

Supporting Information for

Markovnikov-Selective Hydroboration of Vinylarenes

Catalyzed by a Cobalt(II) Coordination Polymer

Guoqi Zhang,^{*,†} Jing Wu,^{†,‡} Sihan Li,^{†,‡} Sean Cass,[†] and Shengping Zheng,[‡]

[†] Department of Sciences, John Jay College and Ph.D. Program in Chemistry, The Graduate Center of the City University of New York, New York, 10019 NY, USA.

[‡] Department of Chemistry, Hunter College, the City University of New York, New York, 10065 NY, USA.

Experimental Details

General Considerations. Unless specified otherwise, all reactions were carried out under a dry N₂ 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. ¹H NMR and ¹³C 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). **1** were prepared according to literature procedures.¹

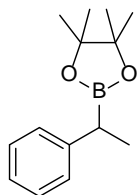
General Procedure for 1-Catalyzed Alkene Hydroboration. In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Alkenes (2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for indicated time periods (5 min for most cases) and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution (Note: the quenching of the reaction at this point was evidenced in a separate experiment, see below. The quenching of reaction by air was also indicated in a similar cobalt-catalyzed alkene hydroboration in the literature, see ref. 7b of the main text). The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the total yields of desired alkylboronates and the ratio of the regioisomeric products by comparing the GC traces with those of authentic samples² (Note: the GC data of minor linear hydroborated products reported below match with those authentic ones as reported in ref. 2, where the linear products were isolated as the major products by this same group and their structures have been confirmed by ¹H and ¹³C NMR spectroscopies along with GC-MS analysis by using the same GC conditions). The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO₂ column chromatography using ethyl

acetate/hexane as an eluent. The pure alkylboronates of major products were characterized by ^1H and ^{13}C NMR spectroscopies.

1-Catalyzed Alkene Hydroboration in the Air. Cobalt catalyst **1** (0.22 mg, 0.5 μmol , 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in CH_2Cl_2 (1.0 mL, 99.9%, extra dry, Acros) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min upon exposure to the air. Alkenes (2.0 mmol) was charged and then pinacolborane (282 mg, 2.2 mmol) was added to the reaction mixture in one portion. The reaction was allowed to stir at room temperature in the air for 5 min, and then the crude reaction mixture was analyzed by GC-MS (dilute solution in CH_2Cl_2). Only < 4% hydroborated adducts were observed.

General Procedure for Catalyst Robustness Screen. In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.11 mg, 0.5 μmol , 0.025 mol%) and KO^tBu (1.12 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), additive (1.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added sequentially. Hexamethylbenzene (31 mg) was finally added as an internal standard for GC analysis. 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 (1 mL) to the solution. The crude product was analyzed by GC-MS to determine the GC yield and ratio of the regioisomeric products from styrene hydroboration. For the reactions indicated in entries 1-6 (Table 3), the additives did not experience significant hydroboration as these additives were almost fully recovered as found in the corresponding GC profiles (> 98%). For styrene hydroboration in the presence of ketones and aldehydes (entries 7-9, Table 3), in each case the additive (ketone or aldehyde) experienced major hydroboration, and the yields are reported in Table 3 in the main text. The identification of three boronate esters have been made by comparing their GC retention time and MS data with the authentic samples that have been previously reported by our group by using the same catalyst.¹ The GC data for those hydroboration adducts of additives are as follows: 15.0 min (entry 7, Table 3); 12.9 min (entry 8, Table 3); 18.3 min (entry 8, Table 3).

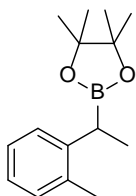
Catalytic details and characterization data



Chemical Formula: $C_{14}H_{21}BO_2$
Molecular Weight: 232.1300

2a²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μ mol, 0.025 mol%) and KO^tBu (1.12 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 (208.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was

quenched by exposing the reaction solution to air and adding CH_2Cl_2 (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil of **2a** was isolated. Yield: 380 mg (82%). 1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.24-7.19 (m, 2H), 7.15-7.11 (m, 1H), 2.43 (q, J = 7.5 Hz, 1H), 1.33 (d, J = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 128.4, 127.9, 125.2, 83.4, 24.70, 24.66, 17.1 ppm. GC-MS (m/z): 232 (calc. 232). t_r (retention time) = 13.6 min (major), t_r = 14.6 min (minor).

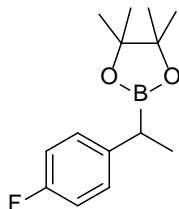


Chemical Formula: $C_{15}H_{23}BO_2$
Molecular Weight: 246.1570

2b²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μ mol, 0.025 mol%) and KO^tBu (1.12 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. 2-Methylstyrene (236.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction

mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil of **2b** was isolated. Yield: 310 mg (63%). 1H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 7.9 Hz, 1H), 7.26-7.19 (m, 2H), 7.19-7.13 (m, 1H), 2.75 – 2.65 (m, 1H), 2.43 (d, J = 2.1 Hz,

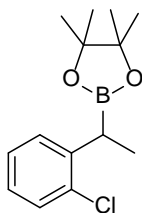
3H), 1.44 (d, $J = 7.5$ Hz, 3H), 1.32 (s, 6H), 1.31 (s, 6H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 143.6, 135.8, 130.3, 127.3, 126.3, 125.3, 83.4, 24.91, 24.86, 20.2, 16.6 ppm. GC-MS (m/z): 246 (calc. 246). $t_r = 14.9$ min (major), $t_r = 16.1$ min (minor). Note: a small amount of impurities (the minor regioisomer) were still observed in the NMR spectra after purification by column chromatography.



Chemical Formula: $\text{C}_{14}\text{H}_{20}\text{BFO}_2$
Molecular Weight: 250.1204

2c²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol , 0.025 mol%) and KO^tBu (1.12 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. 4-Fluorostyrene (244.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5

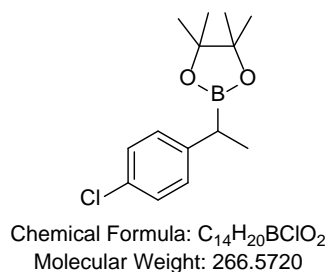
min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil of **2c** was isolated. Yield: 385 mg (77%). ^1H NMR (500 MHz, CDCl_3) δ 7.21-7.17 (m, 2 H), 6.99-6.95 (m, 2H), 2.44 (q, $J = 7.5$ Hz, 1 H), 1.34 (d, $J = 7.5$ Hz, 3 H), 1.24 (s, 6H), 1.22 (s, 6 H); ^{13}C NMR (125 MHz, CDCl_3) δ 161.2 (d, $J = 240$ Hz), 140.8 (d, $J = 3.2$ Hz), 129.3 (d, $J = 7.6$ Hz), 115.2 (d, $J = 21.0$ Hz), 83.7, 24.92, 24.88, 17.5 ppm. GC-MS (m/z): 250 (calc. 250). $t_r = 14.7$ min (major), $t_r = 14.8$ min (minor). Note: a small amount of impurities (the minor regioisomer) were still observed in the NMR spectra after purification by column chromatography.



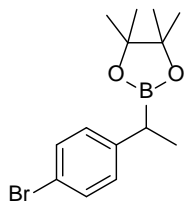
Chemical Formula: $\text{C}_{14}\text{H}_{20}\text{BClO}_2$
Molecular Weight: 266.5720

2d²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol , 0.025 mol%) and KO^tBu (1.12 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. 2-Chlorostyrene (276.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 20

min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO₂ column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil of **2d** was isolated. Yield: 400 mg (75%). ¹H NMR (500 MHz, CDCl₃) δ 7.21-7.17 (m, 2 H), 6.99-6.95 (m, 2H), 2.44 (q, *J* = 7.5 Hz, 1 H), 1.34 (d, *J* = 7.5 Hz, 3 H), 1.24 (s, 6H), 1.22 (s, 6 H); ¹³C NMR (151 MHz, CDCl₃) δ 143.1, 134.1, 129.5, 129.1, 127.1, 126.7, 83.7, 24.96, 24.94, 15.7 ppm. GC-MS (*m/z*): 266 (calc. 266). *t_r* = 16.1 min (major), *t_r* = 17.0 min (minor). Note: a small amount of impurities (the minor regioisomer) were still observed in the NMR spectra after purification by column chromatography.

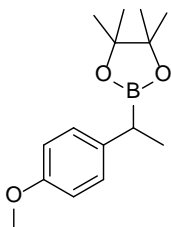


2e²: In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Chlorostyrene (276.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO₂ column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil of **2e** was isolated. Yield: 405 mg (76%). ¹H NMR (500 MHz, CDCl₃) δ 7.22 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.41 (q, *J* = 7.5 Hz, 1H), 1.31 (d, *J* = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H) ppm; ¹³C NMR (151 MHz, CDCl₃) δ 143.8, 131.0, 129.4, 128.6, 83.7, 24.91, 24.87, 17.2 ppm. GC-MS (*m/z*): 266 (calc. 266). *t_r* = 16.4 min (major), *t_r* = 17.1 min (minor).



Chemical Formula: $C_{14}H_{20}BBro_2$
Molecular Weight: 311.0260

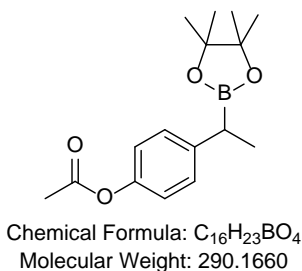
2f²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μ mol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Bromostyrene (364.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 30 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Yellowish oil of **2f** was isolated. Yield: 448 mg (72%). 1H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 2.50 (q, J = 7.6 Hz, 1H), 1.41 (d, J = 7.9 Hz, 3H), 1.31 (s, 6H), 1.30 (s, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 131.5, 129.8, 119.0, 83.7, 24.9, 24.9, 17.2 ppm. GC-MS (m/z): 311 (calc. 311). t_r = 17.5 min (major), t_r = 18.3 min (minor).



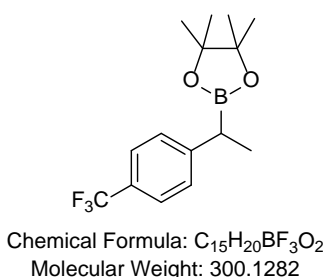
Chemical Formula: $C_{15}H_{23}BO_3$
Molecular Weight: 262.1560

2g²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μ mol, 0.025 mol%) and KO^tBu (1.12 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. 4-Methoxystyrene (268.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Yellowish oil of **2g** was isolated. Yield: 372 mg (71%). 1H NMR (600 MHz, $CDCl_3$) δ 7.16 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H), 2.39 (q, J = 7.5 Hz, 1H), 1.32 (d, J = 7.8 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H) ppm; ^{13}C NMR

(125 MHz, CDCl₃) δ 157.5, 137.2, 128.9, 114.0, 83.4, 55.4, 24.89, 24.85, 17.6 ppm. GC-MS (m/z): 262 (calc. 262). t_r = 17.1 min (major), t_r = 17.9 min (minor).

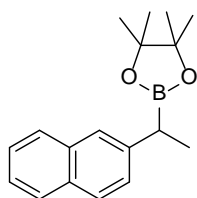


2h²: In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μ mol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Acetoxystyrene (324.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure the product was purified through a SiO₂ column chromatography using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of **2h** was isolated. Yield: 441 mg (76%). ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 2.43 (q, J = 7.6 Hz, 1H), 2.27 (s, 3H), 1.31 (d, J = 7.5 Hz, 3H), 1.21 (s, 6 H), 1.20 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 170.0, 148.5, 142.7, 128.9, 121.5, 83.6, 24.92, 24.89, 21.5, 17.4 ppm. GC-MS (m/z): 290 (calc. 290). t_r = 18.7 min (major), t_r = 19.5 min (minor).



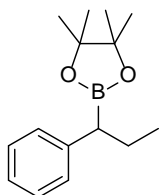
2i²: In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μ mol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 4-Trifluoromethylstyrene (344.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 60 min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO₂ column

chromatography using ethyl acetate/hexane (1:20, v/v) as an eluent. While solid of **2i** was obtained. Yield: 324 mg (54%). ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 2.51 (q, $J = 7.5$ Hz, 1H), 1.36 (d, $J = 7.9$ Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 149.7, 128.7, 128.3, 127.7 (q, $J = 32.2$ Hz), 125.5 (q, $J = 3.8$ Hz), 124.9 (q, $J = 271.8$ Hz), 83.9, 24.92, 24.88, 17.0 ppm. GC-MS (m/z): 300 (calc. 300). $t_r = 13.6$ min (major), $t_r = 14.5$ min (minor).



Chemical Formula: $\text{C}_{18}\text{H}_{23}\text{BO}_2$
Molecular Weight: 282.1900

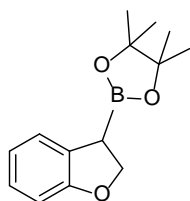
2j²: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol , 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 2-Vinylnaphthalene (308.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 30 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2 (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH_2Cl_2) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO_2 column chromatography using ethyl acetate/hexane (1:20, v/v) as an eluent. White solid of **2j** was isolated. Yield: 502 mg (89%). ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.78 (m, 3H), 7.70 (s, 1H), 7.49 – 7.41 (m, 3H), 2.67 (q, $J = 7.3$ Hz, 1H), 1.48 (d, $J = 7.5$ Hz, 3H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.6, 133.9, 131.7, 127.7, 127.55, 127.50, 127.3, 125.7, 125.3, 124.8, 83.4, 30.2, 24.7, 24.6, 16.9 ppm. GC-MS (m/z): 282 (calc. 282). $t_r = 20.9$ min (major), $t_r = 21.7$ min (minor).



Chemical Formula: $\text{C}_{15}\text{H}_{23}\text{BO}_2$
Molecular Weight: 246.1570

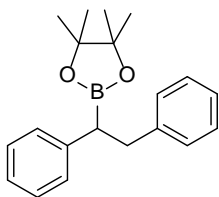
2k³: In a glovebox under N_2 atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol , 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. Trans- β -methylstyrene (236.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH_2Cl_2

(1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO₂ column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Colorless oil of **2k** was isolated. Yield: 453 mg (92%). ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 7.15 (t, *J* = 7.1 Hz, 1H), 2.24 (t, *J* = 7.9 Hz, 1H), 1.93 – 1.86 (m, 1H), 1.72 – 1.67 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 143.3, 128.4, 128.2, 125.1, 83.3, 25.8, 24.7, 24.6, 14.0 ppm. GC-MS (*m/z*): 246 (calc. 246). *t_r* = 14.6 min (major), *t_r* = 14.7 min (minor), *t_r* = 14.9 min (minor).



Chemical Formula: C₁₄H₁₉BO₃
Molecular Weight: 246.1130

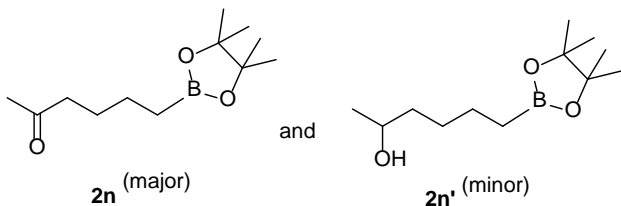
2l³: In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The mixture was stirred for 1 min. 2,3-Benzofuran (236.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the product was purified through a SiO₂ column chromatography using ethyl acetate/hexane (1:40, v/v) as an eluent. Yellowish oil of **2l** was isolated. Yield: 462 mg (94%). ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.23 (m, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 4.79 (dd, *J* = 10.5, 8.3 Hz, 1H), 4.57 (dd, *J* = 11.1, 8.4 Hz, 1H), 3.11 (t, *J* = 10.8 Hz, 1H), 1.31 (s, 6H), 1.30 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 159.7, 128.6, 127.4, 124.6, 120.3, 109.1, 84.0, 73.6, 25.0, 24.6 ppm. GC-MS (*m/z*): 246 (calc. 246). *t_r* = 17.0 min (the only peak).



Chemical Formula: C₂₀H₂₅BO₂
Molecular Weight: 308.2280

2m³: In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol, 0.025 mol%) and KO^tBu (1.12 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. Cis-stilbene or trans-stilbene (360.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂). The reaction mixture was then evaporated under reduced pressure and the crude product was passed through a SiO₂ column chromatography using ethyl acetate/hexane (1:20, v/v) as an eluent. White solid of **2m** was isolated. Yield: 595 mg (95%). ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.28 (m, 4H), 7.28-7.22 (m, 4H), 7.22-7.13 (m, 2H), 3.20 (dd, *J* = 13.4, 9.8 Hz, 1H), 3.01 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.73 (dd, *J* = 9.8, 7.0 Hz, 1H), 1.16 (s, 6H), 1.15 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 142.6, 141.7, 128.9, 128.4, 128.4, 128.1, 125.8, 125.4, 83.4, 38.9, 24.6, 24.5 ppm. GC-MS (*m/z*): 308 (calc. 308). *t_r* = 21.5 min (the only peak).

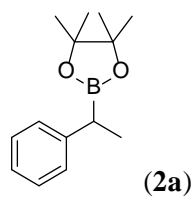


2n and **2n'**⁴: In a glovebox under N₂ atmosphere, cobalt catalyst **1** (0.22 mg, 0.5 μmol, 0.025 mol%) and KO^tBu (1.12 mg, 1 mol%) was dissolved in THF (1.0 mL) in a 5 mL glass vial equipped with a stir bar. The

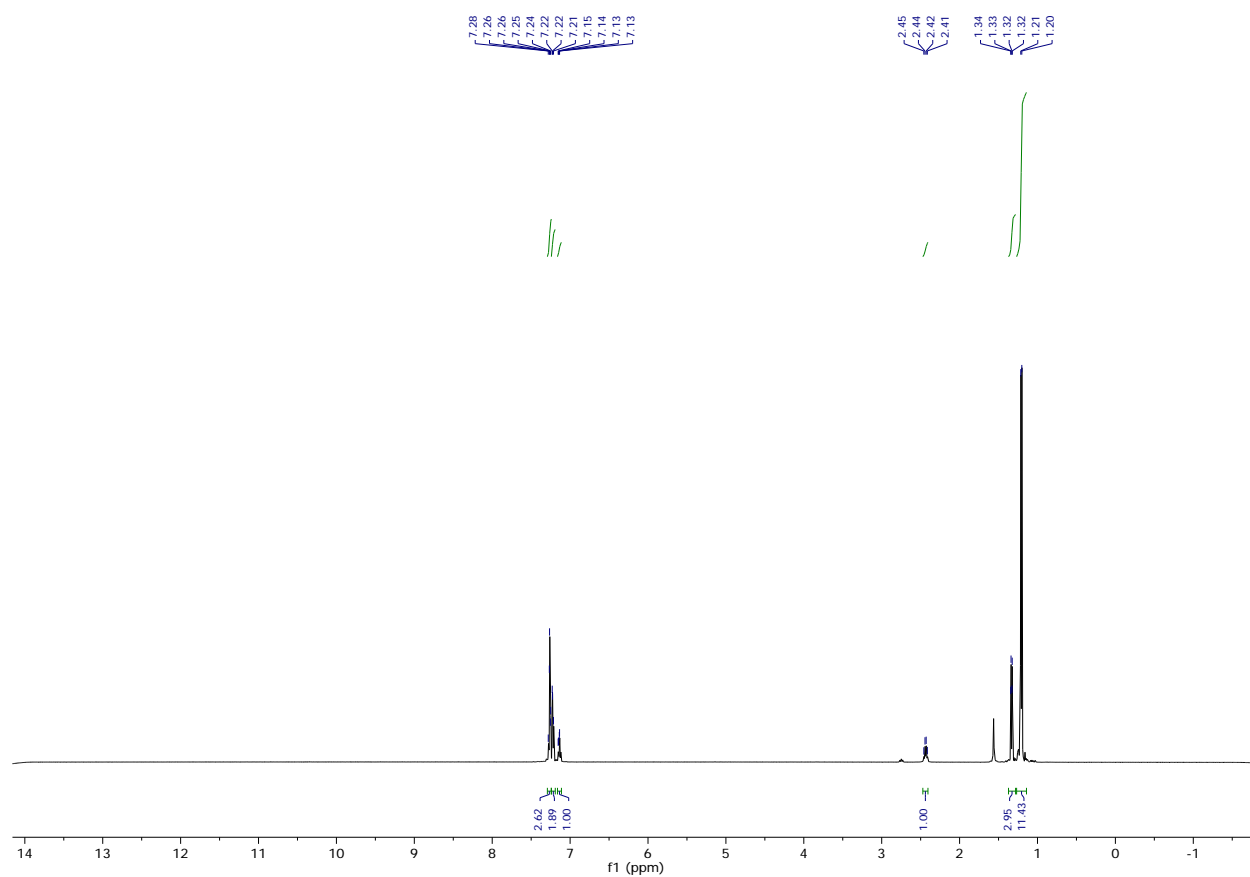
mixture was stirred for 1 min. 5-Hexen-2-one (196.0 mg, 2.0 mmol) and pinacolborane (282 mg, 2.2 mmol) were then added. The reaction mixture was allowed to stir at room temperature for 5 min and then the reaction was quenched by exposing the reaction solution to air and adding CH₂Cl₂ (1 mL) to the solution. The crude reaction mixture was first analyzed by GC-MS (dilute solution in CH₂Cl₂) to determine the ratio of the regioisomeric products by comparing the GC traces with those of authenticated samples. The reaction mixture was then evaporated under reduced pressure and the crude product was passed through a SiO₂ column chromatography using ethyl acetate/hexane (1:20, v/v) as an eluent. Colorless oil of the major product **2n** and minor product **2n'** were isolated, respectively. Yield for **2n**: 325 mg (72%). ¹H NMR (500 MHz, CDCl₃) δ 2.35 (t, *J* = 7.5 Hz, 2H), 2.06 (d, *J* = 1.6 Hz, 3H), 1.55 – 1.47 (m, 2H), 1.38 – 1.30 (m, 2H), 1.17 (t, *J* = 1.4 Hz, 12H), 0.72 (t, *J* = 7.8 Hz, 2H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 209.4, 83.0, 43.7, 29.8, 26.5, 24.8, 23.6 ppm. GC-MS (*m/z*): 226 (calc. 226). Yield for **2n'**: 50 mg (11%). ¹H NMR (500 MHz, CDCl₃) δ 3.86 – 3.74 (m, 1H), 1.79 – 1.65 (m, 1H), 1.54 – 1.37

(m, 6H), 1.25 (s, 12H), 1.18 (d, $J = 6.3$ Hz, 3H), 0.80 (t, $J = 7.2$ Hz, 2H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 83.23, 68.17, 39.31, 28.7, 25.1, 24.1, 23.7 ppm. GC-MS (m/z): 228 (calc. 228). t_r = 13.6 min (major), t_r = 20.1 min (minor).

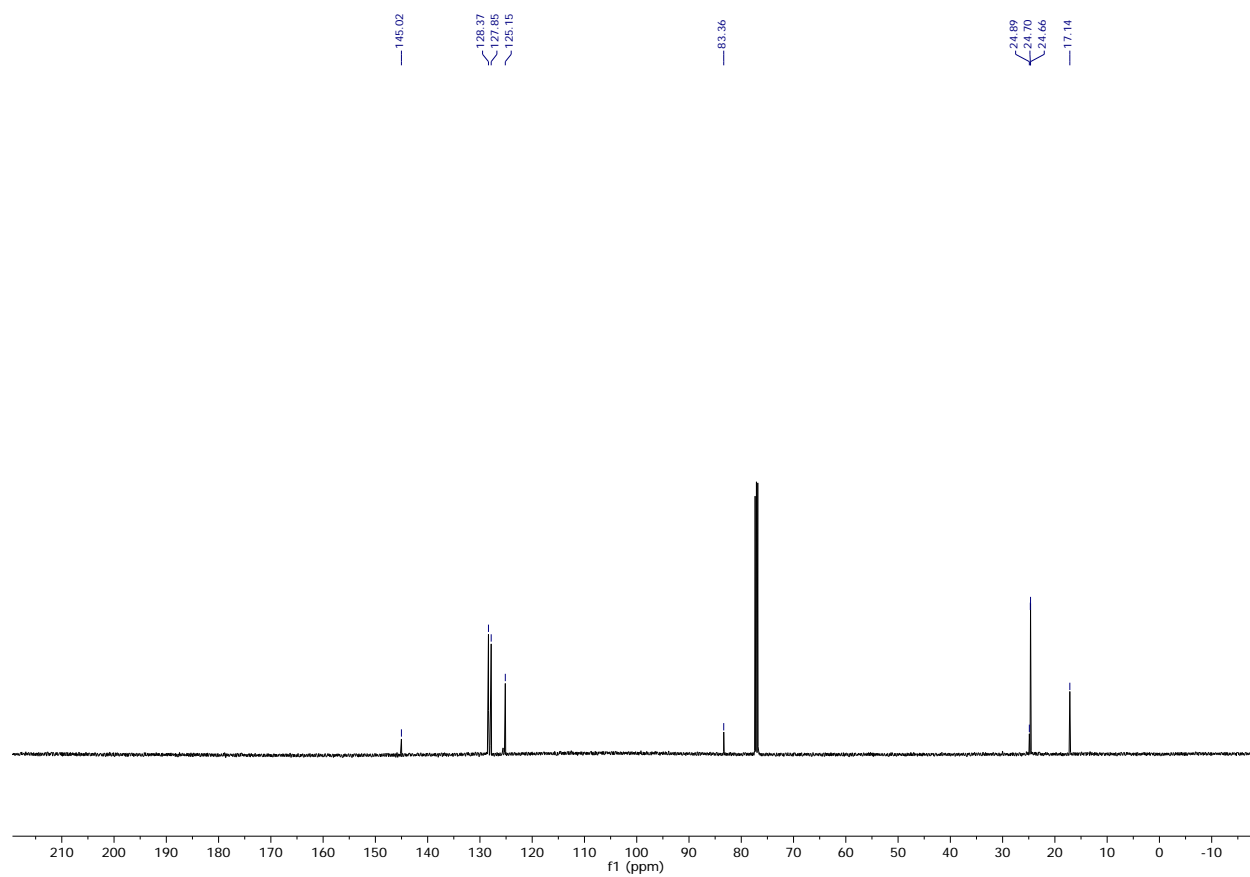
Copies of NMR spectra for isolated compounds:

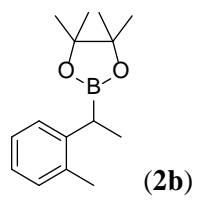


^1H NMR (500 MHz, CDCl_3):

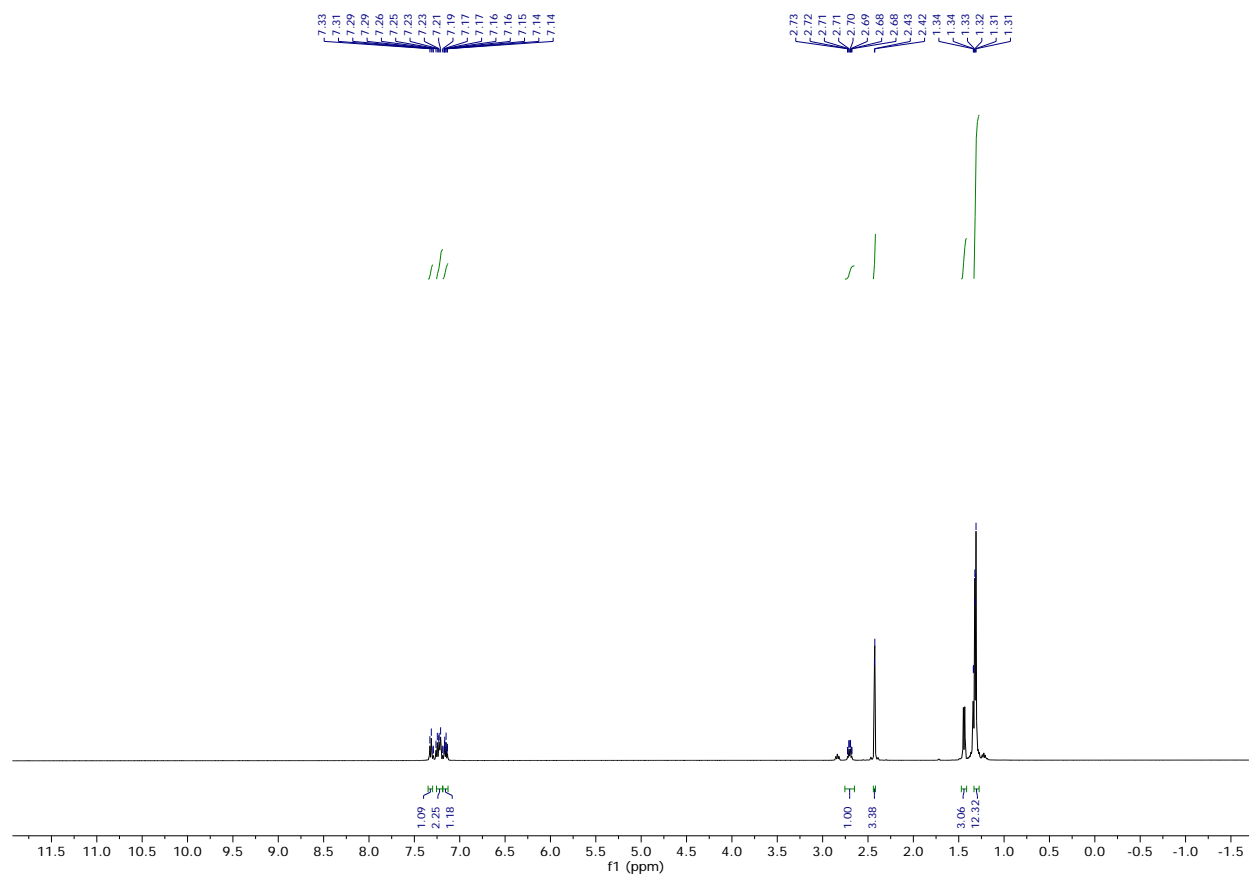


^{13}C NMR (126 MHz, CDCl_3):

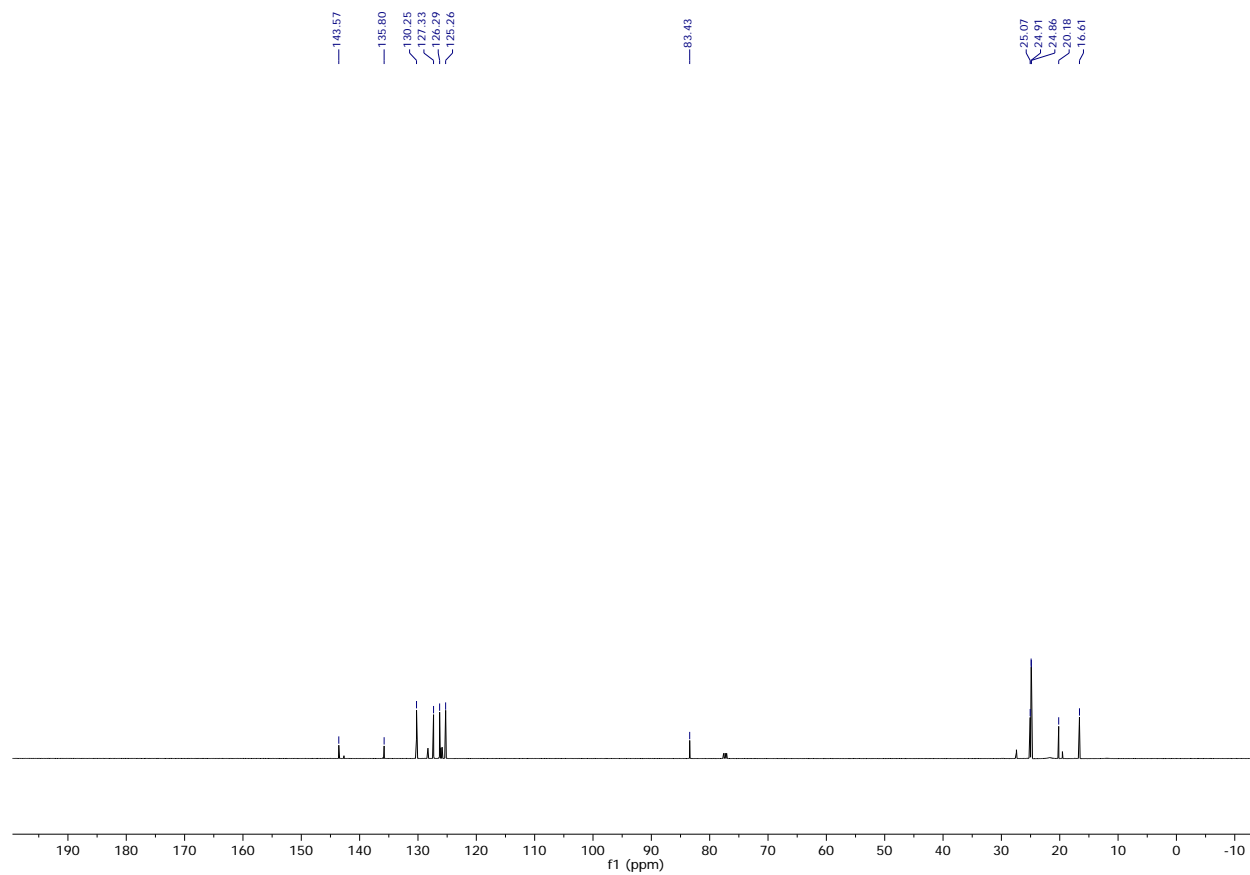


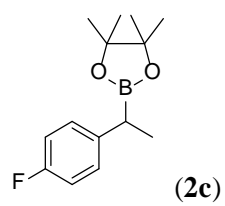


^1H NMR (500 MHz, CDCl_3):

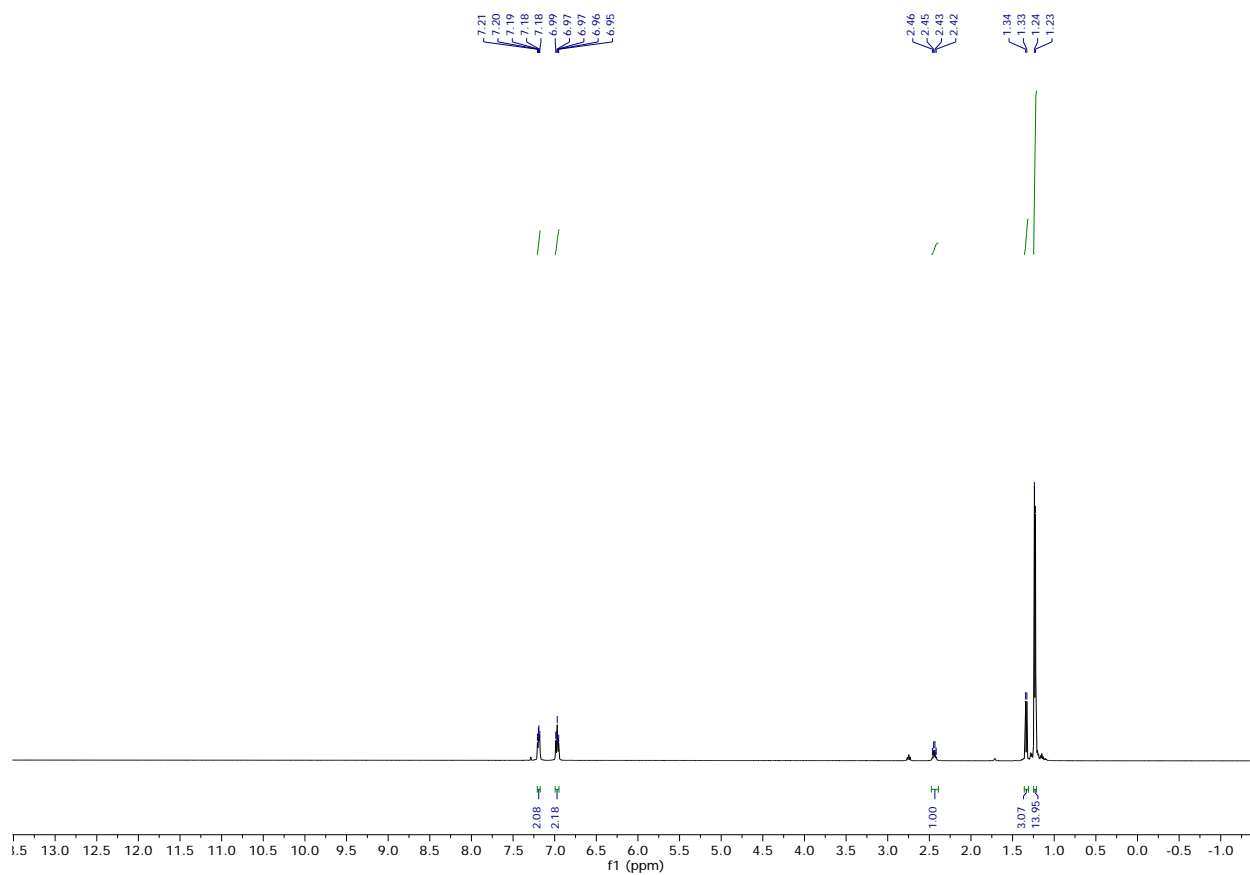


^{13}C NMR (126 MHz, CDCl_3):

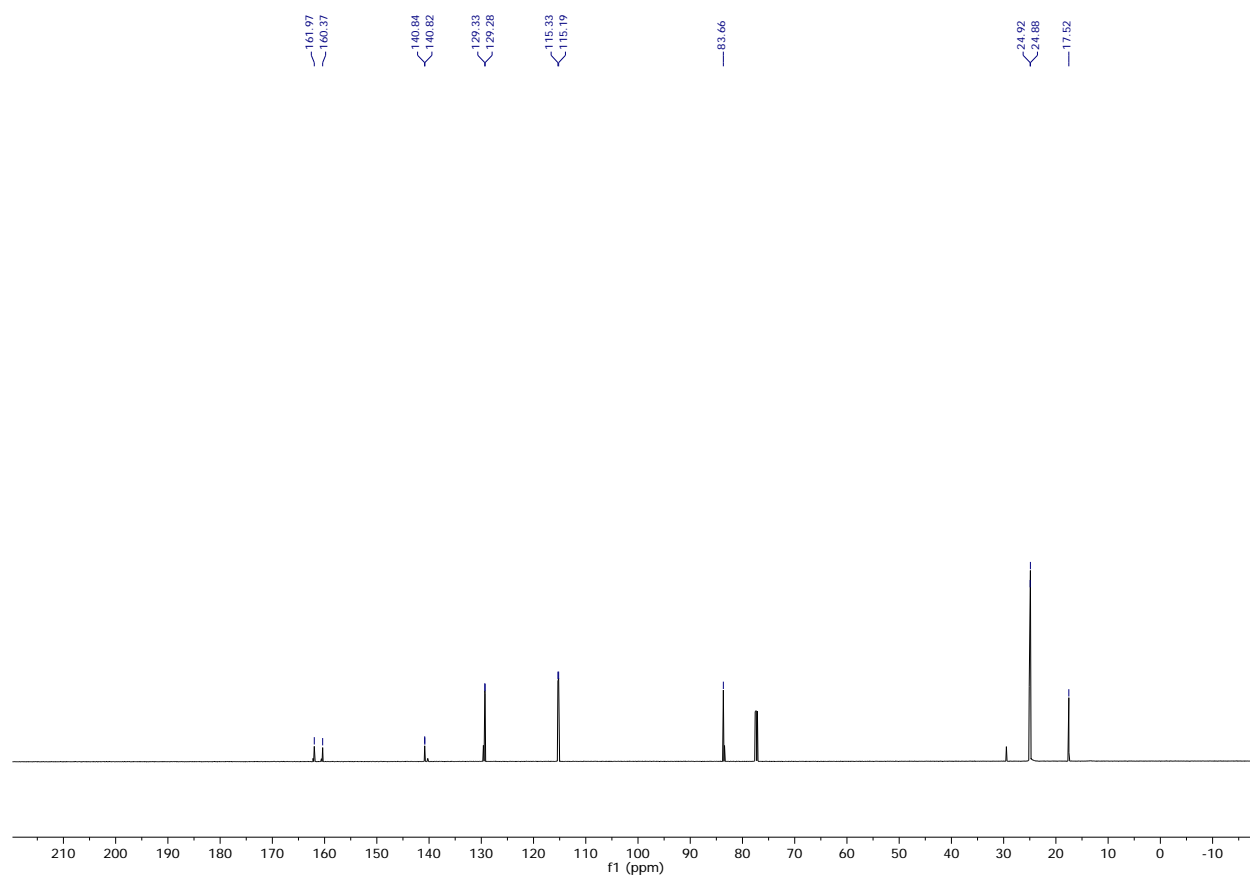


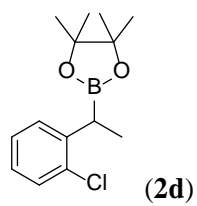


^1H NMR (600 MHz, CDCl_3):

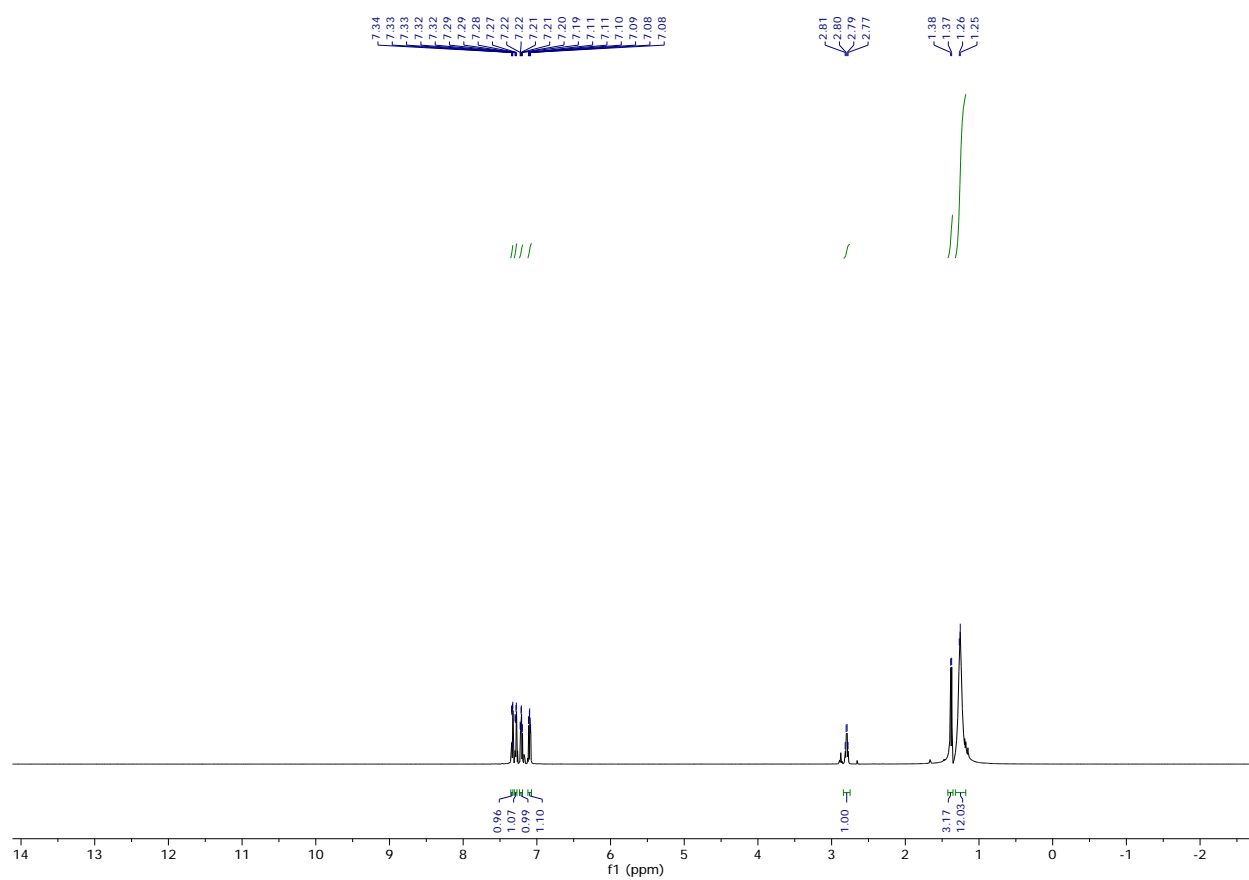


^{13}C NMR (151 MHz, CDCl_3):

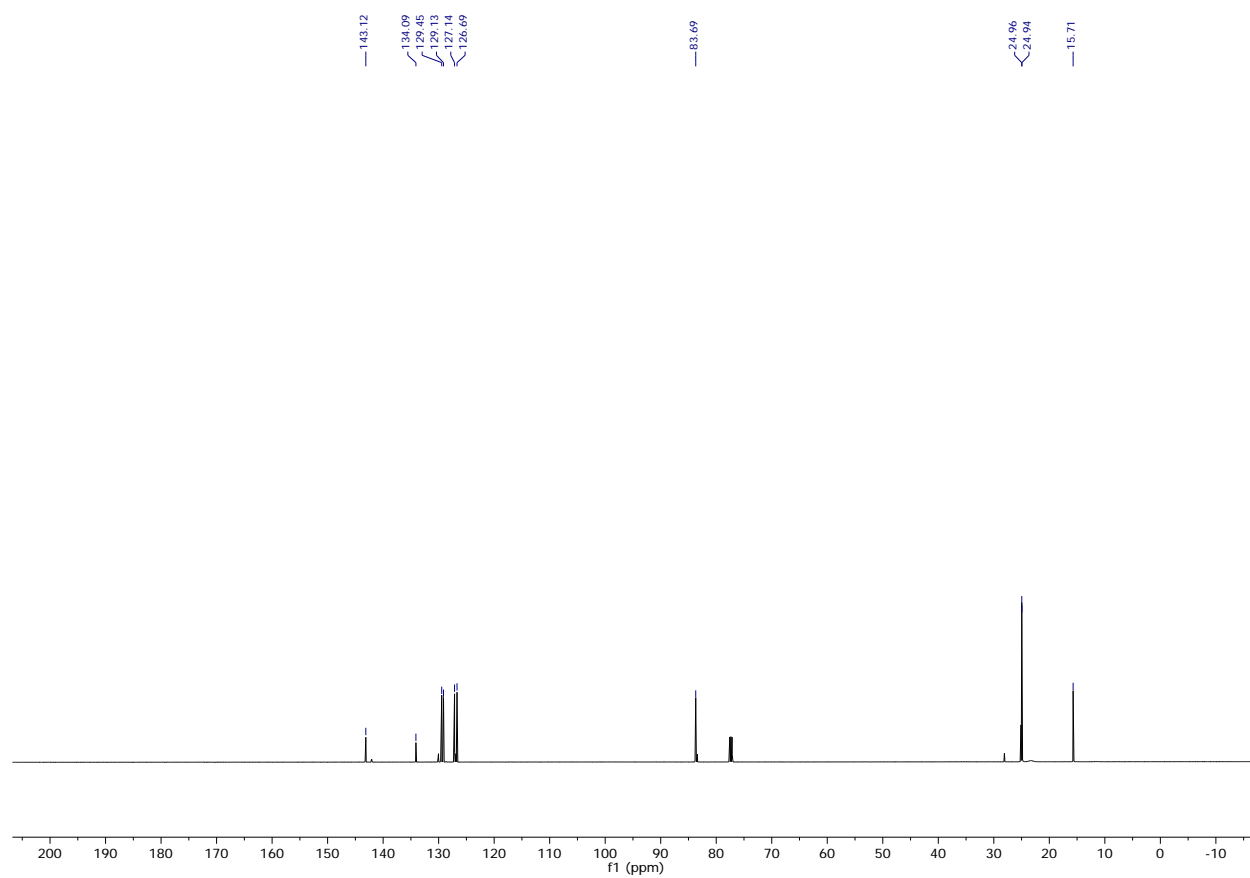


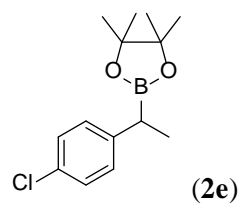


^1H NMR (600 MHz, CDCl_3):

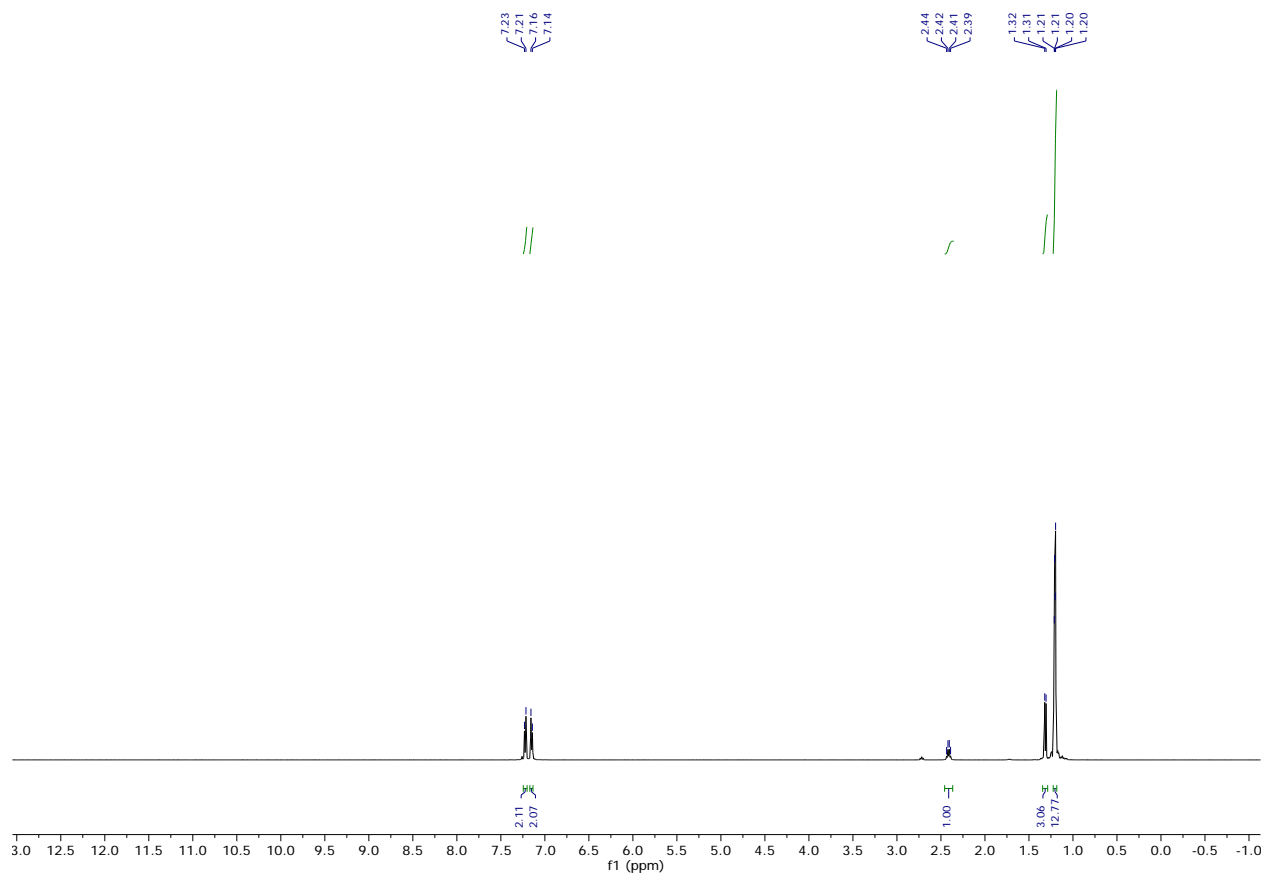


^{13}C NMR (151 MHz, CDCl_3):

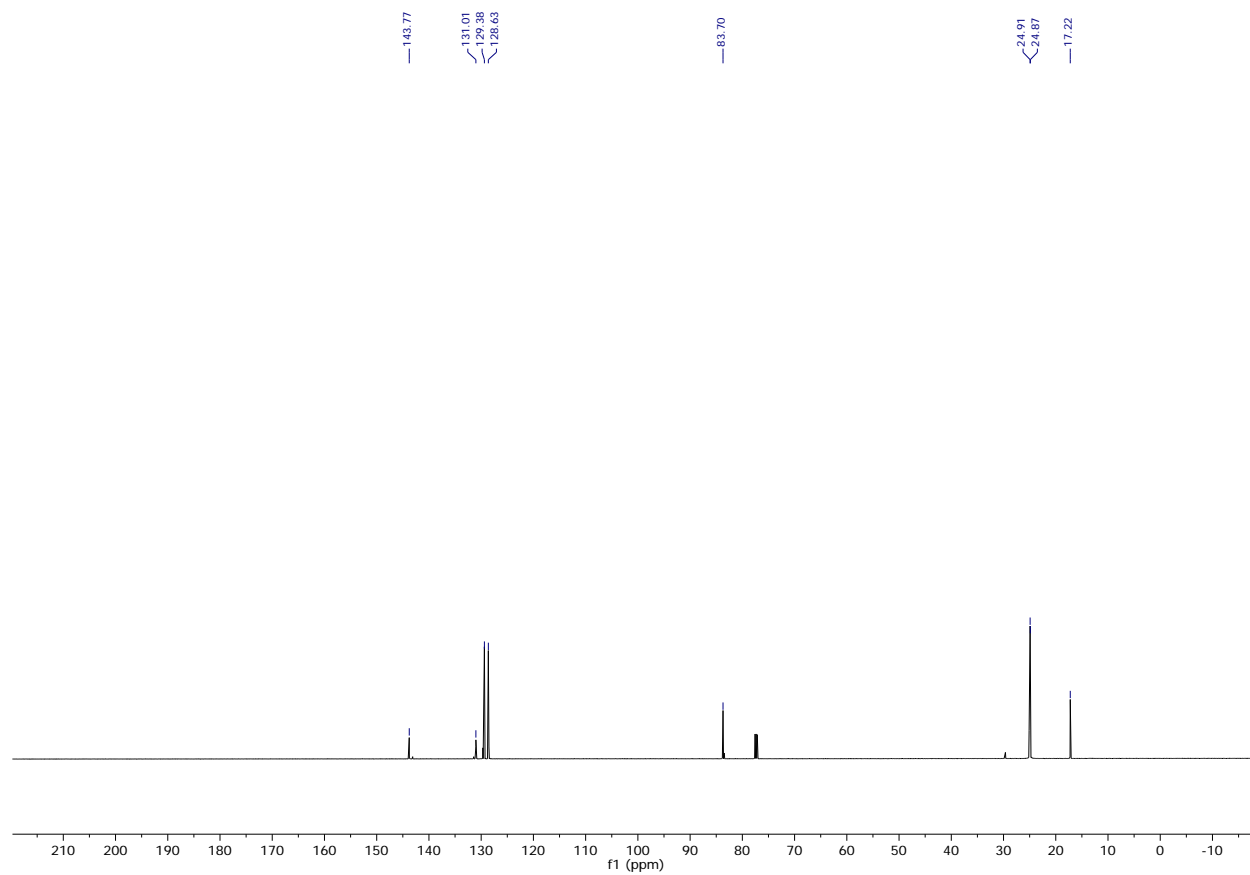


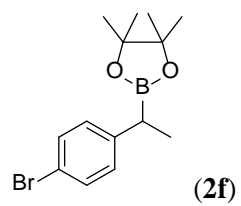


^1H NMR (600 MHz, CDCl_3):

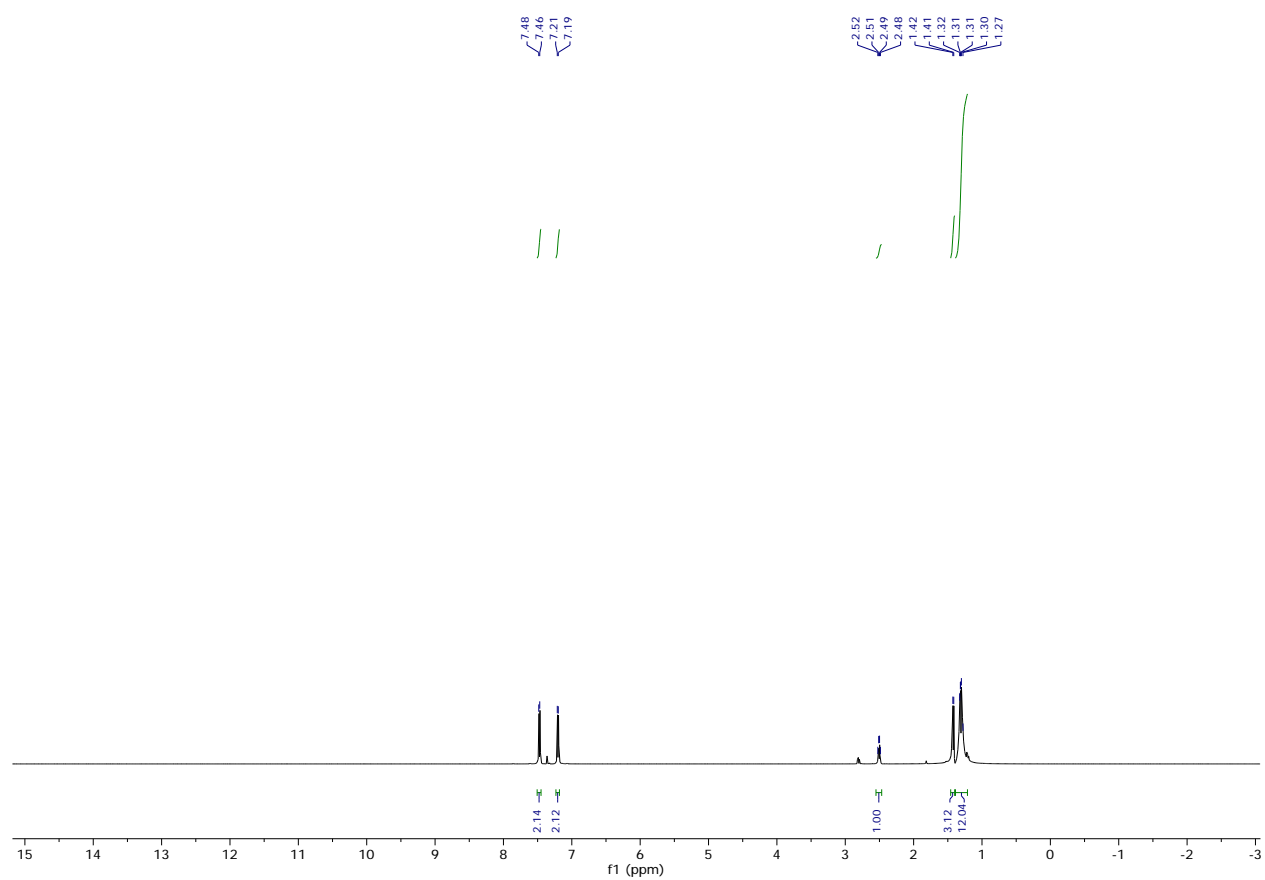


^{13}C NMR (151 MHz, CDCl_3):

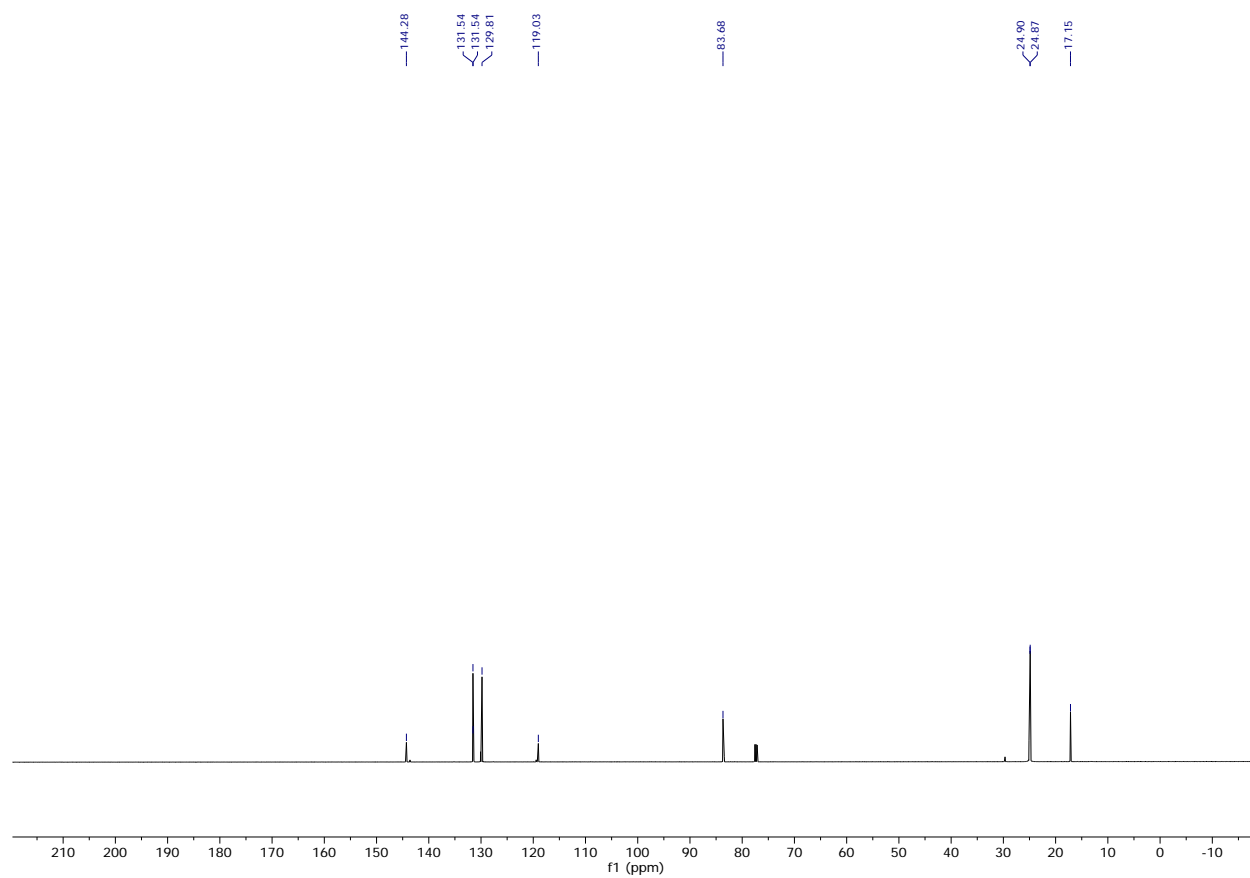


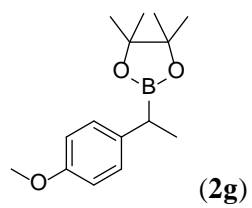


^1H NMR (600 MHz, CDCl_3):

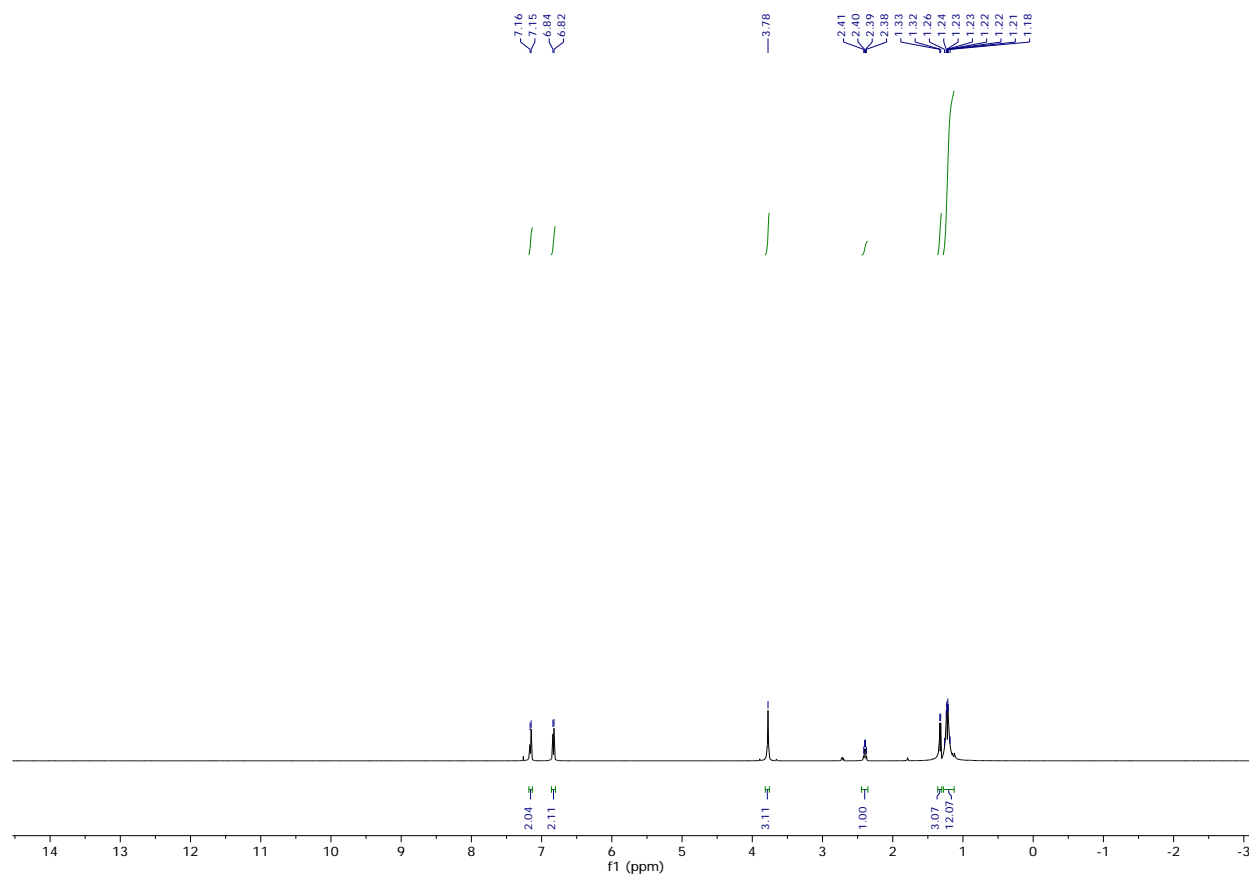


^{13}C NMR (151 MHz, CDCl_3):

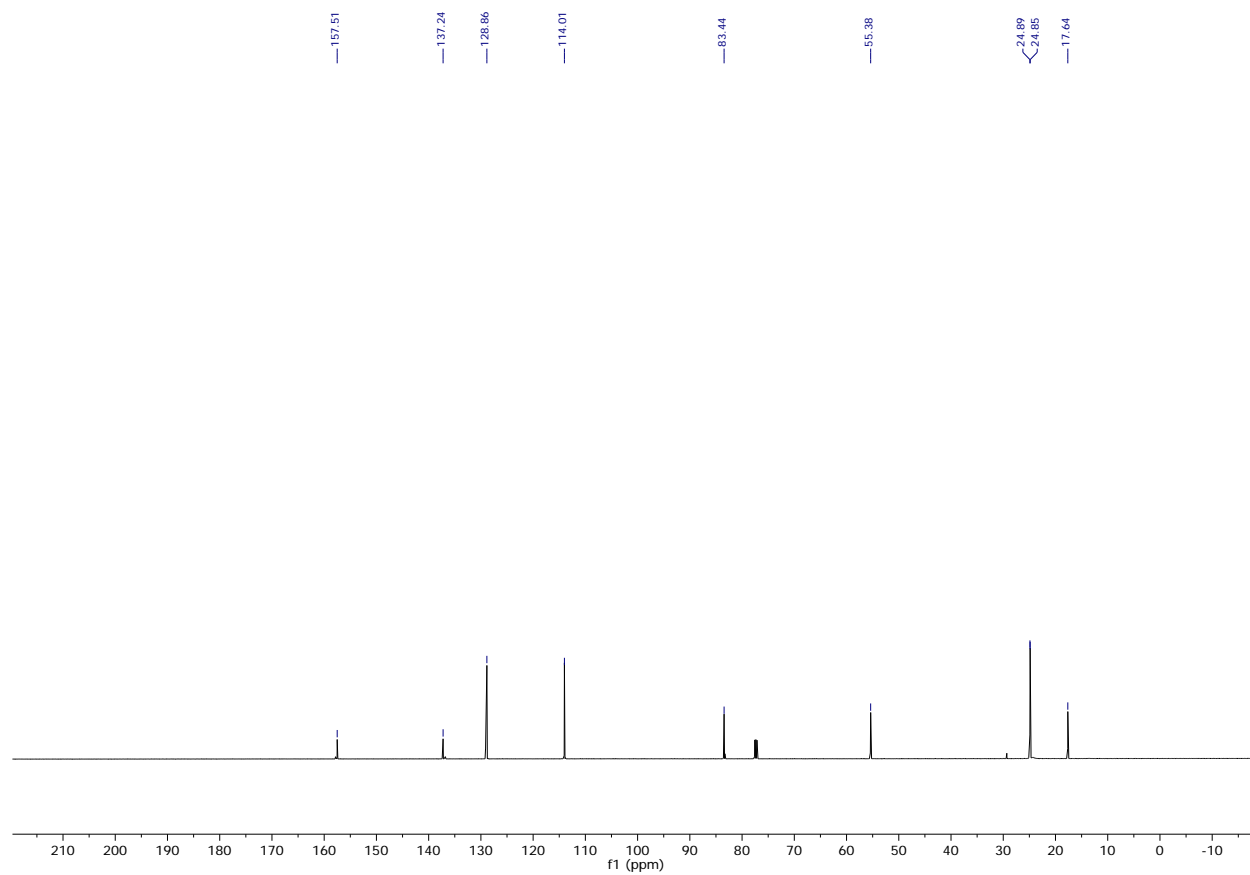


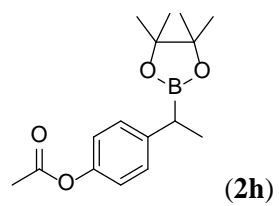


^1H NMR (600 MHz, CDCl_3):

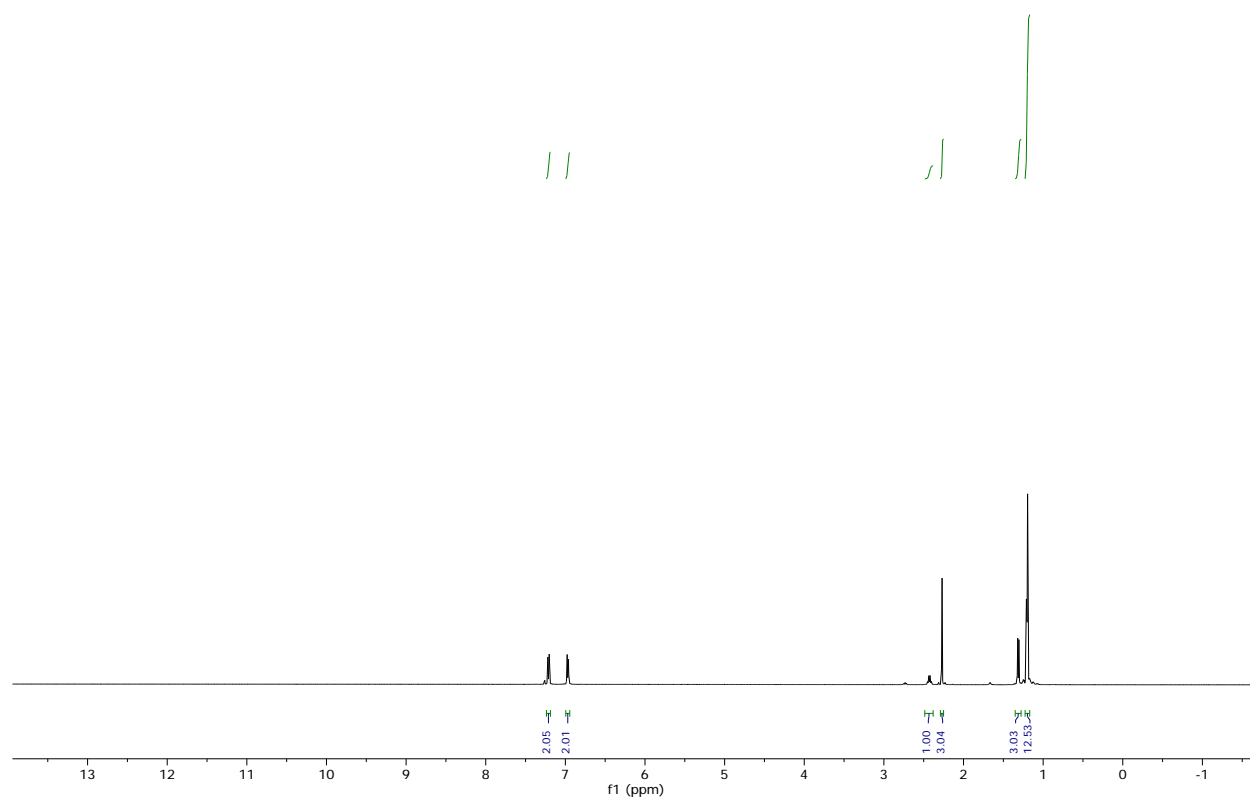


^{13}C NMR (151 MHz, CDCl_3):

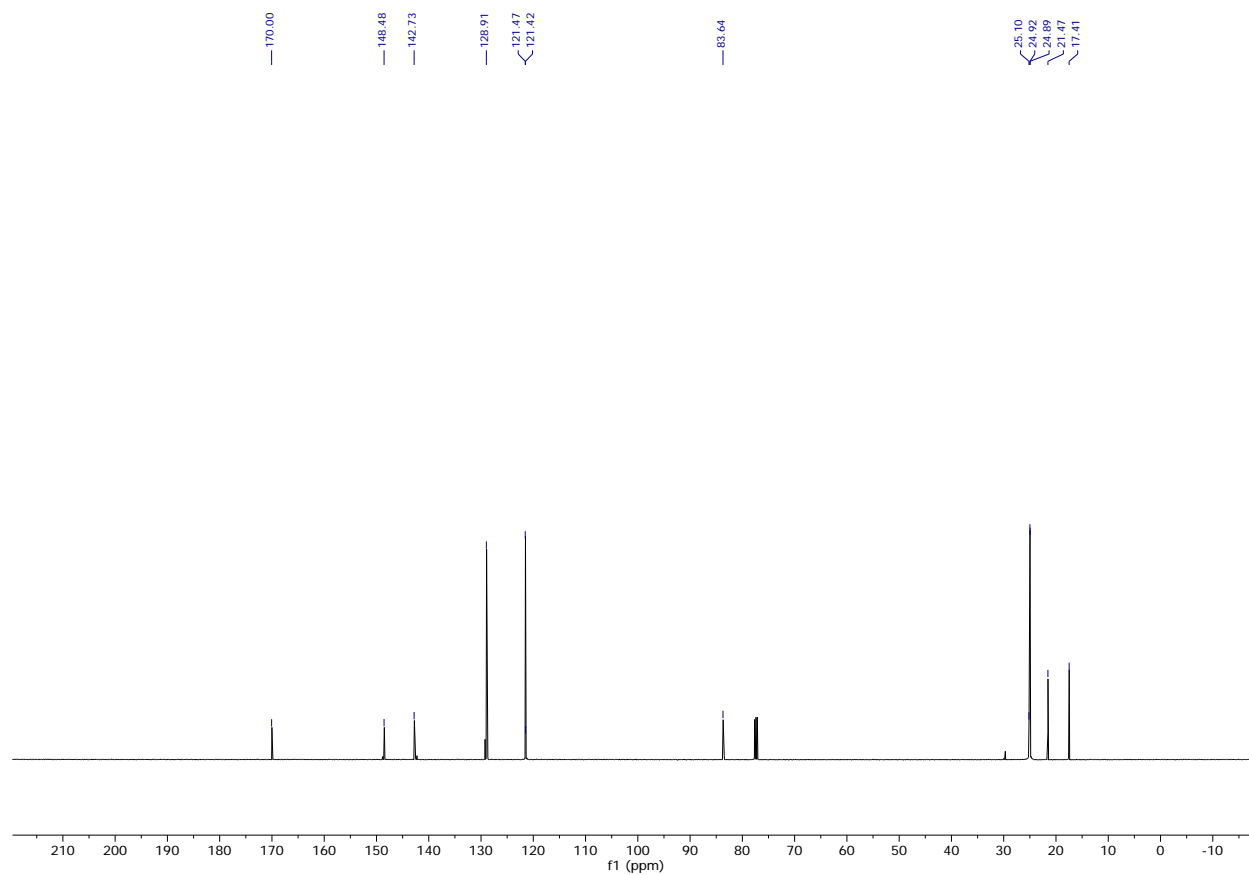


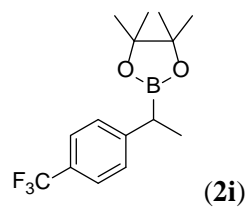


^1H NMR (500 MHz, CDCl_3):

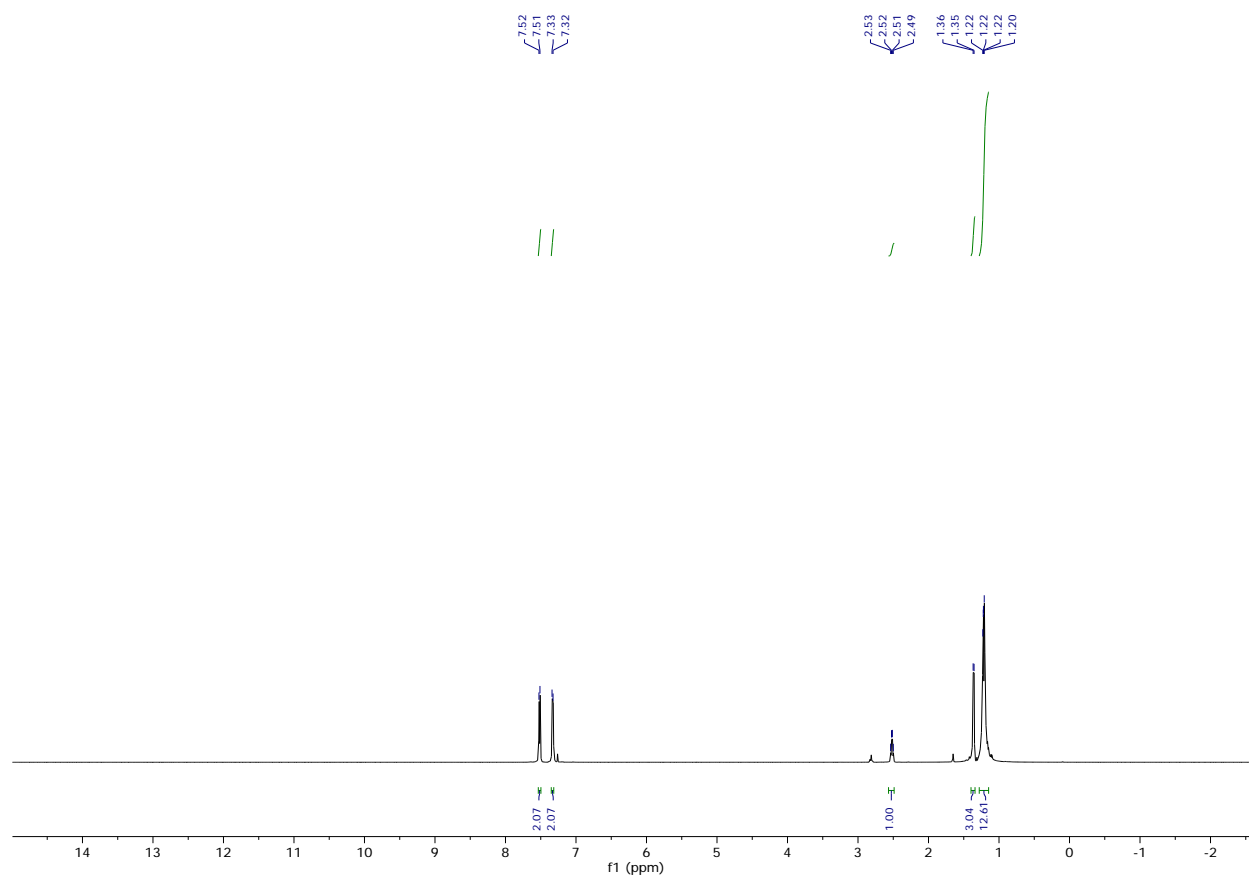


^{13}C NMR (126 MHz, CDCl_3):

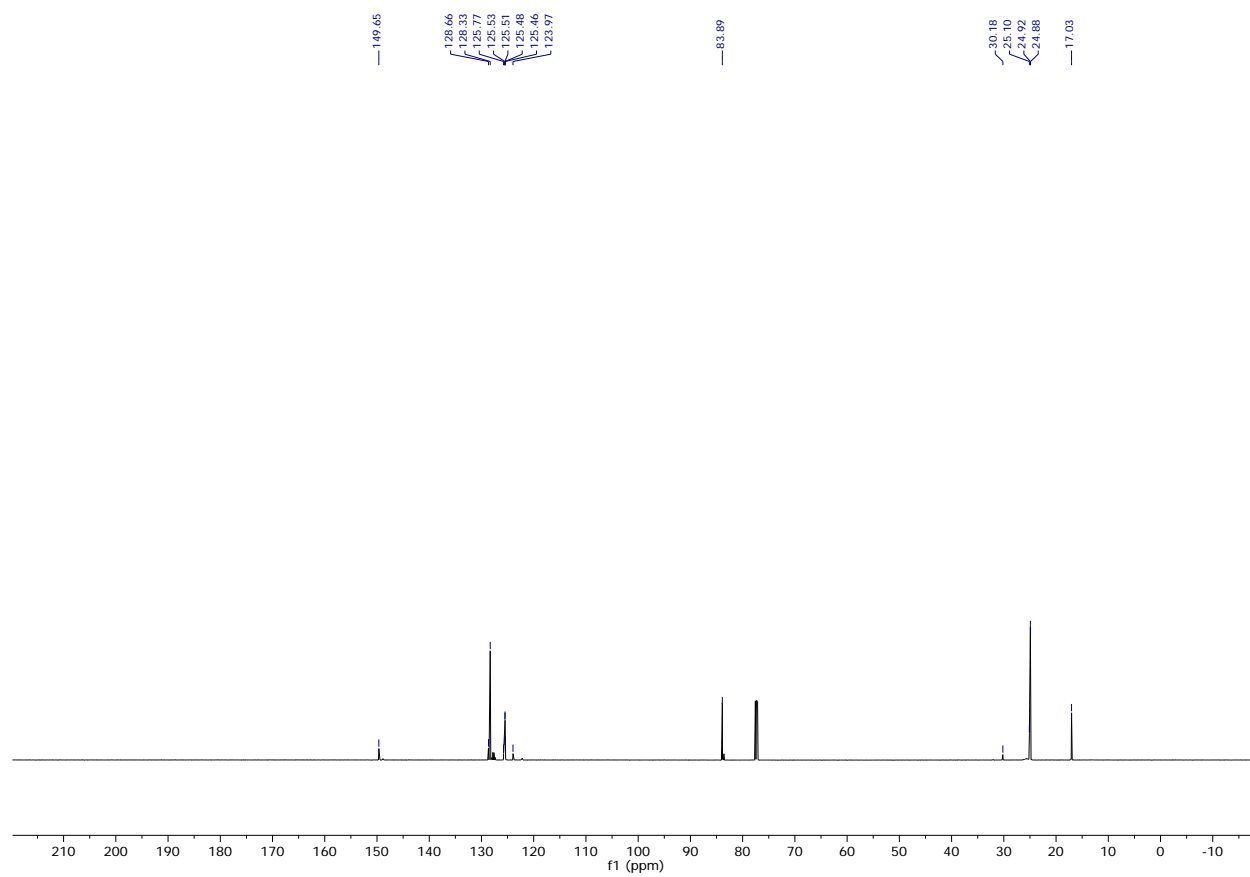


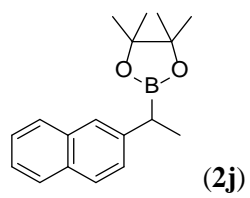


^1H NMR (600 MHz, CDCl_3):

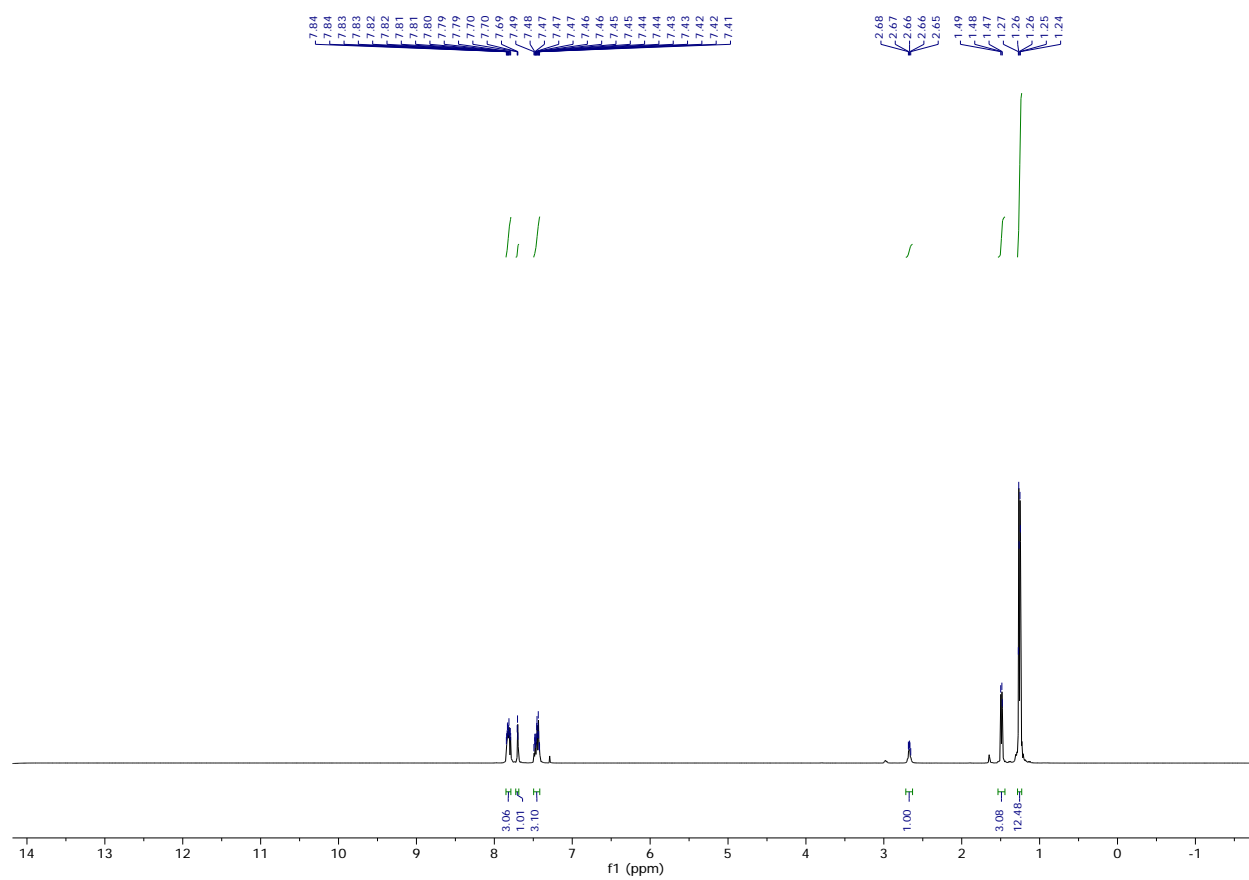


^{13}C NMR (151 MHz, CDCl_3):

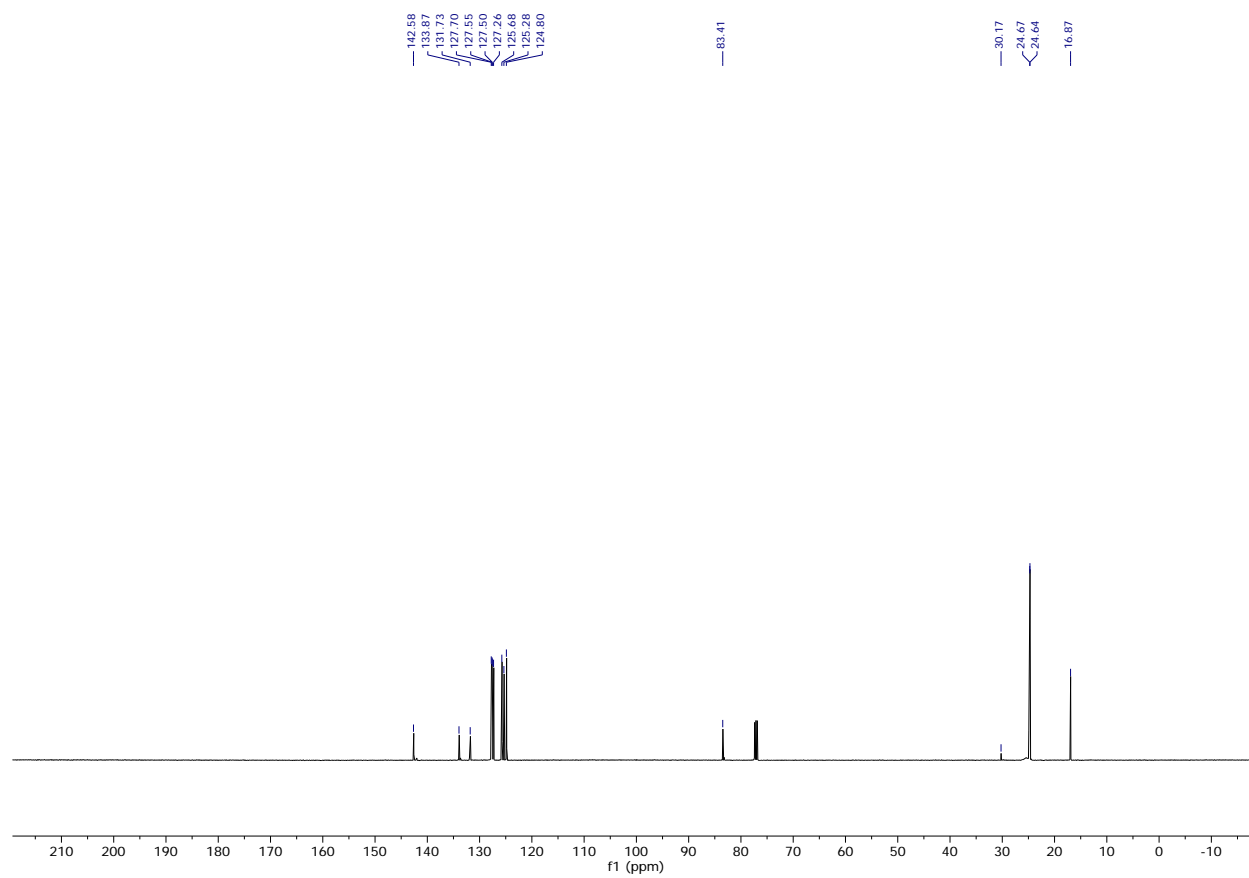


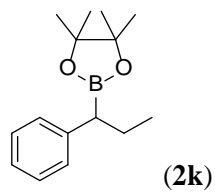


^1H NMR (500 MHz, CDCl_3):

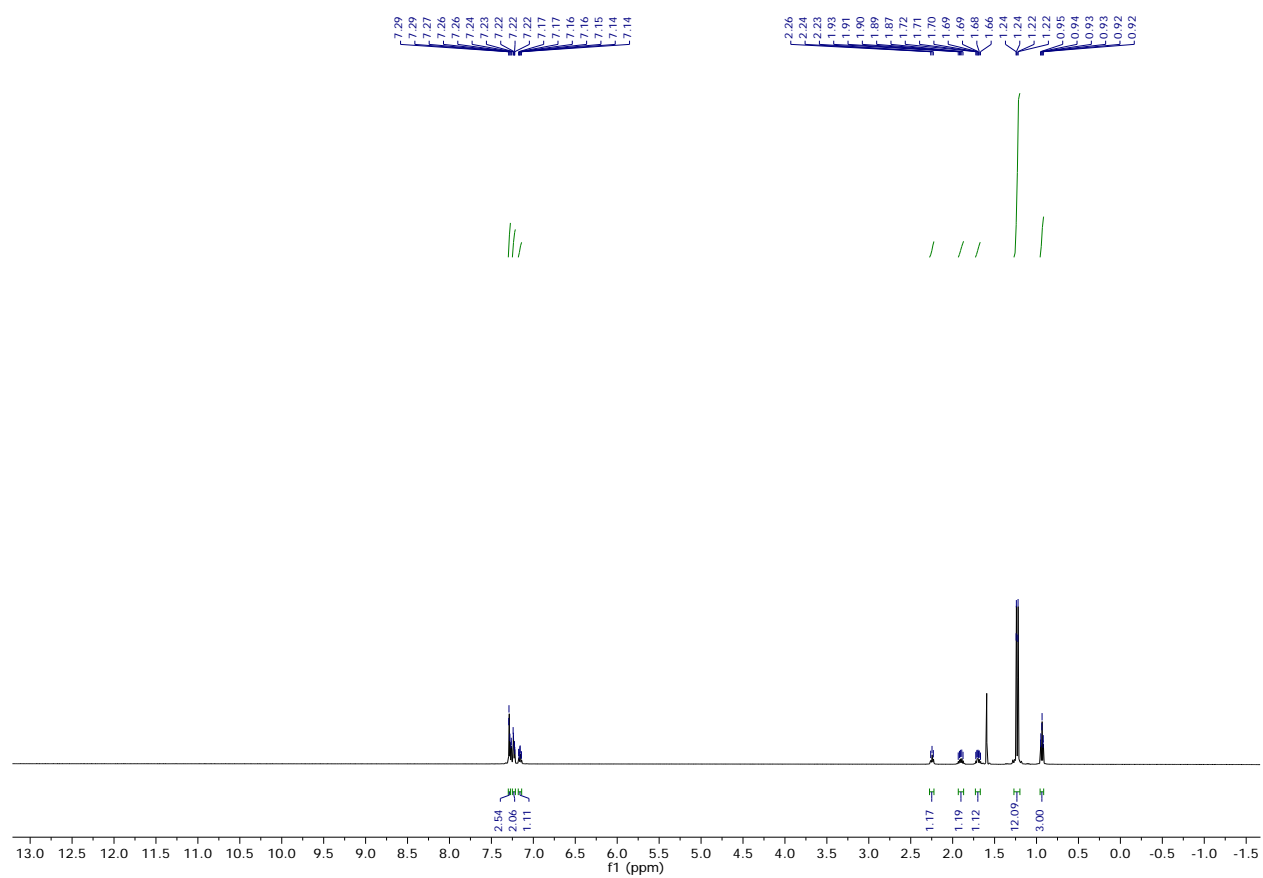


^{13}C NMR (126 MHz, CDCl_3):

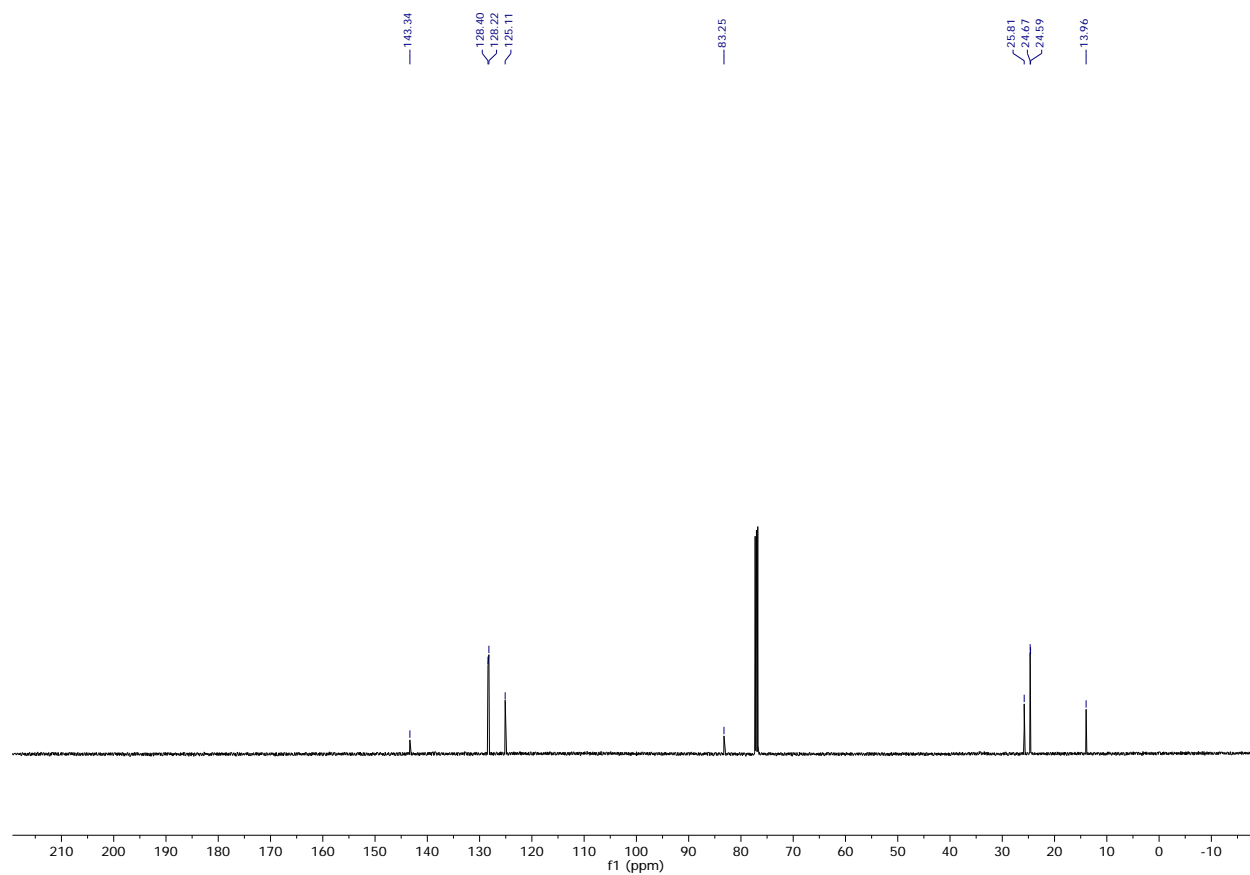


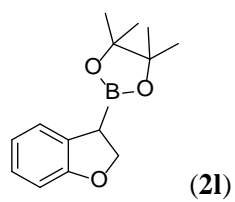


^1H NMR (500 MHz, CDCl_3):

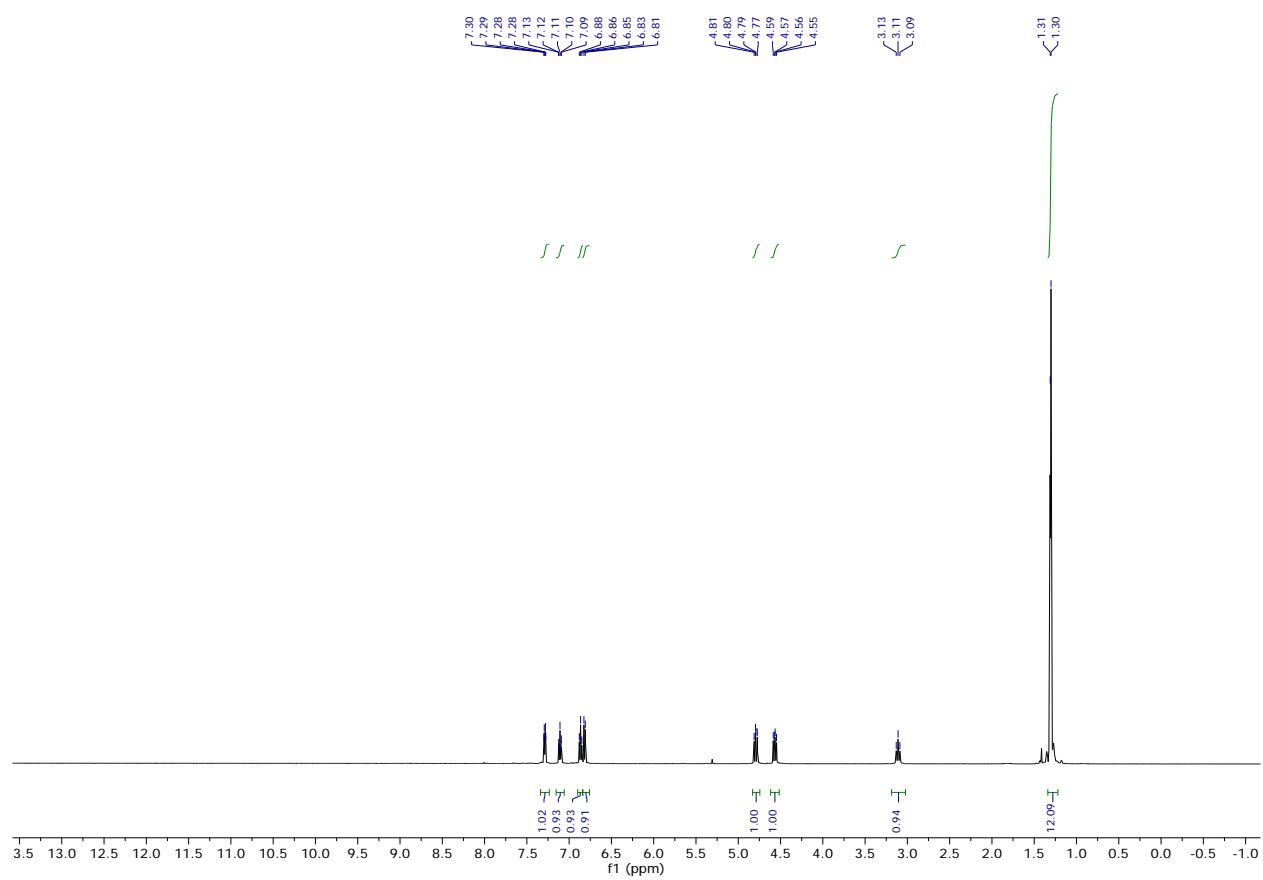


^{13}C NMR (126 MHz, CDCl_3):

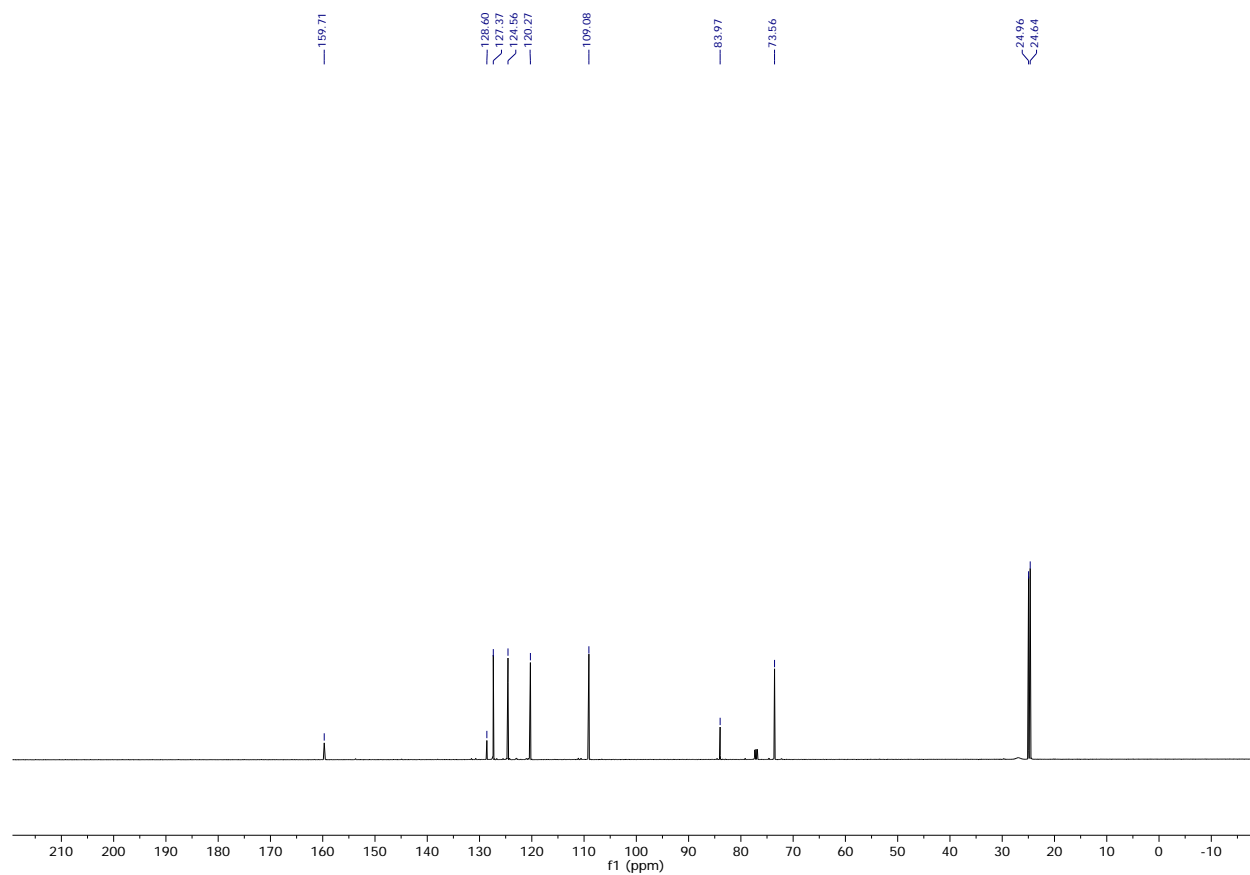


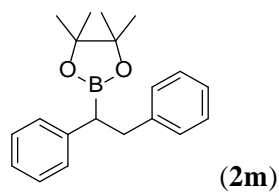


^1H NMR (500 MHz, CDCl_3):

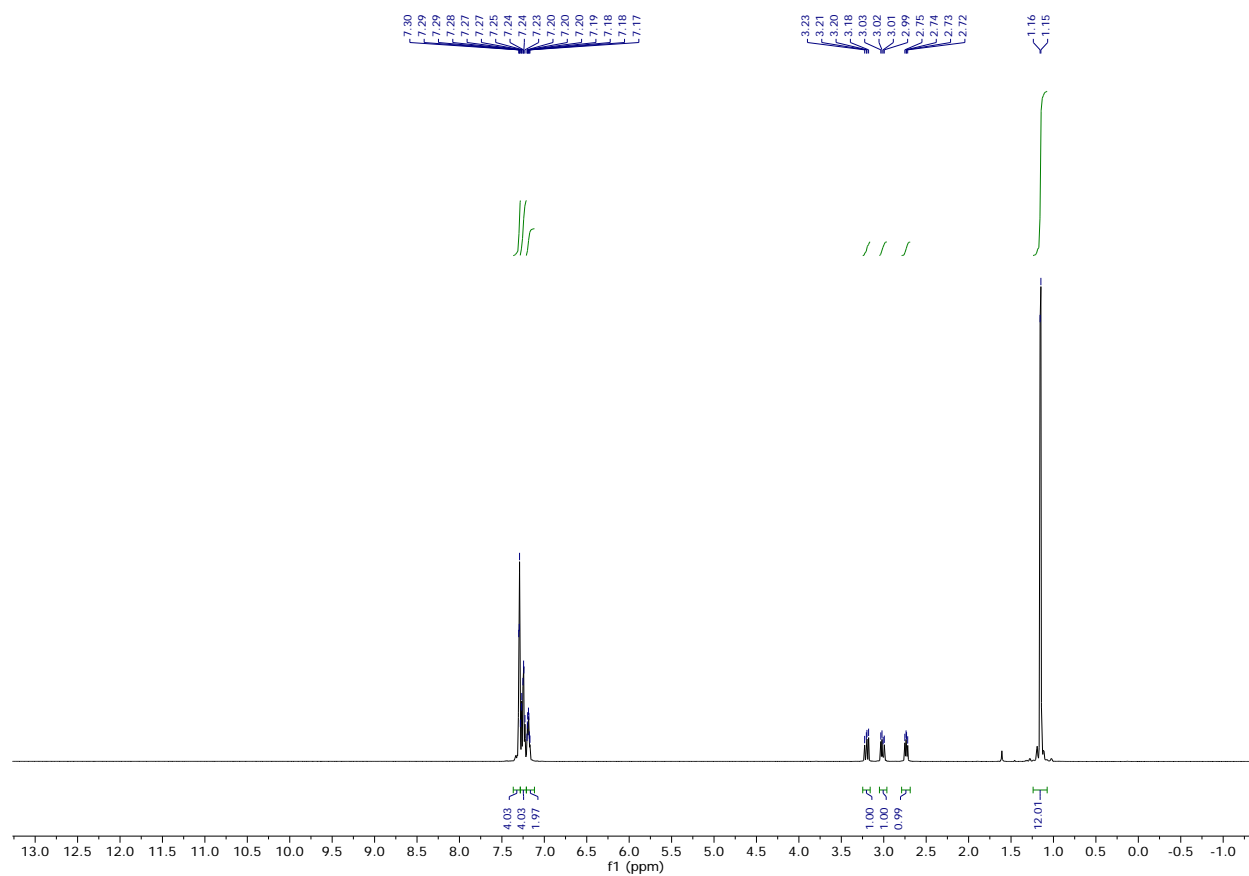


^{13}C NMR (126 MHz, CDCl_3):

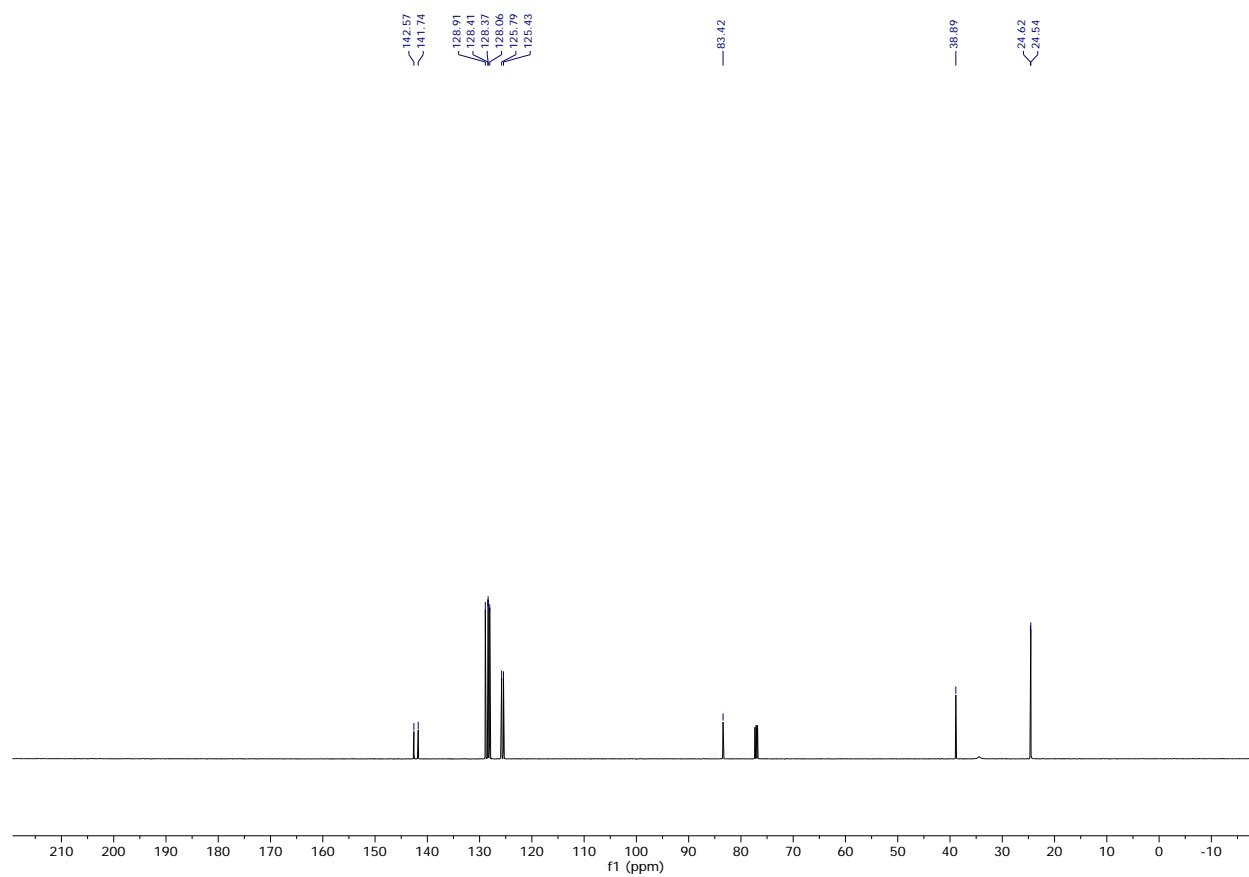


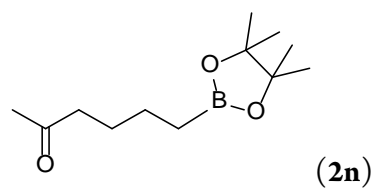


^1H NMR (500 MHz, CDCl_3):

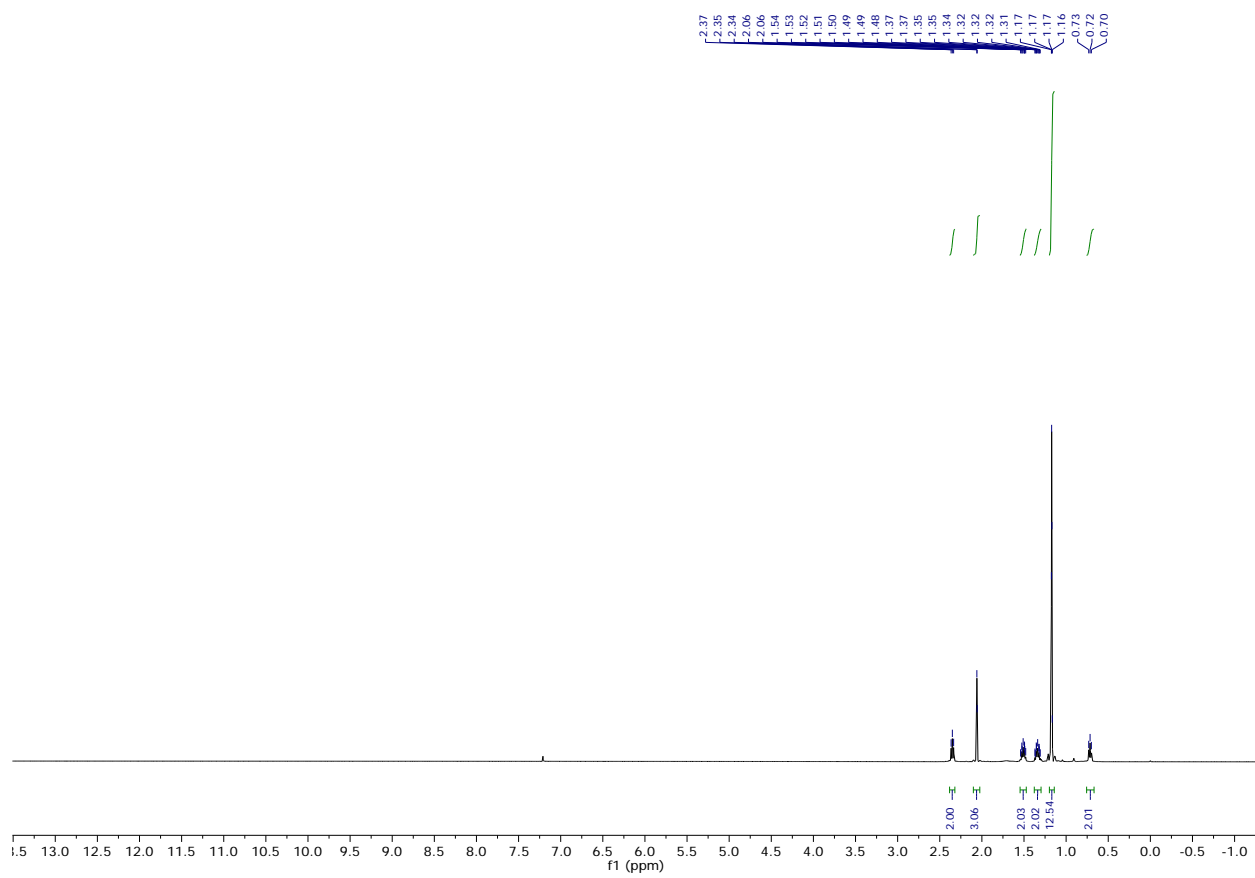


^{13}C NMR (126 MHz, CDCl_3):

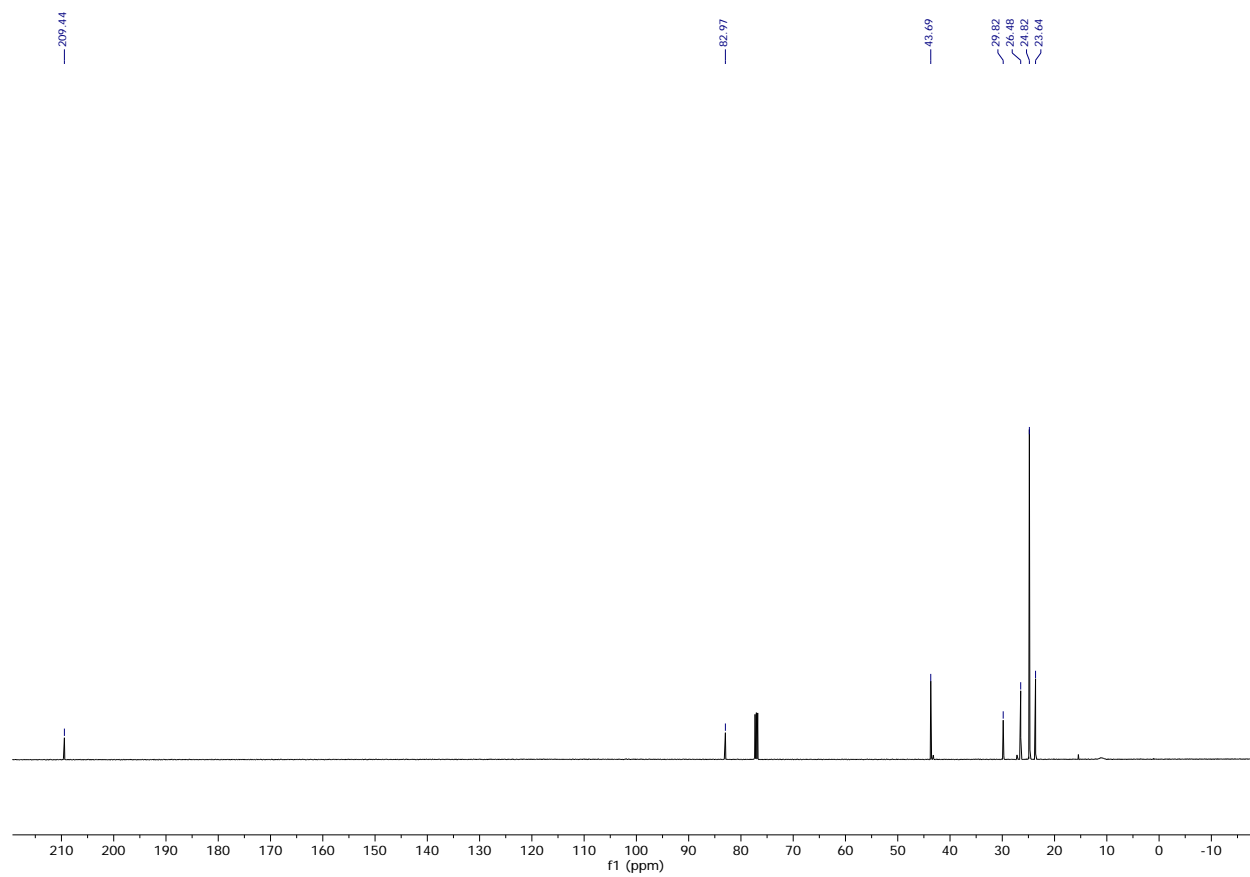


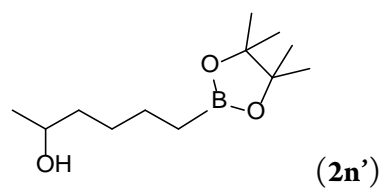


^1H NMR (500 MHz, CDCl_3):

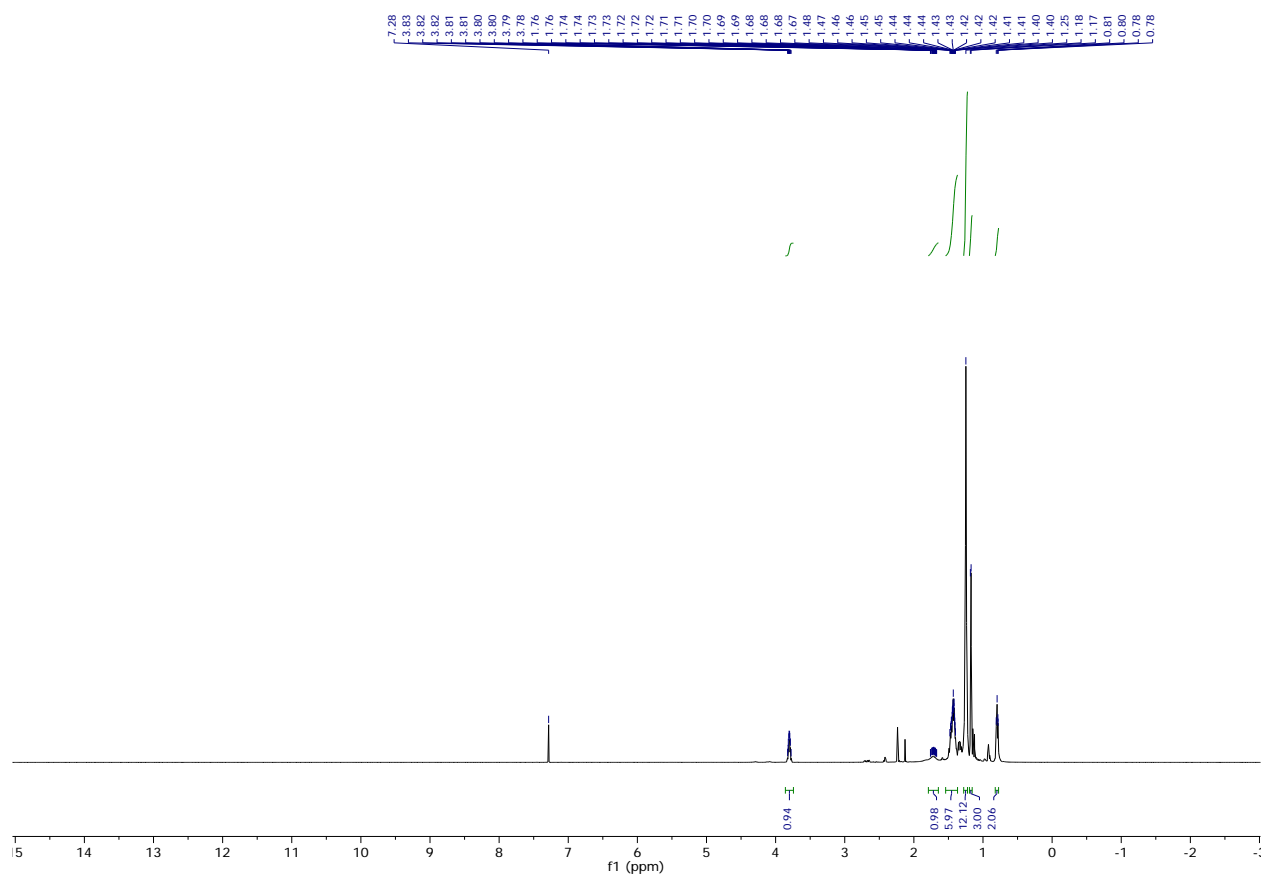


^{13}C NMR (126 MHz, CDCl_3):

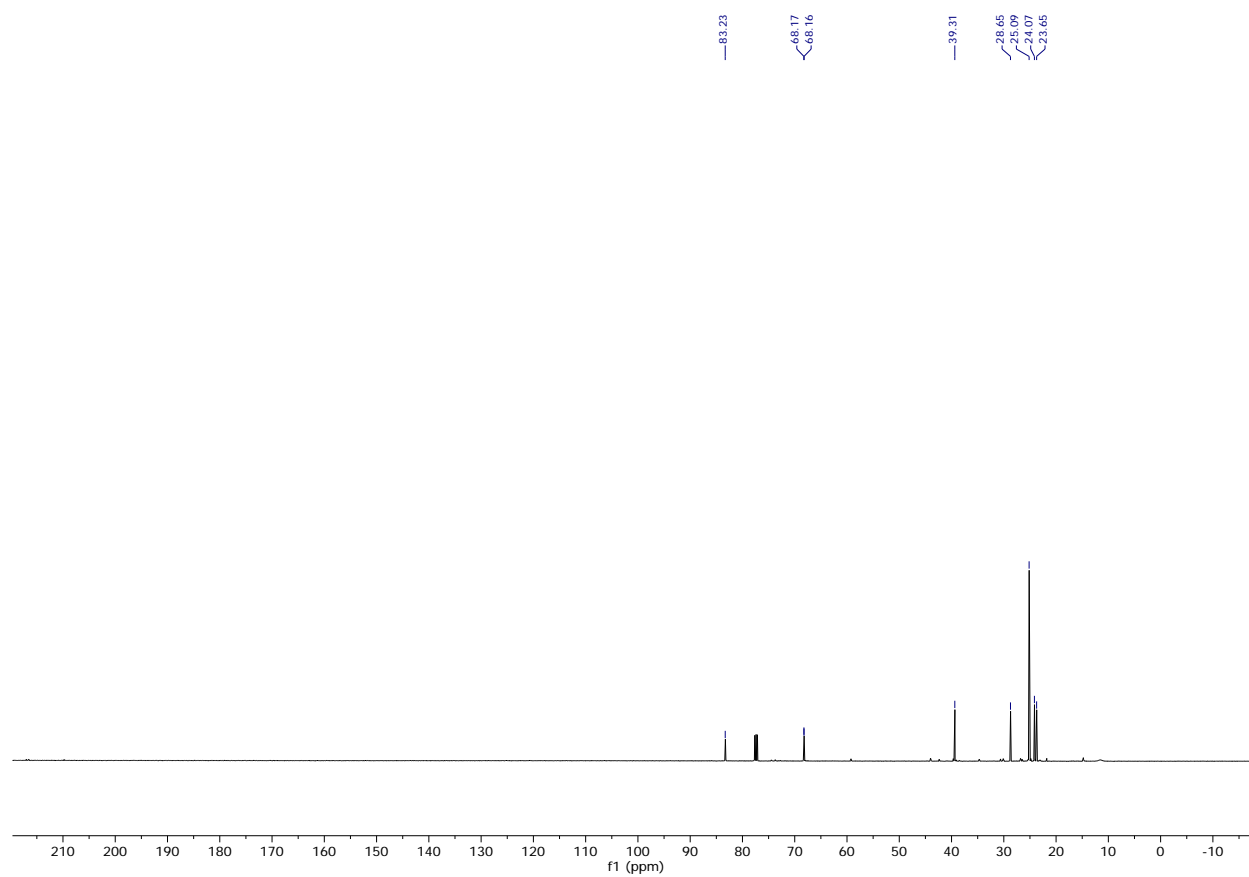




^1H NMR (500 MHz, CDCl_3):



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



References:

- (1) Wu, J.; Zeng, H.; Cheng, J.; Zheng, S.; Golen, G. A.; Manke, D. R.; Zhang, G. *J. Org. Chem.* **2018**, *83*, 9442-9448.
- (2) Zhang, G.; Wu, J.; Wang, M.; Zeng, H.; Cheng, J.; Neary, M. C.; Zheng, S. *Eur. J. Org. Chem.* **2017**, 5814-5818.
- (3) Scheuermann, M. L.; Johnson, E. J.; Chirik, P. J. *Org. Lett.* 2015, *17*, 2716-2719.
- (4) Peng, J.; Docherty, J. H.; Dominey, A. P.; Thomas, S. P. *Chem. Commun.* **2017**, *53*, 4726-4729.