Supplementary Material:

Assembly of a 3-D cobalt(II) supramolecular framework and its applications in hydrofunctionalization of ketones and aldehydes

Figure S1. The FT-IR spectra of ligand **L** (purple line) and complex **1** (green line).

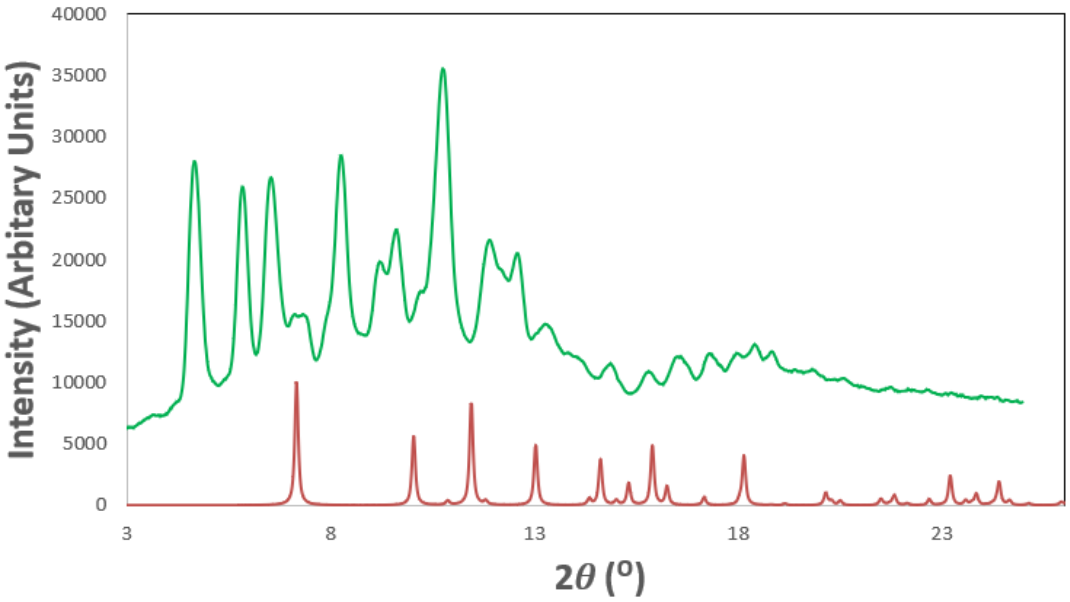
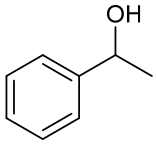


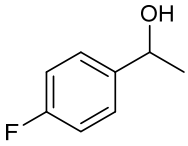
Figure S2. The measured PXRD pattern of sample **1** after being dried in the air (green line) and the calculated PXRD pattern of **1** from the single-crystal X-ray diffraction data (violet line). A possible phase transition is suggested due to the partial loss of co-crystallized solvents.

Experimental Details

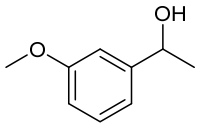
Synthetic procedures and characterization data



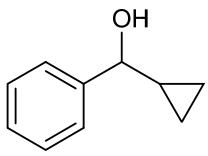
1-Phenylethanol:[43] In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Acetophenone (120.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 112.0 mg (92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27–7.13 (m, 4H), 7.13–7.05 (m, 1H), 4.68 (q, *J* = 6.5 Hz, 1H), 2.16 (s, 1H), 1.30 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.9, 128.5, 127.5, 125.5, 70.4, 29.8, 25.2 ppm.



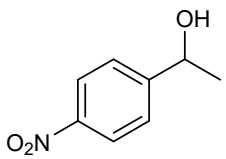
1-(4-Fluorophenyl)ethanol:[43] Method A (by hydroboration): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 4′-Fluoroacetophenone (138.0 mg, 1.0 mmol) and 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 132 mg (94%). Method B (by hydrosilylation): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 4′-Fluoroacetophenone (138.0 mg, 1.0 mmol) and phenylsilane (119.0 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) at room temperature for 2 h. The product was isolated by column chromatography as described above. Yield: 129 mg (92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.84 (q, *J* = 6.5 Hz, 1H), 2.23 (s, 1H), 1.45 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.1 Hz), 141.6 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 8.2 Hz), 115.3 (d, *J* = 21.1 Hz), 69.8, 29.8, 25.3 ppm.



1-(3-Methoxyphenyl)ethanol:[43] In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 140 mg (92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.1 Hz, 1H), 6.99–6.90 (m, 2H), 6.83 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.86 (d, *J* = 6.5 Hz, 1H), 3.82 (s, 3H), 2.29 (s, 1H), 1.49 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 147.7, 129.6, 117.8, 112.9, 111.0, 70.3, 55.3, 25.2 ppm.

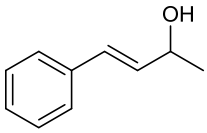


1-Cyclopropyl Phenylmethanol:[43] Method A (by hydroboration): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Cyclopropyl phenyl ketone (146.0 mg, 1.0 mmol) 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 141 mg (95%). Method B (by hydrosilylation): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Cyclopropyl phenyl ketone (146.0 mg, 1.0 mmol) and phenylsilane (119.0 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) at room temperature for 2 h. The product was isolated by column chromatography as described above. Yield: 133 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.39–7.34 (m, 2H), 7.32–7.27 (m, 1H), 4.01 (d, *J* = 8.3 Hz, 1H), 2.09 (s, 1H), 1.22 (tdd, *J* = 8.2, 5.0, 3.2 Hz, 1H), 0.68 – 0.60 (m, 1H), 0.56 (tdd, *J* = 8.6, 5.6, 4.4 Hz, 1H), 0.48 (dtd, *J* = 9.3, 5.2, 4.3 Hz, 1H), 0.38 (ddt, *J* = 9.3, 5.5, 4.6 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 128.5, 127.6, 126.1, 78.6, 19.3, 3.7, 2.9 ppm.

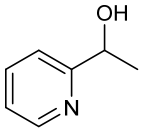


1-(4-Nitrophenyl)ethanol:[43] Method A (by hydroboration): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 4'-Nitroacetophenone (165.0 mg, 1.0 mmol) and 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Yellowish oil was isolated. Yield: 149 mg (89%). Method B (by hydrosilylation): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 4'-Nitroacetophenone (165.0 mg, 1.0 mmol) and phenylsilane (119.0 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) at room temperature for 2 h. The product was isolated by column chromatography as described above. Yield: 140 mg (84%). ^{1}H NMR (600 MHz, $CDCl_3$) 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. ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 147.6, 126.8, 125.5, 124.5, 123.2, 70.1, 26.1 ppm.

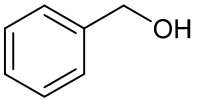


(*E*)-4-Phenylbut-3-en-2-ol:[43] In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 4-Phenyl-3-buten-2-one (146.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 133 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.17–7.12 (m, 1H), 6.47 (dd, *J* = 15.9, 1.2 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.3 Hz, 1H), 4.39 (td, *J* = 6.4, 1.3 Hz, 1H), 1.86 (s, 1H), 1.28 (d, *J* = 6.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 133.7, 129.5, 128.7, 127.7, 126.6, 69.0, 23.5 ppm.

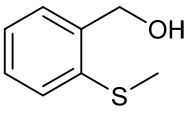


1-(2-pyridyl)ethanol:[43] In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 2-Acetylpyridine (121.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Yellowish oil was isolated. Yield: 101 mg (82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.33 (d, *J* = 4.9 Hz, 1H), 7.71 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.22 (dd, *J* = 7.9, 4.9

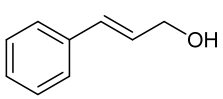
Hz, 1H), 4.87 (q, *J* = 6.5 Hz, 1H), 4.57 (br, 1H), 1.46 (d, *J* = 6.5 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.1, 147.1, 141.9, 133.6, 123.7, 67.63, 67.5, 25.3 ppm.



Benzyl alcohol:[43] Method A (by hydroboration): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Benzaldehyde (106.0 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 95 mg (88%). Method B (by hydrosilylation): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Benzaldehyde (106.0 mg, 1.0 mmol) and phenylsilane (119.0 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) at room temperature for 2 h. The product was isolated by column chromatography as described above. Yield: 92 mg (85%). ^{1}H NMR (600 MHz, $CDCl_3$) 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; ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.98, 128.71, 127.80, 127.14, 65.50 ppm.



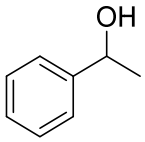
2-Methylthiobenzyl alcohol:[43] In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. 2-Methylthiobenzaldehyde (152.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 139 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 4.6 Hz, 4H), 7.34–7.26 (m, 1H), 4.69 (s, 2H), 2.09 (br, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 136.5, 128.2, 127.8, 126.4, 125.4, 63.1, 16.0 ppm.



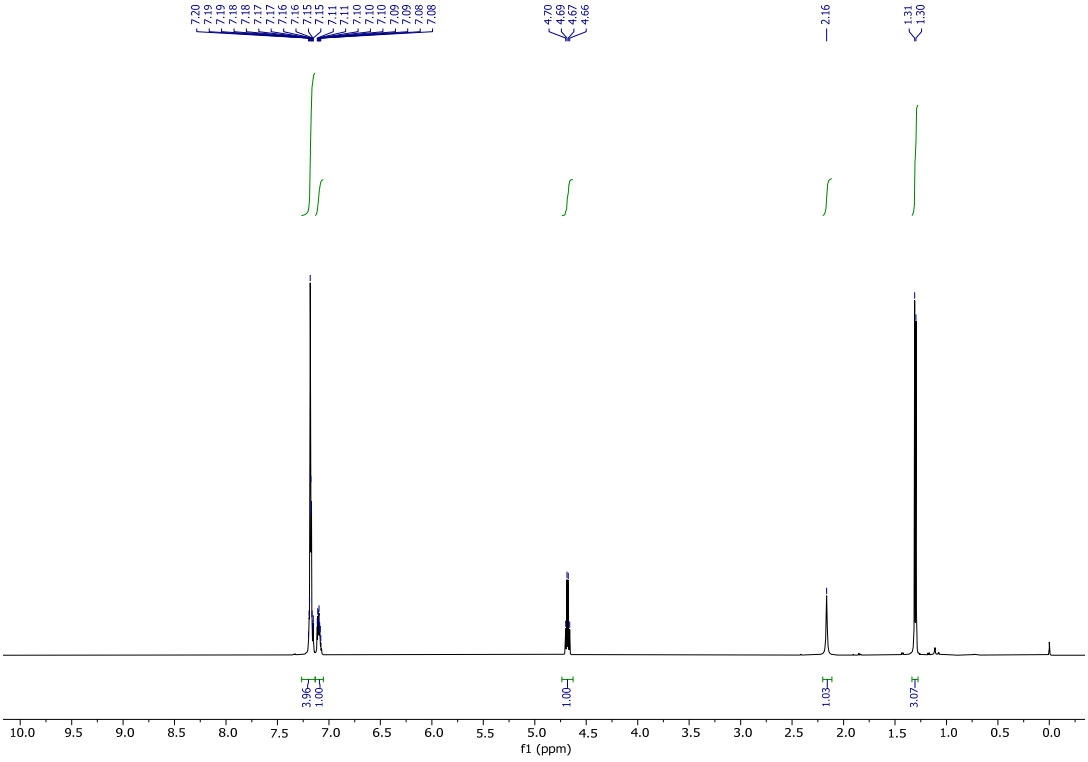
Cinnamyl alcohol:[43] In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Cinnamaldehyde (132.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1

mL) and 30% H_2O_2 (1 mL) stirred at room temperature for 1 h. The solution was extracted with ethyl acetate and washed with brine and water. The organic phase was concentrated under reduced pressure and then purified through flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10, *v*/*v*) as eluent. Colorless oil was isolated. Yield: 115 mg (86%). Method B (by hydrosilylation): In a glovebox under nitrogen atmosphere, **1** (0.63 mg, 1.0 μmol, based on Co(**L**)$_2$(NCS)$_2$) and KO^{t}Bu (1.1 mg, 10 μmol) was placed in a 1.8 mL disposable vial equipped with a stir bar. Cinnamaldehyde (132.0 mg, 1.0 mmol) and phenylsilane (119.0 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 diethyl ether (10 mL) was added. The crude mixture was treated with 2N NaOH (1 mL) at room temperature for 2 h. The product was isolated by column chromatography as described above. Yield: 121 mg (90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.26 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.21 (d, *J* = 6.1 Hz, 2H), 1.90 (s, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.8, 131.2, 128.7, 128.6, 127.8, 126.6, 63.7 ppm.

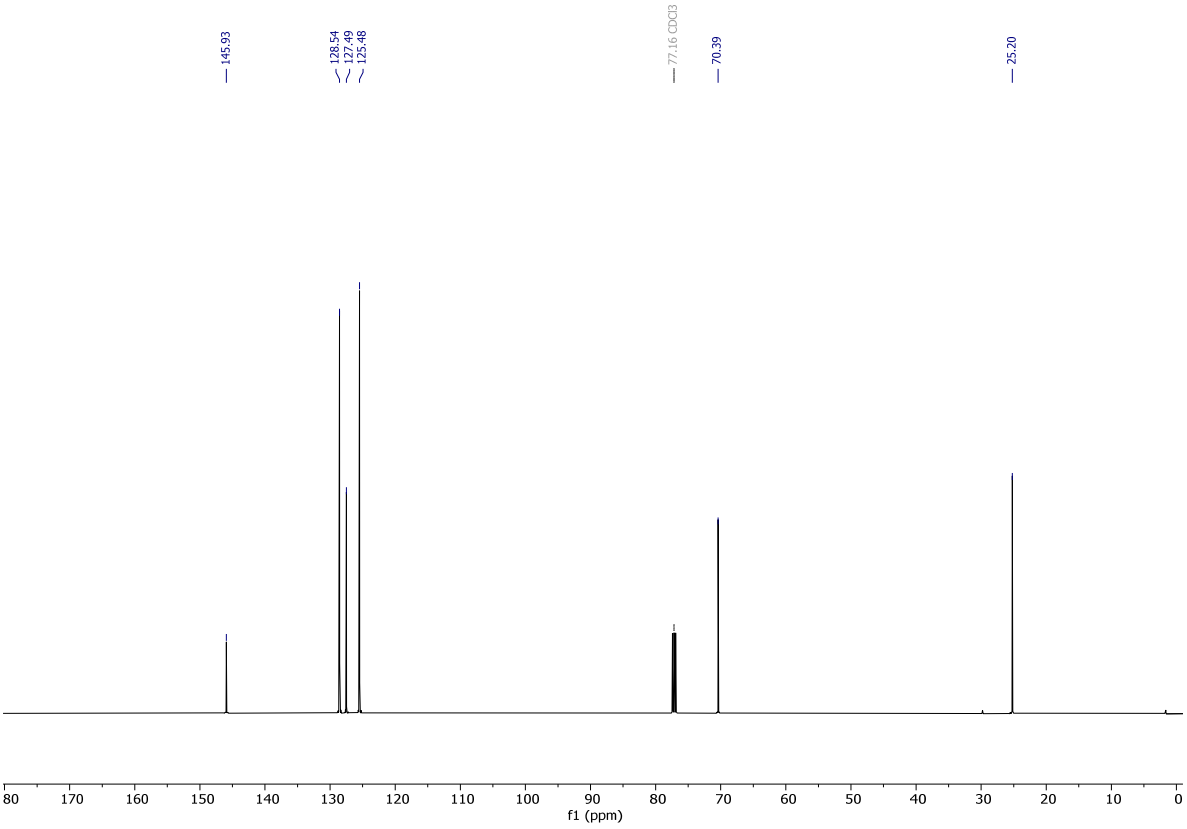
NMR spectra for isolated products:

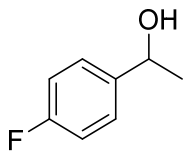


^{1}H NMR (500 MHz, $CDCl_3$):

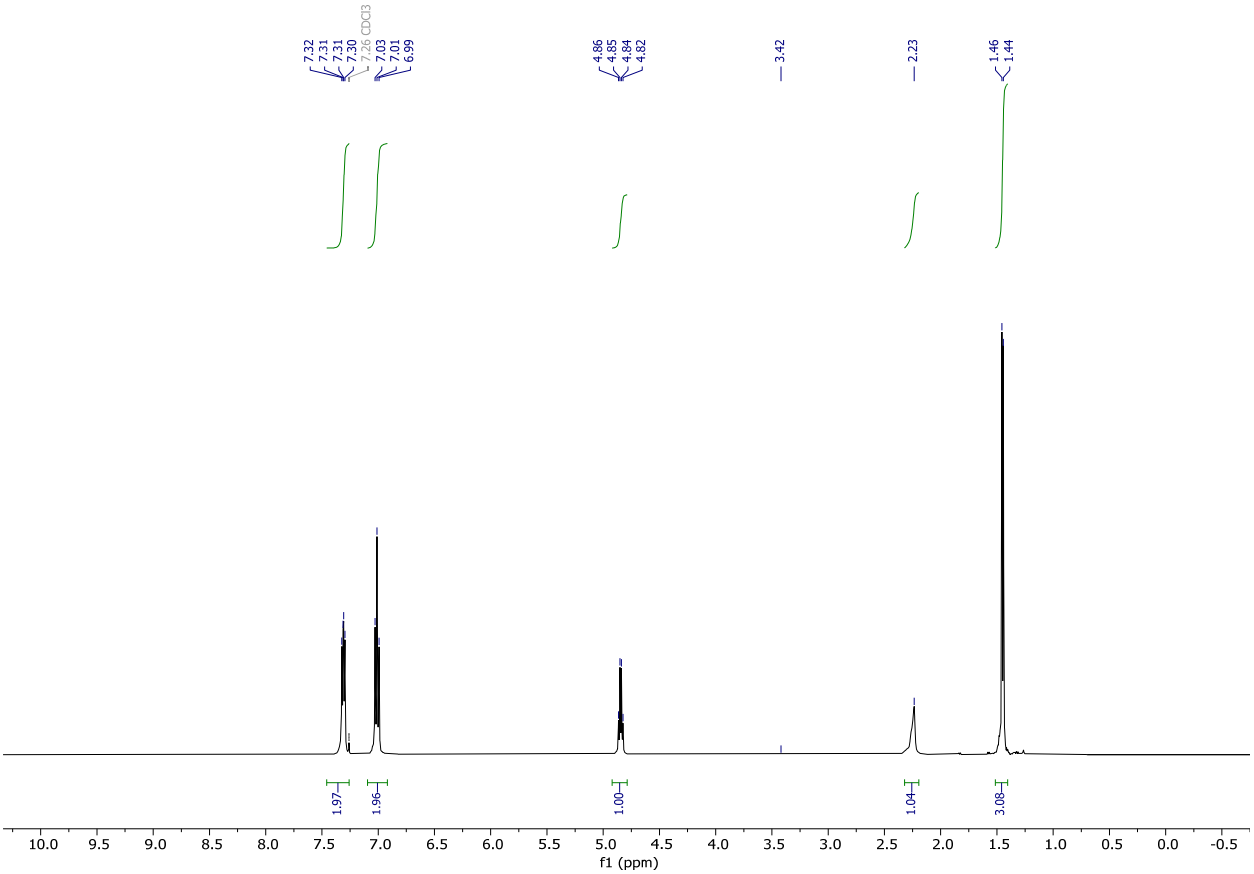


^{13}C NMR (126 MHz, $CDCl_3$):

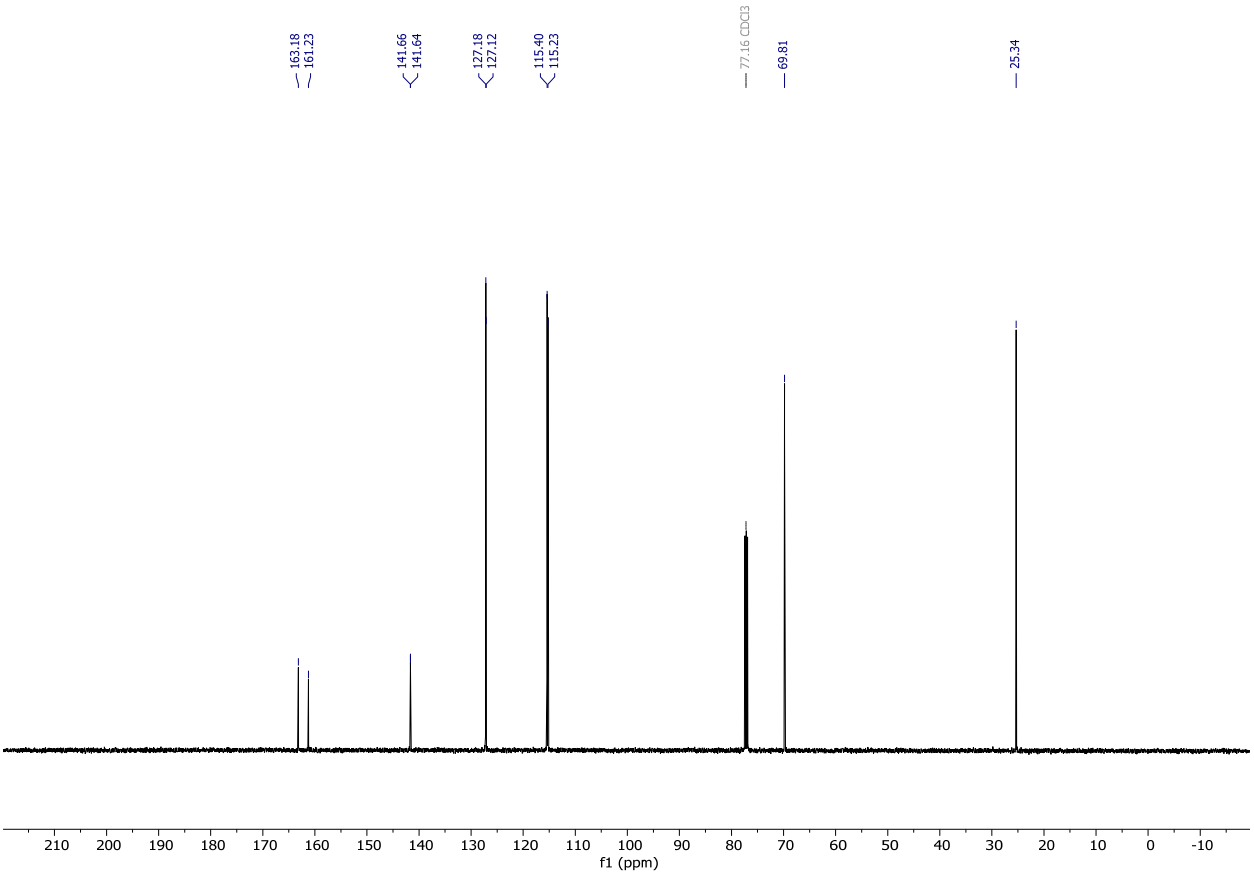


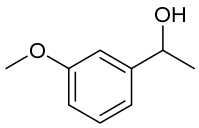


^{1}H NMR (500 MHz, $CDCl_3$):

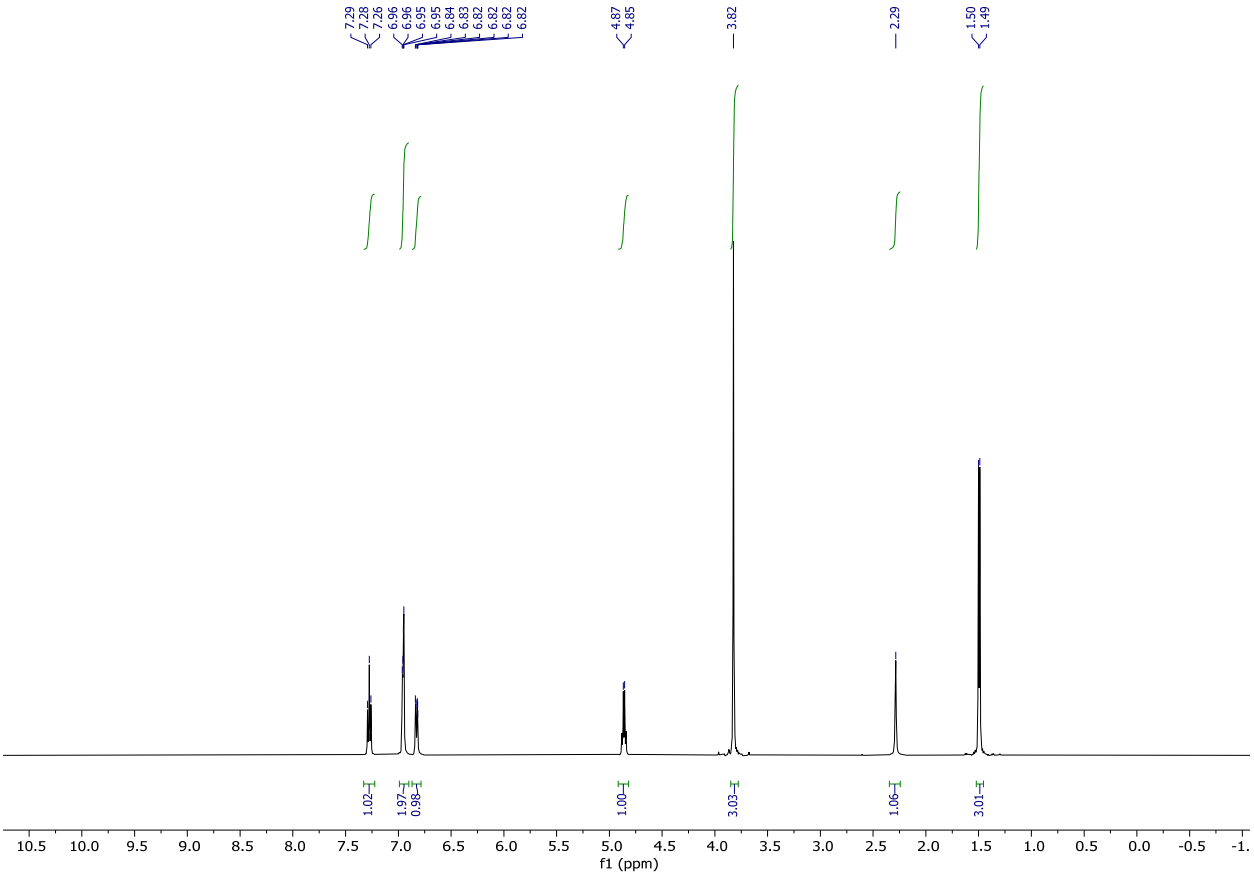


^{13}C NMR (126 MHz, $CDCl_3$):

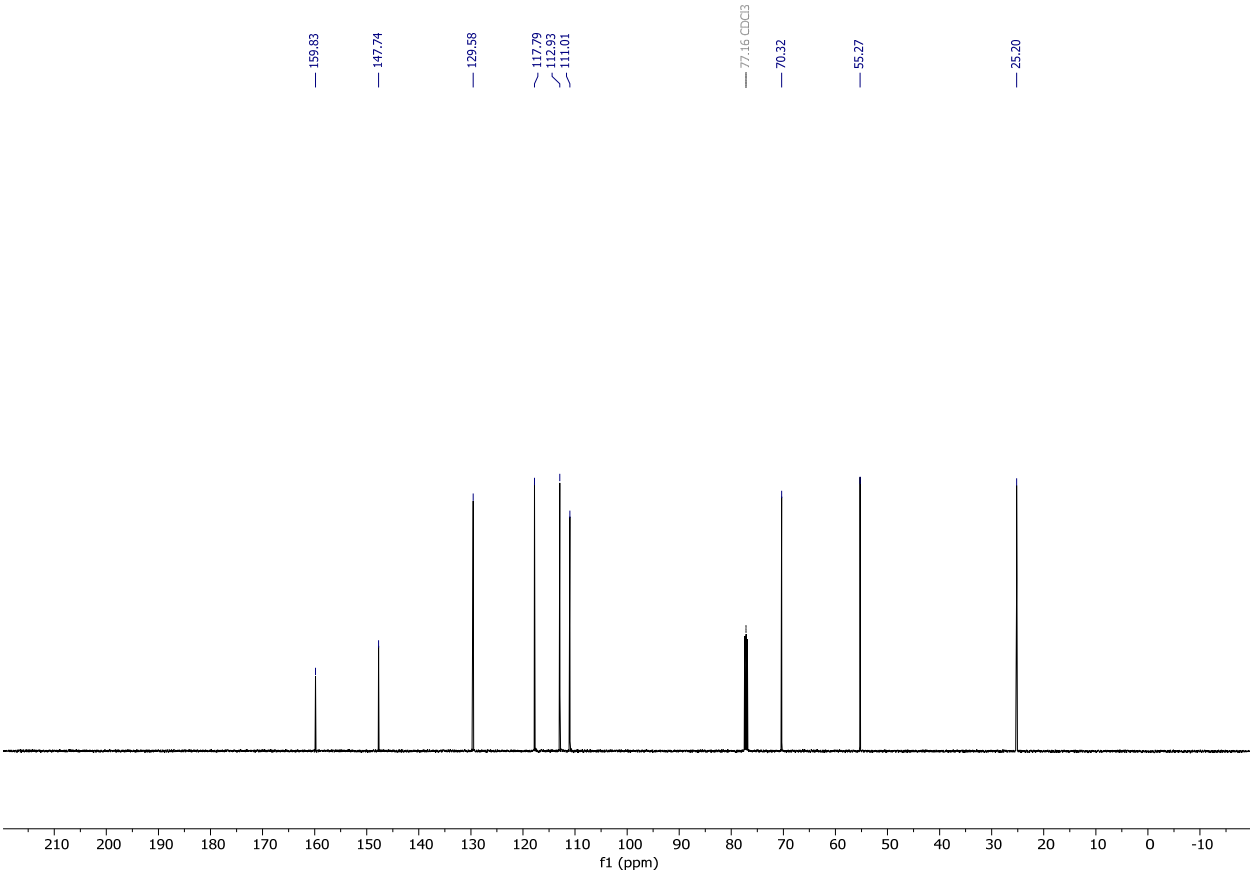


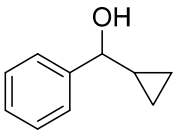


^{1}H NMR (500 MHz, $CDCl_3$):

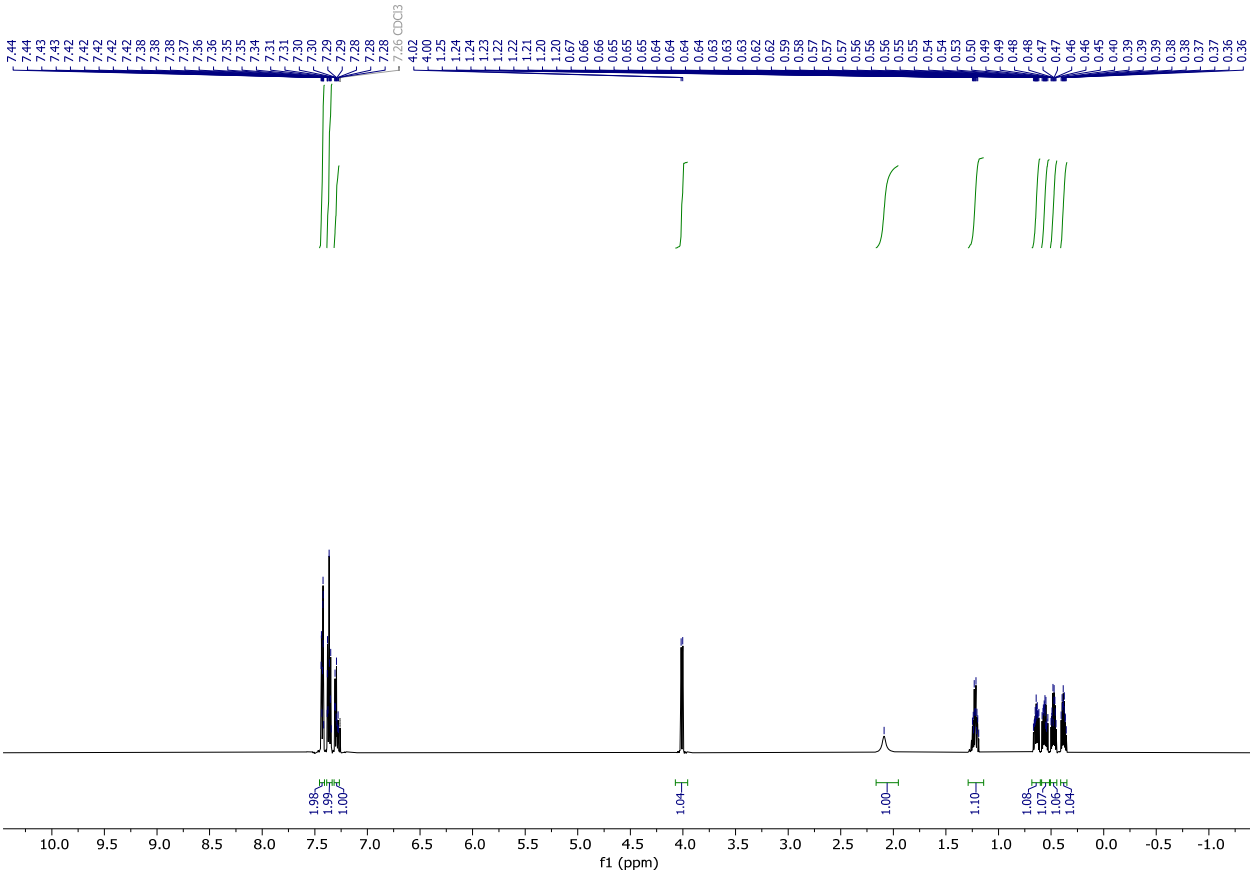


^{13}C NMR (126 MHz, $CDCl_3$):

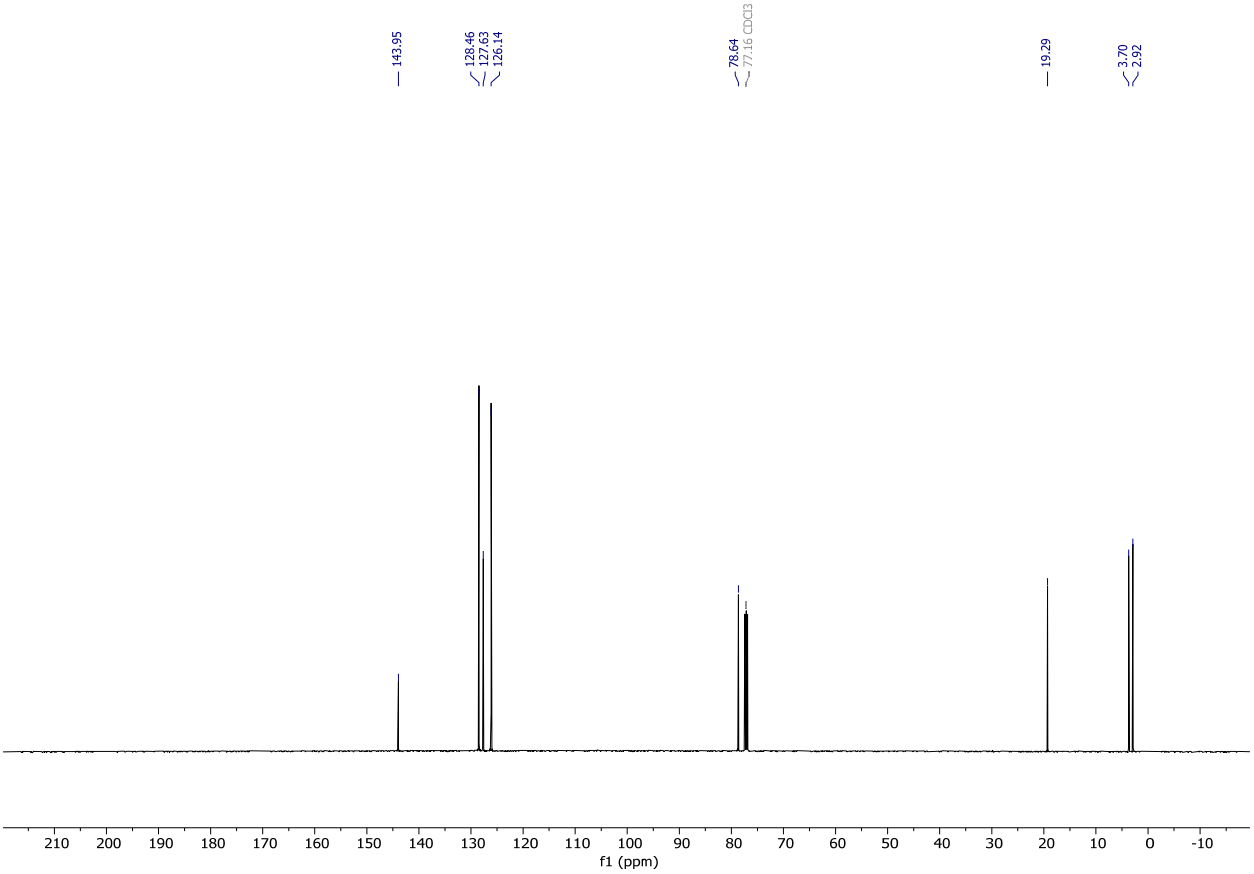


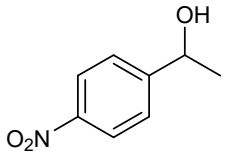


^{1}H NMR (500 MHz, $CDCl_3$):

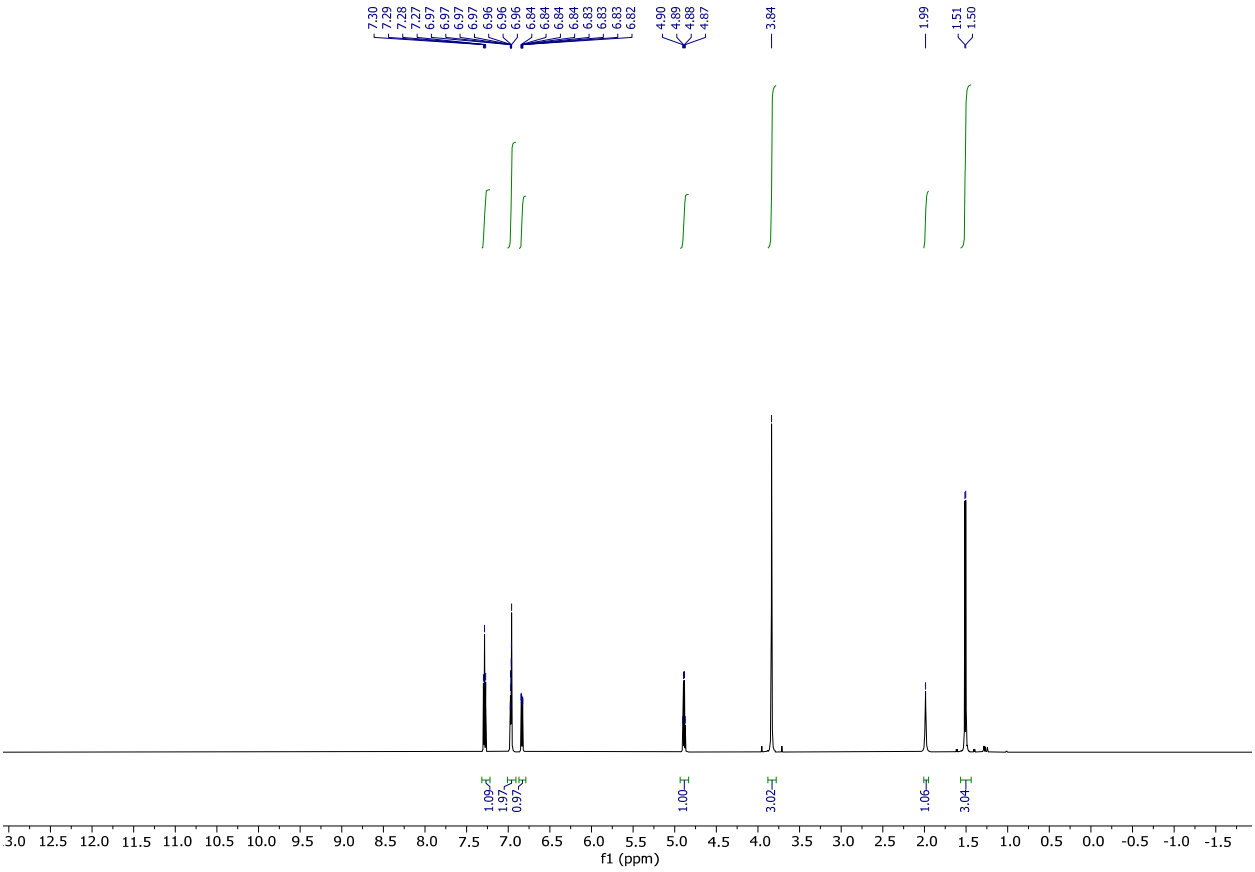


^{13}C NMR (126 MHz, $CDCl_3$):

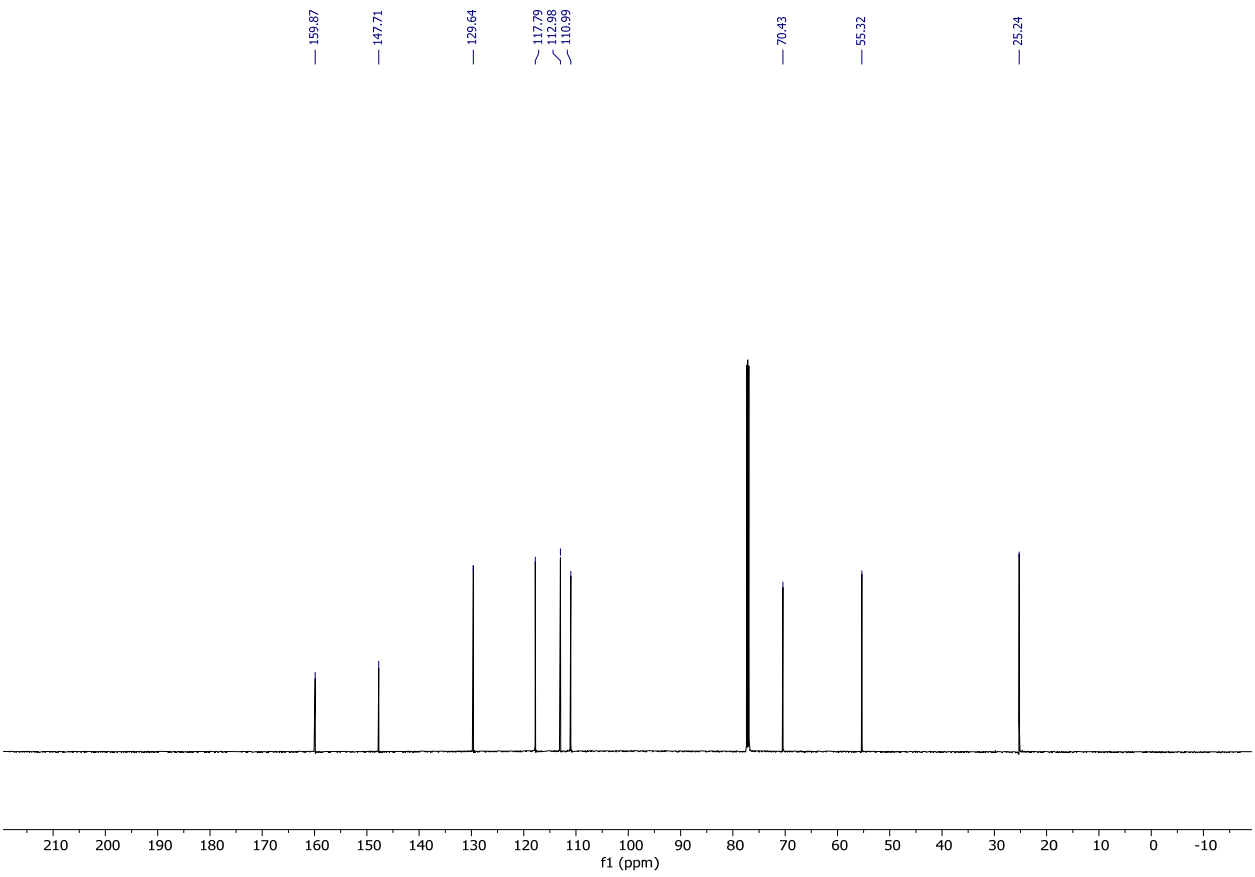


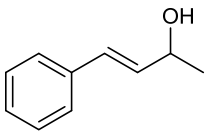


^{1}H NMR (500 MHz, $CDCl_3$):

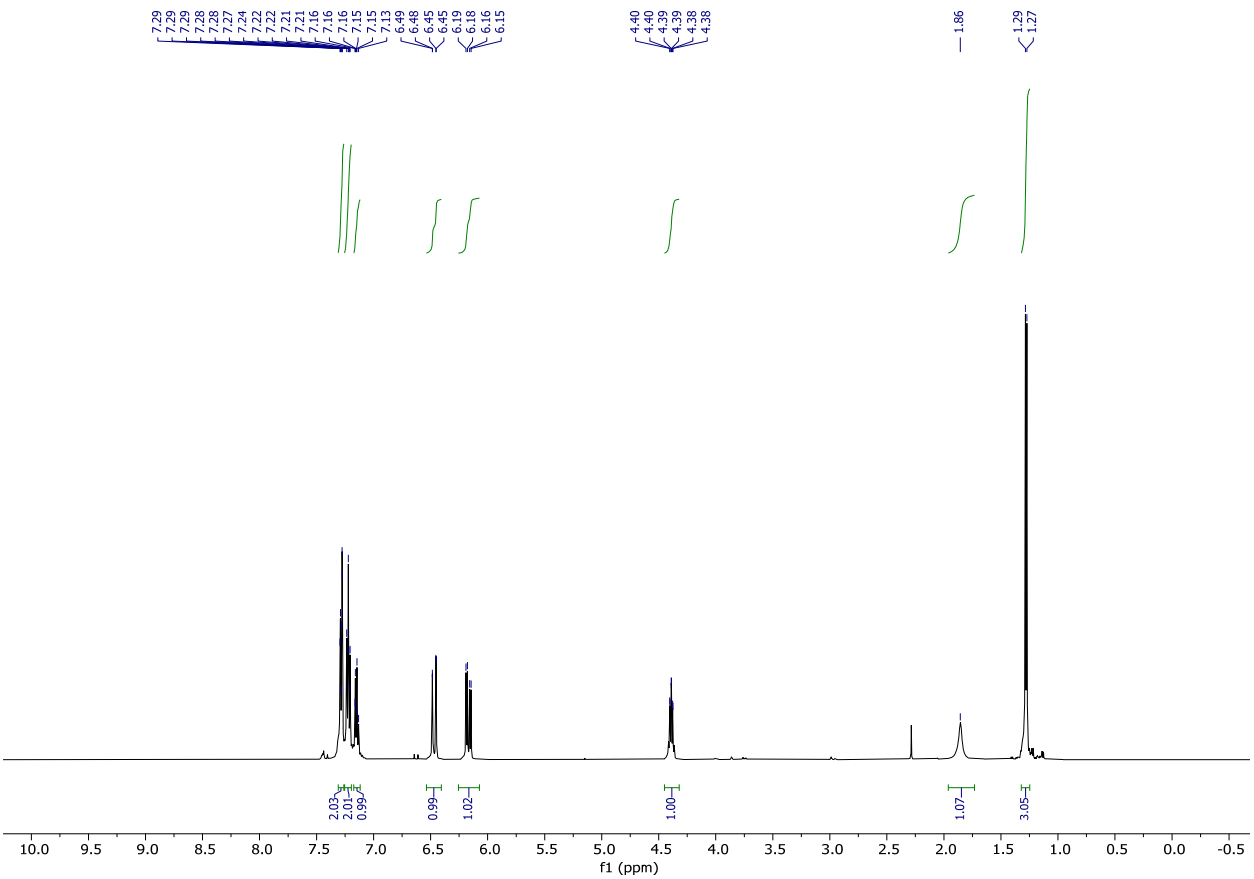


^{13}C NMR (126 MHz, $CDCl_3$):

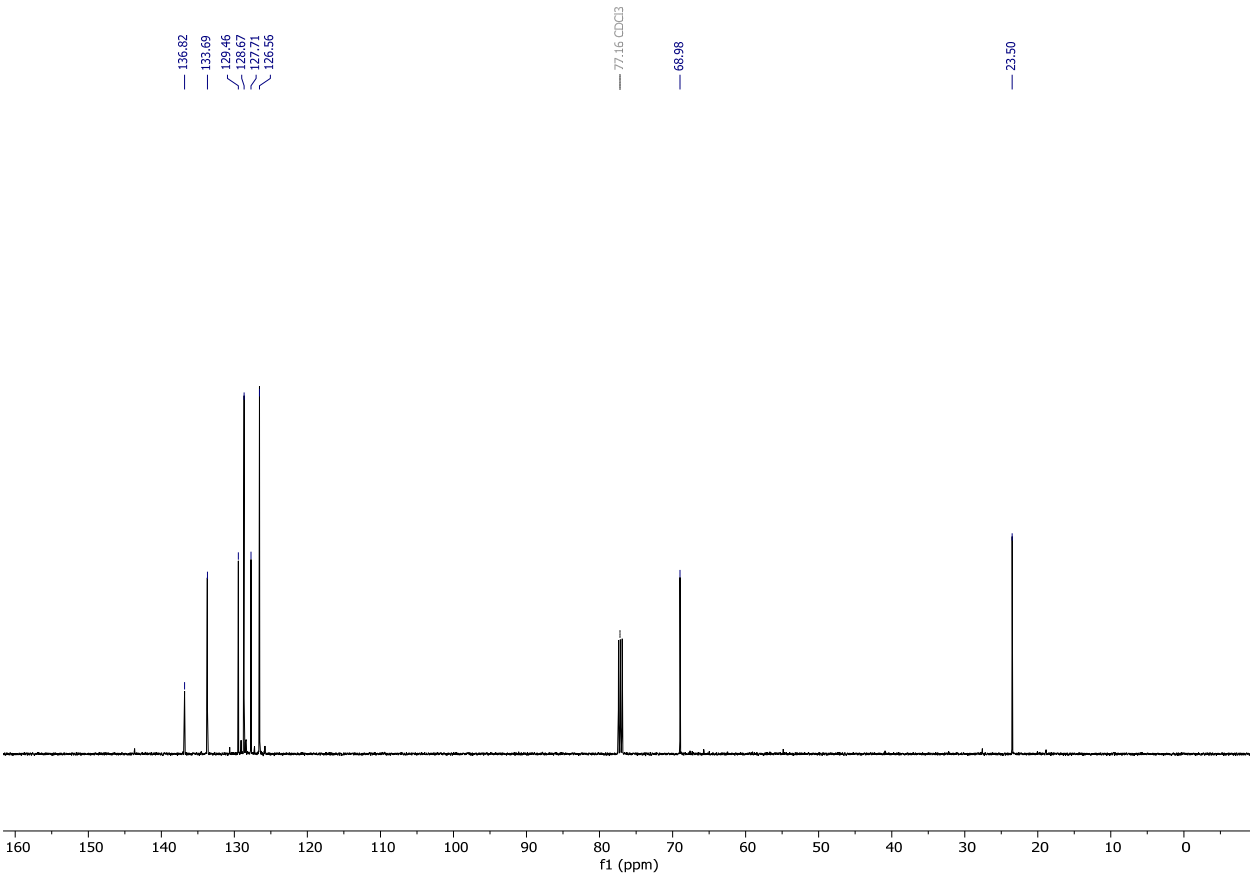


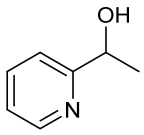


^{1}H NMR (500 MHz, $CDCl_3$):

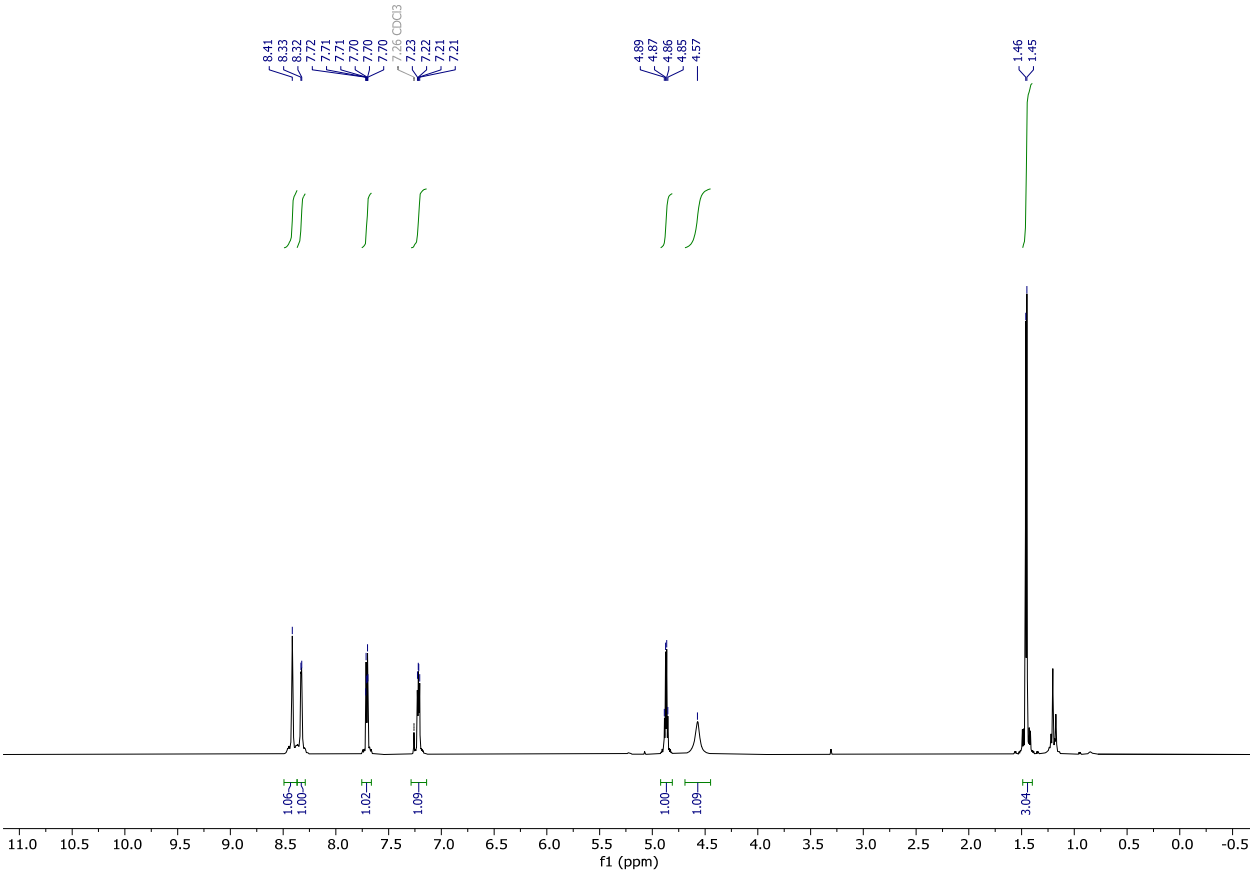


^{13}C NMR (126 MHz, $CDCl_3$):

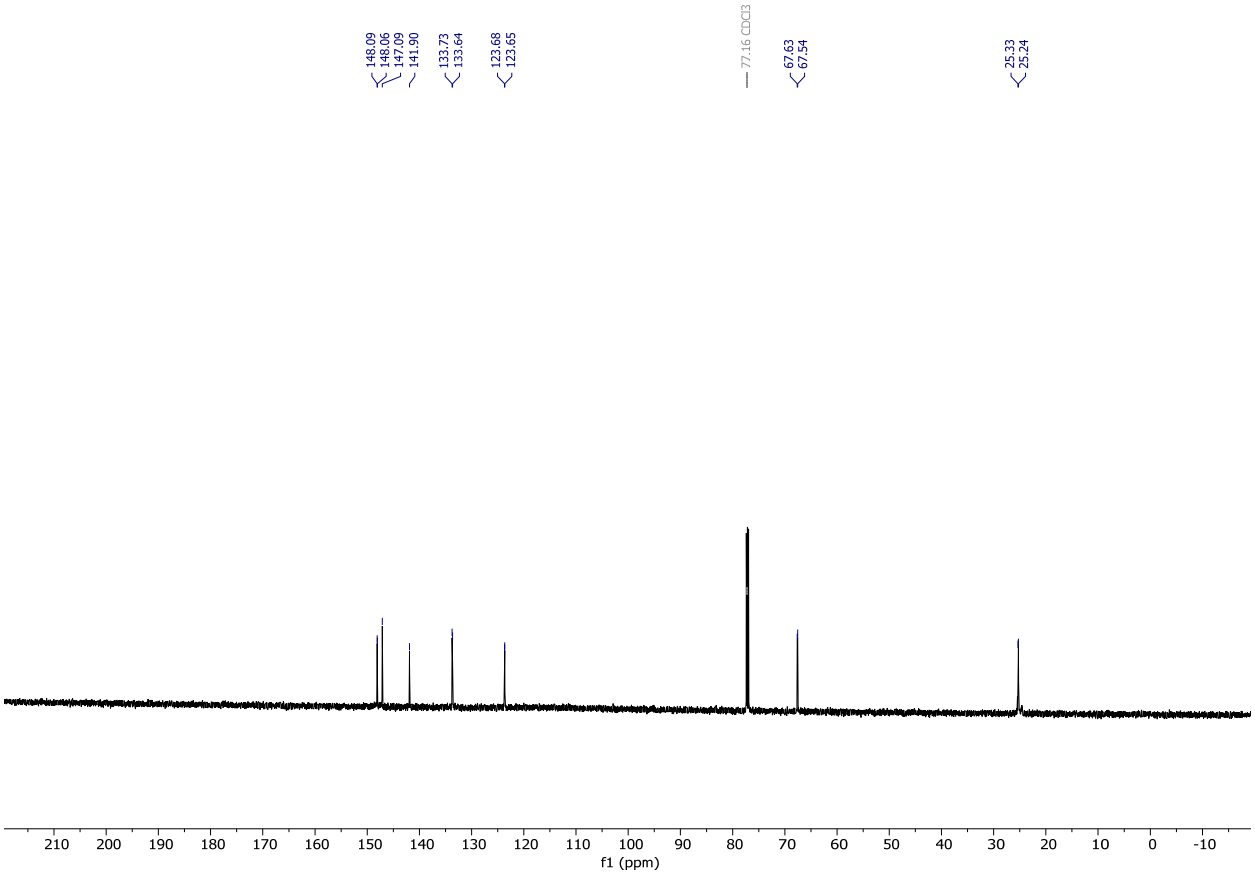


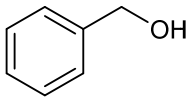


^{1}H NMR (600 MHz, $CDCl_3$):

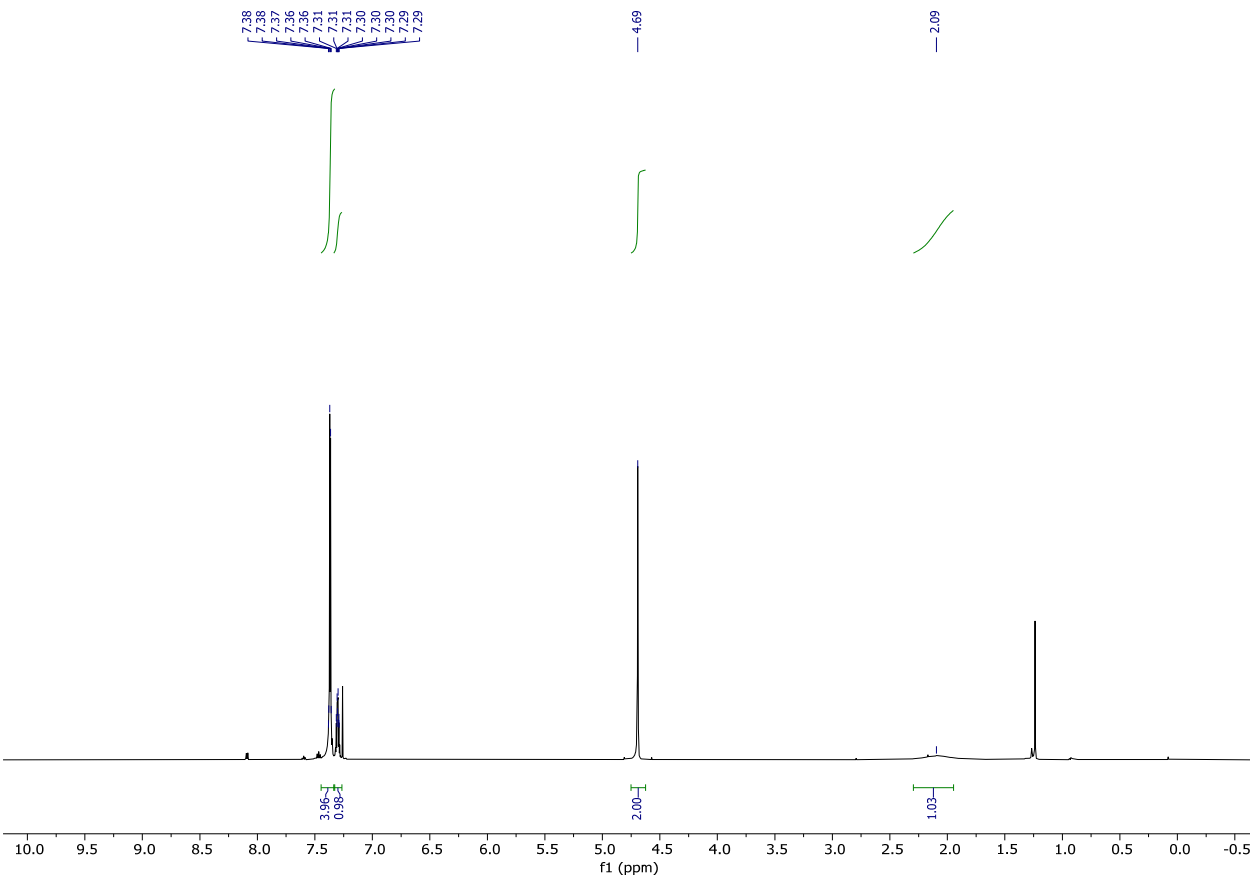


^{13}C NMR (151 MHz, $CDCl_3$):

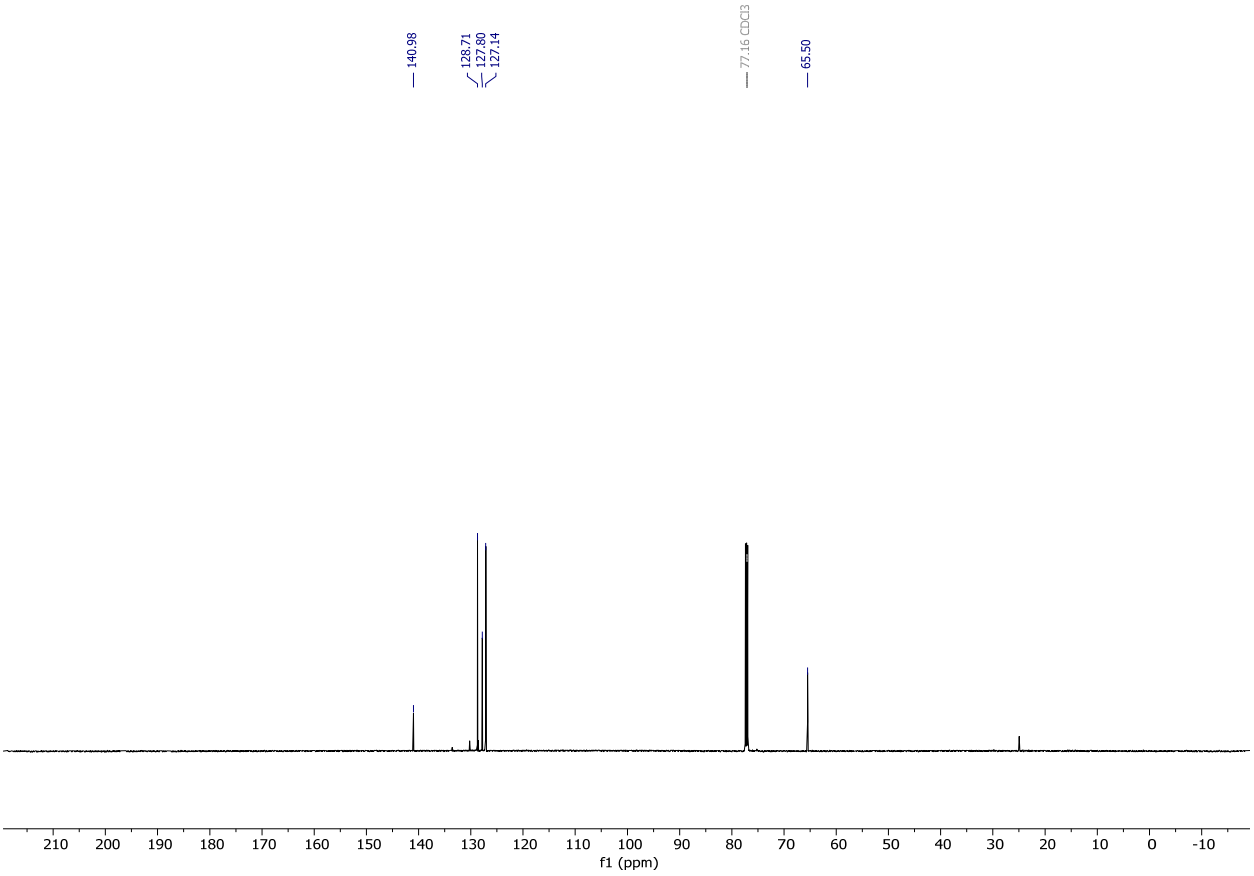


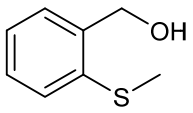


^{1}H NMR (600 MHz, $CDCl_3$):

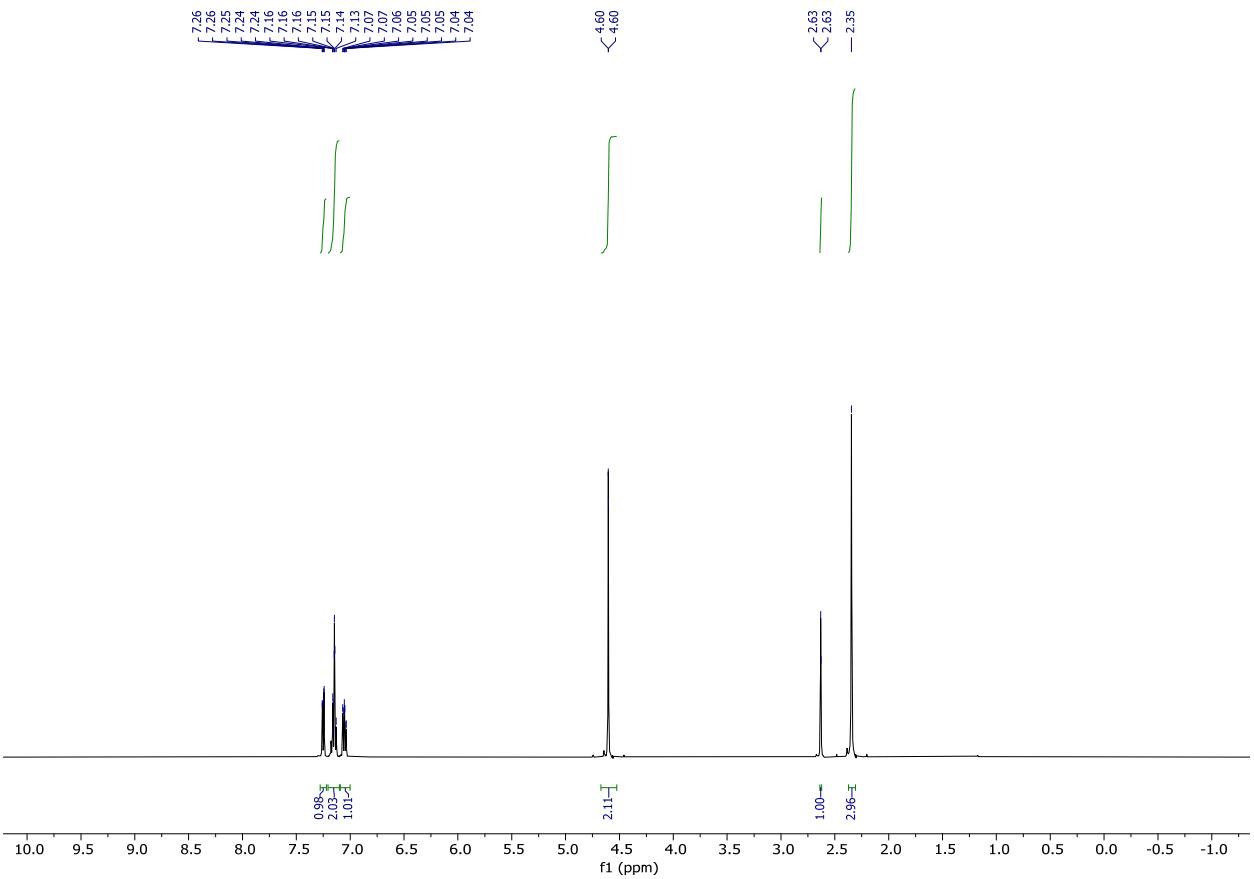


^{13}C NMR (151 MHz, $CDCl_3$):

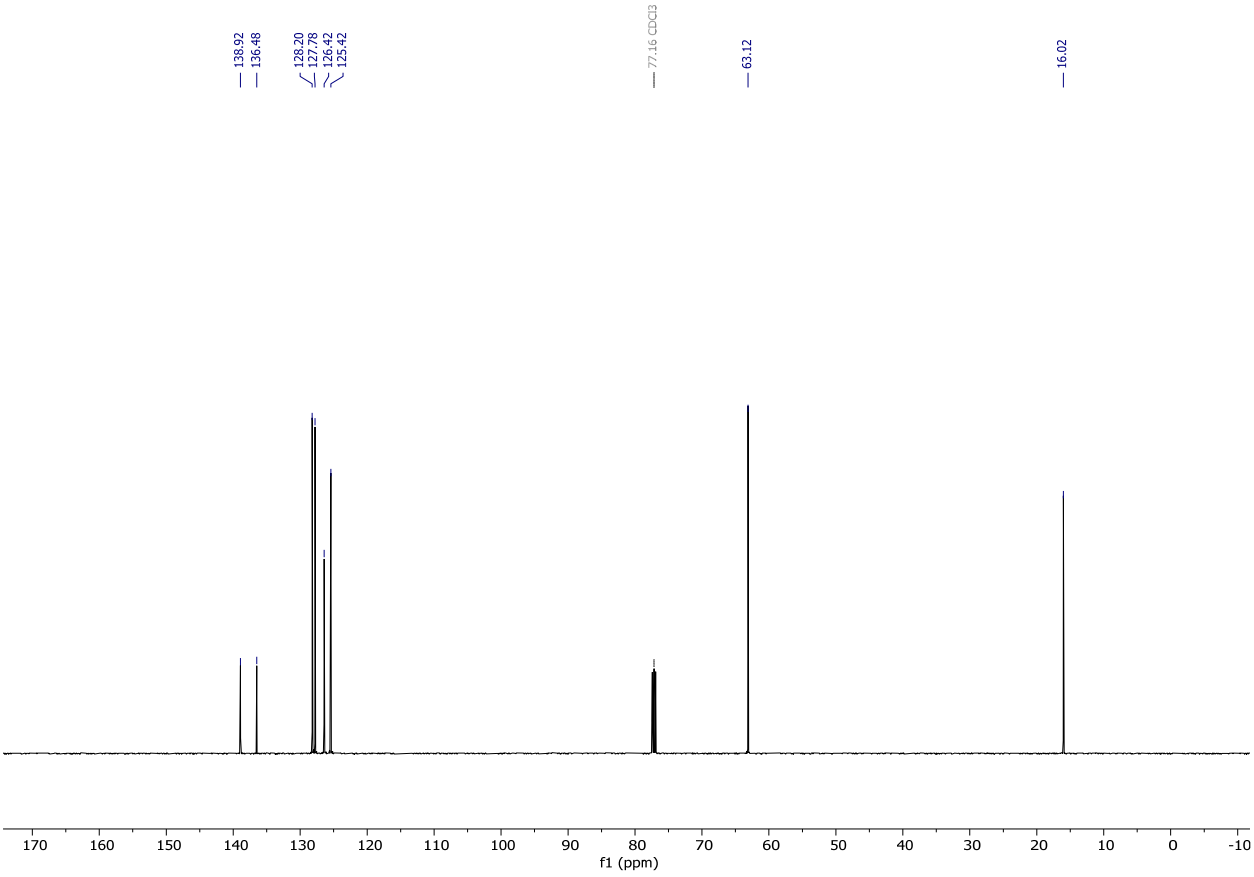


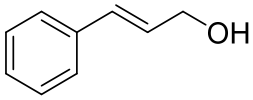


^{1}H NMR (500 MHz, $CDCl_3$):

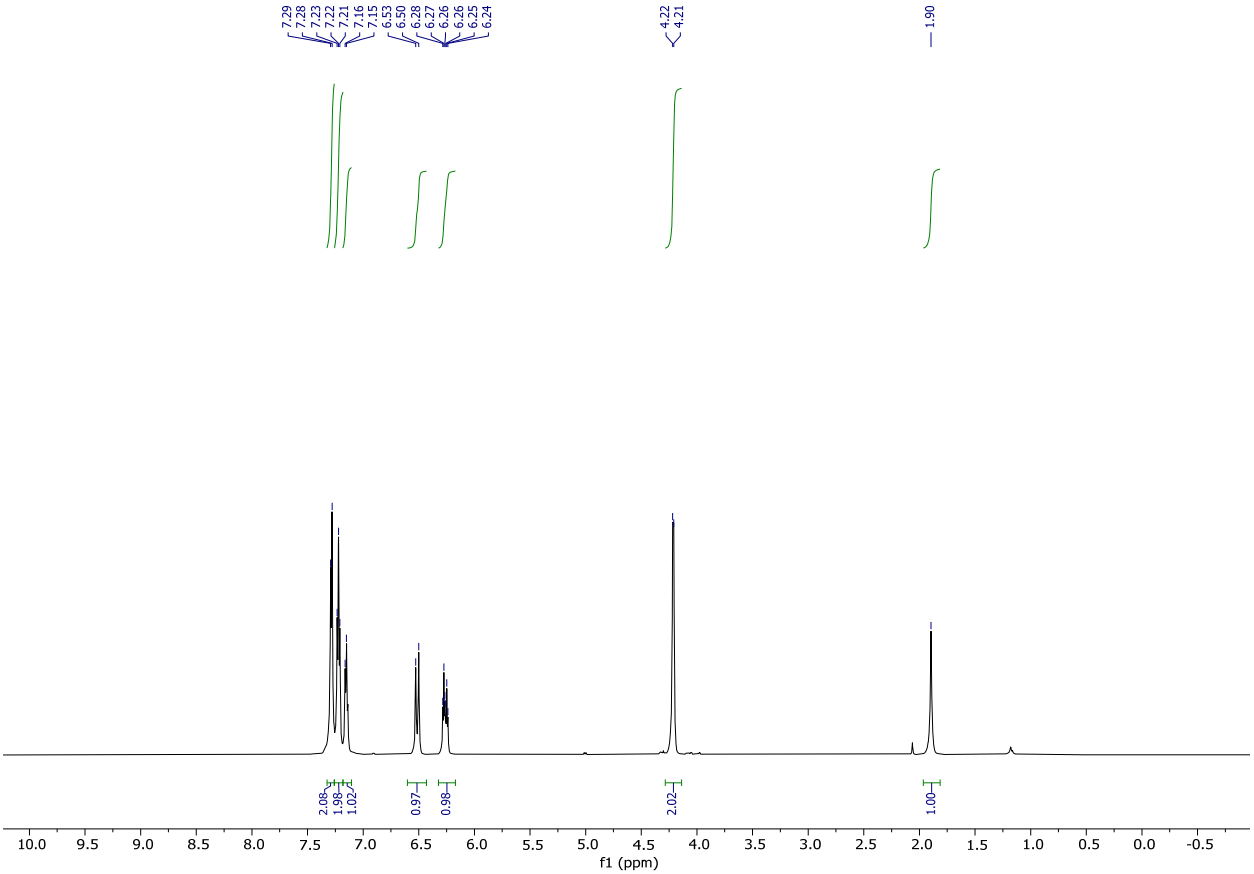


^{13}C NMR (126 MHz, $CDCl_3$):

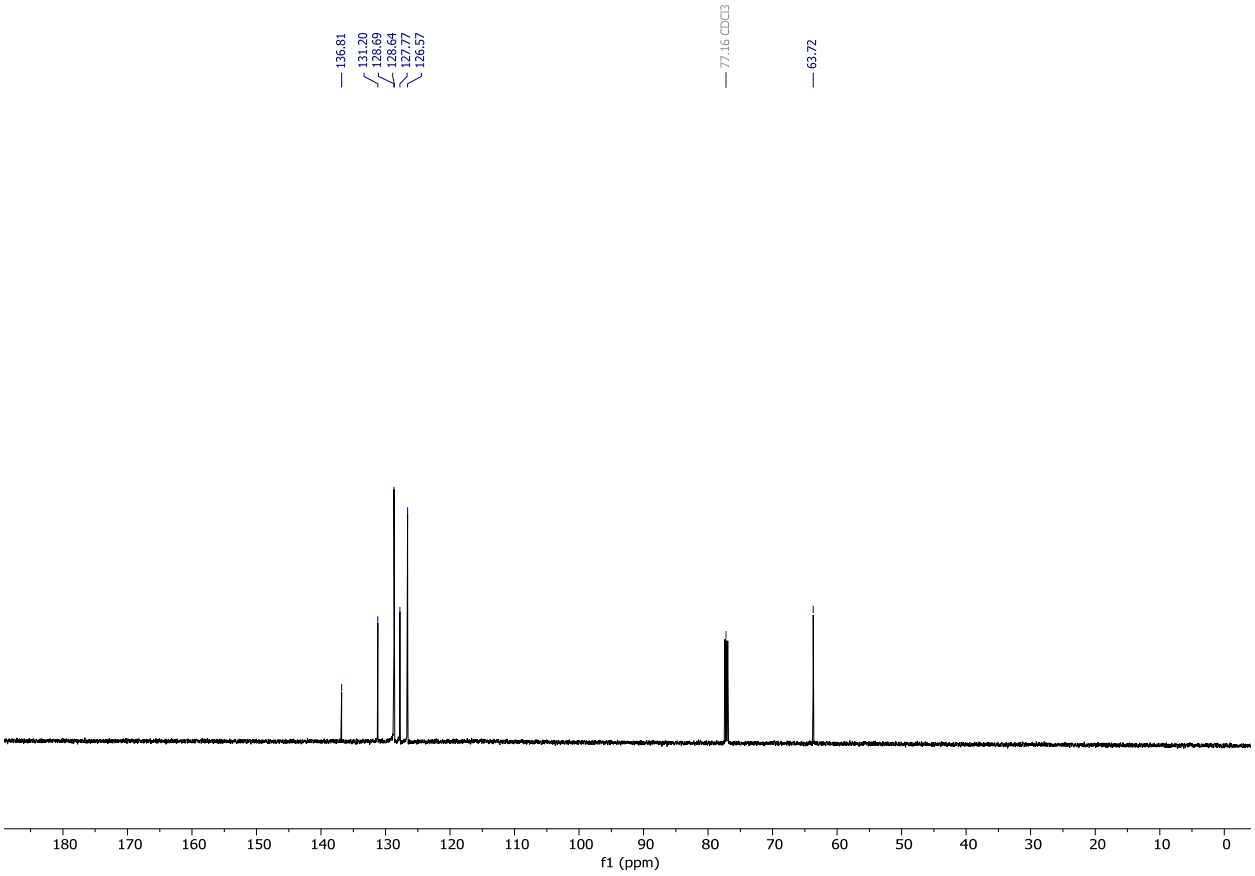




^{1}H NMR (600 MHz, $CDCl_3$):



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


136.81
131.20
128.69
128.64
127.77
126.57
77.16 CDCl3
63.72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)