Supporting Information

Iron-Catalyzed Three-Component 1,2-Azidoalkylation of Conjugated Dienes via Activation of Aliphatic C–H Bonds

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1 General Data

Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{24} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker Avance-400 (400 and 100 MHz) and Bruker Avance-500 (500 and 125 MHz) spectrometers. ^{19}F NMR spectra was using Bruker Avance-400 (377 MHz). Chemical shifts were reported in reference to residual protiated solvent peaks. Accurate mass measurements were acquired at the University of Wisconsin-Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods). Starting materials and solvents were purchased from commercial suppliers (Sigma-Aldrich, Oakwood Products, Alfa Aesar, Tokyo Chemical Industry, Combi-Blocks, Acros Organics or Cayman Chemicals) and used directly without further purification.

2 Experimental Procedures

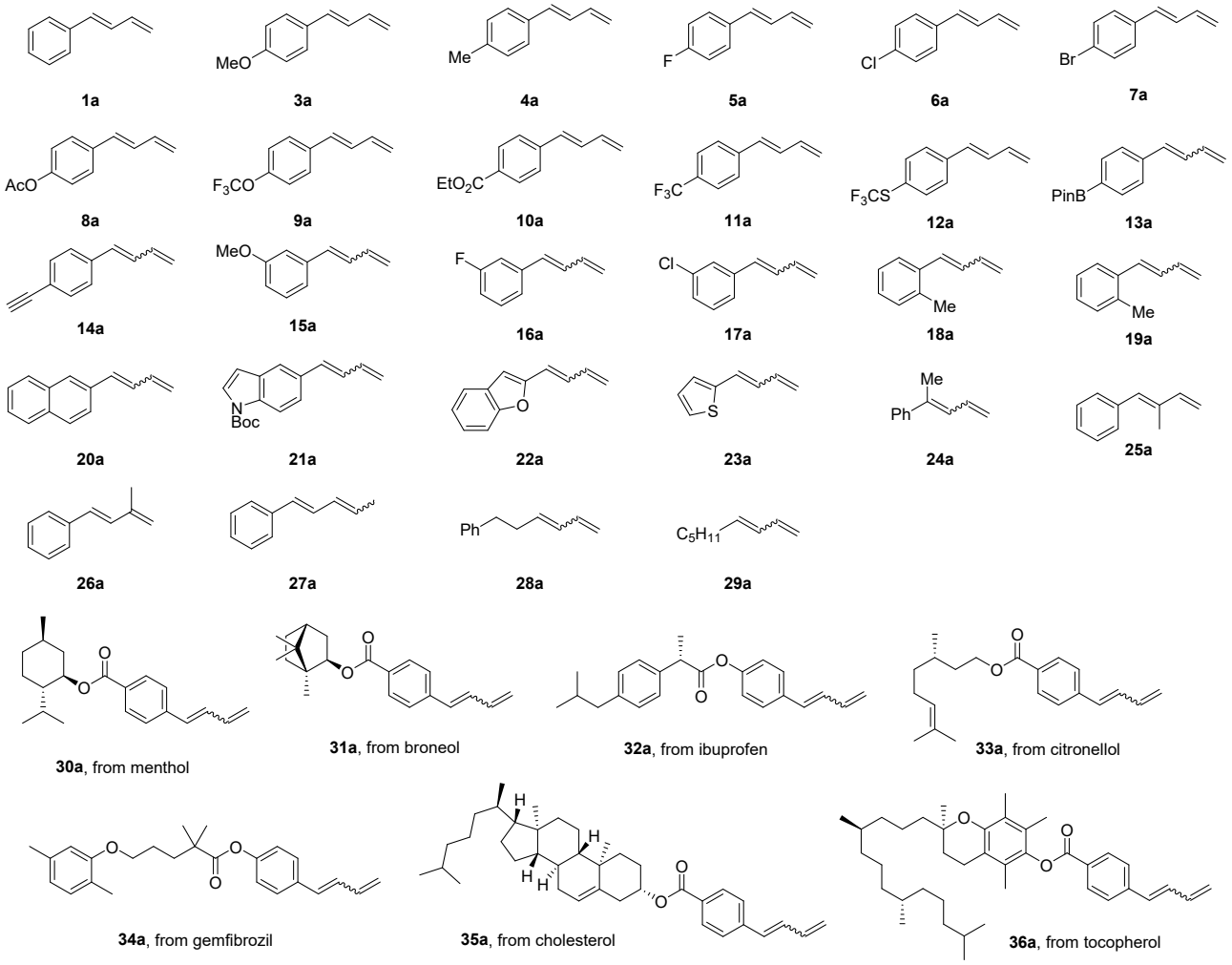
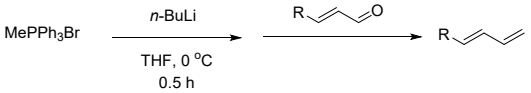


Figure S-1. Number of dienes

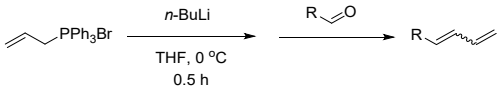
General experimental procedures for preparation of the 1,3-dienes.

Method A



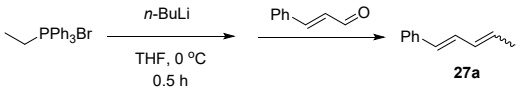
^{n}BuLi (2.4 mL, 6 mmol, 2.5 M in hexane) was added dropwise to a stirred suspension of $MePPh_3Br$ (2.14 g, 6 mmol, 1.2 equiv.) in anhydrous THF (30 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 30 min. Then cinnamaldehydes (5 mmol, 1.0 equiv.) was added, and the reaction was kept stirring for 4-8 h with TLC detection. After the complete consumption of cinnamaldehyde, the mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and then concentrated. The product was purified by column chromatography (SiO_2, hexane) to afford desired 1,3-dienes. **1a**, **3a-7a** were prepared according to method A, all spectroscopic data agree with the literature.[1]

Method B



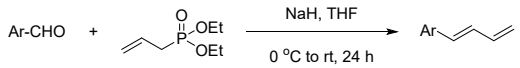
^{n}BuLi (2.4 mL, 6 mmol, 2.5 M in hexane) was added dropwise to a stirred suspension of allylPPh$_3$Br (2.29 g, 6 mmol, 1.2 equiv.) in anhydrous THF (30 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 30 min. Then the aldehyde (5 mmol, 1.0 equiv.) was added, and the reaction was kept stirring for 4-8 h with TLC detection. After the complete consumption of cinnamaldehyde, the mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and then concentrated. The product was purified by column chromatography (SiO_2, hexane) to afford desired 1,3-dienes. **13a-24a, 28a-36a** were prepared according to method B, all spectroscopic data agree with the literature.[2-4]

Method C



^{n}BuLi (2.4 mL, 6 mmol, 2.5 M in hexane) was added dropwise to a stirred suspension of EtPPh$_3$Br (2.22 g, 6 mmol, 1.2 equiv.) in anhydrous THF (30 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 30 min. Then the aldehyde (5 mmol, 1.0 equiv.) was added, and the reaction was kept stirring for 4-8 h with TLC detection. After the complete consumption of cinnamaldehyde, the mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and then concentrated. The product was purified by column chromatography (SiO_2, hexane) to afford desired 1,3-diene. **27a** was prepared according to method C, all spectroscopic data agree with the literature.[5]

Method D



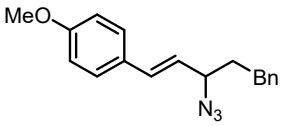
To a stirred solution of diethylallyl phosphonate (535 mg, 3.0 mmol, 1.5 equiv) in THF (25 mL), NaH (72 mg, 3.0 mmol, 1.5 equiv, oil free) was added portion wise under a nitrogen atmosphere at 0°C. The mixture was stirred for 30 min. Then the arylaldehyde (2.0 mmol) in THF (0.5 mL) was added, and the reaction was kept stirring for 24 h with TLC detection. After the complete consumption of arylaldehyde, the mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and then concentrated. The product was purified by column chromatography (SiO_2, hexane) to afford desired 1,3-diene. **8a-12a** was prepared according to method D, all spectroscopic data agree with the literature.[6]

General Experimental Procedures for the synthesis of products:

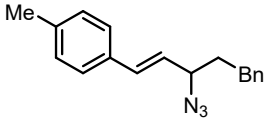
Preparation of 3-50, 52, 53, 60, 64-67, 72: To a flame-dried and N_2-purged Schlenk tube (10 mL) were added Fe(OTf)$_2$ (0.05 M in water, 10 μL, 0.0005 mmol, 0.5 mol%) and a stirring bar. The water was removed under vacuum. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of $TMSN_3$ (28.8 mg, 0.25 mmol, 2.5 equiv.), tert-butyl peroxide (36.6 mg, 0.25 mmol, 2.5 equiv.), 1,3-diene (0.1 mmol, 1.0 equiv.) and R-H (2.0 mL) sequentially. The mixture was stirred at 110 °C for 16 h. Then the solvent was removed under vacuum and the crude residue was purified by column chromatography (SiO_2, EtOAc/hexane = 1:25) to provide the products.

Preparation of 50, 54-59, 61-63, 68: To a flame-dried and N_2-purged Schlenk tube (10 mL) were added Fe(OTf)$_2$ (0.05 M in water, 10 μL, 0.0005 mmol, 0.5 mol%) and a stirring bar. The water was removed under vacuum. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of $TMSN_3$ (28.8 mg, 0.25 mmol, 2.5 equiv.), tert-butyl peroxide (36.6 mg, 0.25 mmol, 2.5 equiv.), 1,3-diene (0.1 mmol, 1.0 equiv.) PhH (1.0 mL) and R-H (1.0 mL) sequentially. The mixture was stirred at 110 °C for 16 h. Then the solvent was removed under vacuum and the crude residue was purified by column chromatography (SiO_2, EtOAc/hexane = 1:25) to provide the products.

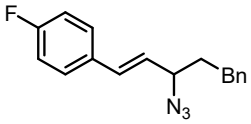
3 Characterization Data for the Products



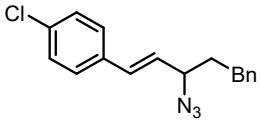
Compound 3. Colorless oil. Yield: 80%. 23.4 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (m, 4H), 7.19 – 7.09 (m, 3H), 6.92 – 6.69 (m, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 5.94 (dd, *J* = 15.7, 8.2 Hz, 1H), 3.95 – 3.87 (m, 1H), 3.73 (s, 3H), 2.74 – 2.60 (m, 2H), 1.98 – 1.79 (m, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 141.1, 133.2, 128.8, 128.6, 128.5, 128.0, 126.2, 124.6, 114.2, 64.3, 55.3, 36.4, 32.1.



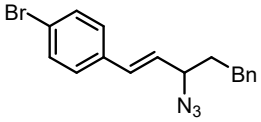
Compound 4. Colorless oil. Yield: 69%. 19.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 – 7.29 (m, 4H), 7.24 – 7.19 (m, 3H), 7.19 – 7.11 (m, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.8, 1.6 Hz, 1H), 4.04 – 3.96 (m, 1H), 2.82 – 2.68 (m, 2H), 2.37 (s, 3H), 2.04 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.1, 138.3, 133.7, 133.3, 129.5, 128.7, 128.6, 126.7, 126.2, 125.9, 64.3, 36.5, 32.2, 21.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3$: 278.1652, observed: 278.1651.



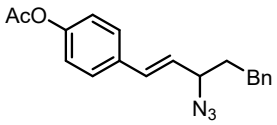
Compound 5. Colorless oil. Yield: 78%. 21.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.19 (m, 3H), 7.10 – 7.00 (m, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.06 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 2.82 – 2.68 (m, 2H), 2.05 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8 (d, *J* = 247.8 Hz), 141.0, 132.5, 132.2 (d, *J* = 3.4 Hz), 128.7, 128.6, 128.4, 128.3, 126.7 (d, *J* = 2.3 Hz), 126.3, 115.7 (d, *J* = 21.7 Hz). 64.1, 36.4, 32.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{16}FN_3$: 282.1401, observed: 282.1399.



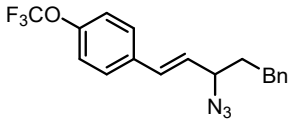
Compound 6. Colorless oil. Yield: 61%. 18.2 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.28 (m, 6H), 7.28 – 7.18 (m, 3H), 6.56 (d, *J* = 15.7 Hz, 1H), 6.11 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.04 – 3.96 (m, 1H), 2.82 – 2.68 (m, 2H), 2.04 – 1.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.0, 134.6, 134.0, 132.4, 129.0, 128.7, 128.6, 128.0, 127.7, 126.3, 64.0, 36.4, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{16}ClN_3$: 298.1106, observed: 298.1104.



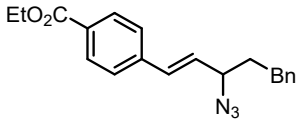
Compound 7. Colorless oil. Yield: 72%. 24.6 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 – 7.46 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 6.57 (d, *J* = 15.7 Hz, 1H), 6.15 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.06 – 3.98 (m, 1H), 2.84 – 2.70 (m, 2H), 1.97 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.0, 135.0, 132.4, 131.9, 128.7, 128.6, 128.3, 127.9, 126.3, 122.2, 63.9, 36.3, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{16}BrN_3$: 342.0600, observed: 342.0600.



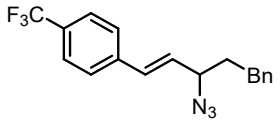
Compound 8. Colorless oil. Yield: 45%. 14.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 7.10 – 7.03 (m, 2H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.09 (dd, *J* = 15.7, 8.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 2.81 – 2.67 (m, 2H), 2.05 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 150.7, 141.0, 133.9, 132.7, 128.7, 128.6, 127.8, 127.3, 126.3, 122.0, 64.0, 36.4, 32.1, 21.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{19}H_{19}N_3O_2$: 322.1550, observed: 322.1551.



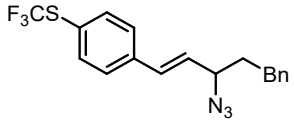
Compound 9. Colorless oil. Yield: 63%. 21.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.16 (m, 5H), 6.59 (d, J = 15.8 Hz, 1H), 6.12 (dd, J = 15.8, 8.0 Hz, 1H), 4.06 – 3.96 (m, 1H), 2.83 – 2.66 (m, 2H), 2.06 – 1.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.0 (q, *J* = 1.8 Hz), 140.9, 134.8, 132.1, 128.7, 128.6, 128.1, 128.1, 126.3, 121.3, 120.6 (q, J = 257.3 Hz), 63.9, 36.3, 32.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.8.



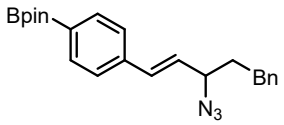
Compound 10. Colorless oil. Yield: 51%. 17.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 – 7.86 (m, 2H), 7.49 – 7.42 (m, 2H), 7.39 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.99 (m, 1H), 2.83 – 2.68 (m, 2H), 2.05 – 1.88 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 140.9, 140.4, 132.6, 130.1, 130.1, 129.7, 128.7, 128.6, 126.6, 126.3, 63.9, 61.1, 36.3, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{20}H_{21}N_3O_2$: 336.1706, observed: 336.1701.



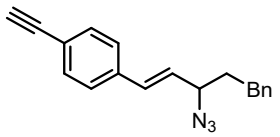
Compound 11. Colorless oil. Yield: 49%. 16.2 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 – 7.57 (m, 2H), 7.52 – 7.45 (m, 2H), 7.32 (m, 2H), 7.25 – 7.19 (m, 3H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.23 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.07 – 3.99 (m, 1H), 2.83 – 2.69 (m, 2H), 2.06 – 1.89 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.9, 139.6, 132.1, 130.1 (q, *J* = 30.7 Hz), 129.8, 128.7, 128.6, 127.0, 126.4, 125.8 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 269.9z Hz), 63.8, 36.3, 32.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.6.



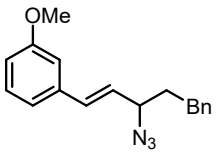
Compound 12. Colorless oil. Yield: 52%. 18.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63 (m, 2H), 7.48 – 7.38 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.22 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.08 – 3.98 (m, 1H), 2.84 – 2.67 (m, 2H), 2.07 – 1.86 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 138.7, 136.7, 132.1, 129.7, 129.6 (q, *J* = 309.5 Hz), 128.7, 128.6, 127.7, 126.4, 123.9 (q, *J* = 2.2 Hz), 63.8, 36.3, 32.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -42.7.



Compound 13. Colorless oil. Yield: 37%. 14.4 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 – 7.75 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 6.61 (d, *J* = 15.7 Hz, 1H), 6.19 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.06 – 3.97 (m, 1H), 2.81 – 2.67 (m, 2H), 2.04 – 1.87 (m, 2H), 1.35 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.1, 138.8, 135.3, 133.6, 128.7, 128.6, 128.1, 126.3, 126.1, 84.0, 64.1, 36.4, 32.2, 25.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{23}H_{28}BN_3O_2$: 390.2347, observed: 390.2340.

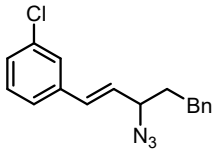


Compound 14. Colorless oil. Yield: 40%. 11.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 – 7.43 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.04 – 3.96 (m, 1H), 2.81 – 2.67 (m, 2H), 2.04 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.0, 136.5, 132.8, 132.6, 128.7, 128.6, 128.3, 126.7, 126.3, 121.9, 83.6, 78.2, 64.0, 36.4, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{19}H_{17}N_3$: 288.1495, observed: 288.1491.

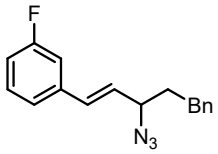


Compound 15. Colorless oil. Yield: 60%. 17.6 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.29 (m, 2H), 7.23 – 7.18 (m, 3H), 7.03 – 6.98 (m, 1H), 6.96 – 6.92 (m, 1H), 6.87 – 6.81 (m, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.04 – 3.96 (m, 1H), 2.82 – 2.68 (m, 2H), 2.04 – 1.87 (m,

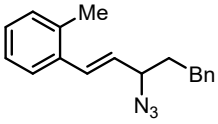
2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 141.1, 137.5, 133.6, 129.8, 128.7, 128.6, 127.3, 126.3, 119.5, 114.0, 112.1, 64.1, 55.4, 36.4, 32.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3O$: 294.1601, observed: 294.1602.



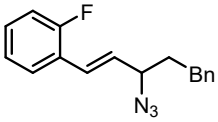
Compound 16. Colorless oil. Yield: 48%. 14.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.36 (m, 1H), 7.33 – 7.28 (m, 2H), 7.24 – 7.16 (m, 6H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.03 – 3.95 (m, 1H), 2.73 (m, 2H), 2.06 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8, 137.8, 134.7, 132.1, 129.9, 128.6, 128.5, 128.5, 128.1, 126.6, 126.2, 124.9, 63.7, 36.2, 32.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{16}ClN_3$: 298.1106, observed: 298.1103.



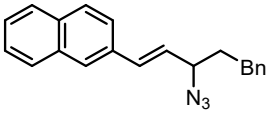
Compound 17. Colorless oil. Yield: 58%. 16.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.28 (m, 3H), 7.24 – 7.18 (m, 3H), 7.18 – 7.14 (m, 1H), 7.12 – 7.05 (m, 1H), 7.01 – 6.94 (m, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.14 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.16 – 3.83 (m, 1H), 2.92 – 2.67 (m, 2H), 2.04 – 1.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 245.8 Hz), 141.0, 138.4 (d, *J* = 7.8 Hz), 132.4 (d, *J* = 2.5 Hz), 130.3 (d, *J* = 8.4 Hz), 128.7, 128.6, 128.5, 126.3, 122.7 (d, *J* = 2.8 Hz), 115.2 (d, *J* = 21.3 Hz), 113.3 (d, *J* = 22.0 Hz), 63.8, 36.3, 32.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{16}FN_3$: 282.1401, observed: 282.1399.



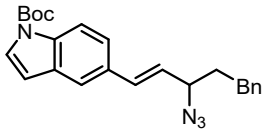
Compound 18. Colorless oil. Yield: 52%. 14.4 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 – 7.42 (m, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.19 (m, 5H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.01 (dd, *J* = 15.6, 8.1 Hz, 1H), 4.07 – 3.99 (m, 1H), 2.83 – 2.69 (m, 2H), 2.37 (s, 3H), 2.05 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.1, 135.8, 135.4, 131.9, 130.5, 128.7, 128.6, 128.3, 128.2, 126.3, 126.3, 126.1, 64.3, 36.4, 32.2, 20.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3$: 278.1652, observed: 278.1649.



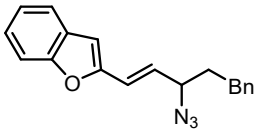
Compound 19. Colorless oil. Yield: 49%. 13.8 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 – 7.42 (m, 1H), 7.36 – 7.29 (m, 2H), 7.25 – 7.17 (m, 4H), 7.17 – 7.09 (m, 1H), 7.09 – 7.02 (m, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 16.0, 8.1 Hz, 1H), 4.06 – 3.98 (m, 1H), 2.82 – 2.68 (m, 2H), 2.05 – 1.88 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.56 (d, *J* = 250.0 Hz), 141.0, 129.7 (d, *J* = 4.9 Hz), 129.6, 128.7, 128.6, 127.9 (d, *J* = 3.5 Hz), 126.3, 126.2 (d, *J* = 3.4 Hz), 124.3 (d, *J* = 3.5 Hz), 124.0 (d, *J* = 12.2 Hz), 116.0 (d, *J* = 22.1 Hz), 64.3, 36.4, 32.2. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{16}FN_3$: 282.1401, observed: 282.1400.



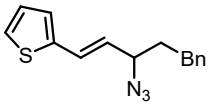
Compound 20. Colorless oil. Yield: 46%. 14.4 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.86 – 7.73 (m, 4H), 7.60 (m, 1H), 7.53 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.12 (m, 3H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.26 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.11 – 4.03 (m, 1H), 2.85 – 2.71 (m, 2H), 2.09 – 1.91 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.1, 133.8, 133.7, 133.5, 133.4, 128.7, 128.6, 128.5, 128.2, 127.8, 127.4, 127.1, 126.6, 126.3, 126.3, 123.6, 64.2, 36.5, 32.2. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{21}H_{19}N_3$: 313.1574, observed: 313.1572.



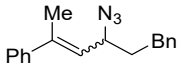
Compound 21. Colorless oil. Yield: 45%. 18.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.12 – 8.07 (m, 1H), 7.61 – 7.55 (m, 2H), 7.42 – 7.36 (m, 1H), 7.36 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 6.14 (dd, *J* = 15.7, 8.2 Hz, 1H), 4.02 (q, *J* = 6.6 Hz, 1H), 2.83 – 2.69 (m, 2H), 2.06 – 1.88 (m, 2H), 1.68 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.8, 141.2, 135.2, 134.2, 131.0, 130.9, 128.7, 128.6, 126.8, 126.2, 125.7, 123.0, 119.5, 115.4, 107.5, 84.0, 64.4, 36.5, 32.2, 28.4.



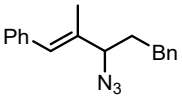
Compound 22. Colorless oil. Yield: 38%. 11.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 – 7.49 (m, 1H), 7.48 – 7.42 (m, 1H), 7.37 – 7.27 (m, 3H), 7.25 – 7.17 (m, 4H), 6.63 (s, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.39 (dd, *J* = 15.6, 7.7 Hz, 1H), 4.07 – 3.99 (m, 1H), 2.83 – 2.70 (m, 2H), 1.99 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.0, 153.4, 141.0, 128.9, 128.9, 128.7, 128.6, 126.3, 125.1, 123.1, 121.6, 121.2, 111.2, 106.0, 63.5, 36.3, 32.1.



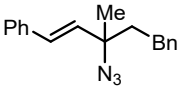
Compound 23. Colorless oil. Yield: 44%. 11.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.28 (m, 2H), 7.26 – 7.15 (m, 4H), 7.04 – 6.91 (m, 2H), 6.73 (dd, *J* = 15.6, 0.9 Hz, 1H), 5.98 (dd, *J* = 15.6, 8.0 Hz, 1H), 4.00 – 3.92 (m, 1H), 2.82 – 2.66 (m, 2H), 2.02 – 1.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.0, 141.0, 128.7, 128.6, 127.6, 126.8, 126.7, 126.5, 126.3, 125.1, 63.9, 36.4, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{15}H_{15}N_3S$: 270.1059, observed: 270.1058.



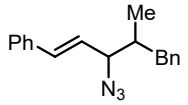
Compound 24. Colorless oil. Yield: 42%. 11.6 mg. *E/Z*: 3:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 – 7.38 (m, 2H, major + minor), 7.37 – 7.26 (m, 10H, major + minor), 7.23 – 7.14 (m, 6H, major + minor), 7.11 – 6.98 (m, 2H, major + minor), 5.73 (d, *J* = 1.4 Hz, 1H, major), 5.47 (d, *J* = 1.5 Hz, 1H, minor), 4.34 – 4.20 (m, 1H, major), 4.02 – 3.83 (m, 1H, minor), 2.93 – 2.68 (m, 2H, major), 2.65 – 2.50 (m, 2H, minor), 2.12 (d, *J* = 1.5 Hz, 3H, minor), 2.07 (d, *J* = 1.4 Hz, 3H, major), 2.03 – 1.94 (m, 2H, major + minor), 1.93 – 1.84 (m, 2H, major + minor). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.0 (minor), 142.5 (major), 141.2(minor), 141.0 (major), 140.7 (major), 140.6 (minor), 128.5 (major), 128.4 (major), 128.4 (minor), 128.4 (minor), 128.4 (major), 128.3 (minor), 128.2 (major), 128.2 (minor), 127.7 (minor), 127.7 (major), 126.1 (minor), 126.0 (major), 125.2 (major), 124.7 (minor), 59.9 (minor), 59.3 (major), 36.8 (minor), 36.7 (major), 32.1 (major), 32.0 (minor), 25.9 (minor), 16.8 (major). **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3$: 278.1652, observed: 278.1651.



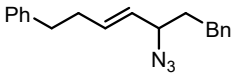
Compound 25. Colorless oil. Yield: 55%. 15.2 mg. *E/Z*: 8:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 – 7.27 (m, 7H), 7.25 – 7.19 (m, 3H), 6.50 (s, 1H), 3.99 (t, *J* = 7.3 Hz, 1H), 2.79 – 2.62 (m, 2H), 2.05 – 1.91 (m, 2H), 1.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.2, 136.9, 135.4, 129.7, 129.2, 128.7, 128.6, 128.4, 127.1, 126.3, 70.3, 34.4, 32.5, 13.6. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3$: 278.1652, observed: 278.1646.



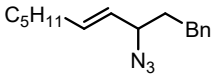
Compound 26. Colorless oil. Yield: 64%. 17.8 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 7.24 – 7.15 (m, 3H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.21 (d, *J* = 16.1 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.05 – 1.91 (m, 2H), 1.55 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 136.5, 131.7, 130.2, 128.8, 128.6, 128.5, 128.1, 126.8, 126.1, 64.9, 42.8, 30.8, 24.2 **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3$: 278.1652, observed: 278.1646.



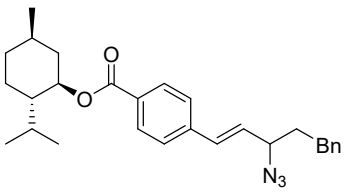
Compound 27. Colorless oil. Yield: 36%. 10.0 mg. *d.r.*: 1:1.1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 – 7.25 (m, 15H, major + minor), 7.25 – 7.16 (m, 6H, major + minor), 6.61 (d, *J* = 16.0 Hz, 2H, major + minor), 6.19 (dd, *J* = 15.8, 8.2 Hz, 2H, major + minor), 4.00 (dd, *J* = 8.2, 4.9 Hz, 1H, minor), 3.93 (dd, *J* = 8.6, 6.4 Hz, 1H, major), 2.87 (dt, *J* = 13.1, 6.3 Hz, 2H, minor), 2.48 – 2.40 (m, 2H, major + minor), 2.09 – 1.96 (m, 2H, major), 0.96 (d, *J* = 6.7 Hz, 3H, major), 0.92 (d, *J* = 6.8 Hz, 3H, minor). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.3 (major), 140.1 (minor), 136.2 (major), 136.2 (minor), 134.9 (major), 134.2 (minor), 129.4 (major), 129.3 (minor), 128.8 (minor), 128.8 (major), 128.6 (major), 128.5 (minor), 128.3 (minor), 128.3 (major), 126.9 (minor), 126.8 (major), 126.2 (major + minor), 125.9 (major), 125.0 (minor), 69.4 (minor), 68.9 (major), 40.2 (minor), 39.9 (major), 39.6 (minor), 39.6 (major), 15.8 (minor), 15.3 (major). **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3$: 278.1652, observed: 278.1653.



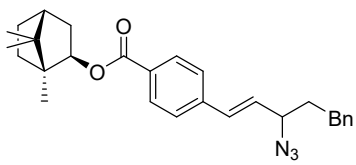
Compound 28. Colorless oil. Yield: 63%. 18.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29 (t, *J* = 7.6 Hz, 4H), 7.24 – 7.12 (m, 6H), 5.81 – 5.70 (m, 1H), 5.46 – 5.36 (m, 1H), 3.81 – 3.73 (m, 1H), 2.91 – 2.69 (m, 2H), 2.67 – 2.58 (m, 2H), 2.49 – 2.35 (m, 2H), 1.89 – 1.71 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.5, 141.3, 134.8, 128.6, 128.5, 128.5, 128.3, 126.2, 126.1, 63.9, 36.3, 35.8, 34.0, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{19}H_{21}N_3$: 292.1808, observed: 292.1803.



Compound 29. Colorless oil. Yield: 39%. 10.1 mg. regioselectivity (1,2- and 1,4-addition): 1.2:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 – 7.25 (m, 4H, major + minor), 7.23 – 7.14 (m, 6H, major + minor), 5.78 – 5.66 (m, 2H, major + minor), 5.44 – 5.30 (m, 2H, major + minor), 3.82 – 3.71 (m, 2H, major + minor), 2.79 – 2.60 (m, 4H, major + minor), 2.48 – 2.34 (m, 2H, major + minor), 2.13 – 2.00 (m, 2H, major + minor), 1.93 – 1.72 (m, 2H, major + minor), 1.51 – 1.38 (m, 4H, major + minor), 1.37 – 1.20 (m, 10H, major + minor), 0.94 – 0.83 (m, 6H, major + minor). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.6 (minor), 141.4 (major), 136.2 (major), 134.3 (minor), 128.7 (major), 128.6 (major + minor), 128.5 (minor), 128.5 (major), 127.4 (minor), 126.2 (major), 126.1 (minor), 64.9 (major), 64.1 (minor), 36.4 (minor), 35.9 (major), 34.7 (minor), 34.1 (major), 32.3 (major), 32.2 (minor), 31.6 (minor), 31.4 (major), 29.0 (major), 25.7 (minor), 22.7 (minor), 22.6 (major), 14.2 (major), 14.1 (minor). **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{16}H_{23}N_3$: 258.1965, observed: 258.1964.

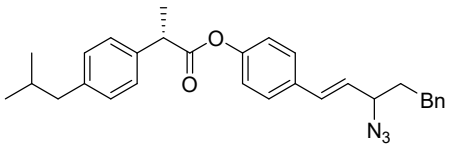


Compound 30. Colorless oil. Yield: 50%. 22.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 – 7.98 (m, 2H), 7.48 – 7.42 (m, 2H), 7.38 – 7.27 (m, 2H), 7.24 – 7.12 (m, 3H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 4.07 – 3.99 (m, 1H), 2.83 – 2.68 (m, 2H), 2.18 – 2.10 (m, 1H), 2.05 – 1.88 (m, 3H), 1.78 – 1.70 (m, 2H), 1.56 (tdd, *J* = 12.4, 6.0, 3.1 Hz, 2H), 1.20 – 1.05 (m, 2H), 0.93 (t, *J* = 7.1 Hz, 7H), 0.80 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 140.9, 140.3, 132.6, 130.5, 130.1, 129.6, 128.7, 128.6, 126.6, 126.3, 75.1, 63.9, 47.5, 41.1, 36.3, 34.5, 32.1, 31.6, 26.7, 23.9, 22.2, 20.9, 16.7. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ calculated for $C_{28}H_{35}N_3O_2$: 468.2621, observed: 468.2618.

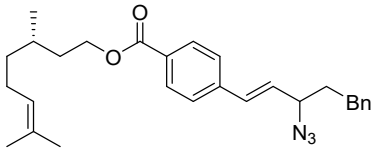


Compound 31. Colorless oil. Yield: 41%. 18.2 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05 – 7.95 (m, 2H), 7.50 – 7.42 (m, 2H), 7.34 – 7.27 (m, 1H), 7.24 – 7.17 (m, 3H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 7.9 Hz, 1H), 5.13 (m, 1H), 4.07 – 3.99 (m, 1H), 2.76 (m, 2H), 2.53 – 2.43 (m, 1H), 2.18 – 2.09 (m, 1H), 2.06 – 1.89 (m, 2H), 1.87 – 1.78 (m, 1H), 1.75 (t, *J* = 4.5 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.37 – 1.28 (m, 1H), 1.17 – 1.09 (m, 1H), 0.98 (s, 3H), 0.93 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 140.9, 140.4, 132.6, 130.5,

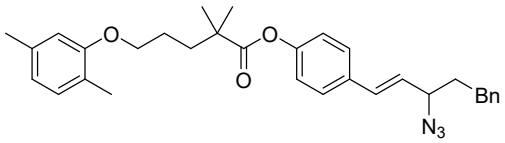
130.1, 129.6, 128.7, 128.6, 126.7, 126.3, 80.7, 63.9, 49.3, 48.0, 45.2, 37.1, 36.3, 32.1, 28.2, 27.6, 19.9, 19.1, 13.8. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ calculated for $C_{28}H_{33}N_3O_2$: 466.2465, observed: 466.2462.



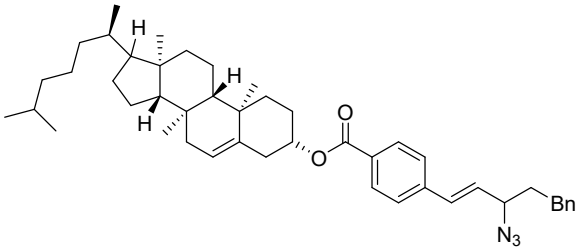
Compound 32. Colorless oil. Yield: 61%. 28.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.34 (m, 2H), 7.31 (dt, *J* = 7.4, 3.5 Hz, 4H), 7.23 – 7.14 (m, 5H), 7.02 – 6.96 (m, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.7, 8.0 Hz, 1H), 4.03 – 3.91 (m, 2H), 2.81 – 2.67 (m, 2H), 2.49 (d, *J* = 7.1 Hz, 2H), 2.04 – 1.83 (m, 3H), 1.62 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.2, 150.9, 141.0, 141.0, 137.3, 133.7, 132.7, 129.7, 128.7, 128.6, 127.7, 127.3, 127.1, 126.3, 121.8, 64.0, 45.4, 45.2, 36.4, 32.1, 30.3, 22.5, 18.7. **HRMS** (ESI-TOF) m/z $[M+NH_4]^+$ calculated for $C_{30}H_{33}N_3O_2$: 485.2911, observed: 485.2907.



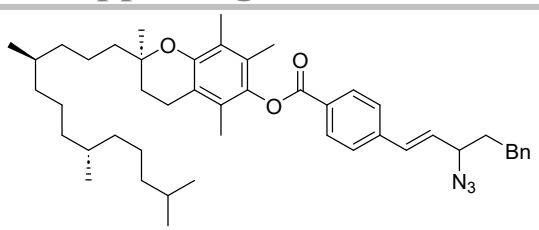
Compound 33. Colorless oil. Yield: 55%. 24.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 – 7.97 (m, 2H), 7.47 – 7.42 (m, 2H), 7.37 – 7.28 (m, 2H), 7.24 – 7.13 (m, 3H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 7.9 Hz, 1H), 5.14 – 5.07 (m, 1H), 4.42 – 4.30 (m, 2H), 4.06 – 3.99 (m, 1H), 2.83 – 2.68 (m, 2H), 2.10 – 1.88 (m, 4H), 1.87 – 1.76 (m, 1H), 1.74 – 1.64 (m, 4H), 1.63 – 1.48 (m, 5H), 1.46 – 1.36 (m, 1H), 1.31 – 1.19 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 140.9, 140.4, 132.6, 131.5, 130.1, 130.1, 129.7, 128.7, 128.6, 126.7, 126.3, 124.7, 63.9, 63.7, 37.1, 36.3, 35.7, 32.1, 29.8, 25.9, 25.6, 19.7, 17.8. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{28}H_{35}N_3O_2$: 446.2802, observed: 446.279.



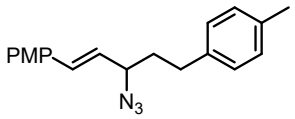
Compound 34. Colorless oil. Yield: 50%. 25.6 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.04 (d, *J* = 8.3 Hz, 3H), 6.73 – 6.58 (m, 3H), 6.12 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.07 – 3.99 (m, 3H), 2.83 – 2.70 (m, 2H), 2.34 (s, 3H), 2.22 (s, 3H), 2.07 – 1.88 (m, 6H), 1.41 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.4, 157.0, 151.0, 141.0, 136.6, 133.7, 132.8, 130.5, 128.7, 128.6, 127.7, 127.1, 126.3, 123.8, 121.9, 120.9, 112.1, 67.9, 64.1, 42.6, 37.3, 36.4, 32.2, 25.4, 25.3, 21.5, 15.9. **HRMS** (ESI-TOF) m/z $[M+NH_4]^+$ calculated for $C_{32}H_{37}N_3O_3$: 529.3173, observed: 529.3171.



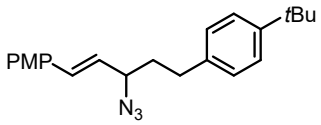
Compound 35. Colorless oil. Yield: 45%. 31.0 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.01 (m, 2H), 7.44 (m, 2H), 7.35 – 7.28 (m, 2H), 7.24 – 7.15 (m, 3H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 7.9 Hz, 1H), 5.45 – 5.40 (m, 1H), 4.92 – 4.82 (m, 1H), 4.06 – 3.99 (m, 1H), 2.83 – 2.68 (m, 2H), 2.47 (d, *J* = 8.1 Hz, 2H), 2.19 – 1.89 (m, 6H), 1.88 – 1.81 (m, 1H), 1.78 – 1.67 (m, 1H), 1.65 – 1.43 (m, 7H), 1.43 – 1.31 (m, 3H), 1.31 – 1.10 (m, 5H), 1.08 (s, 3H), 1.04 – 0.98 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.70 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.8, 140.9, 140.3, 139.8, 132.6, 130.5, 130.1, 129.6, 128.7, 128.6, 126.6, 126.3, 122.9, 74.8, 63.9, 56.9, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.2, 36.8, 36.3, 36.3, 35.9, 32.1, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ calculated for $C_{45}H_{61}N_3O_2$: 698.4656, observed: 698.4642.



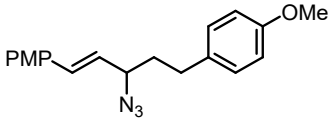
Compound 36. Colorless oil. Yield: 39%. 28.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.25 – 8.20 (m, 2H), 7.58 – 7.51 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.18 (m, 3H), 6.69 (d, *J* = 15.8 Hz, 1H), 6.30 (dd, *J* = 15.8, 7.8 Hz, 1H), 4.10 – 4.02 (m, 1H), 2.85 – 2.70 (m, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.14 (s, 3H), 2.07 (s, 3H), 2.03 (s, 4H), 2.01 – 1.81 (m, 3H), 1.61 – 0.97 (m, 24H), 0.91 – 0.84 (m, 13H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.9, 149.6, 141.0, 140.9, 140.8, 132.5, 130.7, 130.1, 129.2, 128.7, 128.6, 127.0, 126.9, 126.4, 125.3, 123.3, 117.6, 75.2, 63.8, 39.5, 37.6, 37.6, 37.4, 36.3, 33.0, 32.1, 28.1, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.3, 12.0. **HRMS** (ESI-TOF) m/z $[M+NH_4]^+$ calculated for $C_{47}H_{65}N_3O_3$: 737.5364, observed: 737.5358.



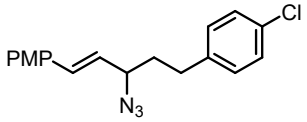
Compound 37. Colorless oil. Yield: 74%. 22.7 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.55 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 8.2 Hz, 1H), 3.97 (q, *J* = 7.4 Hz, 1H), 3.82 (s, 3H), 2.76 – 2.63 (m, 2H), 2.33 (s, 3H), 2.01 – 1.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 138.1, 135.7, 133.3, 129.3, 128.9, 128.5, 128.0, 124.8, 114.2, 64.4, 55.5, 36.6, 31.7, 21.1. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{19}H_{21}N_3O$: 307.1679, observed: 307.1678.



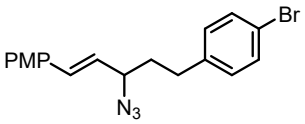
Compound 38. Colorless oil. Yield: 55%. 19.2 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.28 (m, 4H), 7.16 – 7.11 (m, 2H), 6.92 – 6.84 (m, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.82 (s, 3H), 2.78 – 2.63 (m, 2H), 2.03 – 1.85 (m, 2H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 149.1, 138.1, 133.3, 128.9, 128.3, 128.1, 125.5, 124.8, 114.2, 64.4, 55.5, 36.5, 34.5, 31.6, 31.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{22}H_{27}N_3O$: 350.2227, observed: 350.2221.



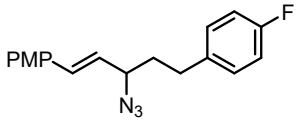
Compound 39. Colorless oil. Yield: 46%. 14.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.29 (m, 2H), 7.14 – 7.08 (m, 2H), 6.91 – 6.80 (m, 4H), 6.54 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.7, 8.2 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 2.74 – 2.60 (m, 2H), 1.99 – 1.81 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 158.1, 133.3, 129.5, 128.9, 128.3, 128.1, 124.8, 114.2, 114.1, 64.3, 55.5, 55.4, 36.7, 31.3, 29.9. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{19}H_{21}N_3O_2$: 324.1706, observed: 324.1703.



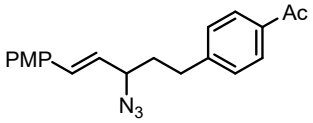
Compound 40. Colorless oil. Yield: 56%. 18.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 – 7.30 (m, 2H), 7.26 – 7.20 (m, 2H), 7.14 – 7.08 (m, 2H), 6.89 – 6.83 (m, 2H), 6.56 – 6.50 (m, 1H), 5.97 (dd, *J* = 15.7, 8.2 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.81 (s, 3H), 2.76 – 2.62 (m, 2H), 1.98 – 1.80 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 139.6, 133.5, 132.0, 130.0, 128.8, 128.7, 128.1, 124.5, 114.3, 64.3, 55.5, 36.4, 31.6. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{18}H_{18}ClN_3O$: 327.1133, observed: 327.1134.



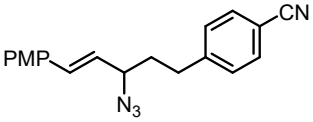
Compound 41. Colorless oil. Yield: 43%. 15.6 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.10 – 7.00 (m, 2H), 6.91 – 6.84 (m, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.7, 8.3 Hz, 1H), 3.99 – 3.91 (m, 1H), 3.82 (s, 3H), 2.75 – 2.61 (m, 2H), 1.99 – 1.81 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 140.1, 133.5, 131.7, 130.4, 128.7, 128.1, 124.5, 120.0, 114.3, 64.3, 55.5, 36.4, 31.6.



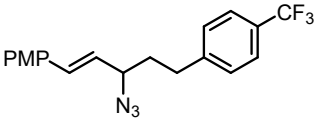
Compound 42. Colorless oil. Yield: 55%. 17.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.30 (m, 2H), 7.18 – 7.10 (m, 2H), 7.02 – 6.92 (m, 2H), 6.92 – 6.83 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.7, 8.2 Hz, 1H), 4.00 – 3.92 (m, 1H), 3.82 (s, 3H), 2.77 – 2.63 (m, 2H), 1.99 – 1.82 (m, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 243.9 Hz), 159.9, 136.8 (d, *J* = 3.2 Hz), 133.4, 130.0 (d, *J* = 7.6 Hz), 128.8, 128.1, 124.6, 115.4 (d, *J* = 21.2 Hz), 114.3, 64.3, 55.5, 36.7, 31.4.**^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.3. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{18}H_{18}FN_3O$: 311.1428, observed: 311.1427.



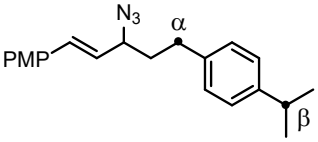
Compound 43. Colorless oil. Yield: 31%. 10.4 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 – 7.87 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.24 (m, 2H), 6.91 – 6.84 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.98 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.82 (s, 3H), 2.86 – 2.72 (m, 2H), 2.59 (s, 3H), 2.03 – 1.86 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.9, 159.9, 147.0, 135.5, 133.6, 128.8, 128.8, 128.7, 128.1, 124.4, 114.3, 64.3, 55.5, 36.2, 32.3, 26.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{20}H_{21}N_3O_2$: 336.1706, observed: 336.1704.



Compound 44. Colorless oil. Yield: 36%. 11.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 – 7.56 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 6.94 – 6.81 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.97 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.82 (s, 3H), 2.87 – 2.72 (m, 2H), 2.01 – 1.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 146.7, 133.7, 132.4, 129.3, 128.4, 128.0, 124.0, 118.9, 114.2, 110.1, 64.1, 55.4, 35.9, 32.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{19}H_{18}N_4O$: 319.1553, observed: 319.1552.

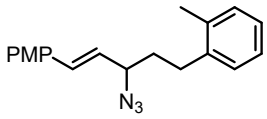


Compound 45. Colorless oil. Yield: 46%. 16.6 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.53 (m, 2H), 7.37 – 7.28 (m, 4H), 6.96 – 6.84 (m, 2H), 6.56 (d, *J* = 15.7 Hz, 1H), 5.98 (dd, *J* = 15.7, 8.2 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.82 (s, 3H), 2.87 – 2.72 (m, 2H), 2.03 – 1.86 (m, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.0, 145.3, 133.7, 128.9, 128.8 (q, *J* = 32.6 Hz), 128.7, 128.1, 125.6 (q, *J* = 3.8 Hz), 124.3, 123.4 (d, *J* = 271.4 Hz), 114.3, 64.3, 55.5, 36.3, 32.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -62.3. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{19}H_{18}F_3N_3O$: 361.1396, observed: 361.1393.

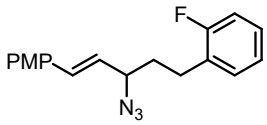


Compound 46. Colorless oil. Yield: 31%. 10.9 mg. α:β = 1.2:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 2H, major + minor), 7.24 – 7.15 (m, 5H, major + minor), 7.14 – 7.09 (m, 4H, major + minor), 6.91 – 6.69 (m, 4H, major + minor), 6.55 (d, *J* = 15.8 Hz, 1H, major), 6.26 (d, *J* = 15.7 Hz, 1H, minor), 5.99 (dd, *J* = 15.7, 8.2 Hz, 1H, minor), 5.75 (dd, *J* = 15.7, 8.4 Hz, 1H, major), 4.06 – 3.94 (m, 1H, major), 3.82 (s, 3H, major),

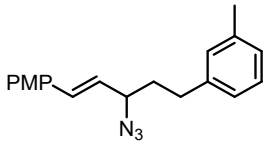
3.81 (s, 3H, minor), 3.77 – 3.67 (m, 1H, major), 2.77 – 2.61 (m, 2H, major), 2.30 (s, 3H, minor), 2.22 (d, 2H. minor), 1.93 – 1.86 (m, 2H, major), 1.40 (s, 3H, minor), 1.34 (s, 3H, minor), 1.25 (d, J = 6.9 Hz, 6H, major). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 159.6, 146.8, 145.2, 138.5, 135.5, 133.3, 132.0, 129.1, 128.5, 128.1, 128.0, 126.7, 126.0, 125.9, 124.8, 114.2, 114.1, 64.4, 62.8, 55.5, 55.5, 48.9, 37.1, 36.6, 33.9, 31.8, 30.6, 28.9, 24.2, 21.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{21}H_{25}N_3O$: 336.2070, observed: 336.2071.



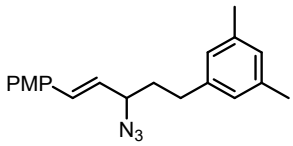
Compound 47. Colorless oil. Yield: 72%. 22.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 – 7.32 (m, 2H), 7.20 – 7.09 (m, 4H), 6.93 – 6.84 (m, 2H), 6.59 (d, J = 15.8 Hz, 1H), 6.03 (dd, J = 15.8, 8.1 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.83 (s, 3H), 2.82 – 2.64 (m, 2H), 2.33 (s, 3H), 1.98 – 1.81 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 139.4, 136.1, 133.3, 130.5, 129.0, 128.8, 128.1, 126.4, 126.2, 124.7, 114.2, 64.7, 55.5, 35.4, 29.6, 19.4. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{19}H_{21}N_3O$: 307.1679, observed: 307.1679.



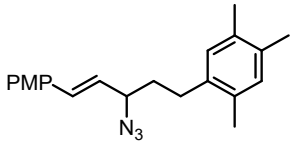
Compound 48. Colorless oil. Yield: 46%. 14.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 2H), 7.23 – 7.15 (m, 2H), 7.11 – 6.98 (m, 2H), 6.91 – 6.83 (m, 2H), 6.57 (d, J = 15.7 Hz, 1H), 6.00 (dd, J = 15.8, 8.1 Hz, 1H), 4.03 – 3.96 (m, 1H), 3.82 (s, 3H), 2.84 – 2.69 (m, 2H), 2.01 – 1.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.3 (d, J = 245.0 Hz), 159.9, 133.4, 130.8 (d, J = 4.9 Hz), 128.8, 128.1, 128.1 (d, J = 16.0 Hz), 128.0 (d, J = 8.1 Hz), 124.6, 124.2 (d, J = 3.7 Hz), 115.5 (d, J = 22.0 Hz), 114.2, 64.5, 55.5, 35.2, 25.8 (d, J = 2.4 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -118.5. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{18}H_{18}FN_3O$: 311.1428, observed: 311.1427.



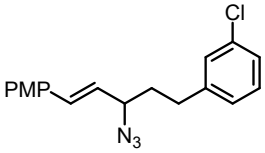
Compound 49. Colorless oil. Yield: 61%. 18.7 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (d, J = 8.8 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.01 (q, J = 7.9 Hz, 3H), 6.91 – 6.80 (m, 2H), 6.55 (d, J = 15.7 Hz, 1H), 6.00 (dd, J = 15.8, 8.2 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.82 (s, 3H), 2.77 – 2.62 (m, 2H), 2.34 (s, 3H), 2.02 – 1.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 141.1, 138.2, 133.3, 129.5, 128.9, 128.5, 128.1, 127.0, 125.6, 124.8, 114.2, 64.4, 55.5, 36.6, 32.1, 21.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{19}H_{21}N_3O$: 308.1757, observed: 308.1763.



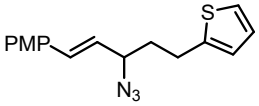
Compound 50. Colorless oil. Yield: 68%. 21.8 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.32 (m, 2H), 6.92 – 6.81 (m, 5H), 6.56 (d, J = 15.8 Hz, 1H), 6.00 (dd, J = 15.7, 8.1 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.83 (s, 3H), 2.75 – 2.59 (m, 2H), 2.30 (s, 6H), 2.01 – 1.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 141.1, 138.1, 133.2, 128.9, 128.0, 127.8, 126.5, 124.8, 114.2, 64.5, 55.5, 36.6, 32.1, 21.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{20}H_{23}N_3O$: 322.1914, observed: 322.1915.



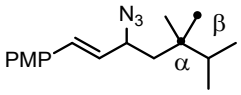
Compound 51. Colorless oil. Yield: 60%. 20.1 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.33 (m, 2H), 6.97 – 6.86 (m, 4H), 6.59 (d, J = 15.7 Hz, 1H), 6.03 (dd, J = 15.8, 8.1 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.83 (s, 3H), 2.67 (m, 2H), 2.26 (s, 3H), 2.22 (s, 3H), 2.22 (s, 3H), 1.88 (m, 2H). **NMR** (126 MHz, $CDCl_3$) δ 159.8, 136.7, 134.3, 134.1, 133.2, 133.2, 131.9, 130.5, 128.9, 128.0, 124.8, 114.2, 64.8, 55.5, 35.6, 29.2, 19.3, 19.3, 18.8. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{21}H_{25}N_3O$: 336.2070, observed: 336.2068.



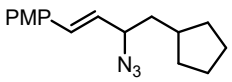
Compound 52. Colorless oil. Yield: 55%. 18.0 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.30 (m, 2H), 7.25 – 7.17 (m, 3H), 6.95 – 6.80 (m, 2H), 6.56 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.82 (s, 3H), 2.78 – 2.64 (m, 2H), 2.00 – 1.83 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 143.2, 134.4, 133.6, 129.9, 128.8, 128.7, 128.1, 126.8, 126.5, 124.4, 114.3, 64.3, 55.5, 36.3, 31.9. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{18}H_{18}ClN_3O$: 327.1133, observed: 327.1135.



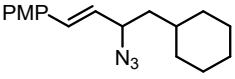
Compound 53. Colorless oil. Yield: 55%. 16.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 – 7.31 (m, 2H), 7.28 – 7.26 (m, 1H), 6.99 – 6.93 (m, 2H), 6.91 – 6.83 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.82 (s, 3H), 2.79 – 2.69 (m, 2H), 2.07 – 1.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 141.4, 133.4, 128.8, 128.2, 128.1, 125.8, 124.6, 120.7, 114.2, 64.4, 55.5, 35.7, 26.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{16}H_{17}N_3OS$: 300.1165, observed: 300.1162.



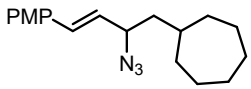
Compound 54. Colorless oil. Yield: 54%. 15.5 mg. α:β = 6:1. Regioselectivity (1,2- and 1,4-addition): 9:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 2H), 6.96 – 6.83 (m, 2H), 6.53 (d, *J* = 15.7 Hz, 1H), 6.00 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.09 – 4.00 (m, 1H), 3.82 (s, 3H), 1.59 – 1.45 (m, 3H), 0.90 (d, *J* = 6.6 Hz, 6H), 0.85 (dd, *J* = 13.7, 6.8 Hz, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$)δ 159.8, 131.9, 129.0, 128.0, 126.6, 114.2, 62.4, 55.5, 44.3, 36.5, 24.8, 24.6, 17.5, 17.5.**HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{17}H_{25}N_3O$: 287.1992, observed: 287.1992.



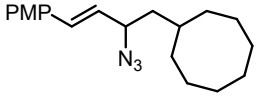
Compound 55. Colorless oil. Yield: 57%. 15.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 2H), 6.92 – 6.83 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.97 (dd, *J* = 15.7, 8.2 Hz, 1H), 4.03 – 3.95 (m, 1H), 3.82 (s, 3H), 1.96 – 1.76 (m, 3H), 1.76 – 1.45 (m, 6H), 1.13 (m, 2H). ^{13}C **NMR** (126 MHz, $CDCl_3$) δ 159.8, 132.7, 129.0, 128.0, 125.4, 114.2, 64.7, 55.5, 41.3, 36.9, 32.8, 32.7, 25.2, 25.2. **HRMS** (ESI-TOF) m/z $[M]^+$ calculated for $C_{16}H_{21}N_3O$: 271.1679, observed: 271.1683.



Compound 56. Colorless oil. Yield: 59%. 16.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 2H), 6.92 – 6.83 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.7, 8.2 Hz, 1H), 4.06 (m, 1H), 3.82 (s, 3H), 1.81 – 1.60 (m, 5H), 1.59 – 1.50 (m, 1H), 1.49 – 1.36 (m, 2H), 1.31 – 1.09 (m, 3H), 1.01 – 0.87 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 132.7, 129.0, 128.0, 125.5, 114.2, 62.9, 55.5, 42.5, 34.3, 33.5, 33.2, 26.6, 26.3, 26.2.

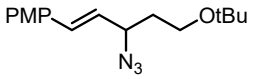


Compound 57. Colorless oil. Yield: 48%. 14.4 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 2H), 6.90 – 6.83 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.82 (s, 3H), 1.79 – 1.39 (m, 13H), 1.28 – 1.16 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 132.7, 129.0, 128.0, 125.4, 114.2, 63.5, 55.5, 43.1, 35.8, 34.7, 34.4, 28.6, 26.4, 26.3.

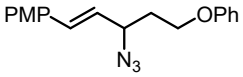


Compound 58. Colorless oil. Yield: 60%. 18.8 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 2H), 6.92 – 6.84 (m, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.8, 8.3 Hz,

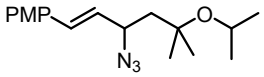
1H), 4.08 – 4.00 (m, 1H), 3.82 (s, 3H), 1.77 – 1.20 (m, 17H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 132.7, 129.0, 128.0, 125.5, 114.2, 63.5, 55.5, 42.9, 33.8, 32.3, 31.9, 27.5, 27.4, 26.4, 25.4, 25.3.



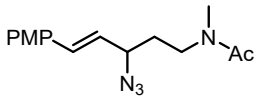
Compound 59. Colorless oil. Yield: 31%. 9.0 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (m, 2H), 6.91 – 6.83 (m, 2H), 6.58 (d, *J* = 15.7 Hz, 1H), 5.98 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.28 – 4.18 (m, 1H), 3.82 (s, 3H), 3.52 – 3.36 (m, 2H), 1.88 – 1.73 (m, 2H), 1.19 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 132.9, 129.0, 128.0, 125.0, 114.2, 73.0, 62.3, 57.8, 55.5, 35.8, 27.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{16}H_{23}N_3O_2$: 290.1863, observed: 290.1859.



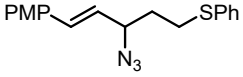
Compound 60. Colorless oil. Yield: 45%. 13.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.32 (m, 2H), 7.34 – 7.27 (m, 2H), 7.00 – 6.94 (m, 1H), 6.94 – 6.84 (m, 4H), 6.62 (d, *J* = 15.7 Hz, 1H), 6.03 (dd, *J* = 15.7, 1.7 Hz, 1H), 4.39 – 4.31 (m, 1H), 4.14 – 4.01 (m, 2H), 3.82 (s, 3H), 2.10 – 2.03 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 158.8, 133.6, 129.6, 128.7, 128.1, 124.3, 121.0, 114.7, 114.2, 64.1, 62.0, 55.5, 34.8. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3O_2$: 310.1550, observed: 310.1548.



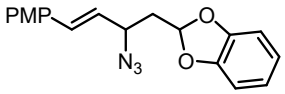
Compound 61. Colorless oil. Yield: 35%. 10.6 mg. Regioselectivity (1,2- and 1,4-addition): 20:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 – 7.30 (m, 2H), 6.90 – 6.81 (m, 3H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.01 (dd, *J* = 15.9, 8.2 Hz, 1H), 4.27 – 4.19 (m, 1H), 3.81 (s, 3H), 1.78 (d, *J* = 7.0 Hz, 2H), 1.26 (s, 1H), 1.24 (s, 3H), 1.20 (s, 3H), 1.11 (dd, *J* = 6.2, 2.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 132.0, 129.1, 128.0, 126.3, 114.2, 74.2, 63.6, 61.6, 55.5, 46.6, 27.2, 26.4, 25.3. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{17}H_{25}N_3O_2$: 304.2019, observed: 304.2016.



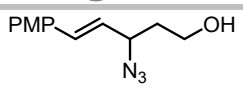
Compound 62. Colorless oil. Yield: 16%. 4.6 mg. Atropisomeric ratio: 1:1.3. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.31 (m, 4H, major + minor), 6.91 – 6.84 (m, 4H, major + minor), 6.60 (d, *J* = 15.8 Hz, 1H, minor), 6.58 (d, *J* = 15.7 Hz, 1H, major), 5.98 (dd, *J* = 15.7, 8.1 Hz, 4H, major + minor), 4.08 – 3.98 (m, 1H, major + minor), 3.82 (s, 3H, minor), 3.81 (s, 3H, major), 3.59 – 3.45 (m, 2H, minor), 3.46 – 3.34 (m, 2H, major), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 2.12 (s, 3H, minor), 2.06 (s, 3H, major), 1.92 – 1.75 (m, 4H, major + minor). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.7 (major), 170.5 (minor), 160.0 (minor), 159.7 (major), 134.0 (minor), 133.2 (major), 128.6 (major), 128.2 (minor), 128.0 (minor), 128.0 (major), 124.1 (major), 123.3 (minor), 114.2 (minor), 114.1 (major), 63.0 (major), 62.2 (minor), 55.4 (minor), 55.3 (major), 47.3 (minor), 44.9 (major), 36.6 (major), 33.5 (minor), 33.2 (minor), 32.5 (major), 21.9 (major), 21.2 (minor). **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{15}H_{20}N_4O_2$: 289.1659, observed: 289.1655.



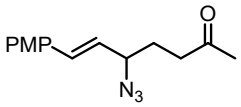
Compound 63. Colorless oil. Yield: 65%. 21.2 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 – 7.27 (m, 6H), 7.24 – 7.15 (m, 1H), 6.91 – 6.81 (m, 2H), 6.57 (d, *J* = 15.7 Hz, 1H), 5.95 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.27 – 4.13 (m, 1H), 3.82 (s, 3H), 3.08 – 2.93 (m, 2H), 2.01 – 1.80 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 135.9, 133.7, 129.7, 129.2, 128.6, 128.1, 126.4, 123.9, 114.2, 63.8, 55.5, 34.5, 30.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{18}H_{19}N_3OS$: 326.1322, observed: 326.1317.



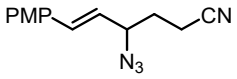
Compound 64. Colorless oil. Yield: 44%. 14.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.31 (m, 2H), 6.92 – 6.85 (m, 2H), 6.85 – 6.72 (m, 4H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.25 (dd, *J* = 5.8, 4.5 Hz, 1H), 6.03 (dd, *J* = 15.7, 8.4 Hz, 1H), 4.44 – 4.34 (m, 1H), 3.82 (s, 3H), 2.31 – 2.13 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 147.3, 147.2, 133.9, 128.3, 128.1, 123.3, 121.6, 121.6, 114.1, 108.8, 108.7, 108.7, 60.4, 55.3, 39.7.



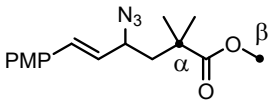
Compound 65. Colorless oil. Yield: 15%. 3.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 2H), 6.91 – 6.83 (m, 2H), 6.60 (d, *J* = 15.7 Hz, 1H), 6.01 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.31 – 4.21 (m, 1H), 3.84 – 3.73 (m, 5H), 1.92 – 1.79 (m, 2H), 1.63 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.9, 133.4, 128.7, 128.1, 124.3, 114.2, 62.7, 59.7, 55.5, 37.5. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{12}H_{15}N_3O_2$: 234.1237, observed: 234.1237.



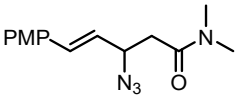
Compound 66. Colorless oil. Yield: 31%. 7.9 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 2H), 6.91 – 6.84 (m, 2H), 6.56 (d, *J* = 15.7 Hz, 1H), 5.94 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.09 – 4.01 (m, 1H), 3.82 (s, 3H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.96 – 1.81 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.7, 159.9, 133.5, 128.7, 128.1, 124.3, 114.3, 64.3, 55.5, 39.6, 30.2, 28.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{14}H_{17}N_3O_2$: 260.1393, observed: 260.1390.



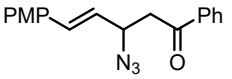
Compound 67. Colorless oil. Yield: 26%. 6.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.32 (m, 2H), 6.91 – 6.85 (m, 2H), 6.66 (d, *J* = 15.7 Hz, 1H), 5.93 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.23 – 4.15 (m, 1H), 3.82 (s, 3H), 2.55 – 2.40 (m, 2H), 1.96 – 1.88 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2, 134.9, 128.3, 128.2, 122.5, 119.0, 114.3, 63.4, 55.5, 30.7, 14.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{13}H_{14}N_4O$: 243.1240, observed: 243.1240.



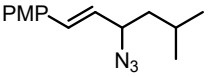
Compound 68. Colorless oil. Yield: 66%. 20.0 mg. α:β = 6:1. Regioselectivity (1,2- and 1,4-addition): 20:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.29 (m, 2H), 6.93 – 6.82 (m, 2H), 6.52 (d, *J* = 15.7 Hz, 1H), 5.93 (dd, *J* = 15.8, 8.5 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.81 (s, 3H), 3.59 (s, 3H), 1.96 (dd, *J* = 14.1, 7.9 Hz, 1H), 1.84 (dd, *J* = 14.2, 6.2 Hz, 1H), 1.24 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.7, 159.8, 133.1, 128.7, 128.1, 124.6, 114.2, 62.3, 55.4, 52.1, 45.1, 41.0, 26.0, 25.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{16}H_{21}N_3O_3$: 304.1656, observed: 304.1651.



Compound 69. Colorless oil. Yield: 34%. 9.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:2). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 2H), 6.89 – 6.83 (m, 2H), 6.64 (d, *J* = 15.7 Hz, 1H), 6.04 (dd, *J* = 15.8, 7.8 Hz, 1H), 4.73 – 4.65 (m, 1H), 3.81 (s, 3H), 3.02 (s, 3H), 2.97 (s, 3H), 2.67 (dd, *J* = 15.6, 8.3 Hz, 1H), 2.50 (dd, *J* = 15.6, 5.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 159.8, 132.9, 128.8, 128.1, 124.2, 114.2, 61.6, 55.5, 38.8, 37.4, 35.7. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{14}H_{18}N_4O_2$: 275.1502, observed: 275.1499.

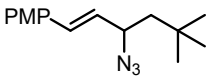


Compound 70. Colorless oil. Yield: 53%. 16.3 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:10). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 – 7.93 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.43 (m, 2H), 7.37 – 7.31 (m, 2H), 6.87 (m, 2H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.08 (dd, *J* = 15.7, 7.8 Hz, 1H), 4.84 – 4.77 (m, 1H), 3.81 (s, 3H), 3.36 (dd, *J* = 17.0, 7.8 Hz, 1H), 3.16 (dd, *J* = 17.0, 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.7, 159.9, 136.8, 133.6, 133.3, 128.9, 128.6, 128.3, 128.1, 123.9, 114.2, 60.6, 55.4, 43.7.



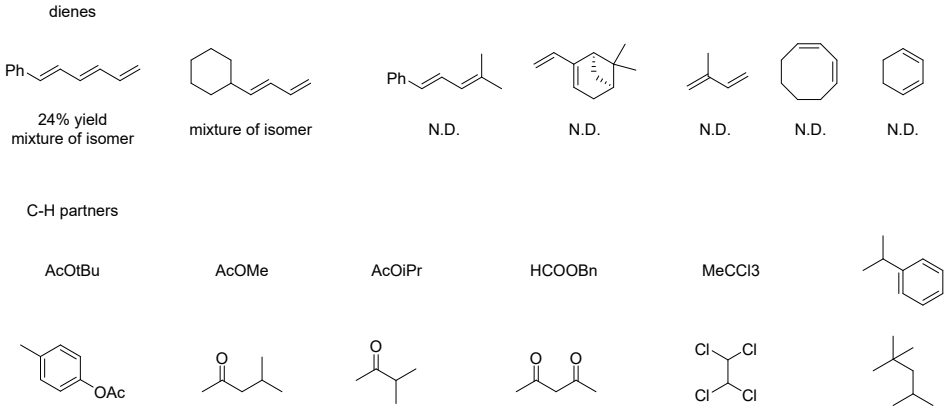
Compound 71. Colorless oil. Yield: 59%. 14.5 mg. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 2H), 6.92 – 6.84 (m, 2H), 6.56 (d, *J* = 15.7 Hz, 1H), 5.96 (dd, *J* = 15.7, 8.3 Hz,

1H), 4.07 – 3.99 (m, 1H), 3.82 (s, 3H), 1.80 – 1.68 (m, 1H), 1.61 – 1.55 (m, 0H), 1.47 – 1.38 (m, 1H), 1.01 – 0.87 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 132.8, 129.0, 128.0, 125.3, 114.2, 63.5, 55.5, 43.9, 25.0, 22.7, 22.5.

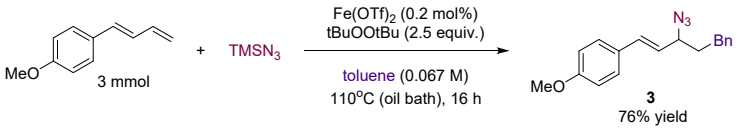


Compound 72. Colorless oil. Yield: 36%. 9.3 mg. Regioselectivity (1,2- and 1,4-addition): 13:1. Purified by column chromatography (SiO_2, EtOAc/hexane = 1:20). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 2H), 6.92 – 6.84 (m, 2H), 6.53 (d, *J* = 15.7 Hz, 1H), 5.98 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.82 (s, 3H), 1.61 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.51 (dd, *J* = 14.4, 5.7 Hz, 1H), 0.98 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.8, 132.1, 129.0, 128.0, 126.5, 114.2, 62.7, 55.5, 48.1, 30.5, 30.1. **HRMS** (ESI-TOF) m/z $[M+Na]^+$ calculated for $C_{15}H_{21}N_3O$: 282.1577, observed: 282.1573.

Some unsuccessful products

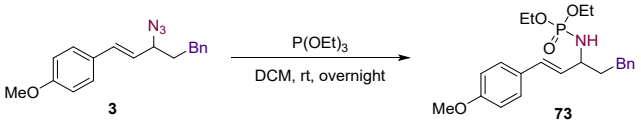


4 Scale up reaction



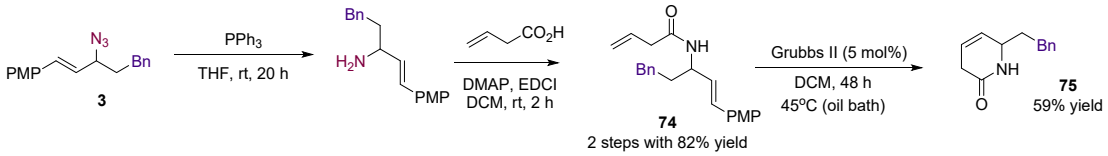
To a flame-dried and N_2-purged Schlenk tube (100 mL) were added $Fe(OTf)_2$ (2.2 mg, 0.006 mmol, 0.2 mol%), and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of $TMSN_3$ (864 mg, 7.5 mmol, 2.5 equiv.), tert-butyl peroxide (1098 mg, 7.5 mmol, 2.5 equiv.), 1,3-diene (480 mg, 3.0 mmol, 1.0 equiv.) and toluene (45 mL) sequentially. The mixture was stirred at 110 °C for 24 h. Then the solvent was removed under vacuum and the crude residue was purified by column chromatography (SiO_2, EtOAc/hexane = 1:25) to provide product **3**.

5 Synthetic application



To a dry dichloromethane solution (1.0 mL) of **3** (58.7 mg, 0.2 mmol, 1.0 equiv.) was added triethylphosphite (66.5 mg, 0.4 mol, 2 equiv.) dropwise for 5 min. The reaction mixture was allowed to stir overnight at r.t., then concentrated under vacuum. The crude residue was purified by flash column chromatography (SiO_2, EtOAc/hexane = 1:3) to give the corresponding product **73** (65.0 mg, 81% yield).

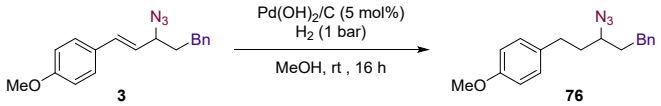
Compound 73. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 – 7.34 (m, 4H), 7.31 – 7.23 (m, 2H), 6.97 – 6.91 (m, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 7.0 Hz, 1H), 4.24 – 4.03 (m, 4H), 3.89 (s, 3H), 3.13 – 3.06 (m, 1H), 2.86 – 2.75 (m, 2H), 2.07 – 1.96 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.33 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3, 141.7, 129.7, 129.6, 129.5 (d, *J* = 3.5 Hz), 128.5, 128.5, 127.6, 126.0, 114.1, 62.4 (d, *J* = 5.2 Hz), 62.3 (d, *J* = 5.0 Hz), 55.3, 53.9, 39.2 (d, *J* = 6.4 Hz), 32.1, 16.3 (d, *J* = 7.2 Hz), 16.2 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.0. **HRMS** (ESI-TOF) m/z $[M-H]^-$ calculated for $C_{22}H_{24}N_5O_4S_2$: 402.1840, observed: 402.1840.



To a solution of **3** (58.7 mg, 0.2 mmol, 1.0 equiv.) in THF/H_2O = 5/1 (1.2 mL) was added PPh_3 (105 mg, 0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir overnight at r.t., then concentrated under vacuum. The crude residue was purified by flash chromatography (SiO_2, DCM/MeOH = 5:1) to afford amine. Then, to a solution of amine, EDCI (38.4 mg, 0.2 mmol, 1.0 equiv.) and DMAP (1.2 mg, 0.01 mmol, 0.1 equiv.) in DCM (2.0 mL) were added but-3-enoic acid (17.2 mg, 0.2 mmol, 1.0 equiv.) and the mixture was stirred at rt for 2 h. The residue was then concentrated under reduced pressure and purified by flash column chromatography (SiO_2, hexane/EtOAc = 2:1) to afford **74** (55 mg, 82% yield). To a flame-dried and N_2-purged Schlenk tube (10 mL) was added Grubbs-II catalyst (4.3 mg, 0.005 mmol, 5 mol%). The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of **74** (30.5 mg, 0.1 mmol, 1.0 equiv.) dissolved in DCM (4.0 mL). Then, the mixture was stirred at 45 °C for 48 h. The mixture was then concentrated under reduced pressure and purified by flash column chromatography (SiO_2, hexane/EtOAc = 1:1) to afford **75** (11.8 mg, 59% yield).

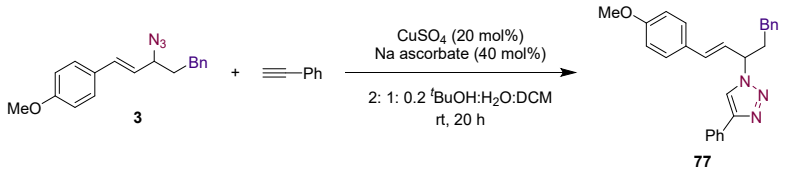
Compound 74. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 – 7.25 (m, 4H), 7.23 – 7.16 (m, 3H), 6.88 – 6.81 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.03 – 5.87 (m, 2H), 5.66 (d, *J* = 8.6 Hz, 1H), 5.27 – 5.19 (m, 2H), 4.72 – 4.63 (m, 1H), 3.80 (s, 3H), 3.01 (d, *J* = 7.2 Hz, 2H), 2.73 – 2.66 (m, 2H), 2.01 – 1.90 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 159.4, 141.6, 131.6, 130.6, 129.5, 128.6, 128.5, 127.7, 127.3, 126.1, 119.9, 114.1, 55.4, 51.1, 41.9, 36.9, 32.4. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{22}H_{25}NO_2$: 336.1958, observed: 336.1955.

Compound 75. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.27 (m, 3H), 7.23 – 7.10 (m, 3H), 6.28 (s, 1H), 5.84 – 5.77 (m, 1H), 5.75 – 5.68 (m, 1H), 4.14 – 4.07 (m, 1H), 3.00 – 2.91 (m, 2H), 2.75 – 2.62 (m, 2H), 1.97 – 1.81 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 141.0, 128.7, 128.4, 126.3, 125.2, 122.3, 53.6, 38.9, 31.4, 30.9. **HRMS** (ESI-TOF) m/z $[M+NH_4]^+$ calculated for $C_{13}H_{15}NO$: 202.1226, observed: 202.1226.



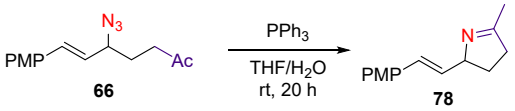
To a MeOH solution (10 mL) **3** (29.3 mg, 0.1 mmol) was added $Pd(OH)_2$ (7.0 mg, 10% on Carbon (wetted with ca. 50% Water)) and the mixture was stirred under atmospheric pressure of H_2 at room temperature for 16h. And then, the reaction mixture was filtered. The filtrate was evaporated under reduced pressure to afford product **76** without further purification (27.2 mg, 92% yield).

Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 7.13 – 7.07 (m, 2H), 6.86 – 6.79 (m, 2H), 3.79 (s, 3H), 2.90 – 2.81 (m, 1H), 2.81 – 2.56 (m, 4H), 1.89 – 1.76 (m, 2H), 1.75 – 1.63 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.0, 142.1, 134.1, 129.4, 128.6, 128.5, 126.0, 114.0, 55.4, 50.7, 39.4, 39.2, 32.5, 31.6.



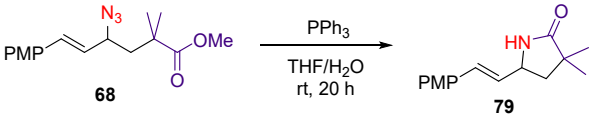
To a flame-dried and N_2-purged Schlenk tube (10 mL) were added $CuSO_4$ (3.2 mg, 0.02 mmol, 0.2 equiv) and sodium ascorbate (8.5 mg, 0.04 mmol, 0.4 equiv) and a stirring bar. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of **3** (29.3 mg, 0.1mmol) and phenylacetylene (20.4 mg, 0.2 mmol, 2 equiv.) dissolved in *t*BuOH/H_2O/DCM (2:1:0.2 v/v, 1.6 mL). Then, the mixture was stirred at room temperature for 20 h. The mixture was diluted with DCM (10 mL), washed with water (5 mL) and brine (5 mL). The organic layer was combined and dried over Na_2SO_4. The residue was evaporated under reduced pressure and purified by flash column chromatography (SiO_2, hexane/EtOAc = 8:1) to afford the product **77** (36.7 mg, 93% yield).

Compound 77. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 – 7.84 (m, 2H), 7.80 (s, 1H), 7.46 – 7.39 (m, 2H), 7.37 – 7.28 (m, 5H), 7.24 – 7.16 (m, 3H), 6.89 – 6.84 (m, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.28 (dd, *J* = 15.8, 7.4 Hz, 1H), 5.25 – 5.17 (m, 1H), 3.81 (s, 3H), 2.73 – 2.54 (m, 3H), 2.48 – 2.37 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 147.9, 140.4, 133.4, 130.9, 128.9, 128.7, 128.6, 128.4, 128.2, 128.1, 126.4, 125.8, 124.5, 118.4, 114.3, 62.9, 55.4, 36.7, 32.1. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{26}H_{25}N_3O$: 396.2070, observed: 396.2068.



To a solution of **66** (58.7 mg, 0.2 mmol, 1.0 equiv.) in THF/H_2O = 5/1 (1.2 mL) was added PPh_3 (105 mg, 0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir overnight at r.t., then concentrated under vacuum. The crude residue was purified by flash chromatography (SiO_2, Hexane/EtOAc = 1:1) to afford **78** (39.5 mg, 92% yield).

Compound 78. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 – 7.25 (m, 2H), 6.85 – 6.79 (m, 2H), 6.49 (d, *J* = 15.5 Hz, 1H), 6.11 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.65 – 4.56 (m, 1H), 3.78 (s, 3H), 2.64 – 2.43 (m, 2H), 2.25 – 2.15 (m, 1H), 2.07 (s, 3H), 1.74 – 1.62 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.3, 159.0, 130.2, 130.1, 129.1, 127.6, 114.0, 74.2, 55.3, 39.1, 30.2, 20.0. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{14}H_{17}NO$: 216.1383, observed: 216.1385.

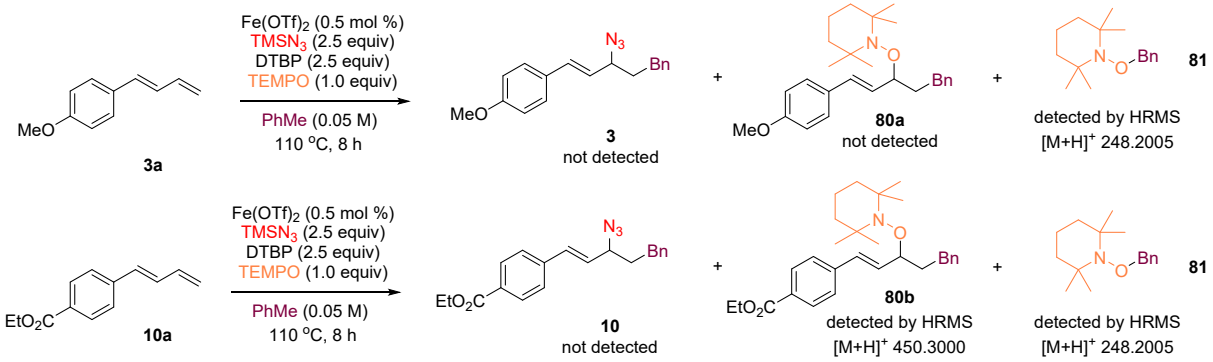


To a solution of **68** (58.7 mg, 0.2 mmol, 1.0 equiv.) in THF/H_2O = 5/1 (1.2 mL) was added PPh_3 (105 mg, 0.4 mmol, 2.0 equiv). The reaction mixture was allowed to stir overnight at r.t., then concentrated under vacuum. The crude residue was purified by flash chromatography (SiO_2, Hexane/EtOAc = 3:1) to afford **79** (47.9 mg, 98% yield).

Compound 79. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.27 (m, 2H), 6.90 – 6.83 (m, 2H), 6.50 (d, *J* = 15.7 Hz, 1H), 5.93 (dd, *J* = 15.7, 7.7 Hz, 1H), 5.56 (s, 1H), 4.27 – 4.19 (m, 1H), 3.81 (s, 3H), 2.24 – 2.15 (m, 1H), 1.83 – 1.75 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 182.5, 159.7, 131.2, 128.9, 128.0, 127.8, 114.3, 55.5, 53.4, 44.5, 40.6, 25.4, 24.8. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{15}H_{19}NO_2$: 246.1489, observed: 246.1488.

6 Mechanistic studies

Reaction in the presence of TEMPO

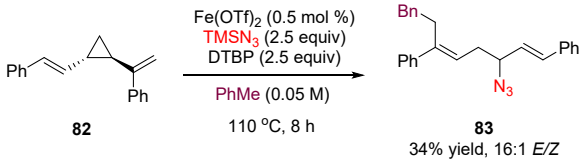


To a flame-dried and N_2-purged Schlenk tube (10 mL) were added $Fe(OTf)_2$ (0.05 M in water, 10 μL, 0.0005 mmol, 0.5 mol%), TEMPO (15.6 mg, 0.1 mmol, 1.0 equiv.) and a stirring bar. The water was removed under vacuum. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of toluene (2.0 mL), $TMSN_3$ (28.8 mg, 0.25 mmol, 2.5 equiv.), tert-butyl peroxide (36.6 mg, 0.25 mmol, 2.5 equiv.) and 1,3-diene (0.1 mmol) sequentially. The mixture was stirred at 110 °C for 8 h. The trapped product **80b** and **81** was detected by HRMS and the product **3** and **10** were not detected.

For **80b: HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{29}H_{40}NO_3$: 450.3003, observed: 450.3000.

For **81: HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{16}H_{26}NO$: 248.2009, observed: 248.2005.

Radical clock experiment

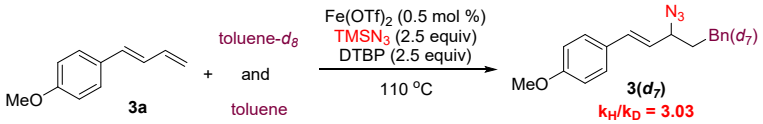


To a flame-dried and N_2-purged Schlenk tube (10 mL) were added $Fe(OTf)_2$ (0.05 M in water, 10 μL, 0.0005 mmol, 0.5 mol%) and a stirring bar. The water was removed under vacuum. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of toluene (2.0 mL), $TMSN_3$ (28.8 mg, 0.25 mmol, 2.5 equiv.), tert-

butyl peroxide (36.6 mg, 0.25 mmol, 2.5 equiv.) and **82** (24.6 mg, 0.1 mmol, 1.0 equiv.) sequentially. The mixture was stirred at 110 °C for 8 h. Then the solvent was removed under vacuum and the crude residue was purified by column chromatography (SiO_2, hexane/EtOAc = 20:1) to provide the ring-opening product **83** (12.9 mg, 34% yield).

Compound 83. Colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 – 7.32 (m, 8H), 7.32 – 7.26 (m, 4H), 7.23 – 7.11 (m, 3H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.08 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.67 (t, *J* = 7.3 Hz, 1H), 3.83 – 3.75 (m, 1H), 2.90 – 2.80 (m, 2H), 2.71 – 2.61 (m, 2H), 2.44 – 2.26 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.5, 142.1, 141.9, 136.1, 133.6, 128.8, 128.7, 128.6, 128.5, 128.3, 127.2, 126.9, 126.8, 126.7, 126.1, 124.1, 64.8, 34.6, 34.1, 32.2. **HRMS** (ESI-TOF) m/z $[M+H]^+$ calculated for $C_{26}H_{25}N_3$: 380.2121, observed: 380.2122.

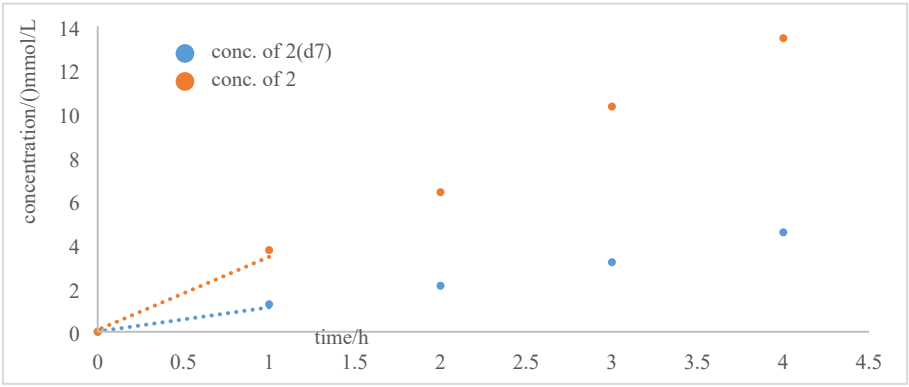
Kinetic isotope effect experiment



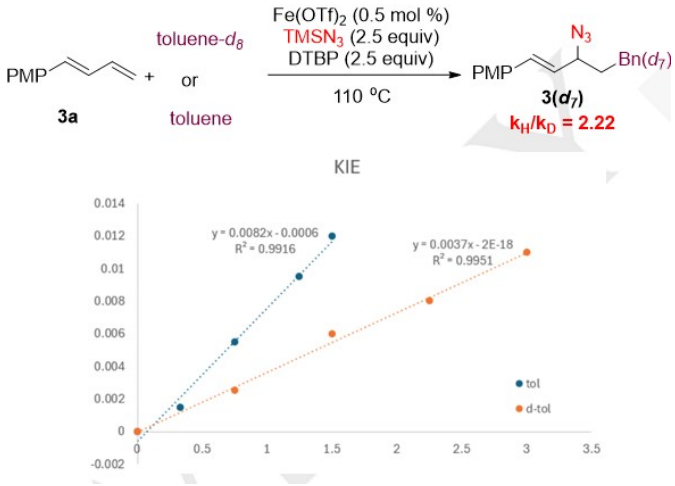
To a flame-dried and N_2-purged Schlenk tube (10 mL) were added $Fe(OTf)_2$ (0.05 M in water, 10 μL, 0.0005 mmol, 0.5 mol%) and a stirring bar. The water was removed under vacuum. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of toluene (1.0 mL), toluene-d_8 (1.0 mL), $TMSN_3$ (28.8 mg, 0.25 mmol, 2.5 equiv.), tert-butyl peroxide (36.6 mg, 0.25 mmol, 2.5 equiv.) and **3a** (16.0 mg, 0.1 mmol, 1.0 equiv.) sequentially. The mixture was stirred at 110 °C for 1 h. Then, the mixture was diluted with DCM, and simply purified by short flash column chromatography on silica gel eluting with DCM. The solvent was removed under vacuum and the concentration of **3(d_7)** was determined by ^{1}H NMR analysis.

All the yields with different reaction time were determined according to above procedure.

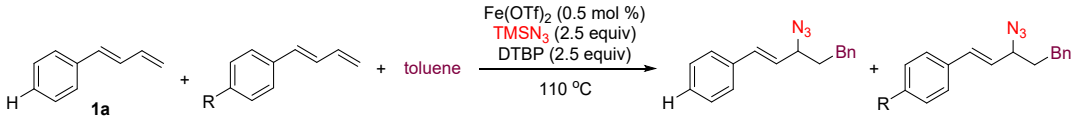
time(min)	concentration of **3** (mM)	concentration of **3-*d*** (mM)
0	0	0
60	3.47	1.26
120	6.39	2.11
180	10.31	3.12
240	13.45	4.56



We also conducted parallel KIE experiments and found that the K_H/K_D = 2.22.

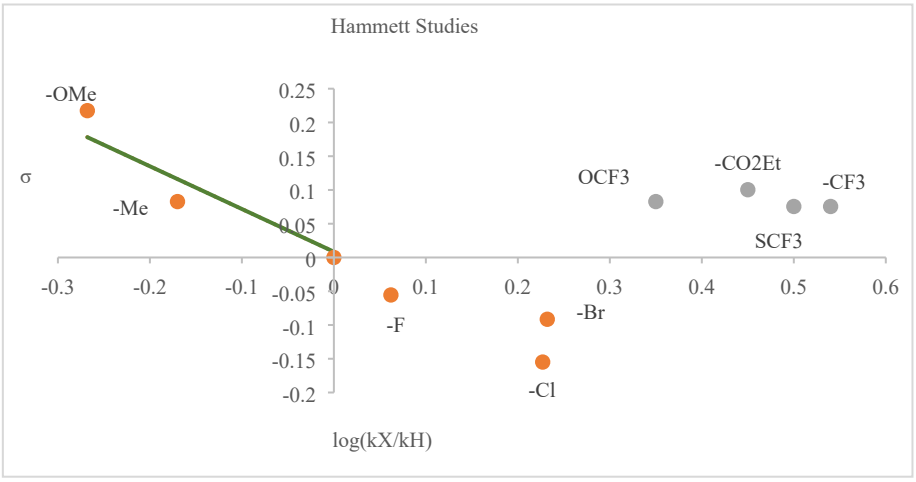


Hammett studies



To a flame-dried and N_2-purged Schlenk tube (10 mL) were added $Fe(OTf)_2$ (0.05 M in water, 10 μL, 0.0005 mmol, 0.5 mol%) and a stirring bar. The water was removed under vacuum. The Schlenk tube was then evacuated and filled with N_2. This cycle was repeated three times and followed by the addition of toluene (2.0 mL), $TMSN_3$ (28.8 mg, 0.25 mmol, 2.5 equiv.), tert-butyl peroxide (36.6 mg, 0.25 mmol, 2.5 equiv.) and **1a** (6.5 mg, 0.05 mmol, 0.05 equiv.) sequentially. The mixture was stirred at 110 °C for 3 h. Then the solvent was removed under vacuum and the product composition was determined by ^1H NMR analysis.

R	para-effect	k_X/k_H	$\log(k_X/k_H)$
OMe	-0.268	1.65	0.217484
Me	-0.17	1.21	0.082785
F	0.062	0.88	-0.05552
Cl	0.227	0.7	-0.1549
Br	0.232	0.81	-0.09151
CF3	0.54	1.19	0.075547
CO2Et	0.45	1.26	0.100371
OCF3	0.35	1.21	0.082785
SCF3	0.5	1.19	0.075547



7 References

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(2) Sardini, S. R.; Brown, M. K. Catalyst Controlled Regiodivergent Arylboration of Dienes. (2017). *J. Am. Chem. Soc.* **139**, 9823-9826.

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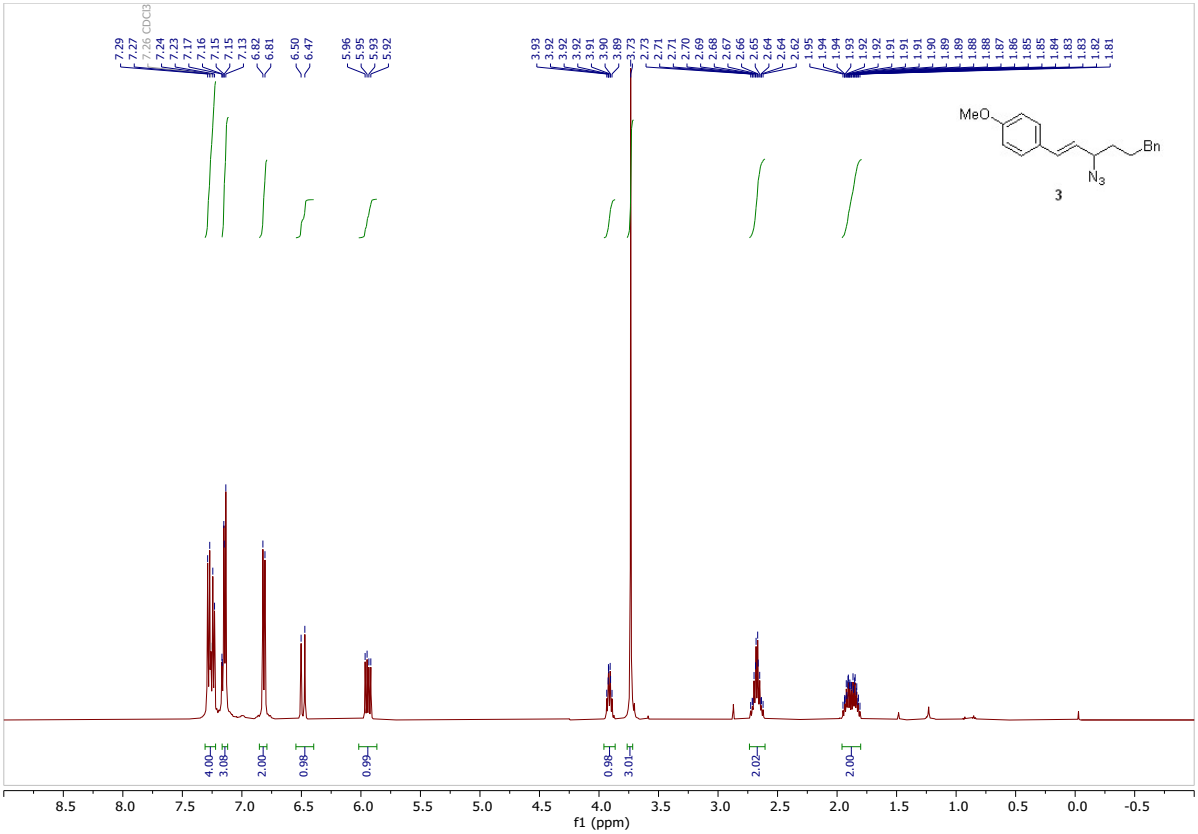
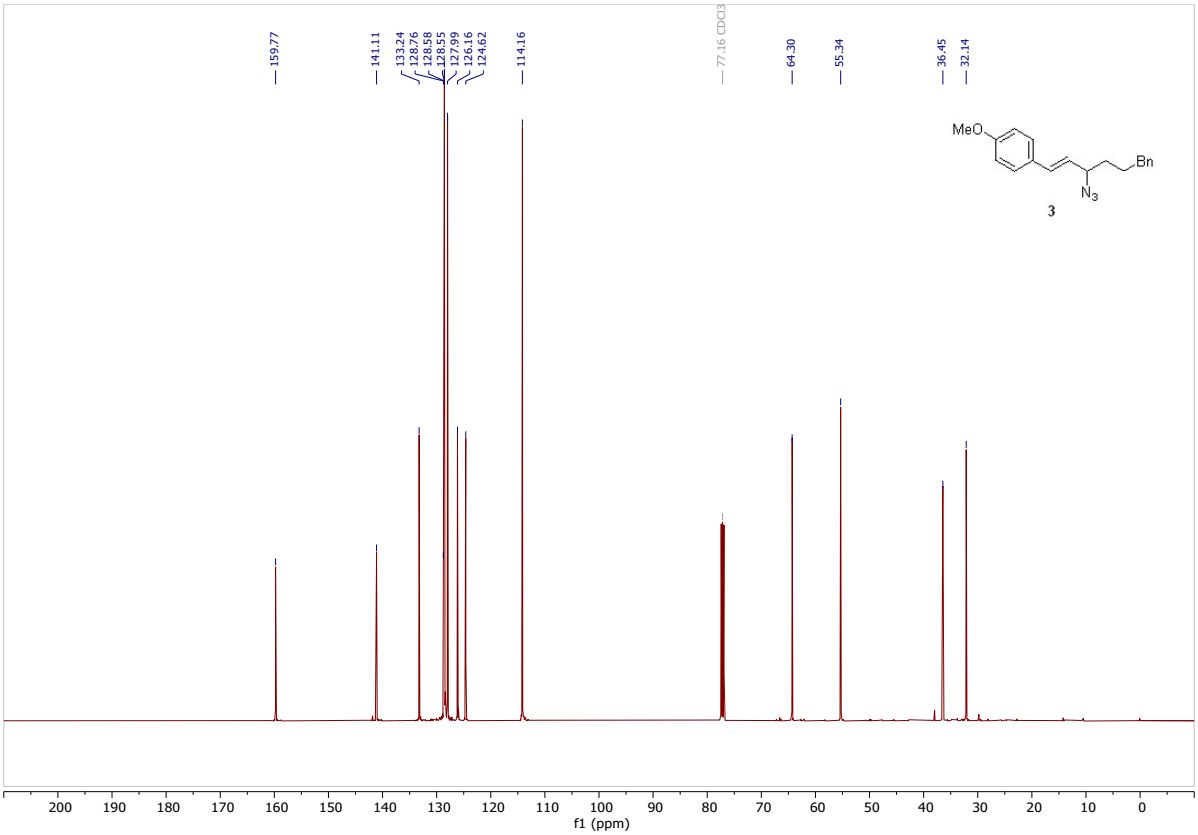
8 NMR spectra

Compound 3

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

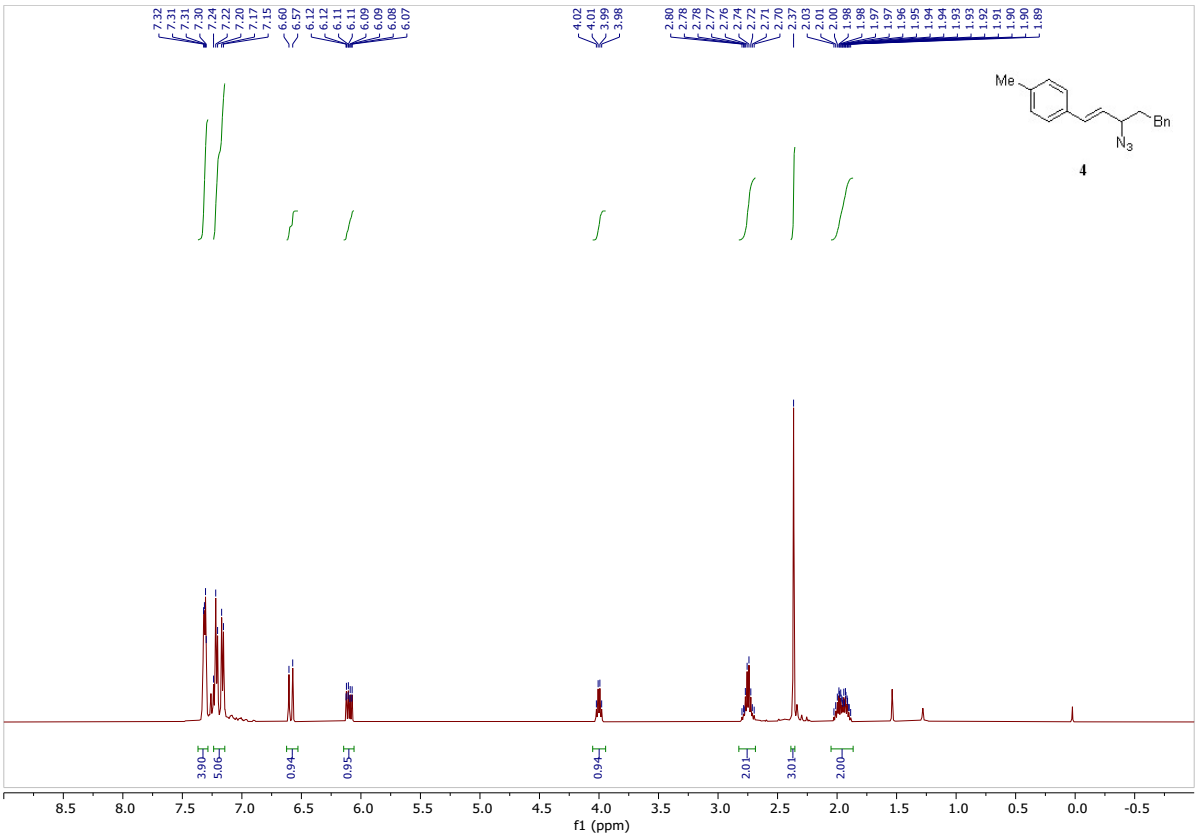


^{13}C NMR (126 MHz, $CDCl_3$)

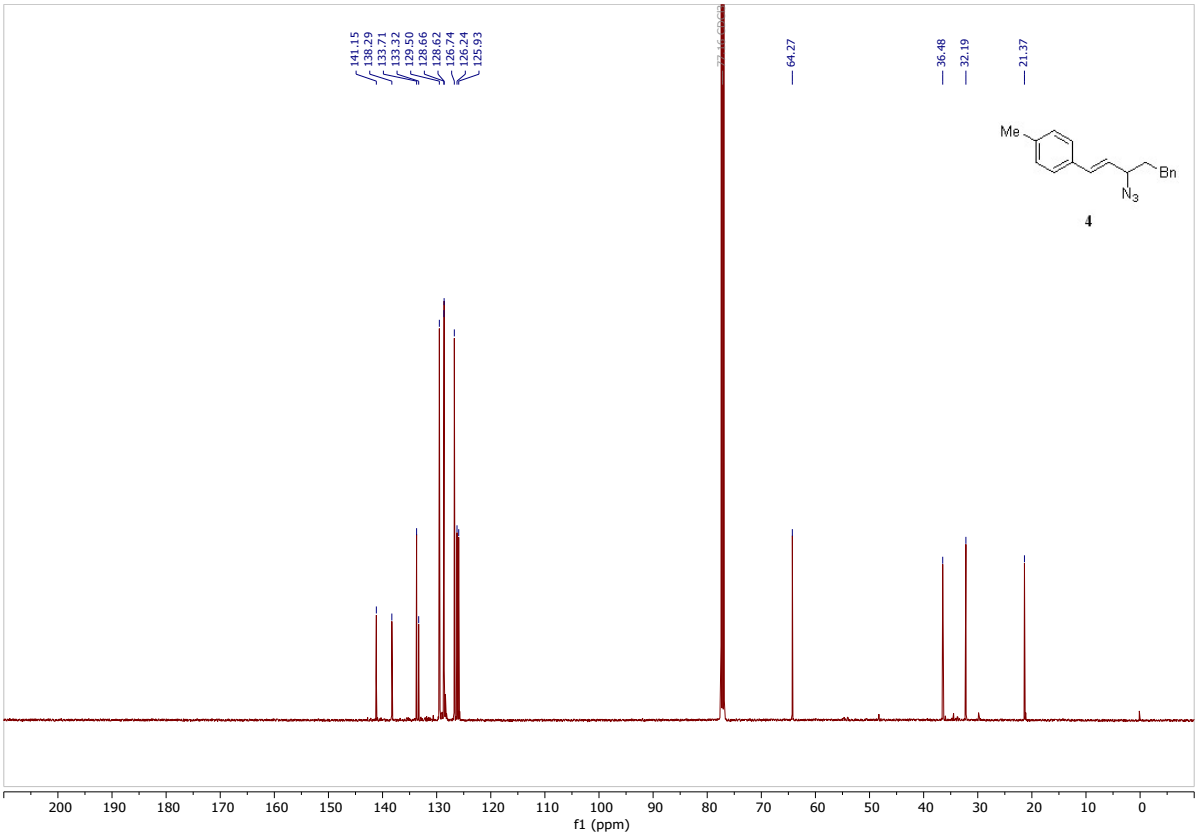


Compound 4

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

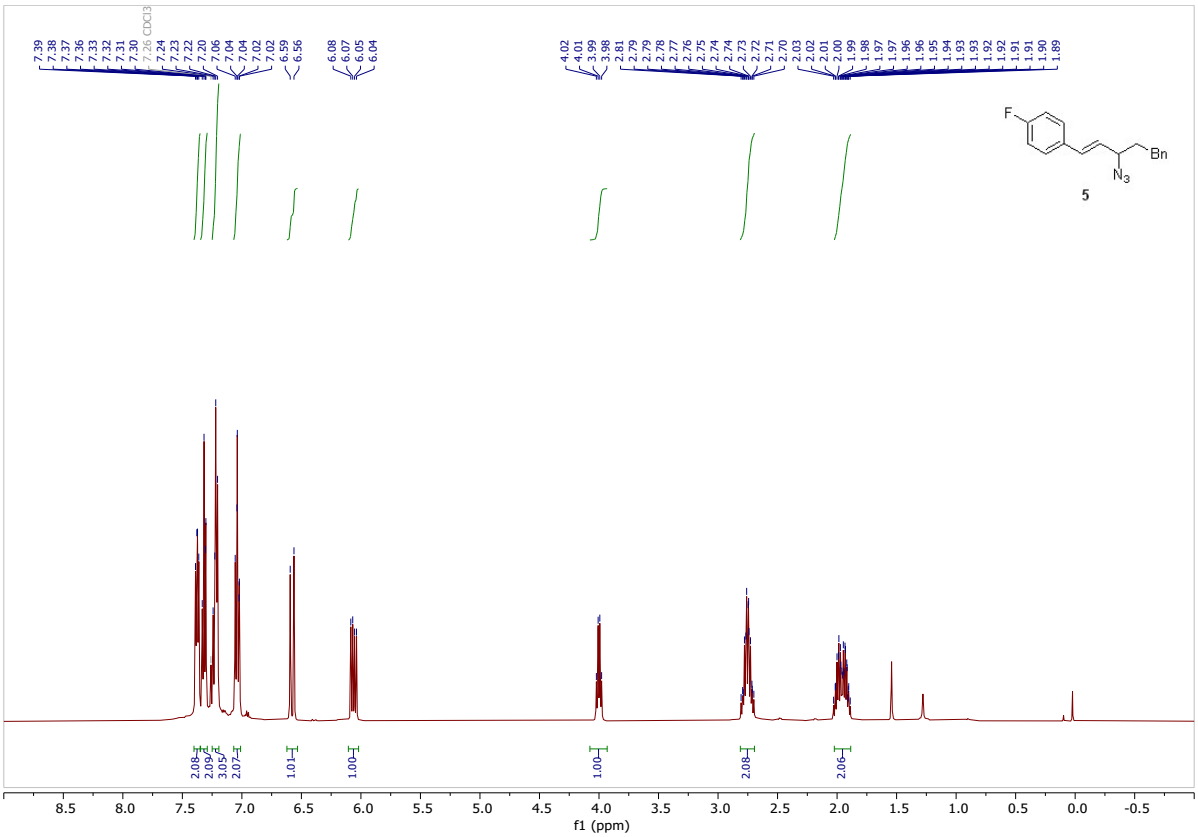


^{13}C NMR (126 MHz, $CDCl_3$)

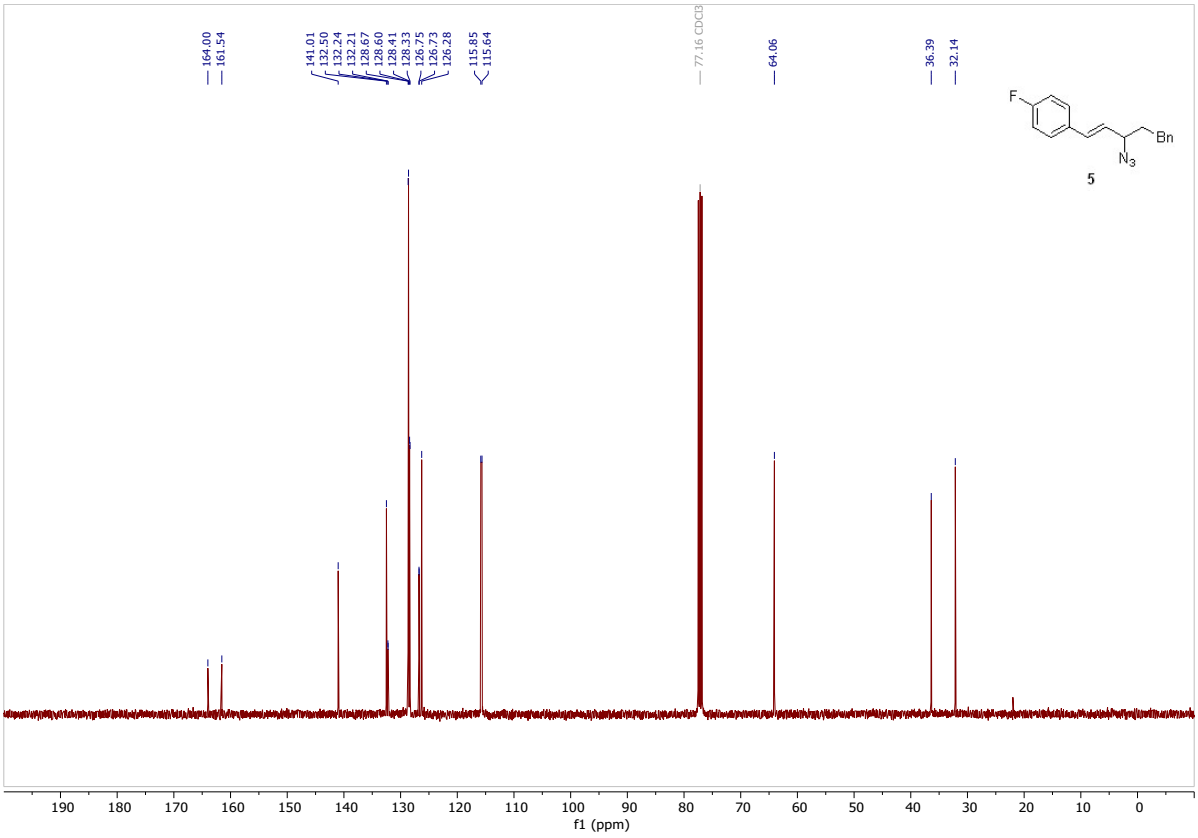


Compound 5

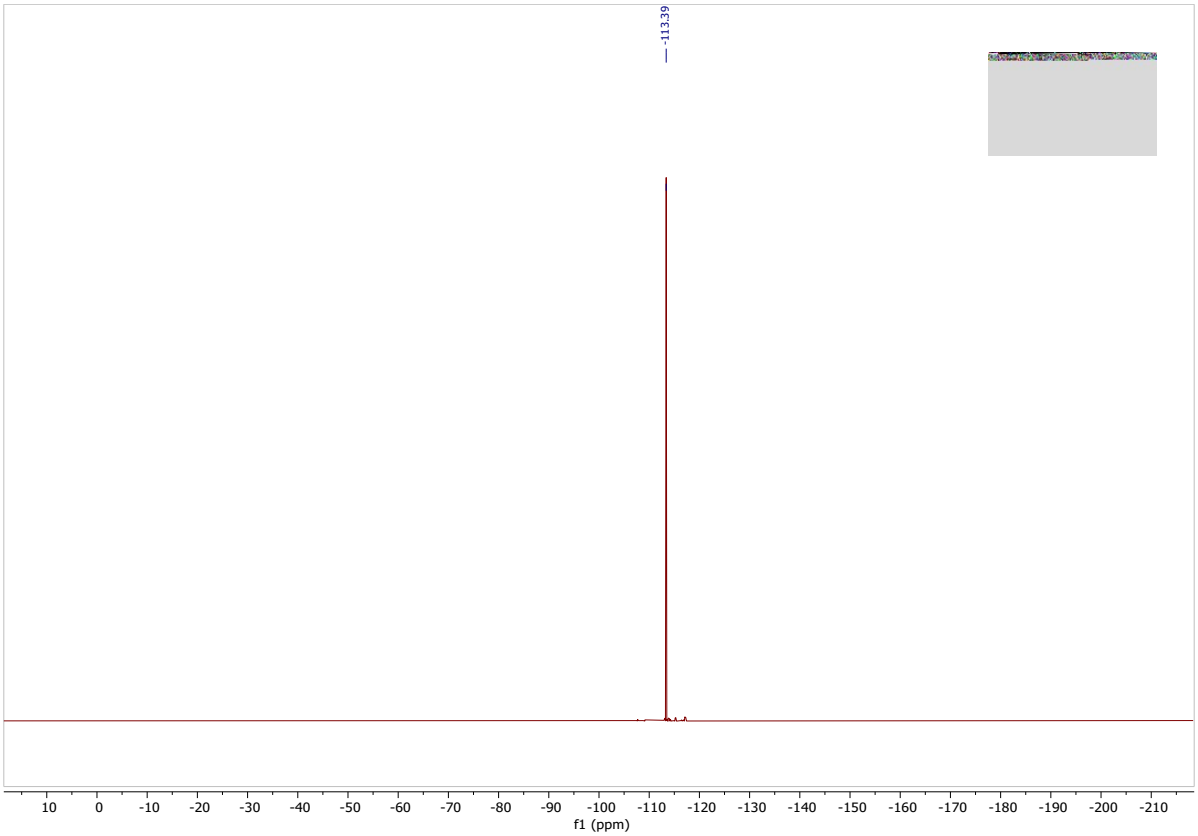
^{1}H NMR (500 MHz, Chloroform-*d*)



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

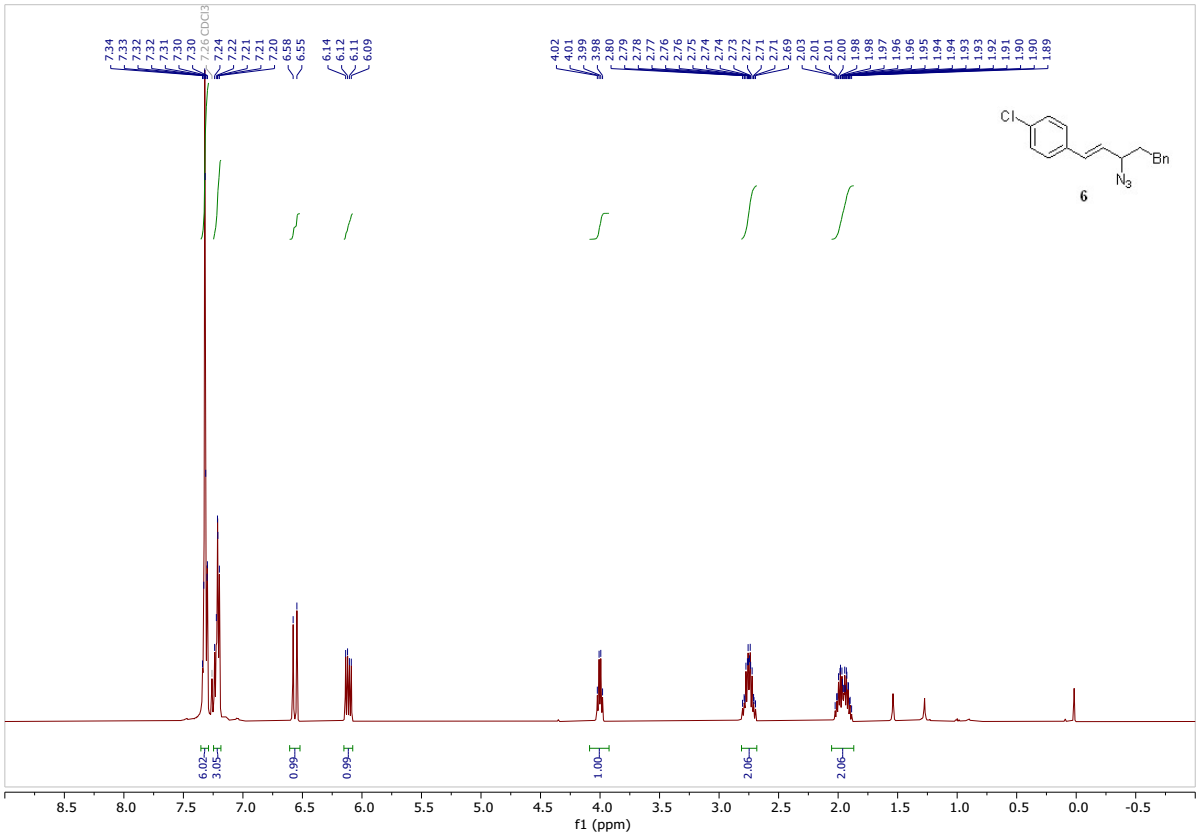


^{19}F NMR (377 MHz, $CDCl_3$)

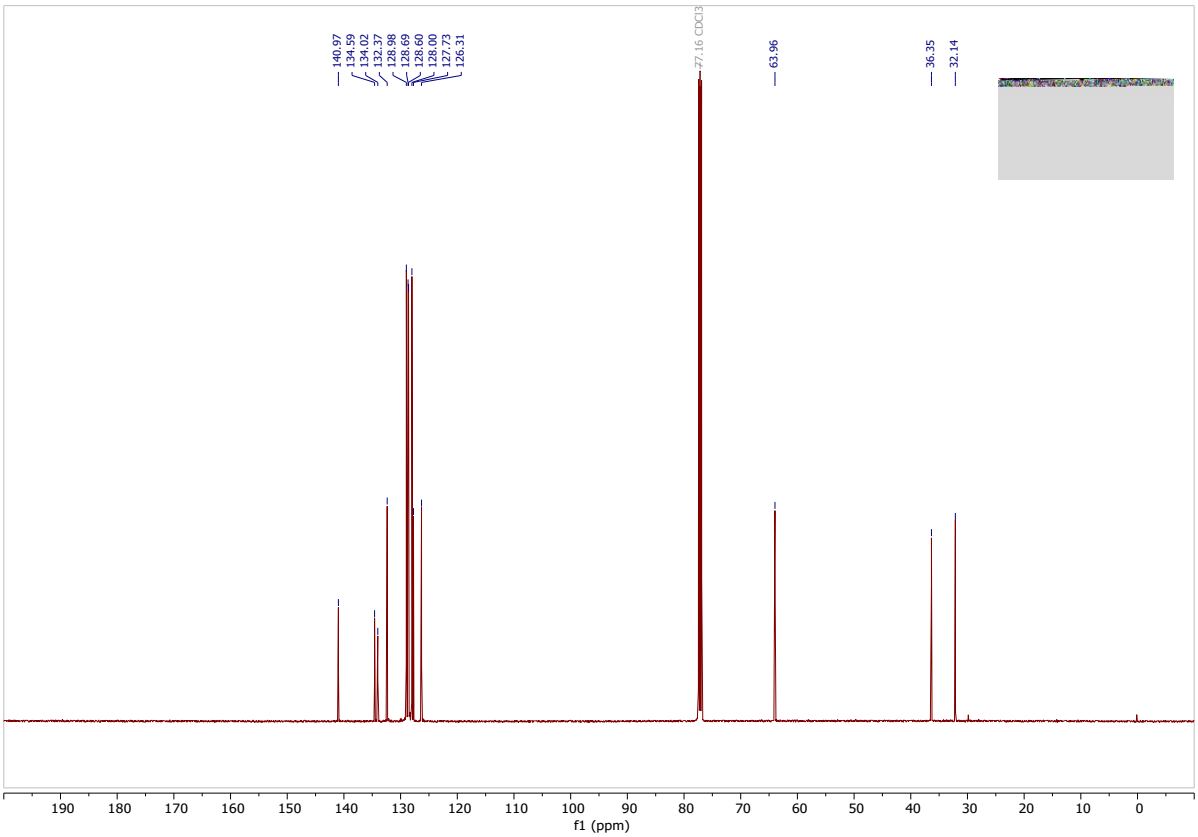


Compound 6

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

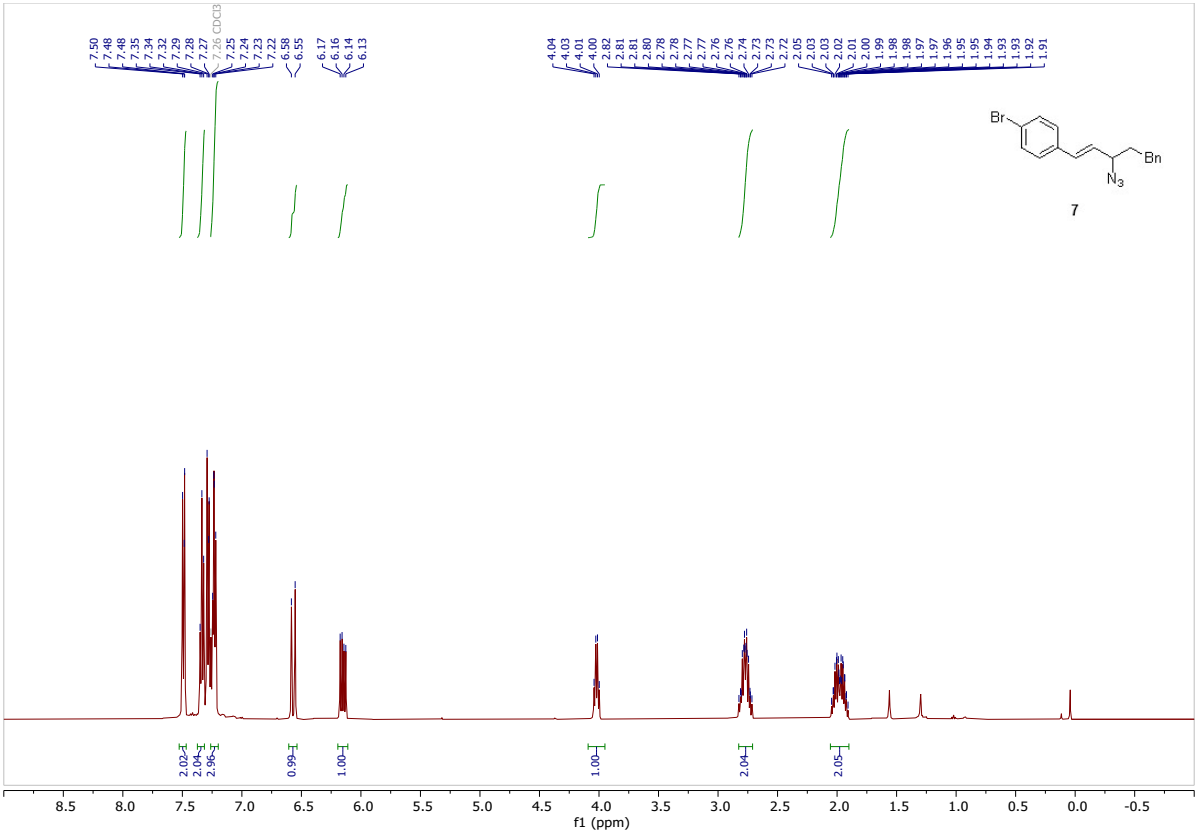


^{13}C NMR (126 MHz, $CDCl_3$)

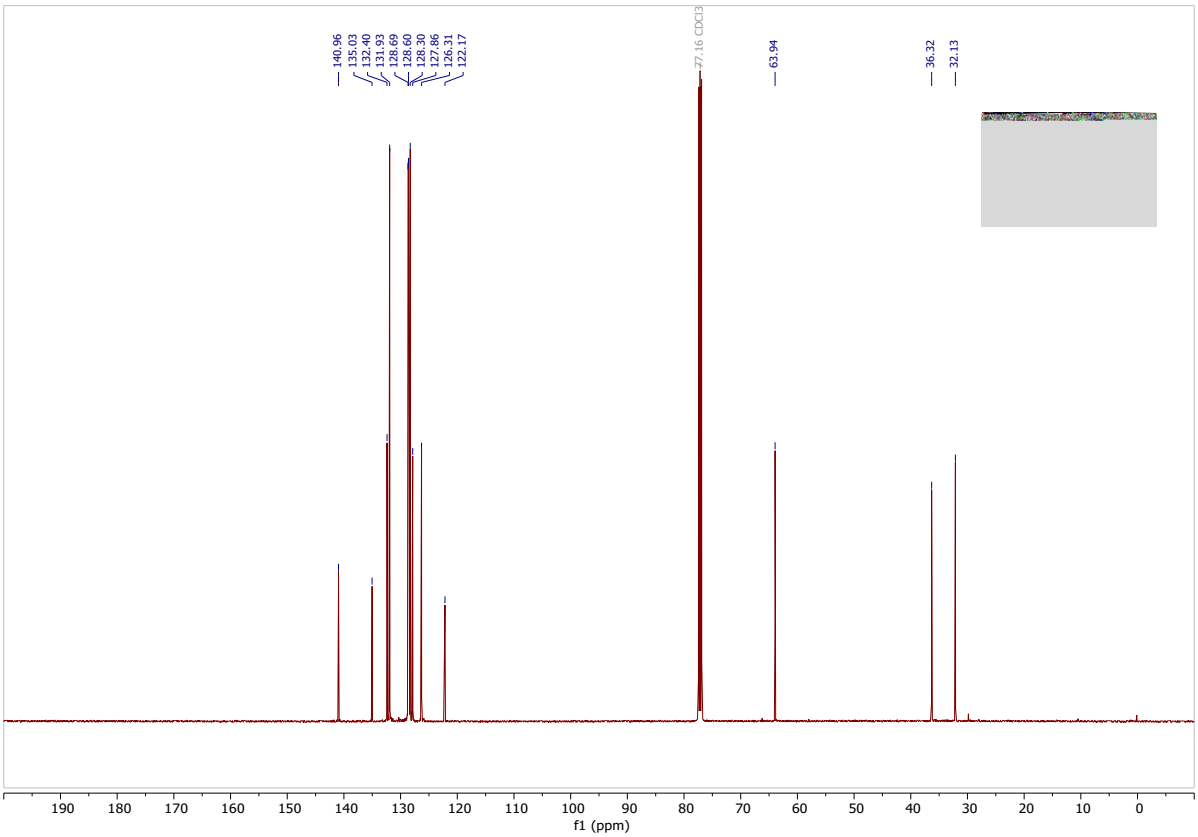


Compound 7

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

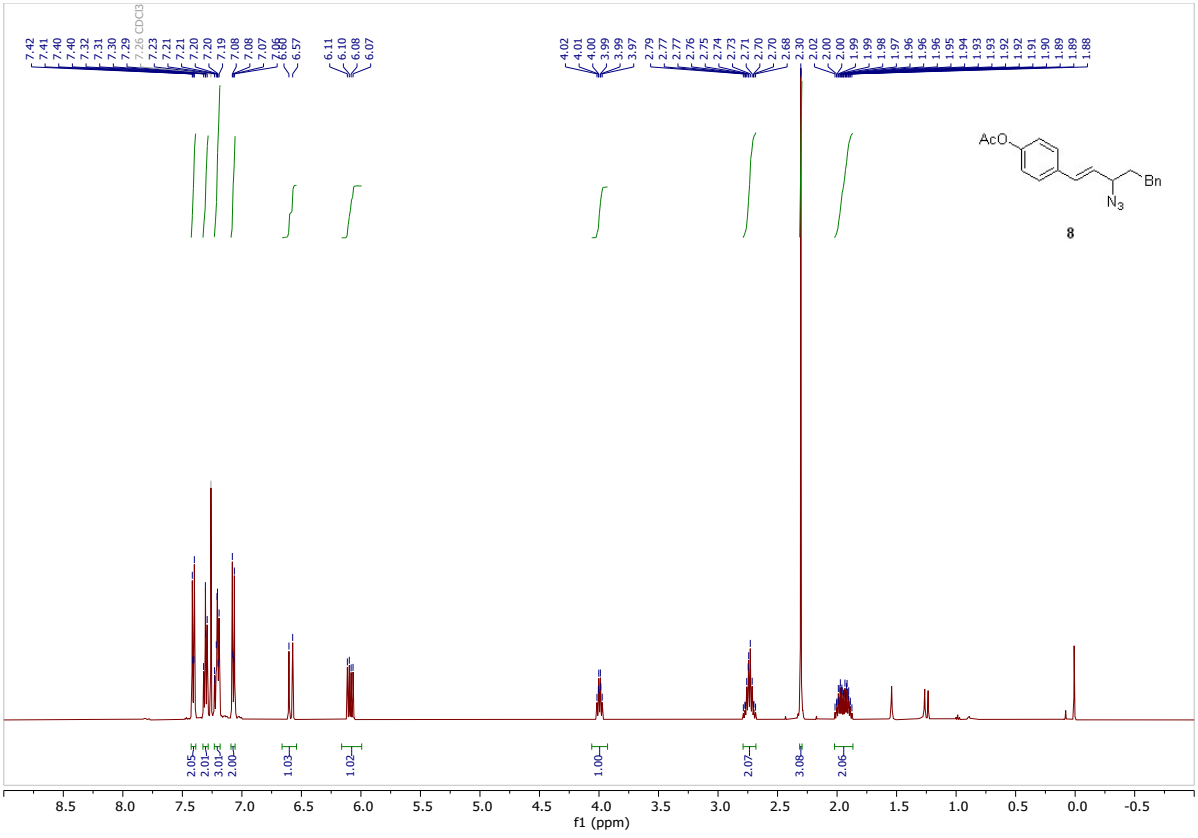


^{13}C NMR (126 MHz, $CDCl_3$)

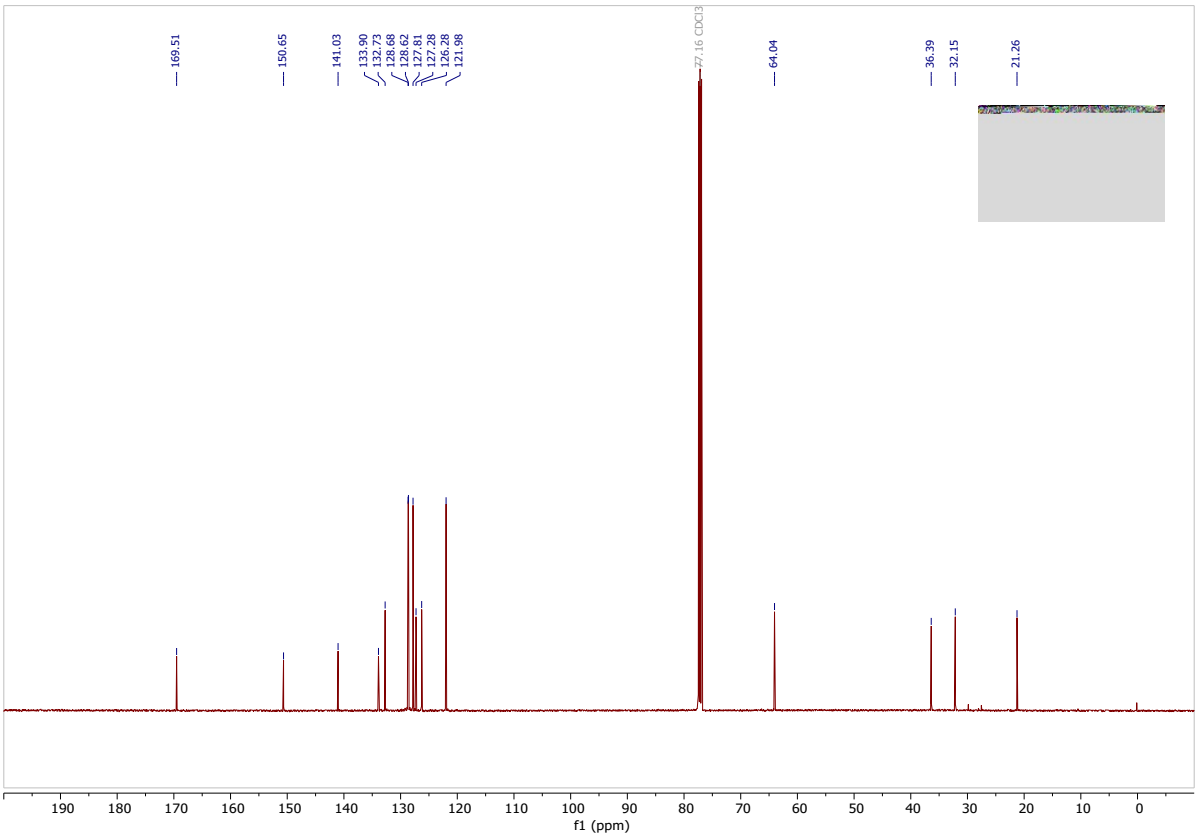


Compound 8

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

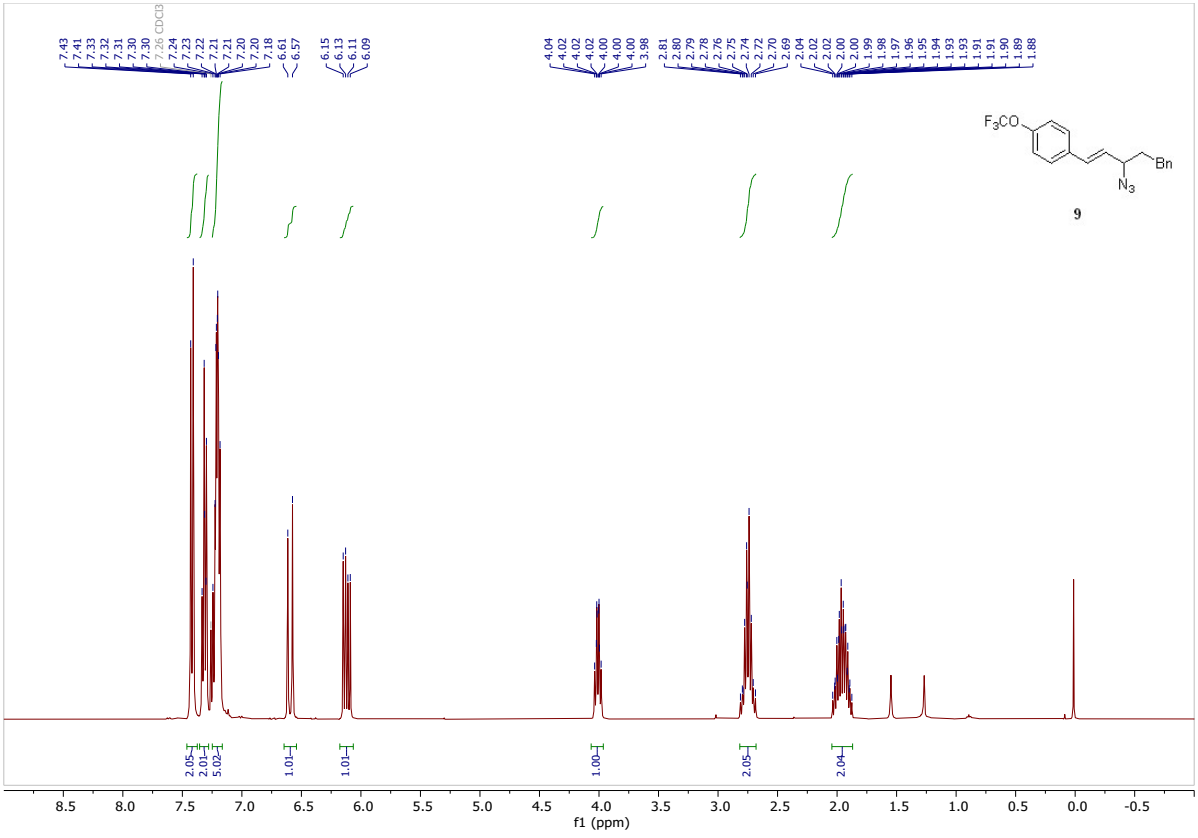


^{13}C NMR (126 MHz, $CDCl_3$)

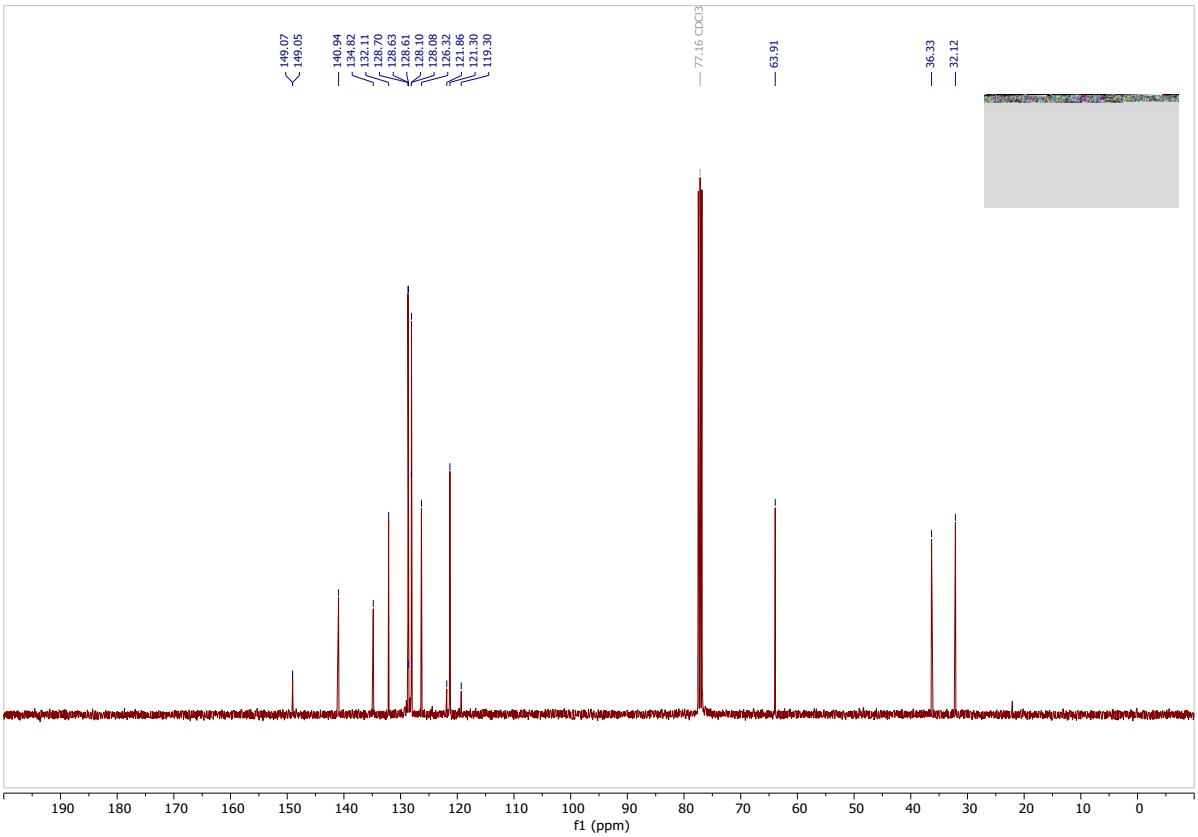


Compound 9

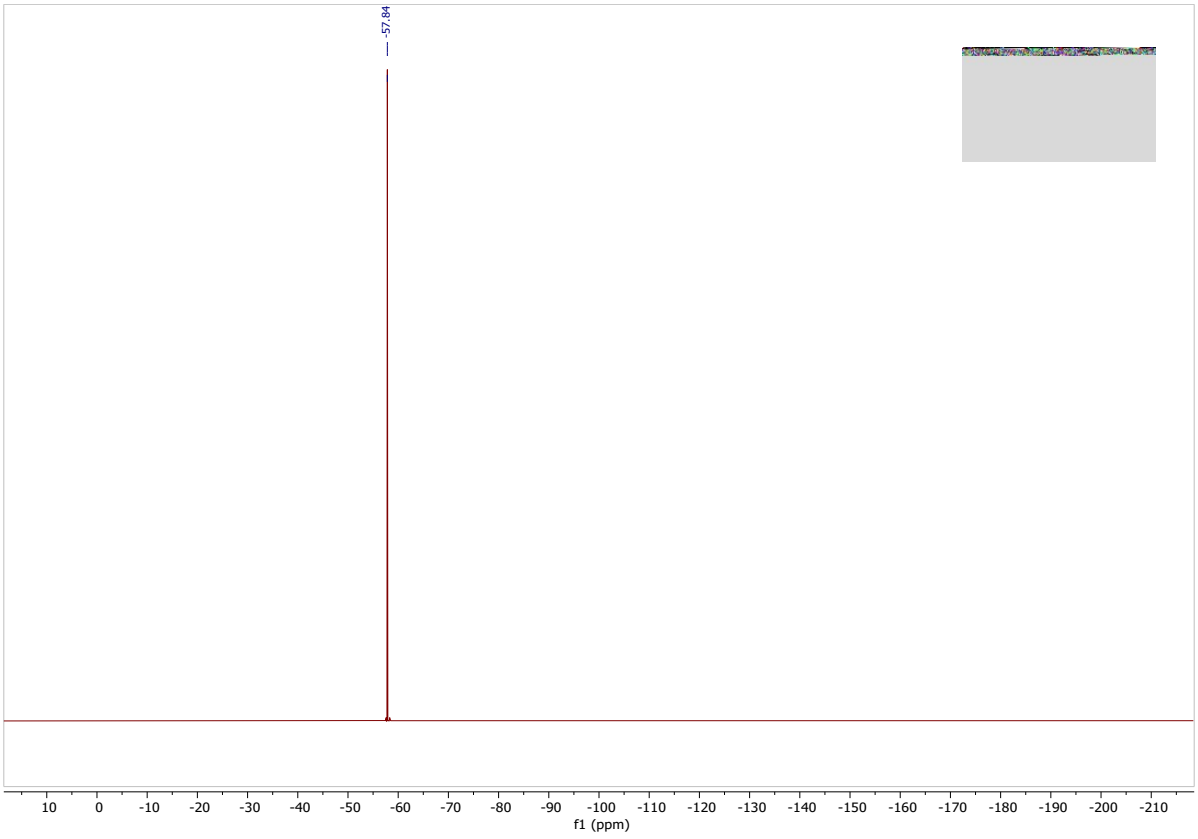
^{1}H NMR (500 MHz, Chloroform-*d*)



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

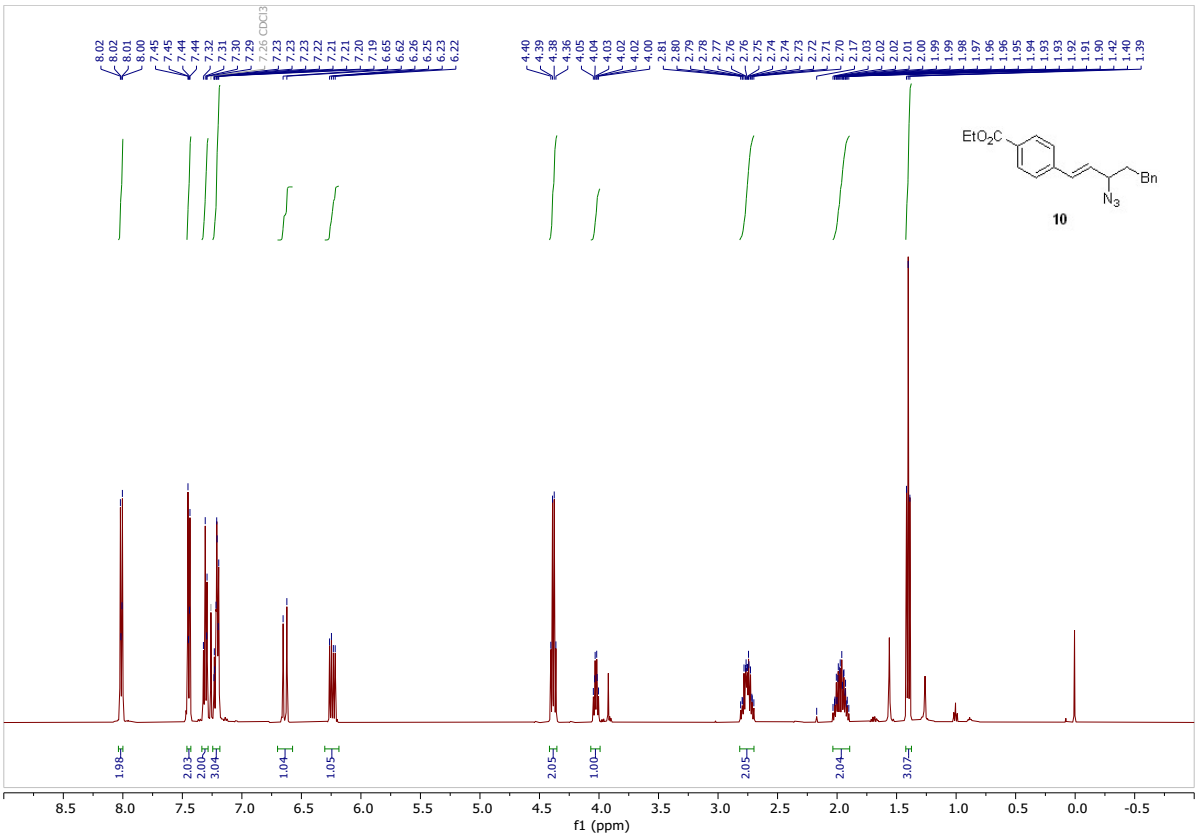


^{19}F NMR (377 MHz, $CDCl_3$)

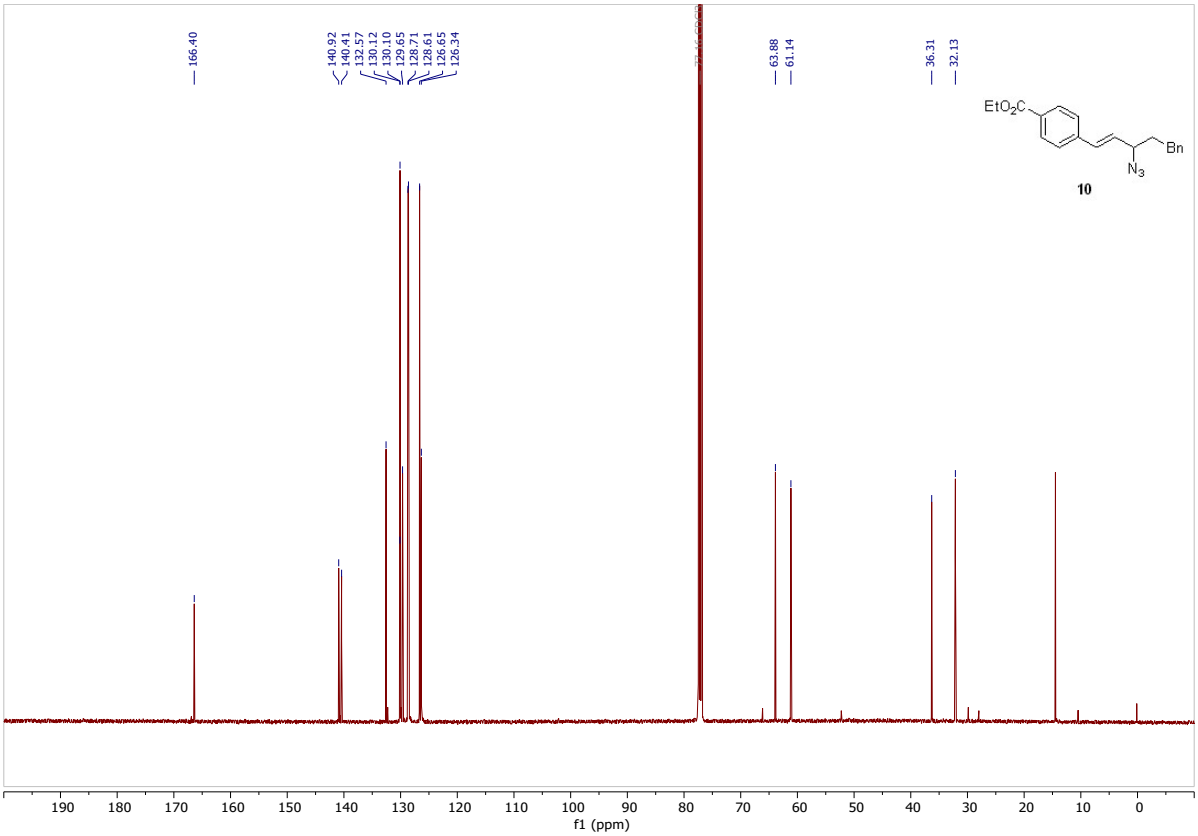


Compound 10

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

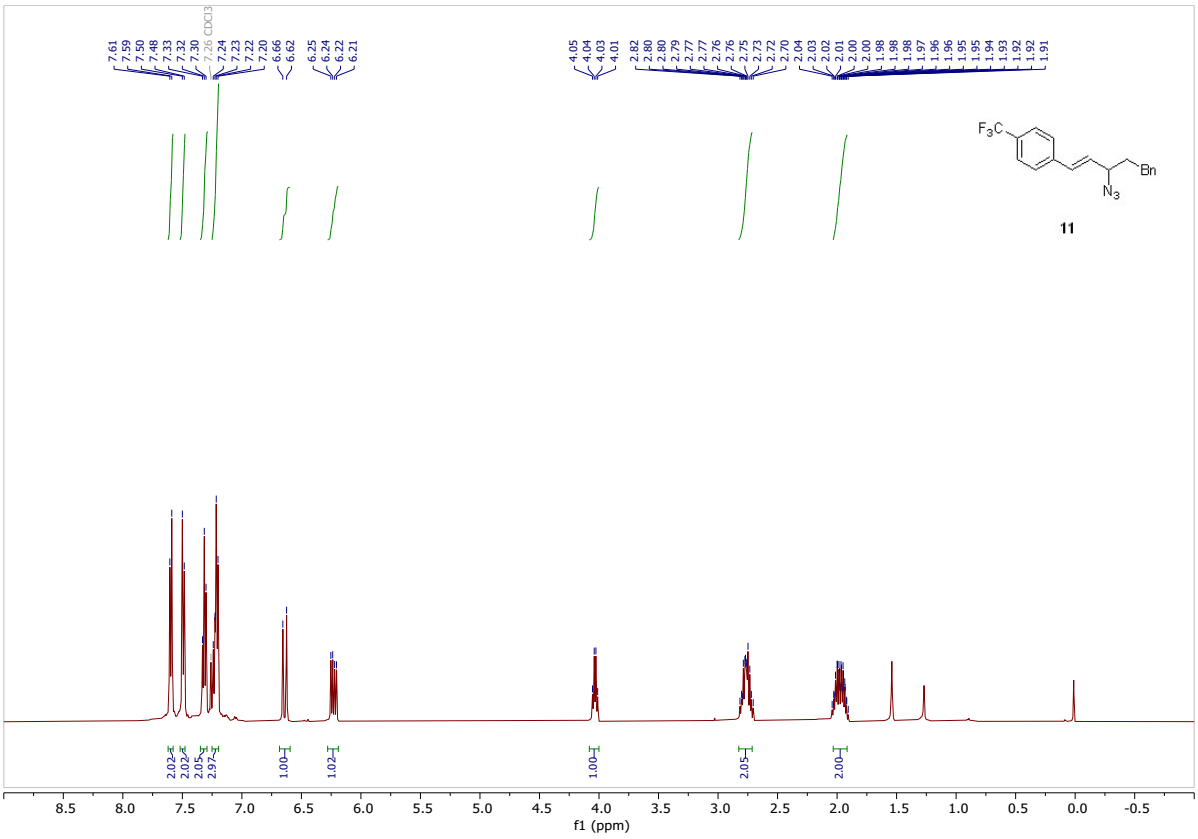


^{13}C NMR (126 MHz, $CDCl_3$)

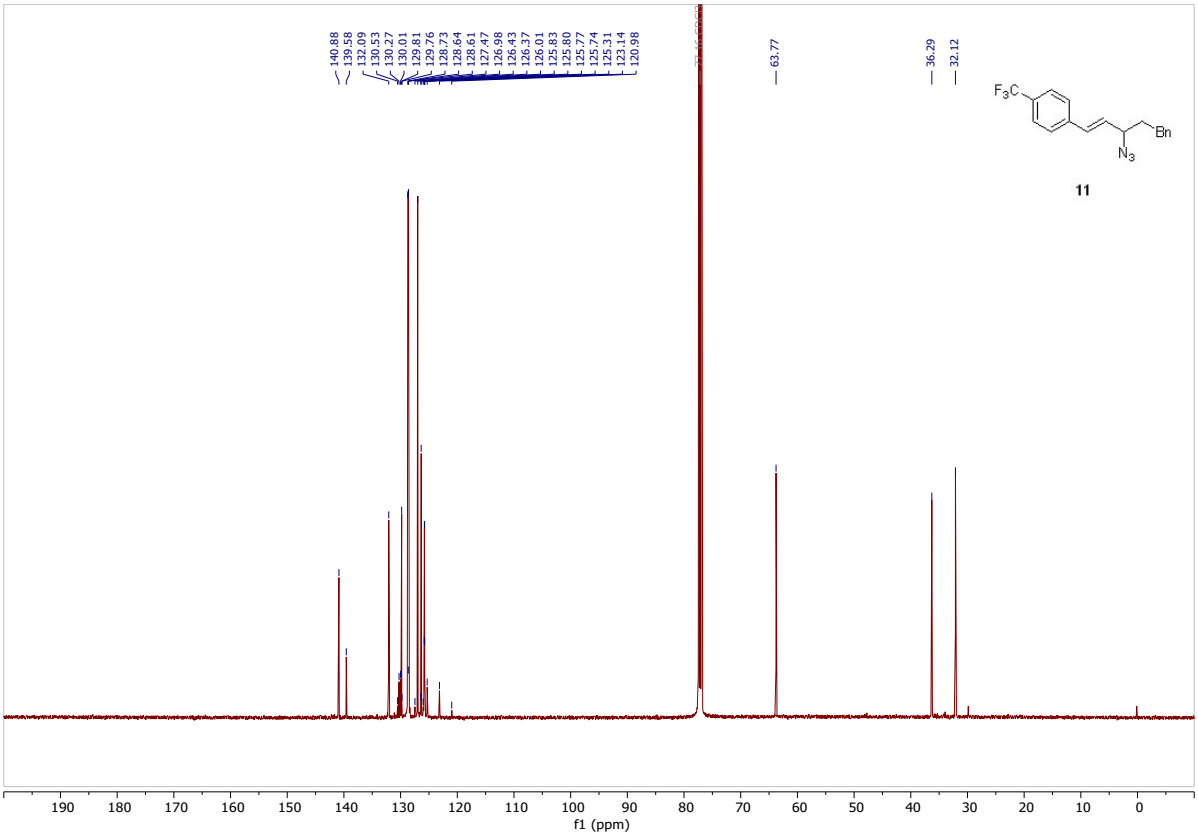


Compound 11

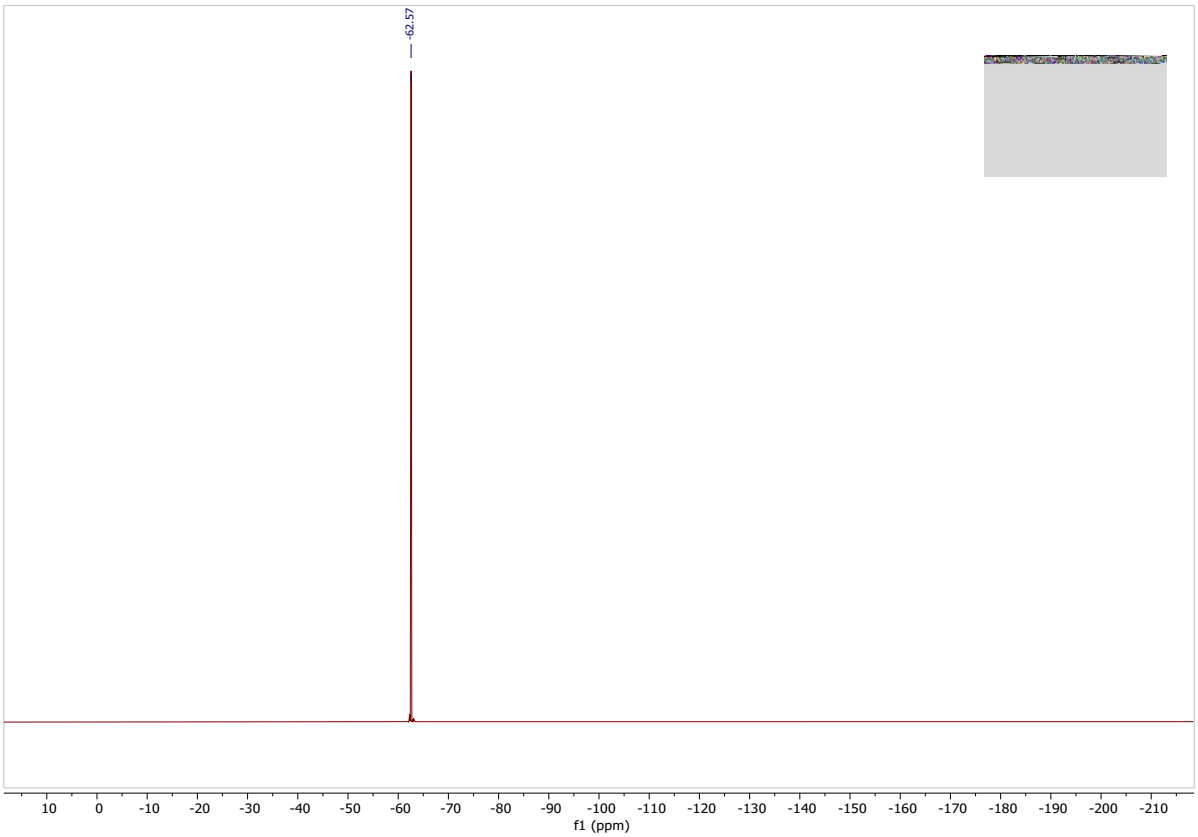
^{1}H NMR (500 MHz, Chloroform-*d*)



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

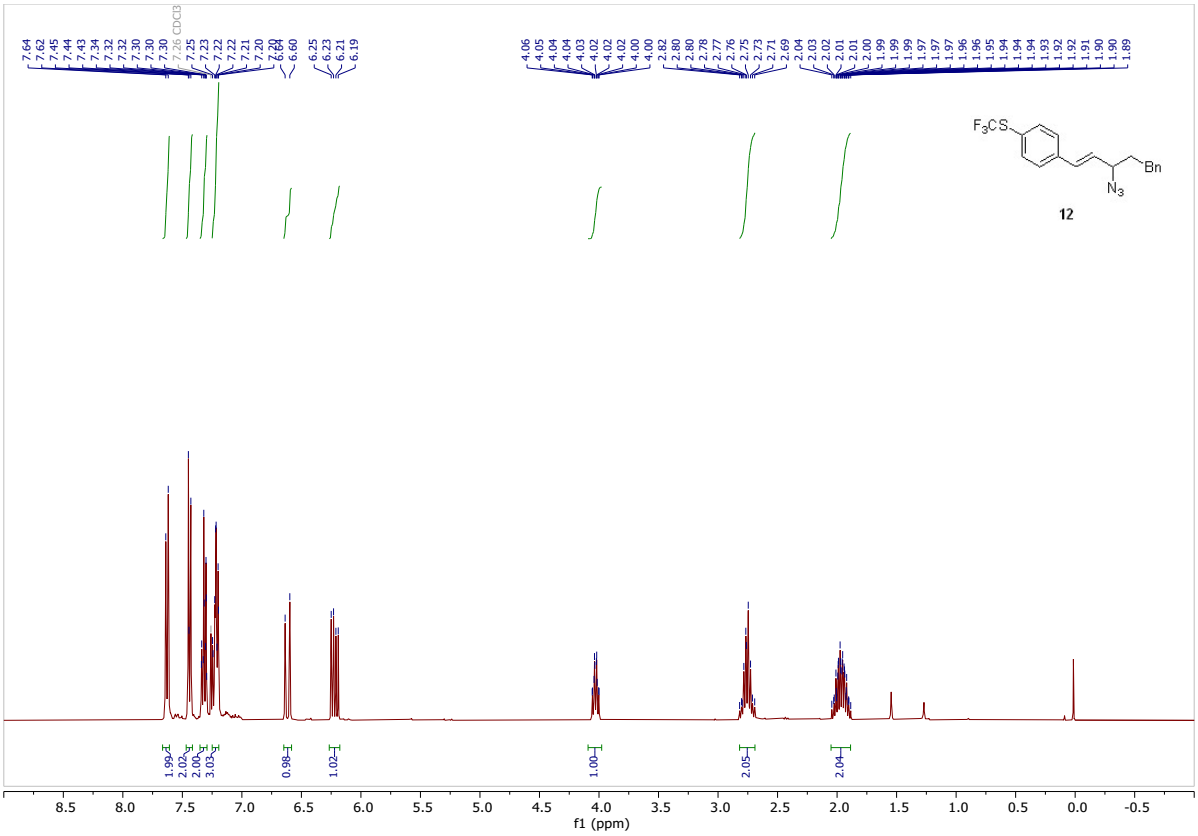


^{19}F NMR (377 MHz, $CDCl_3$)

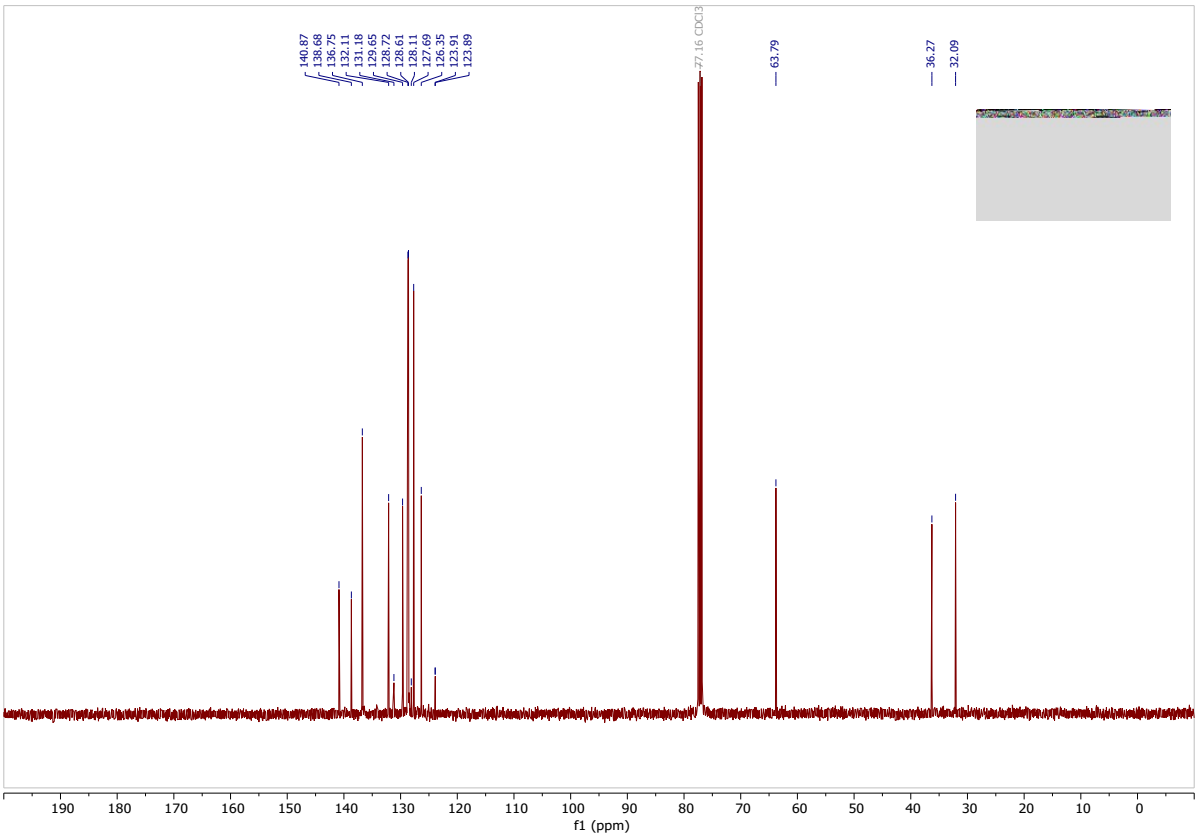


Compound 12

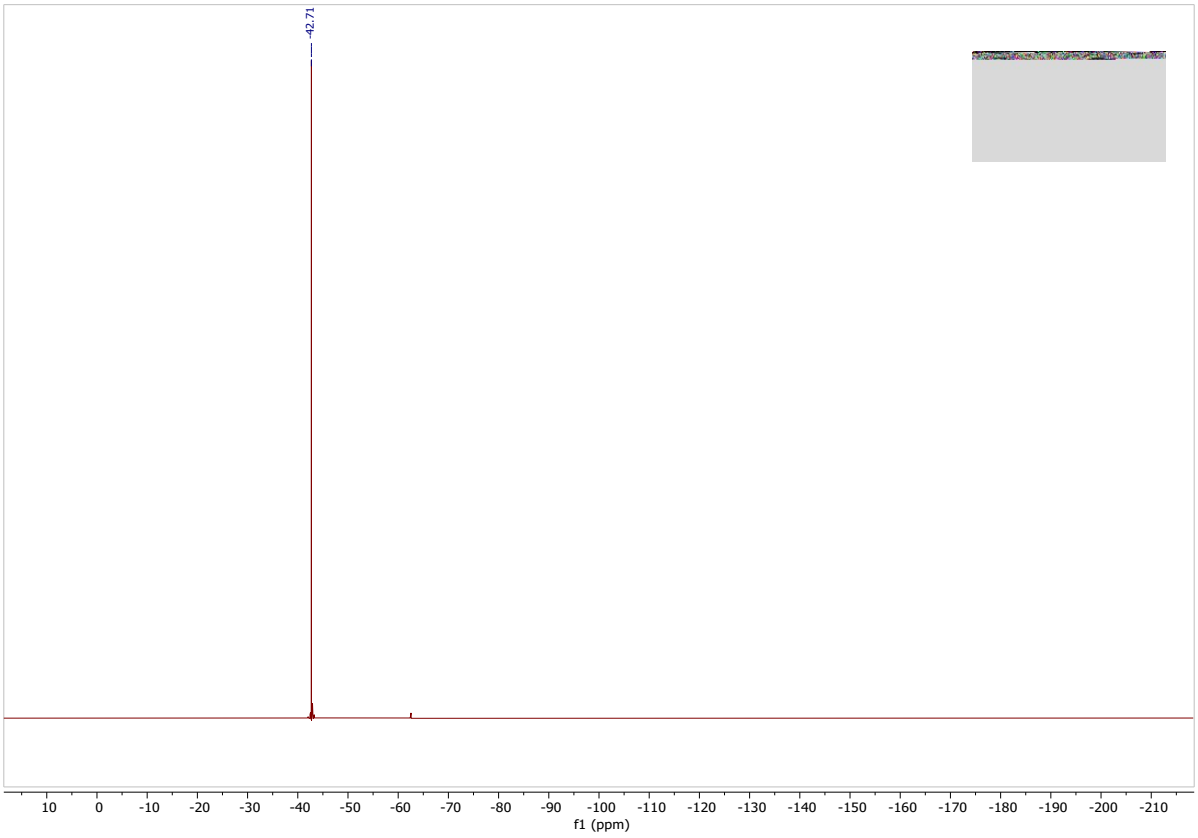
^{1}H NMR (500 MHz, Chloroform-*d*)



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

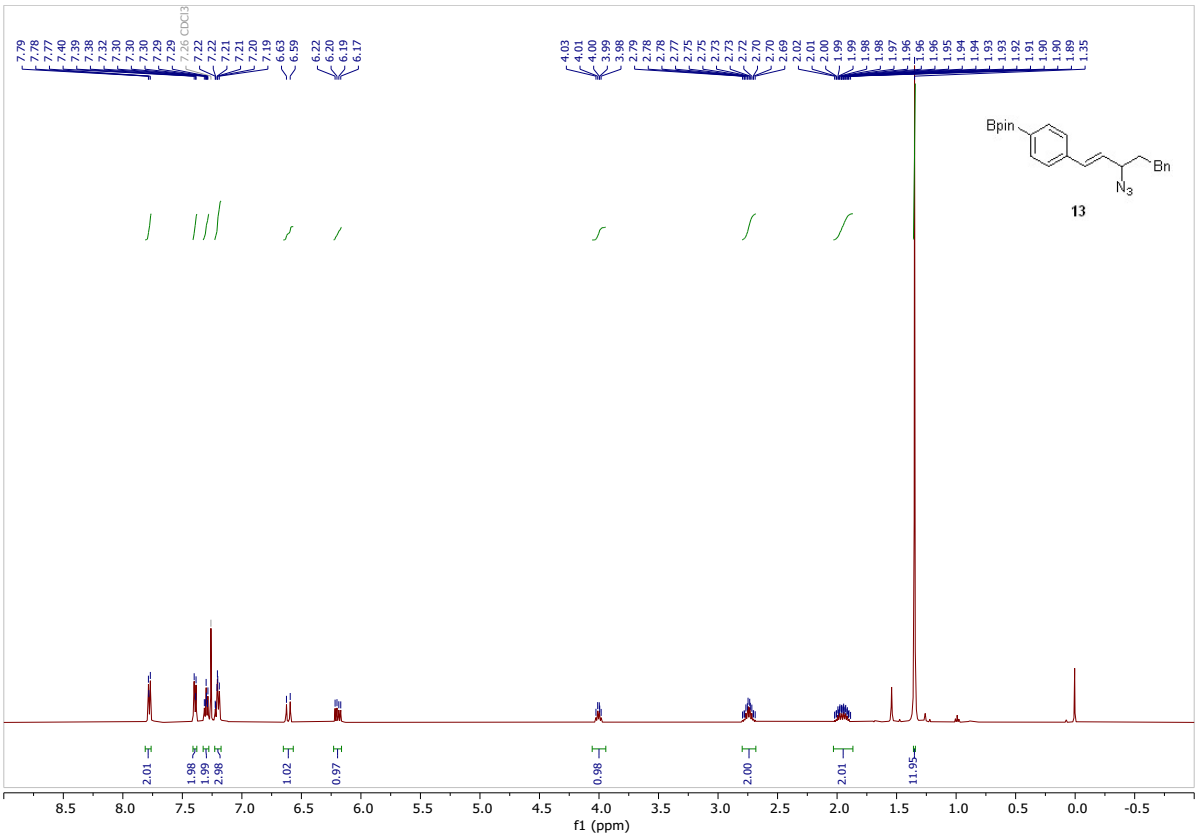


^{19}F NMR (377 MHz, $CDCl_3$)

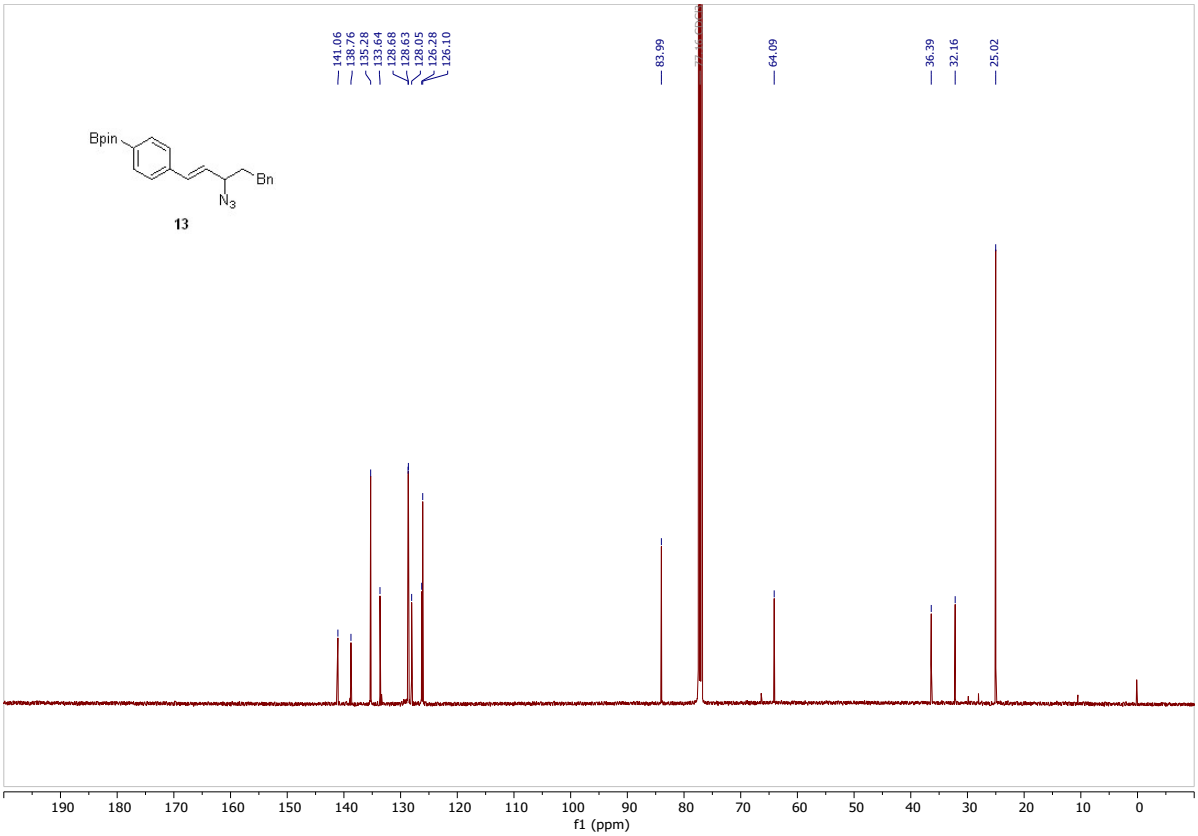


Compound 13

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

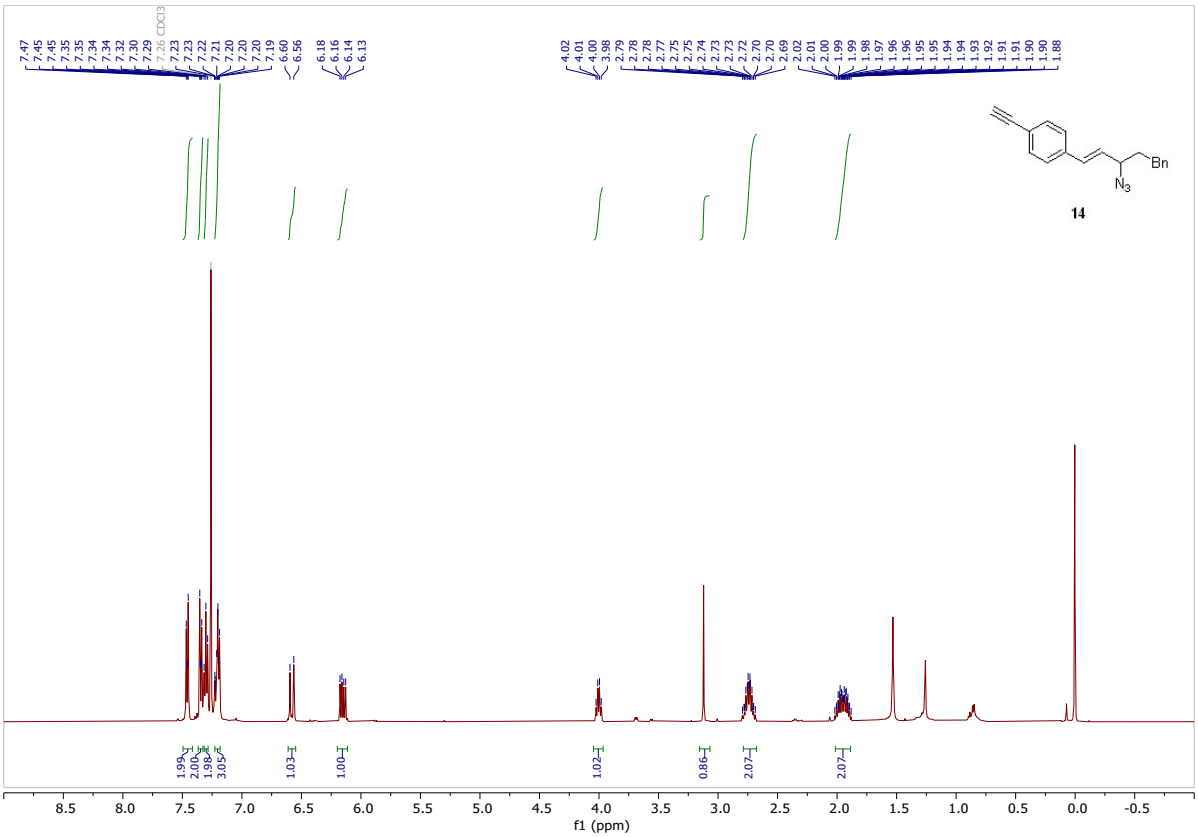


^{13}C NMR (126 MHz, $CDCl_3$)

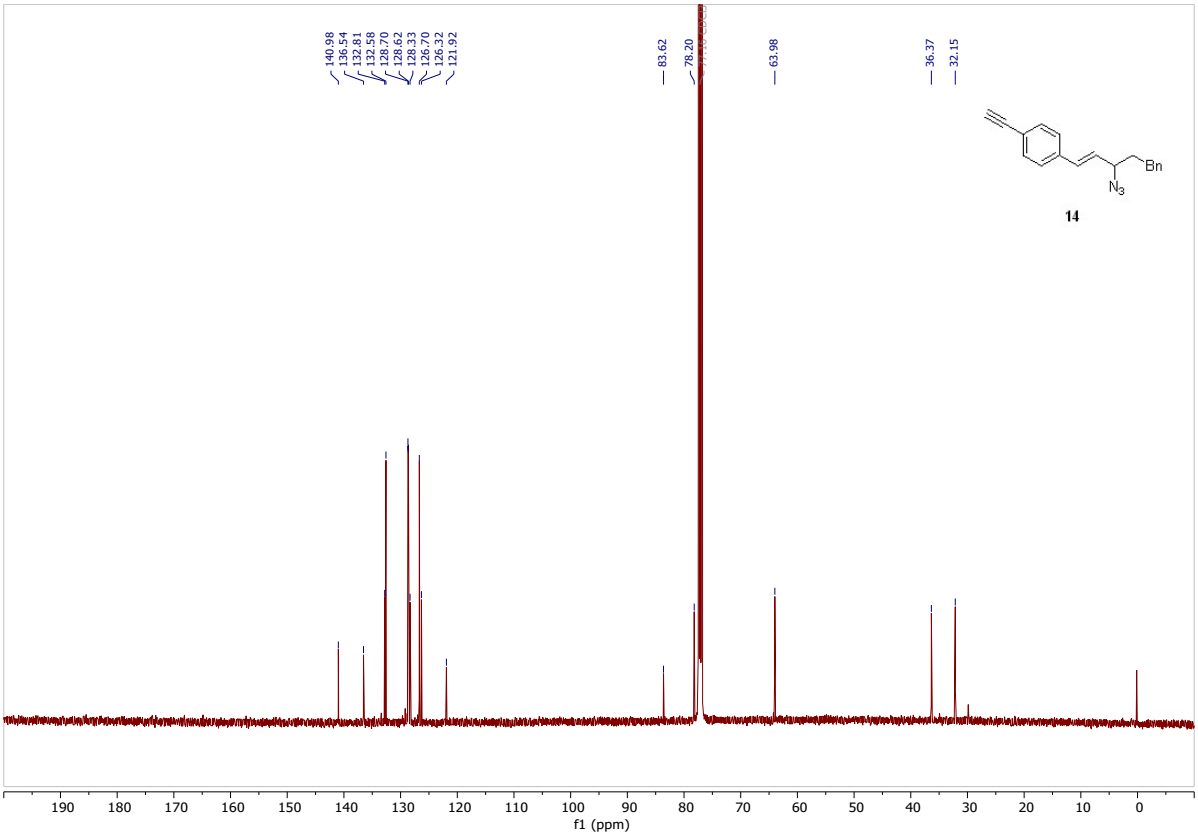


Compound 14

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

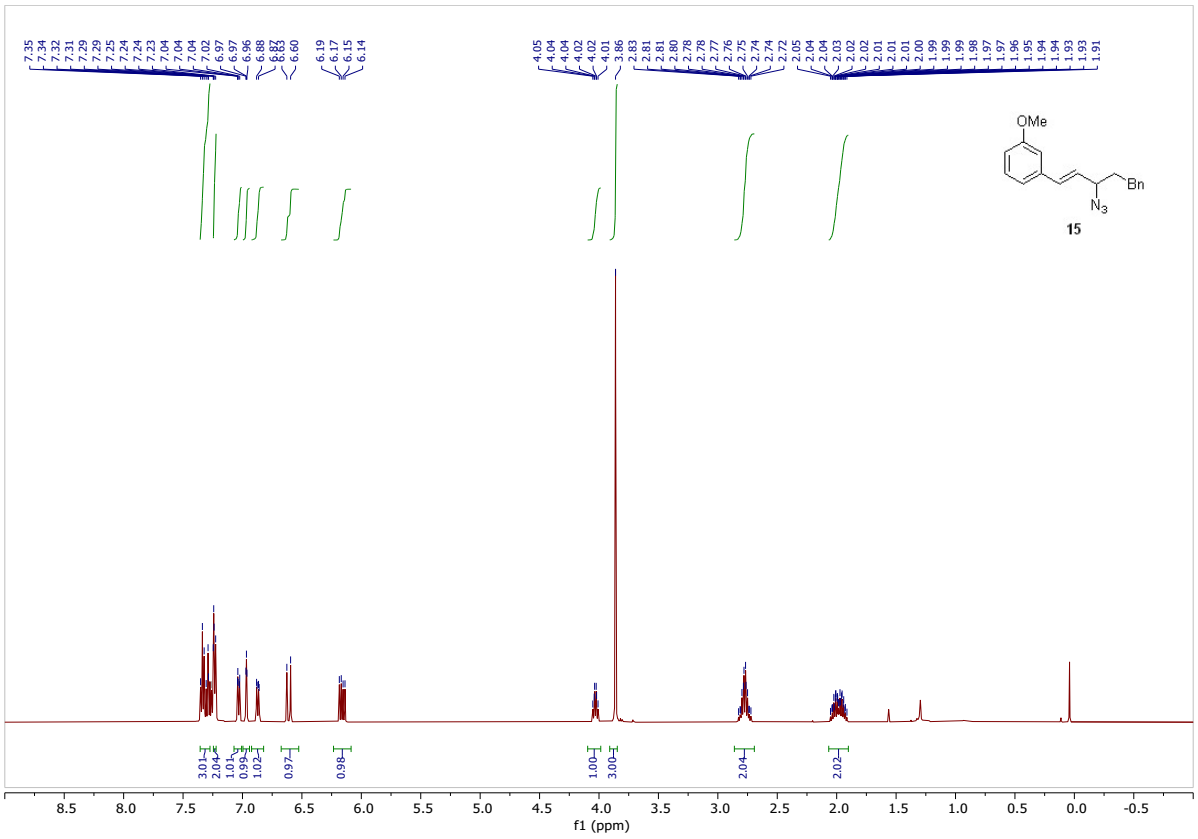


^{13}C NMR (126 MHz, $CDCl_3$)

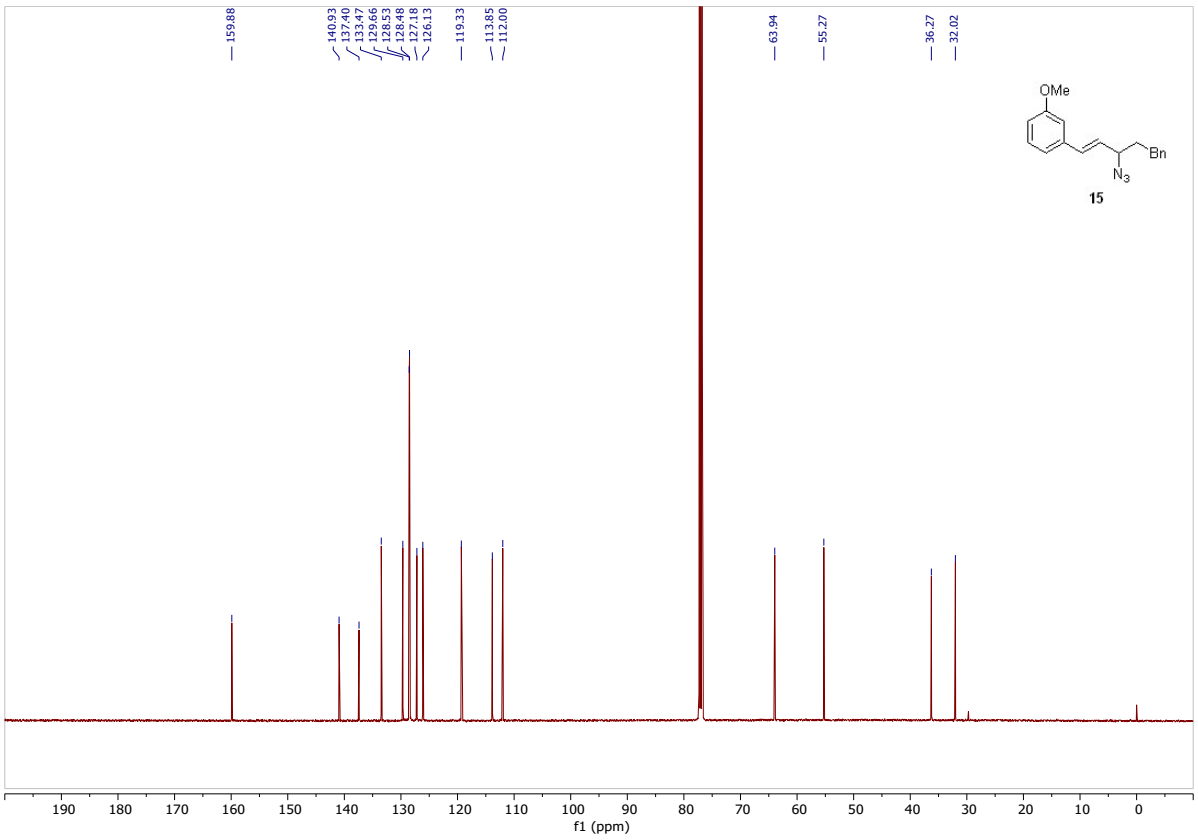


Compound 15

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

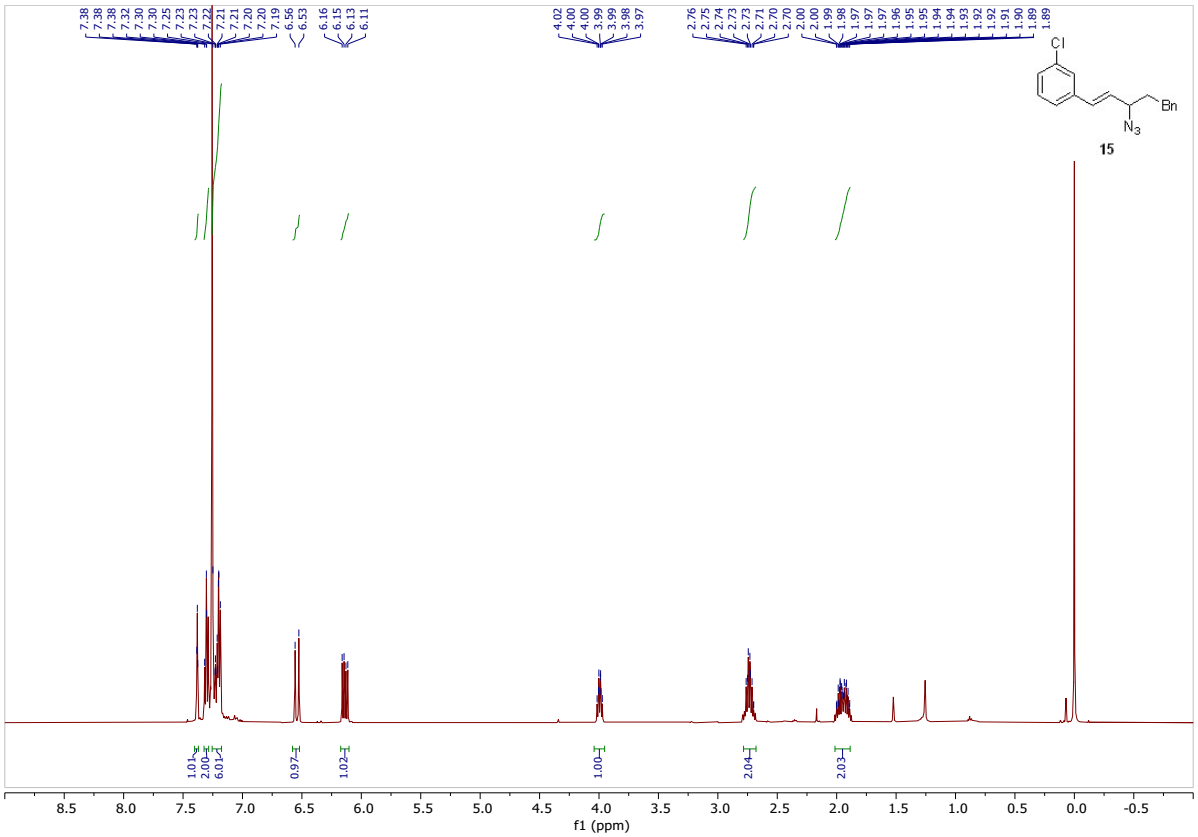


^{13}C NMR (126 MHz, $CDCl_3$)

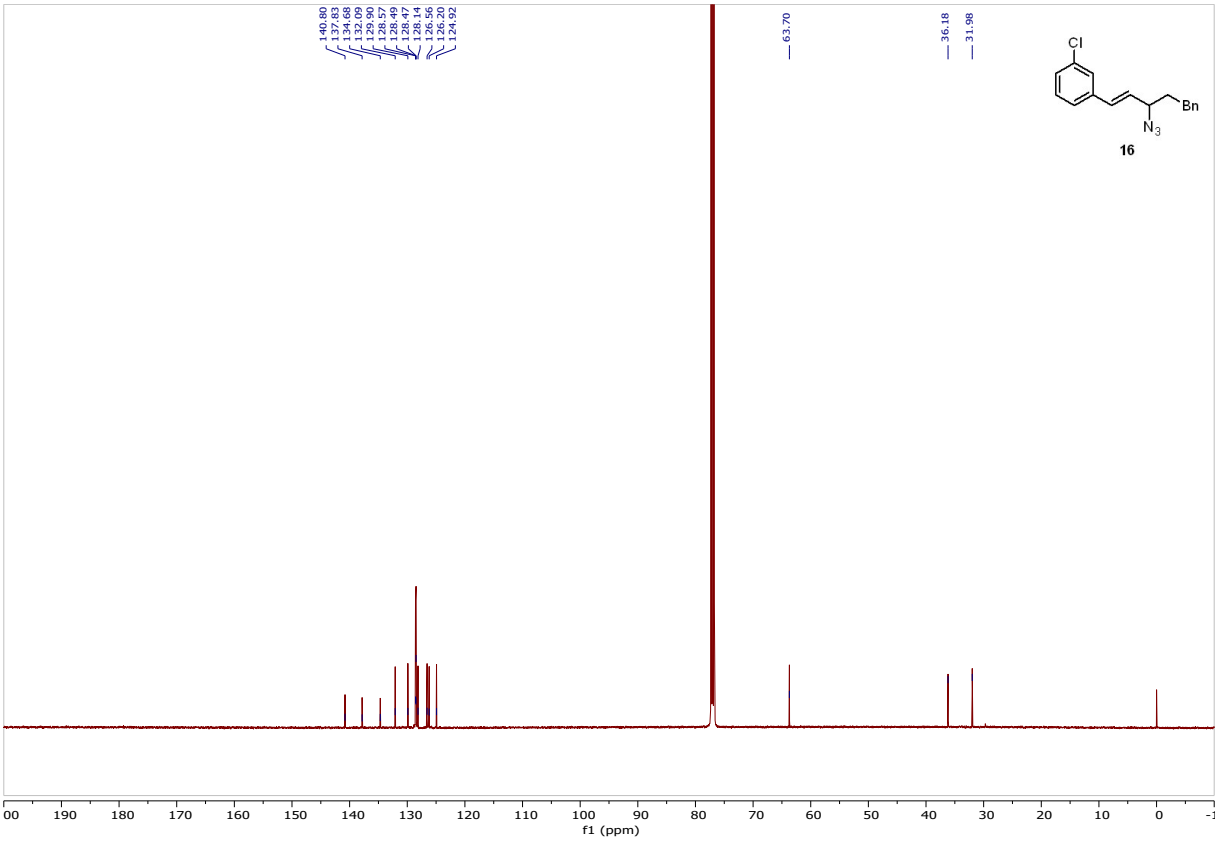


Compound 16

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

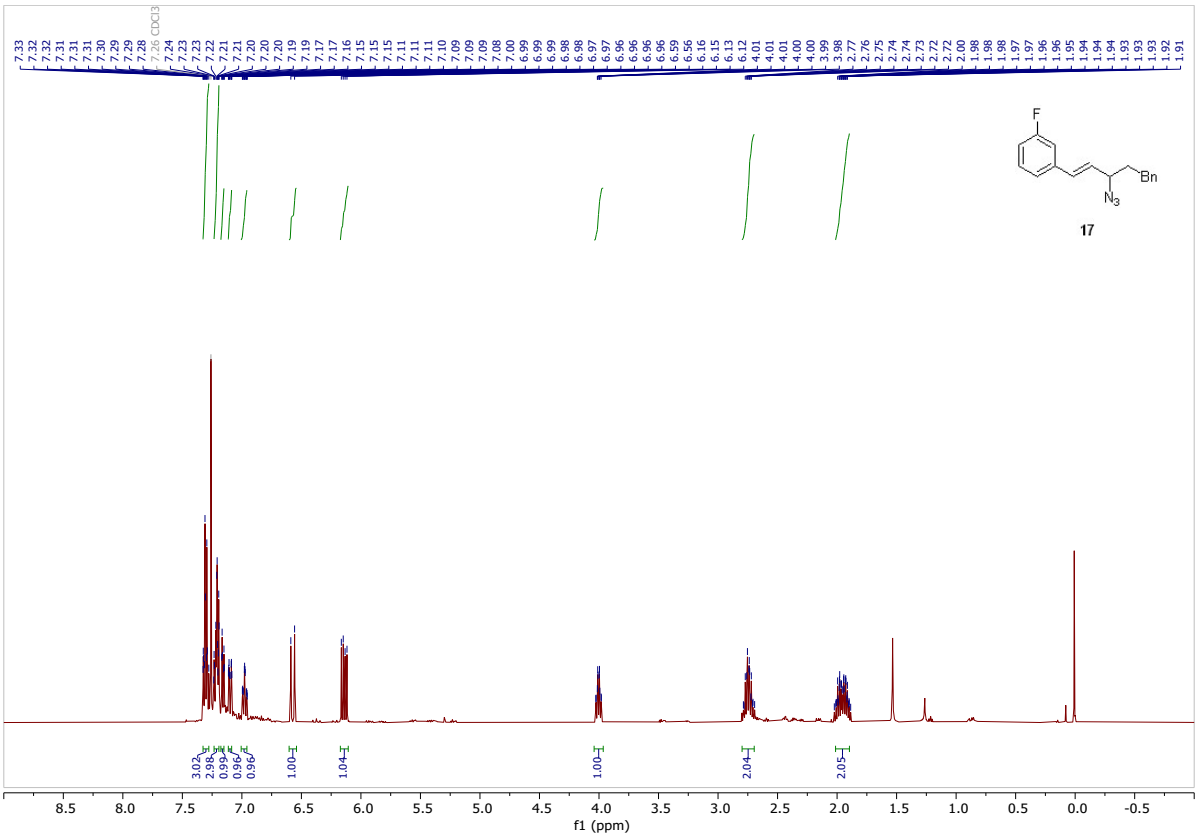


^{13}C NMR (126 MHz, $CDCl_3$)

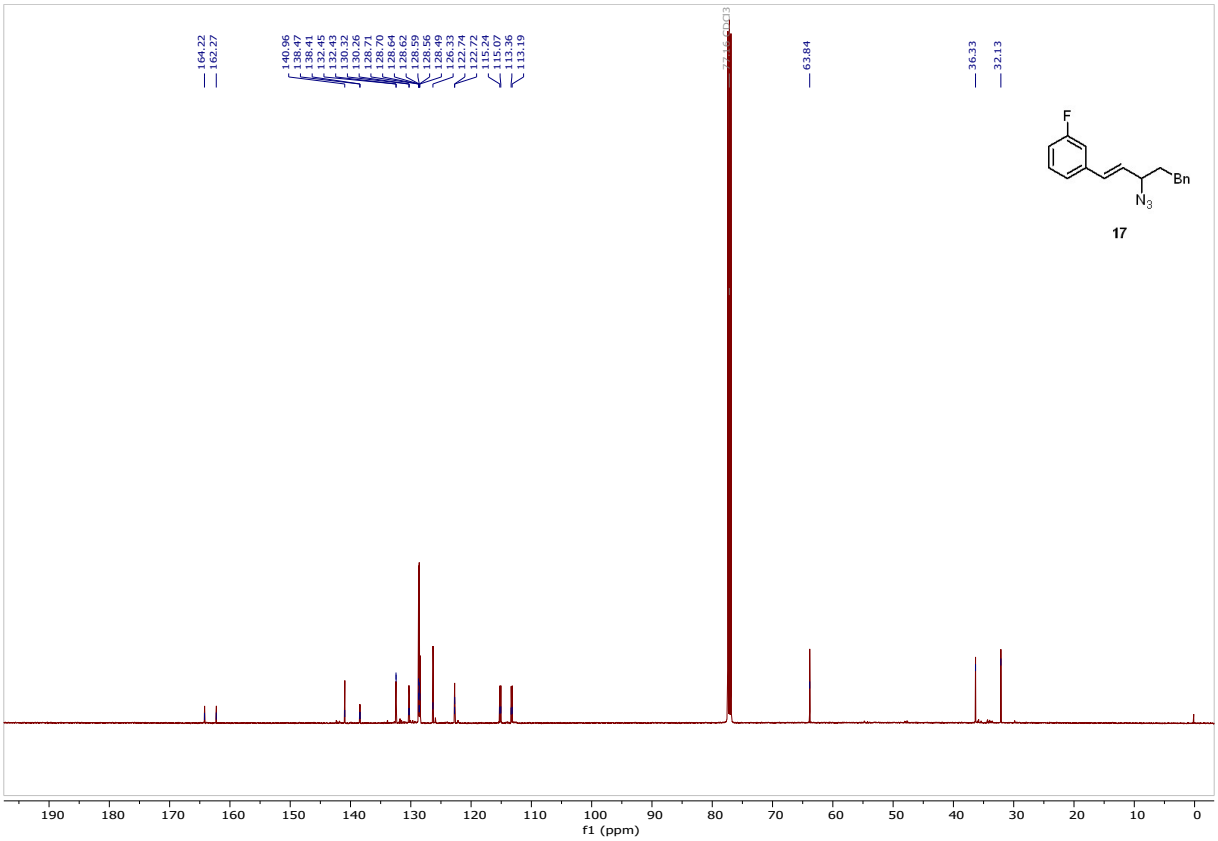


Compound 17

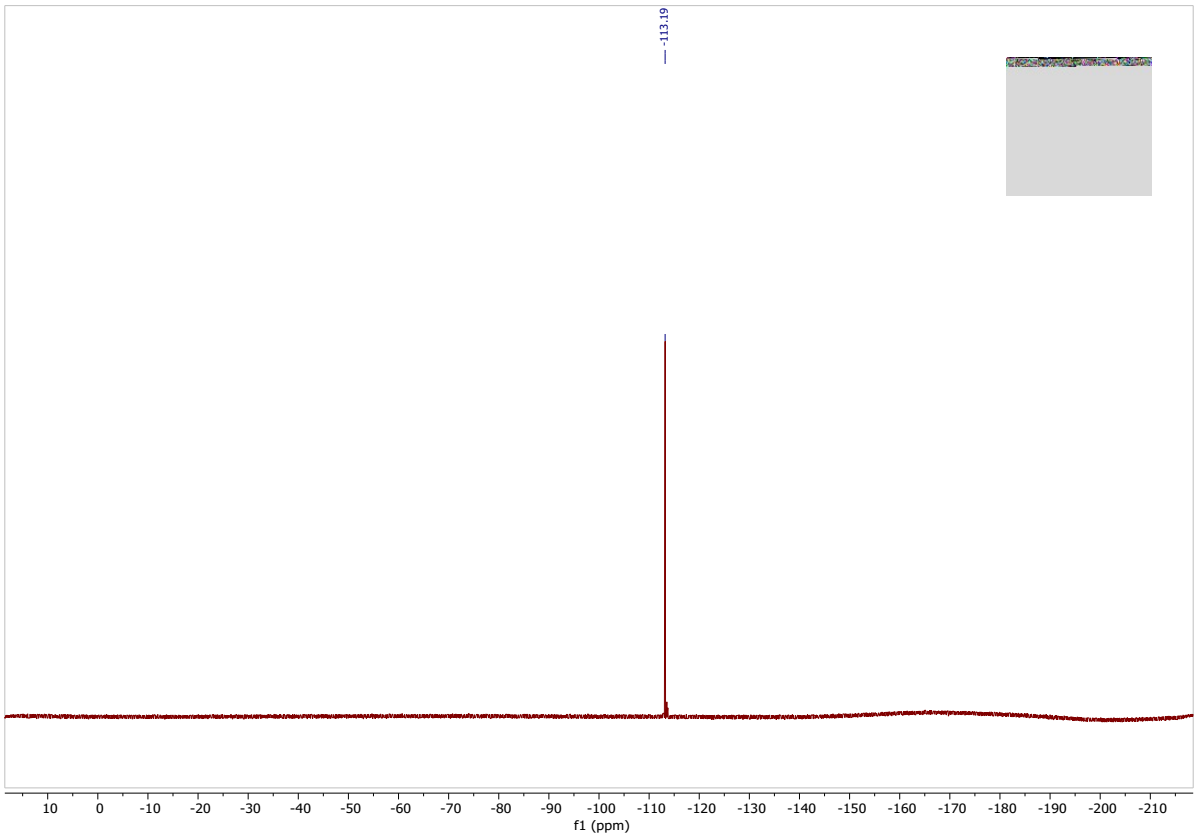
^{1}H NMR (500 MHz, Chloroform-*d*)



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

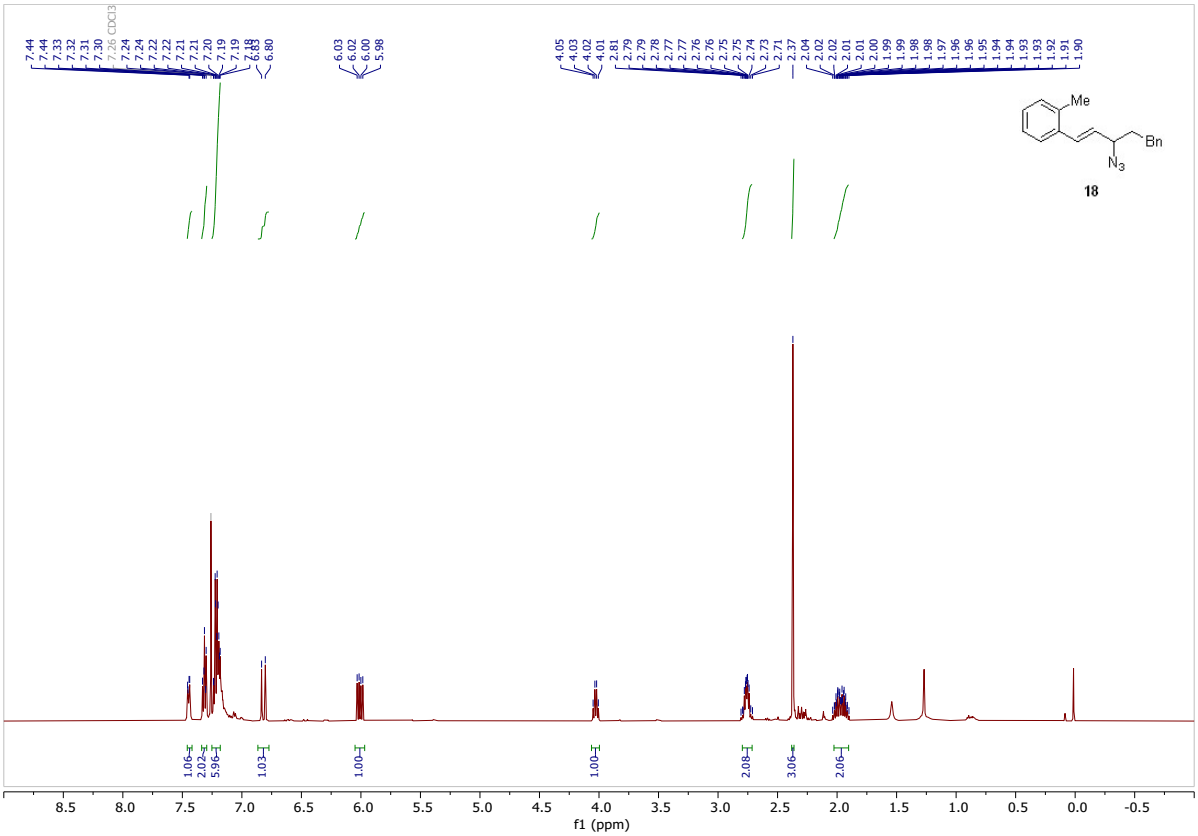


^{19}F NMR (377 MHz, $CDCl_3$)

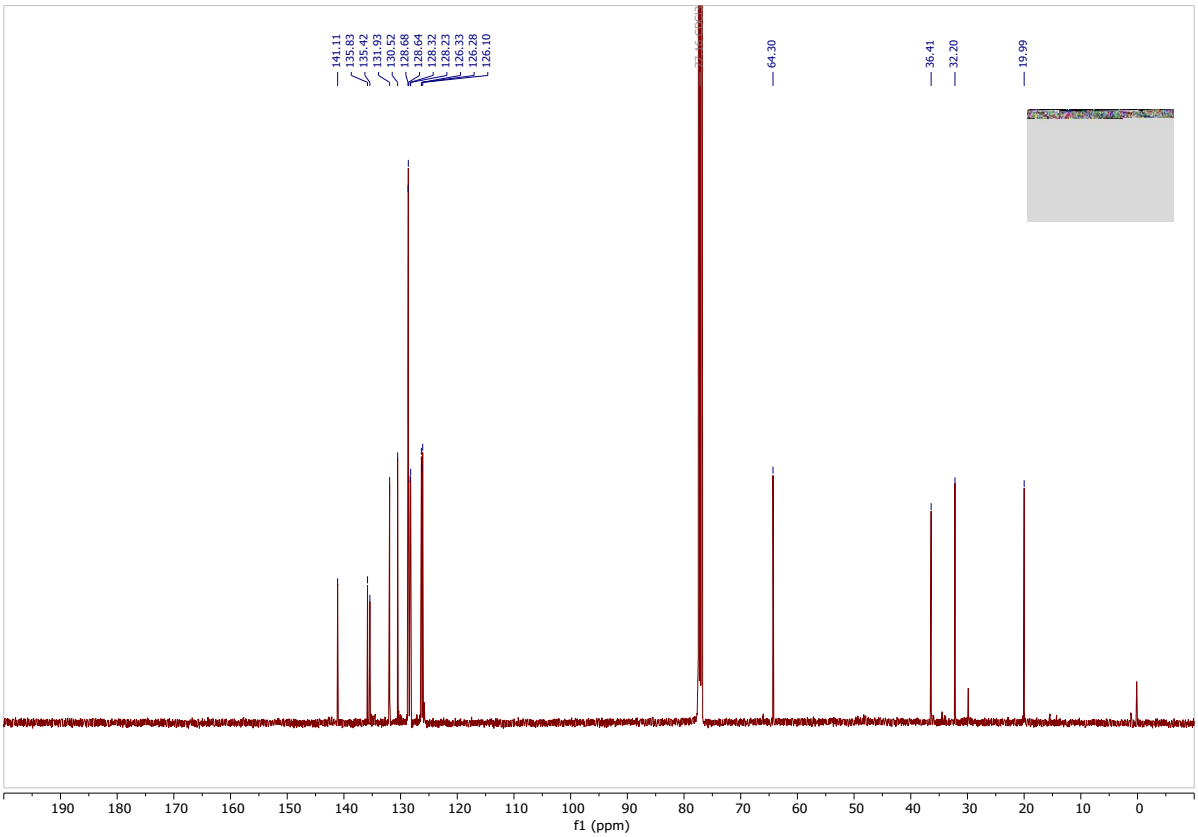


Compound 18

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

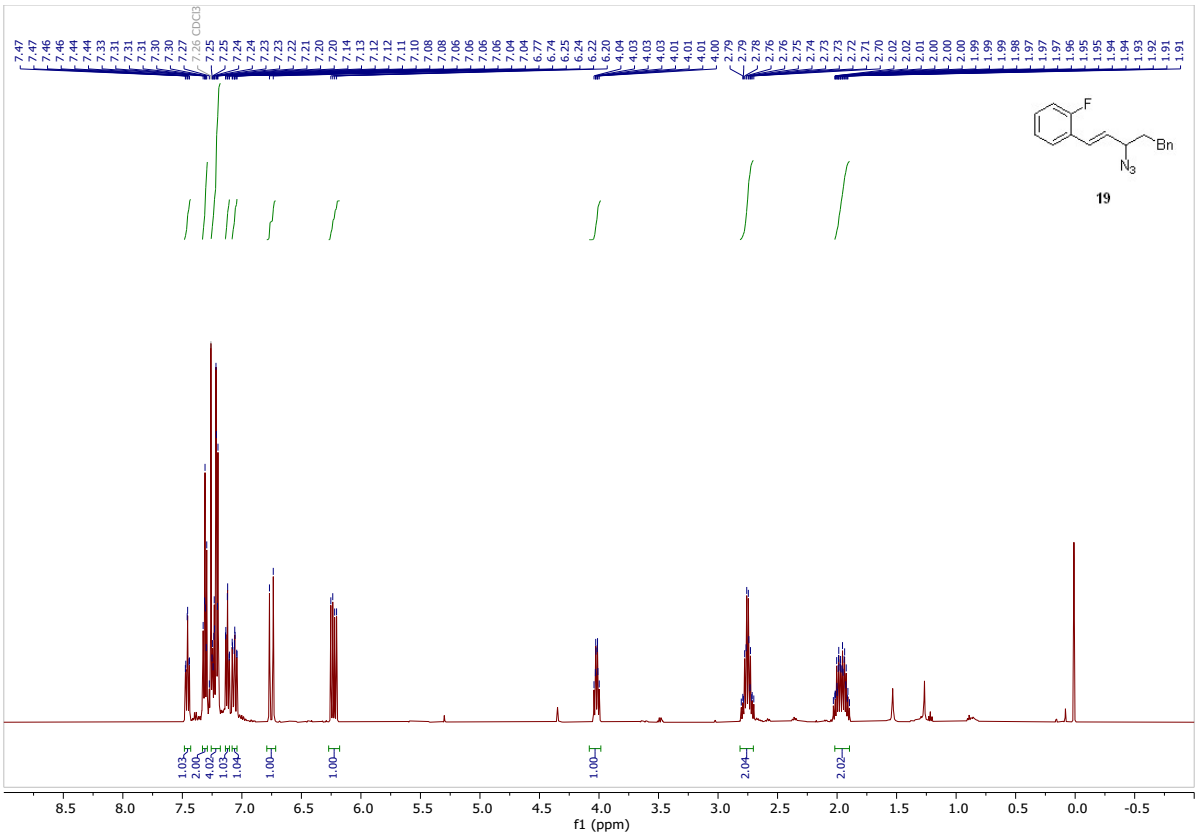


^{13}C NMR (126 MHz, $CDCl_3$)

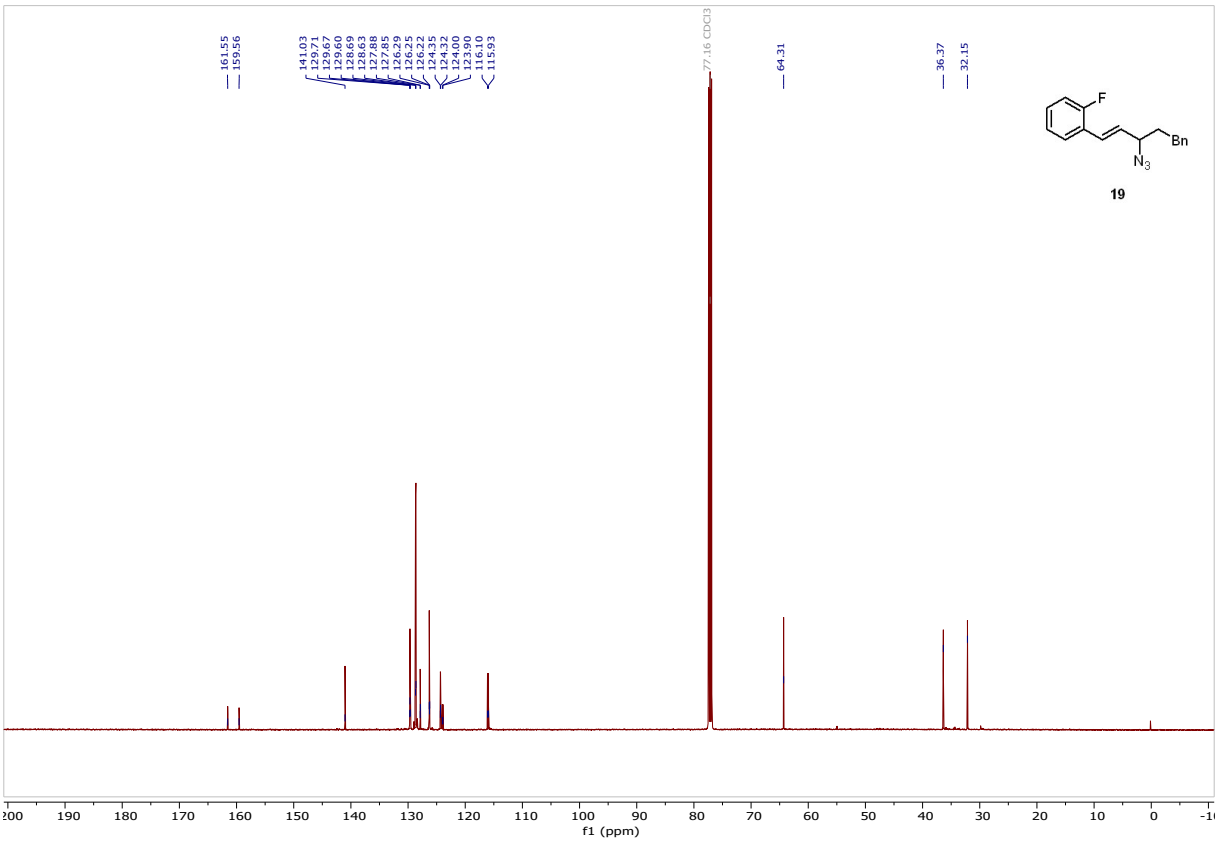


Compound 19

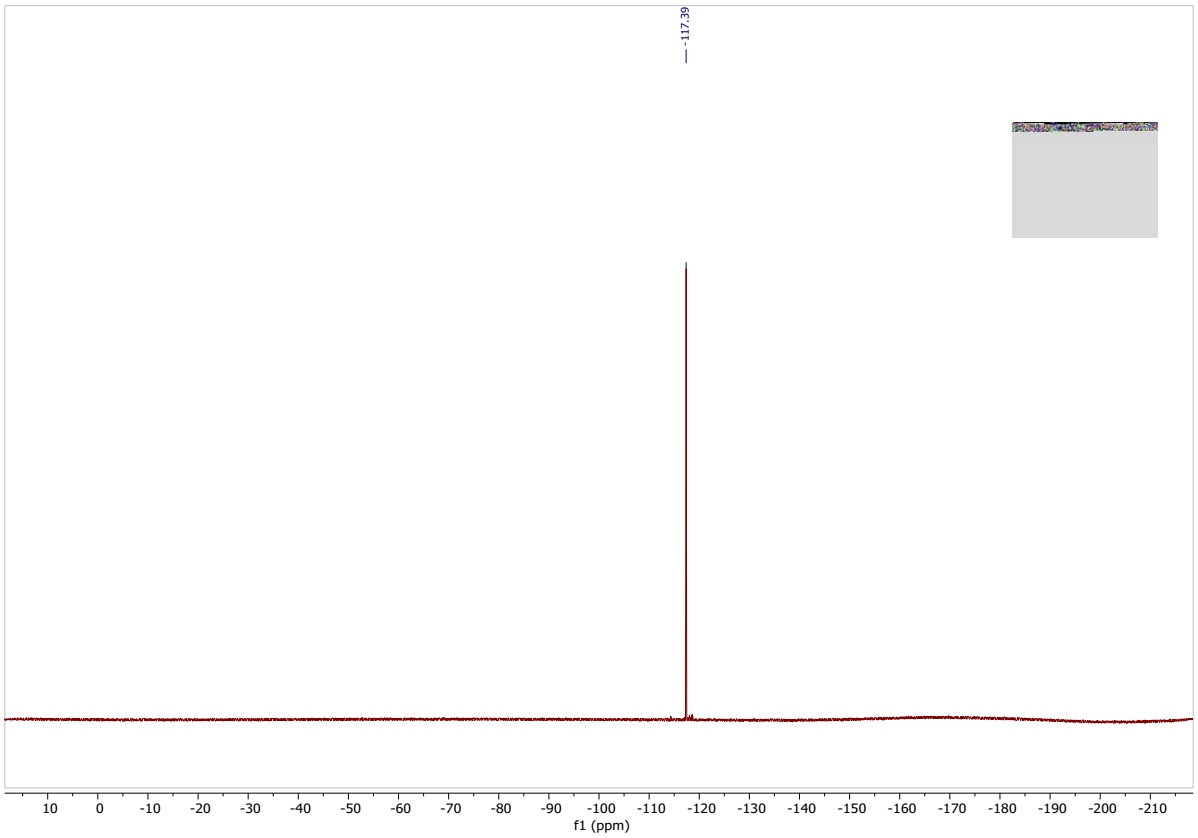
^{1}H NMR (500 MHz, Chloroform-*d*)



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

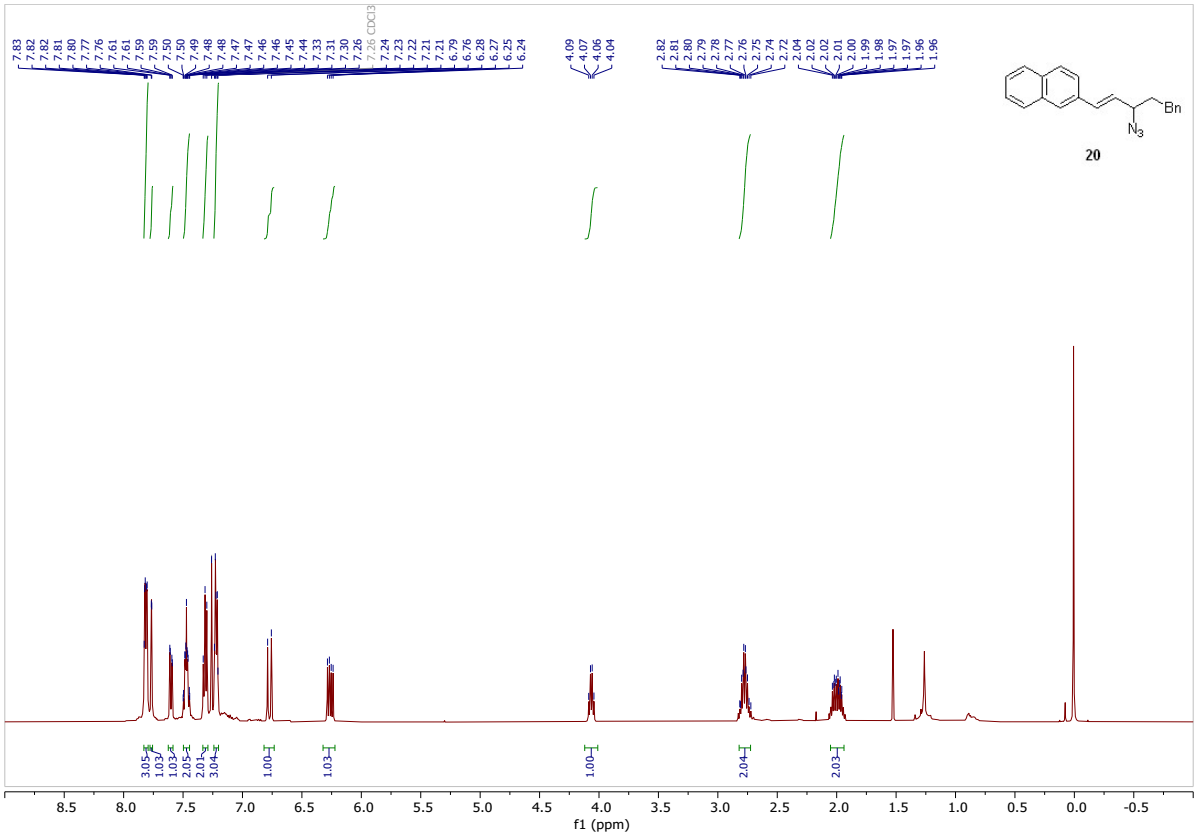


^{19}F NMR (377 MHz, $CDCl_3$)

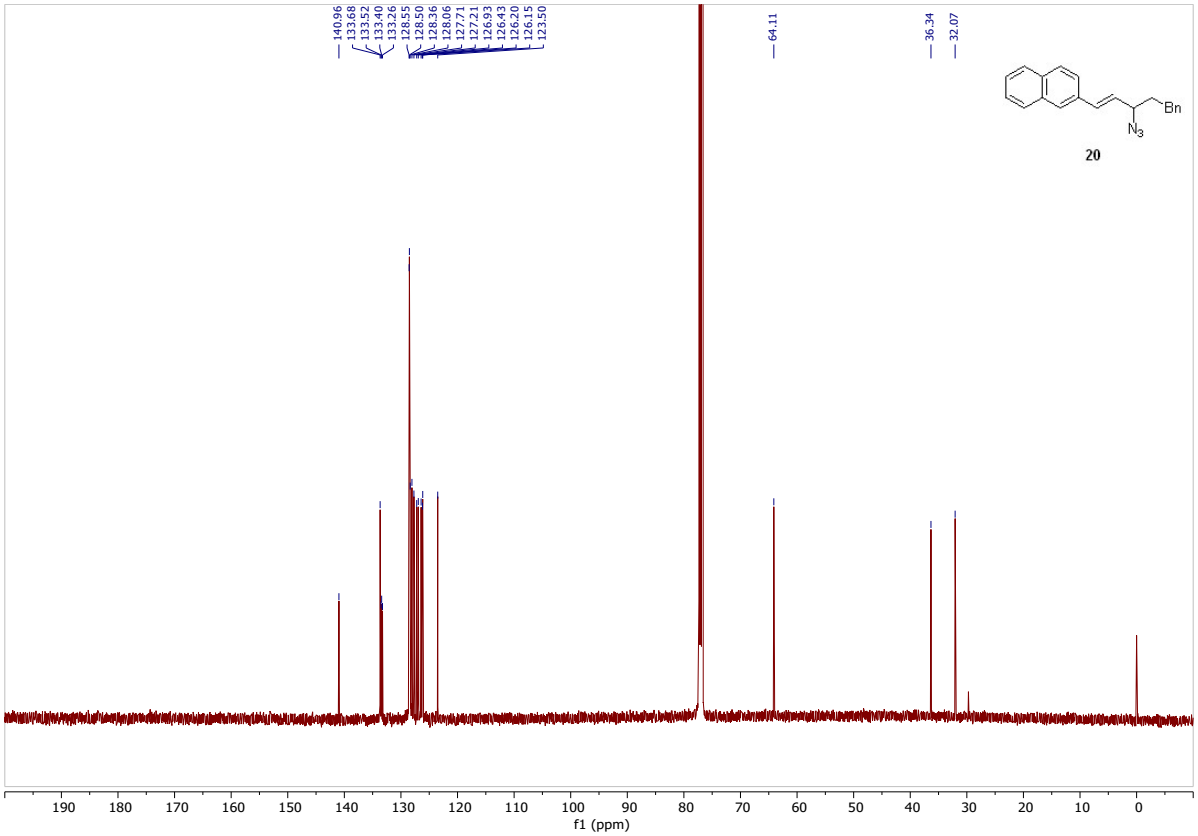


Compound 20

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

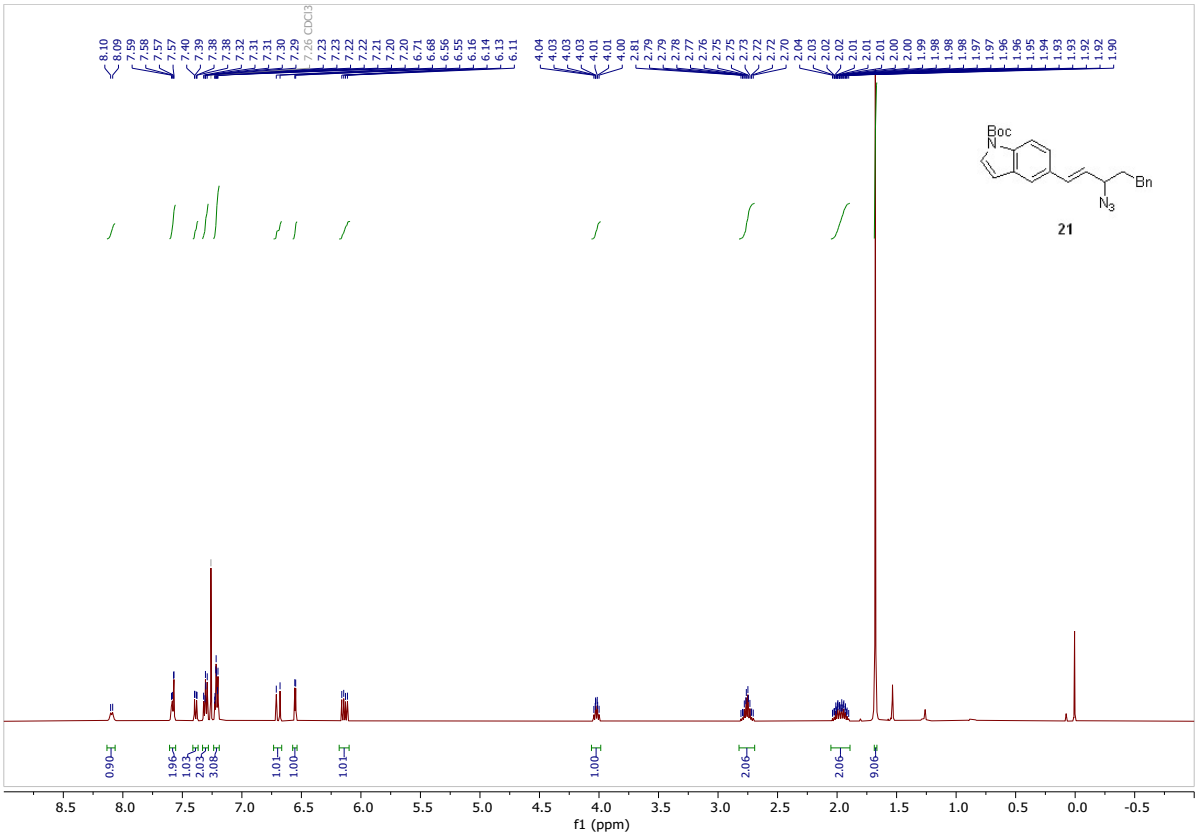


^{13}C NMR (126 MHz, $CDCl_3$)

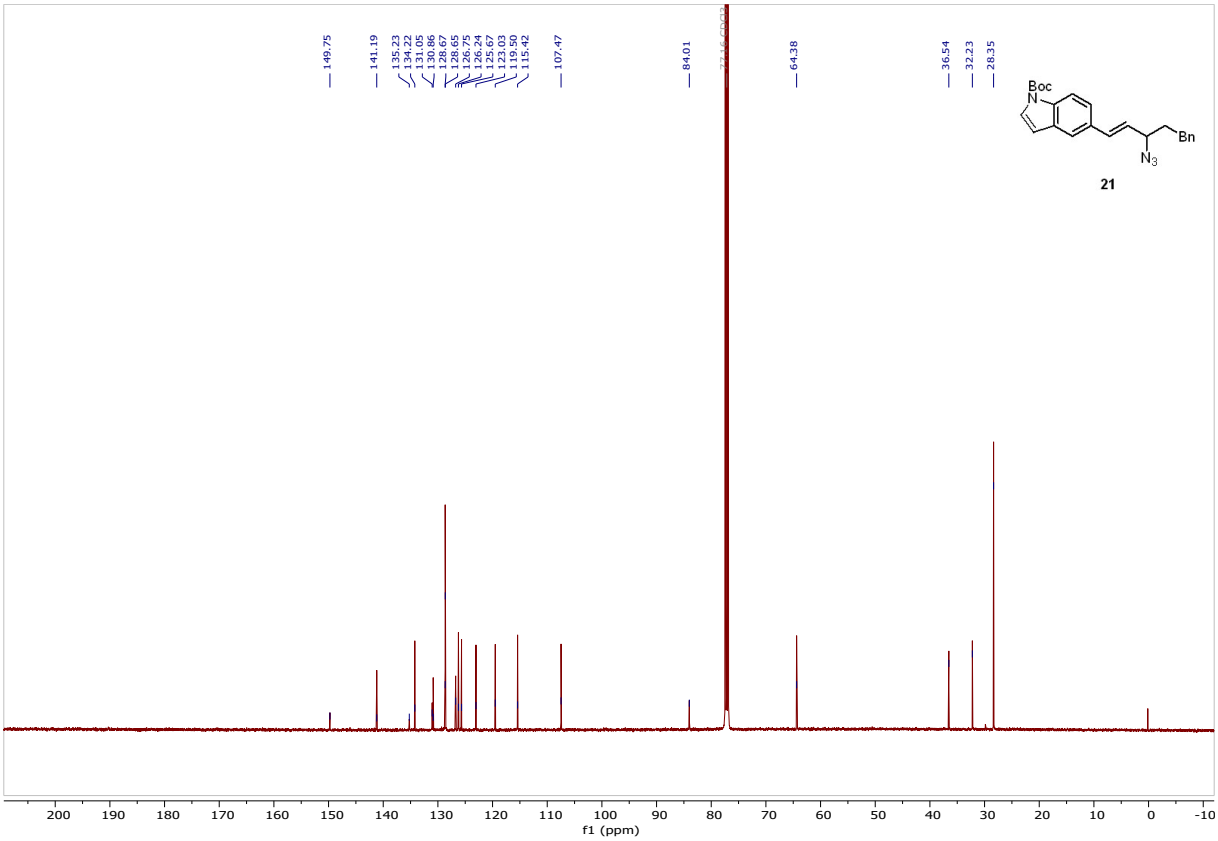


Compound 21

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

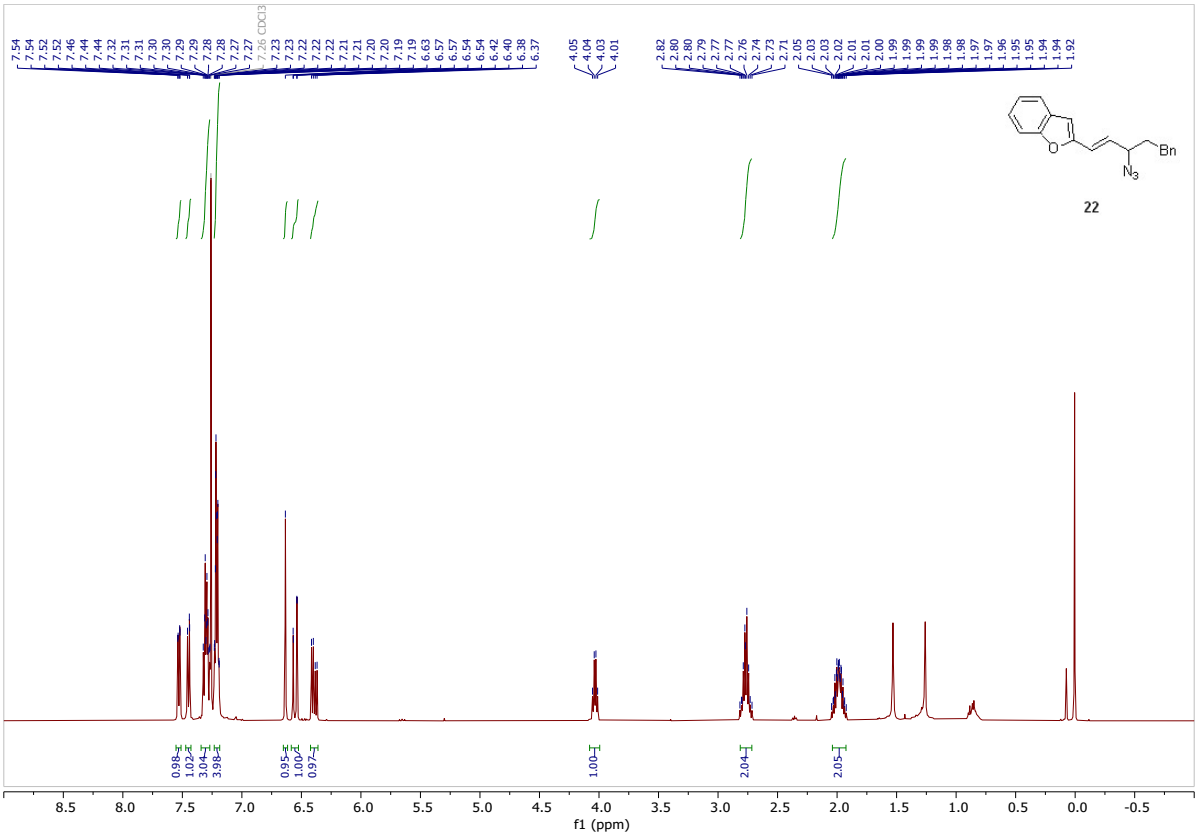


^{13}C NMR (126 MHz, $CDCl_3$)

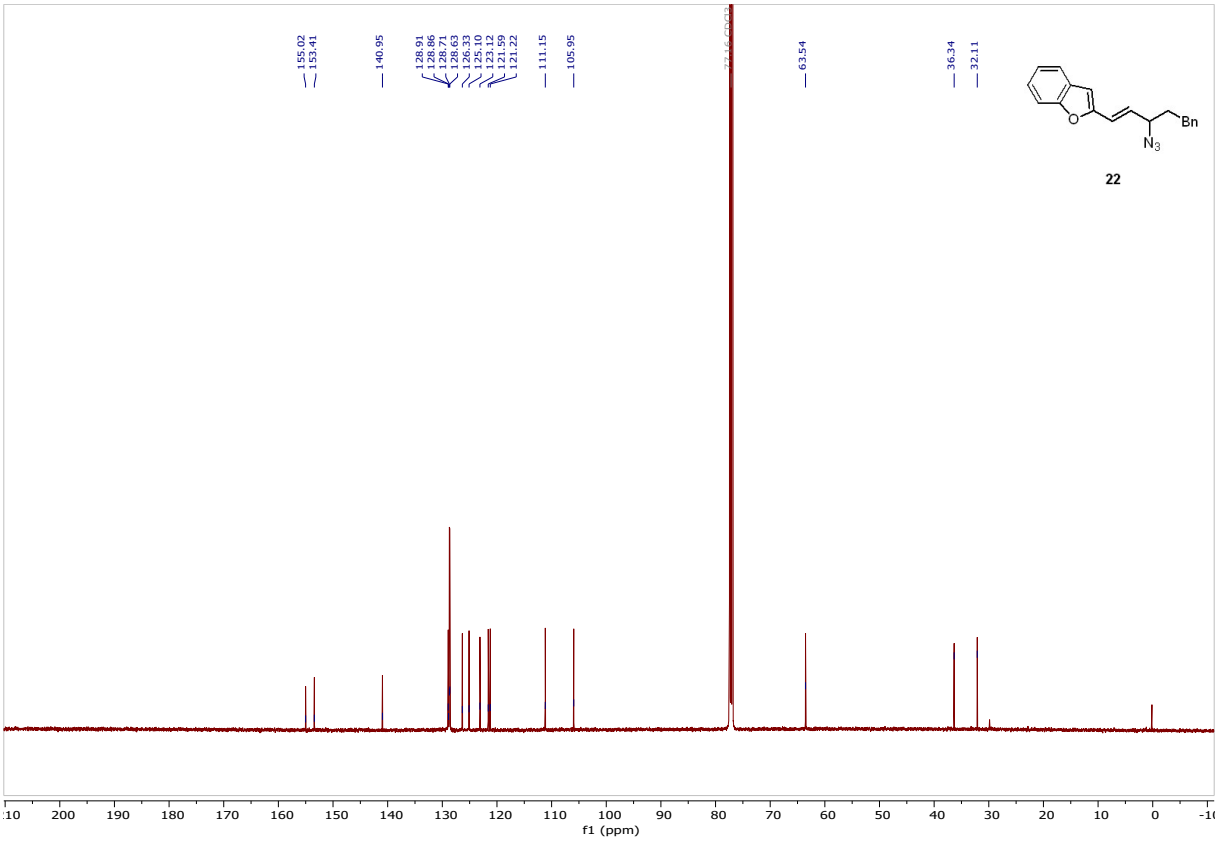


Compound 22

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

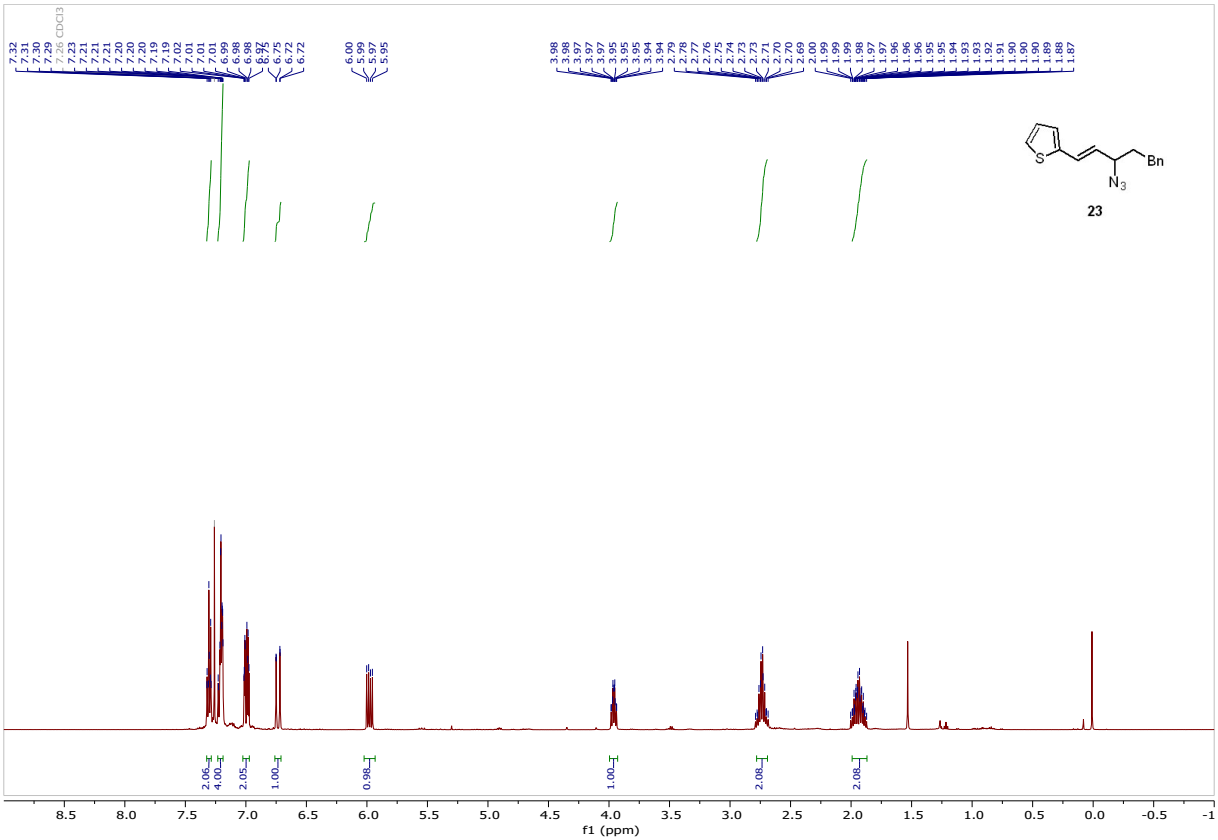


^{13}C NMR (126 MHz, $CDCl_3$)

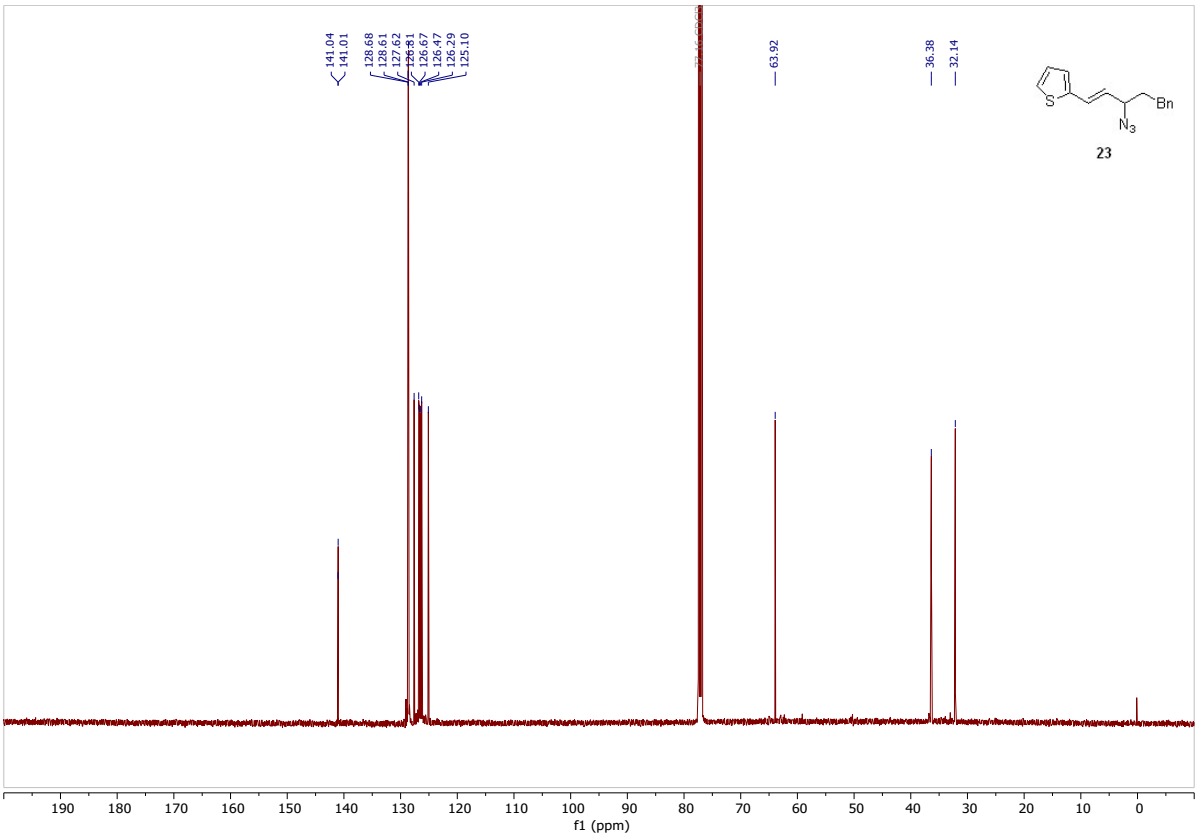


Compound 23

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

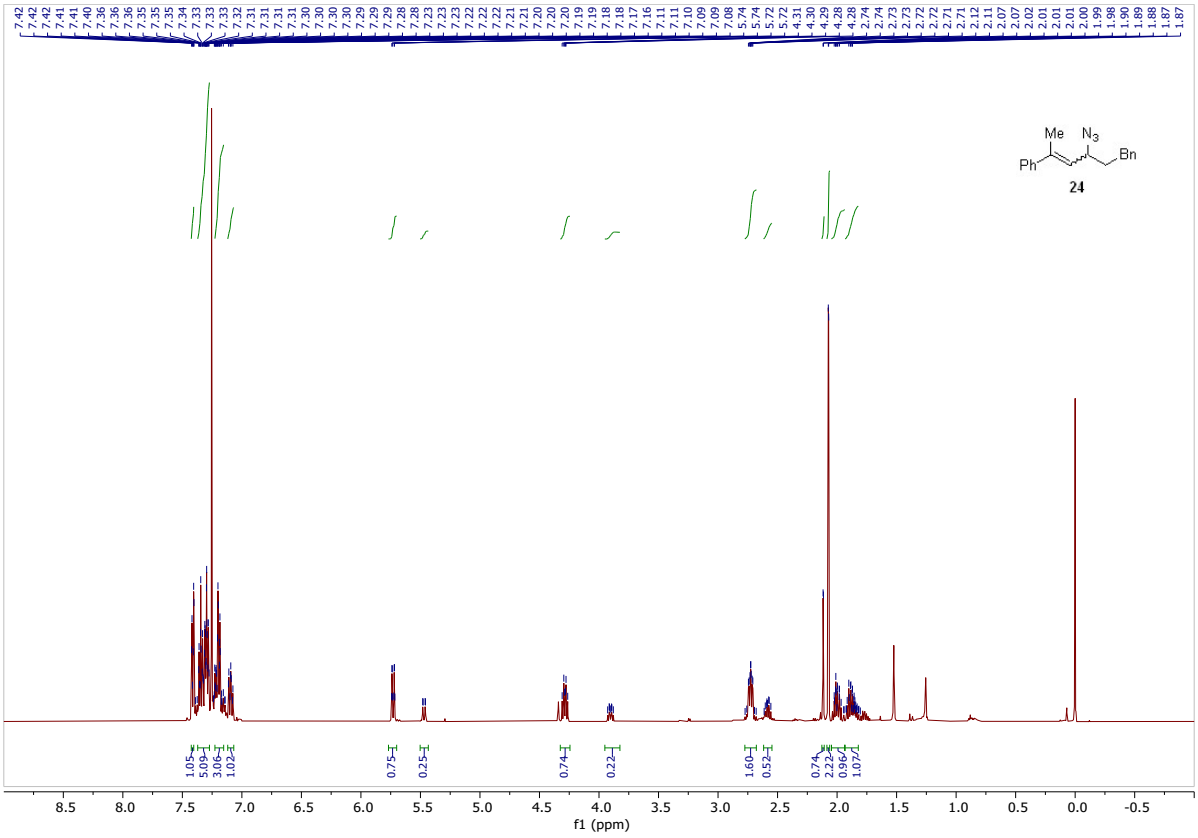


^{13}C NMR (126 MHz, $CDCl_3$)

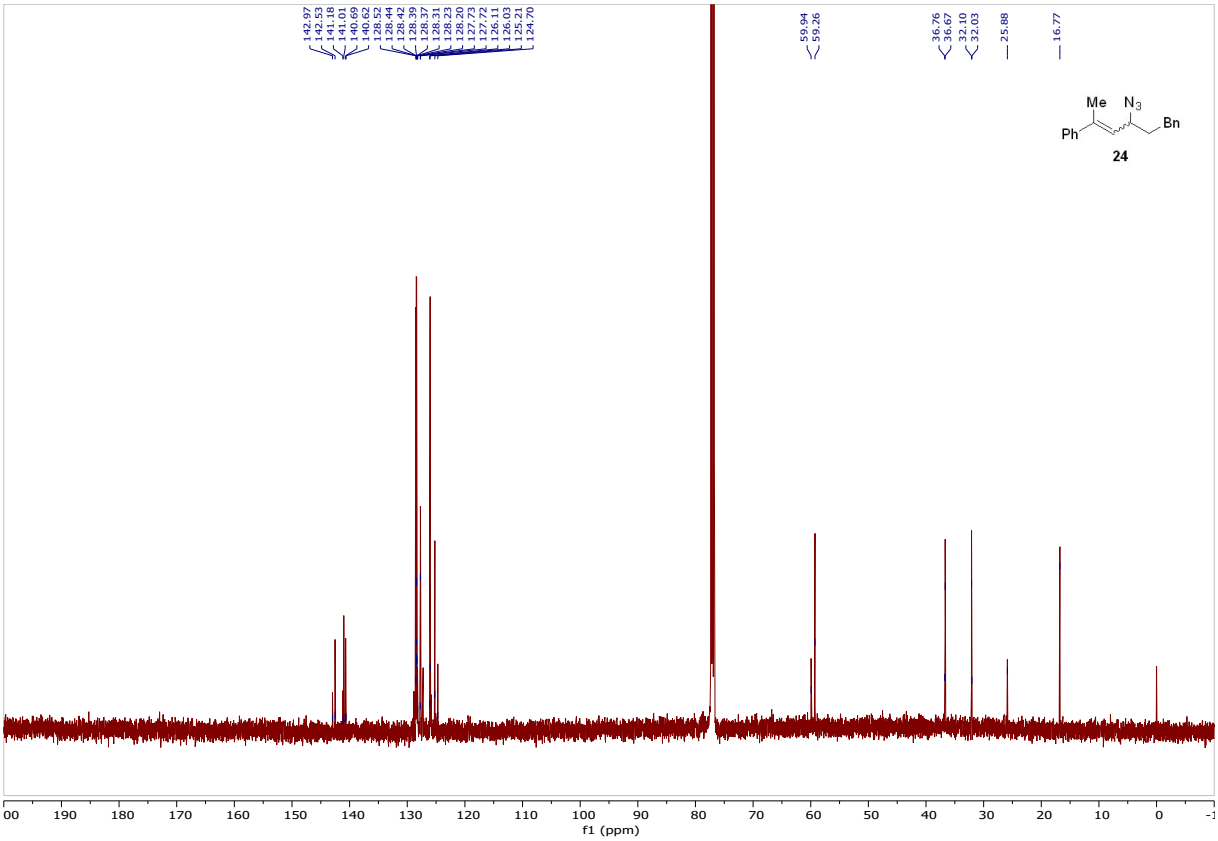


Compound 24

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

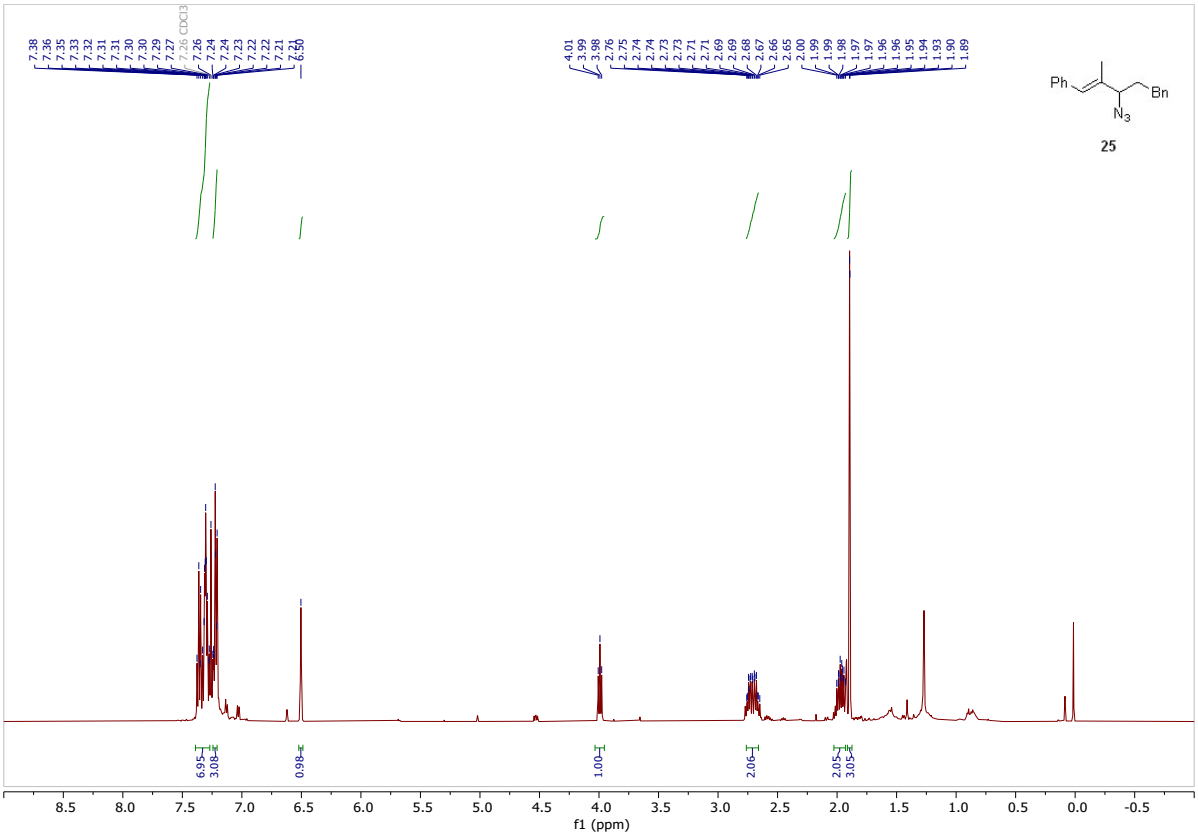


^{13}C NMR (126 MHz, $CDCl_3$)

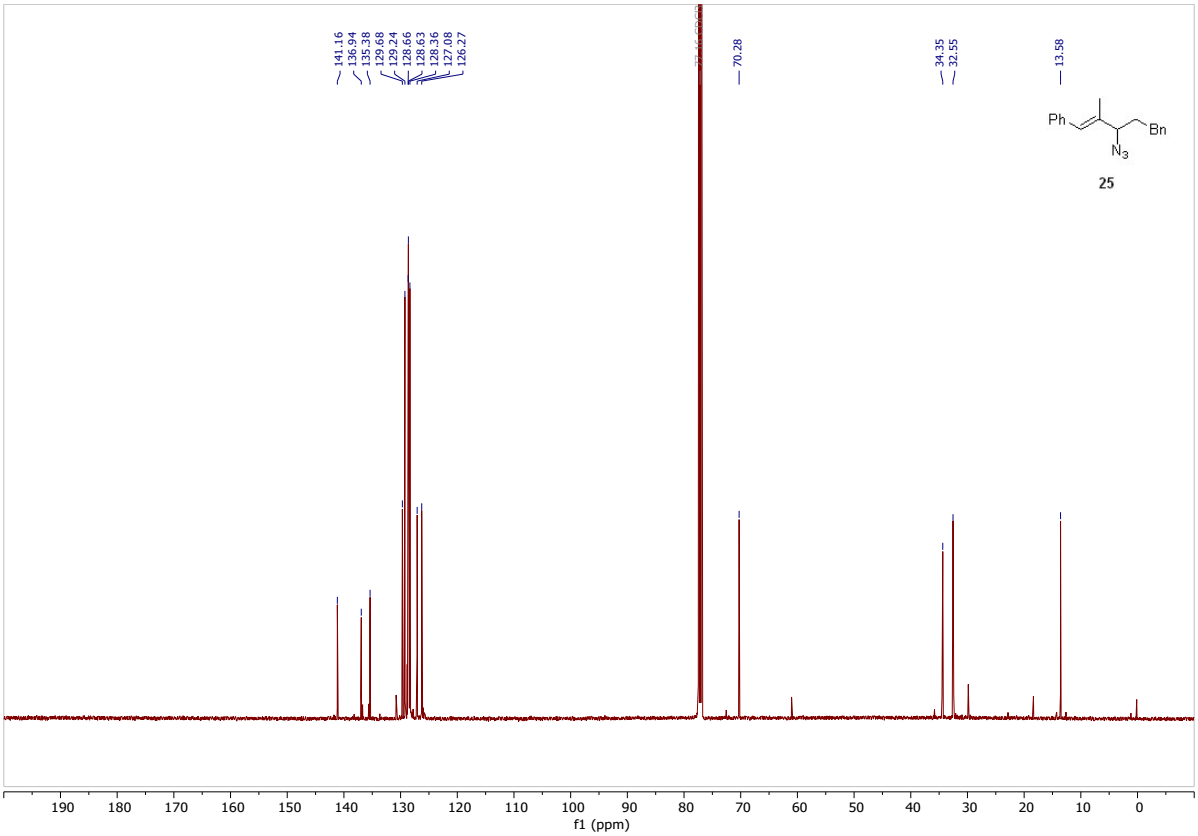


Compound 25

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

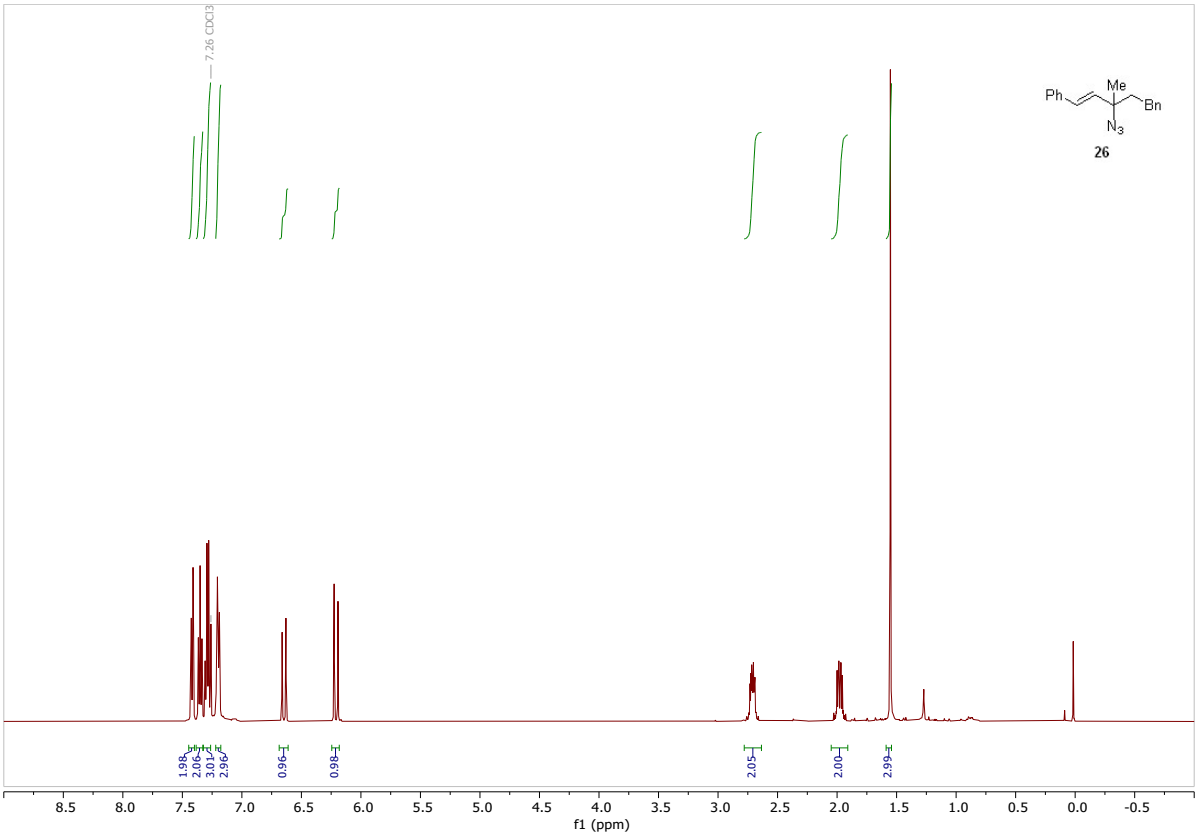


^{13}C NMR (126 MHz, $CDCl_3$)

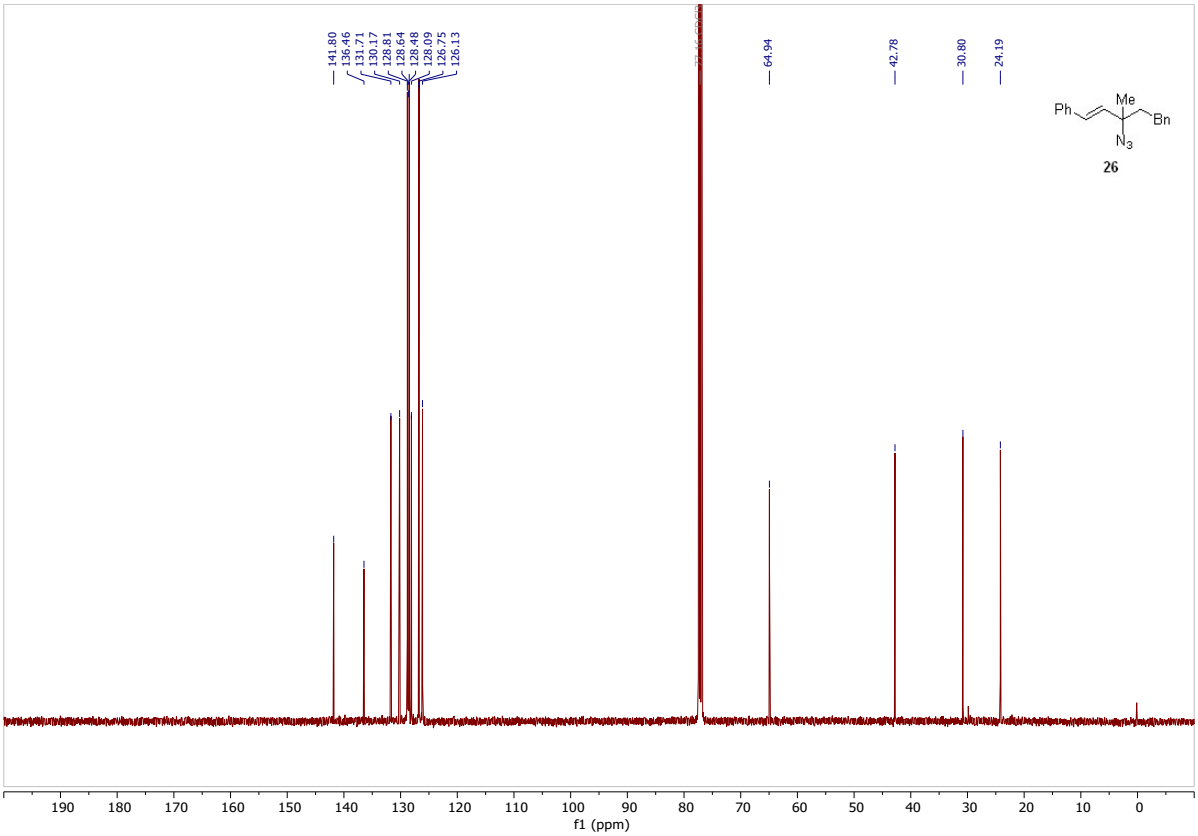


Compound 26

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

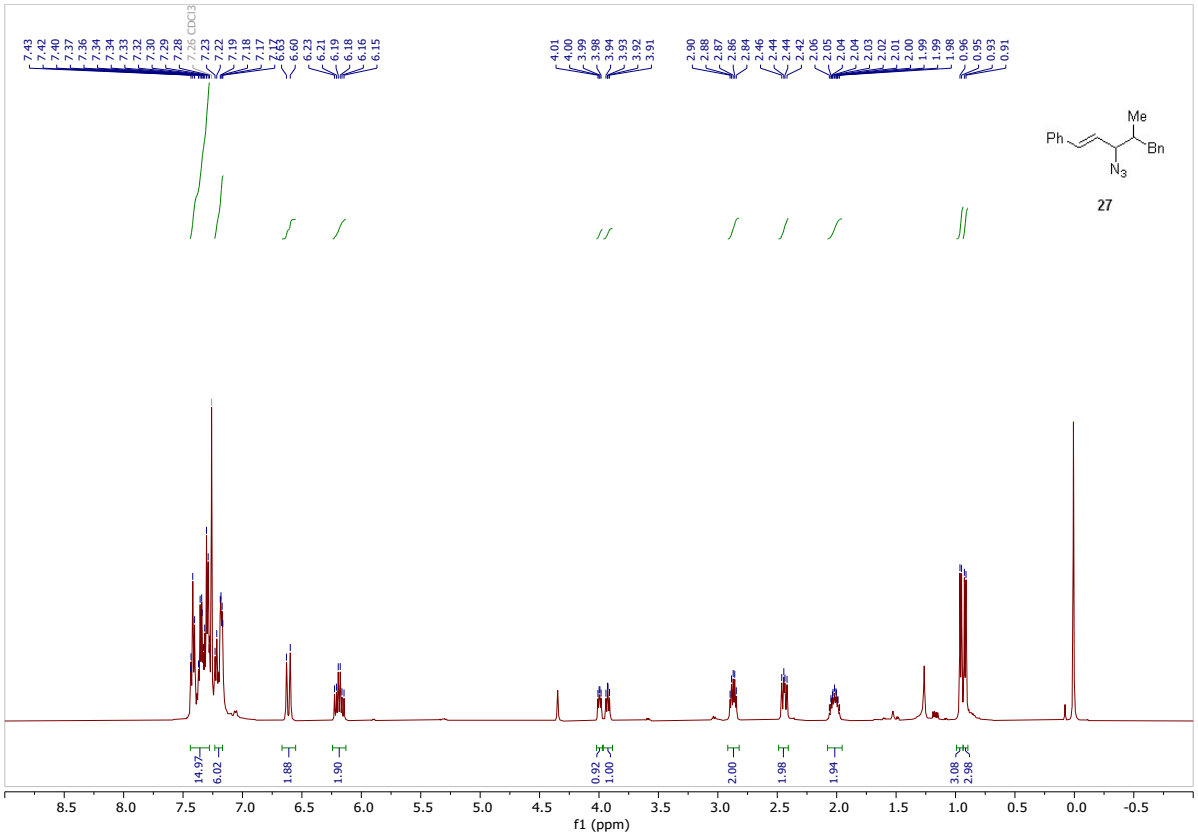


^{13}C NMR (126 MHz, $CDCl_3$)

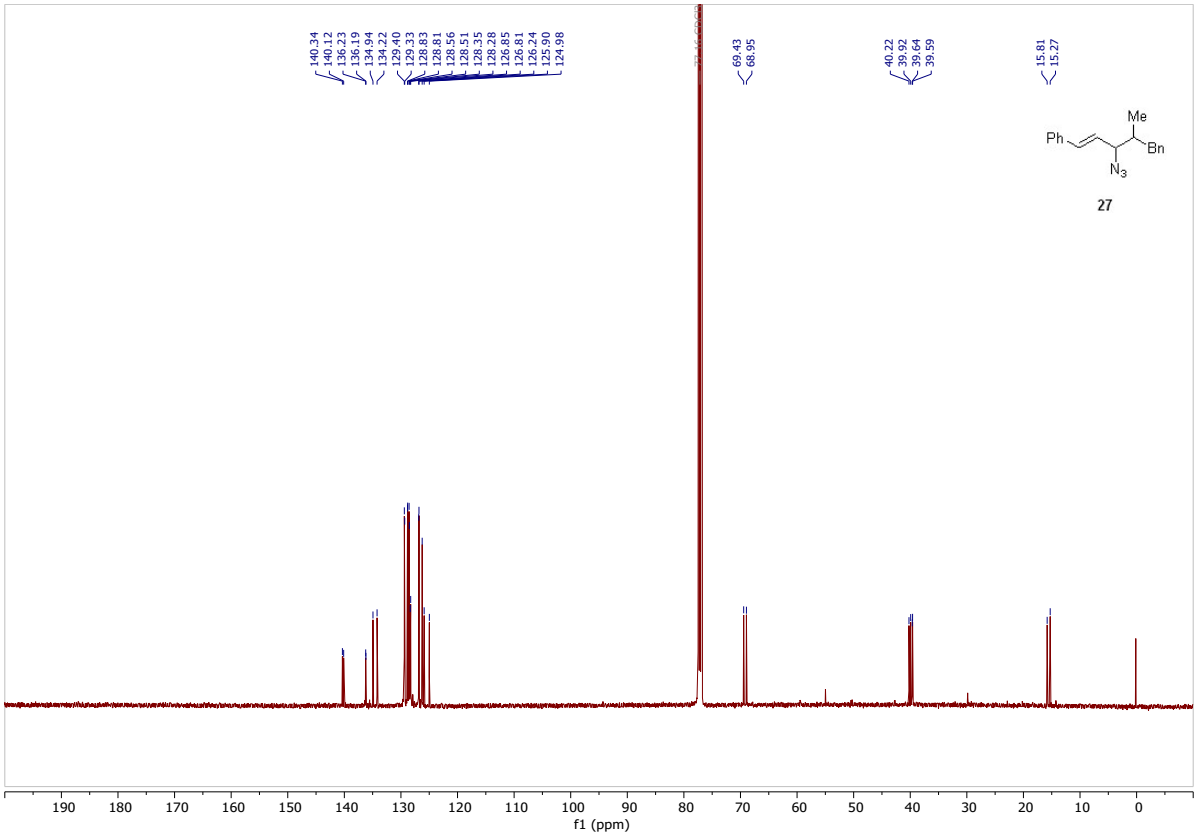


Compound 27

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

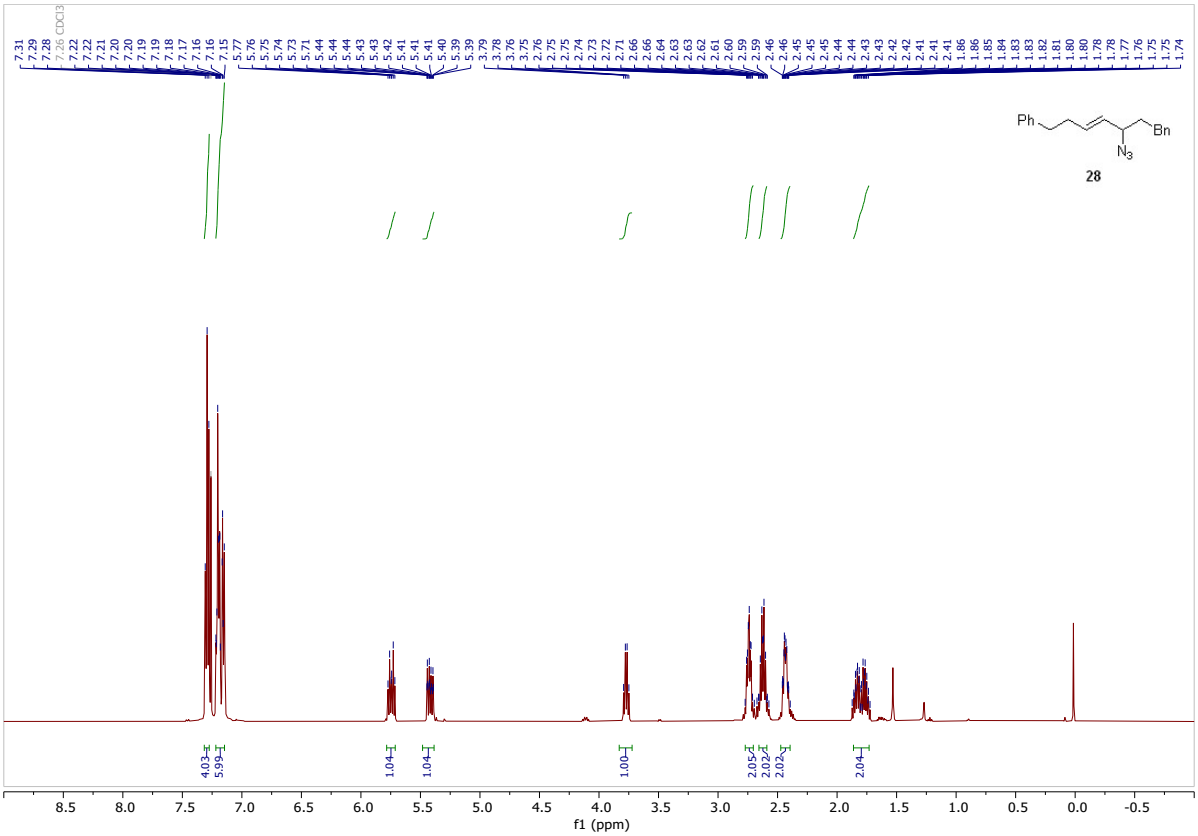


^{13}C NMR (126 MHz, $CDCl_3$)

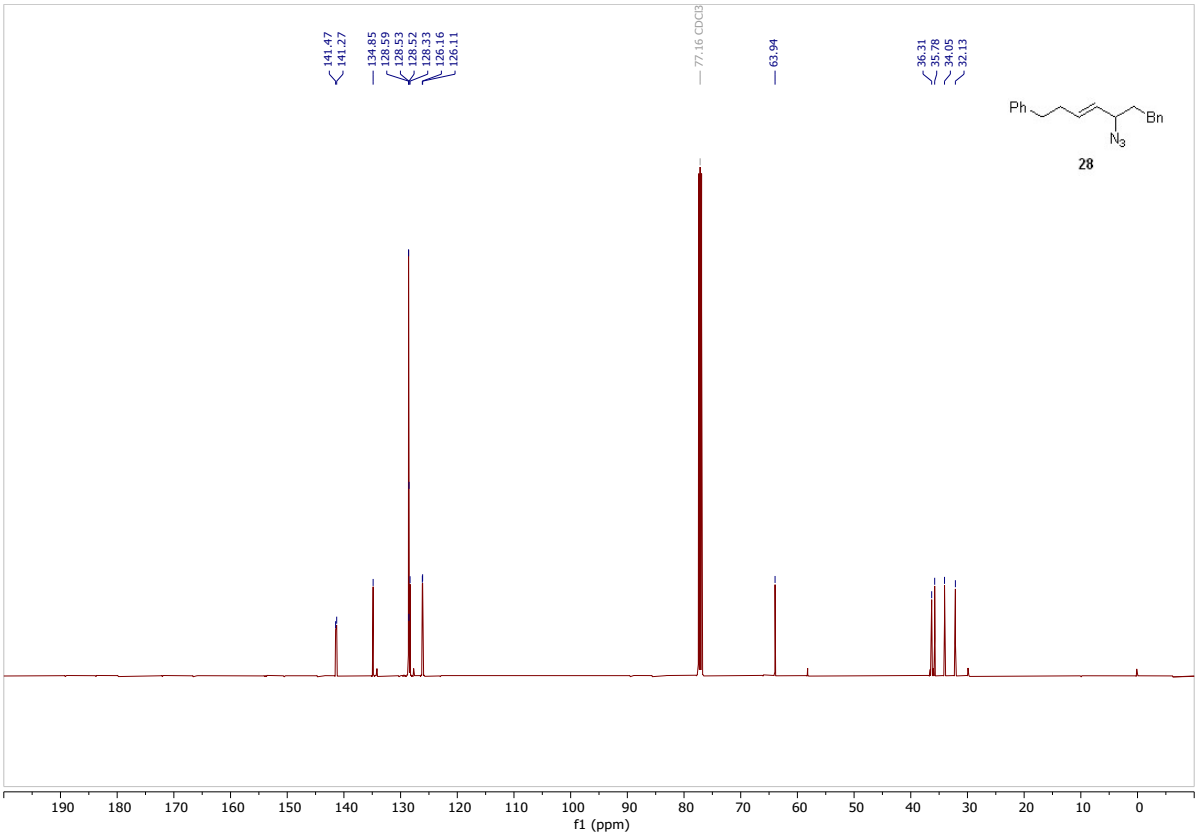


Compound 28

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

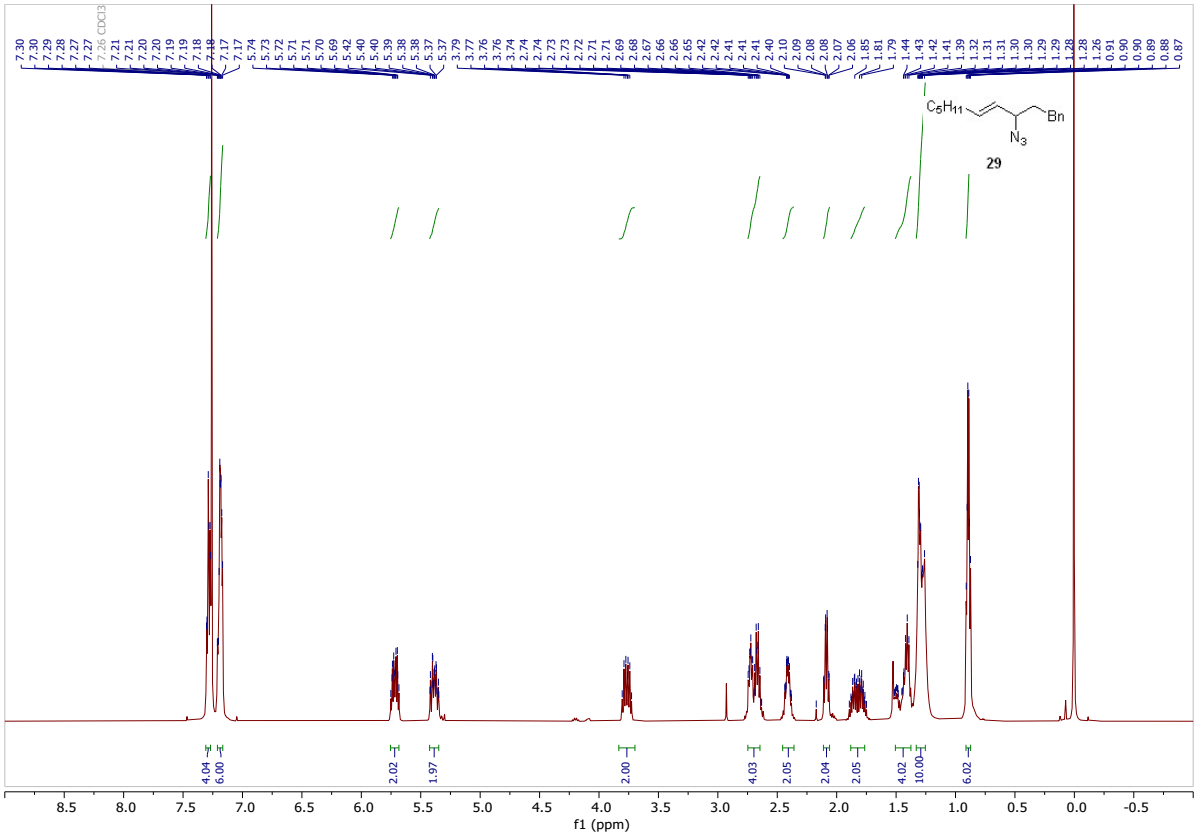


^{13}C NMR (126 MHz, $CDCl_3$)

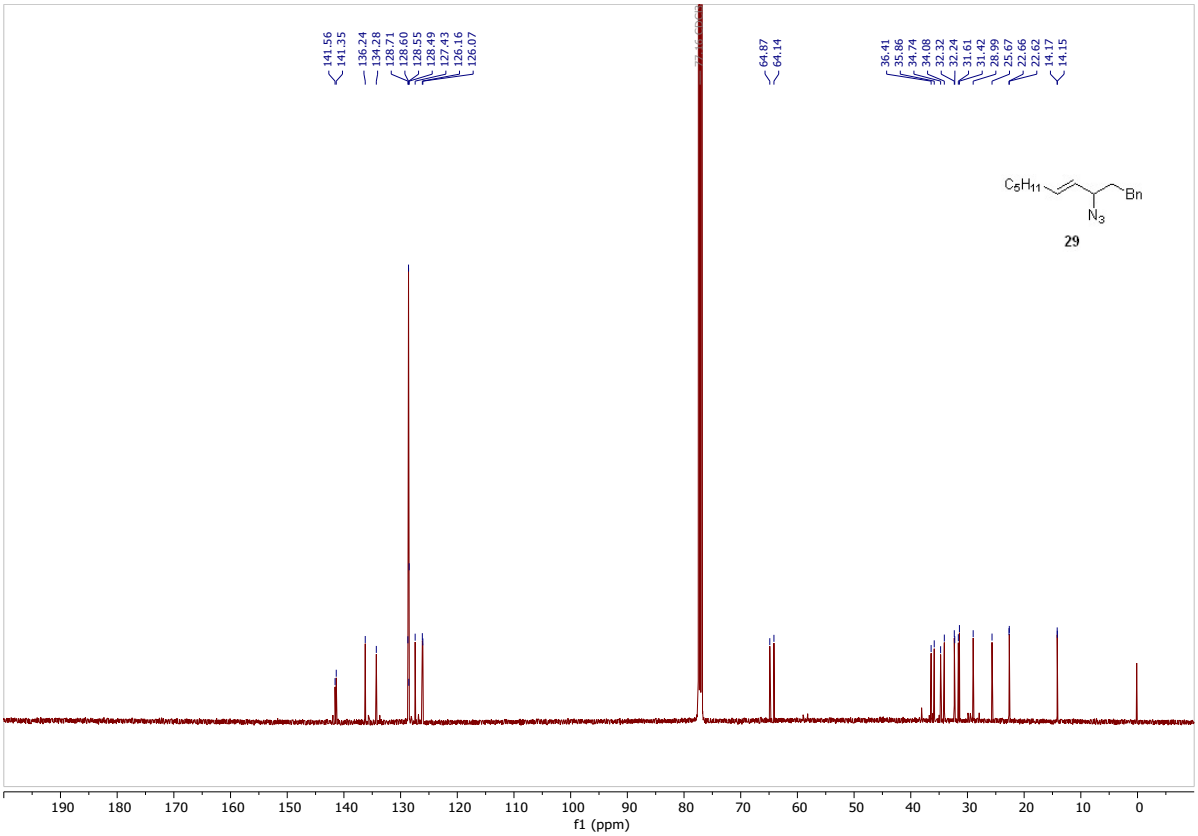


Compound 29

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

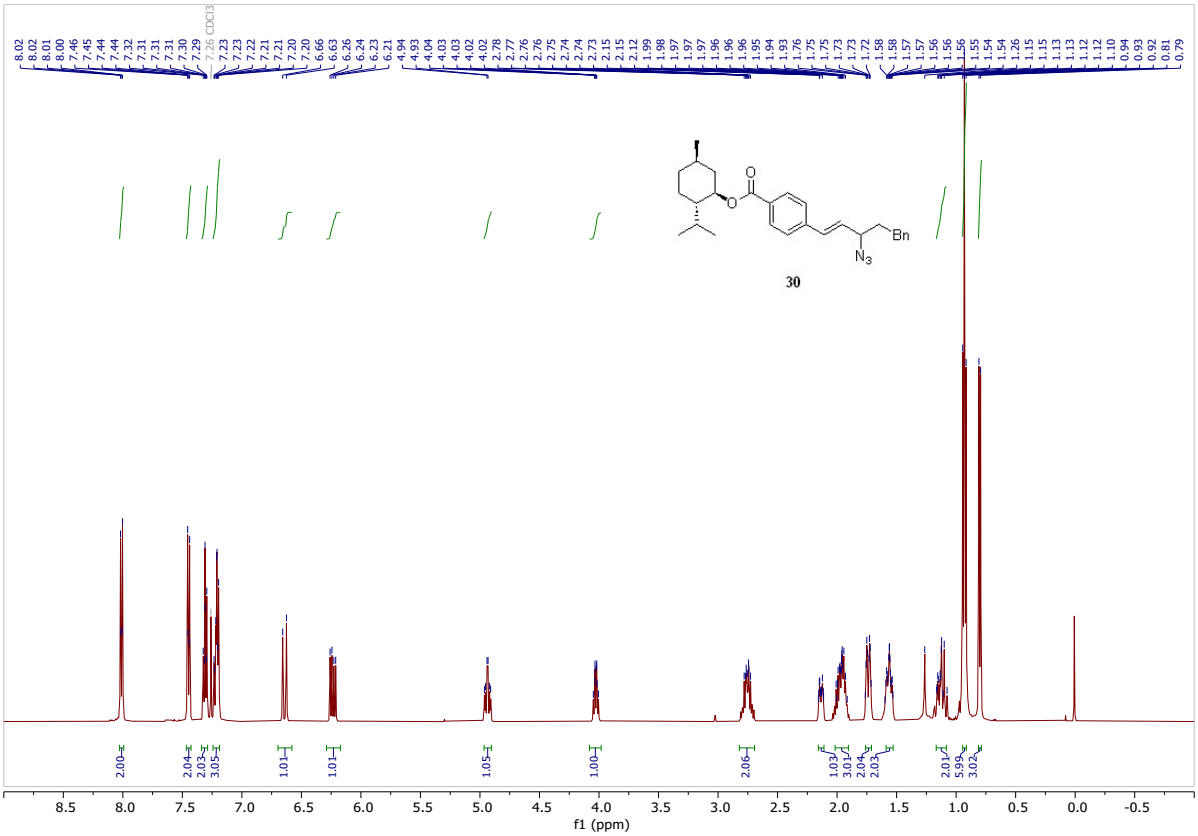


^{13}C NMR (126 MHz, $CDCl_3$)

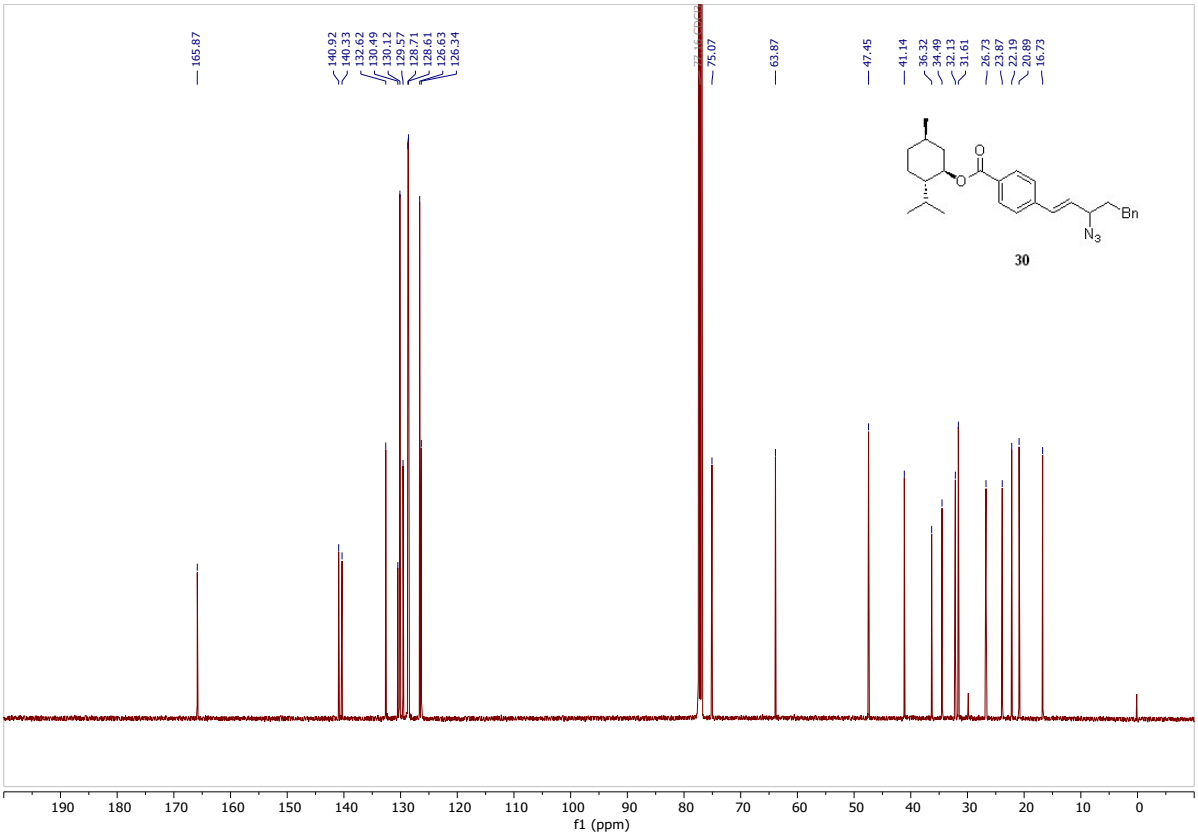


Compound 30

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

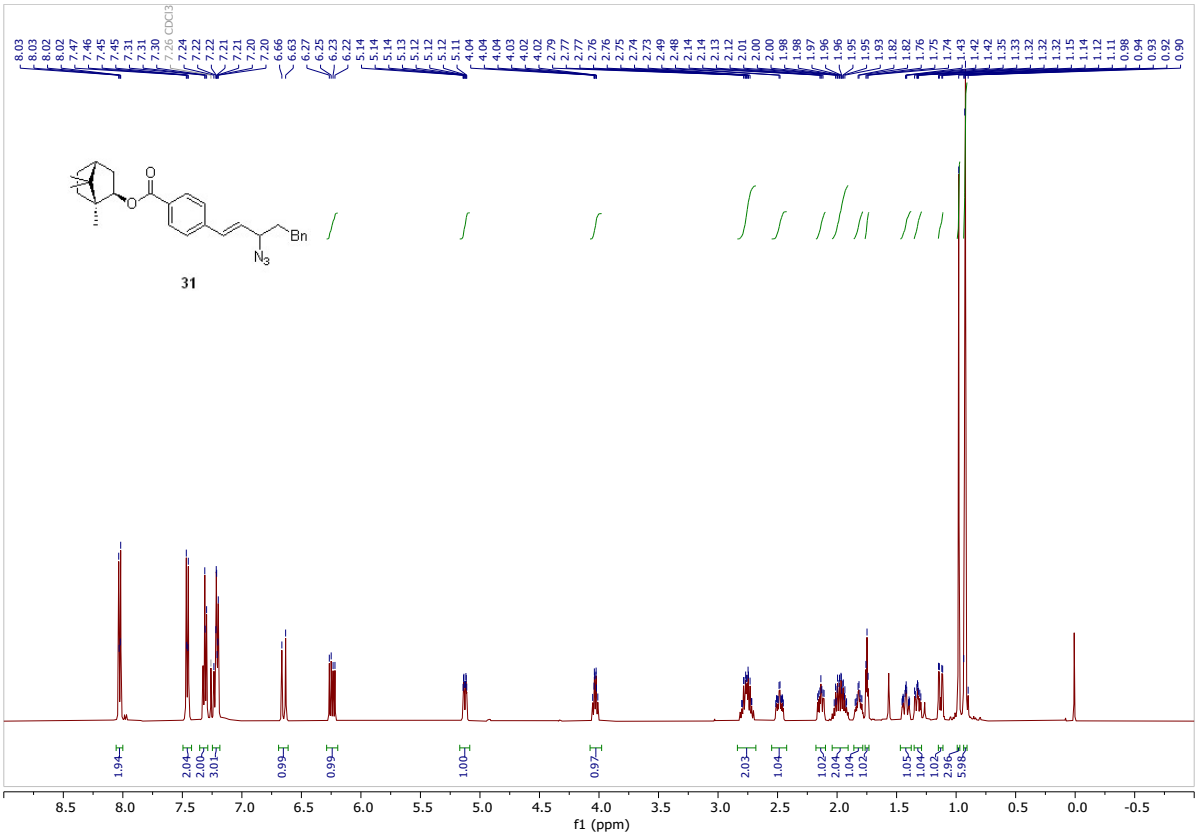


^{13}C NMR (126 MHz, $CDCl_3$)

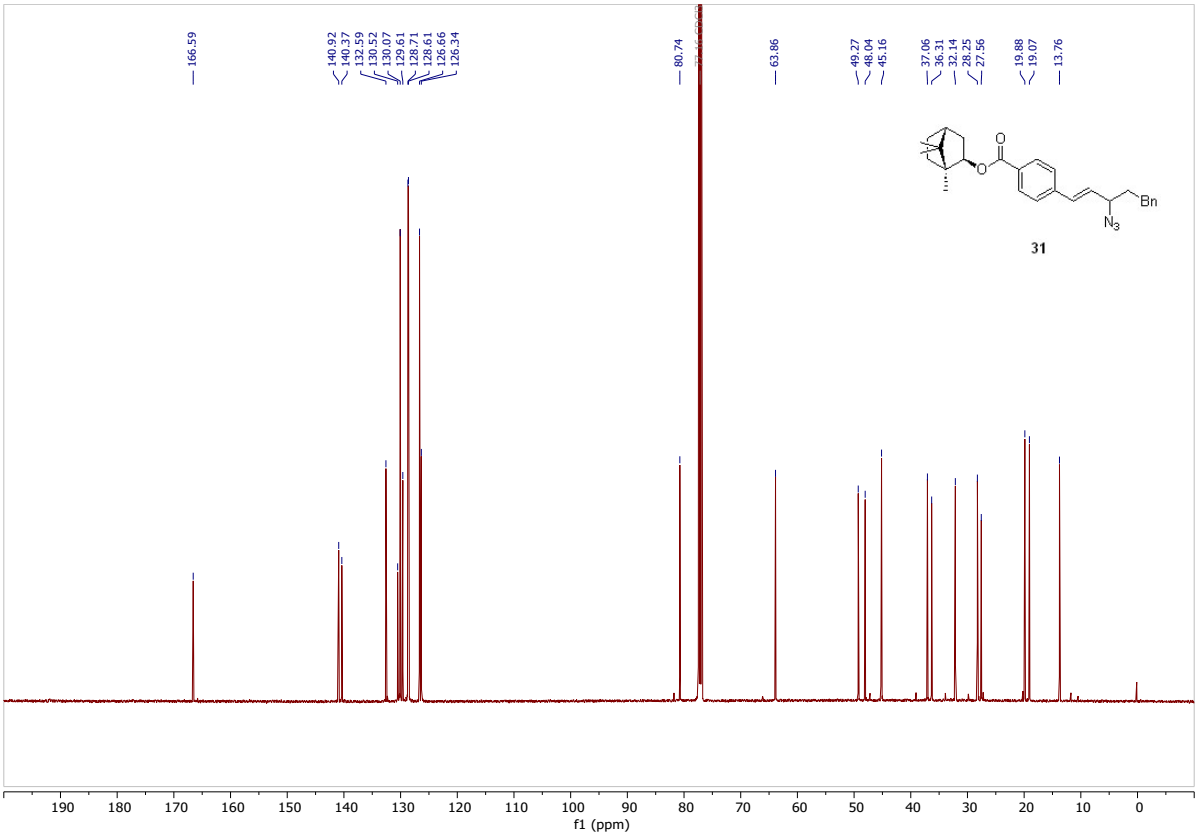


Compound 31

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

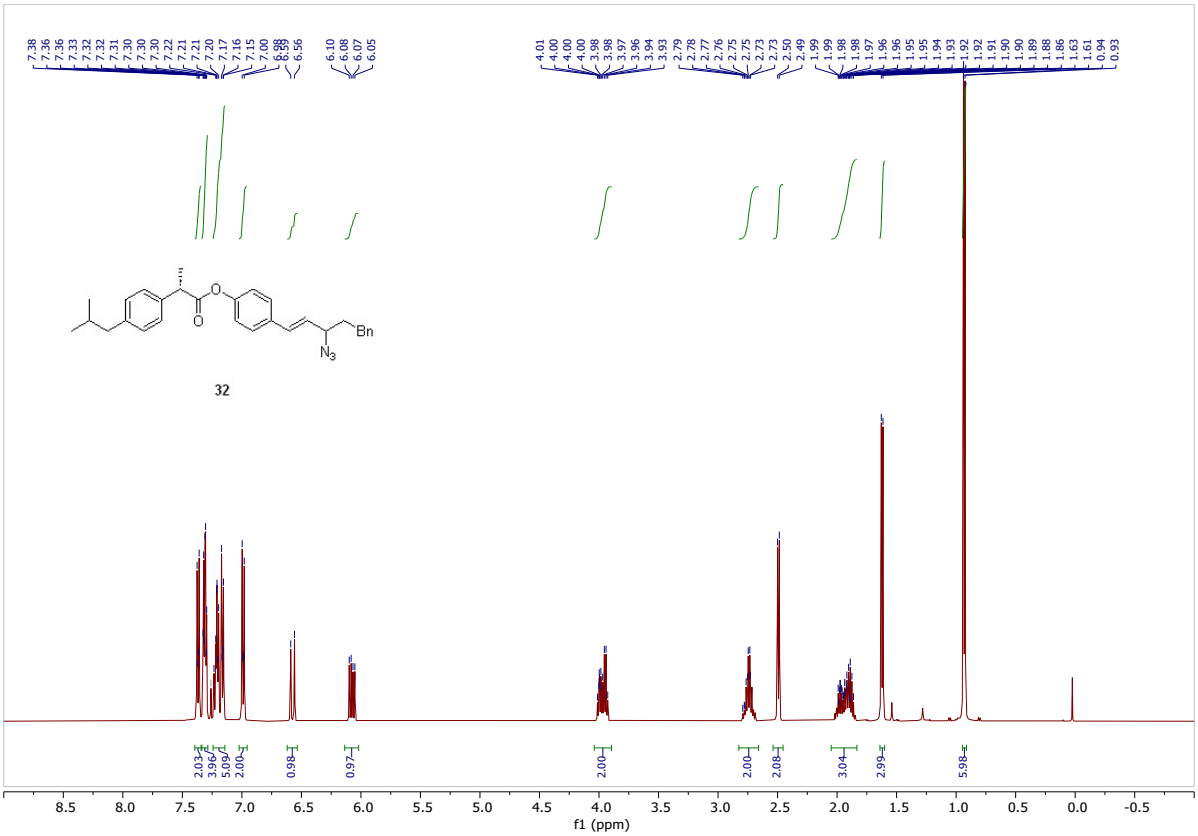


^{13}C NMR (126 MHz, $CDCl_3$)

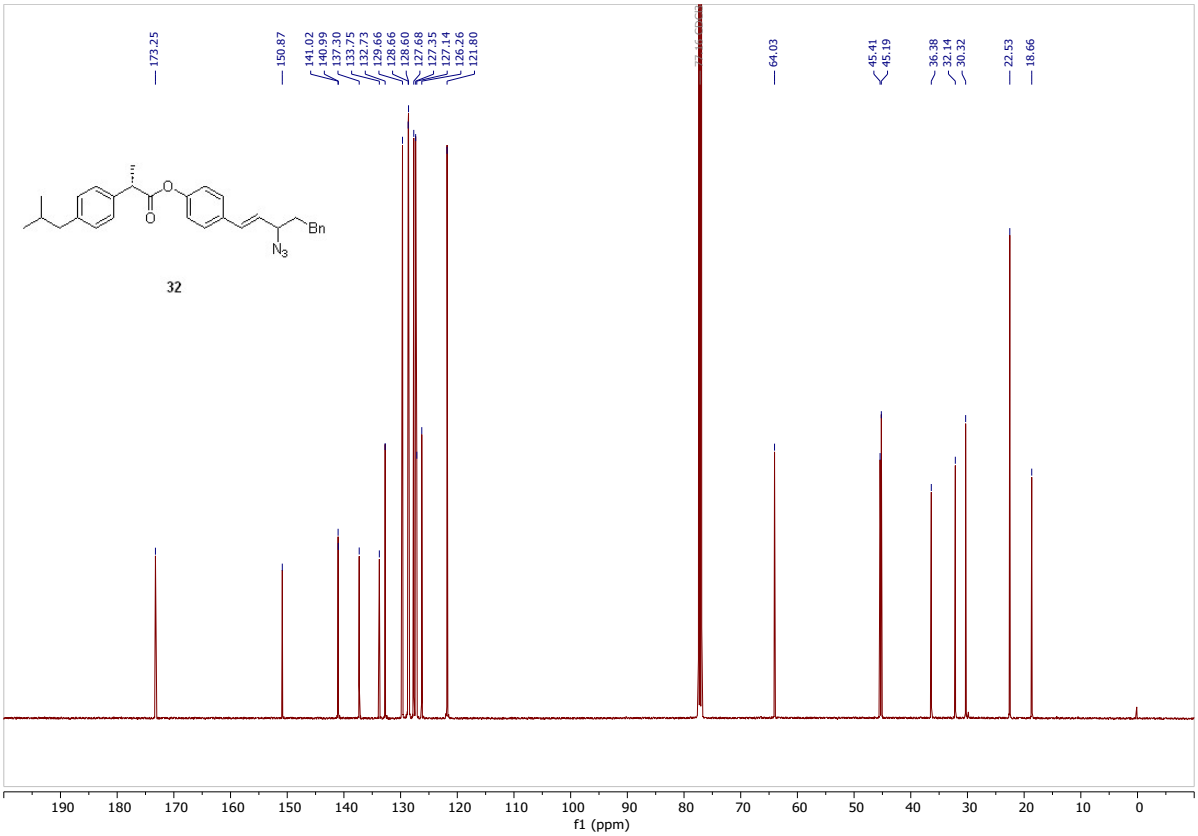


Compound 32

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

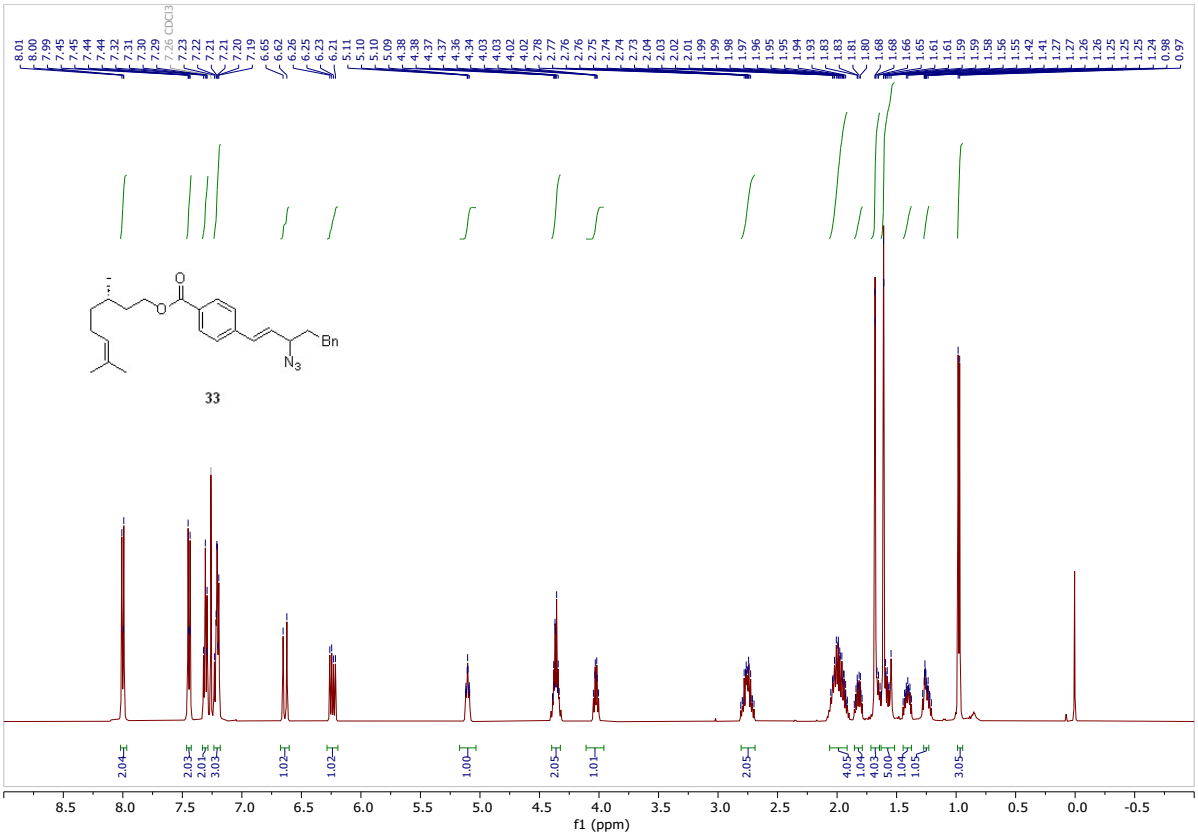


^{13}C NMR (126 MHz, $CDCl_3$)

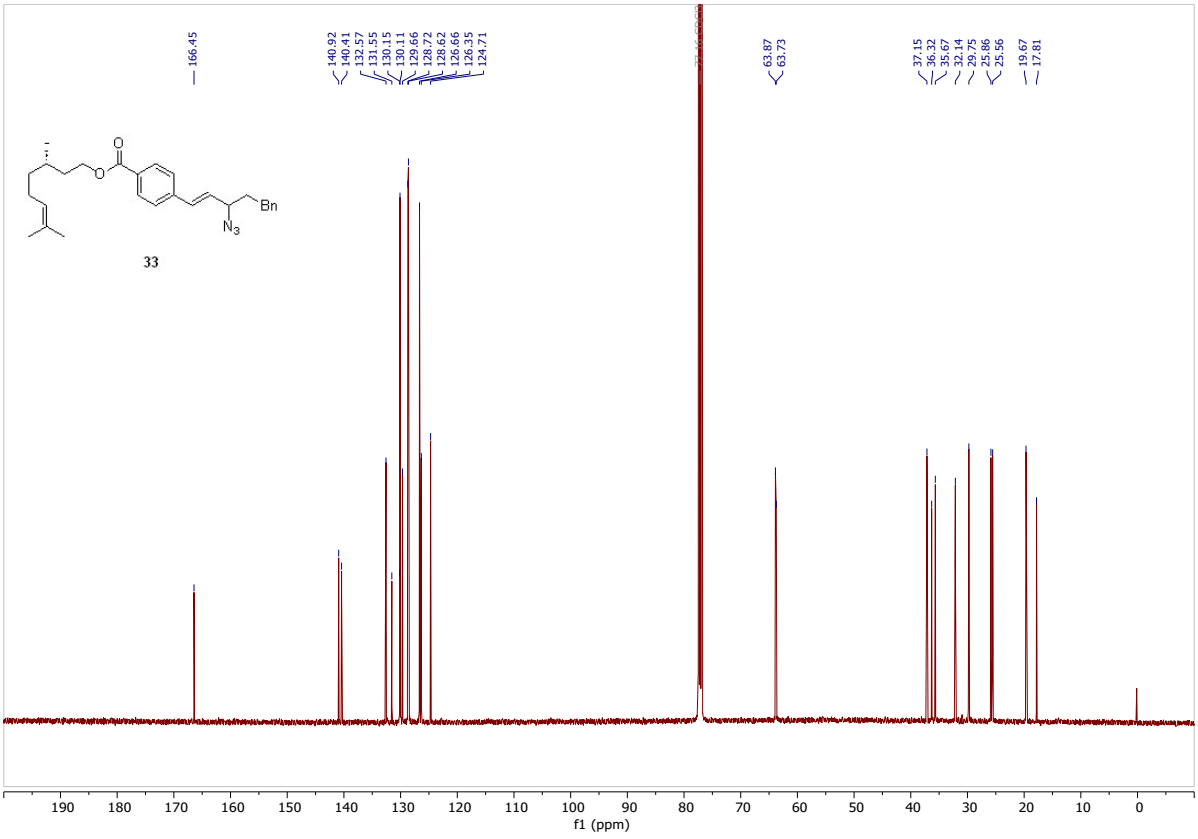


Compound 33

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

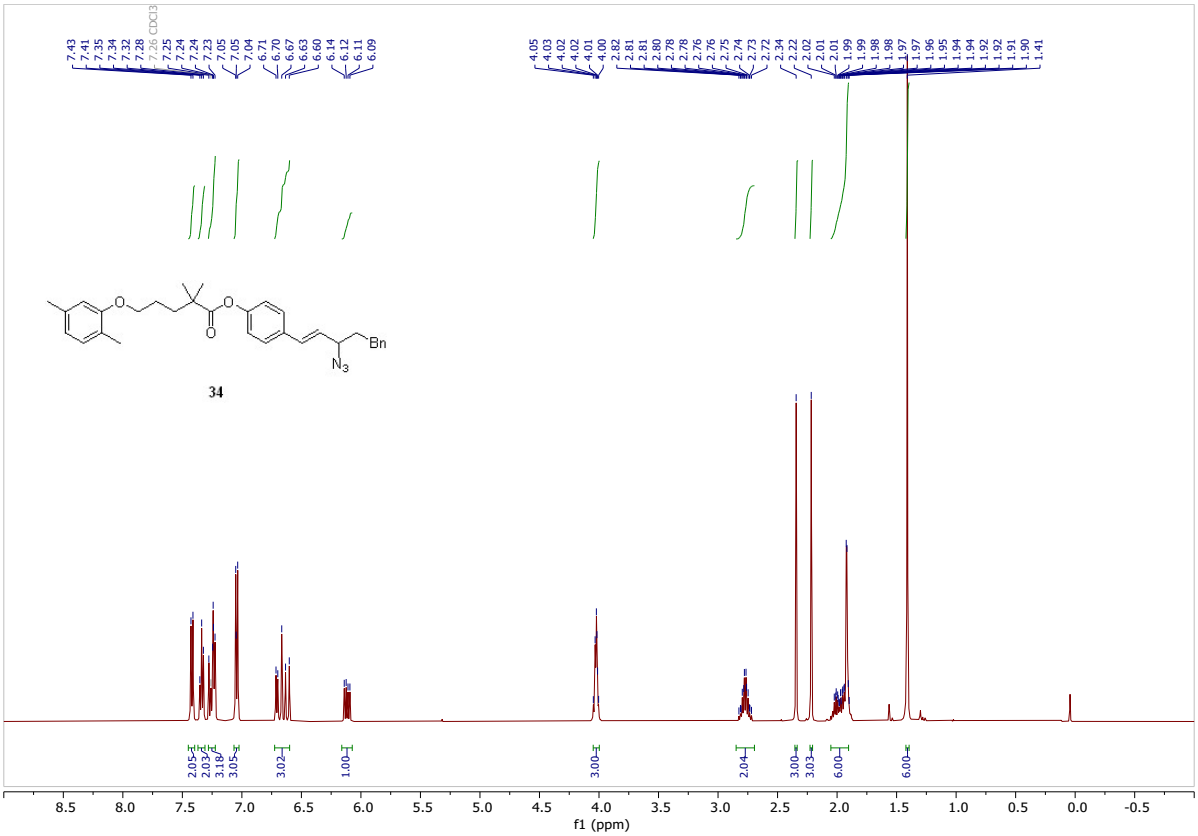


^{13}C NMR (126 MHz, $CDCl_3$)

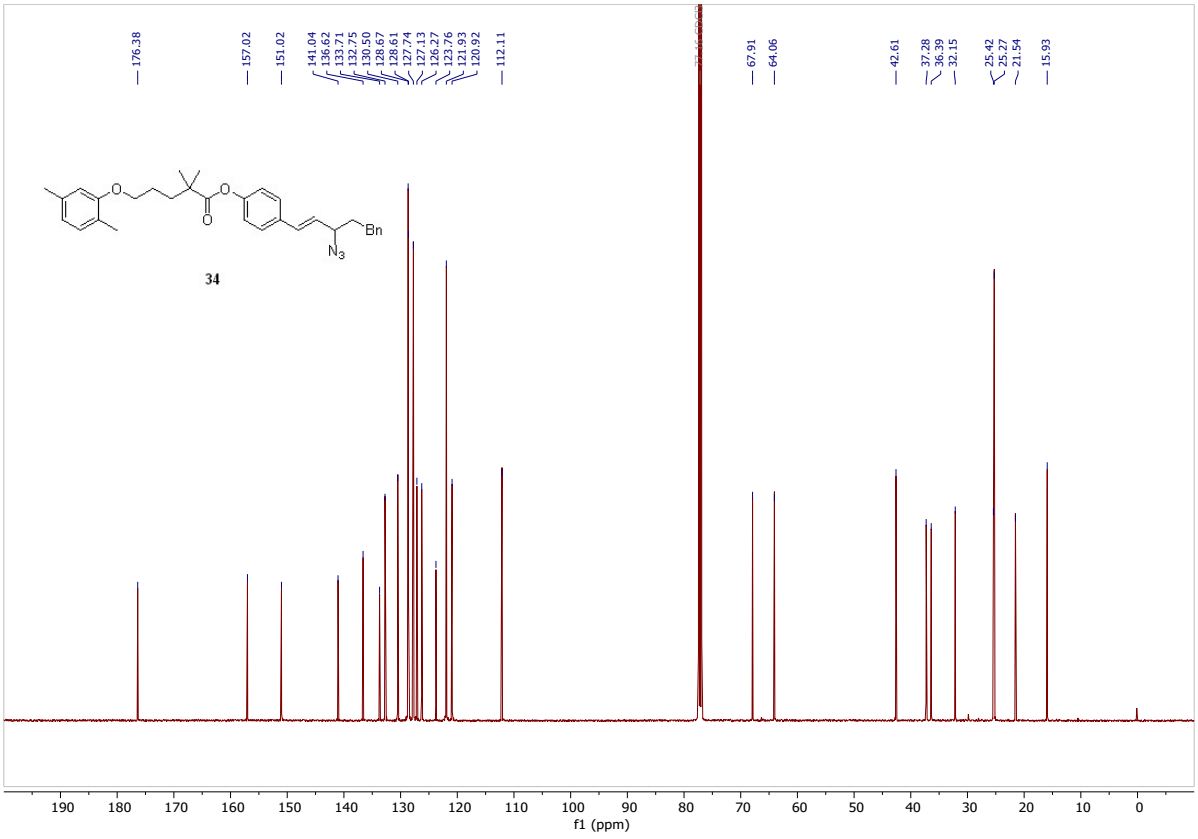


Compound 34

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

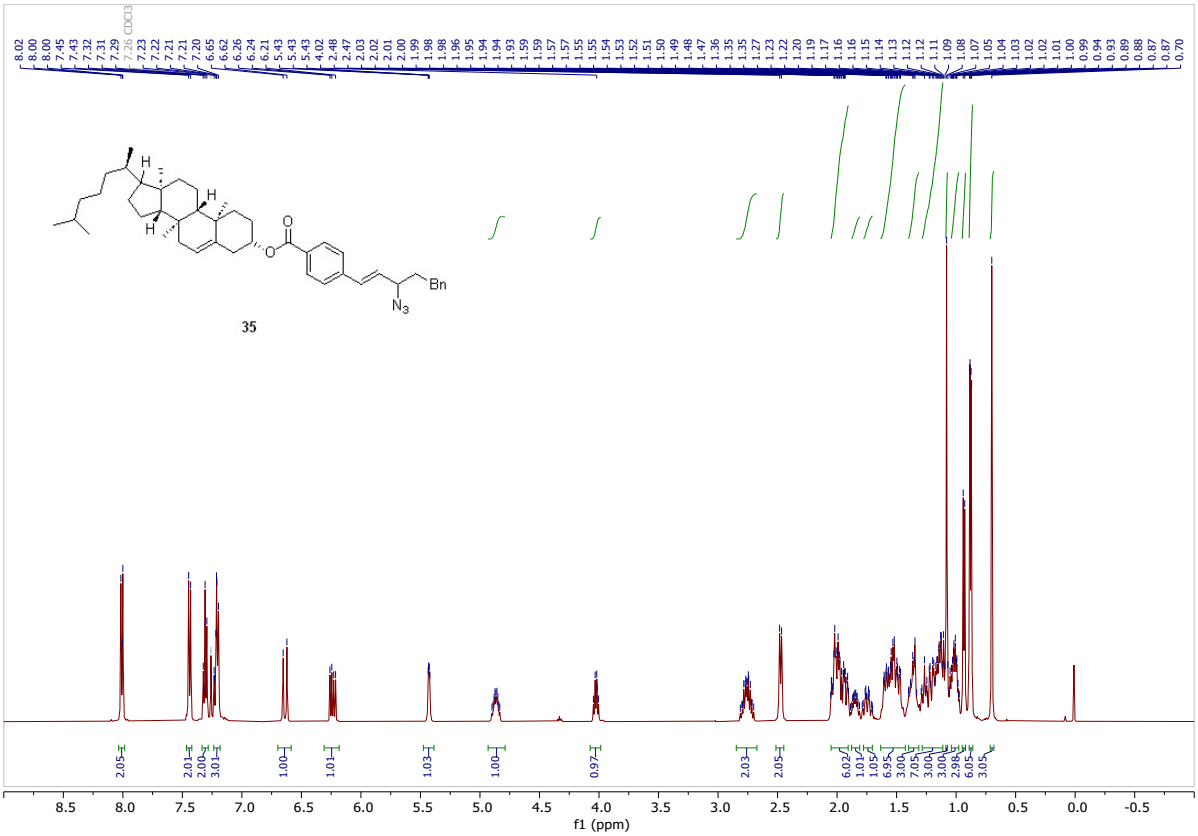


^{13}C NMR (126 MHz, $CDCl_3$)

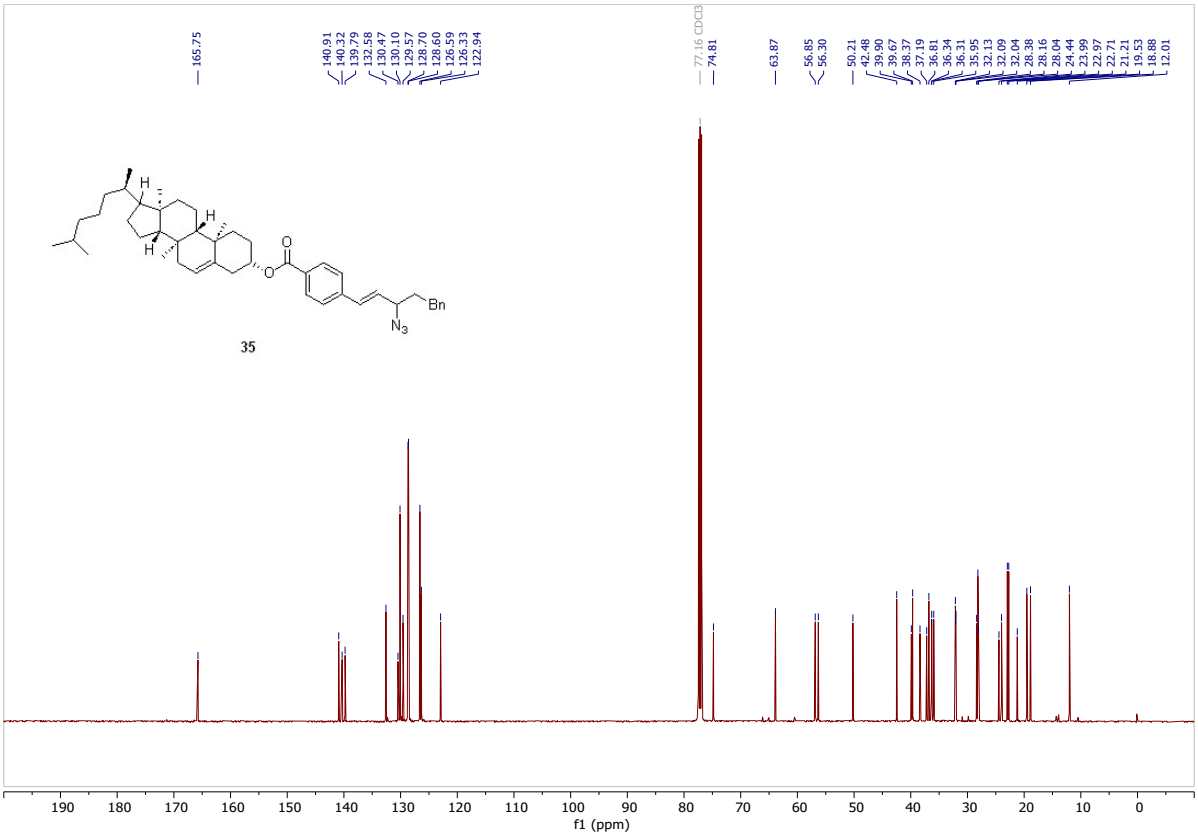


Compound 35

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

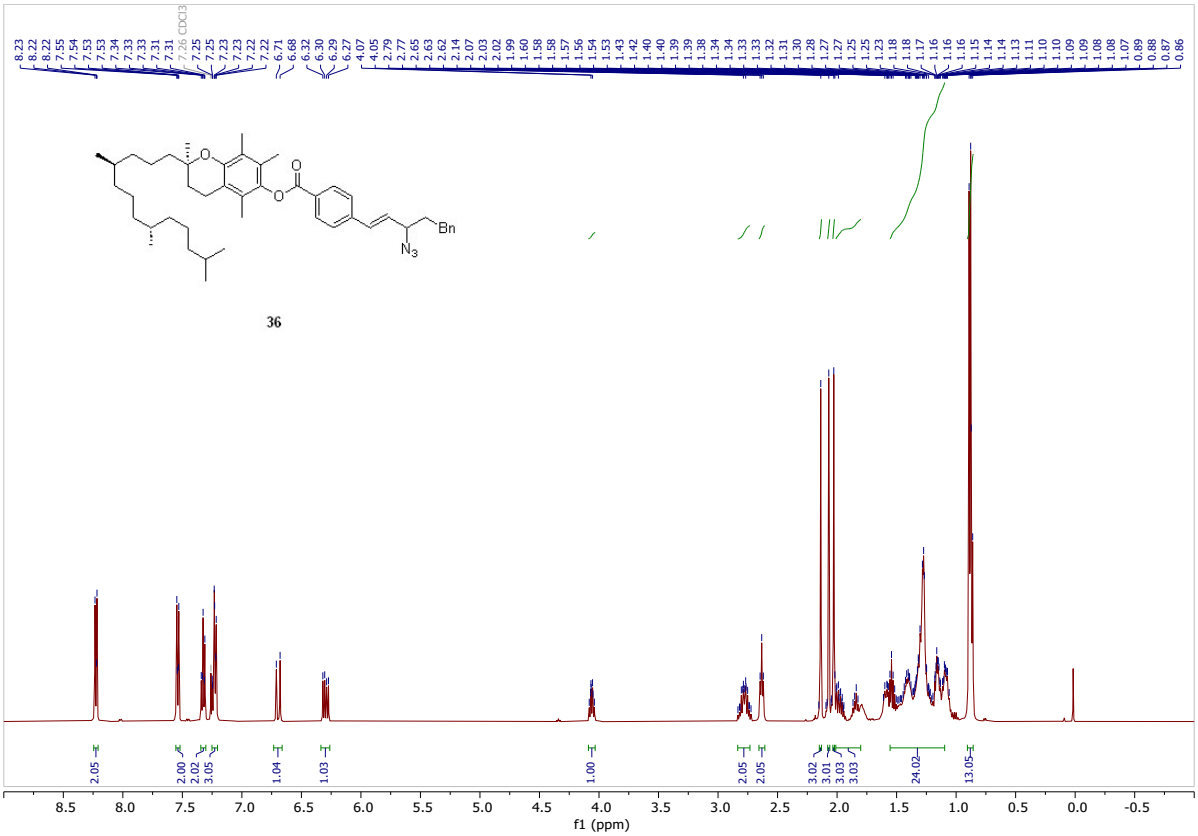


^{13}C NMR (126 MHz, $CDCl_3$)

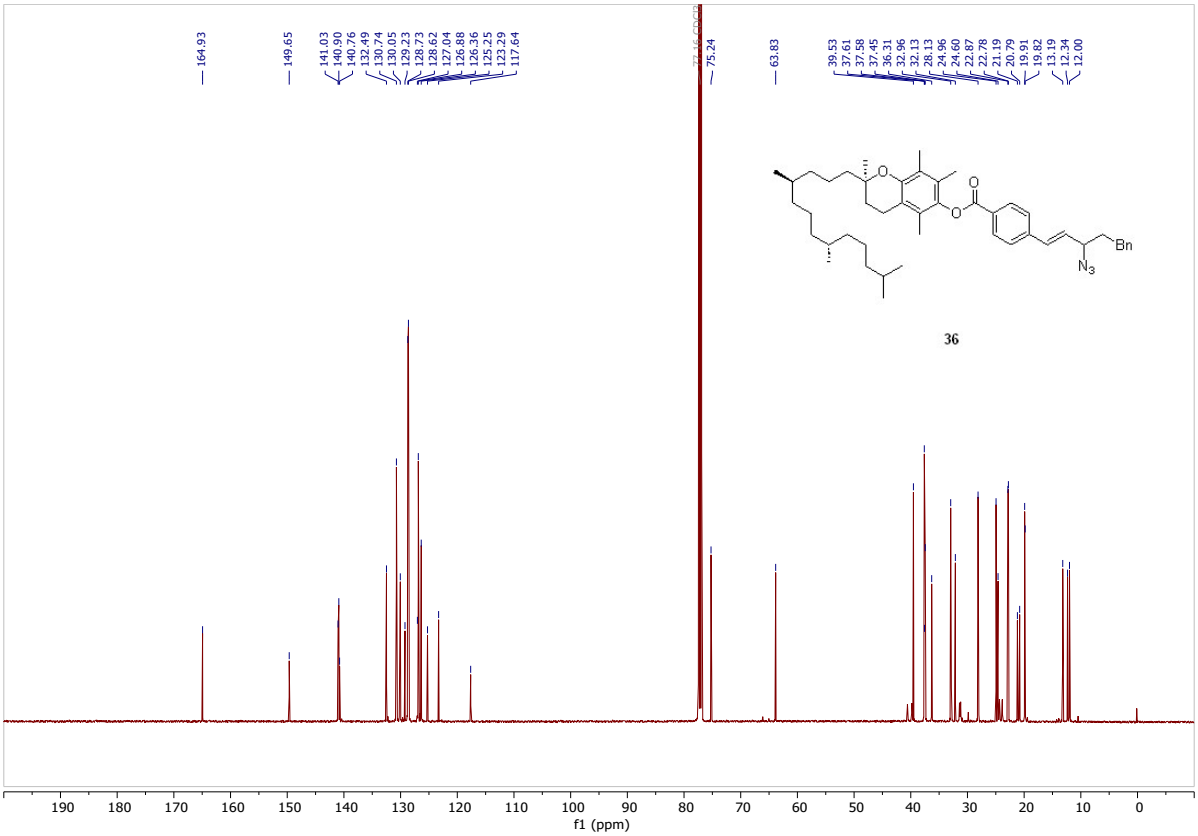


Compound 36

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

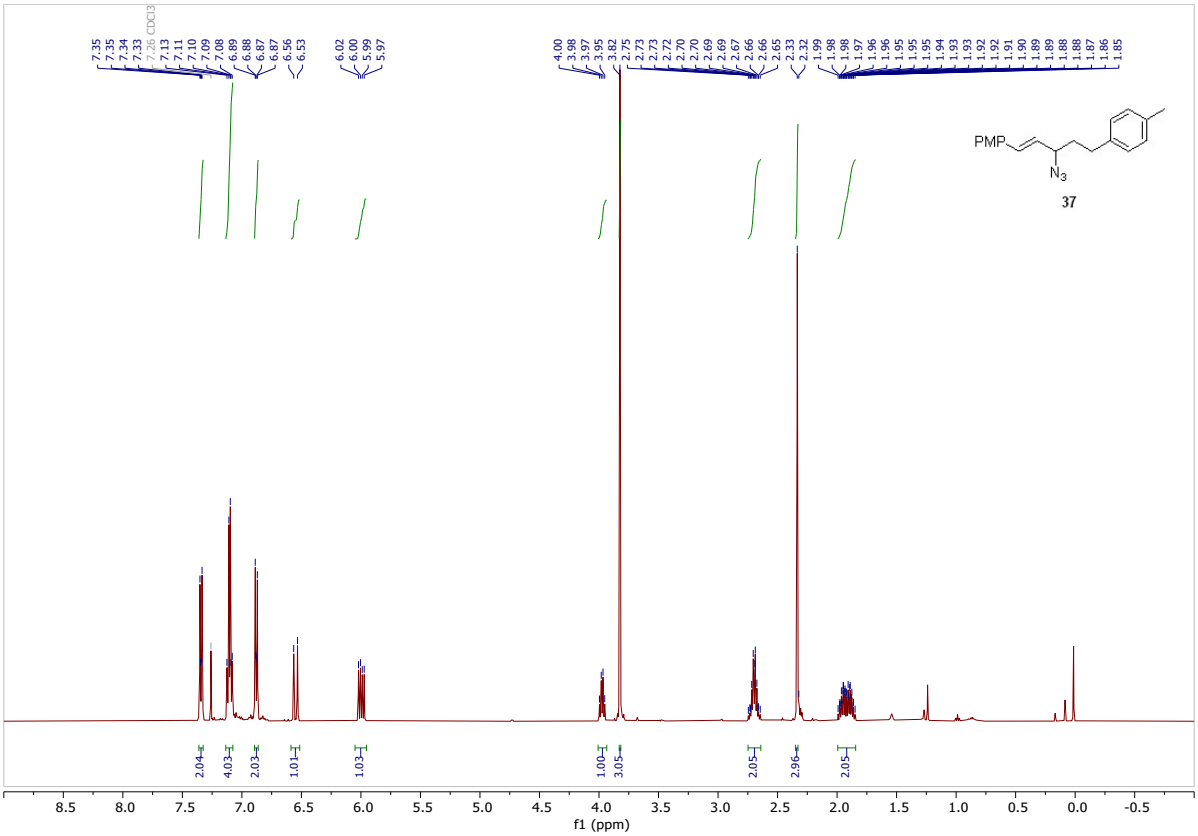


^{13}C NMR (126 MHz, $CDCl_3$)

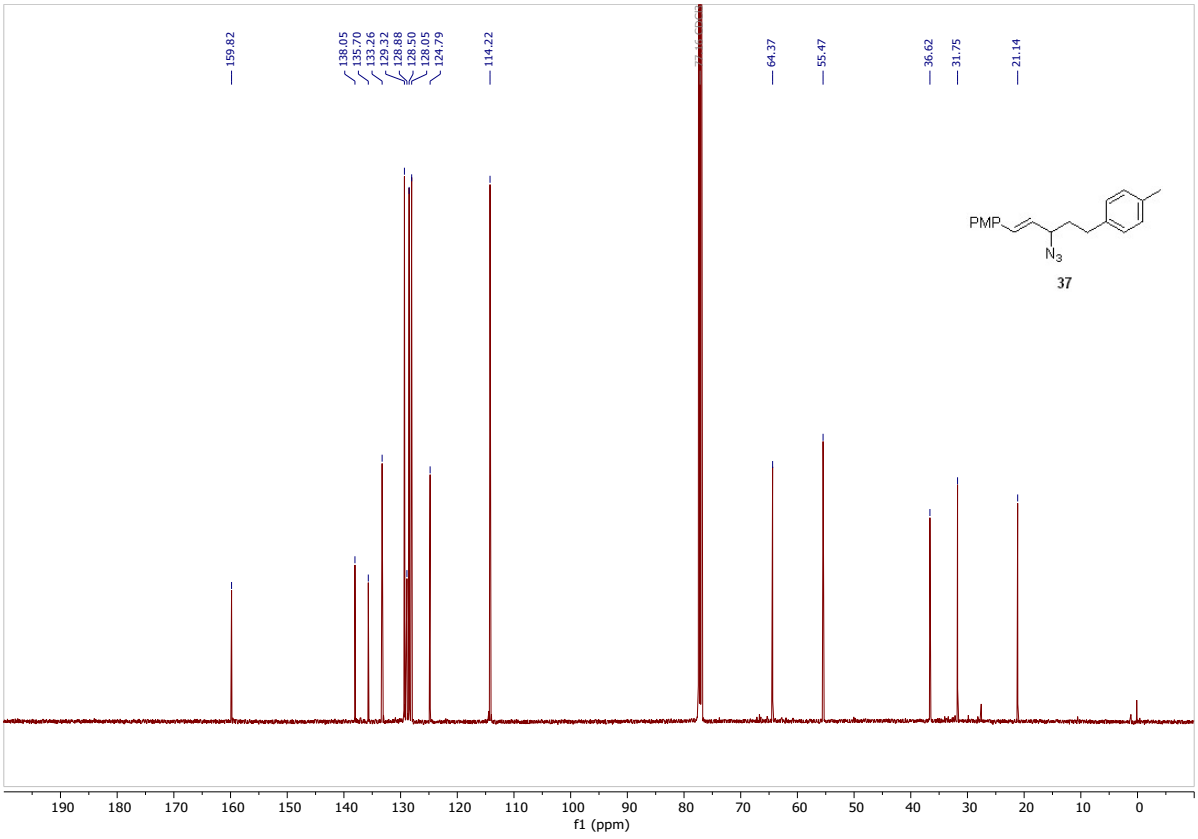


Compound 37

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

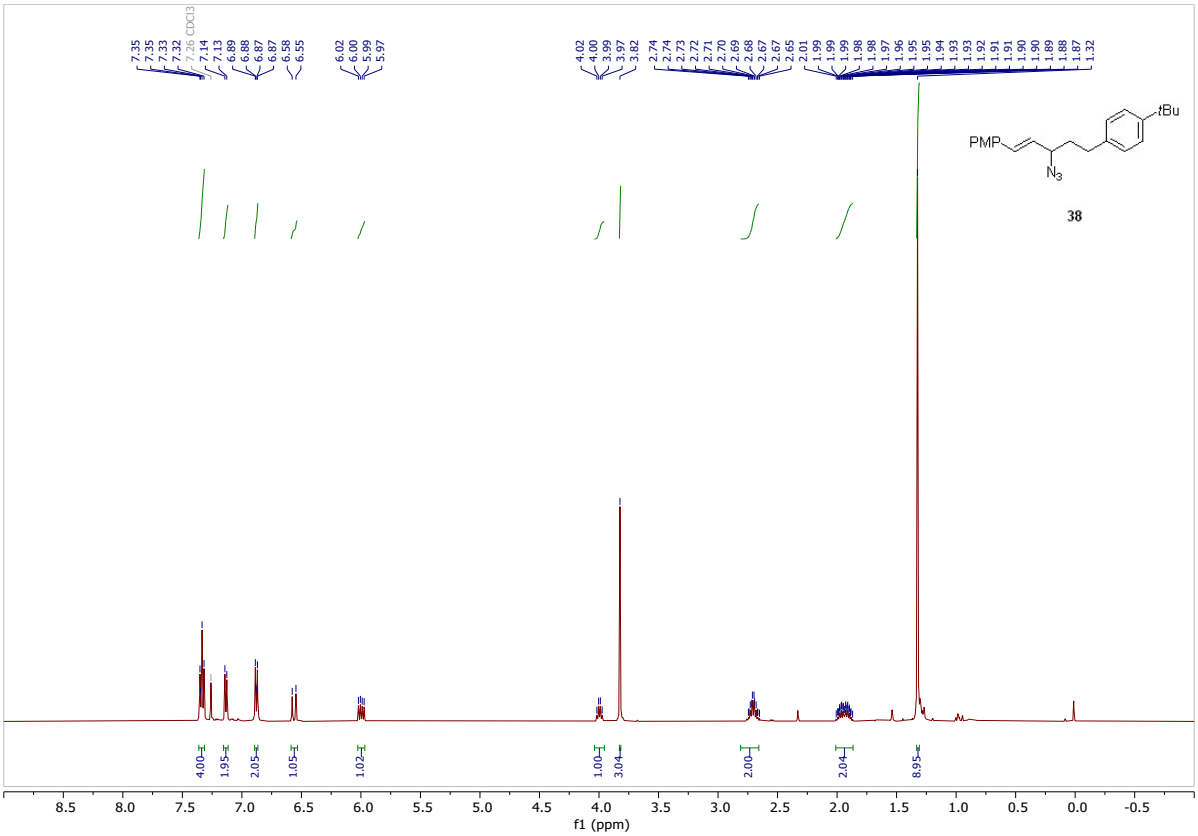


^{13}C NMR (126 MHz, $CDCl_3$)

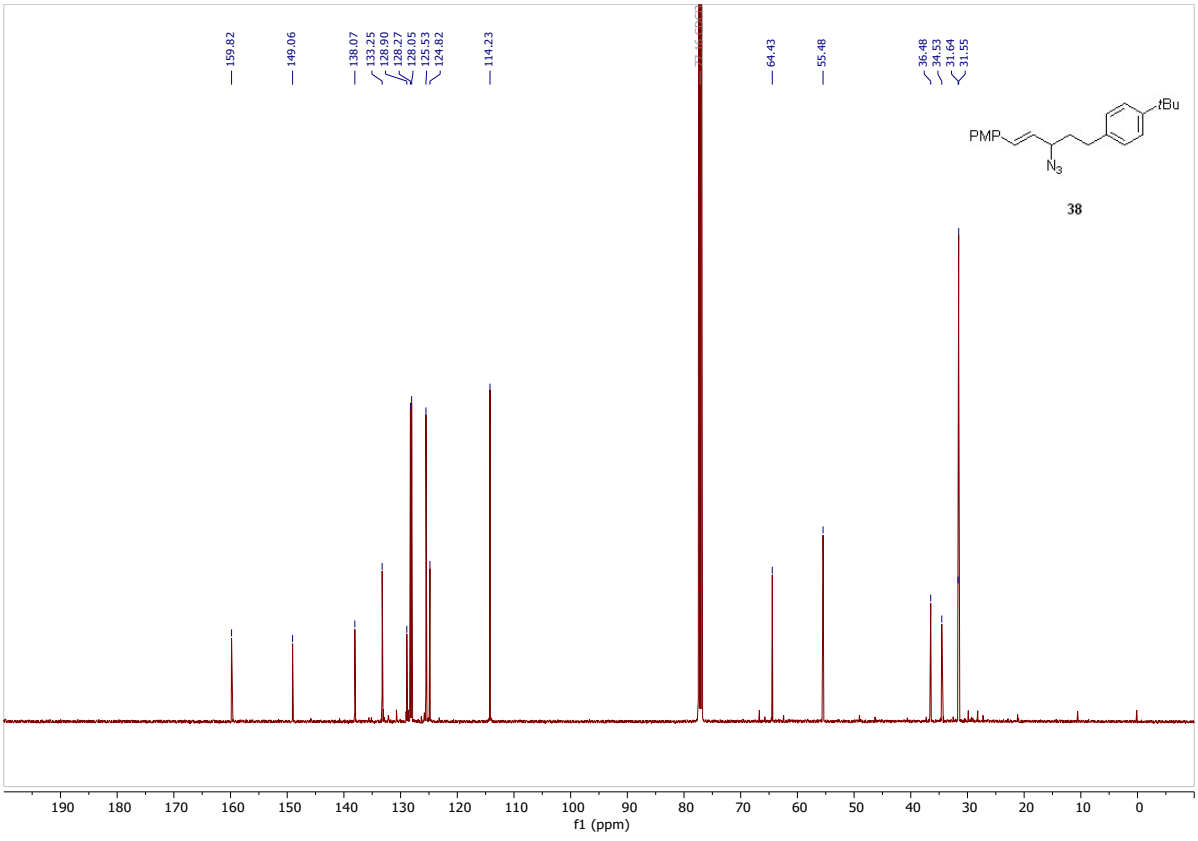


Compound 38

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

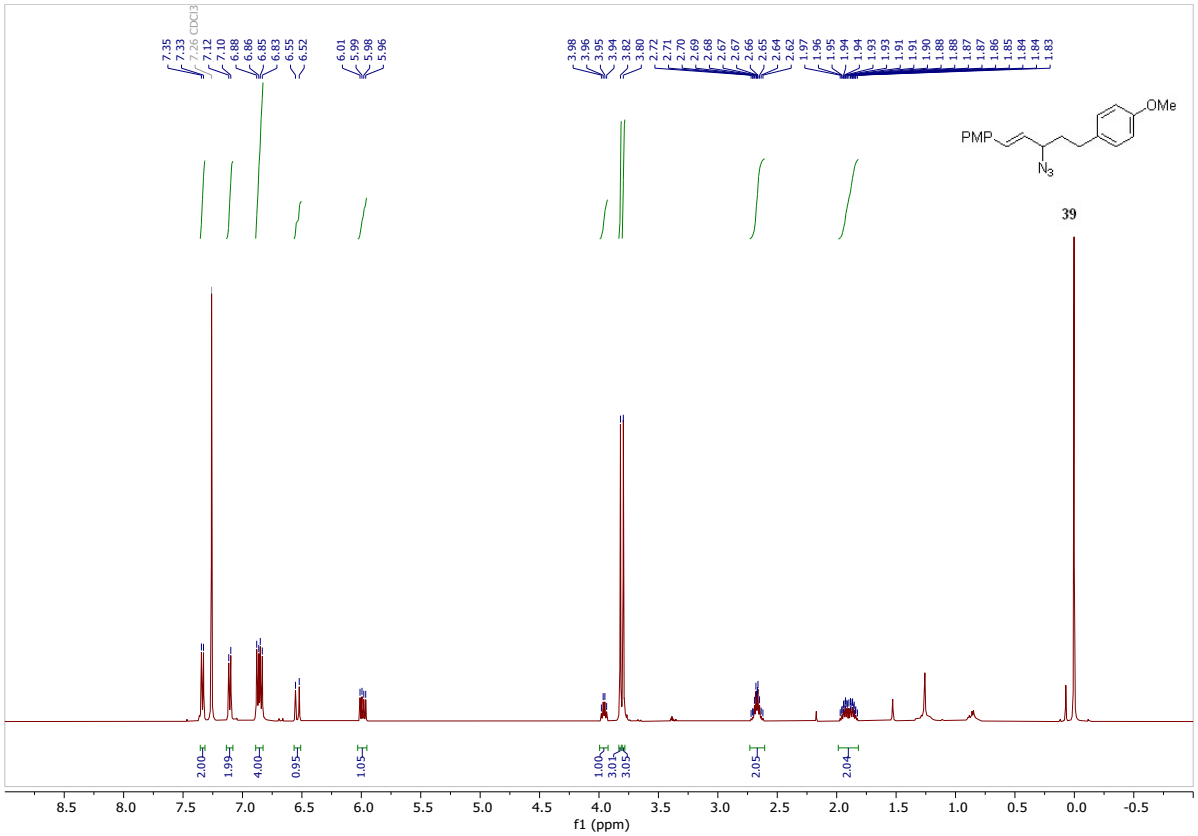


^{13}C NMR (126 MHz, $CDCl_3$)

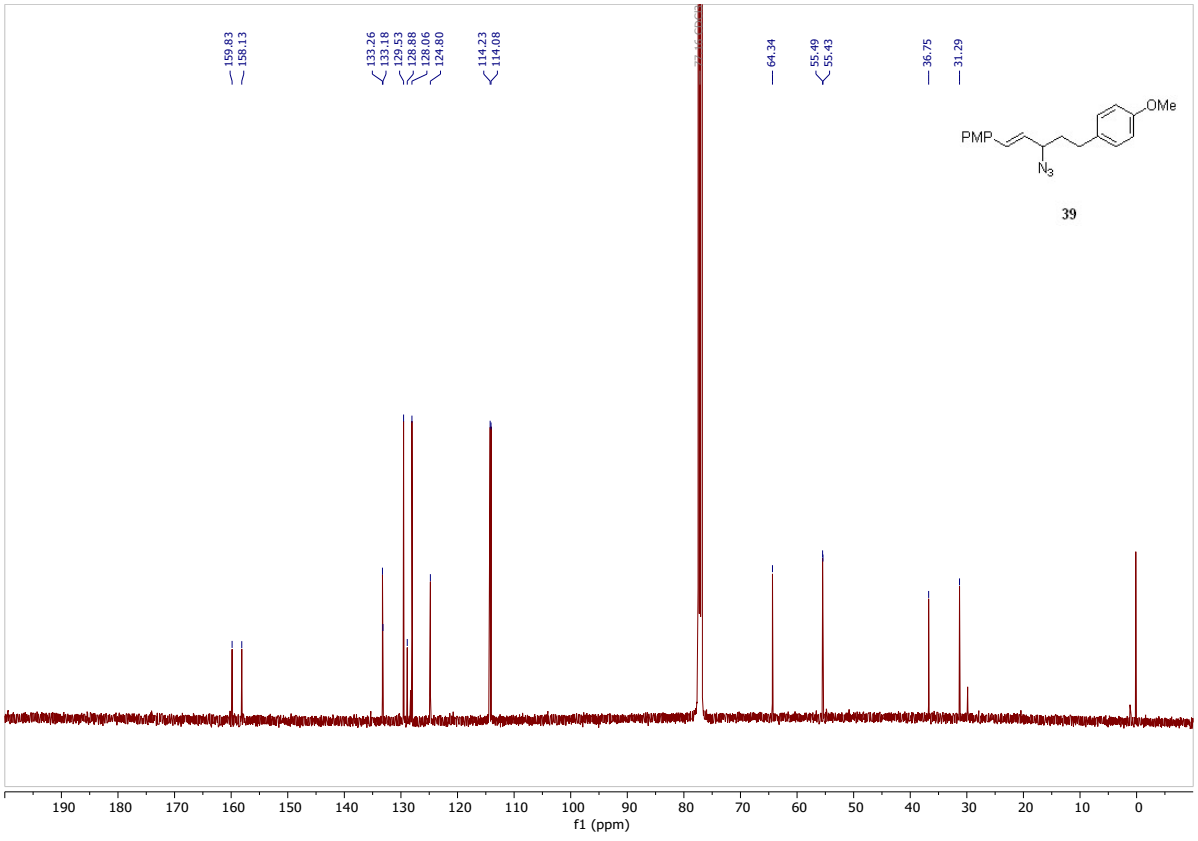


Compound 39

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

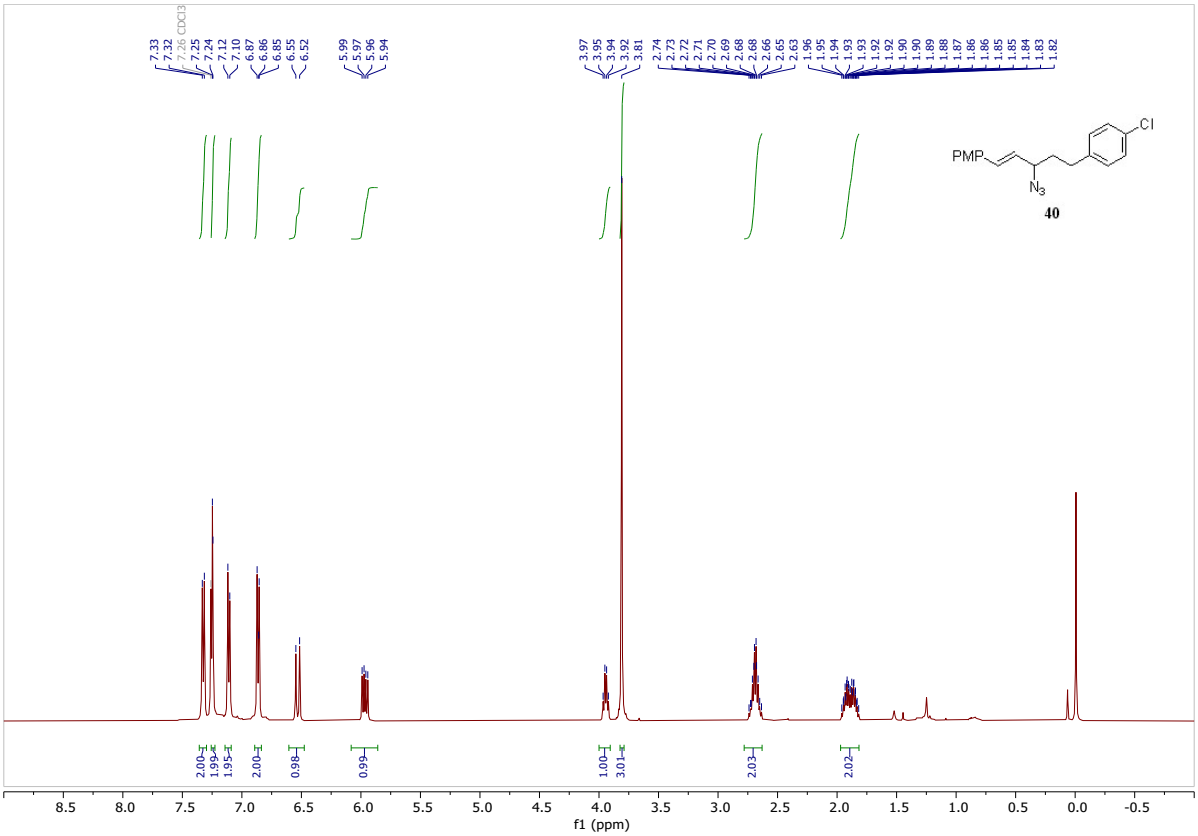


^{13}C NMR (126 MHz, $CDCl_3$)

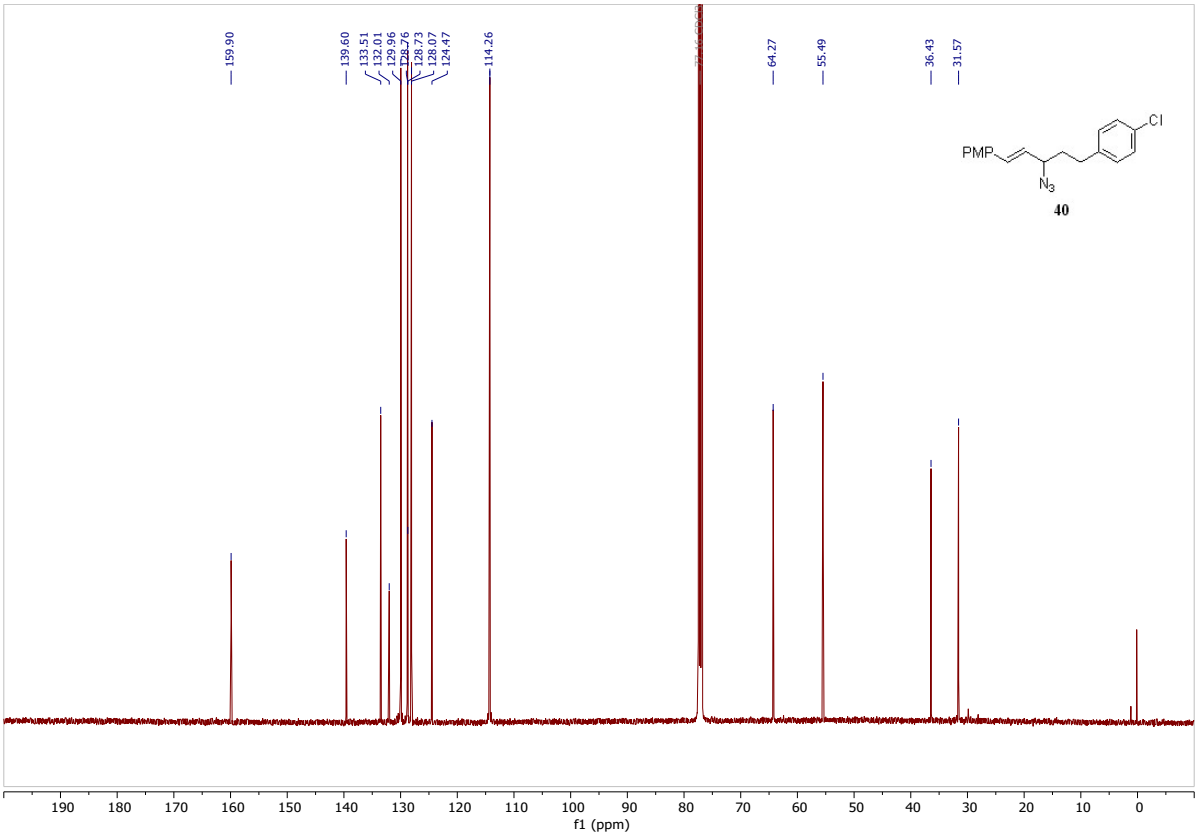


Compound 40

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

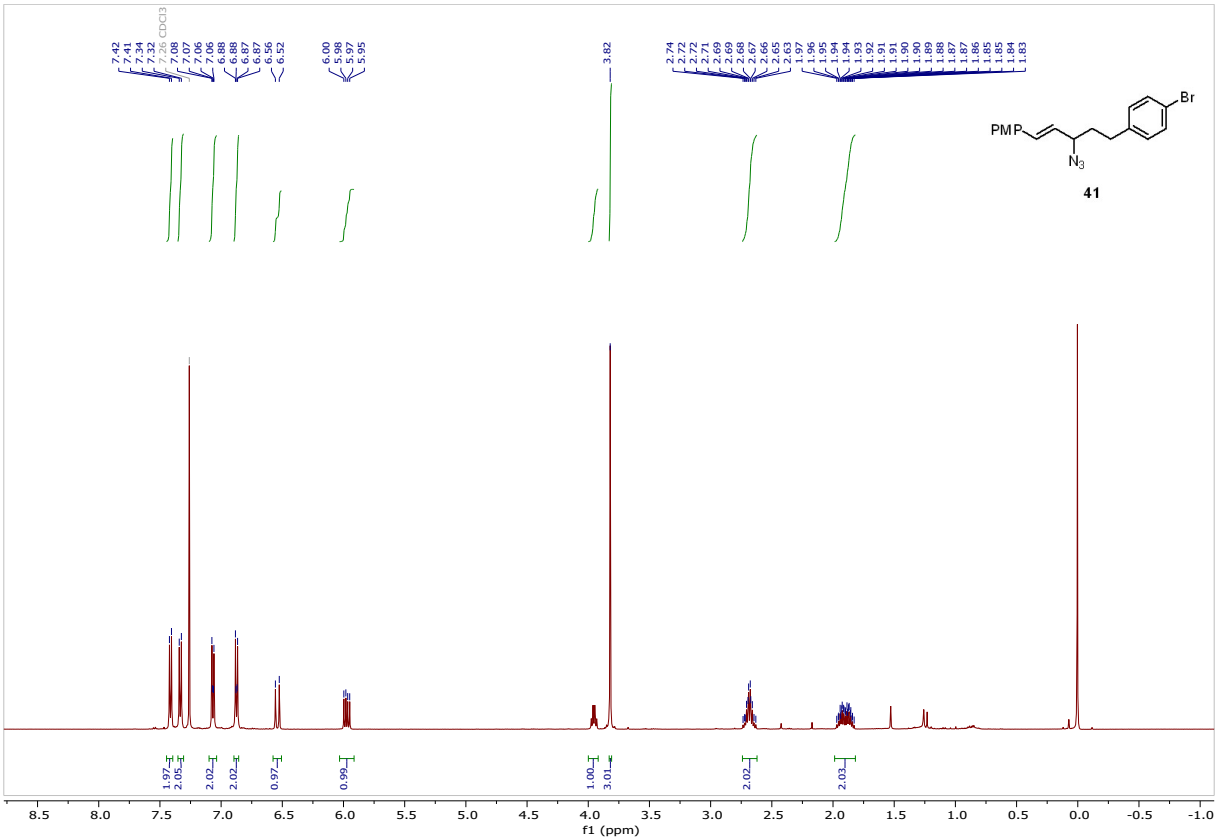


^{13}C NMR (126 MHz, $CDCl_3$)

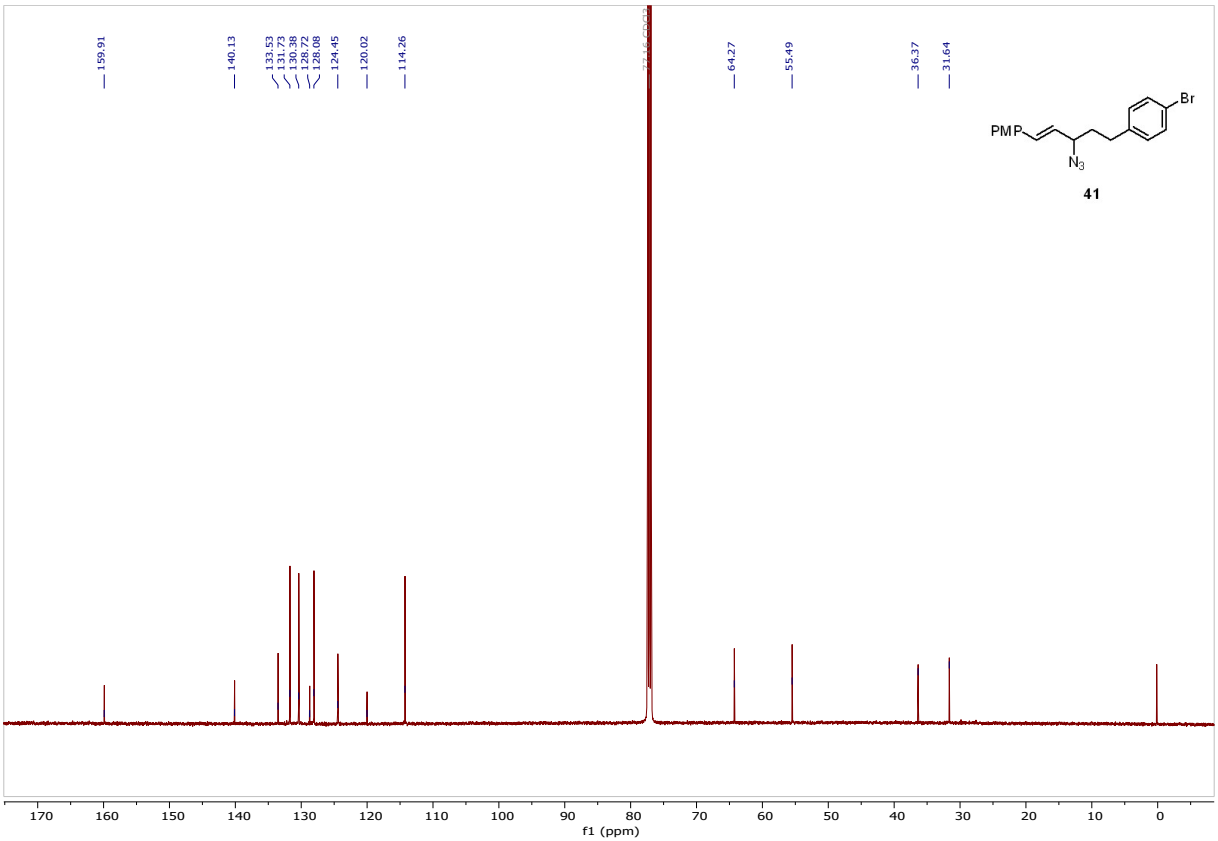


Compound 41

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

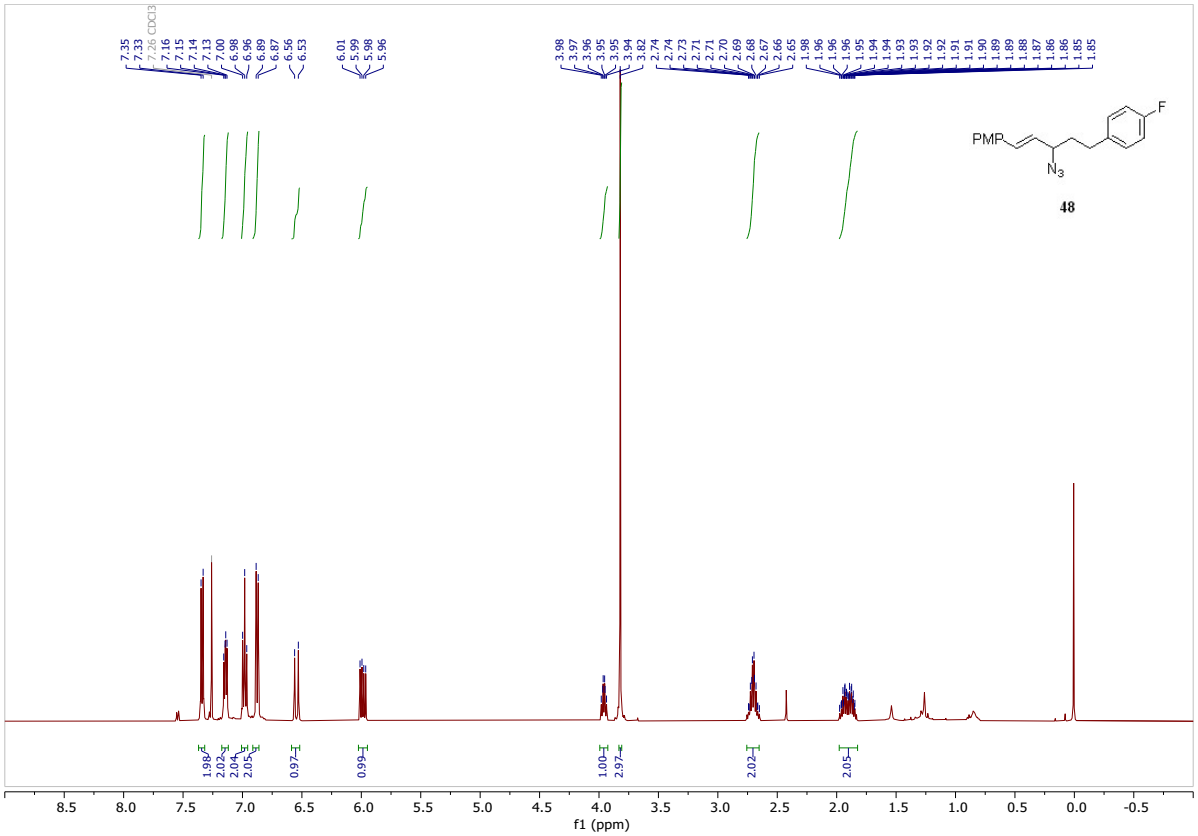


^{13}C NMR (126 MHz, $CDCl_3$)

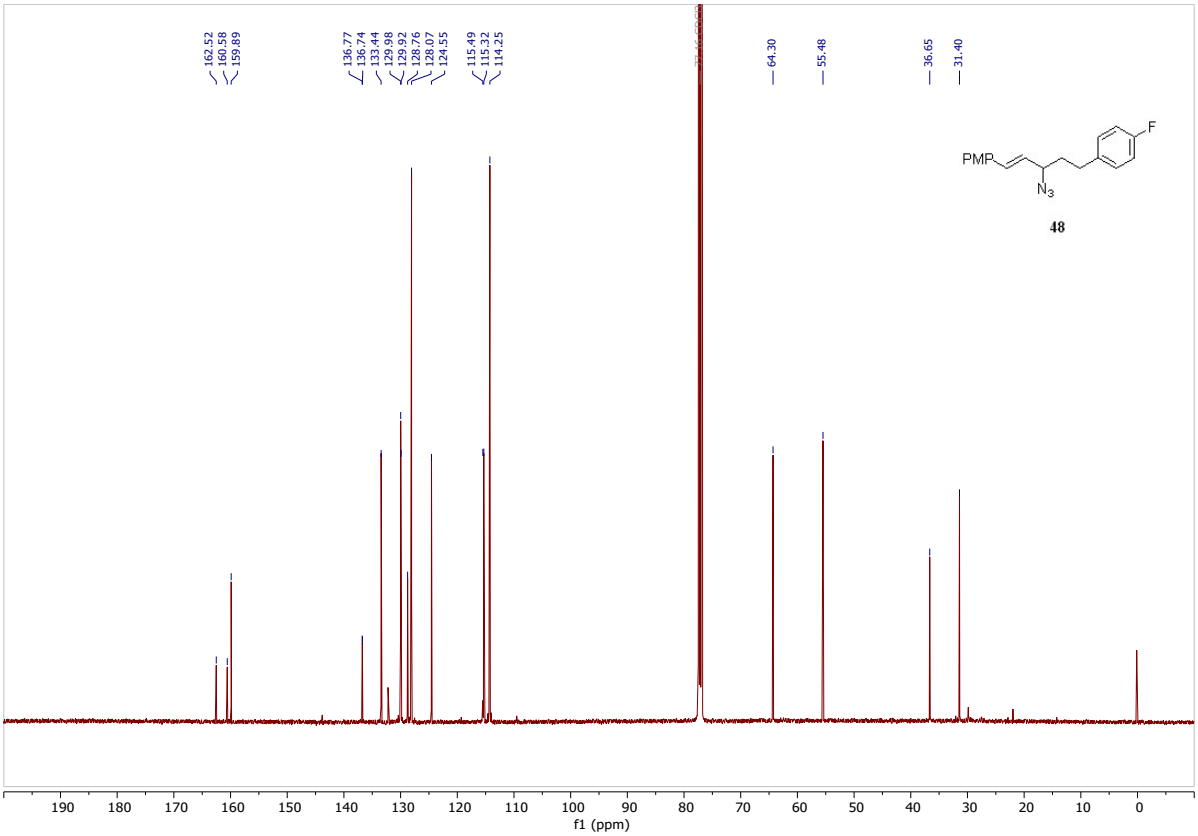


Compound 42

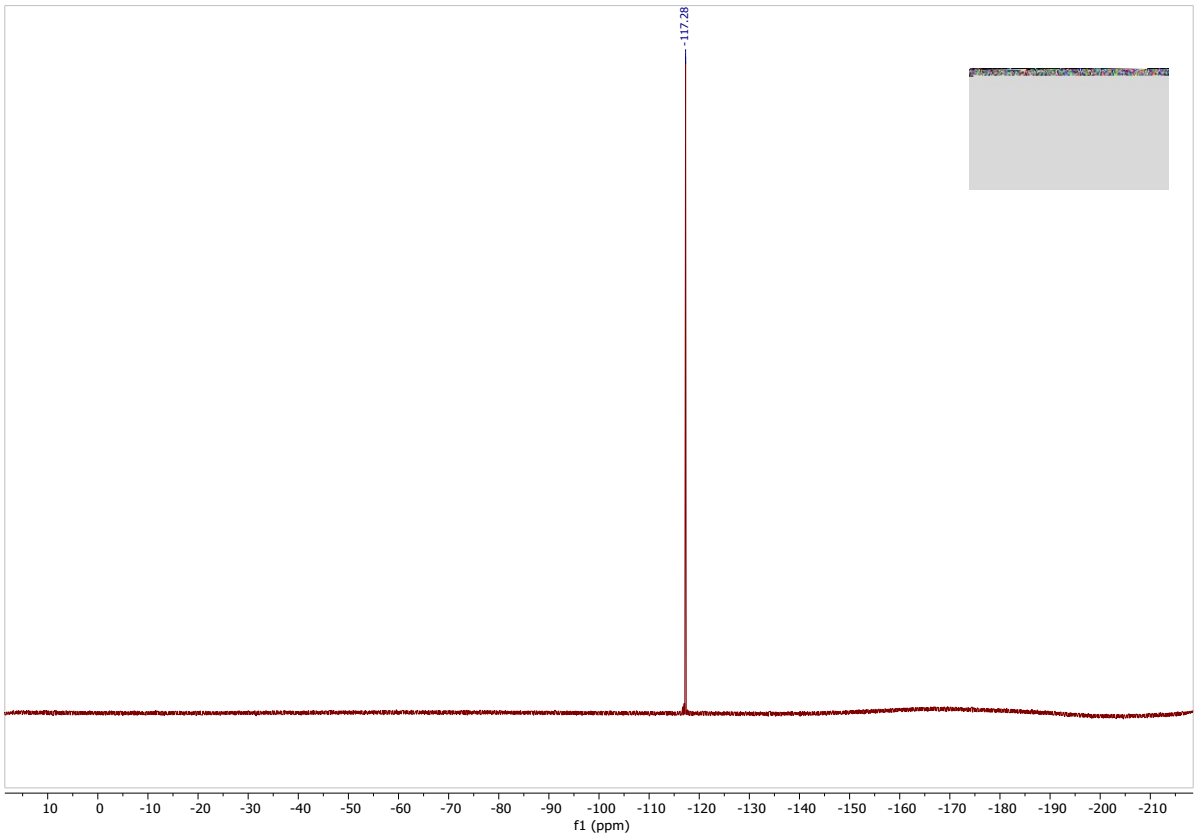
^{1}H NMR (500 MHz, Chloroform-*d*)



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

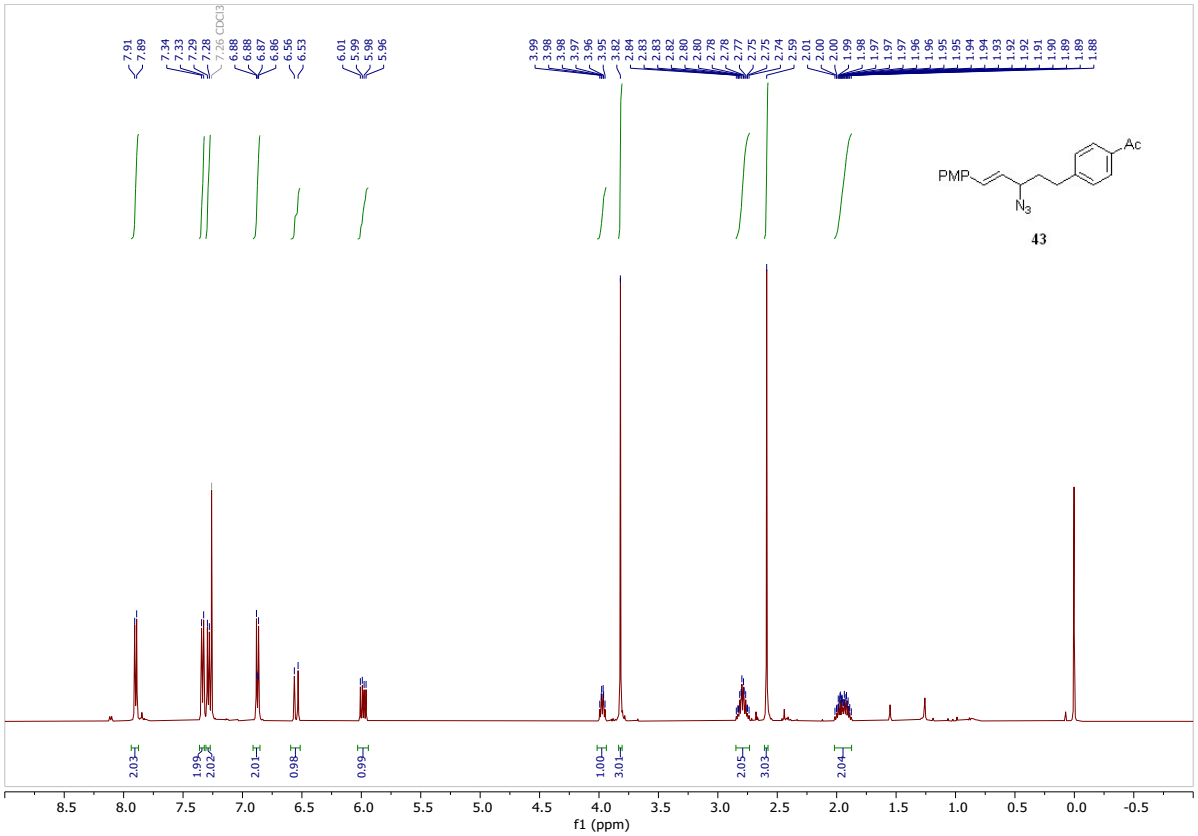


^{19}F NMR (377 MHz, $CDCl_3$)

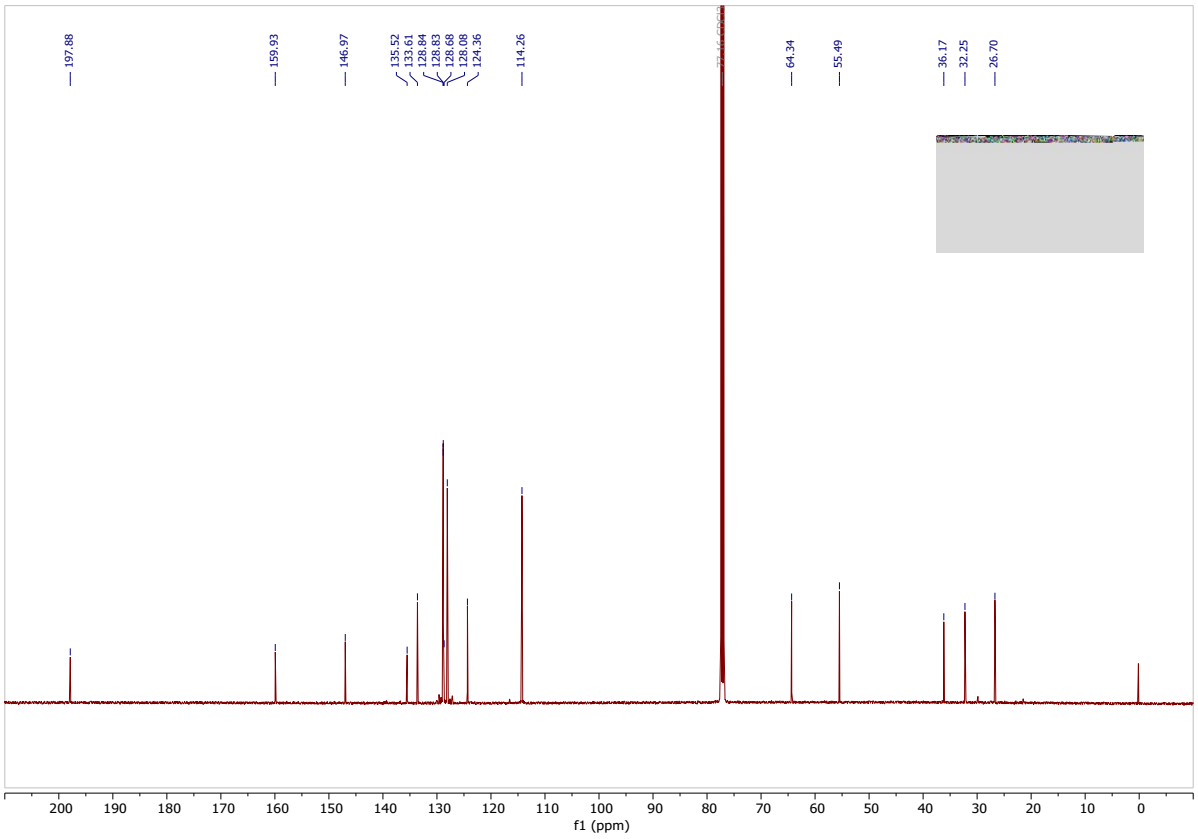


Compound 43

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

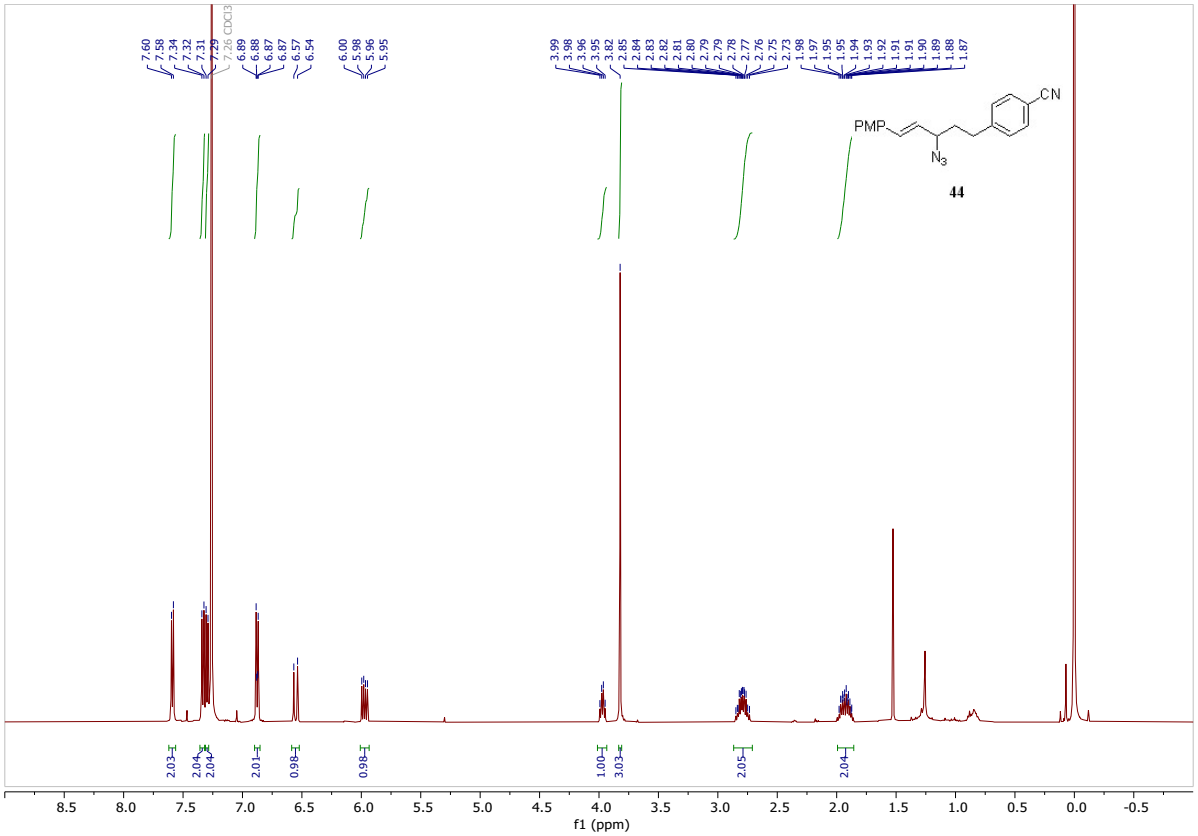


^{13}C NMR (126 MHz, $CDCl_3$)

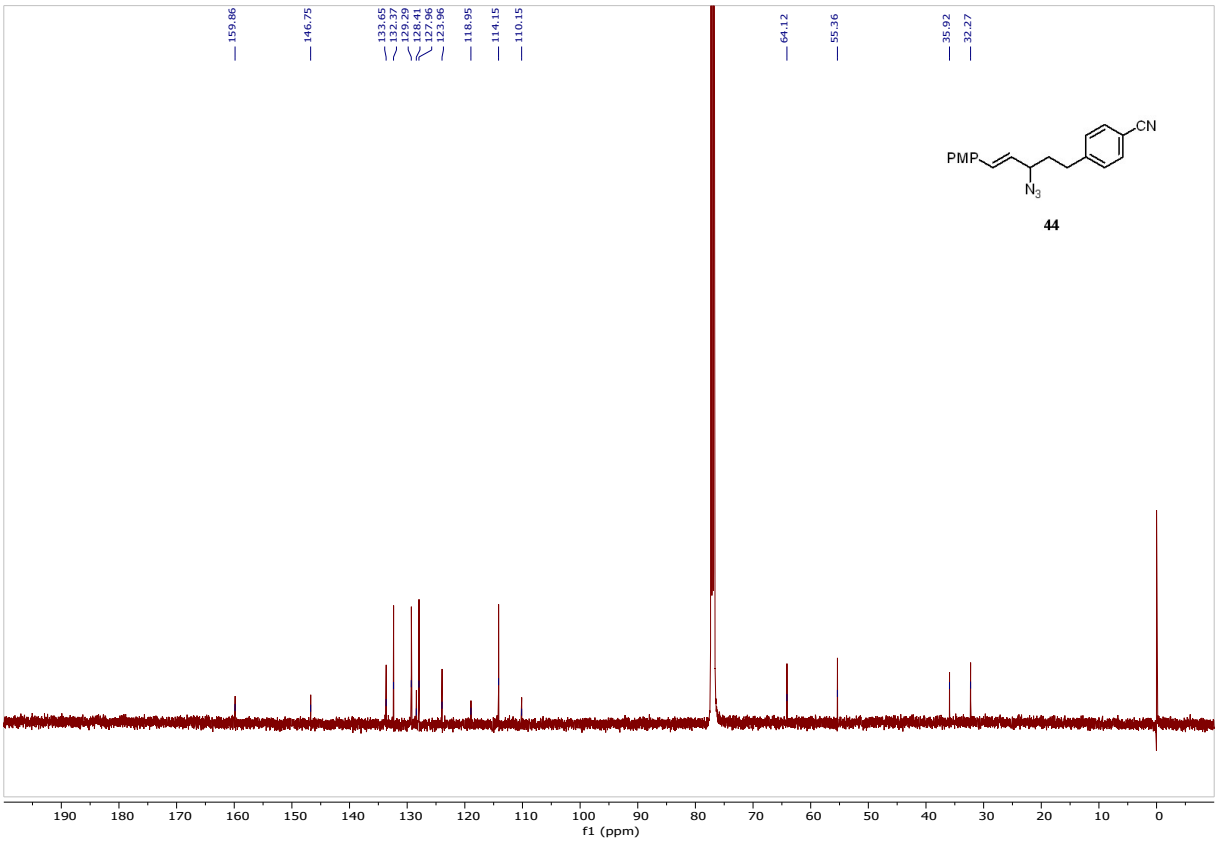


Compound 44

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

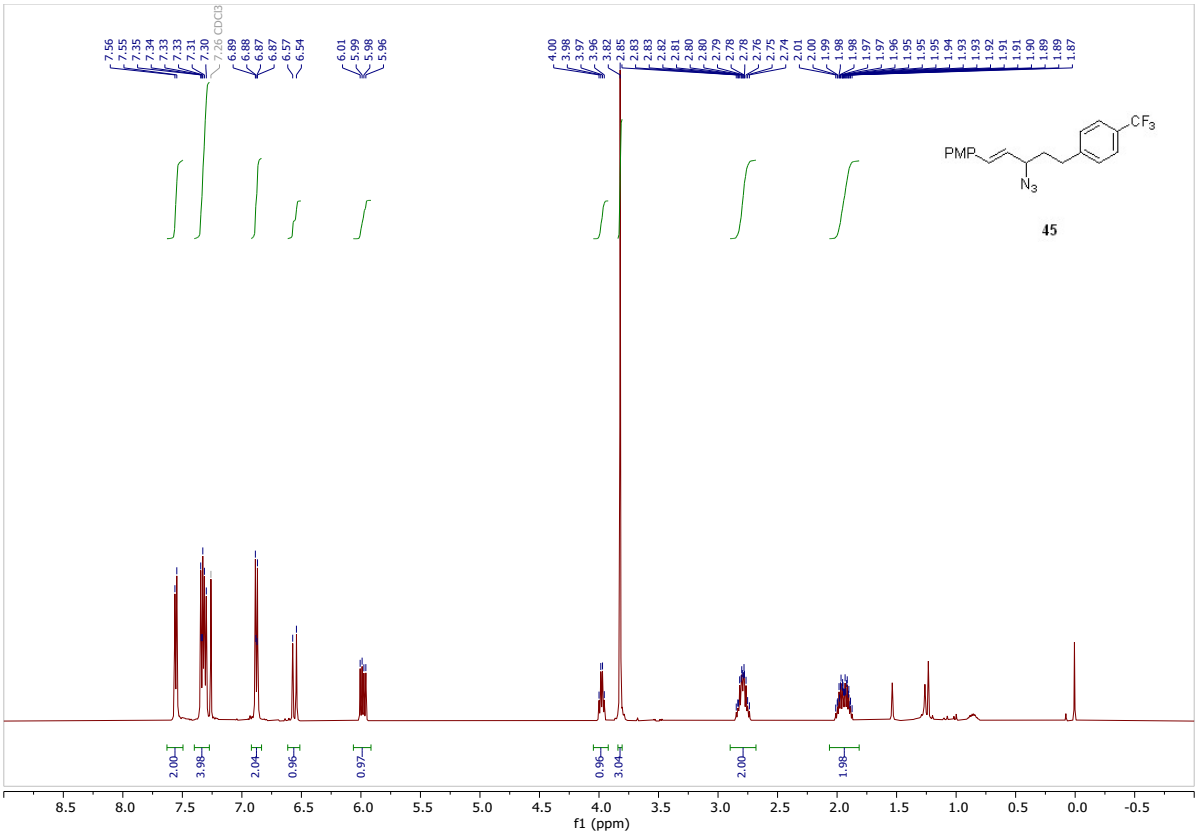


^{13}C NMR (126 MHz, $CDCl_3$)

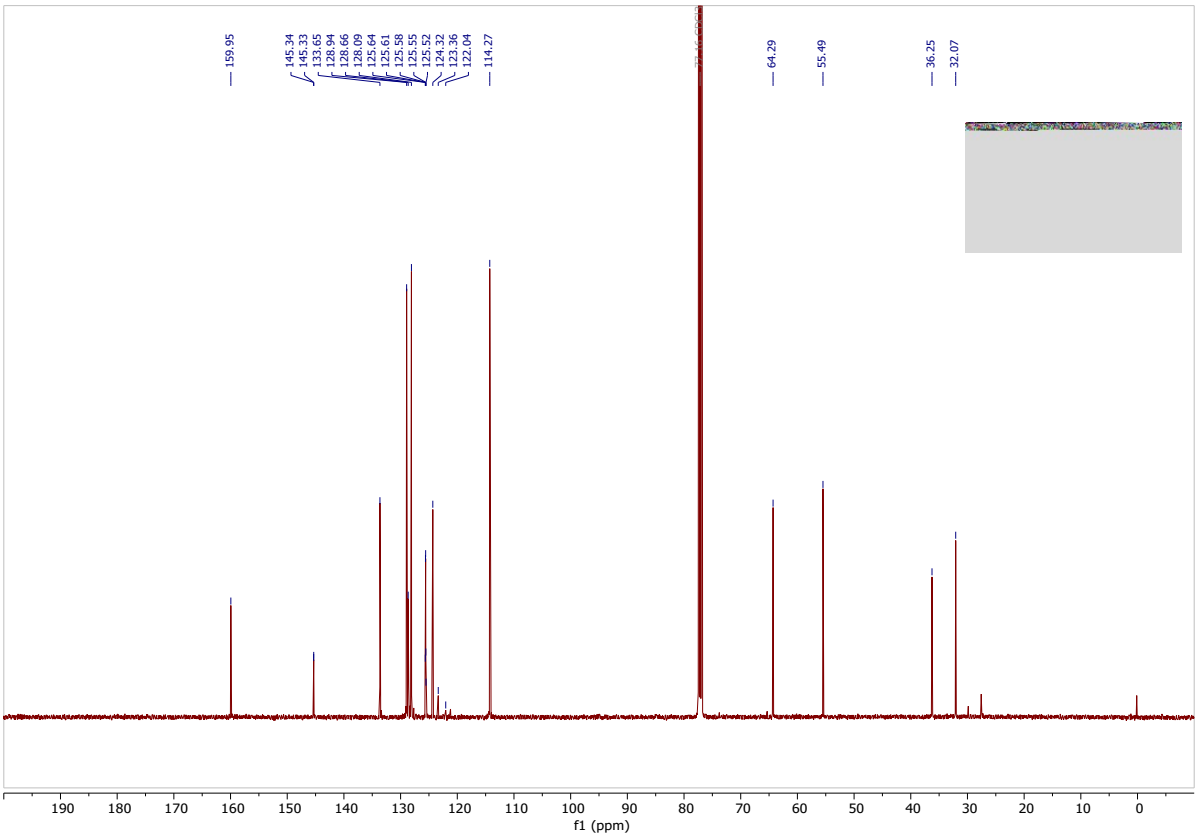


Compound 45

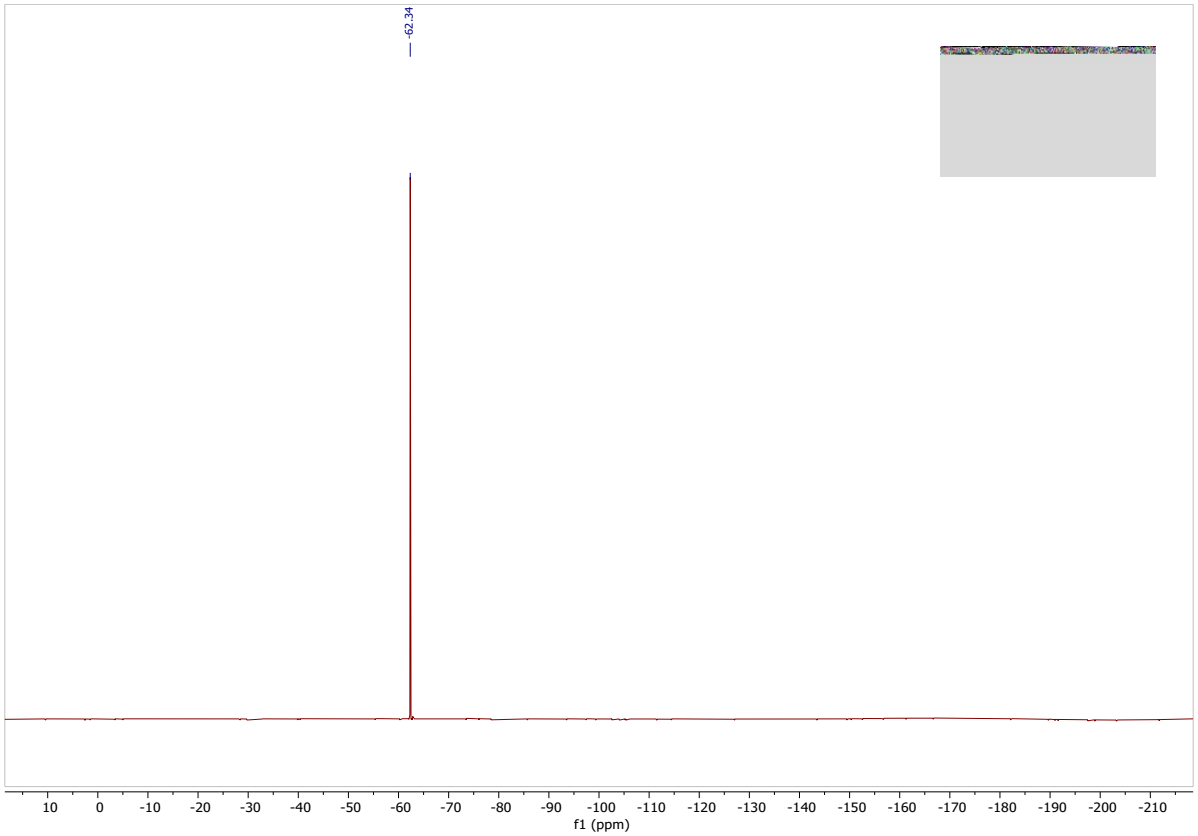
^{1}H NMR (500 MHz, Chloroform-*d*)



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

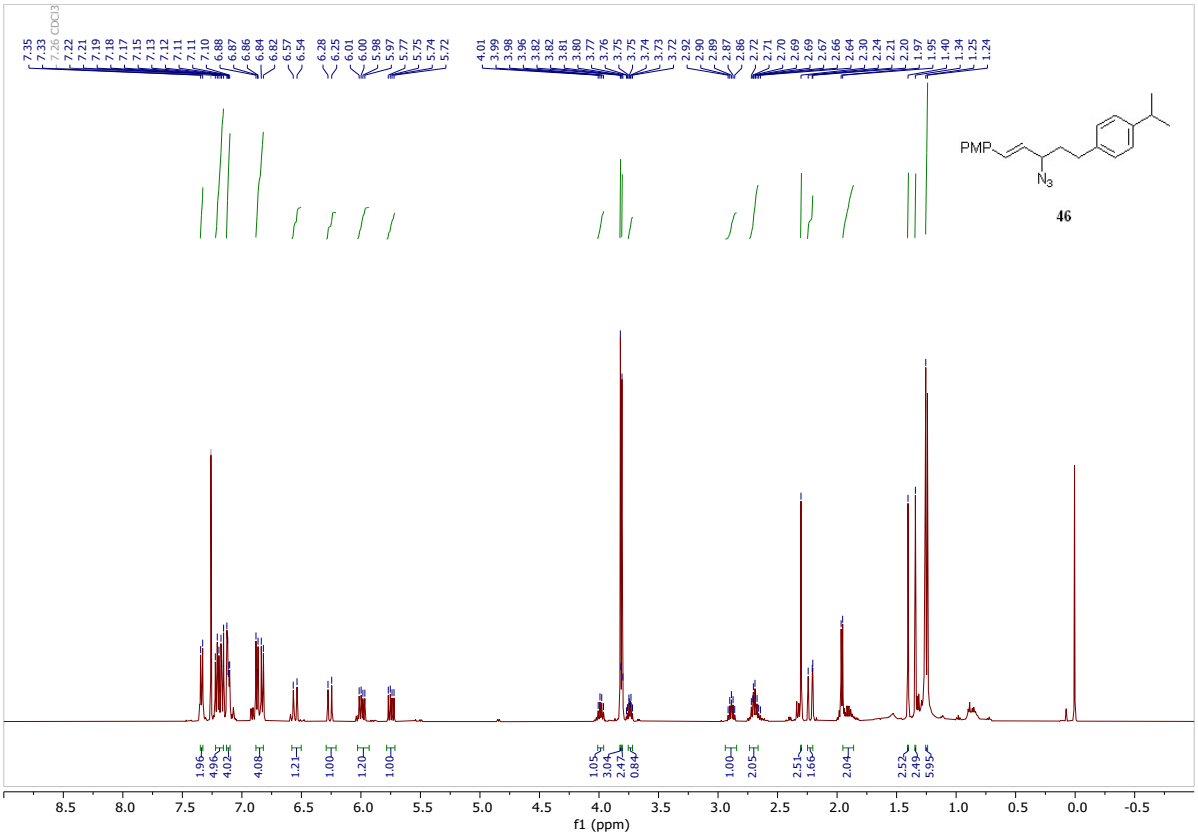


^{19}F NMR (377 MHz, $CDCl_3$)

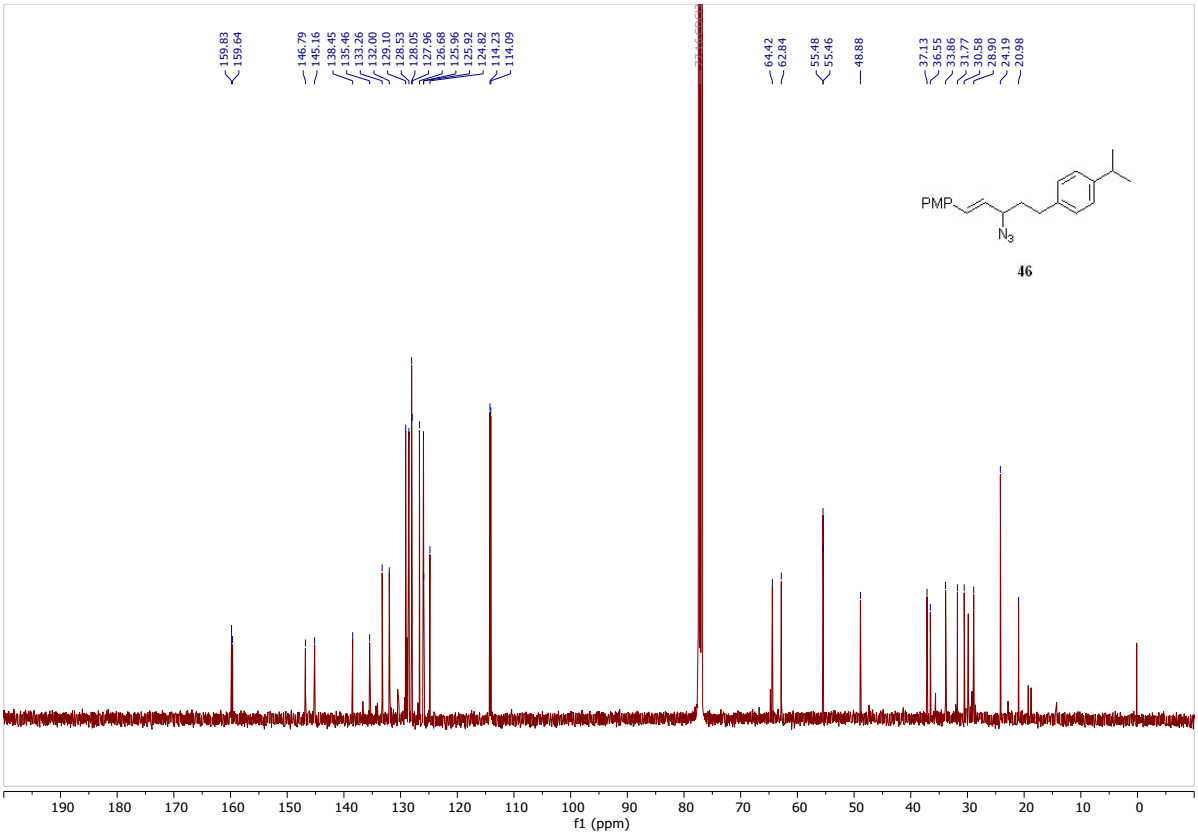


Compound 46

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

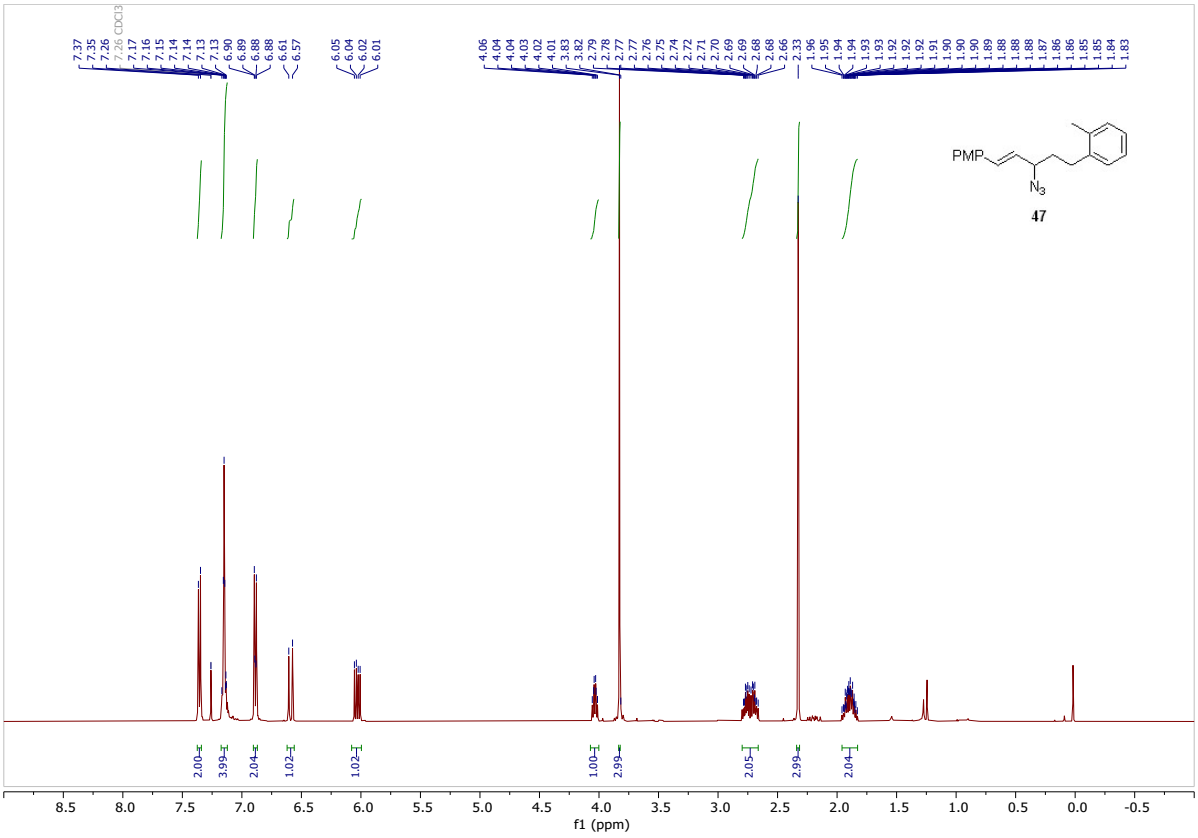


^{13}C NMR (126 MHz, $CDCl_3$)

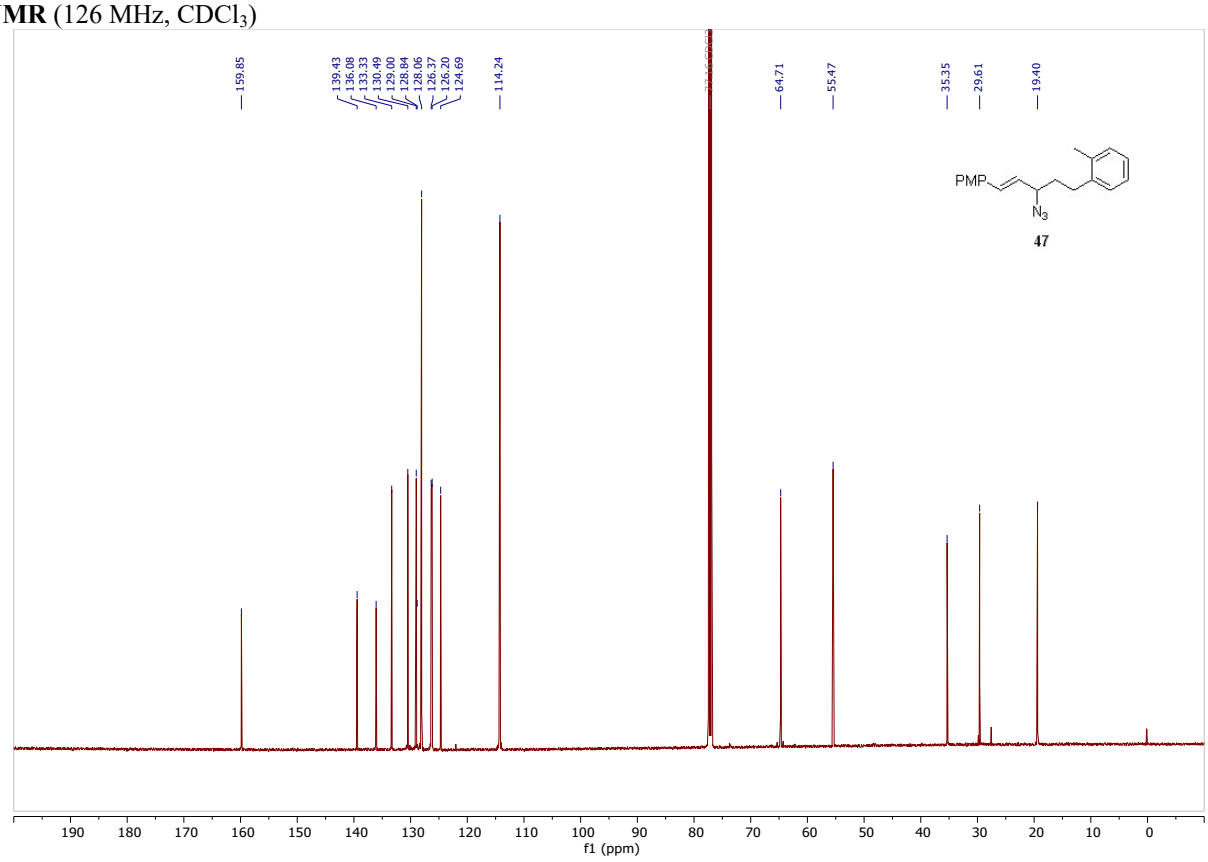


Compound 47

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

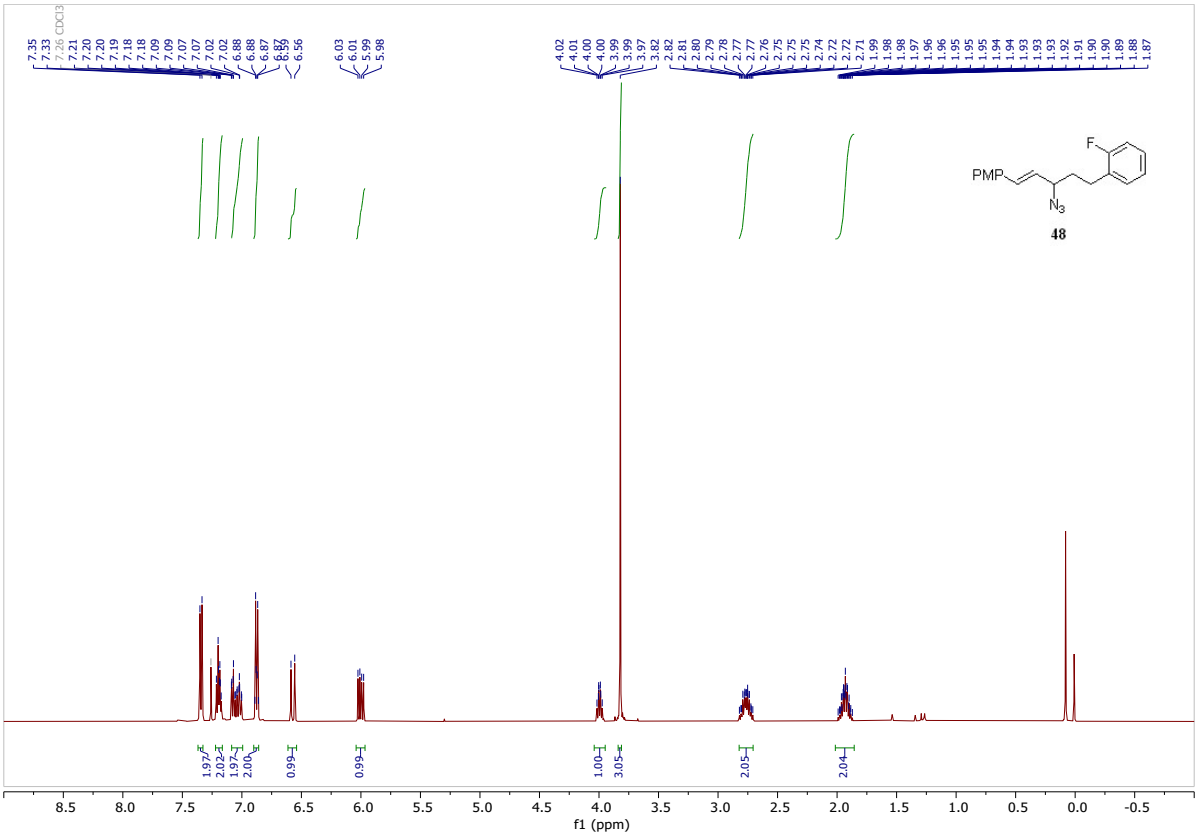


^{13}C NMR (126 MHz, $CDCl_3$)

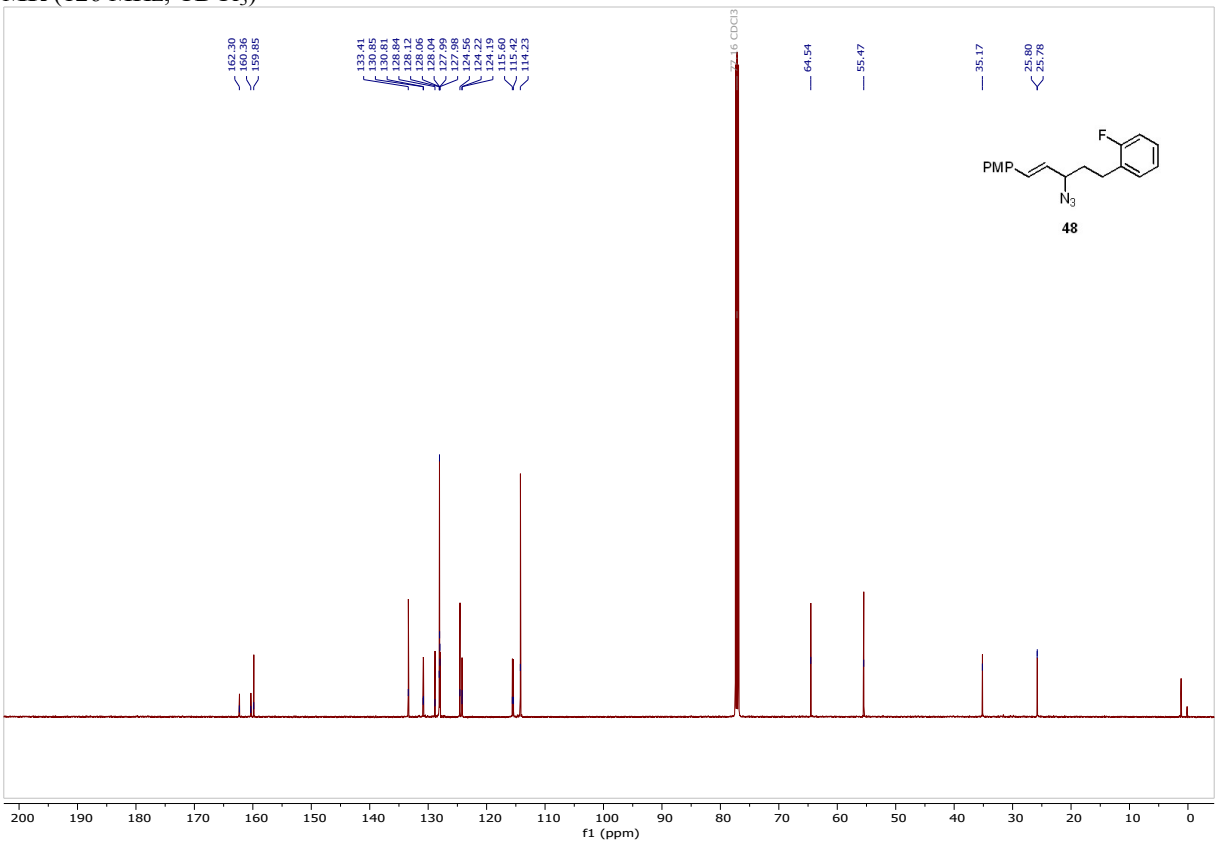


Compound 48

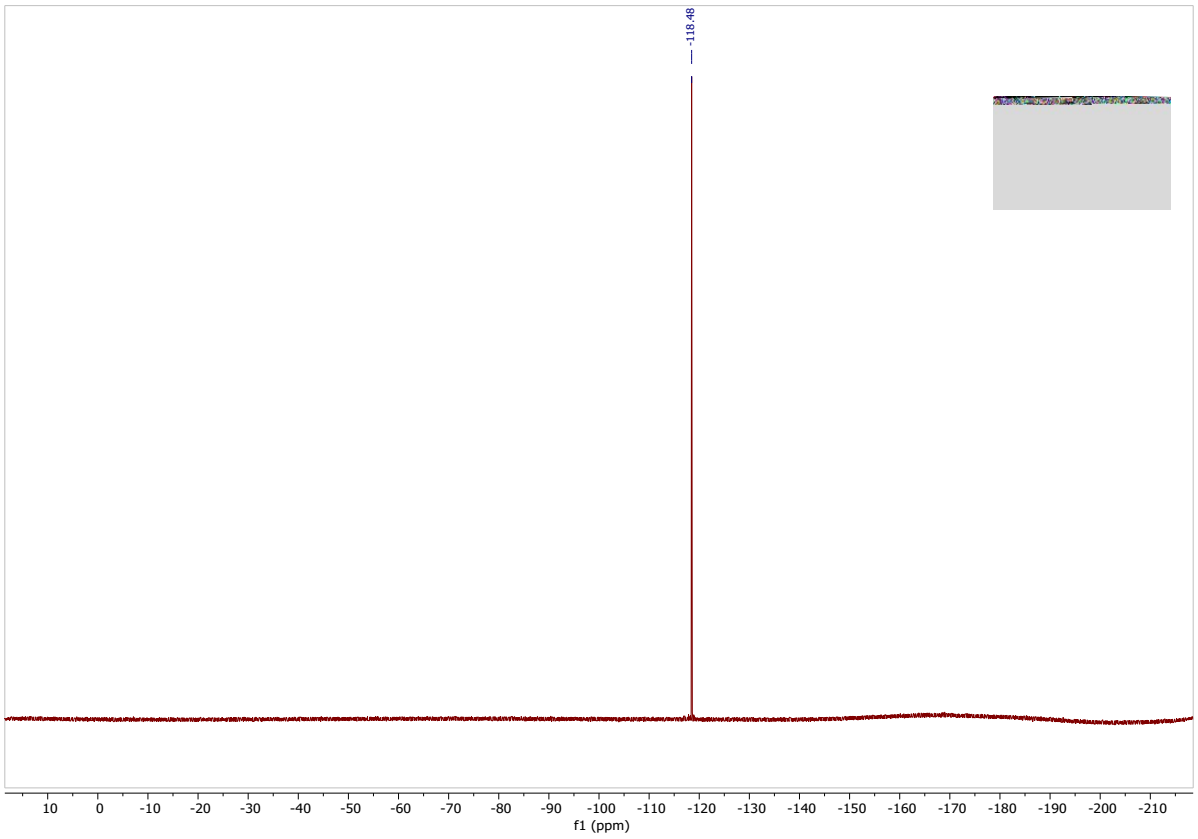
^{1}H NMR (500 MHz, Chloroform-*d*)



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

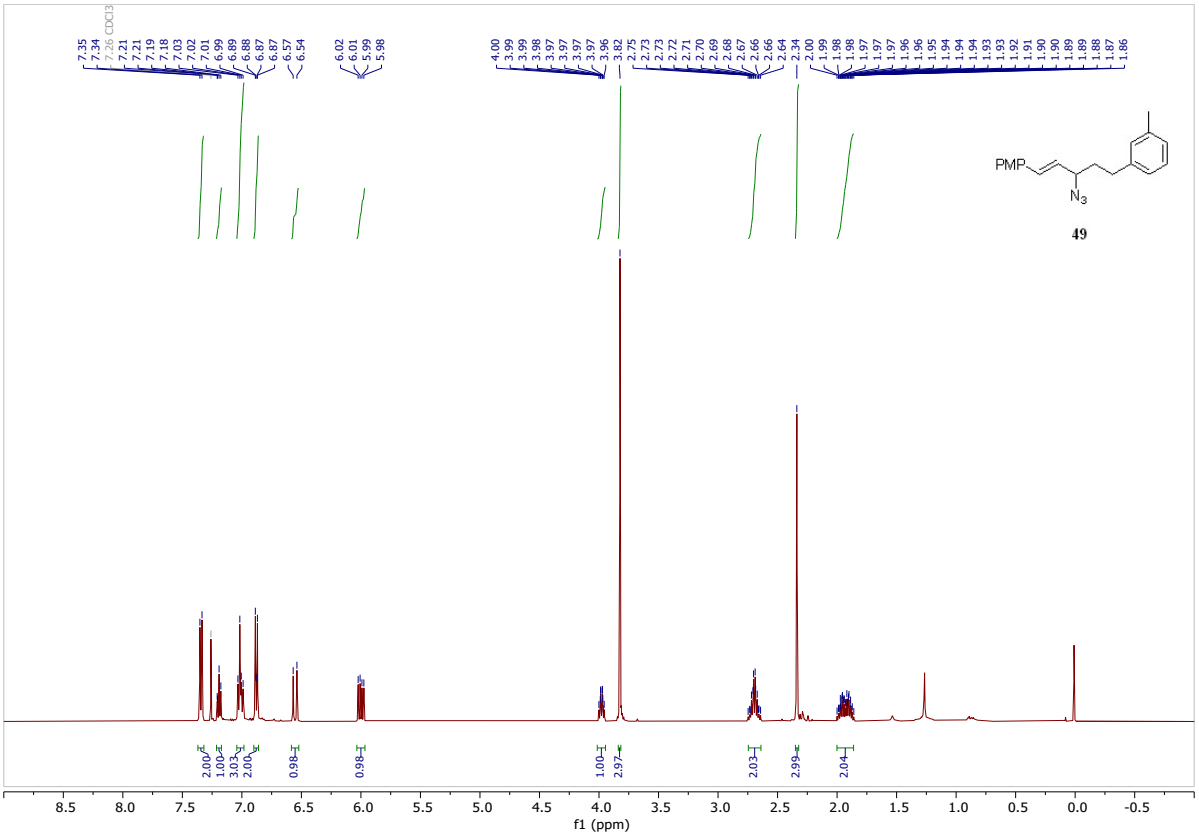


^{19}F NMR (377 MHz, $CDCl_3$)

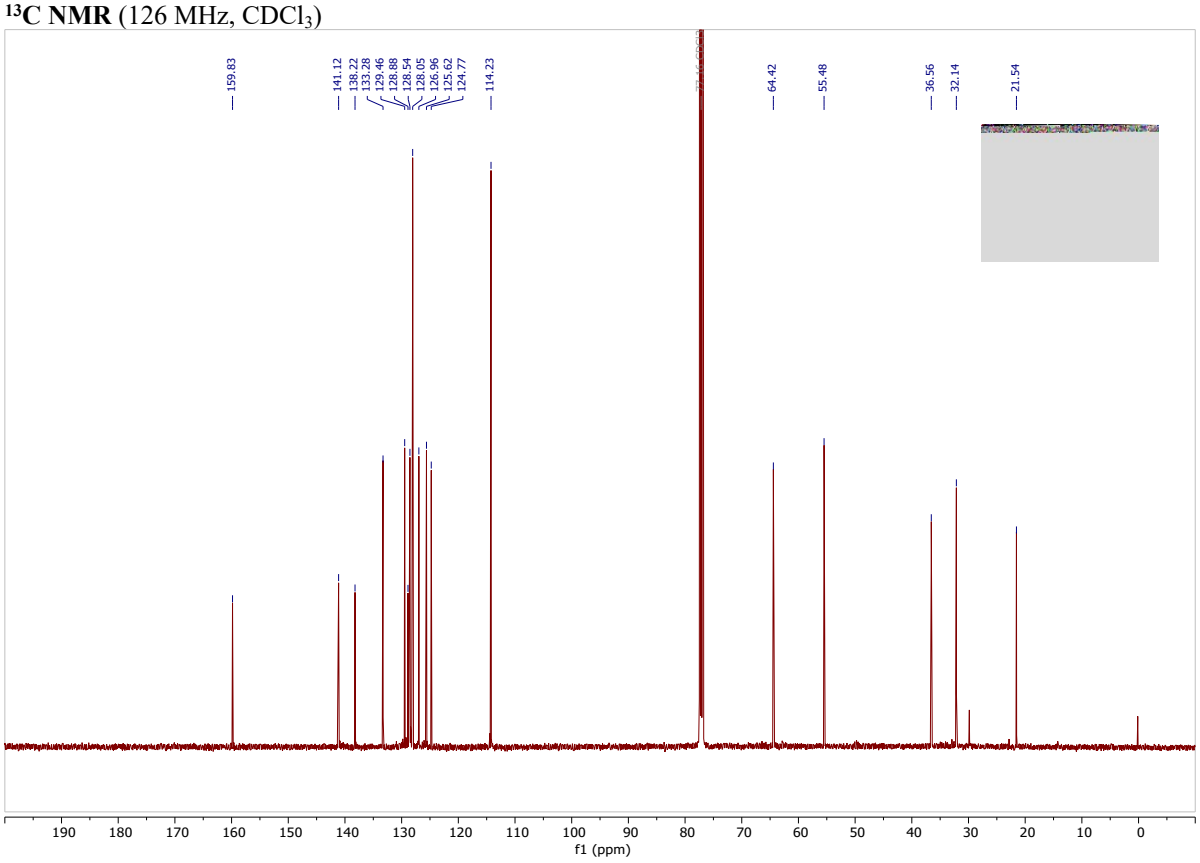


Compound 49

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

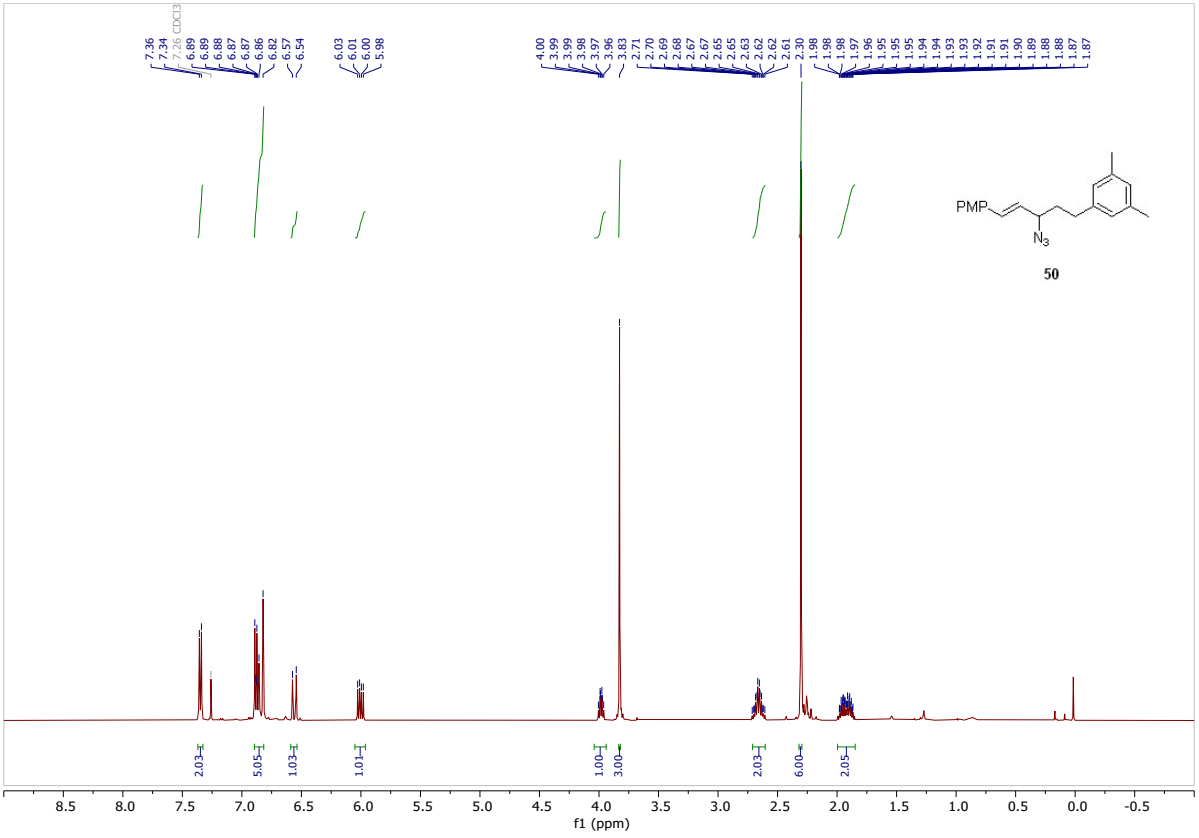


^{13}C NMR (126 MHz, $CDCl_3$)

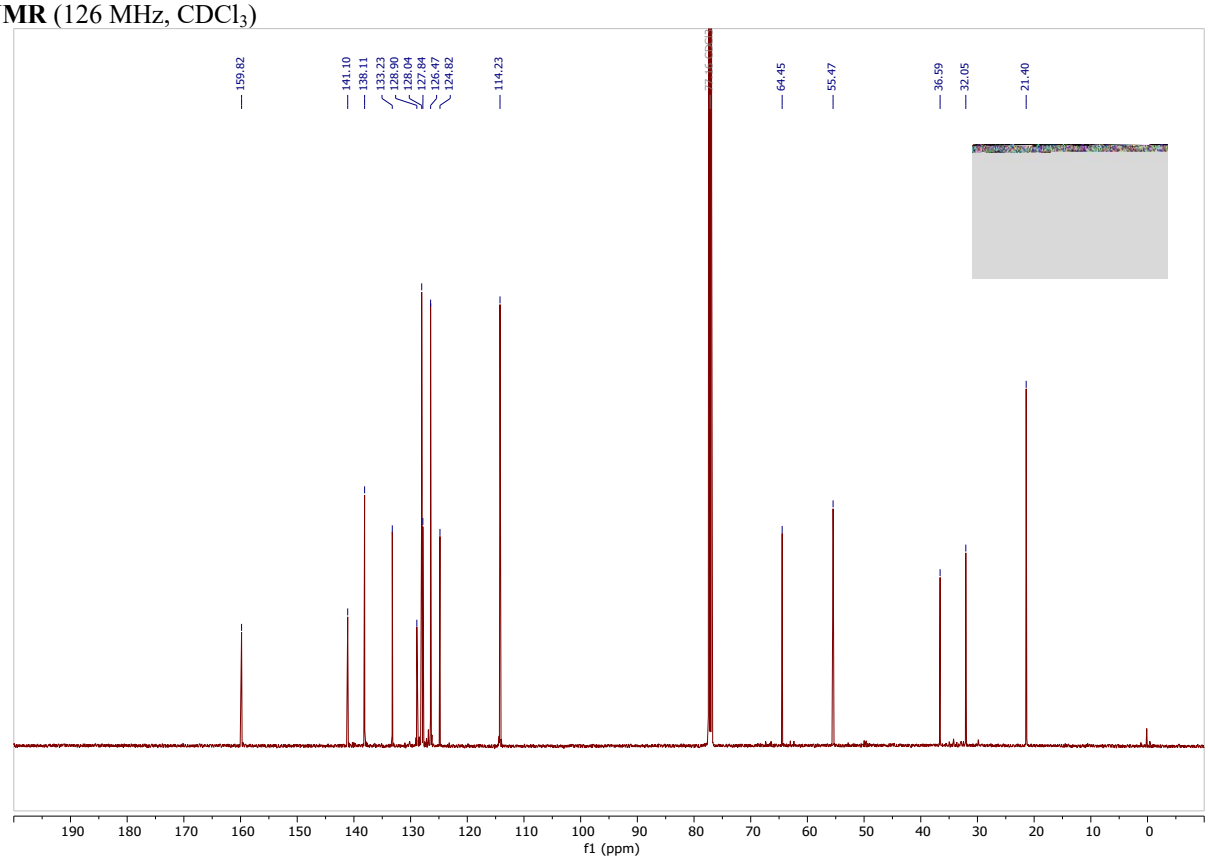


Compound 50

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

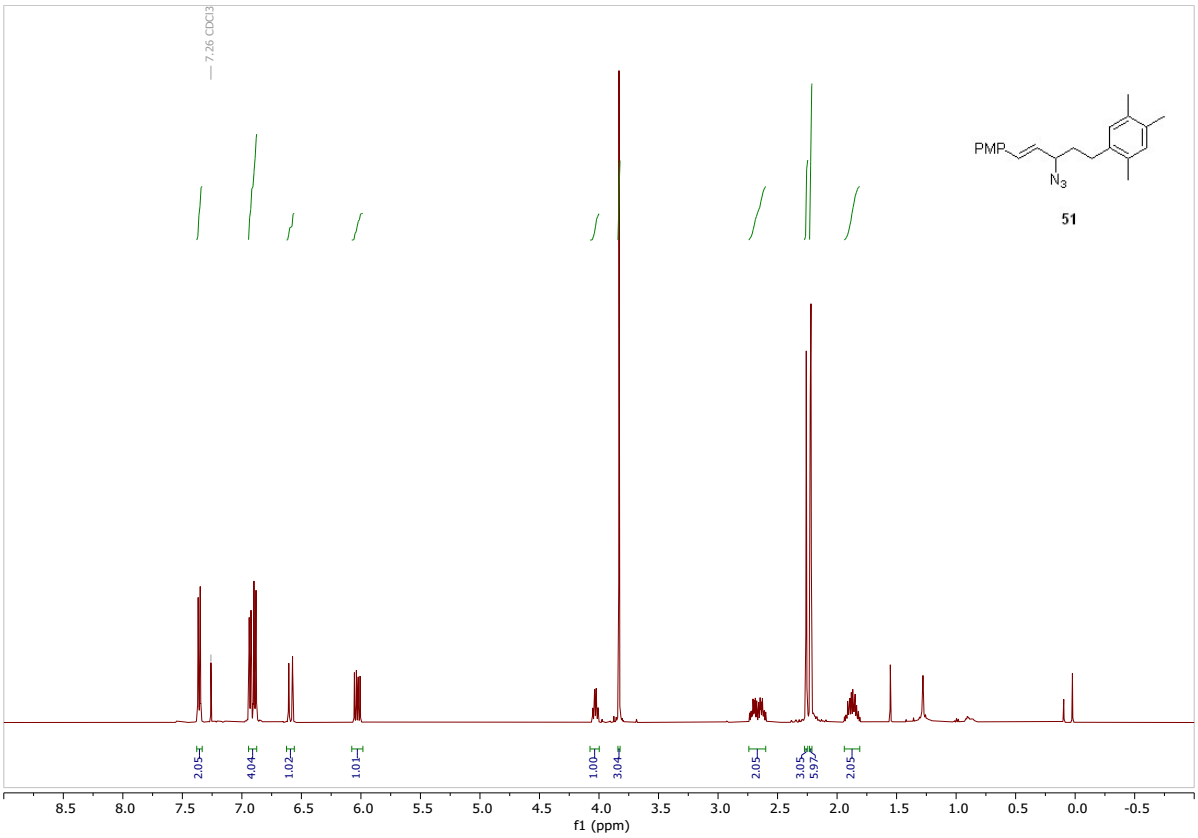


^{13}C NMR (126 MHz, $CDCl_3$)

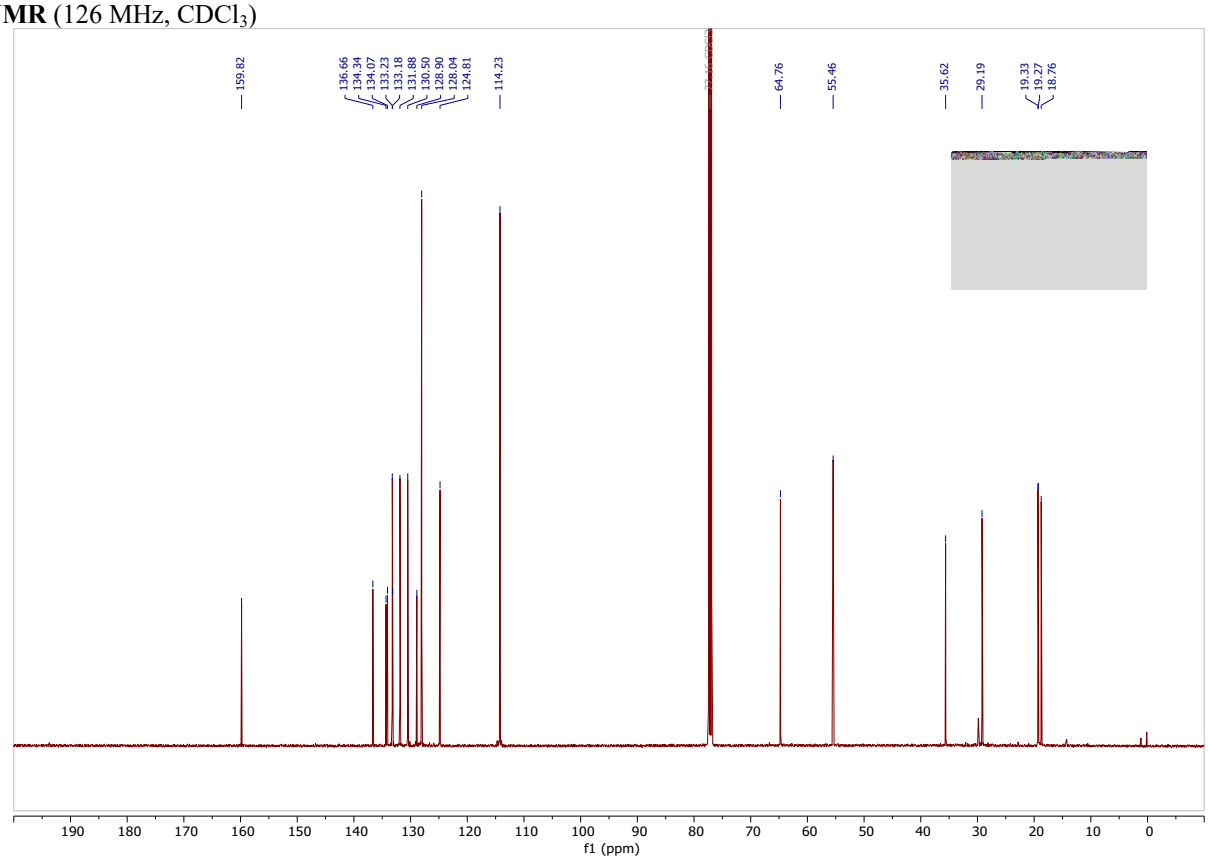


Compound 51

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

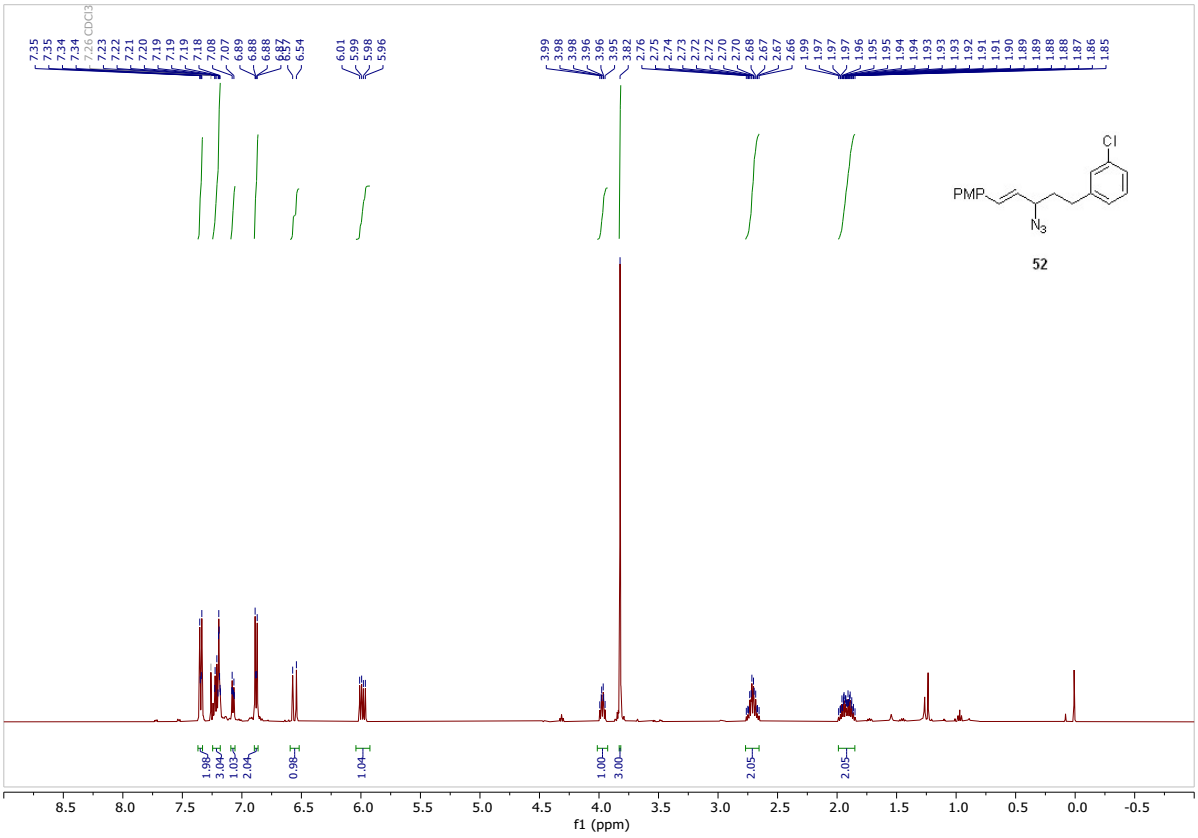


^{13}C NMR (126 MHz, $CDCl_3$)

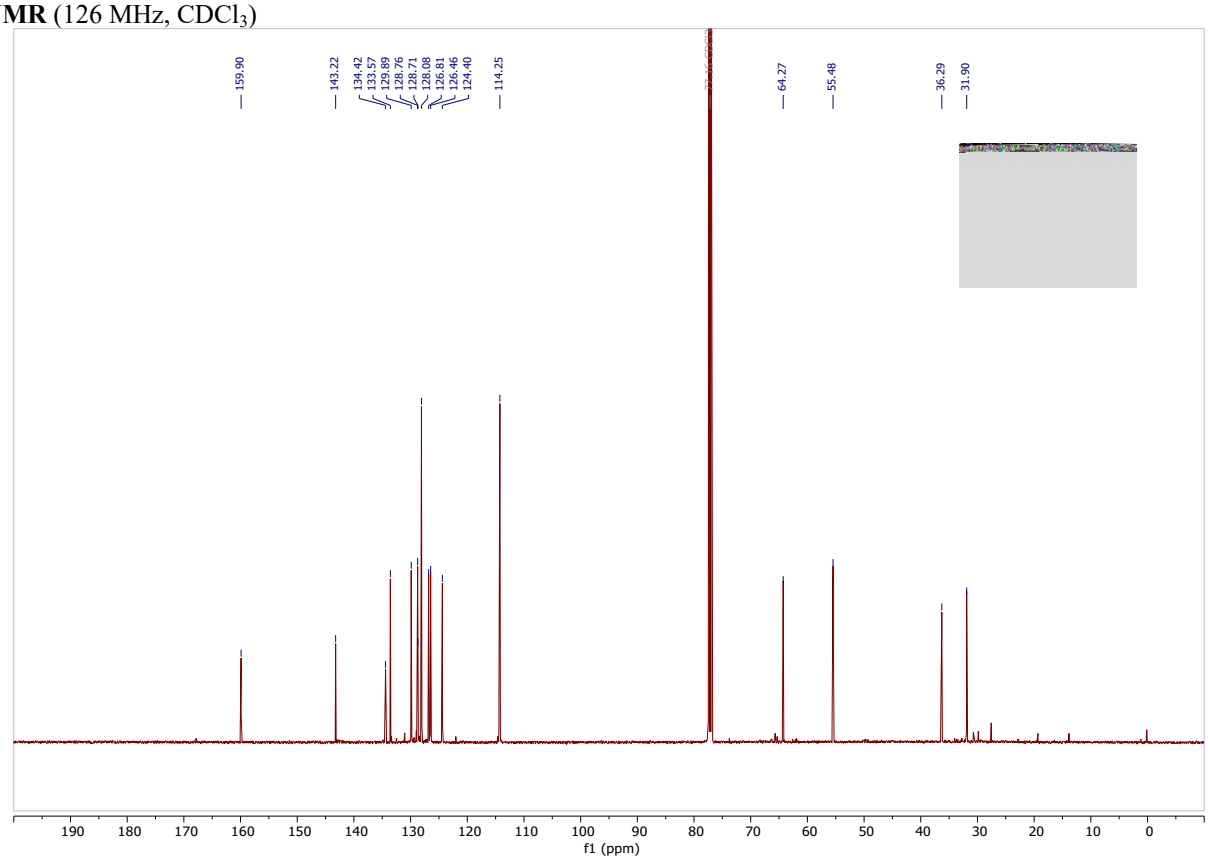


Compound 52

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

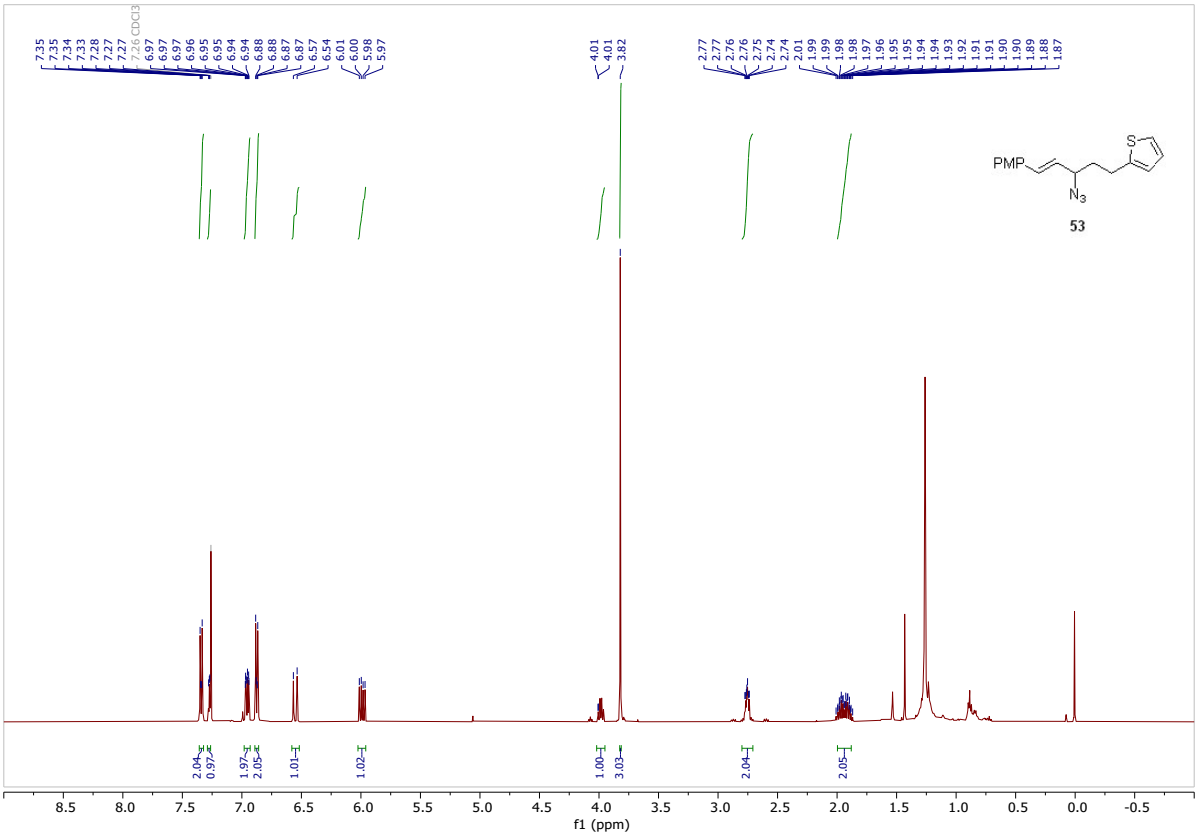


^{13}C NMR (126 MHz, $CDCl_3$)

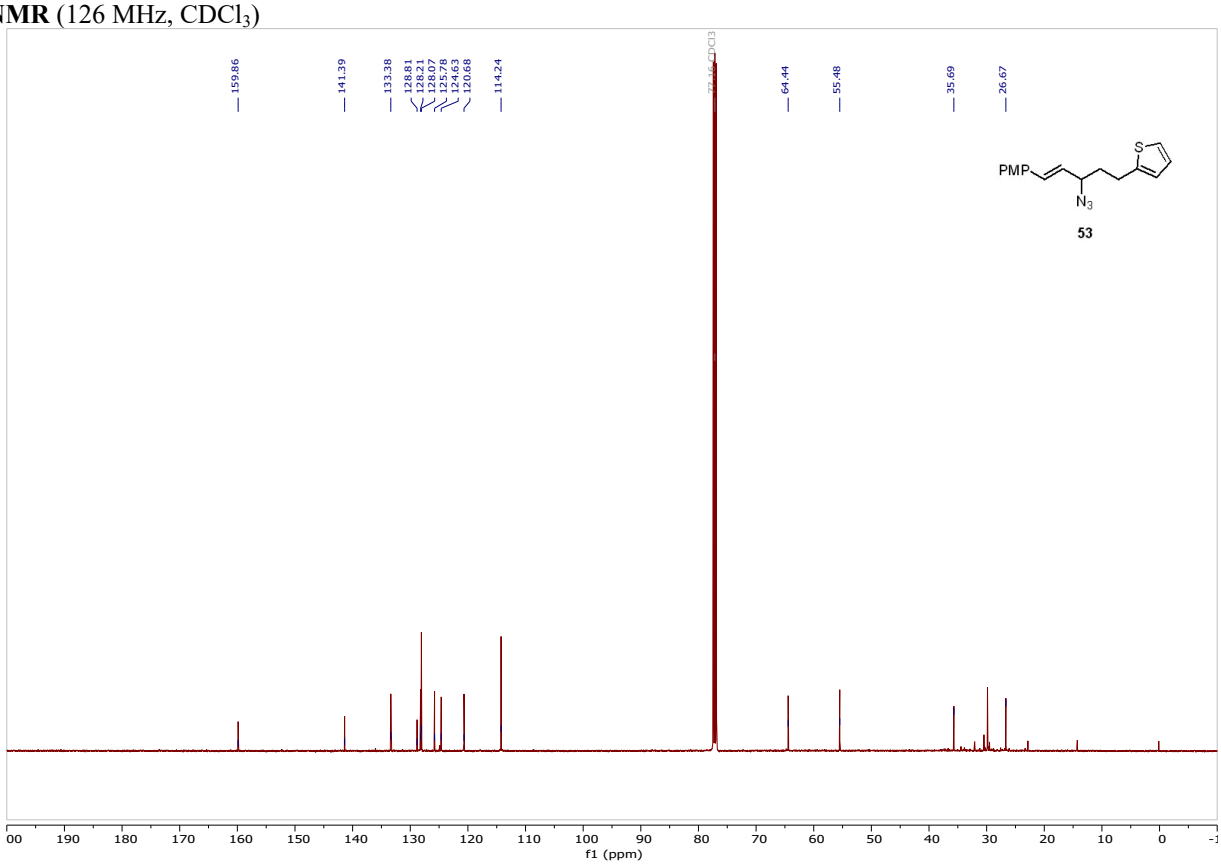


Compound 53

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

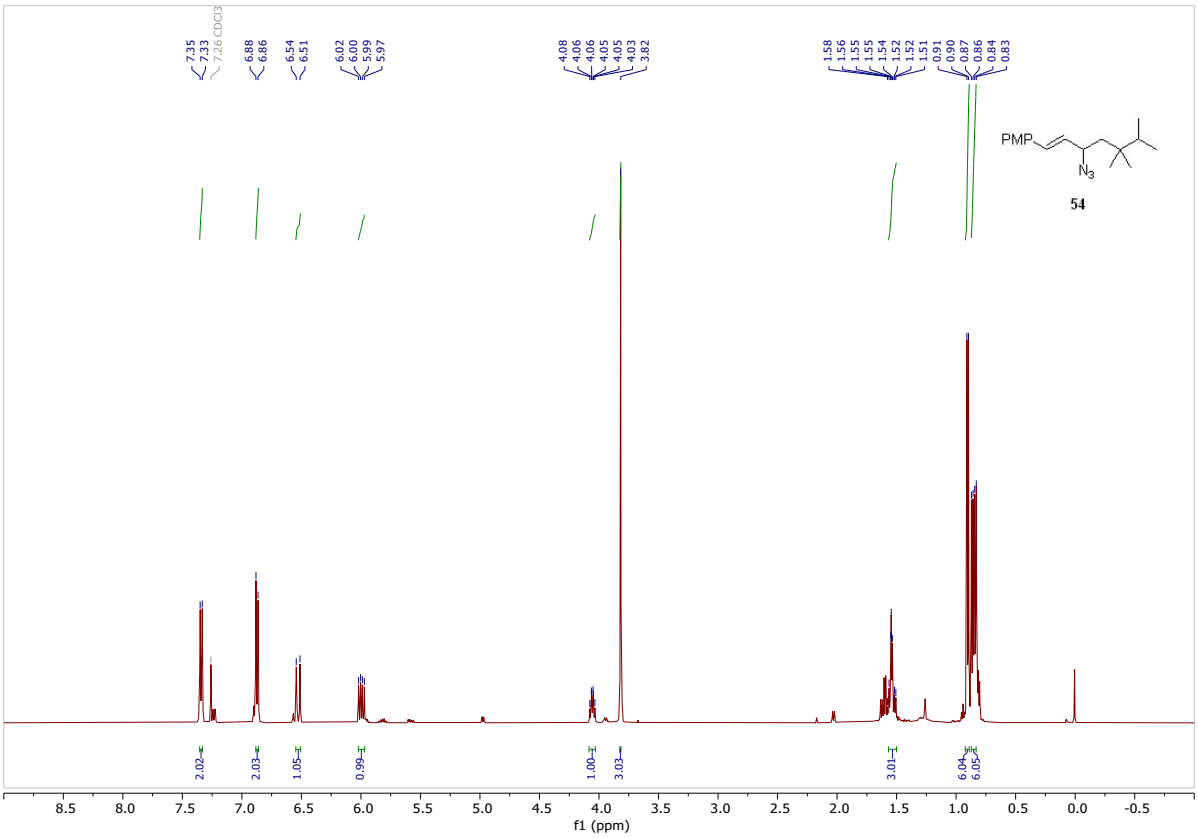


^{13}C NMR (126 MHz, $CDCl_3$)

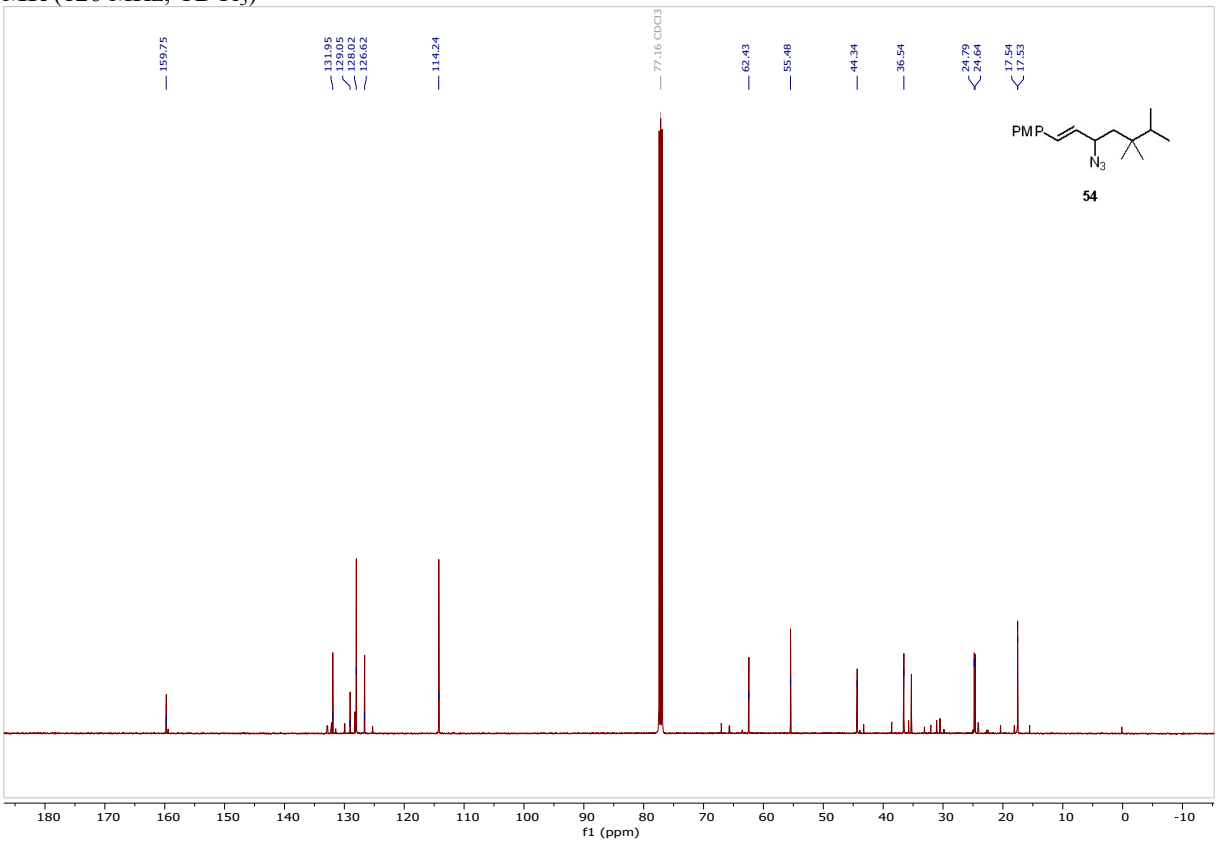


Compound 54

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

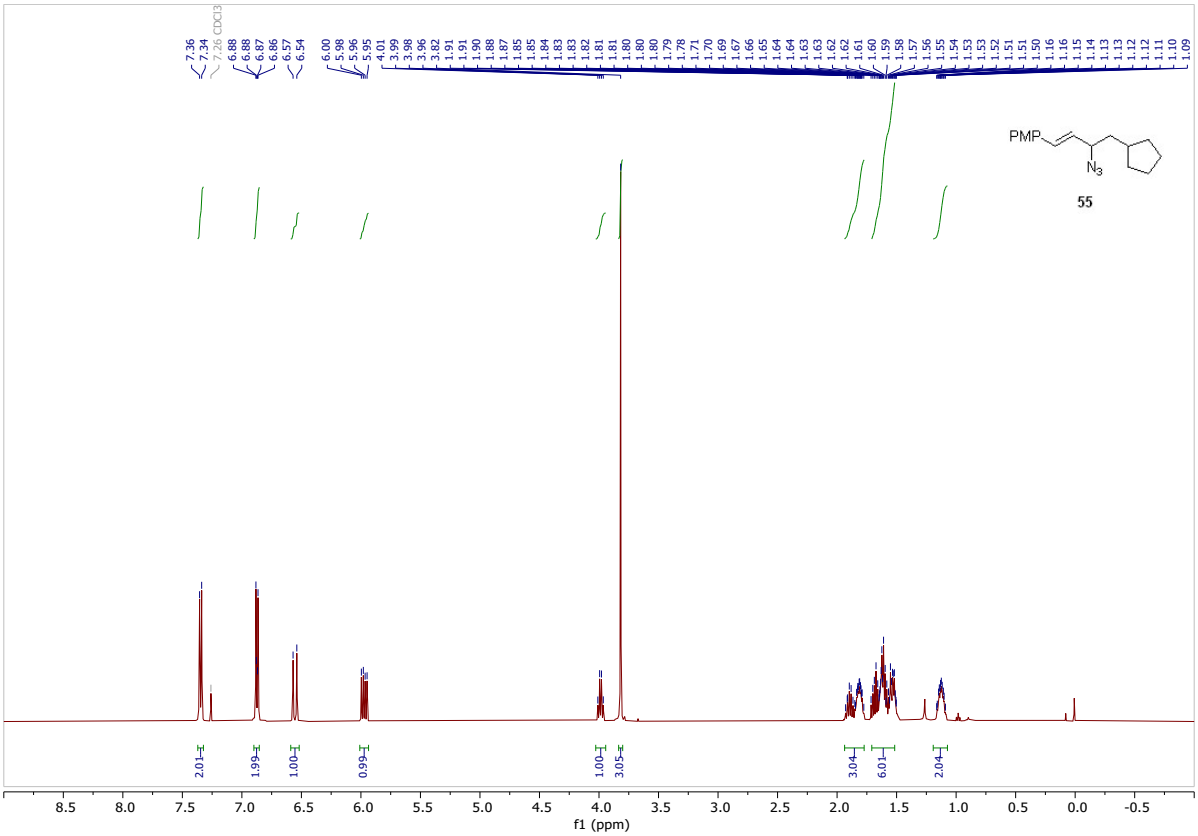


^{13}C NMR (126 MHz, $CDCl_3$)

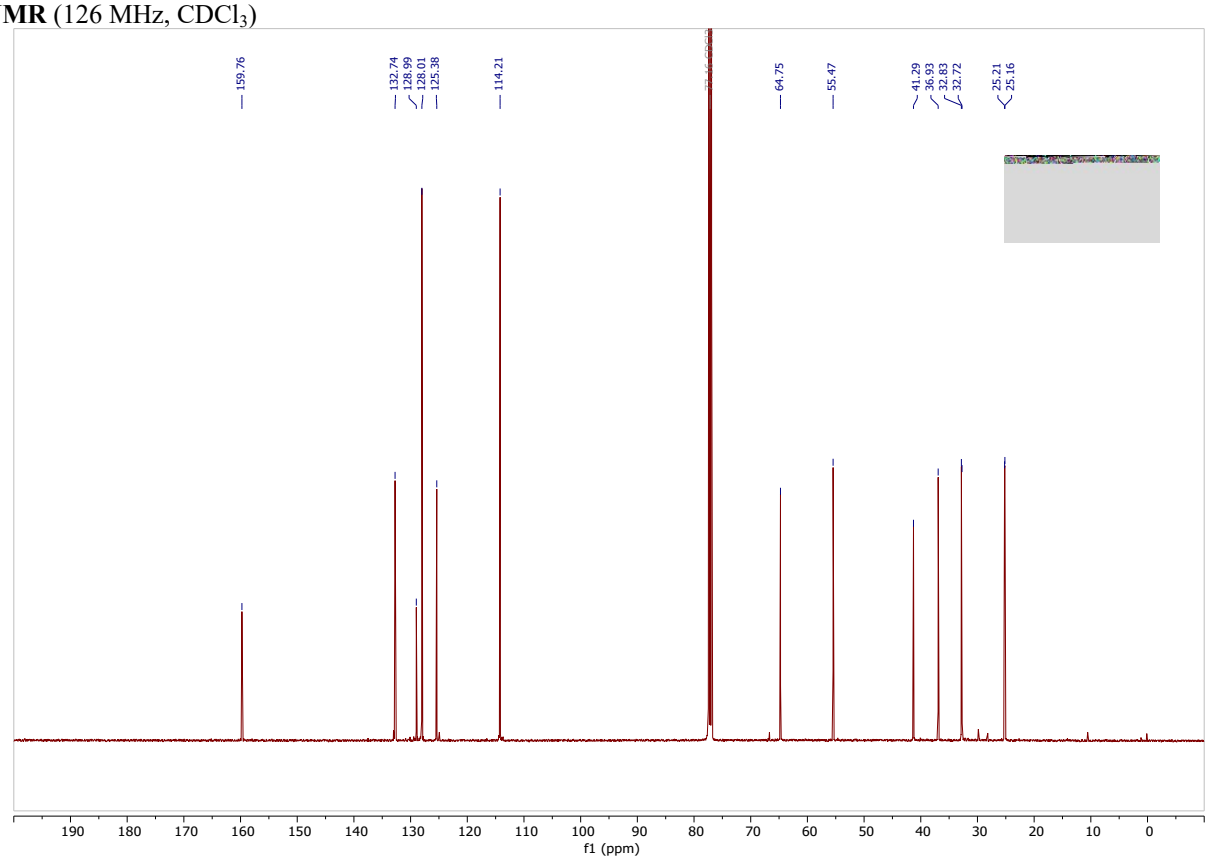


Compound 55

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

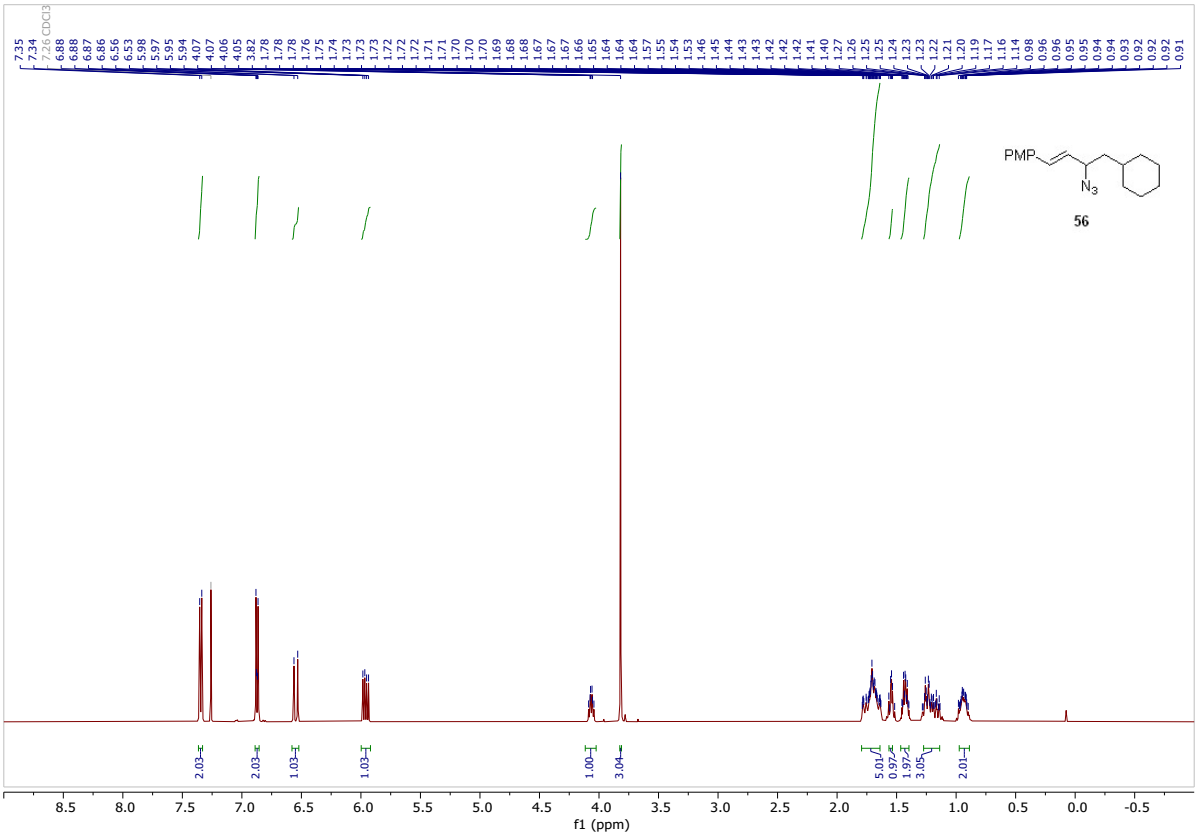


^{13}C NMR (126 MHz, $CDCl_3$)

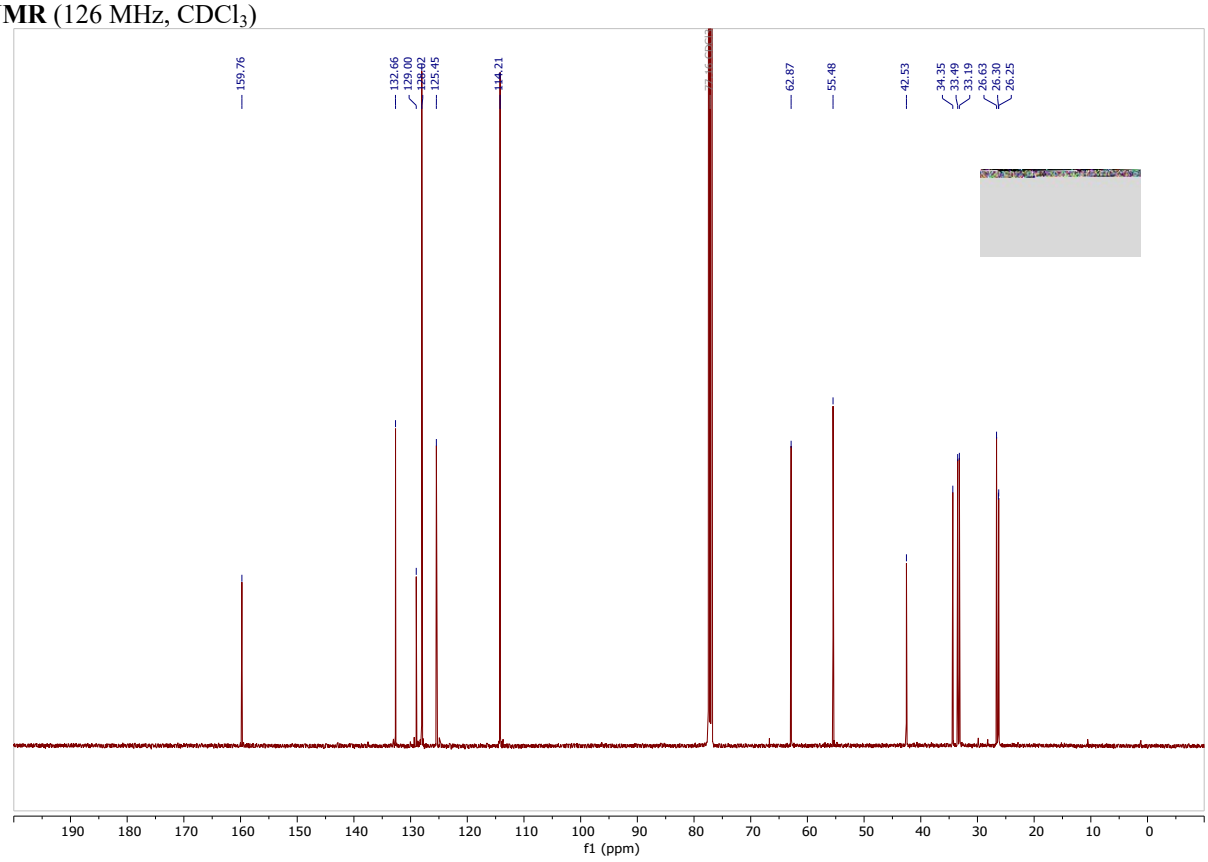


Compound 56

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

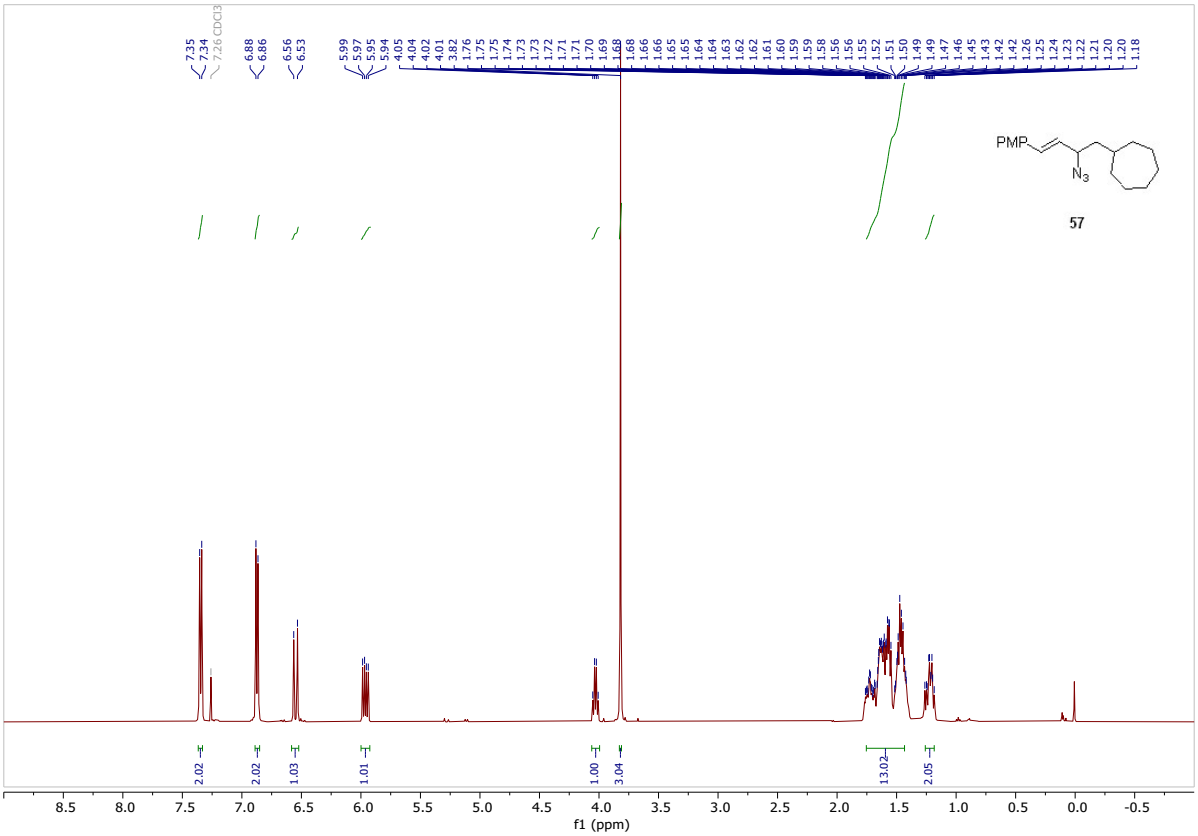


^{13}C NMR (126 MHz, $CDCl_3$)

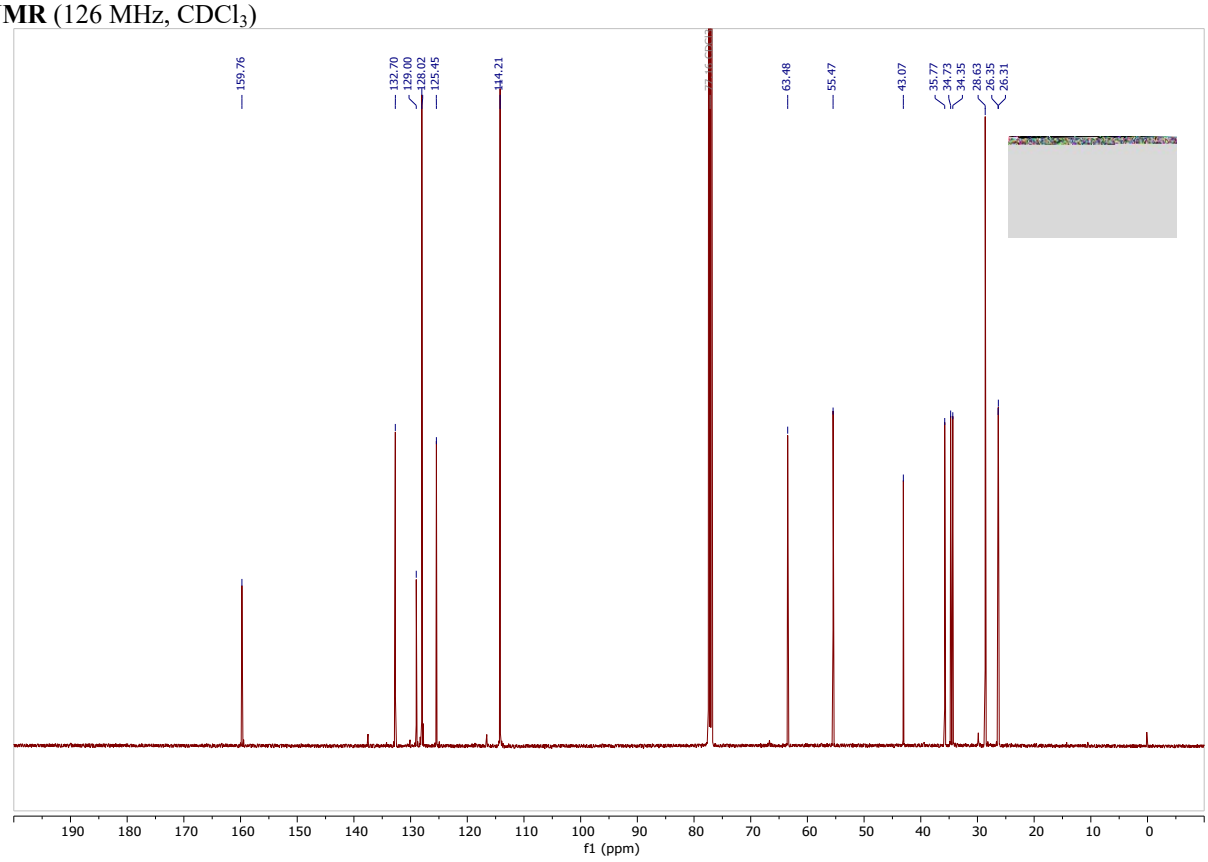


Compound 57

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

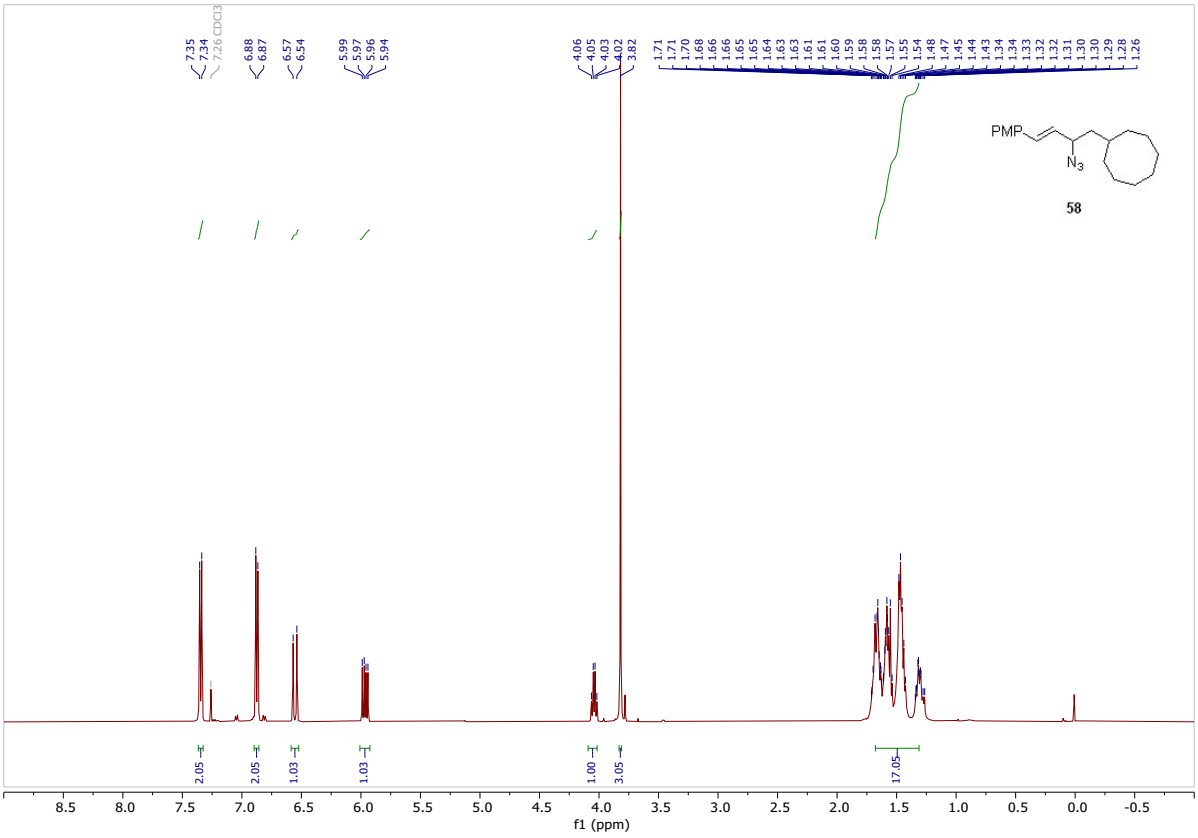


^{13}C NMR (126 MHz, $CDCl_3$)

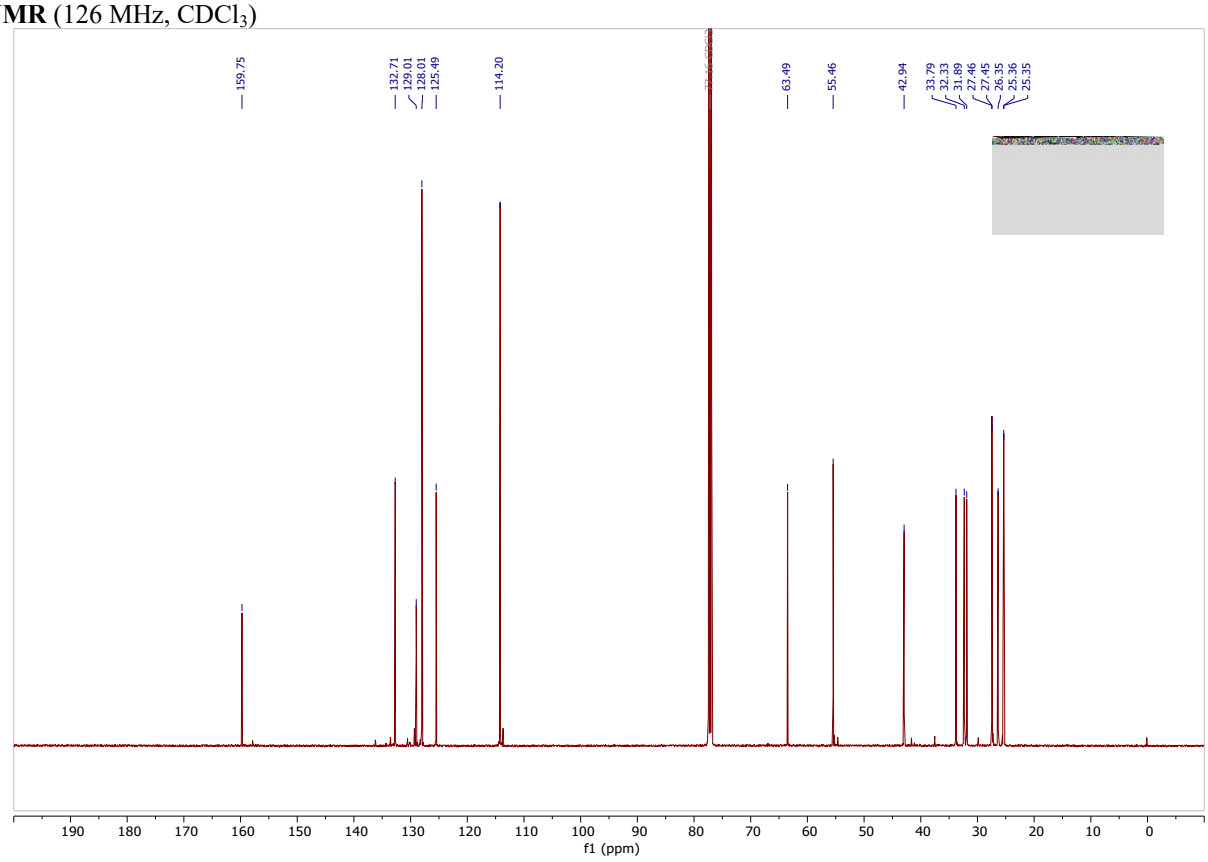


Compound 58

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

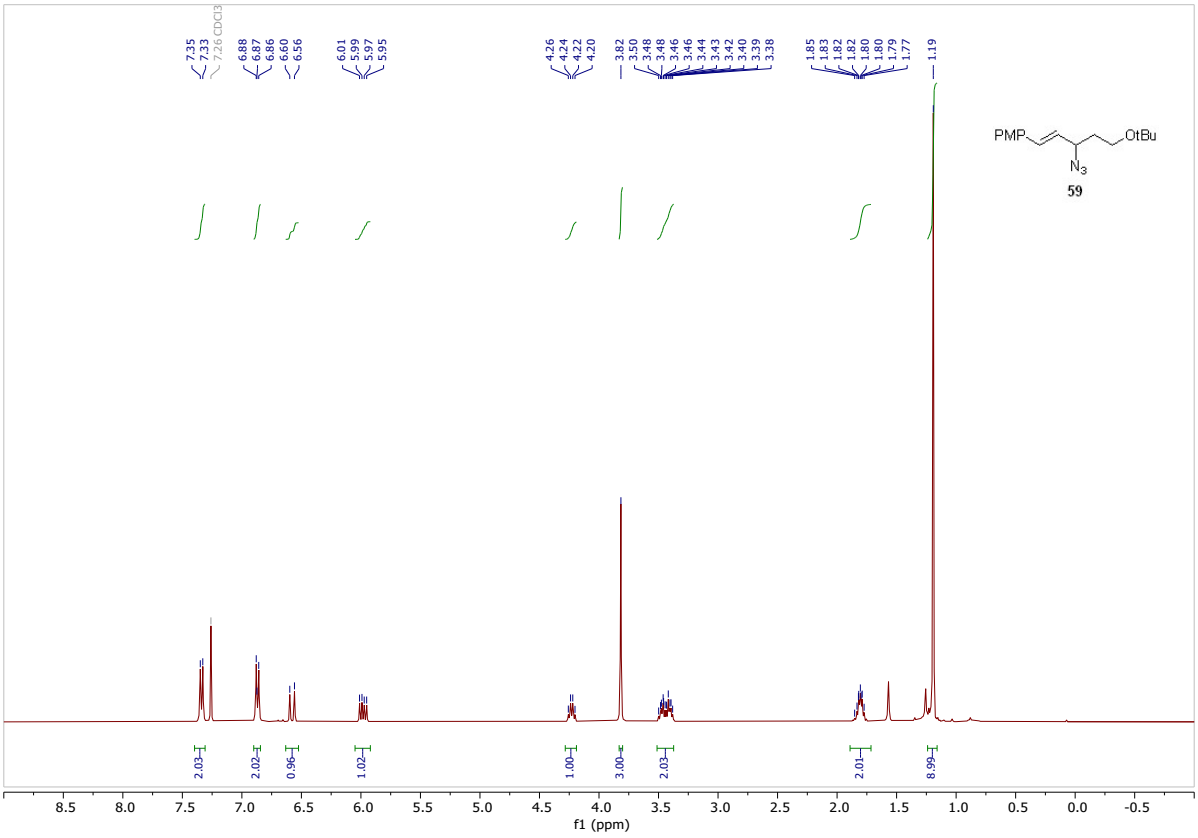


^{13}C NMR (126 MHz, $CDCl_3$)

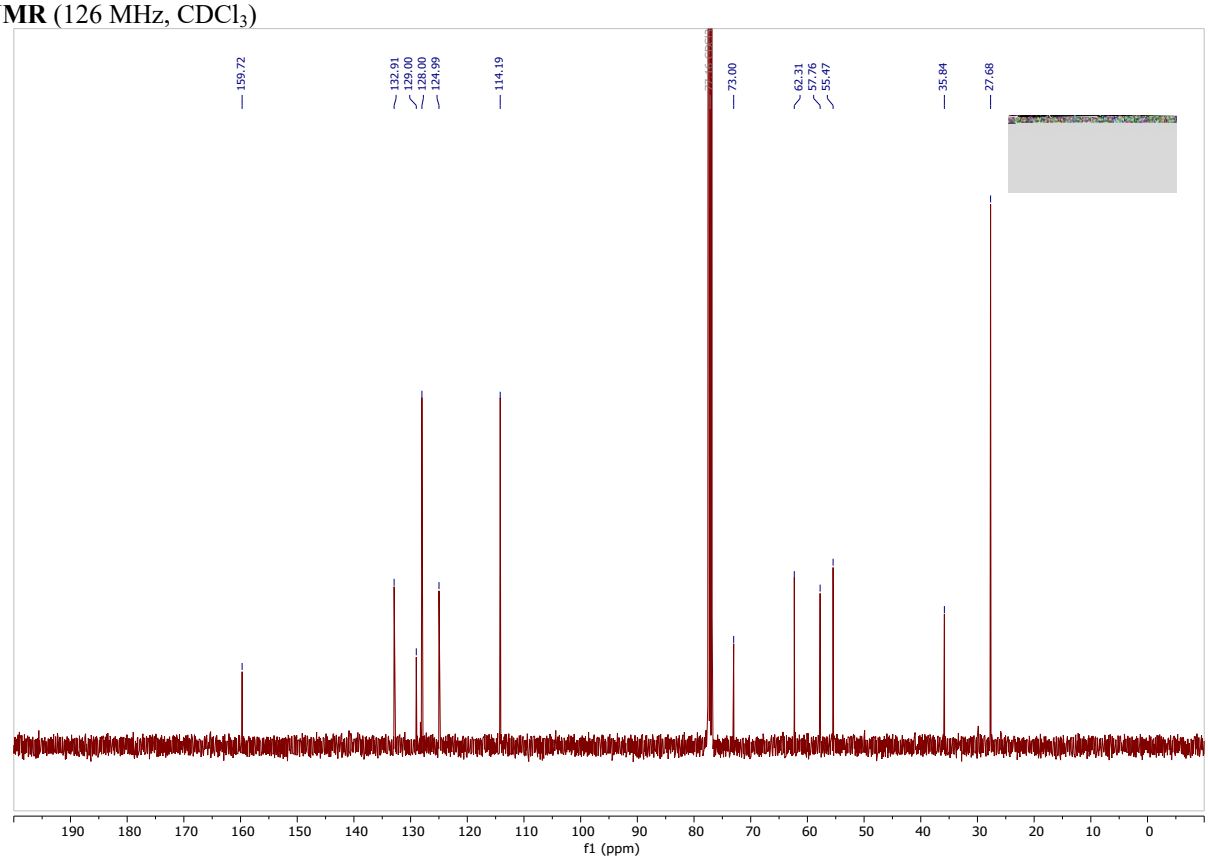


Compound 59

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

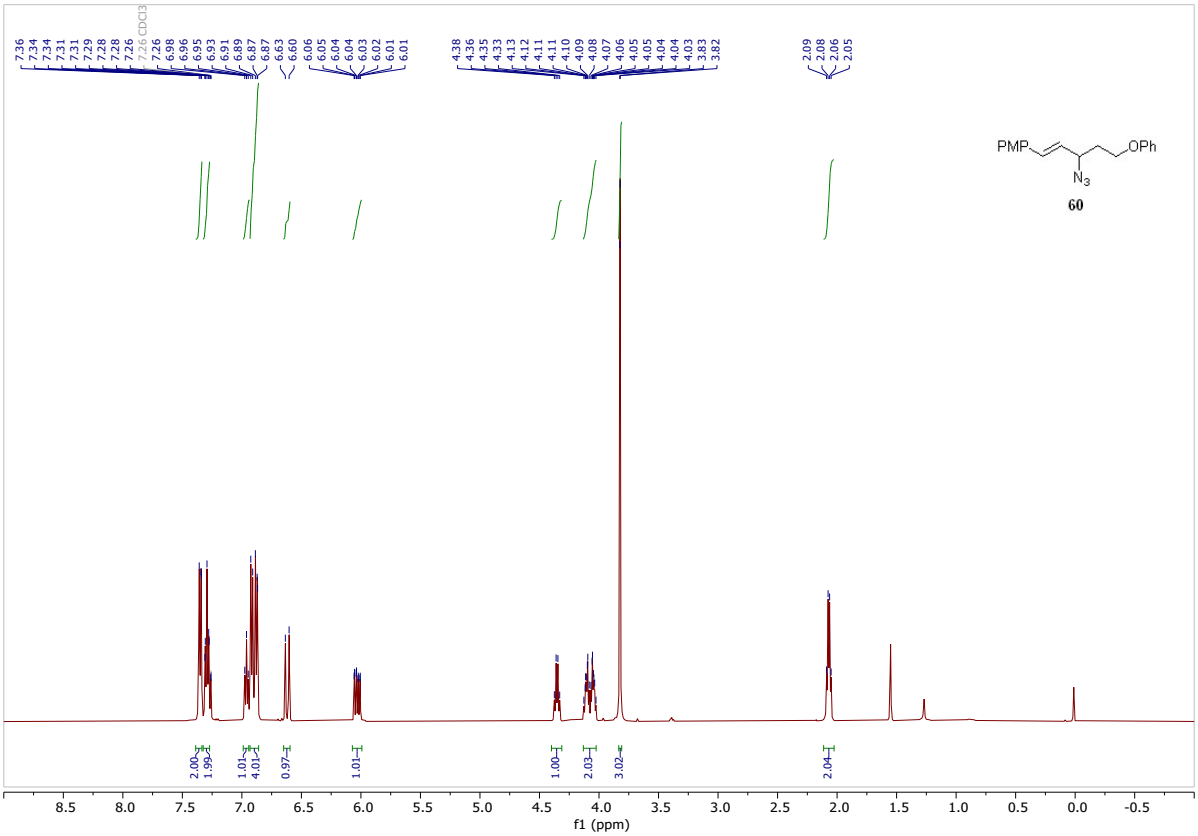


^{13}C NMR (126 MHz, $CDCl_3$)

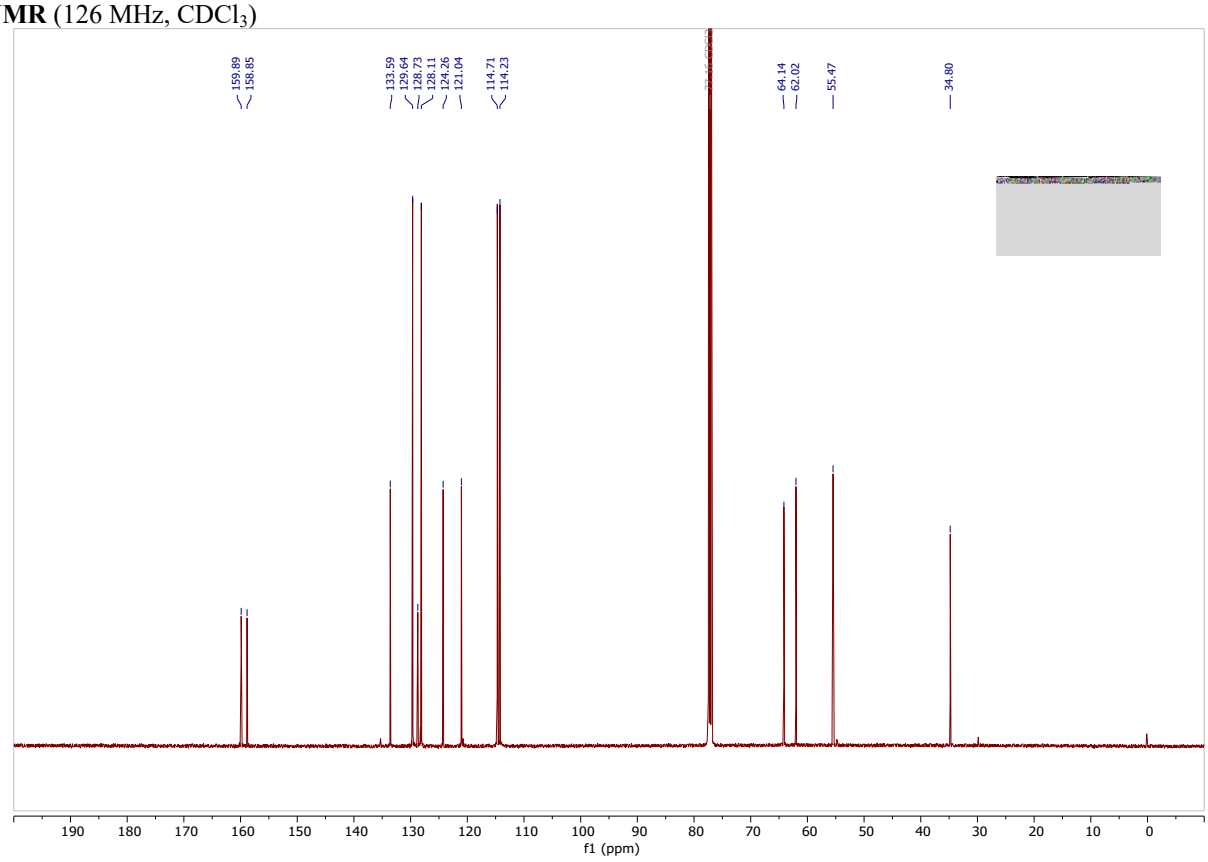


Compound 60

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

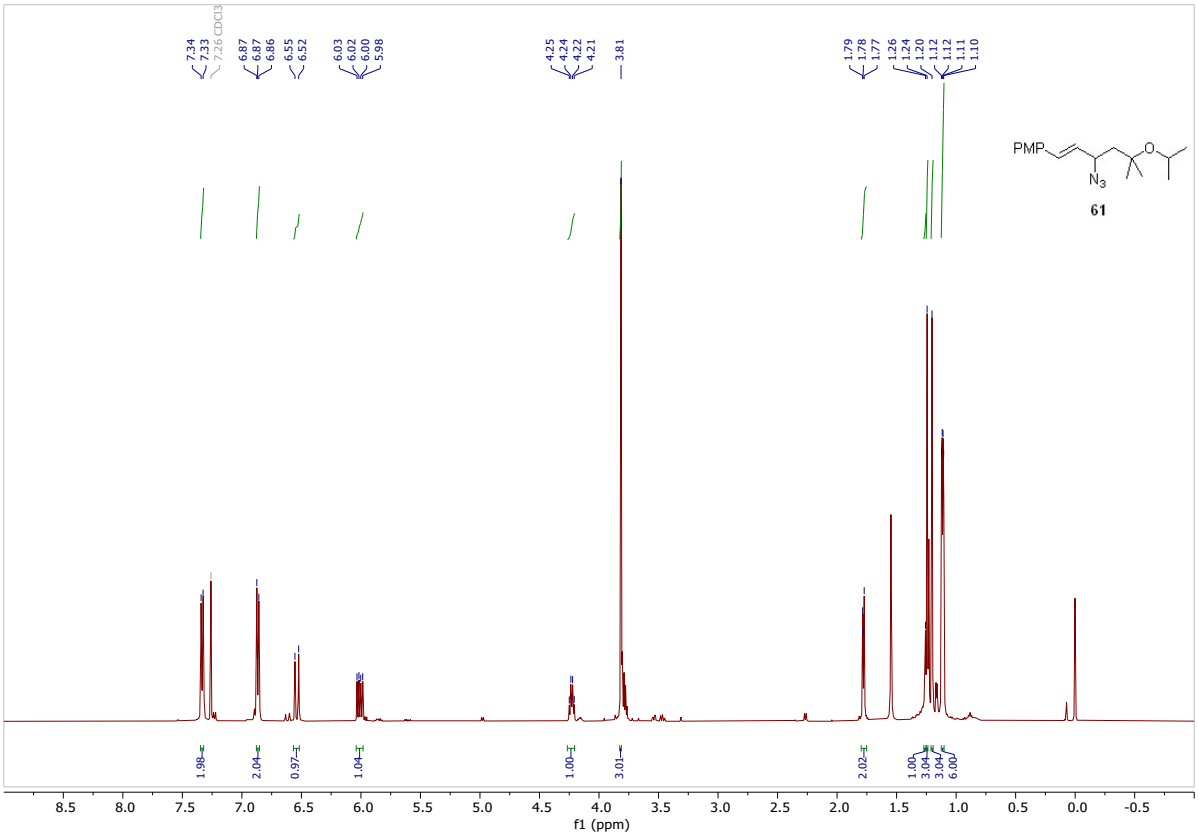


^{13}C NMR (126 MHz, $CDCl_3$)

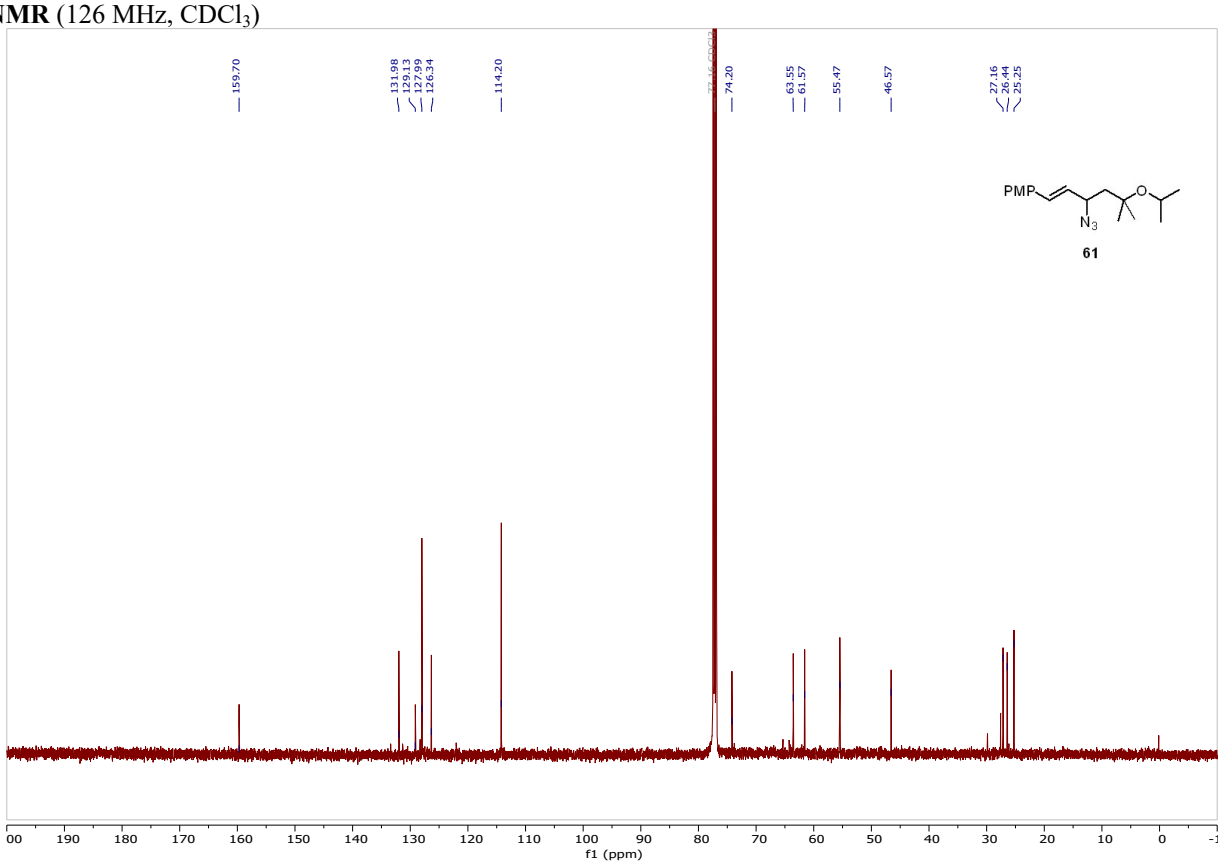


Compound 61

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

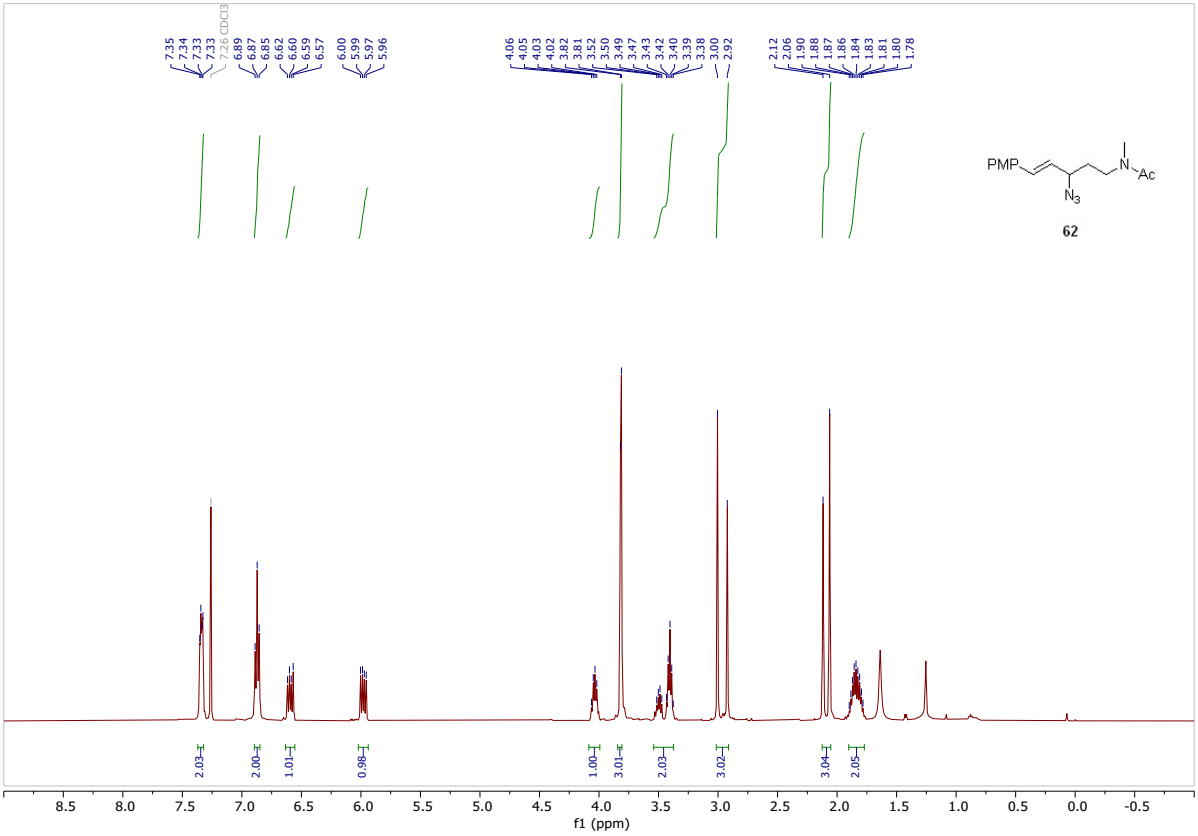


^{13}C NMR (126 MHz, $CDCl_3$)

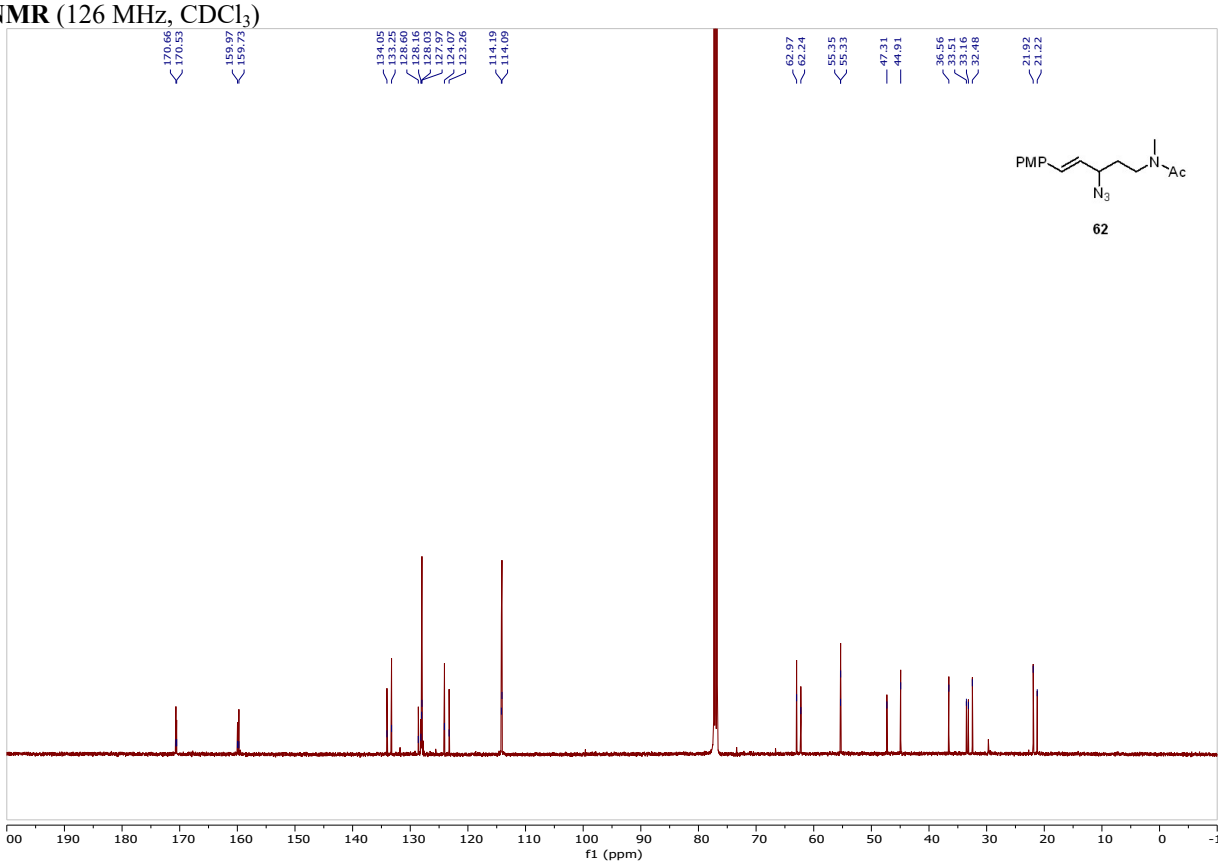


Compound 62

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

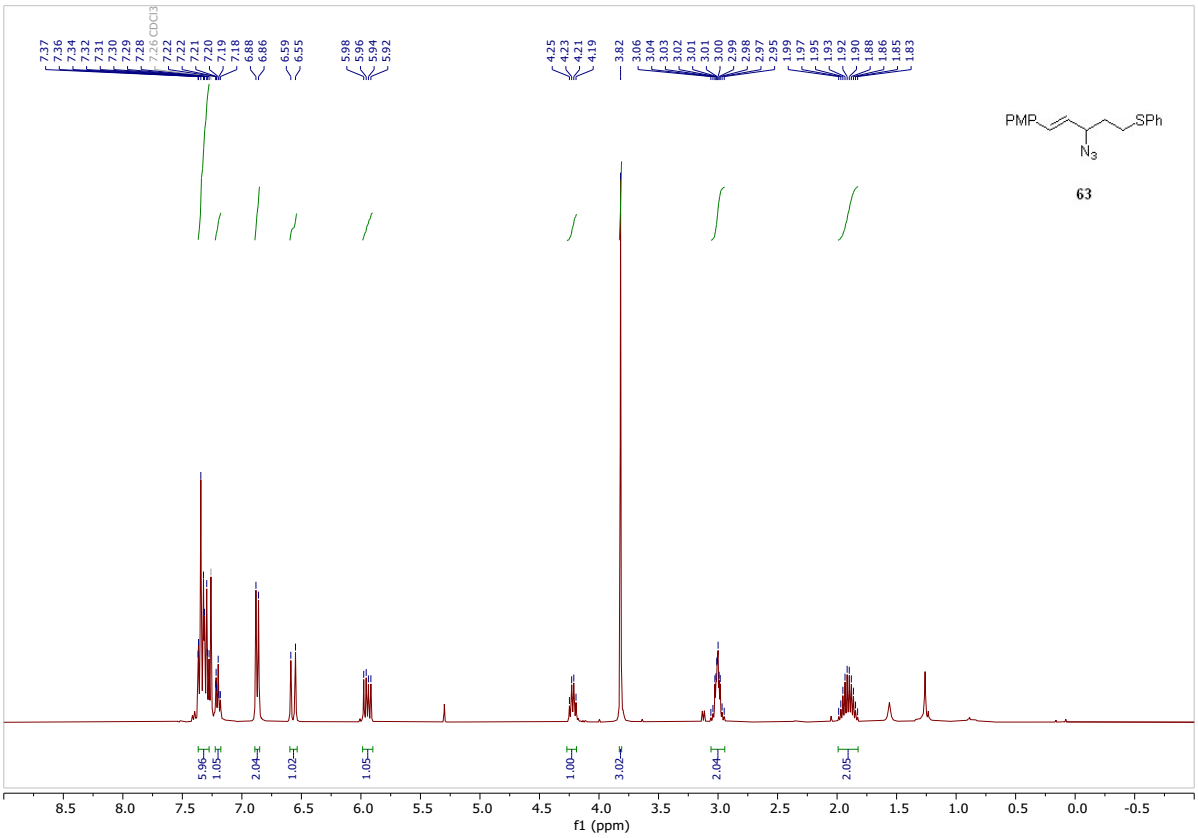


^{13}C NMR (126 MHz, $CDCl_3$)

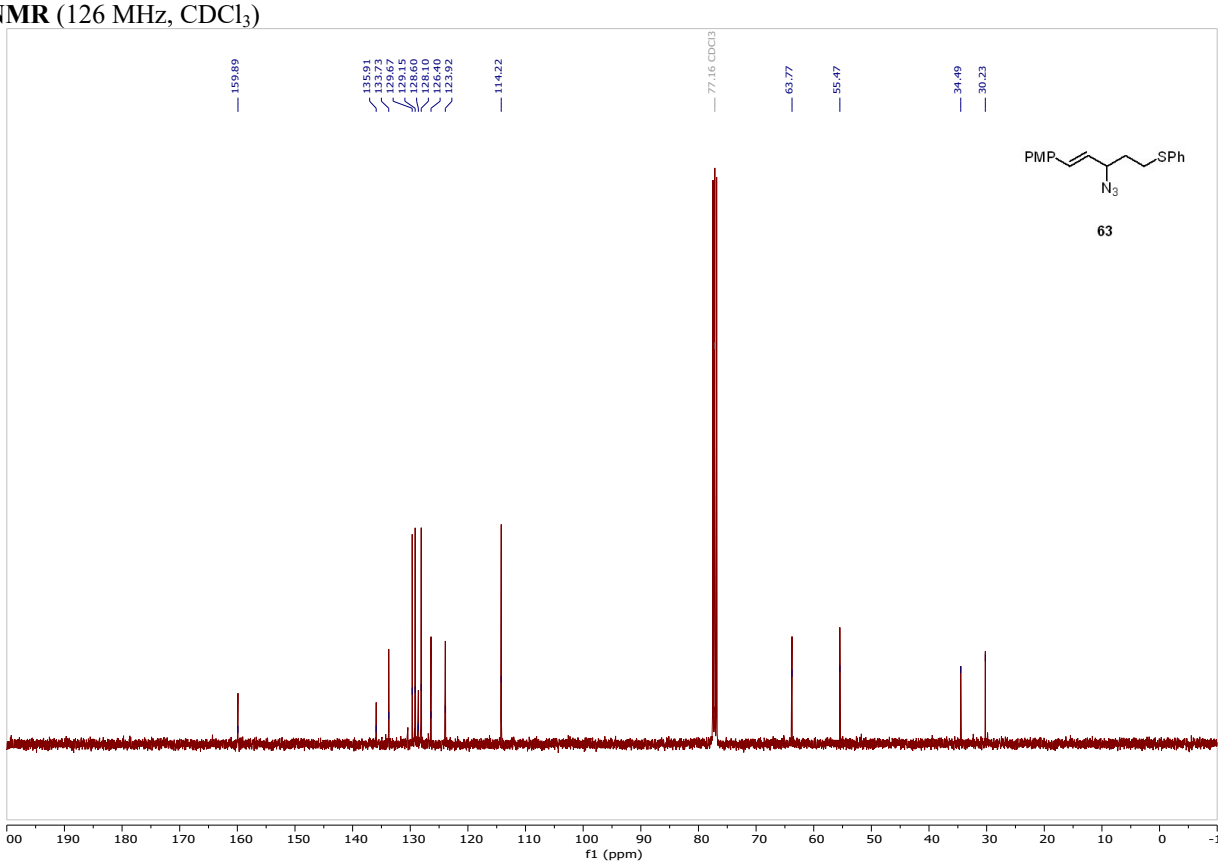


Compound 63

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

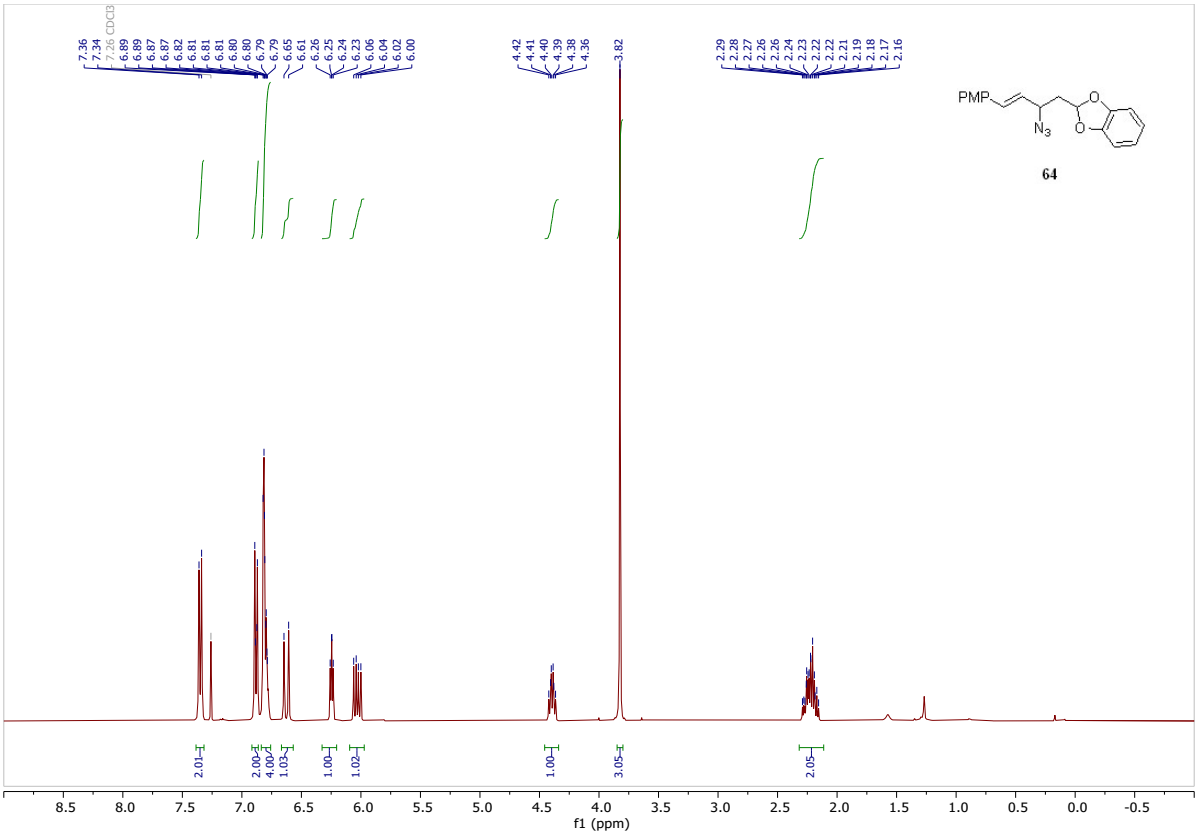


^{13}C NMR (126 MHz, $CDCl_3$)

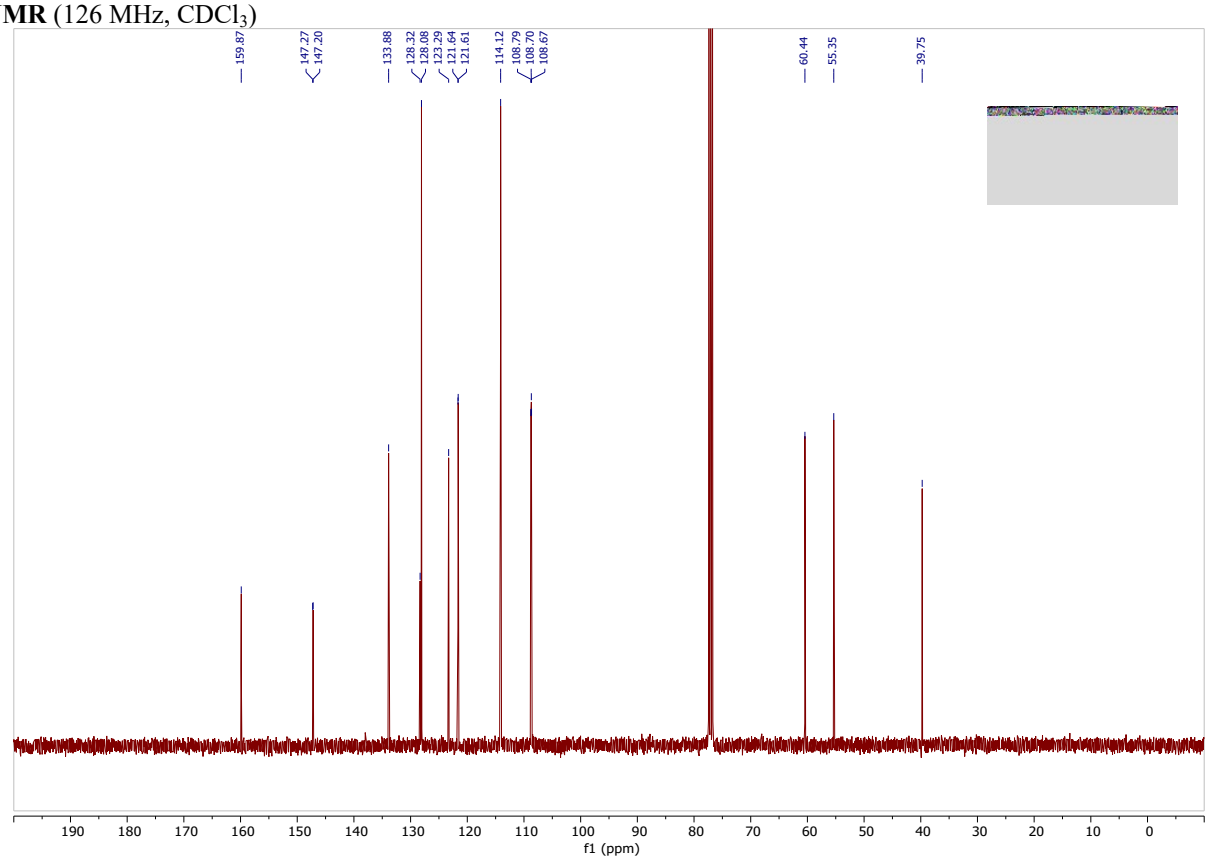


Compound 64

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

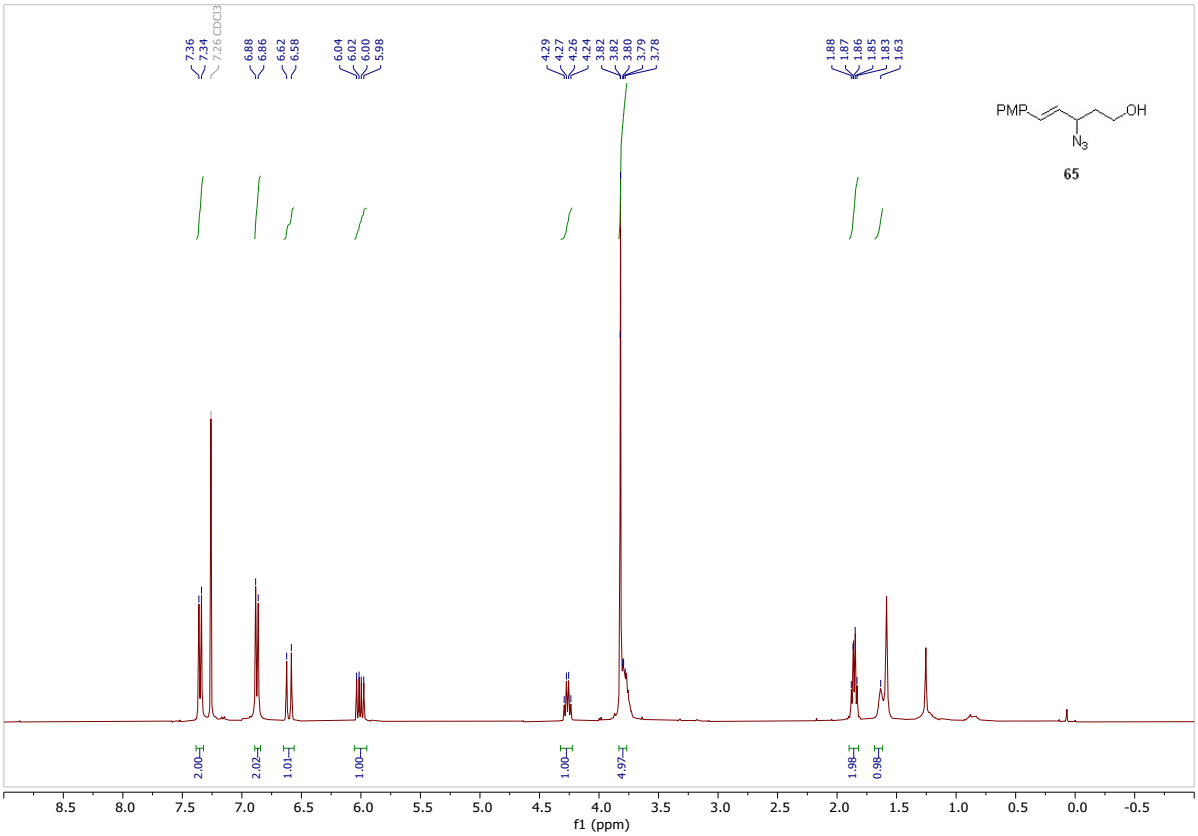


^{13}C NMR (126 MHz, $CDCl_3$)

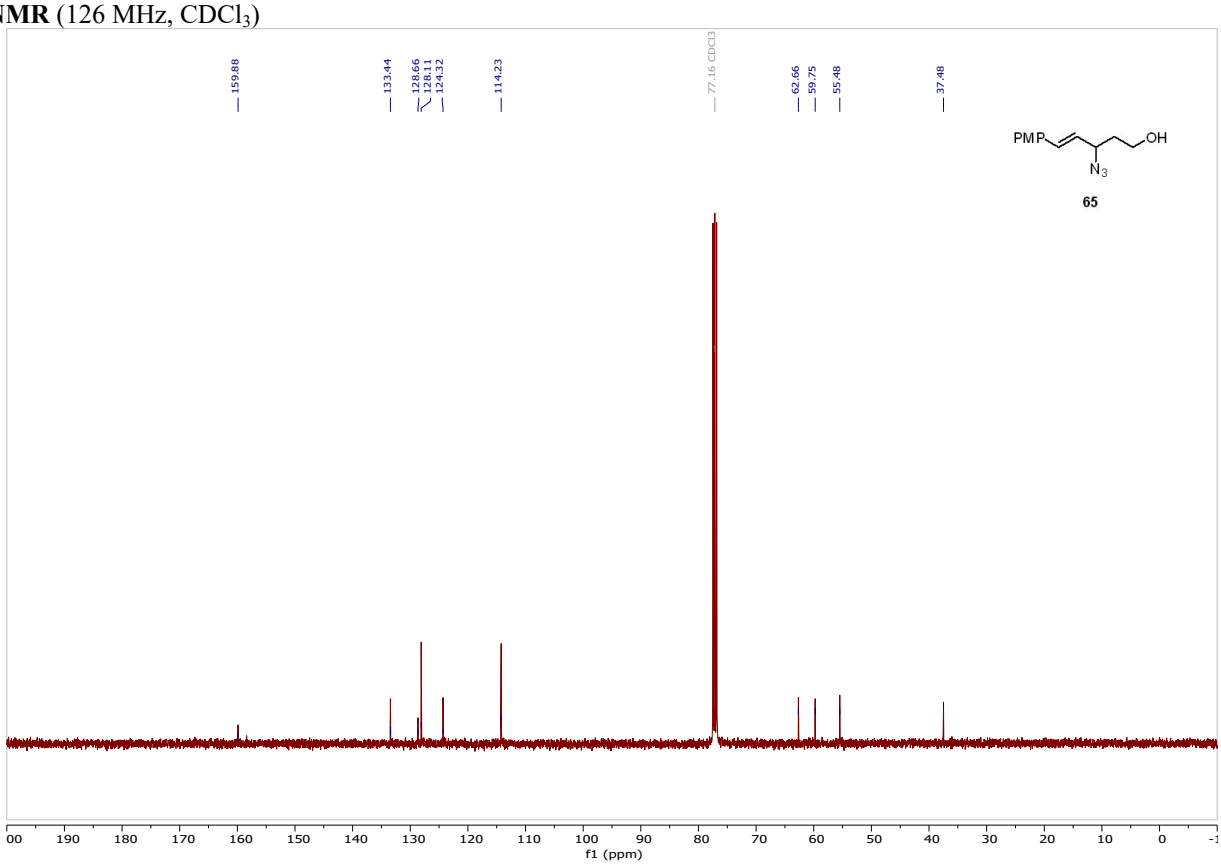


Compound 65

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

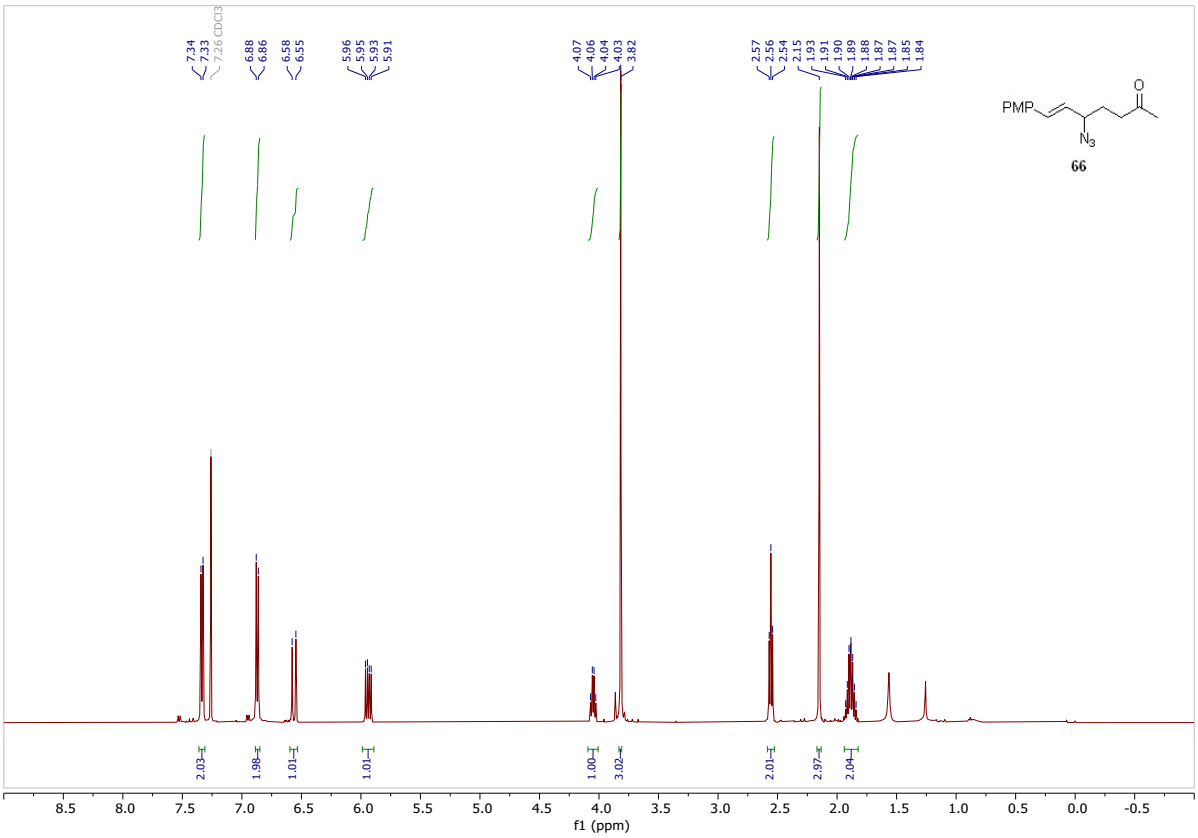


^{13}C NMR (126 MHz, $CDCl_3$)

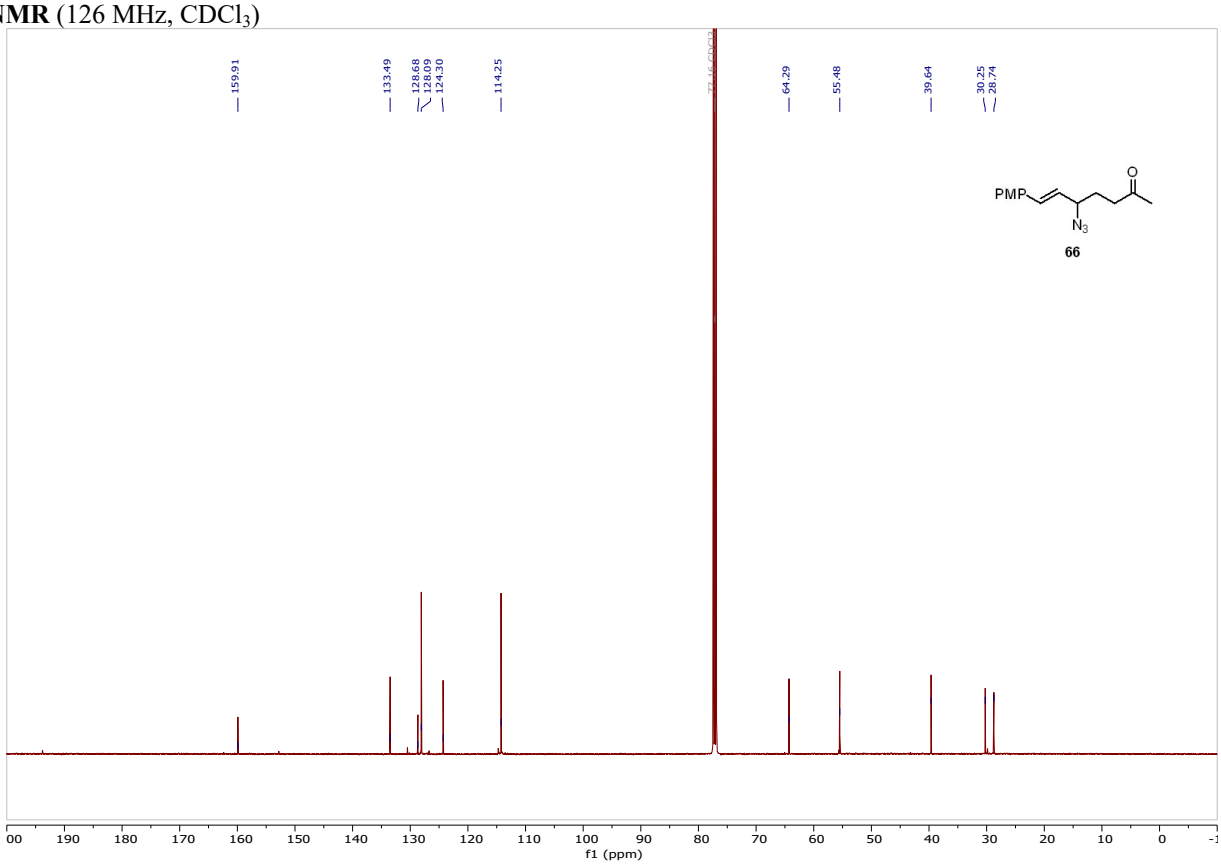


Compound 66

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

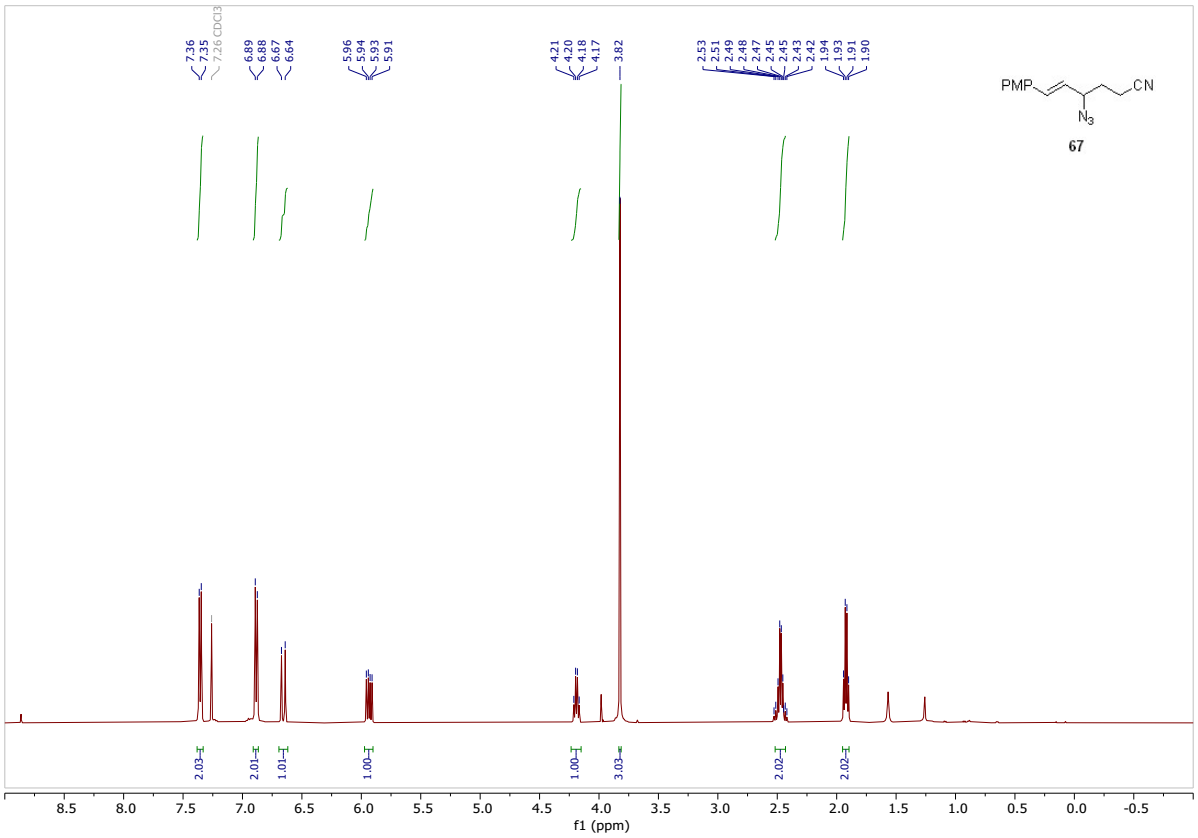


^{13}C NMR (126 MHz, $CDCl_3$)

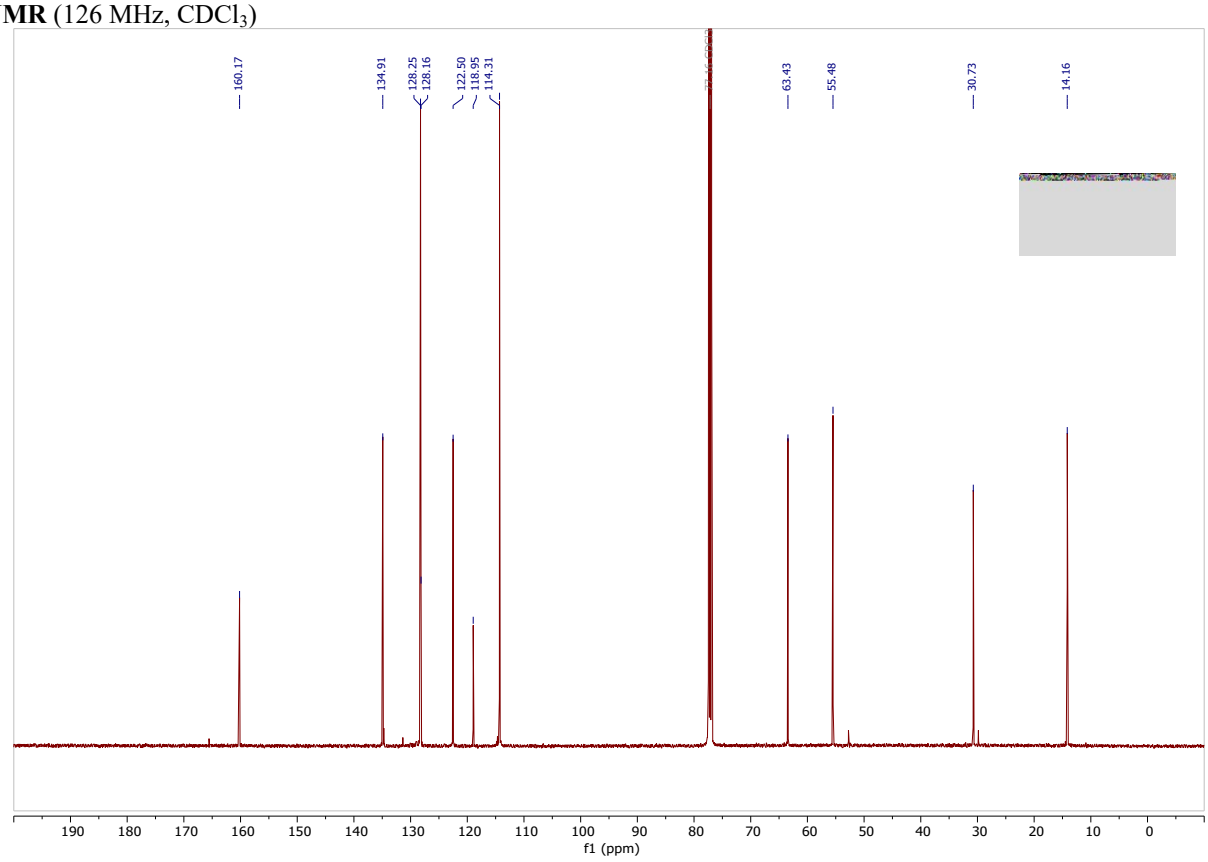


Compound 67

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

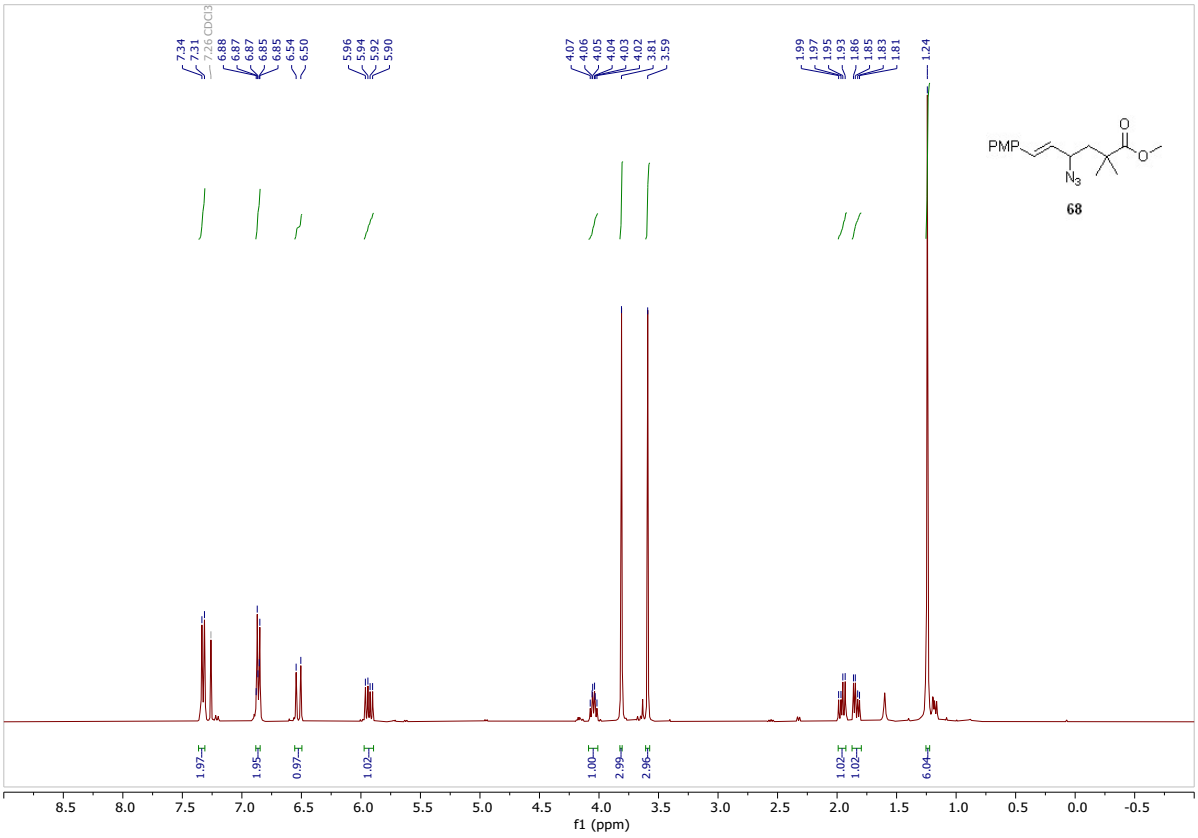


^{13}C NMR (126 MHz, $CDCl_3$)

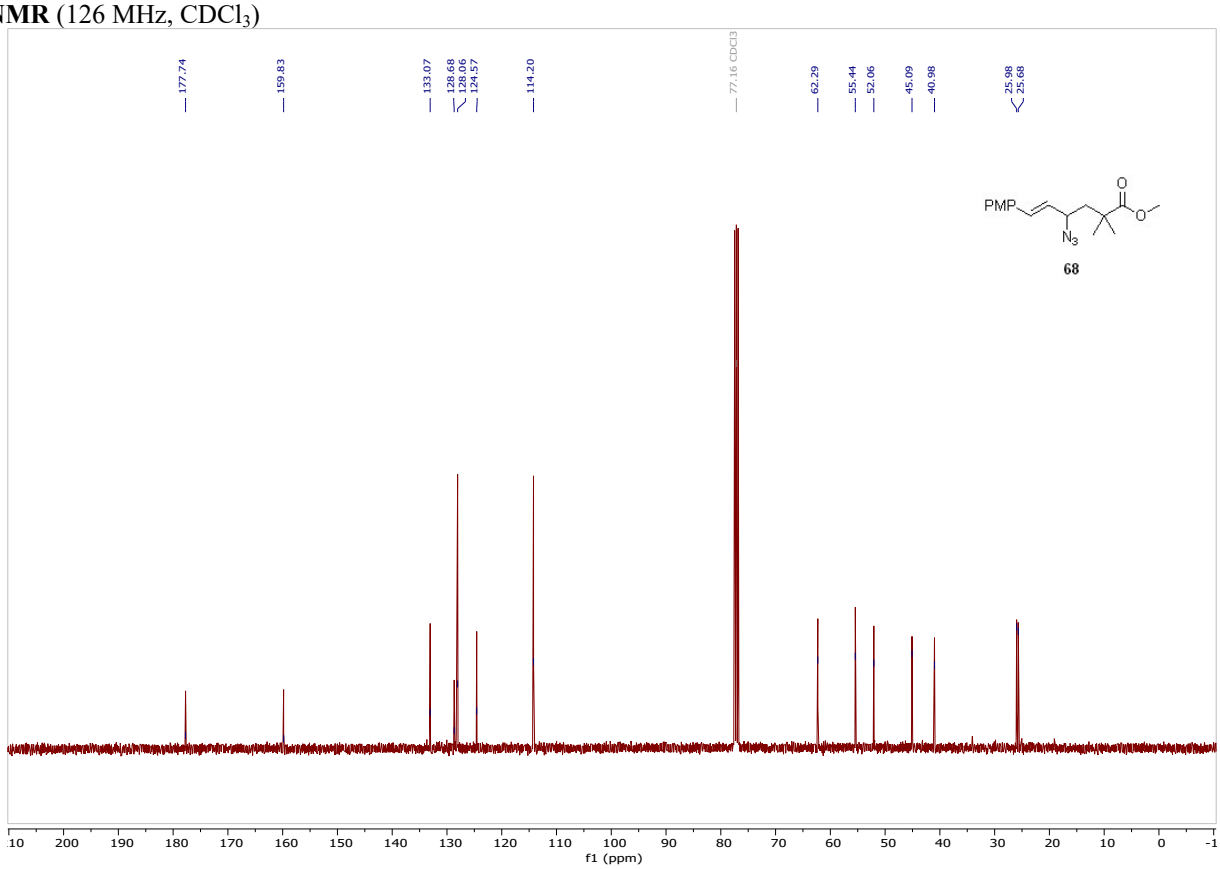


Compound 68

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

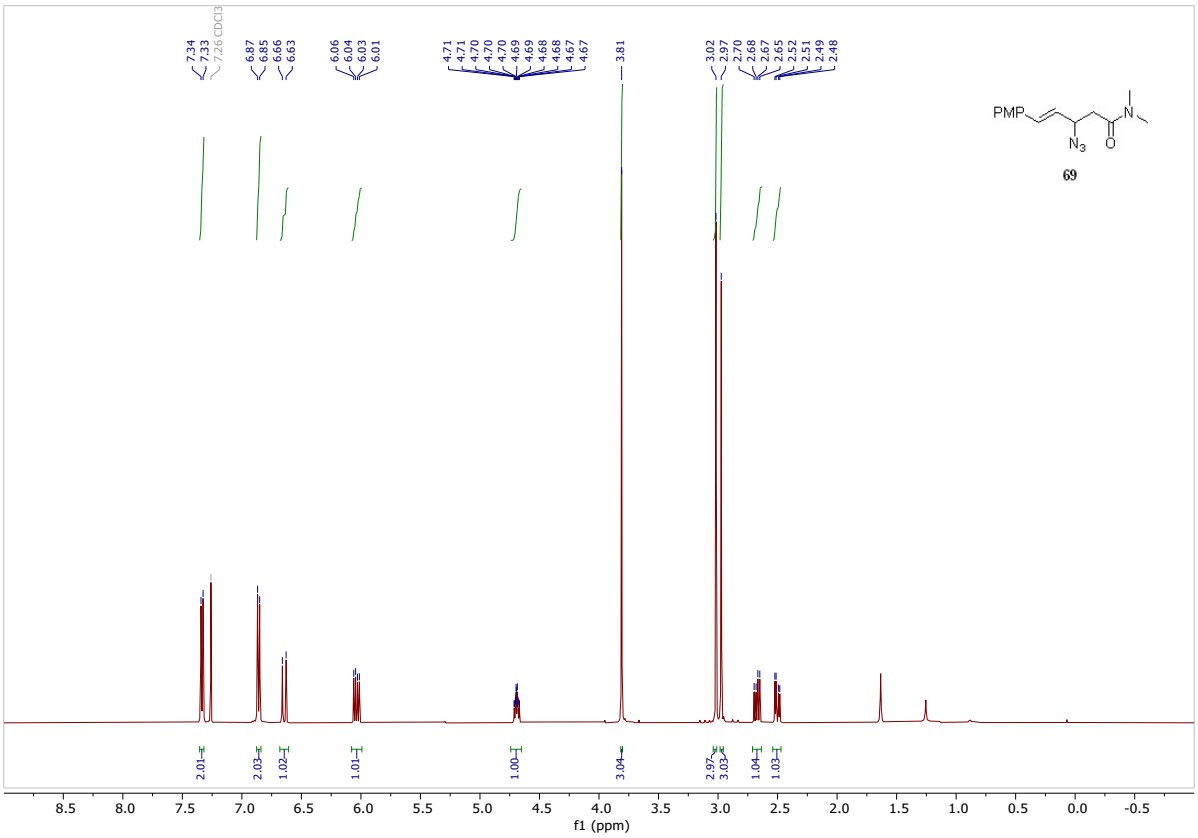


^{13}C NMR (126 MHz, $CDCl_3$)

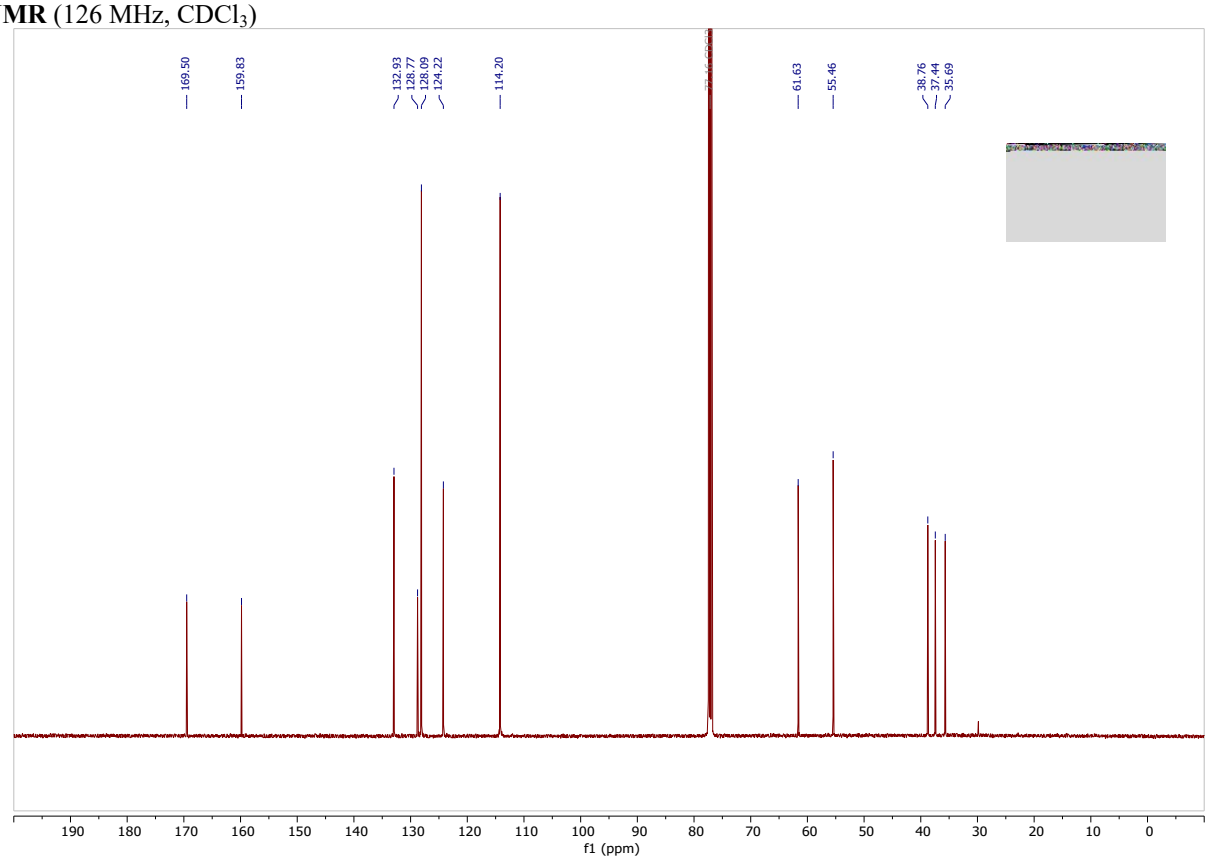


Compound 69

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

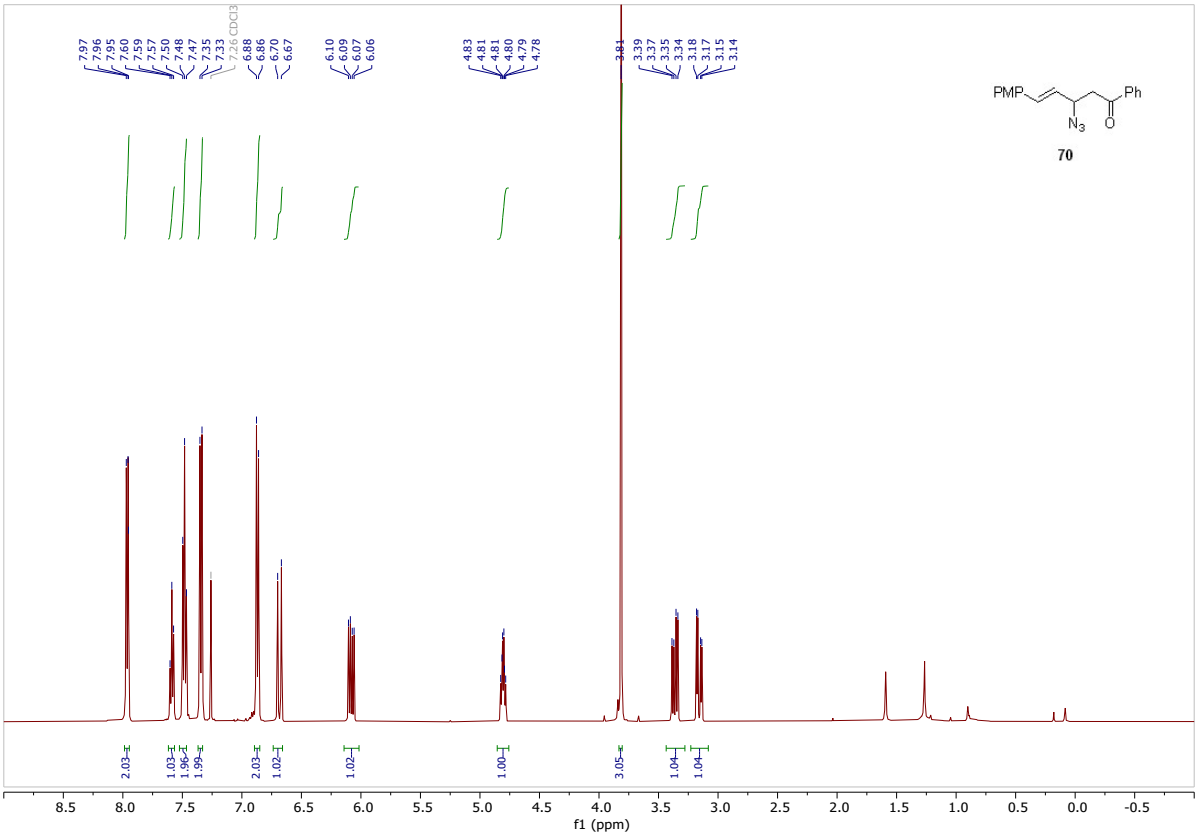


^{13}C NMR (126 MHz, $CDCl_3$)

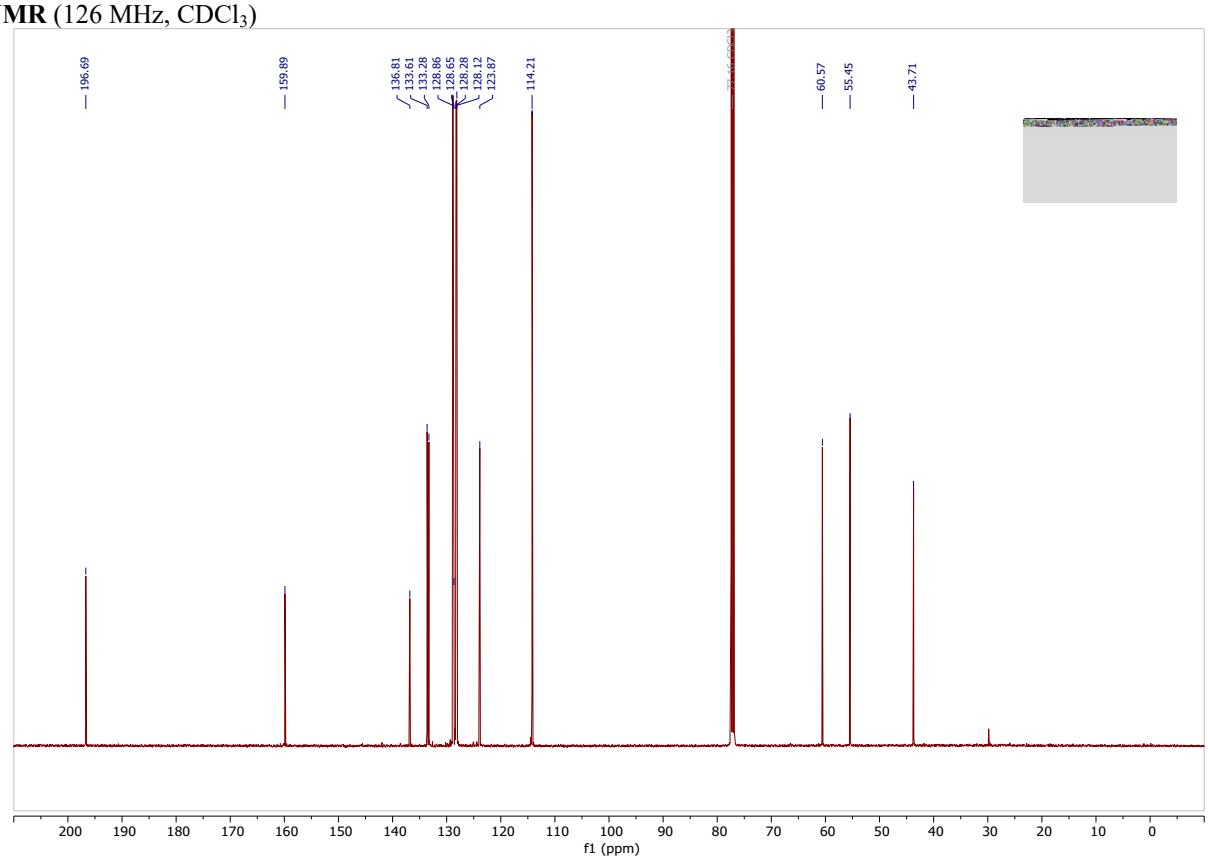


Compound 70

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

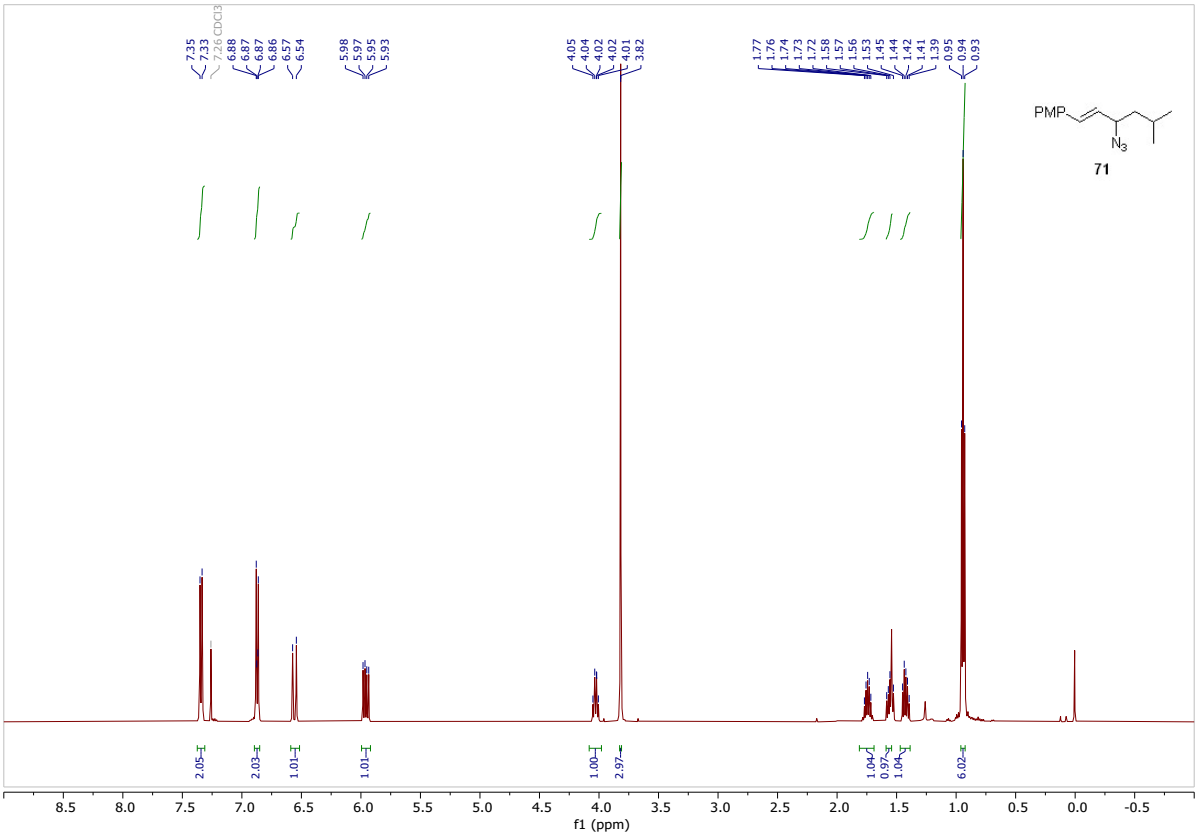


^{13}C NMR (126 MHz, $CDCl_3$)

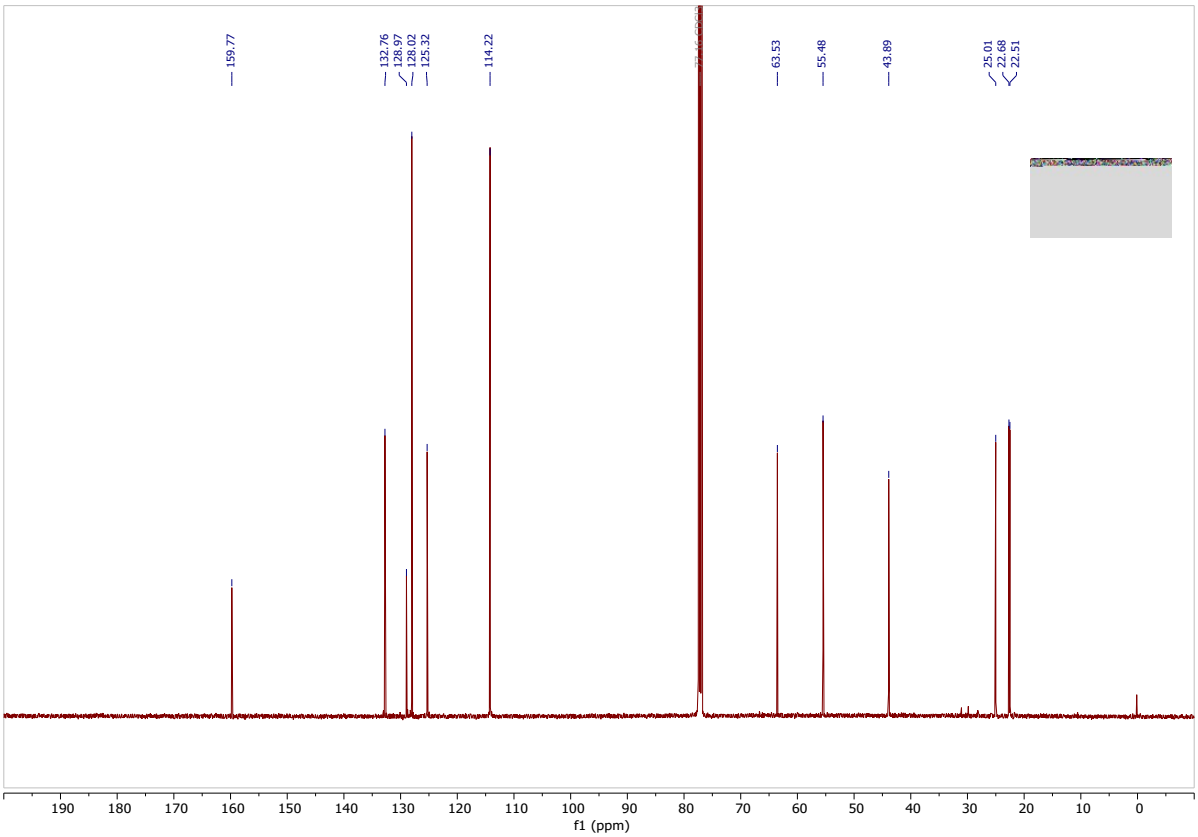


Compound 71

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

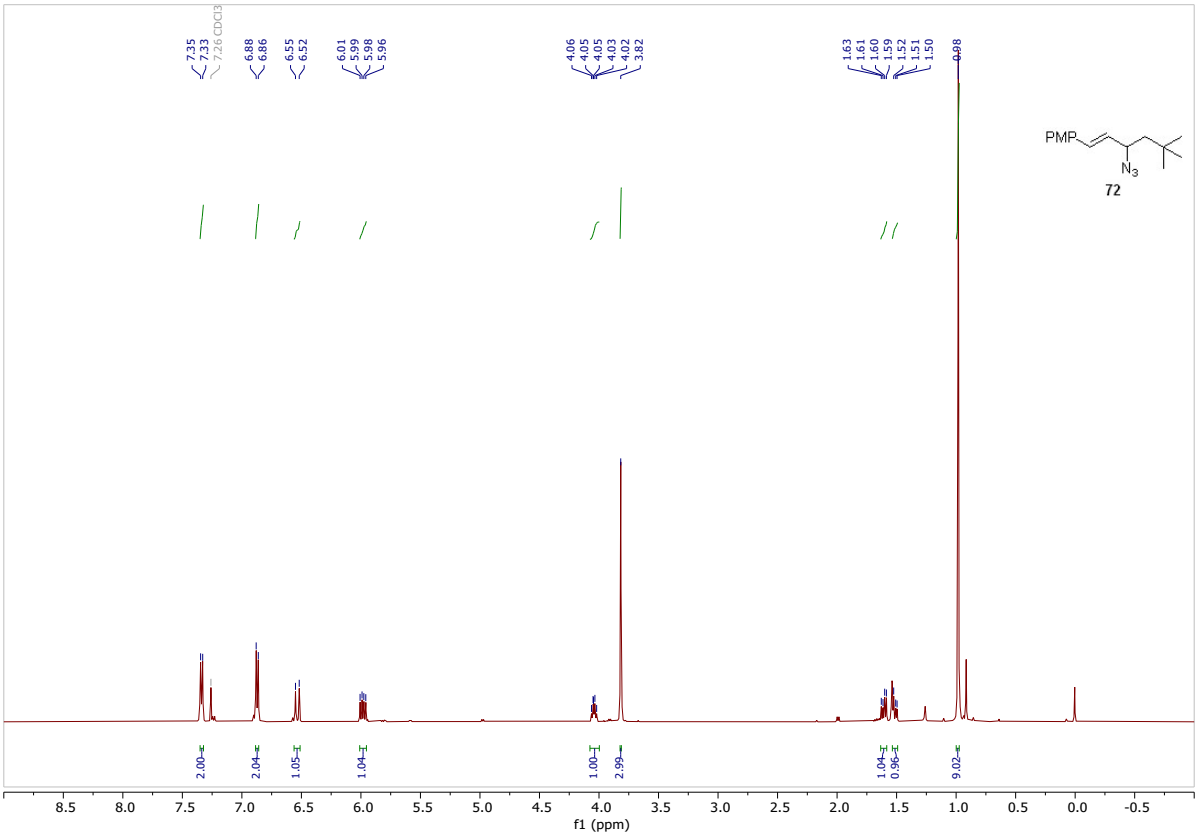


^{13}C NMR (126 MHz, $CDCl_3$)

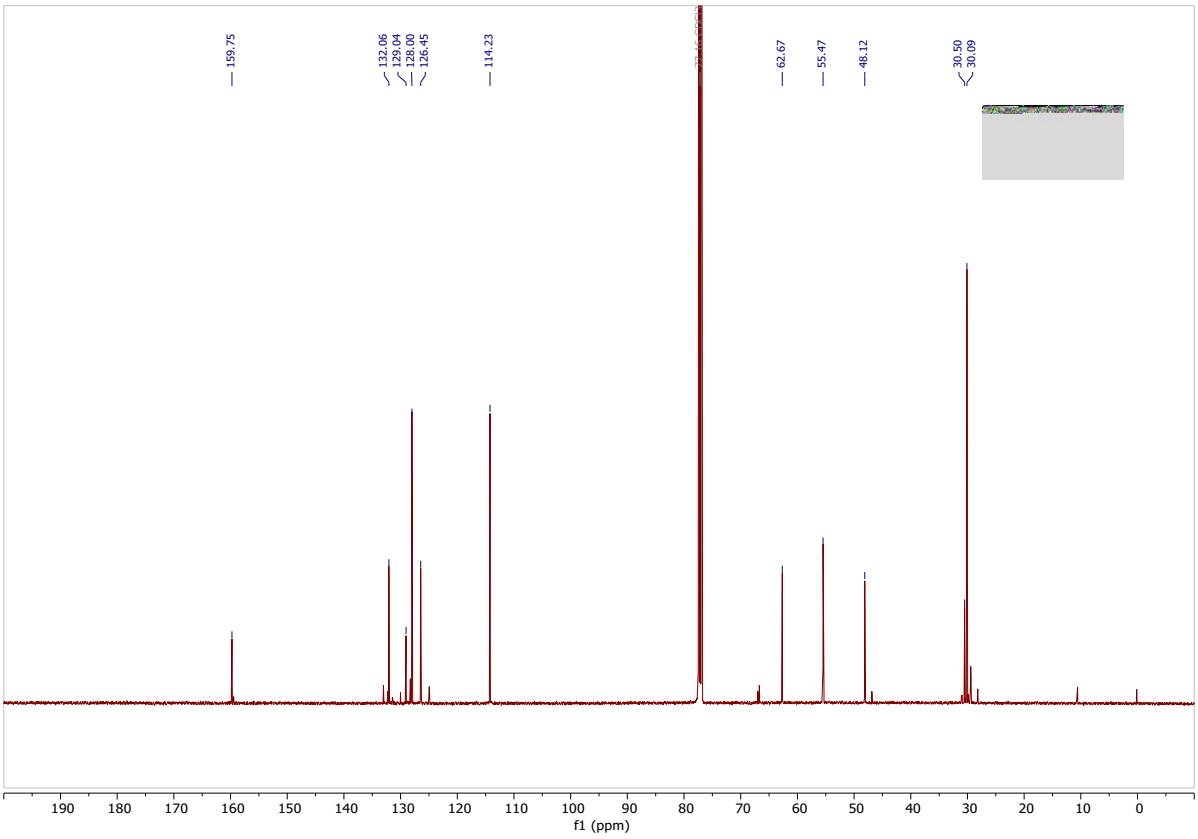


Compound 72

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

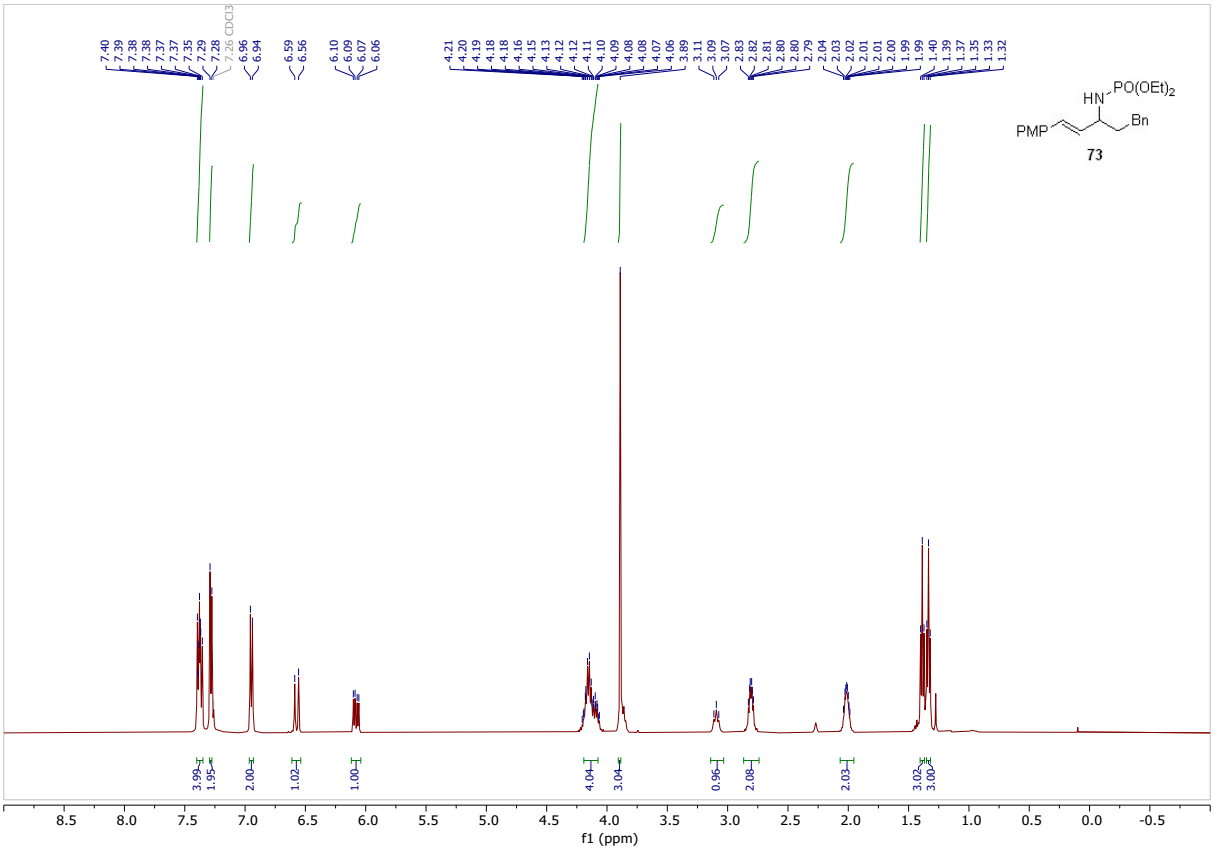


^{13}C NMR (126 MHz, $CDCl_3$)

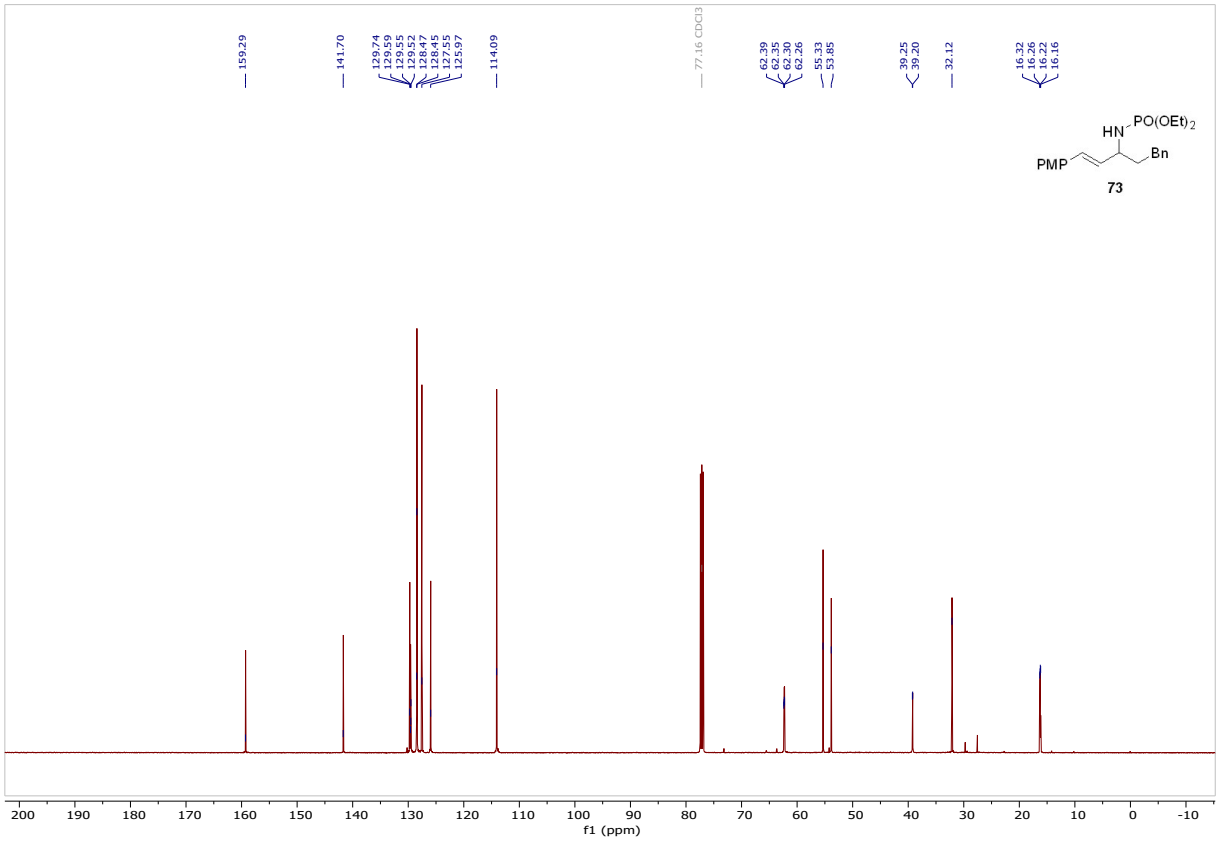


Compound 73

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

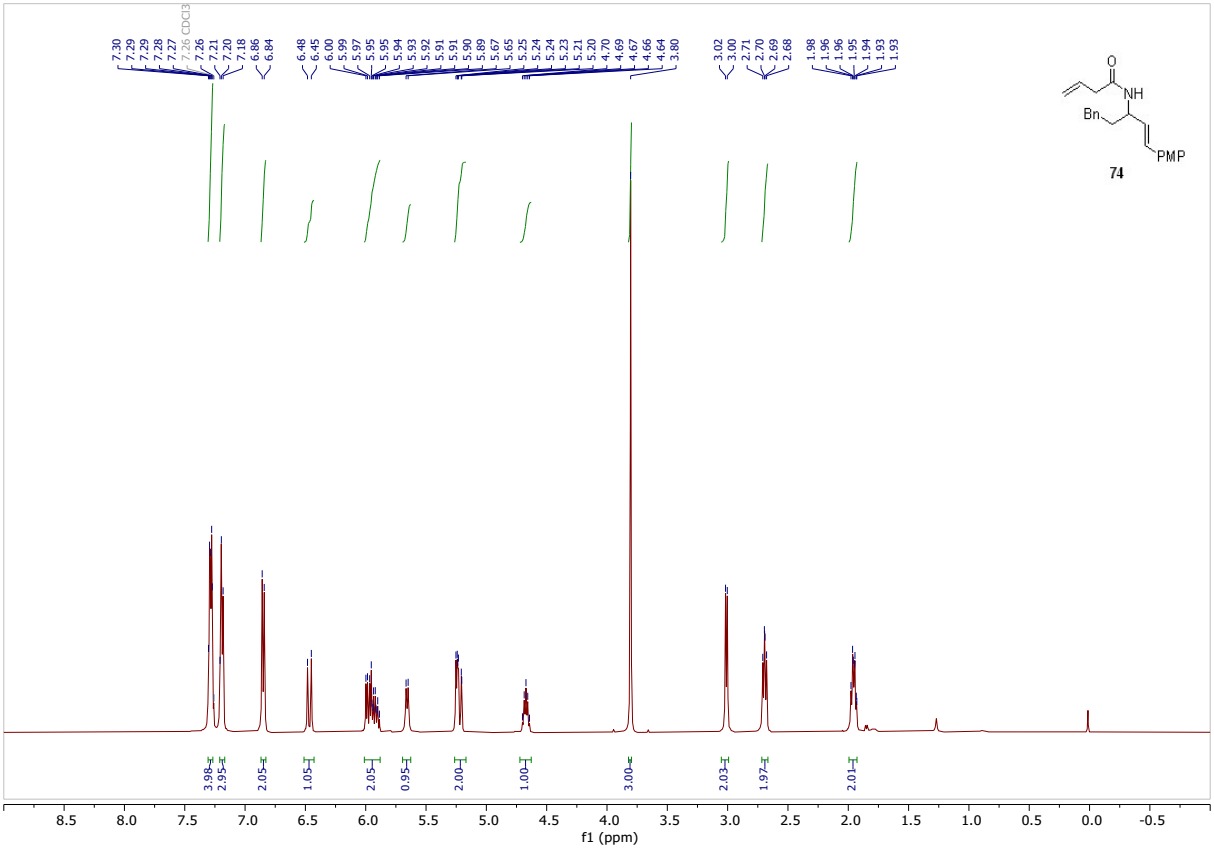


^{13}C NMR (126 MHz, $CDCl_3$)

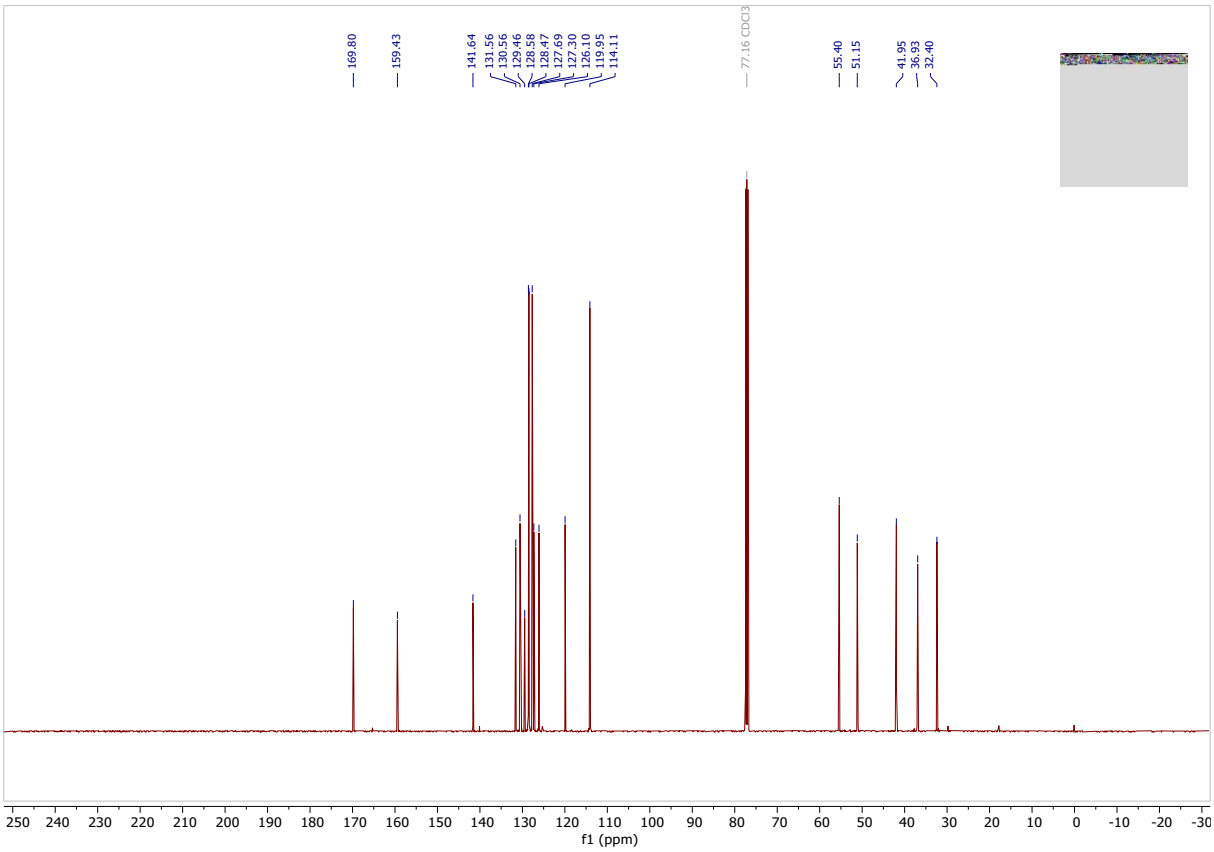


Compound 74

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

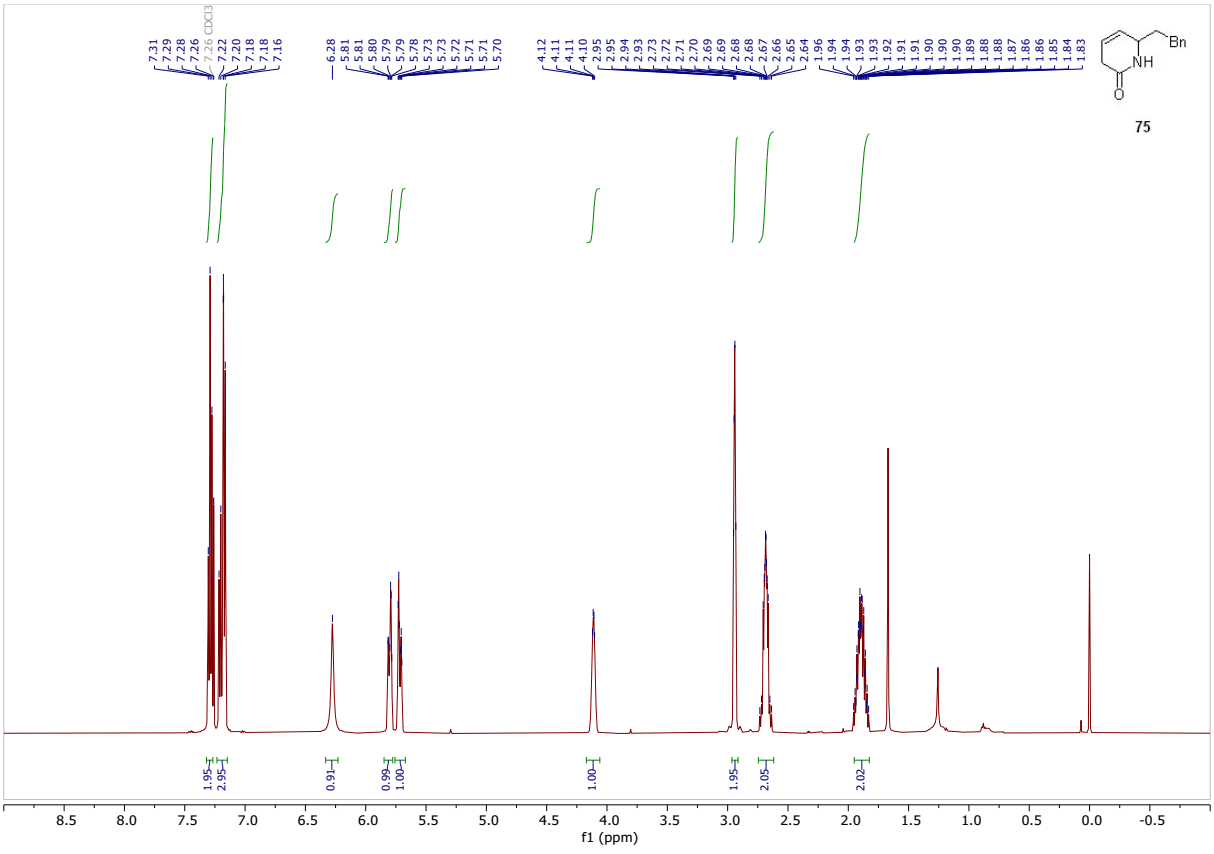


^{13}C NMR (126 MHz, $CDCl_3$)

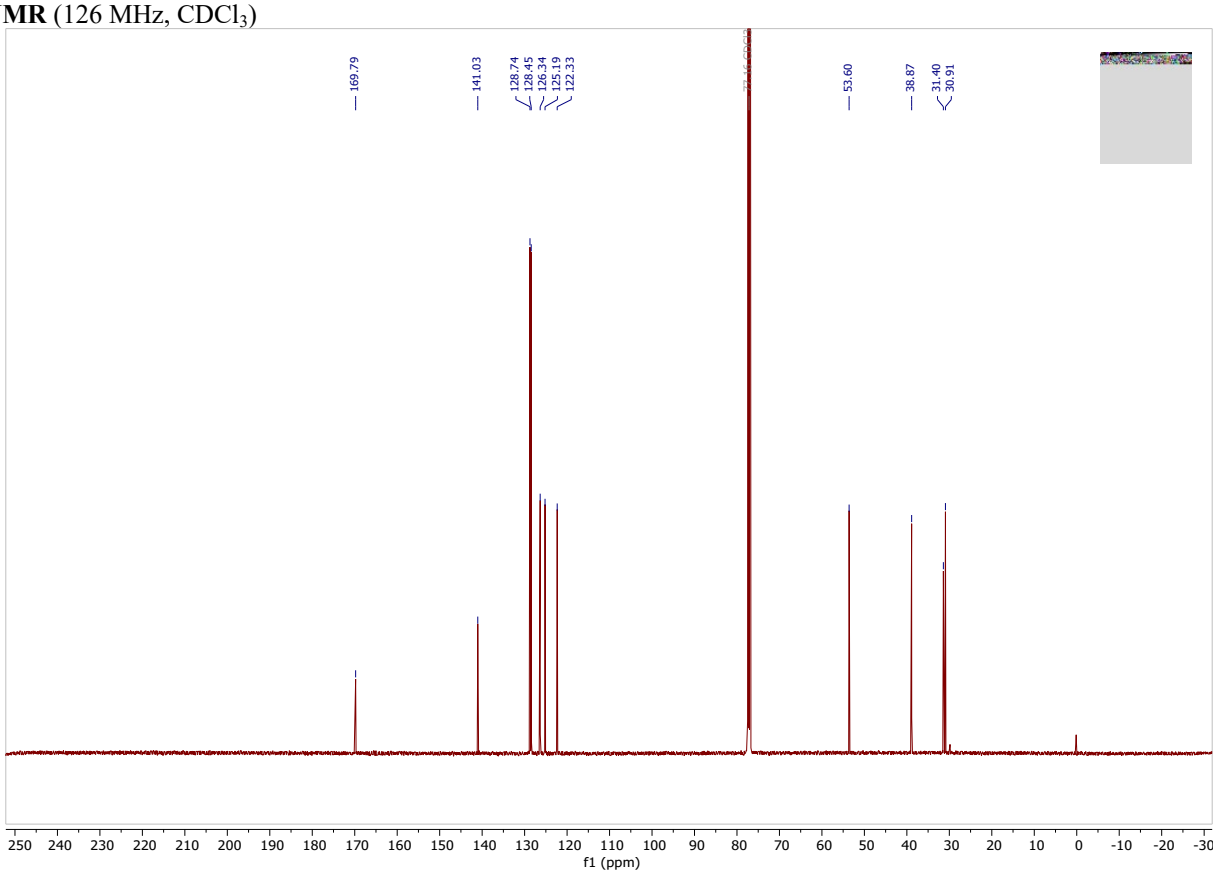


Compound 75

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

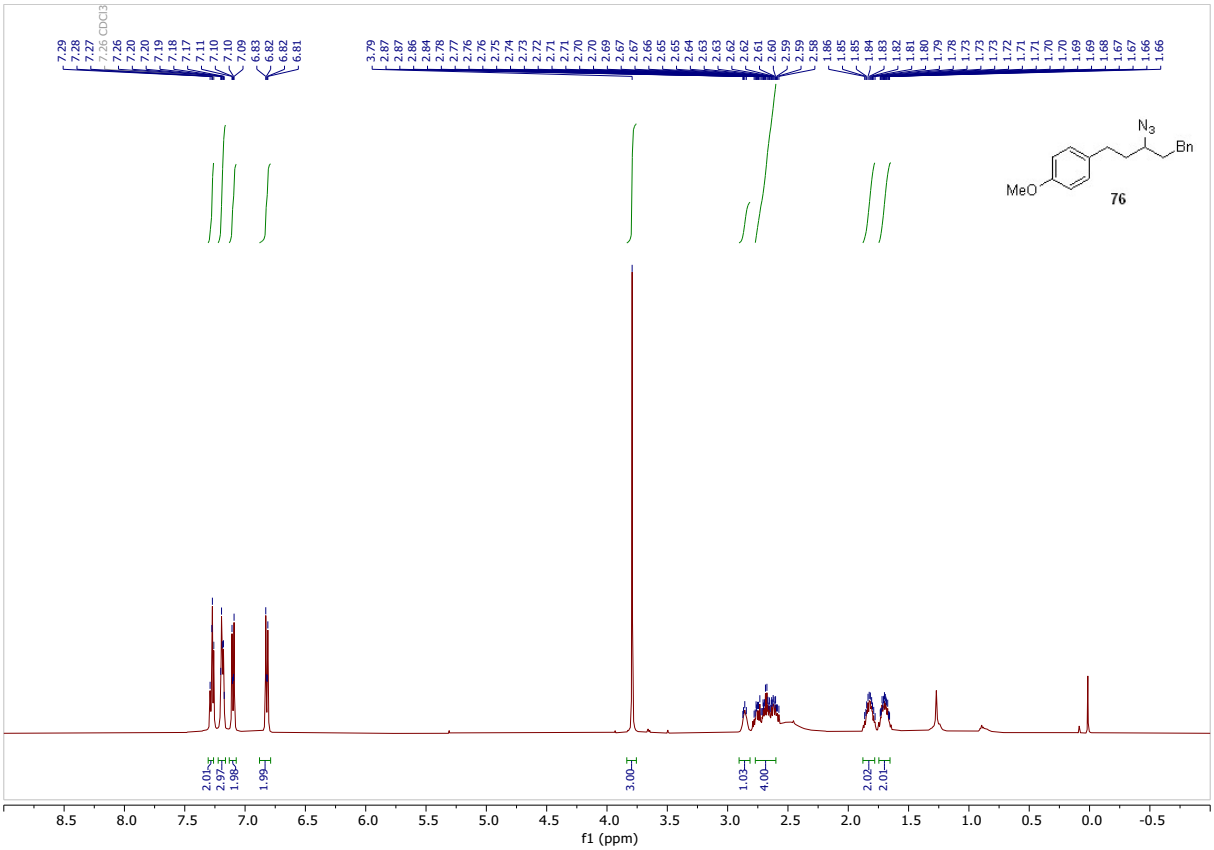


^{13}C NMR (126 MHz, $CDCl_3$)

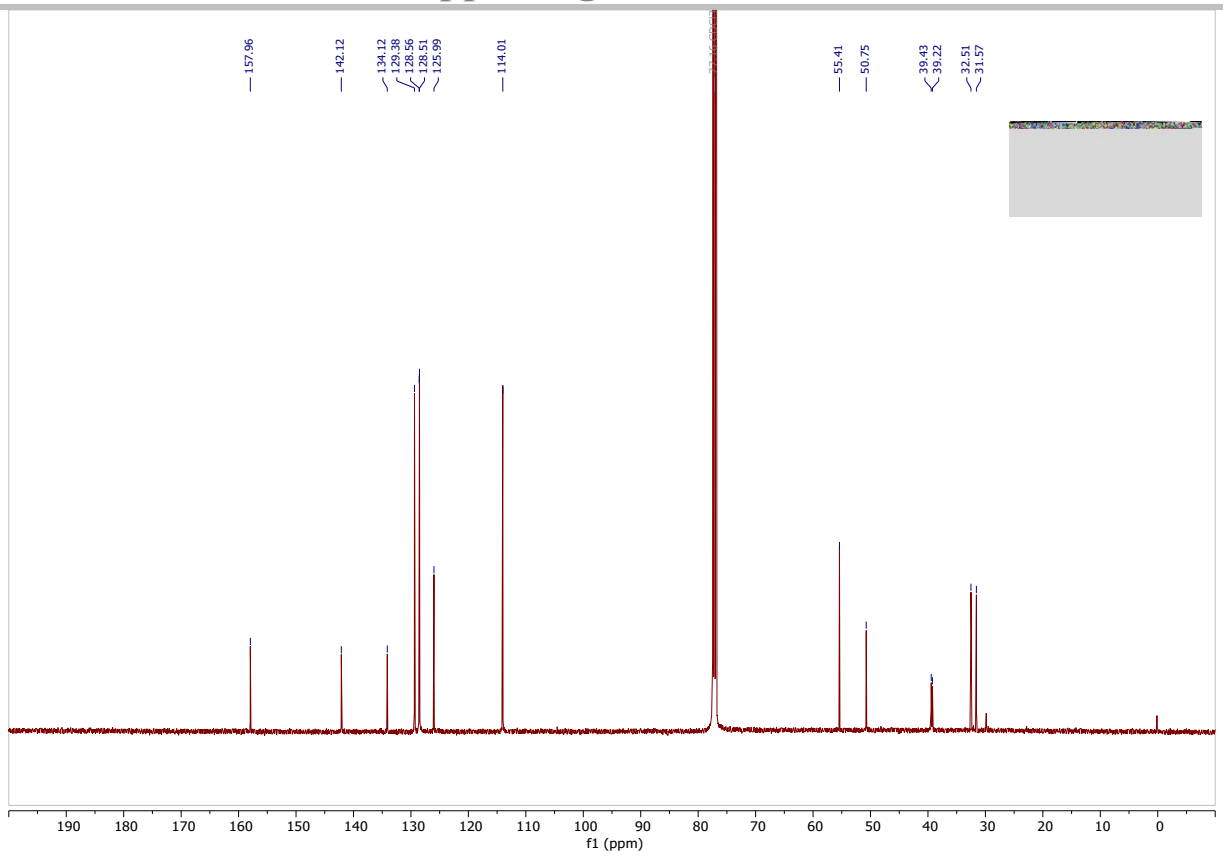


Compound 76

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

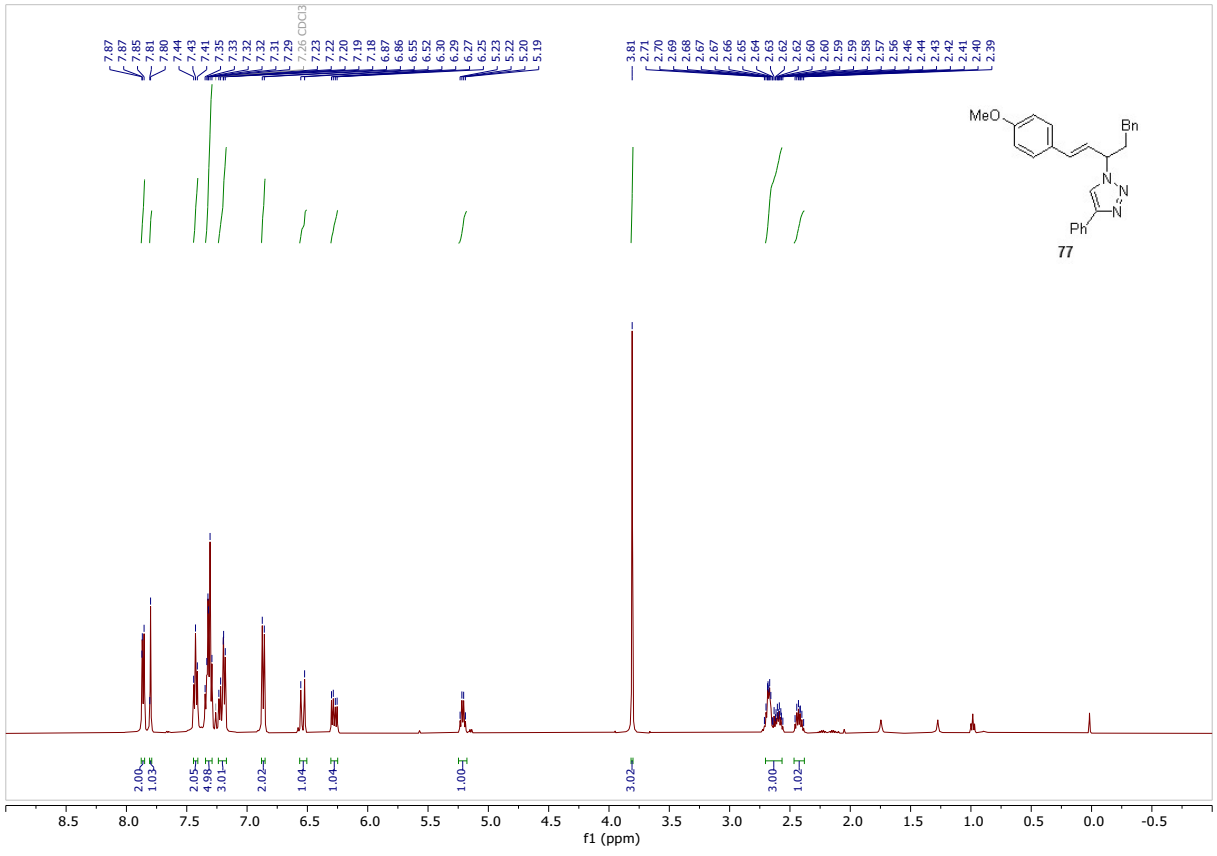


^{13}C NMR (126 MHz, $CDCl_3$)

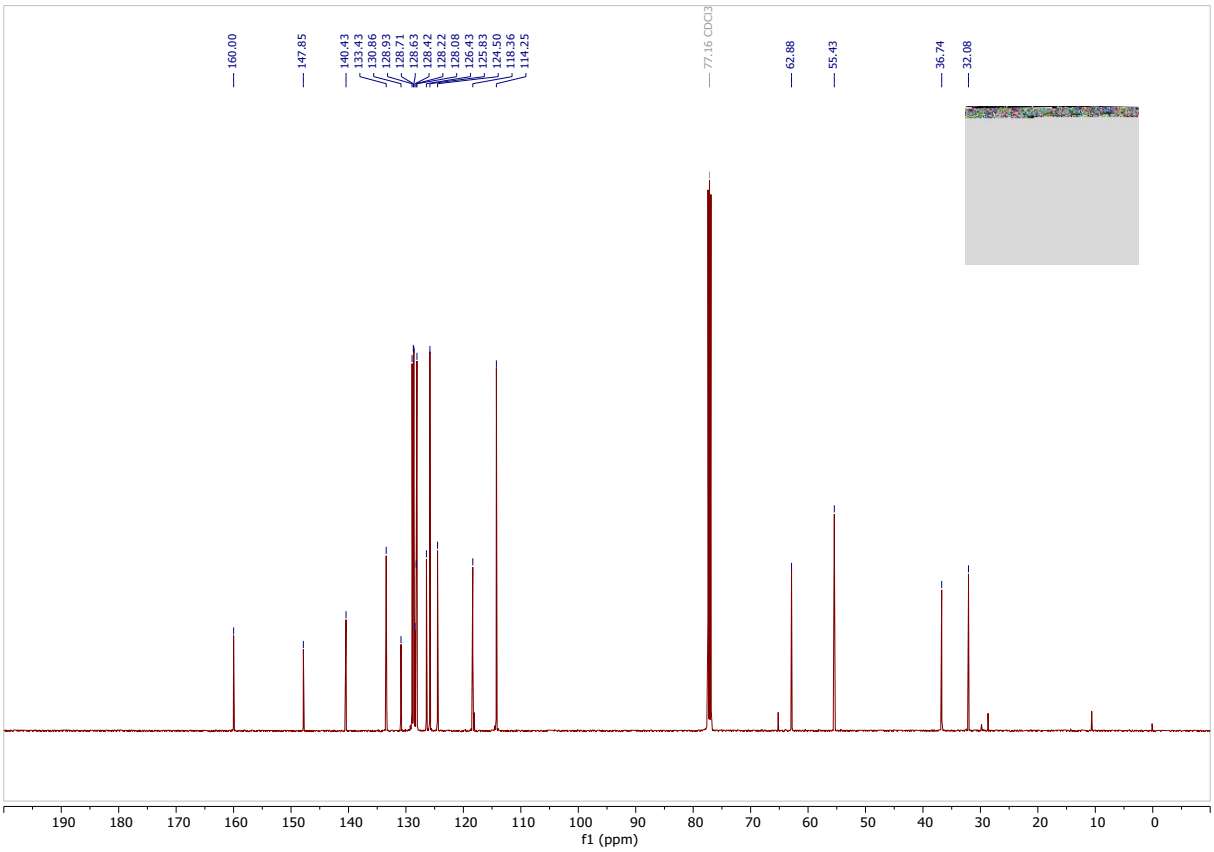


Compound 77

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

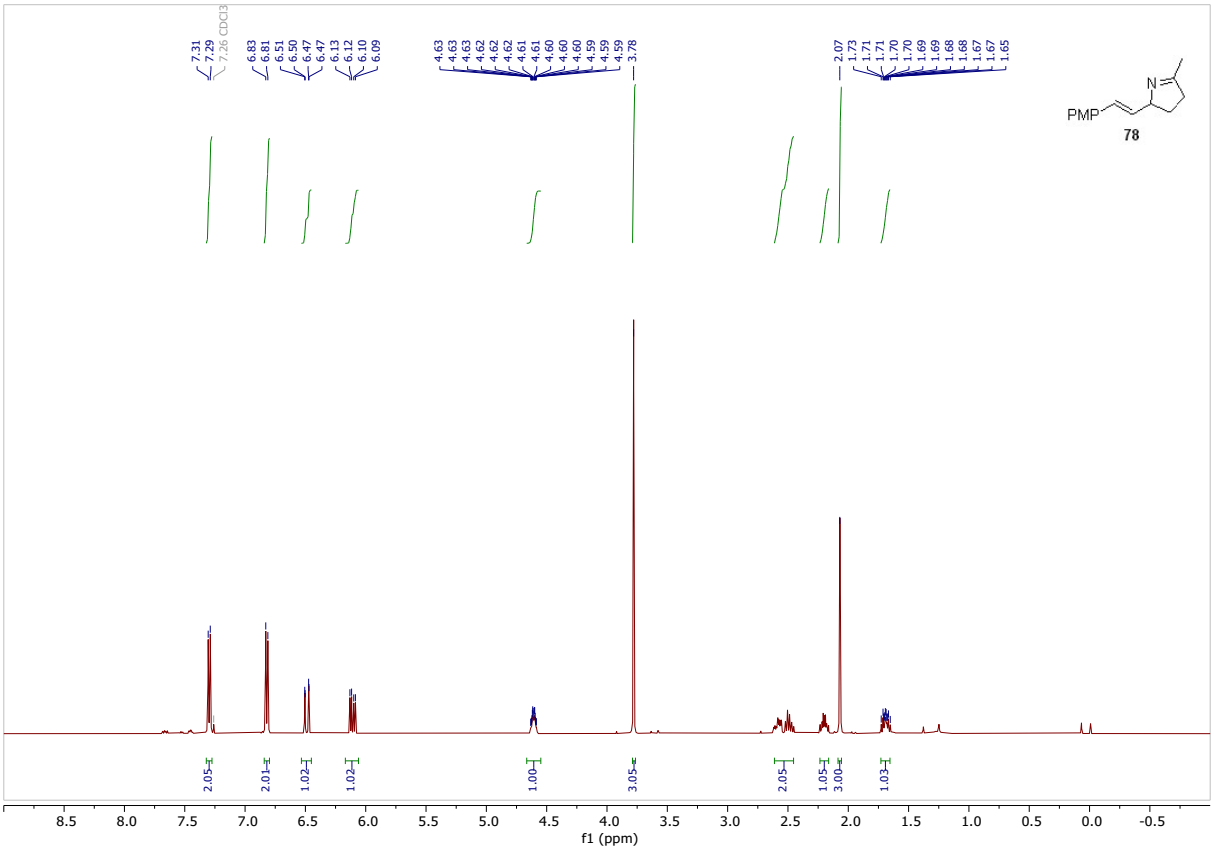


^{13}C NMR (126 MHz, $CDCl_3$)

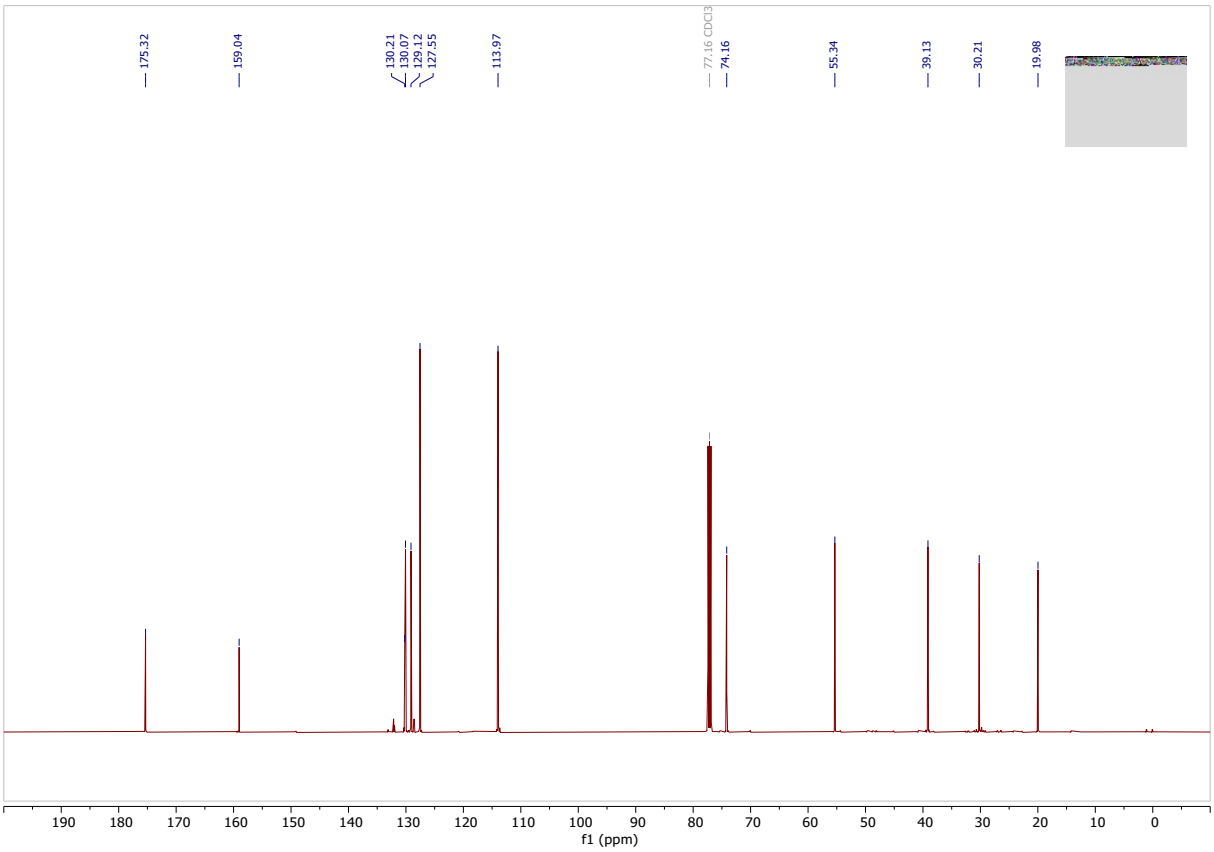


Compound 78

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

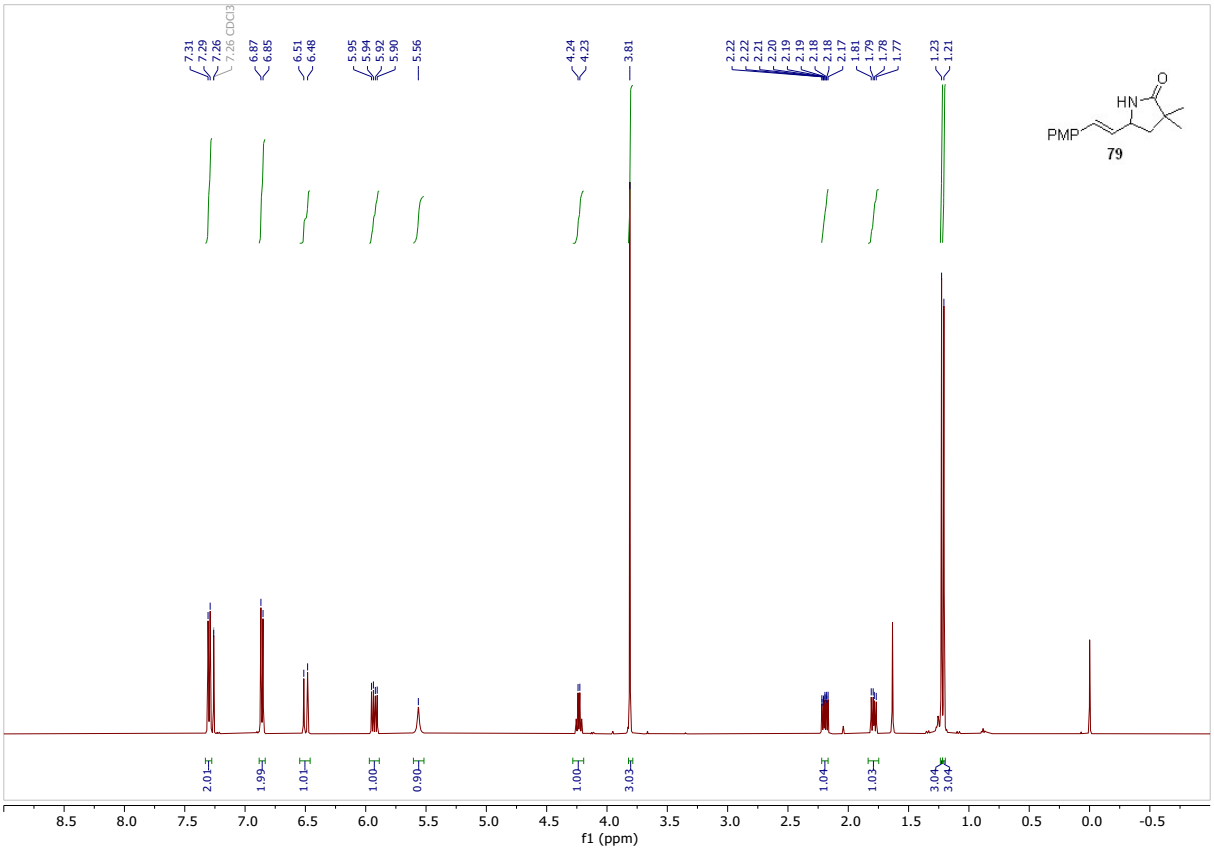


^{13}C NMR (126 MHz, $CDCl_3$)

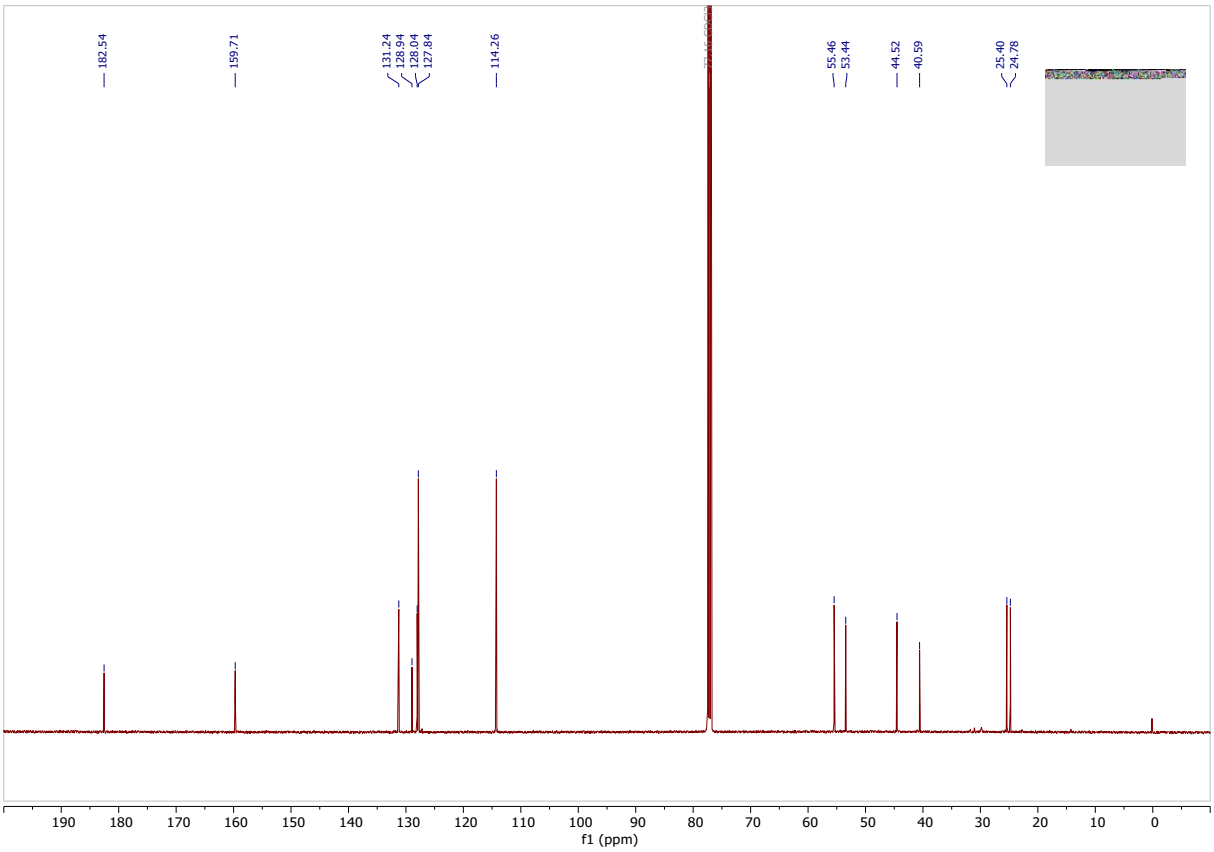


Compound 79

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

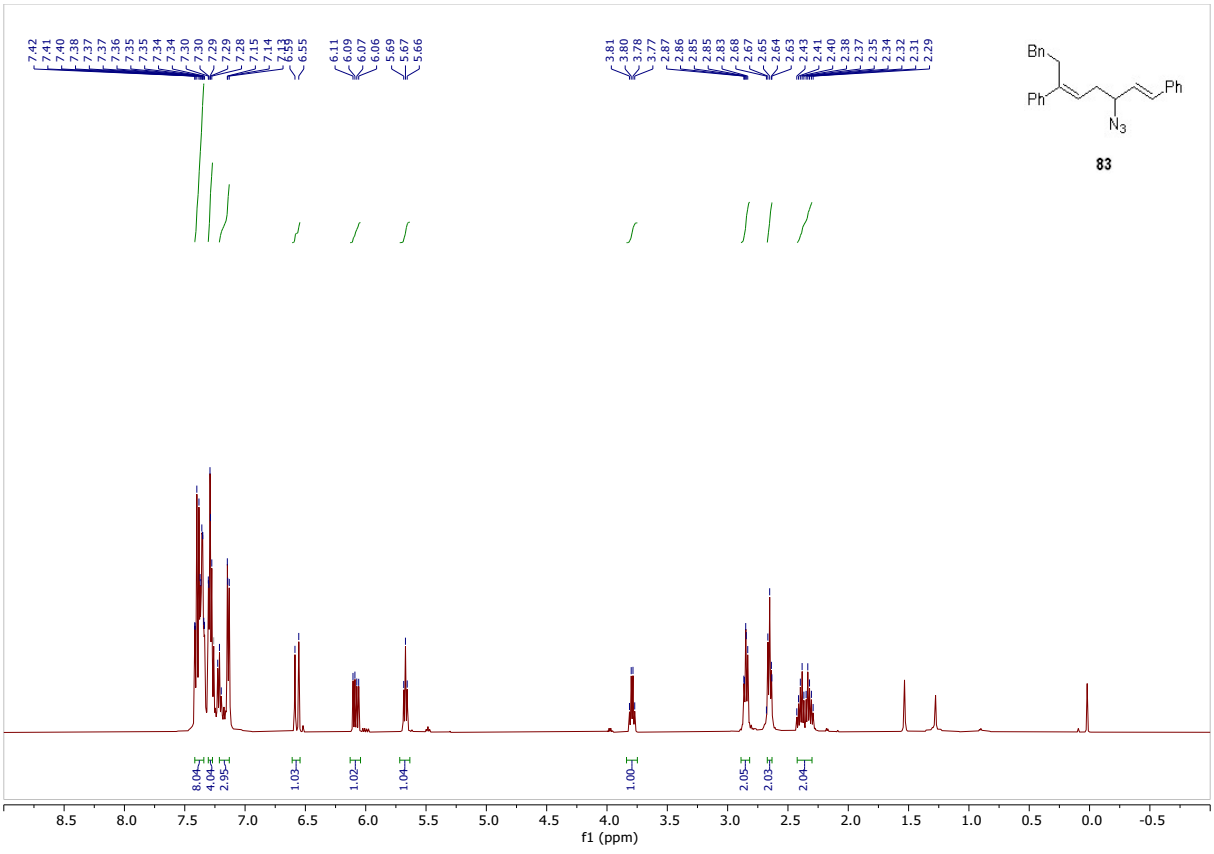


^{13}C NMR (126 MHz, $CDCl_3$)



Compound 83

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



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