SUPPORTING INFORMATION

Mn(I) Phosphine-Amino-Phosphinites: A Highly Modular Class of Pincer Complexes for Enantioselective Transfer Hydrogenation of Aryl-Alkyl ketones

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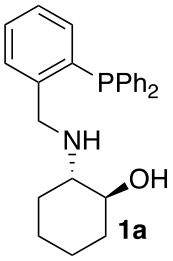
1. General

Reactions were performed under an argon atmosphere using Schlenk techniques and flame-dried glassware or in a glove box. All the chemicals were used as received. Apart from acetone and ethyl acetate, all organic solvents were distilled over standard drying agents (2-propanol, methanol, triethylamine, dichloromethane: calcium hydride; tetrahydrofuran, pentane, hexane: sodium/benzophenone; toluene: sodium) and freshly used or stored over molecular sieves. All solvents, including deionized water, were degassed prior to use by nitrogen bubbling for 1 h.

NMR spectra were measured on Bruker Avance DPX 300 (^{1}H, 300.1; ^{13}C, 75.5; ^{19}F, 282.4; ^{31}P, 121.5), 400 (^{1}H, 400.1; ^{13}C, 100.6; ^{19}F, 376.5; ^{31}P, 162.0) or 500 (^{1}H, 500.2; ^{13}C, 125.8; ^{19}F, 470.7; ^{31}P, 202.5) spectrometers at room temperature (frequencies in MHz). Chemical shifts (δ) are reported in ppm and the multiplicity is indicated as: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, quint = quintet, hept = heptet, br = broad, m = multiplet). ^{1}H and ^{13}C NMR spectra are referenced to the solvent residual peak as internal standard ($CDCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C; CD_2Cl_2: δ 5.32 for ^{1}H, δ 54.00 for ^{13}C), ^{19}F NMR spectra to external $CFCl_3$ and ^{31}P NMR spectra to external 85% H_3PO_4. Infrared spectra were measured on a Nicolet 6700 FT-IR Spectrometer – Thermo Scientific. Wavenumbers (ν) are reported in cm^{-1}. High-resolution mass spectra were measured on a BrukerDaltonics maXis – ESI-Qq-TOF-MS spectrometer (Laboratory of Organic Chemistry, ETH Zürich). The molecular ion is reported in *m*/*z* unit. Elemental analyses were performed on a TruSpec Micro – LECO instrument (Laboratory of Microelemental Analysis, ETH Zürich). Enantiomeric excesses were determined by chiral HPLC on a UltiMate 3000 HPLC – Thermo Fisher Scientific with Chiralpak IB–3 columns and by chiral GC using a Trace1310 GC – Thermo Fisher Scientific gas chromatograph with a β–DEX column at constant oven temperature. Yields were determined by chiral GC using a Trace1310 GC – Thermo Fisher Scientific with a β–DEX column at constant oven temperature or by ^{1}H NMR spectroscopy. All the reactions has been repeated at least twice for confirming the reproducibility.

2. Synthesis of Ligand Precursors (1a-1b)



1a

Synthesis of (1*S*,2*S*)-2-((2-(diphenylphosphaneyl)benzyl) amino)cyclohexan-1-ol (1a): A 0.02M solution of of 2-(diphenylphosphaneyl)benzaldehyde (2.5 g, 8.68 mmol, 1.0 equiv) and (1*S*,2*S*)-2-aminocyclohexan-1-ol (1 g, 8.68 mmol, 1.0 equiv) in anhydrous MeOH was stirred at room temperature for 18 h. After full conversion (monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR), $NaBH_4$ (1.64 g, 5.0 equiv) was added, and the solution was stirred further for 3 h. Then the reaction was quenched with degassed water after confirming the disappearance of the imine proton by ^{1}H NMR. The volatiles were removed by rotary evaporation under inert atmosphere. The aqueous phase was then extracted with CH_2Cl_2. The combined organic layers were washed with degassed H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo for 24 h. The crude product was purified by column chromatography (Hexane: Ethyl acetate = 1:1) to obtain the desired product as a white solid (2.97 g, 88% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.48–7.46 (m, 1H, Ar-*H*), 7.36–7.32 (m, 7H, Ar-*H*), 7.29–7.25 (m, 4H, Ar-*H*), 7.20–7.16 (m, 1H, Ar-*H*), 6.93–6.91 (m, 1H, Ar-*H*), 4.12 (d, *J* = 11.5 Hz, 1H, BzC*H*H), 3.90 (d, *J* = 12.6 Hz, 1H, BzC*H*H), 3.28 (br s, 1H, O*H*), 3.03–2.98 (m, 1H, OC*H*), 2.20–2.15 (m, 1H, NC*H*H), 2.07–2.03 (m, 1H, N*H*), 1.94–1.91 (m, 1H, CyC*H*), 1.68–1.64 (m, 2H, CyC*H*), 1.28–1.11 (m, 4H, CyC*H*), 0.90–0.82 (m, 1H, CyC*H*). **$^{13}C\{^{1}H\}$ APT** (126 MHz, CD_2Cl_2) δ 145.2 (arom.), 145.0 (arom.), 137.3 (d, *J* = 10.6 Hz, arom.), 137.1 (d, *J* = 10.1 Hz, arom.), 136.1 (d, *J* = 13.1 Hz, arom.), 133.9 (arom.), 133.8 (arom.), 133.7 (arom.), 129.4 (arom.), 129.0 (arom.), 128.8 (arom.), 128.7 (arom.), 128.6 (arom.), 127.3 (arom.), 73.8 (O*C*H), 63.4 (N*C*H*)*, 49.7 (d, *J* = 19.9 Hz, Bz*C*H), 33.3 (Cy*C*H), 30.6 (Cy*C*H), 25.3 (Cy*C*H), 24.4 (Cy*C*H). **$^{31}P\{^{1}H\}$ NMR** (203 MHz, CD_2Cl_2) δ –16.0. **HRMS (ESI)** *m*/*z* calcd for $[C_{25}H_{28}NNaOP]^{+}$: 412.18 $[M]^{+}$; found: 412.1801. **EA** Calcd. for $C_{25}H_{28}NOP$: C, 77.10; H, 7.25; N, 3.60s; Found: C, 77.24; H, 7.10; N, 3.66.

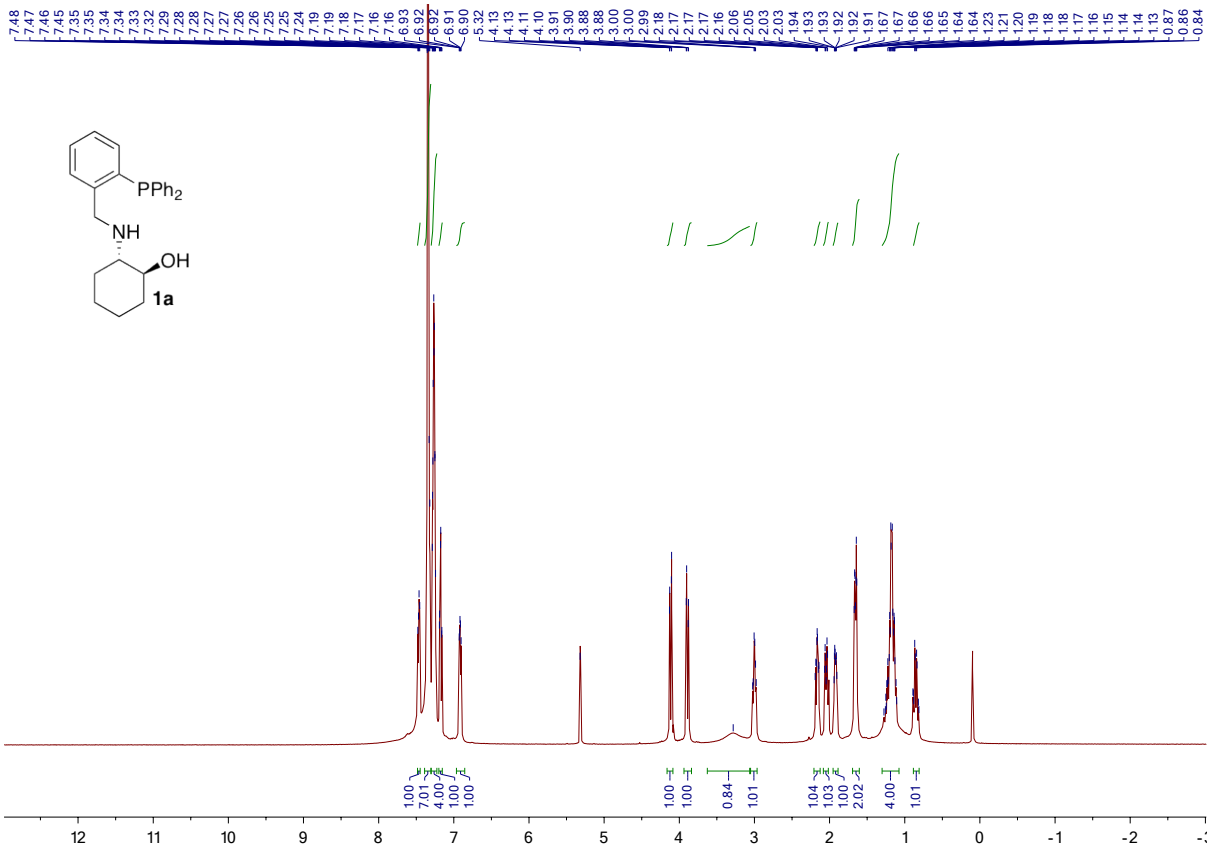


Figure S1. ^{1}H NMR spectrum of **1a** (500 MHz, CD_2Cl_2).

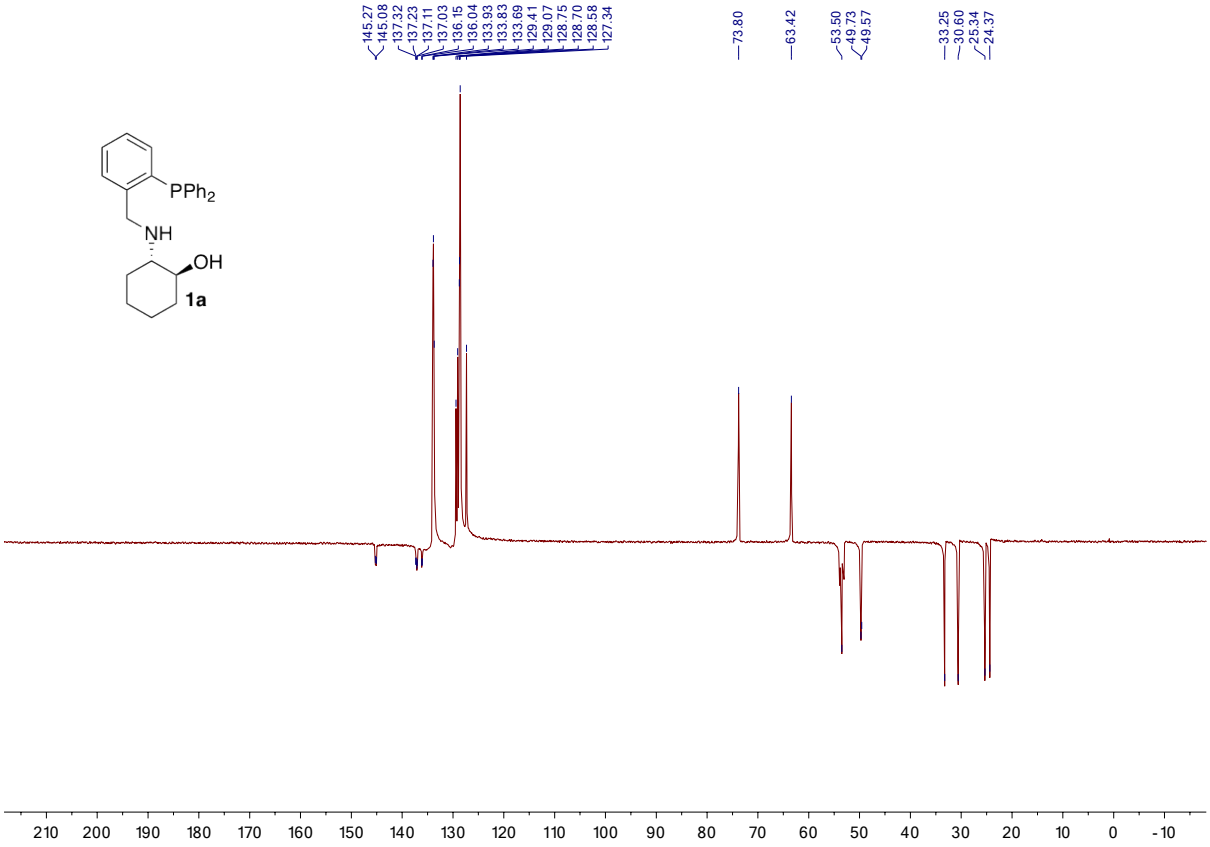


Figure S2. $^{13}C\{^{1}H\}$ APT NMR spectrum of **1a** (126 MHz, CD_2Cl_2).

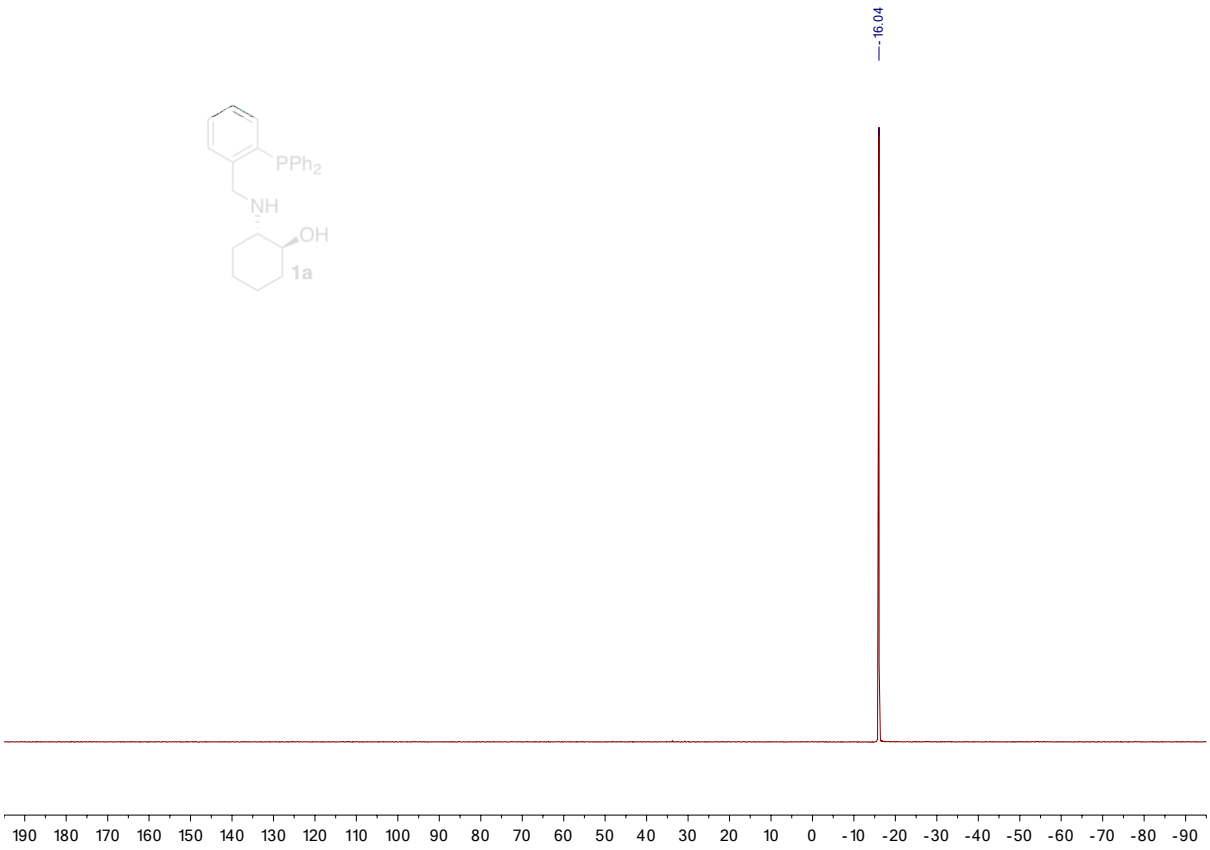
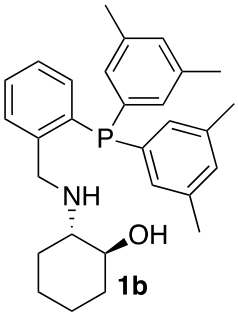


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1a** (203 MHz, CD_2Cl_2).



Synthesis of (1*S*,2*S*)-2-((2-(bis(3,5-dimethylphenyl)phosphene)benzyl) amino)cyclohexan-1-ol (1b): A 0.02M solution of of 2-(3,5-dimethylphenyl phosphaneyl)benzaldehyde (3 g, 8.68 mmol, 1.0 equiv) and (1*S*,2*S*)-2-aminocyclohexan-1-ol (1 g, 8.68 mmol, 1.0 equiv) in anhydrous MeOH was stirred at room temperature for 18 h. After full conversion (monitored by ^{1}H and $^{31}P\{^{1}H\}$ NMR), $NaBH_4$ (1.65 g, 5.0 equiv) was added, and the solution was stirred further for 3 h. The reaction was quenched with degassed water after confirming the disappearance of the imine proton by ^{1}H NMR, and then the volatiles were removed by rotary evaporation under inert atmosphere. The aqueous phase was then extracted with CH_2Cl_2. The combined organic layers were washed with degassed H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo for 24 h. The crude product was purified by column chromatography (Hexane: Ethyl acetate = 1:1) to obtain the desired product as a white solid (3.32 g, 86% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.48-7.46 (m, 1H, Ar-*H*),

7.34–7.30 (m, 1H, Ar-*H*), 7.19–7.15 (m, 1H, Ar-*H*), 6.99 (s, 1H, Ar-*H*), 6.95–6.92 (m, 1H, Ar-*H*), 6.90–6.87 (m, 4H, Ar-*H*), 4.10 (d, *J* = 11.9 Hz, 1H, BzC*H*H), 3.84 (d, *J* = 12.1 Hz, 1H, BzC*H*H), 3.35 (br s, 1H, O*H*), 3.05–3.00 (m, 1H, OC*H*), 2.25 (s, 12H, CH_3*H*), 2.18–2.12 (m, 1H, NC*H*H), 2.05–2.01 (m, 1H, N*H*), 1.95–1.92 (m, 1H, CyC*H*), 1.68–1.64 (m, 2H, CyC*H*),1.28–1.12 (m, 4H, CyC*H*), 0.90–0.81 (m, 1H, CyC*H*). **^{13}C{^{1}H} APT** (126 MHz, CD_2Cl_2) δ 145.0 (arom.), 144.8 (arom.), 138.1 (d, *J* = 7.2 Hz, arom.), 138.0 (d, *J* = 7.2 Hz, arom.), 136.8 (d, *J* = 9.6 Hz, arom.), 136.6 (arom.), 136.5 (d, *J* = 9.6 Hz, arom.), 133.8 (arom.), 131.6 (arom.), 131.6 (arom.), 131.5 (arom.), 131.4 (arom.), 130.5 (d, *J* = 5.0 Hz, arom.), 129.3 (d, *J* = 5.1 Hz, arom.), 128.8 (arom.), 127.2 (arom.), 73.8 (O*C*H), 63.4 (N*C*H), 49.5 (d, *J* = 20.3 Hz, Bz*C*H), 33.3 (Cy*C*H), 30.6 (Cy*C*H), 25.4 (Cy*C*H), 24.4 (Cy*C*H), 21.1 (CH_3). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ –15.9. **HRMS (ESI)** *m*/*z* calcd for $[C_{29}H_{36}NNaOP]^+$: 468.2427 $[M]^+$; found: 468.2423. **EA** Calcd. for $C_{29}H_{36}NOP$: C, 78.17; H, 8.14; N, 3.14; Found: C, 78.21; H, 8.11; N, 3.27.

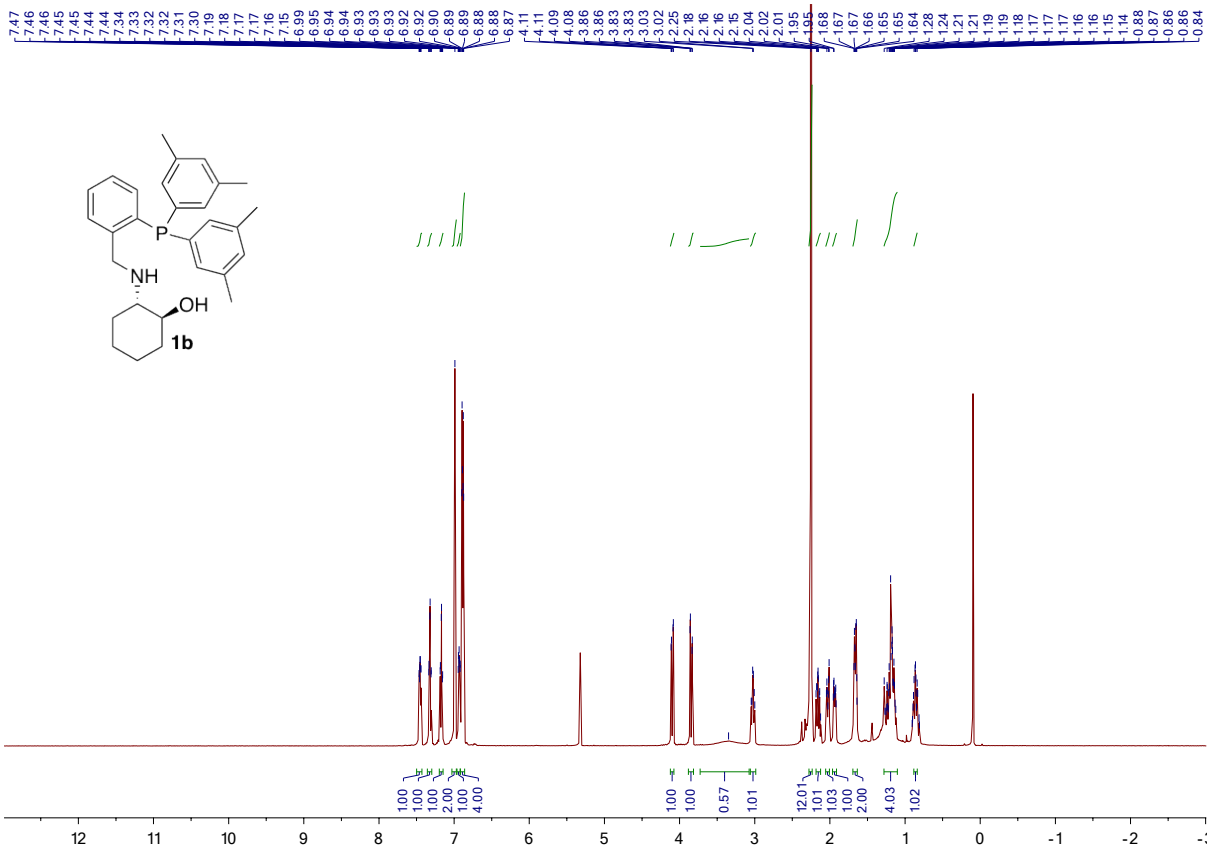


Figure S4. ^{1}H NMR spectrum of **1b** (500 MHz, CD_2Cl_2).

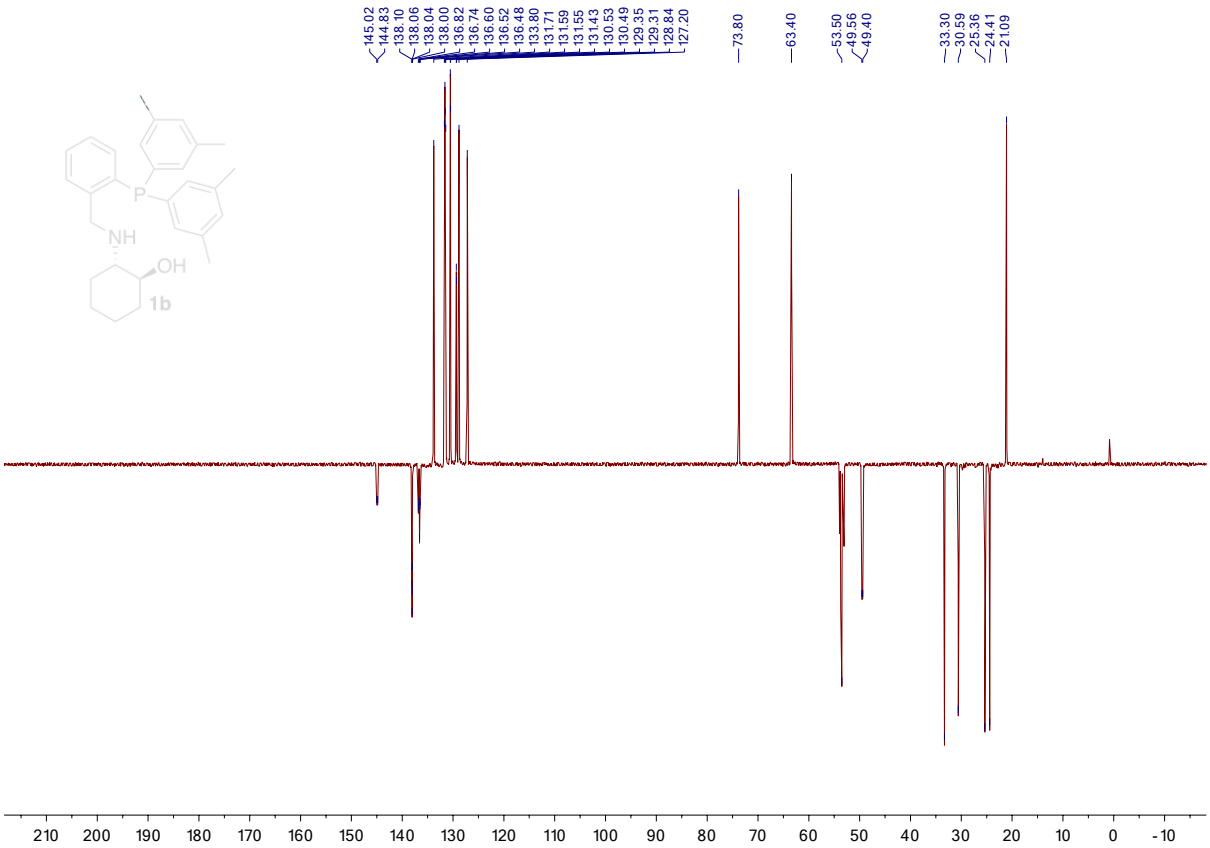


Figure S5. $^{13}C\{^{1}H\}$ APT NMR spectrum of **1b** (126 MHz, CD_2Cl_2).

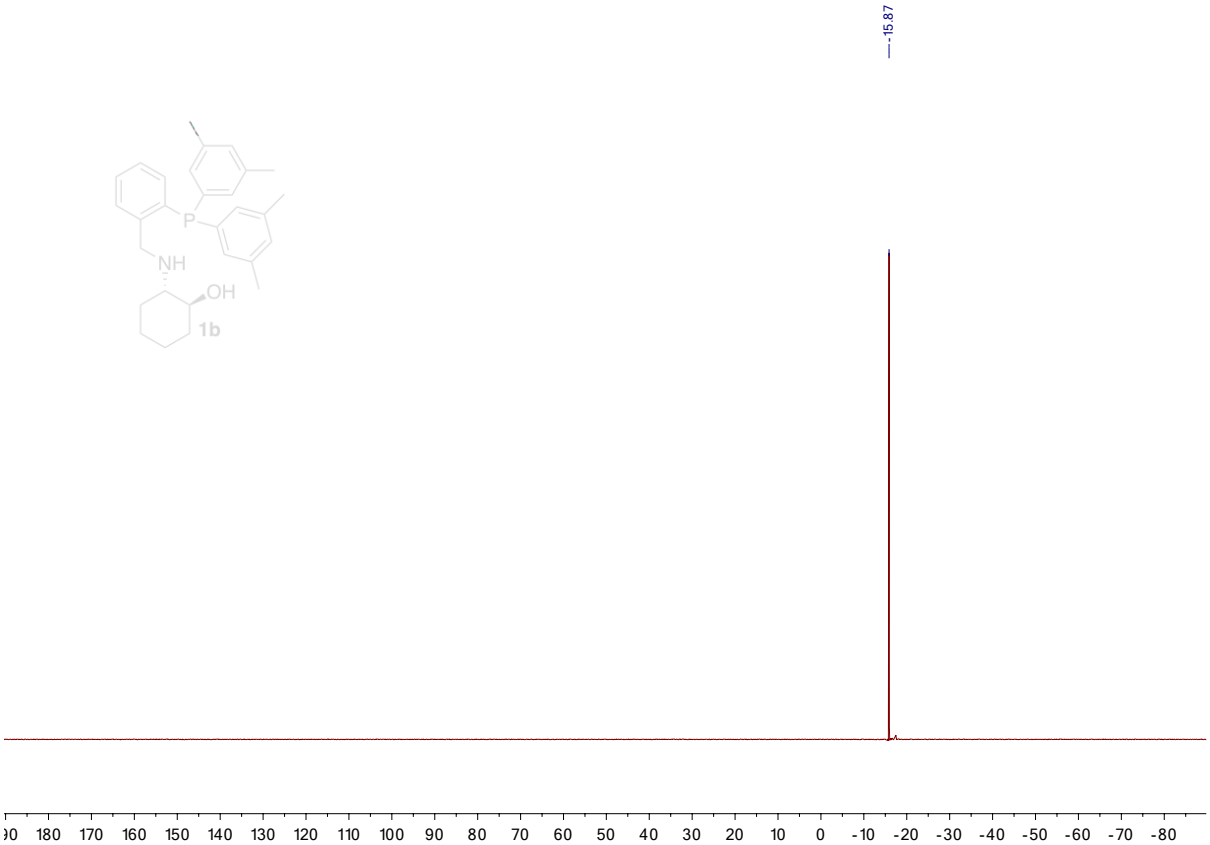


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** (203 MHz, CD_2Cl_2).

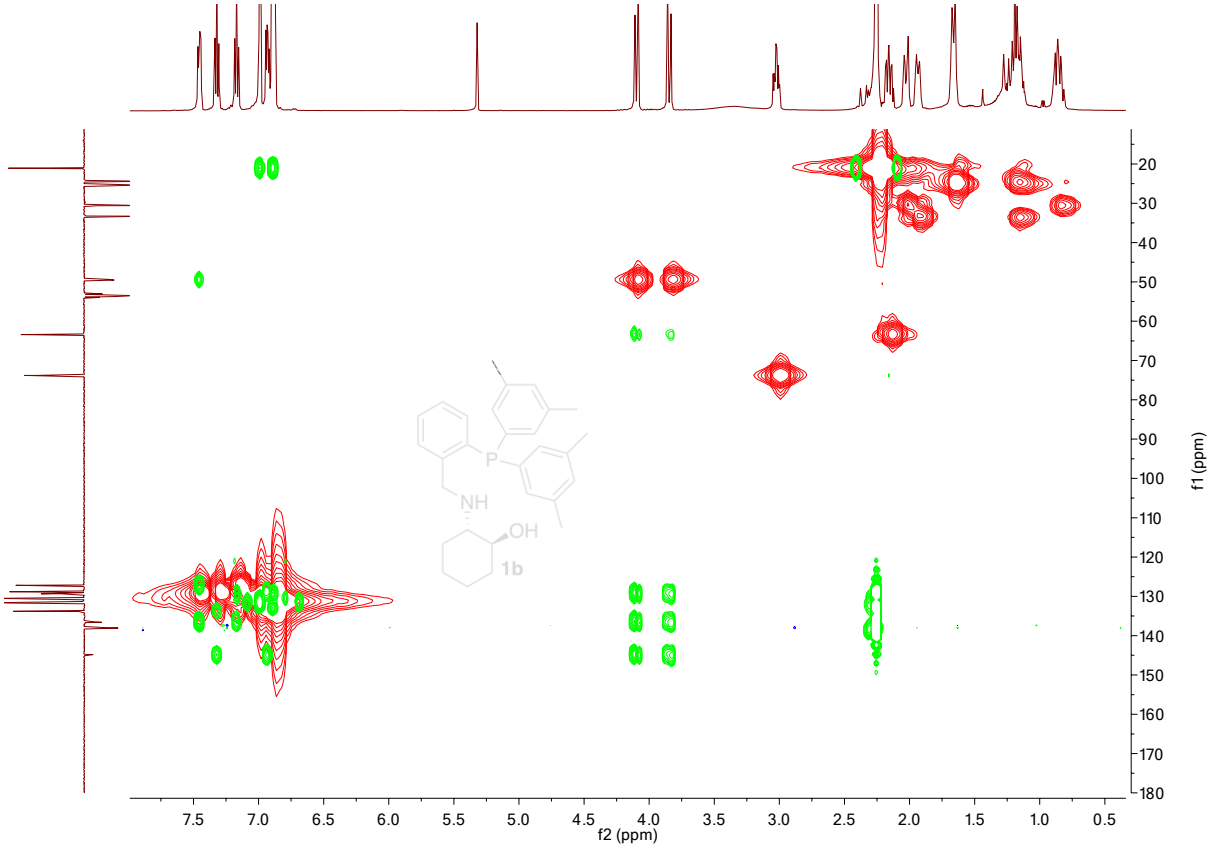


Figure S7. ^{13}C-^{1}HHSQC (red) and ^{13}C-^{1}H HMBC (green) of **1b** superimposed.

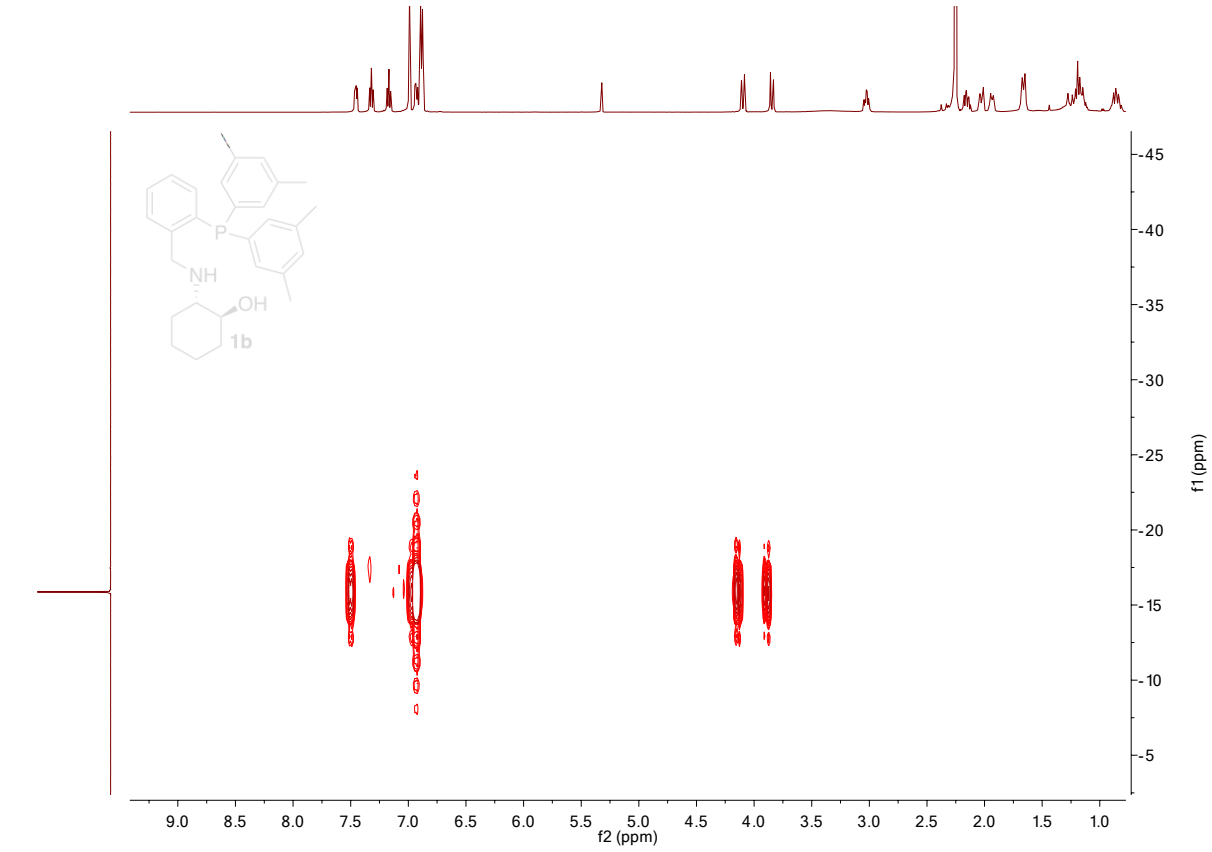
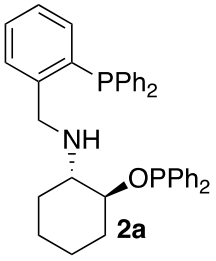


Figure S8. ^{31}P-^{1}H HSQC of ligand processor **1b**.

3. Synthesis of P'(O)N(H)P Ligands (2a-2b)



2a

Synthesis of *N*-(2-(diphenylphosphaneyl)benzyl)-2-((diphenylphosphaneyl)oxy)cyclo-hexan-1-amine (2a): To a 0.2M solution of (1*S*,2*S*)-2-((2-(diphenylphosphaneyl)benzyl)amino)-cycloh-exa-1-ol (1 g, 2.56 mmol, 1.0 equiv) in toluene, trimethylamine (5 mL, 12.84 mmol, 5.0 equiv) was added and stirred at room temperature for 6 h. Then chlorodiphenylphosphine (0.55 mL, 3.08 mmol, 1.2 equiv) was added to the reaction mixture and stirred for 3 h. The formed suspension was then filtered with a cannula over whatman filter paper. After evaporation of the solvent in vacuo (Traces of trimethylamine will be removed), the product was obtained as a white solid with a purity of 95% (by $^{31}P\{^{1}H\}$ NMR) which was directly used for complexation without any further purification. (Note: The mode of addition is highly important, since the by-product (1,1,2,2-tetraaryldiphosphane) will be formed in higher concentration, if both trimethylamine and chloro-diarylphosphine are directly added to the solution of **1a** in toluene.) (1.35 g, 92% yield). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.83–7.57 (m, 1H, Ar-*H*), 7.51–7.47 (m, 4H, Ar-*H*), 7.36–7.29 (m, 9H, Ar-*H*), 7.27–7.20 (m, 8H, Ar-*H*), 7.15–7.11 (m, 1H, Ar-*H*), 6.85–6.82 (m, 1H, Ar-*H*), 3.94 (d, *J* = 13.5 Hz, 1H, BzC*H*H), 3.82 (d, *J* = 13.5 Hz, 1H, BzC*H*H), 3.71–3.61 (m, 1H, OC*H*), 2.64–2.58 (m, 1H, NC*H*H), 2.06–2.02 (m, 1H, N*H*), 1.94–1.91 (m, 1H, CyC*H*), 1.69–1.56 (m, 2H, CyC*H*), 1.45–1.36 (m, 1H, CyC*H*),1.28–1.11 (m, 3H, CyC*H*), 1.06–0.98 (m, 1H, CyC*H*). **^{13}C{^{1}H} APT** (126 MHz, CD_2Cl_2) δ 143.6(d, *J* = 16.6 Hz, arom.), 142.9 (d, *J* = 16.3 Hz, arom.), 137.1 (d, *J* = 10.6 Hz, arom.), 137.0 (d, *J* = 10.6 Hz, arom.), 135.4 (d, *J* = 13.8 Hz, arom.), 135.3(d, *J* = 7.5 Hz, arom.), 135.2 (d, *J* = 7.3 Hz, arom.), 134.0 (d, *J* = 7.8 Hz, arom.), 133.8 (d, *J* = 8.1 Hz, arom.), 133.3 (arom.), 128.9 (arom.), 128.7 (arom.), 128.6 (arom.), 128.6 (arom.), 128.5 (arom.), 128.5 (arom.), 128.5 (arom.), 128.4 (arom.), 128.3 (arom.), 128.2 (arom.), 128.1 (arom.), 126.9 (arom.), 83.5 (d, *J* = 18.4 Hz, O*C*H), 61.6 (d, *J* = 5.6 Hz, N*C*H), 48.9 (d, *J* = 23.4 Hz, Bz*C*H), 32.7(d, *J* = 5.3 Hz, Cy*C*H), 30.1 (Cy*C*H), 24.3 (Cy*C*H), 23.9 (Cy*C*H). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ 106.7, –16.2. **HRMS (ESI)** m/z calcd for $[C_{37}H_{38}NOP_2]^+$: 574.2423 [M]+; found: 574.2423.

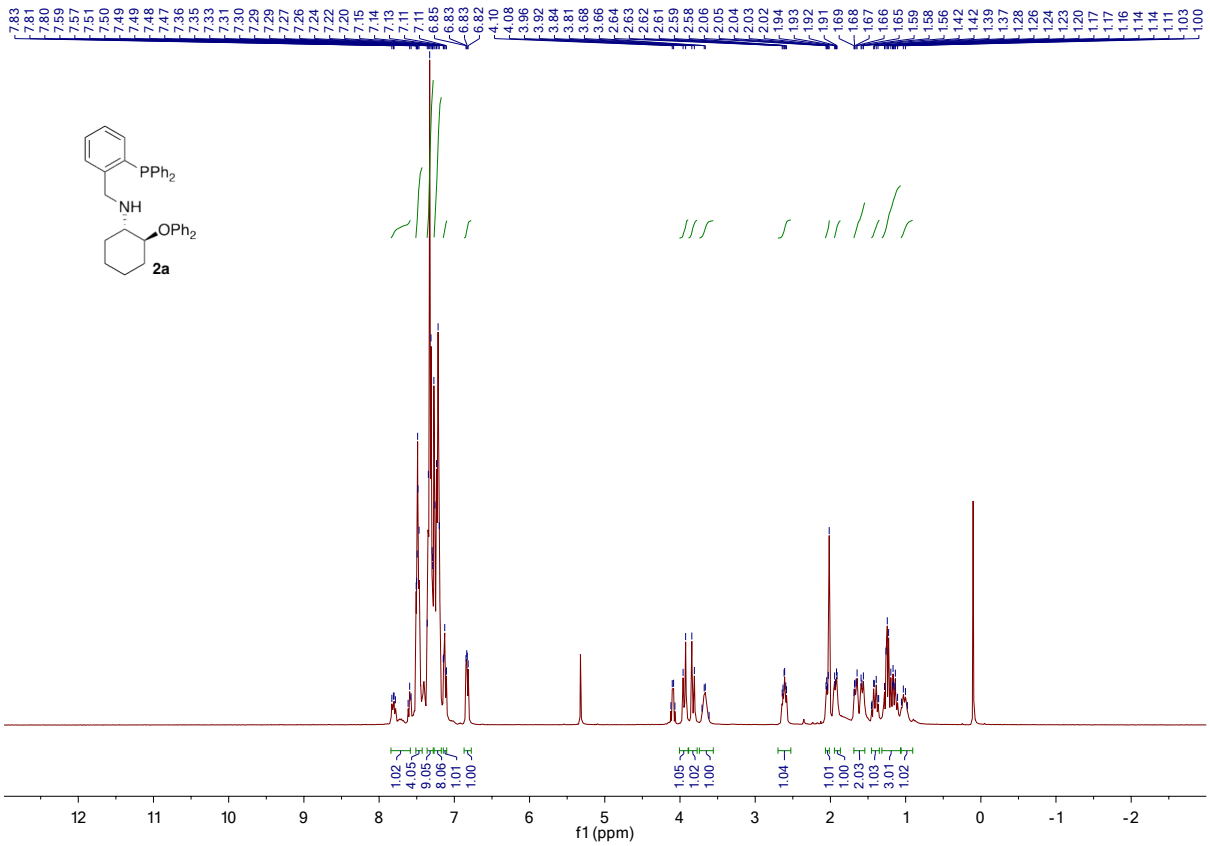


Figure S9. ^{1}H NMR spectrum of **2a** (300 MHz, CD_2Cl_2).

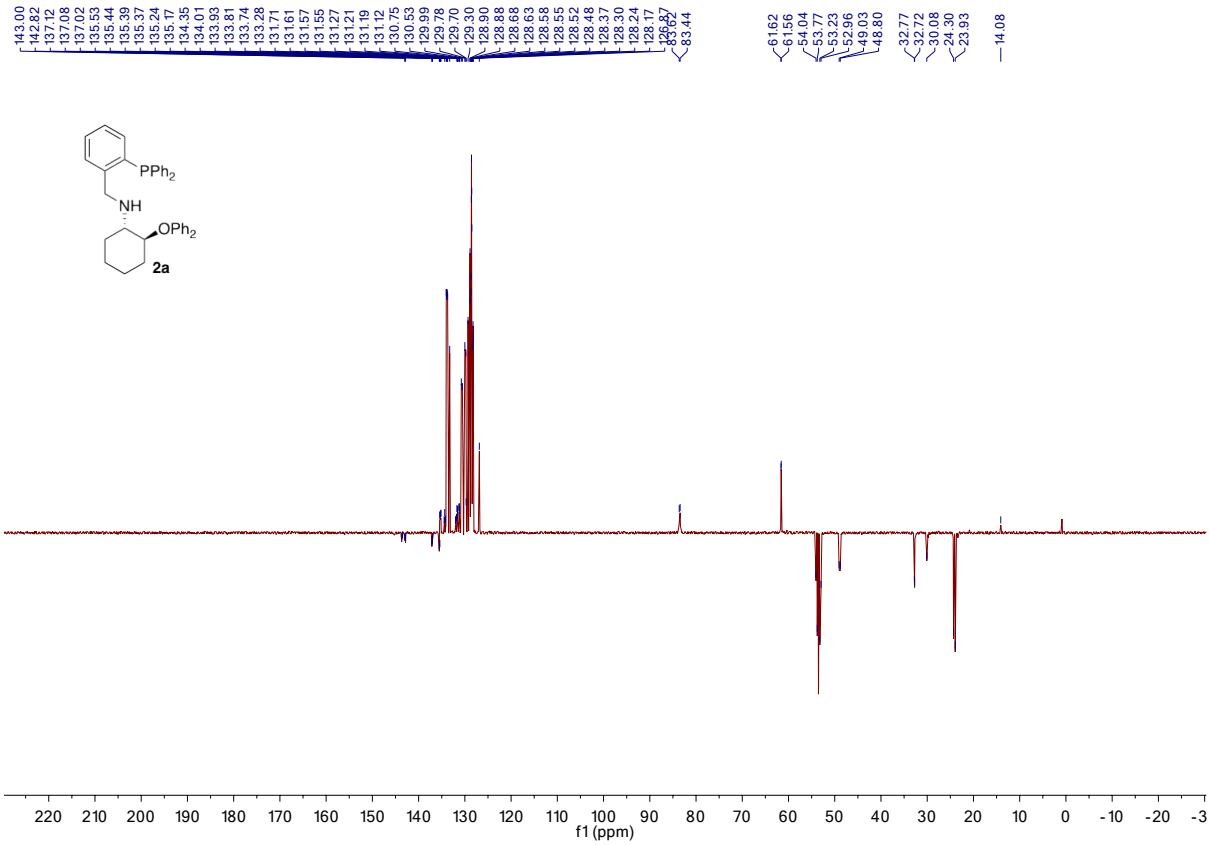


Figure S10. $^{13}C\{^{1}H\}$ APT NMR spectrum of **2a** (101 MHz, CD_2Cl_2).

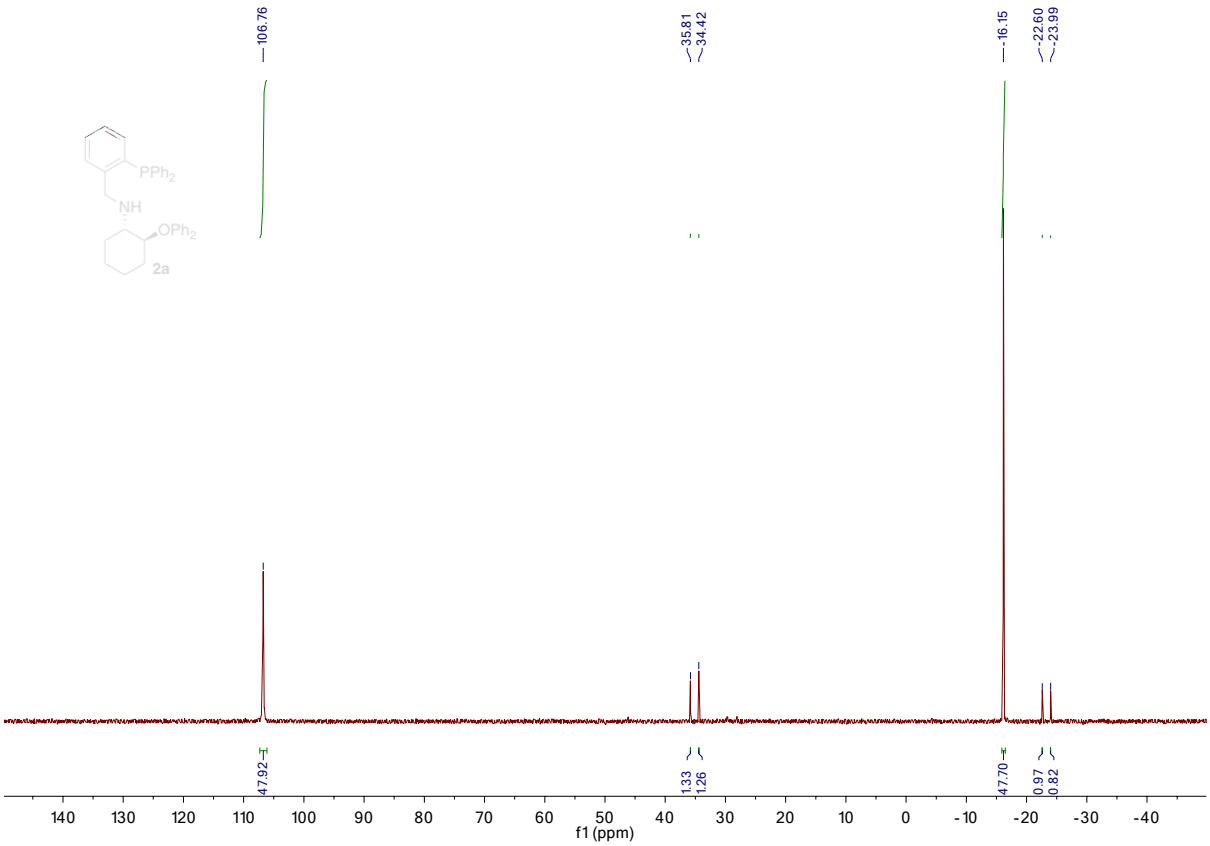
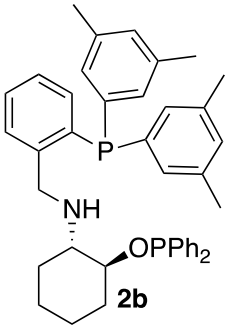


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** (203 MHz, CD_2Cl_2).



Synthesis of *N*-(2-(bis(3,5-dimethylphenyl)phosphene)benzyl)-2-((diphenylphosph-aneyl)oxy)cyclo-hexan-1-amine (2b): To a 0.2M solution of (1*S*,2*S*)-2-((2-(bis(3,5-dimethylphenyl)phosphene) benzyl)amino)cyclohexan-1-ol (1.14 g, 2.56 mmol, 1.0 equiv) in toluene, trimethylamine (1.8 mL, 12.84 mmol, 5.0 equiv) was added and stirred at room temperature for 6 h. Then chloro-diarylphosphine (0.55 mL, 3.08 mmol, 1.2 equiv) was added to the reaction mixture and stirred for 3 h. The formed suspension was then filtered with a cannula over whatman filter paper. After evaporation of the solvent in vacuo (Traces of trimethylamine will be removed), the product was obtained as a white solid with a purity of 96% (by $^{31}P\{^{1}H\}$ NMR) which was directly used for complexation without any further purification. (Note: The mode of addition is highly important, since the by-product (1,1,2,2-tetraaryldiphosphane) will be formed in higher concentration, if both trimethylamine and chloro-diarylphosphine are directly added to the solution of **1a** in toluene.) (1.45 g, 90% yield).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.86–7.55 (m, 1H, Ar-*H*), 7.52–7.46 (m, 4H, Ar-*H*), 7.34–7.09 (m, 9H, Ar-*H*), 6.97 (s, 2H, Ar-*H*), 6.86–6.83 (m, 4H, Ar-*H*), 3.90 (d, *J* = 13.8 Hz, 1H, BzC*H*H), 3.81 (d, *J* = 13.8 Hz, 1H, BzC*H*H), 3.74–3.60 (m, 1H, OC*H*), 2.65–2.57 (m, 1H, NC*H*), 2.27–2.25 (m, 1H, N*H*), 2.23 (s, 12H, CH_3H), 1.93–1.89 (m, 1H, CyC*H*), 1.68–1.64 (m, 1H, CyC*H*), 1.59–1.55 (m, 1H, CyC*H*), 1.43–1.37 (m, 1H, CyC*H*), 1.30–1.27 (m, 1H, CyC*H*),1.22–1.16 (m, 1H, CyC*H*), 1.10–0.98 (m, 1H, CyC*H*), 0.91–0.87 (m, 1H, CyC*H*). **^{13}C{^{1}H} APT** (126 MHz, CD_2Cl_2) δ 145.2 (d, *J* = 24.1 Hz, arom.), 143.1(d, *J* = 17.8 Hz, arom.),138.0 (d, *J* = 7.8 Hz, arom.), 136.7 (d, *J* = 4.5 Hz, arom.), 136.6 (d, *J* = 4.5 Hz, arom.), 135.9 (d, *J* = 13.6 Hz, arom.), 135.4 (d, *J* = 7.1 Hz, arom.), 135.4 (d, *J* = 7.0 Hz, arom.), 133.2 (d, *J* = 7.0 Hz, arom.), 133.2 (arom.), 131.7 (d, *J* = 6.2 Hz, arom.), 131.5 (d, *J* = 6.2 Hz, arom.), 130.7 (arom.), 130.5 (arom.), 130.4 (arom.), 130.4 (arom.),130.0 (arom.), 129.8 (arom.), 128.6 (arom.), 128.3 (d, *J* = 6.6 Hz, arom.), 128.2 (d, *J* = 6.6 Hz, arom.), 126.7 (arom.), 83.6 (d, *J* = 18.6 Hz, OC*H*), 61.5 (d, *J* = 5.7 Hz, NC*H*), 48.9 (d, *J* = 23.1 Hz, BzC*H*), 32.7 (d, *J* = 5.2 Hz, CyC*H*), 30.2(CyC*H*), 24.3(CyC*H*), 24.0(CyC*H*), 21.1 (CH_3). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ –15.9. **HRMS (ESI)** m/z calcd for $[C_{41}H_{45}NOP_2]^+$: 630.3049 [M]+; found: 630.3046.

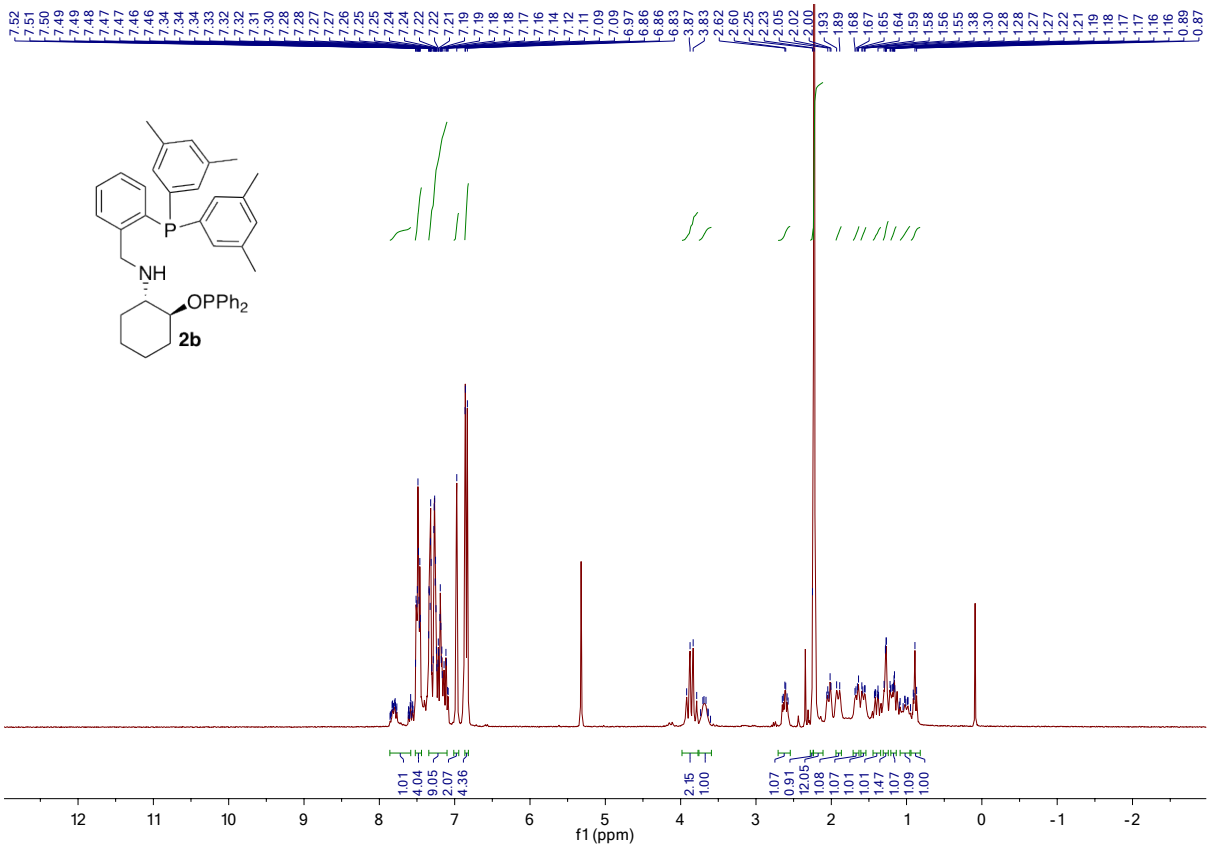


Figure S12. ^{1}H NMR spectrum of **2b** (300 MHz, CD_2Cl_2).

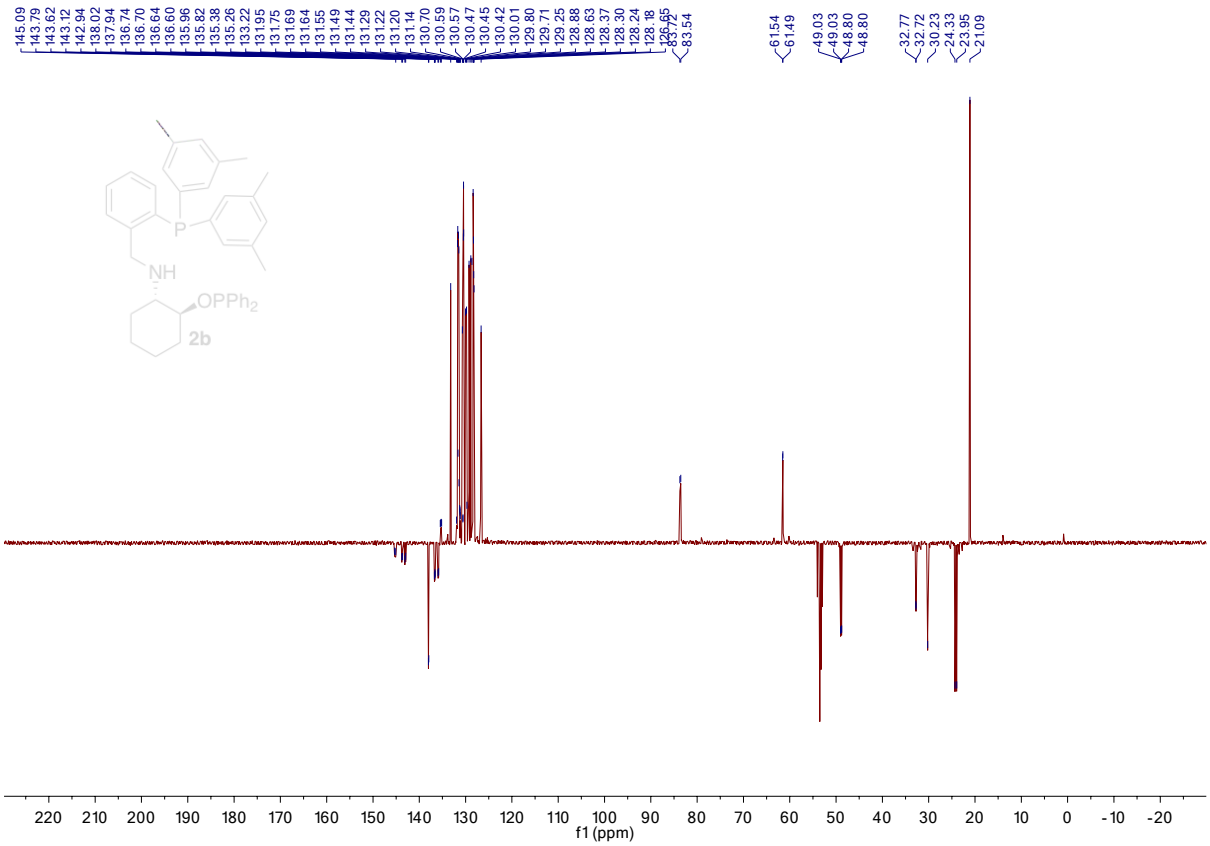


Figure S13. $^{13}C\{^{1}H\}$ APT NMR spectrum of **2b** (101 MHz, CD_2Cl_2).

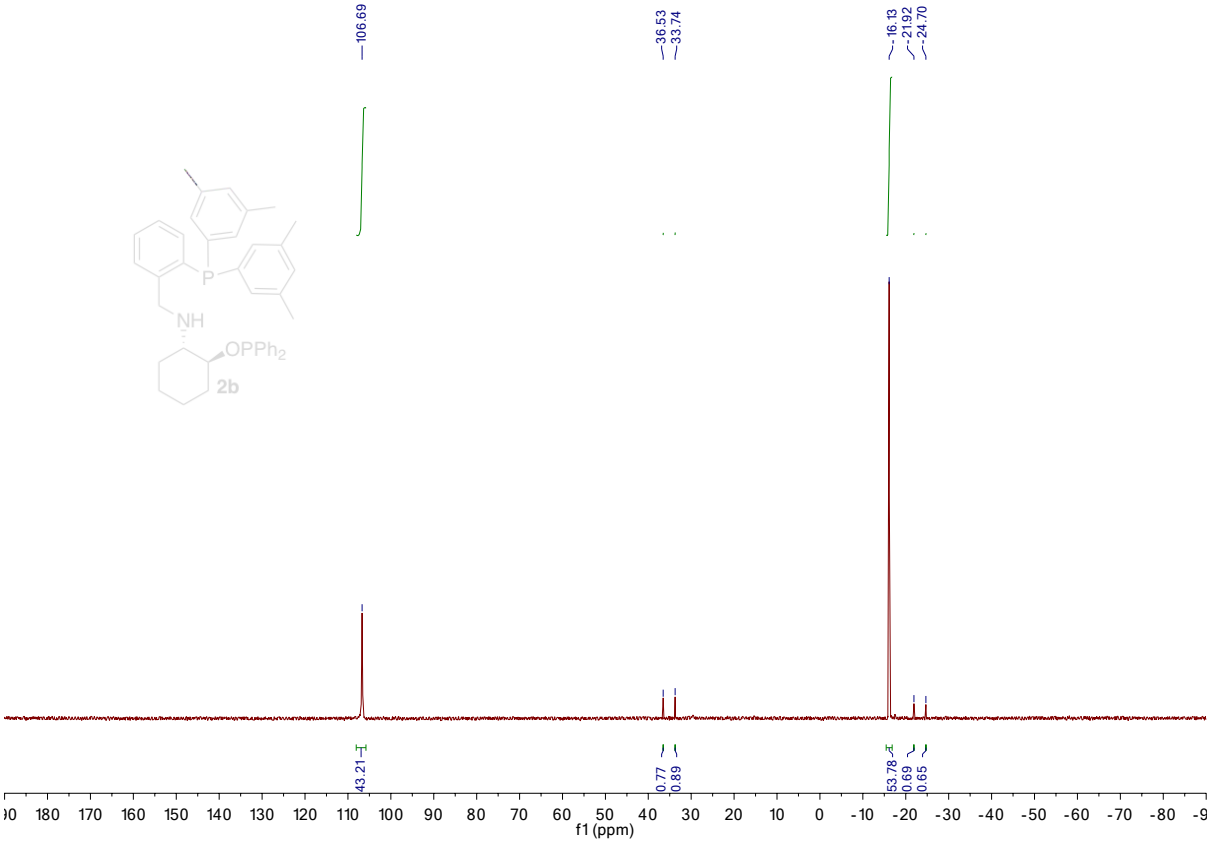


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of **2b** (203 MHz, CD_2Cl_2).

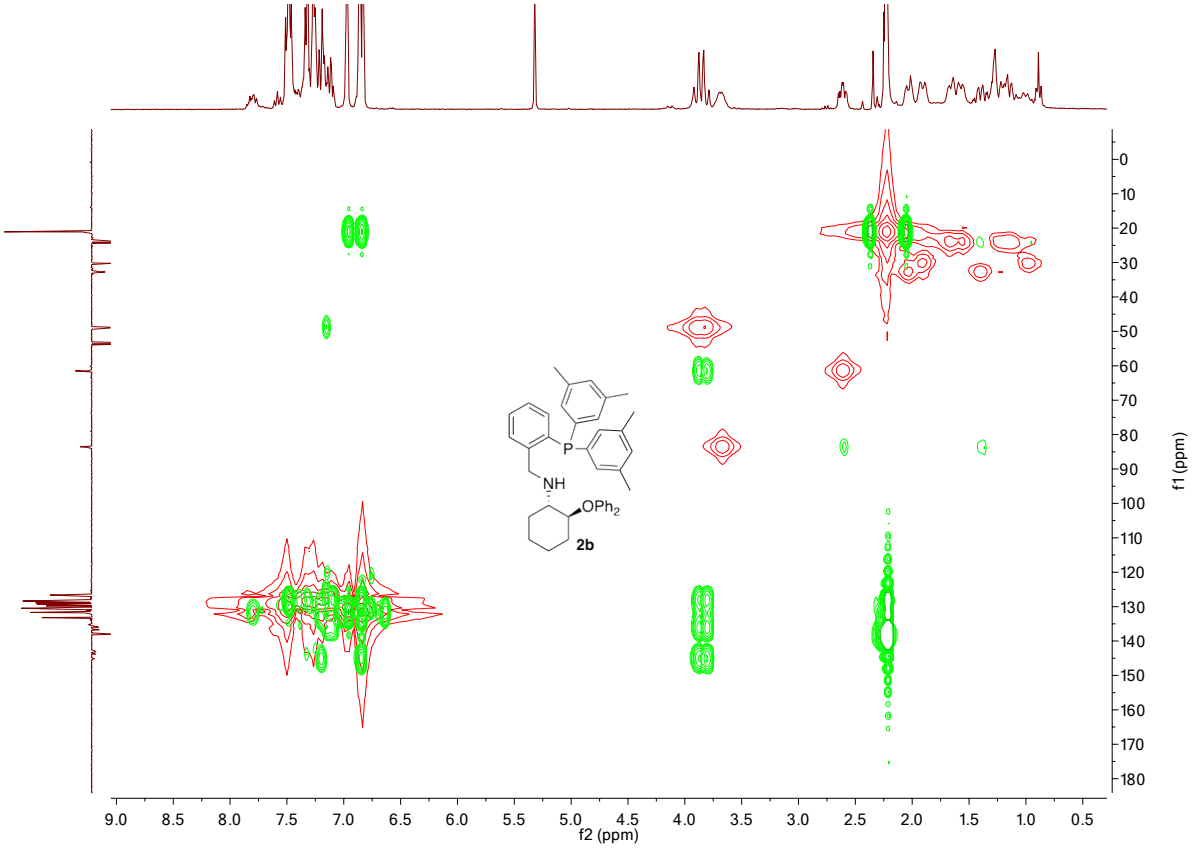


Figure S15. ^{13}C-^{1}HHSQC (red) and ^{13}C-^{1}H HMBC (green) of **2b** superimposed.

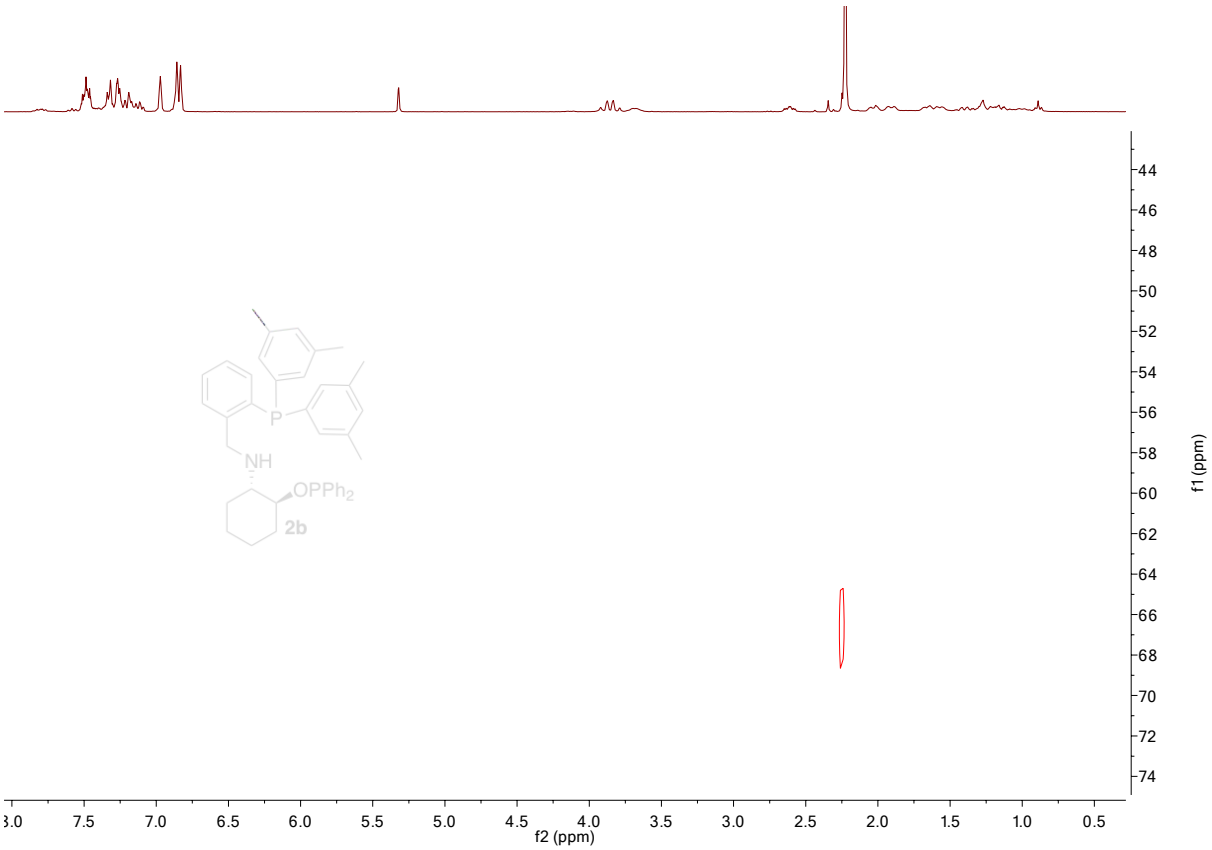
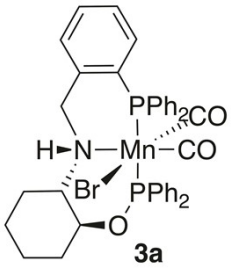


Figure S17. ^{15}N-^{1}H HSQC of ligand **2b**.

4. Synthesis of P'(O)N(H)P manganese complexes (3a-3b)



3a

Synthesis of [MnBr(CO)$_2$(2a)] (3a): A suspension of [MnBr(CO)$_5$] (0.43 g, 1.58 mmol, 1.0 equiv) and **2a** (0.95 g, 1.66 mmol, 1.05 equiv) in anhydrous toluene was stirred at 80 °C for 3 h. Then the amount of solvent was reduced *in vacuo* to ~2 mL and was precipitated with anhydrous hexane. The solids were then filtered with a cannula. The process of precipitation and filtration was carried out several times and then the solid was dried under high *vacuo* (10^{-3}mbar) to give the desired bis(carbonyl) Mn(I) complex [Mn(CO)$_2$(**2a**)]Br (**3a**) as a yellow powder (0.99 g, Yield: 82%). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.16 (t, *J* = 8.9 Hz, 2H, Ar-*H*), 7.98 (t, *J* = 8.2 Hz, 2H, OPAr-*H*), 7.66 (t, *J* = 8.6 Hz, 2H, OPAr-*H*), 7.50–7.40 (m, 9H, OPAr-*H*, PAr-*H*, Ar-*H*), 7.30–7.19 (m, 6H, OPAr-*H*, PAr-*H*), 7.03 (m, 2H, PAr-*H*), 7.07–6.95 (m, 1H, PAr-*H*), 4.18–4.14 (m, 2H, BzC*H*H, OC*H*), 4.00–3.88 (m, 1H, BzC*H*H), 2.75 (m, 3H, N*H*, NC*H*H, CyC*H*), 2.39–2.26 (m, 1H, CyC*H*), 1.87–1.69 (m, 2H, CyC*H*), 1.4–1.20 (m, 3H, CyC*H*), 0.90 (m, 1H, CyC*H*). **^{13}C{^{1}H} APT** (101 MHz, CD_2Cl_2) δ 143.1(arom.), 142.4 (d, *J* = 9.42 Hz, arom.), 142.3 (arom.), 139.6 (d, *J* = 12.9 Hz, arom.), 138.7 (arom.), 137.6 (d, *J* = 8.9 Hz, arom.), 137.0 (arom.), 136.6 (arom.), 134.0 (arom.), 132.9 (d, *J* = 9.6 Hz, arom.), 132.5(d, *J* = 10.6 Hz, arom.), 131.7 (arom.), 131.0 (arom.), 130.8 (arom.), 130.7 (d, *J* = 4.7 Hz, arom.), 130.2 (arom.), 130.1 (d, *J* = 4.7 Hz, arom.), 129.8 (arom.), 129.7 (d, *J* = 10.6 Hz, arom.), 128.9 (d, *J* = 8.3 Hz, arom.), 128.7 (d, *J* = 10.8 Hz, arom.), 128.5 (arom.), 126.0 (arom.), 76.3(O*C*H), 67.0 (N*C*H*)*, 59.7 (d, *J* = 14.0 Hz, Bz*C*H), 35.5 (d, *J* = 7.1 Hz, Cy*C*H), 33.6 (Cy*C*H), 26.2 (Cy*C*H), 25.1 (Cy*C*H), 21.8 (Cy*C*H). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ 160.8 (d, $J_{P,P'}$ = 116.0 Hz), 37.9 (d, $J_{P,P'}$ = 116.0 Hz). **IR** ATR ν: 1930, 1851. **HRMS (ESI)**: *m*/*z* calcd for $[C_{39}H_{37}MnNO_3P_2]^+$: 684.162 [M]+; found: 684.1616. **EA** Calcd. for $C_{39}H_{37}BrMnNO_3P_2$: C, 61.27; H, 4.88; N, 1.83; Found: C, 61.18; H, 4.70; N, 1.87.

X-Ray Structure of [MnBr(CO)$_2$(2a)] (3a):

Empirical formula	$C_{39}H_{37}BrMnNO_3P_2$
Formula weight	764.48
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.5751(3)
b/Å	29.5477(10)

c/Å	12.0766(4)
α/°	90
β/°	108.7480(10)
γ/°	90
Volume/Å^3	3573.4(2)
Z	4
ρ_{calc}g/cm^3	1.421
μ/mm^{-1}	5.460
F(000)	1572.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.982 to 162.328
Index ranges	-13 ≤ h ≤ 13, -36 ≤ k ≤ 37, -12 ≤ l ≤ 14
Reflections collected	53870
Independent reflections	14930 [R_{int} = 0.0456, R_{sigma} = 0.0446]
Data/restraints/parameters	14930/6/873
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0531, wR_2 = 0.1296
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.1308
Largest diff. peak/hole / e Å^{-3}	0.50/-0.44
Flack parameter	0.014(6)

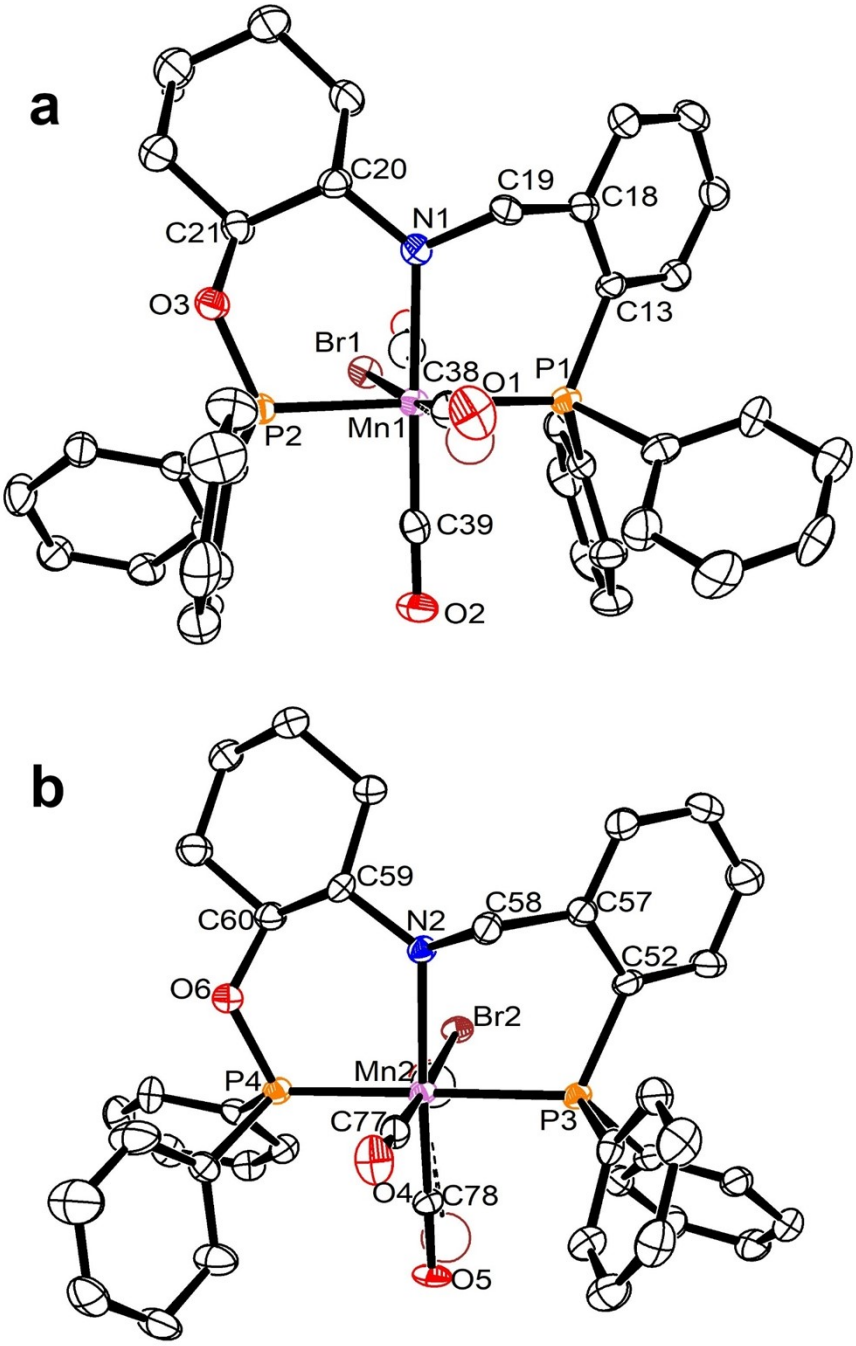


Figure S18: Thermal ellipsoid plot (Ortep-3)[14a] of both crystallographically independent molecules [$MnBr(CO)_2$(**2a**)] (**3a**) with 50 % probability. Both molecules show positional disorder of the Br-atom and one of the carbonyl units. (a) In molecule 1 the disorder (about 8.2 % occupancy) affects the carbonyl group situated trans to the bromine atom while in (b) molecule 2 the disorder (about 6.4 % occupancy) involves the carbonyl molecule situated cis to the bromine atom. The atoms belonging to the minor components are shown with empty spheres while all other non-hydrogen atoms are shown as ellipsoids. The hydrogen atoms were omitted for clarity.

Br1	Mn1	2.5368(12)	Br2	Mn2	2.5297(12)
Mn1	P1	2.3083(19)	Mn2	P3	2.3420(19)
Mn1	P2	2.2274(19)	Mn2	P4	2.2356(19)

Mn1	N1	2.163(6)	Mn2	N2	2.191(6)
C20	C21	1.530(9)	C59	C60	1.533(9)
C13	C18	1.401(10)	C52	C57	1.408(9)

C(59)- N(2)-C(58)	110.0(5)	C(20)- N(1)-C(19)	109.3(5)
O(6)- P(4)-C(60)	119.1(4)	O(3)- P(2)-C(21)	119.1(4)
P(4)- Mn(2)-Br(2)	92.98(6)	P(2)- Mn(1)-Br(1)	89.74(6)
P(4)- Mn(2)-P(3)	178.41(8)	P(2)- Mn(1)-P(1)	178.09(8)
Mn(2)- C(78)-O(5)	178.8(6)	Mn(1)- C(39)-O(2)	178.9(9)
P(4)- Mn(2)-C(78)	90.1(2)	P(2)- Mn(1)-C(39)	90.2(2)
P(3)- Mn(2)-C(78)	89.7(2)	P(1)- Mn(1)-C(39)	88.2(2)

Table T1: Selected distances (Å) and angles (°) of [MnBr(CO)$_2$(2a)] (3a):

A suitable crystal was measured at 100 K on a Bruker Venture Dual Source diffractometer using Cu radiation. The structure was solved with SHELXT[14b] and refined with SHELXL 2018/3[14c] embedded in Olex2.[14d] The crystallographic details are given in Table T1 (CCDC 2083796). The crystal structure analysis of [MnBr(CO)$_2$(2a)] (**3a**) showed some residual density in both molecules, located close to one of the carbonyl ligands. Accordingly, the carbonyl position was described by a mixed occupancy with Br-atoms (8.2% occupancy in molecule 1 and 6.4 % occupancy in molecule 2, respectively). However, if an occasional exchange of the CO/Br-positions is assumed (and not the presence of a complex with the sum formula [MnBr$_2$(CO)(2a)], which has a 17-electron count), there should be residual electron density corresponding to 6.4 % and 8.2 % occupancy of a carbonyl group at the bromide positions, too. Such small electron density of less than 0.5e$^-$/Å^3 per C/O atom is hard to detect and refine in the proximity of an almost fully occupied bromine atom with 35 electrons. Accordingly, for the refinement of the corresponding carbonyl groups the Mn-C, Mn-O and C-O distances were restrained to be similar to the distances (with a standard uncertainty of 0.01) observed in the non-disordered carbonyl group. Interestingly, in molecule 1 (Fig. S18 a) the bromine atom is disordered with the carbonyl group situated in the trans-position, while in molecule 2 (Fig. S18 b) the carbonyl in cis position is affected.

NMR of [MnBr(CO)$_2$(2a)] (3a).

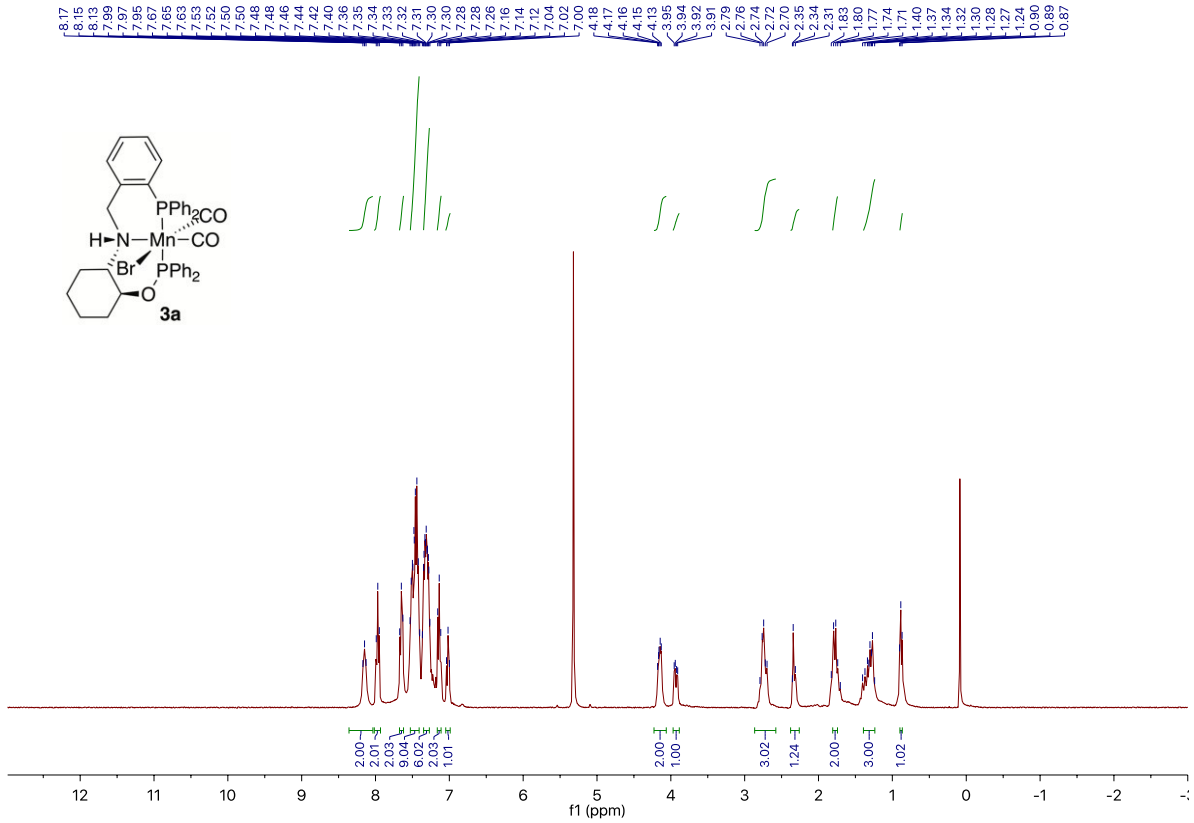


Figure S19. ^{1}H NMR spectrum of **3a** (300 MHz, CD_2Cl_2).

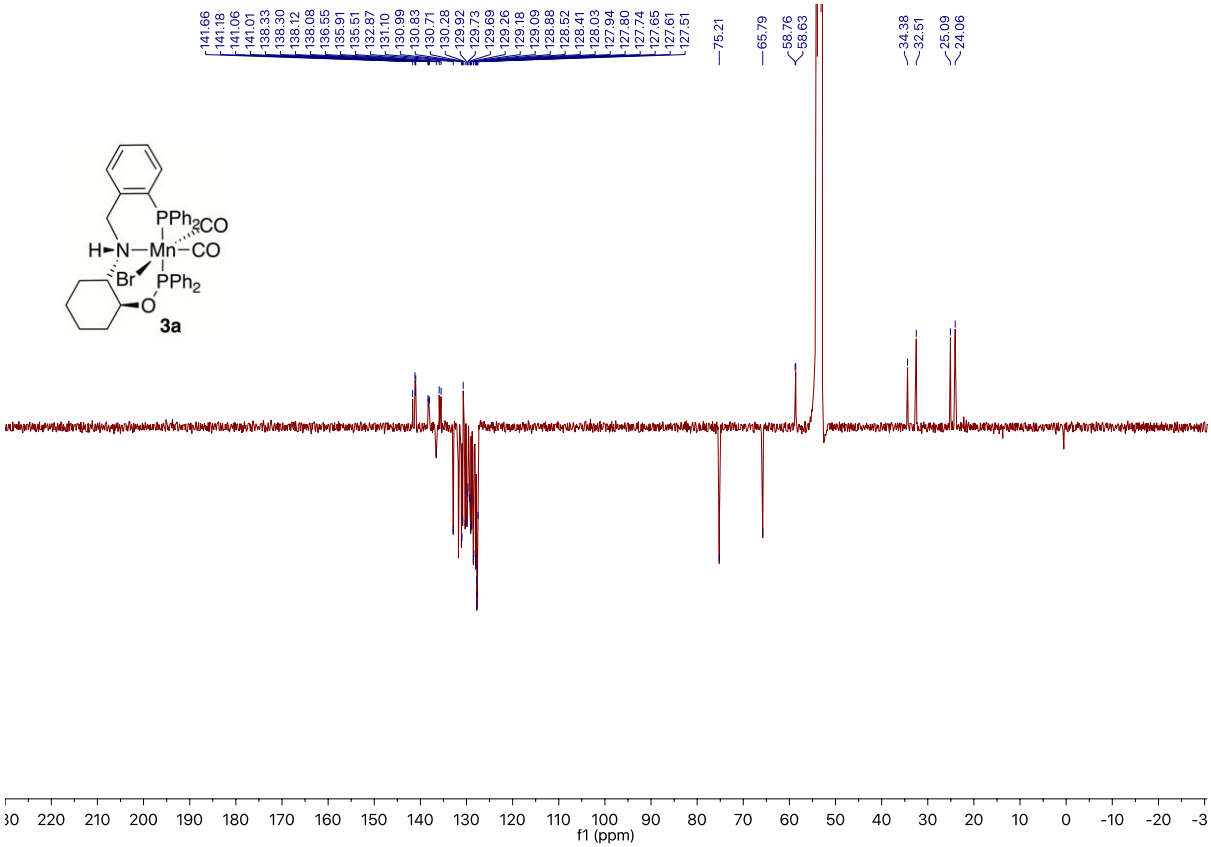


Figure S20. ^{13}C{^{1}H} APT NMR spectrum of **3a** (101 MHz, CD_2Cl_2).

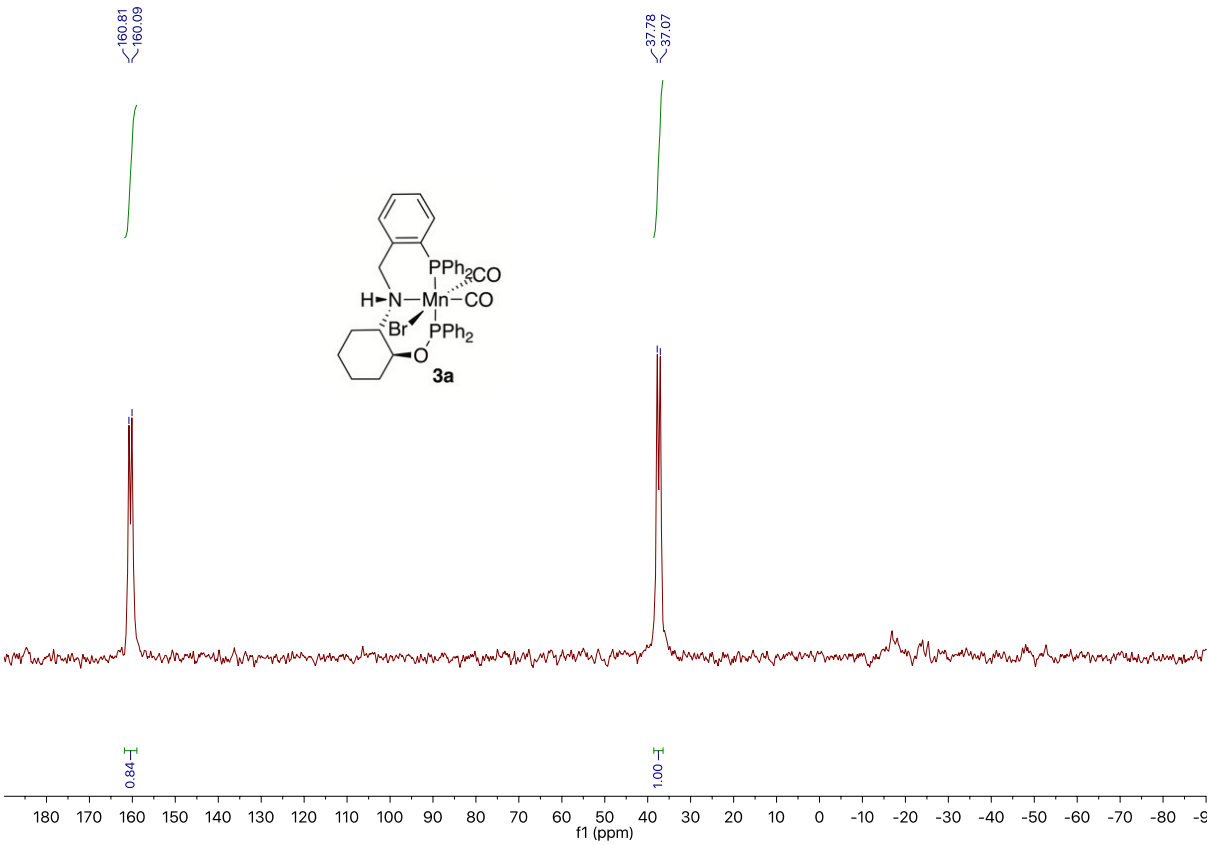


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** (121 MHz, CD_2Cl_2).

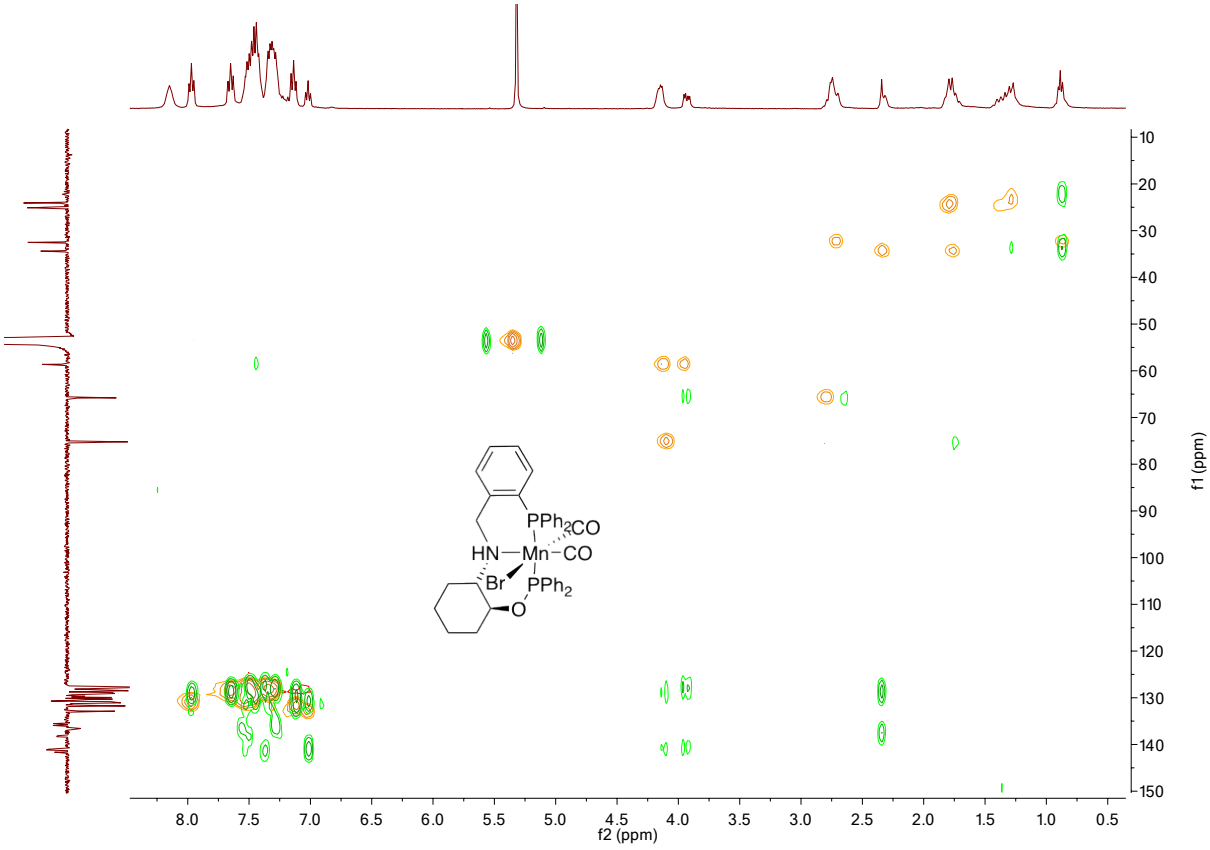


Figure S22. ^{13}C-^{1}HHSQC (red) and ^{13}C-^{1}H HMBC (green) of **3a** superimposed.

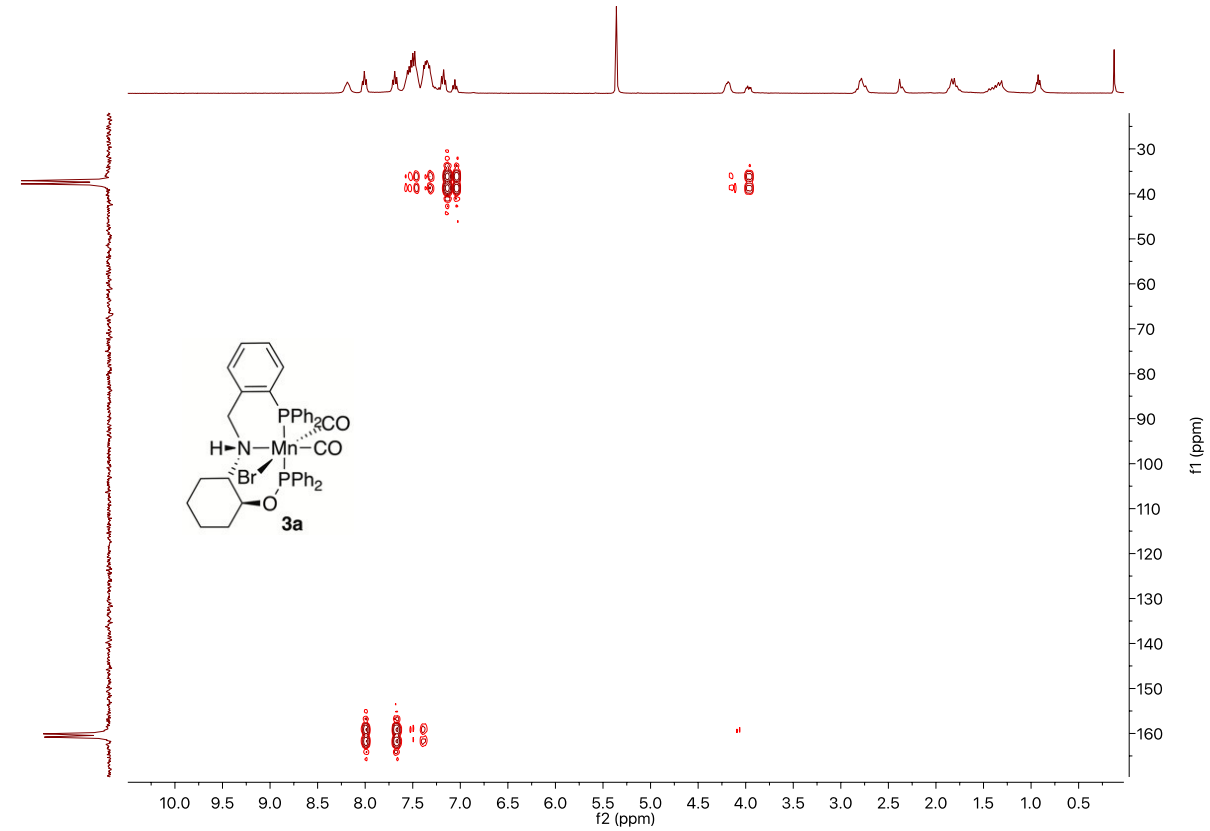


Figure S23. ^{31}P-^{1}H HSQC of [MnBr(CO)$_2$(**2a**)] (**3a**).

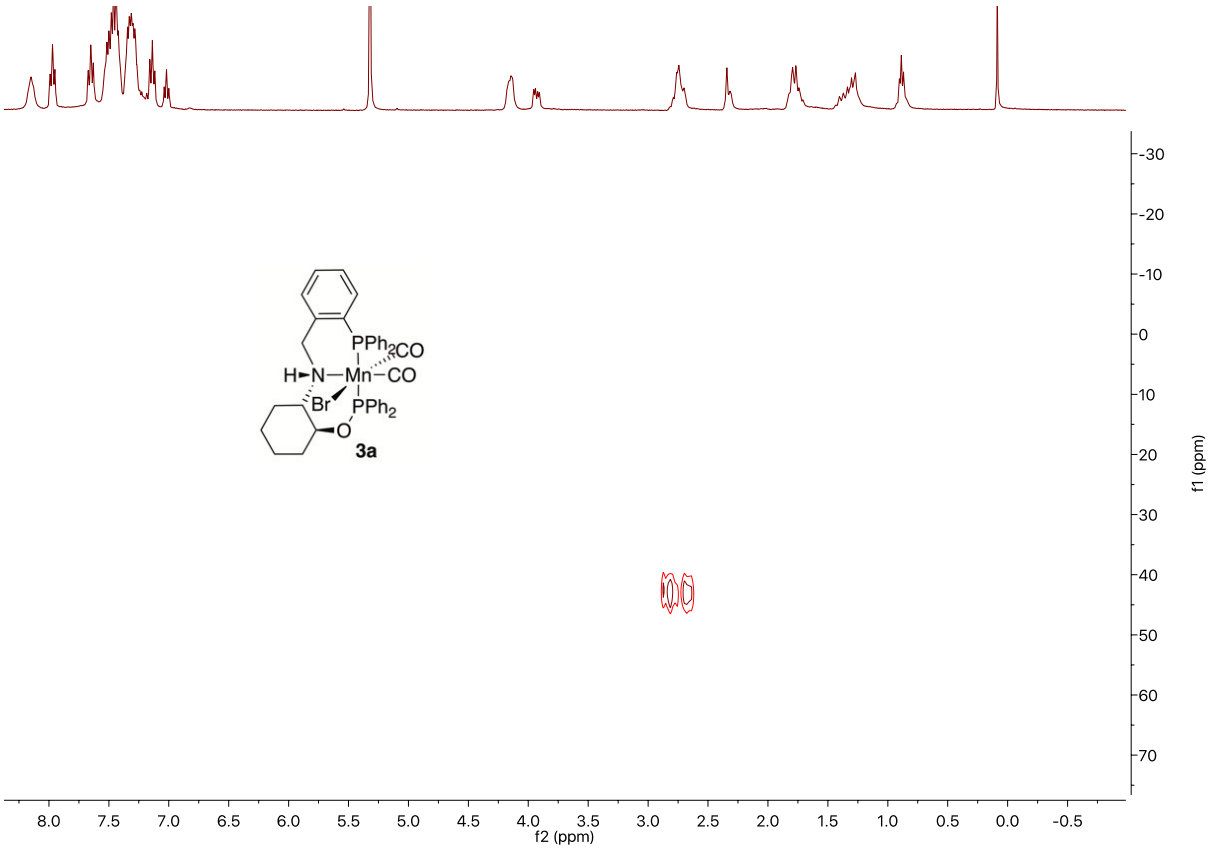


Figure S24. ^{15}N-^{1}H HSQC of [MnBr(CO)$_2$(**2a**)] (**3a**).

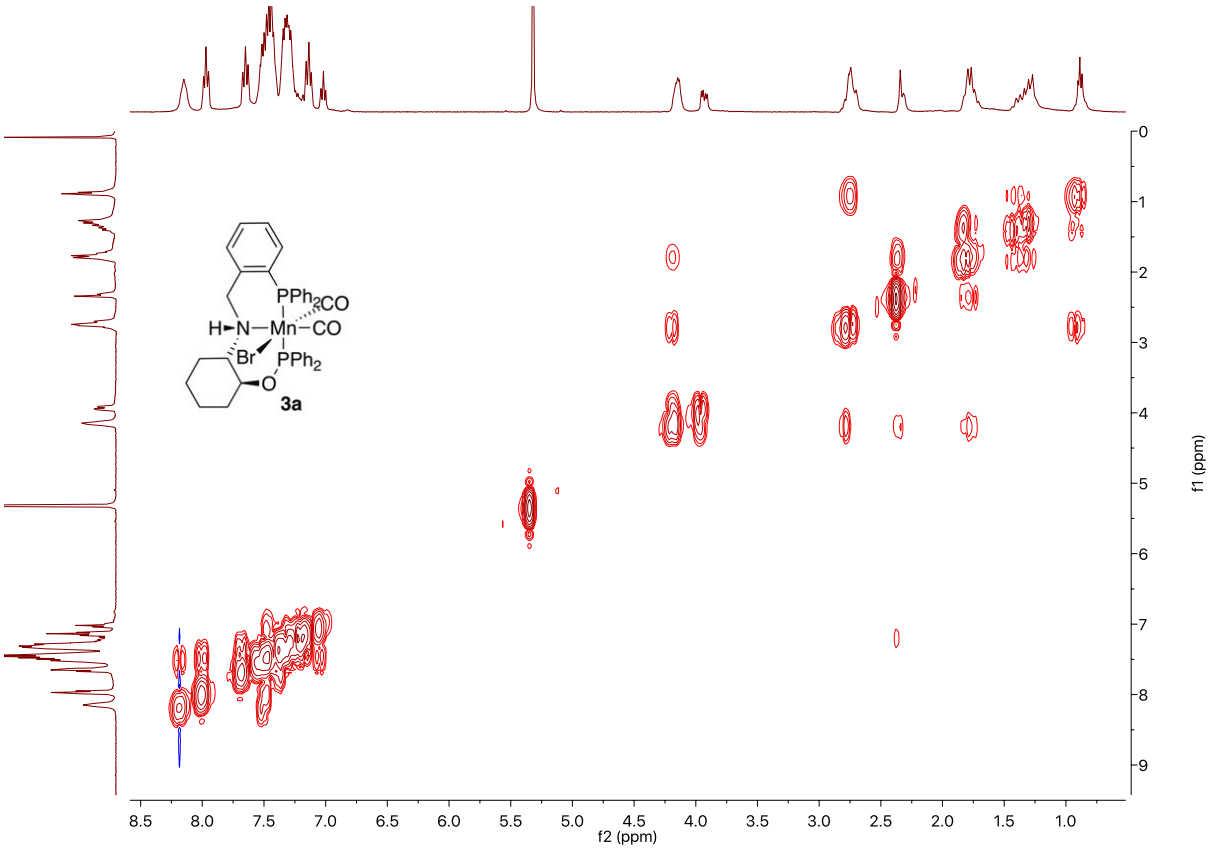
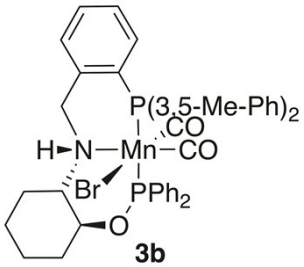


Figure S25. ^{1}H-^{1}H COSY of [MnBr(CO)$_2$(**2a**)] (**3a**).



Synthesis of [MnBr(CO)$_2$(2b)] (3b): A suspension of [MnBr(CO)$_5$] (0.43 g, 1.58 mmol, 1.0 equiv) and **2b** (1.05 g, 1.66 mmol, 1.05 equiv) in anhydrous toluene was stirred at 80 °C for 3 h. Then the amount of solvent was reduced *in vacuo* to ~2 mL and was precipitated with anhydrous hexane. The solids were then filtered with a cannula. The process of precipitation and filtration was carried out several times and then the solid was dried under high *vacuo* (10^{-3}mbar) to give the desired bis(carbonyl) Mn(I) complex [Mn(CO)$_2$(**2b**)]Br (**3b**) as a yellow powder (1.04 g, Yield: 80%). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 7.96–7.93 (m, 2H, OPAr-*H*), 7.74–7.73 (m, 1H, PAr-*H*), 7.69–7.65 (m, 2H, OPAr-*H*), 7.51–7.28 (m, 10H, OPAr-*H*, PAr-*H*), 7.16 (s, 1H, PAr-*H*), 7.03–6.97 (m, 2H, PAr-*H*), 6.73 (d, *J* = 9.3 Hz, PAr-*H*), 4.18–4.12 (m, 2H, BzC*H*H, OC*H*), 3.92–3.88 (m, 1H, BzC*H*H), 2.78–2.71 (m, 3H, N*H*, NC*H*H, CyC*H*), 2.34 (s, 6H, CH_3H), 2.30–2.21 (m, 1H, CyC*H*), 2.17 (s, 6H, CH_3H), 1.82–1.74 (m, 3H, CyC*H*), 1.40–1.27 (m, 2H, CyC*H*), 0.90–0.87 (m, 1H, CyC*H*).

^{13}C{^{1}H} APT (126 MHz, CD_2Cl_2) δ 142.6 (arom.), 142.1 (arom.), 141.6 (d, *J* = 16.8 Hz, arom.), 139.4 (d, *J* = 4.1 Hz, arom.), 139.2 (d, *J* = 4.1 Hz, arom.), 137.6 (d, *J* = 9.6 Hz, arom.), 137.3 (d, *J* = 9.6 Hz, arom.), 135.5 (arom.), 135.1 (arom.), 134.2 (d, *J* = 9.4 Hz, arom.), 133.7 (d, *J* = 9.5 Hz, arom.), 133.5 (arom.), 132.1 (d, *J* = 3.0 Hz, arom.), 131.7 (d, *J* = 11.6 Hz, arom.), 131.4 (d, *J* = 11.6 Hz, arom.), 131.0 (arom.), 130.8 (arom.), 130.0 (d, *J* = 9.8 Hz, arom.), 129.9 (d, *J* = 3.0 Hz, arom.), 129.7 (d, *J* = 4.7 Hz, arom.), 129.3 (d, *J* = 9.7 Hz, arom.), 129.0, 128.9 (d, *J* = 10.3 Hz, arom.), 127.9, (d, *J* = 9.4 Hz, arom.), 127.7 (d, *J* = 9.5 Hz, arom.), 75.6 (O*C*H), 66.3 (N*C*H), 55.8 (d, *J* = 13.6 Hz, Bz*C*H), 34.8 (d, *J* = 6.2 Hz, Cy*C*H), 32.9 (Cy*C*H), 25.5 (Cy*C*H), 24.4 (Cy*C*H), 21.3 (*C*H$_3$), 21.2 (*C*H$_3$). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ 160.9 (d, *J* = 116.0 Hz), 36.6 (d, *J* = 116.0 Hz). **IR** ATR ν: 1931, 1852. **HRMS (ESI)**: *m*/*z* calcd for $[C_{43}H_{45}MnNO_4P_2]^+$: 740.225 [M]+; found: 740.2246. **EA** Calcd. for $C_{43}H_{45}BrMnNO_3P_2$: C, 62.94; H, 5.53; N, 1.71; Found: C, 63.07; H, 5.62; N, 1.56.

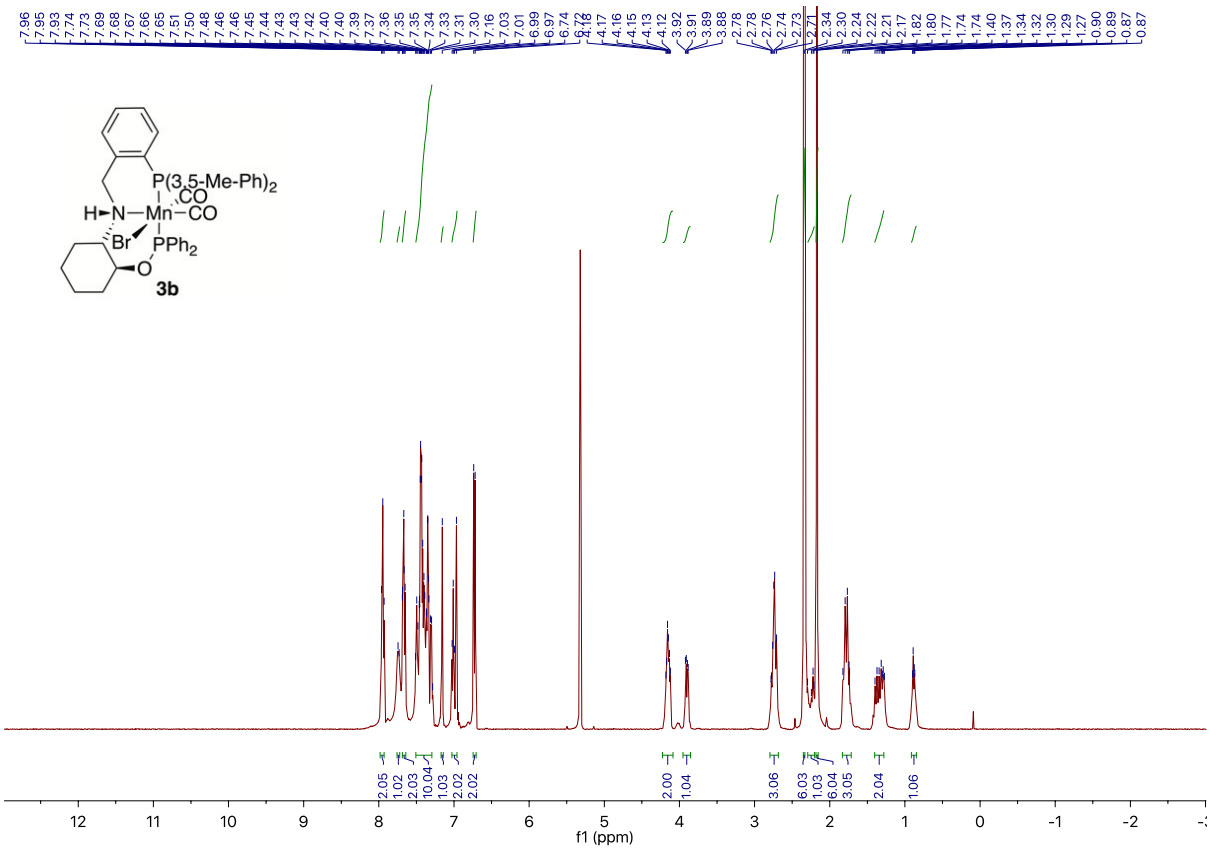


Figure S26. ^{1}H NMR spectrum of **3b** (500 MHz, CD_2Cl_2).

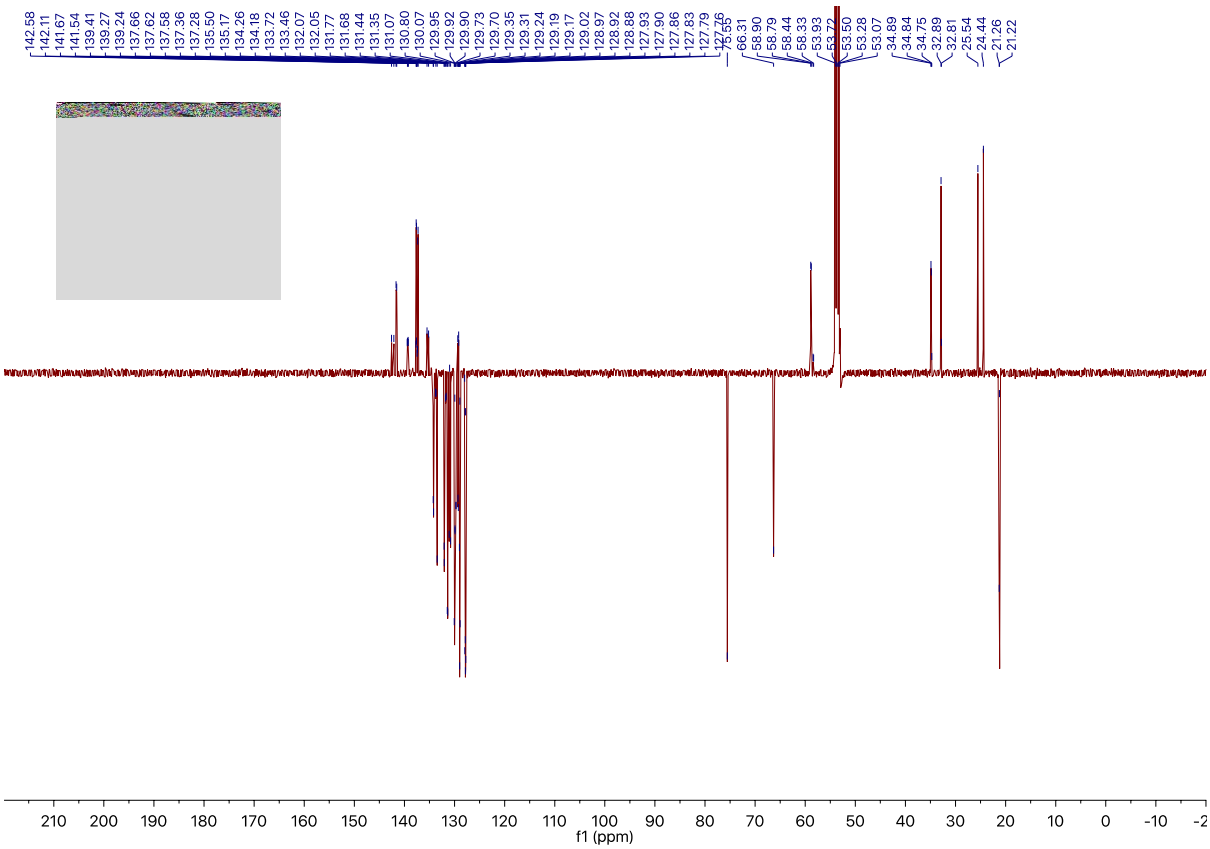


Figure S27. $^{13}C\{^{1}H\}$ APT NMR spectrum of **3b** (126 MHz, CD_2Cl_2).

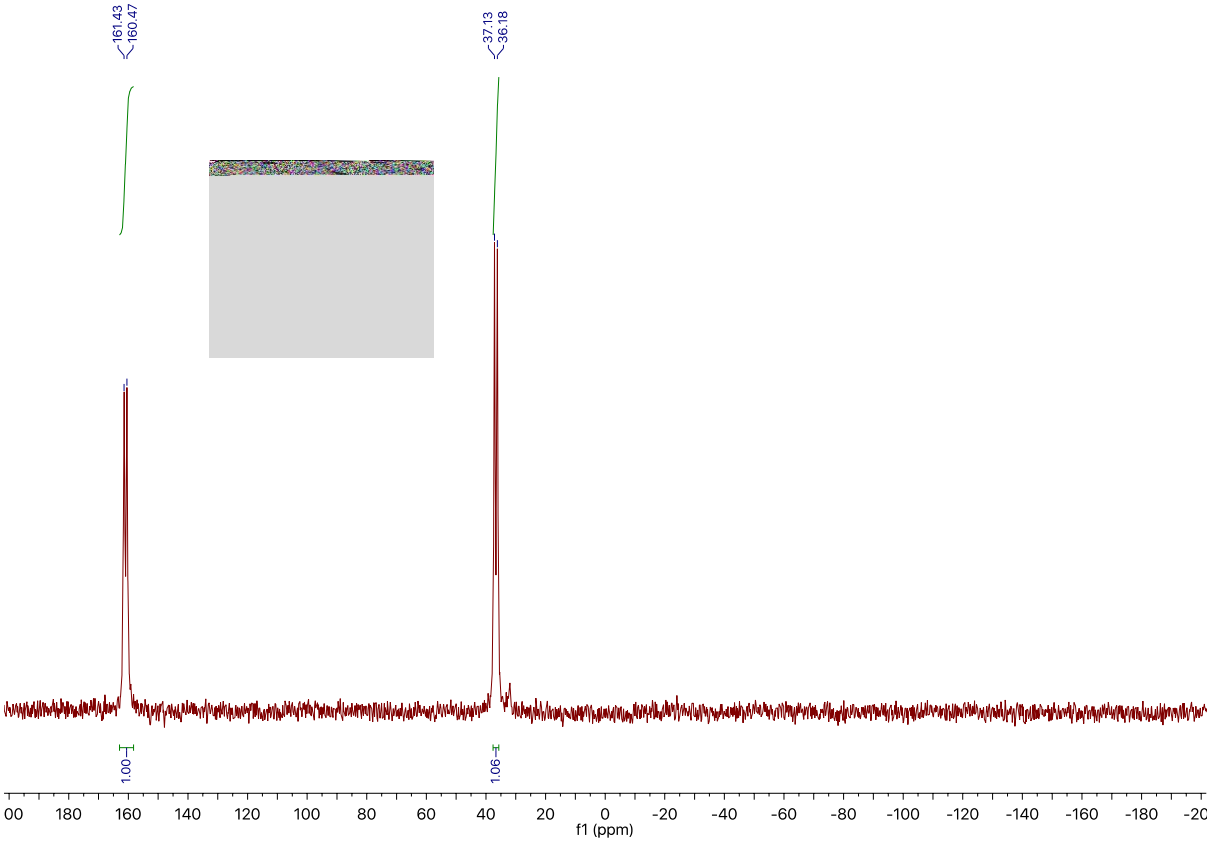


Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of **3b** (203 MHz, CD_2Cl_2).

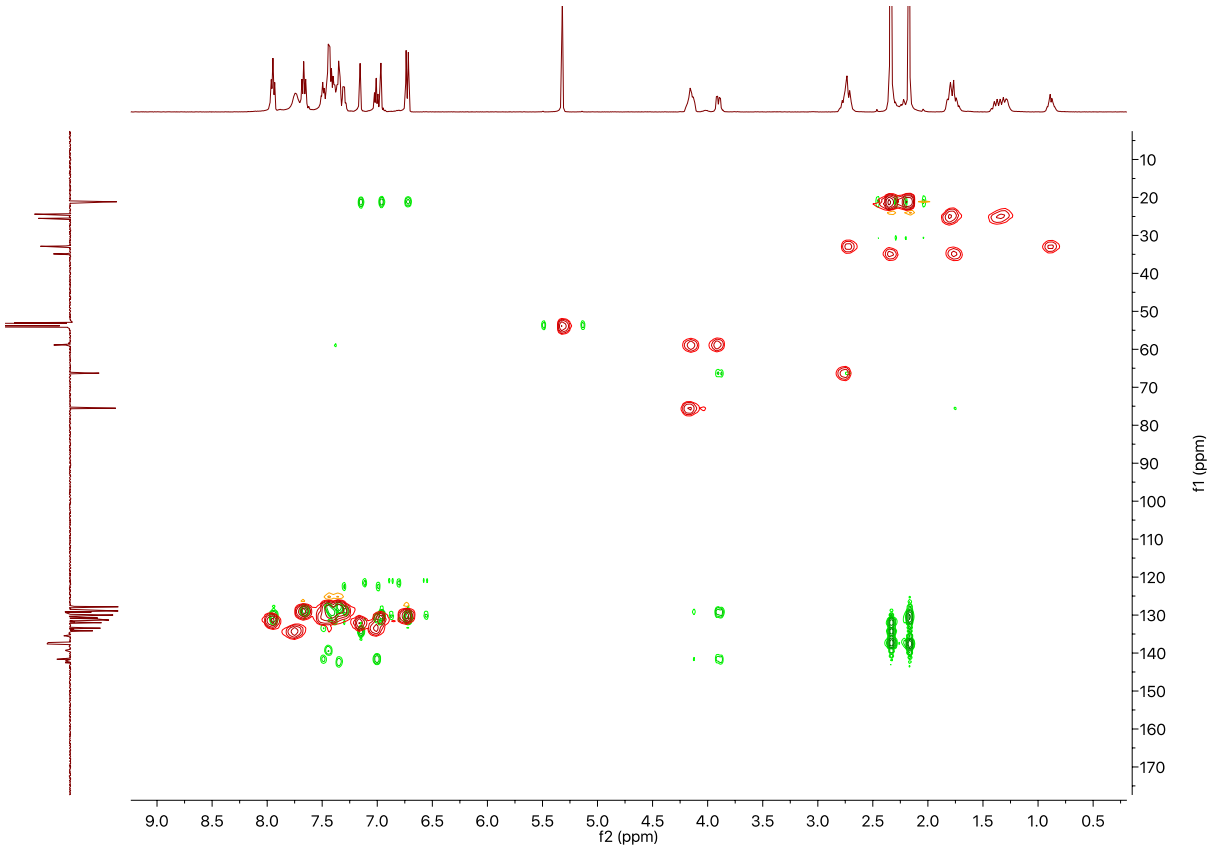


Figure S29. ^{13}C-$^{1}HHSQC$ (red) and ^{13}C-^{1}H HMBC (green) of **3b** superimposed.

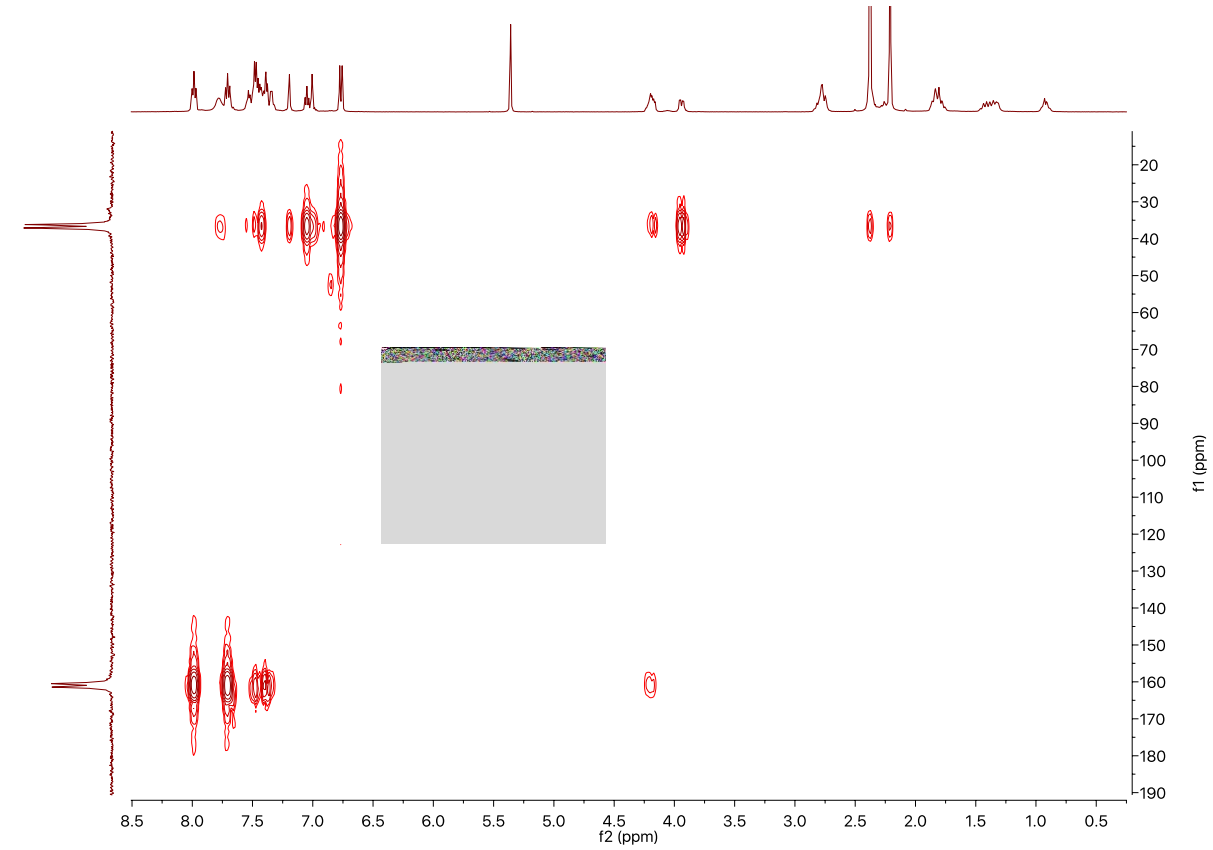


Figure S30. ^{31}P-^{1}H HSQC of [$MnBr(CO)_2$(**2b**)] (**3b**).

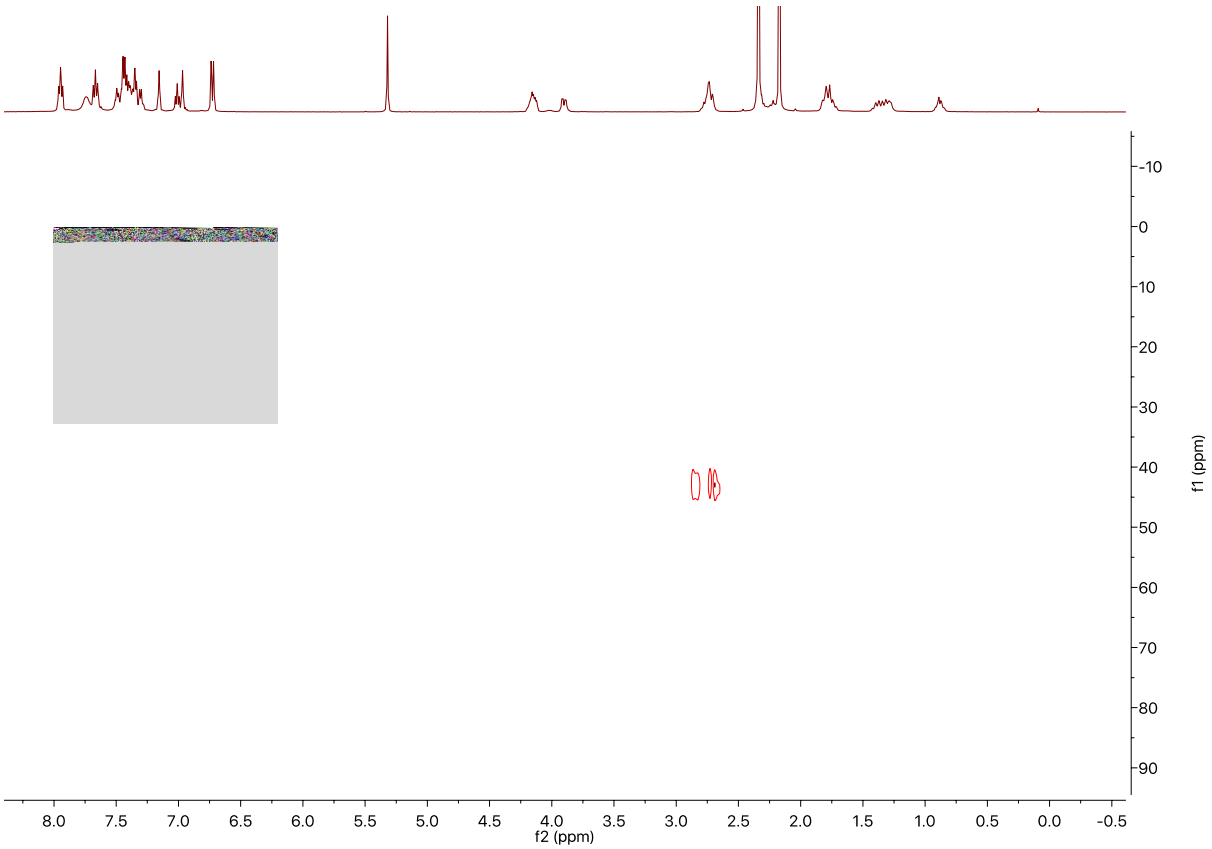


Figure S31. ^{15}N-^{1}H HSQC of [MnBr(CO)$_2$(**2b**)] (**3b**).

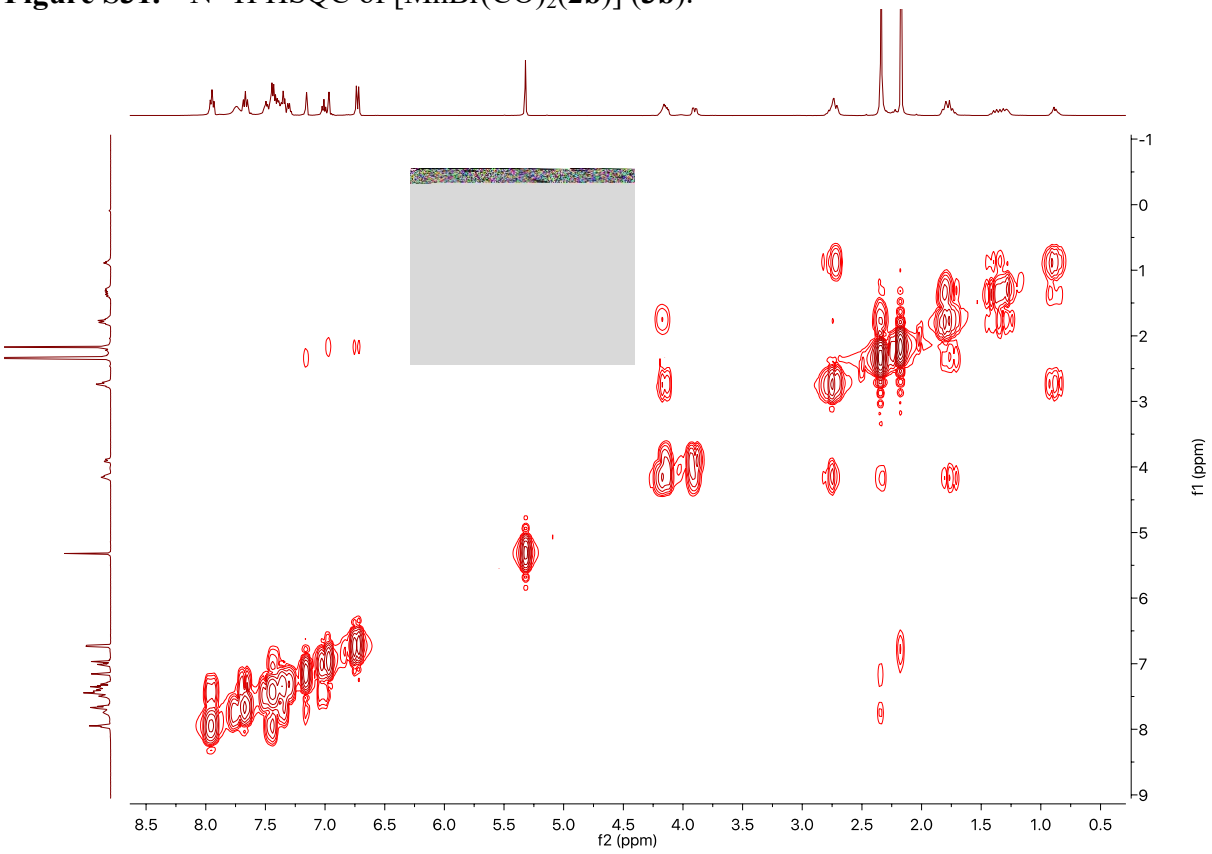
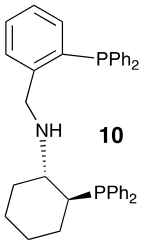


Figure S32. ^{1}H-^{1}H COSY of [MnBr(CO)$_2$(**2b**)] (**3b**).

5. Synthesis and characterization of Ligand (10)



Synthesis of 2-(diphenylphosphaneyl)-N-(2-(diphenylphosphaneyl)benzyl) cyclohexan-1-amine (10): To a 0.02 M solution of 2-(diphenylphosphaneyl)benzaldehyde (0.74 g, 2.56 mmol, 1.0 equiv) and 2-(diphenylphosphino)cyclohexylamine (0.73 g, 2.56 mmol, 1.0 equiv) in anhydrous MeOH was stirred at room temperature for 18 h. After full conversion, $NaBH_4$ (2.4 g, 12.8 mmol, 5.0 equiv) was added, and the solution was stirred further for 18 h. The reaction was quenched with degassed water, and the volatiles were removed by rotary evaporation under inert atmosphere. After addition of degassed water and CH_2Cl_2 to the residue, the layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3x). The combined organic layers were washed with degassed H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was then passed through a short pad of silica and washed with 50:50 mixture of ethyl acetate: hexane. The solution was then concentrated and dried to obtain the product as a white solid with a purity of 92% (by $^{31}P\{^1H\}$ NMR) which was directly used for complexation without any further purification (1.29 g, 90% yield). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.51–7.46 (m, 2H, Ar-*H*), 7.39–7.33 (m, 10H, Ar-*H*), 7.30–7.24 (m, 10H, Ar-*H*), 7.18–7.13 (m, 1H, Ar-*H*), 6.88–6.85 (m, 1H, Ar-*H*), 4.03–3.99 (m, 1H, BzC*H*H), 3.90–3.87 (m, 1H, BzC*H*H), 2.49–2.41 (m, 1H, NC*H*), 2.33–2.28 (m, 1H, NP*H*), 2.16–2.10 (m, 1H, N*H*), 1.71–1.59 (m, 3H, CyC*H*), 1.29–1.26 (m, 3H, CyC*H*), 0.99–0.84 (m, 2H, CyC*H*). **^{13}C{^{1}H} APT** (126 MHz, CD_2Cl_2) δ 137.1, 135.5 (d, *J* = 13.6 Hz, arom.), 134.7, 134.5, 134.0 (d, *J* = 4.6 Hz, arom.),133.7 (d, *J* = 4.6 Hz, arom.), 133.4, 132.7, 132.6, 128.9, 128.7, 128.7, 128.6 (d, *J* = 1.1 Hz, arom.), 128.5 (d, *J* = 1.1 Hz, arom.), 128.4 (d, *J* = 7.1 Hz, arom.), 128.1 (d, *J* = 6.9 Hz, arom.), 127.9, 126.9, 57.4 (d, *J* = 14.4 Hz, N*C*H), 49.2 (d, *J* = 23.4 Hz, Bz*C*H), 40.1 (d, *J* = 13.5 Hz, PCy*C*H), 31.9 (d, *J* = 4.5 Hz, Cy*C*H), 26.6 (d, *J* = 4.6 Hz, Cy*C*H), 25.5 (d, *J* = 4.6 Hz, Cy*C*H), 23.9 (Cy*C*H). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ –9.8, –16.1. **HRMS (ESI)** m/z calcd for $[C_{37}H_{38}NP_2]^+$: 558.2474 [M]+; found:558.2471.

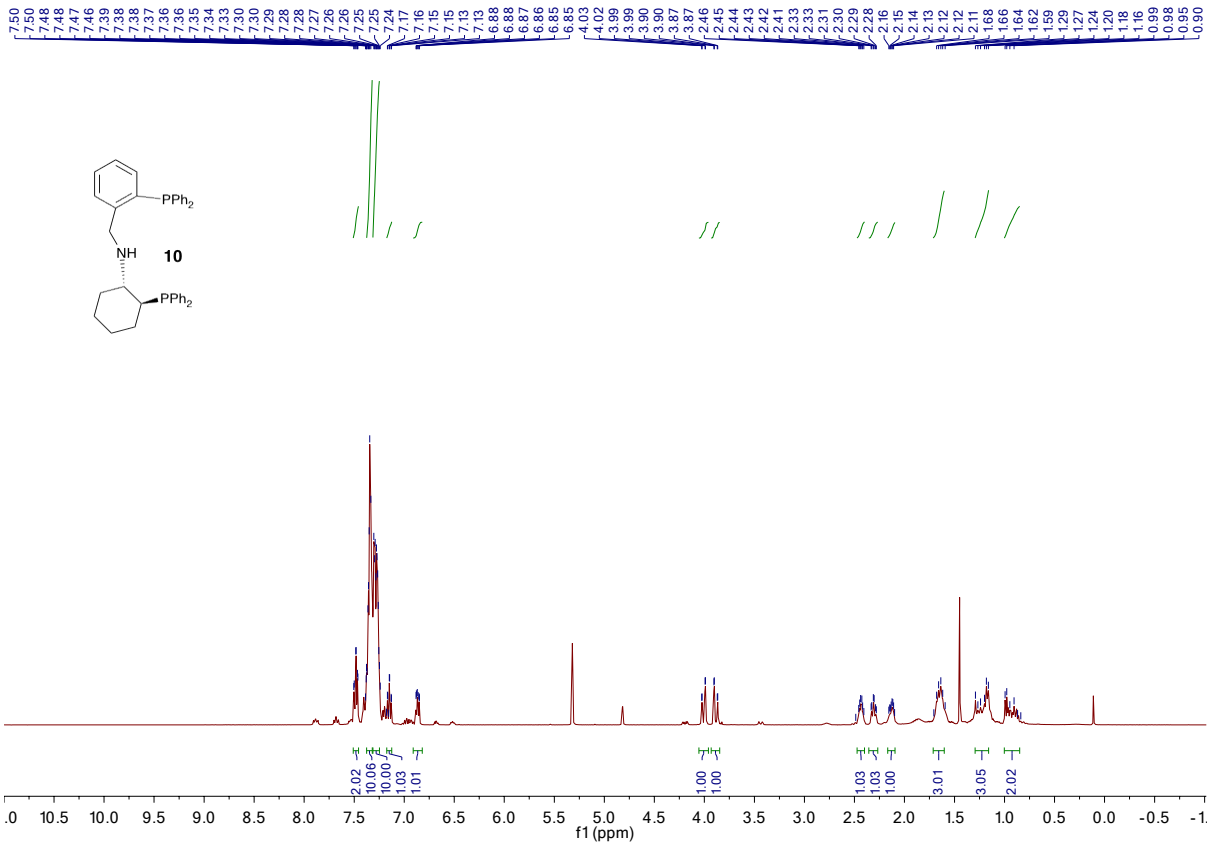


Figure S33. ^{1}H NMR spectrum of **10** (300 MHz, CD_2Cl_2).

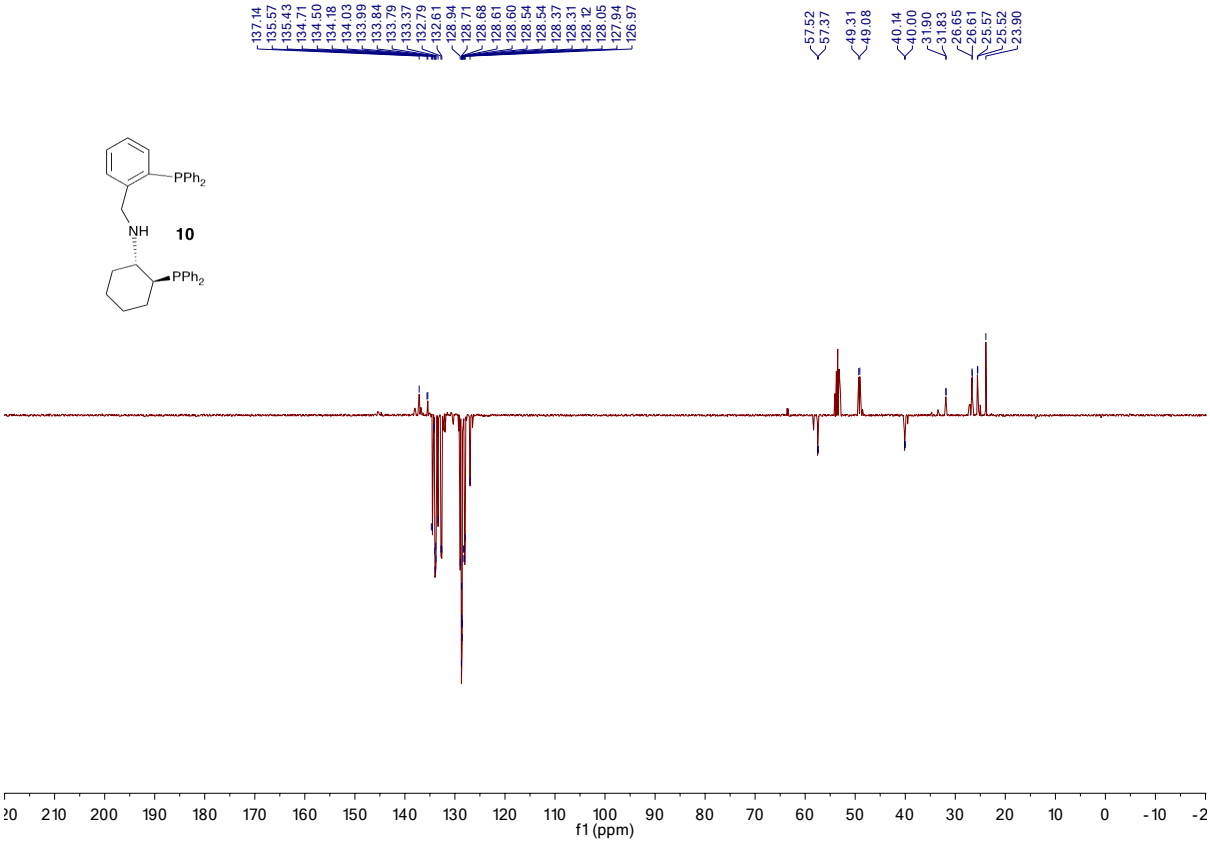


Figure S34. $^{13}C\{^{1}H\}$ APT NMR spectrum of **10** (101 MHz, CD_2Cl_2).

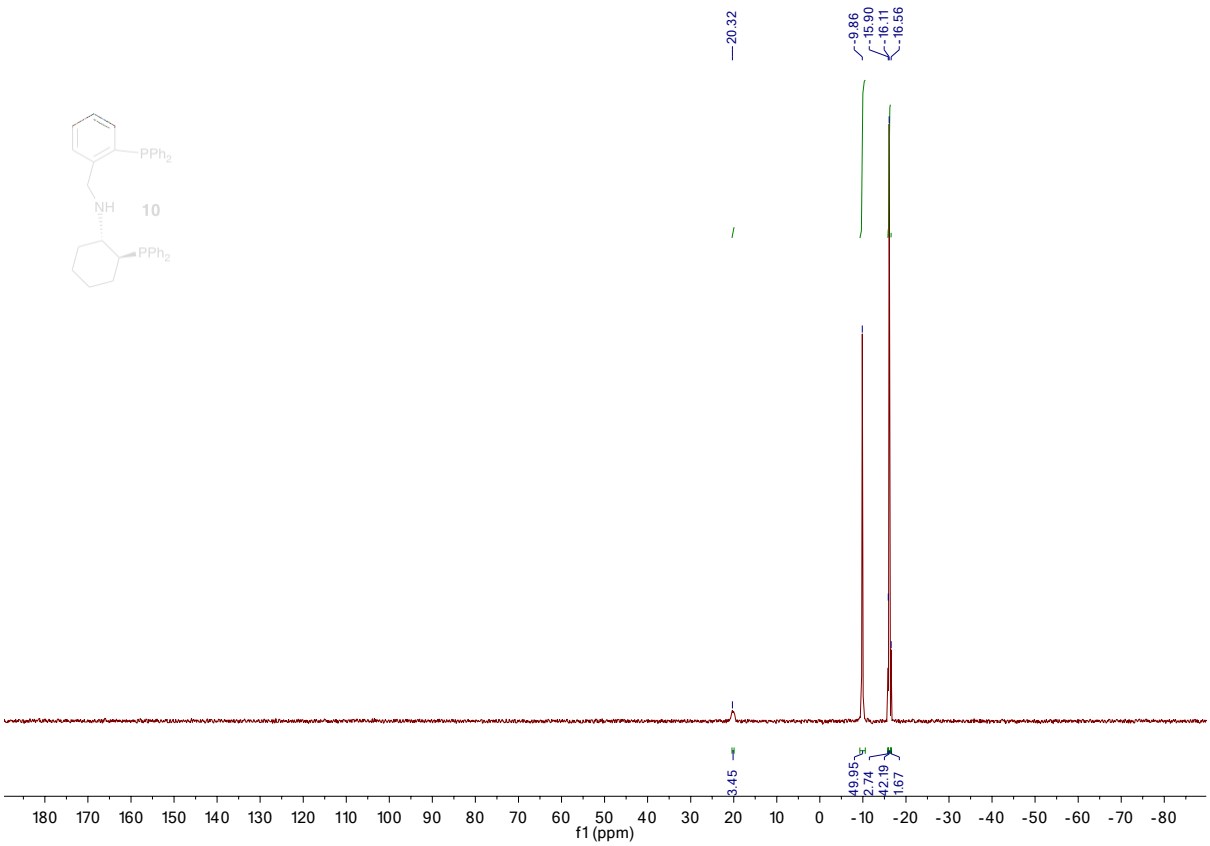


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum of **10** (203 MHz, CD_2Cl_2).

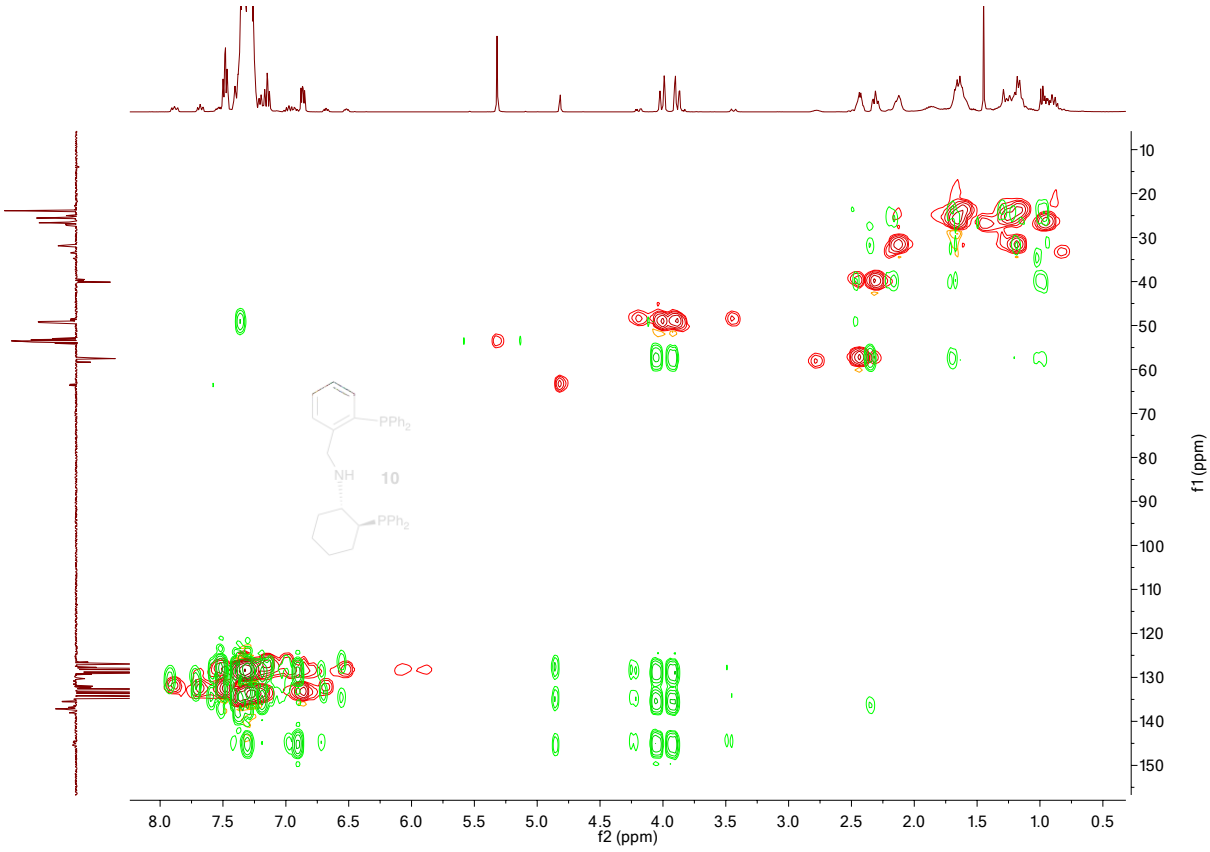


Figure S36. ^{13}C-^{1}HHSQC (red) and ^{13}C-^{1}H HMBC (green) of **10** superimposed.

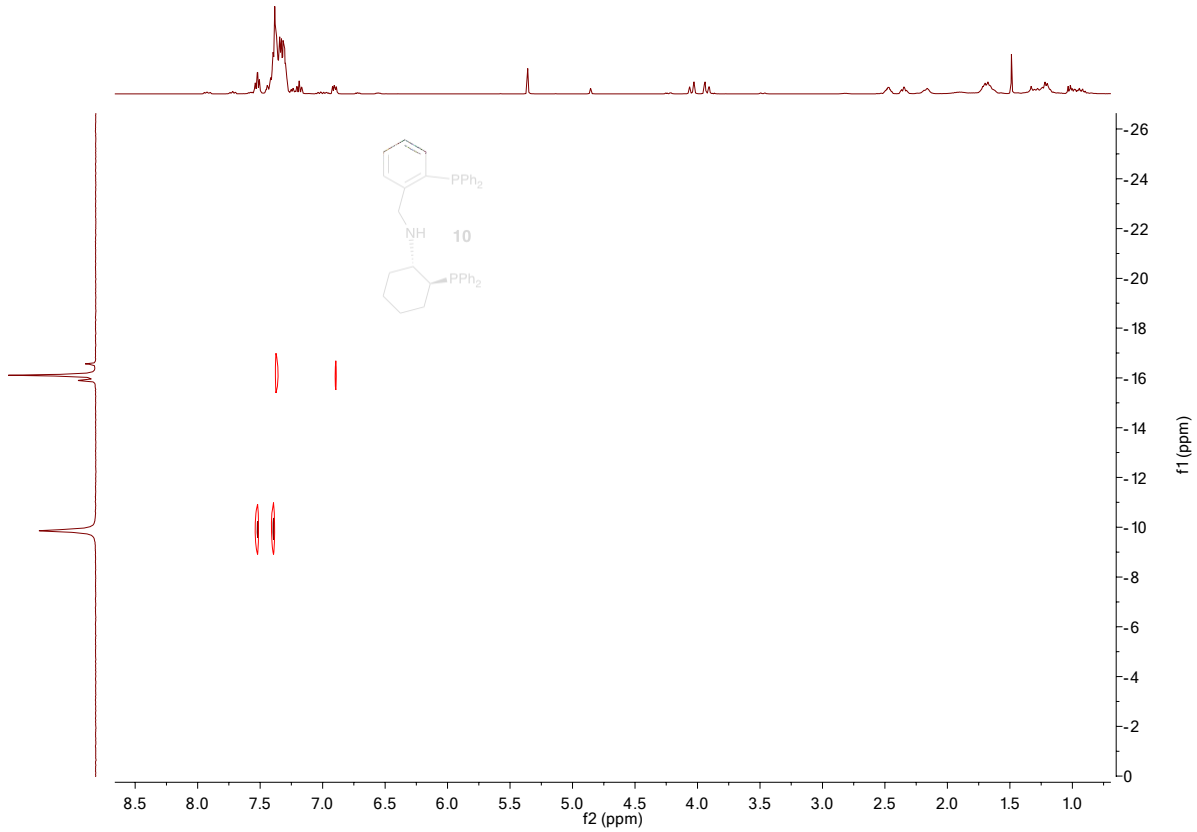


Figure S37. ^{31}P-^{1}H HSQC of ligand **10**.

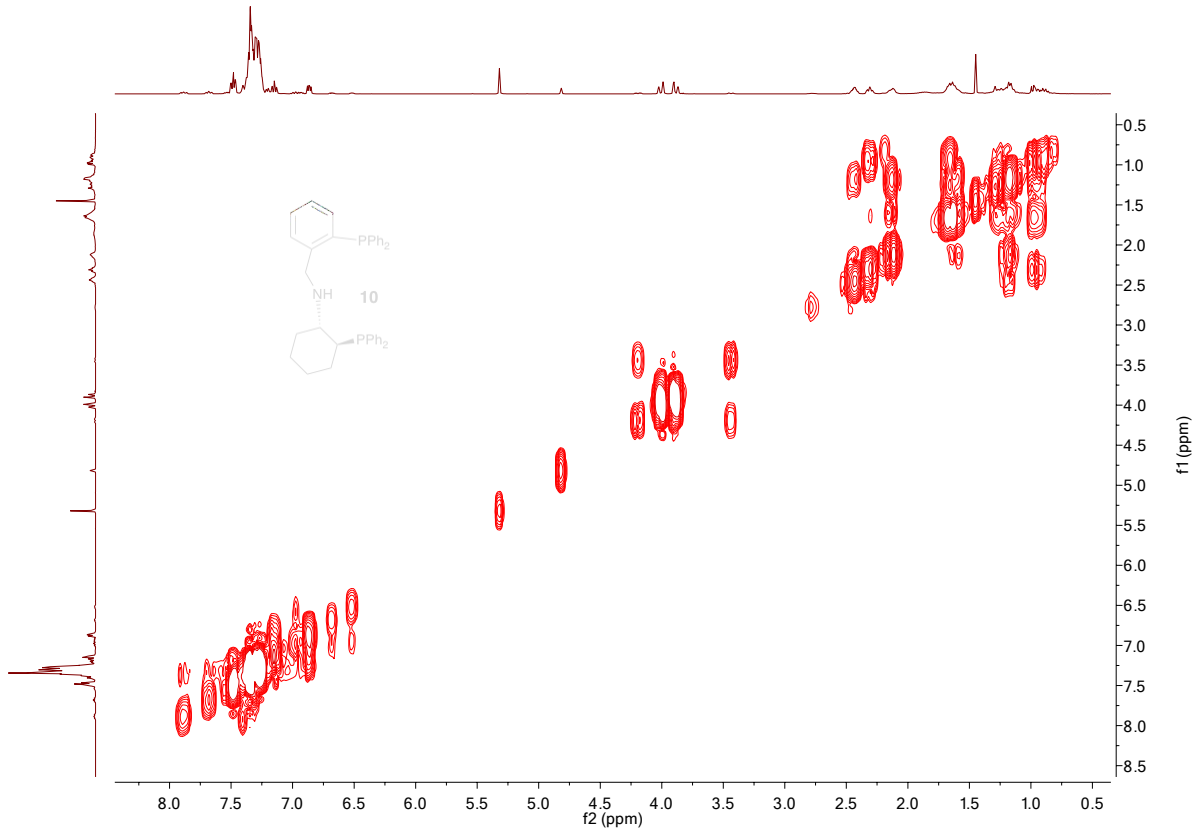
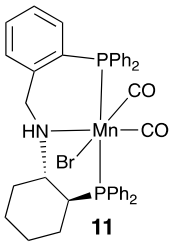


Figure S38. ^{1}H-^{1}H COSY of ligand **10**.

6. Synthesis and characterization of complexes (11)



11

Synthesis of [MnBr(CO)$_2$(10)] (11): A suspension of [MnBr(CO)$_5$] (0.434 g, 1.58 mmol, 1.0 equiv) and **11** (0.926 g, 1.66 mmol, 1.05 equiv) in anhydrous toluene was stirred at 80 °C for 3 h. Then the amount of solvent was reduced *in vacuo* to ~2 mL and was precipitated with anhydrous hexane. The solids were then filtered with a cannula. The process of precipitation and filtration was carried out several times and then the solid was dried under high *vacuo* (10^{-3} mbar) to give the desired bis(carbonyl) Mn(I) complex [Mn(CO)$_2$(**8**)]Br (**9**) as a yellow powder (Yield: 0.898 g, 76%). **^{1}H NMR** (500 MHz, CD_2Cl_2) δ 8.15 (br s, 1H, Ar-*H*), 7.93–7.90 (m, 2H, Ar-*H*), 7.52–7.27 (m, 17H, Ar-*H*), 7.15–7.12 (m, 2H, Ar-*H*), 6.99–6.95 (m, 1H, Ar-*H*), 4.48–4.44 (m, 1H, BzC*H*H), 4.16–4.10 (m, 1H, BzC*H*H), 3.11–3.08 (m, 1H, NCyC*H*H), 2.98–2.90 (m, 1H, PCyC*H*H), 2.73–2.61 (m, 1H, CyC*H*), 2.49–2.40 (m, 1H, CyC*H*), 2.10–2.07 (m, 1H, CyC*H*), 1.92–1.90 (m, 1H, CyC*H*), 1.38–1.07 (m, 4H, CyC*H*). **^{13}C{^{1}H} APT** (126 MHz, CD_2Cl_2) δ 141.9 (d, *J* = 17.6 Hz, arom.), 138.8, 138.6 (d, *J* = 9.2 Hz, arom.), 138.4, 136.9, 136.5, 135.4, (d, *J* = 9.2 Hz, arom.), 134.2 (d, *J* = 9.1 Hz, arom.), 133.9, 133.6, 133.4, 133.1 (d, *J* = 9.1 Hz, arom.), 132.2 (d, *J* = 8.5 Hz, arom.), 131.4, 131.1 (d, *J* = 7.7 Hz, arom.), 130.9, 130.2, 130.0, 129.7, 128.9 (d, *J* = 8.6 Hz, arom.), 128.7, 128.5 (d, *J* = 2.5 Hz, arom.), 128.5, 66.5 (d, *J* = 10.5 Hz, N*C*H), 55.8 (d, *J* = 8.4 Hz, Bz*C*H), 44.4 (d, *J* = 15.4 Hz, P*C*H), 35.3 (d, *J* = 12.3 Hz, Cy*C*H), 29.7 (d, *J* = 6.6 Hz, Cy*C*H), 27.1 (d, *J* = 2.2 Hz, Cy*C*H), 26.2 (Cy*C*H). **^{31}P{^{1}H} NMR** (203 MHz, CD_2Cl_2) δ 77.3 (d, *J* = 117.9 Hz), 51.0 (d, *J* = 117.9 Hz). **IR** ATR ν: 1921, 1842. **HRMS (ESI)**: *m*/*z* calcd for $[C_{39}H_{37}MnNO_2P_2]^+$: 668.1674 [M]+; found: 668.1672. **EA** Calcd. for $C_{43}H_{45}BrMnNO_3P_2$: C, 62.58; H, 4.98; N, 1.87; Found: C, 63.01; H, 5.10; N, 2.21.

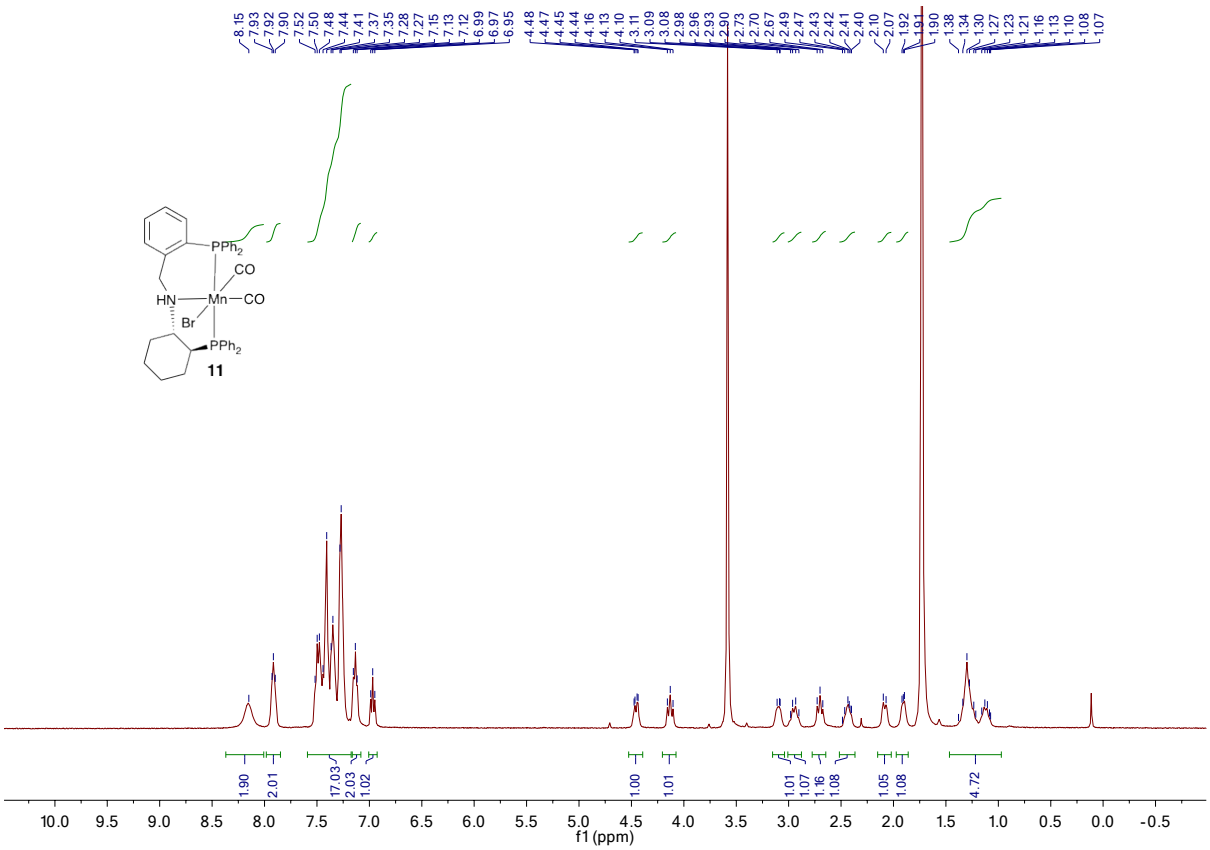


Figure S39. ^{1}H NMR spectrum of **11** (500 MHz, d_8-THF).

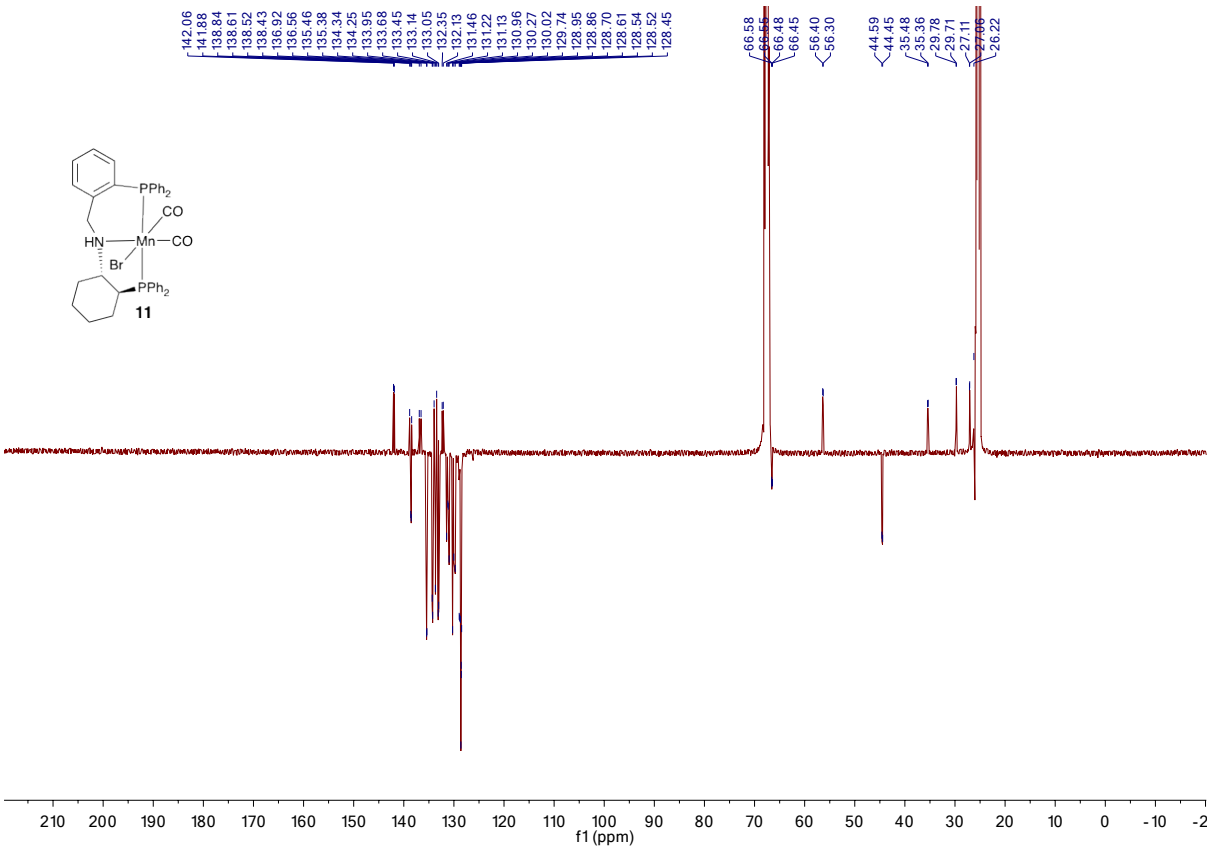


Figure S40. ^{13}C{^{1}H} APT NMR spectrum of **11** (126 MHz, d_8-THF).

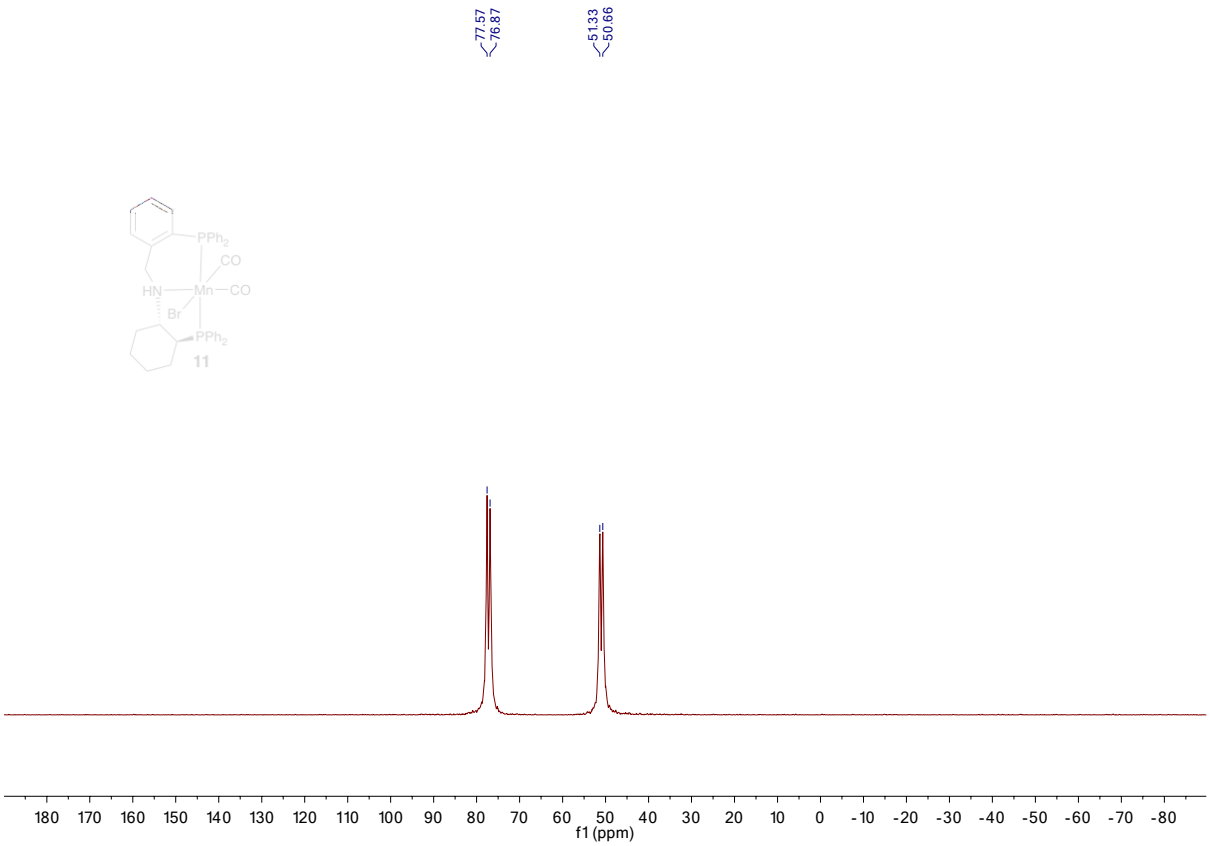


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of **11** (203 MHz, d_8-THF).

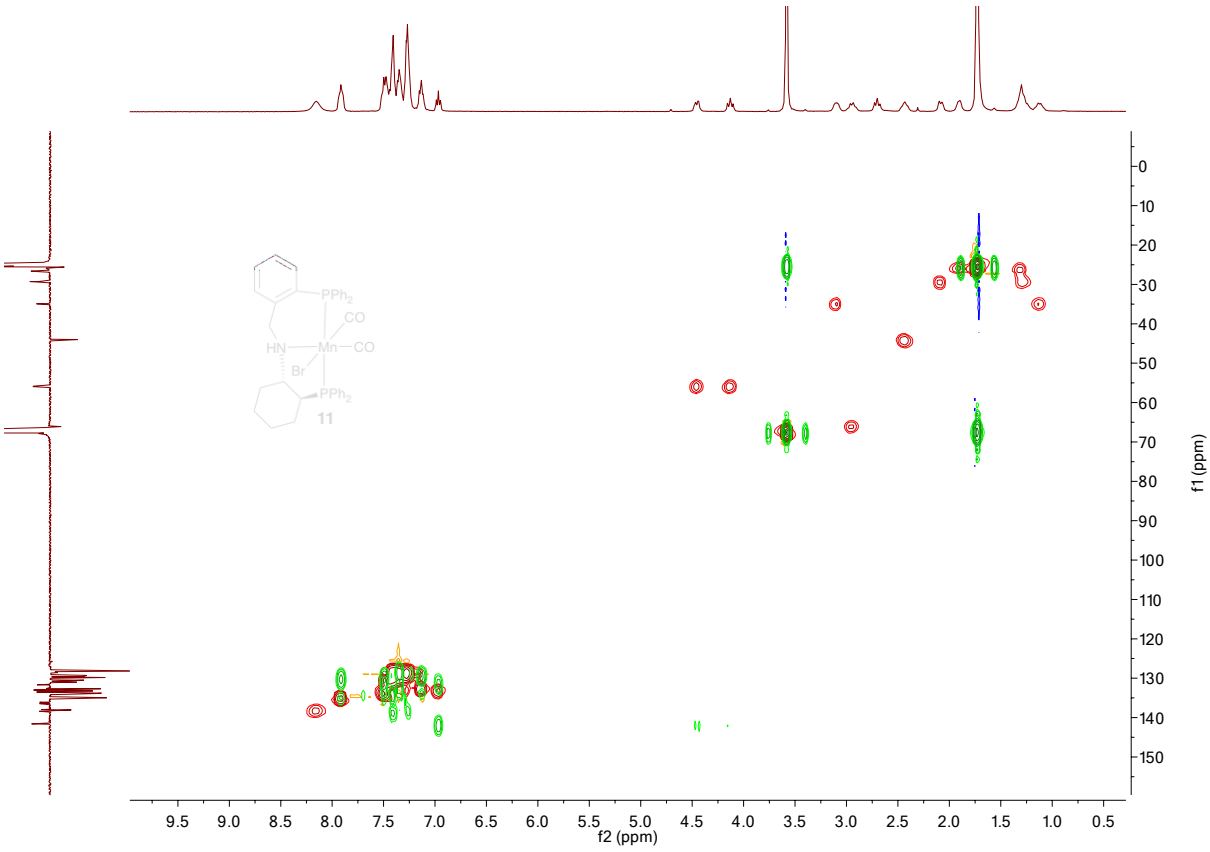


Figure S42. ^{13}C-^{1}HHSQC (red) and ^{13}C-^{1}H HMBC (green) of **9** superimposed.

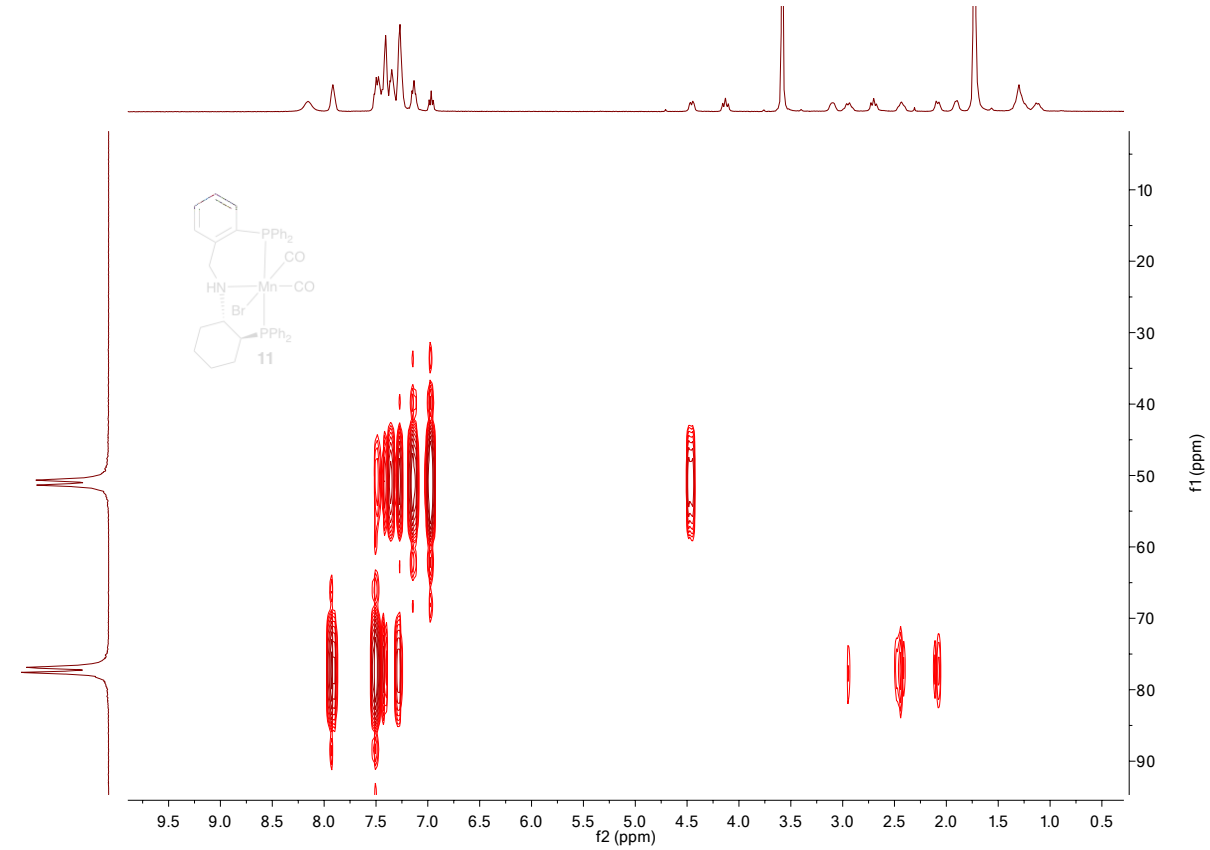


Figure S43. ^{31}P-^{1}H HSQC of [MnBr(CO)$_2$(**10**)] (**11**).

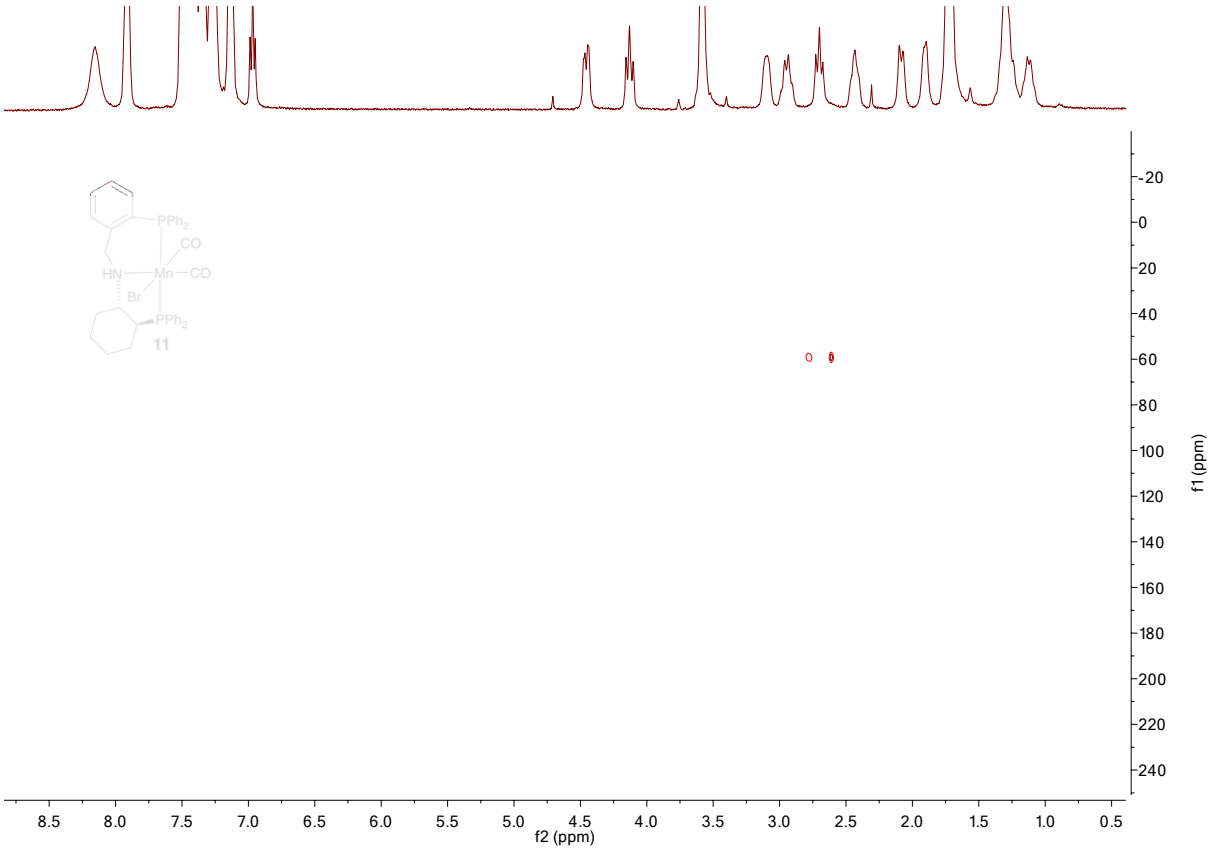


Figure S44. ^{15}N-^{1}H HSQC of [MnBr(CO)$_2$(**10**)] (**11**).

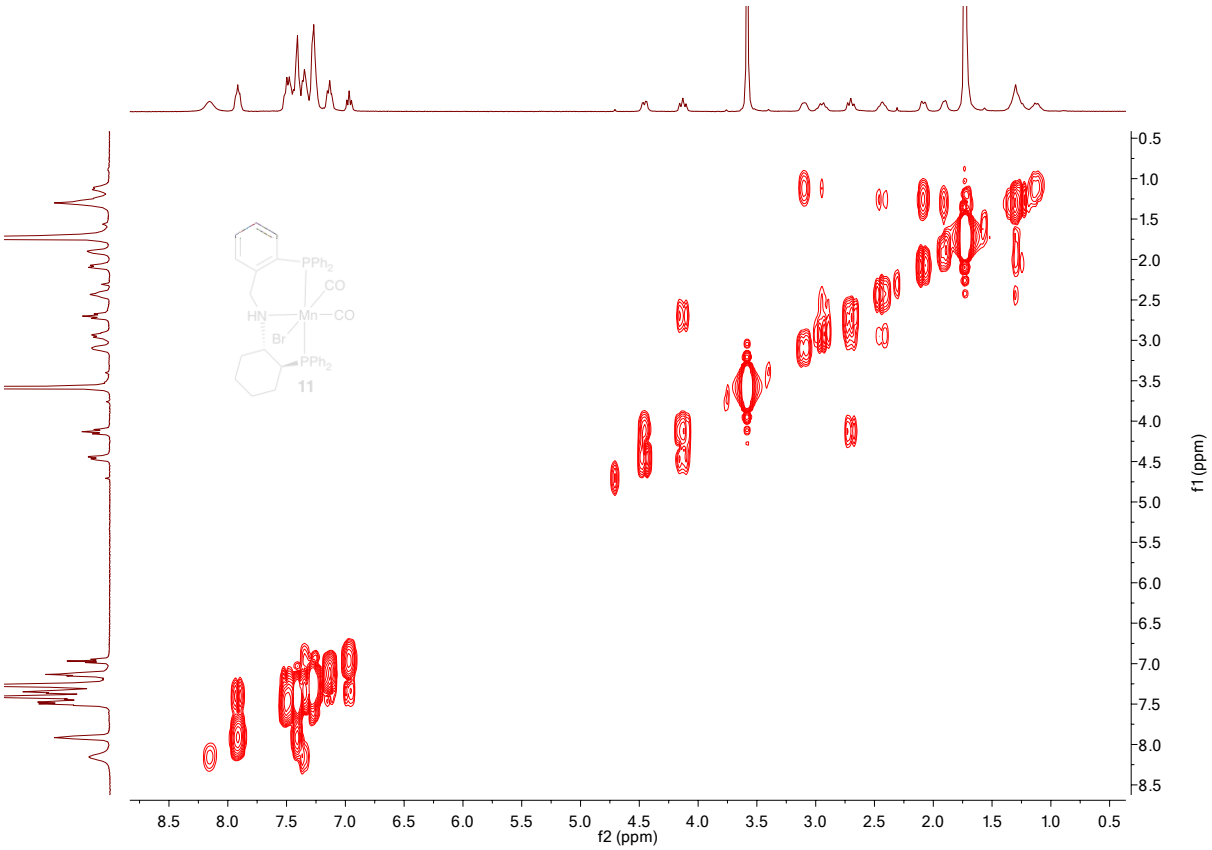


Figure S45. ^{1}H-^{1}H COSY of [MnBr(CO)$_2$(**10**)] (**11**).

7. Comparison of IR between Mn(I) phosphenes and phosphinite pincer complexes

The bond length of **Mn1** with the phosphorous atom **P2** (2.237 A^{o}) is shorter in comparison with **P1** (2.324 A^{o}) which indicates that phosphinite (**P2**) is a weaker electron donor and possess better dπ-pπ back bonding compared to the phosphene (**P1**). Moreover, a comparison was drawn between the bis-phosphene (**11**) and phosphene-phosphinite (**3a**) pincer Mn(I) complex using IR spectroscopy which also revealed the similar observation since complex **3a** (1931 cm^{-1}, 1851 cm^{-1}) possess higher CO stretching frequency than that **11** (1921 cm^{-1}, 1842 cm^{-1}). An analogous trend could also be observed in previously reported bis-phophine and bis-phosphinite Mn(I) complex, were **13** (1921 cm^{-1}, 1842 cm^{-1})[S12] is possessing lower CO stretching frequency than **12** (1921 cm^{-1}, 1842 cm^{-1}).[S12] Hence it is certain that the phosphinite ligands are the better/stronger π-accepting, than their corresponding phosphine ligands.

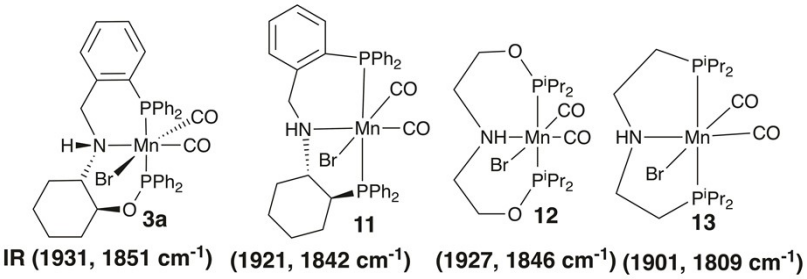


Figure 46. Comparison of IR values between bis-phophene (**11, 13**) and mono/bis-phosphinite (**3a, 12**).

8. Asymmetric Transfer Hydrogenation

Optimization of the transfer hydrogenations with complex **3** and 2-acetonaphthone as benchmark substrate were performed for observing the effect of various parameters on the catalytic system as shown in table 1(The 2-acetonapthone was chosen as the prototypical substrate over acetophenone since the preliminary DFT studies, the π-π interaction between the aryl rings on the ligands phosphene atom and the incoming ketones plays the key role in the enantioselectivity of our reaction). The catalysis was done under inert conditions. In a glove box, a 5 mL micro-vial with a magnetic stirrer was charged with catalyst **3** and 2-acetonaphthone and was sealed with a steel cap (with rubber septum) by a crimper. Freshly

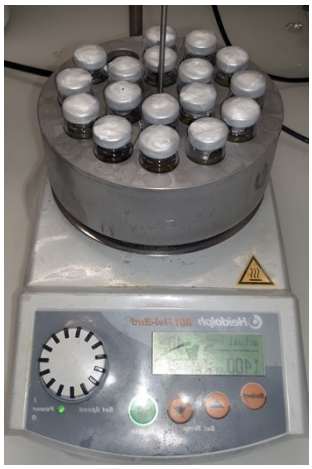


Figure S47. Metallic heating plates with 5 mL micro-vial according to the general procedure.

distilled 2-propanol and suitable base were added consecutively, and the vials was immersed in metallic heating plate after sealing it with teflon as shown in the figure S18 and let it to stir (4000 RPM) for the desired temperature and time.

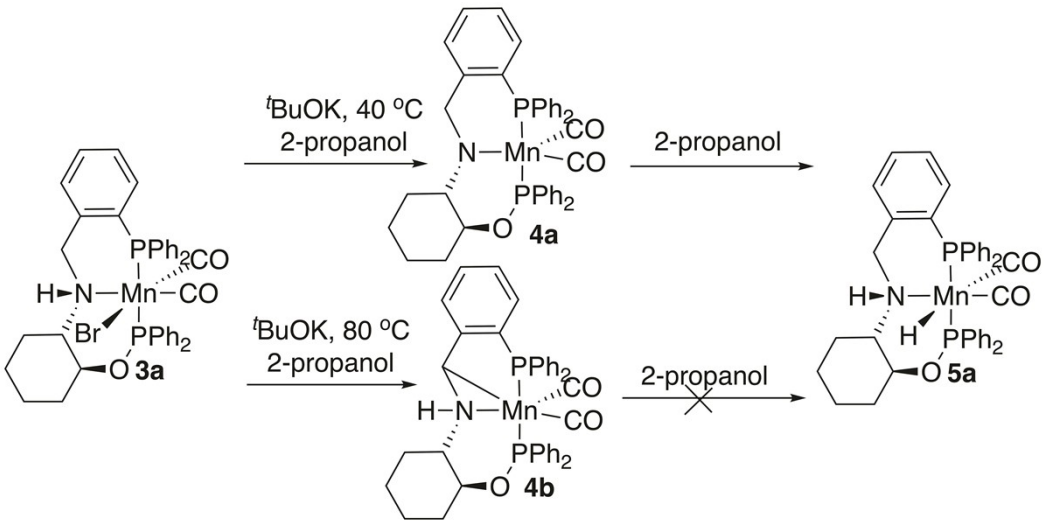
From the optimized parameters, the base and the temperature had the largest effect on the catalytic system. The catalyst requires a strong base in order to abstract the proton due to the higher basicity of the nitrogen atom attached to the manganese. Though KH was marginally

S.No	Concentration (M)	Base	Temp (°C)	catalyst	Catalytic loading (mol%)	ee (%)	Conv (%)
1	0.1	Na^{t}OPent	40	**3a**	2 mol%	74	70
2	0.2	Na^{t}OPent	40	**3a**	2 mol%	74	70
3	0.4	Na^{t}OPent	40	**3a**	2 mol%	74	56
4	0.2	NaO^{t}Bu	40	**3a**	2 mol%	77	25
5	0.2	LiO^{t}Bu	40	**3a**	2 mol%	70	05
6	0.2	KH	40	**3a**	2 mol%	78	91
7	0.2	KO^{t}Bu	40	**3a**	2 mol%	79	88
8	0.2	NaOEt	40	**3a**	2 mol%	76	15
9	0.2	KO^{t}Bu	60	**3a**	2 mol%	74	56
10	0.2	KO^{t}Bu	80	**3a**	2 mol%	62	23
11	0.2	KO^{t}Bu	RT	**3a**	2 mol%	82	61
12	0.2	KO^{t}Bu	40	**3b**	2 mol%	82	91
13[b]	0.2	KO^{t}Bu	40	**3b**	2 mol%	82	91
14	0.2	KO^{t}Bu	40	**3b**	4 mol%	82	92
15	0.2	KO^{t}Bu	40	**3b**	1 mol%	82	69

[a] Yields and enantiomeric excess were determined by GC. [b] PMe_3(30 mol% vs catalyst).

Table T2: optimization of Transfer hydrogenation with catalyst **3**.

the better base for the conversion with one of the best enantioselectivity, ^{t}BuOK was chosen over KH due to the practical convenience. The reactivity of **3a** surprisingly decreased with both decreasing and increasing the temperature from 40 °C. The tendency of Mn(I) complexes to form metal-aziridine intermediate at high temperature and amido species at lower temperature has been previously reported.[1] the combined effect of the higher acidity of the benzylic proton and greater Therefore metal-aziridine intermediate (does not leads to the formation of **5a**) formed at the higher temperature should be the possible reason for the decreased reactivity of **3a** at 80 °C. Therefore, this is a potential reason for the better activity of **3a** at 40 °C over 80 °C. (Scheme 2). However, the activity becomes lower at RT and hence 40 °C has been chosen as the optimum temperature. Addition of PMe_3(30 mol% vs catalyst)[S13] as poisoning agent for Mn(0) nanoparticles did not affect either the activity or enantioselectivity of the reaction (Table T2, entry 13), which is a proof of a homogeneous mechanism.



Scheme 2. Plausible mechanism of formation of manganese hydride **5a** from **3a**.

9. General procedures for catalysis (C1 and C2) and racemic alcohols (C3)

9.1 General ATH Procedure (C1) with [MnBr(CO)$_2$(2a)] (3a)

In a glove box, a 5 mL micro-vial with a magnetic stirrer was charged with catalyst **3b** (9.85 mg, 12.0 mmol, 2 mol%) and the ketone **6 (**0.6 mol**).** Then the micro-vial was sealed with a steel cap (with rubber septum) by a crimper. Freshly distilled 2-propanol (3 mL) and ^{t}BuOK (24 μL, 24.0 mmol, 4 mol%) were added respectively and was sealed with Teflon. Then the reaction vial was immersed in a preheated metallic heating plate and stirred at 1400 RPM. After 18 h the solvent was removed and purified with column chromatography to obtain the isolated yield and enantioselectivities by chiral GC and HPLC.

9.2 General ATH Procedure (C2) with [MnBr(CO)$_2$(2a)] (3a)

Reason for the second condition (C2): In contrary to the other acetophenones**,** the para substituted acetophenones (**6n**-**6r**) were reduced by **3b** with quantitative yield, albeit with significantly lower enantioselectivities (78-82%). Thus, an attempt was made by lower temperature to see if this could lead to a substantial increase in the enantioselectivities of the para substituted acetophenones (**6n**-**6r**) as mentioned in the procedure (**C2**) given below. The same condition was extended as well to the electron deficient meta substituted acetophenones as they also had displayed quantitative conversion under **C1** condition.

C2: In a glove box, a 5 mL micro-vial with a magnetic stirrer was charged with catalyst **3b** (4.95 mg, 6.0 mmol, 1 mol%) and the ketone **6 (**0.6 mol**).** Then the micro-vial was sealed with

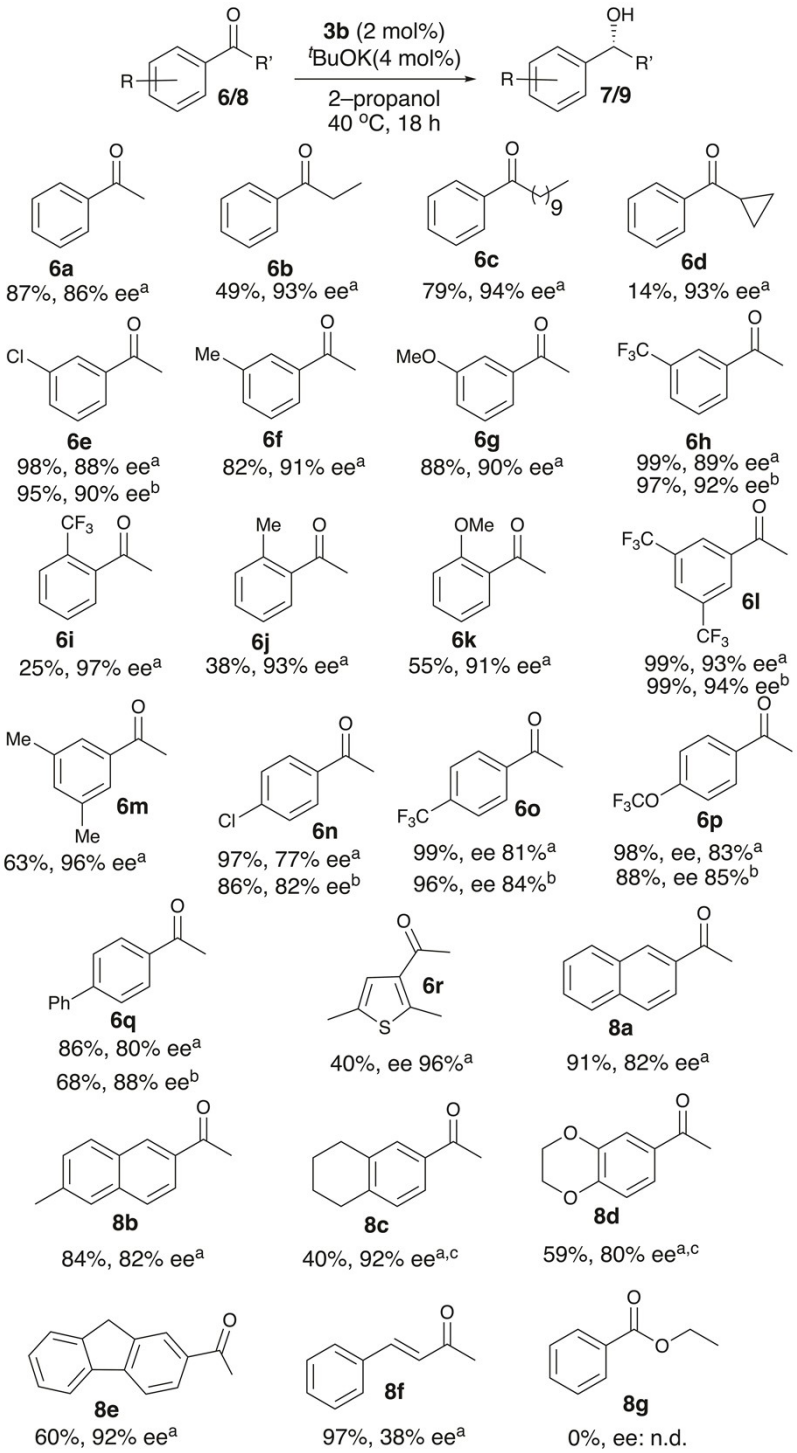
a steel cap (with rubber septum) by a crimper. Freshly distilled 2-propanol (3 mL) and ^{t}BuOK (12 μL, 12.0 mmol, 2 mol%) were added respectively and was sealed with Teflon. Then the reaction vial was immersed in a preheated metallic heating plate and stirred at 1400 RPM. After 24 h the solvent was removed and purified with column chromatography to obtain the isolated yield and enantioselectivities by chiral GC and HPLC.

9.3 General Procedure (C3) for the Reduction of Ketones 6 to Racemic Alcohols 7.

All the racemic alcohols of their corresponding ketones (**6/8**) were prepared by via **C3** in order to compare them with the enantiopure alcohols (**7**) to determine the enantiomeric excess.

C3: Ketone **6/8** (10 mmol) was added to sodium borohydride (493 mg, 12.5 mmol, 1.25 equiv) in EtOH (10 mL) at 0 °C and the solution was warmed to room temperature overnight. Aqueous 1 M HCl solution (50 mL) was added and the aqueous phase was extracted three times with Et2O (3 × 50 mL). The combined organic phases were washed with saturated aqueous NaCl solution (75 mL), dried over MgSO4, and the solvent was removed under reduced pressure. If required, product **7** was purified by flash column chromatography on silica gel.

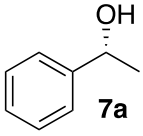
Chart 1: Substrate Scope for the Asymmetric Transfer Hydrogenation of 6 with 3b.



Reactions were performed with 0.6 mol of the substrate in 2-propanol (0.2 M). All the melecules are reported with the isolated yields and the ee values were determined by GC (β-DEX).(a) Optimized condition C1 (catalytic loading 2 mol%, 4 mol% tBuOK, 40 °C, 18 h, 0.2M). (b) Re-optimized condition C2 (catalytic loading 1 mol%, 2 mol% tBuOK, RT, 24 h). (c) The ee values were determined by HPLC (Chiralpak IB-3).

10. Characterization of Catalysis Products

10.1. GC and HPLC trace:



Synthesis of (R)-1-Phenylethan-1-ol, (R)-7a. The synthesis of racemic **7a** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 84% isolated yield (61.5 mg, colorless oil) and with 87.1% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 5H), 4.91 (q, *J* = 6.5, 1H), 2.99 (s, 1H), 1.55 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 145.97, 128.5, 127.5, 125.5, 70.4, 25.2. GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 4.57 min, t_R(major) = 9.95 min, t_R(minor) = 11.56 min. Analytical data are in agreement with literature data.[S1,2,3]

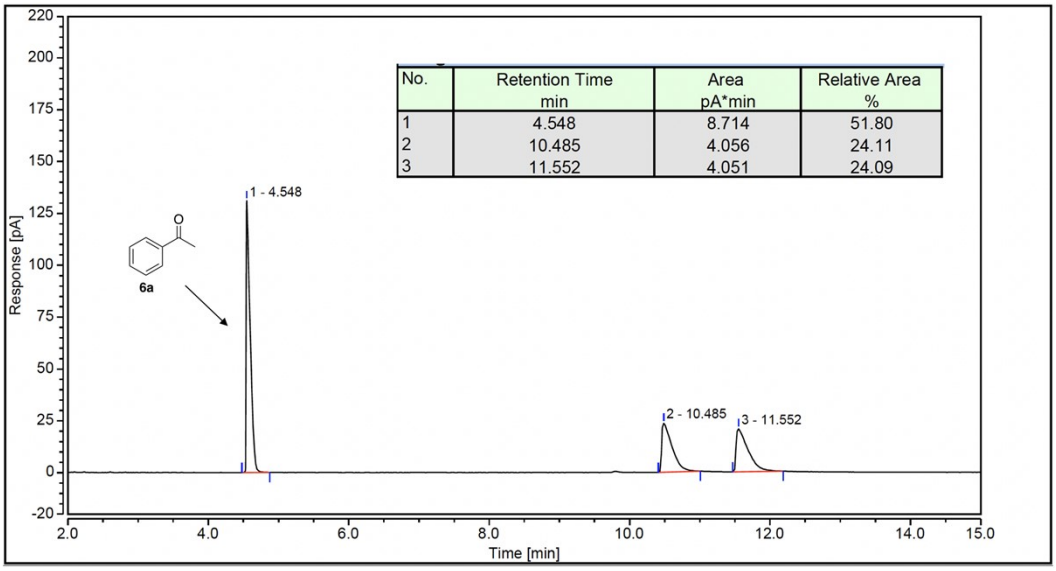


Figure S48: GC trace of 6a and racemic 7a (obtained by general procedure C3).

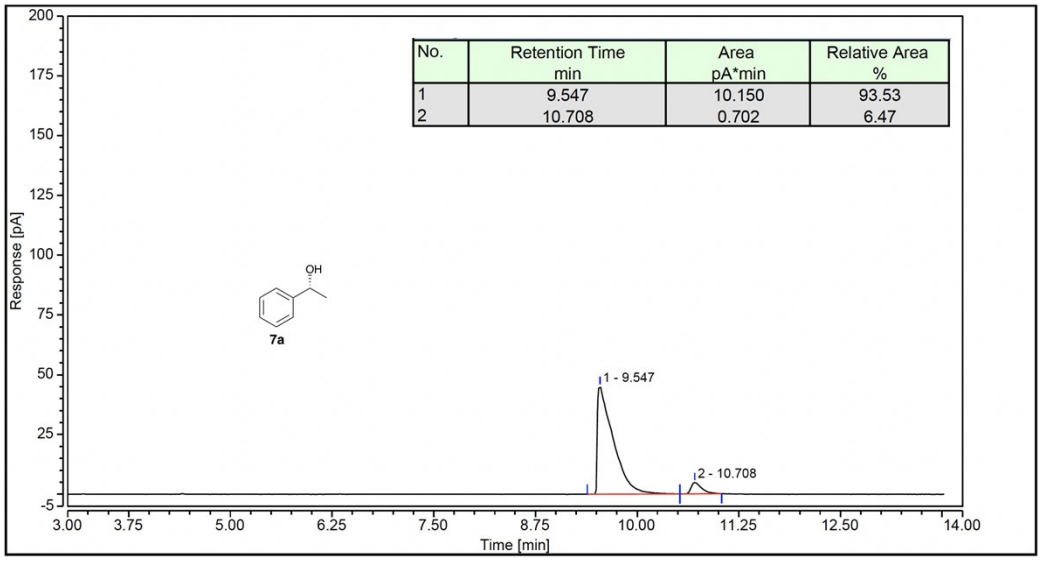
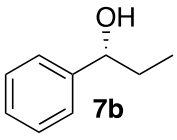
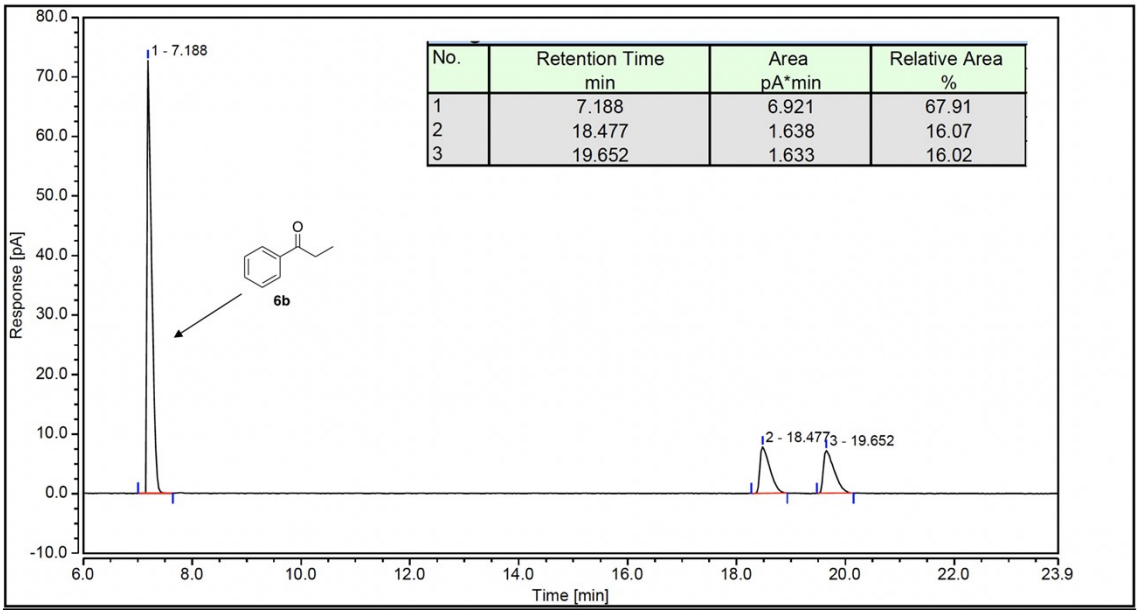


Figure S49: GC trace of enantioenriched 7a (obtained by general procedure C1).



Synthesis of (*R*)-1-phenylpropan-1-ol, (R)-7b. The synthesis of racemic **7b** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 49% isolated yield (40.0 mg, colorless oil) and with 90.2% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 – 7.05 (m, 5H), 4.43 (t, *J* = 6.6 Hz, 1H), 2.41 (s, 1H), 1.83 – 1.49 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 144.6, 128.4, 127.4, 126.1, 75.9, 31.8, 10.2. GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 6.97 min, t_R(major) = 17.46 min, t_R(minor) = 19.60 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.



No.	Retention Time min	Area pA*min	Relative Area %
1	7.188	6.921	67.91
2	18.477	1.638	16.07
3	19.652	1.633	16.02

Figure S50: GC trace of 6b and racemic 7b (obtained by general procedure C3).

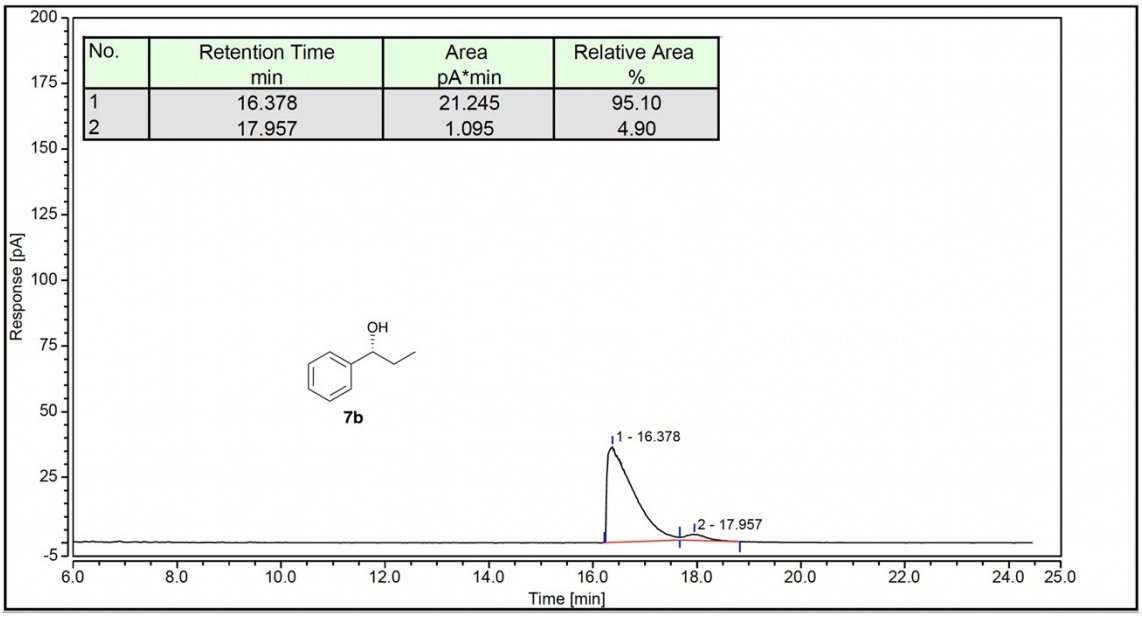
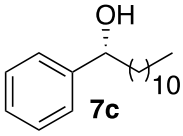


Figure S51: HPLC trace of enantioenriched 7b (obtained by general procedure C1).



Synthesis of (*R*)-1-phenyldodecan-1-ol, (R)-7c. The synthesis of racemic **7c** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 73% isolated yield (114.9 mg, white solid) and with 96.8% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.28 – 7.17 (m, 5H), 4.66 – 4.49 (m, 1H), 1.81 – 1.56 (m, 4H), 1.30 – 1.10 (m, 19H), 0.85 – 0.77 (m, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) 144.9, 128.4, 127.5, 125.9, 74.7, 39.1, 31.9, 29.6, 29.3, 25.8, 22.7, 14.1. GC: β-DEX column, 180 °C isotherm, retention times t_R(SM) = 15.5 min, t_R(major) = 20.7 min, t_R(minor) = 21.1 min. Analytical data are in agreement with literature data.[S4] The absolute configuration was determined to be (*R*) by comparison with literature data.[S4]

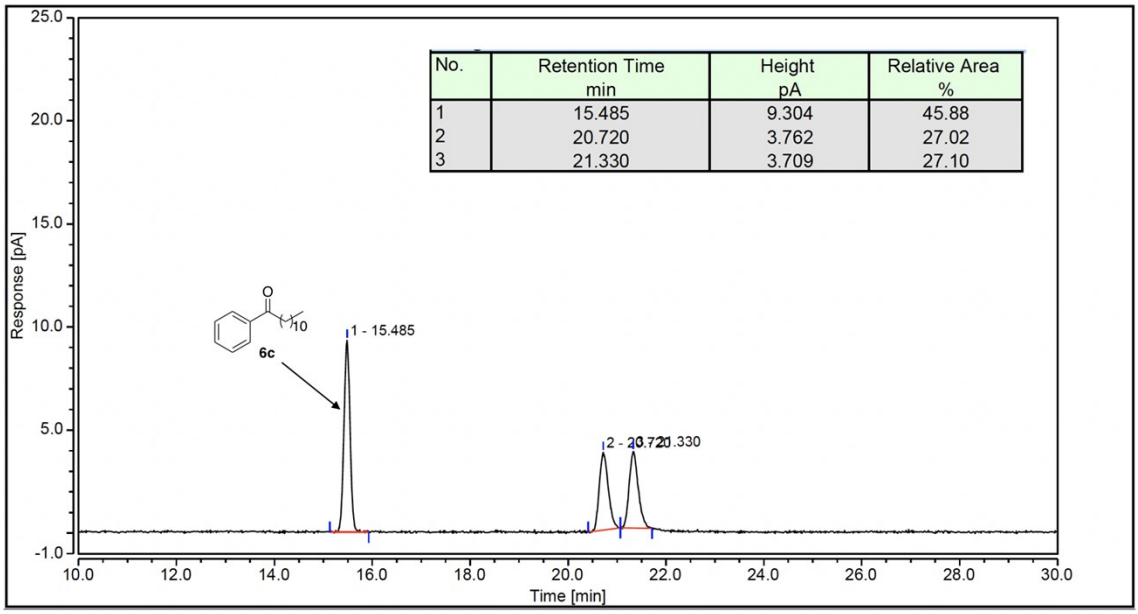


Figure S52: GC trace of 6c and racemic 7c (obtained by general procedure C3).

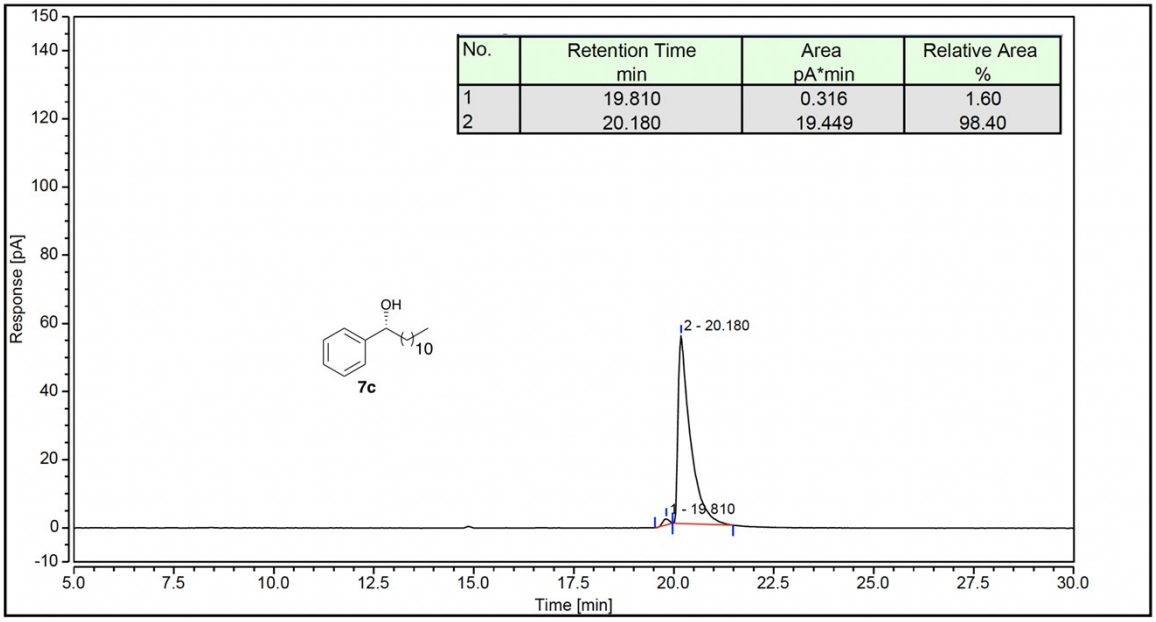
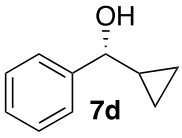
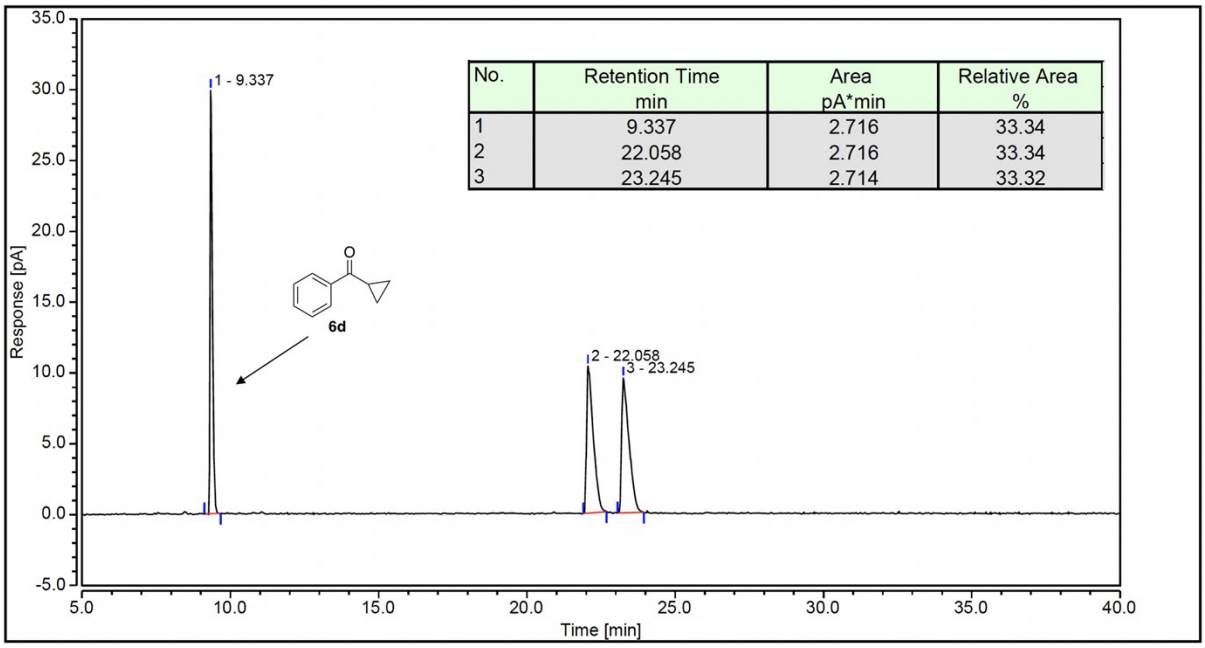


Figure S53: GC trace of enantioenriched 7c (obtained by general procedure C1).

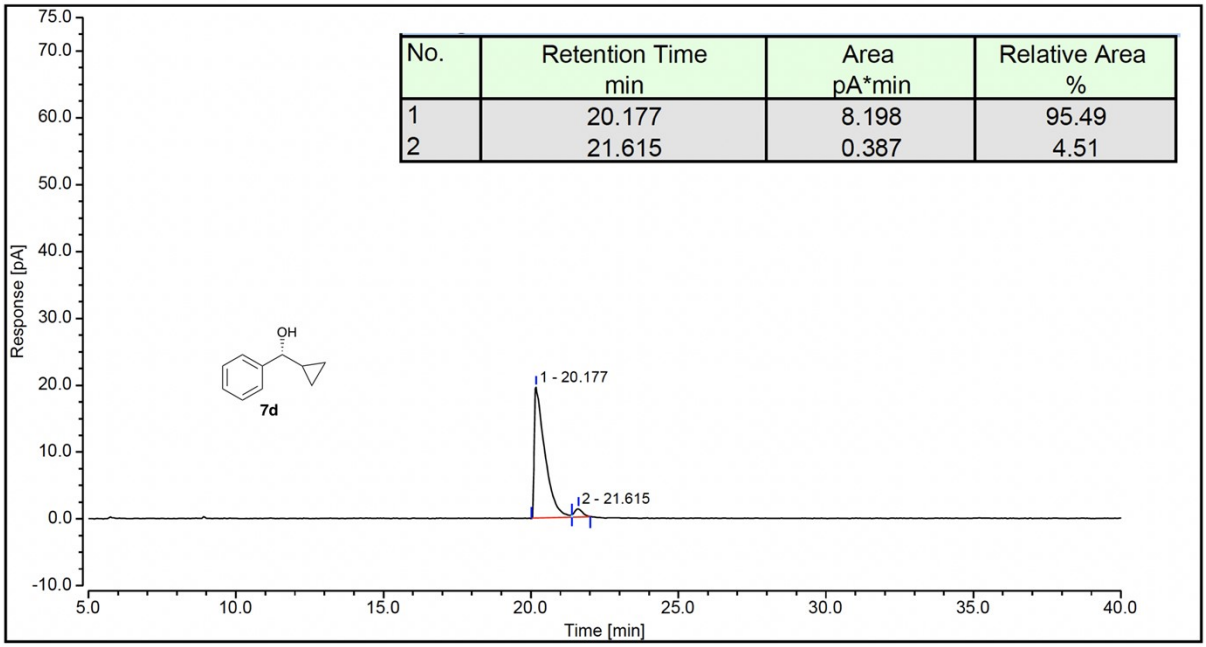


Synthesis of (*R*)-cyclopropyl(phenyl)methanol, (R)-7d. The synthesis of racemic **7d** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 10% isolated yield (8.9 mg, yellowish oil) and with 91% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.46 – 7.09 (m, 5H), 3.87 (d, *J* = 8.3 Hz, 1H), 2.20 (s, 1H), 1.27 – 0.93 (m, 1H), 0.67 – 0.06 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) 143.9, 128.3, 127.5, 126.1, 78.5, 19.2, 3.6, 2.8. GC: β-DEX column, 120 °C isotherm, retention times t_R(SM) = 9.0 min, t_R(major) = 21.9 min, t_R(minor) = 23.5 min. Analytical data are in agreement with literature data.[S4] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.



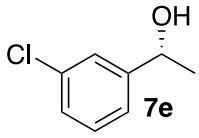
No.	Retention Time min	Area pA*min	Relative Area %
1	9.337	2.716	33.34
2	22.058	2.716	33.34
3	23.245	2.714	33.32

Figure S54: GC trace of 6d and racemic 7d (obtained by general procedure C3).



No.	Retention Time min	Area pA*min	Relative Area %
1	20.177	8.198	95.49
2	21.615	0.387	4.51

Figure S55: GC trace of enantioenriched 7d (obtained by general procedure C1).



Synthesis of (*R*)-1-(3-chlorophenyl)ethan-1-ol, (R)-7e. The synthesis of racemic **7e** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 98% isolated yield (92.1 mg, yellowish oil) and with 87.2% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.21 (m, 4H), 4.91 (q, *J* = 6.4 Hz, 1H), 1.85 (s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 147.8, 134.3, 129.7, 127.5, 125.6, 123.5, 69.8, 25.26. GC: β-DEX

column, 130 °C isotherm, retention times t_R(SM) = 4.5 min, t_R(major) = 11.5 min, t_R(minor) = 13.5 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison (*R*)-**7a.** This compound was obtained in 92% isolated yield (86.4 mg) and with 90.1% ee following general procedure **C2** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 130 °C isotherm, retention times t_R(SM) = 12.0 min, t_R(major) = 13.7 min, t_R(minor) = 13.7 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison (*R*)-**7a**

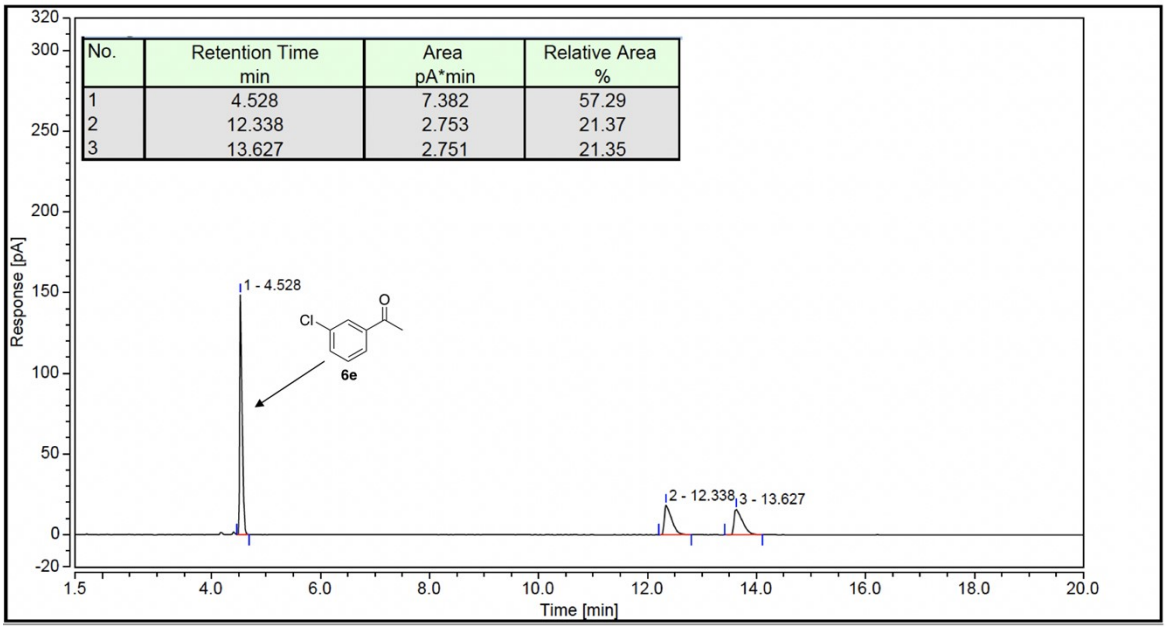


Figure S56: GC trace of 6e and racemic 7e (obtained by general procedure C3).

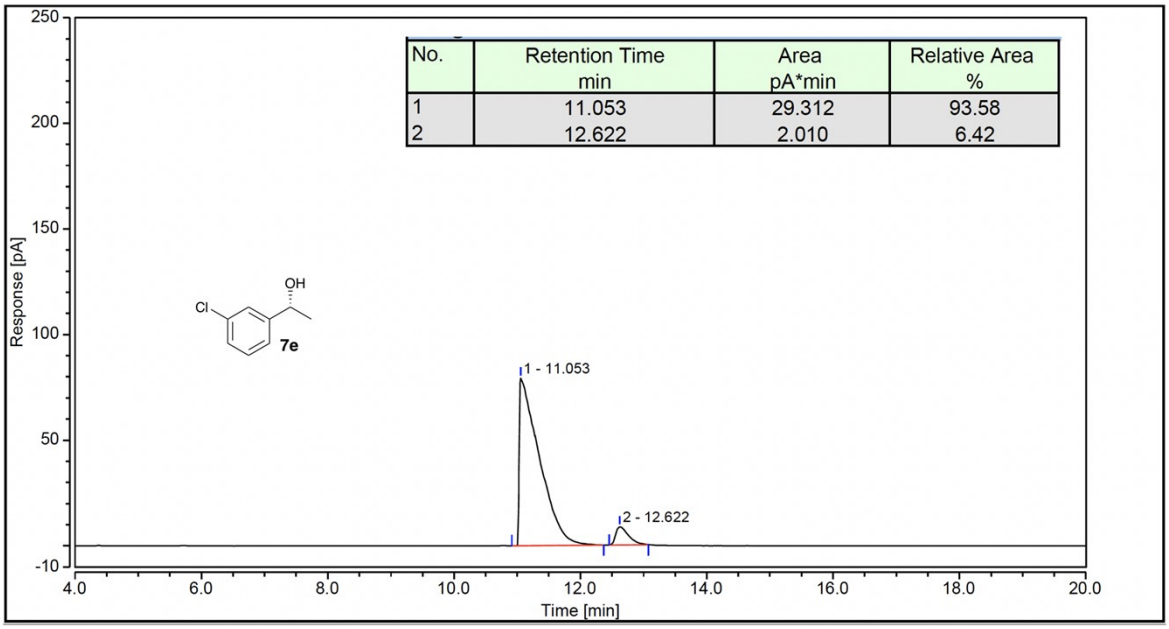


Figure S57: GC trace of enantioenriched 7e (obtained by general procedure C1).

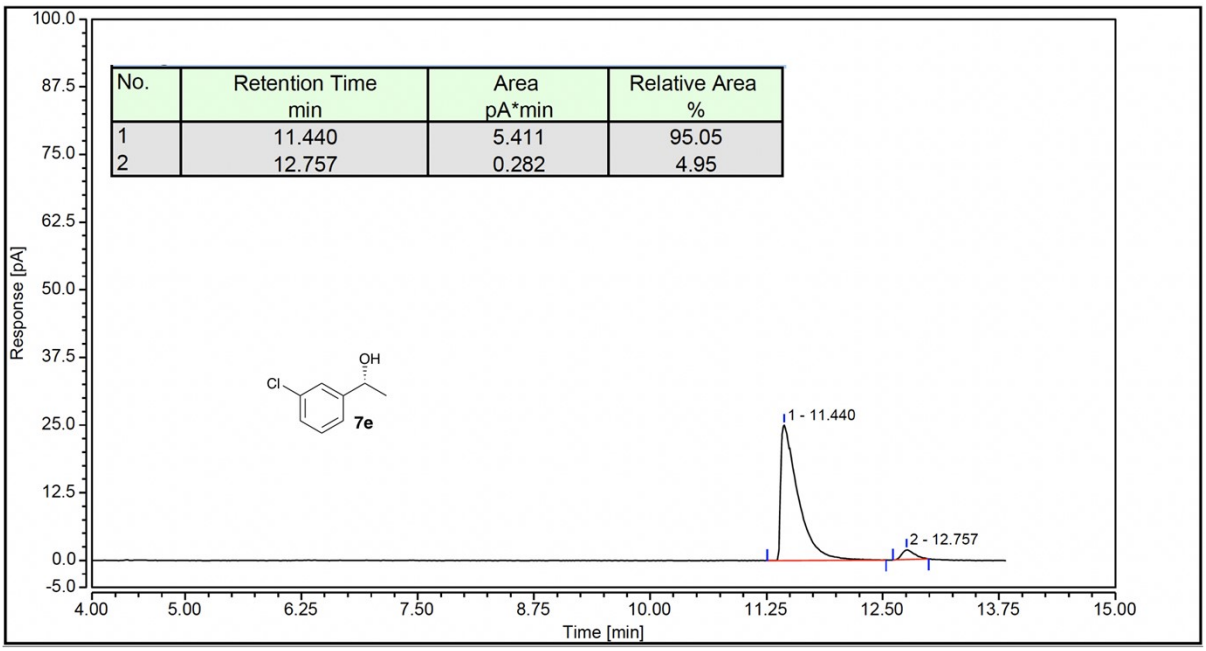
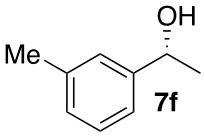
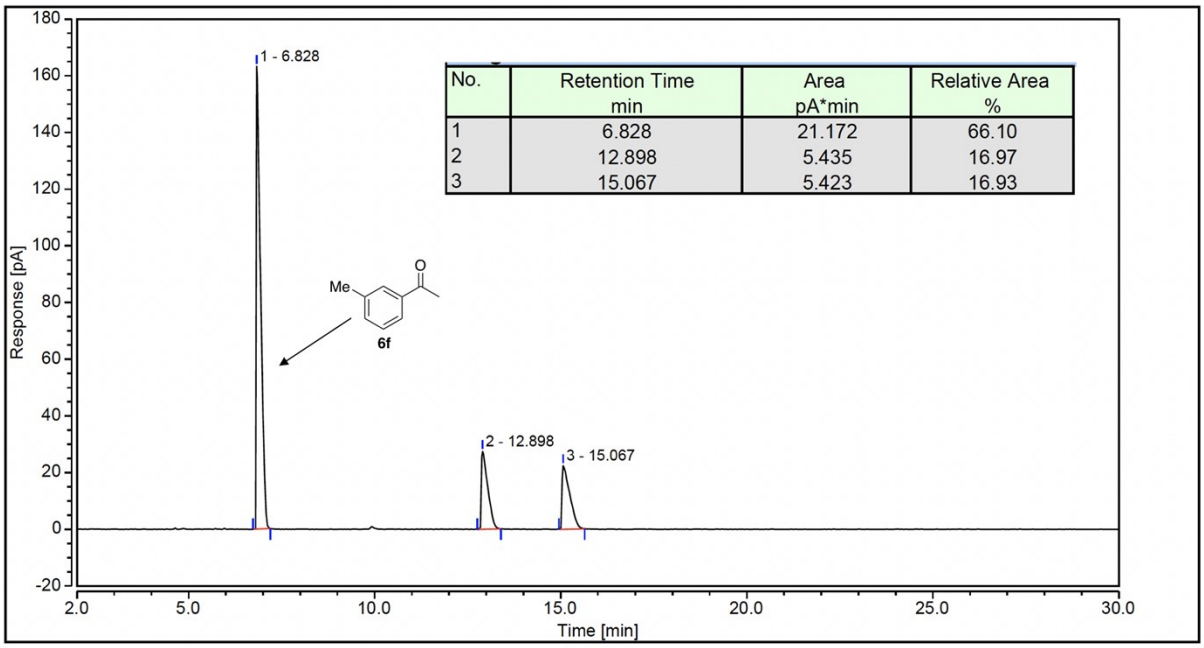


Figure S58: GC trace of enantioenriched 7e (obtained by general procedure C2).

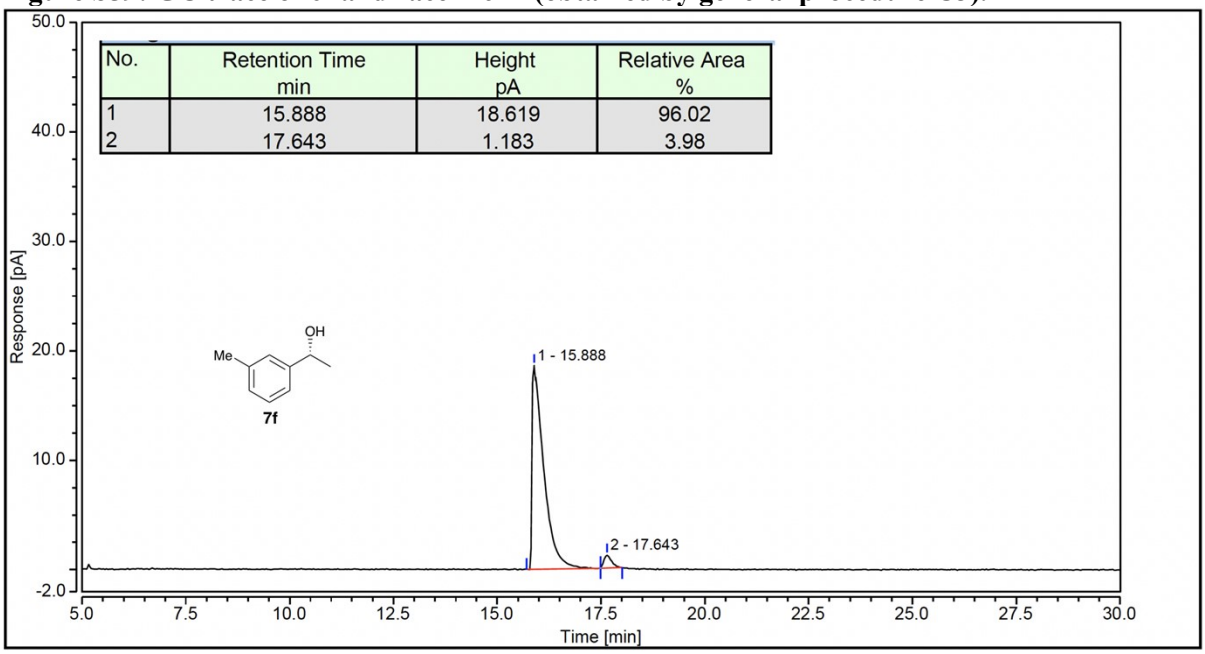


Synthesis of (*R*)-1-(*m*-tolyl)ethan-1-ol, (R)-7f. The synthesis of racemic **7f** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 80% isolated yield (65.4mg, colorless oil) and with 92.0% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.12 (m, 4H), 4.91 (q, *J* = 6.5 Hz, 1H), 2.45 (s, 3H), 2.2.29 (s, 1H), 1.56 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 145.9, 138.1, 128.4, 128.2, 126.2, 122.5, 70.4, 25.2, 21.5.GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 6.8 min, t_R(major) = 16.0 min, t_R(minor) = 19.0 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]



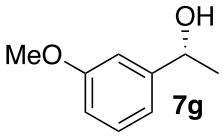
No.	Retention Time min	Area pA*min	Relative Area %
1	6.828	21.172	66.10
2	12.898	5.435	16.97
3	15.067	5.423	16.93

Figure S59: GC trace of 6f and racemic 7f (obtained by general procedure C3).



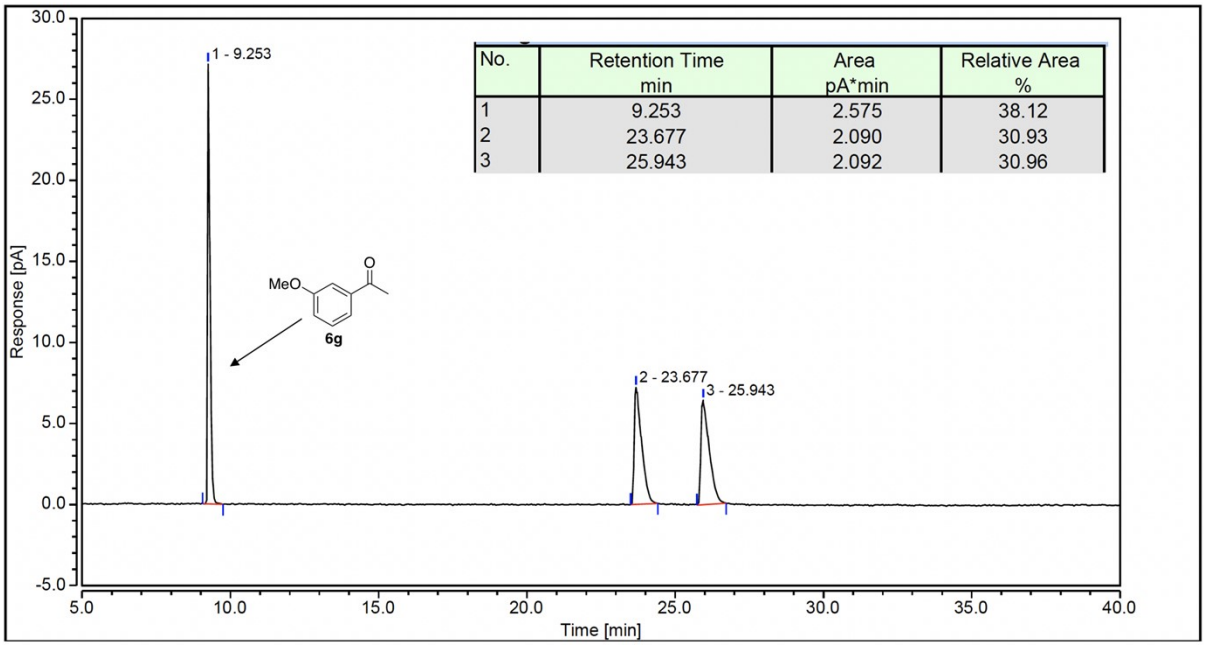
No.	Retention Time min	Height pA	Relative Area %
1	15.888	18.619	96.02
2	17.643	1.183	3.98

Figure S60: GC trace of enantioenriched 7f (obtained by general procedure C1).



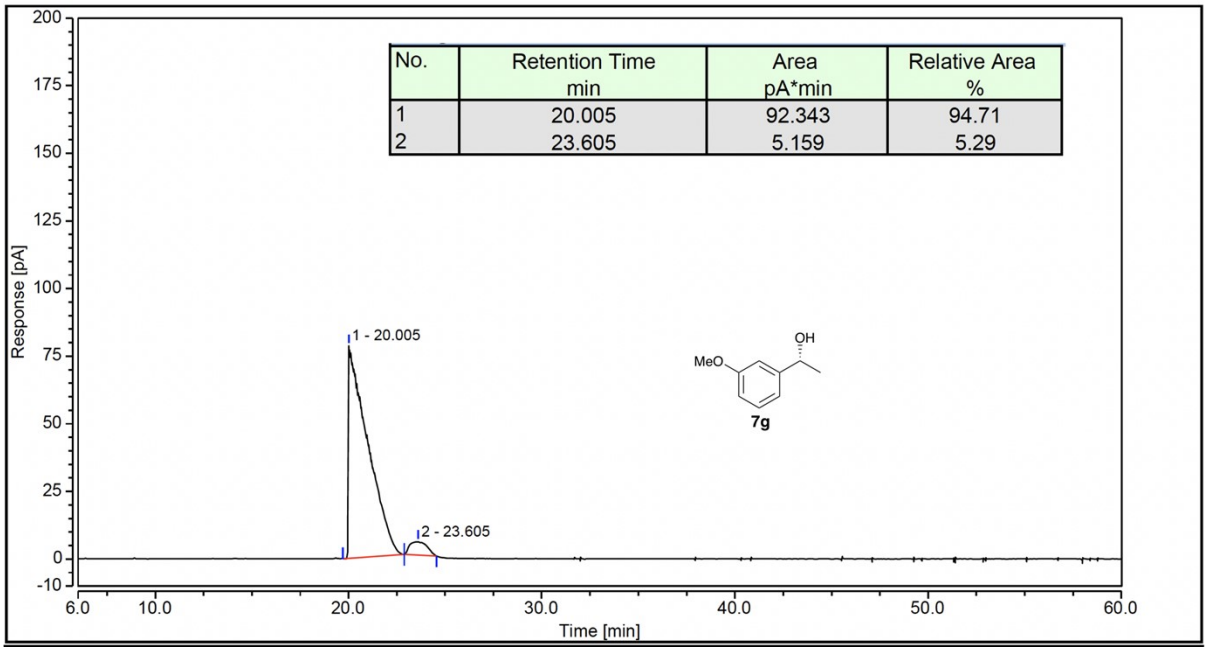
Synthesis of (*R*)-1-(3-methoxyphenyl)ethan-1-ol, (R)-7g. The synthesis of racemic **7g** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 84% isolated yield (76.7 mg, yellowish oil) and with 89.4% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 1H), 7.03 – 6.94 (m, 2H), 6.90 – 6.84 (m, 1H), 4.87z (q, *J* = 6.4 Hz, 1H), 3.85 (s, 4H), 2.73 (s, 1H), 1.52 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 159.7,

14738, 129.5, 117.80, 112.8, 111.0, 70.2, 55.2, 25.2.GC: β-DEX column, 120 °C isotherm, retention times t_R(SM) = 9.1 min, t_R(major) = 22.0 min, t_R(minor) = 25.7 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) (*R*)-**7a**.



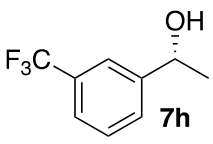
No.	Retention Time min	Area pA*min	Relative Area %
1	9.253	2.575	38.12
2	23.677	2.090	30.93
3	25.943	2.092	30.96

Figure S61: GC trace of racemic 6g and 7g (obtained by general procedure C3).



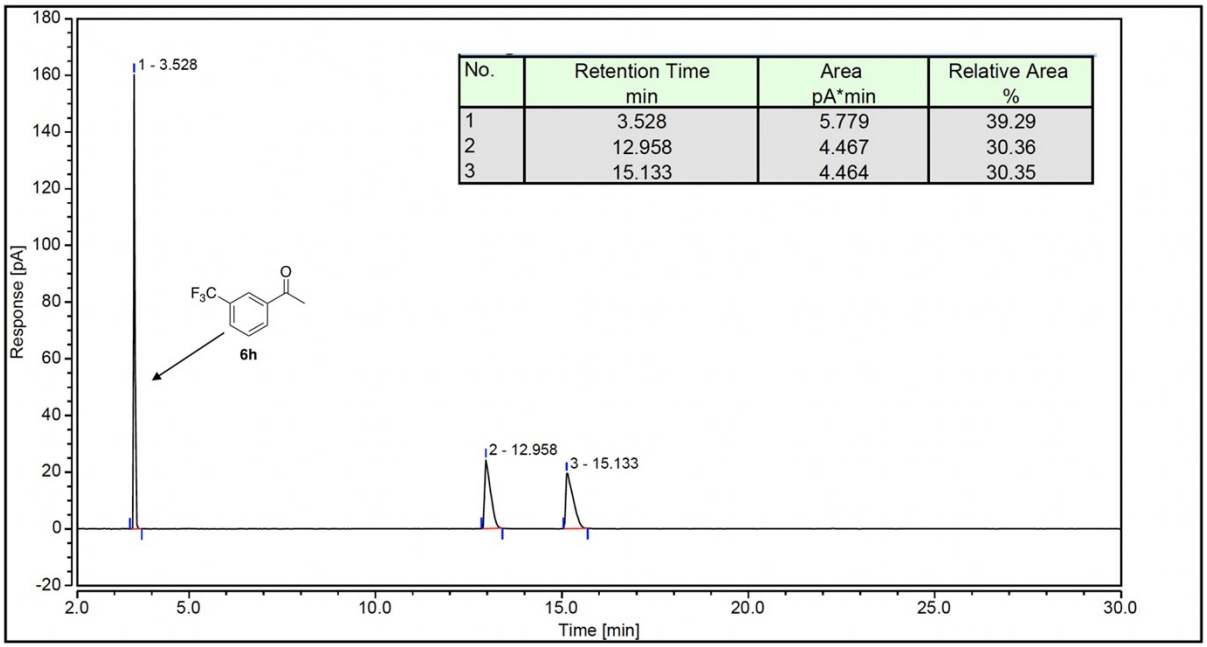
No.	Retention Time min	Area pA*min	Relative Area %
1	20.005	92.343	94.71
2	23.605	5.159	5.29

Figure S62: GC trace of enantioenriched 7g (obtained by general procedure C1).



Synthesis of (*R*)-1-(3-(trifluoromethyl)phenyl)ethan-1-ol, (R)-7h. The synthesis of racemic **7h** and its spectroscopic data has previously been reported.[S2,3] This

compound was obtained in 99% isolated yield (113.0 mg, yellowish oil) and with 85.14% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 3.5 min, t_R(major) = 11.9 min, t_R(minor) = 15.1 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**. This compound was obtained in 95% isolated yield (108.4 mg, yellowish oil) and with 89.5% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 3.5 min, t_R(major) = 12.6 min, t_R(minor) = 15.3 min. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.62 – 7.11 (m, 4H), 4.79 (q, *J* = 6.5 Hz, 1H), 2.62 (d, *J* = 1.0 Hz, 1H), 1.36 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 146.7, 130.8 (q, *J* = 32.1 Hz), 128.9, 128.8, 124.2, 122.2, 69.74. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.



No.	Retention Time min	Area pA*min	Relative Area %
1	3.528	5.779	39.29
2	12.958	4.467	30.36
3	15.133	4.464	30.35

Figure S63: GC trace of 6h and racemic 7h (obtained by general procedure C3).

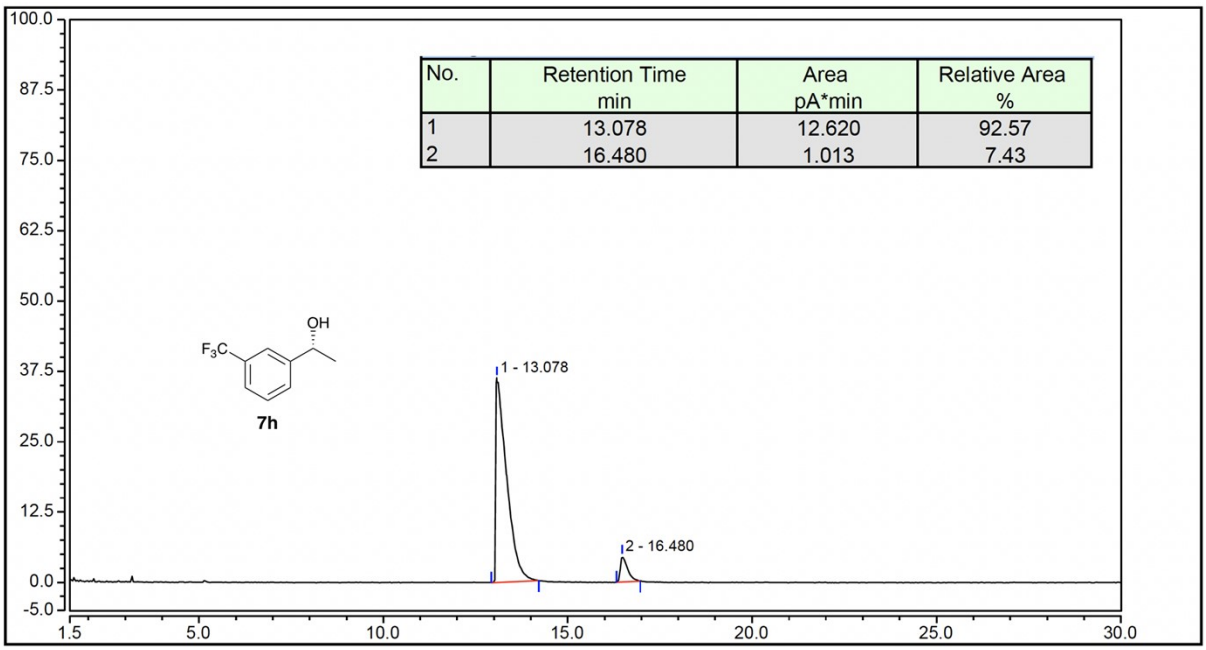


Figure S64: GC trace of enantioenriched 7h (obtained by general procedure C1).

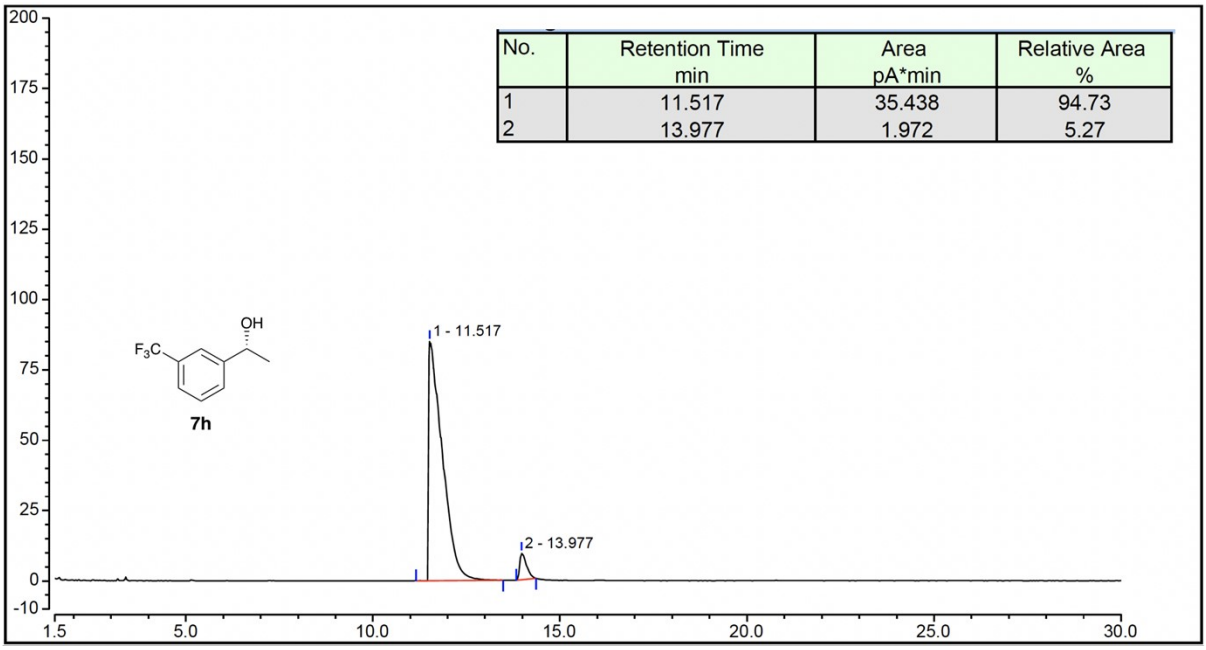
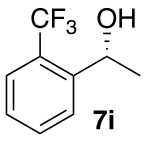
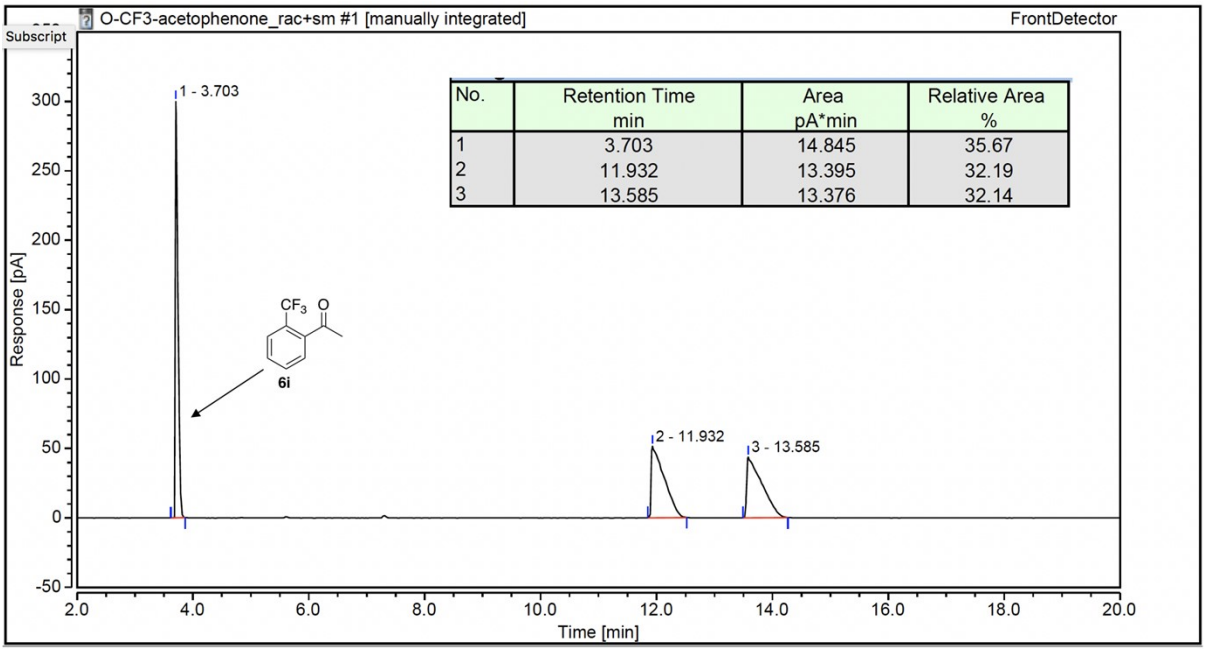


Figure S65: GC trace of enantioenriched 7h (obtained by general procedure C2).



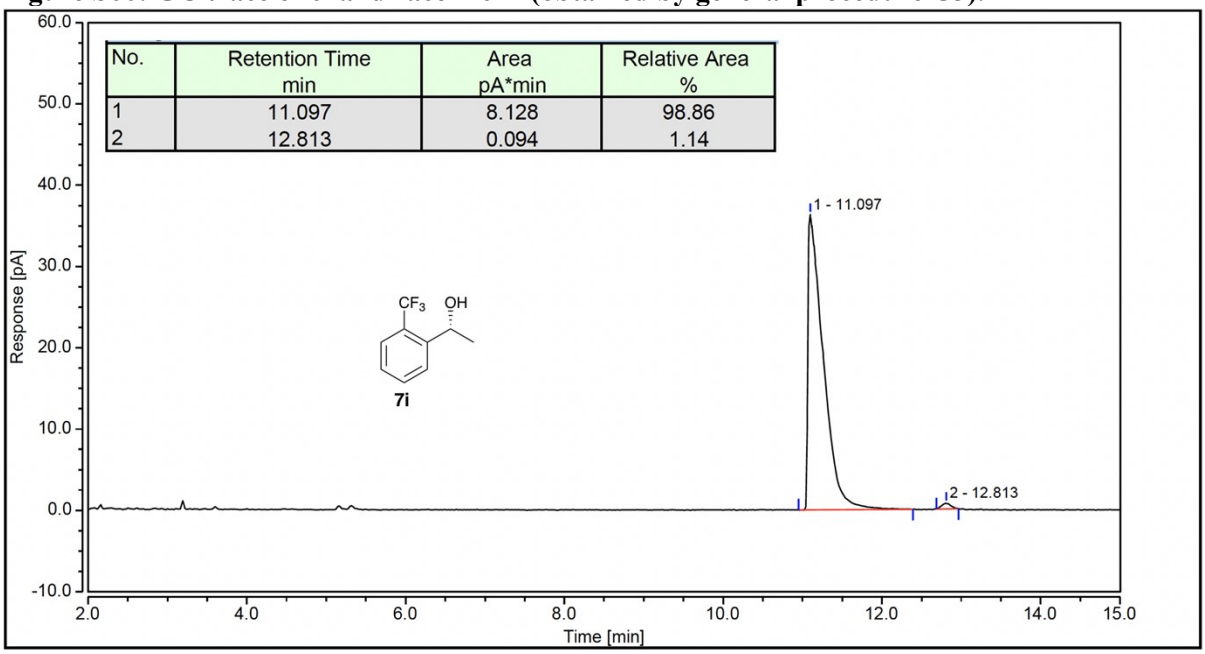
Synthesis of (*R*)-1-(2-(trifluoromethyl)phenyl)ethan-1-ol, (R)-7i. The synthesis of racemic **7i** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 21% isolated yield (23.9 mg, colorless oil) and with 97.7% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.96 – 7.79 (m, 1H), 7.77 – 7.59 (m, 2H), 7.52 – 7.36 (m, 1H), 5.40 (q, *J* = 6.4, 1H), 2.20 (s, 1H), 1.54 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 145.11, 132.3, 127.3, 127.1,

125.3 (q, J = 5.9 Hz), 122.6, 66.7, 25.4. GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 3.5 min, t_R(major) = 11.7 min, t_R(minor) = 14.0 min. Analytical data are in agreement with literature data.[S4] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.



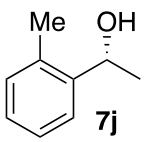
No.	Retention Time min	Area pA*min	Relative Area %
1	3.703	14.845	35.67
2	11.932	13.395	32.19
3	13.585	13.376	32.14

Figure S66: GC trace of 6i and racemic 7i (obtained by general procedure C3).



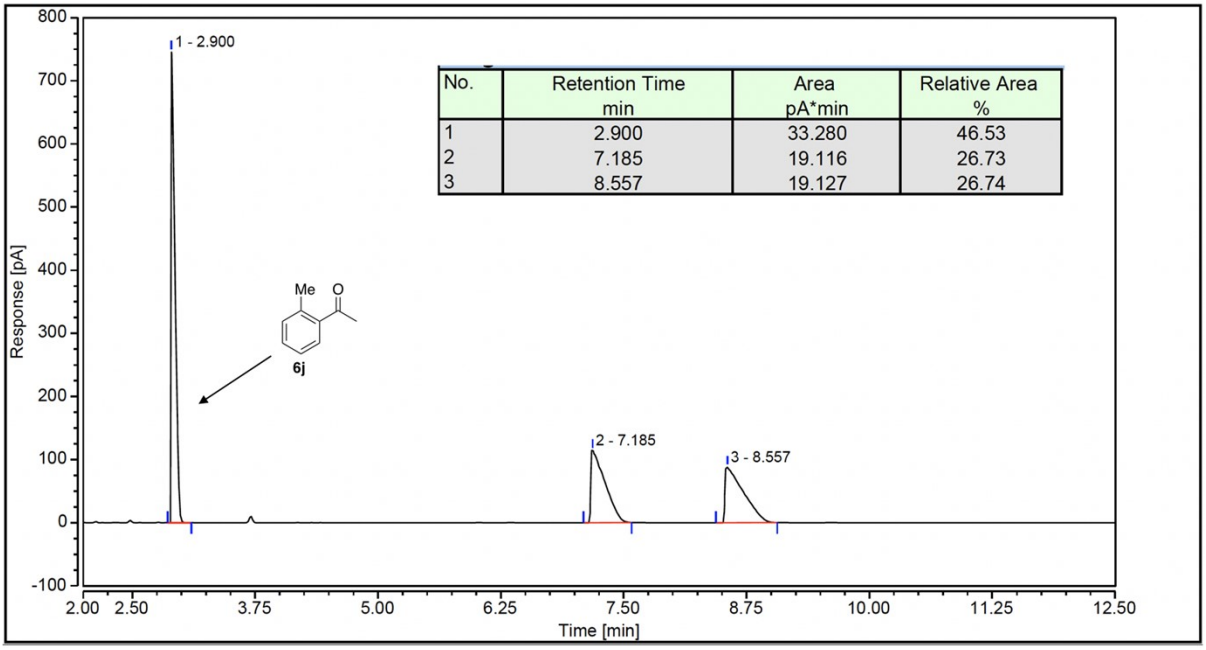
No.	Retention Time min	Area pA*min	Relative Area %
1	11.097	8.128	98.86
2	12.813	0.094	1.14

Figure S67: GC trace of enantioenriched 7i (obtained by general procedure C1).



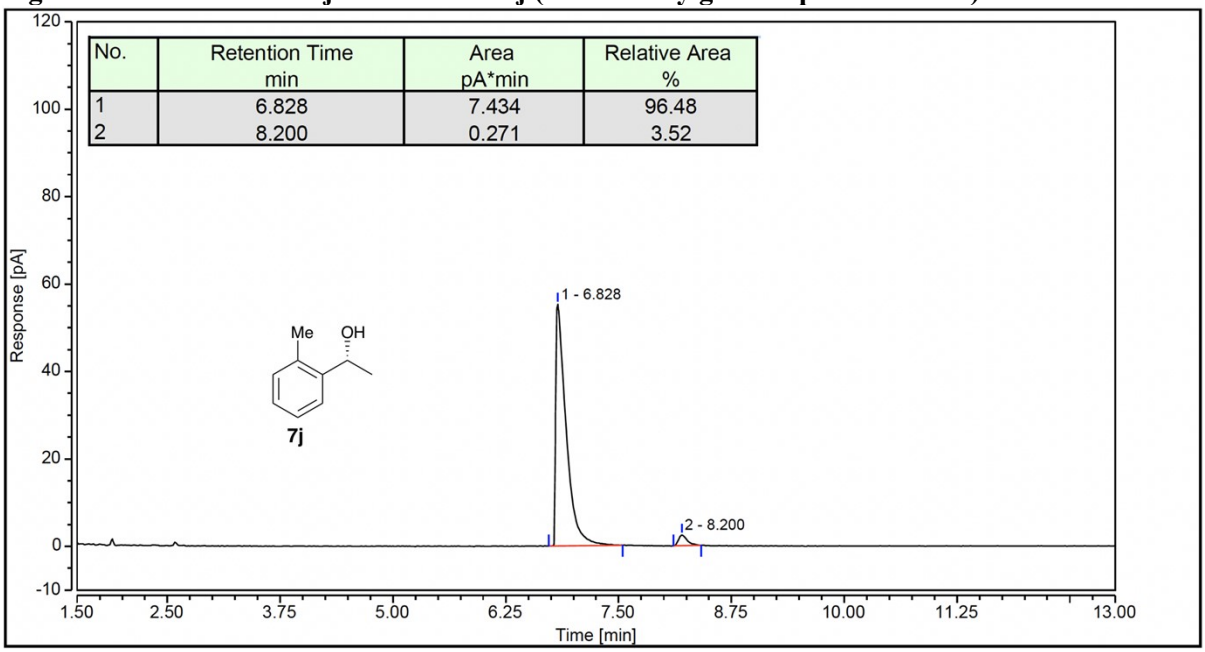
7j **Synthesis of (*R*)-1-(*o*-tolyl)ethan-1-ol, (R)-7j**. The synthesis of racemic **7j** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 35.0%

isolated yield (28.6 mg, yellowish oil) and with 93.0% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 – 7.57 (m, 1H), 7.33 – 7.20 (m, 3H), 5.15 (d, *J* = 6.4 Hz, 1H), 2.71 (s, 1H), 2.42 (s, 3H), 1.53 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 144.0, 134.2, 130.4, 127.1, 126.4, 124.6, 66.7, 23.9, 18.9. GC: β-DEX column, 130 °C isotherm, retention times t_R(SM) = 2.8 min, t_R(major) = 7.0 min, t_R(minor) = 8.8 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.



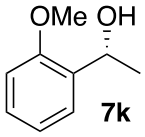
No.	Retention Time min	Area pA*min	Relative Area %
1	2.900	33.280	46.53
2	7.185	19.116	26.73
3	8.557	19.127	26.74

Figure S68: GC trace of 6j and racemic 7j (obtained by general procedure C3).

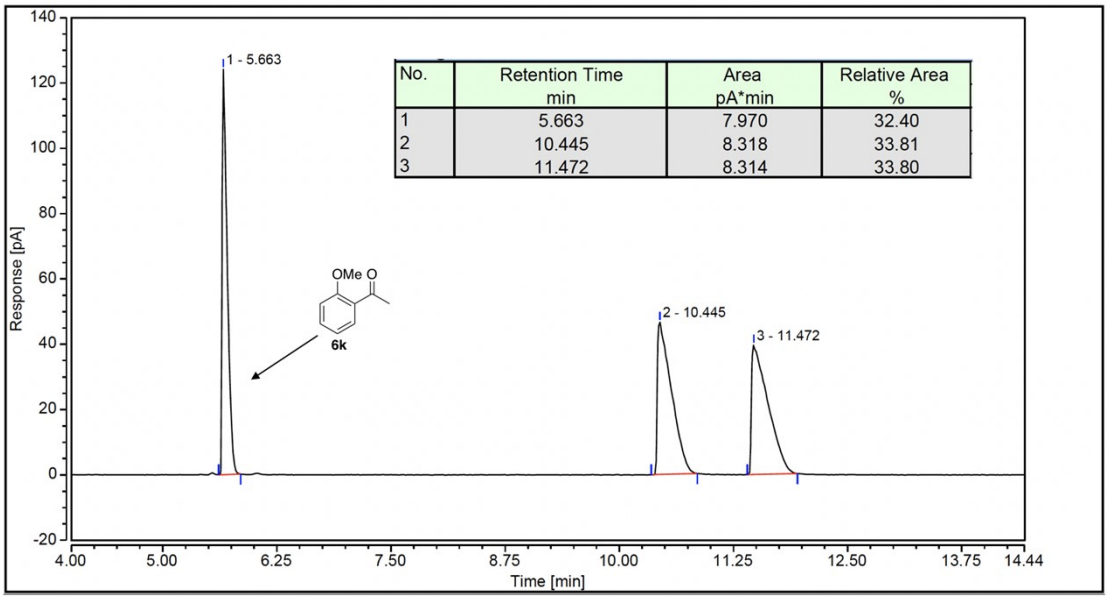


No.	Retention Time min	Area pA*min	Relative Area %
1	6.828	7.434	96.48
2	8.200	0.271	3.52

Figure S69: GC trace of enantioenriched 7j (obtained by general procedure C1).



7k **Synthesis of (*R*)-1-(2-methoxyphenyl)ethan-1-ol, (R)-7k**. The synthesis of racemic **7k** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 55% isolated yield (50.2 mg, yellowish oil) and with 90.8% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 1H), 7.35 – 7.28 (m, 1H), 7.07 – 7.00 (m, 1H), 6.98 – 6.92 (m, 1H), 5.17 (q, *J* = 6.5 Hz, 1H), 3.92 (s, 3H), 2.76 (s, 1H), 1.57 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 156.5, 133.6, 128.3, 126.1, 120.8, 110.5, 66.4, 53.3, 23.0. GC: β-DEX column, 130 °C isotherm, retention times t_R(SM) = 5.5 min, t_R(major) = 10.4 min, t_R(minor) = 10.9 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]



No.	Retention Time min	Area pA*min	Relative Area %
1	5.663	7.970	32.40
2	10.445	8.318	33.81
3	11.472	8.314	33.80

Figure S70: GC trace of 6k and racemic 7k (obtained by general procedure C3).

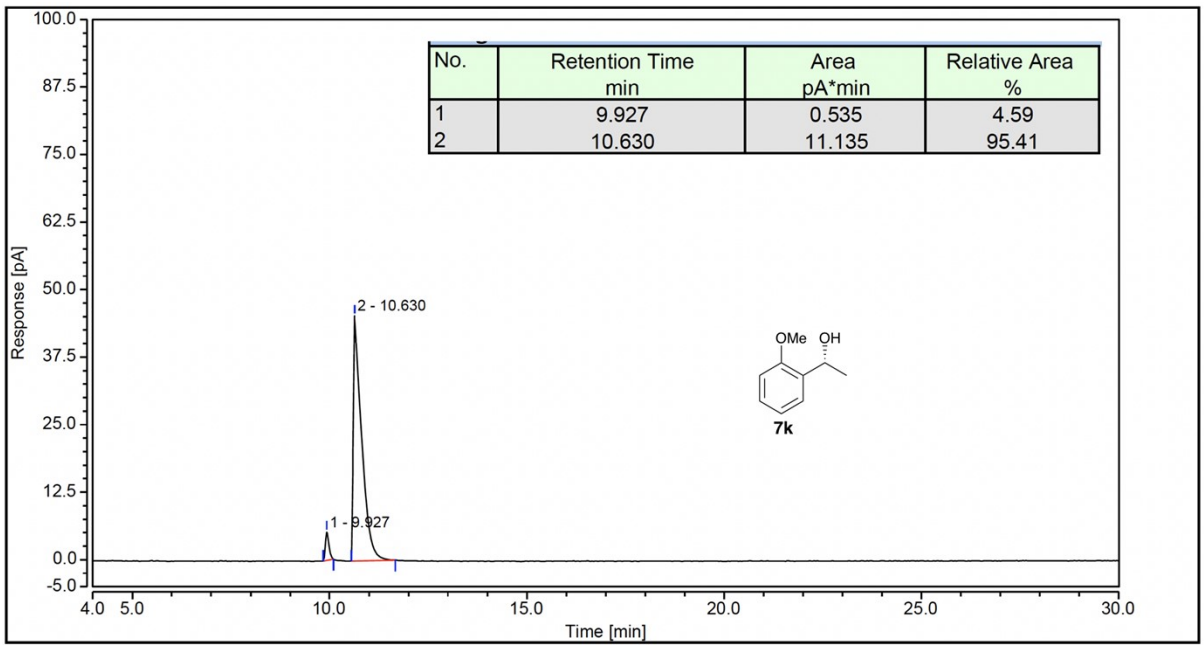
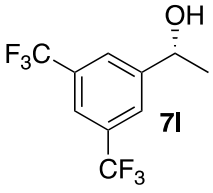


Figure S71: GC trace of enantioenriched 7k (obtained by general procedure C1).



Synthesis of (*R*)-1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-ol, (R)-7l. The synthesis of racemic **7l** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 99% isolated yield (153.3 mg, white solid) and with 92.2% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 100 °C isotherm, retention times t_R(SM) = 10.5 min, t_R(major) = 13.6 min, t_R(minor) = 15.7 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1] This compound was obtained in 99% isolated yield (153.3 mg, white solid) and with 93.9% ee following general procedure **C2** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.99 – 7.82 (m, 3H), 5.11 (q, *J* = 6.5 Hz, 1H), 2.05 (s, 1H), 1.62 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.26, 131.8 (q, *J* = 32.1 Hz), 125.7, 121.3, 69.3, 25.6. GC: β-DEX column, 100 °C isotherm, retention times t_R(SM) = 10.5 min, t_R(major) = 13.8 min, t_R(minor) = 16.4 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with literature data.[S1]

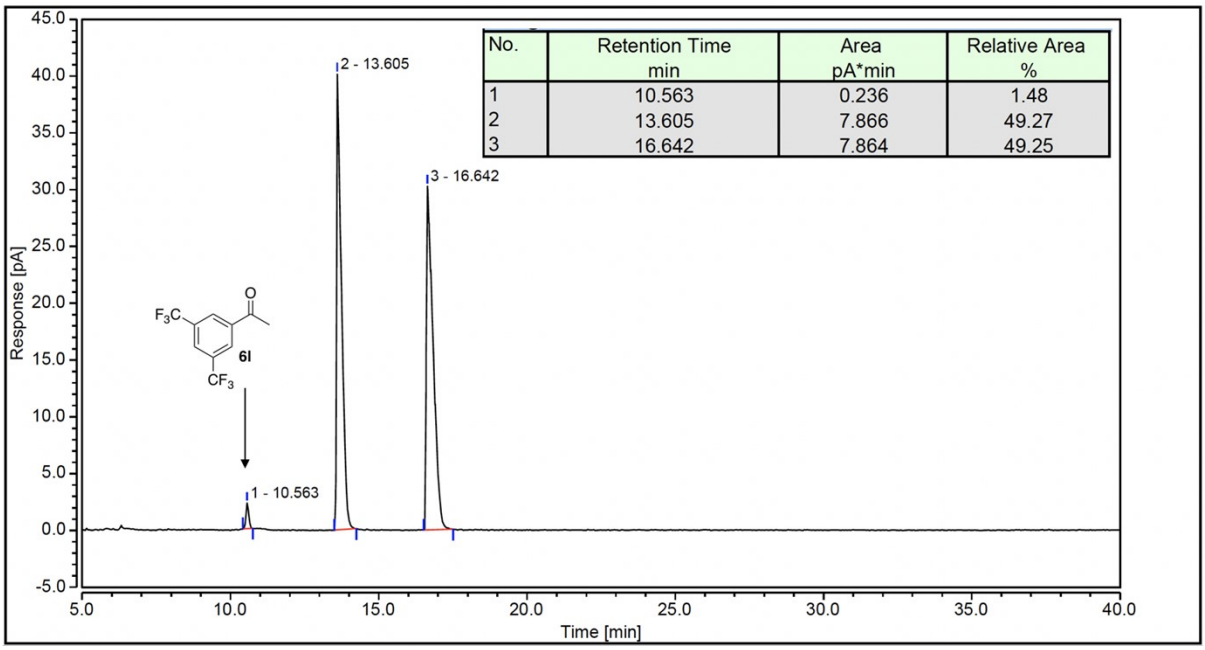


Figure S72: GC trace of 6l and racemic 7l (obtained by general procedure C3).

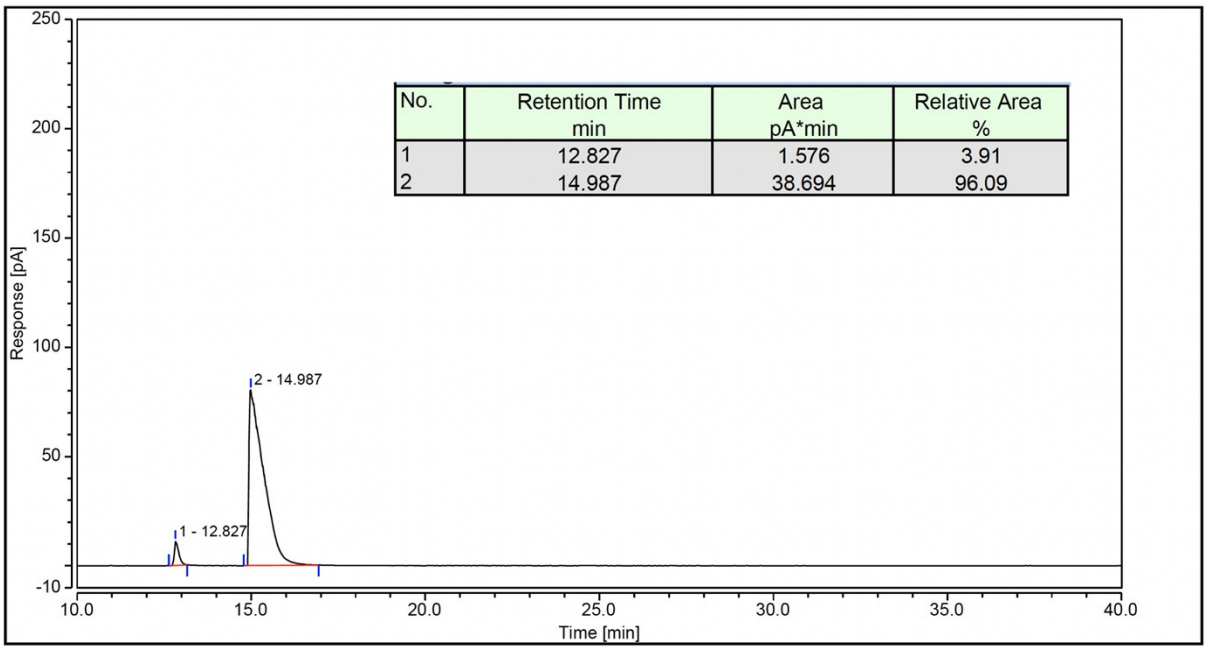


Figure S73: GC trace of enantioenriched 7l (obtained by general procedure C1).

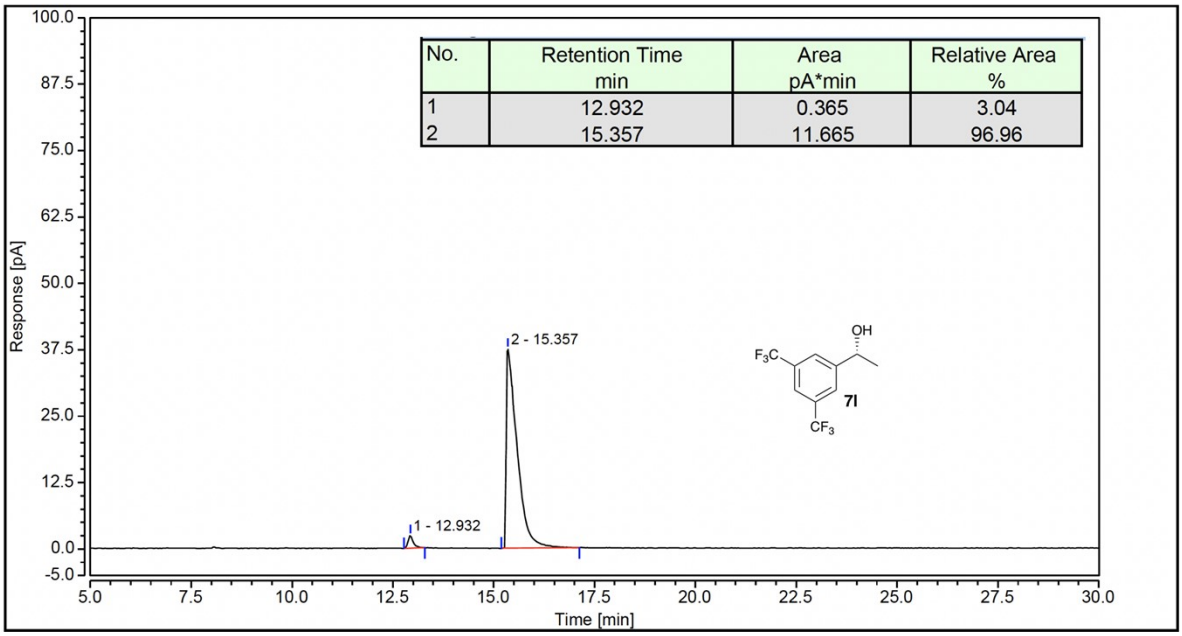
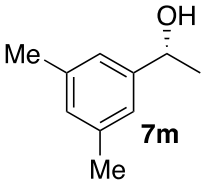


Figure S74: GC trace of enantioenriched 7l (obtained by general procedure C2).



Synthesis of (*R*)-1-(3,5-dimethylphenyl)ethan-1-ol, (R)-7m. The synthesis of racemic **7m** and its spectroscopic data has previously been reported.[S7] This compound was obtained in 60% isolated yield (54.1 mg, colorless oil) and with 94.9% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.10 – 6.97 (m, 3H), 4.89 (q, *J* = 6.5 Hz, 1H), 2.41 (s, 6H), 2.12 (s, 1H), 1.65 – 1.56 (d, *J* = 6.5 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) 145.9, 138.1, 129.1, 123.2, 70.5, 25.1, 21.4. GC: β-DEX column, 100 °C isotherm, retention times t_R(SM) = 17.9 min, t_R(major) = 54.5 min, t_R(minor) = 55.4 min. Analytical data are in agreement with literature data.[S7] The absolute configuration was determined to be (*R*) by comparison with literature data.[S7]

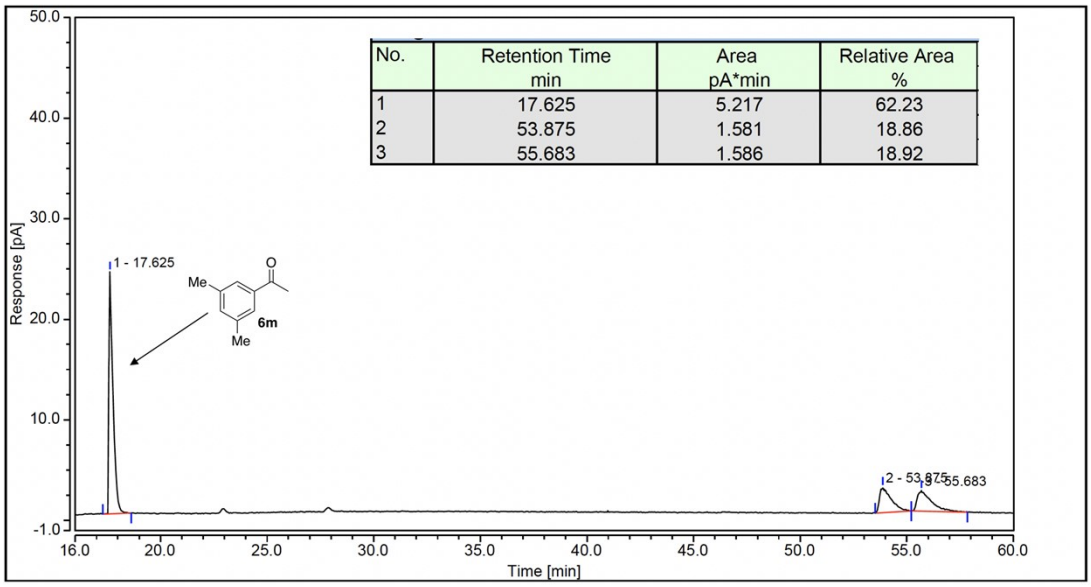


Figure S75: GC trace of 6m and racemic 7m (obtained by general procedure C3).

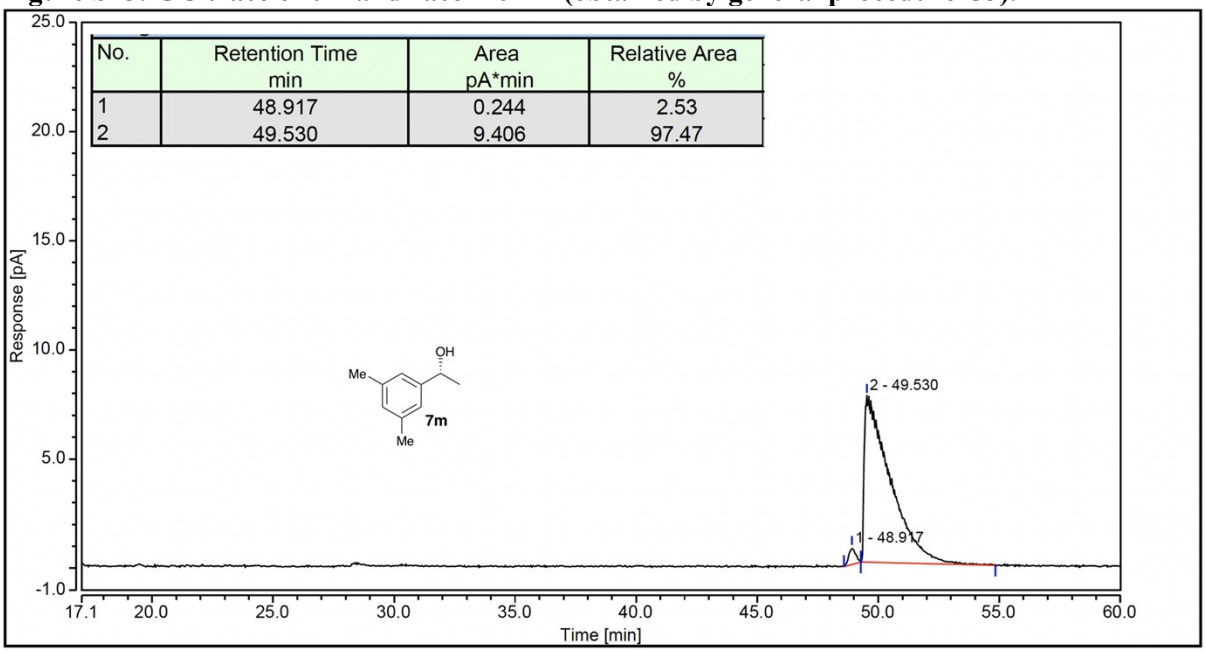
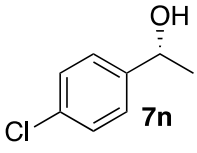


Figure S76: GC trace of enantioenriched 7m (obtained by general procedure C1).



Synthesis of (*R*)-1-(4-chlorophenyl)ethan-1-ol, (R)-7n. The synthesis of racemic **7n** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 97% isolated yield (91.1 mg, yellowish oil) and with 78.0% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 130 °C isotherm, retention times t_R(SM) = 5.3 min, t_R(major) = 11.7 min, t_R(minor) = 14.1 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**. This compound was obtained in 82% isolated yield (77.0 mg,

yellowish oil) and with 81.2% ee following general procedure **C2** using catalyst **3b** (reaction time: 24 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 – 7.16 (m, 4H), 4.86 (d, *J* = 5.9Hz, 1H), 2.83 (br s, 1H), 1.47 (d, *J* = 6.5, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) 144.2, 132.9, 128.5, 126.8, 69.6, 25.2. GC: β-DEX column, 130 °C isotherm, retention times t_R(SM) = 5.2 min, t_R(major) = 11.8 min, t_R(minor) = 14.1 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.

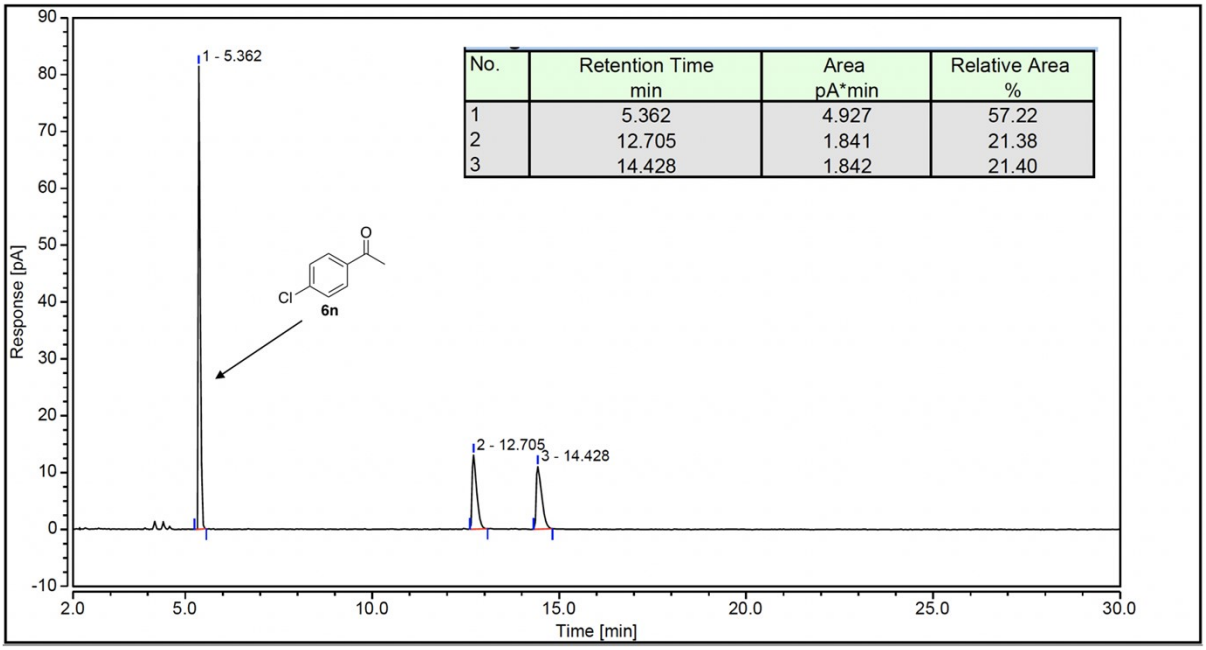


Figure S77: GC trace of 6n and racemic 7n (obtained by general procedure C3).

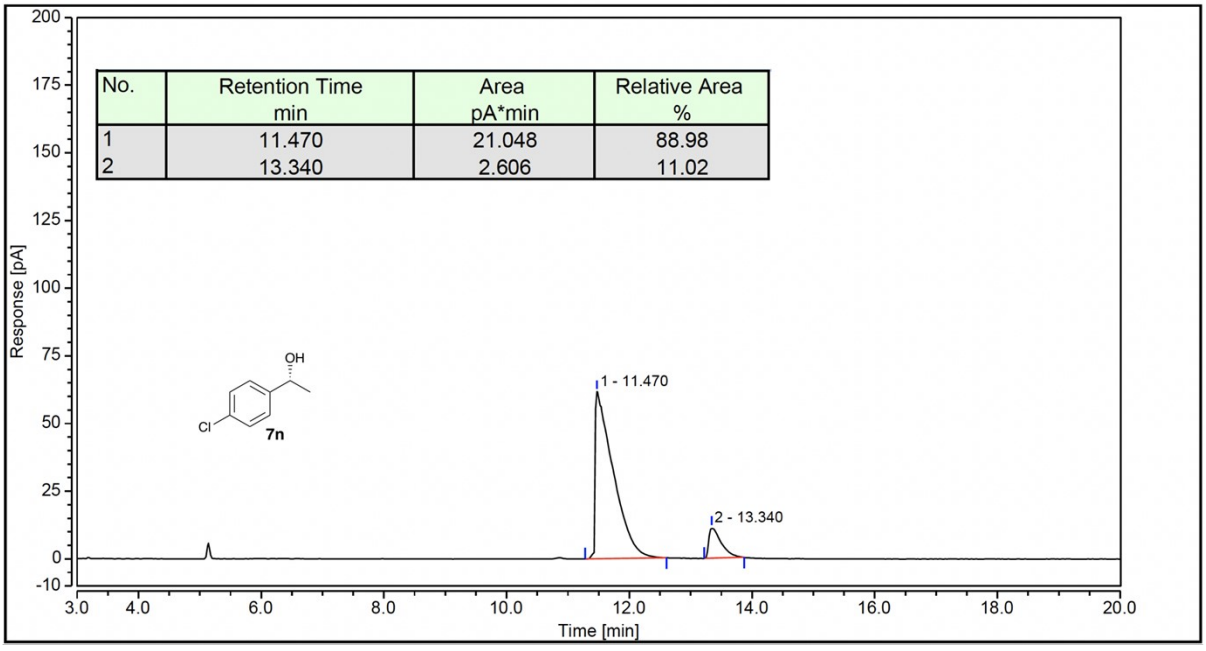


Figure S78: GC trace of enantioenriched 7n (obtained by general procedure C1).

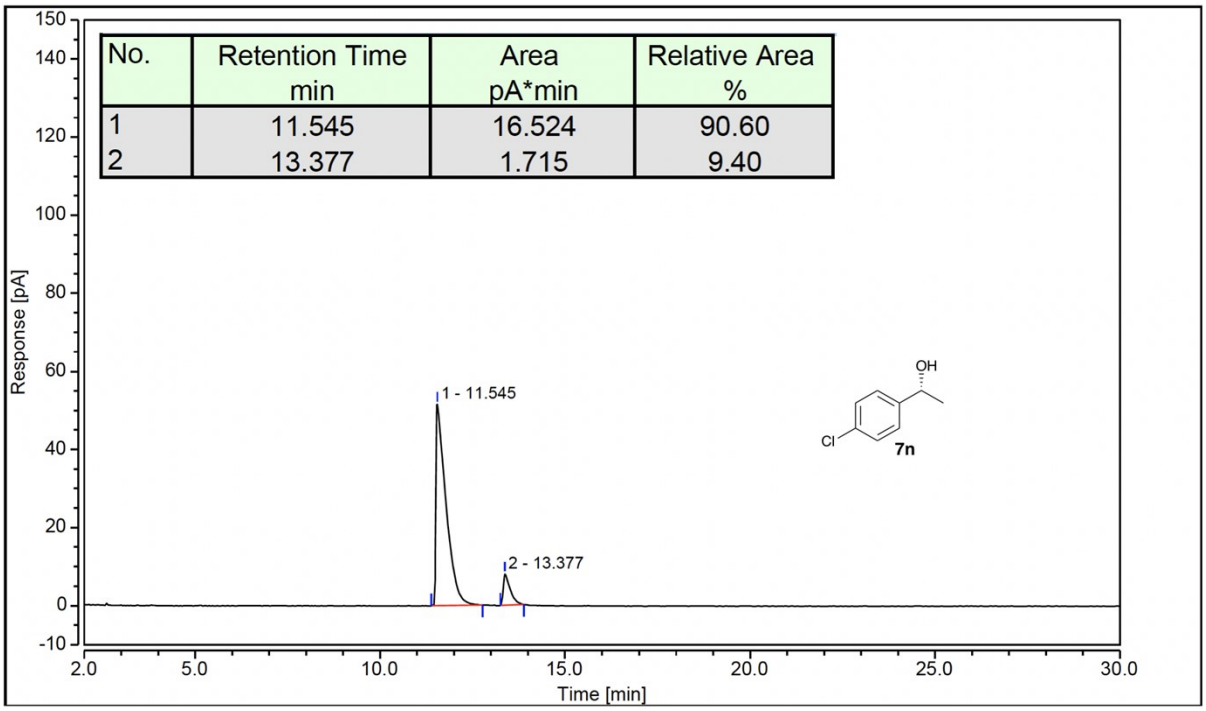
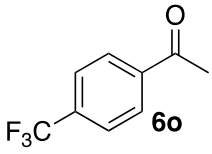


Figure S79: GC trace of enantioenriched 7n (obtained by general procedure C2).



Synthesis of (*R*)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol, (R)-7o. The synthesis of racemic **7o** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 99% isolated yield (112.8 mg, colorless oil) and with 81.2% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 115 °C isotherm, retention times t_R(SM) = 4.0 min, t_R(major) = 12.0 min, t_R(minor) = 15.4 min. Analytical data are in agreement with literature data.[S4] The absolute configuration was determined to be (*R*) by comparison (*R*)-**7a**. This compound was obtained in 97% isolated yield (110.7 mg, colorless oil) and with 83.0% ee following general procedure **C2** using catalyst **3b** (reaction time: 24 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 4.99 (q, *J* = 6.4 Hz, 1H), 2.40 (br s, 1H), 1.55 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) 149.7, 126.0, 125.6, 125.4 (q, *J* = 3.8 Hz), 122.4, 69.7, 25.3. GC: β-DEX column, 130 °C isotherm, retention times t_R(SM) = 4.0 min, t_R(major) = 12.2 min, t_R(minor) = 15.6 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by (*R*)-**7a**.

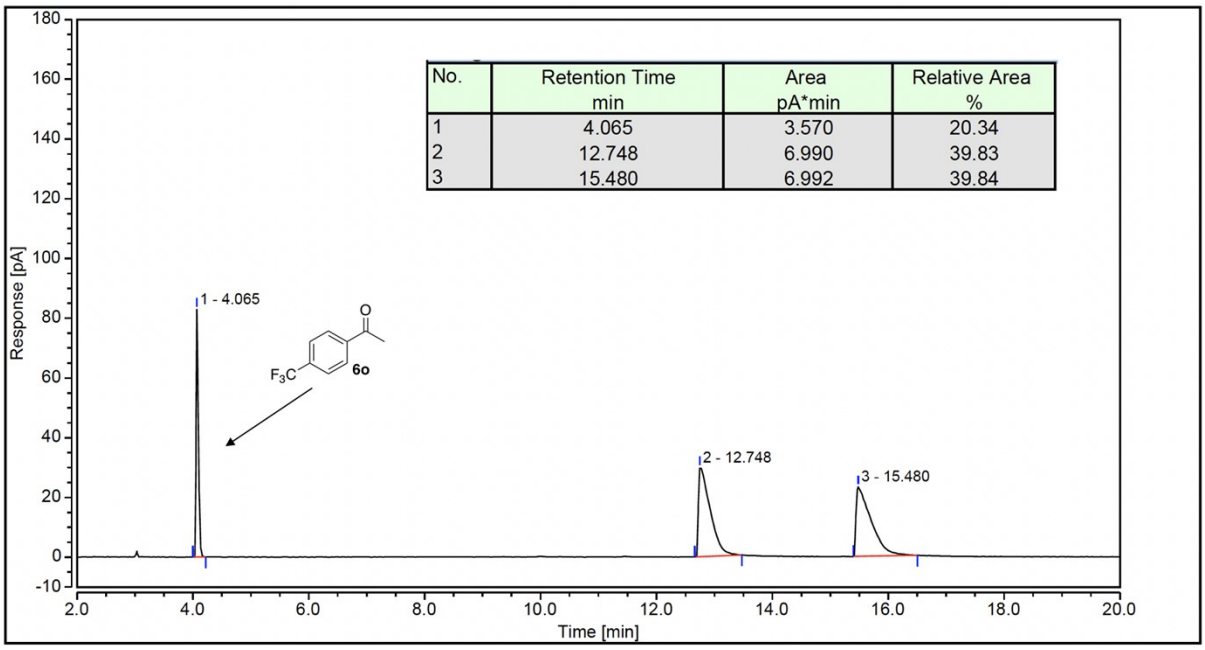


Figure S80: GC trace of 6o and racemic 7o (obtained by general procedure C3).

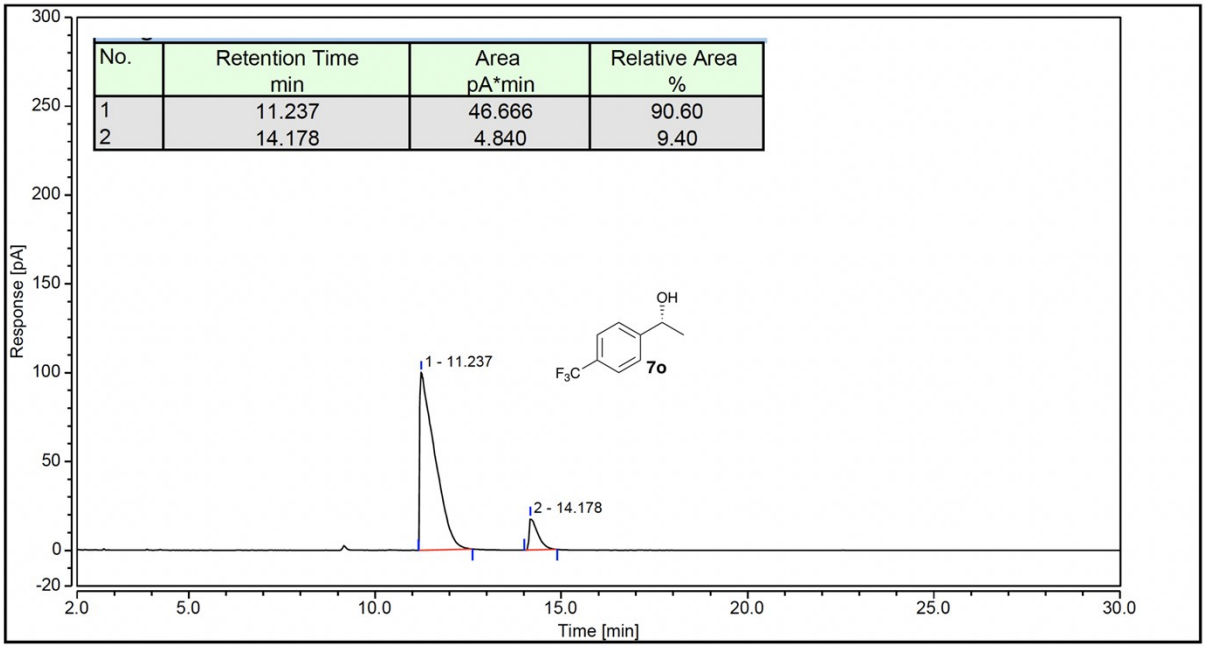


Figure S81: GC trace of enantioenriched 7o (obtained by general procedure C1).

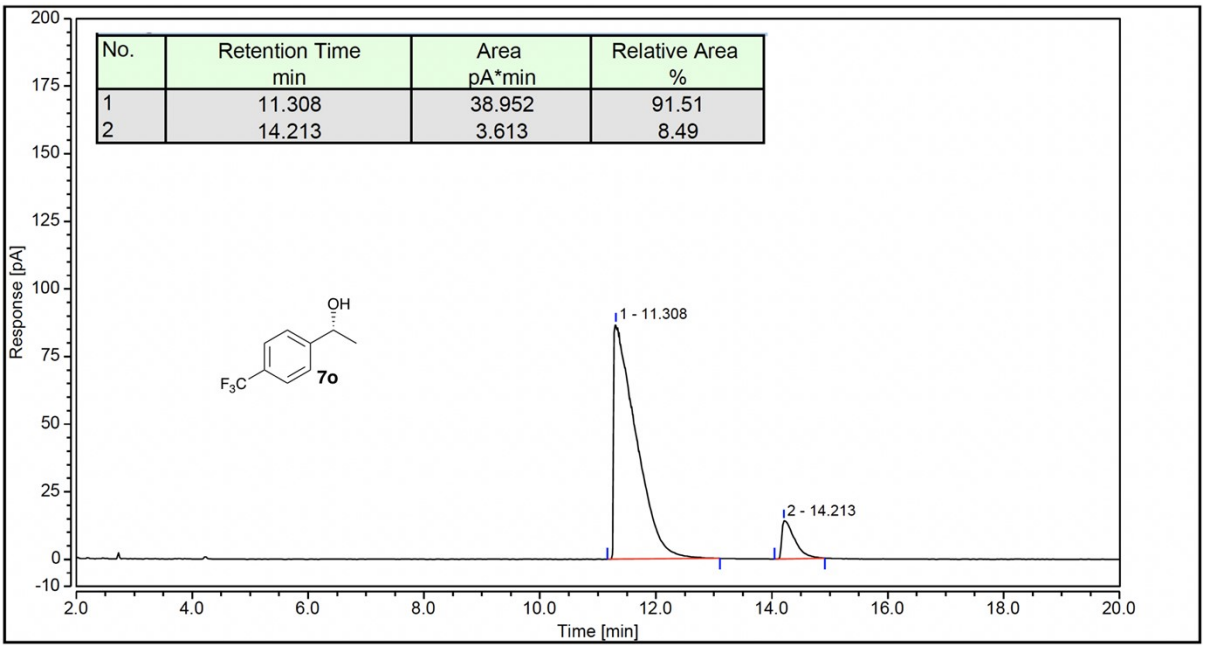
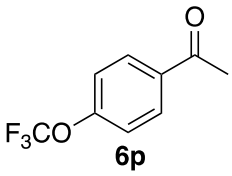


Figure S82: GC trace of enantioenriched 7o (obtained by general procedure C2).



Synthesis of (*R*)-1-(4-(trifluoromethoxy)phenyl)ethan-1-ol, (R)-7p. The synthesis of racemic **7p** and its spectroscopic data has previously been reported.[S5] This compound was obtained in 96% isolated yield (118.7 mg, colorless oil) and with 83.1% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 5.0 min, t_R(major) = 13.5 min, t_R(minor) = 17.7 min. Analytical data are in agreement with literature data.[S5] The absolute configuration was determined to be (*R*) by comparison (*R*)-**7a**. This compound was obtained in 84% isolated yield (103.9 mg, colorless oil) and with 85.1 % ee following general procedure **C2** using catalyst **3b** (reaction time: 24 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.87 (q, *J* = 6.5 Hz, 1H), 1.85 (br s, 1H), 1.42 (d, *J* = 6.5, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) 149.7, 125.6, 125.5 (q, *J* = 3.8 Hz), 122.4, 69.8, 25.4. GC: β-DEX column, 110 °C isotherm, retention times t_R(SM) = 4.9 min, t_R(major) = 13.4 min, t_R(minor) = 17.7 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by comparison (*R*)-**7a**.

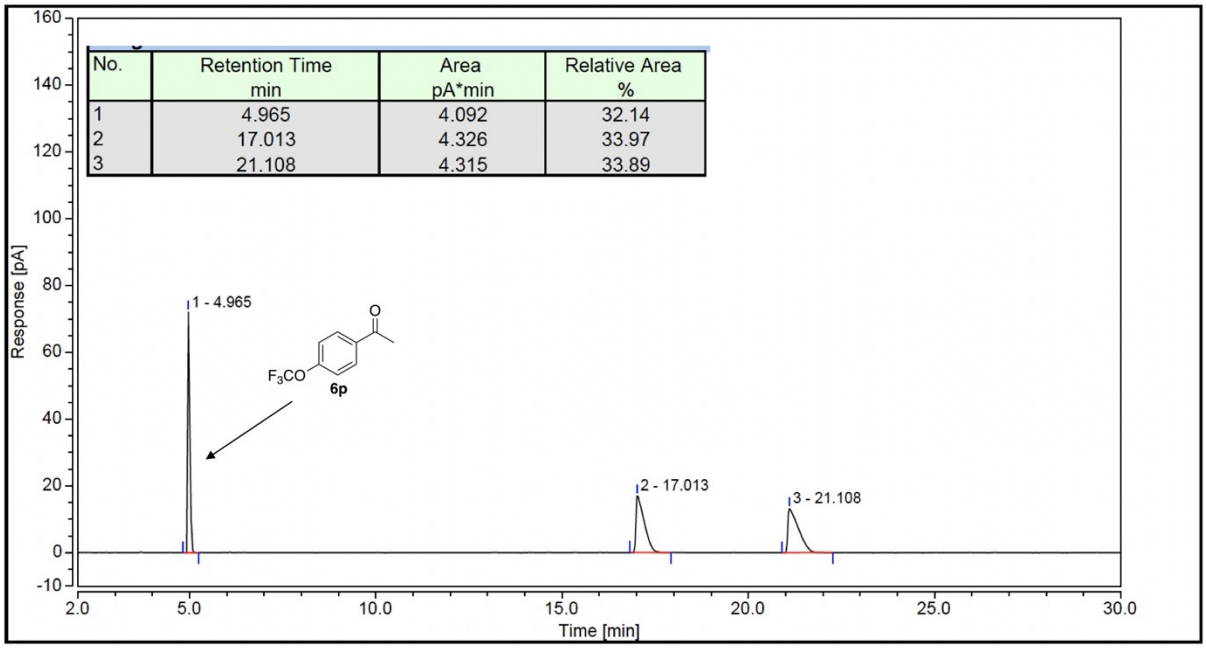


Figure S83: GC trace of 6p and racemic 7p (obtained by general procedure C3).

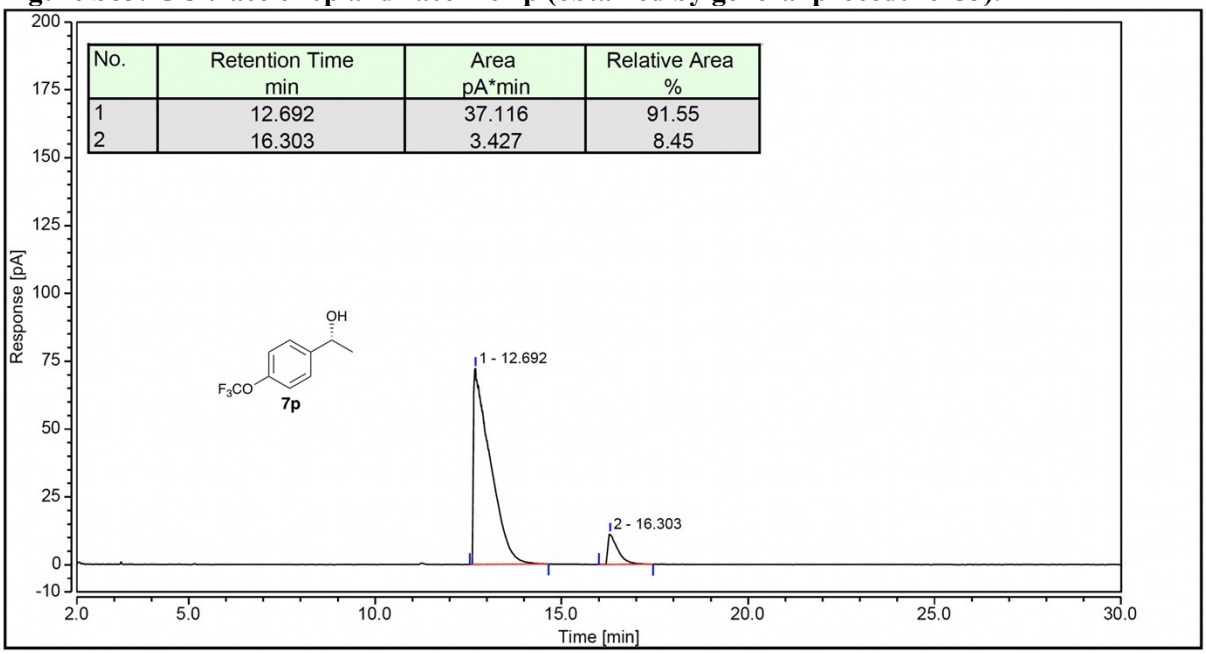


Figure S84: GC trace of enantioenriched 7p (obtained by general procedure C1).

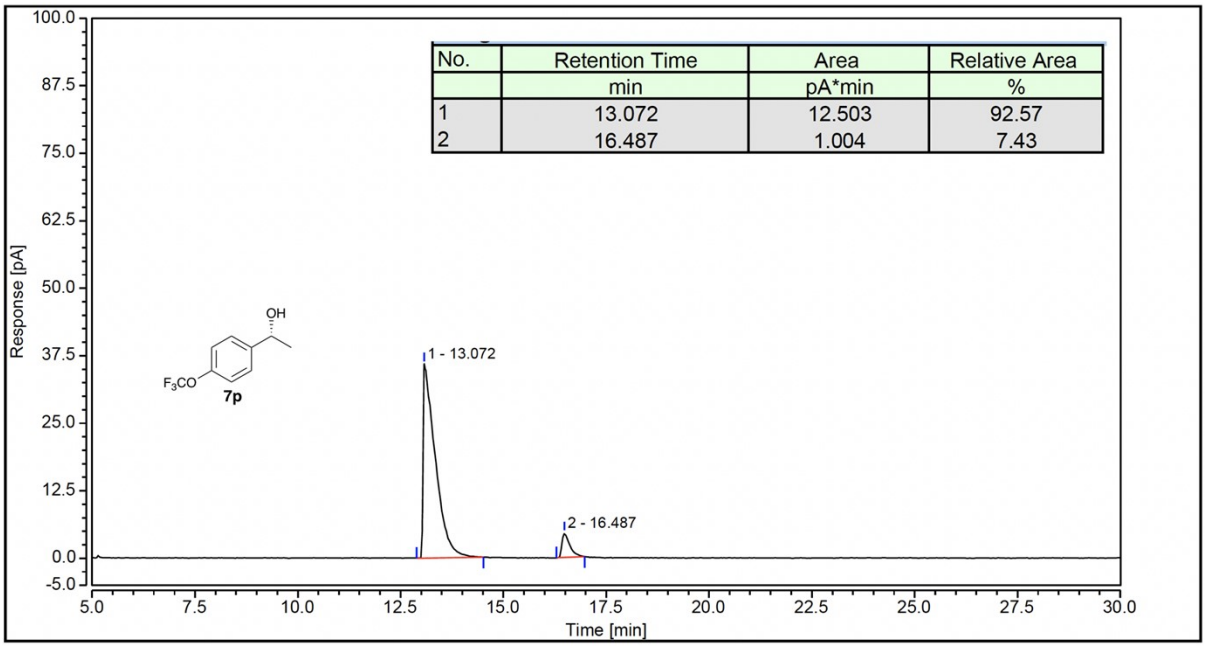
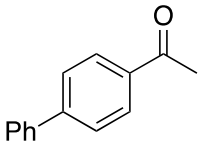


Figure S85: GC trace of enantioenriched 7p (obtained by general procedure C2).



Synthesis of (*R*)-1-([1,1'-biphenyl]-4-yl)ethan-1-ol (R)-7q. The synthesis of racemic **7q** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 86% isolated yield (102.3 mg, white solid) and with 83.6% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). GC: β-DEX column, 160 °C isotherm, retention times t_R(SM) = 20.3 min, t_R(major) = 28.8 min, t_R(minor) = 31.7 min. Analytical data are in agreement with literature data.[S1,2,5] The absolute configuration was determined to be (*R*) by (*R*)-**7a** This compound was obtained in 68% isolated yield (80.9 mg, white solid) and with 87.1% ee following general procedure **C2** using catalyst **3b** (reaction time: 24 h). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 4H), 7.49 – 7.39 (m, 3H), 7.38 – 7.30 (m, 1H), 4.94 (q, *J* = 6.4 Hz, 1H), 1.84 (s, 1H), 1.53 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) 144.3, 140.87, 140.47, 128.7, 127.2, 127.1, 125.8, 70.2, 25.1. GC: β-DEX column, 160 °C isotherm, retention times t_R(SM) = 20.1 min, t_R(major) = 29.2 min, t_R(minor) = 31.9 min. Analytical data are in agreement with literature data.[S4] The absolute configuration was determined to be *(R)* by comparison with (*R*)-**7a**.

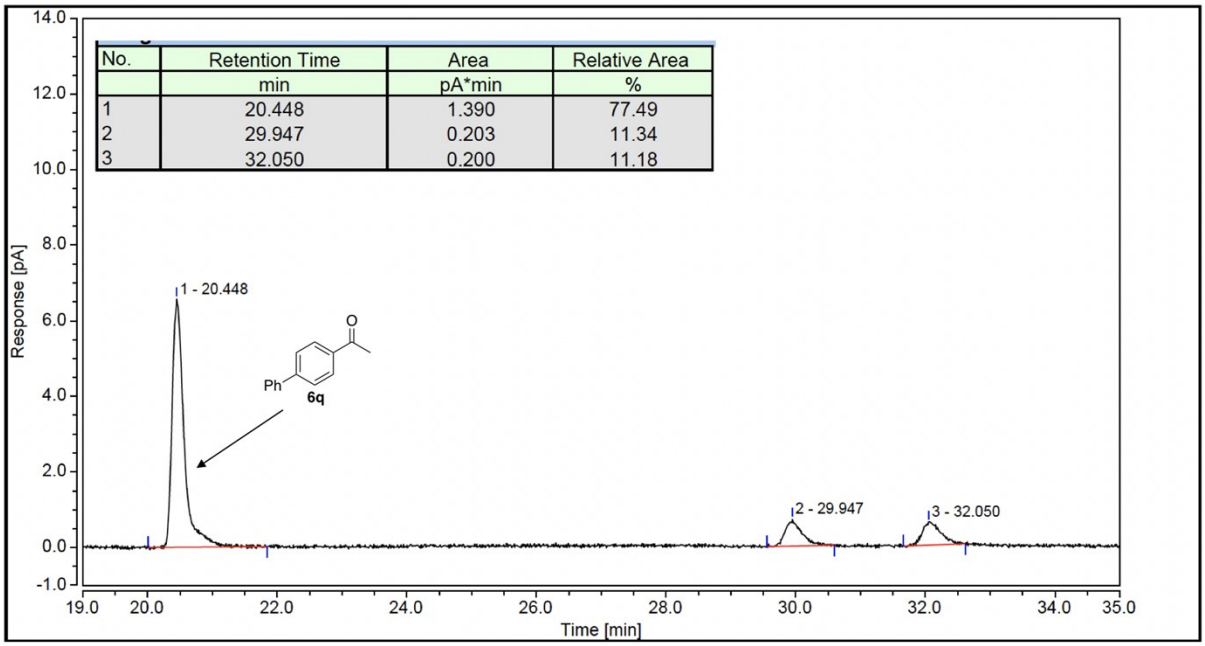


Figure S86: GC trace of 6q and racemic 7q (obtained by general procedure C3).

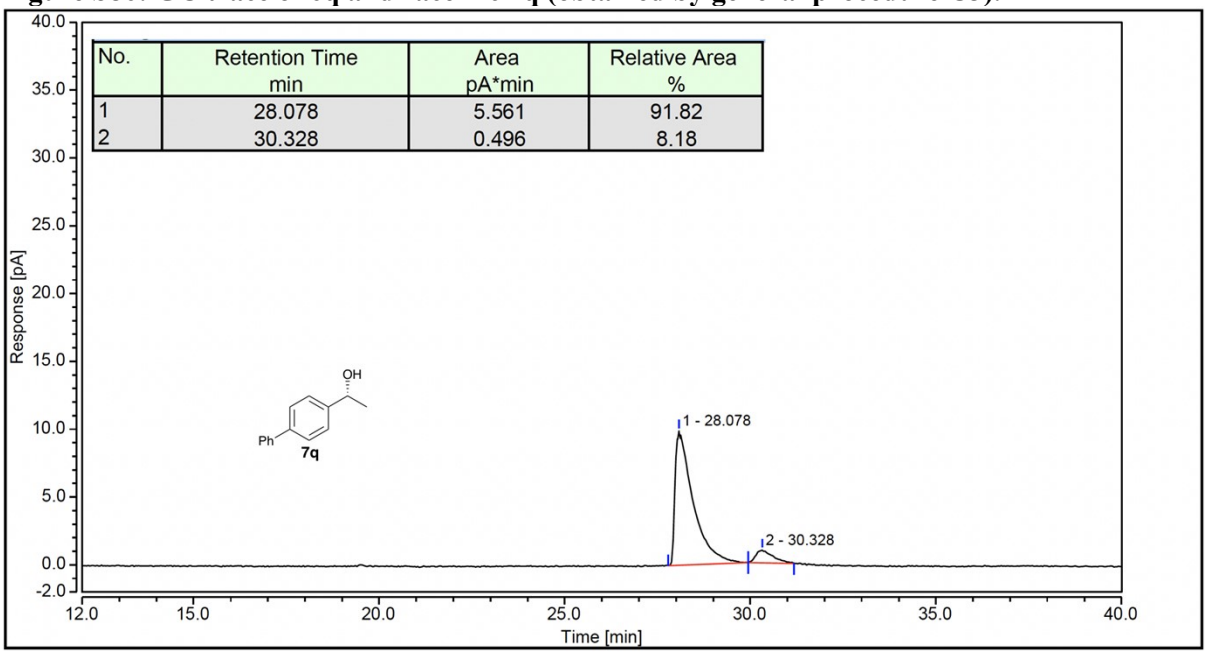


Figure S87: GC trace of enantioenriched 7q (obtained by general procedure C1).

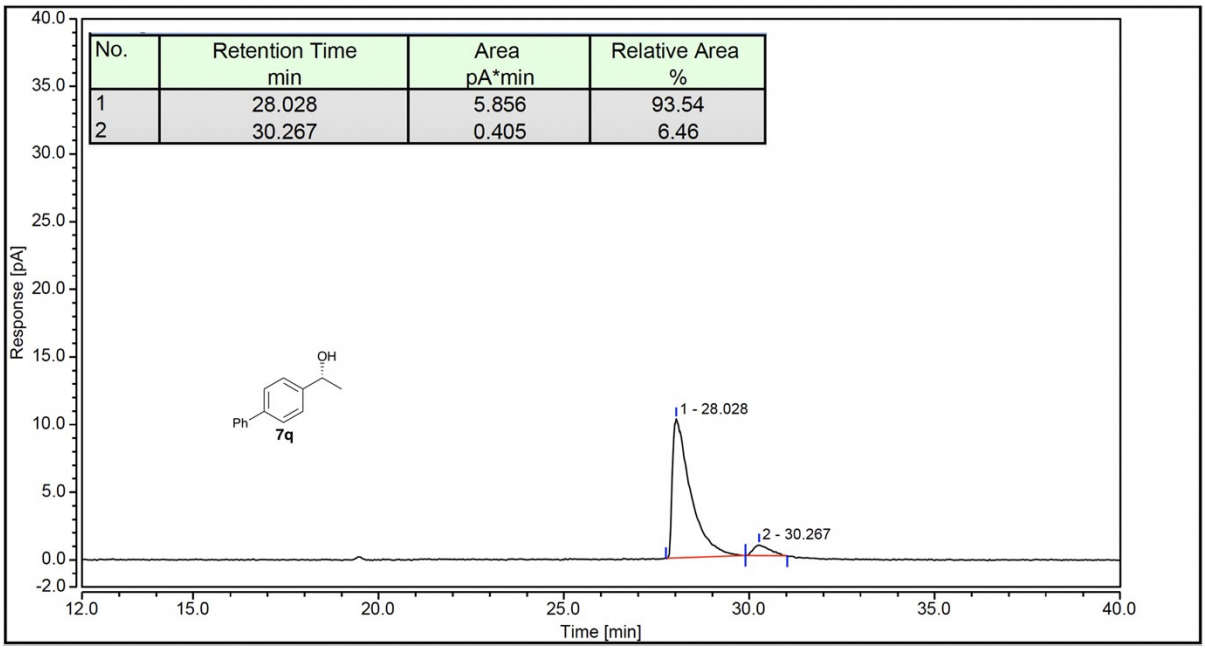
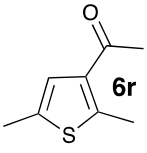


Figure S88: GC trace of enantioenriched 7q (obtained by general procedure C2).



Synthesis of (*R*)-1-(2,5-dimethylthiophen-3-yl)ethan-1-ol (R)-7r. The synthesis of racemic **7r** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 41% isolated yield (38.4 mg, colorless oil) and with 97.2% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.66 (s, 1H), 4.10 (m, 1H), 2.35 (d, *J* = 11.8 Hz, 3H), 2.02 (s, 3H), 1.58 (s, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 141.2, 136.1, 131.6, 123.4, 64.4, 60.4, 23.8, 21.1. GC: β-DEX column, 115 °C isotherm, retention times t_R(SM) = 7.6 min, t_R(major) = 19.2 min, t_R(minor) = 24.4 min. Analytical data are in agreement with literature data.[S4] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.

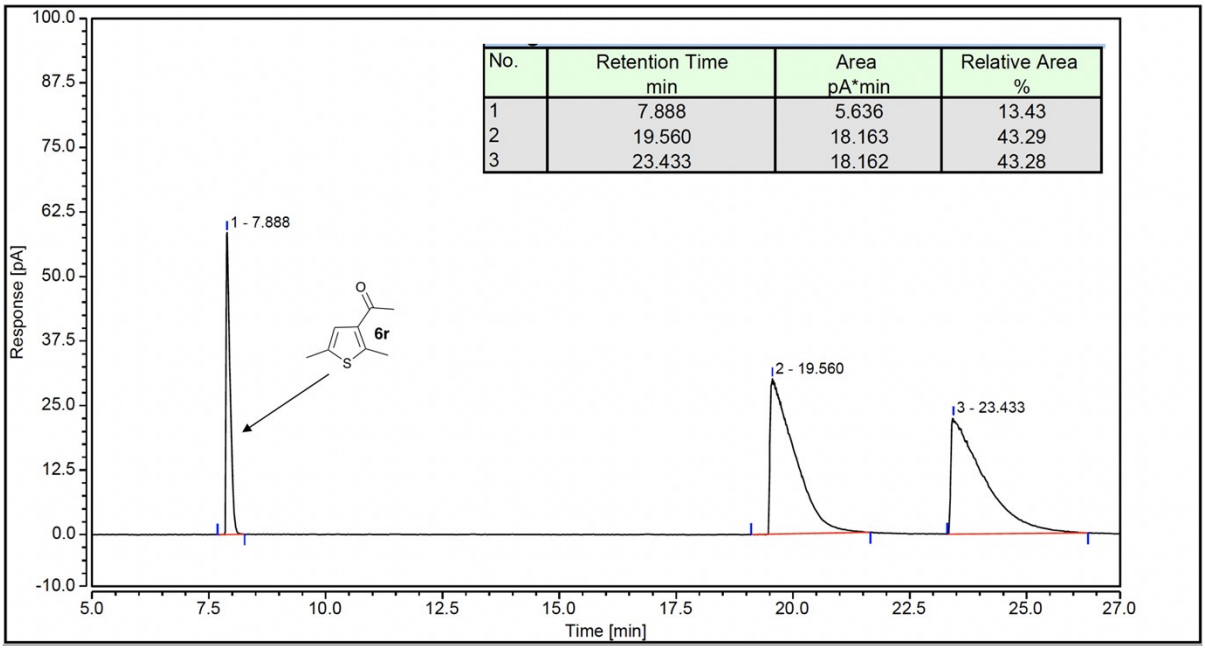


Figure S89: GC trace of 6r and racemic 7r (obtained by general procedure C3).

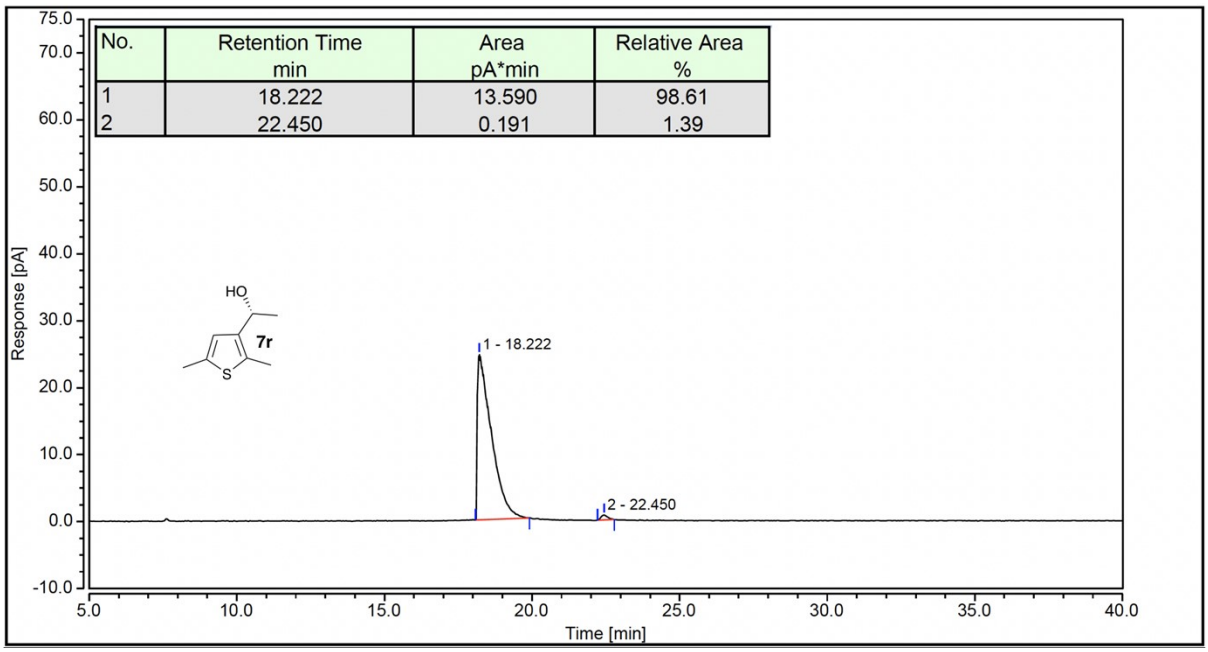
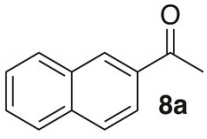


Figure S90: GC trace of enantioenriched 7r (obtained by general procedure C1).



Synthesis of (*R*)-1-(naphthalen-2-yl)ethan-1-ol (R)-9a. The synthesis of racemic **9a** and its spectroscopic data has previously been reported.[S2,3] This compound was obtained in 90% isolated yield (93.0 mg, white solid) and with 82.3% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 4H), 7.44 – 7.36 (m, 3H), 4.99 (q, *J* = 6.5 Hz, 1H), 1.76 (s, 1H), 1.51 (d, *J* =

6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 143.2, 133.3, 132.9, 128.3, 127.9, 127.7, 126.2, 125.8, 123.8, 70.6, 25.2. GC: β-DEX column, 160 °C isotherm, retention times t_R(SM) = 7.6 min, t_R(major) = 11.5 min, t_R(minor) = 12.2 min. Analytical data are in agreement with literature data.[S1,2,3] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**.

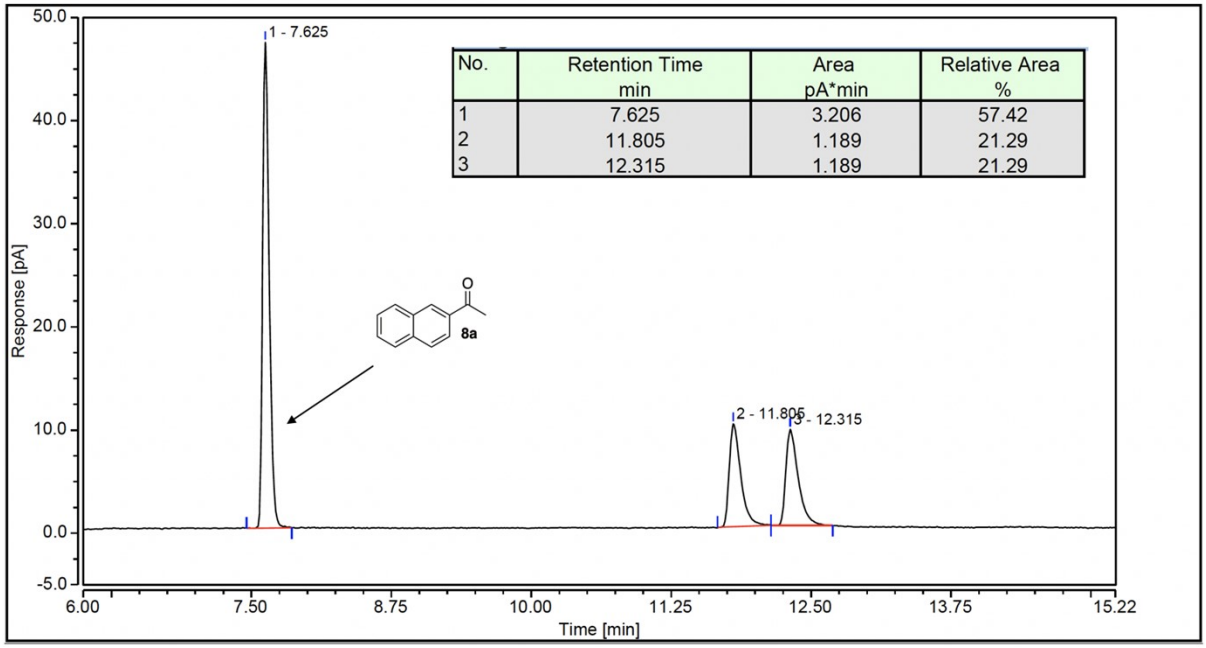


Figure S91: GC trace of 8a and racemic 9a (obtained by general procedure C3).

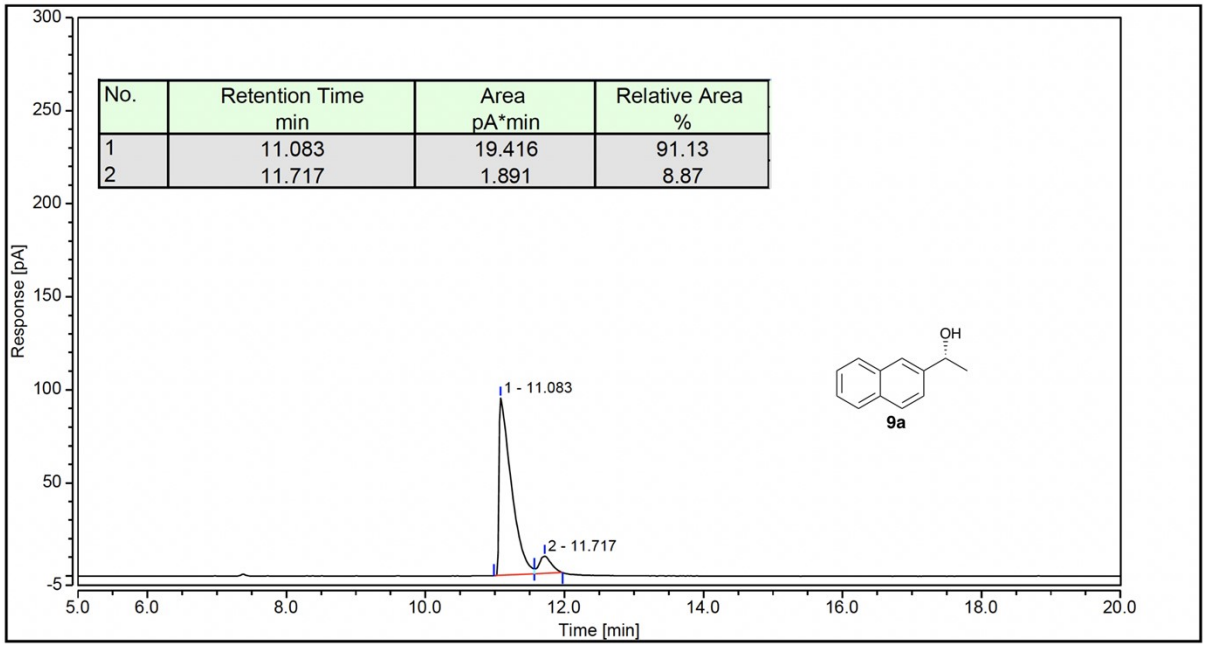
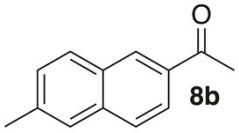


Figure S92: GC trace of enantioenriched 9a (obtained by general procedure C3).



Synthesis of (*R*)-1-(6-methylnaphthalen-2-yl)ethan-1-ol (R)-9b. The synthesis of racemic **9b** and its spectroscopic data has previously been reported.[S9] This compound was obtained in 80% isolated yield (89.4 mg, dirty white solid) and with 81.0% ee following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 – 7.19 (m, 6H), 4.93–4.87 (m, 1H), 2.39 (s, 3H), 1.98 (br s, 1H), 1.45 (d, *J* = 6.4 Hz, 3kH).^{13}C NMR (75 MHz, Chloroform-*d*) 142.2, 135.4, 133.1, 131.5, 128.4, 127.7, 127.6, 126.6, 123.8, 123.6, 70.5, 25.1, 21.7. GC: β-DEX column, 160 °C isotherm, retention times t_R(SM) = 11.4 min, t_R(major) = 16.3 min, t_R(minor) = 17.5 min. Analytical data are in agreement with literature data.[S9] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**. **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 99 : 1, flow rate 1.0 mL/min, λ = 210 nm), retention times t_R((major)-**9b**) = 19.9 min, t_R((minor)-**9b**)= 27.7 min.

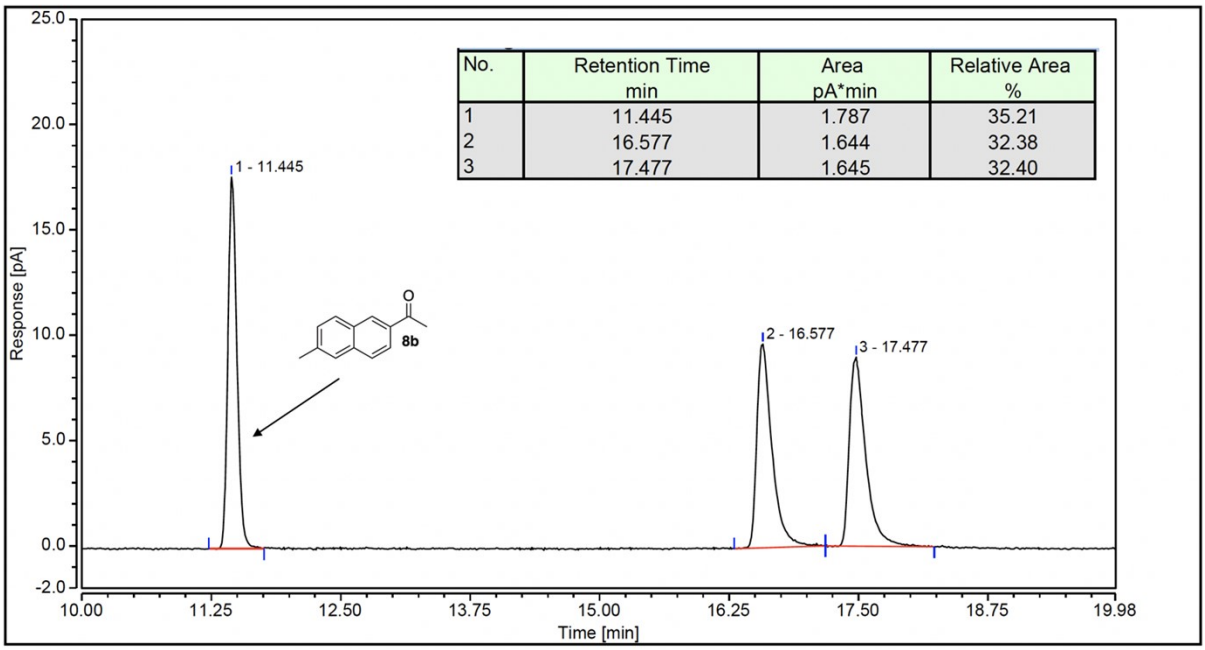


Figure S93: GC trace of 8b and racemic 9b (obtained by general procedure C3).

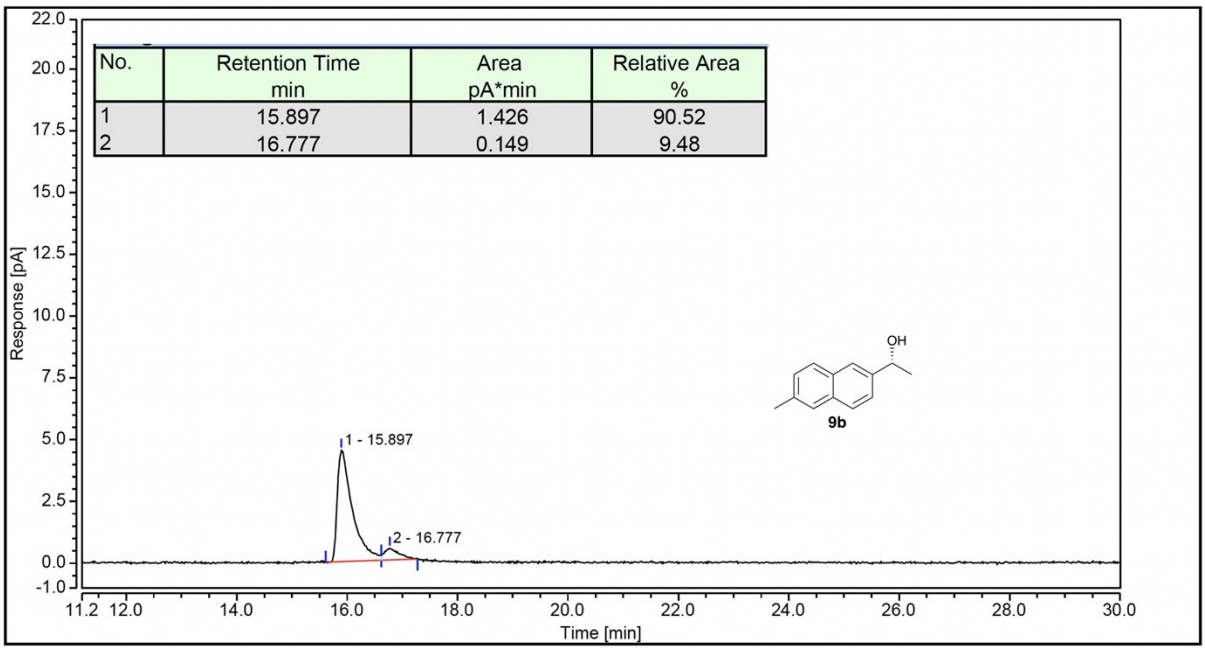
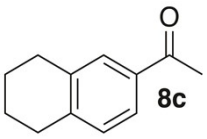


Figure S94: GC trace of enantioenriched 9b (obtained by general procedure C1).



Synthesis of (*R*)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)ethan-1-ol (R)-9c. The synthesis of racemic **9c** and its spectroscopic data has previously been reported.[S5] This compound was obtained in 37% isolated yield (39.1 mg, yellowish oil), following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.24 – 7.02 (m, 3H), 4.90 (q, *J* = 6.4 Hz, 1H), 2.93 – 2.78 (m, 4H), 2.13 (s, 1H), 1.96 – 1.82 (m, 4H), 1.57 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 143.0, 137.2, 136.4, 129.3, 126.1, 122.6, 70.3, 29.5, 29.2, 25.1, 23.3. GC: β-DEX column, 150 °C isotherm, retention times t_R(SM) = 11.6 min, t_R(major) = 15.2 min, t_R(minor) = 15.6 min. Analytical data are in agreement with literature data.[S5] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**. **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 99 : 1, flow rate 1.0 mL/min, λ = 210 nm), retention times t_R((major)-**9c**) = 9.1 min, t_R((minor)-**9c**)= 9.9 min. (ee: 91.8%)

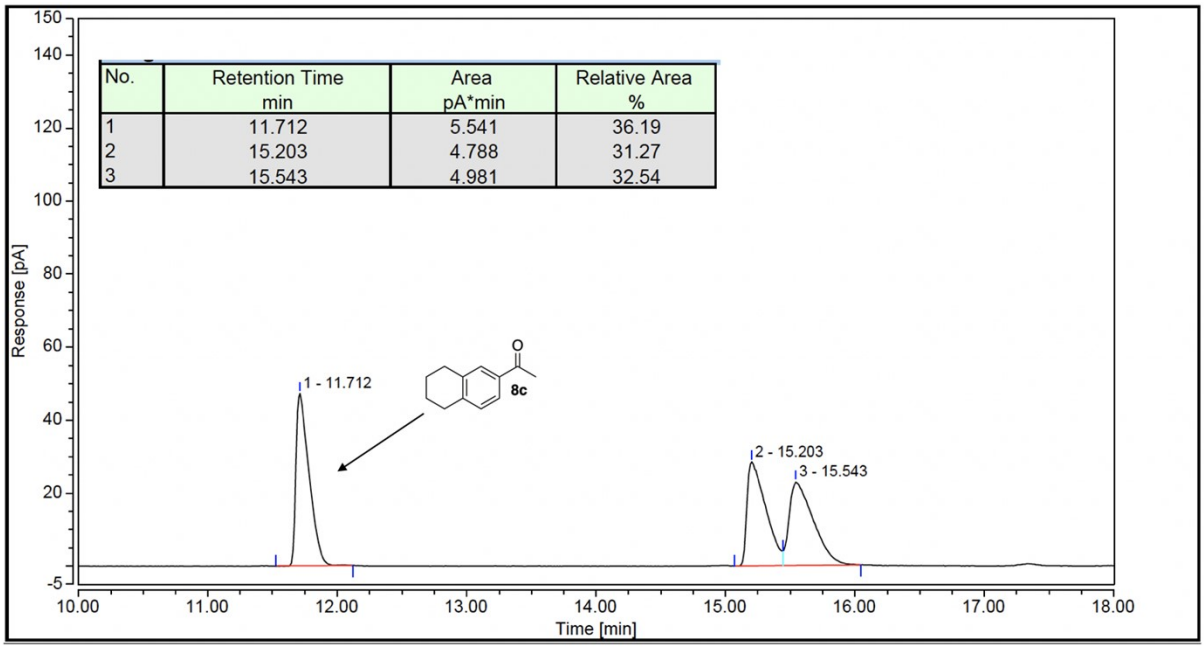


Figure S95: GC trace of 8c and racemic 9c (obtained by general procedure C3).

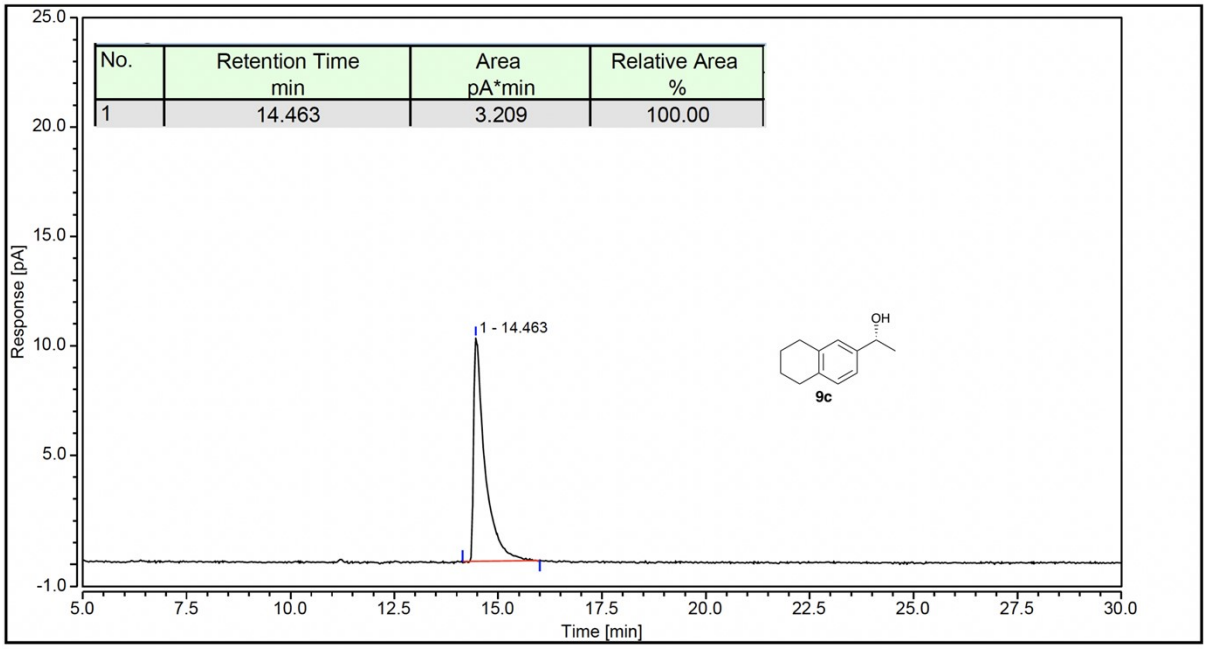


Figure S96: GC trace of enantioenriched 9c (obtained by general procedure C1).

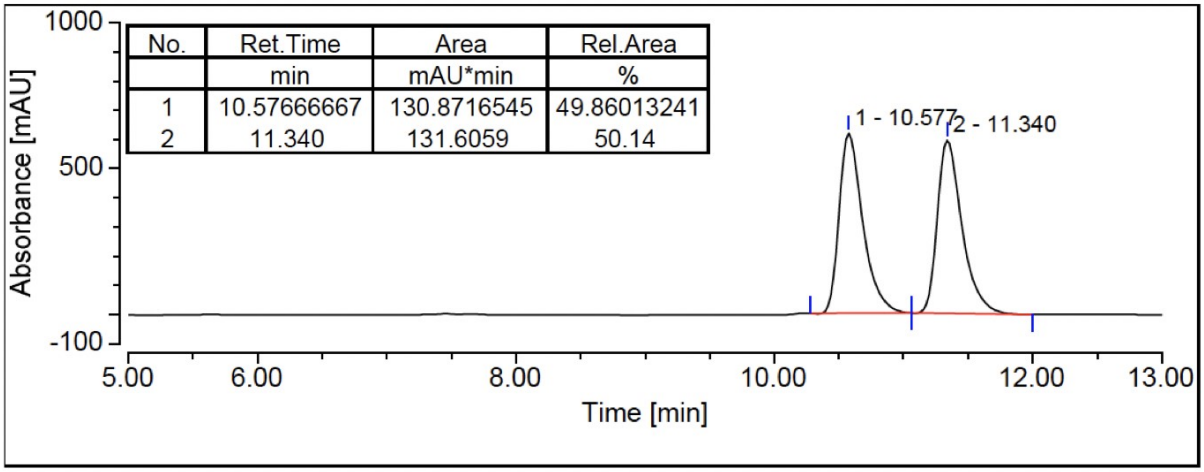


Figure S97: HPLC trace of racemic 9c (obtained by general procedure C3).

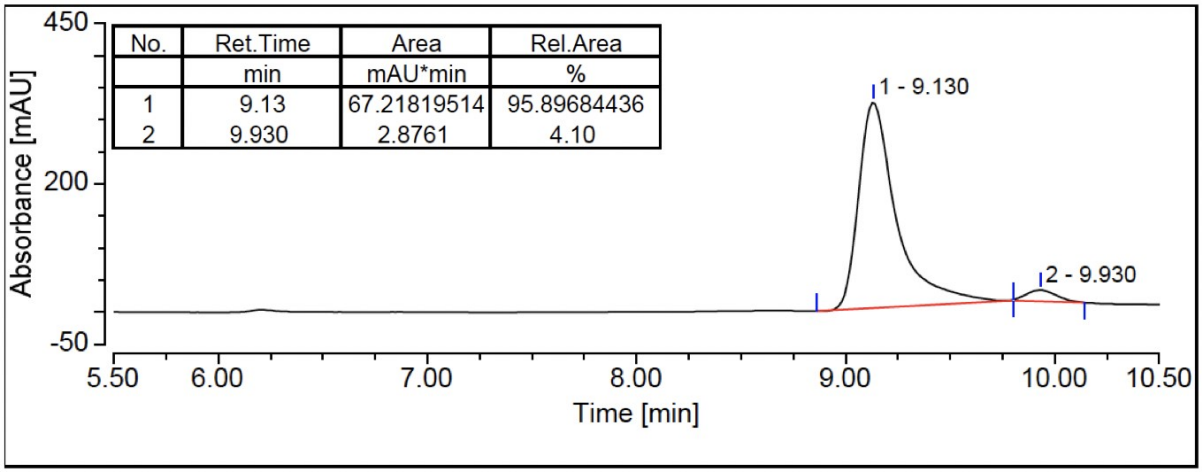
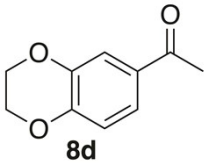


Figure S98: HPLC trace of enantioenriched 9c (obtained by general procedure C1).



8d

Synthesis of (*R*)-1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)ethan-1-ol (R)-9d. The synthesis of racemic **9d** and its spectroscopic data has previously been reported.[S4] This compound was obtained in 61% isolated yield (65.9 mg, colorless oil), following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.96 – 6.71 (m, 3H), 4.75 (q, *J* = 6.4 Hz, 1H), 4.21 (s, 2H), 1.90 (s, 1H), 1.42 (d, *J* = 6.4 Hz, 1H).^{13}C NMR (75 MHz, Chloroform-*d*) 143.4, 142.8, 139.3, 118.5, 117.2, 114.4, 69.9, 64.3, 24.9. GC: β-DEX column, 150 °C isotherm, retention times t_R(SM) = 15.6 min, t_R(product) = 20.1 min, Analytical data are in agreement with literature data.[S4] **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 99 : 1, flow rate 1.0 mL/min, λ = 210 nm), retention times t_R((major)-**9d**) = 30.3 min, t_R((minor)-**9d**)= 38.4 min. (ee: 80.2%)

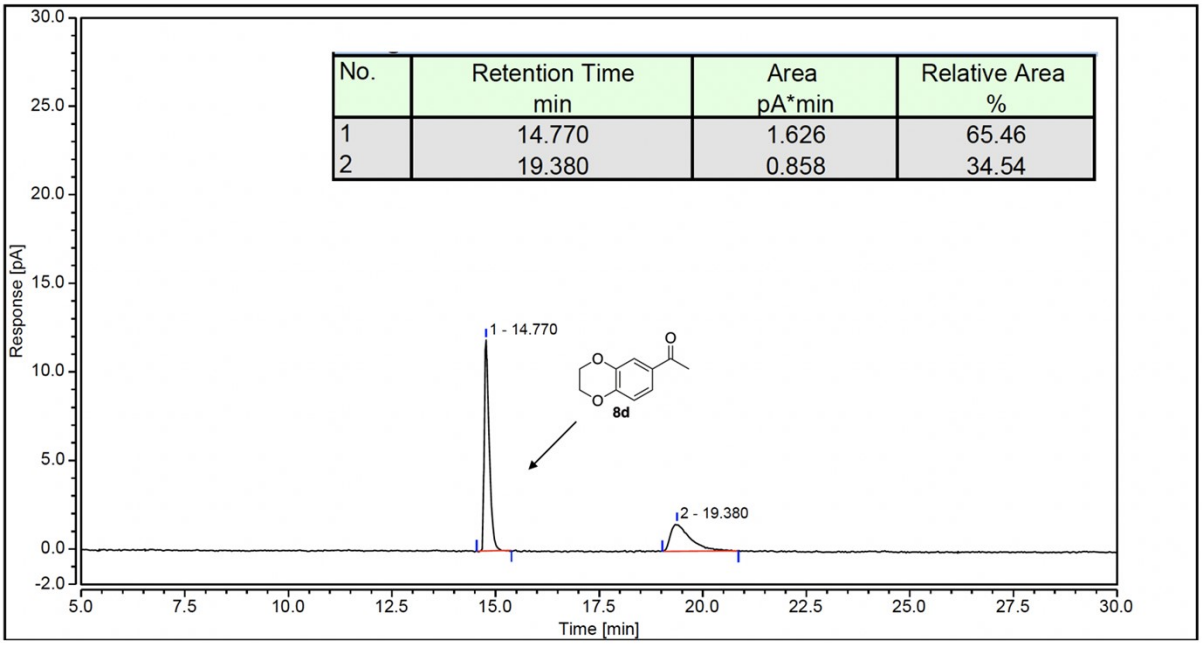


Figure S99: GC trace of 8d and 9d.

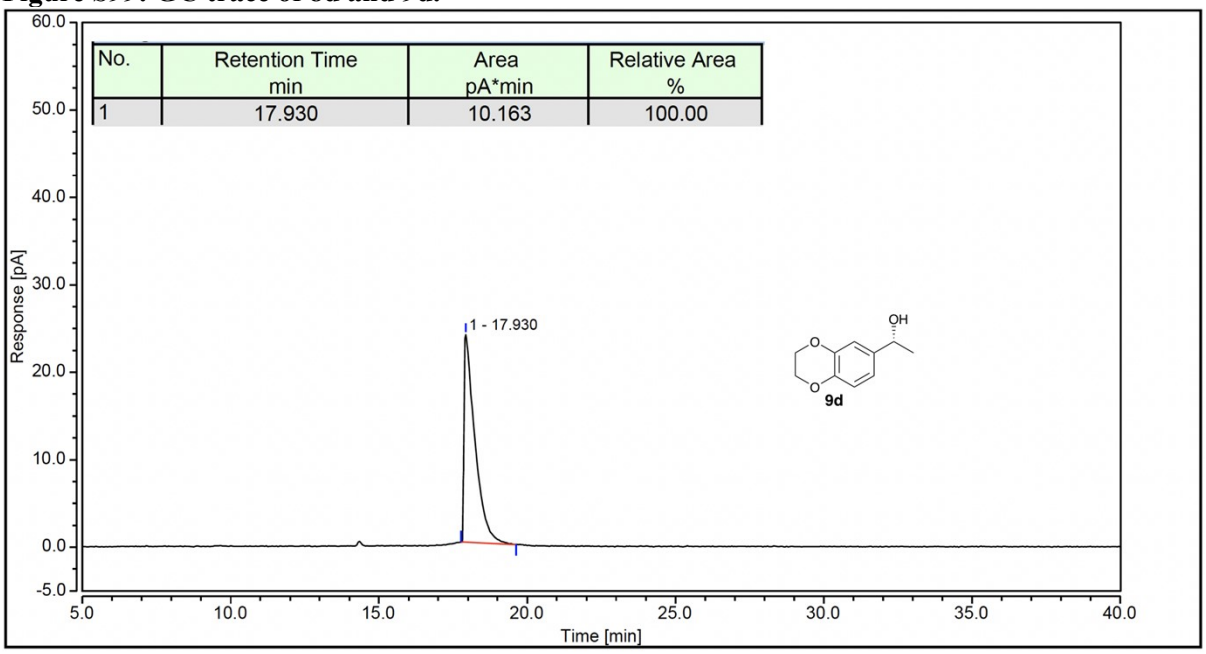


Figure S100: GC trace of 9d (obtained by general procedure C1).

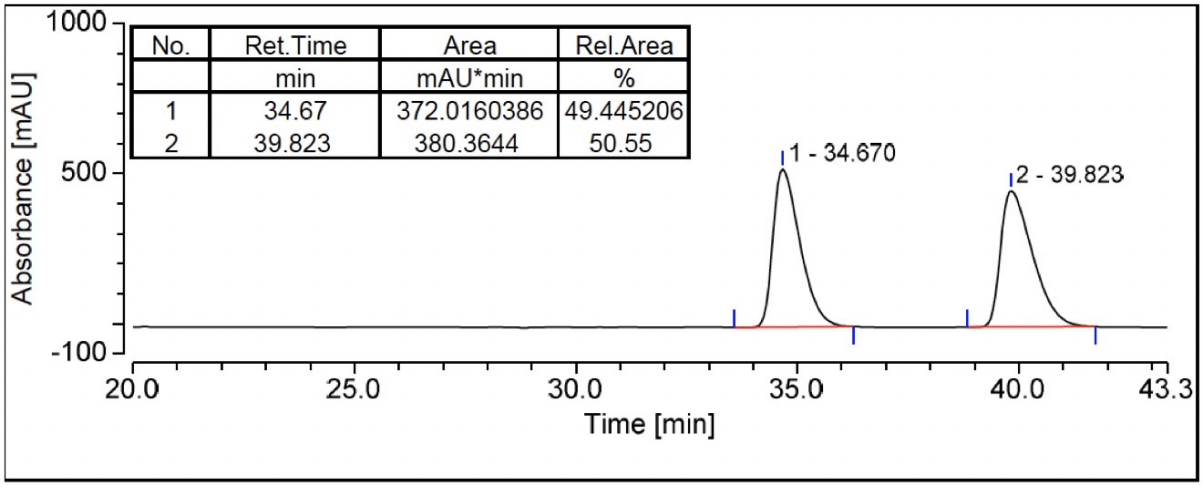


Figure S101: HPLC trace of racemic 9d (obtained by general procedure C3).

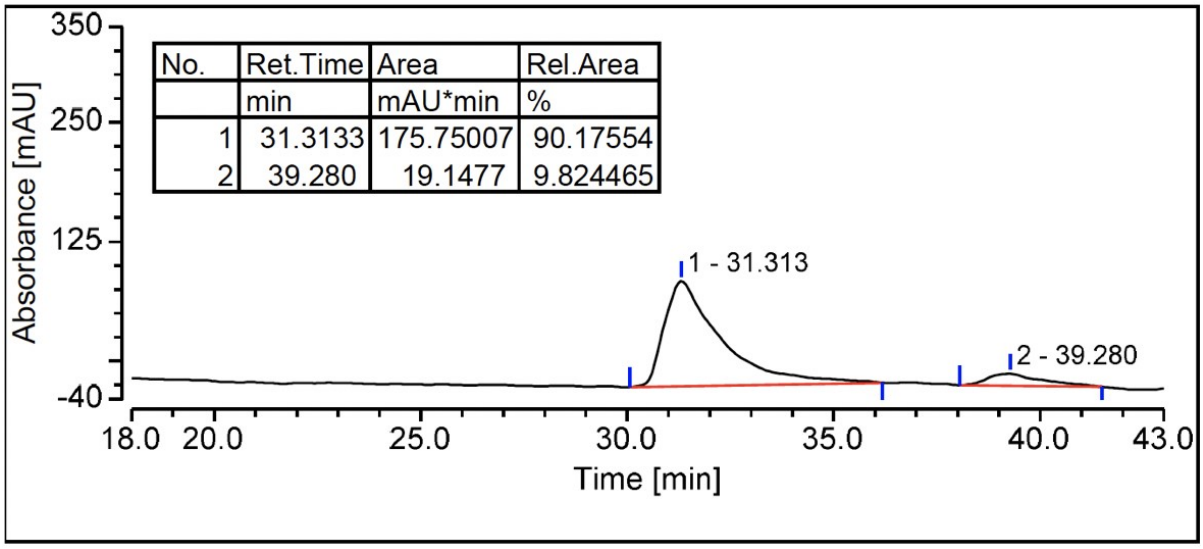
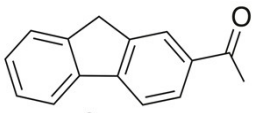


Figure S102: HPLC trace of enantioenriched 9d (obtained by general procedure C1).



8e

Synthesis of (*R*)-1-(9*H*-fluoren-2-yl)ethan-1-ol (R)-9e. The synthesis of racemic **9e** and its spectroscopic data has previously been reported.[S5] This compound was obtained in 60% isolated yield (75.7 mg, white solid) following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.73 – 7.63 (m, 2H), 7.51 – 7.42 (m, 2H), 7.33 – 7.18 (m, 3H), 4.89 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 1H), 1.81 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H).^{13}C NMR (75 MHz, Chloroform-*d*) 144.5, 143.6, 143.3, 141.4, 141.1, 126.7, 125.0, 124.2, 122.1, 119.8, 70.7, 36.9, 25.3. GC: β-DEX column, 180 °C isotherm, retention times t_R(SM) = 18.3 min, t_R(major) = 23.0 min, t_R(minor) = 24.0 min. Analytical data are in agreement with literature data.[S5] The absolute configuration was determined to be (*R*) by comparison with (*R*)-**7a**. **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 99 : 1, flow rate 1.0

mL/min, λ = 210 nm), retention times t_R((major)-**9d**) = 30.3 min, t_R((minor)-**9d**)= 38.4 min. (ee: 91.8%)

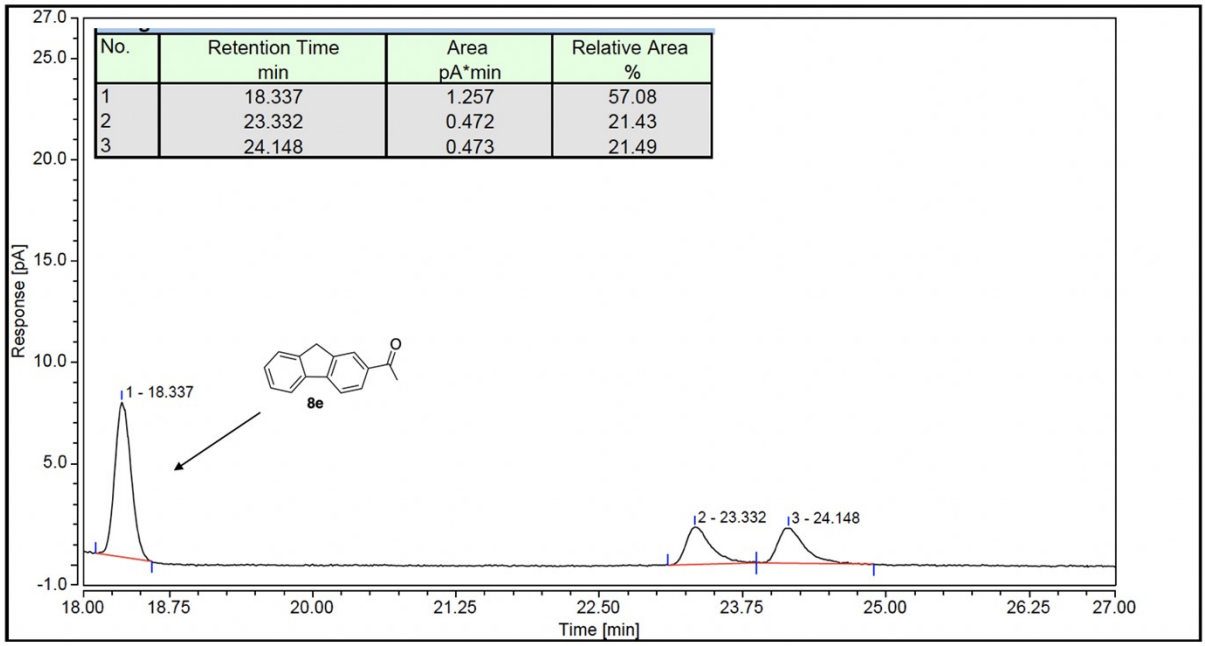


Figure S103: GC trace of racemic 8e and 9e (obtained by general procedure C3).

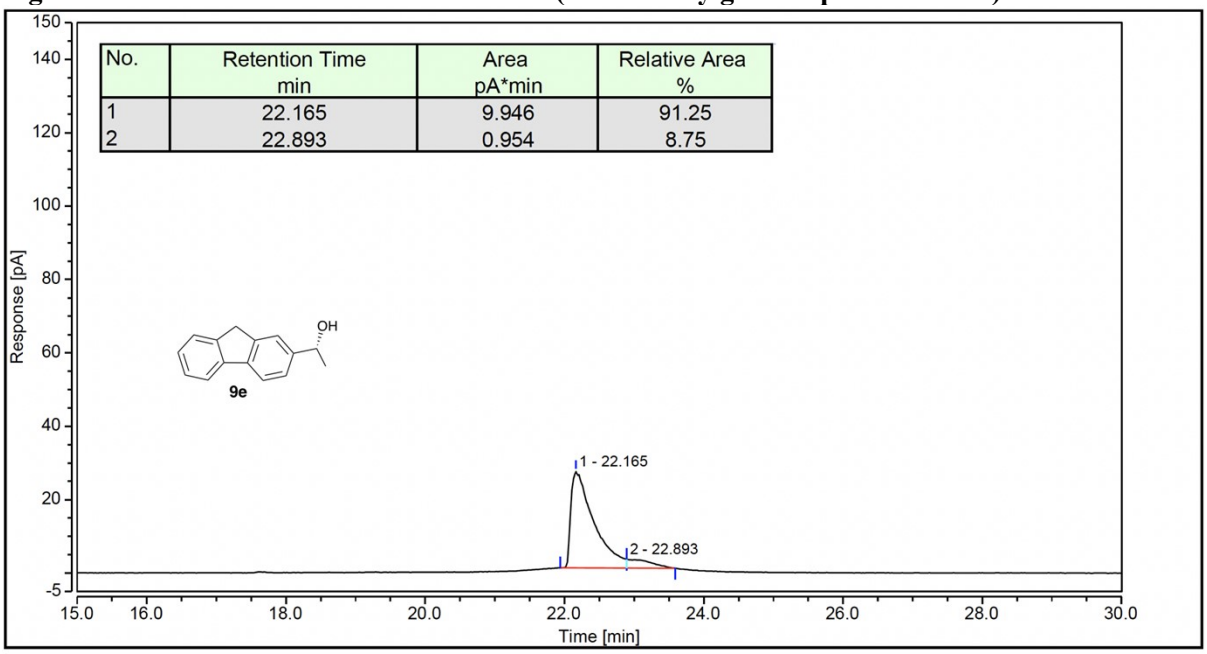


Figure S104: GC trace of enantioenriched 9e (obtained by general procedure C1).

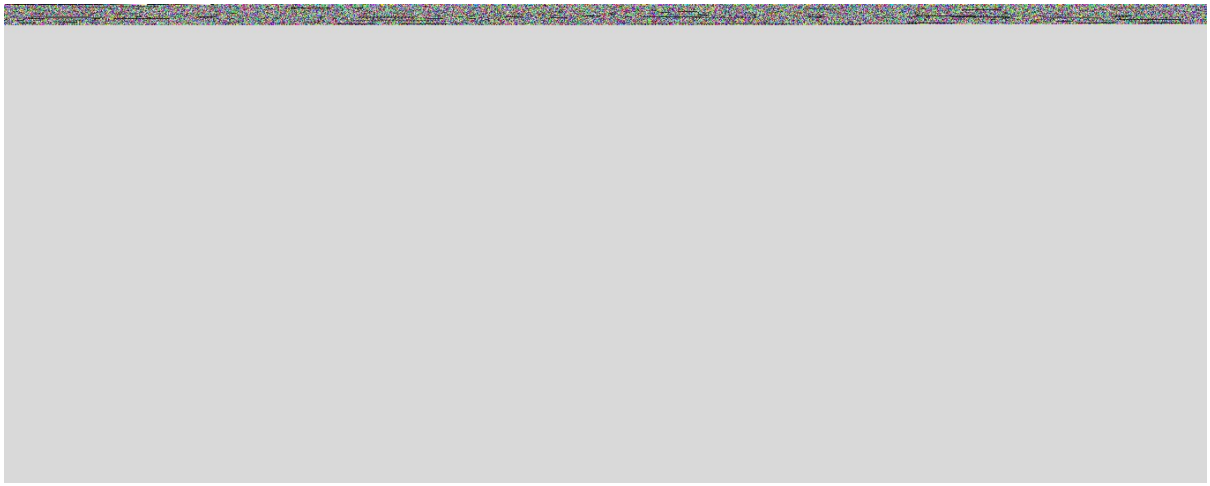
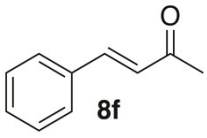


Figure S105: HPLC trace of racemic 9e (obtained by general procedure C3).

Figure S106: HPLC trace of enantioenriched 9e (obtained by general procedure C1).



Synthesis of (*R*,*E*)-4-phenylbut-3-en-2-ol (R)-9f. The synthesis of racemic **9f** and its spectroscopic data has previously been reported.[S2] This compound was obtained in 97.0% isolated yield (86.2 mg, yellowish oil) following general procedure **C1** using catalyst **3b** (reaction time: 18 h). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.41 – 7.00 (m, 4zH), 6.43 (d, *J* = 15.9, 1.2 Hz, 1H), 6.13 (d, *J* = 15.9, 1H), 4.32 (m, 1H), 2.74 (s, 1H), 1.24 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) 143.3, 136.8, 133.6, 129.3, 128.6, 127.6, 126.5, 68.8, 23.4. GC: β-DEX column, 120 °C isotherm, retention times t_R(SM) = 15.2 min, t_R(major) = 20.3 min, t_R(minor) = 20.7 min. Analytical data are in agreement with literature data.[S2] The absolute configuration was determined to be (R) by comparison with literature data.[S2] **HPLC**: Chiralpak IB-3 (hexane : 2-propanol = 99 : 1, flow rate 1.0 mL/min, λ = 210 nm), retention times t_R((major)-**9f**) = 20.3 min, t_R((minor)-**9f**)= 34.9 min. (ee: 37.6%)

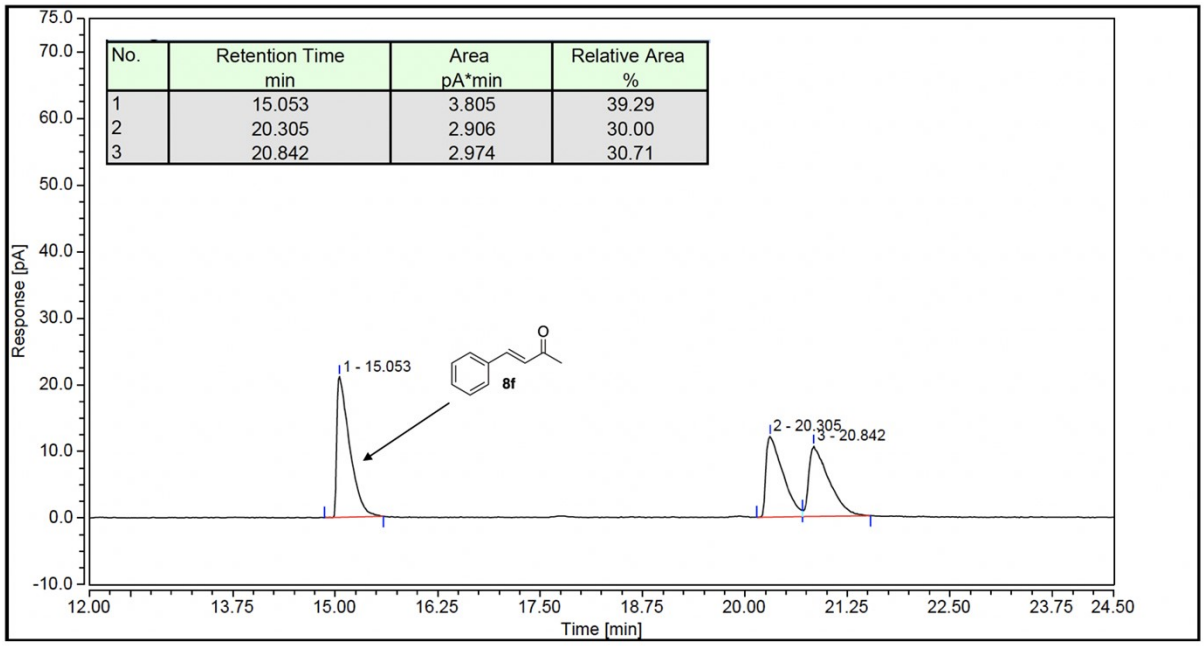


Figure S107: GC trace of 8f and racemic 9f (obtained by general procedure C3).

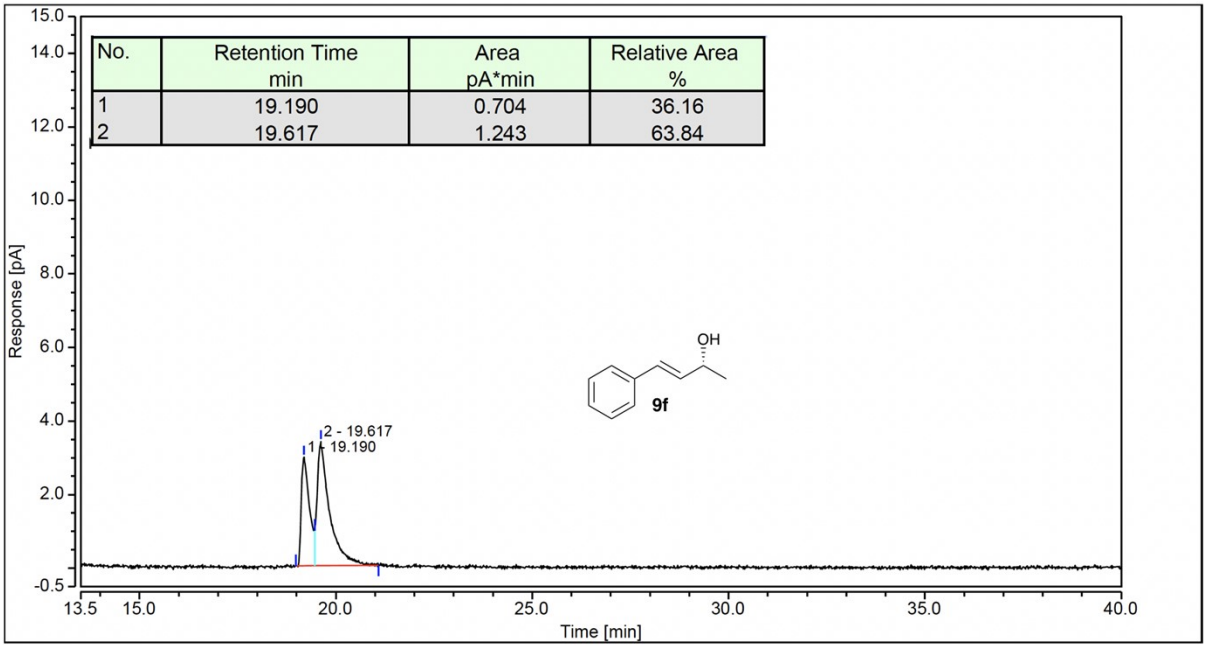


Figure S108: GC trace of enantioenriched 9f (obtained by general procedure C1).

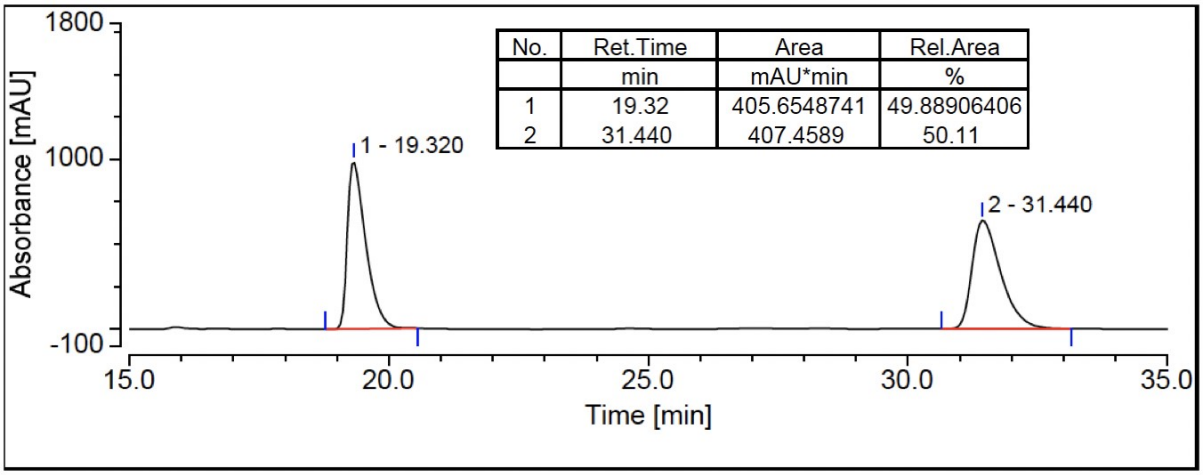


Figure S109: HPLC trace of racemic 9f (obtained by general procedure C3).

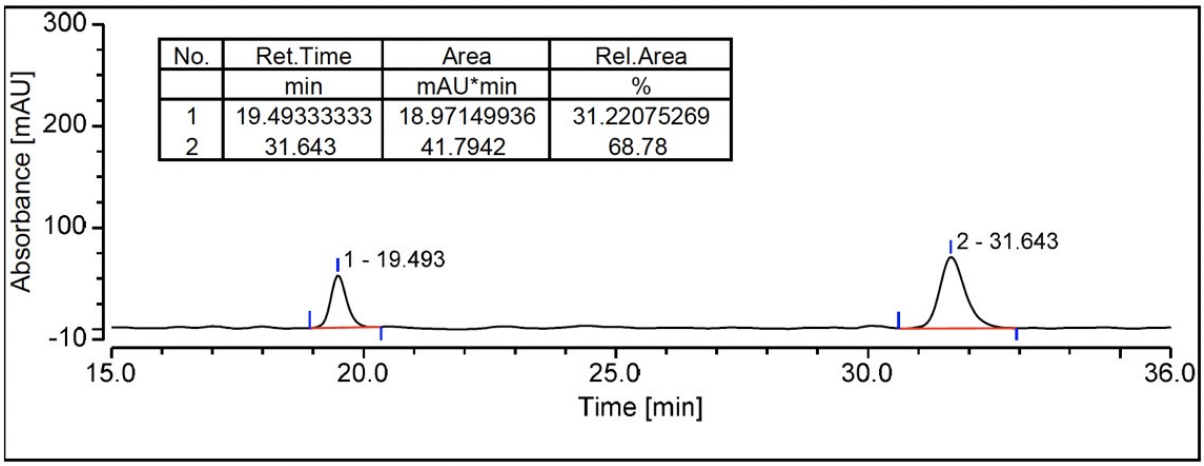


Figure S110: HPLC trace of enantioenriched 9f (obtained by general procedure C1).

10.2. NMR spectra of the alcohols (7/9):

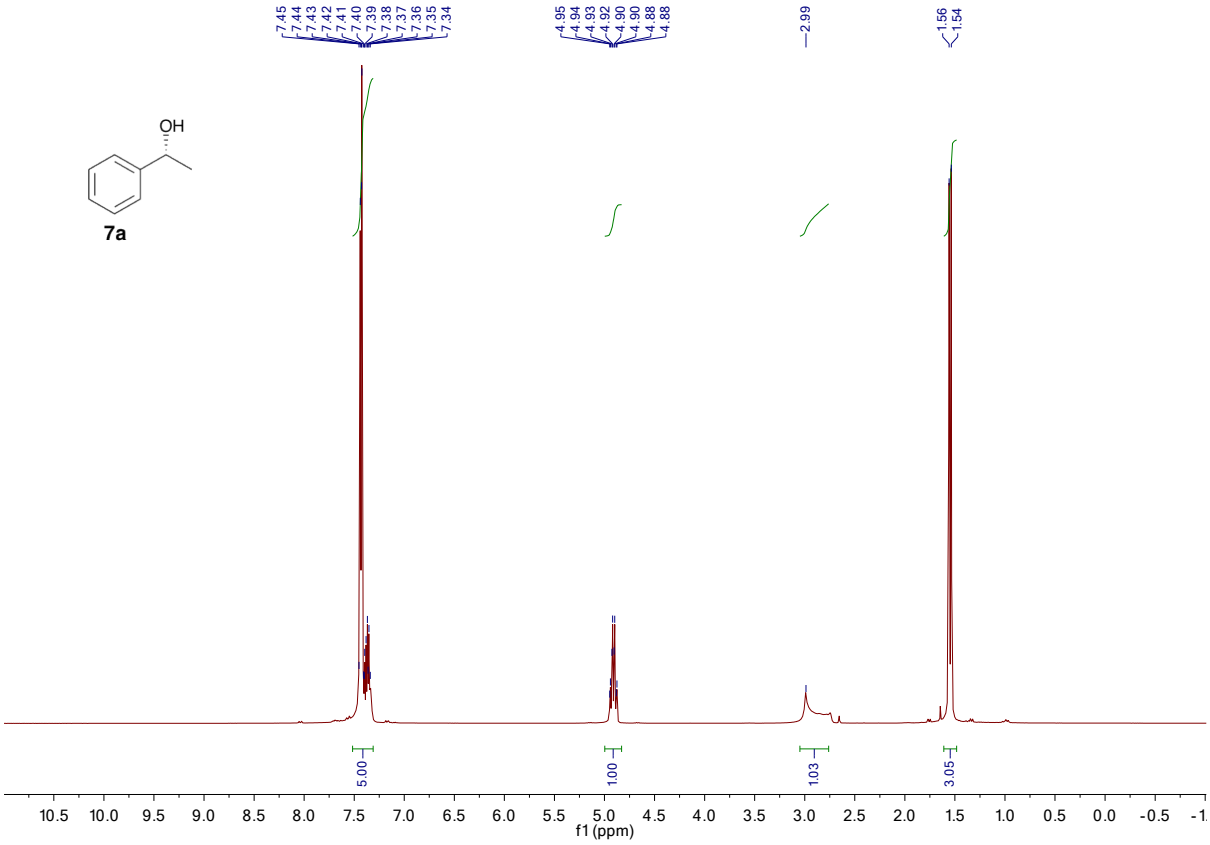


Figure S111. ^{1}H NMR spectrum of **7a** (300 MHz, Chloroform-*d*).

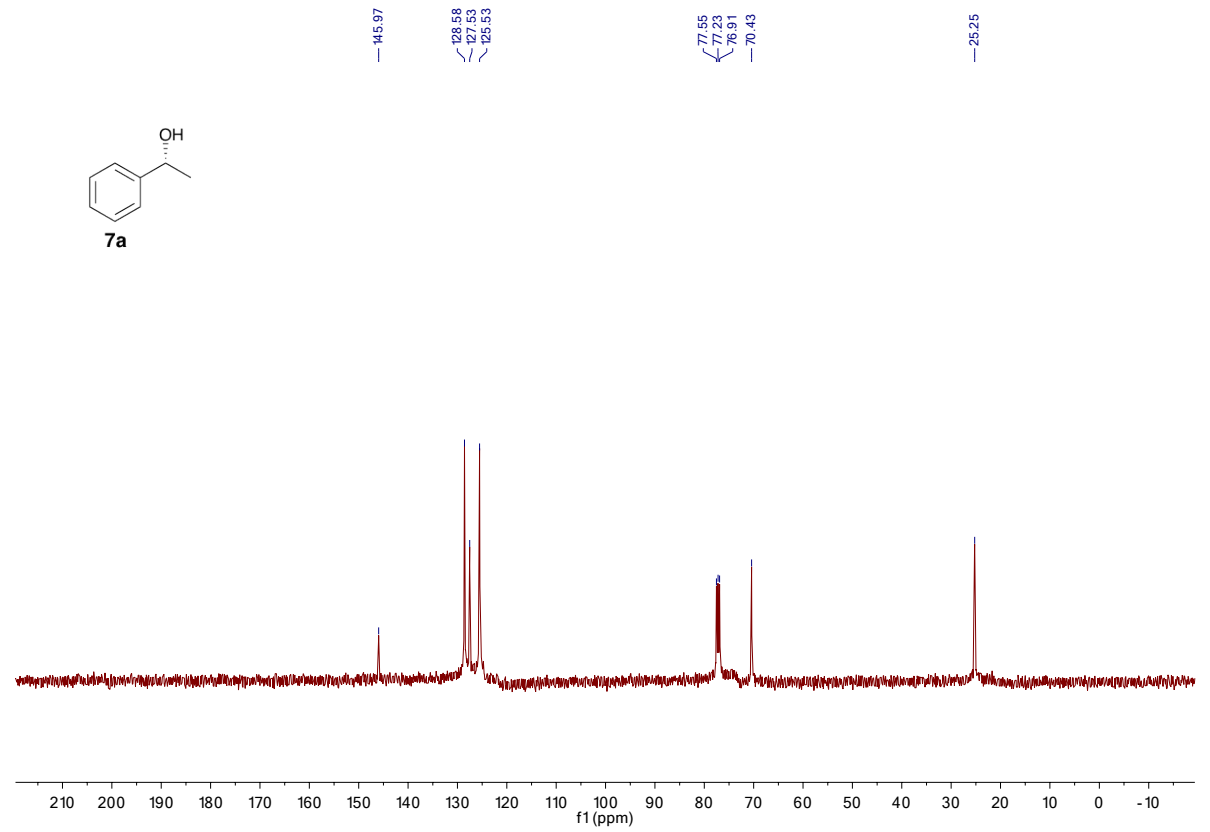


Figure S112. ^{13}C{^{1}H} NMR spectrum of **7a** (75 MHz, Chloroform-*d*).

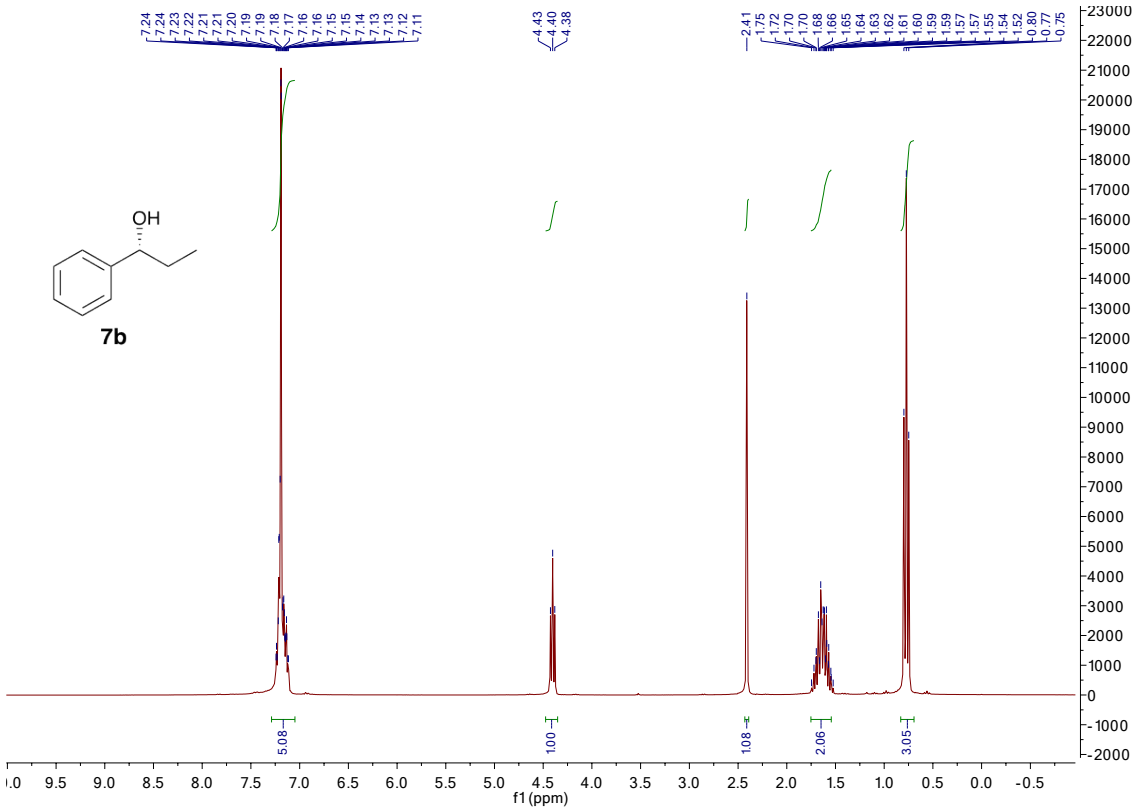


Figure S113. ^{1}H NMR spectrum of **7b** (300 MHz, Chloroform-*d*).

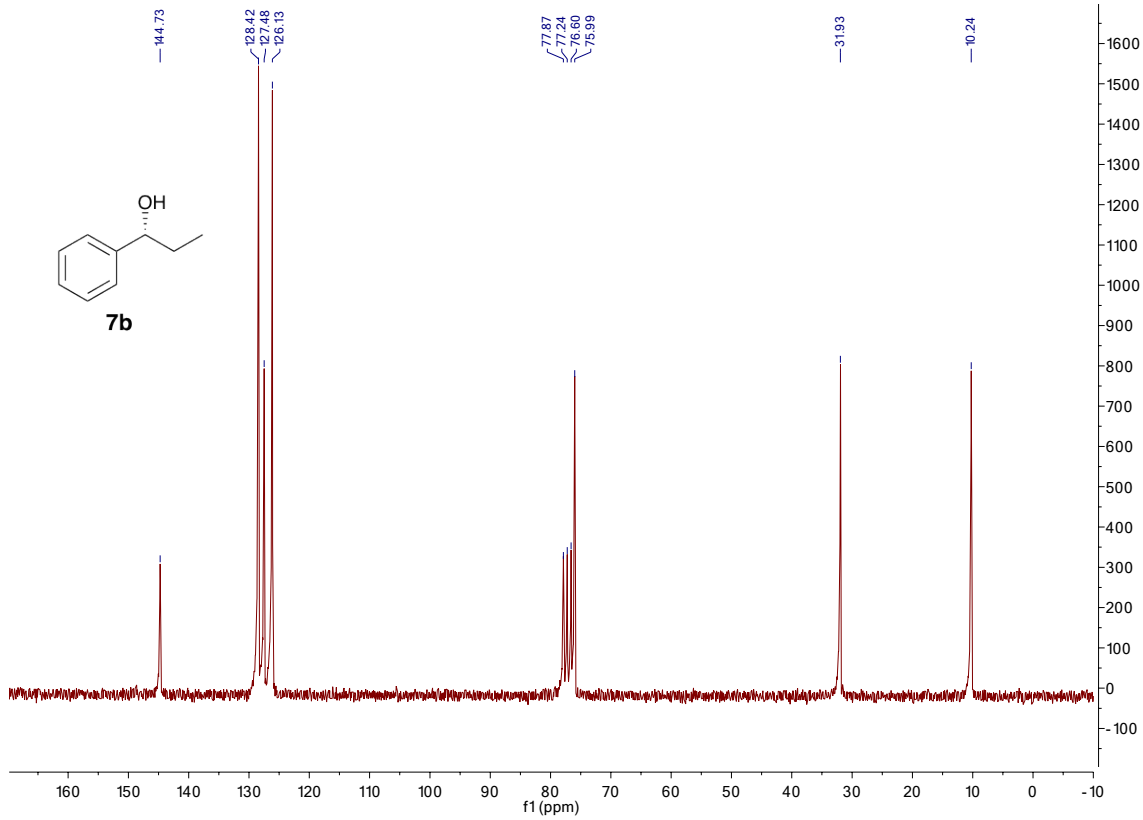


Figure S114. ^{13}C{^{1}H} NMR spectrum of **7b** (75 MHz, Chloroform-*d*).

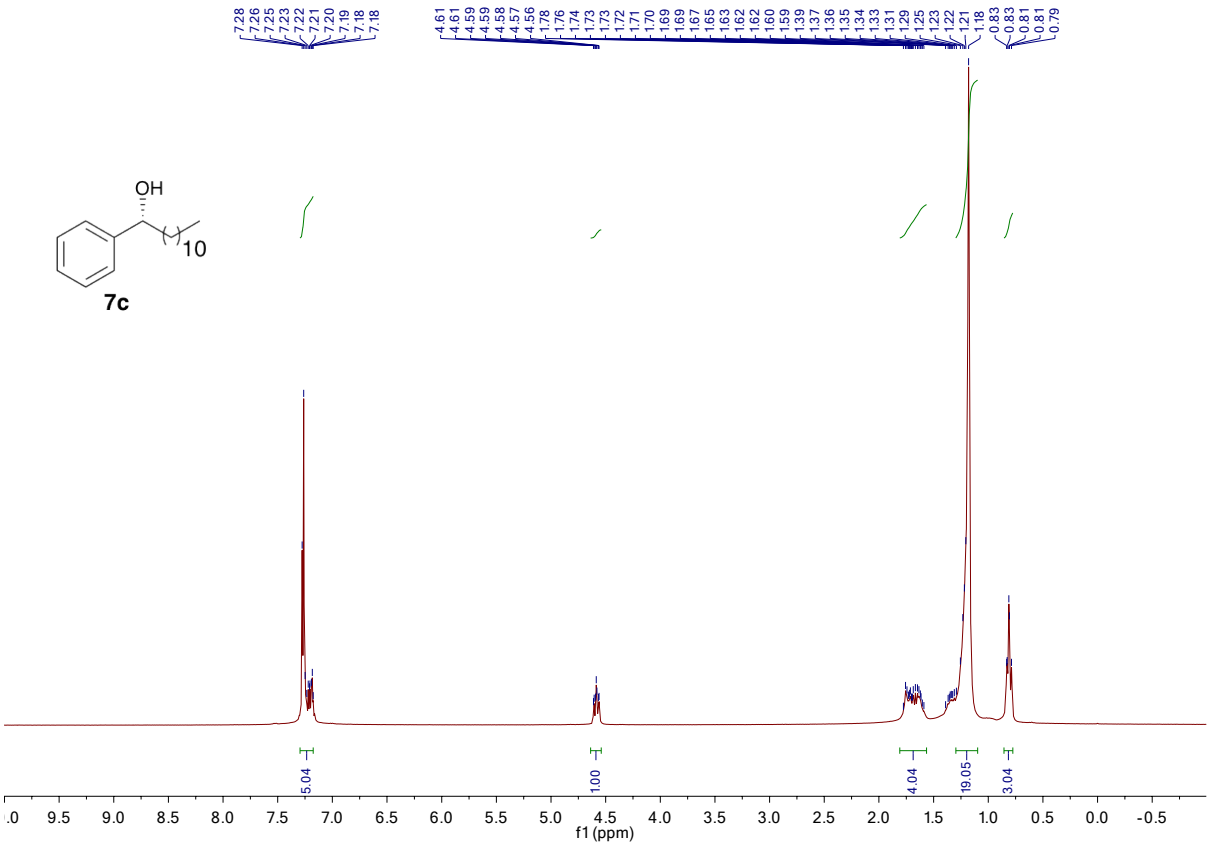


Figure S115. ^{1}H NMR spectrum of **7c** (300 MHz, Chloroform-*d*).

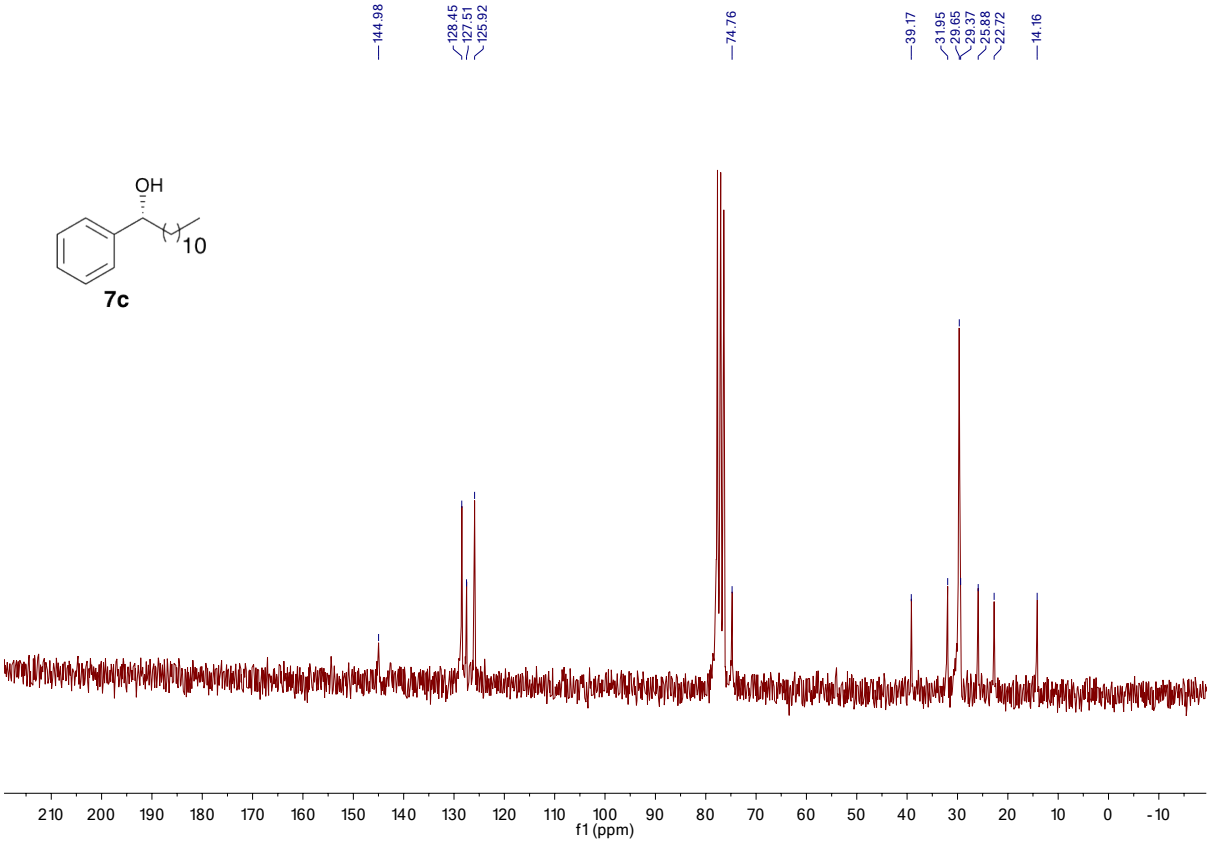


Figure S116. ^{13}C{^{1}H} NMR spectrum of **7c** (75 MHz, Chloroform-*d*).

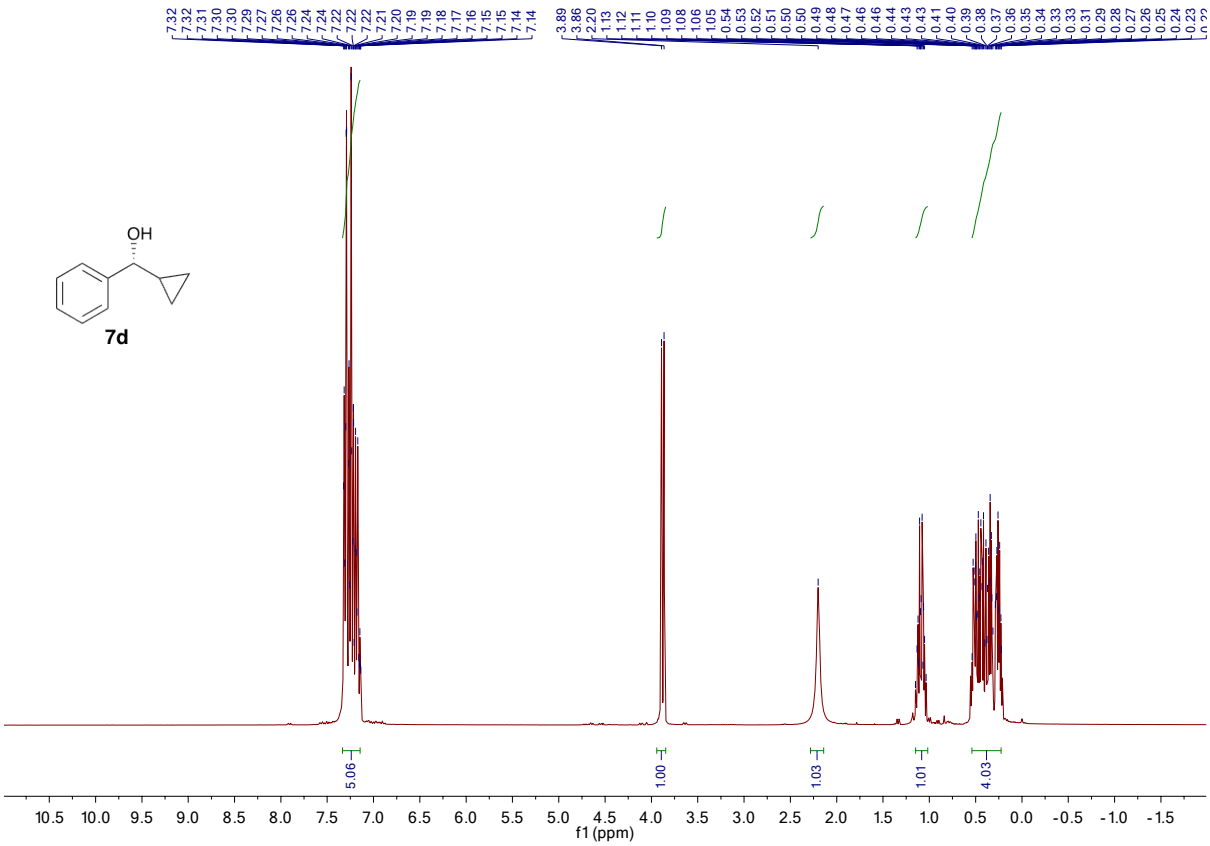


Figure S117. ^{1}H NMR spectrum of **7d** (300 MHz, Chloroform-*d*).

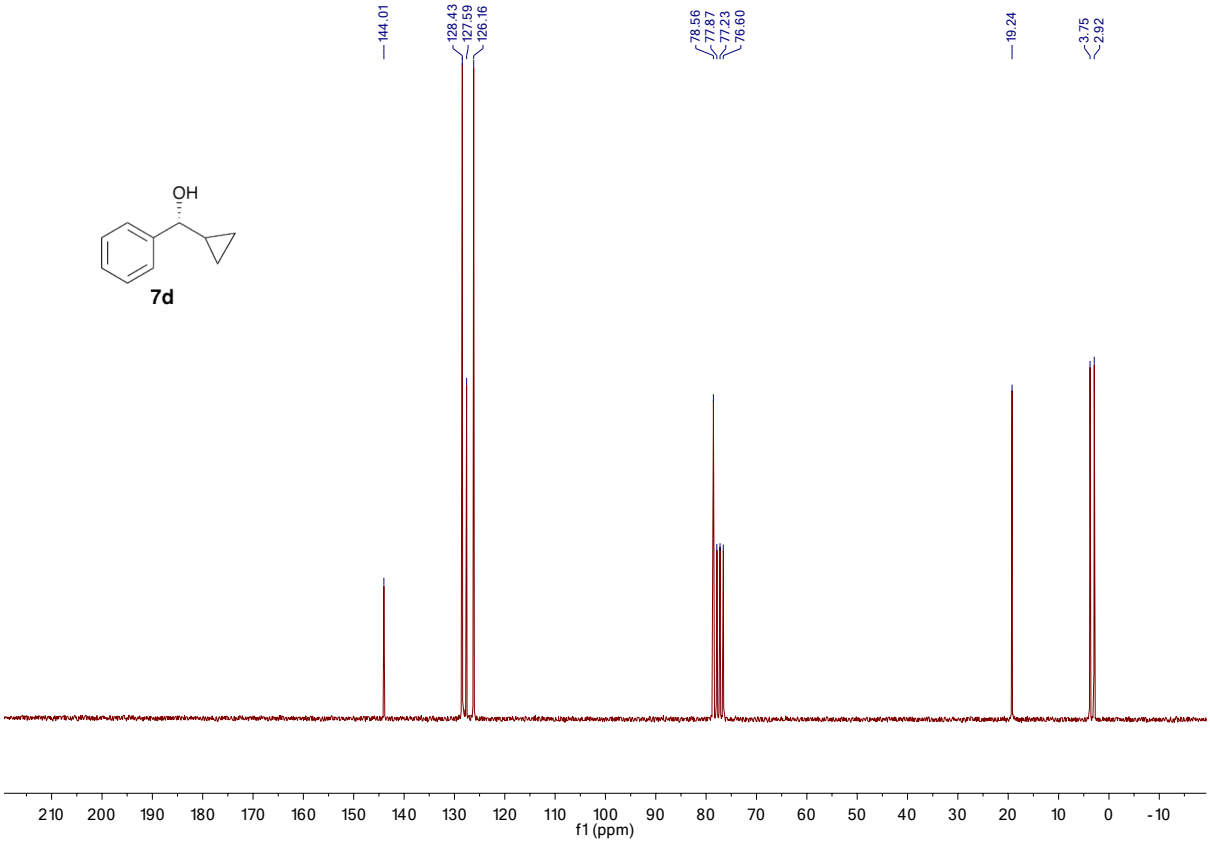


Figure S118. ^{13}C{^{1}H} NMR spectrum of **7d** (75 MHz, Chloroform-*d*).

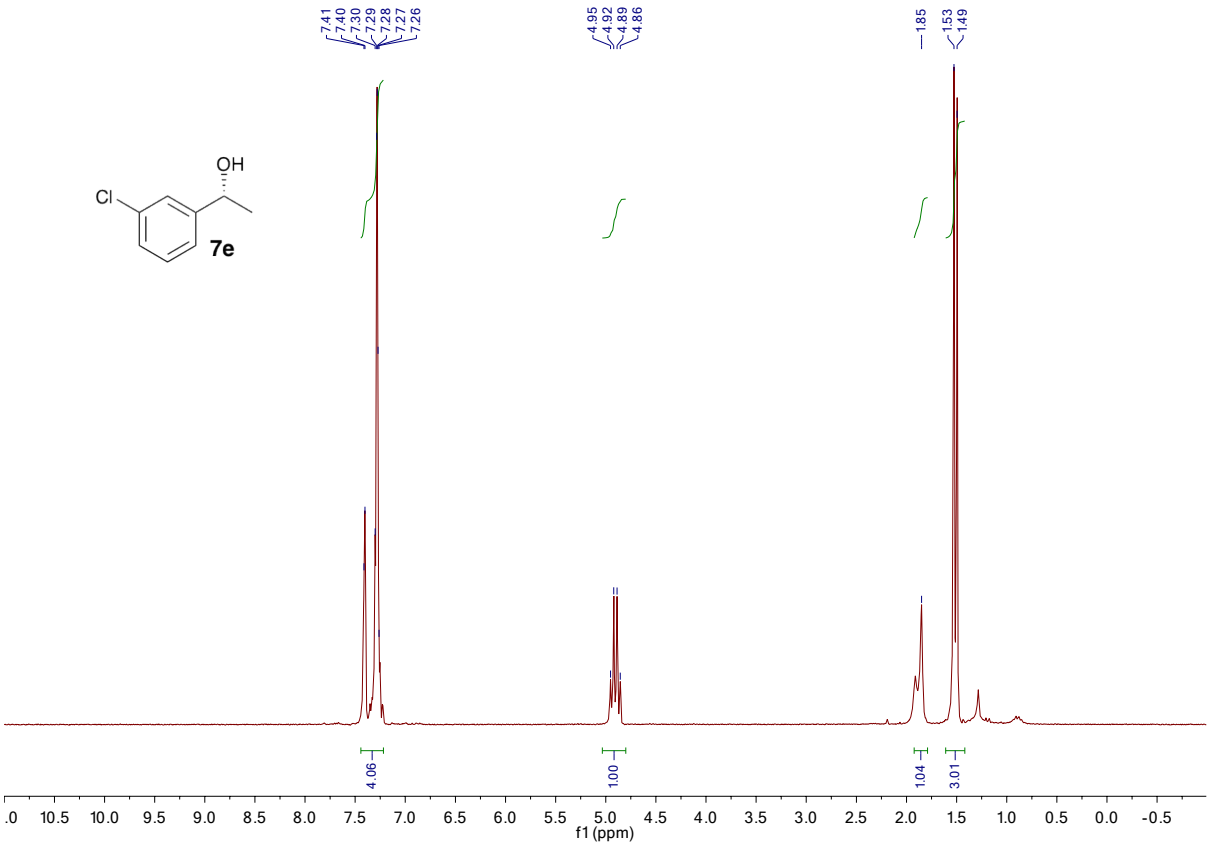


Figure S119. ^{1}H NMR spectrum of **7e** (300 MHz, Chloroform-*d*).

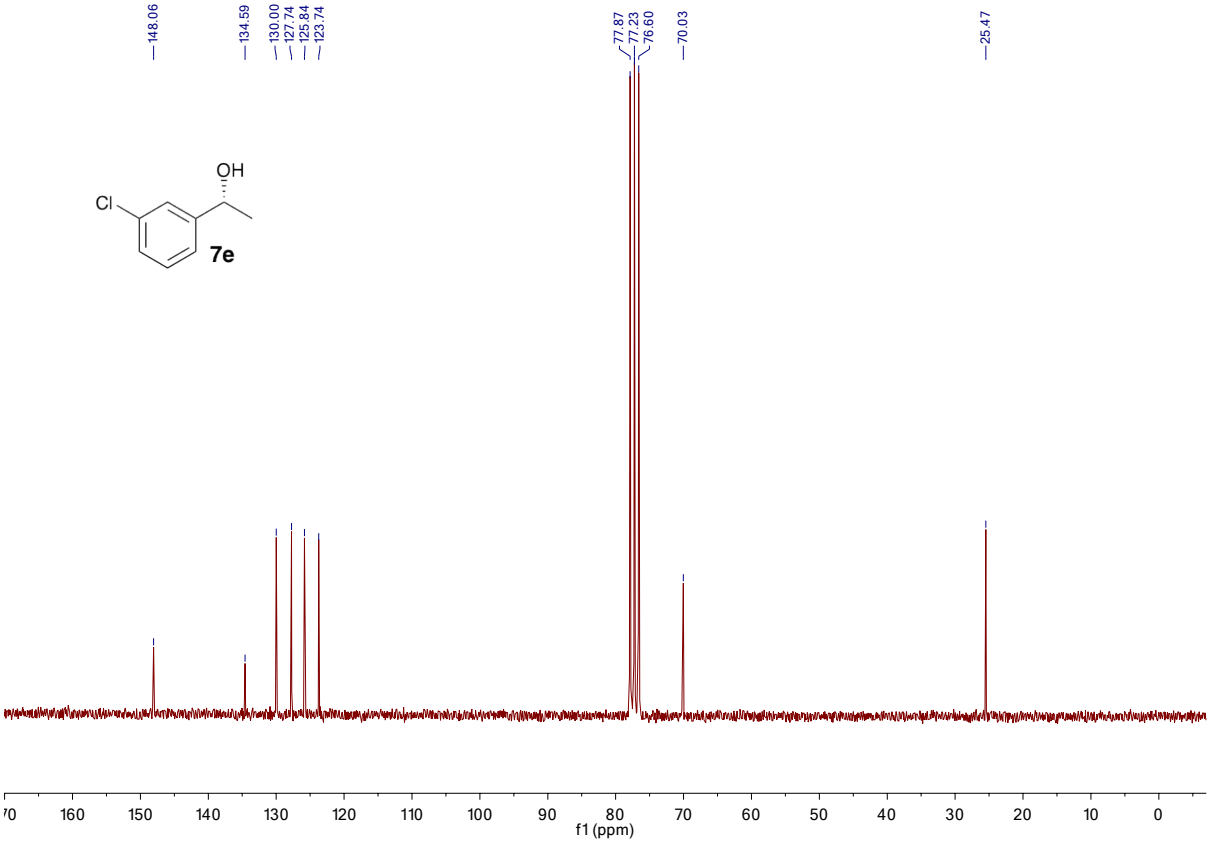


Figure S120. ^{13}C{^{1}H} NMR spectrum of **7e** (75 MHz, Chloroform-*d*).

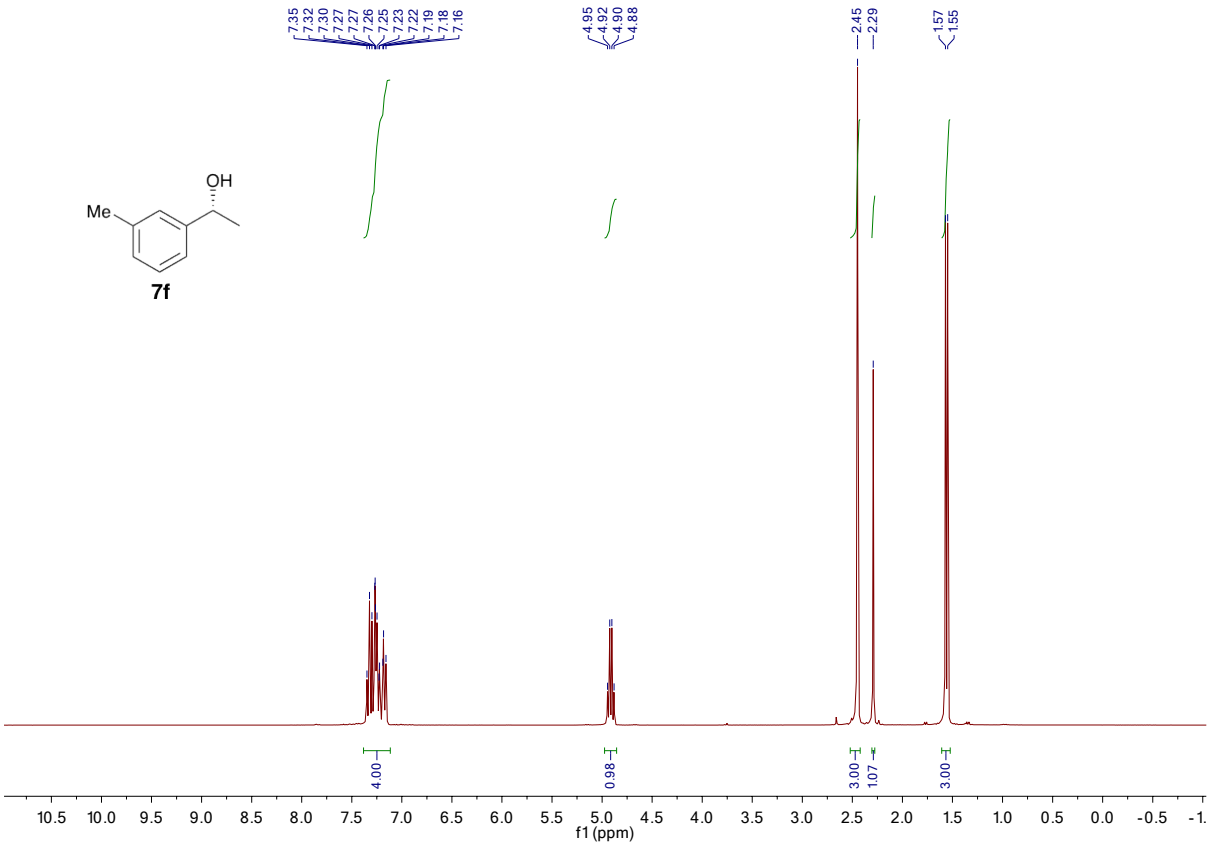


Figure S121. ^{1}H NMR spectrum of **7f** (300 MHz, Chloroform-*d*).

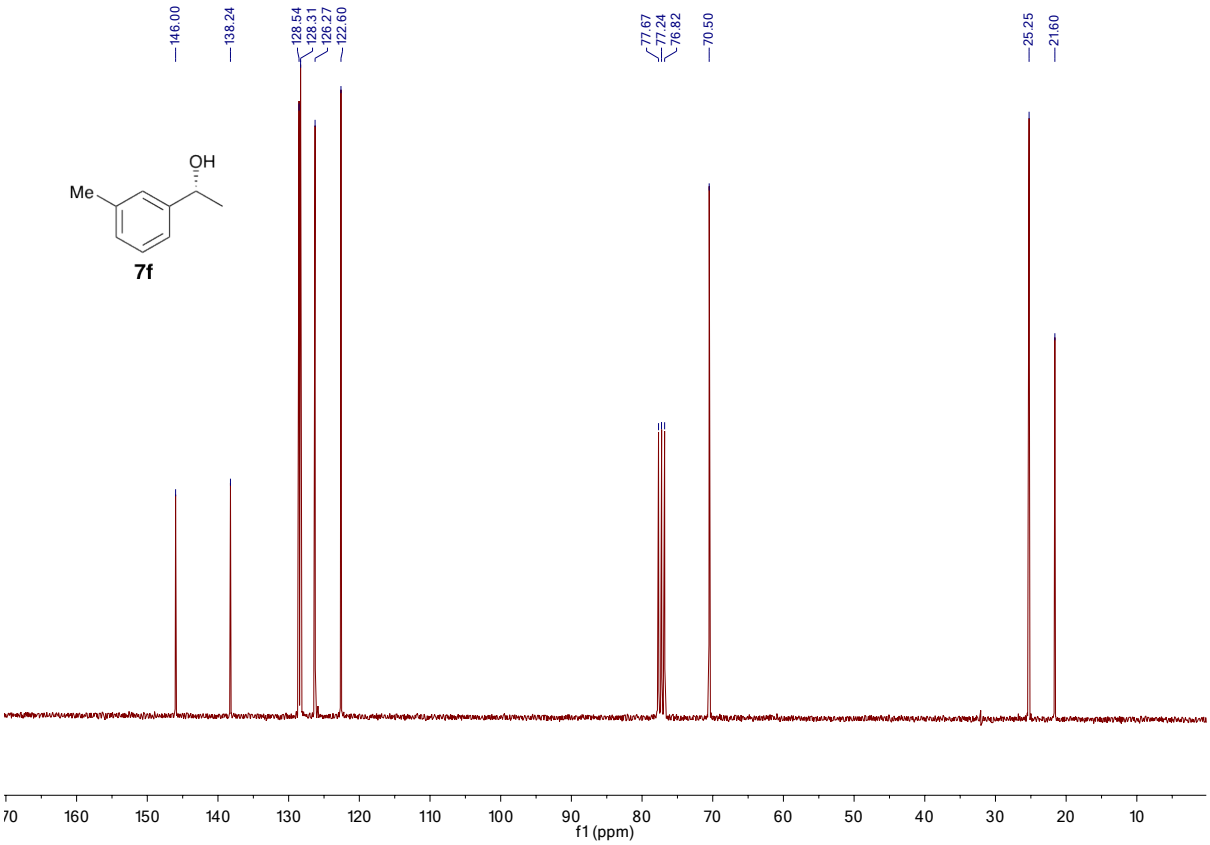


Figure S122. ^{13}C{^{1}H} NMR spectrum of **7f** (75 MHz, Chloroform-*d*).

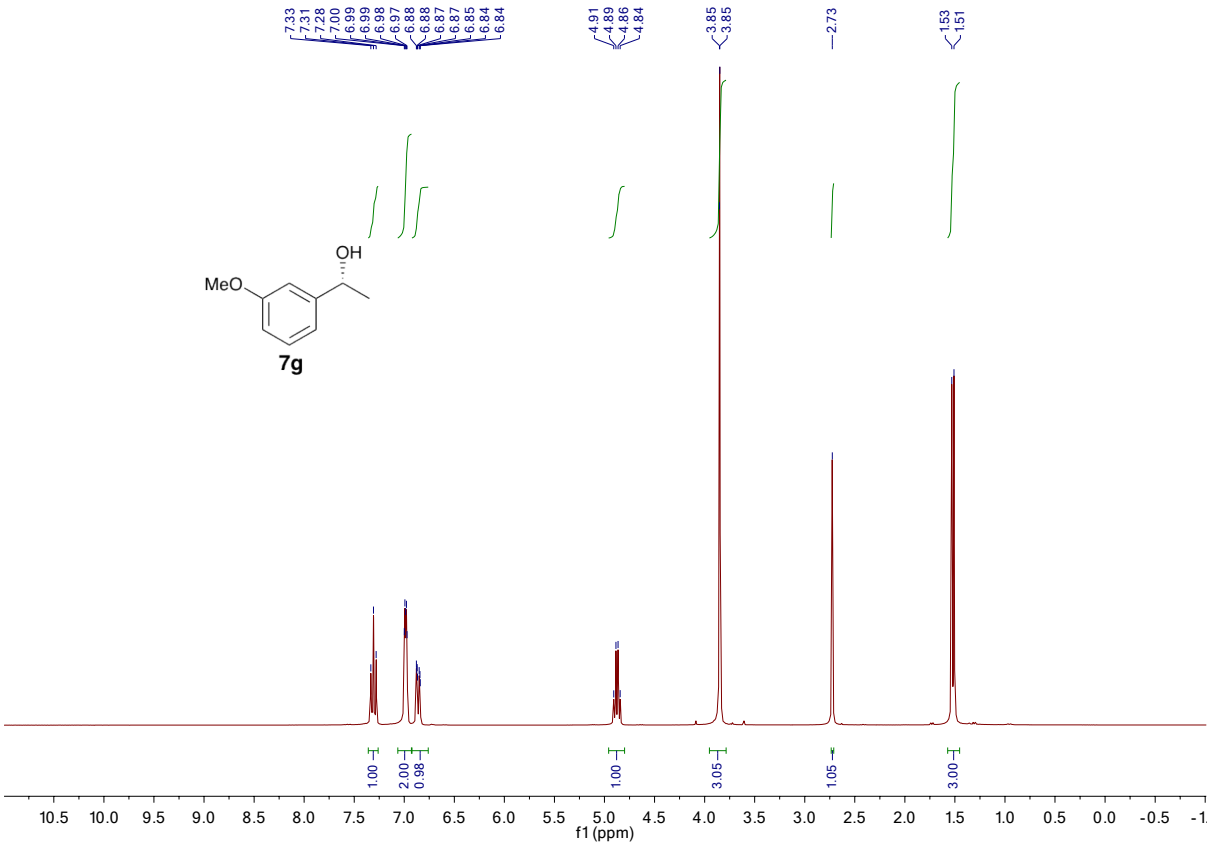


Figure S123. ^{1}H NMR spectrum of **7g** (300 MHz, Chloroform-*d*).

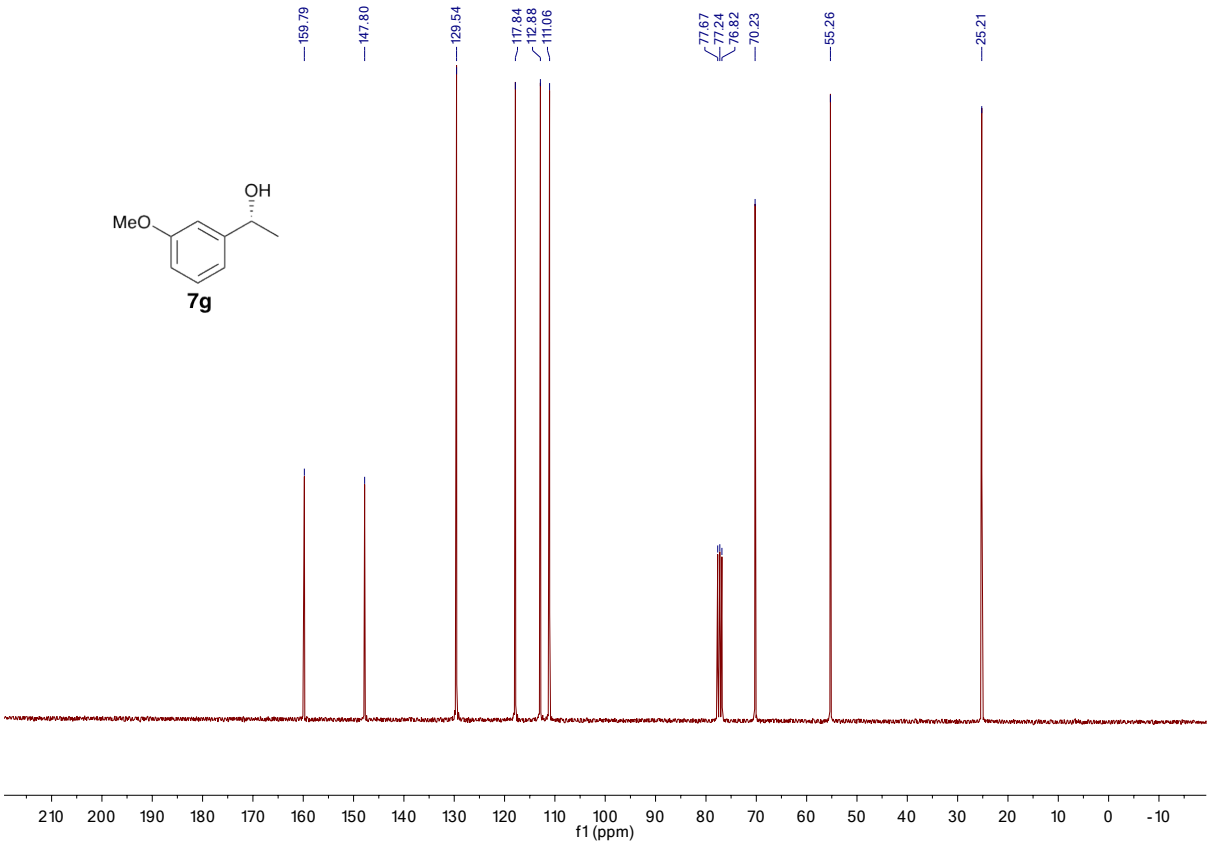


Figure S124. $^{13}C\{^{1}H\}$ NMR spectrum of **7g** (75 MHz, Chloroform-*d*).

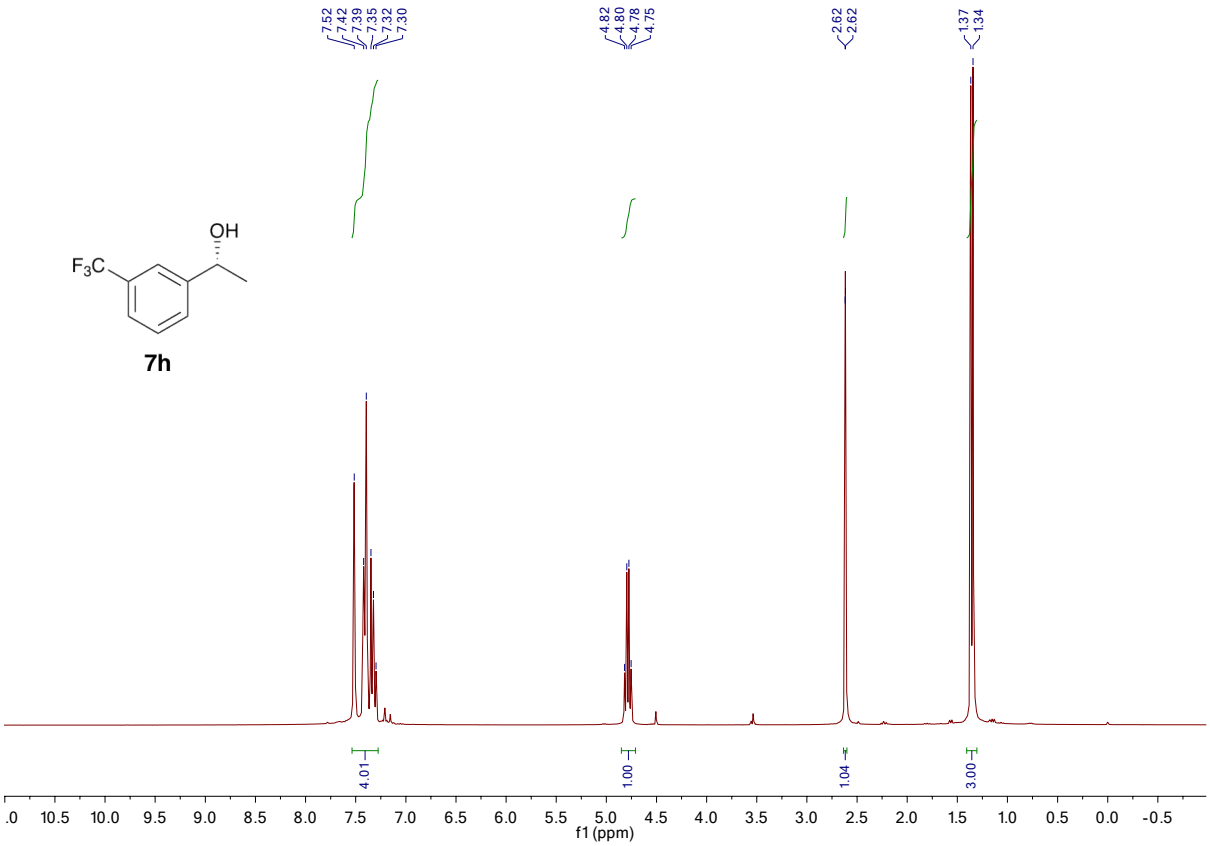


Figure S125. ^{1}H NMR spectrum of **7h** (300 MHz, Chloroform-*d*).

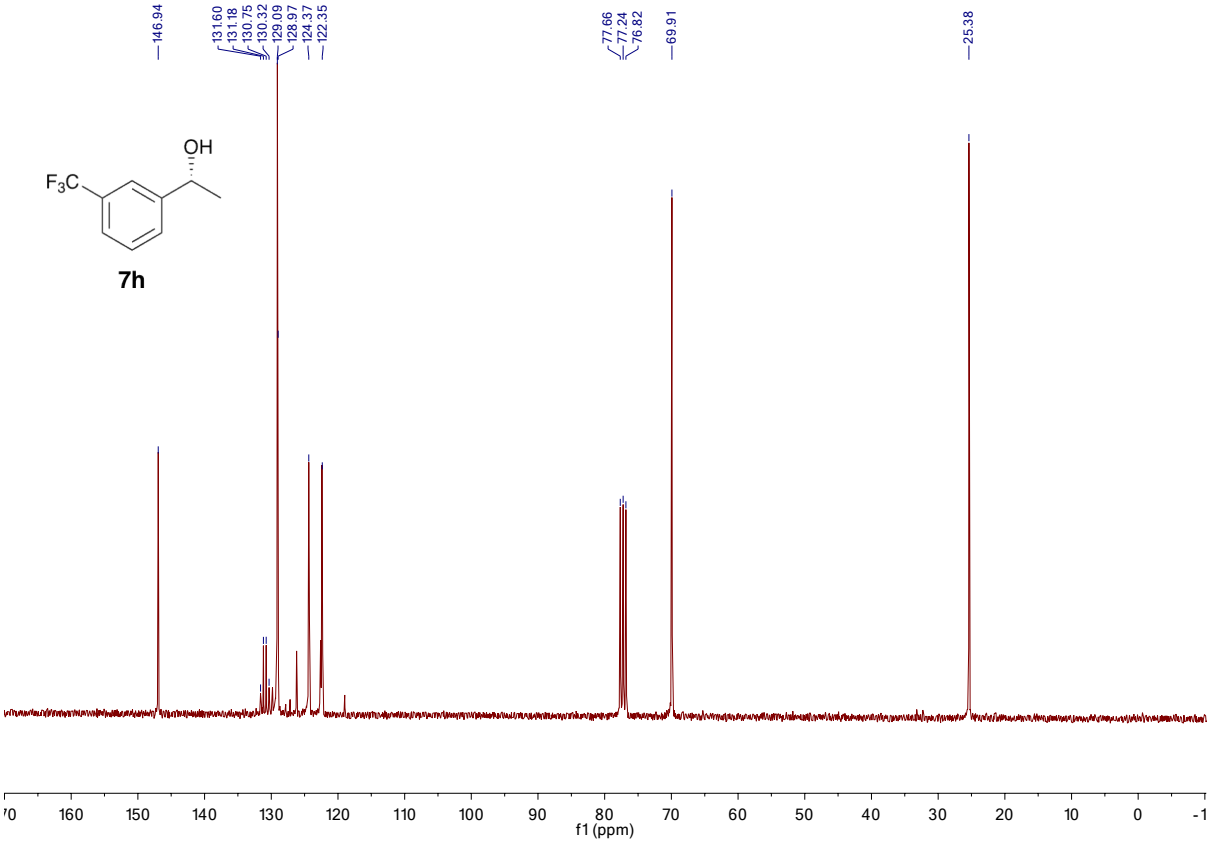


Figure S126. ^{13}C{^{1}H} NMR spectrum of **7h** (75 MHz, Chloroform-*d*).

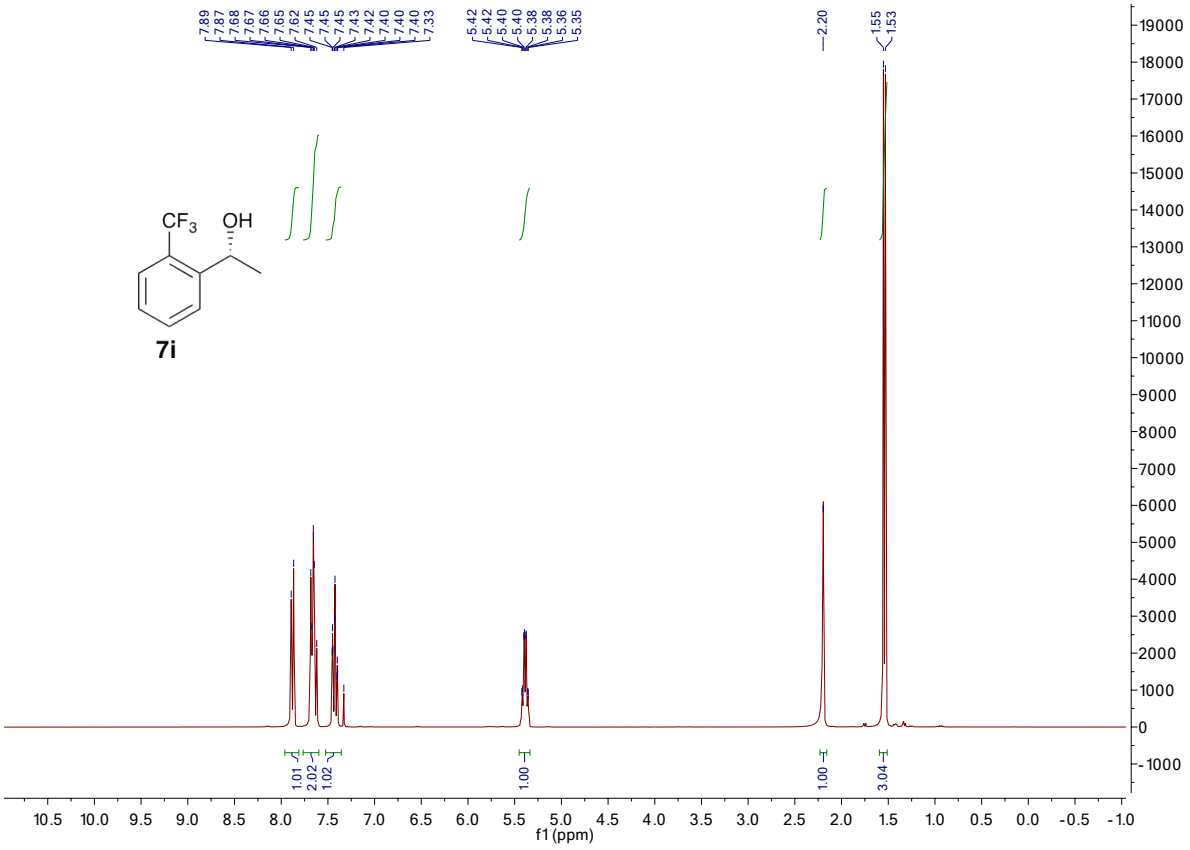


Figure S127. ^{1}H NMR spectrum of **7i** (300 MHz, Chloroform-*d*).

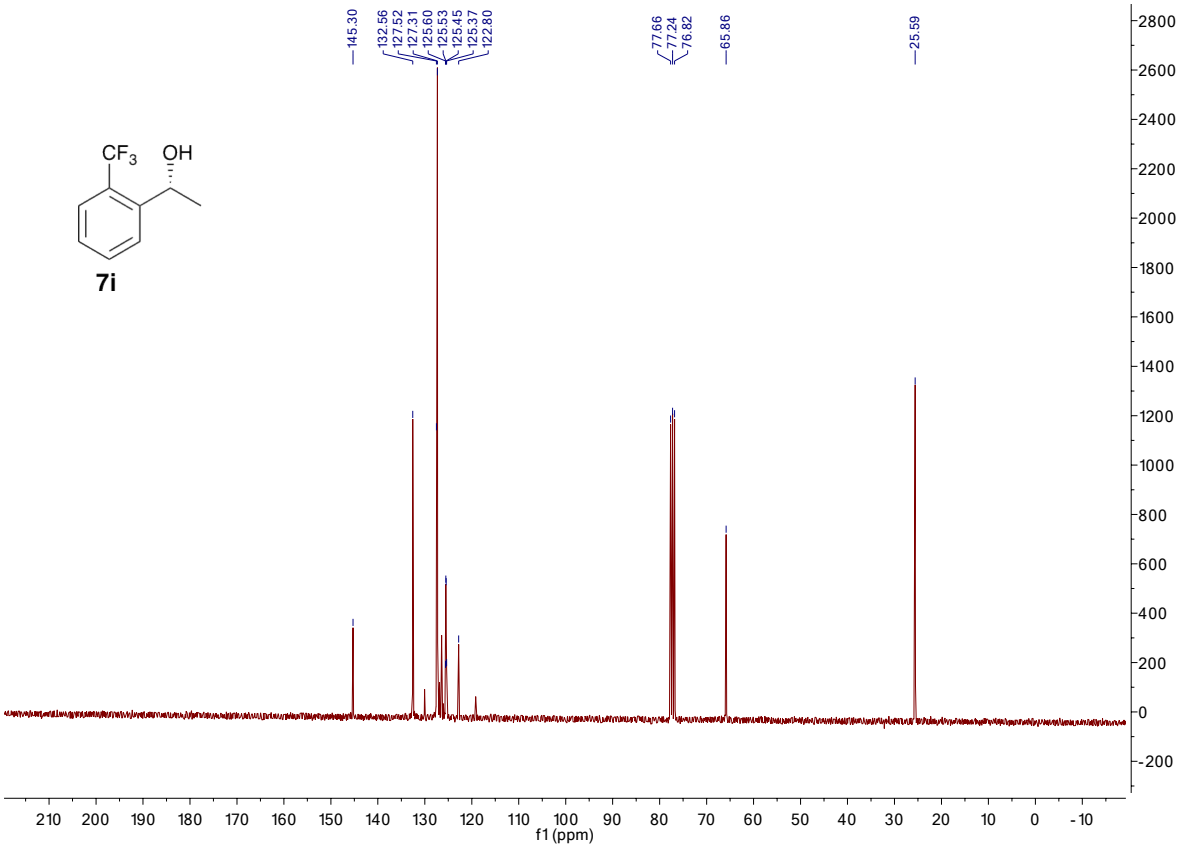


Figure S128. ^{13}C{^{1}H} NMR spectrum of **7i** (75 MHz, Chloroform-*d*).

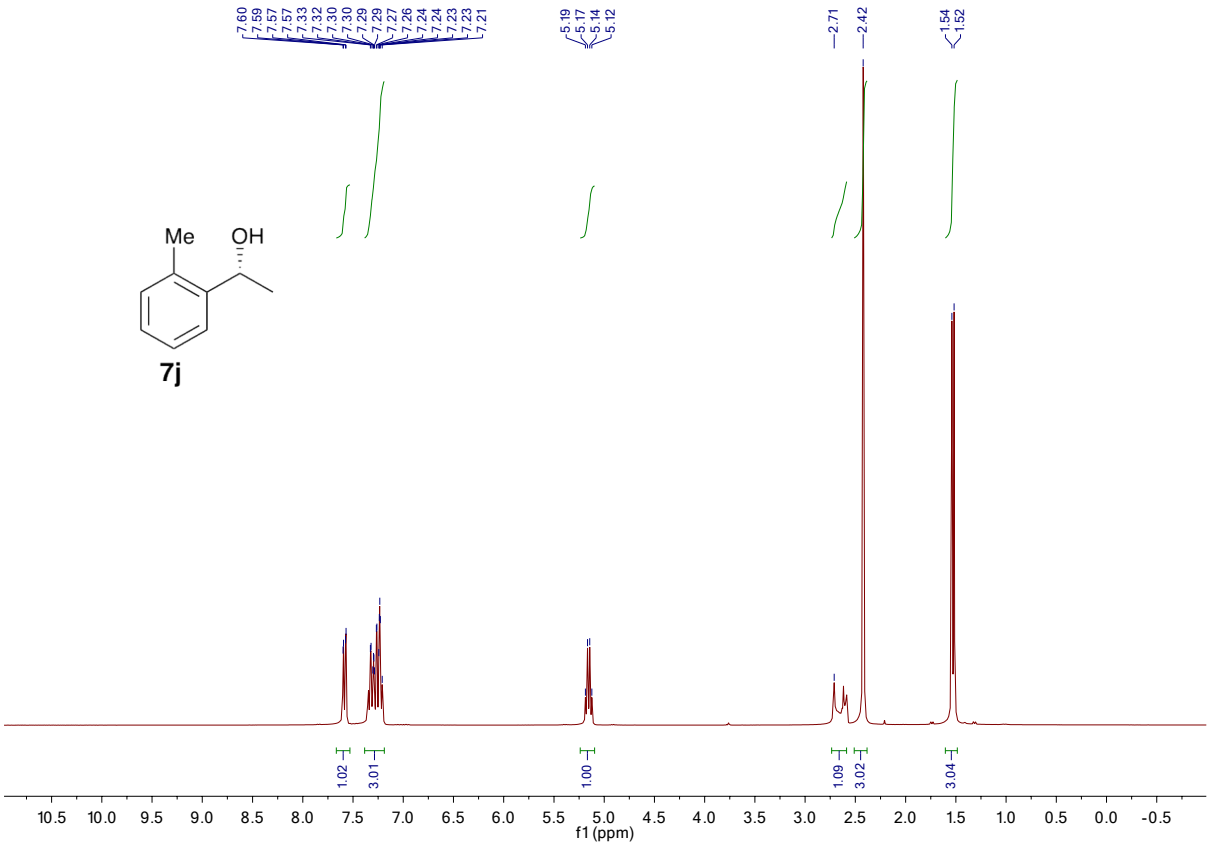


Figure S129. ^{1}H NMR spectrum of **7j** (300 MHz, Chloroform-*d*).

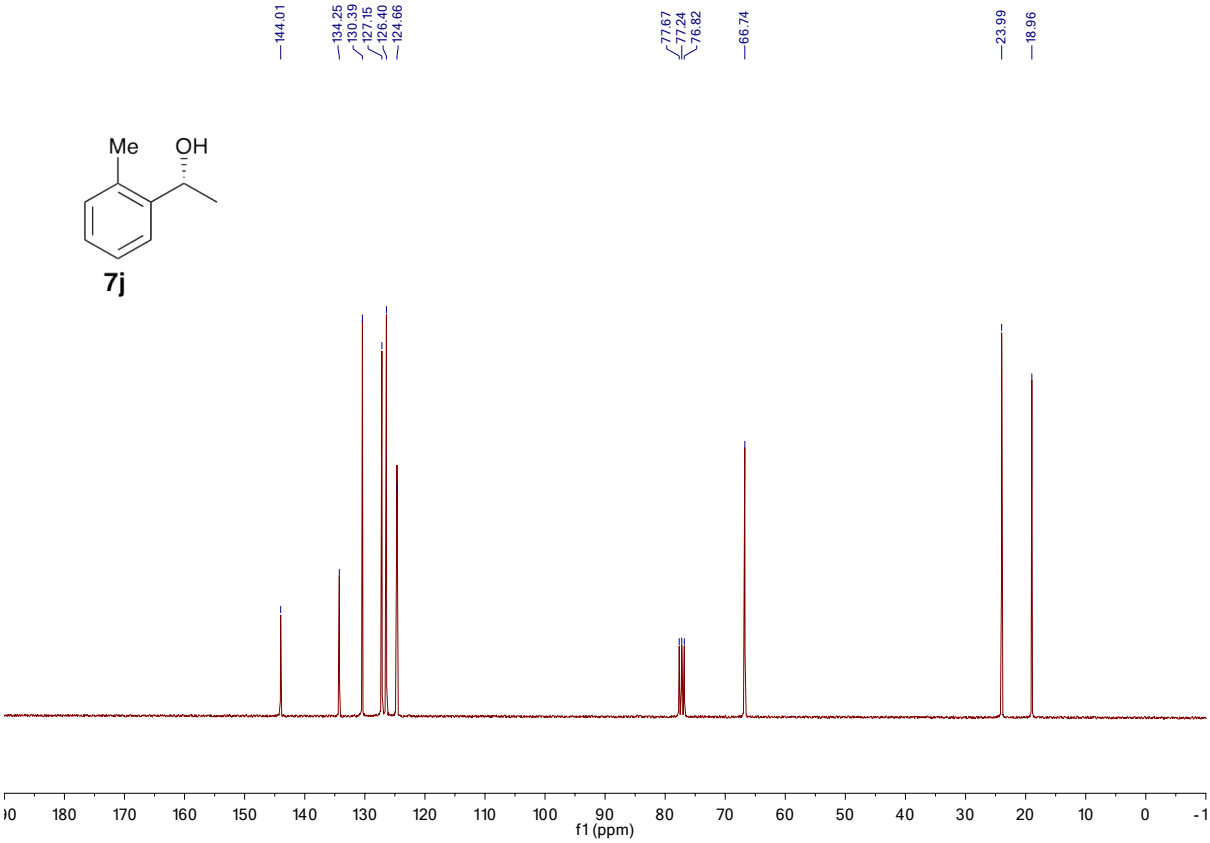


Figure S130. ^{13}C{^{1}H} NMR spectrum of **7j** (75 MHz, Chloroform-*d*).

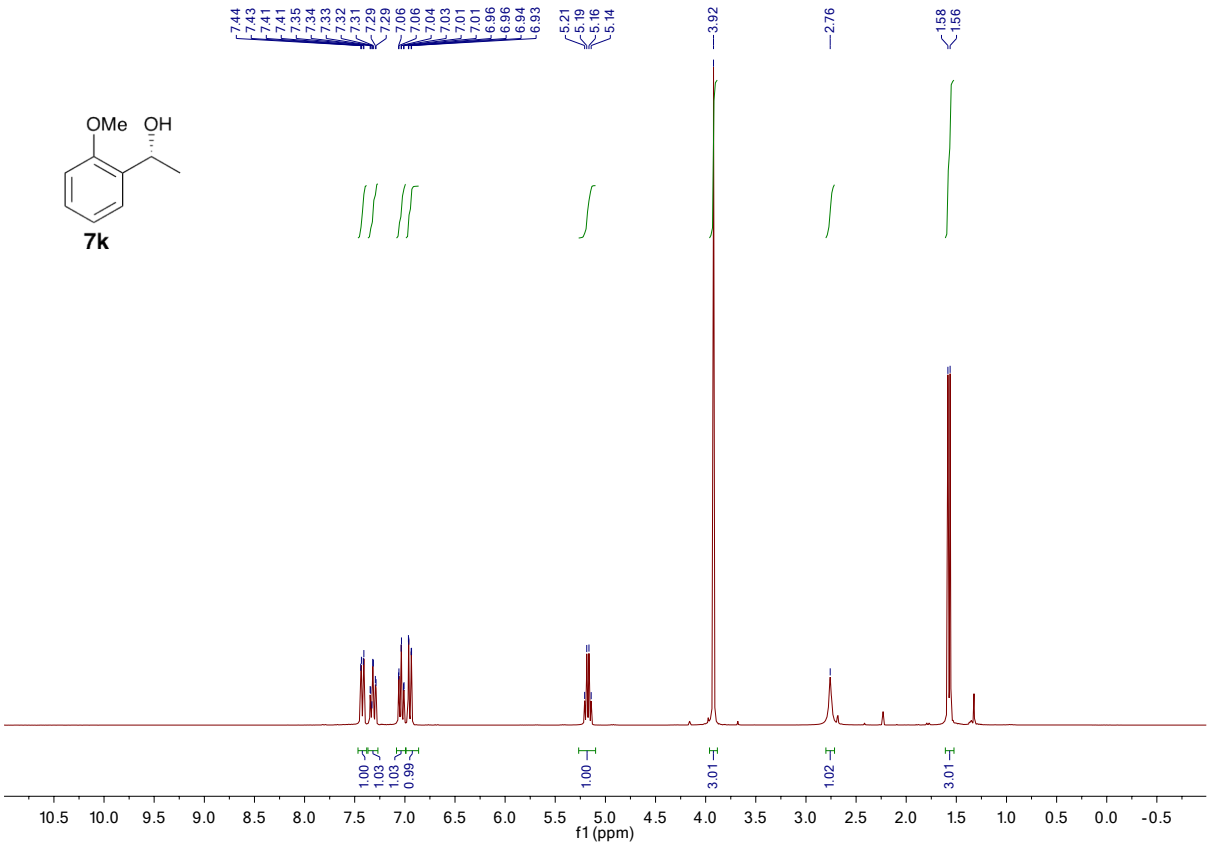


Figure S131. ^{1}H NMR spectrum of **7k** (300 MHz, Chloroform-*d*).

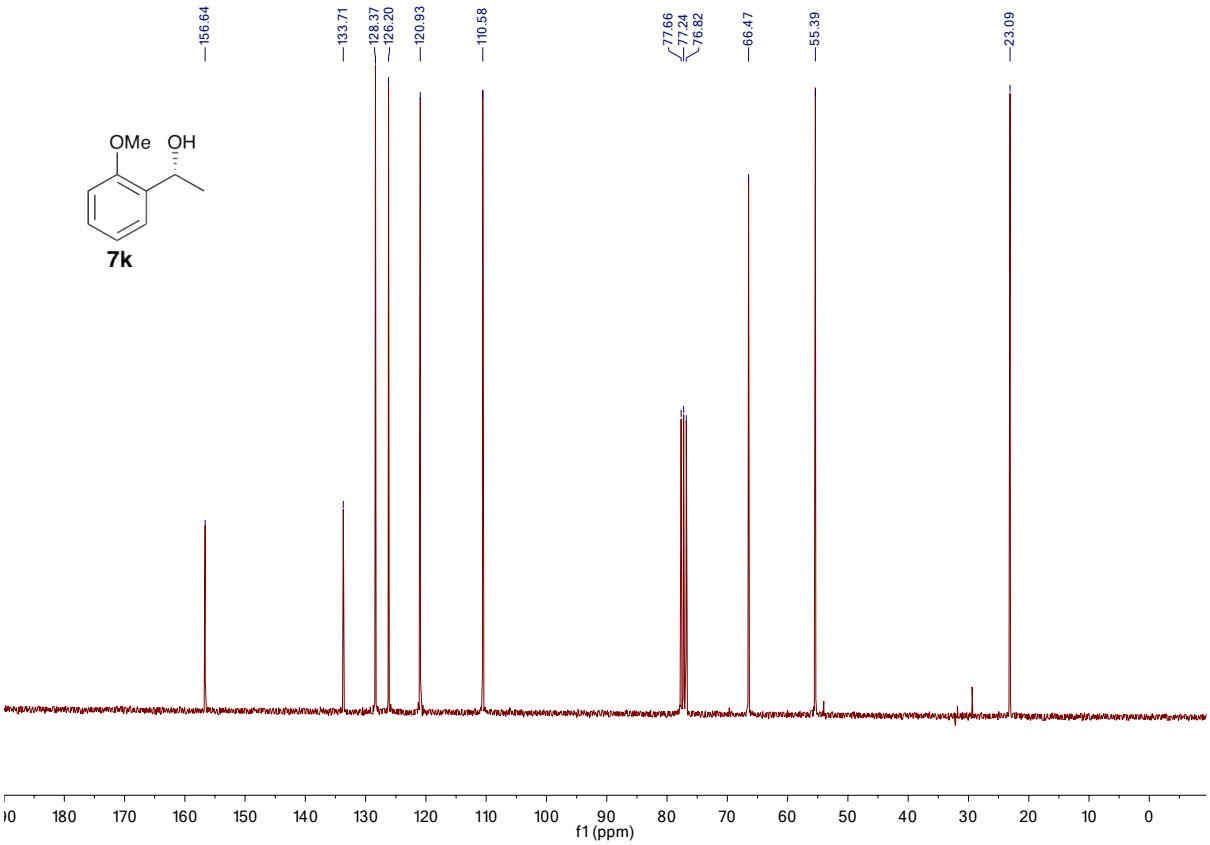


Figure S132. ^{13}C{^{1}H} NMR spectrum of **7k** (75 MHz, Chloroform-*d*).

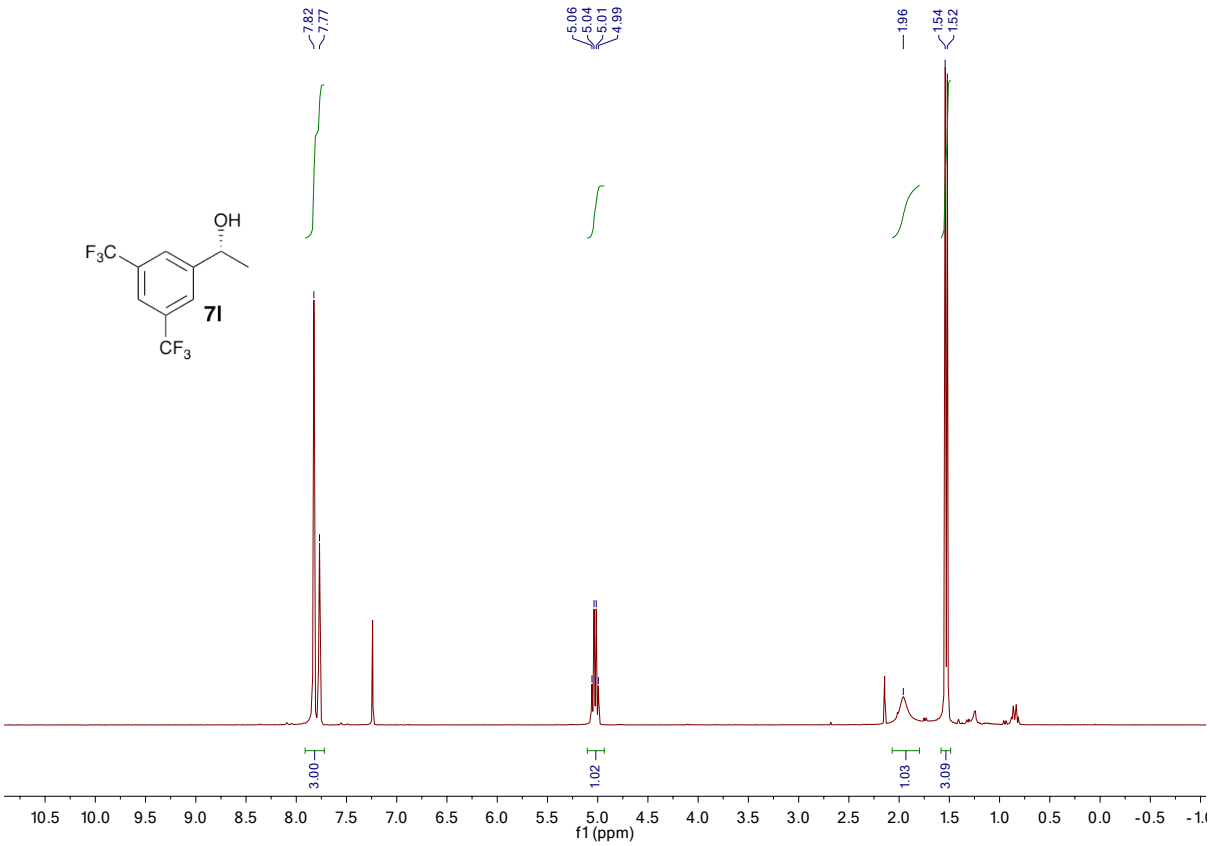


Figure S133. ^{1}H NMR spectrum of **7l** (300 MHz, Chloroform-*d*).

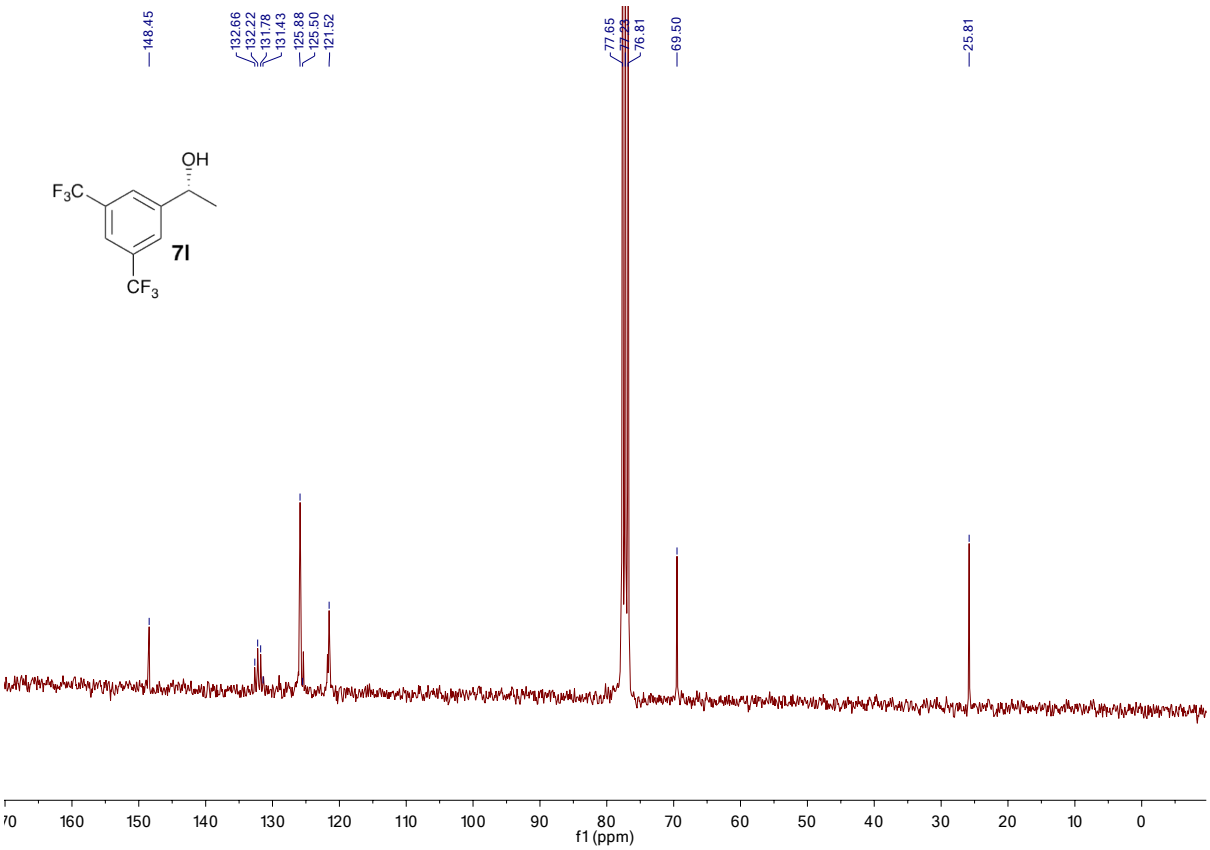


Figure S134. ^{13}C{^{1}H} NMR spectrum of **7l** (75 MHz, Chloroform-*d*).

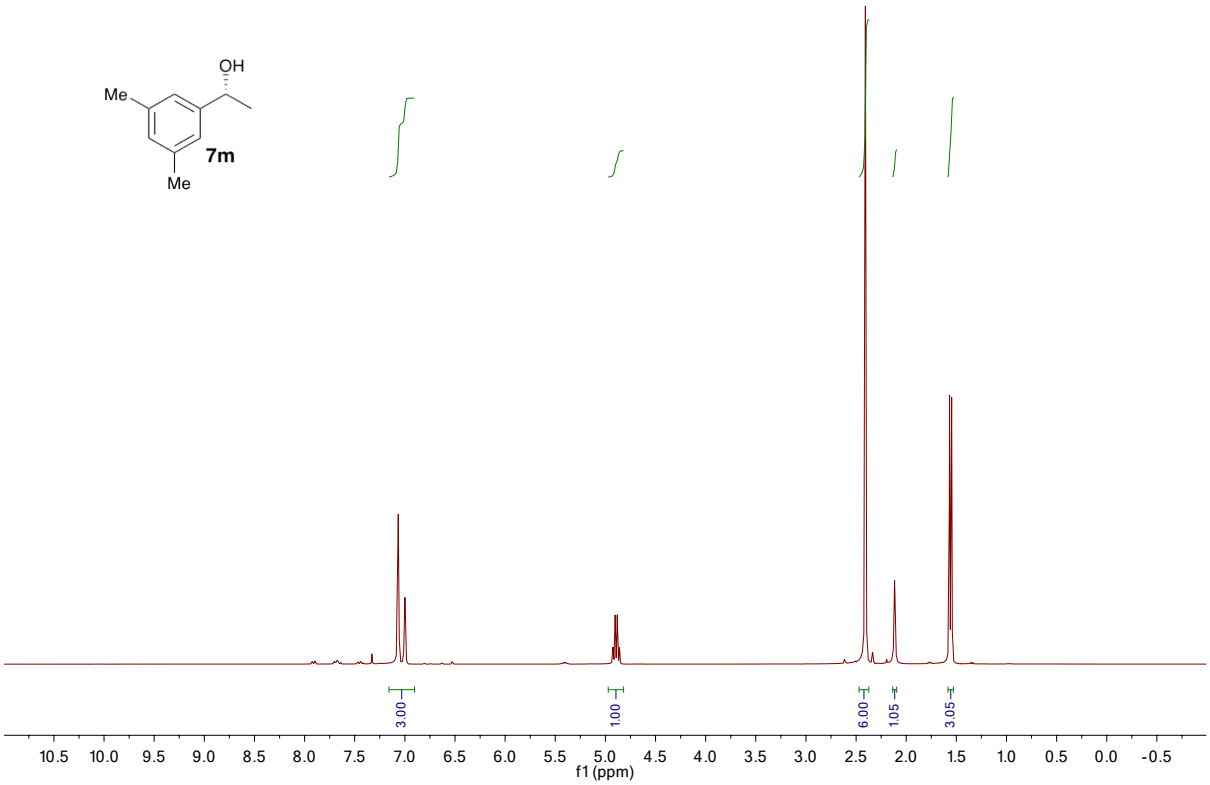


Figure S135. ^{1}H NMR spectrum of **7m** (300 MHz, Chloroform-*d*).

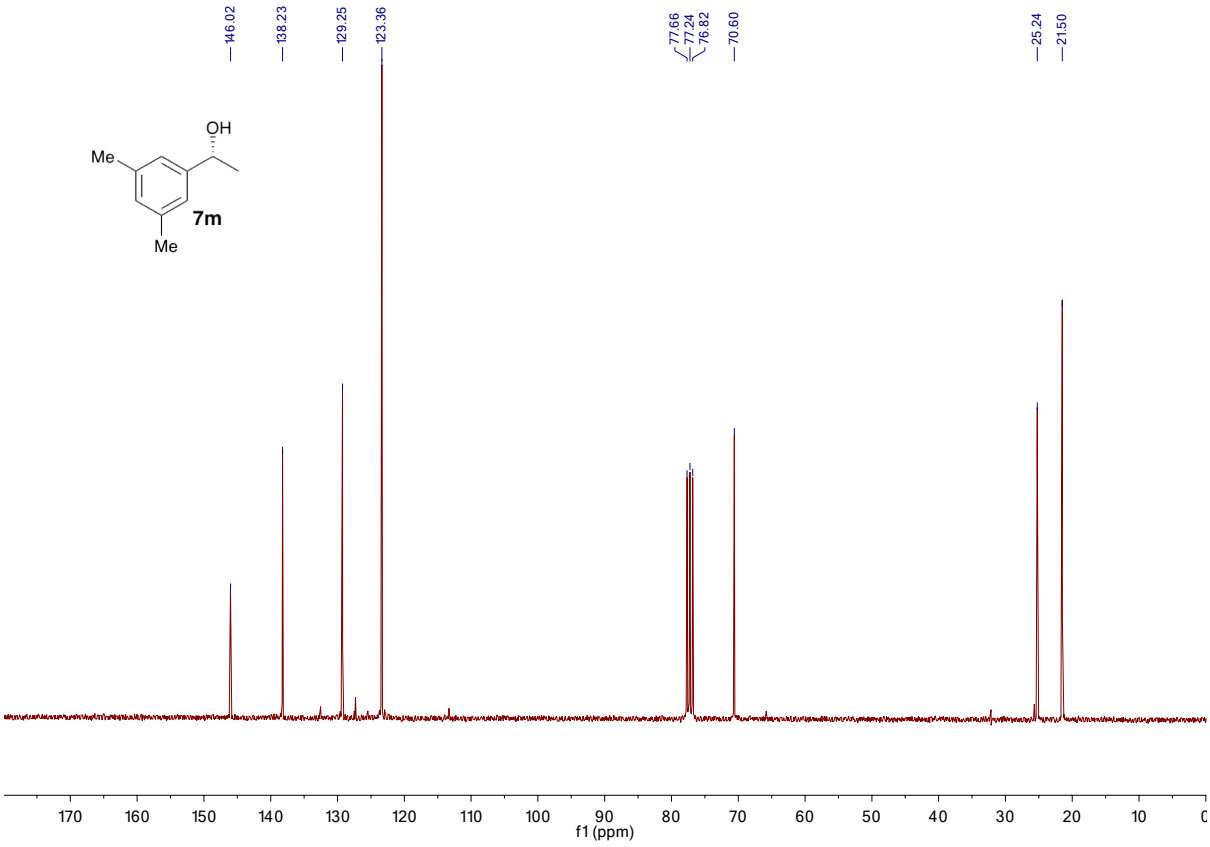


Figure S136. ^{13}C{^{1}H} NMR spectrum of **7m** (75 MHz, Chloroform-*d*).

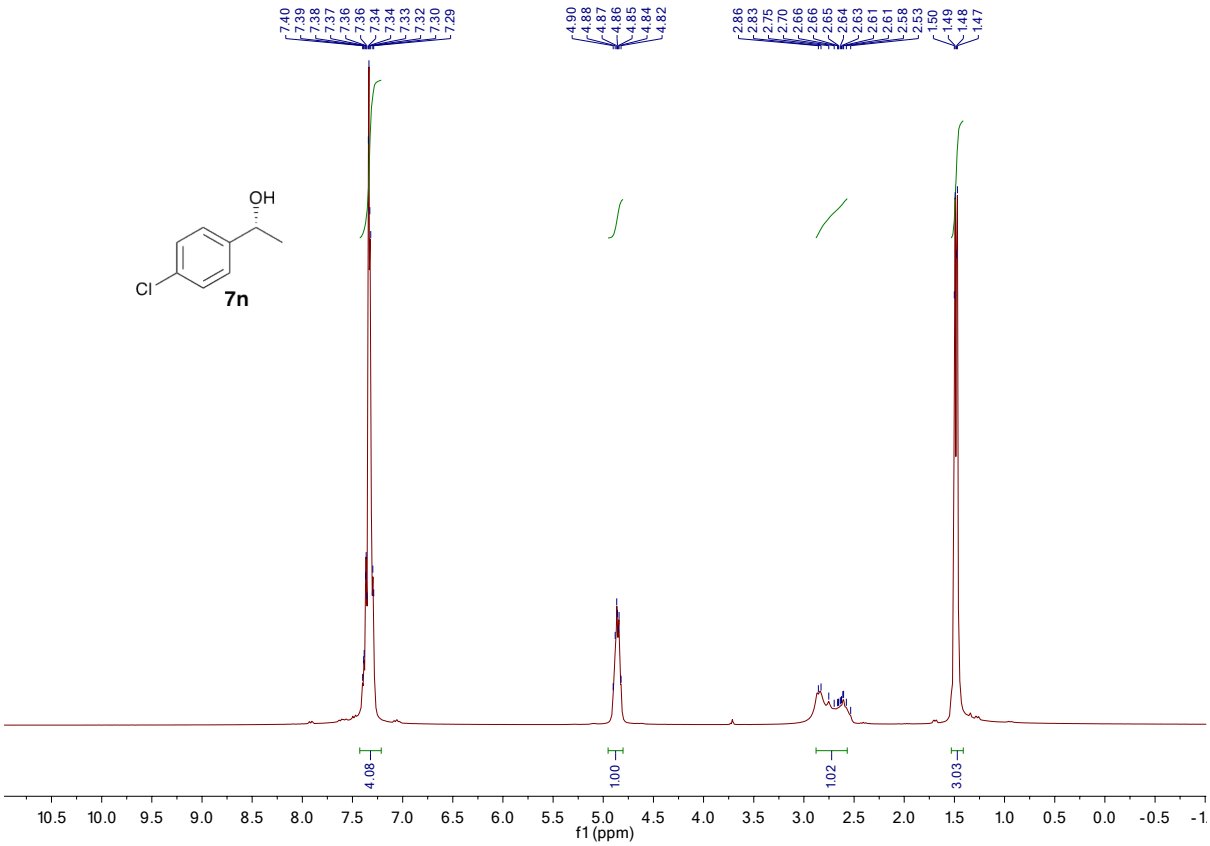


Figure S137. ^{1}H NMR spectrum of **7n** (300 MHz, Chloroform-*d*).

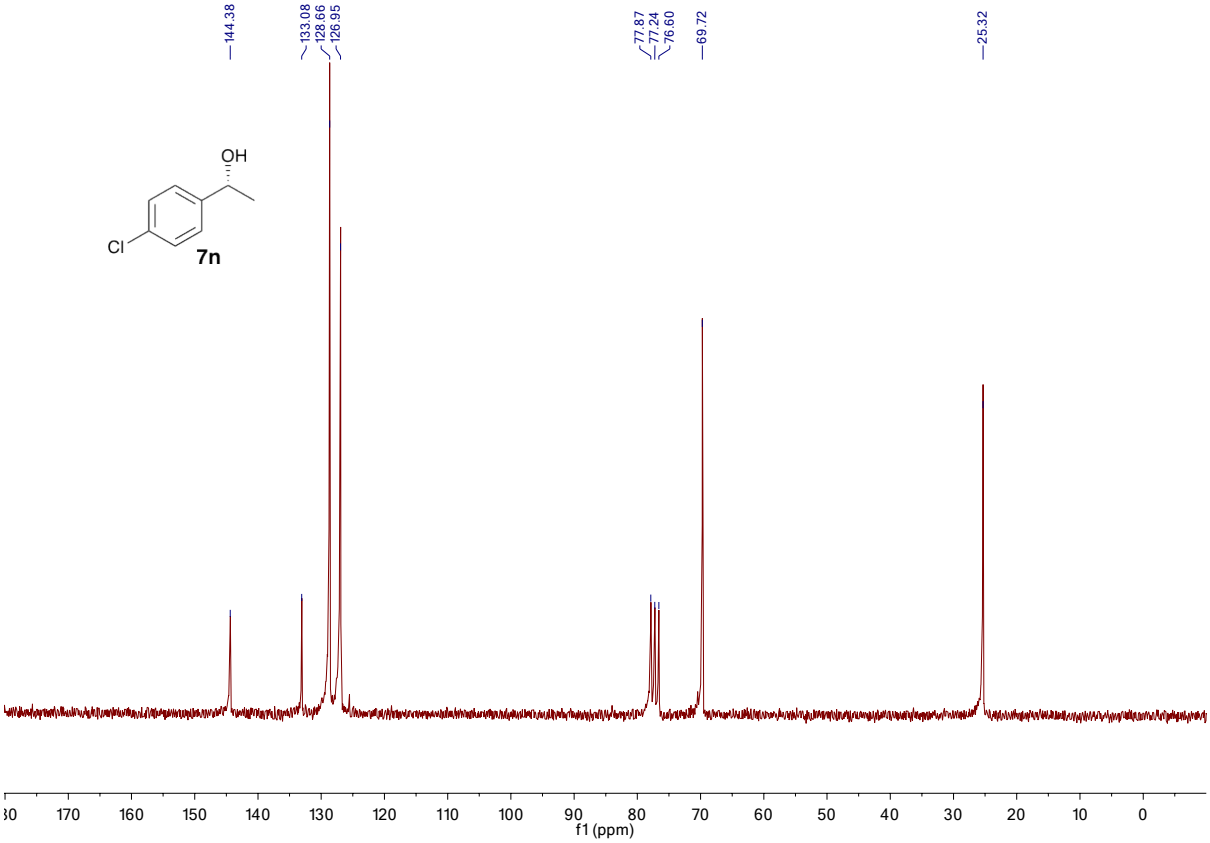


Figure S138. ^{13}C{^{1}H} NMR spectrum of **7n** (75 MHz, Chloroform-*d*).

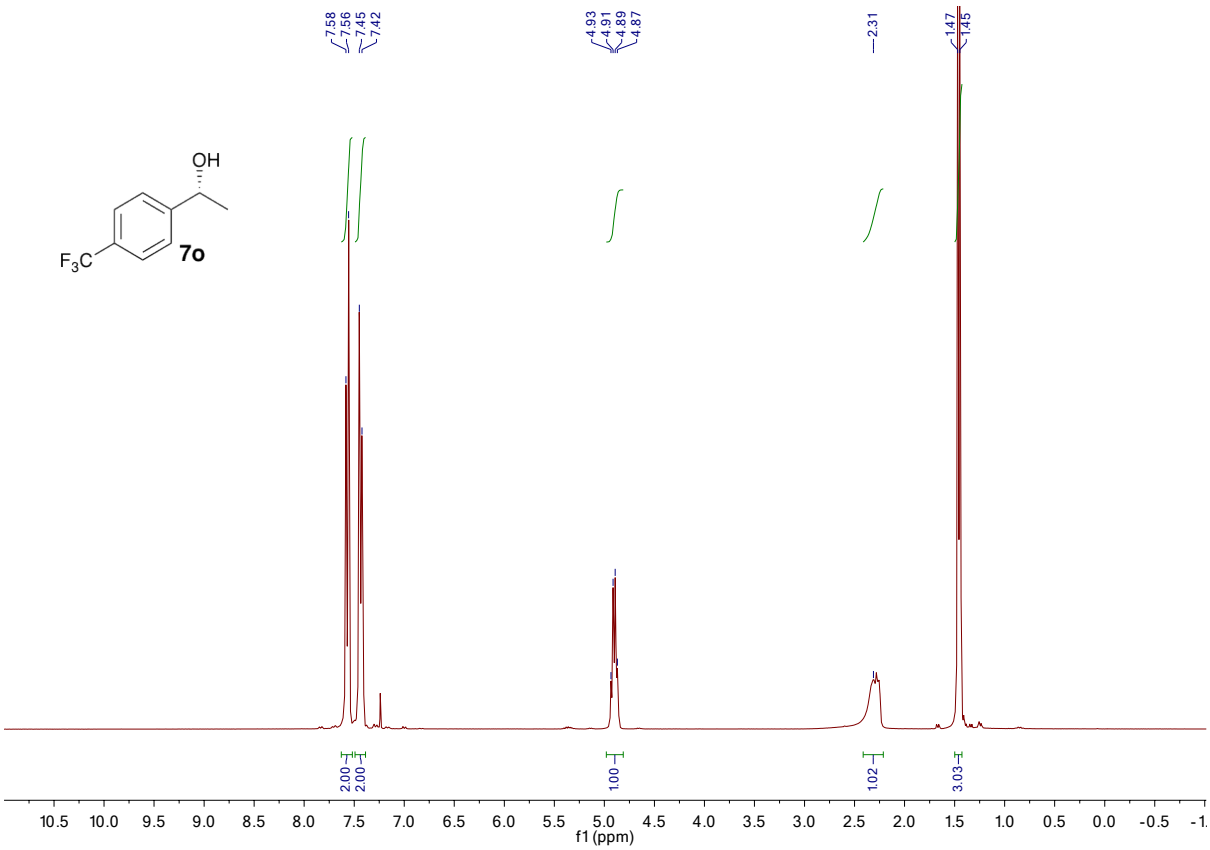


Figure S139. ^{1}H NMR spectrum of **7o** (300 MHz, Chloroform-*d*).

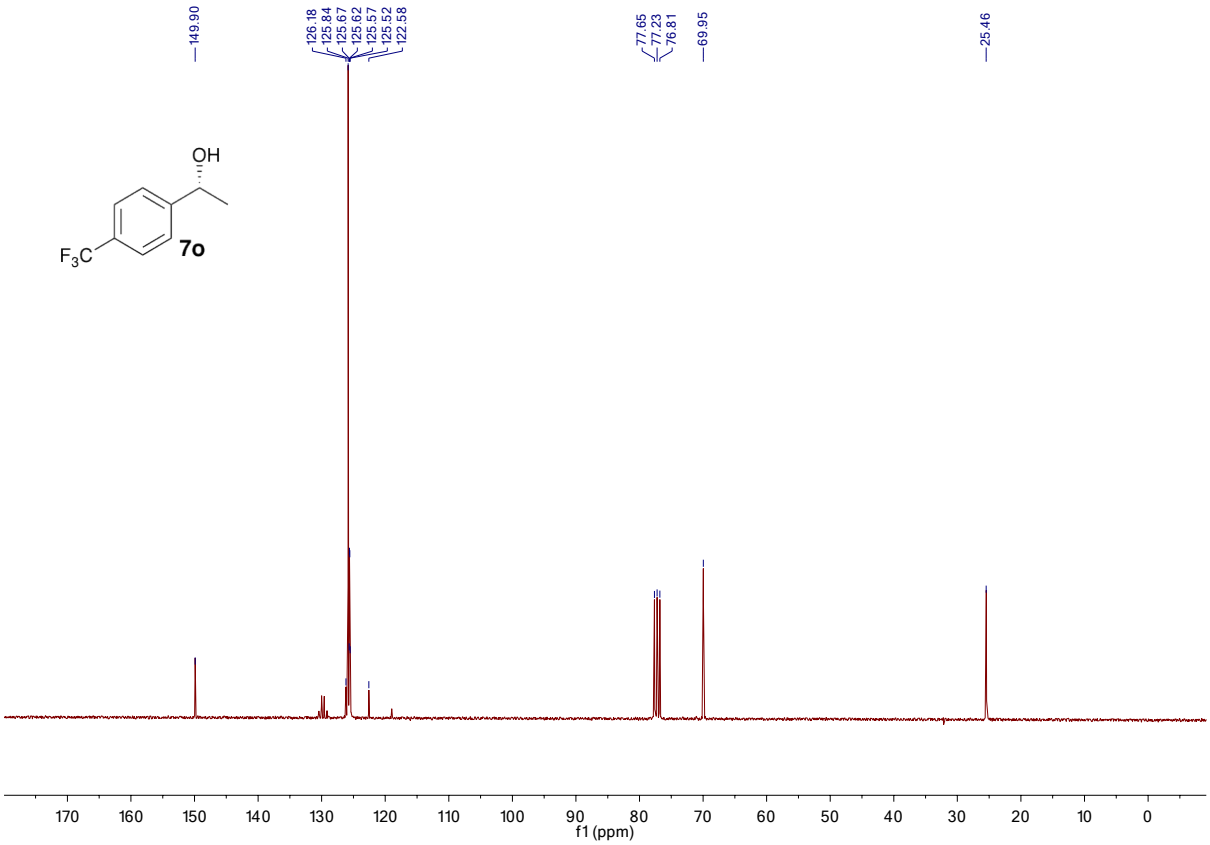


Figure S140. ^{13}C{^{1}H} NMR spectrum of **7o** (75 MHz, Chloroform-*d*).

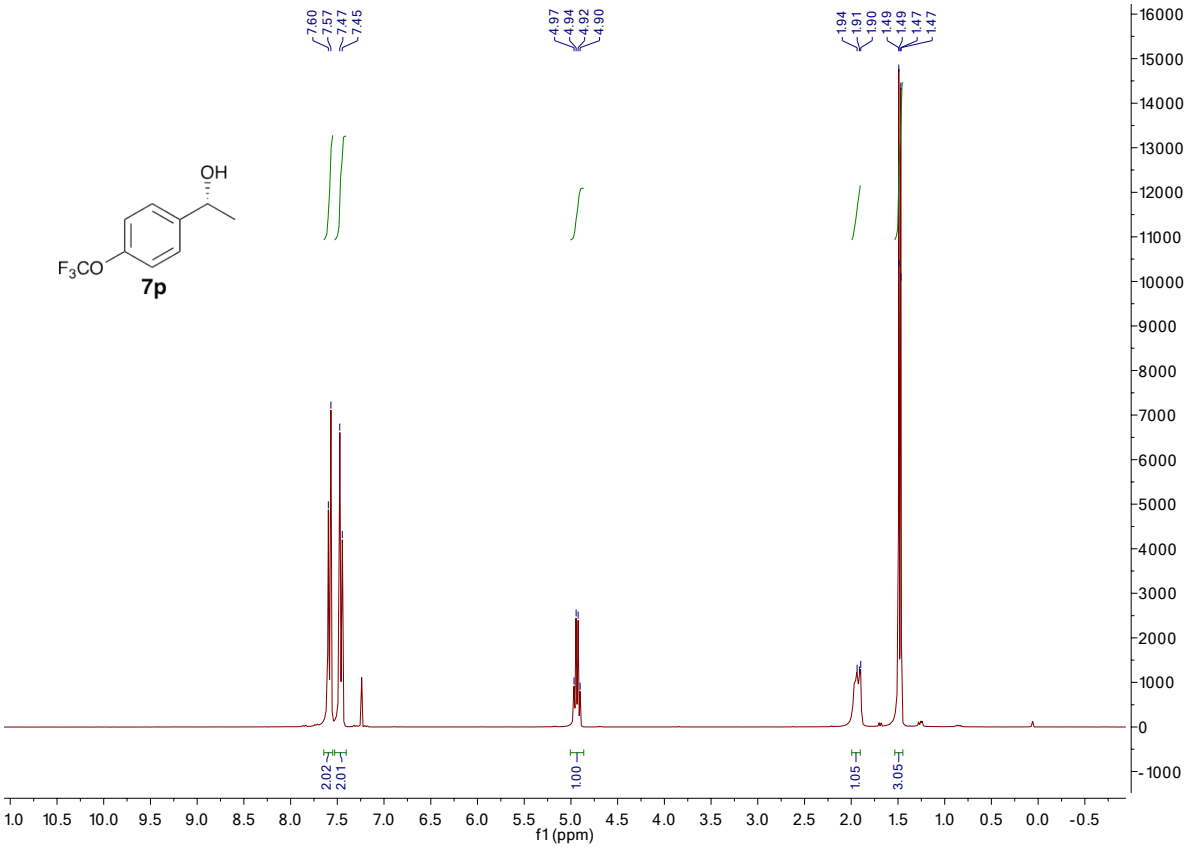


Figure S141. ^{1}H NMR spectrum of **7p** (300 MHz, Chloroform-*d*).

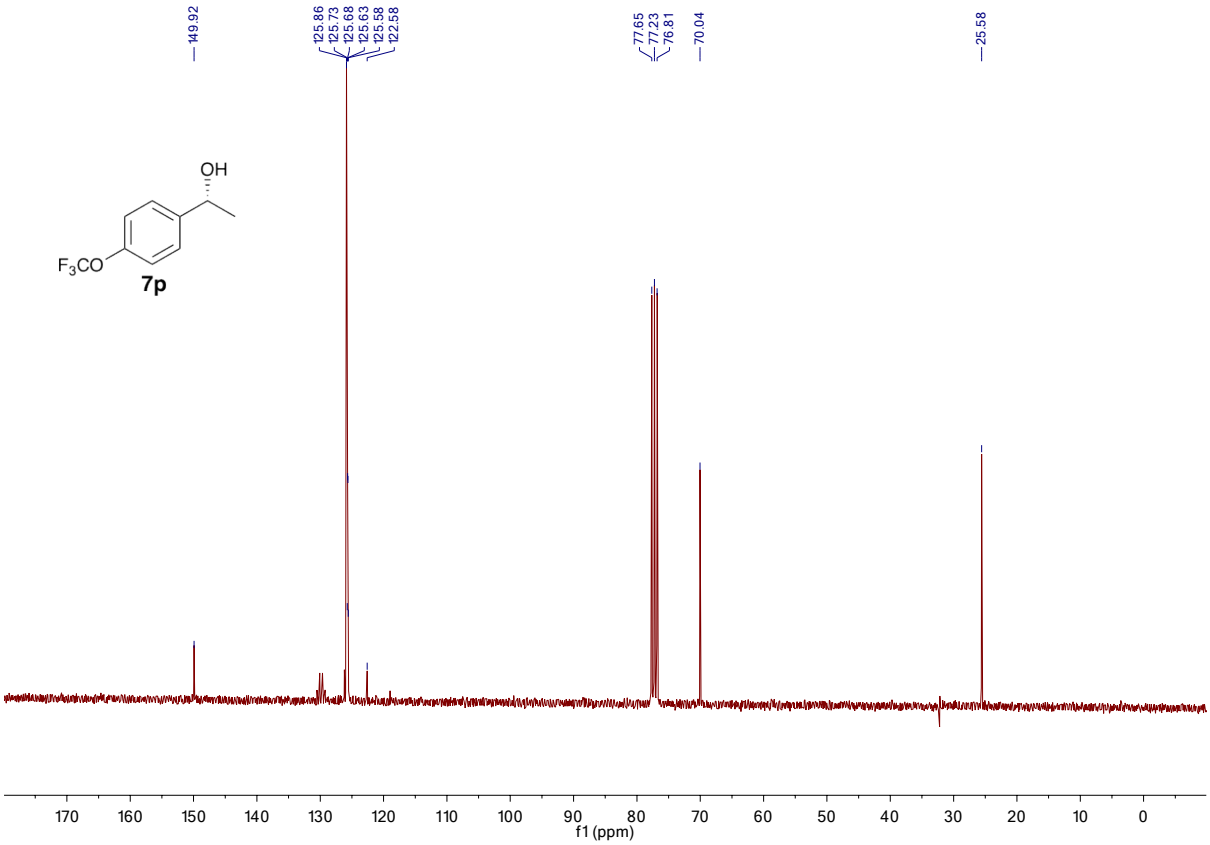


Figure S142. ^{13}C{^{1}H} NMR spectrum of **7p** (75 MHz, Chloroform-*d*).

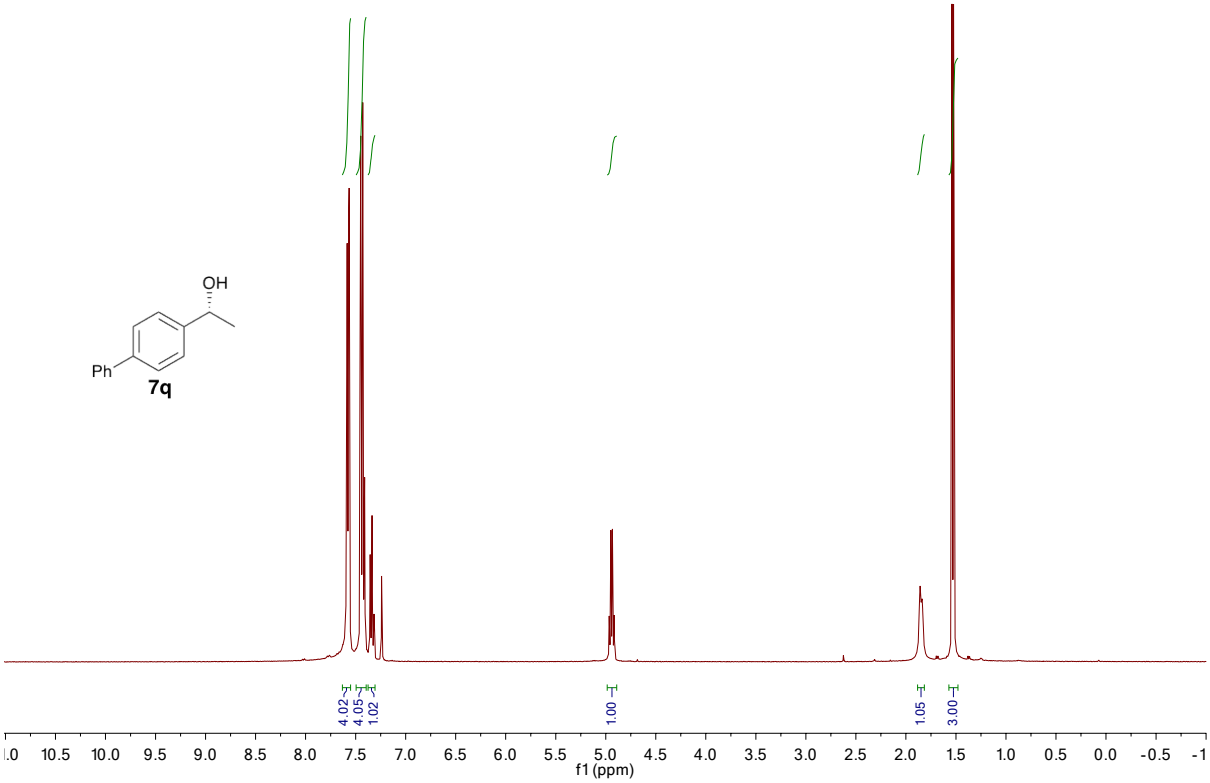


Figure S143. ^{1}H NMR spectrum of **7q** (300 MHz, Chloroform-*d*).

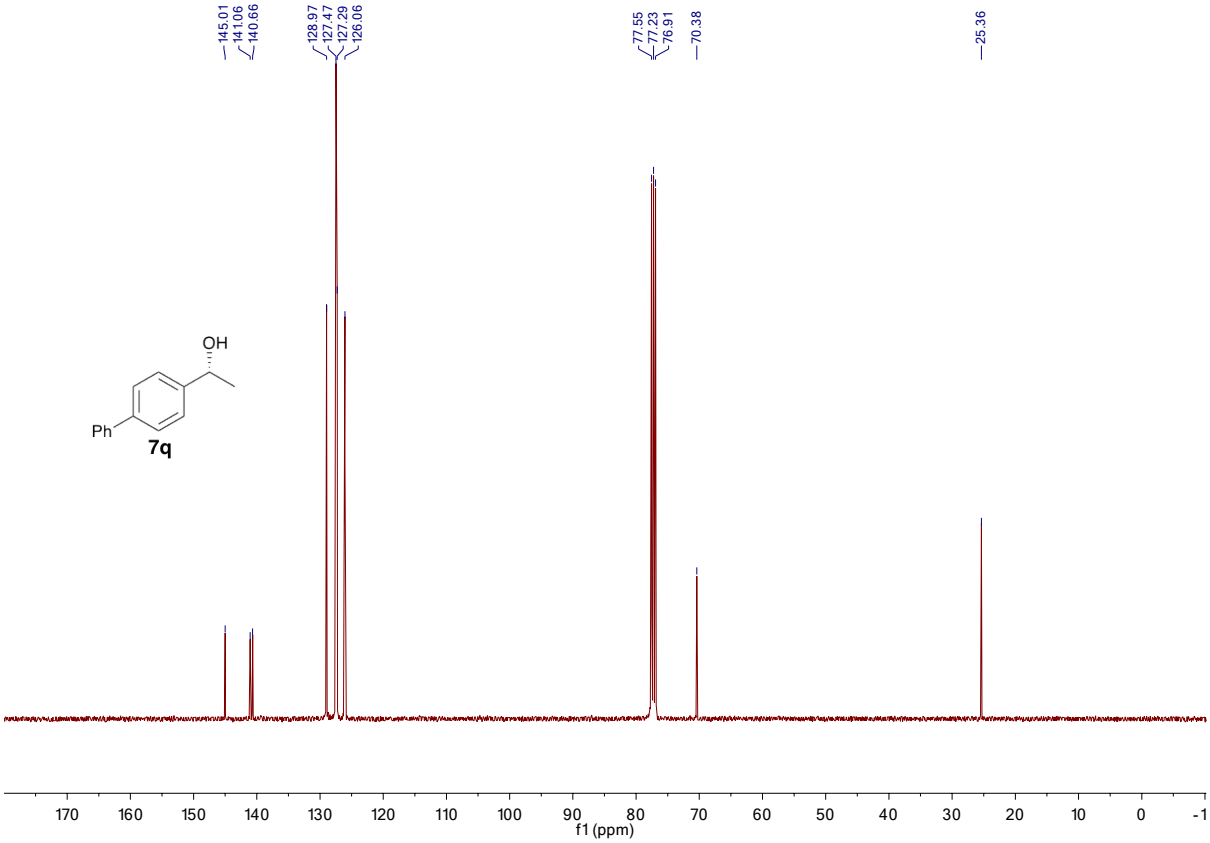


Figure S144. ^{13}C{^{1}H} NMR spectrum of **7q** (75 MHz, Chloroform-*d*).

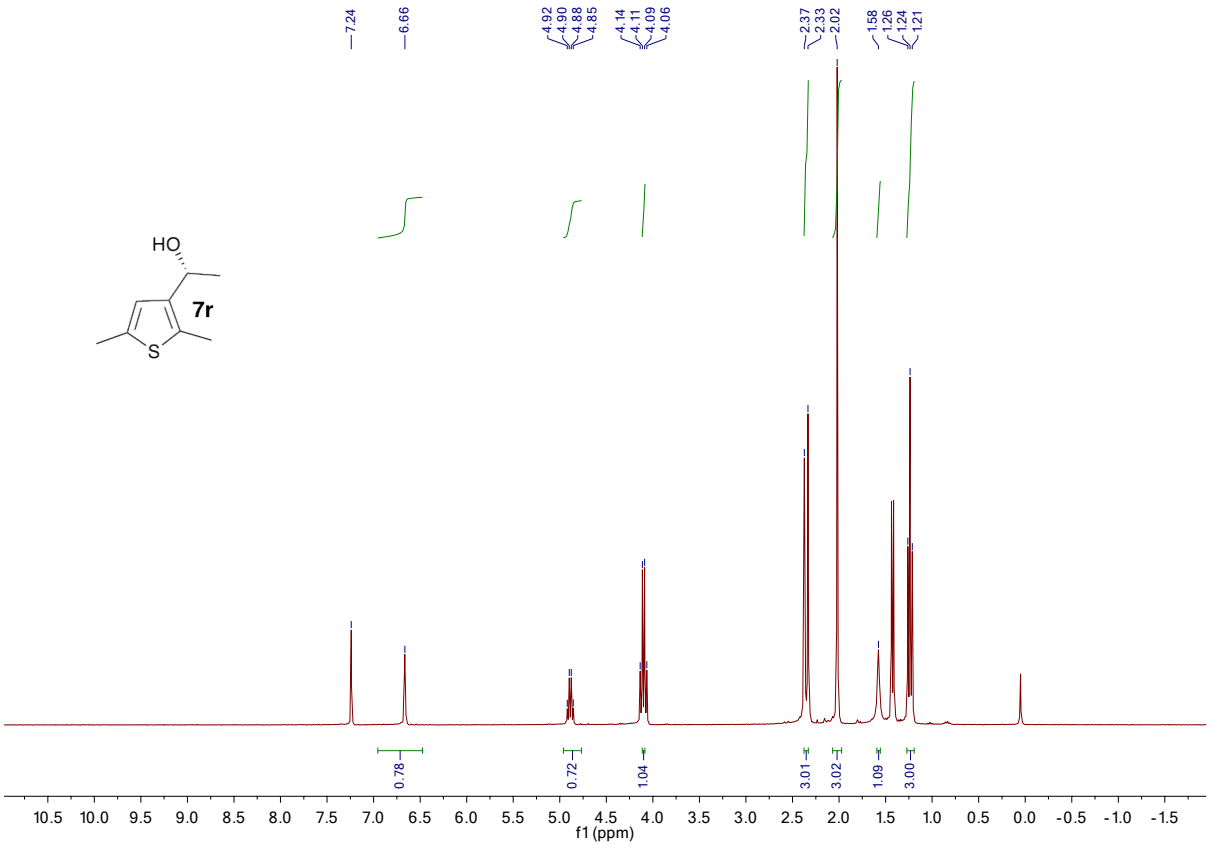


Figure S145. ^{1}H NMR spectrum of **7r** (300 MHz, Chloroform-*d*).

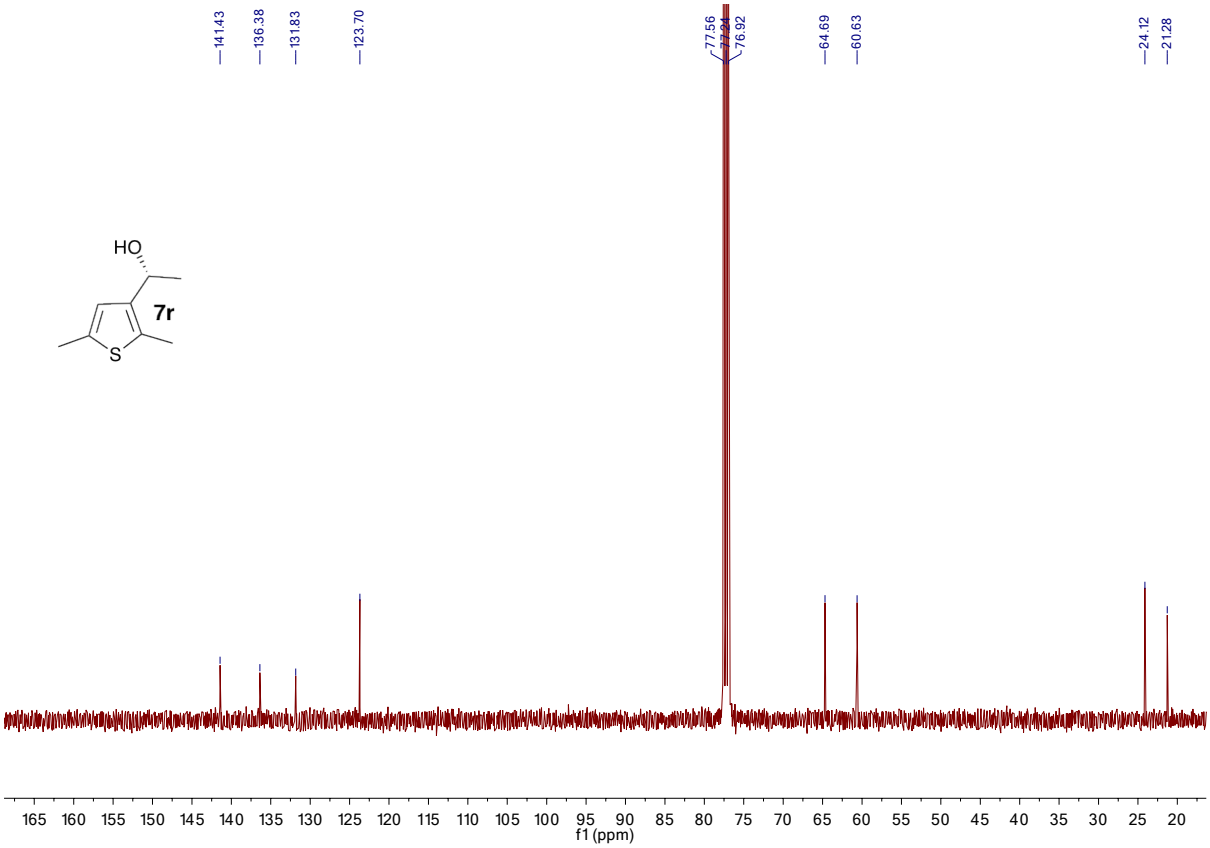


Figure S146. ^{13}C{^{1}H} NMR spectrum of **7r** (75 MHz, Chloroform-*d*).

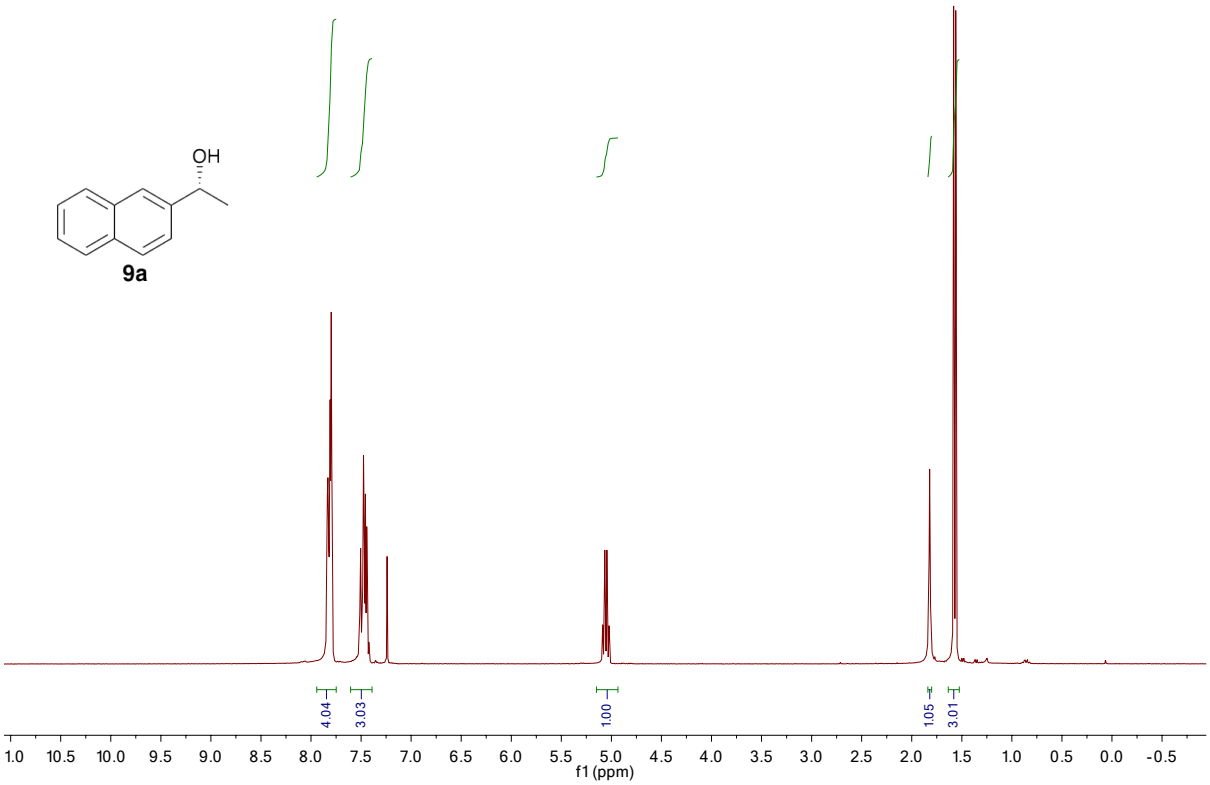


Figure S147. ^{1}H NMR spectrum of **9a** (300 MHz, Chloroform-*d*).

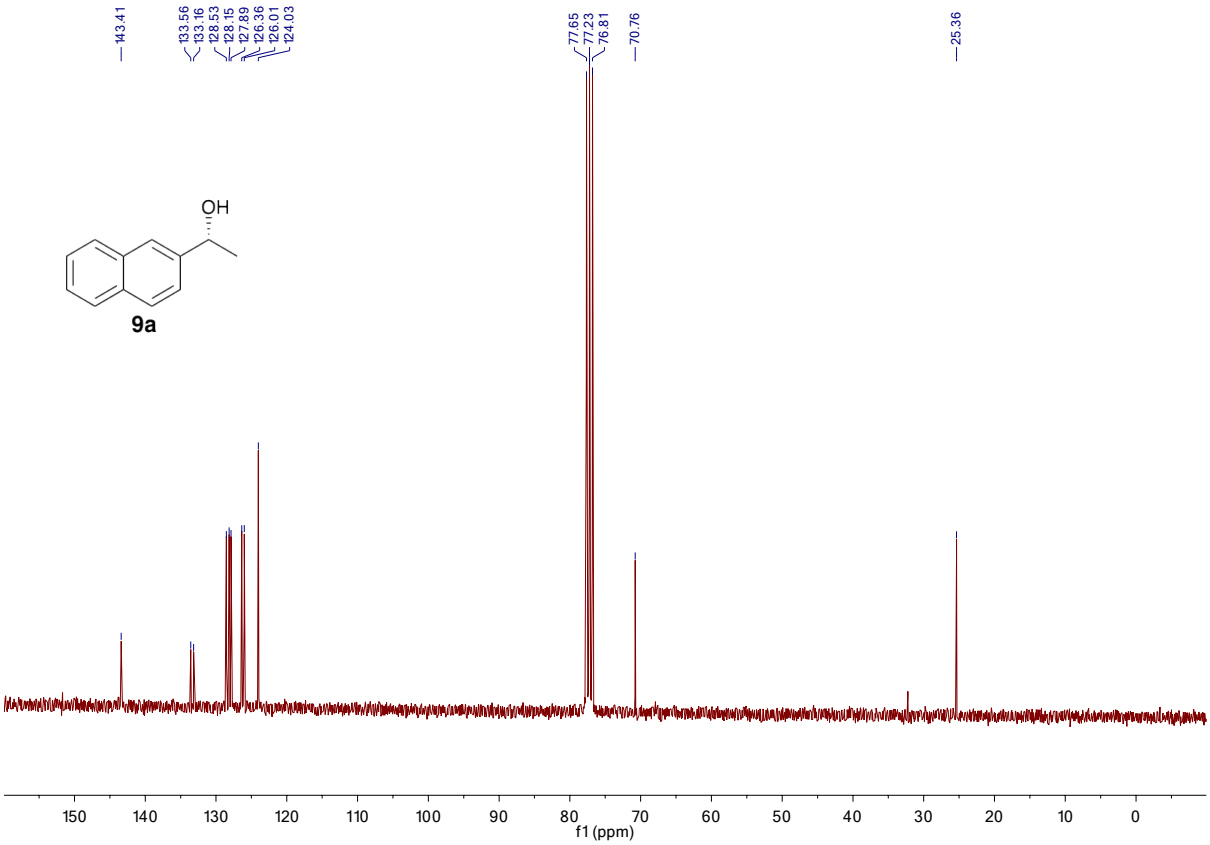


Figure S148. ^{13}C{^{1}H} NMR spectrum of **9a** (75 MHz, Chloroform-*d*).

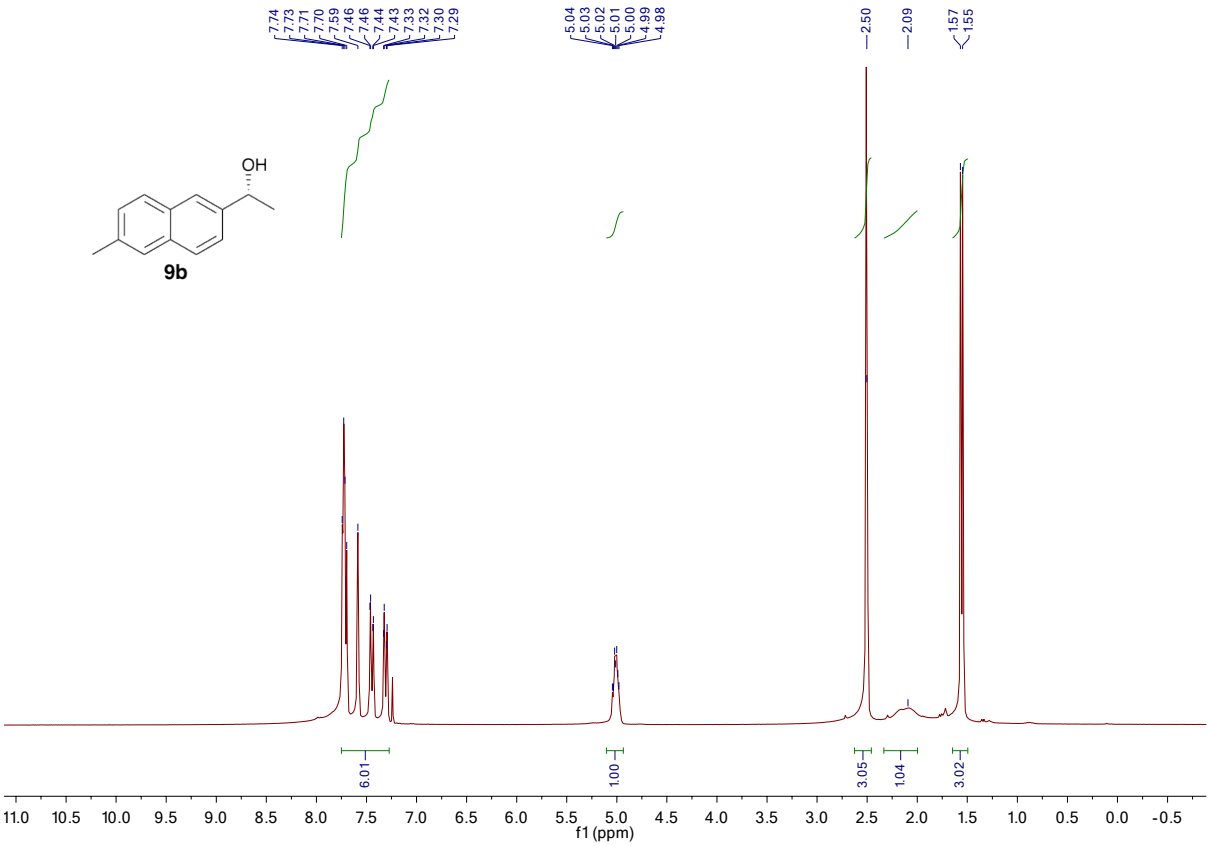


Figure S149. ^{1}H NMR spectrum of **9b** (300 MHz, Chloroform-*d*).

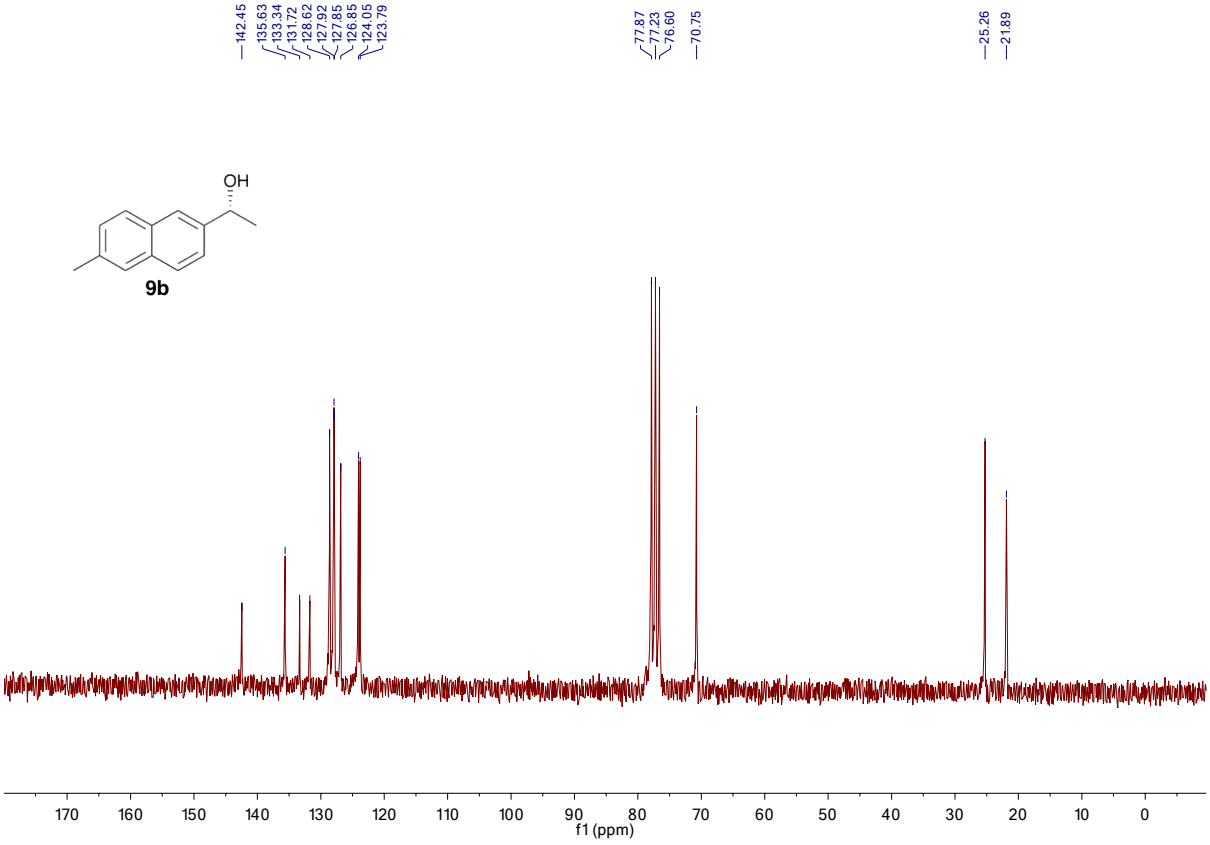


Figure S150. ^{13}C{^{1}H} NMR spectrum of **9b** (75 MHz, Chloroform-*d*).

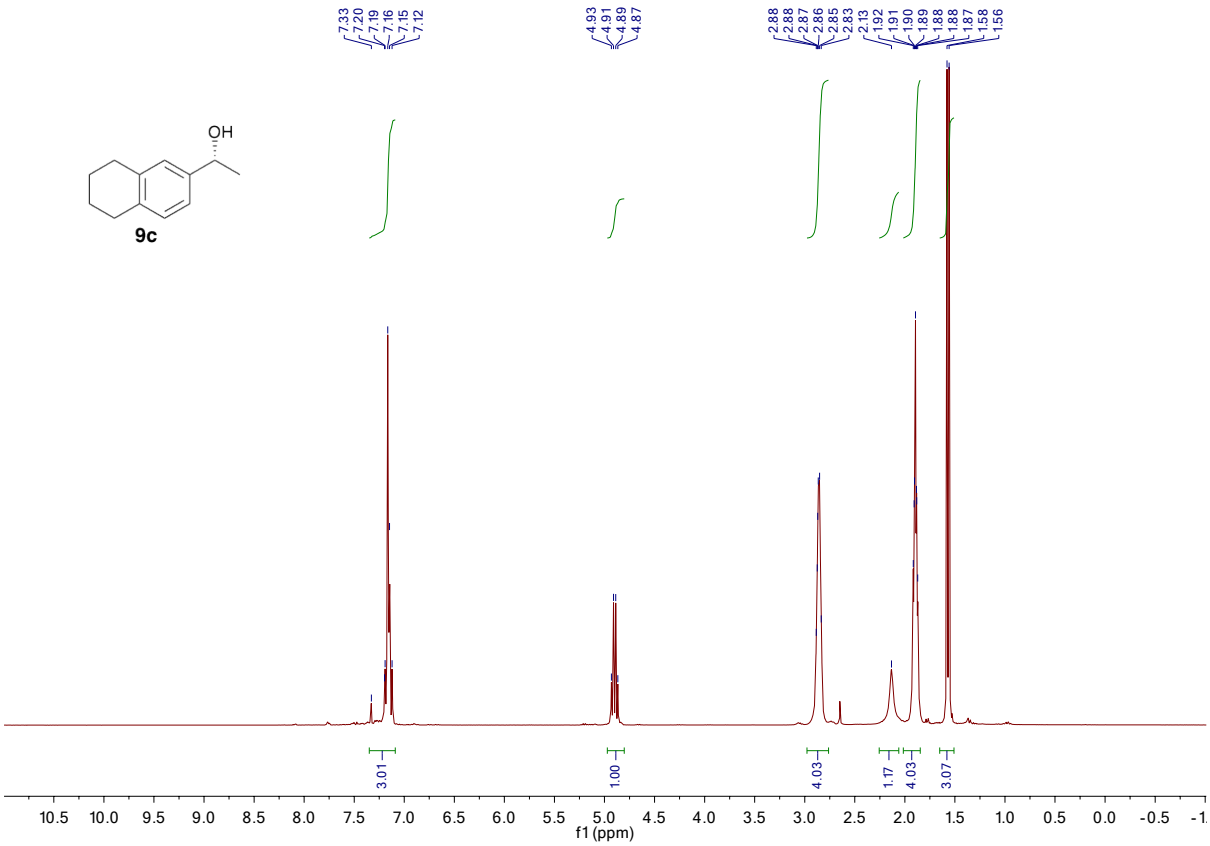


Figure S151. ^{1}H NMR spectrum of **9c** (300 MHz, Chloroform-*d*).

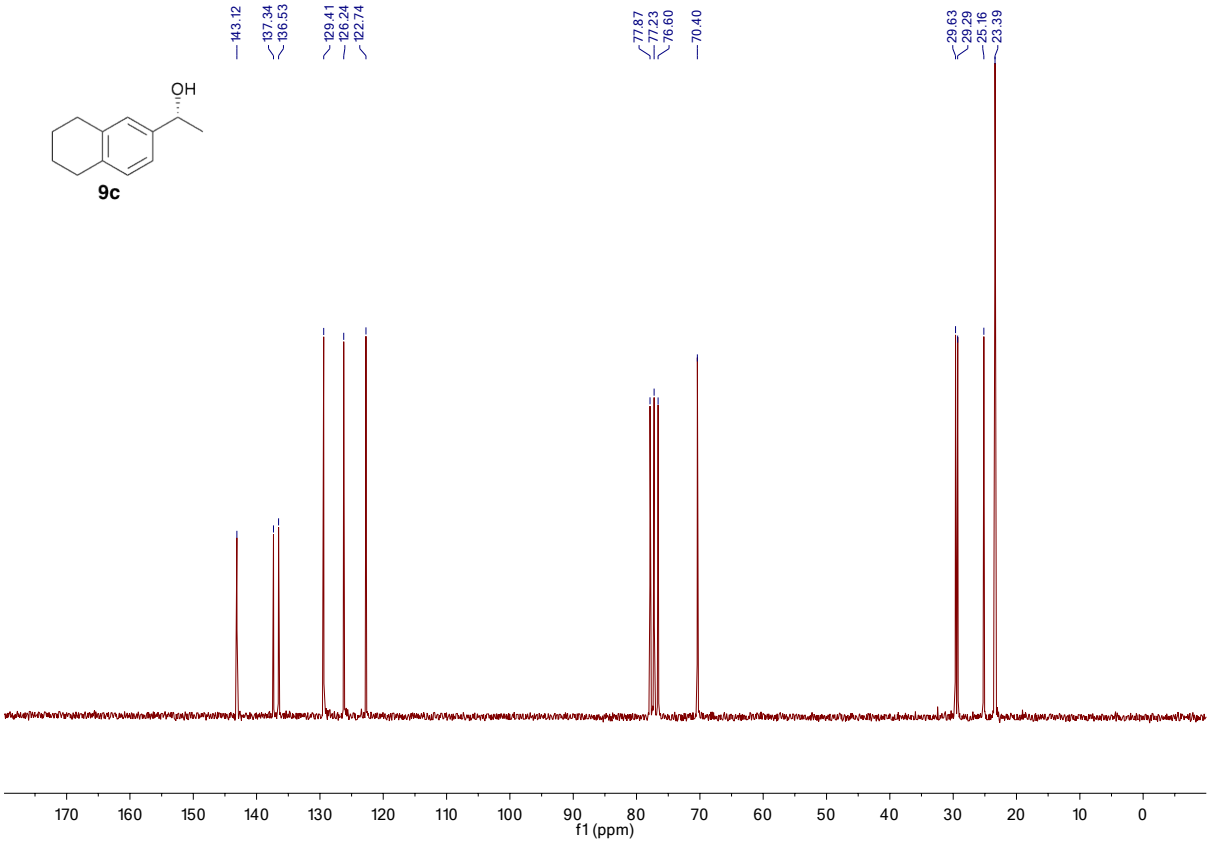


Figure S152. $^{13}C\{^{1}H\}$ NMR spectrum of **9c** (75 MHz, Chloroform-*d*).

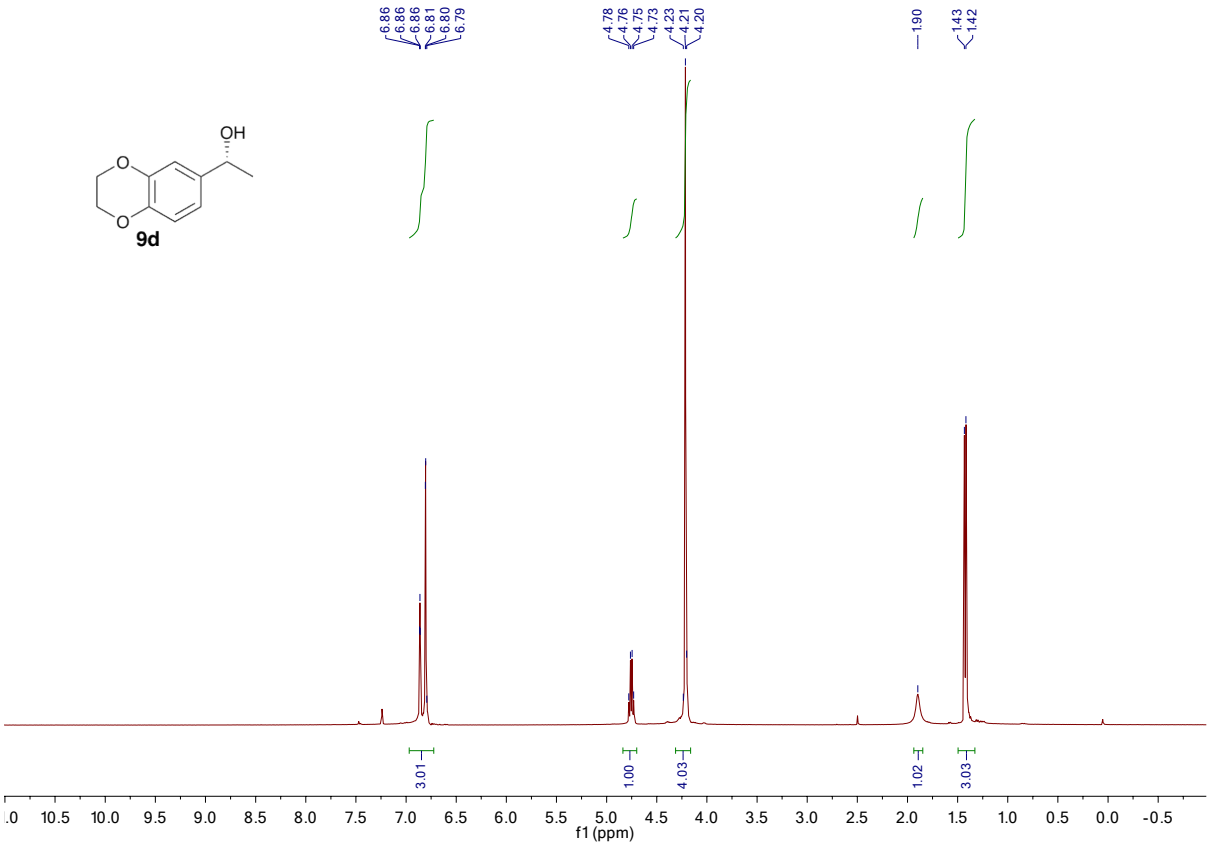


Figure S153. ^{1}H NMR spectrum of **9d** (300 MHz, Chloroform-*d*).

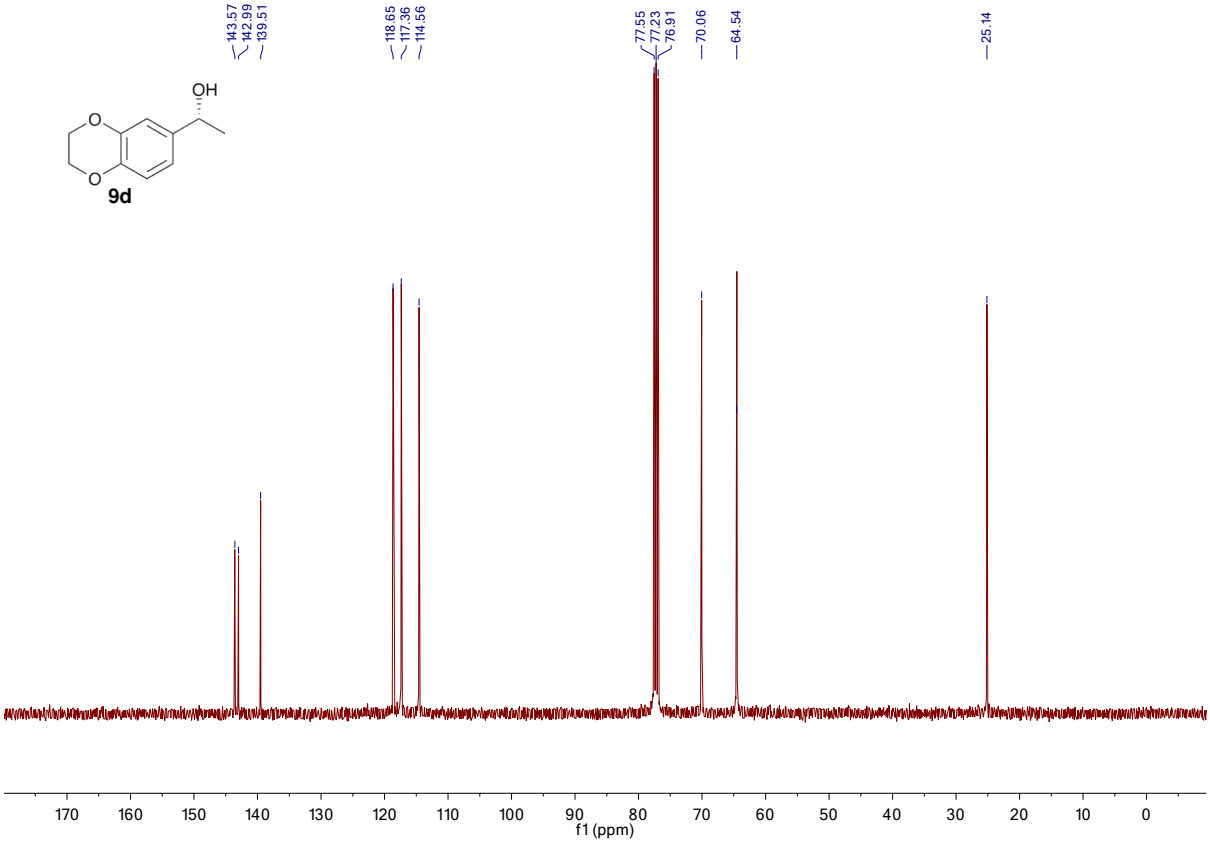


Figure S154. ^{13}C{^{1}H} NMR spectrum of **9d** (75 MHz, Chloroform-*d*).

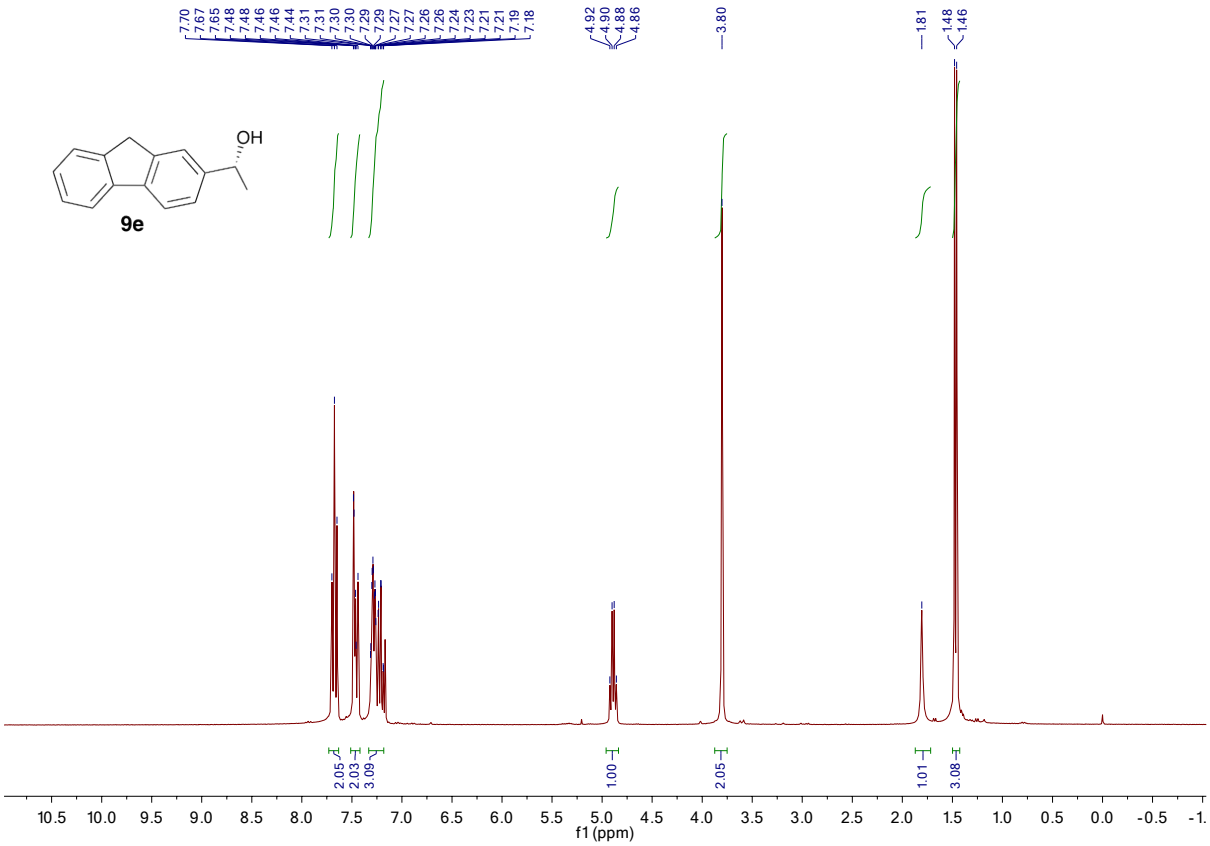


Figure S155. ^{1}H NMR spectrum of **9e** (300 MHz, Chloroform-*d*).

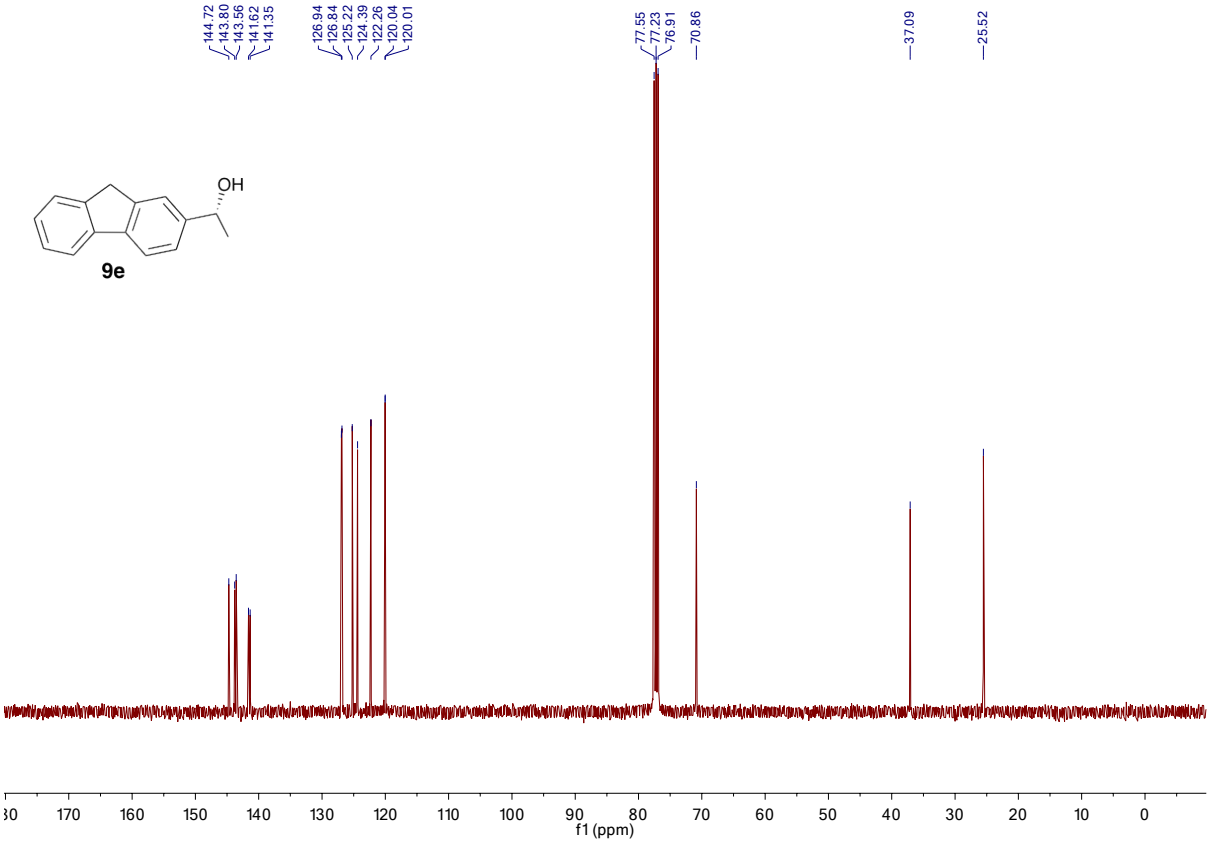


Figure S156. ^{13}C{^{1}H} NMR spectrum of **9e** (75 MHz, Chloroform-*d*).

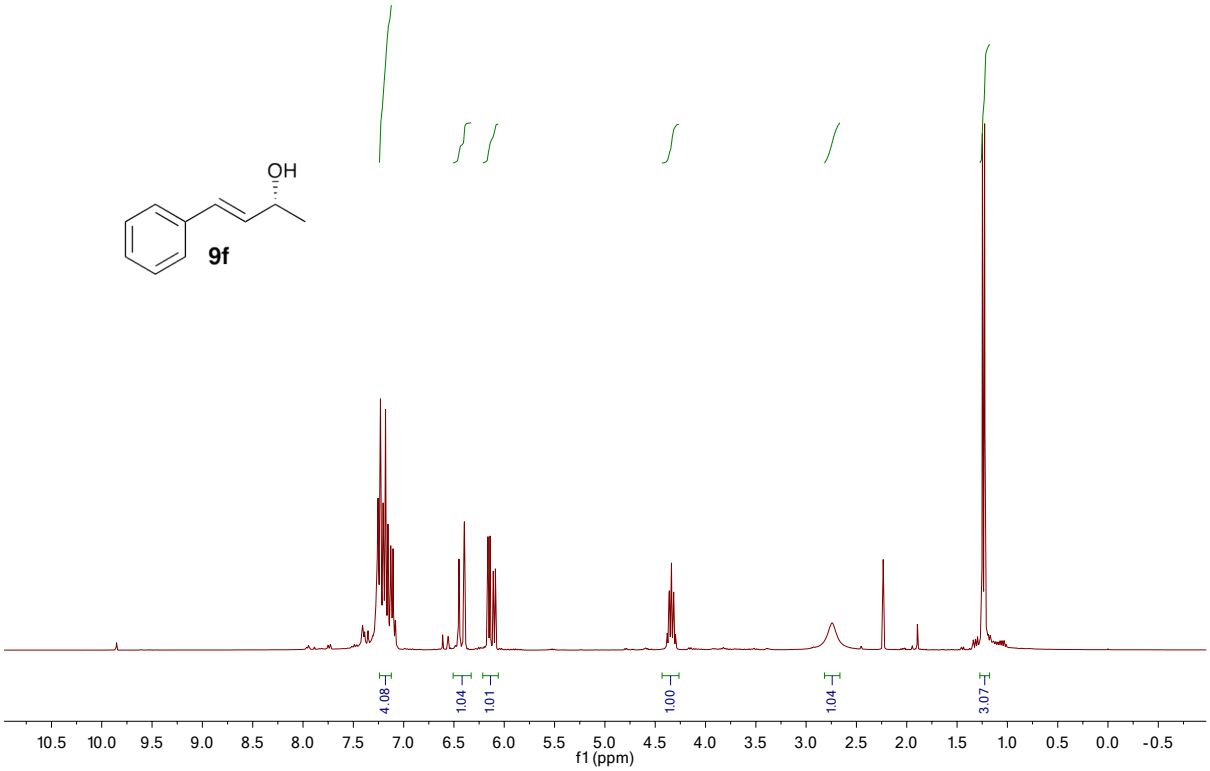


Figure S157. ^{1}H NMR spectrum of **9f** (300 MHz, Chloroform-*d*).

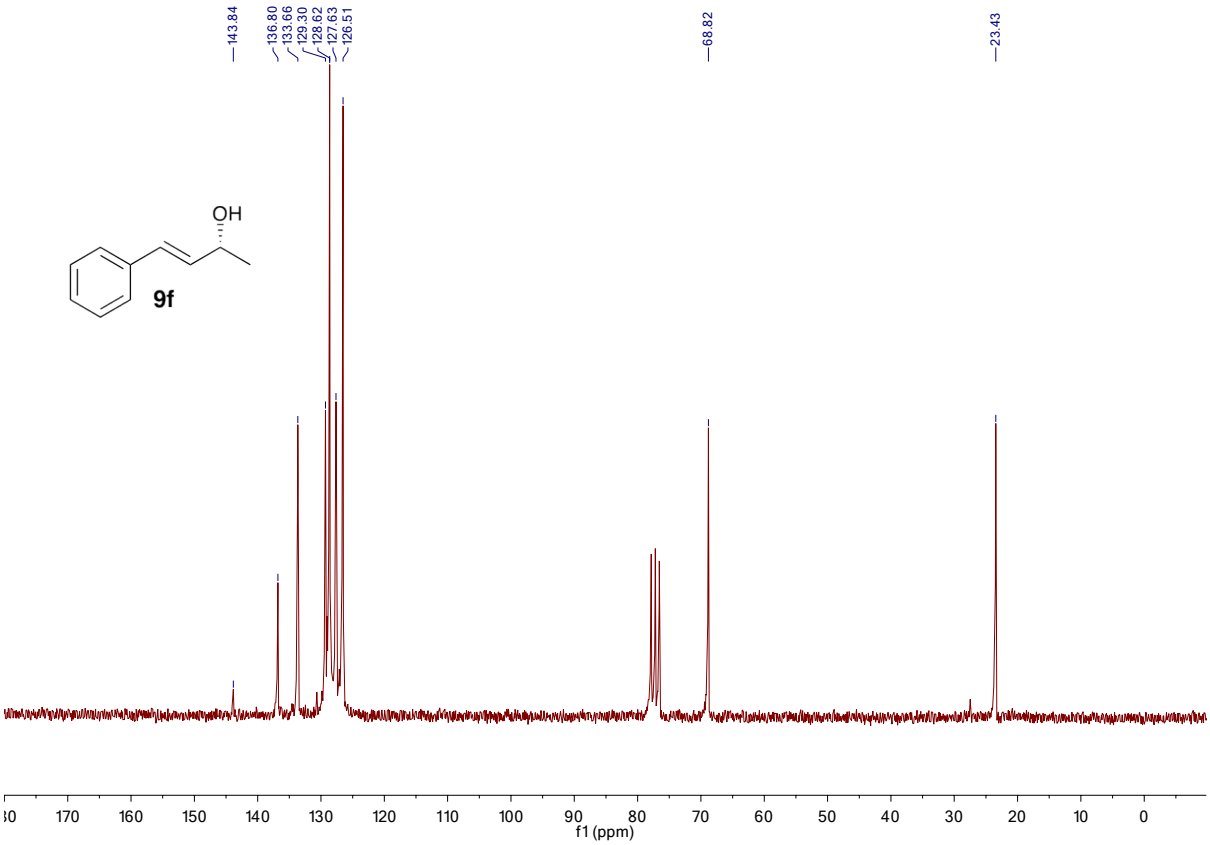


Figure S158. $^{13}C\{^{1}H\}$ NMR spectrum of **9f** (75 MHz, Chloroform-*d*).

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