Supplementary Information:

Iron(II) coordination polymer catalysed hydroboration of ketones

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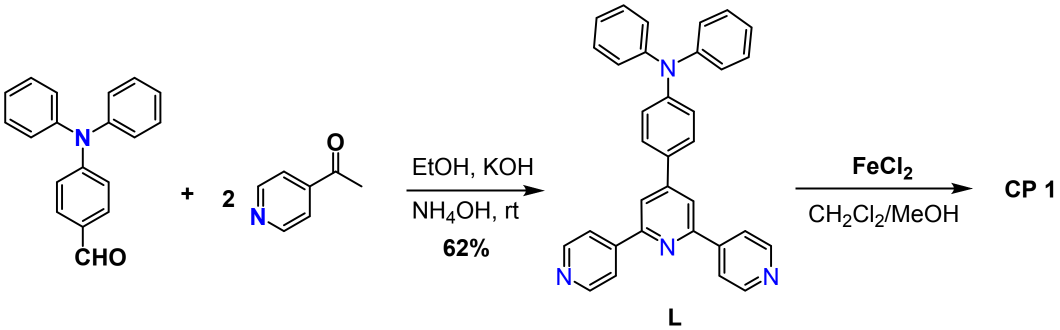
Experimental Details

General Considerations. The catalytic reactions were carried out under a nitrogen atmosphere using standard glove-box technique. Anhydrous grade solvents and liquid reagents used were obtained from Aldrich or Fisher Scientific and stored over 4 Å molecular sieves. FT-IR spectra were recorded on a Shimadzu 8400S instrument with solid samples under N_2 using a Golden Gate ATR accessory. Elemental analyses were performed by Midwest Microlab LLC in Indianapolis. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature on a Bruker AV 500 or 600 MHz NMR spectrometer, with chemical shifts (δ) referenced to the residual solvent signal. GC-MS analysis was obtained using a Shimadzu GCMS-QP2010S gas chromatograph mass spectrometer. Ligand **L** and Fe(tpy)Cl_2 were prepared according to the literature procedure.[1,2]

X-ray Crystallography. An orange colored crystal of **1** was mounted on a Cryoloop with oil. Data were collected at 297 K on a Bruker D8 Venture X-ray instrument using Cu-Kα radiation and data were corrected for absorption with SADABS. Structure was solved by direct methods. All non-hydrogen atoms were refined by full matrix least squares on F^2 and all hydrogen atoms were placed in calculated positions with appropriate riding parameters. Disorder (0.460/0.540) associated with the phenyl ring (atoms C22-C27) was treated using rigid ring constraint and RIGU command. Crystal structures were drawn with the program Mercury v. 2.4. CCDC No. 1839625 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).



Scheme S1. The synthesis of **L** and CP **1**.

Synthesis of L.[2] In a 250 cm^3 round-bottom flask, 4-acetylpyridine (1.21 g, 10.0 mmol) was added to a solution of 4-dimethylaminobenzaldehyde (1.37 g, 5.0 mmol) in EtOH (30 cm^3). KOH pellets (0.56 g, 10 mmol) were then added, followed by aqueous NH_3 (25%, 30 cm^3). The resulting orange solution was stirred at room temperature for 24 h, during which time pale yellow suspension formed. The solid was collected by filtration, washed with H_2O and EtOH and dried in vacuo over P_2O_5. **L** was isolated as a yellowish solid (1.47 g, 62%). ^1H NMR (600 MHz, Chloroform-*d*) δ 8.83 – 8.74 (m, 4H), 8.13 – 8.06 (m, 4H), 8.01 (s, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.32 (dd, J = 8.5, 7.3 Hz, 4H), 7.20 (d, J = 8.7 Hz, 2H), 7.18 (dt, J = 7.9, 1.2 Hz, 4H), 7.14 – 7.09 (m, 2H) ppm; ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.23, 150.43, 147.20, 146.54, 129.66, 128.00, 125.30, 124.04 , 122.84, 121.39, 118.44 ppm.

Synthesis of 1. A solution of **L** (47.6 mg, 0.100 mmol) in MeOH/CH_2Cl_2 (10 mL, 1 : 3, v/v) was placed in a test tube. A blank solution of MeOH/CH_2Cl_2 (6 mL, 1: 1, v/v) was layered on the top of the ligand solution, followed by a solution of $FeCl_2$ (12.6 mg, 0.100 mmol) in MeOH (8 mL). The tube was sealed and allowed to stand at room temperature for a week, during which time X-ray quality orange-red crystals grew on the wall of the tube. The crystals were collected by decanting the solvent and washed with MeOH and then dried in vacuo. Yield: 46.1 mg (86% based on **L**). FT-IR (solid, cm^{-1}) 1609m, 1586s, 1552w, 1537w, 1513s, 1486s, 1372s, 1331w, 1261w, 1241w, 1195m, 1066m, 1009w, 837m, 819s, 772w, 758m, 703s, 675m, 650m. Anal. Calcd. for $C_{66}H_{48}Cl_2FeN_8$: C 73.41, H 4.48, N 10.38%. Found C 73.25, H 4.40, N 10.53%.

General Procedure for Fe^{II}-CP 1-Catalysed Hydroboration. In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol, 0.1 mol% based on the [Fe(**L**)$_2$Cl$_2$] unit) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Ketone (1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. After completion of the reaction, the solvent was evaporated and the crude reaction mixture was first analyzed by GC-MS using a dilute CH_2Cl_2 solution, and then the product was isolated by flash column chromatography with SiO_2 using ethyl acetate/hexane as eluent. The pure products were characterized by ^1H and ^{13}C NMR spectroscopies.

Competing Experiment for Selective Hydroboration of Ketones vs. Aldehydes. In a glove box under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The acetophenone (120.0 mg, 1.0 mmol), benzaldehyde (106.0 mg, 1.0 mmol) and pinacolborane (128.0 mg, 1.0 mmol) were then added sequentially. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and the solvent was evaporated. The products were analyzed by GC-MS using 1,3,5-trimethylbenzene as an internal reference.

Recycling and Reusing Experiment for Hydroboration of Acetophenone. In a glovebox under N_2 atmosphere, catalyst **1** (10.8 mg, 10 μmol, 1 mol%) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a small vial equipped with a stir bar. Acetophenone (120.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. Then, the solid was centrifuged out of suspension and extracted with hexane three times. The combined organic extracts were analyzed by GC-MS using 1,3,5-trimethylbenzene as an internal reference.

The recovered solid catalyst in 1.0 mL THF was charged into a small vial, to which additional KO^{t}Bu (2.2 mg, 20 μmol) was added. Then, acetophenone (120.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were added. The resultant mixture was stirred at room temperature in the glovebox for 4 h. Then, the solid was centrifuged out of suspension and extracted with hexane three times. The combined organic extracts were analyzed by GC-MS using 1,3,5-trimethylbenzene as an internal reference. The results of 5 recycling experiments are summarized in Figure S1.

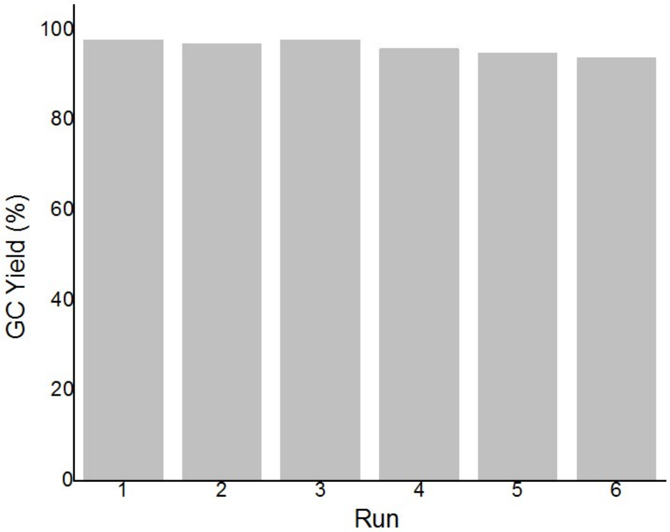


Figure S1. Plot of GC yields (%) of borate ester at different runs in the recycling experiments for CP **1**-catalysed hydroboration of acetophenone.

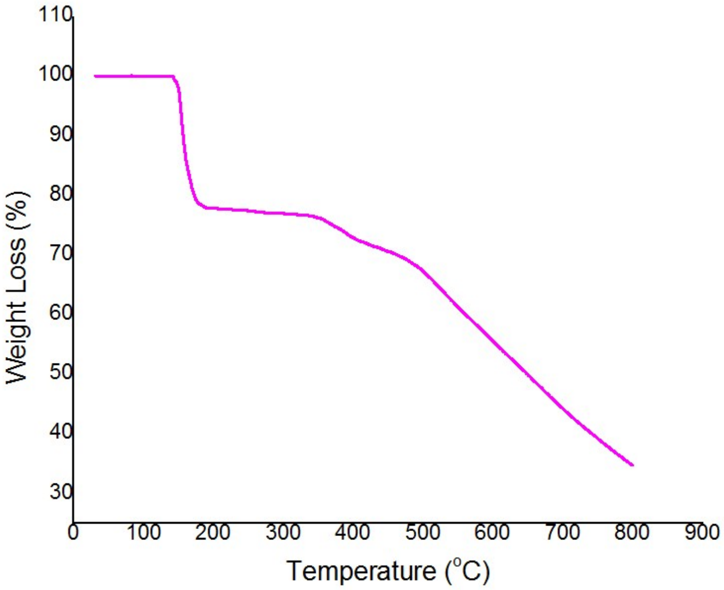
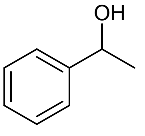


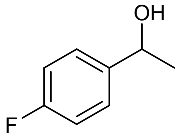
Figure S2. The TGA profile of **1**.

Synthetic details and characterization data



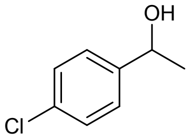
Chemical Formula: $C_8H_{10}O$
Molecular Weight: 122.1670

3a[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Acetophenone (120.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3a** was isolated. Yield: 116.0 mg (95%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 4H), 7.35 – 7.27 (m, 1H), 4.87 (qd, *J* = 6.5, 1.4 Hz, 1H), 2.70 (s, 1H), 1.50 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.89, 128.47, 127.41, 125.45, 70.28, 25.17 ppm.



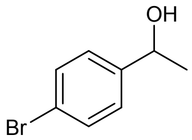
Chemical Formula: C_8H_9FO
Molecular Weight: 140.1574

3b[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4′-Fluoroacetophenone (138.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3b** was isolated. Yield: 131.5 mg (94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 2H), 7.03 (td, *J* = 8.7, 1.6 Hz, 2H), 4.90 (q, *J* = 6.5 Hz, 1H), 1.69 (br, 1H), 1.48 (dt, *J* = 6.5, 1.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.24 (d, *J* = 245.2 Hz), 141.62 (d, *J* = 3.1 Hz), 127.18 (d, *J* = 8.1 Hz), 115.41 (d, *J* = 21.2 Hz), 69.94, 25.46 ppm.



Chemical Formula: C_8H_9ClO
Molecular Weight: 156.6090

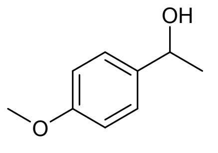
3c[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4′-Chloroacetophenone (154.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3c** was isolated. Yield: 140.9 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.7 Hz, 4H), 4.88 (dd, *J* = 6.6, 1.5 Hz, 1H), 1.85 (s, 1H), 1.47 (dt, *J* = 6.5, 1.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.35, 133.19, 128.73, 126.92, 69.89, 25.42 ppm.



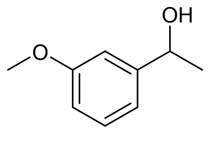
Chemical Formula: C_8H_9BrO
Molecular Weight: 201.0630

3d[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4′-Bromoacetophenone (198.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for

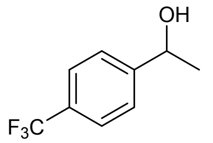
16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3d** was isolated. Yield: 140.5 mg (70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.24 – 7.14 (m, 2H), 4.79 (q, *J* = 6.5 Hz, 1H), 2.52 (s, 1H), 1.42 (dd, *J* = 6.5, 1.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.80, 131.56, 127.22, 121.15, 69.73, 25.27 ppm.


Chemical Formula: $C_9H_{12}O_2$
Molecular Weight: 152.1930

3e[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4′-Methoxyacetophenone (150.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Pale yellow oil of **3e** was isolated. Yield: 133.7 mg (88%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.5, 1.7 Hz, 2H), 6.89 (dd, *J* = 8.6, 1.7 Hz, 2H), 4.84 (d, *J* = 6.5 Hz, 1H), 3.81 (d, *J* = 1.6 Hz, 3H), 2.33 (s, 1H), 1.48 (dd, *J* = 6.5, 1.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.91, 138.12, 126.73, 113.83, 69.92, 55.32, 25.09 ppm.

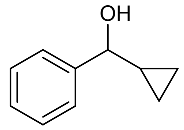

Chemical Formula: $C_9H_{12}O_2$
Molecular Weight: 152.1930

3f[4]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 3′-Methoxyacetophenone (150.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Pale yellow oil of **3f** was isolated. Yield: 144.5 mg (95%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (td, *J* = 7.3, 6.6, 1.7 Hz, 1H), 6.95 (dt, *J* = 5.9, 1.7 Hz, 2H), 6.85 – 6.79 (m, 1H), 4.85 (d, *J* = 6.3 Hz, 1H), 3.82 (d, *J* = 1.6 Hz, 3H), 2.46 (s, 1H), 1.49 (dd, *J* = 6.4, 1.7 Hz, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.72, 147.71, 129.54, 117.76, 112.85, 110.93, 70.26, 55.24, 25.20 ppm.


Chemical Formula: $C_9H_9F_3O$
Molecular Weight: 190.1652

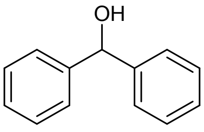
3g[5]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4′-Trifluoromethylacetophenone (188.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Pale yellow oil of **3g** was isolated. Yield: 173 mg (91%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ

7.59 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.92 (q, *J* = 6.5 Hz, 1H), 2.40 (s, 1H), 1.48 (dd, *J* = 6.5, 1.8 Hz, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.78, 129.69 (q, *J* = 32.4 Hz), 127.52, 125.75, 125.53 (q, *J* = 3.8 Hz), 123.20, 69.90, 25.44 ppm.



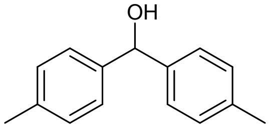
Chemical Formula: $C_{10}H_{12}O$
Molecular Weight: 148.2050

3h[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^tBu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Cyclopropyl phenyl ketone (146.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3h** was isolated. Yield: 103.5 mg (70%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.13 (m, 2H), 7.09 (td, *J* = 7.2, 1.5 Hz, 1H), 3.76 (d, *J* = 8.3 Hz, 1H), 2.29 (s, 1H), 0.99 (tdd, *J* = 8.0, 5.6, 3.1 Hz, 1H), 0.49 – 0.39 (m, 1H), 0.34 (qd, *J* = 8.6, 4.5 Hz, 1H), 0.26 (dq, *J* = 10.0, 4.9 Hz, 1H), 0.16 (dq, *J* = 10.0, 5.0 Hz, 1H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.92, 128.34, 127.49, 126.07, 78.48, 19.16, 3.70, 2.84 ppm.



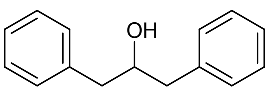
Chemical Formula: $C_{13}H_{12}O$
Molecular Weight: 184.2380

3i[6]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^tBu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Benzophenone (182.1 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3i** was isolated. Yield: 173 mg (94%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.32 (m, 8H), 7.30 (td, *J* = 6.9, 1.7 Hz, 2H), 5.82 (s, 1H), 2.48 (s, 1H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.86, 128.58, 127.64, 126.63, 76.28 ppm.



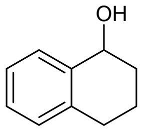
Chemical Formula: $C_{15}H_{16}O$
Molecular Weight: 212.2920

3j[5]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^tBu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4,4′-Dimethylbenzophenone (210.1 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3j** was isolated. Yield: 191mg (90%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 8.2, 1.9 Hz, 4H), 7.21 (dd, *J* = 8.1, 1.9 Hz, 4H), 5.77 (s, 1H), 2.65 (s, 1H), 2.41 (d, *J* = 2.1 Hz, 6H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.19, 137.04, 129.13, 126.50, 75.83, 21.17 ppm.



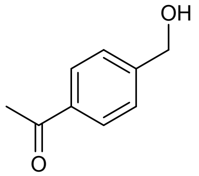
Chemical Formula: $C_{15}H_{16}O$
Molecular Weight: 212.2920

3k[3]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 1,3-Diphenylacetone (210.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3k** was isolated. Yield: 161.2 mg (76%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.2 Hz, 4H), 7.37 – 7.24 (m, 6H), 4.13 (td, *J* = 4.6, 3.9, 2.4 Hz, 1H), 2.94 (dd, *J* = 13.6, 4.6 Hz, 2H), 2.90 – 2.77 (m, 2H), 1.92 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.54, 129.46, 128.51, 126.46, 73.58, 43.36 ppm.



Chemical Formula: $C_{10}H_{12}O$
Molecular Weight: 148.2050

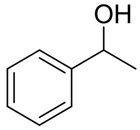
3l[5]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 1-Tetralone (146.2 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The conversion of hydroborated product was determined by GC analysis, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3l** was isolated. Yield: 105 mg (71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 – 7.42 (m, 1H), 7.22 – 7.20 (m, 2H), 7.12 – 7.11 (m, 1H), 4.77 – 4.75 (m, 1H), 2.86 – 2.81 (m, 1H), 2.76 – 2.71 (m, 1H), 2.11 (br, 1H), 2.02 – 1.95 (m, 1H), 1.92 – 1.87 (m, 1H), 1.82 – 1.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 139.08, 127.36, 129.23, 128.93, 127.78, 126.39, 68.35, 32.51, 29.50, 19.01 ppm.



Chemical Formula: $C_9H_{10}O_2$
Molecular Weight: 150.1770

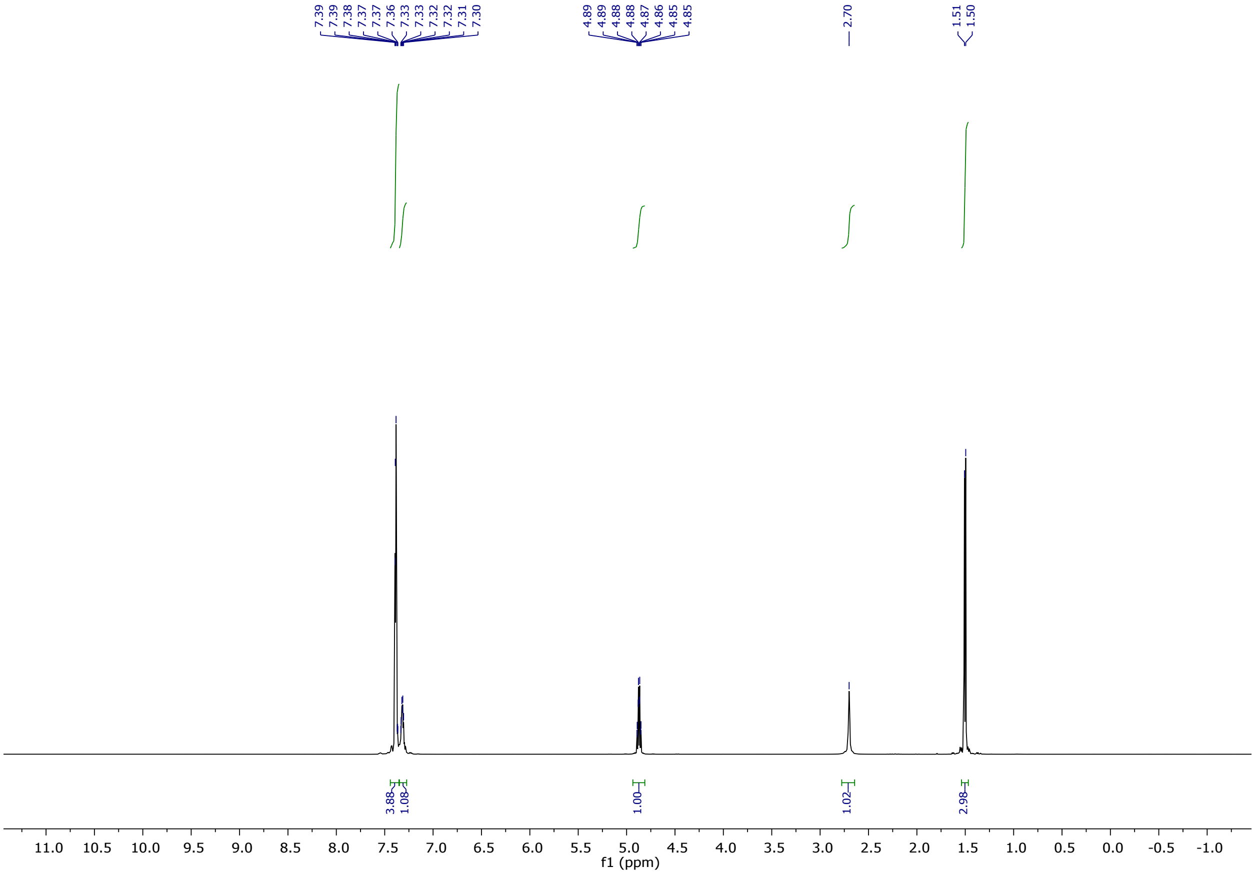
3m[7]: In a glovebox under N_2 atmosphere, catalyst **1** (1.08 mg, 1.0 μmol) and KO^{t}Bu (2.2 mg, 20 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4-Acetylbenzaldehyde (148 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3m** was isolated. Yield: 93 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1, 2H), 7.43 (d, *J* = 8.0, 2H), 4.75 (s, 2H), 2.58 (d, *J* = 1.5 Hz, 3H), 2.35 (br., 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.24, 146.45, 136.31, 128.71, 126.70, 64.62, 26.78 ppm.

Copies of NMR spectra for isolated products:

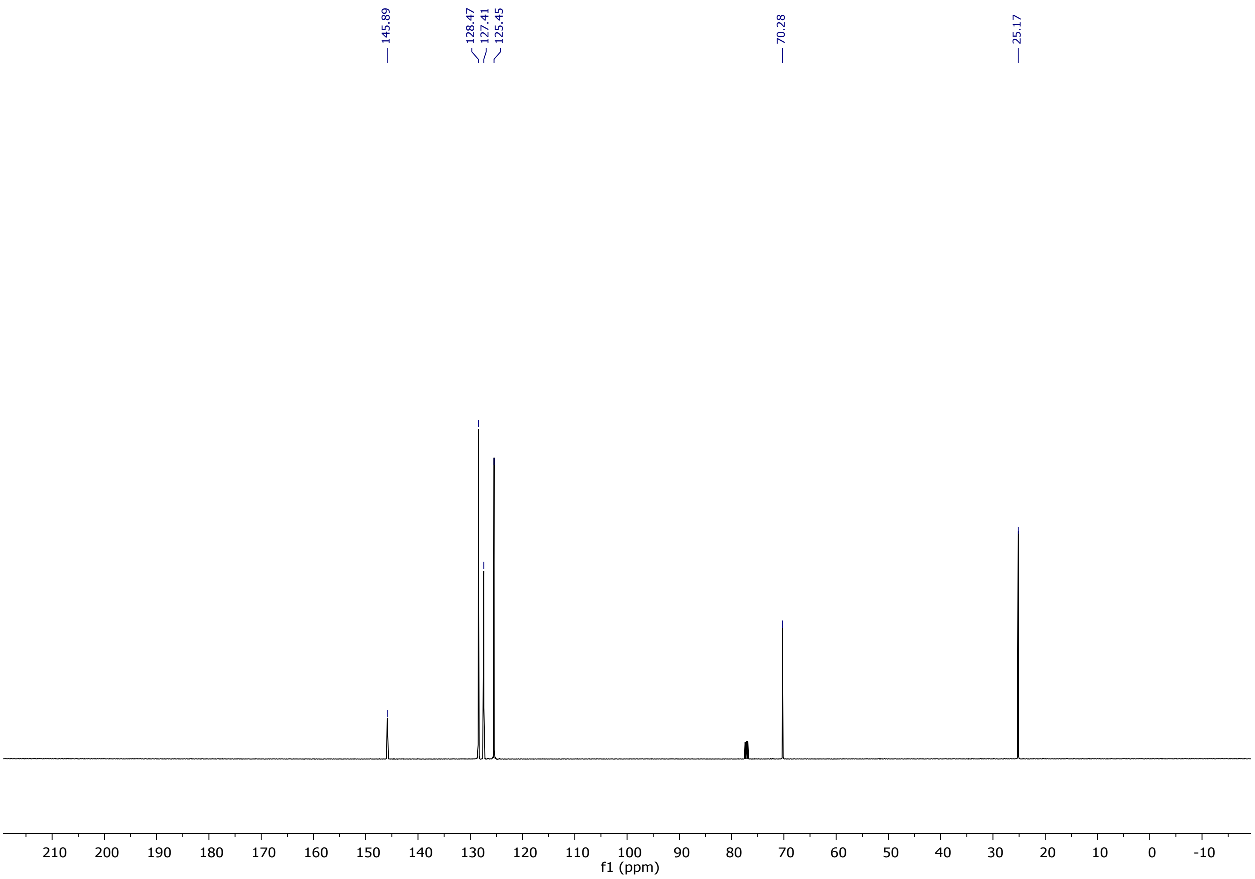


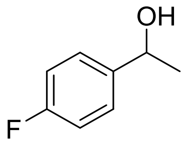
(**3a**)

^{1}H NMR (500 MHz, CDCl$_3$):



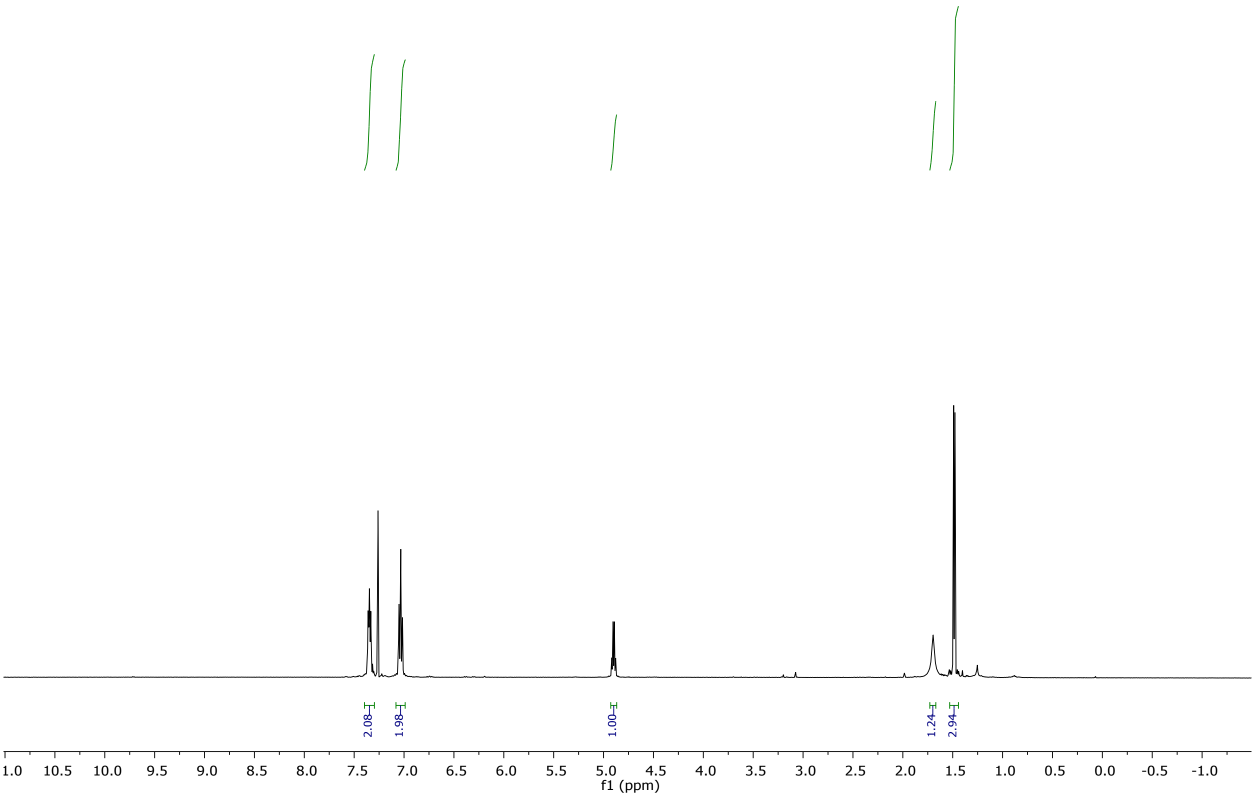
^{13}C NMR (126 MHz, CDCl$_3$):



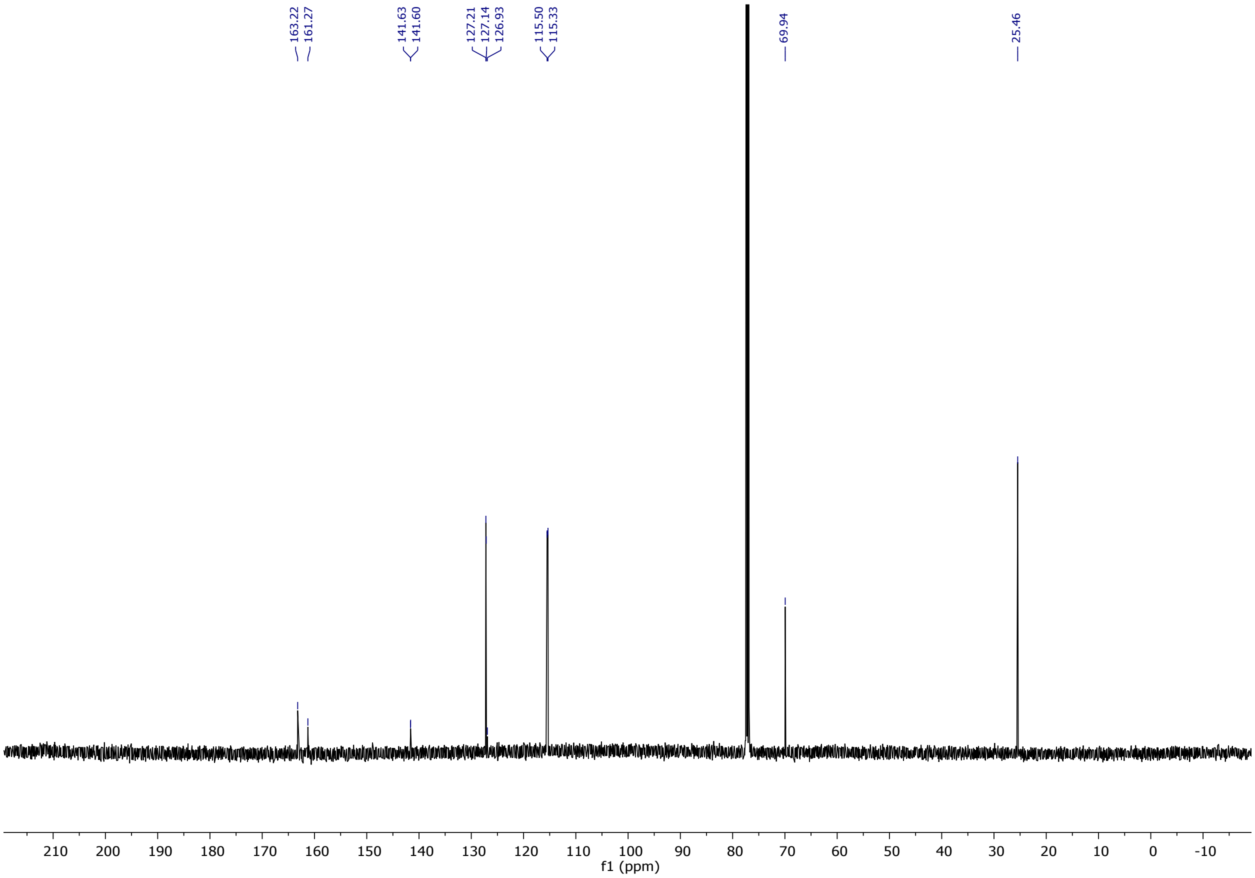


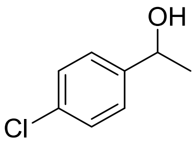
(**6b**)

^{1}H NMR (500 MHz, $CDCl_3$):



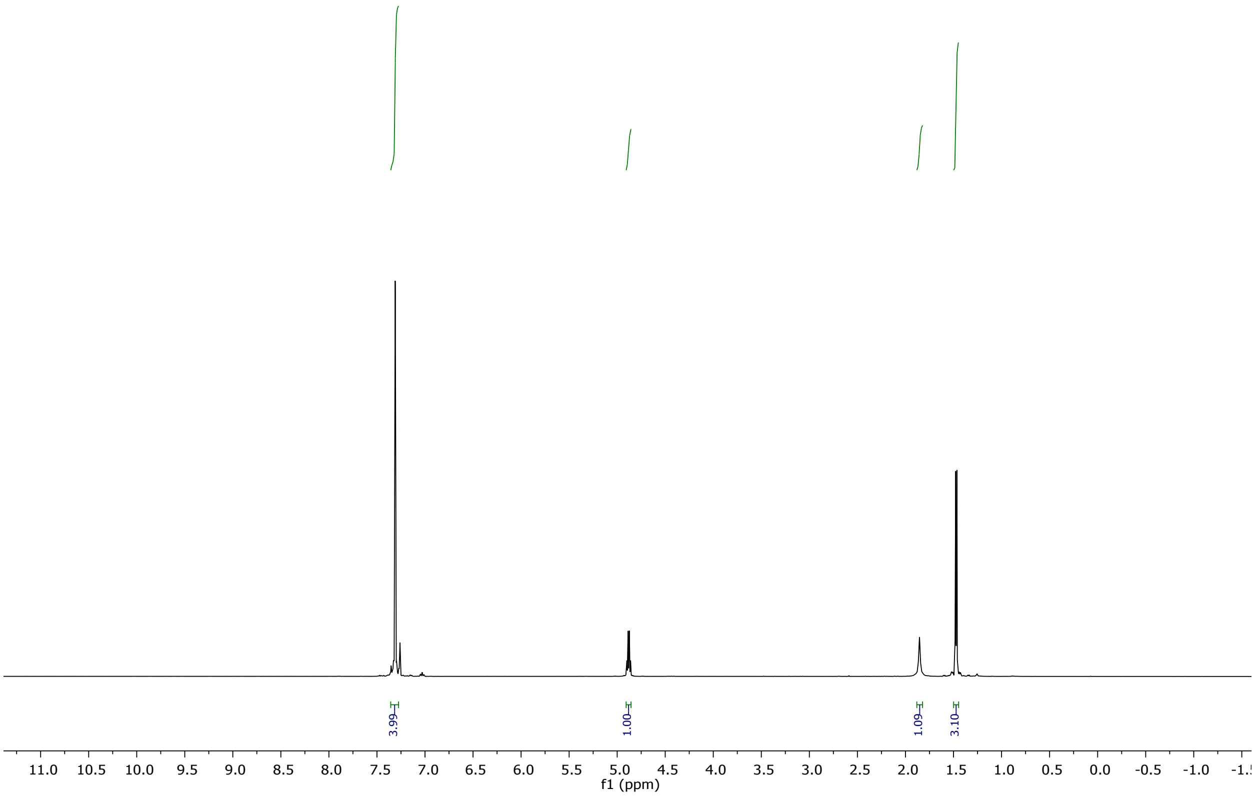
^{13}C NMR (126 MHz, CDCl$_3$):



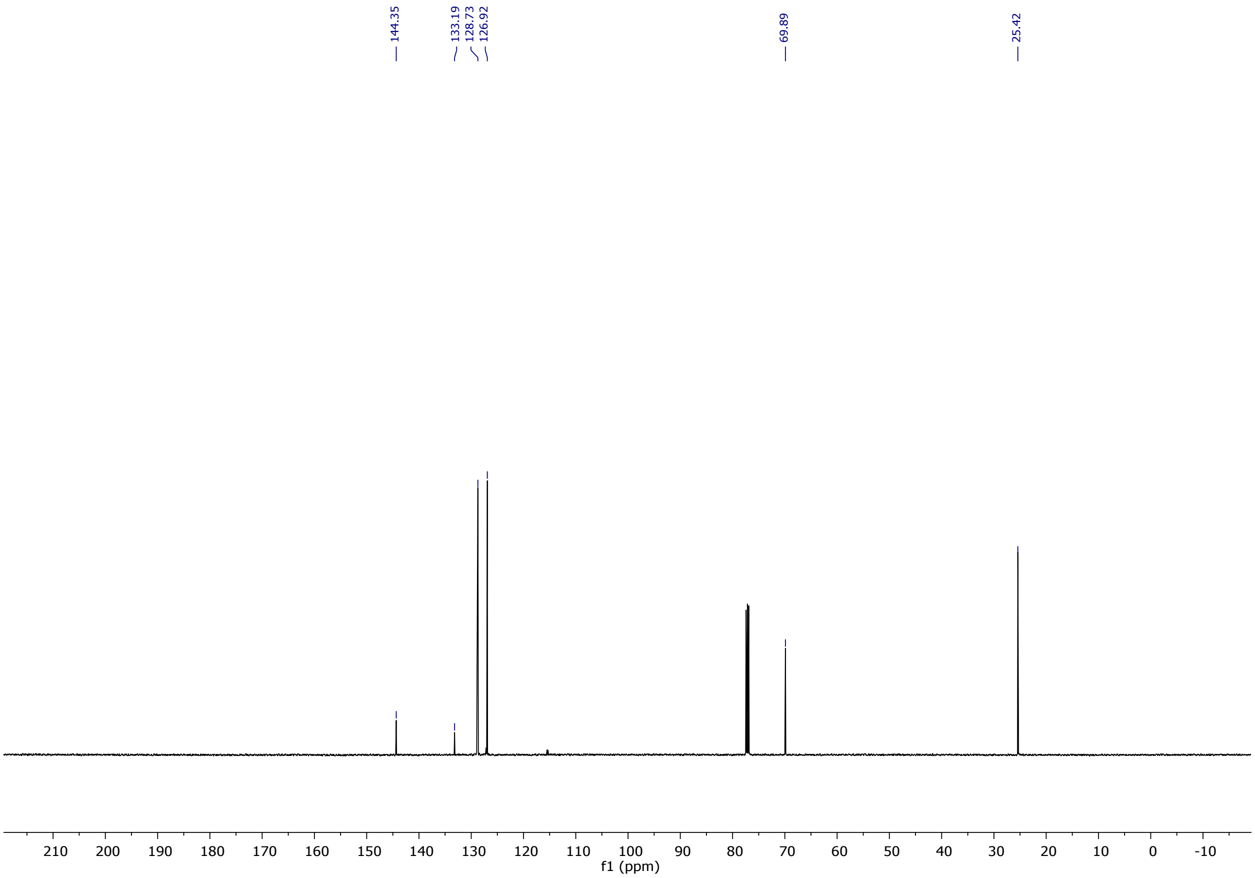


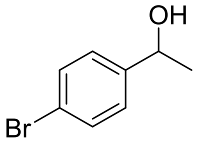
(**6c**)

^{1}H NMR (500 MHz, $CDCl_3$):



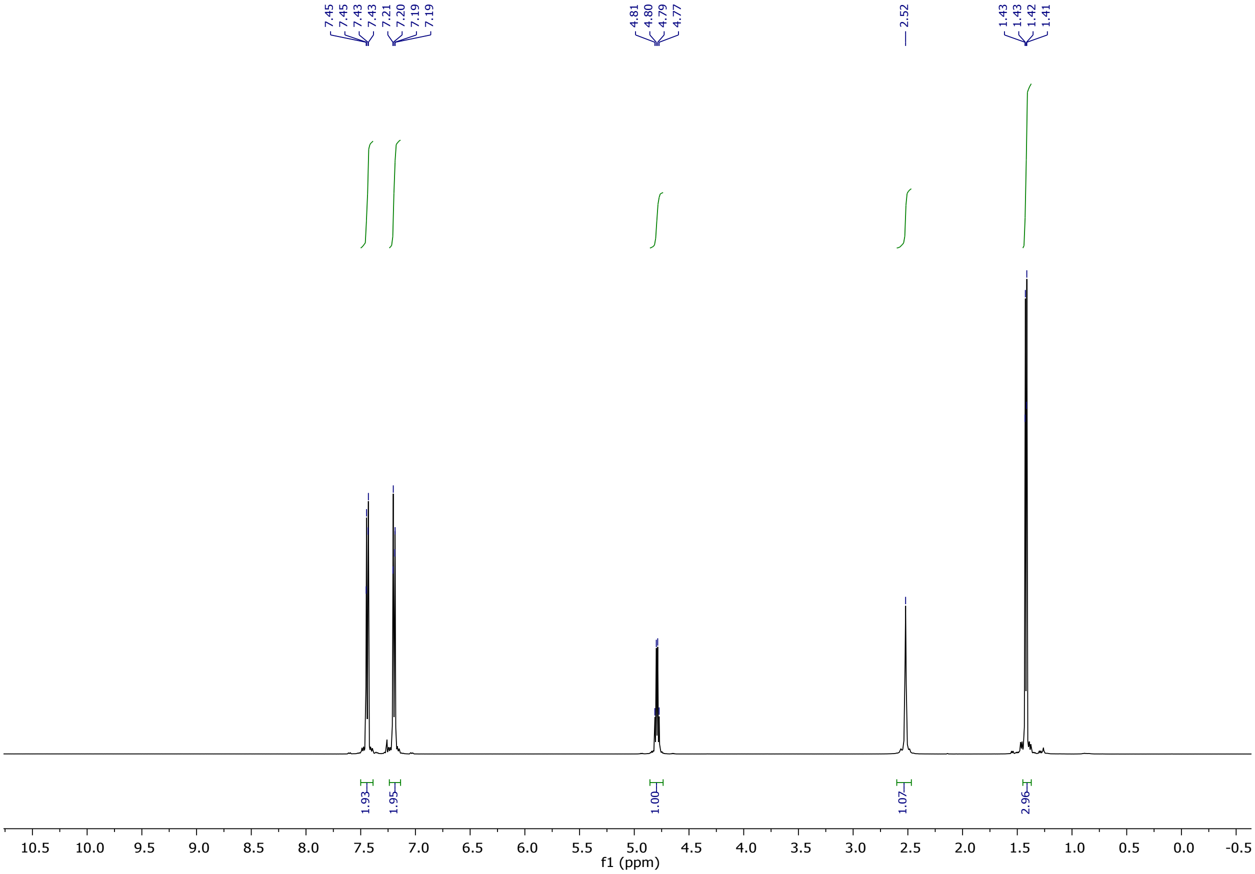
^{13}C NMR (126 MHz, CDCl$_3$):



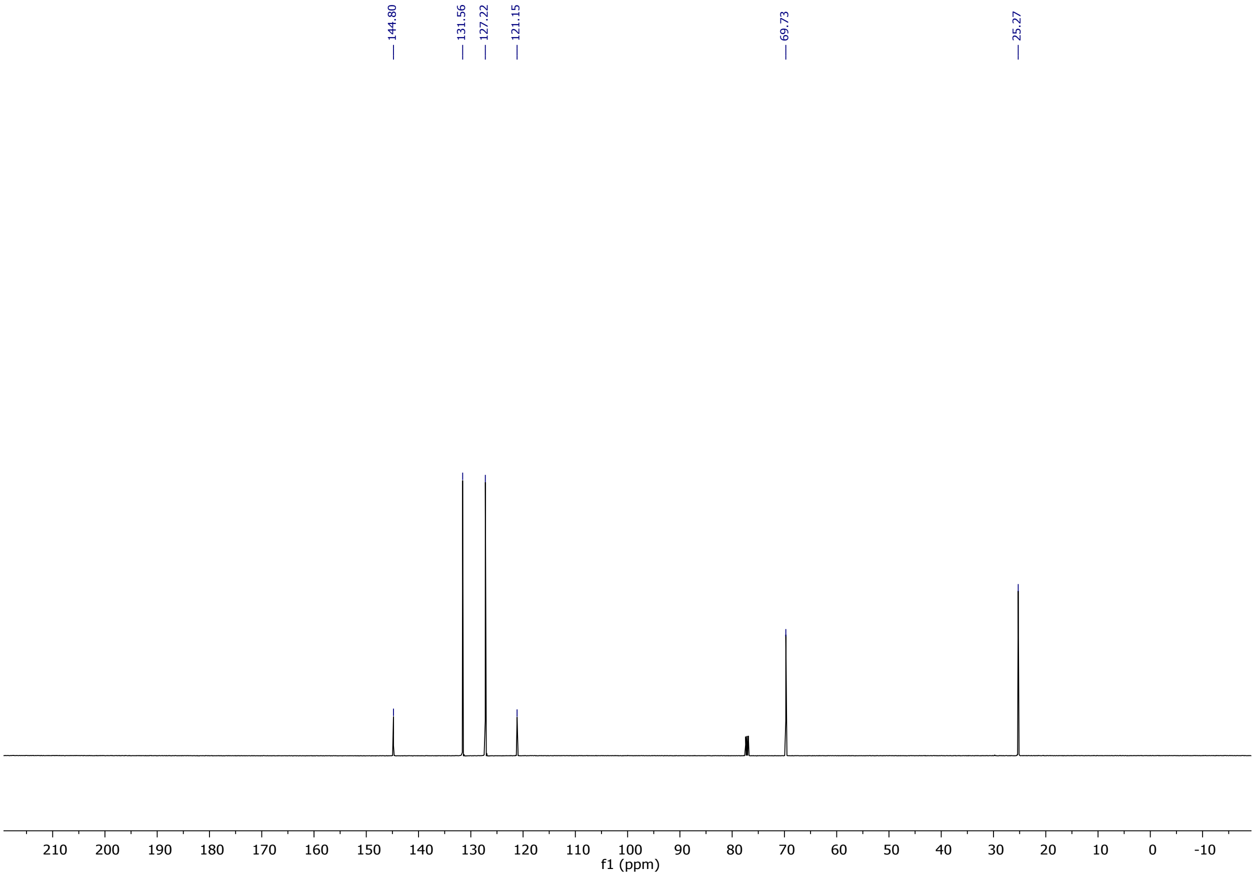


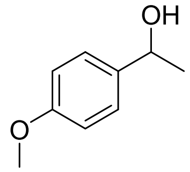
(**3d**)

^{1}H NMR (500 MHz, $CDCl_3$):



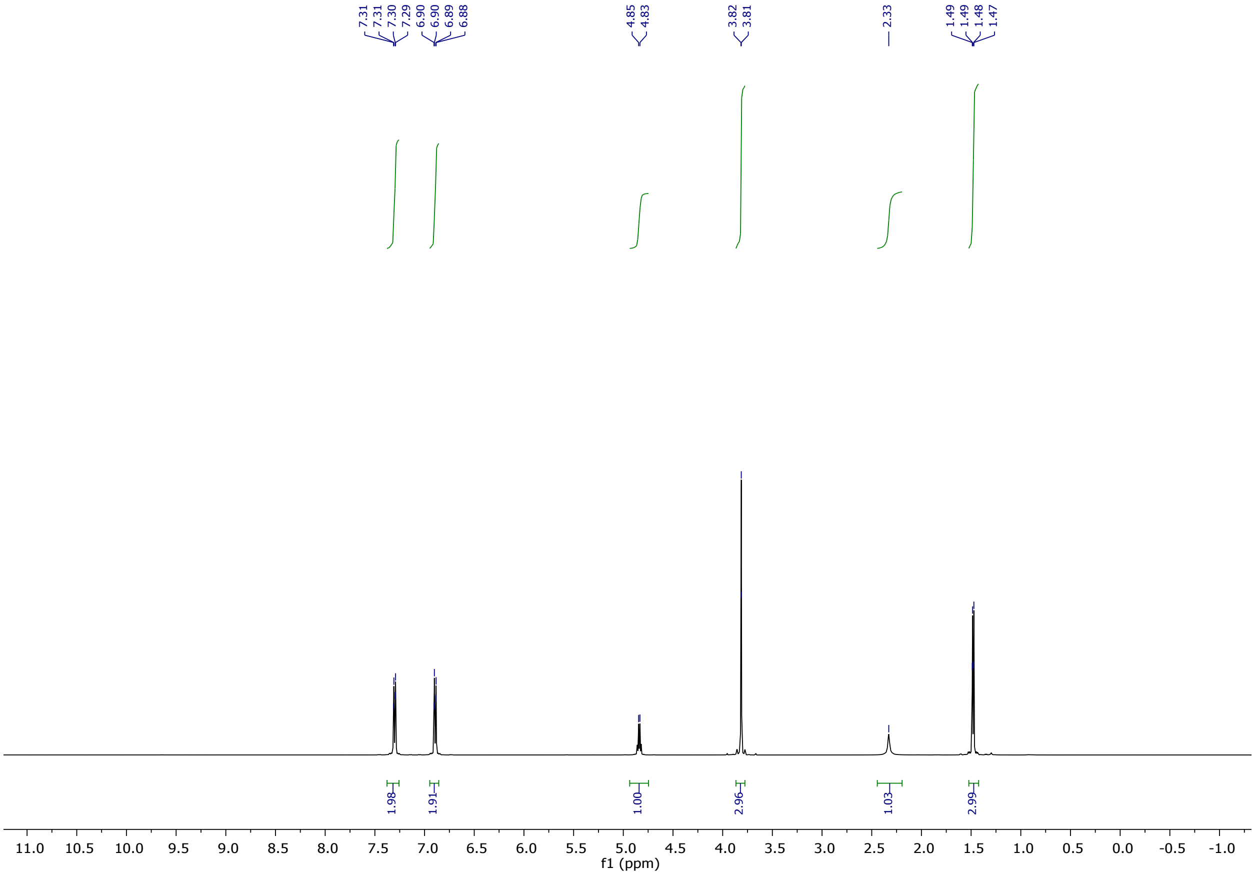
^{13}C NMR (126 MHz, CDCl$_3$):



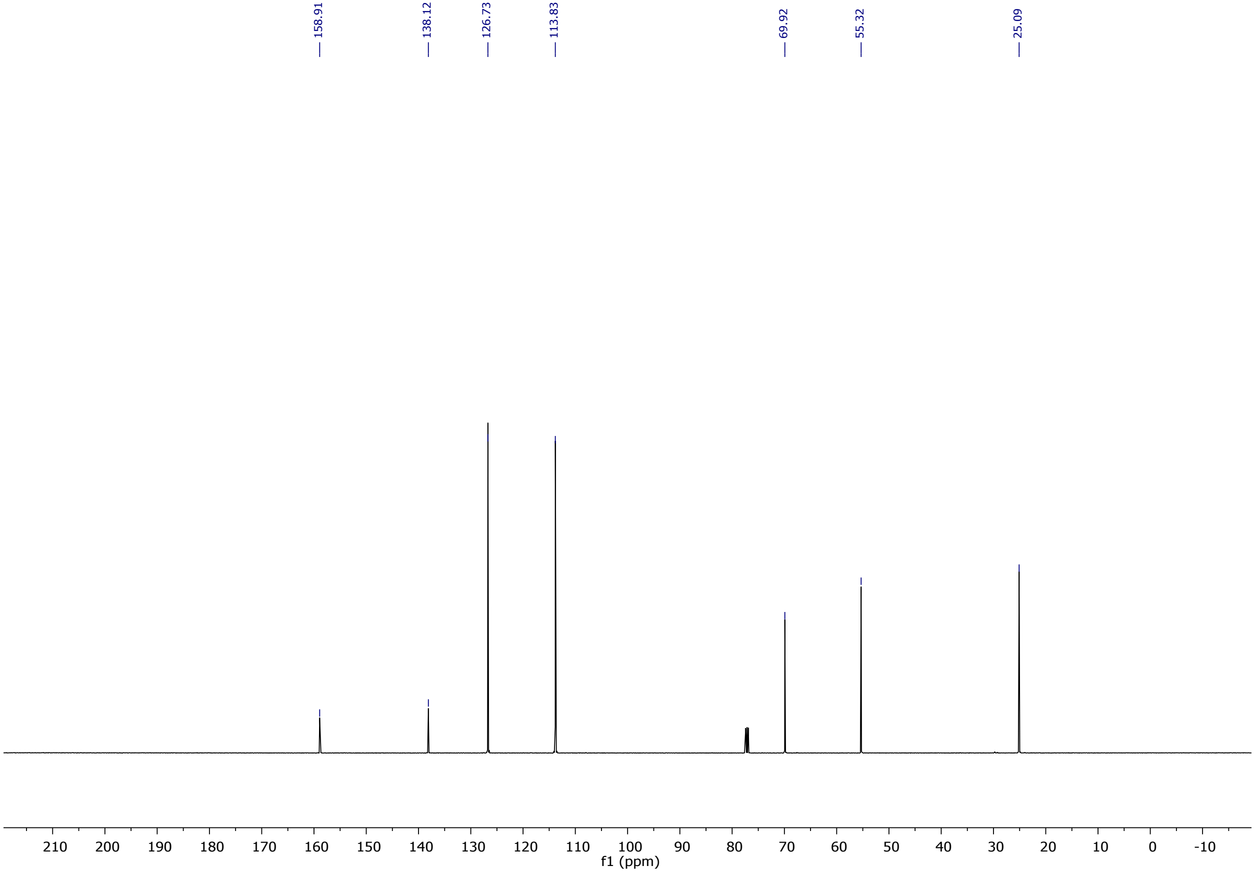


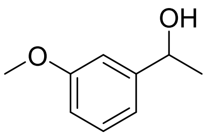
(**3e**)

^{1}H NMR (500 MHz, CDCl$_3$):



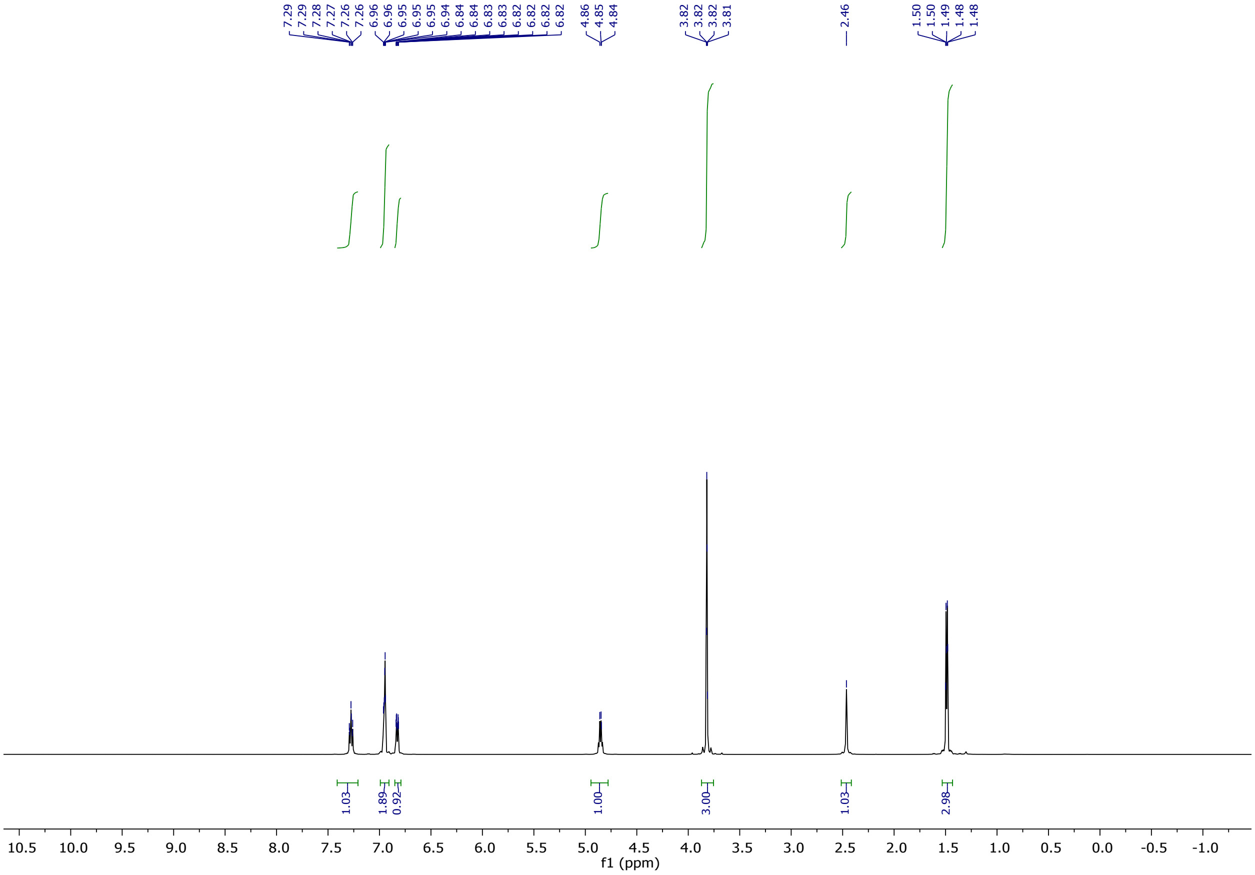
^{13}C NMR (126 MHz, CDCl$_3$):



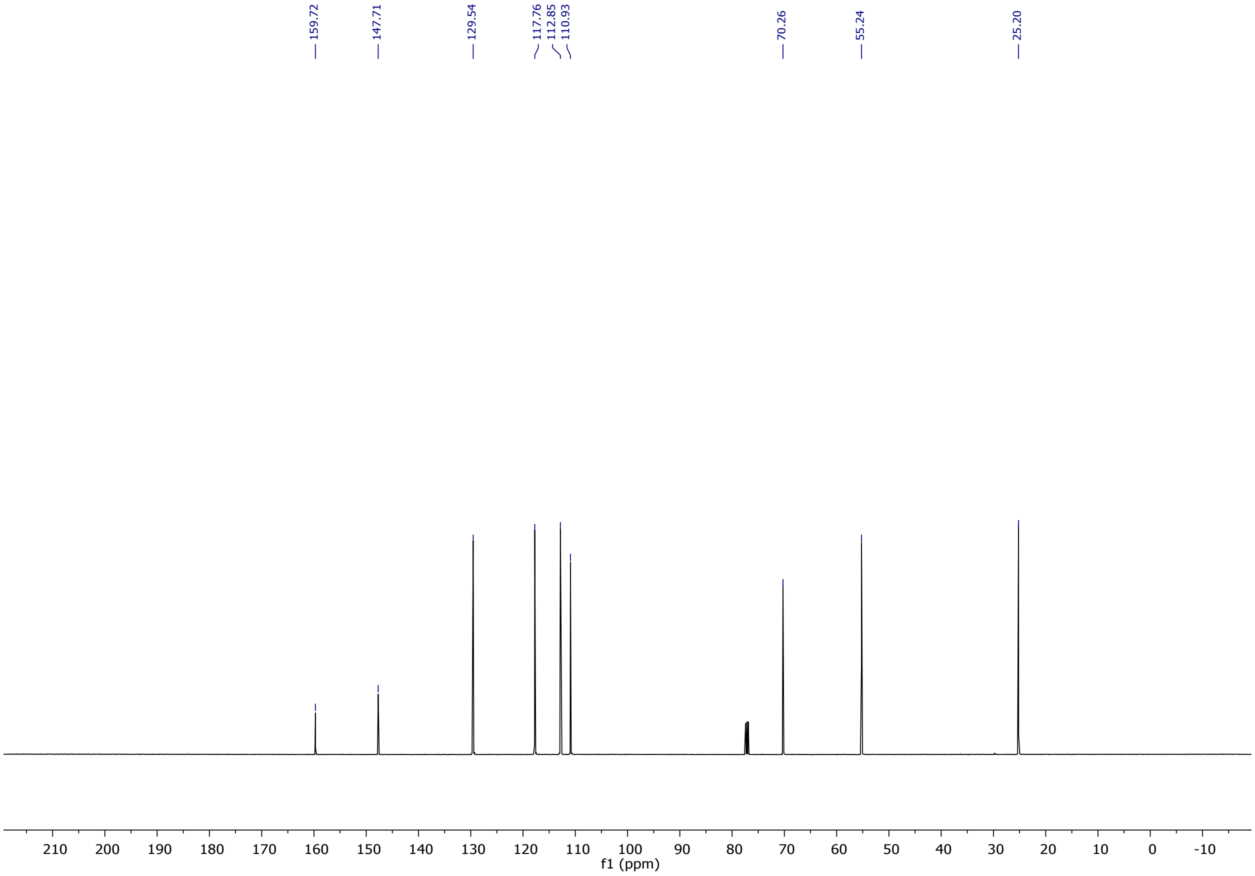


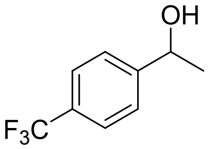
(**3f**)

^{1}H NMR (500 MHz, CDCl$_3$):



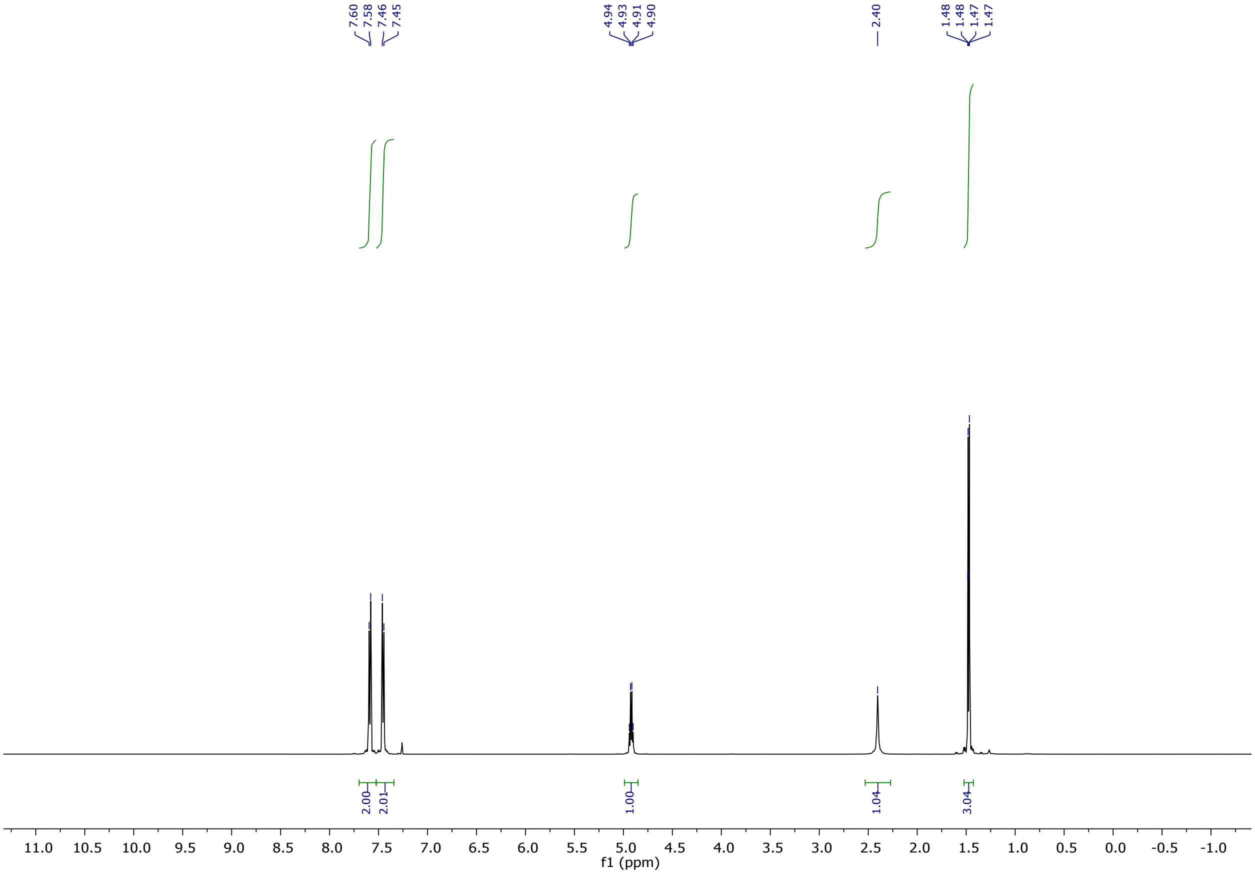
^{13}C NMR (126 MHz, $CDCl_3$):



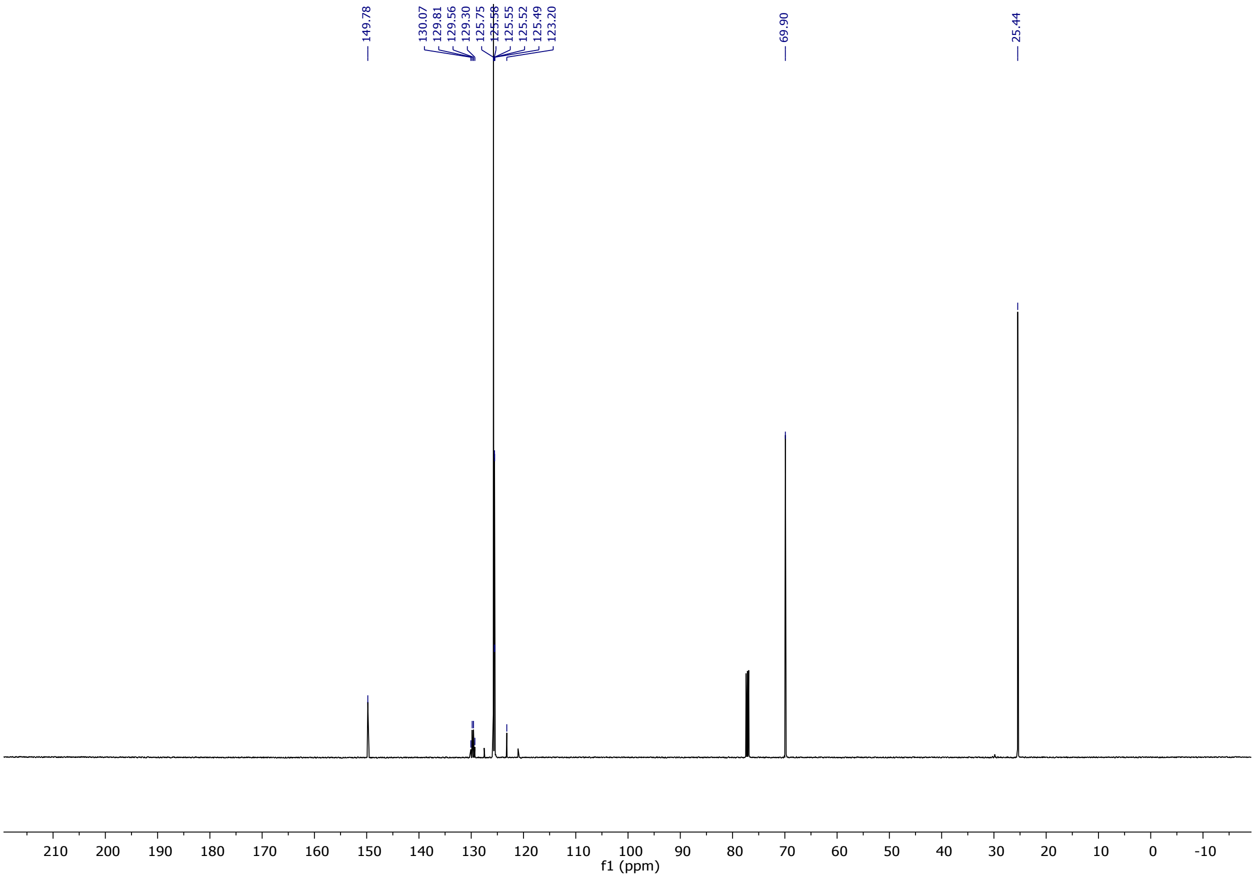


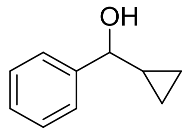
(3g)

^{1}H NMR (500 MHz, $CDCl_3$):



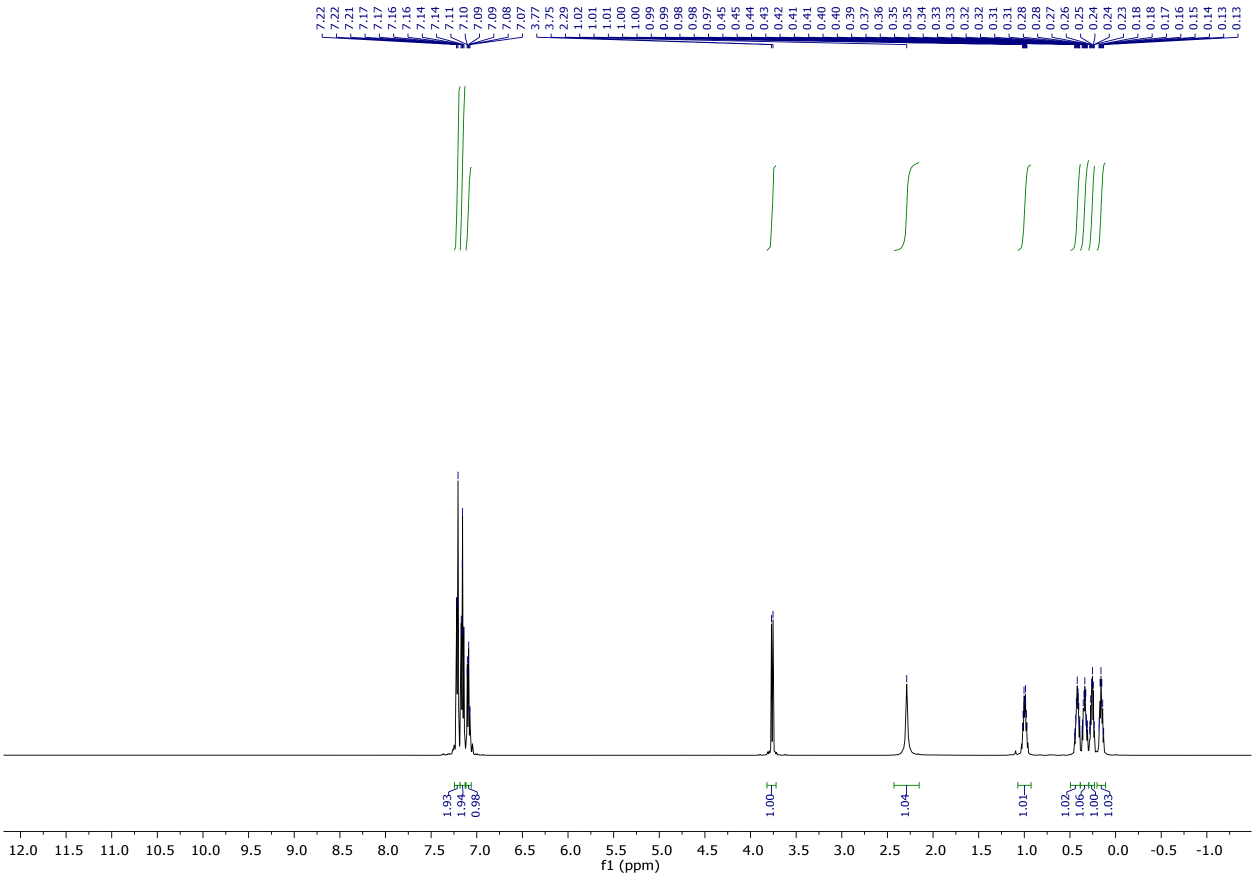
^{13}C NMR (126 MHz, CDCl$_3$):



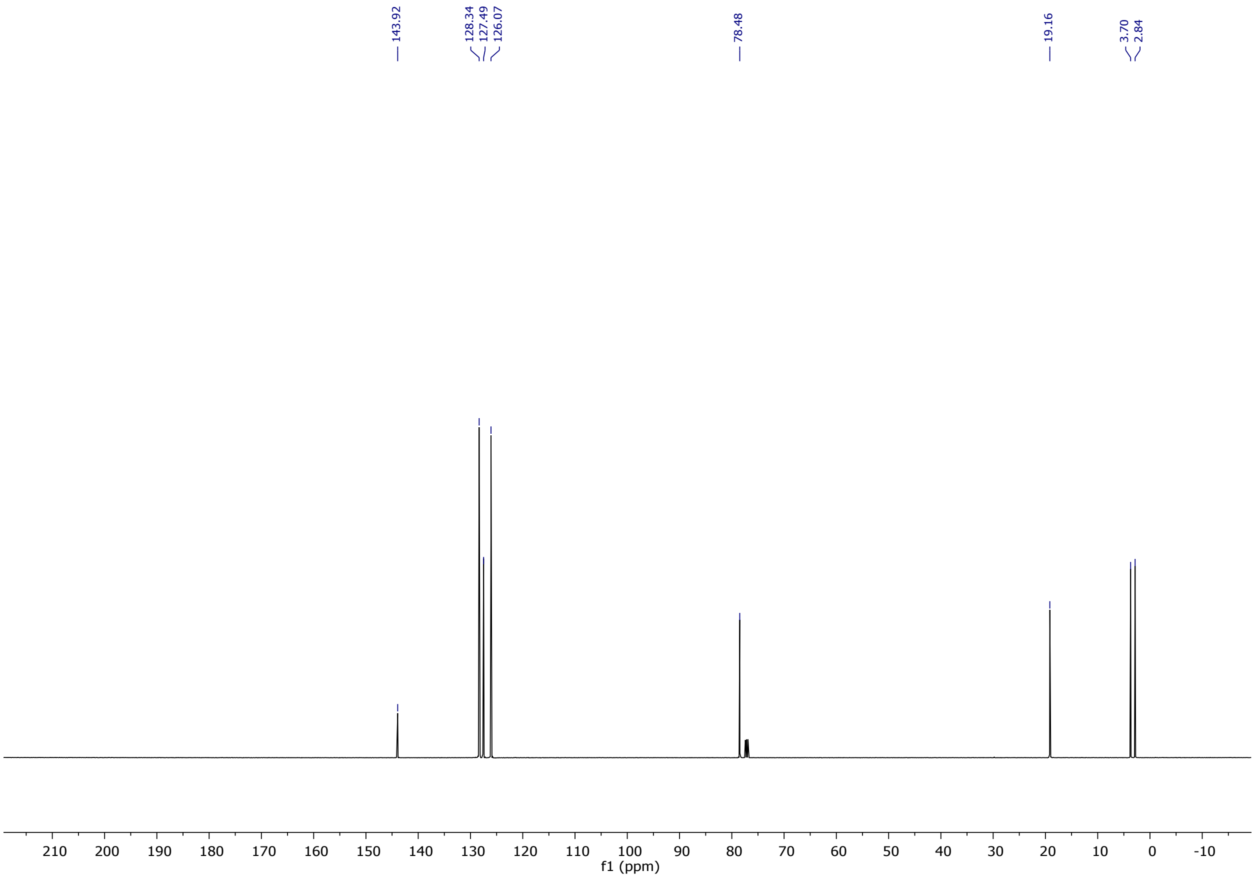


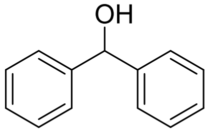
(**3h**)

^{1}H NMR (500 MHz, $CDCl_3$):



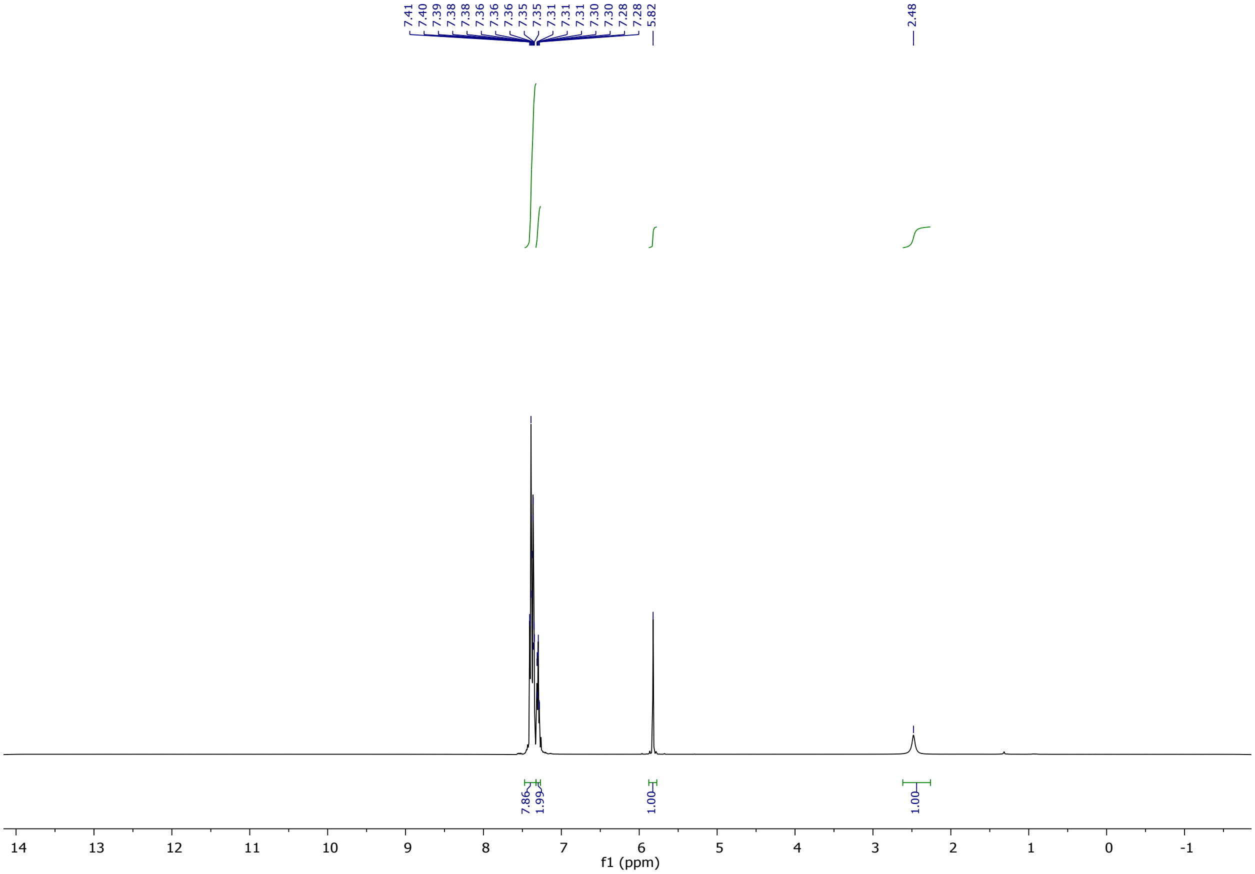
^{13}C NMR (126 MHz, CDCl$_3$):



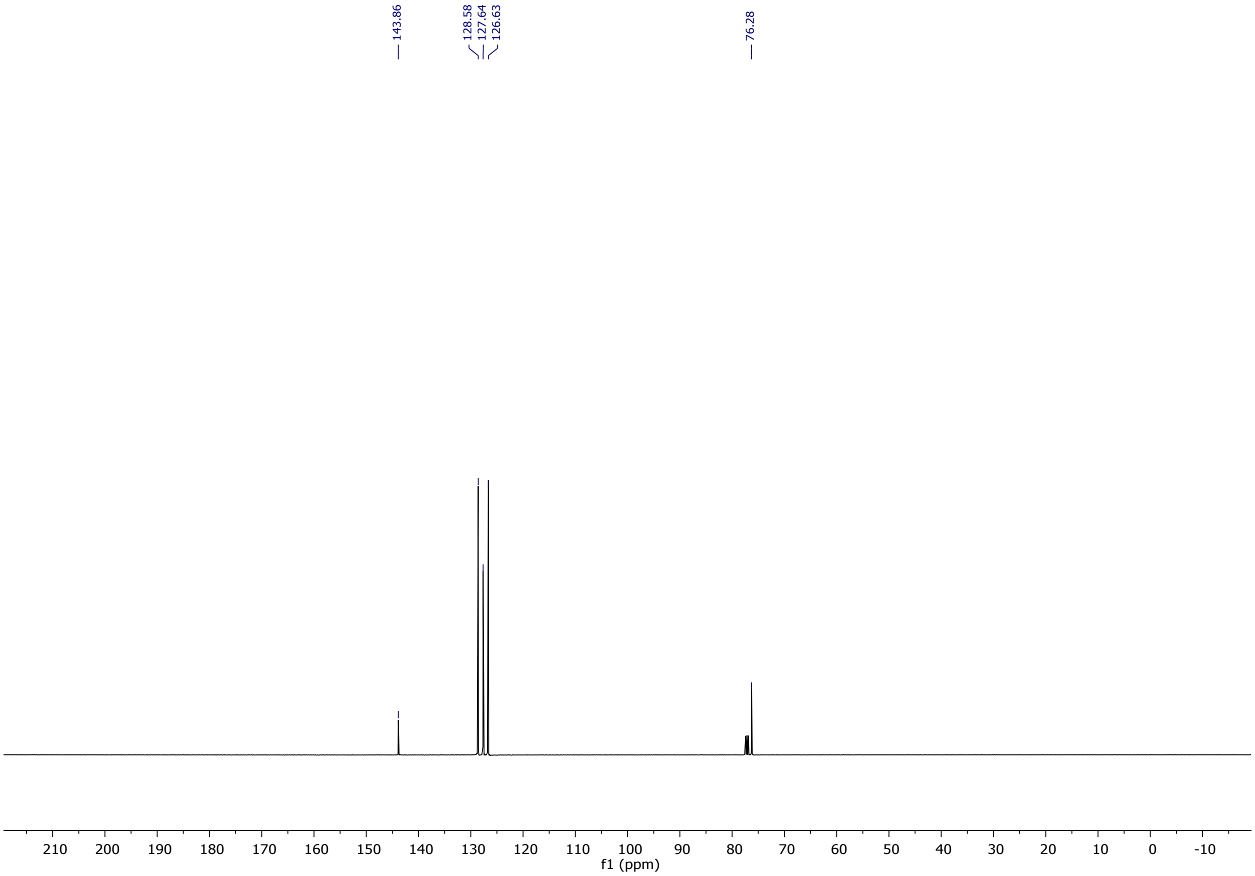


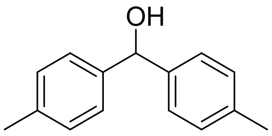
(**3i**)

^{1}H NMR (500 MHz, CDCl$_3$):



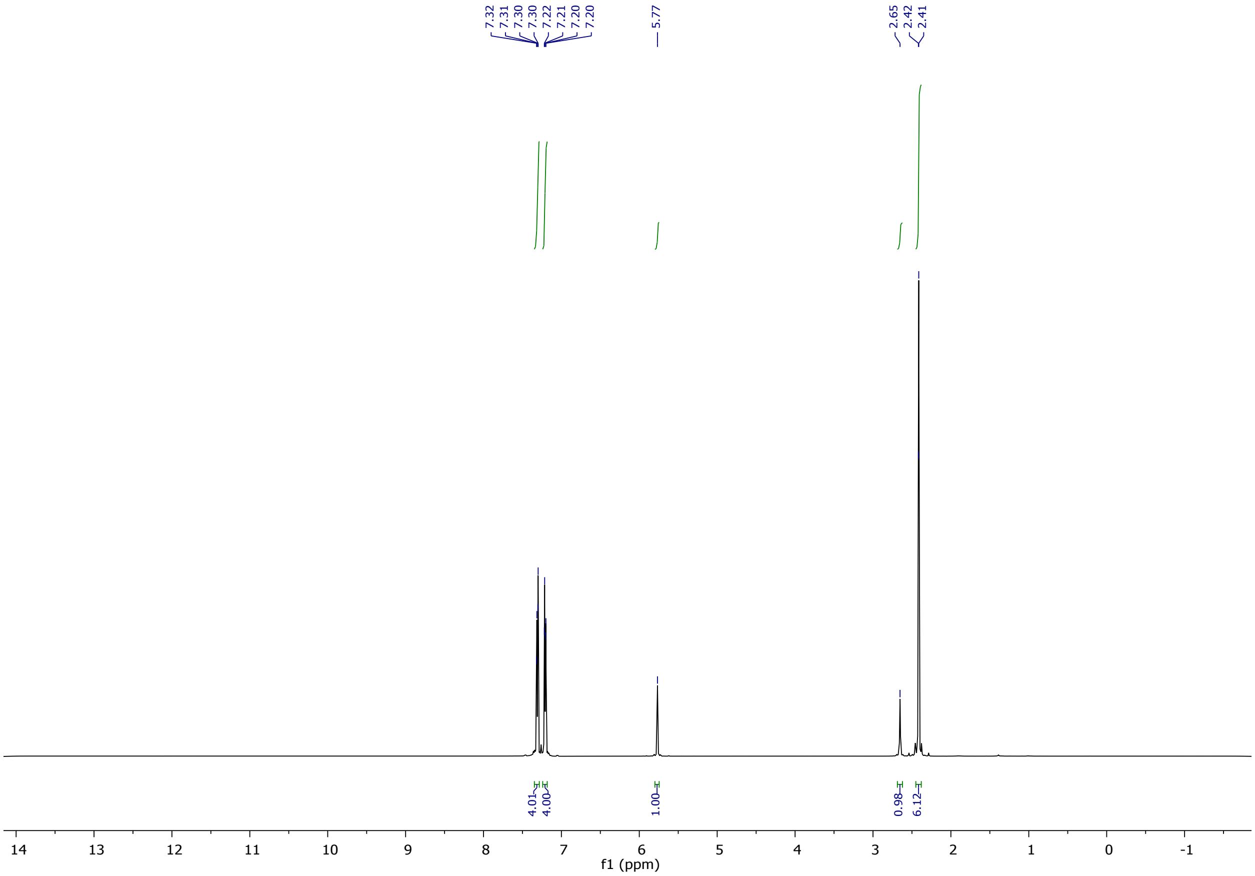
^{13}C NMR (126 MHz, $CDCl_3$):



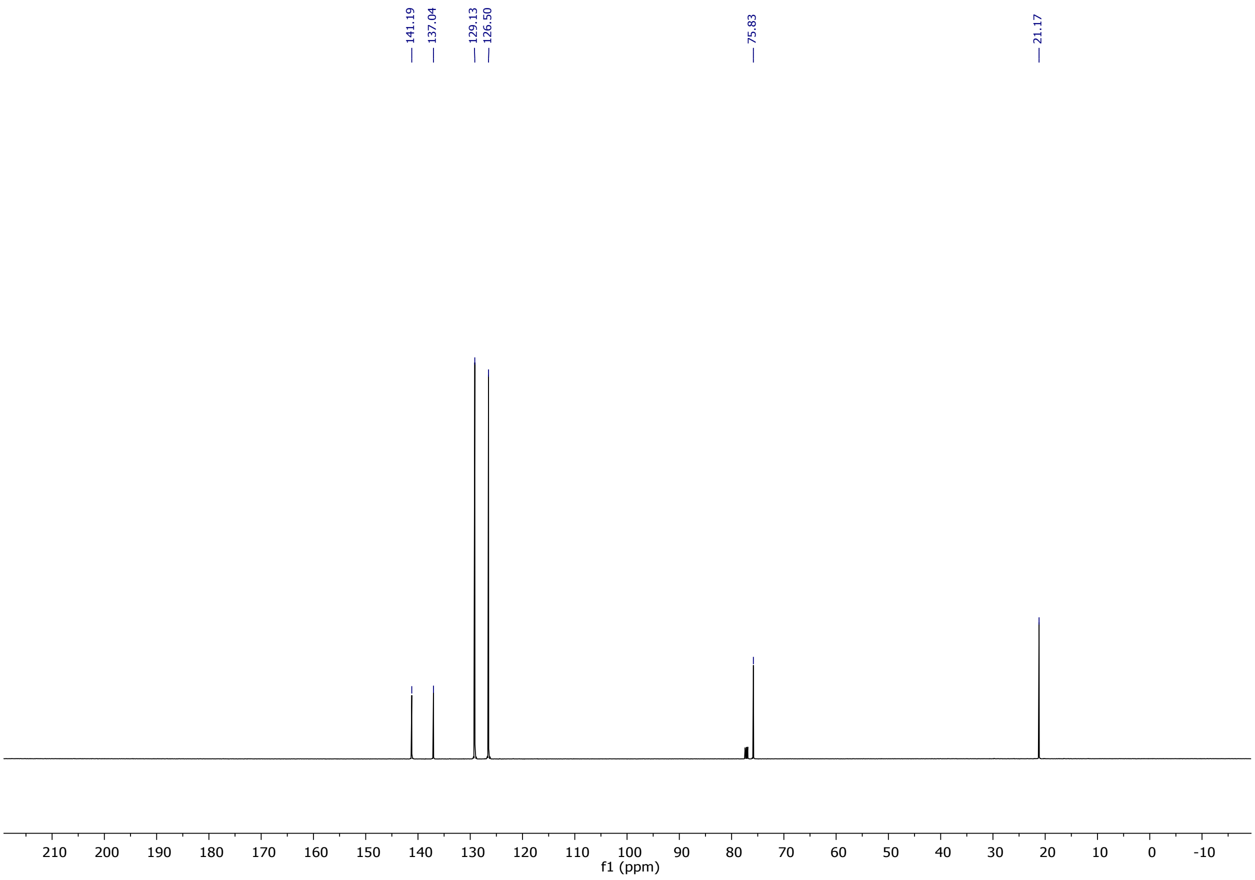


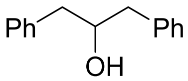
(**3j**)

^{1}H NMR (500 MHz, CDCl$_3$):



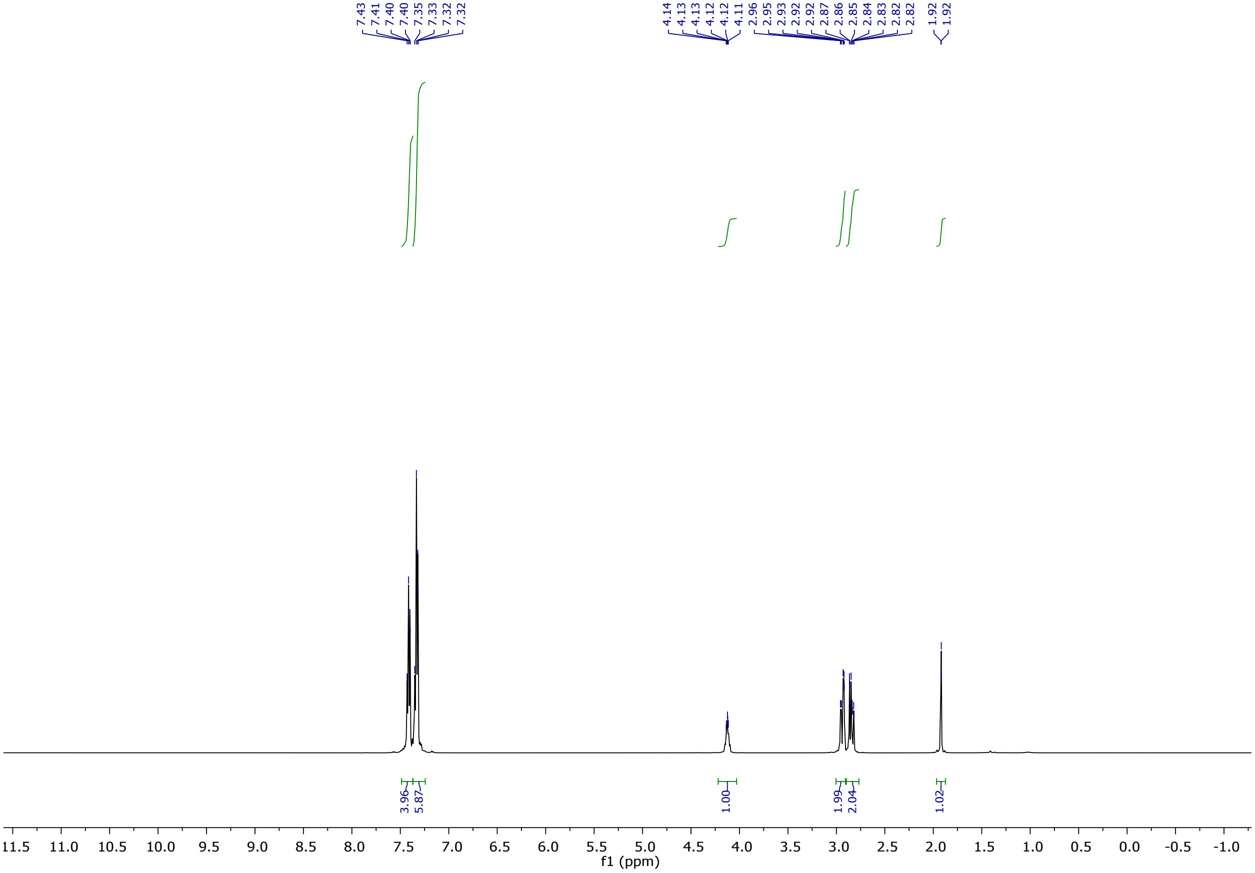
^{13}C NMR (126 MHz, CDCl$_3$):



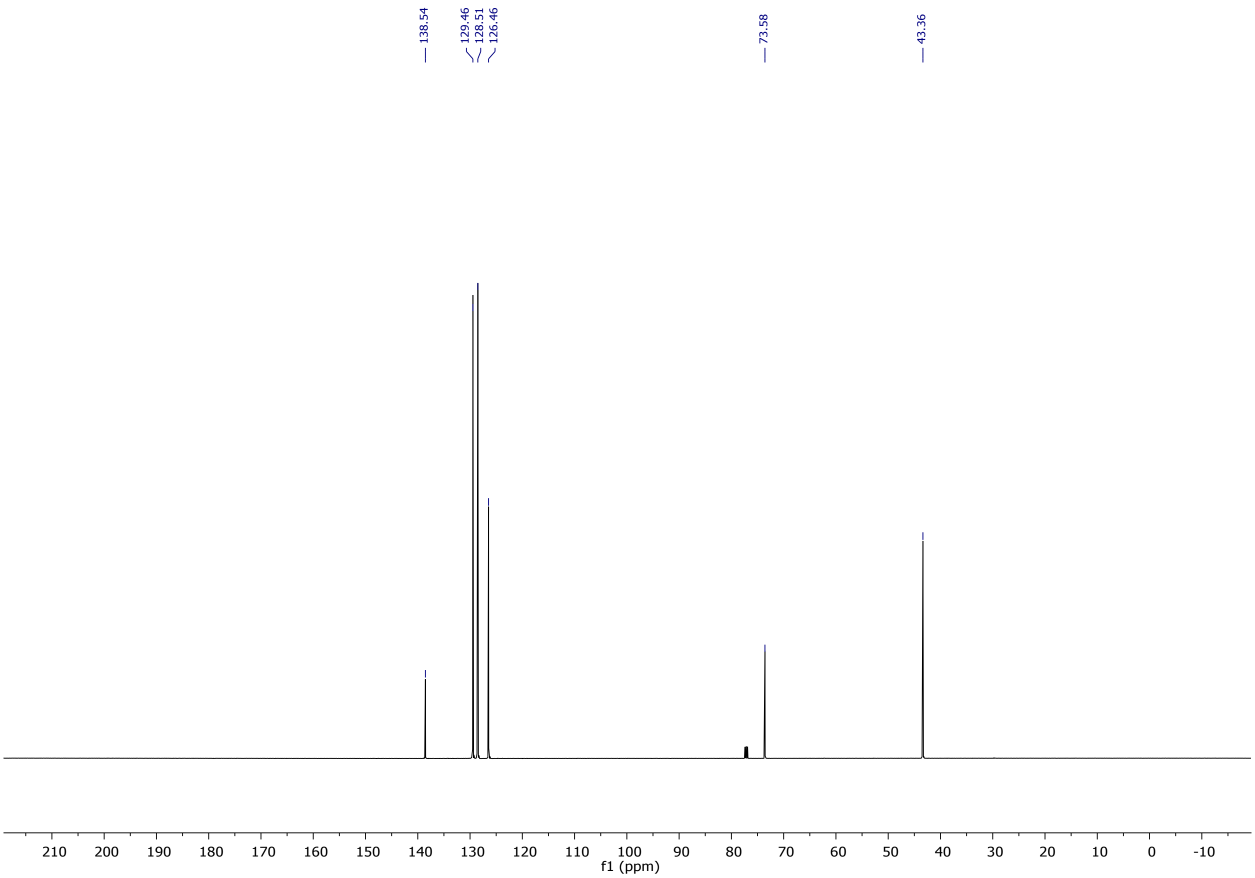


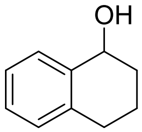
(**3k**)

^{1}H NMR (500 MHz, CDCl$_3$):



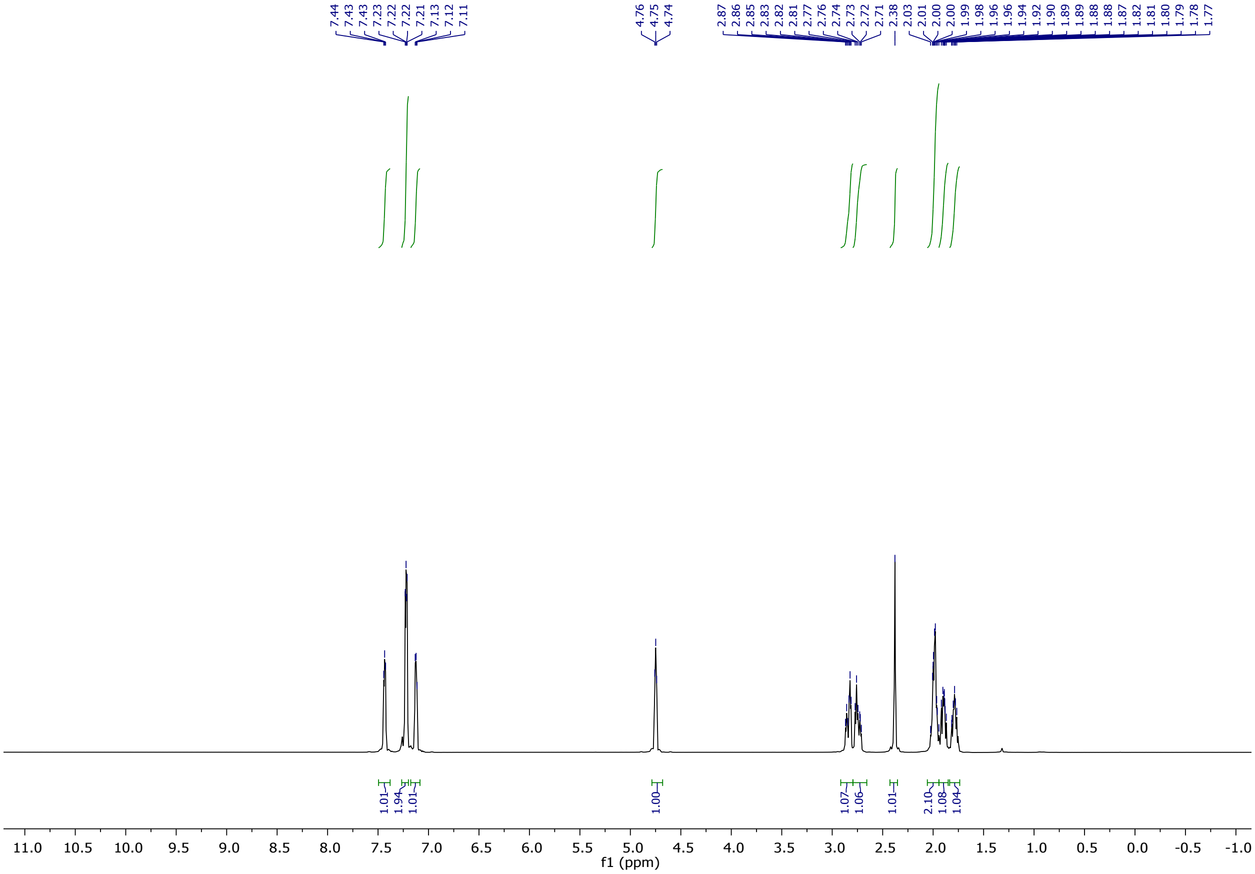
^{13}C NMR (126 MHz, CDCl$_3$):



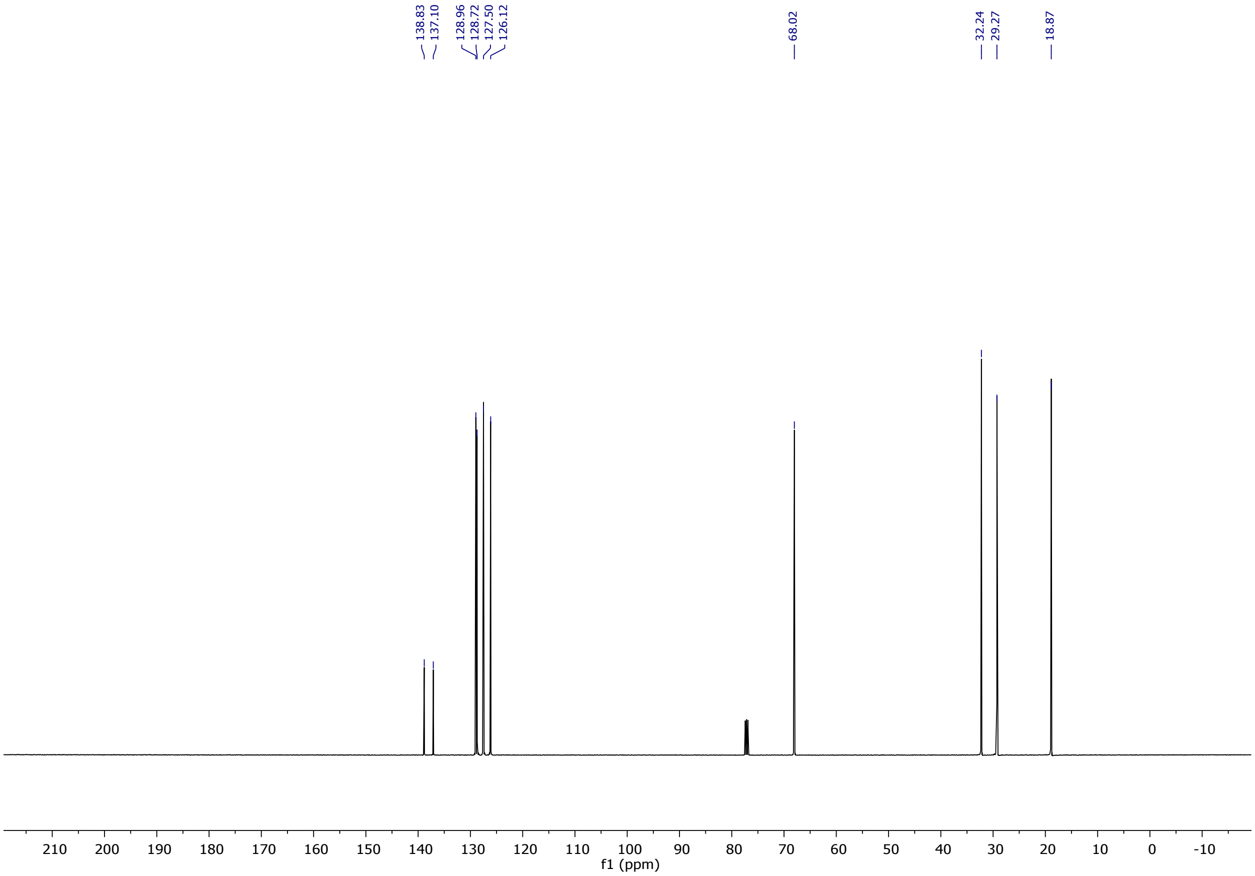


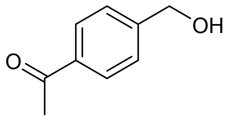
(**3l**)

^{1}H NMR (500 MHz, $CDCl_3$):



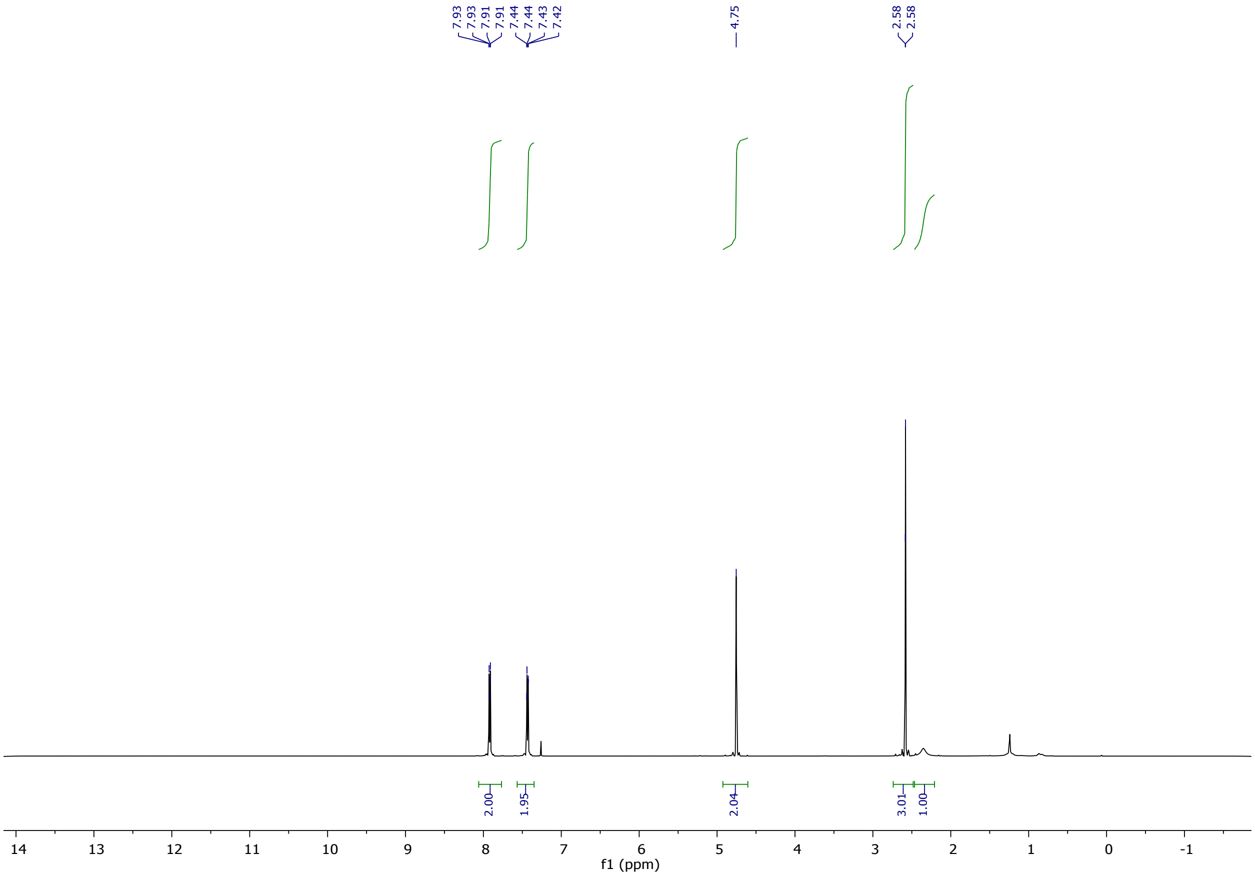
^{13}C NMR (126 MHz, CDCl$_3$):



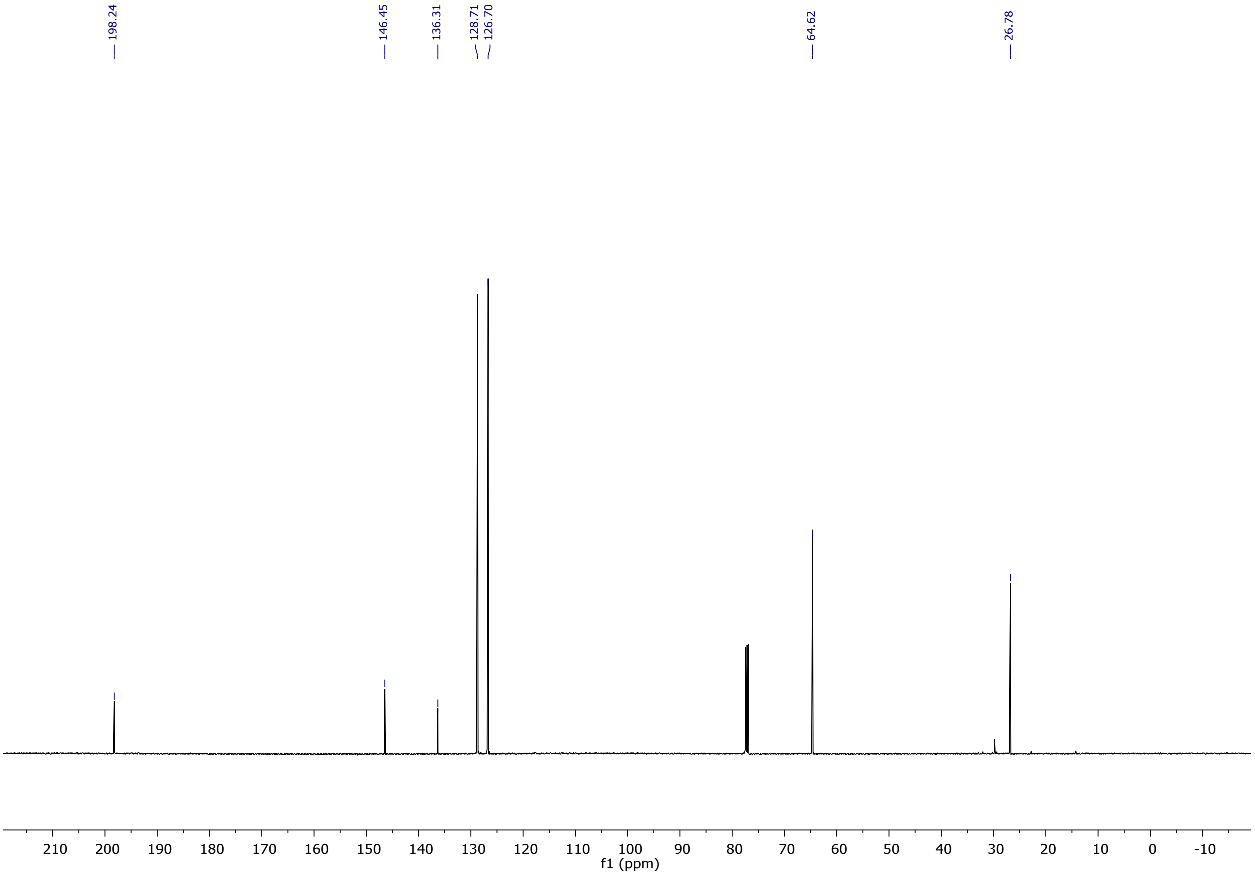


(3m)

^{1}H NMR (500 MHz, CDCl$_3$):



^{13}C NMR (126 MHz, $CDCl_3$):



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