Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Palladium-Mediated C_γ–H Functionalization of Alicyclic Amines

*Ellen Y. Aguilera and Melanie S. Sanford**

ange_202101782_sm_miscellaneous_information.pdf

Supporting Information
Table of Contents

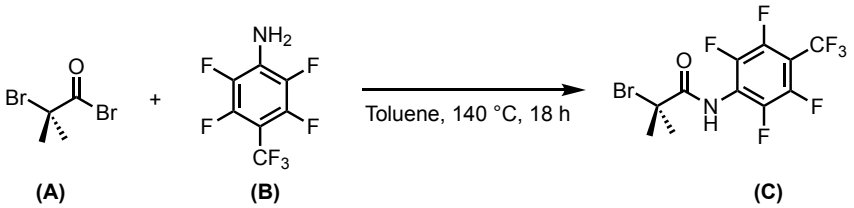
I. General Procedures, Materials, and Methods

Instrument Information. NMR spectra were obtained on a Varian VNMR 700 (699.76 MHz for ^{1}H; 175.95 MHz for ^{13}C) or a Varian VNMR 500 (500.09 MHz for ^{1}H; 470.56 MHz for ^{19}F) or a Varian NMR 400 (128.38 MHz for ^{11}B NMR) spectrometer. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak (most commonly $CDCl_3$) used as an internal reference. ^{19}F chemical shifts are reported in ppm and are referenced on a unified scale to the frequency of the residual solvent peak in the ^{1}H NMR spectrum. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), doublet of triplets (dt), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were obtained at the University of Michigan core facility. X-ray crystallographic data were collected on a Bruker SMART APEX-I CCD-based X-ray diffractometer. Flash chromatography was conducted on a Biotage Isolera One chromatography system using preloaded high-performance silica gel columns (10 g, 25 g, 50 g, or 100 g as appropriate). GC-FID was conducted on a Shimadzu CG-17A system. Melting points were obtained on a OptiMelt automated melting point system.

Materials. All reagents were obtained from a commercial vendor (Aldrich, CombiBlocks, Oakwood, Synthonix, Enamine, Carbosynth, Pressure Chemicals, Matrix, SantaCruz Biotech, or Ontario Chemicals). $Pd(OAc)_2$ was purchased from Pressure Chemical. Acetronitrile and dimethylsulfoxide were purchased from Sigma-Aldrich. Hydrazine monohydrate was purchased from Alfa Aesar. All commercial reagents were used without further purification/drying unless explicitly stated in the experimental section. All reactions were performed under ambient atmosphere unless stated in experimental section.

General Methods. The manipulation of solid reagents was conducted on the benchtop unless otherwise stated. Reactions were conducted under ambient atmosphere unless otherwise stated. Reaction vessels were sealed with either a septum (flask) or a Teflon-lined cap (4 mL or 20 mL vial) with Teflon tape wrapped around the cap. Reactions conducted at elevated temperatures were heated on a hot plate using an aluminum block. Temperature was regulated using an external thermocouple.

II. Synthesis of Starting Materials

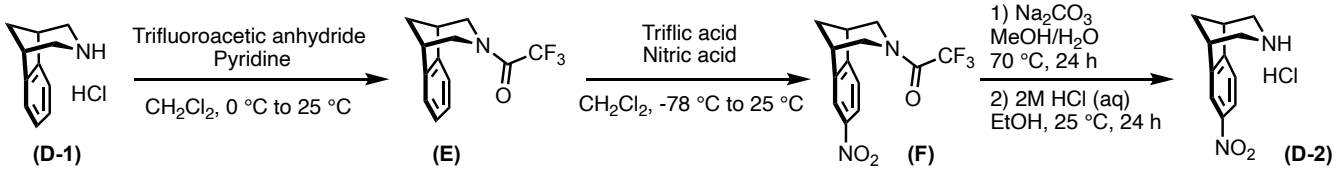


(A) (B) (C)

Synthesis of C: α-Bromo propanamide **C** was synthesized following a literature procedure[1] from starting materials **A** and **B**.

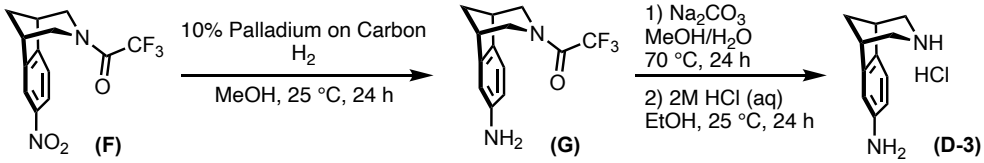
Amine Starting Material Syntheses (D-2 *through* D-8)

Amine starting materials without experimental procedures were purchased from commercial vendors.



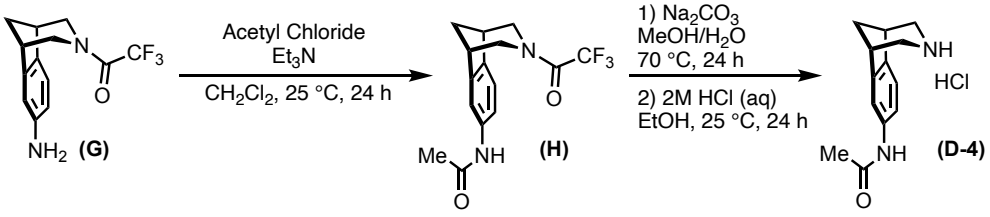
(D-1) (E) (F) (D-2)

Synthesis of D-2: Using a patented procedure,[3] compound **D-2** was obtained as a colorless solid. The ^{1}H NMR spectrum matched that reported in the literature.[3] **D-2** was used as the starting material to prepare substrate **1-B**.



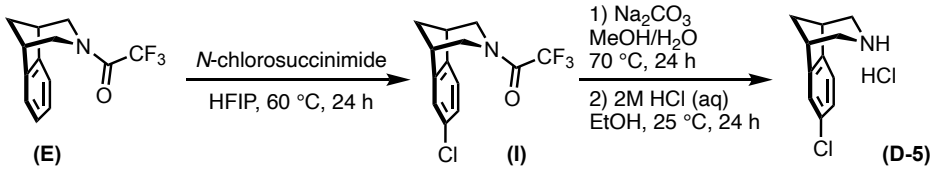
(F) (G) (D-3)

Synthesis of D-3: Using a patented procedure,[3] compound **D-3** was obtained as a colorless solid. The ^{1}H NMR spectrum matched that reported in the literature.[3] **D-3** was used as the starting material to prepare substrate **1-C**.

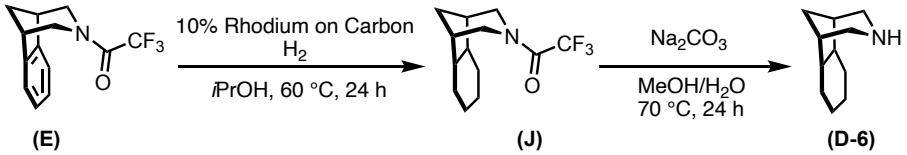


(G) (H) (D-4)

Synthesis of D-4: Using a patented procedure,[3] compound **D-4** was obtained as a colorless solid. The ^{1}H NMR spectrum matched that reported in the literature.[3] **D-4** was used as the starting material to prepare substrate **1-E**.

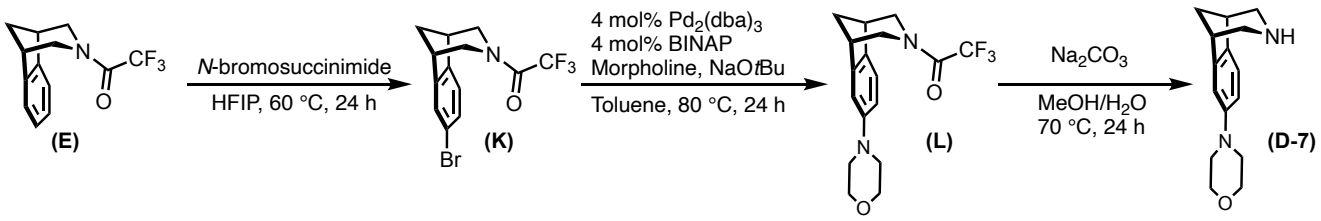


Synthesis of D-5: **D-5** was prepared using a modified literature procedure.[4] In a 20 mL scintillation vial, **E** (2.0 g, 0.0078 mol, 1.0 equiv) was dissolved in hexafluoro-2-propanol (HFIP, 10 mL). To this stirred solution, *N*-chlorosuccinimide (1.0 g, 0.0078 mol, 1.0 equiv) was added, and the reaction vial was sealed. The reaction mixture was stirred at 60 °C for 24 h. The reaction was allowed to cool to rt and was then concentrated under reduced pressure. Purification via column chromatography (gradient elution of 50% EtOAc in hexanes) afforded **I** as a white solid (1.5 g, 67% yield). The ^{1}H NMR spectrum of **I** matched that reported in the literature.[3] Compound **D-5** was prepared from **I** using a literature procedure.[3] Product **D-5** was obtained as a colorless solid (1.1 g, 92% yield), and the ^{1}H NMR spectrum matched that reported in the literature.[3] **D-5** was used as the starting material to prepare substrate **1-D**.

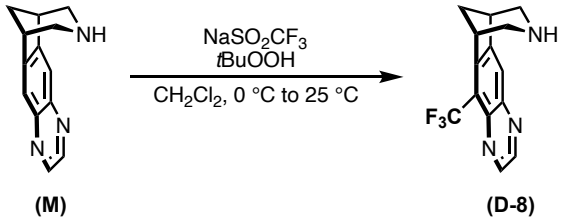


Synthesis of D-6: **D-6** was prepared using a modified literature procedure.[5] Under ambient atmosphere, a 20 mL vial was charged with **E** (1.0 g, 3.9 mmol, 1.0 equiv), rhodium on carbon (39.7 mg, 0.39 mmol, 10%), and *i*PrOH (12 mL). The 20 mL vial was placed in a Parr Reactor, where the reaction was pressurized under 5 atm of hydrogen. The reaction was stirred in the Parr Reactor for 24 h at 60 °C. The reaction was allowed cool to rt and was then removed from the Parr Reactor. The solution was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The crude material was purified by silica gel chromatography (gradient elution of 15% to 30% EtOAc in hexanes), which afforded **J** as a colorless solid (800 mg, 78% yield). Compound **J** (800 mg, 3.0 mmol, 1.0 equiv) and Na_2CO_3 (650 mg, 6.0 mmol, 2.0 equiv) were added to a 20 mL vial followed by a 2:1 MeOH (10 mL)/H_2O (5 mL) mixture. The reaction was stirred at 70 °C for 24 h and then concentrated under reduced pressure. The solid was dissolved in CH_2Cl_2, and an aqueous extraction was performed. The organic layers were combined and concentrated.

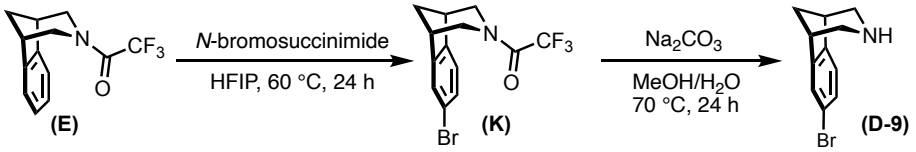
Product **D-6** was obtained as a colorless oil without further purification (480 mg, 97% yield). **D-6** was used as the starting material to prepare substrate **1-G**.



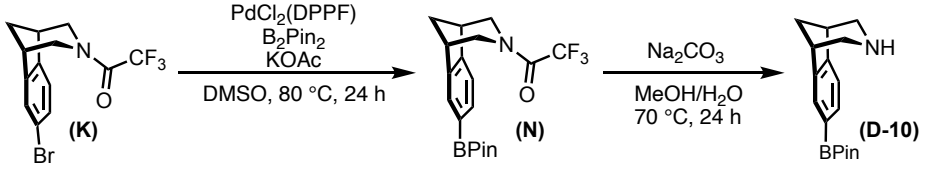
Synthesis of D-7: **D-7** was prepared using a modified literature procedure.[3,4,6] In a 20 mL scintillation vial, **E** (1.0 g, 3.9 mmol, 1.0 equiv) was dissolved in HFIP (10 mL). To this stirred solution, *N*-bromosuccinimide (69.5 mg, 3.9 mmol, 1.0 equiv) was added, and the reaction vial was sealed. The reaction mixture was stirred at 60 °C for 24 h. The reaction was allowed to cool to rt and then concentrated under reduced pressure. Final purification via column chromatography (gradient elution of 50% EtOAc in hexanes) afforded **K** as a colorless solid (700 mg, 54% yield). Under a nitrogen atmosphere, a 20 mL scintillation vial was charged with **K** (700 mg, 2.1 mmol, 1.0 equiv), $Pd_2(dba)_3$ (38.4 mg, 0.042 mmol, 4 mol%), BINAP (52.2 mg, 0.084 mmol, 4 mol%), and NaO*t*Bu (282 mg, 2.9 mmol, 1.4 equiv). The solids in the vial were dissolved in toluene (15 mL) and then morpholine (217 μL, 2.5 mmol, 1.2 equiv) was added. The vial was sealed, and the reaction mixture was stirred at 80 °C for 24 h. The reaction was allowed to warm to rt and then diluted with diethyl ether. An aqueous extraction was performed, and the organic layers were collected and concentrated under reduced pressure. The crude material was purified via silica gel chromatography (gradient elution of 50% EtOAc in hexanes), and compound **L** was obtained as a colorless solid (500 mg, 70% yield). Compound **L** (500 mg, 1.5 mmol, 1.0 equiv) and Na_2CO_3 (350 mg, 3.0 mmol, 2.0 equiv) were dissolved in a 2:1 MeOH (10 mL)/H_2O (5 mL) mixture in a 20 mL vial. The reaction was stirred at 70 °C for 24 h. The reaction solution was then concentrated under reduced pressure. The resulting solids was dissolved in CH_2Cl_2, and an aqueous extraction was performed. The organic layers were combined and concentrated. Product **D-7** was obtained as a colorless oil and was used without further purification to prepare substrate **1-F**.



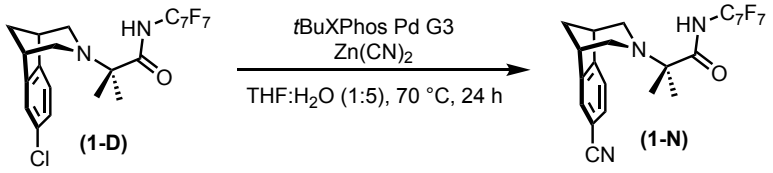
Synthesis of D-8: **D-8** was prepared from compound **M** using a literature procedure.[7] ^1H and ^{19}F NMR spectra of **D-8** matched that reported in the literature.[7] **D-8** was used as the starting material to prepare substrate **1-I**.



Synthesis of D-9: **D-9** was prepared using a modified literature procedure.[3,4] Compound **K** (200.0 mg, 0.6 mmol, 1.0 equiv) and Na_2CO_3 (127.0 mg, 1.2 mmol, 2.0 equiv) were dissolved in a 2:1 MeOH (10 mL)/H_2O (5 mL) mixture in a 20 mL vial. The reaction was stirred at 70 °C for 24 h. The reaction solution was then concentrated under reduced pressure. The resulting solids was dissolved in CH_2Cl_2, and an aqueous extraction was performed. The organic layers were combined and concentrated. Product **D-9** was obtained as a colorless oil and was used without further purification to prepare substrate **1-L**.



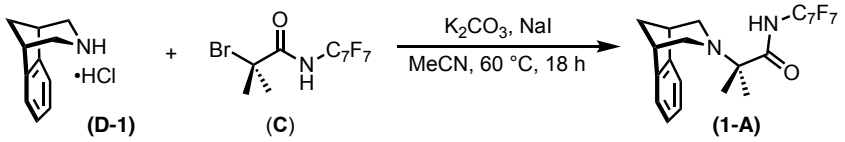
Synthesis of D-10: **D-10** was prepared using a modified literature procedure.[3,8.] In a glovebox, substrate **K** (200.4 mg, 0.60 mmol, 1.0 equiv), $PdCl_2$DPPF (17.5 mg, .024 mmol, 0.04 equiv), B_2Pin_2 (182.2 mg, 0.72 mmol, 1.2 equiv), and KOAc (176.4 mg, 1.8 mmol, 3.0 equiv) were added to a 20 mL vial with a magnetic stir bar. With a syringe, 10 mL of DMSO were added to the vial. This reaction was sealed with a Teflon cap, and heated outside of the glovebox at 80 °C. After 18 h, the reaction was allowed to cool. The resulting mixture was dissolved in EtOAc, and an aqueous extraction was performed. The organic layers were combined, concentrated, and column chromatography (5% EtOAc in Hexanes) was performed to obtain **N**. Compound **N** (140.0 mg, 0.37 mmol, 1.0 equiv) and Na_2CO_3 (78.0 mg, 0.74 mmol, 2.0 equiv) were dissolved in a 2:1 MeOH (6 mL)/H_2O (3 mL) mixture in a 20 mL vial. The reaction was stirred at 70 °C for 24 h. The reaction solution was then concentrated under reduced pressure. The resulting solids was dissolved in CH_2Cl_2, and an aqueous extraction was performed. The organic layers were combined and concentrated. Product **D-10** was obtained as a colorless oil and was used without further purification to prepare substrate **1-M**.



Synthesis of 1-N: **1-N** was prepared using a modified literature procedure.[9] In a glovebox, a medium reaction tube equipped with a magnetic stirbar was charged with *t*BuXPhos Pd

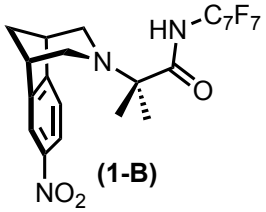
G3 (CAS number: 1447963-75-8) (30.0 mg, 0.038 mmol 5 mol%), substrate **1-D** (370 mg, 0.75 mmol, 1.0 equiv), and $Zn(CN)_2$ (58.0 mg, 0.50 equiv, 0.66 equiv). To this tube, THF was added (0.4 mL) via syringe and capped with a septum cap. The tube was removed from the glovebox, and degassed DI H_2O (1.9 mL) was added to the reaction tube via a syringe. The reaction was stirred vigorously at 70 °C. After 24 h, the reaction mixture was treated with saturated aqueous $NaHCO_3$ (2 mL) and EtOAc (3 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The aqueous layer was treated with 20% aqueous bleach (1 mL) and then disposed of in aqueous cyanide waste. The resulting solid from the organic layer was purified via column chromatography (20% EtOAc in Hexanes).

Directing Group Installation Procedure[1]



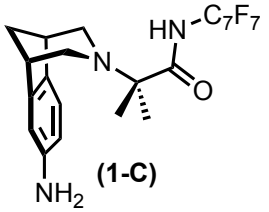
A 20 mL scintillation vial was charged with **D-1** (254 mg, 1.30 mmol, 1.0 equiv), α-bromo propanamide **C** (497 mg, 1.30 mmol, 1.0 equiv), K_2CO_3 (574 mg, 4.16 mmol, 3.2 equiv), and NaI (96.2 mg, 0.65 mmol, 0.5 equiv). Anhydrous acetonitrile (15 mL) was then added. The vial was sealed, and the vial was heated to an external temperature of 60 °C. After 18 h, the reaction was cooled to rt, diluted with EtOAc (~5 mL), and filtered through silica gel. The filtrate was concentrated under reduced pressure. Final purification via column chromatography (gradient elution from 0% to 20% EtOAc in hexanes) afforded product **1-A** (447 mg, 75% yield) as a colorless solid.[1] Amine derivatives **1-B** through **1-K** were prepared in an analogous manner using the appropriate amine starting material (**D-2 through D-8**). Substrate-specific are included below.

Characterization of Directing Group Installation Products (1-B *through* **1-K)**



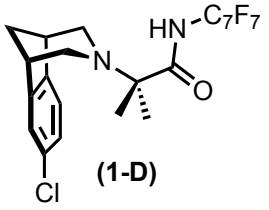
1-B: Isolated yield: 950 mg, 54% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 8.08–8.04 (multiple peaks, 2H), 7.44 (br s, 1H), 7.36 (d, J = 8.1 Hz, 1H), 3.36 (t, J = 7.2 Hz, 2H), 2.89 (t, J = 10.9 Hz, 2H), 2.78 (t, J = 10.3 Hz, 2H), 2.40 (app s, 1H), 1.87 (d, J = 10.9 Hz, 1H), 1.25 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.2, 153.5, 147.7, 147.6, 123.1, 122.2, 116.9, 64.2, 50.6, 50.2, 44.0, 41.2, 41.1, 22.2, 20.7. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –140.8 (app. s, 2F), –143.7 (app. s, 2F).

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}F_7N_3O_3$, 506.1309; found, 506.1316.
Melting point: 125–127 °C
Chromatography conditions: 10% EtOAc in hexanes



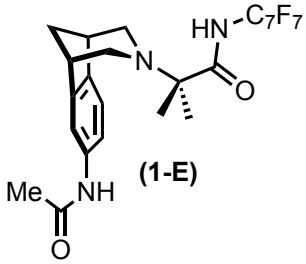
(1-C)

1-C: Isolated yield: 580 mg, 26% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.80 (br s, *NH of amide*, variable integrations), 6.92 (d, *J* = 7.7 Hz, 1H), 6.52 (d, *J* = 2.2 Hz, 1H), 6.36 (dd, *J* = 7.7, 2.2 Hz, 1H), 3.46 (s, 2H), 3.10 (dt, *J* = 13.6, 4.5 Hz, 2H), 2.81-2.72 (multiple peaks, 2H), 2.69–2.61 (multiple peaks, 2H), 2.26 (m, 1H), 1.70 (d, *J* = 10.3 Hz, 1H), 1.22 (s, 3H), 1.21 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.5, 147.0, 145.7, 135.4, 122.3, 112.9, 109.5, 63.8, 50.8, 50.7, 43.8, 41.4, 40.4, 21.9, 21.7. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.9 (m, 2F), –143.0 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{20}F_7N_3O$, 476.1567; found, 476.1577.
Melting point: 114–115 °C
Chromatography conditions: 5% EtOAc in hexanes



(1-D)

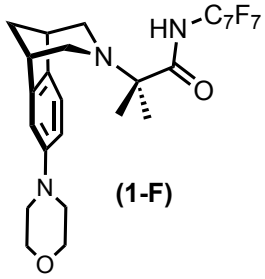
1-D: Isolated yield: 550 mg, 22% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.56 (br s, 1H), 7.15–7.07 (multiple peaks, 3H), 3.21 (dd, *J* = 11.7, 7.2 Hz, 2H), 2.84 (dd, *J* = 10.5, 4.0 Hz, 1H), 2.76 (dd, *J* = 10.5, 4.0 Hz, 1H), 2.73–2.67 (multiple peaks, 2H), 2.32 (m, 1H), 1.76 (d, *J* = 10.6 Hz, 1H), 1.23 (s, 3H), 1.21 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 179.9, 147.7, 144.2, 132.4, 126.9, 122.9, 122.3, 63.9, 50.8, 50.2, 43.8, 41.2, 40.7, 22.5, 20.9. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.3 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}ClF_7N_2O$, 495.1069; found, 495.1083.
Melting point: 90–92 °C
Chromatography conditions: 5% EtOAc in hexanes



(1-E)

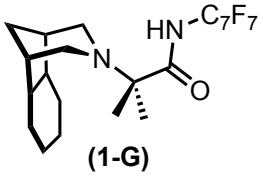
1-E: Isolated yield: 660 mg, 69% (colorless solid)
^{1}H NMR (700 MHz, CD_3OD, 23 ºC): δ 7.53 (br s, 1H), 7.19 (app. t, 2H), 3.22 (s, 1H), 3.17 (s, 1H), 2.93 (d, *J* = 10.6 Hz, 1H), 2.79 (d, *J* = 10.6 Hz, 1H), 2.75 (d, *J* = 10.5 Hz, 2H), 2.28 (m, 1H), 1.98 (s, 3H), 1.82 (d, *J* = 10.5 Hz, 1H), 1.24 (s, 3H), 1.19 (s, 3H).
Note in CD_3OD, amide H's are not observed.

^{13}C NMR (176 MHz, CD_3OD, 23 ºC): δ 178.5, 170.9, 147.5, 142.7, 138.9, 122.9, 119.2, 114.6, 64.8, 52.3, 50.7, 44.5, 42.7, 42.2, 24.4, 23.5, 19.8. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.8 (m, 2F), –143.1 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{24}H_{22}F_7N_3O_2$, 518.1673; found, 518.1676.
Melting point: 145–151°C
Chromatography conditions: 10% EtOAc in hexanes



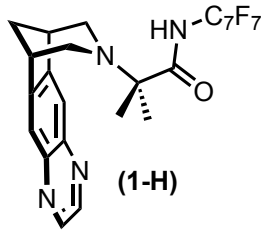
(1-F)

1-F: Isolated yield: 406 mg, 55% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.06 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.3 Hz, 1H), 3.75 (dd, *J* = 5.4, 4.2 Hz, 4H), 3.15 (d, *J* = 6.2 Hz, 2H), 2.95 (q, *J* = 4.3 Hz, 4H), 2.83-2.73 (multiple peaks, 2H), 2.68 (t, *J* = 10.0 Hz, 2H), 2.29 (m, 1H), 1.73 (d, *J* = 10.5 Hz, 1H), 1.22 (s, 3H), 1.21 (s, 3H). *Note in this spectrum, amide H is not observed.*
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.4, 150.9, 146.8, 137.1, 122.1, 113.6, 110.3, 67.0, 63.8, 51.0, 50.5, 49.9, 43.9, 41.7, 40.5, 22.6, 21.1. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.6 (m, 2F), –142.7 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{26}H_{26}F_7N_3O_2$, 546.1986; found, 546.1989.
Melting point: 142–145 °C
Chromatography conditions: 10% EtOAc in hexanes

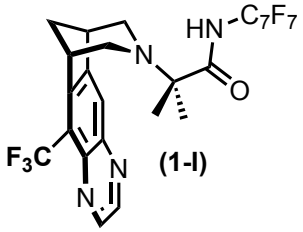


(1-G)

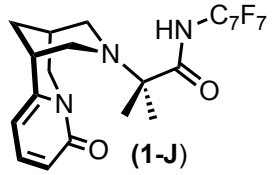
1-G: Isolated yield: 615 mg, 33% (colorless solid)
^{1}H NMR (700 MHz, CD_3OD, 23 ºC): δ 2.90 (d, *J* = 10.5 Hz, 2H), 2.48 (dd, *J* = 10.5, 2.0 Hz, 2H), 2.10 (s, 2H), 2.00–1.94 (multiple peaks, 4H), 1.79 (d, *J* = 8.5 Hz, 2H), 1.62–1.54 (multiple peaks, 2H), 1.43–1.35 (multiple peaks, 8H), 1.31 (d, *J* = 10.5 Hz, 2H). *Note in CD_3OD, amide H is not observed.*
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.2, 64.9, 48.4, 39.6, 38.5, 37.5, 20.6, 20.4, 20.1. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.0 (m, 2F), –143.2 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{25}F_7N_2O$, 467.1928; found, 467.1941.
Melting point: 78–83°C
Chromatography conditions: 5% EtOAc in hexanes



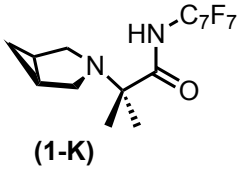
1-H: The ^{1}H, ^{13}C, and ^{19}F NMR spectral data for **1-H** matched that reported in the literature.[1]



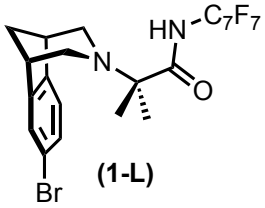
1-I: Isolated yield: 405 mg, 20% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 8.88 (d, *J* = 1.8 Hz, 1H), 8.83 (d, *J* = 1.8 Hz, 1H), 8.01 (s, 1H), 7.38 (s, 1H), 3.98 (app s, 1H), 3.56 (app. s, 1H), 3.14 (m, 1H), 3.01 (d, *J* = 10.6 Hz, 1H), 2.89 (d, *J* = 10.6 Hz, 2H), 2.41 (d, *J* = 11.0 Hz, 1H), 2.00 (d, *J* = 11.0 Hz, 1H), 1.24 (s, 3H), 1.21 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 174.4, 150.1, 149.1, 145.0, 144.1, 143.0, 140.3, 124.9, 124.5 (q, *J* = 276.0 Hz), 121.1 (q, *J* = 30.1 Hz), 64.2, 51.9, 51.6, 42.2, 41.4, 40.8, 21.5, 21.5. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –55.4 (s, 3F), –56.1 (t, 3F), –141.5 (m, 2F), –144.9 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{25}H_{18}F_{10}N_4O$, 581.1394; found, 581.1384.
Melting point: 178–184 °C
Chromatography conditions: 20% EtOAc in hexanes



1-J: The ^{1}H, ^{13}C, and ^{19}F NMR spectral data for **1-J** matched those reported in the literature.[1]

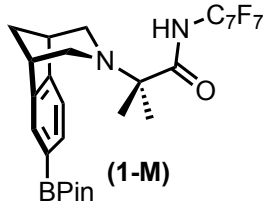


1-K: The ^{1}H, ^{13}C, and ^{19}F NMR spectral data for **1-K** matched those reported in the literature.[1]



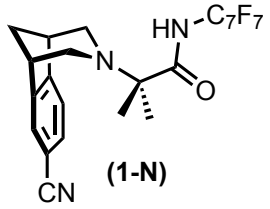
1-L: Isolated yield: 130 mg, 65% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.54 (br s, 1H), 7.26 (app. d, *J* = 6.8 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 3.20 (dt, *J* = 13.9, 4.5 Hz, 2H), 2.86 (dd, *J* = 10.3, 4.1 Hz, 1H), 2.77 – 2.67 (multiple peaks, 3H), 2.31 (m, 1H), 1.75 (d, *J* = 10.6 Hz, 1H), 1.24 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.9, 148.0, 144.8, 129.9, 125.2, 123.4, 120.3, 63.9, 51.0, 50.0, 43.7, 41.2, 40.9, 23.0, 20.4. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.3 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}BrF_7N_2O$, 539.0563; found, 539.0569.
Melting point: 59–61 °C
Chromatography conditions: 5% EtOAc in hexanes



(1-M)

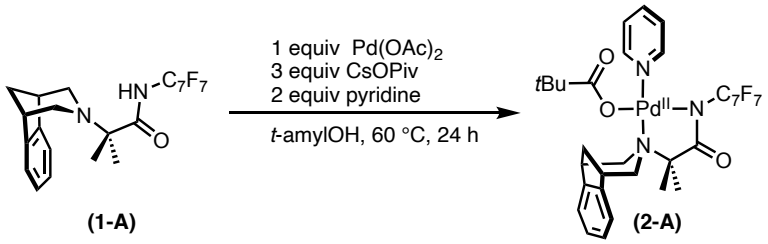
1-M: Isolated yield: 75 mg, 51% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.63 (br s, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.45 (br s, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 3.22 (s, 2H), 2.88-2.76 (multiple peaks, 2H), 2.71 (dd, *J* = 10.5, 5.2 Hz, 2H), 2.29 (m, 1H), 1.75 (d, *J* = 10.5 Hz, 1H), 1.29 (s, 6H), 1.28 (s, 6H), 1.20 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.3, 149.3, 145.0, 134.0, 127.6, 121.2, 83.8, 63.8, 50.7, 50.7, 43.6, 41.4, 41.0, 24.9, 24.7, 22.0, 21.6. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –142.8 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): 31.3.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{30}BF_7N_2O_3$, 587.2238; found, 587.2283.
Melting point: 135–137 °C
Chromatography conditions: 7% EtOAc in hexanes



(1-N)

1-N: Procedure using Synthesis of **1-N** was followed.
Isolated yield: 108 mg, 30% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.48-7.44 (multiple peaks, 2H), 7.42 (br s, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 3.31 (dt, *J* = 5.2, 3.0 Hz, 2H), 2.84 (ddd, *J* = 15.5, 10.5, 3.8 Hz, 2H), 2.75 (t, *J* = 11.6 Hz, 2H), 2.34 (dt, *J* = 10.3, 4.7 Hz, 1H), 1.82 (d, *J* = 10.8 Hz, 1H), 1.23 (s, 3H), 1.22 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.1, 151.4, 147.1, 131.6, 124.9, 122.6, 119.0, 110.6, 64.1, 50.5, 50.4, 43.6, 41.4, 41.0, 21.8, 21.2. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –140.8 (m, 2F), –143.5 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{23}H_{18}F_7N_3O$, 486.1338; found, 486.1360.
Melting point: 120–123 °C
Chromatography conditions: 20% EtOAc in hexanes

Synthesis of 2-A: Pd complex **2-A** was synthesized from **1-A** and $Pd(OAc)_2$ following a literature procedure.[2]

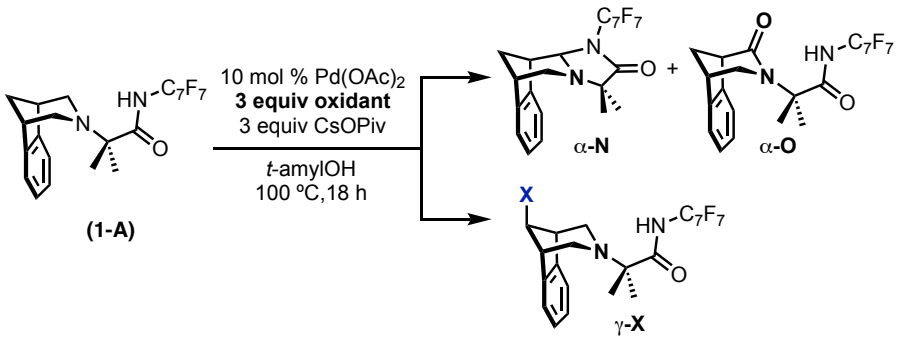


(1-A) **(2-A)**

III. Pd-catalyzed γ-functionalization attempts

General Procedure A (adapted from reference 1): A 4 mL vial was charged with substrate **1-A** (10.1 mg, 0.022 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.50 mg, 0.0022 mmol, 10 mol %), and CsOPiv (15.4 mg, 0.066 mmol, 3.0 equiv) followed by the addition of the desired oxidant (0.066 mmol, 3.0 equiv). With a syringe, *t*-amylOH (0.3 mL) was added. The vial was sealed, and the mixture was stirred at 100 °C. After 18 h at this temperature, the reaction was cooled, diluted with EtOAc, and quenched with hydrazine (3 drops). The resulting mixture was stirred at rt for 10 min. The suspension was then filtered through a plug of Celite, concentrated under vacuum, and analyzed via GC-FID analysis using trimethoxybenzene as internal standard (0.022 mmol, 1.0 equiv).

Table 1. Attempts at Pd-catalyzed γ-functionalization.



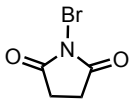
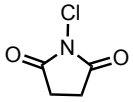
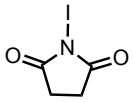
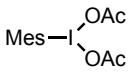
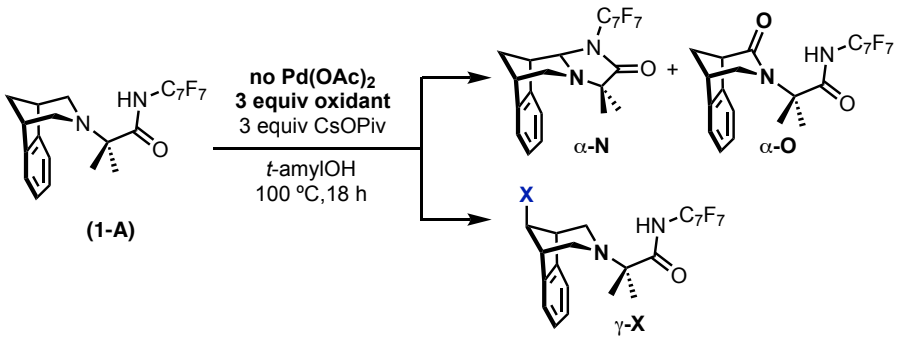
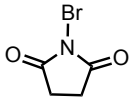
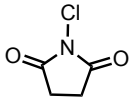
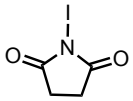
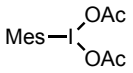
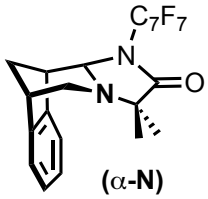
oxidant	X	γ-X	α-N	α-O
PhI	**Ph**	30%	0%	0%
	**Br**	0%	30%	30%
	**Cl**	0%	10%	0%
	**I**	0%	15%	15%
	**OAc**	0%	10%	30%
B_2Pin_2	**BPin**	0%	<1%	0%
S_2Ph_2	**SPh**	0%	0%	0%

Table 2. Control reactions with no Pd.



oxidant	X	γ-X	α-N	α-O
PhI	Ph	0%	<1%	0%
	Br	0%	25%	31%
	Cl	0%	10%	0%
	I	0%	20%	0%
	OAc	0%	10%	15%
B_2Pin_2	BPin	0%	<1%	0%
S_2Ph_2	SPh	0%	10%	0%


(α-N)

α-N: General Procedure A was followed using $Pd(OAc)_2$ and *N*-bromosuccinimide as the oxidant.

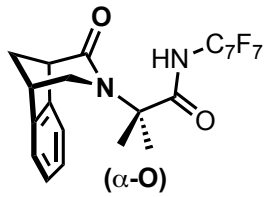
Isolated yield: 2.0 mg, 20% (colorless oil)

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.19 (dd, J = 6.9, 1.3 Hz, 2H), 7.14 (td, J = 6.9, 2.2 Hz, 1H), 6.76 (d, J = 7.3 Hz, 1H), 5.03 (s, 1H), 3.17 (s, 1H), 3.05 (m, 1H), 2.95 (d, J = 5.7 Hz, 1H), 2.87 (m, 1H), 2.55 (ddd, J = 11.5, 5.5, 3.8 Hz, 1H), 1.93 (d, J = 11.5 Hz, 1H), 1.14 (s, 3H), 0.70 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.7, 146.7, 141.1, 127.56, 126.8, 123.5, 122.0, 60.0, 45.7, 43.0, 42.0, 40.8, 29.9, 22.8, 19.3. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

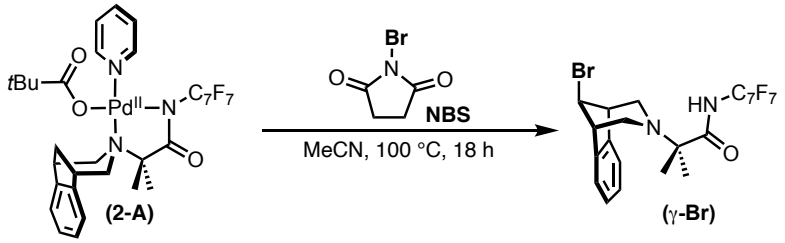
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.2 (t, 3F), –136.3 (m, 1F), –139.1 (m, 1F), –140.5 (m, 1F), –143.2 (m, 1F).

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{17}F_7N_2O$, 459.1302; found, 459.1303.
Chromatography conditions: 7% EtOAc in hexanes



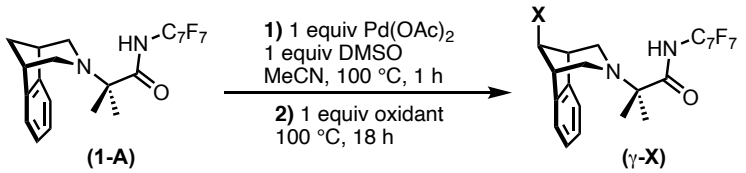
α-O: General Procedure A was followed using $Pd(OAc)_2$ and *N*-bromosuccinimide as the oxidant.
Isolated yield: 2.5 mg, 24% (colorless solid)
^1H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.38 (dd, *J* = 11.7, 7.3 Hz, 2H), 7.25 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.20 (td, *J* = 7.5, 1.2 Hz, 1H), 6.56 (br s, 1H), 3.71 (d, *J* = 4.0 Hz, 1H), 3.66 (dd, *J* = 10.9, 4.0 Hz, 1H), 3.58 (t, *J* = 4.4 Hz, 1H), 3.31 (dt, *J* = 10.9, 1.5 Hz, 1H), 2.53 (ddd, *J* = 11.8, 7.1, 2.9 Hz, 1H), 2.28 (d, *J* = 11.1 Hz, 1H), 1.54 (s, 3H), 1.33 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 172.5, 172.1, 144.0, 143.7, 128.4, 127.8, 122.9, 122.9, 61.9, 49.9, 49.5, 39.9, 37.9, 24.1, 21.5. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.5 (m, 2F), –143.8 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{17}F_7N_2O_2$, 475.1251; found, 475.1237.
Melting point: 199–202 °C
Chromatography conditions: 35% EtOAc in hexanes

IV. γ-Functionalization using Pre-Formed Pd(II) Complex

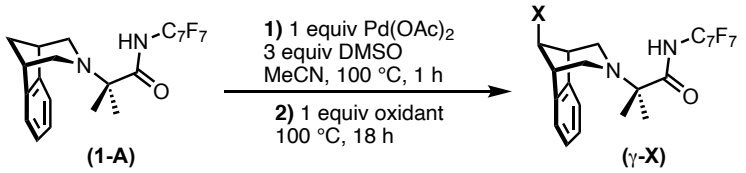


A 4 mL vial was charged with **2-A** (20.0 mg, 0.026 mmol, 1.0 equiv) and *N*-bromosuccinimide (NBS) (4.6 mg, 0.026 mmol, 1.0 equiv) followed by the addition of MeCN (0.5 mL). The vial was sealed, and the mixture was stirred at 100 °C. After 18 h at this temperature, the reaction was cooled, diluted with EtOAc, and quenched with hydrazine (6 drops). This mixture was stirred at rt for 10 min. The resulting suspension was filtered through a plug of Celite and concentrated under vacuum. The product (**γ-Br**) was purified via silica gel column chromatography. Characterization and yield for **γ-Br** is shown below (Section IV).

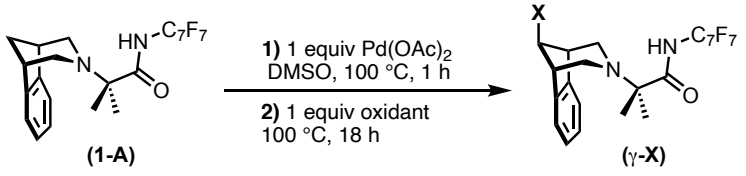
V. *In-situ* Generation of Pd(II) Complex for γ-Functionalization



Procedure A: A 4 mL vial was charged with substrate **1-A** (20.0 mg, 0.0435 mmol, 1.0 equiv), $Pd(OAc)_2$ (10.0 mg, 0.0435 mmol, 1.0 equiv), and acetonitrile (0.6 mL). With a syringe, dimethyl sulfoxide (3.0 μL, 0.0435 mmol, 1.0 equiv) was added. The vial was sealed wih a Teflon-lined cap, and the mixture was stirred at 100 °C. After 1 h at this temperature, the vial was allowed to cool, the cap was removed, and the corresponding oxidant (0.0435 mmol, 1.0 equiv) was added. The vial was re-sealed, and the mixture was heated to 100 °C. After 18 h at this temperature, the reaction was cooled, diluted with EtOAc, and quenched with hydrazine (6 drops). This mixture was stirred at rt for 10 min. The resulting suspension was filtered through a plug of Celite and concentrated under vacuum. The crude material was purified via silica gel column chromatography.

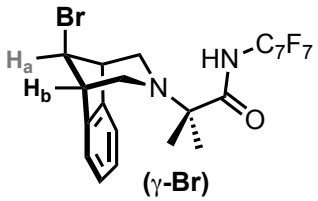


Procedure B: A 4 mL vial was charged with substrate **1-A** (20.0 mg, 0.0435 mmol, 1.0 equiv), $Pd(OAc)_2$ (10.0 mg, 0.0435 mmol, 1.0 equiv), and acetonitrile (0.6 mL). With a syringe, dimethyl sulfoxide (9.3 μL, 0.13 mmol, 3.0 equiv) was added. The vial was sealed with a Teflon-lined cap, and the mixture was stirred at 100 °C. After 1 h at this temperature, the vial was allowed to cool, the cap was removed, and the corresponding oxidant (0.0435 mmol, 1.0 equiv) was added. The vial was re-sealed, and the mixture was stirred and heated to 100 °C. After 18 h at this temperature, the reaction was cooled, diluted with EtOAc, and quenched with hydrazine (6 drops). This mixture was stirred at rt for 10 min. The resulting suspension was filtered through a plug of Celite and concentrated under vacuum. The crude material was purified via silica gel column chromatography.



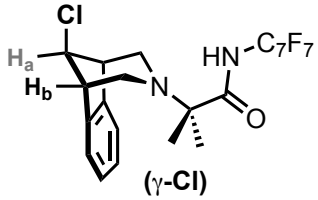
Procedure C: A 4 mL vial was charged with substrate **1-A** (20.0 mg, 0.0435 mmol, 1.0 equiv), $Pd(OAc)_2$ (10.0 mg, 0.0435 mmol, 1.0 equiv), and dimethyl sulfoxide (0.6 mL). The vial was sealed with a Teflon-lined cap, and the mixture was stirred at 100 °C. After 1 h at this temperature, the vial was allowed to cool, the cap was removed, and the

corresponding oxidant (0.13 mmol, 3.0 equiv) was added. The vial was re-sealed, and the mixture was stirred and heated to 100 °C. After 18 h at this temperature, the reaction was cooled, diluted with EtOAc, filtered through a plug of Celite, and concentrated under vacuum. The crude material was purified via silica gel column chromatography.



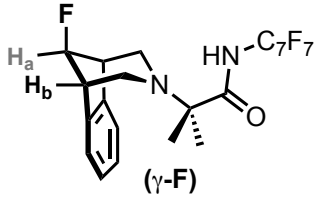
(γ-Br)

γ-Br: Procedure B was followed using *N*-bromosuccinimide as the oxidant.
Isolated yield: 15.5 mg, 66% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.46 (br s, 1H), 7.23–7.20 (multiple peaks, 2H), 7.16 (dd, J = 5.4, 3.2 Hz, 2H), 4.57 (t, J_{ab} = 4.5 Hz, 1H), 3.30 (d, J = 11.0 Hz, 2H), 3.26 (t, J = 4.5 Hz, 2H), 2.69 (dd, J = 11.0, 3.7 Hz, 2H), 1.27 (s, 6H).
Note: J_{ab} value matches the expected J value of ~ 4 Hz in a 5- and 6-membered ring where H_a and H_b are equatorial and trans to each other.[10]
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.8, 142.8, 127.8, 122.0, 64.0, 55.5, 45.2, 44.3, 21.8. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.3 (m, 2F), –143.1 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}BrF_7N_2O$, 539.0491; found, 539.0560.
Melting point: 99–101 °C
Chromatography conditions: 5% EtOAc in hexanes



(γ-Cl)

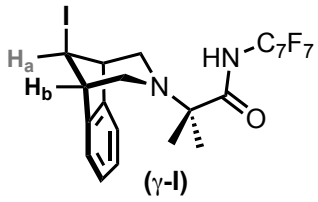
γ-Cl: Procedure B was followed using *N*-chlorosuccinimide as the oxidant.
Isolated yield: 10.8 mg, 50% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.46 (br s, 1H), 7.23 (dd, J = 5.4, 3.1 Hz, 2H), 7.17 (dd, J = 5.4, 3.1 Hz, 2H), 4.45 (t, J_{ab} = 4.6 Hz, 1H), 3.27 (d, J = 12.1 Hz, 2H), 3.24 (t, J = 4.6 Hz, 2H), 2.64 (dd, J = 11.1, 3.7 Hz, 2H), 1.27 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.9, 142.6, 127.8, 122.3, 64.0, 62.1, 45.3, 43.3, 21.8. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.1 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}ClF_7N_2O$, 495.0996; found, 495.1065.
Melting point: 112–114 °C
Chromatography conditions: 5% EtOAc in hexanes



(γ-F)

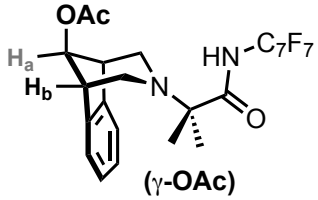
γ-F: Procedure A was followed using *N*-fluorobenzenesulfonimide (NFSI) as the oxidant.
Isolated yield: 9.2 mg, 44% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.53 (br s, 1H), 7.23 (dd, J = 5.4, 3.3 Hz, 2H), 7.19 (dd, J = 5.4, 3.3 Hz, 2H), 4.97 (dt,

$J_{H,F}$ = 56.0, J_{ab} = 5.1 Hz, 1H), 3.32 (t, J = 4.4 Hz, 2H), 3.08 (dd, J = 11.0, 3.3 Hz, 2H), 2.65 (dt, J = 11.0, 3.7 Hz, 2H), 1.25 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.9, 140.5, 128.1, 123.0, 91.0 (d, J = 201.4 Hz), 63.9, 43.5 (d, J = 17.4 Hz), 43.4 (d, J = 2.5 Hz), 21.8. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –63.7 (t, 3F), –149.1 (m, 2F), –150.7 (m, 2F), –198.4 (dt, J = 56.0, 3.8, 1F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}F_8N_2O$, 479.1291; found, 479.1364.
Melting point: 125–127 °C
Chromatography conditions: 3% EtOAc in hexanes



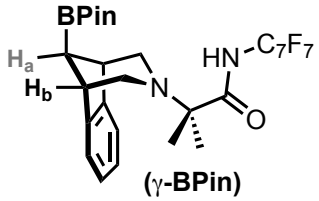
(γ-I)

γ-I: Procedure B was followed using *N*-iodosuccinimide as the oxidant.
Isolated yield: 6.0 mg, 24% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.44 (br s, 1H), 7.21 (dd, J = 5.3, 3.1 Hz, 2H), 7.13 (dd, J = 5.3, 3.1 Hz, 2H), 4.68 (t, J_{ab} = 4.4 Hz, 1H), 3.27 (d, J = 10.7 Hz, 2H), 3.21 (t, J = 3.8 Hz, 2H), 2.77 (dd, J = 11.4, 3.8 Hz, 2H), 1.28 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.8, 142.7, 127.6, 121.6, 63.9, 46.2, 45.4, 37.1, 21.9. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.1 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{18}F_7IN_2O$, 587.0352; found, 587.0423.
Melting point: 107–110 °C
Chromatography conditions: 5% EtOAc in hexanes



(γ-OAc)

γ-OAc: Procedure A was followed using iodomesitylene diacetate as the oxidant.
Isolated yield: 11.9 mg, 53% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.49 (br s, *NH of amide*, variable integrations), 7.22 (dd, J = 5.4, 3.1 Hz, 2H), 7.16 (dd, J = 5.4, 3.1 Hz, 2H), 5.03 (t, J_{ab} = 4.8 Hz, 1H), 3.34 (t, J = 4.1 Hz, 2H), 2.99 (d, J = 10.7 Hz, 2H), 2.63 (dd, J = 10.7, 3.7 Hz, 2H), 2.20 (s, 3H), 1.25 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.0, 170.3, 141.7, 127.8, 122.6, 74.6, 63.9, 43.7, 42.7, 29.9, 21.7, 21.3. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.1 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{24}H_{21}F_7N_2O_3$, 519.1440; found, 519.1509.
Melting point: 110–112 °C
Chromatography conditions: 10% EtOAc in hexanes



γ-BPin: Procedure C was followed using bis(pinacolato) diboron as the oxidant.

Isolated yield: 14.7 mg, 57% (colorless solid)

^{1}H NMR (401 MHz, $CDCl_3$, 23 ºC): δ 7.52 (br s, *NH of amide*, variable integrations), 7.15 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.03 (dd, *J* = 5.3, 3.1 Hz, 2H), 3.36 (t, *J* = 4.0 Hz, 2H), 2.89 (d, *J* = 10.5 Hz, 2H), 2.69 (dd, *J* = 10.5, 2.8 Hz, 2H), 1.94 (t, J_{ab} = 4.0 Hz, 1H), 1.32 (s, 12H), 1.19 (s, 6H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.4, 147.4, 126.5, 121.2, 83.6, 63.9, 48.6, 42.8, 29.9, 25.1, 21.7. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

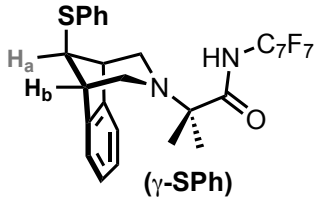
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.6 (m, 2F), –143.0 (m, 2F).

^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 32.8.

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{30}BF_7N_2O_3$, 587.2238; found, 587.2310.

Melting point: 149–153 °C

Chromatography conditions: 5% EtOAc in hexanes



γ-SPh: Procedure C was followed with phenyl disulfide as the oxidant.

Isolated yield: 18.7 mg, 75% (colorless solid)

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.49 (br s, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.20 (multiple peaks, 2H), 7.12 (d, *J* = 10.1 Hz, 2H), 3.86 (t, J_{ab} = 3.5 Hz, 1H), 3.28 (d, *J* = 10.0 Hz, 4H), 2.66 (d, *J* = 10.9 Hz, 2H), 1.28 (s, 6H).

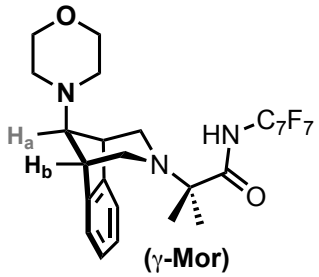
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.0, 144.7, 131.1, 129.3, 127.3, 127.1, 122.0, 64.0, 56.6, 44.6, 44.5, 29.9, 21.9. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.7 (t, 3F), –142.0 (m, 2F), –143.7 (m, 2F).

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{23}F_7N_2OS$, 569.1419; found, 569.1492.

Melting point: 70–75 °C

Chromatography conditions: 5% EtOAc in hexanes



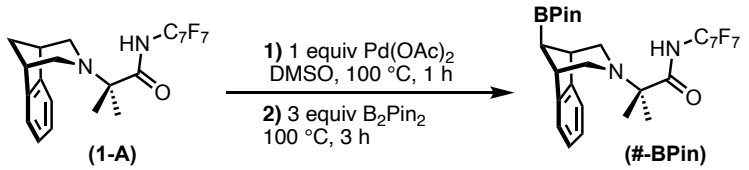
γ-Mor: Procedure C was followed with morpholino benzoate as the oxidant.

Isolated yield: 8.9 mg, 38% (colorless solid)

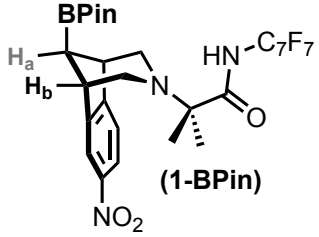
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.53 (br s, *NH of amide*, variable integrations), 7.19 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.12 (dd, *J* = 5.3, 3.1 Hz, 2H), 3.79 (t, *J* = 4.3 Hz, 4H), 3.24 (t, *J* = 4.0 Hz, 2H), 3.15 (d, *J* = 10.0 Hz, 2H), 2.60 (t, J_{ab} = 4.3 Hz, 1H), 2.53 (s, 4H), 2.48 (dd, *J* = 10.0, 3.8 Hz, 2H), 1.24 (s, 6H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.3, 144.2, 127.2, 122.4, 70.3, 67.1, 63.9, 50.9, 43.3, 41.8, 21.7. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.6 (m, 2F), –143.1 (m, 2F).
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{26}H_{26}F_7N_3O_2$, 546.1913; found, 546.1989.
Melting point: 107–109 °C
Chromatography conditions: 75% EtOAc in hexanes

VI. Scope of Pd-Mediated γ-Borylation Reaction



General Procedure: A 4 mL vial was charged with the **corresponding substrate** (1.0 equiv) and $Pd(OAc)_2$ (1.0 equiv). Dimethyl sulfoxide (0.6 mL) was added with a syringe. The vial was sealed with a Teflon-lined cap, and the mixture was stirred at 100 °C. After 1 h at this temperature, the vial was allowed to cool, the cap was removed, and B_2Pin_2 (3.0 equiv) was added. The vial was re-sealed, and the mixture was stirred and heated at 100 °C. After 3 h at this temperature, the reaction was cooled, diluted with dichloromethane, and stirred at rt for 10 min. The resulting suspension was filtered through a plug of Celite and concentrated under vacuum overnight. The crude material was purified via silica gel column chromatography. See substrate-specific notes below.



1-BPin: The general procedure was followed using substrate **1-B** (20.0 mg, 0.040 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.0 mg, 0.040 mmol, 1.0 equiv), and B_2Pin_2 (30.5 mg, 0.120 mmol, 3.0 equiv) as starting materials.

Isolated yield: 12.9 mg, 52% (colorless solid)

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 8.03 (dd, J = 7.9, 2.1 Hz, 1H), 8.00 (d, J = 2.1 Hz, 1H), 7.47 (br s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 3.47 (dt, J = 14.7, 4.1 Hz, 2H), 3.01–2.93 (multiple peaks, 2H), 2.77 (ddd, J = 21.7, 9.9, 4.1 Hz, 2H), 2.01 (t, J_{ab} = 4.8 Hz, 1H), 1.33 (s, 12H), 1.22 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.3, 155.3, 149.4, 147.3, 122.8, 121.6, 116.3, 83.9, 64.2, 48.5, 48.1, 42.8, 42.7, 25.1, 22.2, 20.6. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

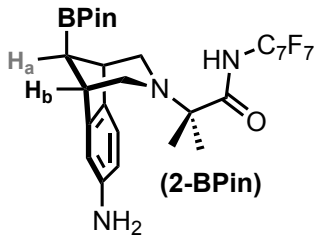
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –140.8 (m, 2F), –143.7 (m, 2F).

^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 32.7.

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{29}BF_7N_3O_5$, 632.2161; found, 632.2155.

Melting point: 115–120 °C

Chromatography conditions: 15% EtOAc in hexanes

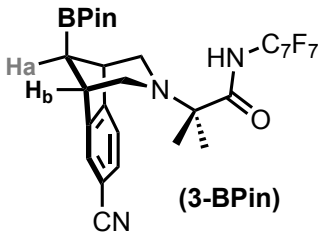


2-BPin: The general procedure was followed using substrate **1-C** (20.0 mg, 0.042 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.5 mg, 0.042 mmol, 1.0 equiv), and B_2Pin_2 (32.0 mg, 0.126 mmol, 3.0 equiv) as starting materials.

Isolated yield: 8.8 mg, 35% (colorless solid)

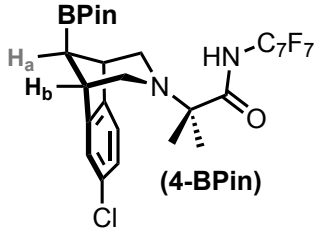
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.81 (br s, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.51 (d, J = 2.1 Hz, 1H), 6.33 (dd, J = 7.7, 2.1 Hz, 1H), 3.44 (app. s, 2H),

3.24 (dt, J = 12.0, 4.2 Hz, 2H), 2.84 (dd, J = 15.2, 10.6 Hz, 2H), 2.70–2.59 (multiple peaks, 2H), 1.89 (t, J_{ab} = 4.1 Hz, 1H), 1.31 (s, 12H), 1.19 (s, 3H), 1.19 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.5, 148.8, 145.3, 137.2, 121.7, 112.4, 109.2, 83.5, 63.9, 48.7, 48.6, 43.0, 42.0, 25.1, 21.9, 21.6. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.9 (m, 2F), –143.1 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 33.9.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{31}BF_7N_3O_3$, 602.2419; found, 602.2417.
Melting point: 107–110 °C
Chromatography conditions: 20% EtOAc in hexanes



(3-BPin)

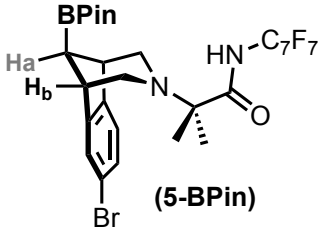
3-BPin: The general procedure was followed using substrate **1-N** (19.9 mg, 0.041 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.2 mg, 0.041 mmol, 1.0 equiv), and B_2Pin_2 (31.2 mg, 0.123 mmol, 3.0 equiv) as starting materials.
Isolated yield: 18 mg, 72% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.48-7.43 (multiple peaks, 2H), 7.43 (br s, 1H), 7.29 (d, J = 7.4 Hz, 1H), 3.43 (s, 2H), 2.94 (t, J = 10.2 Hz, 2H), 2.77-2.67 (multiple peaks, 2H), 1.96 (t, J_{ab} = 4.5 Hz, 1H), 1.32 (s, 12H), 1.21 (s, 3H), 1.20 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.4, 153.2, 148.9, 131.4, 124.4, 122.1, 119.1, 110.2, 83.9, 64.2, 48.4, 48.2, 43.0, 42.6, 25.1, 21.8, 21.0. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –140.8 (m, 2F), –143.6 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 32.2.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{29}H_{29}BF_7N_3O_3$, 612.2190; found, 612.2210.
Melting point: 65–67 °C
Chromatography conditions: 15% EtOAc in hexanes



(4-BPin)

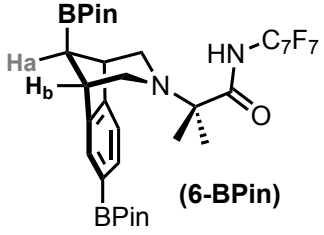
4-BPin: The general procedure was followed using substrate **1-D** (20.0 mg, 0.040 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.0 mg, 0.040 mmol, 1.0 equiv), and B_2Pin_2 (30.5 mg, 0.120 mmol, 3.0 equiv) as starting materials.
Isolated yield: 10.8 mg, 44% (colorless oil)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.59 (br s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.06 (dd, J = 7.8, 2.0 Hz, 1H), 3.34 (dt, J = 13.7, 4.2 Hz, 2H), 2.89 (t, J = 11.4 Hz, 2H), 2.72 (dd, J = 10.7, 4.2 Hz, 1H), 2.65 (dd, J = 10.7, 4.2 Hz, 1H), 1.94 (t, J_{ab} = 4.2 Hz, 1H), 1.32 (s, 12H), 1.21 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.9, 149.5, 146.0, 132.0, 126.5, 122.3, 121.8, 83.7, 64.0, 48.7, 48.1, 42.9, 42.4, 25.1, 25.0, 22.4, 20.8. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.3 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 33.6.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{29}BClF_7N_2O_3$, 621.1921; found, 621.1920.
Chromatography conditions: 10% EtOAc in hexanes



(5-BPin)

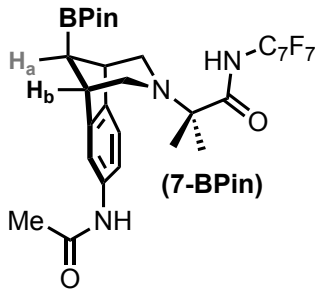
5-BPin: The general procedure was followed using substrate **1-L** (20.0 mg, 0.040 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.0 mg, 0.040 mmol, 1.0 equiv), and B_2Pin_2 (30.5 mg, 0.120 mmol, 3.0 equiv) as starting materials.
Isolated yield: 19.3 mg, 72% (colorless oil)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.57 (br s, 1H), 7.25-7.20 (multiple peaks, 2H), 7.06 (d, J = 7.7 Hz, 1H), 3.33 (dt, J = 13.9, 4.3 Hz, 2H), 2.90 (dd, J = 16.0, 10.6 Hz, 2H), 2.74 (dd, J = 10.6, 4.1 Hz, 1H), 2.63 (dd, J = 10.6, 4.1 Hz, 1H), 1.94 (t, J_{ab} = 4.5 Hz, 1H), 1.32 (s, 12H), 1.21 (s, 3H), 1.18 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.9, 149.8, 146.6, 129.5, 124.6, 122.8, 119.9, 83.7, 64.0, 48.9, 47.9, 42.8, 42.5, 25.1, 25.0, 22.9, 20.4. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –143.3 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 31.9.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{29}BBrF_7N_2O_3$, 665.1416; found, 665.1420.
Chromatography conditions: 10% EtOAc in hexanes



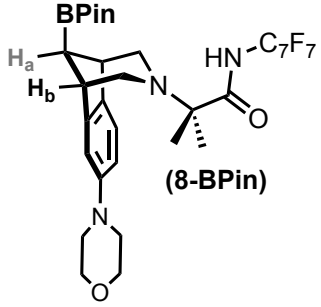
(6-BPin)

6-BPin: The general procedure was followed using substrate **1-M** (20.0 mg, 0.034 mmol, 1.0 equiv), $Pd(OAc)_2$ (7.7 mg, 0.034 mmol, 1.0 equiv), and B_2Pin_2 (26.0 mg, 0.120 mmol, 3.0 equiv) as starting materials.
Isolated yield: 11.6 mg, 48% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.60 (br s, 1H), 7.50-7.44 (multiple peaks, 2H), 7.14 (d, J = 7.2 Hz, 1H), 3.36 (d, J = 4.3 Hz, 2H), 2.90 (dd, J = 10.6, 7.5 Hz, 2H), 2.76-2.64 (multiple peaks, 2H), 1.92 (t, J_{ab} = 4.3 Hz, 1H), 1.32 (s, 12H), 1.29 (s, 6H), 1.28 (s, 6H), 1.17 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.3, 151.1, 146.7, 133.7, 127.0, 120.7, 83.8, 83.6, 63.8, 48.6, 48.6, 43.0, 42.5, 25.1, 25.1, 24.8, 24.7, 21.9, 21.5. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.4 (m, 2F), –142.8 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 30.1.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{34}H_{41}B_2F_7N_2O_5$, 713.3090; found, 713.3115.

Melting point: 155–158 °C
Chromatography conditions: 40% EtOAc in hexanes

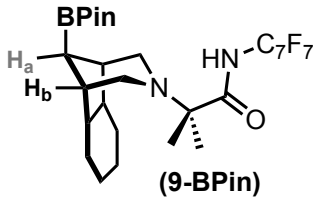


7-BPin: The general procedure was followed using substrate **1-E** (20.0 mg, 0.039 mmol, 1.0 equiv), $Pd(OAc)_2$ (8.8 mg, 0.039 mmol, 1.0 equiv), and B_2Pin_2 (29.7 mg, 0.117 mmol, 3.0 equiv) as starting materials.
Isolated yield: 17.3 mg, 69% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.68 (br s, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.12–7.04 (multiple peaks, 2H), 7.00 (dd, J = 7.8, 2.0 Hz, 1H), 3.34-3.30 (multiple peaks, 2H), 2.87 (dd, J = 13.0, 11.0 Hz, 2H), 2.74–2.62 (multiple peaks, 2H), 2.04 (s, 3H), 1.92 (t, J_{ab} = 4.3 Hz, 1H), 1.31 (s, 12H), 1.20 (s, 3H), 1.17 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.1, 167.9, 148.3, 143.3, 136.6, 121.4, 117.5, 113.5, 83.6, 63.9, 48.8, 48.2, 43.0, 42.4, 25.1, 25.0, 24.3, 22.7, 20.7. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.9 (m, 2F), –143.1 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 31.7.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{30}H_{33}BF_7N_3O_4$, 644.2525; found, 644.2519.
Melting point: 60–65 °C
Chromatography conditions: 25% EtOAc in hexanes



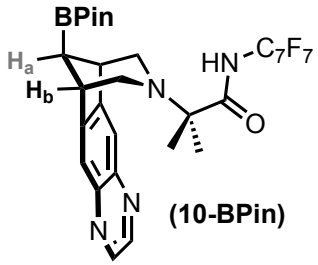
8-BPin: The general procedure was followed using substrate **1-F** (20.0 mg, 0.037 mmol, 1.0 equiv), $Pd(OAc)_2$ (8.3 mg, 0.037 mmol, 1.0 equiv), and B_2Pin_2 (28.2 mg, 0.111 mmol, 3.0 equiv) as starting materials.
Isolated yield: 13.1 mg, 53% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.75 (br s, *NH of amide*, variable integrations), 7.04 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 2.3 Hz, 1H), 6.54 (dd, J = 8.0, 2.3 Hz, 1H), 3.75 (ddd, J = 5.8, 3.8, 2.1 Hz, 4H), 3.29 (dt, J = 15.1, 3.8 Hz, 2H), 2.95 (dddd, J = 17.5, 11.7, 9.5, 4.7 Hz, 4H), 2.91–2.84 (multiple peaks, 2H), 2.67 (ddd, J = 30.5, 10.7, 4.1 Hz, 2H), 1.91 (t, J_{ab} = 4.0, 1H), 1.32 (s, 12H), 1.19 (s, 3H), 1.18 (s, 3H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.4, 150.6, 148.5, 139.0, 121.6, 113.0, 110.0, 83.6, 67.0, 63.8, 49.9, 48.9, 48.4, 43.3, 42.1, 25.1, 22.4, 21.1. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.6 (m, 2F), –142.7 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 33.2.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{32}H_{37}BF_7N_3O_4$, 672.2838; found, 672.2829.
Melting point: 168–171 °C

Chromatography conditions: 15% EtOAc in hexanes



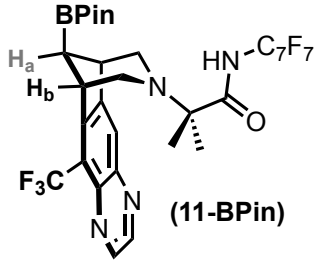
(9-BPin)

9-BPin: The general procedure was followed using substrate **1-G** (20.0 mg, 0.043 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.7 mg, 0.043 mmol, 1.0 equiv), and B_2Pin_2 (32.8 mg, 0.129 mmol, 3.0 equiv) as starting materials.
Isolated yield: 12.3 mg, 48% (colorless solid)
^{1}H NMR (700 MHz, CD_3OD, 23 ºC): δ 2.74 (dt, J = 10.7, 2.2 Hz, 2H), 2.70 (dd, J = 10.7, 1.9 Hz, 2H), 2.20 (s, 2H), 2.02–1.88 (multiple peaks, 5H), 1.77 (d, J = 8.3 Hz, 2H), 1.38 (s, 6H), 1.29 (d, J = 1.0 Hz, 15H), 1.13 (t, J_{ab} = 4.1 Hz, 1H). *Note in CD_3OD, amide H is not observed.*
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.4, 83.2, 65.1, 46.1, 41.4, 40.4, 25.2, 20.6, 20.6, 20.4. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.1 (m, 2F), –143.2 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 31.7.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{36}BF_7N_2O_3$, 593.2780; found, 593.2774.
Melting point: 50–53 °C
Chromatography conditions: 5% EtOAc in hexanes



(10-BPin)

10-BPin: The general procedure was followed using substrate **1-H** (20.0 mg, 0.039 mmol, 1.0 equiv), $Pd(OAc)_2$ (8.8 mg, 0.039 mmol, 1.0 equiv), and B_2Pin_2 (29.7 mg, 0.117 mmol, 3.0 equiv) as starting materials.
Isolated yield: 7.0 mg, 28% (colorless solid)
^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 8.71 (app. s, 2H), 7.77 (app. s, 2H), 7.46 (br s, 1H), 3.63 (t, J = 4.0 Hz, 2H), 3.06 (d, J = 11.0 Hz, 2H), 2.89 (dd, J = 11.0, 4.0 Hz, 2H), 2.05 (t, J_{ab} = 4.0 Hz, 1H), 1.35 (s, 12H), 1.19 (s, 6H).
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.2, 151.5, 144.0, 143.2, 120.4, 83.9, 64.1, 49.7, 42.8, 25.1, 21.5. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (s, 3F), –141.4 (m, 2F), –144.3 (m, 2F).
^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 32.7.
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{30}H_{30}BF_7N_4O_3$, 639.2372; found, 639.2355.
Melting point: 110–115 °C
Chromatography conditions: 30% EtOAc in pentanes



11-BPin: The general procedure was followed using substrate **1-I** (20.0 mg, 0.035 mmol, 1.0 equiv), $Pd(OAc)_2$ (7.9 mg, 0.035 mmol, 1.0 equiv), and B_2Pin_2 (26.7 mg, 0.105 mmol, 3.0 equiv) as starting materials.

Isolated yield: 14.1 mg, 57% (colorless oil)

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 8.86 (d, J = 1.8 Hz, 1H), 8.82 (d, J = 1.8 Hz, 1H), 7.97 (s, 1H), 7.43 (s, 1H), 4.11 (m, 1H), 3.66 (m, 1H), 3.11–2.99 (multiple peaks, 3H), 2.89 (dd, J = 11.0, 4.5 Hz, 1H), 2.02 (t, J_{ab} = 4.0 Hz 1H), 1.35 (s, 12H), 1.21 (s, 3H), 1.19 (s, 3H).

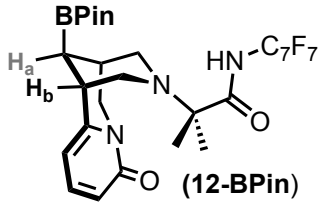
^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 174.5, 151.8, 150.8, 144.8, 144.1, 142.8, 140.1, 124.3 (q, J = 276.9 Hz), 124.1, 120.5 (q, J = 30.2 Hz), 84.1, 64.2, 49.7, 49.4, 43.1, 42.4, 29.9, 25.1, 25.1, 21.41, 21.4. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –55.4 (s, 3F), –56.0 (t, 3F), –141.6 (m, 2F), –144.8 (m, 2F).

^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 35.5.

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{31}H_{29}BF_{10}N_4O_3$, 707.2246; found, 707.2246.

Chromatography conditions: 25% EtOAc in hexanes



12-BPin: The general procedure was followed using substrate **1-J** (20.0 mg, 0.041 mmol, 1.0 equiv), $Pd(OAc)_2$ (9.2 mg, 0.041 mmol, 1.0 equiv), and B_2Pin_2 (31.2 mg, 0.123 mmol, 3.0 equiv) as starting materials.

Isolated yield: 9.1 mg, 36% (light yellow solid)

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 7.71 (s, 1H), 7.03 (dd, J = 9.2, 6.8 Hz, 1H), 6.33 (dd, J = 9.2, 1.4 Hz, 1H), 5.95 (d, J = 7.1 Hz, 1H), 4.18 (d, J = 15.4 Hz, 1H), 3.91 (dd, J = 15.4, 6.4 Hz, 1H), 3.24 (m, 1H), 3.02 (d, J = 11.3 Hz, 1H), 2.79 (d, J = 10.8 Hz, 1H), 2.77–2.70 (multiple peaks, 2H), 2.66 (d, J = 11.3 Hz, 1H), 1.31 (s, 12H), 1.28 (s, 3H), 1.26 (app. d, J_{ab} = 4.9 Hz, 1H), 1.18 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 175.0, 163.3, 151.3, 138.4, 117.1, 104.6, 84.4, 64.6, 54.4, 51.8, 51.2, 36.9, 29.9, 29.6, 25.0, 25.0, 23.8, 17.4. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

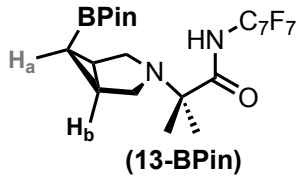
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.1 (t, 3F), –141.0 (m, 2F), –142.8 (m, 2F).

^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 31.7.

HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{28}H_{31}BF_7N_3O_4$, 618.2369; found, 618.2370.

Melting point: 67–72 °C

Chromatography conditions: 60% EtOAc in hexanes



(13-BPin)

13-BPin: The general procedure was followed using substrate **1-K** (20.0 mg, 0.052 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.7 mg, 0.052 mmol, 1.0 equiv), and B_2Pin_2 (40.0 mg, 0.156 mmol, 3.0 equiv) as starting materials.

Isolated yield: 5.2 mg, 20% (colorless oil)

^{1}H NMR (700 MHz, $CDCl_3$, 23 ºC): δ 9.92 (br s, 1H), 3.04 (d, J = 8.5 Hz, 2H), 2.70 (dt, J = 8.5, 2.1 Hz, 2H), 1.74–1.70 (multiple peaks, 2H), 1.31 (s, 6H), 1.13 (s, 12H), 0.02 (t, J_{ab} = 8.5 Hz, 1H).

^{13}C NMR (176 MHz, $CDCl_3$, 23 ºC): δ 176.3, 83.3, 61.8, 47.0, 25.5, 24.7, 20.9, 19.9. *Carbon resonances associated with perfluoroaryl group are not observed.*[1]

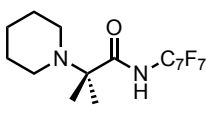
^{19}F NMR (470 MHz, $CDCl_3$, 23 ºC): δ –56.0 (t, 3F), –141.5 (m, 2F), –142.8 (m, 2F).

^{11}B NMR (128 MHz, $CDCl_3$, 23 °C): δ 33.8.

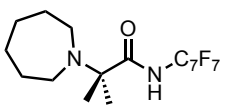
HRMS-electrospray (m/z): $[M]^+$ calcd. for $C_{22}H_{26}BF_7N_2O_3$, 511.1997; found, 511.1995.

Chromatography conditions: 5% EtOAc in pentanes. Performed on water-deactivated silica gel.

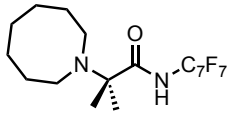
Table 3. Substrates that did not undergo Pd-mediated γ-borylation under these conditions



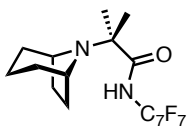
14-BPin, 0%



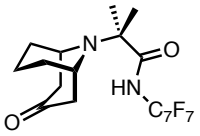
15-BPin, 10%



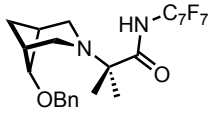
16-BPin, 10%



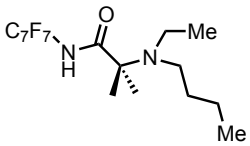
17-BPin, 0%



18-BPin, 0%



19-BPin, 0%



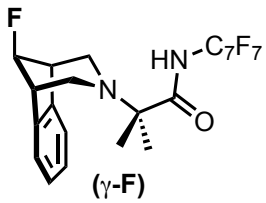
20-BPin, <5%

VII. References

(1) J. J. Topczewski, P. J. Cabrera, N. I. Saper, M. S. Sanford, *Nature* **2016**, *531*, 220–224.
(2) E. Y. Aguilera, M. S. Sanford, *Organometallics* **2019**, *38*, 138–142.
(3) J. W. Coe (Pfizer), WO1999055680A1, **1999**.
(4) R.-J. Tang, T. Milcent, B. Crousse, *J. Org. Chem.* **2018**, *83*, 930–938.
(5) F. Foubelo, M. Yus, *Reduction/Hydrogenation of Aromatic Rings in Arene Chemistry*, John Wiley & Sons, Ltd, **2015**, pp. 337–364.
(6) S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240–7241.
(7) Y. Ji, T. Brueckl, R. D. Baxter, Y. Fujiwara, I. B. Seiple, S. Su, D. G. Blackmond, P. S. Baran, *PNAS* **2011**, *108*, 14411–14415.
(8) S. C. Matthew, B. W. Glasspoole, P. Eisenberger, C. M. Crudden, *J. Am. Chem. Soc.* **2014**, *16*, 5828–5831.
(9) D. T. Cohen, S. L. Buchwald*, Org. Lett*. **2015**, *17*, 202–205.
(10) (a) A. A. Bothner-By in *Geminal and Vicinal Proton-Proton Coupling Constants in Organic Compound,* Vol. 1 (Eds: J. S. Waugh), **1965**, pp. 195-316. (b) E. W. Garbisch, M. G. Griffith, *J. Am. Chem. Soc*. **1968**, *90*, 6543–6544.

VIII. X-Ray Crystallography Data

Structure Determination of γ-F



(γ-F)

Colorless needles of **γ-F** were grown from a hexane solution of the compound at 23 ºC. A crystal of dimensions 0.10 x 0.02 x 0.02 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 7 s for the low angle images, 40 s for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 30204 reflections to a maximum 2θ value of 141.14° of which 3836 were independent and 2148 were greater than 2θ(I). The final cell constants (Table S1) were based on the xyz centroids of 2665 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1)/n with Z = 4 for the formula $C_{22}H_{18}F_8N_2O$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0911 and wR2 = 0.2445 [based on I > 2sigma(I)], R1 = 0.1491 and wR2 = 0.3127 for all data. Additional details are presented in Table 4 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

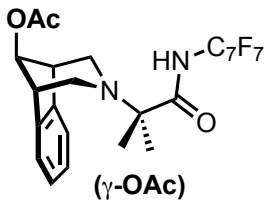
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table 4. Crystal Data and Structural Refinement for **γ-F.**

Empirical Formula	$C_{22}H_{18}F_8N_2O$
Formula Weight	478.38
Temperature	85 (2) K
Wavelength	1.54184 Å
Crystal System	monoclinic
Space Group	P2(1)/n
Unit Cell Dimensions	a = 6.6001(7) Å, α = 90°

	b = 18.5833(15) Å, β = 94.564(9)° c = 16.9595(13) Å, γ = 90°
Volume	2073.5(3) $Å^3$
Z	4
Calculated Density	1.532 Mg/m^3
Absorption Coefficient	1.278 mm^{-1}
F(000)	976
Crystal Size	0.100 x 0.020 x 0.020 mm
Theta Range for Data Collection	3.534 to 70.712
Limiting Indices	$-7 \leq h \leq 7$, $-22 \leq k \leq 22$, $-20 \leq l \leq 20$
Reflections Collected	30204
Independent Reflections	3836
Completeness to Theta	99.5%
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 to 0.42936
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	3836 / 0 / 304
Goodness-of-Fit on F^2	1.046
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0911, wR2 = 0.2445
R indices (all data)	R1 = 0.1491, wR2 = 0.3127
Extinction Coefficient	N/A
Largest Difference Peak and Hole	0.349 and -0.406 $Å^{-3}$

Structural Determination of γ-OAc



Colorless needles of **γ-OAc** were grown from an acetone solution of the compound at 23 °C. A crystal of dimensions 0.20 x 0.12 x 0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 33169 reflections to a maximum 2θ value of 138.49° of which 4179 were independent and 4103 were greater than 2σ(I). The final cell constants (Table S2) were based on the xyz centroids of 19361 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1)/n with Z = 4 for the formula $C_{24}H_{21}F_7N_2O_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0503 and wR2 = 0.1307 [based on I > 2sigma(I)], R1 = 0.0508 and wR2 = 0.1311 for all data. Additional details are presented in Table 5 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

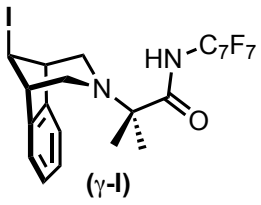
CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

Table 5. Crystal Data and Structural Refinement for **γ-OAc.**

Empirical Formula	$C_{24}H_{21}F_7N_2O_3$
Formula Weight	518.43
Temperature	85 (2) K
Wavelength	1.54184 A
Crystal System	monoclinic
Space Group	P2(1)/n
Unit Cell Dimensions	a = 13.6948(2) Å, α = 90 °

	b = 9.15070(10) Å, β = 102.8070(10)° c = 18.4622(2) Å, γ = 90 °
Volume	2256.07(5) $Å^3$
Z	4
Calculated Density	1.526 Mg/m^3
Absorption Coefficient	1.226 mm^{-1}
F(000)	1064
Crystal Size	0.200 x 0.120 x 0.100 mm
Theta Range for Data Collection	3.658 to 69.245 °
Limiting Indices	$-16\leq h\leq 16$, $-11\leq k\leq 11$, $-22\leq l\leq 22$
Reflections Collected	33169
Independent Reflections	4179
Completeness to Theta	99.9%
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 to 0.77789
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	4179 / 0 / 333
Goodness-of-Fit on F^2	1.064
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0503, wR2 = 0.1307
R indices (all data)	R1 = 0.0508, wR2 = 0.1311
Extinction Coefficient	0.0036(3)
Largest Difference Peak and Hole	0.851 and -0.545 $Å^{-3}$

Structural Determination of γ-I



(γ-I)

Colorless needles of **γ-I** were grown from a hexanes solution of the compound at 23 deg. C. A crystal of dimensions 0.18 x 0.05 x 0.02 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 3 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 32312 reflections to a maximum 2θ value of 138.72° of which 4126 were independent and 3860 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 14962 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2016/6) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{22}H_{18}N_2OF_7I$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0769 and wR2 = 0.2065 [based on I > 2sigma(I)], R1 = 0.0795 and wR2 = 0.2238 for all data. Additional details are presented in Table 6 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8 (Open Access).

CrystalClear Expert 2.0 r16, Rigaku Americas and Rigaku Corporation (2014), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

CrysAlisPro 1.171.38.41 (Rigaku Oxford Diffraction, 2015).

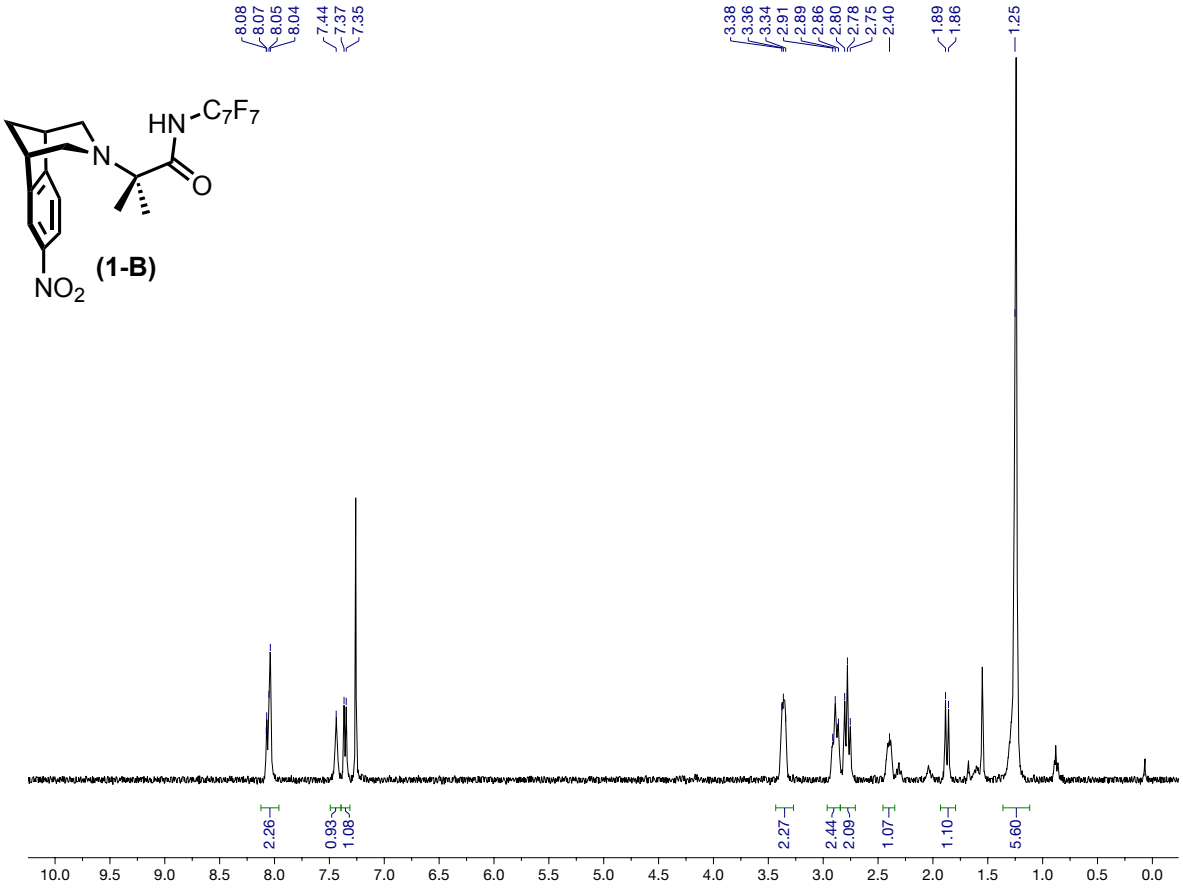
Table 6. Crystal Data and Structural Refinement for **γ-I.**

Empirical Formula	$C_{22}H_{18}F_7IN_2O$
Formula Weight	586.28
Temperature	85 (2) K
Wavelength	1.54184 A
Crystal System	monoclinic
Space Group	P2(1)/c
Unit Cell Dimensions	a = 20.9907(7) Å, α = 90 ° b = 6.6416(2) Å, β = 108.394(4)°

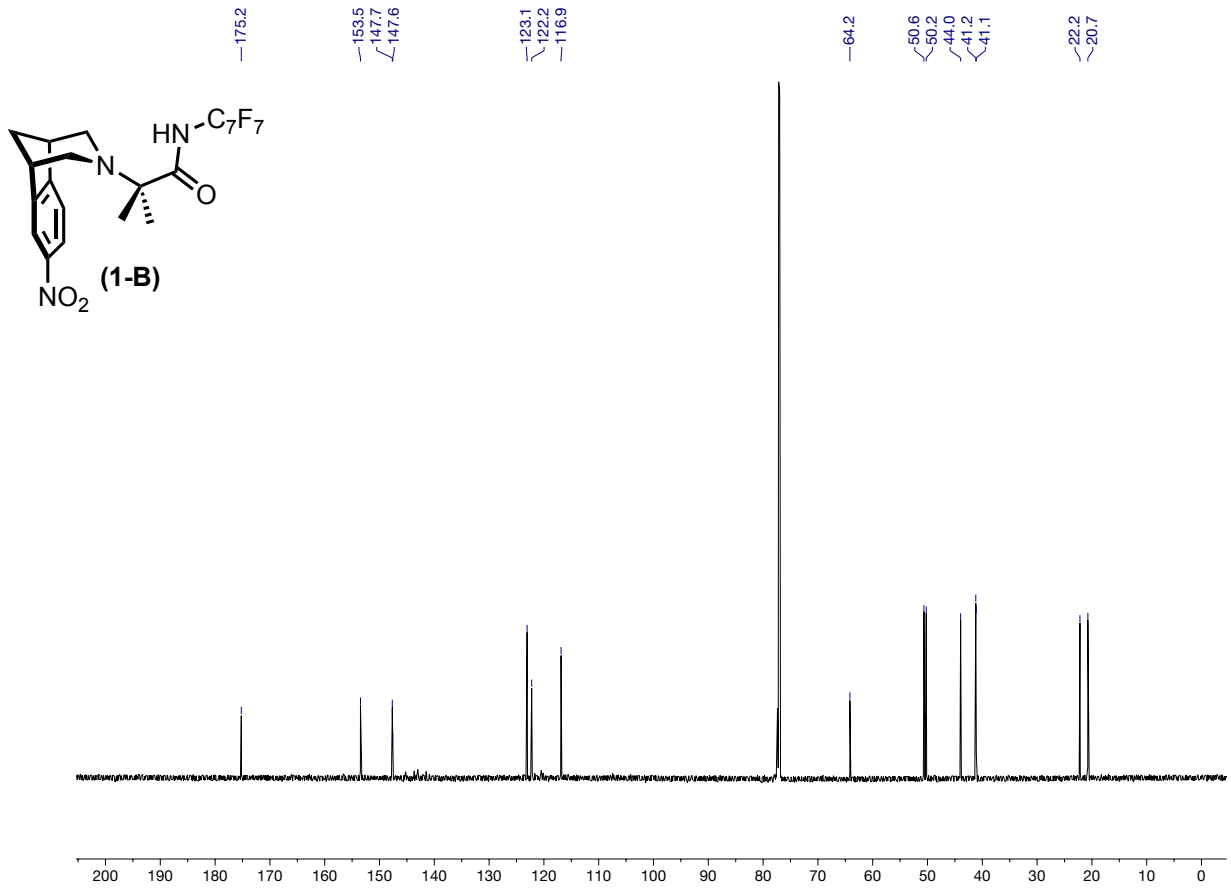
	c = 16.8750(8) Å, γ = 90 °
Volume	2232.38(15) $Å^3$
Z	4
Calculated Density	1.744 Mg/m^3
Absorption Coefficient	11.974 mm^{-1}
F(000)	1152
Crystal Size	0.180 x 0.050 x 0.020 mm
Theta Range for Data Collection	5.264 to 69.362 °
Limiting Indices	$-25 \leq h \leq 25$, $-8 \leq k \leq 7$, $-20 \leq l \leq 18$
Reflections Collected	32312
Independent Reflections	4126
Completeness to Theta	99.7%
Absorption Correction	Semi-empirical from equivalents
Max and Min Transmission	1.00000 to 0.31704
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	4126 / 0 / 300
Goodness-of-Fit on F^2	1.152
Final R Indices [$I>2\sigma(I)$]	R1 = 0.0769, wR2 = 0.2065
R indices (all data)	R1 = 0.0795, wR2 = 0.2238
Extinction Coefficient	n/a
Largest Difference Peak and Hole	2.541 and -0.477 $Å^{-3}$

IX. Spectral Data

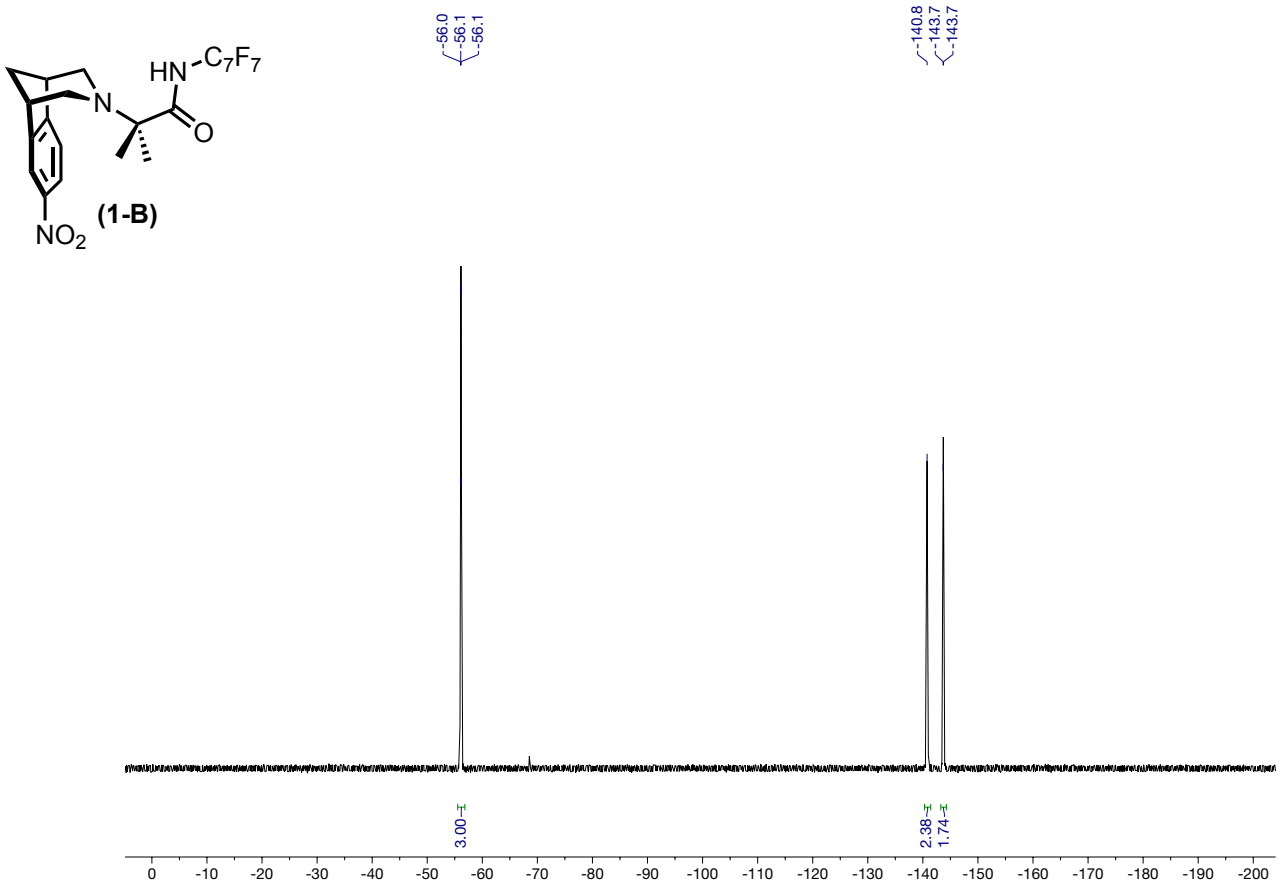
a. Substrate Spectral Data



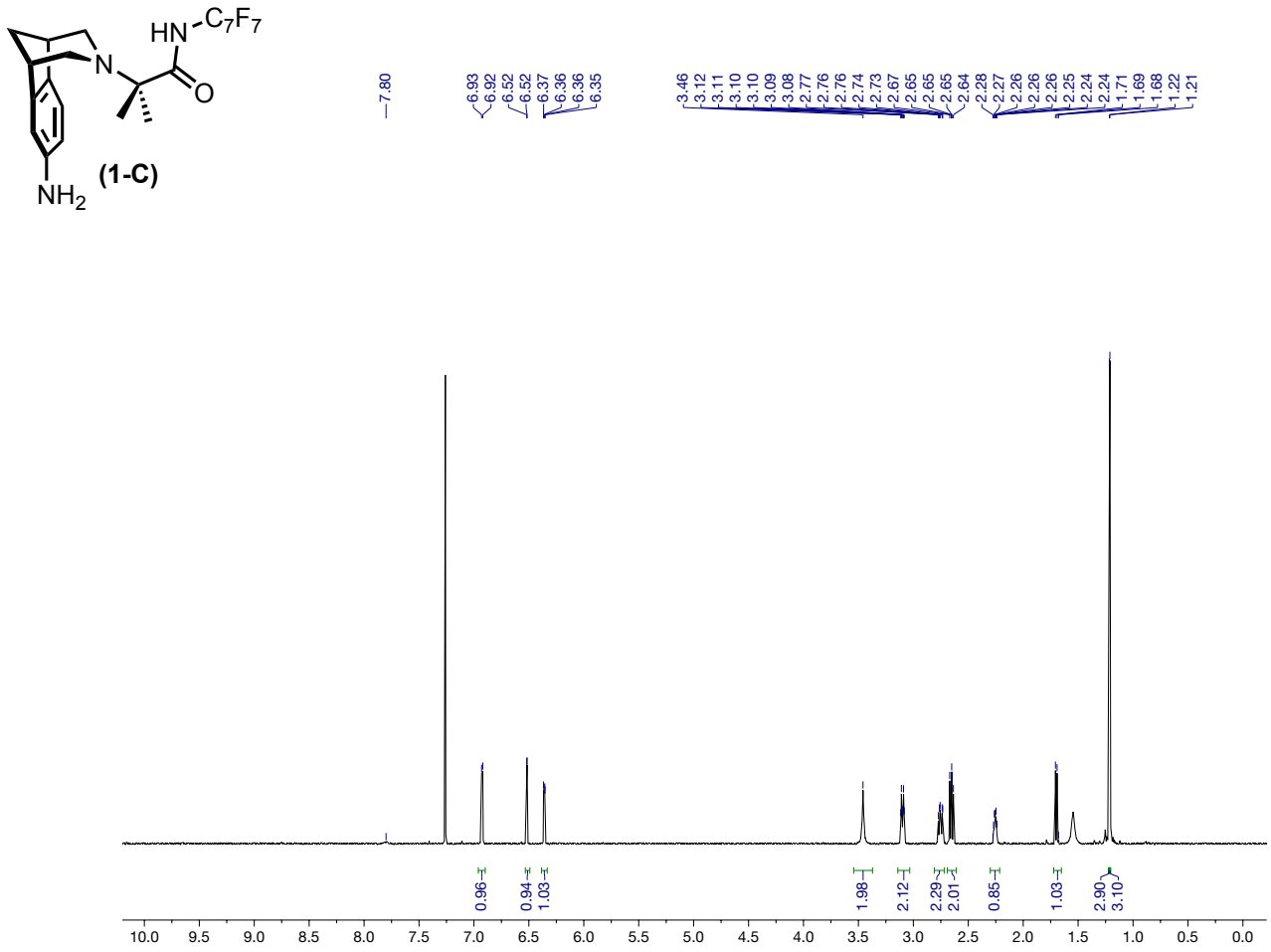
^{1}H NMR Spectrum in $CDCl_3$



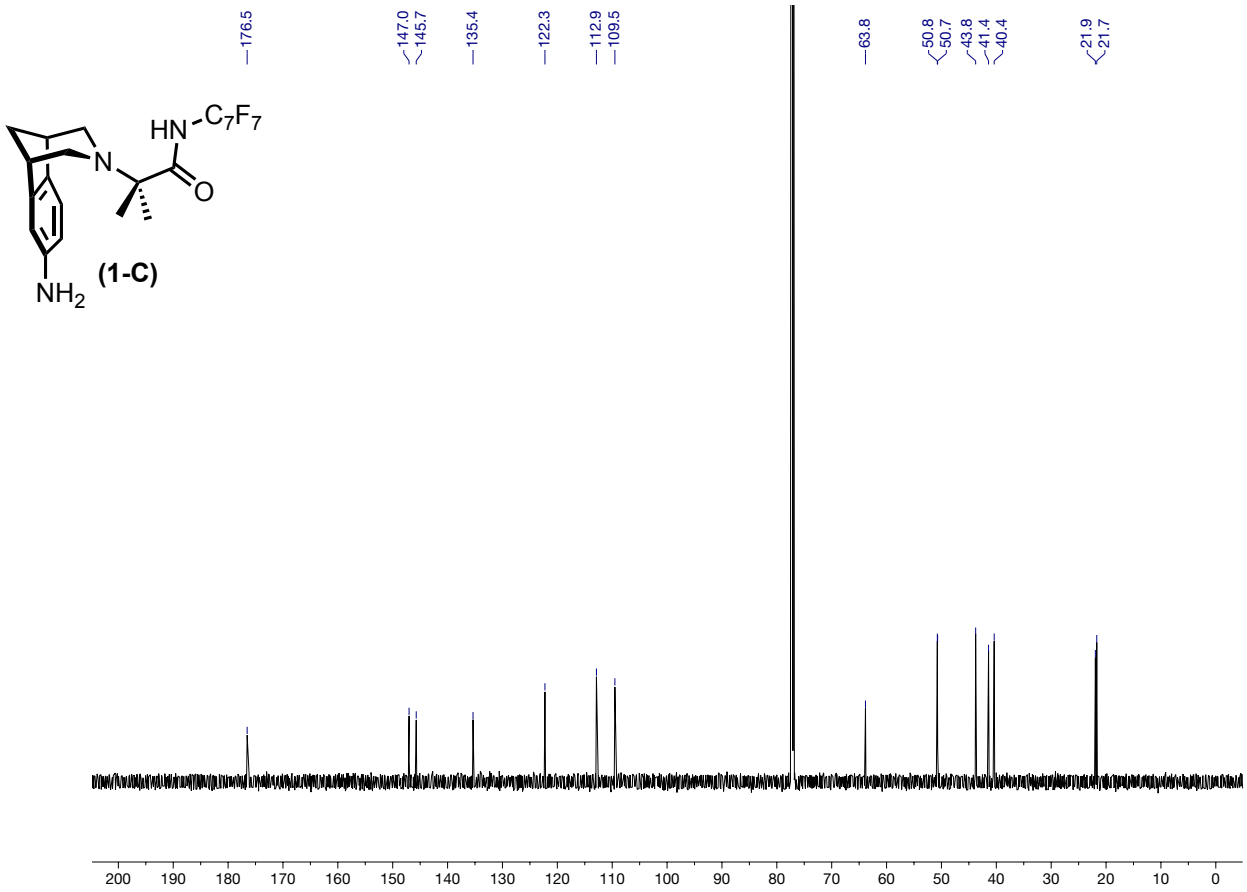
^{13}C NMR Spectrum in $CDCl_3$



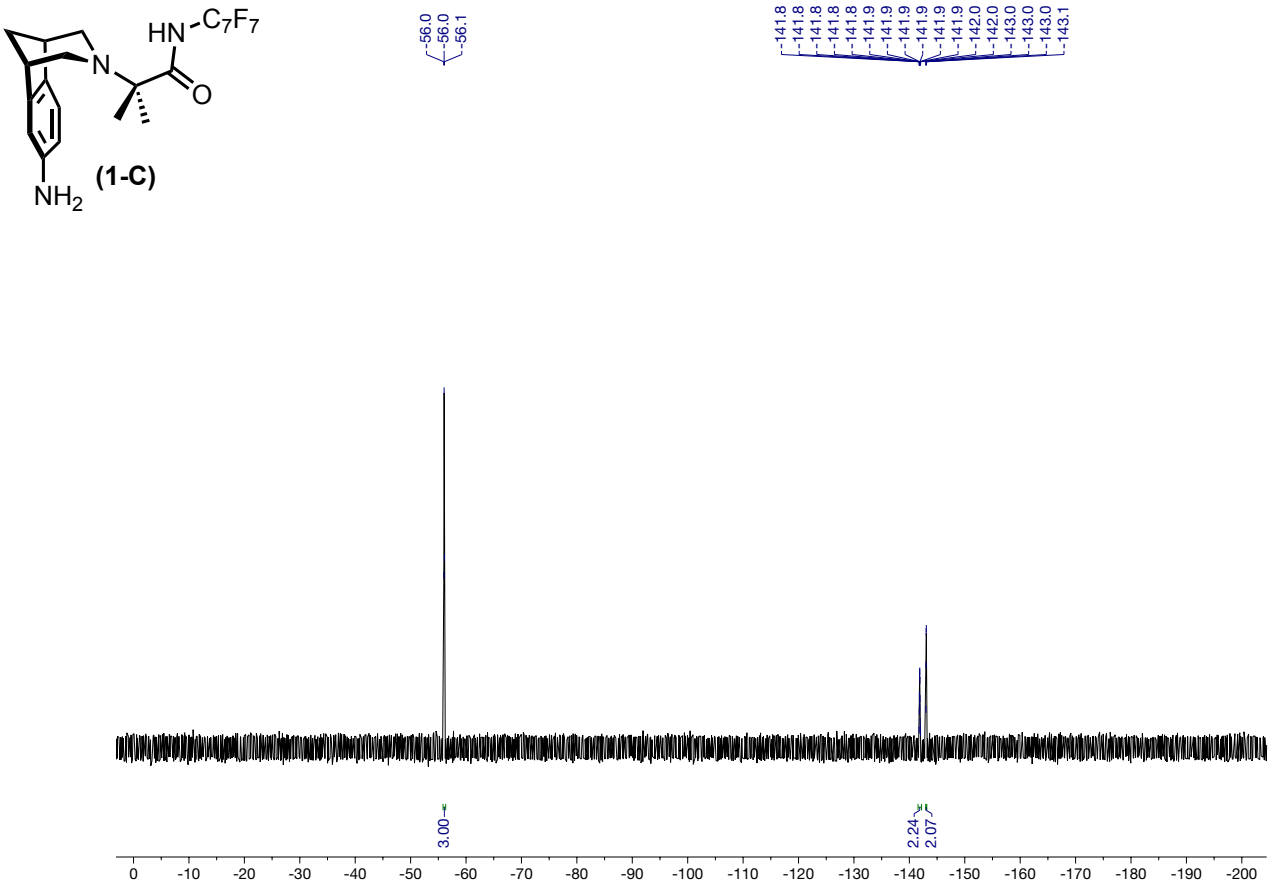
^{19}F NMR Spectrum in $CDCl_3$



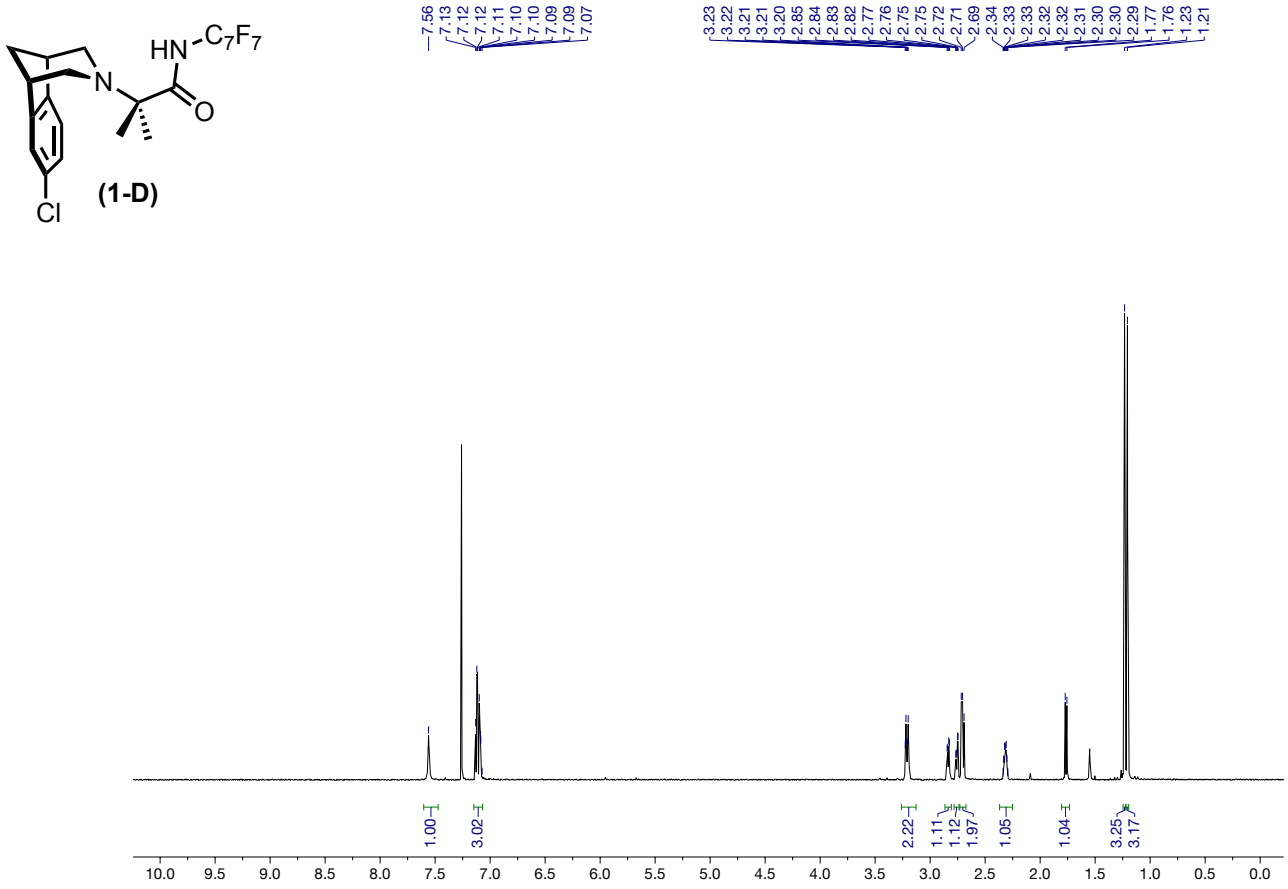
^{1}H NMR Spectrum in $CDCl_3$



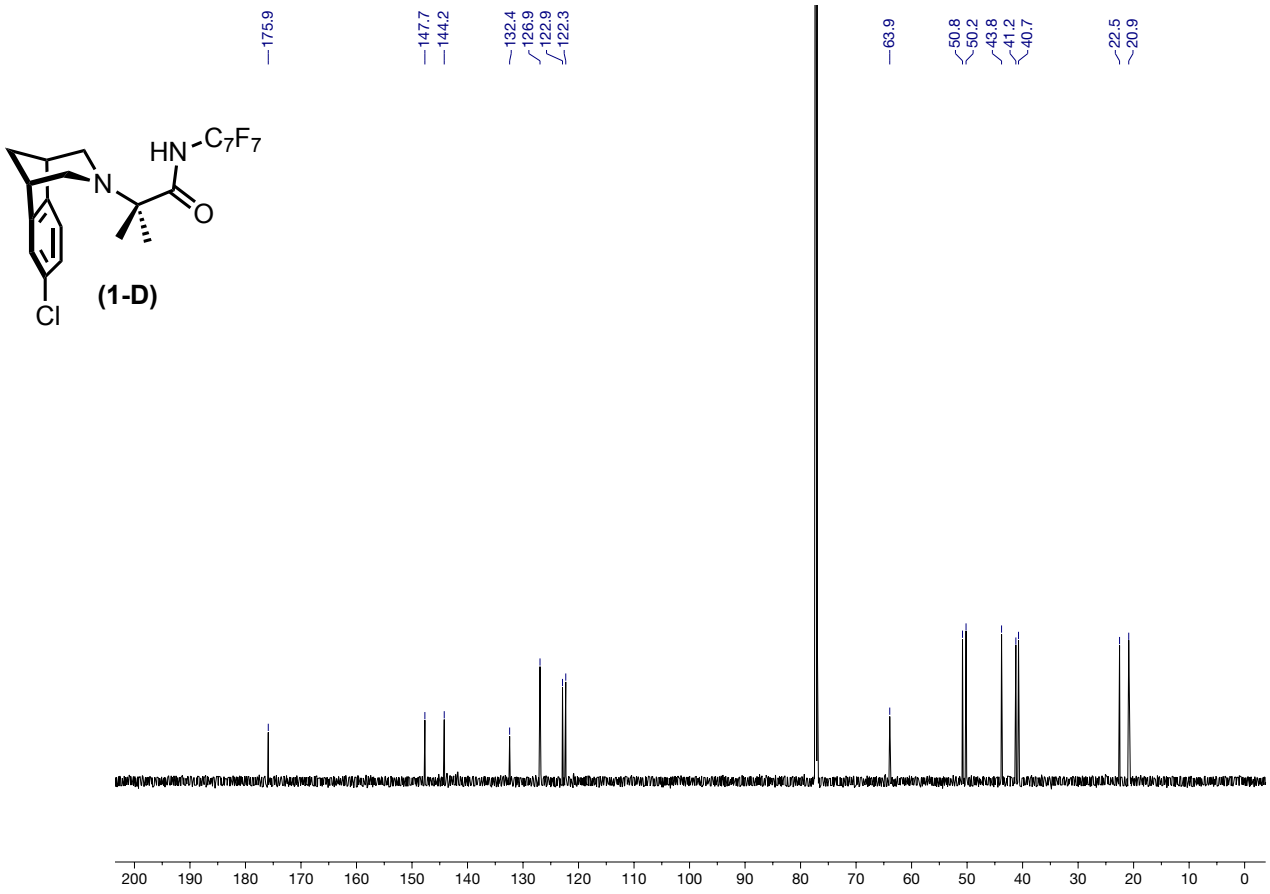
^{13}C NMR Spectrum in $CDCl_3$



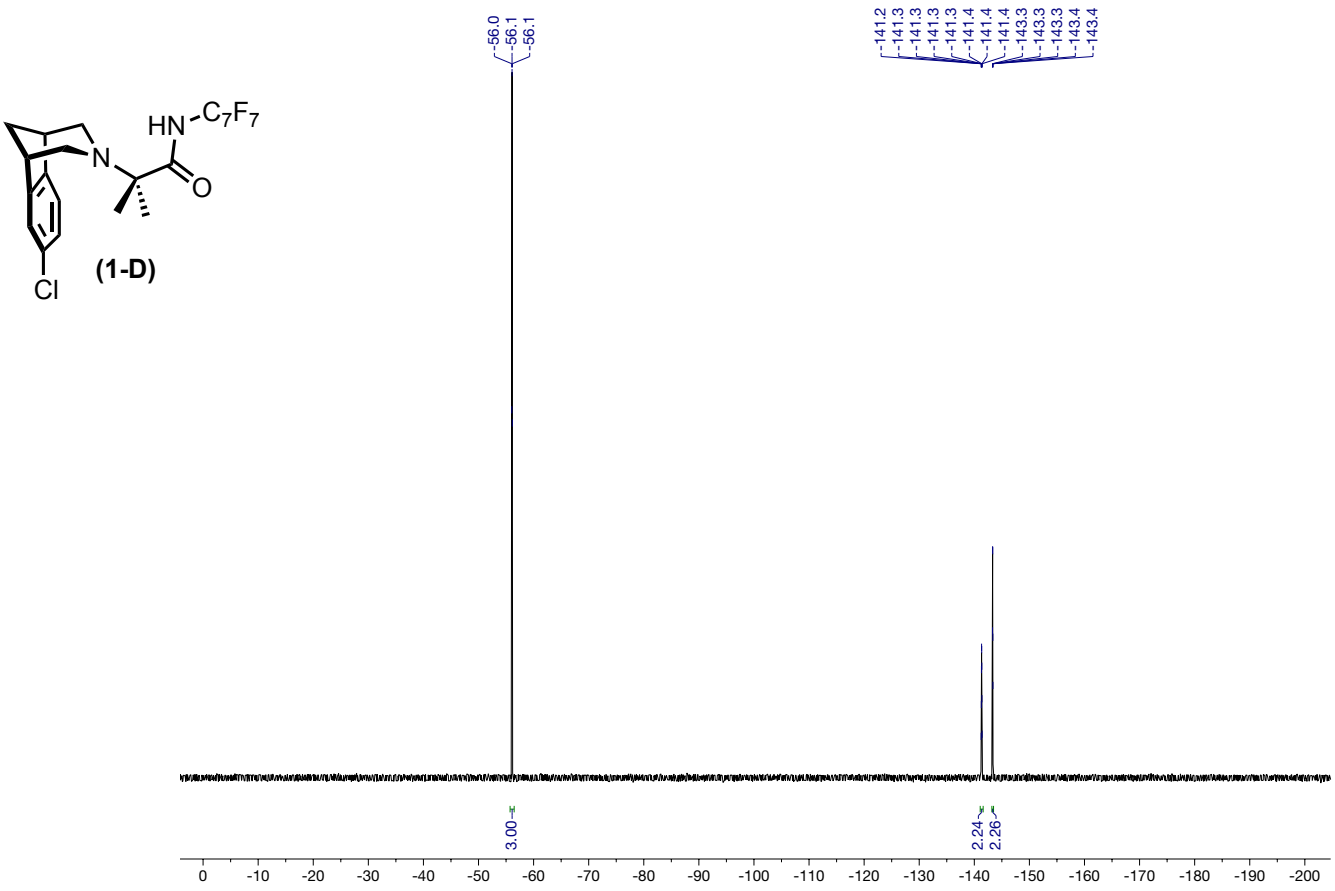
^{19}F NMR Spectrum in $CDCl_3$



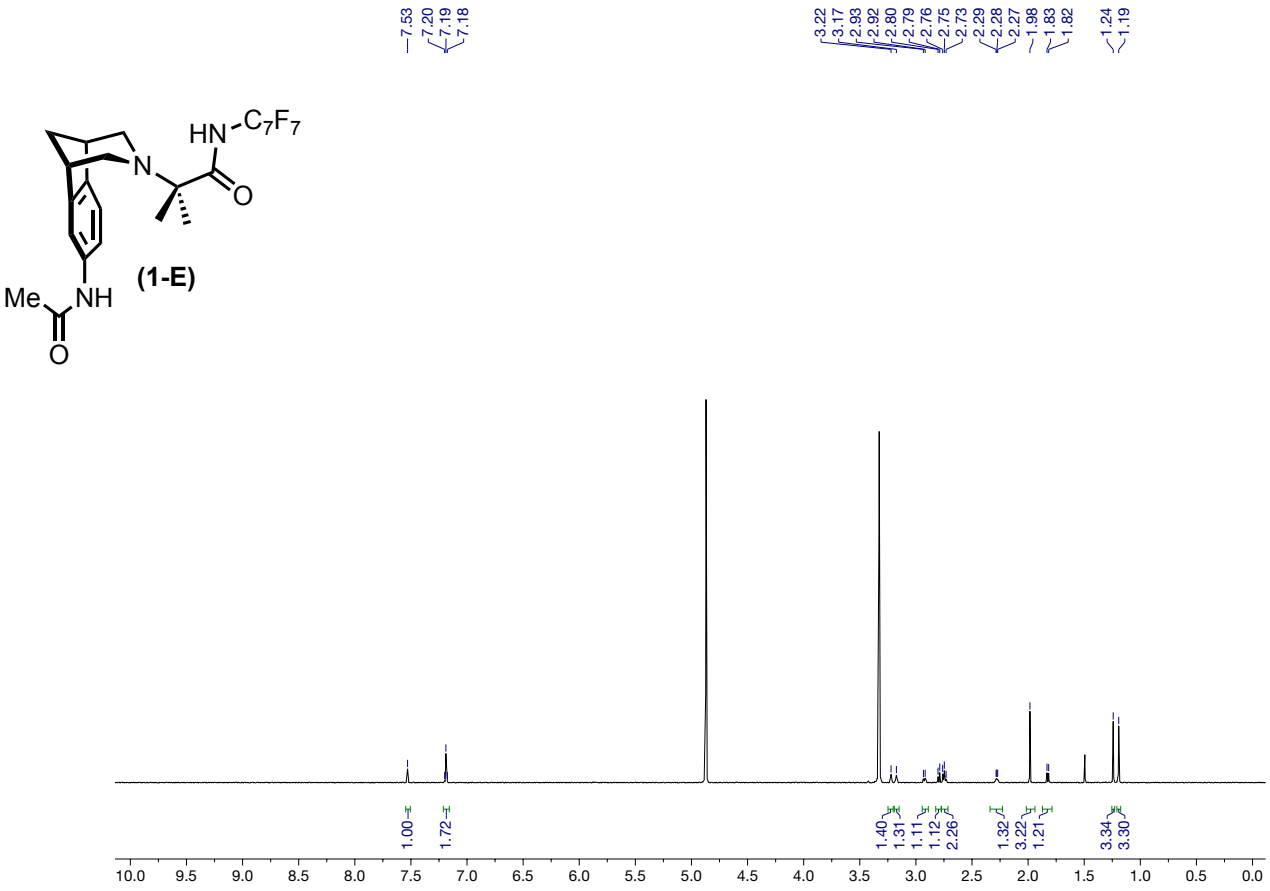
^{1}H NMR Spectrum in $CDCl_3$



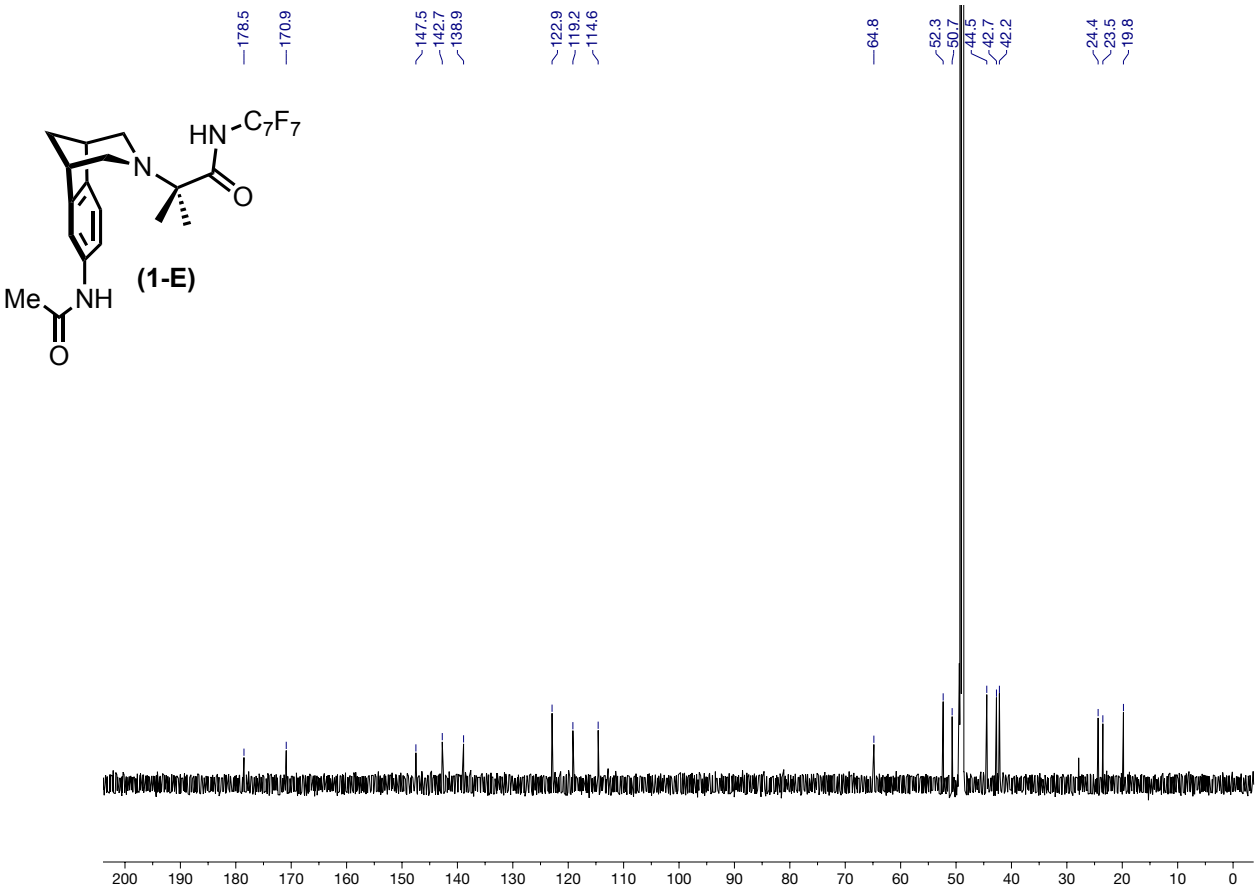
^{13}C NMR Spectrum in $CDCl_3$



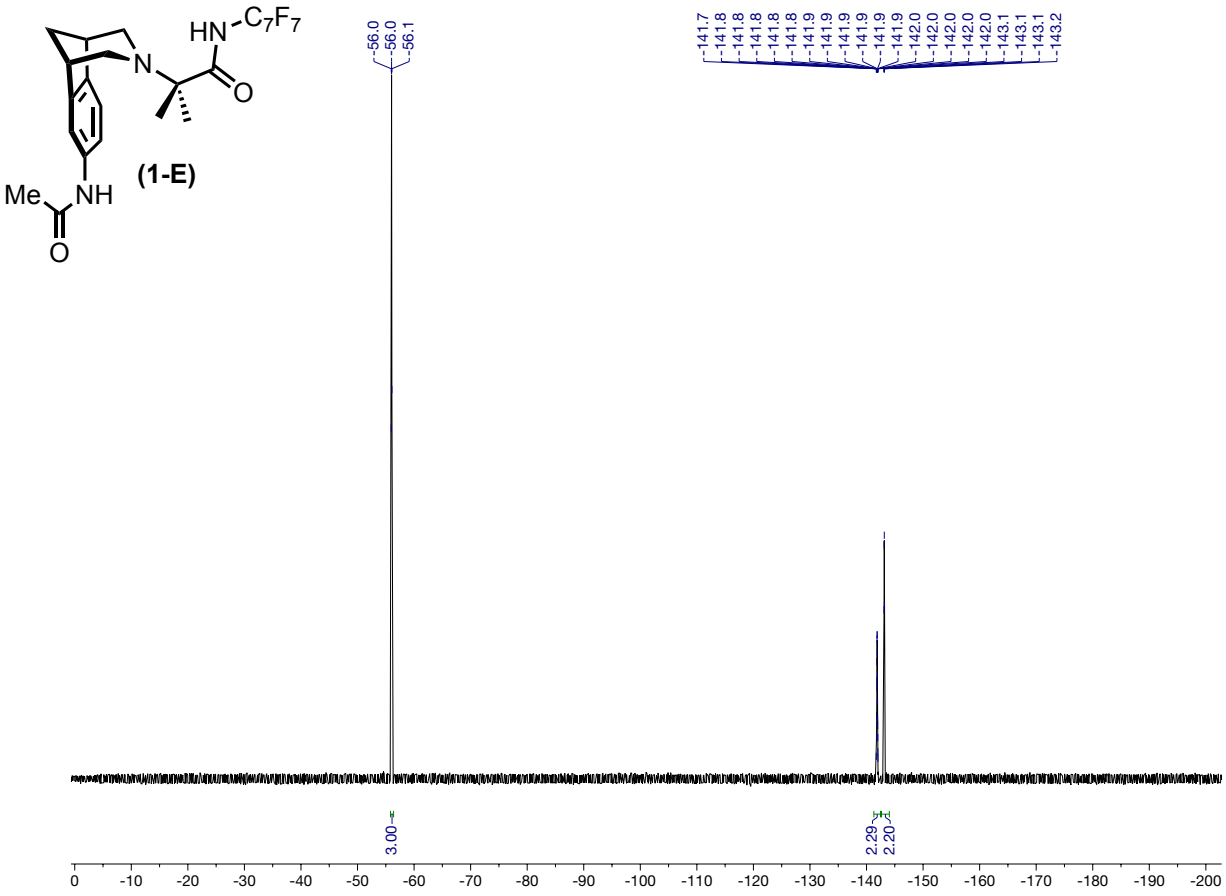
^{19}F NMR Spectrum in $CDCl_3$



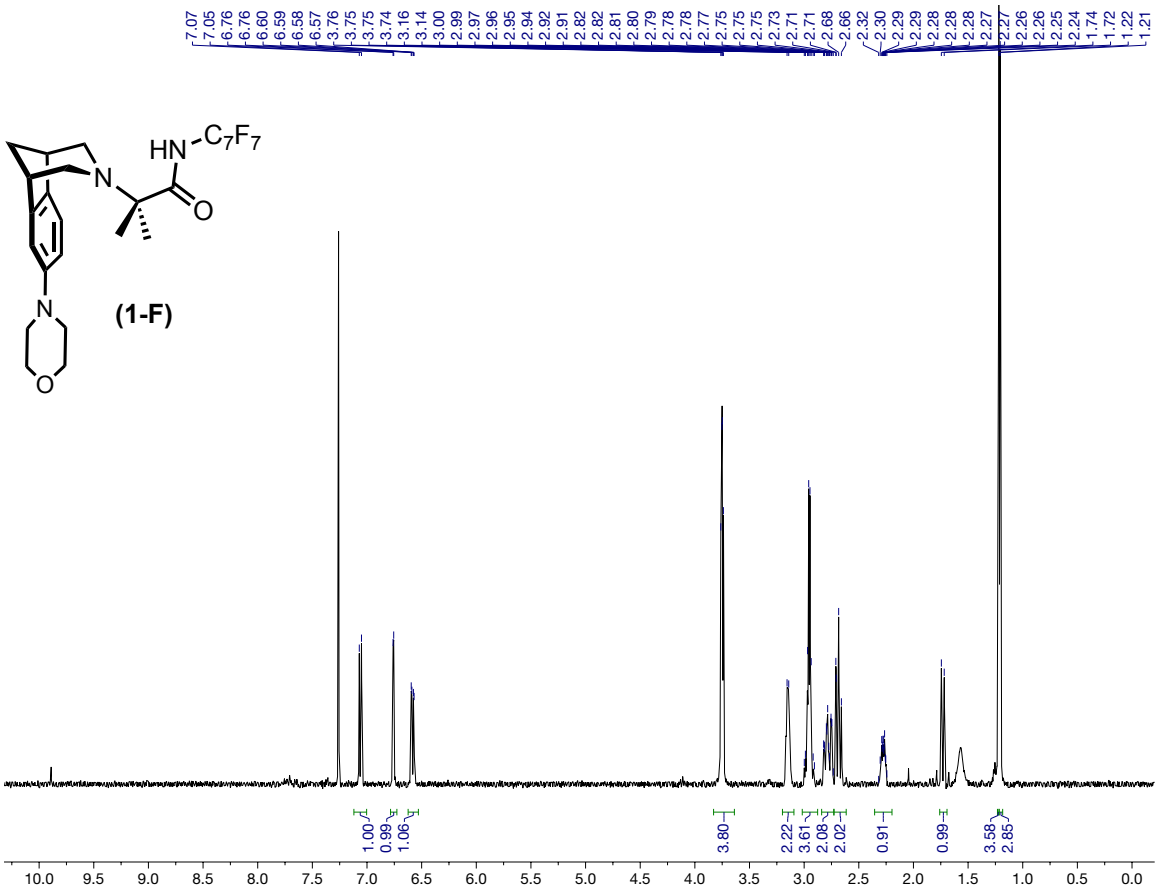
^{1}H NMR Spectrum in CD_3OD



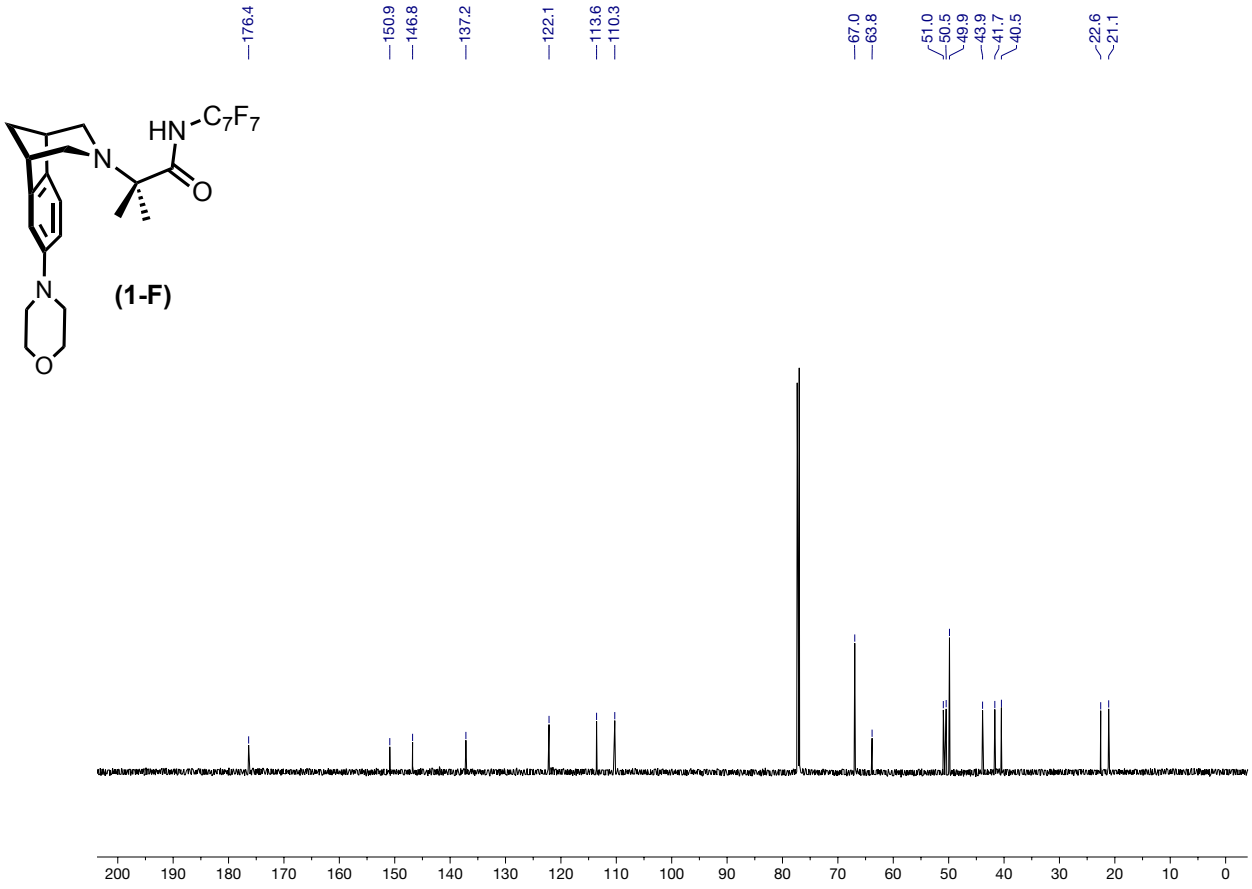
^{13}C NMR Spectrum in CD_3OD



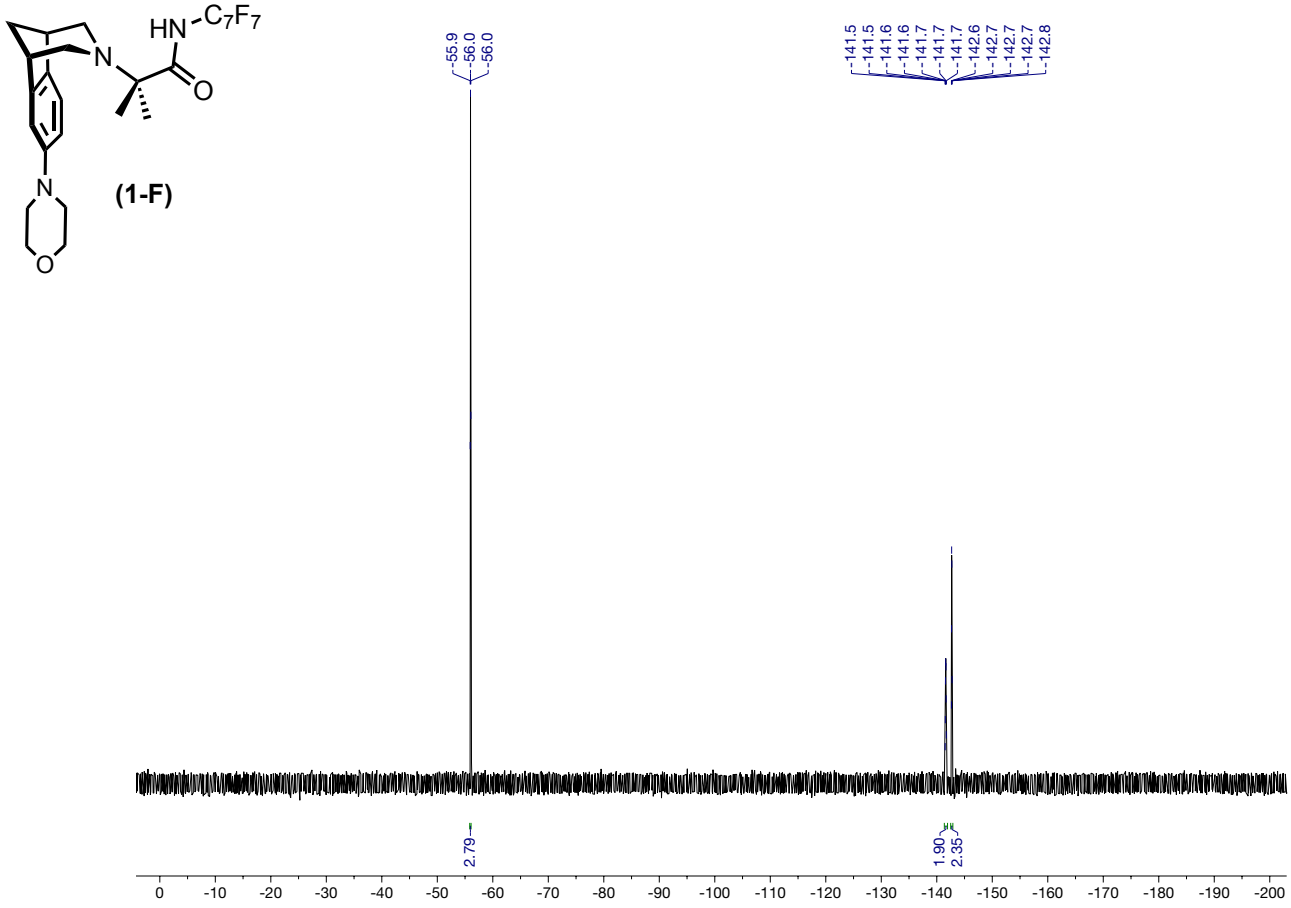
^{19}F NMR Spectrum in $CDCl_3$



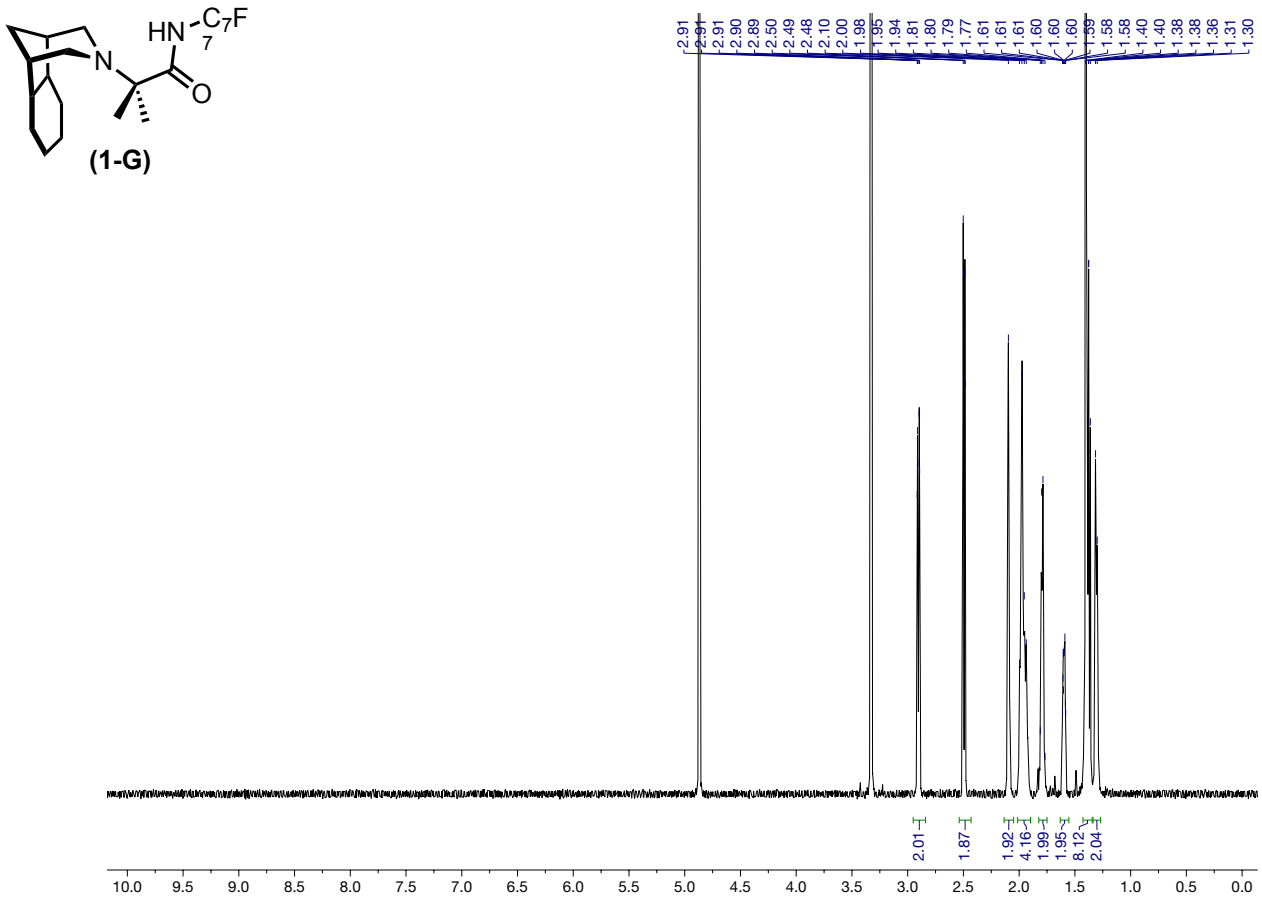
^{1}H NMR Spectrum in $CDCl_3$



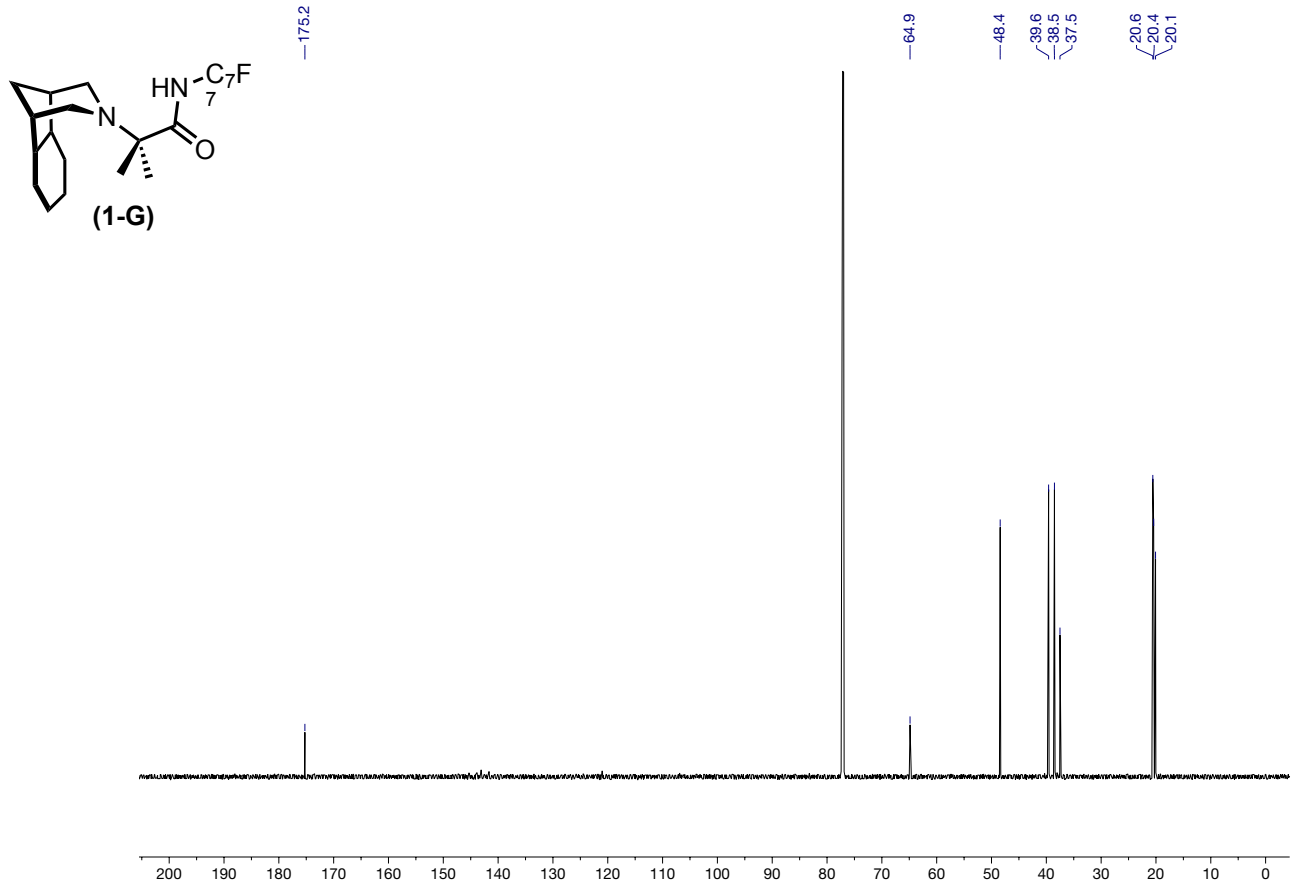
^{13}C NMR Spectrum in $CDCl_3$



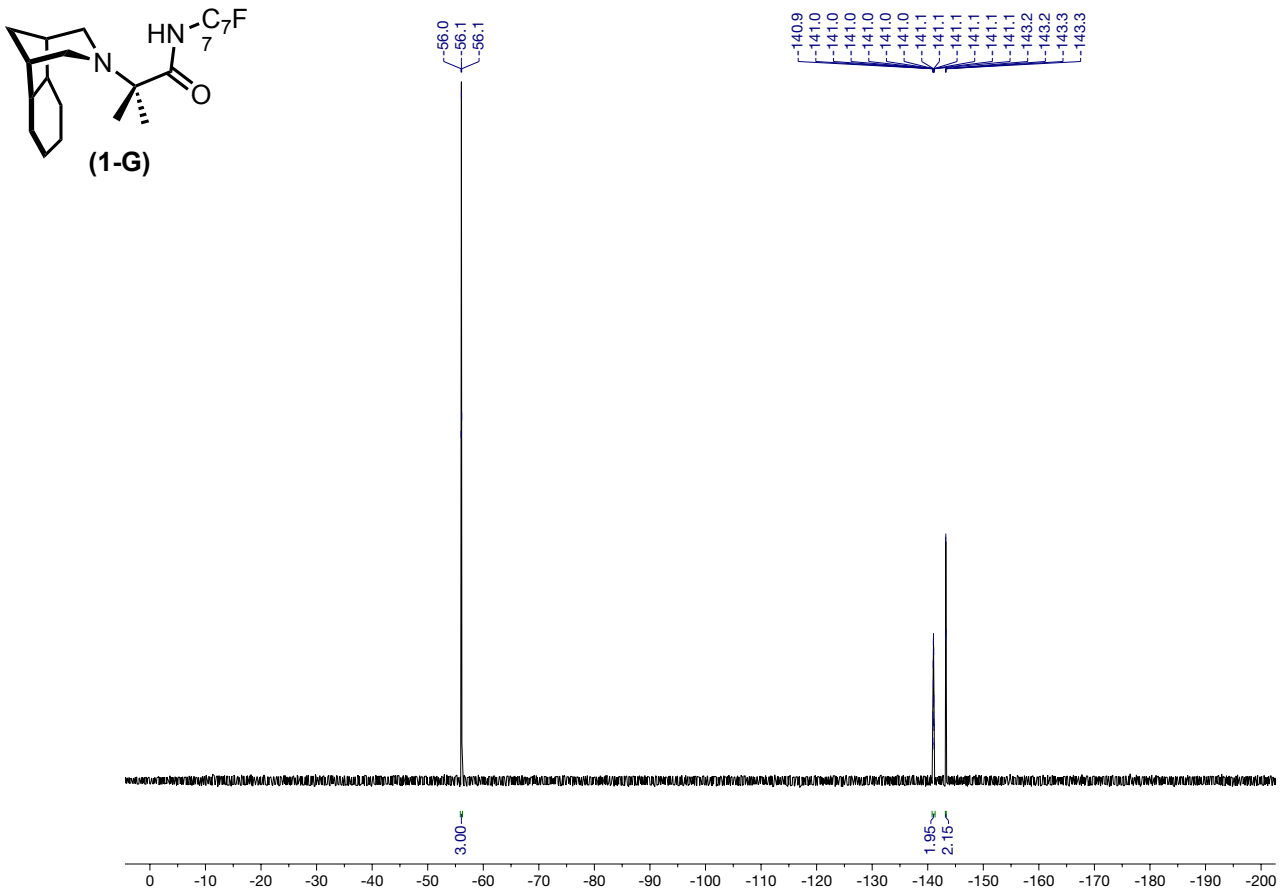
^{19}F NMR Spectrum in $CDCl_3$



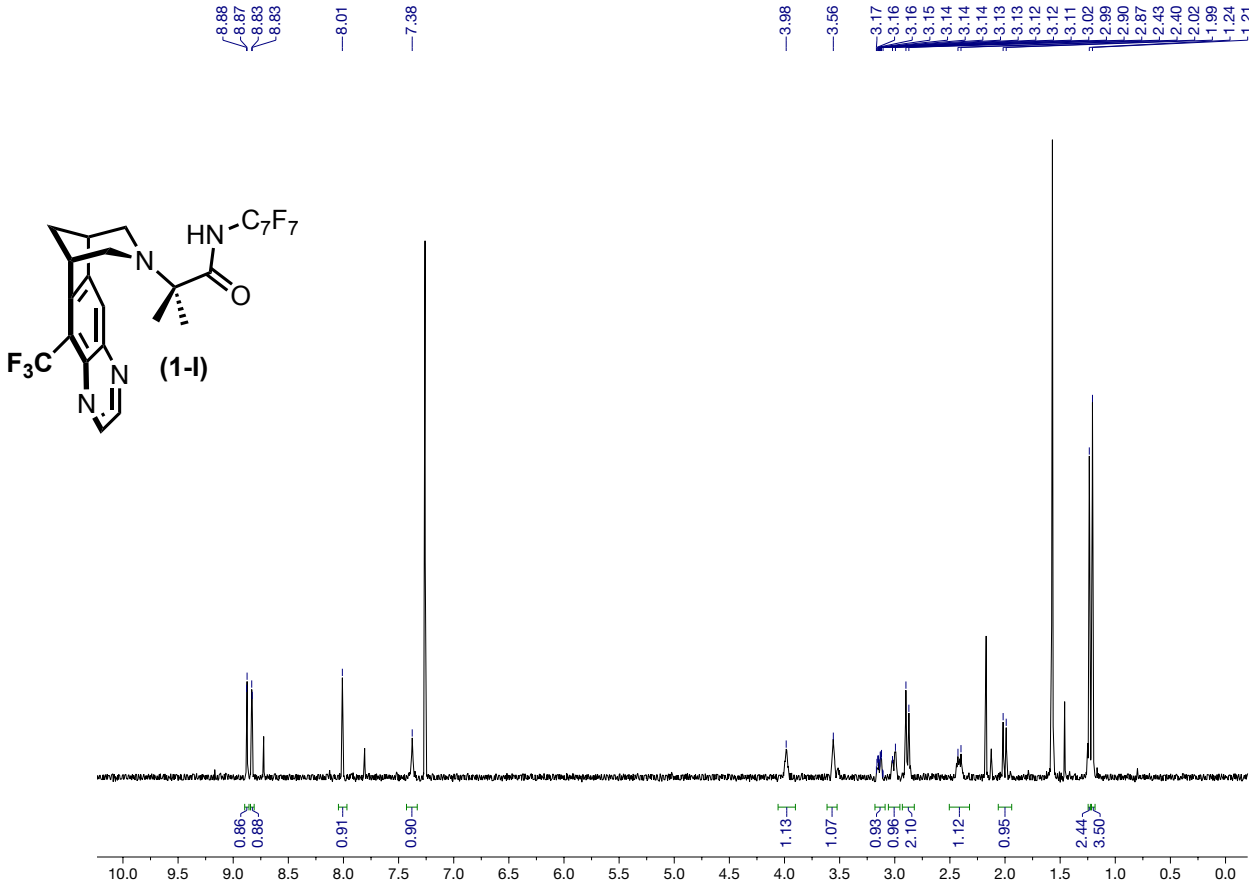
^{1}H NMR Spectrum in CD_3OD



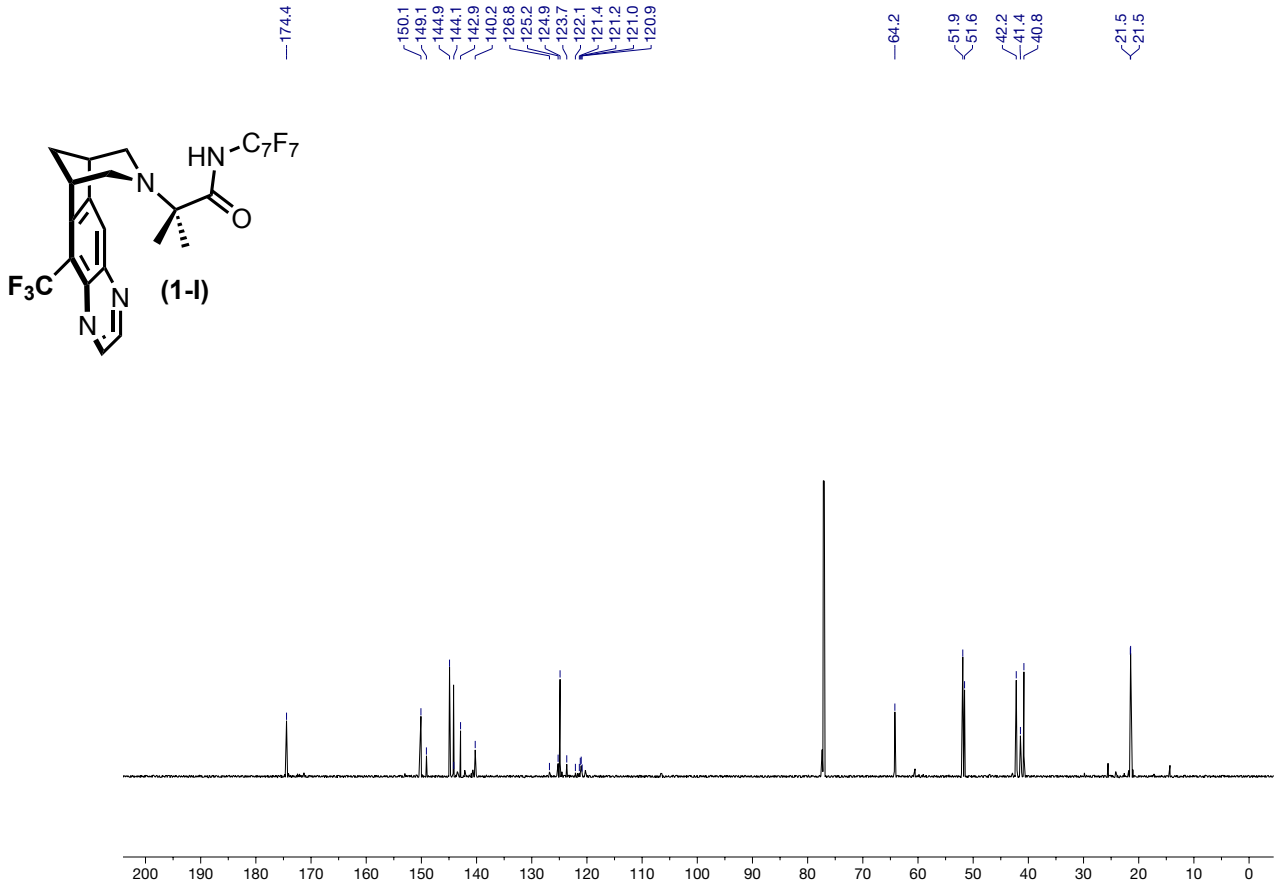
^{13}C NMR Spectrum in $CDCl_3$



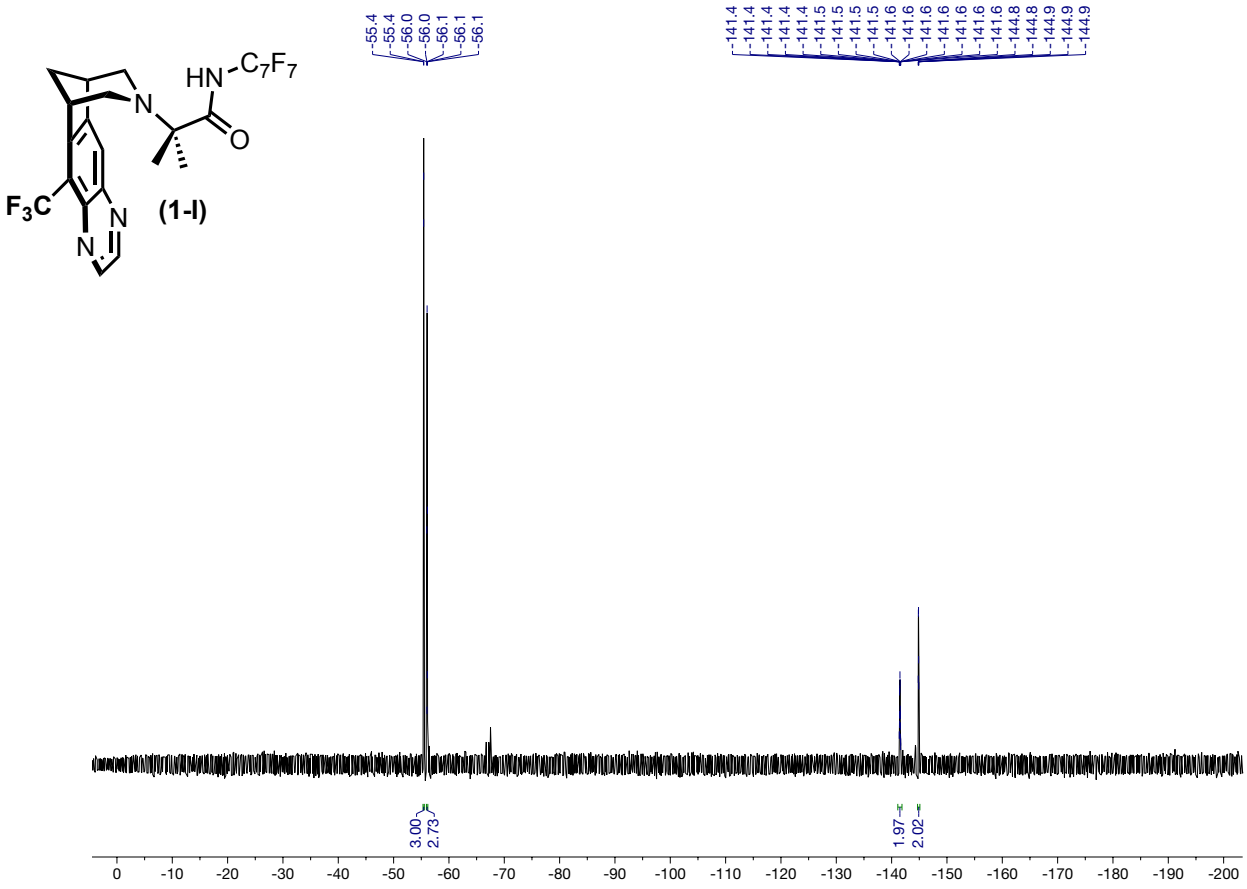
^{19}F NMR Spectrum in $CDCl_3$



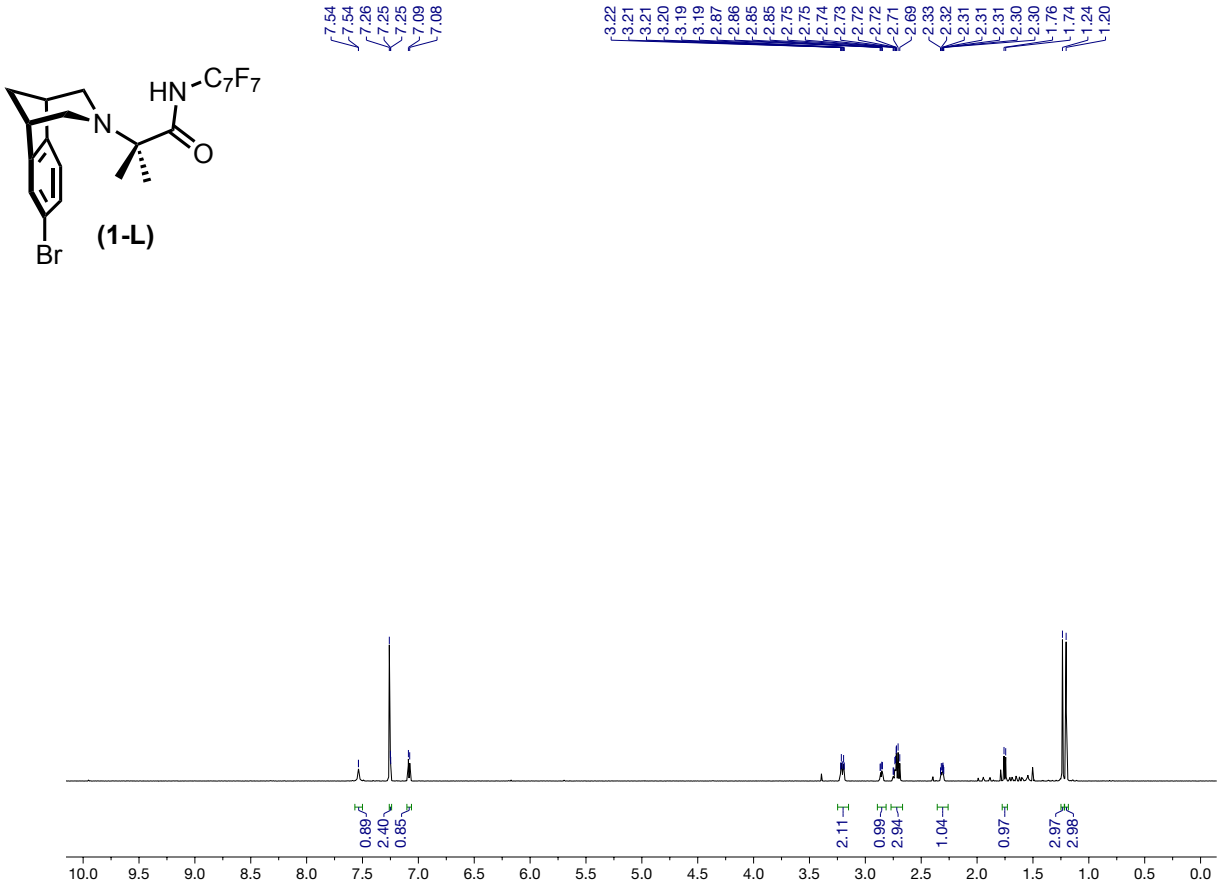
^{1}H NMR Spectrum in $CDCl_3$



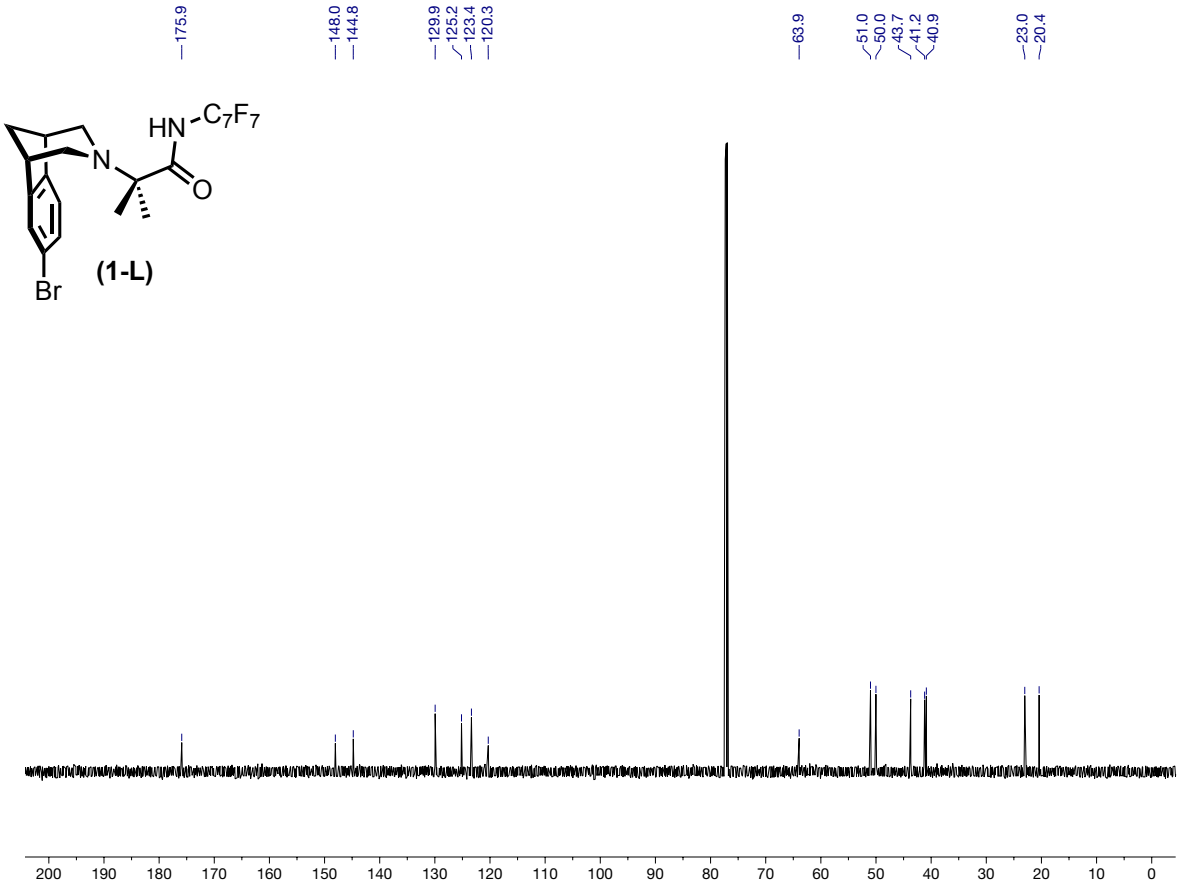
^{13}C NMR Spectrum in $CDCl_3$



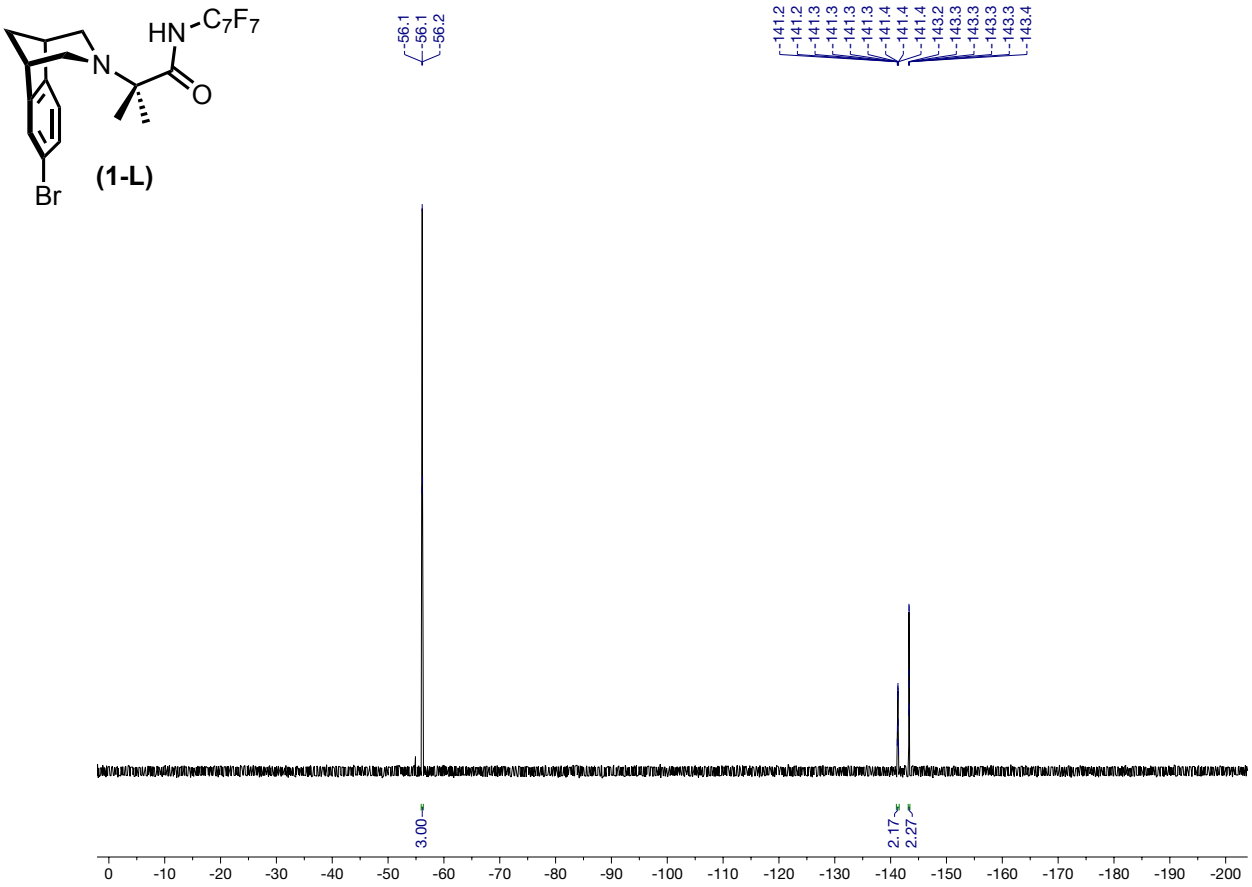
^{19}F NMR Spectrum in $CDCl_3$



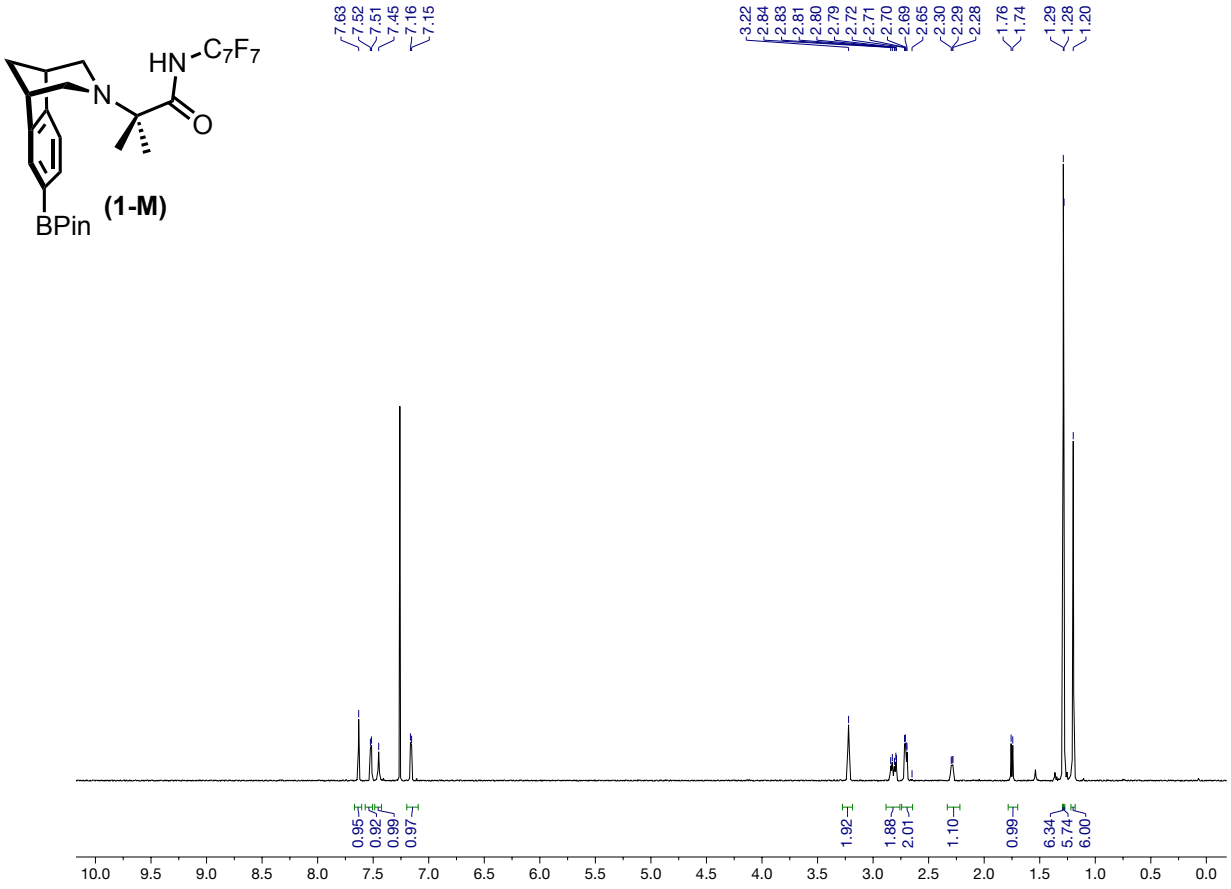
^{1}H NMR Spectrum in $CDCl_3$



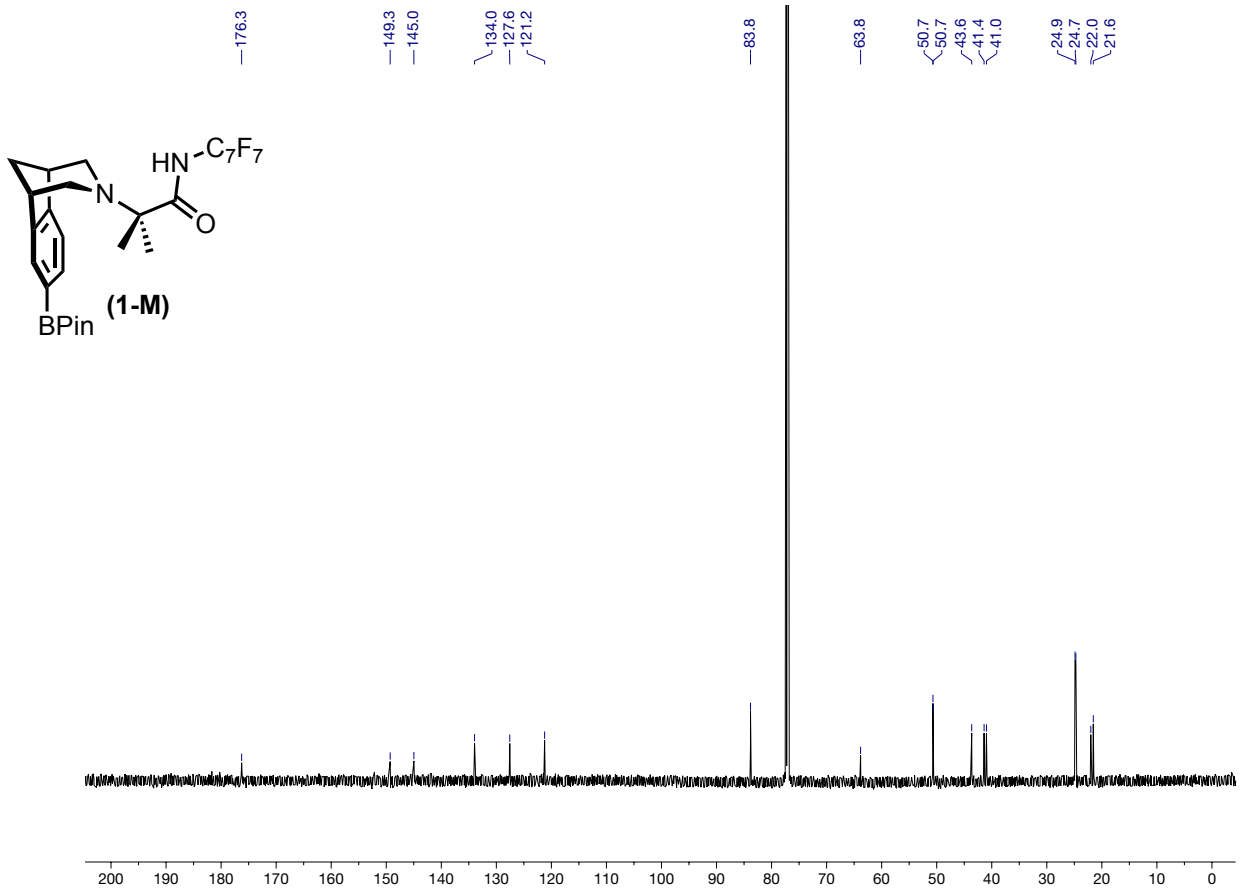
^{13}C NMR Spectrum in $CDCl_3$



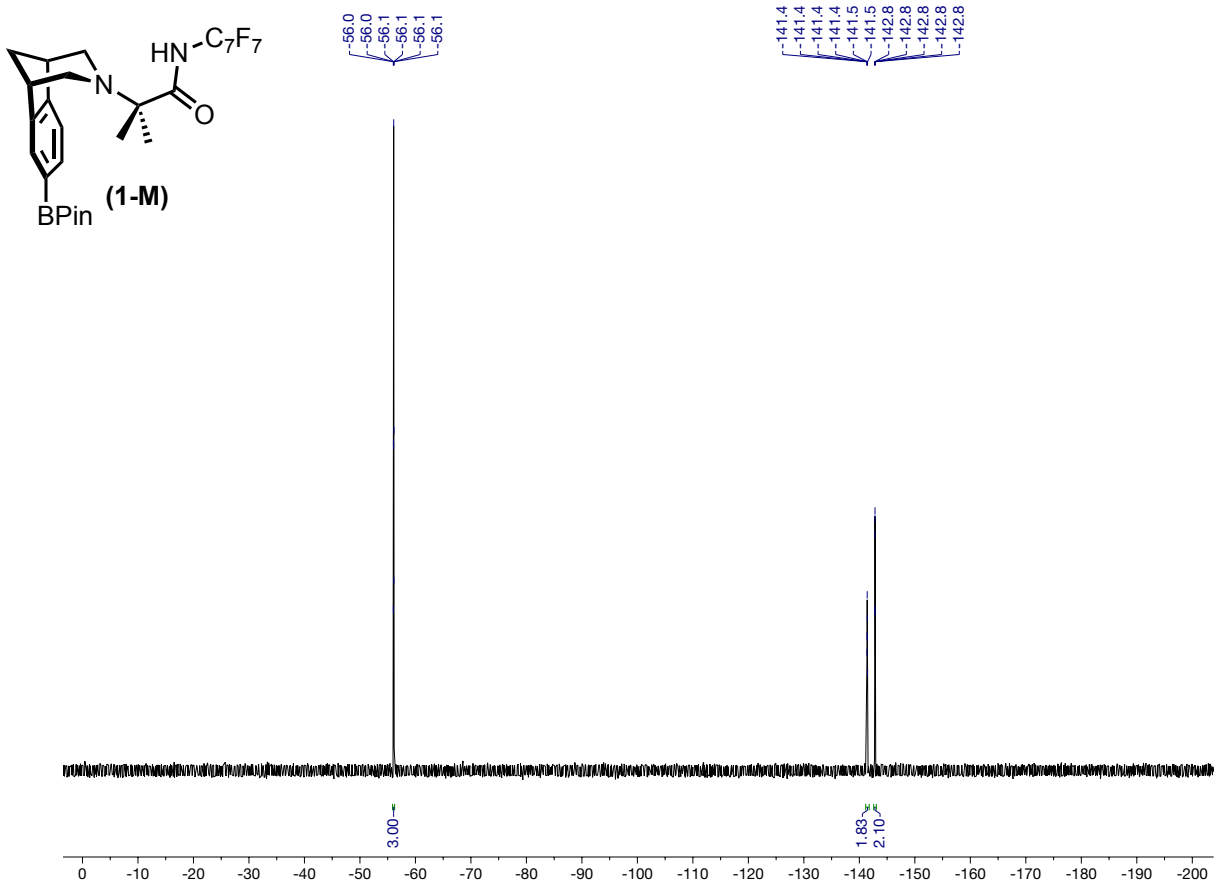
^{19}F NMR Spectrum in $CDCl_3$



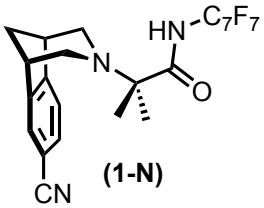
^{1}H NMR Spectrum in $CDCl_3$



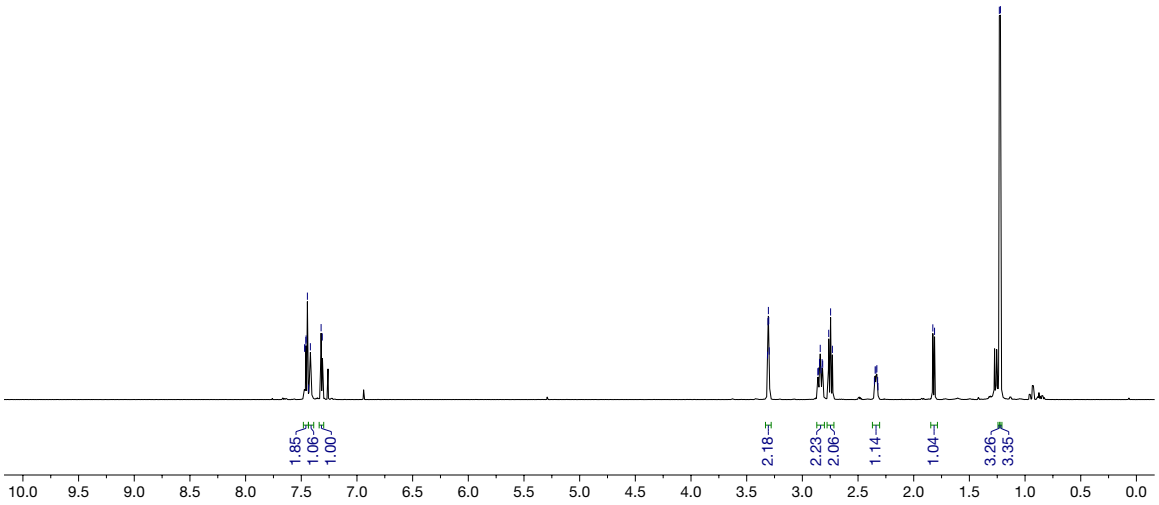
^{13}C NMR Spectrum in $CDCl_3$



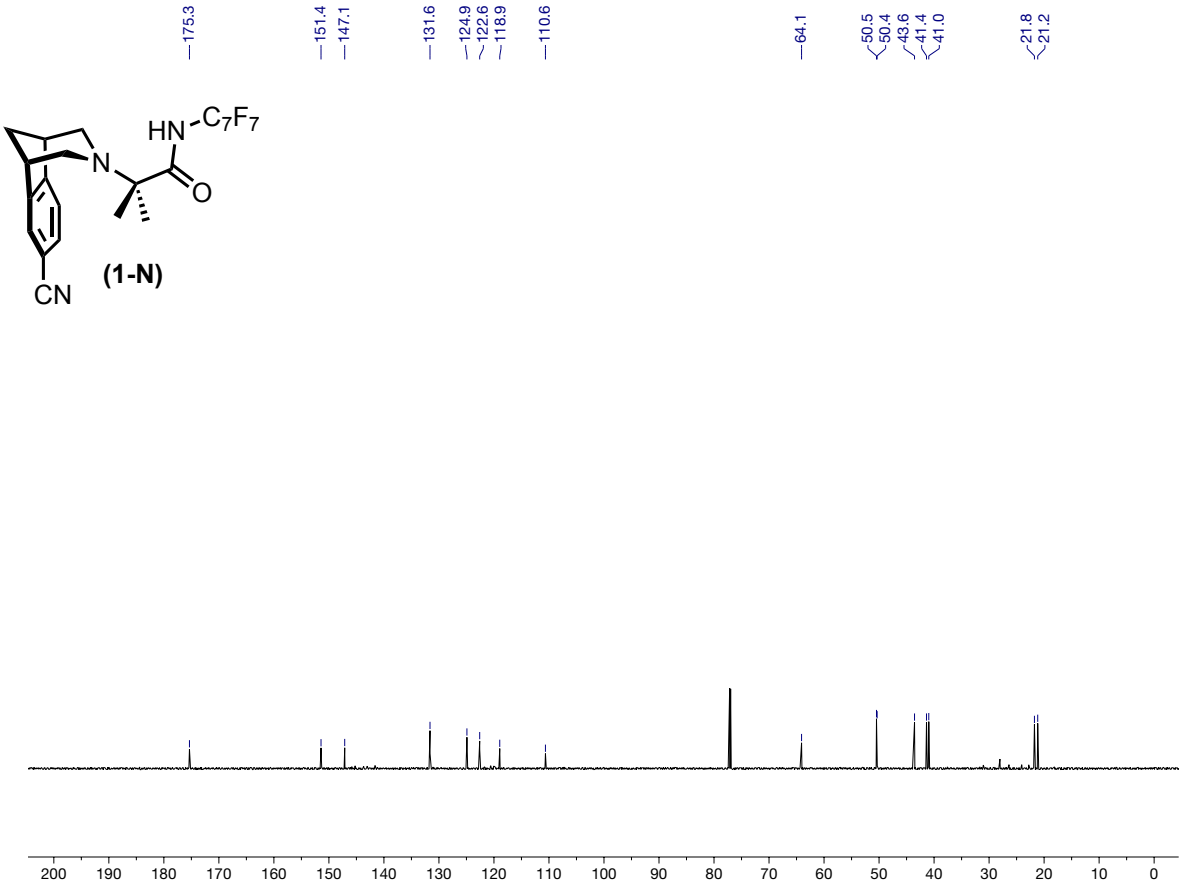
^{19}F NMR Spectrum in $CDCl_3$



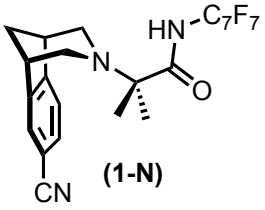
(1-N)



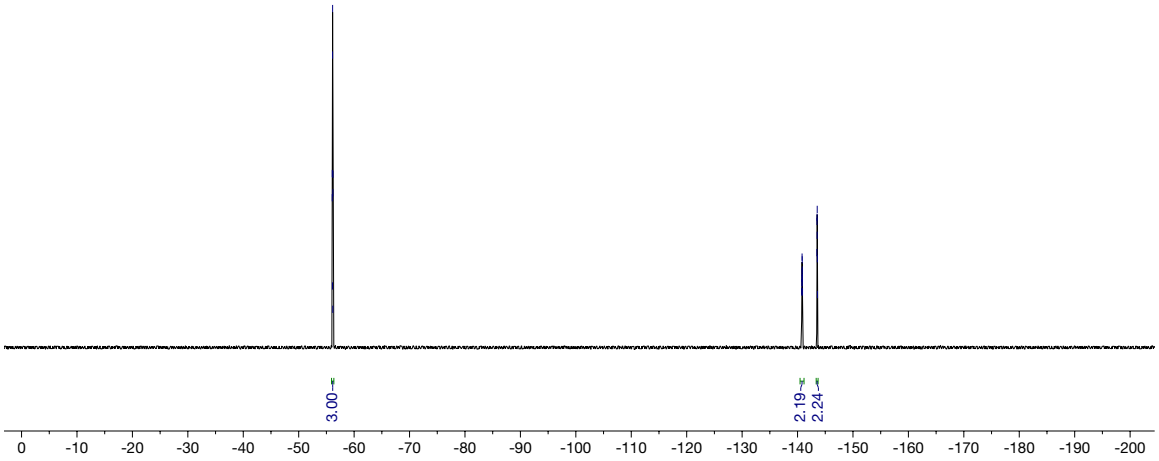
^{1}H NMR Spectrum in $CDCl_3$



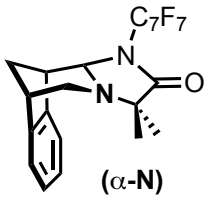
^{13}C NMR Spectrum in $CDCl_3$



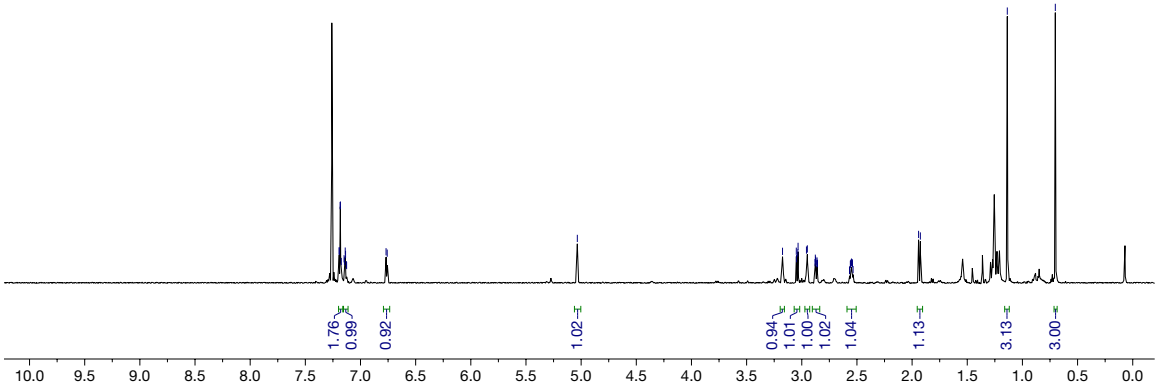
(1-N)



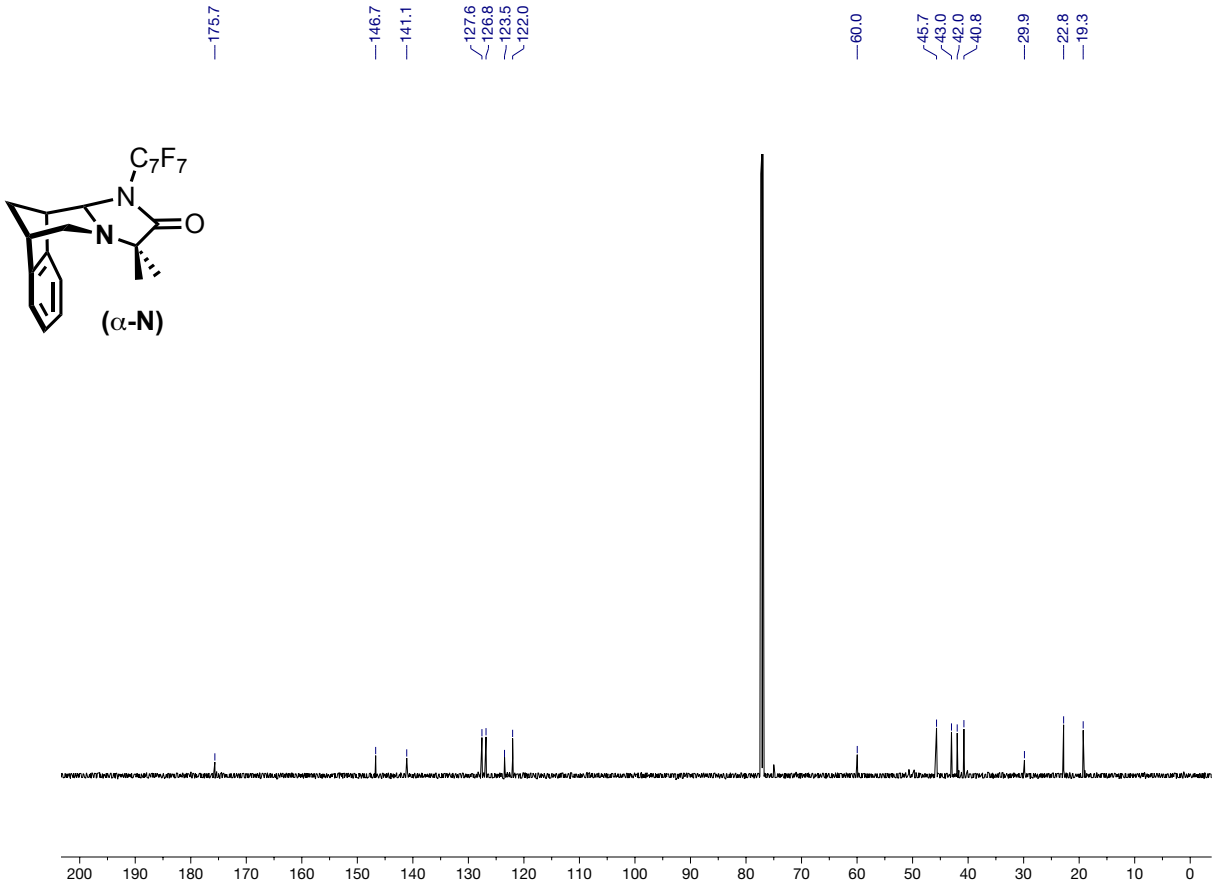
^{19}F NMR Spectrum in $CDCl_3$



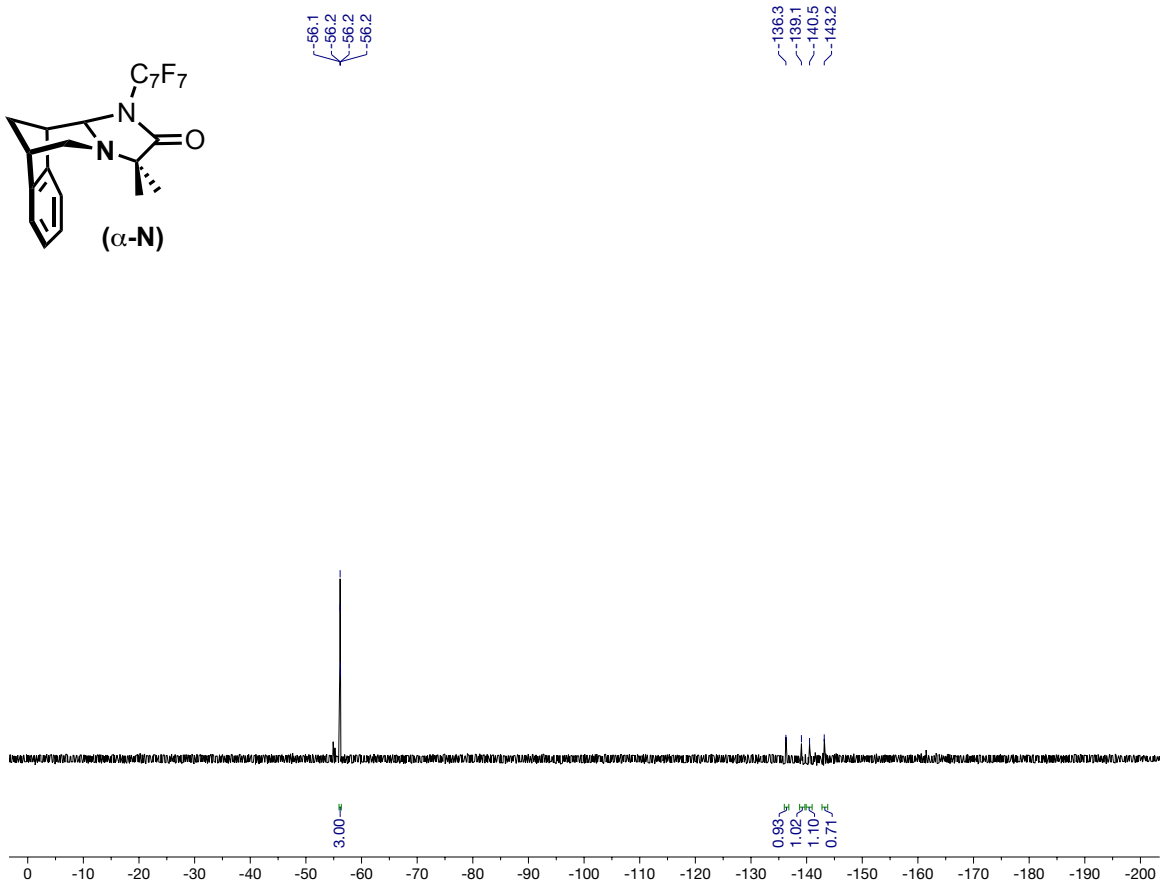
(α-N)



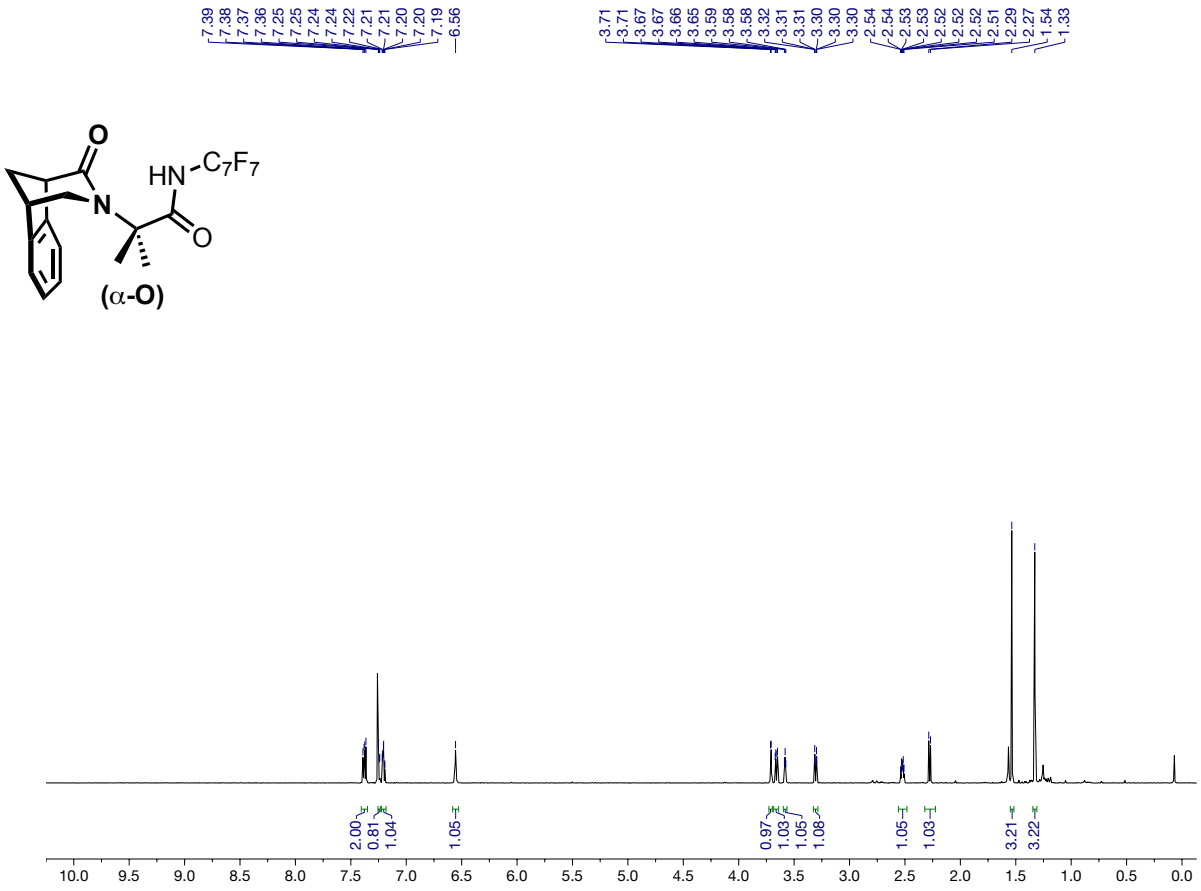
^{1}H NMR Spectrum in $CDCl_3$



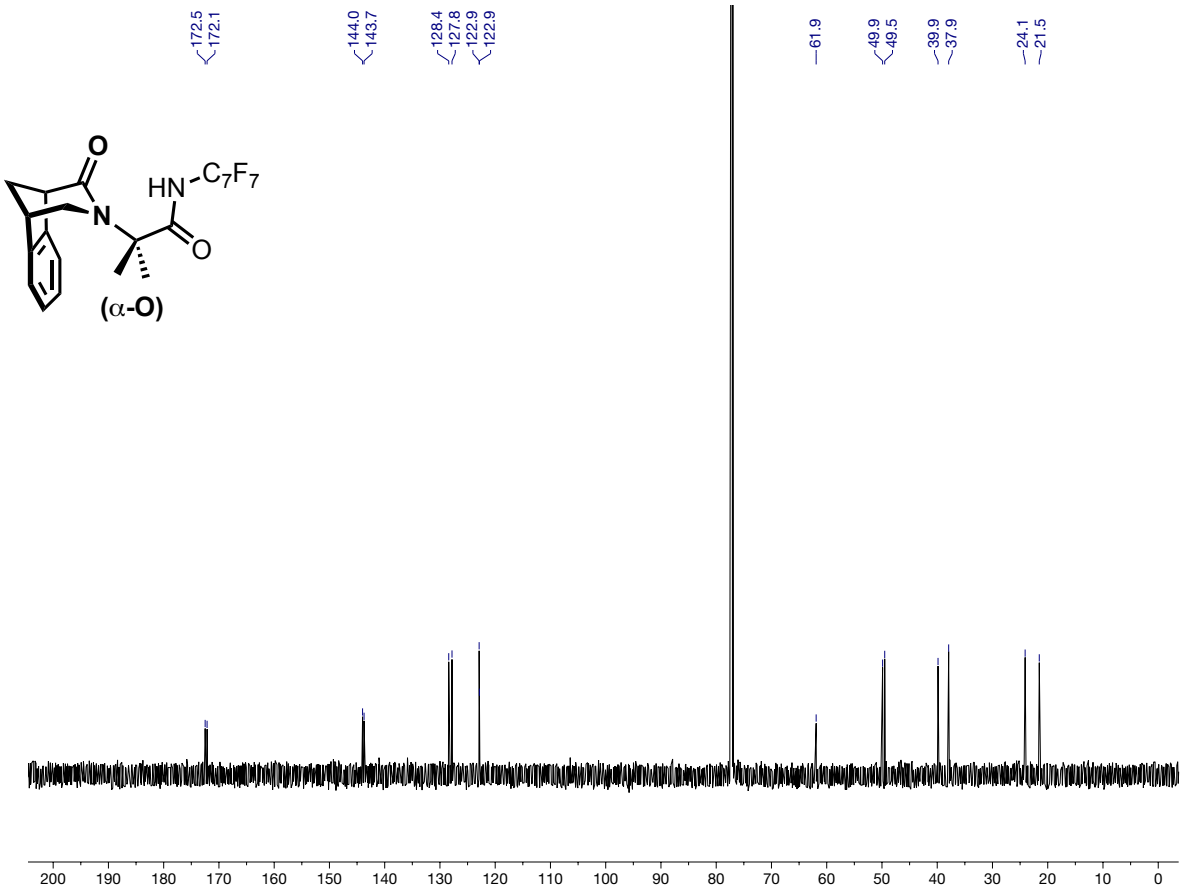
^{13}C NMR Spectrum in $CDCl_3$



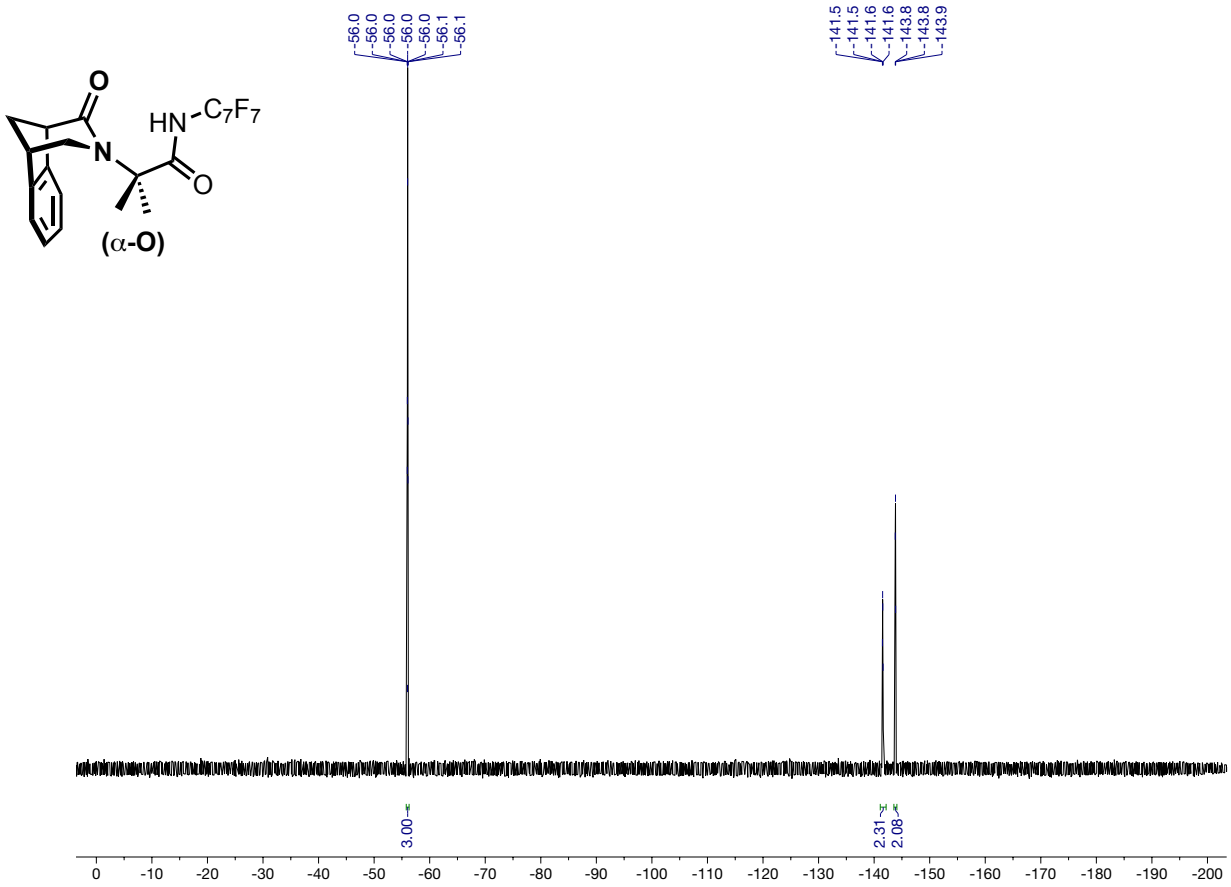
^{19}F NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum in $CDCl_3$

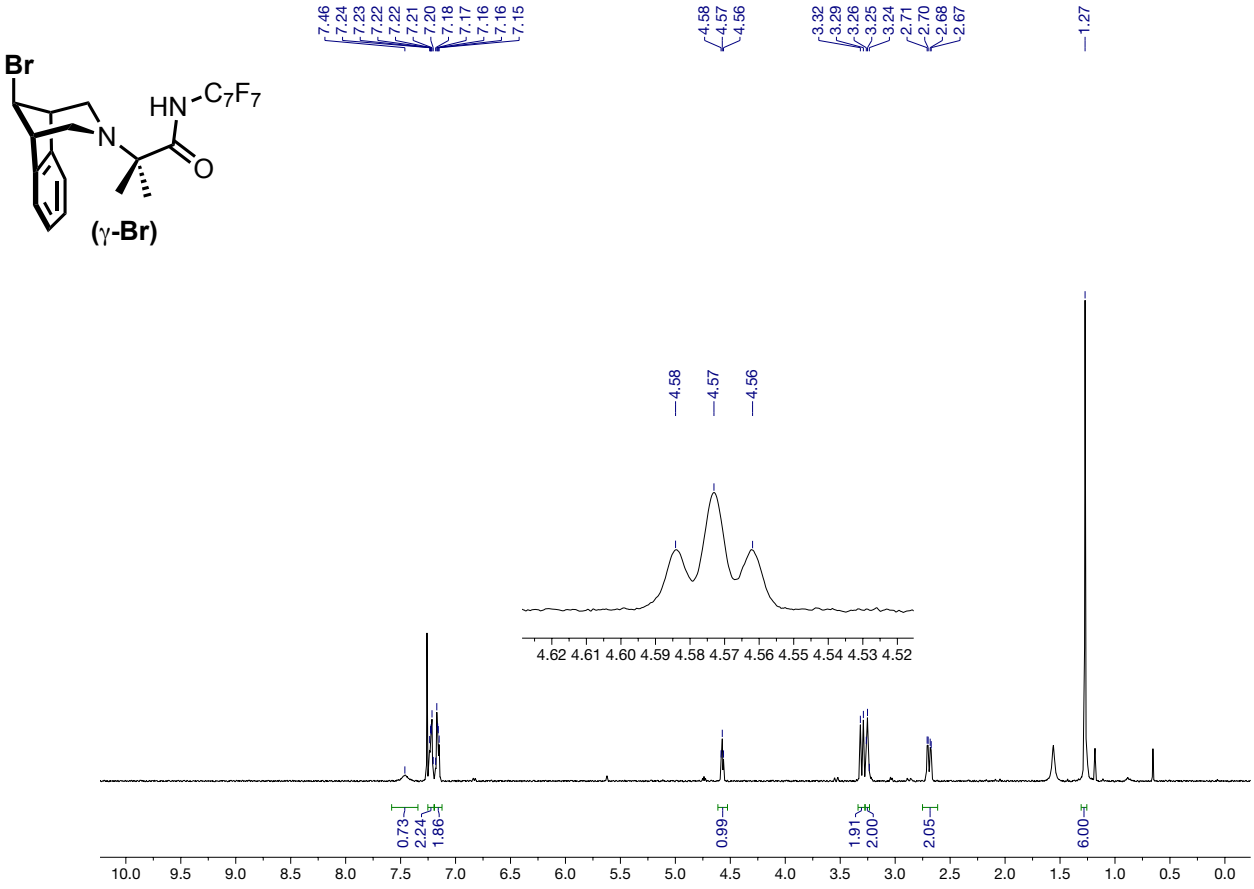


^{13}C NMR Spectrum in $CDCl_3$

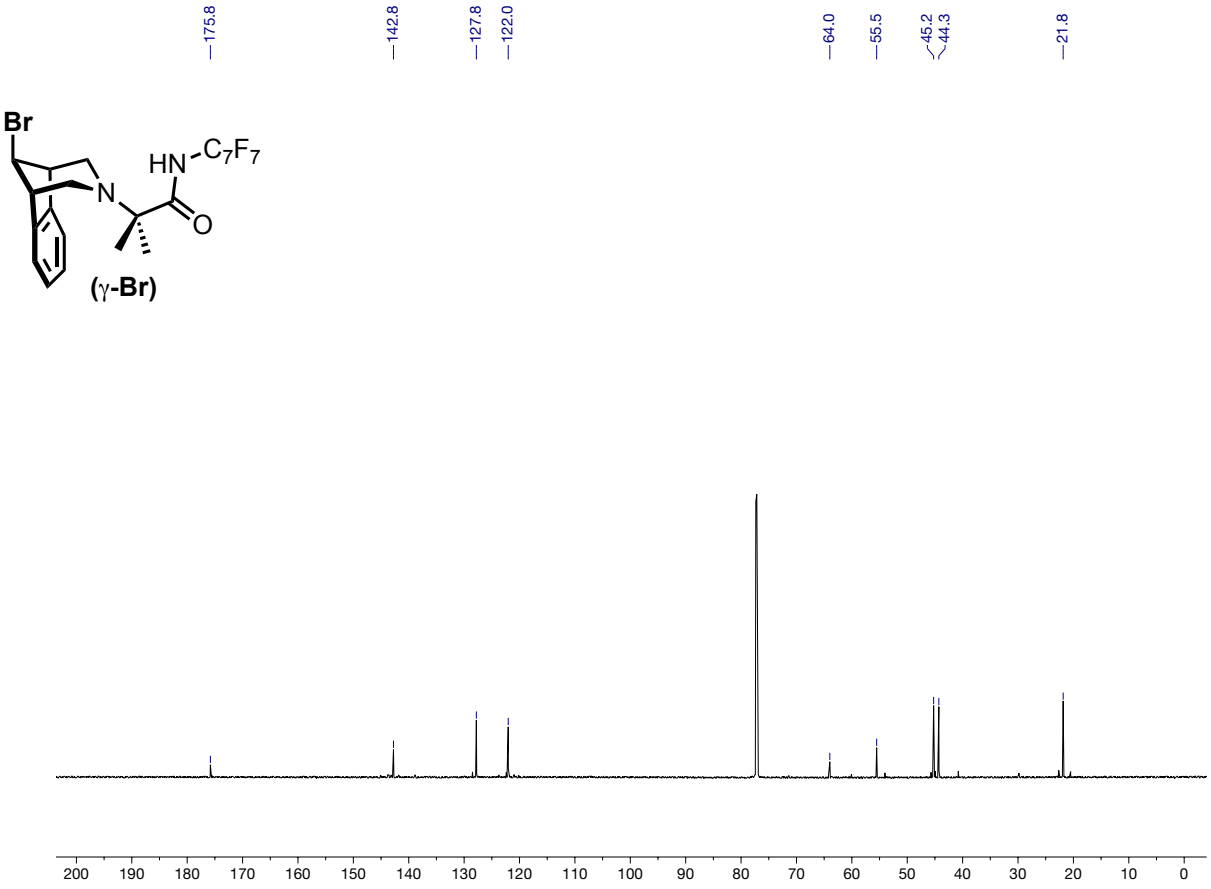


^{19}F NMR Spectrum in $CDCl_3$

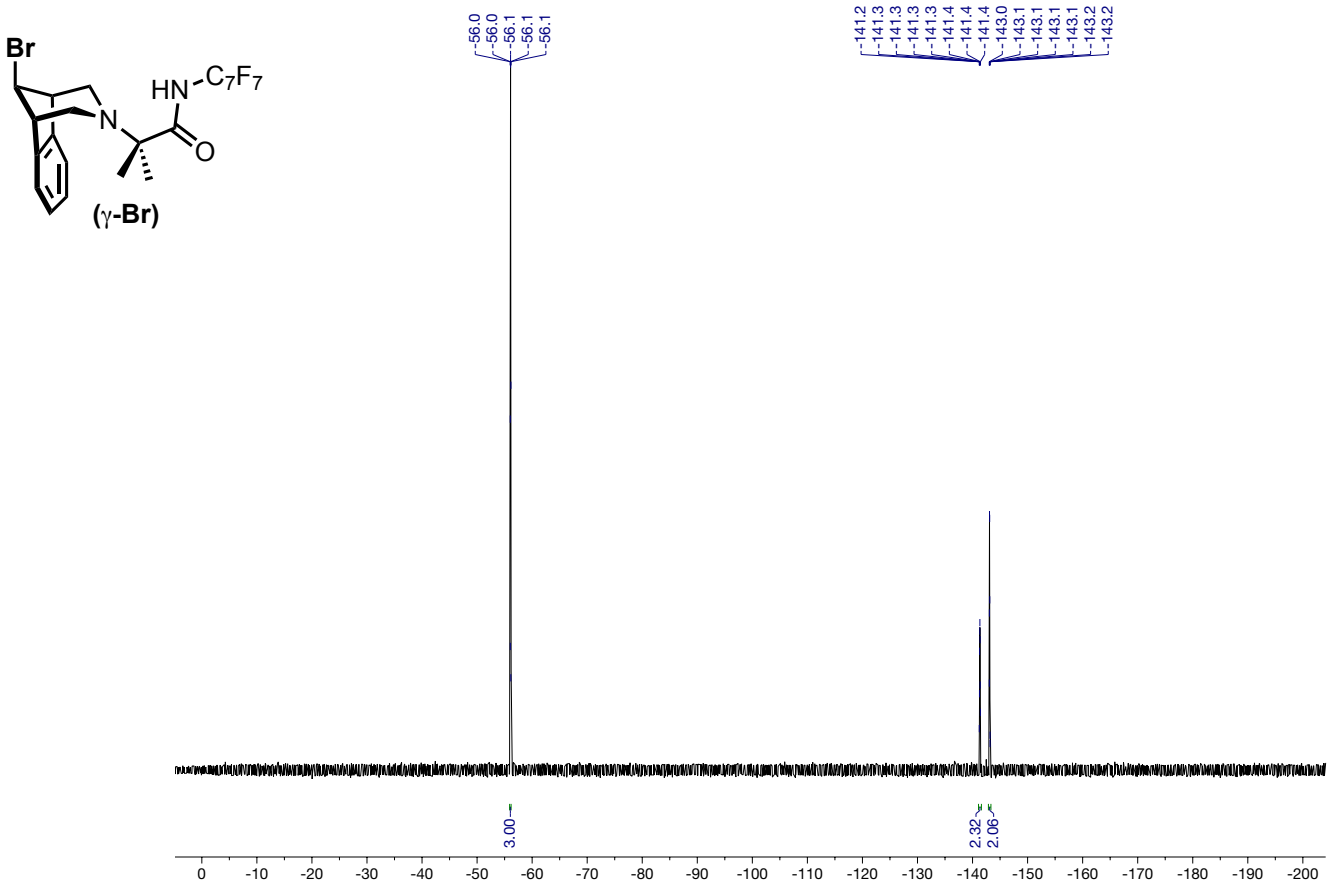
b. Functionalizations Spectra Data



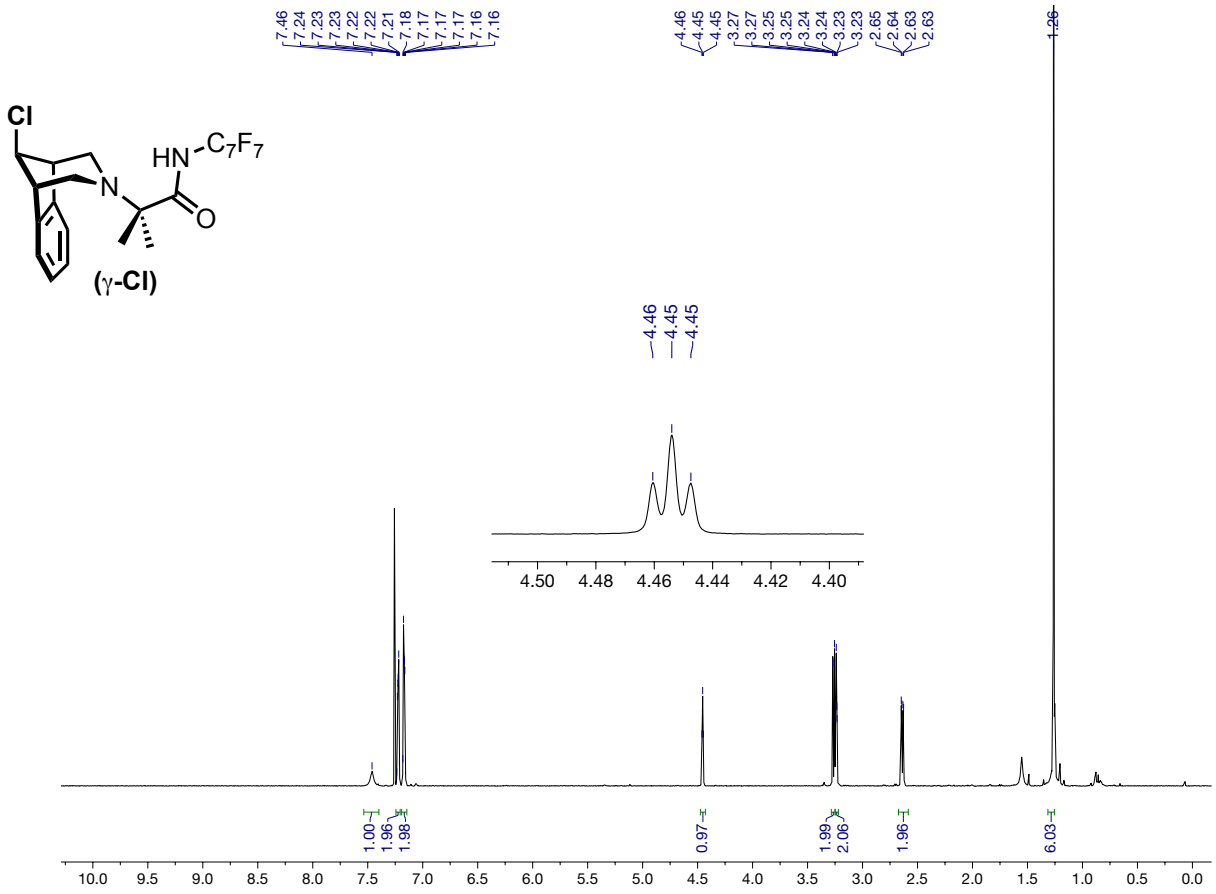
^{1}H NMR Spectrum in $CDCl_3$



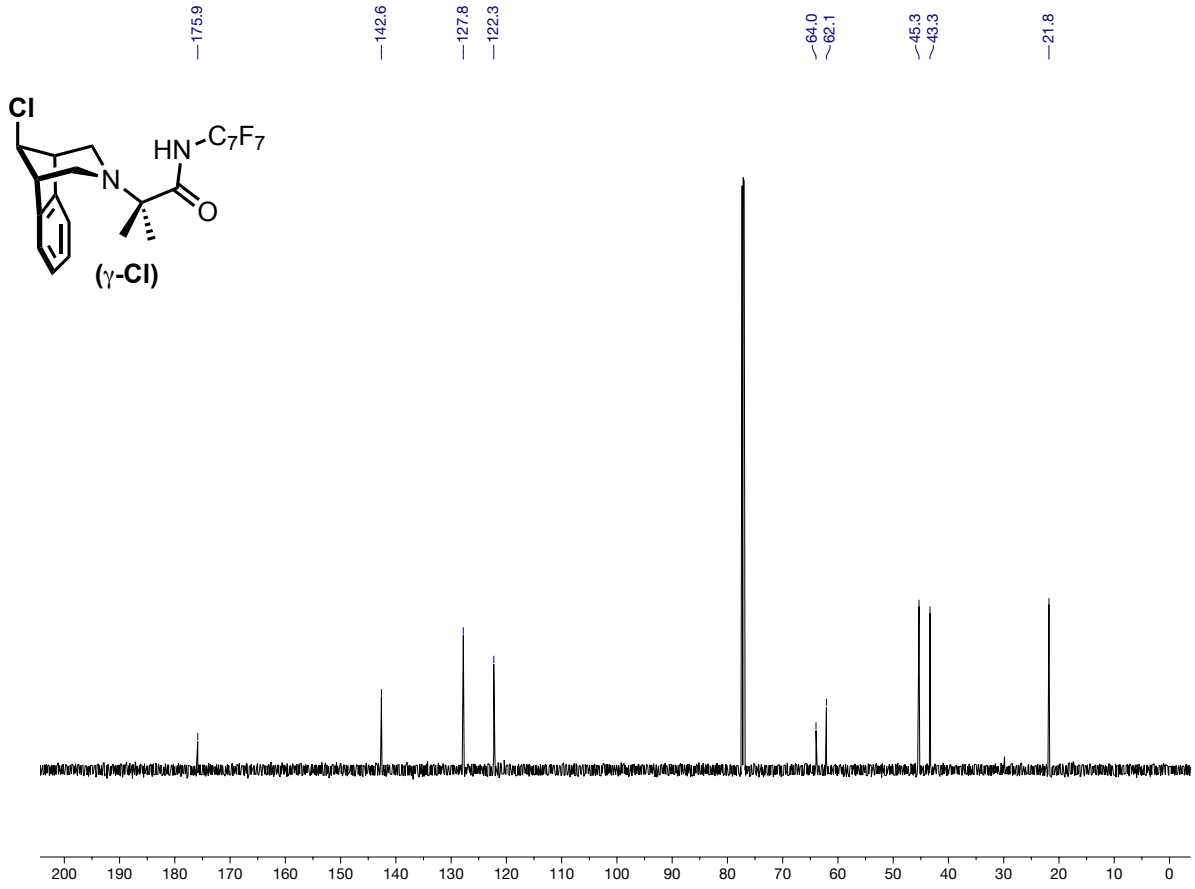
^{13}C NMR Spectrum in $CDCl_3$



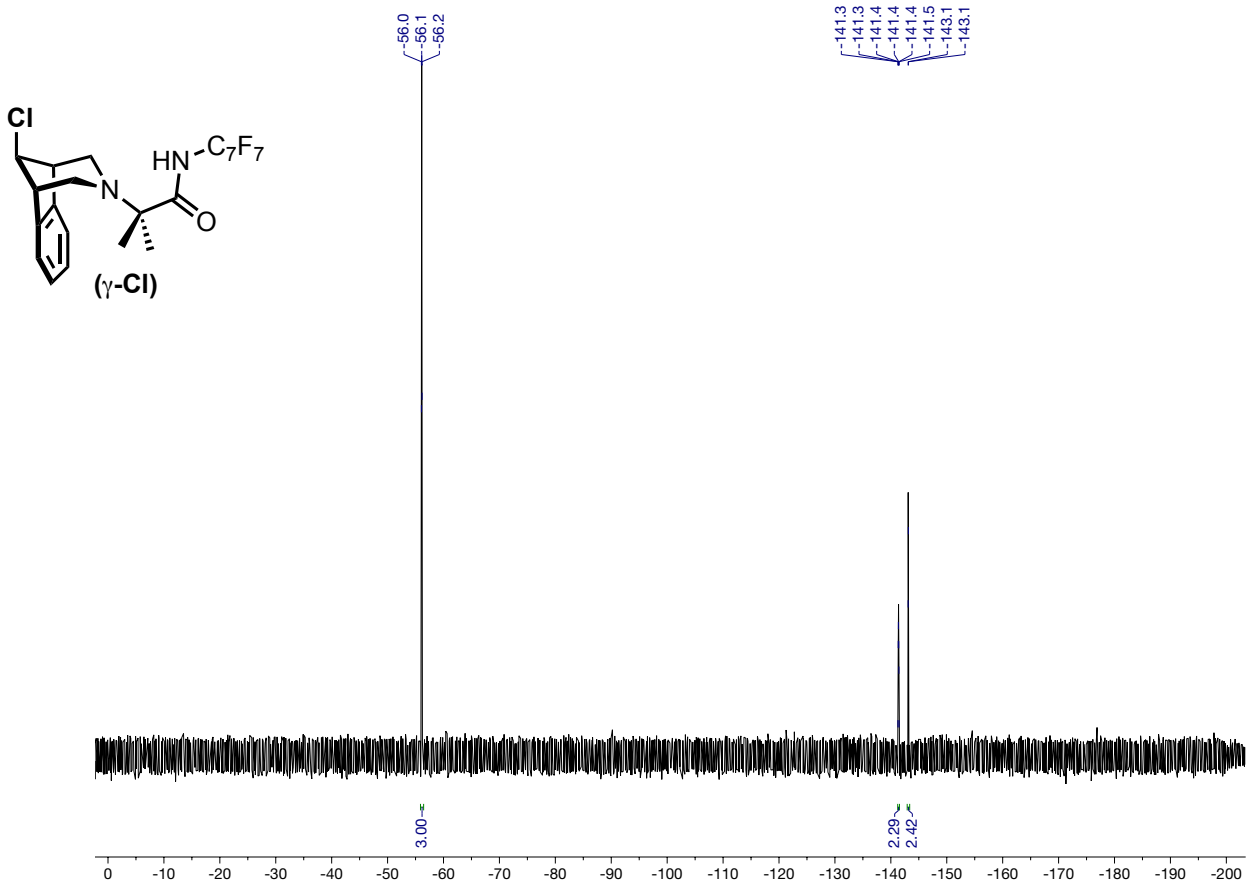
^{19}F NMR Spectrum in $CDCl_3$



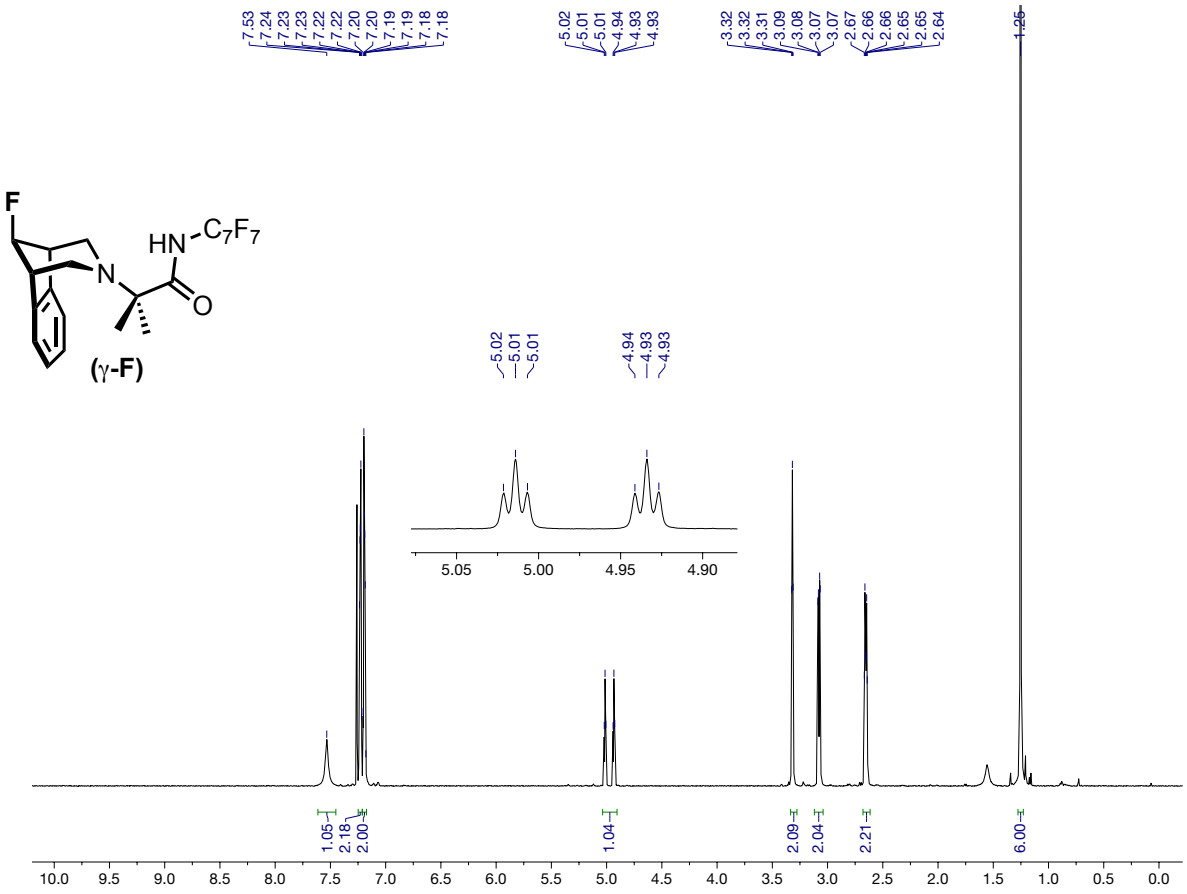
^{1}H NMR Spectrum in $CDCl_3$



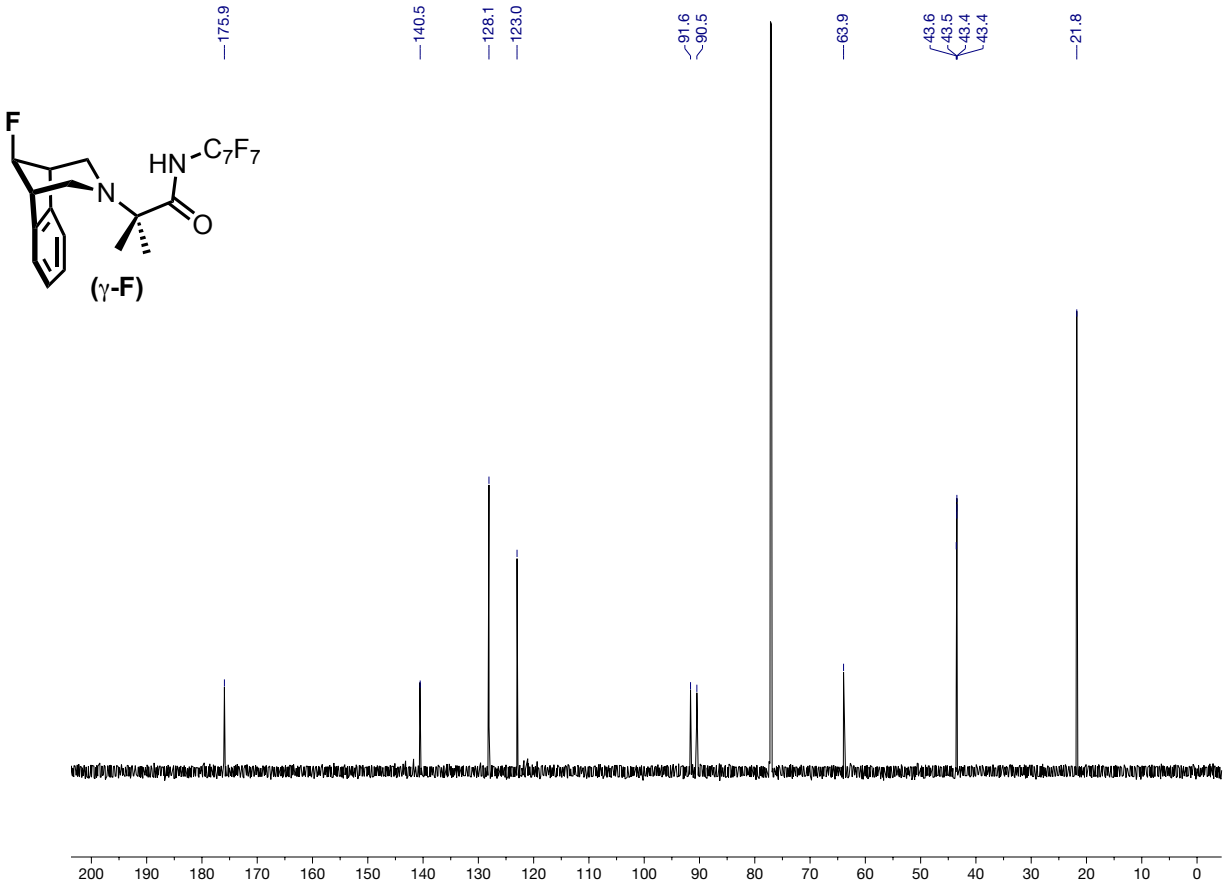
^{13}C NMR Spectrum in $CDCl_3$



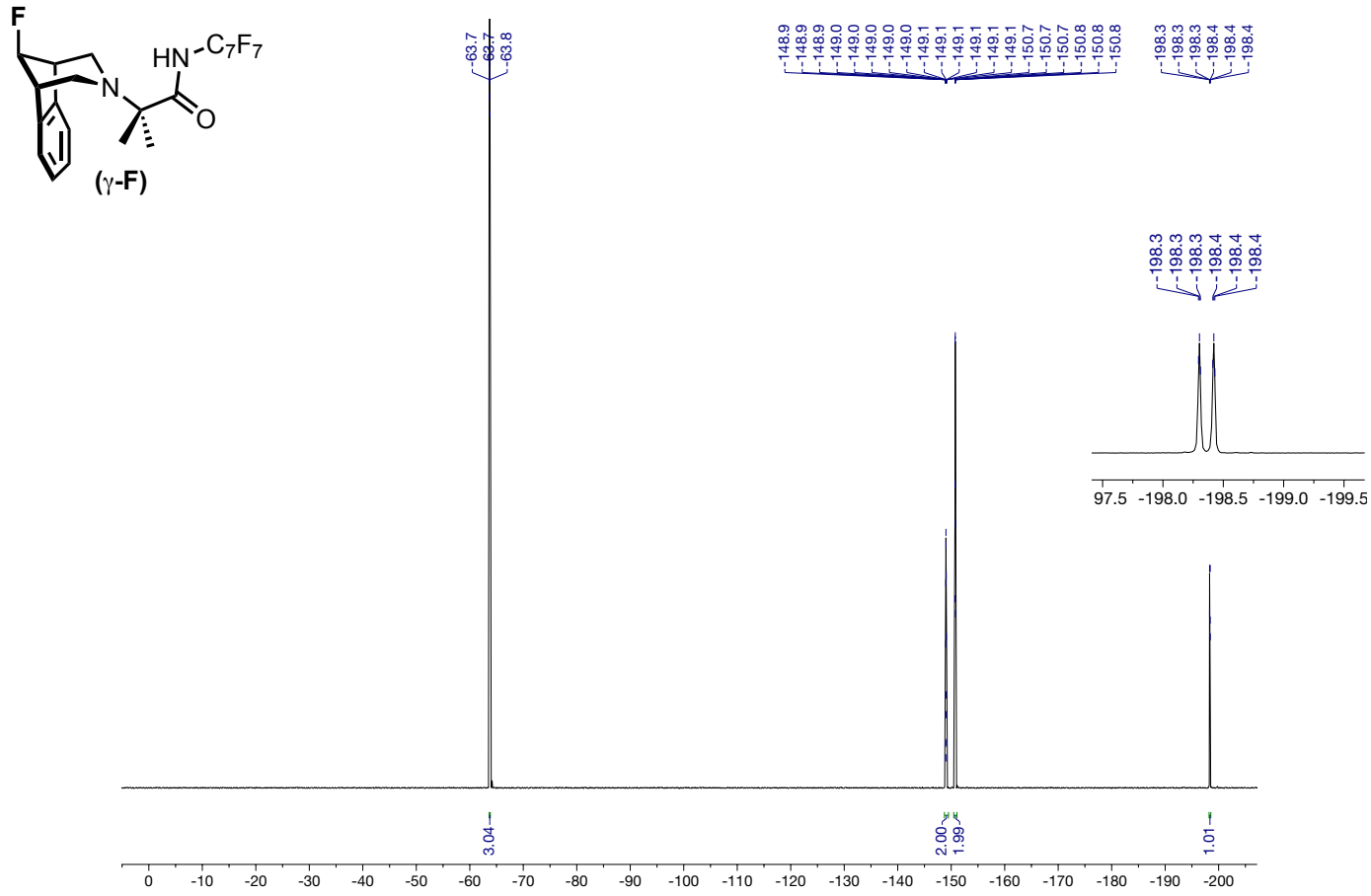
^{19}F NMR Spectrum in $CDCl_3$



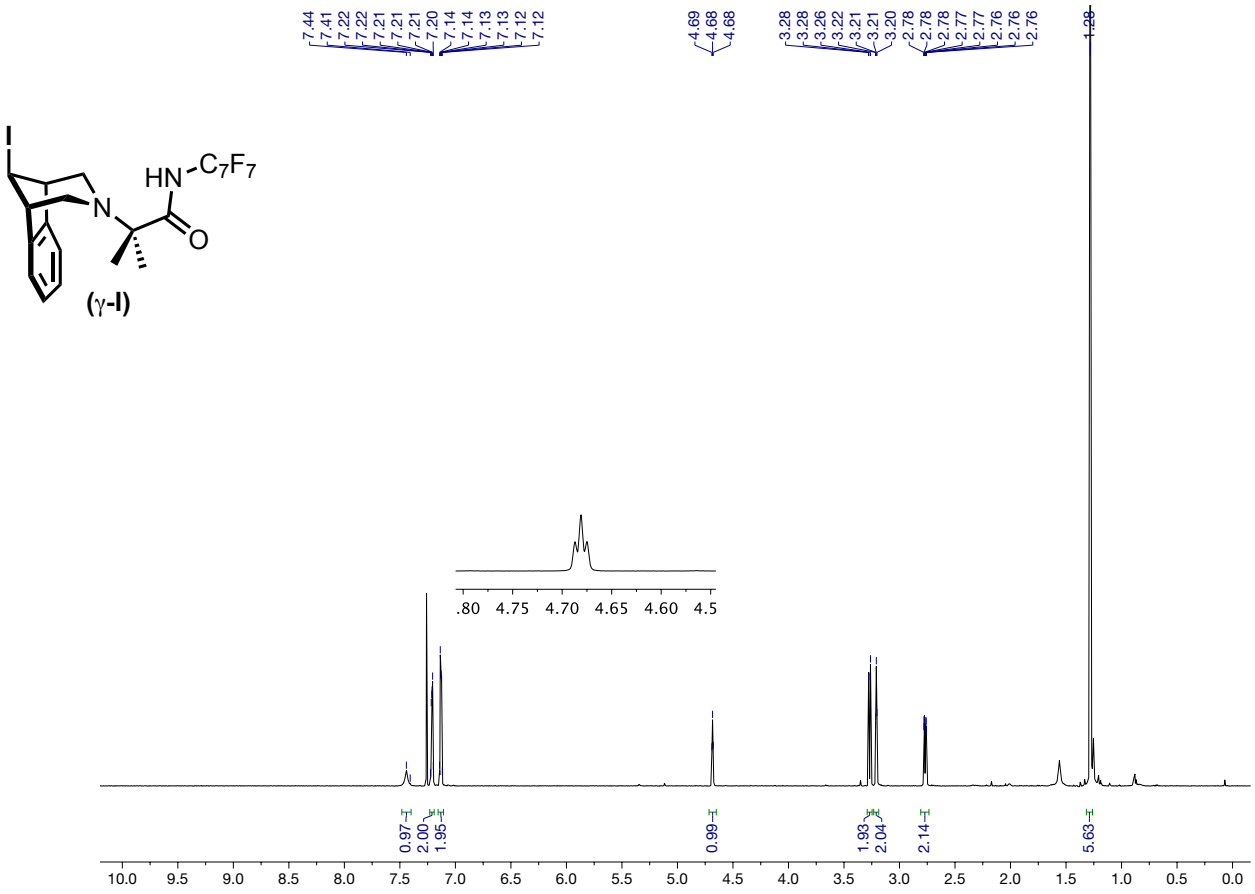
^{1}H NMR Spectrum in $CDCl_3$



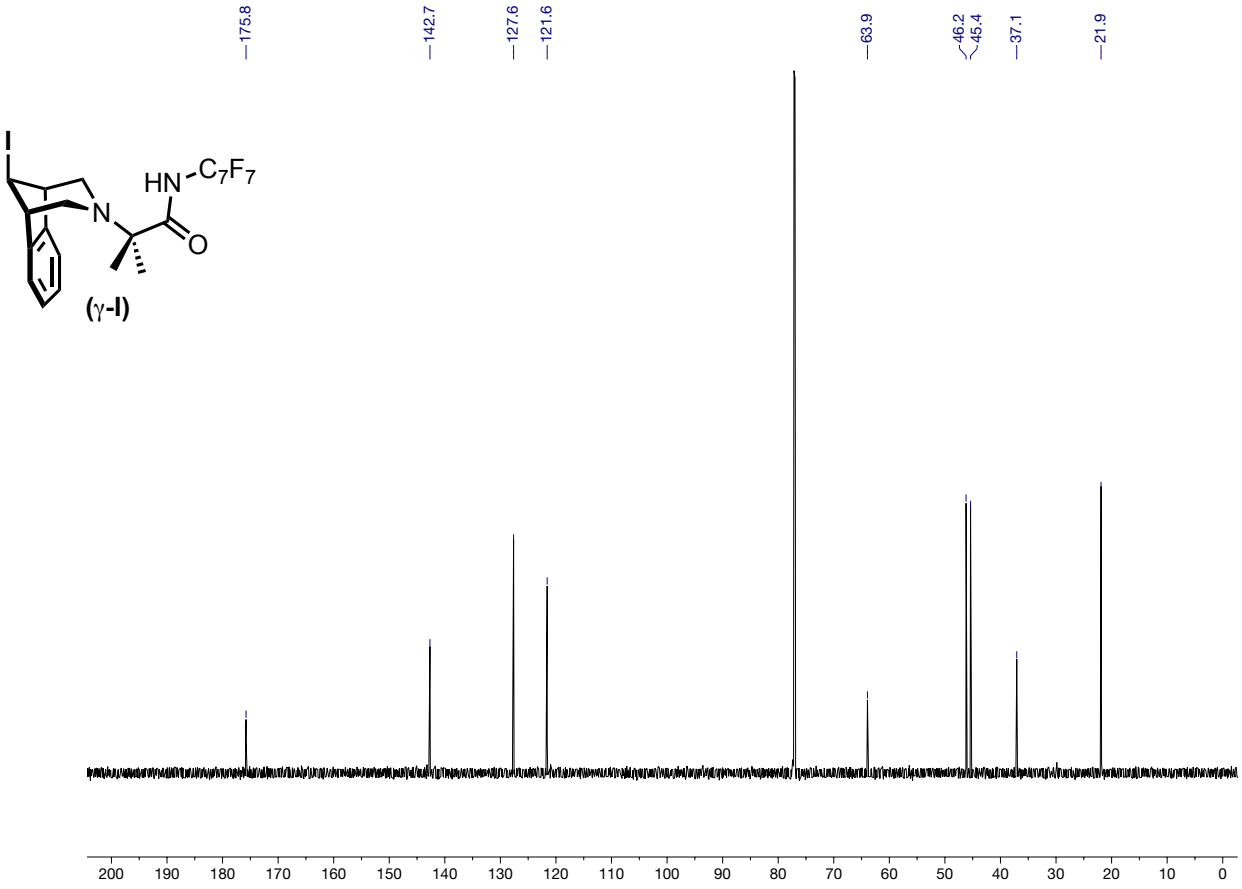
^{13}C NMR Spectrum in $CDCl_3$



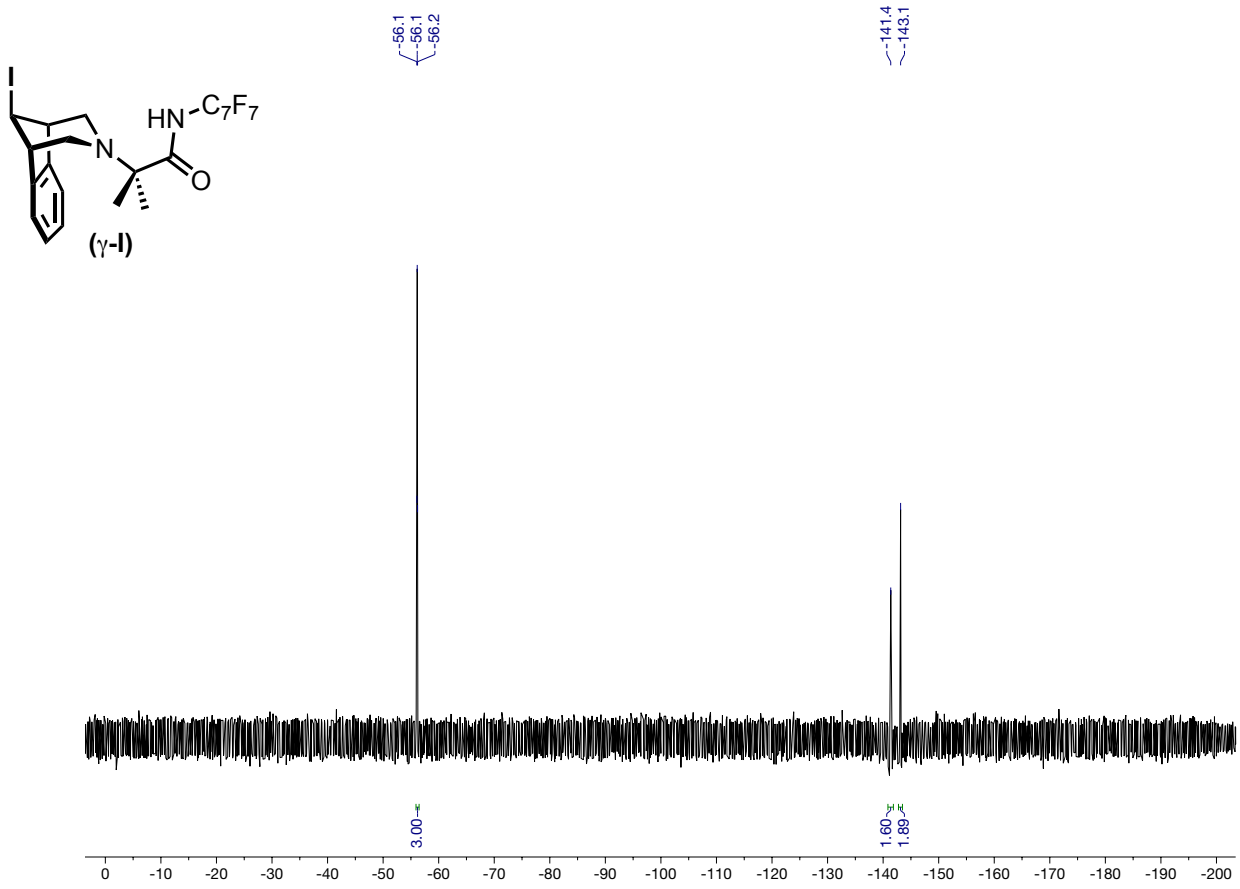
^{19}F NMR Spectrum in $CDCl_3$



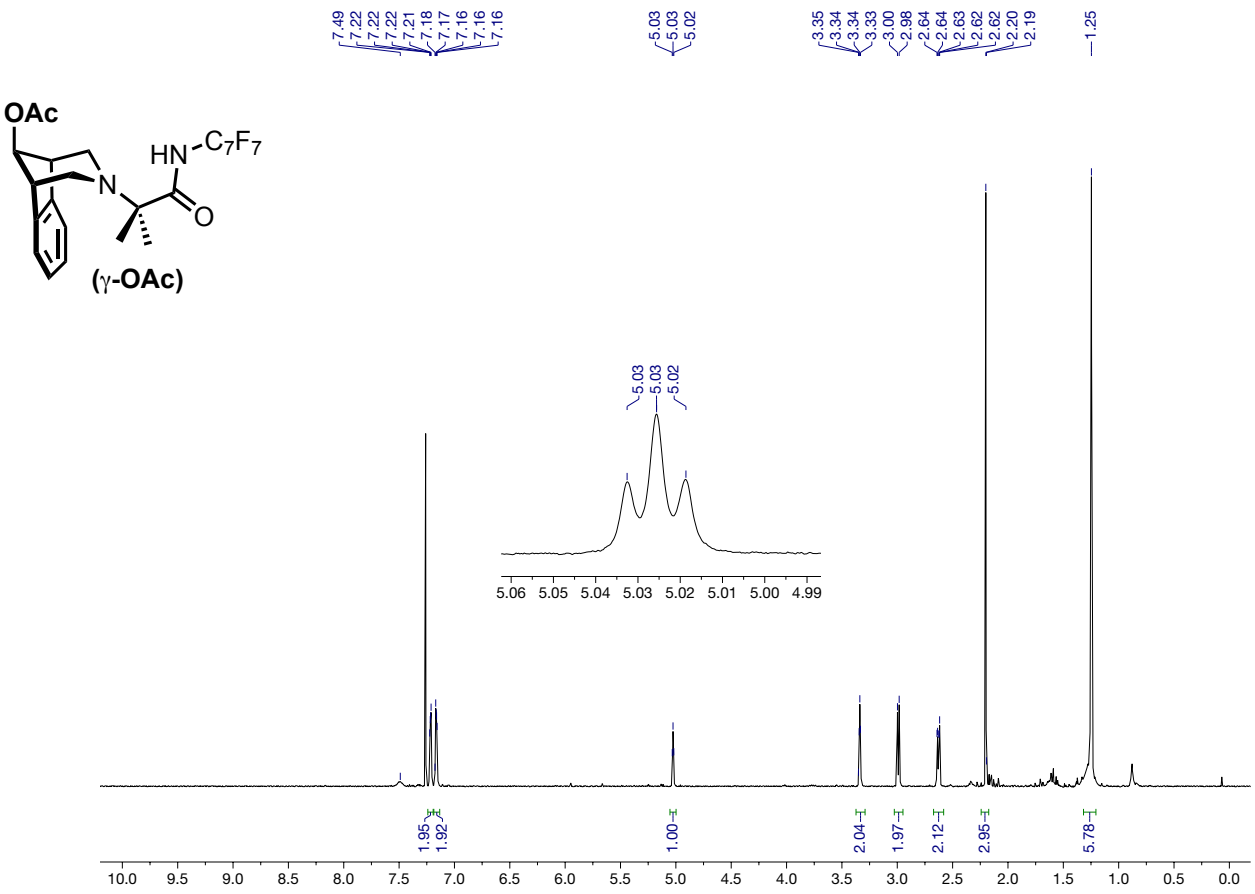
^{1}H NMR Spectrum in $CDCl_3$



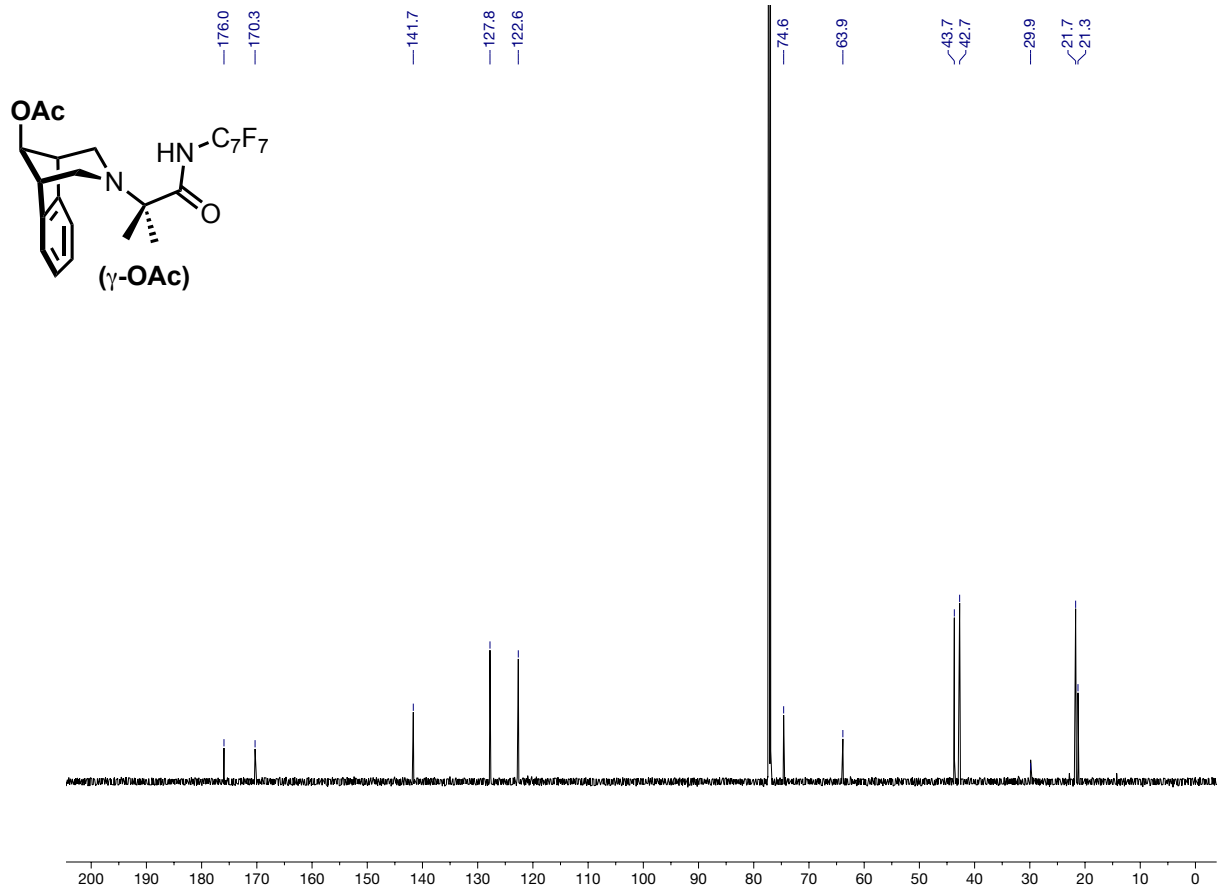
^{13}C NMR Spectrum in $CDCl_3$



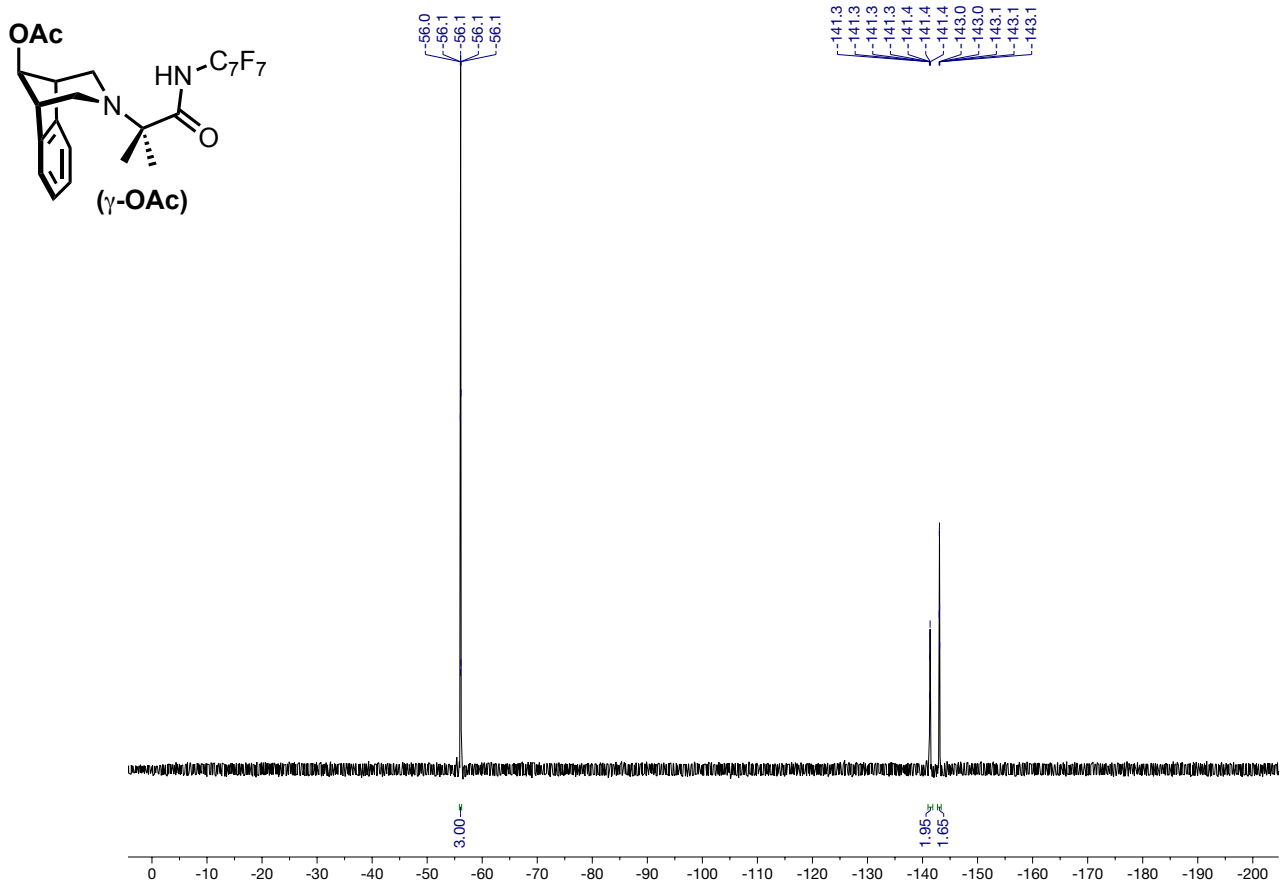
^{19}F NMR Spectrum in $CDCl_3$



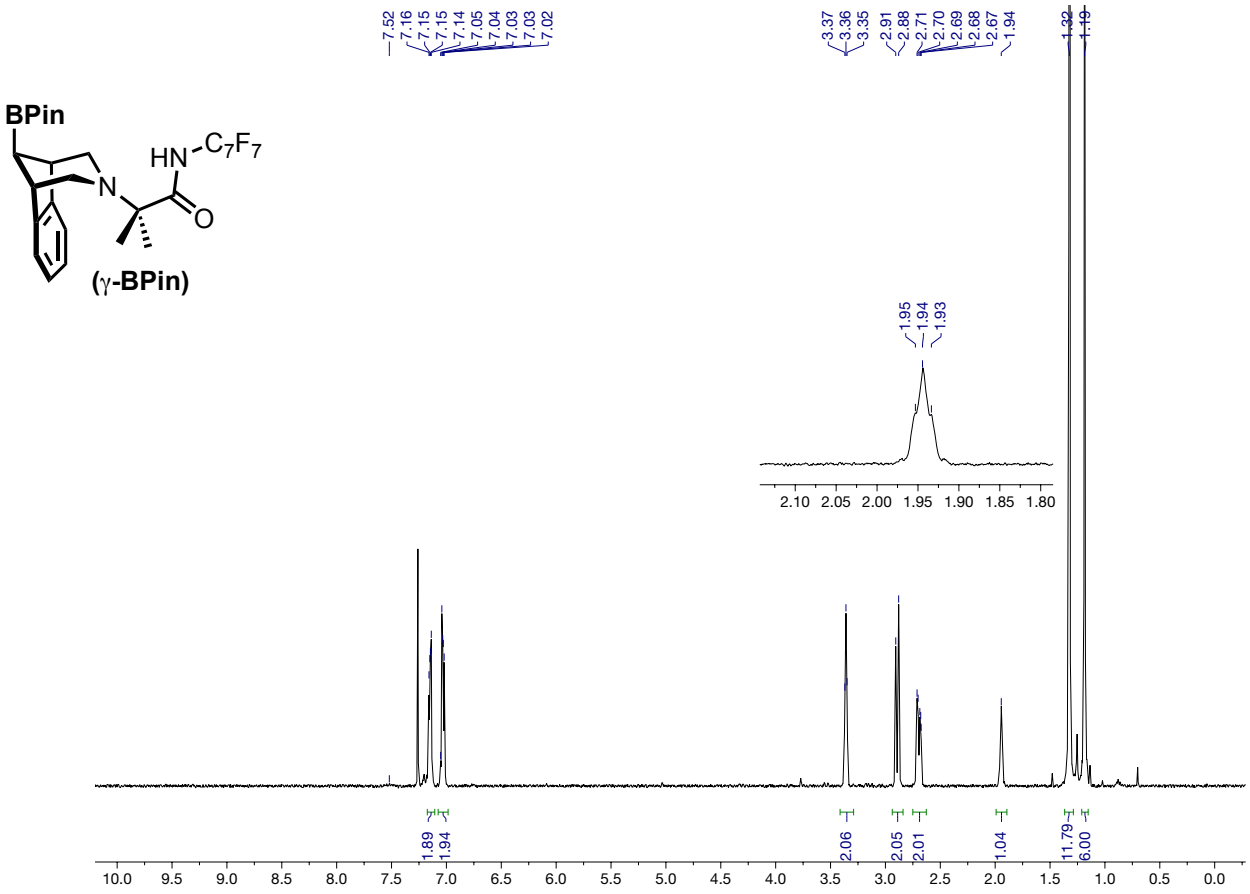
^{1}H NMR Spectrum in $CDCl_3$



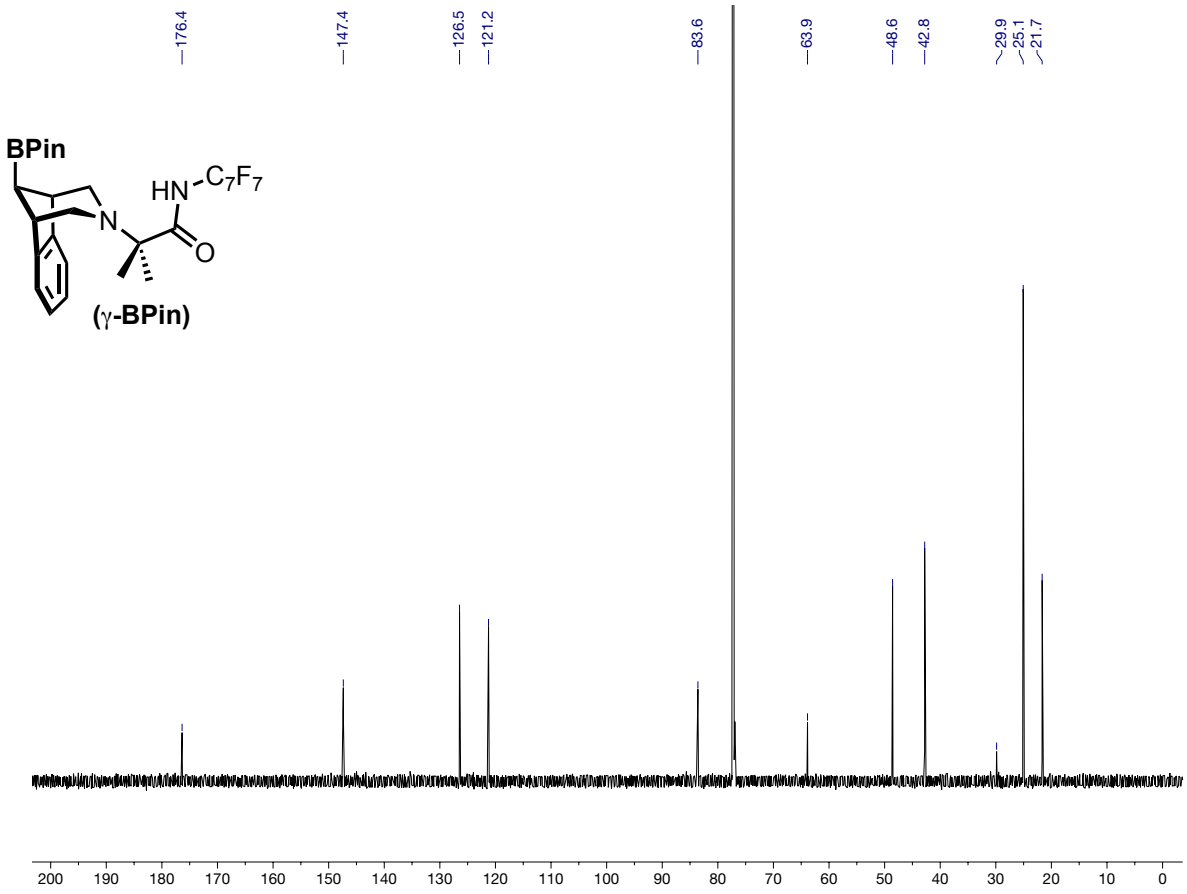
^{13}C NMR Spectrum in $CDCl_3$



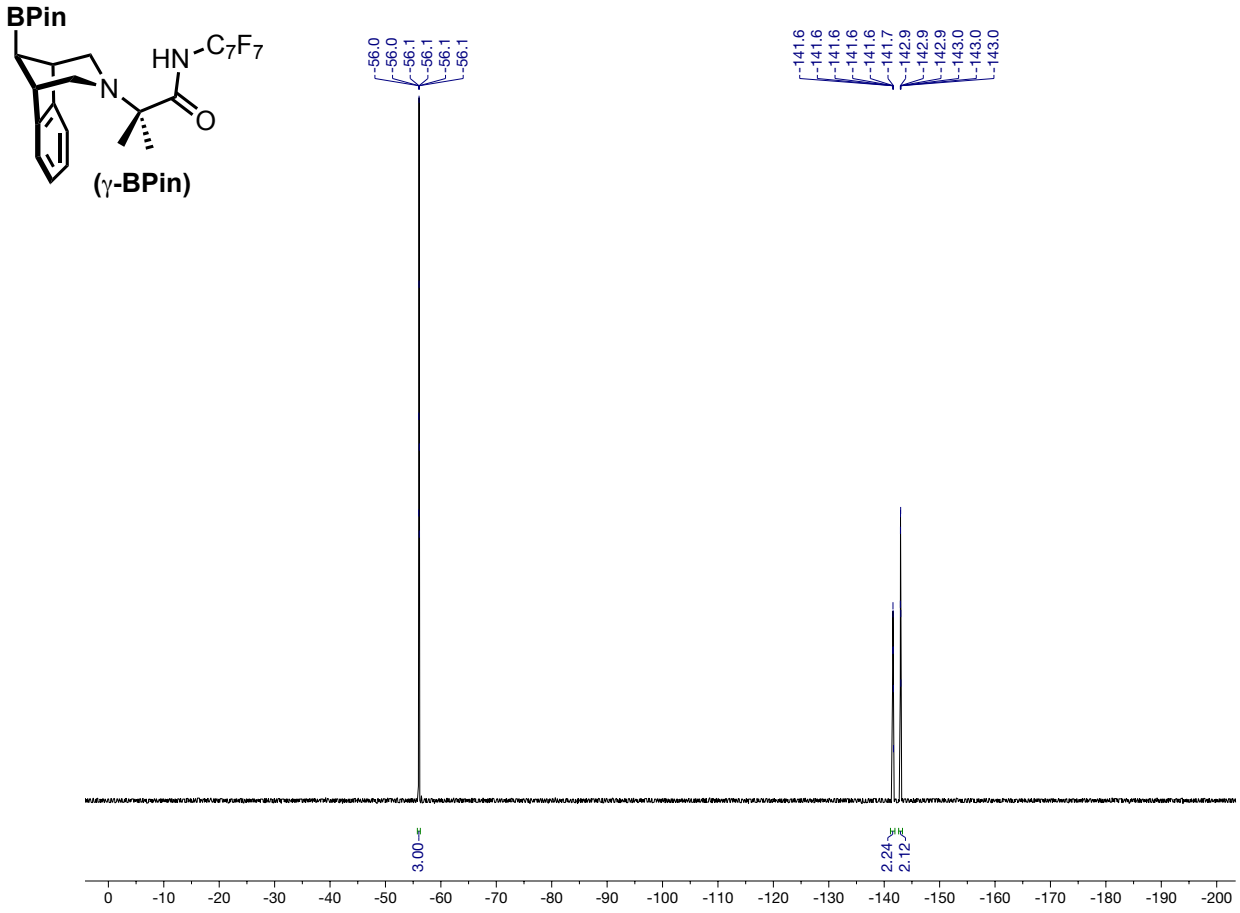
^{19}F NMR Spectrum in $CDCl_3$



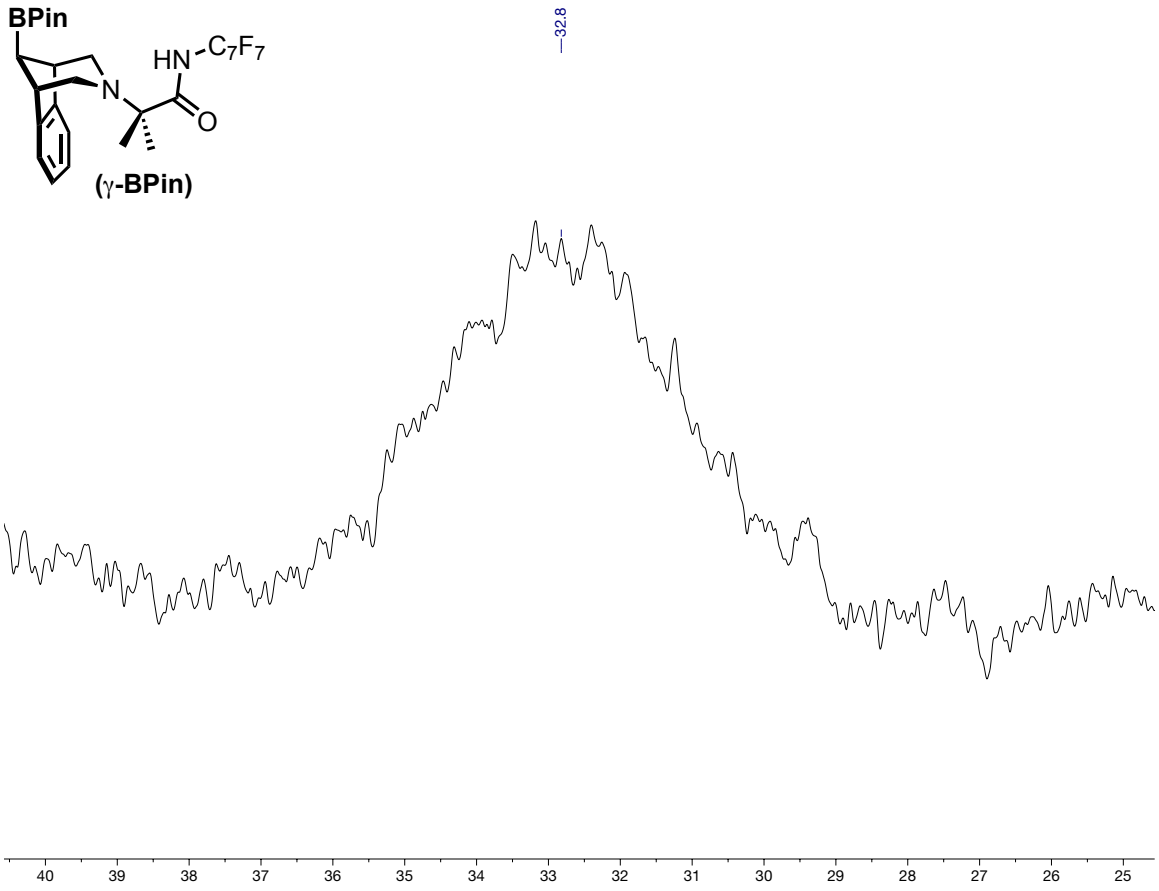
^{1}H NMR Spectrum in $CDCl_3$



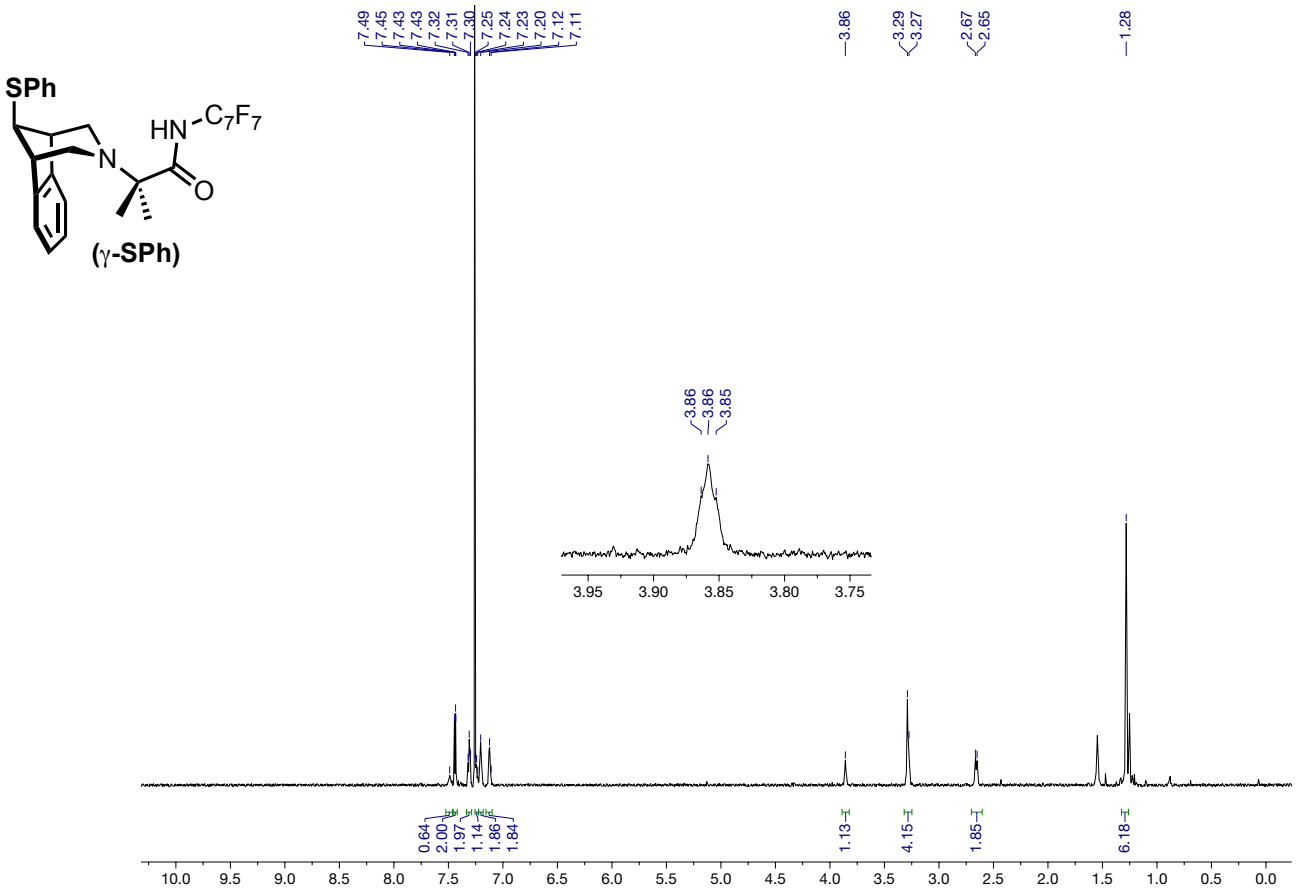
^{13}C NMR Spectrum in $CDCl_3$



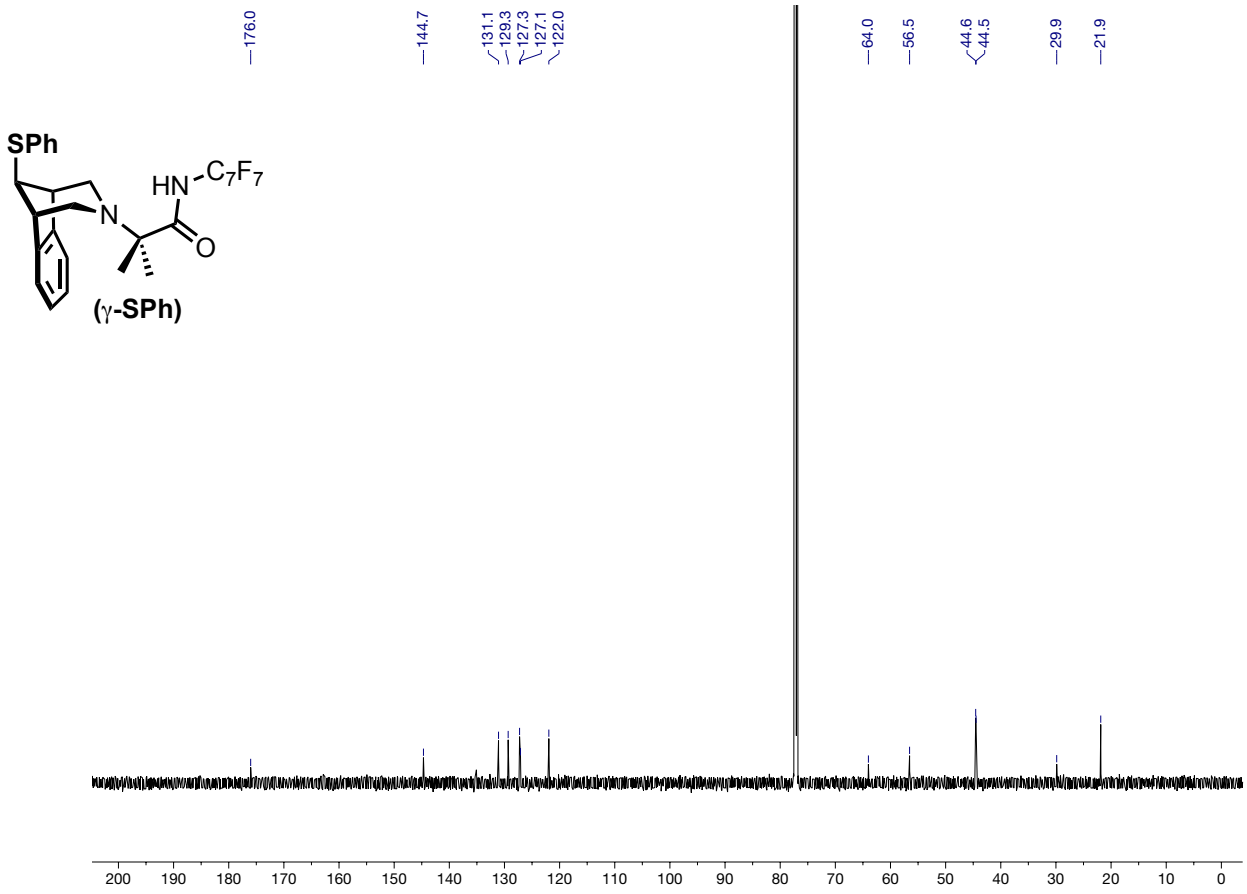
^{19}F NMR Spectrum in $CDCl_3$



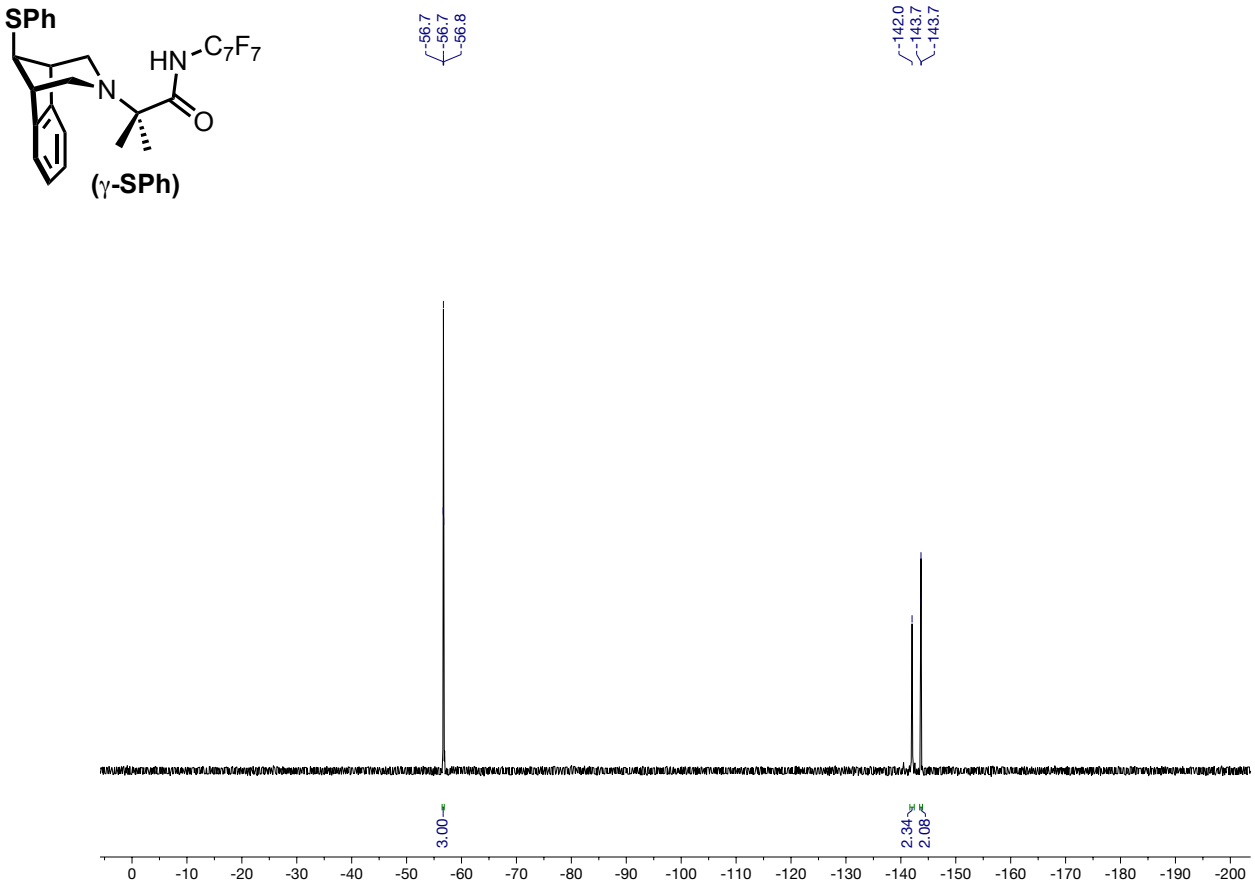
^{11}B NMR Spectrum in $CDCl_3$



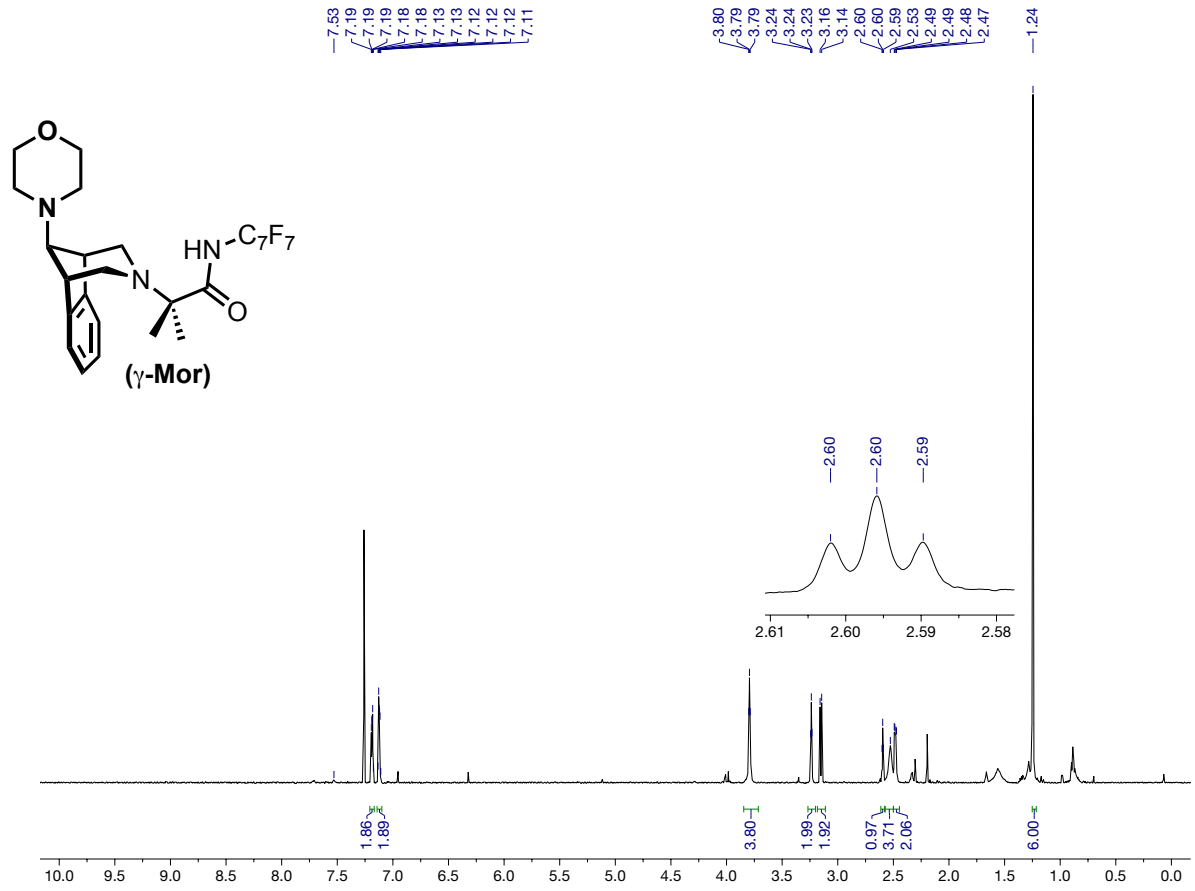
^{1}H NMR Spectrum in $CDCl_3$



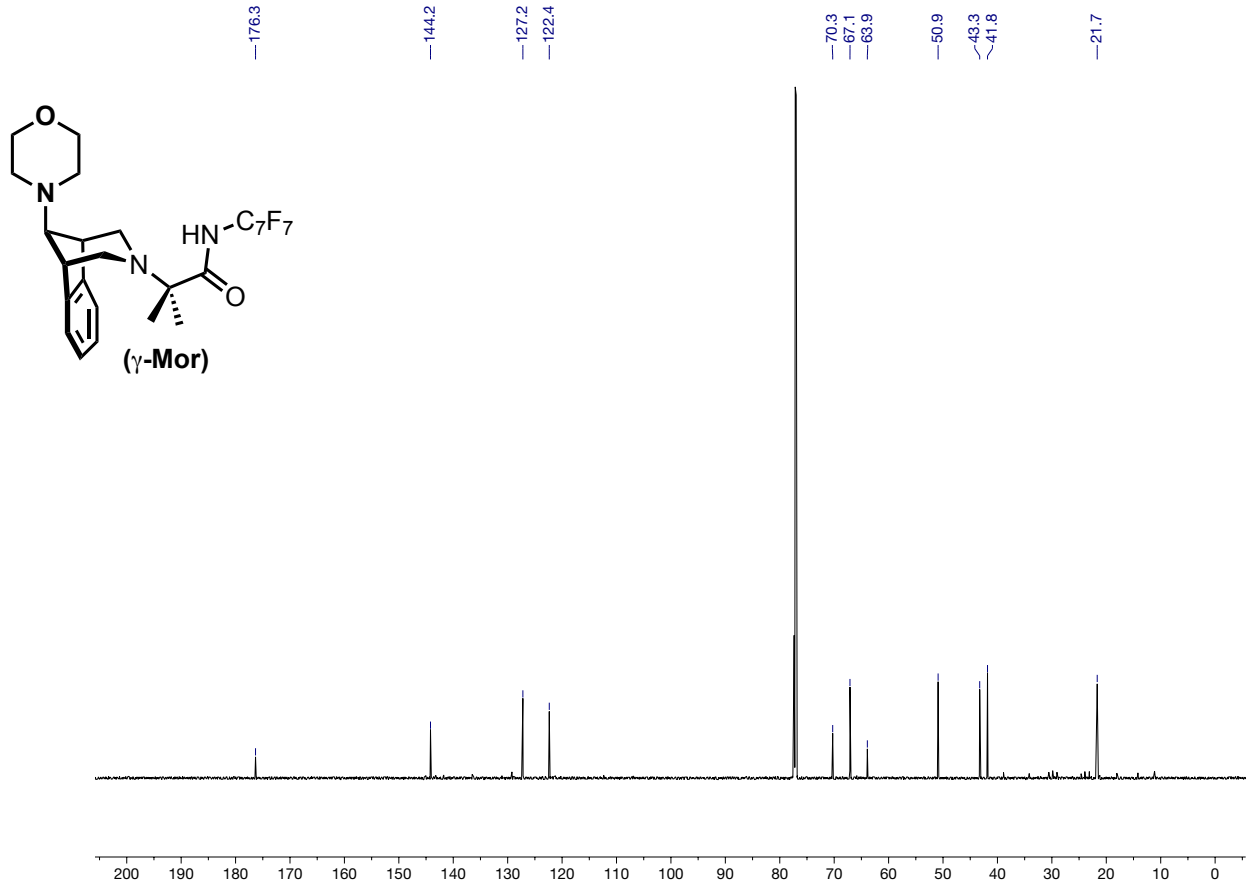
^{13}C NMR Spectrum in $CDCl_3$



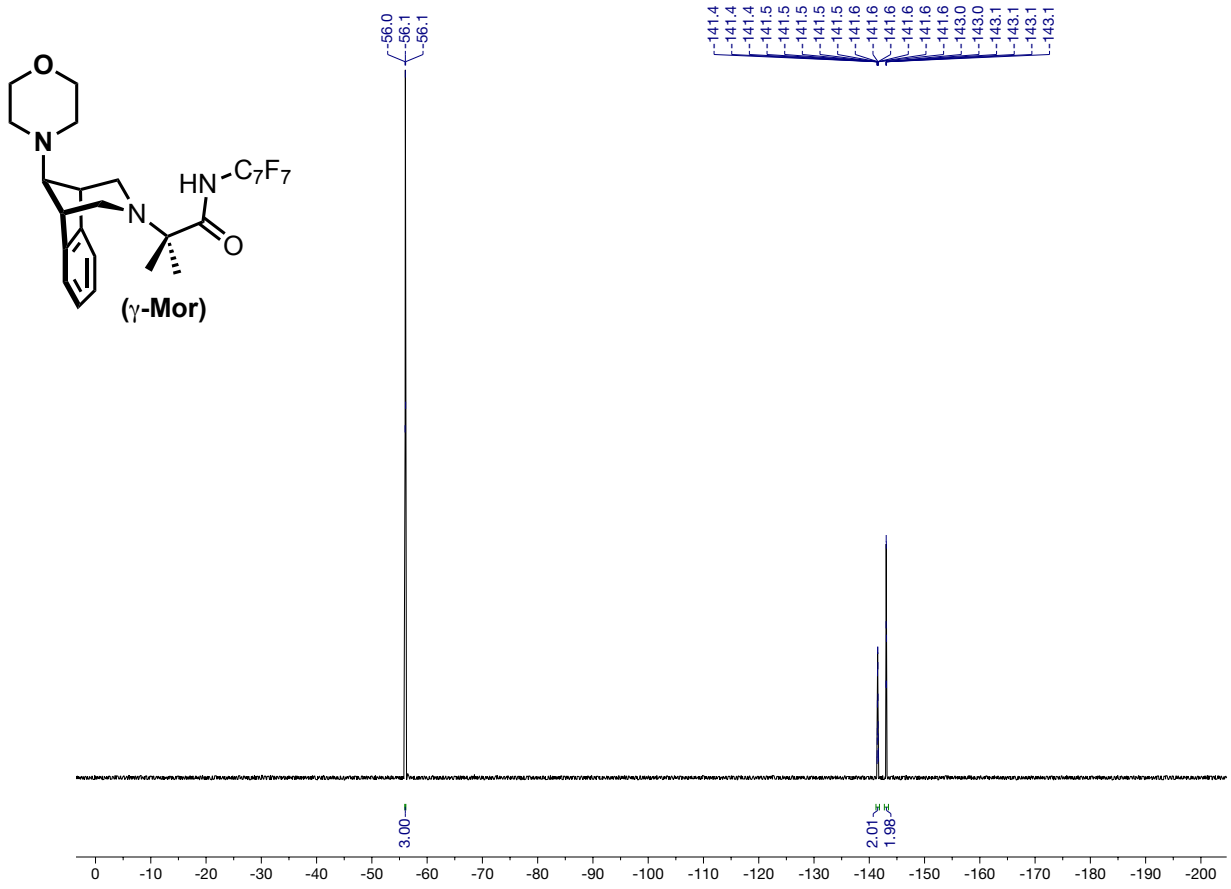
^{19}F NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum in $CDCl_3$

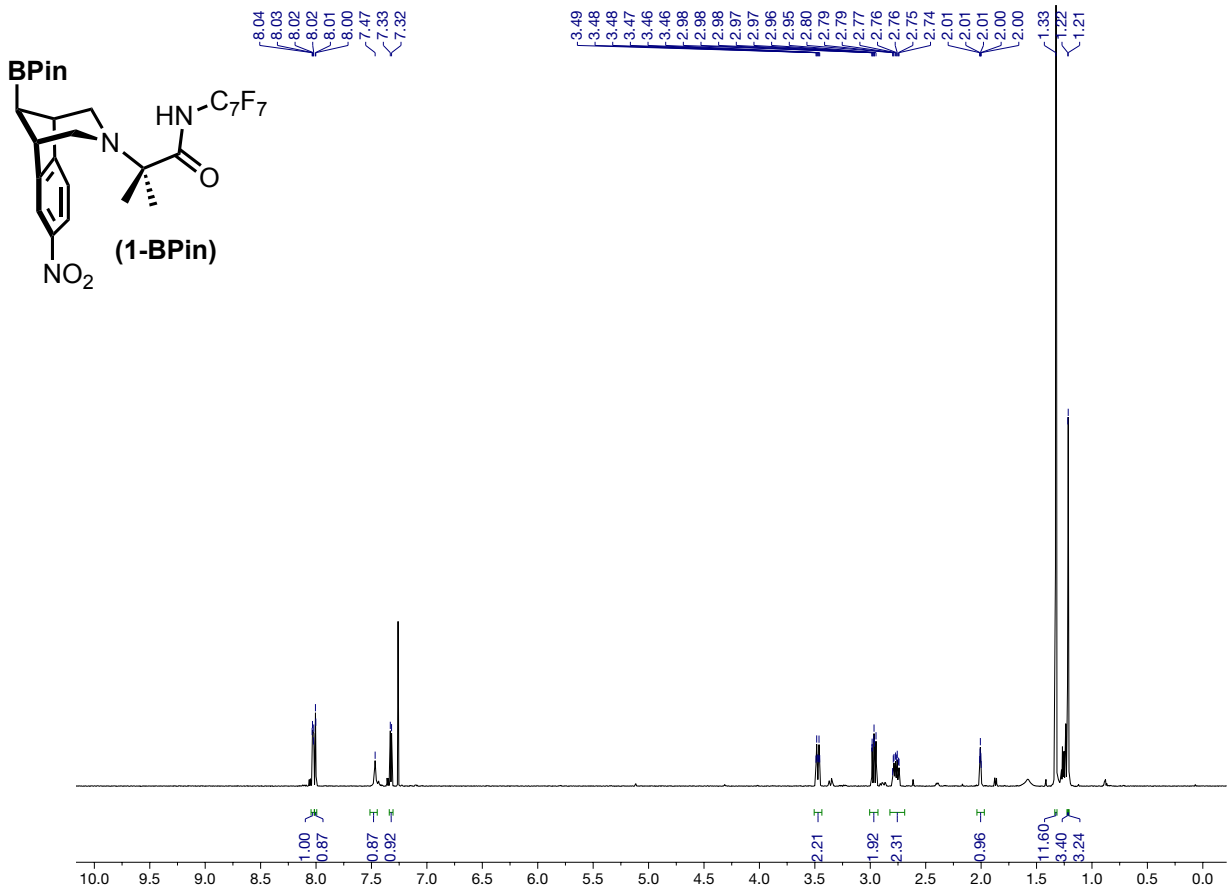


^{13}C NMR Spectrum in $CDCl_3$

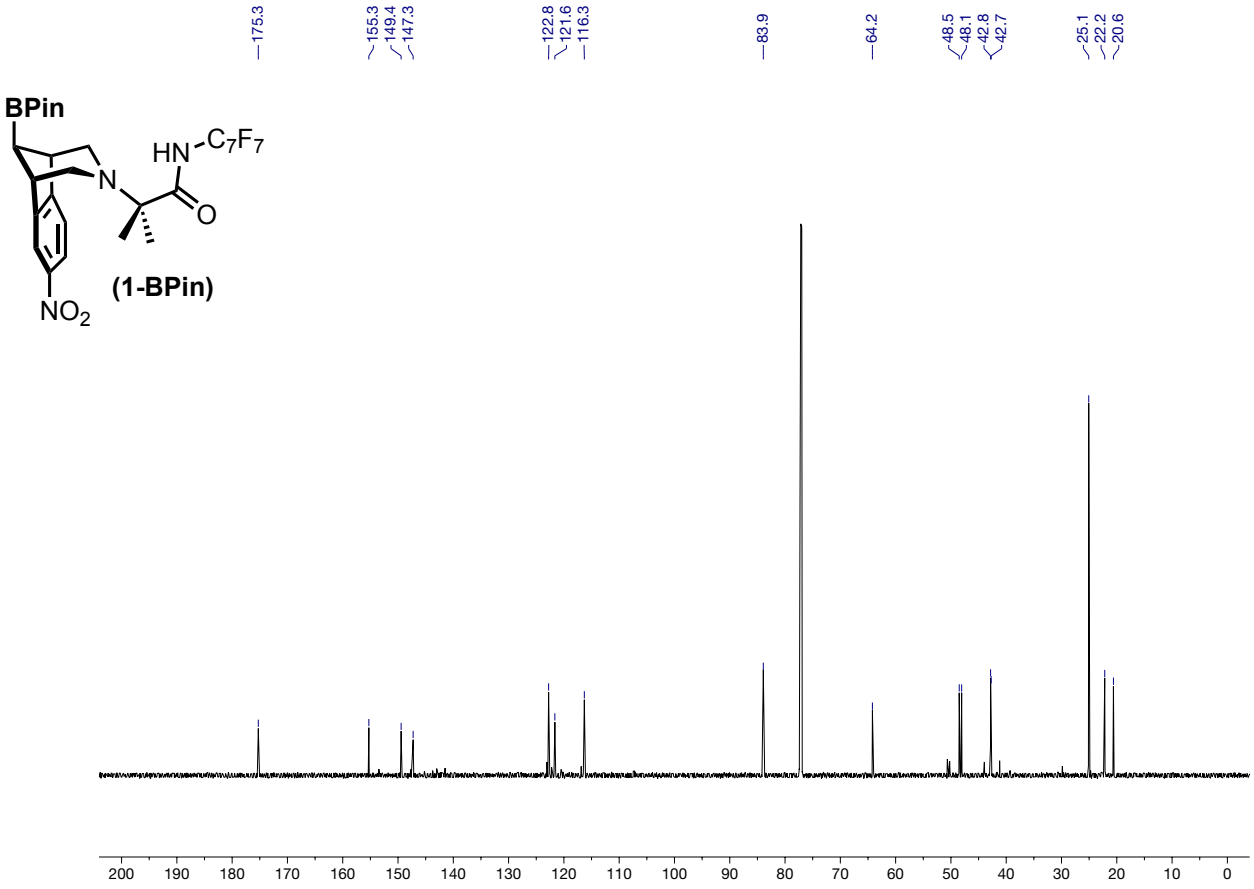


^{19}F NMR Spectrum in $CDCl_3$

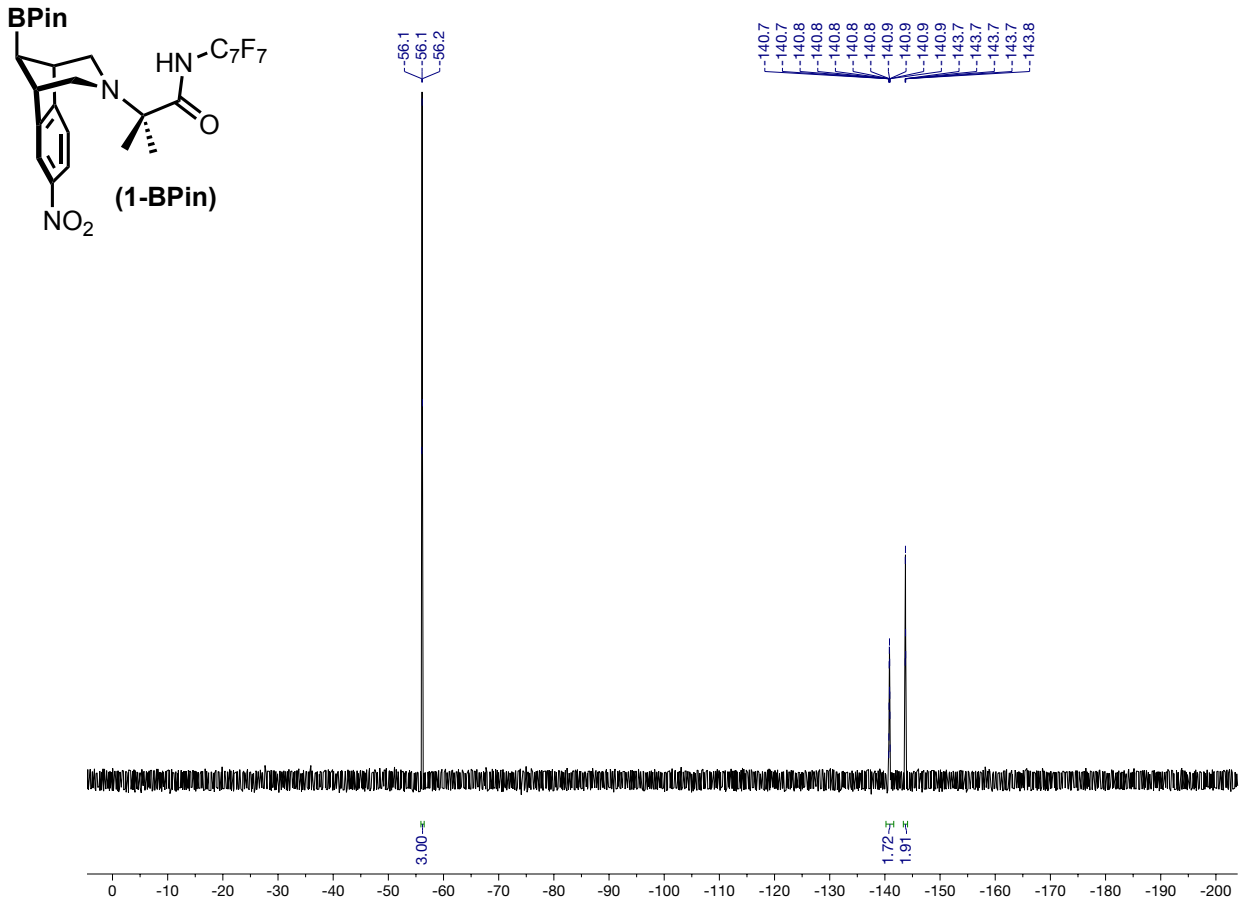
c. Borylation Spectra Data



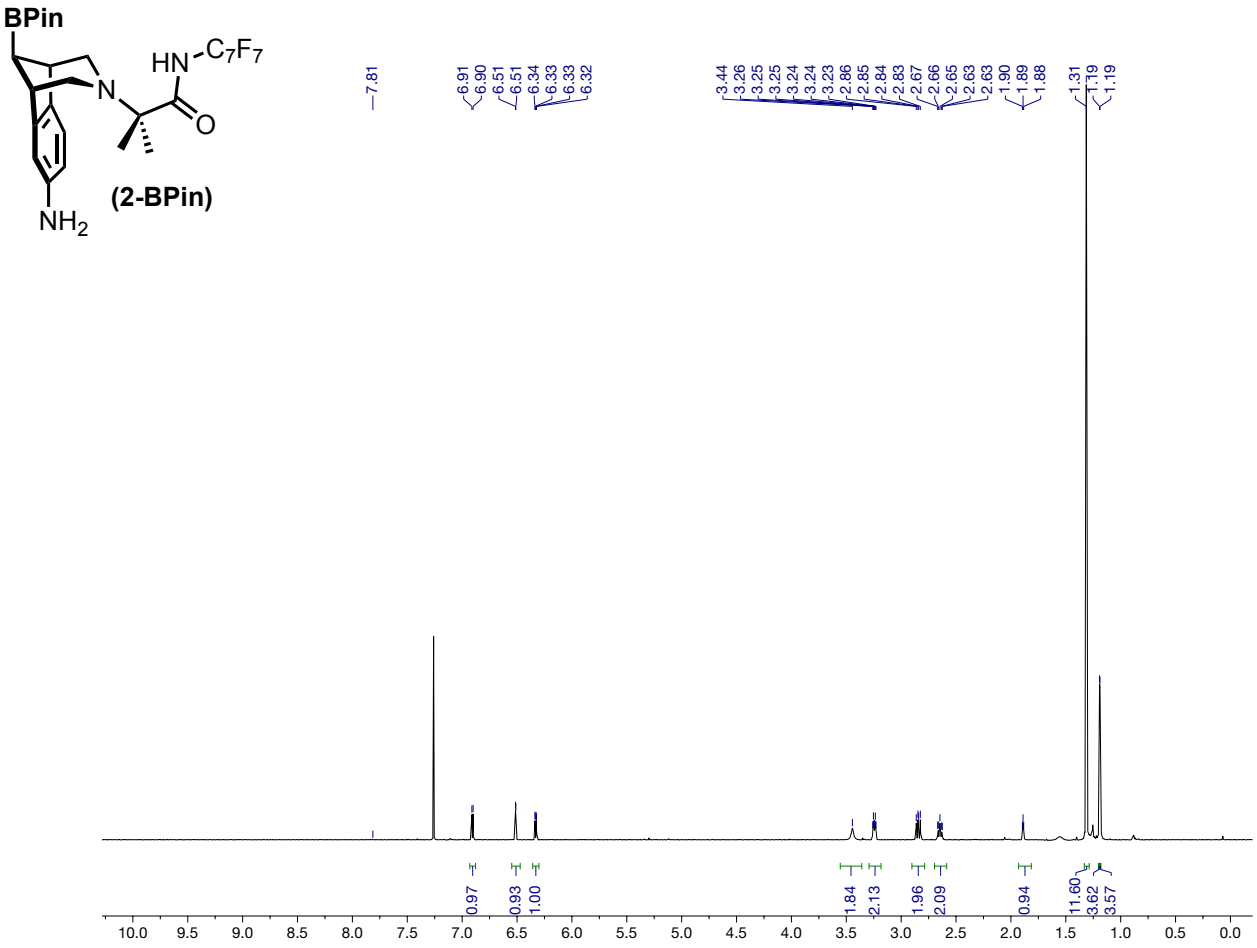
^{1}H NMR Spectrum in $CDCl_3$



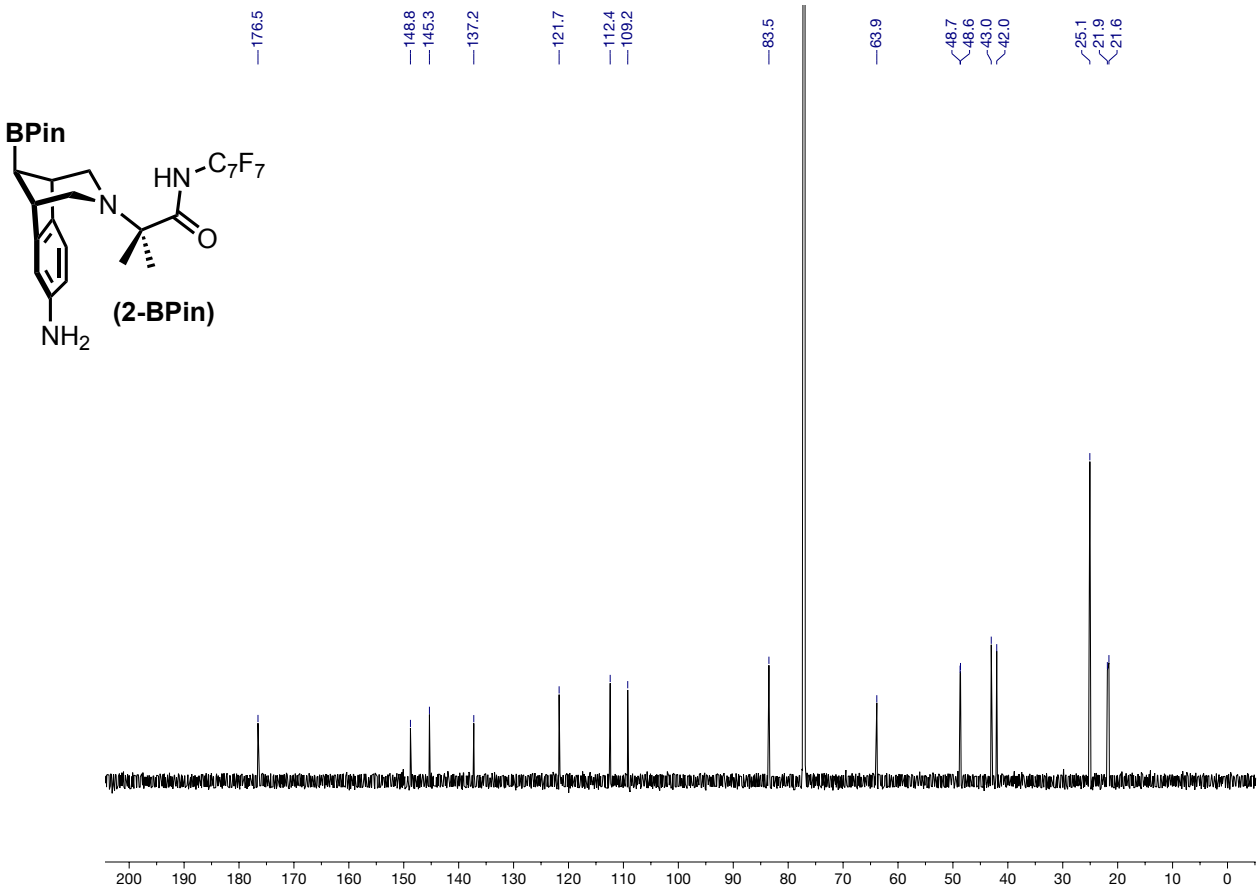
^{13}C NMR Spectrum in $CDCl_3$



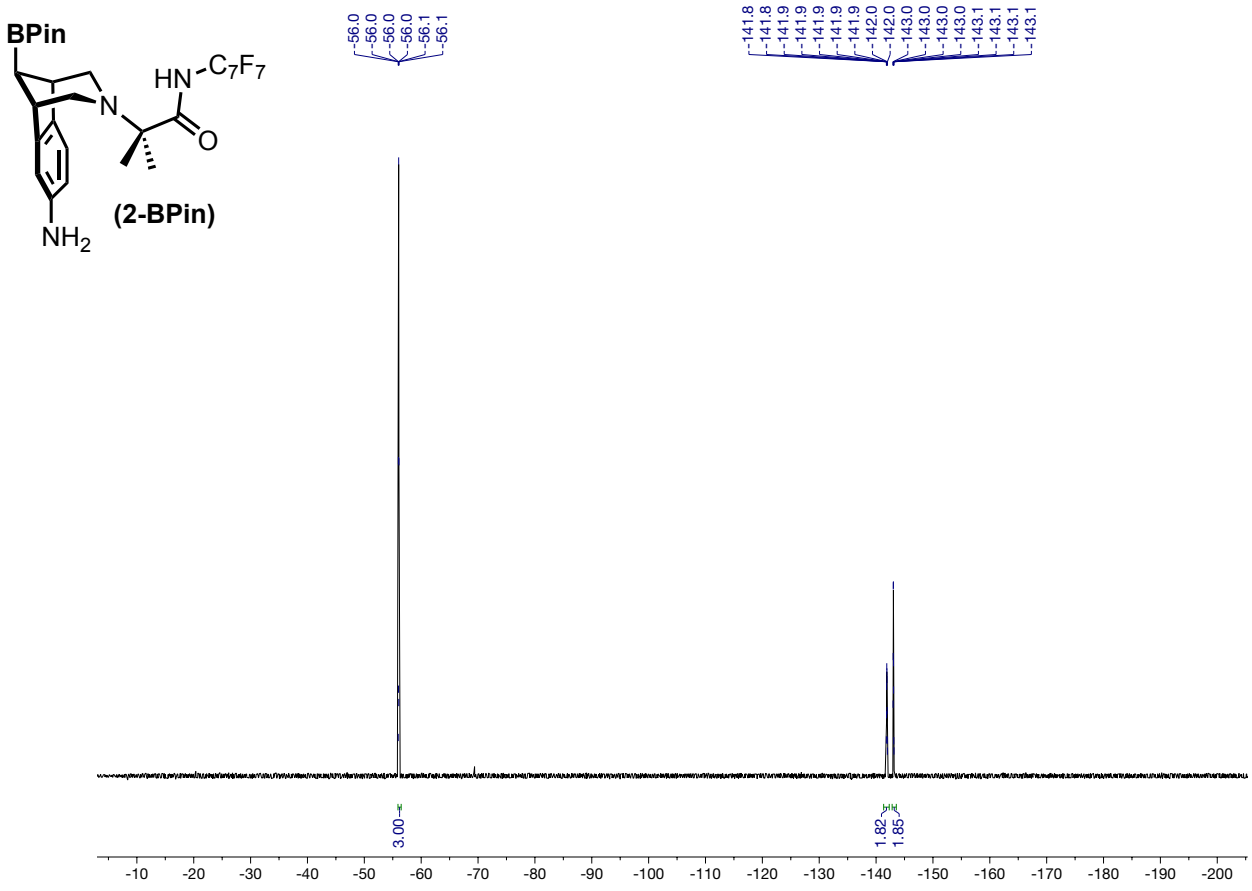
^{19}F NMR Spectrum in $CDCl_3$



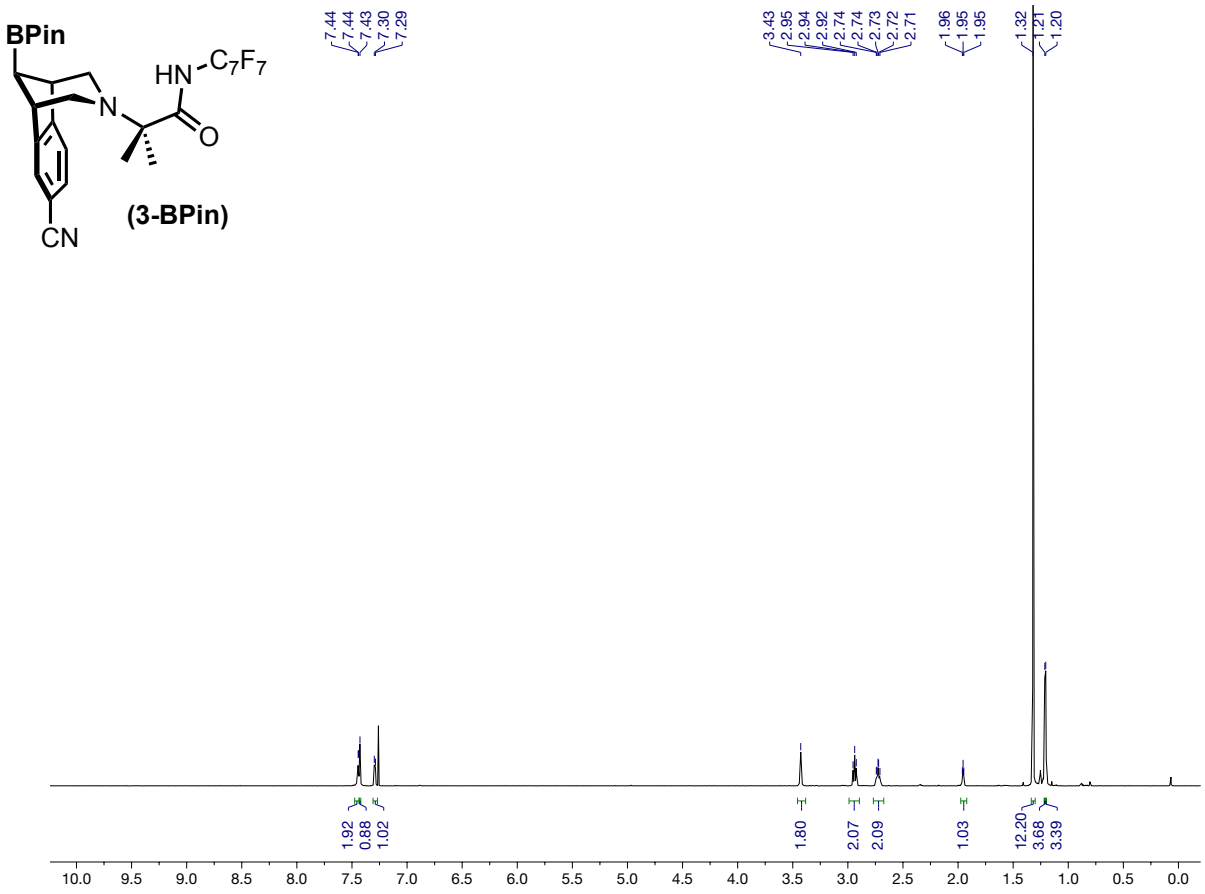
^{1}H NMR Spectrum in $CDCl_3$



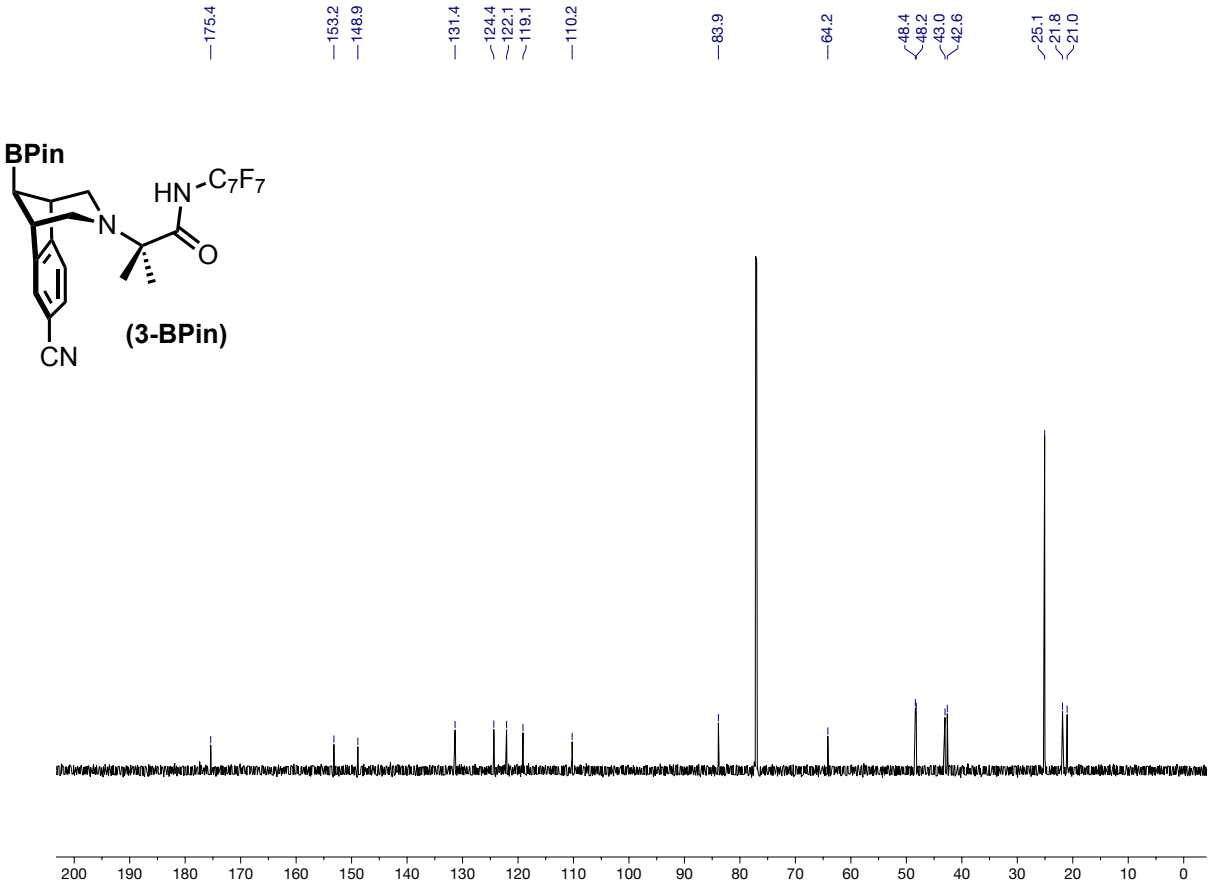
^{13}C NMR Spectrum in $CDCl_3$



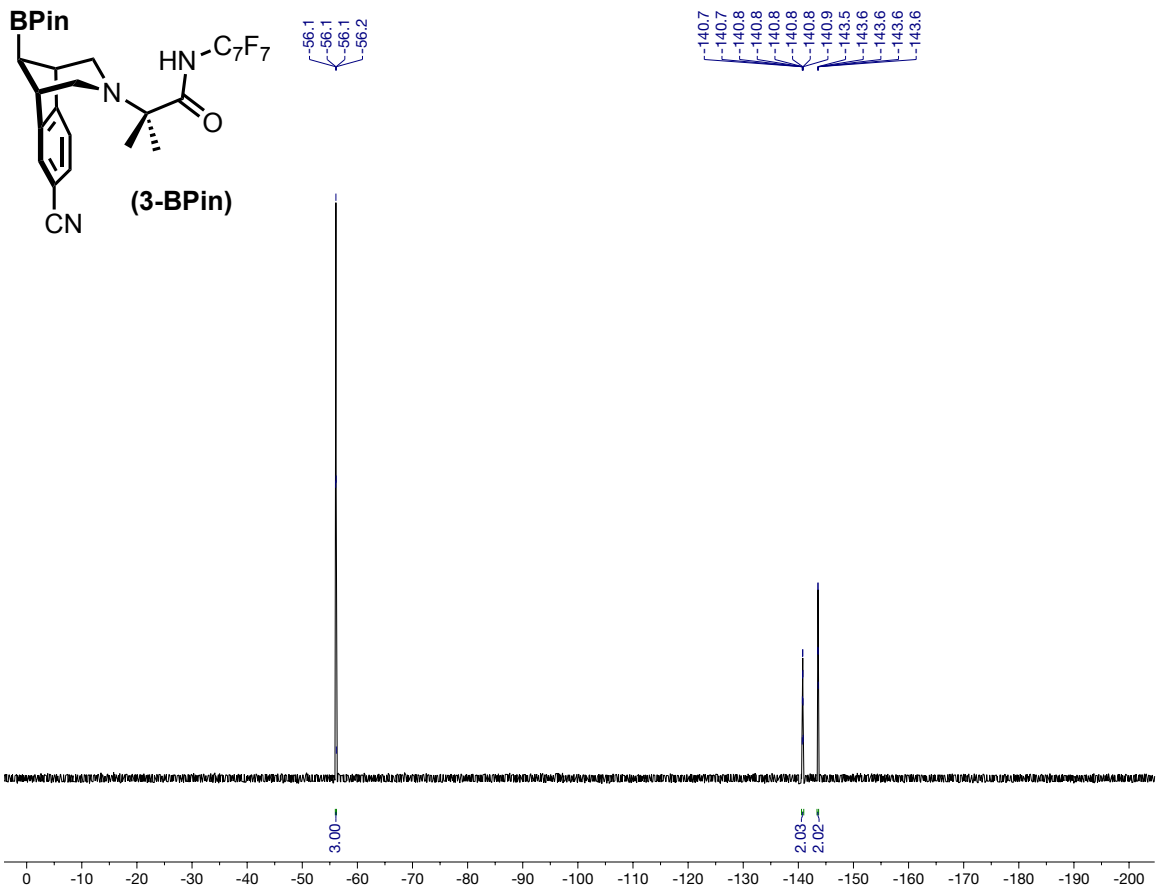
^{19}F NMR Spectrum in $CDCl_3$



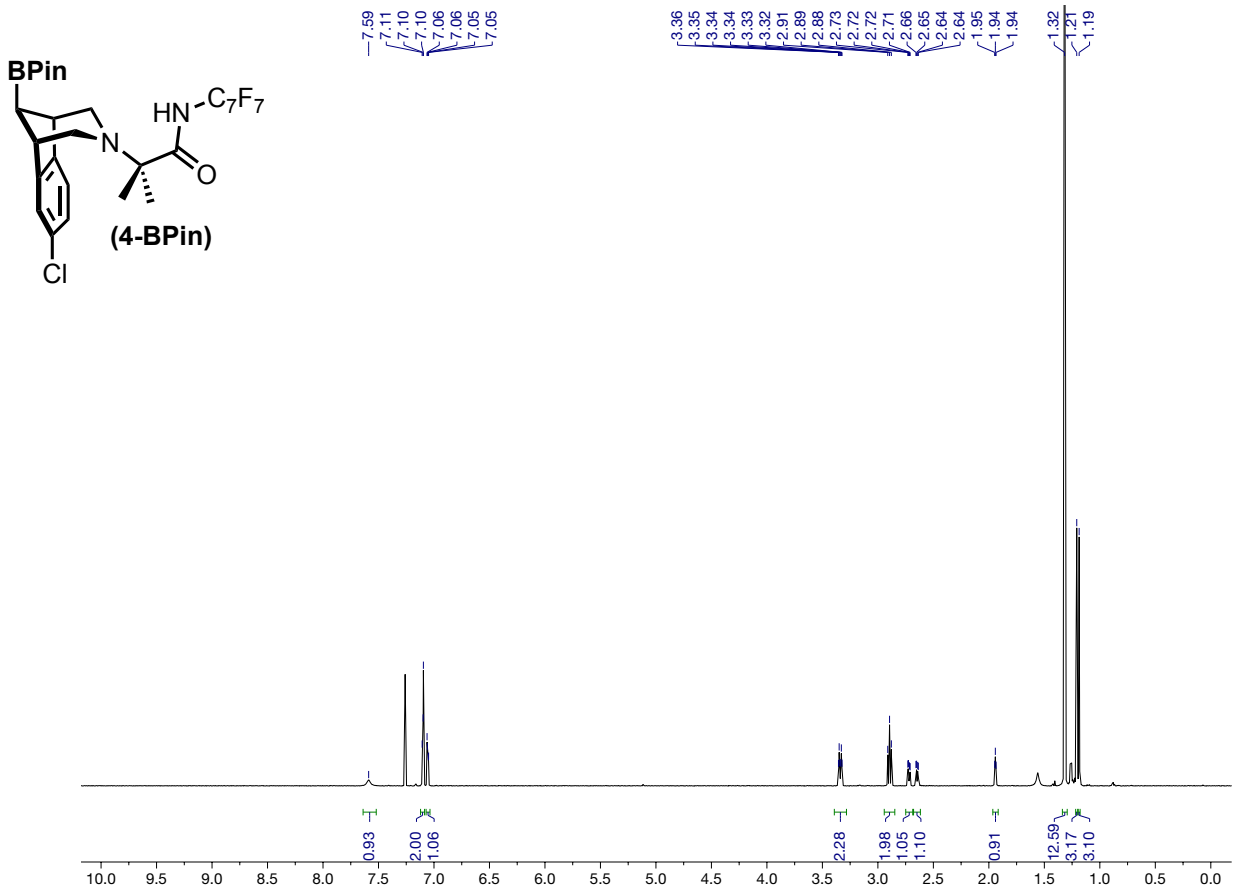
^{1}H NMR Spectrum in $CDCl_3$



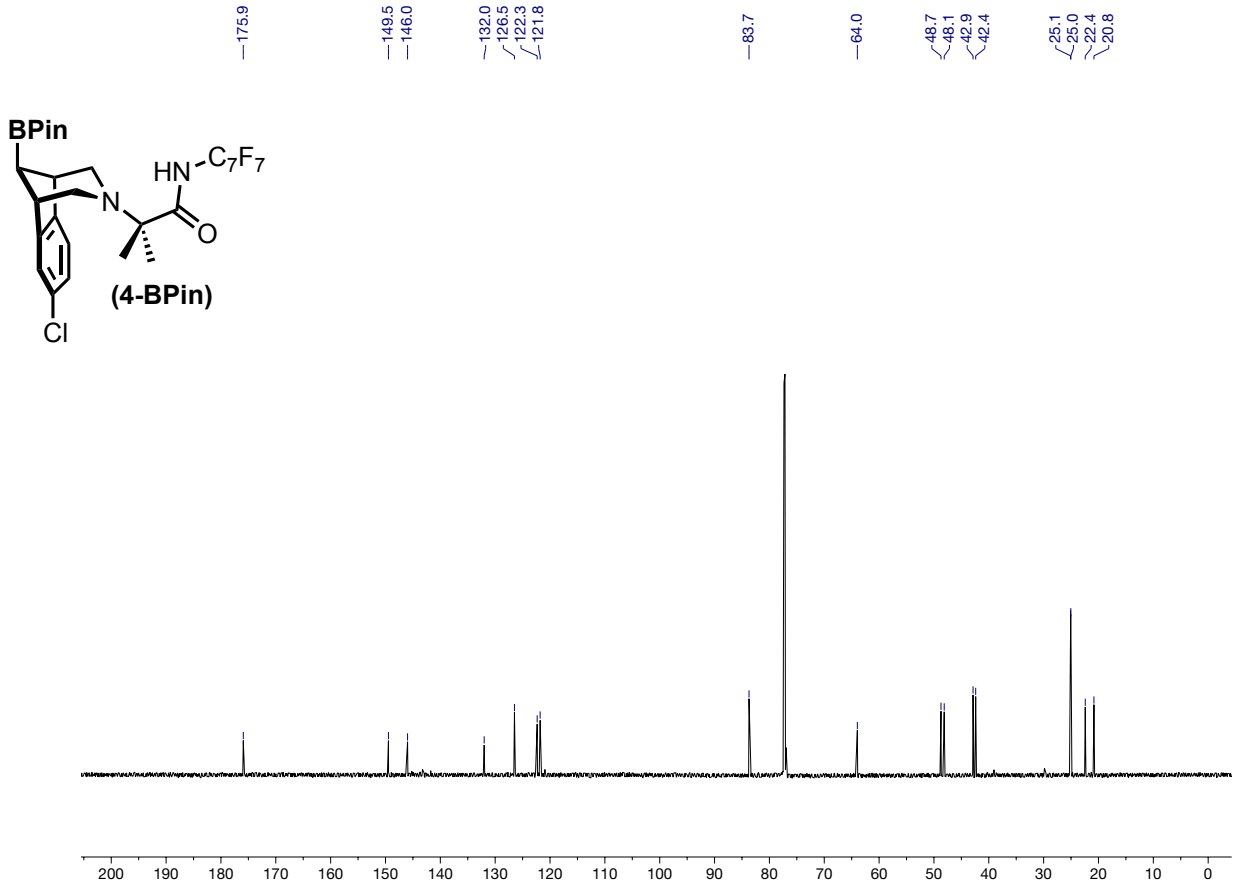
^{13}C NMR Spectrum in $CDCl_3$



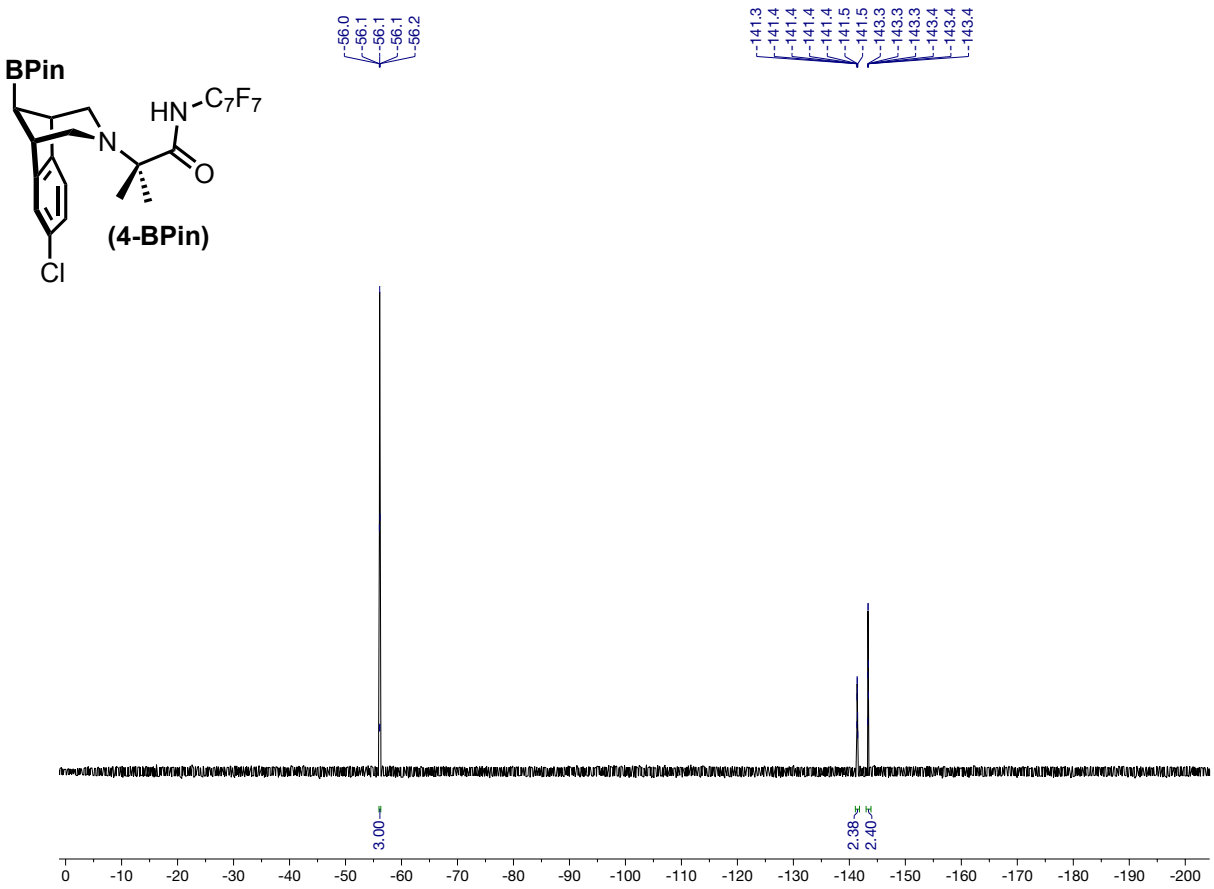
^{19}F NMR Spectrum in $CDCl_3$



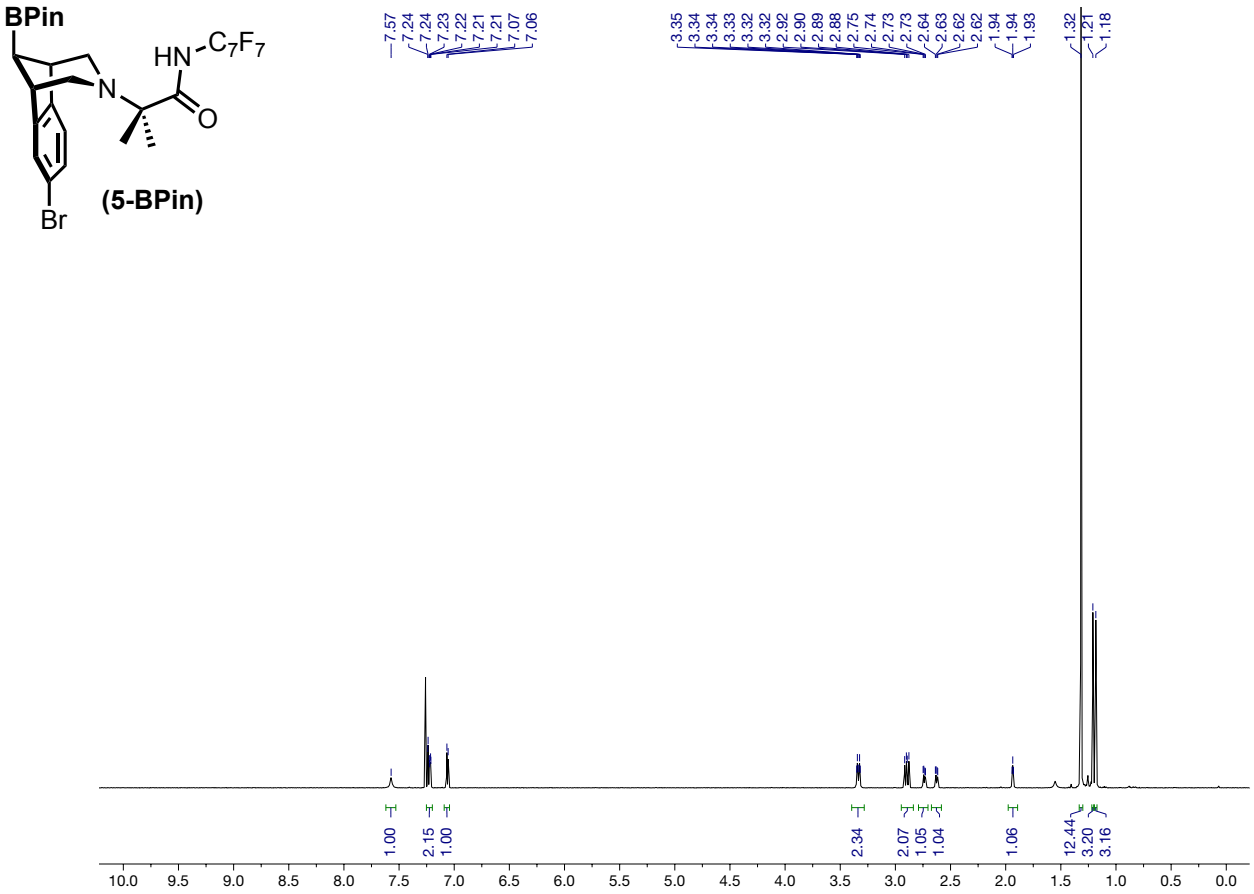
^{1}H NMR Spectrum in $CDCl_3$



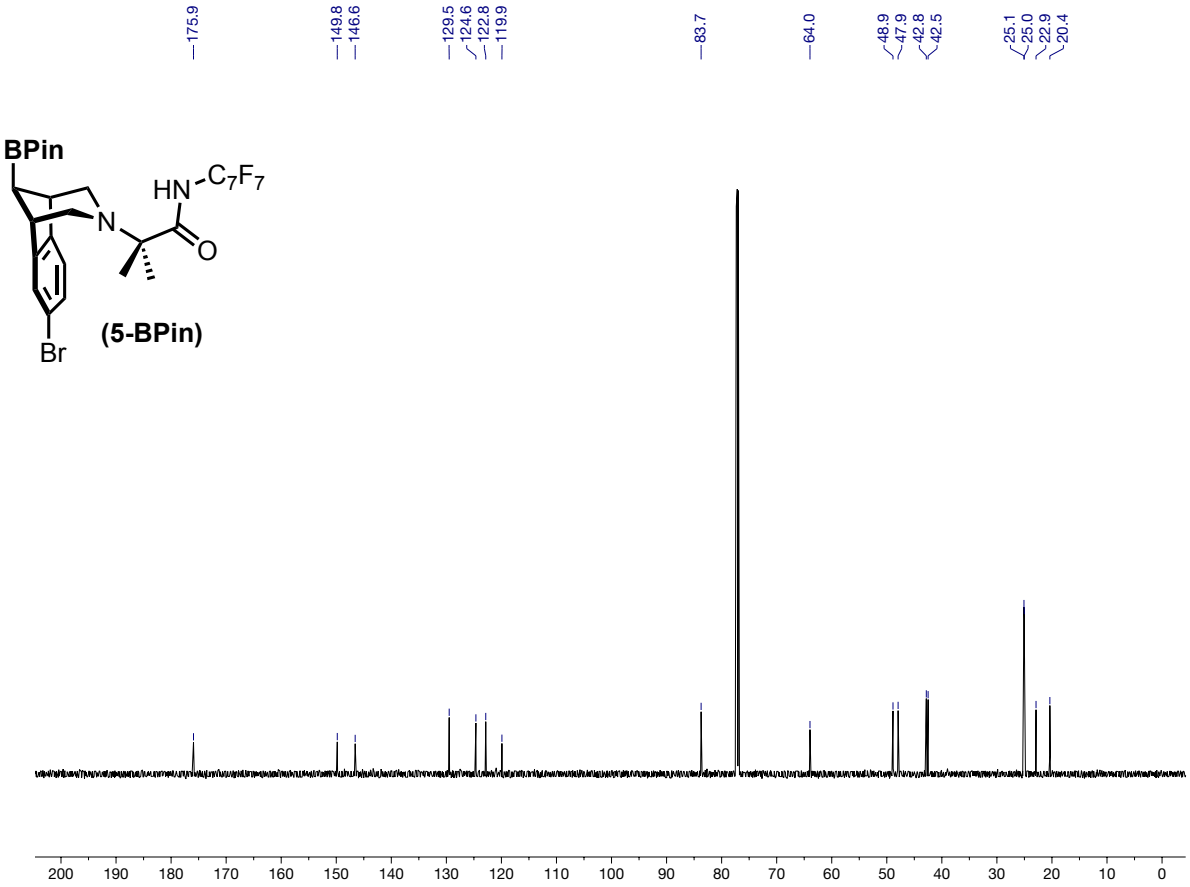
^{13}C NMR Spectrum in $CDCl_3$



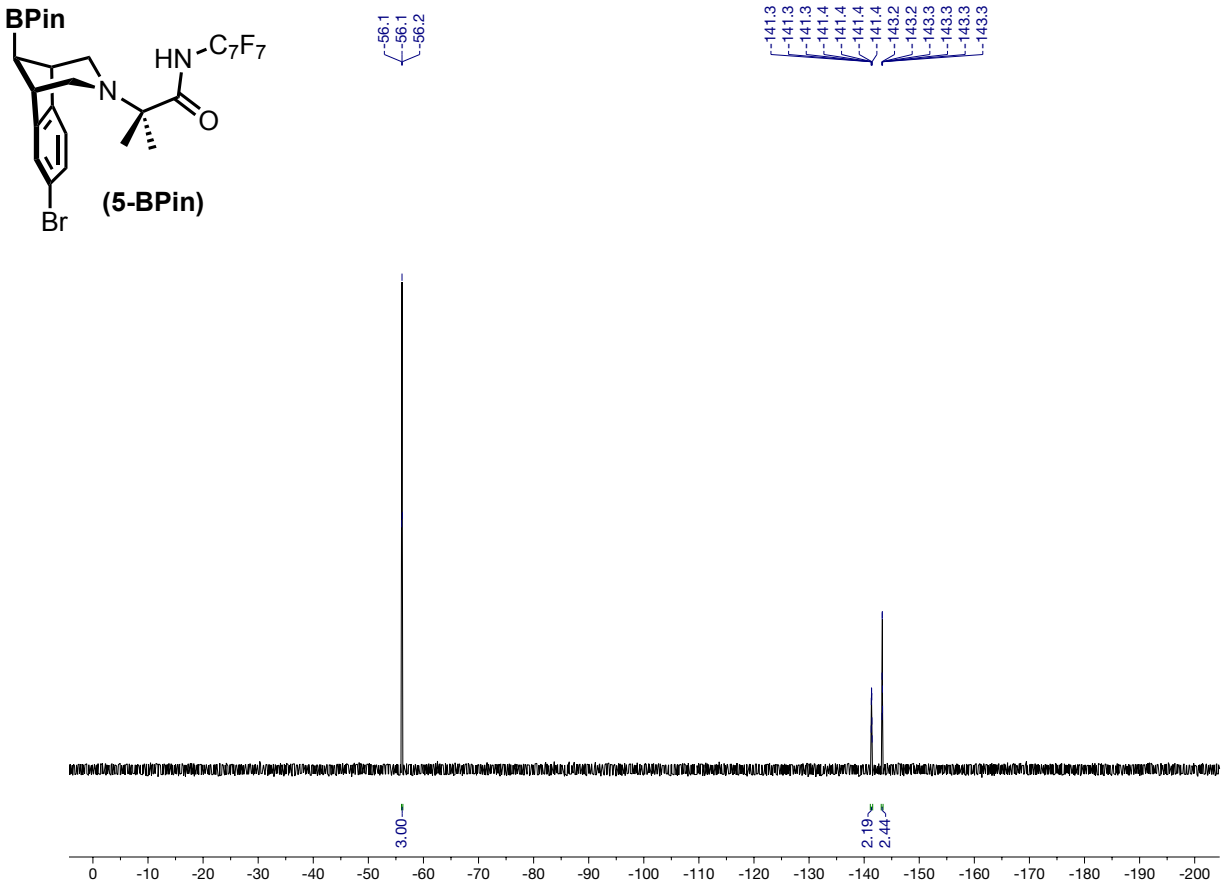
^{19}F NMR Spectrum in $CDCl_3$



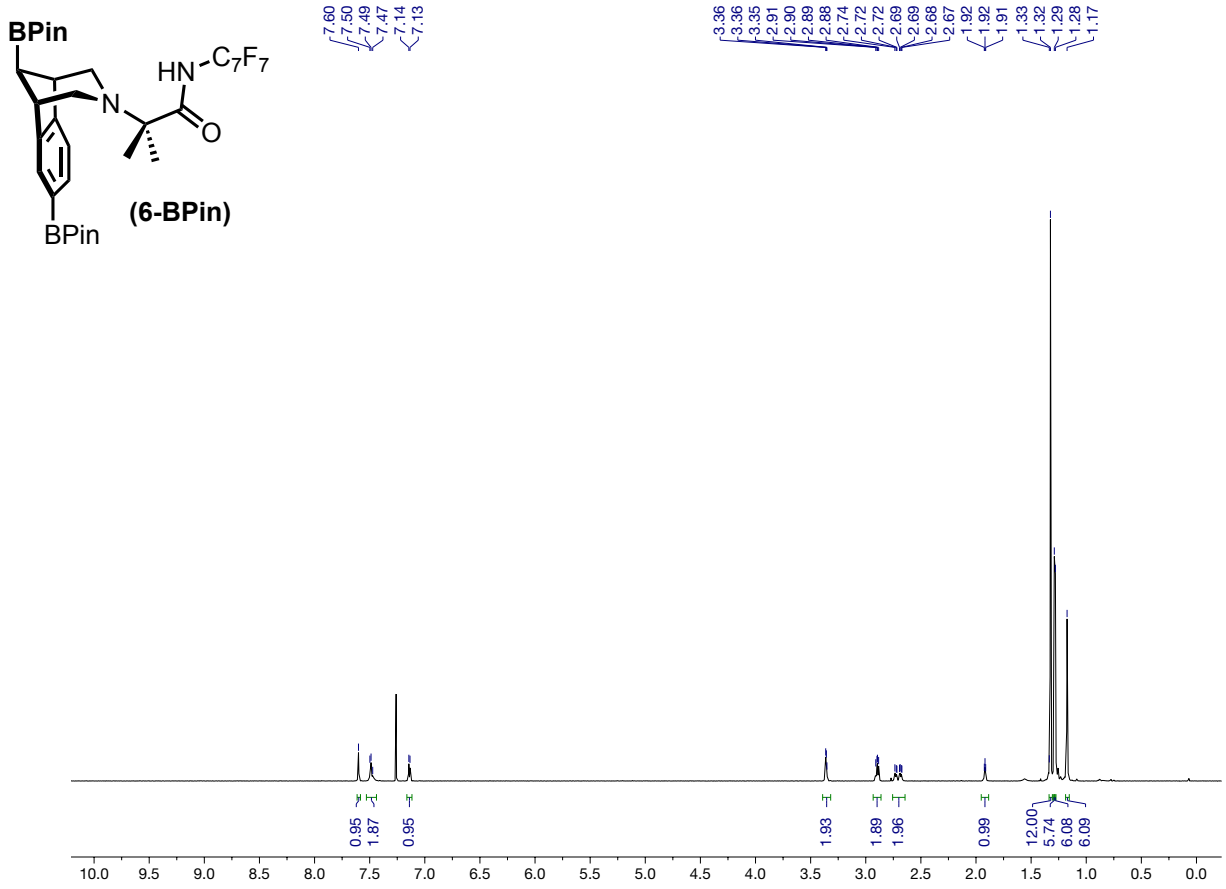
^{1}H NMR Spectrum in $CDCl_3$



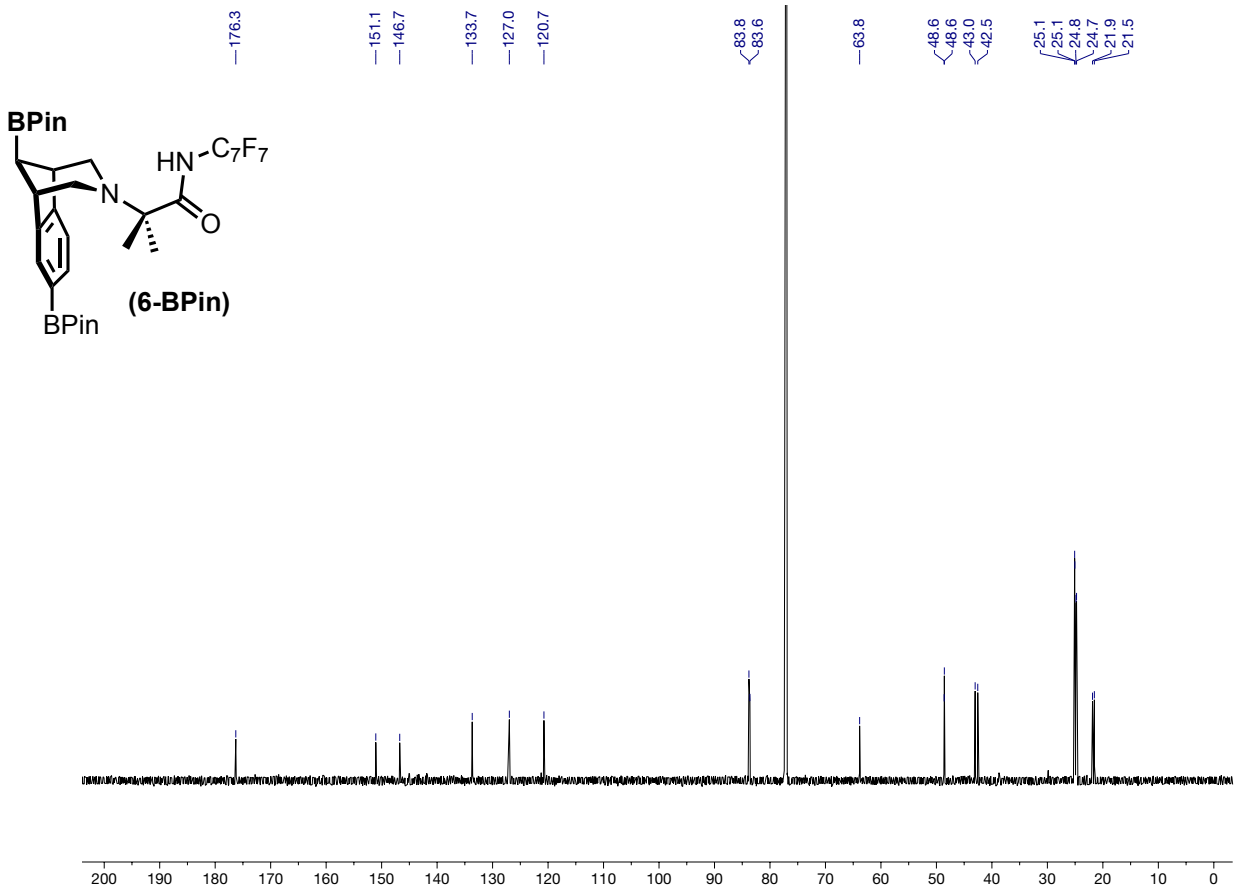
^{13}C NMR Spectrum in $CDCl_3$



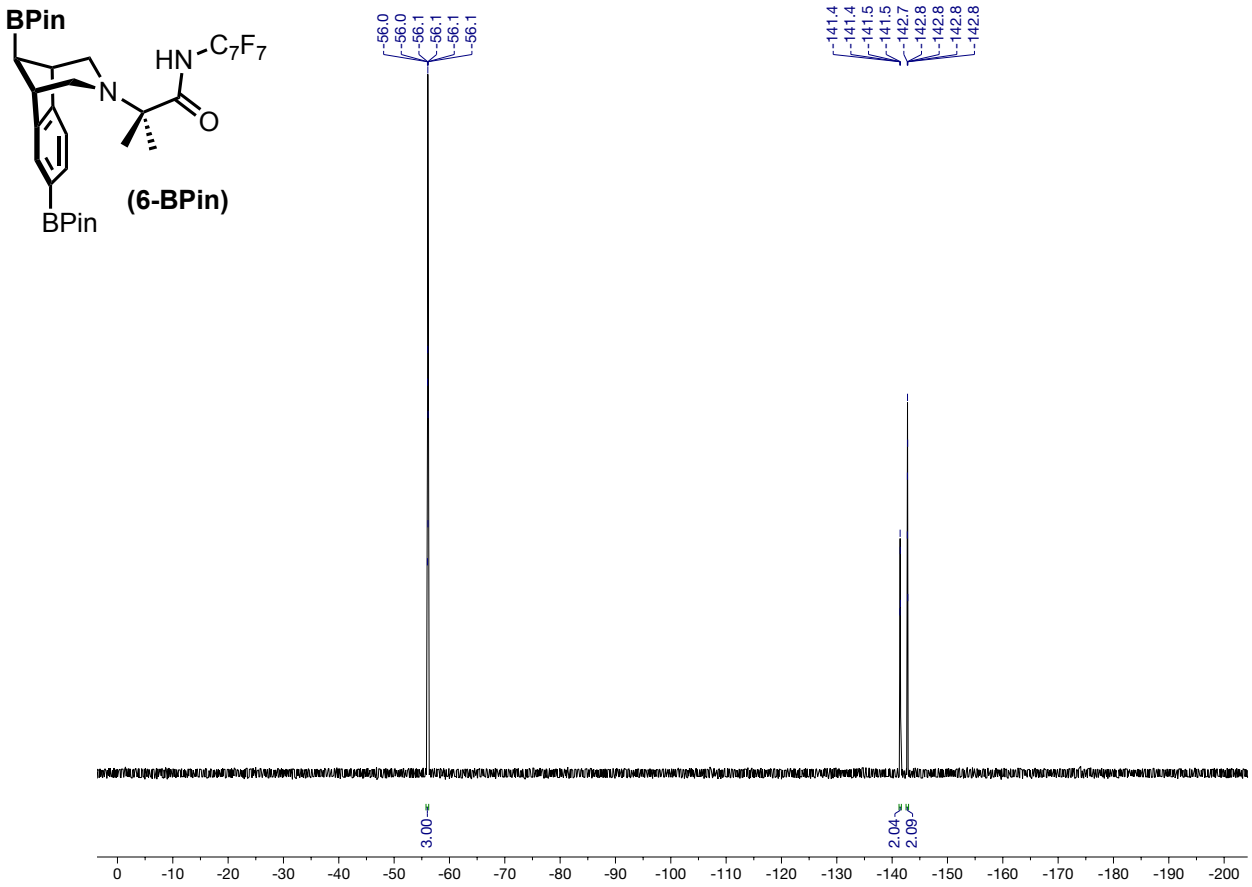
^{19}F NMR Spectrum in $CDCl_3$



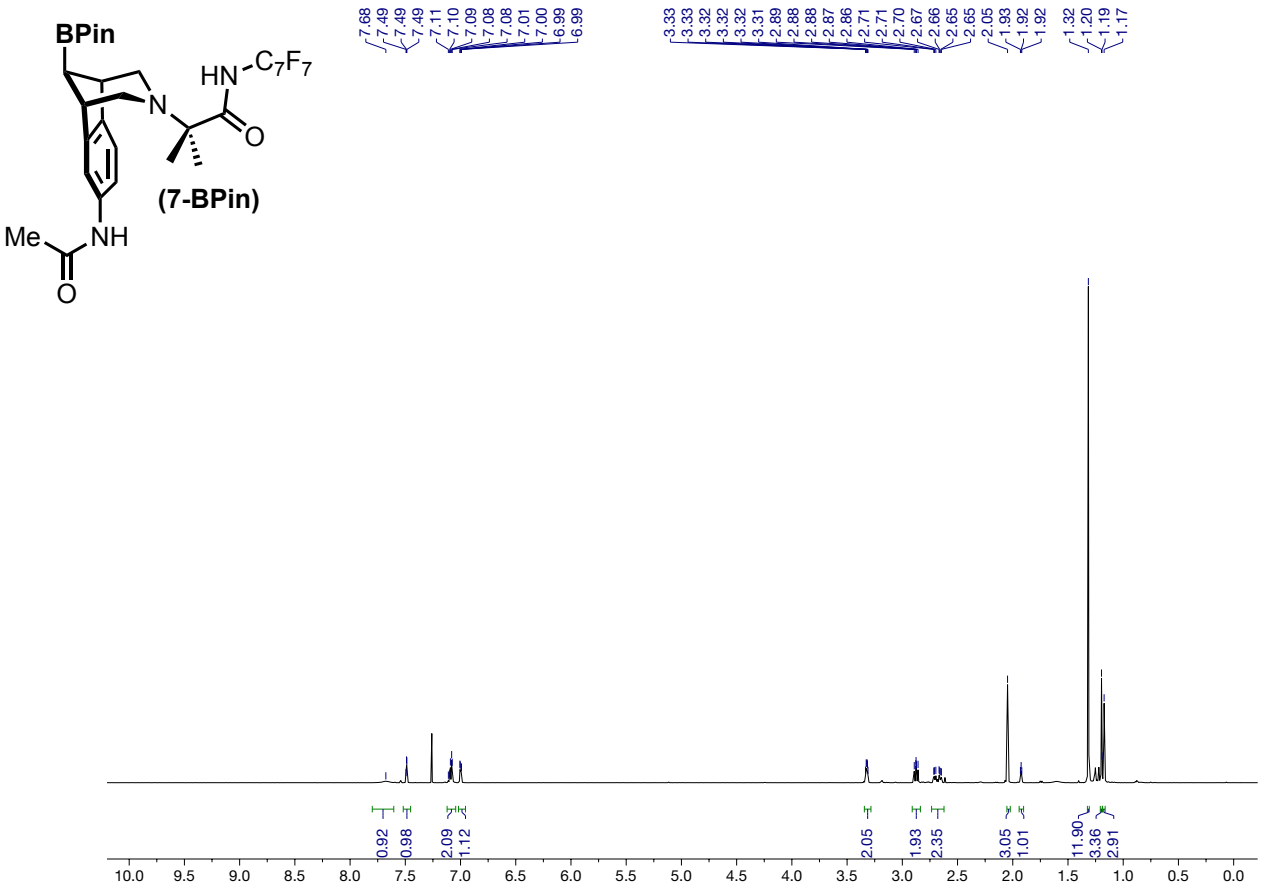
^{1}H NMR Spectrum in $CDCl_3$



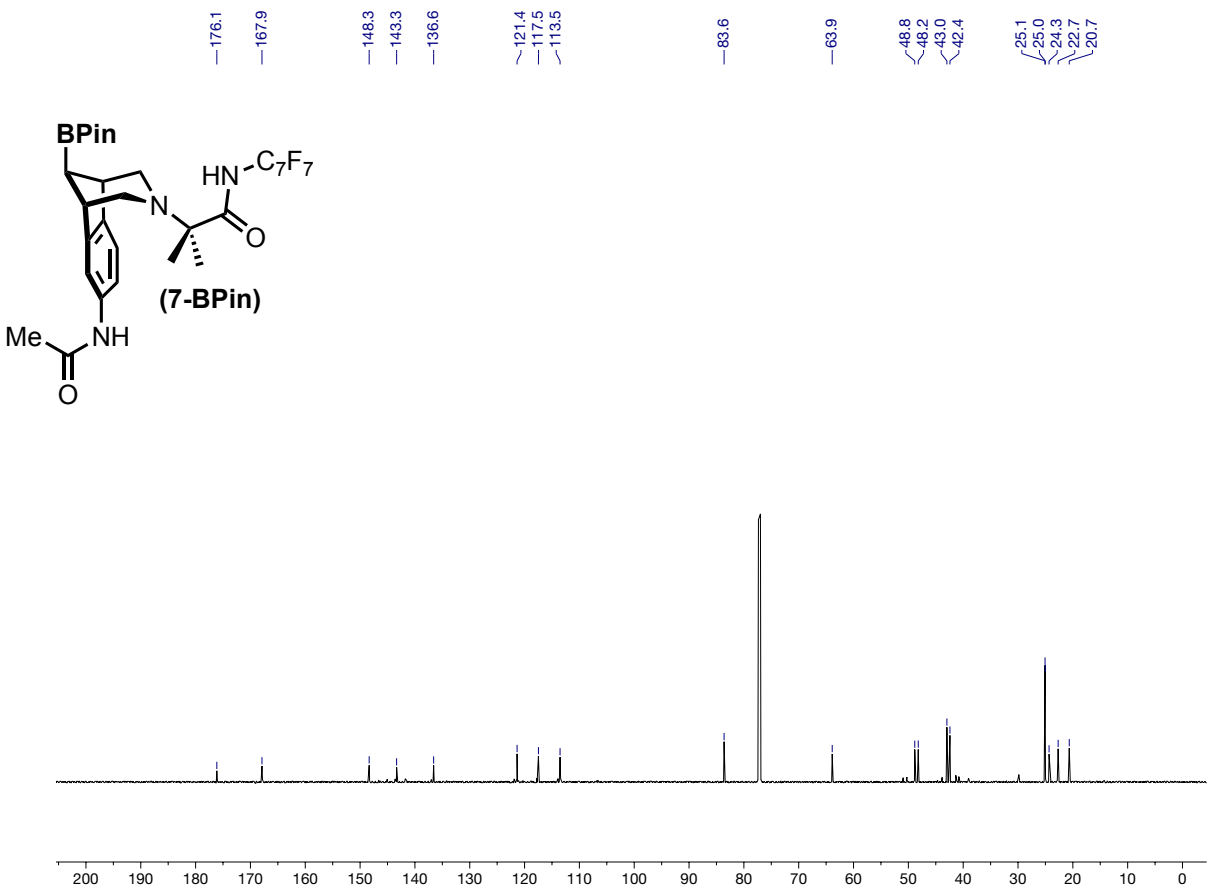
^{13}C NMR Spectrum in $CDCl_3$



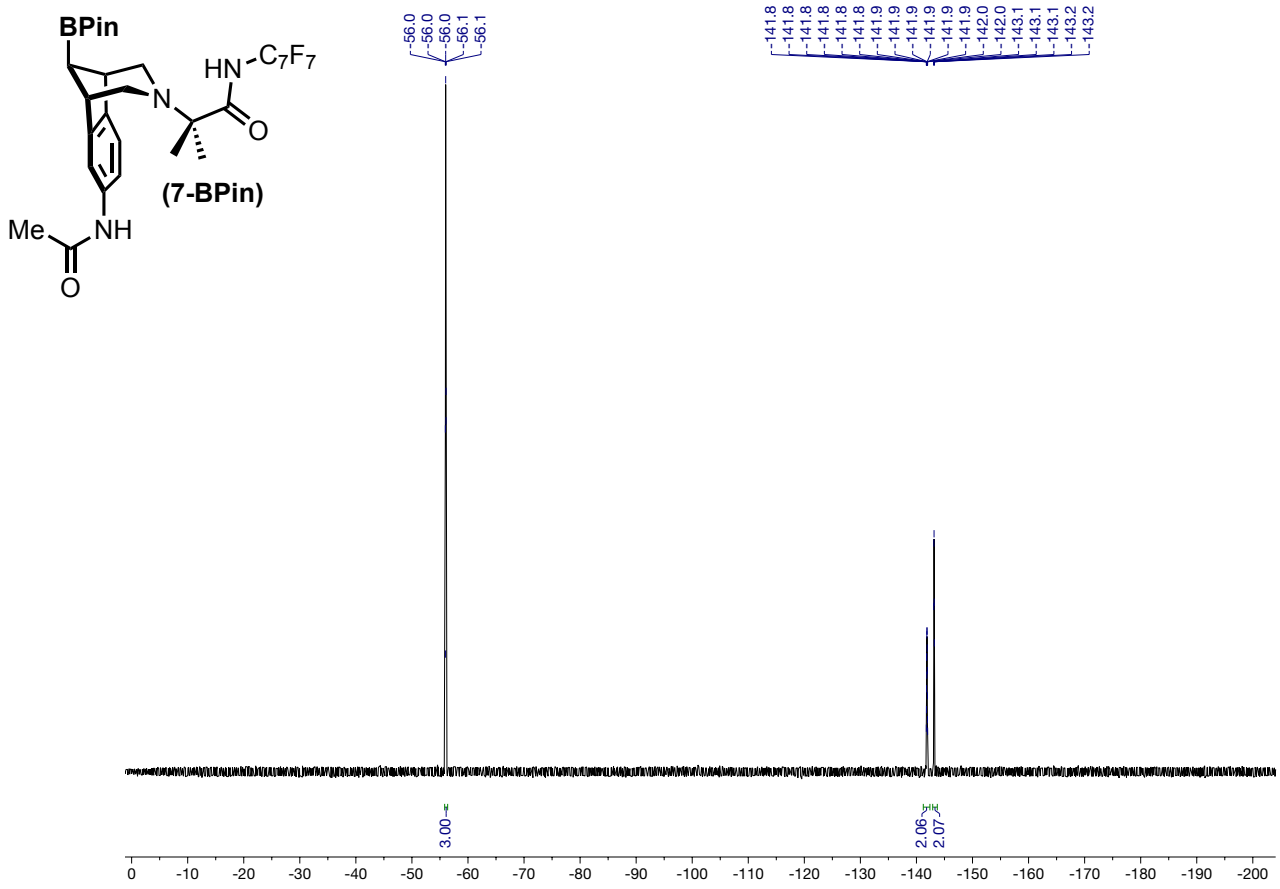
^{19}F NMR Spectrum in $CDCl_3$



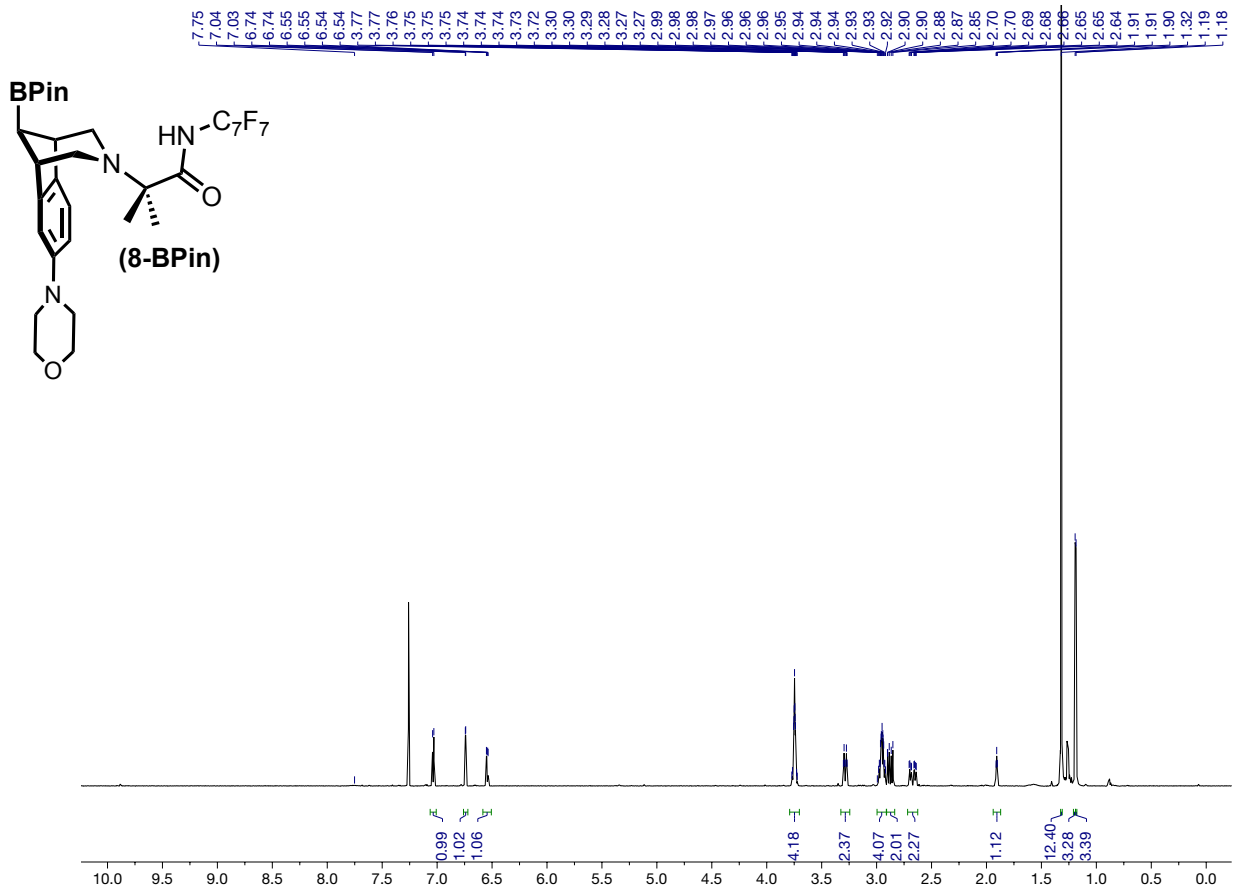
^{1}H NMR Spectrum in $CDCl_3$



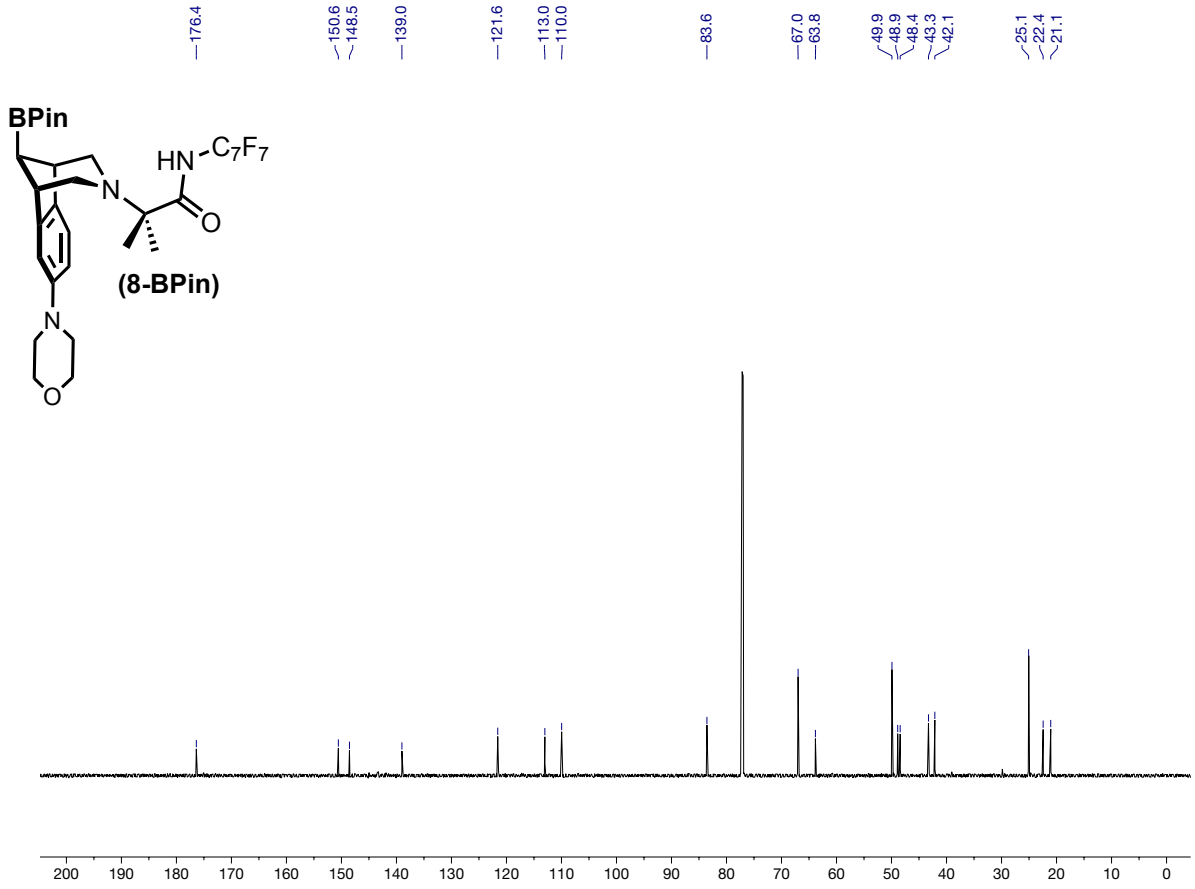
^{13}C NMR Spectrum in $CDCl_3$



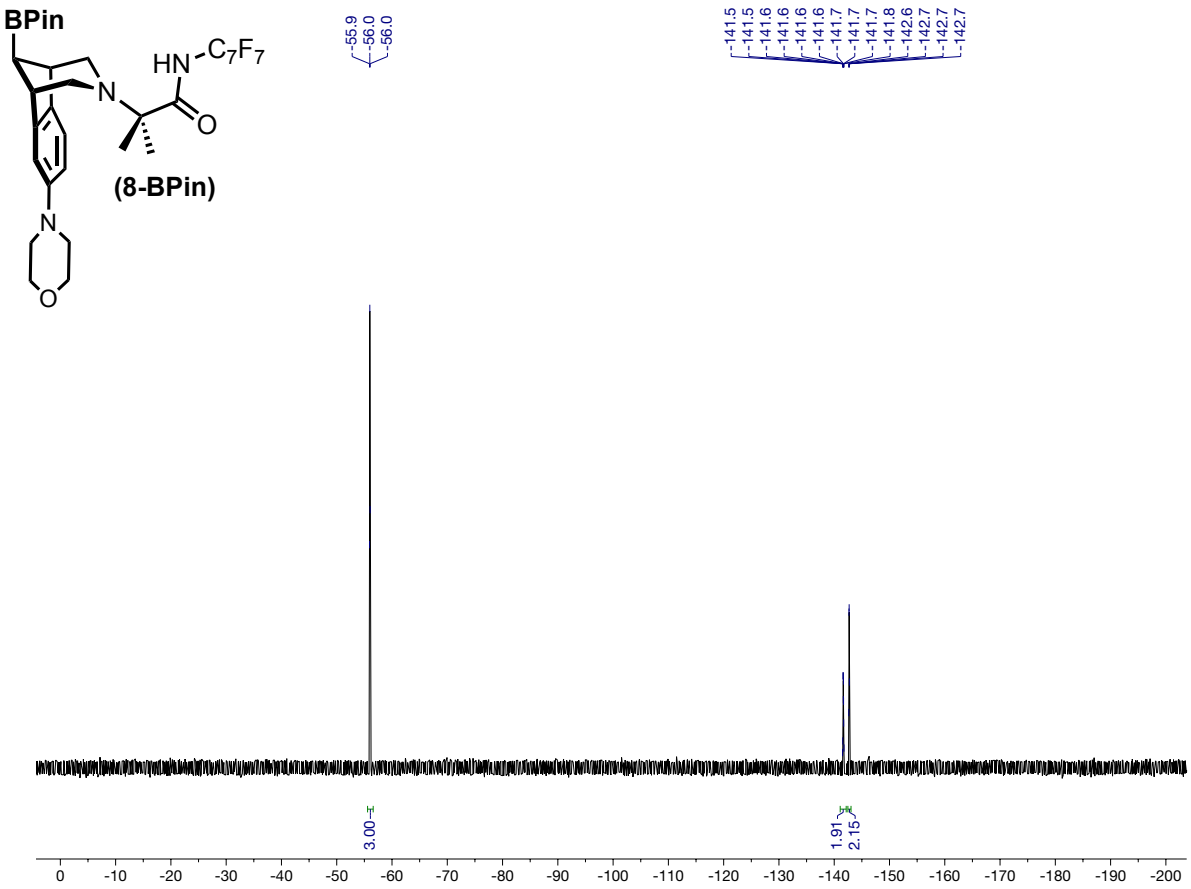
^{19}F NMR Spectrum in $CDCl_3$



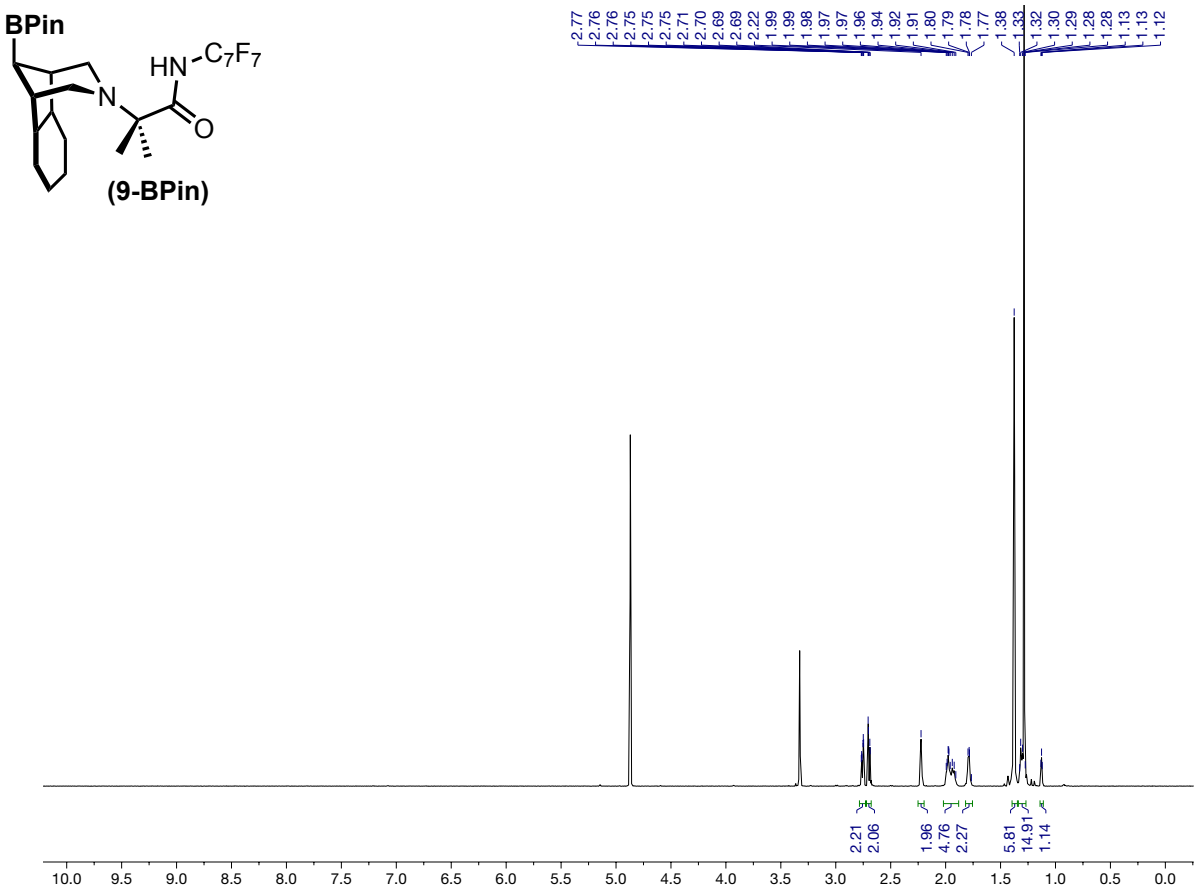
^{1}H NMR Spectrum in $CDCl_3$



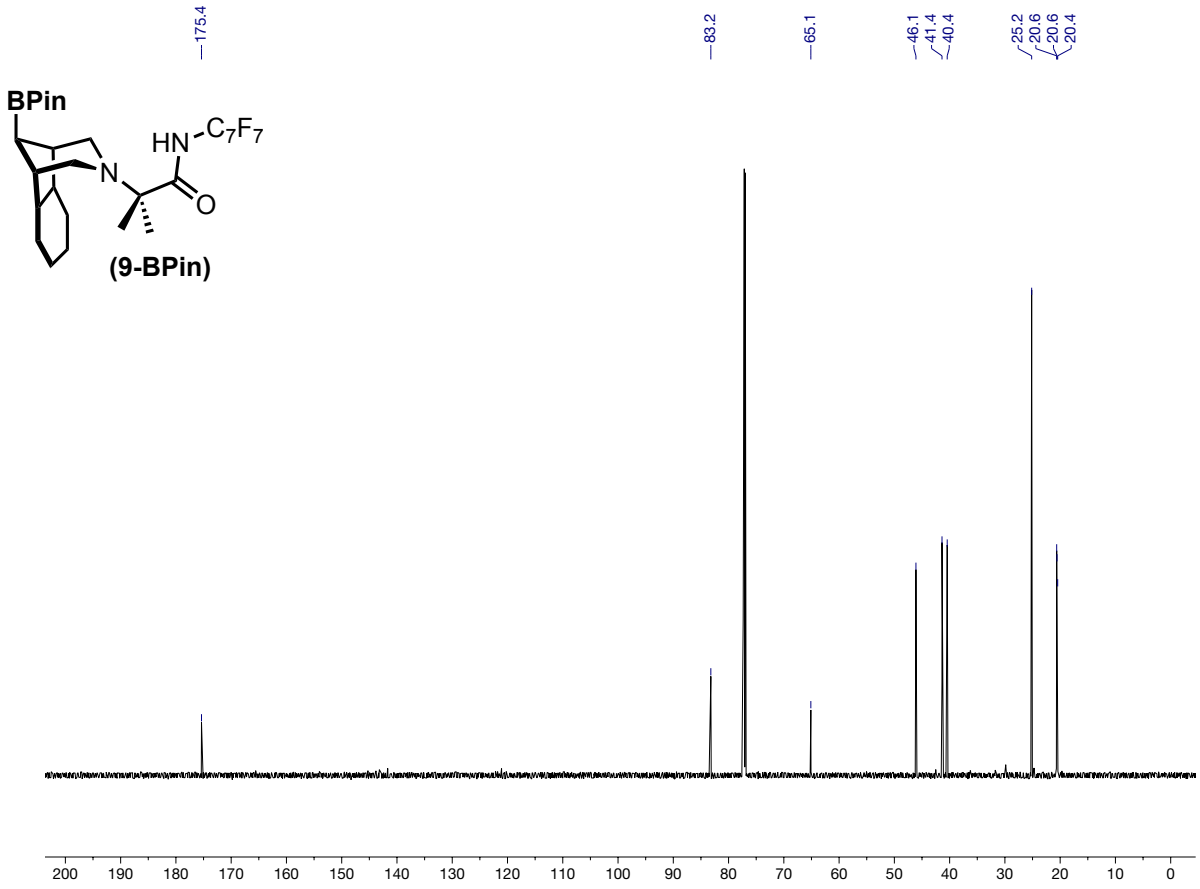
^{13}C NMR Spectrum in $CDCl_3$



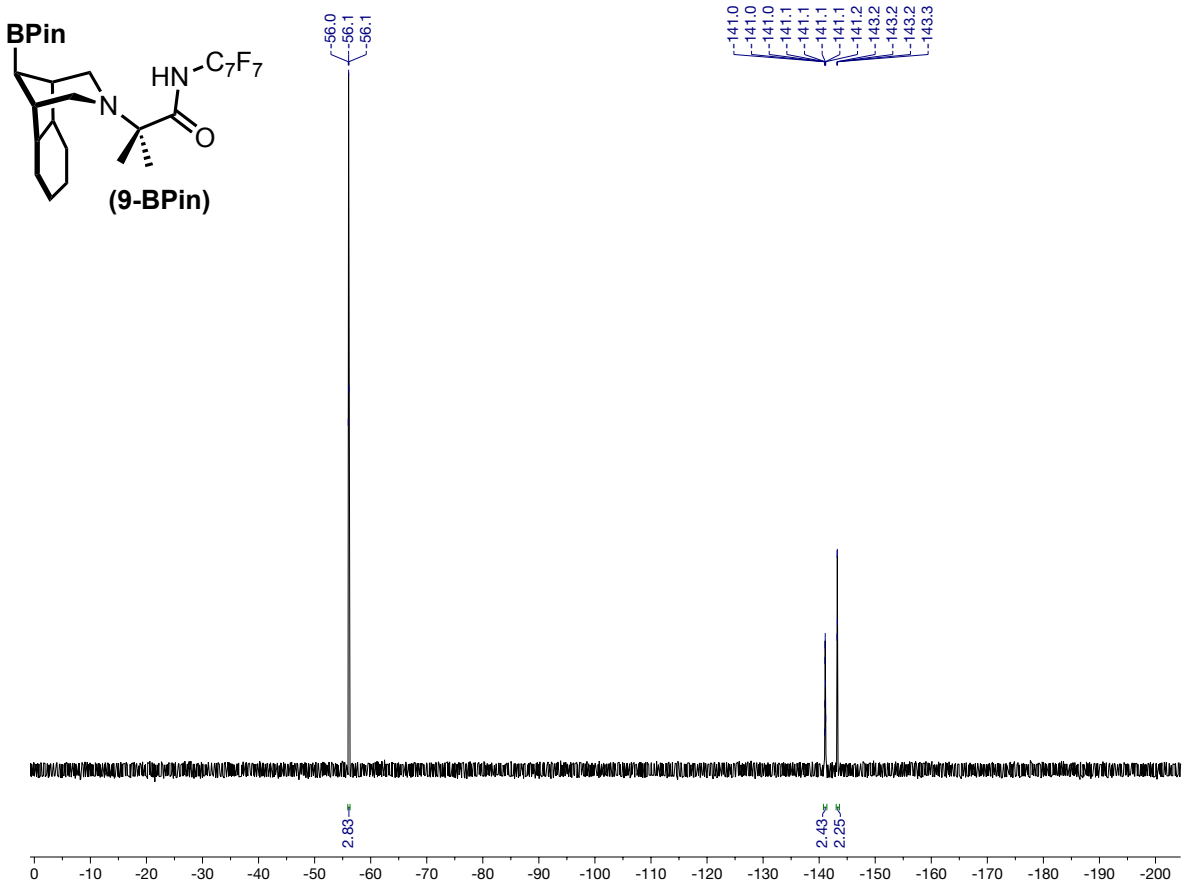
^{19}F NMR Spectrum in $CDCl_3$



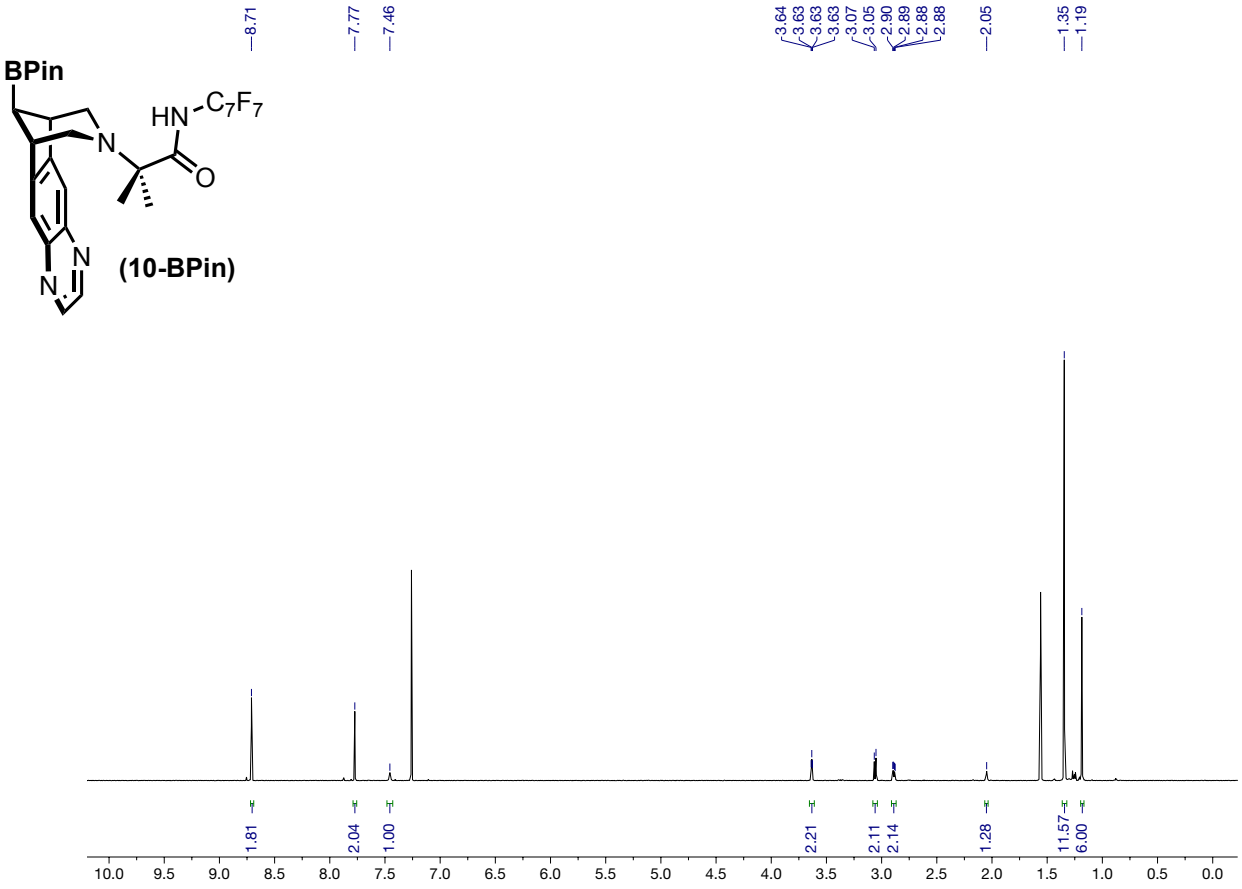
^{1}H NMR Spectrum in CD_3OD



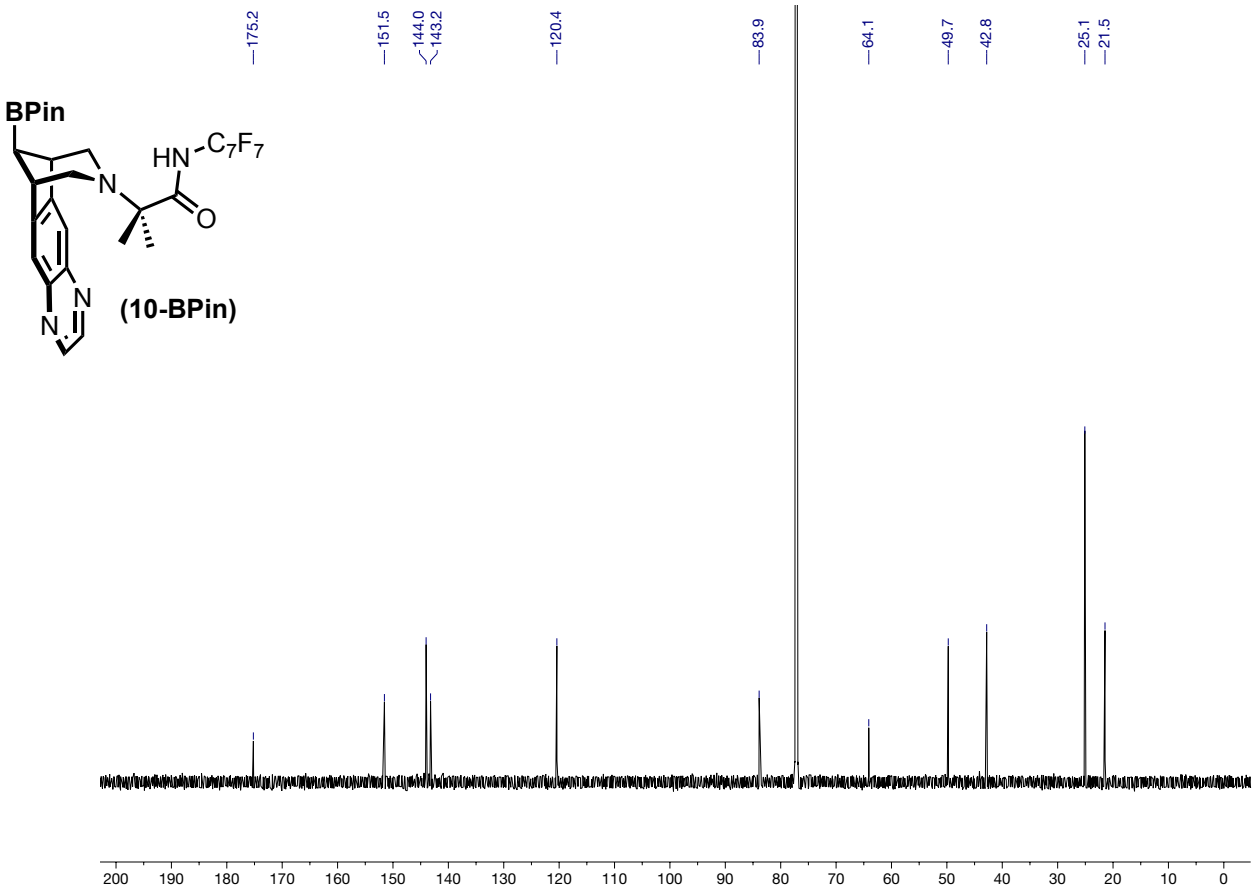
^{13}C NMR Spectrum in $CDCl_3$



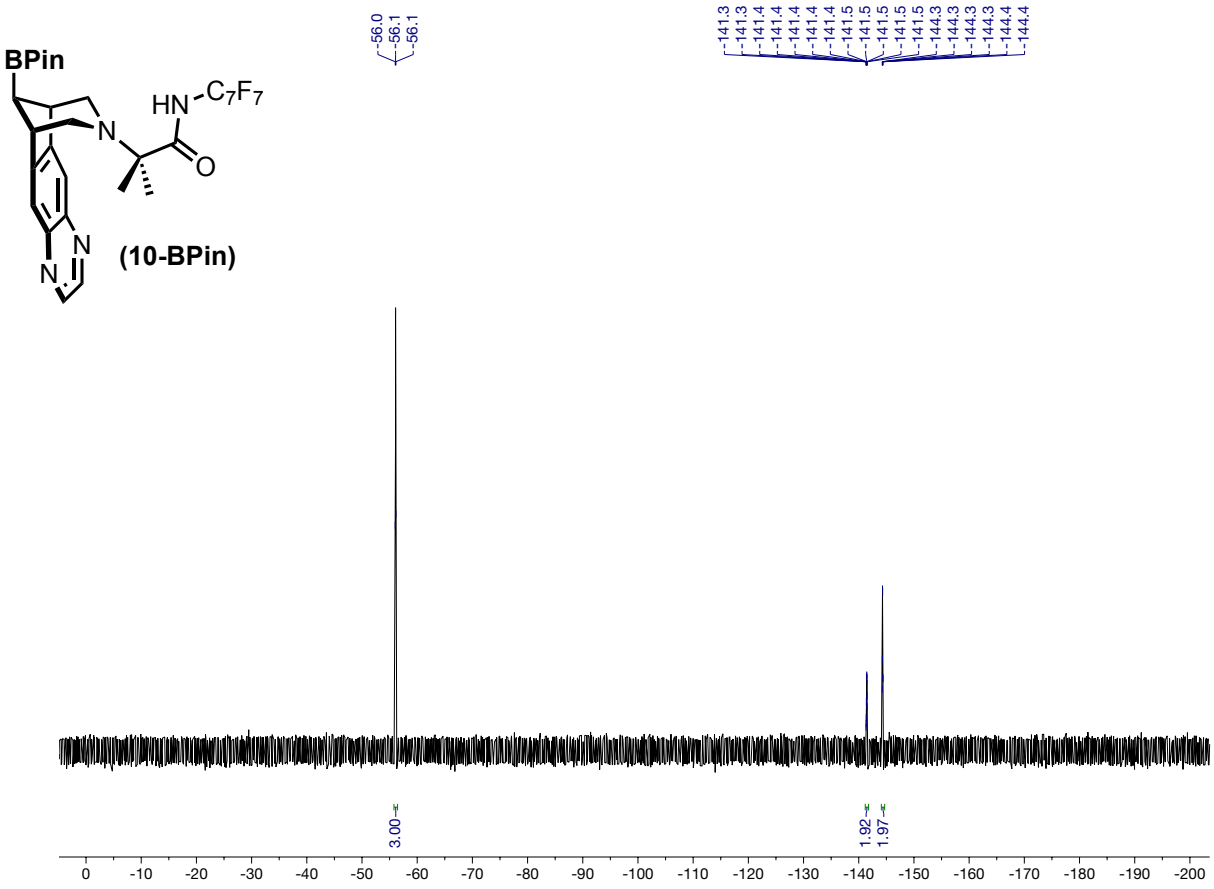
^{19}F NMR Spectrum in $CDCl_3$



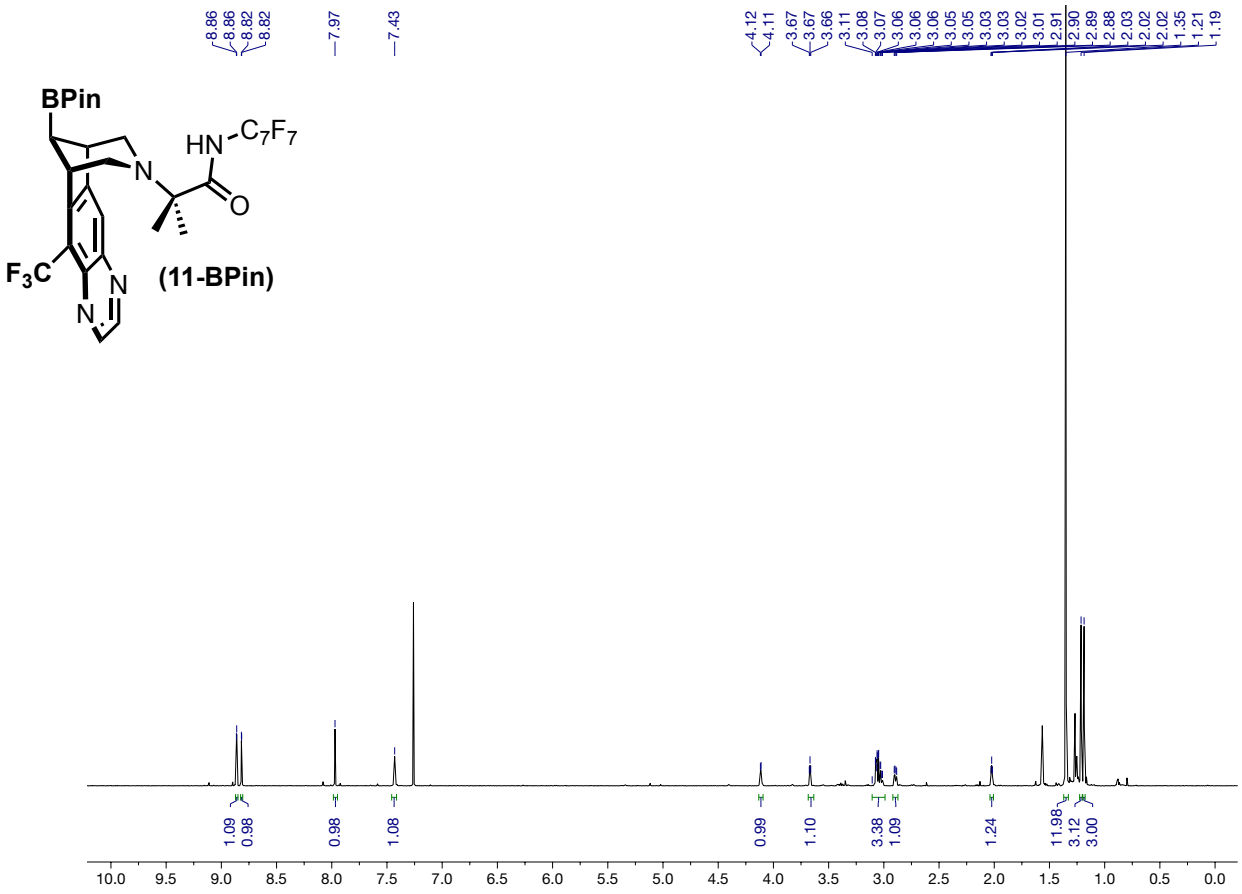
^{1}H NMR Spectrum in $CDCl_3$



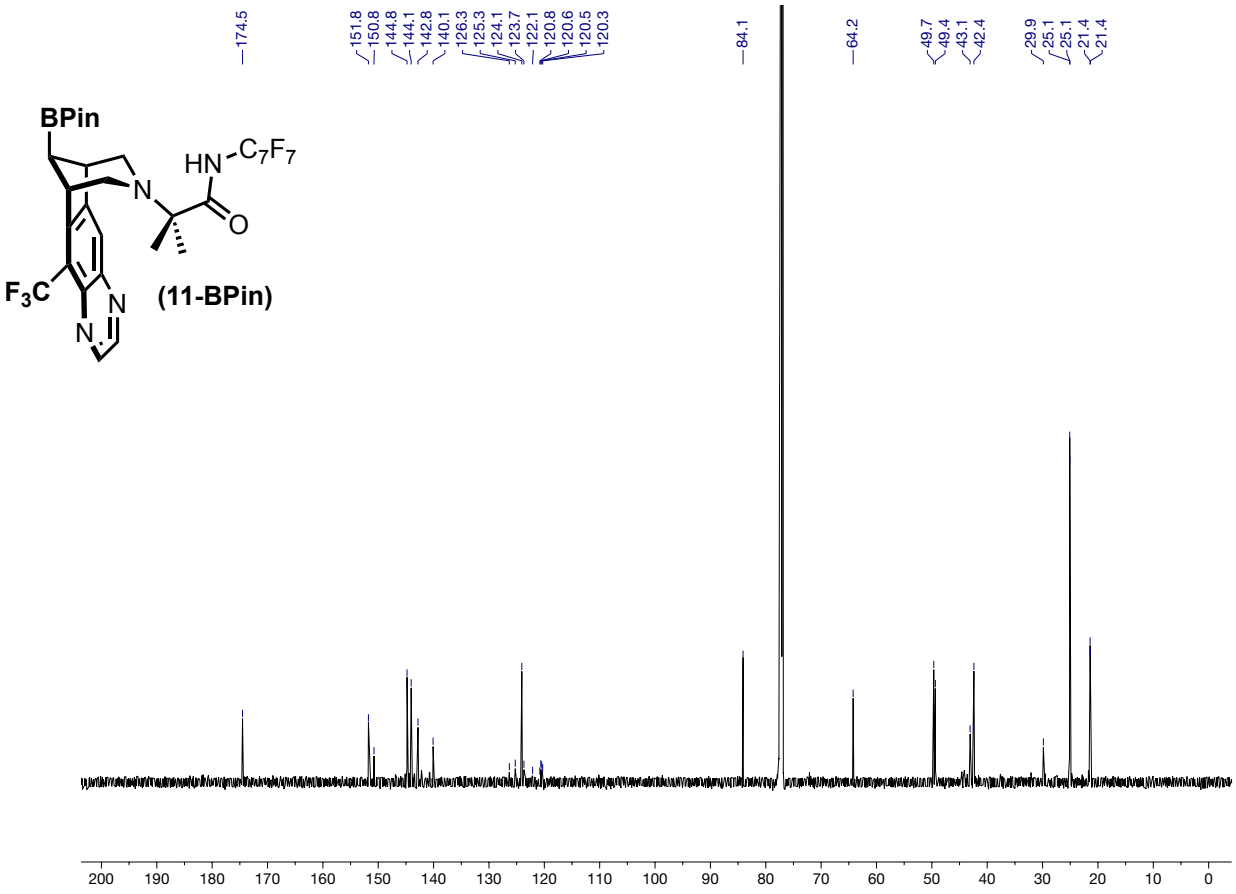
^{13}C NMR Spectrum in $CDCl_3$



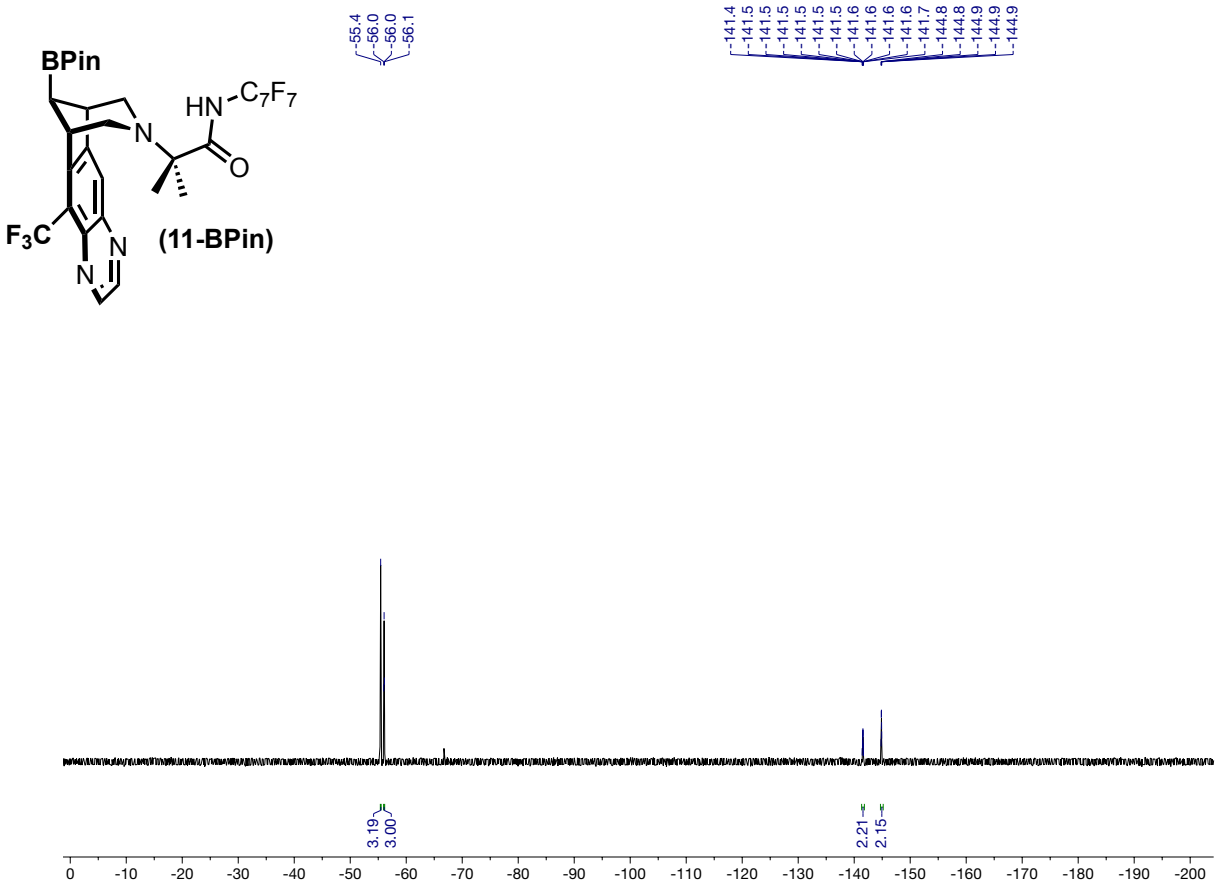
^{19}F NMR Spectrum in $CDCl_3$



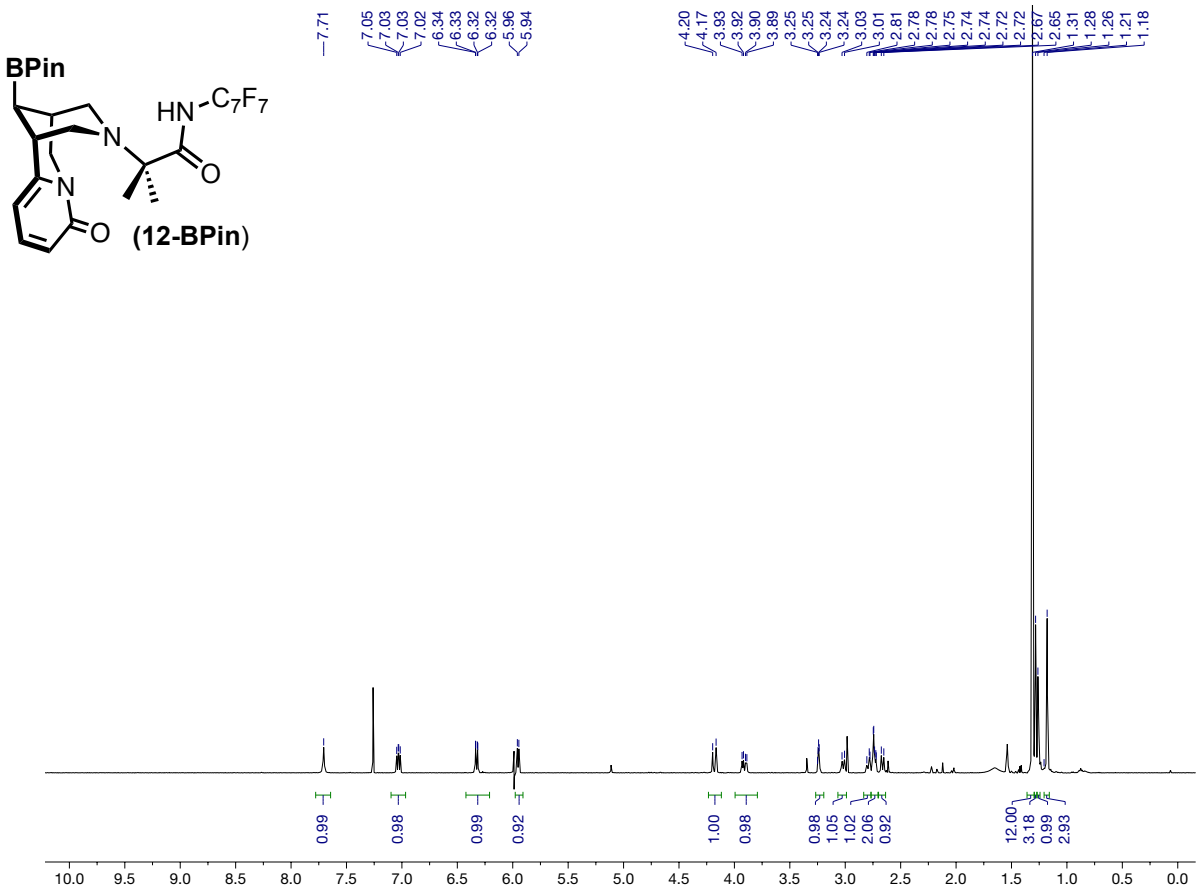
^{1}H NMR Spectrum in $CDCl_3$

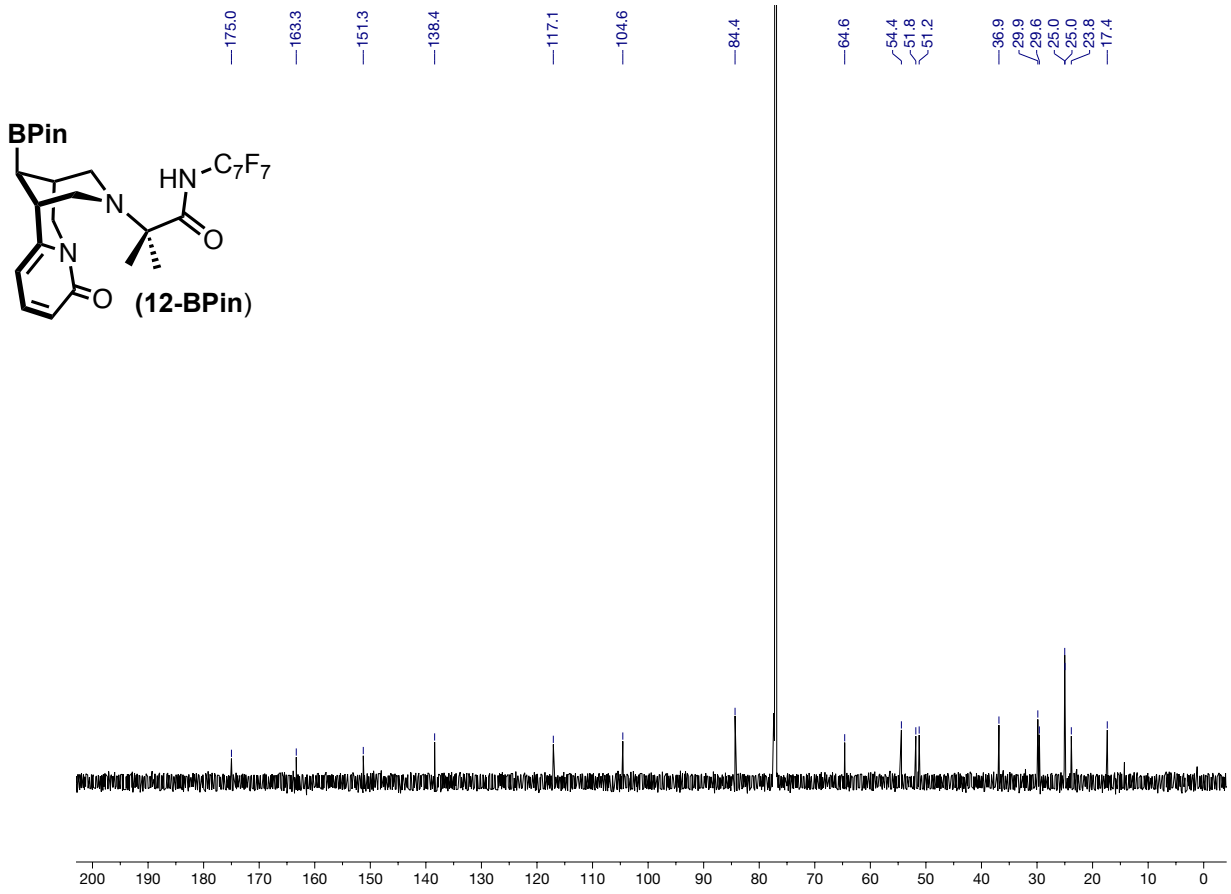


^{13}C NMR Spectrum in $CDCl_3$

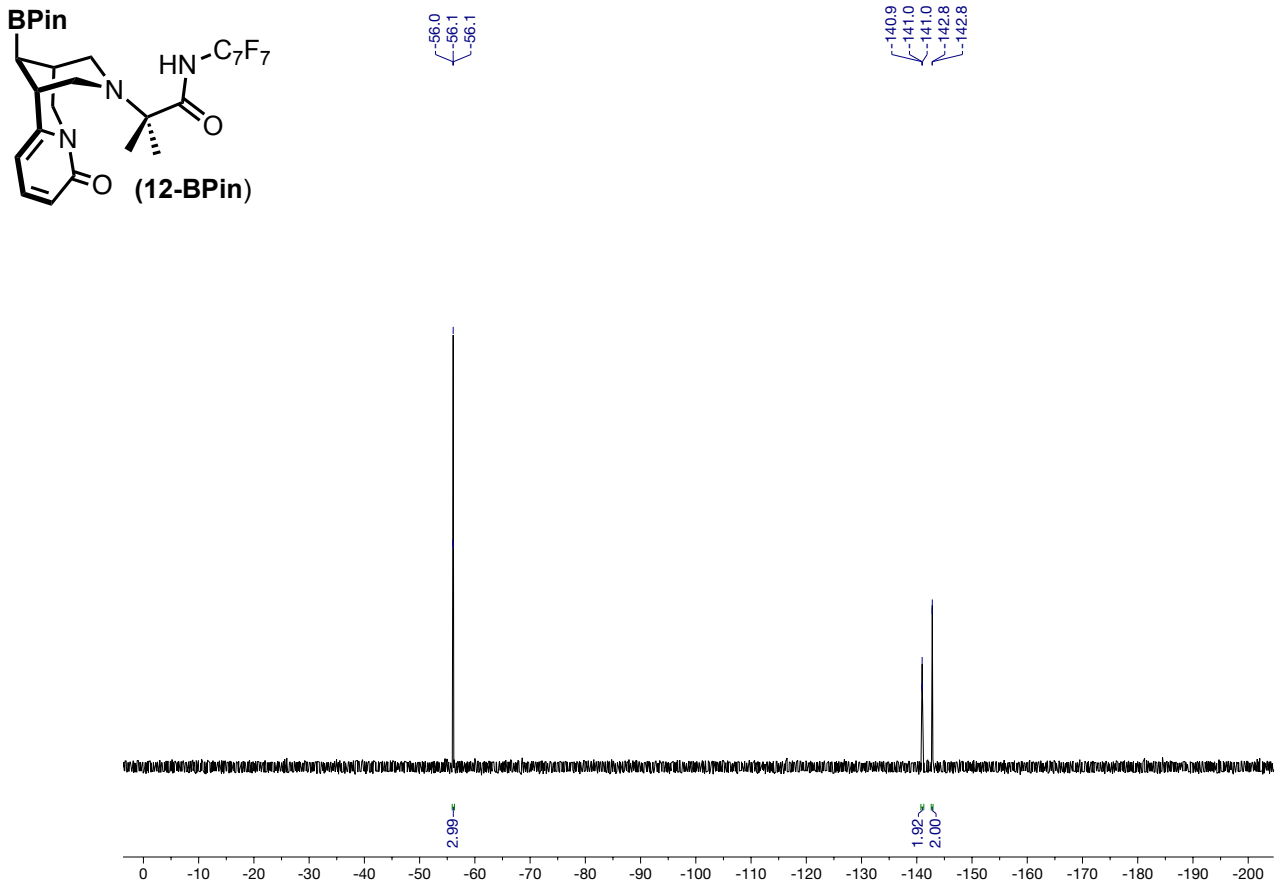


^{19}F NMR Spectrum in $CDCl_3$

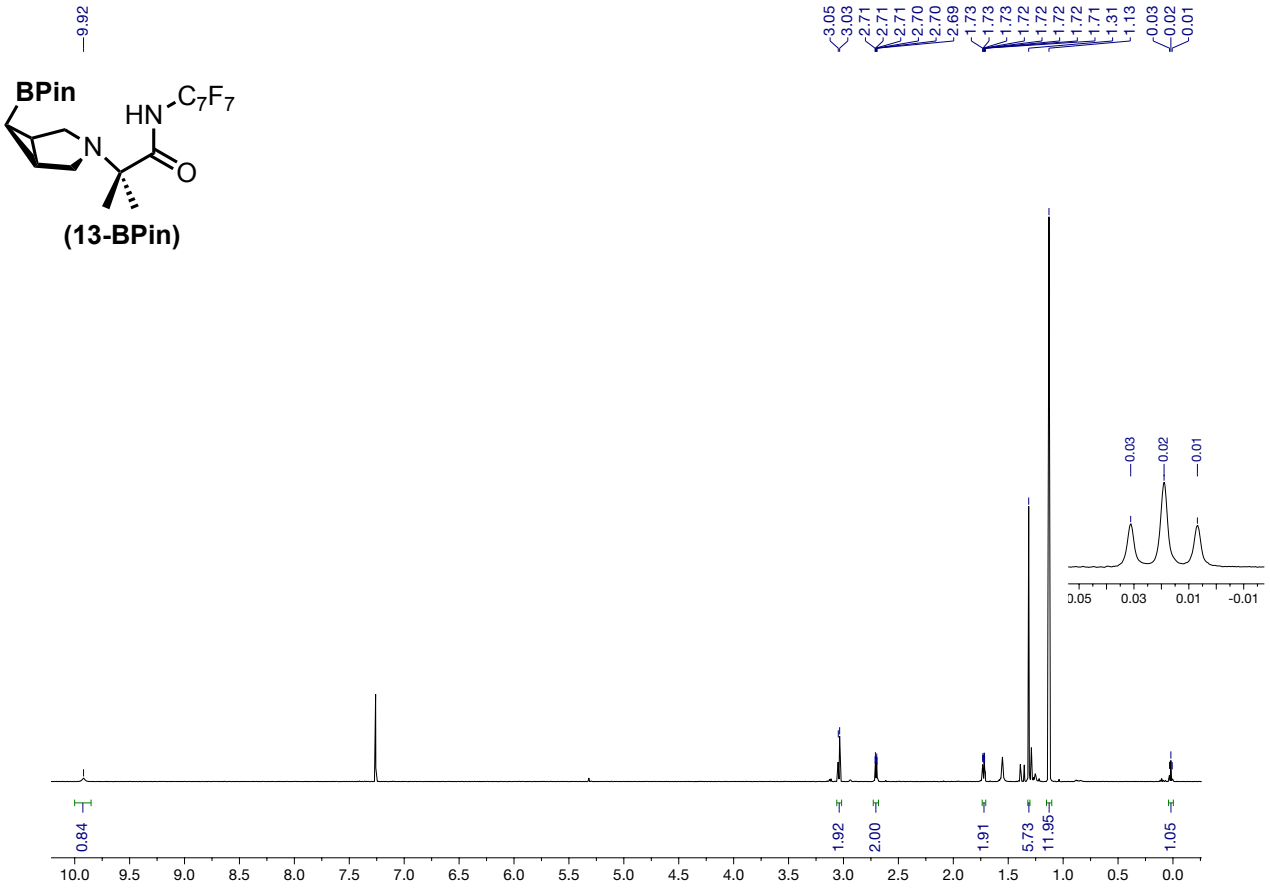

BPin
HN
C_7F_7
N
N
O
O
(12-BPin)
7.71
7.05
7.03
7.03
7.02
6.34
6.33
6.32
6.32
5.96
5.94
4.20
4.17
3.93
3.92
3.90
3.89
3.25
3.25
3.24
3.24
3.03
3.01
2.81
2.78
2.78
2.75
2.74
2.74
2.72
2.72
2.72
2.67
2.65
1.31
1.28
1.26
1.21
1.18
0.99
0.98
0.99
0.92
1.00
0.98
0.98
1.05
1.02
2.06
0.92
12.00
3.18
0.99
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



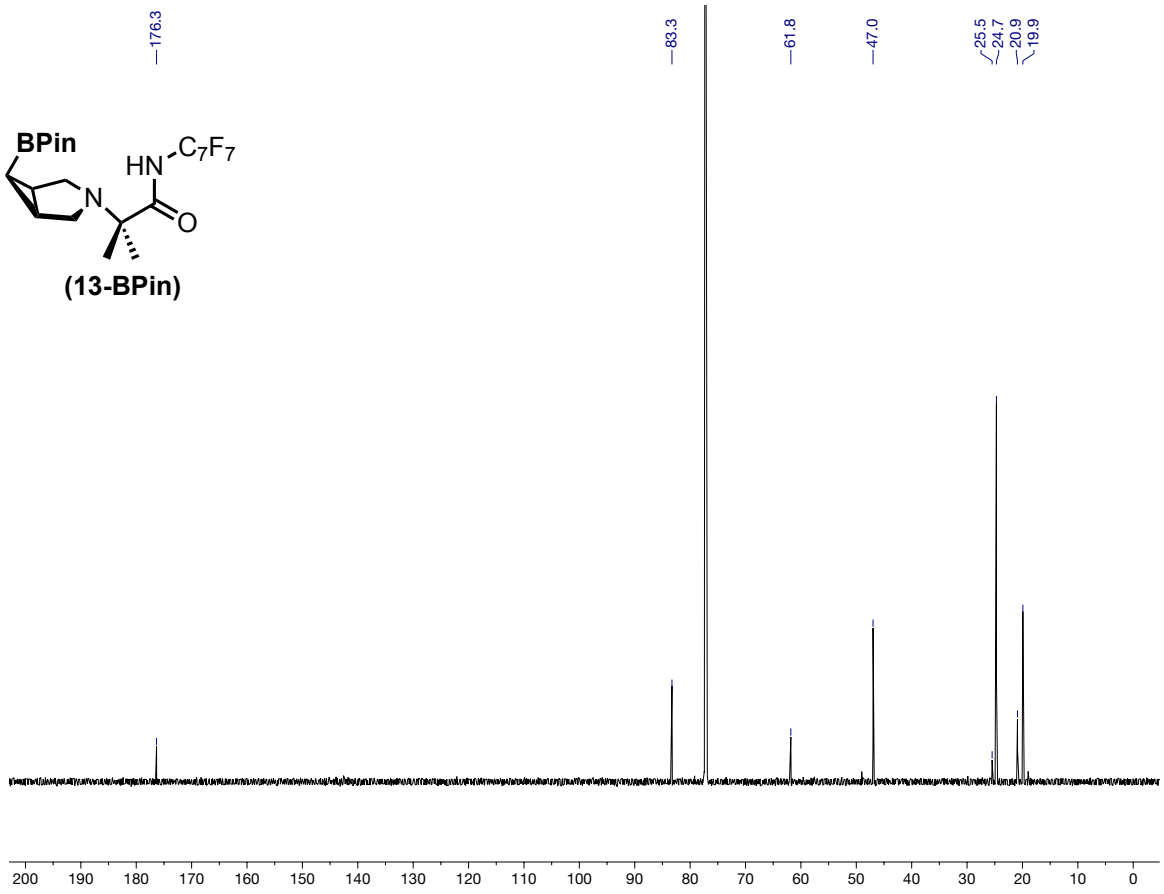
^{13}C NMR Spectrum in $CDCl_3$



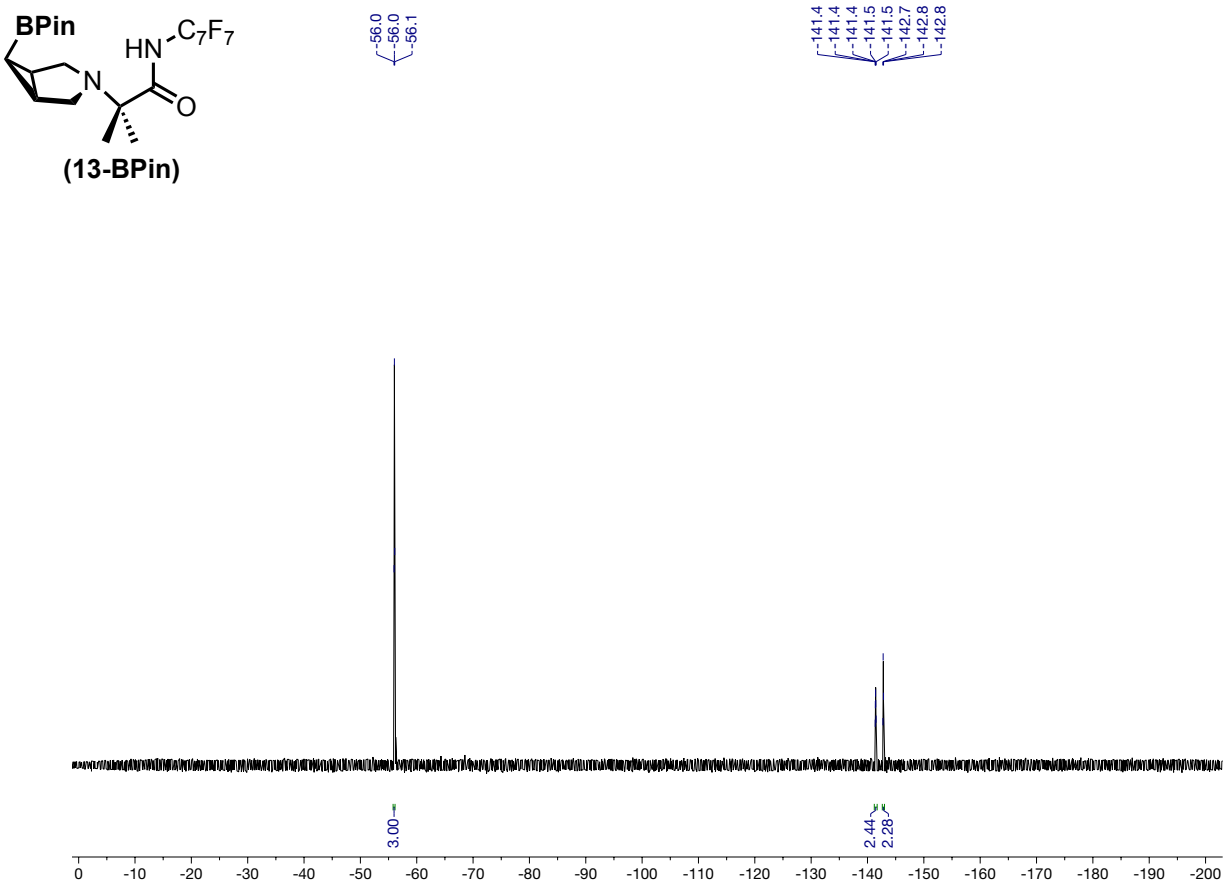
^{19}F NMR Spectrum in $CDCl_3$



^{1}H NMR Spectrum in $CDCl_3$



^{13}C NMR Spectrum in $CDCl_3$



^{19}F NMR Spectrum in $CDCl_3$