1,2-Diaminocyclohexane-derived chiral tetradentate ligands for Mn(I)-catalyzed asymmetric hydrogenation of ketones

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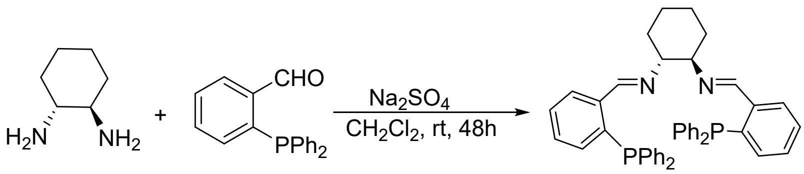
1・General information

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 (Table S1) were used directly without further purification. $MnBr(CO)_5$ (CAS: 14516-54-2) can be purchased from Shijiazhuang chiral chemical CO., LTD., 2-(diphenylphosphino)benzaldehyde (CAS: 50777-76-9), (1R,2R)-(-)-1,2-diaminocyclohexane (CAS: 20439-47-8).^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AV□400 NMR and Bruker AV□500 NMR spectrometers. Chemical shift values in ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances, whereas ^{31}P NMR spectra were referenced externally to H_3PO_4. Elemental analysis was carried out with a Vario EL Ⅲ CHN microanalyzer. Infrared spectroscopy was performed in the solid state on a Bruker ALPHA. A nitrogen-hydrogen-air integrated machine (GX-300A, ZhongXingHuiLi) provides 99% H2, 99% N2 and air as the carrier make up gas used for GC analysis. The 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 (30m *0.25mm *0.25μm, Wuhan Puli Technology Co., Ltd.): injector temp. = 300 °C, flame ionization detector (FID) temp. = 300 °C, column temp. = 80 °C, withdraw time 2 min, then 20 °C /min to 240 °C keeping for 5 min, then 20 °C /min to 280 °C, withdraw time for 5 min; Enantioselectivities (ee, %) were determined by an FuLi GC-9790Plus instrument using a chiral column [CP-Chirasil-Dex CB column (25 m × 0.25 mm × 0.25 μm)], FID temp. = 280 °C, Injector temp. = 250 °C, column temp. = 120 °C isothermal for 2 minutes, 5 °C /min, 180 °C for 30 minutes.

2. Syntheses and characterization of ligands and complexes

2.1 Synthesis of L1

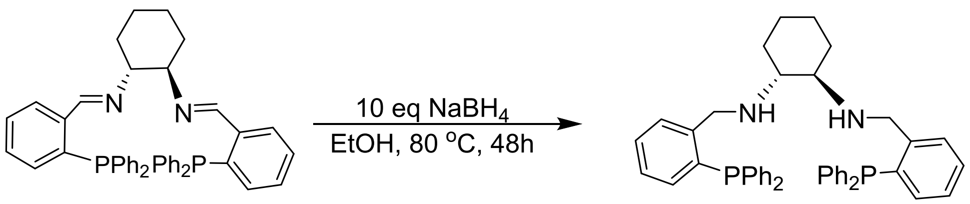


L1

Under nitrogen, a mixture of 2-(diphenylphosphino)benzaldehyde (9.86 g, 34 mmol), (R, R)-1,2-diaminocyclohexane (1.98 g, 17 mmol), anhydrous Na_2SO_4 (20 g, 140 mmol) and 60 mL CH_2Cl_2 in 250 mL Schlenk flask was stirred for 48 h at 25 °C. A pale-orange solution was obtained. The solution was filtered, and then concentrated under reduced pressure to 5 mL. To the solution was added 40 mL of ethanol (Dilute and dissolve the sample) and the resulting solution was cooled to -20 °C (Low temperature reduces the solubility of samples in solution) to give a pale-yellow solid, filtered and dried in vacuo (11.19 g, 90% yield), M.p. 60-62 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 2H), 7.75 (m, *J* = 7.0, 3.5 Hz, 2H), 7.38 – 7.25 (m, 14H), 7.21 (d, *J* = 4.0 Hz, 8H), 6.82 (m, *J* = 6.6, 4.7 Hz, 2H), 3.19 – 3.07 (m, 2H), 1.68 (d, *J* = 8.6 Hz, 2H), 1.48 (d, *J* = 9.4 Hz, 2H), 1.37 (d, *J* = 13.5 Hz, 2H), 1.28 (t, *J* = 9.8 Hz, 2H);^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 159.5, 159.3, 140.2, 140.0, 137.2, 137.1, 137.0, 136.9, 134.1, 134.0, 133.9, 133.8, 133.3, 129.7, 128.8, 128.6, 128.5, 128.4, 128.1, 73.6, 32.5, 24.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ -13.68; IR (ATR, cm^{-1}, KBr): 1636 (m, $\nu_{C=N}$), 2857 (s), 2929 (s), 3050 (s), t. The spectroscopic data correspond to those reported in the literature.[1]

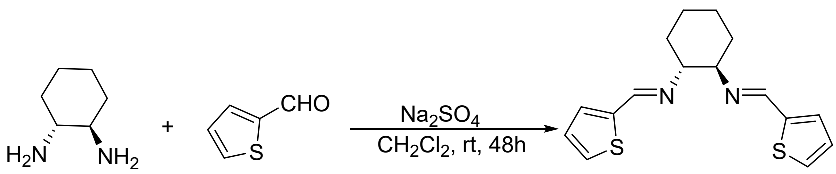
2.2 Synthesis of L2



L1 **L2**

Under nitrogen, a solution of compound (R, R)-**L1** (5.0 g, 7.6 mmol) and $NaBH_4$ (2.8 g, 76 mmol) in absolute ethanol (30 mL) was refluxed with stirring for 48 h. The solution was cooled to room temperature and H_2O (10 mL) was added to destroy excess $NaBH_4$. The mixture solution was extracted with CH_2Cl_2 (30 mL × 3). The combined extract was washed with 10% aqueous NH_4Cl (10 mL × 2), H_2O (10 mL × 2) and the organic layer was dried over anhydrous Na_2SO_4, filtered (Remove the sediments) and concentrated to 5 mL. Then 15 ml of ethanol (Dilute and dissolve the sample) was added and cooled to -30°C (Low temperature reduces the solubility of samples in solution) to give cream-white crystals (4.72 g, 93% yield). M.p. 51-52°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, *J* = 7.8, 4.6 Hz, 2H), 7.29 (tt, *J* = 8.4, 5.6 Hz, 14H), 7.23 – 7.17 (m, 8H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.83 (m, *J* = 7.7, 4.5, 1.3 Hz, 2H), 4.04 (d, *J* = 13.5 Hz, 2H), 3.85 (d, *J* = 13.5 Hz, 2H), 2.19 (br, 2H), 1.99 (d, *J* = 12.9 Hz, 2H), 1.61 (d, *J* = 9.2 Hz, 3H), 1.26 (d, *J* = 6.1 Hz, 2H), 1.09 (t, *J* = 5.7 Hz, 2H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$) δ 133.9, 133.9, 133.8, 133.8, 133.4, 129.0, 128.6, 128.5, 128.5, 128.5, 128.5, 127.1, 60.8, 48.9, 31.5, 24.8, 22.6, 14.1; ^{31}P NMR (243 MHz, $CDCl_3$) δ -15.92; IR (ATR, cm^{-1}, KBr): 1684 (w, $\nu_{C=N}$), 2852 (s), 2924 (s), 3051 (s, ν_{NH}).
The spectroscopic data correspond to those reported in the literature.[1]

2.3 Synthesis of L3

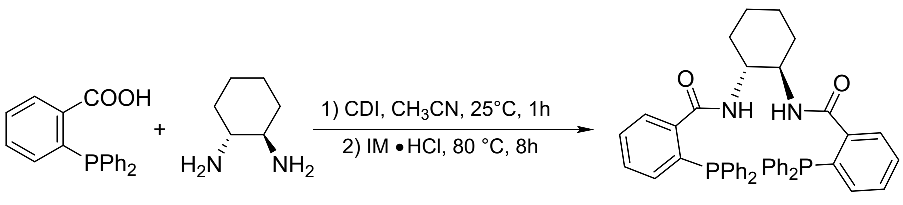


L3

A mixture of 2-thenaldehyde (3.82 g, 34 mmol), (R,R)-1,2-diaminocyclohexane (1.98g, 17 mmol) and anhydrous Na_2SO_4 (20 g, 140 mmol) in CH_2Cl_2 (60 mL) was stirred for 48 h at 25 °C. A pale-orange solution was obtained. The solution was filtered, and then concentrated under reduced pressure to 5 ml. To the solution was added 40 ml of ethanol (Dilute and dissolve the sample) and the resulting solution was cooled to -35°C (Low temperature reduces the solubility of samples in solution) to give a pale-brown solid, filtered and dried in vacuo (5.14 g, 75 % yield). M.p. 75-76 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.18 (m, *J* = 3.5, 0.8 Hz, 1H), 7.00 (m, *J* = 5.0, 3.7 Hz, 1H), 3.41 – 3.31 (m, 2H), 1.94 – 1.74 (m, 3H), 1.48 (t, *J* = 9.4 Hz, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$) δ 154.3, 142.4, 130.1, 128.7, 128.2, 127.3, 127.2, 73.4, 33.6, 33.0, 32.8, 25.0, 24.7, 24.4.
The spectroscopic data correspond to those reported in the literature[2]

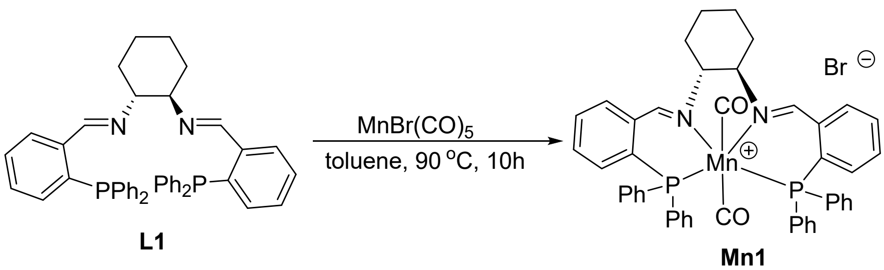
2.4 Synthesis of L4



L4

Under nitrogen, 2-diphenylphosphinylbenzoic acid (10 g, 32.6mmol) and CDI (5.57 g, 33.3mmol) were charged into a clean and dry 250 mL Schlenk flask. After CH_3CN (20 mL) had been added to give a slurry, the resulting mixture was agitated for 2 h at 25 °C to afford a clear and homogenous solution. The solution was transferred to a Reactor containing (R,R)-diaminocyclohexane (1.86 g, 16.3 mmol) and imidazole hydrochloride (1.70 g,16.5 mmol), rinsed with 6 mL CH_3CN. The resulting mixture was then heated at 82 °C for 12 h. After the solution was cooled to 60 °C, a slurry was obtained. 13 mL H_2O was added over 30 min at 60 °C. After 1.0 h, the obtained slurry was cooled to 20 °C (Low temperature reduces the solubility of samples in solution) over 0.5 h. After 0.5 h, the solid was collected by filtration and then washed with CH_3CN/H_2O (2:1, 30 mL) and H_2O (20 mL) successively. After being dried under vacuum at 50 °C, the **L4** was obtained as a pale-yellow solid (4.60 g, 40%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (m, *J* = 7.7, 3.7 Hz, 2H), 7.32 – 7.26 (m, 14H), 7.24 – 7.18 (m, 8H), 6.91 (m, *J* = 7.6, 3.9 Hz, 2H), 6.34 (d, *J* = 6.5 Hz, 2H), 3.77 (s, 2H), 1.89 – 1.82 (m, 2H), 1.64 (d, *J* = 9.5 Hz, 4H), 1.21 (t, *J* = 10.1 Hz, 2H), 1.07 – 0.94 (m, 2H); ^{13}C{H} NMR (150 MHz, $CDCl_3$) δ 169.3, 140.9, 140.7, 137.6, 137.6, 136.6, 136.5, 134.3, 133.9, 133.8, 130.2, 128.8, 128.6, 128.5, 128.5, 128.4, 128.4, 127.5, 127.5, 53.9, 32.0, 24.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ -9.69.
The spectroscopic data correspond to those reported in the literature.[3]

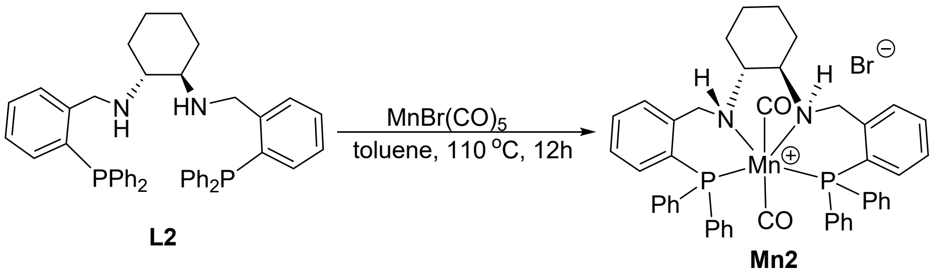
2.5 Preparation of Mn1



L1 **Mn1**

$Mn(CO)_5Br$ (0.54 g, 2.0 mmol) and **L1** (1.32 g, 2.0 mmol) were loaded in a 50 mL Schlenk tube under nitrogen and the contents stirred in dry toluene (10 mL) for 10 h at 90 °C. After cooling to room temperature, the resulting red suspension was cooled to room temperature (Low temperature reduces the solubility of samples in solution) and the precipitate was collected and washed successively *n*-hexane (2 × 5 mL), then dried in vacuo to afford **Mn1** as a red powder (1.50 g, 84% yield). A single crystal of **Mn1** suitable for the X-ray determination was grown by slow diffusion of *n*-hexane into a dichloromethane solution of **Mn1**. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 – 8.54 (m, 2H), 7.99 – 7.90 (m, 2H), 7.73 – 7.67 (m, 3H), 7.64 – 7.55 (m, 10H), 7.50 – 7.43 (m, 6H), 7.17 – 7.07 (m, 5H), 6.54 (s, 2H), 1.94 (s, 2H), 1.70 (s, 2H), 1.45 (s, 2H), 1.24 (s, 2H); $^{13}C\{H\}$ NMR (100 MHz, DMSO-d_6) δ 168.8, 143.5, 139.8, 133.9, 132.3, 131.8, 130.2, 129.7, 71.2, 31.4, 23.6, 19.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.45; IR (ATR, cm^{-1}, KBr): 1612 (s, $\nu_{C=N}$), 1882 (s, ν_{CO}), 1950 (s, ν_{CO}); Anal. Calcd for [$C_{46}H_{40}MnN_2O_2P_2Br$ (*M*w: 848.11)]: C, 65.03; H, 4.75; N, 3.30. Found: C, 64.97; H, 4.78; N, 3.28%.

2.6 Preparation of Mn2

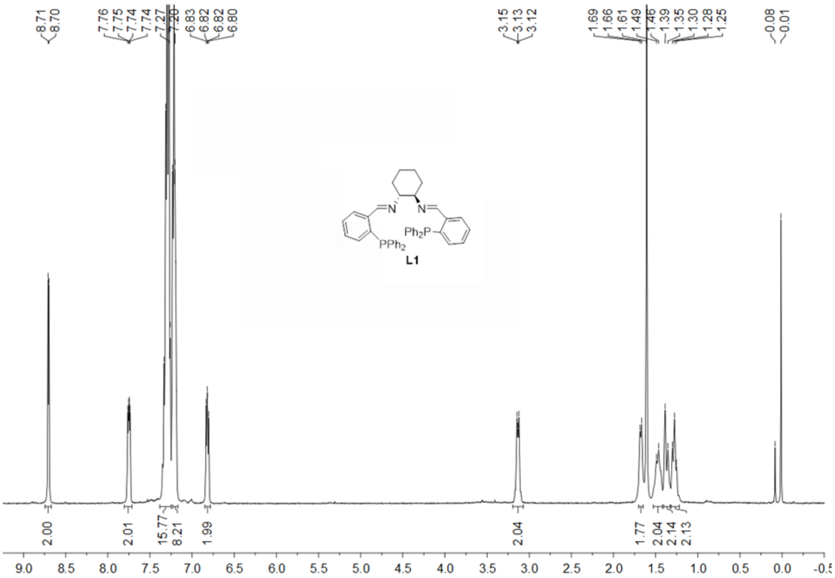


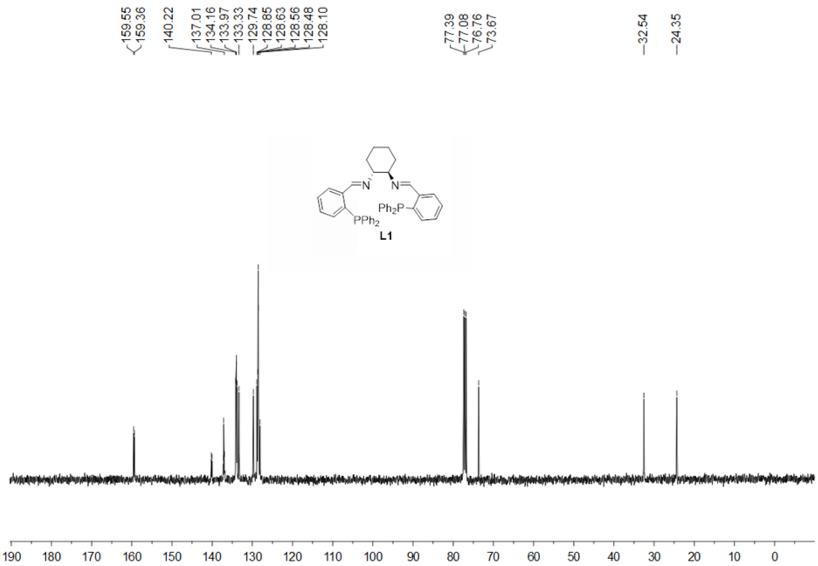
$Mn(CO)_5Br$ (406.0 mg, 1.49 mmol) and **L2** (0.990 mg, 1.49 mmol) were loaded in a 50 mL Schlenk tube under nitrogen and the contents stirred in dry toluene (20 mL) for 12 h at 110 °C. After cooling to room temperature, the reaction mixture was concentrated (Remove low boiling point solvents) under reduced pressure. The residue was dissolved in dichloromethane (2 mL) and *n*-hexane (25 mL) added to form a precipitate (Inert solvents reduce the solubility of samples in solution). The solution above the precipitate was carefully removed by pipette. The precipitate was also washed with *n*-hexane (2 × 20 mL) and then dried to afford **Mn2** as a pale-yellow solid (958.0 mg, 78%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (t, *J* = 7.2 Hz, 4H), 7.78 (d, *J* = 7.0 Hz, 2H), 7.61 (d, *J* = 6.5 Hz, 6H), 7.51 (t, *J* = 6.8 Hz, 12H), 7.33 – 7.27 (m, 2H), 7.26 – 7.13 (m, 2H), 4.42 (d, *J* = 15.5 Hz, 2H), 4.21 (d, *J* = 15.5 Hz, 2H), 3.40 (brs, 2H, NH), 2.60 (s, 2H), 1.87 (d, *J* = 12.0 Hz, 2H), 1.53 (d, *J* = 9.0 Hz, 2H), 1.33 – 1.23 (m, 2H), 0.50 (d, *J* = 10.3 Hz, 2H); $^{13}C\{H\}$ NMR (100 MHz, DMSO-d_6) δ 225.9, 225.6, 140.0, 136.1, 135.4, 133.5, 133.0, 132.3, 132.1, 131.9, 131.3, 130.9, 129.9, 129.7, 129.4, 128.7, 125.3, 60.3, 51.4, 29.4, 23.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.93; IR (ATR, cm^{-1}, KBr): 1622 (s, ν_{NH}), 1852 (s, ν_{CO}), 1930 (s, ν_{CO}), 3233 (s, ν_{NH}); Anal. Calcd for [$C_{46}H_{44}MnN_2O_2P_2Br$ (*M*w: 852.14)]: C, 64.72; H, 5.20; N, 3.28. Found: C, 64.67; H, 5.32; N, 3.24%.

3. NMR Spectra for ligands and complexes

Figure S1 ^{1}H, ^{13}C and ^{31}P NMR spectra for **L1** in $CDCl_3$





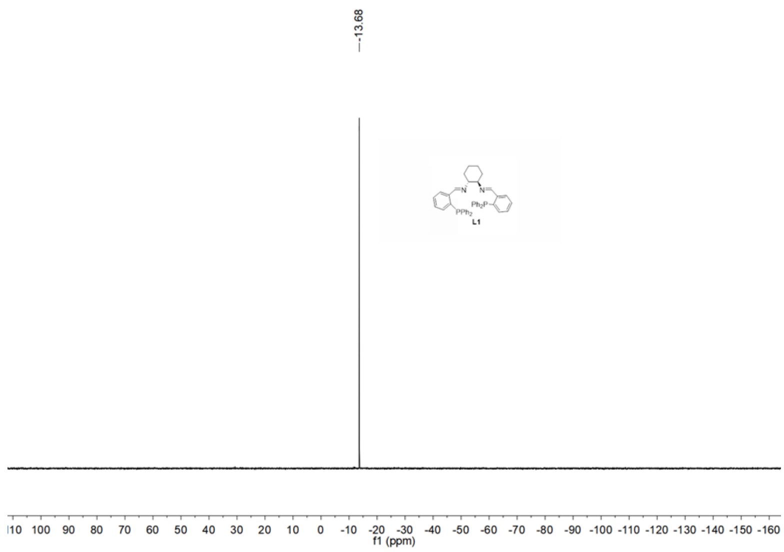
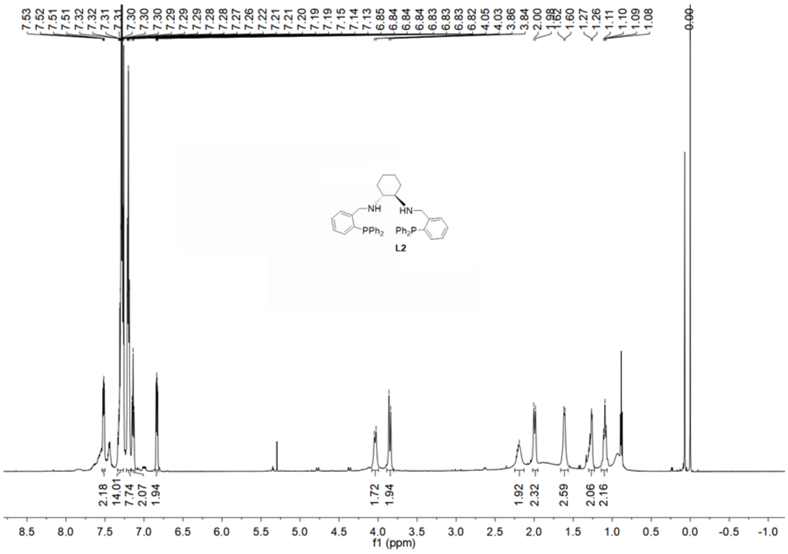
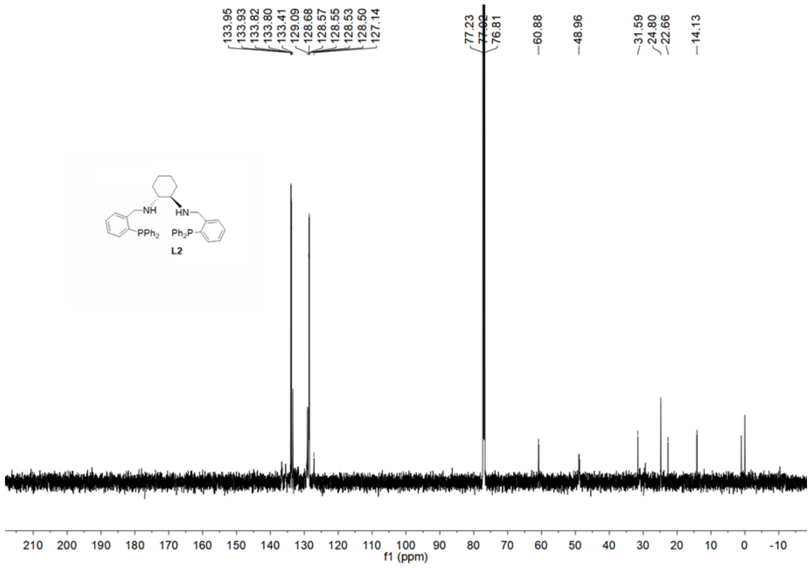


Figure S2 ^{1}H, ^{13}C and ^{31}P NMR spectra for **L2** in $CDCl_3$





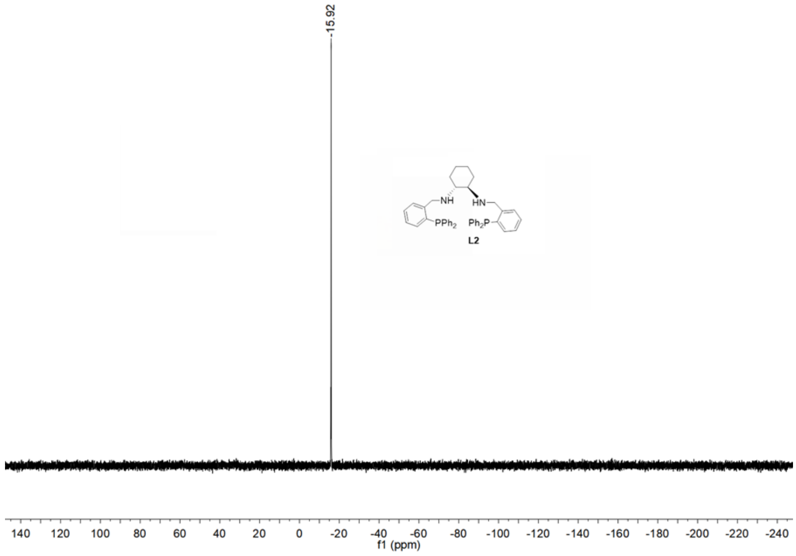
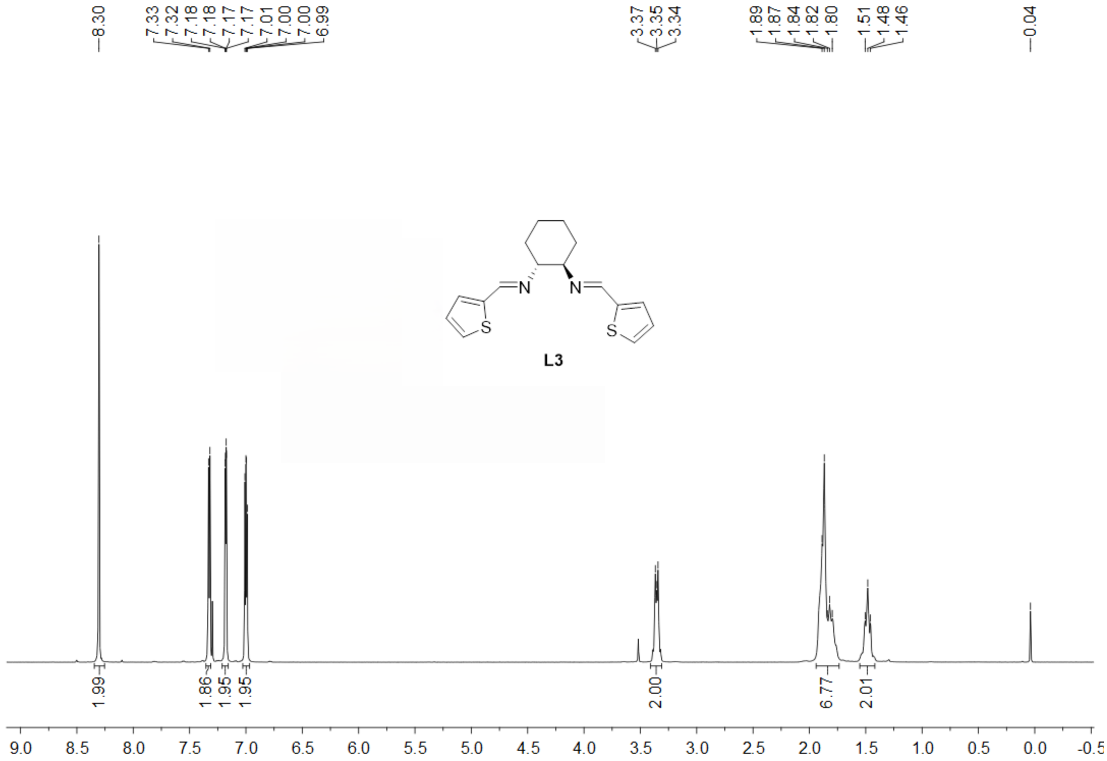


Figure S3 ^{1}H and ^{13}C NMR spectra for **L3** in $CDCl_3$



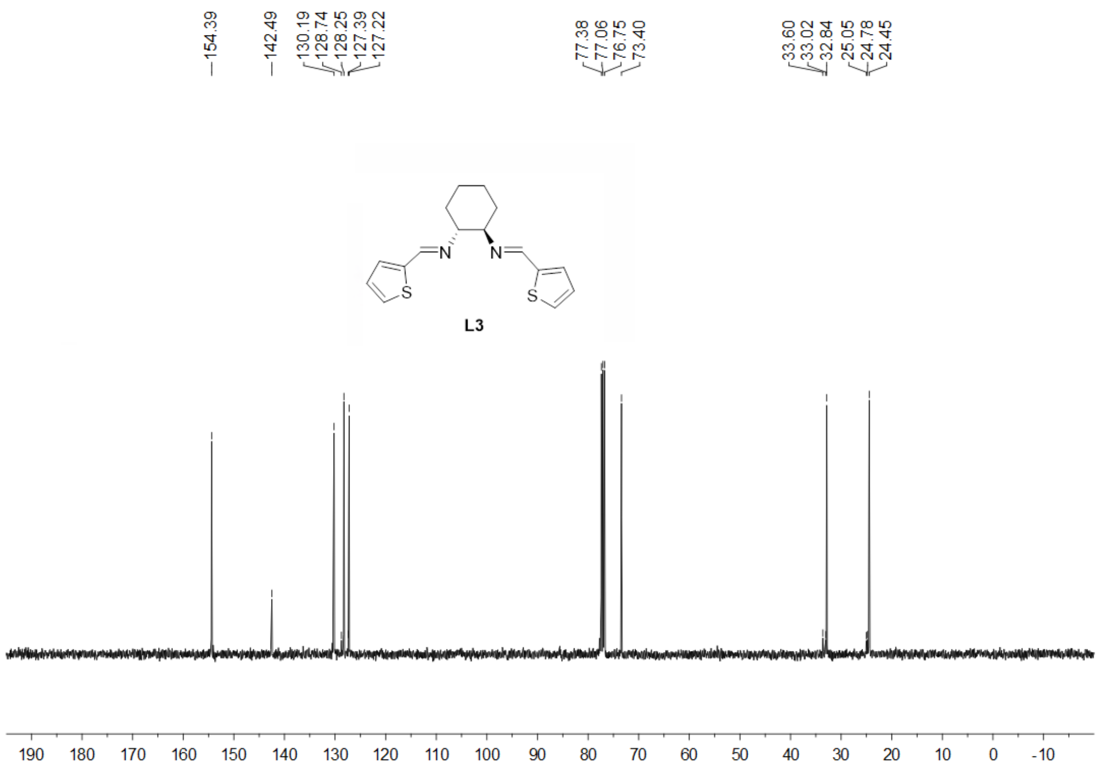
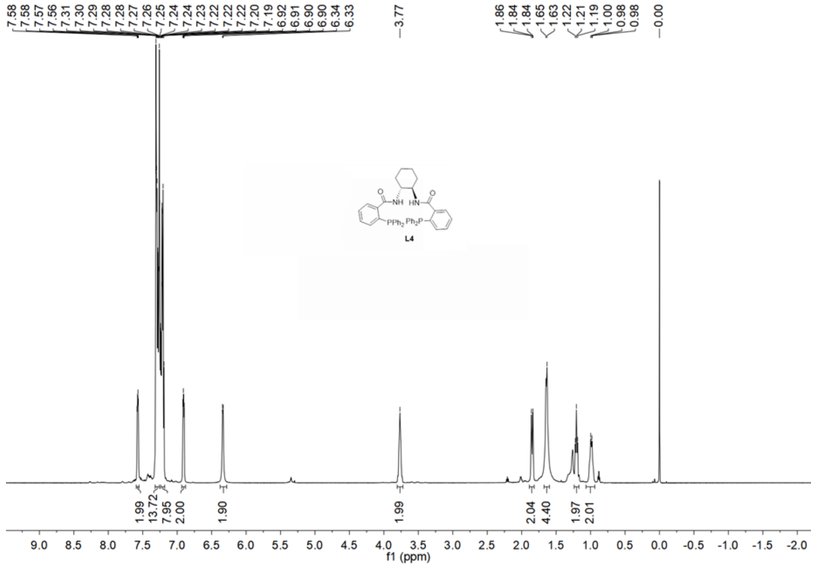
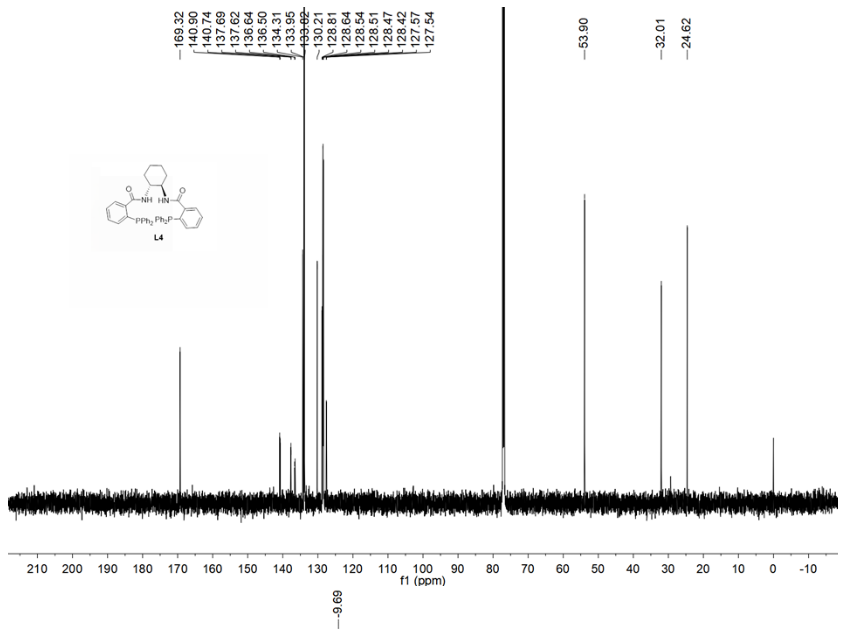


Figure S4 ^{1}H, ^{13}C and ^{31}P NMR spectra for **L4** in $CDCl_3$





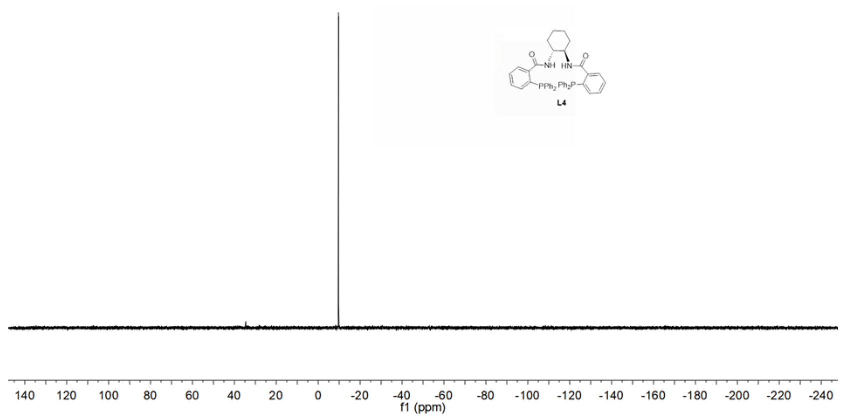
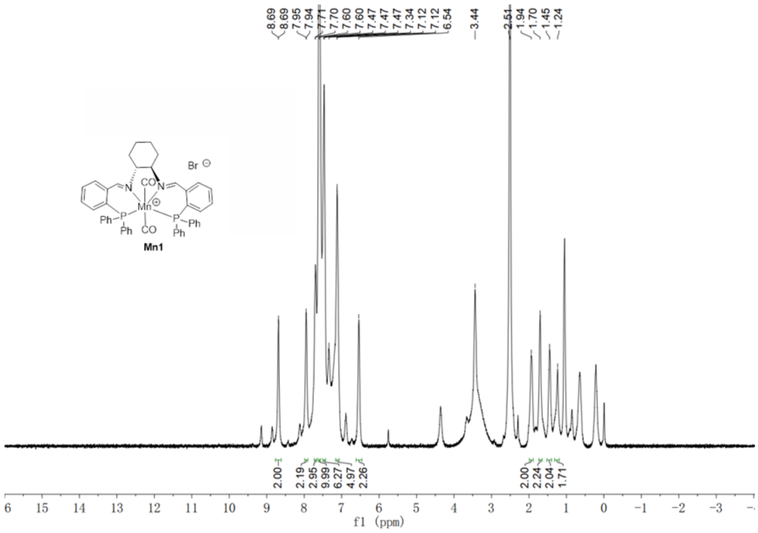
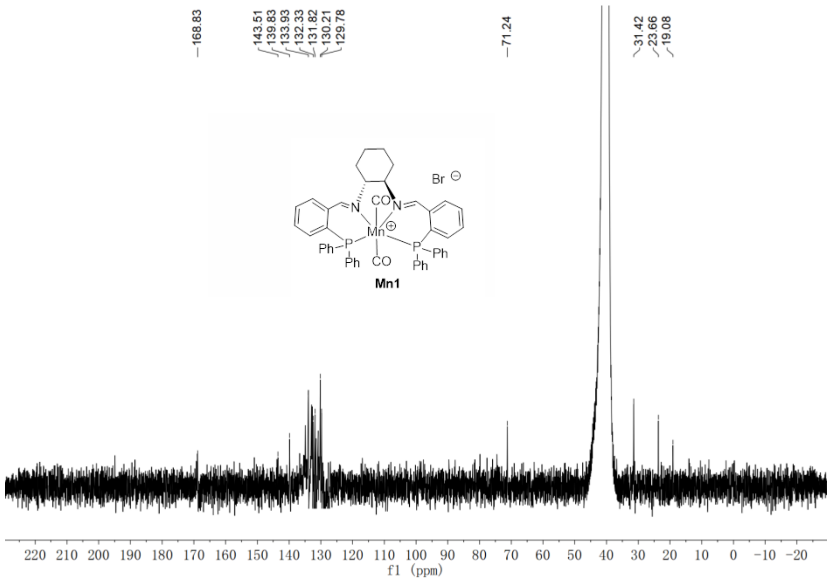


Figure S5 ^{1}H, ^{13}C and ^{31}P NMR spectra for **Mn1** in DMSO-d_6





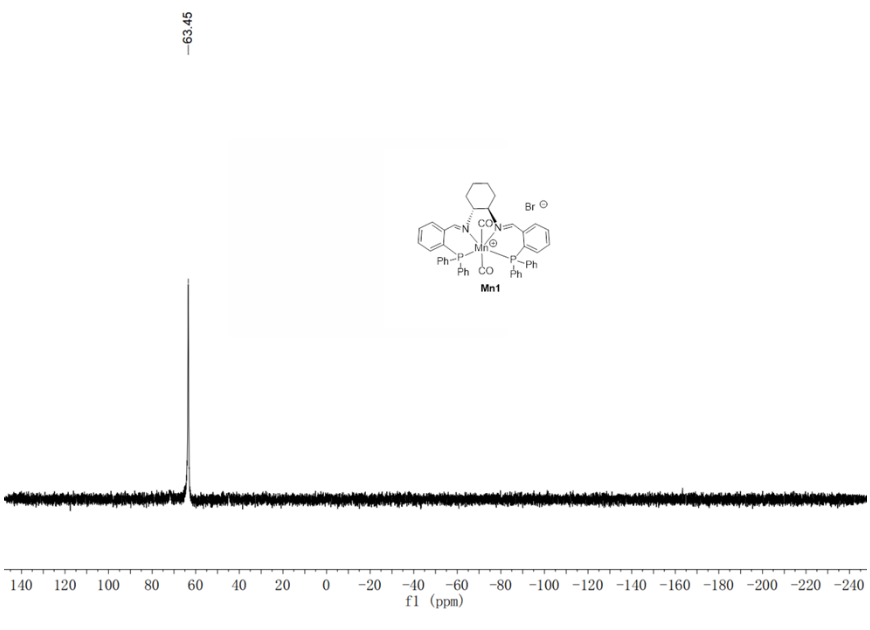
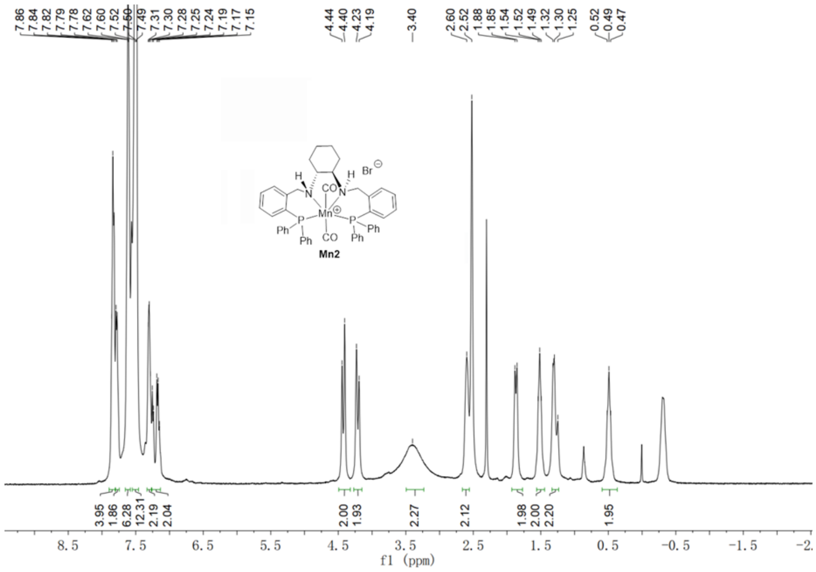
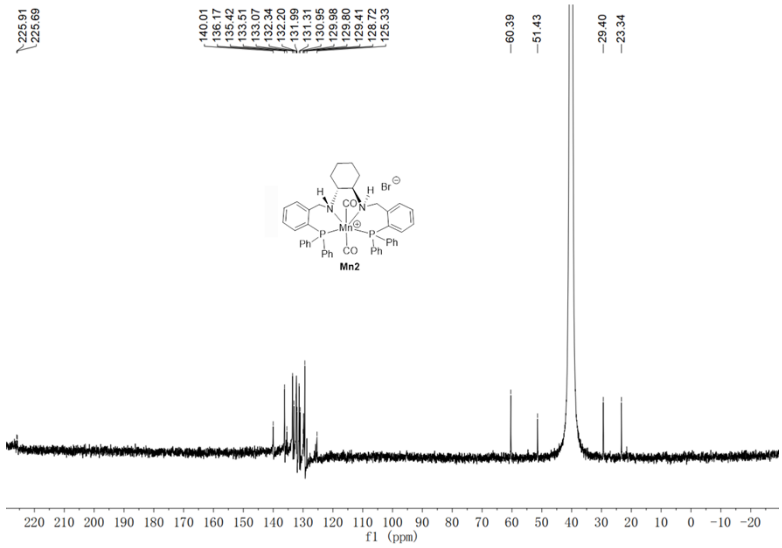


Figure S6 ^{1}H, ^{13}C and ^{31}P NMR spectra for **Mn2** in DMSO-d_6





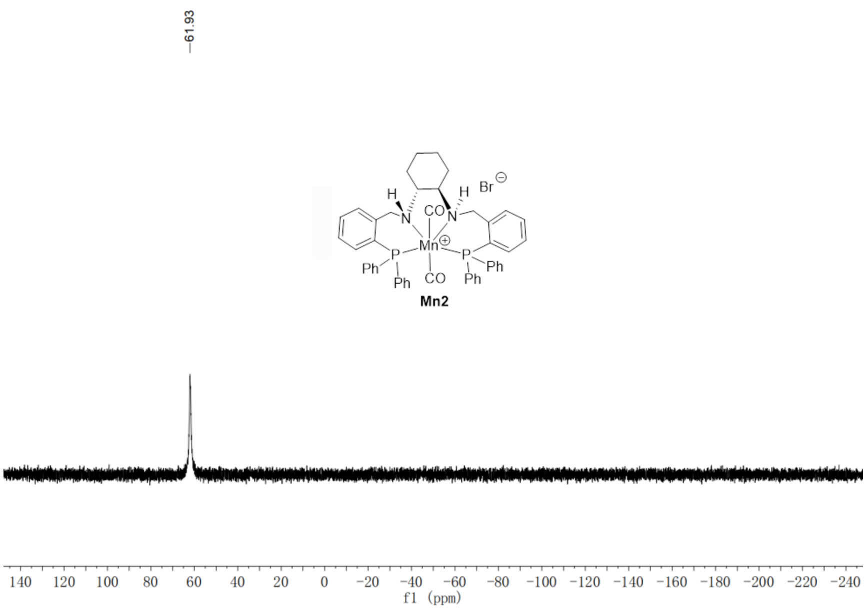


Figure S7 FT-IR spectrum of **L1**

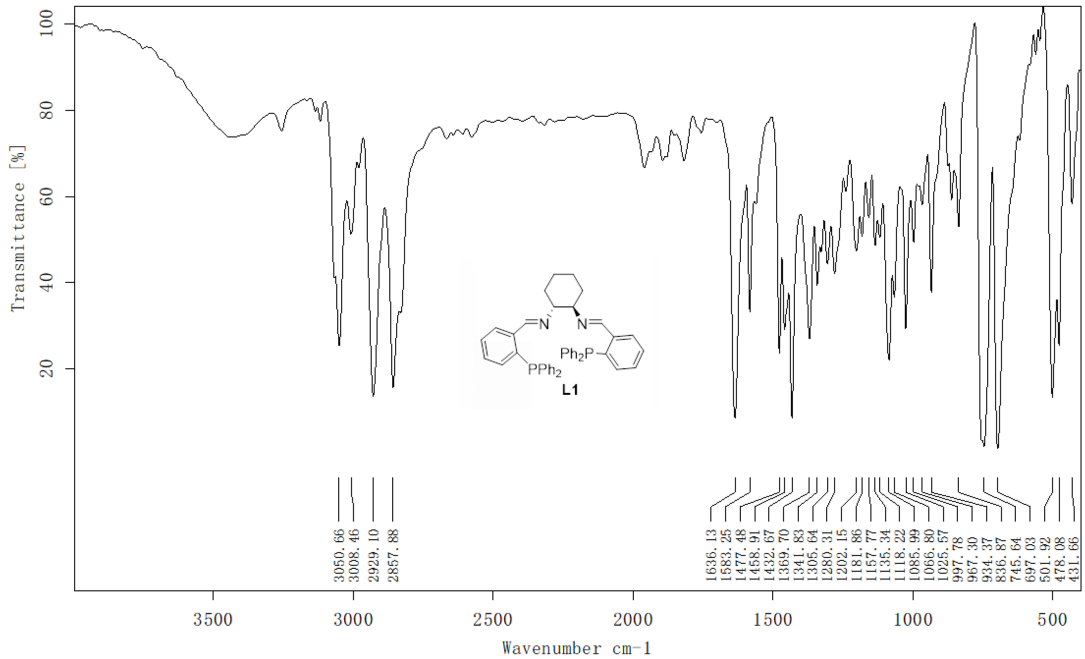


Figure S8 FT-IR spectrum of **L2**

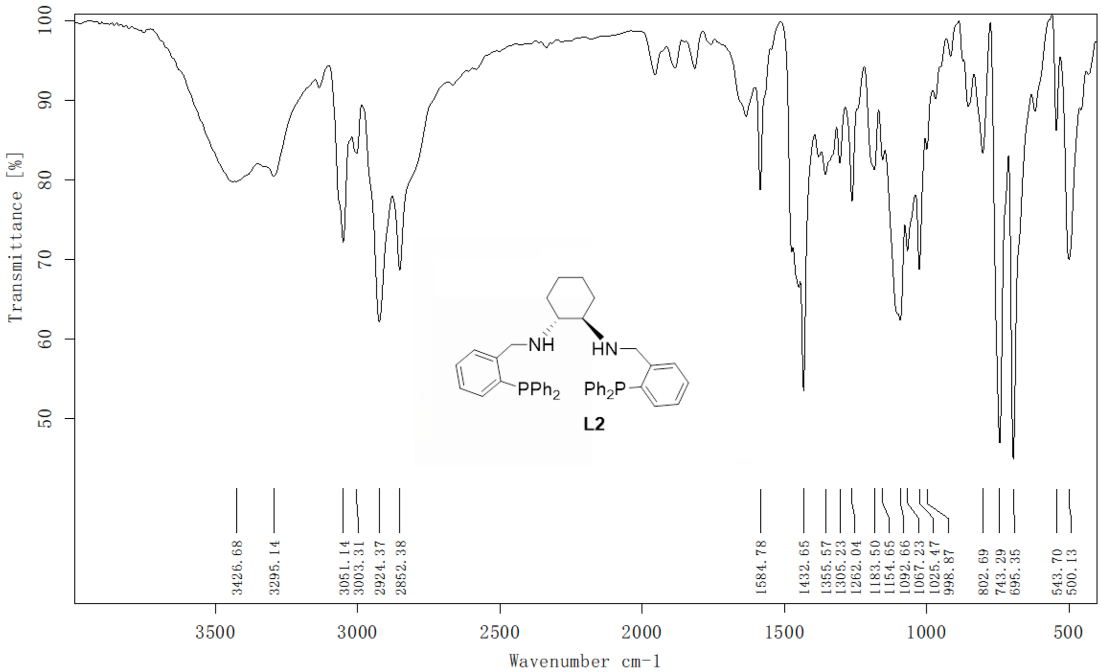


Figure S9 FT-IR spectrum of **Mn1**

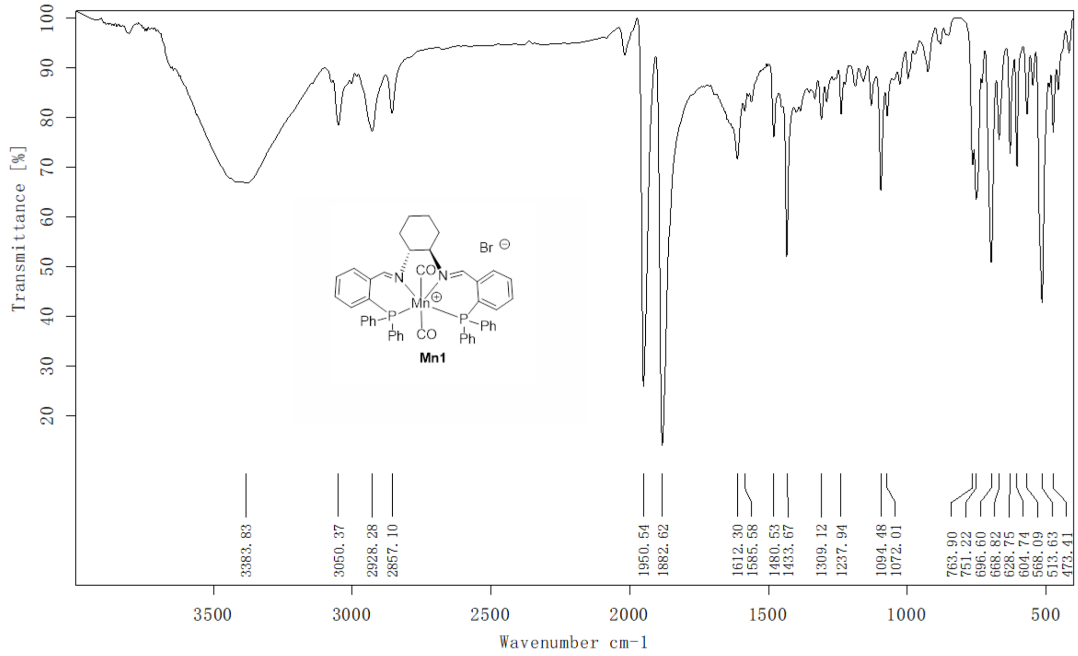
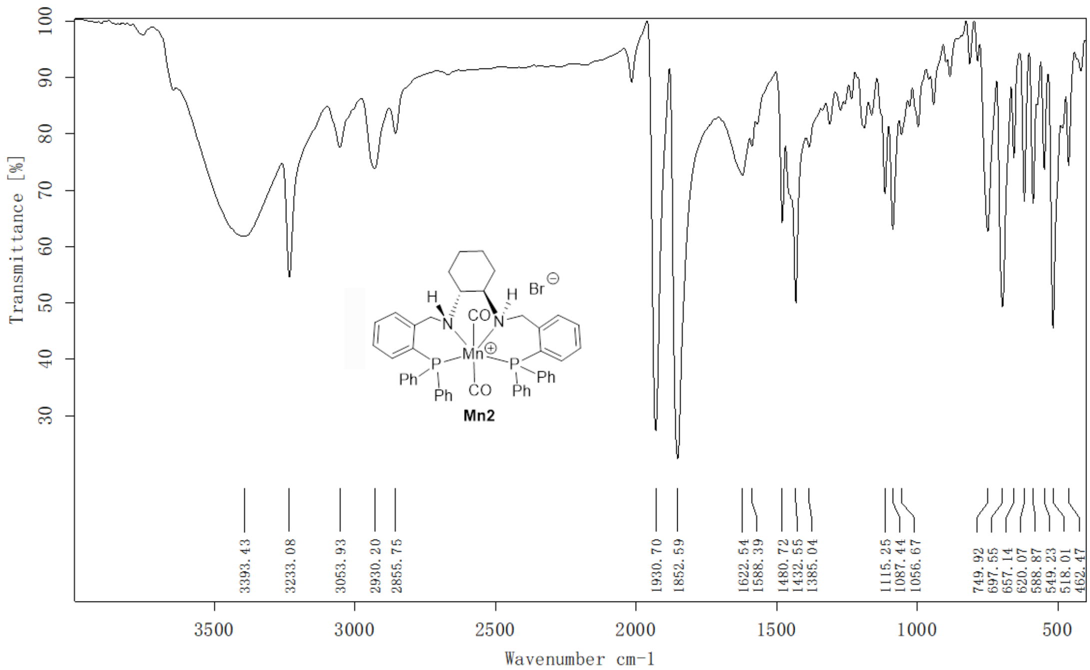


Figure S10 FT-IR spectrum of **Mn2**

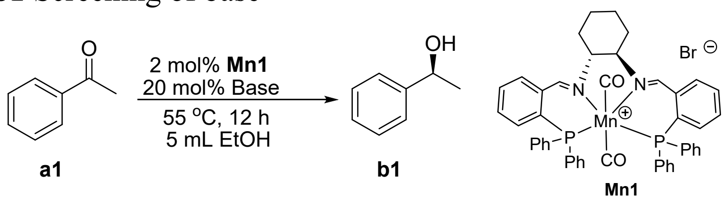


4. Catalytic study

4.1 Optimizing reaction conditions for the ATH of acetophenone (a1) to (*S*)-1-phenylethan-1-ol (b1)

Under a nitrogen atmosphere, a mixture of acetophenone (**a1**) (0.25 mmol), the manganese complex (**Mn1** – **Mn2**) (5 μmol) and base (namely *t*-BuOK, *t*-BuONa, *i*-PrONa, NaOMe KOH, NaOH, K_2CO_3, Na_2CO_3) (0.05 mmol) was dissolved in dry and degassed EtOH (5 mL) and then stirred and heated to the desired temperature (35 - 85 °C). At the specified reaction time (4 – 14 h), 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of EtOH, dodecane introduced, before being analyzed by GC. The composition of the reaction mixture was confirmed by running GC of a mixture of pure ketone, alcohol and dodecane. The enantiomeric excess (ee) of the alcohol was determined by chiral HPLC or GC analysis.

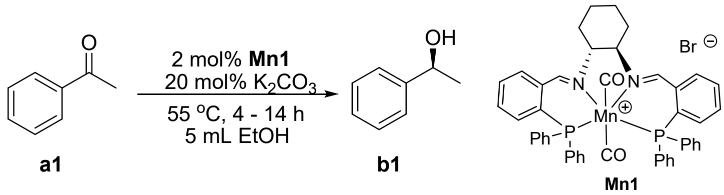
Table S1 Screening of base[a]



Run	Base	Tem. (°C)	Yield (%)[b]	Ee (%)[b]
1	*t*-BuOK	55	99	65
2	*t*-BuONa	55	99	65
3	*t*-BuOLi	55	76	67
4	K_3PO_4	55	31	67
5	CH_3ONa	55	30	68
6	KOH	55	97	73
7	NaOH	55	99	75
8	$LiOH{\cdot}H_2O$	55	63	68
9	**K_2CO_3**	55	98	85
10	DBU	55	8	63
11	$CsCO_3$	55	41	59

[a] Conditions: 0.25 mmol substrate, 5 μmol **Mn1** (2 mol%), 0.05 mmol base (20 mol%), 5 mL EtOH, 50 bar H_2, 55 °C, 12 h; [b] Yields (%) and enantioselectivities (ee, %) were determined by GC (*n*-dodecane was used as an internal standard) and chiral-phase GC using a CP-Chirasil-Dex CB column, respectively.

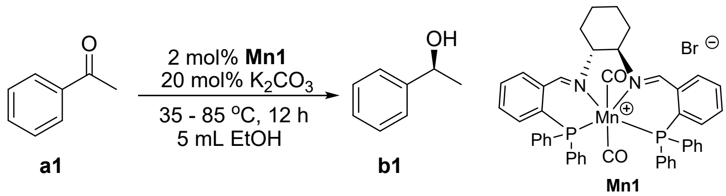
Table S2 Optimizing the time for the AH of **a1**[a]



Run	Time (h)	Tem. (°C)	Yield (%)[b]	Ee (%)[b]
1	4	55	48	73
2	6	55	61	79
3	8	55	76	62
4	10	55	79	73
5	12	55	97	82
6	14	55	99	77

[a] Conditions: 0.25 mmol substrate, 0.05 mmol K_2CO_3, 5 μmol **Mn1** (2 mol%), 0.05 mmol K_2CO_3 (20 mol%), 5 mL EtOH, 50 bar H_2, 55 °C, 4 - 14 h;
[b] Yields (%) and enantioselectivities (ee, %) were determined by GC (*n*-dodecane was used as an internal standard) and chiral-phase GC using a CP-Chirasil-Dex CB column, respectively.

Table S3 Optimizing the temperature for the AH of **a1**[a]



Run	Tem. (°C)	Yield (%)[b]	Ee (%)[b]
1	35	9	50
2	45	11	50
3	55	97	82
4	65	99	71
5	75	99	58
6	85	99	50

[a] Conditions: 0.25 mmol substrate, 0.05 mmol K_2CO_3, 5 μmol **Mn1** (2 mol%), 5 mL EtOH, 50 bar H_2, 35 - 85 °C, 12 h;
[b] Yields (%) and enantioselectivities (ee, %) were determined by GC (*n*-dodecane was used as an internal standard) and chiral-phase GC using a CP-Chirasil-Dex CB column, respectively.

4.2 General procedure for the asymmetric hydrogenation of ketones

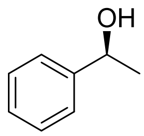
Under a nitrogen atmosphere, a mixture of substrate (**a1** - **a15**) (0.25 mmol), the manganese complex (**Mn1**) (5 μmol, 2 mol%) and K_2CO_3 (0.05 mmol) was dissolved in dry and degassed EtOH (5 mL) and then stirred and heated to the desired temperature (55 °C). At the specified reaction time (12 h), 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of EtOH, dodecane introduced, before being analyzed by GC. The composition of the reaction mixture was confirmed by running GC of a mixture of pure ketone, alcohol and dodecane. The enantiomeric excess (ee) of the alcohol was determined by chiral GC analysis.

5. Characterization of the chiral alcohol products

The reaction mixture was purified by flash gel chromatography (using a gradient of PE/EA) to give the desired product. The enantiomeric excess (ee) of the alcohol was determined by chiral HPLC.

5.1 ^{1}H and ^{13} C{H} NMR spectroscopic data for the isolated chiral alcohol products.[4]

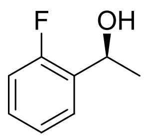
(*S*)-1-phenylethan-1-ol (**b1**)



b1

Colorless oil, 93% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 – 7.29 (m, 4H, Ar-H), 7.24 – 7.19 (m, 1H, Ar-H), 5.17 (s, 1H, OH), 4.73 (q, *J* = 6.5 Hz, 1H, CH), 1.34 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 147.8, 128.4, 126.9, 125.7, 68.5, 26.4.

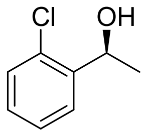
(S)-1-(2-fluorophenyl)ethan-1-ol (**b2**)



b2

Colorless oil, 17% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (td, *J* = 7.7, 1.9 Hz, 1H, Ar-H), 7.26 – 7.10 (m, 2H, Ar-H), 7.05 (m, *J* = 10.9, 8.0, 1.3 Hz, 1H, Ar-H), 5.29 (d, *J* = 4.5 Hz, 1H, OH), 5.04 – 4.95 (m, 1H, CH), 1.32 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 160.5, 158.1, 134.5, 134.4, 128.7, 128.6, 127.4, 127.3, 124.7, 124.6, 115.3, 115.1, 62.5, 62.5, 25.1.

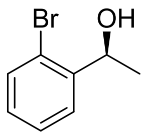
(*S*)-1-(2-chlorophenyl)ethan-1-ol (**b3**)



b3

Colorless oil, 50% isolated yield.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 (m, *J* = 8.0, 1.8 Hz, 1H, Ar-H), 7.31 (m, *J* = 7.1, 6.3, 1.4 Hz, 2H, Ar-H), 7.23 – 7.15 (m, 1H, Ar-H), 5.37 (d, *J* = 4.3 Hz, 1H, OH), 5.03 (qd, *J* = 6.3, 4.2 Hz, 1H, CH), 1.29 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 145.0, 130.7, 129.2, 128.5, 127.7, 127.3, 65.4, 24.7.

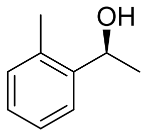
(*S*)-1-(2-bromophenyl)ethan-1-ol (**b4**)



b4

White solid, Mp: 54-56 °C, 38% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66 (m, *J* = 7.8, 1.8 Hz, 1H, Ar-H), 7.55 (m, *J* = 8.0, 1.2 Hz, 1H, Ar-H), 7.41 (td, *J* = 7.5, 1.2 Hz, 1H, Ar-H), 7.19 (td, *J* = 7.6, 1.8 Hz, 1H, Ar-H), 5.44 (d, *J* = 4.0 Hz, 1H, OH), 5.05 – 4.97 (m, 1H, CH), 1.34 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 146.5, 132.5, 129.0, 128.3, 127.6, 121.1, 67.8, 24.8.

(S)-1-(o-tolyl)ethan-1-ol (**b5**)

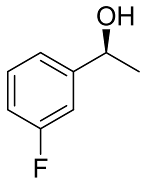


b5

Colorless oil, 14% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 – 7.39 (m, 1H, Ar-H), 7.20 – 7.12 (m, 1H, Ar-H), 7.10 – 7.02 (m, 2H, Ar-H), 5.05 (d, *J* = 4.0 Hz, 1H, OH), 4.92 (m, *J* = 6.4, 4.2 Hz, 1H, CH), 2.26 (s, 3H, CH_3), 1.29 (d, *J* = 6.5 Hz, 3H, CH_3);

$^{13}C\{H\}$ NMR (100 MHz, DMSO-d_6) δ 145.8, 133.9, 130.2, 126.7, 126.2, 125.2, 65.3, 25.0, 19.0.

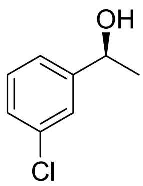
(S)-1-(3-fluorophenyl)ethan-1-ol (**b6**)



b6

Colorless oil, 99% isolated yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.29 (td, *J* = 8.1, 6.0 Hz, 1H, Ar-H), 7.19 – 7.06 (m, 2H, Ar-H), 7.02 – 6.90 (m, 1H, Ar-H), 5.29 (d, *J* = 4.4 Hz, 1H, OH), 4.72 (qd, *J* = 6.4, 4.4 Hz, 1H, CH), 1.30 (d, *J* = 6.6 Hz, 3H, CH_3); $^{13}C\{H\}$ NMR (100 MHz, DMSO-d_6) δ 163.9, 161.5, 151.0, 130.3, 130.2, 121.7, 113.6, 113.4, 112.4, 112.2, 68.0, 68.0, 26.1.

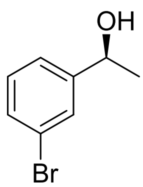
(*S*)-1-(3-chlorophenyl)ethan-1-ol (**b7**)



b7

Colorless oil, 66% isolated yield. ^1H NMR (400 MHz, DMSO-d_6) δ 7.40 (t, *J* = 1.9 Hz, 1H, Ar-H), 7.35 – 7.24 (m, 3H, Ar-H), 5.30 (s, 1H, OH), 4.74 (q, *J* = 6.4 Hz, 1H, CH), 1.33 (d, *J* = 6.5 Hz, 3H, CH_3); $^{13}C\{H\}$ NMR (100 MHz, DMSO-d_6) δ 150.5, 133.3, 130.5, 130.3, 126.8, 125.6, 124.4, 124.3, 67.9, 26.2.

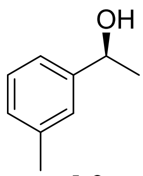
(*S*)-1-(3-bromophenyl)ethan-1-ol (**b8**)



b8

Colorless oil, 73% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (t, *J* = 1.9 Hz, 1H, Ar-H), 7.31 (dt, *J* = 7.7, 1.6 Hz, 1H, Ar-H), 7.26 (dt, *J* = 7.9, 1.5 Hz, 1H, Ar-H), 7.18 (t, *J* = 7.8 Hz, 1H, Ar-H), 5.26 (d, *J* = 4.4 Hz, 1H, OH), 4.68 (qd, *J* = 6.4, 4.3 Hz, 1H, CH), 1.27 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 150.7, 130.6, 129.7, 128.6, 128.4, 124.8, 122.0, 68.0, 26.2.

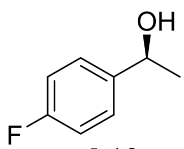
(*S*)-1-(*m*-tolyl)ethan-1-ol (**b9**)



b9

Colorless oil, 42% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 – 7.01 (m, 3H, Ar-H), 6.95 (dt, *J* = 7.4, 1.7 Hz, 1H, Ar-H), 5.07 (d, *J* = 4.2 Hz, 1H, OH), 4.65 (qd, *J* = 6.4, 4.1 Hz, 1H, CH), 2.23 (d, *J* = 1.3 Hz, 3H, CH_3), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 147.8, 147.8, 137.3, 128.3, 127.5, 126.4, 122.8, 68.7, 26.4, 21.5.

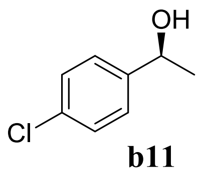
(*S*)-1-(4-fluorophenyl)ethan-1-ol (**b10**)



b10

Colorless oil, 50% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.31 (m, 2H, Ar-H), 7.15 – 7.06 (m, 2H, Ar-H), 5.21 (d, *J* = 4.2 Hz, 1H, OH), 4.73 (qd, *J* = 6.4, 4.2 Hz, 1H, CH), 1.31 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 162.6, 160.2, 143.9, 127.6, 115.0, 67.9, 26.3.

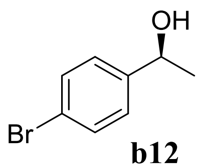
(*S*)-1-(4-chlorophenyl)ethan-1-ol (**b11**)



b11

Colorless oil, 95% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (d, *J* = 1.2 Hz, 4H, Ar-H), 5.28 (d, *J* = 2.9 Hz, 1H, OH), 4.77 – 4.70 (m, 1H, CH), 1.32 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 146.8, 131.4, 128.3, 127.6, 67.9, 26.2.

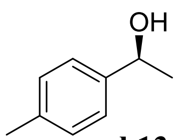
(S)-1-(4-bromophenyl)ethan-1-ol (**b12**)



b12

colorless oil, 90% isolated yield.^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 – 7.47 (m, 2H, Ar-H), 7.36 – 7.28 (m, 2H, Ar-H), 5.30 (s, 1H, OH), 4.73 (q, *J* = 6.4 Hz, 1H, CH), 1.33 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 147.2, 131.3, 128.0, 119.8, 67.9, 26.2.

(S)-1-(p-tolyl)ethan-1-ol (**b13**)

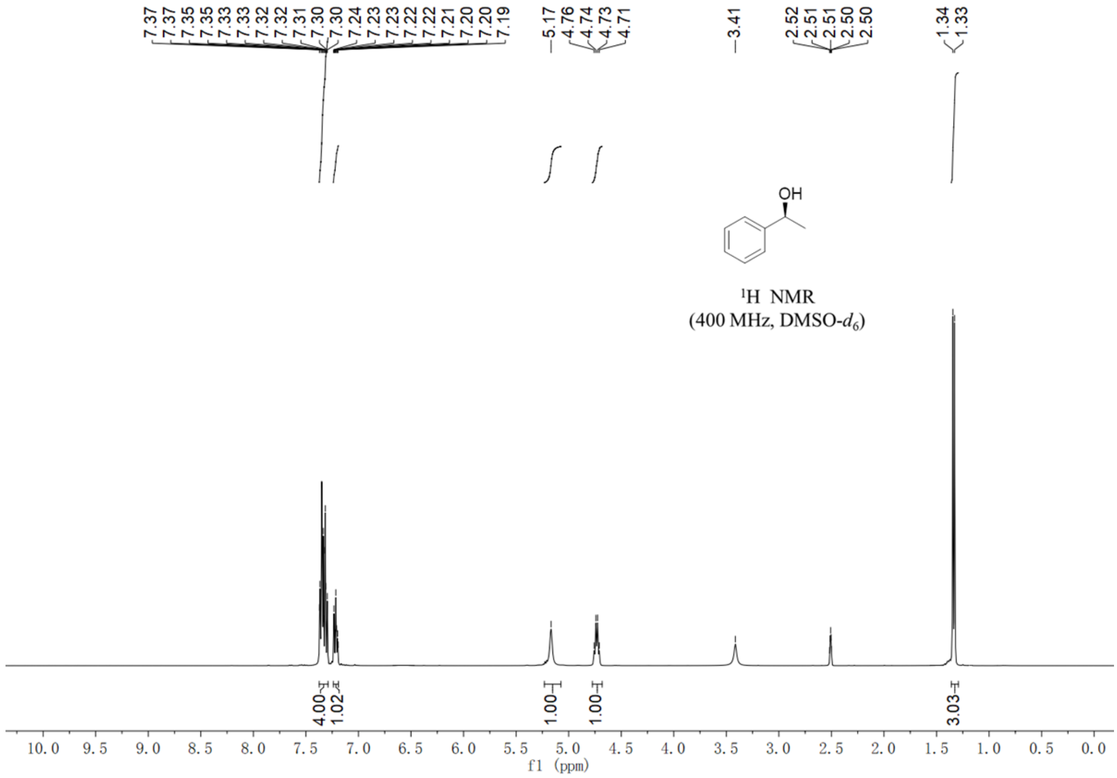


b13

Colorless oil, 59% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 – 7.22 (m, 2H, Ar-H), 7.14 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.10 (d, *J* = 3.9 Hz, 1H, OH), 4.71 (qd, *J* = 6.3, 3.4 Hz, 1H, CH), 2.30 (s, 3H, CH_3), 1.33 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C{H} NMR (100 MHz, DMSO-d_6) δ 144.8, 135.8, 128.9, 125.7, 125.6, 68.3, 26.4, 21.1.

5.2 NMR spectra for chiral alcohol products.

Figure S11 [1]H and [13]C NMR spectra of **b1**; recorded in DMSO-d_6 at ambient temperature



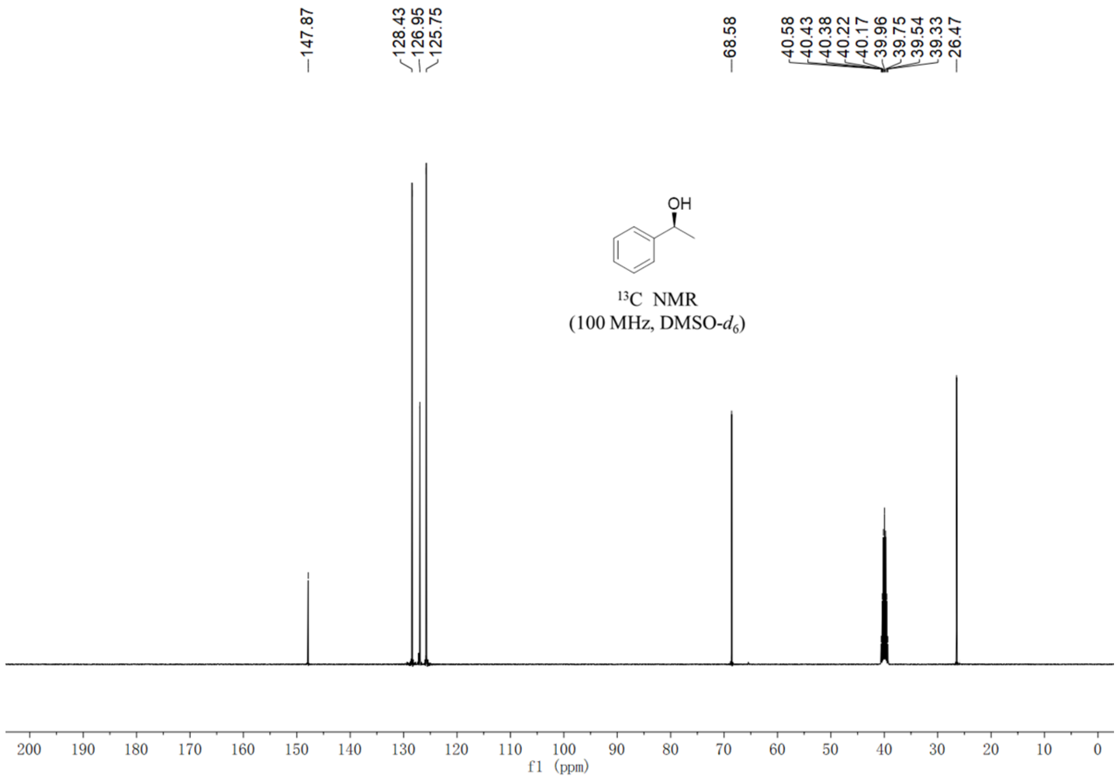
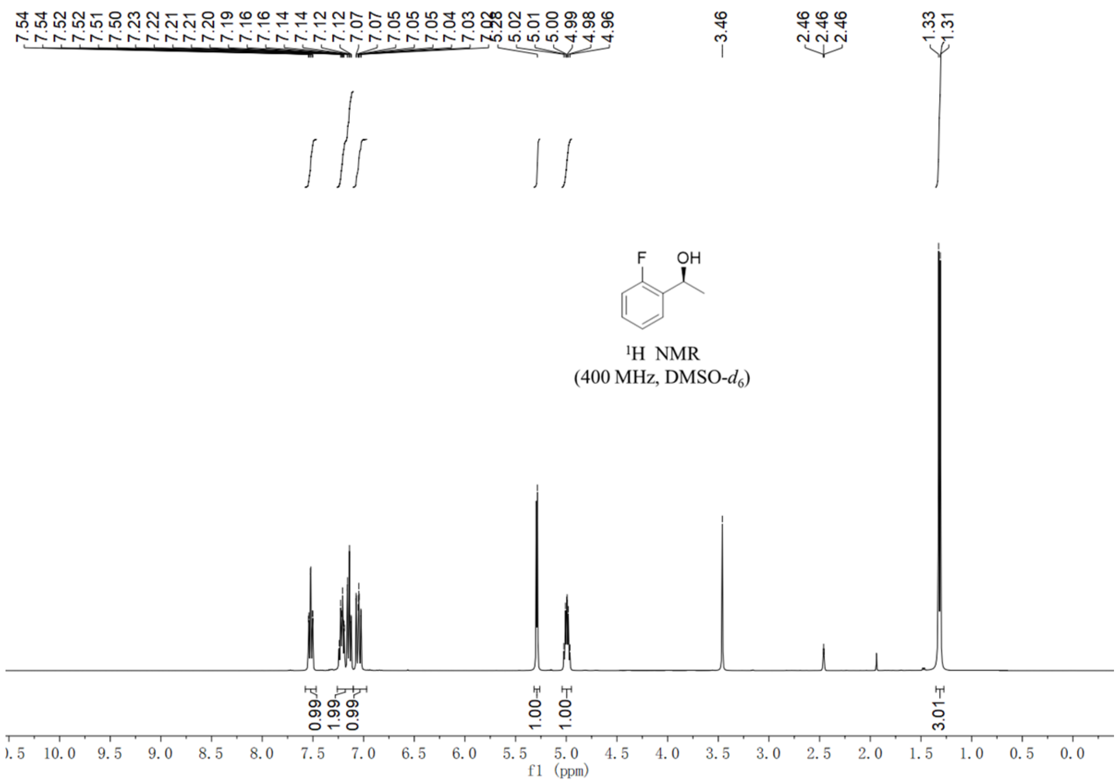


Figure S12 ^{1}H and ^{13}C NMR spectra of **b2** in DMSO-d_6



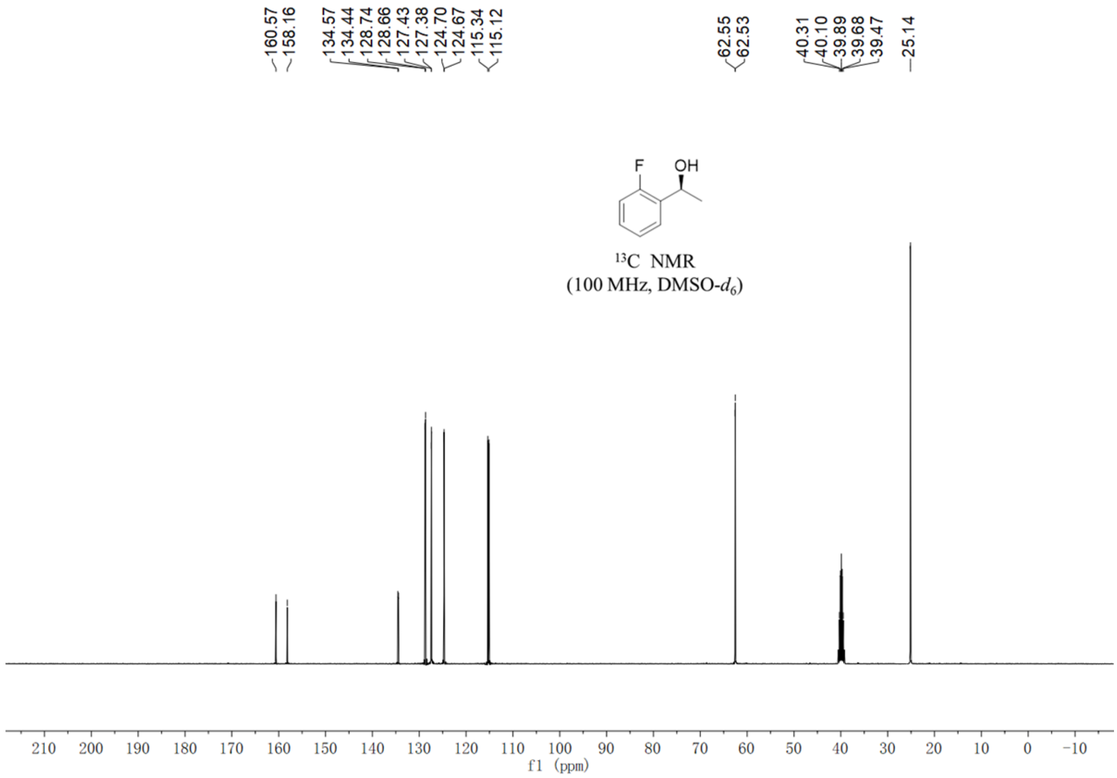
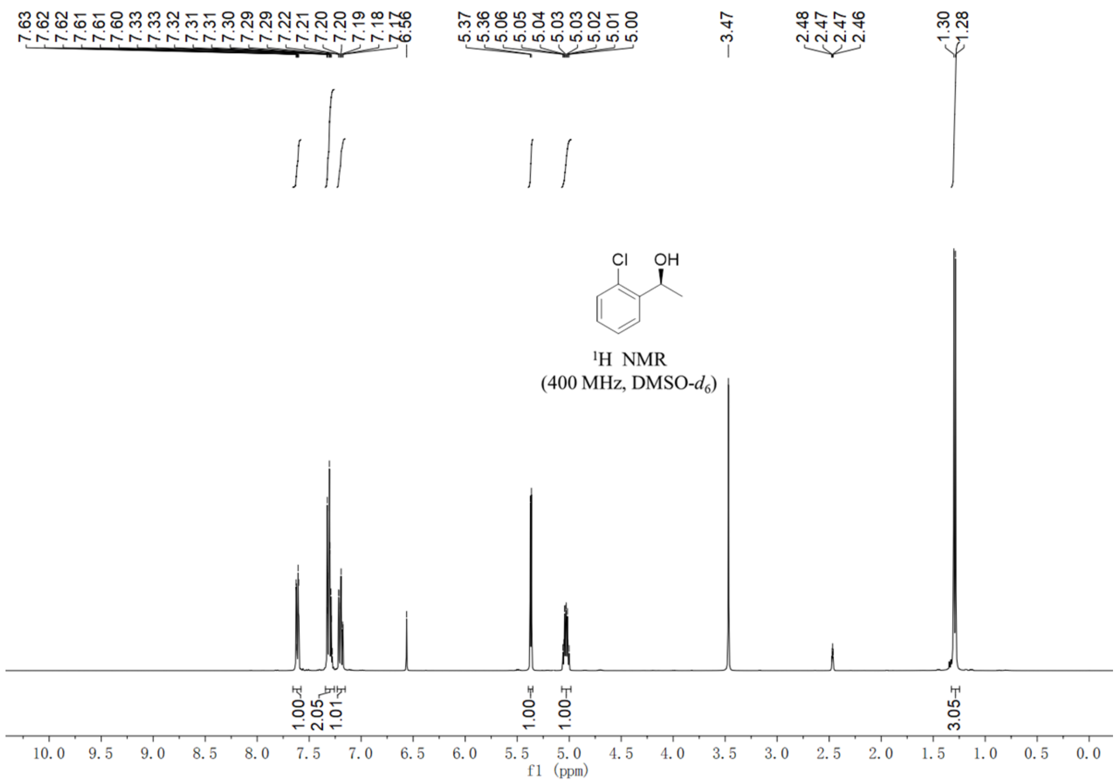


Figure S13 ^{1}H and ^{13}C NMR spectra of **b3** in DMSO-d_6



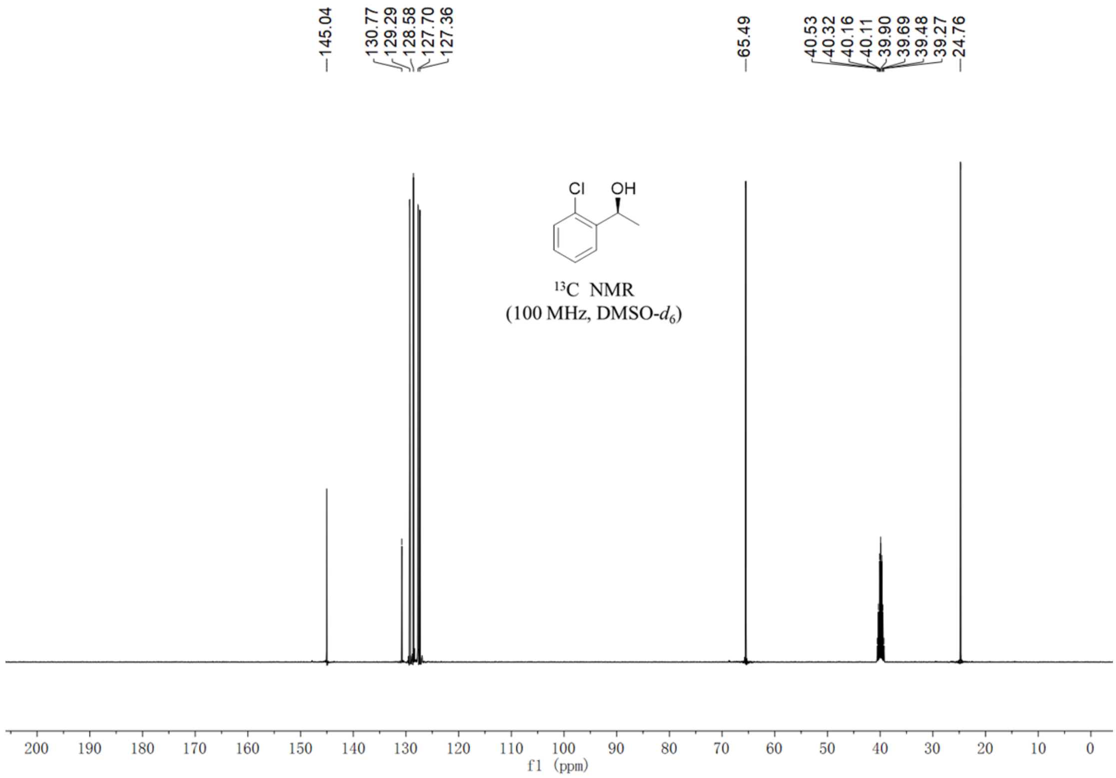
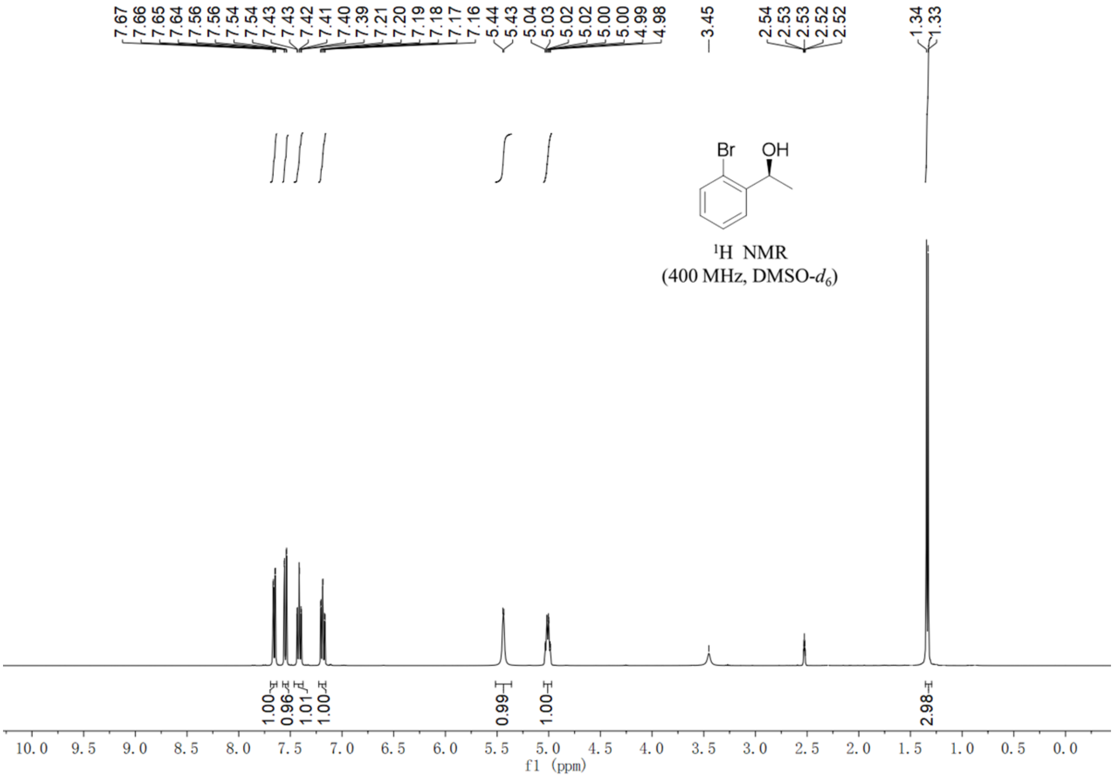


Figure S14 ^{1}H and ^{13}C NMR spectra of **b4**; recorded in DMSO-d_6 at ambient temperature



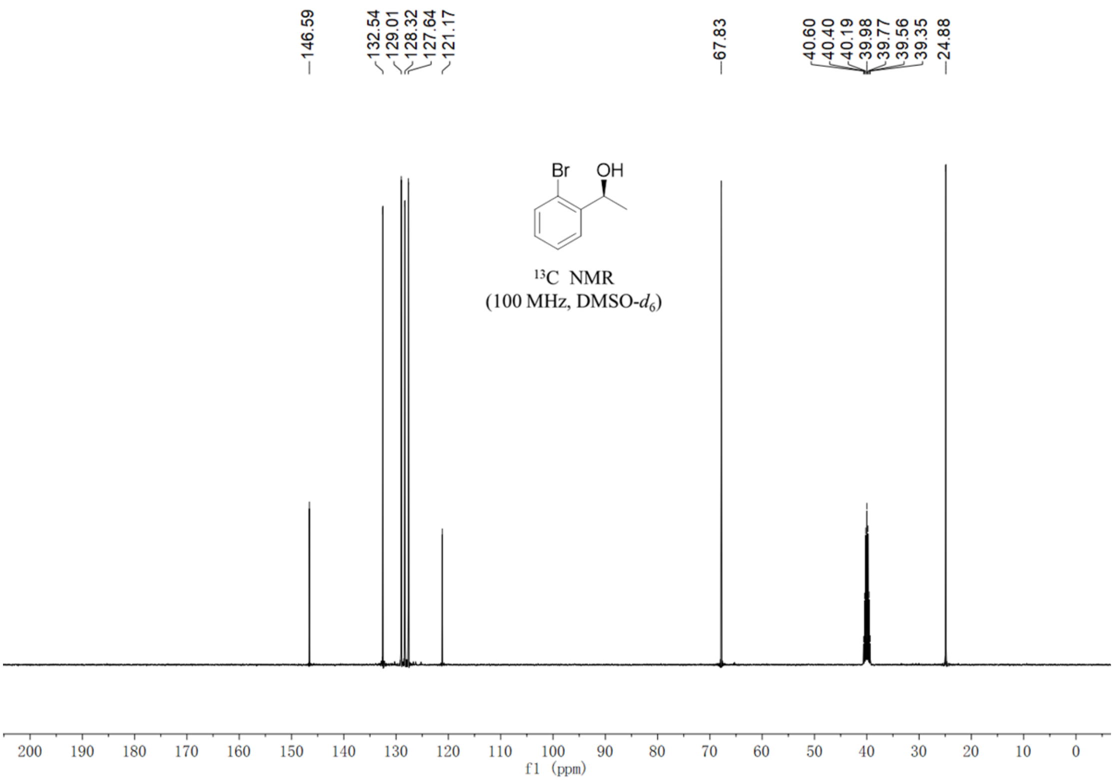
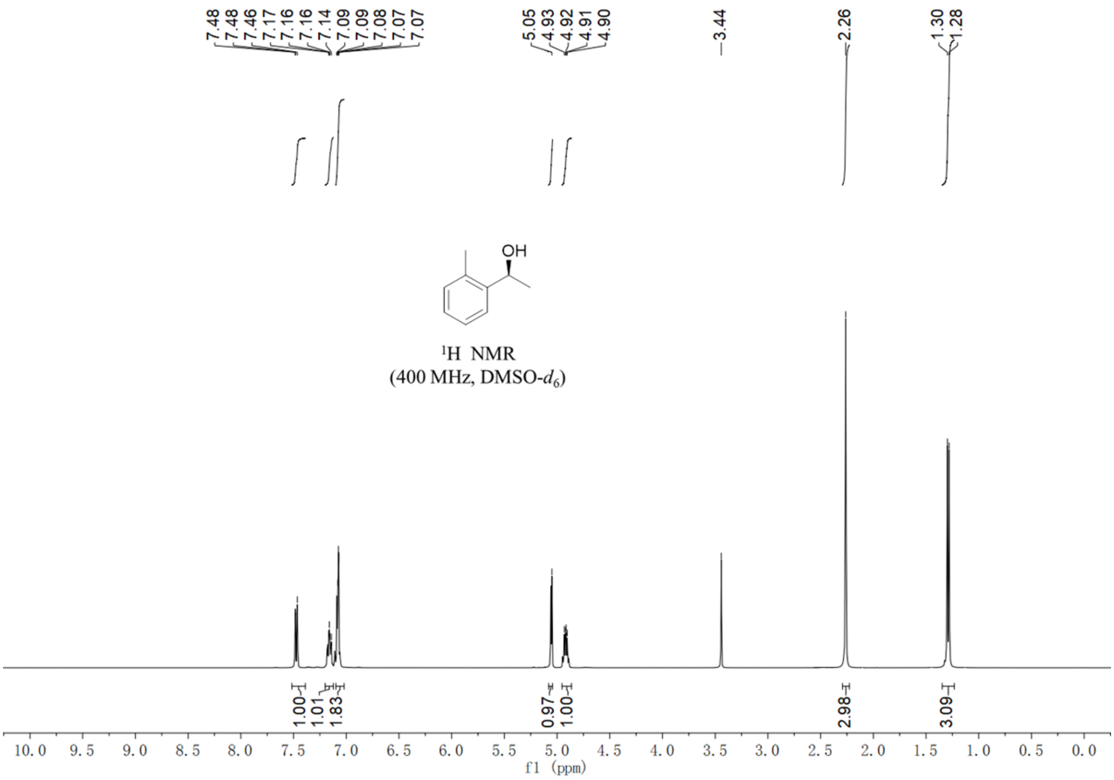


Figure S15 ^{1}H and ^{13}C NMR spectra of **b5**; recorded in DMSO-d_6 at ambient temperature



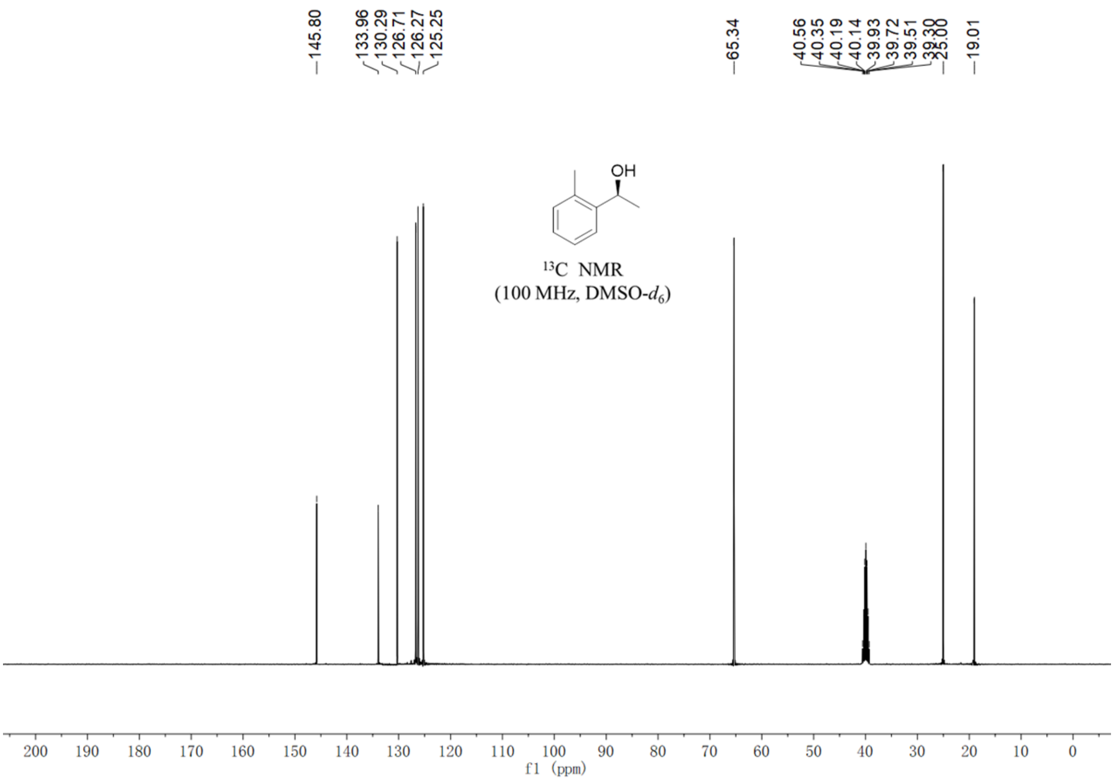
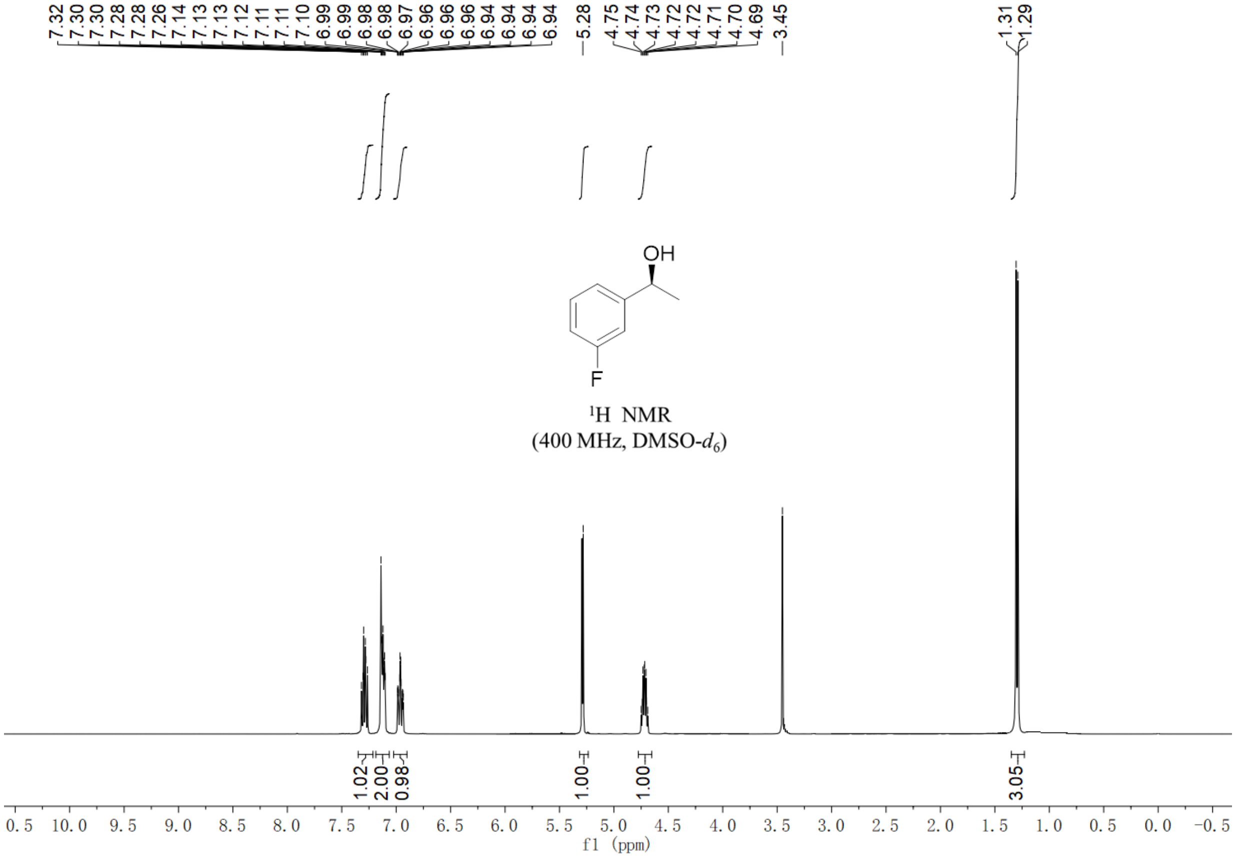


Figure S16 ^{1}H and ^{13}C NMR spectra of **b6**; recorded in DMSO-d_6 at ambient temperature



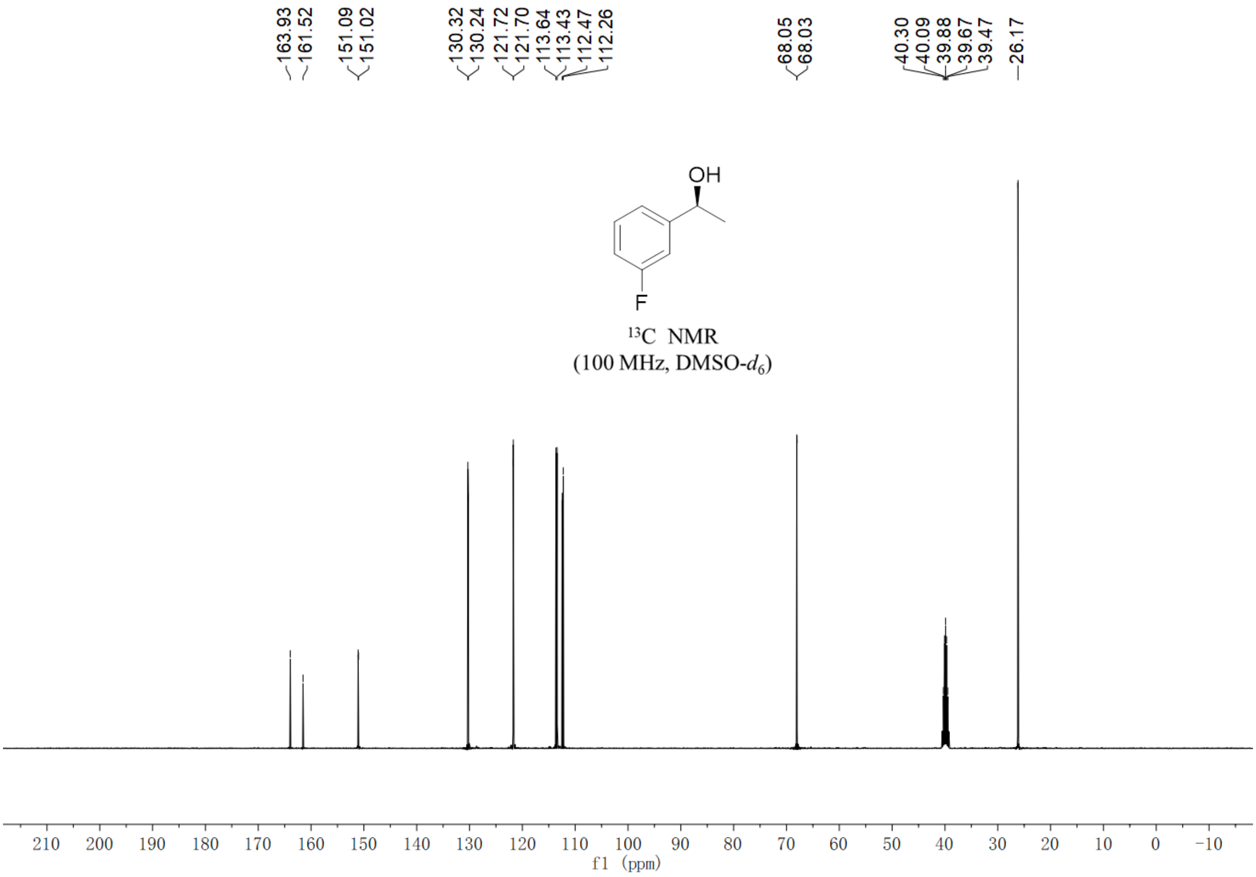
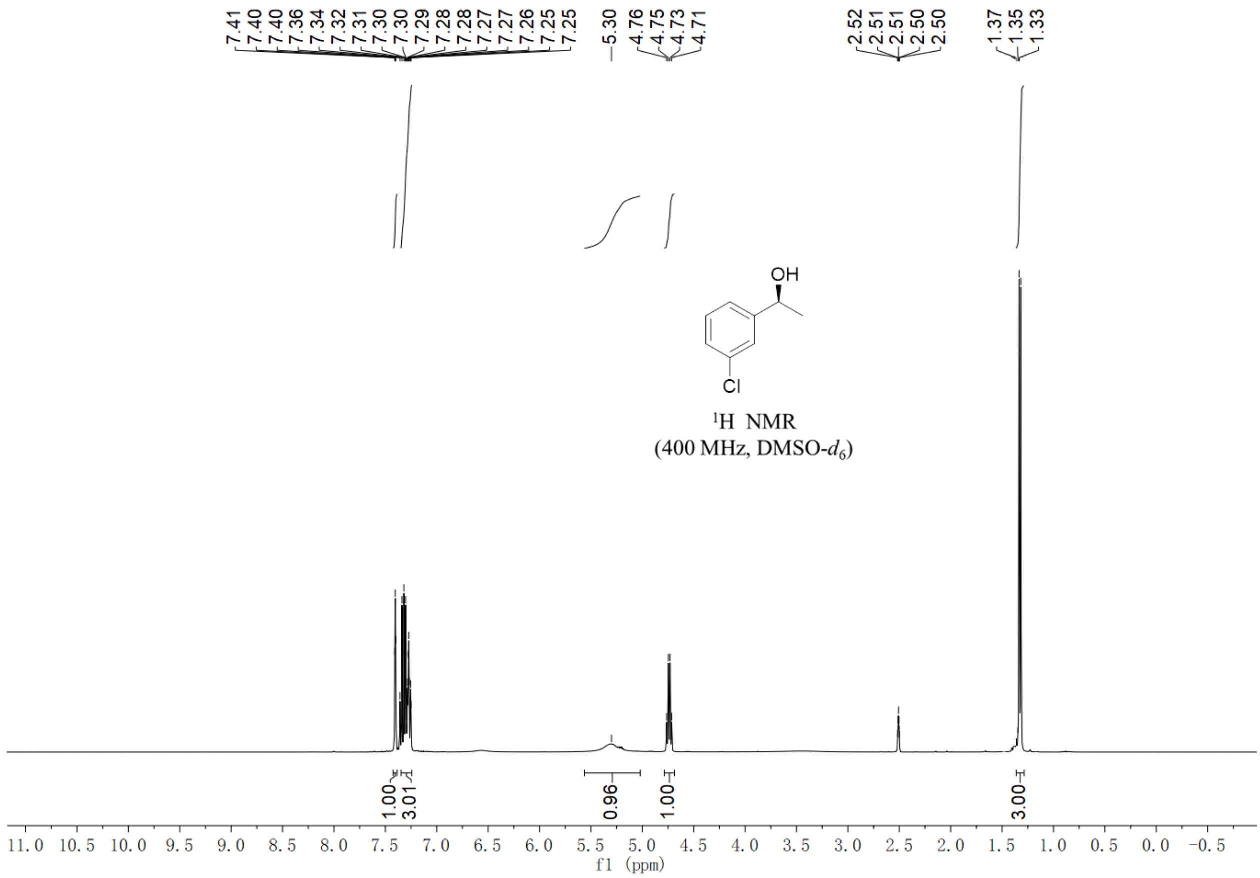


Figure S17 ^{1}H and ^{13}C NMR spectra of **b7**; recorded in DMSO-d_6 at ambient temperature



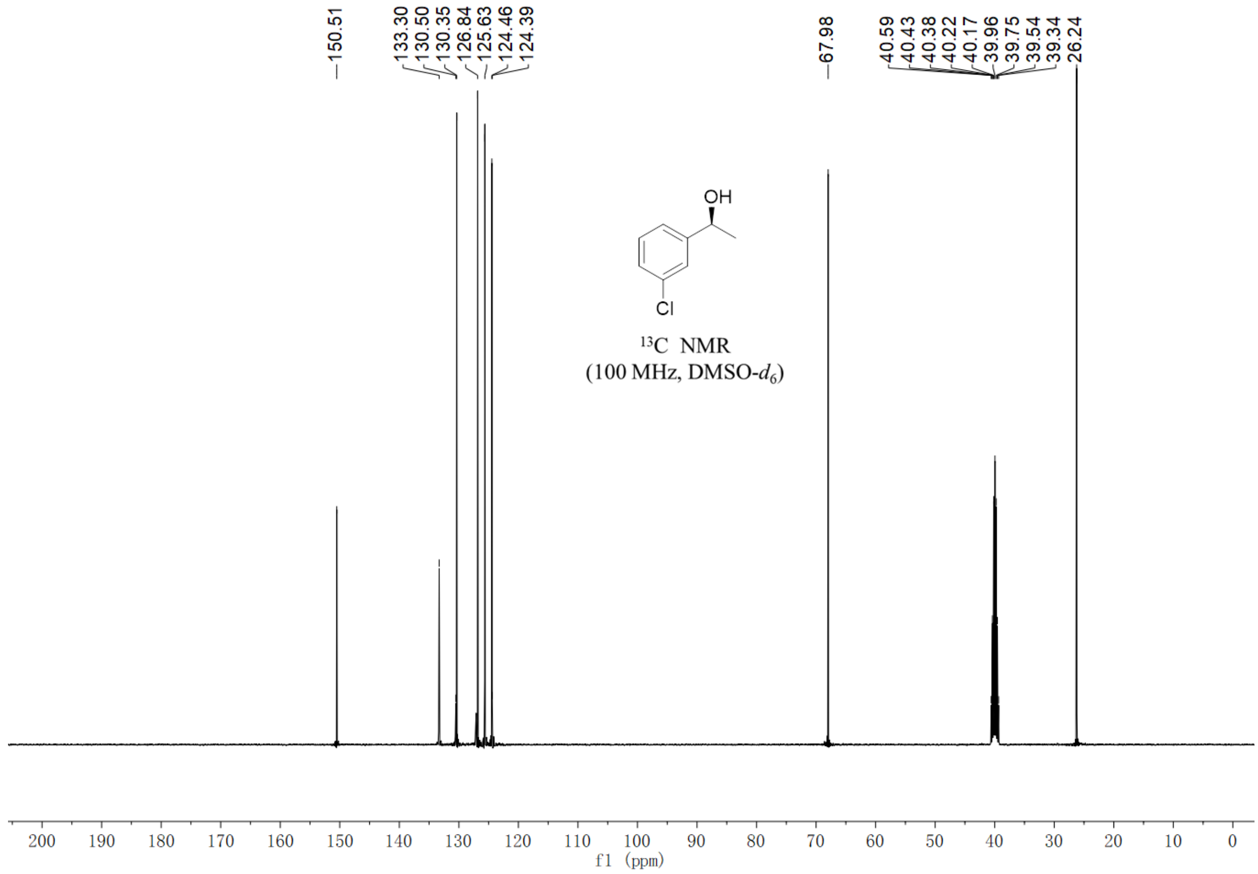
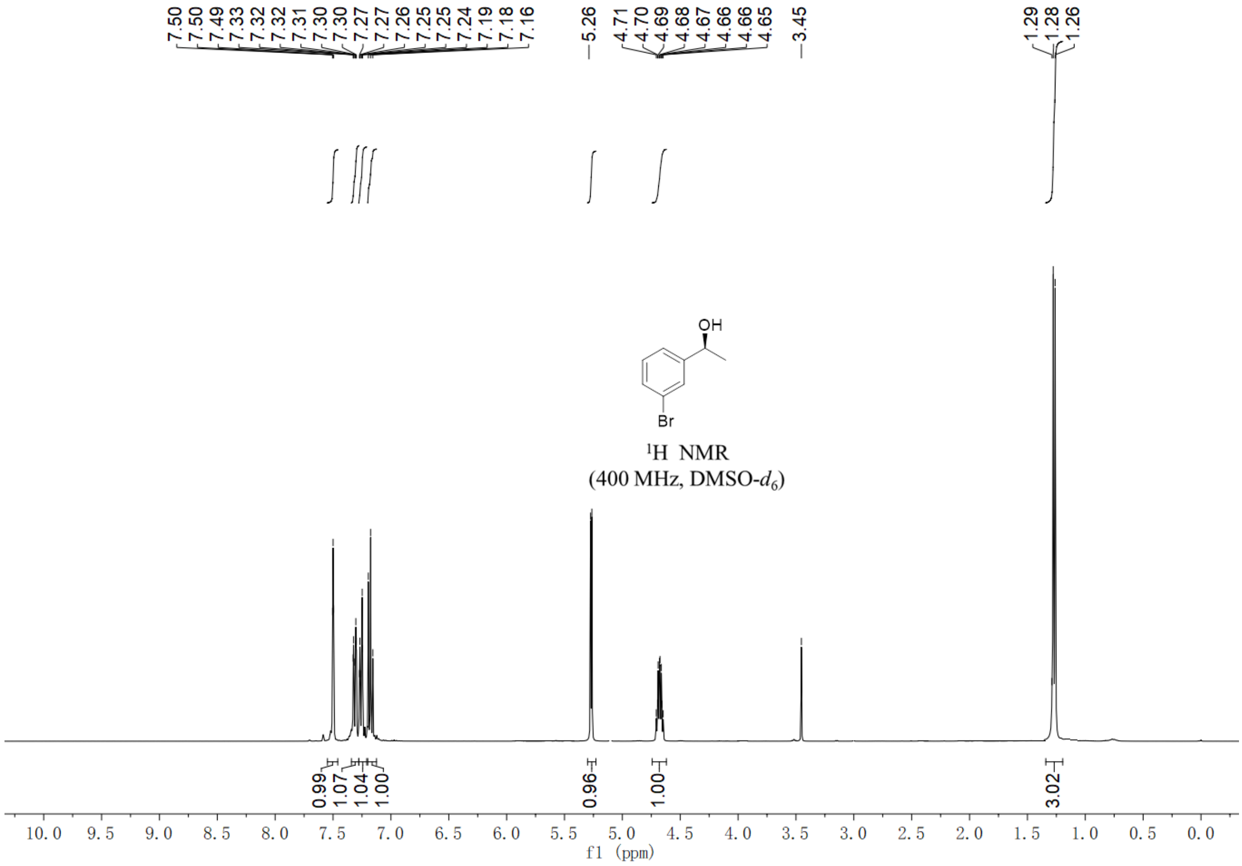


Figure S18 ^{1}H and ^{13}C NMR spectra of **b8**; recorded in DMSO-d_6 at ambient temperature



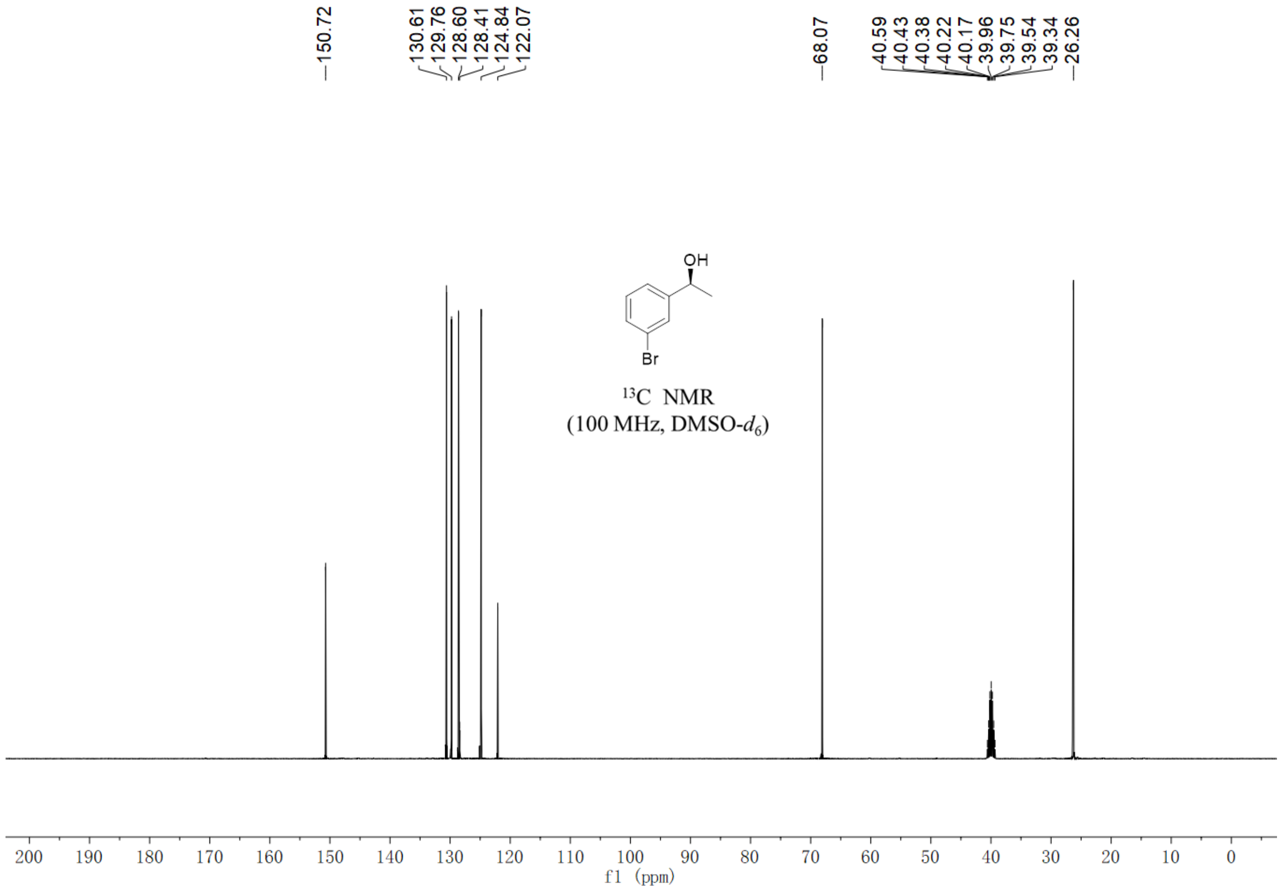
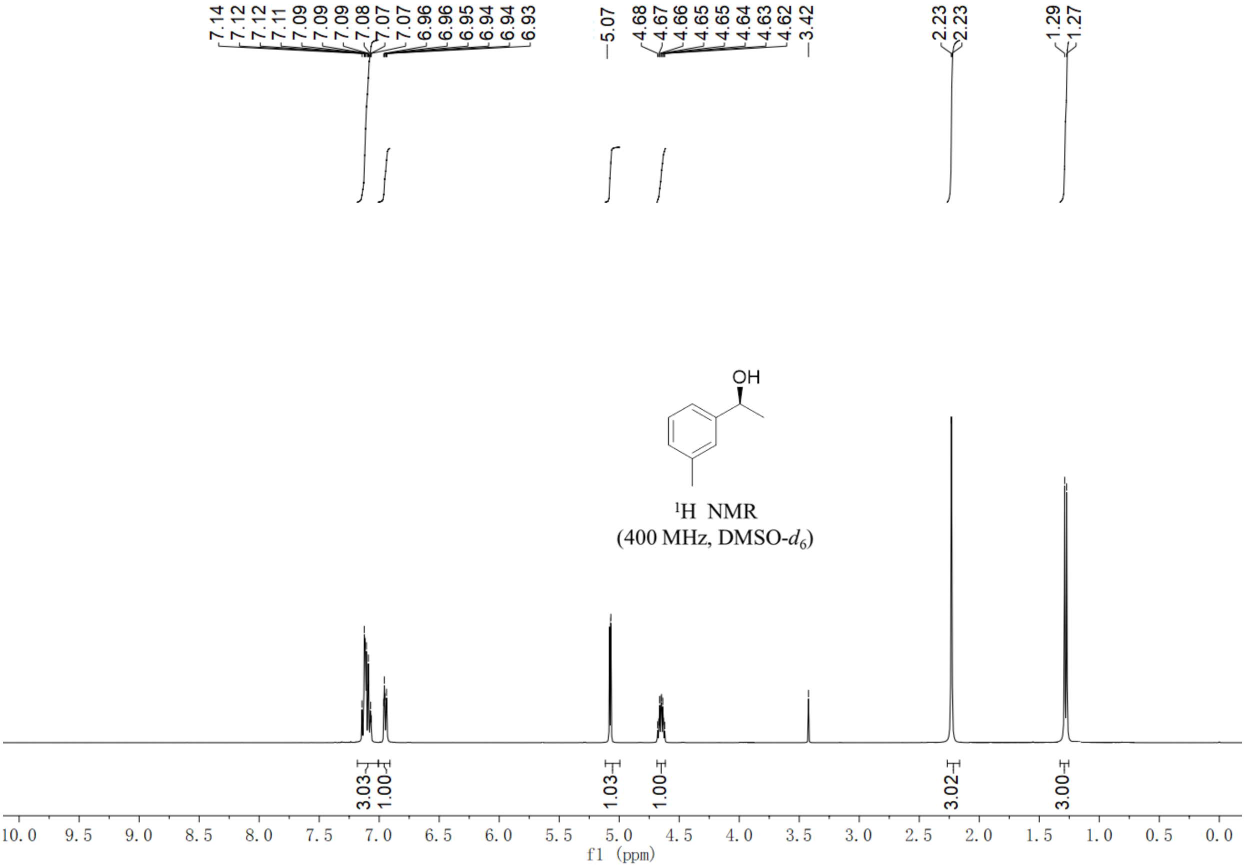


Figure S19 ^{1}H and ^{13}C NMR spectra of **b9**; recorded in DMSO-d_6 at ambient temperature



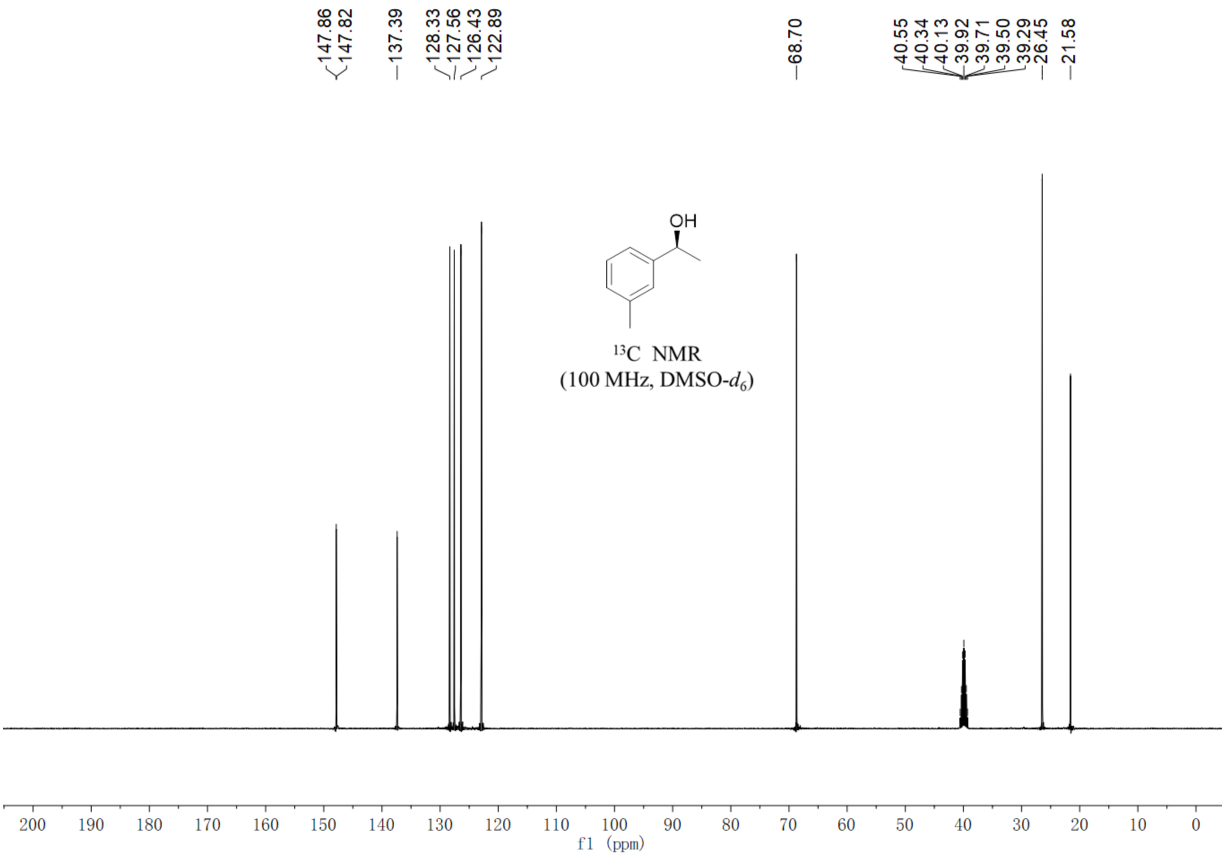
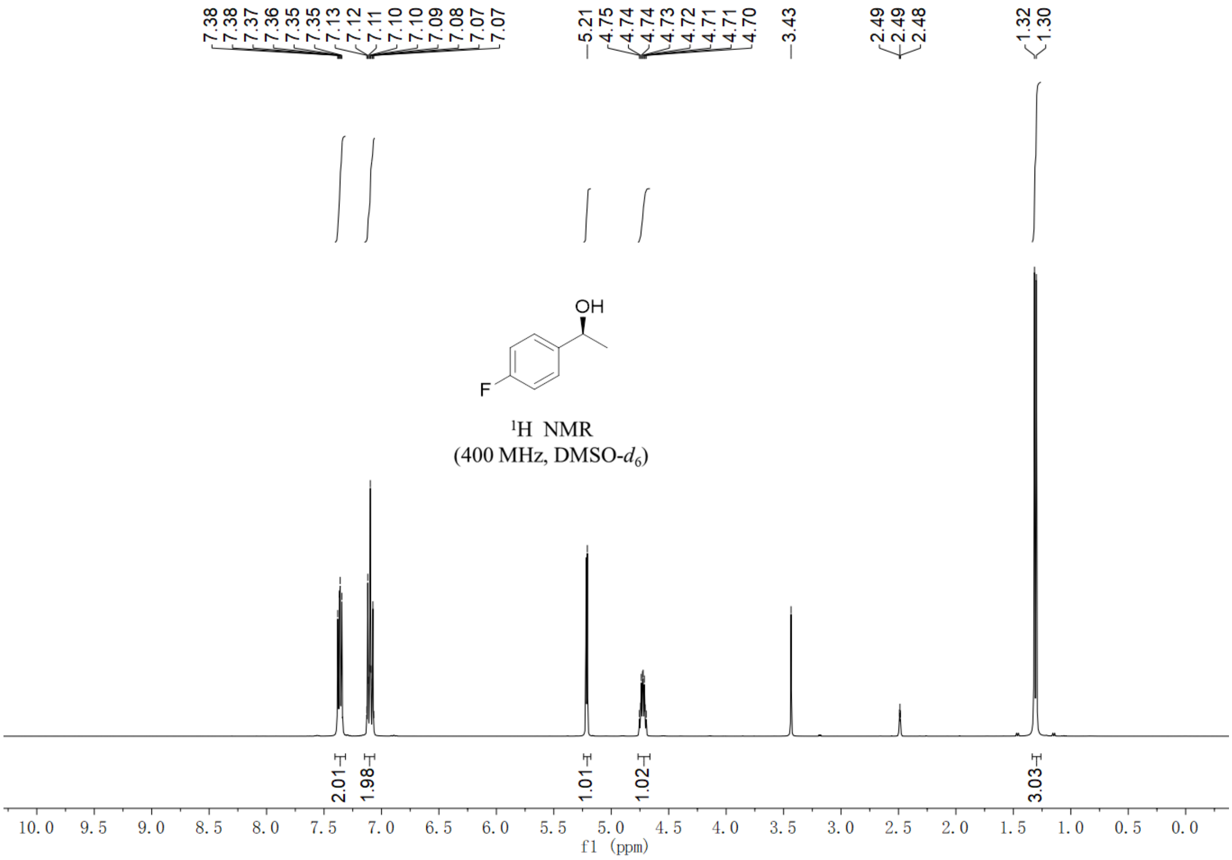


Figure S20 ^{1}H and ^{13}C NMR spectra of **b10**; recorded in DMSO-d_6 at ambient temperature



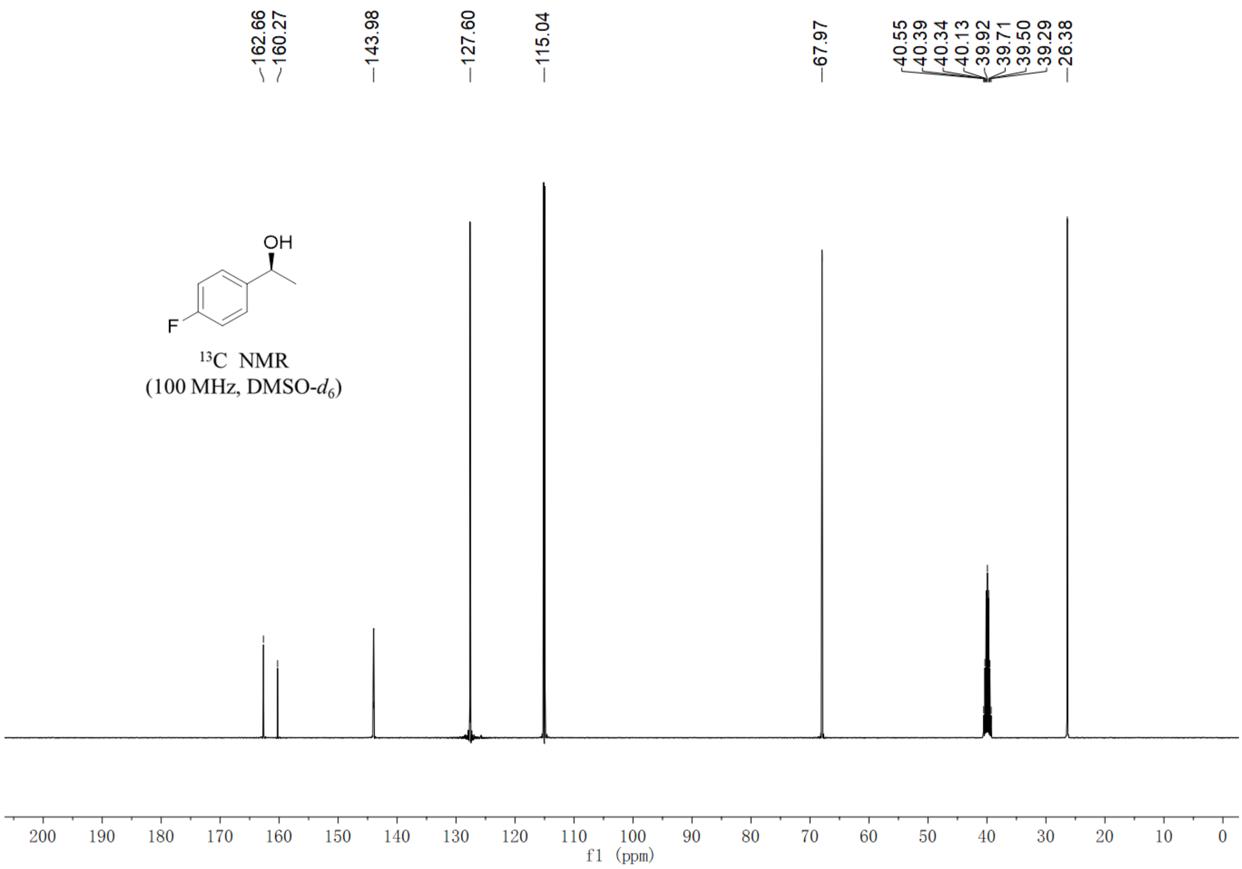
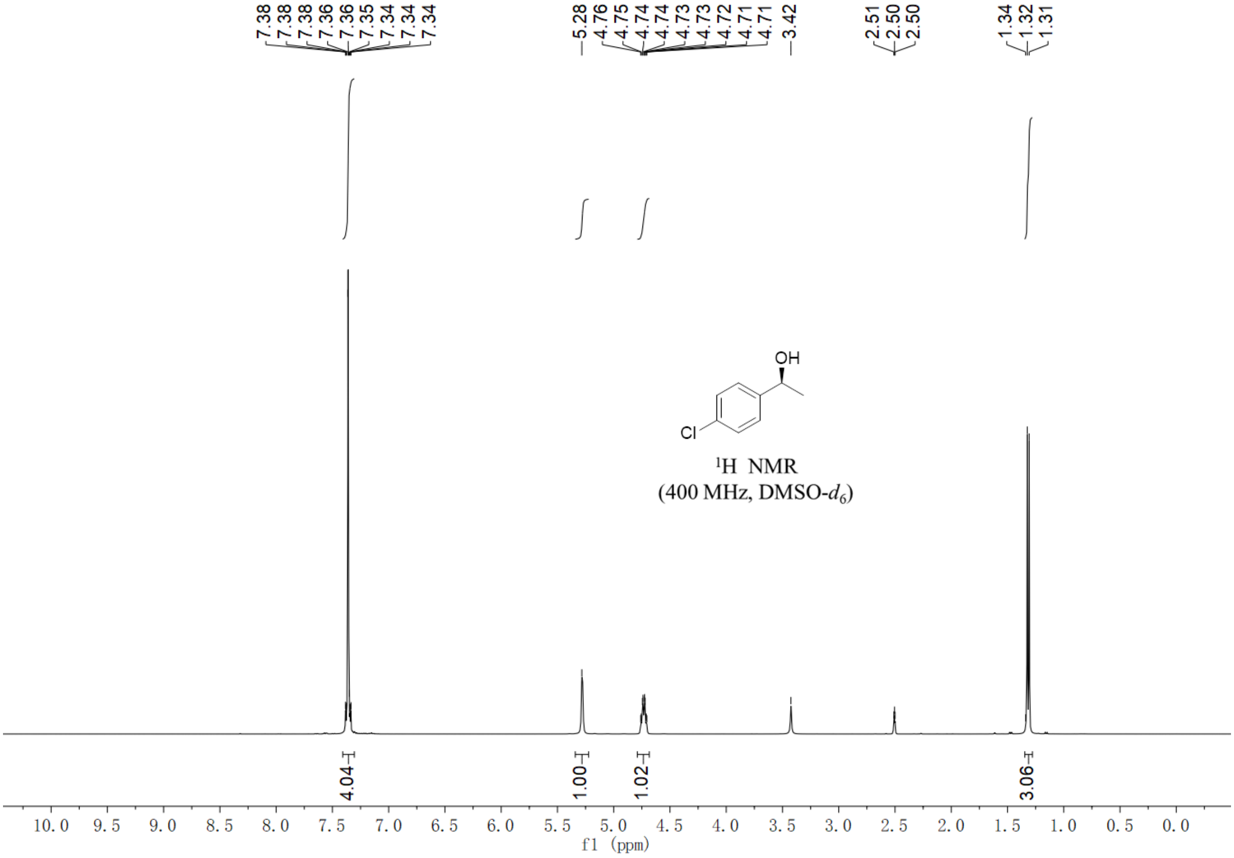


Figure S21 ^{1}H and ^{13}C NMR spectra of **b11**; recorded in DMSO-d_6 at ambient temperature



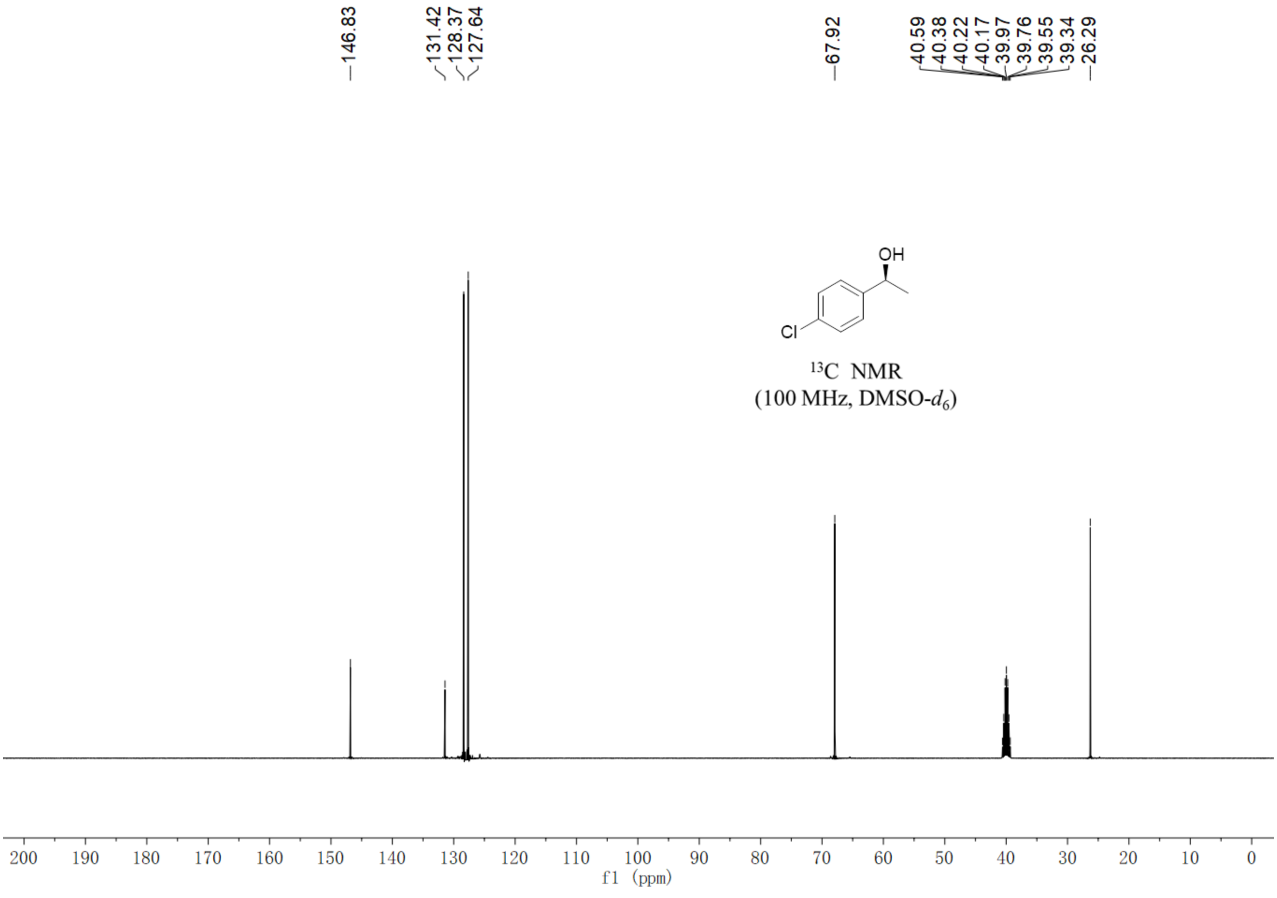
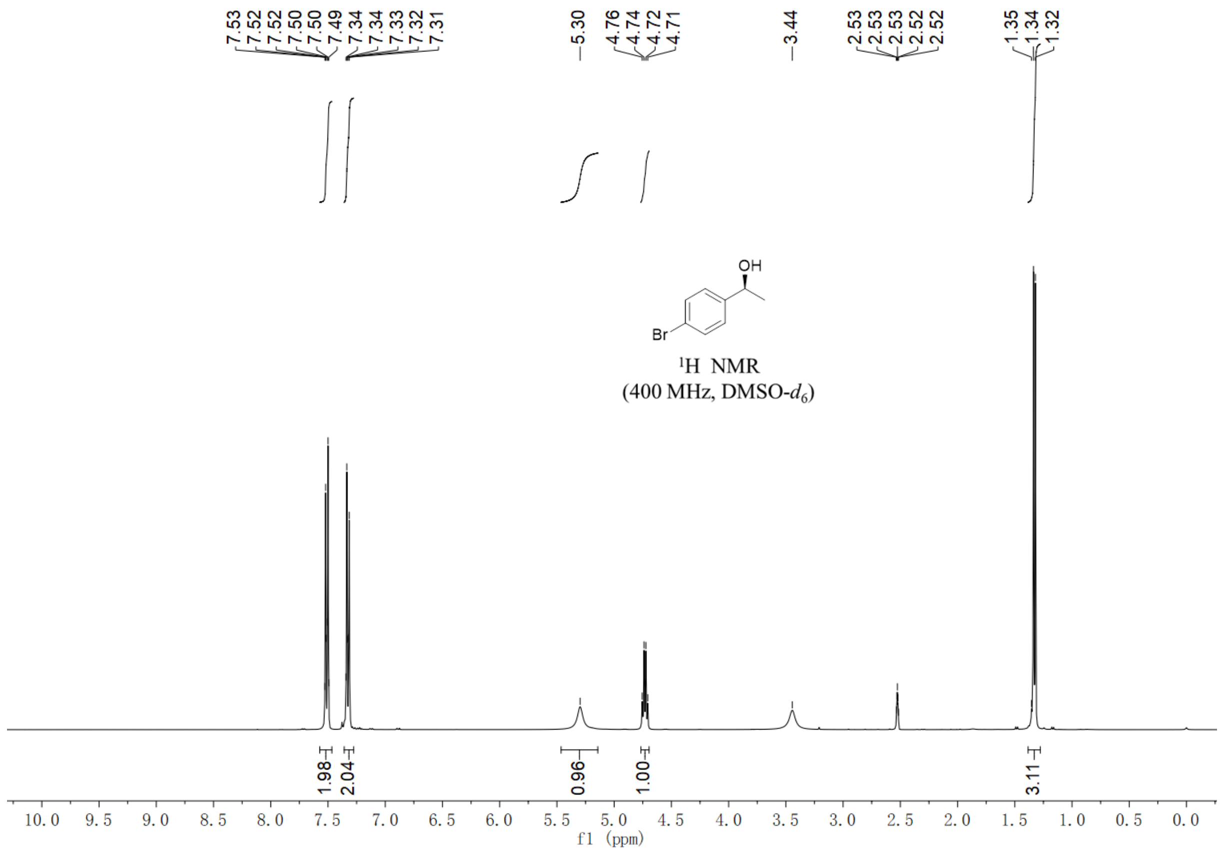


Figure S22 ^{1}H and ^{13}C NMR spectra of **b12**; recorded in DMSO-d_6 at ambient temperature



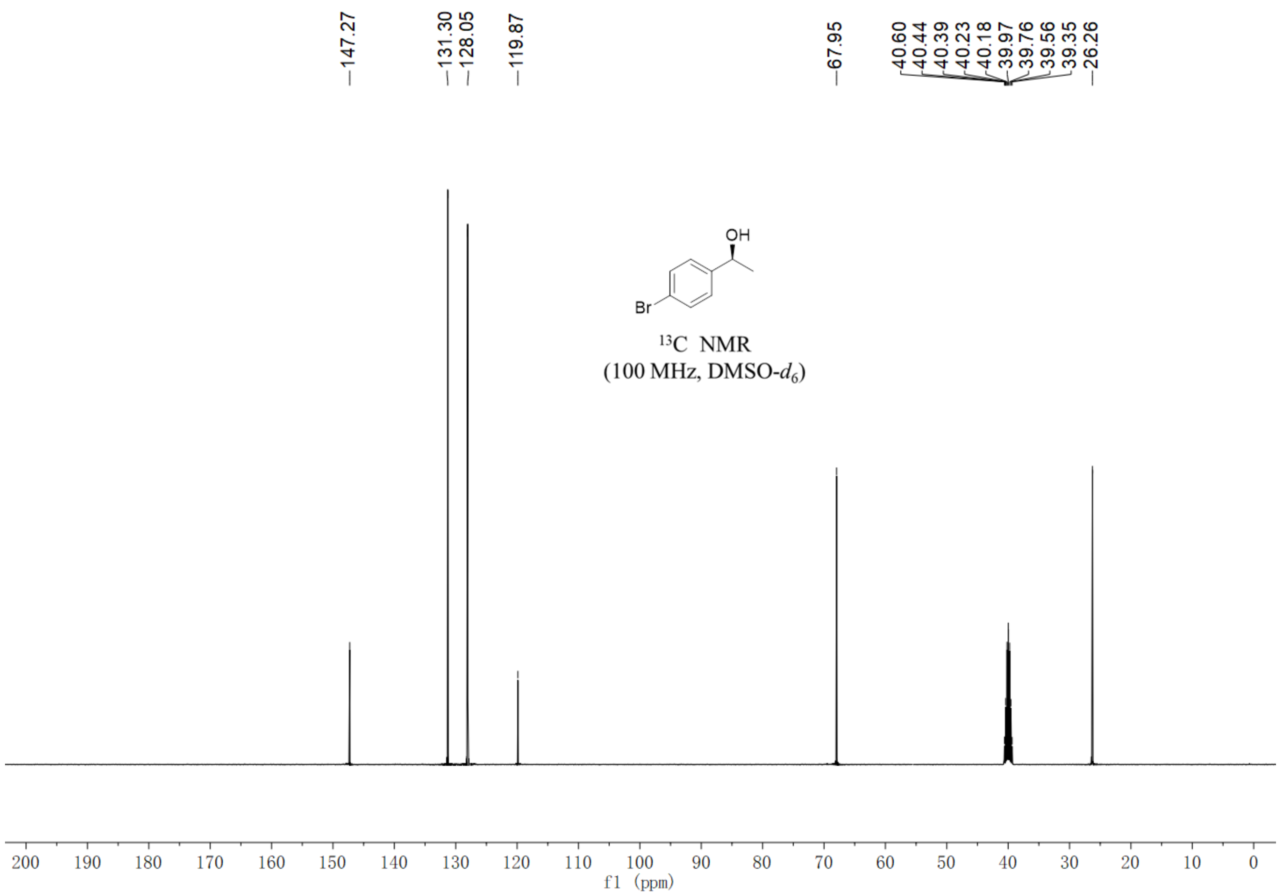
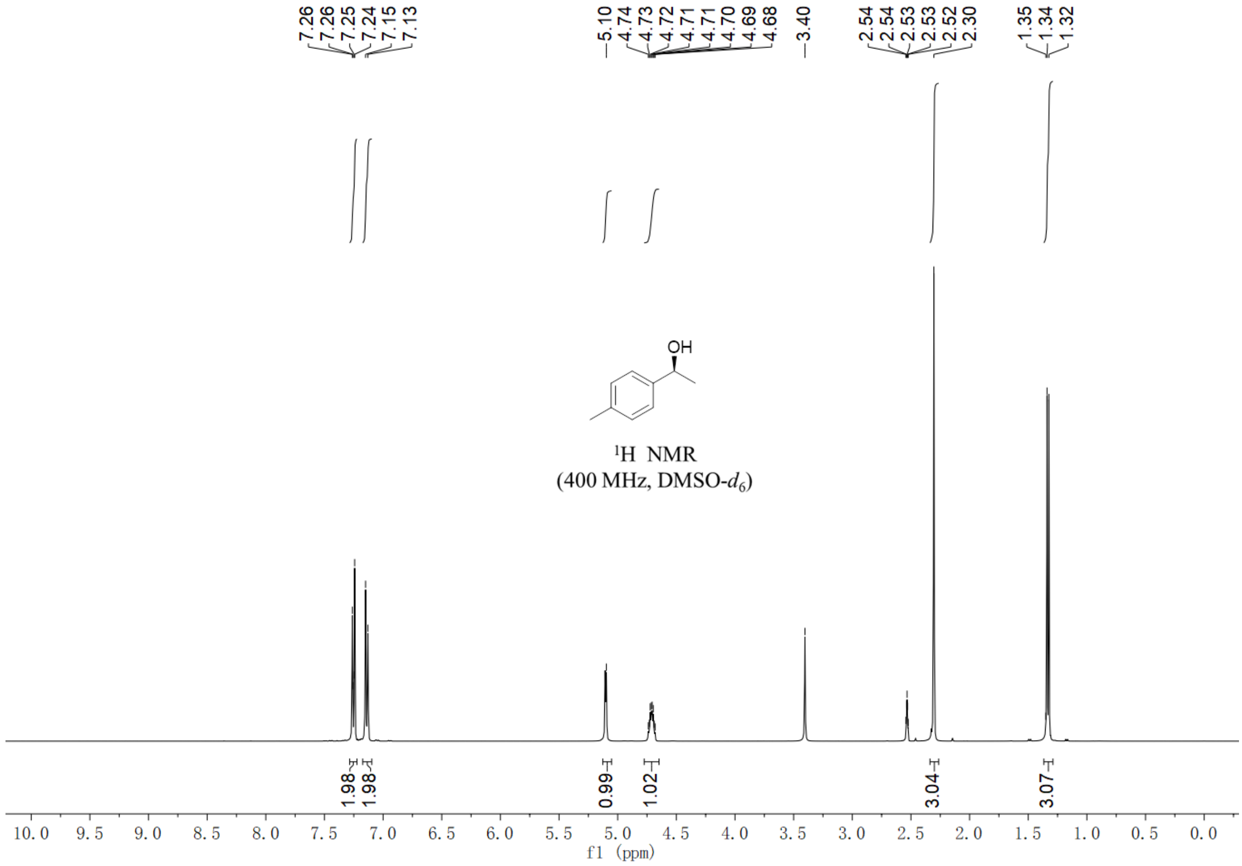
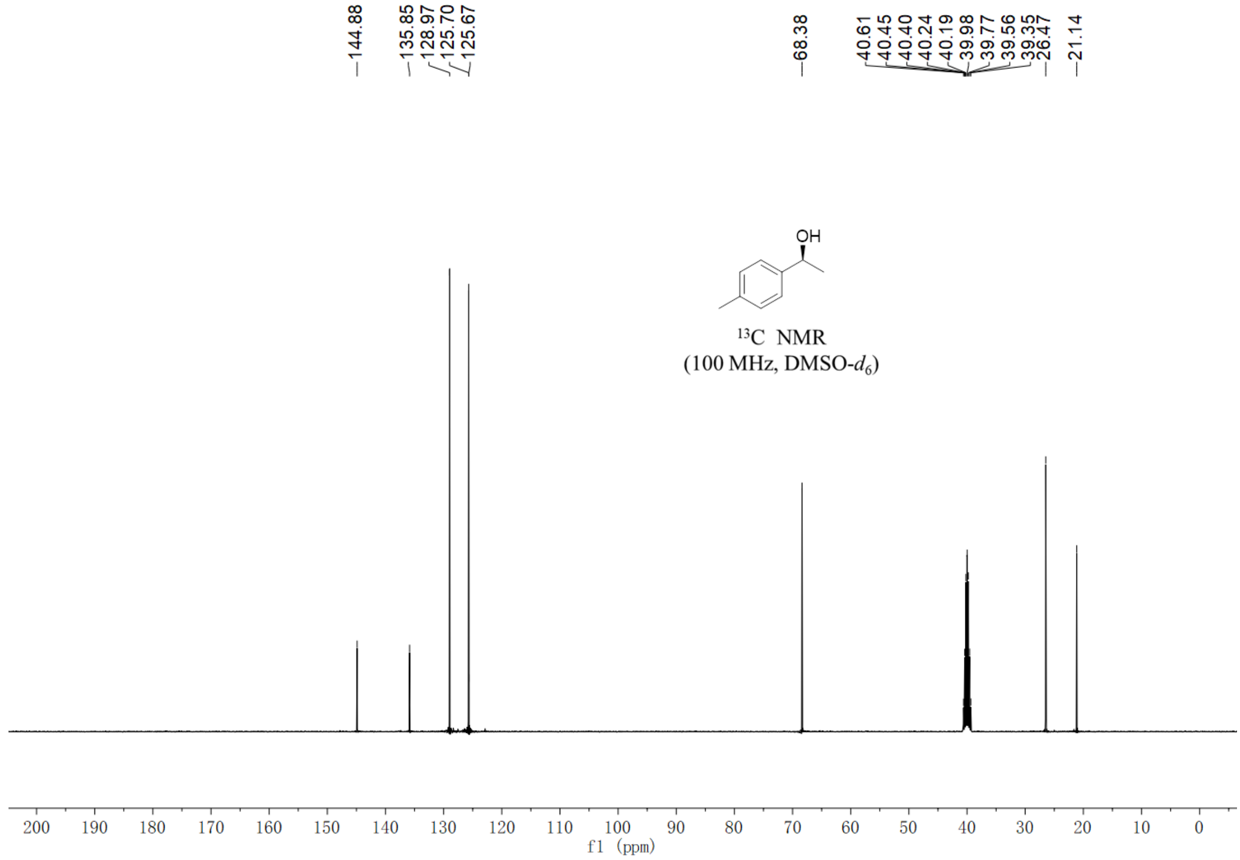


Figure S23 [1]H and [13]C NMR spectra of **b13**; recorded in DMSO-d_6 at ambient temperature

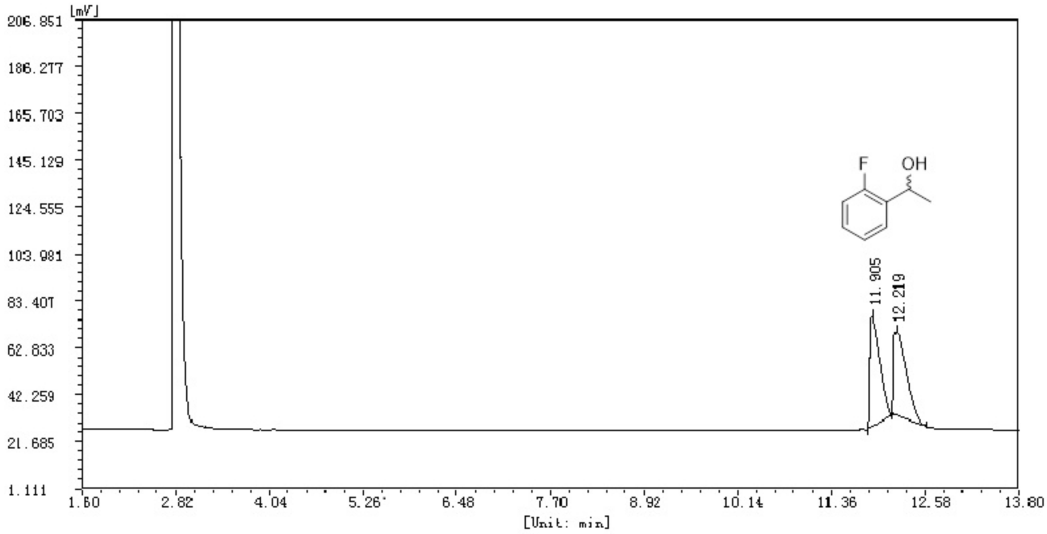




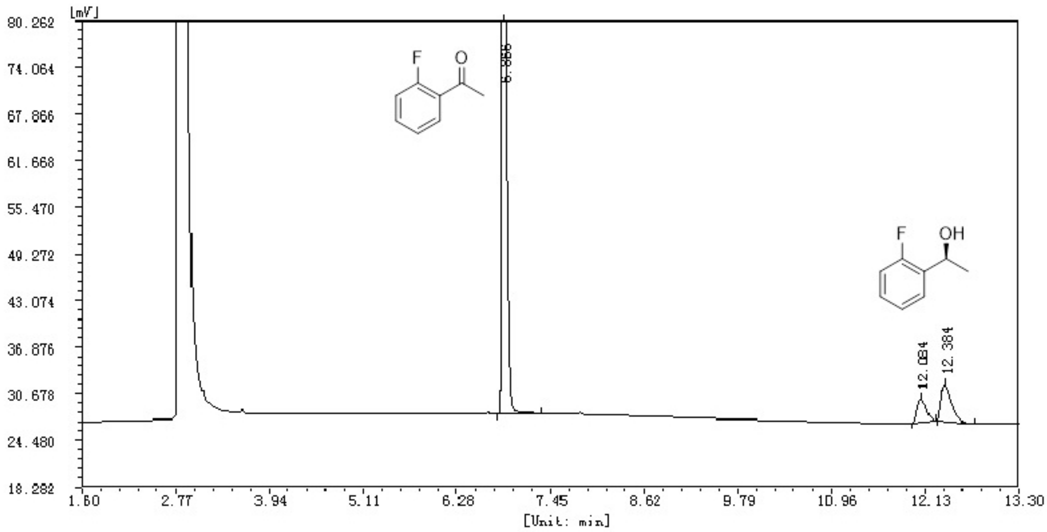
6. GC spectra of the chiral alcohol products

(S)-1-(2-fluorophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



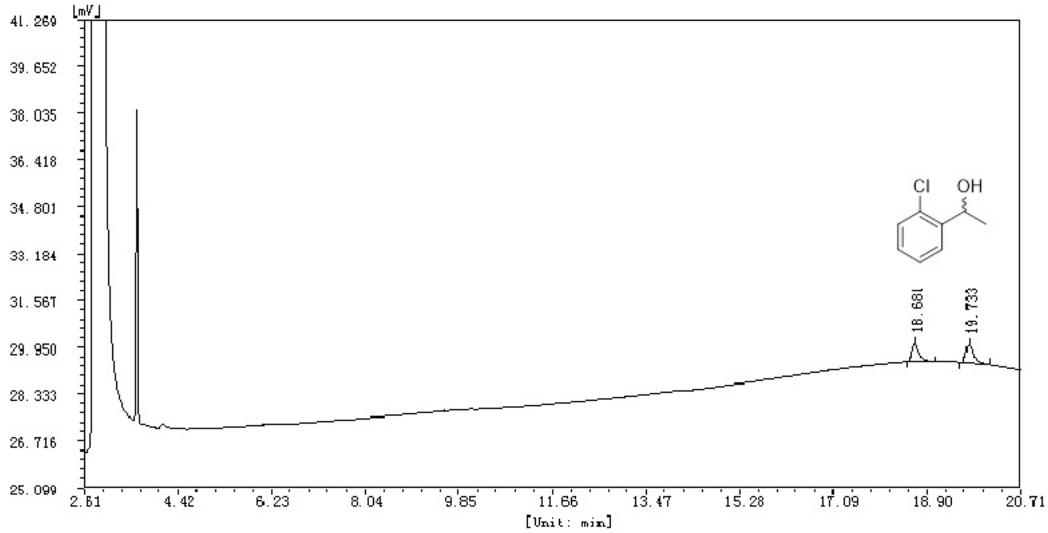
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	11.906	49032.0	431037.1	50.6253
2	12.219	36466.4	420389.4	49.3747



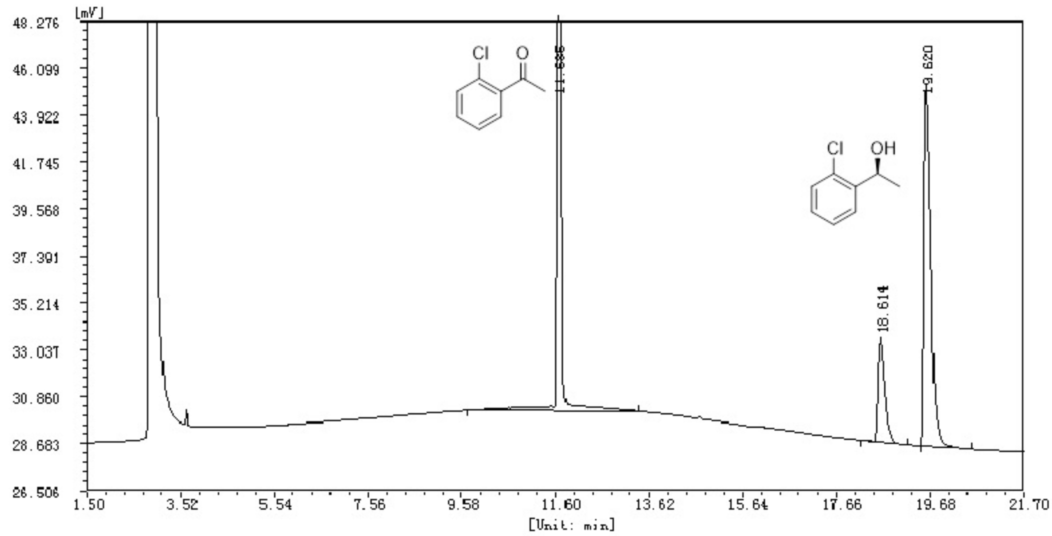
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	6.866	100555.0	350886.4	83.4891
2	12.084	2982.8	25182.8	5.9919
3	12.384	4830.4	44208.9	10.5190

(*S*)-1-(2-chlorophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



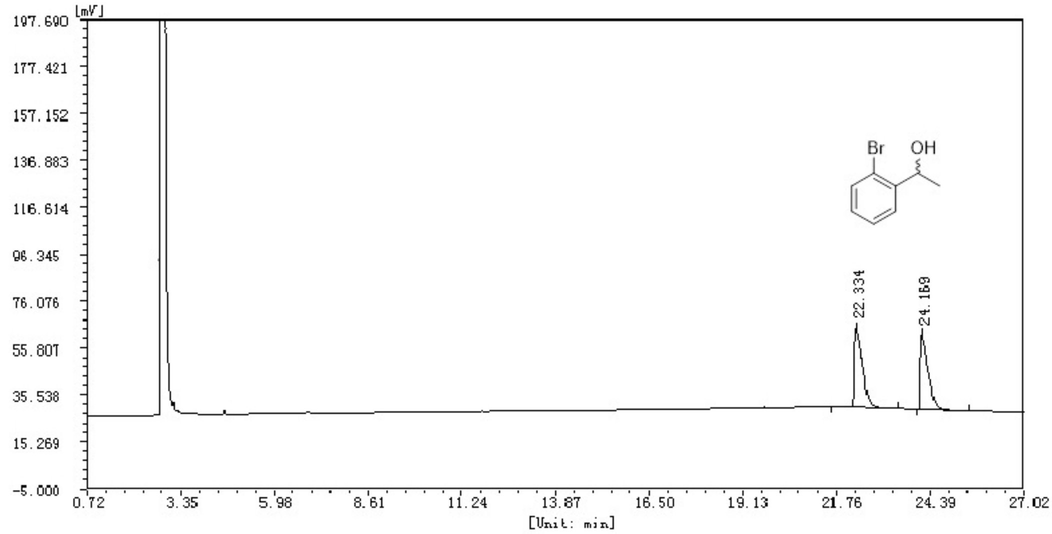
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	18.681	636.7	6632.4	49.4919
2	19.733	672.1	6768.6	50.5081



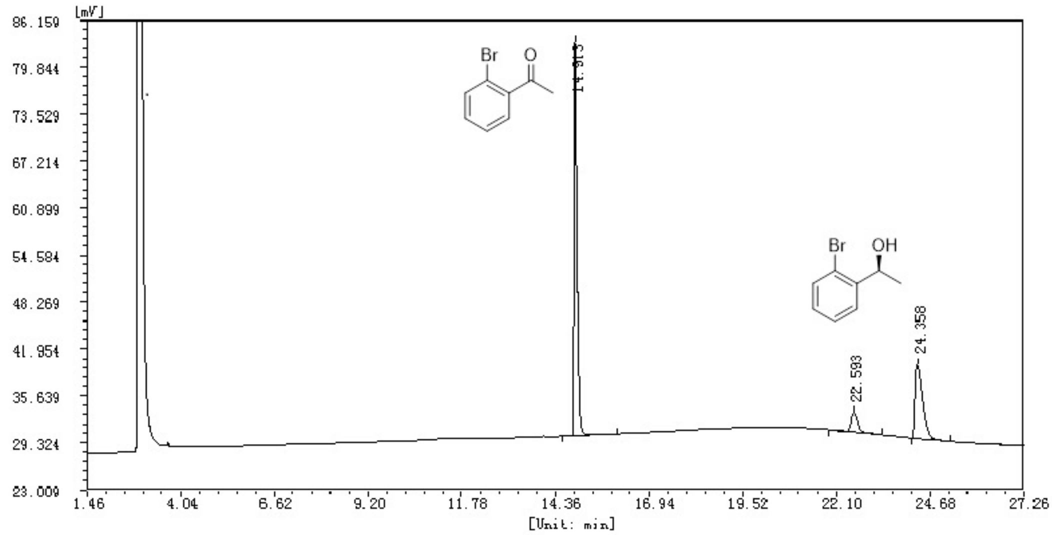
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	11.685	45088.8	232943.6	50.6439
2	18.614	4644.3	48963.7	10.6451
3	19.620	16550.0	178056.2	38.7109

(*S*)-1-(2-bromophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



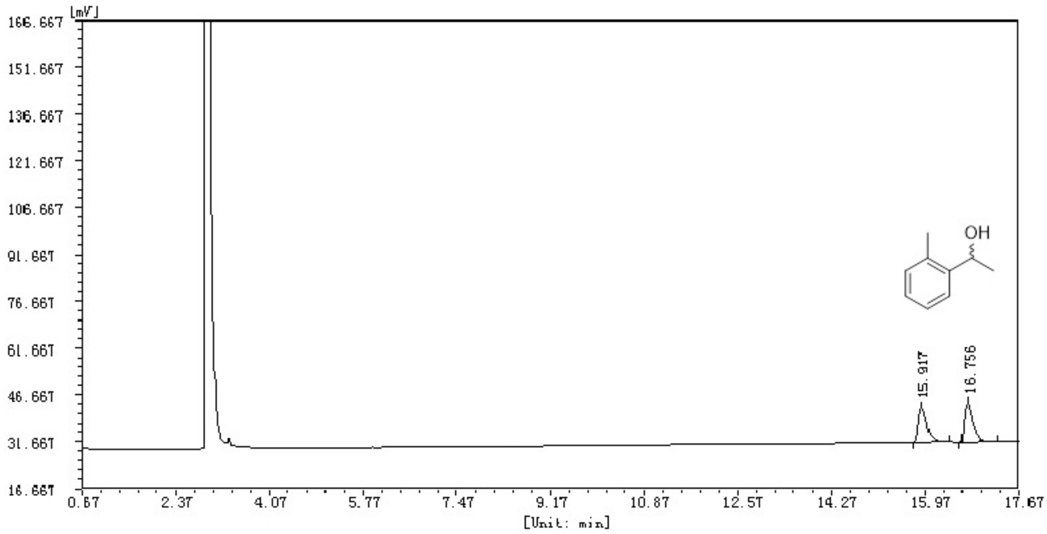
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	22.334	34338.7	558816.8	50.3552
2	24.169	32206.5	550932.8	49.6448



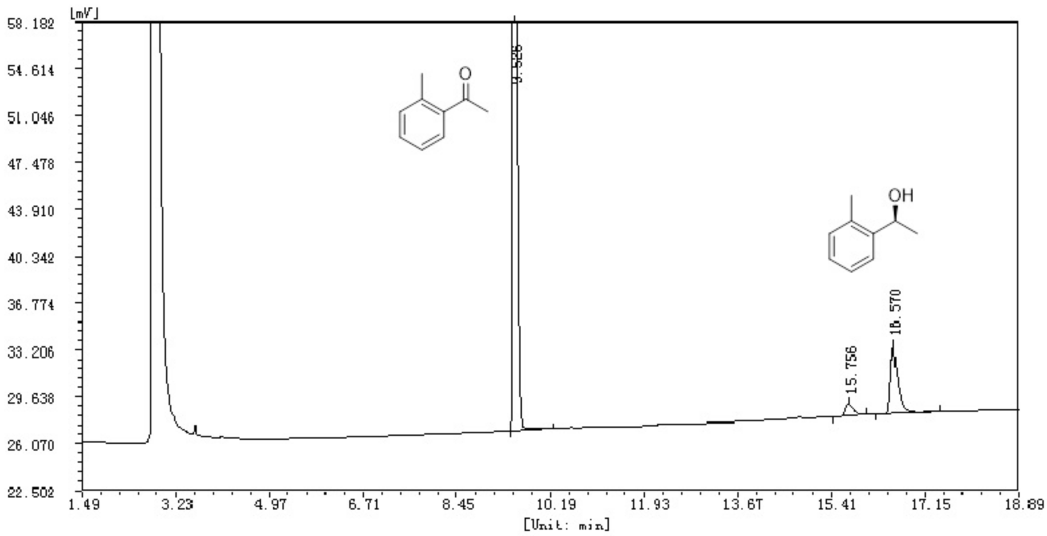
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	14.913	53093.9	305462.5	62.1814
2	22.593	2659.2	38565.9	7.8507
3	24.358	10026.1	147215.5	29.9679

(S)-1-(o-tolyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



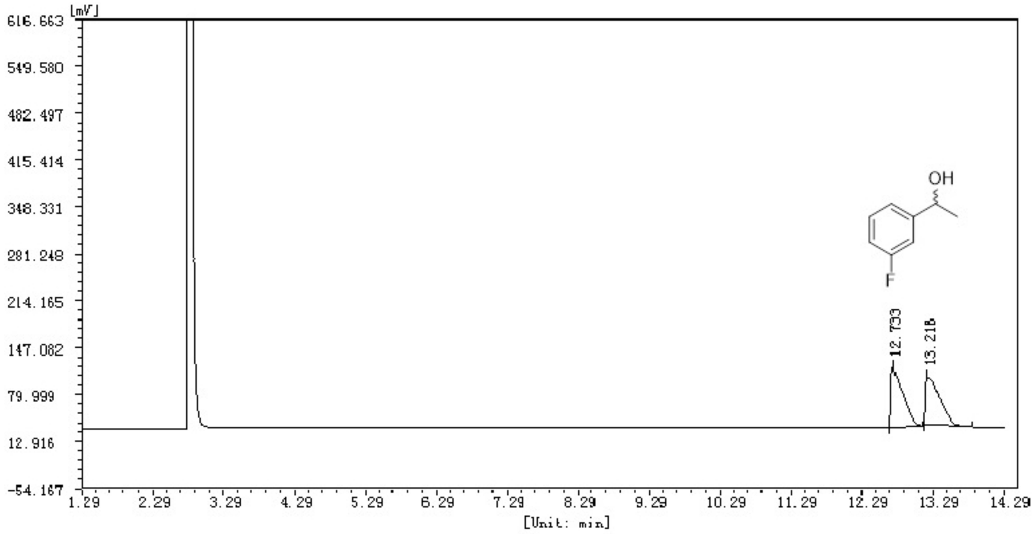
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	15.917	11200.4	129701.5	49.8017
2	16.766	12420.5	130734.3	50.1983



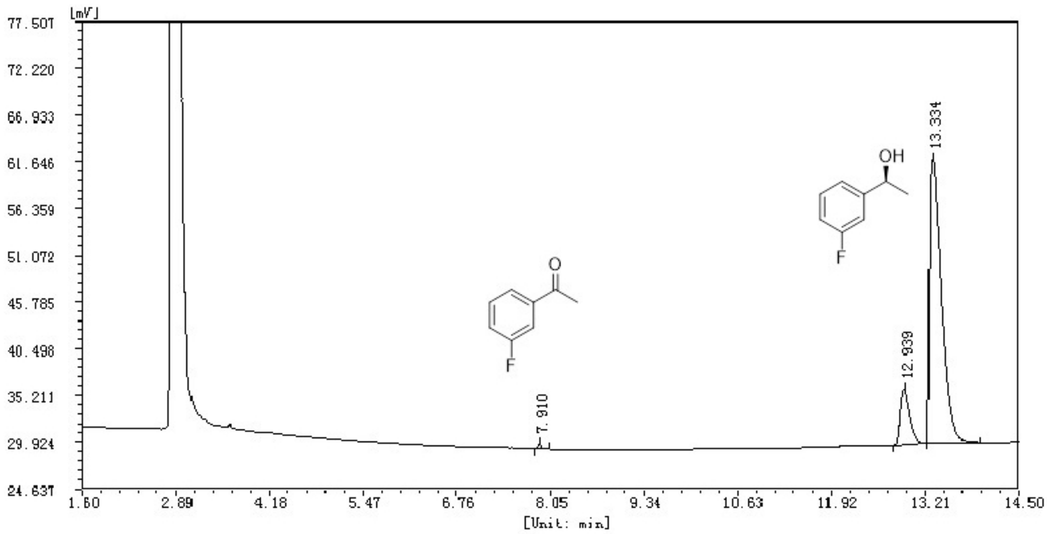
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	9.526	88098.4	400871.0	86.3826
2	15.766	921.1	10053.3	2.1664
3	16.570	5181.6	53140.4	11.4511

(S)-1-(3-fluorophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



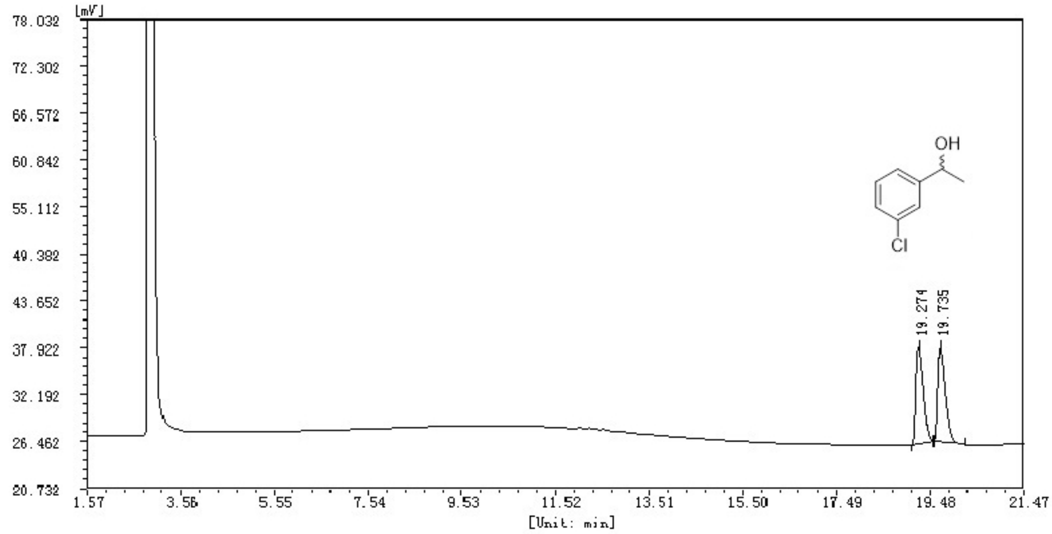
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	12.733	87184.2	1048182.9	50.6160
2	13.216	70567.3	1022668.9	49.3840



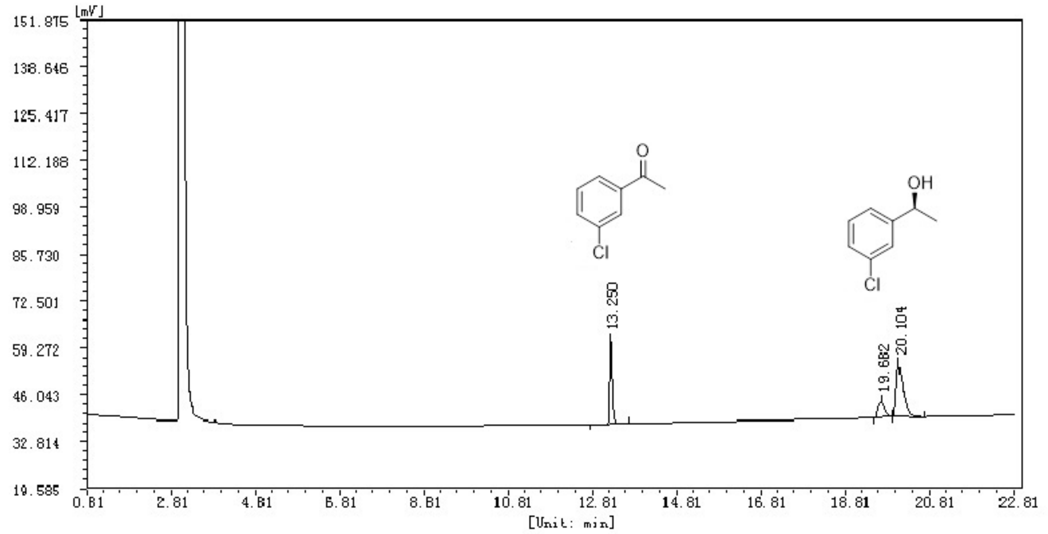
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	7.910	693.7	2150.6	0.5200
2	12.939	6391.9	57229.4	13.8365
3	13.334	32261.4	354229.2	85.6435

(*S*)-1-(3-chlorophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



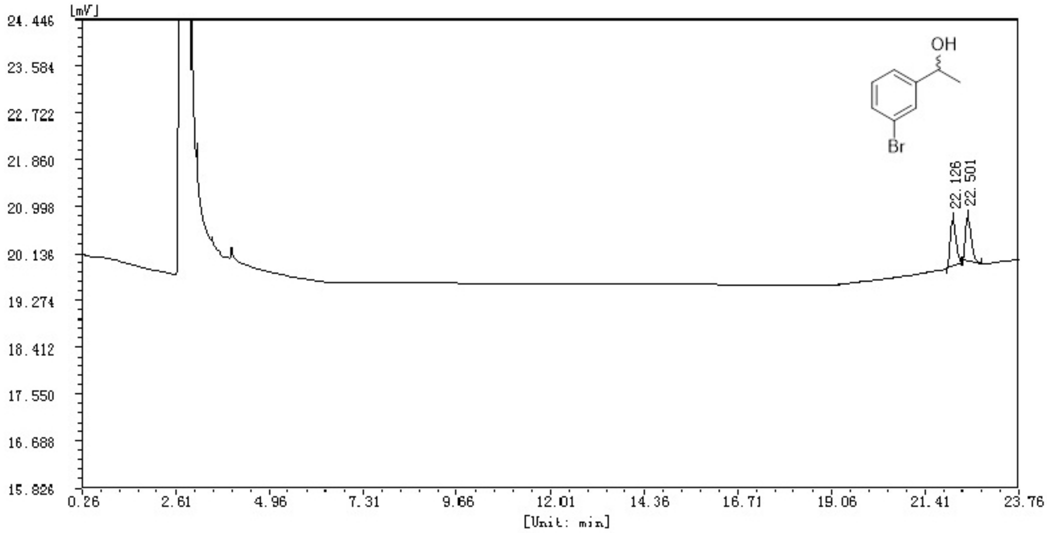
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	19.274	11944.1	131165.1	49.7149
2	19.735	11696.9	132669.4	50.2851



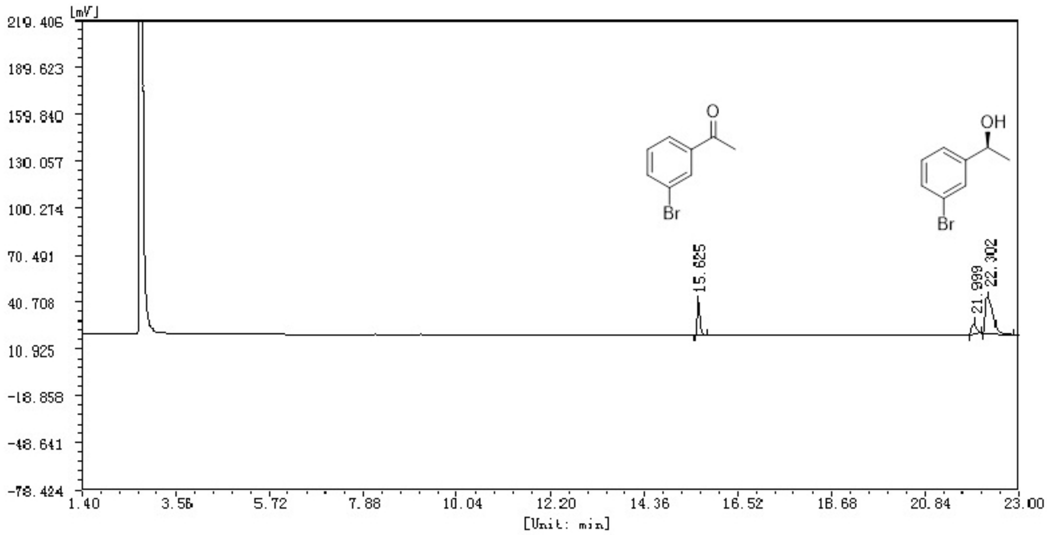
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	13.250	23699.3	103145.1	30.1285
2	19.682	4529.2	51195.3	14.9540
3	20.104	14849.2	188010.6	54.9175

(*S*)-1-(3-bromophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



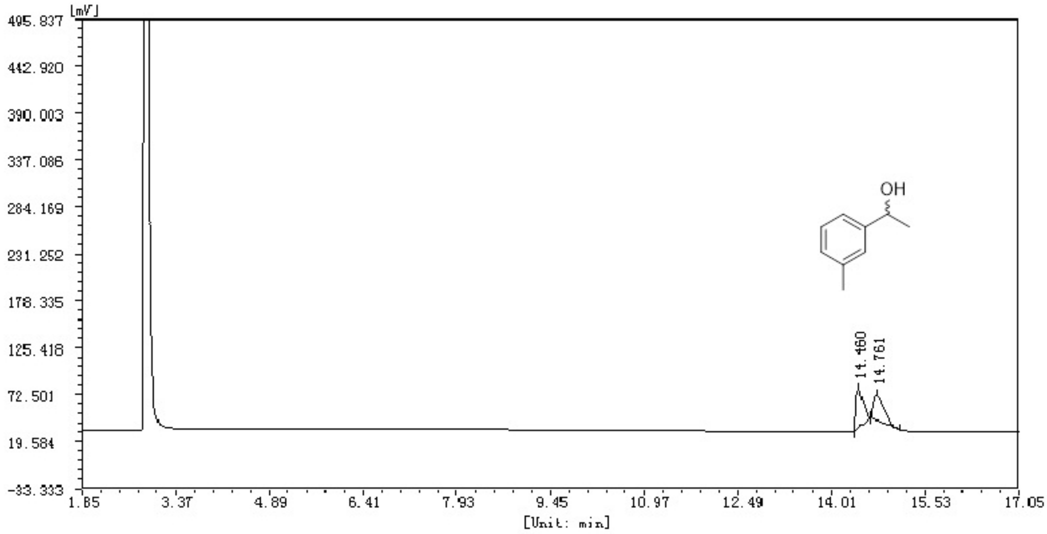
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	22.126	873.7	8730.9	50.6353
2	22.501	822.9	8511.8	49.3647



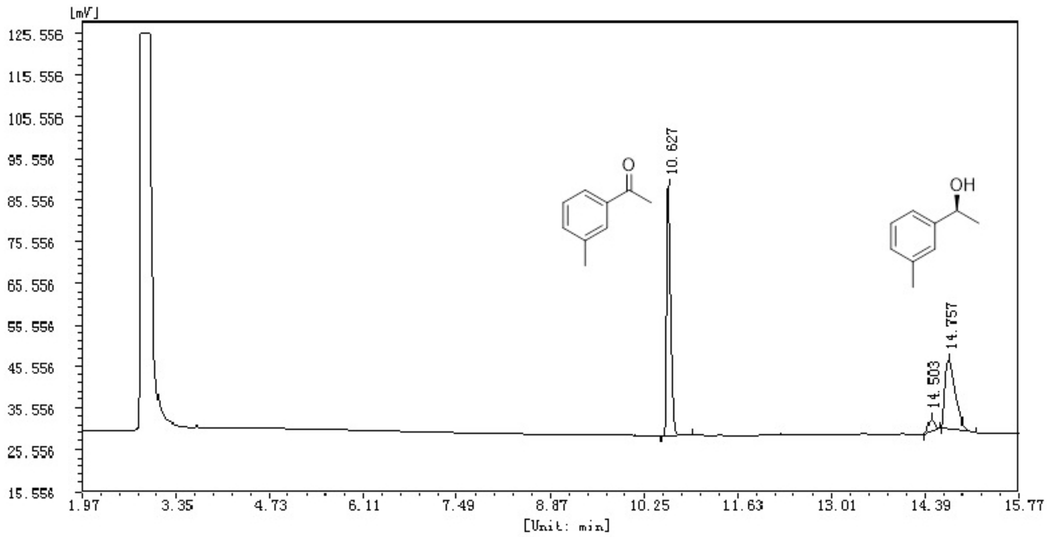
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	15.625	211798.4	98398.5	21.9046
2	21.999	6828.7	56082.7	12.4847
3	22.302	24173.8	294732.2	65.6107

(*S*)-1-(*m*-tolyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



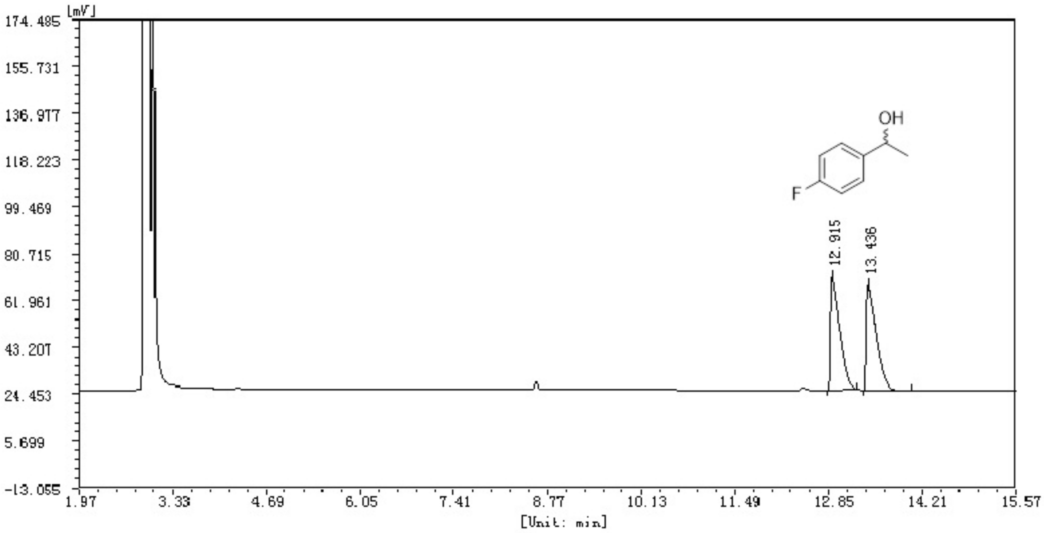
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	14.460	43773.8	362157.1	49.5535
2	14.761	29373.6	368683.2	50.4465



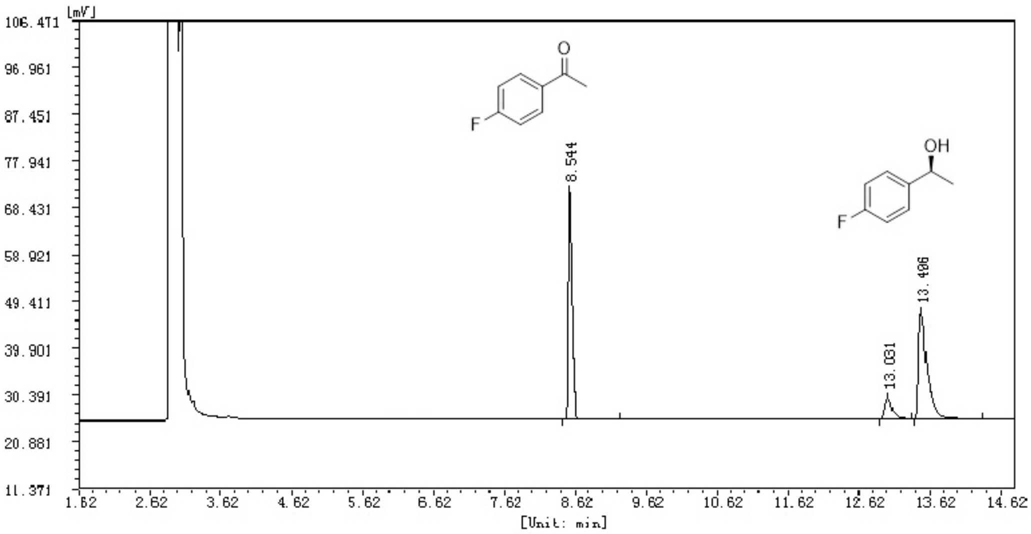
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	10.627	60234.6	248773.4	55.0261
2	14.503	2843.8	21349.8	4.7224
3	14.757	16661.3	181977.3	40.2515

(*S*)-1-(4-fluorophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



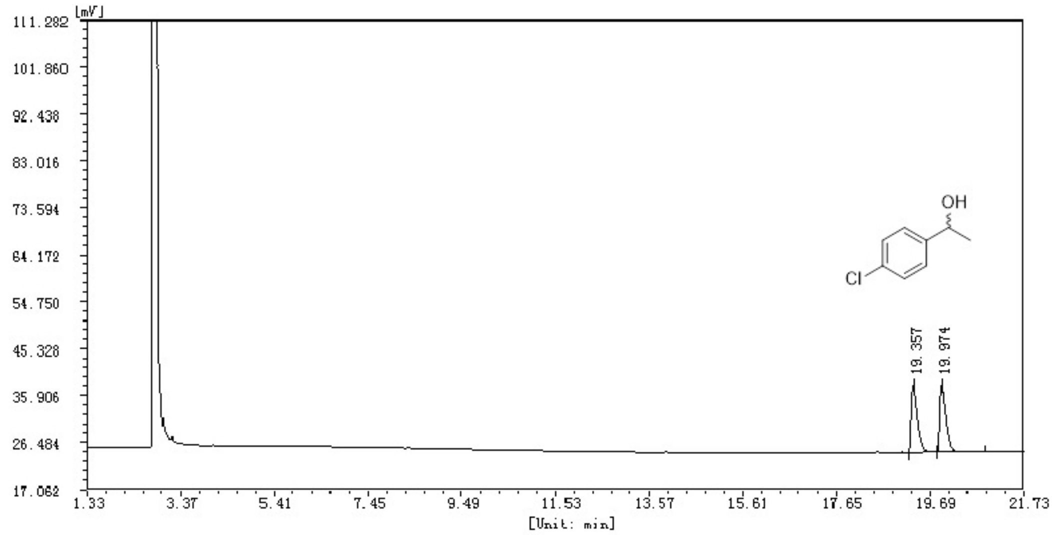
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	12.915	45511.0	419202.5	49.3996
2	13.436	42269.5	429391.6	50.6004



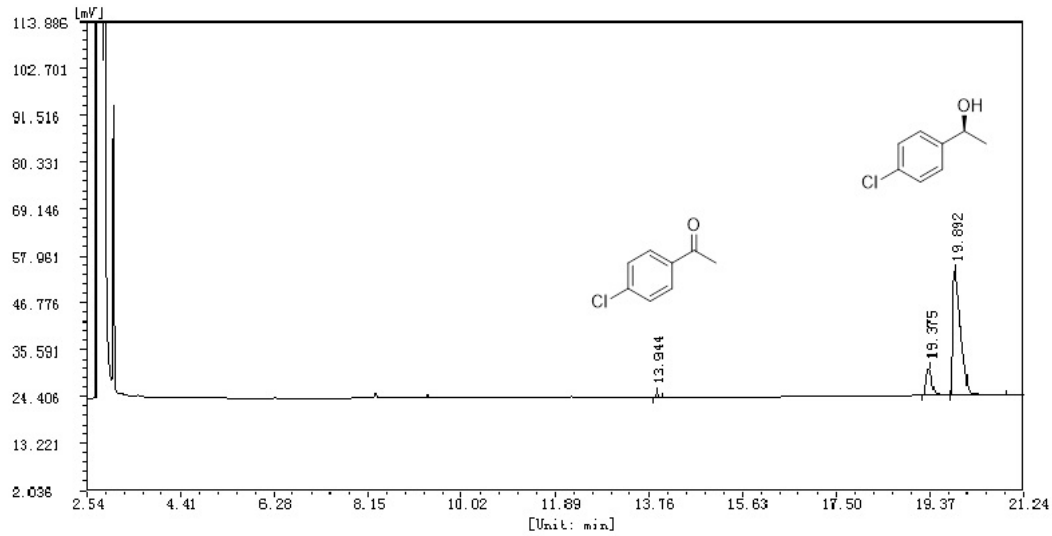
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	8.544	46294.6	178386.2	44.7943
2	13.031	4071.2	32616.7	8.1903
3	13.496	21451.8	187231.6	47.0154

(*S*)-1-(4-chlorophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



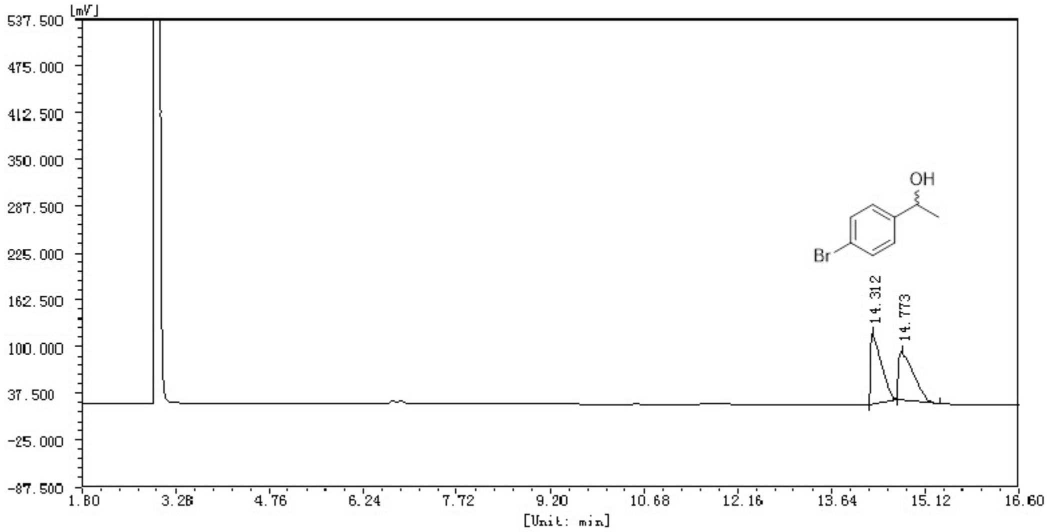
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	19.357	13664.5	128059.3	49.9581
2	19.974	13439.3	128274.0	50.0419



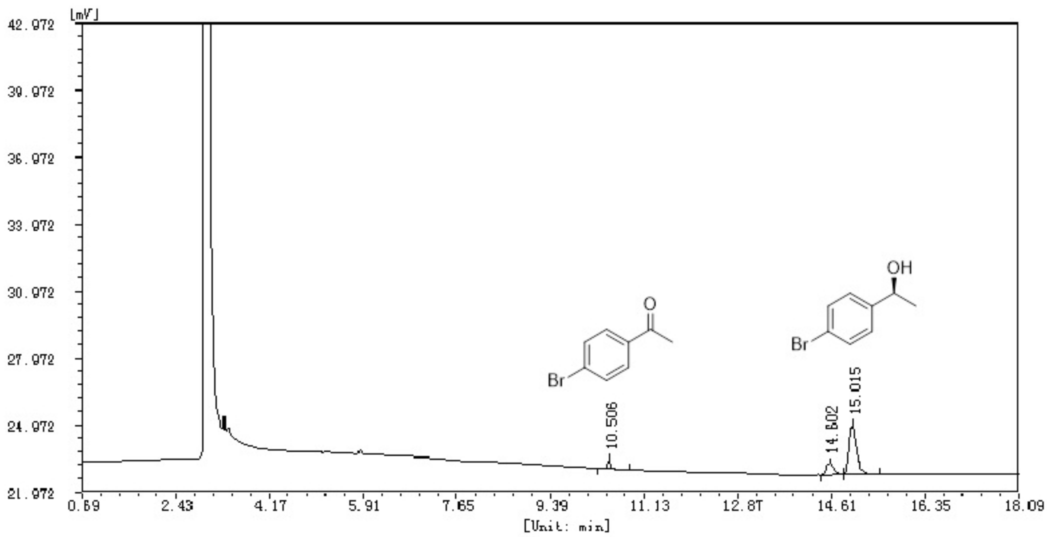
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	13.944	1021.7	4183.2	1.0833
2	19.375	6593.4	58698.1	15.2007
3	19.892	29865.0	323272.7	83.7160

(S)-1-(4-bromophenyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



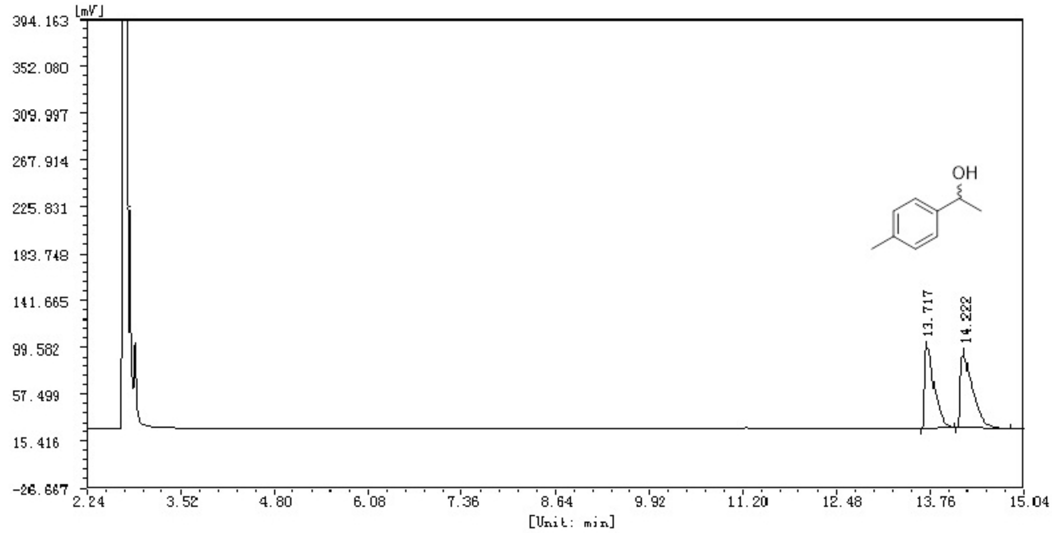
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	14.312	94564.4	1099236.5	50.3354
2	4.773	64299.8	1084588.2	49.6646



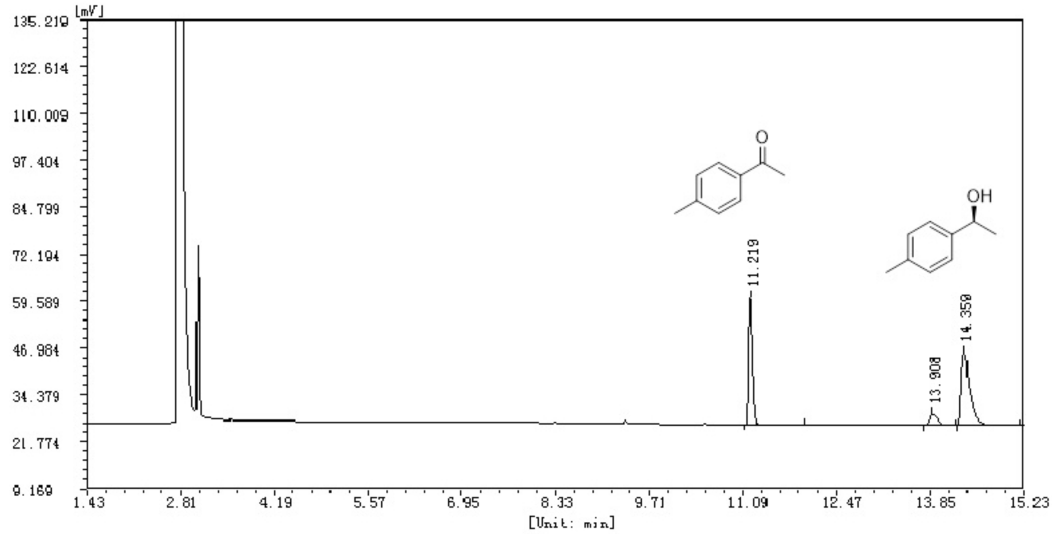
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	10.506	421.5	1729.6	5.9349
2	14.602	492.3	4821.1	16.5433
3	15.015	2232.3	22592.2	77.5218

(S)-1-(p-tolyl)ethan-1-ol

Column	CP-Chirasil-Dex CB column 25m × 0.25 mm × 0.25um
Injector Temp °C	240
Detector Temp °C	260
Injection volume	0.8 uL
Column Temp	120 °C, withdraw time 2 min, then 5 °C /min to 180 °C keeping for 30 min



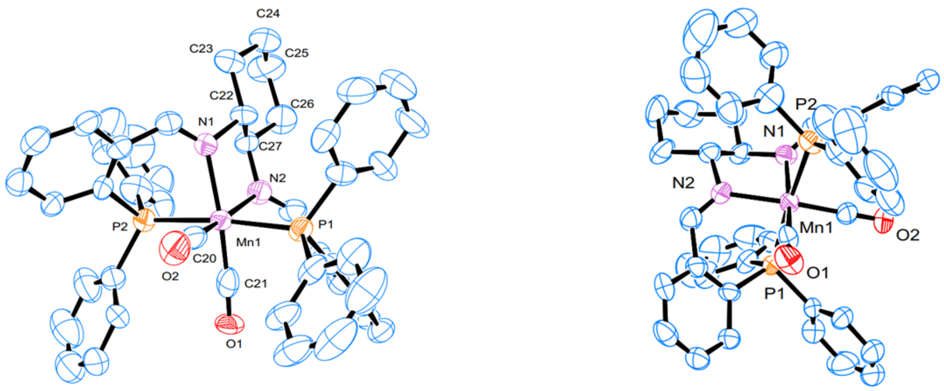
Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	13.717	73670.9	760402.9	49.2768
2	14.222	66368.9	782723.7	50.7232



Entry	Time (min)	Height (AU)	Peak area (AU *S)	Content (%)
1	11.219	34443.0	133145.5	38.1464
2	13.908	3359.4	29904.2	8.5676
3	14.359	19860.6	185988.8	53.2860

7. X-ray structure determination

The single crystal X-ray diffraction studies of **Mn1** were carried out on a Rigaku Sealed Tube CCD (Saturn 724⁺) diffractometer using graphite-mono-chromated Cu-Kα radiation (λ = 1.54178) at 170.00 K. The cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. Structure solution was performed using SHELXT (2015) and structure refinement performed using SHELXL.[5] Crystal data and processing parameters for **Mn1** are summarized in Tables S4.



Mn1 **Mn1**

Chart S1 ORTEP representations of **Mn1**. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms have been omitted for clarity.

Table S4 Crystal data and structure refinement for **Mn1**

Identification code	**Mn1**
CCDC No.	**2408177**
Empirical formula	$C_{46}H_{40}MnN_2O_2P_2$
Formula weight	769.68
Temperature/K	169.99(10)
Crystal system	trigonal
Space group	$P3_121$
a/Å	17.5937(3)
b/Å	17.5937(3)
c/Å	29.4019(7)
α/°	90
β/°	90
γ/°	120

Volume/Å^3	7881.7(3)
Z	6
ρ_{calc}g/cm^3	0.973
μ/mm^{-1}	2.853
F(000)	2406.0
Crystal size/mm^3	0.15 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	5.8 to 155.754
Index ranges	-21 ≤ h ≤ 22, -21 ≤ k ≤ 19, -36 ≤ l ≤ 35
Reflections collected	34069
Independent reflections	10455 [R_{int} = 0.0627, R_{sigma} = 0.0589]
Data/restraints/parameters	10455/108/443
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0674, wR_2 = 0.1839
Final R indexes [all data]	R_1 = 0.0796, wR_2 = 0.1940
Largest diff. peak/hole / e Å^{-3}	0.65/-0.40
Flack parameter	0.102(9)

Table S5 Selected bond distances and bond angles for **Mn-1**

Selected bond distances (Å)		Selected bond angles (°)	
Mn1-P2	2.269(2)	P2-Mn1-P1	174.28(8)
Mn1-N1	2.081(6)	N1-Mn1-P1	103.62(16)
Mn1-N2	2.078(6)	N1-Mn1-P2	81.88(16)
Mn1-C20	1.795(7)	N2-Mn1-P1	81.37(17)
Mn1-C21	1.767(9)	N2-Mn1-P2	101.43(17)
P1-C34	1.820(7)	N2-Mn1-N1	79.0(2)
P1-C41	1.834(4)	C20-Mn1-P1	90.4(3)
P1-C35	1.826(8)	C20-Mn1-P2	87.6(3)
P2-C13	1.831(8)	C21-Mn1-P1	84.2(3)
P2-C7	1.839(4)	C21-Mn1-N1	170.2(3)
P2-C1	1.822(5)	C21-Mn1-C20	91.2(3)

8. DFT studies

Computational methods

All density functional theory (DFT) calculations were performed to understand the mechanism of the enantioselectivity of ketone hydrogenation catalyzed by manganese (Mn) catalysts. B3LYP-D3[6] method combined with a mixed basis sets of SDD (and its ECP)[7] for Mn, K and 6-31G(d)[8] for the other atoms (denoted as BS1) were used to fully optimize all structures in the gas-phase. Then, vibrational frequency calculations on these optimized geometries were carried out at the same level of theory to confirm no imaginary frequency for all local minimum, and one appropriate imaginary frequency for each transition state. The single-point energy calculations are also performed using the SDD/6-311+G(d,p) mixed basis set (denoted as BS2) in PCM solvent model[9] using ethanol solvent to obtain more accurate electronic energies. To examine the effect of DFT functional, a few other common and reliable M06-L, PBE0-D3, and B97X-D methods[10] were also used for the single-point energy calculations on the key intermediates and transition states in dichloromethane solution. In addition, (relative) distortion/interaction energy analysis, non-covalent interactions (NCIs) plot analysis (isovalue=0.50) on the key structures were performed[11]. All DFT calculations were carried out by Gaussian16 program[12]. All 3D images of the optimized structures were shown by CYLview[13]. All free energies are corrected with Grimme's quasi-harmonic approximation for vibrational entropy correction at all frequencies below than 100 cm^{-1} by GoodVibes using default settings[14]. The steric maps were generated by SambVca 2.0 program[15]. The distance of the coordination point from the center of the sphere is defined as 2.3 Angstrom, and the value of mesh spacing for numbering integration is defined as 0.050. Other default parameters are used.

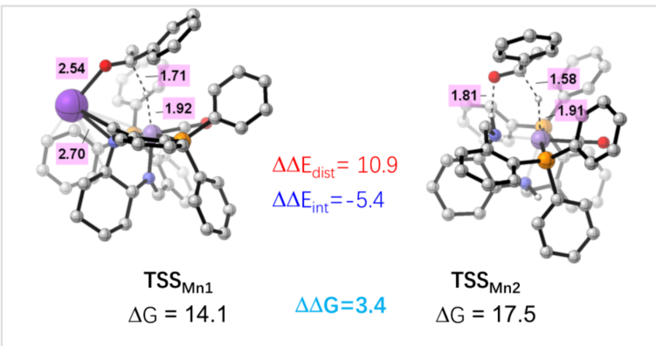
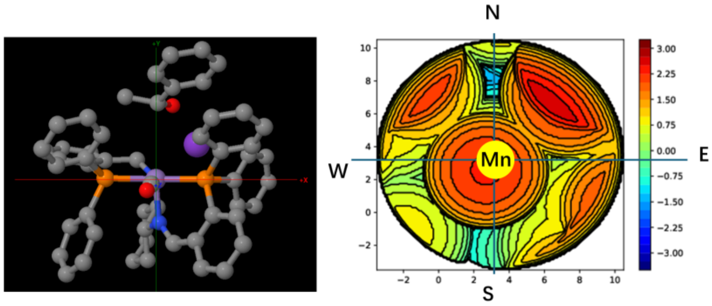


Figure S24 Relative corrected free energies (in kcal/mol) for **TSS_{Mn1}** and **TSS_{Mn2}** calculated by PCM B3LYP-D3/BS2//B3LYP-D3/BS1 in ethanol solution.

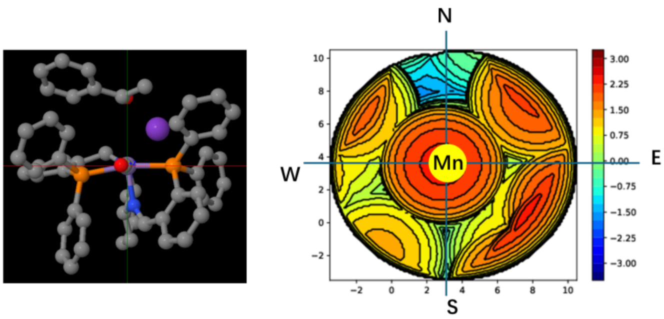


%V_Free	%V_Bur	% Tot/Ex
23.3	76.7	100.0

TSR$_{Mn1}$

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	13.1	31.8	44.9	29.2	70.8
NW	11.3	33.6	44.9	25.1	74.9
NE	6.7	38.2	44.9	15.0	85.0
SE	10.8	34.1	44.9	24.1	75.9

Figure S25 Steric map of Mn-ligand part and substrate for **TSR$_{Mn1}$** with the computed buried volumes (in %).



%V_Free	%V_Bur	% Tot/Ex
24.7	75.3	100.0

TSS$_{Mn1}$

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	11.7	33.2	44.9	26.1	73.9
NW	13.8	31.0	44.9	30.8	69.2
NE	10.1	34.8	44.9	22.5	77.5
SE	8.7	36.2	44.9	19.3	80.7

Figure S26 Steric map of Mn-ligand part and substrate for **TSS$_{Mn1}$** with the computed buried volumes (in %).

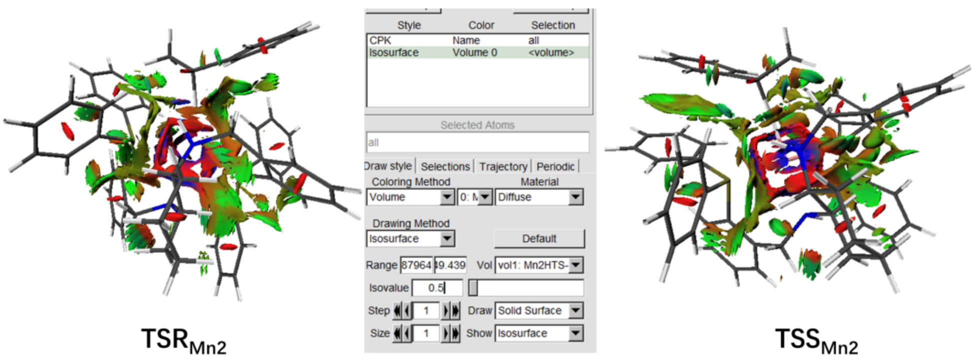


Figure S27 The noncovalent interaction (NCI) plots for **TSR$_{Mn2}$** and **TSS$_{Mn2}$** (red: strong repulsion; green: weak attraction; blue: strong attraction).

Table S6 The relative corrected free energies (in kcal/mol) of transition states in ethanol solution evaluated by the other PCM DFTs/BS2 methods based on the B3LYP-D3/BS1-optimized structures in gas-phase.

	ΔG_{soln} (B3LYP-D3)	ΔG_{soln} (M06-L)	ΔG_{soln} (PBE0-D3)	ΔG_{soln} (ωB97X-D)
Mn1H	0.0	0.0	0.0	0.0
TSR_{Mn1}	15.5	25.6	18.7	21.6
TSS_{Mn1}	14.1	24.8	18.0	20.4
$\Delta\Delta G$	1.4	0.8	0.8	1.3
Mn2H	0.0	0.0	0.0	0.0
TSR_{Mn2}	18.2	25.7	19.1	18.5
TSS_{Mn2}	17.5	25.0	18.6	18.4
$\Delta\Delta G$	0.7	0.6	0.5	0.1

Table S7 The absolute electronic and corrected free energies (in Hartree) of the optimized structures of intermediates and transition states for reaction catalyzed by the Mn catalyst by the B3LYP-D3 method in gas-phase. The free energies (G-qh) are corrected with the quasi-harmonic entropy correction.

	E_{gas}	G_{gas}-qh
Sub	-384.90722	-384.80067
Mn1H	-2740.32620	-2739.63865
TSR_{Mn1}	-3125.24547	-3124.42356
TSS_{Mn1}	-3125.24414	-3124.42118
Mn2H	-2713.80407	-2713.07353
TSR_{Mn2}	-3098.71225	-3097.84949
TSS_{Mn2}	-3098.71312	-3097.85047

Table S8 The absolute electronic energies (in Hartree) for Mn complexes and transition states evaluated by the other PCM (ethanol) DFTs/BS2 methods based on the B3LYP-D3/BS1-optimized structures in gas-phase.

	E_{soln} (B3LYP-D3)	E_{soln} (M06-L)	E_{soln} (PBE0-D3)	E_{soln} (ωB97X-D)
Sub	-385.02010	-384.94953	-384.55286	-384.86927
Mn1H	-2740.93513	-2740.57474	-2738.23350	-2740.11136
TSR_{Mn1}	-3125.95831	-3125.51123	-3122.78429	-3124.97398
TSS_{Mn1}	-3125.96161	-3125.51353	-3122.78654	-3124.97704
Mn2H	-2714.40040	-2714.01585	-2711.70536	-2713.57707
TSR_{Mn2}	-3099.41711	-3098.95014	-3096.25345	-3098.44245
TSS_{Mn2}	-3099.41818	-3098.95106	-3096.25410	-3098.44254

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10 Cartesian coordinates XYZs.

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H	3.639788	-0.983927	-4.569284
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TSS_{Mn1}.xyz

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C	-2.368510	-1.464987	-2.344326
C	3.036803	-1.121951	0.865811
C	1.139254	-0.517637	2.566424
H	1.031771	-0.783028	3.640330
C	-1.534729	-2.281434	-1.459508
H	-1.619024	-3.354154	-1.628471
C	-3.134499	2.278669	-0.621764
C	-2.316516	3.180114	-1.322123
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C	-2.776800	4.453500	-1.656241
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C	-4.062831	4.856732	-1.292485
H	-4.418701	5.851631	-1.546913
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H	-5.903984	4.260402	-0.337265
C	-4.438213	2.685434	-0.288823
H	-5.116488	1.998430	0.205667
C	-3.852023	0.381961	-2.818145
H	-4.319546	1.318238	-2.538046
C	2.493955	-1.133895	2.168905
C	-3.567910	-1.367844	-4.463671
H	-3.792252	-1.798964	-5.435411
C	-3.701686	-0.129115	0.881022
C	-0.332194	-2.788188	0.532233
H	0.754781	-2.839836	0.458470
C	-2.700262	-2.018350	-3.592142
H	-2.251996	-2.968210	-3.875425
C	4.363726	-1.540354	0.664639
H	4.786691	-1.508493	-0.333657
C	-0.254744	-2.961133	3.063031
H	0.836453	-3.066439	3.106175
H	-0.559676	-2.473465	4.001179
C	3.306298	-1.609351	3.212424
H	2.895516	-1.628302	4.220505
C	-4.172686	-1.446757	0.760119
H	-3.949252	-2.016728	-0.135575
C	4.615126	-2.036784	3.002991
H	5.211051	-2.395525	3.838814
C	5.155216	-1.993591	1.716965
H	6.178567	-2.310105	1.533127
C	-0.888244	-4.214757	0.447192

H	-0.551928	-4.706324	-0.474816
H	-1.987409	-4.181673	0.421849
C	-0.122730	0.763948	-1.749763
C	-4.033747	0.577677	2.053772
H	-3.736512	1.621749	2.146562
C	4.115258	0.014469	-2.393313
H	4.275392	-1.056048	-2.478966
C	4.904897	0.882846	-3.146278
H	5.688761	0.482086	-3.784284
C	4.676747	2.260301	-3.093243
H	5.286267	2.937053	-3.687056
C	3.654776	2.760579	-2.286576
H	3.463459	3.827767	-2.240507
C	2.869626	1.892357	-1.527407
H	2.069398	2.277331	-0.908423
C	3.096181	0.512166	-1.563105
C	-0.875943	-4.360034	2.968938
H	-1.973435	-4.282765	2.995479
H	-0.578470	-4.967345	3.833662
C	-0.449341	-5.042069	1.663463
H	-0.871500	-6.052667	1.595494
H	0.644640	-5.155111	1.654539
C	-4.796258	-0.009558	3.067809
H	-5.071718	0.572213	3.945762
C	-4.922236	-2.041704	1.776789
H	-5.271353	-3.064034	1.656364
C	-5.231867	-1.331645	2.939157
H	-5.824296	-1.793074	3.724335
C	1.698441	-4.325451	-3.362714
H	1.577352	-5.187382	-4.013961
C	2.292077	-4.469015	-2.108639
H	2.641200	-5.443743	-1.776609
C	2.447840	-3.359456	-1.271245
H	2.913529	-3.492959	-0.299916
C	2.002991	-2.090440	-1.667569
C	1.416355	-1.956833	-2.939733
H	1.065575	-0.986292	-3.274290
C	1.268940	-3.061023	-3.777525
H	0.811547	-2.931834	-4.755400
H	0.395954	1.742637	0.685440
K	-1.344988	0.886853	3.618539
C	4.763951	3.998409	0.867546
C	3.733808	4.820421	0.413216
C	2.400841	4.491304	0.676274
C	2.076243	3.347537	1.419584
C	3.125336	2.548882	1.899499
C	4.451640	2.855881	1.610467
H	5.799102	4.241362	0.642902
H	3.962724	5.717331	-0.157539
H	1.617145	5.140863	0.300737
H	2.893687	1.673906	2.492439
H	5.242961	2.201348	1.966643
C	0.645360	3.012452	1.797593
O	0.456494	2.559379	2.967177
C	-0.440307	3.909719	1.214393
H	-0.412604	4.876885	1.737909
H	-0.326317	4.082915	0.144770
H	-1.419192	3.456082	1.377503
H	1.300275	0.562912	2.565408

Mn2H.xyz

Mn	0.149329	0.387090	-0.185672
P	2.388615	0.272542	-0.155123
P	-2.043133	0.797676	-0.217713
N	-0.112520	-1.425369	-1.415320
N	-0.015244	-1.163942	1.387080
O	0.409100	2.840121	1.398503
C	3.991368	1.346186	3.522939
H	4.693004	2.086939	3.897227
C	2.893792	0.273313	1.629259
C	-0.207837	-2.661810	-0.575810
H	0.829522	-2.982566	-0.417012
C	2.171603	-0.549242	2.528397
C	-3.103739	-0.164481	-1.400943
C	-1.041402	-1.249669	-2.560103
H	-0.918793	-2.072906	-3.276725
C	1.225601	-1.636133	2.062539
H	1.740529	-2.285734	1.350445
C	3.402689	1.624300	-0.902489
C	2.786306	2.842353	-1.221219
H	1.722082	2.954042	-1.048877
C	3.534588	3.888241	-1.765183
H	3.045804	4.828379	-2.007346
C	4.901136	3.727815	-2.002472
H	5.480603	4.542221	-2.430045
C	5.522548	2.515097	-1.692083
H	6.585504	2.382283	-1.877364
C	4.777750	1.470057	-1.144432

H	5.267093	0.529547	-0.905782
C	3.792818	1.213885	2.146236
H	4.334862	1.865153	1.469534
C	-2.531486	-1.085828	-2.304316
C	3.283522	0.536635	4.406537
H	3.422851	0.635518	5.479670
C	3.235243	-1.213138	-0.879028
C	-0.804652	-2.285848	0.791134
H	-1.793676	-1.871681	0.593164
C	2.385355	-0.407071	3.902418
H	1.835479	-1.045357	4.591220
C	-4.498650	0.008528	-1.399294
H	-4.938123	0.733440	-0.721250
C	-0.962945	-3.832930	-1.228951
H	-1.964855	-3.500781	-1.521492
H	-0.442844	-4.133117	-2.147147
C	-3.388001	-1.822210	-3.141245
H	-2.953231	-2.538251	-3.835209
C	3.885146	-2.202873	-0.126978
H	4.041173	-2.052662	0.937975
C	-4.769867	-1.653523	-3.115807
H	-5.400740	-2.240000	-3.778456
C	-5.331889	-0.722345	-2.241933
H	-6.406897	-0.565135	-2.216852
C	-0.999388	-3.501815	1.712498
H	-1.492284	-3.169768	2.635699
H	-0.029545	-3.927792	1.997882
C	0.317680	1.841331	0.772558
C	3.087344	-1.413995	-2.265577
H	2.626553	-0.633052	-2.869083
C	-3.738994	3.097004	0.073633
H	-4.317389	2.519981	0.789248
C	-4.121981	4.407434	-0.218048
H	-5.001277	4.831117	0.260847
C	-3.374429	5.172778	-1.115440
H	-3.671200	6.194292	-1.339622
C	-2.237286	4.624018	-1.712753
H	-1.642922	5.219040	-2.401713
C	-1.849930	3.316369	-1.418370
H	-0.950891	2.885198	-1.849746
C	-2.602796	2.536166	-0.528411
C	-1.112560	-5.028782	-0.278517
H	-0.121967	-5.440872	-0.035498
H	-1.673727	-5.828156	-0.777622
C	-1.813560	-4.599117	1.016612
H	-1.943336	-5.455207	1.689743
H	-2.819948	-4.222989	0.781350
C	3.549508	-2.581770	-2.873557
H	3.429384	-2.716656	-3.945596
C	4.347149	-3.373236	-0.736064
H	4.850960	-4.128083	-0.137358
C	4.172455	-3.571425	-2.107076
H	4.529736	-4.483250	-2.577916
C	-3.662161	-0.255129	4.046108
H	-3.965701	-0.520994	5.055227
C	-4.109702	-1.001316	2.956010
H	-4.768534	-1.852604	3.109479
C	-3.719160	-0.657964	1.657500
H	-4.084727	-1.251608	0.825573
C	-2.865504	0.431883	1.421616
C	-2.421789	1.176928	2.533791
H	-1.750649	2.017477	2.386034
C	-2.820551	0.840380	3.827348
H	-2.467086	1.434010	4.666531
H	0.251737	1.178047	-1.586746
H	0.803238	-1.455705	-1.855640
H	-0.681430	-0.334314	-3.041023
H	0.976298	-2.258081	2.931162
H	-0.598580	-0.709974	2.090895

TSR_{Mn2}.xyz

Mn	-0.113797	0.062629	0.161088
P	1.929630	-1.012408	0.381011
P	-2.100763	1.177413	0.178008
N	-0.667852	-0.951519	-1.733551
N	-1.118820	-1.766331	0.934628
O	0.476191	1.341106	2.732829
C	2.829419	-1.974803	4.330131
H	3.642914	-1.782947	5.024642
C	1.917308	-1.785935	2.076319
C	-1.167465	-2.334498	-1.453706
H	-0.274788	-2.939983	-1.265178
C	0.756315	-2.464036	2.509082
C	-3.137973	1.173963	-1.362871
C	-1.403336	-0.193555	-2.772551
H	-1.491632	-0.801257	-3.679256
C	-0.333550	-2.873130	1.551291
H	0.110229	-3.444753	0.731954

C	3.534305	-0.109936	0.457506
C	3.564725	1.144023	1.085716
H	2.638776	1.622628	1.379365
C	4.781881	1.767611	1.350907
H	4.789726	2.739984	1.833243
C	5.981593	1.162031	0.971724
H	6.928607	1.656221	1.172688
C	5.958879	-0.071187	0.319604
H	6.887614	-0.545049	0.011955
C	4.741891	-0.708313	0.070137
H	4.736731	-1.679931	-0.412886
C	2.945504	-1.560655	3.001091
H	3.845749	-1.044225	2.691404
C	-2.768526	0.407458	-2.493803
C	1.673139	-2.619435	4.759899
H	1.566183	-2.933407	5.794655
C	2.329990	-2.400267	-0.772304
C	-1.999960	-2.276821	-0.164449
H	-2.757232	-1.506807	-0.319974
C	0.650245	-2.867865	3.843294
H	-0.247421	-3.390682	4.166954
C	-4.365467	1.860008	-1.379570
H	-4.645672	2.464010	-0.524850
C	-1.936540	-2.992543	-2.614666
H	-2.748982	-2.333507	-2.941335
H	-1.259473	-3.119957	-3.468434
C	-3.681647	0.322998	-3.561330
H	-3.410345	-0.271340	-4.430796
C	2.472336	-3.736715	-0.372353
H	2.451869	-3.989362	0.684467
C	-4.901607	0.992456	-3.554266
H	-5.575268	0.902363	-4.402272
C	-5.242330	1.783647	-2.457791
H	-6.181671	2.329357	-2.436268
C	-2.747499	-3.581701	0.168001
H	-3.407576	-3.397969	1.026208
H	-2.043542	-4.366599	0.464984
C	0.254465	0.821826	1.696653
C	2.403183	-2.083561	-2.142419
H	2.312619	-1.045304	-2.465987
C	-3.205520	3.571886	1.331255
H	-4.136666	3.028434	1.460878
C	-3.123139	4.893128	1.771762
H	-3.998389	5.372427	2.202689
C	-1.917167	5.592095	1.674530
H	-1.853421	6.619755	2.022571
C	-0.789942	4.954725	1.153965
H	0.161585	5.478203	1.104406
C	-0.875342	3.634113	0.712829
H	0.001179	3.114281	0.346859
C	-2.087158	2.934309	0.769414
C	-2.572351	-4.328592	-2.213567
H	-1.794739	-5.051086	-1.925254
H	-3.100344	-4.757249	-3.074005
C	-3.531914	-4.111085	-1.037210
H	-4.042425	-5.043888	-0.768618
H	-4.311608	-3.392484	-1.329302
C	2.585487	-3.094966	-3.086974
H	2.638656	-2.837472	-4.141774
C	2.648270	-4.745748	-1.323399
H	2.753650	-5.778289	-0.999800
C	2.697699	-4.428712	-2.682519
H	2.831803	-5.214676	-3.421168
C	-4.803434	-0.882830	3.399006
H	-5.381874	-1.399914	4.159901
C	-5.203246	-0.922231	2.063170
H	-6.098680	-1.467862	1.776296
C	-4.458140	-0.258231	1.083042
H	-4.789876	-0.300474	0.050656
C	-3.296362	0.452909	1.419999
C	-2.907035	0.489922	2.774212
H	-2.008534	1.026862	3.062282
C	-3.654050	-0.168355	3.751136
H	-3.334077	-0.123764	4.788842
H	0.647234	1.327619	-0.802392
H	0.264942	-1.019300	-2.139547
C	4.975399	3.833178	-1.192654
C	4.956515	2.667344	-1.960662
C	3.751812	2.013477	-2.213038
C	2.543931	2.504433	-1.701305
C	2.578763	3.663202	-0.912066
C	3.781282	4.323354	-0.660458
H	5.912958	4.349080	-1.000996
H	5.882448	2.267381	-2.365609
H	3.717747	1.123507	-2.831499
H	1.664161	4.067004	-0.493097
H	3.784124	5.224183	-0.051167
C	1.250914	1.845407	-2.180157

O 1.358951 0.841023 -2.947565
C 0.161660 2.884201 -2.522641
H 0.443137 3.319893 -3.490066
H -0.820577 2.425537 -2.626623
H 0.073731 3.693972 -1.799554
H -0.708130 0.596552 -3.046080
H -1.004347 -3.556969 2.082933
H -1.720855 -1.393616 1.669126

TSS_{Mn2}.xyz

Mn 0.132992 0.060446 0.236560
P 2.474895 0.284691 0.251911
P -2.088155 -0.431373 0.704577
N -0.220964 -0.223045 -1.857586
N 0.467911 -2.165682 0.068774
O 0.248442 0.663943 3.106354
C 3.981512 -1.422972 3.736600
H 4.546434 -1.090940 4.603533
C 3.017945 -0.925277 1.555145
C 0.249059 -1.557309 -2.311216
H 1.342757 -1.494975 -2.328028
C 2.538081 -2.250504 1.485061
C -3.253544 -0.756485 -0.692989
C -1.549860 0.240489 -2.347808
H -1.509286 0.378208 -3.433641
C 1.820487 -2.756967 0.262327
H 2.408115 -2.537948 -0.632720
C 3.320766 1.820727 0.847111
C 2.715871 2.598398 1.848387
H 1.751243 2.315934 2.249520
C 3.348204 3.741929 2.335563
H 2.864410 4.331110 3.110266
C 4.586770 4.136073 1.824080
H 5.072222 5.034280 2.196615
C 5.197331 3.367634 0.832132
H 6.162326 3.662732 0.428243
C 4.573580 2.213603 0.353097
H 5.062887 1.626167 -0.416545
C 3.746766 -0.533350 2.684867
H 4.127093 0.478525 2.758421
C -2.819466 -0.518347 -2.012686
C 3.488160 -2.723397 3.673926
H 3.657693 -3.418875 4.491440
C 3.501543 -0.156248 -1.226601
C -0.148206 -2.585136 -1.238268
H -1.226812 -2.493424 -1.098703
C 2.776997 -3.130617 2.543382
H 2.400763 -4.149499 2.479043
C -4.542411 -1.265499 -0.469920
H -4.879870 -1.430780 0.548426
C -0.218077 -1.954855 -3.723067
H -1.307611 -1.871710 -3.788460
H 0.203338 -1.247819 -4.448333
C -3.689894 -0.834014 -3.067656
H -3.368370 -0.642060 -4.088609
C 4.521062 -1.120357 -1.204662
H 4.778590 -1.613851 -0.271329
C -4.959894 -1.360102 -2.837887
H -5.609882 -1.592862 -3.677173
C -5.395671 -1.568803 -1.528736
H -6.389806 -1.961263 -1.332768
C 0.131093 -4.041504 -1.649188
H -0.277089 -4.714680 -0.883342
H 1.209792 -4.227031 -1.698254
C 0.242076 0.400048 1.955853
C 3.194569 0.487965 -2.439048
H 2.410788 1.244828 -2.480645
C -4.064516 0.293702 2.657065
H -4.322423 -0.758487 2.735216
C -4.745213 1.228592 3.436767
H -5.540500 0.900500 4.101226
C -4.402373 2.582214 3.368165
H -4.933740 3.308409 3.977952
C -3.371721 2.996353 2.523183
H -3.096489 4.045227 2.465971
C -2.684822 2.061338 1.748787
H -1.869162 2.365767 1.102128
C -3.031729 0.706792 1.801410
C 0.153319 -3.400312 -4.073990
H 1.246790 -3.518147 -4.091412
H -0.208241 -3.642993 -5.080594
C -0.446068 -4.357518 -3.035024
H -0.232781 -5.401377 -3.295541
H -1.540425 -4.247706 -3.025100
C 3.888761 0.155649 -3.603961
H 3.641680 0.661534 -4.533826
C 5.203946 -1.456582 -2.376122
H 5.986821 -2.210321 -2.345744

C	4.887499	-0.821646	-3.579079
H	5.419012	-1.084140	-4.490196
C	-1.918191	-4.462047	3.075663
H	-1.809577	-5.396083	3.620385
C	-2.447902	-4.457435	1.785377
H	-2.761445	-5.387904	1.318832
C	-2.584660	-3.255858	1.082926
H	-3.005031	-3.279145	0.083264
C	-2.187195	-2.035049	1.655074
C	-1.663891	-2.055020	2.962950
H	-1.340596	-1.131862	3.430421
C	-1.533392	-3.253664	3.663478
H	-1.123078	-3.240800	4.669559
H	0.029833	1.882619	-0.330985
H	0.384108	0.517723	-2.244563
C	-3.534099	5.045726	-1.419128
C	-2.688168	5.101211	-0.307970
C	-1.479650	4.405409	-0.309684
C	-1.091089	3.642753	-1.420479
C	-1.932579	3.619388	-2.540174
C	-3.149222	4.303730	-2.537340
H	-4.478576	5.583676	-1.415011
H	-2.972311	5.688625	0.561650
H	-0.838894	4.445284	0.566619
H	-1.601197	3.065990	-3.412666
H	-3.791542	4.267552	-3.414112
C	0.258827	2.928032	-1.499913
O	0.522962	2.290810	-2.576215
C	1.398598	3.765604	-0.918086
H	1.454982	4.684319	-1.517161
H	1.266637	4.040515	0.128616
H	2.341177	3.232477	-1.023822
H	1.749055	-3.847927	0.335375
H	-0.109231	-2.550257	0.815306
H	-1.656240	1.236120	-1.925675

Sub.xyz

C	-2.592421	0.111540	-0.000040
C	-1.965675	-1.138809	0.000138
C	-0.576864	-1.220551	0.000042
C	0.205835	-0.054793	-0.000293
C	-0.431453	1.195403	0.000013
C	-1.823996	1.277261	-0.000058
H	-3.677310	0.176482	-0.000038
H	-2.562792	-2.046670	0.000369
H	-0.068454	-2.179283	0.000230
H	0.153129	2.110187	0.000226
H	-2.308636	2.249762	0.000019
C	1.697856	-0.204250	-0.000063
O	2.215625	-1.310996	-0.000078
C	2.557775	1.049636	0.000105
H	2.352038	1.666220	-0.883067
H	2.352725	1.665443	0.883988

H 3.607958 0.753201 -0.000