

Electronic Supplementary Information:

1-D manganese(II)-terpyridine coordination polymers as precatalysts for hydrofunctionalization of carbonyl compounds

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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 N₂ using a Golden Gate ATR accessory. ¹H NMR and ¹³C NMR spectra were obtained at room temperature on a Bruker AV 400, 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. 2,2';6',2''-Terpyridine was purchased from Sigma-Aldrich. 4'-Pyridyl-2,2';6',2''-tpy (**pytpy**) was prepared according to the literature procedure.¹

Synthesis of 1. A solution of **pytpy** (31.0 mg, 0.100 mmol) in MeOH/CH₂Cl₂ (10 mL, 1 : 3, v/v) was placed in a test tube. A blank solution of MeOH/CH₂Cl₂ (4 mL, 1: 1, v/v) was layered on the top of the ligand solution, followed by a solution of MnCl₂ (12.5 mg, 0.100 mmol) in MeOH (8 mL). The tube was sealed and allowed to stand at room temperature for about four weeks, during which time X-ray quality yellow blocks grew at the bottom of the tube. The crystals were collected by decanting the solvent and washed with MeOH and then dried in vacuo. Yield: 37.5 mg (86%). FT-IR (solid, cm⁻¹): 3058m, 1597s, 1571w, 1537s, 1475s, 1407s, 1301w, 1246s, 1165s, 1080s, 1010s, 900w, 847m, 838s, 730m. Anal. Calcd. for C₂₀H₁₄Cl₂MnN₄: C 55.07, H 3.24, N 12.84%. Found C 54.62, H 3.51, N 12.73. In a separate experiment, in a 100 mL flask, **pytpy** (0.62 g, 2.00 mmol) was dissolved in MeOH/CH₂Cl₂ (40 mL, 1 : 3, v/v), to which a solution of MnCl₂ (0.25 g, 2.00 mmol) in MeOH (20 mL) was added dropwise in 3 min. The reaction mixture was allowed to stay for additional 10 min, yellow microcrystals had formed rapidly and were filtered out to give microcrystalline solid of **1** (yield: 0.71 g, 82%). Microanalysis revealed that the composition of this sample was identical to that of **1** and catalytic experiment also confirmed its activity and efficiency for hydroboration of acetophenone.

Synthesis of 2. A solution of **pytpy** (31.0 mg, 0.100 mmol) in MeOH/CH₂Cl₂ (10 mL, 1 : 3, v/v) was placed in a test tube. A blank solution of MeOH/CH₂Cl₂ (4 mL, 1: 1, v/v) was layered on the top of the ligand solution, followed by a solution of MnBr₂ (21.5 mg, 0.100 mmol) in MeOH (8 mL). The tube was sealed and allowed to stand at room temperature for about four weeks, during which time X-ray quality orange crystals grew at the bottom of the tube. The crystals were collected by decanting the solvent and washed with MeOH and then dried in vacuo overnight. Yield: 47.2 mg (90%). FT-IR (solid, cm⁻¹) 3050m, 1633w, 1598s, 1570w, 1535s, 1475m, 1408s, 1246m, 1154m, 1095m, 1076m, 1011s, 904m, 850m, 833m, 798s, 734s, 648s. Anal. Calcd. for C₂₀H₁₄Br₂MnN₄: C 45.75, H 2.69, N 10.67%. Found C 45.11, H 2.67, N 10.89.

General Procedure for 1-Catalysed Hydroboration of Ketones and Aldehydes. In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Ketone or aldehyde (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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was first analysed by GC-MS using a dilute CH₂Cl₂ solution, and then the crude reaction mixture was

purified through flash column chromatography with SiO₂ using ethyl acetate/hexane as an eluent. The alcohol products were characterized by ¹H and ¹³C NMR spectroscopies.

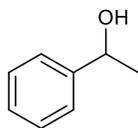
General Procedure for 1-Catalysed Hydrosilylation of Ketones and Aldehydes. In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Ketone or aldehyde (1.0 mmol) and phenylsilane (130.0 mg, 1.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was first analysed by GC-MS using a dilute CH₂Cl₂ solution, and then the crude reaction mixture was treated with 2N NaOH in methanol (5 mL) for 2 h. The solution was extracted with ethyl acetate and washed with brine and water. The filtrate was then purified through a flash column chromatography with SiO₂ using ethyl acetate/hexane as an eluent. The alcohol products were characterized by ¹H and ¹³C NMR spectroscopies.

General Procedure for 1-Catalysed Hydrosilylation of Styrenes. In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Ketone or aldehyde (1.0 mmol) and phenylsilane (130.0 mg, 1.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was first analysed by GC-MS using a dilute CH₂Cl₂ solution, and then the crude mixture was purified through a flash column chromatography with SiO₂ using ethyl acetate/hexane as an eluent. The products were characterized by ¹H and ¹³C NMR spectroscopies.

X-ray Crystallography. Suitable crystals of **1** and **2** were mounted on Cryoloops with Paratone-N oil. Data were collected with a Bruker X8 Kappa Apex II diffractometer using Mo-Kα radiation and corrected for absorption with SADABS and structures solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F². Hydrogen atoms were found from Fourier difference maps and refined isotropically, otherwise they were placed in calculated positions with appropriate riding parameters. CCDC No. 1969921 (**1**) and 1969922 (**2**) contain 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. The crystallographic refinement data are listed in Table S1.

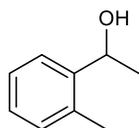
Table S1. X-ray crystallographic data for **1** and **2**.

	1	2
Empirical formula	C ₂₀ H ₁₈ Cl ₂ MnN ₄ O ₂	C ₂₁ H ₁₈ Br ₂ MnN ₄ O
FW	472.22	557.15
T (K)	200(2)	130(2)
Wavelength (Å)	0.71073	0.71073
space group	Monoclinic, <i>P2/n</i>	Triclinic, <i>P-1</i>
cell dimensions (Å, deg)	a = 8.9559(9) b = 11.5794(11) c = 10.6239(11) α = 90 β = 114.012(5) γ = 90	a = 8.8113(2) b = 10.2327(3) c = 11.4867(3) α = 95.1760(10) β = 91.4490(10) γ = 94.4070(10)
V(Å ³)	1006.40(17)	1027.87(5)
Z, ρ (Mg/m ³)	2, 1.558	2, 1.800
μ (mm ⁻¹)	7.987	4.550
F (000)	482	550
crystal size (mm)	0.17 × 0.15 × 0.10	0.360 × 0.250 × 0.060
θ range (deg)	3.82 to 69.21	2.56 to 36.85
index ranges	-10 ≤ h ≤ 10 -14 ≤ k ≤ 13 -12 ≤ l ≤ 12	-14 ≤ h ≤ 14 -17 ≤ k ≤ 17 -19 ≤ l ≤ 19
reflections collected	11286	45159
unique reflections	1762 [R(int) = 0.0584]	10067 [R(int) = 0.0373]
goodness of fit on F ²	1.074	1.037
R ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0557	0.0325
wR ₂ (all data)	0.1400	0.0726

Synthetic details and characterization data

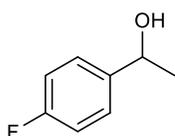
Chemical Formula: C₈H₁₀O
Molecular Weight: 122.1670

3a:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3a** was isolated. Yield: 112.0 mg (92%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.31 (m, 4H), 7.30-7.26 (m, 1H), 4.91 (q, *J* = 6.5 Hz, 1H), 1.66 (br., 1H), 1.51 (d, *J* = 6.4 Hz, 3H) ppm; ¹³C NMR (151 MHz, Chloroform-*d*) δ 145.9, 128.6, 127.6, 125.5, 70.6, 29.8, 25.3 ppm.



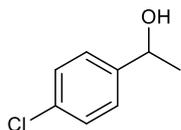
Chemical Formula: C₉H₁₂O
Molecular Weight: 136.1940

3b:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 2'-methylacetophenone (134.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3b** was isolated. Yield: 95.2 mg (70%). ¹H NMR (600 MHz, CDCl₃) δ 7.54 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.27 (td, *J* = 7.4, 1.6 Hz, 1H), 7.21 (td, *J* = 7.4, 1.6 Hz, 1H), 7.17 (dd, *J* = 7.7, 1.8 Hz, 1H), 5.14 (q, *J* = 6.5 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H) ppm; ¹³C NMR (151 MHz, CDCl₃) δ 143.9, 134.3, 130.4, 127.2, 126.4, 124.6, 66.8, 24.0, 19.0 ppm.



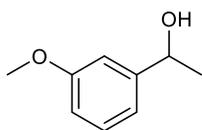
Chemical Formula: C₈H₉FO
Molecular Weight: 140.1574

3c:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3c** was isolated. Yield: 125 mg (89%). ¹H NMR (600 MHz, CDCl₃) δ 7.33 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 4.88 (q, *J* = 6.4 Hz, 1H), 1.86 (s, 1H), 1.47 (d, *J* = 6.6 Hz, 3H) ppm; ¹³C NMR (151 MHz, CDCl₃) δ 162.2 (d, *J* = 245.1 Hz), 141.6 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 8.2 Hz), 115.4 (d, *J* = 21.1 Hz), 69.9, 29.8, 25.4 ppm.



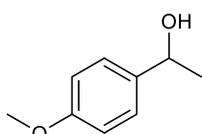
Chemical Formula: C_8H_9ClO
Molecular Weight: 156.6090

3d:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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: 140.9 mg (90%). 1H NMR (600 MHz, $CDCl_3$) δ 7.28 (dt, $J = 9.2, 2.5$ Hz, 2H), 7.25 (dd, $J = 7.3, 4.6$ Hz, 2H), 4.79 (q, $J = 6.5$ Hz, 1H), 2.71 (s, 1H), 1.41 (d, $J = 6.6$ Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 133.2, 128.8, 127.1, 69.9, 25.5 ppm.



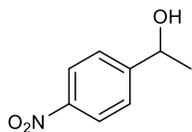
Chemical Formula: $C_9H_{12}O_2$
Molecular Weight: 152.1930

3e:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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 **3e** was isolated. Yield: 144.4 mg (95%). 1H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, $J = 8.1$ Hz, 1H), 7.01 – 6.91 (m, 2H), 6.83 (dd, $J = 8.3, 2.6$ Hz, 1H), 4.89 (q, $J = 6.5$ Hz, 1H), 3.84 (s, 3H), 1.99 (s, 1H), 1.51 (d, $J = 6.6$ Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 147.7, 129.6, 117.8, 113.0, 111.0, 70.4, 55.3, 25.2 ppm.



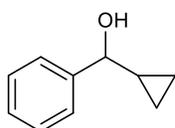
Chemical Formula: $C_9H_{12}O_2$
Molecular Weight: 152.1930

3f:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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 **3f** was isolated. Yield: 142.0 mg (93%). 1H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 4.86 (q, $J = 6.4$ Hz, 1H), 3.81 (s, 3H), 1.74 (s, 1H), 1.48 (d, $J = 6.5$ Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 138.1, 126.8, 114.0, 70.1, 55.4, 29.8, 25.1 ppm.



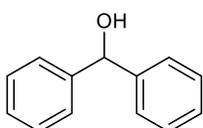
Chemical Formula: $C_8H_9NO_3$
Molecular Weight: 167.1640

3g:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4'-Nitroacetophenone (165.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Yellowish oil of **3g** was isolated. Yield: 147.1 mg (88%). ¹H NMR (600 MHz, CDCl₃) δ 8.18 (td, $J = 6.7, 3.4$ Hz, 2H), 7.53 (td, $J = 6.7, 3.4$ Hz, 2H), 5.07 – 4.96 (m, 1H), 2.06 (s, 1H), 1.64 – 1.38 (m, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 153.7, 147.6, 126.8, 125.5, 124.5, 123.2, 70.1, 26.1 ppm.



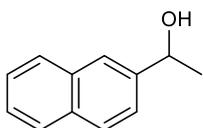
Chemical Formula: $C_{10}H_{12}O$
Molecular Weight: 148.2050

3h:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3h** was isolated. Yield: 110.0.7 mg (74%). ¹H NMR (600 MHz, CDCl₃) δ 7.28 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 7.08 (t, $J = 7.5$ Hz, 1H), 3.75 (d, $J = 8.8$ Hz, 1H), 2.24 (s, 1H), 0.99 (dtd, $J = 13.1, 8.3, 4.8$ Hz, 1H), 0.41 (tt, $J = 8.7, 4.9$ Hz, 1H), 0.33 (tt, $J = 8.7, 4.9$ Hz, 1H), 0.25 (dq, $J = 10.0, 5.0$ Hz, 1H), 0.15 (dq, $J = 9.9, 5.0$ Hz, 1H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 144.1, 128.6, 127.7, 126.3, 78.8, 19.4, 3.9, 3.1 ppm.



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

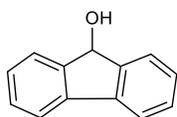
3i:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Benzophenone (182.1 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3i** was isolated. Yield: 173.0 mg (94%). ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.40 (m, 4H), 7.38 – 7.35 (m, 4H), 7.32 – 7.28 (m, 2H), 5.88 (s, 1H), 2.26 (s, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃) δ 143.9, 128.6, 127.7, 126.6, 76.4 ppm.



Chemical Formula: $C_{12}H_{12}O$
Molecular Weight: 172.2270

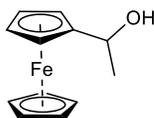
3j:³ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μ mol, based on $Mn(L)Cl_2$) and KO^tBu (1.1 mg, 10 μ mol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 2-Acetylnaphthalene (170.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at

room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3j** was isolated. Yield: 125.5mg (73%). ¹H NMR (600 MHz, CDCl₃) δ 7.93 – 7.79 (m, 3H), 7.78 (d, *J* = 2.9 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.49 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.00 (q, *J* = 6.6 Hz, 1H), 3.05 (s, 1H), 1.58 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 143.5, 133.5, 133.1, 128.4, 128.2, 127.9, 126.3, 125.9, 124.1, 124.0, 70.5, 25.3 ppm.



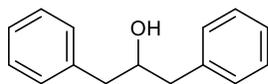
Chemical Formula: C₁₃H₁₀O
Molecular Weight: 182.2220

3k:⁴ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Fluorenone (180.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. White solid of **3k** was isolated. Yield: 173.0 mg (95%). ¹H NMR (600 MHz, CD₃OD) δ 7.71 – 7.63 (m, 2H), 7.63 – 7.56 (m, 2H), 7.36 (td, *J* = 7.5, 1.5 Hz, 2H), 7.30 (td, *J* = 7.4, 1.4 Hz, 2H), 5.49 (s, 1H), 4.94 (s, 1H) ppm; ¹³C NMR (151 MHz, CD₃OD) δ 148.2, 142.2, 130.6, 129.4, 126.9, 121.6, 76.2 ppm.



Chemical Formula: C₁₂H₁₄FeO
Molecular Weight: 230.0880

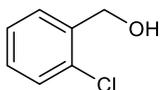
3l:³ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 1-acetylferrocene (228.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Yellow solid of **3l** was isolated. Yield: 211.5 mg (92%). ¹H NMR (600 MHz, CDCl₃): δ 4.51 (q, *J* = 6.4 Hz, 1H), 4.22 (m, 9H), 2.03 (s, 1H), 1.44 (d, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 95.1, 68.8, 68.3, 68.3, 66.7, 66.5, 65.7, 23.8 ppm.



Chemical Formula: C₁₅H₁₆O
Molecular Weight: 212.2920

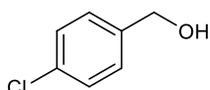
3m:⁴ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 1,3-Diphenylacetone (210.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **3m** was isolated. Yield: 193.2 mg (91%). ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.16 (m, 4H), 7.15 – 6.89 (m, 6H), 3.91 (tq, *J* = 8.2, 4.1 Hz,

1H), 2.72 (dd, $J = 13.8, 5.0$ Hz, 2H), 2.62 (dd, $J = 13.9, 8.3$ Hz, 2H), 1.68 (d, $J = 3.7$ Hz, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 138.77, 129.7, 128.8, 126.7, 73.82, 43.6 ppm.



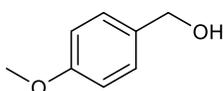
Chemical Formula: $\text{C}_7\text{H}_7\text{ClO}$
Molecular Weight: 142.5820

4a:⁴ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 2-Chlorobenzaldehyde (140.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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 **4a** was isolated. Yield: 136.9 mg (92%). ^1H NMR (600 MHz, CDCl_3) δ 7.46 (dd, $J = 7.6, 2.1$ Hz, 1H), 7.35 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.27 (td, $J = 7.5, 1.6$ Hz, 1H), 7.23 (td, $J = 7.6, 1.9$ Hz, 1H), 4.75 (s, 2H), 2.53 (s, 1H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 138.4, 132.9, 129.6, 129.1, 128.9, 127.3, 63.0 ppm.



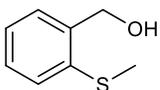
Chemical Formula: $\text{C}_7\text{H}_7\text{ClO}$
Molecular Weight: 142.5820

4b:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4-Chlorobenzaldehyde (140.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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 **4b** was isolated. Yield: 131.0 mg (95%). ^1H NMR (600 MHz, CDCl_3) δ 7.31 (dd, $J = 9.4, 2.8$ Hz, 2H), 7.23 (d, $J = 9.4$ Hz, 2H), 4.56 (s, 2H), 3.09 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 139.4, 133.5, 128.8, 128.5, 64.4 ppm.



Chemical Formula: $\text{C}_8\text{H}_{10}\text{O}_2$
Molecular Weight: 138.1660

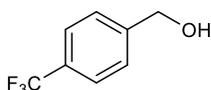
4c:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4-Methoxybenzaldehyde (136.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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 **4c** was isolated. Yield: 131.0 mg (95%). ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.54 (s, 2H), 3.79 (s, 3H), 3.10 (s, 1H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 159.2, 133.4, 128.8, 114.0, 64.8, 55.4 ppm.



Chemical Formula: $\text{C}_8\text{H}_{10}\text{OS}$
Molecular Weight: 154.2270

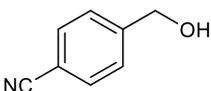
4d:³ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 2-Methylthiobenzaldehyde (152.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir

at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Yellowish oil of **4d** was isolated. Yield: 141.8 mg (92%). ¹H NMR (500 MHz, CDCl₃) δ 7.38 (s, 1H), 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 1H), 4.76 (s, 2H), 2.50 (s, 3H), 1.74 (s, 1H) ppm; ¹³C NMR (151 MHz, CDCl₃) δ 139.0, 136.8, 128.5, 128.2, 126.7, 125.6, 63.7, 16.2 ppm.



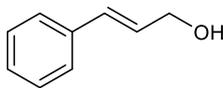
Chemical Formula: C₈H₇F₃O
Molecular Weight: 176.1382

4e:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4'-Trifluoromethylbenzaldehyde (178.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **4e** was isolated. Yield: 169.0 mg (96%). ¹H NMR (600 MHz, CDCl₃) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 4.80 (s, 2H), 2.58 (s, 1H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 145.2, 130.05 (q, *J* = 32.3 Hz), 127.2, 125.7 (q, *J* = 3.8 Hz), 125.3, 123.5, 121.74 64.7 ppm.



Chemical Formula: C₈H₇NO
Molecular Weight: 133.1500

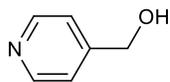
4f:⁴ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 4'-Cyanobenzaldehyde (131.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **4f** was isolated. Yield: 118.5 mg (89%). ¹H NMR (600 MHz, CDCl₃) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 4.70 (s, 2H) ppm (H^{OH} signal is missing); ¹³C NMR (151 MHz, CDCl₃) δ 146.8, 132.5, 127.2, 119.1, 111.0, 64.0 ppm.



Chemical Formula: C₉H₁₀O
Molecular Weight: 134.1780

4g:² In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol, based on Mn(L)Cl₂) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. *Trans*-cinnamaldehyde (132.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **4g** was isolated. Yield: 126.5 mg (94%). ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.22 (m, 2H), 7.19 (dd, *J* = 8.5, 6.6 Hz, 2H), 7.15 – 7.10 (m, 1H), 6.47 (dt, *J* = 15.9, 1.7 Hz, 1H), 6.22 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.17 (dd, *J* = 5.7, 1.6 Hz,

2H), 2.76 (s, 1H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 136.9, 131.1, 128.8, 128.8, 127.6, 126.7, 63.7 ppm.



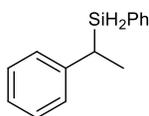
Chemical Formula: $\text{C}_6\text{H}_7\text{NO}$
Molecular Weight: 109.1280

4h:³ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. Pyridine-4-carboxaldehyde (107.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:5, v/v) as eluent. Colorless oil of **4h** was isolated. Yield: 92.6 mg (85%). ^1H NMR (600 MHz, CDCl_3) δ 8.36 (d, $J = 5.9$ Hz, 2H), 7.23 (d, $J = 5.8$ Hz, 2H), 5.26-3.86 (br. 1H, overlapping, H^{OH}), 4.66 (s, 2H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 151.7, 149.4, 121.6, 63.1 ppm.



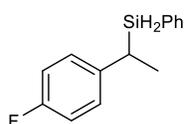
Chemical Formula: $\text{C}_8\text{H}_{18}\text{O}$
Molecular Weight: 130.2310

4i:⁴ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. 1-Octanal (128.0 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 2 h. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydroborated product was detected by GC-MS, 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 **4i** was isolated. Yield: 113.2 mg (87%). ^1H NMR (600 MHz, CDCl_3) δ 3.74 – 3.47 (m, 2H), 2.01 (s, 1H), 1.54 (dt, $J = 15.1, 6.8$ Hz, 2H), 1.45 – 1.01 (m, 10H), 0.89 – 0.79 (m, 3H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 63.2, 33.0, 32.1, 29.7, 29.6, 26.0, 22.9, 14.4 ppm.



Chemical Formula: $\text{C}_{14}\text{H}_{16}\text{Si}$
Molecular Weight: 212.3670

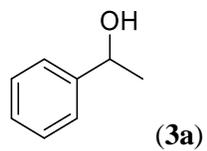
5a:⁵ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was loaded in a 3.8 mL glass vial equipped with a stir bar. Styrene (104.0 mg, 1.0 mmol) and phenylsilane (130.0 mg, 1.2 mmol) were then added. The neat mixture was allowed to stir at room temperature for 80 min. At completion of the reaction, the reaction was exposed to the air and the solvent was evaporated. The hydrosilylated product was detected by GC-MS, 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 **5a** was isolated. Yield: 191.1 mg (90%). ^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.47 (m, 3H), 7.46 – 7.34 (m, 4H), 7.29 – 7.19 (m, 3H), 4.49 (s, 2H), 2.80 – 2.71 (m, 1H), 1.60 (d, $J = 7.5$ Hz, 3H) ppm; ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 136.0, 131.7, 130.1, 128.7, 128.2, 127.5, 125.4, 25.7, 16.7 ppm.



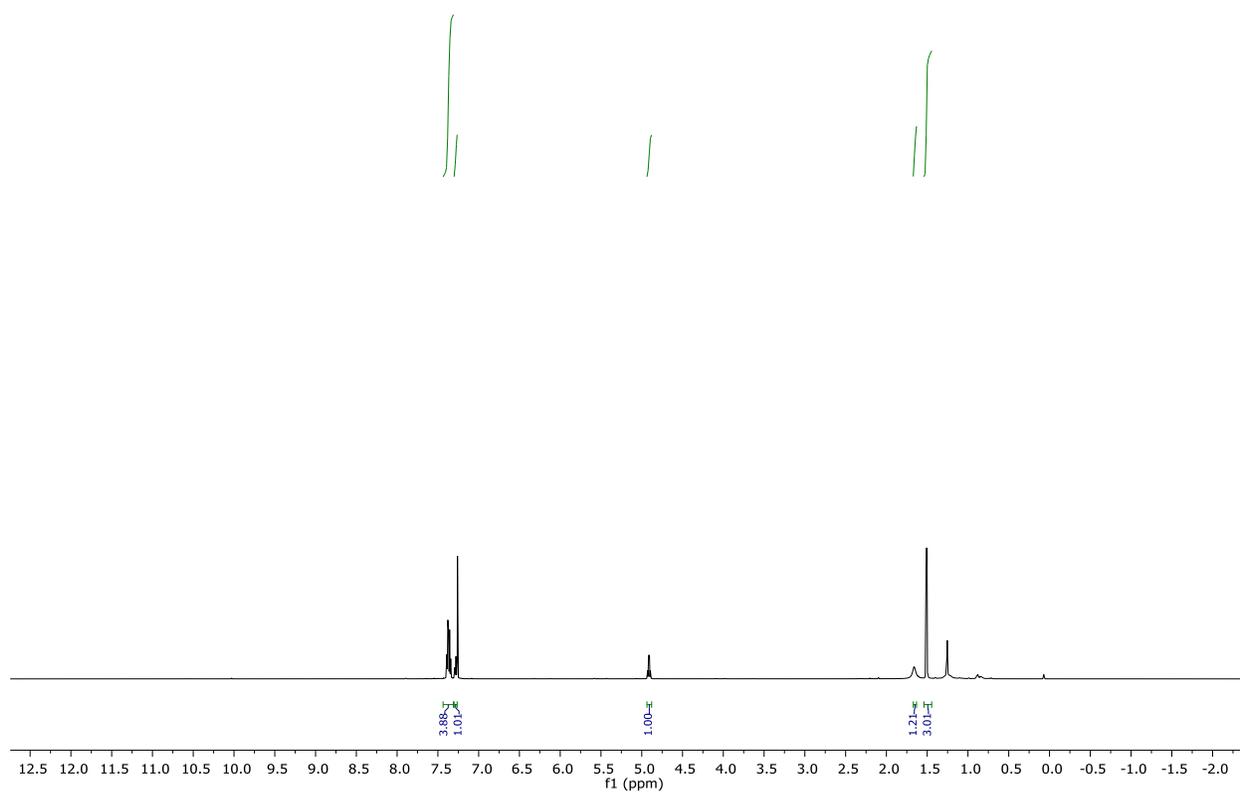
Chemical Formula: $\text{C}_{14}\text{H}_{15}\text{FSi}$
Molecular Weight: 230.3574

5b:⁵ In a glovebox under nitrogen atmosphere, CP **1** (0.44 mg, 1.0 μmol , based on $\text{Mn}(\text{L})\text{Cl}_2$) and KO^tBu (1.1 mg, 10 μmol) was loaded in a 3.8 mL glass vial equipped with a stir bar. Styrene (104.0 mg, 1.0 mmol) and phenylsilane (130.0 mg, 1.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 16. At completion of the

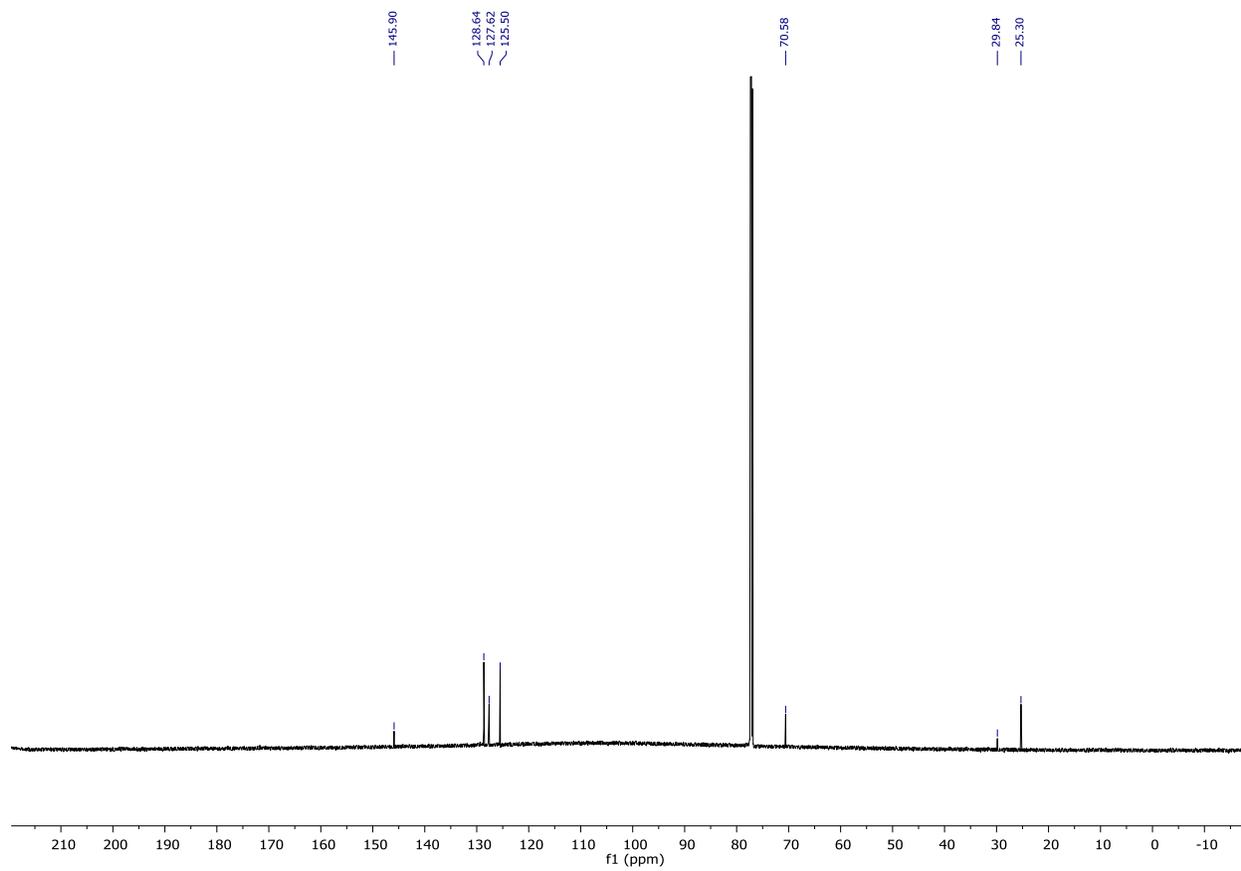
reaction, the reaction was exposed to the air and the solvent was evaporated. The hydrosilylated product was detected by GC-MS, and then the crude reaction mixture was purified through flash column chromatography with SiO₂ using ethyl acetate/hexane (1:10, v/v) as eluent. Colorless oil of **5b** was isolated. Yield: 133.4 mg (58%). ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.39 (m, 3H), 7.34 (dd, *J* = 7.7, 6.9 Hz, 2H), 7.05 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 4.33 (d, *J* = 3.2 Hz, 2H), 2.66 – 2.60 (m, 1H), 1.46 (d, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 161.21 (d, *J* = 219.3 Hz), 140.1, 135.6, 134.83 (d, *J* = 221.4 Hz), 131.1, 129.9, 128.3 (d, *J* = 7.7 Hz), 127.9, 115.11 (d, *J* = 21.1 Hz), 24.6, 16.6 ppm.

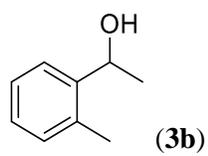
NMR spectra for isolated products:

¹H NMR (600 MHz, CDCl₃):

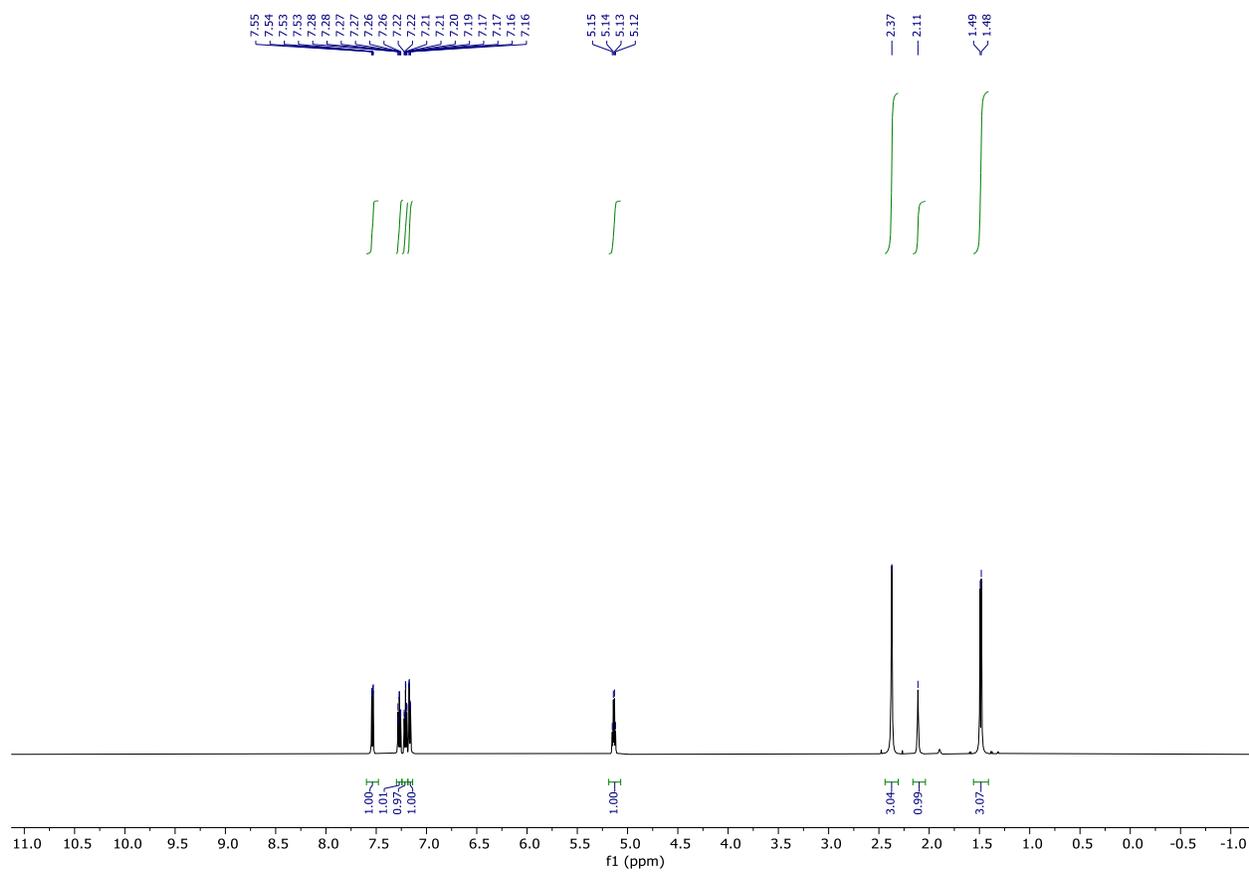


^{13}C NMR (151 MHz, CDCl_3):

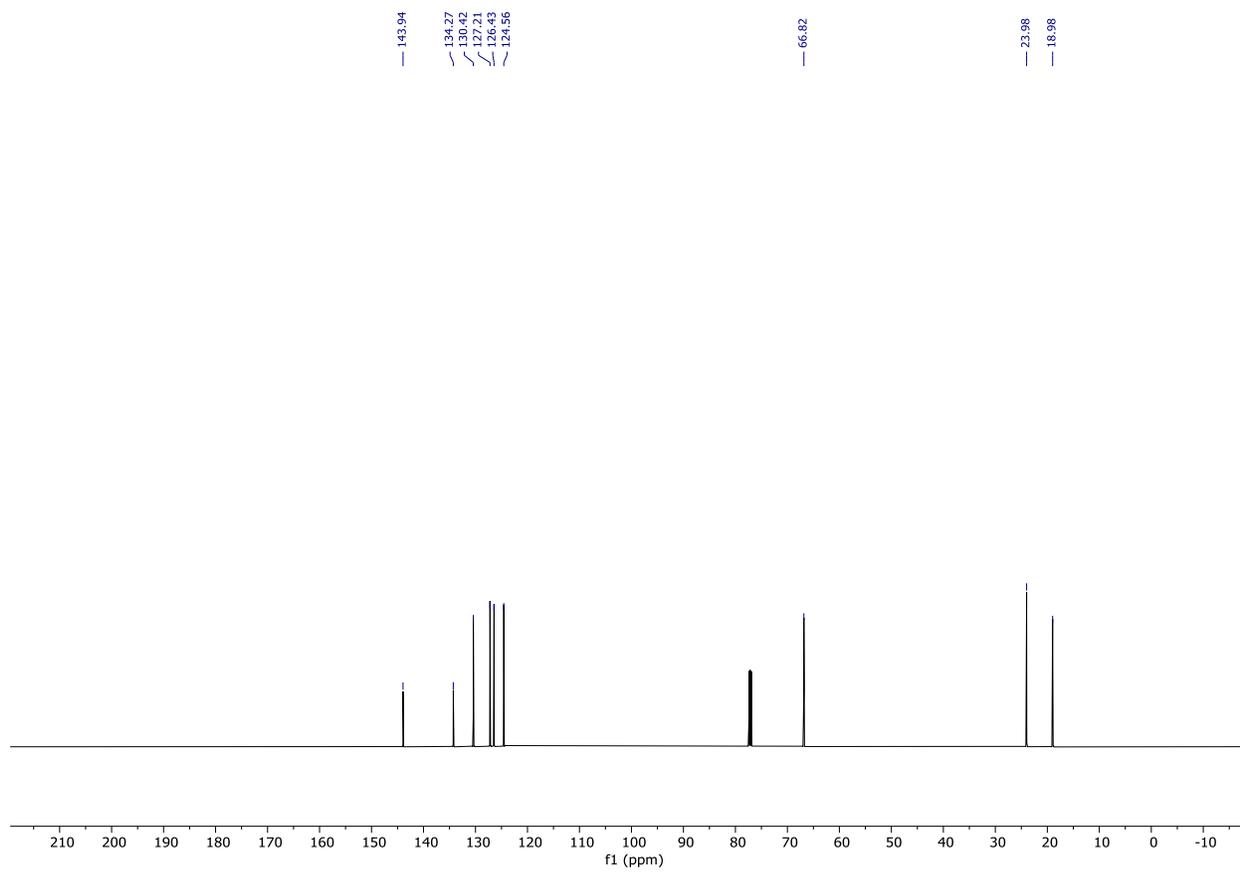


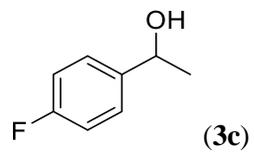


^1H NMR (600 MHz, CDCl_3):

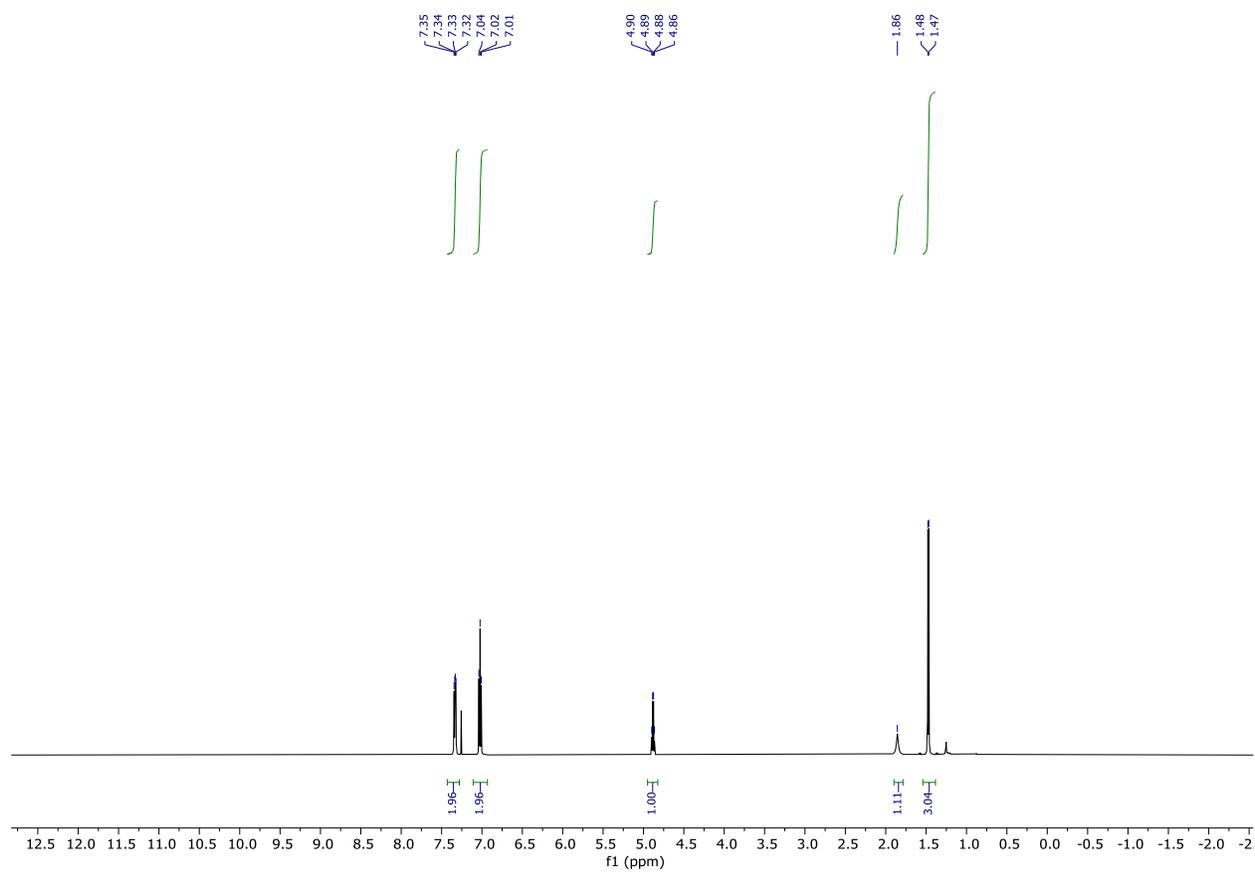


^{13}C NMR (151MHz, CDCl_3):

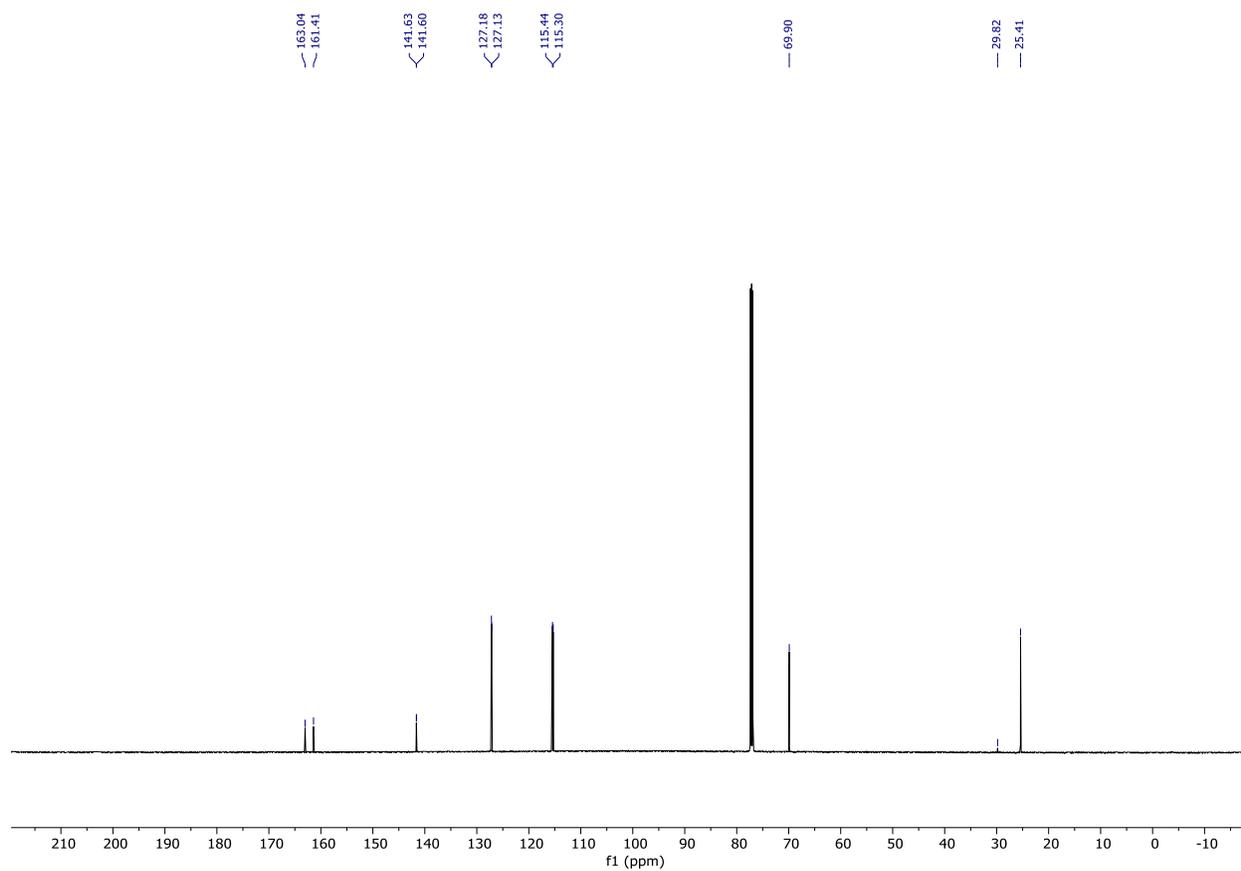


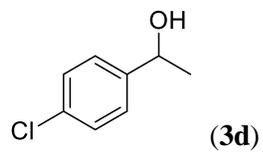


^1H NMR (600 MHz, CDCl_3):

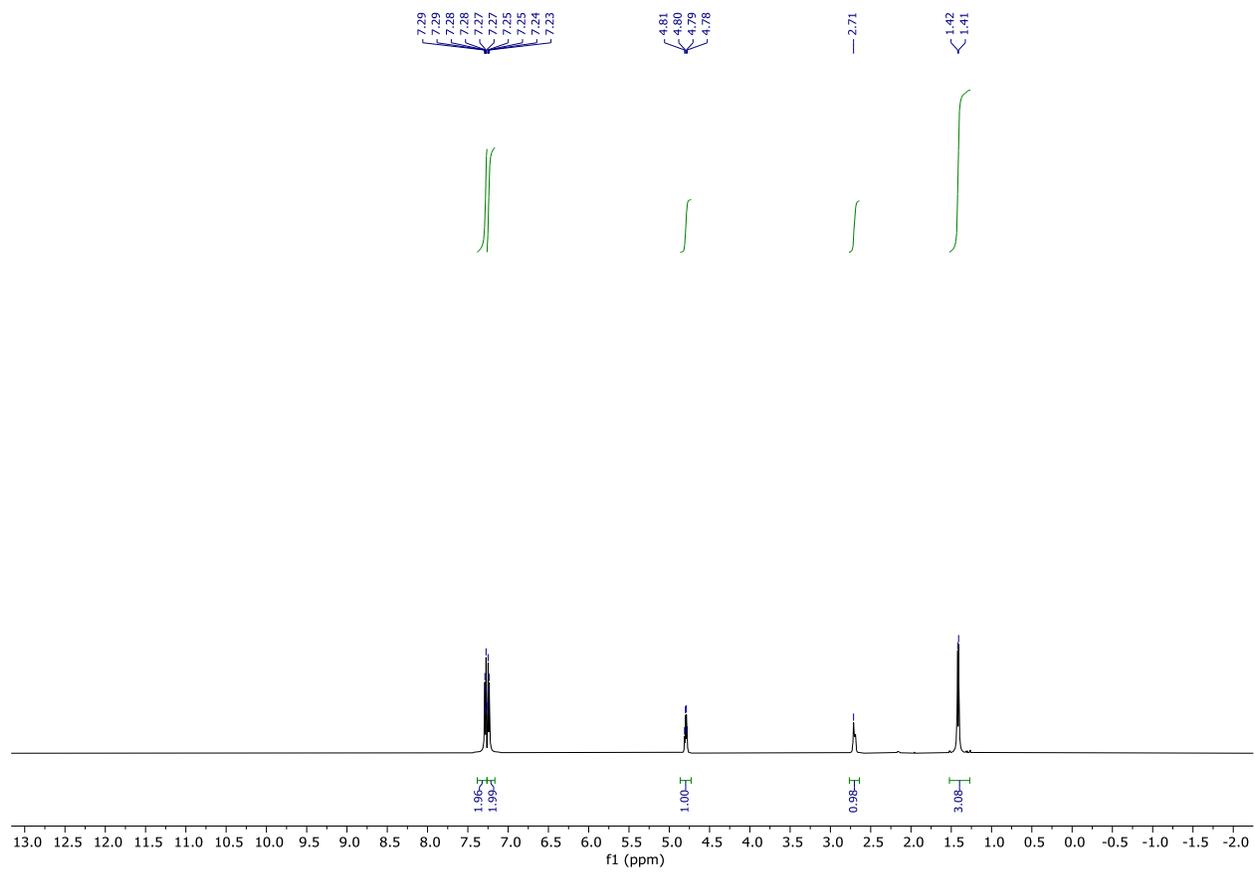


^{13}C NMR (151MHz, CDCl_3):

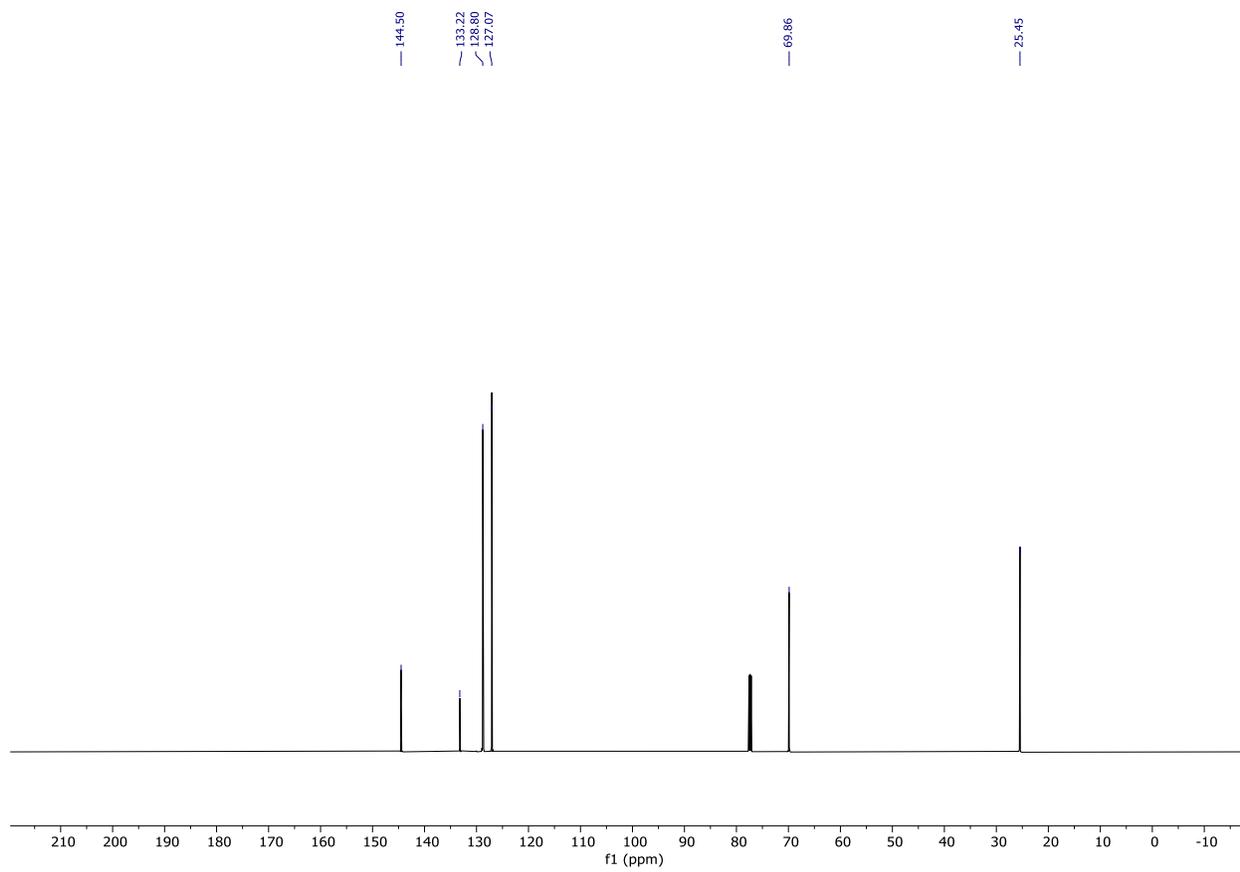


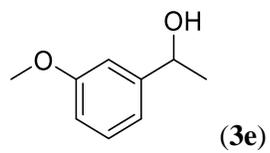


^1H NMR (600 MHz, CDCl_3):

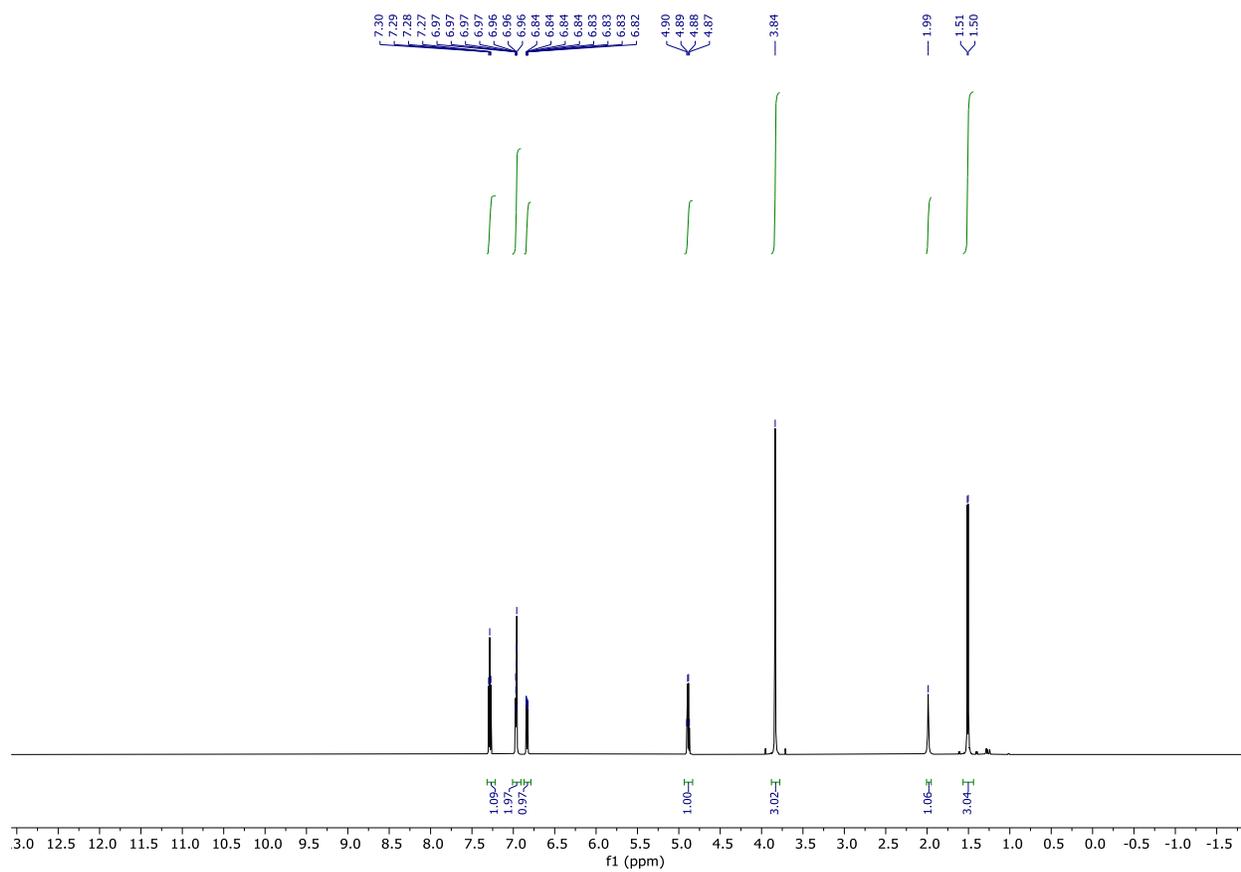


^{13}C NMR (151 MHz, CDCl_3):

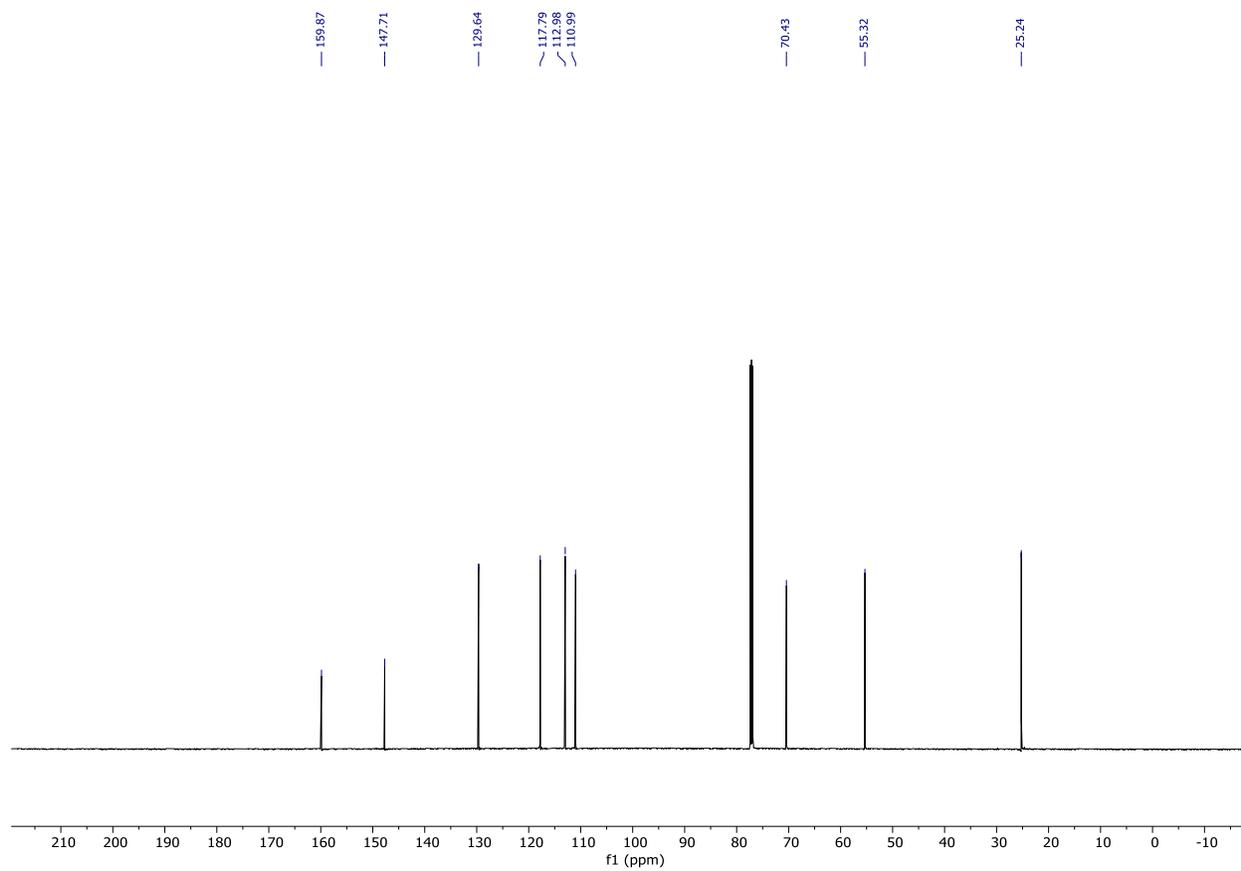


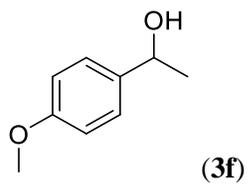


^1H NMR (600 MHz, CDCl_3):

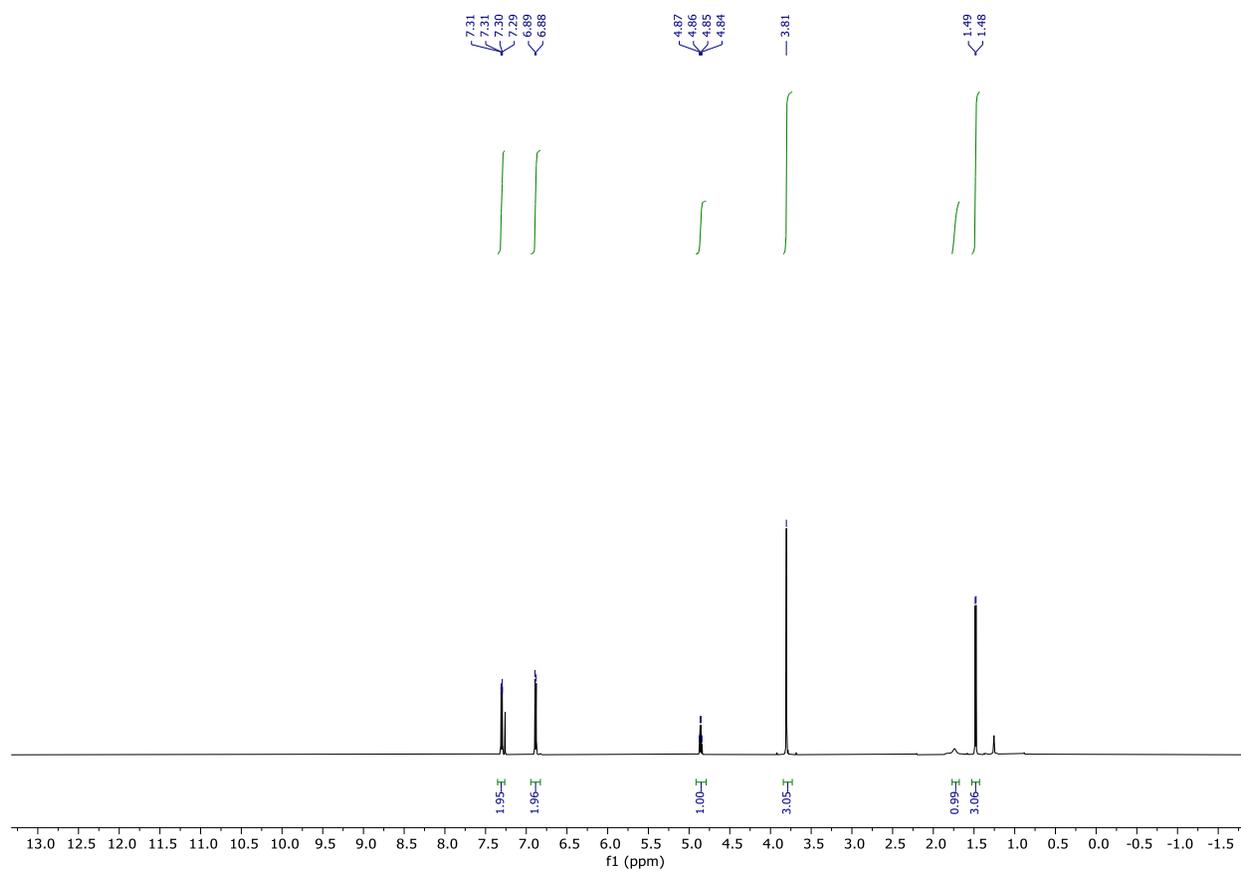


^{13}C NMR (151 MHz, CDCl_3):

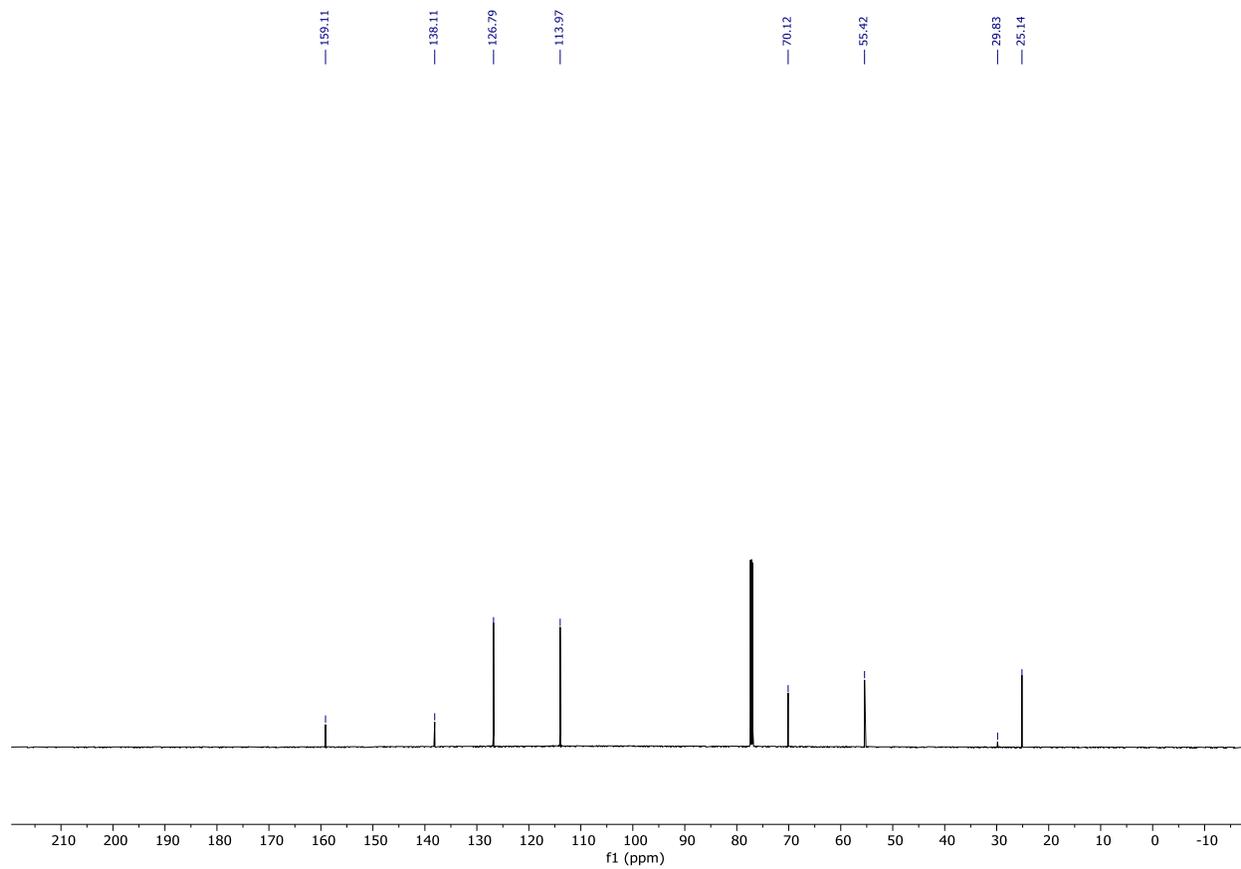


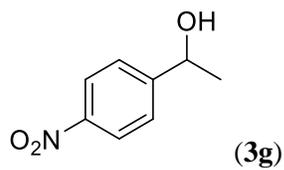


$^1\text{H NMR}$ (600 MHz, CDCl_3):

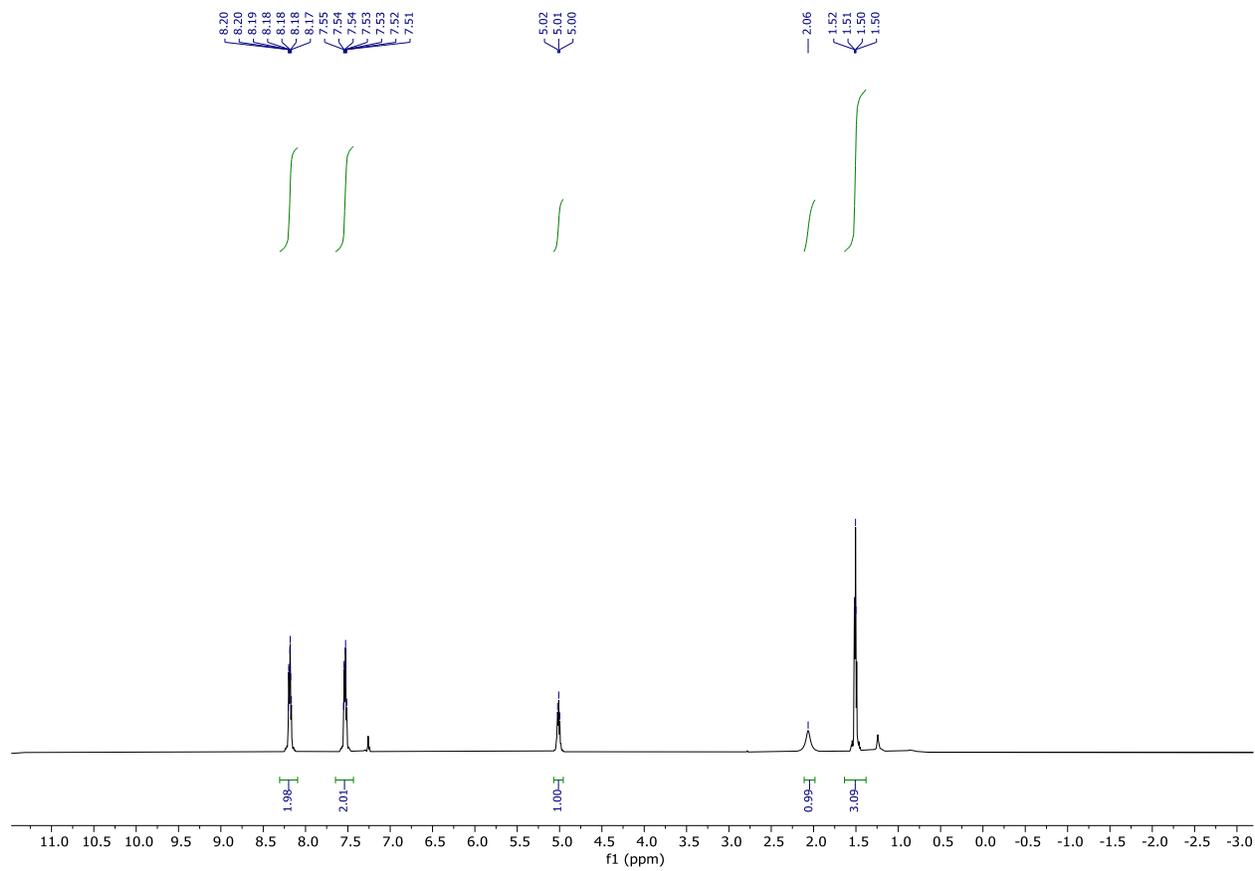


^{13}C NMR (151 MHz, CDCl_3):

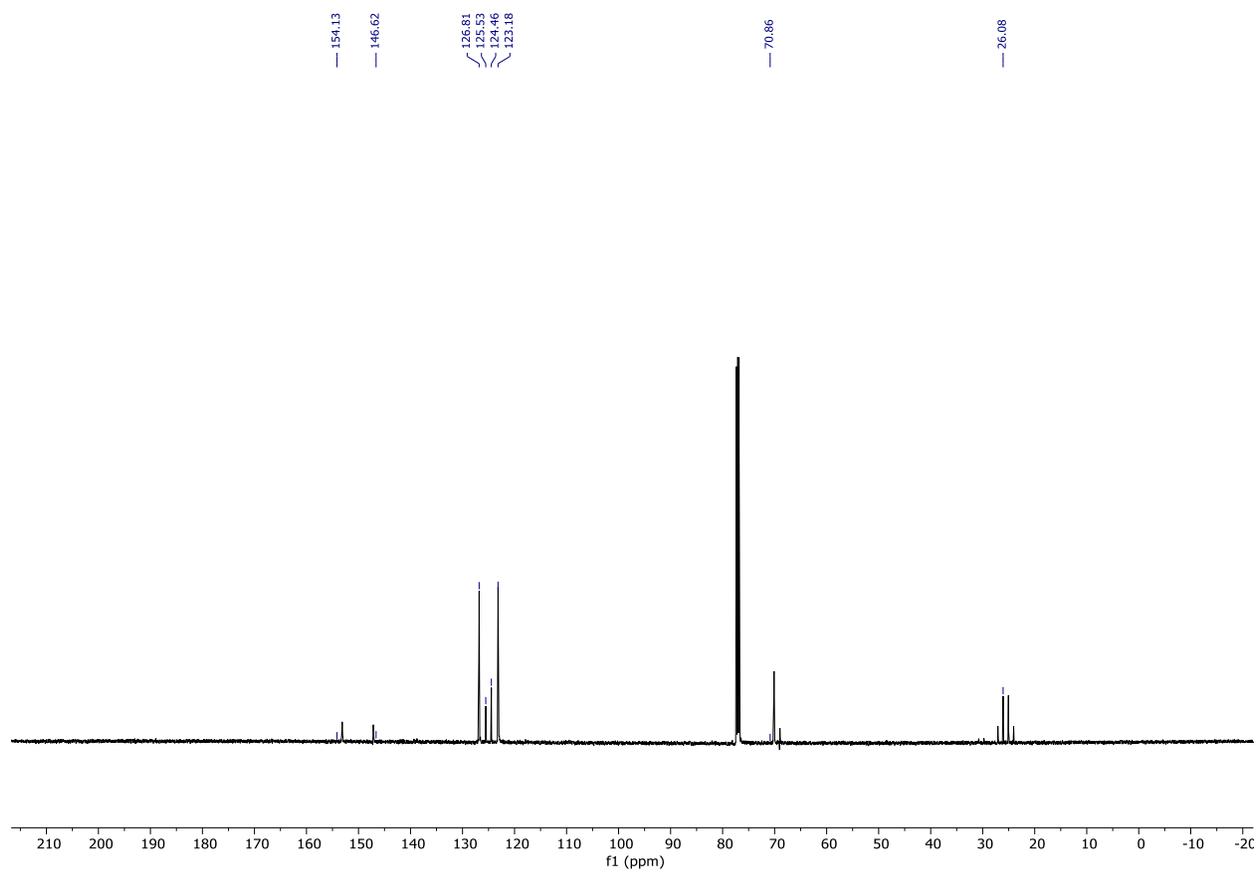


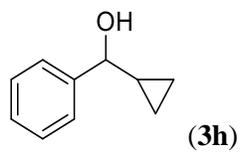


$^1\text{H NMR}$ (600 MHz, CDCl_3):

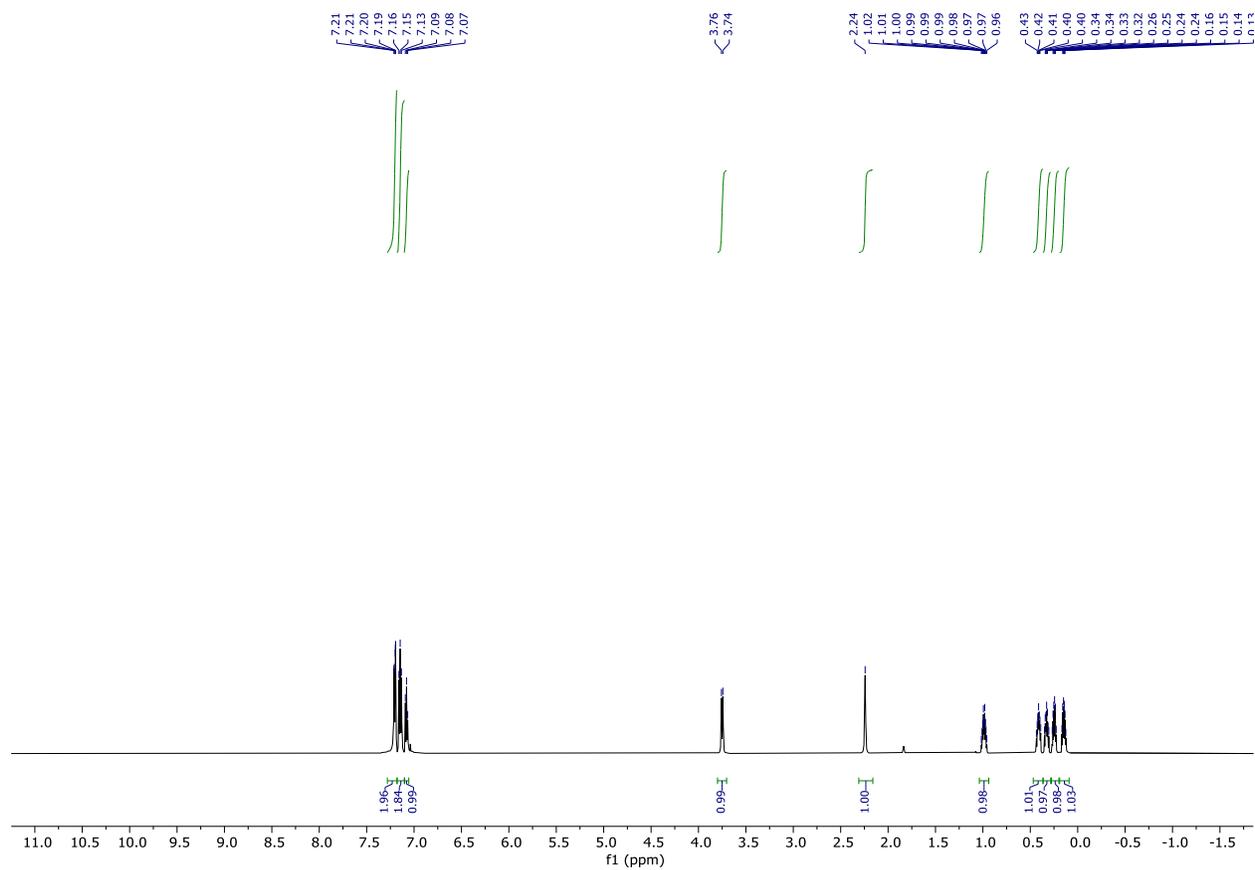


^{13}C NMR (151 MHz, CDCl_3):

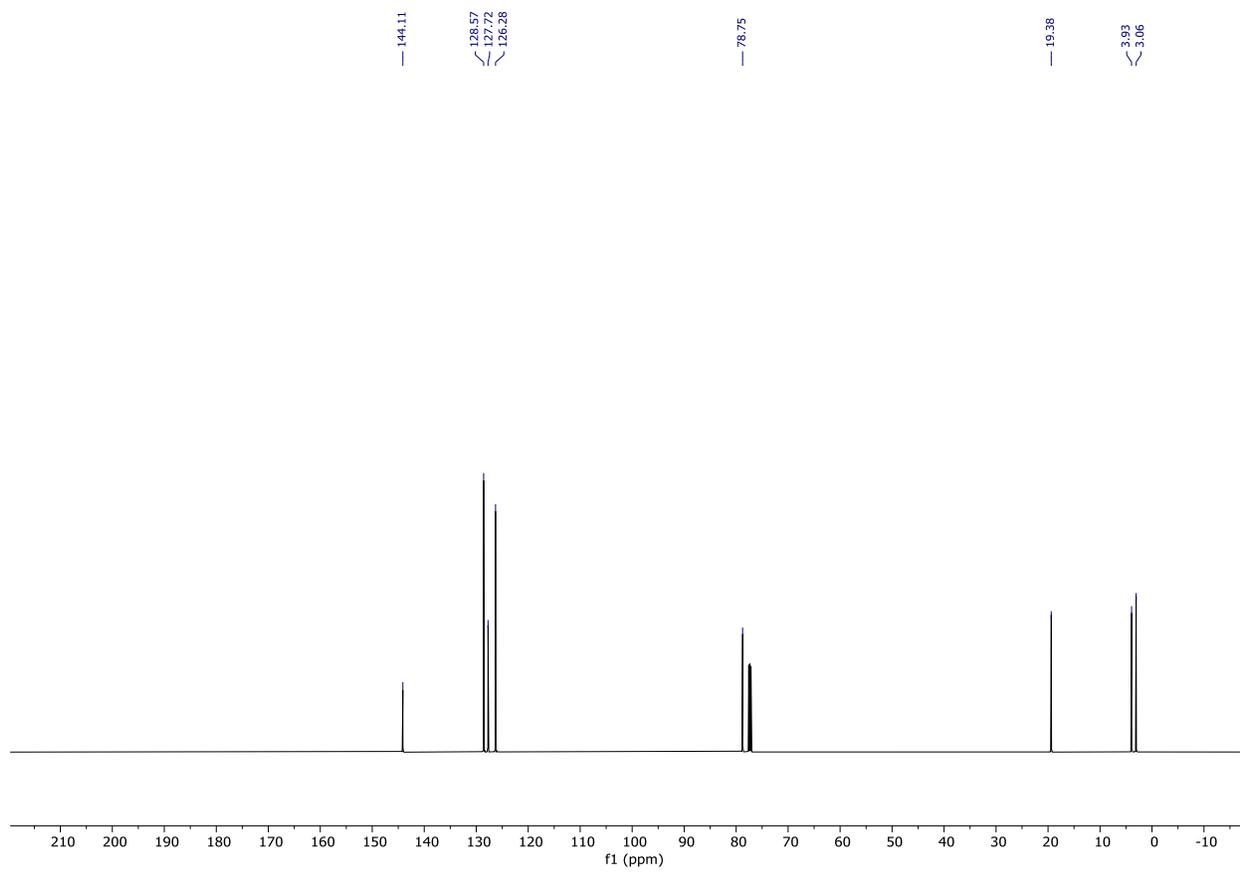


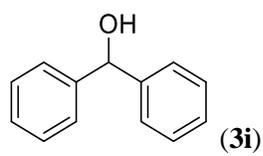


^1H NMR (600 MHz, CDCl_3):

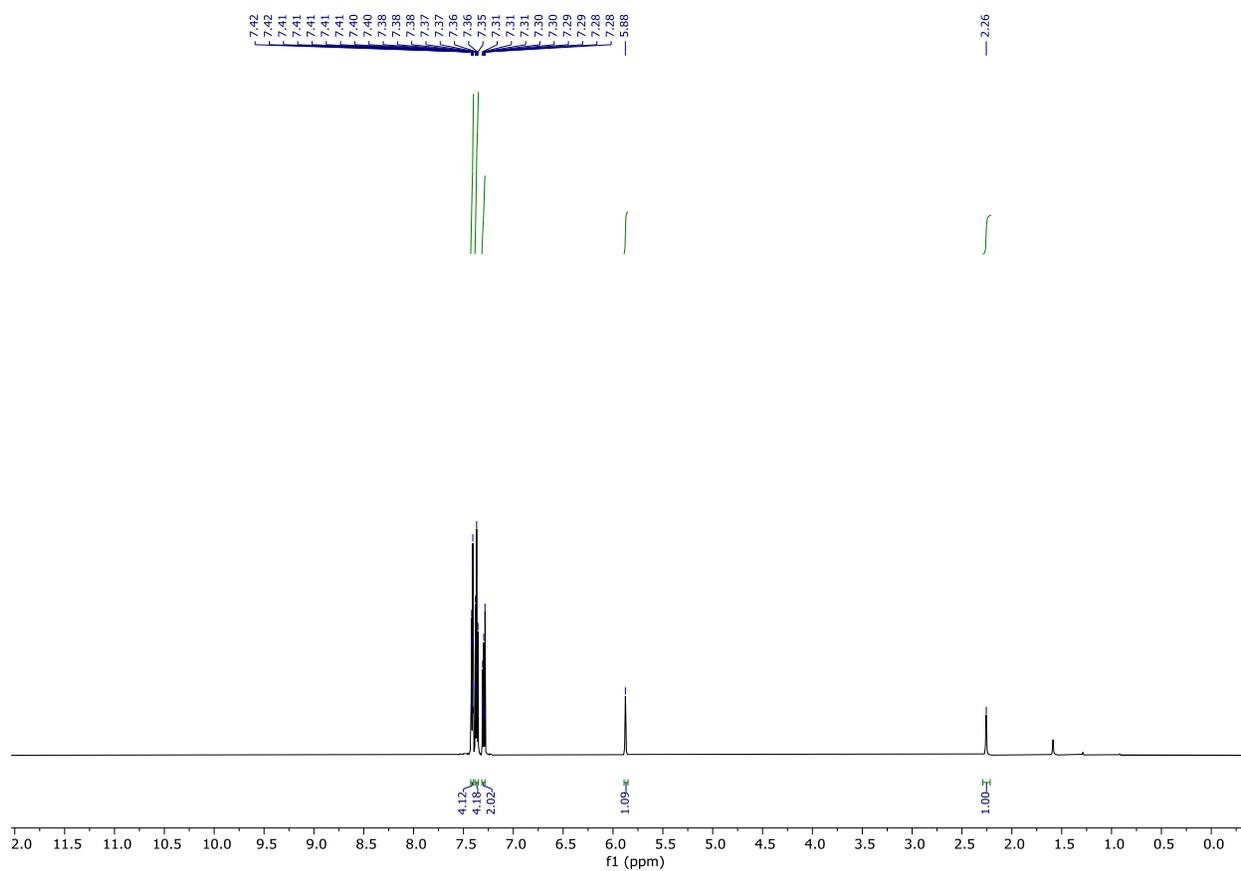


^{13}C NMR (151 MHz, CDCl_3):

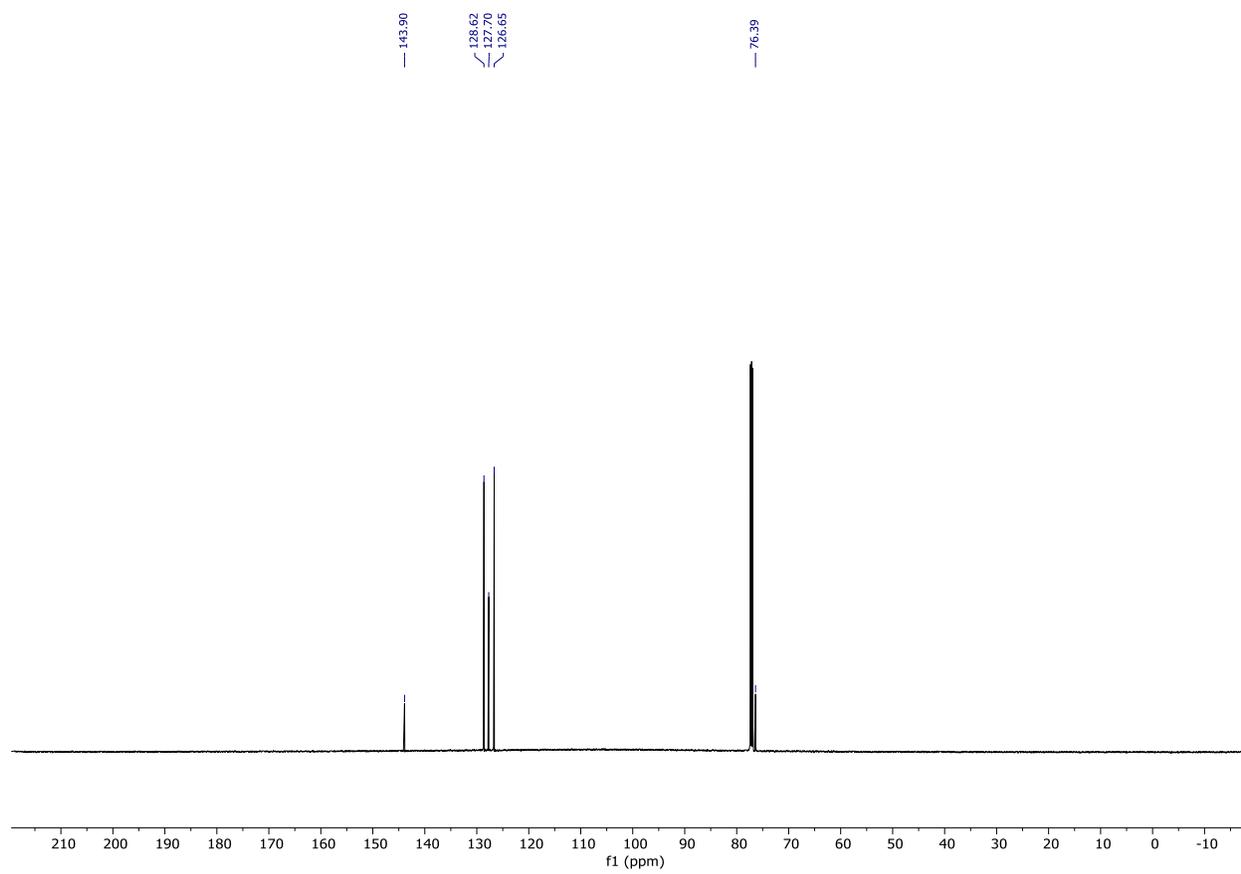


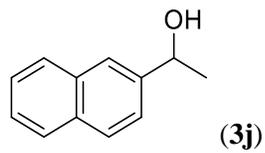


^1H NMR (600 MHz, CDCl_3):

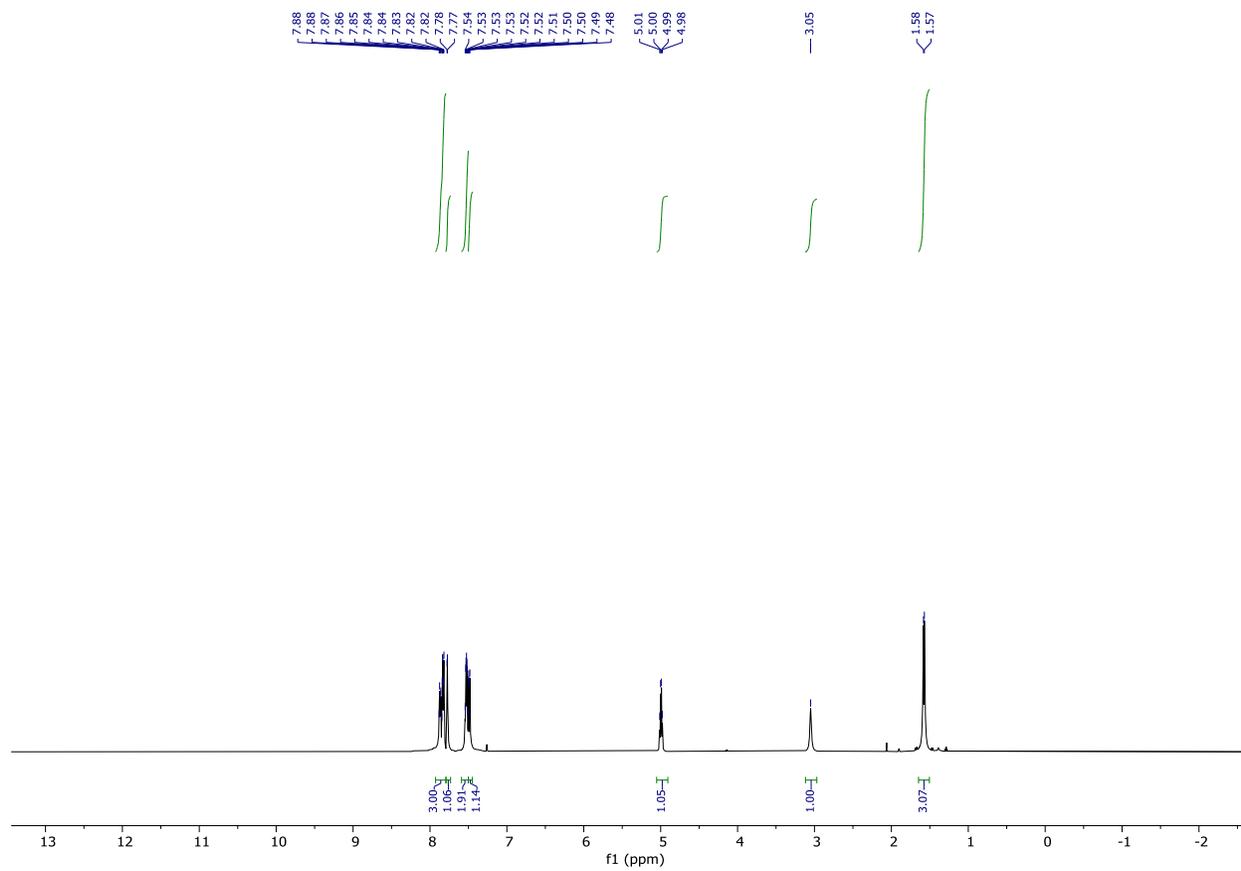


^{13}C NMR (151 MHz, CDCl_3):

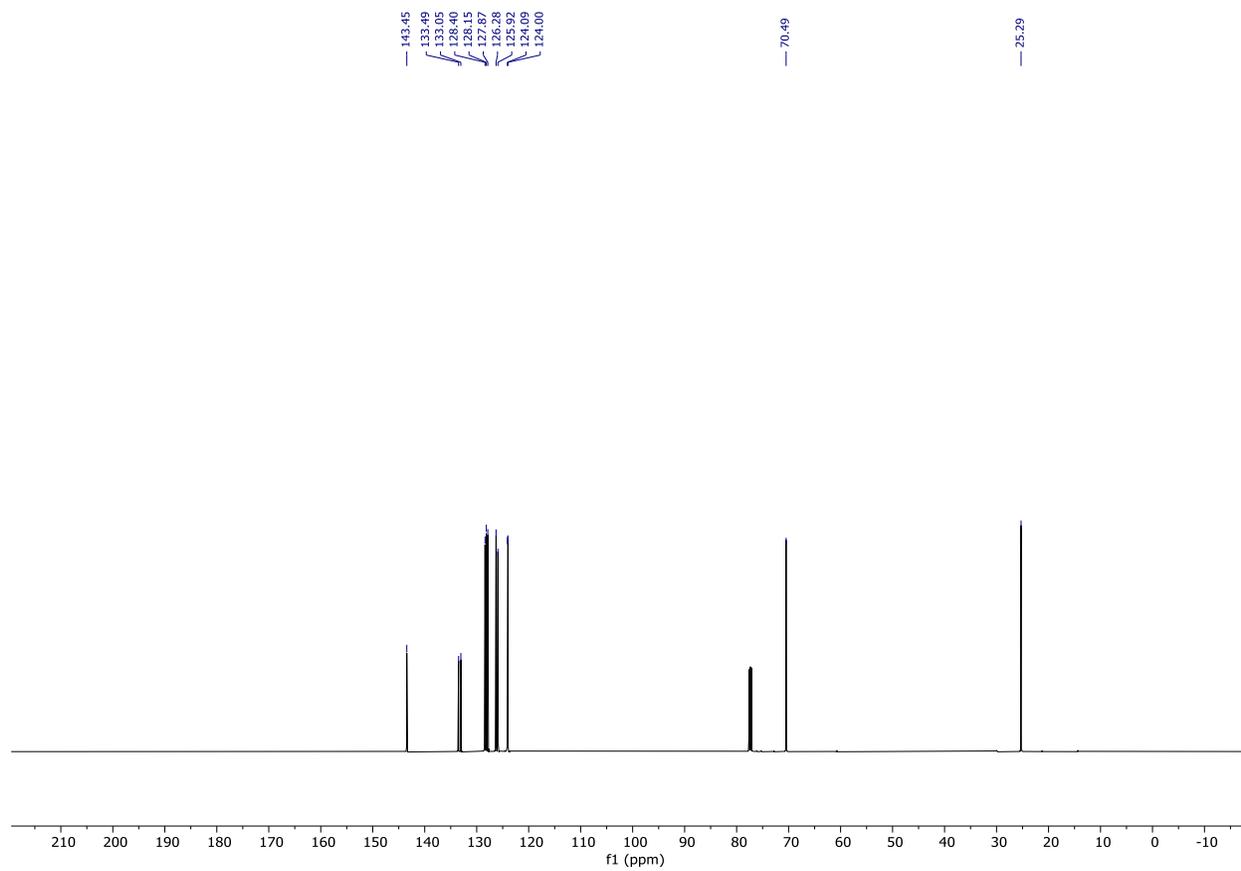


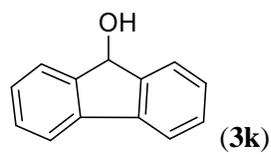


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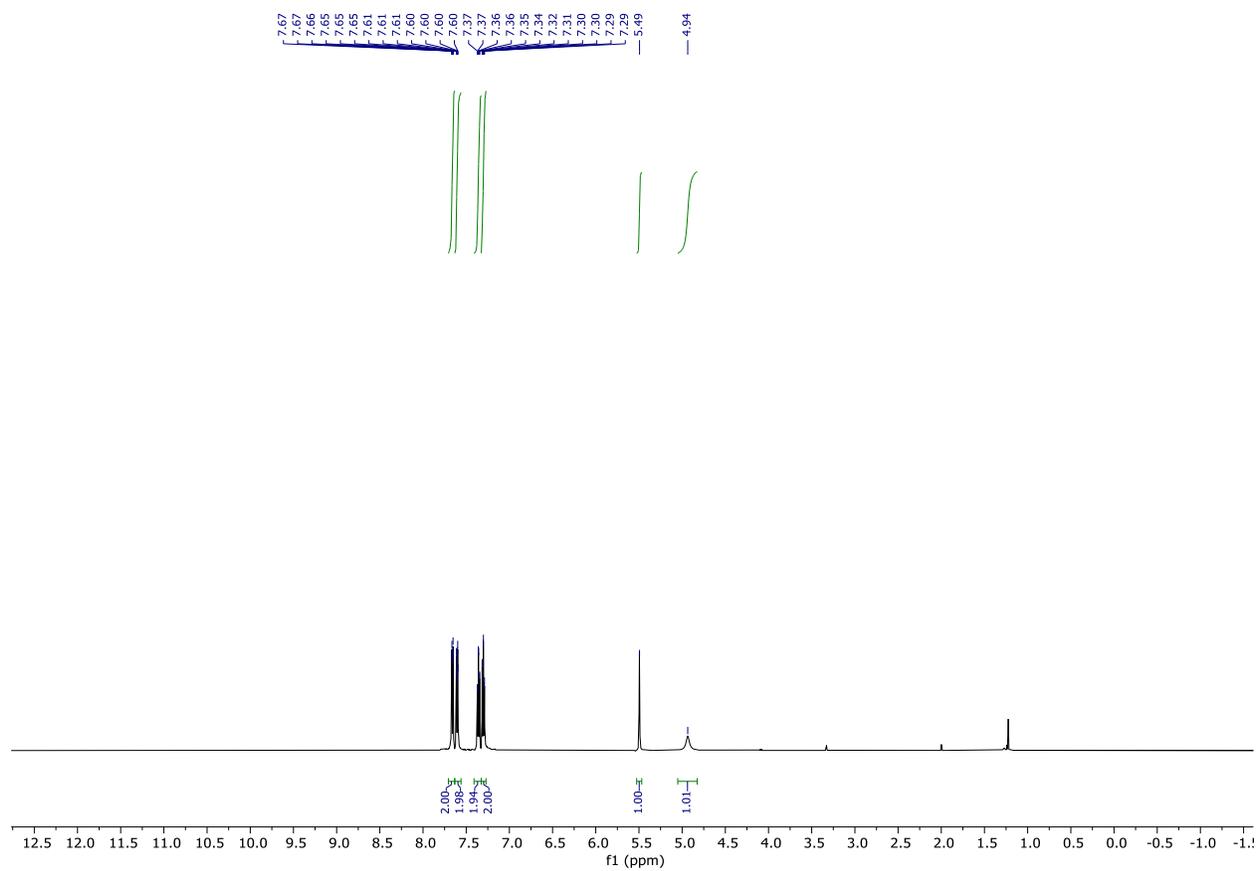


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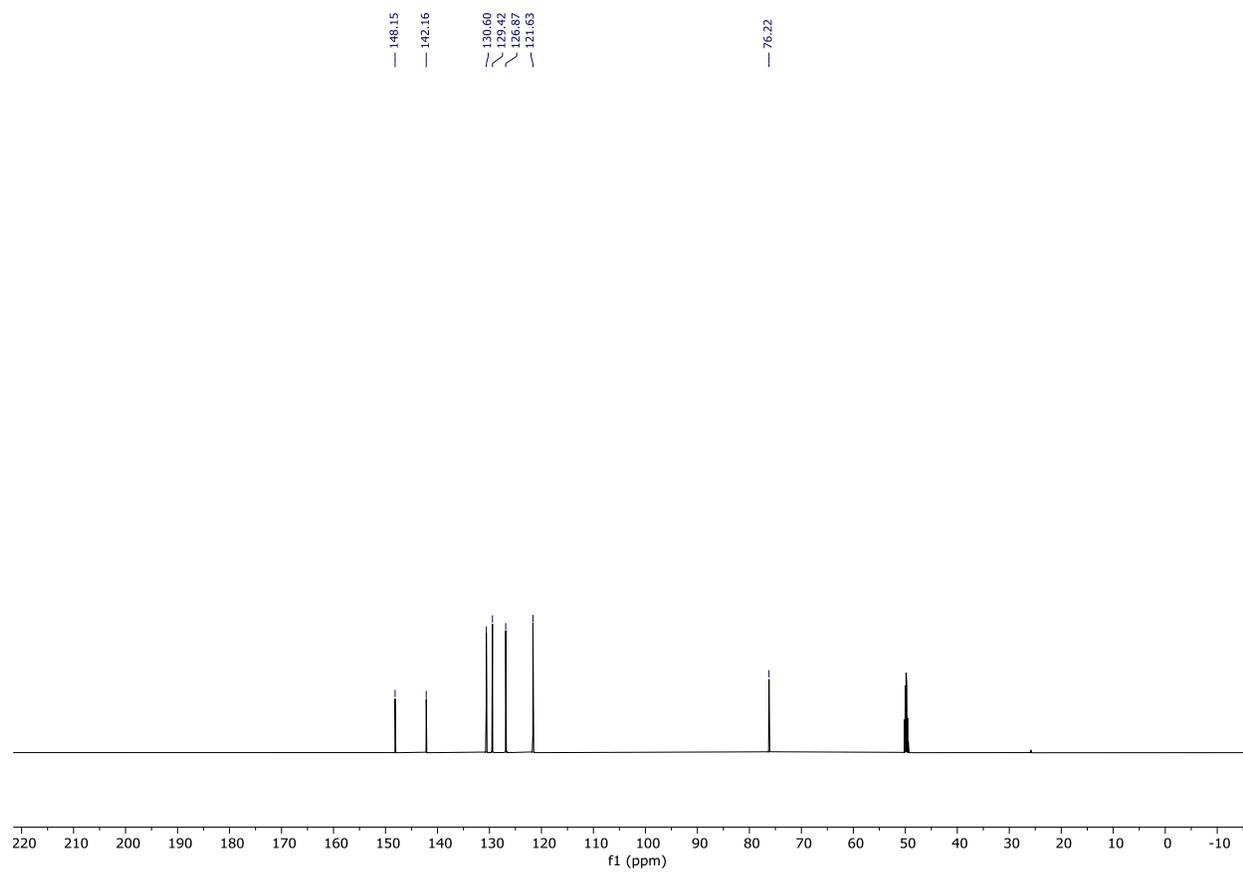


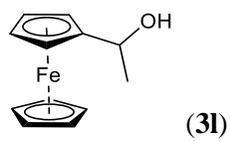


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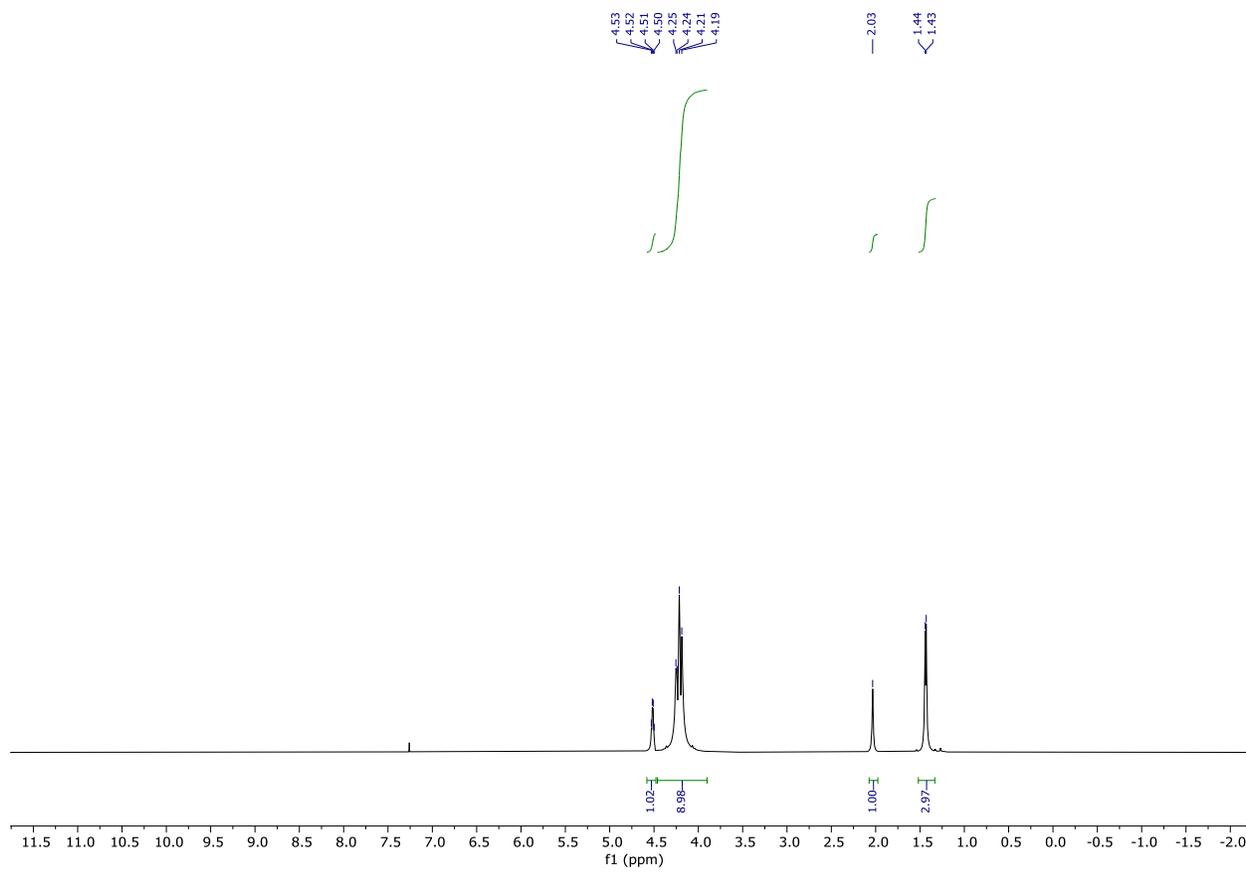


^{13}C NMR (151 MHz, CD_3OD):

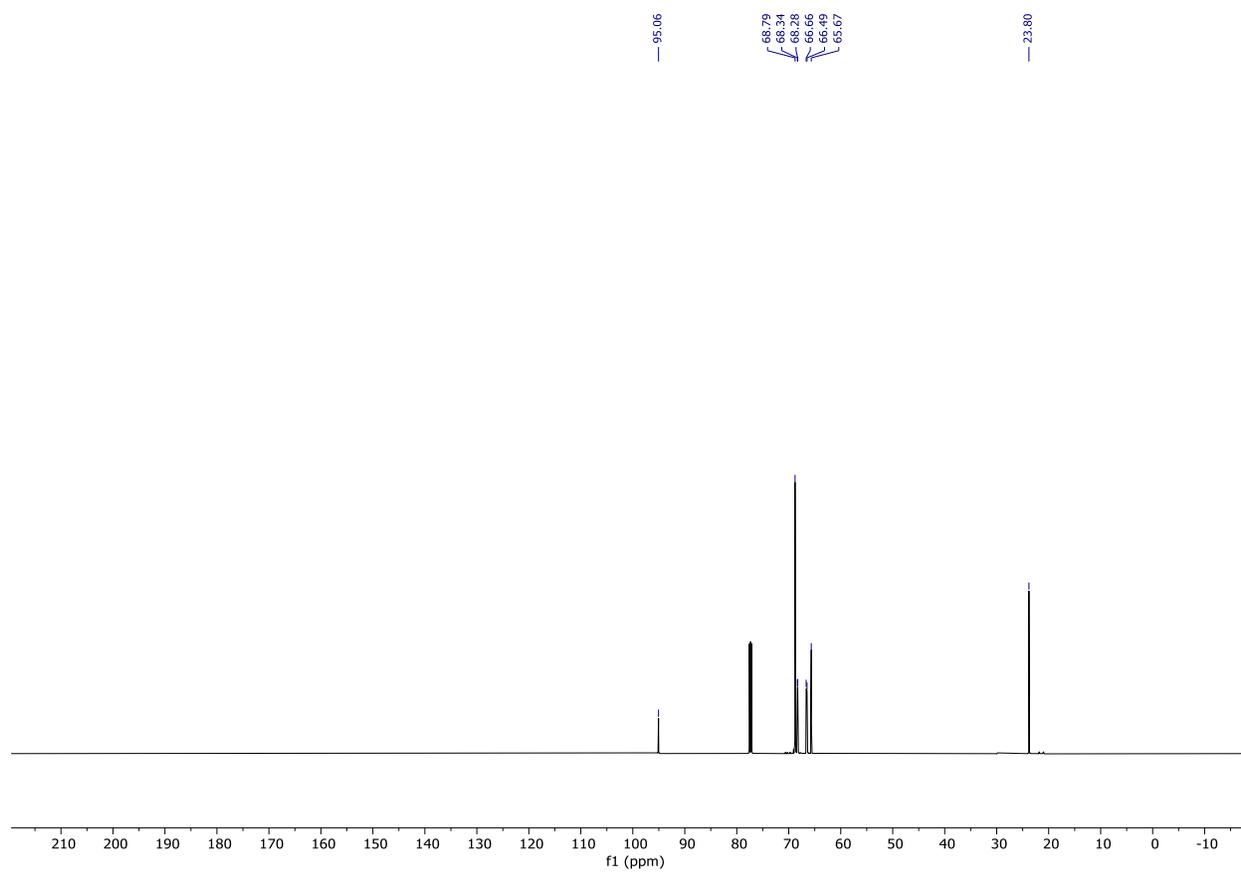


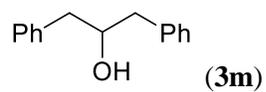


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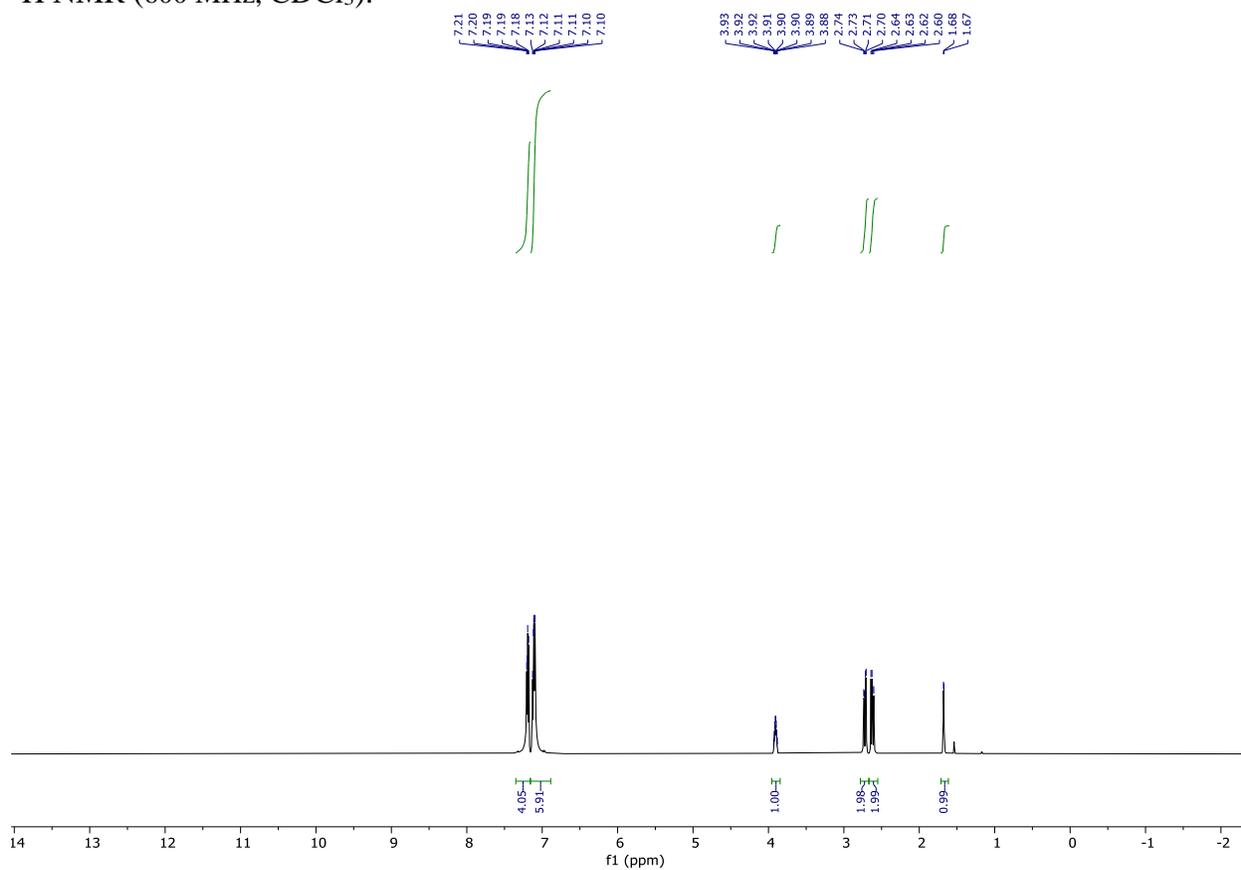


^{13}C NMR (151 MHz, CDCl_3):

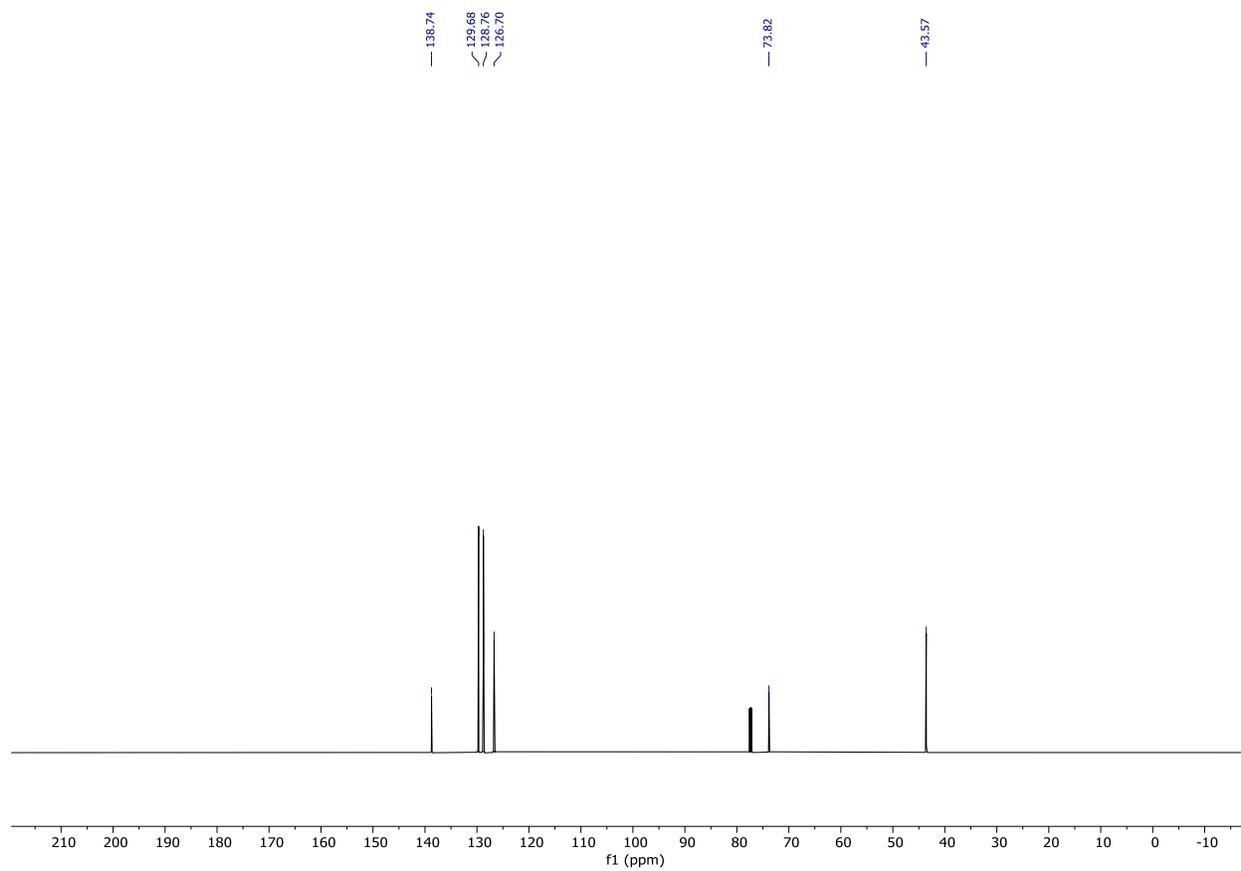


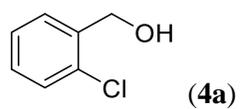


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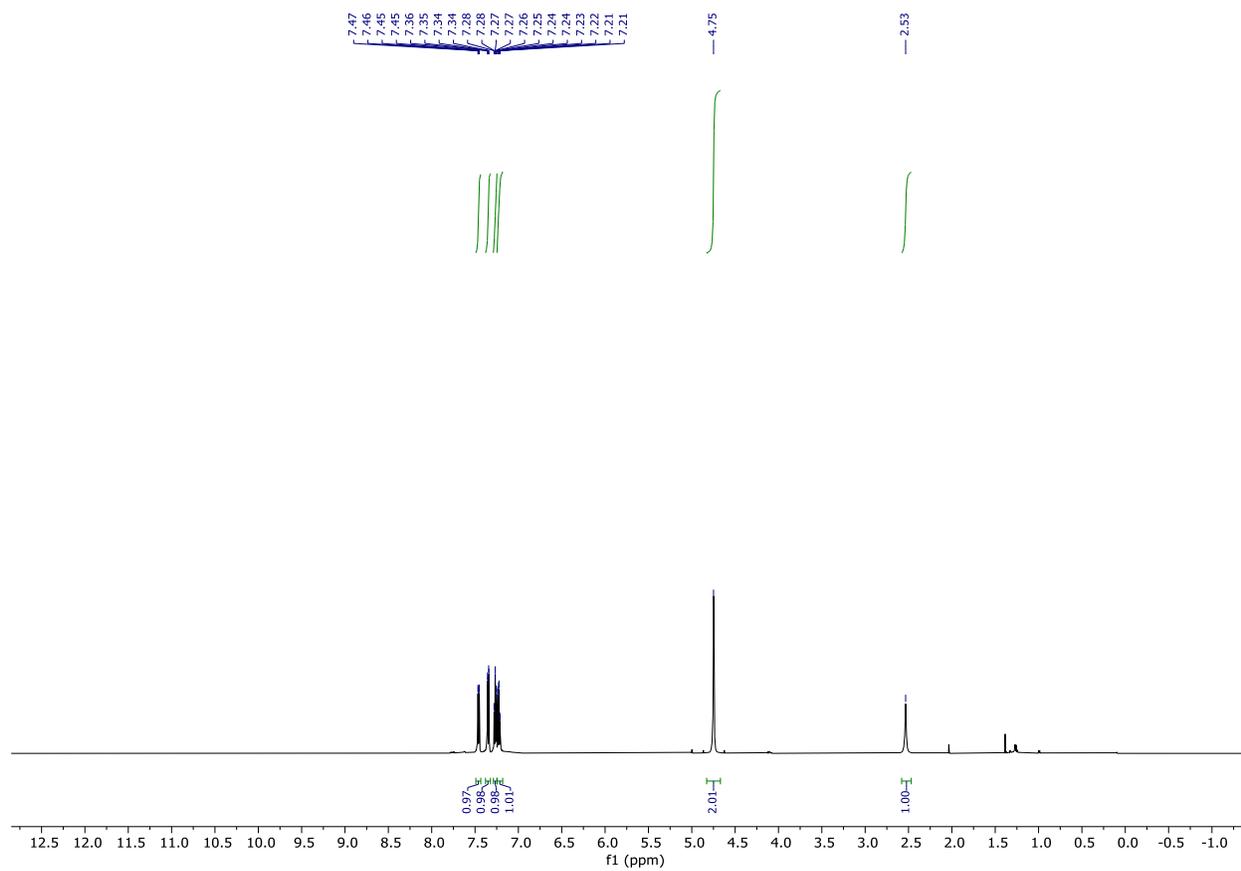


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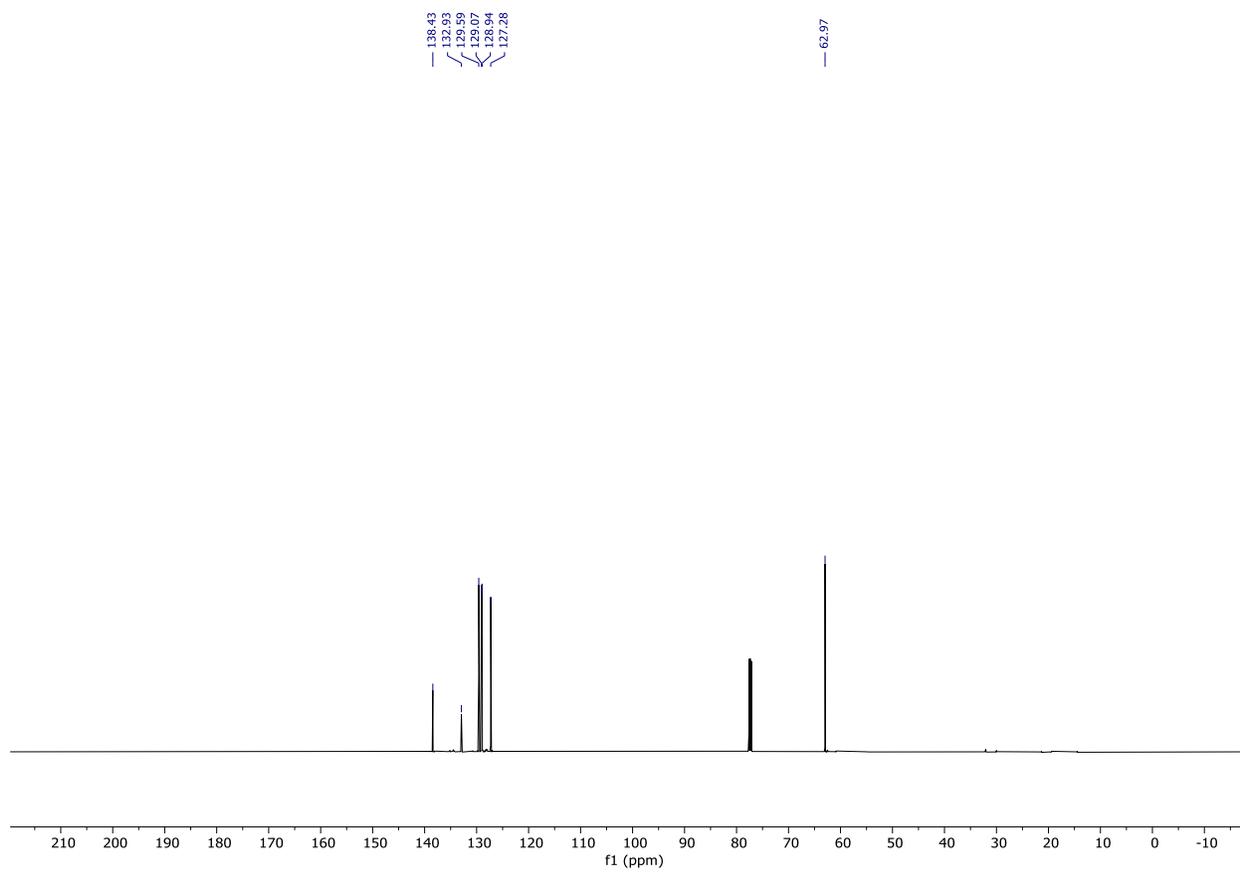


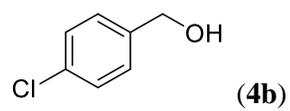


¹H NMR (600 MHz, CDCl₃):

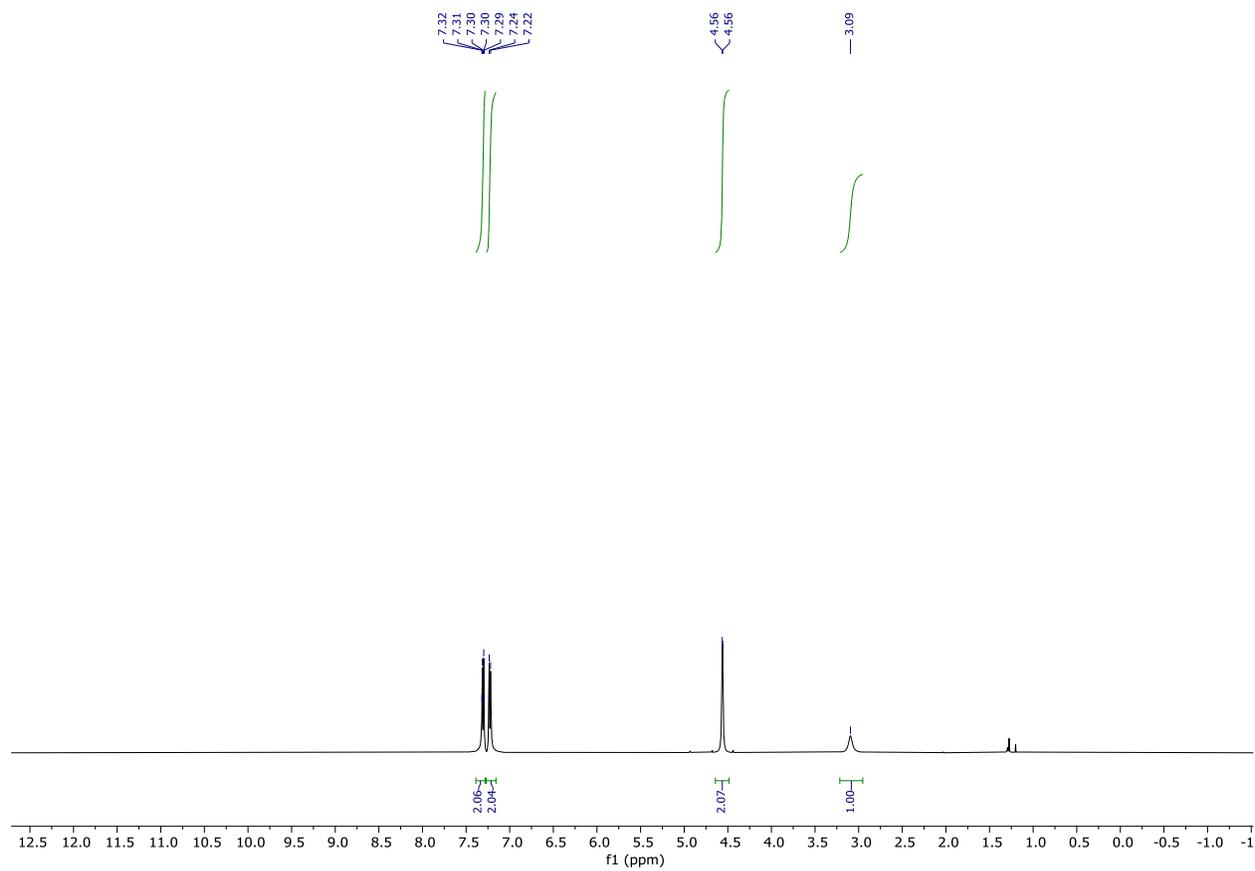


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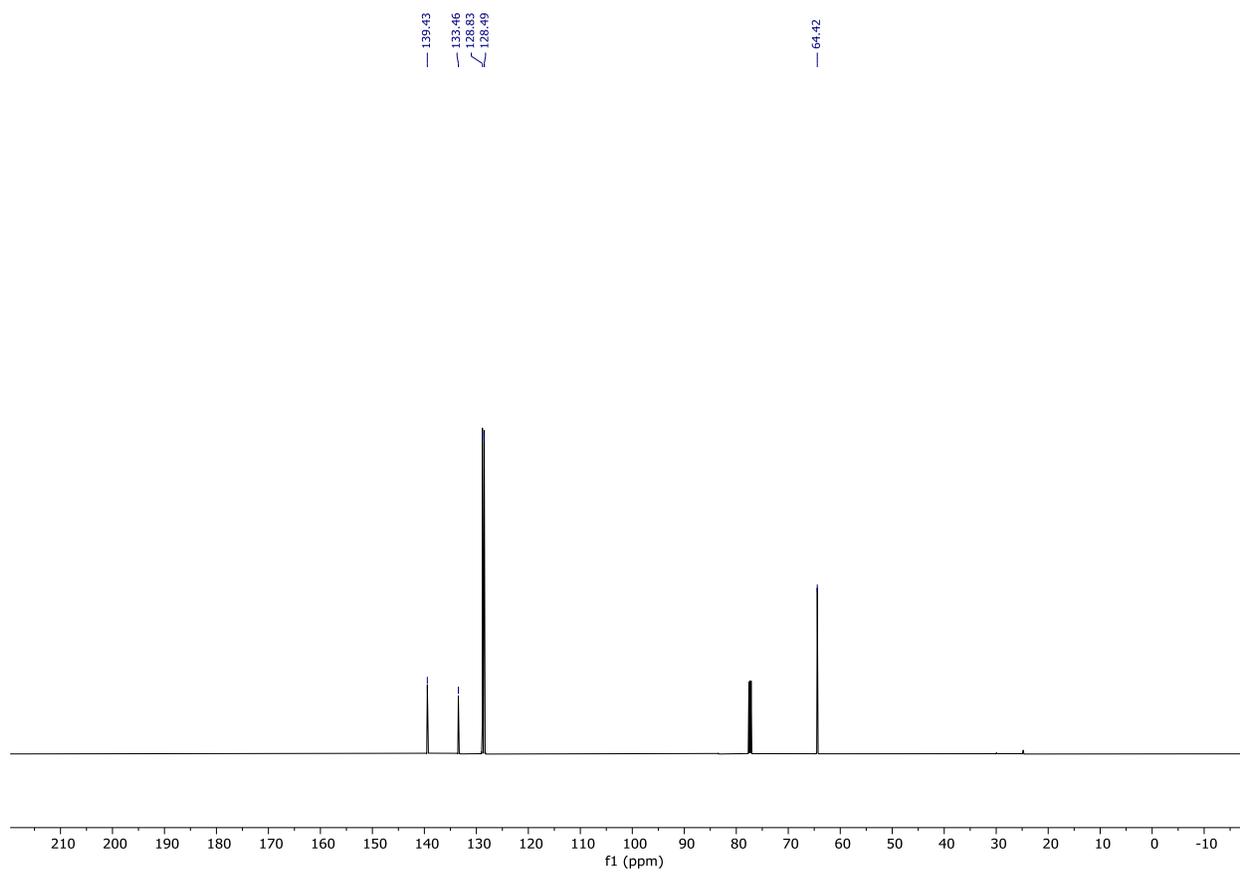


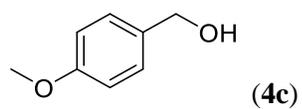


¹H NMR (600 MHz, CDCl₃):

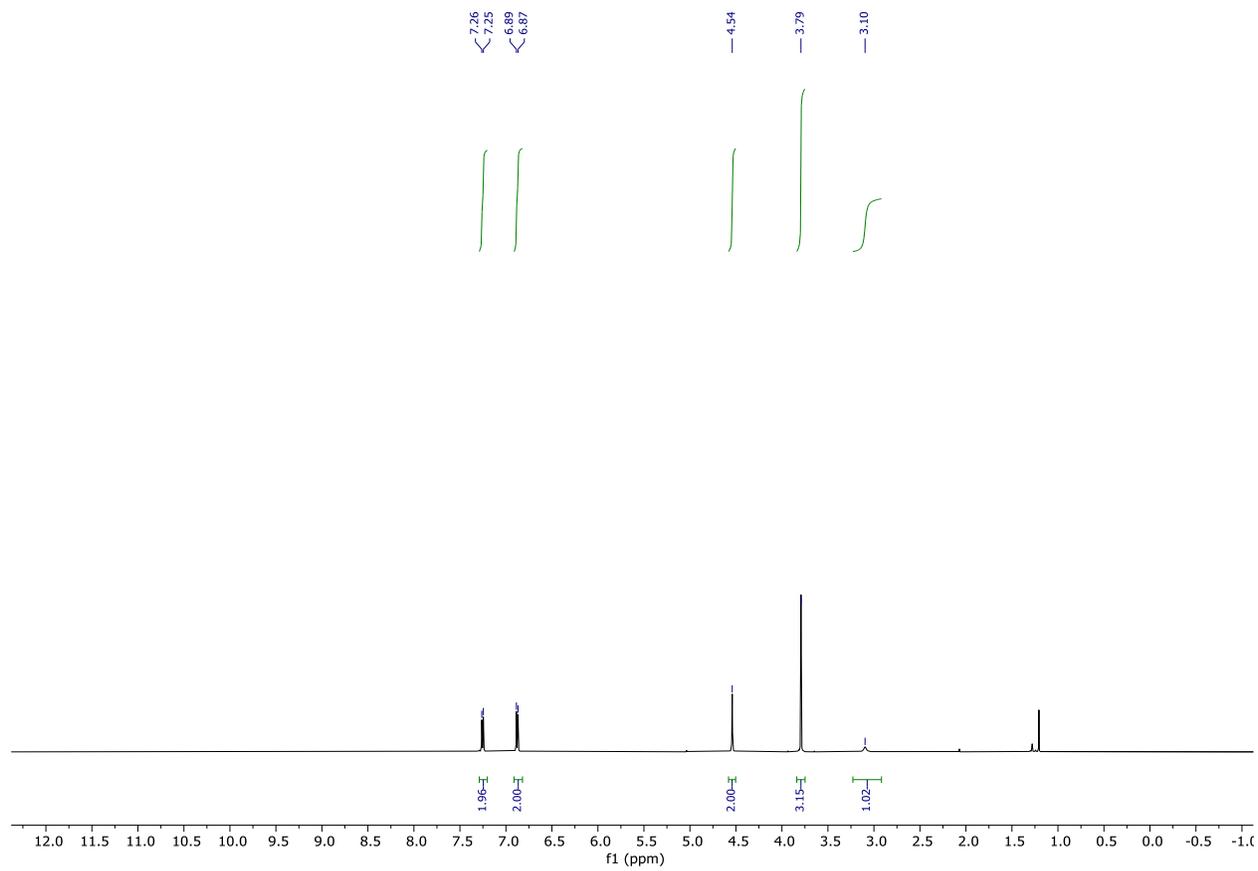


^{13}C NMR (151 MHz, CDCl_3):

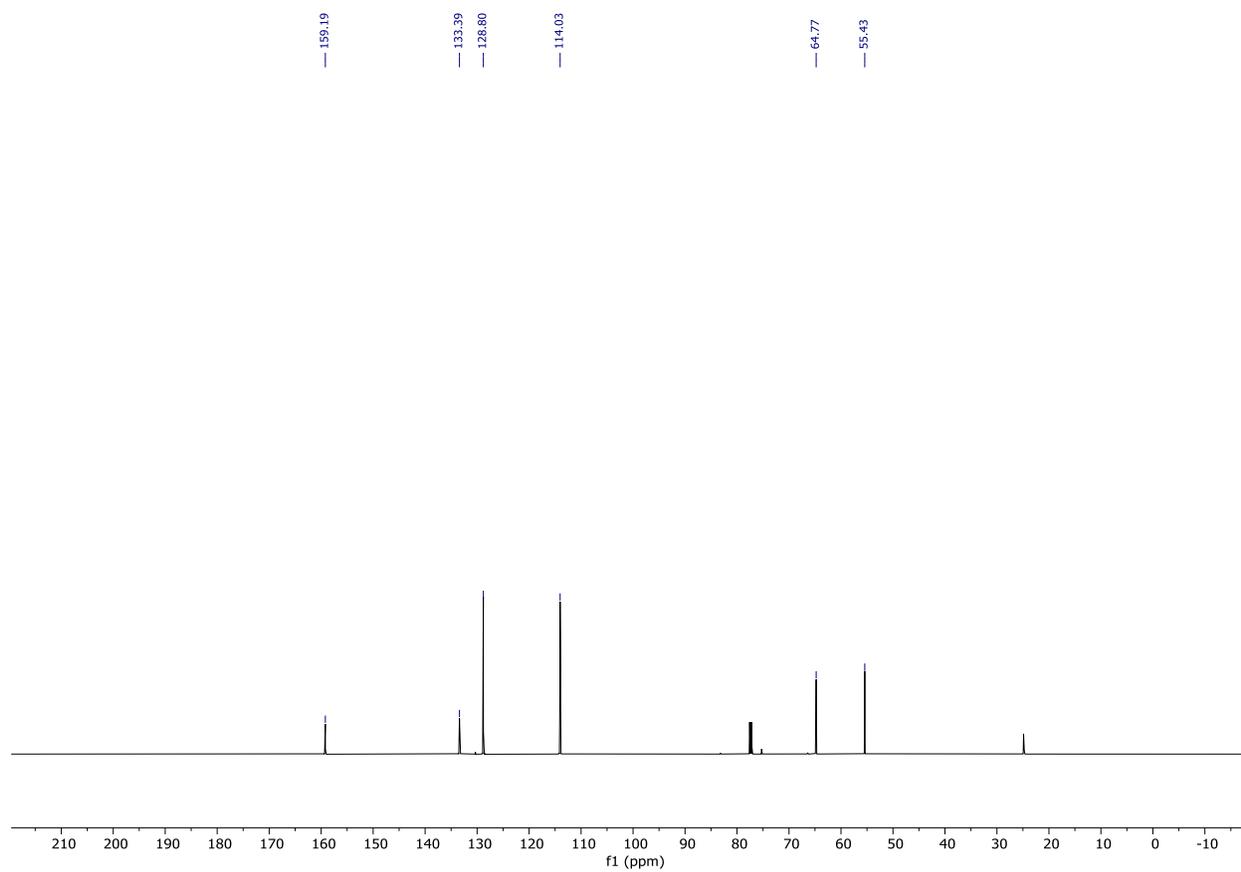


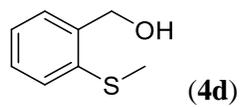


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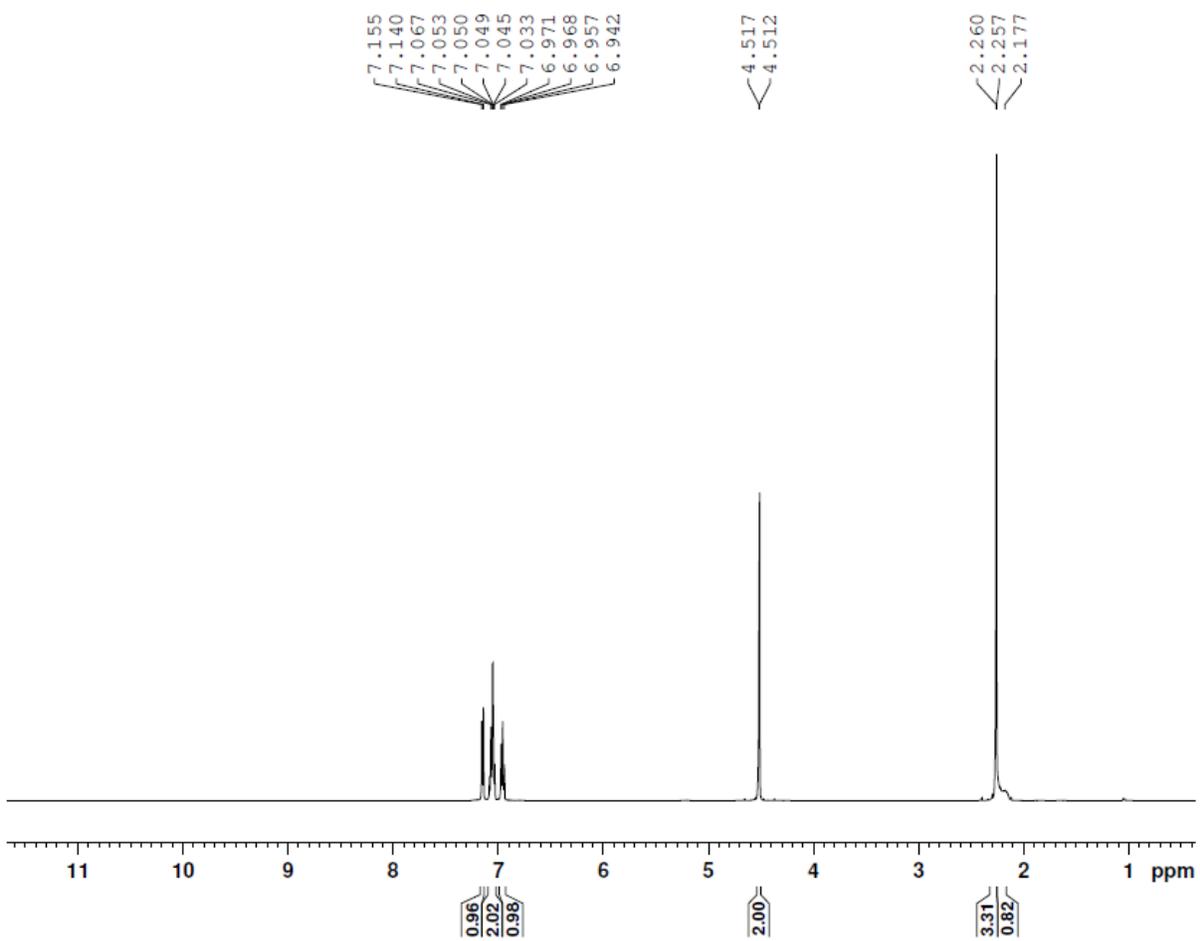


^{13}C NMR (151 MHz, CDCl_3):

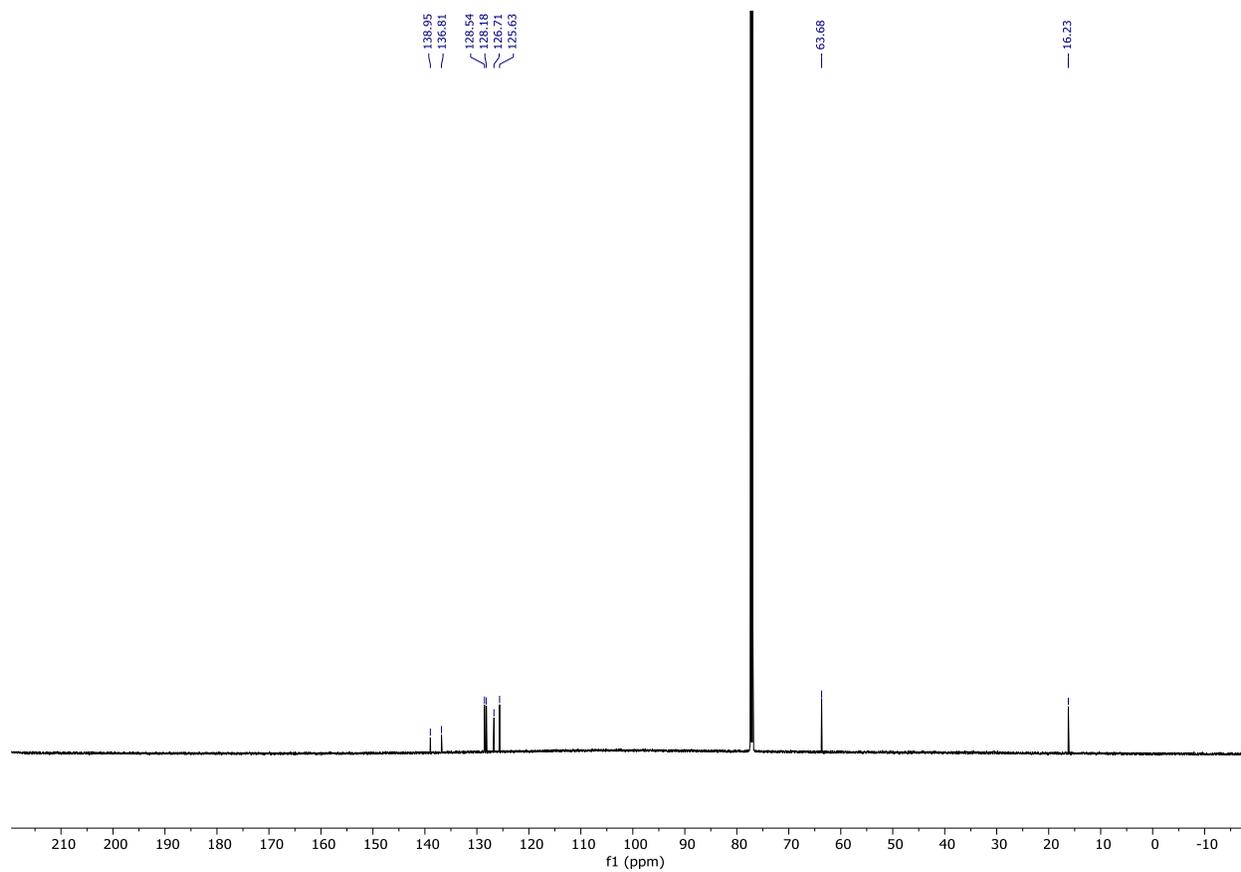


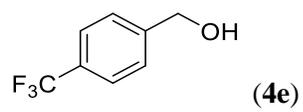


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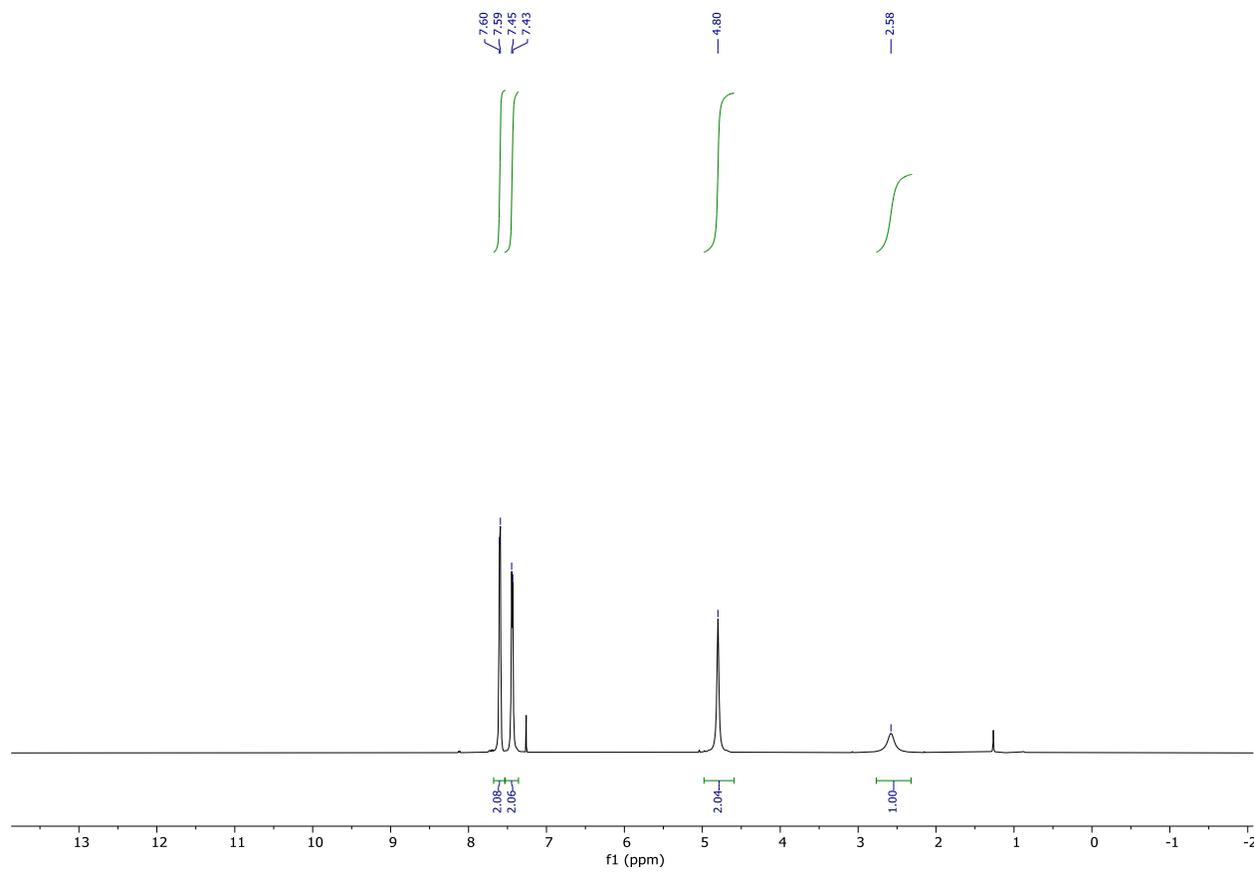


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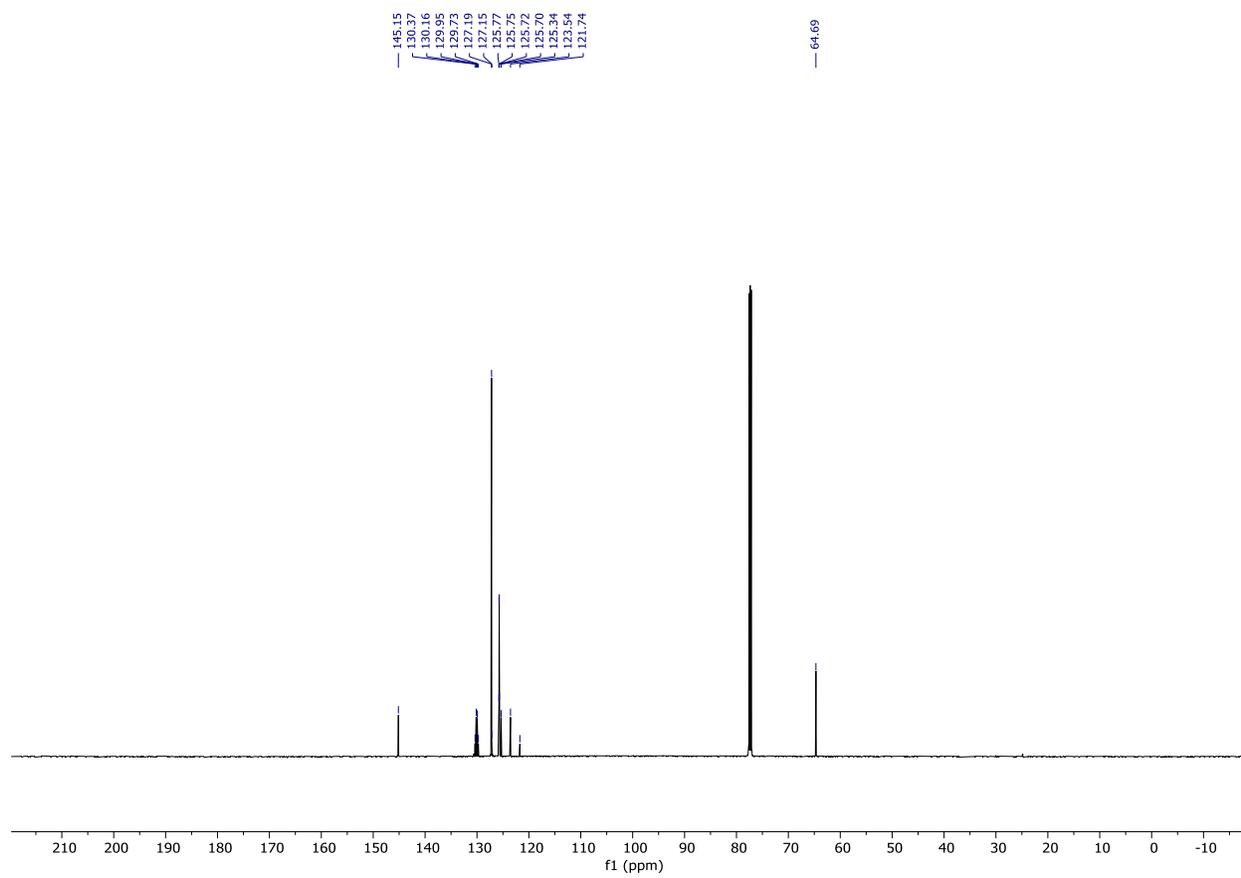


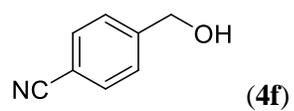


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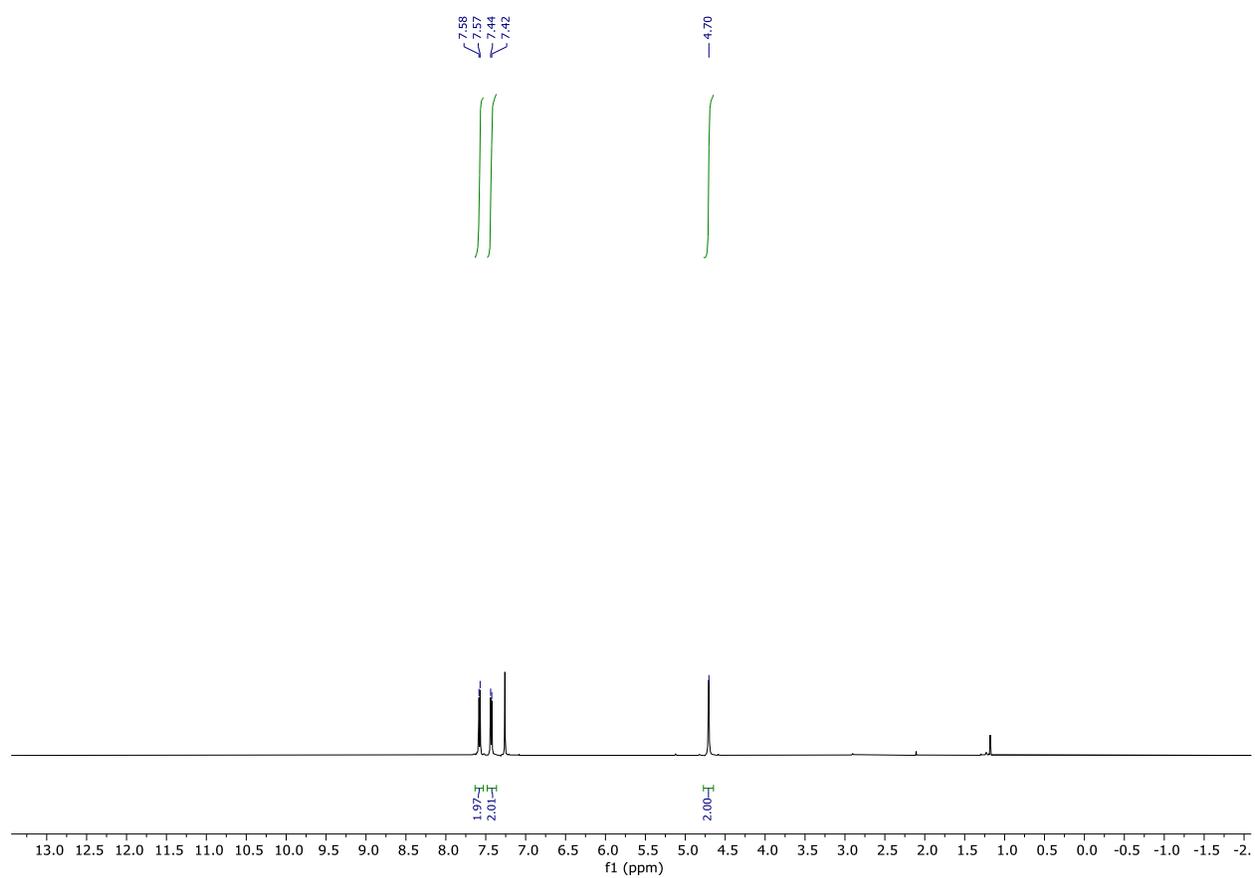


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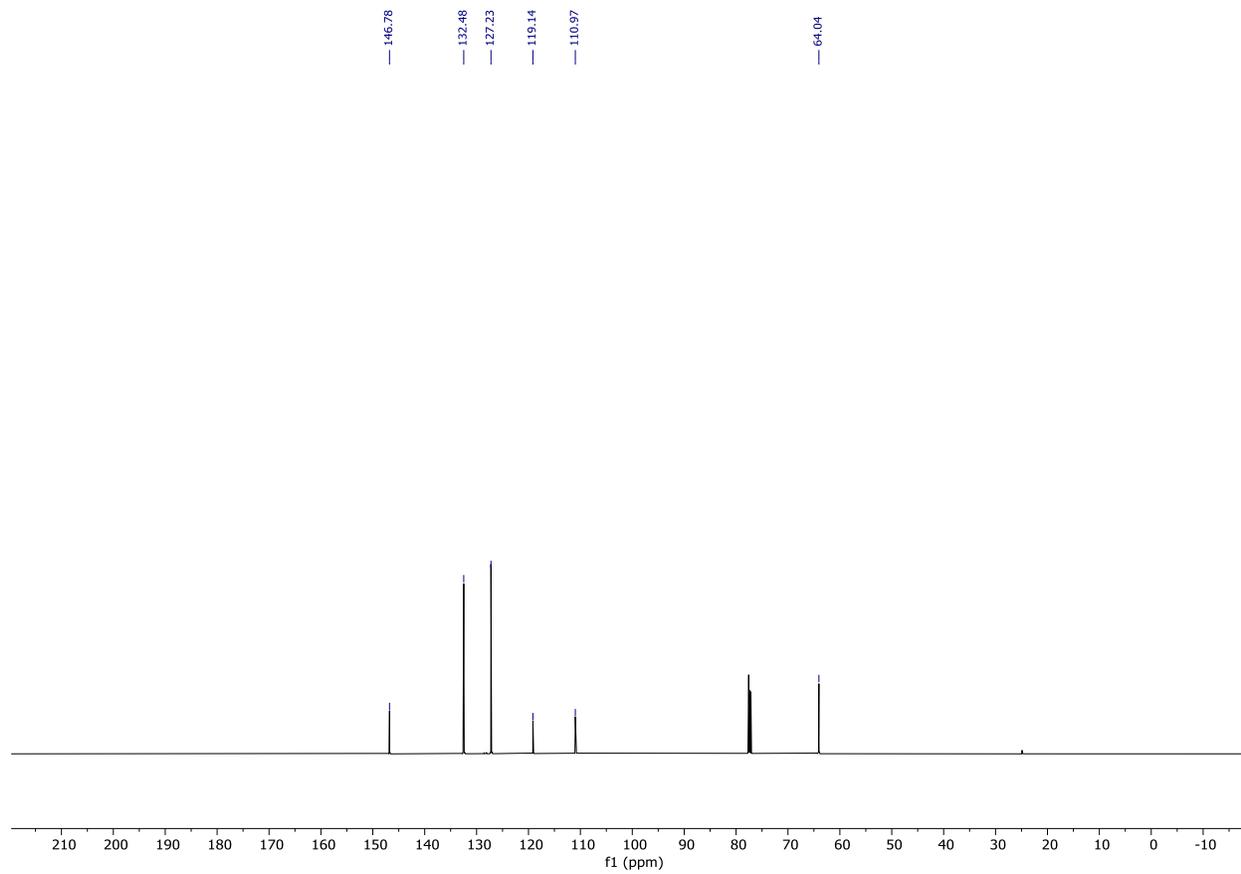


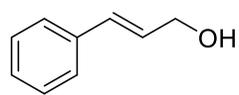


^1H NMR (600 MHz, CDCl_3):



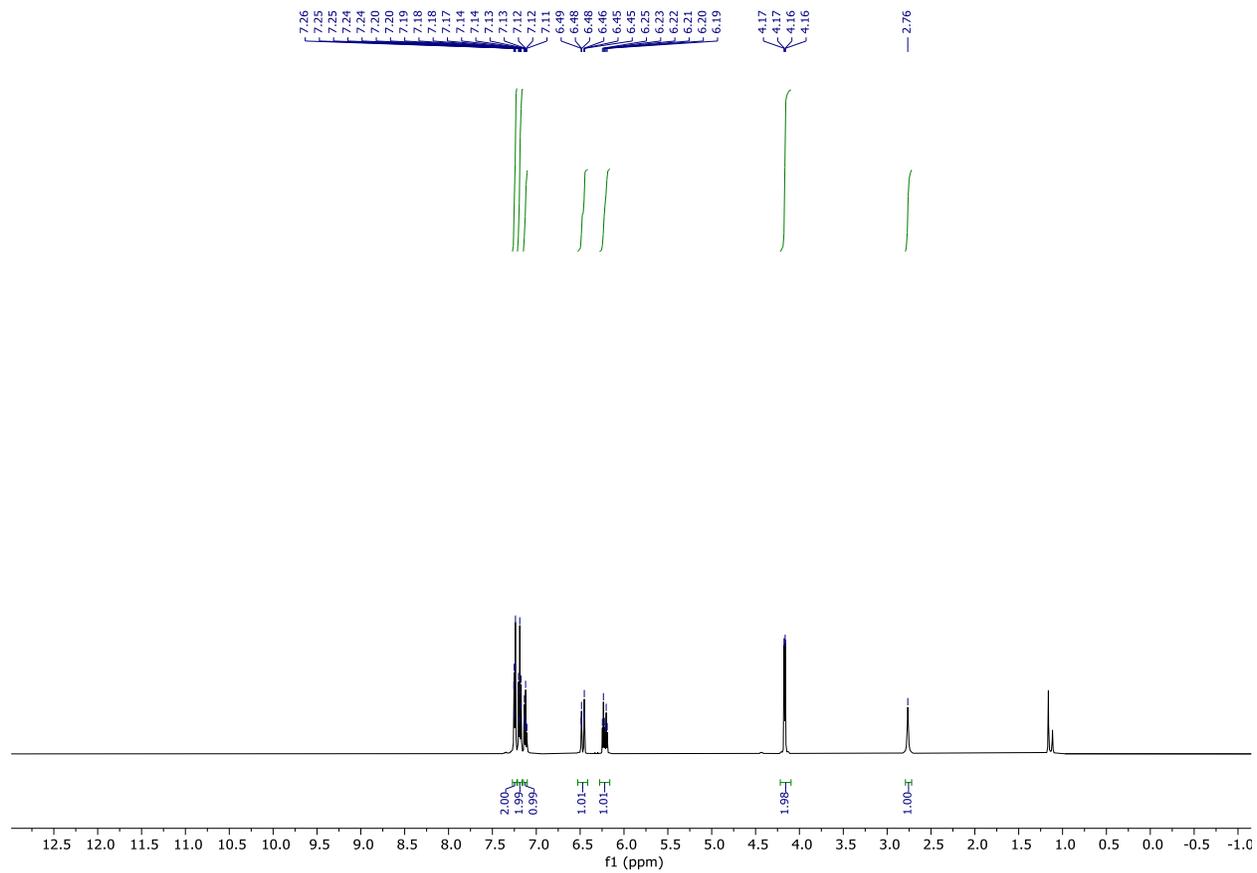
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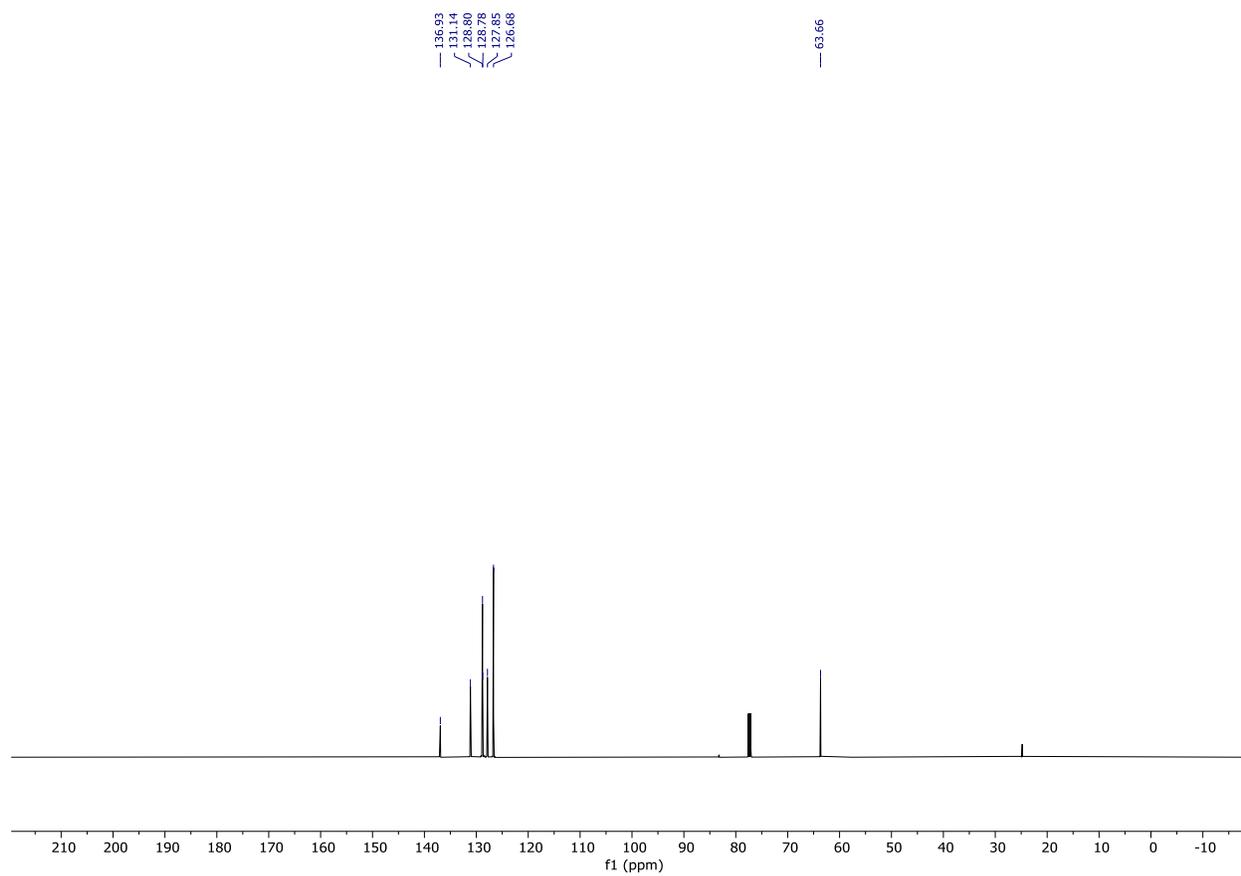


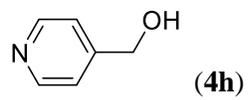
(4g)

^1H NMR (500 MHz, CDCl_3):

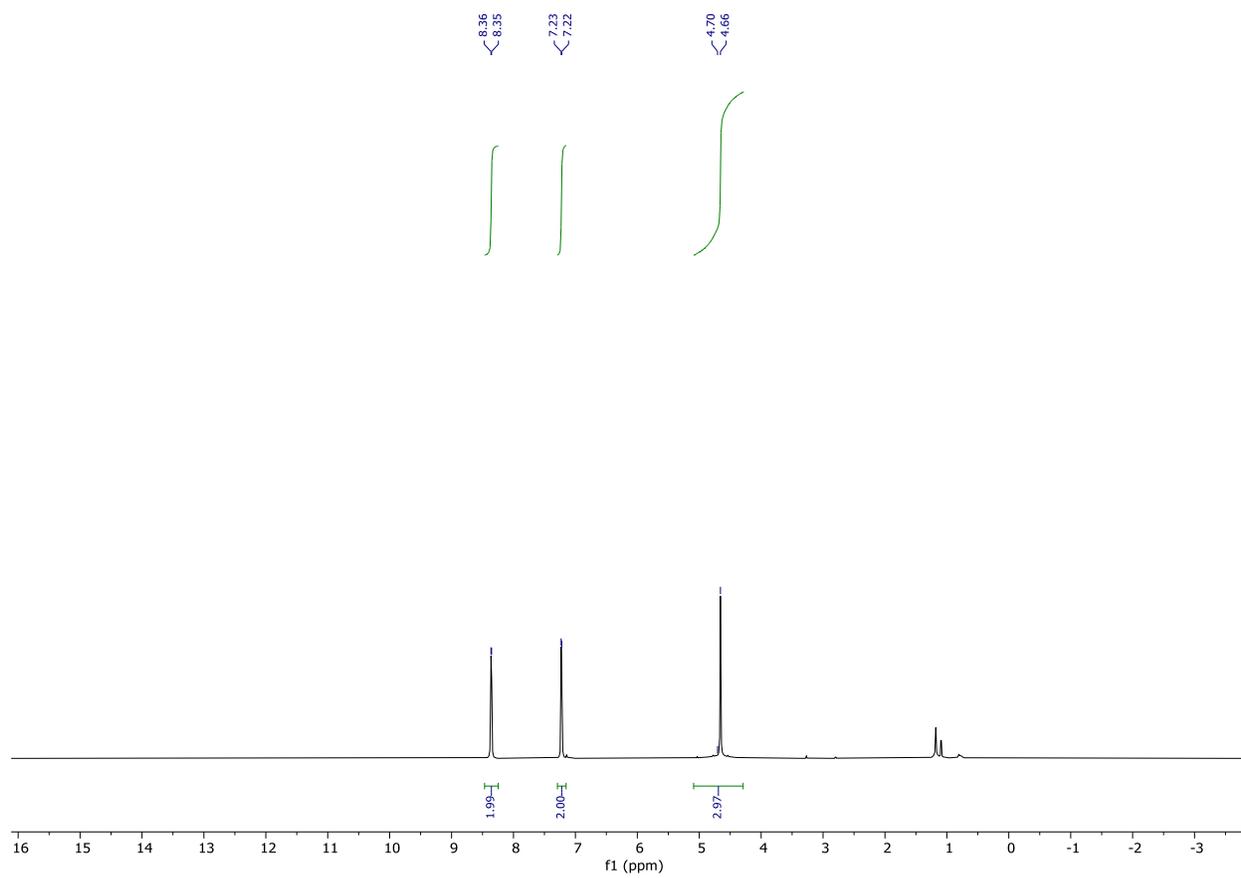


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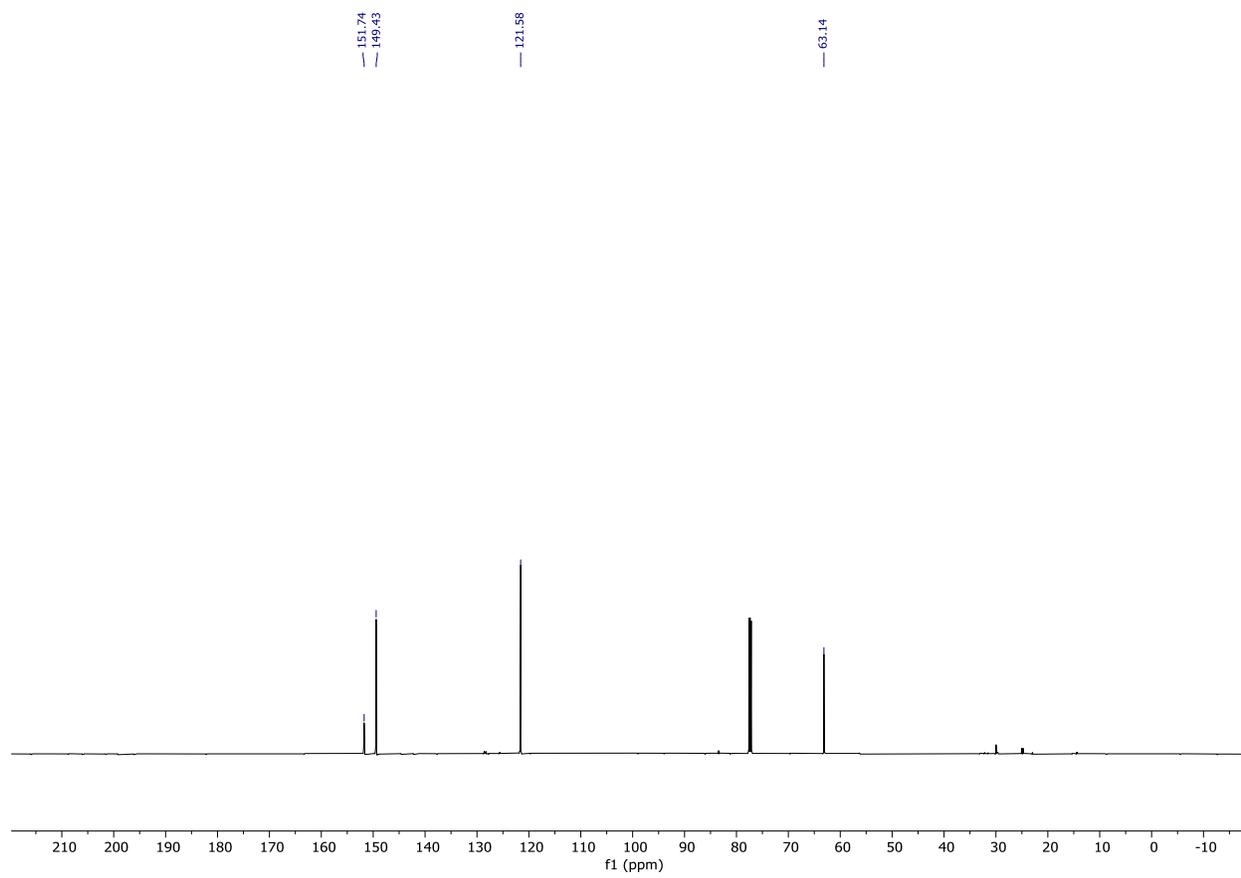


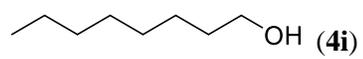


¹H NMR (600 MHz, CDCl₃):

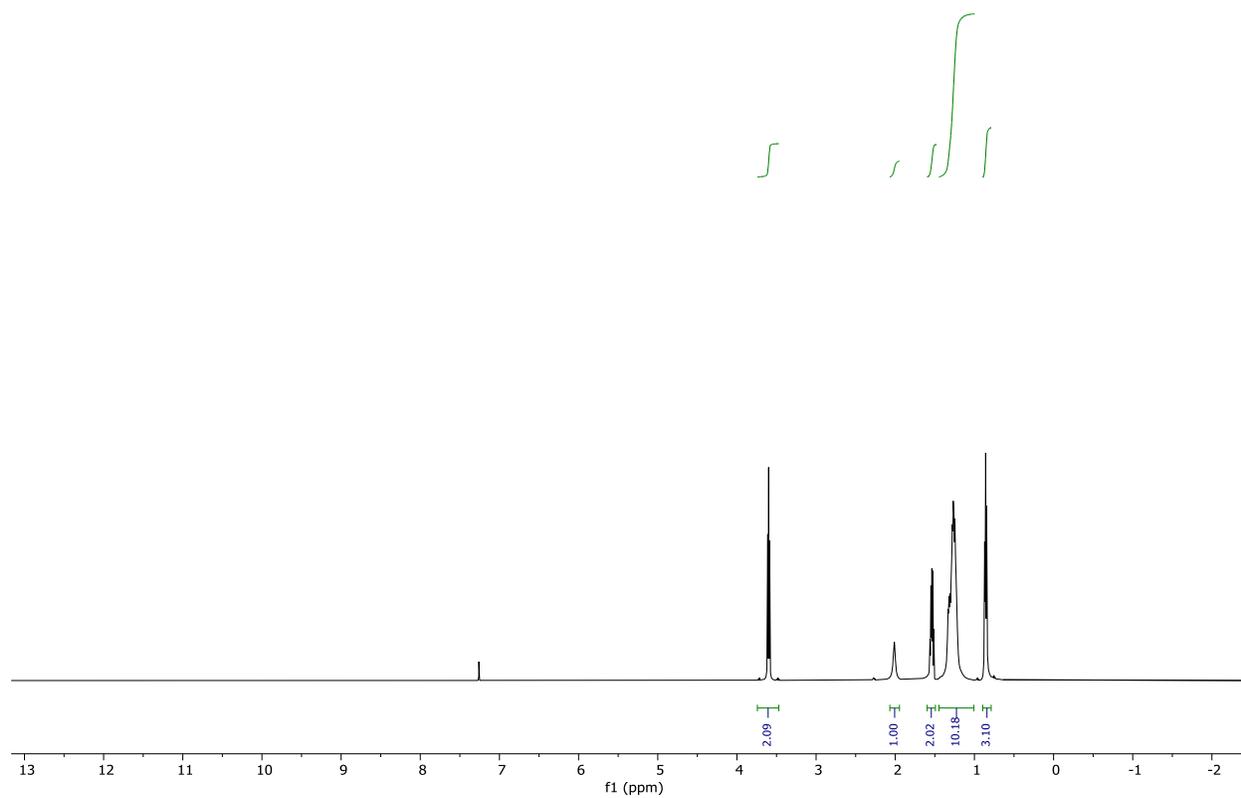


^{13}C NMR (151 MHz, CDCl_3):

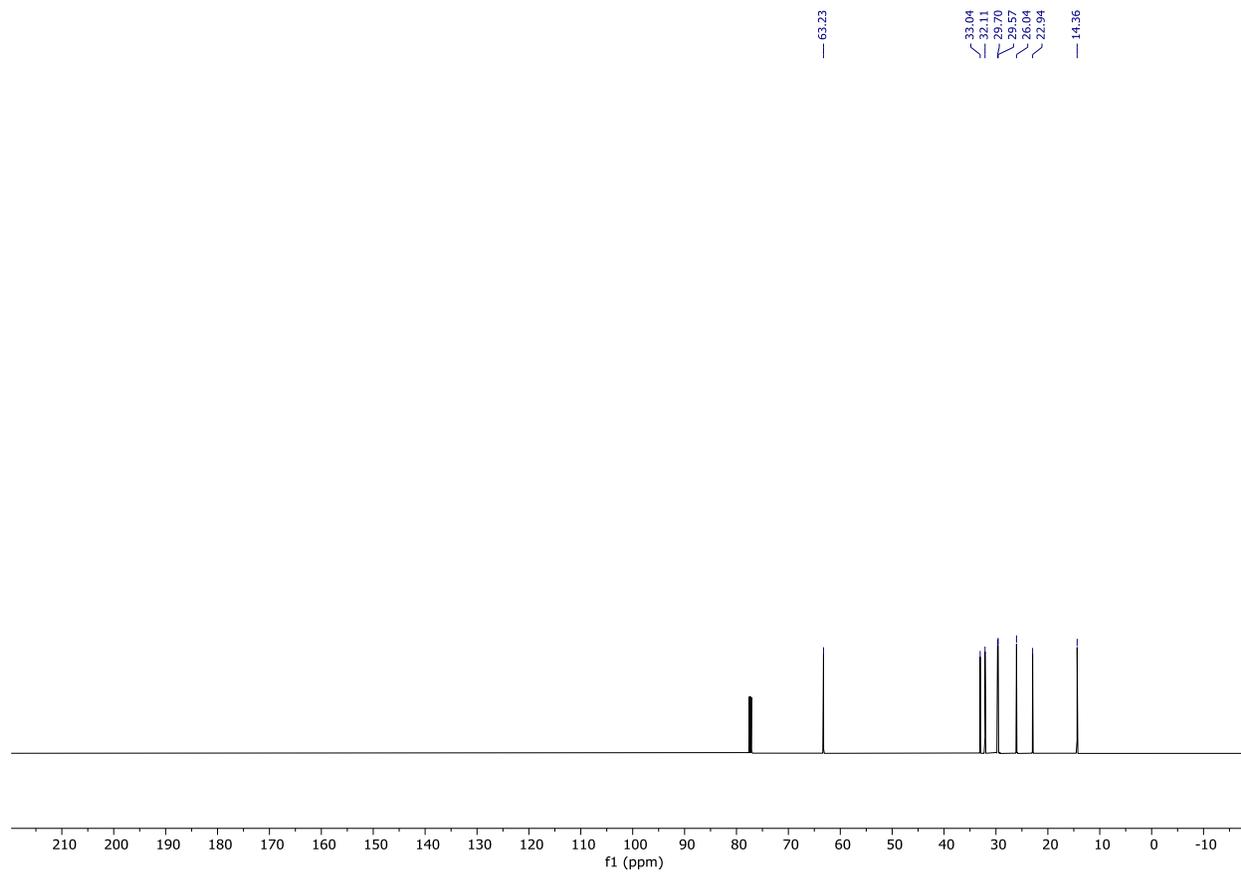


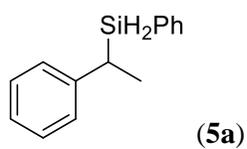


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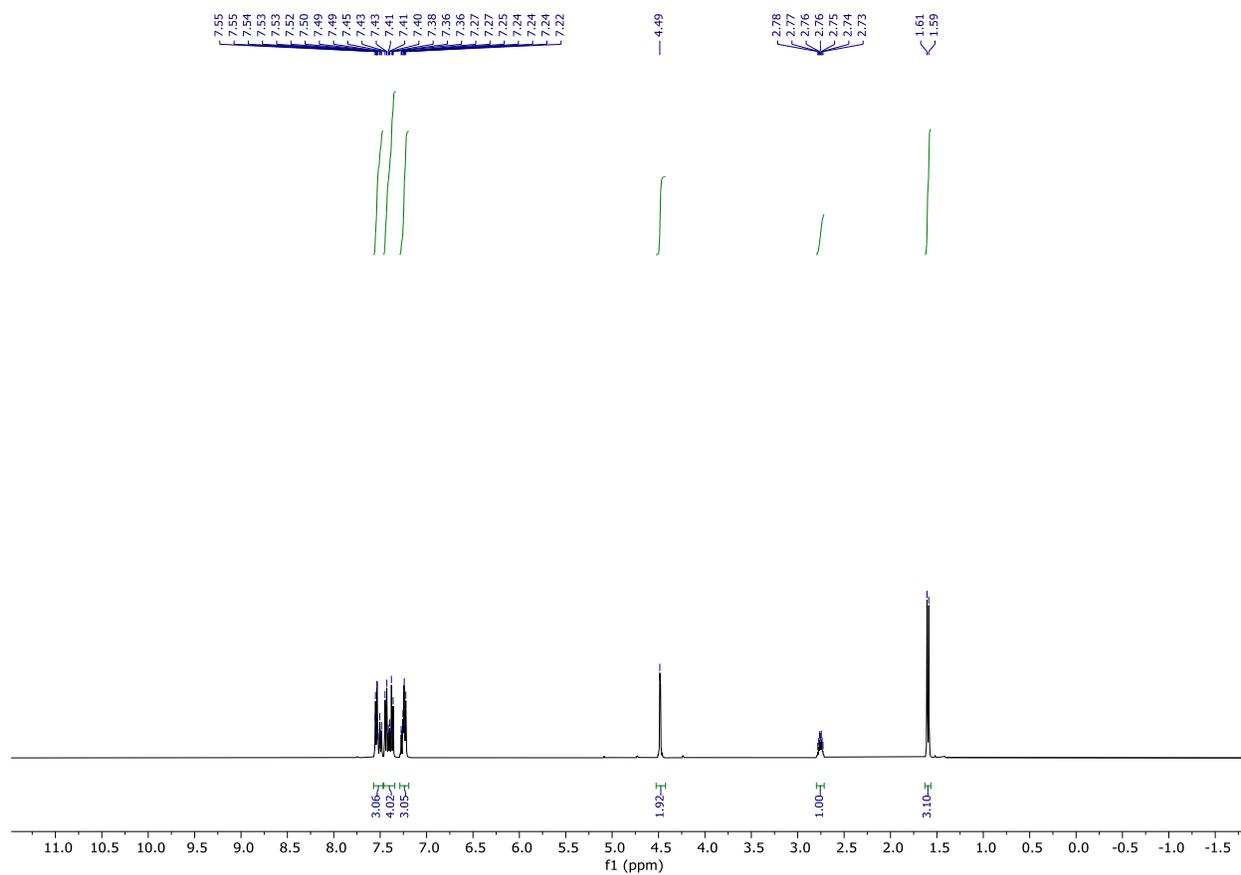


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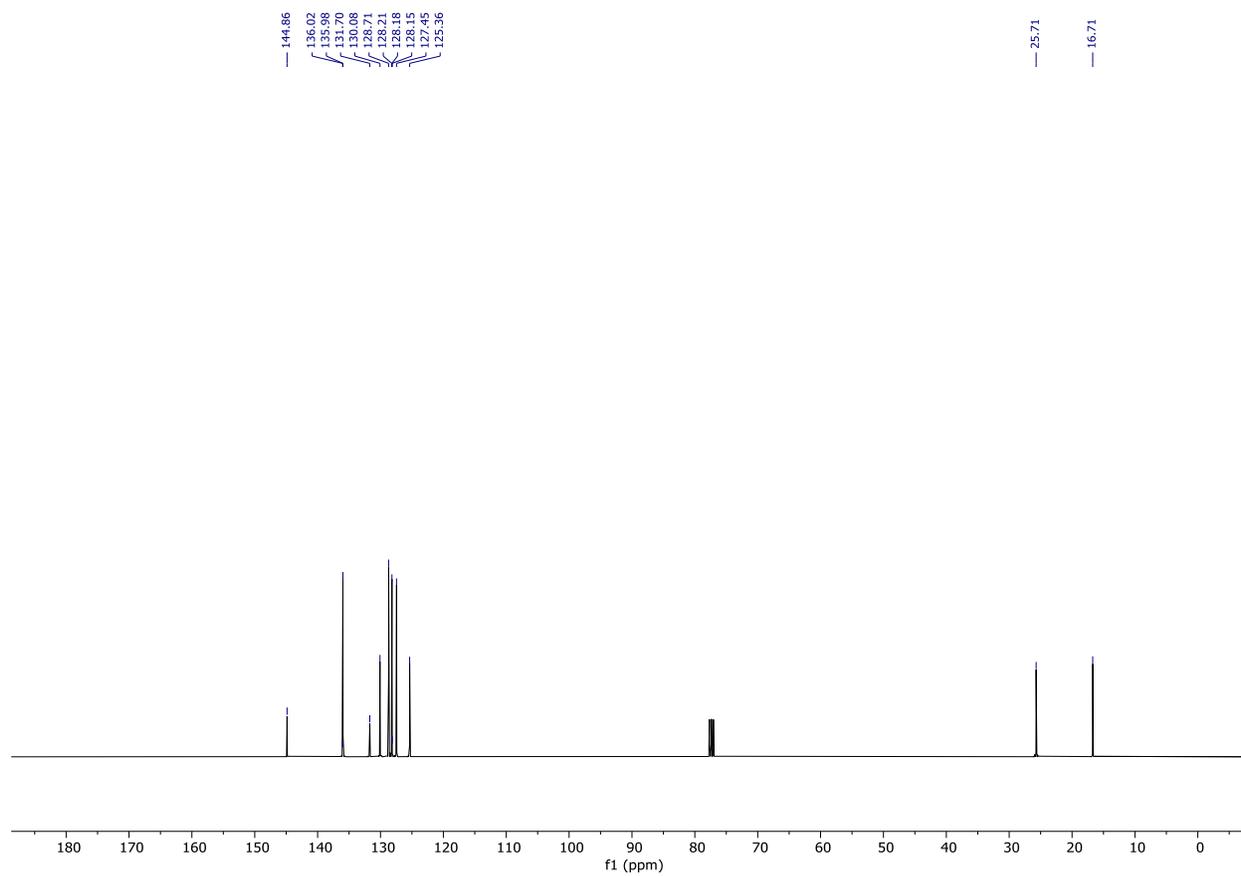


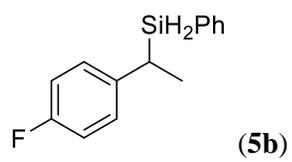


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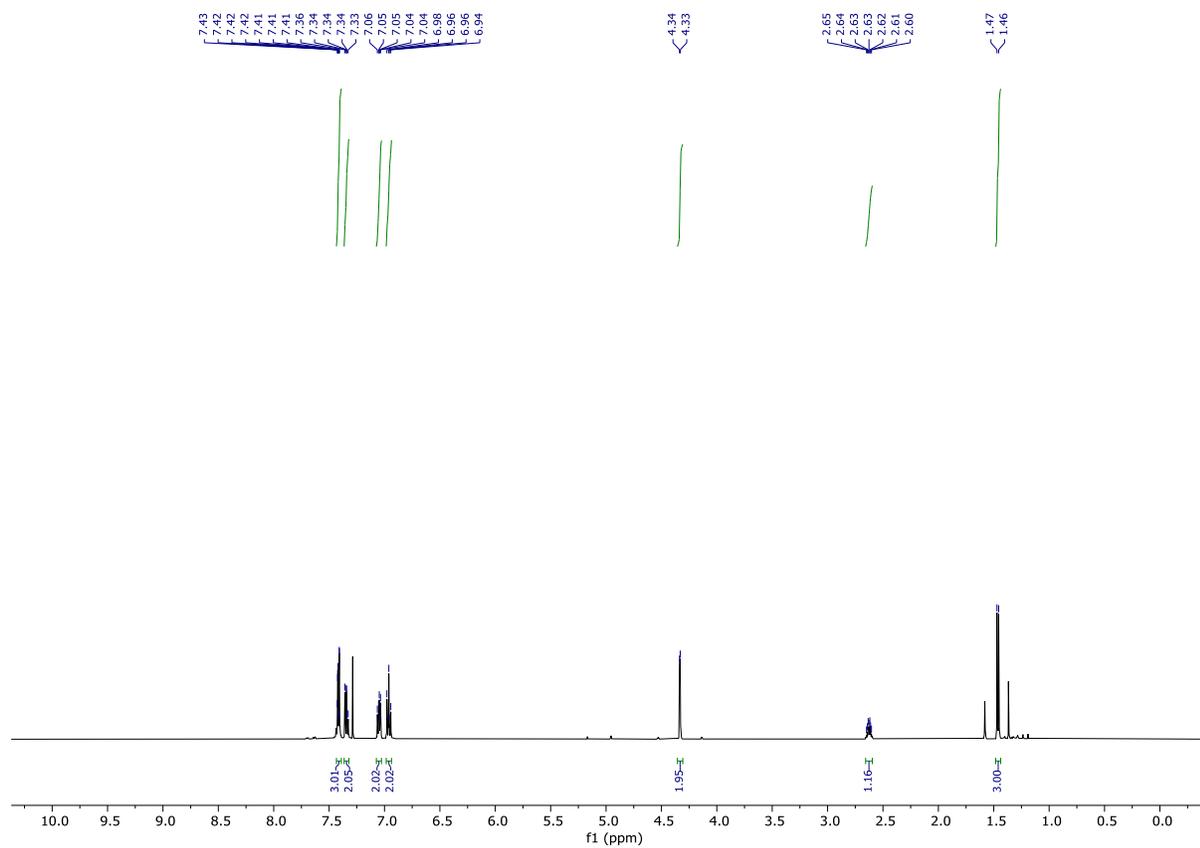


^{13}C NMR (101 MHz, CDCl_3):

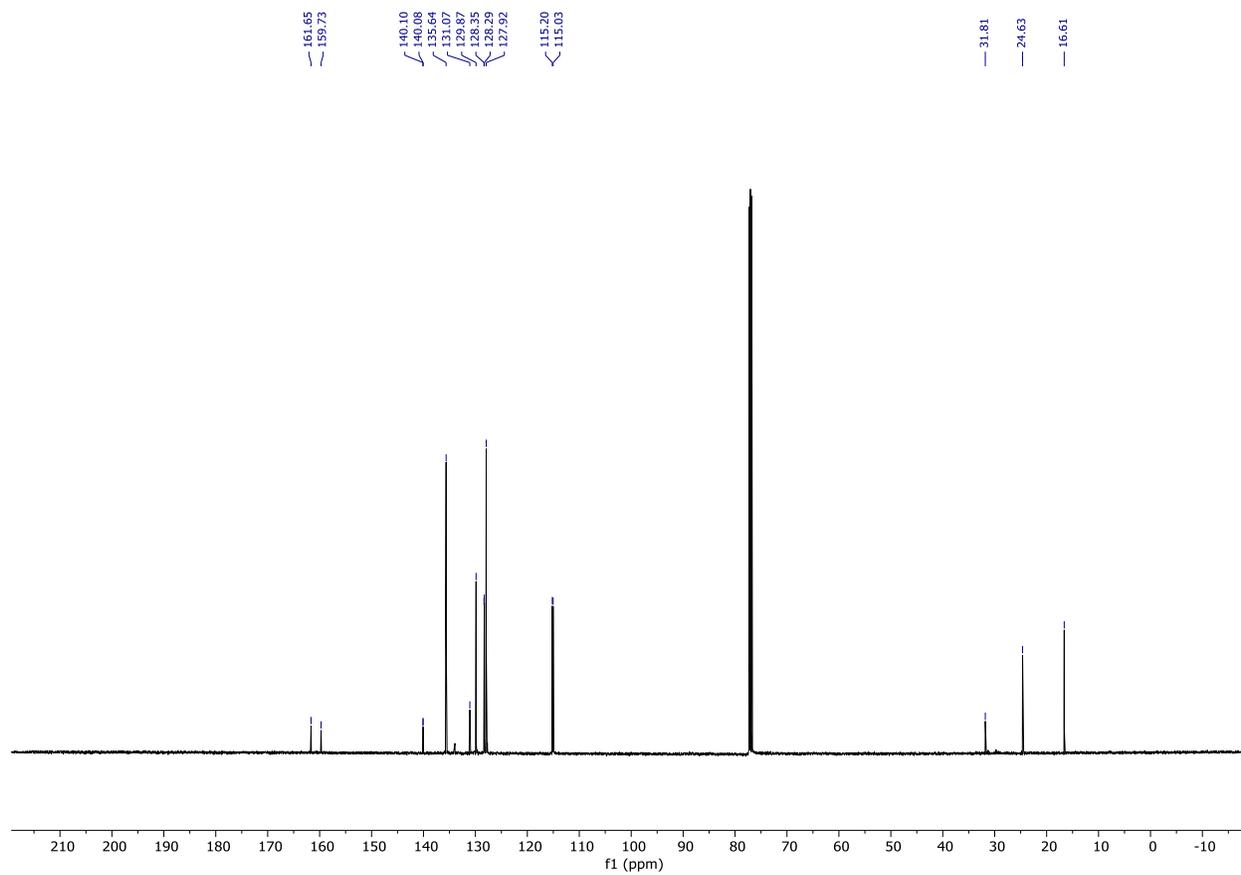




^1H NMR (500 MHz, CDCl_3):



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



References:

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2. H. Zeng, J. Wu, S. Li, C. Hui, A. Ta, S.-Y. Cheng, S. Zheng, G. Zhang, *Org. Lett.* 2019, **21**, 401.
3. G. Zhang, J. Cheng, K. Davis, M. G. Bonifacio, C. Zajaczkowski, *Green Chem.*, 2019, **21**, 1114.
4. G. Zhang, J. Wu, S. Zheng, M. C. Neary, J. Mao, M. Flores, R. J. Trovitch, P. A. Dub. *J. Am. Chem. Soc.*, 2019, **141**, 15230.
5. M. W. Gribble, M. T. Pirnot, J. S. Bandar, R. Y. Liu, S. L. Buchwald, *J. Am. Chem. Soc.*, 2017, **139**, 2192.