Robust and efficient hydrogenation of carbonyl compounds catalyzed by *NN*-Mn(I) complexes

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Table of Contents

1.	General information	S2
2.	Synthesis and characterization of the manganese complexes	S4
3.	NMR ($^{1}H/^{13}C$) and IR spectra for **L1** – **L6** and their manganese complexes (**Mn1** – **Mn6**)	S9
4.	Catalyst optimization using **Mn1** as the precatalyst	S24
5	Single crystal X-ray diffraction studies	S31
6.	Characterization of selected alcohol products	S32
7.	References	S72

1. General information

All manipulations and their complexes were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. All the liquid substrates and solid substrates were used directly without further purification. Isopropyl alcohol (*i*-PrOH, 99.5+%, AR) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The bases (*t*-BuOK, *t*-BuONa, *i*-PrONa, NaOEt, NaOMe KOH, NaOH, $CsCO_3$, Na_2CO_3, $LiOH·H_2O$, LiOH, $Ca(OH)_2$, K_2CO_3, Na_2CO_3) are analytical reagent (98%, AR). $NaBHEt_3$ (1 M in THF) was purchased from Sigma-Aldrich, $MnBr(CO)_5$ and 6,7-dihydroquinolin-8(5H)-one were purchased from Shijiazhuang chiral chemical Co., LTD.. ^1H and ^{13}C NMR spectra were recorded on Bruker AV-400 NMR and Bruker AV-500 NMR spectrometers. Chemical shift values in ^1H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances. Chemical shifts (δ) are reported in ppm and spin-spin coupling constant (J) are expressed in Hz, and other data are reported as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. Infrared spectroscopy was performed in the solid state on a Bruker ALPHA. Elemental analysis was carried out with a Vario EL III CHN microanalyzer. GC analysis was carried out on a FuLi GC-9790Plus instrument (Zhe Jiang FuLi Analytical Instrument) using a PB-FFAP column (30m × 0.32mm × 0.25μm, Wuhan Puli Technology Co., Ltd.) or RB-WAX (30 m × 0.25 mm × 0.25 μm, Wuhan Puli Technology Co., Ltd.): injector temp. 300 °C; detector temp. 300 °C; column temp. 80 ºC; withdraw time 5 min, then 20 ºC/min to 200 ºC keeping for 5 min. and then 30 ºC/min to 250 ºC; withdraw time for 10 min.

Table S1 CAS numbers for substrates and products

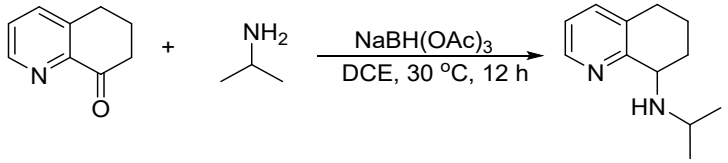
Products	CAS number	Substrates	CAS number
1-Phenylethanol	13323-81-4	Acetophenone	98-86-2
1-(4-Fluorophenyl)ethanol	403-41-8	4'-Fluoroacetophenone	403-42-9
1-(4-Chlorophenyl)ethanol	3391-10-4	4'-Chloroacetophenone	99-91-2
1-(4-Bromophenyl)ethanol	5391-88-8	4'-Bromoacetophenone	99-90-1
1-(4-Methylphenyl)ethanol	536-50-5	4'-Methylacetophenone	122-00-9
1-(4-Methoxyphenyl)ethanol	3319-15-1	4'-Methoxyacetophenone	100-06-1
1-(4-Nitrophenyl)ethanol	6531-13-1	4-Nitroacetophenone	100-19-6
4-(1-Hydroxyethyl)benzonitrile	52067-35-3	4-Acetylbenzonitrile	1443-80-7
1-(3-Methoxy-phenyl)ethanol	23308-82-9	3-Methoxyacetophenone	586-37-8
1-(3-Methyllphenyl)ethanol	25675-28-9	3'-Methylacetophenone	585-74-0
1-(3-Fluorophenyl)ethanol	402-63-1	3'-Fluoroacetophenone	455-36-7
1-(3-Chlorophenyl)ethanol	6939-95-3	3'-Chloroacetophenone	99-02-5
1-(3-Bromophenyl)ethanol	52780-14-0	3'-Bromoacetophenone	2142-63-4
1-(2-Methoxyphenyl)ethanol	13513-82-1	2'-Methoxyacetophenone	579-74-8
1-(2-Methylphenyl) ethanol	7287-82-3	2'-Methylacetophenone	577-16-2
1-(2-Fluorophenyl)ethanol	445-26-1	2'-Fluoroacetophenone	445-27-2
1-(2-Chlorophenyl)ethanol	13524-04-4	2'-Chloroacetophenone	2142-68-9
1-(2-Bromophenyl)ethanol	5411-56-3	2'-Bromoacetophenone	2142-69-0
1-(2,4-Dichlorophenyl)ethanol	1475-13-4	2',4'-Dichloroacetophenone	2234-16-4
1-(2,6-Dichlorophenyl)ethanol	53066-19-6	2',6'-Dichloroacetophenone	2040-05-3
1-(3,4-Dichlorophenyl)ethanol	1475-11-2	3',4'-Dichloroacetophenone	2642-63-9
1-Phenyl-1-butanol	614-14-2	Butyrophenone	495-40-9
1-(4-Methylphenyl)-1-propanol	25574-04-3	4'-Methylpropiophenone	5337-93-9

1-(3-chlorophenyl)propan-1-ol	32019-30-0	3'-Chloropropiophenone	34841-35-5
2-Methyl-1-phenyl-1-propanol	611-69-8	Isobutyrophenone	611-70-1
1-(1-Naphthyl)ethanol	57605-95-5	1'-Acetonaphthone	941-98-0
1-(2-Naphthyl)eyhanol	40295-80-5	2-Acetonaphthone	93-08-3
Cyclohexyl(phenyl)methanol	945-49-3	Benzoylcyclohexane	712-50-5
Benzhydrol	91-01-0	Benzophenone	119-61-9
1,2,3,4-Tetrahydro-1-naphthol	529-33-9	1-Tetralone	529-34-0
6,7,8,9-tetrahydro-5H-benzo [7]annulen-5-ol	35550-94-8	1-Benzosuberone	826-73-3
5,6,7,8-Tetrahydroquinolin-8-ol	14631-46-0	6,7-Dihydro-5H-quinolin-8-one	56826-69-8
1-(thiophen-2-yl)ethan-1-ol	78002-44-5	2-Acetylthiophene	88-15-3
1-Pyidin-2-yl-ethanol	18728-61-5	2-Acetylpyridine	1122-62-9
1-(2-Furyl)ethanol	4208-64-4	2-Acetylfuran	1192-62-7
1-(5-methylfuran-2-yl)ethan-1-ol	14003-15-7	2-Acetyl-5-methylfuran	1193-79-9
Cyclohexanol	108-93-0	Cyclohexanone	108-94-1
Cycloheptanol	502-41-0	Cycloheptanone	502-42-1
Cyclooctanol	96-41-3	Cyclooctanone	502-49-8
Cyclododecanol	1724-39-6	Cyclododecanone	830-13-7
4-Phenylcyclohexanol	5437-46-7	4-Phenylcyclohexanone	4894-75-1
4-t-Butylcyclohexanol	98-52-2	4-t-Butylcyclohexanone	98-53-3
3-Quinuclidinol	1619-34-7	3-Quinuclidinone	3731-38-2
DL-Menthol	89-78-1	Menthone	10458-14-7
1-phenylhexan-3-ol	2180-43-0	1-Phenylhexan-3-one	29898-25-7
4-Phenyl-2-butanol	2344-70-9	Benzylacetone	2550-26-7
4-phenyl-3-buten-2-ol	17488-65-2	Benzalacetone	122-57-6
Benzyl alcohol	100-51-6	Benzaldehyde	100-52-7
4-Methylbenzyl alcohol	589-18-4	p-Tolualdehyde	104-87-0
4-Fluorobenzyl alcohol	459-56-3	4-Fluorobenzaldehyde	459-57-4
4-Methoxybenzyl alcohol	105-13-5	p-Anisaldehyde	123-11-5
2-Naphthalenemethanol	1592-38-7	2-Naphthaldehyde	66-99-9
2-(Hydroxymethyl)pyridine	586-98-1	2-Pyridinecarboxaldehyde	1121-60-4
2-Thiophenemethanol	636-72-6	2-Thenaldehyde	98-03-3
Furfuryl alcohol	98-00-0	Furfural	98-01-1
1-Heptanol	111-70-6	Heptaldehyde	111-71-7
1-Octanol	111-87-5	Octanal	124-13-0

2 Synthesis and characterization of the ligands and manganese(I) complexes

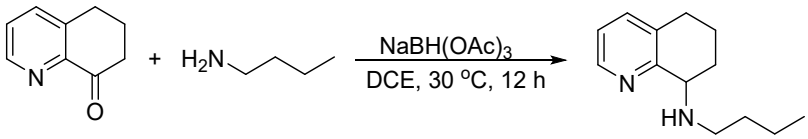
2.1. Synthesis of N-R-8-N(H)$C_9H_{10}N$ [L1 – L4][2]

2.1.1 Preparation of *N*-isopropyl-5,6,7,8-tetrahydroquinolin-8-amine (**L1**)



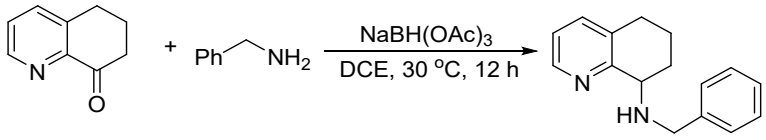
Similar to our previous work,[1,2a,2b] a mixture of 5,6,7-trihydroquinolin-8-one (1.47 g, 10 mmol), propan-2-amine (0.71 g, 12 mmol, 1.2 eq.) and sodium triacetoxyborohydride (6.33 g, 30 mmol, 3.0 eq.) were loaded in a 250 mL flask followed by 1,2-dichloroethane (DCE, 80 mL). The reaction mixture was stirred at 30 °C for 12 h. An aqueous saturated solution of $NaHCO_3$ (100 mL) was added to quench the reaction (pH > 8) and the mixture extracted with ethyl acetate (3 × 30 mL). The combined organic phases were dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The residue was purified by flash column chromatography using a gradient of petroleum ether/ EtOAc from 200:1 to 5:1 to afford **L1** as a yellow oil (1.72 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 4.1 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 7.5, 4.7 Hz, 1H), 3.88 (d, *J* = 6.3 Hz, 1H), 3.71 (s, 1H), 3.11 – 2.99 (m, 1H), 2.76 (dd, *J* = 13.3, 5.2 Hz, 2H), 2.12 (t, *J* = 11.5 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.79 – 1.68 (m, 2H), 1.16 (dd, *J* = 9.7, 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 146.8, 136.8, 132.3, 121.7, 55.1, 46.0, 29.2, 28.8, 24.6, 22.0, 19.6.

2.1.2 Preparation of *N*-butyl-5,6,7,8-tetrahydroquinolin-8-amine (**L2**)



Using a similar procedure and molar ratios to that described for **L1**, **L2** was obtained as a yellow oil (1.92 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.4 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.74 (t, *J* = 6.3 Hz, 1H), 2.78 – 2.66 (m, 4H), 2.17 – 2.05 (m, 1H), 1.96 (dd, *J* = 11.7, 6.2 Hz, 1H), 1.72 (ddd, *J* = 13.5, 9.5, 3.9 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.37 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 146.8, 146.7, 136.8, 136.7, 132.3, 121.7, 121.6, 58.1, 47.5, 47.5, 32.5, 28.8, 28.6, 20.6, 19.6, 14.0.

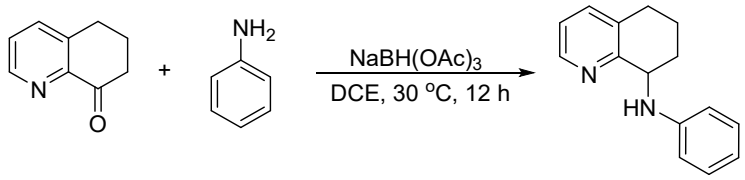
2.1.3 Preparation of *N*-benzyl-5,6,7,8-tetrahydroquinolin-8-amine (**L3**)



Using a similar procedure and molar ratios to that described for **L1**, **L3** was obtained as a yellow oil (2.25 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.1 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 14.3, 7.1 Hz, 3H), 7.22 – 7.16 (m, 1H), 7.00 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.94 (s, 1H), 3.82 (dd, *J* = 7.3, 5.6 Hz, 1H), 3.01 (s, 1H), 2.85 – 2.74 (m, 1H), 2.73 – 2.64 (m, 1H), 2.15 (dt, *J* =

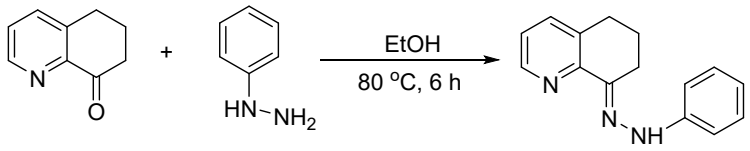
12.1, 5.1 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.83 – 1.74 (m, 1H), 1.72 – 1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 146.8, 140.5, 140.5, 136.9, 132.5, 128.4, 128.3, 127.1, 126.9, 121.9, 57.6, 51.8, 28.9, 28.6, 19.7.

2.1.4 Preparation of *N*-phenyl-5,6,7,8-tetrahydroquinolin-8-amine (**L4**)



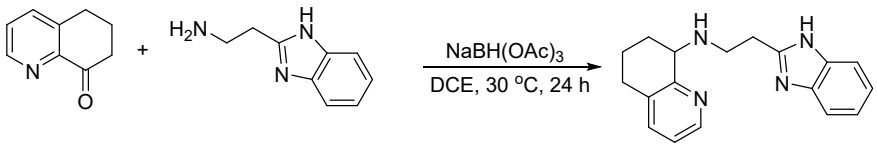
Using a similar procedure and molar ratios to that described for **L1**, **L4** was obtained as a white solid (1.32 g, 58%). Mp: 105 - 106 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.2 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 2H), 7.14 (dd, *J* = 7.6, 4.7 Hz, 1H), 6.79 – 6.71 (m, 3H), 4.51 (t, *J* = 5.5 Hz, 1H), 2.85 (q, *J* = 6.6 Hz, 2H), 2.01 – 1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 148.1, 147.2, 137.1, 132.8, 129.2, 122.3, 117.6, 113.8, 53.9, 29.1, 28.5, 19.2.

2.2. Preparation of 8-(2-phenylhydrazineylidene)-5,6,7,8-tetrahydroquinoline (L5)[2c]



The 5,6,7-trihydroquinolin-8-one (1.47 g, 10 mmol) was combined with freshly distilled phenylhydrazine (1.08 g, 10 mmol) in ethanol (10 mL) and the solution heated on a steam bath for 6 h. After cooling the red solution to room temperature, the resulting yellow crystals were collected by suction filtration, washed with cold ethanol (5 - 10 mL) and dried to give **L5** as a yellow solid (1.20 g, 50%). Mp: 114 – 115 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 14.00 (s, 1H), 8.51 (d, *J* = 4.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.15 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.83 (dd, *J* = 8.8, 4.3 Hz, 1H), 2.88 (t, *J* = 6.1 Hz, 2H), 2.85 – 2.80 (m, 2H), 2.05 – 1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 151.0, 145.3, 145.0, 136.8, 135.3, 133.0, 129.2, 121.8, 119.6, 112.8, 112.8, 34.1, 30.2, 22.8.

2.3. Preparation of *N*-(2-(1H-benzo[d]imidazol-2-yl)ethyl)-5,6,7,8-tetrahydroquinolin-8-amine (L6)

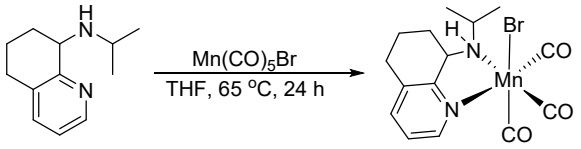


Using a similar procedure and molar ratios to that described for **L1**, **L6** was obtained as a yellow oil (1.65 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.3 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.49 – 7.42 (m, 1H), 7.21 – 7.11 (m, 3H), 3.95 (d, *J* = 6.4 Hz, 1H), 3.29 – 3.09 (m, 4H), 2.81 (dd, *J* = 12.2, 5.8 Hz, 2H), 2.17 (dd, *J* = 12.0, 5.2 Hz, 1H), 1.96 (dd, *J* = 12.1, 6.5 Hz, 1H), 1.89 – 1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.7, 146.5, 137.4, 133.1, 122.3, 121.7, 114.7, 57.0, 45.0, 29.0,

28.8, 28.7, 19.7.

2.4 Synthesis of manganese(I) complexes (Mn1 – Mn6)

2.4.1 Preparation of (N-*i*-Pr-8-$NHC_9H_{10}N$)$Mn(CO)_3Br$ (**Mn1**)[2]

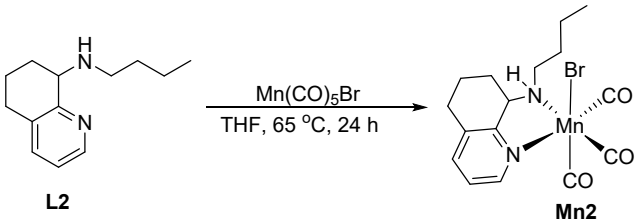


L1 **Mn1**

To a 25 mL Schlenk flask maintained under nitrogen, a solution of **L1** (190 mg, 1 mmol) in THF (5 mL) was added followed by an orange solution of $Mn(CO)_5Br$ (275 mg, 1 mmol) in THF (10 mL). The reaction mixture was then stirred and heated to 65 °C for 24 h. Once cooled to room temperature the mixture was concentrated under reduced pressure. The solid residue was washed with hexane (10 mL) and then dried to give **Mn1** as a yellow solid (365 mg, 89%). Single crystals of **Mn1** were obtained by layering a saturated solution of the complex in dichloromethane with diethyl ether at 5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 25.1 Hz, 1H), 7.54 (d, *J* = 4.7 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 4.21 (t, *J* = 13.5 Hz, 1H), 3.64 (t, *J* = 12.1 Hz, 1H), 3.30 – 3.16 (m, 1H), 2.90 – 2.79 (m, 1H), 2.68 (d, *J* = 6.0 Hz, 1H), 2.18 (d, *J* = 5.5 Hz, 1H), 1.85 – 1.74 (m, 1H), 1.56 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 222.9, 222.8, 222.1, 158.3, 152.1, 139.3, 135.1, 125.1, 63.0, 48.4, 27.6, 27.6, 23.2, 20.8, 19.1; IR (ATR, cm^{-1}, KBr): 1906 (s, ν_{CO}), 1922 (s, ν_{CO}), 2017 (s, ν_{CO}); Anal. Calcd for [$C_{15}H_{18}BrMnN_2O_3$ (Mw: 409.16)]: C, 44.03; H, 4.43; N, 6.85. Found: C, 44.11; H, 4.48; N, 6.84%.

2.4.2 Preparation of (N-*n*-Bu-8-$NHC_9H_{10}N$)$Mn(CO)_3Br$ (**Mn2**)

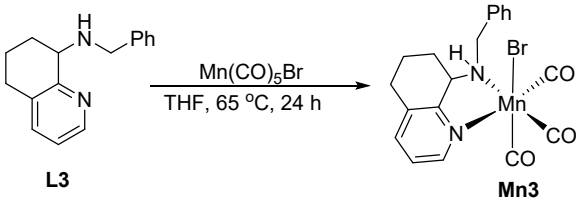


L2 **Mn2**

Using a similar procedure and molar ratios to that described for **Mn1**, **Mn2** was isolated as a yellow powder (392 mg, 92%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.76 (d, *J* = 4.9 Hz, 1H), 7.77 (s, 1H), 7.51 – 7.43 (m, 1H), 4.20 – 4.08 (m, 1H), 3.58 (d, *J* = 10.7 Hz, 1H), 3.32 (s, 1H), 3.16 (d, *J* = 5.3 Hz, 2H), 2.87 – 2.73 (m, 2H), 2.05 – 1.93 (m, 2H), 1.85 – 1.75 (m, 2H), 1.65 – 1.58 (m, 1H), 1.44 (dd, *J* = 14.4, 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 223.1, 222.5, 221.9, 158.0, 151.9, 139.3, 135.0, 125.1, 63.5, 51.0, 31.1, 28.7, 27.2, 20.7, 20.3, 14.2; IR (ATR, cm^{-1}, KBr): 1916 (s, ν_{CO}), 1938 (s, ν_{CO}), 2017(s, ν_{CO}); Anal. Calcd for [$C_{16}H_{20}BrMnN_2O_3$ (Mw: 423.19)]: C, 45.41; H, 4.76; N, 6.62. Found: C, 45.49; H, 4.78; N, 6.60%.

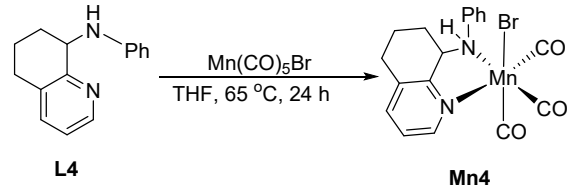
2.4.3 Preparation of (N-Bn-8-$NHC_9H_{10}N$)$Mn(CO)_3Br$ (**Mn3**)



Using a similar procedure and molar ratios to that described for **Mn1**, **Mn3** was isolated as a yellow powder (413 mg, 90%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.76 (s, 1H), 7.75 (s, 1H), 7.53 (s, 1H), 7.41 (d, *J* = 29.7 Hz, 5H), 4.63 – 4.47 (m, 1H), 4.33 (d, *J* = 42.5 Hz, 2H), 3.33 (s, 1H), 2.77 (d, *J* = 14.7 Hz, 2H), 2.62 – 2.55 (m, 1H), 1.95 (s, 1H), 1.67 (d, *J* = 99.8 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 222.4, 220.7, 219.9, 160.0, 150.5, 139.1, 135.3, 129.3, 128.9, 128.7, 128.4, 128.1, 127.7, 124.2, 62.9, 53.8, 27.6, 26.0, 21.4; IR (ATR, cm^{-1}, KBr): 1904 (s, ν_{CO}), 1936 (s, ν_{CO}), 2019 (s, ν_{CO}); Anal. Calcd for [$C_{19}H_{18}BrMnN_2O_3$ (Mw: 457.21)]: C, 49.91; H, 3.97; N, 6.13. Found: C, 49.91; H, 4.02; N, 6.15%.

2.4.4 Preparation of (N-Ph-8-$NHC_9H_{10}N$)$Mn(CO)_3Br$ (**Mn4**)

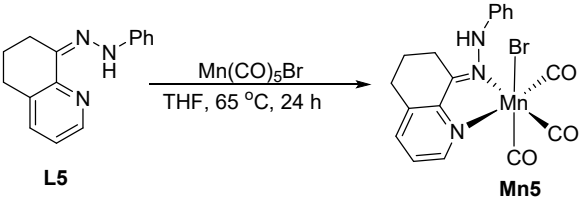


Using a similar procedure and molar ratios to that described for **Mn1**, **Mn4** was isolated as a yellow powder (365 mg, 82%).

^{1}H NMR (400 MHz, DMSO-d_6)* δ 8.79 (s, 1H), 7.84 (s, 1H), 7.50 (d, *J* = 29.6 Hz, 5H), 7.21 (s, 1H), 5.78 (br, 1H), 5.06 (s, 1H), 2.81 (d, *J* = 35.1 Hz, 2H), 1.92 (dd, *J* = 55.8, 25.3 Hz, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 223.1, 222.5, 220.7, 158.6, 157.2, 152.2, 150.9, 147.5, 139.4, 135.3, 129.9, 125.5, 64.1, 27.5, 27.2, 20.6; IR (ATR, cm^{-1}, KBr): 1907 (s, ν_{CO}), 1949 (s, ν_{CO}), 2023(s, ν_{CO}); Anal. Calcd for [$C_{18}H_{16}BrMnN_2O_3$ (Mw: 443.18)]: C, 48.78; H, 3.64; N, 6.32. Found: C, 48.81; H, 3.68; N, 6.31%.

***Mn4** may be contaminated with traces of paramagnetic material giving broad ^{1}H NMR peaks

2.4.5 Preparation of (N-Ph-8-$NHC_9H_{10}N$)$Mn(CO)_3Br$ (**Mn5**)

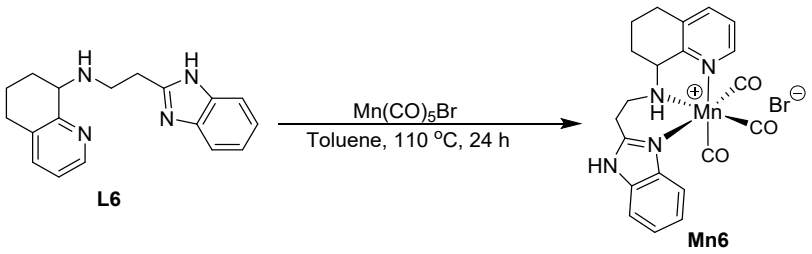


Using a similar procedure and molar ratios to that described for **Mn1**, **Mn5** was isolated as a yellow powder (408 mg, 89%).

^{1}H NMR (400 MHz, DMSO-d_6)* δ 9.79 (br, 1H), 8.99 (d, *J* = 5.2 Hz, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.99 (t, *J* = 6.9 Hz, 1H), 2.98 (t, *J* = 17.2 Hz, 4H), 1.98 – 1.83 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 223.2, 221.2, 219.0, 167.6, 151.8, 145.0, 140.2, 138.7, 129.0, 126.5, 122.2, 118.1, 28.6, 27.6, 21.1; IR (ATR, cm^{-1}, KBr): 1919 (s, ν_{CO}), 1942 (s, ν_{CO}), 2027 (s, ν_{CO}); Anal. Calcd for [$C_{18}H_{15}BrMnN_3O_3$ (*M*w: 456.18)]: C, 47.39; H, 3.31; N, 9.21. Found: C, 47.40; H, 3.33; N, 9.28%.

***Mn5** may be contaminated with traces of paramagnetic material giving broad ^{1}H NMR peaks.

2.4.6 Preparation of **Mn6**



To a 25 mL Schlenk flask maintained under nitrogen, a solution of **L6** (292 mg, 1 mmol) in toluene (5 mL) was added followed by an orange solution of $Mn(CO)_5Br$ (275 mg, 1 mmol) in toluene (10 mL). The reaction mixture was then stirred and heated at 110 °C for 24 h. Once cooled to room temperature the mixture was concentrated under reduced pressure. The solid residue was washed with *n*-hexane (10 mL) and then dried to give **Mn6** as a green-yellow solid (426 mg, 83%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.73 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 6.3 Hz, 2H), 6.86 (br, 1H), 4.54 (d, *J* = 4.9 Hz, 1H), 3.07 (br, 2H), 2.80 (br, 2H), 2.22 (br, 1H), 2.07 (dd, *J* = 22.2, 11.9 Hz, 2H), 1.90 (d, *J* = 9.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 220.2, 219.8, 218.9, 159.7, 158.8, 151.5, 151.4, 140.0, 139.8, 135.7, 135.6, 125.5, 125.1, 123.9, 123.7, 123.4, 123.0, 117.0, 113.4, 67.4, 65.1, 27.5, 26.6, 25.5, 21.1; IR (ATR, cm^{-1}, KBr): 1912 (s, ν_{CO}), 1930 (s, ν_{CO}), 2027(s, ν_{CO}); Anal. Calcd for [$C_{21}H_{20}BrMnN_4O_3$ (Mw: 511.26)]: C, 49.34; H, 3.94; N, 10.96. Found: C, 49.40; H, 3.98; N, 10.94%.

2.4.7 Complexes **Mn7** – **Mn10** was synthesized and characterized according to the procedure reported by ourselves.[2]

3. NMR ($^{1}H/^{13}C$) and IR spectra for L1 – L6 and their manganese complexes (Mn1 – Mn6)

Figure S1 The ^{1}H and ^{13}C NMR spectra for **L1** in $CDCl_3$

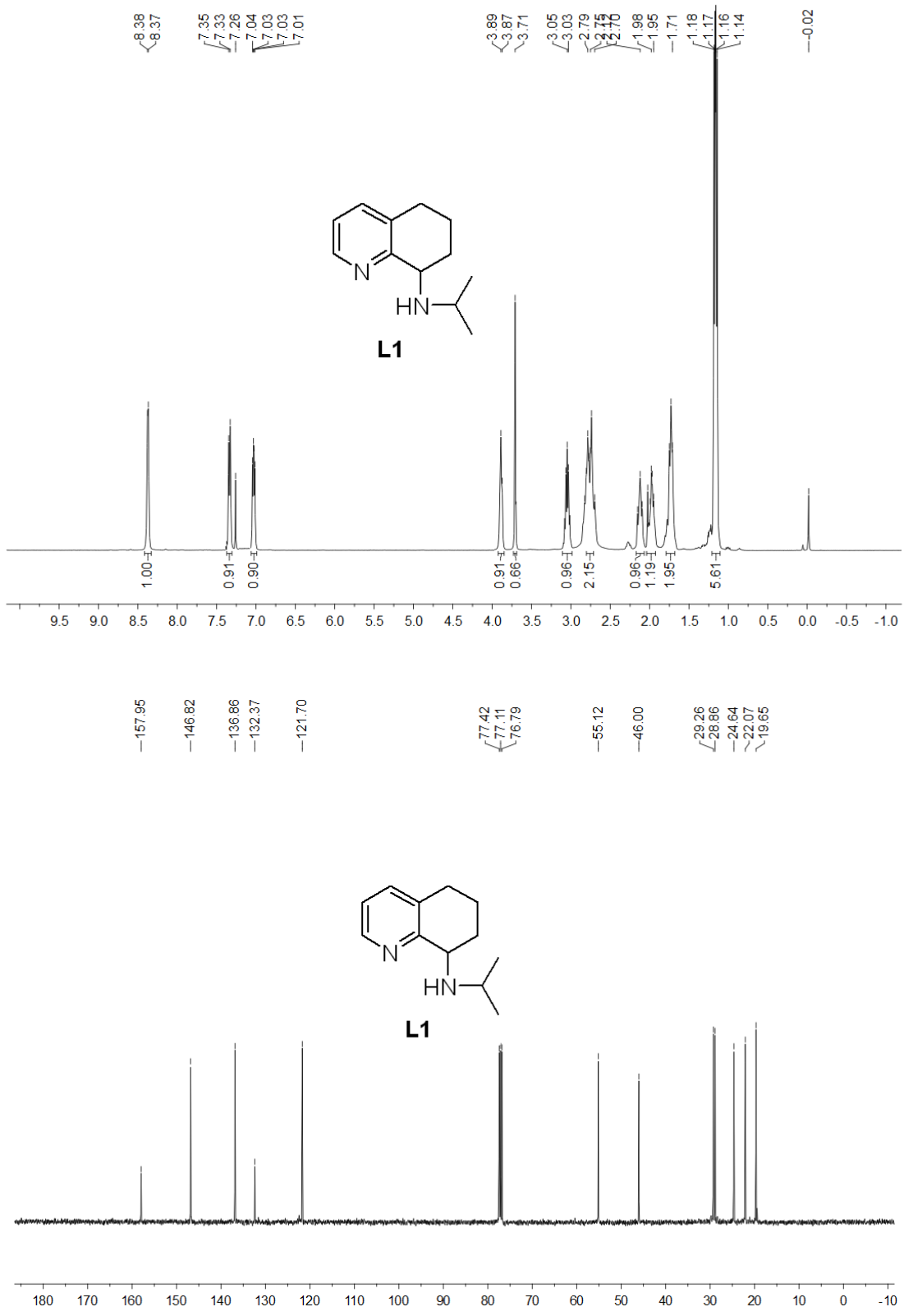


Figure S2 The ^{1}H and ^{13}C NMR spectra for **L2** in $CDCl_3$

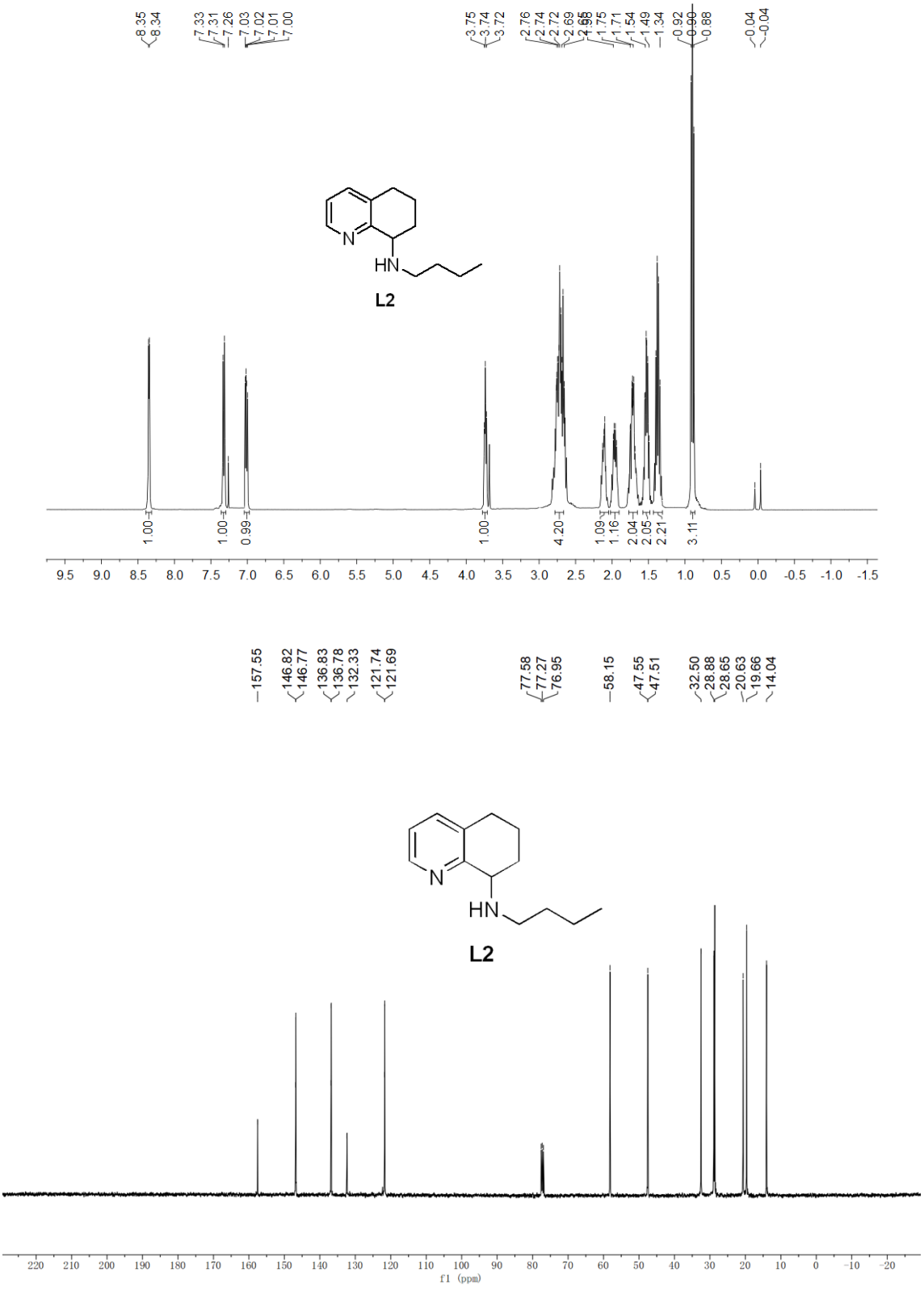


Figure S3 The ^{1}H and ^{13}C NMR spectra for **L3** in $CDCl_3$

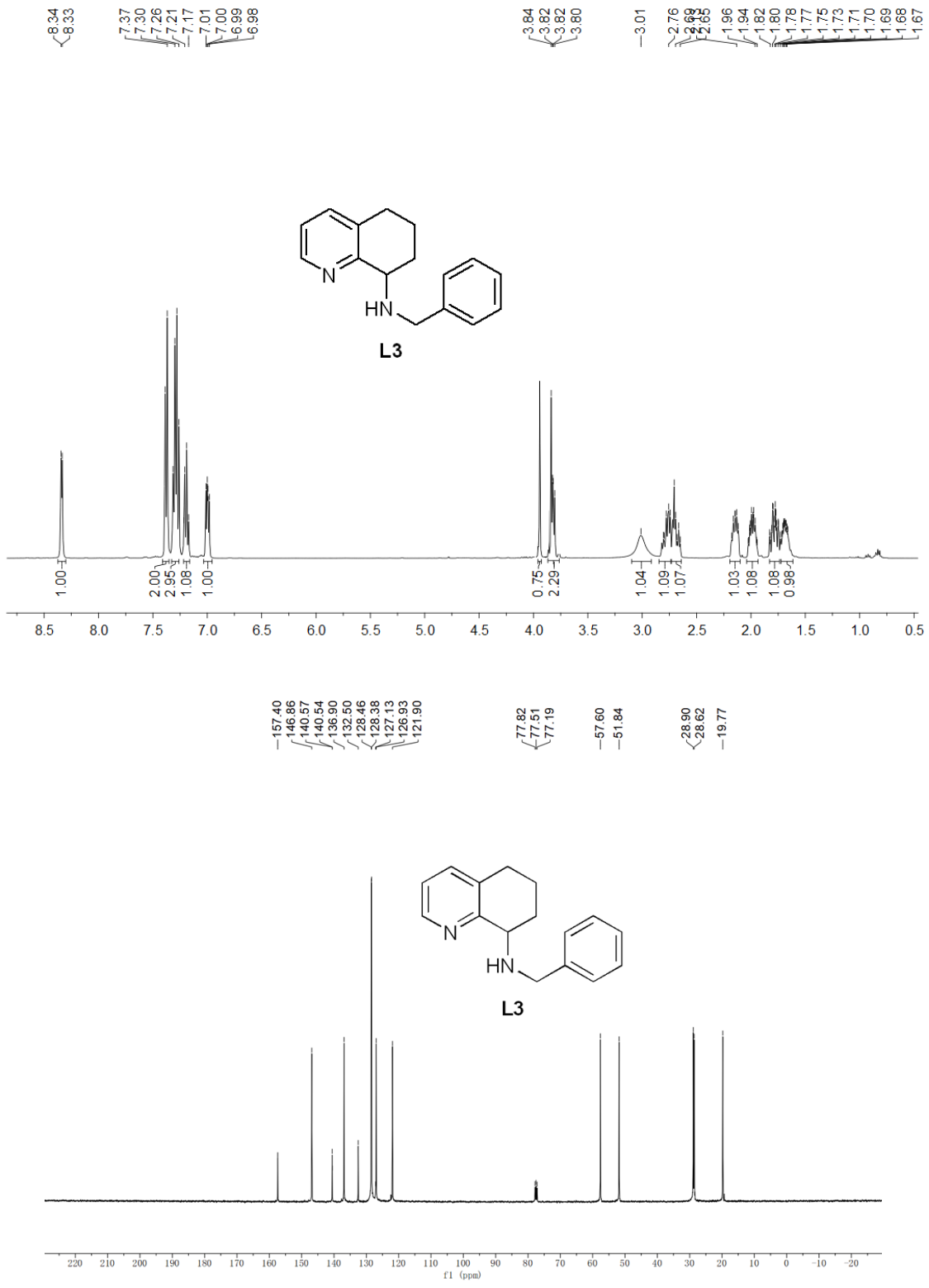


Figure S4 The ^{1}H and ^{13}C NMR spectra for **L4** in $CDCl_3$

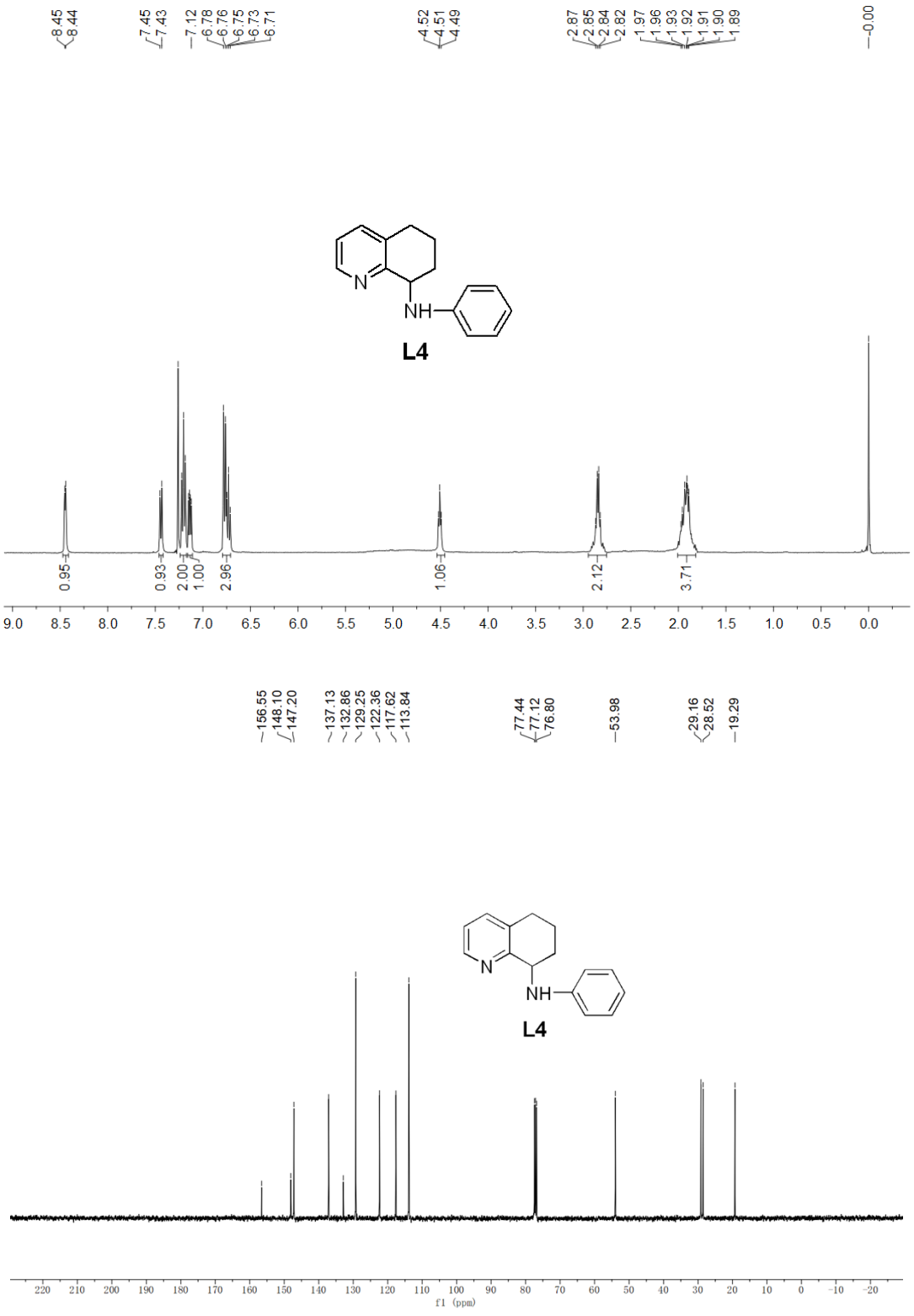


Figure S5 The ^{1}H and ^{13}C NMR spectra for **L5** in $CDCl_3$

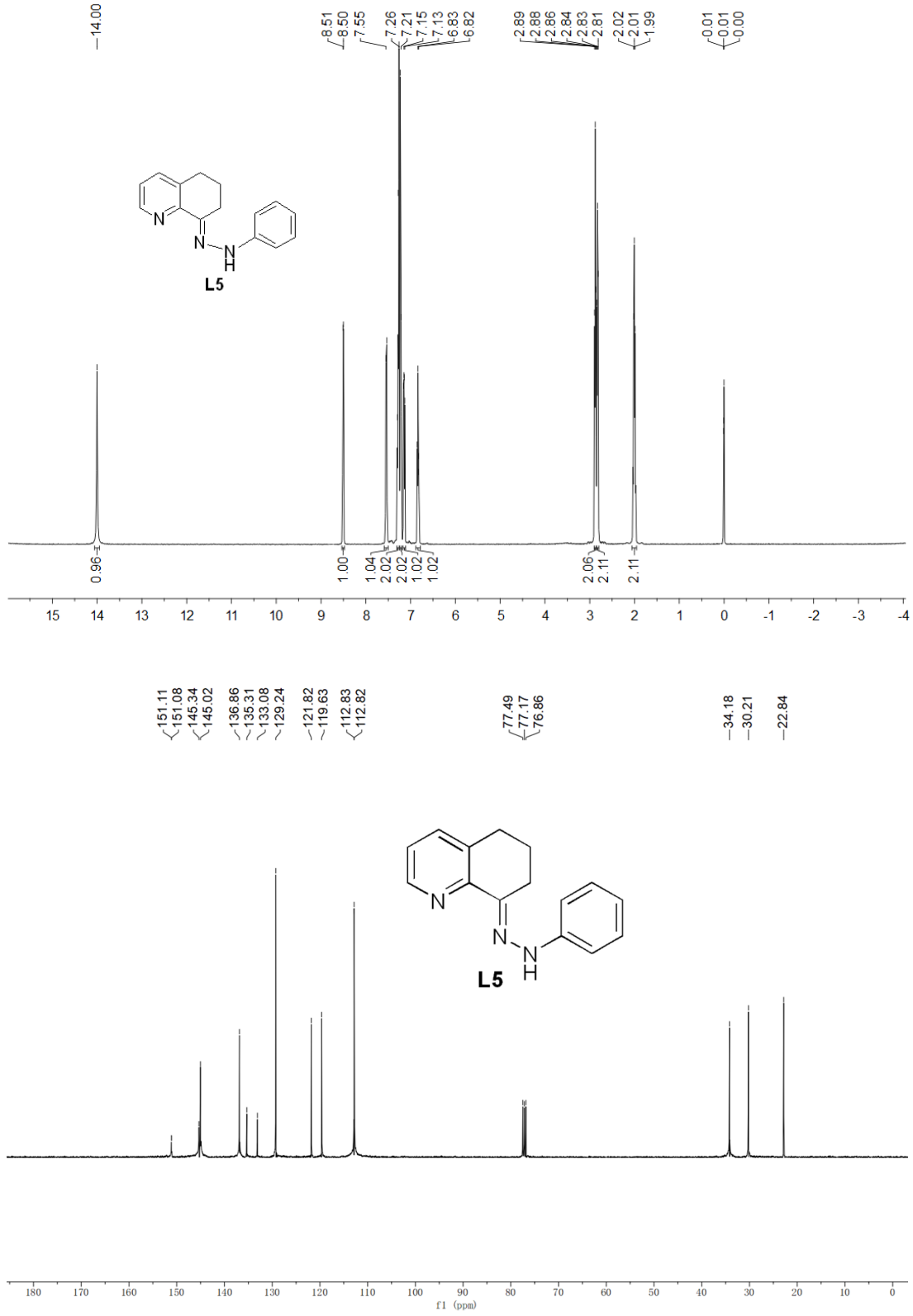


Figure S6 The ^{1}H and ^{13}C NMR spectra for **L6** in $CDCl_3$

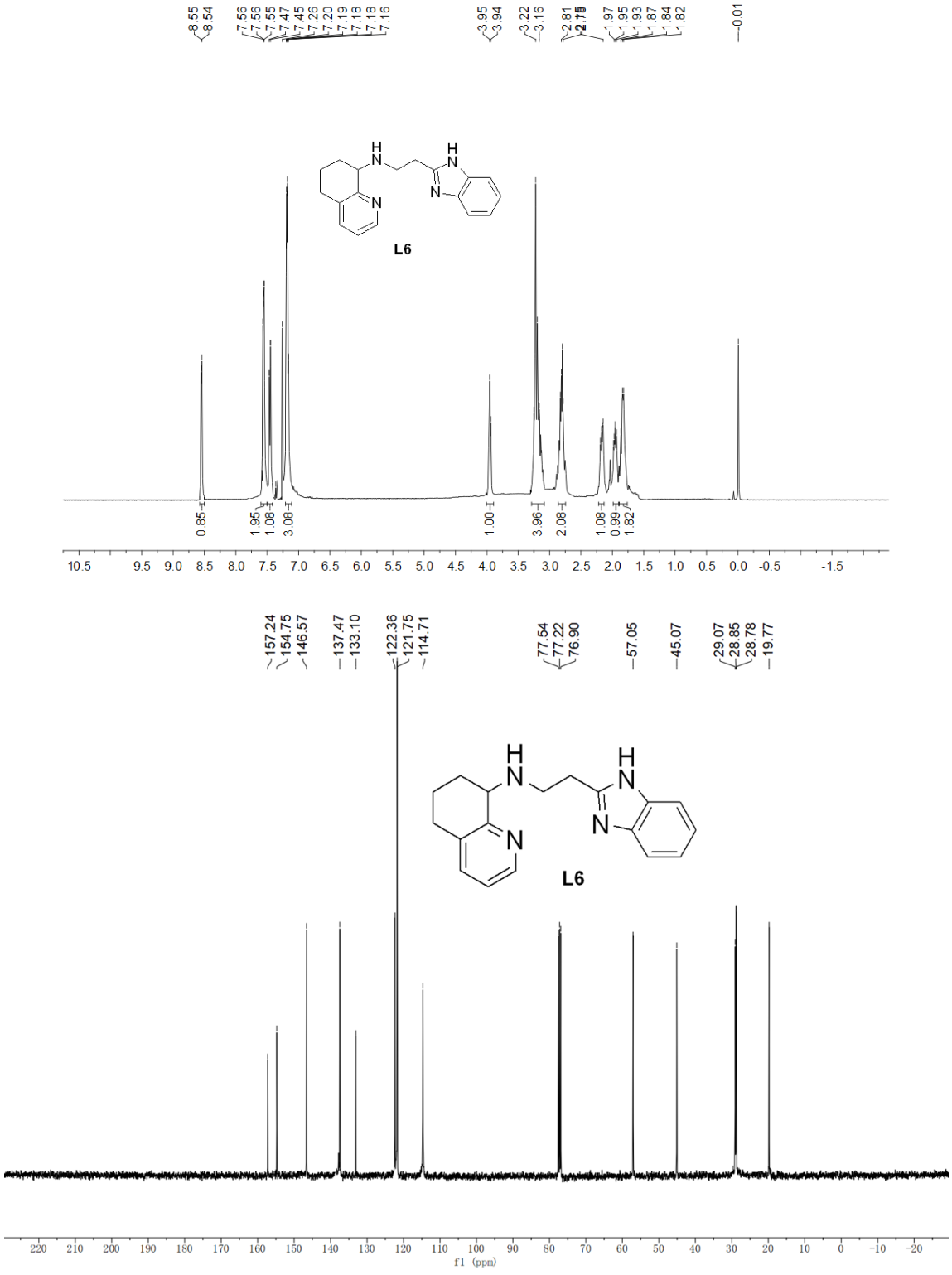


Figure S7 The ^{1}H NMR (in $CDCl_3$) and ^{13}C NMR (in DMSO-d_6) spectra for **Mn1**

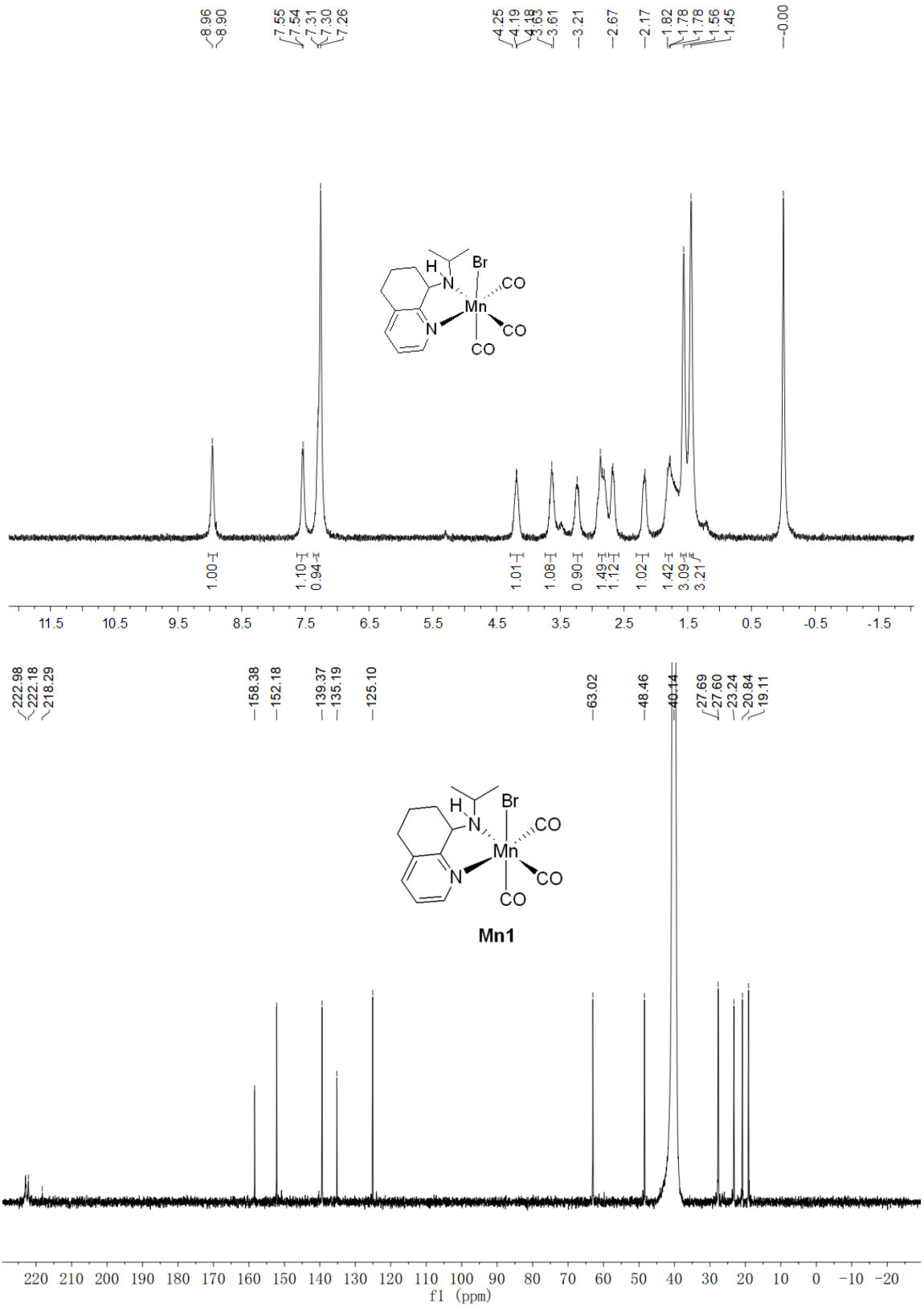


Figure S8 The ^{1}H and ^{13}C NMR spectra for **Mn2** in DMSO-d_6

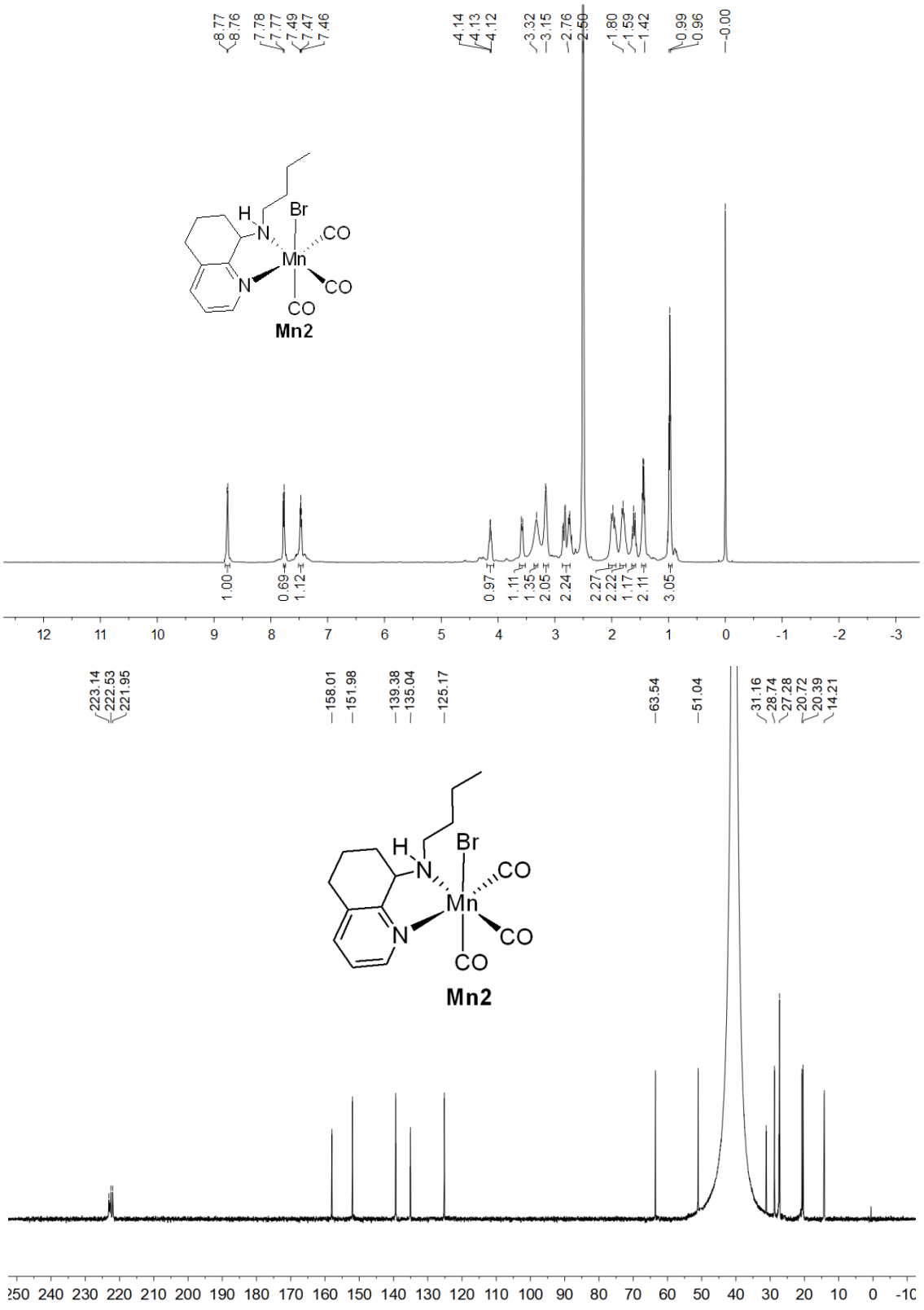


Figure S9 The ^{1}H and ^{13}C NMR spectra for **Mn3** in DMSO-d_6

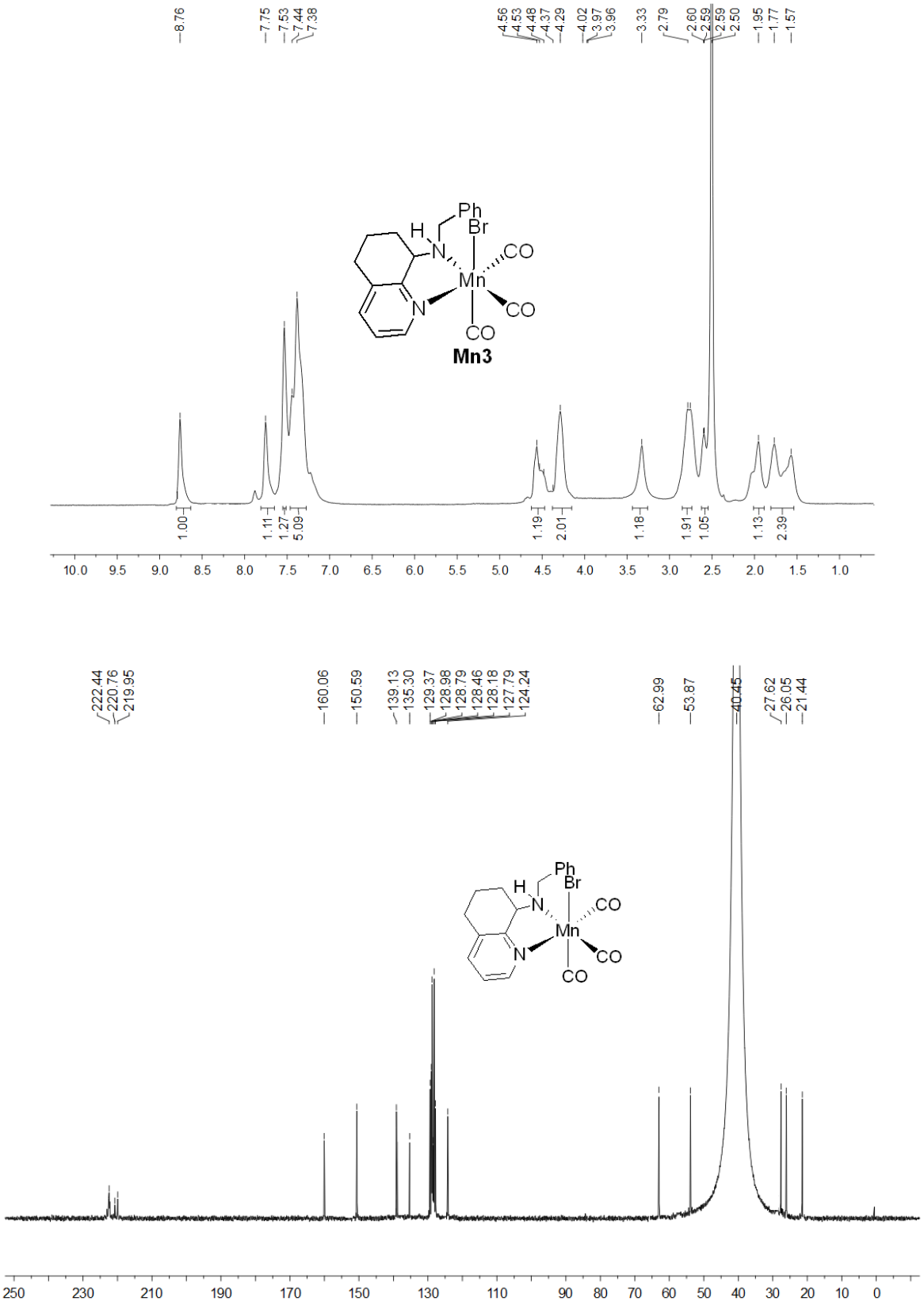
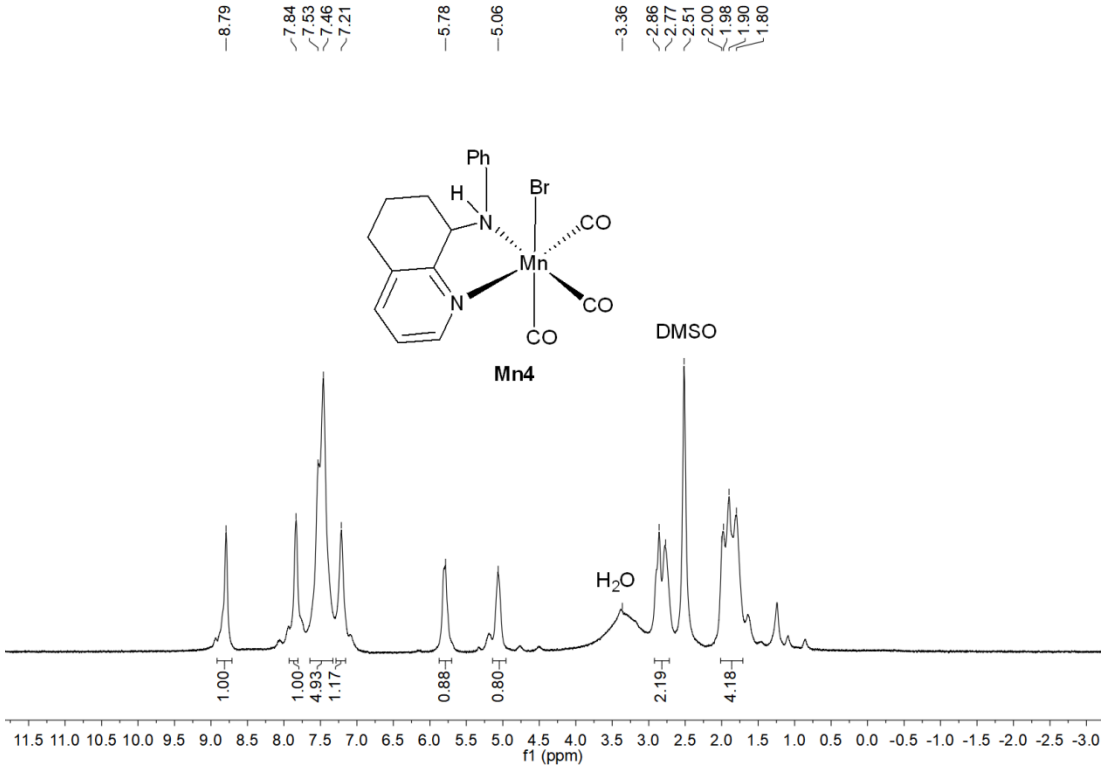


Figure S10 The ^{1}H and ^{13}C NMR spectra for **Mn4** in DMSO-d_6



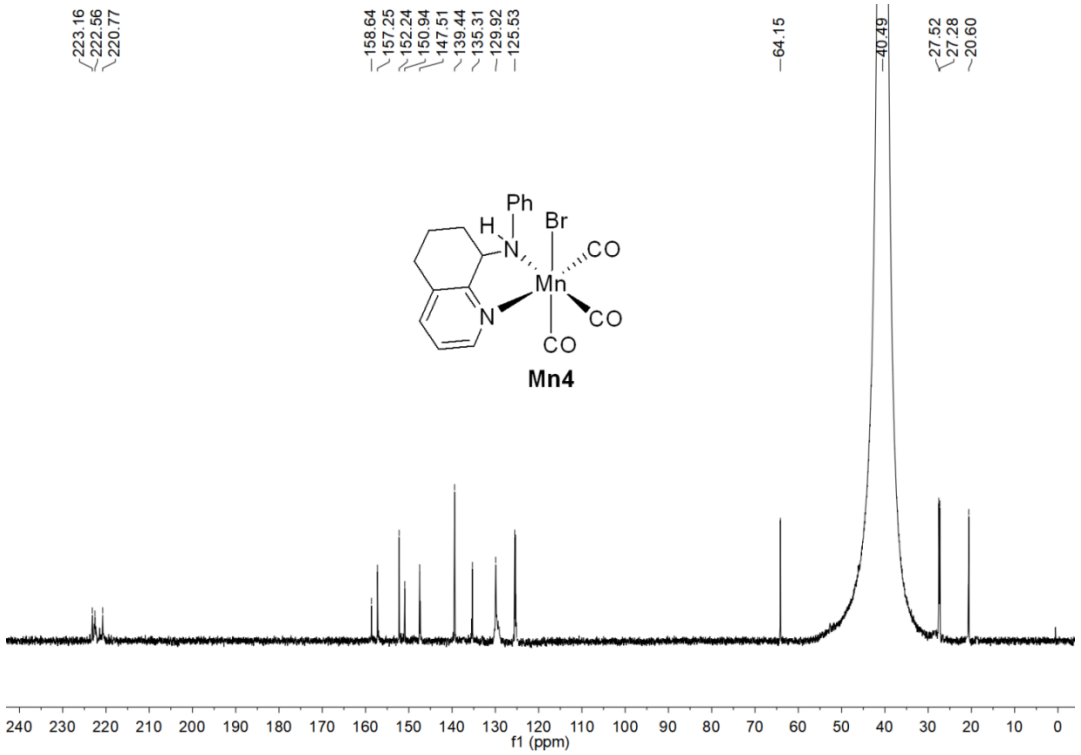


Figure S11 The ^{1}H and ^{13}C NMR spectra for **Mn5** in DMSO-d_6

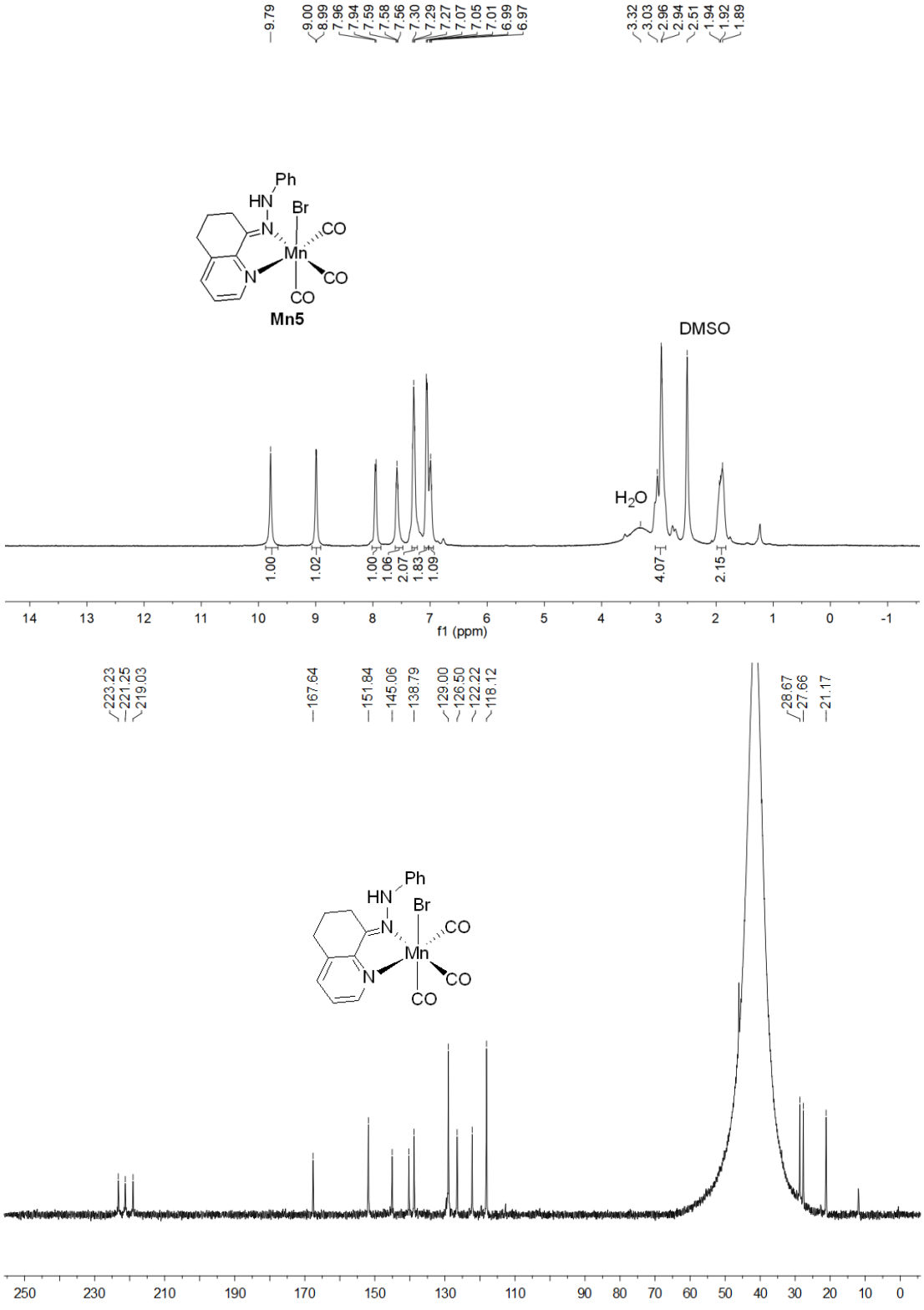


Figure S12 The ^{1}H and ^{13}C NMR spectra for **Mn6** in DMSO-d_6

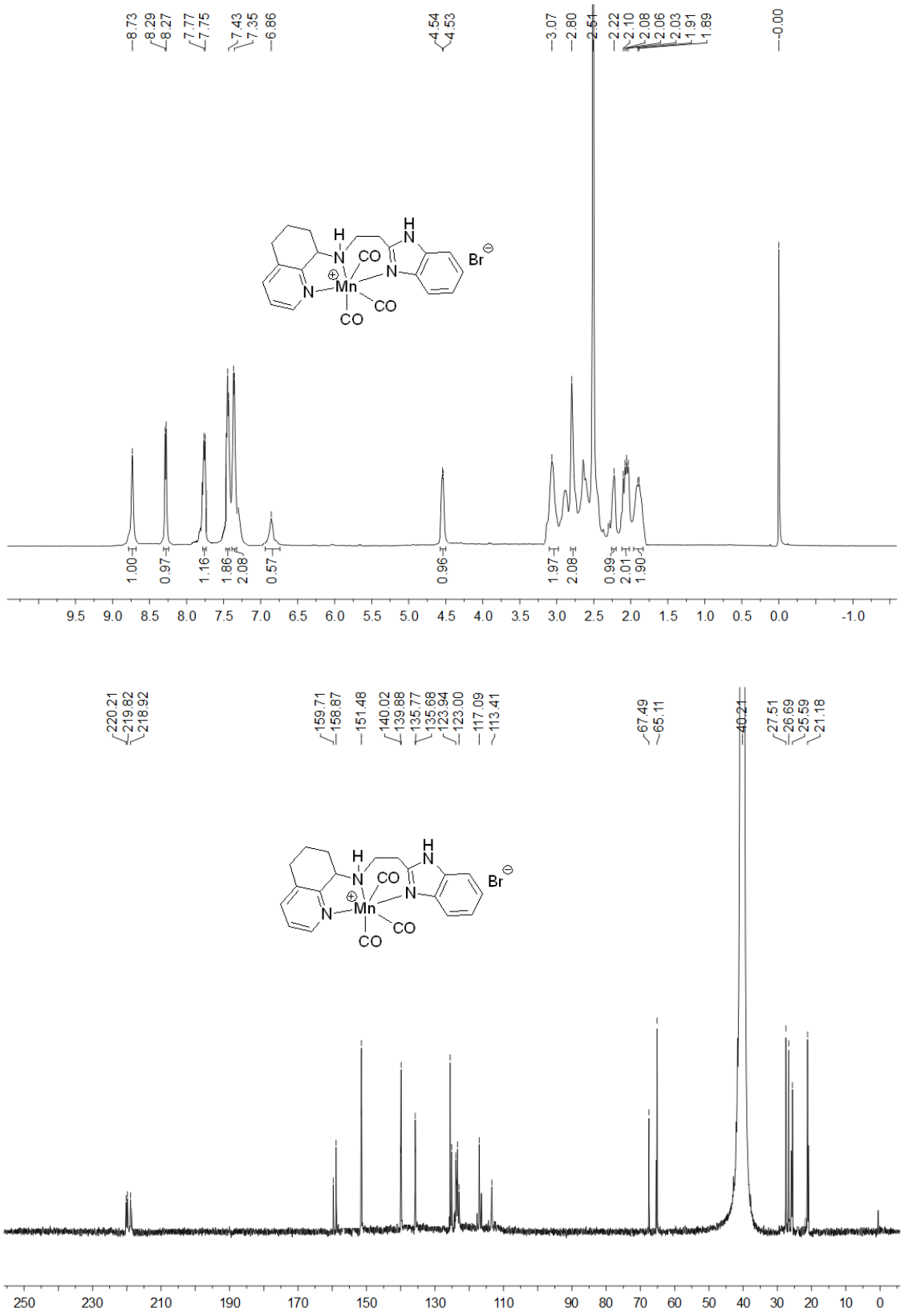


Figure S13 FT-IR spectrum of **Mn1**; recorded in the solid state on a Bruker ALPHA.

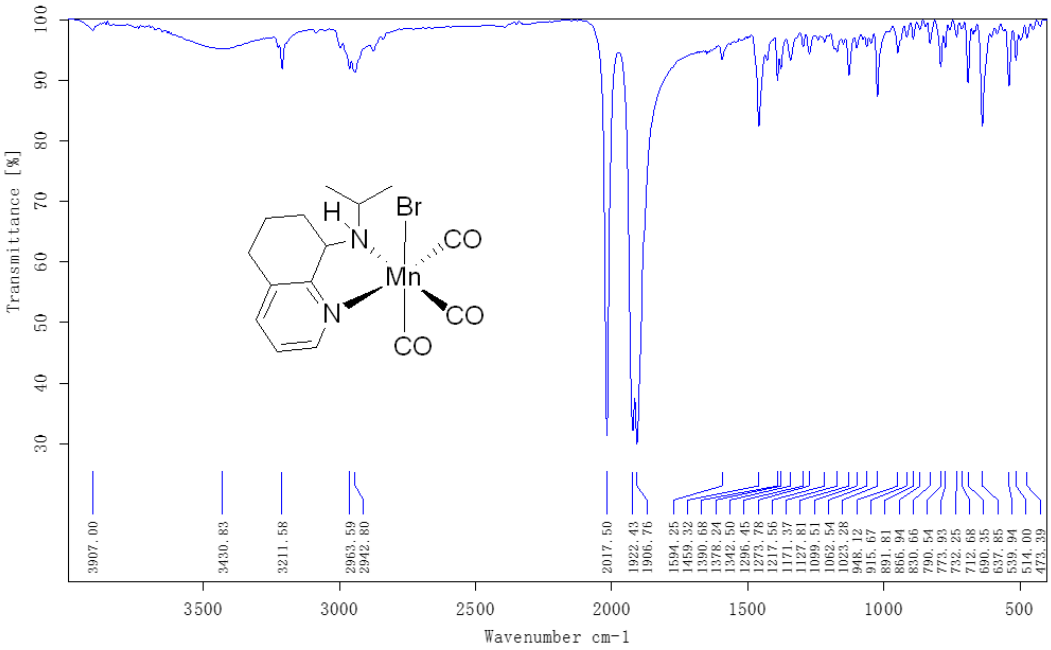


Figure S14 FT-IR spectrum of **Mn2**; recorded in the solid state on a Bruker ALPHA.

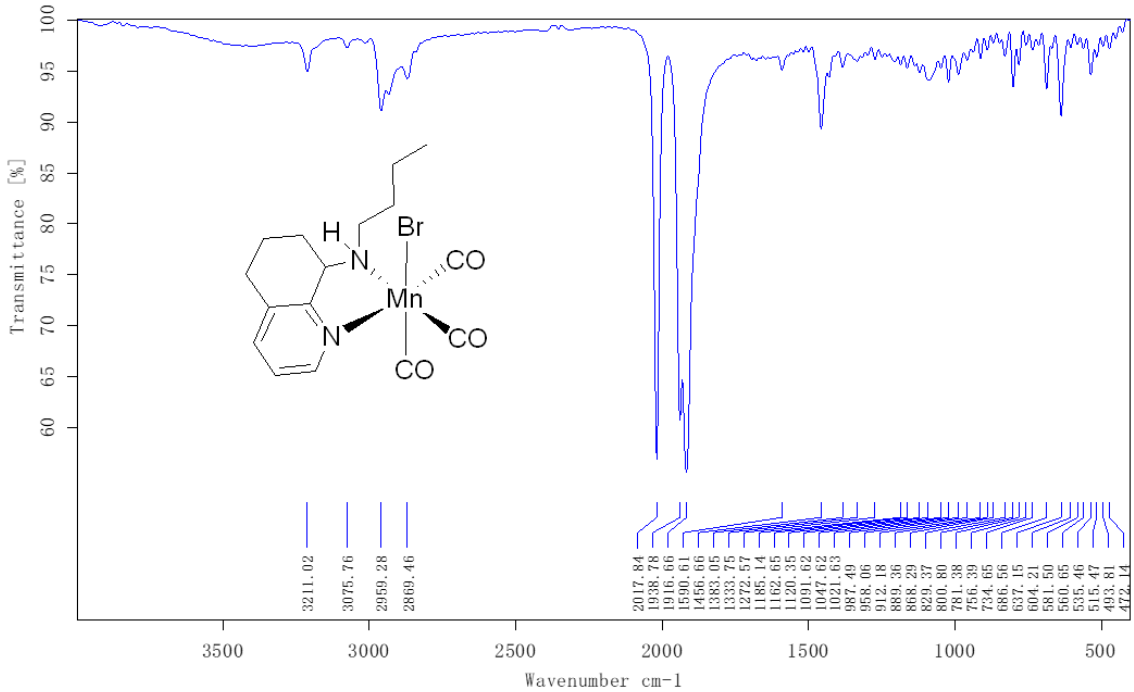


Figure S15 FT-IR spectrum of **Mn3**; recorded in the solid state on a Bruker ALPHA.

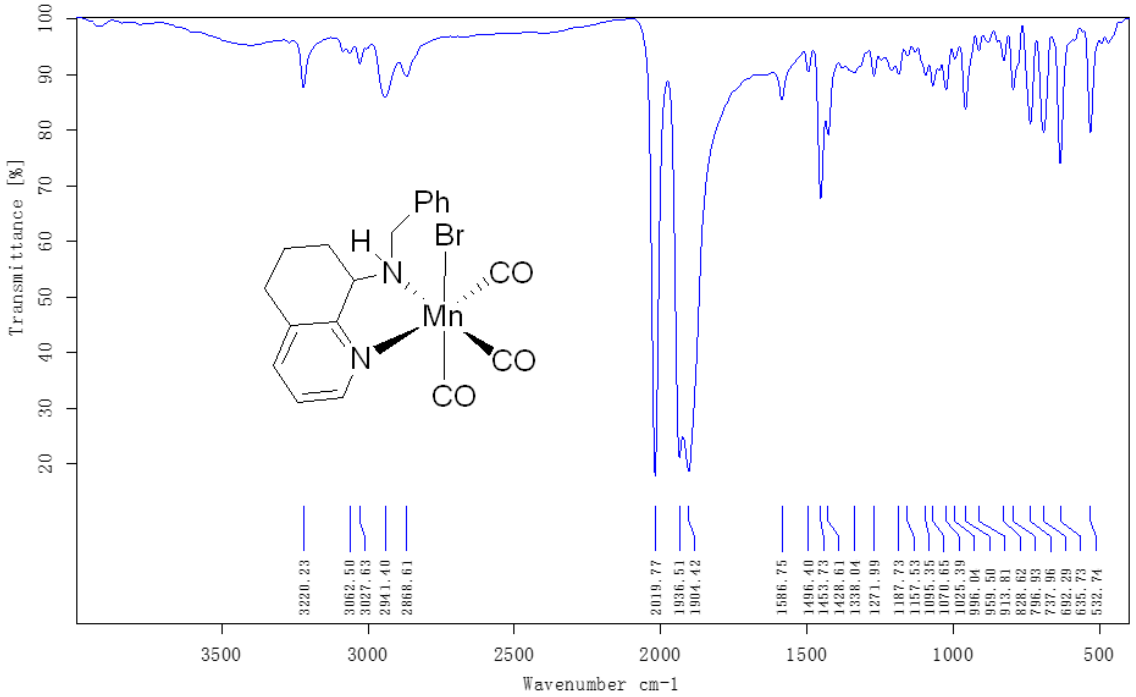


Figure S16 FT-IR spectrum of **Mn**4; recorded in the solid state on a Bruker ALPHA.

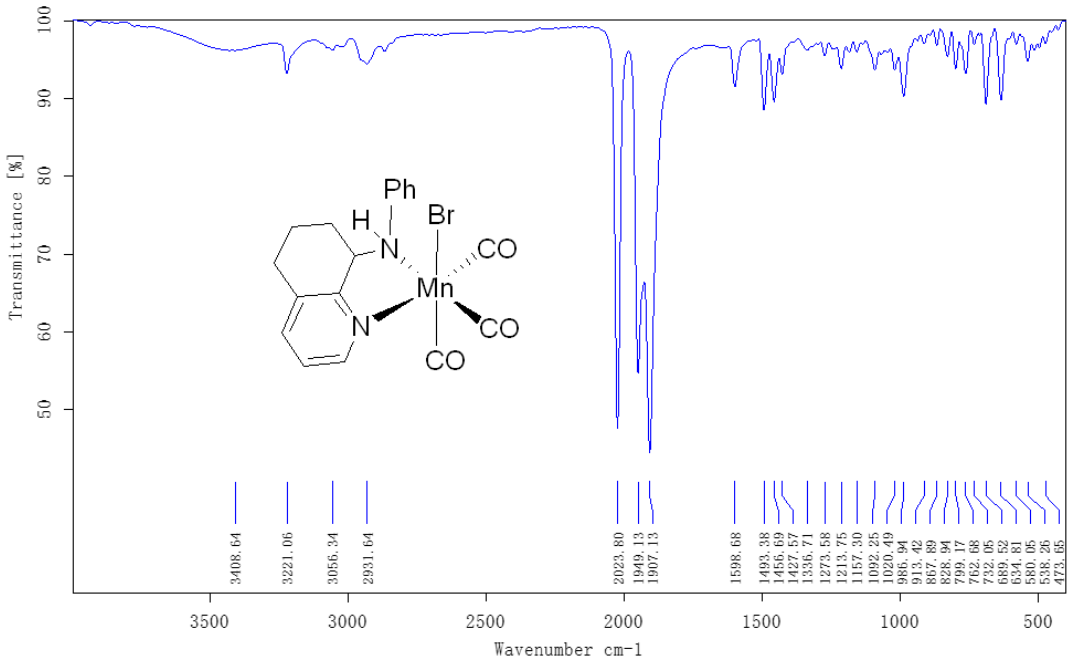


Figure S17 FT-IR spectrum of **Mn5**; recorded in the solid state on a Bruker ALPHA.

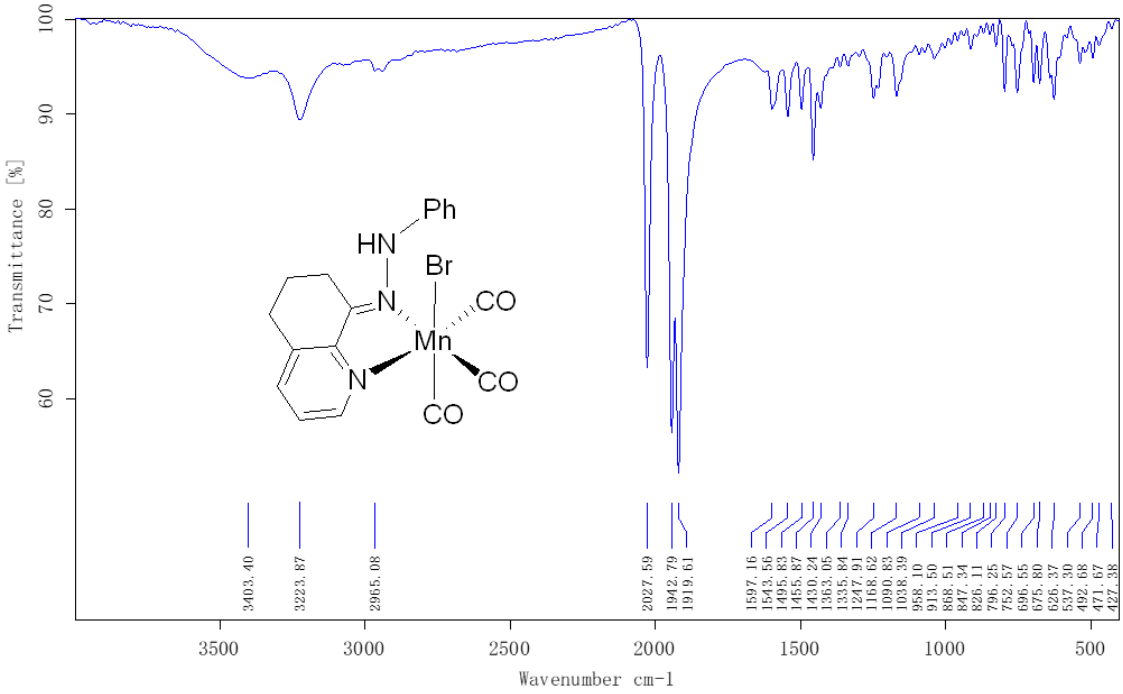
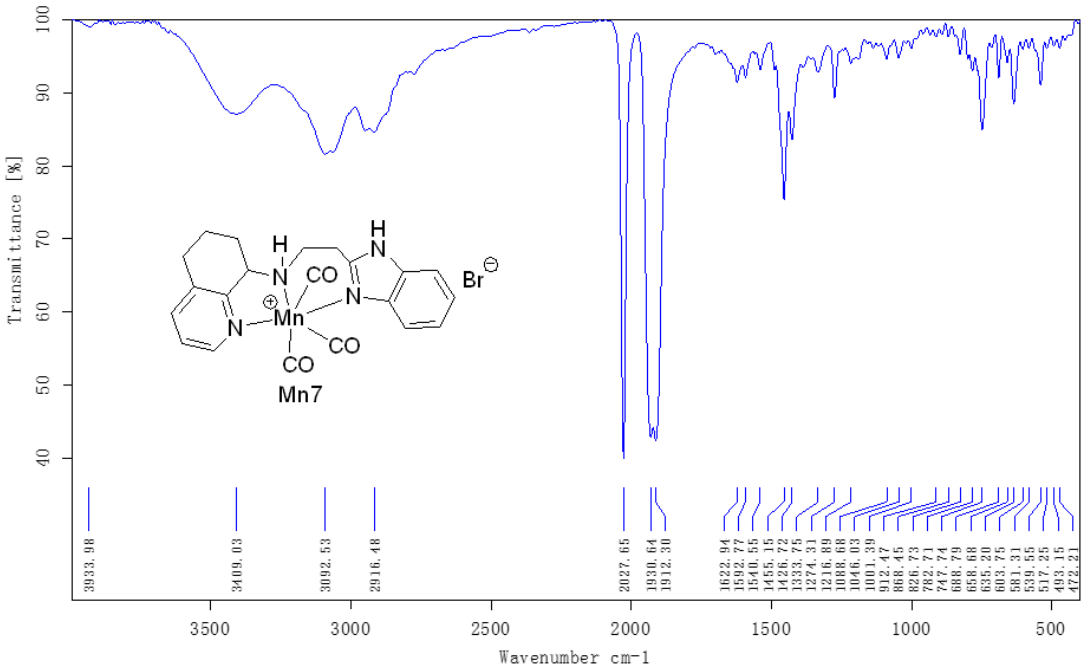


Figure S18 FT-IR spectrum of **Mn6**; recorded in the solid state on a Bruker ALPHA.



4. Catalyst optimization using Mn1 as the precatalyst

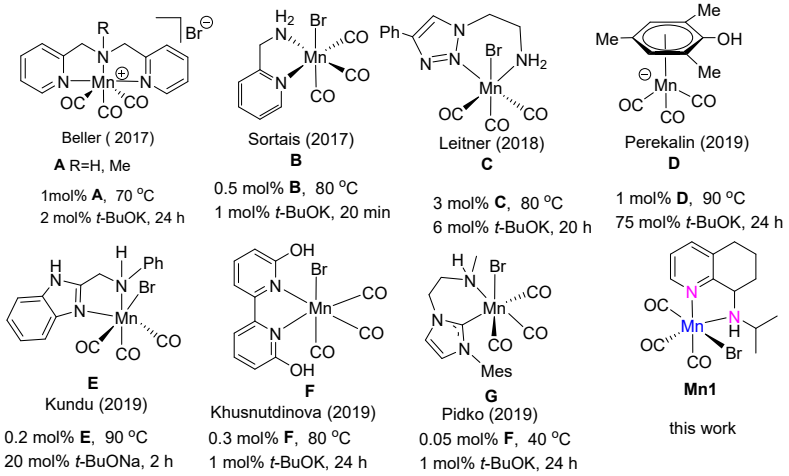


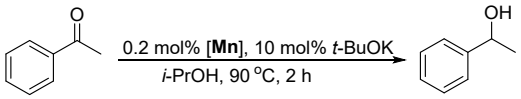
Chart S1 Selected examples of catalysts used for TH ketones

4.1 General Procedure for catalytic study

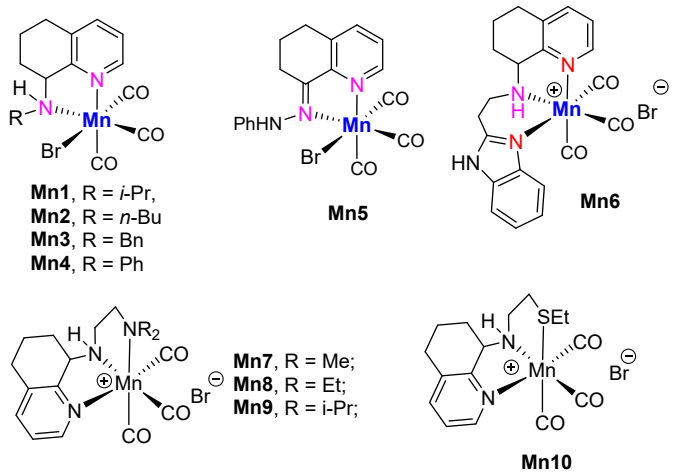
Under a N_2 atmosphere, a 25 or 250 mL dried Schlenk tube, containing a stirrer bar, was charged with acetophenone (**a1**, 2.0 – 25.0 mmol), the manganese complex (**Mn1** - **Mn10**, 5.0 – 10.0 µmol), the desired amount of base (*t*-BuOK, *t*-BuONa, *i*-PrONa, NaOEt, NaOMe KOH, NaOH, $CsCO_3$, Na_2CO_3, $LiOH{\cdot}H_2O$, LiOH, $Ca(OH)_2$, K_2CO_3, Na_2CO_3, $NaBHEt_3$, NaHMDS, KHMDS) (0.2 – 1.25 mmol) and *i*-PrOH (5 – 25 mL). The Schlenk tube was sealed and the contents stirred and heated to 90 °C for the desired reaction time (20 – 120 min). After cooling to room temperature, the pressure was slowly released. The reaction mixture was filtered through a plug of silica gel and then analyzed by GC.

4.2 Optimizing reaction conditions

Table S2 Evaluation of manganese catalysts, **Mn1** - **Mn10**, for the transfer hydrogenation of acetophenone.[a]

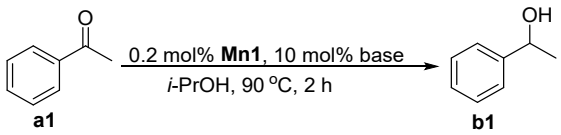


Entry	[**Mn**]	Conversion %[b]
1	**Mn1**	97
2	**Mn2**	90
3	**Mn3**	87
4	**Mn4**	58
5	**Mn5**	69
6	**Mn6**	41
7	**Mn7**	85
8	**Mn8**	82
9	**Mn9**	78
10	**Mn10**	81
11	**none**	5



[a] Conditions: 5.0 mmol acetophenone, 10 μmol (0.2 mol%) [**Mn**], 0.5 mmol *t*-BuOK (10 mol%), 5 mL *i*-PrOH, 90 °C (oil temperature), 2 h;
[b] Determined by GC with dodecane as the internal standard.

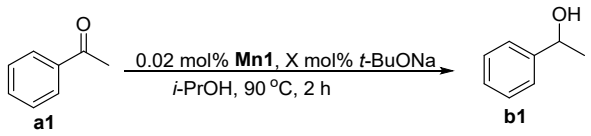
Table S3 Screening of the type of base[a]



Entry	Base	Conversion (%)[b]
1	*t*-BuOK	97
2	*t*-BuONa	99
3	*i*-PrONa	94
4	EtONa	90
5	MeONa	89
6	$NaBHEt_3$	55
7	KHMDS	86
8	NaHMDS	91
9	Cs_2CO_3	45
10	Na_2CO_3	32
11	$LiOH·H_2O$	76
12	NaOH	94
13	KOH	91
14	$Ca(OH)_2$	4
15	$Ba(OH)_2$	14
16[c]	*t*-BuONa	5
17	none	none
18[d]	*t*-BuONa	6

[a] Conditions: 5.0 mmol acetophenone, 10 μmol (0.2 mol%) **Mn1**, 0.5 mmol base (10 mol%), 5 mL *i*-PrOH, 90 °C (oil temperature), 2 h;
[b] Determined by GC with dodecane as the internal standard;
[c] In the absence of **Mn1**;
[d] $Mn(CO)_5Br$ was used as catalyst.

Table S4 Evaluation of the base loading[a]



Entry	X mol% *t*-BuONa	Conversion (%)[b]
1	25	89
2	20	85
3	15	81
4	10	78
5	5	61
6	2.5	57
7	1.25	38
8	0	NR
9[c]	5	92

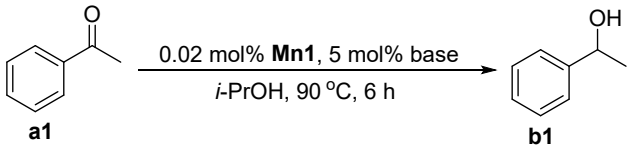
[a] Conditions: 25 mmol acetophenone, 5 μmol **Mn1**, X mol of *t*-BuONa (0 - 25 mol%), 10 mL *i*-PrOH (2.5 M), 90 °C (oil temperature), 2 h;

[b] Determined by GC with dodecane as the internal standard;

[c] 6 h.

NR = no reaction.

Table S5 Optimization of the reaction parameters for transfer hydrogenation of acetophenone (**a1**)

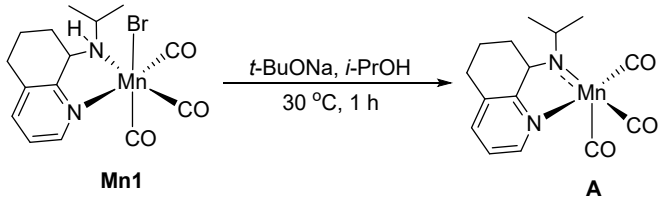


Entry	Base	Conversion (%)[b]	TON
1	*t*-BuOK	80	4000
2	*t*-BuONa	92	4600
3	NaOH	76	3800
4	KOH	75	3750
5	MeONa	73	3650
6	None	nd	--

[a] Conditions: 25 mmol acetophenone, 5 μmol **Mn1**, 1.25 mol base (5 mol%), 10 mL *i*-PrOH (2.5 M), 90 °C (oil temperature), 6 h, TON = turnover number;

[b] Determined by GC with dodecane as the internal standard.

4.3 Investigation of the active species A



Mn1 **A**

A dry 25 mL Schlenk flask, containing a stir bar, was charged sequentially with **Mn1** (0.204 g, 0.50 mmol), *t*-BuONa (0.245 g, 2.50 mmol) and *i*-PrOH (10 mL). The reaction mixture was stirred at 30 °C for 1 h forming a red solution. After the volatiles were removed under reduced pressure, the residue was dissolved in diethyl ether (10 mL) and filtered through Celite. The diethyl ether filtrate was concentrated to 1 mL and THF (2 mL) added and the mixture kept at -20 °C overnight. The resulting red precipitate was collected and dried to give **A** (98 mg, 59%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 – 8.80 (m, 1H), 7.55 – 7.53 (m, 1H), 7.32 – 7.29 (m, 1H), 4.18 (d, *J* = 3.8 Hz, 1H), 3.71 – 3.56 (m, 1H), 3.23 -3.21(m, 1H), 2.94 – 2.72 (m, 2H), 2.72 – 2.61 (m, 1H), 1.56 (d, *J* = 6.1 Hz, 6H), 1.52 – 1.42 (d, *J* = 5.8 Hz, 6H); IR (ATR, cm^{-1}, KBr): 1905 (s, ν_{CO}), 2003 (s, ν_{CO}), 2019 (s, ν_{CO}).

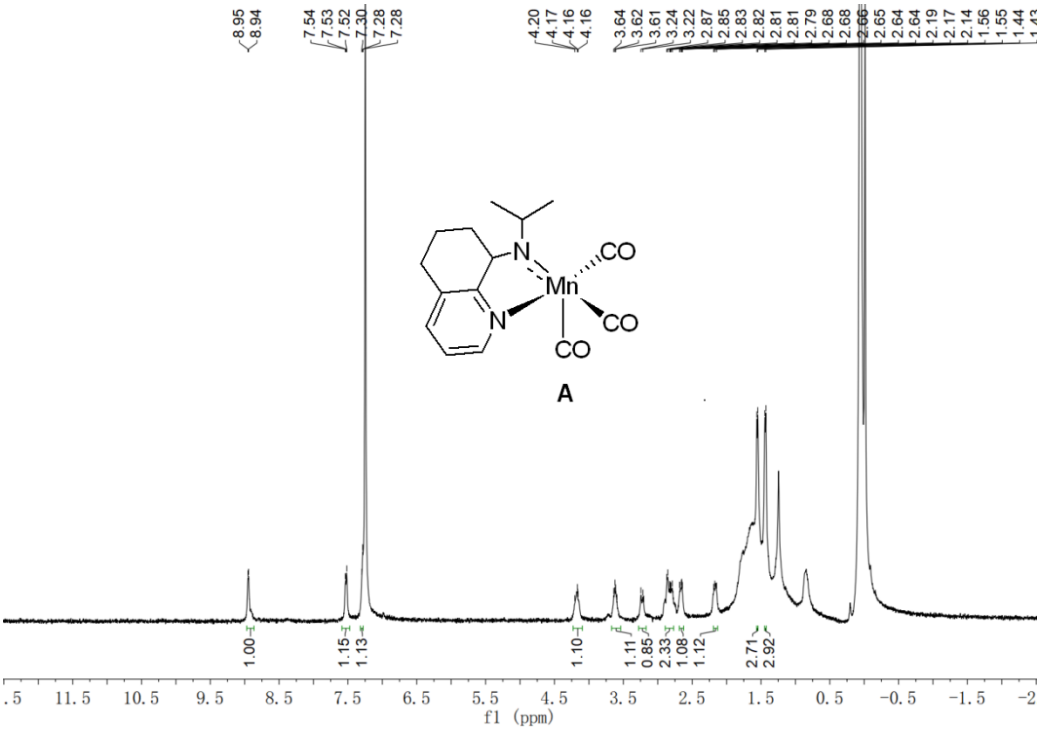


Figure S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **A**

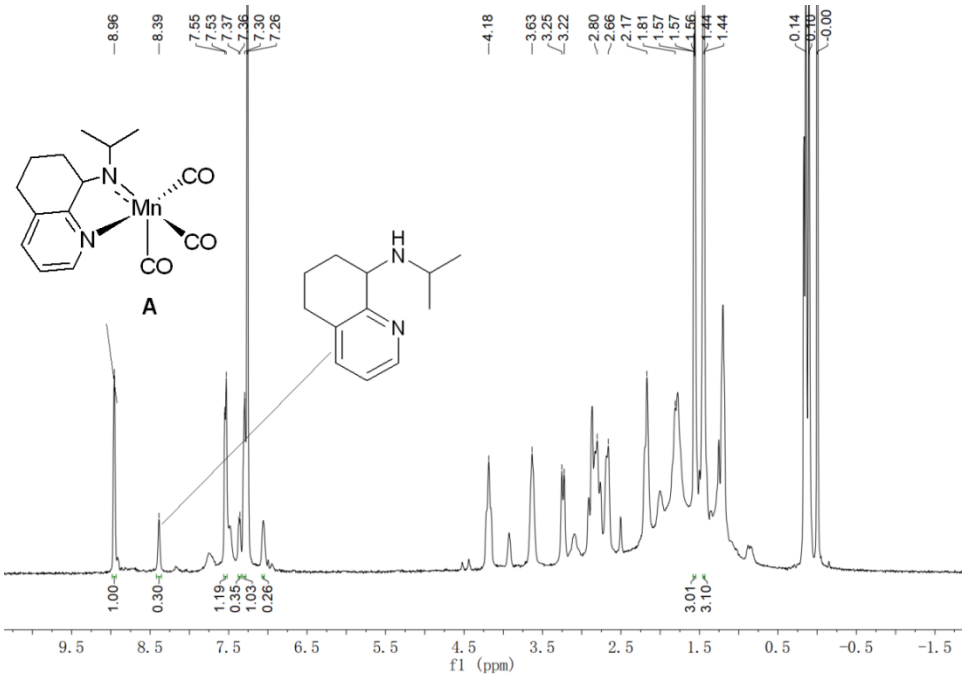


Figure S20 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of crude **A** in $CDCl_3$

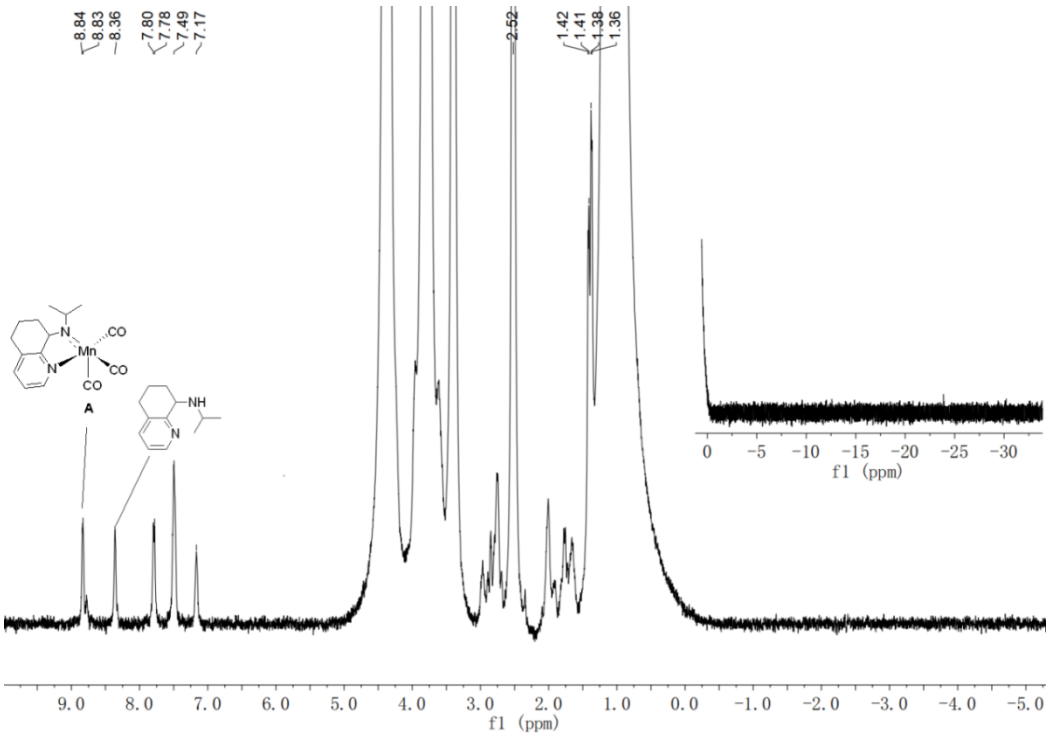


Figure S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the active species formed from the reaction of **Mn1** with *t*-BuONa in an isopropyl alcohol solution of *t*-BuONa.

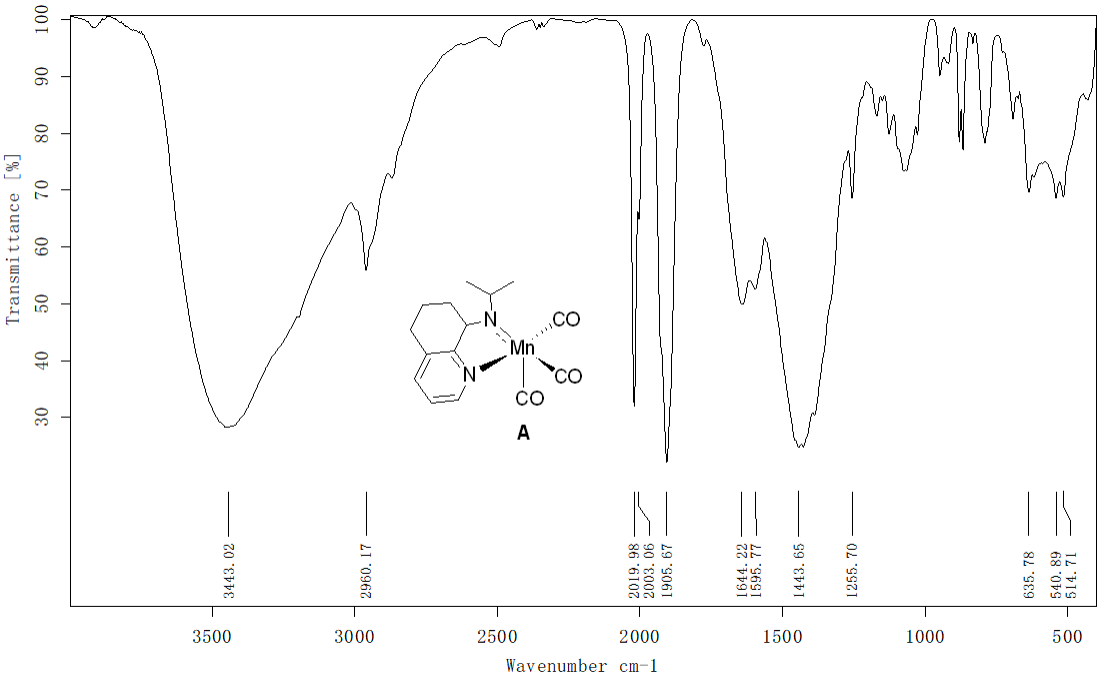
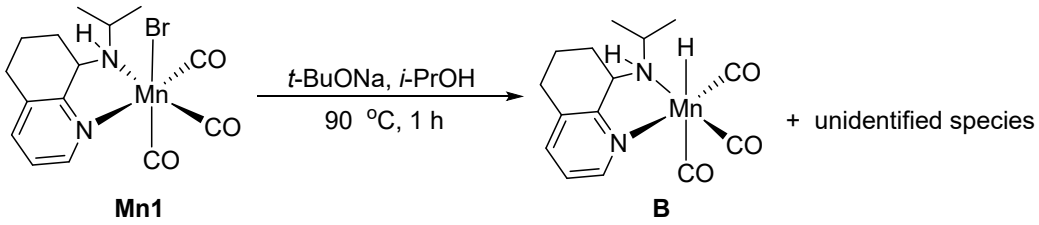


Figure S22 FT-IR spectrum of **A**; recorded in the solid state on a Bruker ALPHA.

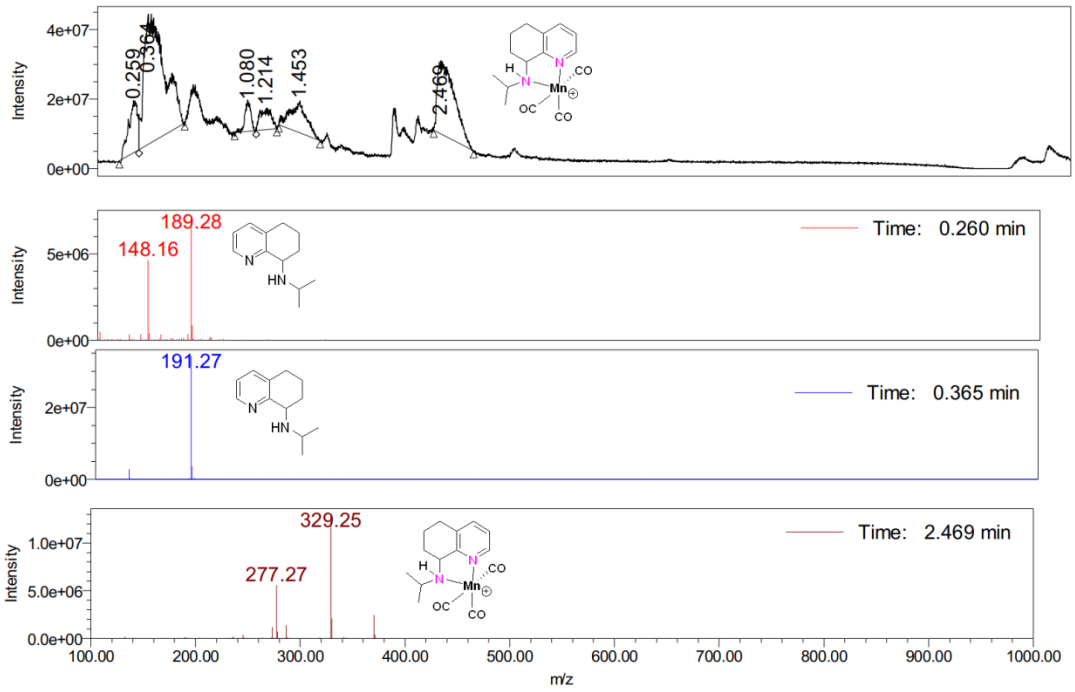
4.4 Investigation of the active species B



MS for $[C\text{-}H]^+$ found 329.25

A dry 25 mL Schlenk flask, containing a stir bar, was charged sequentially with **Mn1** (0.102 g 0.25 mmol), *t*-BuONa (0.122 g, 1.25 mmol) and *i*-PrOH (10 mL), the reaction mixture was stirred at 90 °C for 1 h. Once cooled to room temperature, the mixture was filtered and the solvent removed under reduce pressure. The resulting yellowish residue was washed with a minimum amount of pentane and dried to give crude **B** as a yellow powder (41 mg). However, **B** proved very sensitive and was found to be contaminated with some unidentified paramagnetic impurity leading to a poorly resolved ^{1}H NMR spectrum. ESI found [($C_{15}H_{18}MnN_2O_3$) (**B**-H)$^+$] = 329.25; Calcd for [($C_{15}H_{18}MnN_2O_3$) (**B**-H) $^+$] = 329.26; IR (ATR, cm^{-1}, KBr): 1896 (s, ν_{CO}), 1923 (s, ν_{CO}), 2020 (s, ν_{CO}).

Figure 23 ESI-MS (*m/z*) spectrum of **B**



ESI mass spectra recorded in acetone (1 mL) using the 3200 QTRAP 1200 infinity series instrument. Acetonitrile, flow rate = 1 mL/ min, electronic energy = 50 eV, Q1MS scan range = 100 -1000. The base peak corresponds to [**B**-H]$^+$ at *m/z* 329.25.

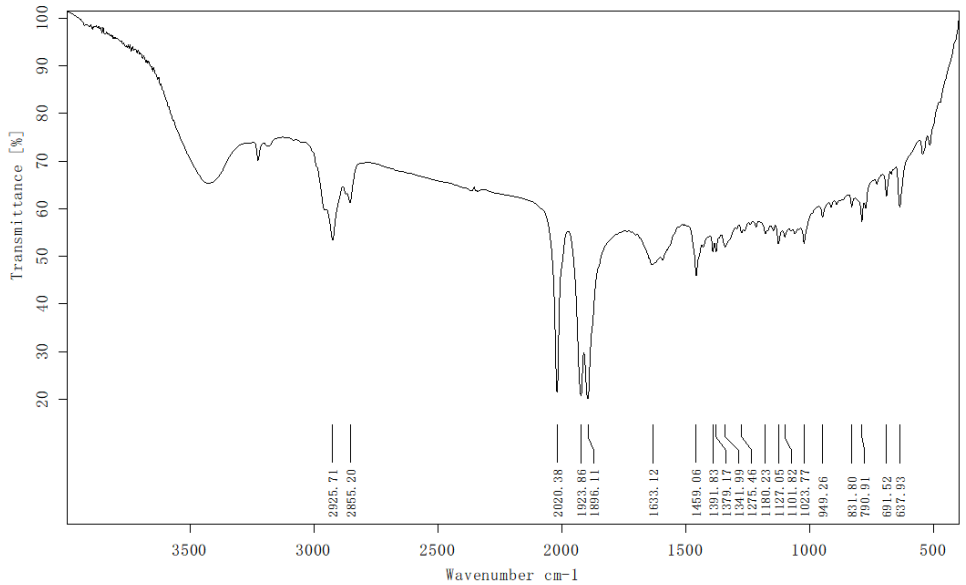


Figure 24 FT-IR spectrum of **B**; recorded in the solid state on a Bruker ALPHA.

5. Single crystal X-ray diffraction studies

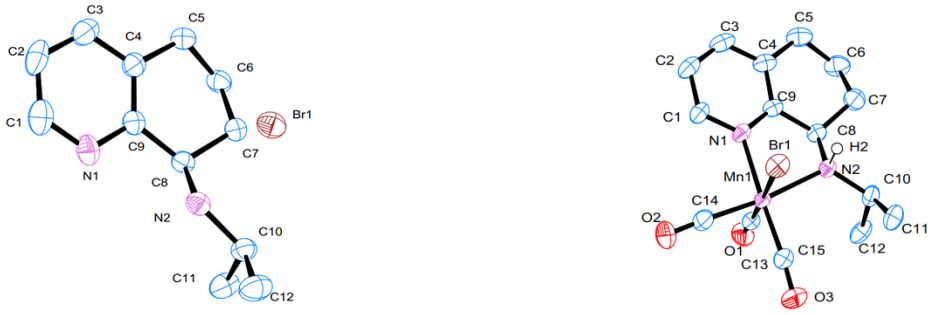


Figure S25 ORTEP representations of [**L1**H]Br (left) and **Mn1** (right). The thermal ellipsoids are shown at the 30% probability level, while the hydrogen atoms have been omitted for clarity.

Table S6 Crystal data and structure refinement for [**L1**H]Br and **Mn1**.

Identification code	[**L1**H]Br	**Mn1**
CCDC No.	2248092	2248093
Empirical formula	$C_{24}H_{38}Br_2N_4$	$C_{15}H_{18}BrMnN_2O_3$
Formula weight	542.40	409.16
Temperature/K	169.98(10)	169.99(10)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
a/Å	17.4207(4)	21.7602(3)
b/Å	7.60980(10)	12.71564(11)
c/Å	19.8264(4)	16.6797(2)
α/°	90	90
β/°	95.023(2)	111.0588(14)
γ/°	90	90
Volume/Å^3	2618.25(9)	4306.96(9)
Z	4	8
ρ_{calc}g/cm^3	1.376	1.262
μ/mm^{-1}	4.045	7.247
F(000)	1120.0	1648.0
Crystal size/mm^3	0.2 × 0.05 × 0.02	0.3 × 0.2 × 0.15
Radiation	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.48 to 150.57	8.204 to 153.546
Index ranges	-21 ≤ h ≤ 21, -8 ≤ k ≤ 9, -24 ≤ l ≤ 24	-25 ≤ h ≤ 27, -15 ≤ k ≤ 7, -20 ≤ l ≤ 20
Reflections collected	21032	15658
Independent reflections	5239 [R_{int} = 0.0422, R_{sigma} = 0.0346]	4369 [R_{int} = 0.0218, R_{sigma} = 0.0186]
Data/restraints/parameters	5239/24/295	4369/0/202
Goodness-of-fit on F^2	0.852	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0513, wR_2 = 0.1535	R_1 = 0.0337, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.1627	R_1 = 0.0351, wR_2 = 0.0961
Largest diff. peak/hole / e Å^{-3}	1.03/-0.81	0.82/-0.47

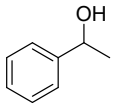
6. Characterization of selected alcohol products

The reaction mixtures were purified by flash gel chromatography (eluent: petroleum ether / ethyl acetate = 200:1 to 10:1) to give the desired product.

6.1. ^{1}H and ^{13}C NMR of selected alcohol products

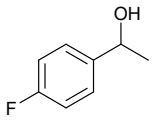
These spectroscopic data of selected alcohol products correspond to those reported in the literature.[3-6]

6.1.1 1-Phenylethanol (**b1**, entry 1, Table 2)



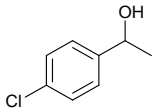
92% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 -7.30 (m, 5H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.60 (brs, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 128.5, 127.5, 125.4, 70.3, 25.2.

6.1.2 1-(4-Fluorophenyl)ethan-1-ol (**b2**, Table 3)



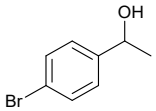
93% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.10-7.04 (m, 2H),4.92 (q, *J* = 6.4 Hz, 1H), 1.92 (s, 1H), 1.52 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ162.1, 141.5, 127.1, 115.3, 69.78, 25.30.

6.1.3 1-(4-Chlorophenyl)ethan-1-ol (**b3**, Table 3)



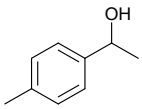
95% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 4H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.04 (s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 133.0, 128.6, 126.8, 69.7, 25.3.

6.1.4 1-(4-Bromophenyl)ethan-1-ol (**b4**, Table 3)



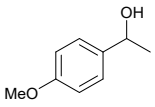
95% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.29-7.25 (m, 2H), 4.88 (q, *J* = 6.4 Hz, 1H), 2.05 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 131.4, 127.2, 121.0, 69.5, 25.1.

6.1.5 1-(4-Tolyl)ethan-1-ol (**b5**, Table 3)



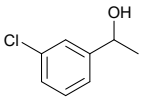
91% yield, Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8 Hz, 2H), 7.214 (d, *J* = 8 Hz, 2H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.40 (s, 3H), 1.88 (s, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.1, 129.2, 125.3, 70.2, 25.1, 21.1.

6.1.6 1-(4-Methoxyphenyl)ethan-1-ol (**b6**, Table 3)



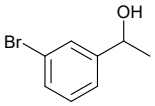
85% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 6.95-6.92 (m, 2H),4.90 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 1H), 1.88 (brs, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.0, 126.7, 126.6, 113.9, 113.8, 70.0, 55.3, 25.0.

6.1.7 1-(3-Chlorophenyl)ethan-1-ol (**b8**, Table 3)



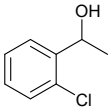
93% yield, Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.34-7.28 (m, 3H),4.93 (q, *J* = 6.4 Hz, 1H), 1.94 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 134.3, 129.8, 127.6, 125.6, 123.6, 69.6, 25.2.

6.1.8 1-(3-Bromophenyl)ethan-1-ol (**b9**, Table 3)



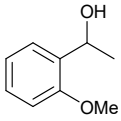
96% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 1H), 7.46-6.42 (m, 1H), 7.34-7.31 (m, 1H), 7.27-7.24 (m, 1H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.05 (brs, 1H), 1.52 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 130.4, 130.1, 128.6, 124.1, 122.5, 69.5, 25.2.

6.1.9 1-(2-Chlorophenyl)ethan-1-ol (**b10**, Table 3)



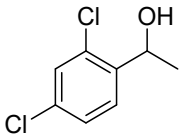
95% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 1H), 7.38-7.32 (m, 3H), 5.34 (q, *J* = 6.4 Hz, 1H), 2.06 (brs, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 131.5, 129.3, 128.3, 127.2, 126.5, 66.8, 23.5.

6.1.10 1-(1-Tolyl)ethan-1-ol (**b16**, Table 3)



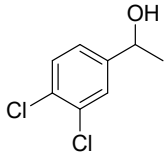
81% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.32-7.28 (m, 1H), 7.03-6.99 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.14 (q, *J* = 6.4 Hz, 1H), 4.92 (s, 3H), 2.69 (brs, 1H), 1.56 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 133.7, 128.2, 126.1, 120.8, 110.4, 66.1, 55.3, 23.1.

6.1.11 1-(2,4-Dichlorophenyl)ethan-1-ol (**b17**, Table 3)[6d,6e]



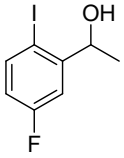
95% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 1H), 7.29 (s, 1H), 7.21 (dd, *J* = 8.4, 2.1 Hz, 1H), 5.15 (q, *J* = 6.4 Hz, 1H), 3.15 (s, 1H), 1.39 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 133.3, 132.0, 129.0, 127.4, 127.4, 66.4, 23.5.

6.1.12 1-(3,4-Dichlorophenyl)ethan-1-ol (**b18**, Table 3)[6b]



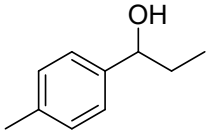
94% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.78 (q, *J* = 6.5 Hz, 1H), 2.76 (s, 1H), 1.41 (d, *J* = 6.6 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 132.4, 131.0, 130.3, 127.4, 124.8, 69.1, 25.1.

6.1.13 1-(5-fluoro-2-iodophenyl)ethan-1-ol (**b20**, Table 3)[6c]



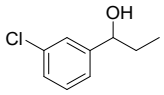
95% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.37 (dd, *J* = 10.0, 3.1 Hz, 1H), 6.79 (ddd, *J* = 8.6, 7.8, 3.1 Hz, 1H), 5.06 (qd, *J* = 6.3, 1.3 Hz, 1H), 2.06 (brs, 1H), 1.49 (d, *J* = 6.4 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.3, 150.0, 149.9, 140.3 (dd, *J* = 13.1, 7.4 Hz), 116.5 (dd, *J* = 22.1, 17.9 Hz), 113.7 (dd, J = 23.3, 10.9 Hz), 73.4 (d, J = 11.6 Hz), 23.7 (d, J = 11.9 Hz).

6.1.14 1-(*p*-Tolyl)propan-1-ol (**b21**, Table 3)[6b]



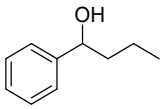
95% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.47 (t, *J* = 6.7 Hz, 1H), 2.41 (s, 1H), 2.33 (s, 3H), 1.83 – 1.61 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 137.0, 129.0, 126.0, 75.8, 31.8, 21.1, 10.2.

6.1.15 1-(3-Chlorophenyl)propan-1-ol (**b22**, Table 3)



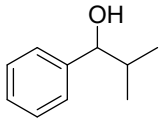
94% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.2 Hz, 1H), 7.25 (d, *J* = 2.2 Hz, 2H), 7.21 (d, *J* = 1.9 Hz, 1H), 4.57 (t, *J* = 6.5 Hz, 1H), 1.93 (s, 1H), 1.81 – 1.71 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 134.3, 129.6, 127.5, 126.1, 124.1, 75.3, 31.9, 9.9.

6.1.16 1-Phenylbutan-1-ol (**b23**, Table 3)[6b]



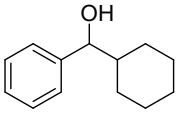
96% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.26 (dd, *J* = 9.0, 4.6 Hz, 1H), 4.65 (dd, *J* = 7.5, 5.9 Hz, 1H), 1.94 (s, 1H), 1.78 (dddd, *J* = 15.5, 10.1, 6.1, 3.7 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.47 – 1.37 (m, 1H), 1.35 – 1.23 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 128.4, 127.4, 125.9, 74.4, 41.2, 19.0, 13.9.

6.1.17 2-Methyl-1-phenylpropan-1-ol (**b24**, Table 2)[6]



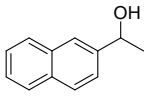
92% yield, colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 5H), 4.34 (d, *J* = 6.9 Hz, 1H), 1.99 – 1.93 (m, 1H), 1.91 (br, s, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 128.1, 127.4, 126.5, 80.0, 35.2, 19.0, 18.2.

6.1.18 Cyclohexyl(phenyl)methanol (**b25**, Table 3)[6b]



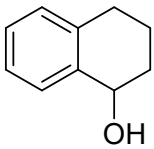
92% yield, colorless oil, Mp: 39 - 40 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (ddt, *J* = 14.9, 12.2, 7.3 Hz, 5H), 4.30 (d, *J* = 7.2 Hz, 1H), 2.16 (br, s, 1H), 1.98 – 1.92 (m, 1H), 1.74 (dt, *J* = 12.2, 3.1 Hz, 1H), 1.61 (ddd, *J* = 11.6, 5.9, 3.0 Hz, 2H), 1.39 – 1.31 (m, 1H), 1.24 – 1.18 (m, 1H), 1.17 – 1.10 (m, 2H), 1.06 – 0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 128.1, 127.3, 126.6, 79.3, 44.9, 29.3, 28.8, 26.4, 26.1, 26.0.

6.1.19 1-(Naphthalen-2-yl)ethan-1-ol (**b28**, Table 3)[6]



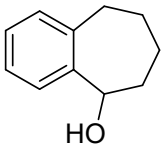
93% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 4H), 7.57-7.51 (m, 3H),5.12 (q, *J* = 6.4 Hz, 1H), 1.90 (brs, 1H), 1.64 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 133.3, 132.9, 128.3, 127.9, 127.7, 126.1, 125.8, 123.8, 123.8, 70.5, 25.1.

6.1.20 1,2,3,4-tetrahydronaphthalen-1-ol (**b31**, Table 3)[7]



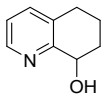
72% yield, yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 5.6, 3.6 Hz, 1H), 7.13 (dt, *J* = 7.4, 3.6 Hz, 2H), 7.04 (dd, *J* = 5.5, 3.6 Hz, 1H), 4.66 (t, *J* = 4.6 Hz, 1H), 2.76 (dt, *J* = 17.1, 5.6 Hz, 1H), 2.66 (ddd, *J* = 16.8, 7.9, 5.4 Hz, 1H), 2.47 (s, 1H), 1.90 (dddd, *J* = 12.0, 9.5, 6.2, 3.6 Hz, 2H), 1.80 (ddt, *J* = 11.4, 7.6, 3.8 Hz, 1H), 1.76 – 1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.1, 128.9, 128.7, 127.5, 126.1, 68.0, 32.3, 29.3, 18.9.

6.1.21 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol (**b32**, Table 3)[7]



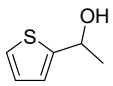
94% yield, white solid, Mp: 99 - 100 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.19 (dtd, *J* = 20.4, 7.4, 1.4 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 4.94 – 4.90 (m, 1H), 2.94 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.78 – 2.66 (m, 1H), 2.11 – 2.02 (m, 2H), 1.96 (t, *J* = 8.0 Hz, 1H), 1.83 – 1.78 (m, 2H), 1.57 – 1.42 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 140.8, 129.5, 126.9, 126.1, 124.6, 74.0, 36.6, 35.7, 27.8, 27.6.

6.1.22 5,6,7,8-Tetrahydroquinolin-8-ol (**b33**, Table 3)[5]



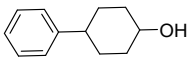
88% yield, pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.6 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.07 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.71 (dd, *J* = 7.5, 5.5 Hz, 1H), 4.44 (br, 1H, O*H*), 2.83 – 2.70 (m, 2H), 2.26 – 2.12 (m, 1H), 2.03 – 1.91 (m, 1H), 1.88 – 1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 146.6, 137.1, 131.9, 122.4, 68.4, 30.9, 28.4, 19.2.

6.1.23 1-(Thiophen-2-yl)ethan-1-ol (**b37**, Table 3)[6]



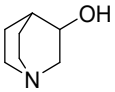
78% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 1H), 7.03-7.00 (m, 2H), 5.18 (q, *J* = 6.4 Hz, 1H), 2.11 (brs, 1H), 1.65 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 141.9, 110.1, 105.1, 63.5, 21.2.

6.1.24 4-Phenylcyclohexan-1-ol (**b44**, entry 6, Table 4)[8]



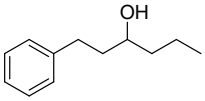
85% yield, white solid, Mp: 116 - 117°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.18 (dd, *J* = 9.0, 7.4 Hz, 3H), 3.68 (tt, *J* = 10.5, 4.4 Hz, 1H), 2.49 (tt, *J* = 12.0, 3.5 Hz, 1H), 2.13 – 2.06 (m, 2H), 1.97 – 1.91 (m, 2H), 1.54 (dd, *J* = 12.2, 3.0 Hz, 2H), 1.49 – 1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 128.3, 126.7, 126.0, 70.6, 43.4, 35.9, 32.4, 27.7.

6.1.25 Quinuclidin-3-ol (**b48**, entry 10, Table 4) [9]



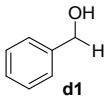
60% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (s, 1H), 3.78 (dt, *J* = 7.9, 3.6 Hz, 1H), 3.05 (ddd, *J* = 14.1, 8.3, 2.3 Hz, 1H), 2.85 (ddd, *J* = 10.5, 5.7, 2.6 Hz, 1H), 2.72 (ddq, *J* = 10.3, 7.7, 2.8 Hz, 2H), 2.65 – 2.49 (m, 2H), 1.95 (tdd, *J* = 10.3, 5.1, 2.4 Hz, 1H), 1.78 (q, *J* = 3.3 Hz, 1H), 1.66 (tt, *J* = 9.5, 4.7 Hz, 1H), 1.46 (dddd, *J* = 13.3, 10.4, 5.7, 2.9 Hz, 1H), 1.39 – 1.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.0, 57.6, 47.1, 46.1, 28.1, 24.6, 18.7.

6.1.26 1-Phenylhexan-3-ol (**b50**, entry 12, Table 4)[10]



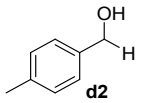
90% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.12 (m, 3H), 3.60 (ddd, *J* = 9.4, 7.4, 4.7 Hz, 1H), 2.77 (ddd, *J* = 13.8, 9.7, 5.9 Hz, 1H), 2.64 (ddd, *J* = 13.8, 9.7, 6.7 Hz, 1H), 2.13 (br, s, 1H), 1.82 – 1.64 (m, 2H), 1.44 (dd, *J* = 5.8, 3.8 Hz, 2H), 1.34 (td, *J* = 7.4, 7.0, 2.9 Hz, 1H), 0.91 (t, *J* = 6.8 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 142.37, 128.47, 128.43, 125.80, 71.08, 39.78, 39.14, 32.12, 18.87, 14.17.

6.1.27 Benzyl alcohol (**d1**, entry 1, Table 5)[3]



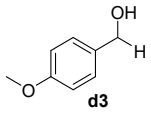
85% yield, colorless oil. **^{1}**H NMR (500 MHz, $CDCl_3$) δ 7.46–7.22 (m, 5H), 4.67 (s, 2H), 2.66 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 128.5, 127.6, 127.0, 65.1

6.1.28 4-Methylbenzyl alcohol (**d2**, entry 2, Table 5)[3]



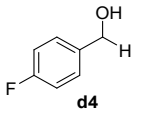
95% yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J*=8.1 Hz, 2H), 7.19 (d, *J*=7.9 Hz, 2H), 4.65 (s, 2H), 2.37 (s, 3H), 1.87 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 137.3, 129.2, 127.1, 65.2, 21.1.

6.1.29 4-Methoxybenzyl alcohol (**d3**, entry 3, Table 5).[3]



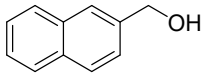
81% yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ7.31 (d, *J*=8.7 Hz, 2H), 6.92 (d, *J*=8.4 Hz, 2H), 4.63 (s, 2H), 3.83 (s, 3H), 1.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 133.2, 128.6, 113.9, 64.7, 55.2.

6.1.30 4-Fluorobenzyl alcohol (**d4**, entry 4, Table 5).[3]



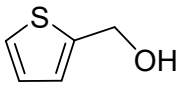
94% yield, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.07 (m, 2H), 4.68 (s, 2H), 1.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2 (d, $J_{C\text{-}F}$ = 245.4 Hz), 136.5 (d, $J_{C\text{-}F}$=3.1 Hz), 128.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 64.2.

6.1.31 Naphthalen-2-ylmethanol (**d5**, entry 5, Table 5)[11]



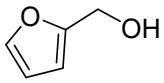
95% yield, white solid, Mp: 80 – 81 ^{o}C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dt, *J* = 8.9, 4.9 Hz, 3H), 7.74 (s, 1H), 7.43 (ddd, *J* = 10.0, 8.0, 3.1 Hz, 3H), 4.78 (s, 2H), 2.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 133.4, 132.9, 128.3, 127.9, 127.7, 126.2, 125.9, 125.4, 125.2, 65.4.

6.1.32 thiophen-2-ylmethanol (**d7**, entry 7, Table 5)[12]



93% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 4.4, 1.9 Hz, 1H), 6.93 (d, *J* = 4.6 Hz, 2H), 4.71 (s, 2H), 3.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 126.8, 125.4, 125.4, 59.6.

6.1.33 1-(furan-2-yl)ethan-1-ol (**d8**, entry 8, Table 5)[12]



82% yield, colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 1.0 Hz, 1H), 6.32 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.04 (s, 1H), 4.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.2, 110.3, 107.5, 57.2.

6.2. NMR spectra for selected alcohol products

Figure S26 ^{1}H and ^{13}C NMR spectra of 1-phenylethanol in $CDCl_3$

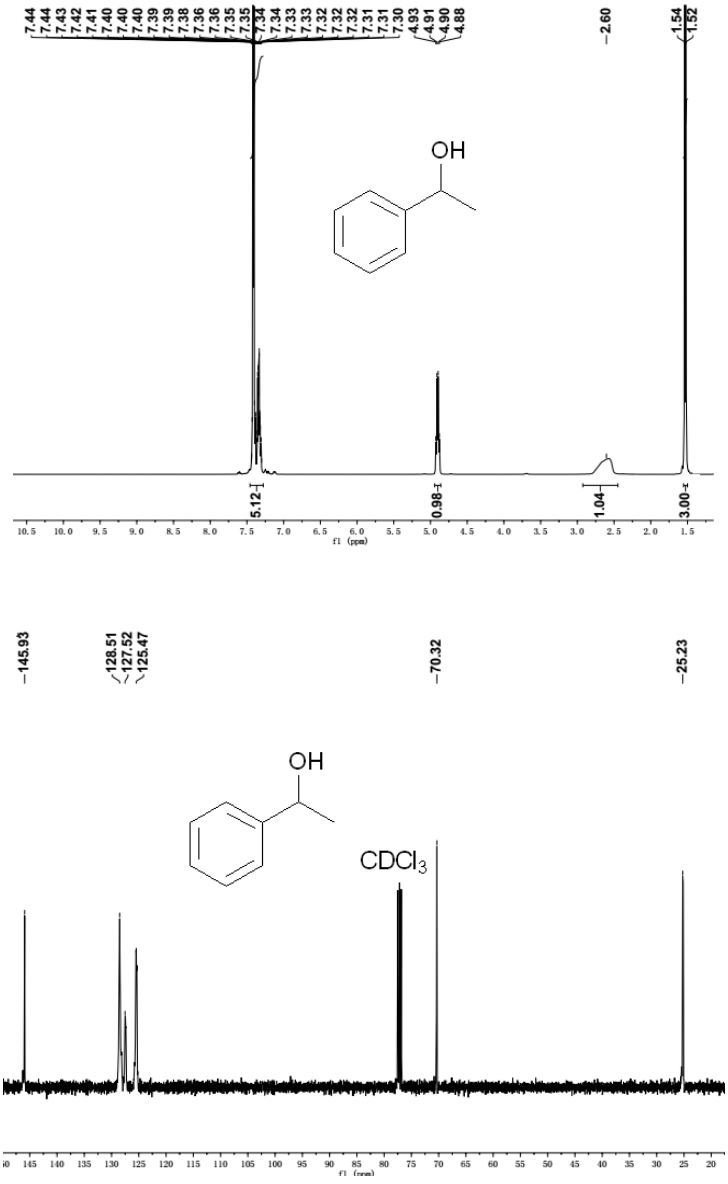


Figure S27 ^{1}H and ^{13}C NMR spectra of 1-(4-fluorophenyl)ethan-1-ol in $CDCl_3$

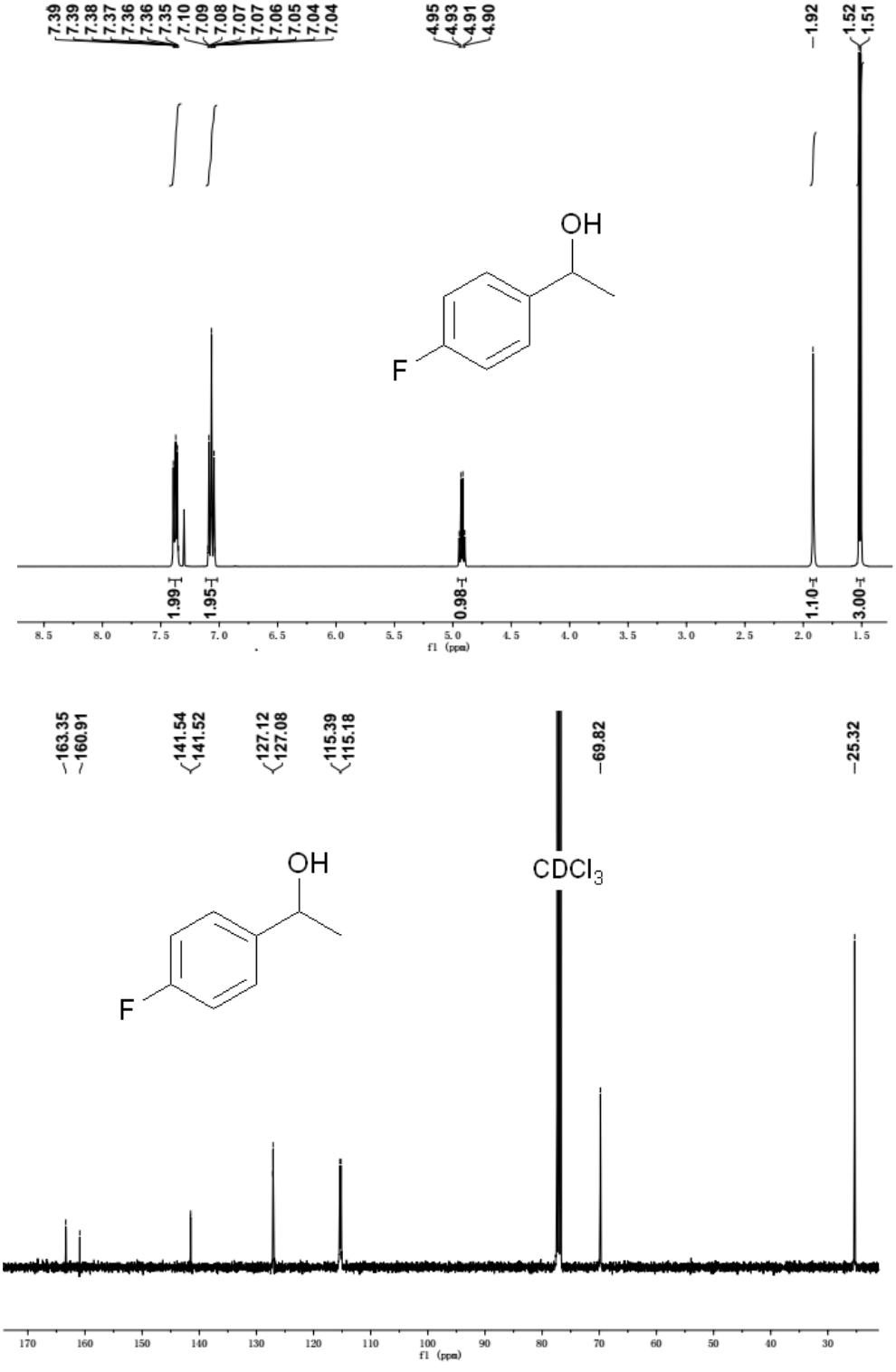


Figure S28 ^{1}H and ^{13}C NMR spectra of 1-(4-chlorophenyl)ethan-1-ol in $CDCl_3$

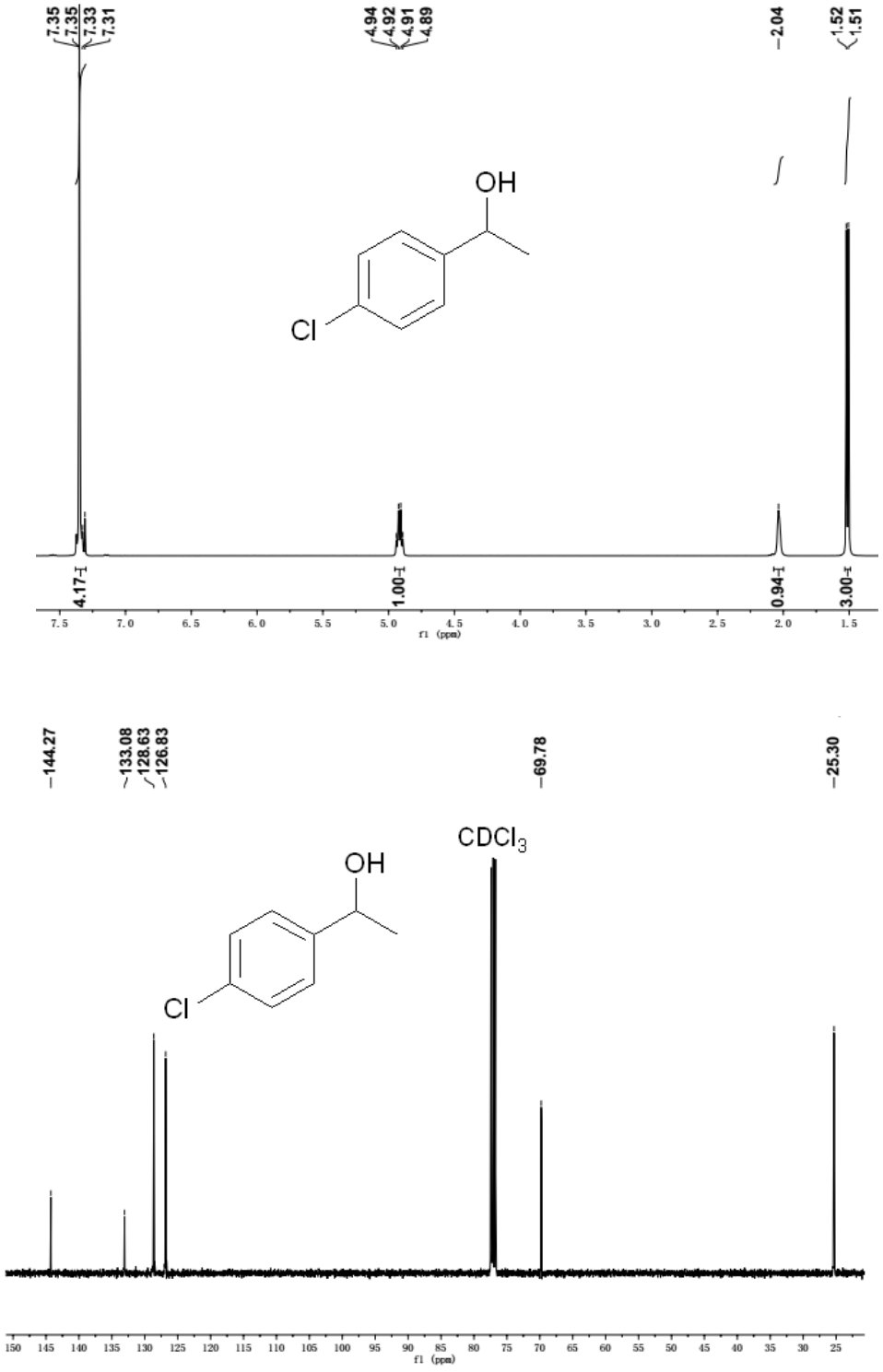
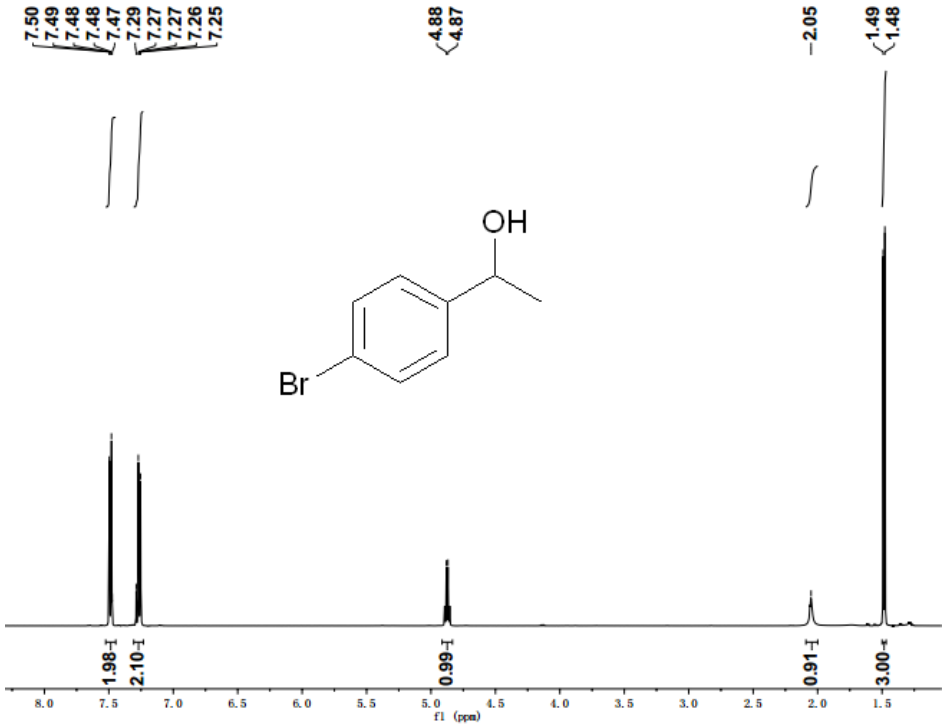


Figure S29 ^{1}H and ^{13}C NMR spectra of 1-(4-bromophenyl)ethan-1-ol in $CDCl_3$



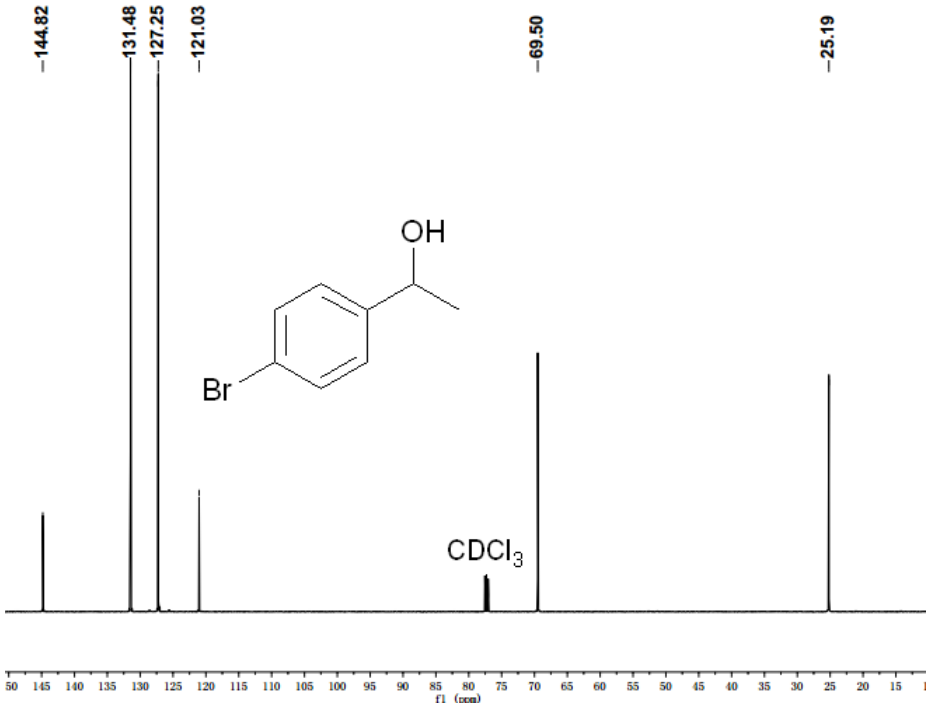
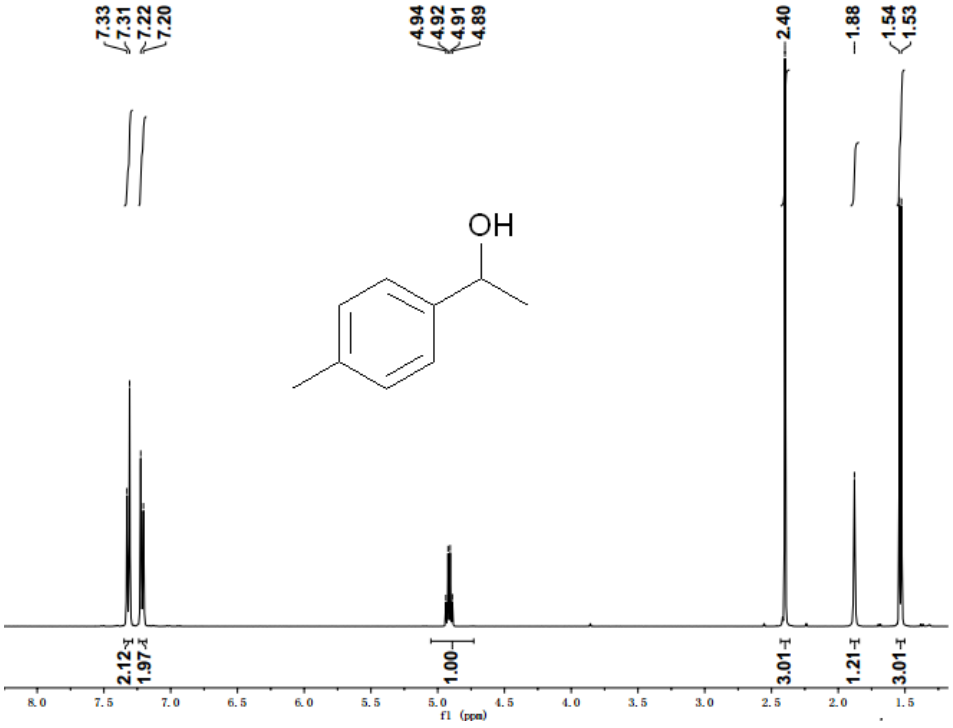


Figure S30 ^{1}H and ^{13}C NMR spectra of 1-(p-tolyl)ethan-1-ol in $CDCl_3$



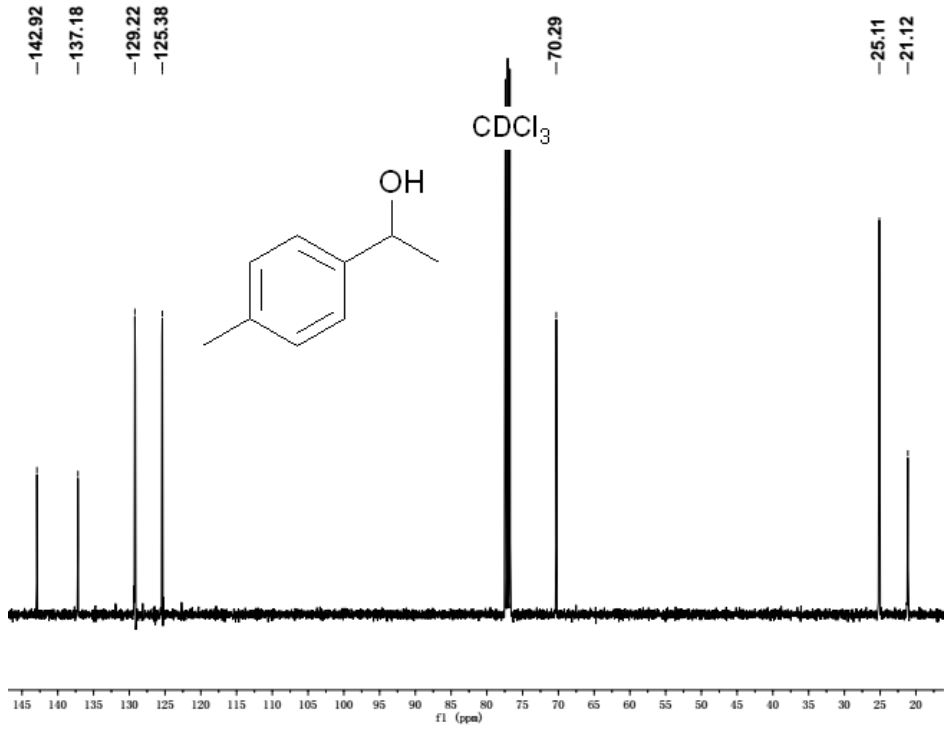


Figure S31 ^{1}H and ^{13}C NMR spectra of 1-(4-methoxyphenyl)ethan-1-ol in $CDCl_3$

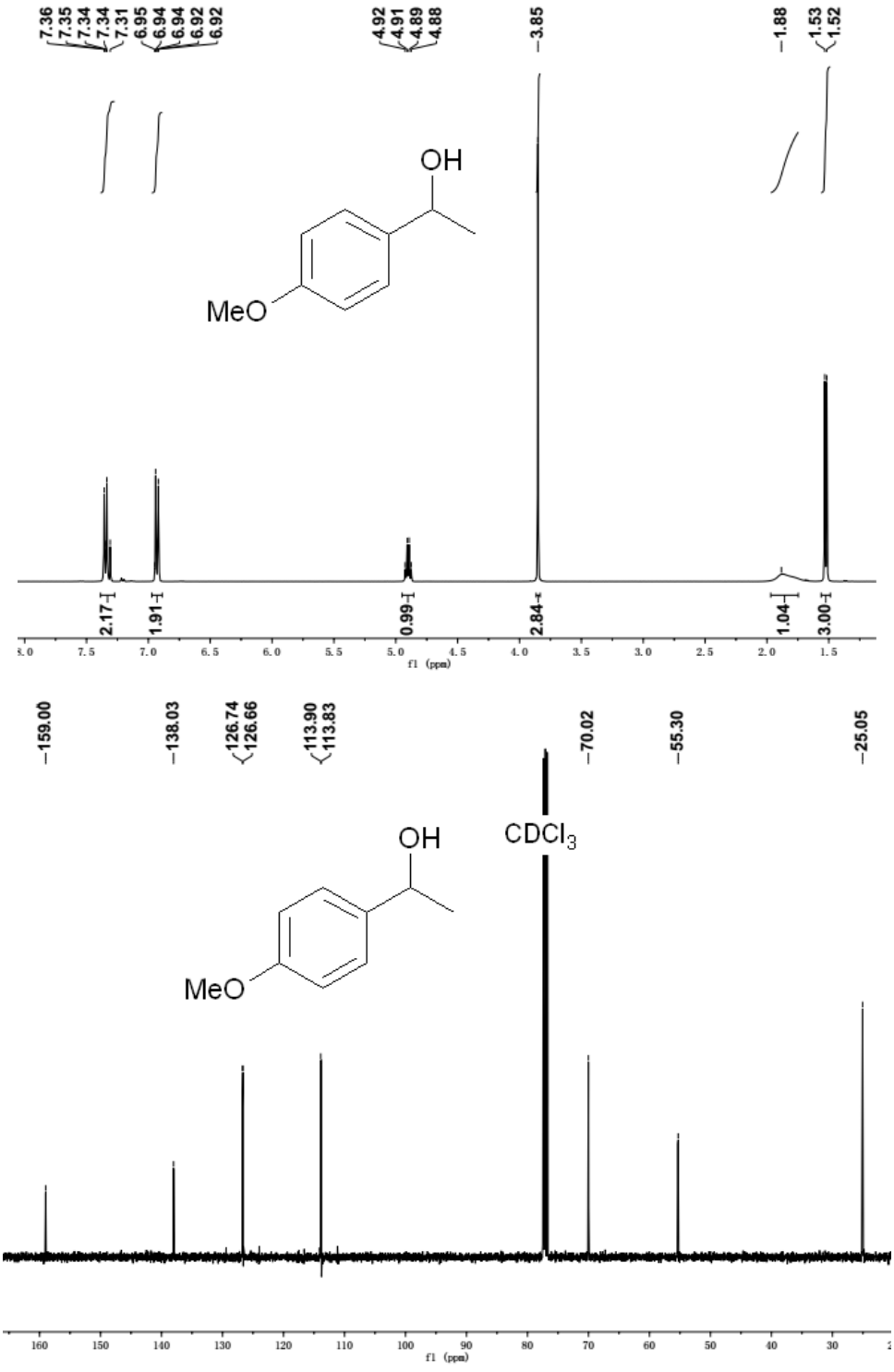


Figure S32 ^{1}H and ^{13}C NMR spectra of 1-(3-chlorophenyl)ethan-1-ol in $CDCl_3$

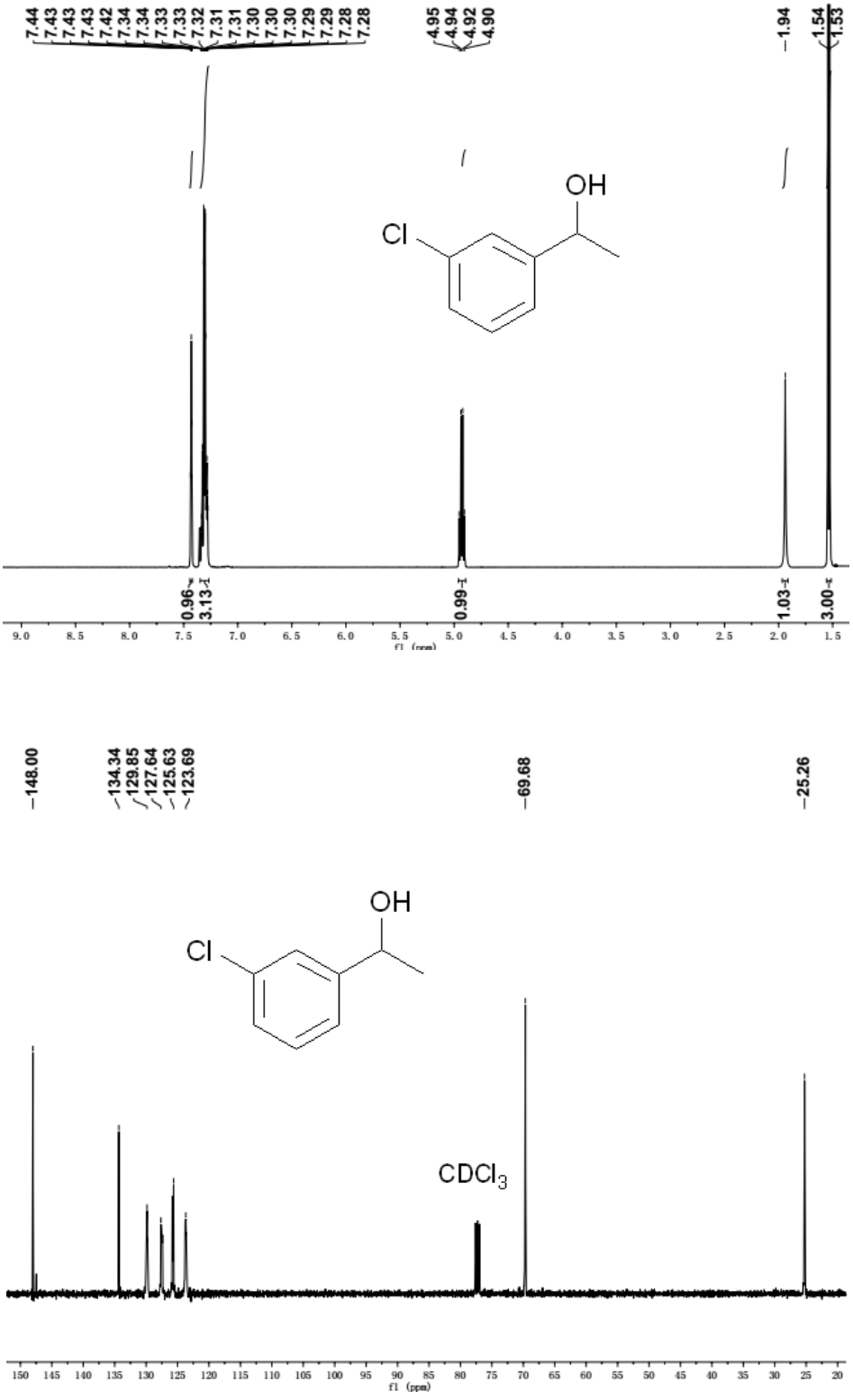


Figure S33 ^{1}H and ^{13}C NMR spectra of 1-(3-bromophenyl)ethan-1-ol in $CDCl_3$

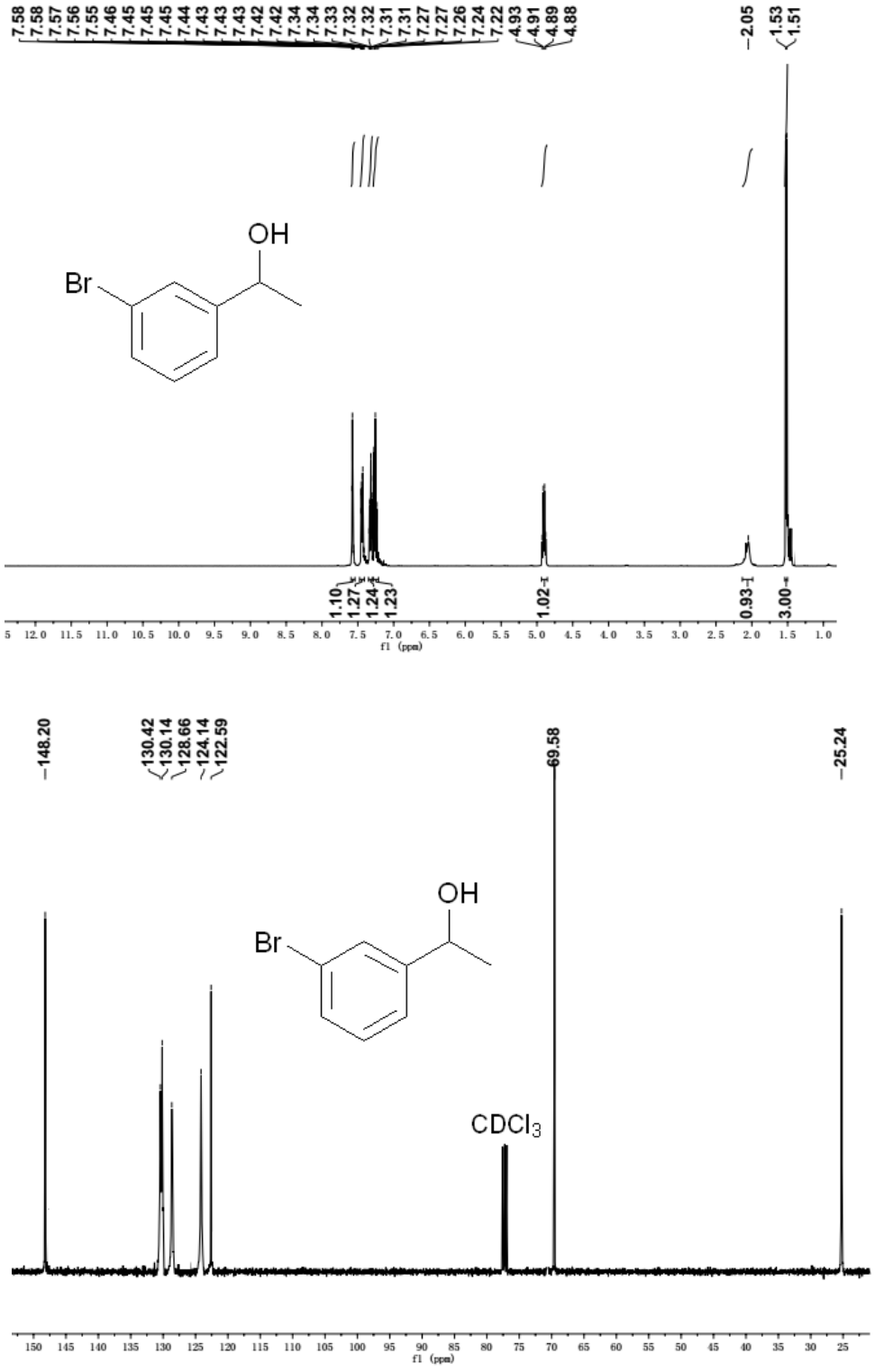


Figure S34 ^{1}H and ^{13}C NMR spectra of 1-(2-chlorophenyl)ethan-1-ol in $CDCl_3$

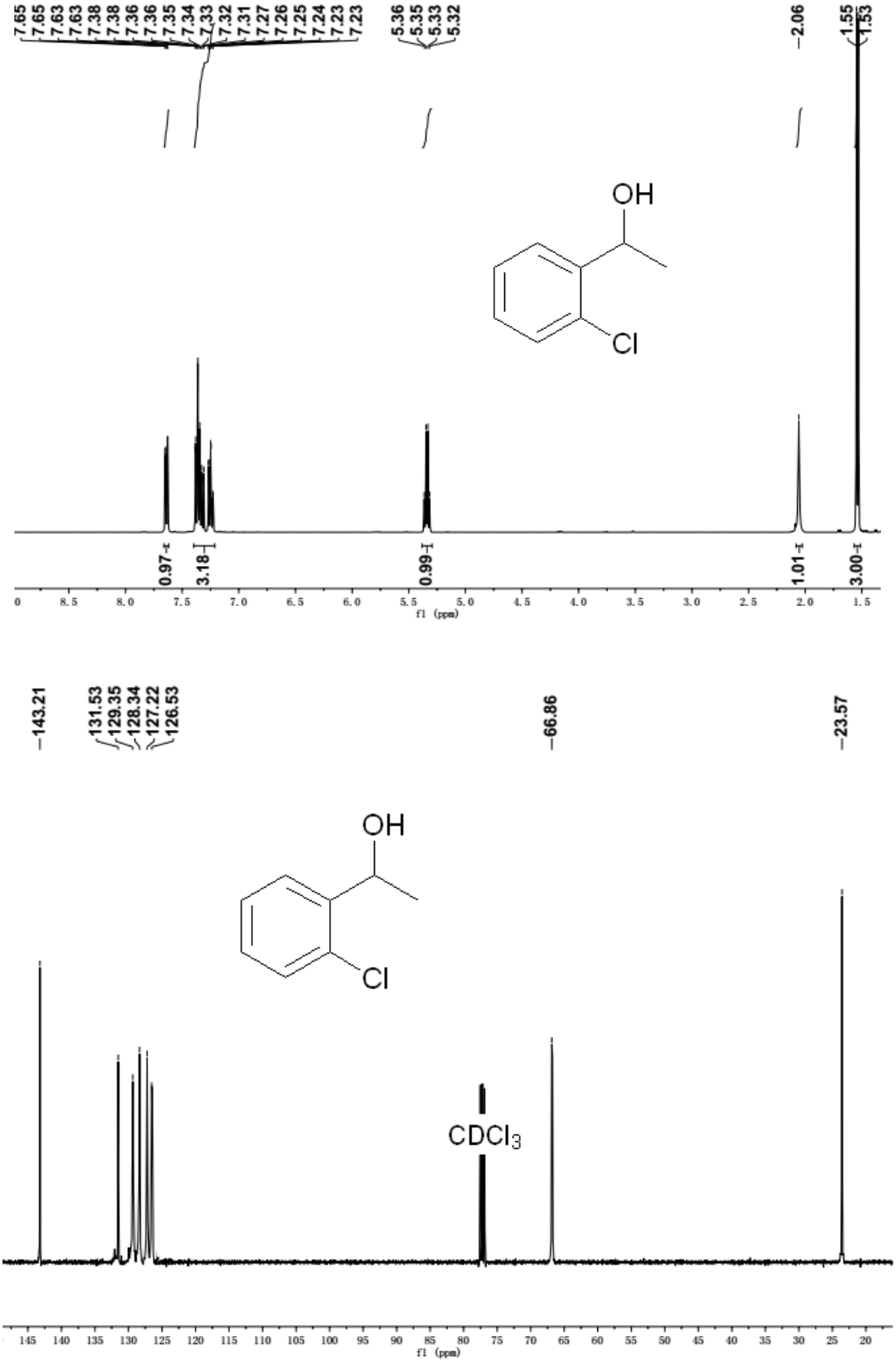


Figure S35 ^{1}H and ^{13}C NMR spectra of 1-(1-tolyl)ethan-1-ol in $CDCl_3$

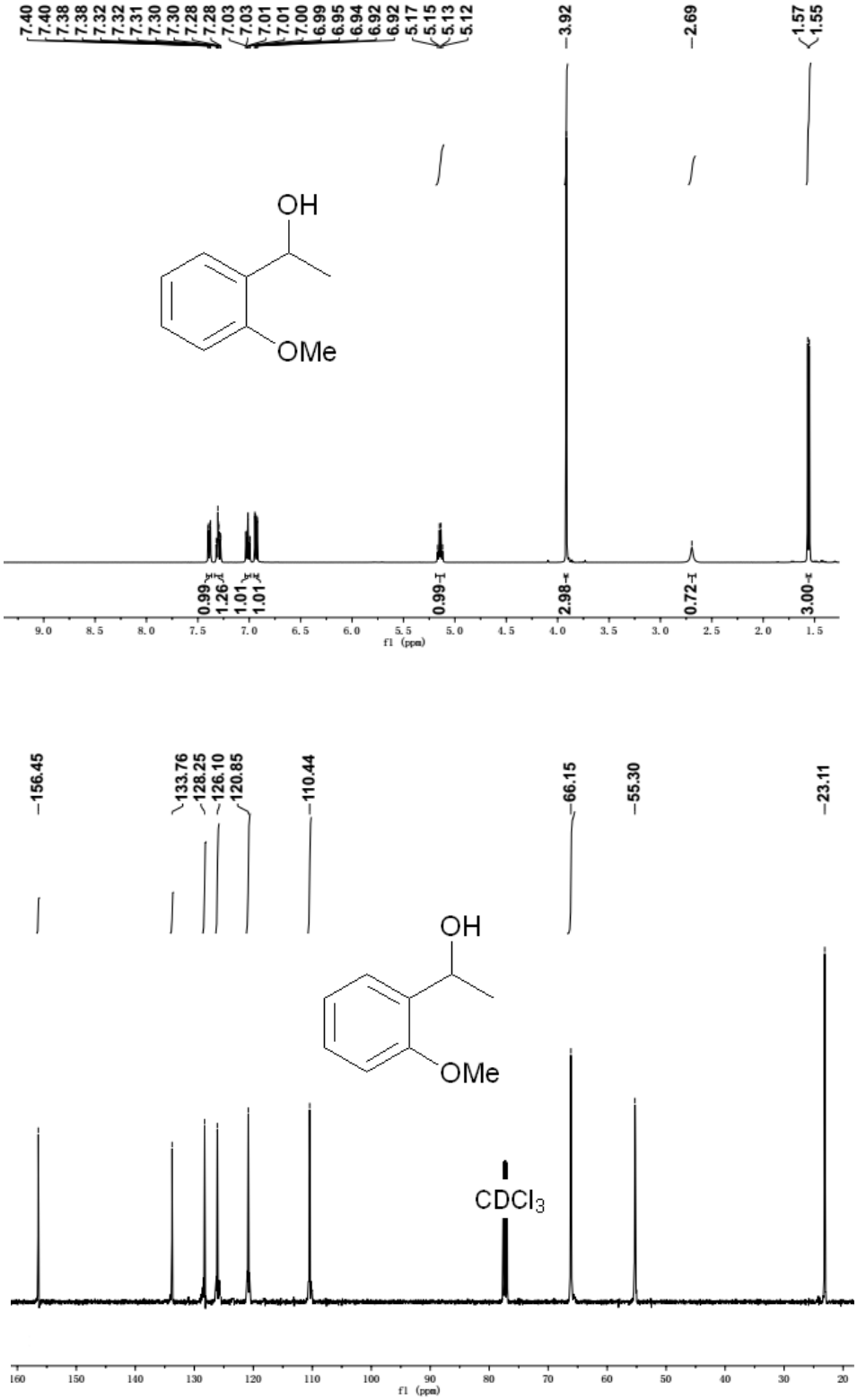
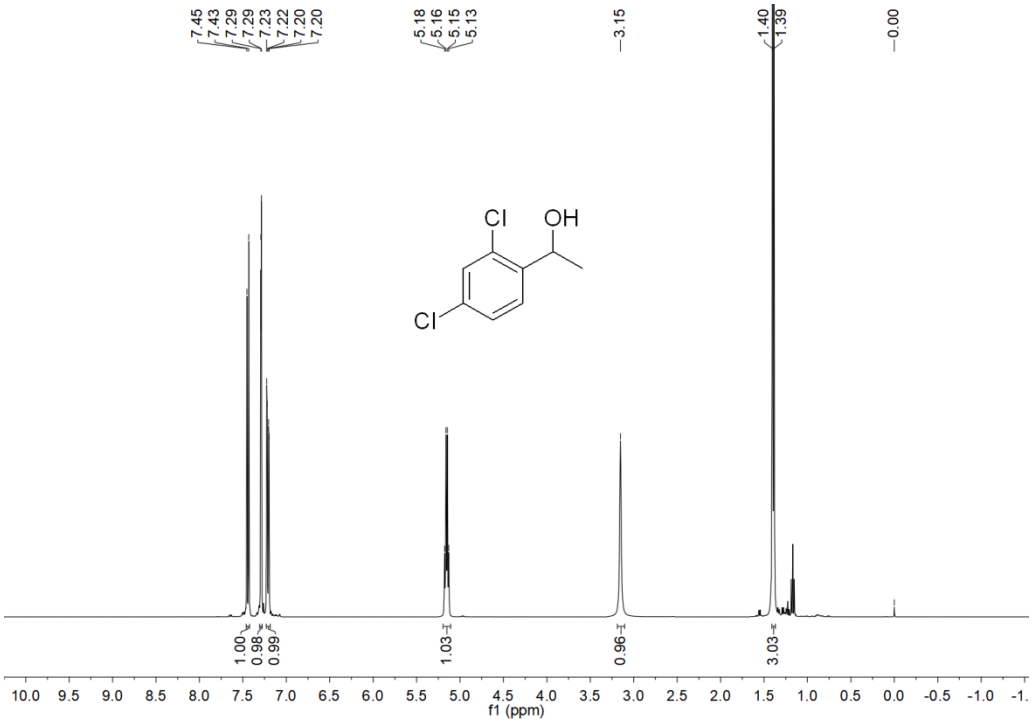


Figure S36 ^{1}H and ^{13}C NMR spectra of 1-(2,4-dichlorophenyl)ethan-1-ol in $CDCl_3$



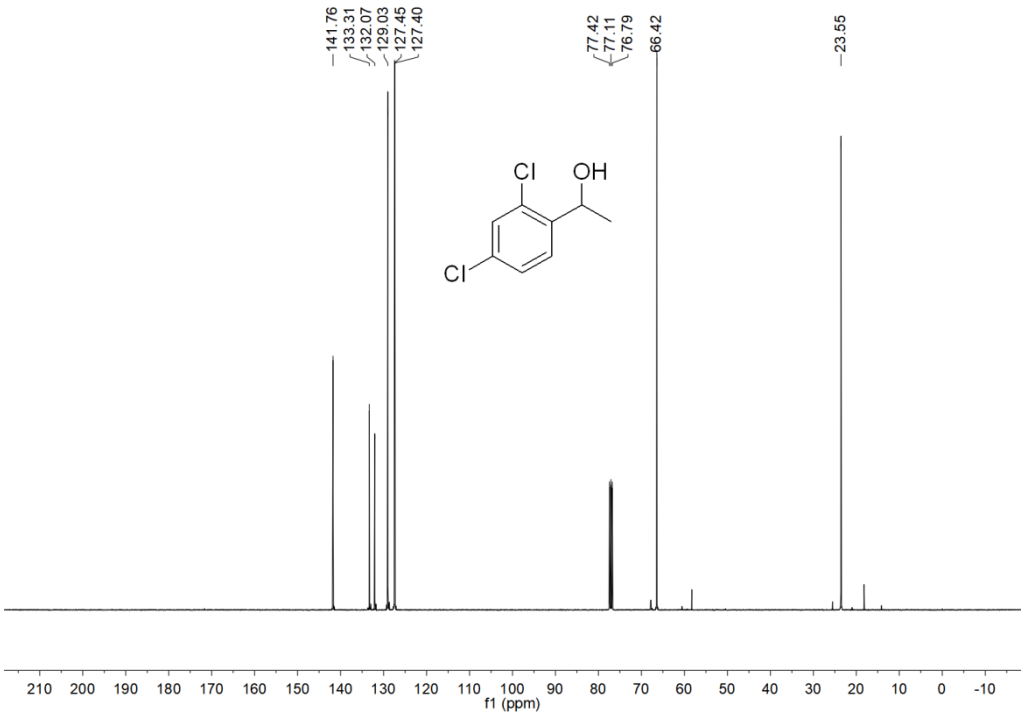
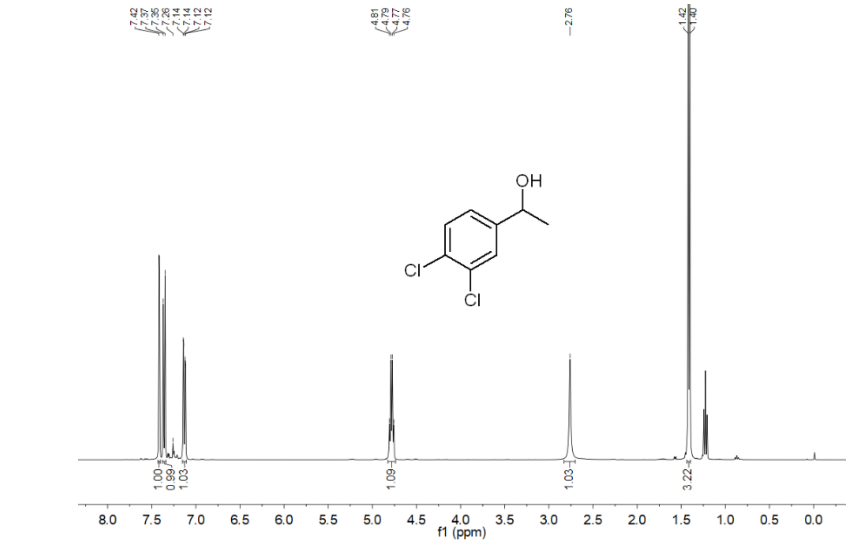


Figure S37 ^{1}H and ^{13}C NMR spectra of 1-(3,4-dichlorophenyl)ethan-1-ol in $CDCl_3$



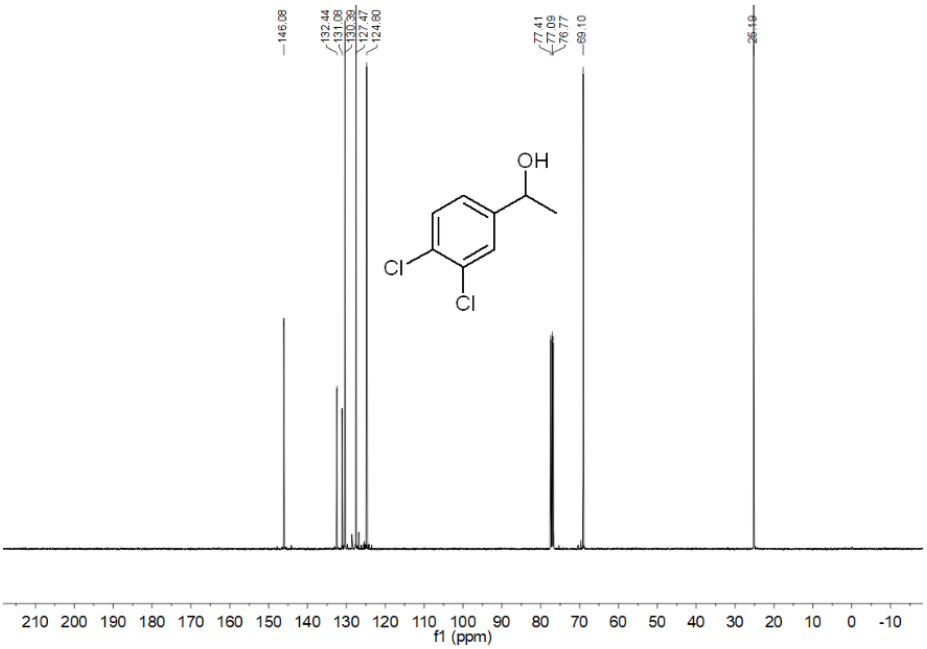


Figure S38 ^{1}H and ^{13}C NMR spectra of 1-(5-fluoro-2-iodophenyl)ethan-1-ol in $CDCl_3$

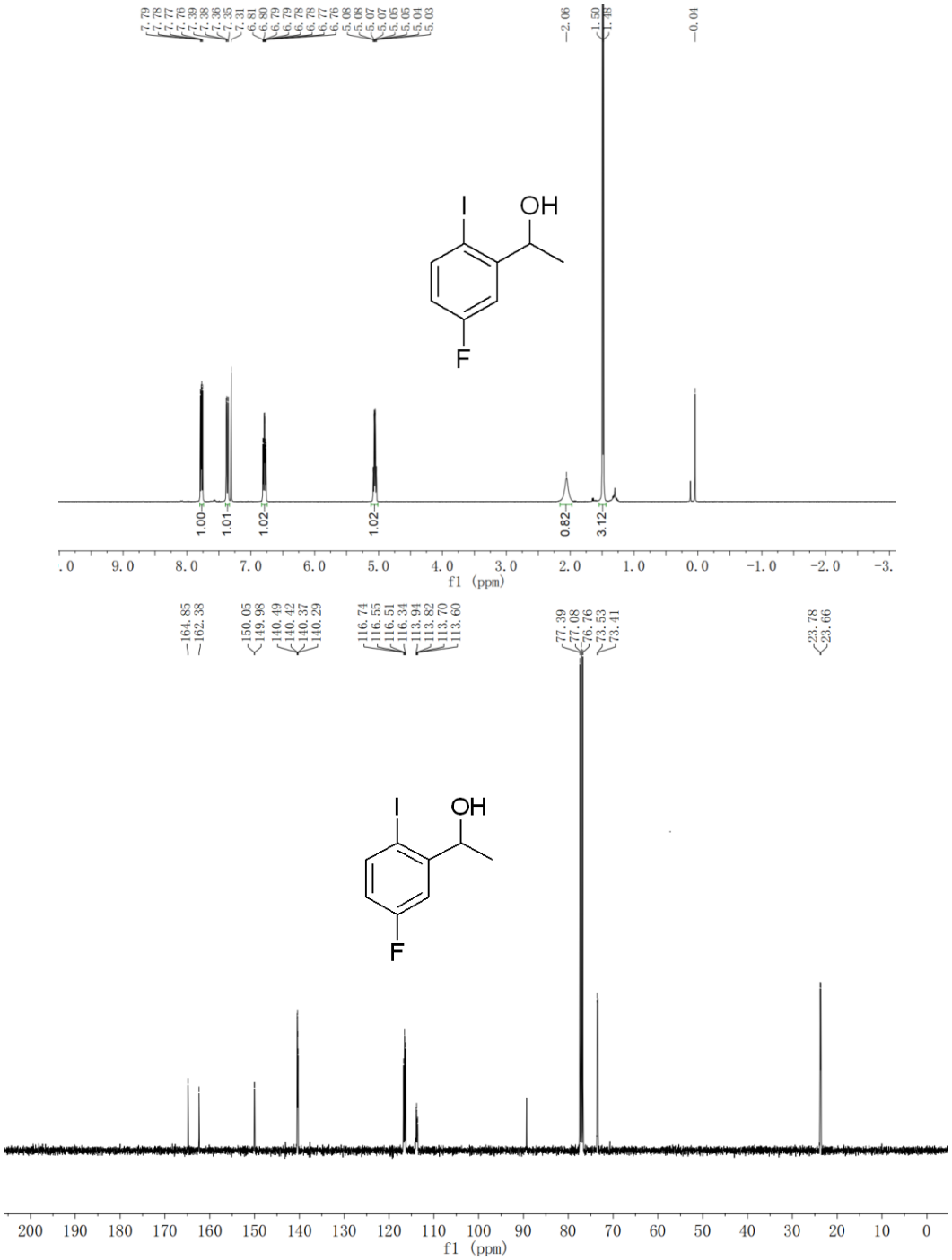
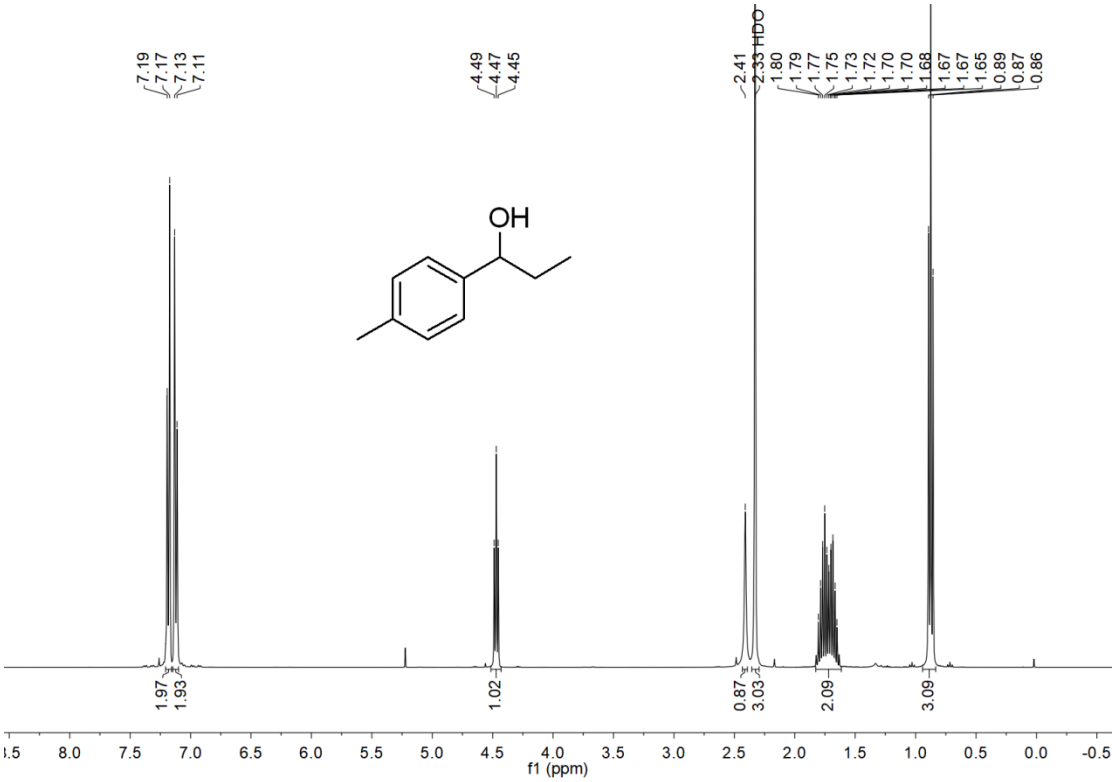


Figure S39 ^{1}H and ^{13}C NMR spectra of 1-(p-tolyl)propan-1-ol in $CDCl_3$



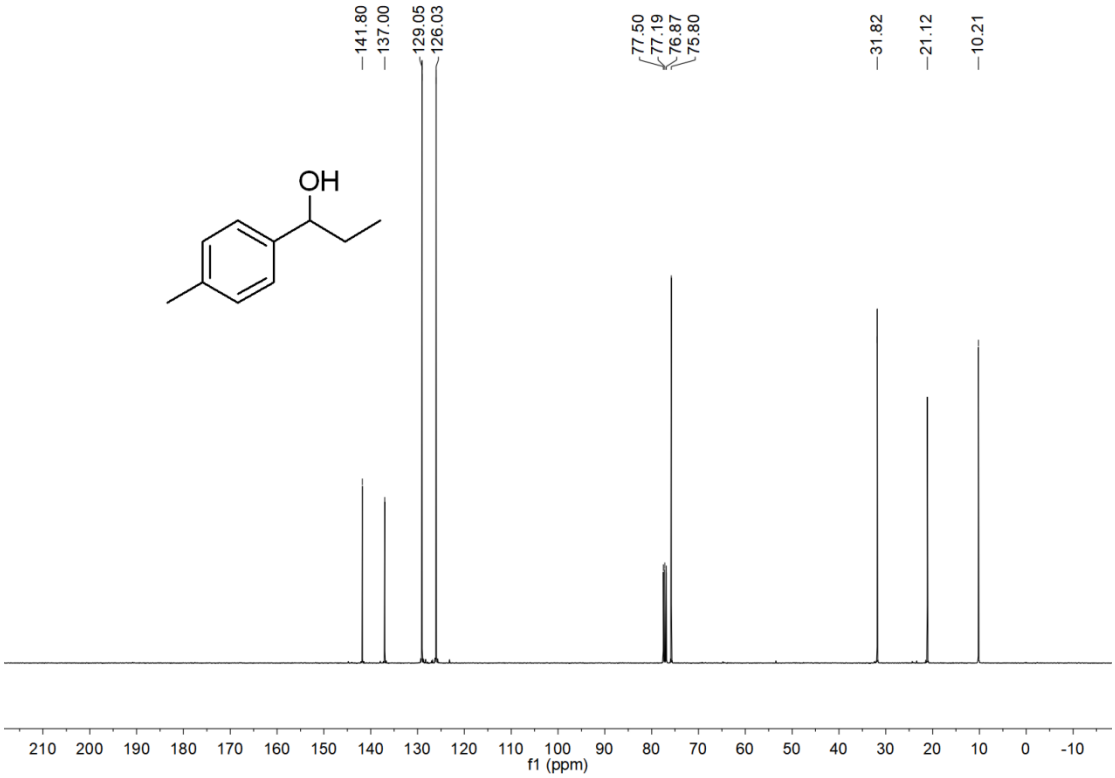


Figure S40 ^{1}H and ^{13}C NMR spectra of 1-(3-chlorophenyl)propan-1-ol in $CDCl_3$

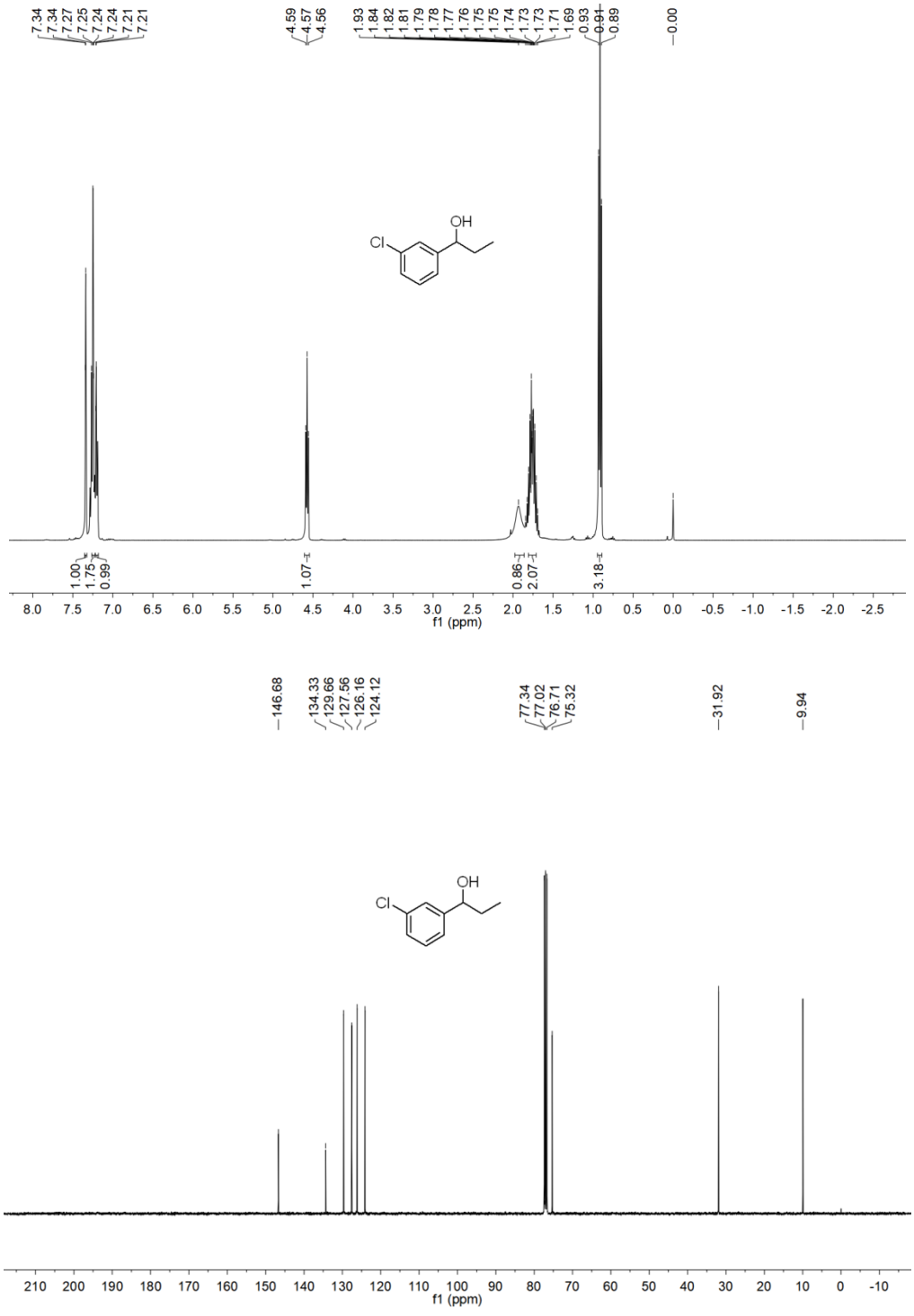


Figure S41 ^{1}H and ^{13}C NMR spectra of 1-phenylbutan-1-ol in $CDCl_3$

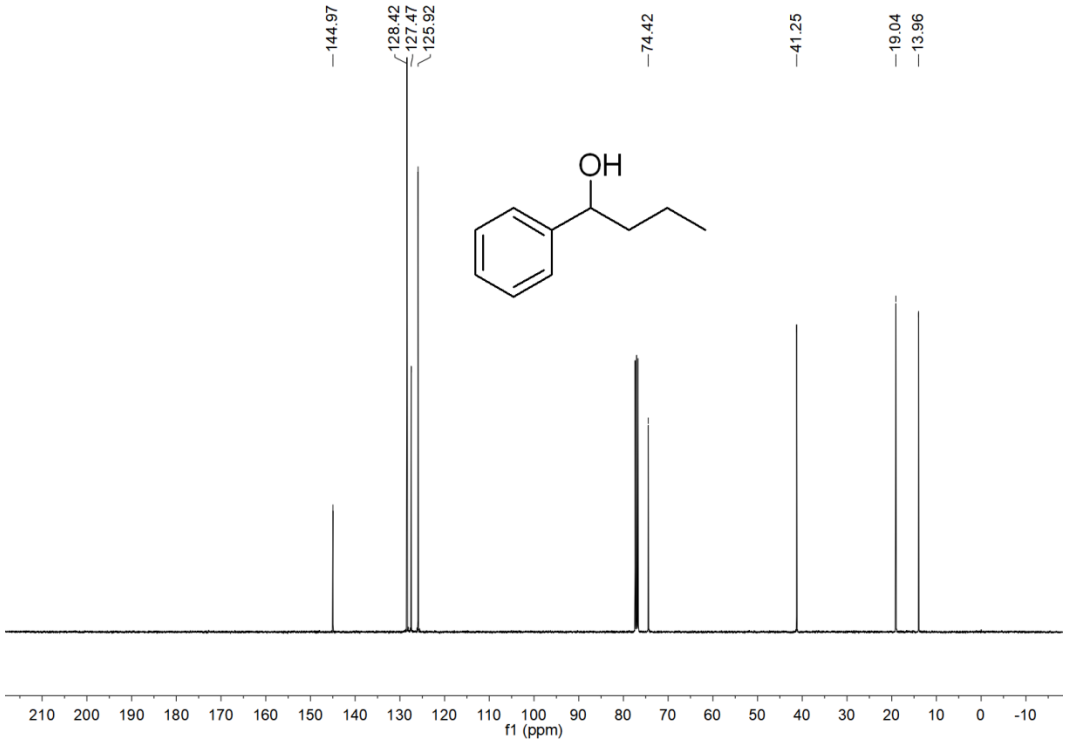


Figure S42 ^{1}H and ^{13}C NMR spectra of 2-methyl-1-phenylpropan-1-ol in $CDCl_3$

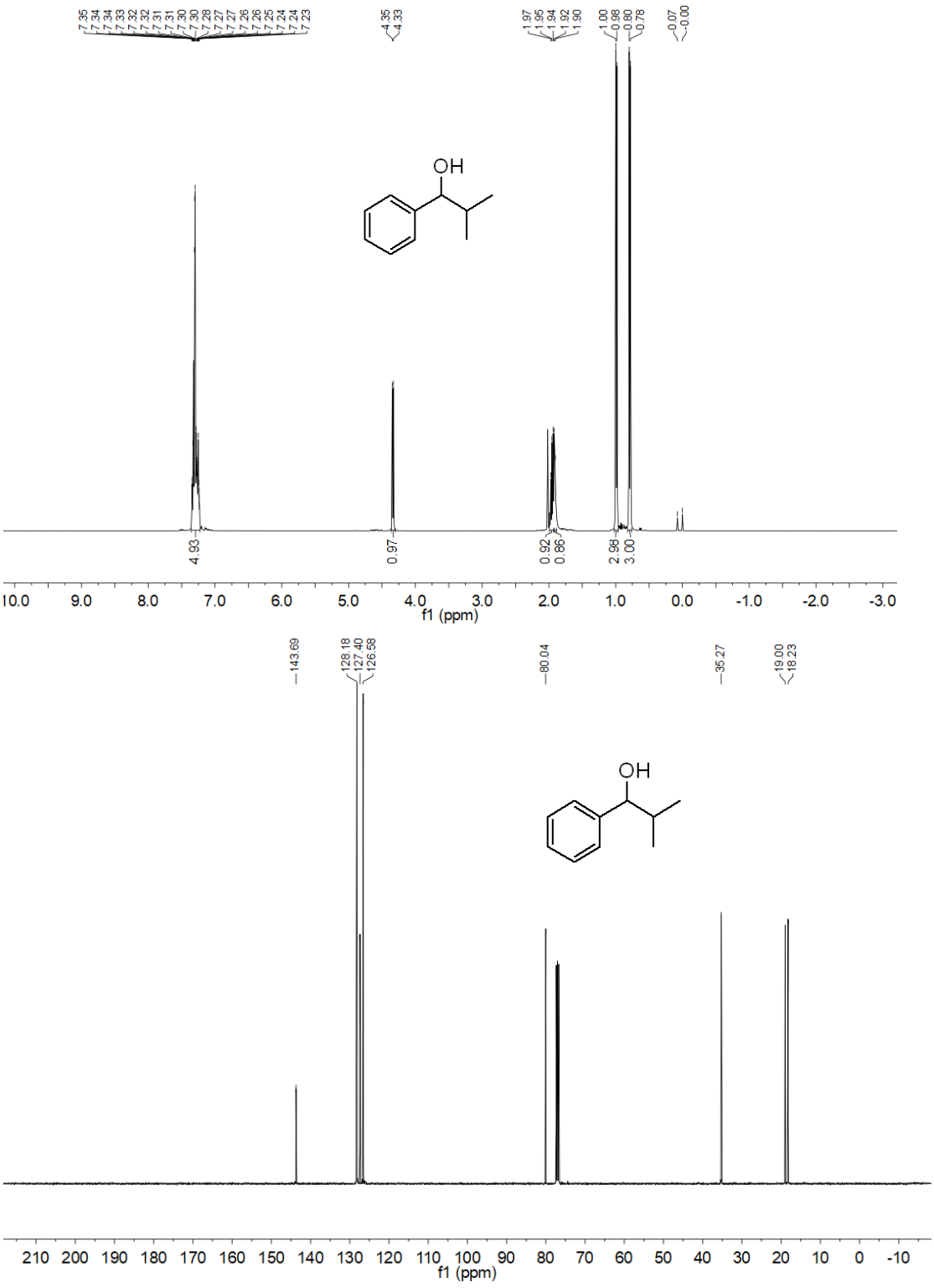


Figure S43 ^{1}H and ^{13}C NMR spectra of cyclohexyl(phenyl)methanol in $CDCl_3$

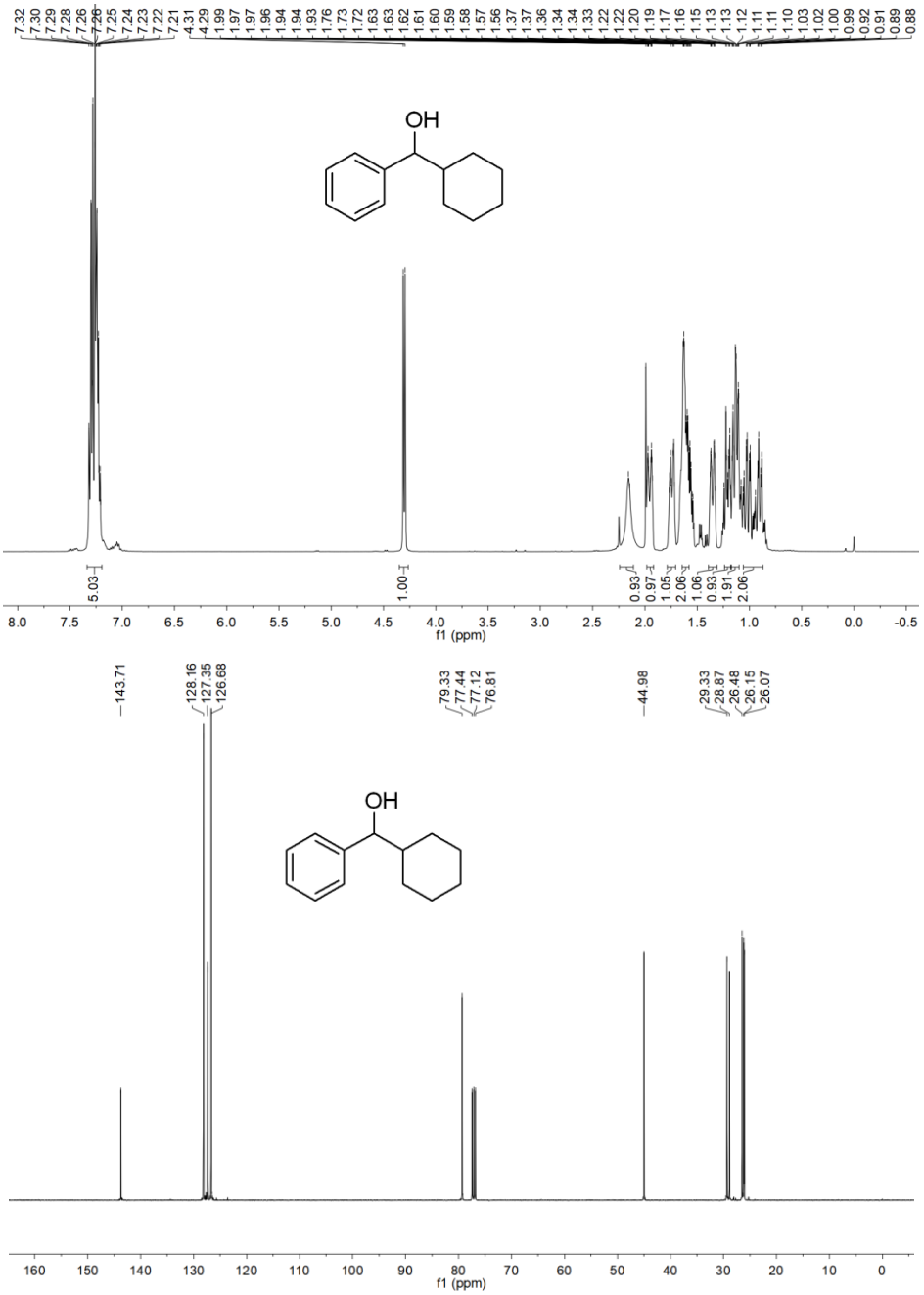


Figure S44 ^{1}H and ^{13}C NMR spectra of 1-(naphthalen-2-yl)ethan-1-ol in $CDCl_3$

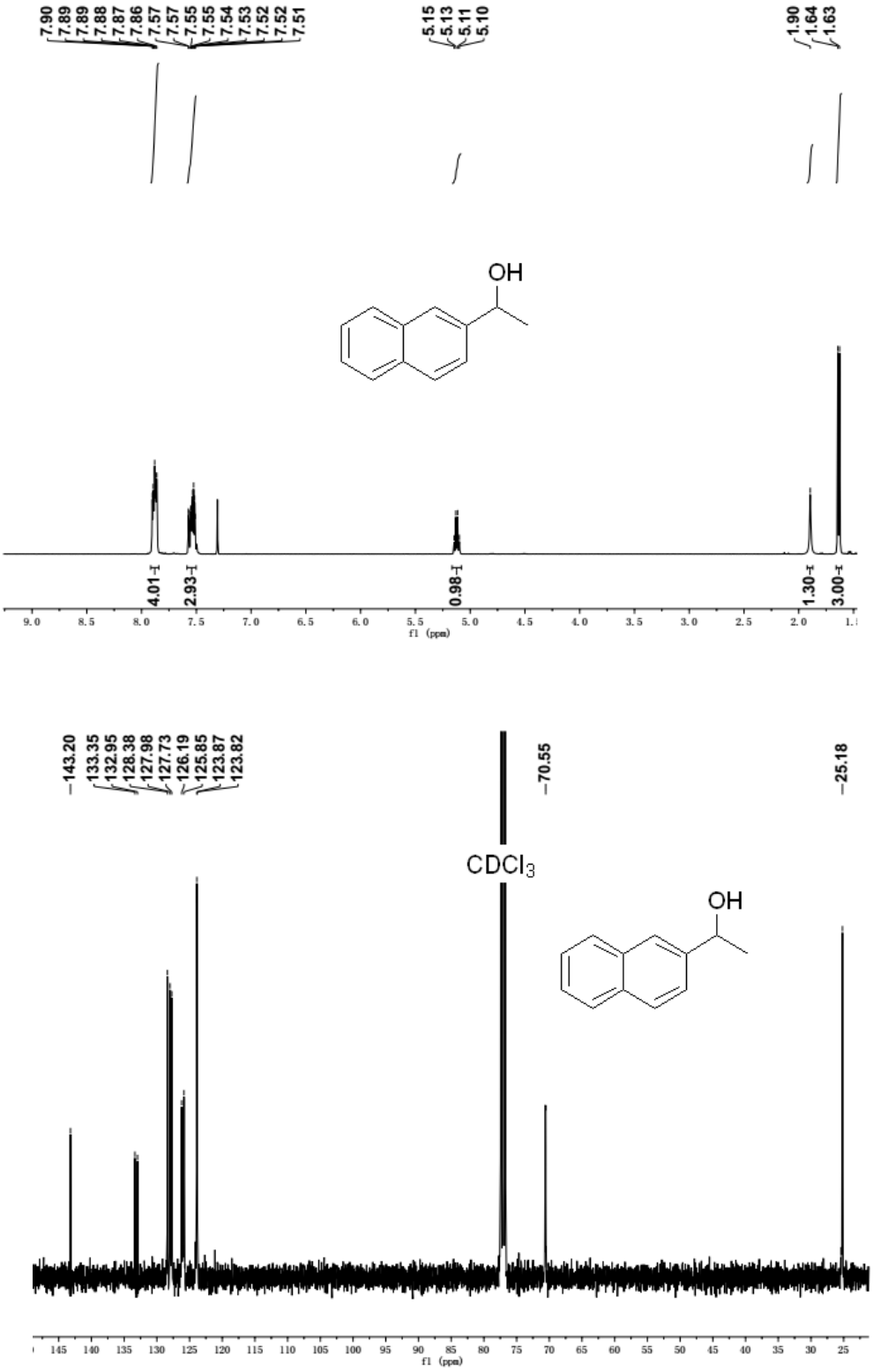
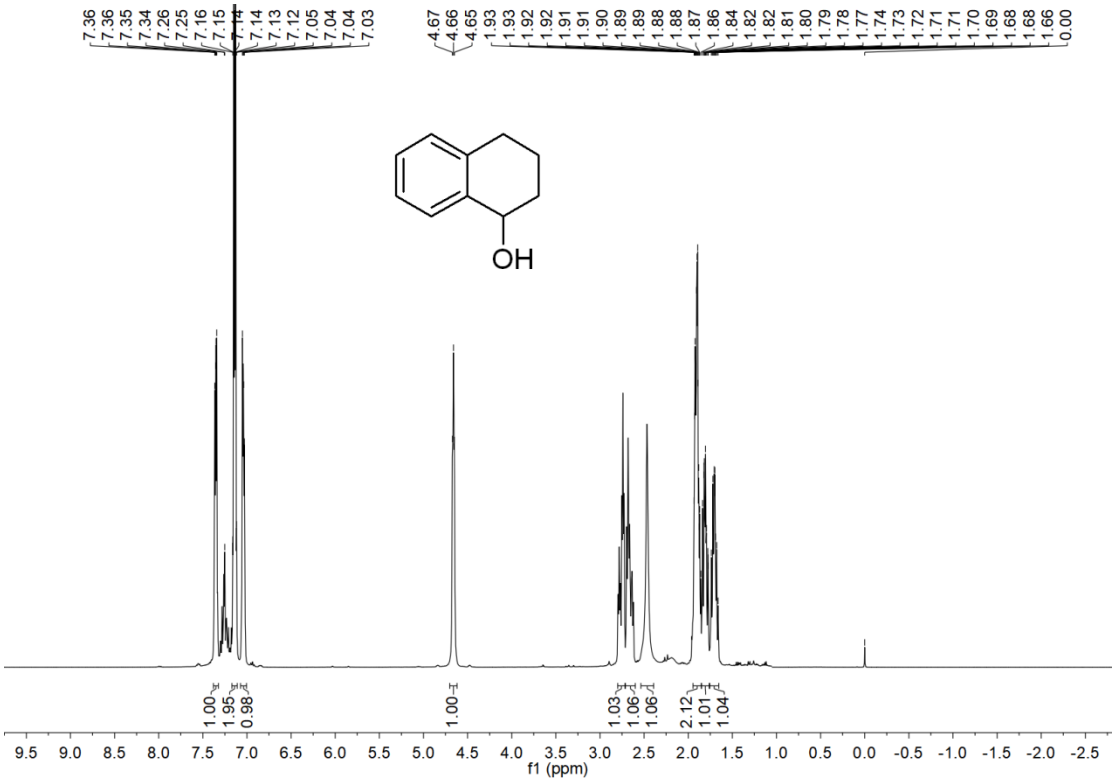


Figure S45 ^{1}H and ^{13}C NMR spectra of 1,2,3,4-tetrahydronaphthalen-1-ol in $CDCl_3$



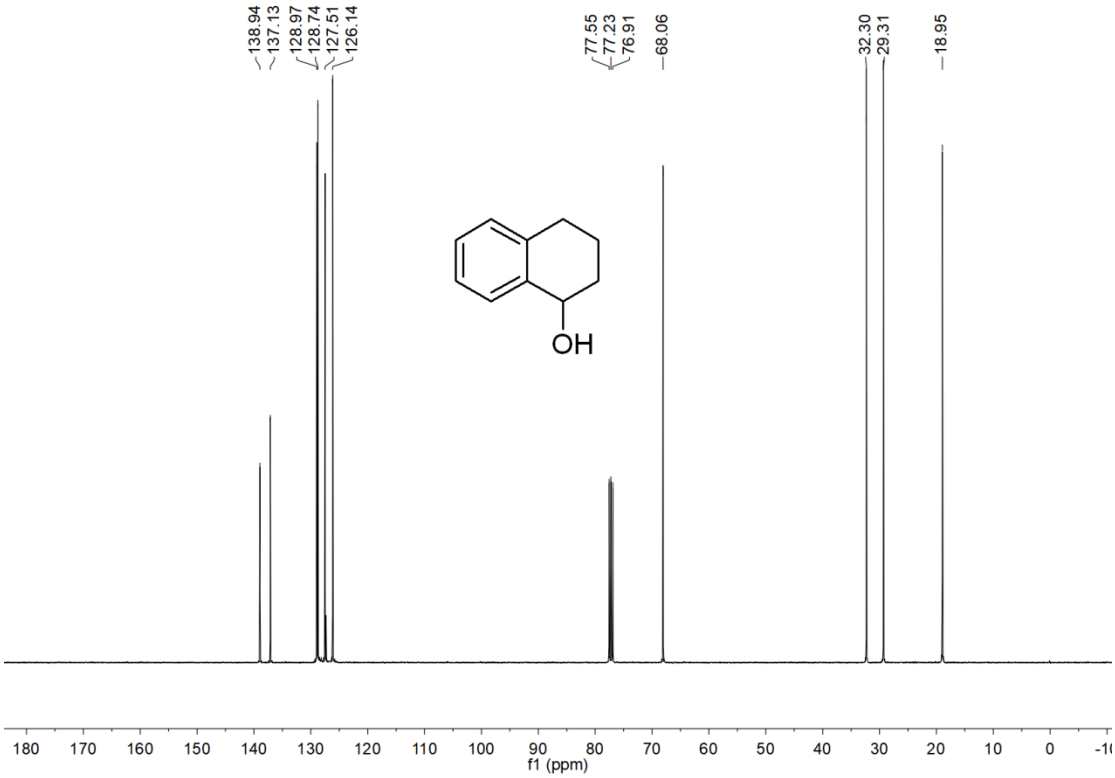


Figure S46 ^{1}H and ^{13}C NMR spectra of 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ol in $CDCl_3$

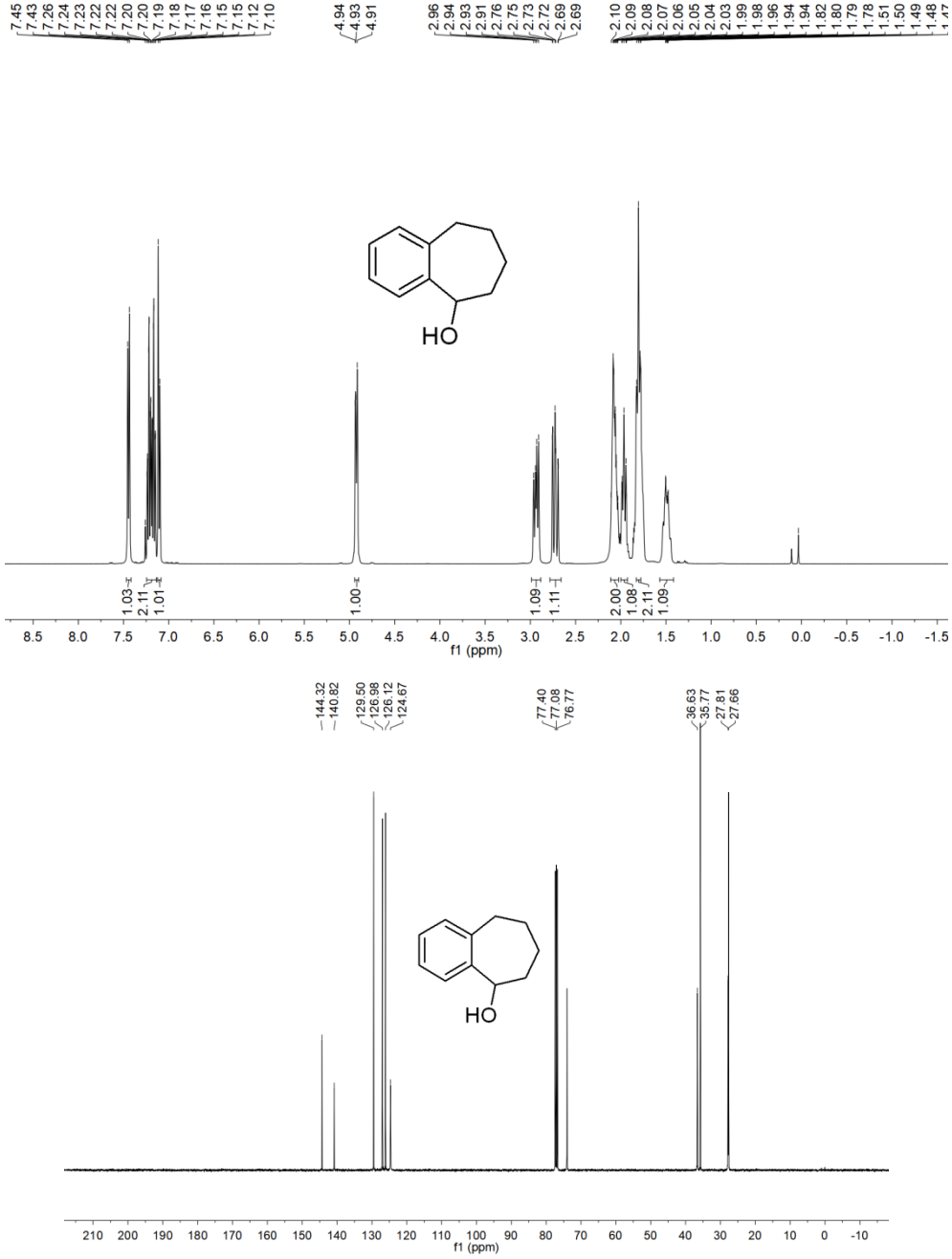


Figure S47 ^{1}H and ^{13}C NMR spectra of 1-(thiophen-2-yl)ethan-1-ol in $CDCl_3$

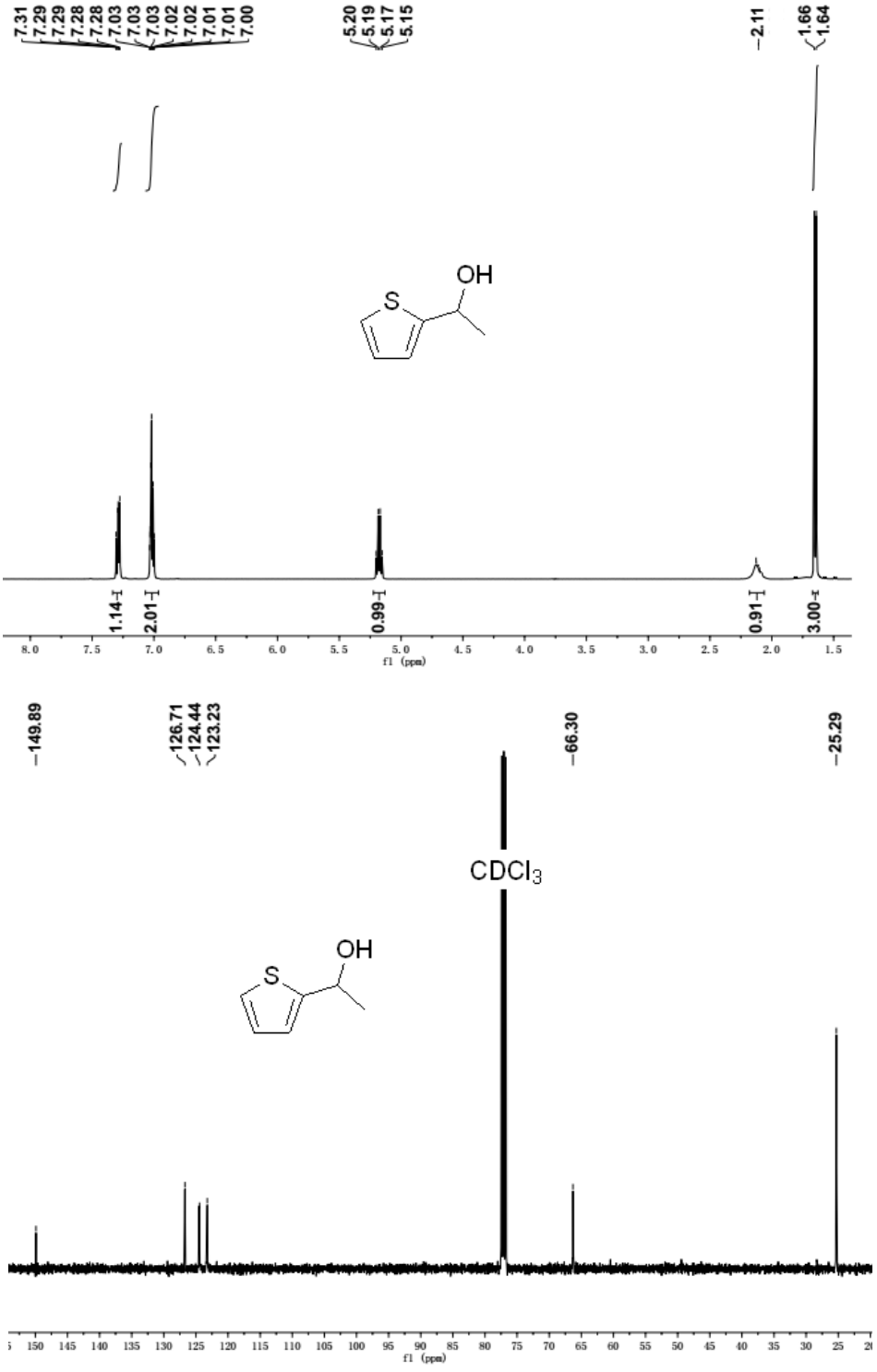


Figure S48 ^{1}H and ^{13}C NMR spectra of 5,6,7,8-tetrahydroquinolin-8-ol in $CDCl_3$

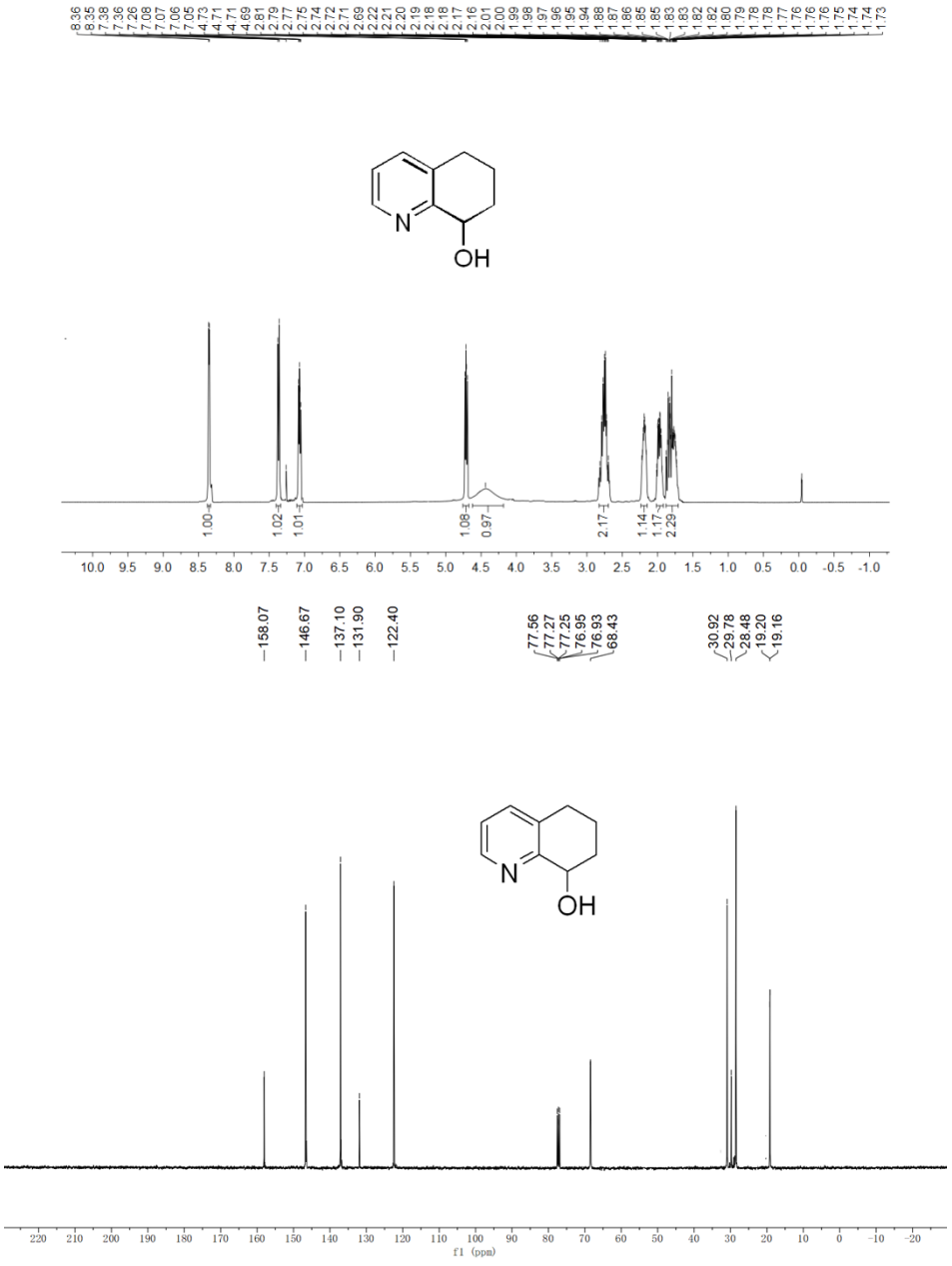


Figure S49 ^{1}H and ^{13}C NMR spectra of 4-phenylcyclohexan-1-ol in $CDCl_3$

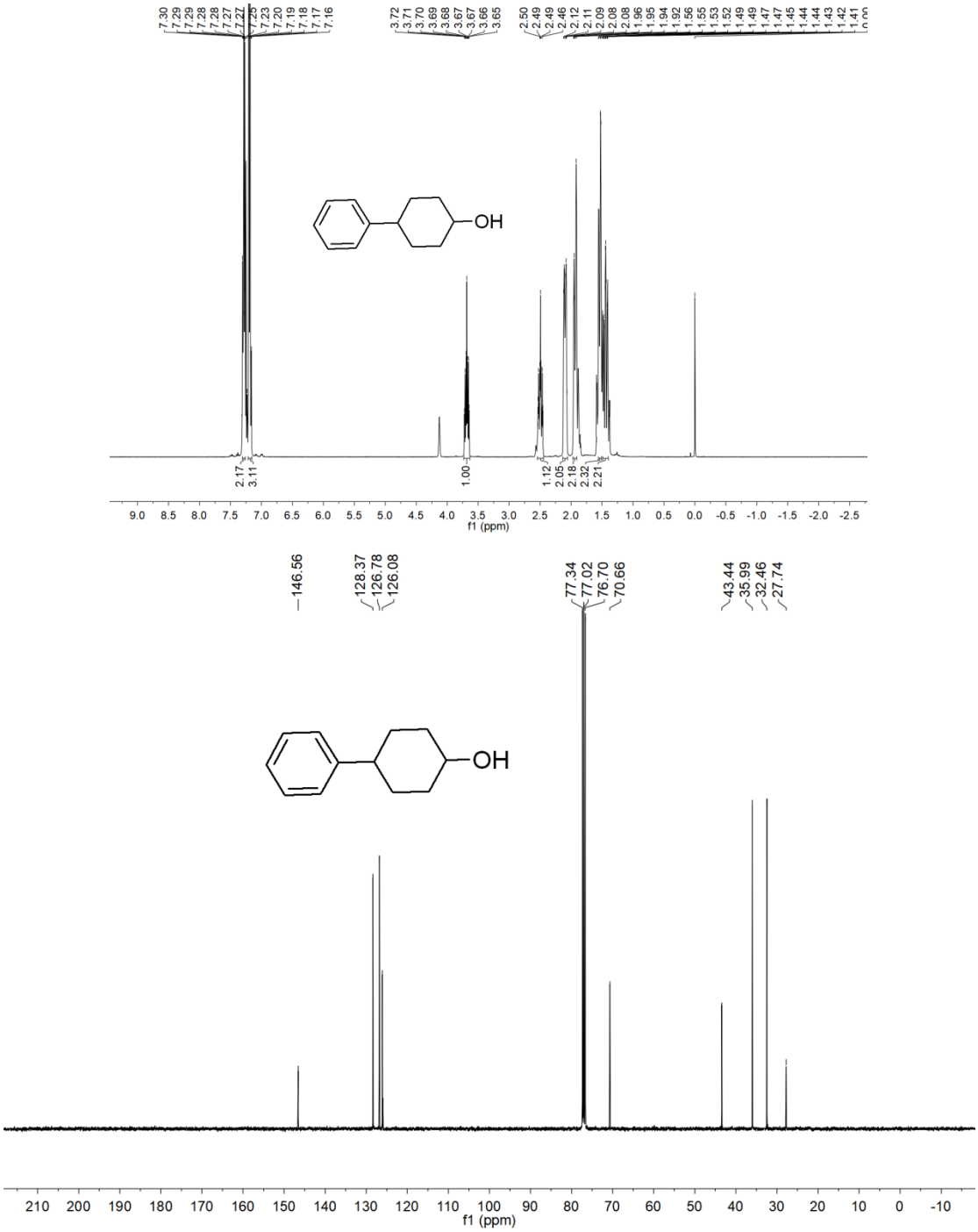


Figure S50 ^{1}H and ^{13}C NMR spectra of quinuclidin-3-ol in $CDCl_3$

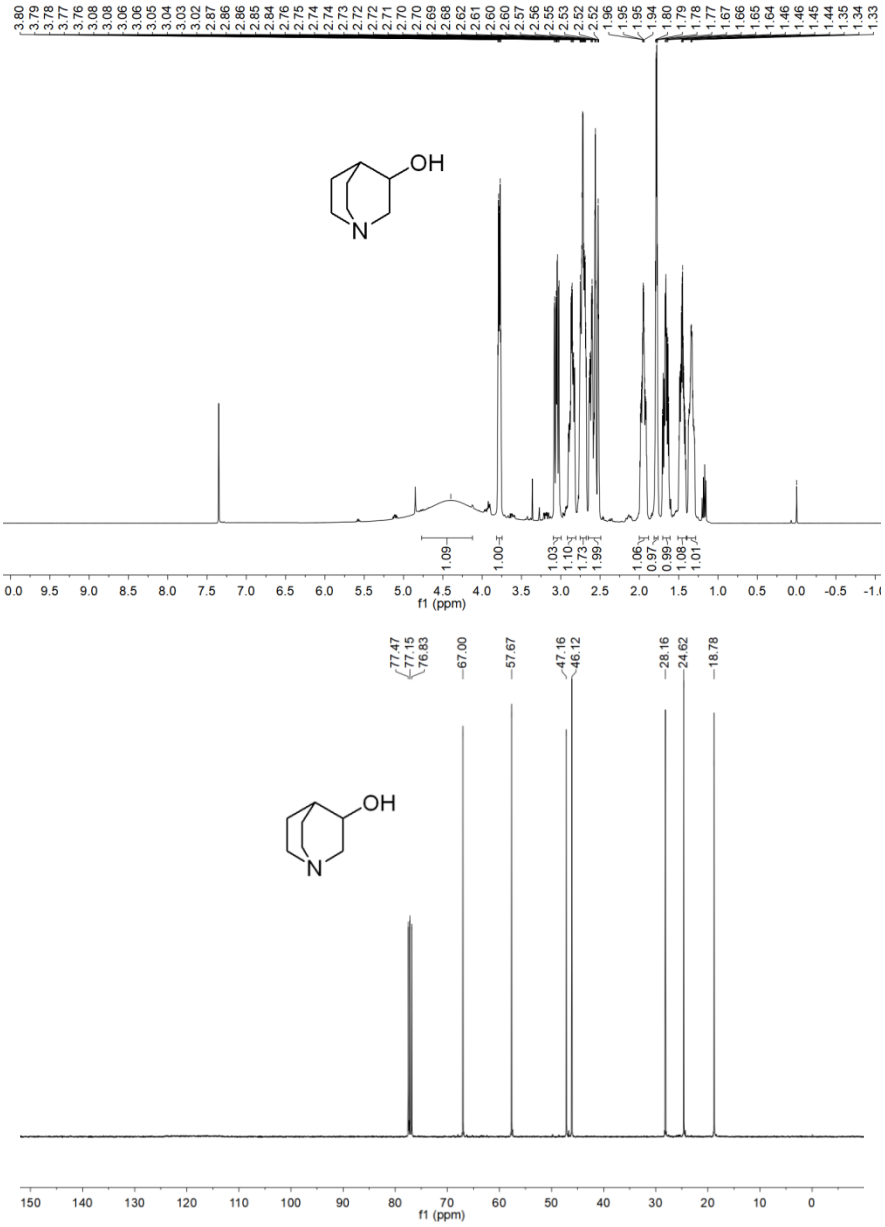


Figure S51 ^{1}H and ^{13}C NMR spectra of 4-phenylcyclohexan-1-ol in $CDCl_3$

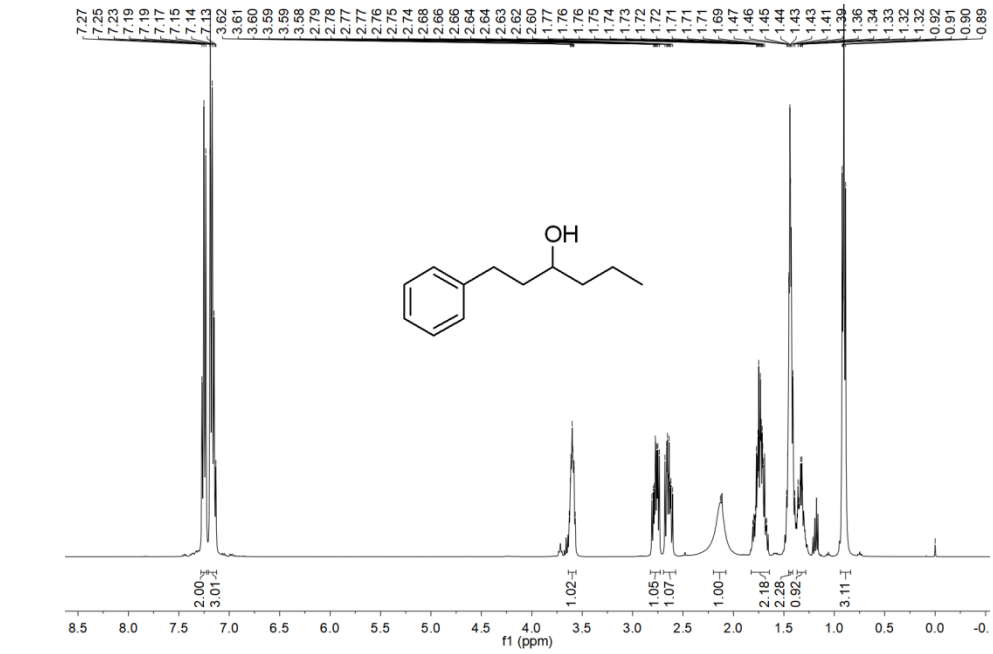
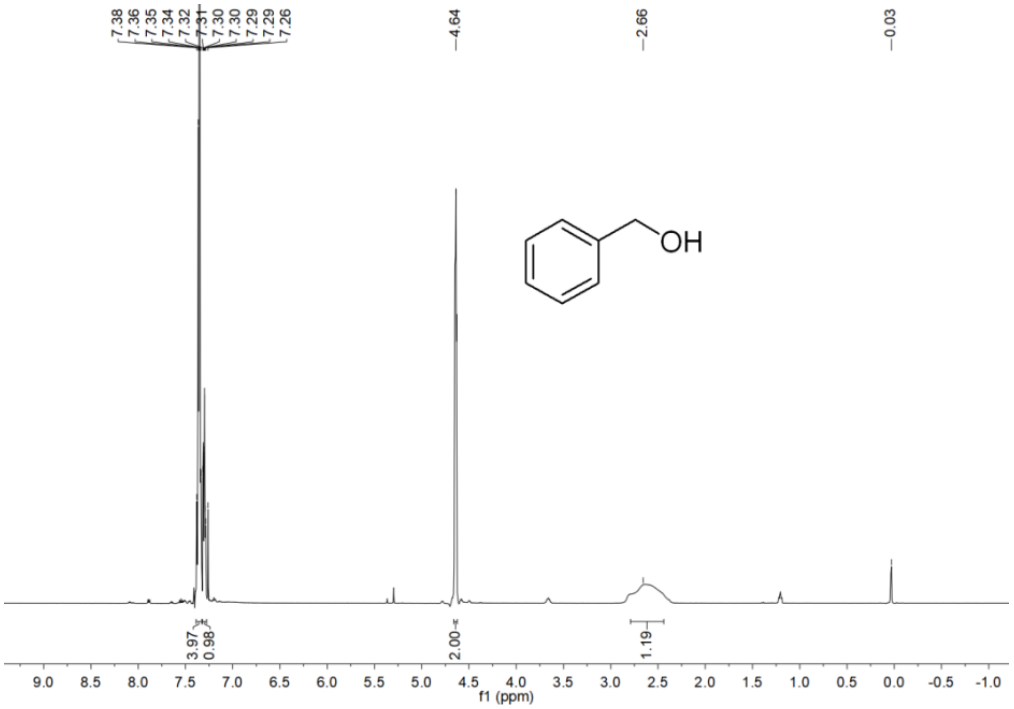


Figure S52 ^{1}H and ^{13}C NMR spectra of phenylmethanol in $CDCl_3$



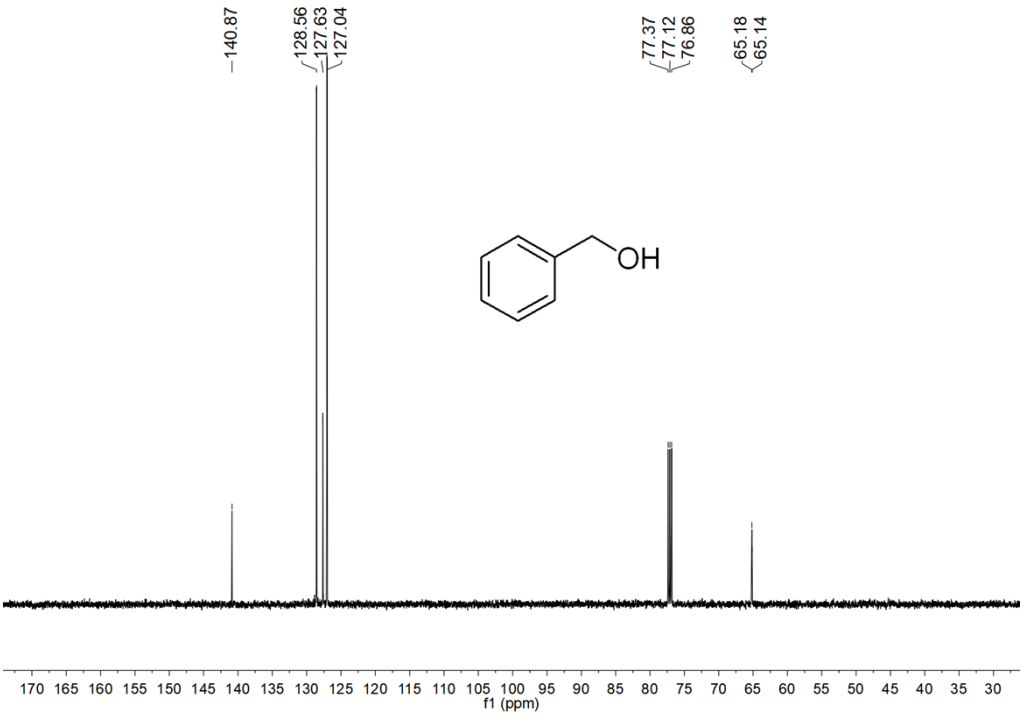
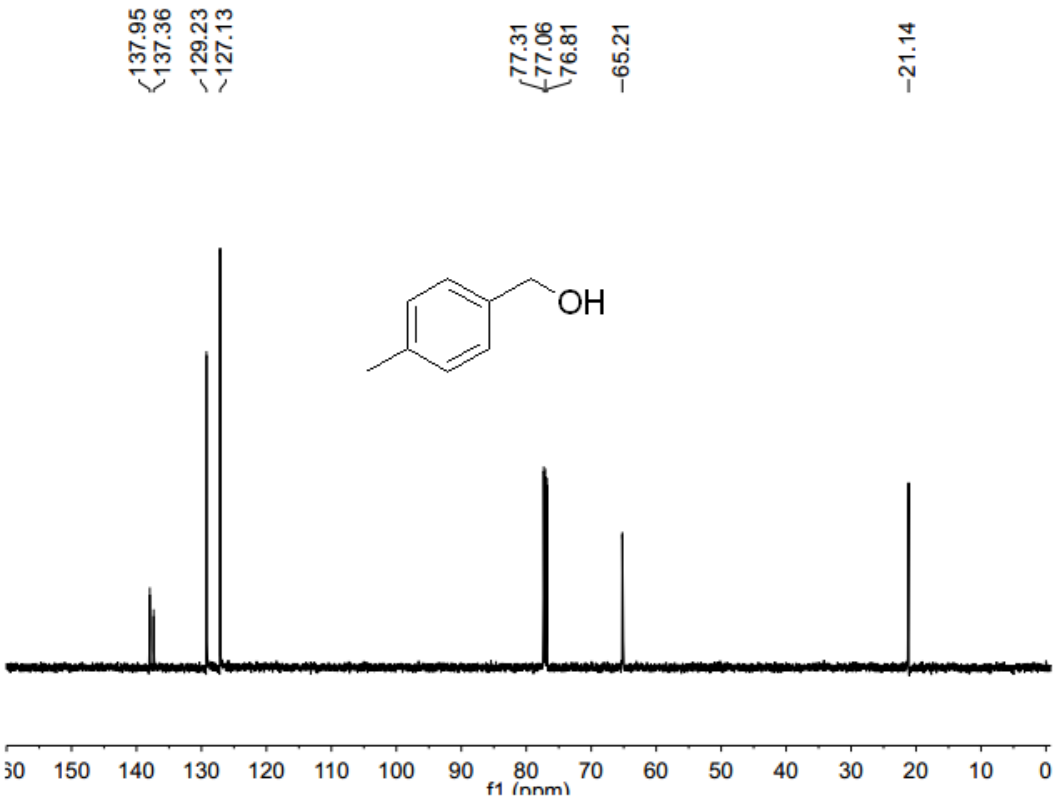


Figure S53 ^{1}H and ^{13}C NMR spectra of *p*-tolylmethanol in $CDCl_3$



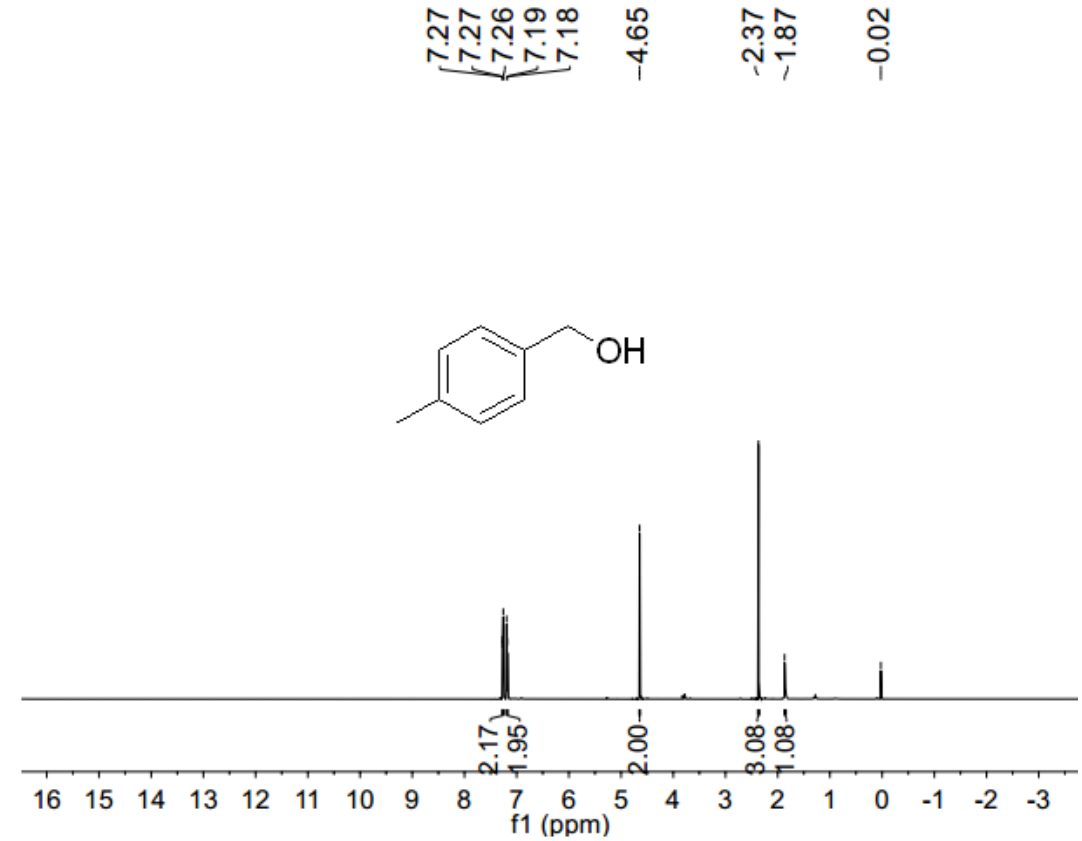


Figure S54 ^{1}H and ^{13}C NMR spectra of (4-methoxyphenyl)methanol in $CDCl_3$

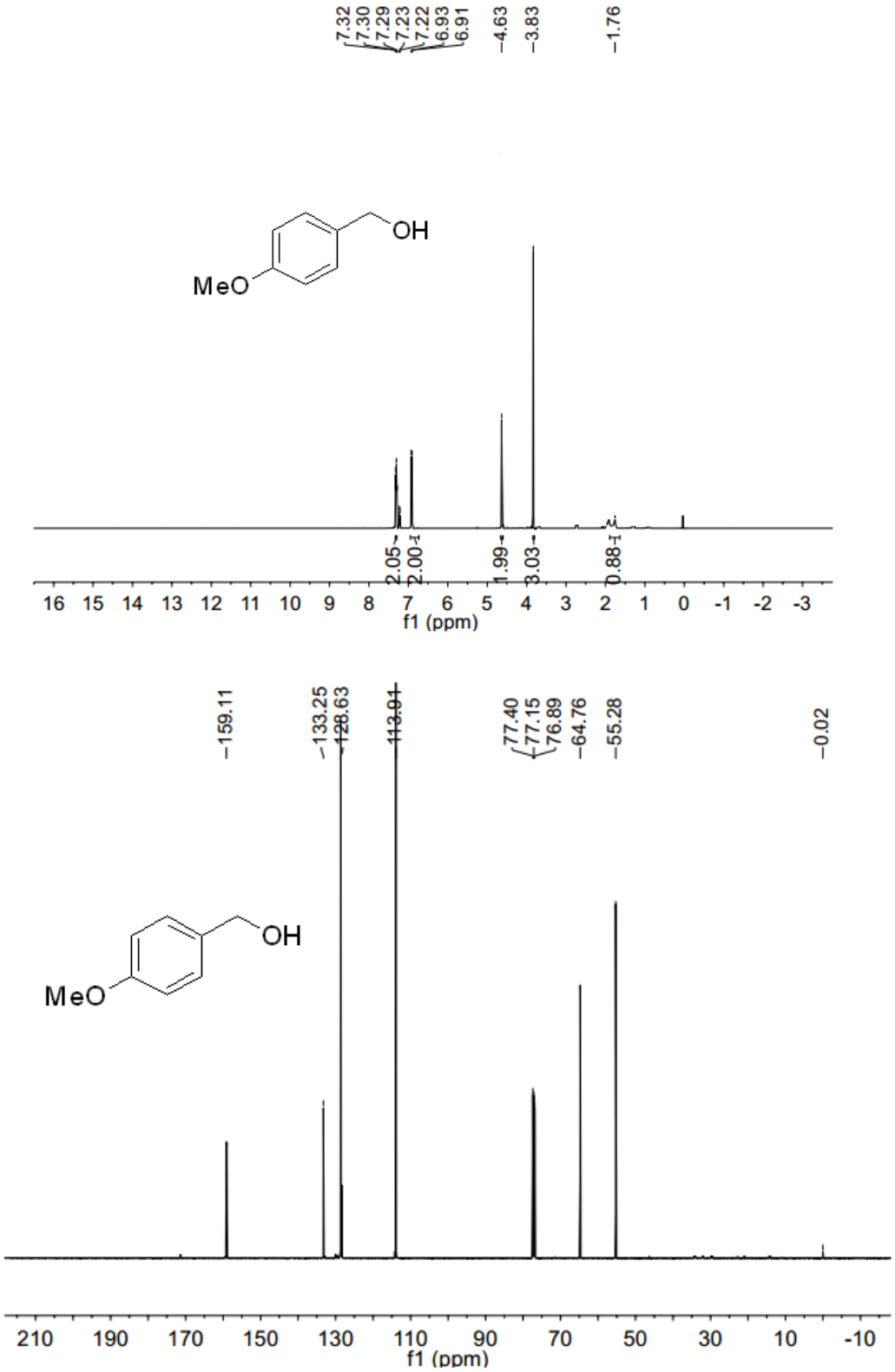


Figure S55 ^{1}H and ^{13}C NMR spectra of (4-fluorophenyl)methanol in $CDCl_3$

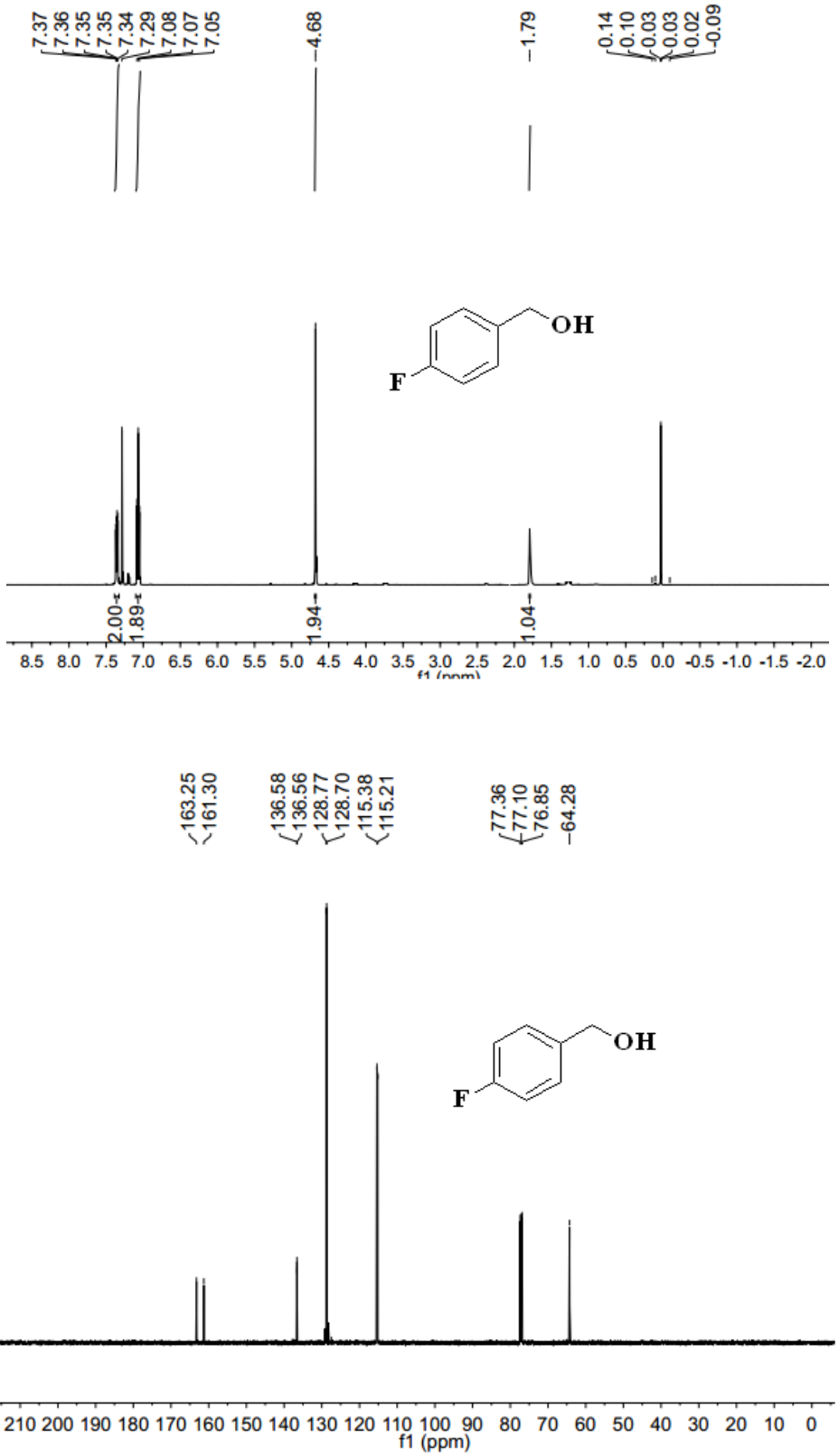


Figure S56 ^{1}H and ^{13}C NMR spectra of naphthalen-2-ylmethanol in $CDCl_3$

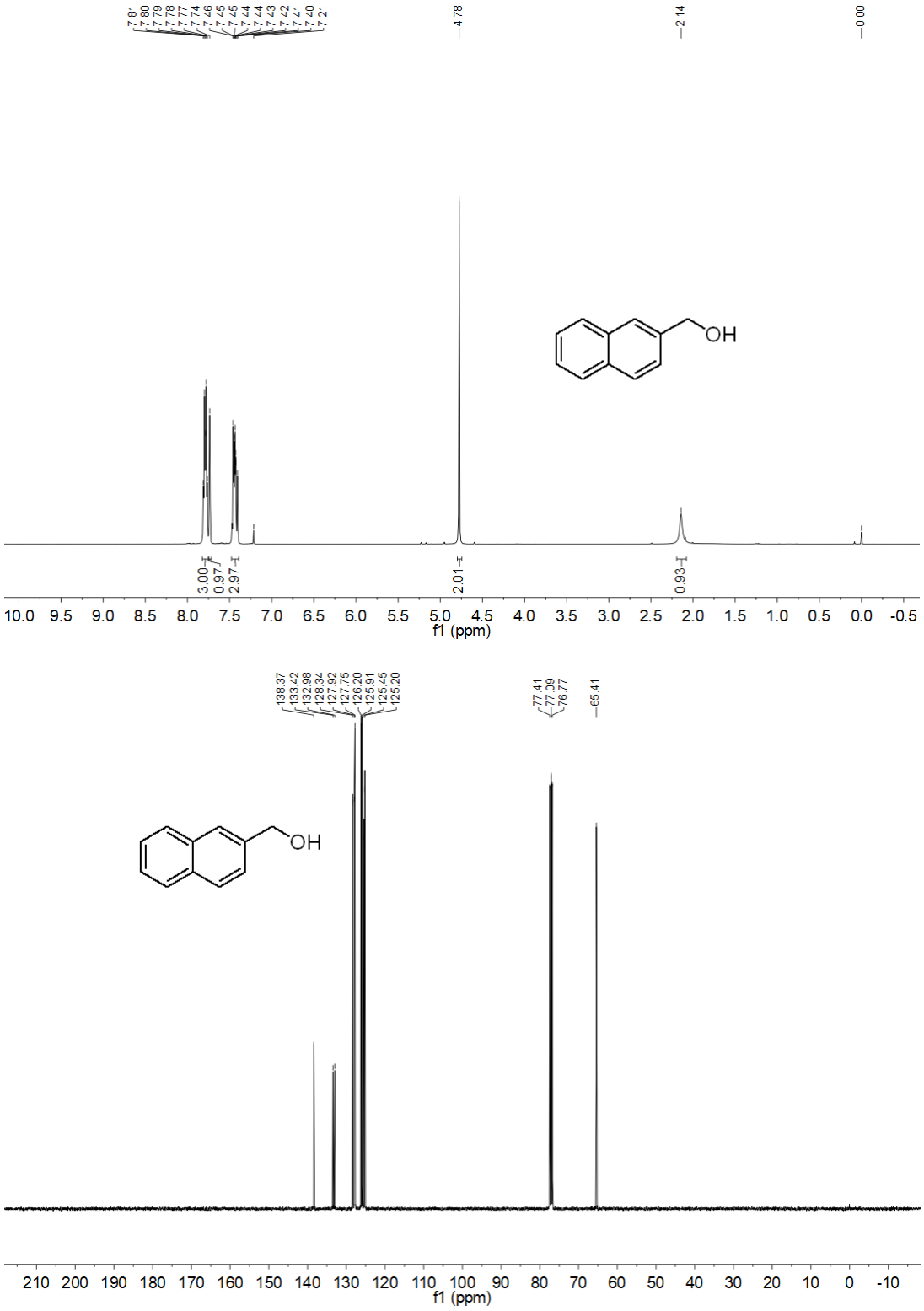


Figure S57 ^{1}H and ^{13}C NMR spectra of thiophen-2-ylmethanol in $CDCl_3$

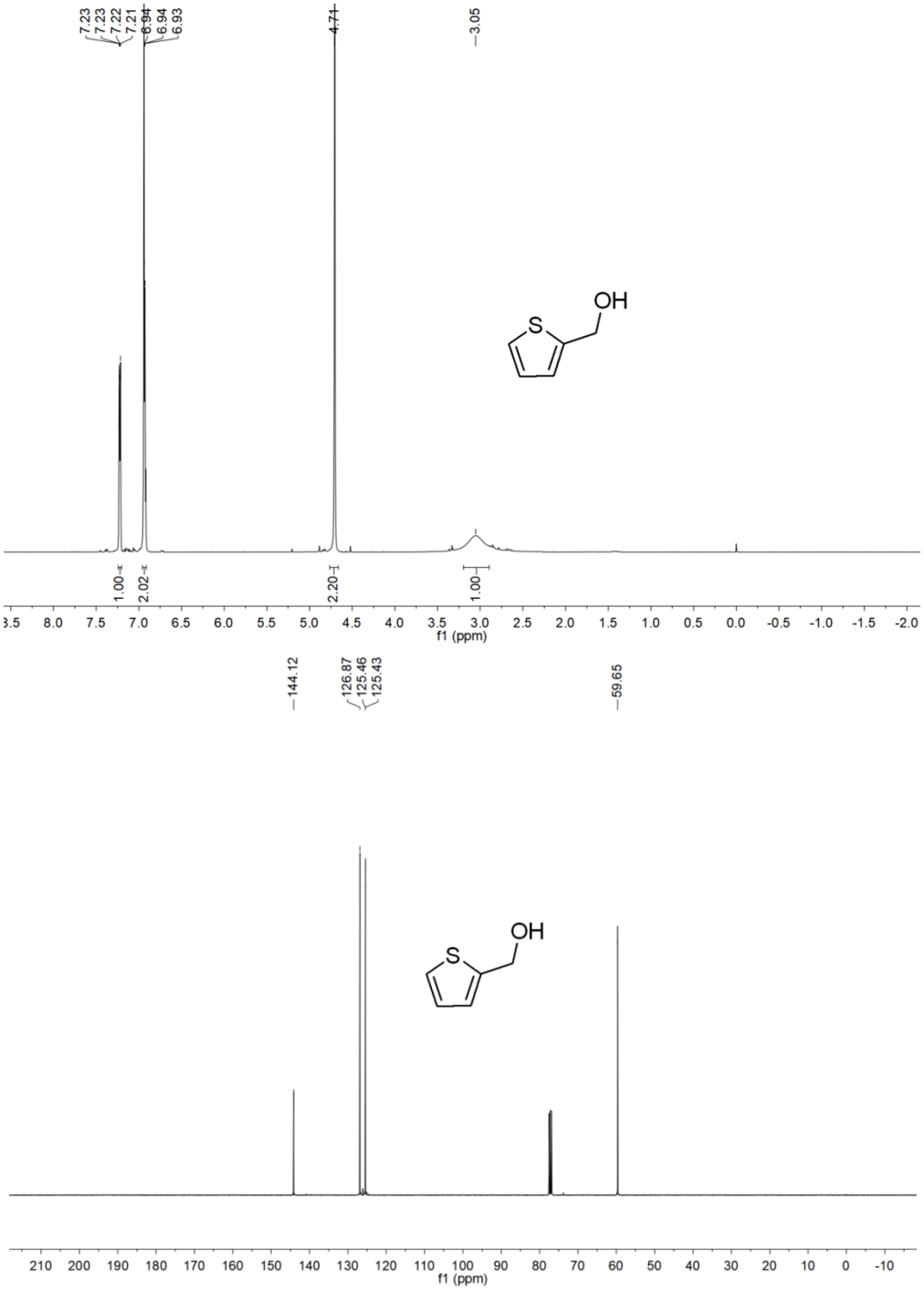
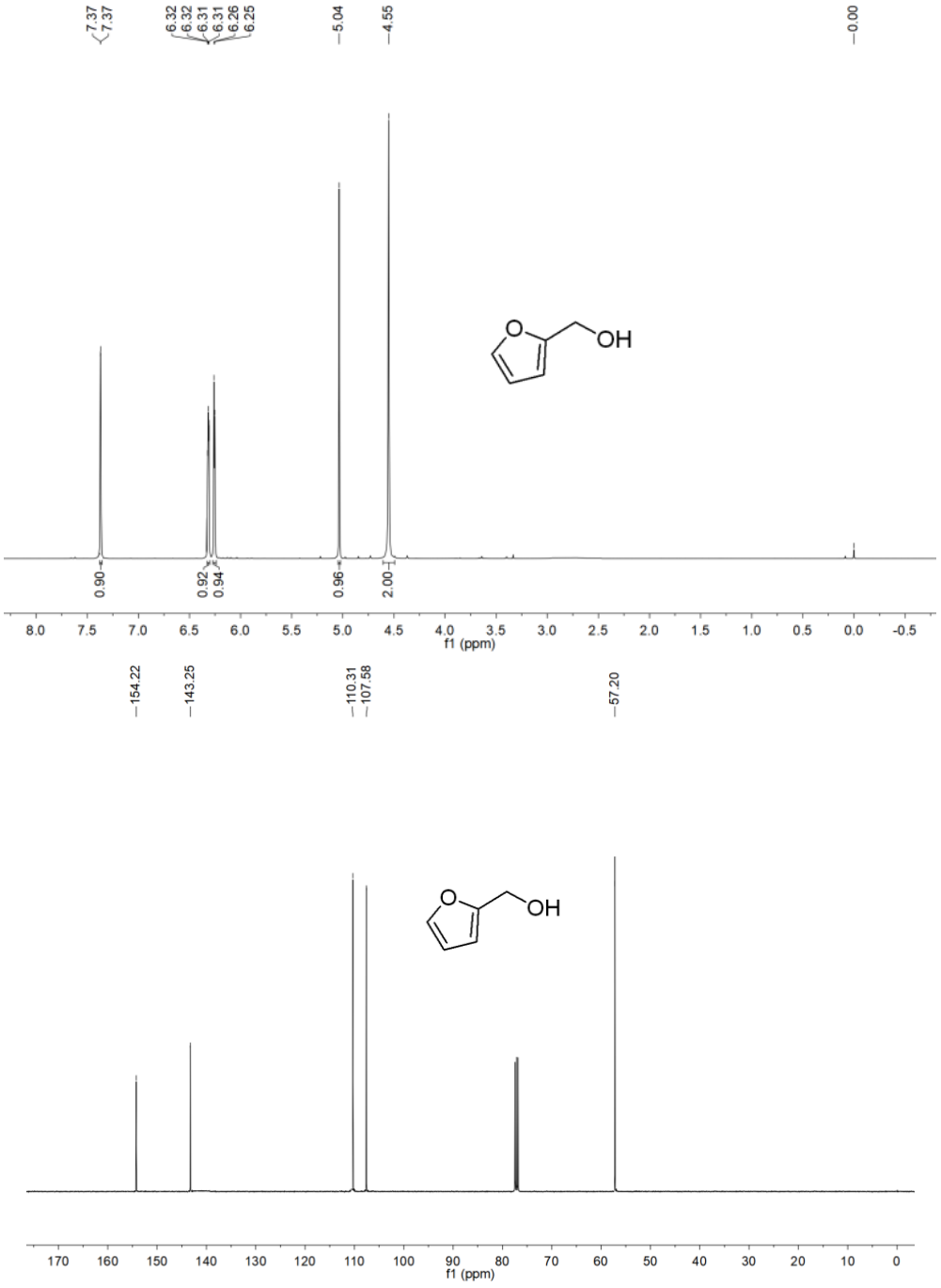


Figure S58 ^{1}H and ^{13}C NMR spectra of 1-(furan-2-yl)ethan-1-ol in $CDCl_3$



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