Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Materials

Giant N-heterocyclic carbene-containing macrocycles for cobalt-catalysed hydroboration of alkynes

Guoqi Zhang,*

General Considerations

Unless specified otherwise, all reactions were carried out under a dry nitrogen atmosphere using standard glsovebox and Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Anhydrous grade solvents (stored over 4 Å molecular sieves) and alkyne substrates were purchased from Sigma-Aldrich, Fisher Scientific and TCI America. Pinacolborane was purchased from Acros or Alfa Aesar and redistilled under reduced pressure prior to use. FT-IR spectra were recorded on a Shimadzu 8400S instrument with solid samples under N_2 using a Golden Gate ATR accessory. ^{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. HR-MS data were obtained on an Agilent 6550 QToF coupled to an Agilent 1290 Infinity LC system. GC-MS analysis was obtained using a Shimadzu GCMS-QP2010S gas chromatograph mass spectrometer. Precursor **3** was prepared according to the previous procedure.[1]

Synthesis of 2b

A solution of 1,4-bis(bromomethyl)-2,5-dimethylbenzene (139 mg, 0.47 mmol) in acetonitrile (50 cm^3) was added dropwise to a solution of 2,6-di(1*H*-imidazol-1-yl)pyridine (100 mg, 0.47 mmol) in acetonitrile (80 cm^3) over a period of 4 h. The mixture was then heated to reflux for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was redissolved in water (100 cm^3) and NH_4PF_6 (1.0 g, 6.1 mmol) was added to the solution, which was sonicated for 20 min and then filtered to give a light yellow solid and washed with water. After recrystallization of the crude product with water and acetonitrile, colorless crystals of **2b** were afforded. Yield: 80 mg (26%). FT-IR (solid, cm^{-1}): 1614w, 1538w, 1464m, 1220m, 1114m, 1079m, 1007w, 828s, 737s, 628m. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.40 (s, 2 H), 10.15 (s, 2 H), 8.83 (s, 2 H), 8.72 (d, J = 2.0 Hz, 2 H), 8.63 (t, J = 8.0 Hz, 2 H), 8.26 (d, J = 8.5 Hz, 2 H), 8.22 (d, J = 8.0 Hz, 2 H), 8.09 (t, J = 2.0 Hz, 2 H), 7.99 (s, 2 H), 7.27 (s, 2 H), 7.11 (s, 2 H), 5.56 (s, 8 H), 2.36 (s, 6 H), 2.27 (s, 6 H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.13, 136.09, 135.47, 134.72, 134.18, 133.07, 132.43, 131.07, 130.41, 124.38, 123.52, 120.09, 119.84, 114.90, 114.59, 50.63, 50.44, 18.17 ppm. HR-MS (ESI, positive): m/z 1289.2031 $[M + Na]^+$ (Calcd. 1289.2053); 1121.2511 $[M – PF_6]^+$ (Calcd. 1121.2514).

Synthesis of 4a

To a 100 mL Pyrex tube was added **3** (0.20 g, 0.455 mmol), dibromo-*p*-xylene (0.120 g, 0.455 mmol) and MeCN (10 cm^3) under Ar. The tube was sealed and placed in an oil bath. The reaction was run at 150 °C overnight. The reaction was then cooled to room temperature and filtered. The resulting solid product was suspended in a 100 cm^3 water solution and followed by addition of NH_4PF_6 (1.0 g, 6.1 mmol). The suspension was sonicated for 1 hour and then the solution was filtered, washed with water and dried in vacuo to give a while solid. Yield: 0.315 g (83 %). FT-IR (solid, cm^{-1}): 2975w, 1608m, 1532m, 1462s, 1219s, 981s, 799m, 721m. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.13 (s, 4 H), 8.70 (d, J = 8.5 Hz, 8 H), 8.47 (d, J = 16.0 Hz, 8 H), 8.15-8.01 (m, 16 H), 7.70-7.59 (m, 14 H), 5.58 (s, 8 H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.05, 150.18, 139.69, 137.22, 135.79, 135.34, 135.05, 129.65, 129.15, 128.68, 127.53, 123.21, 122.10, 121.73, 117.82, 52.02 ppm. HR-MS (ESI, positive): m/z 410.4832 $[M - 3(PF_6)]^{3+}$ (calc. 410.4829), 688.2061 $[M - 2(PF_6)]^{2+}$ (calc. 688.2065), 834.1782 $[M + 2H]^{2+}$ (calc. 834.1785).

Synthesis of 4b

4b was prepared according to the same procedure as for **4a**, except the use of 1,4-di(bromomethyl)-3,5-dimethylbenzene (1.01g, 2.16 mmol) as the starting material. **4b** was isolated in 76 % yield (0.72 g) 92 % after anion exchange. Suitable single crystals were obtained by slow evaporation of an acetonitrile/water solution of the product over 2 weeks. FT-IR (solid, cm^{-1}): 2947w, 1599w, 1546m, 1447w, 1398w, 1243m, 1190m, 1072m, 982m, 822s, 738m. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.10 (s, 4 H), 8.70 (d, J = 7.5 Hz, 8 H), 8.51 (s, 4 H), 8.45 (s, 4 H), 8.14 (d, J = 7.0 Hz, 4 H), 8.04 (d, J = 8.0 Hz, 8 H), 7.98 (s, 4 H), 7.63 (m, 6 H), 7.32 (s, 4 H), 5.55 (s, 8 H), 2.40 (s, 12 H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.06, 150.20, 139.68, 137.24, 135.82, 135.35, 134.75, 132.83, 131.25, 129.66, 129.13, 128.63, 127.54, 123.37, 122.15, 121.70, 117.83, 50.12, 18.32 ppm. HR-MS (ESI, positive): m/z 285.6362 $[M - 4(PF_6)]^{4+}$ (the only peak, calc. 285.6356).

General Procedure for Catalytic Hydroboration of Alkynes. In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. Alkynes (1.0 mmol) and pinacolborane (1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The

crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (SiO_2) using ethyl acetate/hexane as an eluent. The alkenylboronate product was characterized by ^{1}H and ^{13}C NMR spectroscopies.

X-ray Structural Determinations

Suitable crystal of the compound **2b** was mounted on Cryoloops with Paratone-N oil. Data were collected with a Bruker APEX II CCD using Mo-Kα radiation and corrected for absorption with SADABS and structures solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2. Hydrogen atoms were found from Fourier difference maps and refined isotropically, otherwise they were placed in calculated positions with appropriate riding parameters. For **4b**, a small colorless rod with approximate orthogonal dimensions 0.047 × 0.057 × 0.168 mm^3 was placed and optically centered on the Bruker Venture Photon 100 CMOS system at –83 °C (190 K). Indexing of the unit cell used a random set of reflections collected from three series of 0.5° wide omega-scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Data were collected on a Cu-Ka radiation with 0.5° wide scans, variable time per frame dependent upon detector 2θ angle and varying phi and omega angles such that nearly all unique reflections were collected at least once but owing to the weak diffraction the data collection was abandoned with some high angle data missing. The crystal to detector distance was 5.00 cm, thus providing a complete sphere of data to $2\theta_{max}$ = 135.93°.

For refinement details: all crystallographic calculations were performed on an Intel Xeon E5-1620v2 at 3.70GHz an eight core processor and 16 GB of extended memory. Data collected were corrected for Lorentz and polarization effects with Saint[2] and absorption using Blessing's method and merged as incorporated with the program Sadabs.[3,4] The SHELXTL[5] program package was implemented to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences and intensity statistics indicated the centrosymmetric triclinic space group P-1 (no. 2). The structure was determined by direct methods with a majority of the fully occupied non-hydrogen atoms being located directly using the program XT.[6] The structure refined with XL.[7] The data collected were merged for least squares refinement to 5112 unique data [R(int)=0.0316]. The main molecule suffers a disorder in a terminal phenyl group that is directly linked to the presence of acetonitrile at 50:50. Two independent PF_6^- ions were located and refined

with one ordered and the other suffering from rotational disorder in one plane of the molecule that was optimized to 0.63:0.37. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and throughout the final refinement stages. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. We were unable to obtain better quality of single crystals for this compound, considering its difficulty in crystallization.

CCDC Nos. 2171899 and 2171900 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Figures for crystal structures were drawn with the program Mercury v. 2.4. The crystallographic refinement data are listed below.

2b: $C_{21}H_{21}F_{12}N_5P_2$, M = 394.43, colorless block, triclinic, space group P-1, a = 9.2706(3), b = 9.6225(3), c = 14.6054(5) Å, α = 88.2720(10), β = 72.8160(10), γ = 83.8840(10), U = 1237.65(7) Å^3, Z = 2, D_c = 1.700 Mg m^{-3}, μ(Mo-Kα) = 0.289 mm^{-1}, T = 100(2) K. Total 21658 reflections, 3965 unique. Refinement of 4545 reflections (363 parameters) with I >2σ (I) converged at final R_1 = 0.0376 (R_1 all data = 0.0435), wR_2 = 0.0973 (wR_2 all data = 0.1022), GOF = 1.053.

4b: $C_{84}H_{75}F_{24}N_{13}P_4$, M = 1846.45, colorless block, triclinic, space group P-1, a = 8.9230(3), b = 12.4296(3), c = 18.4932(6) Å, α = 88.9900(18), β = 87.0124(19), γ = 85.1082(17), U = 2026.52(11) Å^3, Z = 1, D_c = 1.513 Mg m^{-3}, μ(Mo-Kα) = 1.842 mm^{-1}, T = 100(2) K. Total 8389 reflections, 3336 unique. Refinement of 5112 reflections (667 parameters) with I >2σ (I) converged at final R_1 = 0.0555 (R_1 all data = 0.0997), wR_2 = 0.1275 (wR_2 all data = 0.1461), GOF = 1.027.

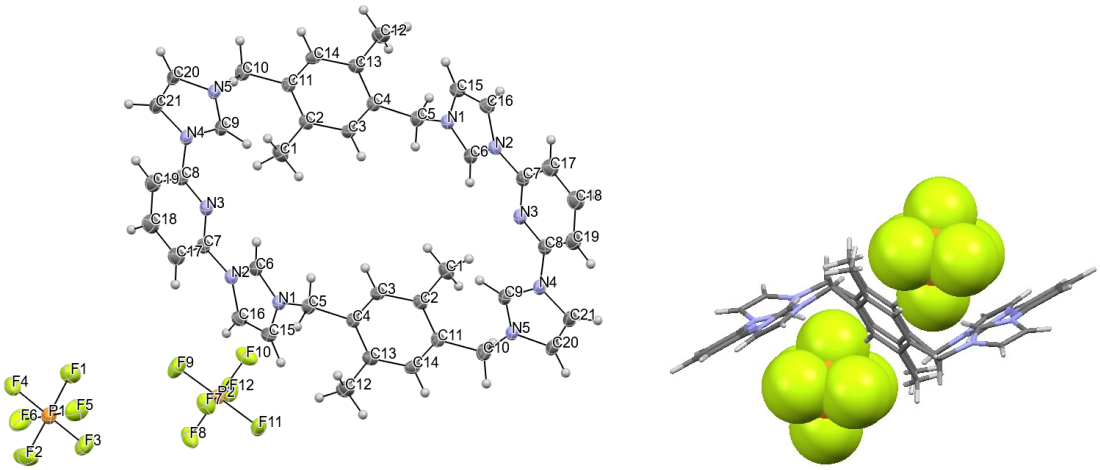


Fig. S1. (a) The ORTEP structure of **2b** drawn with ellipsoids at 50% thermal probability showing the atomic displacement parameters. (b) The space-filling representation of **2b** showing a "partial chair" conformation with two of its PF_6^- counteranions in the cell.

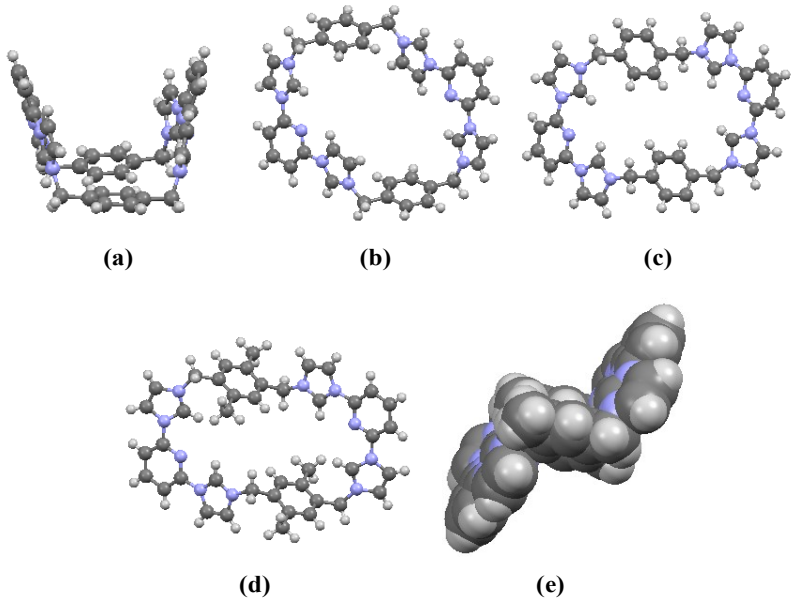


Fig. S2. The distinct conformations found in the polymorphs of TxSB **2a** and **2b** crystals. For **2a**: (a) "boat" conformer; (b) "partial chair" conformer; and (c) "chair" conformer; for **2b**: (d) "chair" conformer and (e) a side-view of the chair with space-filling representation.

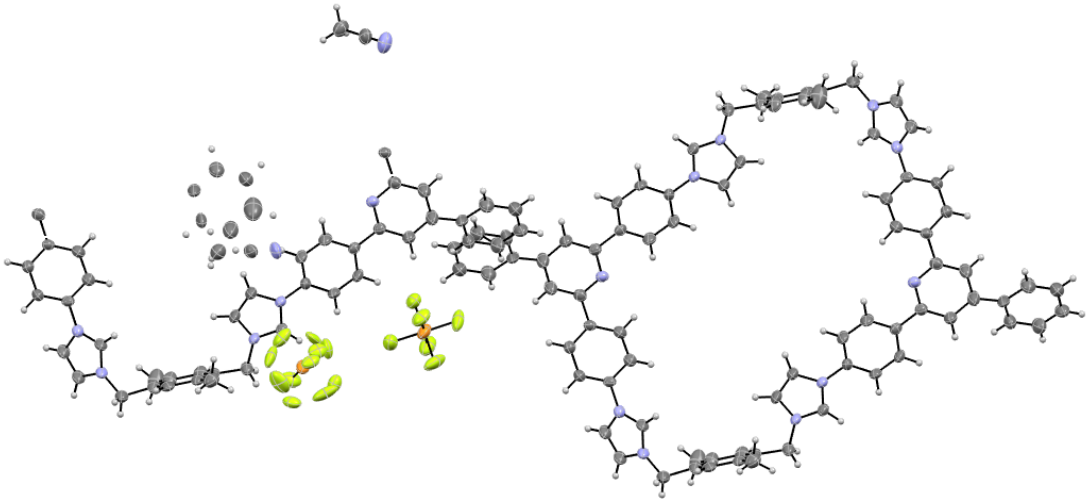
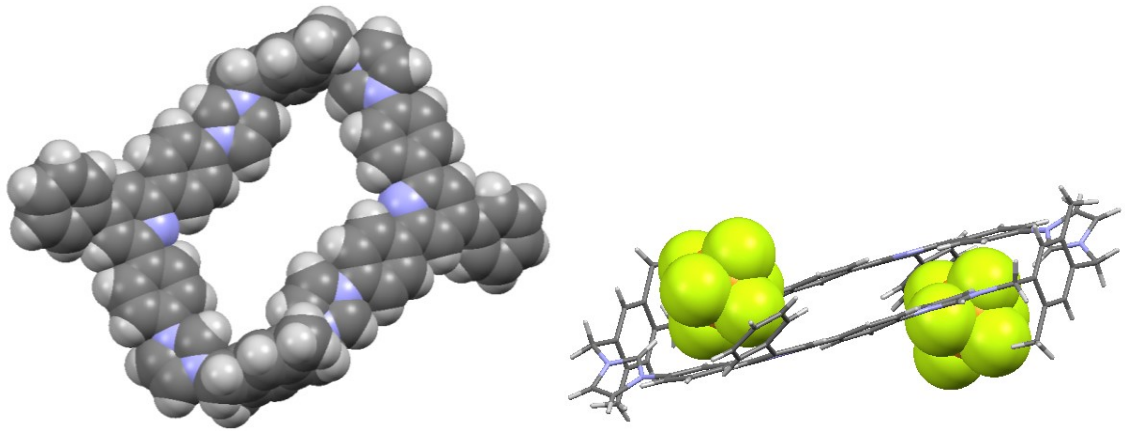


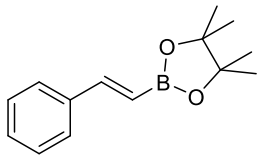
Fig. S3. The ORTEP structure of **4b** in the unit cell drawn with ellipsoids at 50% thermal probability, showing the actual atomic displacement parameters.



(a) **(b)**

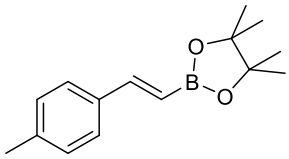
Fig. S4. (a) The space-filling representation of **4b** showing a "partial chair" conformation. (b) The side-view of **4b** showing two of the PF_6^- anions locating at above or below the macrocycle.

Catalytic details and characterization data



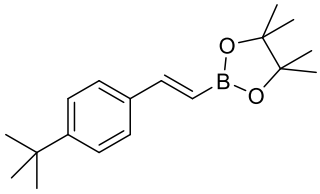
Chemical Formula: $C_{14}H_{19}BO_2$
Molecular Weight: 230.1140

5a:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. Phenylacetylene (102 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS. The GC yield was determined to be 83%, corresponding to a turnover number (TON) of 830 and a turnover frequency (TOF) of 52 h^{-1}. The mixture was then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give colorless oil. Yield: 166 mg (72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.41 (d, *J* = 18.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.18 (d, *J* = 18.5 Hz, 1H), 1.32 (s, 13H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 137.6, 129.0, 128.7, 127.2, 83.5, 29.8, 24.9 ppm. GC-MS (m/z): 230 (calc. 230).



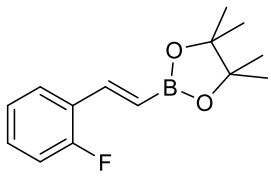
Chemical Formula: $C_{15}H_{21}BO_2$
Molecular Weight: 244.1410

5b:[9] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. *p*-Tolylacetylene (166 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give colorless oil. Yield: 185 mg (76%). δ ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.36 (m, overlapping, 1H,), 7.15 (d, *J* = 8.2 Hz, 2H), 6.12 (d, *J* = 18.5 Hz, 1H), 2.35 (s, 3H), 1.32 (s, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.6, 139.1, 134.9, 129.4, 127.1, 83.4, 24.9, 21.4 ppm. GC-MS (m/z): 244 (calc. 244).



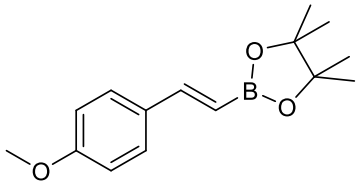
Chemical Formula: $C_{18}H_{27}BO_2$
Molecular Weight: 286.2220

5c:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 4-*tert*-Butylphenylacetylene (158 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give colorless oil. Yield: 200 mg (70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.35 (m, *overlapping*, 2H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.320 (s, *overlapping*, 9H,), 1.317 (s, *overlapping*, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.3, 149.5, 134.9, 127.0, 125.6, 83.4, 34.8, 31.4, 25.0 ppm. GC-MS (m/z): 286 (calc. 286).



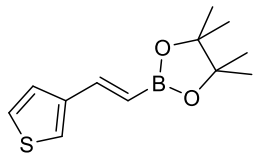
Chemical Formula: $C_{14}H_{18}BFO_2$
Molecular Weight: 248.1044

5d:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 4-Fluorophenylacetylene (120 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give yellowish oil. Yield: 112 mg (45%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, overlapping, 2H), 7.21 – 7.16 (m, 1H), 7.04 (t, J = 7.1 Hz, 1H), 6.96 (dd, J = 10.7, 8.2 Hz, 1H), 6.16 (d, J = 18.6 Hz, 1H), 1.24 (s, 13H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7 (d, J = 251.5 Hz), 141.3 (d, J = 4.0 Hz), 130.2 (d, J = 8.3 Hz), 127.4 (d, J = 3.3 Hz), 124.1 (d, J = 3.3 Hz), 115.8 (d, J = 22.0 Hz), 83.5, 24.8 ppm. GC-MS (m/z): 248 (calc. 248).



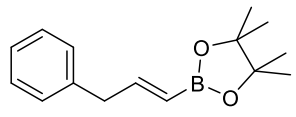
Chemical Formula: $C_{15}H_{21}BO_3$
Molecular Weight: 260.1400

5e:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 4-Ethynylanisole (132 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give yellowish oil. Yield: 166 mg (64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.35 (d, J = 18.4 Hz, 1H), 6.91 – 6.81 (m, 2H), 6.01 (d, J = 18.4 Hz, 1H), 3.80 (s, 3H), 1.30 (s, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 149.2, 130.5, 128.6, 114.1, 83.3, 55.4, 24.9 ppm. GC-MS (m/z): 260 (calc. 260).



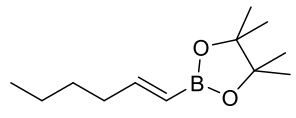
Chemical Formula: $C_{12}H_{17}BO_2S$
Molecular Weight: 236.1360

5f:[9] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 3-Ethynylthiophene (108 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give brownish solid. Yield: 182 mg (77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, J = 18.4 Hz, 1H), 7.26 – 7.20 (m, overlapping, 2H), 7.18 (t, J = 4.1 Hz, 1H), 5.87 (d, J = 18.4 Hz, 1H), 1.23 (s, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 141.3, 126.1, 125.0, 124.9, 83.3, 24.8 ppm. GC-MS (m/z): 236 (calc. 236).



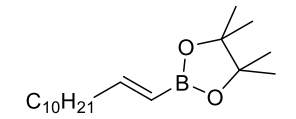
Chemical Formula: $C_{15}H_{21}BO_2$
Molecular Weight: 244.1410

5g:[9] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 3-Phenyl-1-propyne (116 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:20, v/v) as an eluent to give colorless oil. Yield: 154 mg (63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (q, J = 7.6 Hz, 2H), 7.21 (p, J = 6.4, 5.9 Hz, 3H), 6.79 (dt, J = 17.9, 6.5 Hz, 1H), 5.47 (dd, J = 17.3, 4.9 Hz, 1H), 3.51 (d, J = 6.4 Hz, 2H), 1.28 (s, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.6, 139.2, 129.1, 128.6, 126.3, 83.3, 42.4, 24.9 ppm. GC-MS (m/z): 244 (calc. 244).



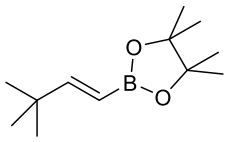
Chemical Formula: $C_{12}H_{23}BO_2$
Molecular Weight: 210.1240

5h:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 1-Hexyne (82 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent to give colorless oil. Yield: 178 mg (85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 – 6.59 (m, 1H), 5.42 (dt, J = 18.0, 1.9 Hz, 1H), 2.21 – 2.11 (m, 2H), 1.43 – 1.37 (m, 2H), 1.33 (t, J = 7.6 Hz, 2H), 1.26 (t, J = 2.3 Hz, 12H), 0.89 (td, J = 7.3, 2.6 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 83.1, 35.6, 30.5, 24.9, 22.4, 14.0 ppm. GC-MS (m/z): 210 (calc. 210).



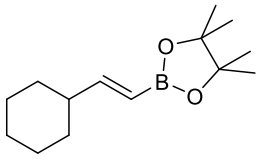
Chemical Formula: $C_{18}H_{35}BO_2$
Molecular Weight: 294.2860

5i:[9] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 1-Dodecyne (166 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent to give colorless oil. Yield: 165 mg (56%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.63 (d, J = 18.0 Hz, 1H), 5.42 (d, J = 18.0 Hz, 1H), 2.17 – 2.10 (m, 2H), 1.40 (q, J = 7.2 Hz, 2H), 1.25 (s, overlapping, 12H), 1.25 (s, overlapping, 14H), 0.88 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 83.1, 36.0, 32.1, 29.8, 29.7, 29.7, 29.5, 29.4, 28.4, 24.9, 22.8, 14.3 ppm. GC-MS (m/z): 294 (calc. 294).



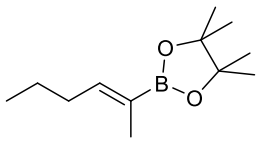
Chemical Formula: $C_{12}H_{23}BO_2$
Molecular Weight: 210.1240

5j:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 1-tert-Butylacetylene (82 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent to give colorless oil. Yield: 193 mg (92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.62 (d, J = 18.4 Hz, 1H), 5.34 (d, J = 18.3 Hz, 1H), 1.25 (s, 12H), 1.00 (s, 9H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 83.1, 35.1, 28.9, 24.9 ppm. GC-MS (m/z): 210 (calc. 210).



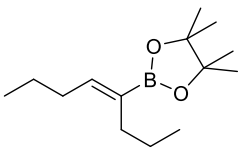
Chemical Formula: $C_{14}H_{25}BO_2$
Molecular Weight: 236.1620

5k:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 1-Cyclohexylacetylene (108 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent to give colorless oil. Yield: 177 mg (75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.58 (dd, J = 18.2, 6.2 Hz, 1H), 5.38 (dd, J = 18.2, 1.5 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.73 (td, J = 13.6, 6.6 Hz, 4H), 1.64 (dd, J = 12.8, 1.7 Hz, 1H), 1.27 (s, overlapping, 12H), 1.25 – 1.22 (m, overlapping, 2H), 1.19 – 1.06 (m, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 83.1, 43.4, 32.1, 26.3, 26.1, 24.9 ppm. GC-MS (m/z): 236 (calc. 236).



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

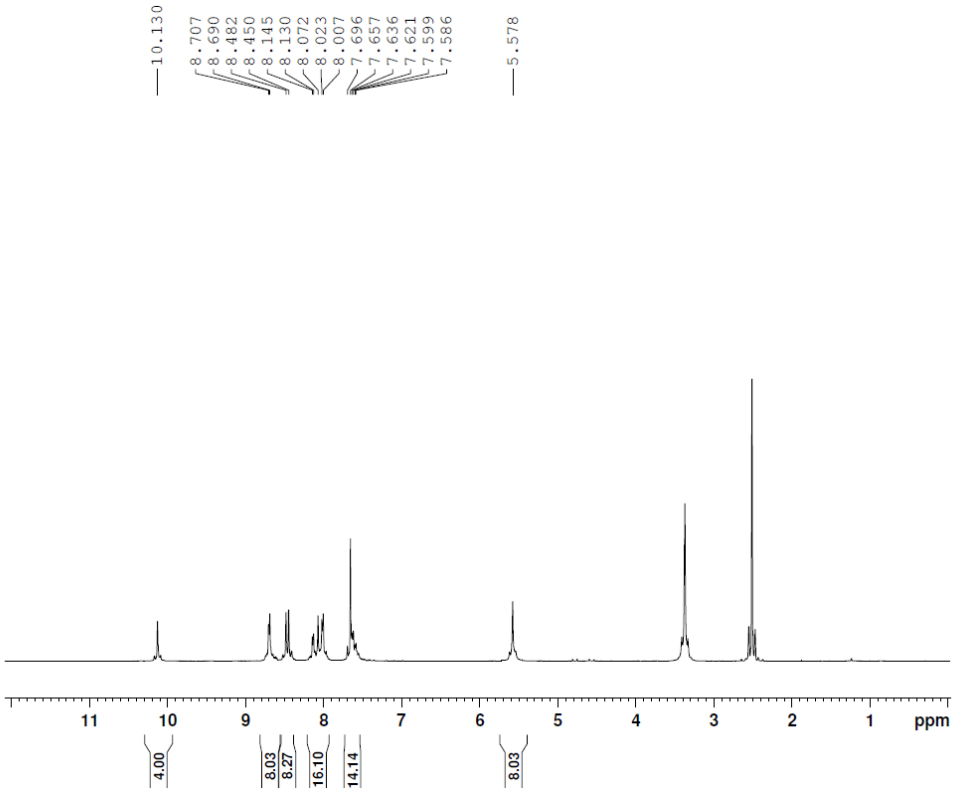
5l:[9] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 2-Hexyne (82 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent to give colorless oil. Yield (mixture, **5l** : regioisomer = 2:1): 168 mg (80%). **5l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 – 6.28 (m, 1H), 2.11 – 2.07 (m, 2H), 1.66 (s, 3H), 1.45 – 1.39 (m, 2H), 1.25 (s, 12H), 0.90 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 83.2, 30.9, 24.9, 24.9, 22.2, 14.2, 14.0 ppm. GC-MS (m/z): 210 (calc. 210).

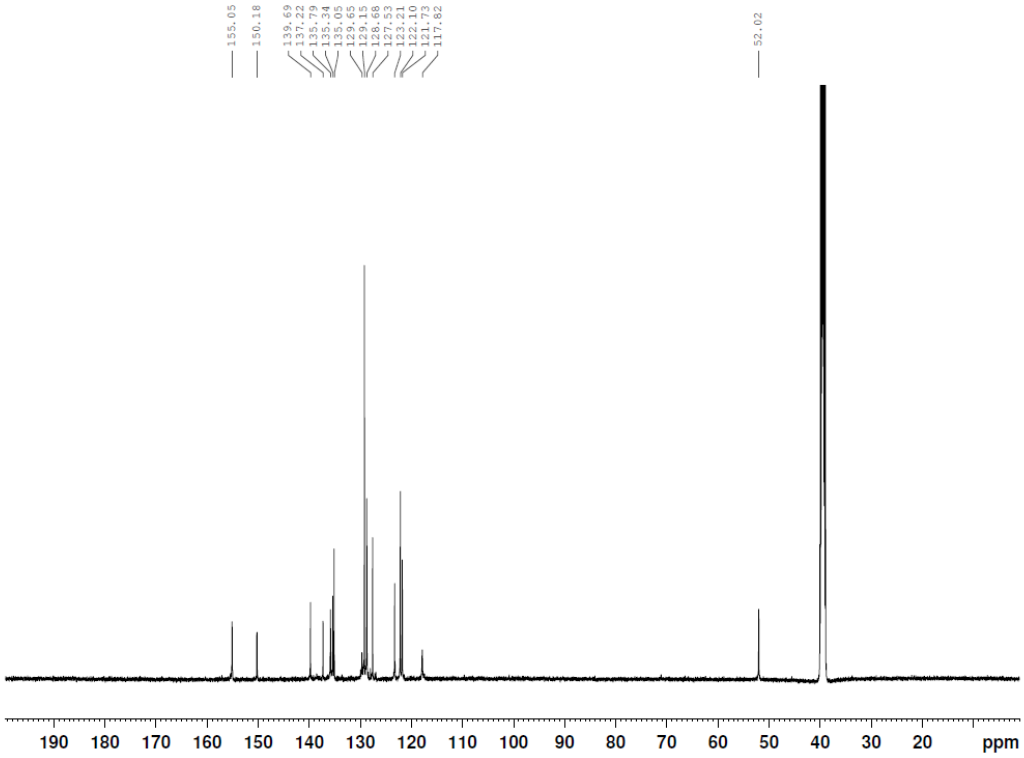


Chemical Formula: $C_{14}H_{27}BO_2$
Molecular Weight: 238.1780

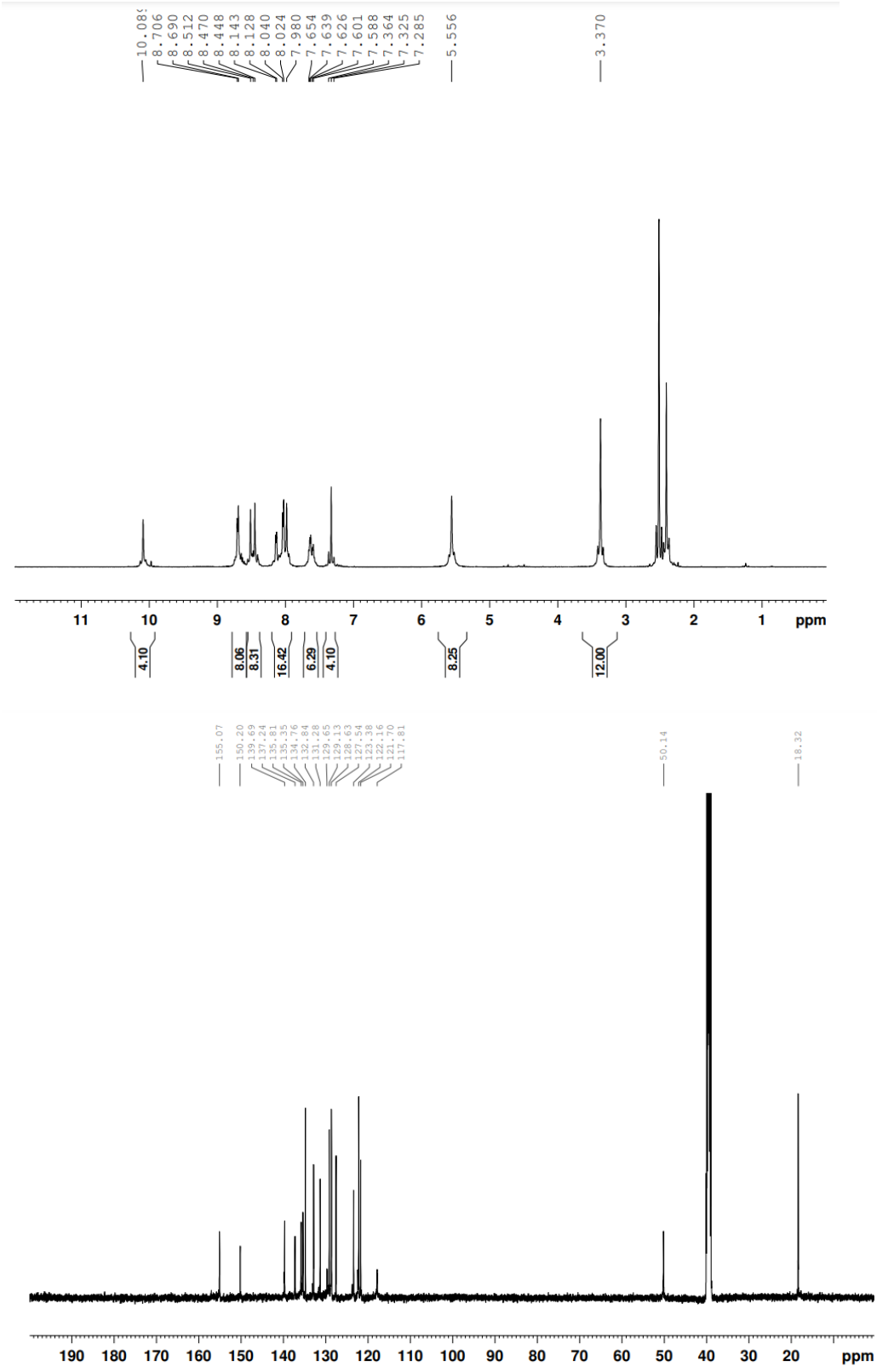
5m:[8] In a glovebox under N_2 atmosphere, **4b** (1.72 mg, 1.0 μmol, 0.1 mol%) was dissolved in THF (0.5 mL) in a 3.8 mL glass vial equipped with a stir bar, to which $CoCl_2$ (0.52 mg, 0.4 mol%) and $NaHBEt_3$ (10 μL, 1 M in THF, 1 mol%) were subsequently added. 4-Octyne (110 mg, 1.0 mmol) and pinacolborane (155 mg, 1.2 mmol, 1.2 eq.) were then added. The reaction mixture was allowed to stir at room temperature for 16 h. The reaction was exposed to the air and quenched with aq. $NaHCO_3$, and then extracted with Et_2O. The crude reaction mixture was analyzed by GC-MS and then purified through column chromatography (silica gel) using ethyl acetate/hexane (1:40, v/v) as an eluent to give colorless oil. Yield: 209 mg (88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31 – 6.27 (m, 1H), 2.13 – 2.08 (m, overlapping, 4H), 1.44 – 1.38 (m, 2H), 1.38 – 1.33 (m, 2H), 1.25 (s, 12H), 0.91 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 4H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 83.1, 30.8, 30.7, 24.9, 23.5, 22.6, 14.24, 14.20 ppm. GC-MS (m/z): 238 (calc. 238).

^{1}H and ^{13}C NMR spectra of **4a** (DMSO-d_6):

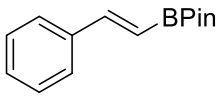




^{1}H and ^{13}C NMR spectra of **4b** (DMSO-d_6):

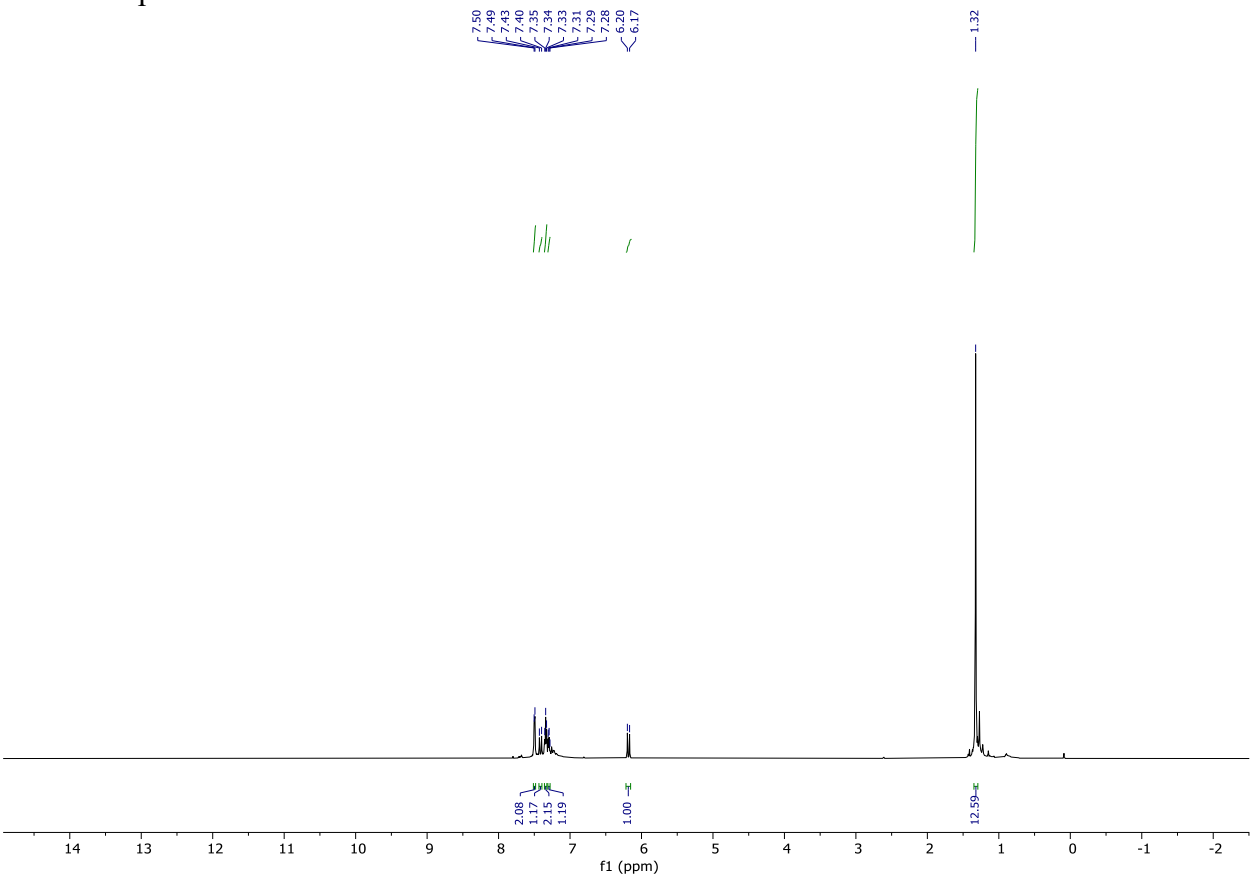


Copies of ^{1}H and ^{13}C NMR spectra for products **5a**-**m**.

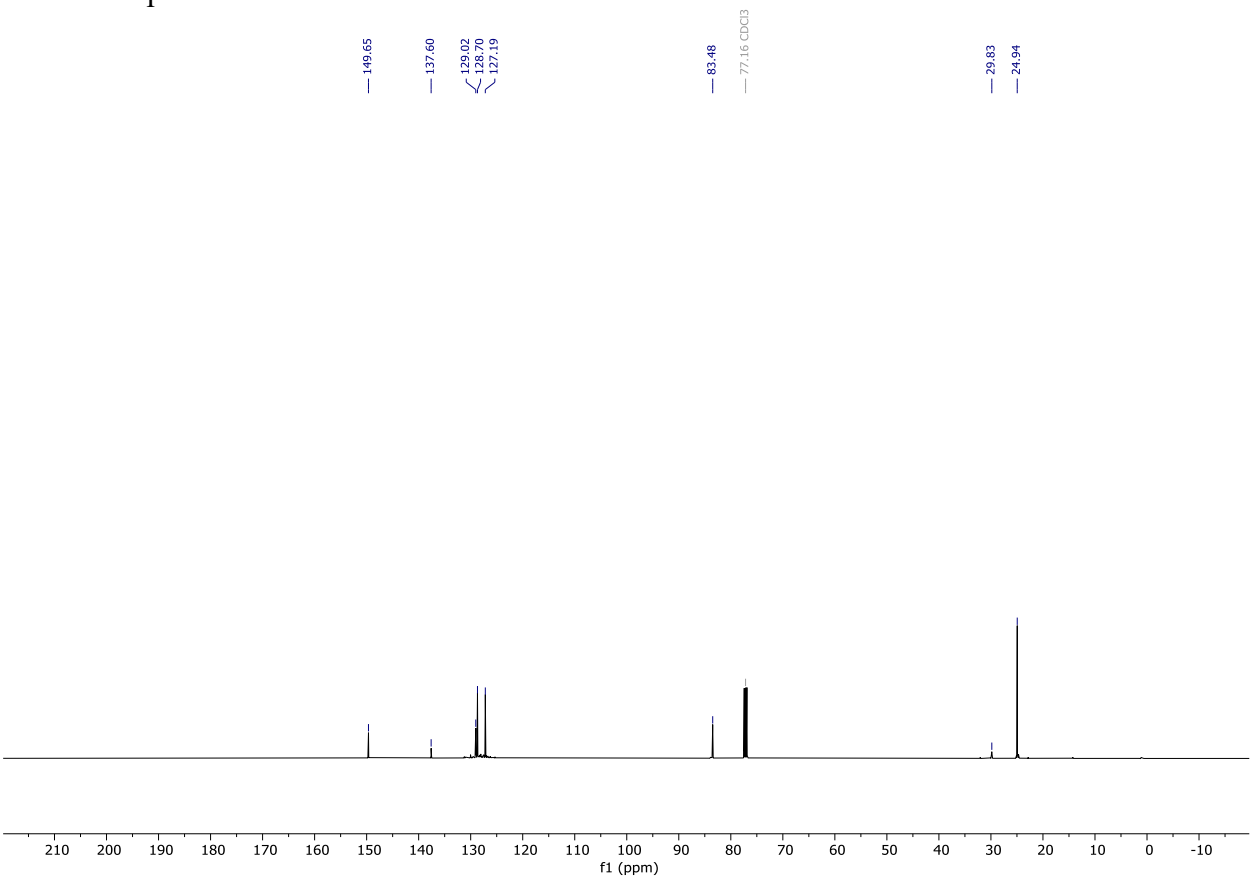


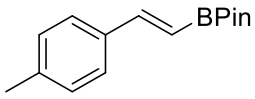
5a

^{1}H NMR spectrum:



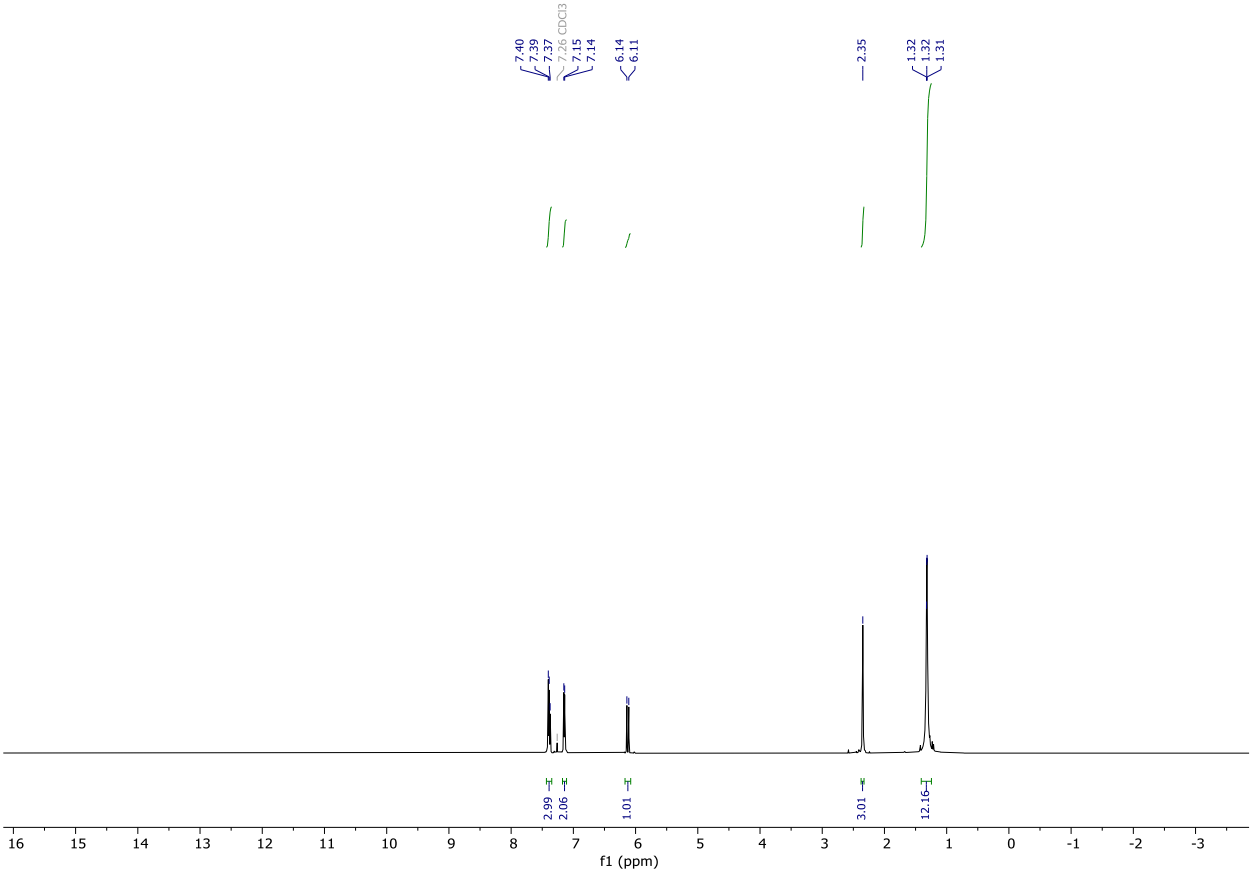
^{13}C NMR spectrum:



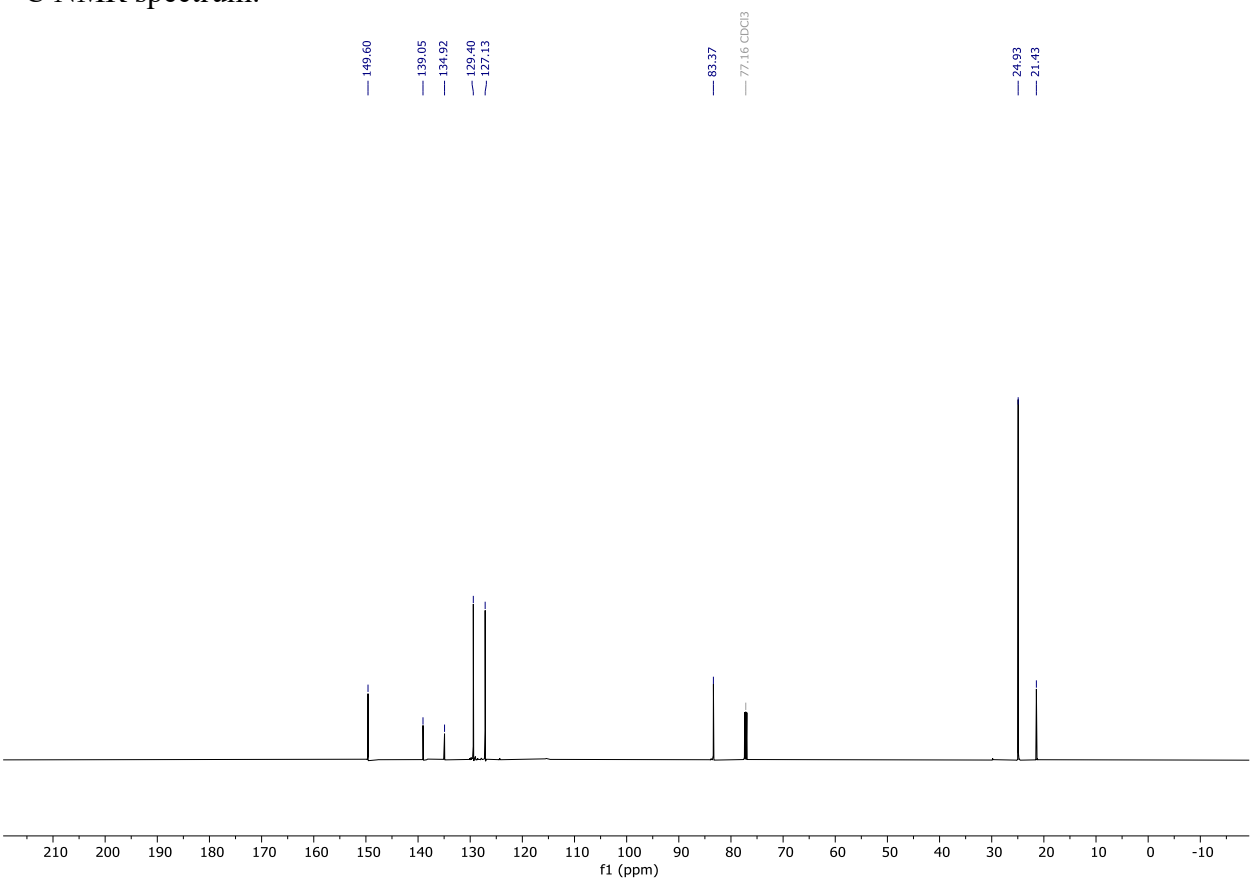


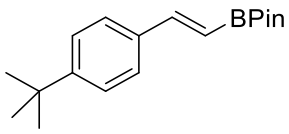
5b

^{1}H NMR spectrum:



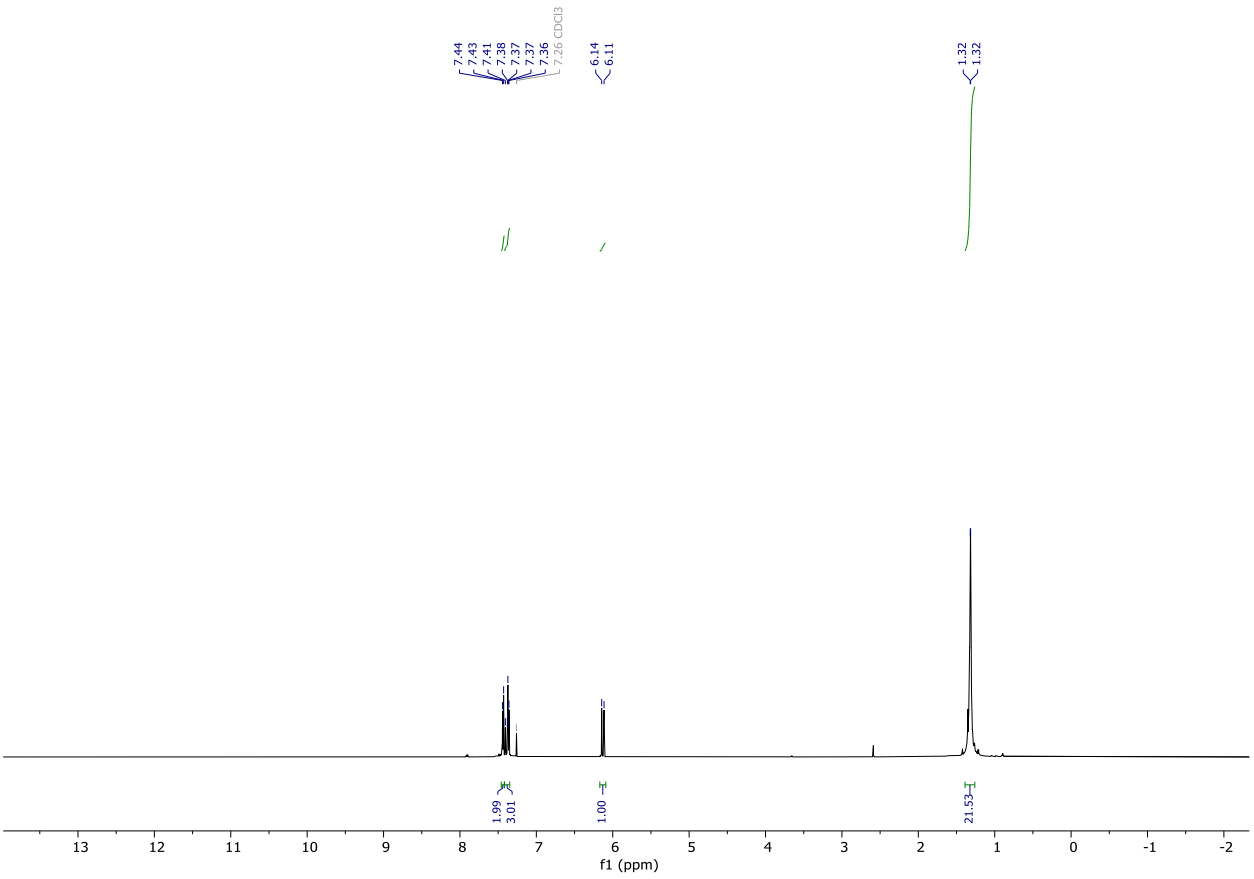
^{13}C NMR spectrum:



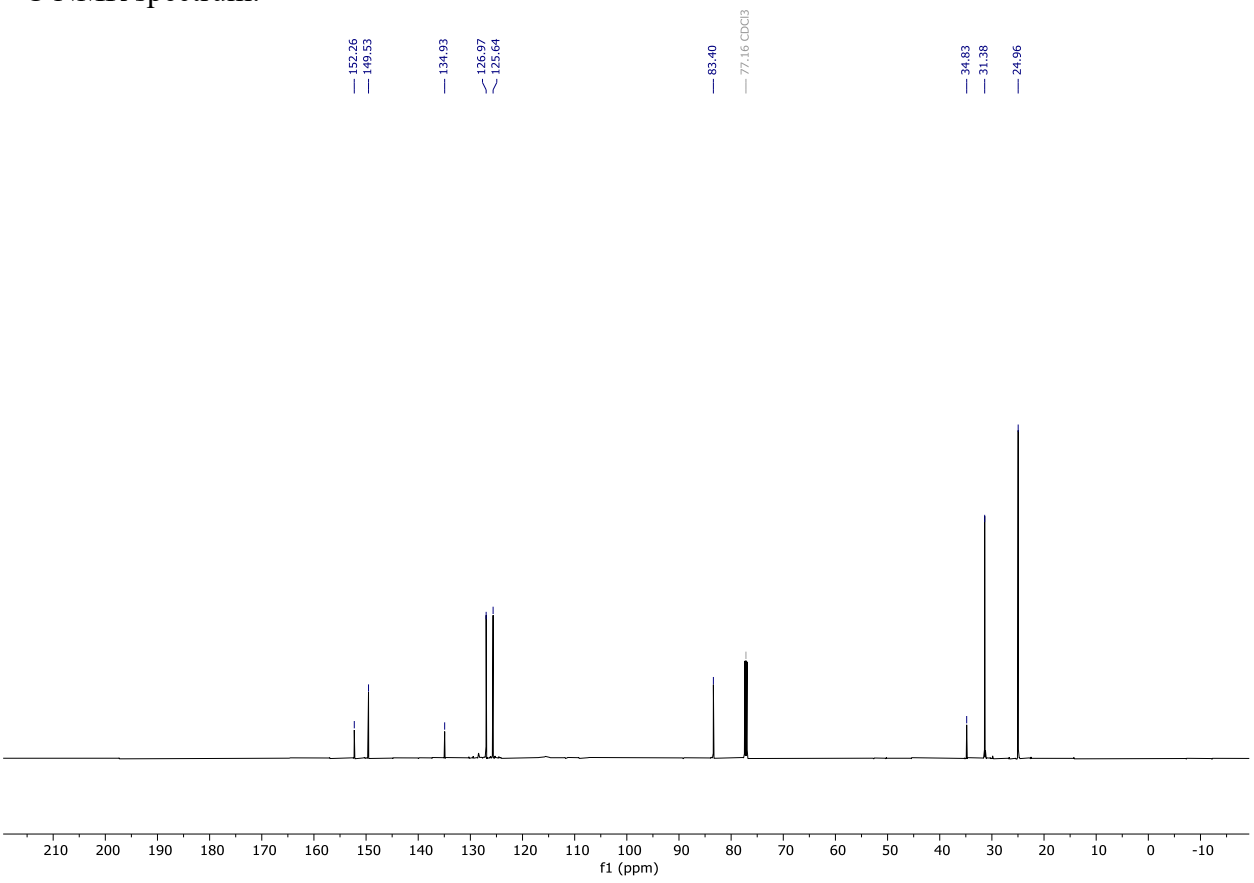


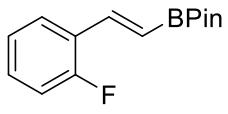
5c

^{1}H NMR spectrum:



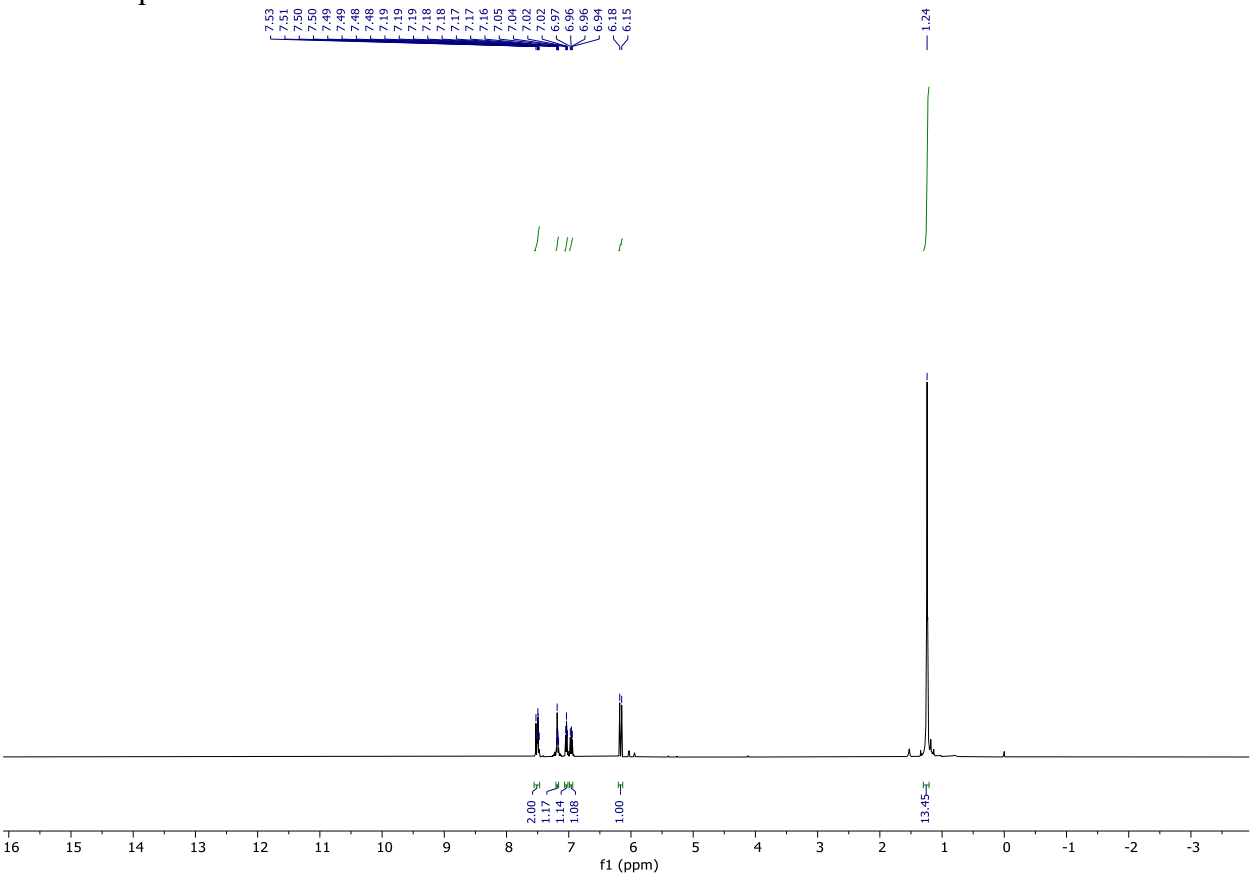
^{13}C NMR spectrum:



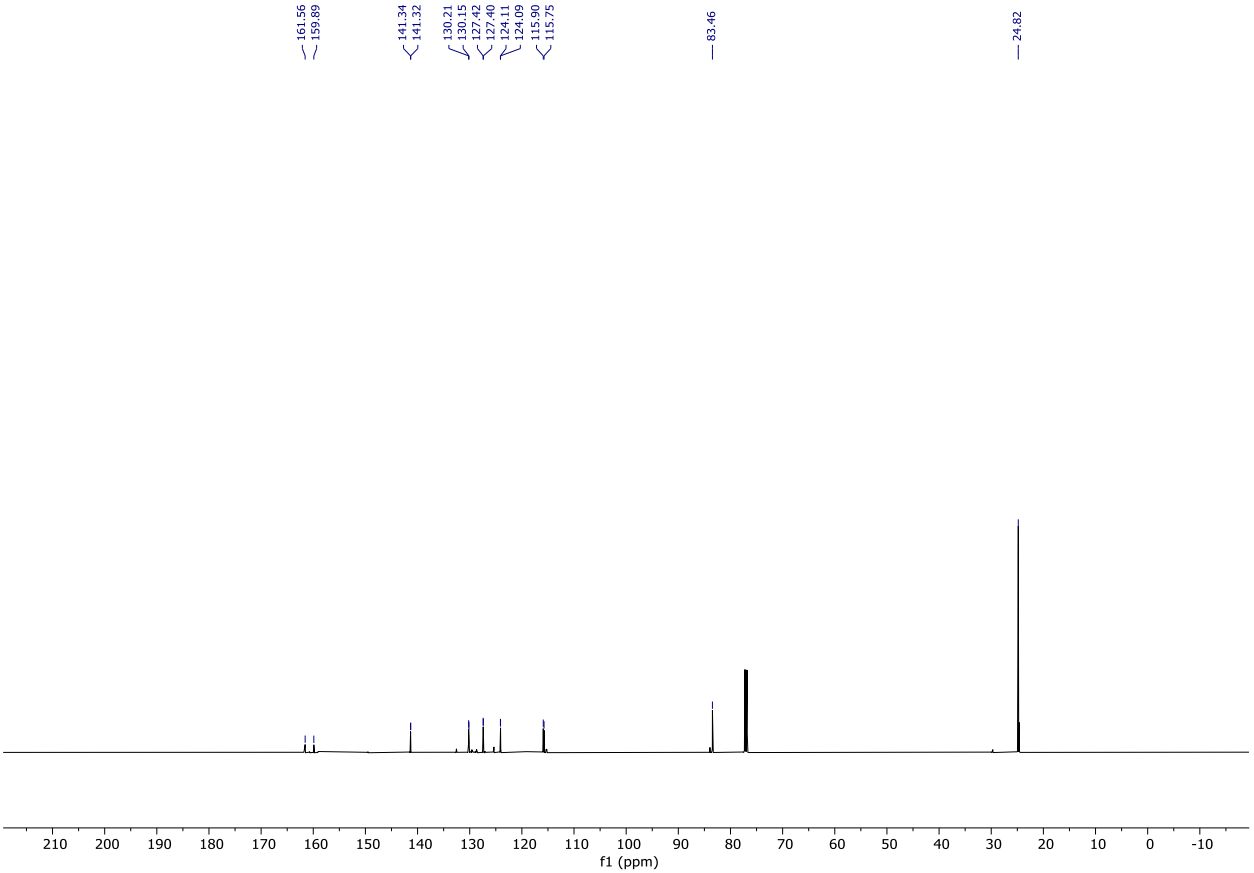


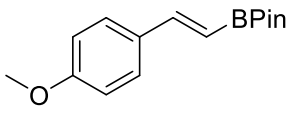
5d

^{1}H NMR spectrum:



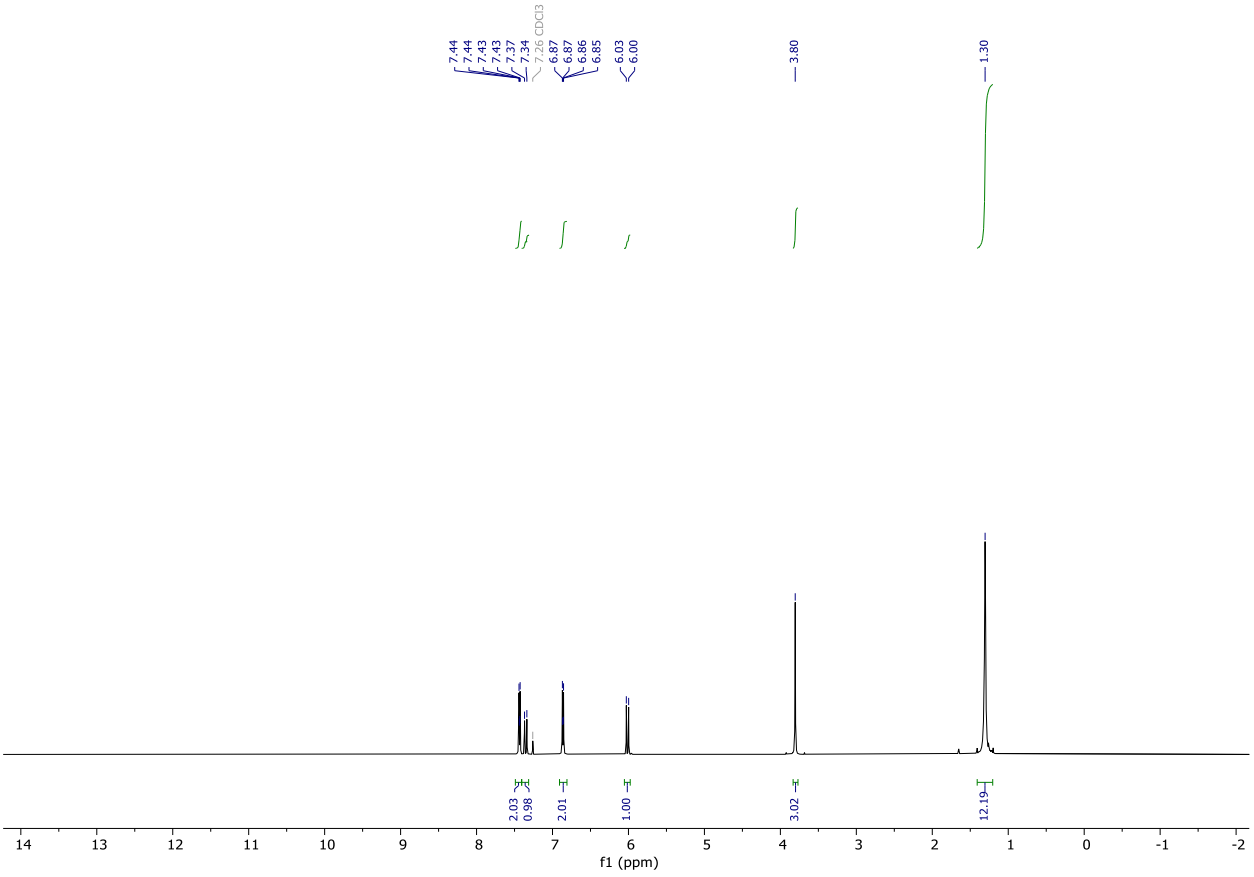
^{13}C NMR spectrum:



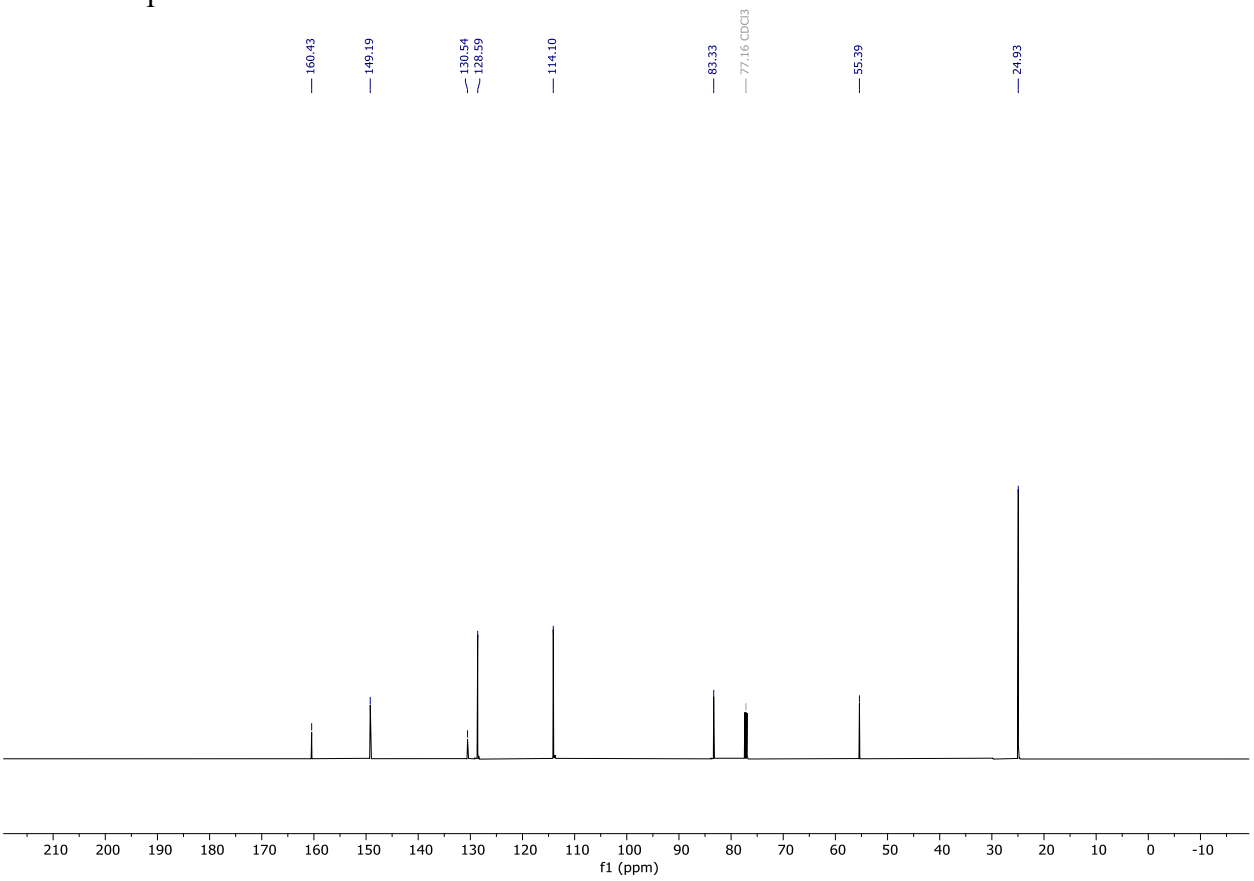


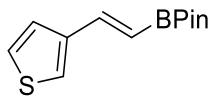
5e

^{1}H NMR spectrum:



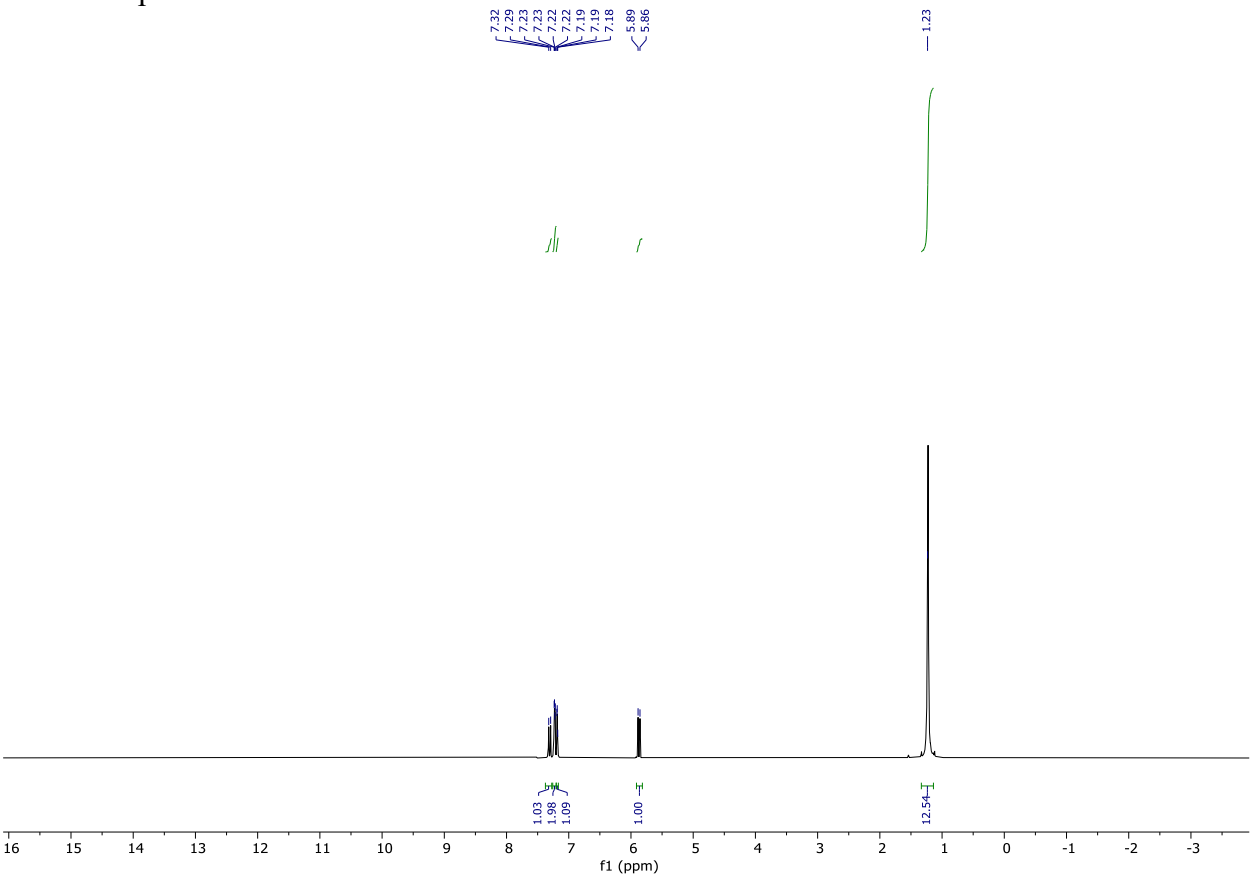
^{13}C NMR spectrum:



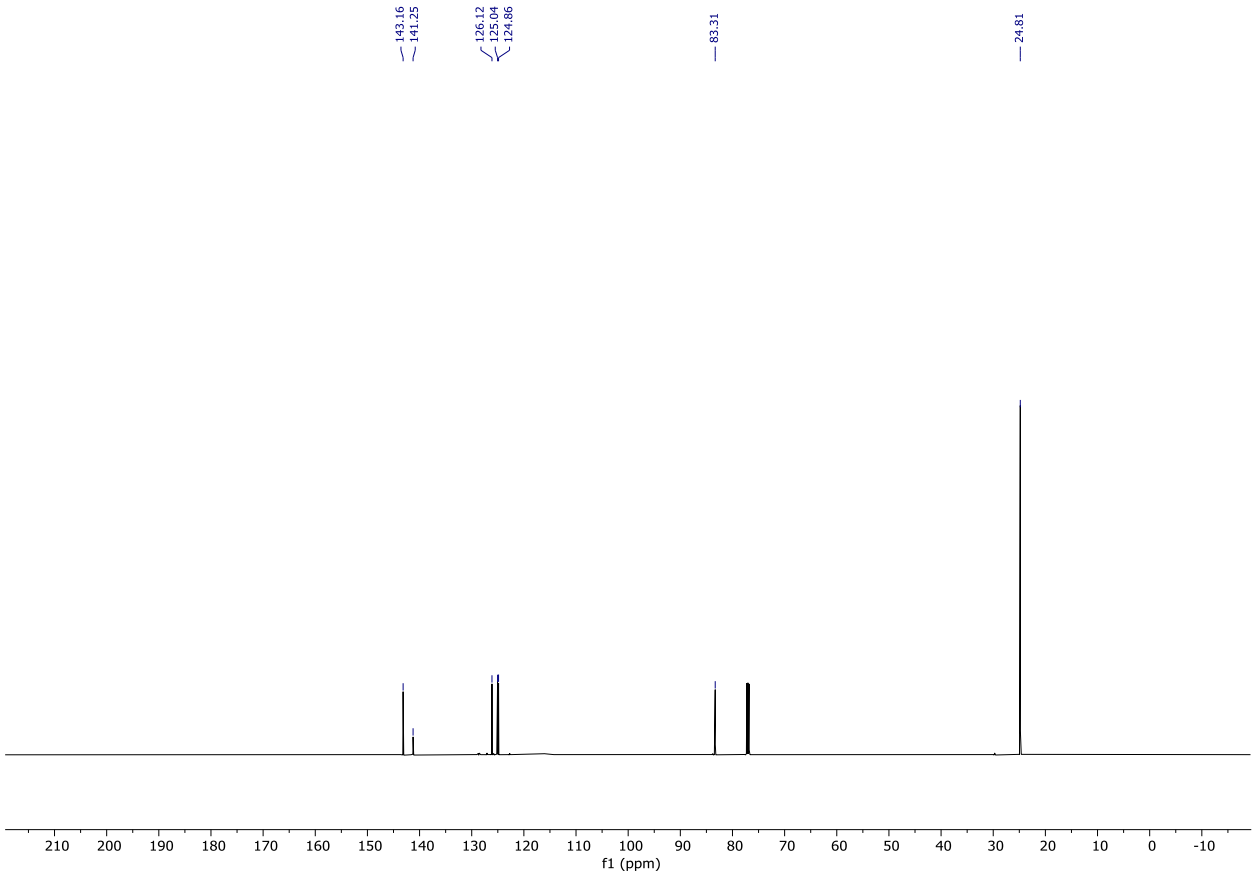


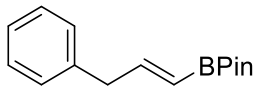
5f

^{1}H NMR spectrum:



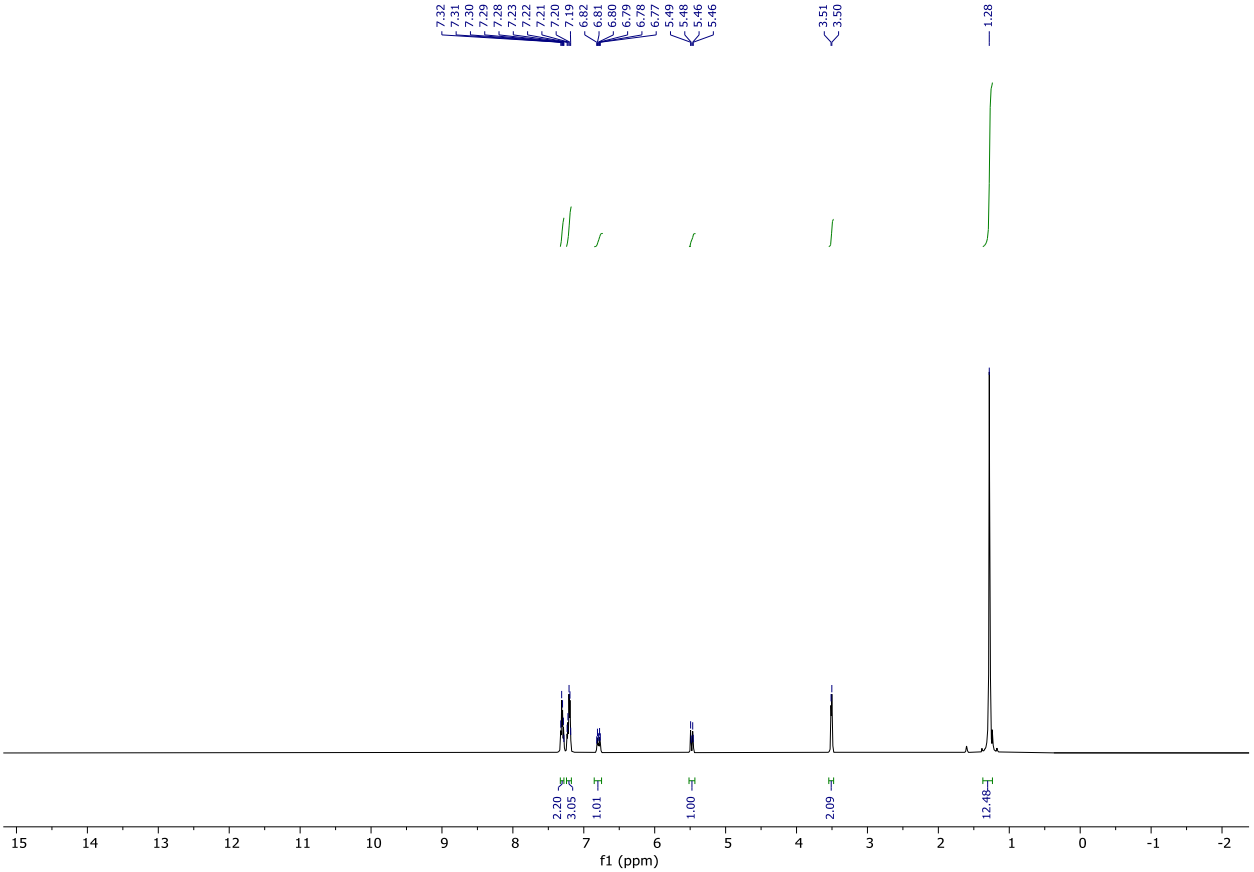
^{13}C NMR spectrum:



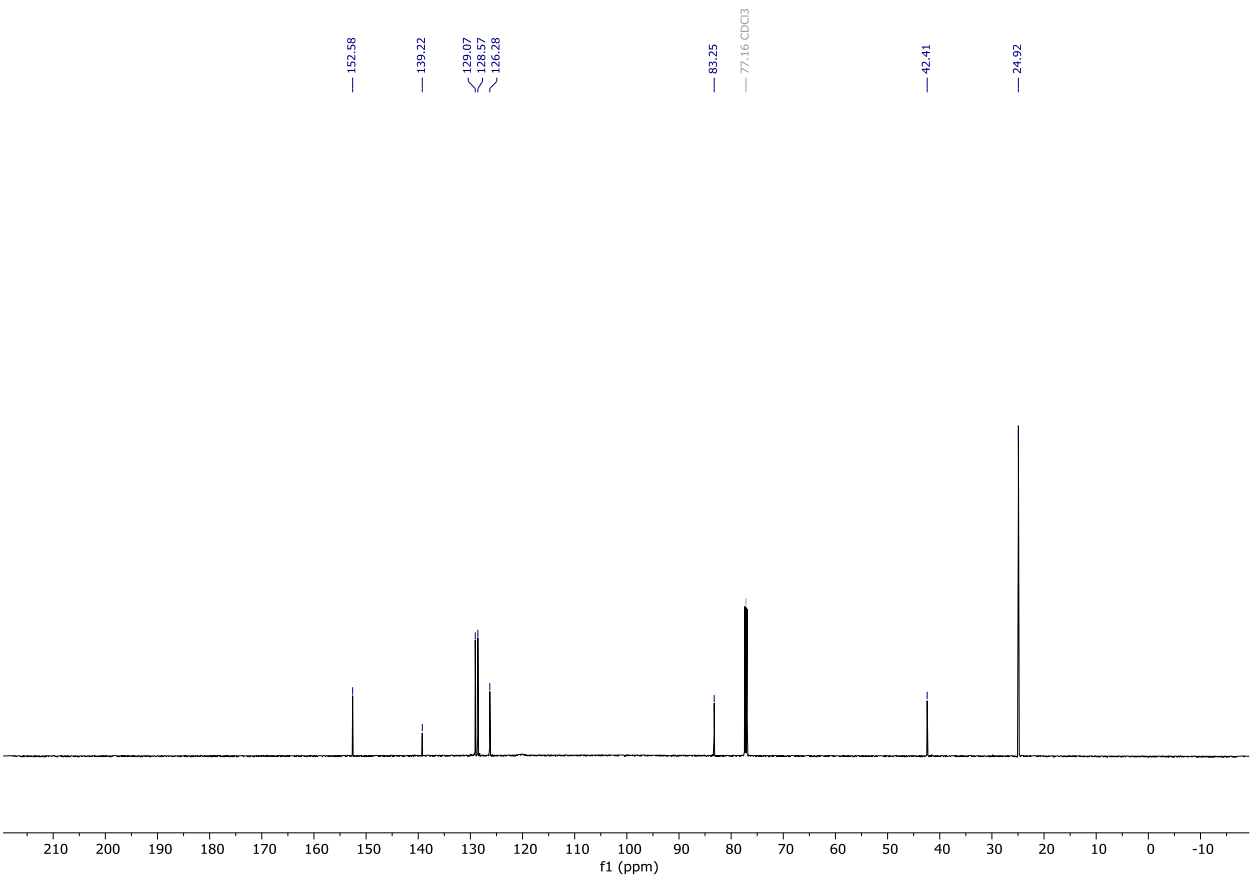


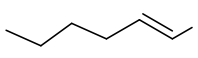
5g

^{1}H NMR spectrum:



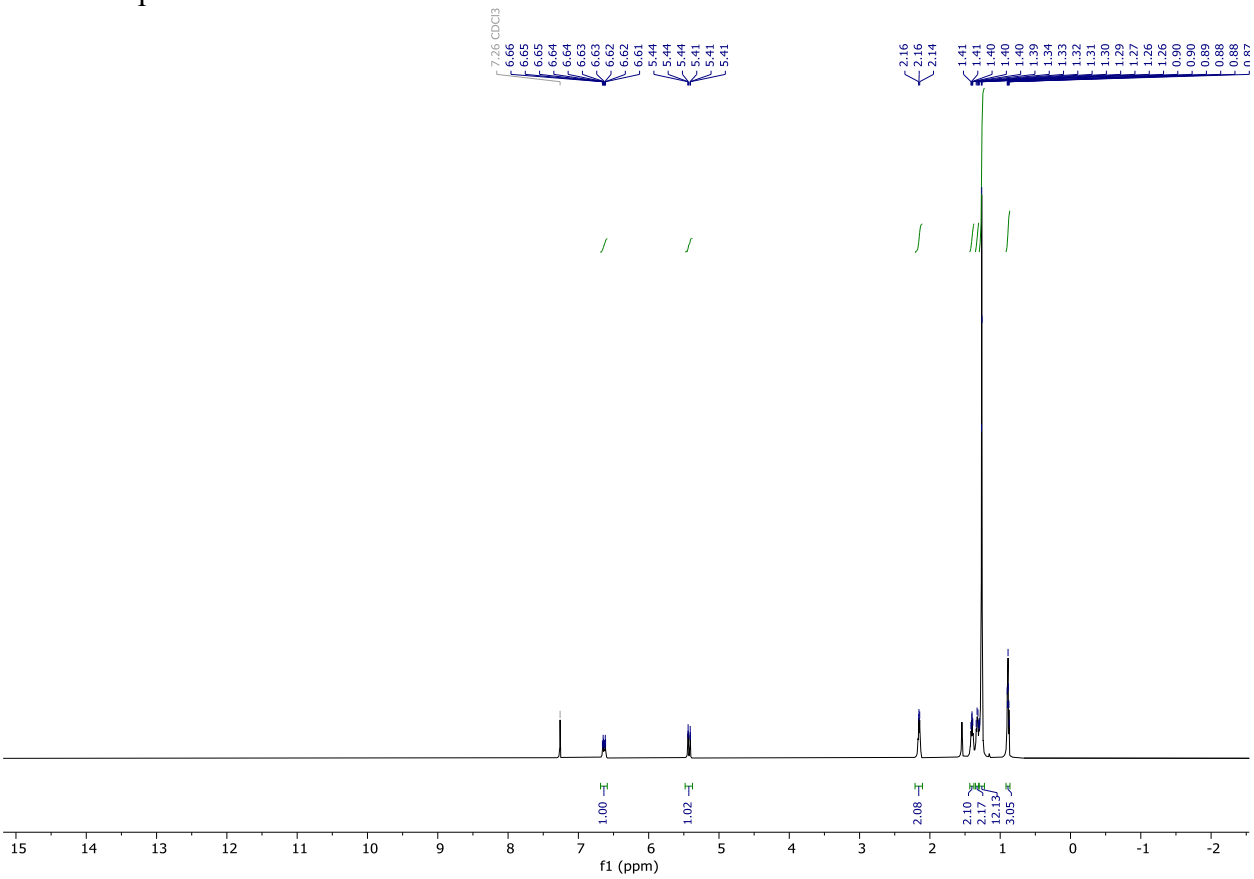
^{13}C NMR spectrum:



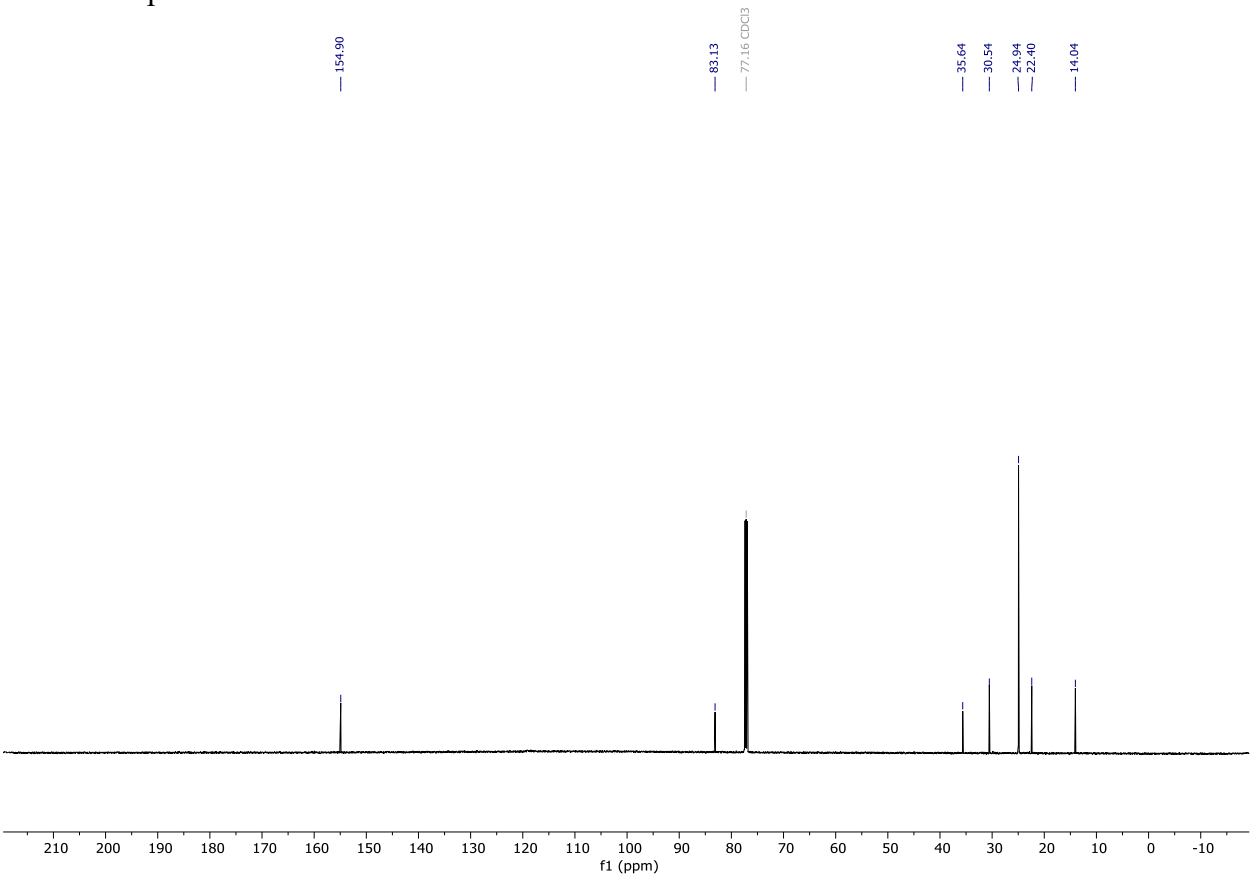


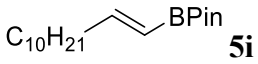
5h

^{1}H NMR spectrum:



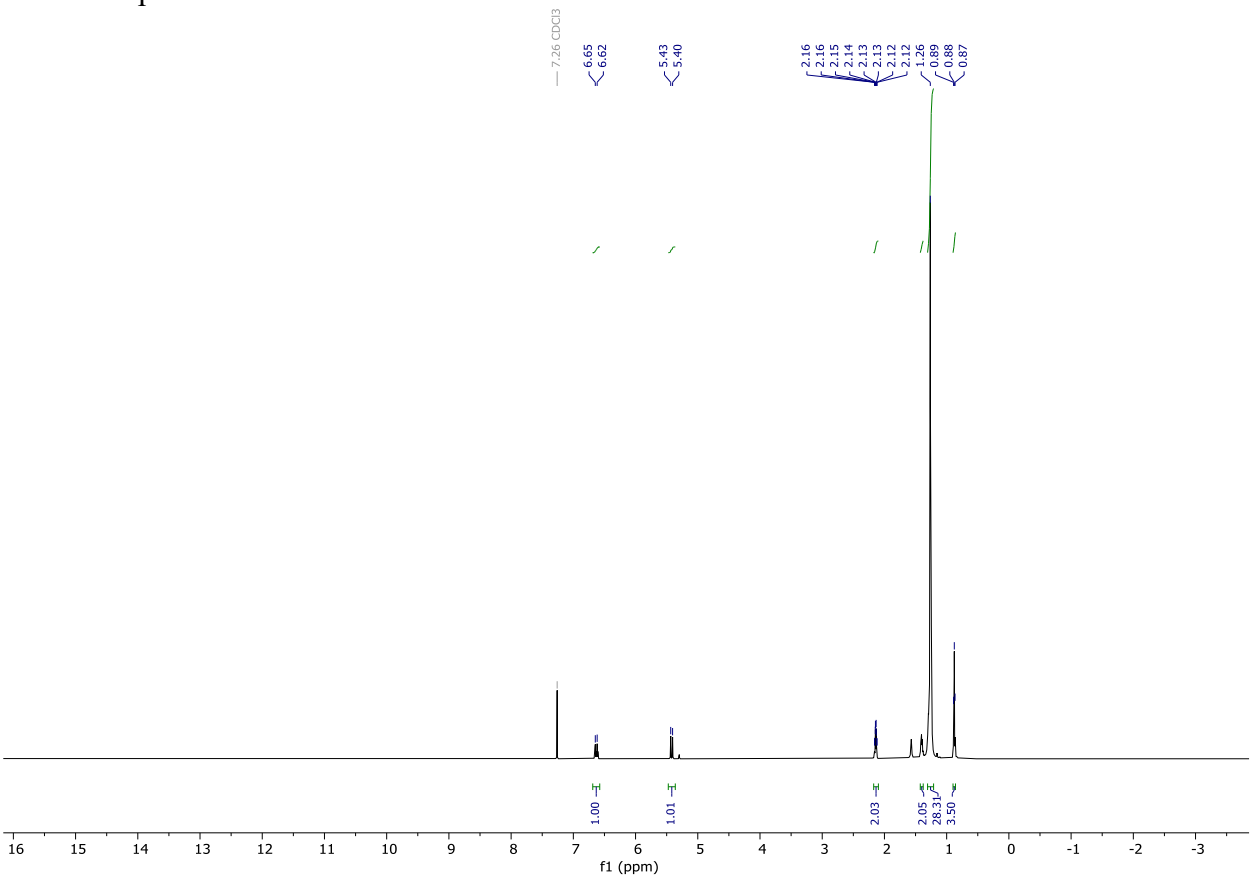
^{13}C NMR spectrum:



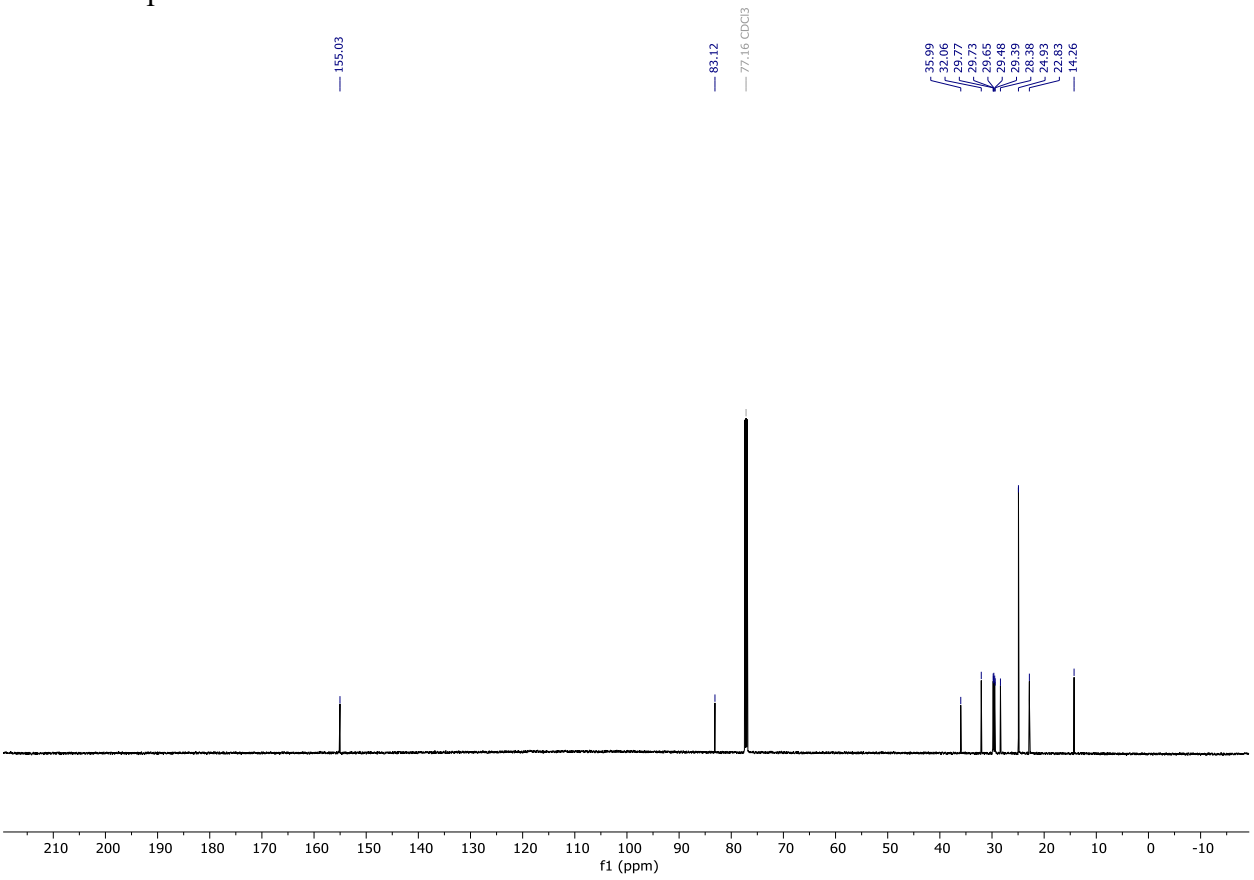


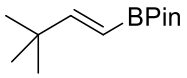
5i

^{1}H NMR spectrum:



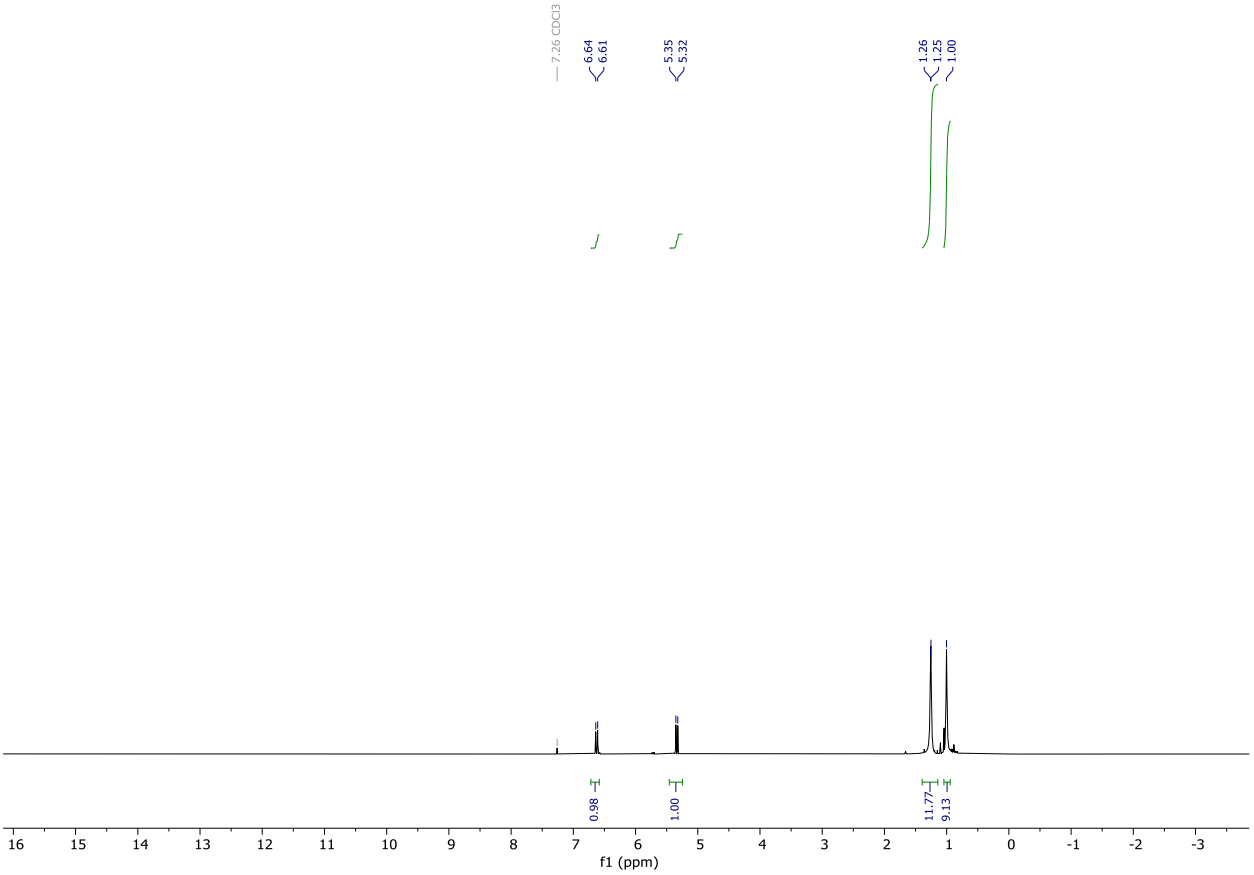
^{13}C NMR spectrum:



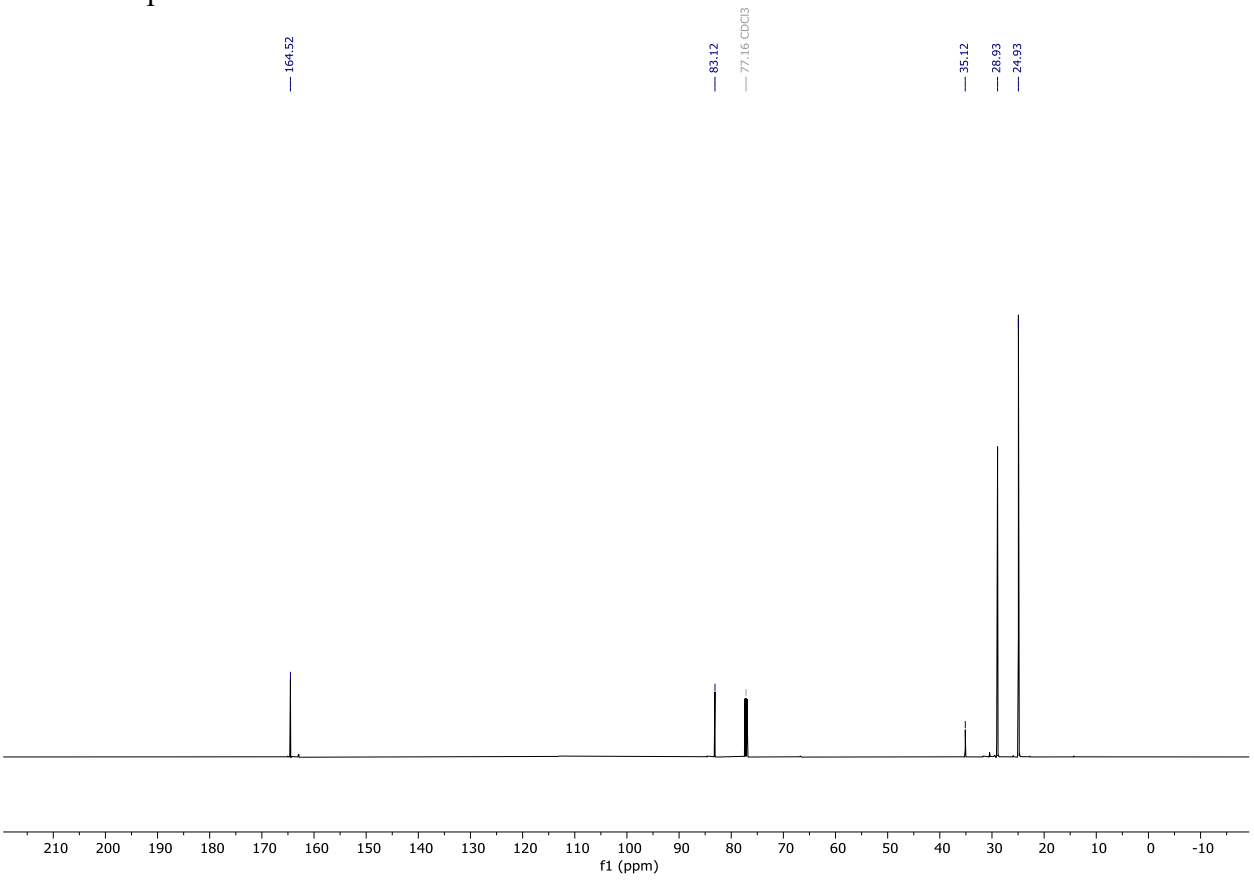


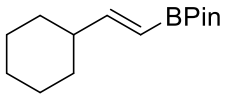
5j

^{1}H NMR spectrum:



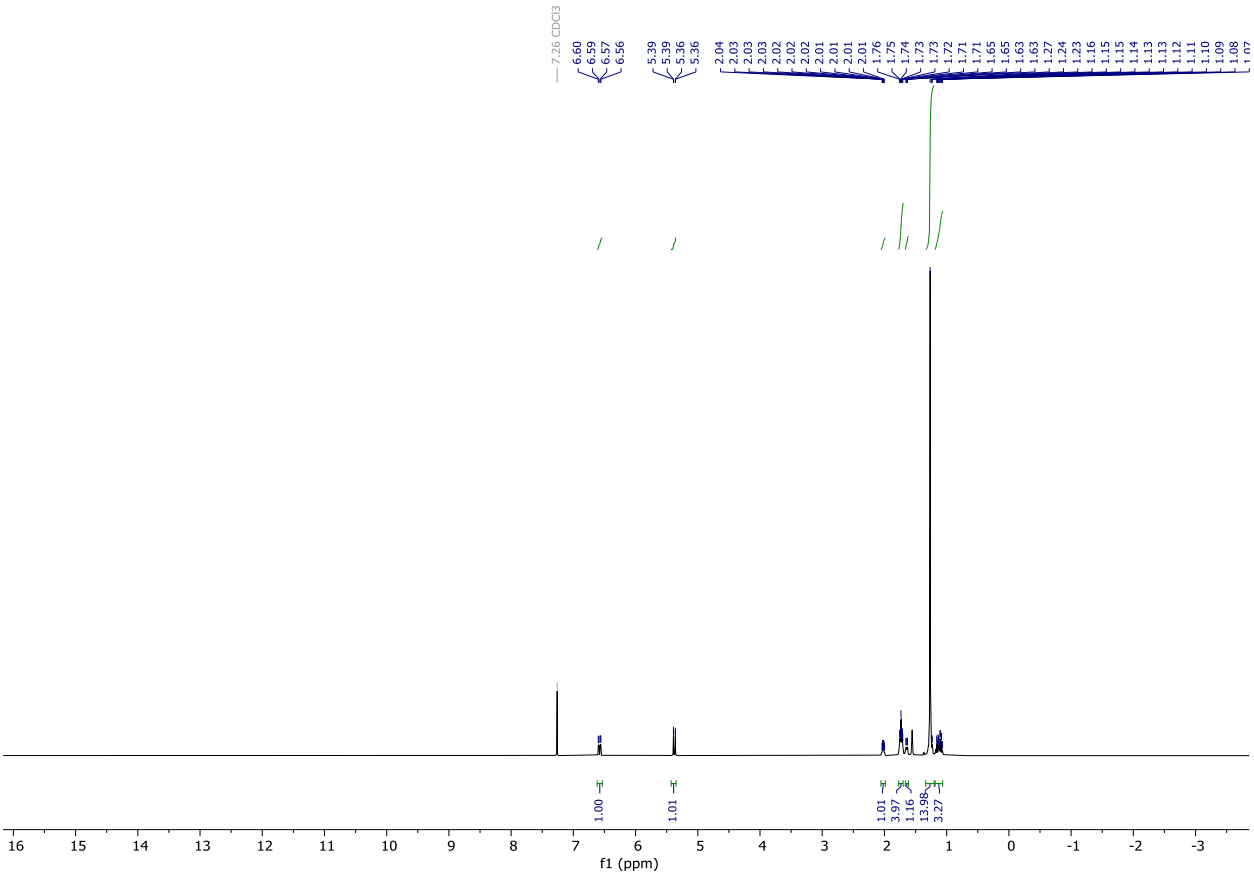
^{13}C NMR spectrum:



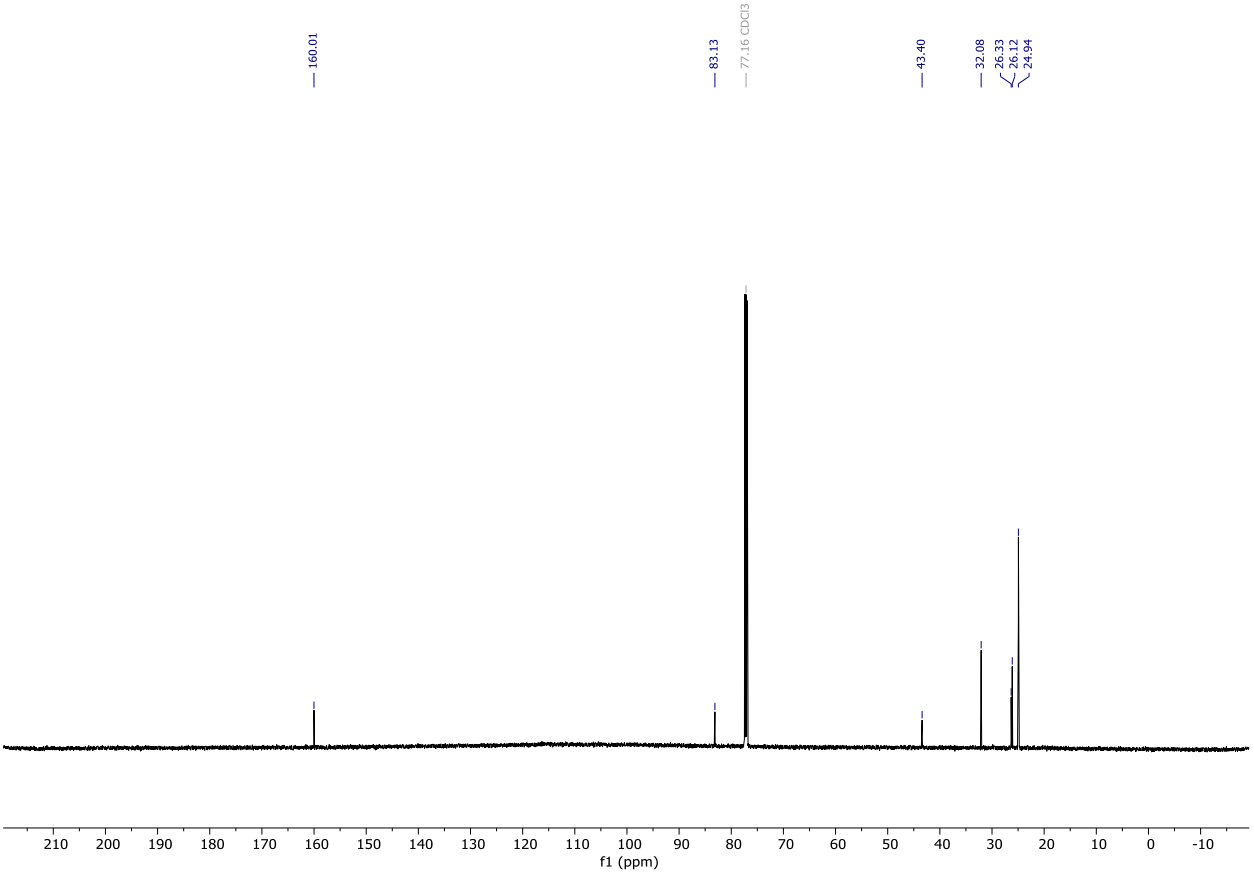


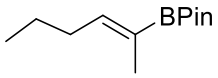
5k

^{1}H NMR spectrum:



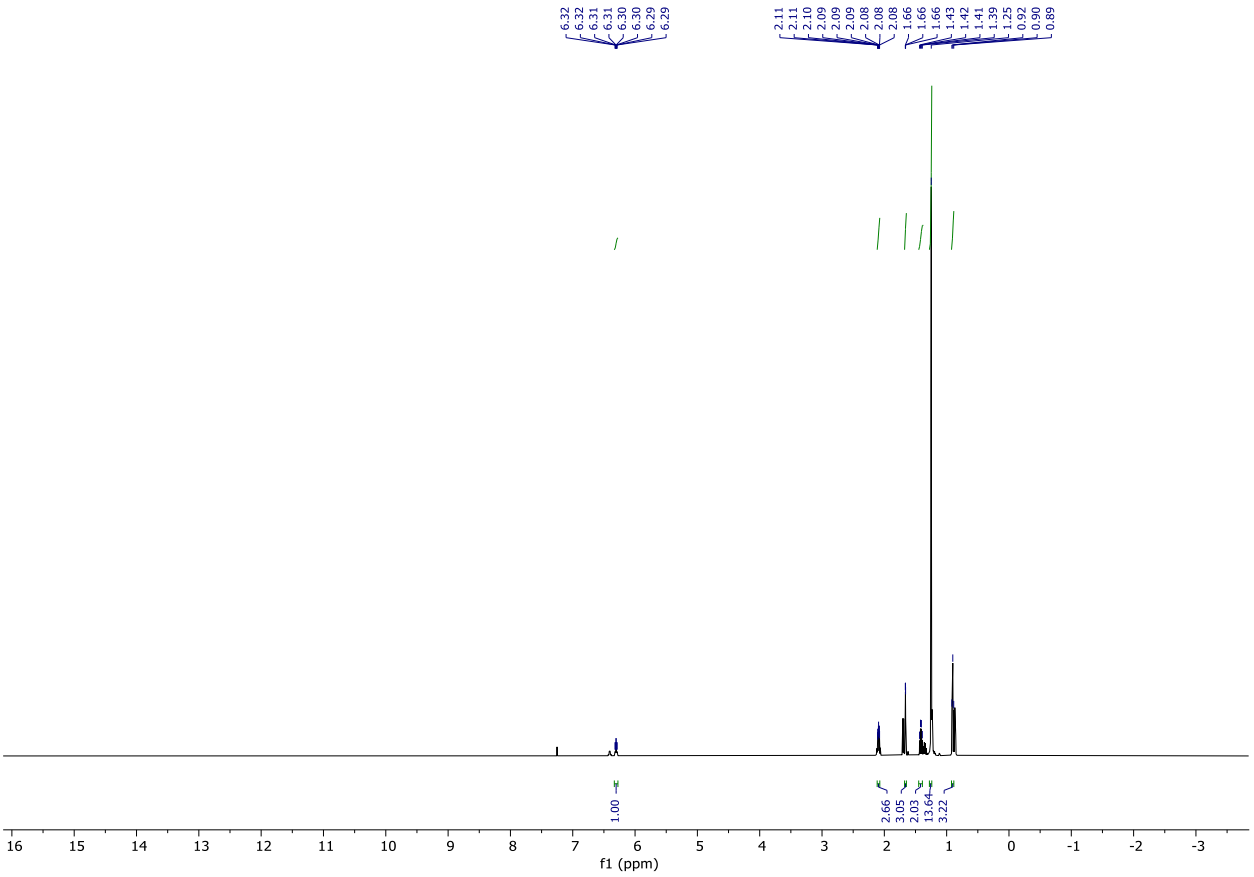
^{13}C NMR spectrum:



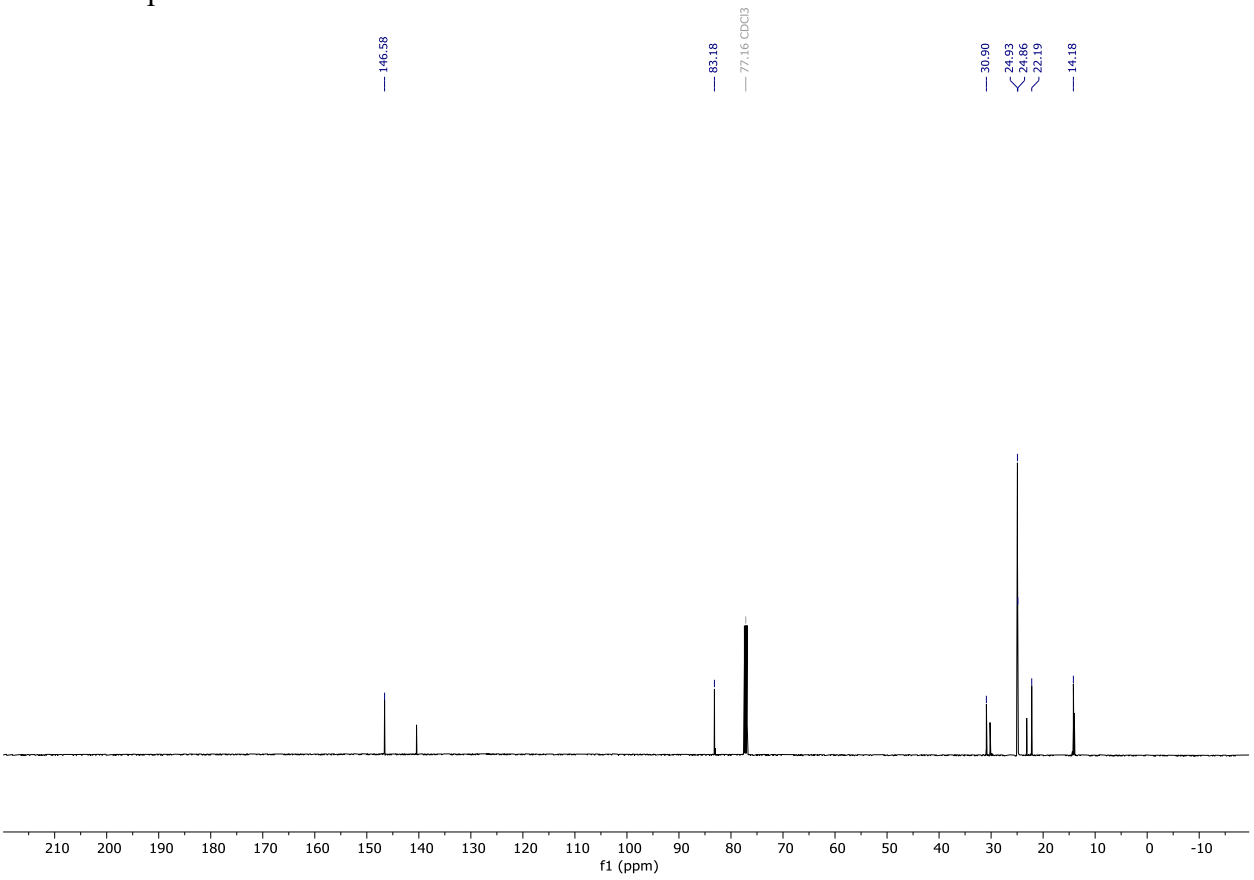


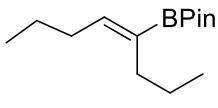
5l (+ regioisomer)

^{1}H NMR spectrum:



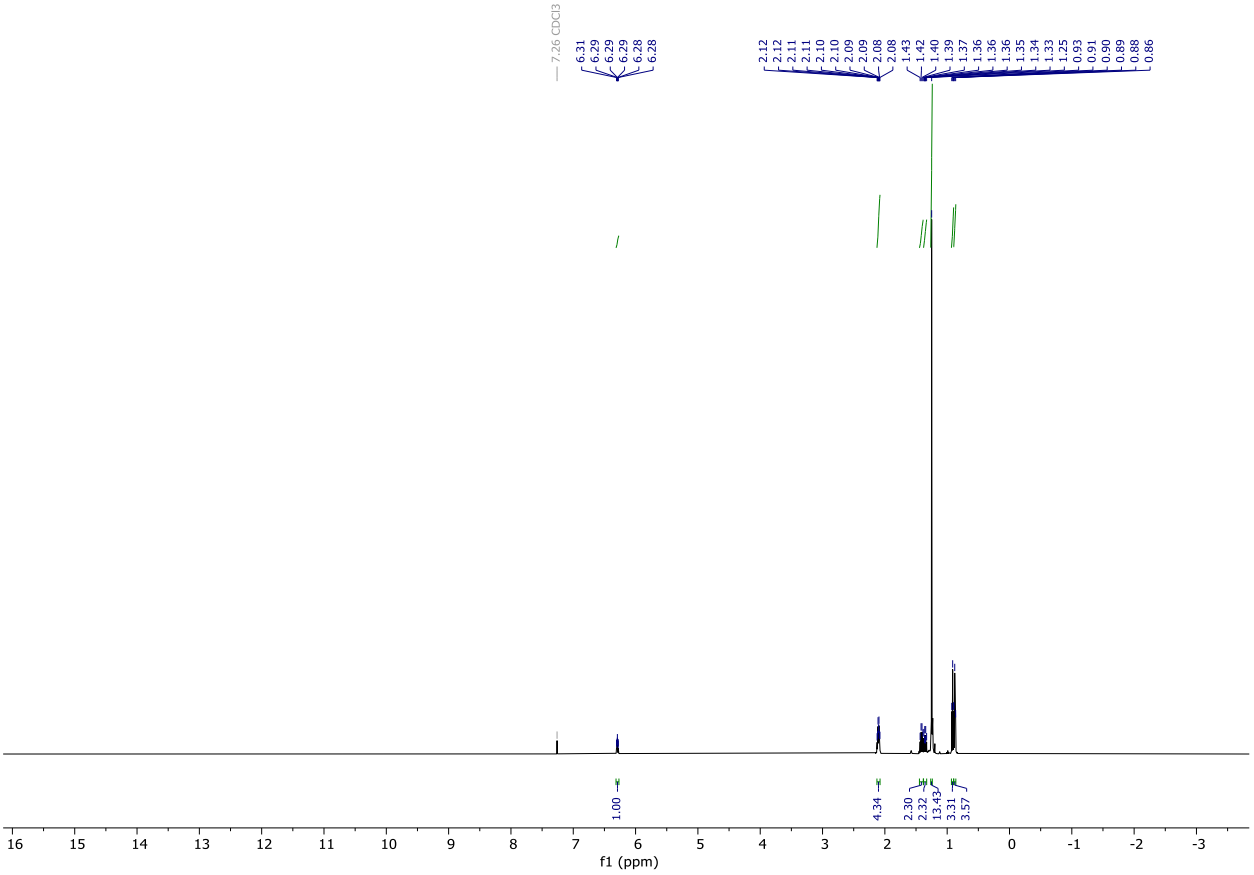
^{13}C NMR spectrum:



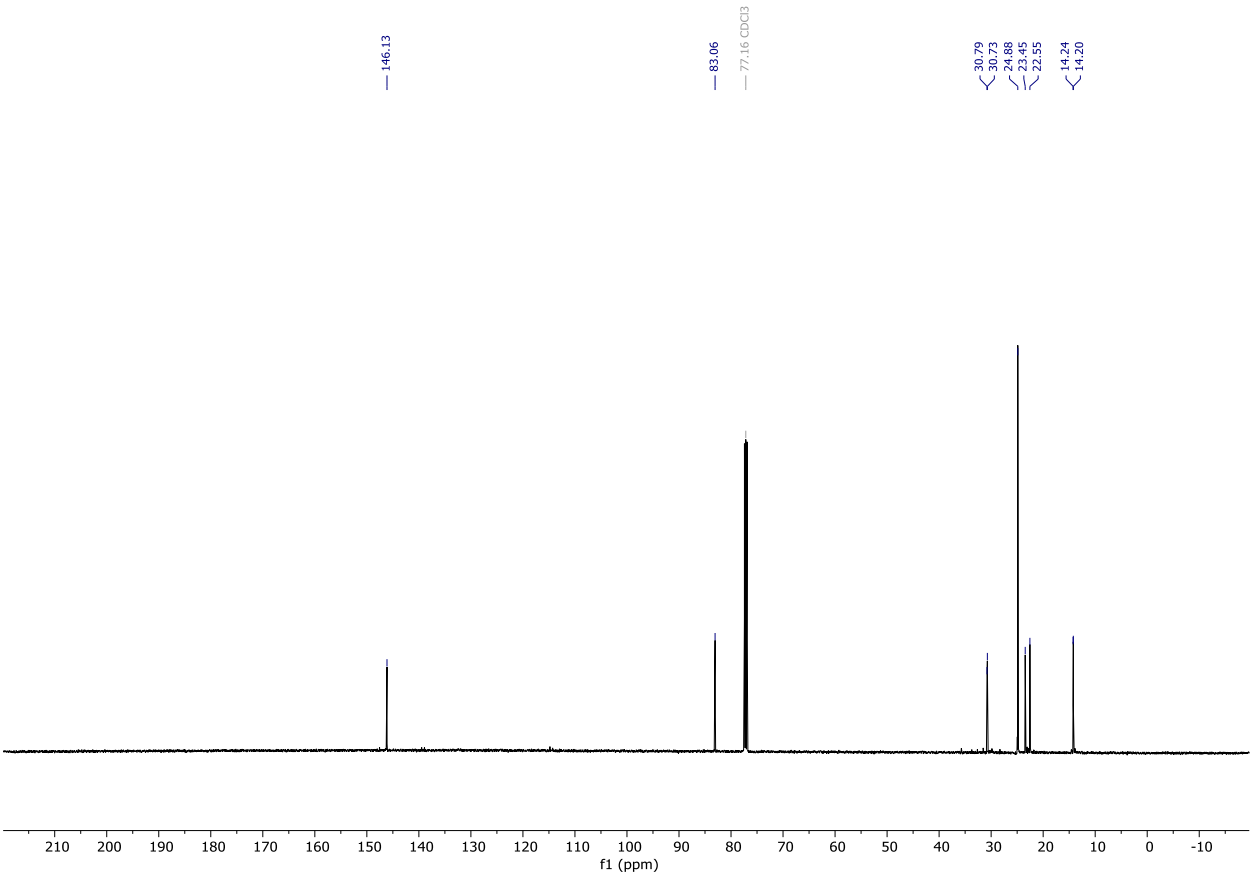


5m

^{1}H NMR spectrum:



^{13}C NMR spectrum:



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