Electronic Supplementary Information for

Constructing Reactive Fe and Co Complexes from Isolated Picolyl-Functionalized *N*-Heterocyclic Carbenes

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1. NMR spectra

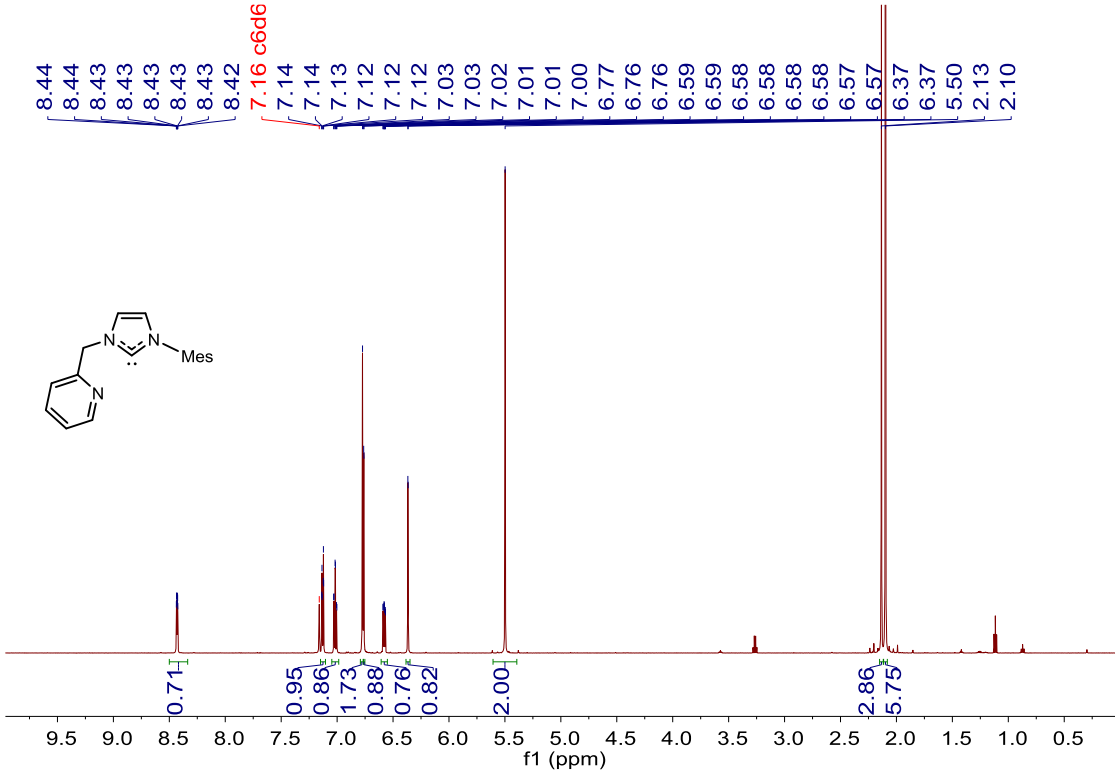


Figure S1. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **2a**.

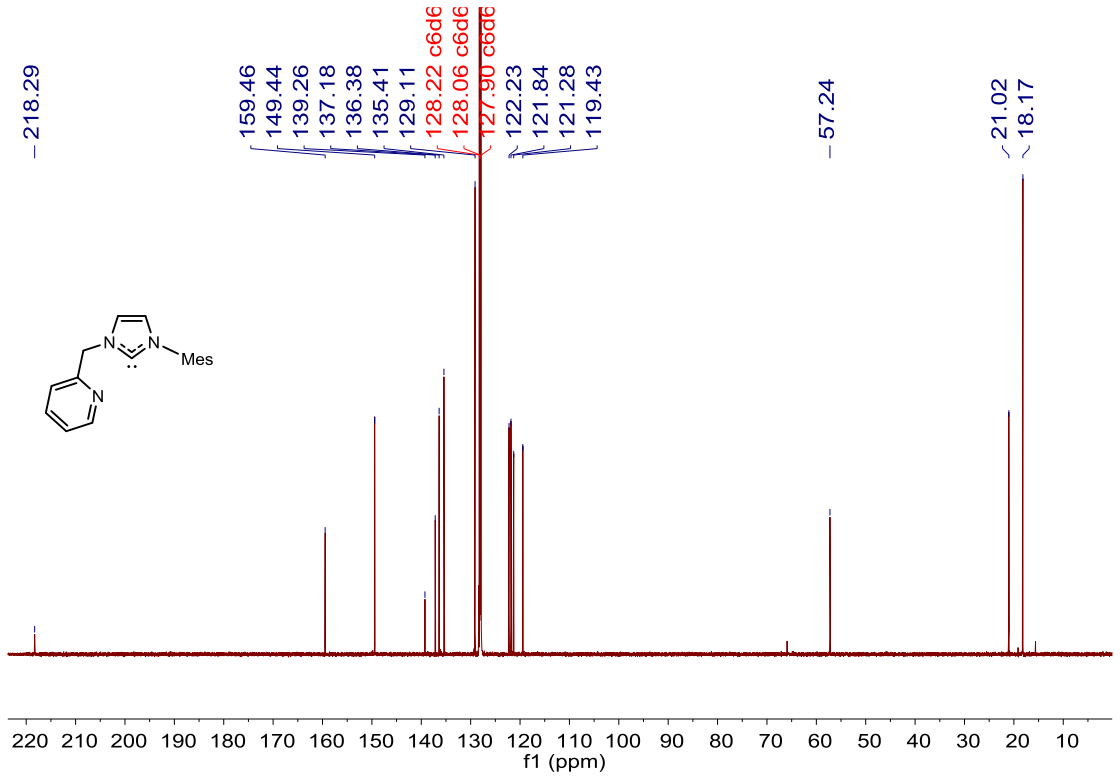


Figure S2. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **2a**.

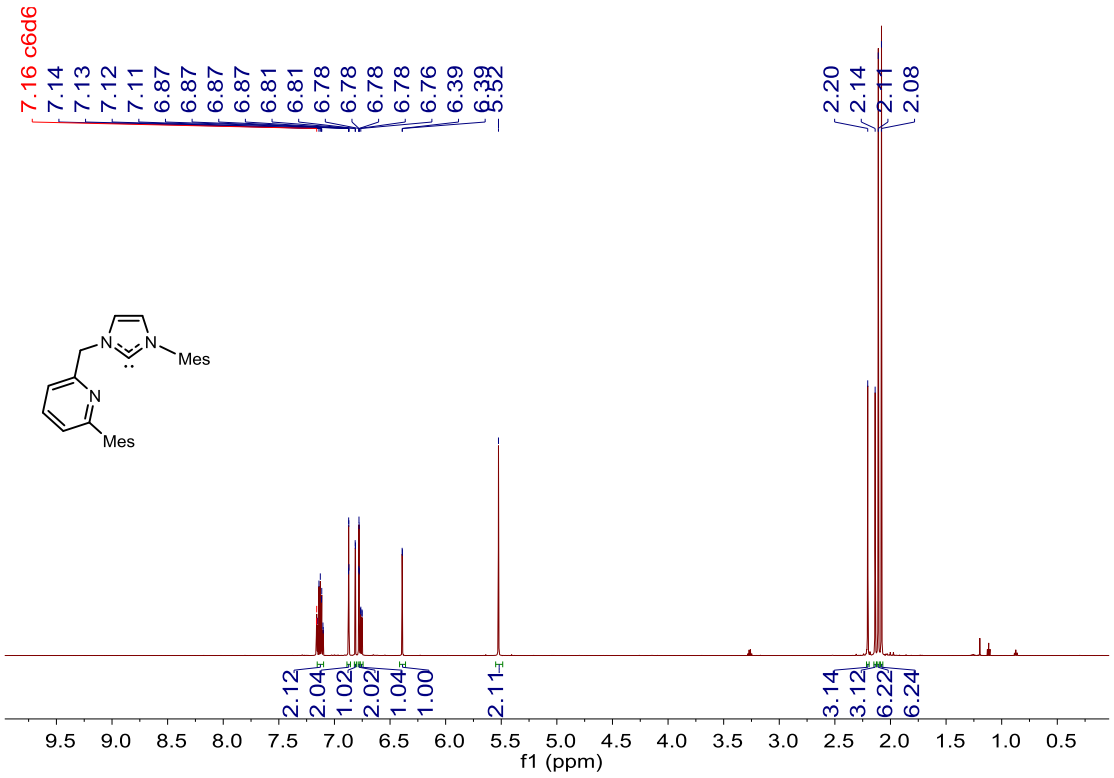


Figure S3. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **2b**.

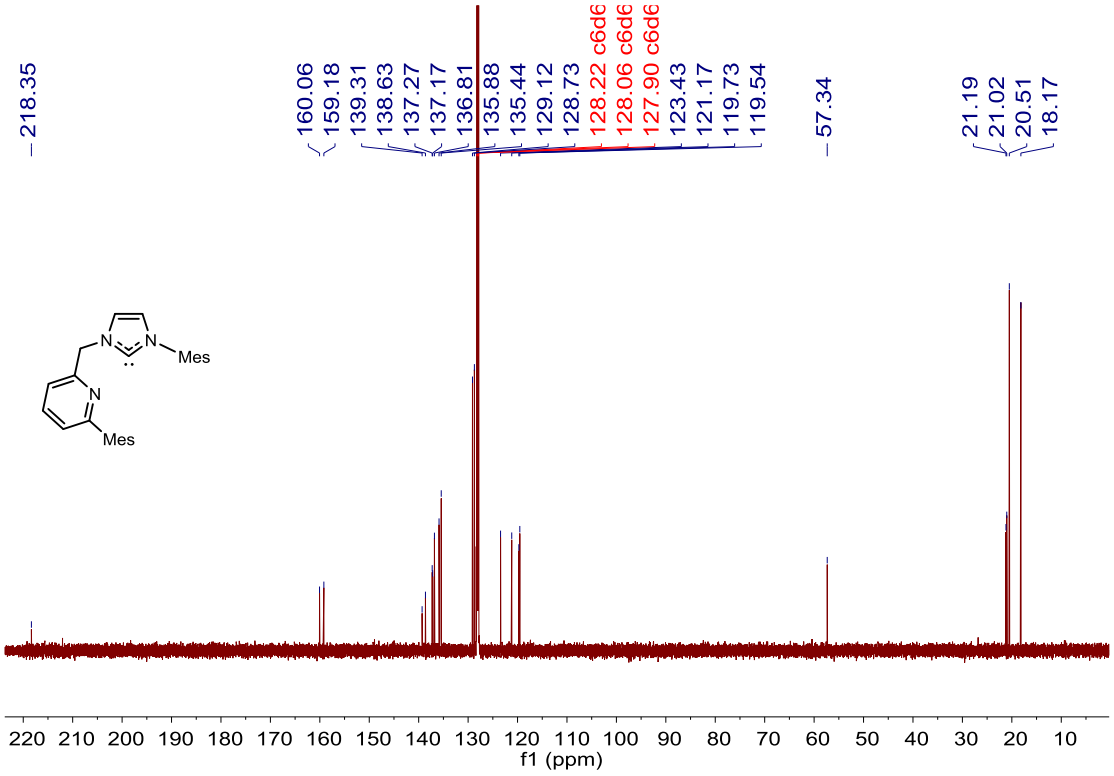


Figure S4. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **2b**.

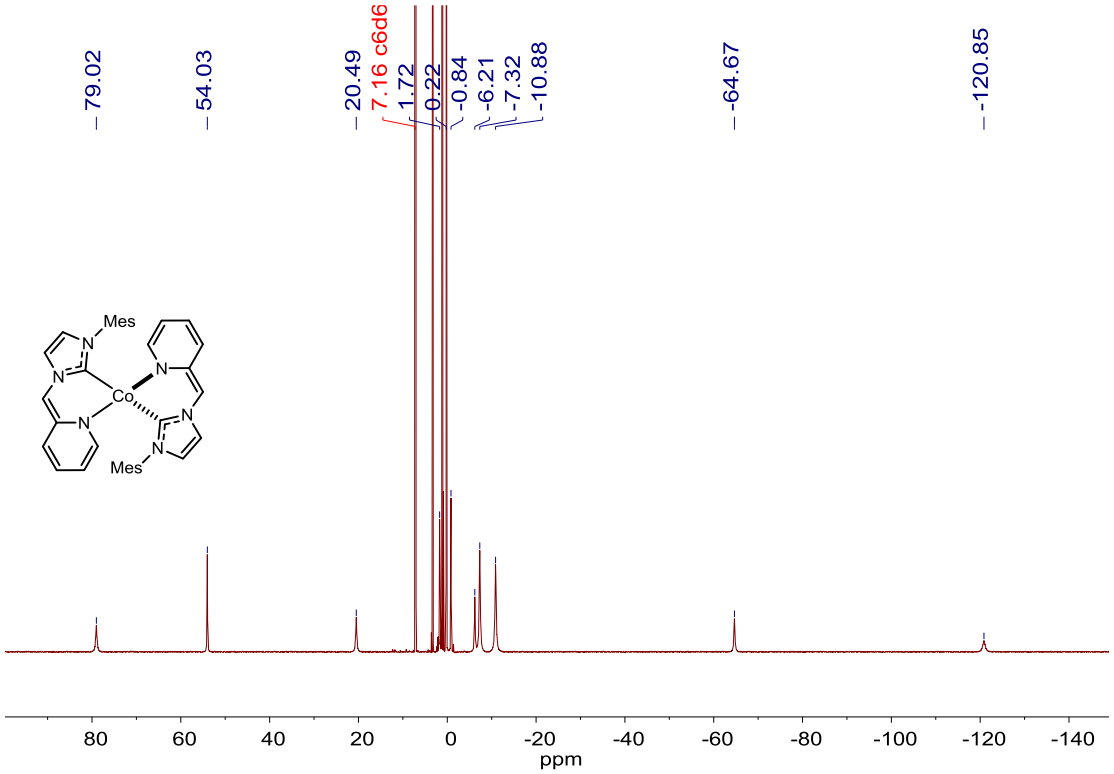


Figure S5. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **3[Co]**.

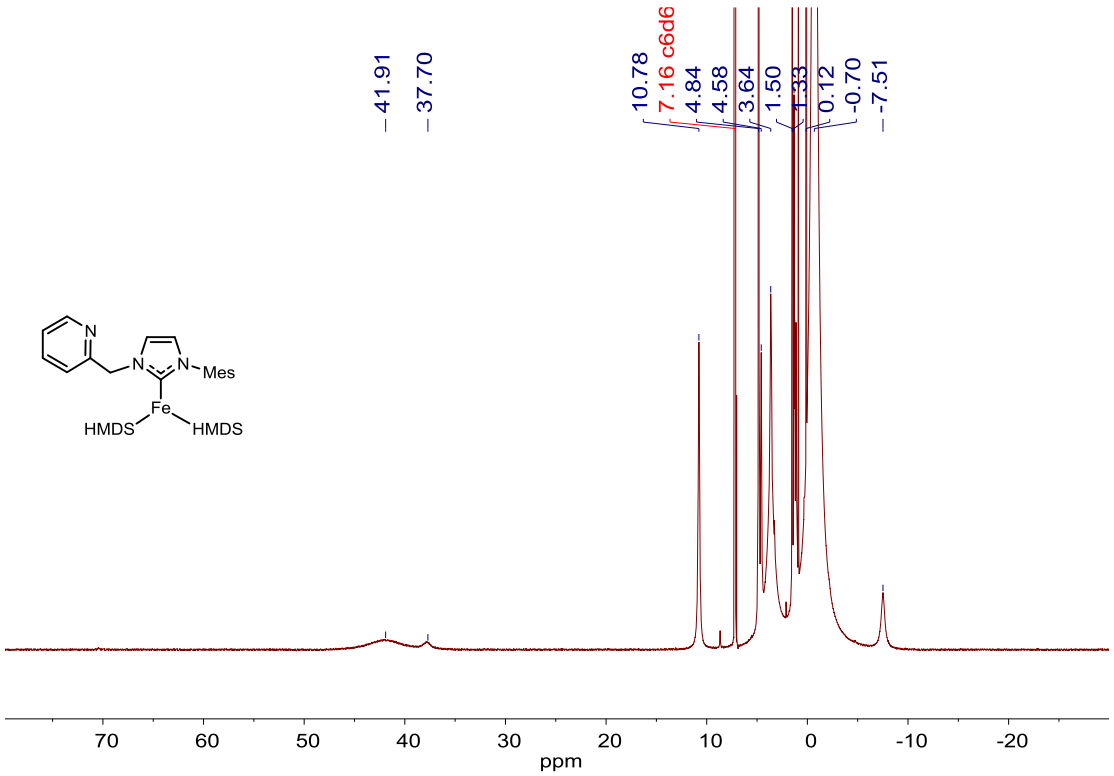
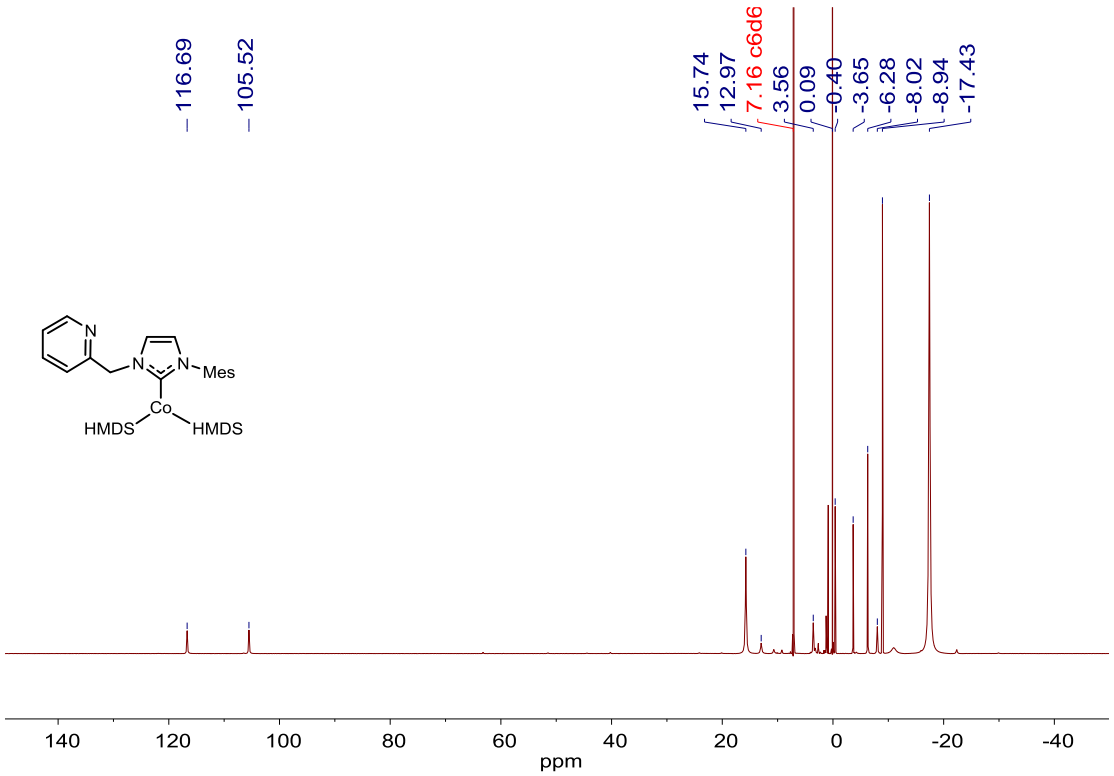


Figure S6. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **4[Fe]**.



Fgure S7. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **4[Co]**.

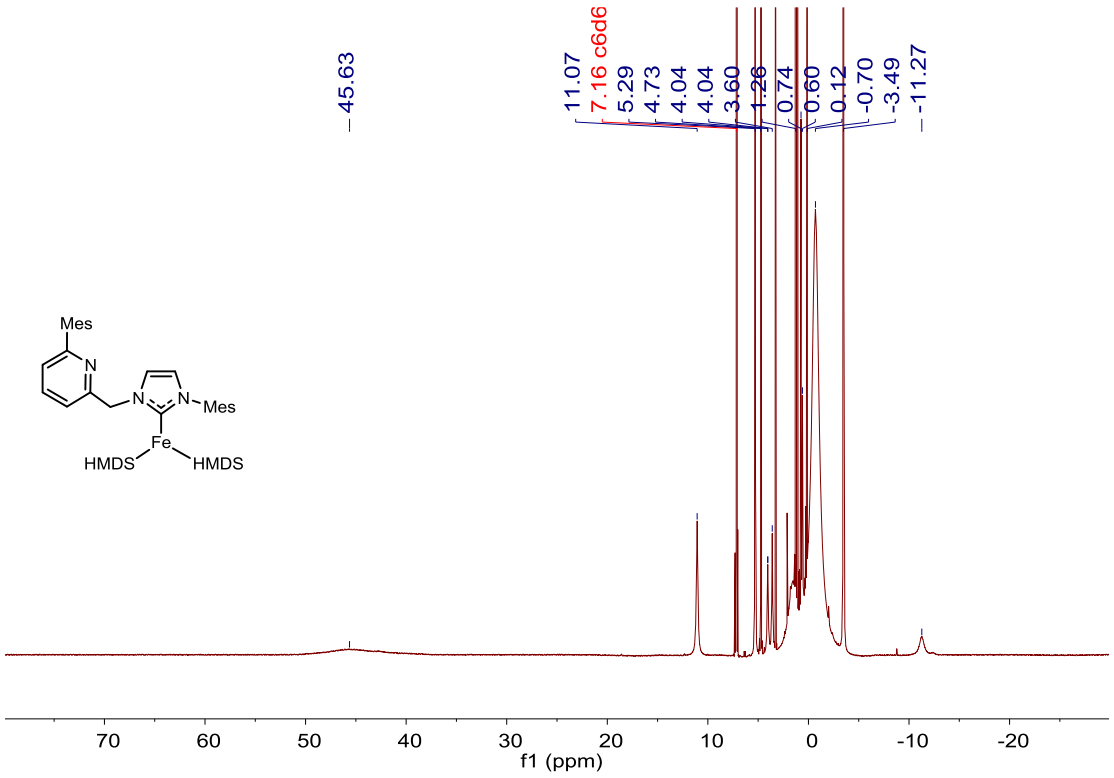


Figure S8. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **5[Fe]**.

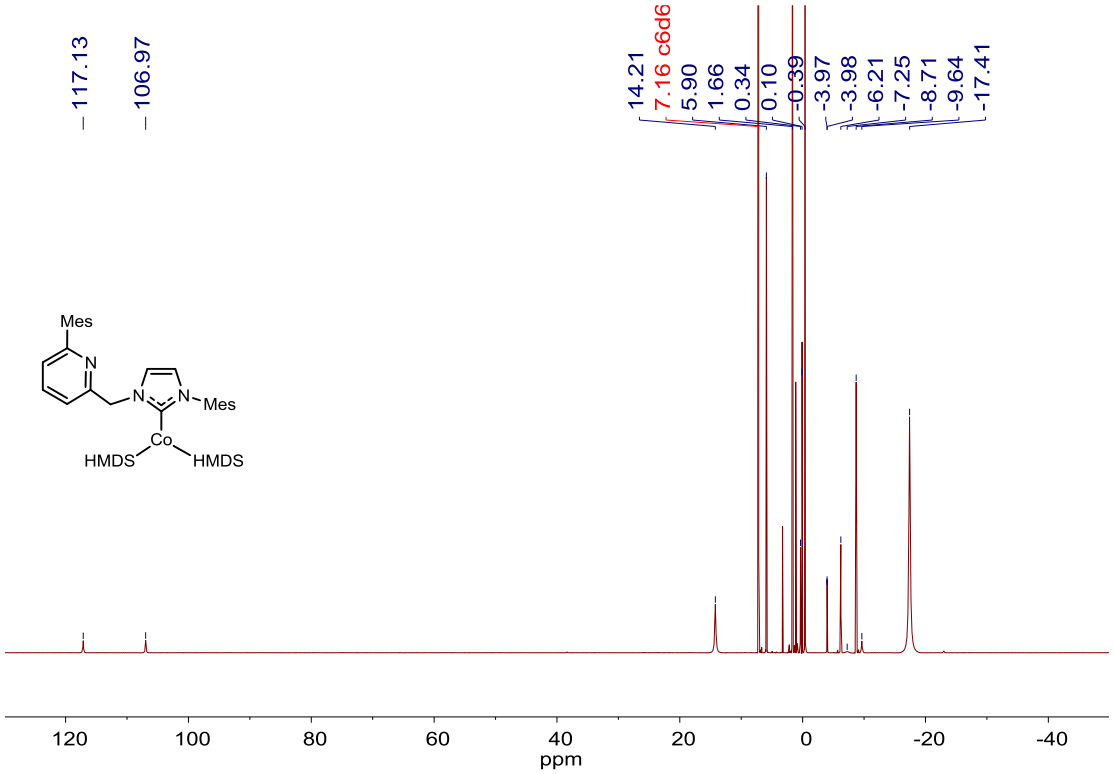


Figure S9. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **5[Co]**.

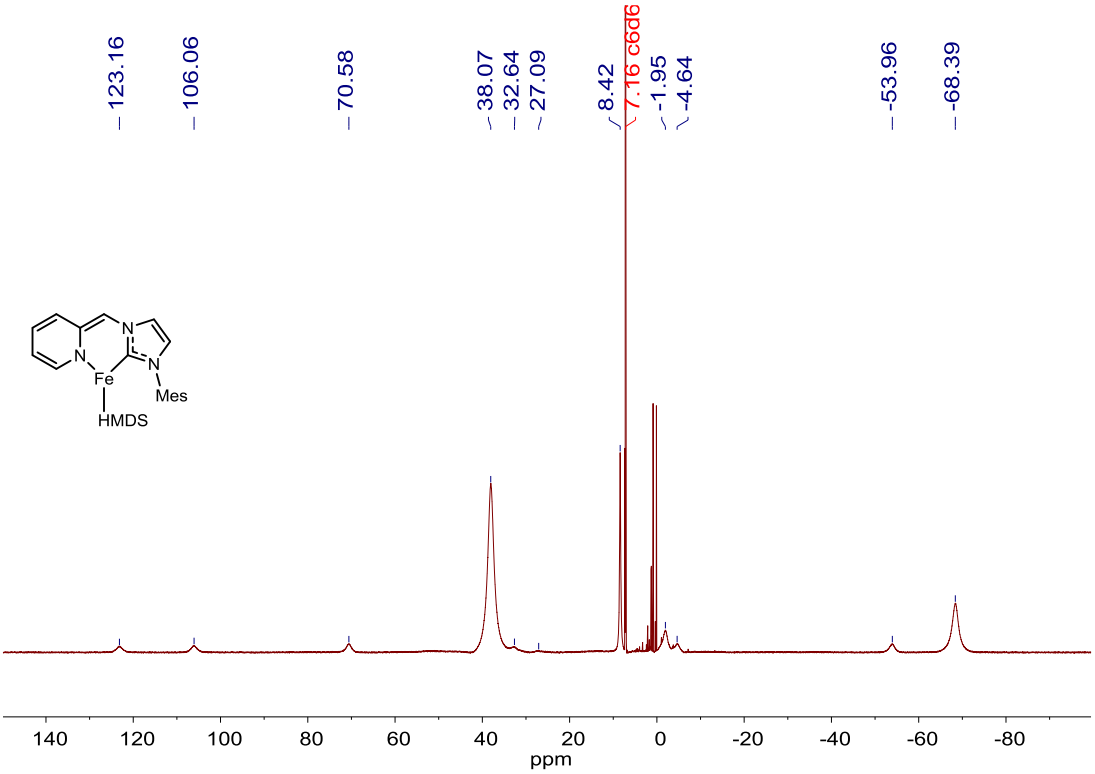


Figure S10. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **6'[Fe]**.

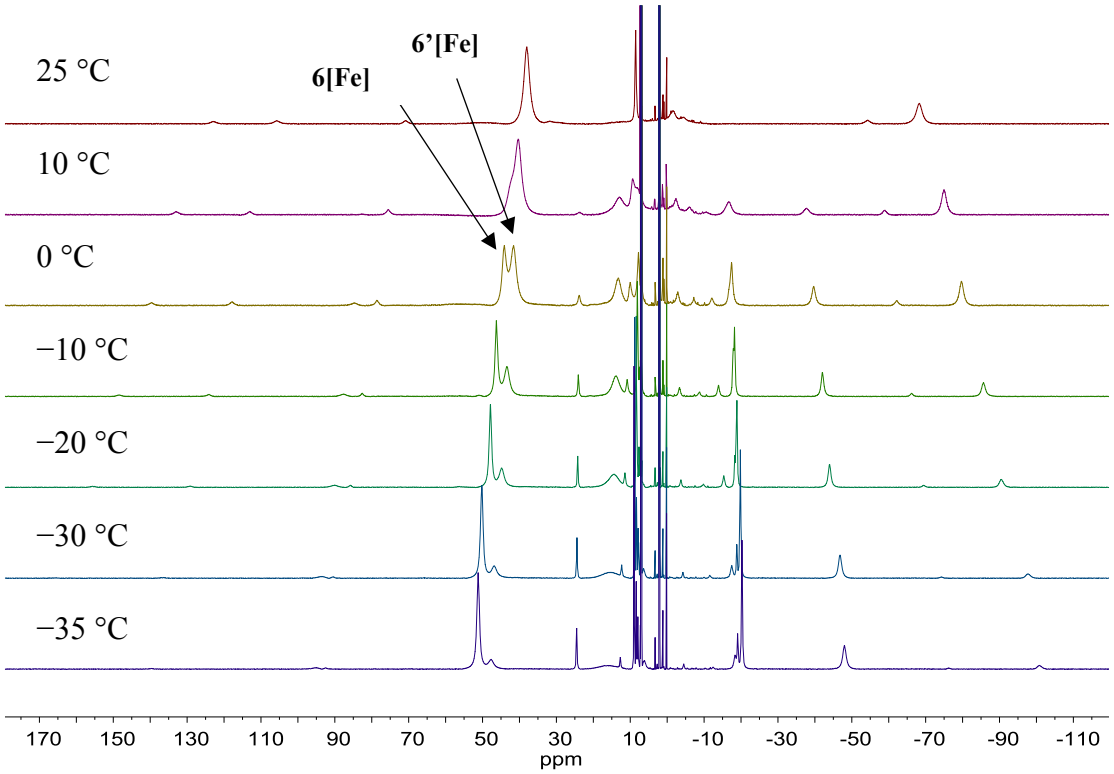


Figure S11. Variable temperature ^{1}H NMR (600 MHz, toluene-d_8) spectrum of **6'[Fe]** under Ar.

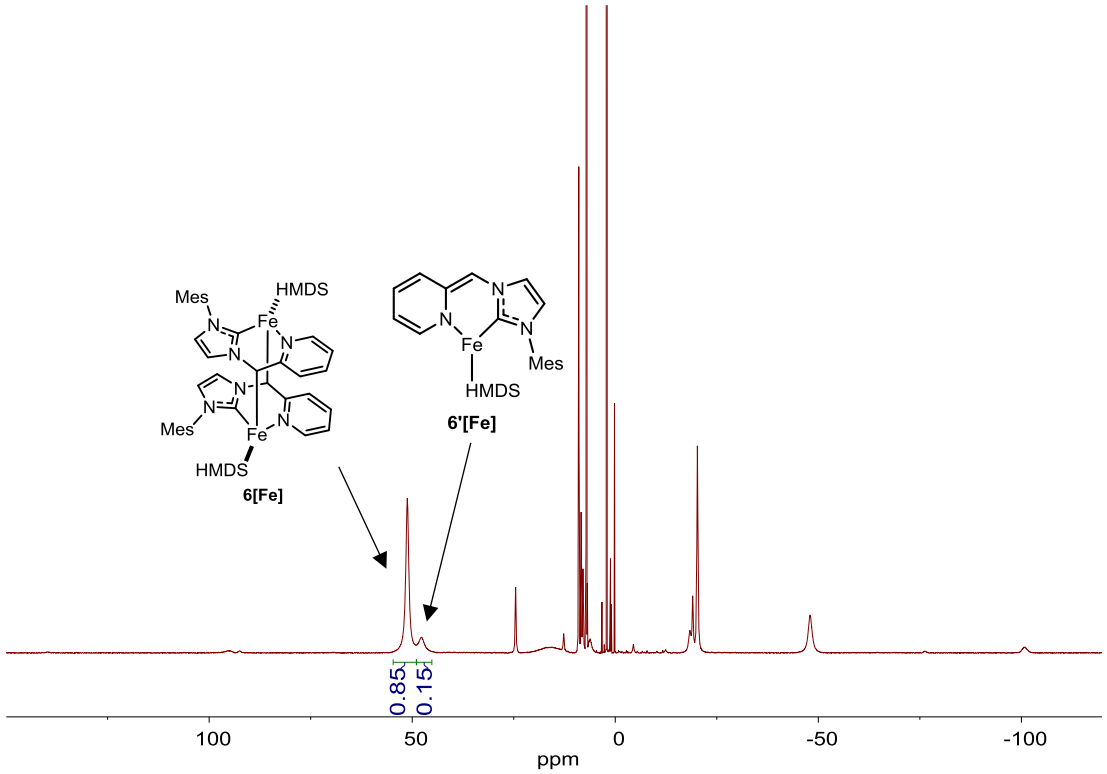


Figure S12. ^{1}H NMR (600 MHz, toluene-d_8) spectrum of **6'[Fe]** and **6[Fe]** mixture at −35 °C under Ar.

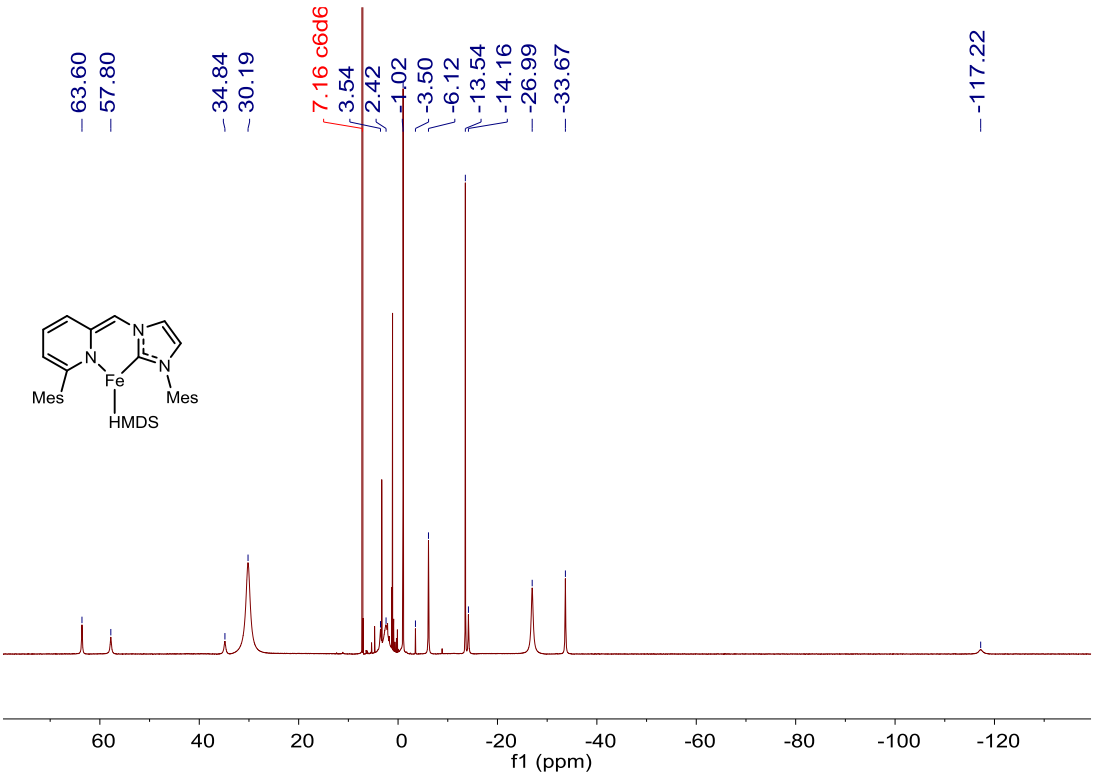


Figure S13. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **7[Fe]**.

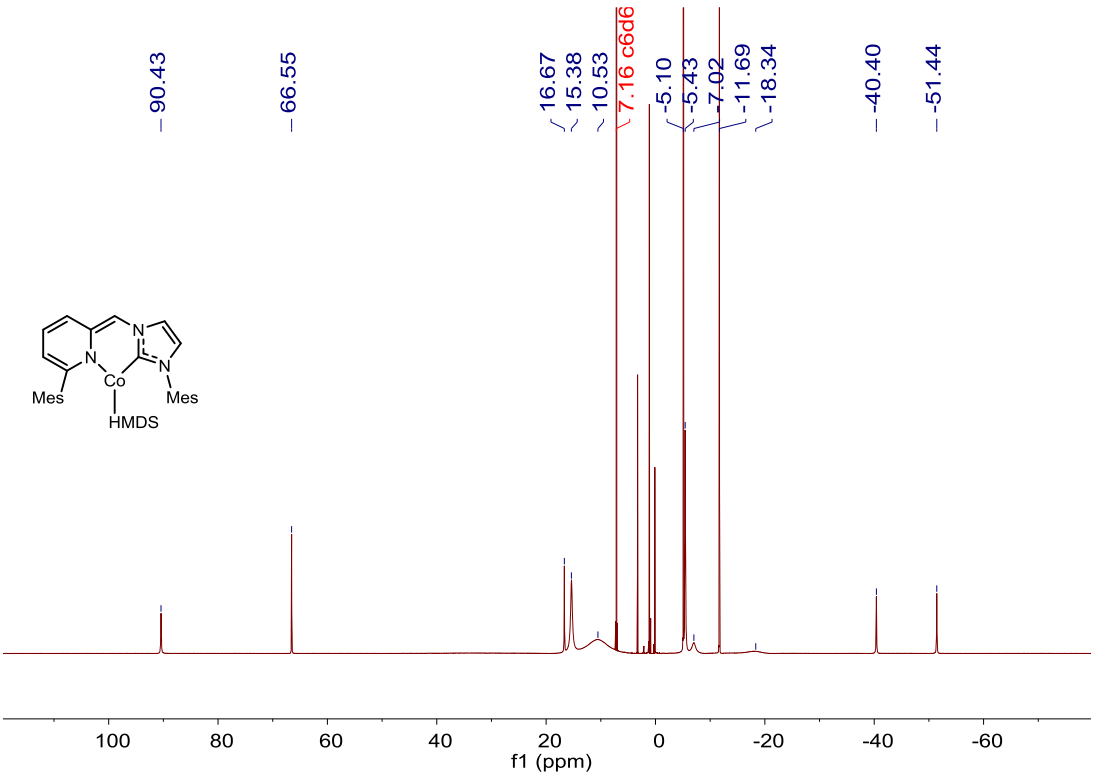


Figure S14. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **7[Co]**.

2. X-ray crystallography

The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex2 software package.[1] The structures were solved by direct methods and refined using SHELX-2016 software package.[2,3] All non-hydrogen atoms were refined anisotropically, except for the disordered ligand in **3[Co]**, and the disordered Me group in **7[Co], [Co$_2$(HMDS)$_2$L$_2$]**. Selected crystallographic data are summarized in Tables S1−S3.

Table S1. Selected crystallographic data for compounds **2a**, **2b**, **3[Co]**, **4[Fe]**, and **4[Co]**.

	2a	**2b**	**3[Co]**	**4[Fe]**	**4[Co]**
Empirical formula	$C_{18}H_{19}N_3$	$C_{27}H_{29}N_3$	$C_{36}H_{36}N_6Co$	$C_{30}H_{55}N_5Si_4Fe$	$C_{30}H_{55}N_5Si_4Co$
FW (g·mol^{-1})	277.36	395.53	611.64	654.00	657.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	C2/c	$P2_1/n$	$P2_1/n$
Z	4	4	8	4	4
a (Å)	7.7983(7)	18.539(2)	33.543(2)	12.1005(11)	12.1070(4)
b (Å)	33.609(4)	10.7159(14)	9.3669(7)	21.0469(18)	21.0094(6)
c (Å)	5.9283(6)	11.6654(15)	22.9162(18)	15.0905(14)	15.1110(6)
α (deg)	90	90	90	90	90
β (deg)	102.610(4)	96.770(4)	113.068(3)	100.064(5)	100.431(2)
γ (deg)	90	90	90	90	90
V (Å^3)	1516.3(3)	2301.3(5)	6624.4(8)	3784.1(6)	3780.1(2)
D_{calcd}, (g·cm^{-3})	1.215	1.142	1.227	1.148	1.155
μ (mm^{-1})	0.073	0.067	0.551	0.550	0.606
F(000)	592	848	2568	1408	1412
no. of obsd reflns	3522	5267	7590	8726	8699
no. of params refnd	193	279	367	376	376
goodness of fit	1.042	1.005	1.025	1.014	1.009
R_1 (I>2σ)	0.0537	0.0611	0.0675	0.0392	0.0419
wR_2 (I>2σ)	0.1390	0.1576	0.1663	0.1002	0.0959

Table S2. Selected crystallographic data for compounds **5[Fe]**, **5[Co]**, **6[Fe]**, **7[Fe]** and **7[Co]**.

	5[Fe]	**5[Co]**	**6[Fe]**	**7[Fe]**	**7[Co]**
Empirical formula	$C_{39}H_{65}N_5Si_4Fe$	$C_{39}H_{65}N_5Si_4Co$	$C_{48}H_{72}N_8Si_4Fe_2$	$C_{33}H_{46}N_4Si_2Fe$	$C_{33}H_{46}N_4Si_2Co$
FW ($g \cdot mol^{-1}$)	772.17	775.25	985.19	610.77	613.85
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbca	Pbca
Z	4	4	4	8	8
a (Å)	23.467(8)	23.374(2)	14.4692(11)	19.7886(13)	17.3185(11)
b (Å)	10.283(3)	10.2831(9)	28.2574(19)	17.2735(11)	19.7038(12)
c (Å)	20.491(7)	20.3862(15)	17.2321(13)	19.8837(12)	19.7936(12)
α (deg)	90	90	90	90	90
β (deg)	114.286(11)	114.097(4)	113.491(3)	90	90
γ (deg)	90	90	90	90	90
V ($Å^3$)	4507(2)	4472.9(7)	6461.6(8)	6796.6(7)	6754.4(7)
D_{calcd}, ($g \cdot cm^{-3}$)	1.138	1.144	1.013	1.194	1.207
μ (mm^{-1})	0.472	0.522	0.556	0.541	0.606
F(000)	1664	1648	2096	2608	2616
no. of obsd reflns	10306	10224	14854	7820	7784
no. of params refnd	460	460	577	373	373
goodness of fit	0.981	0.996	0.998	1.002	0.998
R_1 ($I>2\sigma$)	0.0796	0.0544	0.0608	0.0452	0.0520
wR_2 ($I>2\sigma$)	0.1625	0.1252	0.1622	0.1094	0.1240

Table S3. Selected crystallographic data for compound **[$Co_2(HMDS)_2L_2$]**.

	[$Co_2(HMDS)_2L_2$]
Empirical formula	$C_{48}H_{72}N_8Si_4Co_2$
FW ($g \cdot mol^{-1}$)	991.35
Crystal system	Monoclinic
Space Group	$P2_1/n$
Z	4
a (Å)	11.4169(4)
b (Å)	27.5089(9)
c (Å)	18.1503(6)
α (deg)	90
β (deg)	107.825
γ (deg)	90
V ($Å^3$)	5426.8(3)
D_{calcd}, ($g \cdot cm^{-3}$)	1.213
μ (mm^{-1})	0.738
F(000)	2104
no. of obsd reflns	12477
no. of params refnd	575
goodness of fit	1.017
R_1 ($I>2\sigma$)	0.0416
wR_2 ($I>2\sigma$)	0.1013

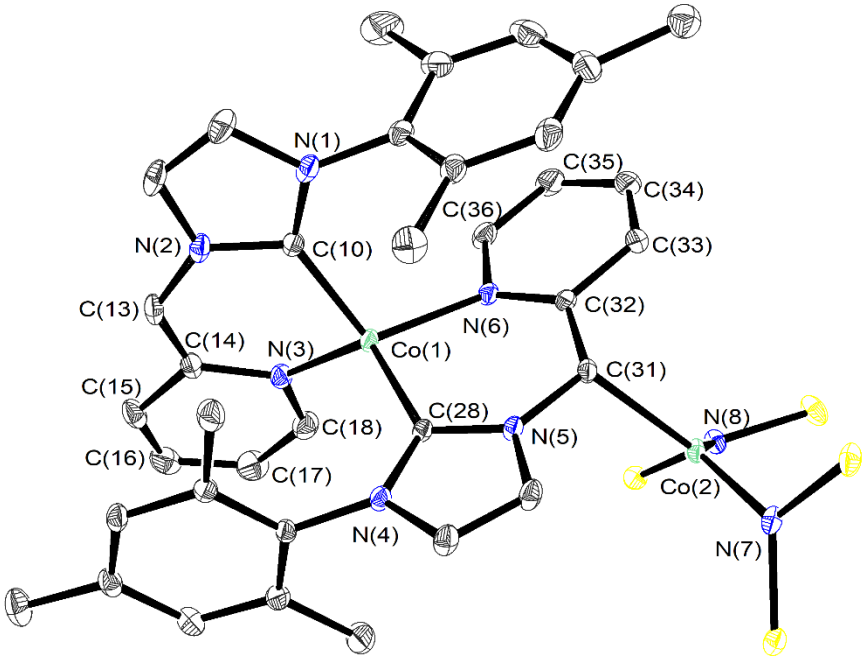


Figure S15. X-ray structures of **[$Co_2(HMDS)_2L_2$]**. Ellipsoids are shown at 30% probability. Hydrogen atoms and the HMDS methyl groups have been omitted for clarity. Only one disordered component is shown. Selected bond lengths (Å) and angles (°): Co(1)–C(10) 1.966(2), Co(1)–N(3) 1.960(2), Co(1)–C(28) 1.969(3), Co(1)–N(6) 2.017(2), N(3)–C(18) 1.360(4), C(18)–C(17) 1.353(4), C(17)–C(16) 1.411(5), C(16)–C(15) 1.330(5), C(15)–C(14) 1.447(4), C(14)–N(3) 1.396(3), C(14)–C(13) 1.361(3), C(13)–N(2) 1.405(3), N(6)–C(36) 1.361(4), C(36)–C(35) 1.362(3), C(35)–C(34) 1.492(5), C(34)–C(33) 1.358(4), C(33)–C(32) 1.417(3), C(32)–N(6) 1.357(3), C(32)–C(31) 1.460(3), C(31)–N(5) 1.464(3), C(10)–Co(1)–N(3) 95.44(9), N(3)–Co(1)–C(28) 120.96(9), C(28)–Co(1)–N(6) 94.14(8), N(6)–Co(1)–C(10) 112.31(9), N(2)–C(13)–C(14) 127.2(2), N(5)–C(31)–C(32) 121.1(2); Co(2)–C(31) 2.148(2), Co(2)–N(7) 1.935(2), Co(2)–N(8) 1.931(2), C(31)–Co(2)–N(7) 112.32(9), N(7)–Co(2)–N(8) 127.55(9), N(8)–Co(2)–C(31) 119.95(9).

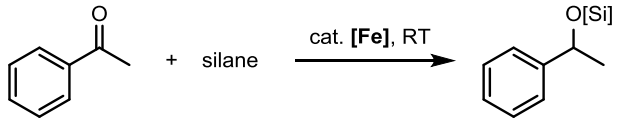
3. Hydrosilylation of ketones

General Experimental Procedure for Initial Catalytic Performance Evaluation.

In a nitrogen glovebox, catalyst (0.025–0.05 mol%), hexamethylbenzene (30.1 mg, 0.19 mmol, internal standard), acetophenone (390 μL, 3.34 mmol), silane ($PhSiH_3$ or PMHS), solvent (toluene or THF) and a stirbar were charged in a 2-dram borosilicate glass vial. The vial was fitted with a PTFE-lined rubber septum screw cap. The reaction was left stirring at room temperature for the specified time. An NMR sample was prepared using 0.1 mL of the reaction mixture in 0.4 mL of $CDCl_3$. The conversion of the

reaction were determined by ^{1}H NMR signals of the products compared to internal standard. The results are summarized in Table S4.

Table S4. Hydrosilylation of acetophenone.[a]



Entry	Catalyst	Loading (mol%)	Silane	Solvent	Time (h)	Conversion[b] (%)
1	**3[Fe]**	0.05	H_3SiPh	0.5 mL toluene	2	100
2	**3[Fe]**	0.025	H_3SiPh	0.5 mL toluene	3	80
3	**3[Co]**	0.025	H_3SiPh	0.5 mL toluene	3	40
4	**4[Fe]**	0.025	H_3SiPh	0.5 mL toluene	3	15
5	**4[Co]**	0.025	H_3SiPh	0.5 mL toluene	3	9
6	**5[Fe]**	0.025	H_3SiPh	0.5 mL toluene	3	5
7	**5[Co]**	0.025	H_3SiPh	0.5 mL toluene	3	7
8	**6[Fe]**	0.025	H_3SiPh	0.5 mL toluene	3	12
9	**7[Fe]**	0.025	H_3SiPh	0.5 mL toluene	3	60
10	**7[Co]**	0.025	H_3SiPh	0.5 mL toluene	3	32
11	**3[Fe]**	0.05	PMHS	-	2	100
12	**3[Fe]**	0.05	PMHS	0.3 mL toluene	2	100
13	**3[Fe]**	0.05	PMHS	0.3 mL THF	2	100
14	**$Fe(HMDS)_2$**	0.05	PMHS	-	3	5

[a] General conditions: acetophenone (3.3 mmol), $PhSiH_3$ (4.0 mmol) for entries 1–10 or PMHS (0.5 mL neat for entries 11 and 14; 0.2 mL with additional 0.3 mL of solvent for entries 12 and 13). [b] Conversions are determined by ^{1}H NMR spectroscopy with C_6Me_6 as internal standard.

4. Characterization of isolated alcohols

1-Phenylethanol

Colorless oil. 383.1 mg, 94%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 4.90 (q, *J* = 6.5 Hz, 1H), 1.88 (s, 1H), 1.50 (dd, *J* = 6.5, 1.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.95, 128.64, 127.61, 125.52, 70.56, 25.29.

1-(4-Methoxyphenyl)ethanol

Colorless oil. 488.1 mg, 96%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.6, 1.6 Hz, 2H), 6.91 – 6.84 (m, 2H), 4.85 (q, *J* = 6.3 Hz, 1H), 3.80 (s, 3H), 1.48 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.12, 138.14, 126.79, 113.98, 70.11, 55.43, 25.16.

1-(4-Bromophenyl)ethanol

Colorless oil. 643.9 mg, 96%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.26 – 7.23 (m, 2H), 4.87 (qd, *J* = 6.4, 3.1 Hz, 1H), 1.85 (d, *J* = 3.3 Hz, 1H),1.47 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.91, 131.70, 127.29, 121.31, 69.94, 25.40.

1-(4-Cyanophenyl)ethanol

Colorless oil. 466.4 mg, 95%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.51 – 7.45 (m, 2H), 4.96 (qd, *J* = 6.5, 3.0 Hz, 1H), 1.99 (d, *J* = 3.6 Hz, 3H), 1.50 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.19, 132.50, 126.19, 118.99, 111.26, 69.82, 25.56.

1-(3-Aminophenyl)ethanol

White solid. 393.5 mg, 86%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.7 Hz, 1H), 6.75 (ddt, *J* = 7.6, 1.6, 0.8 Hz, 1H), 6.72 (dt, *J* = 2.1, 1.2 Hz, 1H), 6.60 (ddd, *J* = 7.9, 2.4, 1.0 Hz, 1H), 4.81 (q, *J* = 6.5 Hz, 1H), 3.68 (s, 2H), 1.76 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.38, 146.74, 129.61, 115.76, 114.37, 112.11, 70.58, 25.16.

1-(2-Pyridyl)ethanol

Colorless oil. 367.1 mg, 89%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (ddt, *J* = 4.1, 2.0, 1.0 Hz, 1H), 7.67 (tdd, *J* = 7.5, 1.7, 0.8 Hz, 1H), 7.27 (dq, *J* = 7.9, 1.0 Hz, 1H), 7.20 – 7.16 (m, 1H), 4.88 (q, *J* = 6.6 Hz, 1H), 4.37 (s, 1H), 1.49 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.21, 148.24, 136.90, 122.32, 119.90, 68.99, 24.37.

1-(2-Furyl)ethanol

Colorless oil. 338.6 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 (dt, *J* = 3.3, 0.8 Hz, 1H), 4.88 (qd, *J* = 6.5, 4.6 Hz, 1H), 2.02 (d, *J* = 5.0 Hz, 1H), 1.54 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.73, 142.05, 110.26, 105.24, 63.77, 21.40.

1-(2,4,6-Trimethylphenyl)ethanol

White solid. 535.0 mg, 98%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.37 (q, *J* = 6.7 Hz, 1H), 2.42 (s, 6H), 2.25 (s, 3H), 1.68 (s, 1H), 1.53 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.79, 136.58, 135.80, 130.28, 67.64, 21.75, 20.83, 20.66.

Diphenylmethanol

White solid. 601.4 mg, 98%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 4H), 7.36 – 7.31 (m, 4H), 7.29 – 7.25 (m, 2H), 5.86 (d, *J* = 3.5 Hz, 1H), 2.19 (dd, *J* = 3.5, 1.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.95, 128.66, 127.74, 126.69, 76.44.

Cycloheptanol

Colorless oil. 345.1 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.85 (tt, *J* = 8.5, 4.3 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.65 (dddd, *J* = 14.2, 8.8, 6.8, 3.1 Hz, 2H), 1.56 (dddt, *J* = 11.1, 8.1, 4.7, 3.0 Hz, 6H), 1.49 – 1.35 (m, 2H), 1.30 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 72.96, 37.78, 28.25, 22.77.

1-Cyclopropylethanol

Colorless oil. 231.9 mg, 81%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.11 – 3.05 (m, 1H), 1.55 (d, *J* = 3.3 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 0.91 (qt, *J* = 8.2, 5.0 Hz, 1H), 0.54 – 0.45 (m, 2H), 0.31 – 0.23 (m, 1H), 0.22 – 0.14 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 73.15, 22.59, 19.40, 3.14, 2.39.

5-Hexen-2-ol

Colorless oil. 282.3 mg, 84%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.0, 1.3 Hz, 1H), 2.29 – 2.01 (m, 2H), 1.60 – 1.49 (m, 2H), 1.38 (d, *J* = 3.9 Hz, 1H), 1.20 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.64, 114.91, 67.86, 38.41, 30.31, 23.62.

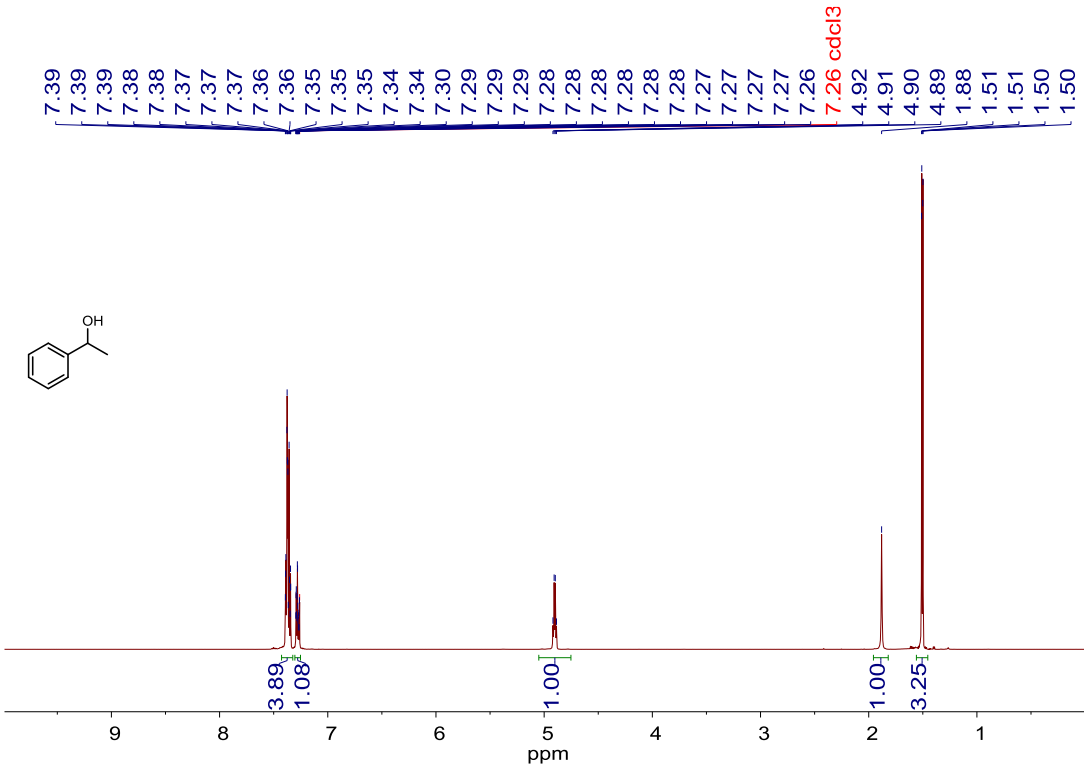


Figure S16. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-Phenylethanol**.

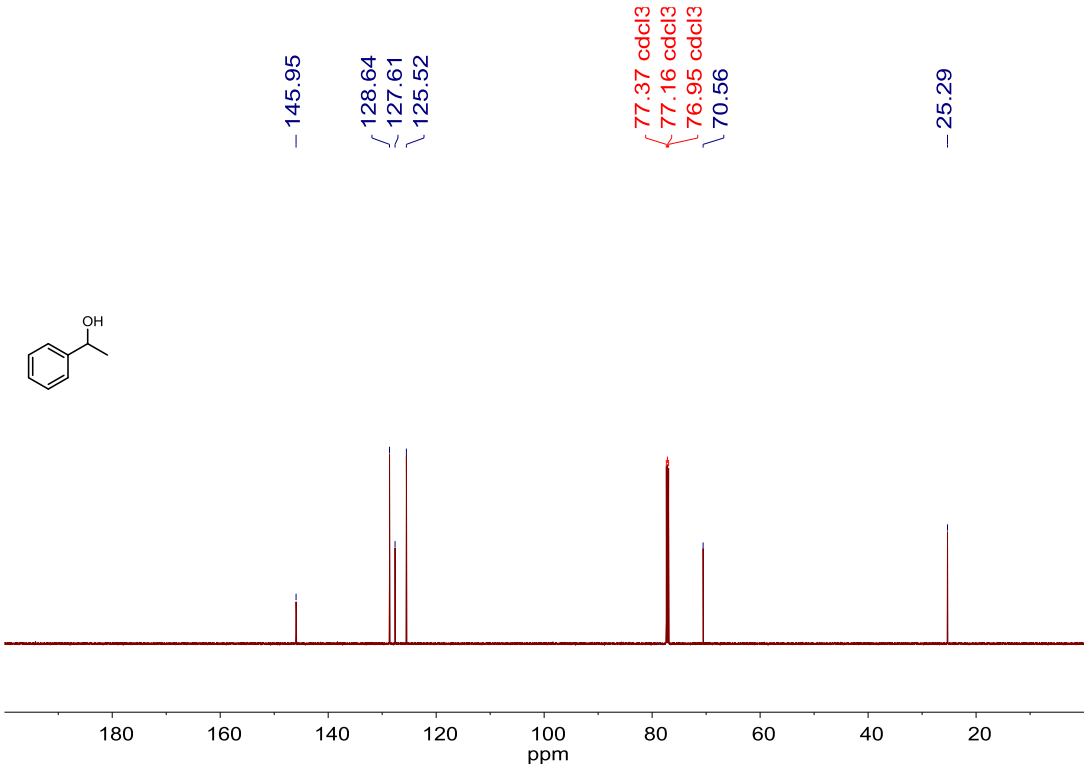


Figure S17. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-Phenylethaol**.

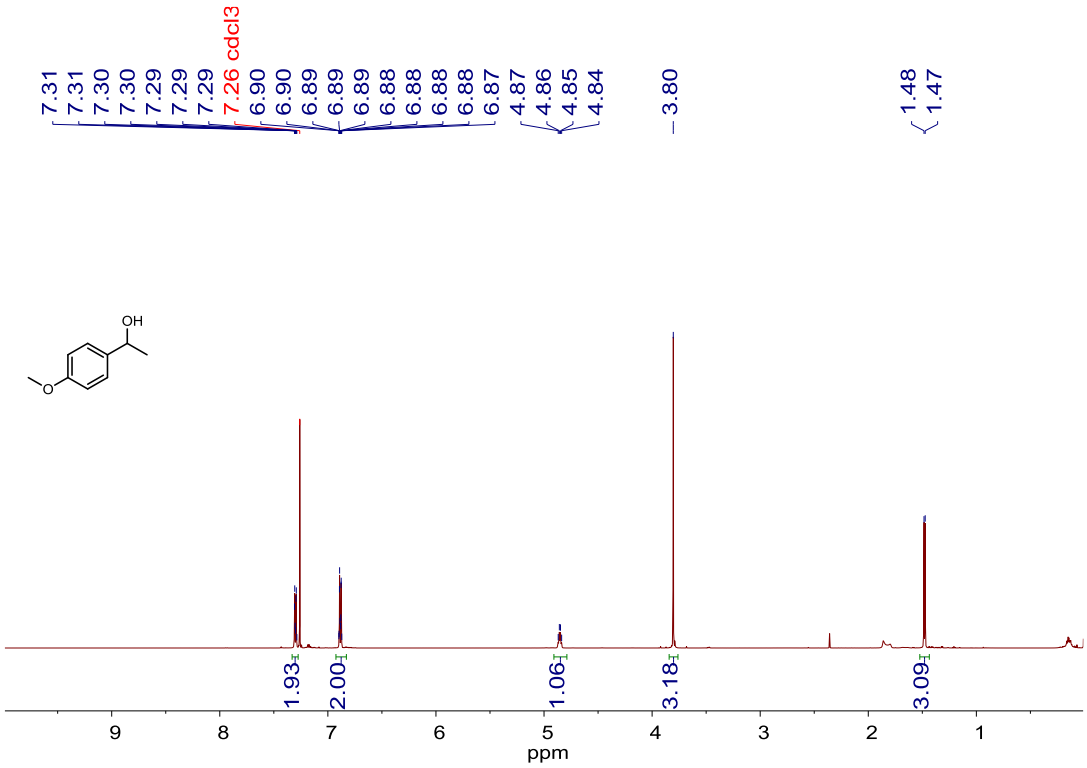


Figure S18. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(4-Methoxyphenyl)ethanol**.

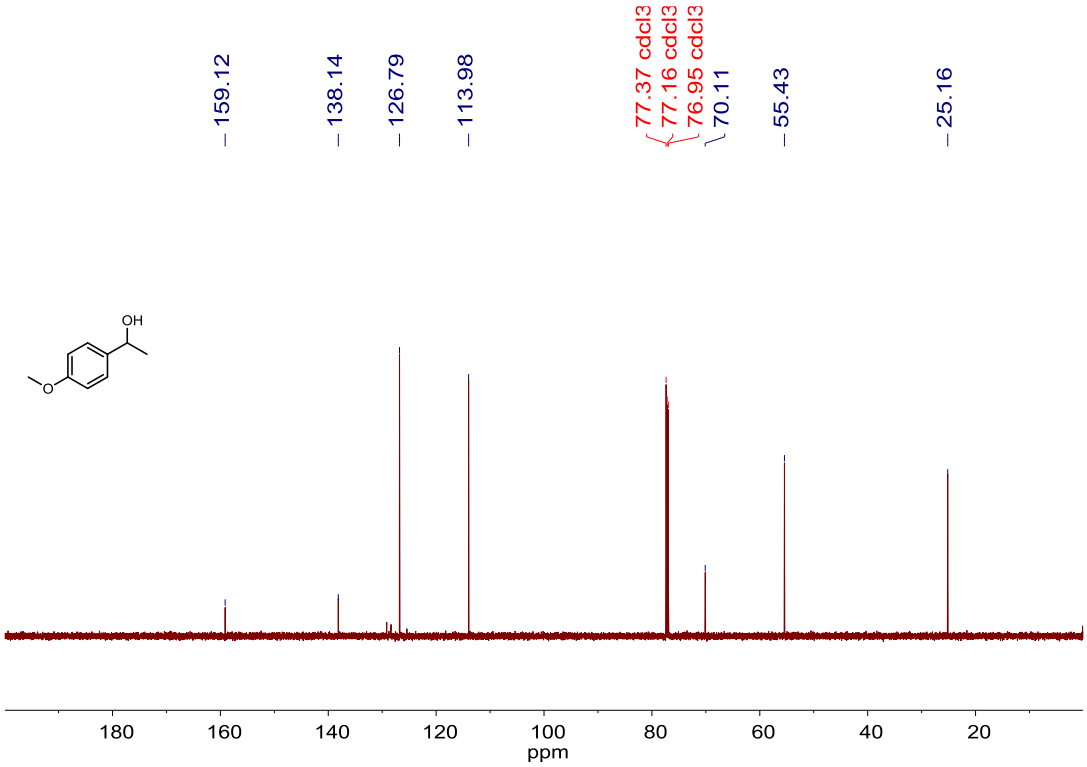


Figure S19. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(4-Methoxyphenyl)ethanol**.

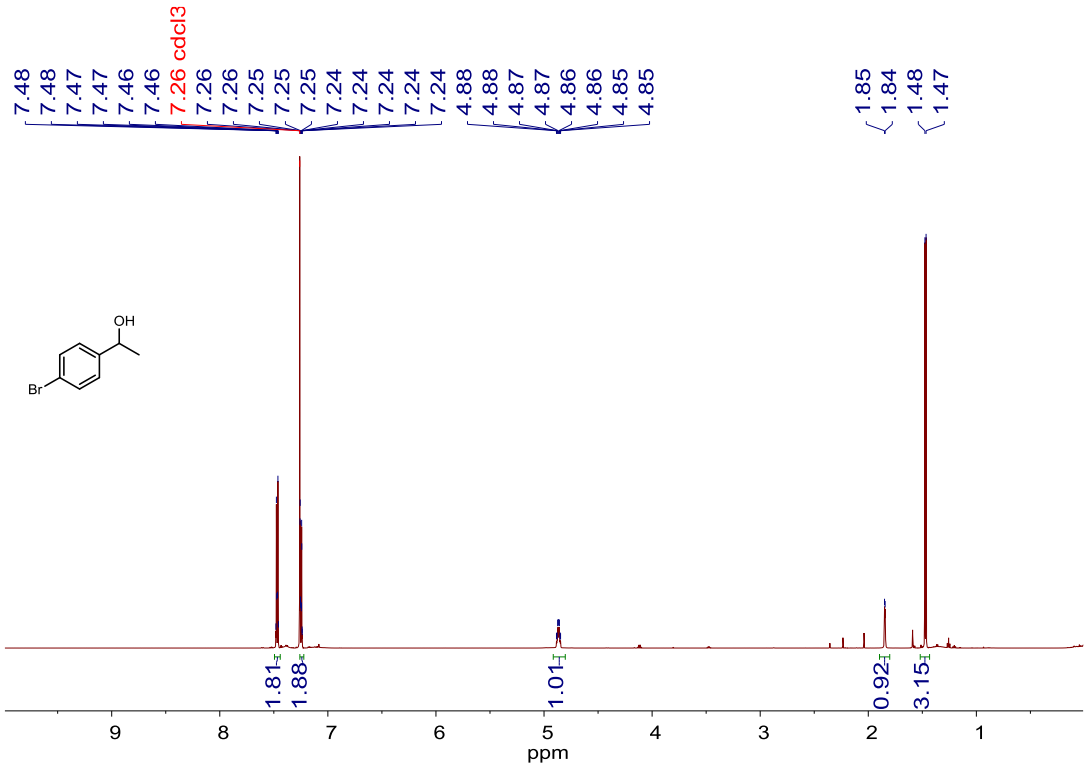


Figure S20. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(4-Bromophenyl)ethanol**.

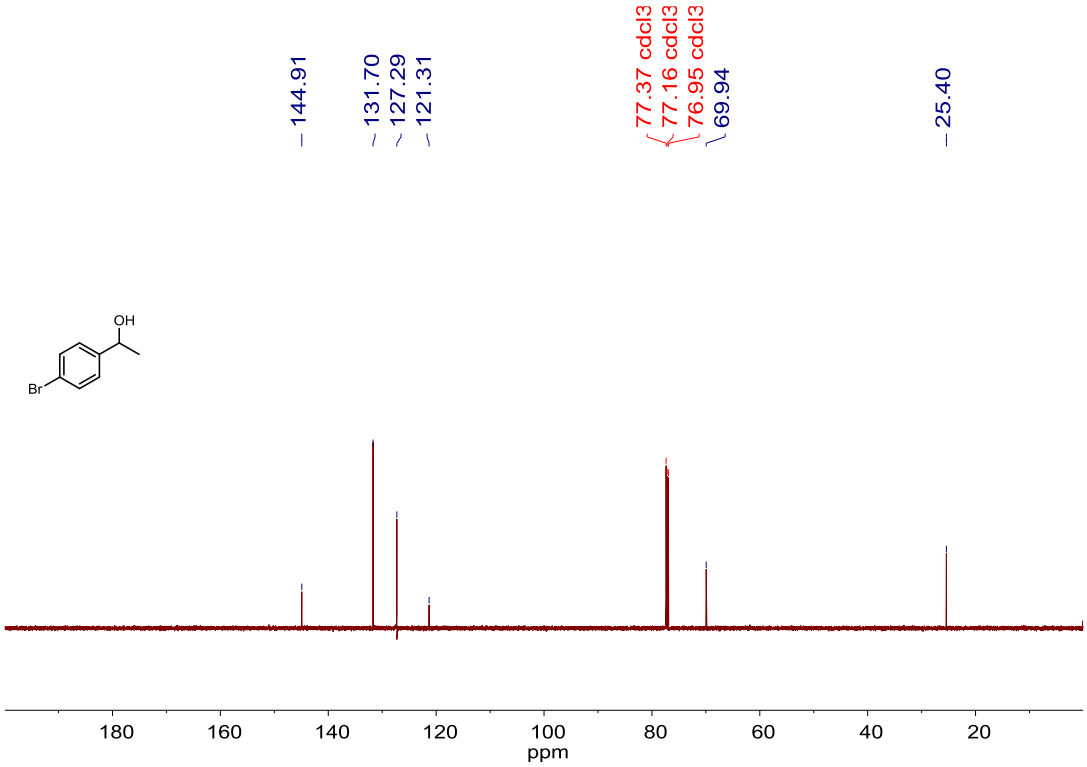


Figure S21. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(4-Bromophenyl)ethanol**.

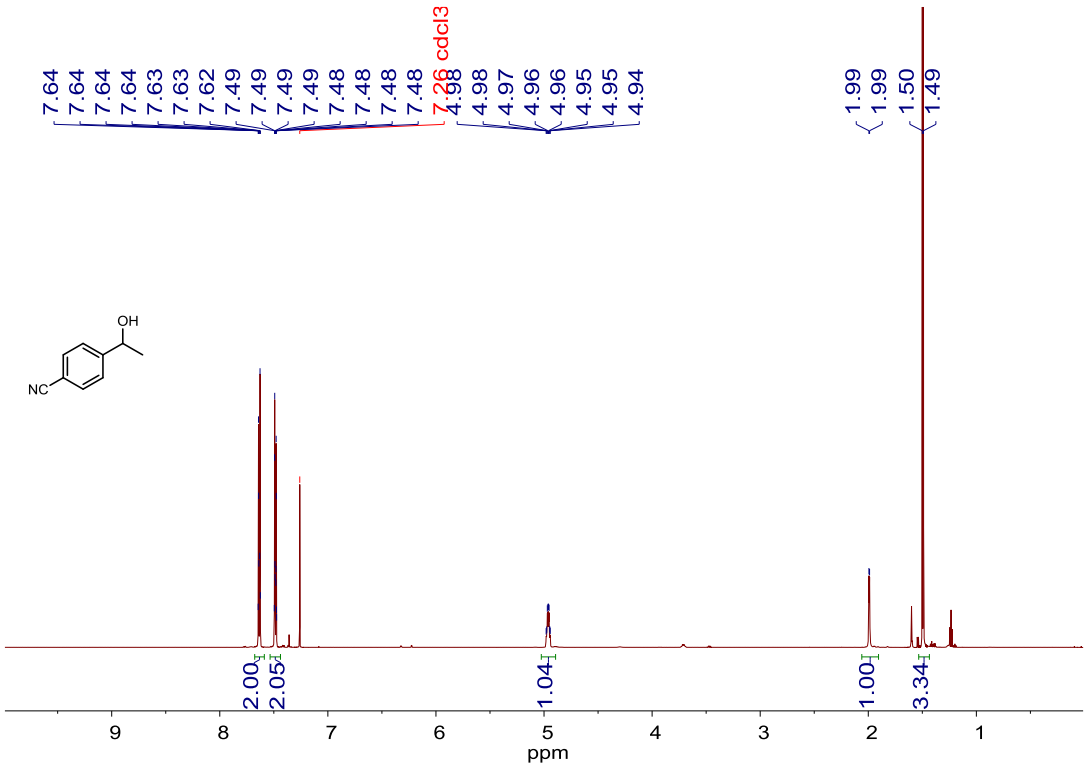


Figure S22. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(4-Cyanophenyl)ethanol**.

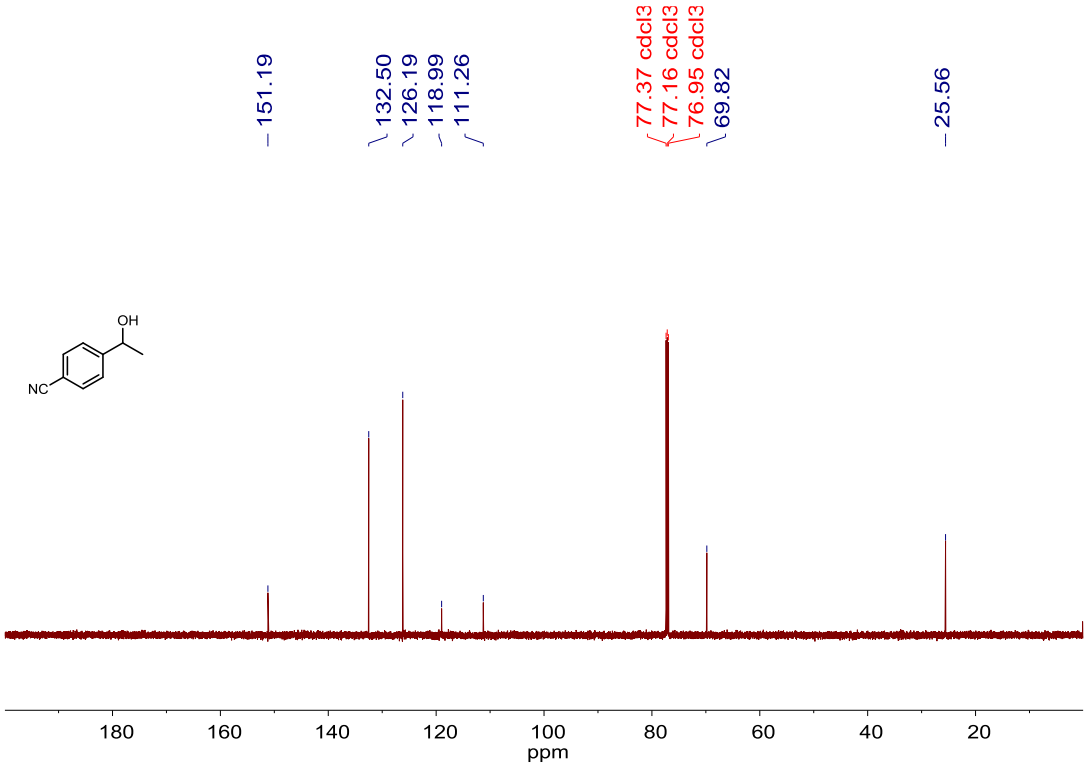


Figure S23. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(4-Cyanophenyl)ethanol**.

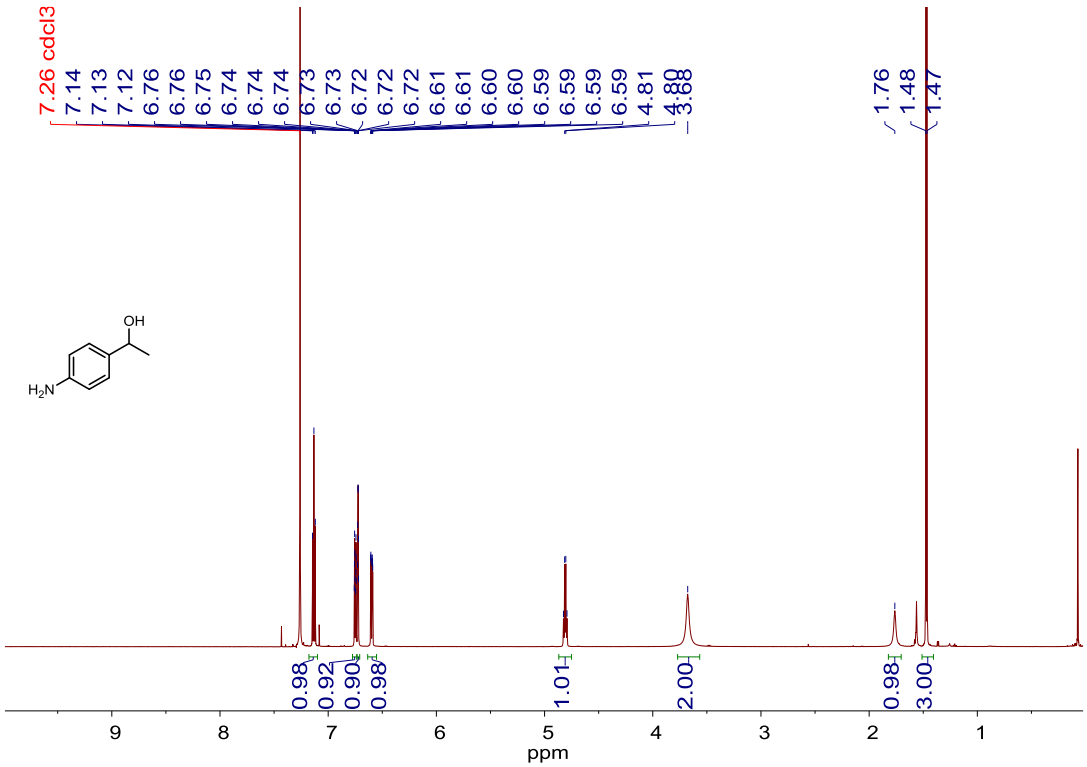


Figure S24. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(3-Aminophenyl)ethanol**.

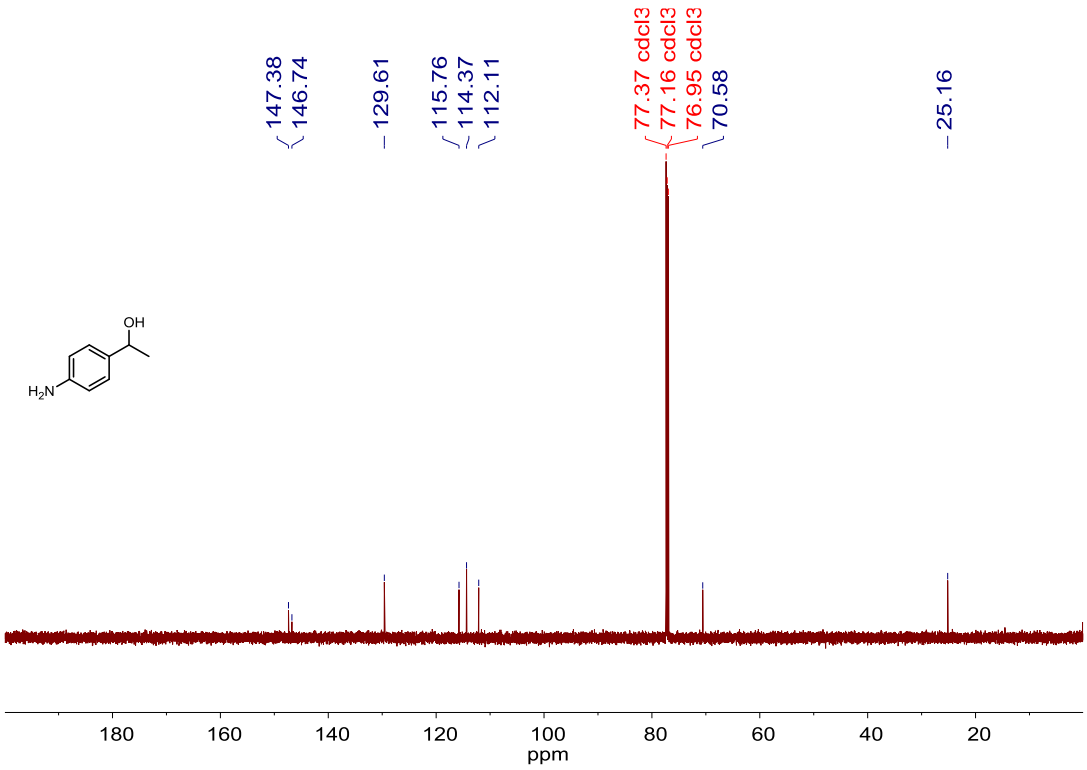


Figure S25. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(3-Aminophenyl)ethanol**.

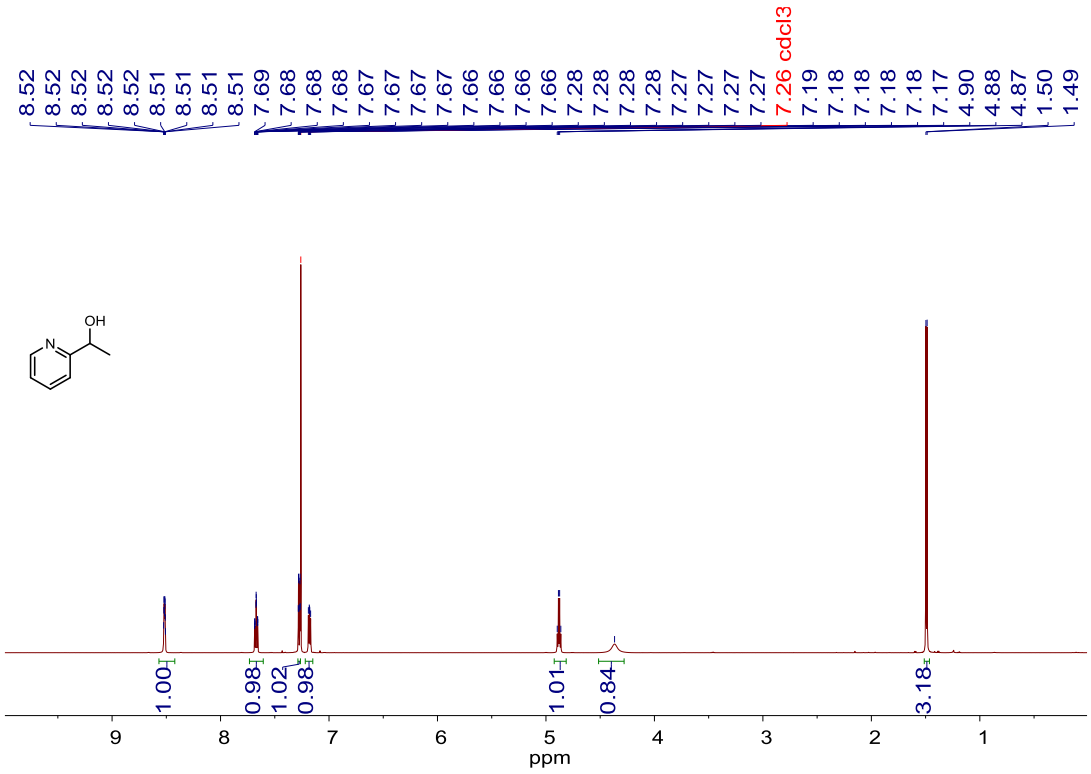


Figure S26. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(2-Pyridyl)ethanol**.

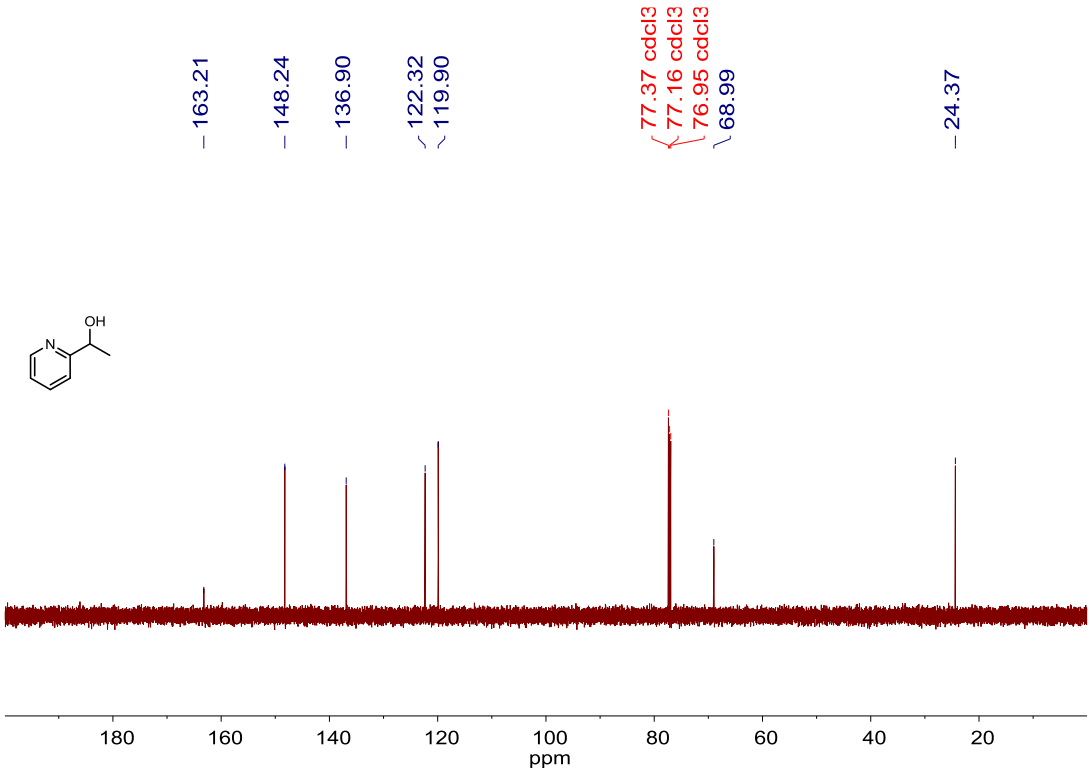


Figure S27. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(2-Pyridyl)ethanol**.

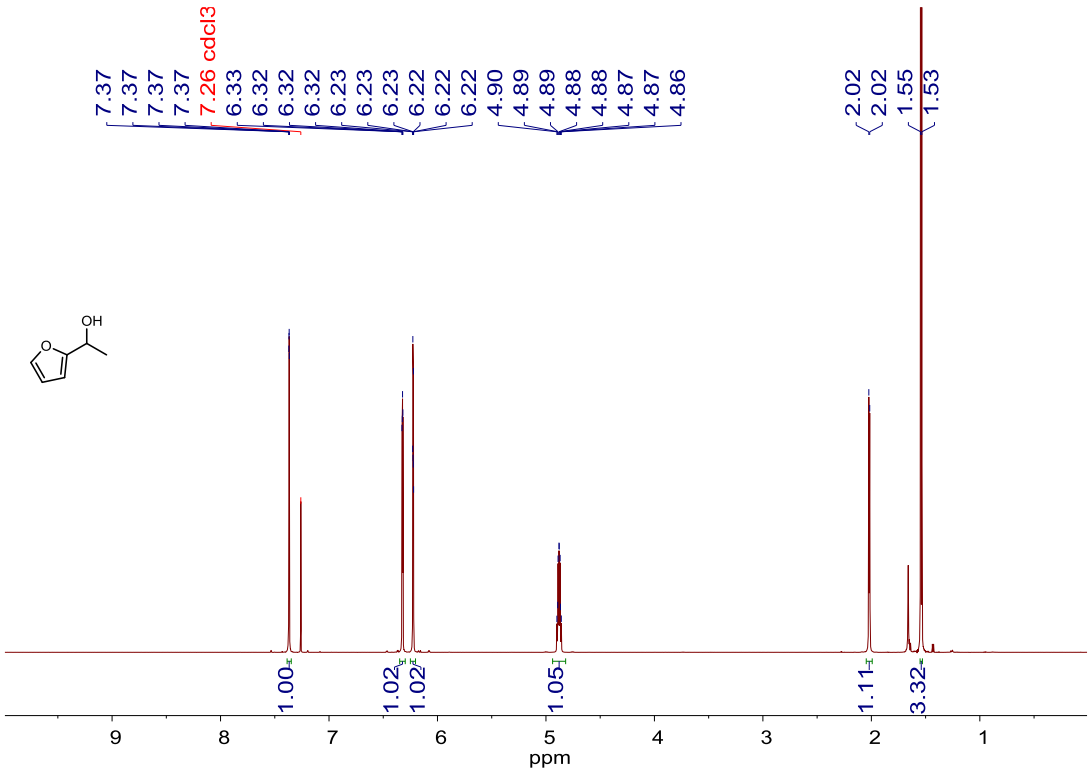


Figure S28. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(2-Furyl)ethanol**.

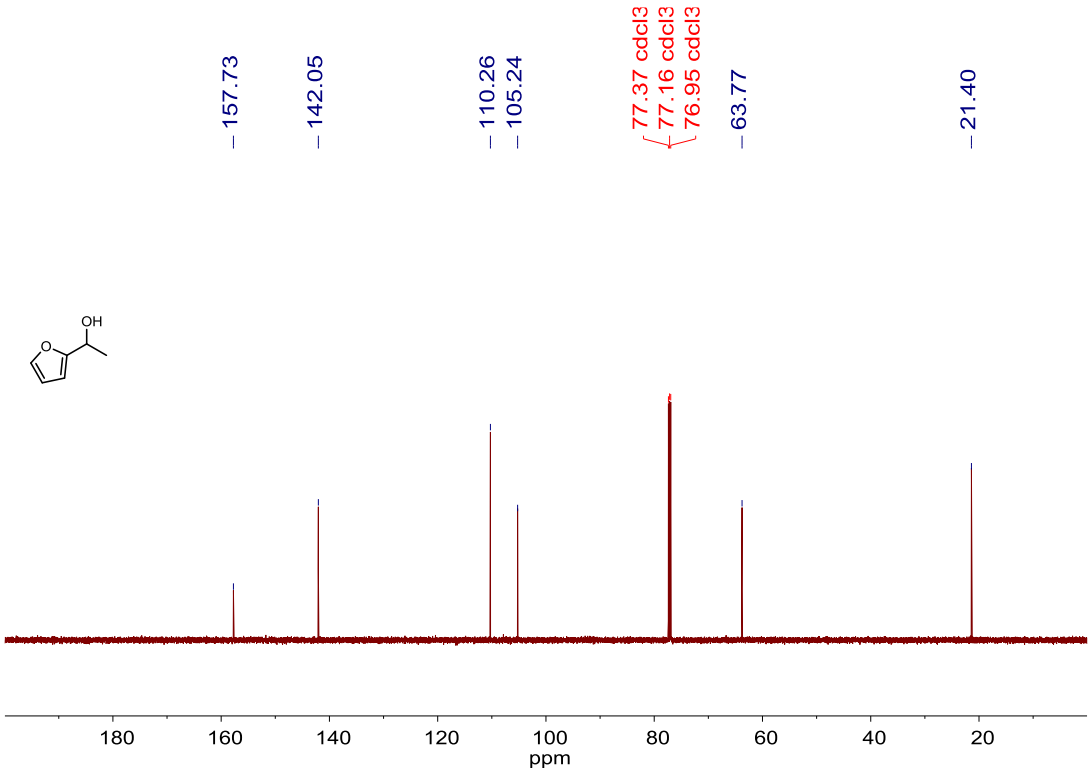


Figure S29. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(2-Furyl)ethanol**.

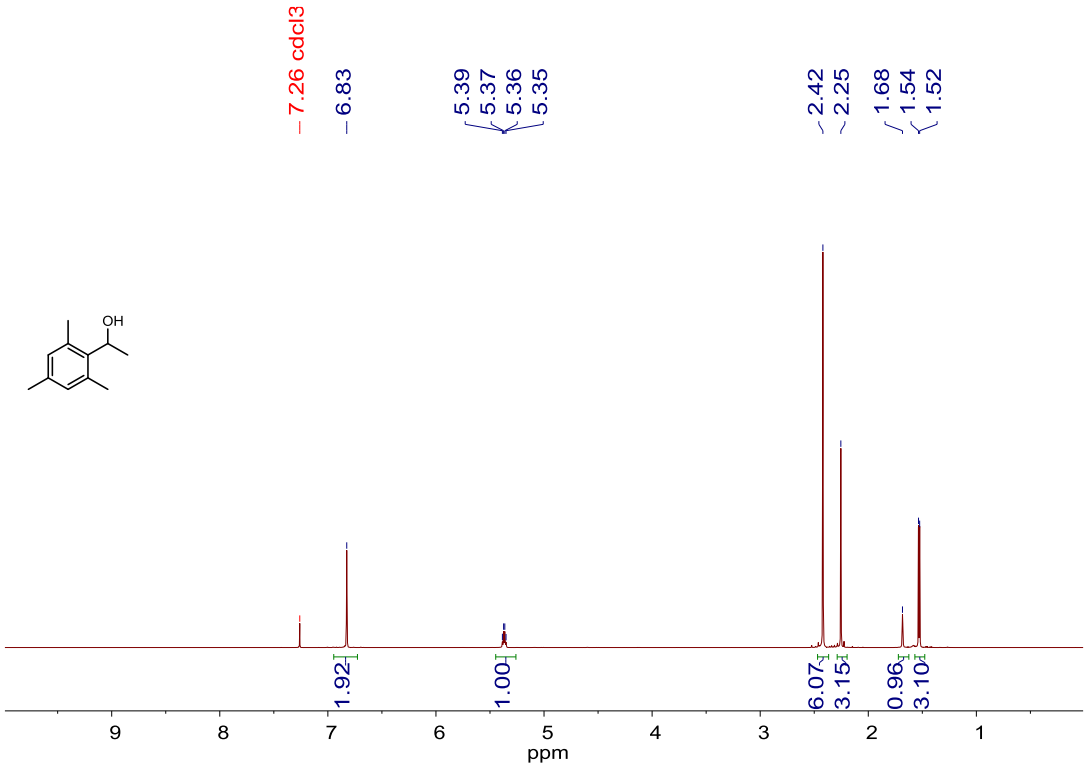


Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-(2,4,6-Trimethylphenyl)ethanol**.

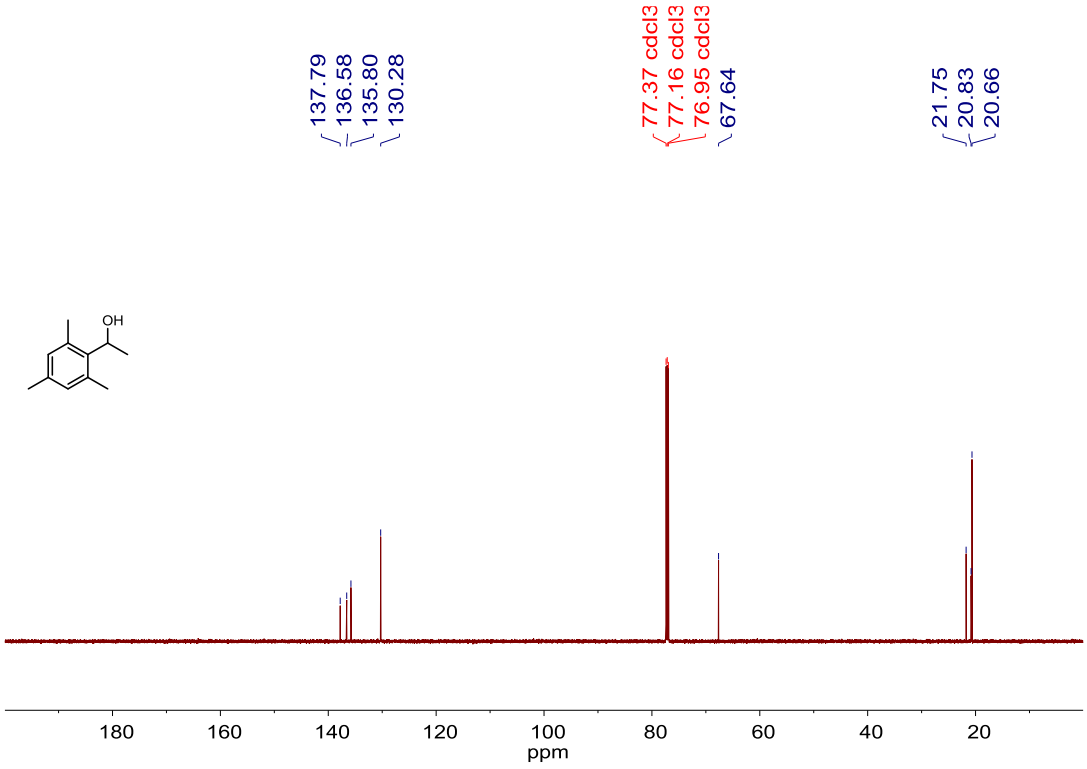


Figure S31. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-(2,4,6-Trimethylphenyl)ethanol**.

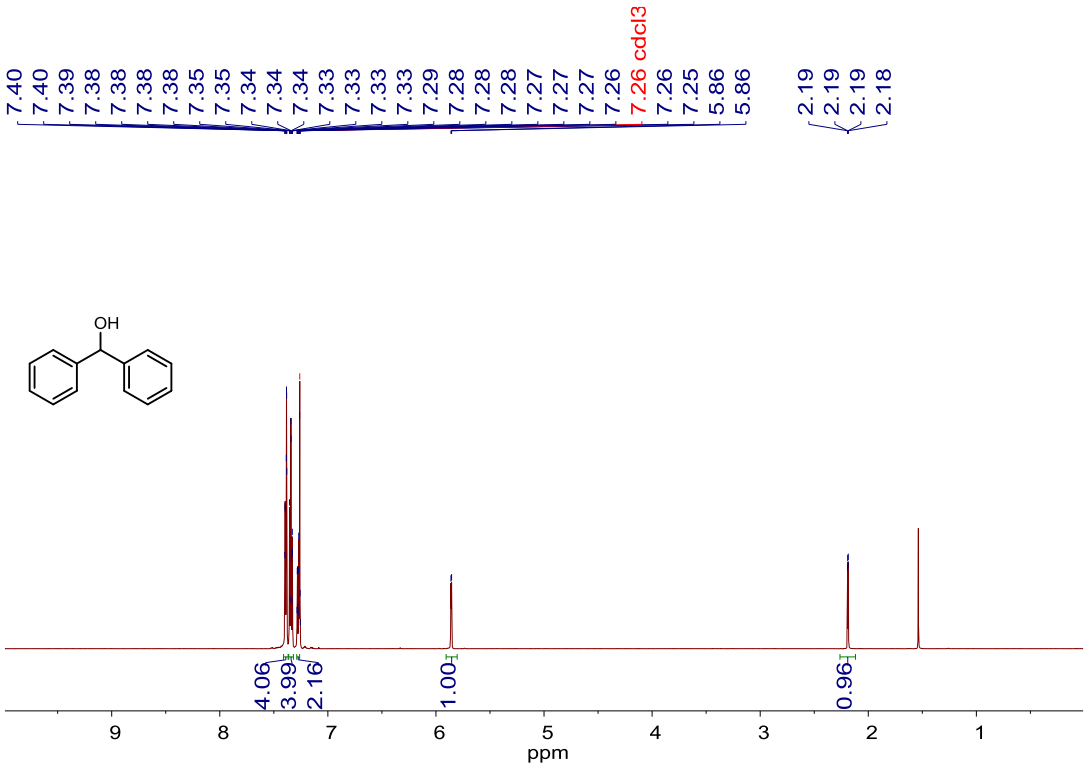


Figure S32. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **Diphenylmethanol**.

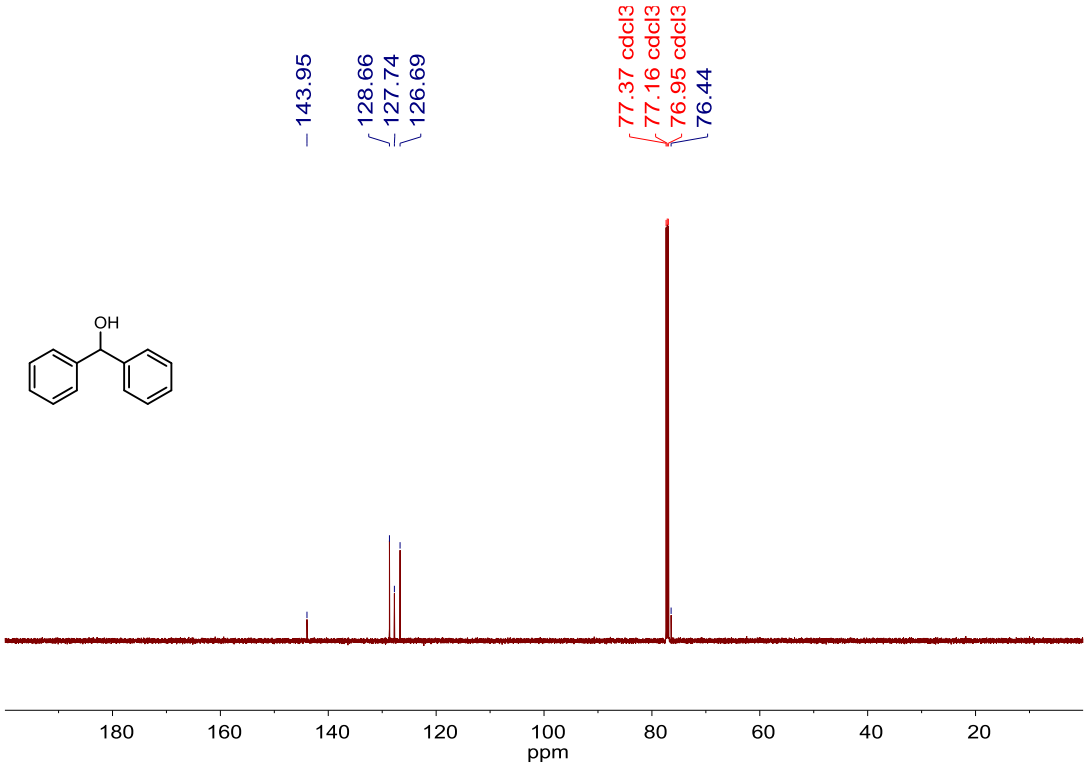


Figure S33. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **Diphenylmethanol**.

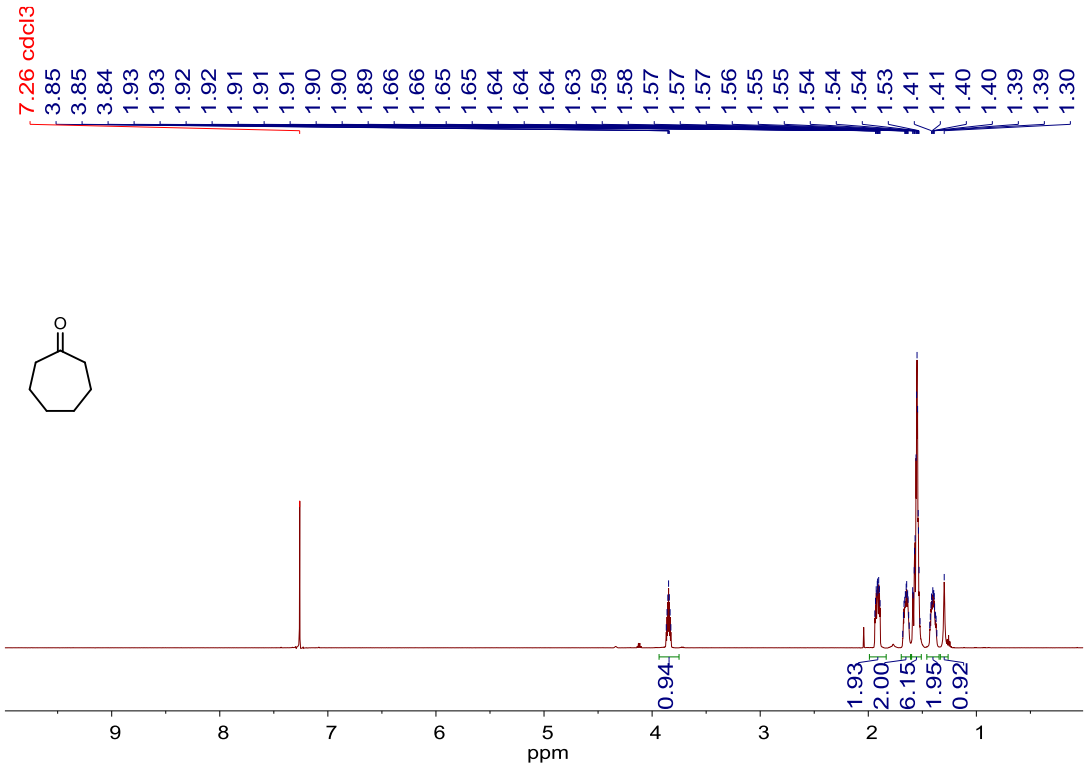


Figure S34. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **Cyclpheptanol**.

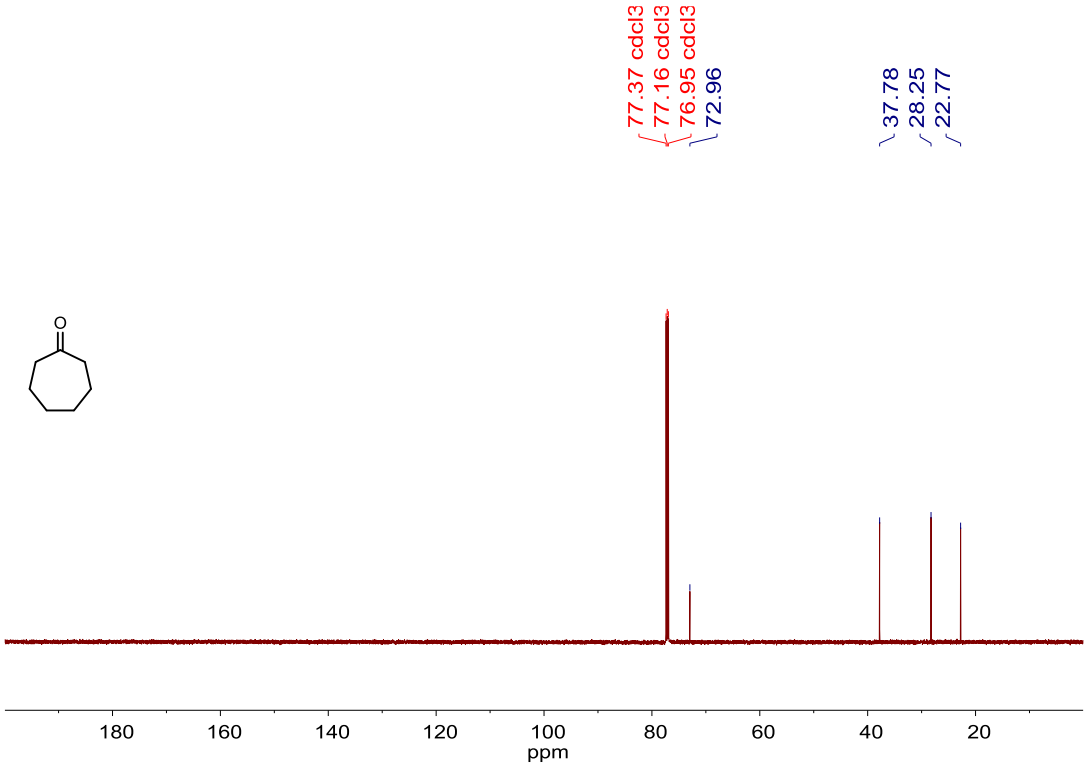


Figure S35. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **Cyclpheptanol**.

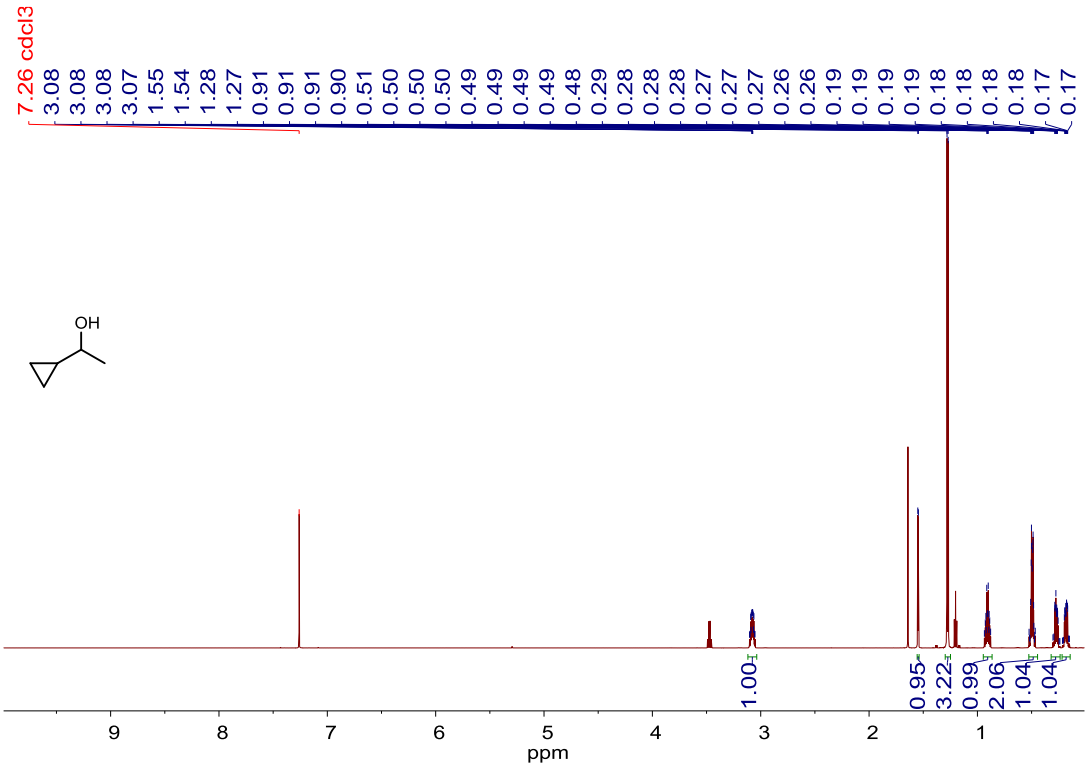


Figure S36. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-Cyclopropylethanol**.

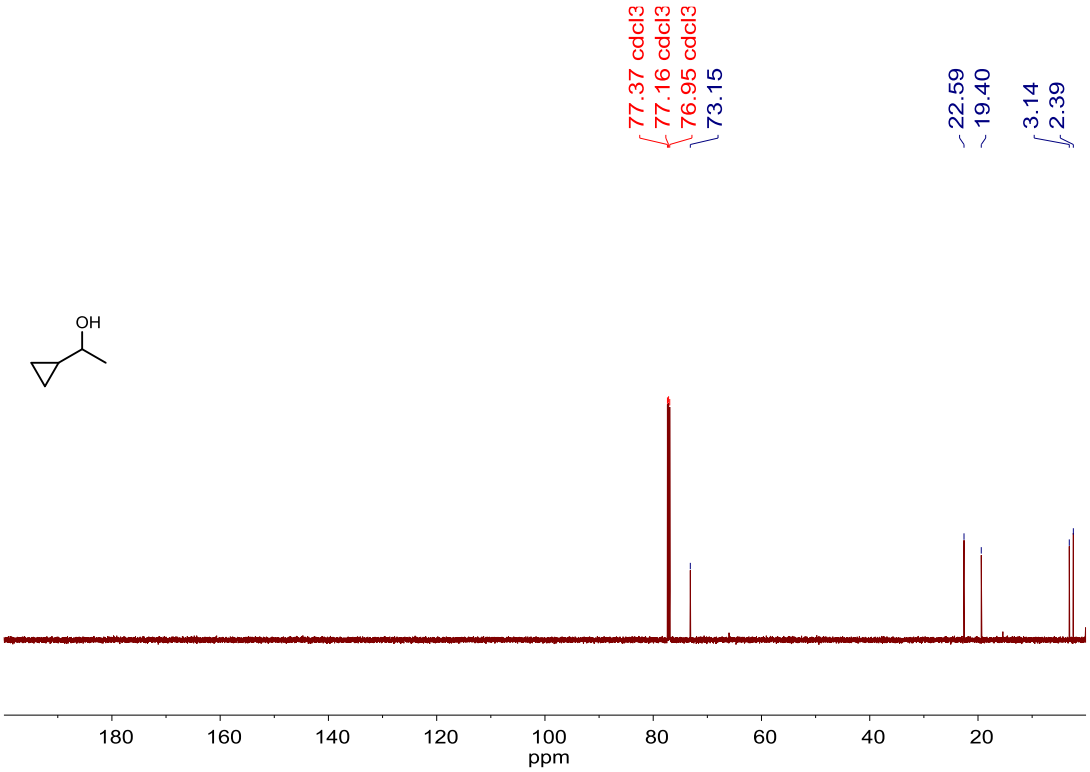


Figure S37. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-Cyclopropylethanol**.

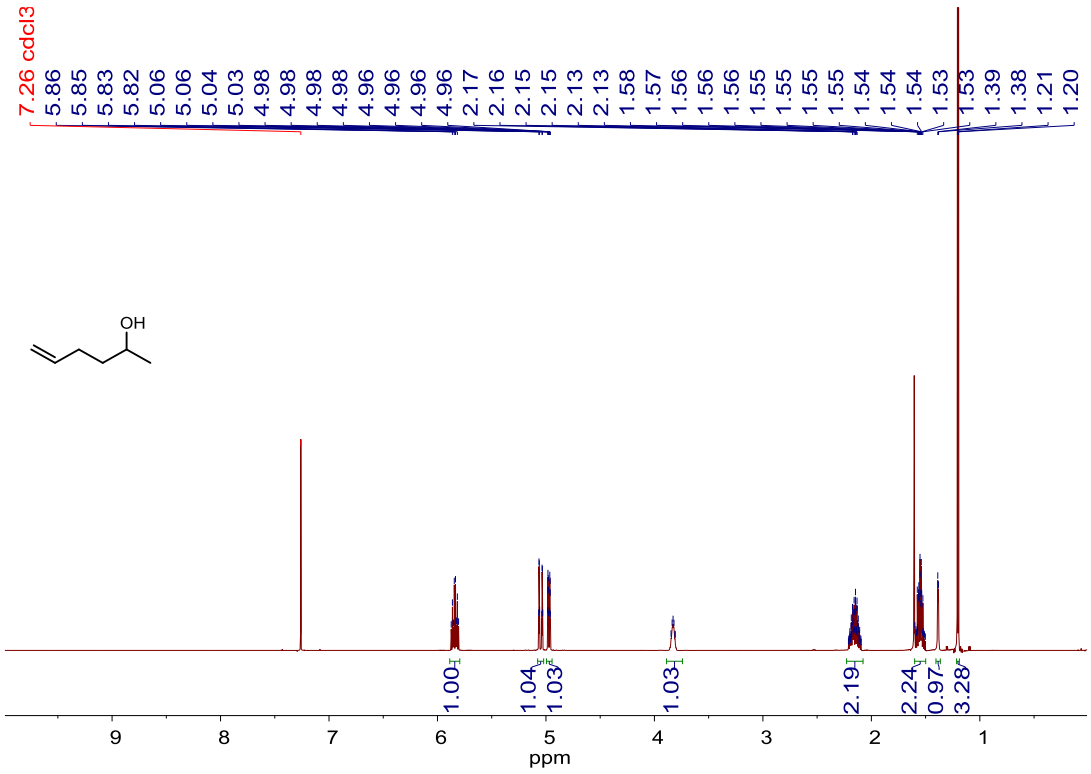


Figure S38. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5-Hexen-2-ol**.

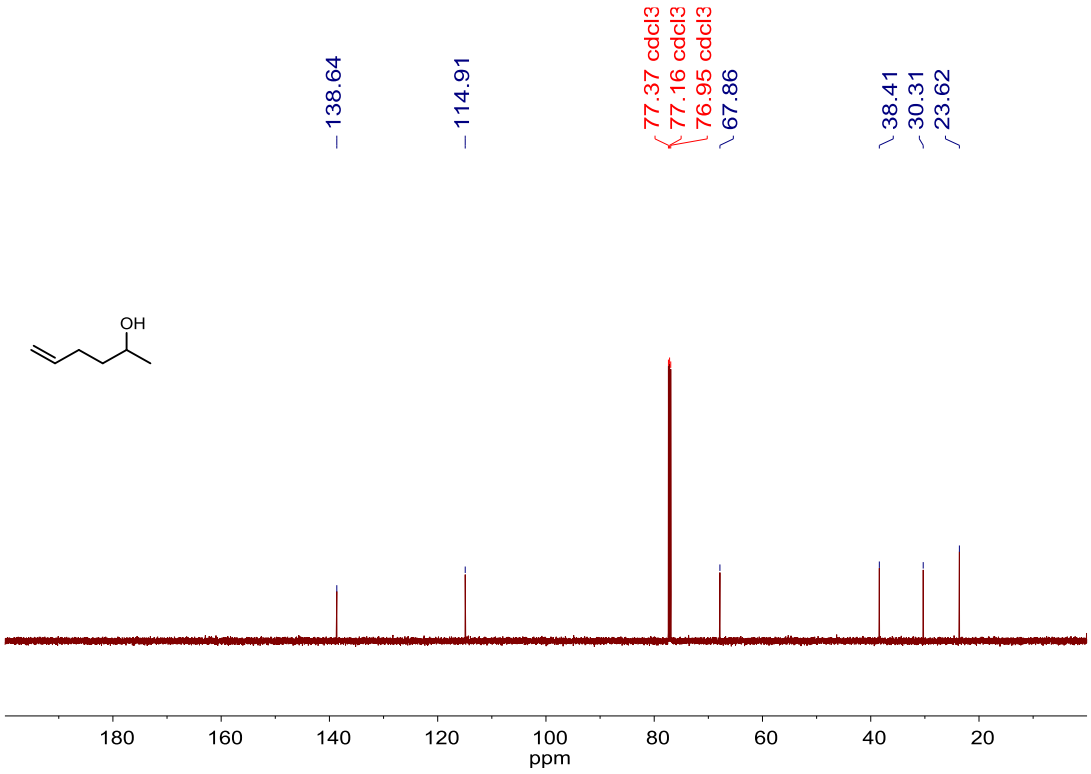


Figure S39. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5-Hexen-2-ol**.

5. References

(1) *Apex2 Software Package*; Bruker AXS Inc.: Madison, WI, 2013.

(2) Sheldrick, G. M. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3.

(3) http://shelx.uni-ac.gwdg.de/SHELX/index.php. (accessed on January 30, 2017).