Efficient transfer hydrogenation of ketones by molybdenum complexes through comprehensively verifying auxiliary ligands

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Table of contents

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. $Mo(CO)_6$, $NaBHEt_3$ (1 M in THF) were purchased from Sigma-Aldrich. $Mo(\eta^3\text{-allyl})(CO)_2(CH_3CN)_2Br$ and $Mo(PPh_3)_2(CO)_2(CH_3CN)_2$ were prepared according to literature procedures.[1,2] The tridentate ligands (**L1** – **L4**) containing 5,6,7,8-tetrahydroquinolin-8-amine were prepared using a previously reported procedure.[3] ^1H, ^{13}C and ^{31}P 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, 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. GC was performed using a FuLi 9790II instrument using an Agilent HP-INNOWAX column (30m × 0.320mm × 0.25μm, Part number: 19091N-113I): injector temp. 300 °C, detector 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.

Table S1 CAS numbers for substrates and products

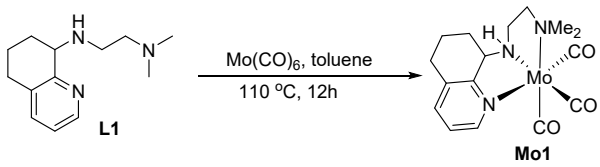
Products	CAS number	Substrates	CAS number
1-Phenylethanol	13323-81-4	Acetophenone	98-86-2
1-(4-Fluorophenyl)ethanol	403-41-8	4'-Fluoroacetophenone	403-42-9
1-(4-Chlorophenyl)ethanol	3391-10-4	4'-Chloroacetophenone	99-91-2
1-(4-Bromophenyl)ethanol	5391-88-8	4'-Bromoacetophenone	99-90-1
1-(4-Methylphenyl)ethanol	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-(2Methylphenyl) 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-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
Benzoylcyclohexane	712-50-5	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
1-Indanol	6351-10-6	1-Indanone	83-33-0
1-(Hydroxyphenylmethyl) cyclohexan-1-ol	1135-72-4	1-Hydroxycyclohexyl phenyl ketone	947-19-3
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
Cyclopentanol	96-41-3	Cyclopentanone	120-92-3
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
Cyclopentadecanol	4727-17-7	Cyclopentadecanone	502-72-7
4-Phenylcyclohexanol	5437-46-7	4-Phenylcyclohexanone	4894-75-1
4-t-Butylcyclohexanone	98-53-3	4-t-Butylcyclohexanol	98-52-2
3-Quinuclidinol	1619-34-7	3-Quinuclidinone	3731-38-2
3-Heptanone	106-35-4	3-Hydroxyheptane	589-82-2
2-Pentanone	107-87-9	2-Pentanol	6032-29-7
3-Penten-2-one	625-33-2	3-Penten-2-ol	1569-50-2

2. Syntheses and characterization of the ligands and complexes

2.2.1 Synthesis of $[8\text{-}(2\text{-}R_2N)C_2H_4NHC_9H_{10}N](CO)_3Mo$ (Mo1 – Mo3)[1,2]

a) $R_2N = Me_2N$, **Mo1**



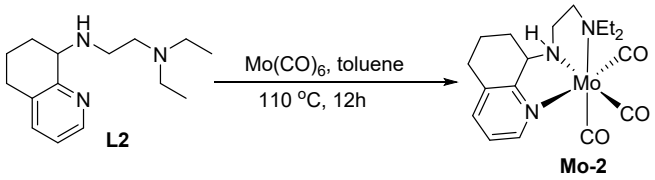
Under a N_2 atmosphere, a mixture of *N*[1],*N*[1]-dimethyl-N[2]-(5,6,7,8-tetrahydroquinolin- 8-yl)ethane-1,2-diamine (**L1**, 219 mg, 1 mmol) and $Mo(CO)_6$ (265 mg, 1 mmol) in 10 mL toluene was added to a 25 mL Shrek bottle. the reaction mixture was kept stirring at 110 °C for 12 h, and the resulting orange-red suspension was cooled to room temperature. The orange precipitate was filtered off, washed three times with 2 mL of toluene, and afterward redissolved in 2 mL DCM. Ether (20 mL) was added until product precipitation occurred. The resulting organe solid was filtered off, washed two times with 5 mL of ether, and dried in vacuo to yield 325 mg (81%) of **Mo1** as an orange solid. Crystals suitable for X-ray analysis were obtained were obtained by slowly allowing a layer of ether to diffuse into a saturated solution of **Mo1** in DCM.

^{1}H NMR (500 MHz, DMSO-*d*) δ 8.67 (d, *J* = 4.7 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.6, 5.4 Hz, 1H), 5.78 (s, 1H), 4.21 – 4.15 (m, 1H), 2.80 – 2.76 (m, 3H), 2.74 (s, 3H), 2.46 (s, 1H), 2.15 (d, *J* = 9.1 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.99-1.93 (m, 3H), 1.90 (s, 3H), 1.75 (dd, *J* = 14.3, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-*d*) δ 157.67, 150.02, 138.38, 135.78, 123.67, 62.73, 61.57, 55.90, 47.50, 42.32, 28.02, 26.96, 21.38, CO not observed; FT-IR (cm^{-1}, KBr): 1728 (s, ν_{CO}), 1771 (s, ν_{CO}), 1897 (s, ν_{CO}), 3278 (m, ν_{NH}); Anal. Calcd for **Mo1** (399.31) [$C_{16}H_{21}MoN_3O_3$]: C, 48.13; H, 5.30; N, 10.52; Found: C,

48.11, H, 5.34, N, 10.45.

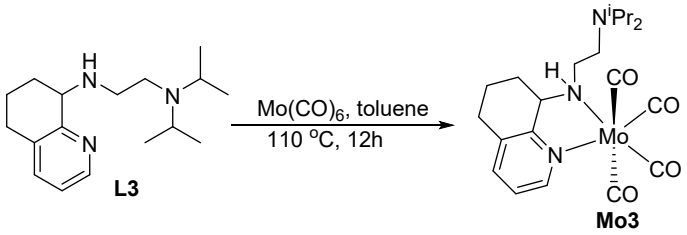
Caution: Carbon monoxide is released upon addition/heating of the suspension. Allow for adequate ventilation and use of personal safety equipment.

b) $R_2N = Et_2N$, **Mo2**



Using a similar procedure and molar ratios (**L2**, 247 mg, 1 mmol and $Mo(CO)_6$, 265 mg, 1 mmol) to that described for **Mo1**, **Mo2** was isolated as an orange power (375 mg, 87%). ^{1}H NMR (500 MHz, DMSO-*d*) δ 8.64 (d, *J* = 4.3 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.31 (dd, *J* = 7.6, 5.4 Hz, 1H), 5.77 (s, 1H, NH), 4.21 – 4.12 (m, 1H), 3.25-3.21 (m, 1H), 2.94 – 2.90 (m, 1H), 2.77 (d, *J* = 6.7 Hz, 3H), 2.43 (d, *J* = 11.5 Hz, 1H), 2.31 (d, *J* = 7.9 Hz, 1H), 2.17-2.13 (m, 1H), 2.07-2.03 (m, 1H), 2.00 – 1.92 (m, 2H), 1.92 – 1.83 (m, 2H), 1.81-1.74 (m, 1H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 158.03, 149.89, 138.62, 136.00, 123.85, 63.07, 56.74, 53.80, 47.58, 44.87, 41.92, 28.40, 27.34, 21.76, 9.61, 9.50, CO not observed; FT-IR (cm^{-1}, KBr): 1728 (s, ν_{CO}), 1775 (s, ν_{CO}), 1894 (s, ν_{CO}), 3274 (m, ν_{NH}); Anal. Calcd for **Mo2** (427.37) [$C_{18}H_{25}MoN_3O_3$]: C, 50.59; H, 5.90; N, 9.83; Found: C, 50.61, H, 5.94, N, 9.75.

c) $R_2N = i\text{-}Pr_2N$, **Mo3**

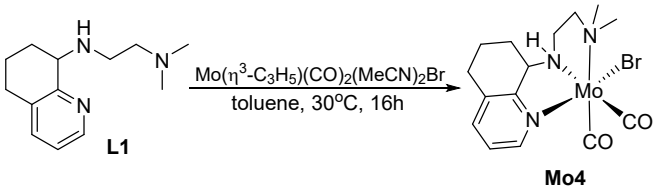


Using a similar procedure and molar ratios (**L3**, 275 mg, 1 mmol and $Mo(CO)_6$, 265 mg, 1 mmol) to that described for **Mo1**, **Mo3** was isolated as an orange power (415 mg, 85%).

^{1}H NMR (500 MHz, DMSO-*d*) δ 8.59 (d, *J* = 4.7 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 7.6, 5.4 Hz, 1H), 4.52 – 4.45 (m, 1H), 3.84 (s, 1H), 3.08 – 2.94 (m, 4H), 2.82-2.65 (m, 4H), 1.99 (d, *J* = 10.6 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.54 (dd, *J* = 23.1, 11.1 Hz, 1H), 1.20 (d, *J* = 6.5 Hz, 1H), 1.01 (dd, *J* = 13.3, 6.5 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-*d*) δ 208.91(C=O), 206.71(C=O), 158.61, 150.11, 138.93, 135.63, 123.67, 64.35, 48.74, 46.77, 44.32, 28.16, 27.67, 21.15, 20.56, 19.29; FT-IR (cm^{-1}, KBr): 1815 (s, ν_{CO}), 1861 (s, ν_{CO}), 1885 (s, ν_{CO}), 2006 (s, ν_{CO}), 3207 (m, ν_{NH}); Anal. Calcd for **Mo3** (483.43) [$C_{21}H_{29}MoN_3O_4$]: C, 52.18; H, 6.05; N, 8.69; Found: C, 52.13, H, 6.08, N, 8.61.

2.2.2 Synthesis of [8-(2-R_2N)$C_2H_4NHC_9H_{10}N$](CO)$_2$MoBr (**Mo4 – Mo6**)

a) $R_2N = Me_2N$, **Mo4**

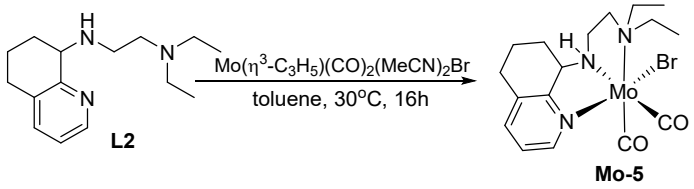


In a 25 mL Shrek bottle, a mixture of N^1,N^1-dimethyl-N^2-(5,6,7,8-tetrahydroquinolin- 8-yl)ethane-1,2-diamine (**L1**, 219 mg, 1 mmol) and Mo(η^3-C_3H_5)(CO)$_2$(MeCN)$_2$Br (355 mg, 1 mmol) in 10 mL toluene. the reaction mixture was kept

stirring at 30 °C for 16 h. An orange suspension was obtained and the solvent was concentrated to 3 mL in vacuo, the orange-brown solid was filtered and was washed two times with 2 mL of toluene, and afterward redissolved in 2 mL DCM. Ether (20 mL) was added until product precipitation occurred again. The resulting brown solid was filtered off, washed two times with 5 mL of ether, and dried in vacuo to yield 310 mg (68%) of **Mo4** as a pale-brown power.

^{1}H NMR (500 MHz, DMSO-*d*) δ 8.49 (br, 1H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.51-7.48 (m, 2H), 4.58 (s, 1H), 4.21 (br, 1H), 2.94 – 2.91 (m, 2H), 2.85-2.76 (m, 2H), 2.56 (s, 3H), 2.21-2.18 (m, 2H), 2.06-2.02 (m, 2H), 1.79 (s, 3H), 1.41 – 1.19 (m, 2H); ^{13}C NMR (125 MHz, DMSO-*d*) δ 157.04, 149.77, 143.08, 136.15, 125.54, 60.69, 59.95, 53.65, 49.96, 41.97, 27.84, 26.38, 21.10; FT-IR (cm^{-1}, KBr): 1841 (s, ν_{CO}), 1934 (s, ν_{CO}), 3424 (m, ν_{NH}); Anal. Calcd for **Mo4** (451.21) [$C_{15}H_{21}BrMoN_3O_2$]: C, 39.93; H, 4.69; N, 9.31; Found: C, 39.98, H, 4.71, N, 9.28.

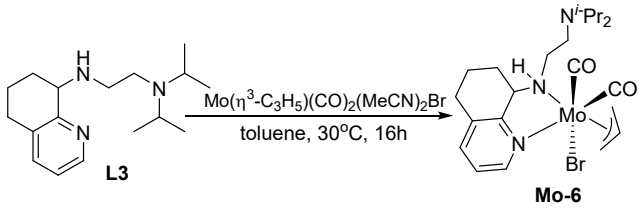
b) R_2N = Et_2N, **Mo5**



Using a similar procedure and molar ratios (**L2**, 247 mg, 1 mmol and Mo(n^3-C_3H_5)$(CO)_2$ $(MeCN)_2$Br, 355 mg, 1 mmol) to that described for **Mo4**, **Mo5** was isolated as a pale-brown power (365 mg, 76%).

^{1}H NMR (500 MHz, DMSO) δ 8.49 – 8.45 (m, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.34 (m, 1H), 3.71 (d, *J* = 10.3 Hz, 1H), 3.17 – 3.11 (m, 2H), 3.06 – 3.00 (m, 2H), 2.82 (s, 4H), 2.65 – 2.63 (m, 1H), 2.37 – 2.36 (m, 1H), 2.30 (s, 1H), 2.02 (s, 1H), 1.84 – 1.77 (m, 2H), 1.26 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-*d*) δ 152.19, 147.01, 138.24, 138.16, 133.63, 123.92, 59.20, 57.03, 50.34, 46.97, 42.32, 27.71, 26.02, 20.36, 19.92; FT-IR (cm^{-1}, KBr): 1908 (s, ν_{CO}), 2025 (s, ν_{CO}), 3418 (m, ν_{NH}); Anal. Calcd for **Mo5** (479.26) [$C_{17}H_{25}BrMoN_3O_2$]: C, 42.60; H, 5.26; N, 8.77; Found: C, 42.51, H, 5.30, N, 8.68.

c) R_2N = *i*-Pr_2N, **Mo6**

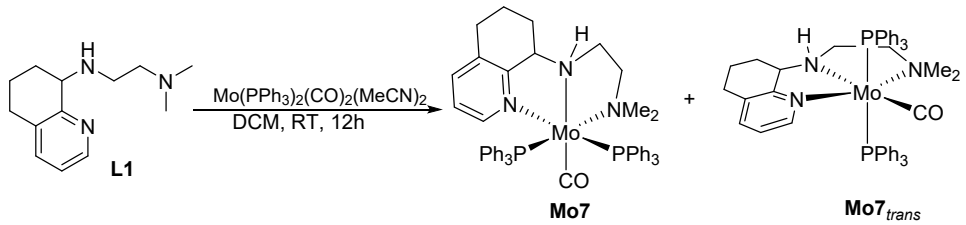


Using a similar procedure and molar ratios (**L3**, THQ-NNN^{Pr2}, 275 mg, 1 mmol and Mo(n^3-C_3H_5)$(CO)_2(MeCN)_2$Br, 355 mg, 1 mmol) to that described for **Mo4**, **Mo6** was isolated as a pale-brown power (410 mg, 74%).

1H NMR (500 MHz, DMSO-*d*) δ 8.38 (t, *J* = 52.4 Hz, 1H), 7.74 (ddd, *J* = 28.5, 27.7, 7.7 Hz, 1H), 7.53 – 7.32 (m, 1H), 4.40 (s, 1H), 3.76 (d, *J* = 49.5 Hz, 2H), 3.31 (s, 6H), 3.07 (d, *J* = 45.4 Hz, 2H), 2.78 (s, 2H), 2.00 (s, 1H), 1.83 – 1.63 (m, 2H), 1.35 (s, 2H), 1.21 – 1.16 (m, 1H), 1.12 – 0.92 (m, 12H);^{13}C NMR (125 MHz, DMSO-*d*) δ155.70, 149.31, 139.44, 138.27, 134.70, 125.19, 124.26, 123.97, 65.38, 62.49, 56.81, 53.58, 48.55, 28.06, 27.82, 21.39, 20.78, 15.64; FT-IR (cm^{-1}, KBr): 1846 (s, ν_{CO}), 1930 (s, ν_{CO}), 3445 (m, ν_{NH}); Anal. Calcd for **Mo6** (551.41) [$C_{22}H_{35}BrMoN_3O_2$]: C, 47.92; H, 6.76; N, 7.62; Found: C, 47.87, H, 6.81, N, 7.60.

2.2.3 Synthesis of [8-(2-R_2N/RS)$C_2H_4NHC_9H_{10}N$](CO)Mo(PPh_3)$_2$ (**Mo7** and **Mo8**)[4]

a) R_2N = Me_2N, **Mo7**

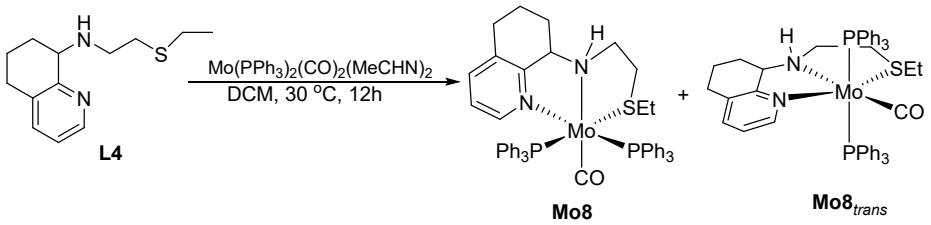


In a 25 mL Shrek bottle, a mixture of N^1,N^1-dimethyl-N^2-(5,6,7,8-tetrahydroquinolin- 8-yl)ethane-1,2-diamine (**L1**, 219 mg, 1 mmol) and $Mo(PPh_3)_2(CO)_2(MeCN)_2$ (758 mg, 1 mmol) in 10 mL CH_2Cl_2. the reaction mixture was kept stirring at rt for 12 h. The solvent was concentrated to 2 mL in vacuo and ether (20 mL) was added until product precipitation occurred, the pale yellow solid was filtered and was washed two times with 5 mL of ether, and dried in vacuo to yield 462 mg (53%) of **Mo7**/**Mo7** *trans* as a pale-yellow power.

The $^{31}P\{^1H\}$ spectrum is recorded immediately following dissolution, the isomers: **Mo7**(84%) and **Mo7**$_{trans}$ (16%) were observed. On standing in deuterated DMSO for 12 h. the ratio of **Mo7**/**Mo7**$_{\mathbf{trans}}$ changed to 80%: 20% by ^{31}P $\{^1H\}$ NMR spectroscopy.

^1H NMR (500 MHz, DMSO) δ 8.72 (d, *J* = 5.1 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.60 (m, 18H), 7.56 (dd, *J* = 7.1, 3.0 Hz, 12H), 7.48 – 7.46 (m, 1H), 6.43 (s, 1H), 4.25 – 4.18 (m, 1H), 2.86 (s, 3H), 2.83 – 2.80 (m, 2H), 2.16 (dd, *J* = 9.4, 2.9 Hz, 2H), 2.07 (d, *J* = 12.4 Hz, 2H), 2.00 – 1.96 (m, 1H), 1.90 (d, *J* = 11.8 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*) δ 158.19, 157.22, 156.12, 149.69, 148.43, 146.91, 146.23, 143.02, 140.37, 137.90, 137.05, 135.81, 135.53, 135.17, 134.36, 134.25, 134.00, 132.98, 132.38, 132.36, 131.99, 131.90, 130.85, 130.72, 129.18, 129.07, 128.92, 128.81, 126.16, 123.86, 122.60, 122.20, 60.87, 58.36, 53.63, 49.89, 45.65, 27.60, 25.77, 21.13, 19.47; ^{31}P NMR (202 MHz, DMSO-*d*) δ 25.67, 17.44(*trans*); FT-IR (cm^{-1}, KBr): 1886 (s, ν_{CO}), 3424 (m, ν_{NH}); Anal. Calcd for **Mo7** (867.88) [$C_{50}H_{51}MoN_3OP_2$]: C, 69.20; H, 5.92; N, 4.84; Found: C, 69.16, H, 5.98, N, 4.76.

b) RS = EtS, **Mo8**



Using a similar procedure and molar ratios (**L4**, 222 mg, 1 mmol and $Mo(PPh_3)_2(CO)_2(MeCN)_2$ 758 mg, 1 mmol) to that described for **Mo7**, **Mo8**/**Mo8**$_{trans}$ was isolated as a pale-brown power (546 mg, 67%)

The $^{31}P\{^1H\}$ spectrum is recorded immediately following dissolution, the isomers **Mo8**(55%) and **Mo8**$_{trans}$ (45%) were observed.

^1H NMR (500 MHz, DMSO) δ 8.45 (s, 1H), 8.11 (s, 1H), 7.95 – 7.88 (m, 3H), 7.84 – 7.76 (m, 5H), 7.75 – 7.69 (m, 4H), 7.62 (dd, *J* = 11.7, 7.1 Hz, 5H), 7.58 – 7.52 (m, 3H), 7.48 (d, *J* = 3.2 Hz, 6H), 7.44 (d, *J* = 5.2 Hz, 2H), 7.31 (s, 2H), 7.20 – 7.16 (m, 1H), 3.03 – 3.01 (m, 1H), 2.79 (s, 4H), 2.56 (d, *J* = 7.3 Hz, 2H), 2.16 (d, *J* = 6.2 Hz, 2H), 2.01 (s, 2H), 1.75 (s, 2H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*) δ 203.98 (C=O), 151.88, 147.09, 144.41, 139.34, 138.30, 138.11, 137.44, 137.32, 135.49, 134.36, 134.25, 134.06, 133.80, 133.60, 133.04, 132.92, 132.80, 132.35, 132.33, 131.99, 131.89, 130.84, 130.71, 129.43, 129.34, 129.16, 129.09, 129.05, 128.79, 124.07, 123.95, 56.93, 47.22, 45.12, 34.88, 32.69, 27.71, 25.44, 19.82, 15.10; ^{31}P NMR (202 MHz, DMSO-*d*) δ 50.65, 17.36 (*trans*); FT-IR (cm^{-1}, KBr): 1888 (s, ν_{CO}), 3425 (m, ν_{NH}); Anal. Calcd for **Mo8** (807.81) [$C_{44}H_{45}MoN_2OP_2S$]: C, 65.42; H, 5.62; N, 3.47; Found: C, 65.48, H, 5.68, N, 3.46.

3 NMR and IR spectra for molybdenum complexes

3.1 ^{1}H, ^{13}C and ^{31}P NMR spectra for molybdenum complexes

Figure S1 The ^{1}H and ^{13}C NMR spectra for **Mo1** in DMSO-*d*

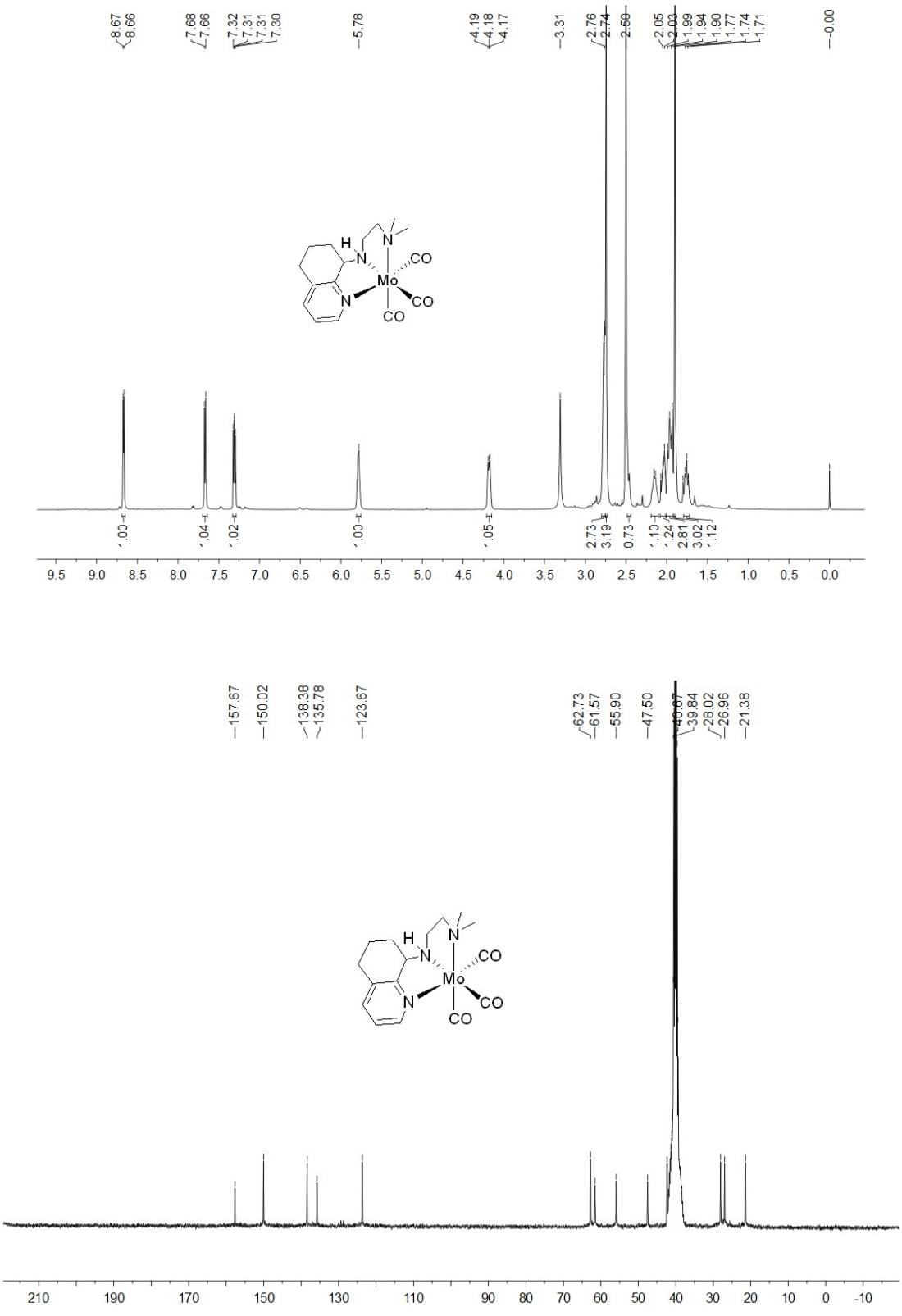


Figure S2 The ^{1}H and ^{13}C NMR spectra for **Mo2** in DMSO-*d*

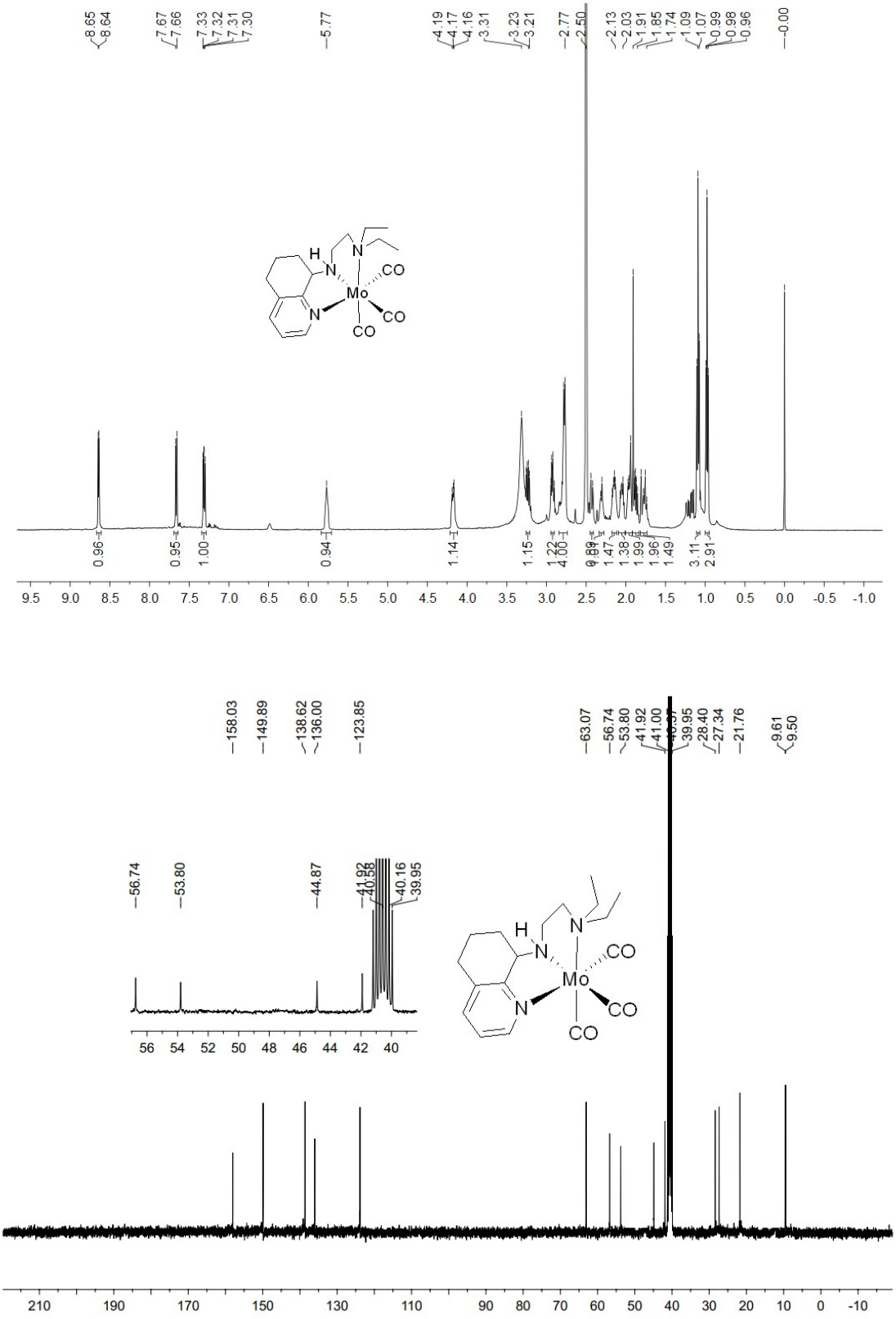


Figure S3 The ^{1}H and ^{13}C NMR spectra for **Mo3** in DMSO-*d*

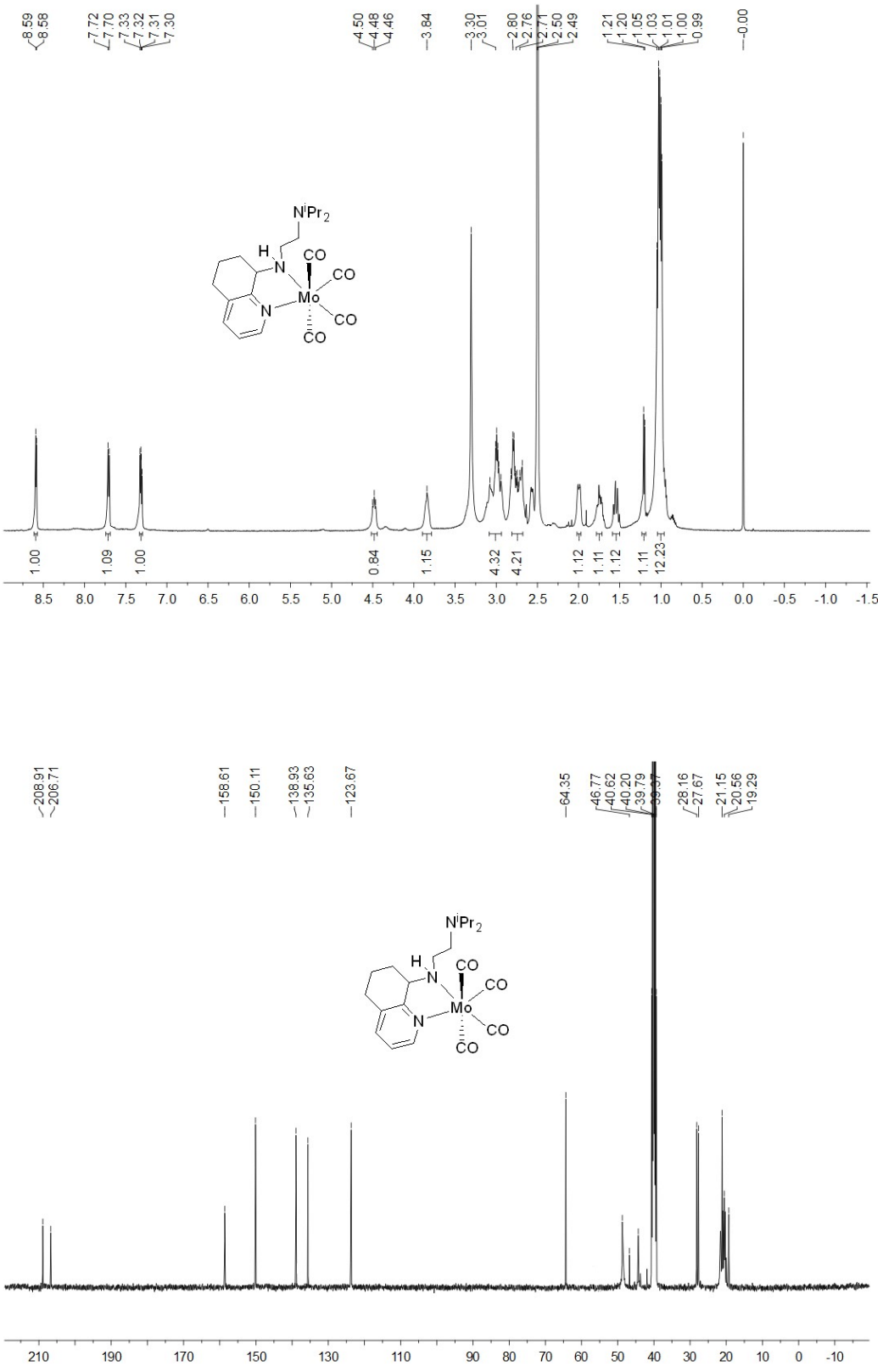


Figure S4 The ^{1}H and ^{13}C NMR spectra for Mo4 in DMSO-*d* at 80 °C

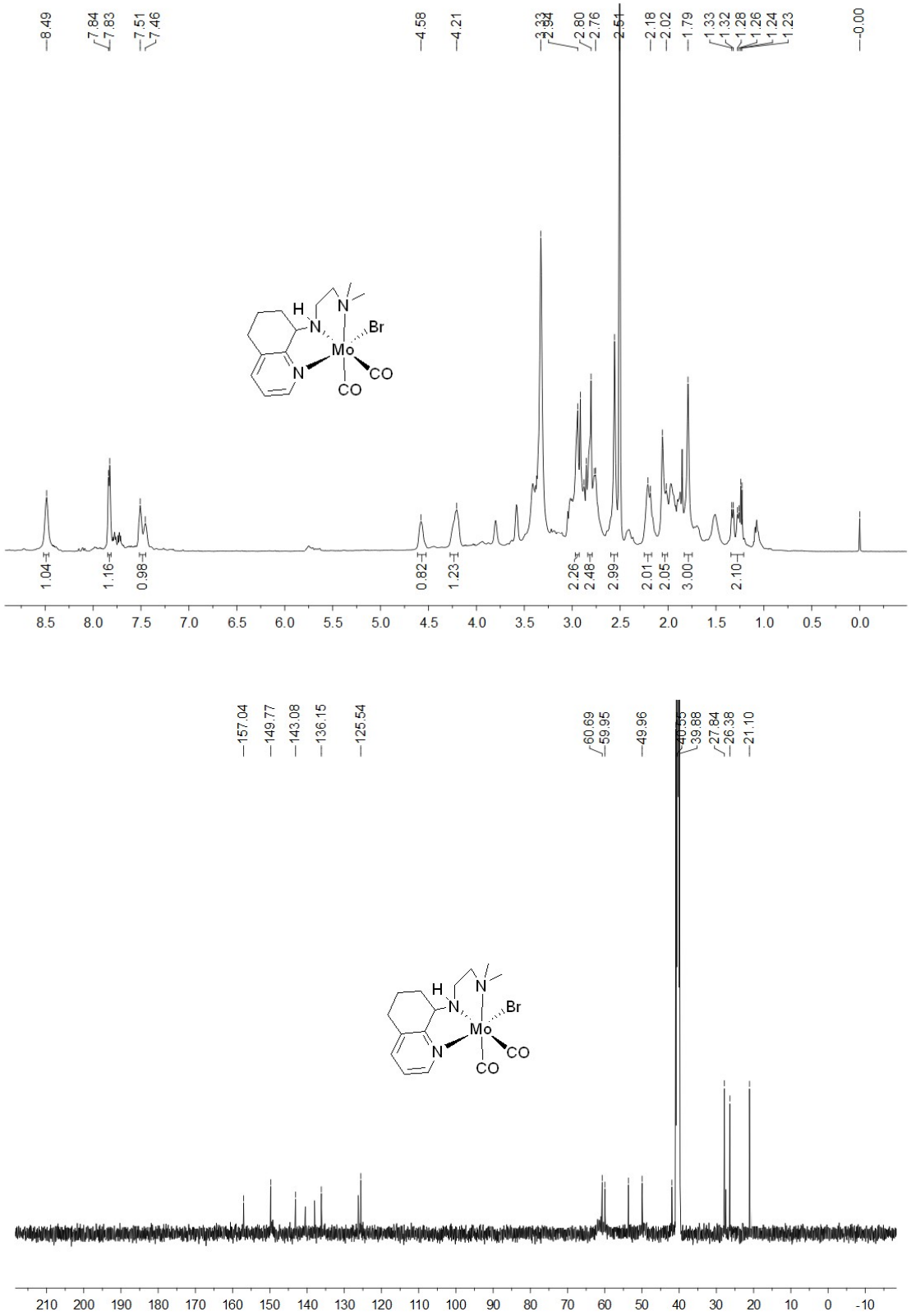


Figure S5 The ^{1}H and ^{13}C NMR spectra for Mo5 in DMSO-*d* at 80 °C

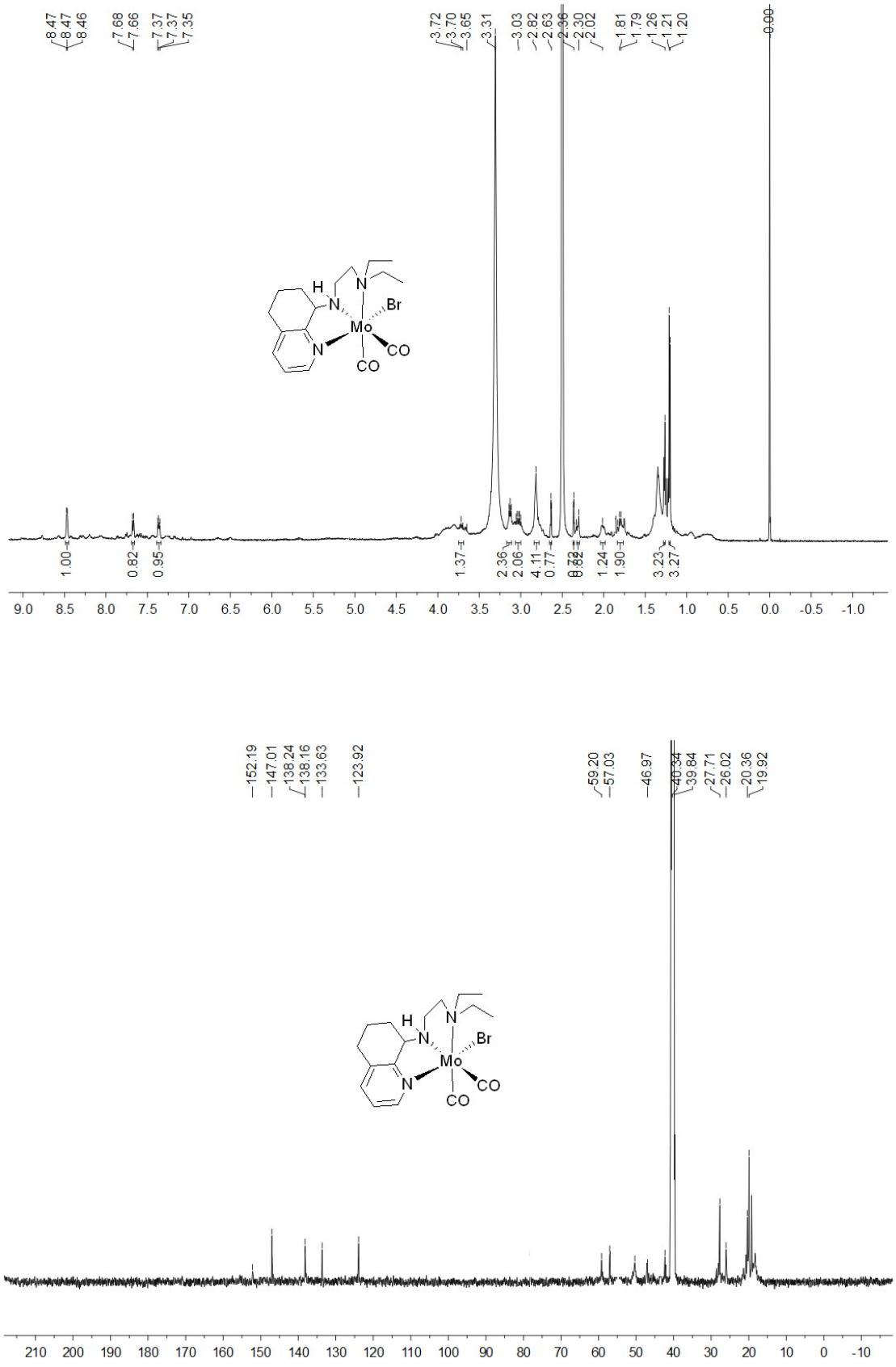


Figure S6 The ^{1}H and ^{13}C NMR spectra for Mo6 in DMSO-*d*

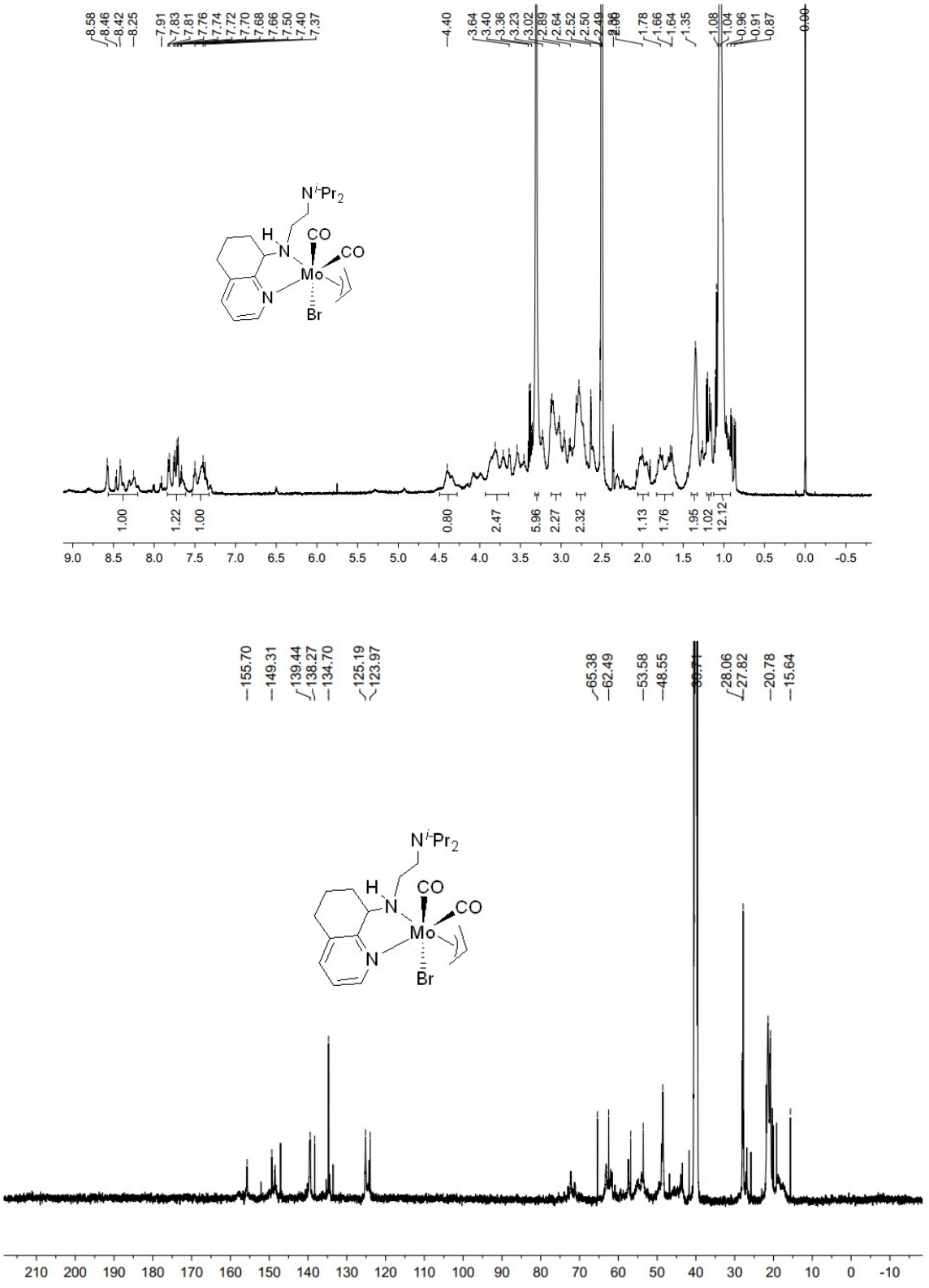


Figure S7 The ^{1}H, ^{13}C and ^{31}P NMR spectra for Mo7 and Mo7$_{trans}$ in DMSO-*d*

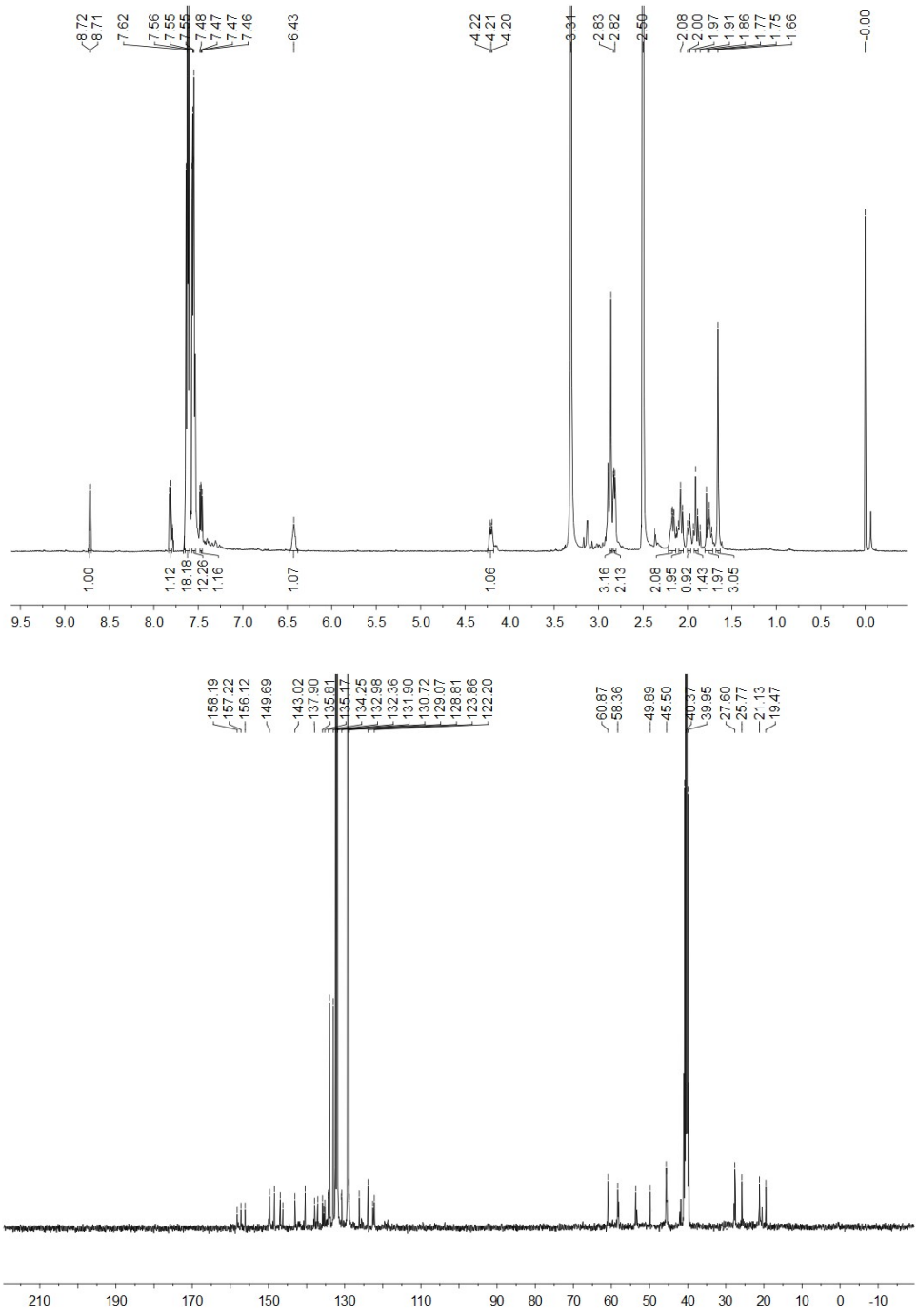
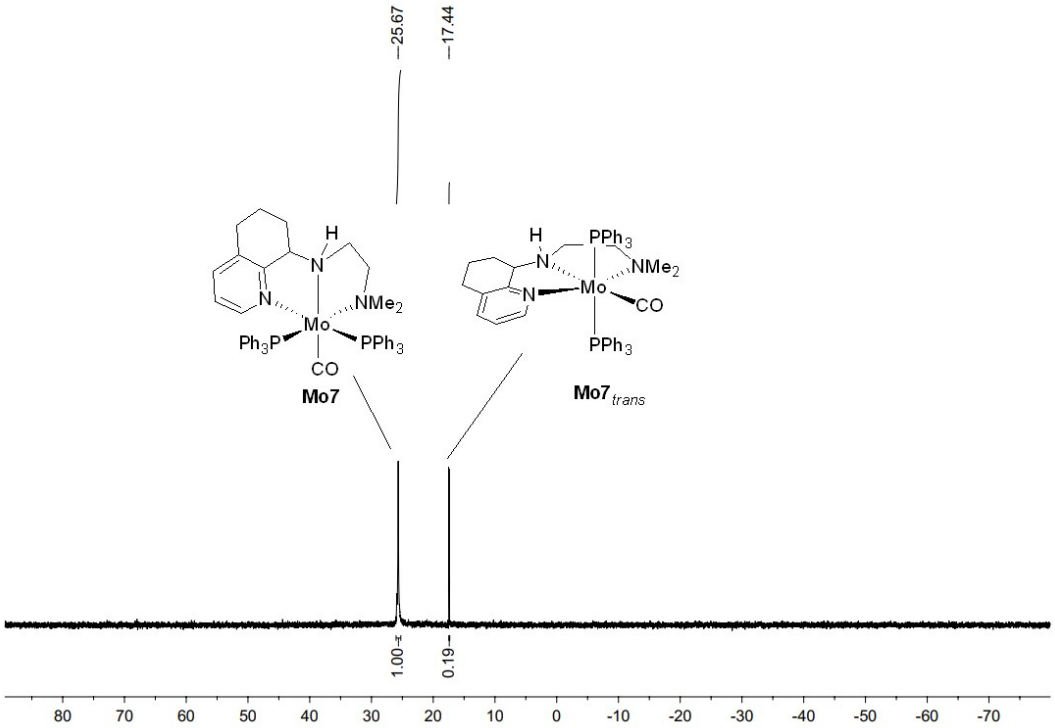
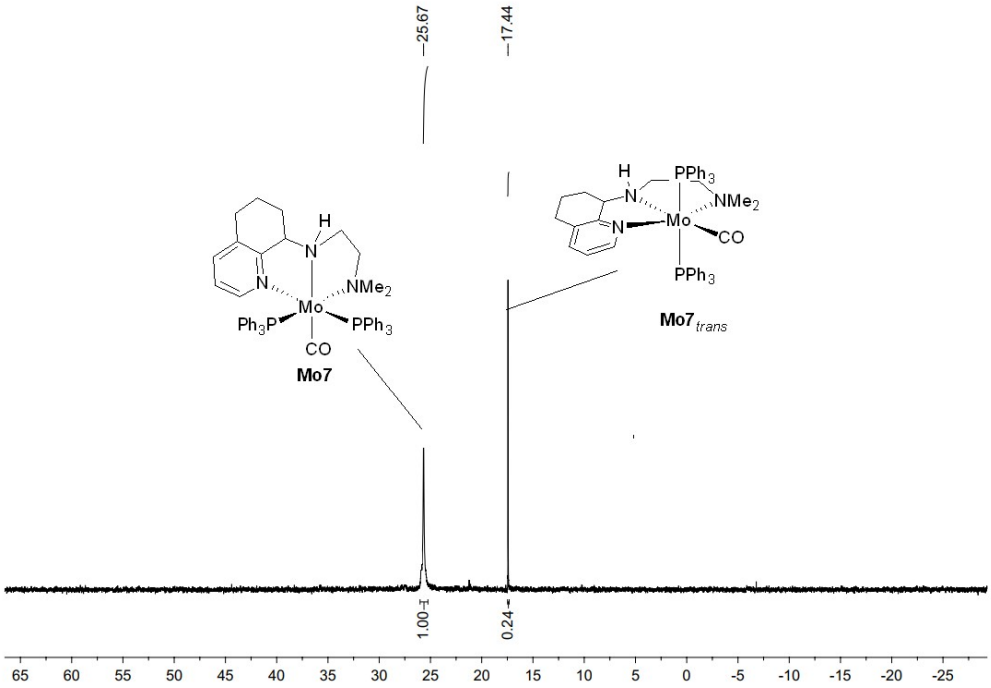


Figure S8 The ^{31}P {^{1}H} NMR spectrum of Mo7/Mo7$_{trans}$ in DMSO-*d*, spectrum recorded following dissolution



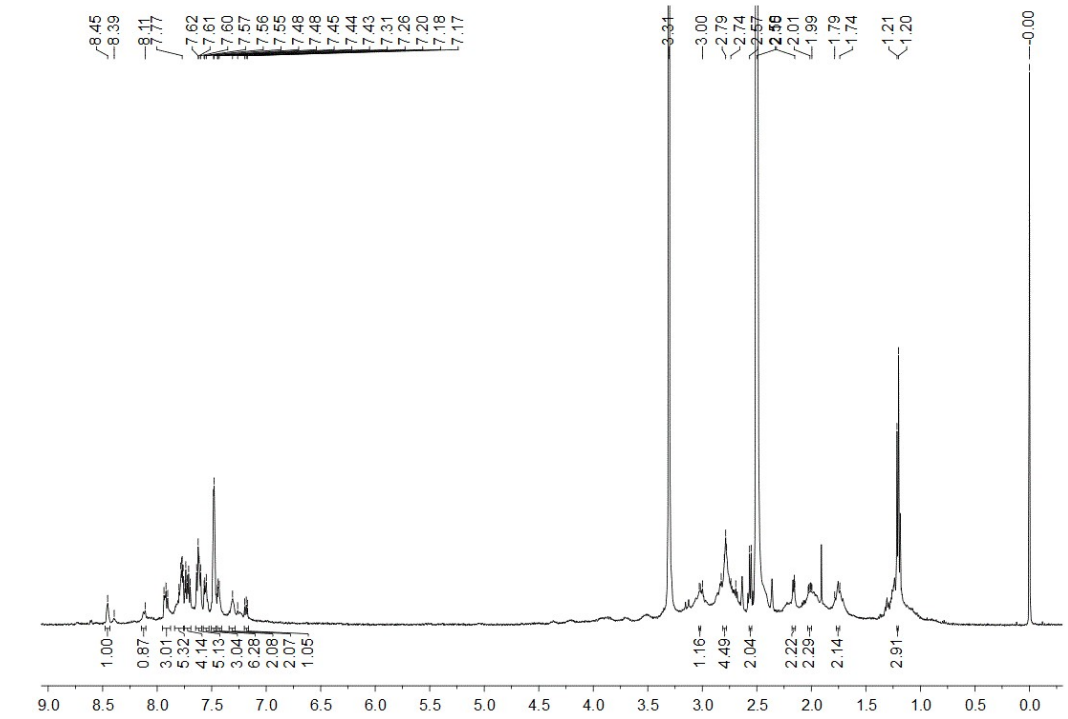
[^{31}P{^{1}H} NMR (202 MHz, DMSO-*d*) spectrum recorded following dissolution (ratio of **Mo7**/**Mo7**$_{trans}$ = 84:16)]

Figure S9 The ^{31}P {^{1}H} NMR spectrum of Mo7/Mo7$_{trans}$ in DMSO-*d*; spectrum recorded after standing in DMSO-*d* for 8 h



^{31}P{^{1}H} NMR (202 MHz, DMSO-*d*) spectrum recorded after standing in DMSO-*d* for 12 hours (ratio of **Mo7**/**Mo7**$_{trans}$ = 80:20)

Figure S10 The ^{1}H, ^{13}C and ^{31}P NMR spectra for Mo8/Mo8$_{trans}$ in DMSO-*d*



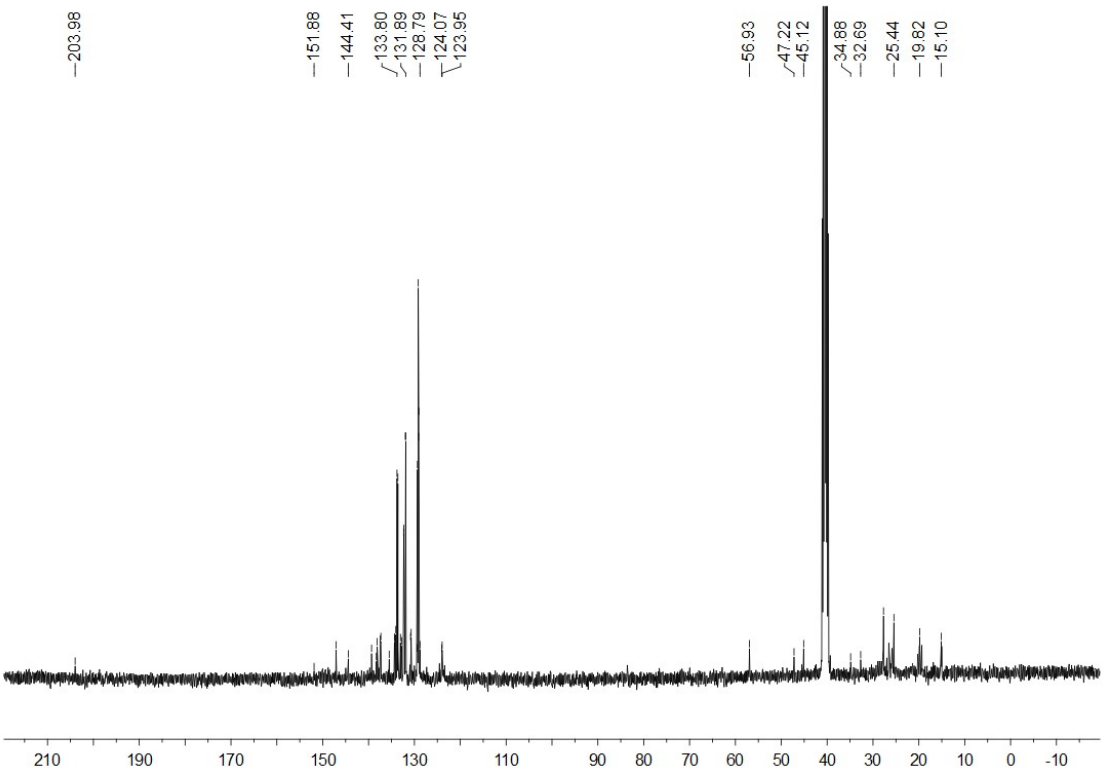
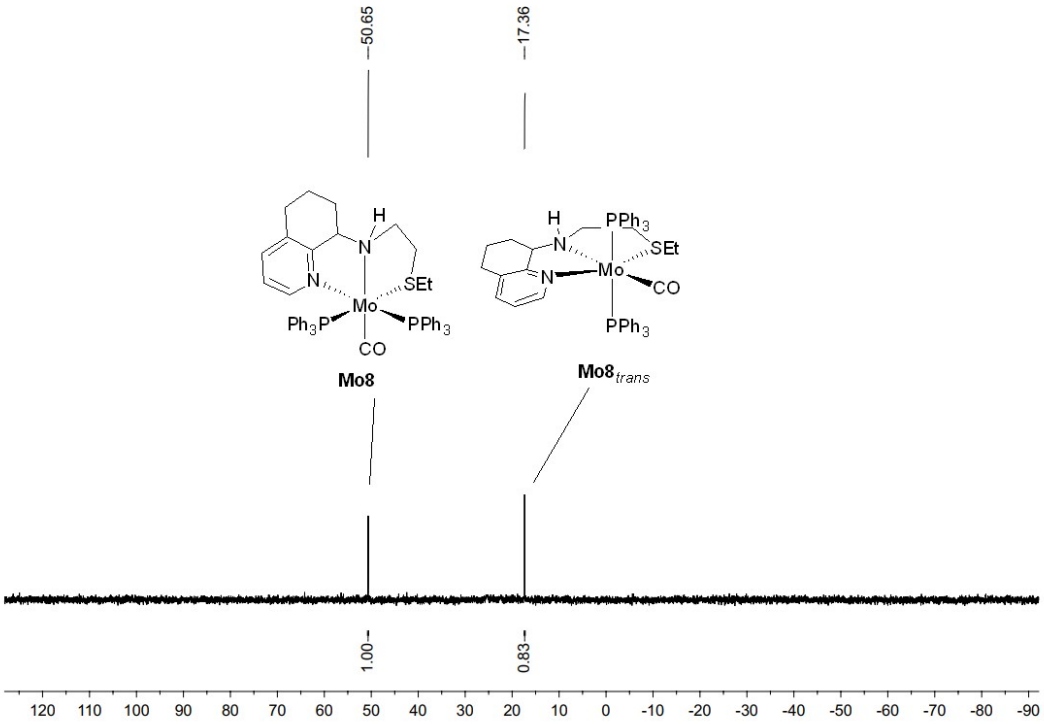


Figure S11 The ^{31}P {^{1}H} NMR spectrum of Mo8/Mo8$_{trans}$ in DMSO-*d*; spectrum recorded following dissolution



[^{31}P{^{1}H} NMR (202 MHz, DMSO-*d*) spectrum recorded following dissolution (ratio of **Mo8**/**Mo8**$_{trans}$ = 55:45)]

3.2 IR spectra for molybdenum complexes

Figure S12 FT-IR spectrum for **Mo1**

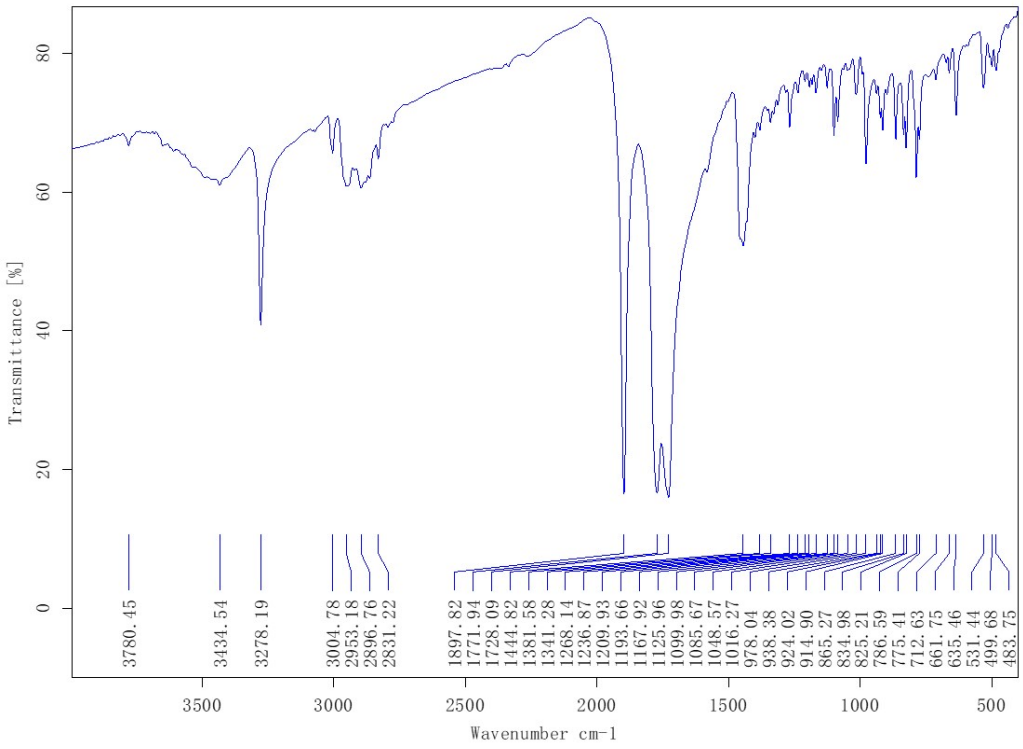


Figure S13 IR spectrum for **Mo2**

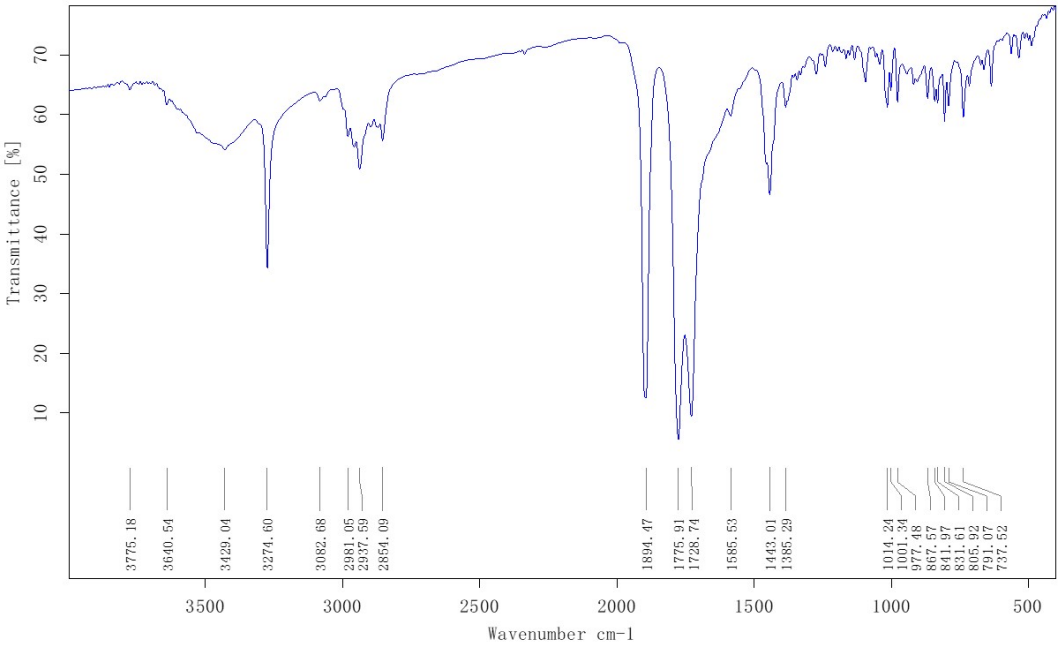


Figure S14 IR spectrum for **Mo3**

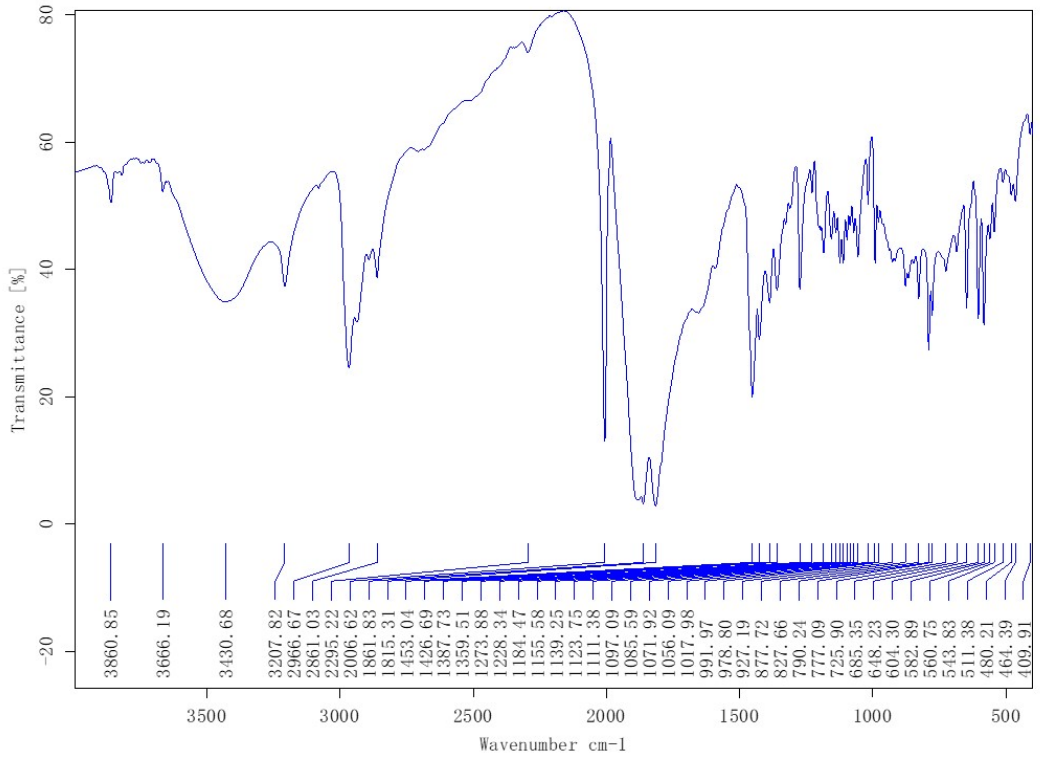


Figure S15 IR spectrum for **Mo4**

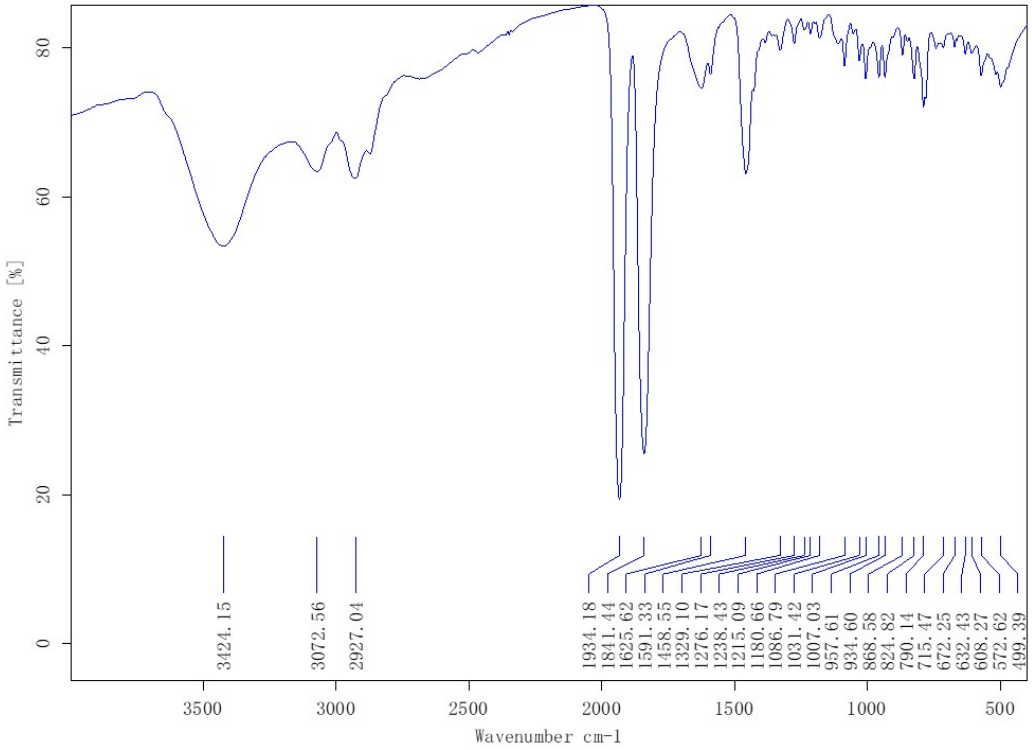


Figure S16 IR spectrum for **Mo5**

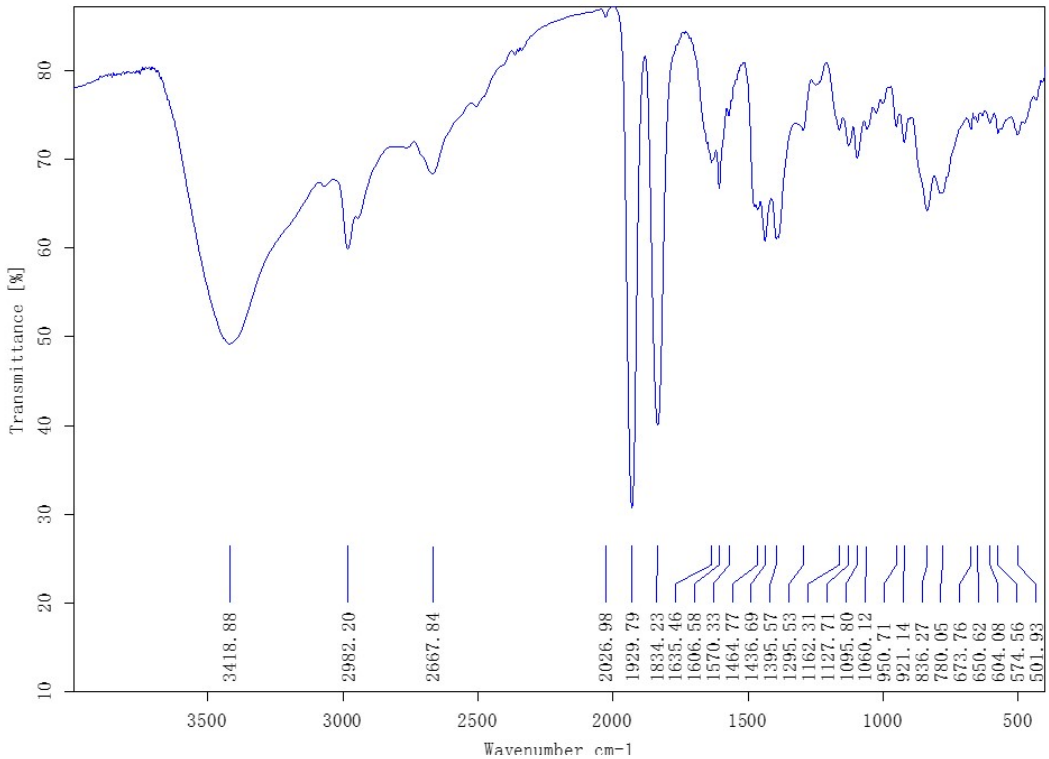


Figure S17 IR spectrum for **Mo6**

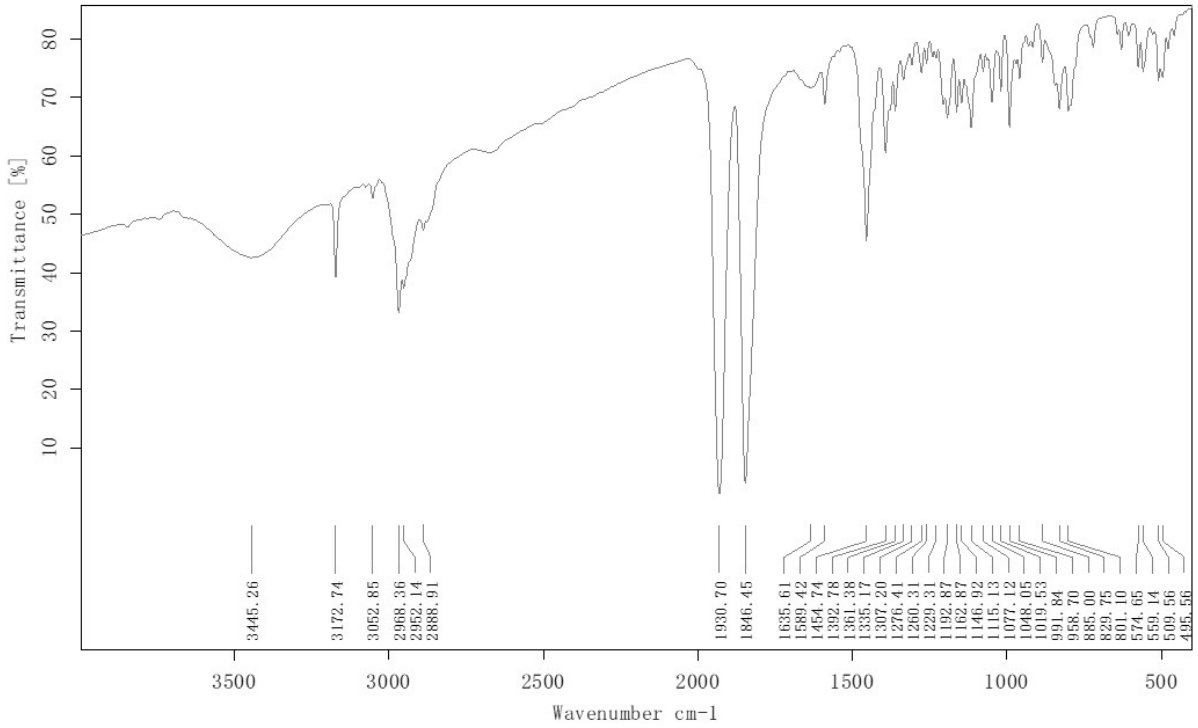


Figure S18 IR spectrum for **Mo7/Mo7**$_{trans}$

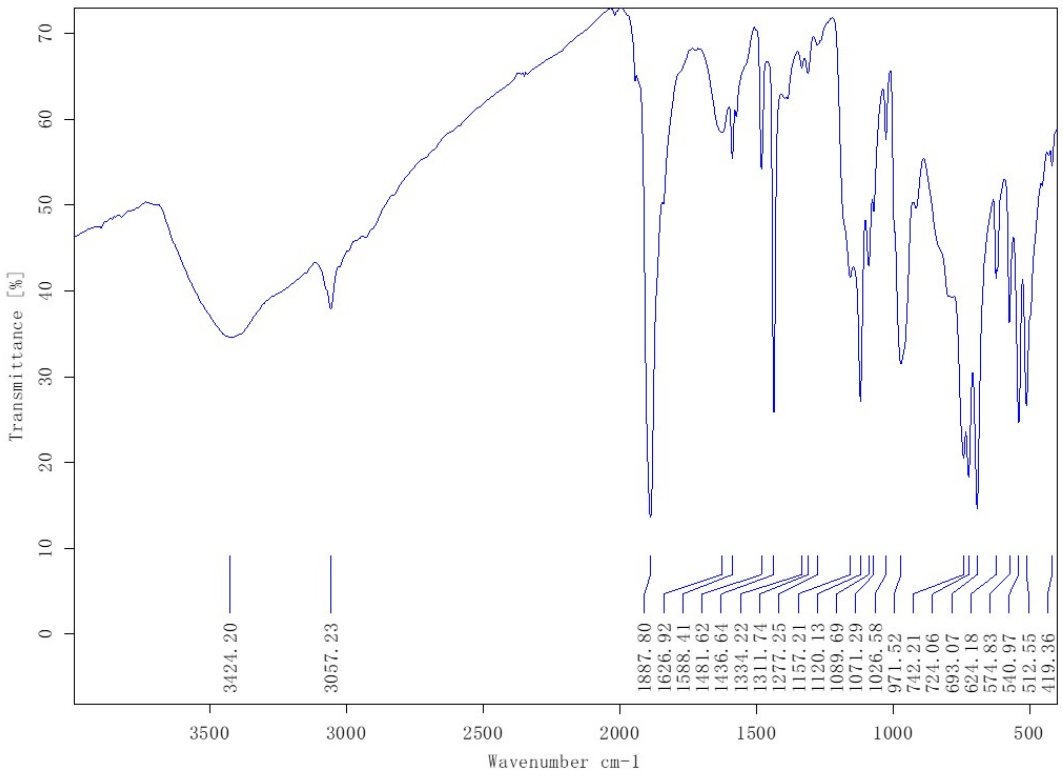
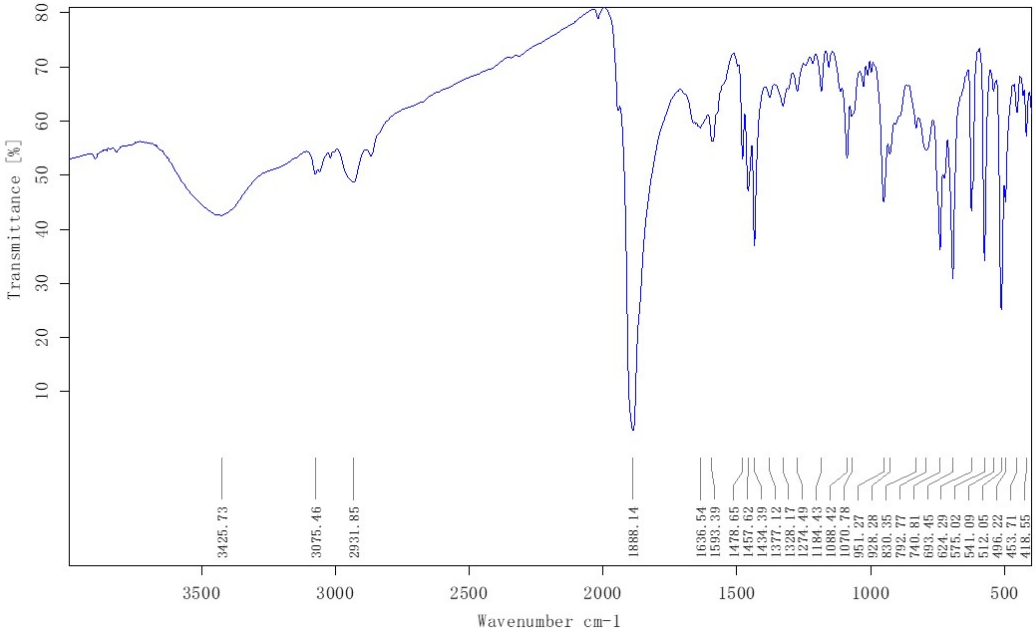


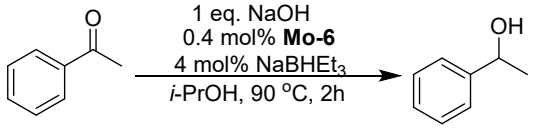
Figure S18 IR spectrum for **Mo8/ Mo8**$_{trans}$



4. Catalytic study

Under nitrogen. a 25 mL dried Schlenk tube was charged with selected ketonic substrate (2.5 mmol), molybdenum complex (**Mo6**, 10 umol), $NaHBEt_3$ (0.1 mmol), the desired amount of base (NaOH) (2.5 mmol) and dry and degassed 2-propanol (5 mL). The mixture was put to the desired temperature of bath (oil temperature, 20 – 110 °C) and the contents stirred. After 2 h, the mixture was cooled to room temperature, and the pressure slowly released. The reaction mixture was filtered through a plug of silica gel and then analyzed by GC, the composition of the reaction mixture was confirmed by running GC on a mixture of pure ketone, alcohol and dodecane. All yields and conversions were determined by GC using dodecane as internal standard (Table S2).

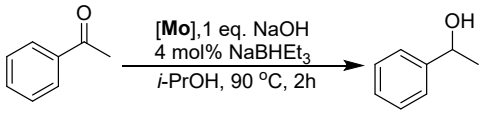
Table S2 Transfer hydrogenation of acetophenone to 1-phenylethanol using **Mo-6** at different temperature[a]



Entry	T(°C)	t(h)	Conv.%[b]
1	20	2	5
2	30	2	16
3	60	2	28
4	90	2	95
5	110	2	96

[a]Conditions: 2.5 mmol acetophenone, 10 μmol (0.4 mol%) **Mo6**, 2.5 mmol (1 eq.) NaOH, 0.1 mmol $NaBHEt_3$ (4 mol%), 5 mL *i*-PrOH, 30 ~ 110 °C (oil temperature), 2 hours, 1 atm N_2; [b] Determined by GC with dodecane as the internal standard.

Table S3 Transfer hydrogenation of acetophenone to 1-phenylethanol using **Mo1** ~ **Mo9** over different run time.[a]



Entry	[**Mo**]	t(h)	Conv.%[b]	t(h)	Conv.%[b]	t(h)	Conv.%[b]	t(h)	Conv.%[b]
1	**Mo1**	0.5	15	1.0	46	1.5	62	2.0	88
2	**Mo2**	0.5	12	1.0	39	1.5	58	2.0	75
3	**Mo3**	0.5	17	1.0	48	1.5	72	2.0	89
4	**Mo4**	0.5	38	1.0	71	1.5	85	2.0	92
5	**Mo5**	0.5	35	1.0	57	1.5	78	2.0	85
6	**Mo6**	0.5	48	1.0	75	1.5	92	2.0	95
7	**Mo7**	0.5	28	1.0	62	1.5	82	2.0	91
8	**Mo8**	0.5	24	1.0	54	1.5	75	2.0	82

[a] Conditions: 2.5 mmol acetophenone, 10 μmol (0.4 mol%) molybdenum complex (**Mo1** – **Mo8**), 10 mg (2.5 mmol, 1 eq.) NaOH, 0.1 mmol (4 mol%) $NaBHEt_3$, 5 mL *i*-PrOH, 90 °C (oil temperature), 0.5 - 2 h, 1 atm N_2; [b]Determined by GC with dodecane as the internal standard.

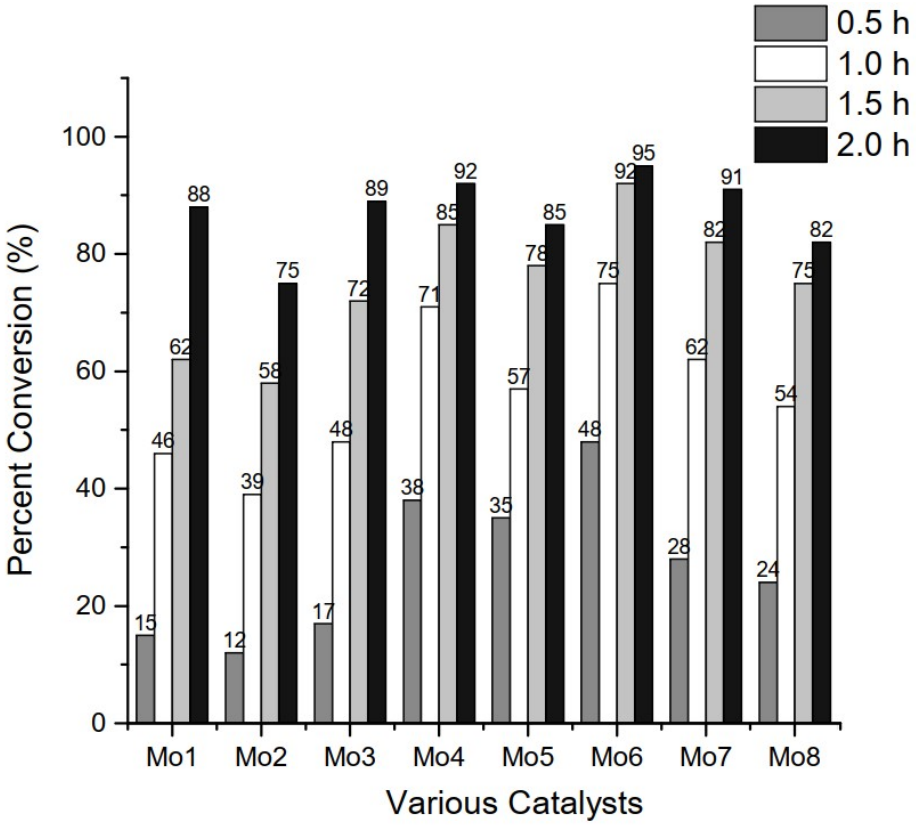


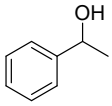
Figure S19 Comparison of molybdenum catalysts for transfer hydrogenation of acetophenone under the conditions in Table S3

5. Characterization of selected alcohol products

The reaction mixture was purified by flash gel chromatography (eluent: petroleum ether / ethyl acetate = 200:1 to 50:1) to give the desired product.

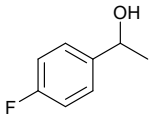
5.1. ^{1}H and ^{13}C NMR of the selected alcohol products

5.1.1 1-phenylethanol (entry 6, Table 1)



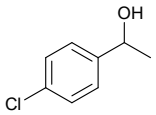
89% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 -7.30 (m, 5H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.60 (brs, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.93, 128.51, 127.52, 125.47, 70.32, 25.23.

5.1.2 1-(4-fluorophenyl)ethan-1-ol (entry 3, Table 4)



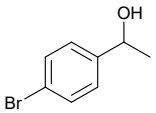
90% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.10-7.04 (m, 2H),4.92 (q, *J* = 6.4 Hz, 1H), 1.92 (s, 1H), 1.52 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ162.1, 141.5, 127.1,115.3, 69.78, 25.30.

5.1.3 1-(4-chlorophenyl)ethan-1-ol (entry 4, Table 4)



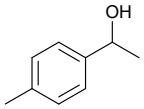
87% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 4H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.04 (s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.27, 133.08, 128.63, 126.83, 69.78, 25.30.

5.1.4 1-(4-bromophenyl)ethan-1-ol (entry 5, Table 4)



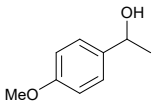
88% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.29-7.25 (m, 2H), 4.88 (q, *J* = 6.4 Hz, 1H), 2.05 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.82, 131.48, 127.25, 121.03, 69.50, 25.19.

5.1.5 1-(4-tolyl)ethan-1-ol (entry 6, Table 4)



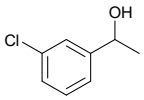
57% yield, Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8 Hz, 2H), 7.214 (d, *J* = 8 Hz, 2H), 4.91 (q, *J* = 6.4 Hz, 1H), 2.40 (s, 3H), 1.88 (s, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.92, 137.18, 129.22, 125.38, 70.29, 25.11, 21.12.

5.1.6 1-(4-methoxyphenyl)ethan-1-ol (entry 8, Table 4)



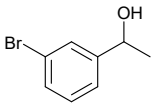
75% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 6.95-6.92 (m, 2H),4.90 (q, *J* = 6.4 Hz, 1H), 3.85 (s, 1H), 1.88 (brs, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.00, 138.03, 126.74, 126.66, 113.90, 113.83, 70.02, 55.30, 25.05.

5.1.7 1-(3-chlorophenyl)ethan-1-ol (entry 11, Table 4)



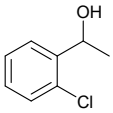
91% yield, Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.34-7.28 (m, 3H),4.93 (q, *J* = 6.4 Hz, 1H), 1.94 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.00, 134.34, 129.85, 127.64, 125.63, 123.69, 69.68, 25.26.

5.1.8 1-(3-bromophenyl)ethan-1-ol (entry 11, Table 4)



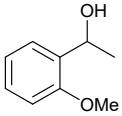
88% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 1H), 7.46-6.42 (m, 1H), 7.34-7.31 (m, 1H), 7.27-7.24 (m, 1H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.05 (brs, 1H), 1.52 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.20, 130.42, 130.14, 128.66, 124.14, 122.59, 69.58, 25.24.

5.1.9 1-(2-chlorophenyl)ethan-1-ol (entry 18, Table 4)



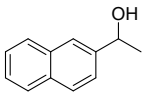
89% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 1H), 7.38-7.32 (m, 3H), 5.34 (q, *J* = 6.4 Hz, 1H), 2.06 (brs, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.21, 131.53, 129.35, 128.34, 127.22, 126.53, 66.86, 23.57.

5.1.10 1-(1-tolyl)ethan-1-ol (entry 22, Table 4)



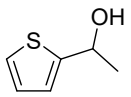
64% yield, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.32-7.28 (m, 1H), 7.03-6.99 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 5.14 (q, *J* = 6.4 Hz, 1H), 4.92 (s, 3H), 2.69 (brs, 1H), 1.56 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.45, 133.76, 128.25, 126.10, 120.85, 110.44, 66.15, 55.30, 23.11.

5.1.11 1-(naphthalen-2-yl)ethan-1-ol (entry 8, Table 5)



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 143.20, 133.35, 132.95, 128.38, 127.98, 127.73, 126.19, 125.85, 123.87, 123.82, 70.55, 25.18.

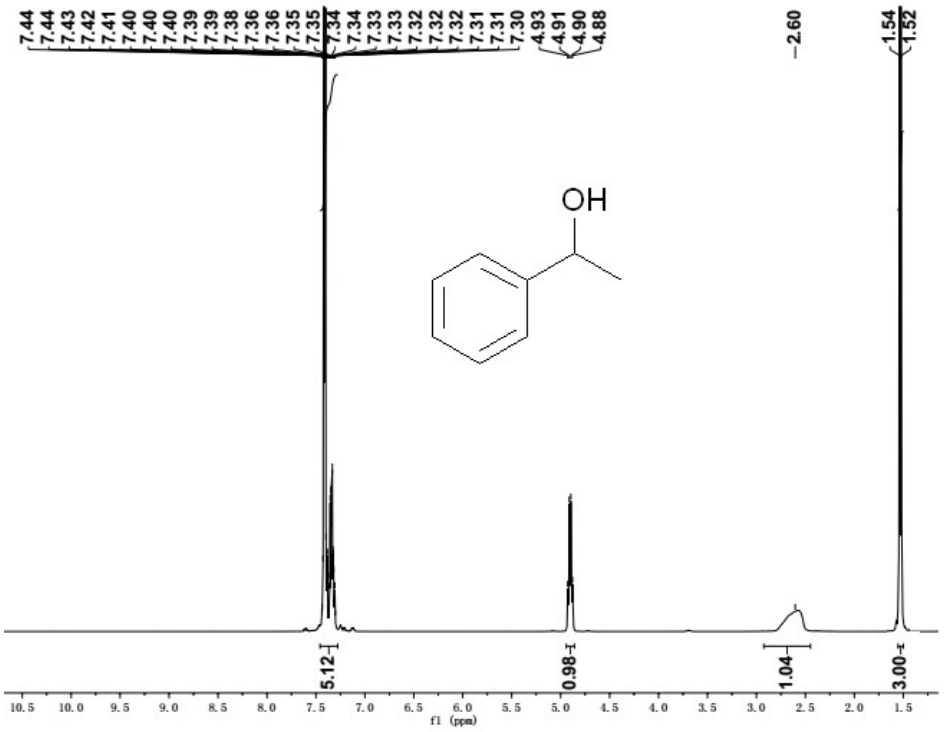
5.1.12 1-(thiophen-2-yl)ethan-1-ol (entry 13, Table 5)



68% 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 157.68, 141.92, 110.13, 105.11, 63.57, 21.26.

5.2. Copies of NMR spectra for the selected alcohol products

Figure S20 ^{1}H and ^{13}C NMR spectra of 1-phenylethanol in $CDCl_3$



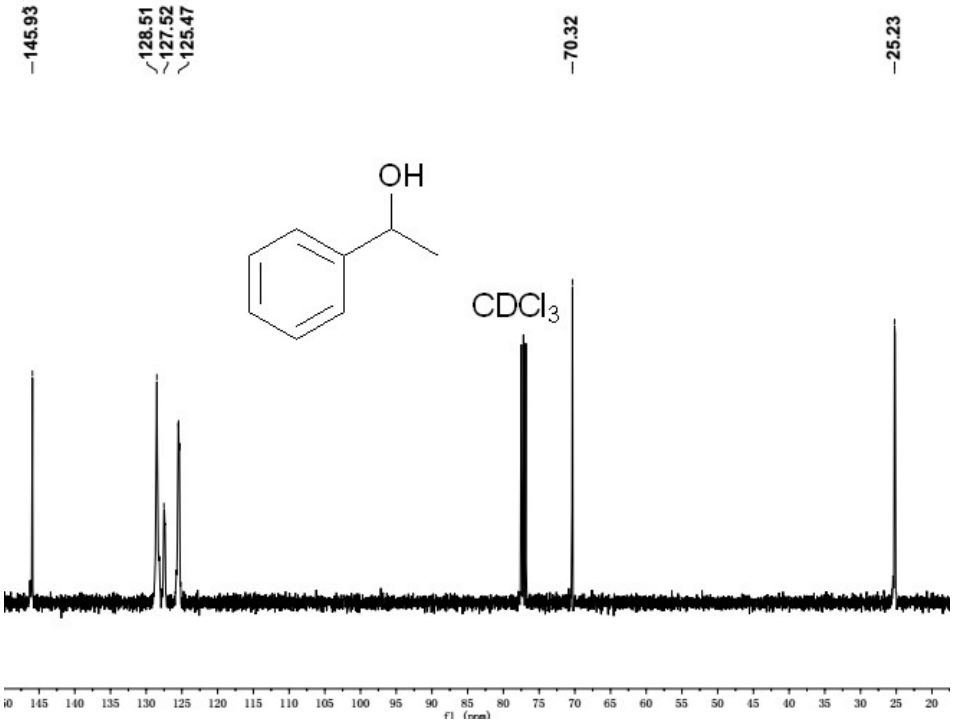


Figure S21 ^{1}H and ^{13}C NMR spectra of 1-(4-fluorophenyl)ethan-1-ol in $CDCl_3$

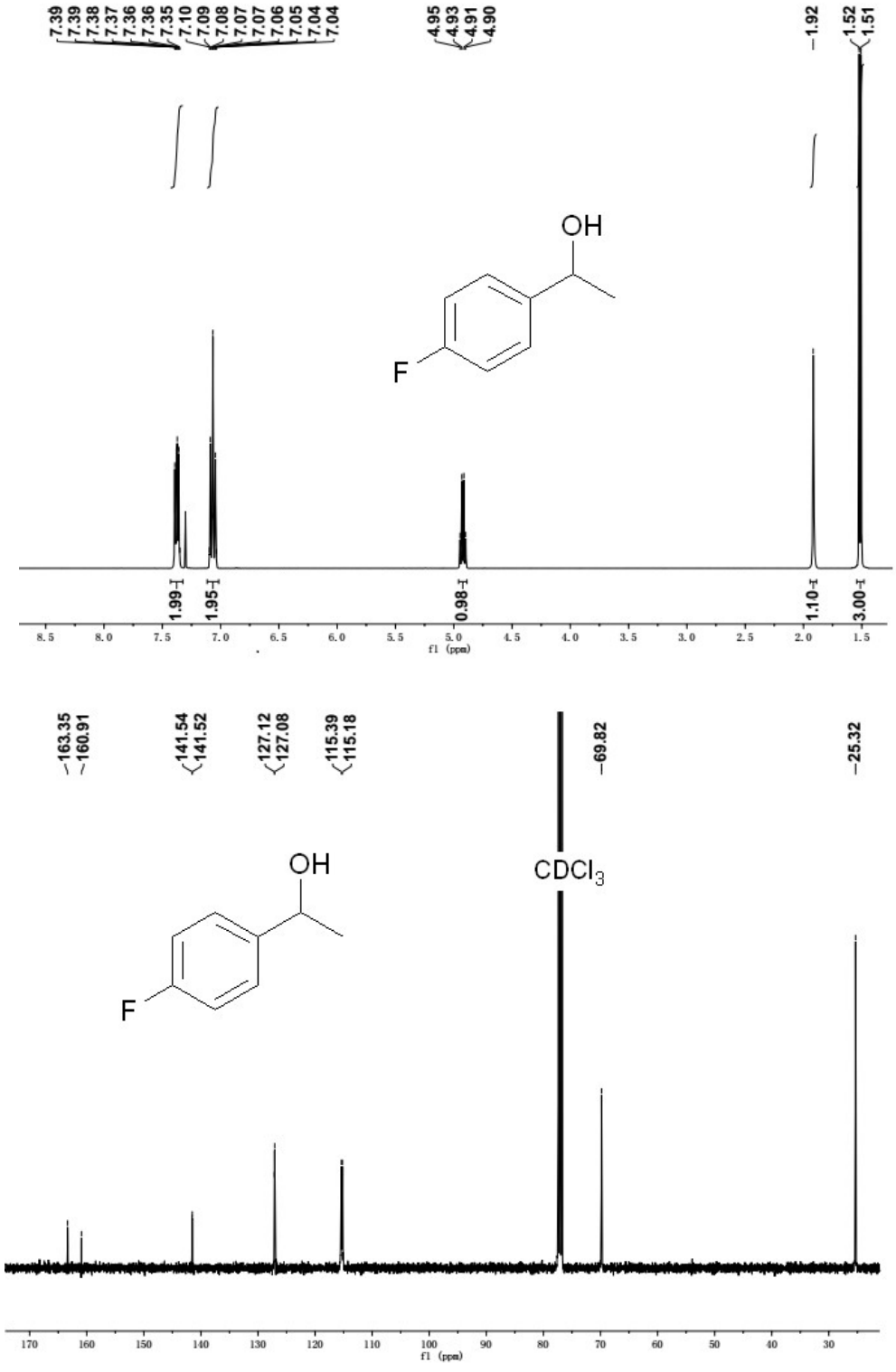


Figure S22 ^{1}H and ^{13}C NMR spectra of 1-(4-chlorophenyl)ethan-1-ol in $CDCl_3$

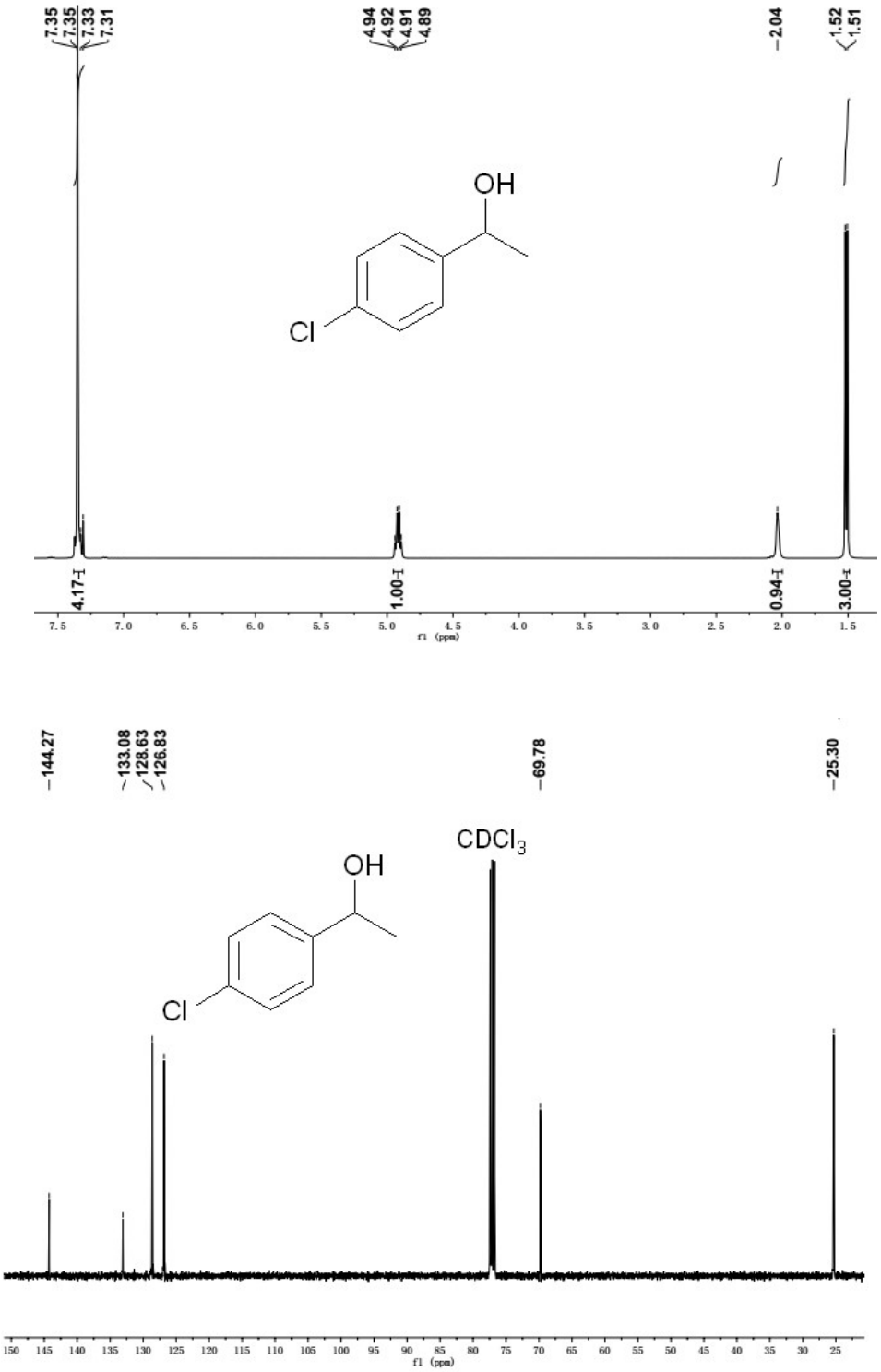
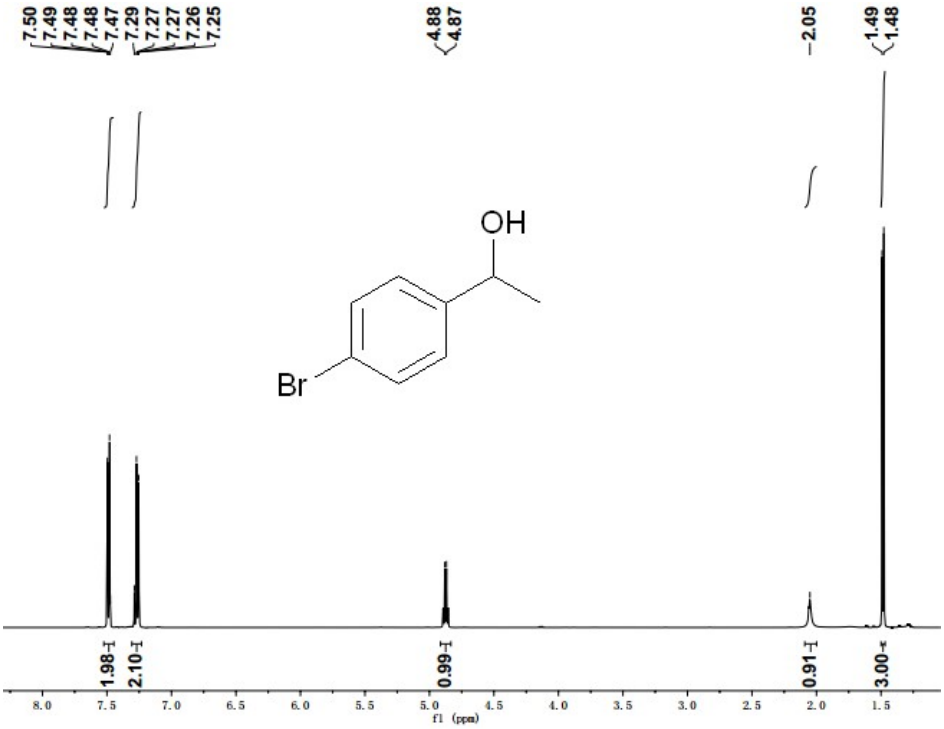


Figure S23 ^{1}H and ^{13}C NMR spectra of 1-(4-bromophenyl)ethan-1-ol in $CDCl_3$



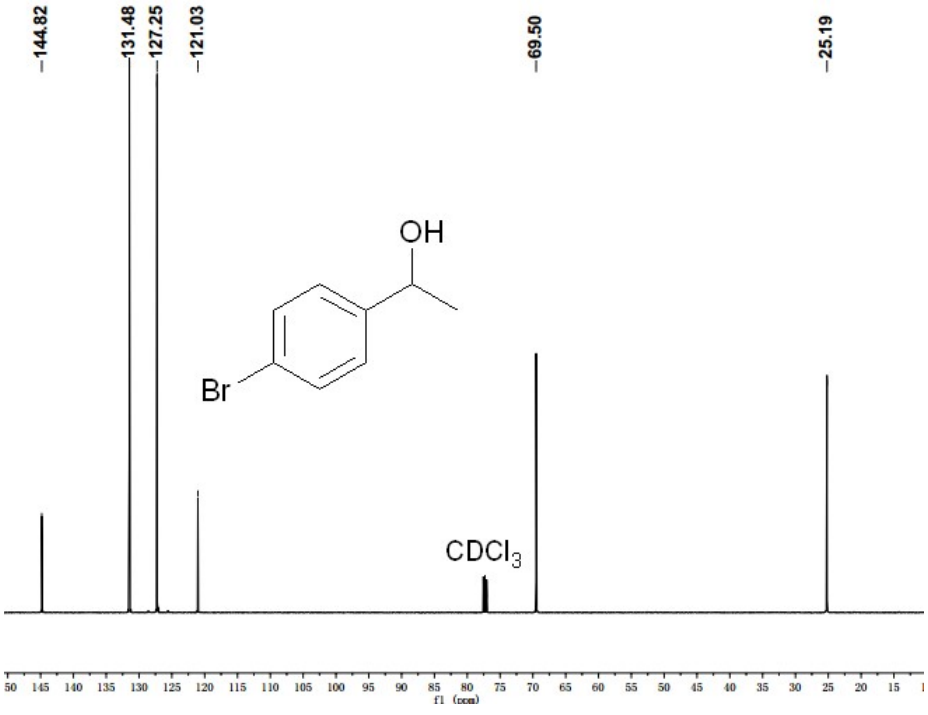
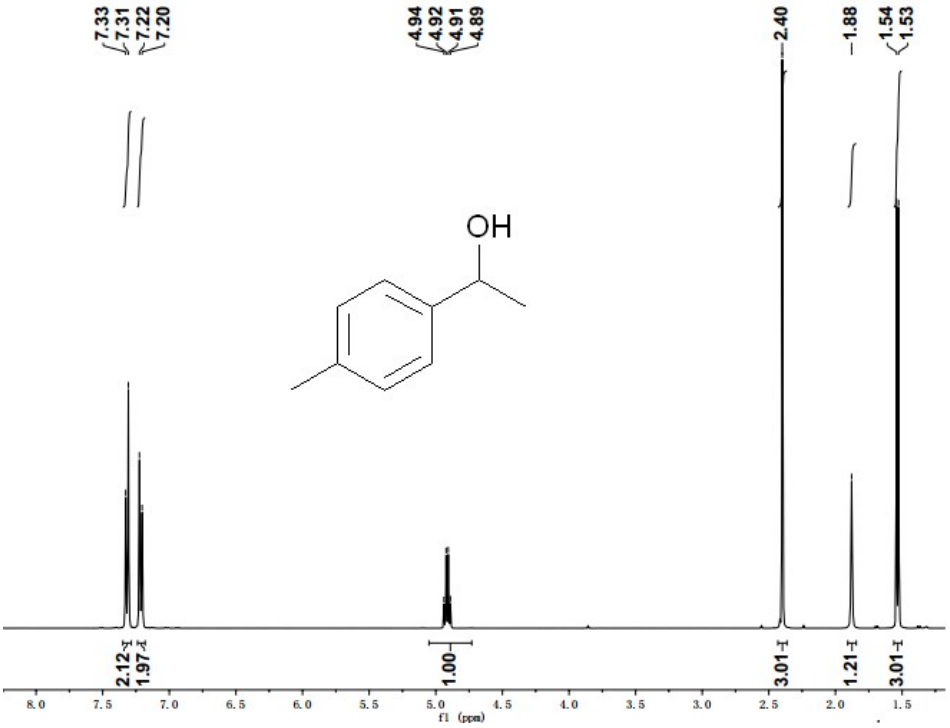


Figure S24 ^{1}H and ^{13}C NMR spectra of 1-(p-tolyl)ethan-1-ol in $CDCl_3$



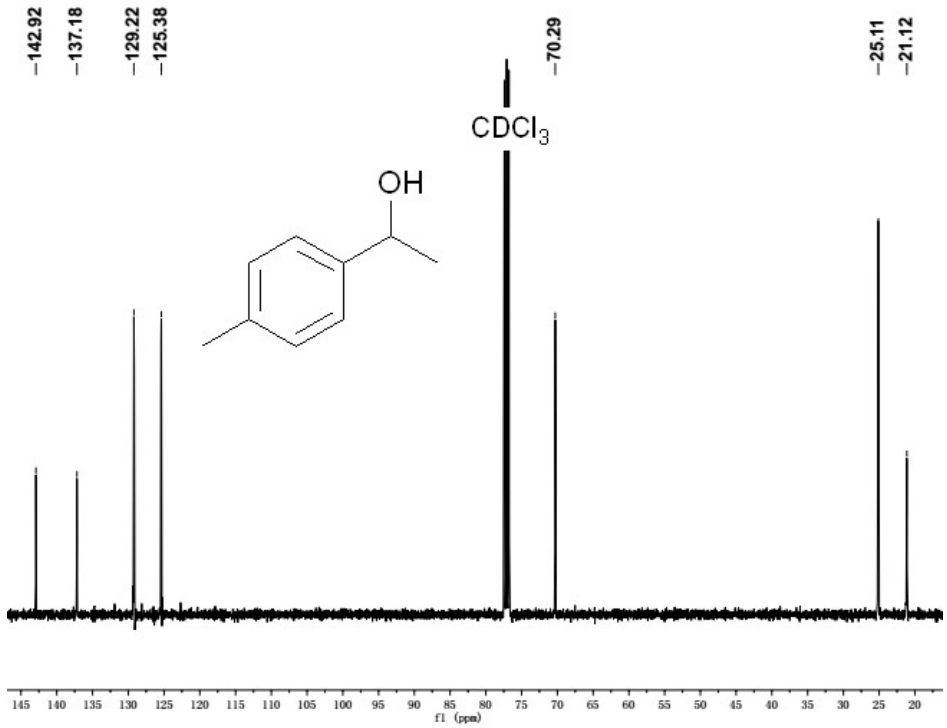


Figure S25 ^{1}H and ^{13}C NMR spectra of 1-(4-methoxyphenyl)ethan-1-ol in $CDCl_3$

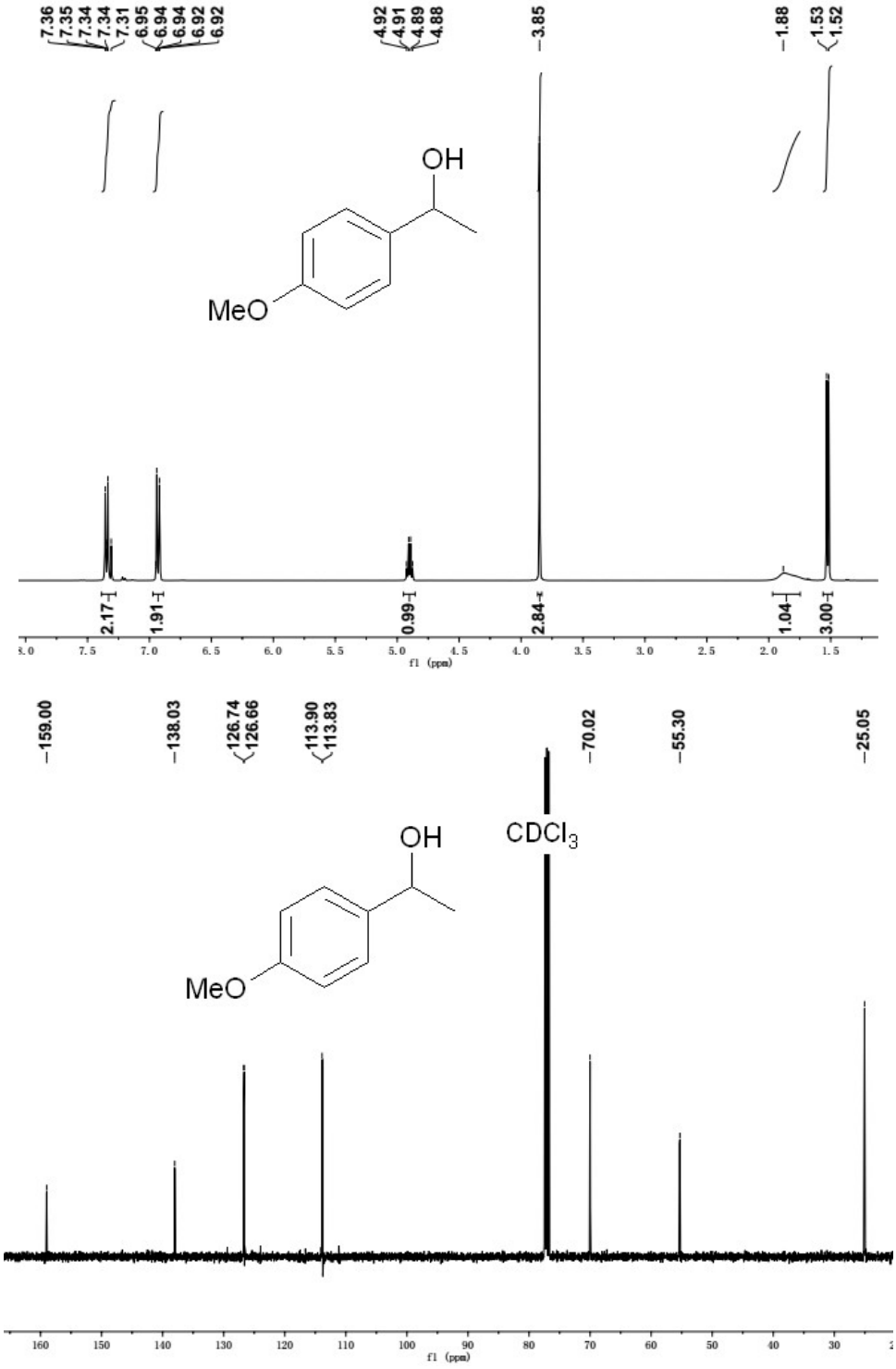


Figure S26 ^{1}H and ^{13}C NMR spectra of 1-(3-chlorophenyl)ethan-1-ol

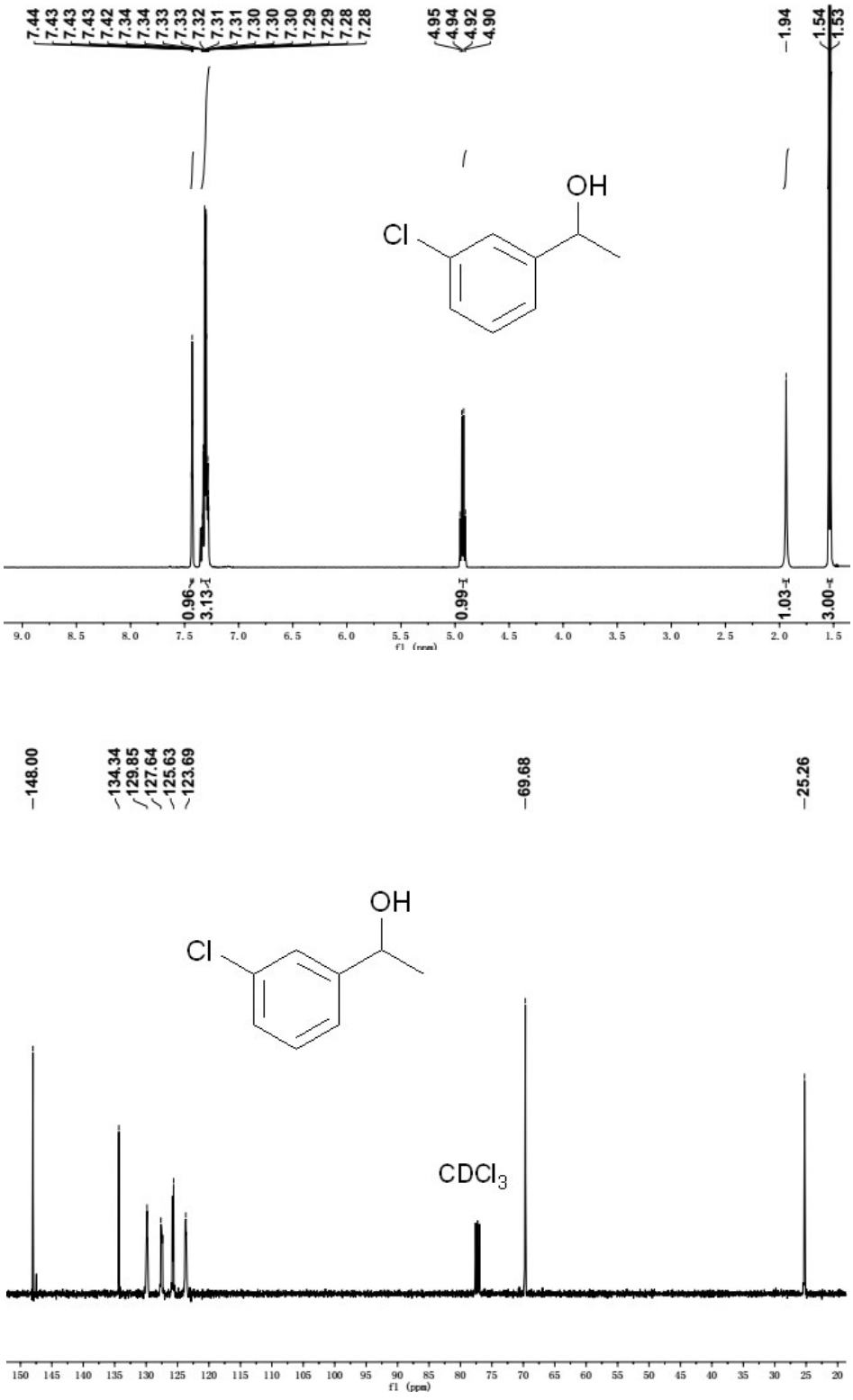


Figure S27 ^{1}H and ^{13}C NMR spectra of 1-(3-bromophenyl)ethan-1-ol

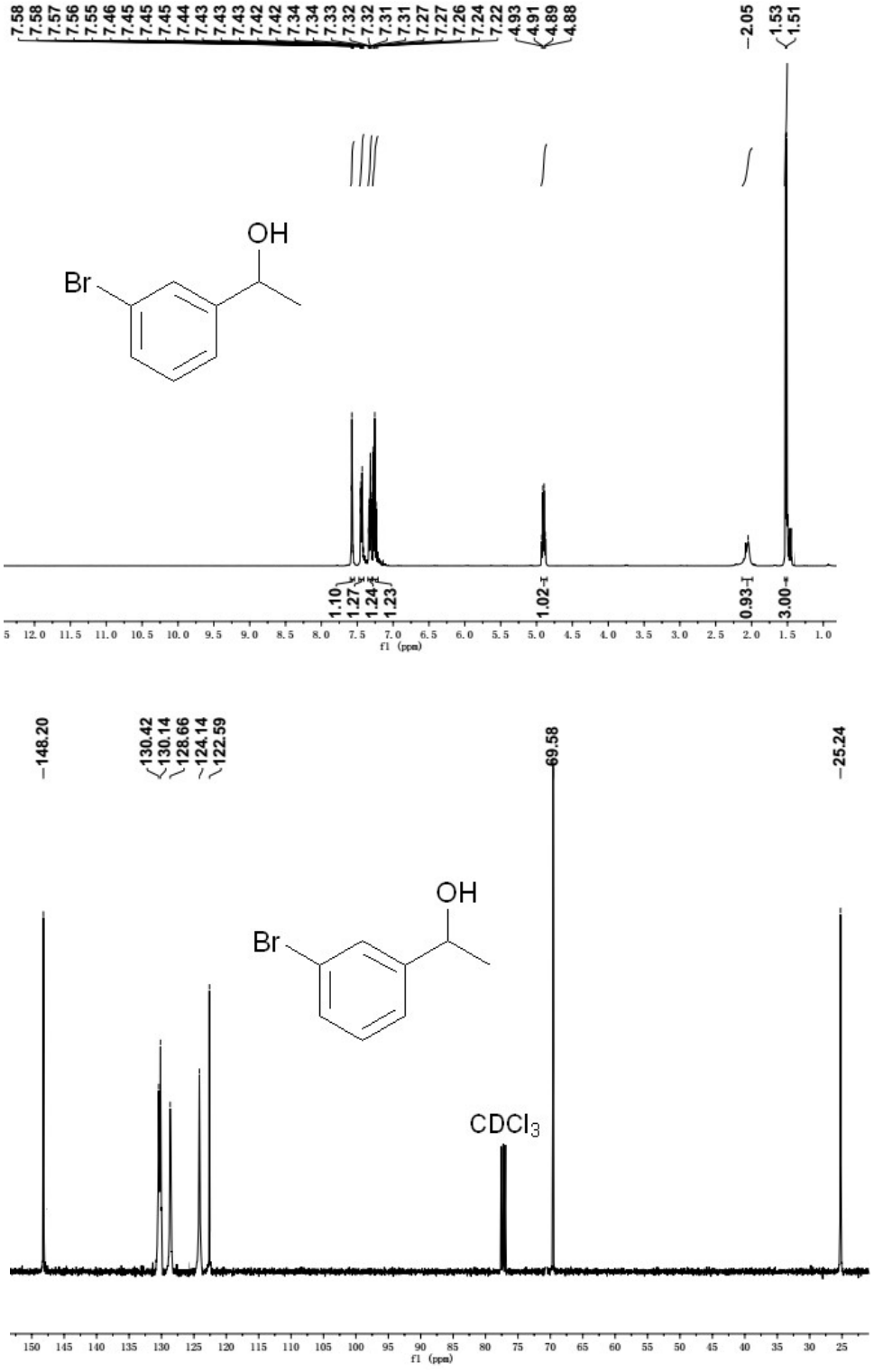
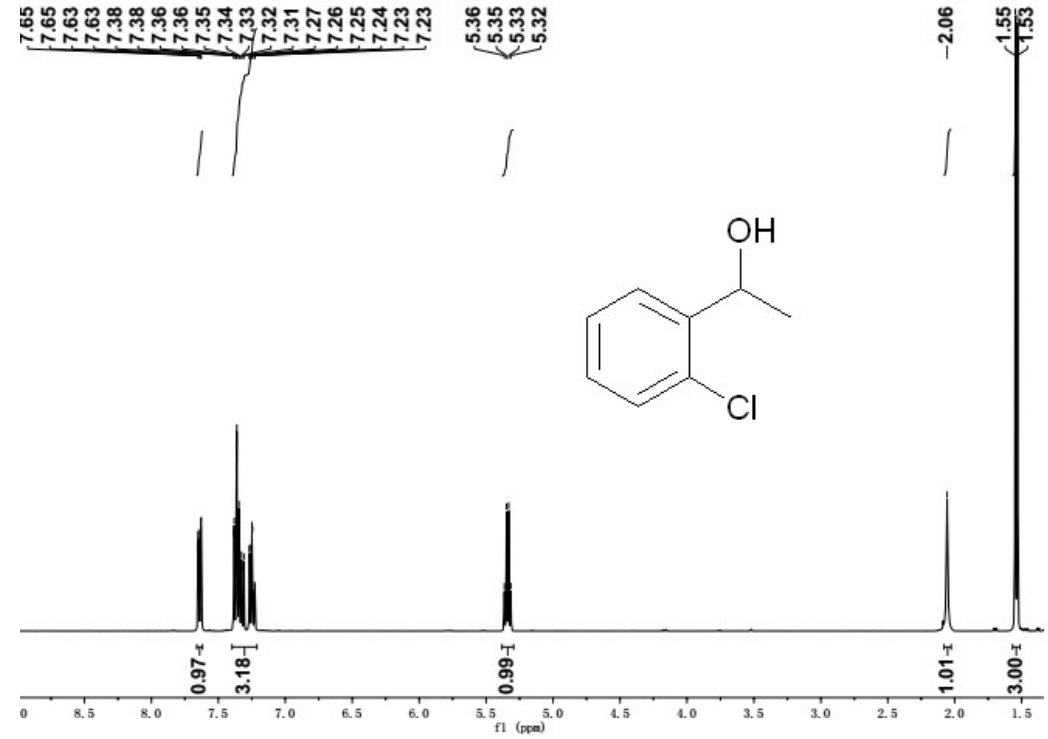


Figure S28 ^{1}H and ^{13}C NMR spectra of 1-(2-chlorophenyl)ethan-1-ol



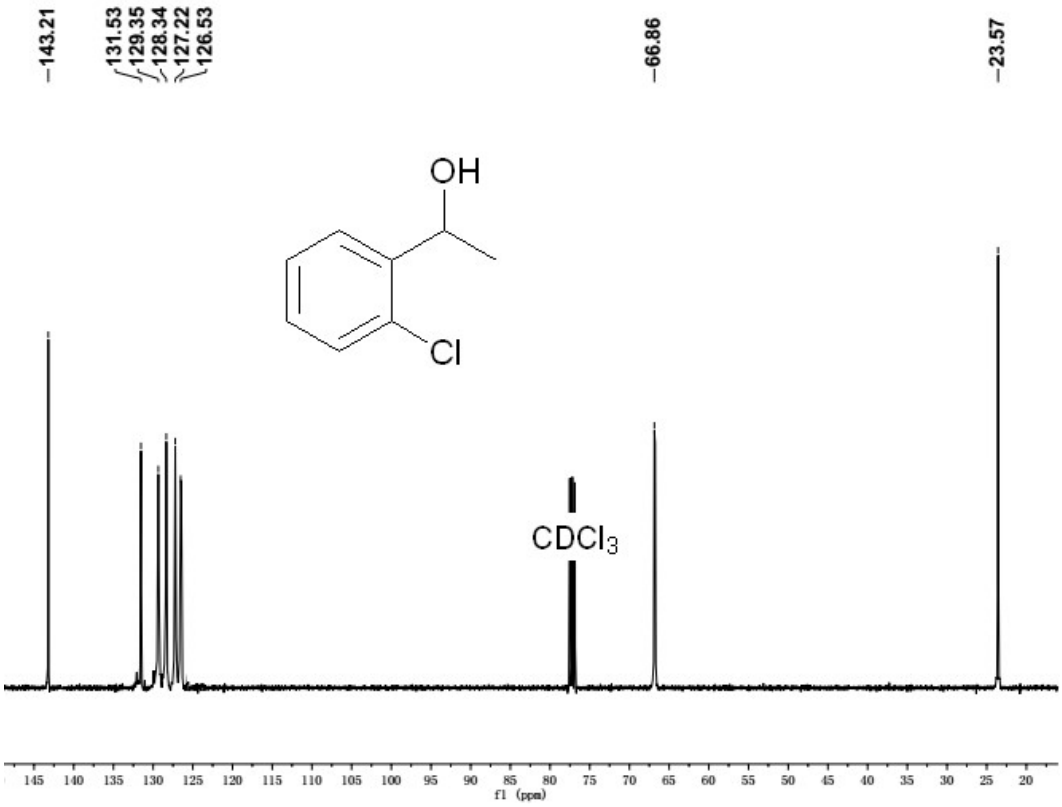


Figure S29 ^{1}H and ^{13}C NMR spectra of 1-(1-tolyl)ethan-1-ol

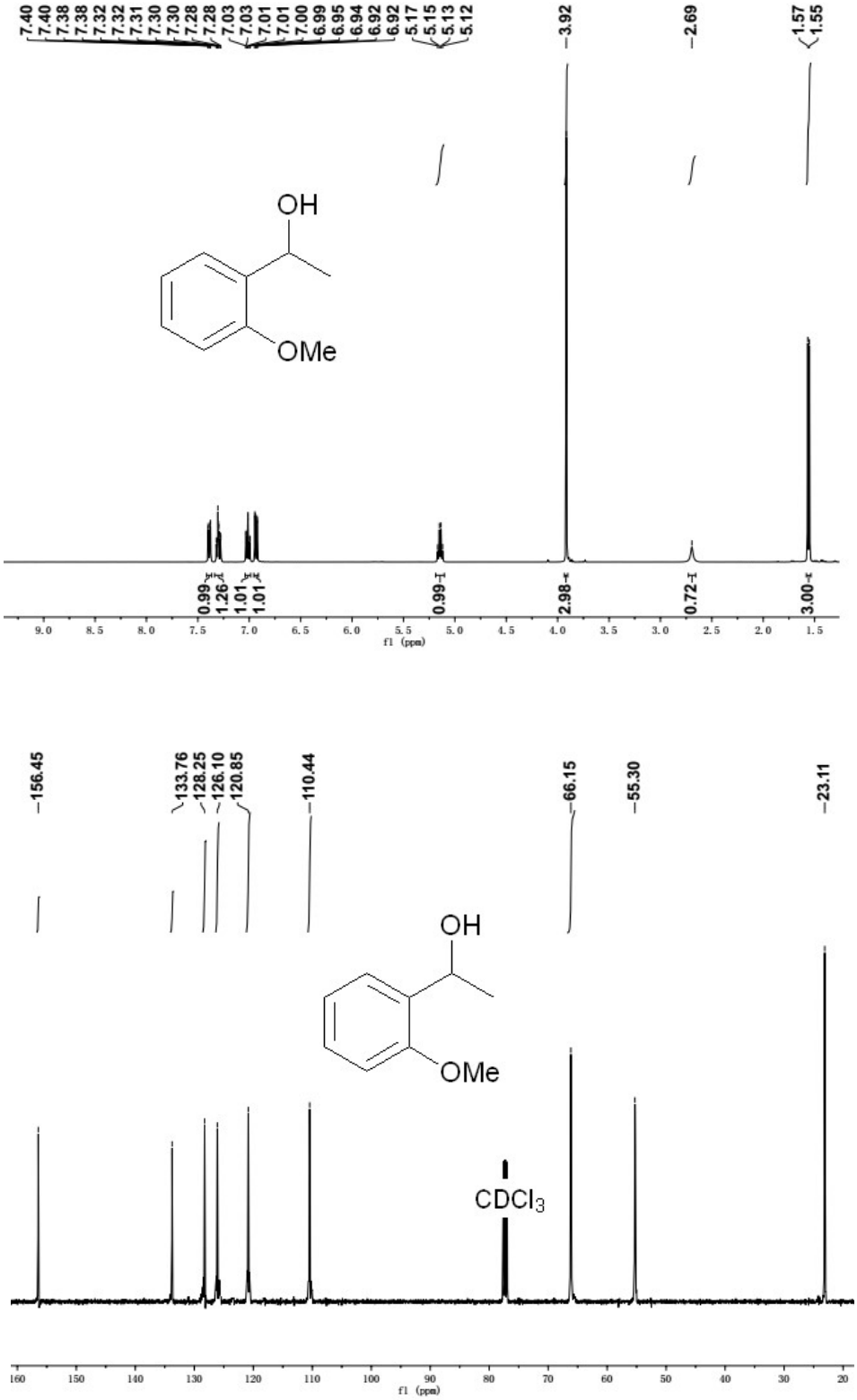


Figure S30 ^{1}H and ^{13}C NMR spectra of 1-(naphthalen-2-yl)ethan-1-ol

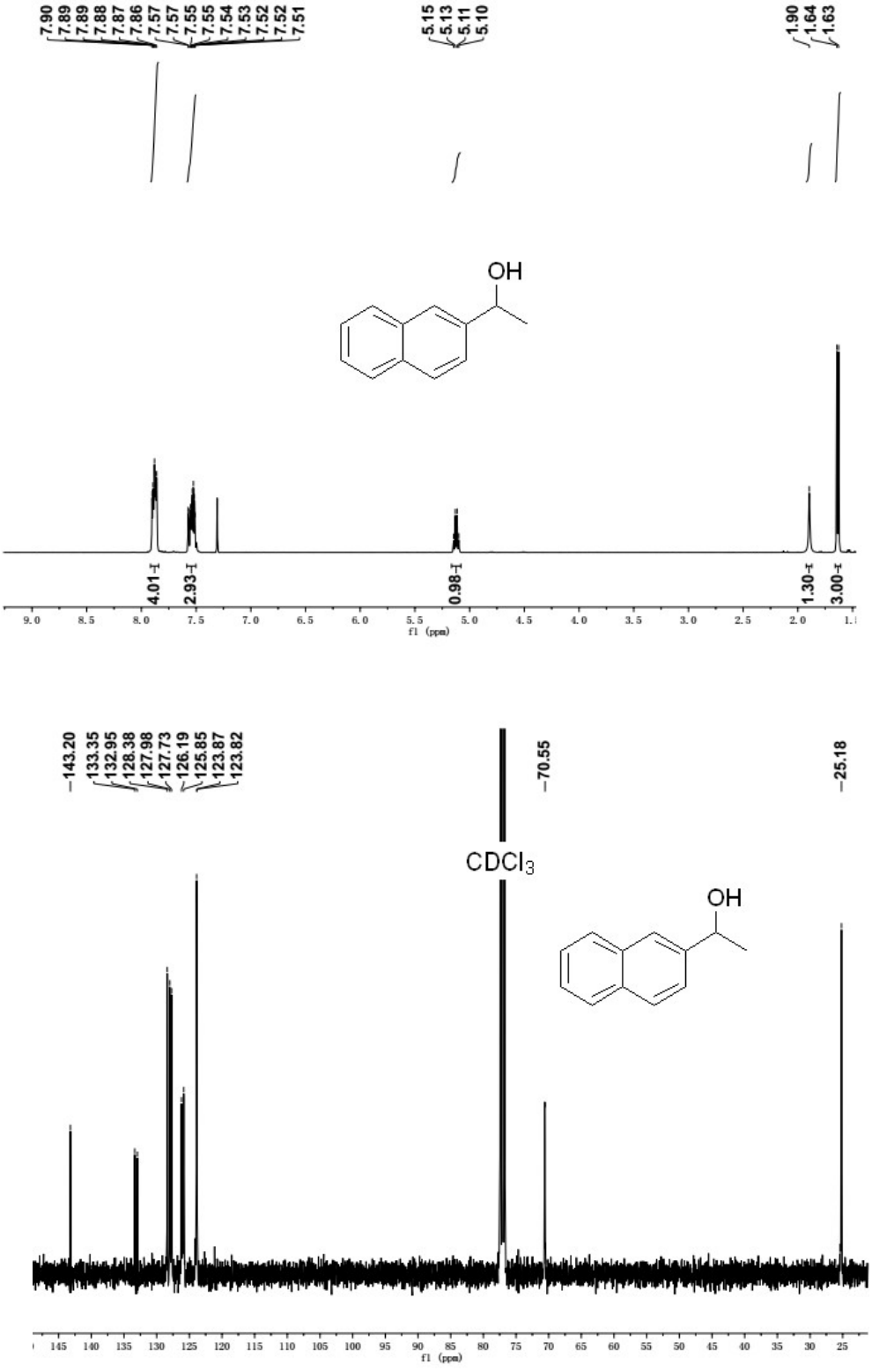
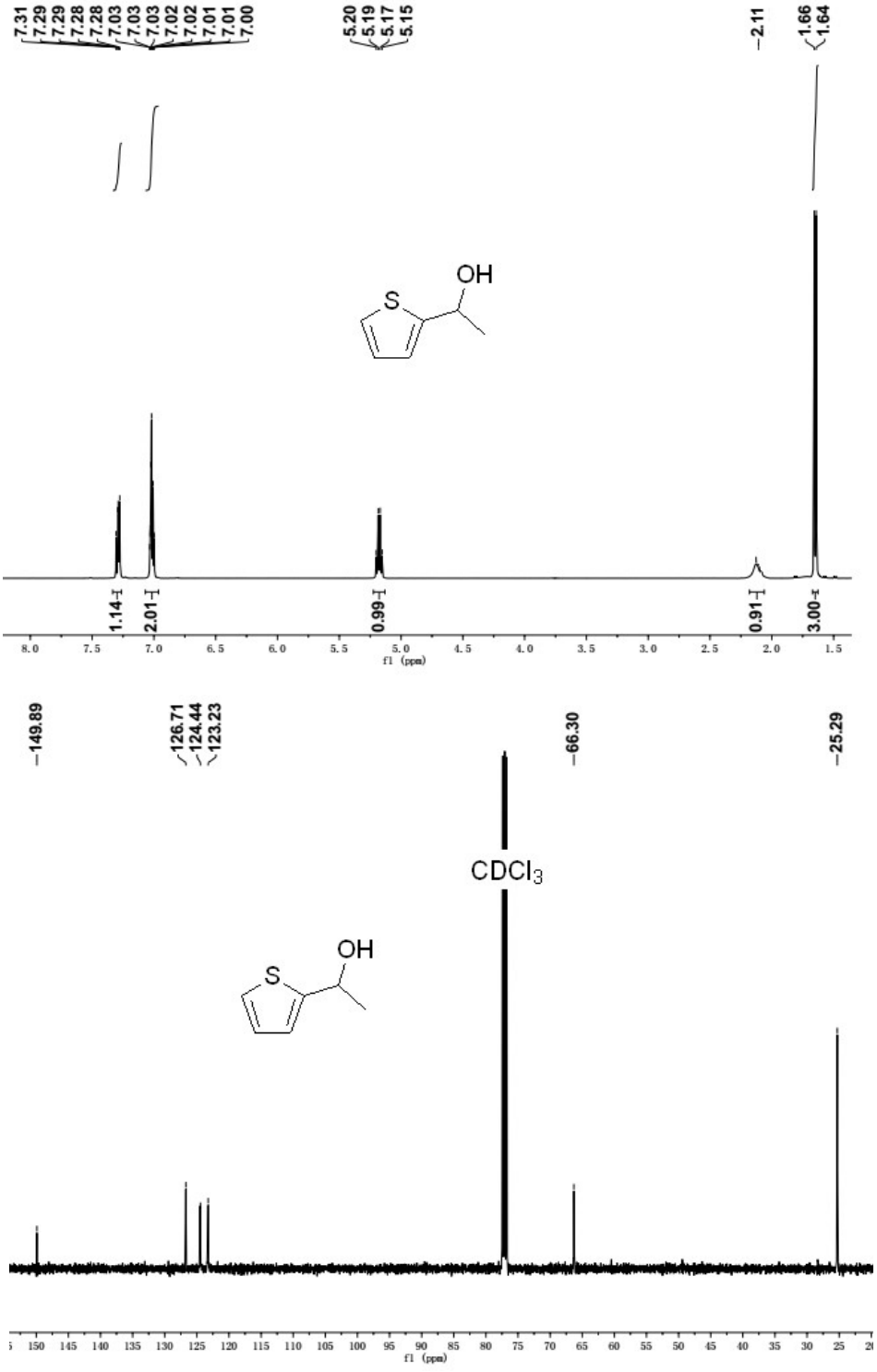


Figure S31 ^{1}H and ^{13}C NMR spectra of 1-(thiophen-2-yl)ethan-1-ol



6. X-ray structure determination

Table S4 crystal data and structure refinement for **Mo1**, **Mo3** and **Mo6**.

Identification code	**Mo1**	**Mo3**	**Mo6**
CCDC	2164839	2164840	2164841
Empirical formula	$C_{16}H_{21}MoN_3O_3$	$C_{21}H_{29}MoN_3O_4$	$C_{22}H_{35}BrMoN_3O_2$
Formula weight	399.30	483.41	548.37
Temperature/K	170.00(11)	169.99(10)	169.99(13)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	Ia	$P2_1/c$
a/Å	8.2042(2)	14.5555(2)	13.78177(12)
b/Å	8.6141(2)	10.47576(13)	8.83757(7)
c/Å	12.2400(4)	15.7041(2)	19.27005(17)
α/°	83.525(2)	90	90
β/°	78.867(2)	109.6233(17)	98.1502(9)
γ/°	78.108(2)	90	90
Volume/Å^3	828.13(4)	2255.48(6)	2323.34(4)
Z	2	4	4
ρ_{calc}g/cm^3	1.601	1.4235	1.5676
μ/mm^{-1}	6.637	5.008	6.804
F(000)	408.0	1002.5	1119.5
Crystal size/mm^3	0.35 × 0.25 × 0.2	0.15 × 0.12 × 0.08	0.24 × 0.18 × 0.12
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/	7.382 to 150.828	10.34 to 150.08°	6.48 to 150.46°
Index ranges	-10 ≤ h ≤ 9, -10 ≤ k ≤ 10, -12 ≤ l ≤ 15	-18 ≤ h ≤ 18, -11 ≤ k ≤ 12, -19 ≤ l ≤ 17	-17 ≤ h ≤ 17, -8 ≤ k ≤ 10, -24 ≤ l ≤ 24
Reflections collected	9490	7902	17413
Independent reflections	3261 [R_{int} = 0.0171, R_{sigma} = 0.0156]	3542 [R_{int} = 0.0181, R_{sigma} = 0.0200]	4623 [R_{int} = 0.0272, R_{sigma}= 0.0207]
Data/restraints/parameters	3261/0/210	3542/0/266	4623/0/265
Goodness-of-fit on F^2	1.052	1.038	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0192, wR_2 = 0.0493	R_1= 0.0189, wR_2= 0.0509	R_1= 0.0280, wR_2= 0.0771
Final R indexes [all data]	R_1 = 0.0193, wR_2 = 0.0493	R_1= 0.0190, wR_2= 0.0510	R_1= 0.0292, wR_2= 0.0778
Largest diff. peak/hole / e Å^{-3}	0.37/-0.50	0.35/-0.43	0.44/-0.85

7. Reference

(1) S. Anderson, D. J. Cook, and A. F. Hill, *Organometallics,* 2001, **20***,* 2468-2476.

(2) (a) J. Ellermann, M. Moll and N. Will, *J. Organomet. Chem,.*1989, **378**, 73-79; (b) O. Oztopcu, C. Holzhacker, M. Puchberger, M. Weil, K. Mereiter, L. F. Veiros and K. Kirchner, *Organometallics,* 2013, **32**, 3042-3052.

(3) Z. Wang, Q. Lin, N. Ma, S. Liu, M. Han, X. Yan, Q. Liu, G. A. Solan, and W. -H. Sun, *Catal. Sci. Technol*., 2021, **11**, 8026–8036.

(4) (a) S. Chakraborty, O. Blacque, T. Fox and H. Berke, *Chem. Asian J.,* 2014, **9**, 328-337; (b) Z. Wang, X. Chen, B. Liu, Q. Liu, G. A. Solan, X. Yang and W.-H. Sun, *Catal. Sci. Technol.*, 2017, **7**, 1297-1304