Supporting Information

Thioether–NHC bidentate manganese complexes as efficient phosphine-free catalysts for hydrogenation at room temperature

Mariia Hruzd,[a,b] Sabrina L. Kleynemeyer,[c] Christophe Michon,[a] Stéphanie Bastin,[c] Eric Pollet,[b,d] Vincent Ritleng*[a] and Jean-Baptiste Sortais*[b,c]

a Université de Strasbourg, Ecole européenne de Chimie, Polymères et Matériaux, CNRS, LIMA, UMR 7042, 25 rue Becquerel, Strasbourg, France

E-mail : vritleng@unistra.fr

b University of Strasbourg Institute for Advanced Study (USIAS), Strasbourg, France

c LCC-CNRS, Université de Toulouse, CNRS, UPS, Toulouse, France.

E-mail : jean-baptiste.sortais@lcc-toulouse.fr

d Université de Strasbourg, Ecole européenne de Chimie, Polymères et Matériaux, CNRS, ICPEES, UMR 7515, 25 rue Becquerel, Strasbourg, France

Table of Contents

Experimental Details

General Information

Materials and Methods

All manipulations were performed using standard Schlenk techniques under an atmosphere of argon. All solvents were dried using standard methods and stored over activated molecular sieves (4 Å). Deionized water and acetonitrile were deoxygenated by bubbling argon for 1 hour before use. $CDCl_3$ was passed through a short column of basic alumina, deoxygenated by argon bubbling (1 hour), and kept over 4 Å molecular sieves. C_6D_6 was deoxygenated by argon bubbling (1 hour) and kept over 4 Å molecular sieves. N-Mesitylimidazole was prepared according to known procedures [S1]. All other chemicals were purchased from usual chemical providers and used as received. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV254 plates. *Column chromatography* was carried out using Macherey-Nagel silica gel (Kieselgel 60, 40–60 μm). Autoclaves (50 mL, Maximator) were used for the hydrogenation.

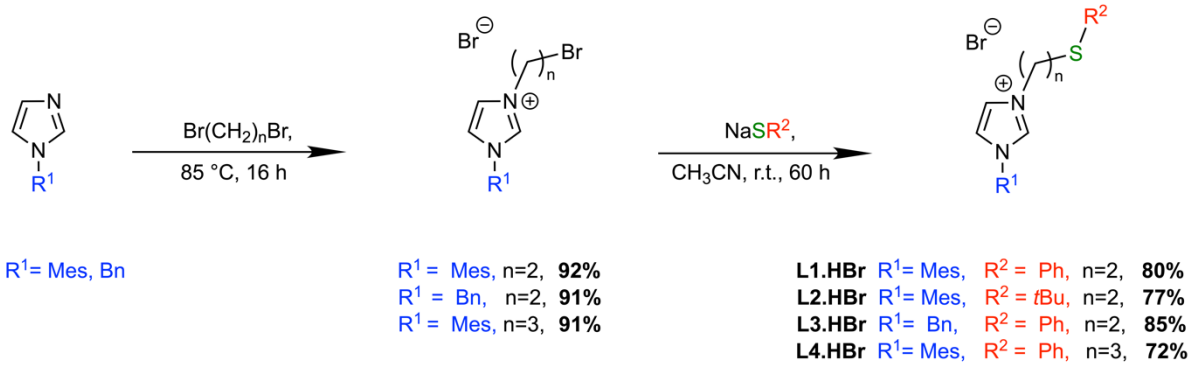
Characterization Techniques (Equipment)

Gas chromatography analyses were conducted on an Agilent GC system with FID detectors using an Agilent HP-1 column (30 m, 0.35 mm, 0.25 μm), with hydrogen as the carrier gas and dodecane as an internal standard. *^{1}H, ^{13}C, and ^{19}F NMR spectra* were acquired on Bruker Avance III HD 400 MHz and Bruker Avance III HD 500 MHz spectrometers. The chemical shifts are referenced to the residual deuterated or ^{13}C solvent peaks. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hertz (Hz), respectively. The following abbreviations are used to classify the multiplicity of the observed signals: s = singlet, br.s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tt = triplet of triplet, sext = sextet, m = multiplet. *IR spectra in solid state* were recorded on a PerkinElmer Spectrum 2 spectrometer using an ATR sampling accessory. *IR spectra in THF* were recorded in 0.3 cm CaF_2 cells with 0.05 cm spacer on PerkinElmer Spectrum 2. *Elemental analyses* were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, Institut de Chimie, UMR 7177, Université de Strasbourg. *High-resolution mass spectra* were recorded on Bruker micrOTOF and Bruker micrOTOF-Q mass spectrometers by the Service de Spectrométrie de Masse, Institut de Chimie, UMR 7177, and the Laboratoire de Spectrométrie de Masse BioOrganique, IPHC, UMR 7178 of the Université de Strasbourg. *Single-crystal X-ray diffraction data:* the crystals were placed in oil, and a single crystal was selected, mounted on a micro mount, and placed in a low-temperature N_2 stream. X-ray diffraction data collection for **1** and **2** crystals was carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX4 software) [S2] from reflections taken from one set of 180 frames, each at 1s exposure. The structures were solved using the program SHELXT-2018 [S3]. The refinement and all further calculations were carried out using SHELXL-2019 [S4]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. X-ray diffraction data collection for **3** and **4** crystals was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 40mm. The cell parameters were determined (APEX3 software) [S5] from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014 [S3]. The refinement and all further calculations were carried out using SHELXL-2018 [S4]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters.

Experimental Procedures

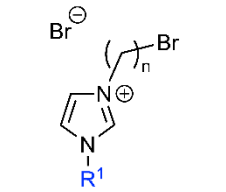
Synthesis of NHC-thioether bidentate ligands (L1.HBr-L4.HBr).

The preparation of functionalized thioether imidazolium salts NHC-SR (**L1.HBr-L4.HBr**) (**Scheme S1**) was carried out using a previously developed two-step procedure.[S6,S7] This involved the quaternization of the corresponding N-substituted imidazoles with 1,2-dibromoethane[S8] or 1,3-dibromopropane [S79, followed by nucleophilic substitution of bromine with the desired commercial or in situ generated sodium thiolate. [S10,S11]



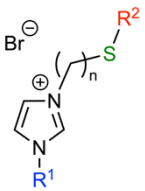
Scheme S1. Synthesis of NHC-thioether bidentate ligands (**L1.HBr–L4.HBr**).

Quaternisation of N-substituted-imidazoles.



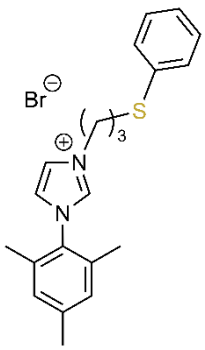
A mixture of N-substituted imidazoles (0.01 mmol) and 1,2-dibromobutane or 1,3-dibromopropane (0.03 mmol) was heated at 85 °C for 16-24 h, during which a white solid formed. After completion of the reaction, the excess of 1,2-dibromobutane or 1,3-dibromopropane was distilled off under reduced pressure, and the resulting solid residue was dissolved in 30 mL of CH_2Cl_2. The suspension was then filtered through Celite, and the solvent was removed under vacuum to yield a white solid. [S8,S9]

Functionalization of imidazoliums salts (L1.HBr-L4.HBr).



Appropriate thiol (1.5 equiv.) was dissolved in acetonitrile, followed by the addition of a solution of sodium hydroxide (1.5 equiv.) in water. The resulting mixture was stirred at room temperature under argon for 30 minutes. The corresponding imidazolium precursor (1.0 equiv.) was then added, and the solution was stirred at room temperature for 64 hours. Afterward, the solvent was removed under a vacuum, and the solid residue was redissolved in CH_2Cl_2 and filtered through Celite. The volatiles were evaporated under reduced pressure, giving an orange-brown oil. This oil was passed through a silica plug, eluting first with CH_2Cl_2 to remove unreacted thiolate, followed by a gradual elution with 90:10 CH_2Cl_2/MeOH. The final products, **L1.HBr–L4.HBr** were obtained as white solids after evaporation of the solvents. [S10,S11]

*Synthesis of 1-mesityl-3-(3-(phenylthio)propan)-1H-imidazol-3-ium bromide(**L4.HBr**):*



Thiophenol (1.9 g, 17.24 mmol, 1.5 equiv.) was dissolved in acetonitrile (25 mL). Sodium hydroxide (690 mg, 17.24 mmol, 1.5 equiv.) in deoxygenated water (1.5 mL) was added, and the resulting mixture was stirred for 30 minutes at room temperature under argon. Then, imidazolium salt (4.5 g, 11.49 mmol, 1 equiv.) was added, and the solution was stirred for 64 hours at room temperature. After this time, the solvent was removed under vacuum, and the solid residue was suspended in CH_2Cl_2 and filtered through Celite. The volatiles were removed under reduced pressure, and the resulting orange-brown oil was passed through a plug of silica, eluting first with CH_2Cl_2 (to remove unreacted thiolate) and then gradually with 90:10 CH_2Cl_2/MeOH. Compound **L4.HBr** was obtained as a white solid after concentration. Yield: 3.5 g, 72%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 10.44 (s, 1H, C*H* – Im_2), 7.71 (t, $^3J_{HH}$ = 1.8 Hz, 1H, C*H* – $Im_{4,5}$), 7.37 – 7.32 (m, 2H, C*H*-Ph), 7.31– 7.26 (m, 2H, C*H*-Ph), 7.22 – 7.17 (m, 1H, C*H*-Ph), 7.14 (t, $^3J_{HH}$ = 1.8 Hz, 1H, C*H* – $Im_{4,5}$), 6.99 (s, 2H, C*H*– Mes), 4.91 (t, $^3J_{HH}$ = 7.0 Hz, 2H, N – CH_2), 3.05 (t, $^3J_{HH}$ = 6.7 Hz, 2H, S – CH_2), 2.37 (p, $^3J_{HH}$ = 6.8 Hz, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.05 (s, 6H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 141.2 (*C*), 137.9 (*C*), 135.0 (*C*), 134.1 (*C*), 130.6 (*C*H), 129.8 (*C*H), 129.5 (*C*H), 129.1 (*C*H), 126.4 (*C*H), 123.6 (*C*H – $Im_{4,5}$), 123.4 (*C*H – $Im_{4,5}$), 48.8 (N – *C*H_2), 30.1 (S – *C*H_2), 29.8 (*C*H_2), 21.1 (*C*H_3), 17.6 (*C*H_3).

HRMS (ESI): m/z: calcd for $[C_{21}H_{25}N_2S]^+$: 337.1733, found: 337.1731, εr = 0.7

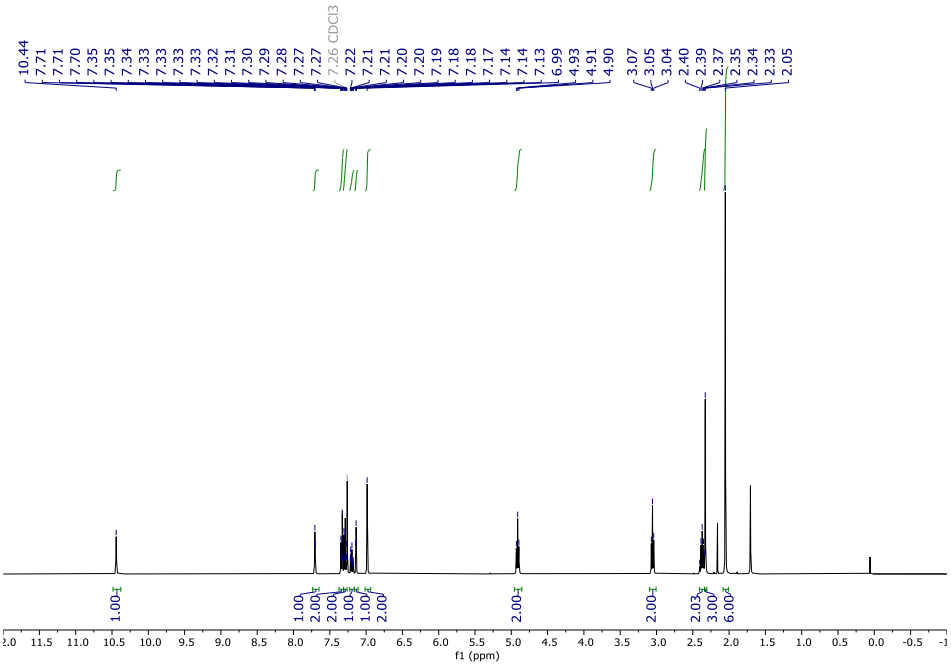


Figure S2. ^{1}H NMR of **L4.HBr** (400 MHz, $CDCl_3$).

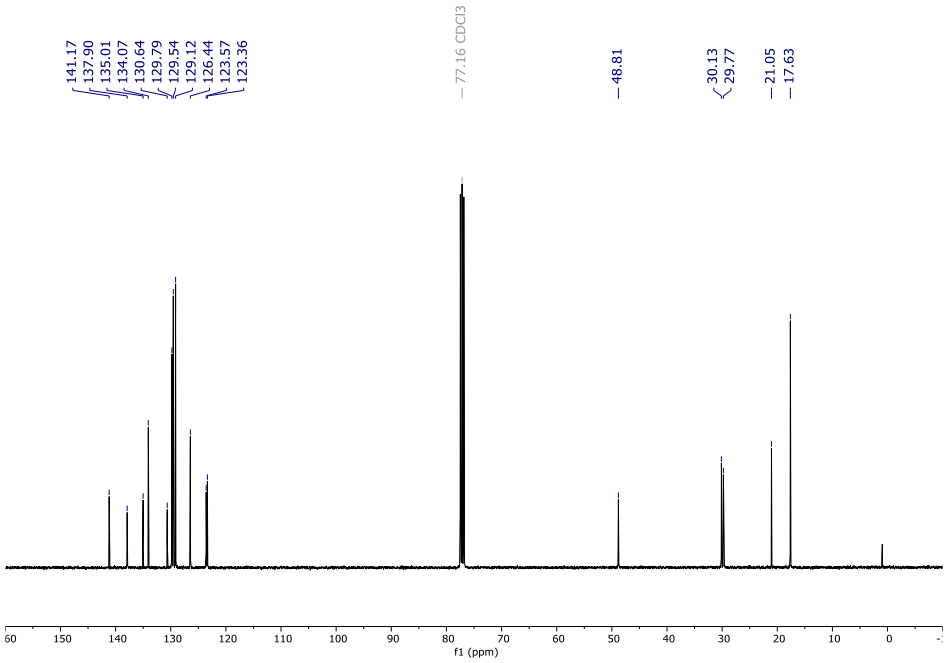
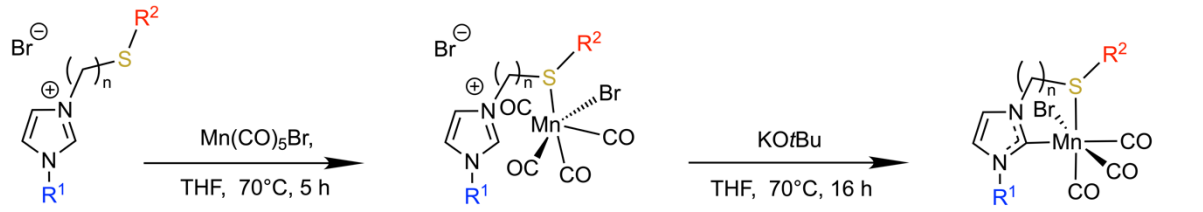


Figure S3. $^{13}C\{^{1}H\}$ NMR of **L4.HBr** (101 MHz, $CDCl_3$).

General procedure for the synthesis of thioether-NHC Manganese(I) complexes (1–4).

In a Schlenk tube under an argon atmosphere, the appropriate ligand, **L1.HBr–L4.HBr** (1 eq.) and $Mn(CO)_5Br$ (1 eq.) were dissolved in distilled THF and heated to 70 °C (**Scheme S4)**. After 5 hours, the reaction mixture was cooled to room temperature, and KO*t*Bu (1.05 eq.) was gradually and slowly added. The reaction mixture was then heated to 70 °C and stirred overnight. Upon cooling to r.t., the THF was removed under vacuum. The crude product was dissolved in CH_2Cl_2 (complex **4** in THF), filtrated through Celite, dried, and reprecipitated twice from a THF/n-hexane mixture, and washed twice with n-pentane, yielding the desired yellow complex (**1–4**).

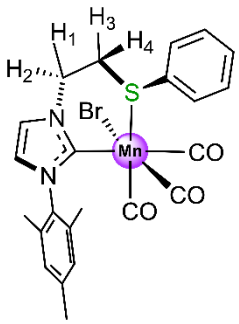


R^1= Mes, Bn
R^2 = Ph, *t*Bu
n=2,3

R^1 = Mes, Bn
R^2 = Ph, *t*Bu
n=2,3

1, R^1= Mes, R^2 = Ph, n=2, **85 %**
2, R^1= Mes, R^2 = *t*Bu, n=2, **77 %**
3, R^1= Bn, R^2 = Ph, n=2, **88 %**
4, R^1= Mes, R^2 = Ph, n=3, **66 %**

Scheme S4. Synthesis of NHC-thioether manganese(I) complexes (**1–4**).



Complex 1. According to the general procedure, complex **1** (341 mg, 85%) was obtained as a yellow powder from **L1.HBr** (300 mg, 0.74 mmol), $Mn(CO)_5Br$ (204 mg, 0.74 mmol), and KO*t*Bu (87 mg, 0.78 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of n-pentane into a solution of complex **1** in CH_2Cl_2 at r.t.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.65 – 7.56 (m, 2H, C*H* – Ph), 7.45 – 7.38 (m, 3H, C*H* – Ph), 7.19 (d, J_{HH} = 1.8 Hz, 1H, C*H* – Im), 6.98 (s, 2H, 2C*H* – Mes), 6.94 (d, J_{HH} = 1.8 Hz, 1H, C*H* – Im), 5.29 (t, J_{HH} = 13.1 Hz, 1H, N-CH_2 – H_2), 4.35 (dd, J_{HH} = 14.4 Hz, J_{HH} = 2.7 Hz, 1H, N-CH_2 – H_1), 3.64 (dd, J_{HH} = 12.3 Hz, J_{HH} = 4.2 Hz, 1H, S-CH_2 – H_3), 3.05 (td, J_{HH} = 12.3 Hz, J_{HH} = 1.8 Hz 1H, S-CH_2 – H_4), 2.34 (s, 3H, CH_3 – Mes), 2.18 (s, 3H, CH_3 – Mes), 2.08 (s, 3H, CH_3 – Mes).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ 222.5 (Mn – *C*O), 219.5 (Mn – *C*O), 216.1 (Mn – *C*O), 189.9 (Mn – *C* (NHC)), 139.8 (*C*), 137.9 (*C*), 136.5 (*C*), 135.4 (*C*), 135.1 (*C*), 130.6 (*C*H), 129.8 (*C*H), 129.67 (*C*H), 129.65 (*C*H), 129.1 (CH), 124.8 (*C*H – Im), 122.9 (*C*H – Im), 48.0 (N – CH_2), 34.9 (S – CH_2), 21.3 (CH_3 – Mes), 18.9 (CH_3 – Mes), 18.2 (CH_3 – Mes).

IR (solid, ATR): ῡ [cm^{-1}] 2014 (s, ῡ CO), 1932 (s, ῡ CO), 1909 (s, ῡ CO).

IR (THF): ῡ [cm^{-1}] 2019 (s, ῡ CO), 1939 (s, ῡ CO), 1906 (s, ῡ CO);

Elemental analysis: (calcd., found for $C_{23}H_{22}BrMnN_2O_3S$): C (51.03, 51.42), H (4.10, 4.31), N (5.17, 5.38).

HRMS (ESI): m/z: calcd for $[C_{23}H_{22}MnN_2O_3S]^+$: 467.0726, found: 461.0727, εr = 0.08 ppm.

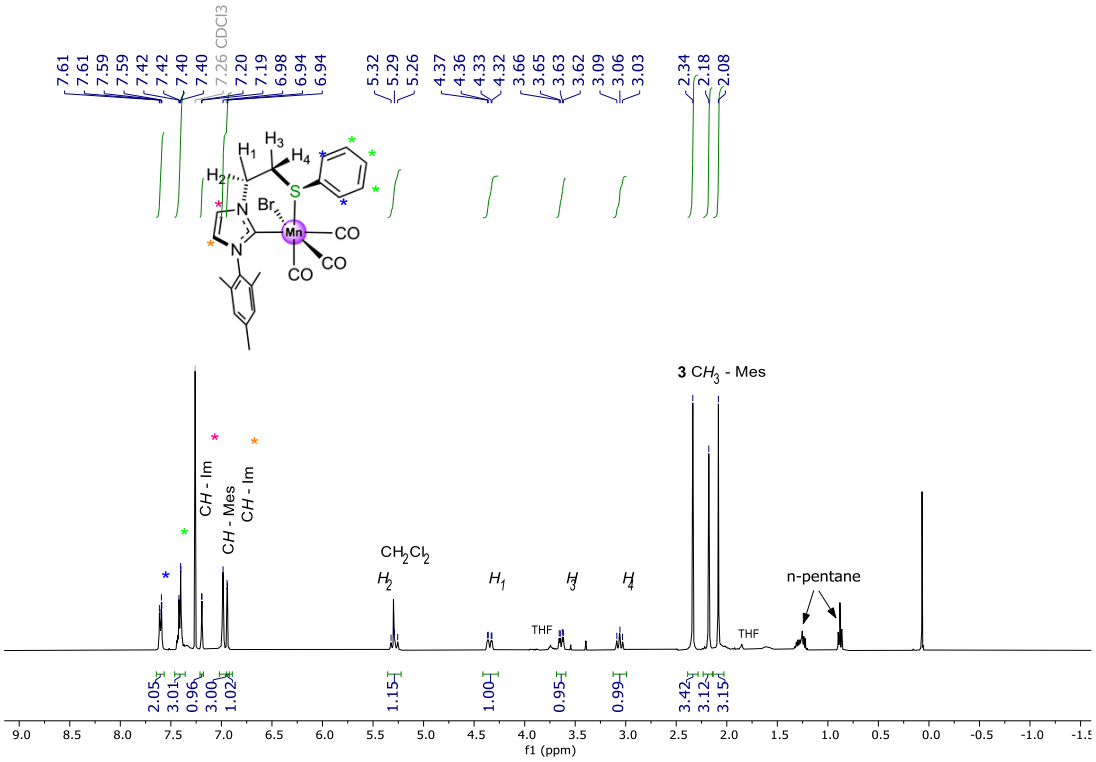


Figure S5. ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$).

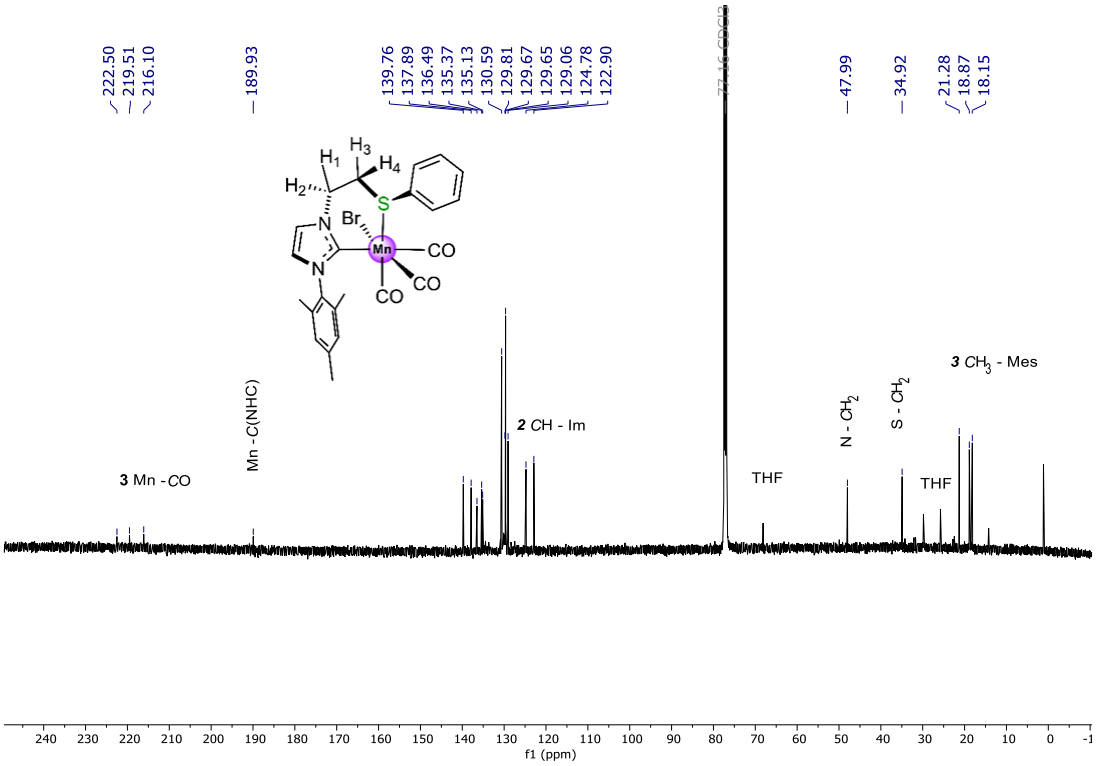


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (126 MHz, $CDCl_3$).

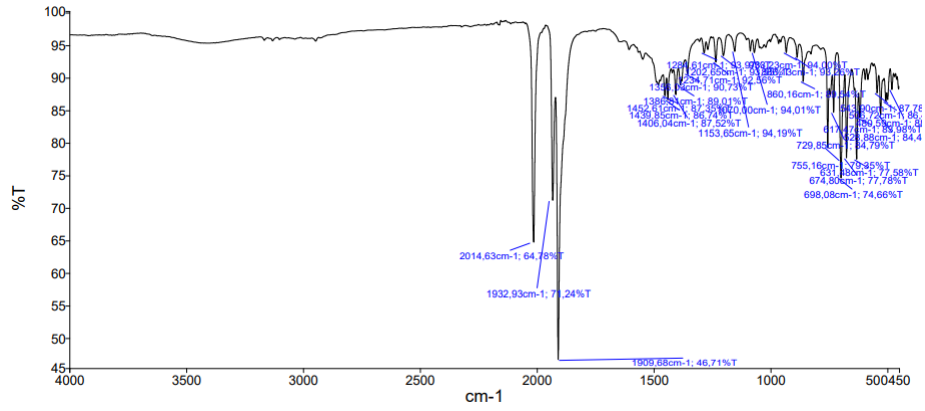


Figure S7. IR (ATR) spectrum of **1.**

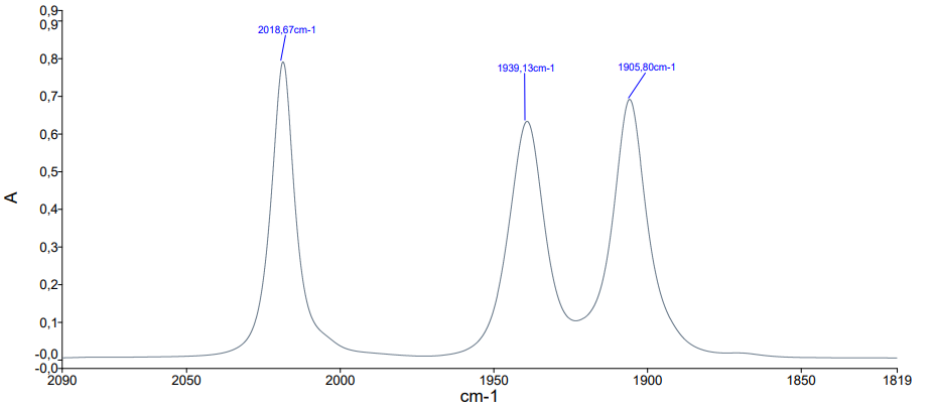
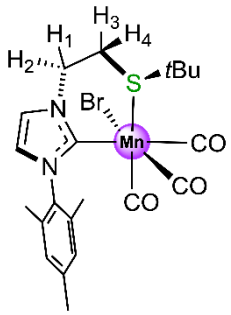


Figure S8. IR (in THF) spectrum of **1**.



Complex 2. According to general procedure, complex **2** (313 mg, 77%) was obtained as a yellow powder from **L2.HBr** (300 mg, 0.78 mmol), $Mn(CO)_5Br$ (215 mg, 0.78 mmol), and KO*t*Bu (92 mg, 0.82 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of n-pentane into a solution of complex **2** in CH_2Cl_2 at r.t..

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.13 (d, J_{HH} = 1.8 Hz, 1H, C*H* – Im), 7.00 (br. s, 1H, C*H* – Mes), 6.99 (br. s, 1H, C*H* – Mes), 6.87 (d, J_{HH} = 1.8 Hz, 1H, C*H* – Im), 5.35 (ddd, J_{HH} = 14.3, J_{HH} = 12.7, J_{HH} = 1.5 Hz, 1H, N-CH_2 – *H*$_2$), 4.22 (ddd, J_{HH} = 14.5 Hz, J_{HH} = 4.6 Hz, J_{HH} = 2.4 Hz, 1H, N-CH_2 – *H*$_1$), 3.31 (dd, J_{HH} = 11.7 Hz, J_{HH} = 4.6 Hz, J_{HH} = 1.6 Hz, 1H, S-CH_2 – *H*$_3$), 2.46 (ddd, J_{HH} = 12.7, J_{HH} = 11.6, J_{HH} = 2.4 Hz, 1H, S-CH_2 – *H*$_4$), 2.35 (s, 3H, C*H*$_3$ – Mes), 2.15 (s, 3H, C*H*$_3$ – Mes), 2.02 (s, 3H, C*H*$_3$ – Mes), 1.47 (s, 9H, C(C*H*$_3$)$_3$).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ 224.2 (Mn – *C*O), 220.0 (Mn – *C*O), 216.9 (Mn – *C*O), 189.7 (Mn – *C* (NHC)), 139.7 (*C*(CH_3) – Mes), 137.7 (*C*(CH_3) – Mes), 136.3 (*C* – Mes), 135.6 (*C*(CH_3) – Mes), 129.5 (*C*H – Mes), 129.0 (*C*H – Mes), 124.5 (*C*H – Im), 122.6 (*C*H – Im), 49.3 (*C*(CH_3)$_3$), 47.5 (N – *C*H_2), 29.8 (C(*C*H_3)$_3$), 27.7 (S – *C*H_2), 21.3 (*C*H_3 – Mes), 18.8 (*C*H_3 – Mes), 18.2 (*C*H_3 – Mes).

IR (solid, ATR): ῡ [cm^{-1}] 2008 (s, ῡ CO), 1923 (s, ῡ CO), 1901 (s, ῡ CO);

IR (THF): ῡ [cm^{-1}] 2017 (s, ῡ CO), 1940 (s, ῡ CO), 1894 (s, ῡ CO);

Elemental analysis: (calcd., found for $C_{21}H_{26}BrMnN_2O_3S \cdot 1/6\ CH_2Cl_2$): C (47.48, 47.38), H (4.96, 4.95), N (5.23, 5.21).

HRMS (ESI): m/z: calcd for $[C_{21}H_{26}MnN_2O_3S]^+$: 441.1039, found: 441.1039, εr = 0.14 ppm.

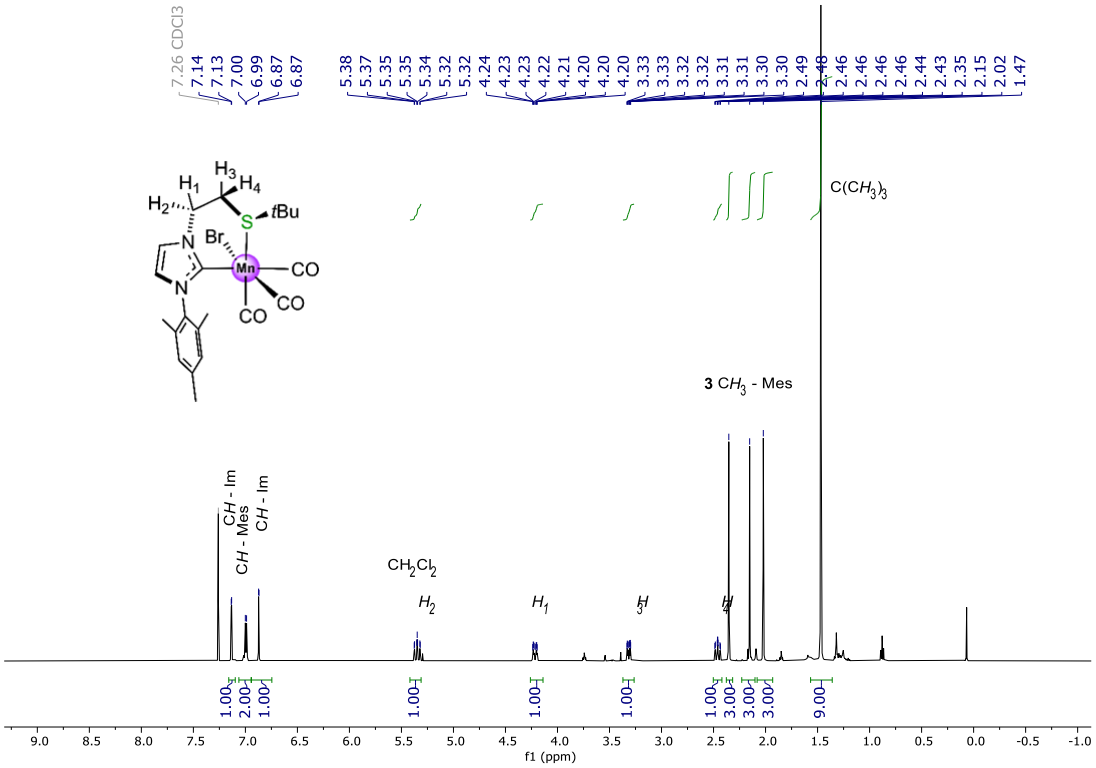


Figure S9. ^{1}H NMR spectrum **of 2** (500 MHz, $CDCl_3$).

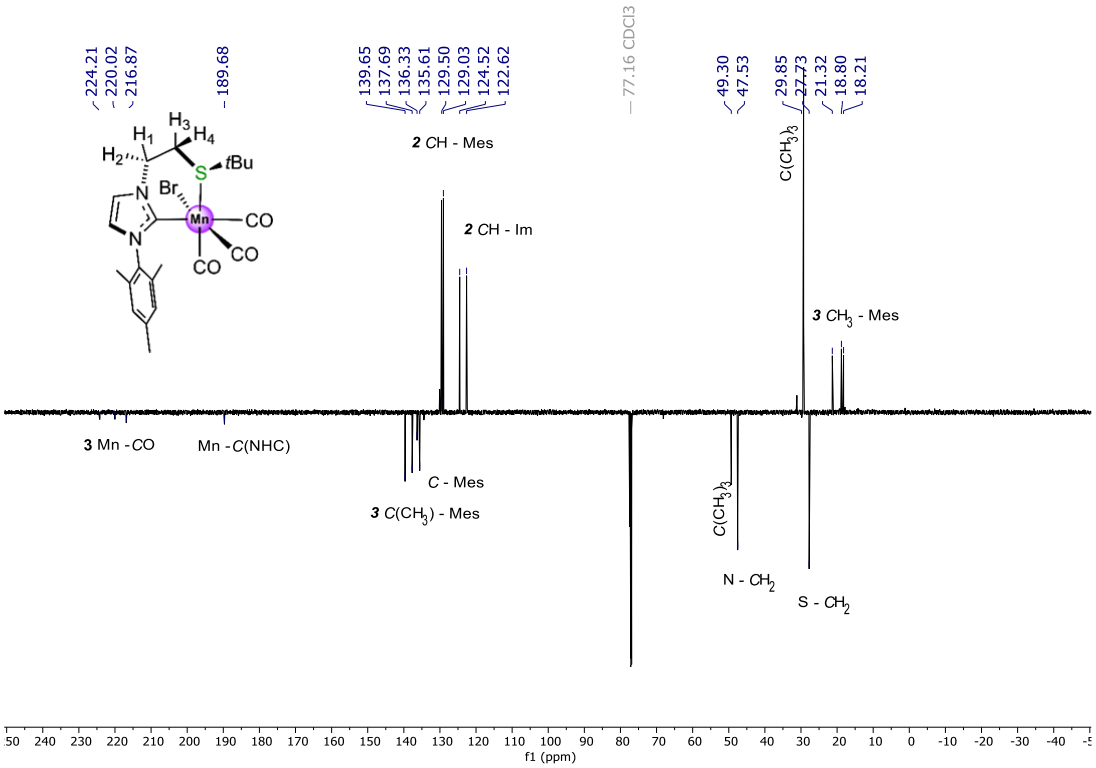


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum **of 2** (126 MHz, $CDCl_3$,).

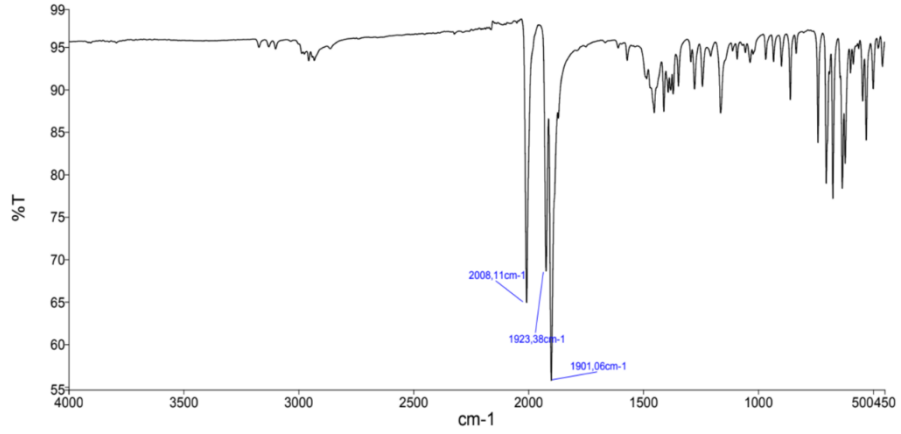


Figure S11. IR spectrum of **2**.

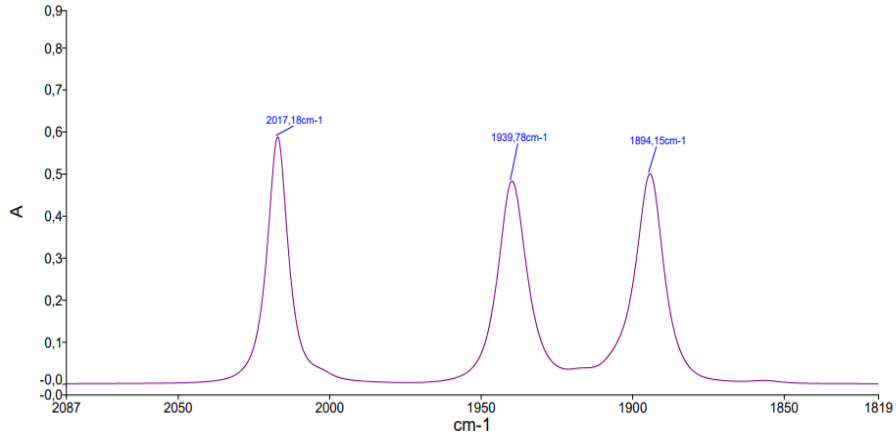
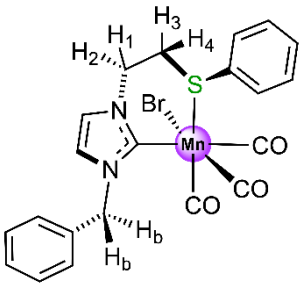


Figure S12. IR (THF) spectrum of **2**.



Complex 3. According to general procedure, complex **3** (362 mg, 88%) was obtained as a yellow powder from **3** (300 mg, 0.80 mmol), $Mn(CO)_5Br$ (220 mg, 0.80 mmol), and KO*t*Bu (94 mg, 0.84 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of n-pentane into a solution of complex **3** in CH_2Cl_2 at r.t.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): 7.69 – 7.60 (m, 2H), 7.52 – 7.30 (m, 8H), 7.04 (s, 1H), 6.79 (s, 1H), 5.94 – 5.80 (m, 1H, CH_2 – *H_b*), 5.73-5.59 (m, 1H, CH_2 – *H_b*), 4.96 (br s, 1H, N-CH_2 – *H_2*), 4.58 (br s, 1H, N-CH_2 – *H_1*), 3.28 (br s, 1H, S-CH_2 – *H_3*), 3.11 (br s, 1H, S-CH_2 – *H_4*). *N.B.* All signals overlap for both isomers.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ 223.4 (Mn – *C*O, Major isomer), 222.5 (Mn – *C*O, Major isomer), 222.3 (Mn – *C*O, Minor isomer), 222.1 (Mn – *C*O, Minor isomer), 215.4 (Mn – *C*O, Major isomer), 215.3 (Mn – *C*O, Minor isomer), 188.8 (Mn – *C* (NHC), Minor isomer), 187.5 (Mn – *C* (NHC), Major isomer), 136.5 (*C*, Major isomer), 136.3 (*C*, Minor isomer), 136.2 (*C*, Minor isomer), 136.1 (*C*, Major isomer), 130.1 (*C*H), 129.9 (*C*H), 129.8 (*C*H), 129.7 (*C*H), 129.0 (*C*H), 128.6 (*C*H), 128.4 (*C*H, Major isomer), 128.3 (*CH*, Minor isomer), 123.6 (*C*H – Im, Major isomer), 123.5 (*C*H – Im, Minor isomer), 122.0 (*C*H –Im, Major isomer), 121.9 (*C*H – Im, Minor isomer), 55.4 (CH_2, Major isomer), 55.0 (CH_2, Minor isomer), 49.1 (N – CH_2, Major isomer), 49.0 (N – CH_2, Minor isomer), 35.6 (S – CH_2, Minor isomer), 35.5 (S – CH_2, Major isomer).

IR (solid, ATR): ῡ [cm^{-1}] 2014 (s, ῡ CO), 1927 (s, ῡ CO), 1898 (s, ῡ CO).

IR (THF): ῡ [cm^{-1}] 2019 (s, ῡ CO), 1939 (s, ῡ CO), 1900 (s, ῡ CO).

Elemental analysis: (calcd., found for $C_{21}H_{18}BrMnN_2O_3S \cdot 1/6\ CH_2Cl_2$): C (48.16, 48.17), H (3.60, 3.58), N (5.31, 5.10).

HRMS (ESI): m/z: calcd for $[C_{21}H_{18}MnN_2O_3S]^+$: 433.0413, found: 433.0411, εr = 0.42 ppm.

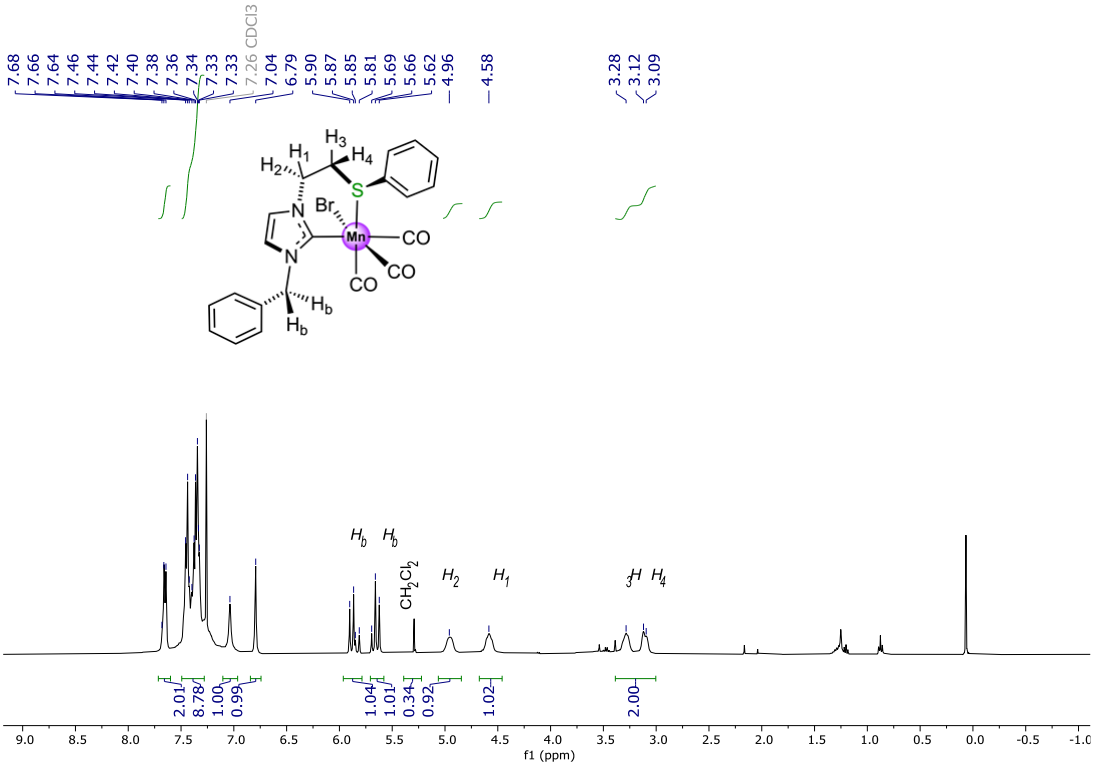


Figure S13. ^{1}H NMR spectrum **of 3** (500 MHz, $CDCl_3$).

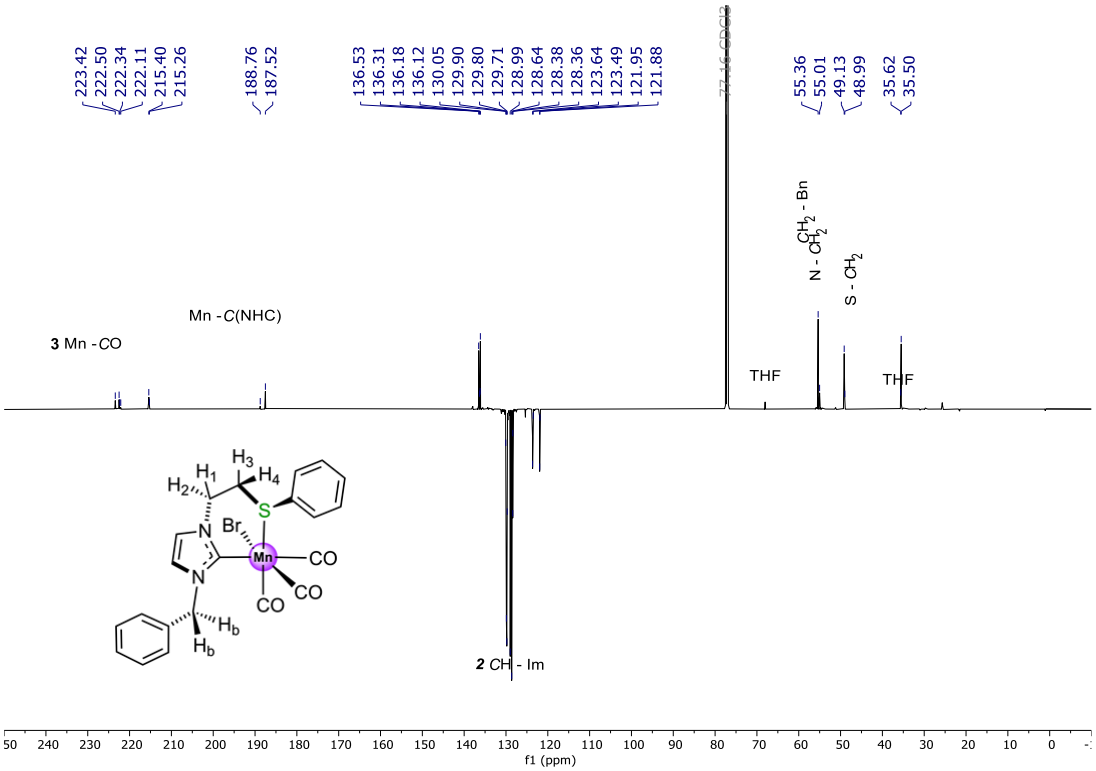


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3** (126 MHz, $CDCl_3$).

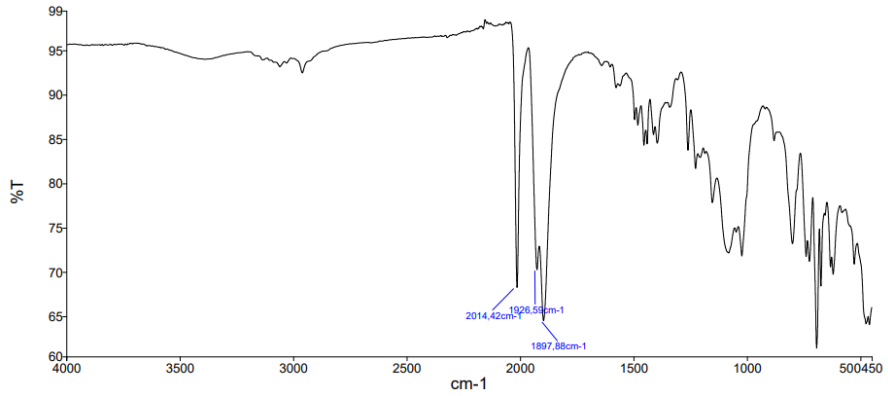


Figure S15. IR (ATR) spectrum of **3**.

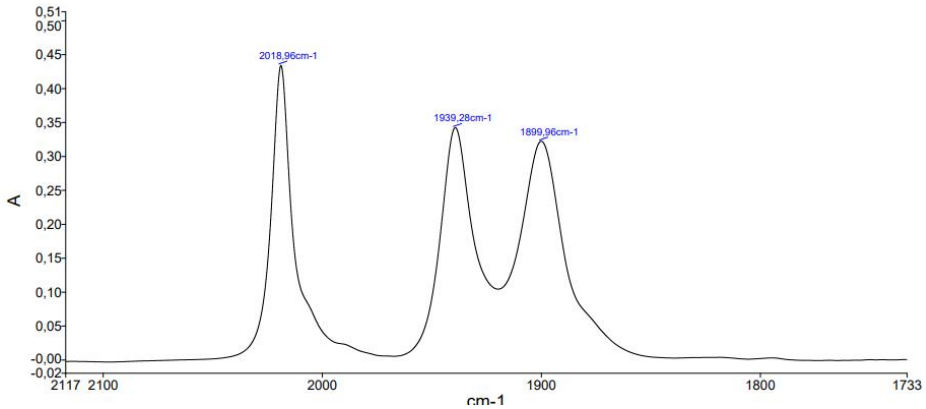
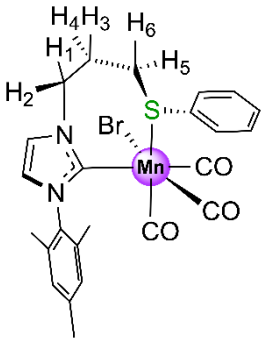


Figure S16. IR (THF) spectrum of **3**.



Complex 4. According to general procedure, complex **4** (264 mg, 66%) was obtained as a yellow powder from **L4.HBr** (300 mg, 0.72 mmol), $Mn(CO)_5Br$ (198 mg, 0.72 mmol), and KO*t*Bu (85 mg, 0.76 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of n-hexane into a solution of complex **4** in toluene at r.t.

^{1}H NMR (400 MHz, C_6D_6, 25°C): δ 7.38 (d, *J* = 7.4 Hz, 2H, C*H* – Ph), 6.96 (t, *J* = 7.6 Hz, 2H, C*H* – Ph), 6.87 (t, *J* = 7.4 Hz, 1H, C*H* – Ph), 6.81 (s, 1H, C*H* – Mes), 6.77 (s, 1H, C*H* – Mes), 6.10 (s, 1H, C*H* – Im), 6.03 (d, *J* = 1.8 Hz, 1H, C*H* – Im), 5.89 – 5.72 (m, 1H, N-CH_2), 3.31 – 3.19 (m, 1H, N-CH_2), 2.55 – 2.45 (m, 1H, S-CH_2), 2.40 – 2.29 (m, 1H, S-CH_2), 2.18 (s, 3H, CH_3 – Mes), 2.12 (s, 3H, CH_3 – Mes), 2.04 (s, 3H, CH_3 – Mes), 1.38 – 1.24 (m, 2H, CH_2).

^{1}H NMR (400 MHz, CD_2Cl_2, 25°C): δ 7.54 (d, *J* = 6.8 Hz, 2H, C*H* – Ph), 7.45 – 7.38 (m, 3H, C*H* – Ph), 7.23 (d, *J* = 1.9 Hz, 1H, C*H* – Im), 7.05 – 6.88 (m, 3H, C*H* – Im, C*H* – Mes), 5.58 (t, *J* = 13.3 Hz, 1H, N-CH_2), 4.09 (d, *J* = 14.2 Hz, 1H, N-CH_2), 3.21 – 3.06 (m, 2H, S-CH_2), 2.33 (s, 3H, CH_3 – Mes), 2.30 – 2.21 (m, 2H, CH_2), 2.15 (s, 2H, CH_3 – Mes), 2.08 (s, 3H, CH_3 – Mes).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25°C): 192.0 (Mn – *C* (NHC)), 139.6 (*C*), 138.0 (*C*), 137.1 (*C*), 136.2 (*C*), 135.2 (*C*), 129.9 (*C*H), 129.3 (*C*H), 129.1 (*C*H), 128.9 (*C*H), 128.5 (*C*H), 123.9 (*C*H – Im), 123.7 (*C*H – Im), 48.9 (N – CH_2), 37.5 (S – CH_2), 28.9 (– CH_2 –), 21.1 (CH_3 – Mes), 18.9 (CH_3 – Mes), 18.7 (CH_3 – Mes). (The signals for CO ligands were not detected due to the lower solubility of **4** in C_6D_6 and instability in CD_2Cl_2)

Elemental analysis: (calcd., found for $C_{24}H_{24}MnN_2O_3SBr$): C (51.90, 51.08), H (4.36, 4.54), N (5.04, 4.75).

IR (solid, ATR): ῡ [cm^{-1}] 2010 (s, ῡ CO), 1925 (s, ῡ CO), 1894 (s, ῡ CO).

HRMS (ESI): m/z: calcd for $[C_{24}H_{24}MnN_2O_3S]^+$: 475.0882, found: 475.0880, εr = 0.65 ppm.

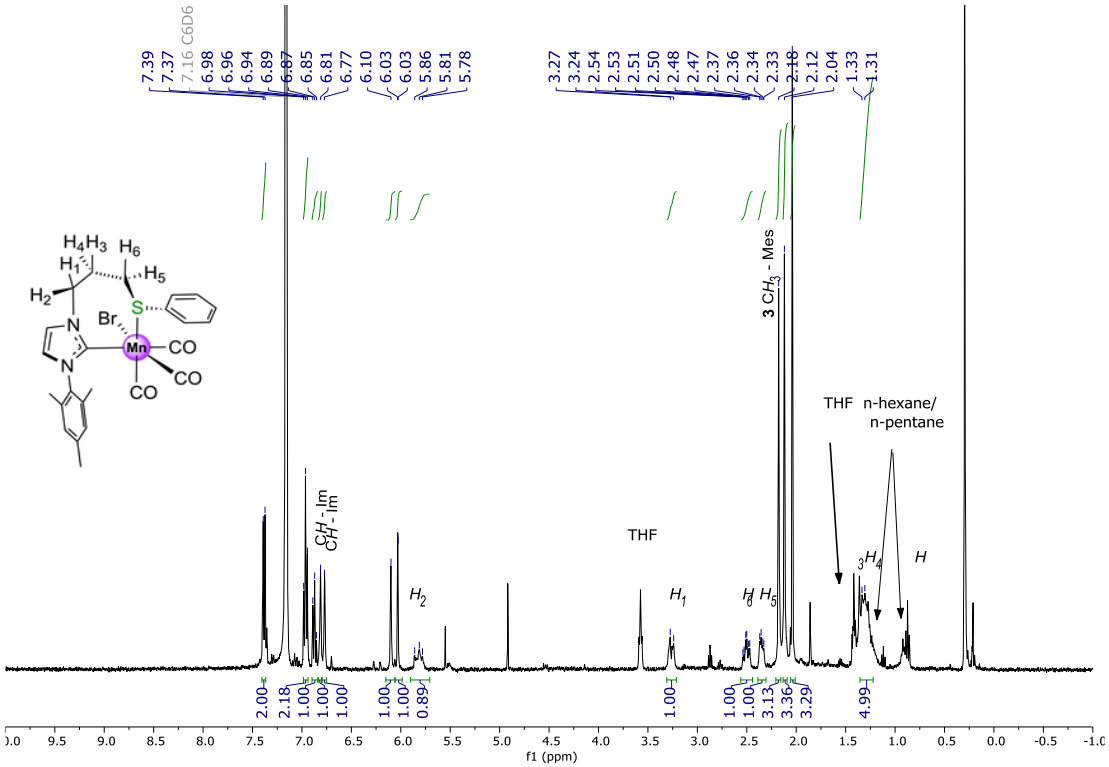


Figure S17.1. ^{1}H NMR spectrum of **4** (400 MHz, C_6D_6).

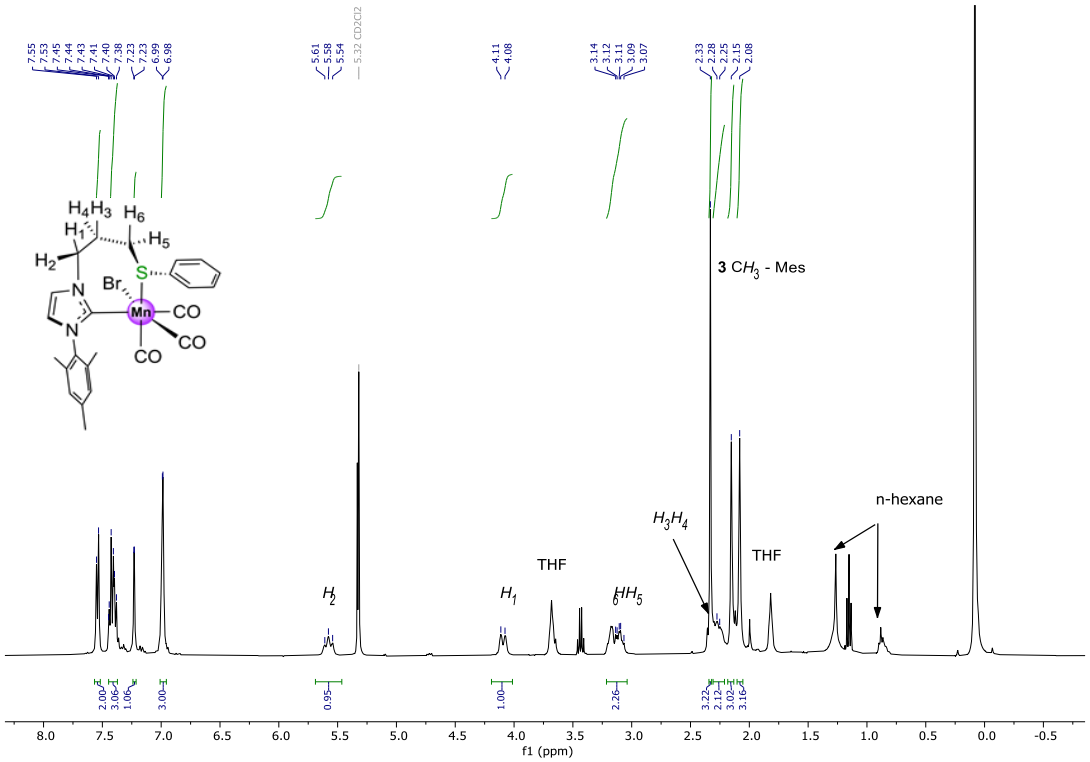


Figure S17.2. ^{1}H NMR spectrum of **4** (400 MHz, CD_2Cl_2).

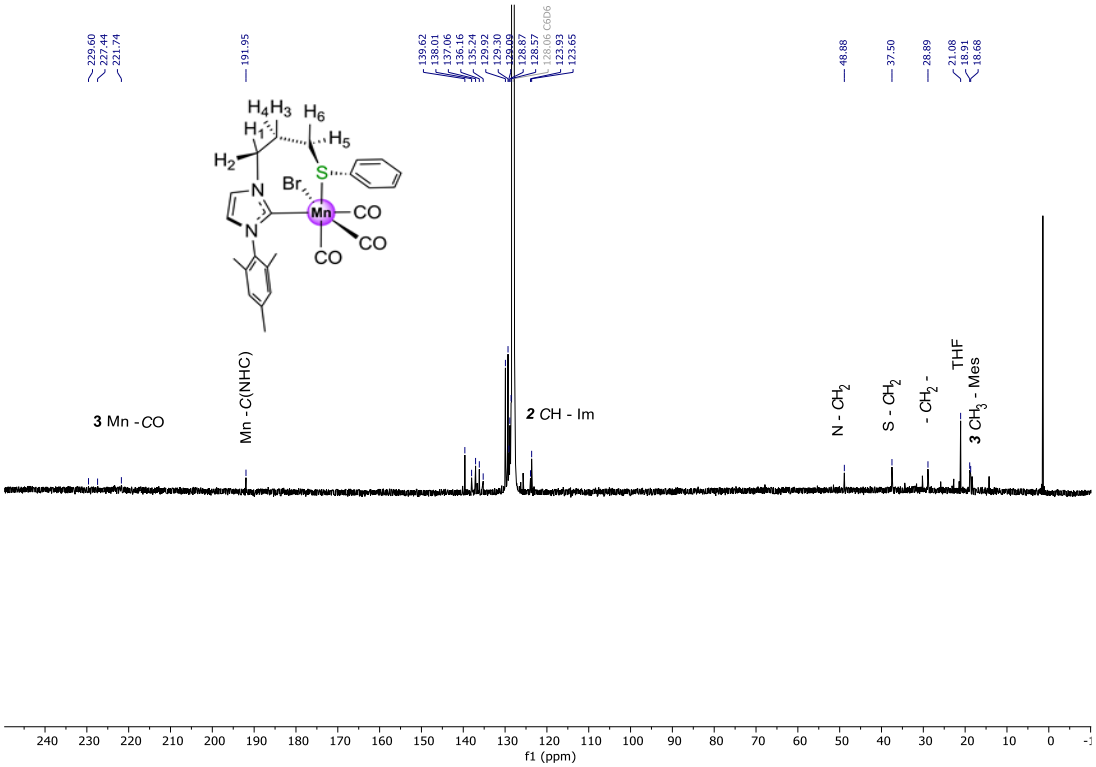


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum **of 4** (126 MHz, C_6D_6).

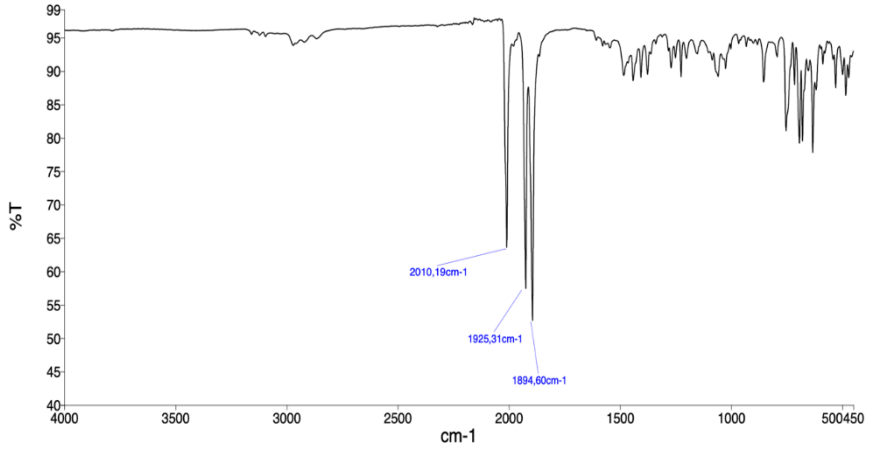


Figure S19. IR (ATR) spectrum of **4**.

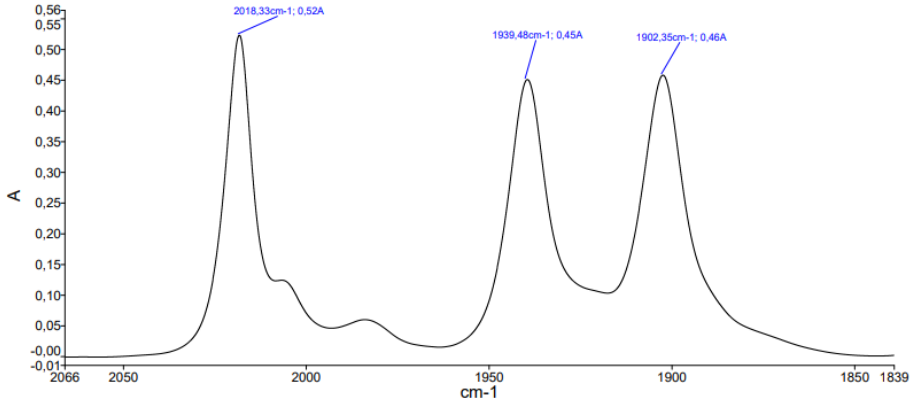


Figure S20. IR(THF) spectrum of **4**.

Characterisation Data

Table S1. Selected bond lengths (Å) and angles (°) for complexes **1-4** with esd's in parentheses.

	1	**2**	**3**	**4**
Mn–C_{NHC}	2.064(4)	2.064(4)	2.049(5)	2.077(13)
Mn–S	2.4054(11)	2.4059(13)	2.3881(15)	2.402(4)
Mn–Br	2.5440(6)	2.5325(8)	2.5240(10)	2.542(2)
C_{NHC}–Mn–S	89.50(11)	91.22(13)	87.84(14)	91.2(4)
C_{NHC}–Mn–Br	90.04(10)	86.16(12)	89.52(14)	88.6(4)
S–Mn–Br	88.48(3)	87.84(4)	85.00(4)	90.44(11)
N1C_{NHC}–MnS	+29.4(3)	+25.5(4)	-42.8(4)	-37.0(1)

Single-crystal X-ray diffraction data

Complex 1: X-ray crystal Data for C_{23} H_{22} Br Mn N_2 O_3 S, (*M* = 541.33), were carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX4 software) [S2] from reflections taken from one set of 180 frames, each at 1s exposure. The structures were solved using the program SHELXT-2018 [S3]. The refinement and all further calculations were carried out using SHELXL-2019 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX4 [S2]; transmission factors: T_{min}/T_{max} = 0.6924/0.7456. The compound crystallises in a chiral group P212121 and the structure_Flack parameter is 0.027(5).

Crystallographic data for **1**

Compound	1	
Empirical formula	C23 H22 Br Mn N2 O3 S	
CCDC	2406905	
Formula weight	541.33	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.4010(3) Å	α = 90°
	b = 15.8222(7) Å	β = 90°
	c = 16.6388(7)Å	γ = 90°
Volume	2211.67(16) $Å^3$	
Z	4	
Density (calculated)	1.626 Mg/m^3	
Absorption coefficient	2.526 mm^{-1}	
F(000)	1096	
Crystal size	0.140 x 0.100 x 0.080 mm	
Crystal color	yellow	
Theta range for data collection	2.448 to 28.036°.	
Index ranges	-9<=h<=11, -20<=k<=20, -22<=l<=22	
Reflections collected	39013	
Independent reflections	5340 [R(int) = 0.0565]	
Completeness to theta = 25.242	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6924	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5340 / 0 / 283	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0661	
R indices (all data)	R1 = 0.0388, wR2 = 0.0693	
Largest diff. peak and hole	0.361 and -0.621 $e.Å^{-3}$	

Complex 2: X-Ray crystal Data for $C_{21}H_{26}BrMnN_2O_3S$, (M = 521.35), were carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX4 software) [S2] from reflections taken from one set of 180 frames, each at 1s exposure. The structures were solved using the program SHELXT-2018 [S3]. The refinement and all further calculations were carried out using SHELXL-2019 [S4]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX4 [S2]; transmission factors: T_{min}/T_{max} = 0.4878/0.7528.

Crystallographic data for **2**

Compound	2	
Empirical formula	C21 H26 Br Mn N2 O3 S	
CCDC	2406906	
Formula weight	521.35	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.7798(7) Å	α = 90°
	b = 8.0924(3) Å	β = 101.904(2)°
	c = 18.2707(8) Å	γ = 90°
Volume	2282.93(17) $Å^3$	
Z	4	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	7.803 mm^{-1}	
F(000)	1064	
Crystal size	0.200 x 0.130 x 0.120 mm	
Crystal color	yellow	
Theta range for data collection	2.862 to 66.759°.	
Index ranges	-18<=h<=18, -9<=k<8, -21<=l<=21	
Reflections collected	24271	
Independent reflections	4019 [R(int) = 0.0733]	
Completeness to theta = 66.759	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.4878	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4019 / 0 / 268	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0657, wR2 = 0.1925	
R indices (all data)	R1 = 0.0712, wR2 = 0.2010	
Largest diff. peak and hole	1.299 and -1.710 $e.Å^{-3}$	

Complex 3: X-Ray crystal Data for C_{21} H_{18} Br Mn N_2 O_3 S, (*M* = 513.28), were carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 40mm. The cell parameters were determined (APEX3 software) [S5] from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014 [S3]. The refinement and all further calculations were carried out using SHELXL-2018 [S4]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3 [S5]; transmission factors: T_{min}/T_{max} = 0.6597/0.7456. The SQUEEZE instruction in PLATON [S12] was applied. The residual electron density was assigned to 1/4 molecules of dichloromethane solvent.

Crystallographic data for **3** + 0.25 CH_2Cl_2

Compound	3	
Empirical formula	C21 H18 Br Mn N2 O3 S + 0.25 CH_2Cl_2	
CCDC	2406904	
Formula weight	513.28	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.1743(9) Å	α = 91.696(3)°
	b = 10.9691(11) Å	β = 100.136(3)°
	c = 12.8226(14) Å	γ = 91.504(3)°
Volume	1130.7(2) $Å^3$	
Z	2	
Density (calculated)	1.508 Mg/m^3	
Absorption coefficient	2.466 mm^{-1}	
F(000)	516	
Crystal size	0.160 x 0.120 x 0.100 mm	
Crystal color	yellow	
Theta range for data collection	1.614 to 28.082°.	
Index ranges	-10<=h<=10, -14<=k<14, -16<=l<=16	
Reflections collected	43287	
Independent reflections	5471 [R(int) = 0.0878]	
Completeness to theta = 25.242	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6597	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5471 / 0 / 261	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0654, wR2 = 0.1816	
R indices (all data)	R1 = 0.1023, wR2 = 0.2108	
Largest diff. peak and hole	1.796 and -1.243 $e.Å^{-3}$	

Complex 4: X-Ray crystal Data for $C_{24}H_{24}BrMnN_2O_3S$, (M = 555.37), were carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 40mm. The cell parameters were determined (APEX3 software) [S5] from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014 [S3]. The refinement and all further calculations were carried out using SHELXL-2018 [S4]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3 [S5]; transmission factors: T_{min}/T_{max} = 0.5628/0.7456. The compound crystallises in a chiral group P21 and the structure Flack parameter is 0.011(19).

Crystallographic data for **4** + Toluene

Compound	4	
Empirical formula	C24 H24 Br Mn N2 O3 S + Toluene	
CCDC	2406903	
Formula weight	647.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.999(2) Å	α = 90°
	b = 14.802(5) Å	β = 91.389(11)°
	c = 12.675(4) Å	γ = 90°
Volume	1500.2(8) $Å^3$	
Z	2	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	1.875 mm^{-1}	
F(000)	664	
Crystal size	0.140 x 0.120 x 0.100 mm	
Crystal color	yellow	
Theta range for data collection	1.607 to 28.001°.	
Index ranges	-10<=h<=10, -19<=k<19, -16<=l<=16	
Reflections collected	20413	
Independent reflections	7121 [R(int) = 0.1450]	
Completeness to theta = 25.242	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6597	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7121 / 1 / 356	
Goodness-of-fit on F^2	0.956	
Final R indices [I>2sigma(I)]	R1 = 0.0794, wR2 = 0.1682	
R indices (all data)	R1 = 0.1687, wR2 = 0.2173	
Largest diff. peak and hole	1.431 and -0.838 $e.Å^{-3}$	

Experimental procedures for the catalytic hydrogenations

General procedure for the catalytic hydrogenation of alkenes

Procedure_A:

Complex **4** (13.9 mg, 0.025 mmol, 1 mol%) was weighed in air and transferred into a 10 mL Schlenk tube. The tube was then degassed and purged with argon. An autoclave connected to the Schlenk line was charged with the catalyst dissolved in distilled 2-MeTHF (1.0 mL), followed by the addition of $NaHBEt_3$ (50 µL, 2 mol%) in 2-MeTHF (0.5 mL), and alkene (2.5 mmol), in that order. The Schlenk tube was rinsed with an additional 2-MeTHF (0.5 mL) to ensure complete transfer of the catalyst solution.

Procedure_B:

Complex **4** (20.8 mg, 0.038 mmol, 1.5 mol%) was weighed in air and transferred into a 10 mL Schlenk tube. The tube was degassed and purged with argon. The autoclave, connected to the Schlenk line, was charged with the catalyst dissolved in distilled 2-MeTHF (1.0 mL), $NaHBEt_3$ (50 µL, 2 mol%) in 2-MeTHF (0.5 mL), and alkene (2.5 mmol), in that order. The Schlenk tube was subsequently rinsed with 2-MeTHF (0.5 mL).

Procedure_C:

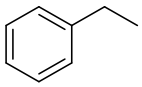
Complex **4** (11 mg, 0.020 mmol, 2 mol%) was weighed in air and transferred into a 10 mL Schlenk tube. The tube was degassed and purged with argon. The autoclave, connected to the Schlenk line, was then charged with the catalyst dissolved in distilled 2-MeTHF (1.0 mL), $NaHBEt_3$ (50 µL, 5 mol%) in 2-MeTHF (0.5 mL), and alkenes (1 mmol), in that order. The Schlenk tube was rinsed with an additional 2-MeTHF (0.5 mL) to ensure complete transfer.

Reaction Conditions:

The autoclave was immediately pressurized with hydrogen (50 bar) and stirred in an oil bath at 30 °C for 18 hours. After cooling to room temperature and releasing the hydrogen, the reaction mixture was filtered through a small silica pad (2 cm, in a Pasteur pipette) and washed with dichloromethane. A 0.05 mL filtrate sample was analysed by gas chromatography (GC) to determine conversion. The solvent was then carefully removed under reduced pressure using a rotary evaporator to yield the pure product, characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

^{1}H, ^{13}C, and ^{19}F NMR spectra of isolated alkanes

Ethylbenzene ($\mathbf{b_1}$)



According to the general procedure **A**, styrene $\mathbf{a_1}$ (285 µL, 2.5 mmol) afforded the title compound $\mathbf{b_1}$ as an oil (186 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.24 – 7.15 (m, 2H, CH_{Ar}), 7.14 – 7.05 (m, 3H, CH_{Ar}), 2.56 (q, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.15 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 144.4 (*C*), 128.5 (*C*H), 128.0 (*C*H), 125.7 (*C*H), 29.0 (*C*H_2), 15.8 (*C*H_3).

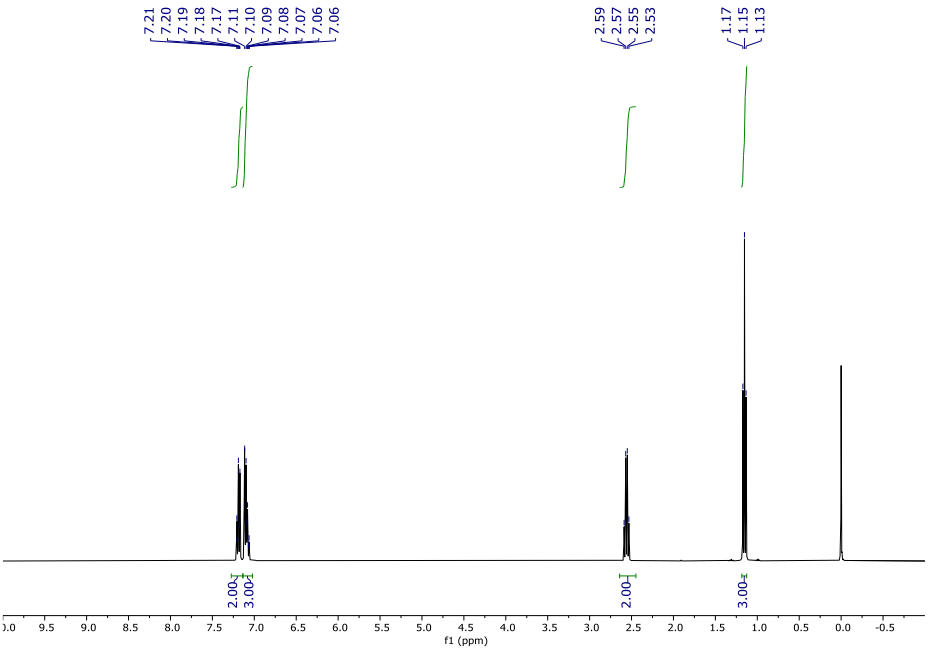


Figure S21: ^{1}H NMR spectrum of $\mathbf{b_1}$ (400 MHz, $CDCl_3$).

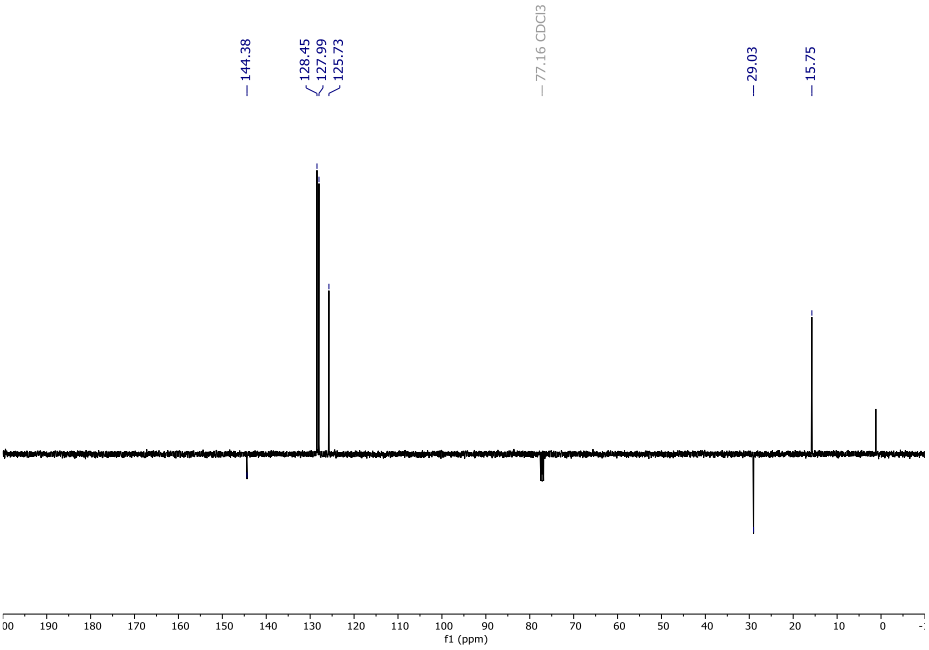
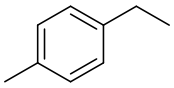


Figure S22: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_1}$ (101 MHz, $CDCl_3$).

1-Ethyl-4-methylbenzene (b_2)



According to the general procedure **A**, 4-methylstyrene $\mathbf{a_2}$ (330 µL, 2.5 mmol) afforded the title compound $\mathbf{b_2}$ as an oil (262 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.25-7.17 (m, 4H, CH_{Ar}), 2.73 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.44 (s, 3H, CH_3), 1.35 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 141.3 (*C*), 135.1 (*C*), 129.1 (*C*H), 127.9 (*C*H), 28.6 (CH_2), 21.1 (CH_3), 15.9 (CH_3).

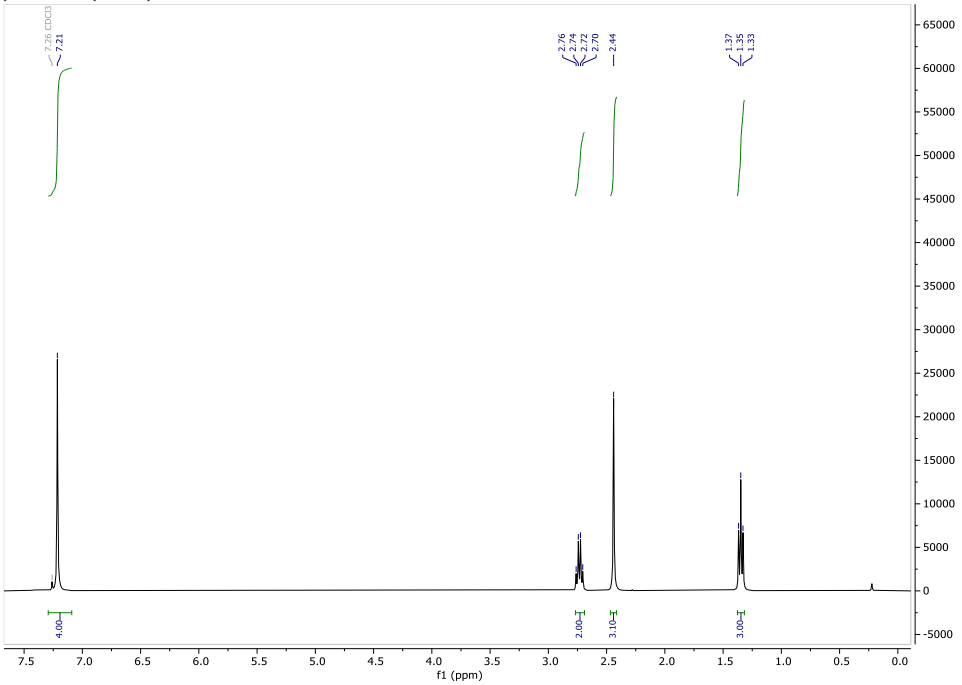


Figure S23: ^{1}H NMR spectrum of $\mathbf{b_2}$ (400 MHz, $CDCl_3$).

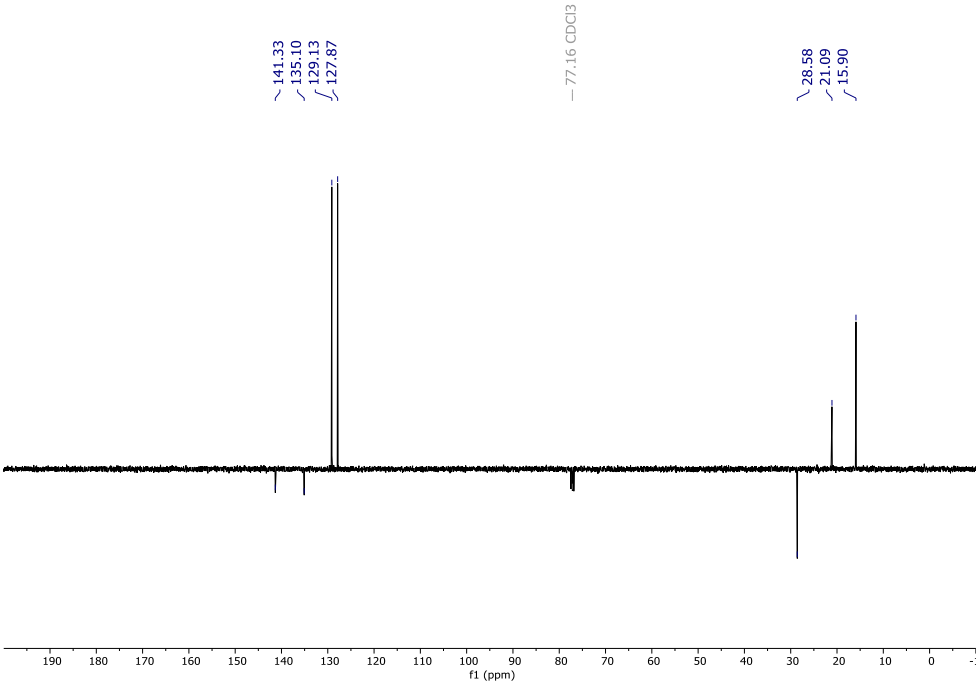
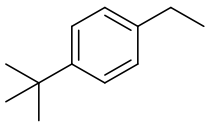


Figure S24: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_2}$ (101 MHz, $CDCl_3$).

1-*tert*-Butyl-4-ethylbenzene (b_3)



According to the general procedure **A**, 4-*tert*-butylstyrene $\mathbf{a_3}$ (458 µL, 2.5 mmol) afforded the title compound $\mathbf{b_3}$ as an oil (374 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.59 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{Ar}), 7.41 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{Ar}), 2.90 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.59 (s, 9H, 3CH_3), 1.51 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 148.4 (*C*), 141.2 (*C*), 127.7 (*C*H), 125.3 (*C*H), 34.5 (*C*(CH_3), 31.8 (C(*C*H_3)$_3$), 28.5 (*C*H_2), 15.7 (*C*H_3).

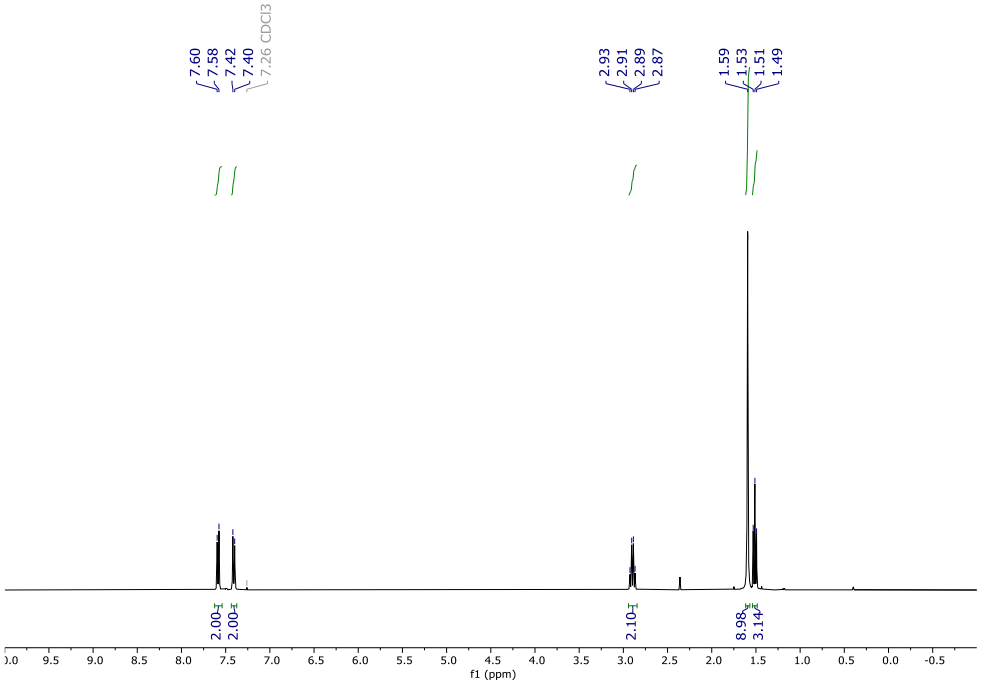


Figure S25: ^{1}H NMR spectrum of $\mathbf{b_3}$ (400 MHz, $CDCl_3$).

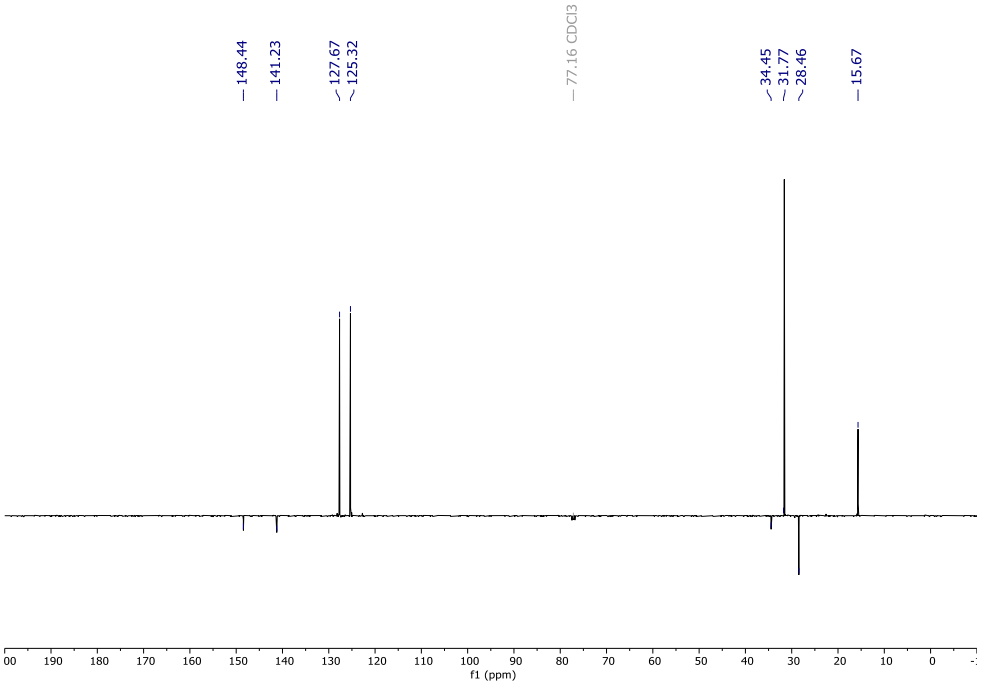
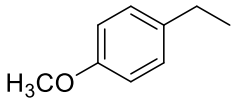


Figure S26: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_3}$ (101 MHz, $CDCl_3$).

1-Ethyl-4-methoxybenzene (b_4)



According to the general procedure **A**, 4- methoxystyrene $\mathbf{a_4}$ (333 µL, 2.5 mmol) afforded the title compound $\mathbf{b_4}$ as an oil (320 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.31 – 7.15 (m, 2H, CH_{Ar}), 6.97 – 6.92 (m, 2H, CH_{Ar}), 3.87 (s, 3H, OCH_3), 2.71 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.33 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C):** δ 157.8 (*C*), 136.4 (*C*), 128.8 (*C*H_2), 113.8 (*C*H_2), 55.2 (O*C*H_3), 28.1 (*C*H_2), 16.0 (*C*H_3).

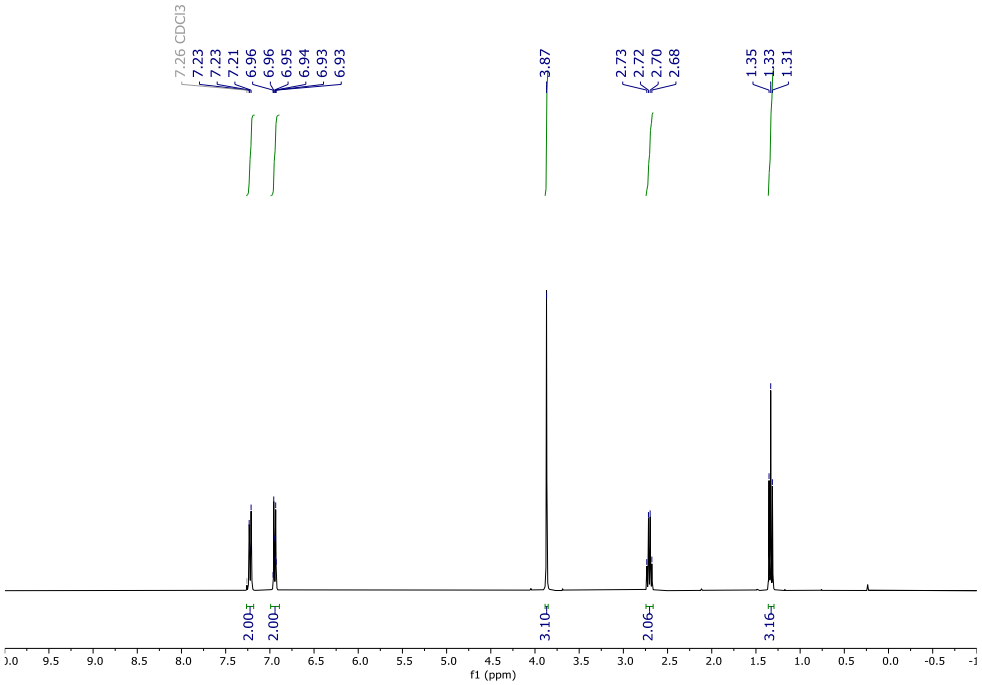


Figure S27: ^{1}H NMR spectrum of $\mathbf{b_4}$ (400 MHz, $CDCl_3$).

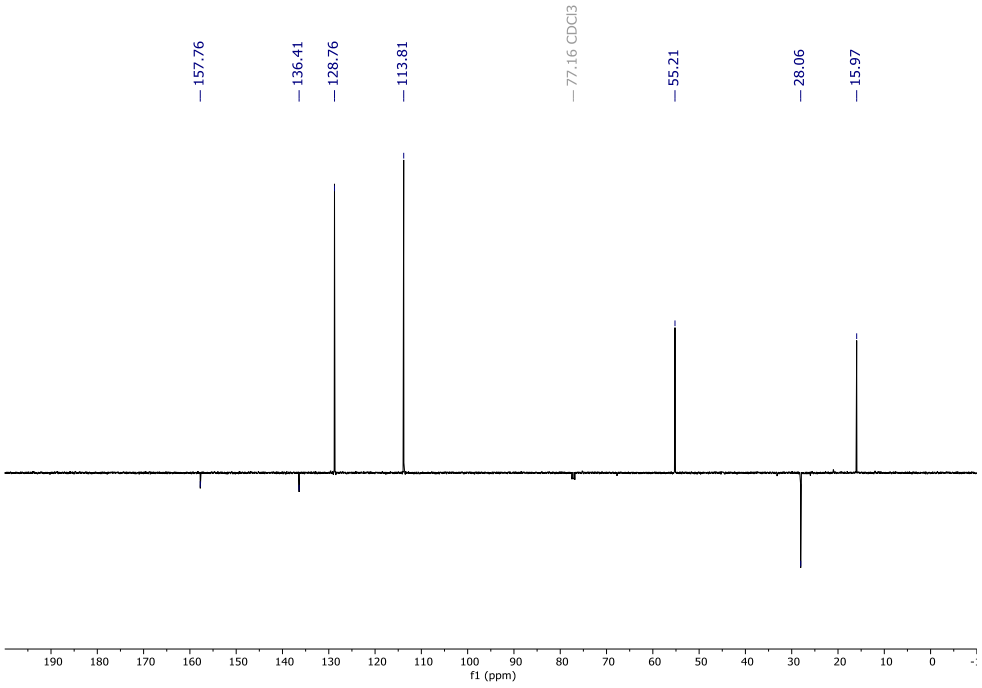
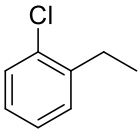


Figure S28: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_4}$ (101 MHz, $CDCl_3$).

1-Chloro-2-ethylbenzene (b_5)



According to the general procedure **A**, 2-chlorostyrene $\mathbf{a_5}$ (318 µL, 2.5 mmol) afforded the title compound $\mathbf{b_5}$ as an oil (300 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.46 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH_{Ar}), 7.36 – 7.26 (m, 2H, CH_{Ar}), 7.22 (td, J_{HH} = 7.4, 2.0 Hz, 1H, CH_{Ar}), 2.89 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.37 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 141.7 (*C*), 133.9 (*C*), 129.6 (*C*H), 129.5 (*C*H), 127.2 (*C*H), 126.9 (*C*H), 26.9 (CH_2), 14.2 (CH_3).

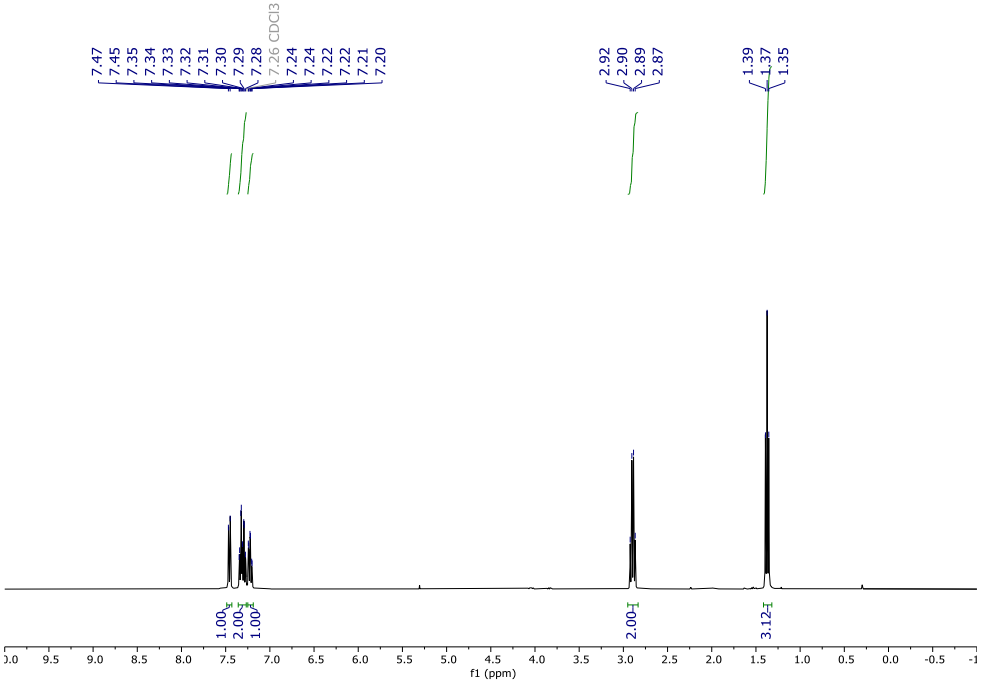


Figure S29: ^{1}H NMR spectrum of $\mathbf{b_5}$ (400 MHz, $CDCl_3$).

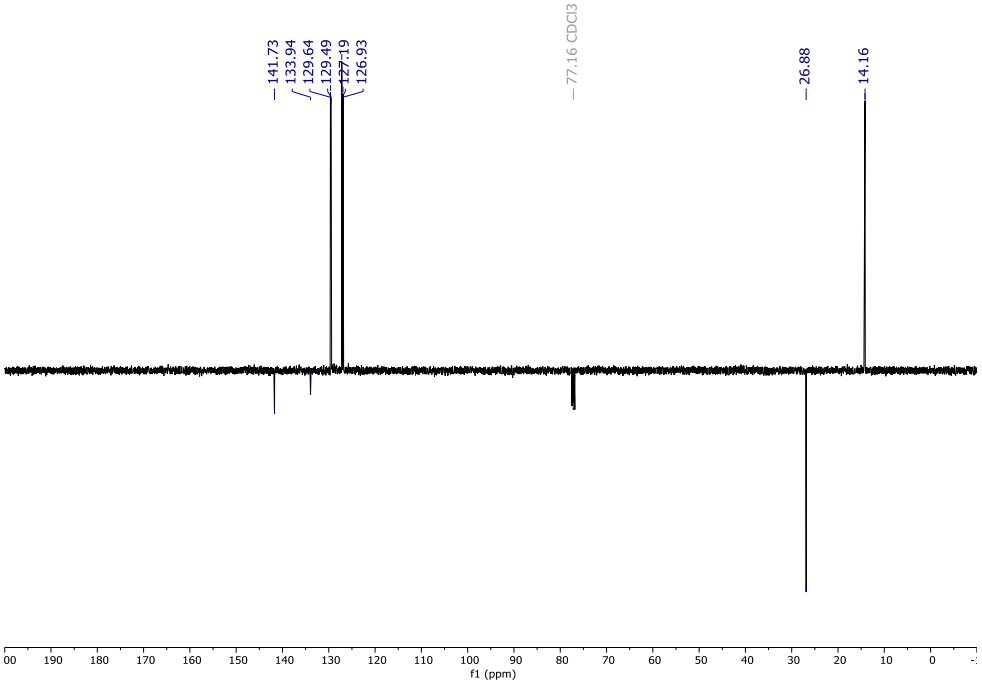
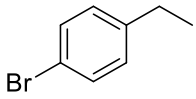


Figure S30: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_5}$ (101 MHz, $CDCl_3$).

1-Ethyl-4-bromobenzene (b_6)



According to the general procedure **A**, 4-bromostyrene $\mathbf{a_6}$ (327 µL, 2.5 mmol) afforded the title compound $\mathbf{b_6}$ as an oil (405 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.46 – 7.43 (m, 2H, CH_{Ar}), 7.13 – 7.09 (m, 2H, CH_{Ar}), 2.65 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.27 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 143.2 (*C*), 131.4 (*C*H), 129.7 (*C*H), 119.4 (*C*), 28.4 (*C*H_2), 15.6 (*C*H_3).

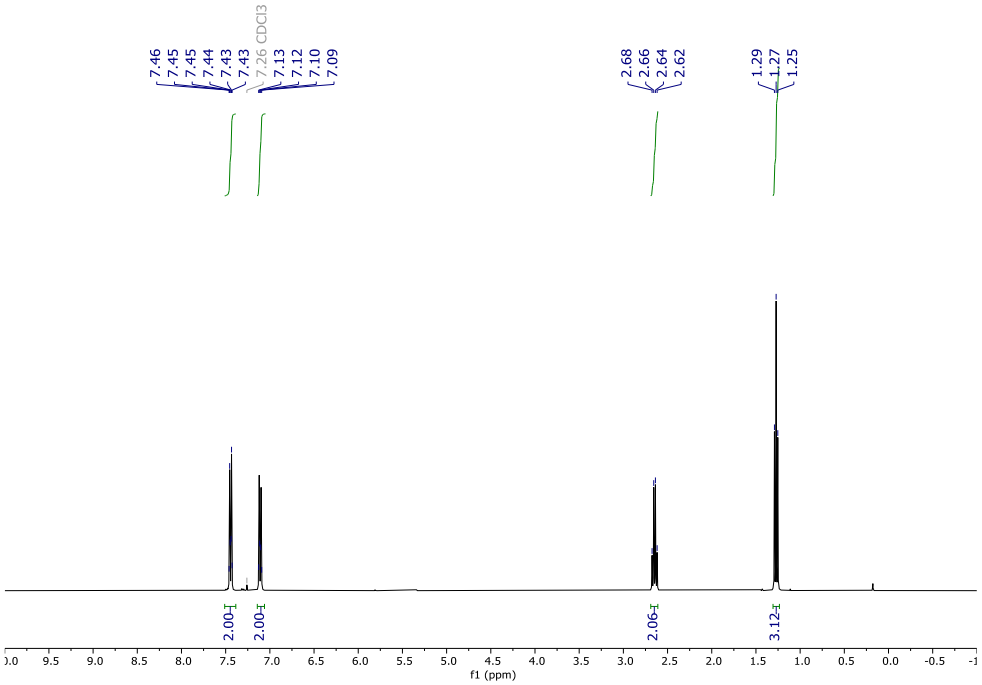


Figure S31: ^{1}H NMR spectrum of $\mathbf{b_6}$ (400 MHz, $CDCl_3$).

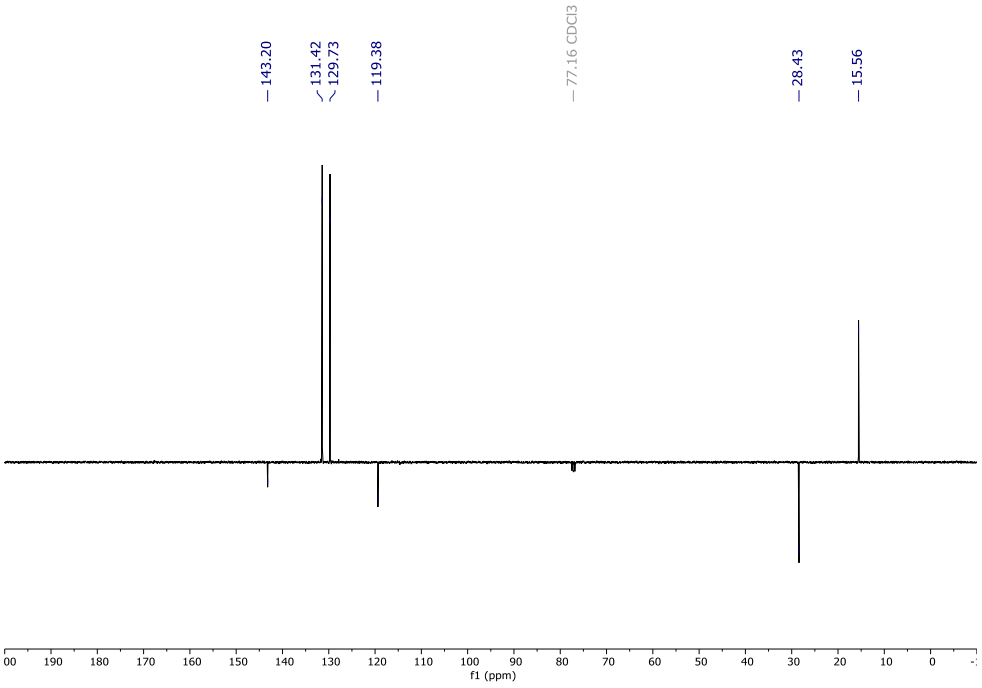
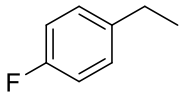


Figure S32: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_6}$ (101 MHz, $CDCl_3$).

1-Ethyl-4-fluorobenzene (b_7)



According to the general procedure **A**, 4-fluorostyrene $\mathbf{a_7}$ (300 µL, 2.5 mmol) afforded the title compound $\mathbf{b_7}$ as an oil (248 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.17 – 7.14 (m, 2H, CH_{Ar}), 7.04 – 6.93 (m, 2H, CH_{Ar}), 2.64 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.24 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 161.0 (d, *C*, J_{CF} = 243.4 Hz), 140.0 (d, *C*, J_{CF} = 3.0 Hz), 129.3 (d, *C*H, J_{CF} = 8.1 Hz), 115.1 (d, *C*H, J_{CF} = 21.2 Hz), 28.2 (*C*H$_2$), 15.9 (*C*H$_3$).
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -118.2.

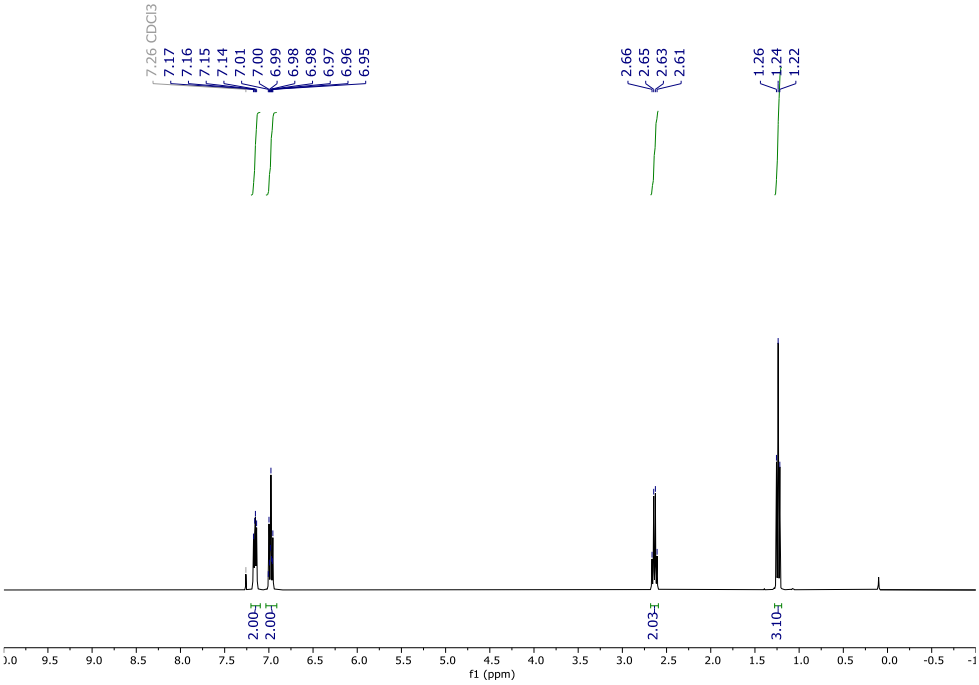


Figure S33: ^{1}H NMR spectrum of $\mathbf{b_7}$ (400 MHz, $CDCl_3$).

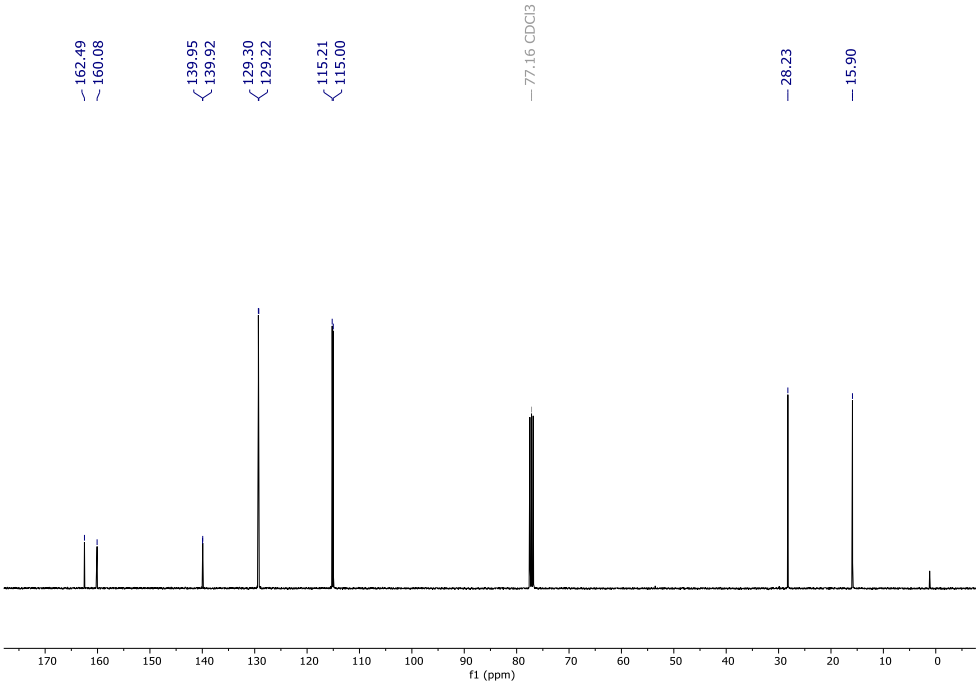


Figure S34: ^{13}C{^{1}H} NMR spectrum of $\mathbf{b_7}$ (101 MHz, $CDCl_3$).

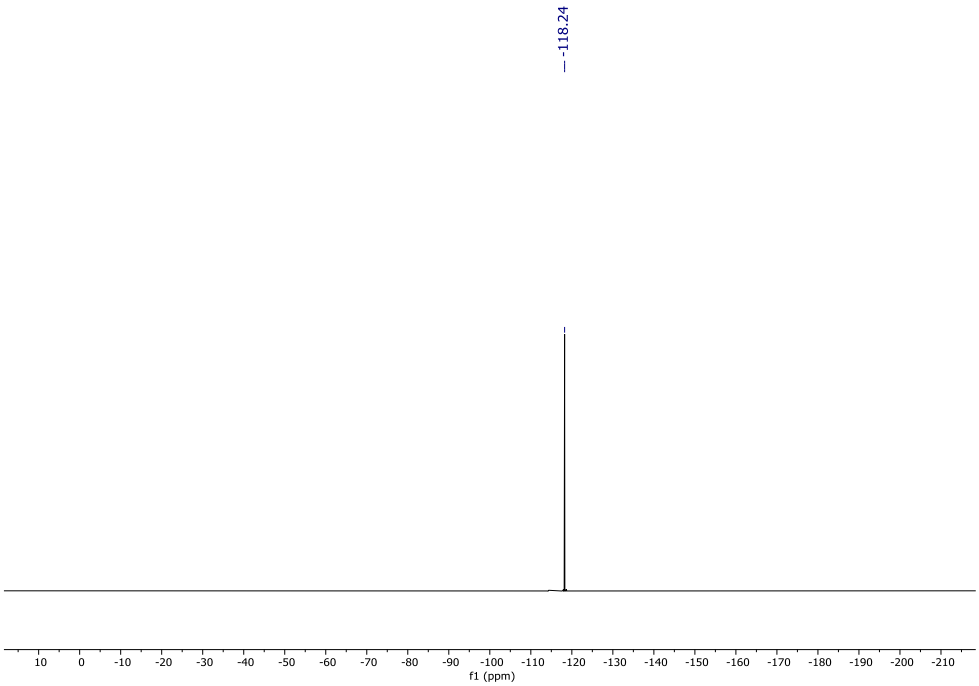
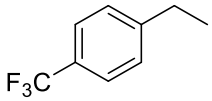


Figure S35: $^{19}F\{^{1}H\}$ NMR spectrum of **b$_7$** (377 MHz, $CDCl_3$).

1-Ethyl-4-(trifluoromethyl)benzene (b$_8$)



According to the general procedure **A**, 4-(trifluoromethyl)styrene **a$_8$** (370 µL, 2.5 mmol) afforded the title compound **b$_8$** as an oil (360 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.58 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, C*H*$_{Ar}$), 7.33 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, C*H*$_{Ar}$), 2.74 (q, $^{3}J_{HH}$ = 7.6 Hz, 2H, C*H*$_2$), 1.30 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H, C*H*$_3$).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 148.4 (q, J_{CF} = 1.3 Hz, *C*), 128.3 (*C*H), 128.2 (q, J_{CF} = 32.4 Hz, *C*), 125.4 (q, J_{CF} = 3.8 Hz, *C*H), 124.7 (q, J_{CF} = 272.7 Hz, *C*F$_3$), 28.9 (*C*H$_2$), 15.4 (*C*H$_3$).
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -62.3 (C*F*$_3$).

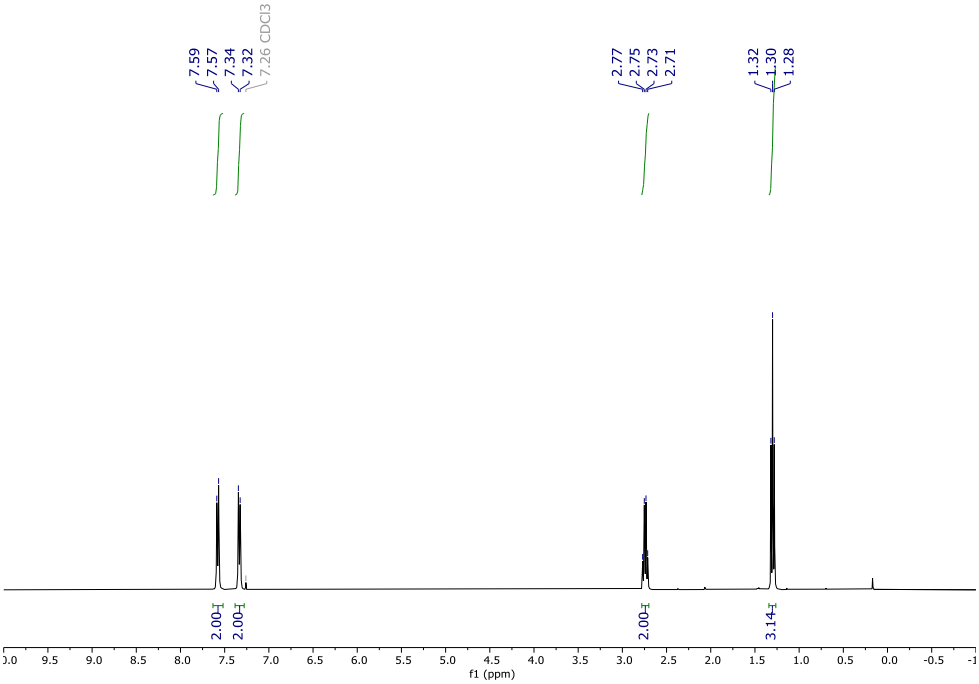


Figure S36: ^{1}H NMR spectrum of **b$_8$** (400 MHz, $CDCl_3$).

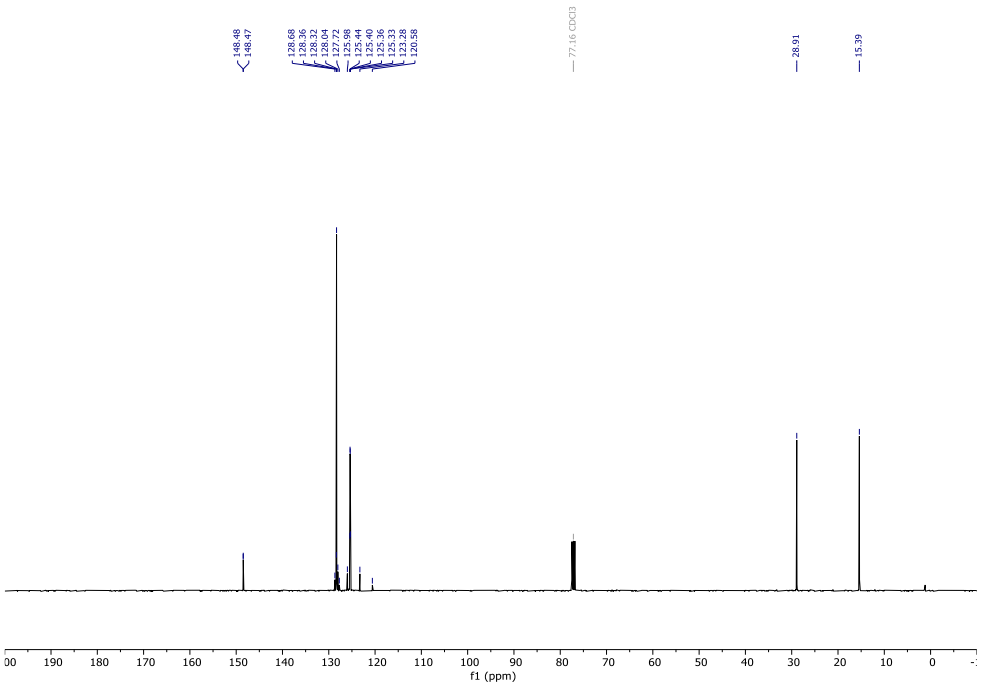


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **b_8** (101 MHz, $CDCl_3$).

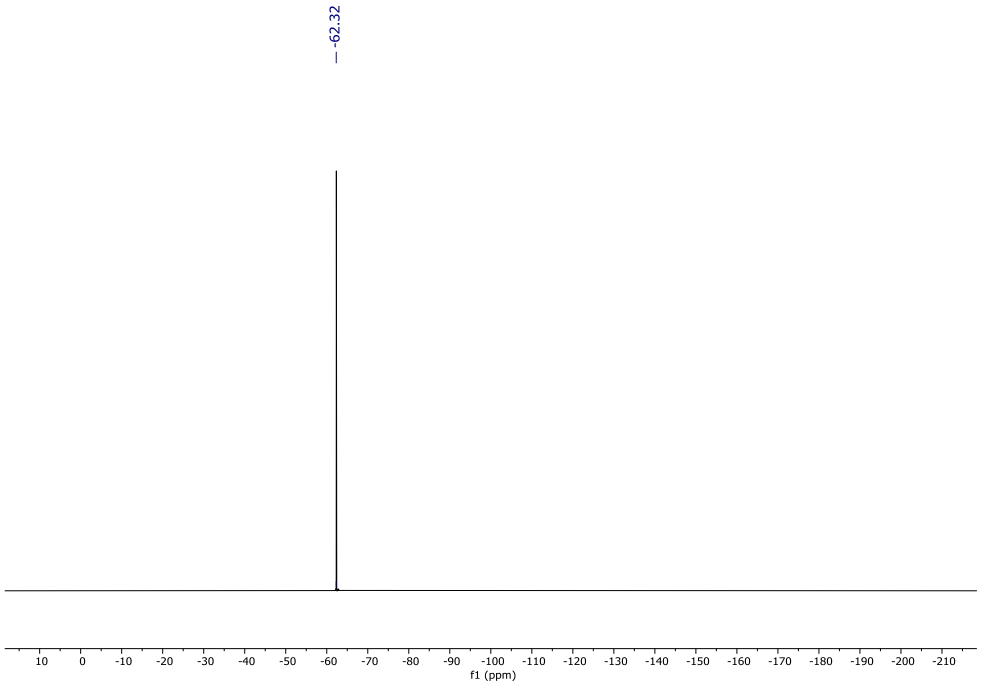
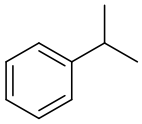


Figure S38: $^{19}F\{^{1}H\}$ NMR spectrum of **b_8** (377 MHz, $CDCl_3$).

(1-Methylethyl)benzene (b_9)



According to the general procedure **A**, α-methylstyrene $\mathbf{a_9}$ (325 µL, 2.5 mmol) afforded the title compound $\mathbf{b_9}$ as an oil (241 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.49 – 7.41 (m, 2H, CH_{Ar}), 7.41 – 7.36 (m, 2H, CH_{Ar}), 7.35 – 7.30 (m, 1H, CH_{Ar}), 3.06 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*), 1.42 (d, *J* = 7.0 Hz, 6H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 149.0 (*C*), 128.5 (*C*H), 126.5 (*C*H), 125.9 (*C*H), 34.3 (*C*H), 24.2 (*C*H_3).

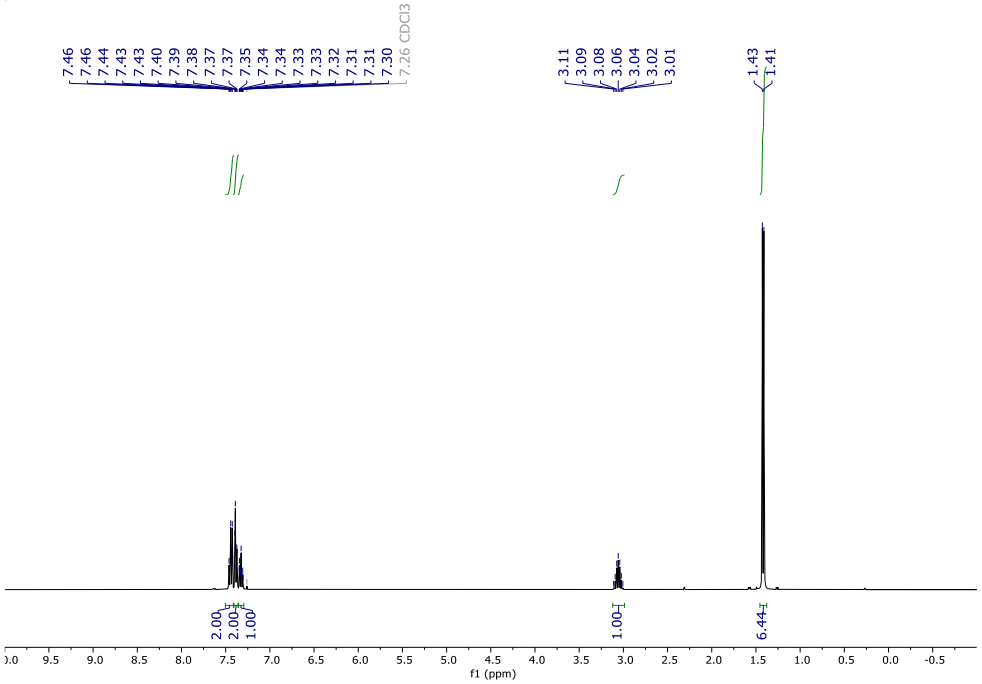


Figure S39: ^{1}H NMR spectrum of $\mathbf{b_9}$ (400 MHz, $CDCl_3$).

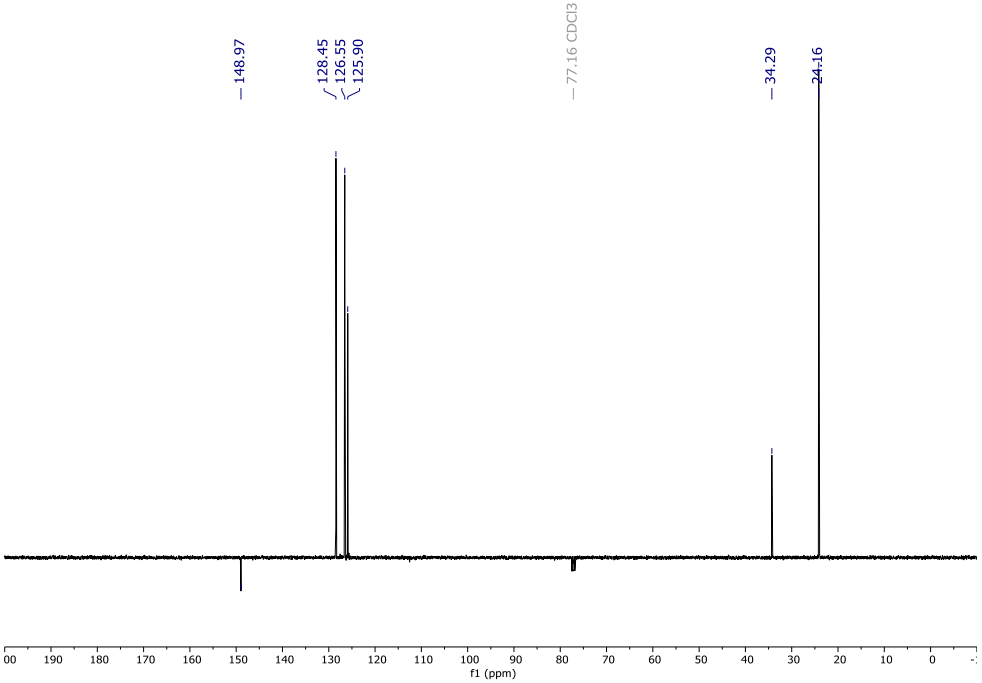
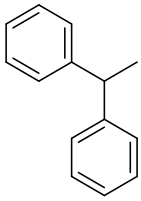


Figure S40: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_9}$ (101 MHz, $CDCl_3$).

1,1-Diphenylethane (b_{10})



According to the general procedure C, 1,1-diphenylethylene **a_{10}** (177 µL, 1 mmol) afforded the title compound **b_{10}** as an oil (165 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.26 – 7.02 (m, 10H, CH_{Ar}), 4.04 (q, $^3J_{HH}$ = 7.2 Hz, 1H, C*H*), 1.54 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 146.5 (*C*), 128.5 (*C*H), 127.7 (*C*H), 126.1 (*C*H), 44.9 (*C*H), 22.0 (*C*H_3).

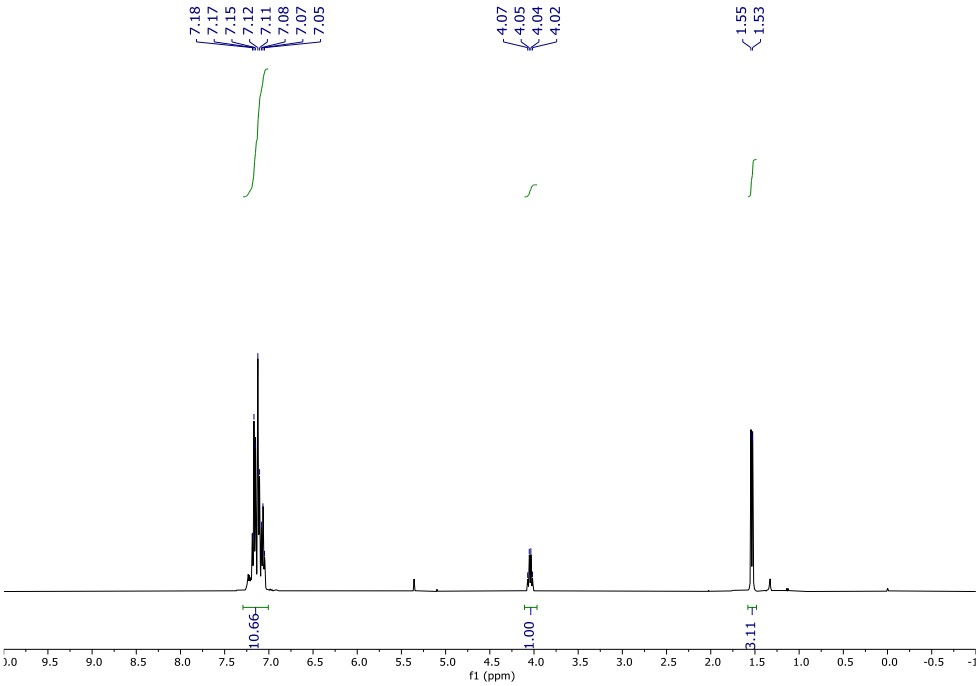


Figure S41: ^{1}H NMR spectrum of **b_{10}** (400 MHz, $CDCl_3$).

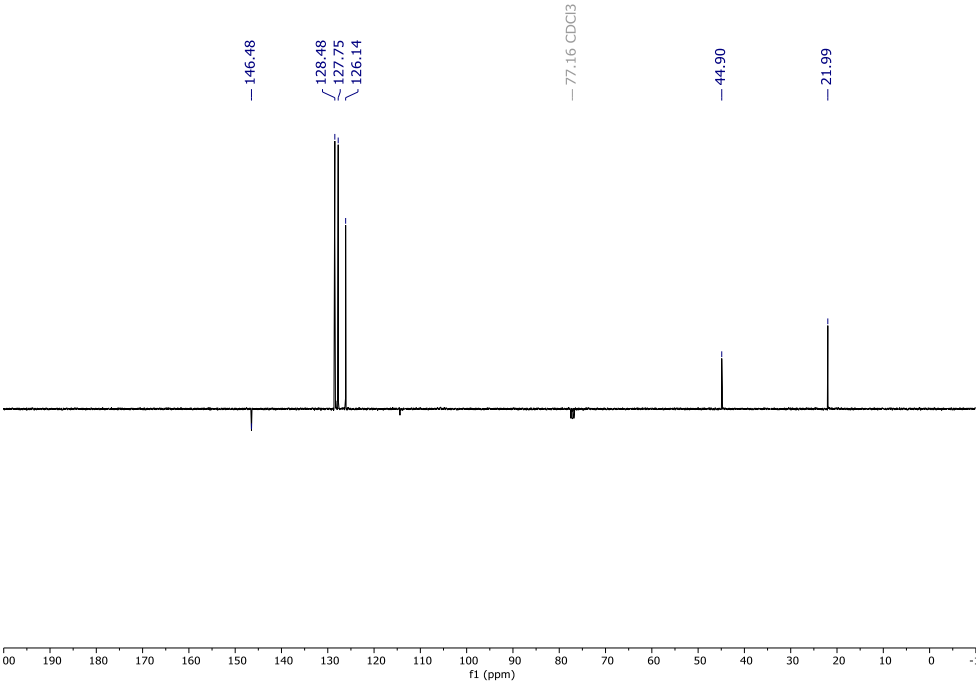
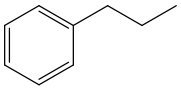


Figure S42: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **b_{10}** (101 MHz, $CDCl_3$).

1-Propylbenzene (b_{11})



According to the general procedure B, *trans*-β-methylstyrene **a_{11}** (325 µL, 2.5 mmol) afforded the title compound **b_{11}** as an oil (253 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.29 – 7.27 (m, 2H, CH_{Ar}), 7.25 – 7.15 (m, 3H, CH_{Ar}), 2.59 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH_2), 1.65 (sext, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH_2), 0.95 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 142.8 (*C*), 128.6 (*C*H), 128.3 (*C*H), 125.7 (*C*H), 38.2 (*C*H_2), 24.7 (*C*H_2), 14.0 (*C*H_3).

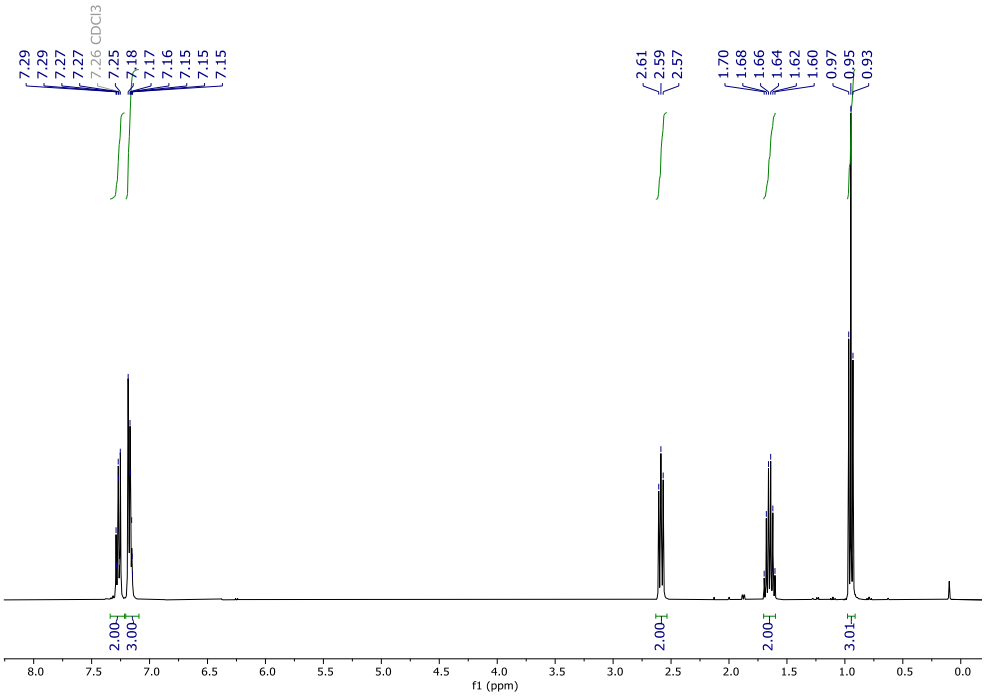


Figure S43: ^{1}H NMR spectrum of **b_{11}** (400 MHz, $CDCl_3$).

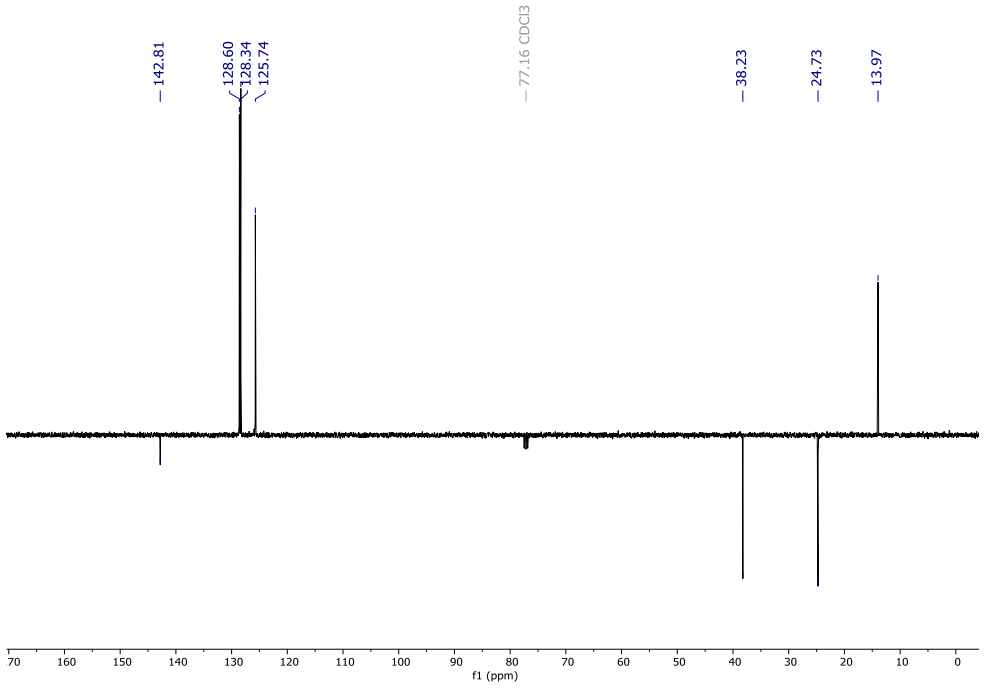


Figure S44: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **b_{11}** (101 MHz, $CDCl_3$).

n-Dodecane (b_{14})

According to the general procedure A, 1-dodecene **a_{14}** (556 µL, 2.5 mmol) afforded the title compound **b_{14}** as an oil (402 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.36 – 1.20 (m, 20H, CH_2), 0.89 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 32.2 (*C*H_2), 29.95 (*C*H_2), 29.90 (*C*H_2), 29.6 (*C*H_2), 22.9 (*C*H_2), 14.3 (*C*H_3).

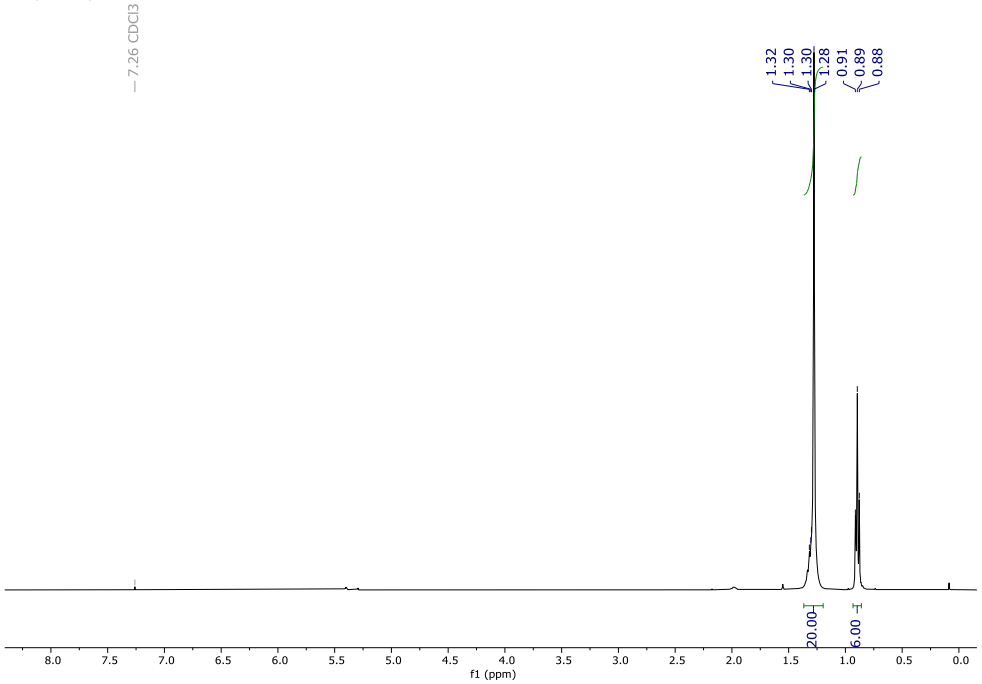


Figure S45: ^{1}H NMR spectrum of **b_{14}** (400 MHz, $CDCl_3$).

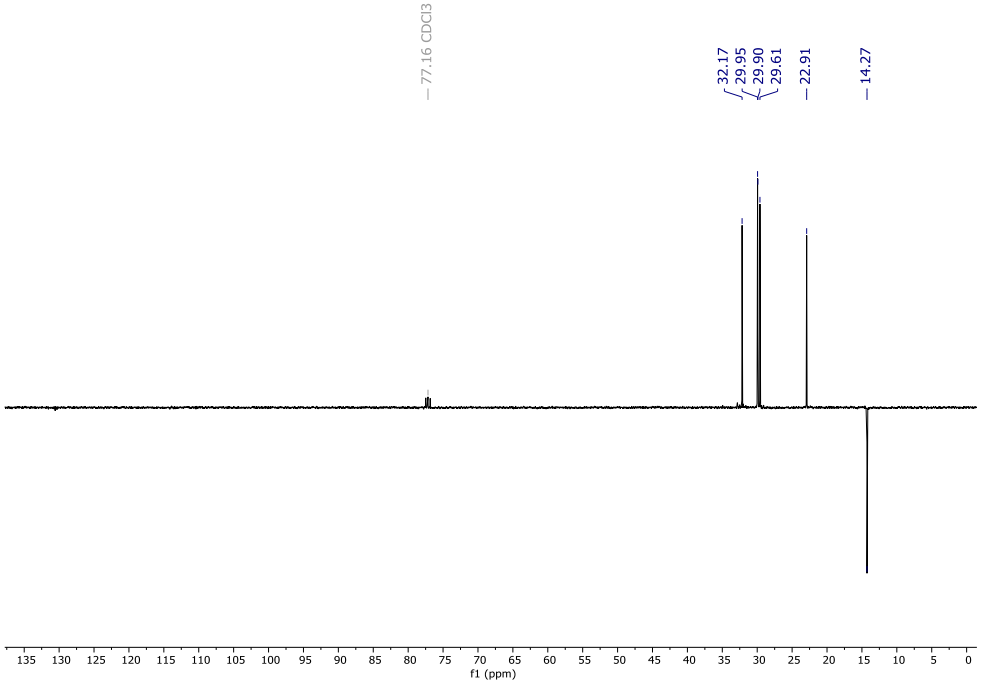
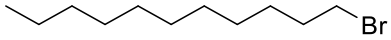


Figure S46: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **b_{14}** (101 MHz, $CDCl_3$).

11-Bromo-undecane (b_{15})



According to the general procedure **A**, 11-bromo-1-undecene $\mathbf{a_{15}}$ (550 µL, 2.5 mmol) afforded the title compound $\mathbf{b_{15}}$ as an oil (560 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.40 (t, $^3J_{HH}$ = 6.8 Hz, 2H, BrCH_2), 1.85 (p,$^3J_{HH}$ = 6.8 Hz, 2H, BrCH$_2$CH_2), 1.46 – 1.38 (m, 2H,), 1.37 – 1.17 (m, 14H, 7CH_2), 0.88 (t, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 34.1 (BrCH_2), 33.0 (CH_2), 32.0 (CH_2), 29.73 (CH_2), 29.70 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 28.9 (CH_2), 28.3 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

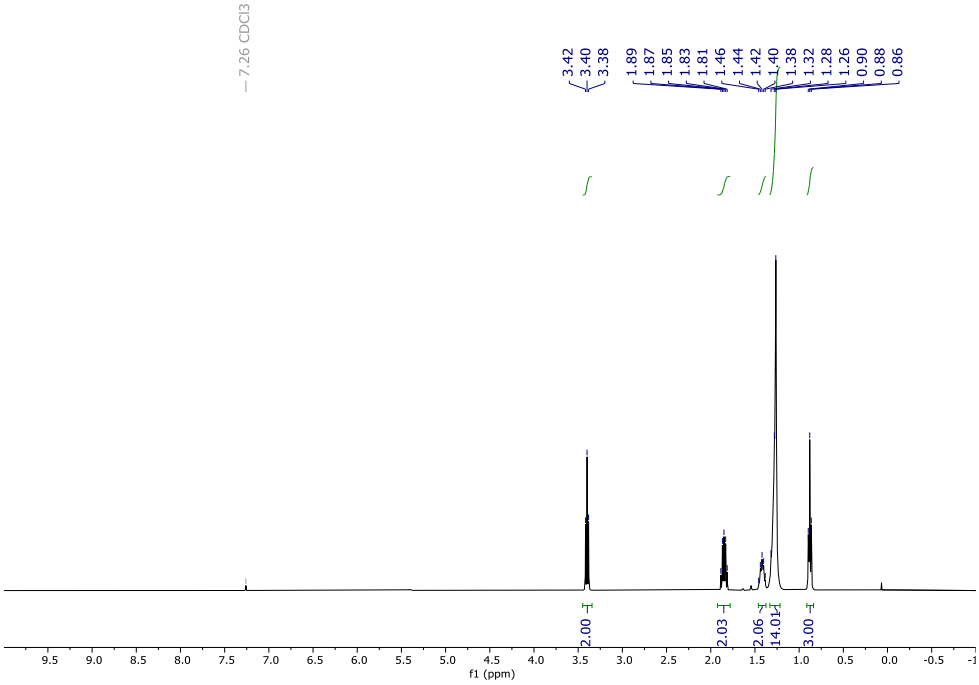


Figure S47: ^{1}H NMR spectrum of $\mathbf{b_{15}}$ (400 MHz, $CDCl_3$).

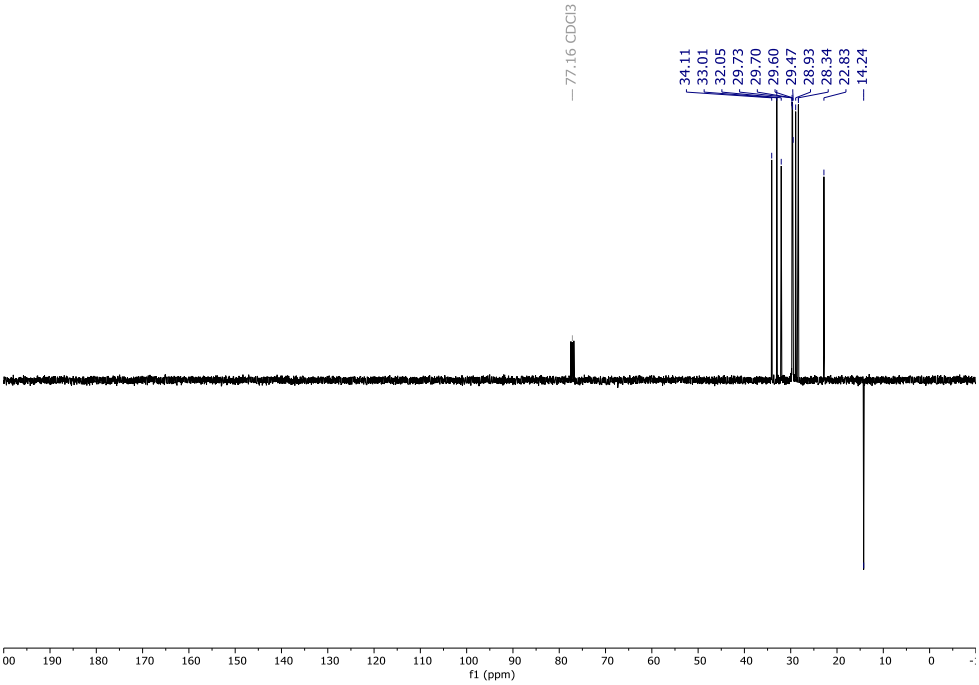
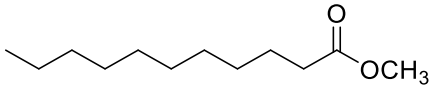


Figure S48: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{b_{15}}$ (101 MHz, $CDCl_3$).

Methyl undecanoate (b_{16})



According to the general procedure **B**, methyl-10-undecenoate **a_{16}** (562 µL, 2.5 mmol) afforded the title compound **b_{16}** as an oil (491 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.62 (s, 3H, OCH_3), 2.26 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2), 1.63 – 1.49 (m, 2H, CH_2), 1.33 – 1.16 (m, 14H, 7CH_2), 0.84 (t, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 174.3 (C=O), 51.4 (OCH_3), 34.2 (CH_2), 32.0 (CH_2), 29.64 (CH_2), 29.55 (CH_2), 29.40 (CH_2), 29.35 (CH_2), 29.2 (CH_2), 25.0 (CH_2), 22.8 (CH_2), 14.1 (CH_3).

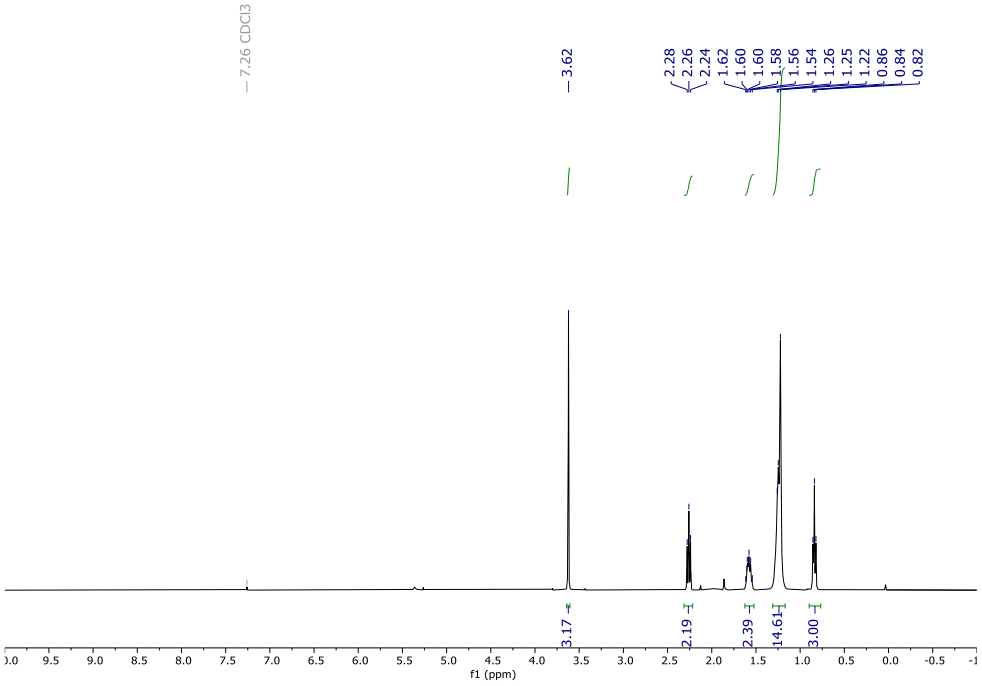


Figure S49: ^{1}H NMR spectrum of **b_{16}** (400 MHz, $CDCl_3$).

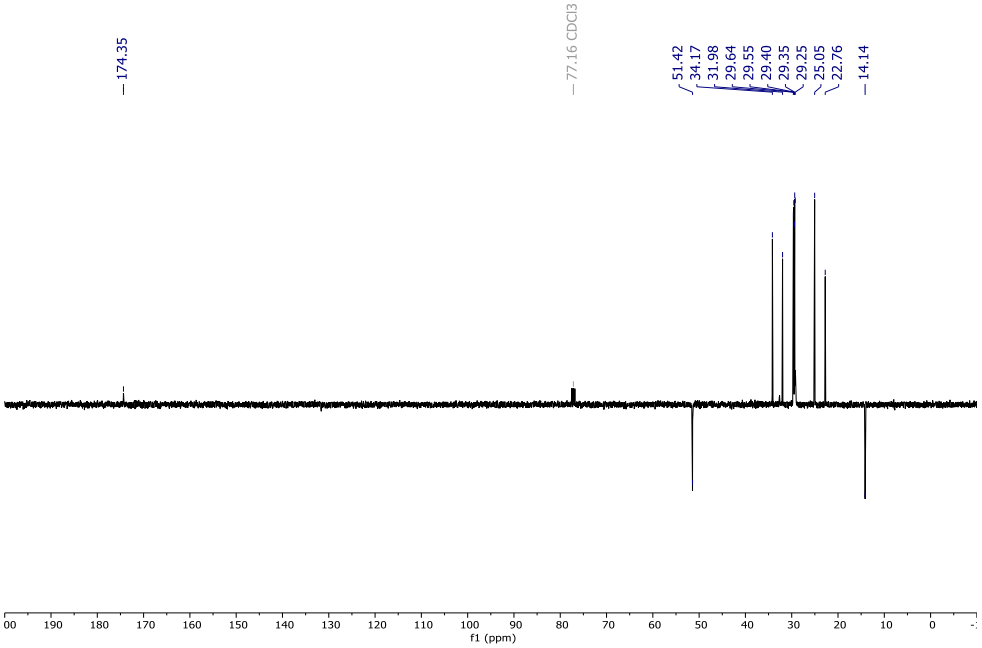
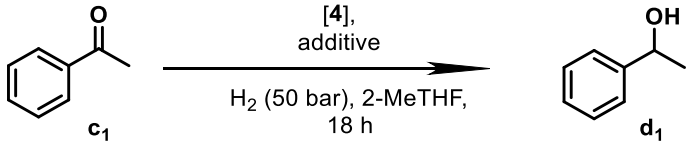


Figure S50: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **b_{16}** (101 MHz, $CDCl_3$).

Table S2. Optimisation of the parameters for the hydrogenation of acetophenone with pre-catalyst **4.**



Entry	**Catalyst (mol%)**	**Additive**	**T (°C)**	**GC conversion d_1(%)**
1[a]	1 (0.025)	$NaHBEt_3$	30	63
2[a]	1 (0.025)	$NaHBEt_3$	60	30
3[b]	3 (0.03)	$NaHBEt_3$	30	98
4[b]	3 (0.03)	$KHBEt_3$	30	98

[a] Acetophenone (2.5 mmol), additive (3 mol%), 2-MeTHF (2 ml); [b] Acetophenone (1 mmol), additive (7 mol%), 2-MeTHF (3 ml).

General Procedure for the catalytic hydrogenation of ketones

Procedure_D:

Complex **4** (16.7 mg, 0.030 mmol, 3 mol%) was weighed in air and transferred into a 10 mL Schlenk tube. The tube was then degassed and purged with argon. An autoclave connected to the Schlenk line was charged with the catalyst dissolved in distilled 2-MeTHF (1.0 mL), followed by $NaHBEt_3$ (70 µL, 7 mol%) in 2-MeTHF (0.5 mL), and the ketone (1 mmol) in 2-MeTHF (0.5 mL), in that order. The Schlenk tube was rinsed with an additional 2-MeTHF (1 mL) to ensure complete transfer.

Procedure_E:

Complex **4** (13.8 mg, 0.025 mmol, 5 mol%) was weighed in open air and transferred into a 10 mL Schlenk tube. The tube was degassed and purged with argon. An autoclave connected to the Schlenk line was charged with the catalyst dissolved in distilled 2-MeTHF (1.0 mL), followed by $NaHBEt_3$ (50 µL, 10 mol%) in 2-MeTHF (1.0 mL), and the ketone (0.5 mmol) in 2-MeTHF (1.0 mL), in that order. The Schlenk tube was rinsed with an additional 2-MeTHF (1 mL) to ensure complete transfer.

Reaction Conditions:

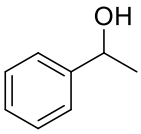
The autoclave was immediately pressurized with hydrogen (50 bar) and stirred in an oil bath at 30 °C (for procedure_E: at 60 °C) for 18 hours. After the reaction, the autoclave was cooled to room temperature, and the hydrogen pressure was released. The reaction mixture was then filtered through a small silica pad (2 cm, in a Pasteur pipette) and washed with dichloromethane. The solvent was removed under reduced pressure using a rotary evaporator.

Product purification:

The crude product was purified by column chromatography on silica gel using a petroleum ether/ethyl acetate mixture (9:1) as the eluent. This process yielded the corresponding alcohols, typically obtained with over 95% purity as determined by NMR spectroscopy.

^{1}H, ^{13}C, and ^{19}F NMR spectra of isolated alcohols

1-Phenylethanol (d_1)



According to the general procedure **D**, acetophenone **c_1** (118 µL, 1 mmol) afforded the title compound **d_1** as an oil (107 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.32 – 7.22 (m, 4H, C*H*$_{Ar}$), 7.23 – 7.12 (m, 1H, C*H*$_{Ar}$), 4.80 (q, $^{3}J_{HH}$ = 6.5 Hz, 1H, C*H*CH$_3$), 1.89 (br. s, 1H, O*H*), 1.41 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, C*H*$_3$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 145.9 (*C*), 128.6 (*C*H), 127.6 (*C*H), 125.5 (*C*H), 70.5 (*C*HOH), 25.3 (*C*H$_3$).

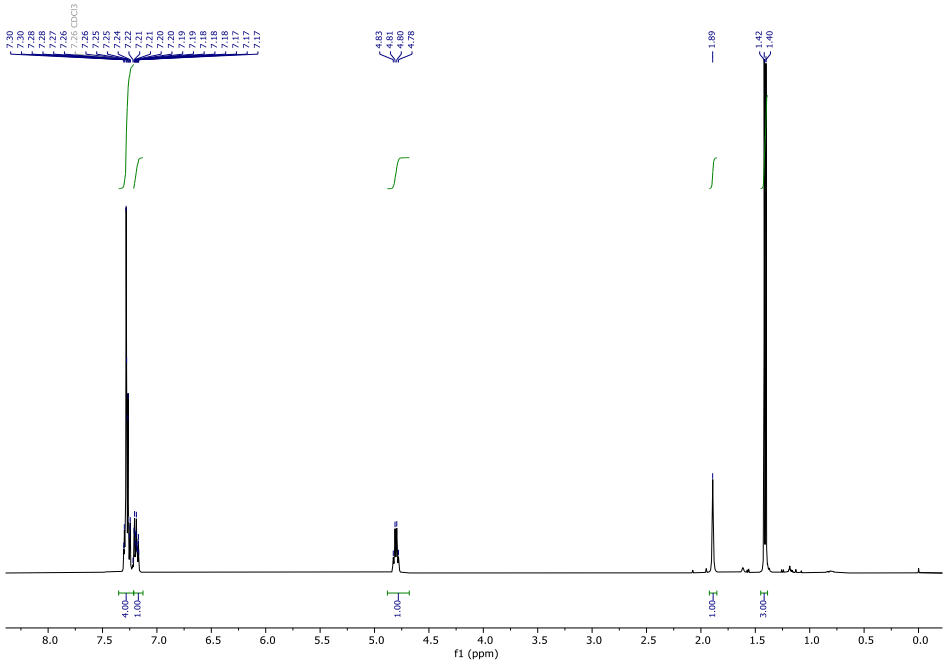


Figure S51: ^{1}H NMR spectrum of **d_1** (400 MHz, $CDCl_3$).

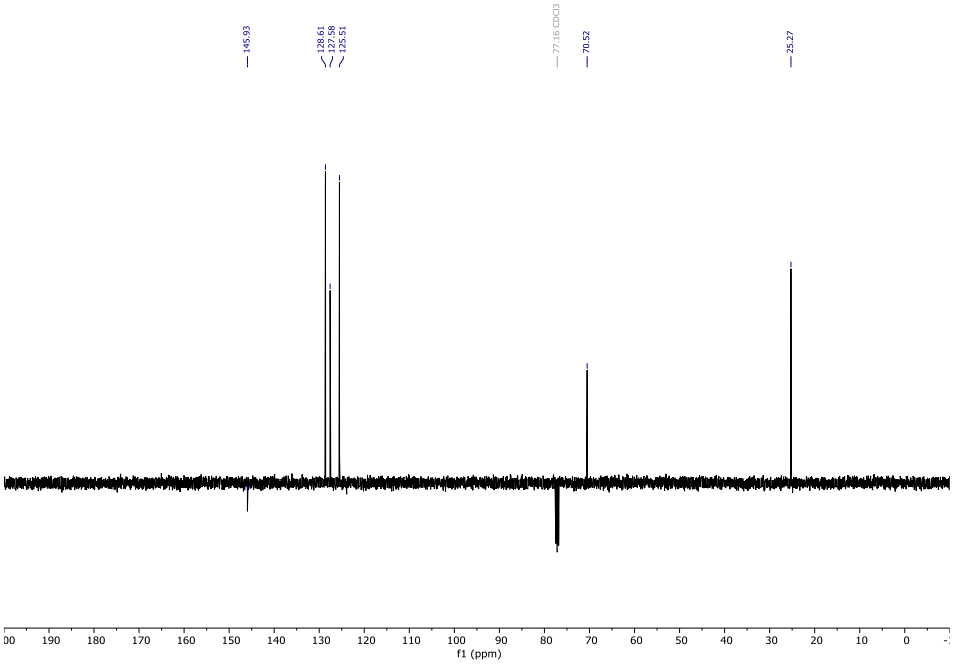
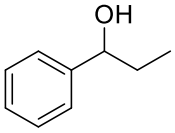


Figure S52: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **d_1** (101 MHz, $CDCl_3$).

1-Phenylpropanol (d_2)



According to the general procedure **D**, propiophenone $\mathbf{c_2}$ (134 µL, 1 mmol) afforded the title compound $\mathbf{d_2}$ as an oil (117 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.31 – 7.21 (m, 4H, CH_{Ar}), 7.21 – 7.15 (m, 1H, CH_{Ar}), 4.48 (t, $^3J_{HH}$ = 6.7 Hz, 1H, CHCH$_2$), 2.07 (br. s, 1H, OH), 1.81 – 1.56 (m, 2H, CH_2), 0.82 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 144.7 (*C*), 128.5 (*C*H), 127.5 (*C*H), 126.1 (*C*H), 76.1(*C*HOH), 31.9 (*C*H$_2$), 10.2 (*C*H$_3$).

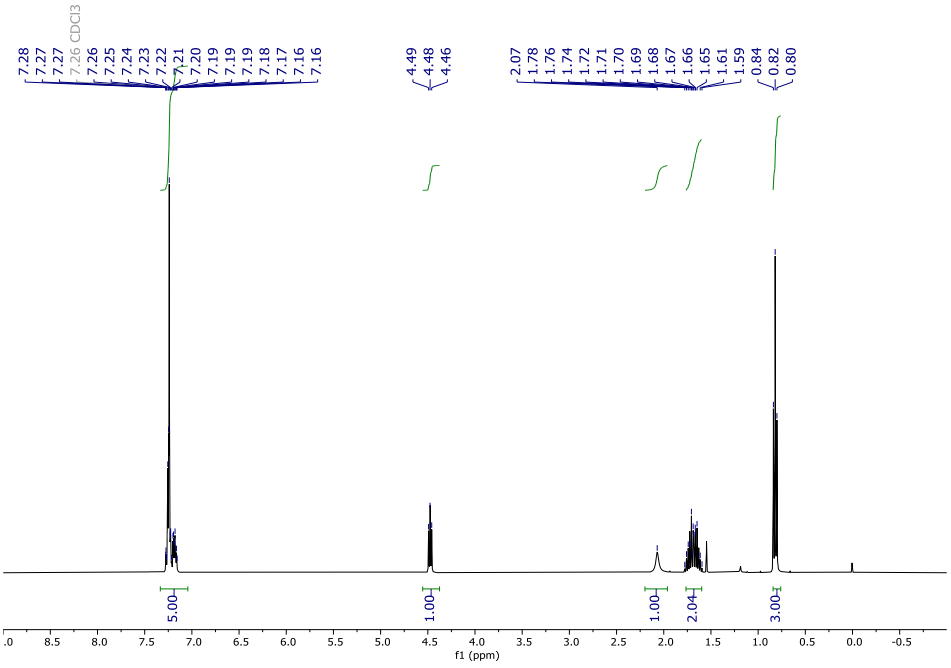


Figure S53: ^{1}H NMR spectrum of $\mathbf{d_2}$ (400 MHz, $CDCl_3$).

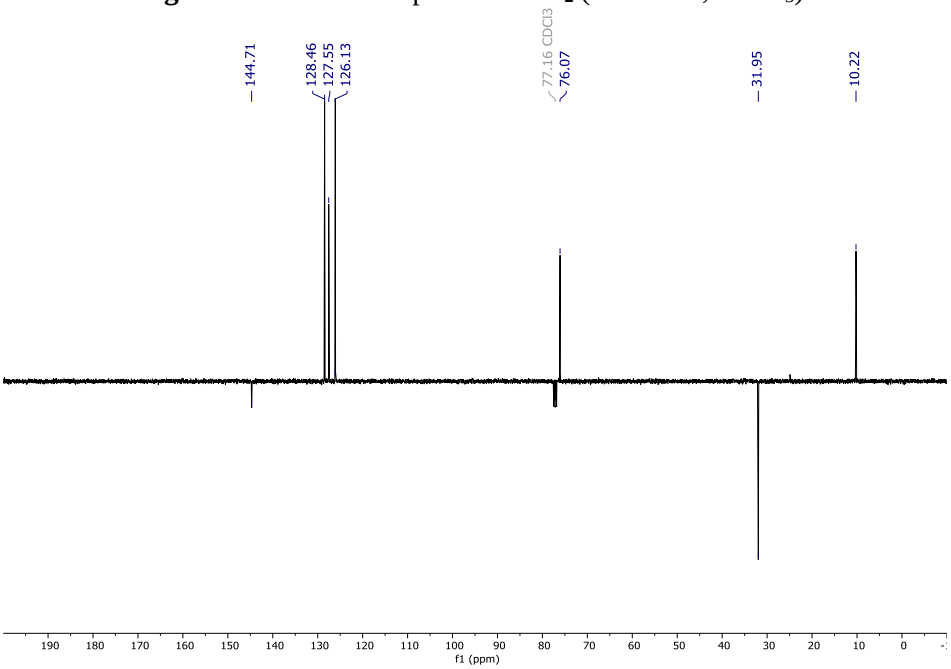
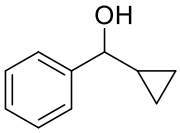


Figure S54: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{d_2}$ (101 MHz, $CDCl_3$).

α-Cyclopropylphenyl methanol (d_4)



According to the general procedure **D**, cyclopropyl phenyl ketone $\mathbf{c_4}$ (138 µL, 1 mmol) afforded the title compound $\mathbf{d_4}$ as an oil (122 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.46 – 7.40 (m, 2H, C*H*$_{Ar}$), 7.39 – 7.33 (m, 2H, C*H*$_{Ar}$), 7.32 – 7.26 (m, 1H, C*H*$_{Ar}$), 4.01 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C*H*OH), 2.11 (br. s, 1H, O*H*), 1.28 – 1.17 (m, 1H), 0.67 – 0.60 (m, 1H), 0.60 – 0.52 (m, 1H), 0.50 – 0.45 (m, 1H), 0.42 – 0.34 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 144.0 (*C*), 128.5 (*C*H), 127.6 (*C*H), 126.1 (*C*H), 78.6 (*C*HOH), 19.3 (*C*H), 3.7 (CH_2), 2.9 (CH_2).

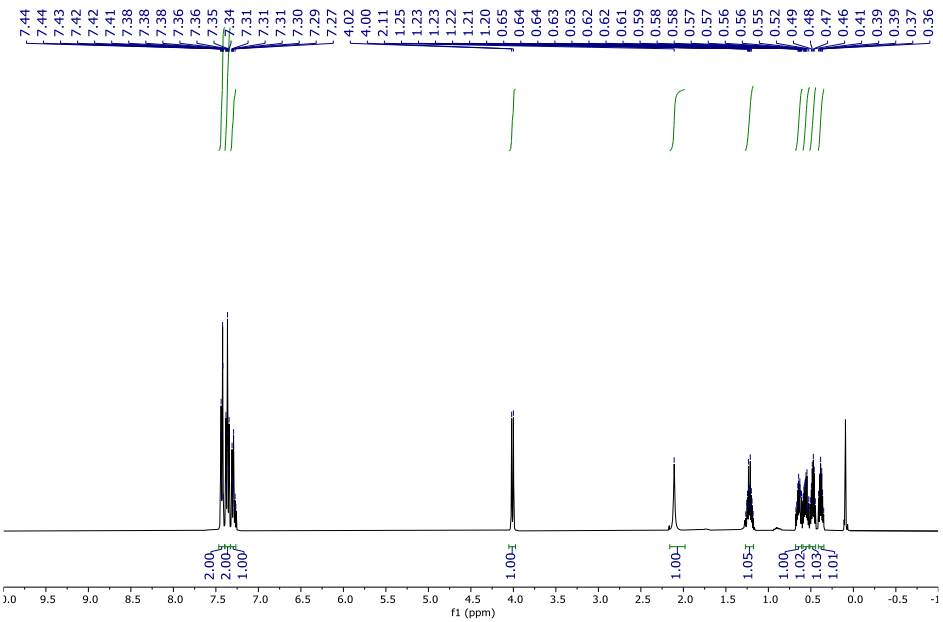


Figure S55: ^{1}H NMR spectrum of $\mathbf{d_4}$ (400 MHz, $CDCl_3$).

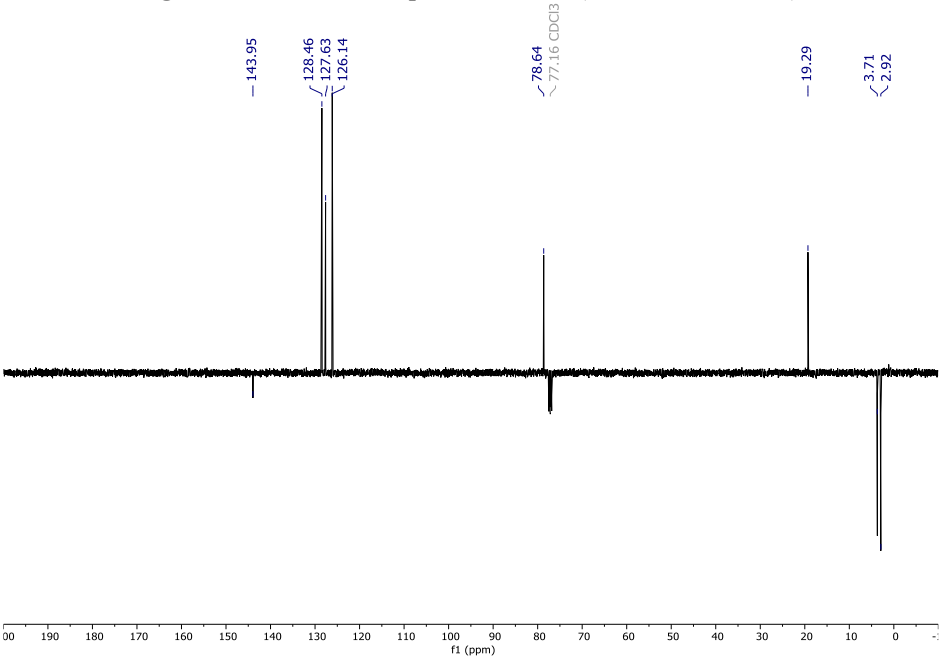
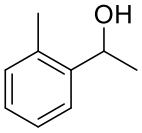


Figure S56: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{d_4}$ (101 MHz, $CDCl_3$).

1-(2-Methylphenyl)ethanol (d_5)



According to the general procedure **D**, 2-methylacetophenone $\mathbf{c_5}$ (132 µL, 1 mmol) afforded the title compound $\mathbf{d_5}$ as an oil (113 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.43 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C*H*$_{Ar}$), 7.16 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, C*H*$_{Ar}$), 7.13 – 7.01 (m, 2H, C*H*$_{Ar}$), 5.05 (q, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*CH$_3$), 2.27 (s, 3H, C*H*$_3$), 1.73 (br. s, 1H, O*H*), 1.39 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CHC*H*$_3$);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 144.0 (*C*), 134.4 (*C*), 130.5 (*C*H), 127.3 (*C*H), 126.5 (*C*H), 124.6 (*C*H), 67.0 (*C*HOH), 24.1 (*C*H$_3$), 19.0 (*C*H$_3$).

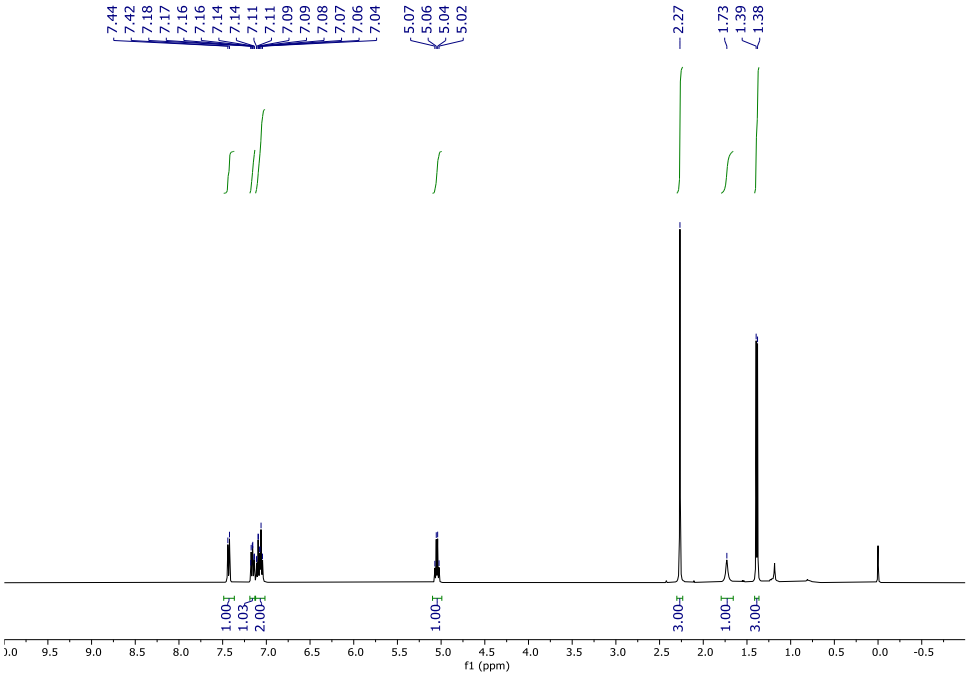


Figure S57: ^{1}H NMR spectrum of $\mathbf{d_5}$ (400 MHz, $CDCl_3$).

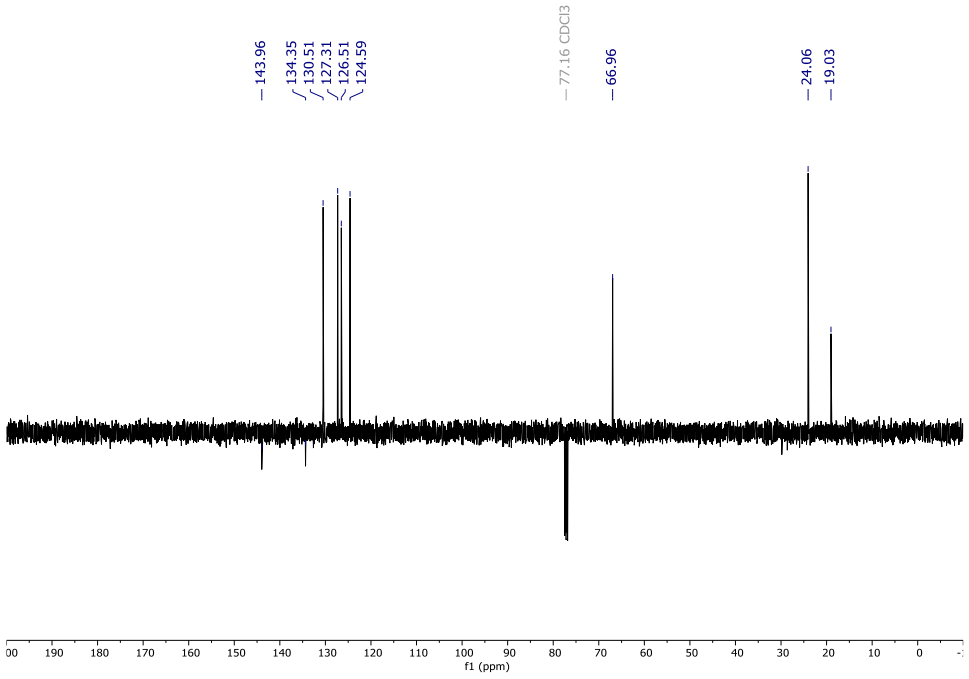
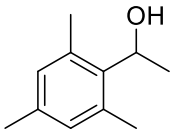


Figure S58: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{d_5}$ (101 MHz, $CDCl_3$).

1-(2,4,6-Trimethylphenyl) ethanol (d_6)



According to the general procedure **D**, 2,4,6-trimethylacetophenone **c_6** (162 µL, 1 mmol) afforded the title compound **d_6** as a white solid (110 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 6.84 (s, 2H, C*H*$_{Ar}$), 5.36 (q, $^3J_{HH}$ = 6.7 Hz, 1H, C*H*CH$_3$), 2.43 (s, 6H, 2C*H*$_{3ortho\text{-}Mes}$), 2.27 (s, 3H, C*H*$_{3para\text{-}Mes}$), 1.90 (br. s, 1H, O*H*), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CHC*H*$_3$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 137.8 (*C*), 136.5 (*C*), 135.7 (*C*), 130.2 (*C*H), 67.6 (*C*HOH), 21.7 (*C*H$_3$), 20.8 (*C*H$_3$), 20.6 (*C*H$_3$).

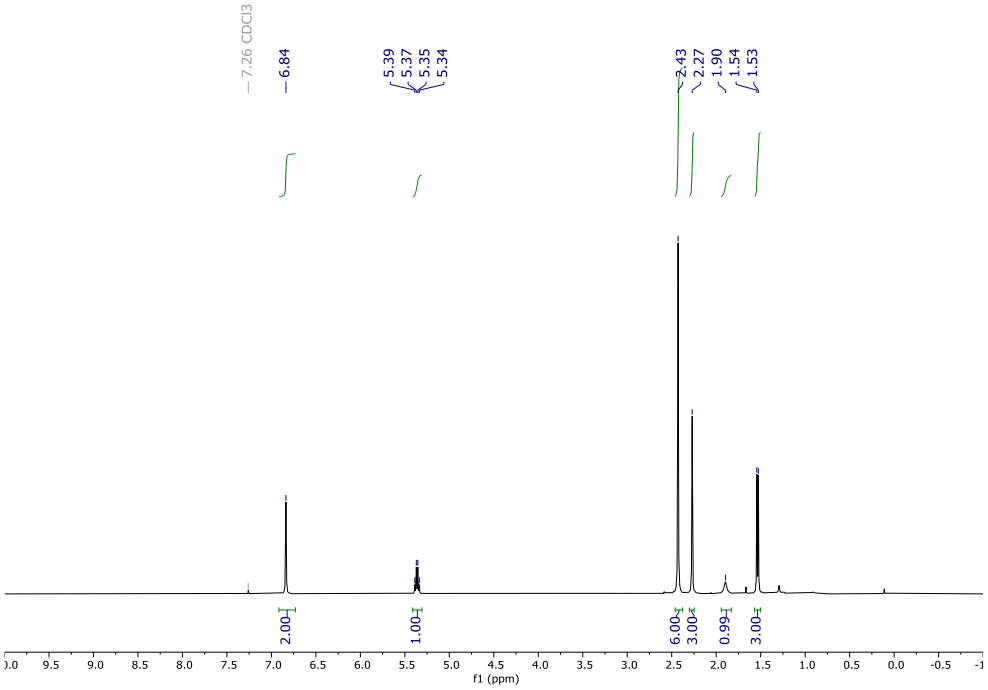


Figure S59: ^{1}H NMR spectrum of **d_6** (400 MHz, $CDCl_3$).

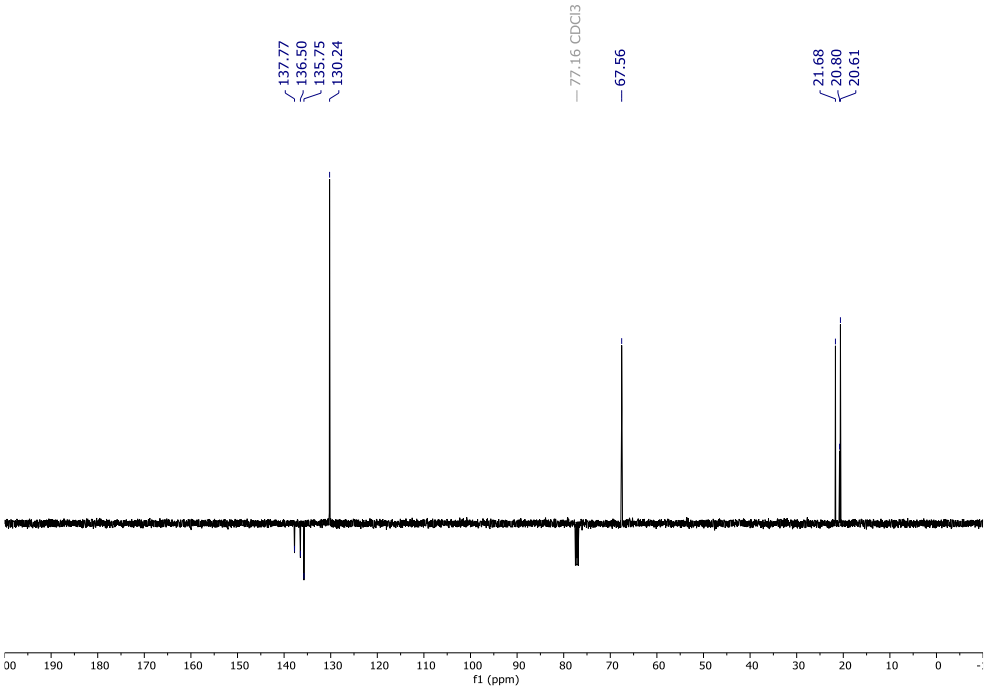
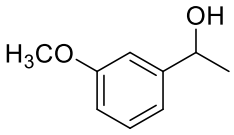


Figure S60: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **d_6** (101 MHz, $CDCl_3$).

1-(3-Methoxyphenyl)ethanol (d_7)



According to the general procedure **D**, 3-methoxyacetophenone **c**$_7$ (138 µL, 1 mmol) afforded the title compound **d**$_7$ as an oil (122 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.23 – 7.19 (m, 1H), 6.92 – 6.85 (m, 2H), 6.79 – 6.75 (m, 1H), 4.79 (q, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*OH), 3.75 (s, 3H, OCH_3), 2.30 (br. s, 1H, OH), 1.43 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 159.8 (*C*), 147.7 (*C*), 129.6 (*C*H), 117.8 (*C*H), 112.9 (*C*H), 111.0 (*C*H), 70.3 (*C*HOH), 55.3 (O*C*H$_3$), 25.2 (*C*H$_3$).

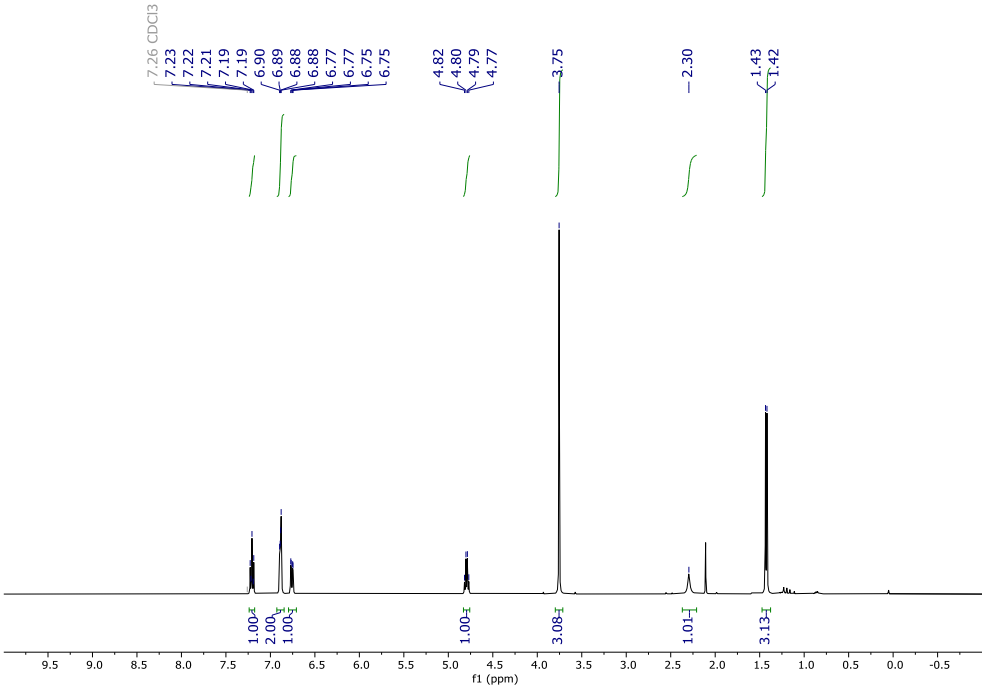


Figure S61: ^{1}H NMR spectrum of **d**$_7$ (400 MHz, $CDCl_3$).

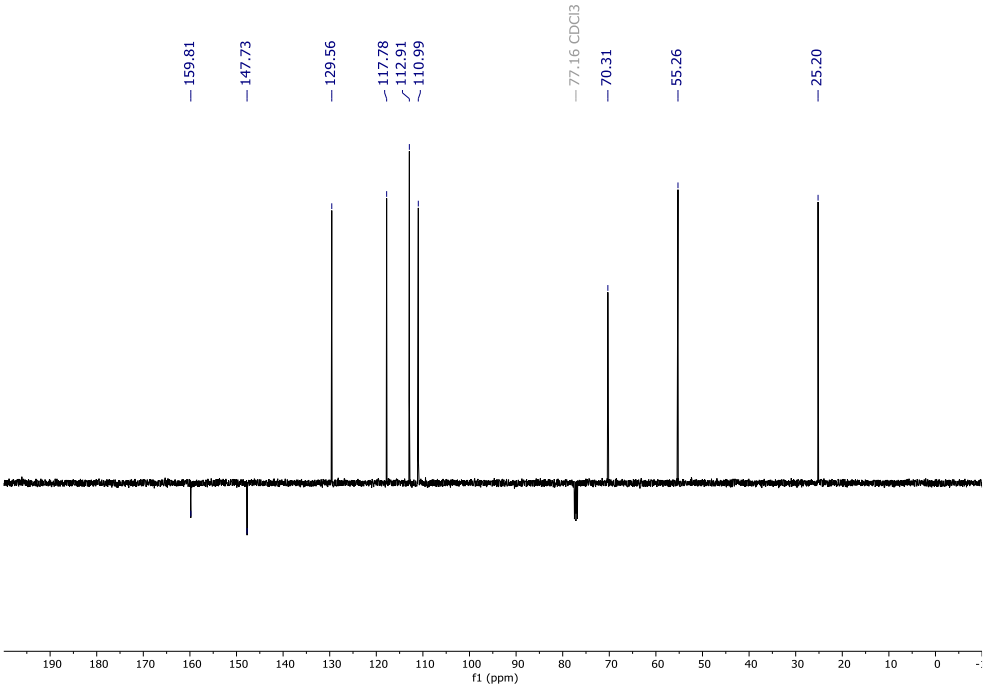
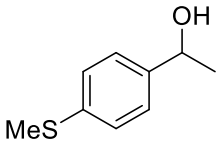


Figure S62: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **d**$_7$ (101 MHz, $CDCl_3$).

1-(4-Methylthiophenyl)ethanol (d_8)



According to the general procedure **D**, 4-methylthioacetophenone $\mathbf{c_8}$ (167 mg, 1 mmol) afforded the title compound $\mathbf{d_8}$ as a white solid (143 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.20 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C*H*Ar), 7.15 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C*H*Ar), 4.75 (q, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*OH), 2.39 (s, 3H, SCH_3), 2.03 (br. s, 1H, O*H*), 1.38 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 142.9 (*C*), 137.5 (*C*), 126.9 (*C*H), 126.1 (*C*H), 70.0 (*C*HOH), 25.8 (CH*C*H_3), 16.1 (S*C*H_3).

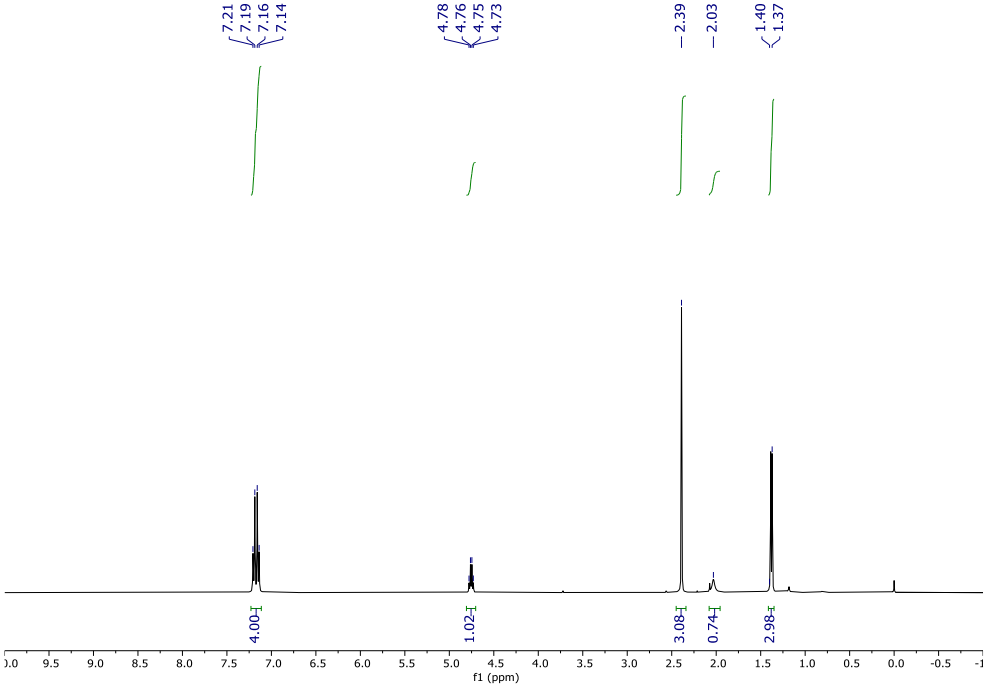


Figure S63: ^{1}H NMR spectrum of $\mathbf{d_8}$ (400 MHz, $CDCl_3$).

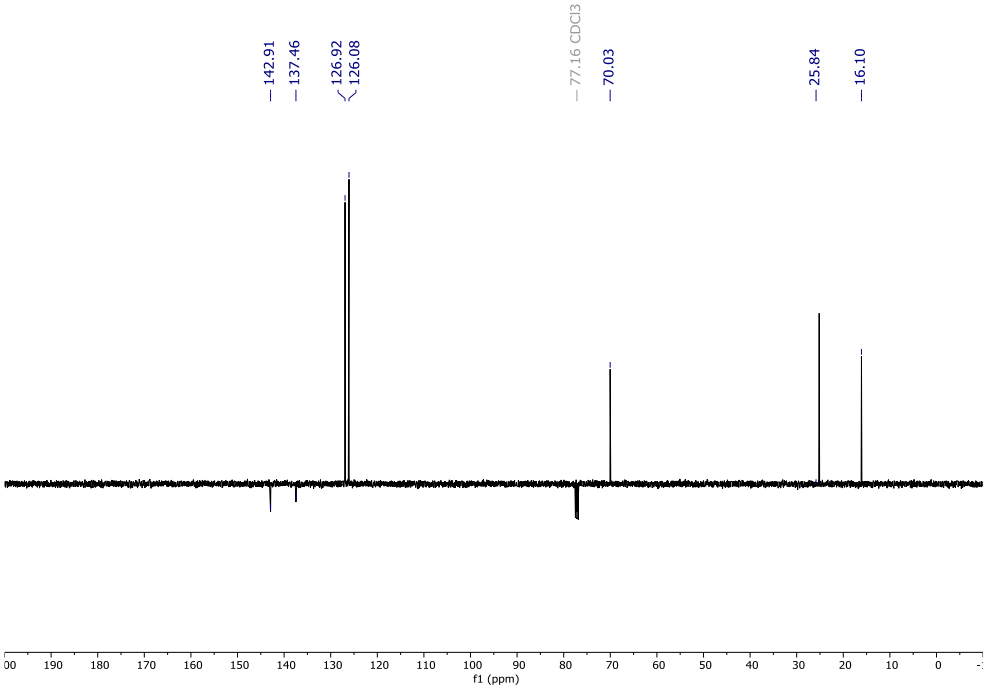
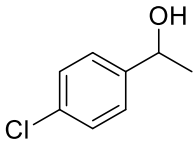


Figure S64: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of $\mathbf{d_8}$ (101 MHz, $CDCl_3$).

1-(4-Chlorophenyl)ethanol (d_9)



According to the general procedure **D**, 4-Chloroacetophenone **c_9** (130 µL, 1 mmol) afforded the title compound **d_9** as an oil (132 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.28 – 7.18 (m, 4H, C*H*$_{Ar}$), 4.79 (q, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*CH_3), 2.09 (br. s, 1H, O*H*), 1.40 (d,$^3J_{HH}$ = 6.5 Hz, 3H, C*H*$_3$);
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 144.4 (*C*), 133.1 (*C*), 128.7 (*C*H), 126.9 (*C*H), 69.8 (*C*HOH), 25.4 (*C*H_3).

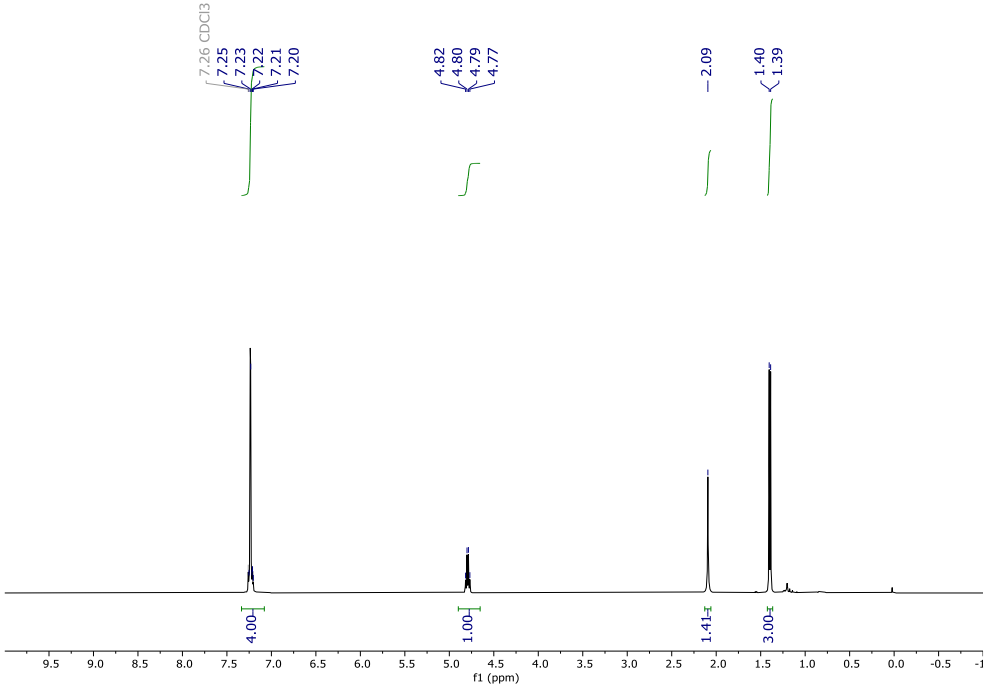


Figure S65: ^{1}H NMR spectrum of **d_9** (400 MHz, $CDCl_3$).

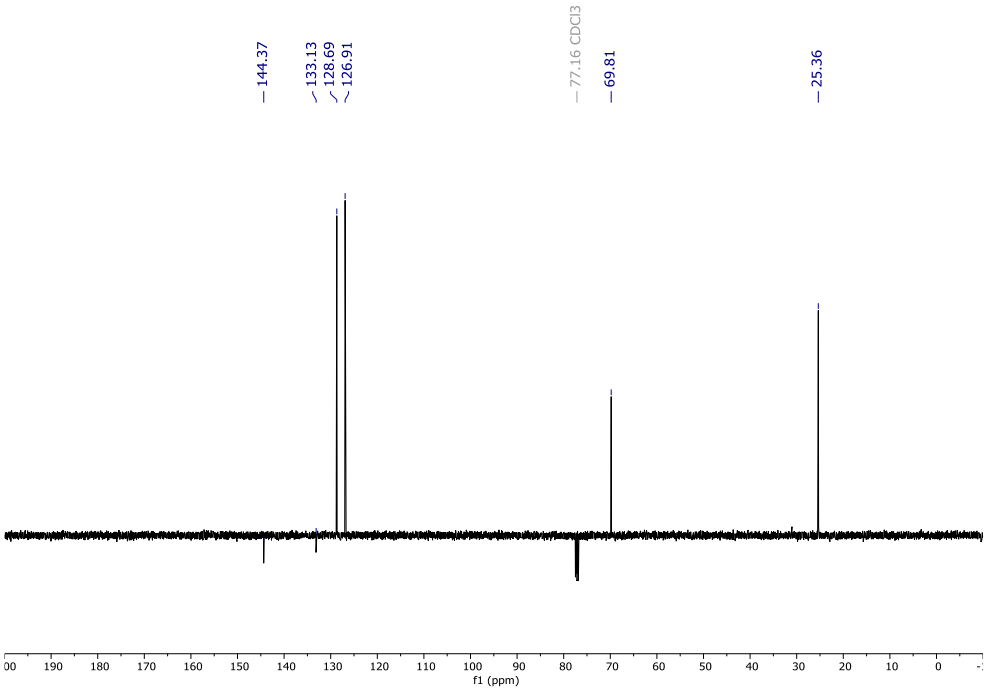
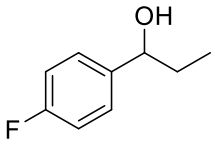


Figure S66: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **d_9** (101 MHz, $CDCl_3$).

1-(4-Fluorophenyl)propanol (d_{10})



According to the general procedure **D**, 1-(4-fluorophenyl)propan-1-one **c_{10}** (139 µL, 1 mmol) afforded the title compound **d_{10}** as an oil (113 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.36 – 7.23 (m, 2H, CH_{Ar}), 7.04 – 6.98 (m, 2H, CH_{Ar}), 4.55 (t, $^{3}J_{HH}$ = 6.6 Hz, 1H, CHOH), 2.13 (br. s, 1H, OH), 1.84 – 1.64 (m, 2H,CH_2CH$_3$), 0.88 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 162.2 (d, *C*, $^{1}J_{CF}$ = 245.1 Hz), 140.4 (d, *C*, $^{4}J_{CF}$ = 2.9 Hz), 127.7 (d, *C*H, $^{3}J_{CF}$ = 8.8 Hz), 115.4 (d, *C*H, $^{2}J_{CF}$ = 21.2 Hz), 75.4 (*C*HOH), 32.1 (*C*H$_2$), 10.1 (*C*H$_3$).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -115.3.

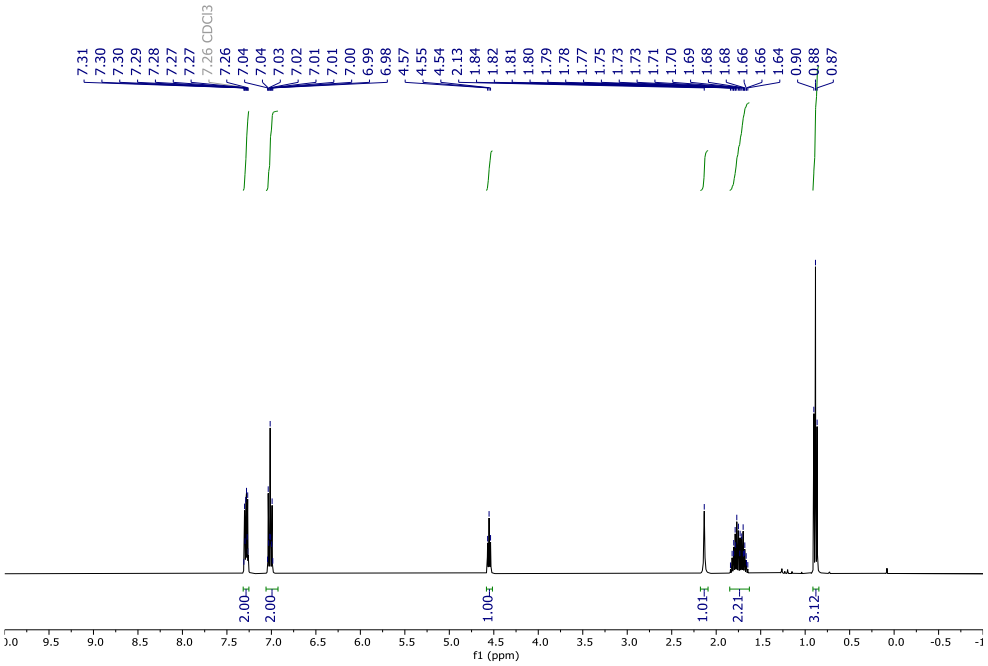


Figure S67: ^{1}H NMR spectrum of **d_{10}** (400 MHz, $CDCl_3$).

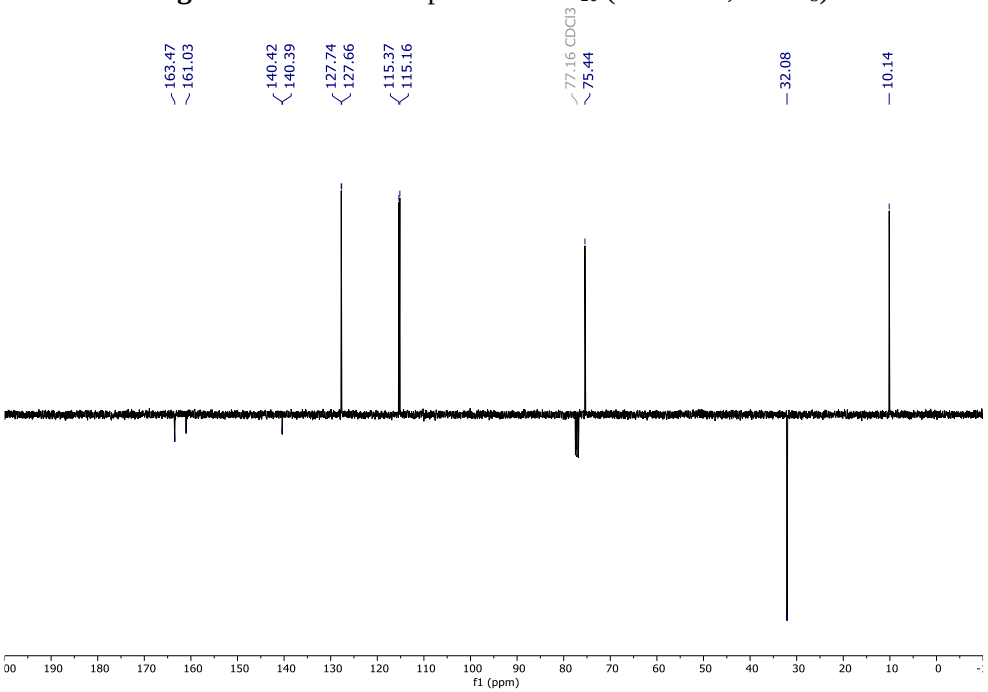


Figure S68: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **d_{10}** (101 MHz, $CDCl_3$).

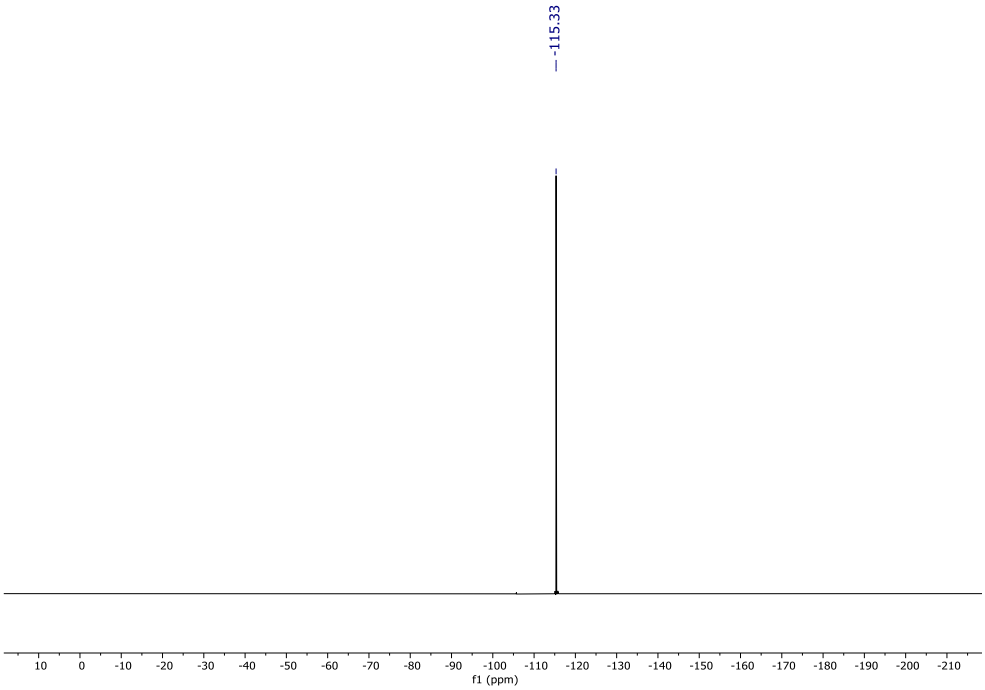
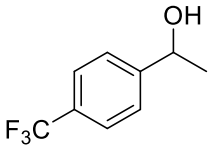


Figure S69: $^{19}F\{^{1}H\}$ NMR spectrum of **d_{10}** (377 MHz, $CDCl_3$).

1-(4-Trifluoromethylphenyl)ethanol (d_{11})



According to the general procedure **D**, 4-(trifluoromethyl)-acetophenone **c_{11}** (189 mg, 1 mmol) afforded the title compound **d_{11}** as an oil (156 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.59 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_{Ar}), 7.47 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_{Ar}), 4.93 (q, $^{3}J_{HH}$ = 6.5 Hz, 1H, C*H*OH), 2.26 (br. s, 1H, O*H*), 1.49 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 149.8 (q, $^{5}J_{CF}$ = 2.0 Hz, *C*), 129.7 (q, $^{2}J_{CF}$ = 32.3 Hz, *C*), 125.8 (*C*H), 125.6 (q, $^{3}J_{CF}$ = 4.0 Hz, *C*H), 124.3 (q, $^{1}J_{CF}$ = 275.5 Hz, *C*F_3), 69.9 (*C*HOH), 25.5 (*C*H_3).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -62.5 (CF_3).

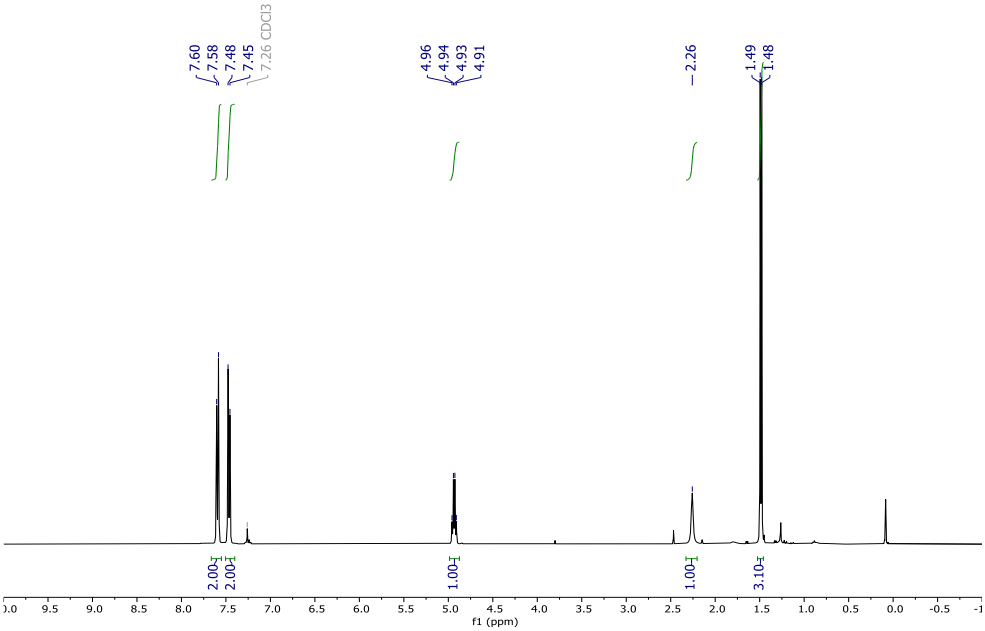


Figure S70: ^{1}H NMR spectrum of **d_{11}** (400 MHz, $CDCl_3$).

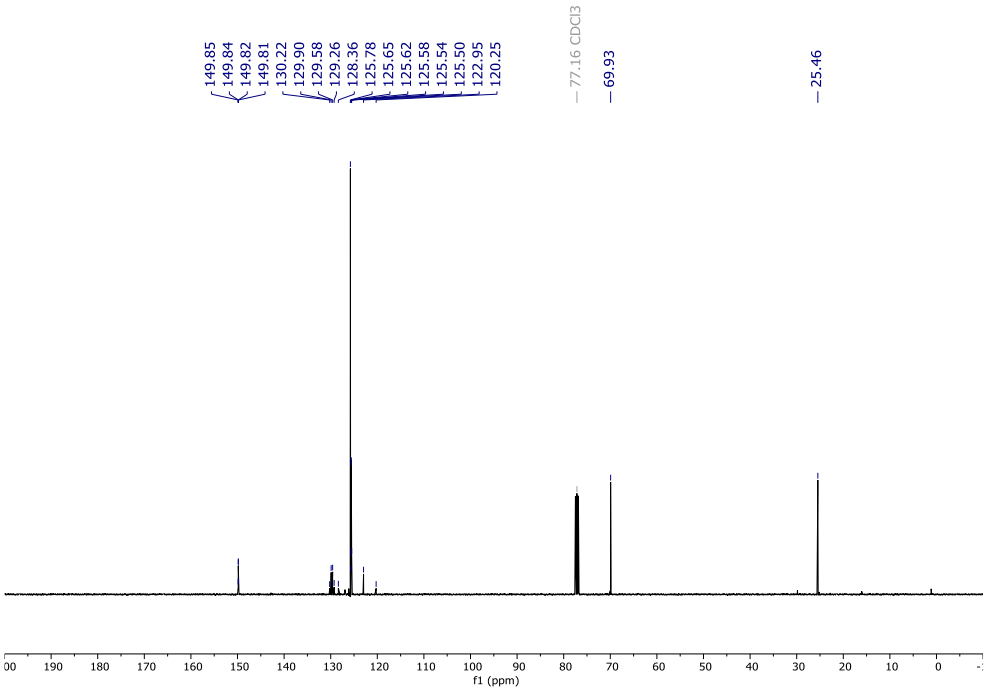


Figure S71: $^{13}C\{^{1}H\}$ NMR of **d_{11}** (101 MHz, $CDCl_3$).

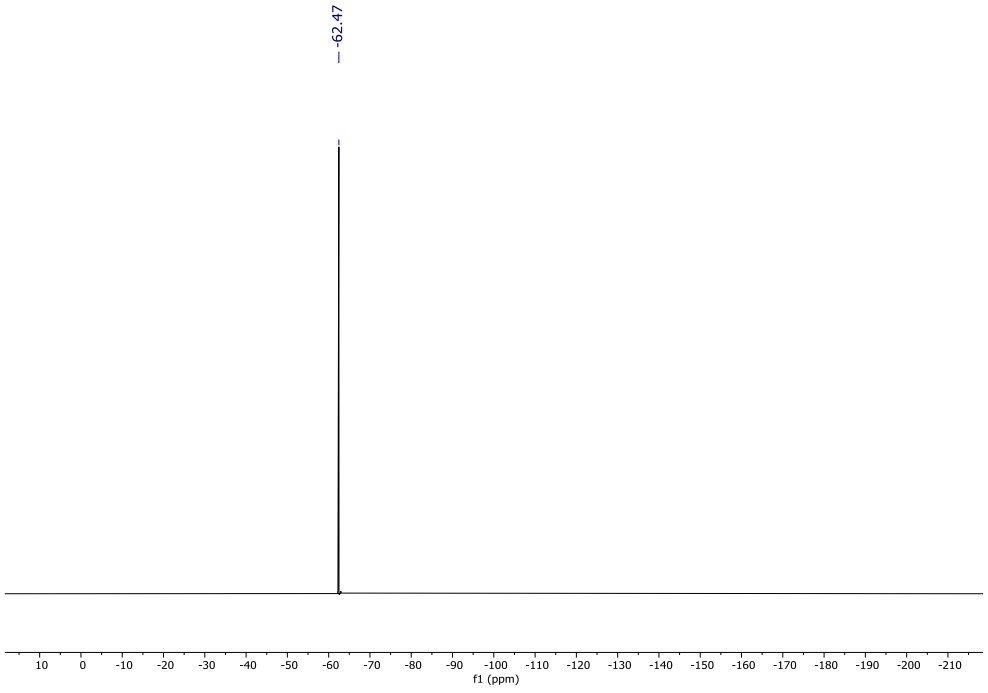
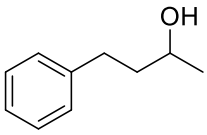


Figure S72: $^{19}F\{^{1}H\}$ NMR spectrum of **d_{11}** (377 MHz, $CDCl_3$).

4-phenylbutan-2-ol (d_{13})



According to the general procedure **D**, benzylacetone **c_{13}** (150 µL, 1 mmol) afforded the title compound **d_{13}** as an oil (127 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.33 – 7.27 (m, 2H, CH_{Ar}), 7.24 – 7.17 (m, 3H, CH_{Ar}), 3.84 (sext, t, $^{3}J_{HH}$ = 6.2 Hz, 1H), 2.81 – 2.65 (m, 2H), 1.82 – 1.76 (m, 2H), 1.68 (br. s, 1H), 1.24 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 142.2 (*C*), 128.5 (*C*H), 125.9 (*C*H), 67.6 (*C*HOH), 40.9 (CH_2), 32.2 (CH_2), 23.7 (CH_3).

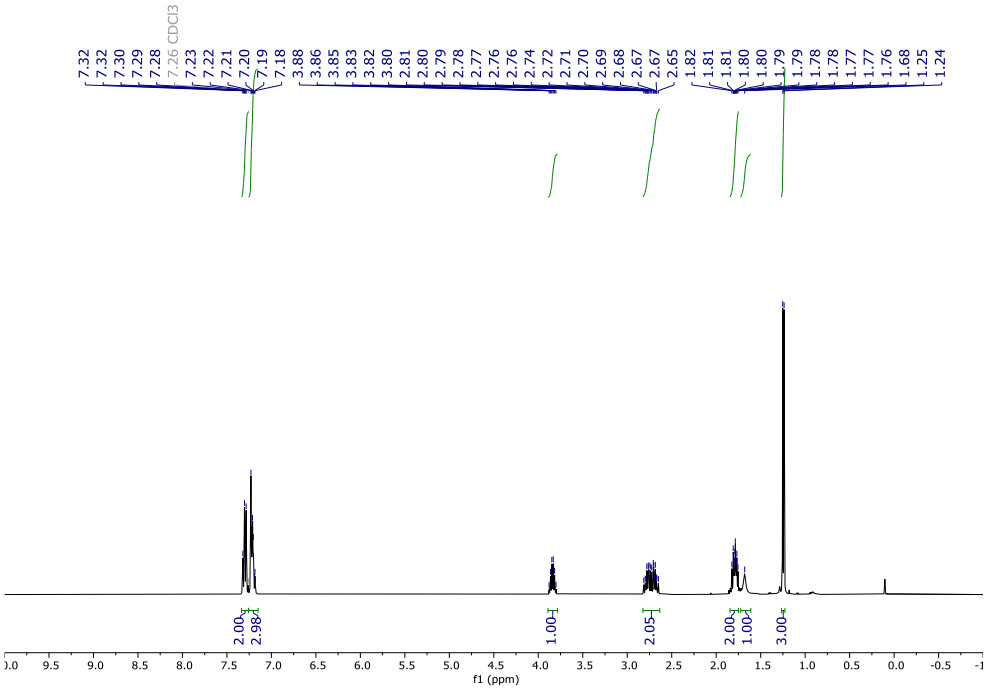


Figure S73: ^{1}H NMR spectrum of **d_{13}** (400 MHz, $CDCl_3$).

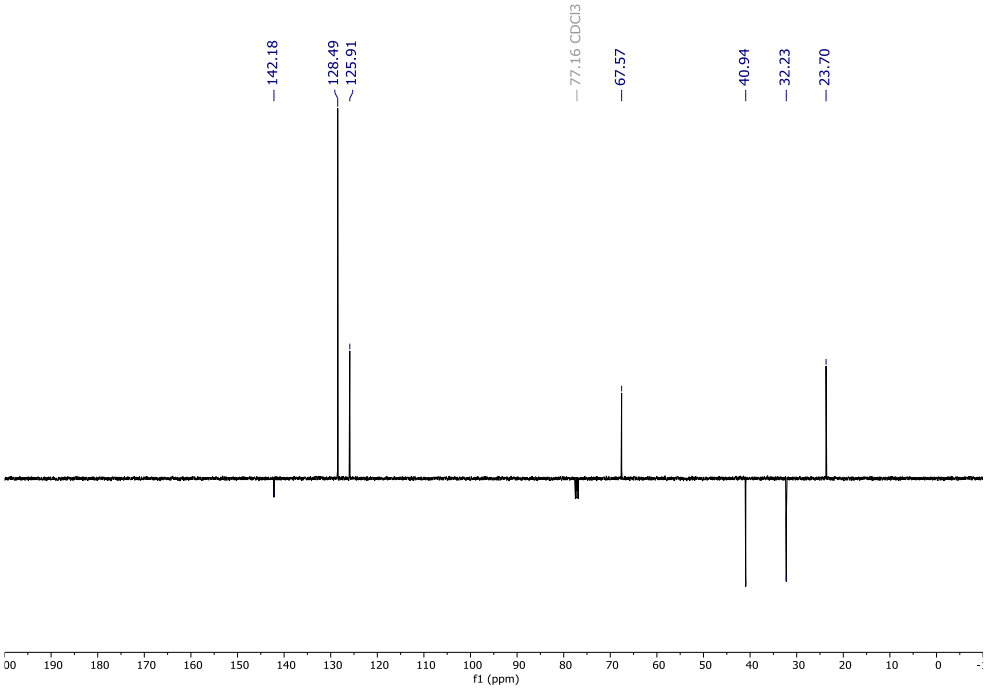
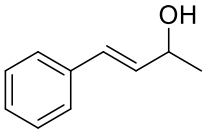


Figure S74: ^{13}C{^{1}H} NMR spectrum using the J-MOD sequence of **d_{13}** (101 MHz, $CDCl_3$).

4-Phenyl-3-buten-2-ol (d_{14}) and 4-Phenylbutan-2-ol (d_{13})

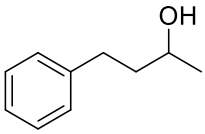
According to the general procedure **E** (hydrogenation performed at 60 °C), 4-phenyl-3-buten-2-one **c_{14}** (74 mg, 0.5 mmol) afforded a mixture of 4-phenyl-3-buten-2-ol (**d_{14}**) and 4-phenylbutan-2-ol (**d_{13}**) in a ration **d_{14}**:**d_{13}** = 67:33, as an oil (73 mg, 98 %).

4-Phenyl-3-buten-2-ol d_{14}



^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.28 – 7.07 (m, 5H, C*H*$_{Ar}$), 6.46 (d, $^3J_{HH}$ = 16.0 Hz, 1H, C*H*), 6.16 (dd, $^3J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*), 4.37 (p, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*OH), 2.05 (br. s, 1H, O*H*), 1.27 (d, $^3J_{HH}$ = 6.4 Hz, 1H, C*H*$_3$);

4-Phenylbutan-2-ol d_{13}



^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.28 – 7.07 (m, 5H, C*H*$_{Ar}$), 3.71 (sext, $^3J_{HH}$ = 6.1 Hz, 1H, C*H*OH), 2.80 – 2.42 (m, 2H, C*H*$_2$), 2.05 (br. s, 1H, O*H*), 1.81-1.54 (m, 2H, C*H*$_2$), 1.12 (d, $^3J_{HH}$ = 6.1 Hz, 3H, C*H*$_3$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ 142.2(*C*), 136.8(*C*), 133.7(*C*H), 129.4(*C*H), 128.6(*C*H), 128.5(*C*H), 127.7(*C*H), 126.5(*C*H), 125.9(*C*H), 68.9(*C*HOH), 67.5(*C*HOH), 40.9(*C*H$_2$), 32.2(*C*H$_2$), 23.6(*C*H$_3$),23.5(*C*H$_3$).

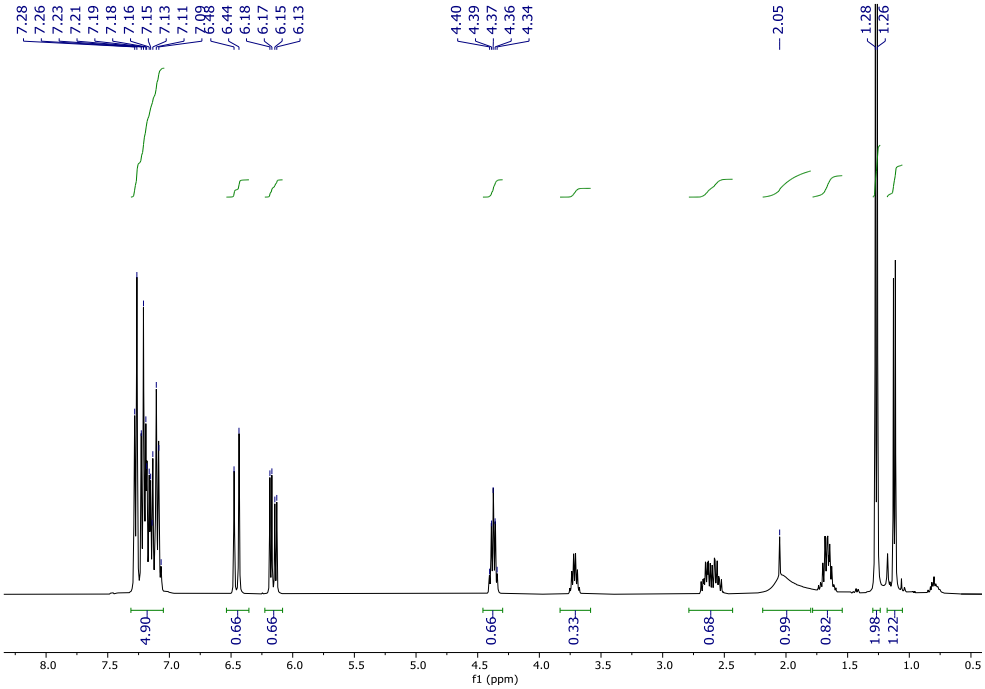


Figure S75: ^{1}H NMR spectrum of **d_{14}** and **d_{13}** (400 MHz, $CDCl_3$).

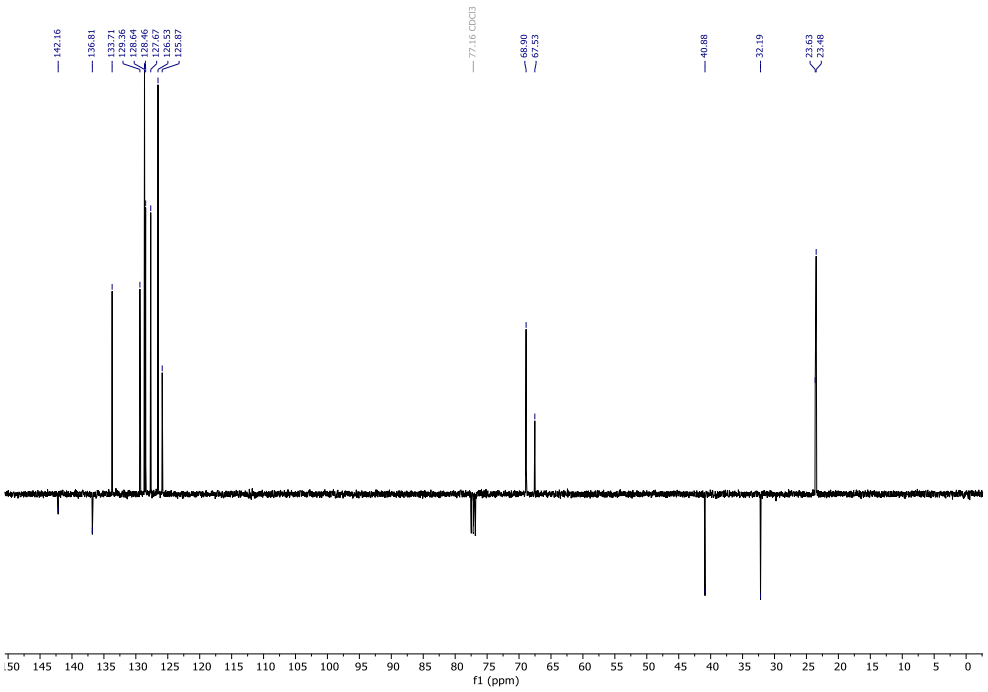


Figure S76: $^{13}C\{^{1}H\}$ NMR spectrum using the J-MOD sequence of $\mathbf{d_{14}}$ and $\mathbf{d_{13}}$ (101 MHz, $CDCl_3$).

References

[S1] A. J. Arduengo III, F. P. Gentry, Jr., P. K. Taverkere and H. E. Howard III, US Patent 6177 575, 2001.
[S2] "M86-EXX278V1 APEX4 User Manual", Bruker Corporation, 2021.
[S3] G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3-8.
[S4] G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8.
[S5] "M86-EXX229V1 APEX3 User Manual", Bruker AXS Inc., Madison, USA, 2016.
[S6] W. G. Chen, J. Egly, A. I. Pobtador-Bahamonde, A. Maisse-Francois, S. Bellemin-Laponnaz, T. Achard, *Dalton Trans.*, 2020, **49**, 3243–3252.
[S7] V. Mechrouk, B. Leforestier, W. Chen, A. Poblador-Bahamonde, A. Maisse-Francois, S. Bellemin-Laponnaz and T. Achard, *Chem. Eur. J.*, 2024, **30**, e202401390.
[S8] Y. Dan, T. Haoyun, X. Linfei, H. Han Vinh, *Dalton Trans.*, 2011, **40**, 8788-8795.
[S9] T. Qiaoqi, S. Chandan, H. Yuan, H. Han Vinh, *Org. Biomol. Chem.*, 2020, **18**, 2487-2491.
[S10] J. Egly, M. Bouché, W. Chen, A. Maisse-François, T. Achard and S. Bellemin-Laponnaz, *Eur. J. Inorg. Chem.*, 2018, **2**, 159–166.
[S11] F. Ulm, A. I. Poblador-Bahamonde, S. Choppin, S. Bellemin-Laponnaz, M. J. Chetcuti, T. Achard, V. Ritleng, *Dalton Trans.*, 2018, **47**, 17134–17145.
[S12] A.L. Spek, *J.Appl.Cryst*., 2003, **36**, 7-13.