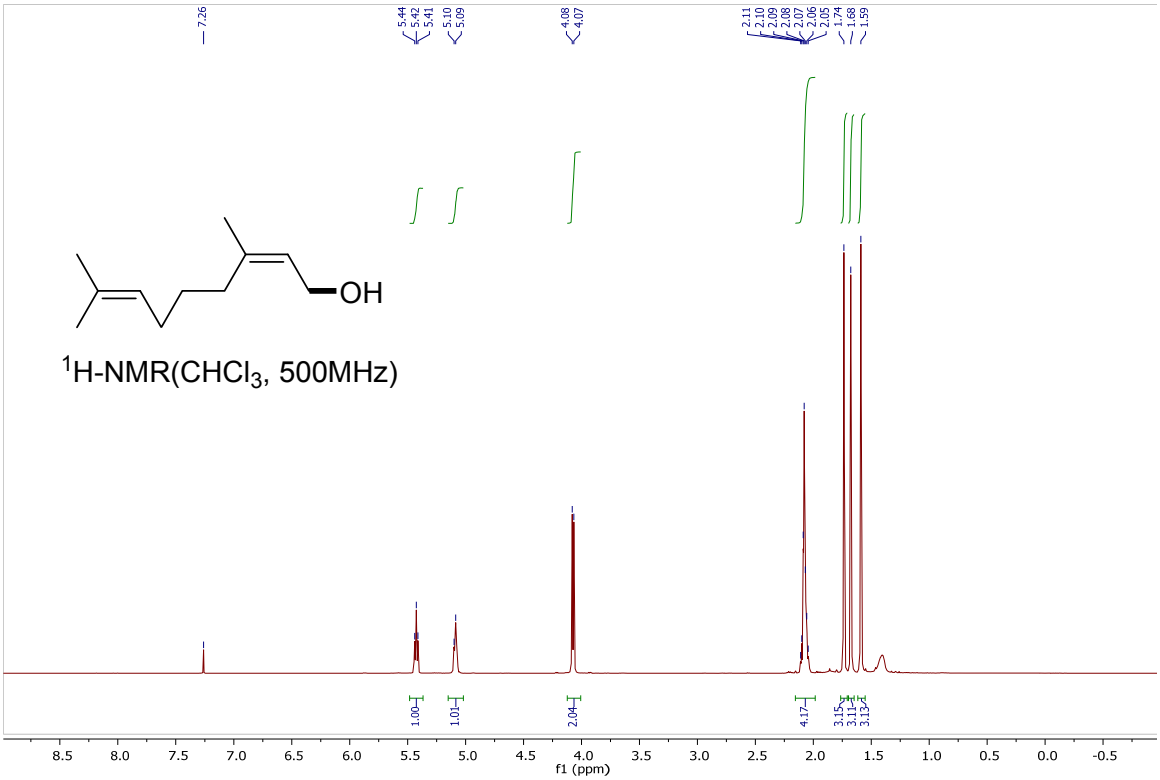
^{13}C-NMR($CDCl_3$, 126MHz)

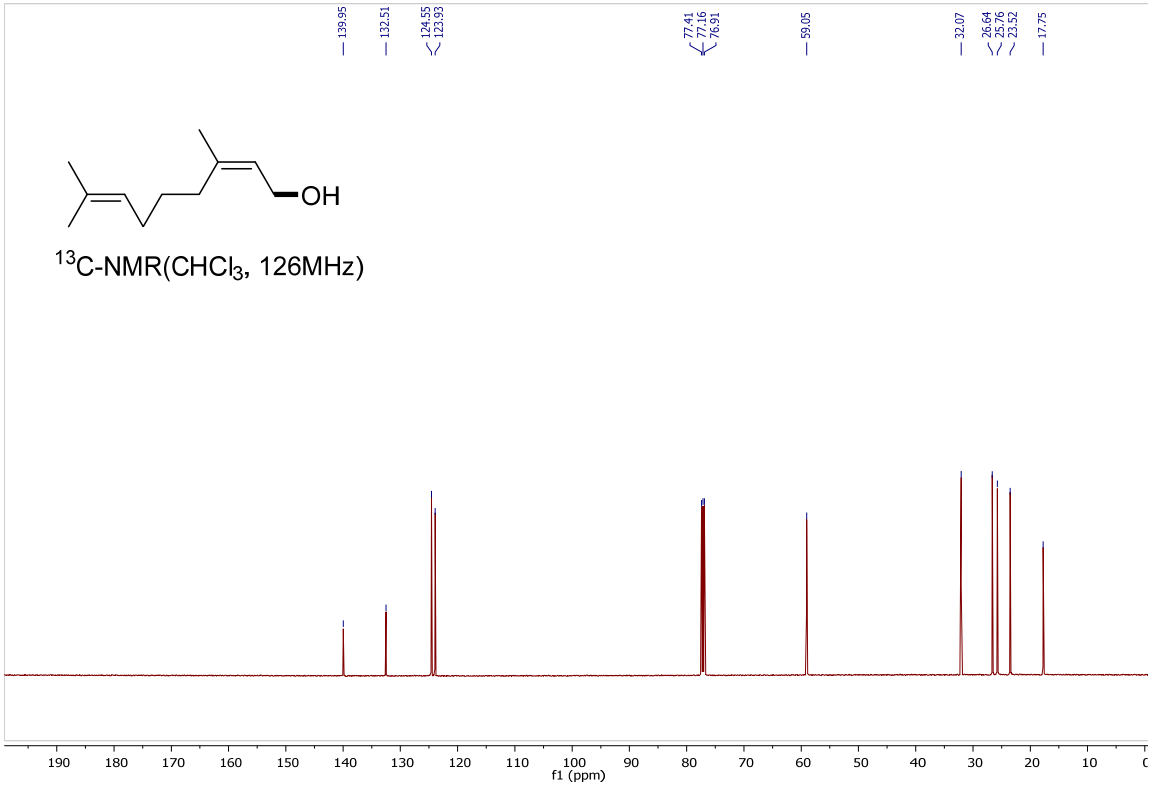


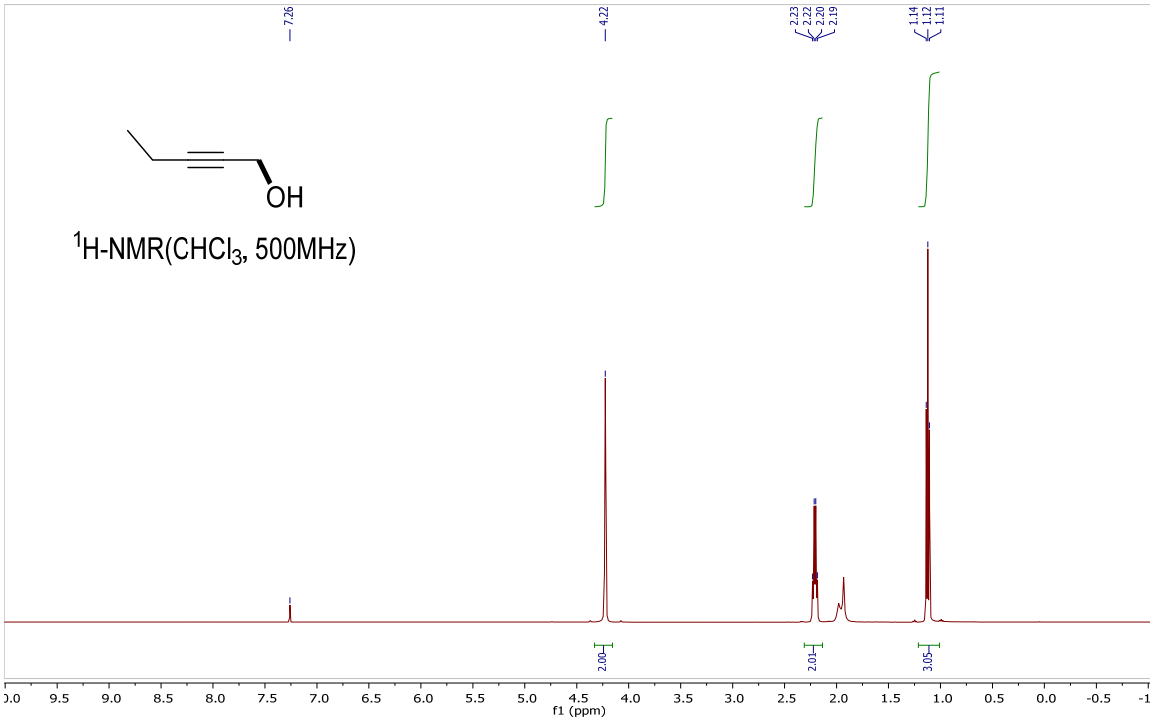
^{1}H-NMR($CDCl_3$, 500MHz)



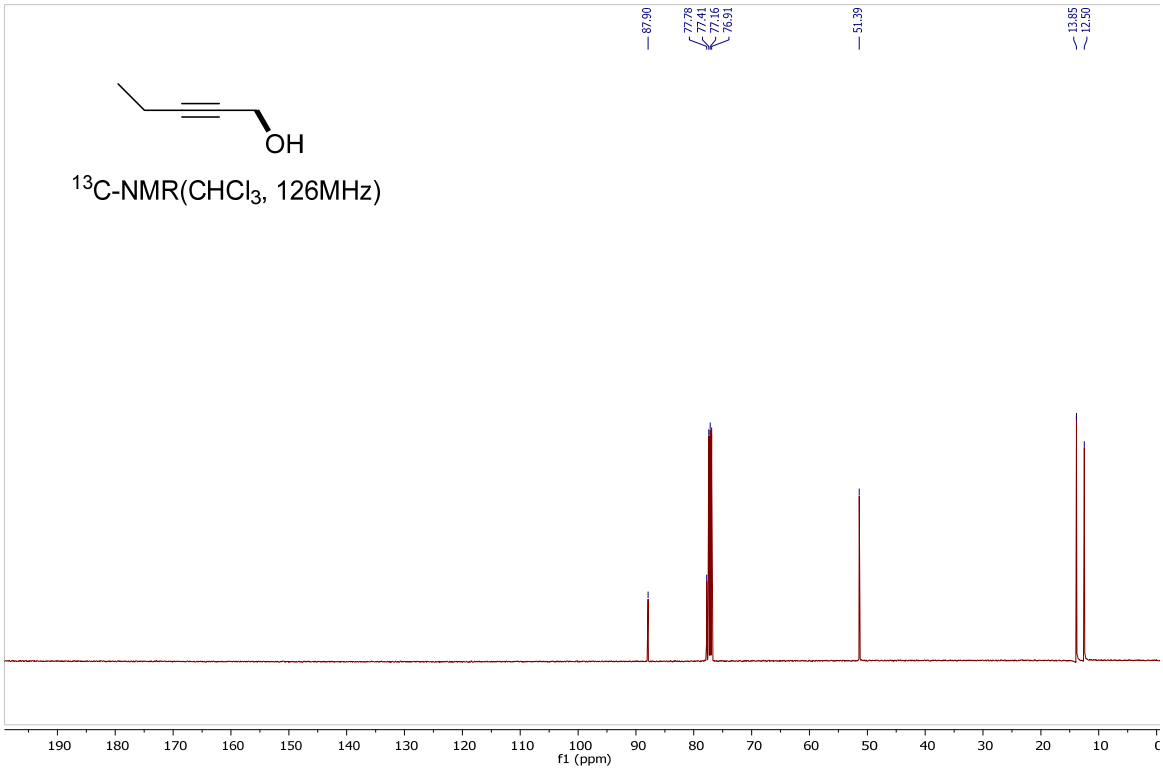
^{13}C-NMR($CDCl_3$, 126MHz)


7.26
5.44
5.42
5.41
5.10
5.09
4.08
4.07
2.11
2.10
2.09
2.08
2.07
2.06
2.05
1.74
1.68
1.59
OH
1H-NMR(CHCl3, 500MHz)
1.00
1.01
2.04
4.17
3.15
3.11
3.13
f1 (ppm)

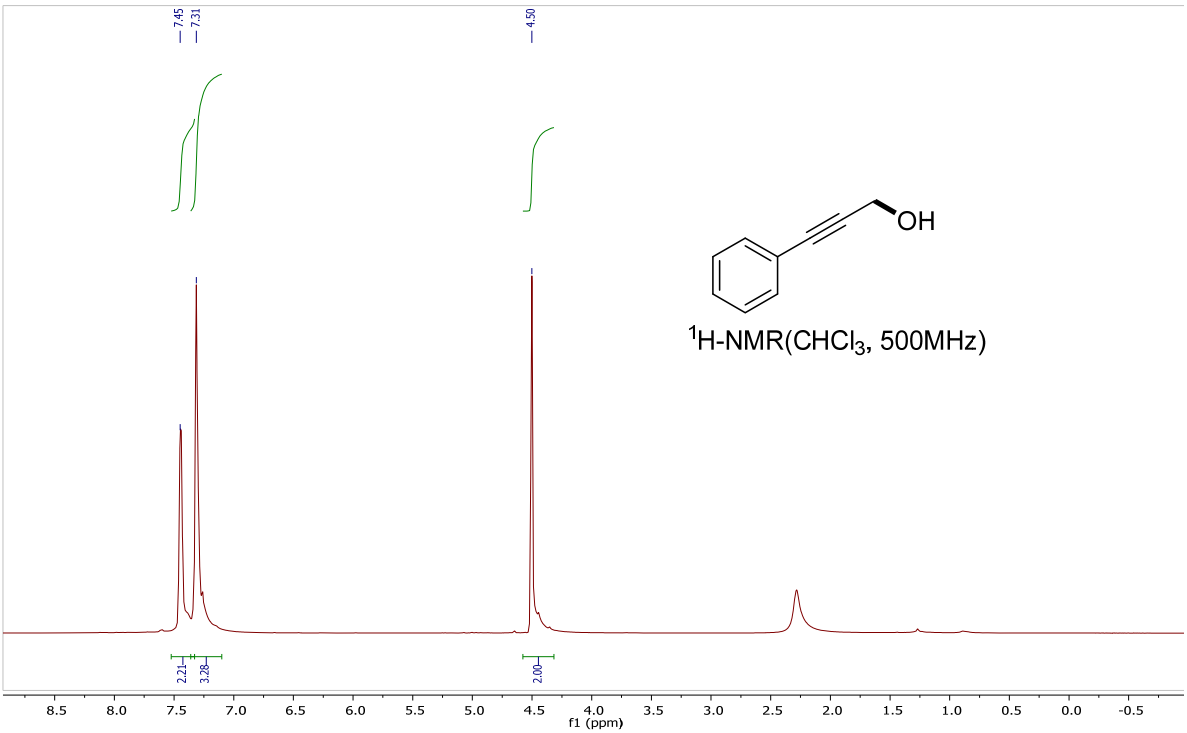

139.95
132.51
124.55
123.93
77.41
77.16
76.91
59.05
32.07
26.64
25.76
23.52
17.75
OH
13C-NMR(CHCl3, 126MHz)
f1 (ppm)



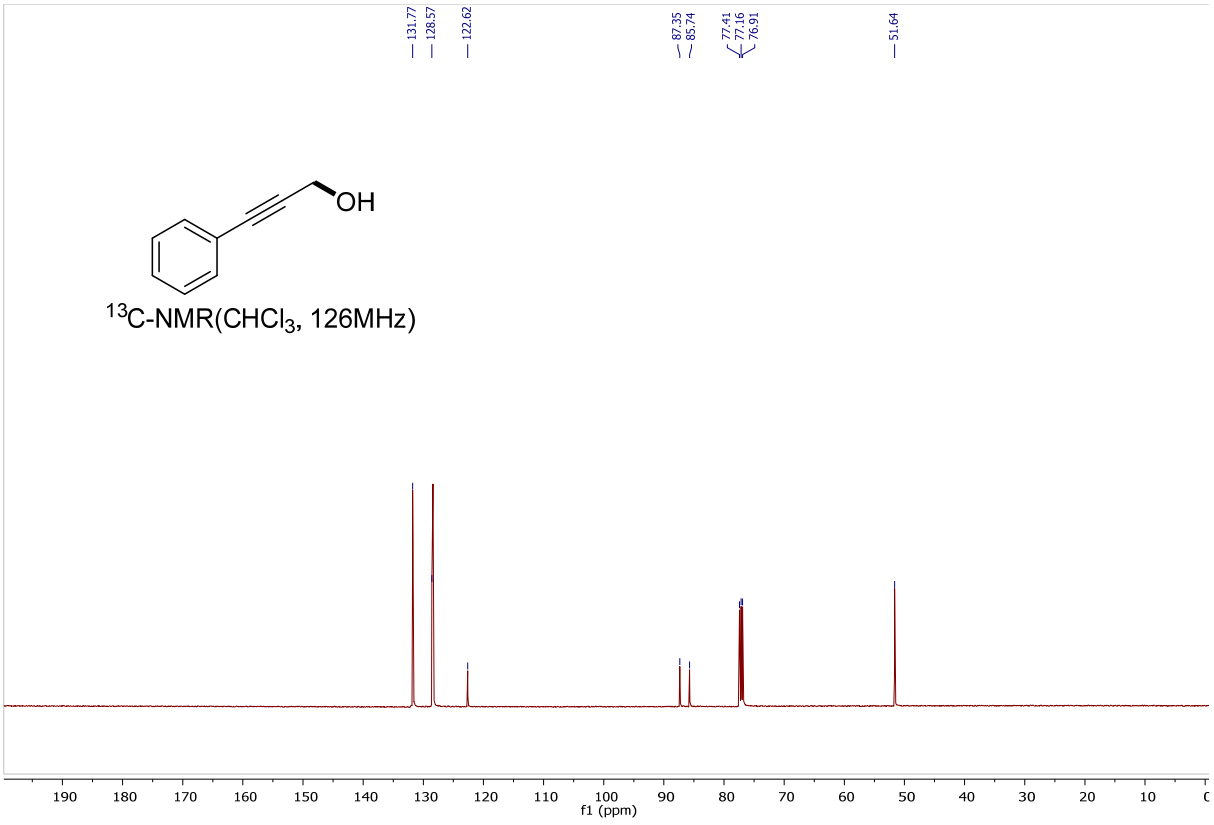
^{1}H-NMR($CHCl_3$, 500MHz)



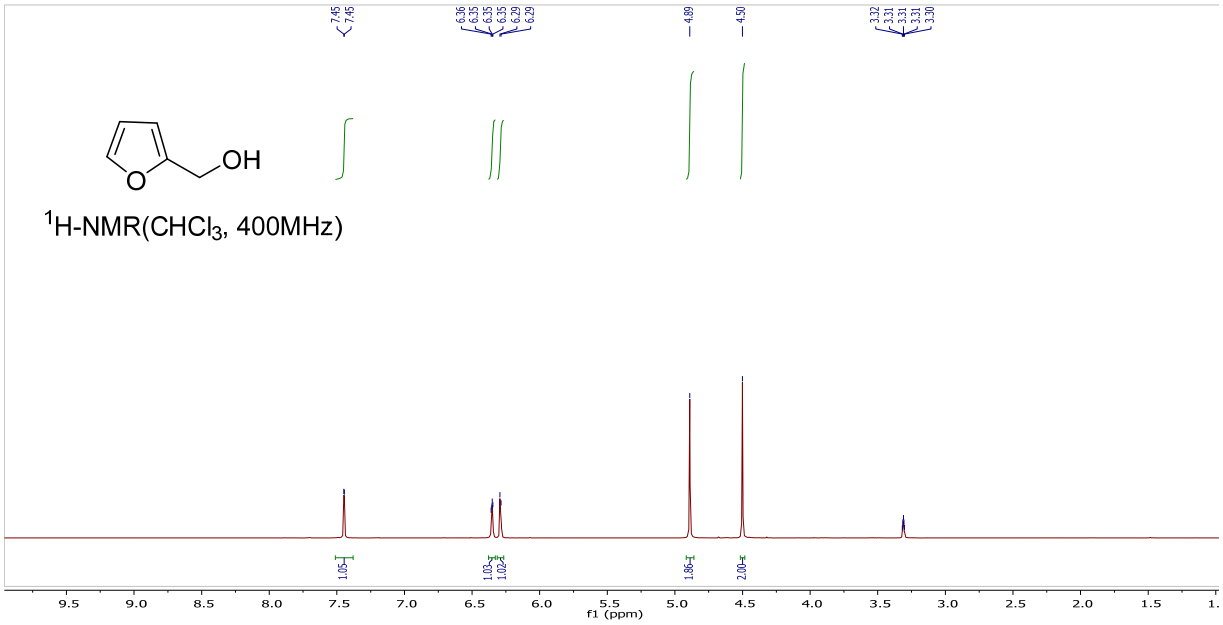
^{13}C-NMR($CHCl_3$, 126MHz)



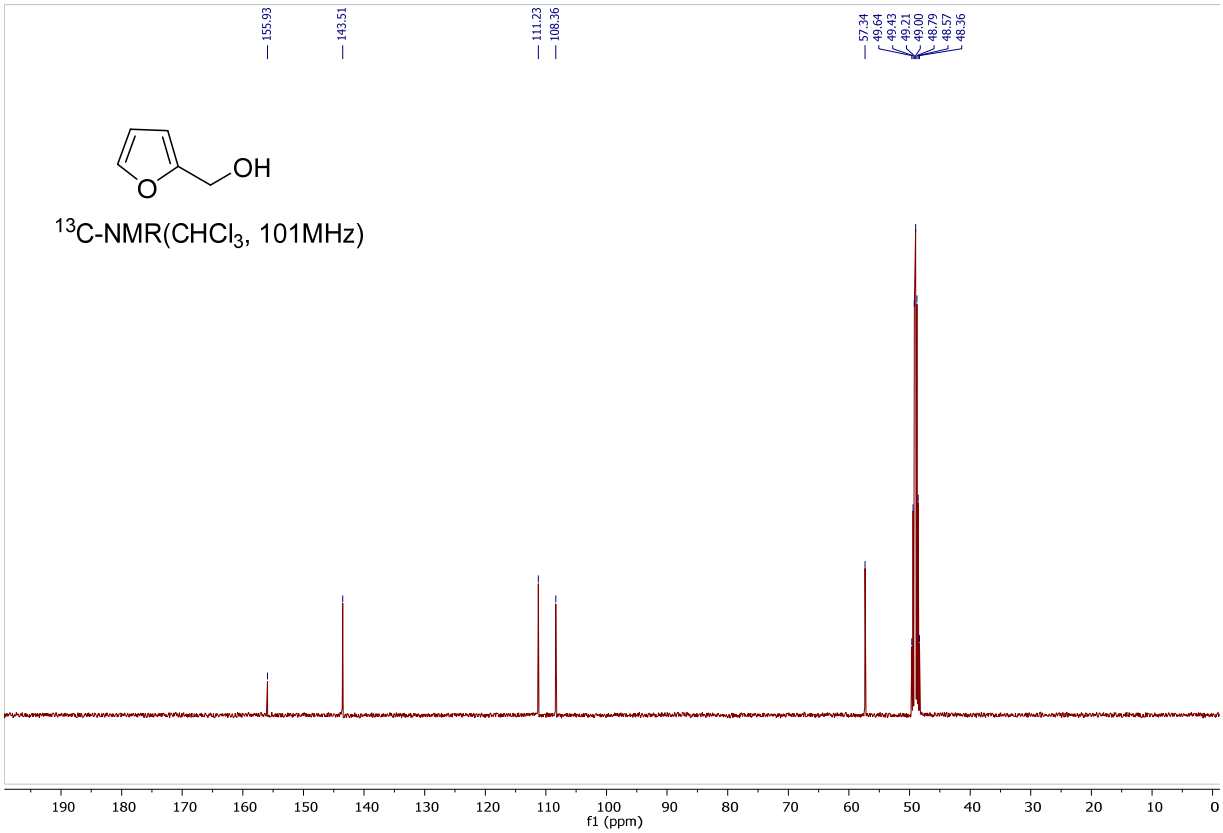
^{1}H-NMR($CHCl_3$, 500MHz)



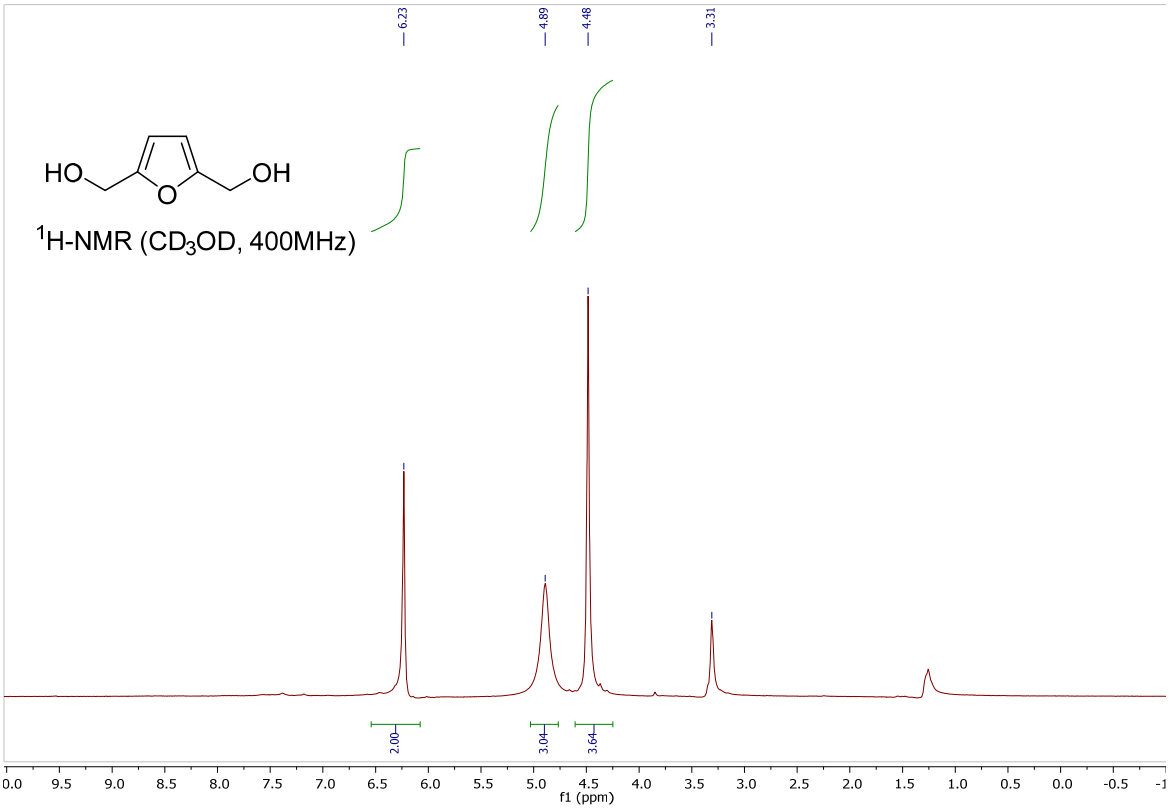
^{13}C-NMR($CHCl_3$, 126MHz)

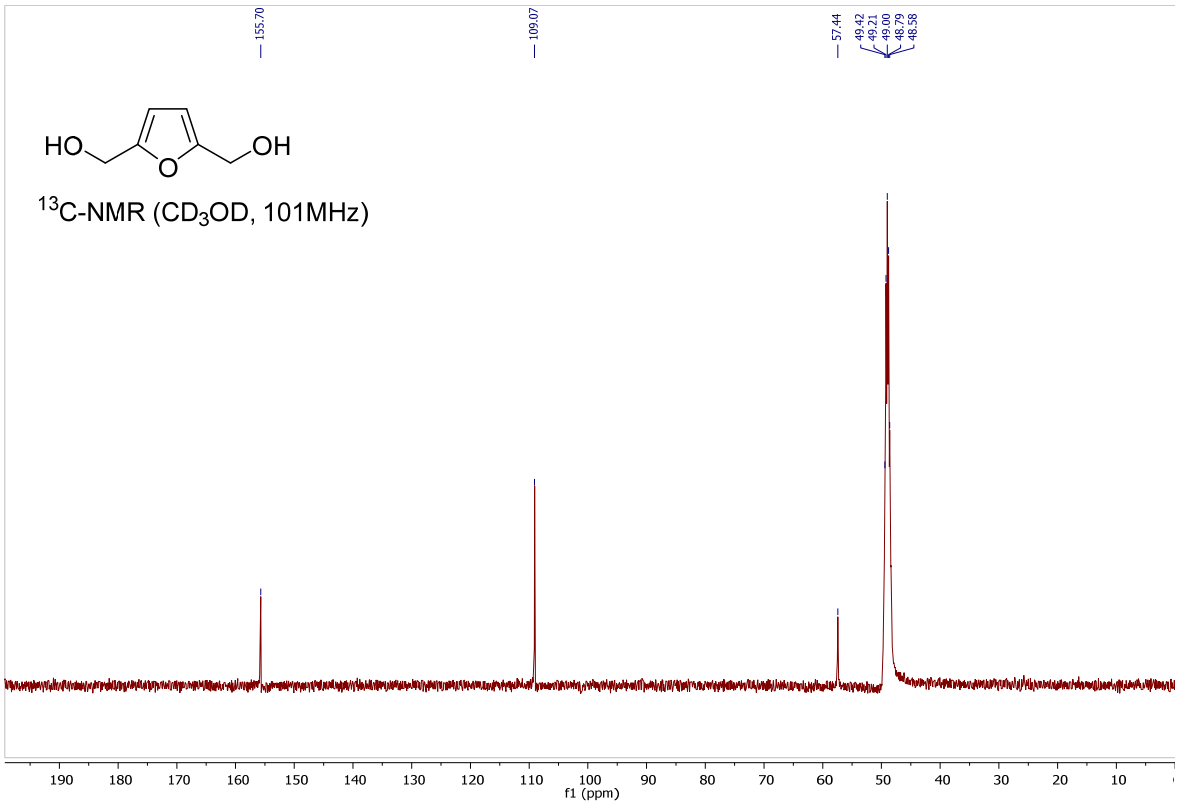


^{1}H-NMR($CHCl_3$, 400MHz)



^{13}C-NMR($CHCl_3$, 101MHz)


6.23
4.89
4.48
3.31
HO
OH
O
^{1}H-NMR (CD_3OD, 400MHz)
2.00
3.04
3.64
f1 (ppm)


155.70
109.07
57.44
49.42
49.21
49.00
48.79
48.58
HO
OH
O
^{13}C-NMR (CD_3OD, 101MHz)
f1 (ppm)