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Supporting Information:

Highly Efficient and Selective Hydroboration of Terminal and Internal Alkynes Catalysed by a Cobalt(II) Coordination Polymer

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Experimental Details

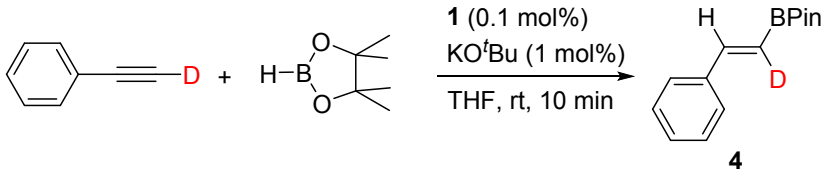
General Considerations. Unless specified otherwise, all reactions were carried out under a dry N_2 atmosphere using standard glove-box and Schlenk techniques. Anhydrous grade solvents and reagents used were obtained from Aldrich or Fisher Scientific and stored over 4 Å molecular sieves. All chemicals of analytical grade including the alkene substrates and additives are used as received from Aldrich, Alfa Aesar, Acros or Fisher Scientific without further purification. ^{1}H 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 (column: SHRX1-5MS, thickness: 0.25 m, diameter: 0.25 mm, length: 30.0 m; conditions: 30-200 °C, 10 °C/min, injection temperature: 100 °C; solvent cutoff: 3 min). Co(tpy)Cl_2 and **1** were prepared according to literature procedures.[1]

General Procedure for 1-Catalyzed Alkyne Hydroboration. In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Alkynes (1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for indicated time periods (10-30 min) and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the yield and selectivity of desired alkenylboronates. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane as an eluent. The pure alkenylboronate products were characterized by ^{1}H and ^{13}C NMR spectroscopies.

Mercury-poisoning Experiment for Hydroboration of Phenylacetylene. In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min and then Hg (~0.5 g) was added. Alkynes (1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS using hexamethylbenzene as an internal standard and 84% yield of **2a** was observed.

Chemoselective Hydroboration of Alkyne vs. Alkene. In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Styrene (104 mg, 1.0 mmol), phenylacetylene (102 mg, 1.0 mmol) and pinacolborane (128 mg, 1.0 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS using hexamethylbenzene as an internal standard. The results show 88% conversion of phenylacetylene and >95% recycle of styrene.

Deuterium-Labeling Experiment. In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Phenylacetylene-D1 (103 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol, 1.1 eq.) were then added. The reaction mixture was allowed to stir at room temperature for additional 10 min. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The product was isolated (201 mg, 86%) by column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. The product was characterized by ^1H, ^2H and ^{13}C NMR spectroscopies.



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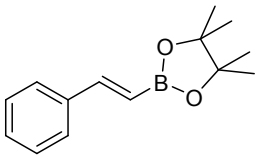
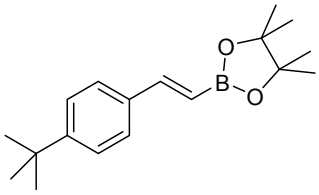
Catalytic reactions and characterization details



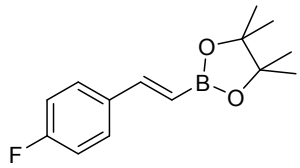
Chemical Formula: $C_{14}H_{19}BO_2$
Molecular Weight: 230.1140

2a[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Phenylacetylene (102 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2a** was isolated. Yield: 189 mg (82%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 18.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 7.3 Hz, 1H), 6.17 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 137. 8, 129.3, 128.9, 127.4, 83.7, 25.2 ppm. GC-MS (m/z): 230 (calc. 230).



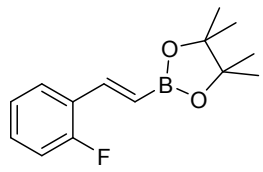
Chemical Formula: $C_{18}H_{27}BO_2$
Molecular Weight: 286.2220

2b[3]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-tert-Butylphenylacetylene (158 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **3c** was isolated. Yield: 172 mg (60%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.44 (s, 1H), 7.40 (d, J = 8.4 Hz, 2H), 6.17 (d, J = 18.4 Hz, 1H), 1.35 (s, 24H, overlapping) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4, 149.7, 135.0, 127.1, 125.8, 83.6, 35.0, 31.6, 25.1 ppm. GC-MS (m/z): 286 (calc. 286).



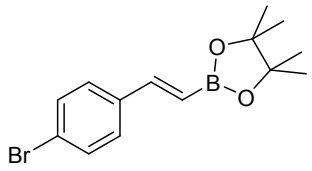
Chemical Formula: $C_{14}H_{18}BFO_2$
Molecular Weight: 248.1044

2c[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Fluorophenylacetylene (120 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Yellowish oil of **2c** was isolated. Yield: 154 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.35 (d, J = 18.5 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.07 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 161.9, 148.2, 128.7 (d, J = 8.2 Hz), 115.6 (d, J = 21.7 Hz), 83.4, 24.8 ppm. GC-MS (m/z): 248 (calc. 248).



Chemical Formula: $C_{14}H_{18}BFO_2$
Molecular Weight: 248.1044

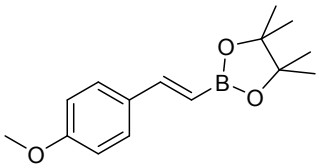
2d[3]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 2-Fluorophenylacetylene (120 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 20 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Yellowish oil of **2d** was isolated. Yield: 184 mg (74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H, overlapping), 7.26 (s, 1H), 7.15 – 7.09 (m, 1H, overlapping), 7.07 – 6.99 (m, 1H), 6.24 (d, J = 18.7 Hz, 1H), 1.31 (s, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 159.8, 141.4 (d, J = 4.0 Hz), 130.3 (d, J = 8.5 Hz), 127.5 (d, J = 3.3 Hz), 125.4 (d, J = 11.6 Hz), 124.2 (d, J = 3.6 Hz), 115.9 (d, J = 22.1 Hz), 83.5, 24.9 ppm. GC-MS (m/z): 248 (calc. 248).



Chemical Formula: $C_{14}H_{18}BBrO_2$
Molecular Weight: 309.0100

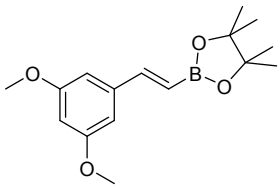
2e[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Bromophenylacetylene (180 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Yellowish oil of **2d** was isolated. Yield: 185 mg (60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 6.6 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 18.5 Hz, 1H), 6.15 (dd, J = 18.4, 2.5 Hz, 1H), 1.31 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.1, 136.4, 133.6, 131.8, 131.7, 128.6, 123.0, 83.6, 24.9 ppm. GC-MS (m/z): 309 (calc. 309).

^{1}H NMR (500 MHz, Chloroform-*d*)



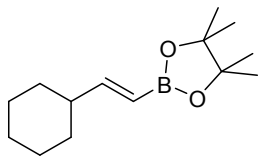
Chemical Formula: $C_{15}H_{21}BO_3$
Molecular Weight: 260.1400

2f[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Methoxyphenylacetylene (132 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 30 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Yellowish oil of **2d** was isolated. Yield: 161 mg (62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 18.5 Hz, 1H), 6.85 (d, J = 8.3 Hz, 2H), 6.02 (d, J = 17.7 Hz, 1H), 3.78 (s, 3H), 1.30 (s, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 149.1, 133.6, 128.5, 114.0, 113.9, 83.2, 55.2, 24.8 ppm. GC-MS (m/z): 260 (calc. 260).



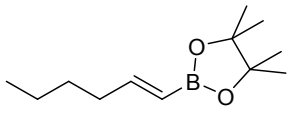
Chemical Formula: $C_{16}H_{23}BO_4$
Molecular Weight: 290.1660

2g[4]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 3,5-Dimethoxyphenylacetylene (162 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Yellowish oil of **2g** was isolated. Yield: 189 mg (65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 18.3 Hz, 1H), 6.65 (s, 2H), 6.41 (s, 1H), 6.13 (d, J = 18.4 Hz, 1H), 3.77 (s, 6H), 1.30 (s, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 149.4, 139.5, 105.0, 101.3, 83.4, 55.3, 24.8 ppm. GC-MS (m/z): 290 (calc. 290).
^{1}H NMR (500 MHz, Chloroform-*d*)



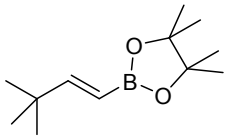
Chemical Formula: $C_{14}H_{25}BO_2$
Molecular Weight: 236.1620

2h[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Ethynylcyclohexane (108 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2h** was isolated. Yield: 213 mg (90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.55 (dd, J = 18.2, 6.1 Hz, 1H), 5.35 (d, J = 18.2 Hz, 1H), 2.08 – 1.91 (m, 1H), 1.74 – 1.66 (m, 4H), 1.64 – 1.59 (m, 1H), 1.24 (d, J = 2.2 Hz, 14H, overlapping), 1.14 – 1.02 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 115.2, 83.0, 43.3, 31.9, 26.2, 26.0, 24.8 ppm. GC-MS (m/z): 236 (calc. 236).



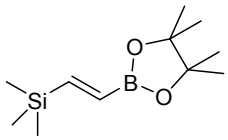
Chemical Formula: $C_{12}H_{23}BO_2$
Molecular Weight: 210.1240

2i[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 1-Hexyne (82 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2i** was isolated. Yield: 172 mg (82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (dt, J = 17.9, 6.4 Hz, 1H), 5.42 (dd, J = 18.0, 1.6 Hz, 1H), 2.18 – 2.11 (m, 2H), 1.39 (q, J = 7.3 Hz, 2H), 1.35 – 1.30 (m, 2H), 1.26 (s, 12H), 0.91 – 0.85 (m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 83.3, 35.9, 30.7, 25.1, 22.6, 14.3 ppm. GC-MS (m/z): 210 (calc. 210).



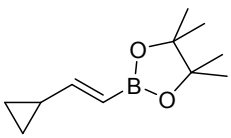
Chemical Formula: $C_{12}H_{23}BO_2$
Molecular Weight: 210.1240

2j[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 3,3-Dimethyl-1-butyne (82 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2j** was isolated. Yield: 168 mg (80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (d, J = 17.6 Hz, 1H), 5.34 (d, J = 18.5 Hz, 1H), 1.26 (s, 12H), 1.01 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 83.1, 35.1, 28.9, 24.9 ppm. GC-MS (m/z): 210 (calc. 210).



Chemical Formula: $C_{11}H_{23}BO_2Si$
Molecular Weight: 226.1980

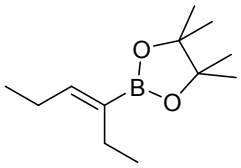
2k[3]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Trimethylsilylacetylene (98 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2k** was isolated. Yield: 192 mg (85%). ^{1}H NMR (5600 MHz, $CDCl_3$) δ 7.12 (d, J = 21.8 Hz, 1H), 6.24 (d, J = 21.8 Hz, 1H), 1.28 (s, 12H), 0.07 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 83.5, 24.9, -1.71 ppm. GC-MS (m/z): 226 (calc. 226).



Chemical Formula: $C_{11}H_{19}BO_2$
Molecular Weight: 194.0810

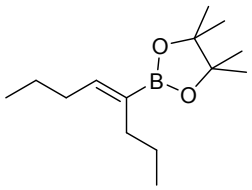
2l[3]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Ethynylcyclopropane (132 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The

reaction mixture was allowed to stir at room temperature for 5 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2l** was isolated. Yield: 167 mg (86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.06 (dd, J = 17.8, 9.3 Hz, 1H), 5.49 (d, J = 17.8 Hz, 1H), 1.51 (dt, J = 8.8, 4.5 Hz, 1H), 0.86 – 0.73 (m, 2H), 1.25 (s, 12H), 0.53 (dd, J = 4.6, 2.1 Hz, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 82.9, 24.8, 17.1, 7.9 ppm. GC-MS (m/z): 194 (calc. 194).



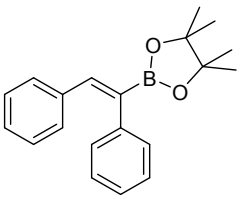
Chemical Formula: $C_{12}H_{23}BO_2$
Molecular Weight: 210.1240

2m[3]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 3-Hexyne (82 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2m** was isolated. Yield: 185 mg (88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (t, J = 7.1 Hz, 1H), 2.12 (m, 4H, overlapping), 1.25 (s, 12H), 0.99 (t, J = 7.6 Hz, 3H), 0.93 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 83.0, 24.8, 21.7, 21.6, 15.0, 13.9 ppm. GC-MS (m/z): 210 (calc. 210).



Chemical Formula: $C_{14}H_{27}BO_2$
Molecular Weight: 238.1780

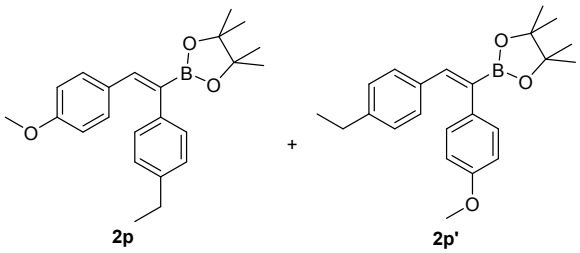
2n[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Octyne (110 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2n** was isolated. Yield: 155 mg (65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.28 (t, J = 7.1 Hz, 1H), 2.11 – 2.06 (m, 4H), 1.43 – 1.37 (m, 2H), 1.37 – 1.31 (m, 2H), 1.23 (s, 12H), 0.90 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.3, 83.2, 30.96, 30.89, 25.0, 23.6, 22.7, 14.41, 14.37 ppm. GC-MS (m/z): 238 (calc. 238).



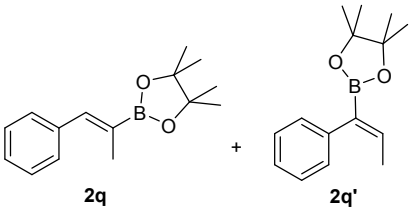
Chemical Formula: $C_{20}H_{23}BO_2$
Molecular Weight: 306.2120

2o[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Diphenylacetylene (178 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 30 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was

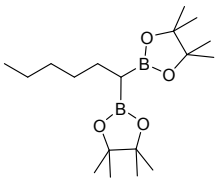
analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. White solid of **2o** was isolated. Yield: 168 mg (55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.29 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.0 Hz, 1H), 7.20 (d, J = 8.1 Hz, 2H), 7.17 – 7.12 (m, 3H), 7.11 – 7.06 (m, 2H), 1.34 (s, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 130.3, 129.2, 128.6, 128.2, 127.9, 126.6, 84.1, 25.1 ppm. GC-MS (m/z): 306 (calc. 306).



2p + 2p'(1:1): In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Ethylphenyl-4-methoxyphenylacetylene (238 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 30 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. A mixture of **2p + 2p'** as white solid was isolated. Yield: 306 mg (84%). ^{1}H NMR (**2p** or **2p'**, 600 MHz, $CDCl_3$) δ 7.28 (s, 2H), 7.12-7.08 (m, 2H, overlapping), 7.03-7.00 (m, 2H, overlapping), 6.96 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.74 (s, 3H), 2.65 (q, J = 7.6 Hz, 2H), 1.30 (s, 12H), 1.25 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 130.3, 129.2, 128.6, 128.2, 127.9, 126.6, 84.1, 25.1 ppm. GC-MS (m/z): 364 (calc. 364). ^{1}H NMR (**2p'**, 600 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.12-7.08 (m, 4H, overlapping), 7.03-7.00 (m, 2H, overlapping), 6.82 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 2.56 (q, J = 7.6 Hz, 2H), 1.30 (s, 12H), 1.18 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (**2p** + **2p',** 151 MHz, $CDCl_3$) δ 158.9, 158.0, 143.7, 142.8, 142.5, 141.9, 137.8, 134.5, 132.9, 131.5, 130.00, 129.96, 129.8, 128.7, 127.8, 127.4, 113.7, 113.2, 83.66, 83.61, 55.1, 28.6, 24.8, 15.4, 15.2 ppm. GC-MS (m/z): 364 (calc. 364).



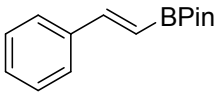
2q + 2q' (2.5:1)[2]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 1-Phenylpropyne (116 mg, 1.0 mmol) and pinacolborane (141 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 30 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. A mixture of **2q + 2q'** as white solid was isolated. Yield: 127 mg (52%). ^{1}H NMR (**2q** + **2q'**, 500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 4H), 7.30 – 7.21 (m, 2H), 7.21 – 7.17 (m, 2H), 6.79 – 6.73 (m, 1H), 2.03 (s, 1H, $H^{C=CH}$-**2q'**), 1.80 (d, J = 7.0 Hz, 3H, $H^{C=CH}$-**2q**), 1.35 (s, 5H, H^{Bpin}-**2q'**), 1.30 (s, 12H, H^{Bpin}-**2q**). ^{13}C NMR (**2q** + **2q',** 126 MHz, $CDCl_3$) δ 143.1, 142.7, 140.1, 138.2, 129.7, 129.4, 128.4, 128.1, 127.4, 126.2, 83.84, 83.76, 25.18, 25.08, 16.34, 16.26 ppm. GC-MS (m/z): 244 (calc. 244).



Chemical Formula: $C_{18}H_{36}B_2O_4$
Molecular Weight: 338.1020

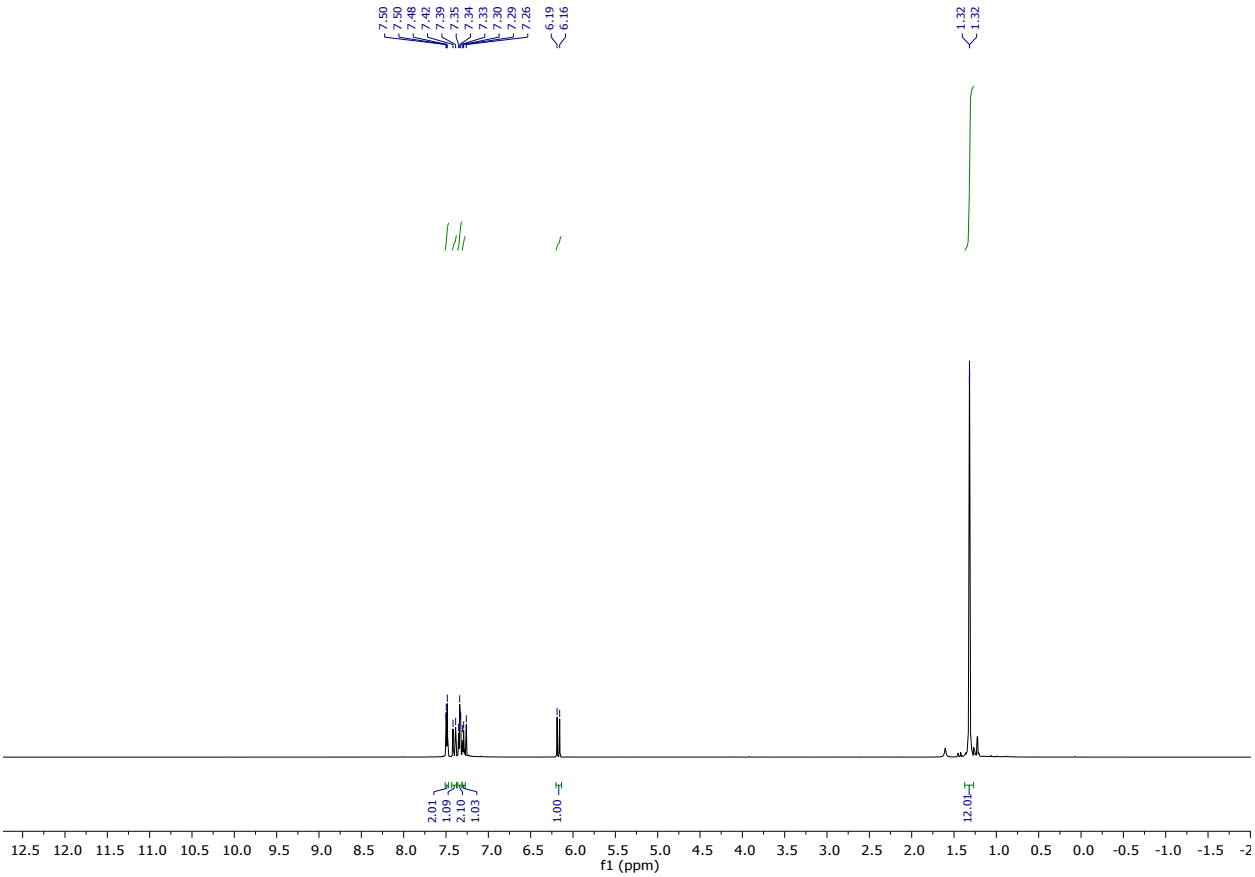
3[5]: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.25 μmol, 0.025 mol%) and KO^{t}Bu (0.56 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 3.8 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 1-Hexyne (82 mg, 1.0 mmol) and pinacolborane (256 mg, 2.0 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 10 min. The reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (2 mL) to the solution. The crude reaction mixture was analyzed by GC-MS and then purified through a column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **3** was isolated. Yield: 196 mg (58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (q, J = 7.7 Hz, 2H), 1.28-1.21 (m, 6H), 1.20 (s, 12H), 1.19 (s, 12H), 0.82 (t, J = 6.9 Hz, 3H, H^{CH3}), 0.68 (t, J = 7.9 Hz, 1H, H^{CH}) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.1, 32.5, 32.1, 25.9, 25.1, 24.8, 22.8, 14.3 ppm. GC-MS (m/z): 338 (calc. 338).

Copies of NMR spectra for isolated products.

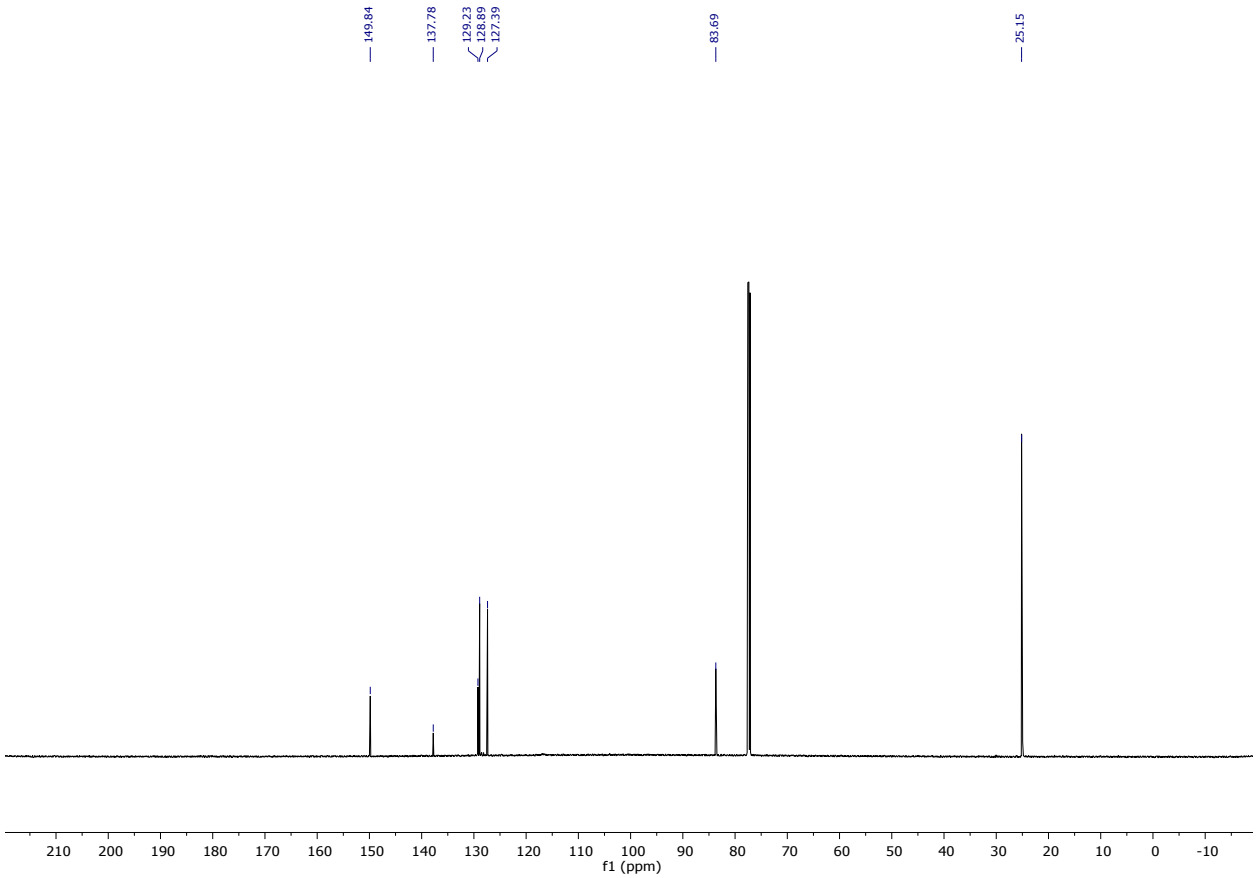


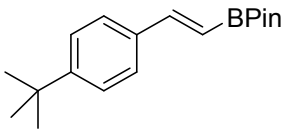
2a

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



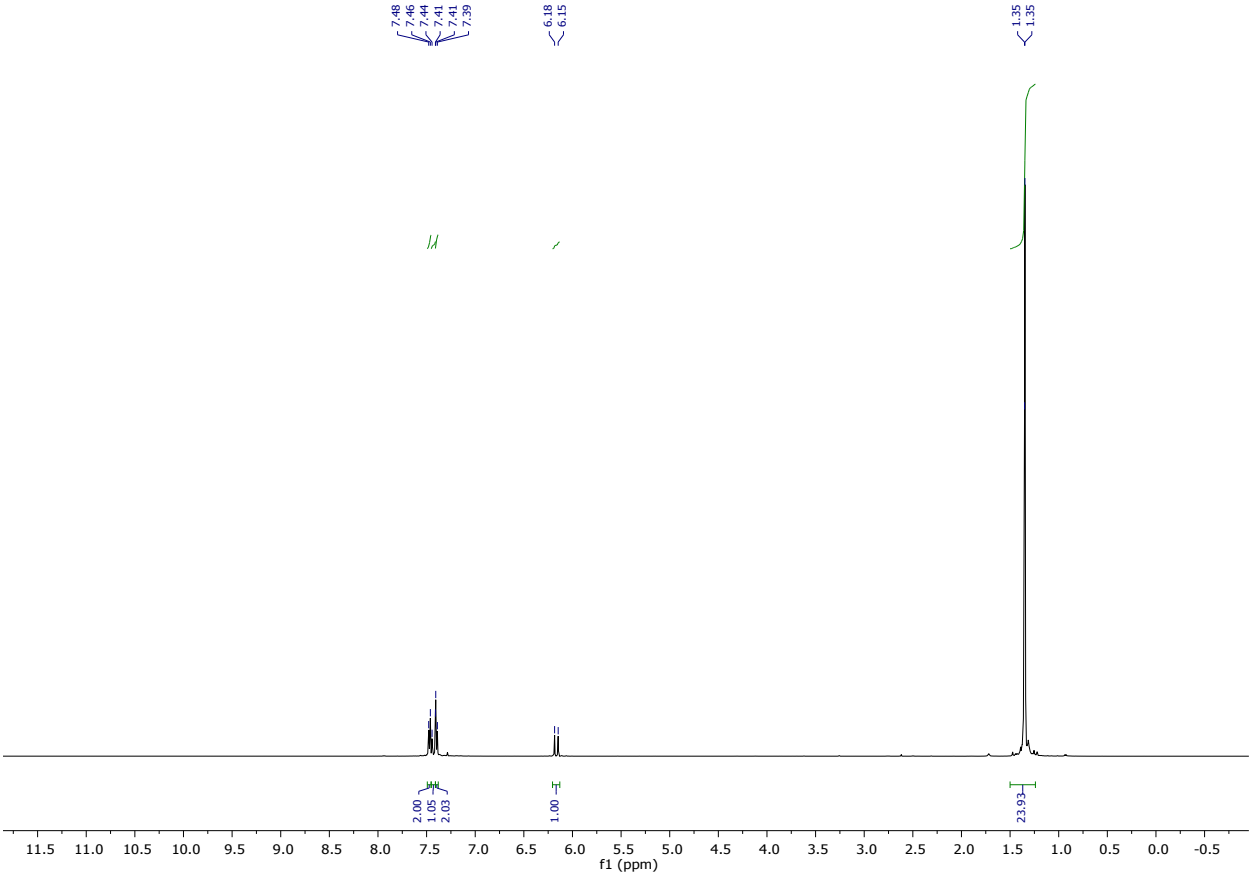
^{13}C NMR (151 MHz, $CDCl_3$):


149.84
137.78
129.23
128.89
127.39
83.69
25.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

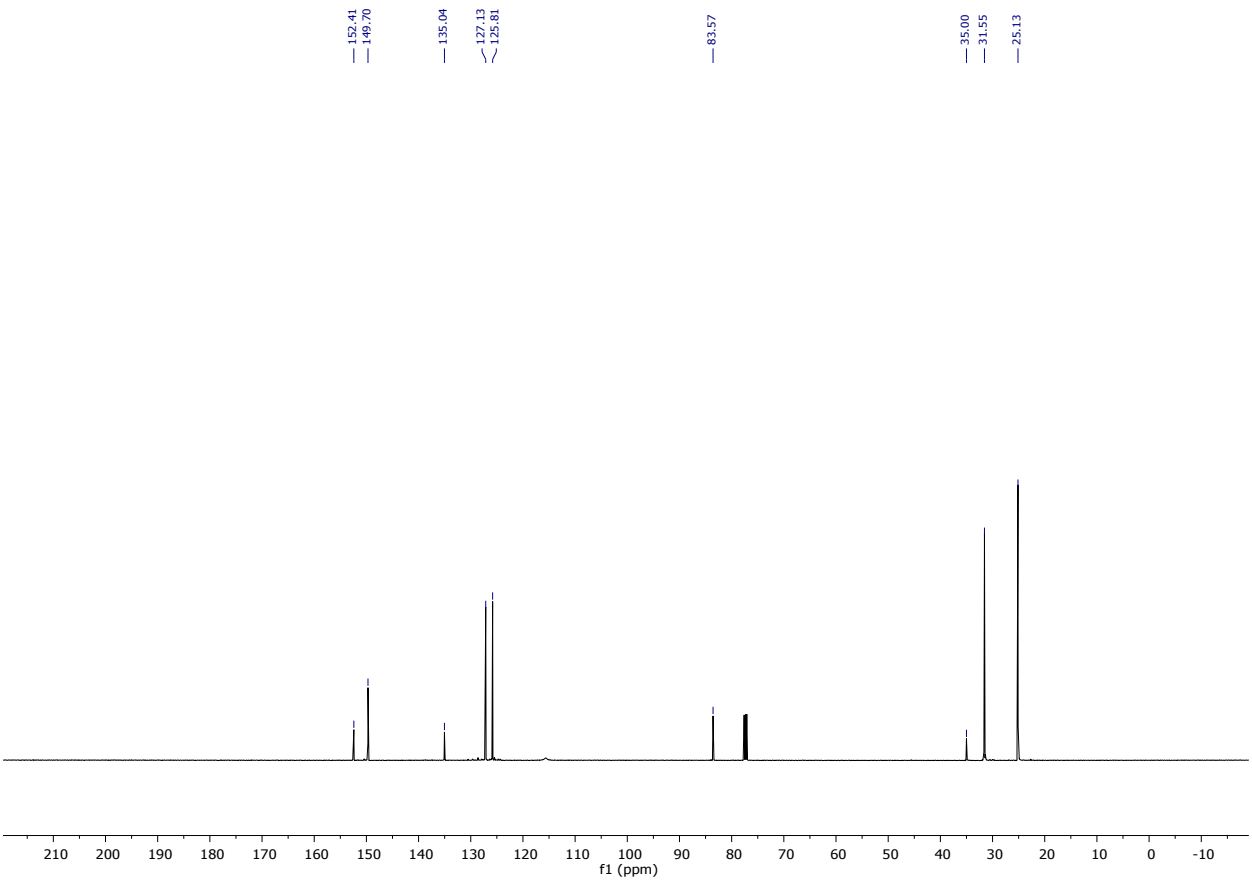


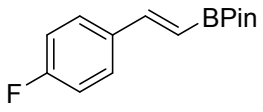
2b

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



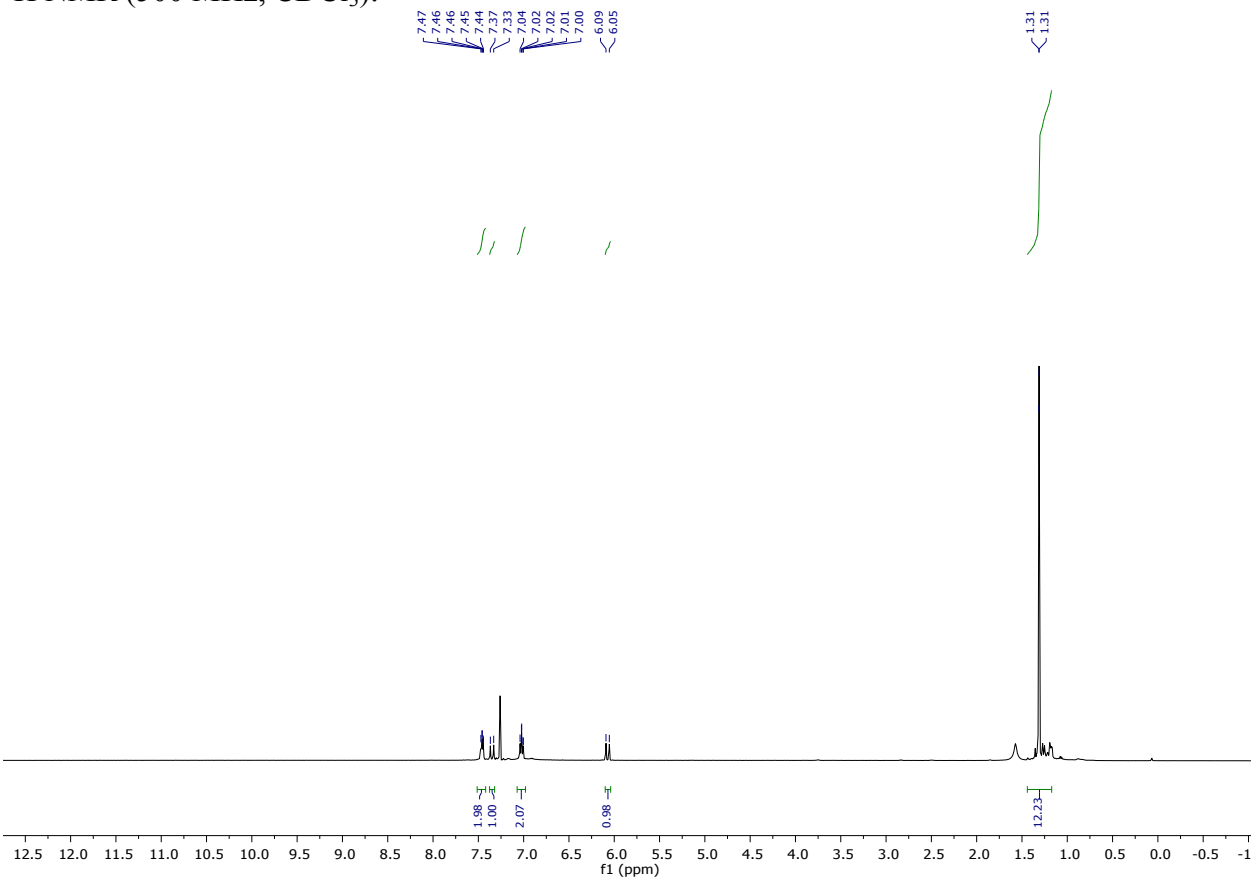
^{13}C NMR (126 MHz, $CDCl_3$):



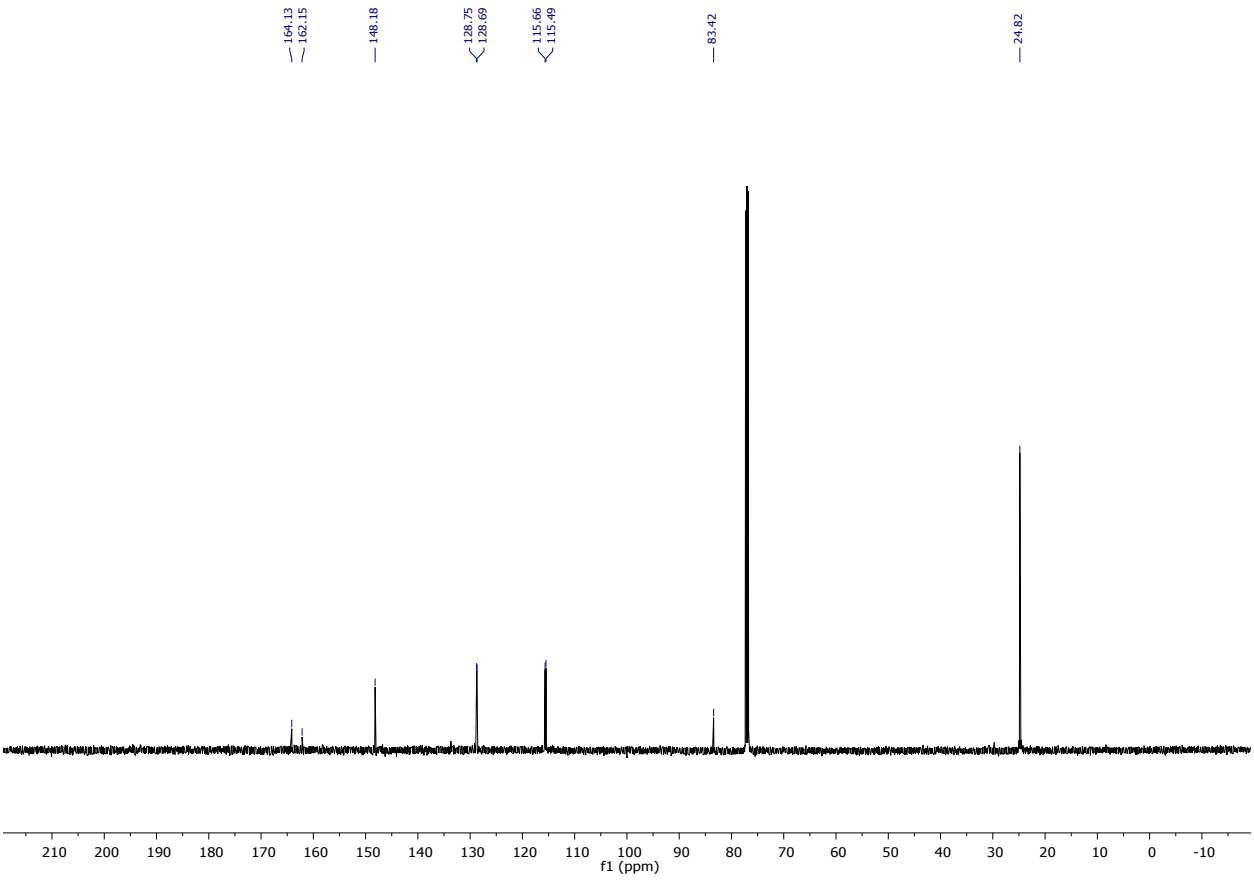


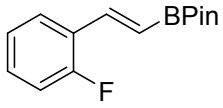
2c

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



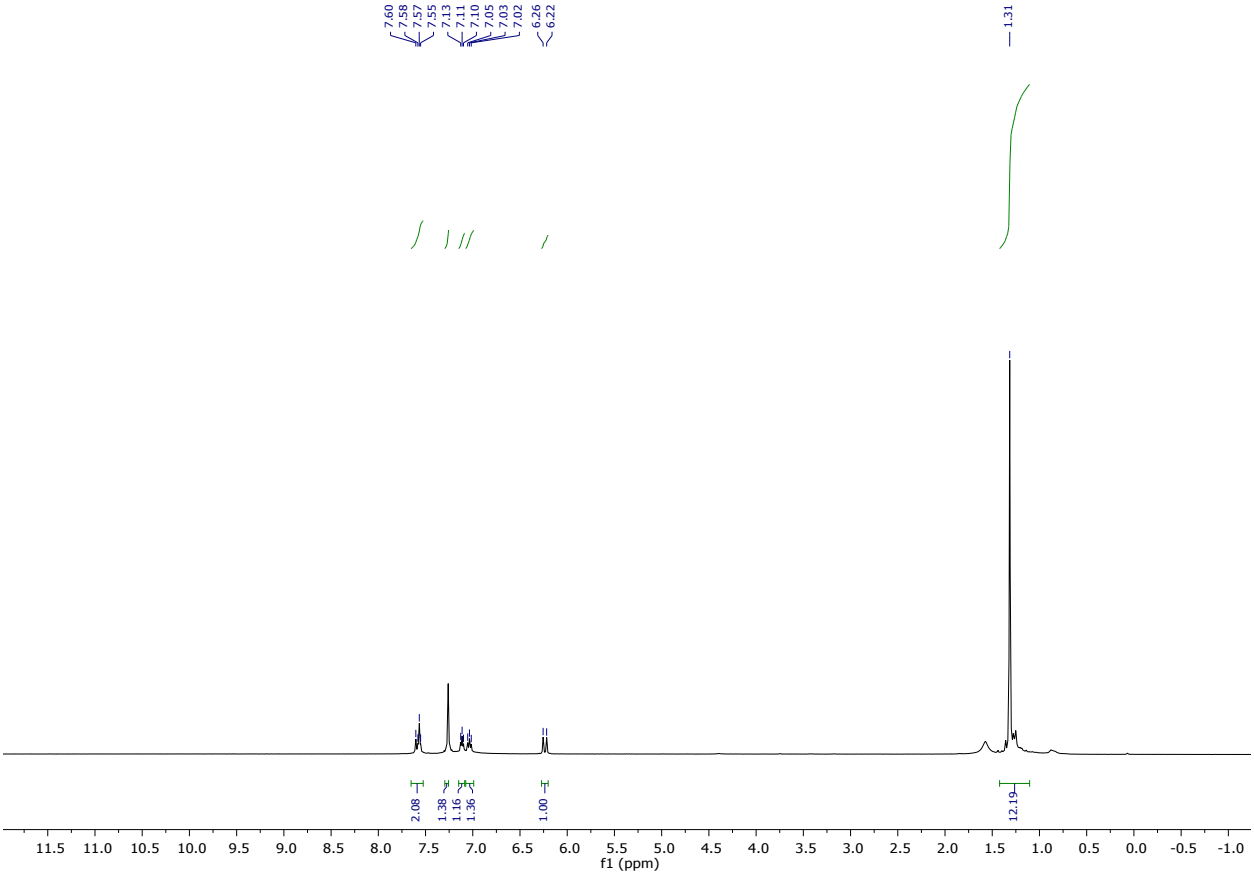
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



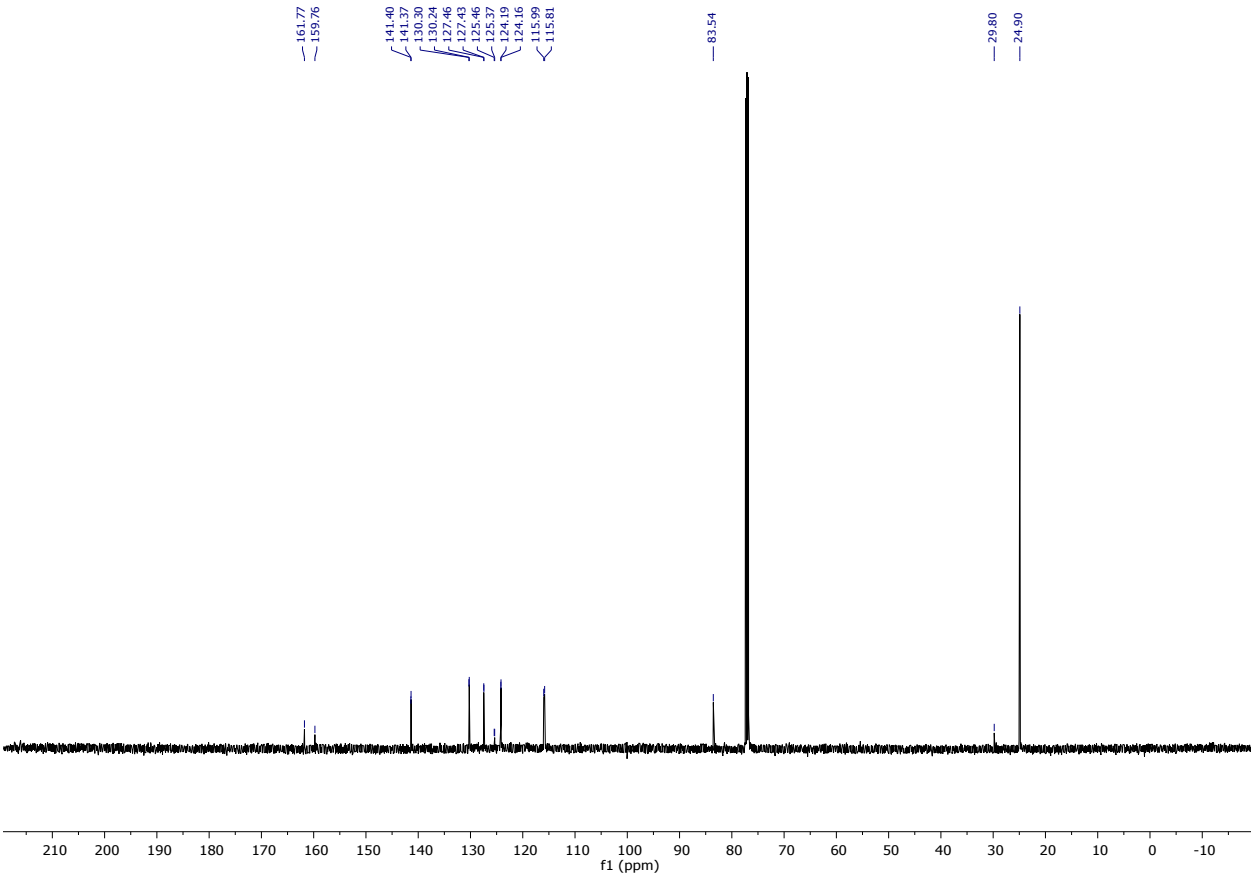


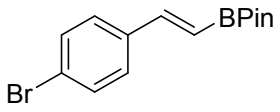
2d

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



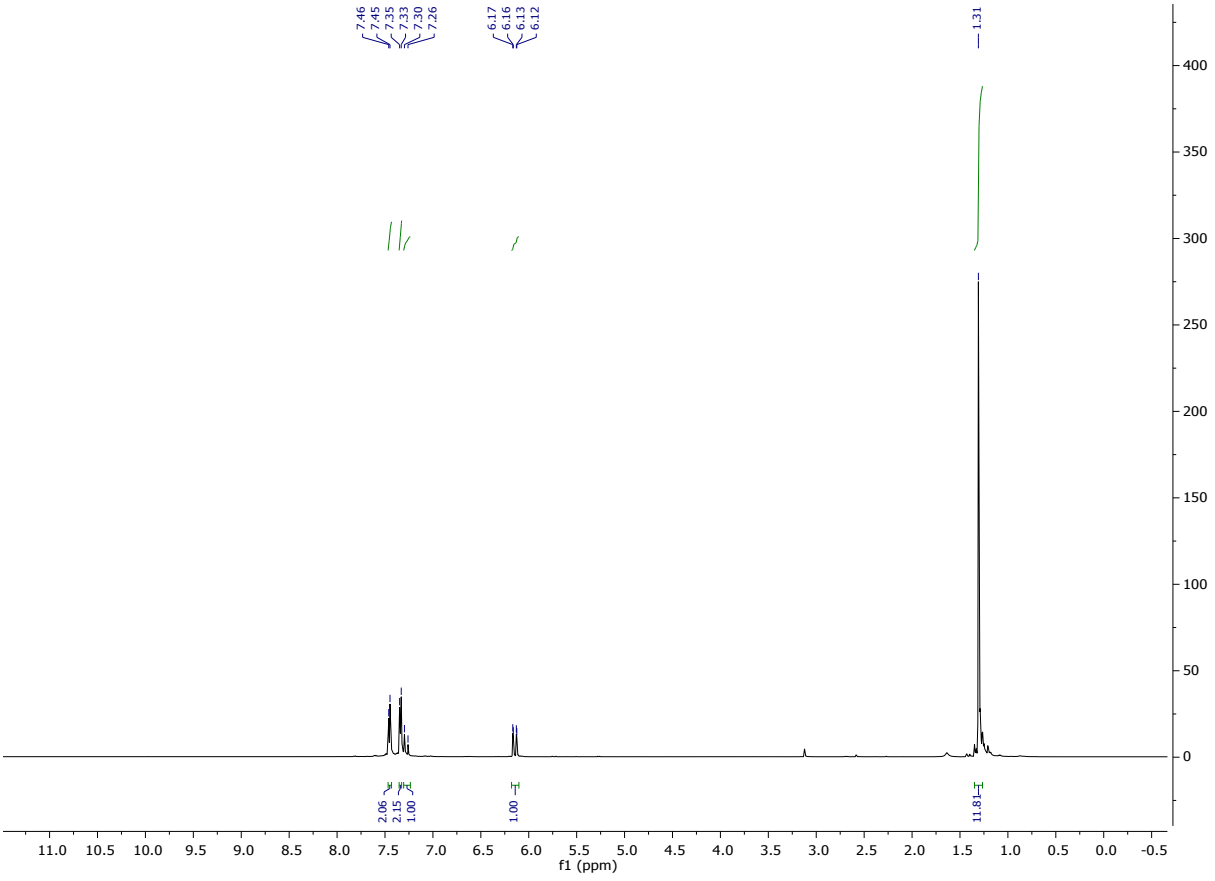
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



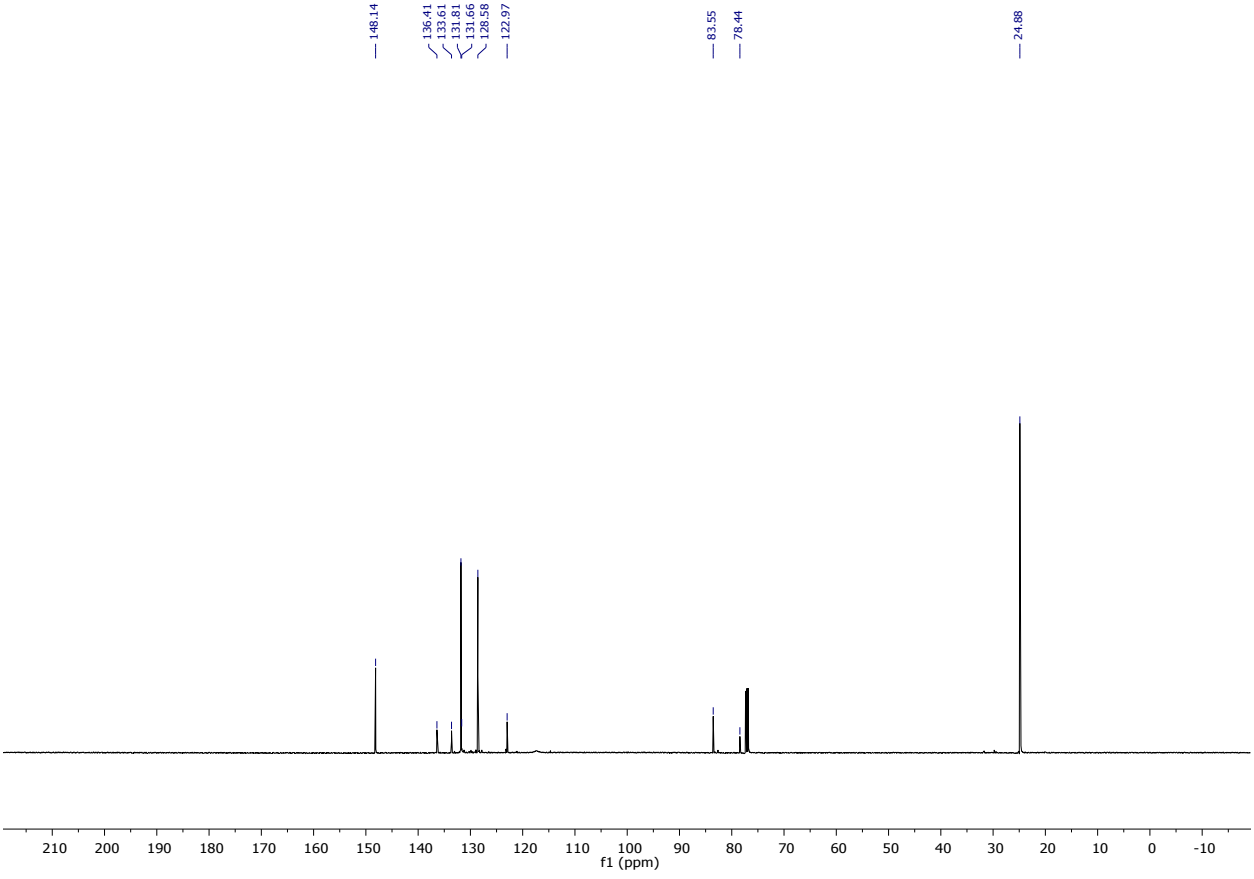


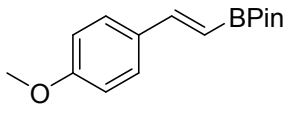
2e

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



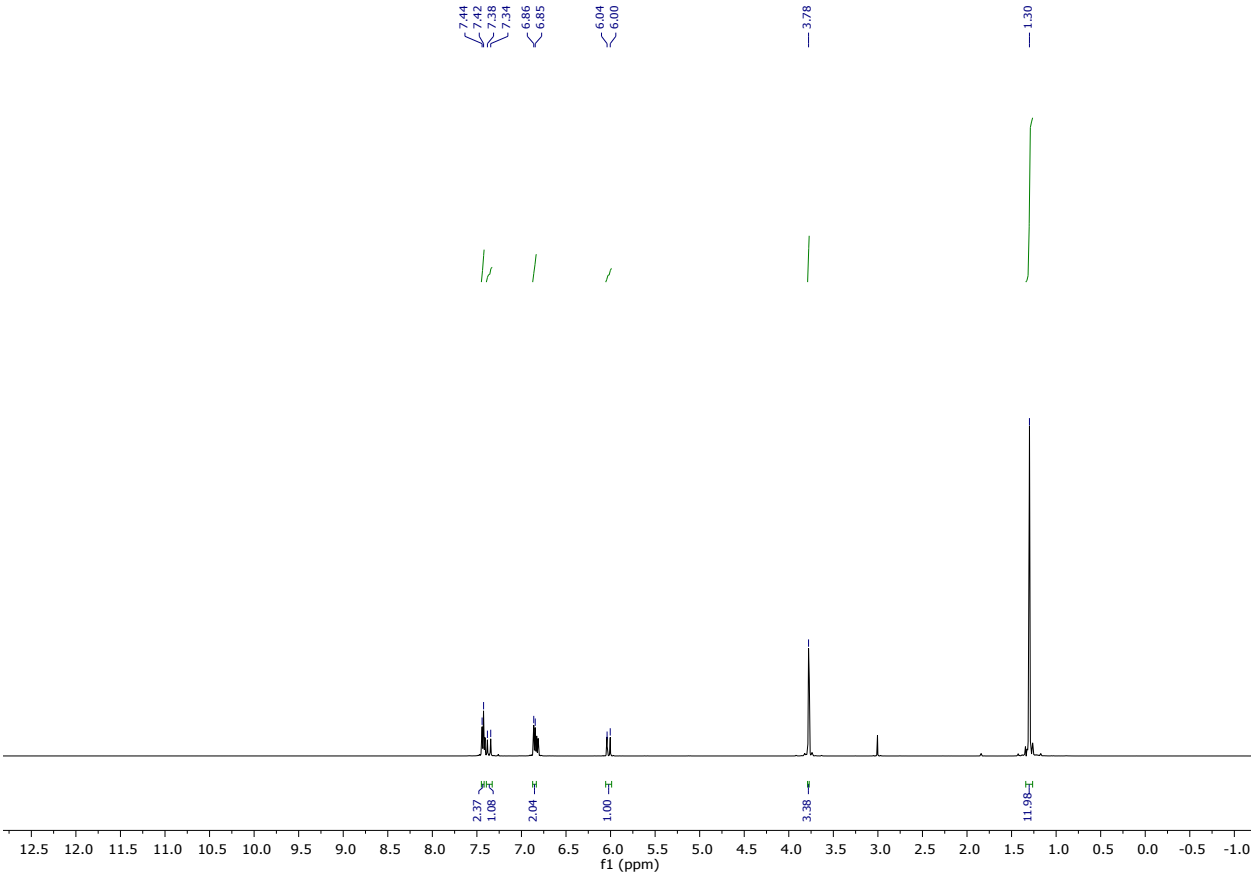
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



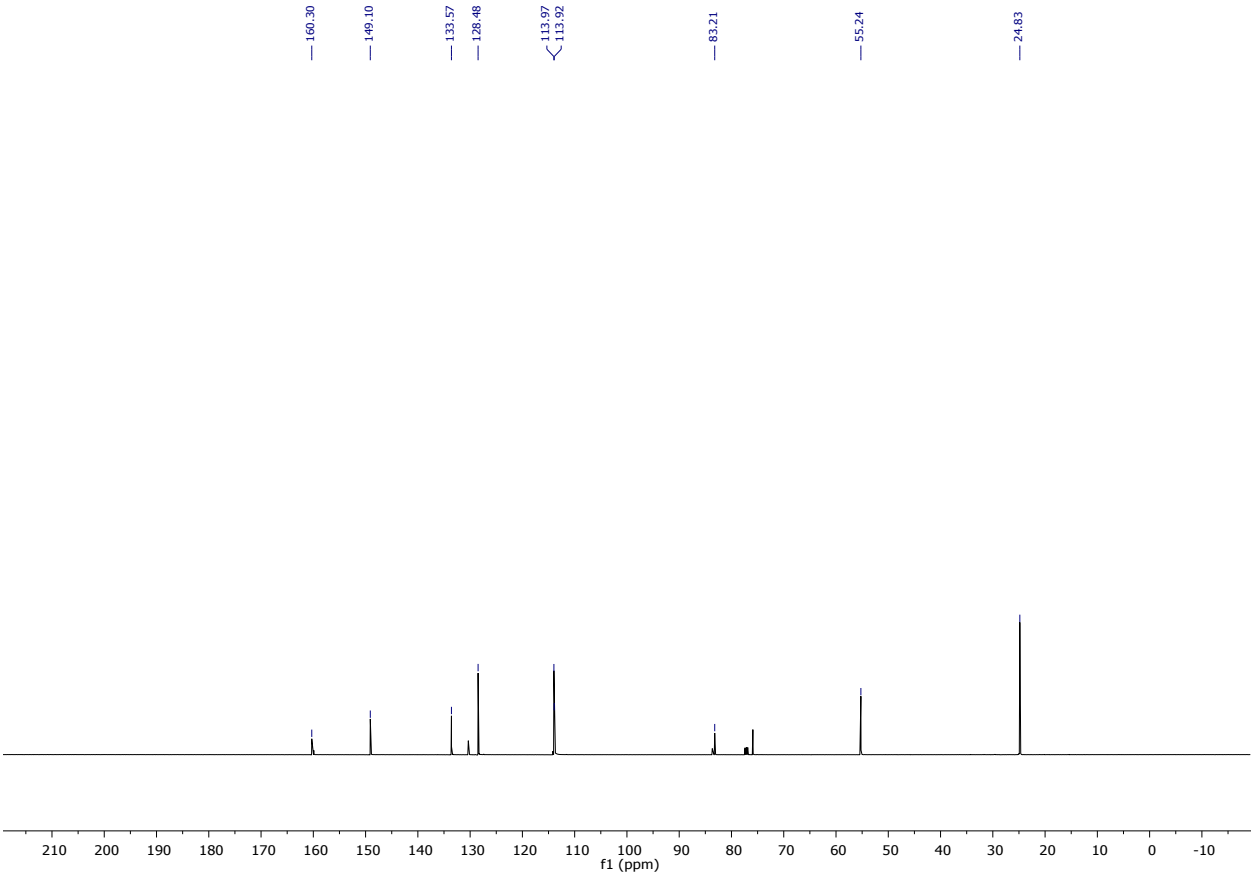


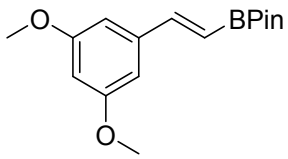
2f

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



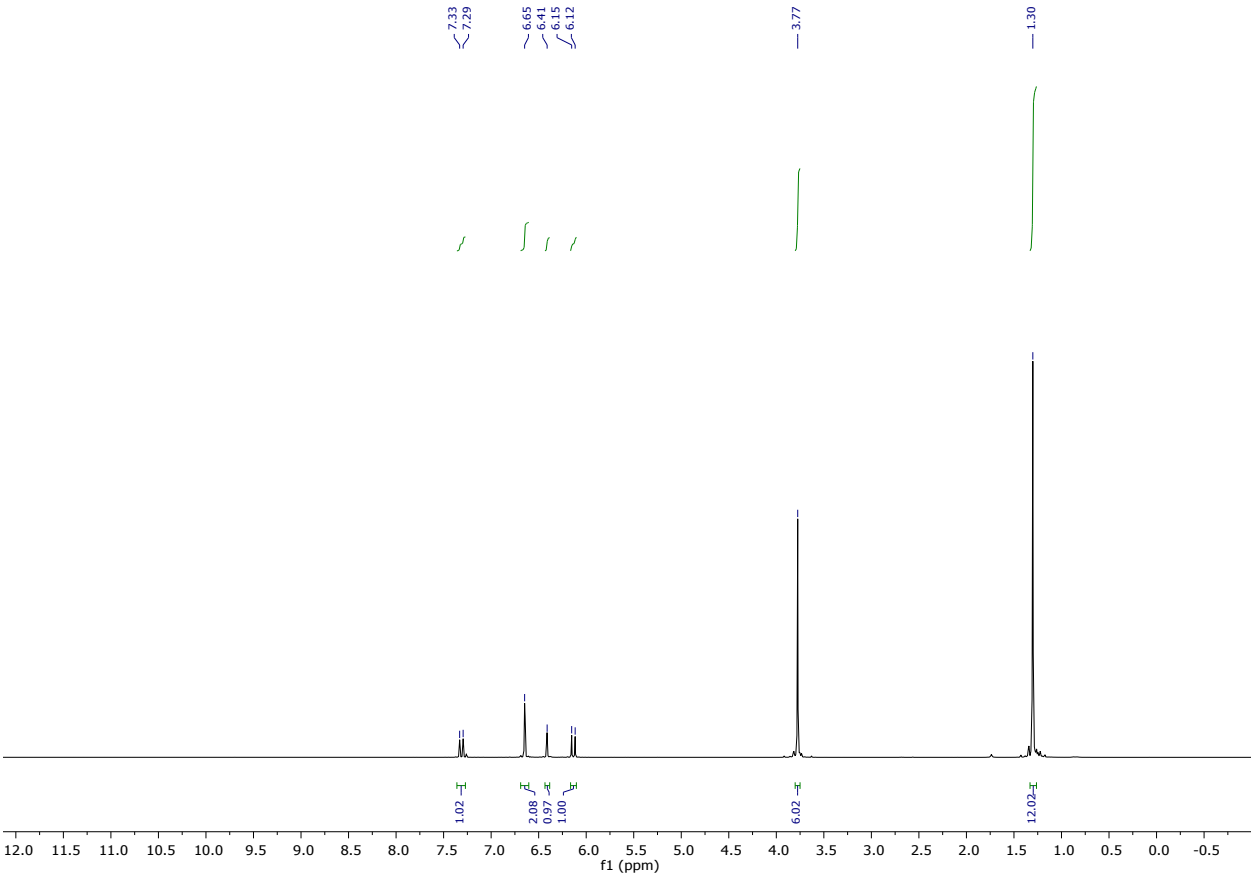
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



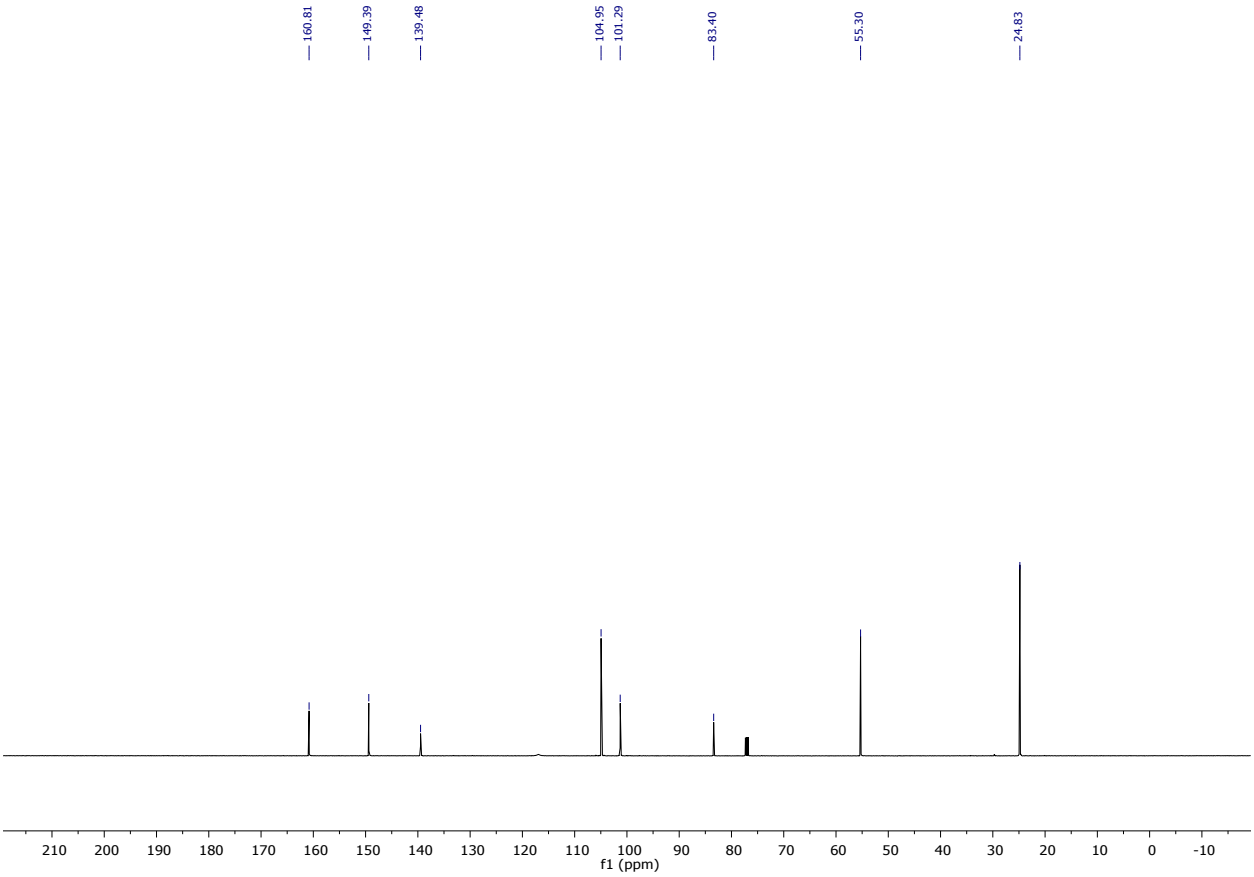


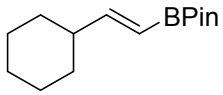
2g

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



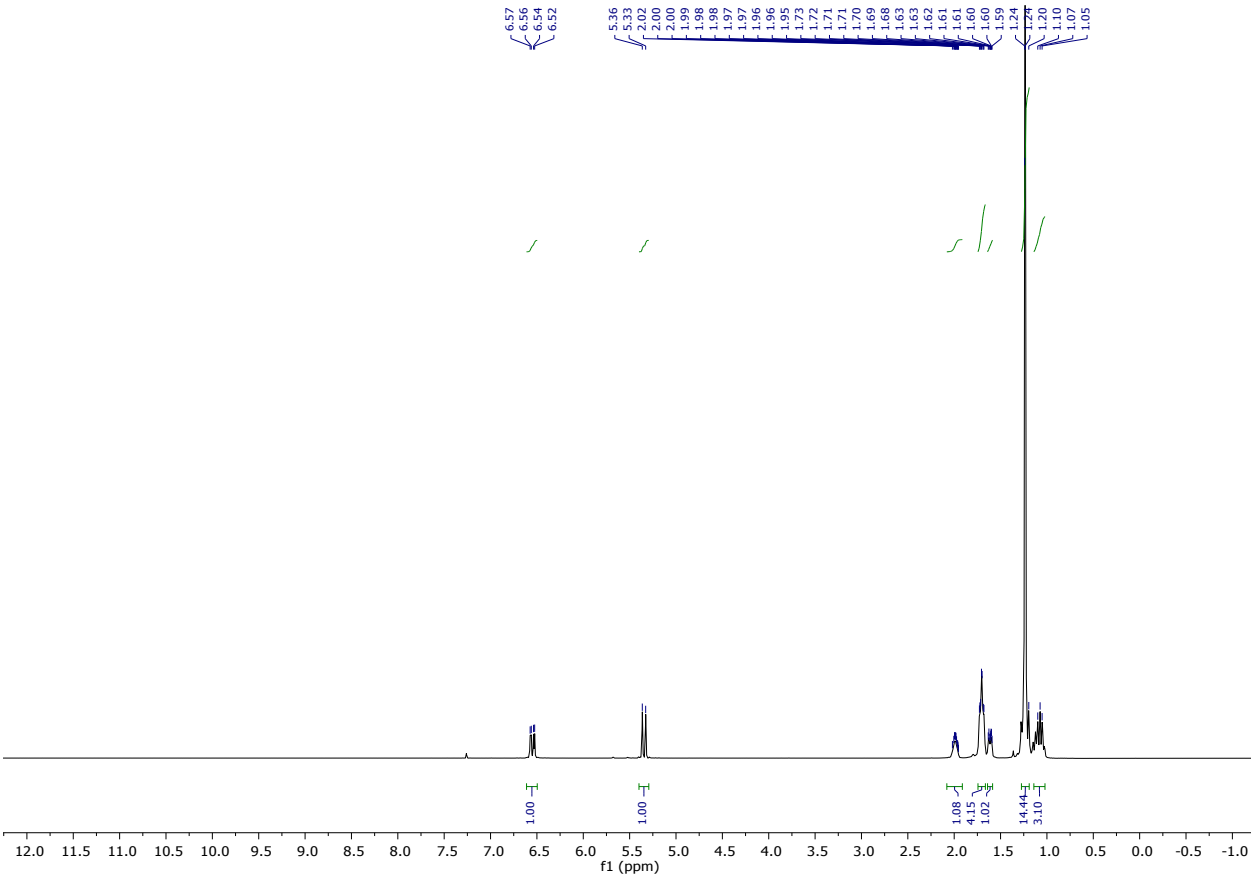
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



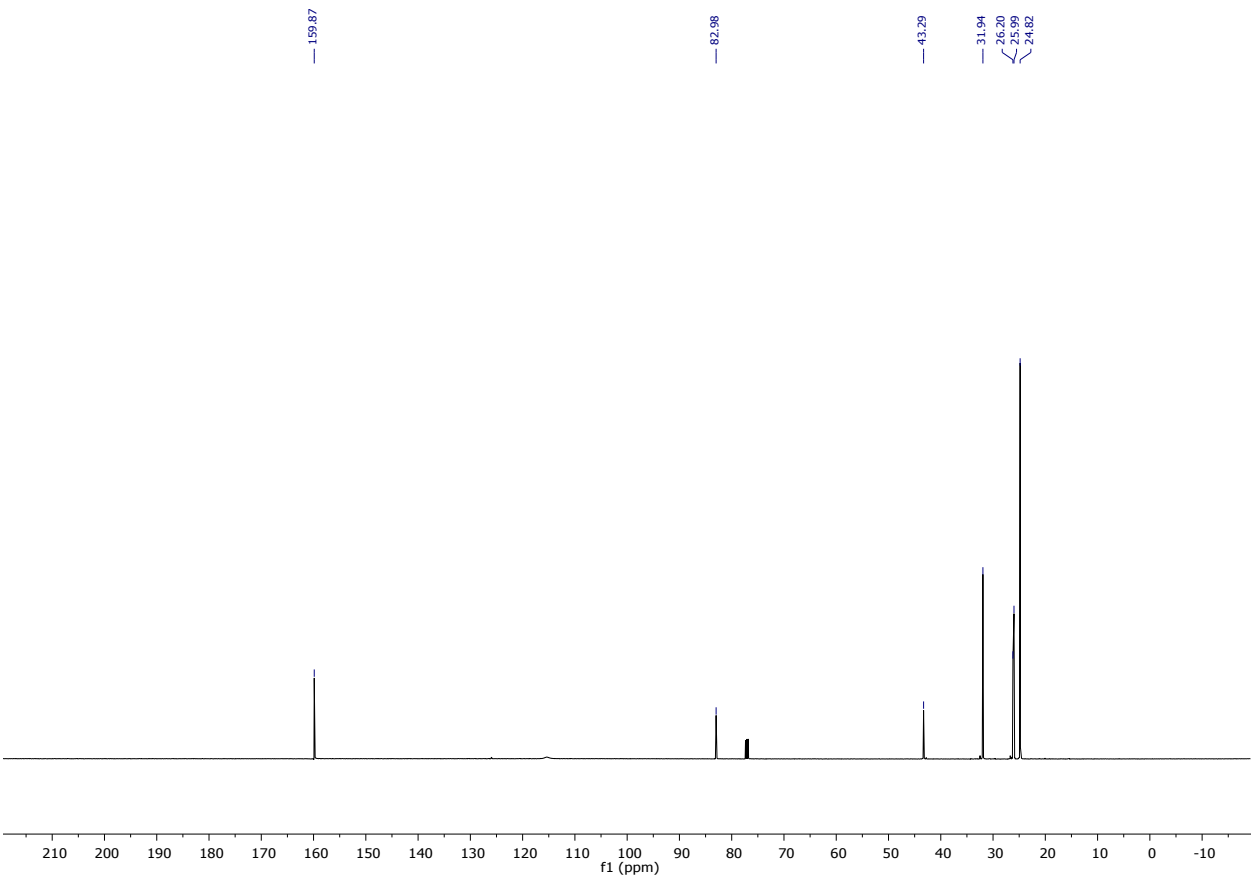


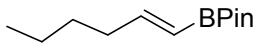
2h

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



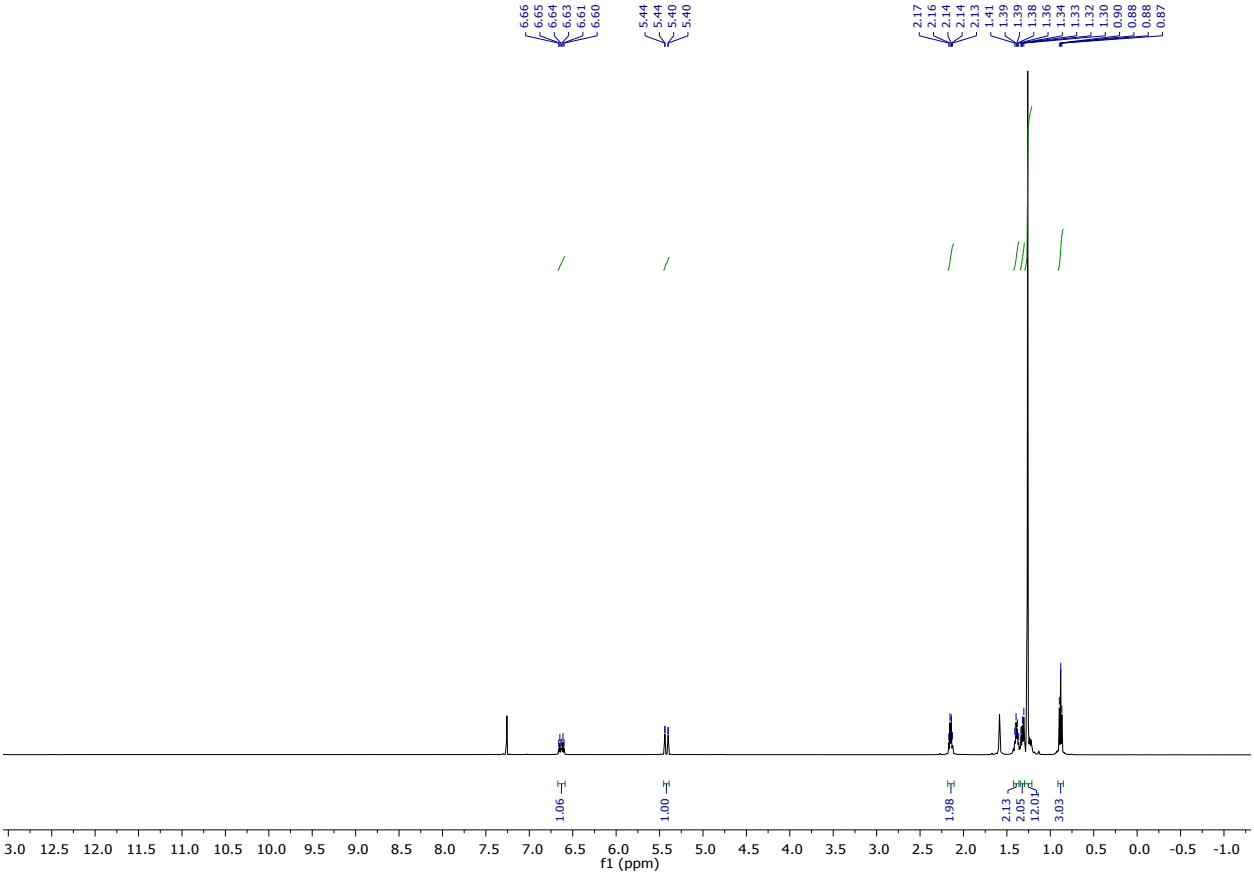
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



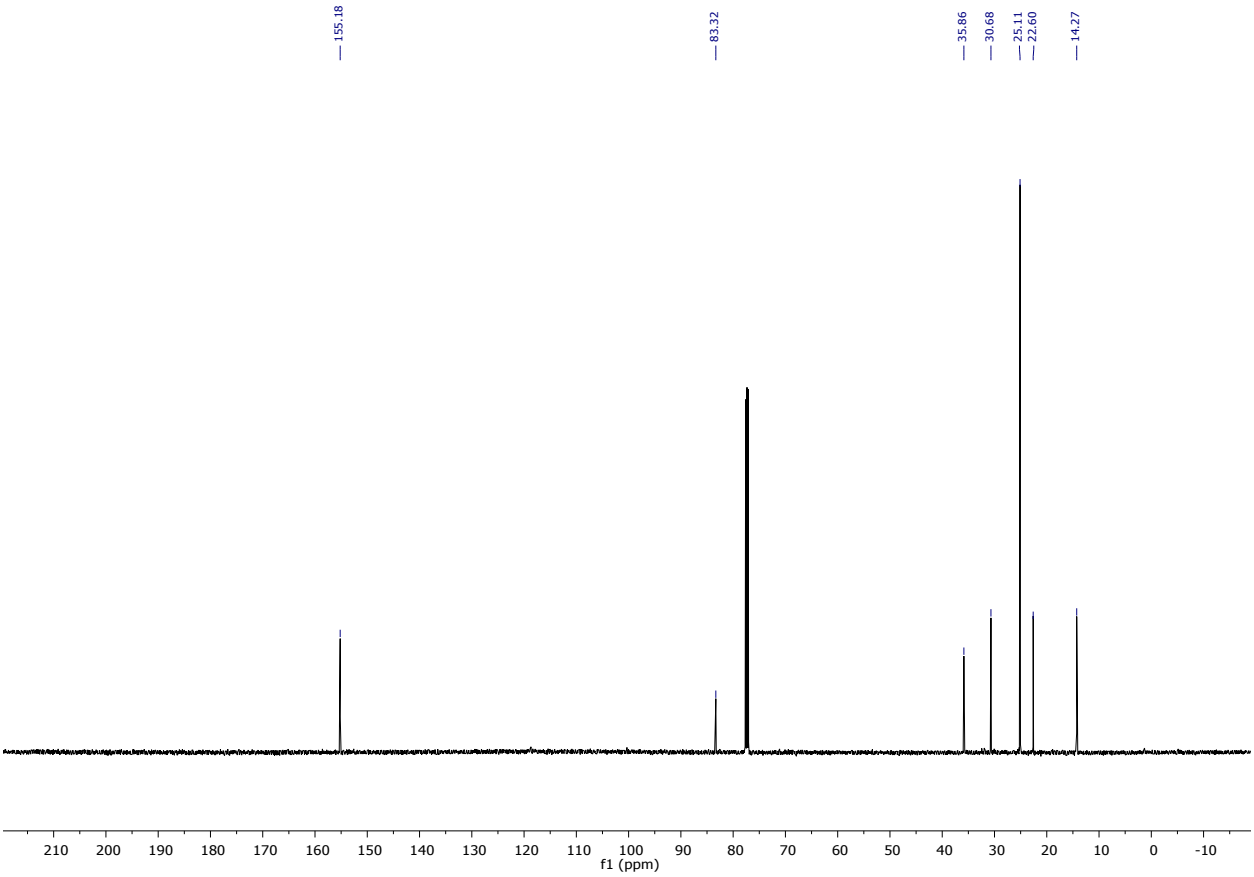


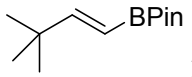
2i

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



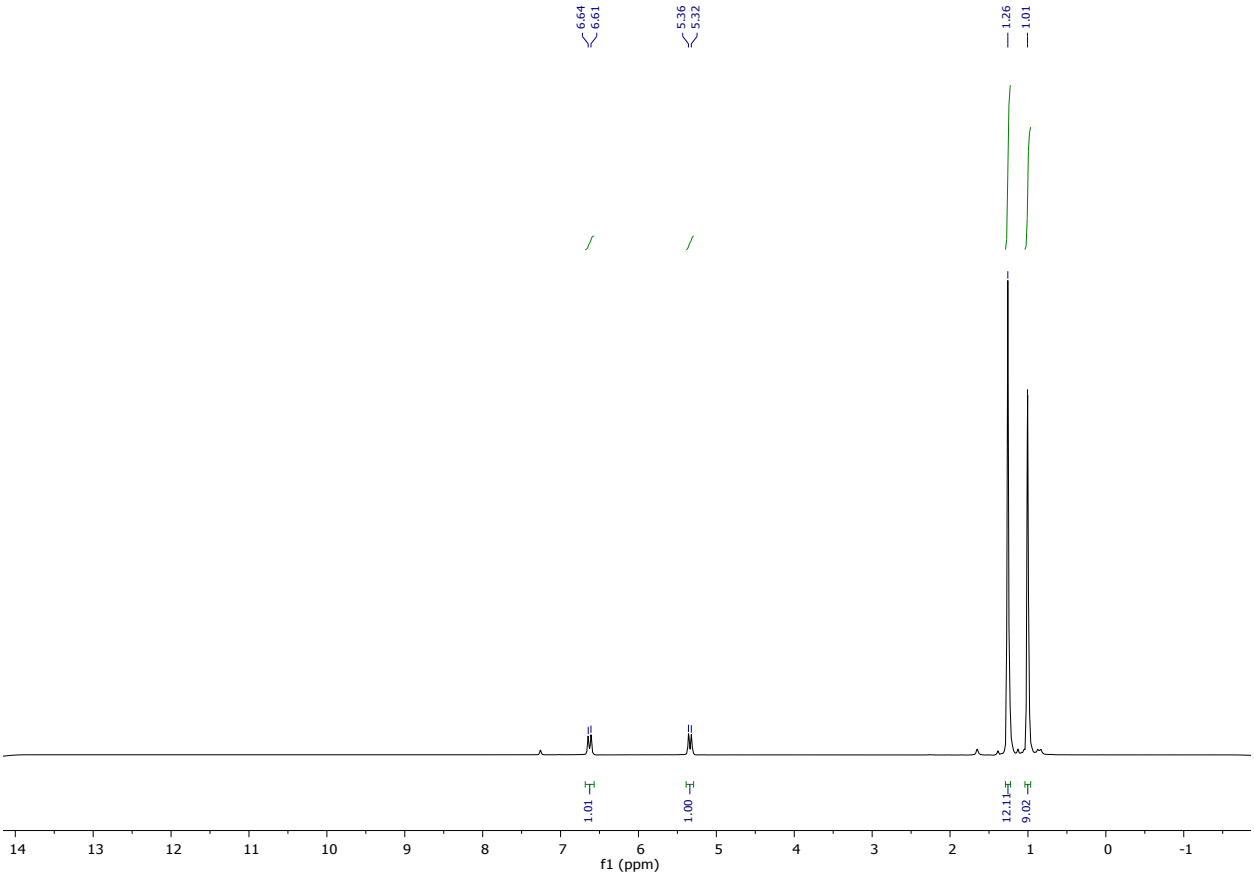
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



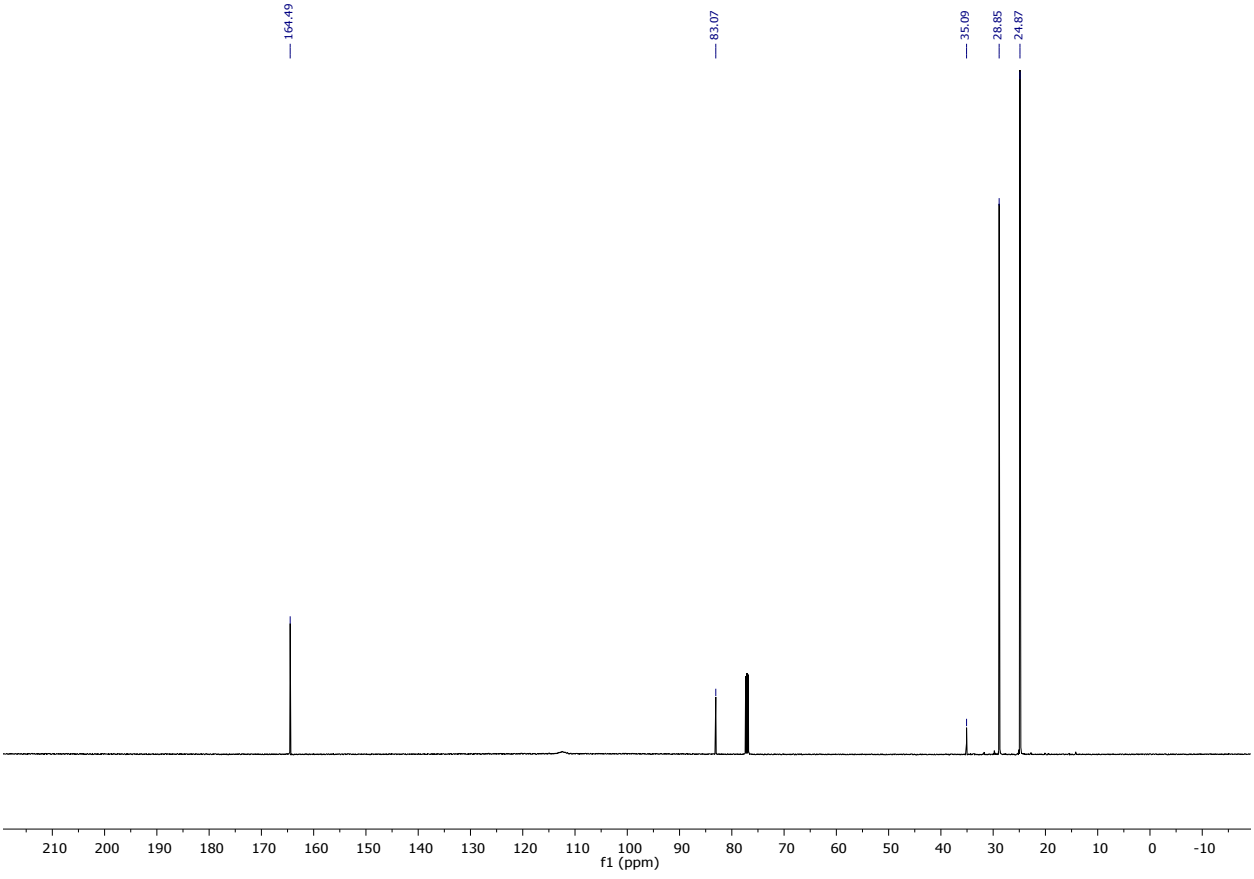


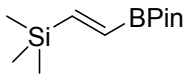
2j

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



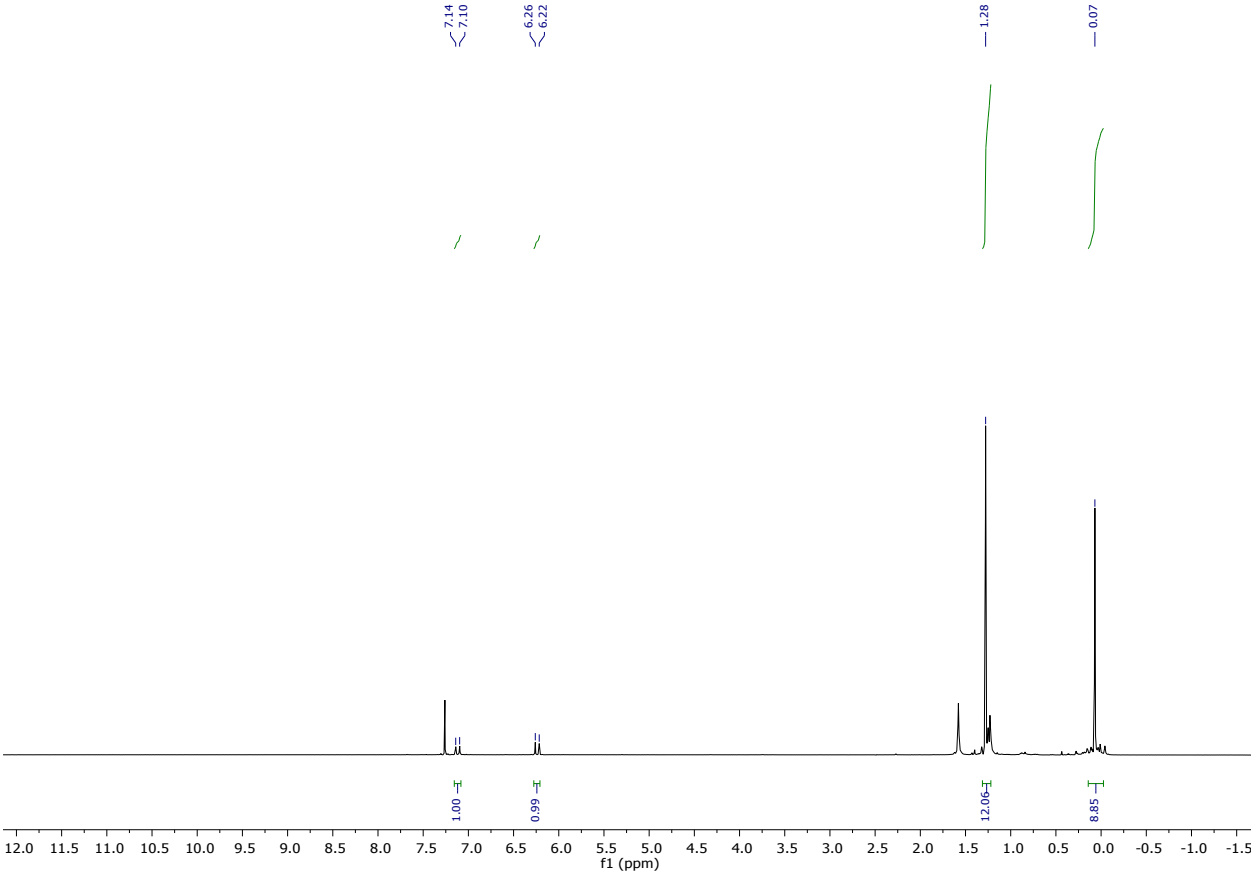
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



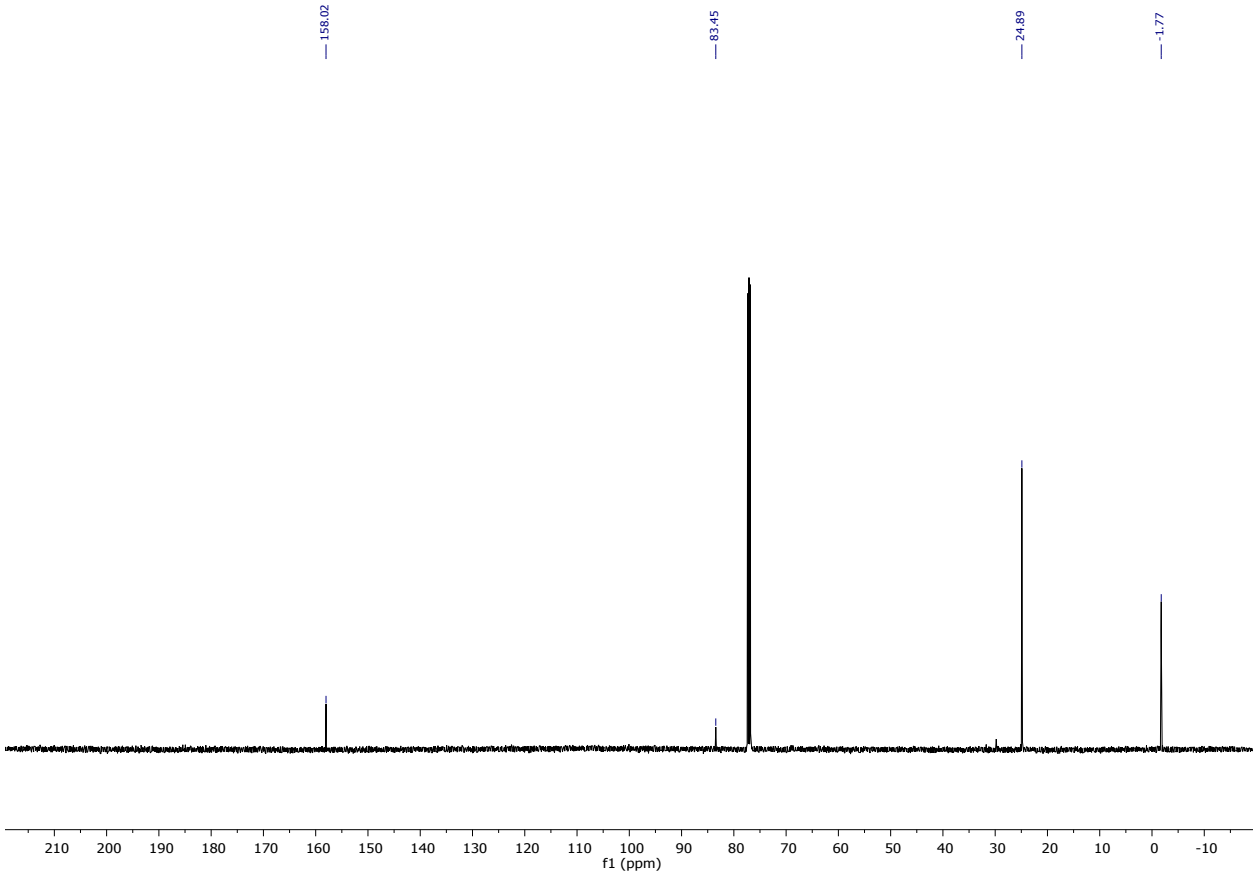


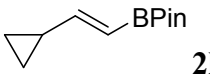
2k

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



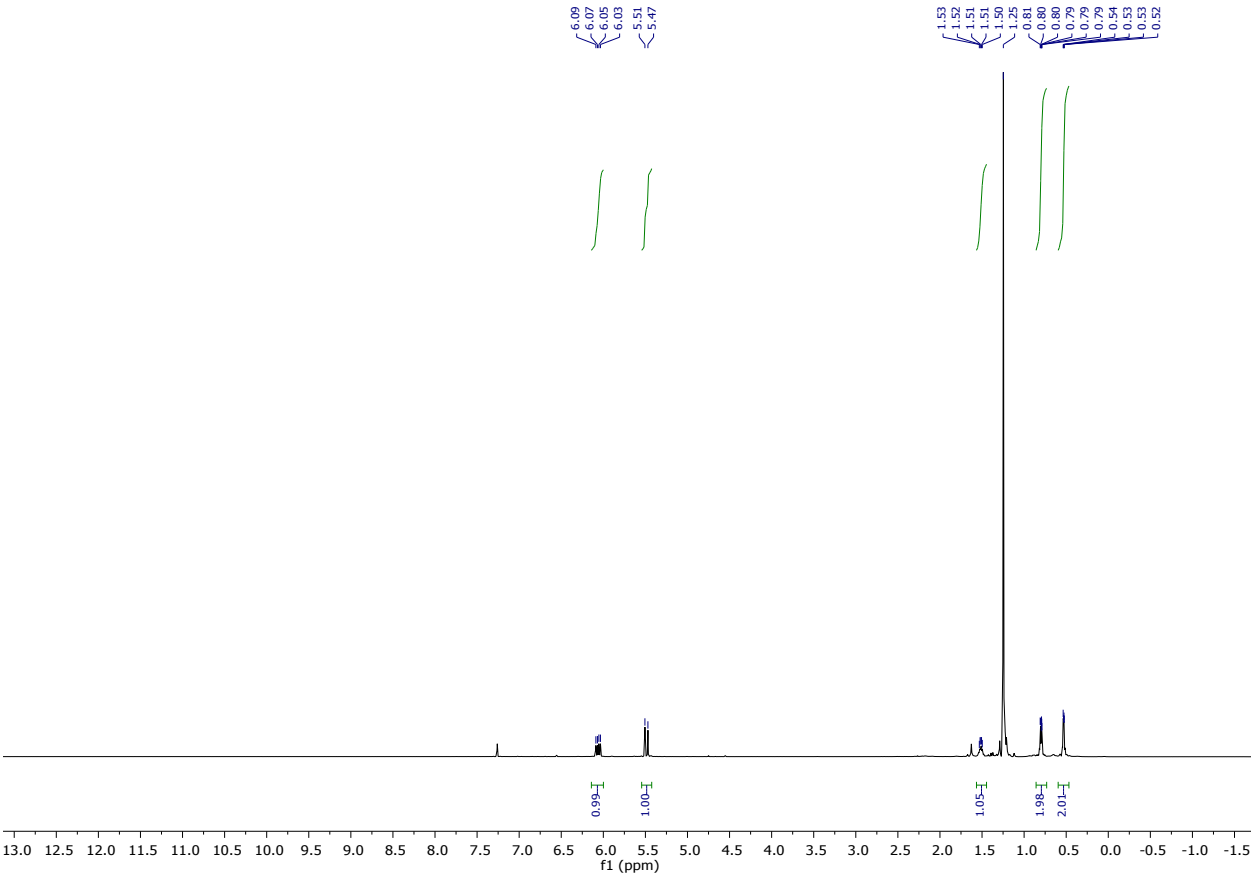
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



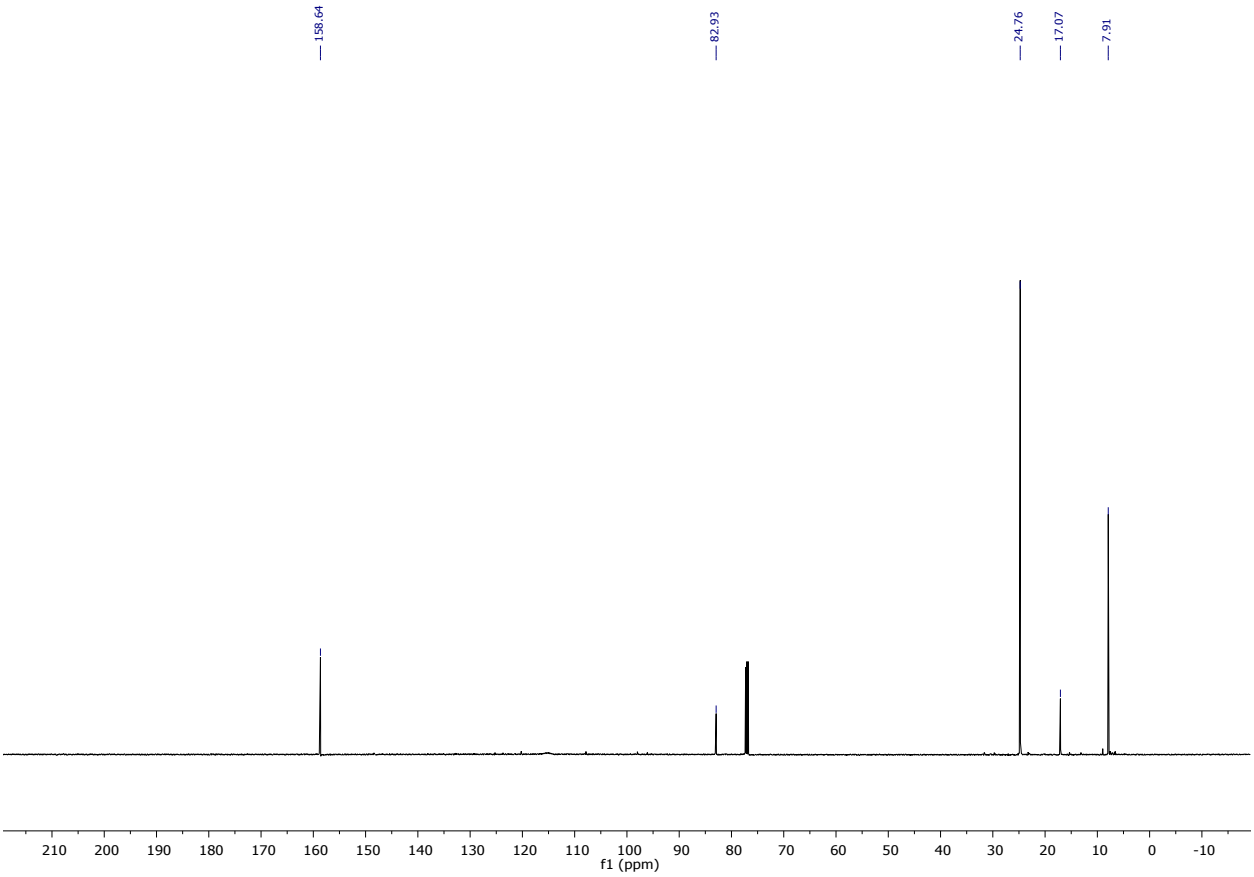


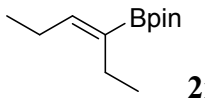
2l

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



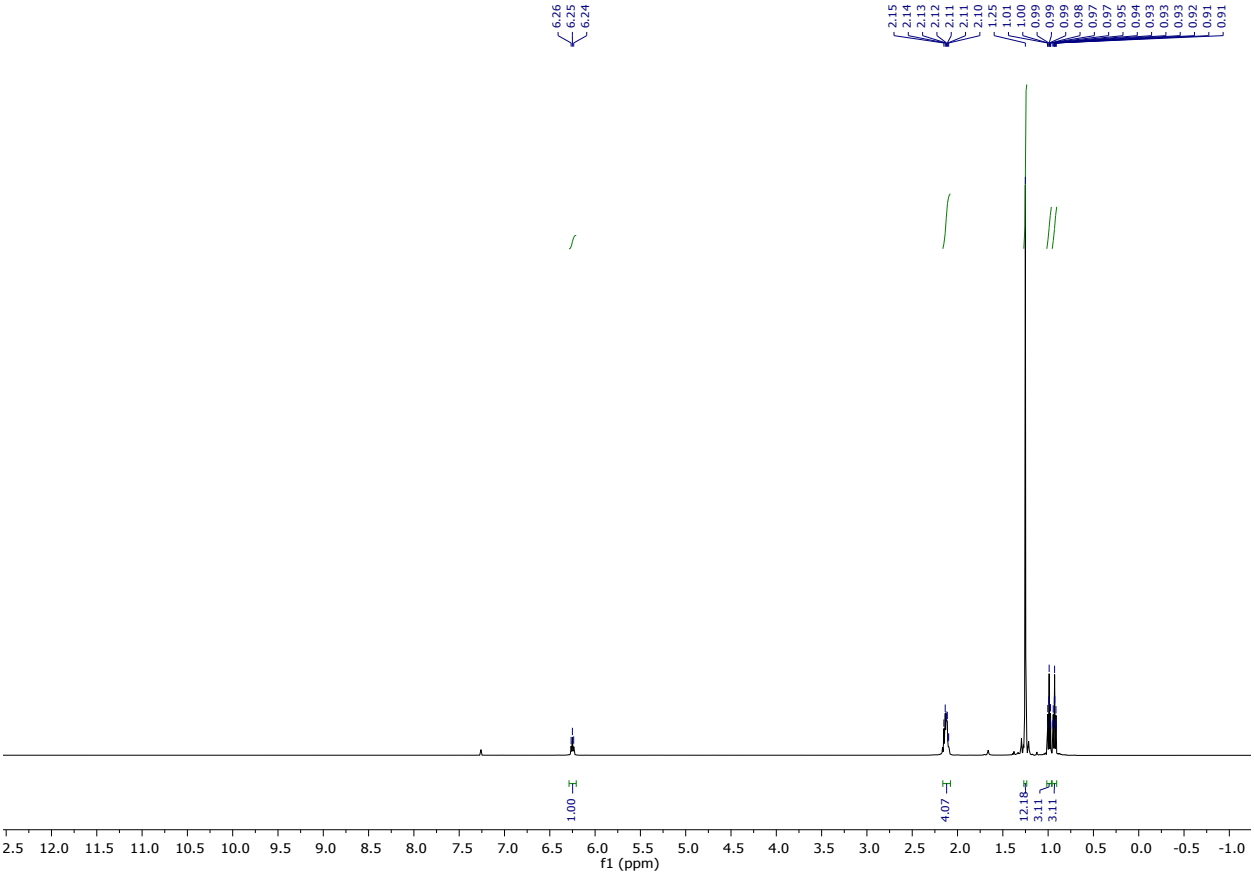
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



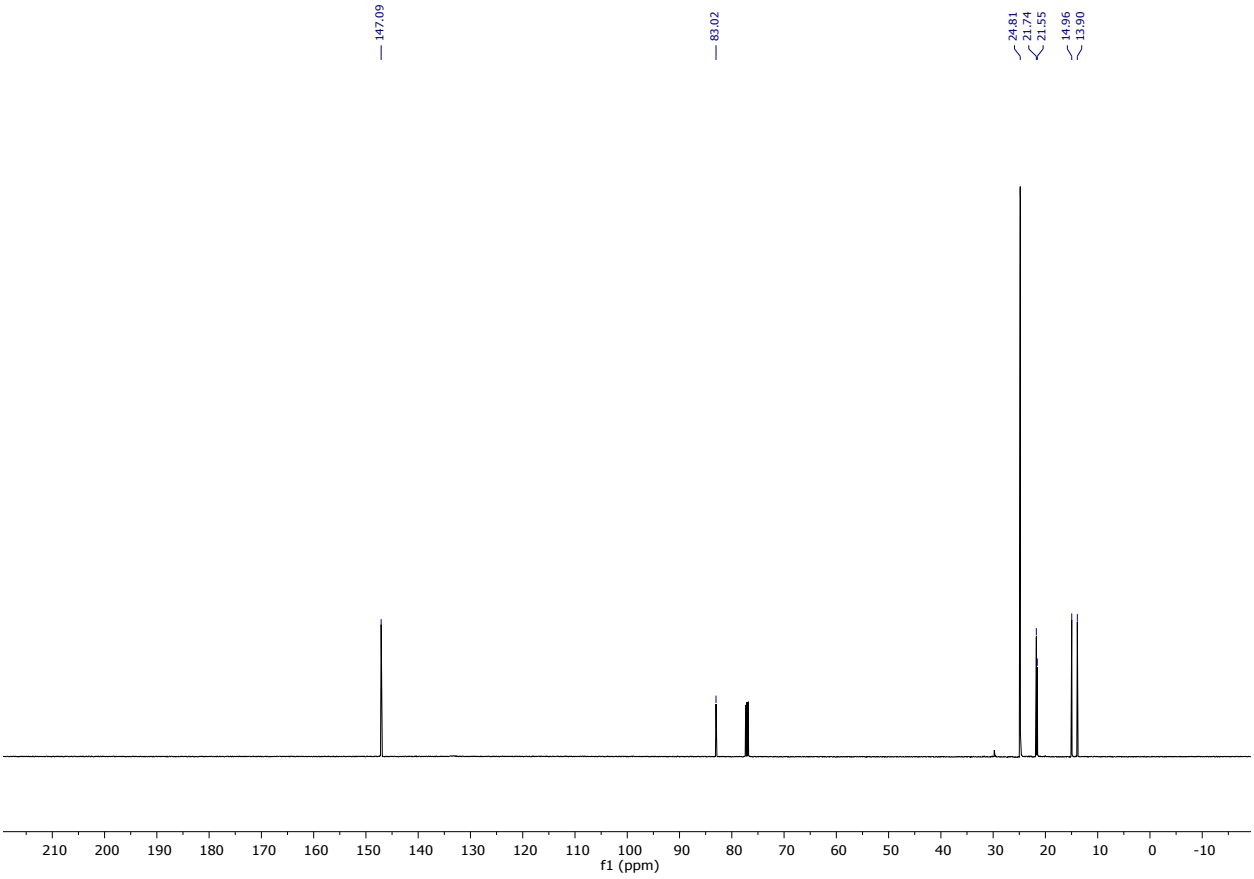


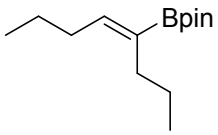
2m

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



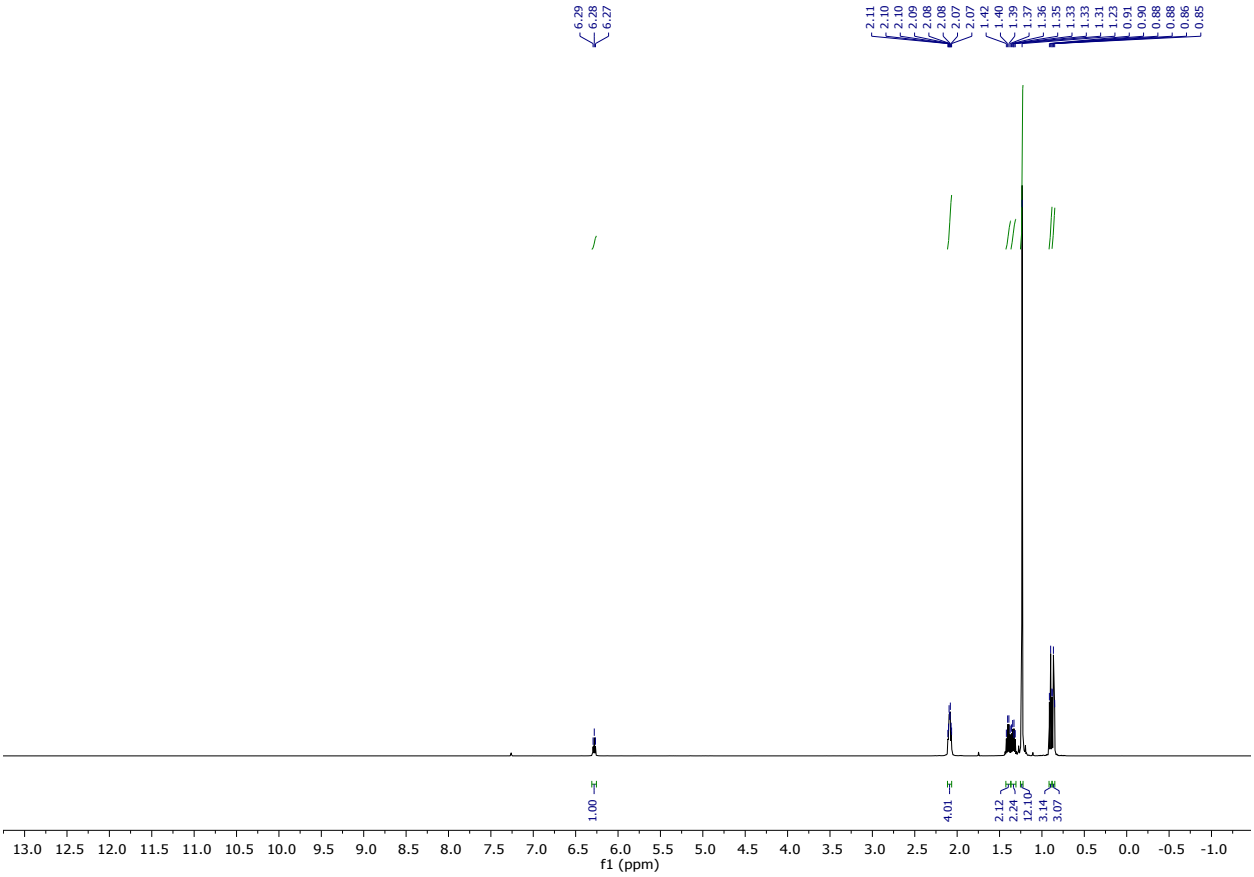
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



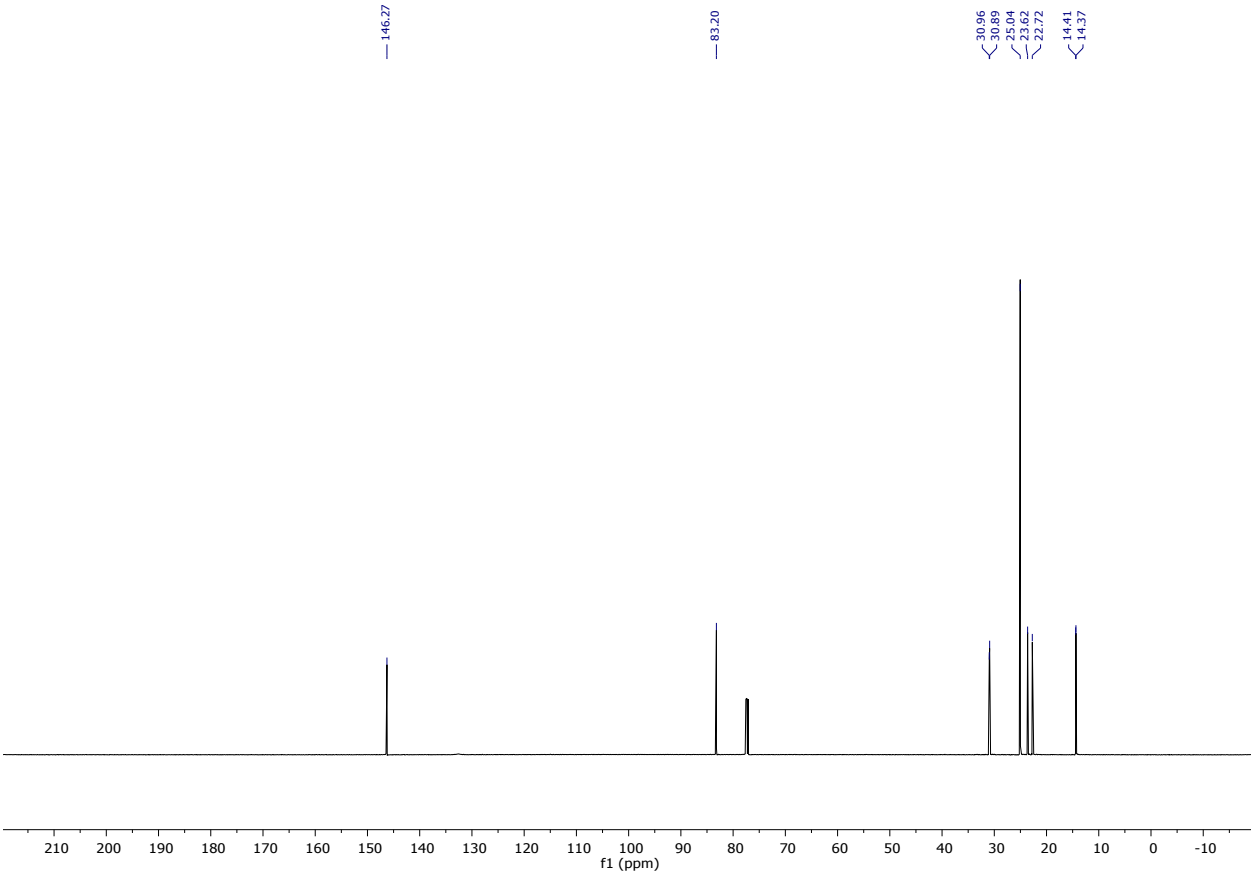


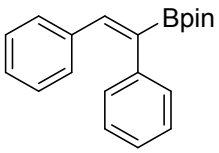
2n

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



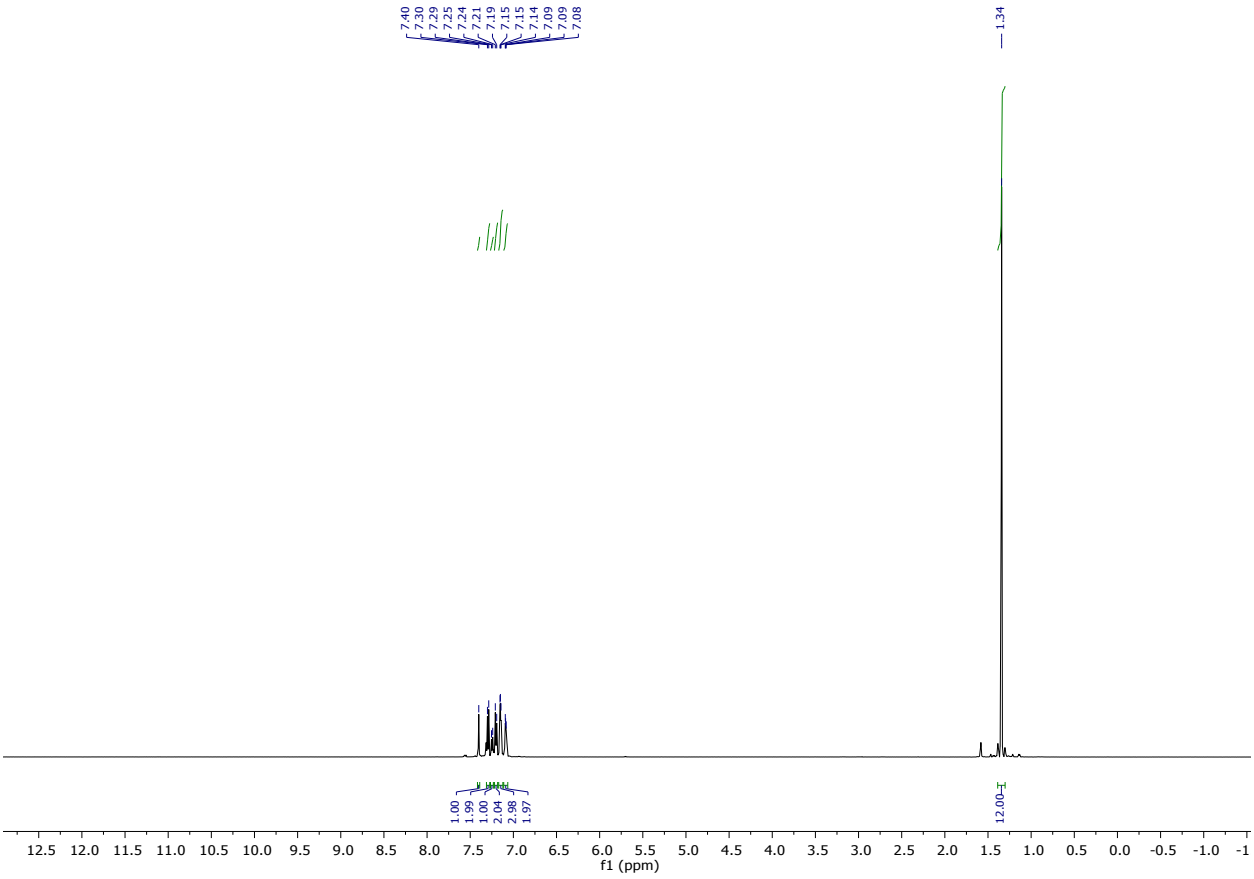
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



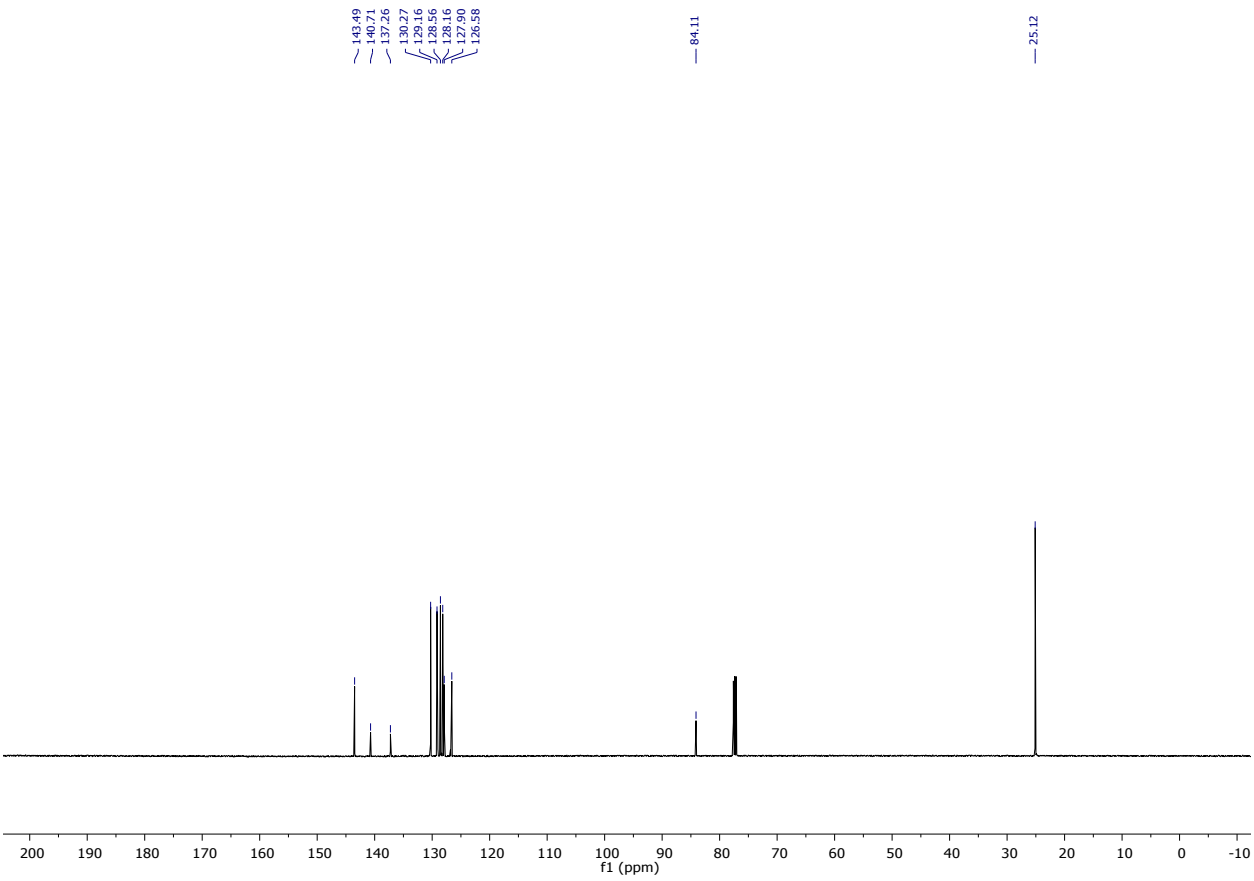


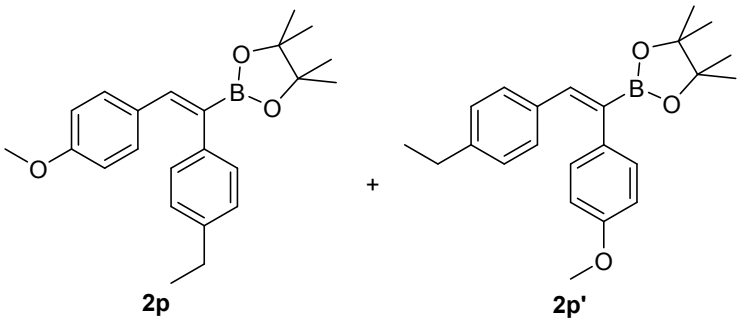
2o

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



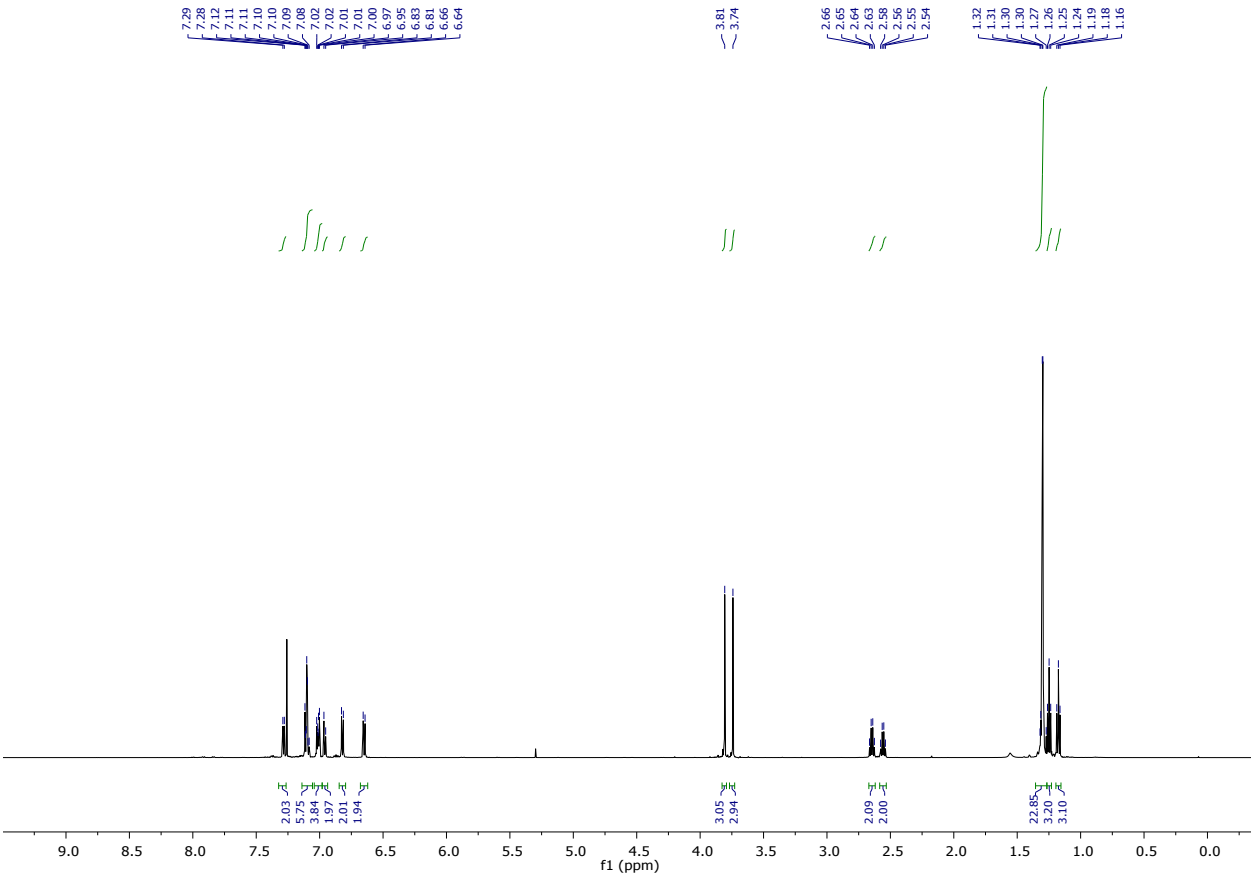
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



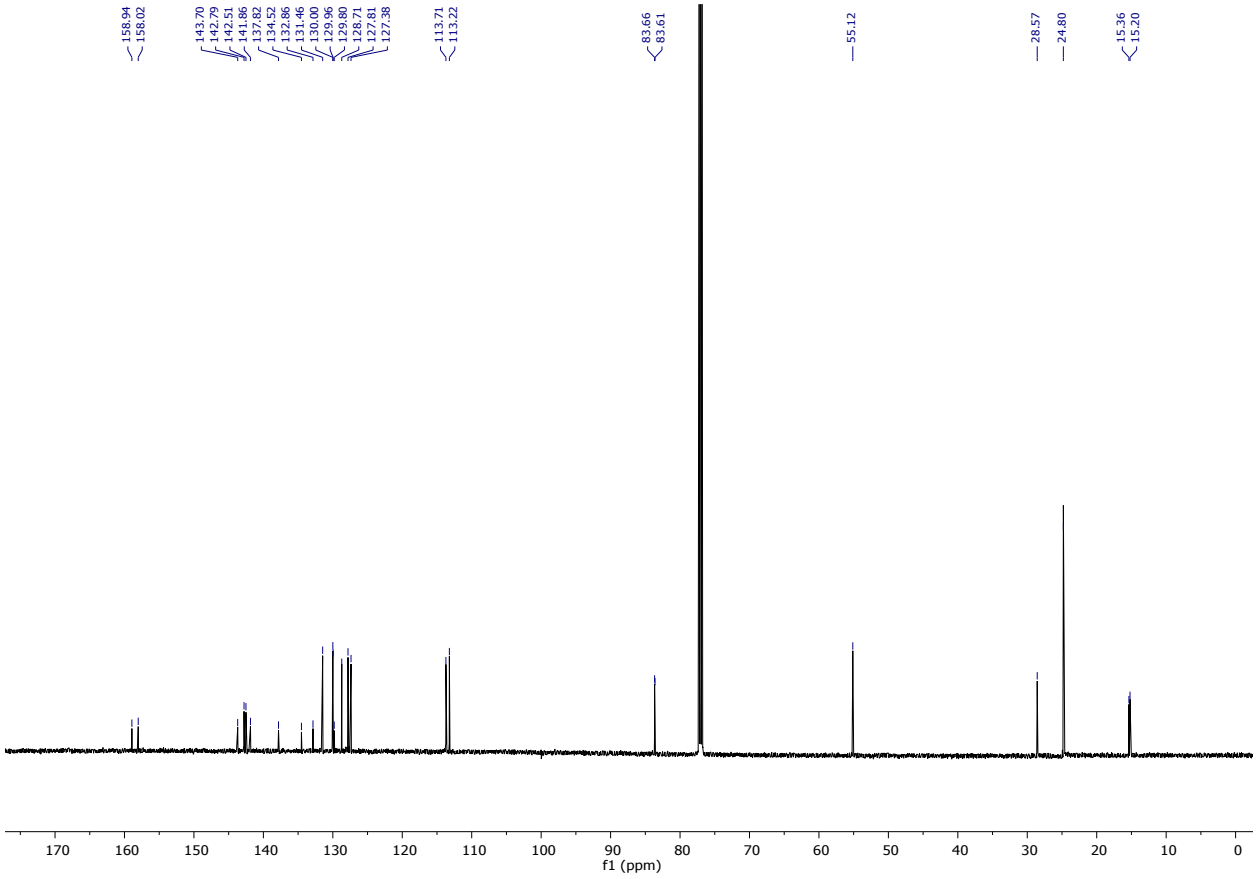


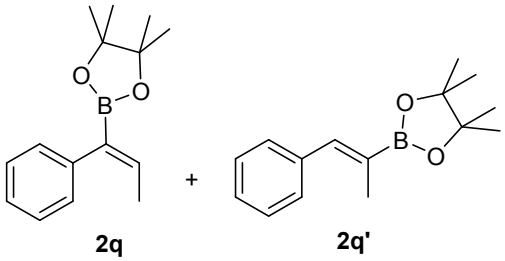
1 : 1

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



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

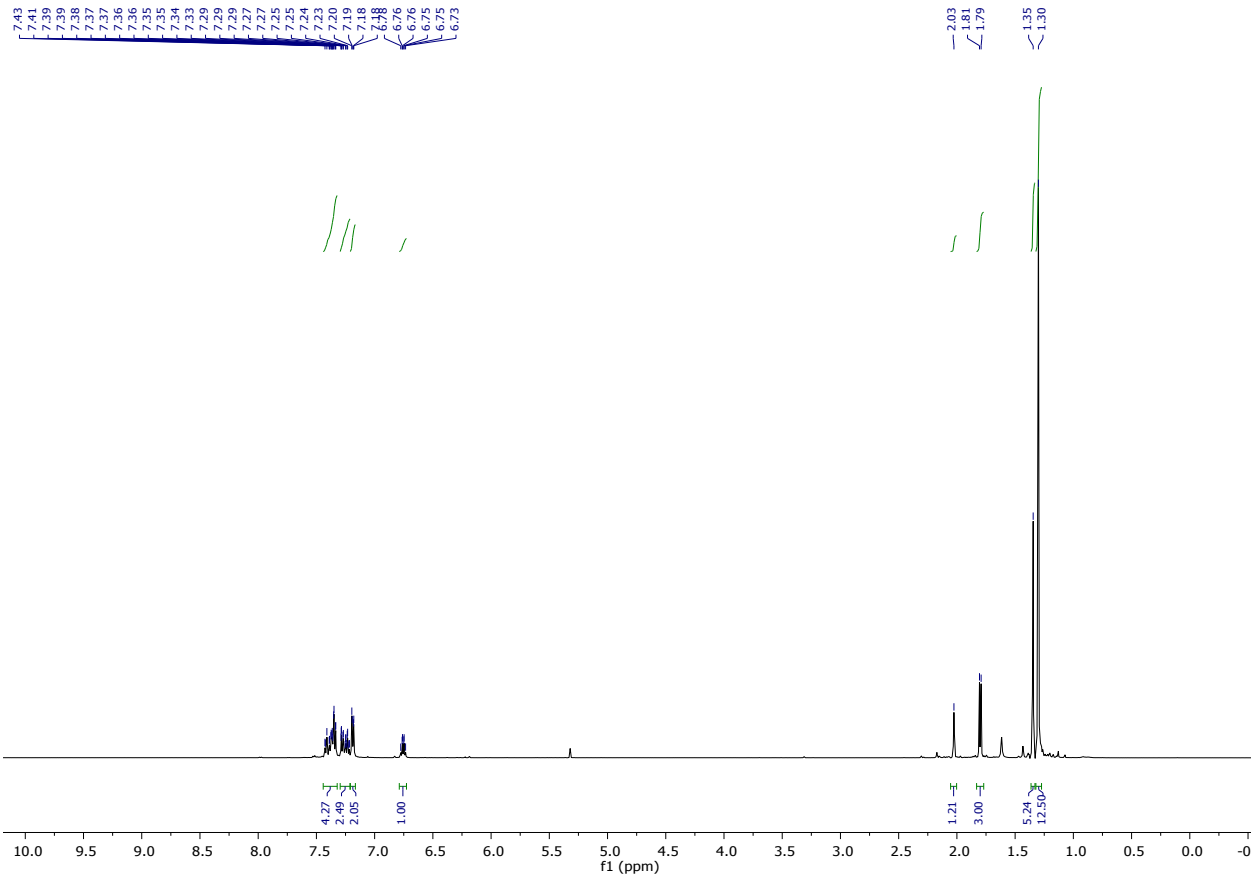




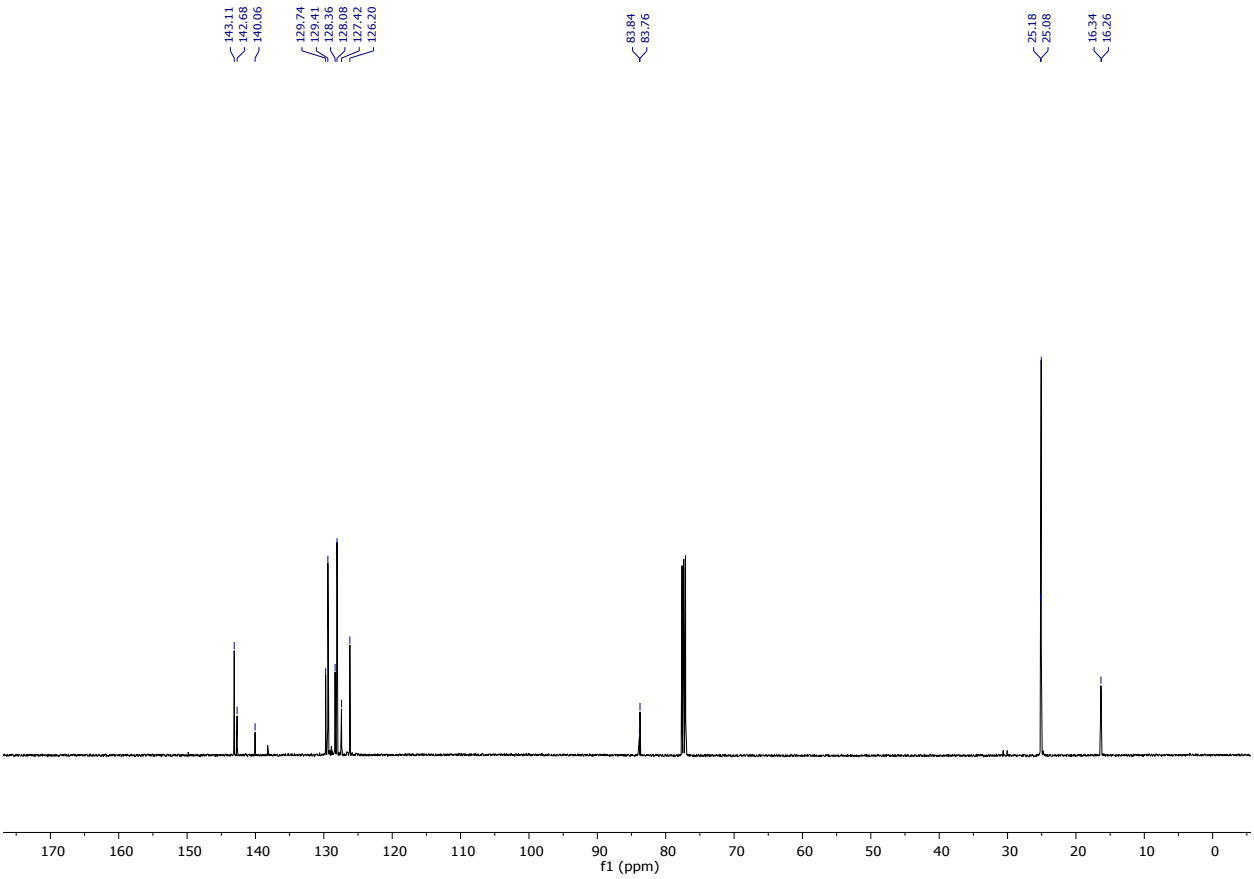
2q + **2q'**

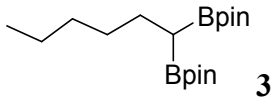
2.5 : 1

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



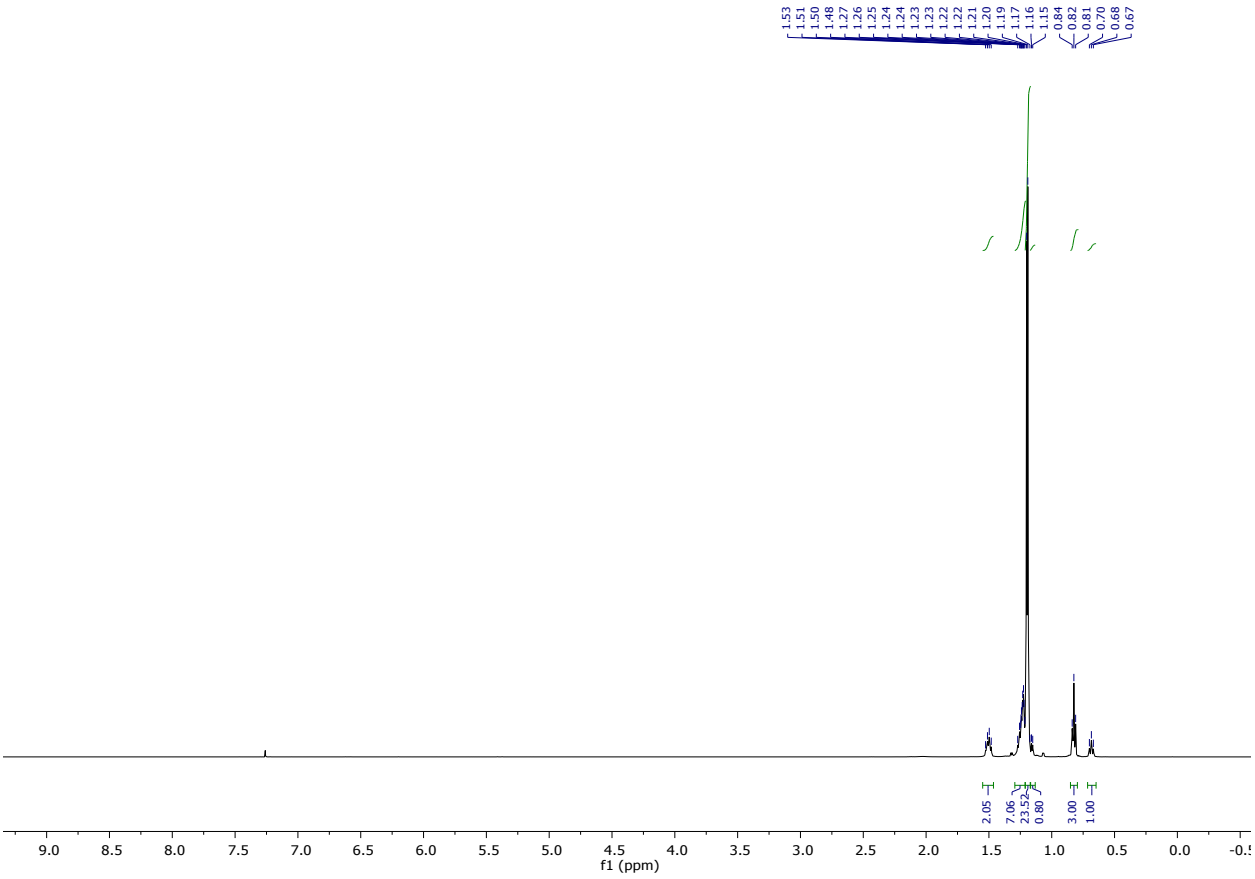
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



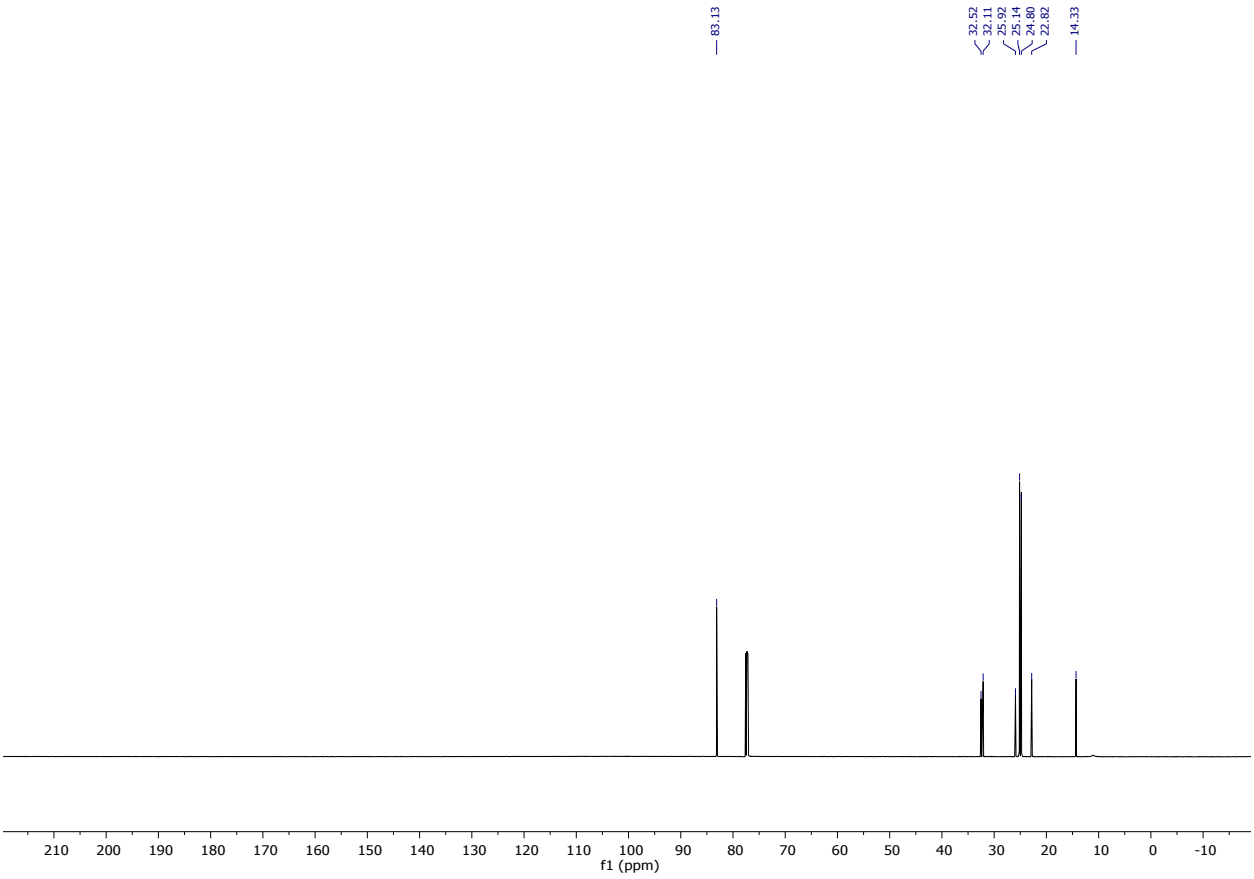


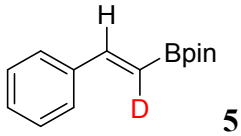
3

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



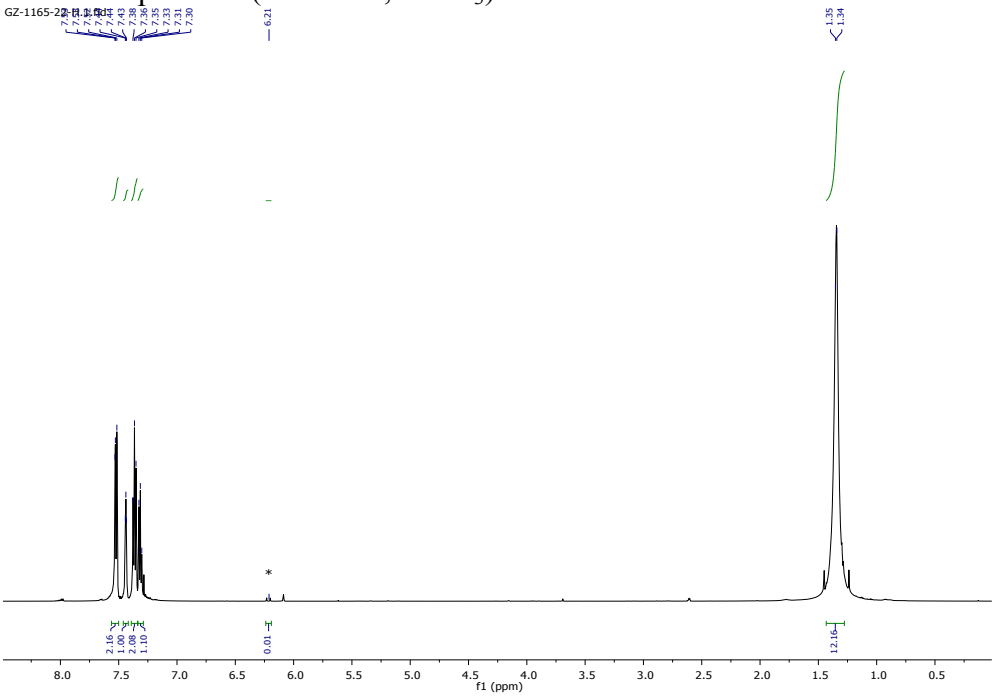
^{13}C NMR spectrum (126 MHz, $CDCl_3$):



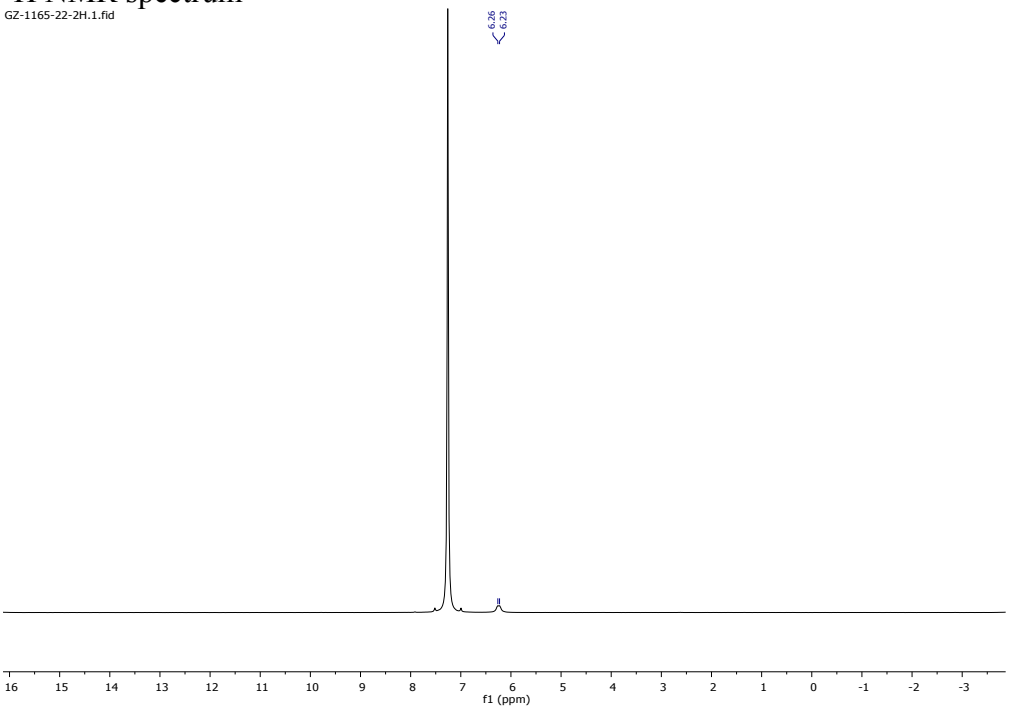


5

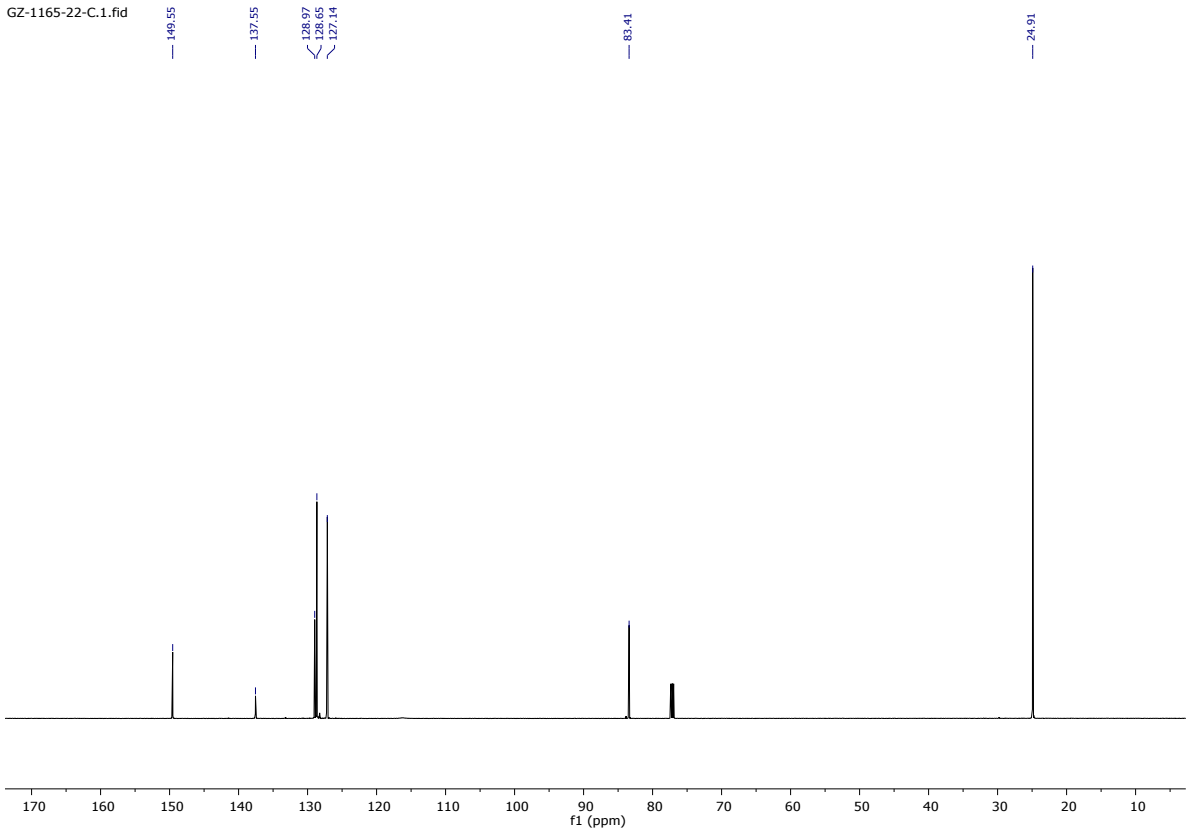
^{1}H NMR spectrum (500 MHz, $CDCl_3$):



^{2}H NMR spectrum



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



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