Enantioselective Catalytic Fluorinative Aza-Semi-Pinacol Rearrangement

Fedor Romanov-Michailidis, Marion Pupier, Céline Besnard, Thomas Bürgi, Alexandre Alexakis*

**Département de Chimie Organique, Université de Genève, 30, quai Ernest Ansermet CH-1211 Genève 4, Switzerland*

SUPPORTING INFORMATION

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General Methods

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker (^{1}H, 300 MHz), a Bruker (^{1}H, 400 MHz), or a Bruker (^{1}H, 500 MHz) spectrometers, using deuterated solvents $CDCl_3$, CD_2Cl_2 or C_6D_6. Chemical shifts (δ) are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Scalar coupling constants (J) are reported in hertz (Hz).

All reactions were carried out in heat-gun dried glassware equipped with magnetic stirrer bars under an inert atmosphere of dry nitrogen or argon. ^{1}H NMR, TLC or GC-MS control of the crude reaction mixtures was routinely performed to ensure complete conversions of the starting material. 3 Å and 4 Å molecular sieves were powdered and heated at 260 °C during overnight prior to use. 1,2-Dichloroethane, 1-chlorobenzene and chloroform were distilled over P_2O_5 and stored over activated 4 Å molecular sieves. MeOH and EtOH were distilled over CaH_2 under argon, and stored over activated 4 Å molecular sieves. Acrylonitrile, 1-fluorobenzene and hexafluorobenzene were distilled over P_2O_5 and stored over activated 4 Å molecular sieves. Benzene and 1,4-dioxane were distilled over Na/benzophenone under argon, and stored over activated 4 Å molecular sieves. Toluene, THF, Et_2O, CH_2Cl_2 and CH_3CN were dried by passage through a column of activated alumina, under nitrogen atmosphere. KHMDS and KO*t*-Bu were sublimed under high vacuum prior to use. NaH (60% *w/w* suspension in mineral oils) was washed with anhydrous *n*-hexane prior to use.

All other chemical reagents were purchased from commercial suppliers and used as such without further purification. Toluene, THF, Et_2O, CH_2Cl_2 and CH_3CN were dried by passage through a column of activated alumina, under nitrogen atmosphere. C_6H_5F, *c*-Hex, and $^{i}Pr_2O$ were distilled over CaH_2 and stored over activated 4 Å molecular sieves. Selectfluor™, Na_2CO_3, and Na_3PO_4 were finely powdered and dried under high vacuum (10^{-2} mbar) at 80 °C for 2 h prior to use. LiCl was dried under high vacuum (10^{-2} mbar) at 140 °C for 4 h prior to use. Mg^0 was activated by heating at 200 °C under high vacuum (10^{-2} mbar) for overnight, followed by sublimation of a seed of iodine prior to use. Grignard solutions were titrated according to the method of Knochel *et al.*[1]

Electrospray-ionization high-resolution mass (ESI-HRMS) spectra were recorded on a QSTAR Pulsar (AB/MDS Sciex) apparatus. Electron-impact high-resolution mass (EI-HRMS) spectra were recorded on a DFS-Thermofischer instrument.

Chiral separations were performed on Agilent 1290 Infinity HPLC or Waters TharSFC SFC instruments. *n*-Hexane/isopropanol or CO_2/methanol eluents. Retention times are cited in minutes. X-ray data were measured using Cu radiation on a SuperNova Dual source equipped with an Atlas detector.

The preparation of enantiopure chiral phosphoric acids $\mathbf{L_1}$, $\mathbf{L_2}$, $\mathbf{L_3}$ and $\mathbf{L_4}$ was already described beforehand.[2] $[\alpha]_D$ values are given in deg.cm.g^{-1}.dm^{-1}; concentration *c* is listed in g.(100 mL)$^{-1}$.

VCD Study

IR and VCD Measurements

Enantiomerically pure β-fluoro cyclobutylimines $\mathbf{B_4}$ and *ent*-$\mathbf{B_4}$ were prepared by carrying out the fluorination/semi-pinacol reaction with enantiomeric phosphoric acids (R_a)-$\mathbf{L_3}$ and (S_a)-$\mathbf{L_3}$, respectively. The optical purity was increased from 92:8 to > 99.5:0.5 *e.r.* by crystallizing out the racemate from *n*-hexane/Et_2O/CH_2Cl_2 (the mother liquor was kept). IR and Vibrational Circular Dichroism (VCD) spectra of enantiomeric compounds $\mathbf{B_4}$ and *ent*-$\mathbf{B_4}$ were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm^{-1}) in front of the photoelastic modulator was used to enhance the signal/noise ratio. Spectra were recorded with a transmission cell equipped with CaF_2 windows and a 0.2 mm Teflon spacer. Solutions in CD_2Cl_2 at concentrations of 5.6 mg in 0.2 ml CD_2Cl_2 were measured. Both enantiomers were measured under identical conditions and subtracted to each other in order to eliminate artifacts. Samples were measured at a resolution of 4 cm^{-1} by averaging about 24'000 scans for both enantiomers. Spectra are presented without further data processing.

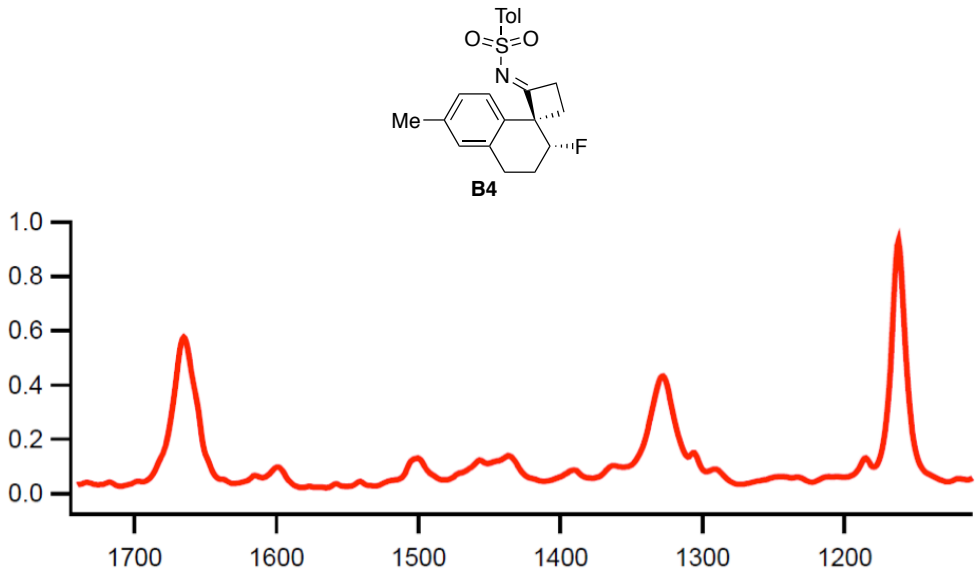

Figure 1. Experimental IR spectrum of compound $\mathbf{B_4}$.

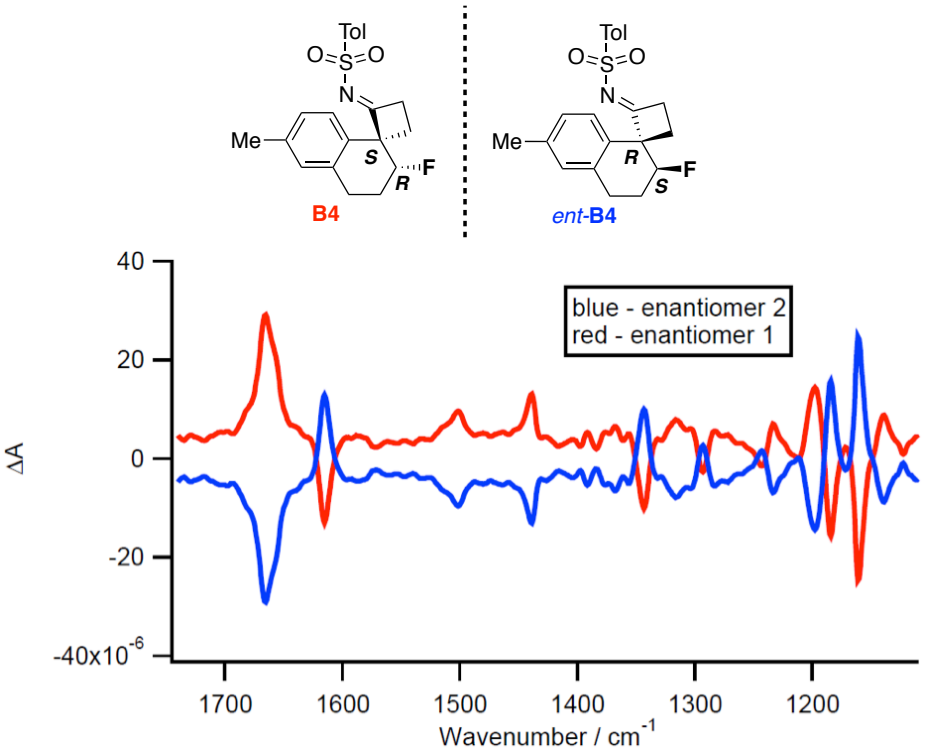

Figure 2. Experimental VCD spectra of enantiomers $\mathbf{B_4}$ (red, enantiomer 1) and *ent*-$\mathbf{B_4}$ (blue, enantiomer 2).

Calculations

Calculations of several conformers of *ent*-$\mathbf{B_4}$ were done at the DFT B3PW91 level using a 6-31G(d,p) basis set. Frequencies were scaled by 0.98. VCD spectra were constructed from calculated rotational strengths assuming Lorentzian band shape with a half-width at half maximum of 5 cm^{-1}. All calculations were performed using Gaussian 09, Revision C.01.

Five conformers were located; four of them are within about one kcal/mol, according to the calculations. For comparison with the experimental IR and VCD spectra a Boltzmann weighted average of the calculated spectra of the conformers was used.

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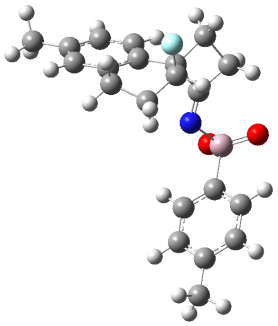

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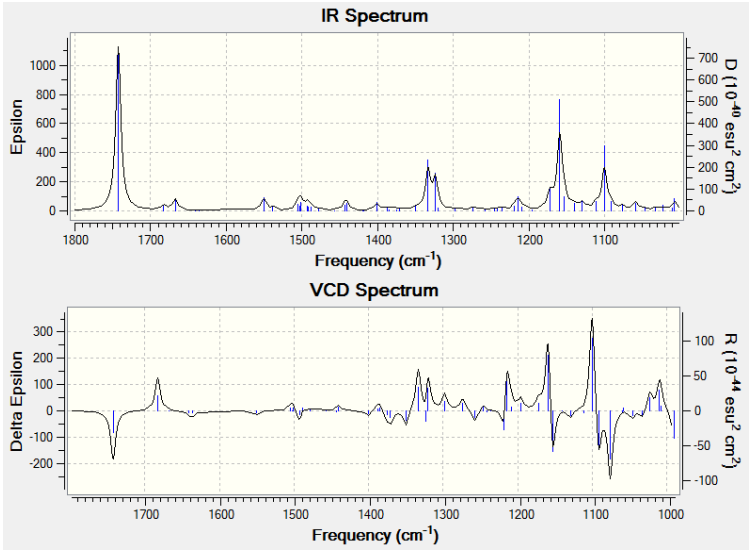

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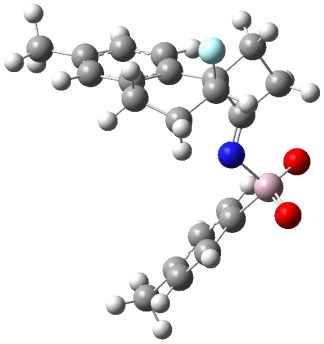

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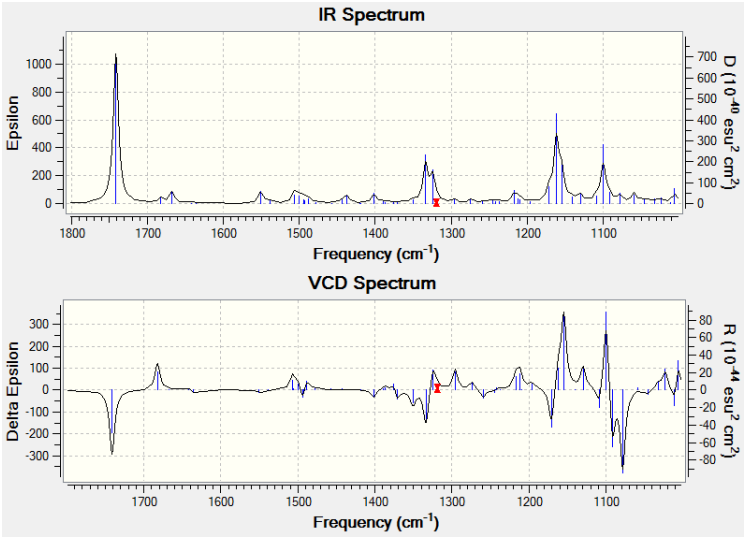

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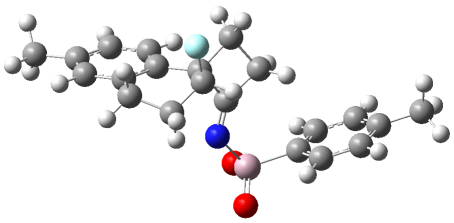

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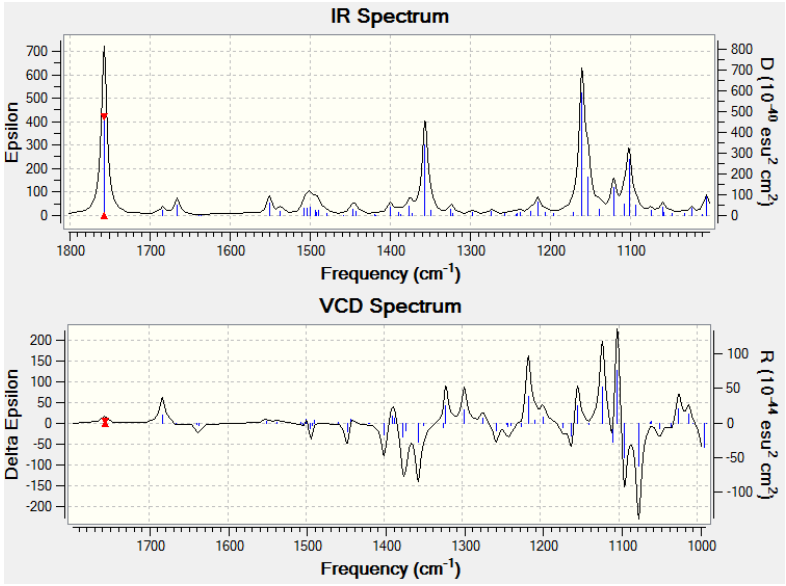

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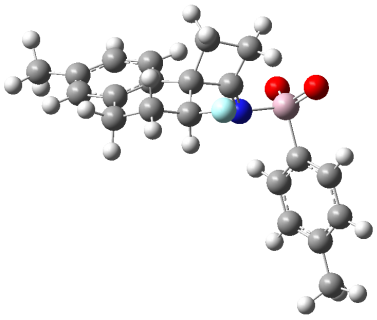

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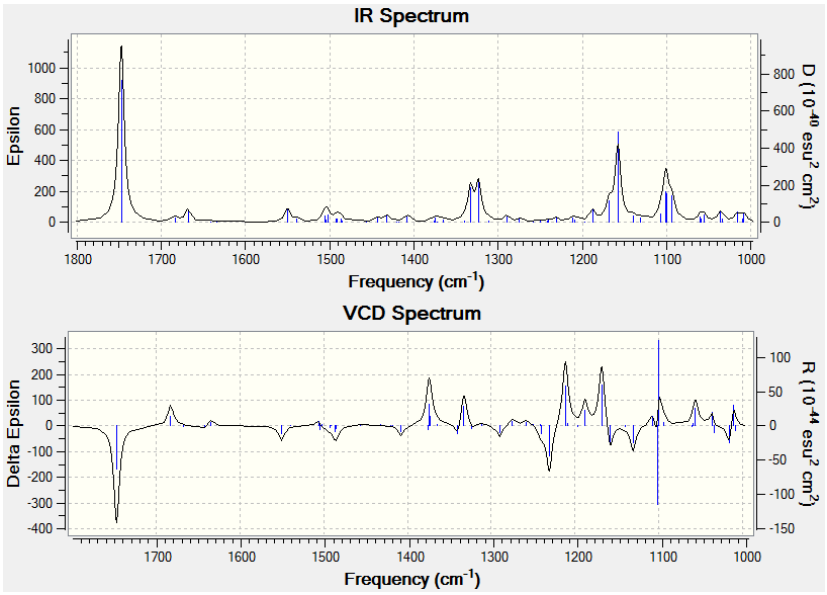

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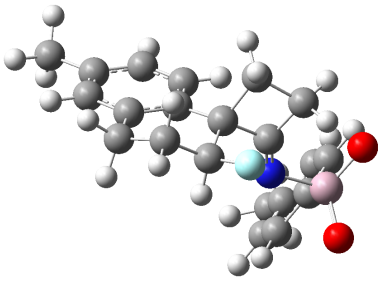

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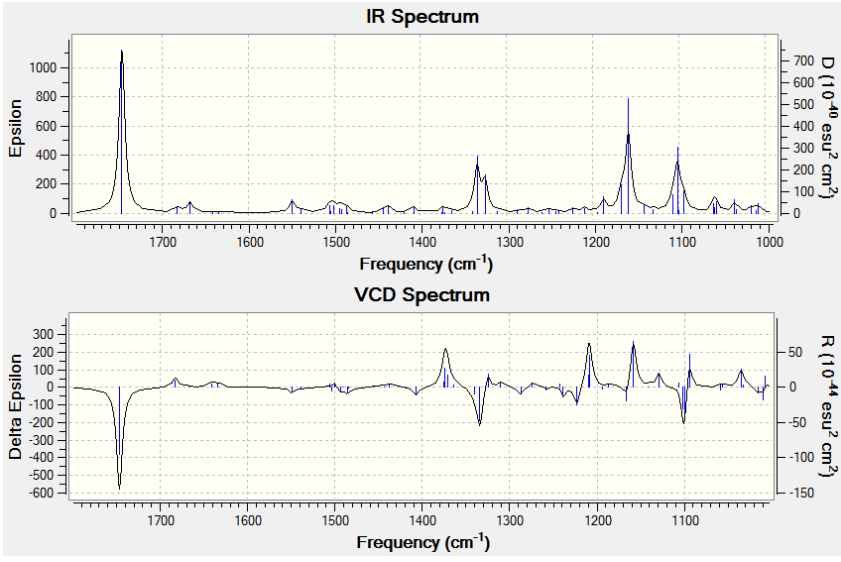


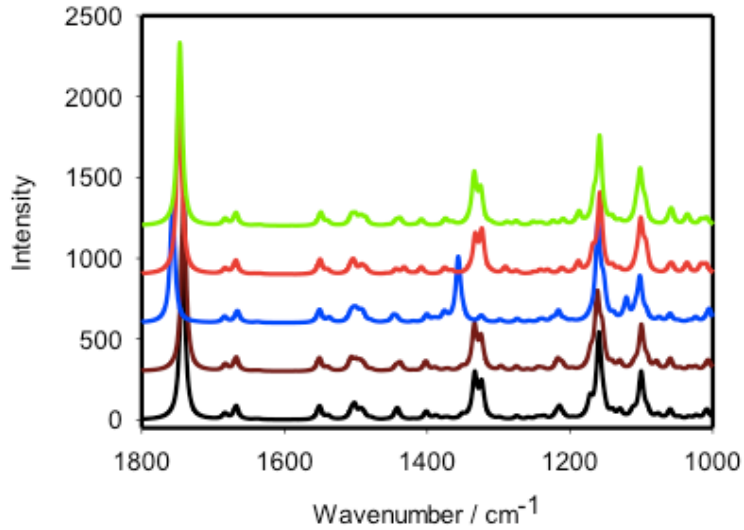


Figure 3. Calculated IR spectra for different conformers of *ent*-**B**$_4$: conformer **1**, **2**, **3**, **4**, **5** (from bottom to top). According to the Boltzmann distribution, the relative populations are: **1** (9.9%), **2** (14.8%), **3** (too high in energy), **4** (52.3%), **5** (23.0%), **6** (not stable).

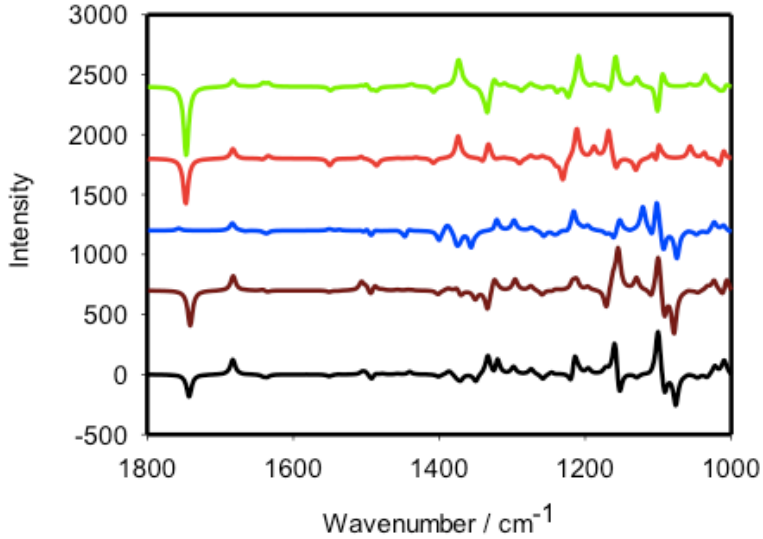


Figure 4. Calculated VCD for different conformers of *ent*-**B**$_4$: conformer **1**, **2**, **3**, **4**, **5** (from bottom to top).

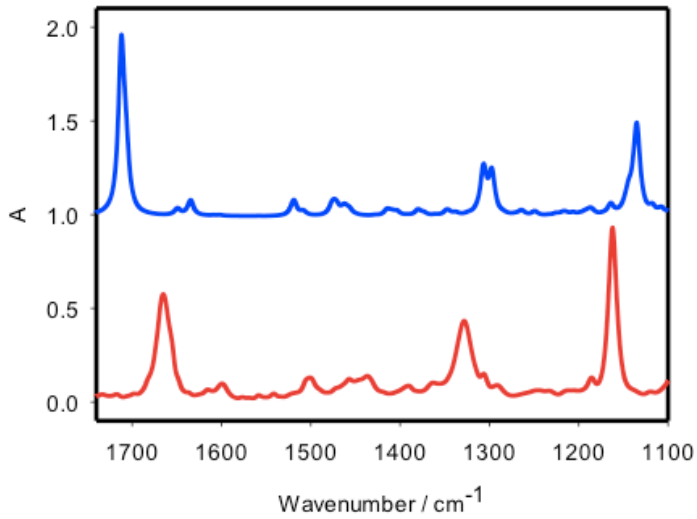


Figure 5. Comparison of Boltzmann-averaged IR spectra of *ent*-**B**$_4$, experimental (bottom) and calculated (top).

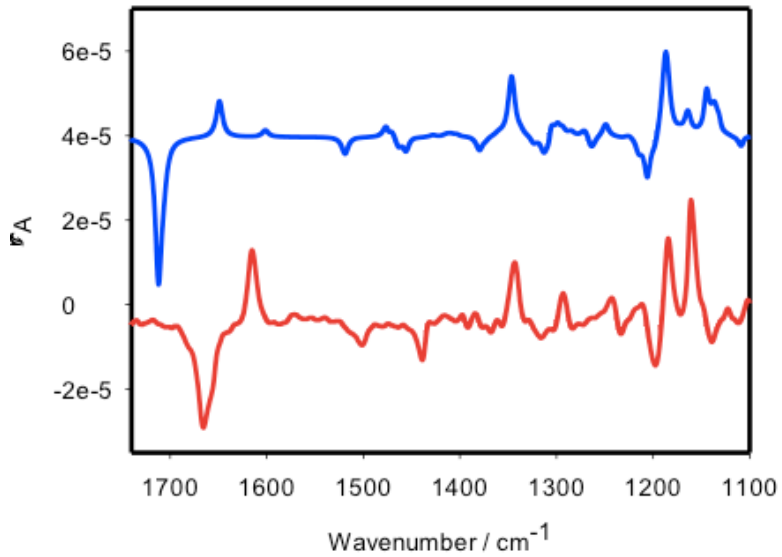
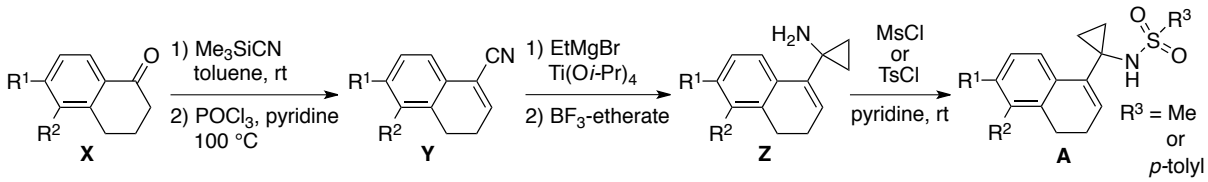


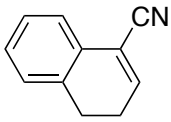
Figure 6. Comparison of Boltzmann-averaged VCD spectra of *ent*-**B**$_4$, experimental (bottom) and calculated (top).

Preparation of Protected Allylic Cyclopropylamines (A_x)



Characterization of Products

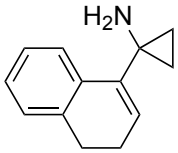
3,4-dihydronaphthalene-1-carbonitrile (Y_1)



3,4-dihydronaphthalene-1-carbonitrile
Chemical Formula: $C_{11}H_9N$
Molecular Weight: 155.20

A mixture of α-tetralone **X**$_1$ (1.0 mL, 7.46 mmol, 1.0 equiv.), Me_3SiCN (1.20 mL, 8.95 mmol, 1.2 equiv.), and ZnI_2 (60 mg, 0.19 mmol, 2.5 mol%) in anhydrous toluene (4.0 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (2.09 mL, 22.4 mmol, 3.0 equiv.) and anhydrous pyridine (12 mL) were added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 95:5). Colorless oil. Isolated yield 53% (615 mg, 3.96 mmol). **R**$_f$ (silica gel, *n*-Hex/Et_2O 9:1) 0.43. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.47 (1H, *m*, C^{ar}*H*), 7.24-7.32 (2H, *m*, C^{ar}*H*), 7.12-7.17 (1H, *m*, C^{ar}*H*), 6.89 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.86 (2H, *t*, *J* 8.1, benzylic CH_2), 2.50 (2H, *td*, J_1 8.1, J_2 4.9, allylic CH_2) ppm.

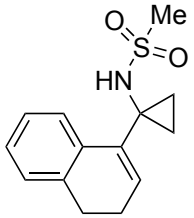
1-(3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_1)



1-(3,4-dihydronaphthalen-1-yl) cyclopropanamine
Chemical Formula: $C_{13}H_{15}N$
Molecular Weight: 185.26

To a cooled (-78 °C, dry ice/acetone bath) solution of 3,4-dihydronaphthalene-1-carbonitrile **Y_1** (615 mg, 3.96 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (1.30 mL, 4.36 mmol, 1.1 equiv.) in anhydrous Et_2O (20 mL) was added EtMgBr (3.0 M solution in Et_2O, 2.90 mL, 8.71 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca*. 48% *w/w*, 999 μL, 7.92 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Dark-orange oil. Isolated yield 52% (380 mg, 2.05 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 1:1) 0.15. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (1H, *d*, *J* 7.6, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.16-7.19 (2H, *m*, C^{ar}*H*), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

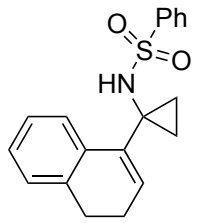
***N*-(1-(3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_1-Ms)**



N-(1-(3,4-dihydronaphthalen-1-yl) cyclopropyl)methanesulfonamide
Chemical Formula: $C_{14}H_{17}NO_2S$
Molecular Weight: 263.36

To a cooled (0 °C, ice/water bath) solution of 1-(3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_1** (650 mg, 3.51 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (20 mL) were added sequentially Et_3N (1.48 mL, 10.5 mmol, 3.0 equiv.), followed by MsCl (326 μL, 4.21 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 2 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). White crystalline solid. Isolated yield 90% (832 mg, 3.16 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48 (1H, *d*, *J* 7.5, C^{ar}*H*), 7.24-7.28 (1H, *m*, C^{ar}*H*), 7.19-7.22 (2H, *m*, C^{ar}*H*), 6.23 (1H, *t*, *J* 4.7, olefinic C=C*H*), 5.10 (1H, *brs*, sulfonamide N*H*), 2.74 (2H, *t*, *J* 8.0, benzylic CH_2), 2.74 (3H, *s*, methanesulfonyl CH_3), 2.31 (2H, *td*, J_1 8.3, J_2 4.7, allylic CH_2), 1.36-1.37 (2H, *m*, cyclopropylic CH_2), 1.06-1.09 (2H, *m*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.0 (C*q*), 135.5 (C*q*), 132.4 (C*q*), 128.61 (*C*H), 128.59 (*C*H), 127.8 (*C*H), 127.0 (*C*H), 122.9 (*C*H), 41.7 (*C*H_3), 36.5 (C*q*-N), 27.7 (*C*H_2), 22.9 (*C*H_2), 13.8 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{17}NO_2S$, expected $(M+H)^+$ *m/z* 264.1053, observed $(M+H)^+$ *m/z* 264.1055.

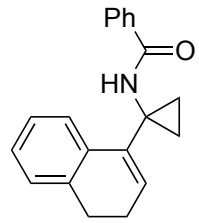
***N*-(1-(3,4-dihydronaphthalen-1-yl)cyclopropyl)benzenesulfonamide (A_1-Ps)**



N-(1-(3,4-dihydronaphthalen-1-yl) cyclopropyl)benzenesulfonamide
Chemical Formula: $C_{19}H_{19}NO_2S$
Molecular Weight: 325.42

To a cooled (0 °C, ice/water bath) solution of 1-(3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_1** (630 mg, 3.40 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (18 mL) were added sequentially Et_3N (1.43 mL, 10.2 mmol, 3.0 equiv.), followed by $PhSO_2Cl$ (522 μL, 4.08 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 2 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). White crystalline solid. Isolated yield 92% (1.02 g, 3.13 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.43. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.48 (1H, *d*, *J* 7.5, C^{ar}*H*), 7.24-7.28 (1H, *m*, C^{ar}*H*), 7.19-7.22 (2H, *m*, C^{ar}*H*), 6.23 (1H, *t*, *J* 4.7, olefinic C=C*H*), 5.10 (1H, *brs*, sulfonamide N*H*), 2.74 (2H, *t*, *J* 8.0, benzylic CH_2), 2.74 (3H, *s*, methanesulfonyl CH_3), 2.31 (2H, *td*, J_1 8.3, J_2 4.7, allylic CH_2), 1.36-1.37 (2H, *m*, cyclopropylic CH_2), 1.06-1.09 (2H, *m*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.0 (C*q*), 135.5 (C*q*), 132.4 (C*q*), 128.61 (*C*H), 128.59 (*C*H), 127.8 (*C*H), 127.0 (*C*H), 122.9 (*C*H), 41.7 (*C*H_3), 36.5 (C*q*-N), 27.7 (*C*H_2), 22.9 (*C*H_2), 13.8 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{19}H_{19}NO_2S$, expected $(M+H)^+$ *m/z* 326.1210, observed $(M+H)^+$ *m/z* 326.1212.

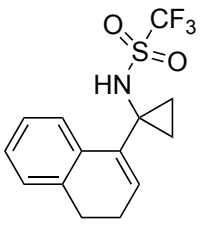
***N*-(1-(3,4-dihydronaphthalen-1-yl)cyclopropyl)benzamide (A_1-Bz)**



N-(1-(3,4-dihydronaphthalen-1-yl) cyclopropyl)benzamide
Chemical Formula: $C_{20}H_{19}NO$
Molecular Weight: 289.37

To a cooled (0 °C, ice/water bath) solution of 1-(3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_1** (380 mg, 2.05 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (25 mL) were added sequentially Et_3N (865 μL, 6.15 mmol, 3.0 equiv.), followed by benzoyl chloride (476 μL, 4.10 mmol, 2.0 equiv.). The resultant mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 1 h of stirring, the crude mixture was treated with saturated aqueous NaCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). White crystalline solid. Isolated yield 98% (581 mg, 2.01 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61-7.68 (3H, *m*, C^{ar}*H*), 7.43 (1H, *t*, *J* 7.8, C^{ar}*H*), 7.34 (2H, *t*, *J* 7.2, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.14-7.18 (2H, *m*, C^{ar}*H*), 6.66 (1H, *brs*, amide N*H*), 6.44 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.74 (2H, *t*, *J* 7.9, benzylic CH_2), 2.28-2.34 (2H, *m*, allylic CH_2), 1.26-1.30 (2H, *m*, cyclopropylic CH_2), 1.16-1.19 (2H, *m*, cyclopropylic CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.5 (amide C*q*), 137.4 (C*q*), 135.6 (C*q*), 135.1 (C*q*), 133.9 (C*q*), 131.5 (*C*H), 129.6 (*C*H), 128.6 (*C*H), 128.2 (*C*H), 127.0 (*C*H), 126.9 (*C*H), 126.5 (*C*H), 122.9 (*C*H), 34.6 (C*q*-N), 27.8 (*C*H_2), 23.1 (*C*H_2), 14.1 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{20}H_{19}NO$, expected $(M+H)^+$ *m/z* 290.1540, observed $(M+H)^+$ *m/z* 290.1541.

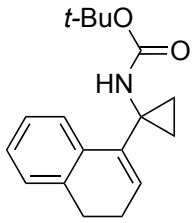
***N*-(1-(3,4-dihydronaphthalen-1-yl)cyclopropyl)-1,1,1-trifluoromethanesulfonamide (A_1-Tf)**



N-(1-(3,4-dihydronaphthalen-1-yl)cyclo propyl)-1,1,1-trifluoromethanesulfonamide
Chemical Formula: $C_{14}H_{14}F_3NO_2S$
Molecular Weight: 317.33

To a cooled (-78 °C, dry ice/acetone bath) solution of 1-(3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_1** (450 mg, 2.43 mmol, 1.0 equiv.) and Et_3N (1.02 mL, 7.29 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (15 mL) was added Tf_2O (411 µL, 2.43 mmol, 1.0 equiv.). The resultant solution was stirred at -78 °C for 1 h, and then slowly brought to ambient temperature during overnight. The reaction mixture was hydrolysed with 10% (*w/w*) aqueous HCl and extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/Et_2O 95:5). Yellow crystalline solid. Isolated yield 92% (709 mg, 2.24 mmol). **R_f** (silica gel, *n*-Hex/Et_2O 4:1) 0.58. **^{1}H NMR** (400 MHz, C_6D_6): δ 7.04-7.13 (2H, *m*, C^{ar}*H*), 6.96-7.01 (2H, *m*, C^{ar}*H*), 5.92 (1H, *t*, *J* 4.6, olefinic C=C*H*), 5.06 (1H, *brs*, amine N*H*), 2.45 (2H, *t*, *J* 8.1, benzylic CH_2), 1.83-1.89 (2H, *m*, allylic CH_2), 0.86-0.89 (2H, *m*, cyclopropylic CH_2), 0.66-0.70 (2H, *m*, cyclopropylic CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -76.6 (3F, *s*, CF_3) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ 137.2 (C*q*), 135.0 (C*q*), 132.6 (C*q*), 129.9 (*C*H), 128.5 (*C*H), 127.6 (*C*H), 126.7 (*C*H), 122.8 (*C*H), 119.8 (*q*, $J^{C\text{-}F}$ 320, *C*F_3), 37.6 (cyclopropylic N-C*q*), 27.5 (*C*H_2), 22.9 (*C*H_2), 14.2 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{14}F_3NO_2S$, expected $(M+H)^+$ *m/z* 318.0771, observed $(M+H)^+$ *m/z* 318.0772.

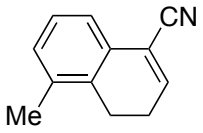
***tert*-butyl (1-(3,4-dihydronaphthalen-1-yl)cyclopropyl)carbamate (A_1-Boc)**



tert-butyl (1-(3,4-dihydronaphthalen-1-yl)cyclopropyl)carbamate
Chemical Formula: $C_{18}H_{23}NO_2$
Molecular Weight: 285.38

A mixture composed of 1-(3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_1** (433 mg, 2.34 mmol, 1.0 equiv.), Boc_2O (751 µL, 3.51 mmol, 1.5 equiv.), Et_3N (658 µL, 4.68 mmol, 2.0 equiv.), and catalytic DMAP (15 mg, 0.12 mmol, 5 mol%) in anhydrous CH_2Cl_2 (15 mL) was stirred at ambient temperature for 16 h. Upon completion, the reaction mixture was hydrolysed with 10% (*w/w*) aqueous HCl and extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 9:1). Colorless waxy solid. Isolated yield 71% (474 mg, 1.66 mmol). **R_f** (silica gel, *n*-Hex/Et_2O 4:1) 0.67. **^{1}H NMR** (400 MHz, C_6D_6): δ 7.68 (1H, *d*, *J* 7.5, C^{ar}*H*), 7.17-7.19 (1H, *m*, C^{ar}*H*), 7.06 (1H, *td*, J_1 7.4, J_2 1.3, C^{ar}*H*), 6.96 (1H, *d*, *J* 8.1, C^{ar}*H*), 5.65 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.44 (2H, *t*, *J* 8.0, benzylic CH_2), 1.82-1.87 (2H, *m*, allylic CH_2), 1.22 (9H, *s*, *tert*-butylic CH_3), 0.76-0.80 (2H, *m*, cyclopropylic CH_2), 0.57-0.61 (2H, *m*, cyclopropylic CH_2) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ 147.7 (carbamate C*q*), 137.0 (C*q*), 136.8 (C*q*), 132.6 (C*q*), 128.2 (*C*H), 127.9 (*C*H), 127.6 (*C*H), 127.0 (*C*H), 124.2 (*C*H), 84.6 (O-C*q*), 37.7 (cyclopropylic N-C*q*), 27.8 (*C*H_2), 27.2 (*tert*-butylic *C*H_3), 23.1 (*C*H_2), 13.5 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{18}H_{23}NO_2$, expected $(M+H)^+$ *m/z* 286.1802, observed $(M+H)^+$ *m/z* 286.1807.

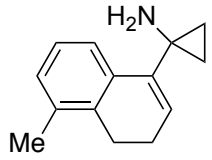
5-methyl-3,4-dihydronaphthalene-1-carbonitrile (Y_2)



5-methyl-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{12}H_{11}N$
Molecular Weight: 169.22

A mixture of 5-methyl-1-tetralone **X_2** (760 mg, 4.75 mmol, 1.0 equiv.), Me_3SiCN (765 μL, 5.70 mmol, 1.2 equiv.), and ZnI_2 (40 mg, 0.12 mmol, 2.5 mol%) in anhydrous toluene (3.0 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (1.33 mL, 14.3 mmol, 3.0 equiv.) and anhydrous pyridine (8.0 mL) were slowly added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 95:5). Light-orange crystalline solid. Isolated yield 75% (605 mg, 3.58 mmol). **R_f** (silica gel, *n*-Hex/Et_2O 4:1) 0.55. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.47 (1H, *m*, C^{ar}*H*), 7.24-7.32 (2H, *m*, C^{ar}*H*), 7.12-7.17 (1H, *m*, C^{ar}*H*), 6.89 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.86 (2H, *t*, *J* 8.1, benzylic CH_2), 2.50 (2H, *td*, J_1 8.1, J_2 4.9, allylic CH_2) ppm.

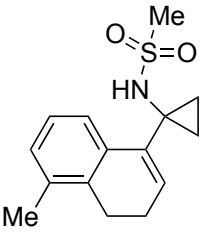
1-(5-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_2)



1-(5-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine
Chemical Formula: $C_{14}H_{17}N$
Molecular Weight: 199.29

To a cooled (-78 °C, dry ice/acetone bath) solution of 5-methyl-3,4-dihydronaphthalene-1-carbonitrile **Y_2** (600 mg, 3.55 mmol, 1.0 equiv.) and Ti(O^{i}Pr)$_4$ (1.17 mL, 3.91 mmol, 1.1 equiv.) in anhydrous Et_2O (20 mL) was added EtMgBr (3.0 M solution in Et_2O, 2.60 mL, 7.81 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca.* 48% *w/w*, 900 μL, 7.10 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Beige viscous oil. Isolated yield 44% (312 mg, 1.57 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 1:1) 0.12. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (1H, *d*, *J* 7.6, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.16-7.19 (2H, *m*, C^{ar}*H*), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

***N*-(1-(5-methyl-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_2)**

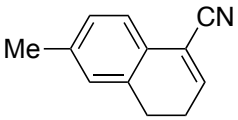


N-(1-(5-methyl-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{15}H_{19}NO_2S$
Molecular Weight: 277.38

To a cooled (0 °C, ice/water bath) solution of 1-(5-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_2** (312 mg, 1.57 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (12 mL) were added sequentially Et_3N (662 μL, 4.71 mmol, 3.0 equiv.), followed by MsCl (147 μL, 1.88 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an

additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/EtOAc 3:2) 0.33. **^{1}H NMR** (400 MHz, C_6D_6): δ 7.31 (1H, *d*, *J* 7.7, C^{ar}*H*), 7.11 (1H, *t*, *J* 7.6, C^{ar}*H*), 6.95 (1H, *d*, *J* 7.5, C^{ar}*H*), 5.98 (1H, *t*, *J* 4.6, olefinic C=C*H*), 5.41 (1H, *brs*, sulfonamide N*H*), 2.33 (2H, *t*, *J* 8.2, benzylic CH_2), 2.33 (3H, *s*, methanesulfonyl CH_3), 2.04 (3H, *s*, CH_3), 1.88 (2H, *td*, J_1 8.4, J_2 4.6, allylic CH_2), 1.21 (2H, *brs*, cyclopropylic CH_2), 0.80 (2H, *brs*, cyclopropylic CH_2) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ 136.2 (C*q*), 135.3 (C*q*), 135.0 (C*q*), 132.7 (C*q*), 129.8 (*C*H), 128.1 (olefinic *C*H), 126.5 (*C*H), 121.9 (*C*H), 41.5 (methanesulfonyl *C*H_3), 36.7 (C*q*-N), 23.5 (*C*H_3), 22.8 (*C*H_2), 19.8 (*C*H_2), 14.2 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{19}NO_2S$, expected $(M+H)^+$ *m/z* 278.1210, observed $(M+H)^+$ *m/z* 278.1215.

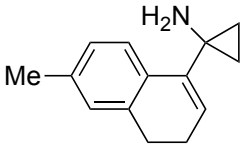
6-methyl-3,4-dihydronaphthalene-1-carbonitrile (Y_3)



6-methyl-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{12}H_{11}N$
Molecular Weight: 169.22

A mixture of 6-methyl-1-tetralone $\mathbf{X_3}$ (1.20 g, 7.49 mmol, 1.0 equiv.), Me_3SiCN (1.20 mL, 8.99 mmol, 1.2 equiv.), and ZnI_2 (60 mg, 0.12 mmol, 2.5 mol%) in anhydrous toluene (5.0 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (2.10 mL, 22.5 mmol, 3.0 equiv.) and anhydrous pyridine (12 mL) were slowly added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 95:5). White crystalline solid. Isolated yield 69% (875 mg, 5.17 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/Et_2O 4:1) 0.58. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (1H, *d*, *J* 7.8, C^{ar}*H*), 7.09 (1H, *d*, *J* 7.8, C^{ar}*H*), 6.97 (1H, *s*, C^{ar}*H*), 6.82 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.81 (2H, *t*, *J* 8.2, benzylic CH_2), 2.48 (2H, *td*, J_1 8.4, J_2 4.8, allylic CH_2), 2.34 (3H, *s*, CH_3) ppm.

1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_3)

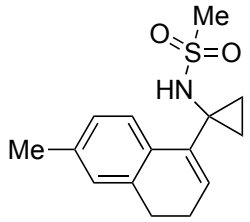


1-(6-methyl-3,4-dihydronaphthalen -1-yl)cyclopropanamine
Chemical Formula: $C_{14}H_{17}N$
Molecular Weight: 199.29

To a cooled (-78 °C, dry ice/acetone bath) solution of 6-methyl-3,4-dihydronaphthalene-1-carbonitrile $\mathbf{Y_3}$ (800 mg, 4.73 mmol, 1.0 equiv.) and Ti(O^{i}Pr)$_4$ (1.56 mL, 5.20 mmol, 1.1 equiv.) in anhydrous Et_2O (24 mL) was added EtMgBr (3.0 M solution in Et_2O, 3.47 mL, 10.4 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca.* 48% *w/w*, 1.20 mL, 9.46 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Beige viscous oil. Isolated yield 44% (312 mg, 1.57 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/EtOAc 1:1) 0.12. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (1H, *d*, *J* 7.6, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.16-7.19 (2H, *m*, C^{ar}*H*), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1

8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

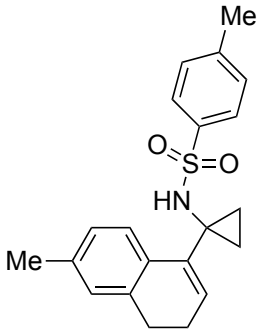
_N_-(1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_3)



N-(1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{15}H_{19}NO_2S$
Molecular Weight: 277.38

To a cooled (0 °C, ice/water bath) solution of 1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_3** (300 mg, 1.53 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (12 mL) were added sequentially Et_3N (662 µL, 4.71 mmol, 3.0 equiv.), followed by MsCl (147 µL, 1.88 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 3:2) 0.37. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.21 (1H, *d*, *J* 7.8, C^{ar}H), 6.98 (1H, *d*, *J* 7.7, C^{ar}H), 6.78 (1H, *s*, C^{ar}H), 5.88 (1H, *t*, *J* 4.6, olefinic C=C*H*), 5.09 (1H, *brs*, sulfonamide N*H*), 2.37 (2H, *t*, *J* 8.0, benzylic CH_2), 2.31 (3H, *s*, methanesulfonyl CH_3), 2.16 (3H, *s*, CH_3), 1.88 (2H, *td*, J_1 8.2, J_2 4.7, allylic CH_2), 1.15 (2H, *brs*, cyclopropylic CH_2), 0.76 (2H, *brs*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 137.1 (C*q*), 136.9 (C*q*), 135.9 (C*q*), 130.3 (C*q*), 129.3 (*C*H), 127.64 (olefinic *C*H), 127.55 (*C*H), 123.6 (*C*H), 41.4 (methanesulfonyl *C*H_3), 36.4 (C*q*-N), 27.9 (*C*H_2), 23.1 (*C*H_3), 21.2 (*C*H_2), 14.0 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{19}NO_2S$, expected $(M+H)^+$ *m/z* 278.1210, observed $(M+H)^+$ *m/z* 278.1216.

4-methyl-*N*-(1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropyl)benzenesulfonamide (A_4)

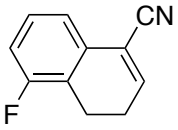


4-methyl-*N*-(1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropyl)benzenesulfonamide
Chemical Formula: $C_{21}H_{23}NO_2S$
Molecular Weight: 353.48

To a cooled (0 °C, ice/water bath) solution of 1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_3** (211 mg, 1.06 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were added sequentially Et_3N (447 µL, 3.18 mmol, 3.0 equiv.), followed by TsCl (242 mg, 1.27 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 3:2) 0.37. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.59 (2H, *d*, *J* 8.3, C^{ar}H), 7.33 (1H, *d*, *J* 7.8, C^{ar}H), 6.94 (1H, *d*, *J* 8.2, C^{ar}H), 6.64 (1H, *s*, C^{ar}H), 6.58 (2H, *d*, *J* 8.0, C^{ar}H), 6.12 (1H, *brs*, sulfonamide N*H*), 5.59 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.12 (3H, *s*, CH_3), 1.99 (2H, *t*, *J* 8.0, benzylic CH_2), 1.86 (3H, *s*, CH_3), 1.68 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.33 (2H, *brs*, cyclopropylic CH_2), 0.76 (2H, *brs*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 142.0 (C*q*), 139.8 (C*q*),

136.9 (C*q*), 136.6 (C*q*), 134.7 (C*q*), 130.3 (C*q*), 128.9 (*C*H), 128.7 (*C*H), 127.7 (olefinic *C*H), 127.4 (*C*H), 126.9 (*C*H), 123.6 (*C*H), 36.5 (C*q*-N), 27.2 (CH_2), 22.8 (CH_2), 21.2 (CH_3), 21.1 (CH_3), 13.7 (cyclopropylic CH_2) ppm. **ESI-HRMS (positif)** M = $C_{21}H_{23}NO_2S$, expected $(M+H)^+$ *m/z* 354.1523, observed $(M+H)^+$ *m/z* 354.1527.

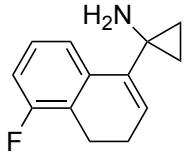
5-fluoro-3,4-dihydronaphthalene-1-carbonitrile (Y_5)



5-fluoro-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{11}H_8FN$
Molecular Weight: 173.19

A mixture of 5-fluoro-1-tetralone **X_5** (730 mg, 4.45 mmol, 1.0 equiv.), Me_3SiCN (716 μL, 5.34 mmol, 1.2 equiv.), and ZnI_2 (38 mg, 0.11 mmol, 2.5 mol%) in anhydrous toluene (3.5 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (1.25 mL, 13.4 mmol, 3.0 equiv.) and anhydrous pyridine (8 mL) were slowly added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 9:1). Faint-yellow crystalline solid. Isolated yield 57% (440 mg, 2.54 mmol). **R_f** (silica gel, *n*-Hex/Et_2O 4:1) 0.58. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.44-7.47 (1H, *m*, C^{ar}*H*), 7.24-7.32 (2H, *m*, C^{ar}*H*), 7.12-7.17 (1H, *m*, C^{ar}*H*), 6.89 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.86 (2H, *t*, *J* 8.1, benzylic CH_2), 2.50 (2H, *td*, J_1 8.1, J_2 4.9, allylic CH_2) ppm.

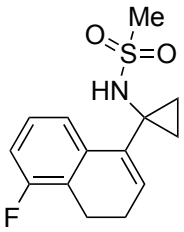
1-(5-fluoro-3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_5)



1-(5-fluoro-3,4-dihydronaphthalen-1-yl)cyclopropanamine
Chemical Formula: $C_{13}H_{14}FN$
Molecular Weight: 203.26

To a cooled (-78 °C, dry ice/acetone bath) solution of 5-fluoro-3,4-dihydronaphthalene-1-carbonitrile **Y_5** (440 mg, 2.54 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (830 μL, 2.79 mmol, 1.1 equiv.) in anhydrous Et_2O (15 mL) was added EtMgBr (3.0 M solution in Et_2O, 1.90 mL, 5.60 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca.* 48% *w/w*, 641 μL, 5.08 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Orange oil. Isolated yield 48% (248 mg, 1.22 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 1:1) 0.14. **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.65 (1H, *d*, *J* 7.6, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.16-7.19 (2H, *m*, C^{ar}*H*), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

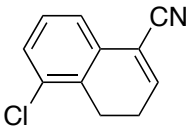
***N*-(1-(5-fluoro-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_5)**



N-(1-(5-fluoro-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{14}H_{16}FNO_2S$
Molecular Weight: 281.35

To a cooled (0 °C, ice/water bath) solution of 1-(5-fluoro-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_5** (168 mg, 0.83 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (6.5 mL) were added sequentially Et_3N (350 μL, 2.49 mmol, 3.0 equiv.), followed by MsCl (78 μL, 1.0 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). White amorphous solid. 95% (222 mg, 0.79 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 3:2) 0.36. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.13 (1H, *d*, *J* 8.7, C^{ar}*H*), 6.97 (1H, *q*, *J* 8.0, C^{ar}*H*), 6.81 (1H, *t*, *J* 8.9, C^{ar}*H*), 5.90 (1H, *t*, *J* 4.6, olefinic C=C*H*), 5.44 (1H, *brs*, sulfonamide N*H*), 2.51 (2H, *t*, *J* 8.0, benzylic CH_2), 2.26 (3H, *s*, methanesulfonyl CH_3), 1.75 (2H, *td*, J_1 8.2, J_2 4.7, allylic CH_2), 1.16 (2H, *brs*, cyclopropylic CH_2), 0.71 (2H, *brs*, cyclopropylic CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -118.0 (1F, *s*, C^{ar}*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 160.4 (*d*, $J^{C\text{-}F}$ 241, *ipso*(F)-C*q*), 135.2 (*d*, $J^{C\text{-}F}$ 3.4, olefinic C*q*), 135.1 (*d*, $J^{C\text{-}F}$ 5.0, *meta*(F)-C*q*), 129.9 (*para*(F)-*C*H), 128.1 (olefinic *C*H), 123.2 (*d*, $J^{C\text{-}F}$ 17.1, *ortho*(F)-C*q*), 119.7 (*d*, $J^{C\text{-}F}$ 2.9, *meta*(F)-*C*H), 114.7 (*d*, $J^{C\text{-}F}$ 22.5, *ortho*(F)-*C*H), 41.5 (methanesulfonyl *C*H_3), 36.5 (C*q*-N), 22.0 (*C*H_2), 19.1 (*d*, $J^{C\text{-}F}$ 3.4, *C*H_2), 14.1 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{16}FNO_2S$, expected $(M+H)^+$ *m/z* 282.0959, observed $(M+H)^+$ *m/z* 282.0962.

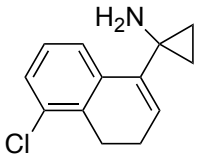
5-chloro-3,4-dihydronaphthalene-1-carbonitrile (Y_6)



5-chloro-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{11}H_8ClN$
Molecular Weight: 189.64

A mixture of 5-chloro-3,4-dihydronaphthalen-1(2*H*)-one **X_6** (1.24 g, 6.84 mmol, 1.0 equiv.), Me_3SiCN (1.10 mL, 8.21 mmol, 1.2 equiv.), and ZnI_2 (55 mg, 0.17 mmol, 2.5 mol%) in anhydrous toluene (5.0 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (1.92 mL, 20.5 mmol, 3.0 equiv.) and anhydrous pyridine (12 mL) were slowly added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 95:5). Yellow crystalline solid. Isolated yield 51% (662 mg, 3.49 mmol). **R_f** (silica gel, *n*-Hex/Et_2O 4:1) 0.50. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.47 (1H, *m*, C^{ar}*H*), 7.24-7.32 (2H, *m*, C^{ar}*H*), 7.12-7.17 (1H, *m*, C^{ar}*H*), 6.89 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.86 (2H, *t*, *J* 8.1, benzylic CH_2), 2.50 (2H, *td*, J_1 8.1, J_2 4.9, allylic CH_2) ppm.

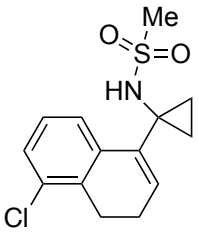
1-(5-chloro-3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_6)



1-(5-chloro-3,4-dihydronaphthalen-1-yl)cyclopropanamine
Chemical Formula: $C_{13}H_{14}ClN$
Molecular Weight: 219.71

To a cooled (-78 °C, dry ice/acetone bath) solution of 5-chloro-3,4-dihydronaphthalene-1-carbonitrile **Y_6** (657 mg, 3.46 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (1.14 mL, 3.81 mmol, 1.1 equiv.) in anhydrous Et_2O (20 mL) was added EtMgBr (3.0 M solution in Et_2O, 2.54 mL, 7.61 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca.* 48% *w/w*, 874 μL, 6.92 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Dark-orange oil. Isolated yield 42% (322 mg, 1.47 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 1:1) 0.10. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (1H, *d*, *J* 7.6, $C^{ar}H$), 7.23-7.28 (1H, *m*, $C^{ar}H$), 7.16-7.19 (2H, *m*, $C^{ar}H$), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

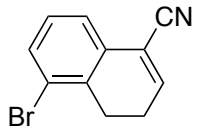
***N*-(1-(5-chloro-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_6)**



N-(1-(5-chloro-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{14}H_{16}ClNO_2S$
Molecular Weight: 297.80

To a cooled (0 °C, ice/water bath) solution of 1-(5-chloro-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_6** (322 mg, 1.47 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were added sequentially Et_3N (620 μL, 4.41 mmol, 3.0 equiv.), followed by MsCl (137 μL, 1.76 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). White crystalline solid. Isolated yield 93% (407 mg, 1.37 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.21. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (1H, *d*, *J* 7.0, $C^{ar}H$), 7.28 (1H, *dd*, J_1 8.0, J_2 1.1, $C^{ar}H$), 7.20 (1H, *t*, *J* 7.8, $C^{ar}H$), 6.29 (1H, *t*, *J* 4.7, olefinic C=C*H*), 5.25 (1H, *brs*, sulfonamide N*H*), 2.88 (2H, broad *t*, *J* 8.0, benzylic CH_2), 2.71 (3H, *s*, methanesulfonyl CH_3), 2.34 (2H, *td*, J_1 8.2, J_2 4.7, allylic CH_2), 1.33-1.35 (2H, *m*, cyclopropylic CH_2), 1.05-1.08 (2H, *m*, cyclopropylic CH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.1 (C*q*), 134.5 (C*q*), 134.4 (C*q*), 133.9 (C*q*), 129.8 (*C*H), 128.8 (*C*H), 127.5 (*C*H), 121.7 (*C*H), 41.8 (CH_3), 36.6 (C*q*-N), 23.9 (CH_2), 22.3 (CH_2), 13.7 (cyclopropylic CH_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{16}ClNO_2S$, expected $(M+H)^+$ *m/z* 298.0664, observed $(M+H)^+$ *m/z* 298.0665.

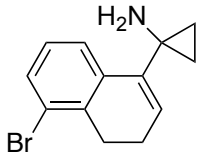
5-bromo-3,4-dihydronaphthalene-1-carbonitrile (Y_7)



5-bromo-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{11}H_8BrN$
Molecular Weight: 234.09

A mixture of 5-bromo-1-tetralone $\mathbf{X_7}$ (930 mg, 4.13 mmol, 1.0 equiv.), Me_3SiCN (670 μL, 4.96 mmol, 1.2 equiv.), and ZnI_2 (35 mg, 0.10 mmol, 2.5 mol%) in anhydrous toluene (3.0 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (1.16 mL, 12.4 mmol, 3.0 equiv.) and anhydrous pyridine (7.0 mL) were slowly added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 95:5). White crystalline solid. Isolated yield 69% (643 mg, 2.75 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/Et_2O 9:1) 0.68. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (1H, *d*, *J* 7.8, $C^{ar}H$), 7.09 (1H, *d*, *J* 7.8, $C^{ar}H$), 6.97 (1H, *s*, $C^{ar}H$), 6.82 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.81 (2H, *t*, *J* 8.2, benzylic CH_2), 2.48 (2H, *td*, J_1 8.4, J_2 4.8, allylic CH_2), 2.34 (3H, *s*, CH_3) ppm.

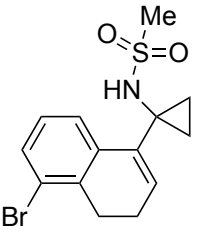
1-(5-bromo-3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_7)



1-(5-bromo-3,4-dihydronaphthalen -1-yl)cyclopropanamine
Chemical Formula: $C_{13}H_{14}BrN$
Molecular Weight: 264.16

To a cooled (-78 °C, dry ice/acetone bath) solution of 5-bromo-3,4-dihydronaphthalene-1-carbonitrile $\mathbf{Y_7}$ (643 mg, 2.75 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (904 μL, 3.02 mmol, 1.1 equiv.) in anhydrous Et_2O (15 mL) was added EtMgBr (3.0 M solution in Et_2O, 2.02 mL, 6.05 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca.* 48% *w/w*, 700 μL, 5.50 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Beige viscous oil. Isolated yield 44% (312 mg, 1.57 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/EtOAc 1:1) 0.15. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (1H, *d*, *J* 7.5, $C^{ar}H$), 7.42 (1H, *dd*, J_1 7.1, J_2 0.9, $C^{ar}H$), 7.11 (1H, *t*, *J* 7.9, $C^{ar}H$), 6.10 (1H, *t*, *J* 4.6, olefinic C=C*H*), 3.21 (1H, *brs*, amino NH_2), 2.88 (2H, *t*, *J* 8.1, benzylic CH_2), 2.28 (2H, *td*, J_1 8.4, J_2 4.6, allylic CH_2), 0.98-1.01 (2H, *m*, cyclopropylic CH_2), 0.81-0.84 (2H, *m*, cyclopropylic CH_2) ppm.

***N*-(1-(5-bromo-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_7)**

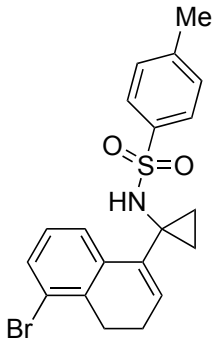


N-(1-(5-bromo-3,4-dihydronaphthalen -1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{14}H_{16}BrNO_2S$
Molecular Weight: 342.25

To a cooled (0 °C, ice/water bath) solution of 1-(5-bromo-3,4-dihydronaphthalen-1-yl)cyclopropanamine $\mathbf{Z_7}$ (175 mg, 0.66 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were added sequentially Et_3N (662 μL, 4.71 mmol, 3.0 equiv.), followed by MsCl (147 μL, 1.88 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an

additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/EtOAc 3:2) 0.37. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.33 (1H, *dd*, J_1 8.1, J_2 0.8, C^{ar}*H*), 7.19 (1H, *d*, *J* 7.7, C^{ar}*H*), 6.80 (1H, *t*, *J* 7.9, C^{ar}*H*), 5.86 (1H, *t*, *J* 4.7, olefinic C=C*H*), 5.15 (1H, *brs*, sulfonamide N*H*), 2.65 (2H, *t*, *J* 8.1, benzylic CH_2), 2.19 (3H, *s*, methanesulfonyl CH_3), 1.74 (2H, *td*, J_1 8.2, J_2 4.7, allylic CH_2), 1.11 (2H, *brs*, cyclopropylic CH_2), 0.67 (2H, *brs*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 136.2 (C*q*), 135.3 (C*q*), 135.1 (C*q*), 131.9 (*C*H), 130.1 (*C*H), 128.1 (*C*H), 124.7 (olefinic C*q*), 122.9 (olefinic *C*H), 41.5 (methanesulfonyl *C*H_3), 36.3 (C*q*-N), 27.2 (*C*H_2), 22.4 (*C*H_2), 14.3 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{16}BrNO_2S$, expected $(M+H)^+$ *m/z* 342.0158, 344.0138; observed $(M+H)^+$ *m/z* 342.0162, 344.0142.

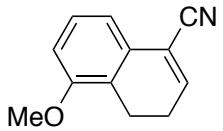
_N_-(1-(5-bromo-3,4-dihydronaphthalen-1-yl)cyclopropyl)-4-methylbenzenesulfonamide (A_8)



N-(1-(5-bromo-3,4-dihydronaphthalen-1-yl) cyclopropyl)-4-methylbenzenesulfonamide
Chemical Formula: $C_{20}H_{20}BrNO_2S$
Molecular Weight: 418.35

To a cooled (0 °C, ice/water bath) solution of 1-(5-bromo-3,4-dihydronaphthalen-1-yl)cyclopropanamine $\mathbf{Z_7}$ (161 mg, 0.61 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were added sequentially Et_3N (257 µL, 1.83 mmol, 3.0 equiv.), followed by TsCl (140 mg, 0.73 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). $\mathbf{R_f}$ (silica gel, *n*-Hex/EtOAc 3:2) 0.37. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.37 (2H, *d*, *J* 8.3, C^{ar}*H*), 7.23 (1H, *dd*, J_1 8.0, J_2 1.0, C^{ar}*H*), 7.07 (1H, *d*, *J* 7.6, C^{ar}*H*), 6.72 (1H, *t*, *J* 7.8, C^{ar}*H*), 6.56 (2H, *d*, *J* 7.9, C^{ar}*H*), 5.56 (1H, *t*, *J* 4.7, olefinic C=C*H*), 5.54 (1H, *brs*, sulfonamide N*H*), 2.08 (2H, *brs*, benzylic CH_2), 1.96 (3H, *s*, CH_3), 1.54 (2H, *td*, J_1 8.2, J_2 4.7, allylic CH_2), 1.18 (2H, *brs*, cyclopropylic CH_2), 0.67 (2H, *brs*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 142.4 (C*q*), 139.5 (C*q*), 136.7 (C*q*), 135.1 (C*q*), 134.0 (C*q*), 131.2 (*C*H), 128.9 (*C*H), 128.8 (*C*H), 128.4 (olefinic *C*H), 127.7 (*C*H), 127.3 (*C*H), 124.5 (C*q*), 122.7 (*C*H), 36.3 (C*q*-N), 26.5 (*C*H_2), 21.9 (*C*H_2), 21.2 (*C*H_3), 14.0 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{20}H_{20}BrNO_2S$, expected $(M+H)^+$ *m/z* 418.0471, 420.0451; observed $(M+H)^+$ *m/z* 418.0474, 420.0454.

5-methoxy-3,4-dihydronaphthalene-1-carbonitrile (Y_8)

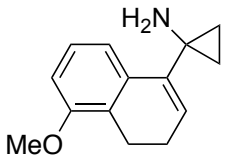


5-methoxy-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{12}H_{11}NO$
Molecular Weight: 185.22

A mixture of 5-methoxy-1-tetralone $\mathbf{X_8}$ (1.21 g, 6.84 mmol, 1.0 equiv.), Me_3SiCN (1.10 mL, 8.21 mmol, 1.2 equiv.), and ZnI_2 (55 mg, 0.17 mmol, 2.5 mol%) in anhydrous toluene (5.0 mL) was stirred at ambient temperature for 8 h. Then, $POCl_3$ (1.92 mL, 20.5 mmol, 3.0 equiv.) and anhydrous pyridine (12 mL) were slowly added, and the whole mixture was heated at 80 °C for 8 h. The

cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 9:1). Faint-pink crystalline solid. Isolated yield 60% (763 mg, 4.12 mmol). $\mathbf{R}_f$ (silica gel, *n*-Hex/Et_2O 4:1) 0.57. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44-7.47 (1H, *m*, C^{ar}*H*), 7.24-7.32 (2H, *m*, C^{ar}*H*), 7.12-7.17 (1H, *m*, C^{ar}*H*), 6.89 (1H, *t*, *J* 4.8, olefinic C=C*H*), 2.86 (2H, *t*, *J* 8.1, benzylic CH_2), 2.50 (2H, *td*, J_1 8.1, J_2 4.9, allylic CH_2) ppm.

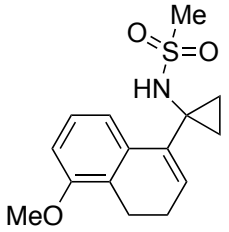
1-(5-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropanamine ($\mathbf{Z_8}$)



1-(5-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropanamine
Chemical Formula: $C_{14}H_{17}NO$
Molecular Weight: 215.29

To a cooled (-78 °C, dry ice/acetone bath) solution of 5-methoxy-3,4-dihydronaphthalene-1-carbonitrile $\mathbf{Y_8}$ (763 mg, 4.12 mmol, 1.0 equiv.) and Ti(O^{i}Pr)$_4$ (1.36 mL, 4.53 mmol, 1.1 equiv.) in anhydrous Et_2O (24 mL) was added EtMgBr (3.0 M solution in Et_2O, 3.02 mL, 9.06 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca*. 48% *w/w*, 1.04 mL, 8.24 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Dark-orange oil. Isolated yield 44% (392 mg, 1.82 mmol). $\mathbf{R}_f$ (silica gel, *n*-Hex/EtOAc 1:1) 0.10. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (1H, *d*, *J* 7.6, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.16-7.19 (2H, *m*, C^{ar}*H*), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

***N*-(1-(5-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide ($\mathbf{A_9}$)**

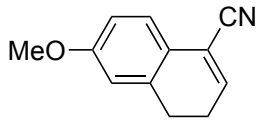


N-(1-(5-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{15}H_{19}NO_3S$
Molecular Weight: 293.38

To a cooled (0 °C, ice/water bath) solution of 1-(5-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropanamine $\mathbf{Z_8}$ (392 mg, 1.82 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (15 mL) were added sequentially Et_3N (767 μL, 5.46 mmol, 3.0 equiv.), followed by MsCl (169 μL, 1.76 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Light-orange glassy solid. 88% (470 mg, 1.60 mmol). $\mathbf{R}_f$ (silica gel, *n*-Hex/EtOAc 3:2) 0.33. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.14 (1H, *t*, *J* 8.0, C^{ar}*H*), 7.10 (1H, *d*, *J* 7.3, C^{ar}*H*), 6.55 (1H, *dd*, J_1 8.0, J_2 0.5, C^{ar}*H*), 5.95 (1H, *t*, *J* 4.6, olefinic C=C*H*), 5.36 (1H, *brs*, sulfonamide N*H*), 3.36 (3H, *s*, CH_3-O), 2.74 (2H,

broad *t*, *J* 7.6, benzylic CH_2), 2.31 (3H, *s*, methanesulfonyl CH_3), 1.90 (2H, *td*, J_1 8.3, J_2 4.7, allylic CH_2), 1.22 (2H, *brs*, cyclopropylic CH_2), 0.79 (2H, *brs*, cyclopropylic CH_2) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 156.9 (C*q*), 135.8 (C*q*), 134.0 (C*q*), 129.0 (*C*H), 127.3 (*C*H), 124.8 (C*q*), 116.6 (*C*H), 110.2 (*C*H), 55.0 (*C*H_3-O), 41.4 (methanesulfonyl *C*H_3), 36.7 (C*q*-N), 22.5 (*C*H_2), 19.8 (*C*H_2), 14.1 (cyclopropylic *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{19}NO_3S$, expected $(M+H)^+$ *m/z* 294.1159, observed $(M+H)^+$ *m/z* 294.1157.

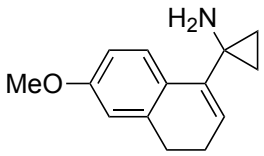
6-methoxy-3,4-dihydronaphthalene-1-carbonitrile (Y_9)



6-methoxy-3,4-dihydro naphthalene-1-carbonitrile
Chemical Formula: $C_{12}H_{11}NO$
Molecular Weight: 185.22

A mixture of 6-methoxy-1-tetralone **X_9** (1.80 g, 10.2 mmol, 1.0 equiv.), Me_3SiCN (1.64 mL, 12.2 mmol, 1.2 equiv.), and ZnI_2 (70 mg, 0.25 mmol, 2.5 mol%) in anhydrous DME (5.0 mL) was stirred at 60 °C for 8 h. Then, $POCl_3$ (2.09 mL, 22.4 mmol, 3.0 equiv.) and anhydrous pyridine (12 mL) were added, and the whole mixture was heated at 80 °C for 8 h. The cooled reaction mixture was poured over ice-cold 1 N HCl, and extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane → *n*-hexane/Et_2O 95:5). White crystalline solid. Isolated yield 85% (1.61 g, 8.69 mmol). **R_f** (silica gel, *n*-Hex/Et_2O 9:1) 0.43. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (1H, *d*, *J* 8.4, C^{ar}*H*), 6.49 (1H, *d*, *J* 2.4, C^{ar}*H*), 6.45 (1H, *dd*, J_1 8.4, J_2 2.6, C^{ar}*H*), 5.97 (1H, *t*, *J* 4.8, olefinic C=C*H*), 3.23 (3H, *s*, CH_3-O), 2.15 (2H, *t*, *J* 8.2, benzylic CH_2), 1.59 (2H, *td*, J_1 8.3, J_2 4.8, allylic CH_2) ppm.

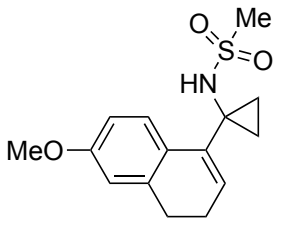
1-(6-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropanamine (Z_9)



1-(6-methoxy-3,4-dihydronaph thalen-1-yl)cyclopropanamine
Chemical Formula: $C_{14}H_{17}NO$
Molecular Weight: 215.29

To a cooled (-78 °C, dry ice/acetone bath) solution of 6-methoxy-3,4-dihydronaphthalene-1-carbonitrile **Y_9** (1.61 g, 8.69 mmol, 1.0 equiv.) and $Ti(O^iPr)_4$ (2.86 mL, 9.56 mmol, 1.1 equiv.) in anhydrous Et_2O (50 mL) was added EtMgBr (3.0 M solution in Et_2O, 6.37 mL, 19.1 mmol, 2.2 equiv.) over a period of 1 h *via* syringe pump. The resultant yellow solution was stirred at this temperature for 30 min. The reaction mixture was warmed up to ambient temperature over a period of 1 h. The mixture was cooled back down to 0 °C (ice/water bath), and BF_3•Et_2O (*ca*. 48% *w/w*, 2.19 mL, 17.4 mmol, 2.0 equiv.) was added. After the mixture was stirred at ambient temperature for 1 h, 1 N aqueous HCl and diethyl ether were added. 1 N aqueous NaOH was added to the resultant two-phase mixture, which was subsequently extracted with diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 4:1 → 3:2). Dark-orange oil. Isolated yield 52% (380 mg, 2.05 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 1:1) 0.15. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (1H, *d*, *J* 7.6, C^{ar}*H*), 7.23-7.28 (1H, *m*, C^{ar}*H*), 7.16-7.19 (2H, *m*, C^{ar}*H*), 6.02 (1H, *t*, *J* 4.6, olefinic C=C*H*), 2.75 (2H, *t*, *J* 7.9, benzylic CH_2), 2.25 (2H, *td*, J_1 8.2, J_2 4.6, allylic CH_2), 1.84 (2H, *brs*, NH_2), 0.88-0.93 (2H, *m*, cyclopropylic CH_2), 0.78-0.82 (2H, *m*, cyclopropylic CH_2) ppm.

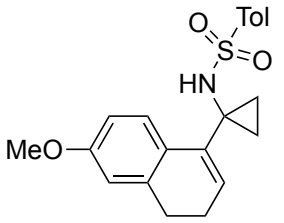
***N*-(1-(6-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide (A_{10})**



N-(1-(6-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropyl)methanesulfonamide
Chemical Formula: $C_{15}H_{19}NO_3S$
Molecular Weight: 293.38

To a cooled (0 °C, ice/water bath) solution of 1-(6-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_9** (325 mg, 1.51 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were added sequentially Et_3N (637 µL, 4.53 mmol, 3.0 equiv.), followed by MsCl (145 µL, 1.81 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 3:2) 0.37. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.25 (1H, *d*, *J* 8.4, C^{ar}*H*), 6.72 (1H, *d*, *J* 9.1, C^{ar}*H*), 6.69 (1H, *s*, C^{ar}*H*), 5.83 (1H, *t*, *J* 4.6, olefinic C=C*H*), 5.21 (1H, *brs*, sulfonamide N*H*), 3.38 (3H, *s*, C*H*$_3$-O), 2.35 (2H, *t*, *J* 8.2, benzylic C*H*$_2$), 2.34 (3H, *s*, methanesulfonyl C*H*$_3$), 1.87 (2H, *td*, J_1 8.2, J_2 4.7, allylic C*H*$_2$), 1.18 (2H, *brs*, cyclopropylic C*H*$_2$), 0.78 (2H, *brs*, cyclopropylic C*H*$_2$) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 159.5 (C*q*), 138.8 (C*q*), 135.7 (C*q*), 126.0 (*C*H), 125.9 (olefinic C*q*), 124.9 (*C*H), 114.8 (*C*H), 111.7 (olefinic *C*H), 54.8 (*C*H$_3$-O), 41.4 (methanesulfonyl *C*H$_3$), 36.5 (C*q*-N), 28.3 (*C*H$_2$), 23.0 (*C*H$_2$), 14.0 (cyclopropylic *C*H$_2$) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{19}NO_3S$, expected $(M+H)^+$ *m/z* 294.1159, observed $(M+H)^+$ *m/z* 294.1162.

***N*-(1-(6-methoxy-3,4-dihydronaphthalen-1-yl)cyclopropyl)-4-methylbenzenesulfonamide (A_{11})**



N-(1-(6-methoxy-3,4-dihydronaphthalen-1-yl) cyclopropyl)-4-methylbenzenesulfonamide
Chemical Formula: $C_{21}H_{23}NO_3S$
Molecular Weight: 369.48

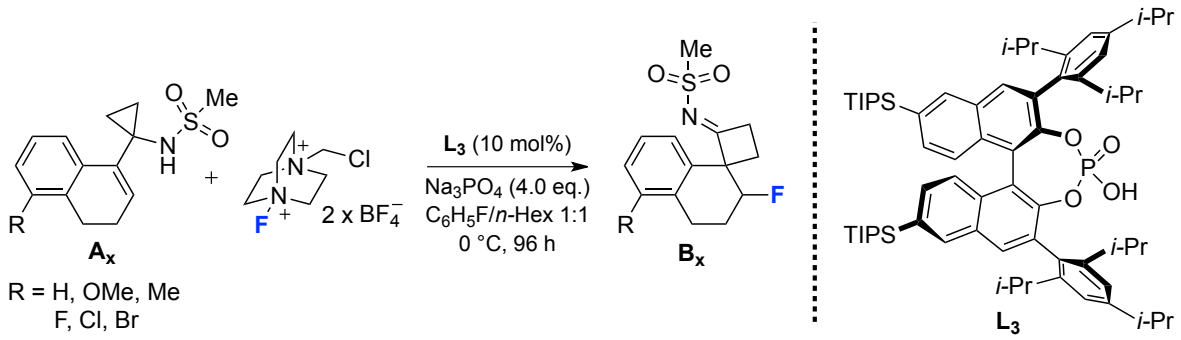
To a cooled (0 °C, ice/water bath) solution of 1-(6-methyl-3,4-dihydronaphthalen-1-yl)cyclopropanamine **Z_9** (325 mg, 1.51 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were added sequentially Et_3N (637 µL, 4.53 mmol, 3.0 equiv.), followed by TsCl (345 mg, 1.81 mmol, 1.2 equiv.). The resultant dark-brown mixture was stirred at 0 °C for 30 min, and then brought slowly to ambient temperature. After an additional 6 h of stirring, the crude mixture was poured into 1 N aqueous HCl, and then extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and liberated of solvents *in vacuo*. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Beige oil. 95% (414 mg, 1.49 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 3:2) 0.37. **^{1}H NMR** (500 MHz, C_6D_6): δ 7.59 (2H, *d*, *J* 8.2, C^{ar}*H*), 7.35 (1H, *d*, *J* 8.5, C^{ar}*H*), 6.67 (1H, *dd*, J_1 8.5, J_2 2.7, C^{ar}*H*), 6.60 (2H, *d*, *J* 8.0, C^{ar}*H*), 6.56 (1H, *d*, *J* 2.7, C^{ar}*H*), 6.15 (1H, *brs*, sulfonamide N*H*), 5.53 (1H, *t*, *J* 4.6, olefinic C=C*H*), 3.35 (3H, *s*, C*H*$_3$-O), 1.95 (2H, *t*, *J* 7.9, benzylic C*H*$_2$), 1.86 (3H, *s*, C*H*$_3$), 1.66 (2H, *td*, J_1 8.2, J_2 4.6, allylic C*H*$_2$), 1.35 (2H, *brs*, cyclopropylic C*H*$_2$), 0.79 (2H, *brs*, cyclopropylic C*H*$_2$) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 159.2 (C*q*), 142.1 (C*q*), 139.8 (C*q*), 138.8 (C*q*), 134.4 (C*q*), 128.9 (*C*H), 127.7 (*C*H), 126.0 (olefinic C*q*), 125.4 (*C*H), 124.8 (*C*H), 114.6 (*C*H), 111.0 (olefinic *C*H), 54.8 (*C*H$_3$-O), 36.5 (C*q*-N), 27.5 (*C*H$_2$),

22.7 (CH_2), 21.0 (CH_3), 13.7 (cyclopropylic CH_2) ppm. **ESI-HRMS (positif)** M = $C_{21}H_{23}NO_3S$, expected $(M+H)^+$ *m/z* 370.1472, observed $(M+H)^+$ *m/z* 370.1475.

General Procedure for the Fluorination-Initiated *aza*-Semi-Pinacol Rearrangement: Preparation of Racemates

To a well-stirred solution of allylic cyclopropylamine $\mathbf{A_x}$ (0.20 mmol, 1.0 equiv.) in anhydrous CH_3CN (2.5 mL, 0.08 M) were added powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.) and anhydrous Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.). The resultant colorless mixture was stirred at 0 °C for 24 h. Saturated aqueous $Na_2S_2O_3$ was then added to quench the reaction. The layers were separated and the aqueous layer was extracted with methyl *tert*-butyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Conversions and diastereomer ratios (*d.r.*) were determined by ^1H and ^{19}F NMR analysis of the crude compounds. Pure material ($\mathbf{B_x}$) was obtained after purification by flash chromatography on silica gel, using an adequate *n*-hexane/EtOAc mixture as eluent. Enantiomer separations were performed by chiral HPLC.

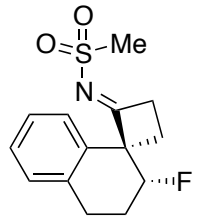
General Procedure for the Fluorination-Initiated *aza*-Semi-Pinacol Rearrangement: Enantioselective Reaction



To a well-stirred solution of allylic cyclopropylamine $\mathbf{A_x}$ (0.20 mmol, 1.0 equiv.) and (R_a)-TIPS-TRIP ($\mathbf{L_3}$) (24 mg, 0.02 mmol, 10 mol%) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M) were added powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.) and anhydrous Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.). The resultant heterogeneous mixture was stirred at 0 °C for 96 h. Saturated aqueous $Na_2S_2O_3$ was then added to quench the reaction. The layers were separated and the aqueous layer was extracted with methyl *tert*-butyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Conversions and diastereomer ratios (*d.r.*) were determined by ^1H and ^{19}F NMR analysis of the crude compounds. Pure material ($\mathbf{B_x}$) was obtained after purification by flash chromatography on silica gel, using an adequate *n*-hexane/EtOAc mixture as eluent. Enantiomer ratios (*e.r.*) were determined by chiral HPLC analysis of purified compounds.

Characterization of Products

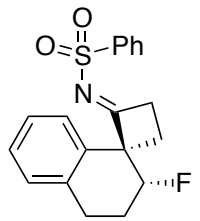
β-Fluoro Cyclobutylimine (B_1-Ms)



Chemical Formula: $C_{14}H_{16}FNO_2S$
Molecular Weight: 281.35

According to the General Procedure: allylic cyclopropylamine **A_1-Ms** (53 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Colorless oil. Isolated yield 85% (48 mg, 0.17 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.25. > 20:1 *d.r.* (^{1}H NMR). 92:8 *e.r.* Chiral HPLC. Chiralcel OD-H. *n*-Hex/*i*-PrOH 90:10. 1.0 mL/min. t_R 14.1 (minor), 22.3 (major). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18-7.25 (3H, *m*, C^{ar}*H*), 7.12 (1H, *d*, *J* 6.6, C^{ar}*H*), 5.03 (1H, *ddd*, J_1^{H-F} 49.1, J_2 9.8, J_3 3.1, α-fluoro C*H*), 3.47-3.64 (2H, *m*, CH_2), 3.03 (3H, *s*, methanesulfonyl CH_3), 2.77-3.06 (3H, *m*, CH_2), 2.33-2.41 (1H, *m*, CH_2), 2.06-2.29 (2H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -187.1 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 198.8 (*d*, J^{C-F} 4.6, imine C*q*), 135.8 (*d*, J^{C-F} 5.1, C*q*), 134.7 (*d*, J^{C-F} 1.2, C*q*), 129.0 (*C*H), 127.9 (*C*H), 127.4 (*d*, J^{C-F} 1.5, *C*H), 127.4 (*C*H), 91.3 (*d*, J^{C-F} 180.0, *C*H-F), 63.6 (*d*, J^{C-F} 20.6, α-imine C*q*), 41.6 (methanesulfonyl *C*H_3), 38.0 (*C*H_2), 28.1 (*d*, J^{C-F} 5.8, *C*H_2), 26.6 (*d*, J^{C-F} 9.9, *C*H), 25.5 (*d*, J^{C-F} 19.3, *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{16}FNO_2S$, expected $(M+H)^+$ *m/z* 282.0959, observed $(M+H)^+$ *m/z* 282.0960. **$[\alpha]^{20}_D$** -37.2 (*c* = 1.00, $CHCl_3$).

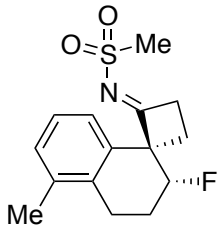
β-Fluoro Cyclobutylimine (B_1-Ps)



Chemical Formula: $C_{19}H_{18}FNO_2S$
Molecular Weight: 343.42

According to the General Procedure: allylic cyclopropylamine **A_1-Ps** (65 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Colorless oil. Isolated yield 67% (46 mg, 0.13 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.33. > 20:1 *d.r.* (^{1}H NMR). 88.5:11.5 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 18.1 (major), 27.6 (minor). **^{1}H NMR** (400 MHz, C_6D_6): δ 7.93 (2H, *dd*, J_1 8.0, J_2 1.6, C^{ar}*H*), 6.96-6.99 (1H, *m*, C^{ar}*H*), 6.78-6.92 (5H, *m*, C^{ar}*H*), 6.65-6.69 (1H, *m*, C^{ar}*H*), 4.59 (1H, *ddd*, J_1^{H-F} 49.1, J_2 9.6, J_3 3.0, α-fluoro C*H*), 3.41-3.59 (2H, *m*, CH_2), 2.36-2.45 (2H, *m*, CH_2), 2.13-2.21 (1H, *m*, CH_2), 1.82-1.90 (1H, *m*, CH_2), 1.54-1.77 (2H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -186.4 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ 214.9 (*d*, J^{C-F} 5.1, imine C*q*), 142.1 (*d*, J^{C-F} 2.1, C*q*), 137.6 (*d*, J^{C-F} 6.7, C*q*), 128.8 (*d*, J^{C-F} 0.9, *C*H), 127.6 (*d*, J^{C-F} 1.9, *C*H), 127.0 (*C*H), 126.8 (*d*, J^{C-F} 0.6, *C*H), 94.2 (*d*, J^{C-F} 173.0, *C*H-F), 56.1 (*d*, J^{C-F} 19.7, α-imine C*q*), 39.3 (*C*H_2), 38.8 (*C*H_2), 32.5 (*d*, J^{C-F} 11.7, *C*H), 32.3 (*d*, J^{C-F} 18.8, *C*H_2), 24.0 (*C*H_3), 20.3 (*C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{19}H_{18}FNO_2S$, expected $(M+H)^+$ *m/z* 344.1116, observed $(M+H)^+$ *m/z* 344.1119. **$[\alpha]^{20}_D$** +3.8 (*c* = 1.00, $CHCl_3$).

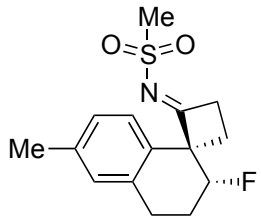
β-Fluoro Cyclobutylimine (B_2)



Chemical Formula: $C_{15}H_{18}FNO_2S$
Molecular Weight: 295.37

According to the General Procedure: allylic cyclopropylamine **A_2** (55 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Pale-yellow oil. Isolated yield 84% (50 mg, 0.17 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.28. > 20:1 *d.r.* (^{1}H NMR). 95:5 *e.r.* Chiral HPLC. Chiralcel OD-H. *n*-Hex/*i*-PrOH 90:10. 1.0 mL/min. t_R 9.8 (minor), 12.6 (major). **^{1}H NMR** (400 MHz, C_6D_6): δ 6.93-6.98 (2H, *m*, C^{ar}*H*), 6.82-6.86 (1H, *m*, C^{ar}*H*), 4.72 (1H, *ddd*, J_1^{H-F} 49.4, J_2 9.5, J_3 2.8, α-fluoro C*H*), 3.43 (2H, *t*, *J* 8.8, benzylic CH_2), 2.27-2.44 (2H, *m*, diastereotopic CH_2), 2.37 (3H, *s*, methanesulfonyl CH_3), 2.07 (1H, *ddd*, J_1 14.7, J_2 8.3, J_3 6.5, CH_2), 1.81-1.98 (2H, *m*, CH_2), 1.82 (3H, *s*, CH_3), 1.66-1.76 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -187.2 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (100 MHz, C_6D_6): δ 197.4 (*d*, J^{C-F} 5.5, imine C*q*), 136.3 (C*q*), 136.1 (*d*, J^{C-F} 4.6, C*q*), 133.4 (*d*, J^{C-F} 1.6, C*q*), 129.1 (*C*H), 127.3 (*C*H), 125.5 (*d*, J^{C-F} 1.3, *C*H), 90.9 (*d*, J^{C-F} 179.3, *C*H-F), 63.8 (*d*, J^{C-F} 20.5, α-imine C*q*), 41.0 (methanesulfonyl *C*H$_3$), 37.9 (*C*H$_2$), 28.0 (*d*, J^{C-F} 5.5, *C*H$_2$), 25.2 (*d*, J^{C-F} 19.4, *C*H$_2$), 24.0 (*d*, J^{C-F} 9.4, *C*H$_2$), 19.6 (*C*H$_3$) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{18}FNO_2S$, expected (M+H)$^+$ *m/z* 296.1116, observed (M+H)$^+$ *m/z* 296.1119. **$[\alpha]^{20}_D$** -35.6 (*c* = 1.00, $CHCl_3$).

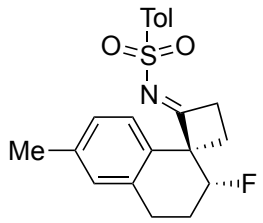
β-Fluoro Cyclobutylimine (B_3)



Chemical Formula: $C_{15}H_{18}FNO_2S$
Molecular Weight: 295.37

According to the General Procedure: allylic cyclopropylamine **A_3** (59 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Colorless oil. Isolated yield 86% (51 mg, 0.17 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.23. > 20:1 *d.r.* (^{1}H NMR). 93:7 *e.r.* Chiral HPLC. Chiralpak IB. *n*-Hex/THF 95:5. 1.2 mL/min. t_R 9.6 (minor), 21.8 (major). **^{1}H NMR** (500 MHz, C_6D_6): δ 6.95 (1H, *d*, *J* 8.0, C^{ar}*H*), 6.81 (1H, *d*, *J* 8.9, C^{ar}*H*), 6.57 (1H, *s*, C^{ar}*H*), 4.70 (1H, *ddd*, J_1^{H-F} 49.2, J_2 9.0, J_3 2.8, α-fluoro C*H*), 3.41 (2H, *t*, *J* 8.6, diastereotopic CH_2), 2.51-2.58 (1H, *m*, CH_2), 2.29-2.43 (2H, *m*, CH_2), 2.36 (3H, *s*, methanesulfonyl CH_3), 2.04 (3H, *s*, CH_3), 1.81-1.96 (2H, *m*, CH_2), 1.69-1.77 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -186.9 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 197.3 (*d*, J^{C-F} 6.1, imine C*q*), 137.1 (C*q*), 134.8 (*d*, J^{C-F} 1.3, C*q*), 133.1 (*d*, J^{C-F} 4.3, C*q*), 129.5 (*C*H), 128.4 (*C*H), 127.6 (*d*, J^{C-F} 0.9, *C*H), 91.1 (*d*, J^{C-F} 180.0, *C*H-F), 63.3 (*d*, J^{C-F} 20.9, α-imine C*q*), 41.0 (methanesulfonyl *C*H$_3$), 37.8 (*C*H$_2$), 27.7 (*d*, J^{C-F} 5.9, *C*H$_2$), 26.1 (*d*, J^{C-F} 9.1, *C*H$_2$), 25.6 (*d*, J^{C-F} 19.4, *C*H$_2$), 20.9 (*C*H$_3$) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{18}FNO_2S$, expected (M+H)$^+$ *m/z* 296.1116, observed (M+H)$^+$ *m/z* 296.1120. **$[\alpha]^{20}_D$** -26.8 (*c* = 1.00, $CHCl_3$).

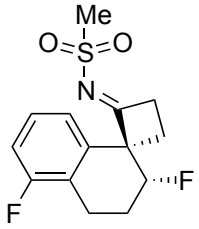
β-Fluoro Cyclobutylimine (B_4)



Chemical Formula: $C_{21}H_{22}FNO_2S$
Molecular Weight: 371.47

According to the General Procedure: allylic cyclopropylamine **A_4** (59 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). White crystalline solid. Isolated yield 83% (62 mg, 0.17 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.38. > 20:1 *d.r.* (^{1}H NMR). 92:8 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/THF 90:10. 1.0 mL/min. t_R 34.7 (major), 40.0 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.90 (2H, *d*, *J* 8.3, C^{ar}*H*), 6.94 (1H, *d*, *J* 8.0, C^{ar}*H*), 6.75 (1H, *d*, *J* 7.9, C^{ar}*H*), 6.65 (2H, *d*, *J* 8.0, C^{ar}*H*), 6.50 (1H, *s*, C^{ar}*H*), 4.64 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.2, J_2 9.5, J_3 2.9, α-fluoro C*H*), 3.47-3.61 (2H, *m*, diastereotopic CH_2), 2.40-2.48 (2H, *m*, CH_2), 2.18-2.24 (1H, *m*, CH_2), 2.00 (3H, *s*, CH_3), 1.89-1.95 (1H, *m*, CH_2), 1.76 (3H, *s*, CH_3), 1.72-1.82 (1H, *m*, CH_2), 1.61-1.69 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -186.5 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 196.9 (*d*, $J^{C\text{-}F}$ 5.2, imine C*q*), 143.7 (C*q*), 138.1 (C*q*), 137.0 (C*q*), 134.6 (*d*, $J^{C\text{-}F}$ 1.6, C*q*), 133.3 (*d*, $J^{C\text{-}F}$ 4.8, C*q*), 129.6 (*C*H), 129.4 (*C*H), 128.1 (*C*H), 127.6 (*C*H), 91.4 (*d*, $J^{C\text{-}F}$ 179.7, *C*H-F), 63.6 (*d*, $J^{C\text{-}F}$ 20.6, α-imine C*q*), 38.4 (*C*H_2), 28.1 (*d*, $J^{C\text{-}F}$ 5.8, *C*H_2), 26.3 (*d*, $J^{C\text{-}F}$ 9.5, *C*H_2), 25.6 (*d*, $J^{C\text{-}F}$ 19.3, *C*H_2), 21.1 (*C*H_3), 20.9 (*C*H_3) ppm. **ESI-HRMS (positif)** M = $C_{21}H_{22}FNO_2S$, expected $(M+H)^+$ *m/z* 372.1429, observed $(M+H)^+$ *m/z* 372.1432. **$[\alpha]^{20}_D$** -30.9 (*c* = 1.00, $CHCl_3$).

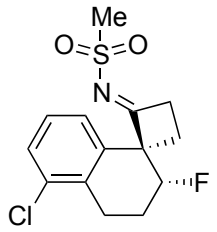
β-Fluoro Cyclobutylimine (B_5)



Chemical Formula: $C_{14}H_{15}F_2NO_2S$
Molecular Weight: 299.34

According to the General Procedure: allylic cyclopropylamine **A_5** (56 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Colorless oil. Isolated yield 82% (49 mg, 0.16 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.30. > 20:1 *d.r.* (^{1}H NMR). 94.5:5.5 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 25.0 (major), 26.9 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 6.70-6.78 (2H, *m*, C^{ar}*H*), 6.64 (1H, *td*, J_1 8.0, J_2 1.4, C^{ar}*H*), 4.56 (1H, *ddd*, $J_1^{H\text{-}F}$ 48.8, J_2 9.2, J_3 2.7, α-fluoro C*H*), 3.37 (2H, *t*, *J* 8.4, benzylic CH_2), 2.55-2.62 (1H, broad *m*, diastereotopic CH_2), 2.35 (3H, *s*, methanesulfonyl CH_3), 2.26-2.37 (2H, *m*, CH_2), 1.66-1.86 (2H, *m*, CH_2), 1.51-1.62 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -115.6 (1F, *s*, C^{ar}*F*), -187.9 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 196.0 (*d*, $J^{C\text{-}F}$ 5.9, imine C*q*), 160.6 (*d*, $J^{C\text{-}F}$ 244, *ipso*(F)-C*q*), 138.4 (*t*, $J^{C\text{-}F}$ 4.4, *meta*(F)-C*q*), 128.5 (*para*(F)-*C*H), 123.1 (*dd*, $J_1^{C\text{-}F}$ 3.9, $J_2^{C\text{-}F}$ 2.8, *meta*(F)-*C*H), 123.0 (*d*, $J^{C\text{-}F}$ 1.7, *ortho*(F)-C*q*), 113.9 (*d*, $J^{C\text{-}F}$ 21.7, *ortho*(F)-*C*H), 90.4 (*d*, $J^{C\text{-}F}$ 180.1, *C*H-F), 62.9 (*dd*, $J_1^{C\text{-}F}$ 21.2, $J_2^{C\text{-}F}$ 2.2, α-imine C*q*), 41.0 (methanesulfonyl *C*H_3), 37.8 (*C*H_2), 27.7 (*d*, $J^{C\text{-}F}$ 5.5, *C*H_2), 24.2 (*d*, $J^{C\text{-}F}$ 19.7, *C*H_2), 19.7 (*dd*, $J_1^{C\text{-}F}$ 9.3, $J_2^{C\text{-}F}$ 4.5, *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{15}F_2NO_2S$, expected $(M+NH_4)^+$ *m/z* 317.1130, observed $(M+NH_4)^+$ *m/z* 317.1133. **$[\alpha]^{20}_D$** -50.0 (*c* = 1.00, $CHCl_3$).

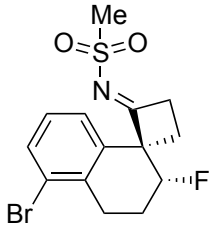
β-Fluoro Cyclobutylimine (B_6)



Chemical Formula: $C_{14}H_{15}ClFNO_2S$
Molecular Weight: 315.79

According to the General Procedure: allylic cyclopropylamine **A_6** (60 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Colorless oil. Isolated yield 79% (50 mg, 0.16 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.20. > 20:1 *d.r.* (^{1}H NMR). 94.5:5.5 *e.r.* Chiral HPLC. Chiralpak IB. *n*-Hex/THF 95:5. 1.2 mL/min. t_R 20.1 (minor), 24.4 (major).**^{1}H NMR** (500 MHz, C_6D_6): δ 7.02 (1H, *dd*, J_1 7.9, J_2 1.1, C^{ar}*H*), 6.82 (1H, *d*, *J* 7.8, C^{ar}*H*), 6.70 (1H, *t*, *J* 7.9, C^{ar}*H*), 4.56 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.0, J_2 9.5, J_3 2.8, α-fluoro C*H*), 3.33-3.42 (2H, *m*, diastereotopic CH_2), 2.63 (1H, *dtd*, J_1 17.9, J_2 6.0, J_3 2.9, diastereotopic CH_2), 2.25-2.41 (2H, *m*, CH_2), 2.36 (3H, *s*, methanesulfonyl CH_3), 1.68-1.85 (2H, *m*, CH_2), 1.51-1.62 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -184.4 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 196.2 (*d*, $J^{C\text{-}F}$ 5.3, imine C*q*), 138.3 (*d*, $J^{C\text{-}F}$ 4.7, C*q*), 134.5 (C*q*), 133.2 (*d*, $J^{C\text{-}F}$ 1.5, C*q*), 128.5 (*C*H), 128.4 (*C*H), 126.2 (*C*H), 90.5 (*d*, $J^{C\text{-}F}$ 180.0, *C*H-F), 63.4 (*d*, $J^{C\text{-}F}$ 20.9, α-imine C*q*), 41.0 (methanesulfonyl *C*H$_3$), 37.9 (*C*H$_2$), 27.8 (*d*, $J^{C\text{-}F}$ 5.5, *C*H$_2$), 24.8 (*d*, $J^{C\text{-}F}$ 7.7, *C*H$_2$), 24.6 (*d*, $J^{C\text{-}F}$ 2.3, *C*H$_2$) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{15}ClFNO_2S$, expected $(M+NH_4)^+$ *m/z* 333.0835, observed $(M+NH_4)^+$ *m/z* 333.0834. **$[\alpha]^{20}_D$** -49.6 (*c* = 1.00, $CHCl_3$).

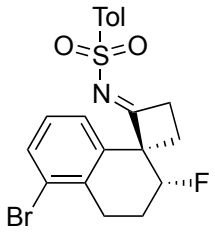
β-Fluoro Cyclobutylimine (B_7)



Chemical Formula: $C_{14}H_{15}BrFNO_2S$
Molecular Weight: 360.24

According to the General Procedure: allylic cyclopropylamine **A_7** (68 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). Colorless oil. Isolated yield 80% (58 mg, 0.16 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.26. > 20:1 *d.r.* (^{1}H NMR). 94.5:5.5 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 8.6 (minor), 9.8 (major). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.22 (1H, *dd*, J_1 7.9, J_2 1.3, C^{ar}*H*), 6.85 (1H, *d*, *J* 7.8, C^{ar}*H*), 6.61 (1H, *t*, *J* 7.9, C^{ar}*H*), 4.56 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.1, J_2 9.5, J_3 2.8, α-fluoro C*H*), 3.32-3.41 (2H, *m*, diastereotopic CH_2), 2.58-2.67 (1H, *m*, CH_2), 2.36 (3H, *s*, methanesulfonyl CH_3), 2.24-2.40 (2H, *m*, CH_2), 1.67-1.81 (2H, *m*, CH_2), 1.51-1.61 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -186.5 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 196.3 (*d*, $J^{C\text{-}F}$ 5.1, imine C*q*), 138.4 (*d*, $J^{C\text{-}F}$ 4.8, C*q*), 134.7 (*d*, $J^{C\text{-}F}$ 1.7, C*q*), 131.9 (*C*H), 128.6 (*C*H), 127.0 (*d*, $J^{C\text{-}F}$ 0.7, *C*H), 125.6 (C*q*), 90.6 (*d*, $J^{C\text{-}F}$ 180.2, *C*H-F), 63.4 (*d*, $J^{C\text{-}F}$ 20.9, α-imine C*q*), 41.0 (methanesulfonyl *C*H$_3$), 37.9 (*C*H$_2$), 27.9 (*d*, $J^{C\text{-}F}$ 5.5, *C*H$_2$), 27.8 (*d*, $J^{C\text{-}F}$ 9.5, *C*H$_2$), 25.0 (*d*, $J^{C\text{-}F}$ 19.6, *C*H$_2$) ppm. **ESI-HRMS (positif)** M = $C_{14}H_{15}BrFNO_2S$, expected $(M+H)^+$ *m/z* 360.0064, observed $(M+H)^+$ *m/z* 360.0065. **$[\alpha]^{20}_D$** -39.7 (*c* = 1.00, $CHCl_3$).

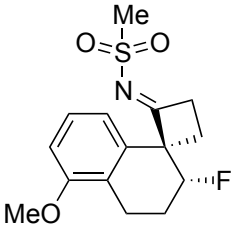
β-Fluoro Cyclobutylimine (B_8)



Chemical Formula: $C_{20}H_{19}BrFNO_2S$
Molecular Weight: 436.34

According to the General Procedure: allylic cyclopropylamine **A_8** (84 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 95:5 → 4:1). White crystalline solid. Isolated yield 77% (67 mg, 0.15 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.32. > 20:1 *d.r.* (^{1}H NMR). 90.5:9.5 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/THF 90:10. 1.0 mL/min. t_R 13.0 (minor), 14.7 (major). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.90 (2H, *d*, *J* 8.3, C^{ar}*H*), 7.1§7 (1H, *dd*, J_1 7.8, J_2 1.1, C^{ar}*H*), 6.85 (1H, *dd*, J_1 7.8, J_2 0.6, C^{ar}*H*), 6.66 (2H, *d*, *J* 8.5, C^{ar}*H*), 6.55 (1H, *t*, *J* 7.9, C^{ar}*H*), 4.47 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.1, J_2 10.1, J_3 3.0, α-fluoro C*H*), 3.40-3.58 (2H, *m*, diastereotopic CH_2), 2.56 (1H, *dq*, J_1 17.8, J_2 3.3, CH_2), 2.28-2.36 (1H, *m*, CH_2), 2.16-2.25 (1H, *m*, CH_2), 1.77 (3H, *s*, CH_3), 1.71-1.81 (1H, *m*, CH_2), 1.56-1.69 (1H, *m*, CH_2), 1.41-1.51 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -188.2 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 195.9 (*d*, $J^{C\text{-}F}$ 4.3, imine C*q*), 144.0 (C*q*), 138.7 (*d*, $J^{C\text{-}F}$ 5.3, C*q*), 137.8 (C*q*), 134.5 (C*q*), 131.8 (*C*H), 129.7 (*C*H), 128.6 (*C*H), 128.4 (*C*H), 127.1 (*C*H), 125.5 (C*q*), 90.8 (*d*, $J^{C\text{-}F}$ 179.8, *C*H-F), 63.7 (*d*, $J^{C\text{-}F}$ 20.6, α-imine C*q*), 38.5 (*C*H_2), 28.3 (*d*, $J^{C\text{-}F}$ 5.5, *C*H_2), 28.0 (*d*, $J^{C\text{-}F}$ 10.0, *C*H_2), 25.0 (*d*, $J^{C\text{-}F}$ 19.5, *C*H_2), 21.1 (*C*H_3) ppm. **ESI-HRMS (positif)** M = $C_{20}H_{19}BrFNO_2S$, expected $(M+H)^+$ *m/z* 436.0377, 438.0357; observed $(M+H)^+$ *m/z* 436.0385, 438.0365. **$[\alpha]^{20}_D$** -33.3 (*c* = 1.00, $CHCl_3$).

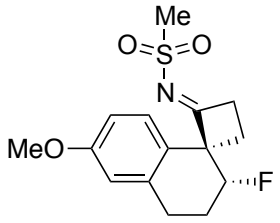
β-Fluoro Cyclobutylimine (B_9)



Chemical Formula: $C_{15}H_{18}FNO_3S$
Molecular Weight: 311.37

According to the General Procedure: allylic cyclopropylamine **A_9** (59 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). Colorless oil. Isolated yield 87% (54 mg, 0.17 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.11. > 20:1 *d.r.* (^{1}H NMR). 95:5 *e.r.* Chiral HPLC. Chiralcel OD-H. *n*-Hex/*i*-PrOH 85:15. 1.0 mL/min. t_R 20.4 (major), 24.0 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 6.98 (1H, *t*, *J* 8.0, C^{ar}*H*), 6.74 (1H, *d*, *J* 7.7, C^{ar}*H*), 6.33 (1H, *dd*, J_1 8.1, J_2 0.6, C^{ar}*H*), 4.71 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.2, J_2 9.6, J_3 2.9, α-fluoro C*H*), 3.43 (2H, *t*, *J* 8.6, benzylic CH_2), 3.24 (3H, *s*, methoxy CH_3-O), 2.80 (1H, *dtd*, J_1 17.9, J_2 6.0, J_3 3.1, diastereotopic CH_2), 2.52 (1H, *ddd*, J_1 14.9, J_2 8.3, J_3 6.6, CH_2), 2.35-2.42 (1H, *m*, CH_2), 2.36 (3H, *s*, methanesulfonyl CH_3), 1.82-1.99 (2H, *m*, CH_2), 1.67-1.77 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -187.3 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 197.1 (*d*, $J^{C\text{-}F}$ 5.2, imine C*q*), 157.1 (C*q*), 137.4 (*d*, $J^{C\text{-}F}$ 4.4, C*q*), 128.1 (*C*H), 124.2 (C*q*), 119.5 (*C*H), 108.7 (*C*H), 91.0 (*d*, $J^{C\text{-}F}$ 179.4, *C*H-F), 63.5 (*d*, $J^{C\text{-}F}$ 20.7, α-imine C*q*), 54.8 (methoxy *C*H_3-O), 41.0 (methanesulfonyl *C*H_3), 37.9 (*C*H_2), 27.8 (*d*, $J^{C\text{-}F}$ 5.3, *C*H_2), 24.8 (*d*, $J^{C\text{-}F}$ 19.3, *C*H_2), 20.9 (*d*, $J^{C\text{-}F}$ 9.4, *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{18}FNO_3S$, expected $(M+H)^+$ *m/z* 312.1065, observed $(M+H)^+$ *m/z* 312.1063. **$[\alpha]^{20}_D$** -45.5 (*c* = 1.00, $CHCl_3$).

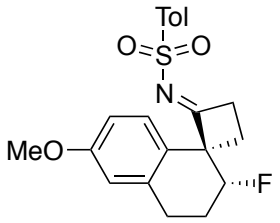
β-Fluoro Cyclobutylimine (B_{10})



Chemical Formula: $C_{15}H_{18}FNO_3S$
Molecular Weight: 311.37

According to the General Procedure: allylic cyclopropylamine **A_{10}** (59 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). Colorless oil. Isolated yield 84% (52 mg, 0.17 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.13. > 20:1 *d.r.* (^{1}H NMR). 93:7 *e.r.* Chiral HPLC. Chiralcel OD-H. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 24.3 (major), 30.9 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 6.94 (1H, *d*, *J* 8.7, C^{ar}*H*), 6.62 (1H, *dd*, J_1 8.7, J_2 2.8, C^{ar}*H*), 6.41 (1H, *d*, *J* 2.8, C^{ar}*H*), 4.68 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.1, J_2 9.0, J_3 2.7, α-fluoro C*H*), 3.41 (2H, *t*, *J* 8.7, benzylic CH_2), 3.27 (3H, *s*, methoxy CH_3-O), 2.49-2.55 (1H, *m*, diastereotopic CH_2), 2.37-2.43 (1H, *m*, CH_2), 2.36 (3H, *s*, methanesulfonyl CH_3), 2.26-2.35 (1H, *m*, CH_2), 1.78-1.94 (2H, *m*, CH_2), 1.67-1.75 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -187.0 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 197.4 (*d*, $J^{C\text{-}F}$ 6.1, imine C*q*), 159.3 (C*q*), 136.4 (*d*, $J^{C\text{-}F}$ 1.5, C*q*), 128.9 (*d*, $J^{C\text{-}F}$ 0.9, *C*H), 127.1 (*C*H), 113.7 (*d*, $J^{C\text{-}F}$ 26.2, *C*H), 91.1 (*d*, $J^{C\text{-}F}$ 180.2, *C*H-F), 63.1 (*d*, $J^{C\text{-}F}$ 20.9, α-imine C*q*), 54.8 (methoxy *C*H$_3$-O), 41.0 (methanesulfonyl *C*H$_3$), 37.7 (*C*H$_2$), 27.8 (*d*, $J^{C\text{-}F}$ 5.8, *C*H$_2$), 26.3 (*d*, $J^{C\text{-}F}$ 9.1, *C*H$_2$), 25.5 (*d*, $J^{C\text{-}F}$ 19.6, *C*H$_2$) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{18}FNO_3S$, expected $(M+H)^+$ *m/z* 312.1065, observed $(M+H)^+$ *m/z* 312.1065. **$[\alpha]^{20}_D$** -40.6 (*c* = 1.00, $CHCl_3$).

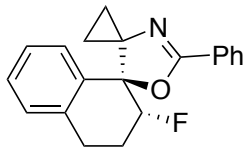
β-Fluoro Cyclobutylimine (B_{11})



Chemical Formula: $C_{21}H_{22}FNO_3S$
Molecular Weight: 387.47

According to the General Procedure: allylic cyclopropylamine **A_{11}** (77 mg, 0.20 mmol, 1.0 equiv.), chiral phosphoric acid (R_a)-TIPS-TRIP (**L_3**) (24 mg, 0.02 mmol, 10 mol%), powdered Selectfluor™ (177 mg, 0.50 mmol, 2.5 equiv.), and dried Na_3PO_4 (131 mg, 0.80 mmol, 4.0 equiv.) in anhydrous C_6H_5F/*n*-Hex 1:1 (*v/v*) (total volume: 2.5 mL, 0.08 M). Purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). White crystalline solid. Isolated yield 78% (60 mg, 0.16 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.19. > 20:1 *d.r.* (^{1}H NMR). 92.5:7.5 *e.r.* Chiral HPLC. Chiralcel OD-H. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 11.5 (major), 20.4 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.91 (2H, *d*, *J* 8.3, C^{ar}*H*), 6.93 (1H, *d*, *J* 8.6, C^{ar}*H*), 6.65 (2H, *d*, *J* 8.3, C^{ar}*H*), 6.56 (1H, *dd*, J_1 8.7, J_2 2.7, C^{ar}*H*), 6.35 (1H, *d*, *J* 2.7, C^{ar}*H*), 4.63 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.2, J_2 9.4, J_3 2.9, α-fluoro C*H*), 3.48-3.60 (2H, *m*, benzylic CH_2), 3.24 (3H, *s*, methoxy CH_3-O), 2.40-2.47 (2H, *m*, diastereotopic CH_2), 2.20 (1H, *ddd*, J_1 14.8, J_2 8.6, J_3 6.1, CH_2), 1.92 (1H, *qd*, J_1 9.8, J_2 1.8, CH_2), 1.77 (3H, *s*, CH_3), 1.70-1.81 (1H, *m*, CH_2), 1.60-1.69 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -186.6 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 197.1 (*d*, $J^{C\text{-}F}$ 5.3, imine C*q*), 159.2 (C*q*), 143.8 (C*q*), 138.1 (C*q*), 136.3 (*d*, $J^{C\text{-}F}$ 1.5, C*q*), 129.7 (*C*H), 129.0 (*d*, $J^{C\text{-}F}$ 1.2, *C*H), 113.6 (*d*, $J^{C\text{-}F}$ 29.0, *C*H), 91.3 (*d*, $J^{C\text{-}F}$ 179.8, *C*H-F), 63.4 (*d*, $J^{C\text{-}F}$ 20.6, α-imine C*q*), 54.7 (methoxy *C*H$_3$-O), 38.2 (*C*H$_2$), 28.1 (*d*, $J^{C\text{-}F}$ 5.7, *C*H$_2$), 26.6 (*d*, $J^{C\text{-}F}$ 9.5, *C*H$_2$), 25.6 (*d*, $J^{C\text{-}F}$ 19.5, *C*H$_2$), 21.1 (*C*H$_3$) ppm. **ESI-HRMS (positif)** M = $C_{21}H_{22}FNO_3S$, expected $(M+H)^+$ *m/z* 388.1378, observed $(M+H)^+$ *m/z* 388.1380. **$[\alpha]^{20}_D$** -46.6 (*c* = 1.00, $CHCl_3$).

Undesired Fluorocyclization Product

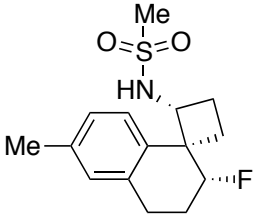


Chemical Formula: $C_{20}H_{18}FNO$
Molecular Weight: 307.36

^{1}H NMR (500 MHz, C_6D_6): δ 8.07-8.12 (2H, *m*, C^{ar}*H*), 7.73-7.77 (1H, *m*, C^{ar}*H*), 6.95-7.07 (5H, *m*, C^{ar}*H*), 6.80-6.84 (1H, *m*, C^{ar}*H*), 4.92 (1H, *ddd*, $J_1^{H\text{-}F}$ 47.9, J_2 7.7, J_3 2.2, α-fluoro C*H*), 2.65-2.73 (1H, *m*, CH_2), 2.39 (1H, *dt*, J_1 17.0, J_2 5.8, CH_2), 1.96-2.13 (1H, *m*, CH_2), 1.72-1.82 (1H, *m*, CH_2), 1.62-1.67 (1H, *m*, CH_2), 1.44-1.50 (1H, *m*, CH_2), 1.34-1.41 (1H, *m*, CH_2), 0.63 (1H, *ddd*, J_1 12.7, J_2 7.6, J_3 5.1, cyclopropylic CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -194.8 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 161.3 (C*q*), 136.2 (C*q*), 131.1 (*C*H), 129.8 (C*q*), 128.6 (*C*H), 128.5 (*C*H), 128.4 (*C*H), 127.2 (*C*H), 92.3 (*d*, $J^{C\text{-}F}$ 176.9, *C*H-F), 84.3 (*d*, $J^{C\text{-}F}$ 24.3, C*q*-O), 58.1 (C*q*-N), 26.2 (*d*, $J^{C\text{-}F}$ 20.1, *C*H$_2$), 25.3 (*d*, $J^{C\text{-}F}$ 8.0, *C*H$_2$), 13.1 (cyclopropylic *C*H$_2$), 12.0 (*d*, $J^{C\text{-}F}$ 7.4, cyclopropylic *C*H$_2$) ppm. **ESI-HRMS (positif)** M = $C_{20}H_{18}FNO$, expected $(M+H)^+$ *m/z* 308.1446, observed $(M+H)^+$ *m/z* 308.1446. **$[\alpha]^{20}_D$** +33.1 (*c* = 1.00, $CHCl_3$).

Diastereoselective Reduction

Characterization of Products
Fluorinated Amine (C_3)

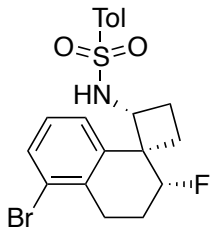


Chemical Formula: $C_{15}H_{20}FNO_2S$
Molecular Weight: 297.39

To a cooled (-78 °C, dry ice/acetone bath) solution of β-fluoro cyclobutylimine **B_3** (25 mg, 0.08 mmol, 1.0 equiv.) in anhydrous THF (4.5 mL) was added L-Selectride (1.0 M solution in THF, 200 μL, 0.20 mmol, 2.5 equiv.) dropwise *via* syringe. The resultant pale-orange solution was then stirred at -78 °C for 6 h. Upon completion, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). White crystalline solid. Isolated yield 87% (21 mg, 0.07 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 4:1) 0.19. > 20:1 *d.r.* (^{1}H NMR). 93:7 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 21.9 (minor), 25.4 (major). **^{1}H NMR** (500 MHz, C_6D_6): δ 6.99 (1H, *d*, *J* 8.0, C^{ar}*H*), 6.88 (1H, *d*, *J* 8.2, C^{ar}*H*), 6.68 (1H, *s*, C^{ar}*H*), 4.49 (1H, *ddd*, J_1 49.5, J_2 4.9, J_3 1.5, α-fluoro C*H*), 3.58-3.63 (2H, *m*, N*H* + C*H*-N), 2.83 (1H, *ddd*, J_1 17.6, J_2 11.4, J_3 6.7, diastereotopic CH_2), 2.45 (1H, *ddd*, J_1 17.2, J_2 7.1, J_3 2.2, CH_2), 2.04-2.13 (2H, *m*, CH_2), 2.09 (3H, *s*, methanesulfonyl CH_3), 1.92-2.03 (1H, *m*, CH_2), 2.00 (3H, *s*, CH_3), 1.85-1.92 (2H, *m*, CH_2), 1.51-1.59 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -188.6 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 137.5 (C*q*), 136.8 (C*q*), 131.0 (C*q*), 130.5 (*C*H), 127.5 (*C*H), 126.5 (*C*H), 95.3 (*d*, $J^{C\text{-}F}$ 176, α-fluoro *C*H), 53.3 (*d*, $J^{C\text{-}F}$ 11.6, *C*H-N), 51.8 (*d*, $J^{C\text{-}F}$ 19.7, α-carbonyl C*q*), 41.5 (methanesulfonyl *C*H$_3$), 28.5 (*C*H$_2$), 26.1 (*d*,

$J^{C\text{-}F}$ 3.4, CH_2), 24.6 (*d*, $J^{C\text{-}F}$ 4.5, CH_2), 23.8 (*d*, $J^{C\text{-}F}$ 20.5, CH_2), 20.9 (CH_3) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{20}FNO_2S$, expected $(M+H)^+$ *m/z* 298.1272, observed $(M+H)^+$ *m/z* 298.1274. $[\alpha]^{20}_D$ +36.1 (*c* = 1.00, $CHCl_3$).

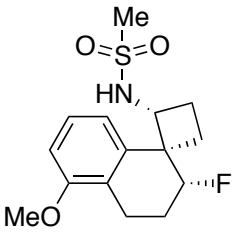
Fluorinated Amine (C_8)



Chemical Formula: $C_{20}H_{21}BrFNO_2S$
Molecular Weight: 438.35

To a cooled (-78 °C, dry ice/acetone bath) solution of β-fluoro cyclobutylimine **B_8** (35 mg, 0.08 mmol, 1.0 equiv.) in anhydrous THF (4.5 mL) was added L-Selectride (1.0 M solution in THF, 200 μL, 0.20 mmol, 2.5 equiv.) dropwise *via* syringe. The resultant pale-orange solution was then stirred at -78 °C for 6 h. Upon completion, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). White crystalline solid. Isolated yield 94% (32 mg, 0.075 mmol). $\mathbf{R}_f$ (silica gel, *n*-Hex/EtOAc 4:1) 0.24. > 20:1 *d.r.* (^{1}H NMR). 90.5:9.5 *e.r.* Chiral HPLC. Chiralcel OJ-H. *n*-Hex/*i*-PrOH 80:20. 0.9 mL/min. t_R 8.4 (major), 11.1 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.42 (2H, *dd*, J_1 6.6, J_2 1.7, $C^{ar}H$), 7.20 (1H, *d*, *J* 7.9, $C^{ar}H$), 6.91 (1H, *d*, *J* 7.9, $C^{ar}H$), 6.73 (2H, *d*, *J* 7.0, $C^{ar}H$), 6.65 (1H, *t*, *J* 7.8, $C^{ar}H$), 4.84 (1H, *d*, *J* 10.2, sulfonamide N*H*), 4.25 (1H, *dd*, $J_1^{H\text{-}F}$ 49.1, J_2 4.9, α-fluoro C*H*), 3.72 (1H, *q*, *J* 8.9, C*H*-N), 2.65-2.72 (1H, *m*, diastereotopic CH_2), 2.38 (1H, *dd*, J_1 17.8, J_2 6.9, CH_2), 1.98 (3H, *s*, CH_3), 1.89-1.96 (1H, *m*, CH_2), 1.79-1.84 (2H, *m*, CH_2), 1.65-1.74 (1H, *m*, CH_2), 1.53-1.62 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): δ -189.1 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): δ 143.0 (C*q*), 139.4 (C*q*), 137.1 (C*q*), 136.5 (C*q*), 131.4 (*C*H), 129.7 (*C*H), 126.8 (*C*H), 126.32 (*C*H), 126.30 (*C*H), 94.4 (*d*, $J^{C\text{-}F}$ 176, *C*H-F), 53.8 (*d*, $J^{C\text{-}F}$ 11.1, *C*H-N), 52.4 (*d*, $J^{C\text{-}F}$ 19.2, α-carbonyl C*q*), 28.0 (CH_3), 26.4 (*d*, $J^{C\text{-}F}$ 4.5, CH_2), 26.3 (CH_2), 23.3 (*d*, $J^{C\text{-}F}$ 20.6, CH_2), 21.3 (CH_2) ppm. **ESI-HRMS (positif)** M = $C_{20}H_{21}BrFNO_2S$, expected $(M+H)^+$ *m/z* 437.0460, 439.0440; observed $(M+H)^+$ *m/z* 437.0465, 439.0445. $[\alpha]^{20}_D$ +31.3 (*c* = 1.00, $CHCl_3$).

Fluorinated Amine (C_9)

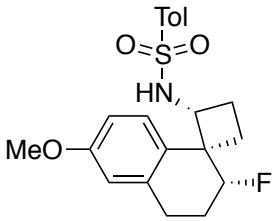


Chemical Formula: $C_{15}H_{20}FNO_3S$
Molecular Weight: 313.39

To a cooled (-78 °C, dry ice/acetone bath) solution of β-fluoro cyclobutylimine **B_9** (25 mg, 0.08 mmol, 1.0 equiv.) in anhydrous THF (4.5 mL) was added L-Selectride (1.0 M solution in THF, 200 μL, 0.20 mmol, 2.5 equiv.) dropwise *via* syringe. The resultant pale-orange solution was then stirred at -78 °C for 6 h. Upon completion, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). White crystalline solid. Isolated yield 89% (22 mg, 0.07 mmol). $\mathbf{R}_f$ (silica gel, *n*-Hex/EtOAc 3:2) 0.10. > 20:1 *d.r.* (^{1}H NMR). 95:5 *e.r.* Chiral HPLC. Chiralpak IC. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. t_R 23.5 (major), 32.1 (minor). **^{1}H NMR** (500 MHz, C_6D_6): δ 7.06 (1H, *t*, *J* 8.0, $C^{ar}H$), 6.81 (1H, *d*, *J* 7.9, $C^{ar}H$), 6.43 (1H, *d*, *J* 8.0, $C^{ar}H$), 4.46 (1H,

ddd, $J_1^{H\text{-}F}$ 49.4, J_2 4.8, J_3 1.6, α-fluoro C*H*), 3.91 (1H, broad *d*, *J* 10.3, sulfonamide N*H*), 3.63 (1H, *q*, *J* 8.8, C*H*-N), 3.25 (3H, *s*, methoxy CH_3-O), 2.86-2.89 (2H, *m*, diastereotopic CH_2), 2.07-2.14 (1H, *m*, CH_2), 2.03 (3H, *s*, methanesulfonyl CH_3), 1.89-1.97 (3H, *m*, CH_2), 1.63-1.71 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): *δ* -188.3 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): *δ* 157.6 (C*q*), 135.4 (C*q*), 127.2 (*C*H), 126.7 (C*q*), 118.5 (*C*H), 108.6 (*C*H), 95.0 (*d*, $J^{C\text{-}F}$ 175.5, *C*H-F), 54.8 (*C*H_3-O), 53.4 (*d*, $J^{C\text{-}F}$ 11.5, *C*H-N), 51.9 (*d*, $J^{C\text{-}F}$ 19.6, α-carbonyl C*q*), 41.4 (methanesulfonyl *C*H_3), 28.7 (*C*H_2), 26.4 (*d*, $J^{C\text{-}F}$ 3.4, *C*H_2), 23.0 (*d*, $J^{C\text{-}F}$ 20.5, *C*H_2), 19.2 (*d*, $J^{C\text{-}F}$ 4.6, *C*H_2) ppm. **ESI-HRMS (positif)** M = $C_{15}H_{20}FNO_3S$, expected $(M+H)^+$ *m/z* 314.1221, observed $(M+H)^+$ *m/z* 314.1223. **$[\alpha]^{20}_D$** +28.9 (*c* = 1.00, $CHCl_3$).

Fluorinated Amine (C_{11})



Chemical Formula: $C_{21}H_{24}FNO_3S$
Molecular Weight: 389.48

To a cooled (-78 °C, dry ice/acetone bath) solution of β-fluoro cyclobutylimine **B_{11}** (92.5:7.5 *e.r.*, 31 mg, 0.08 mmol, 1.0 equiv.) in anhydrous THF (4.5 mL) was added L-Selectride (1.0 M solution in THF, 200 μL, 0.20 mmol, 2.5 equiv.) dropwise *via* syringe. The resultant pale-orange solution was then stirred at -78 °C for 6 h. Upon completion, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc 9:1 → 4:1). Colorless oil. Isolated yield 89% (27 mg, 0.07 mmol). **R_f** (silica gel, *n*-Hex/EtOAc 3:2) 0.26. > 20:1 *d.r.* (^{1}H NMR). 92:8 *e.r.* Chiral HPLC. Chiralcel OD-H. *n*-Hex/*i*-PrOH 80:20. 1.0 mL/min. **t_R** 15.9 (major), 18.4 (minor). **^{1}H NMR** (500 MHz, C_6D_6): *δ* 7.55 (2H, *d*, *J* 8.3, C^{ar}*H*), 7.00 (1H, *d*, *J* 8.6, C^{ar}*H*), 6.72 (2H, *d*, *J* 8.3, C^{ar}*H*), 6.69 (1H, *dd*, J_1 8.6, J_2 2.8, C^{ar}*H*), 6.49 (1H, *d*, *J* 2.7, C^{ar}*H*), 4.43 (1H, *ddd*, $J_1^{H\text{-}F}$ 49.6, J_2 5.0, J_3 1.5, α-fluoro C*H*), 4.39 (1H, *d*, *J* 10.4, sulfonamide N*H*), 3.75 (1H, *q*, *J* 8.6, C*H*-N), 3.33 (3H, *s*, methoxy CH_3-O), 2.80 (1H, *ddd*, J_1 17.5, J_2 10.9, J_3 7.0, diastereotopic CH_2), 2.37 (1H, *ddd*, J_1 17.0, J_2 6.6, J_3 2.9, CH_2), 1.91-2.02 (2H, *m*, CH_2), 1.90 (3H, *s*, CH_3), 1.80-1.89 (2H, *m*, CH_2), 1.57-1.65 (1H, *m*, CH_2) ppm. **^{19}F NMR** (376 MHz, C_6D_6): *δ* -187.8 (1F, *s*, C(sp^3)-*F*) ppm. **^{13}C NMR** (125 MHz, C_6D_6): *δ* 159.0 (C*q*), 142.8 (C*q*), 139.8 (C*q*), 138.9 (C*q*), 129.6 (*C*H), 127.8 (*C*H), 127.1 (*C*H), 126.0 (C*q*), 114.3 (*C*H), 113.4 (*C*H), 95.3 (*d*, $J^{C\text{-}F}$ 175.7, *C*H-F), 54.7 (methoxy *C*H_3-O), 53.6 (*d*, $J^{C\text{-}F}$ 11.4, *C*H-N), 51.6 (*d*, $J^{C\text{-}F}$ 19.7, α-carbonyl C*q*), 28.5 (*C*H_2), 26.4 (*d*, $J^{C\text{-}F}$ 3.5, *C*H_2), 25.1 (*d*, $J^{C\text{-}F}$ 4.9, *C*H_2), 23.8 (*d*, $J^{C\text{-}F}$ 20.4, *C*H_2), 21.1 (*C*H_3) ppm. **ESI-HRMS (positif)** M = $C_{21}H_{24}FNO_3S$, expected $(M+H)^+$ *m/z* 390.1534, observed $(M+H)^+$ *m/z* 390.1531. **$[\alpha]^{20}_D$** +40.8 (*c* = 1.00, $CHCl_3$).

References and Notes

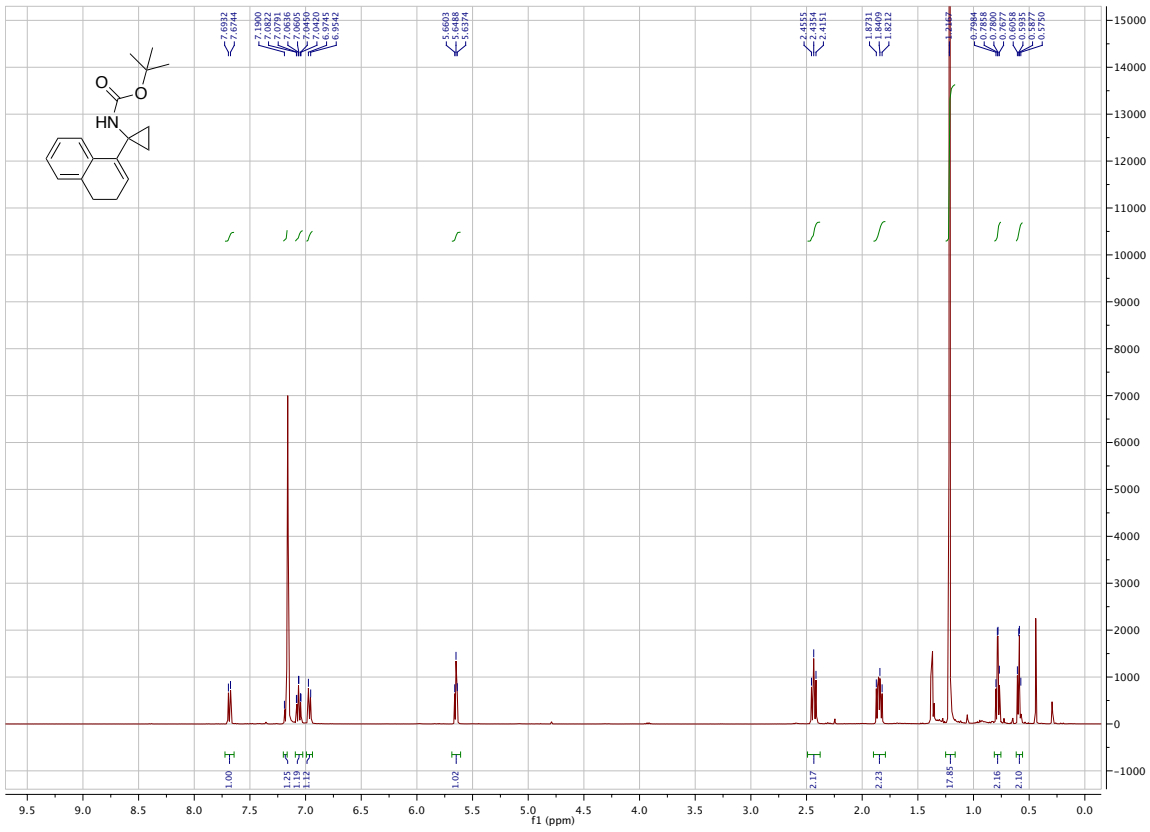
(1) A. Krasovskiy, P. Knochel, *Synthesis* **2006**, *5*, 890-891.

(2) (a) F. Romanov-Michailidis, L. Guénée, A. Alexakis, *Angew. Chem., Int. Ed.* **2013**, *52*, 9266-9270; (b) F. Romanov-Michailidis, L. Guénée, A. Alexakis, *Org. Lett.* **2013**, *15*, 5890-5893.

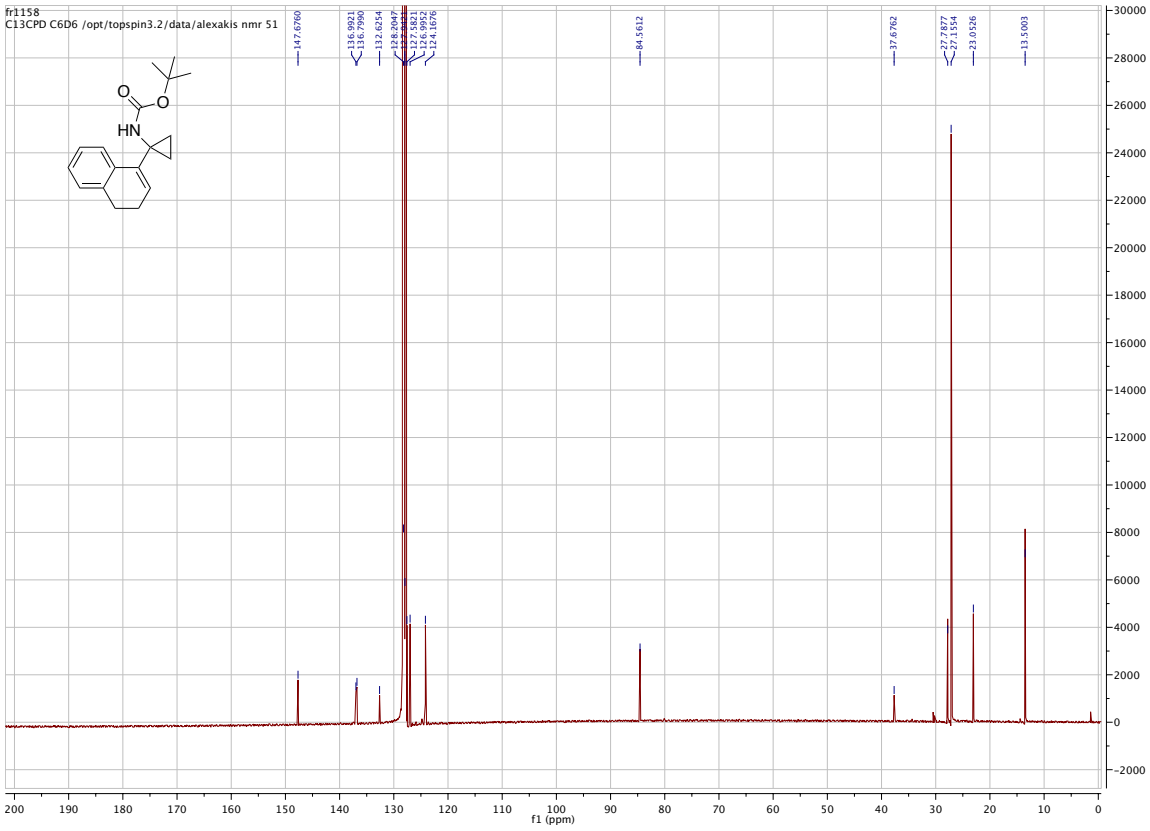
NMR Spectra

Substrate (A_1-Boc)

^{1}H NMR 400 MHz, C_6D_6

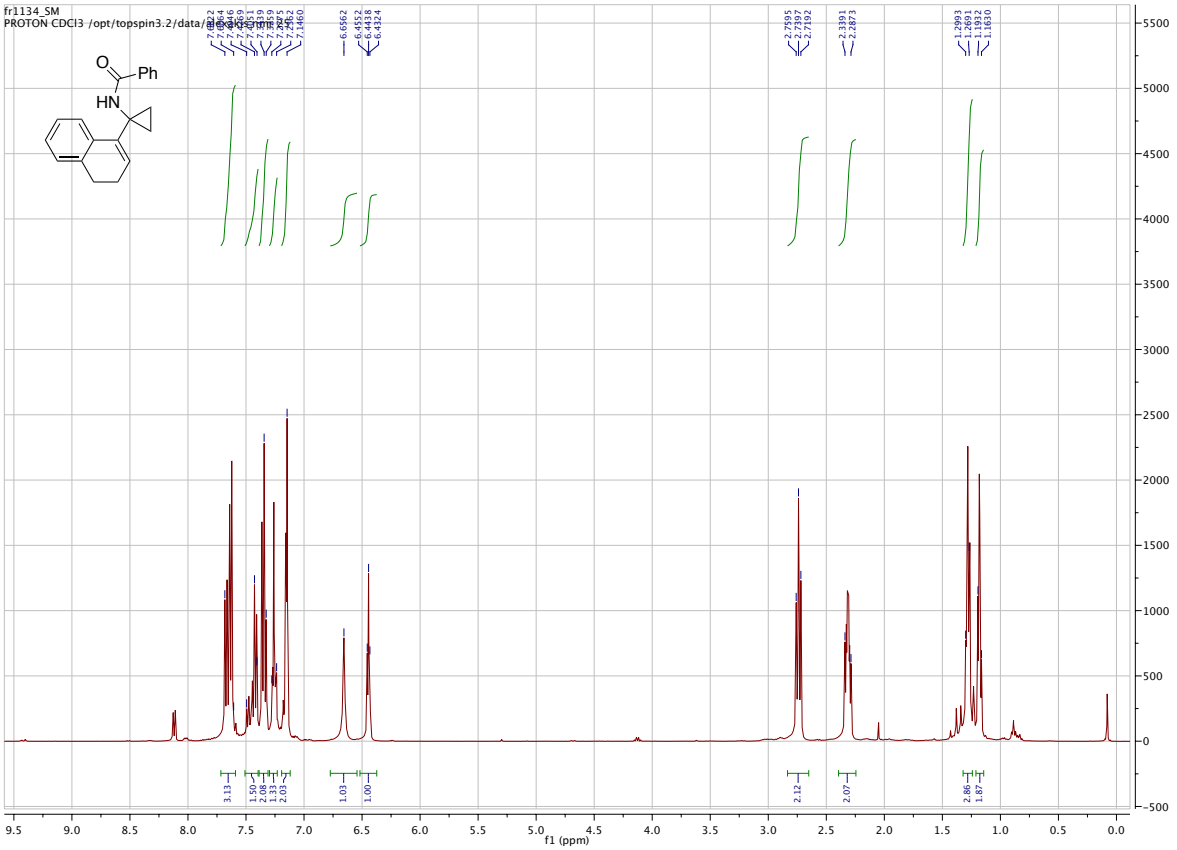


^{13}C NMR 100 MHz, C_6D_6

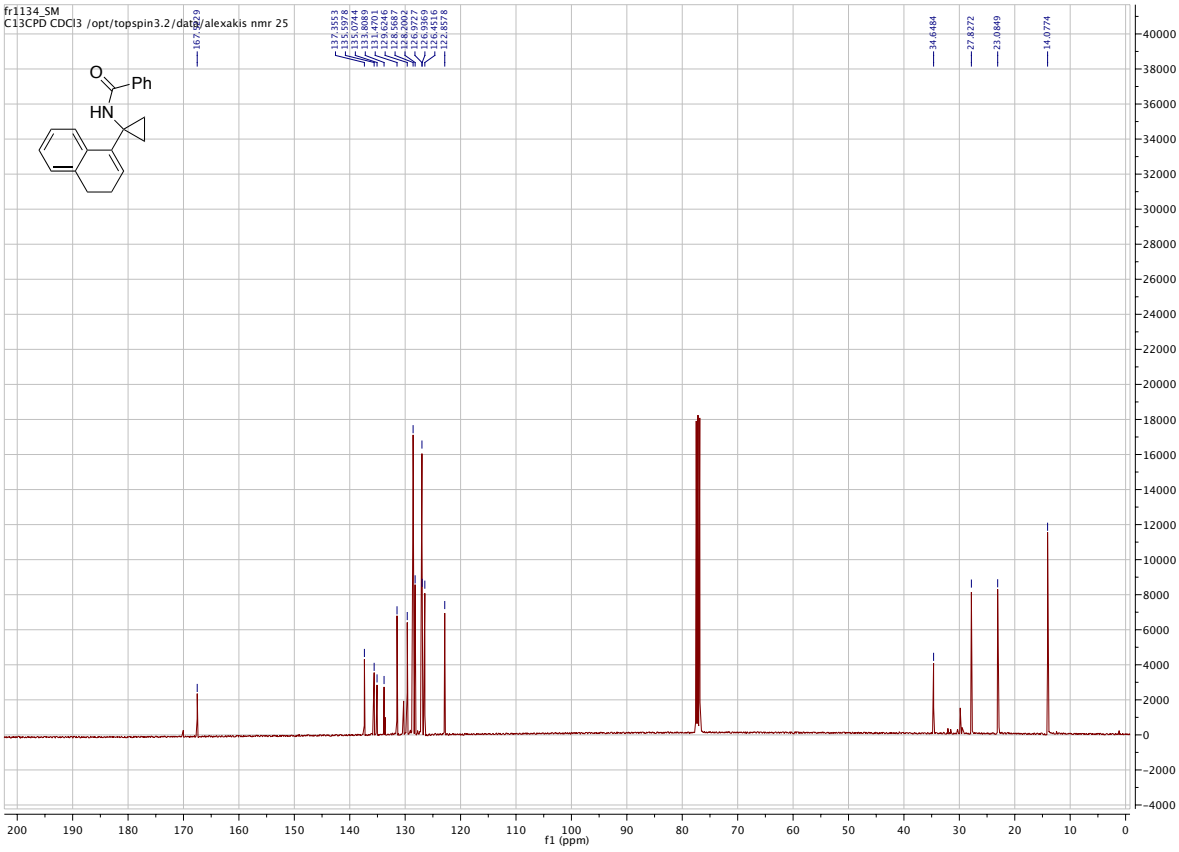


Substrate (A_1-Bz)

^{1}H NMR 400 MHz, $CDCl_3$

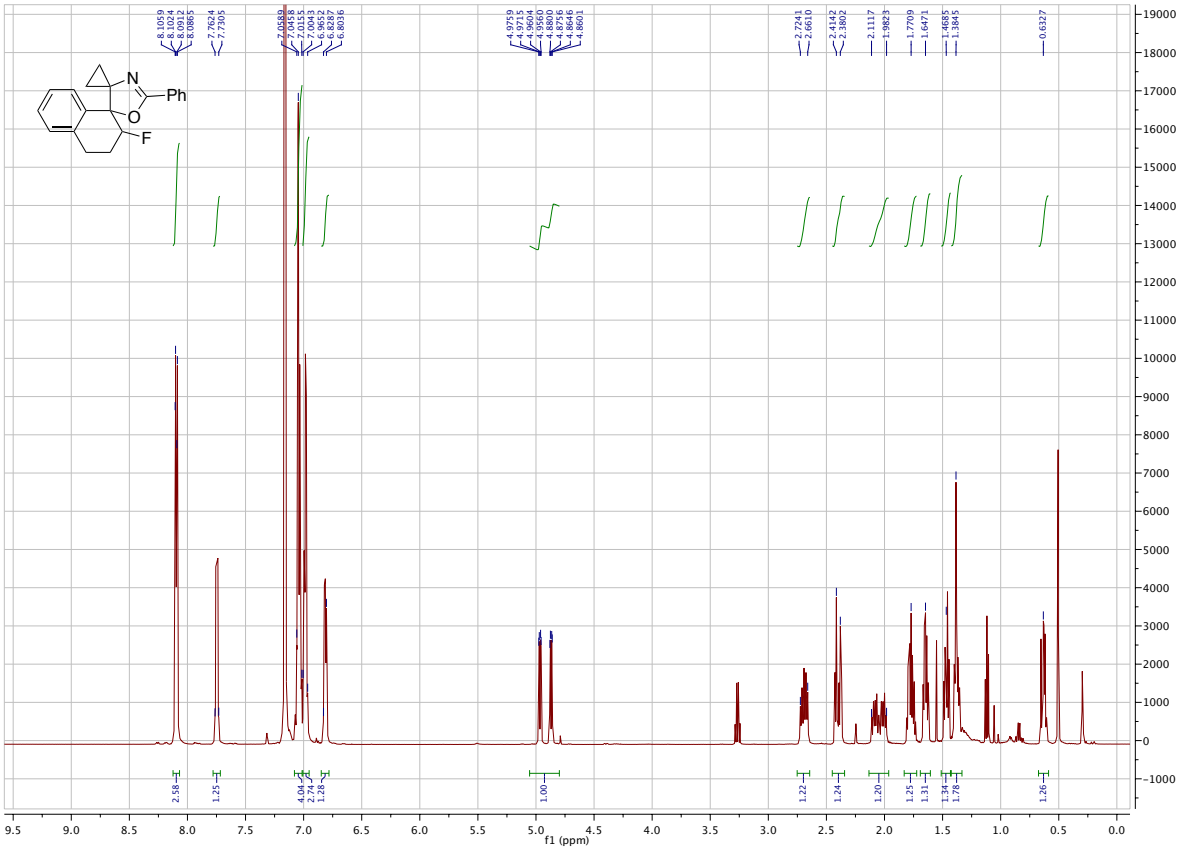


^{13}C NMR 100 MHz, $CDCl_3$

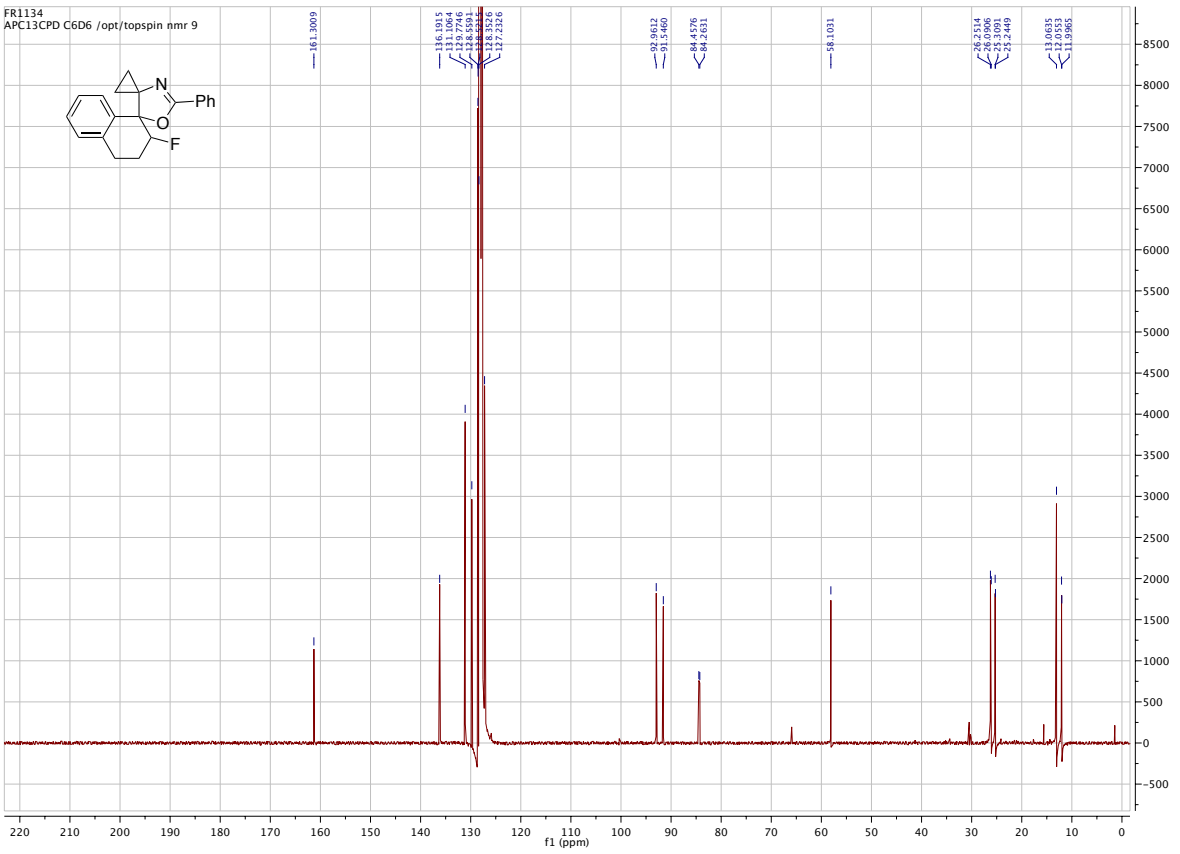


Fluorocyclization Product

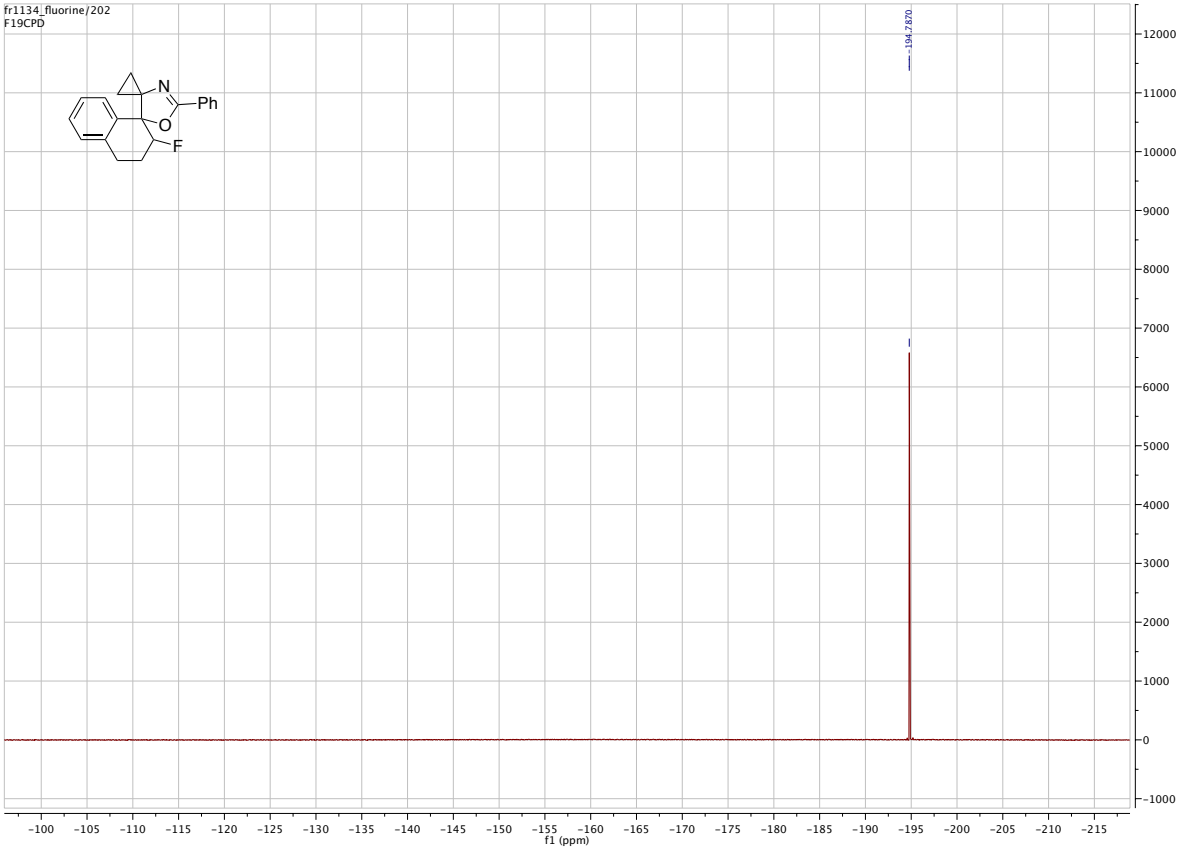
^{1}H NMR 500 MHz, C_6D_6



^{13}C NMR 125 MHz, C_6D_6

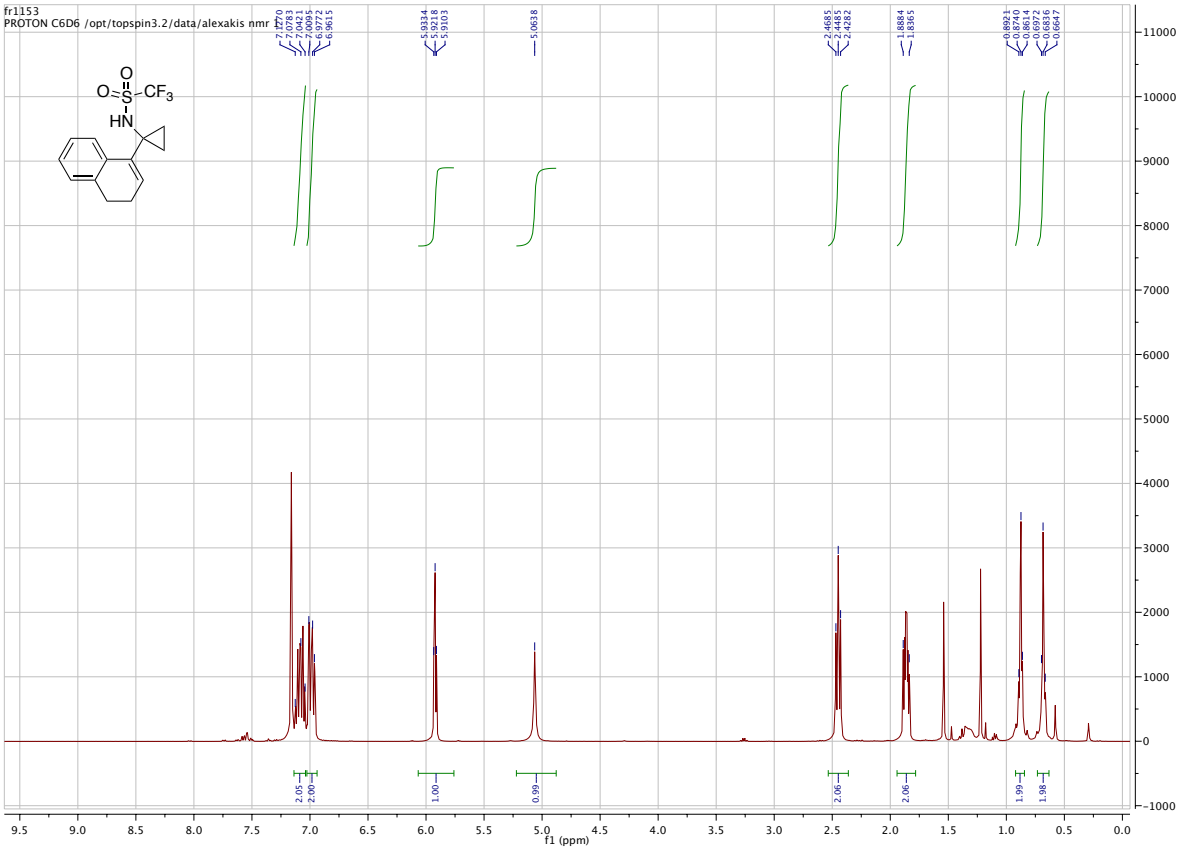


^{19}F NMR 375 MHz, C_6D_6

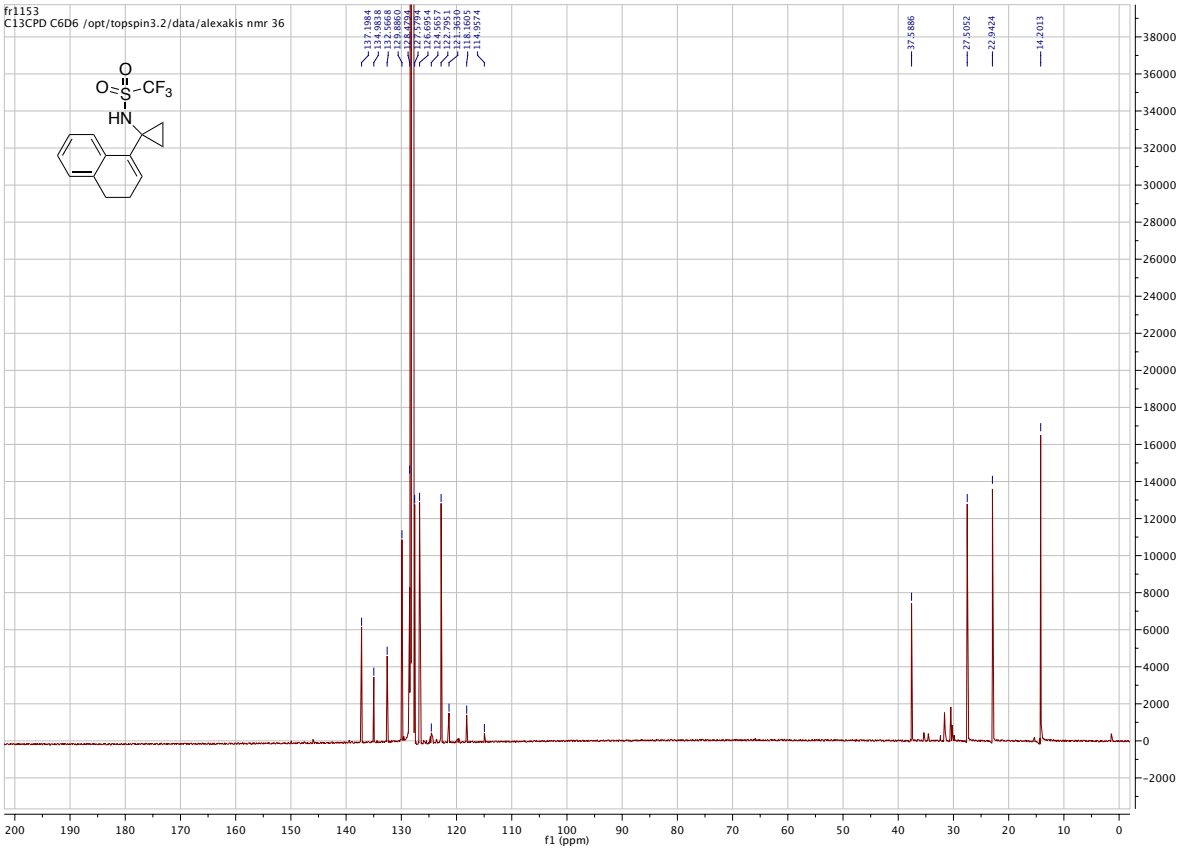


Substrate (A_1-Tf)

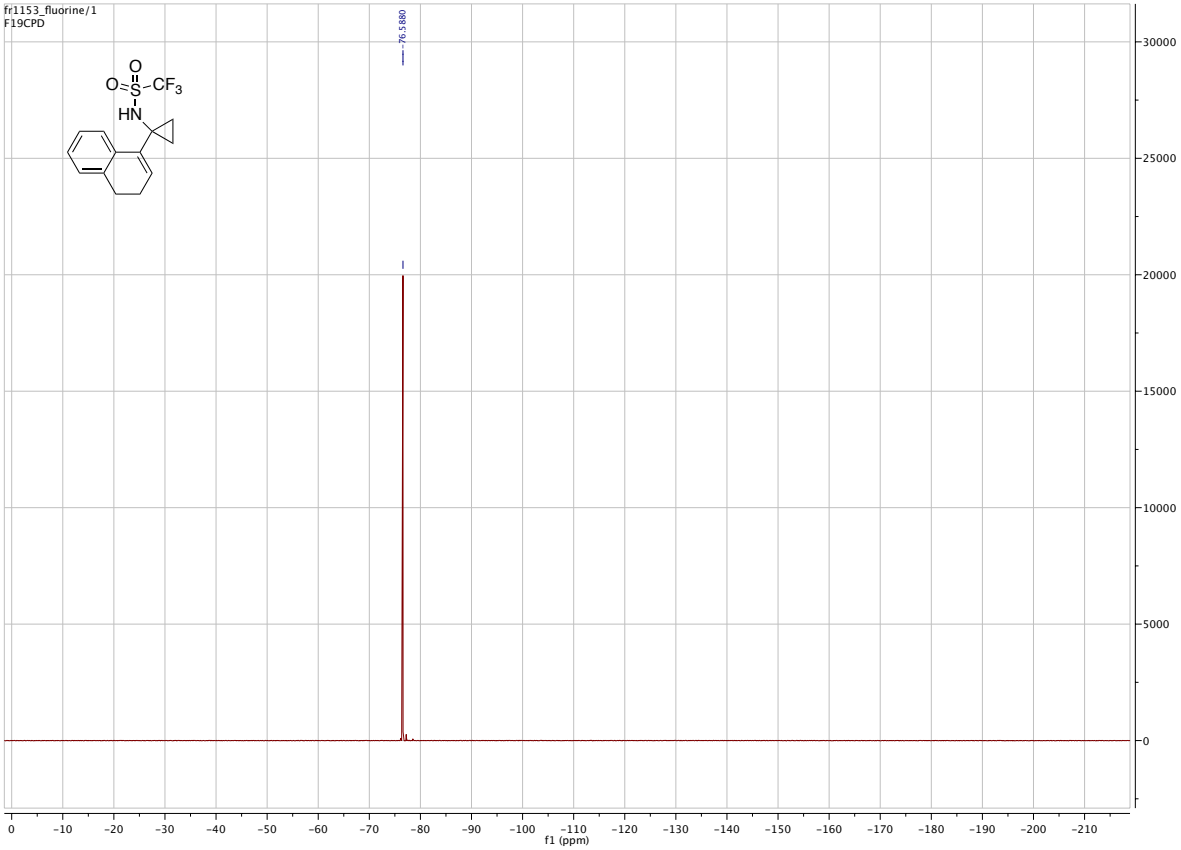
^{1}H NMR 400 MHz, C_6D_6



^{13}C NMR 100 MHz, C_6D_6

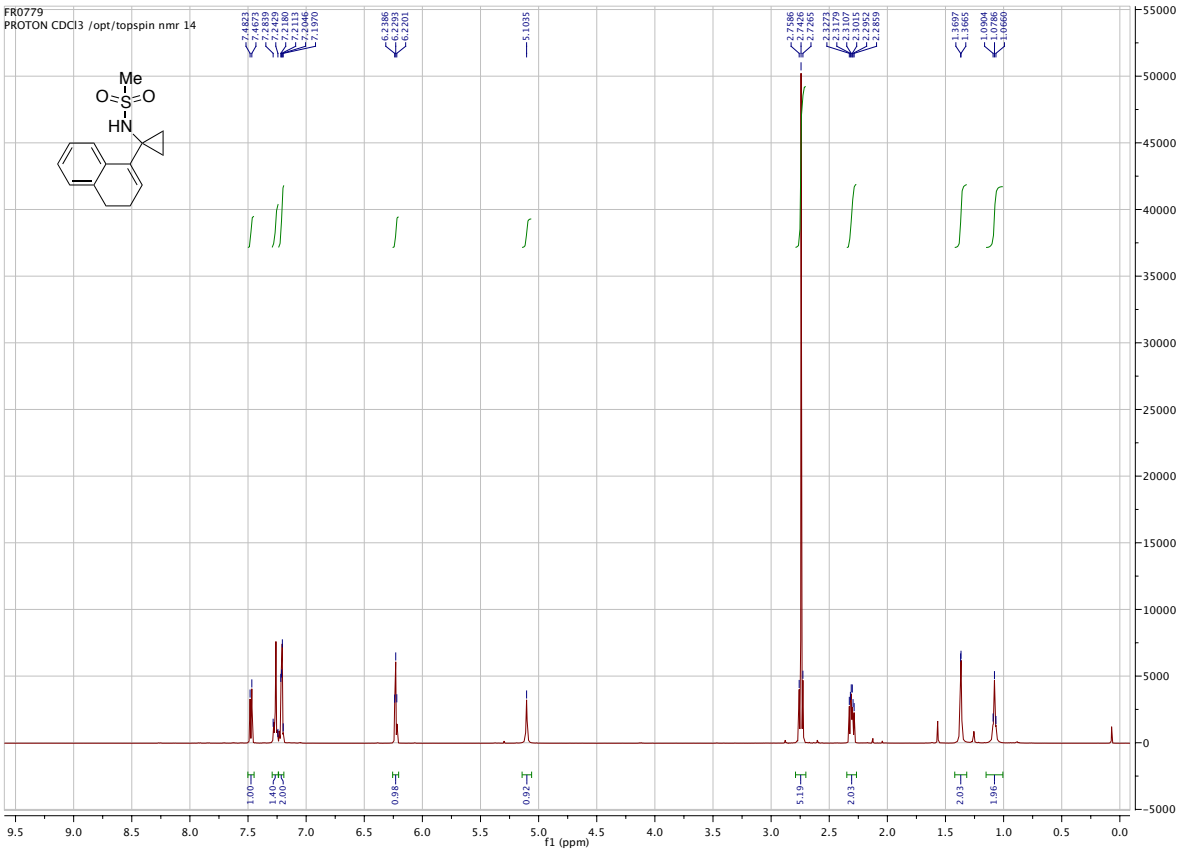


^{19}F NMR 375 MHz, C_6D_6

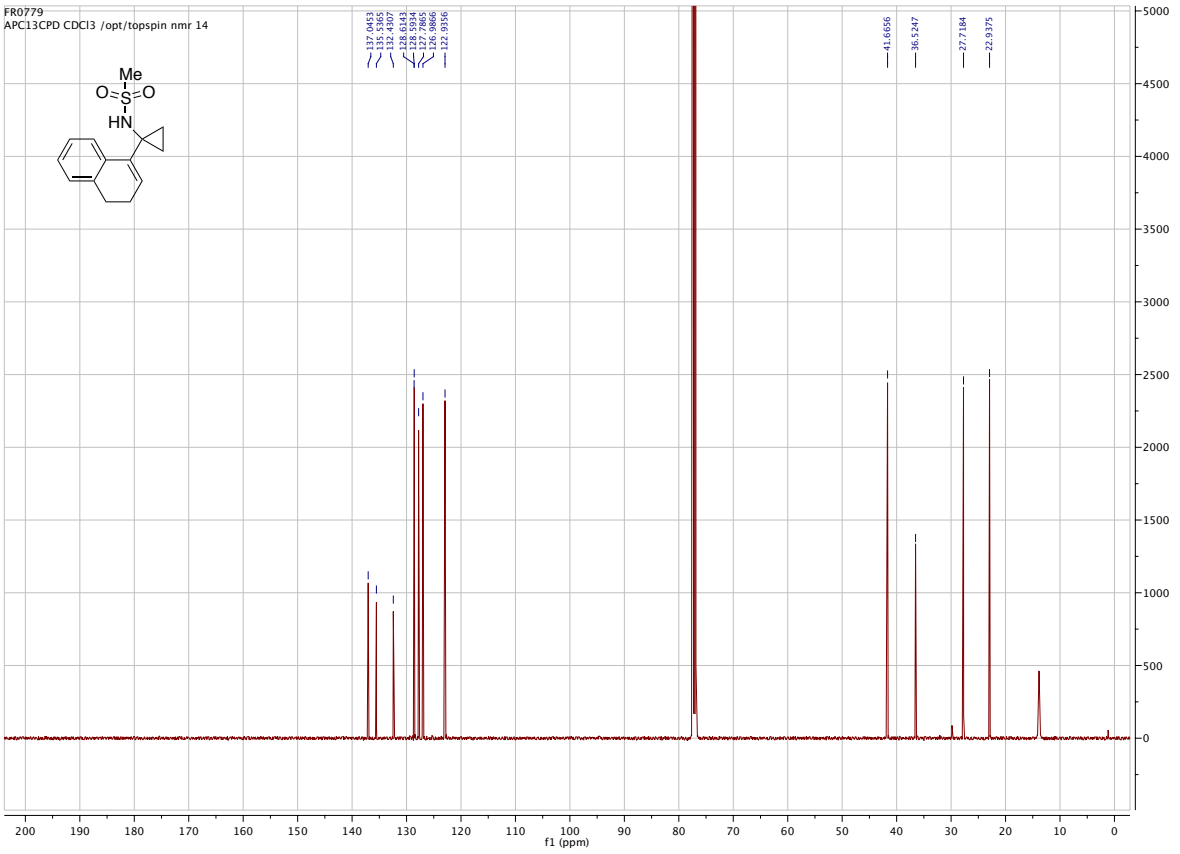


Substrate (A_1-Ms)

^{1}H NMR 500 MHz, $CDCl_3$

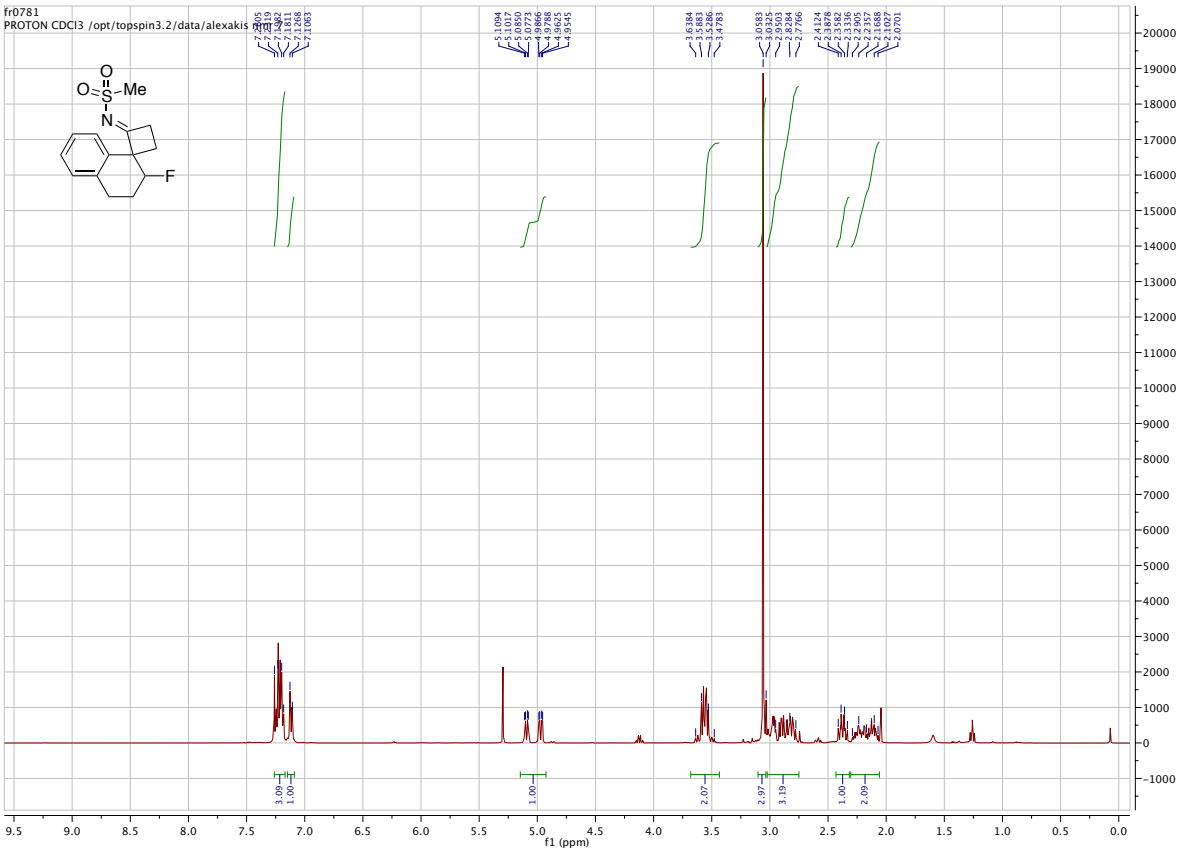


^{13}C NMR 125 MHz, $CDCl_3$

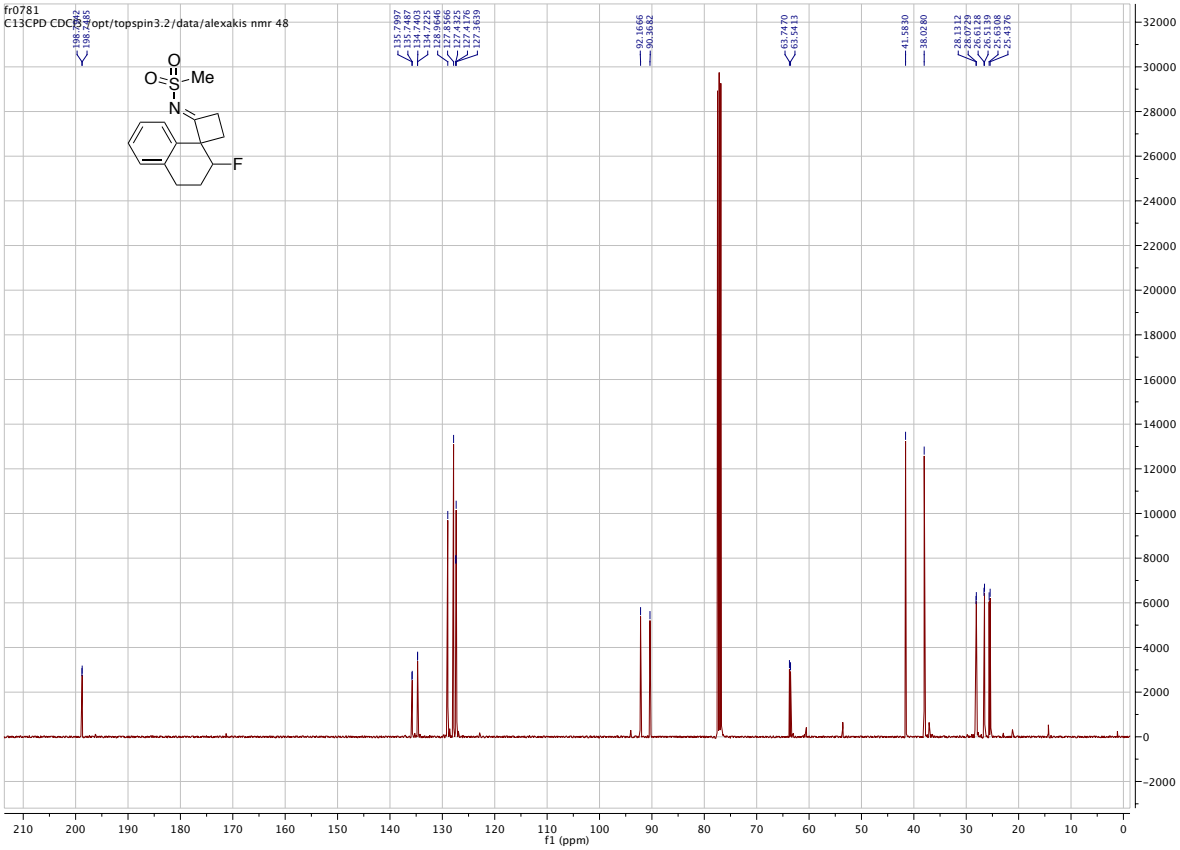


β-Fluoro Cyclobutylimine (B_1-Ms)

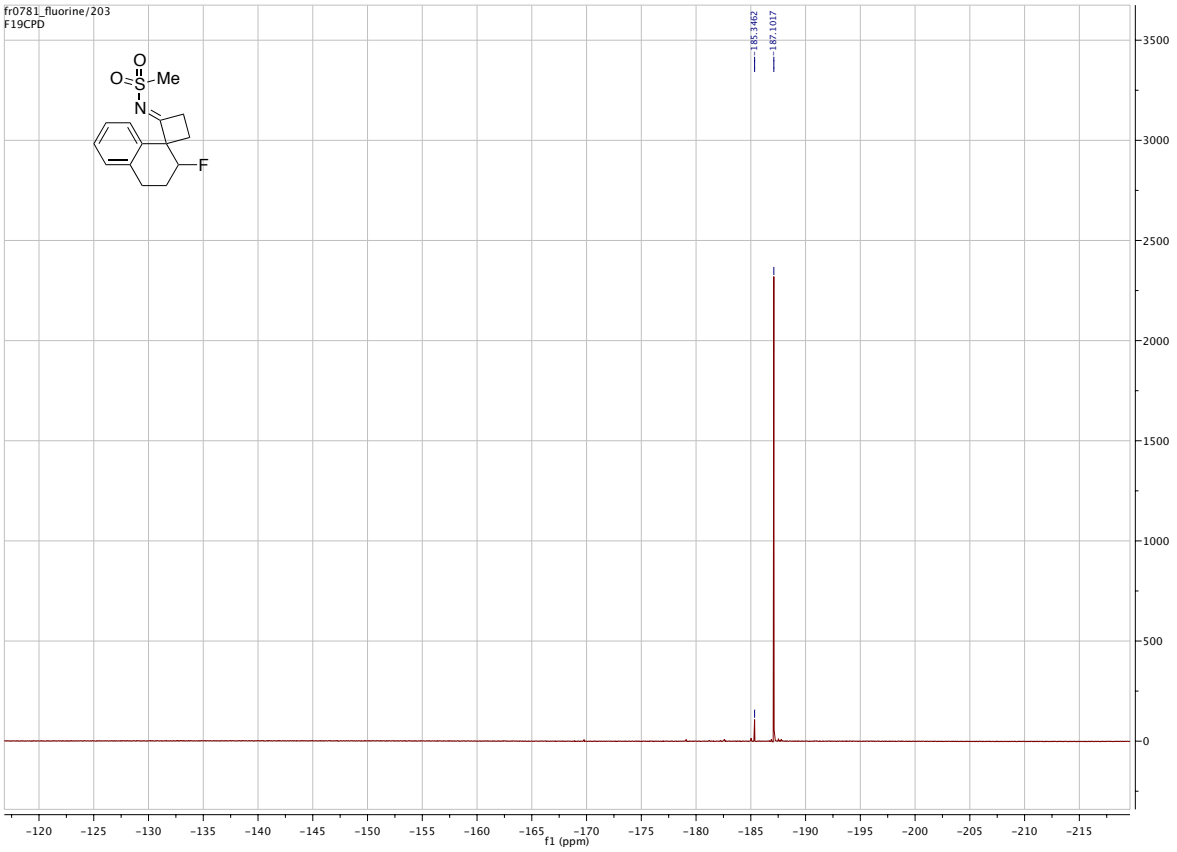
^{1}H NMR 400 MHz, $CDCl_3$



^{13}C NMR 100 MHz, $CDCl_3$

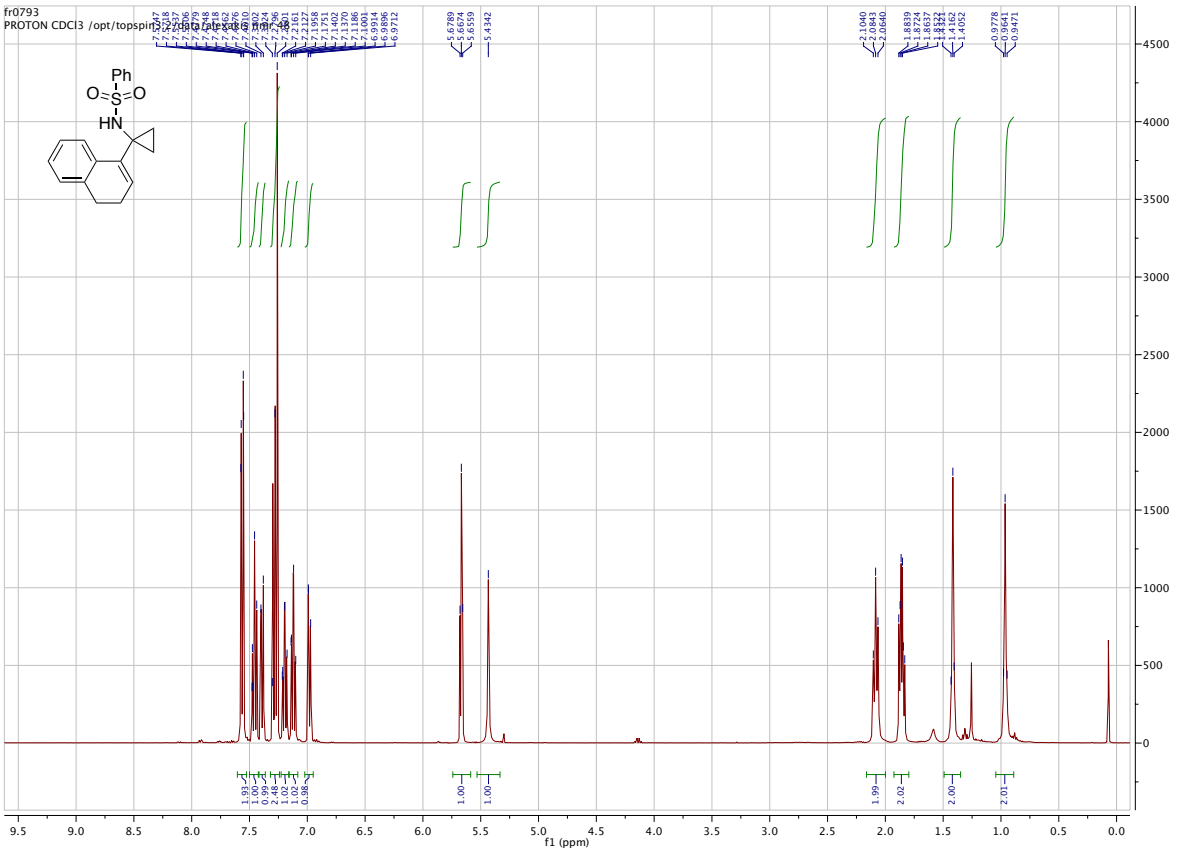


^{19}F NMR 375 MHz, $CDCl_3$

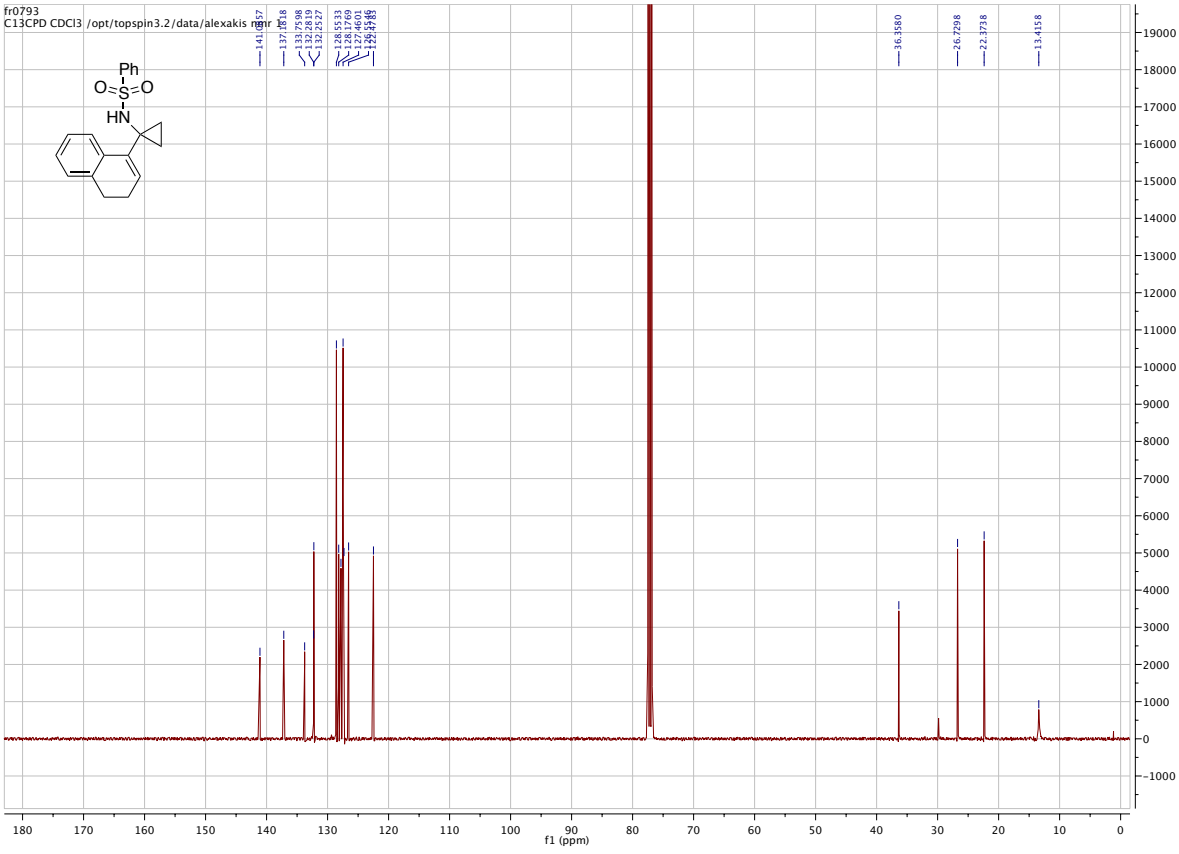


Substrate (A_1-Ps)

^{1}H NMR 400 MHz, $CDCl_3$

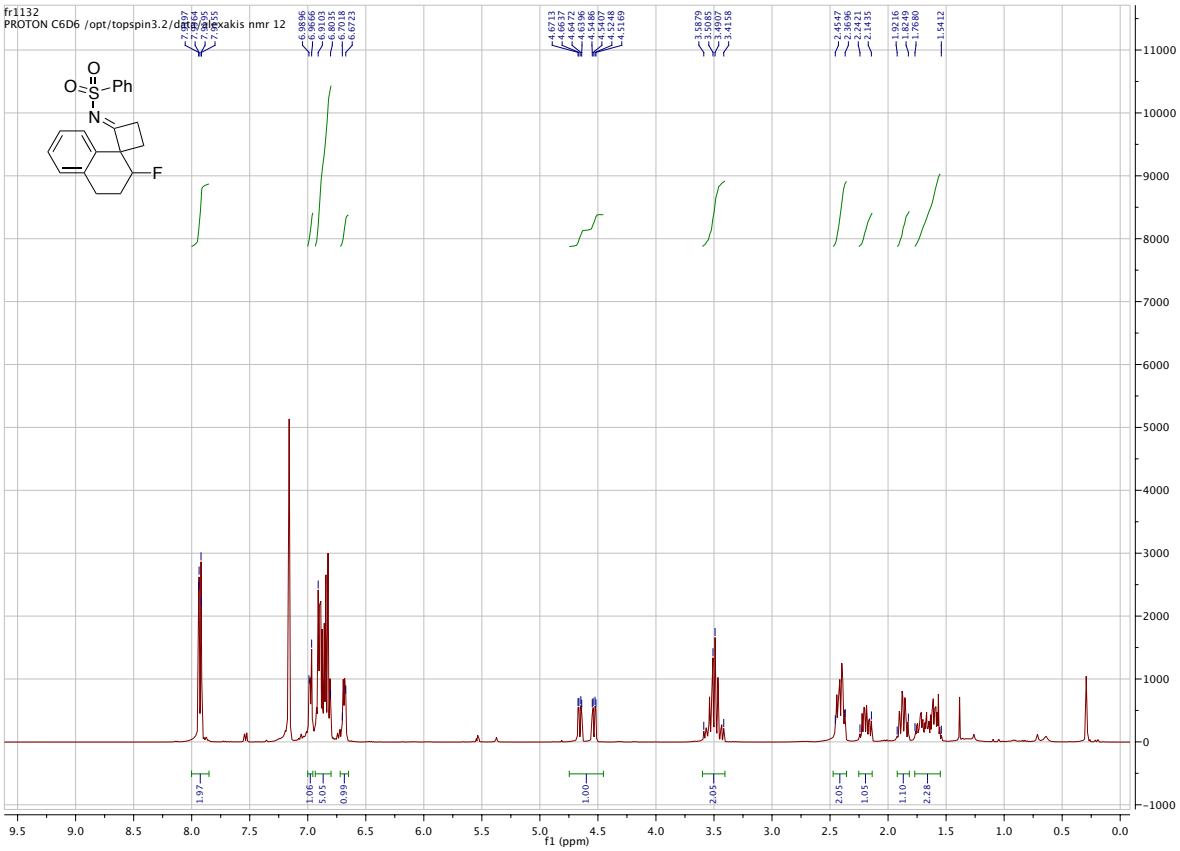


^{13}C NMR 100 MHz, $CDCl_3$

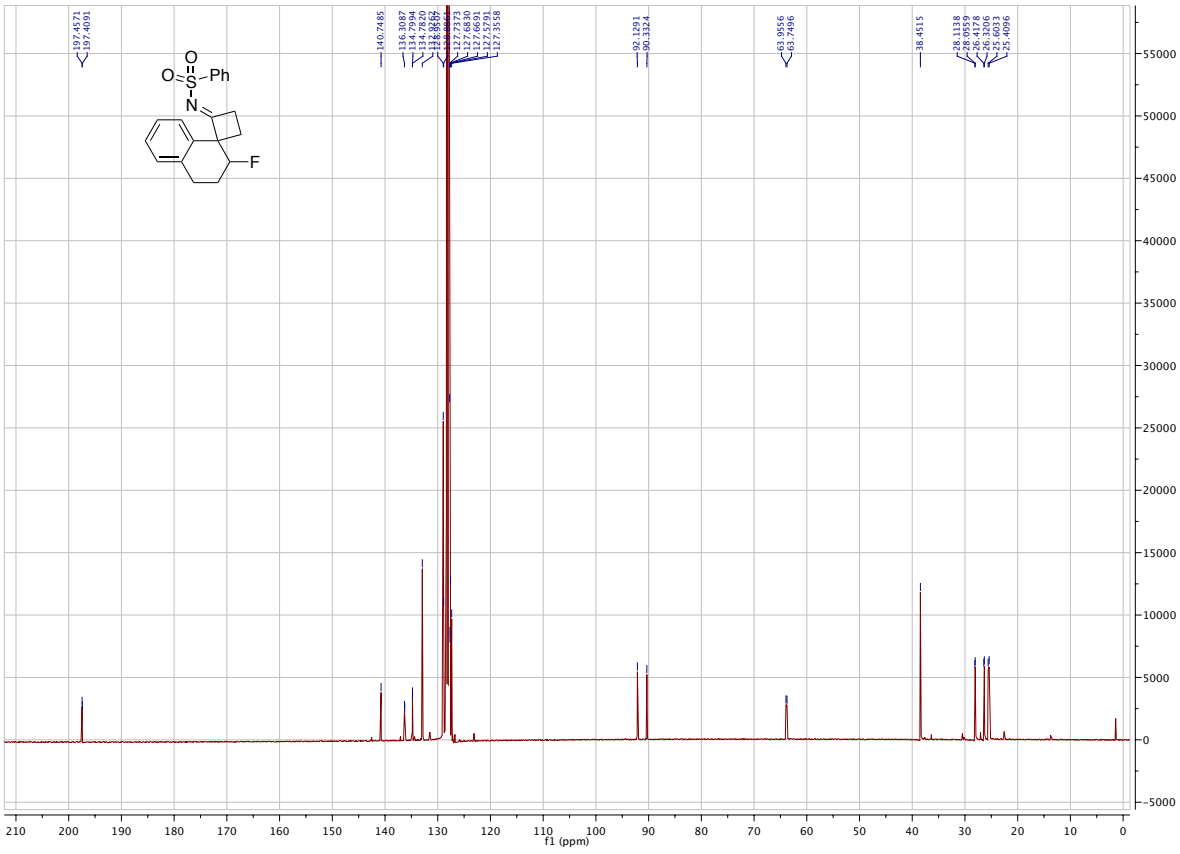


β-Fluoro Cyclobutylimine (B_1-Ps)

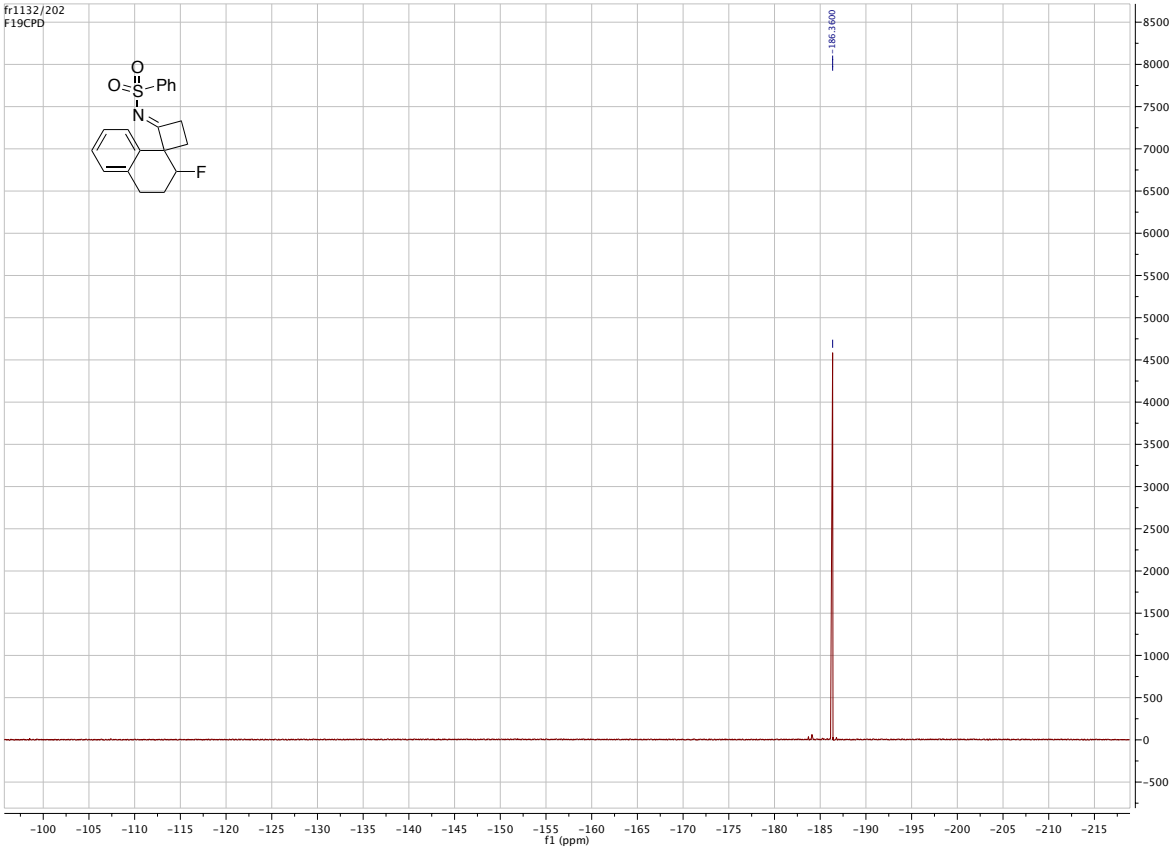
^{1}H NMR 400 MHz, C_6D_6



^{13}C NMR 100 MHz, C_6D_6

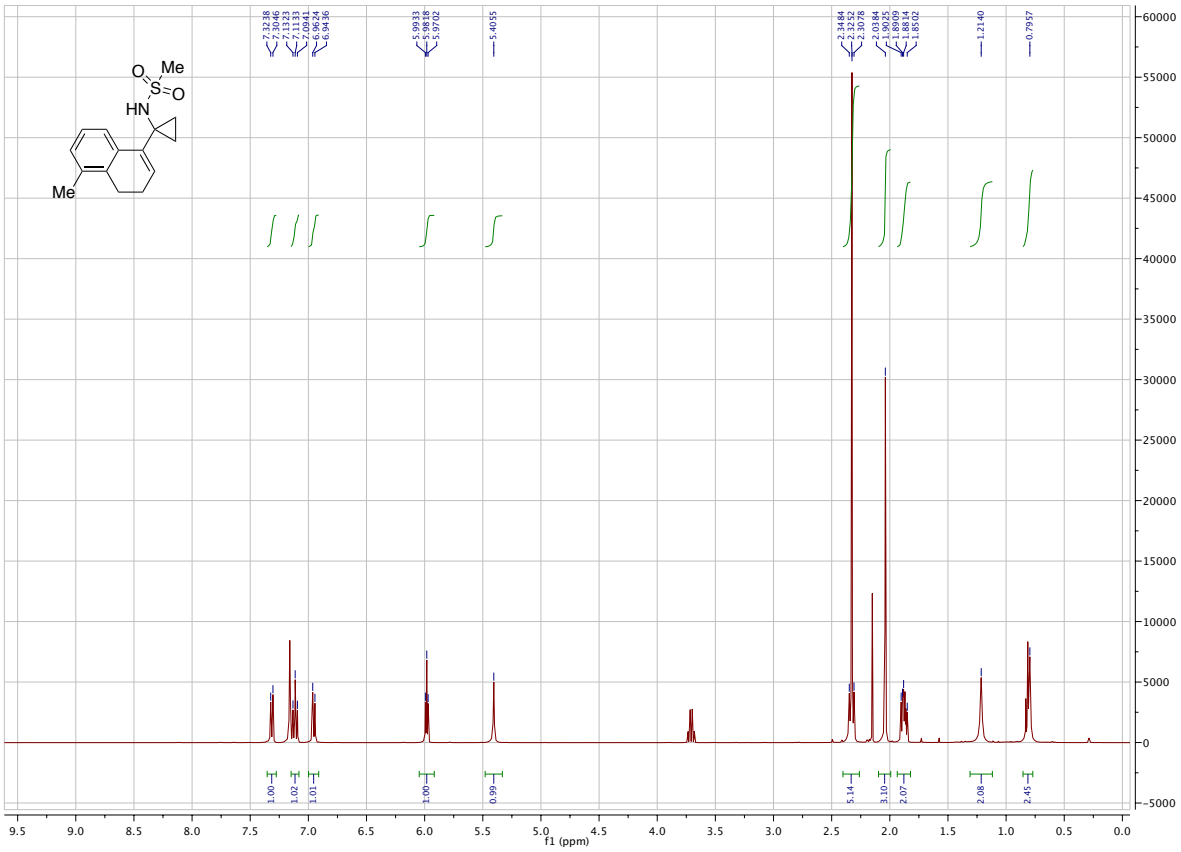


^{19}F NMR 375 MHz, C_6D_6

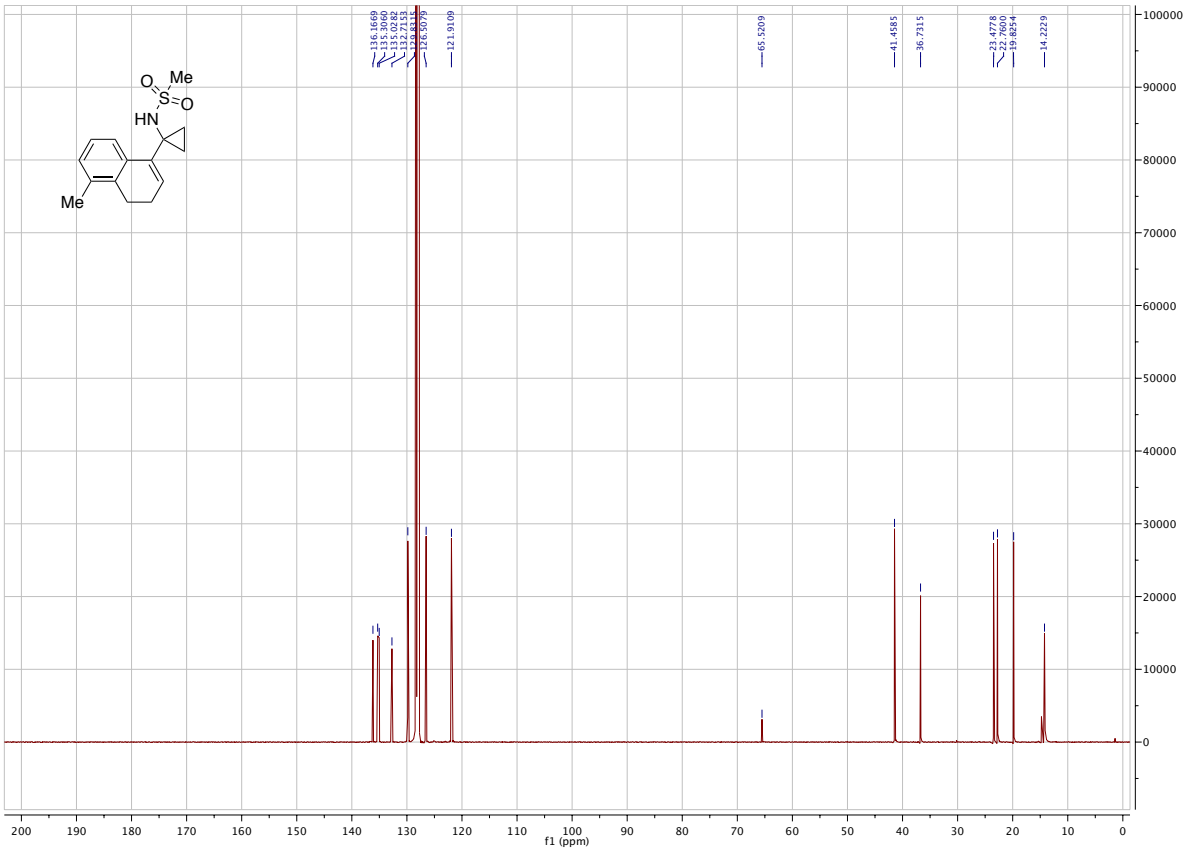


Substrate (A_2)

^{1}H NMR 400 MHz, C_6D_6

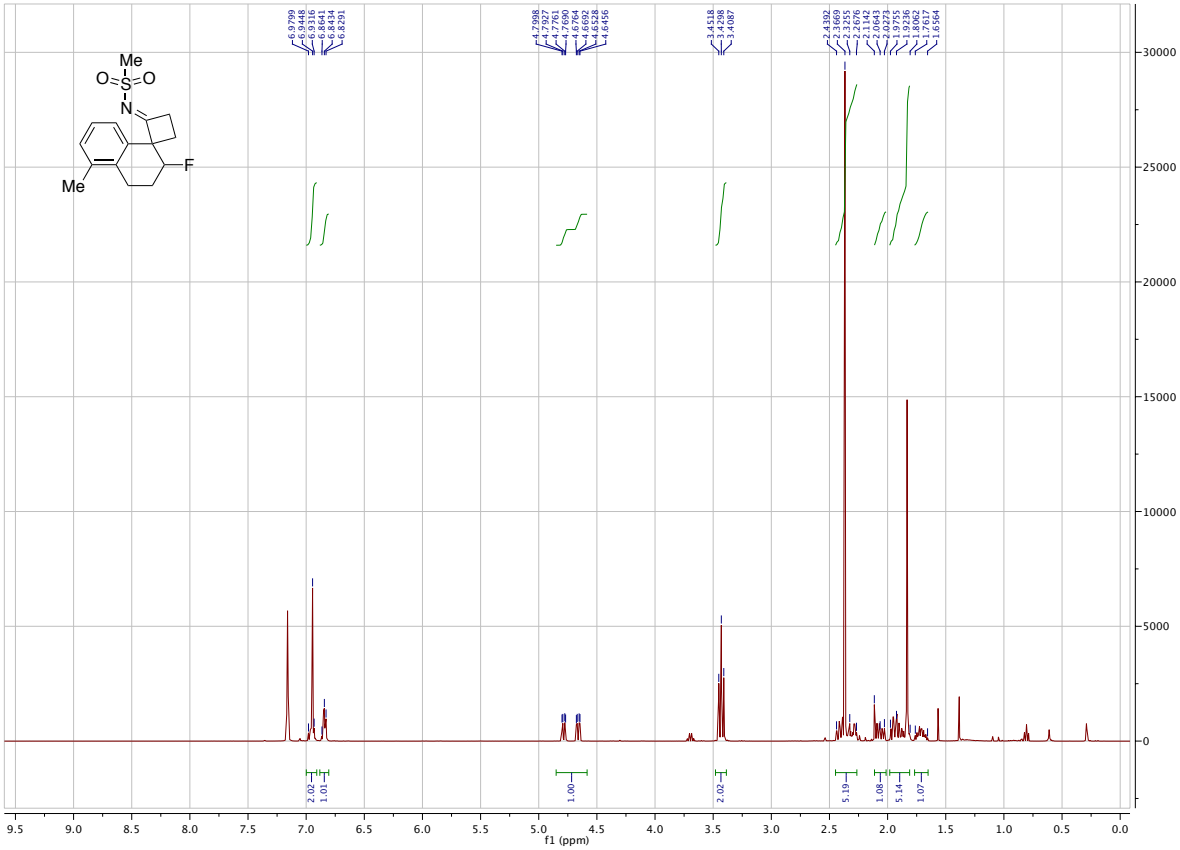


^{13}C NMR 100 MHz, C_6D_6

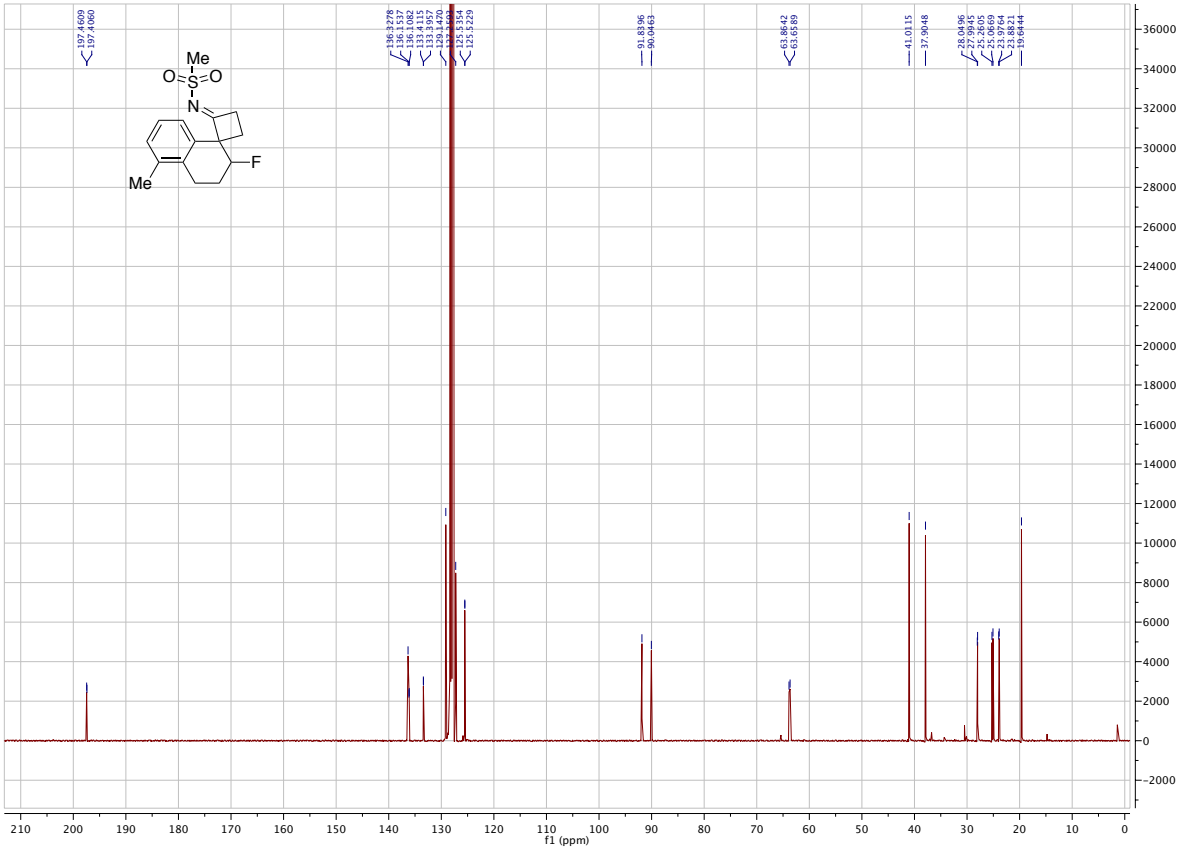


β-Fluoro Cyclobutylimine (B_2)

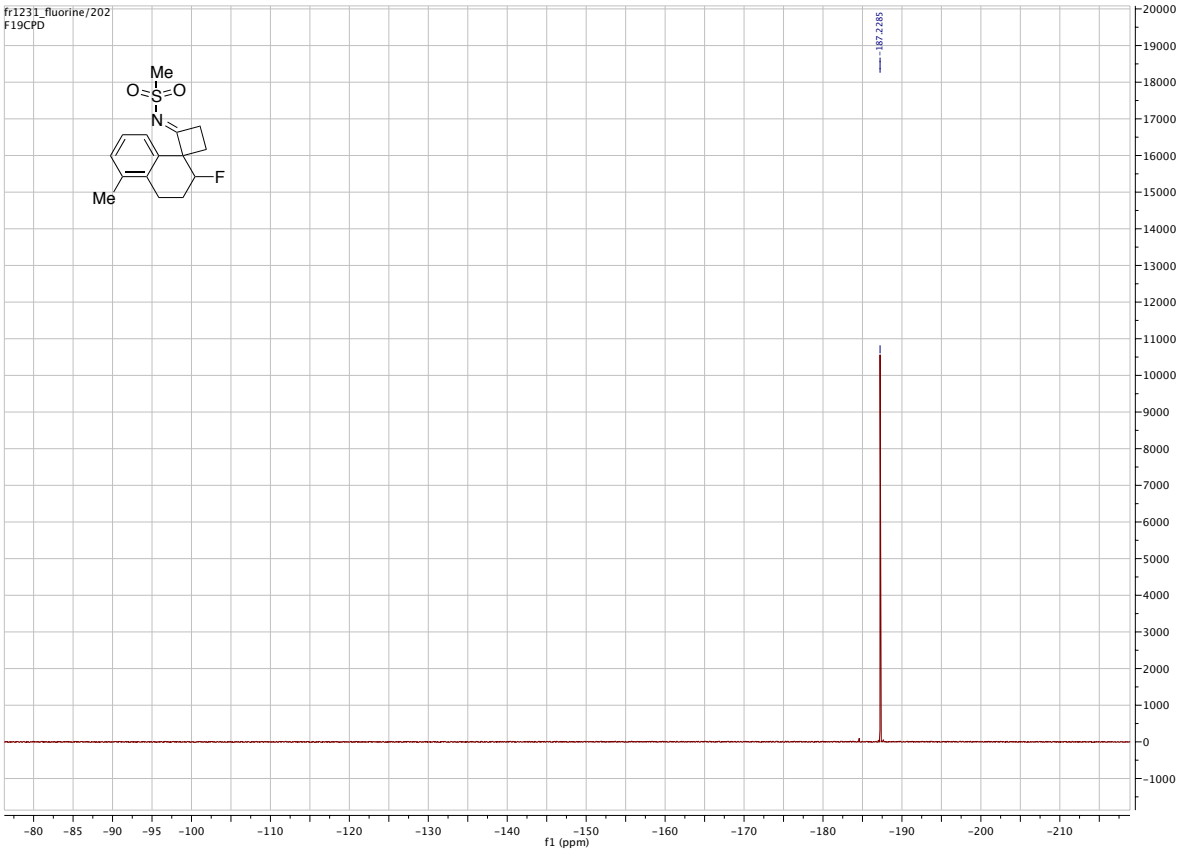
^{1}H NMR 400 MHz, C_6D_6



^{13}C NMR 100 MHz, C_6D_6

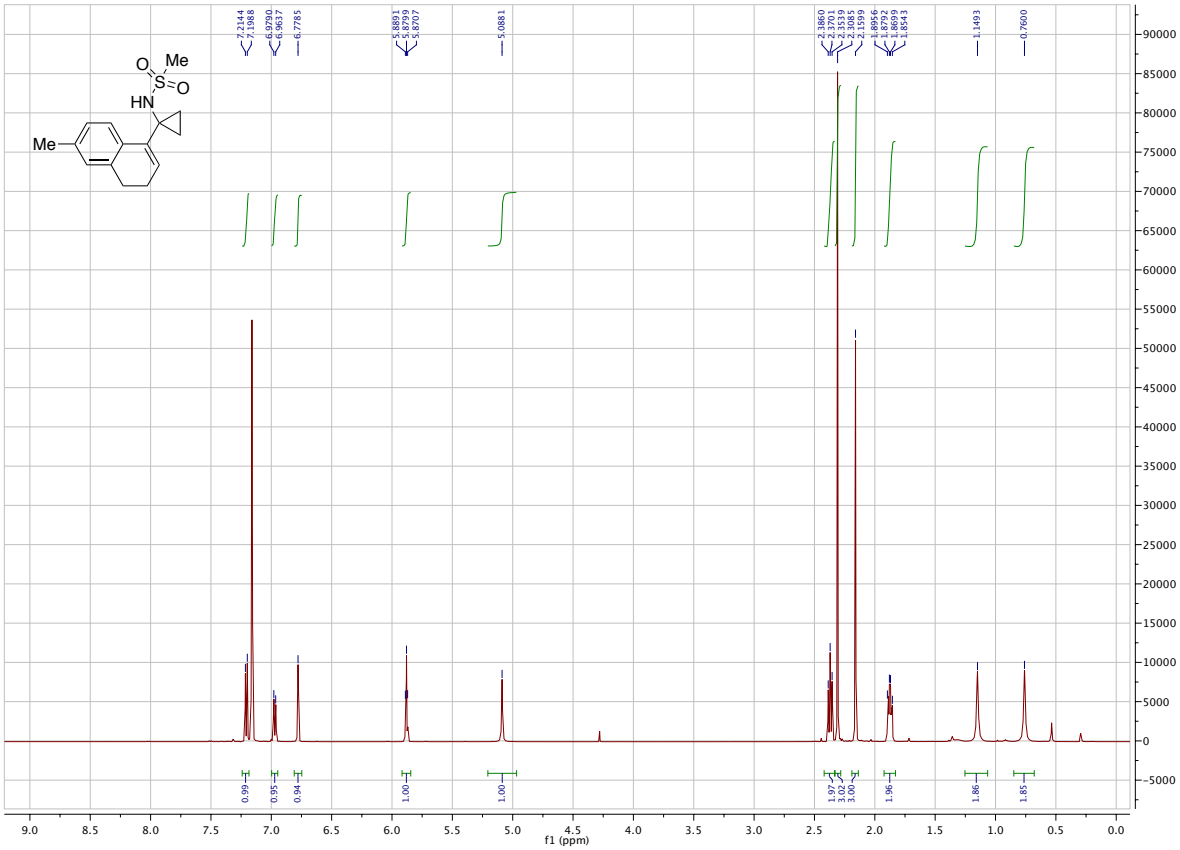


^{19}F NMR 375 MHz, C_6D_6

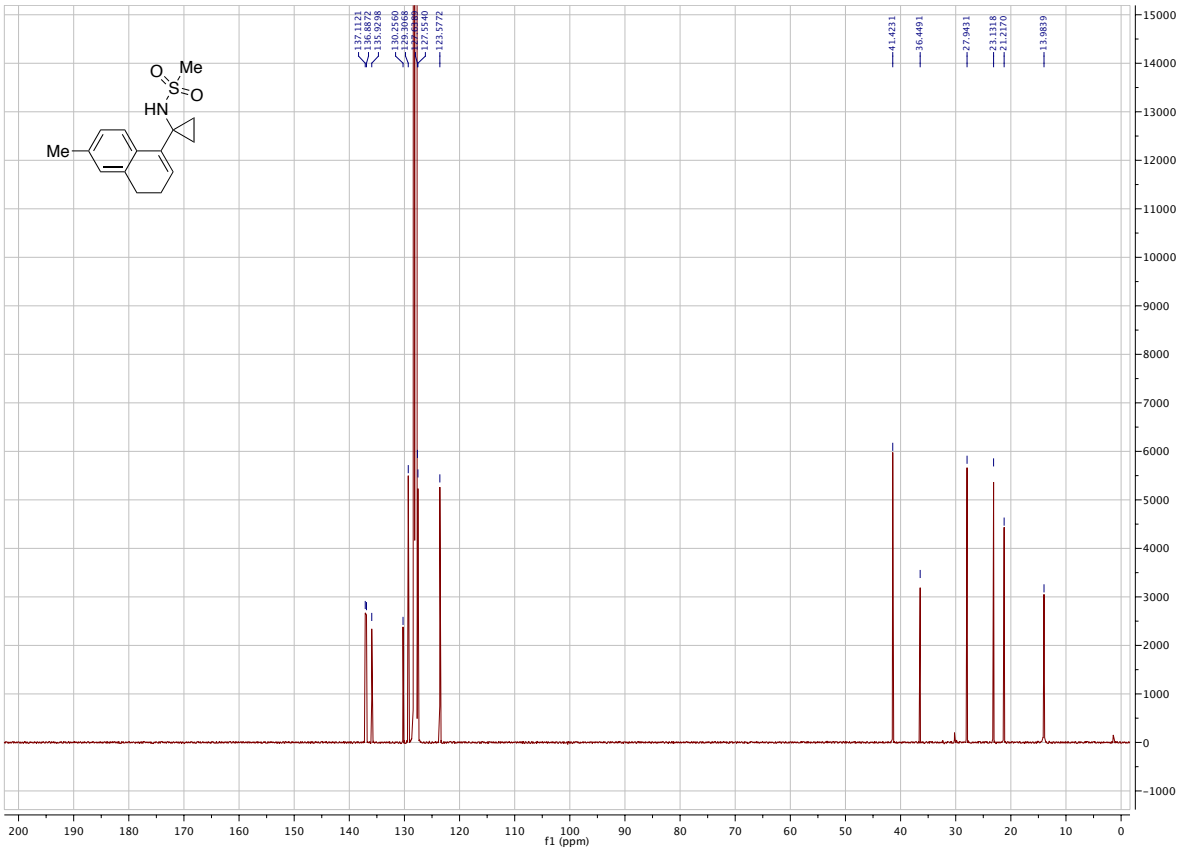


Substrate (A_3)

^{1}H NMR 500 MHz, C_6D_6



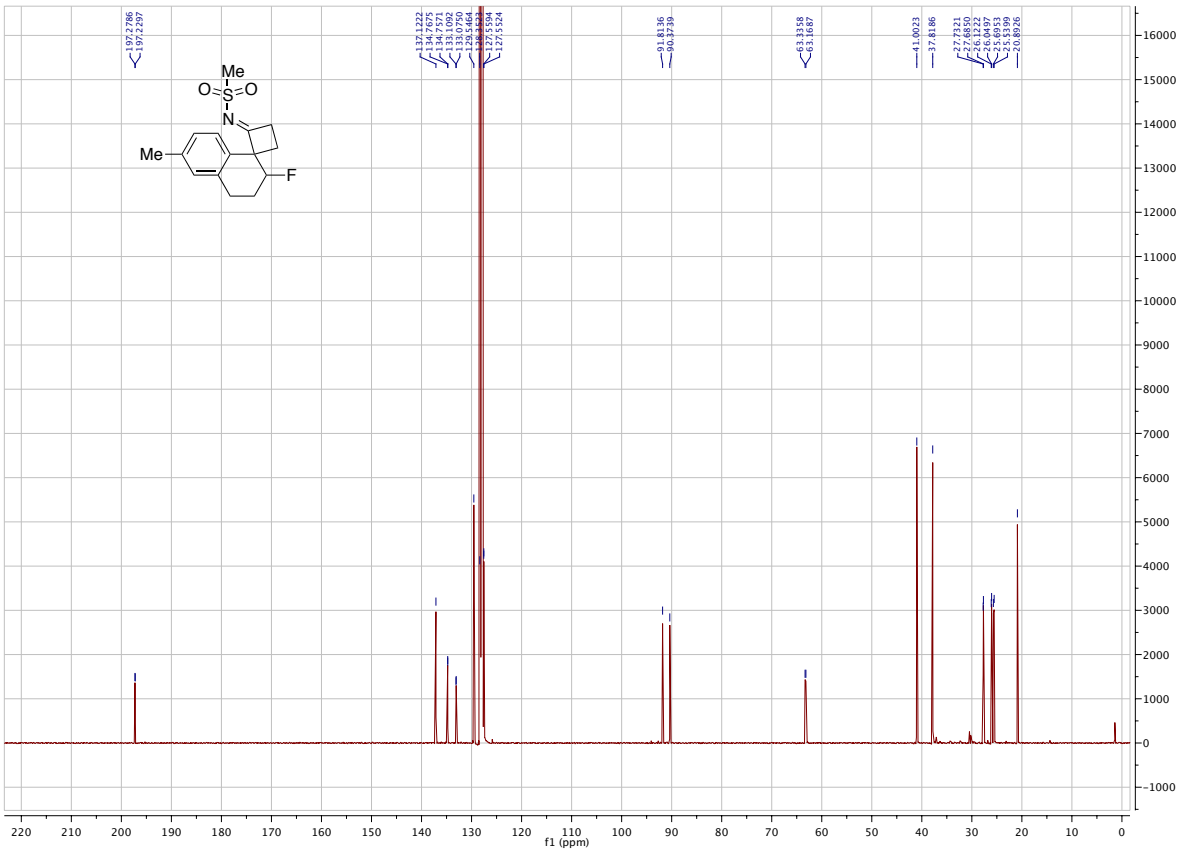
^{13}C NMR 125 MHz, C_6D_6



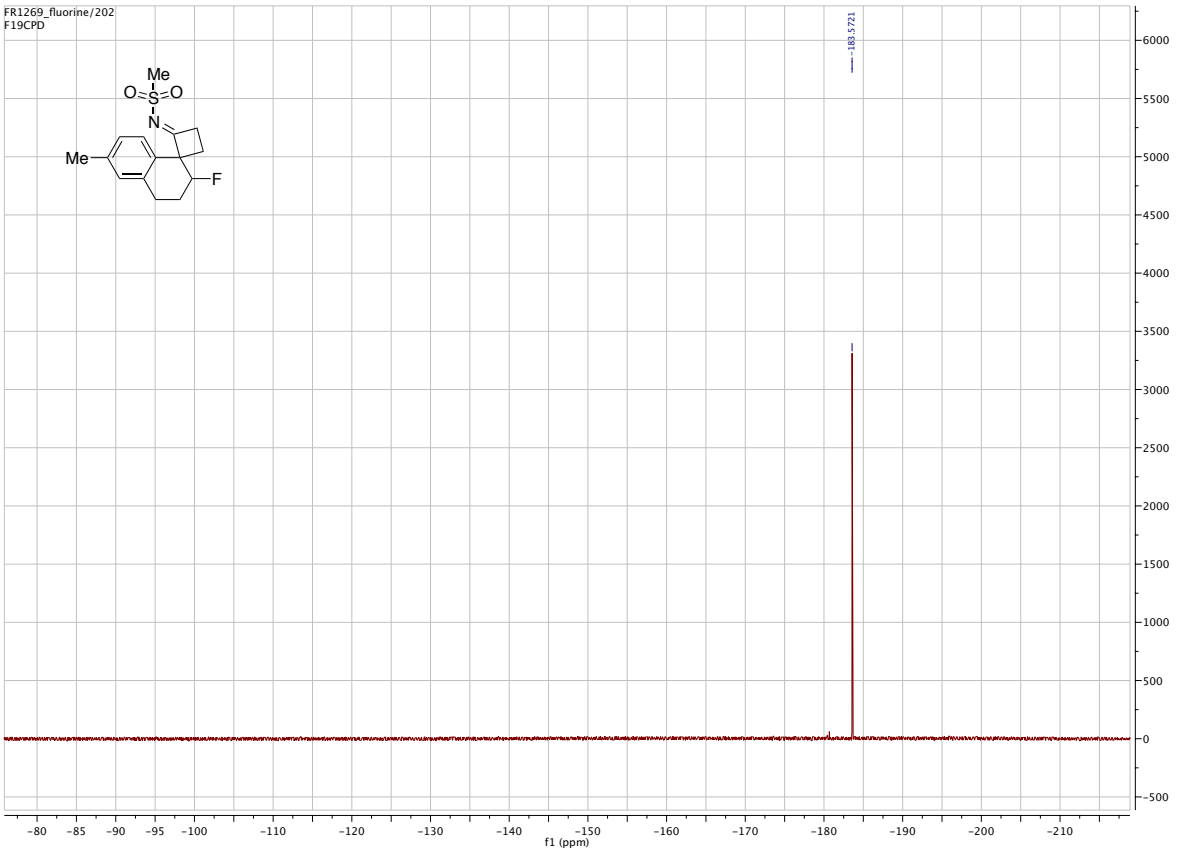
β-Fluoro Cyclobutylimine (B_3)

^{1}H NMR 500 MHz, C_6D_6

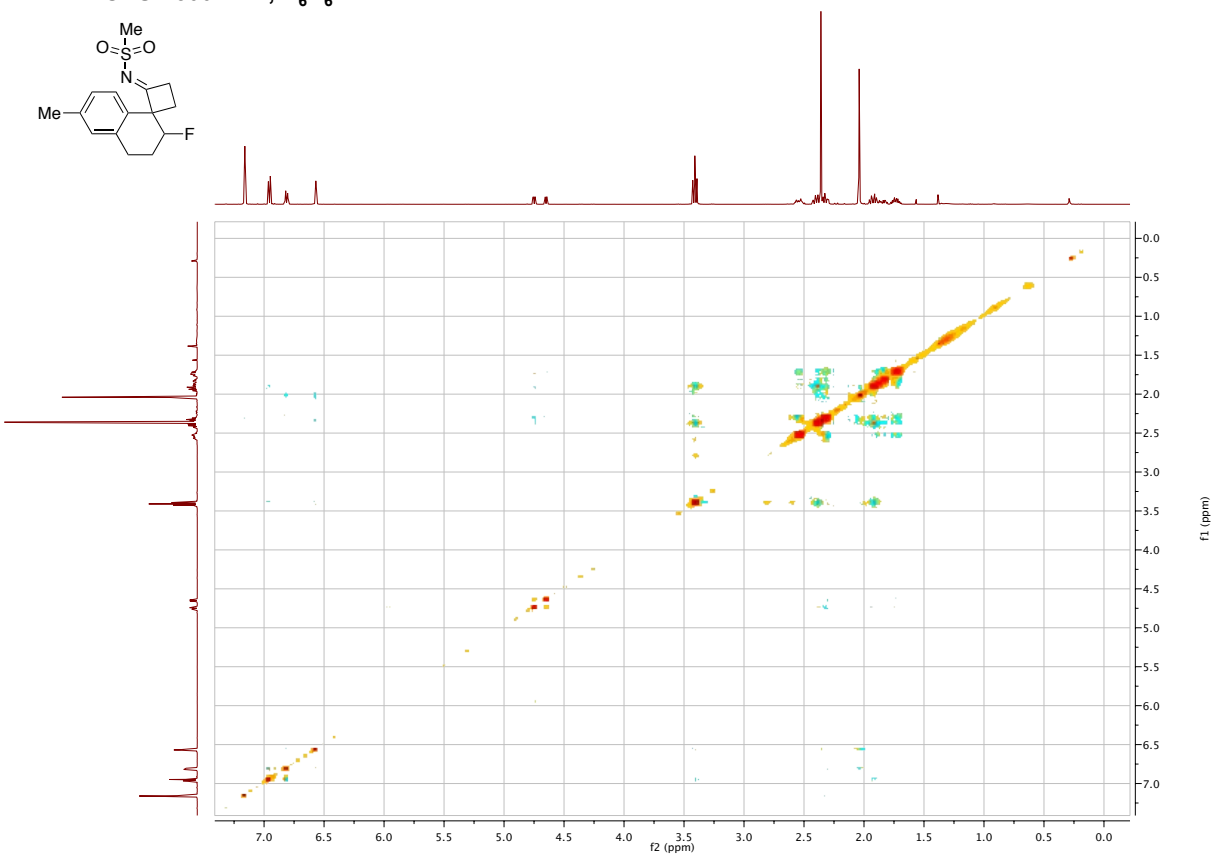
^{13}C NMR 125 MHz, C_6D_6



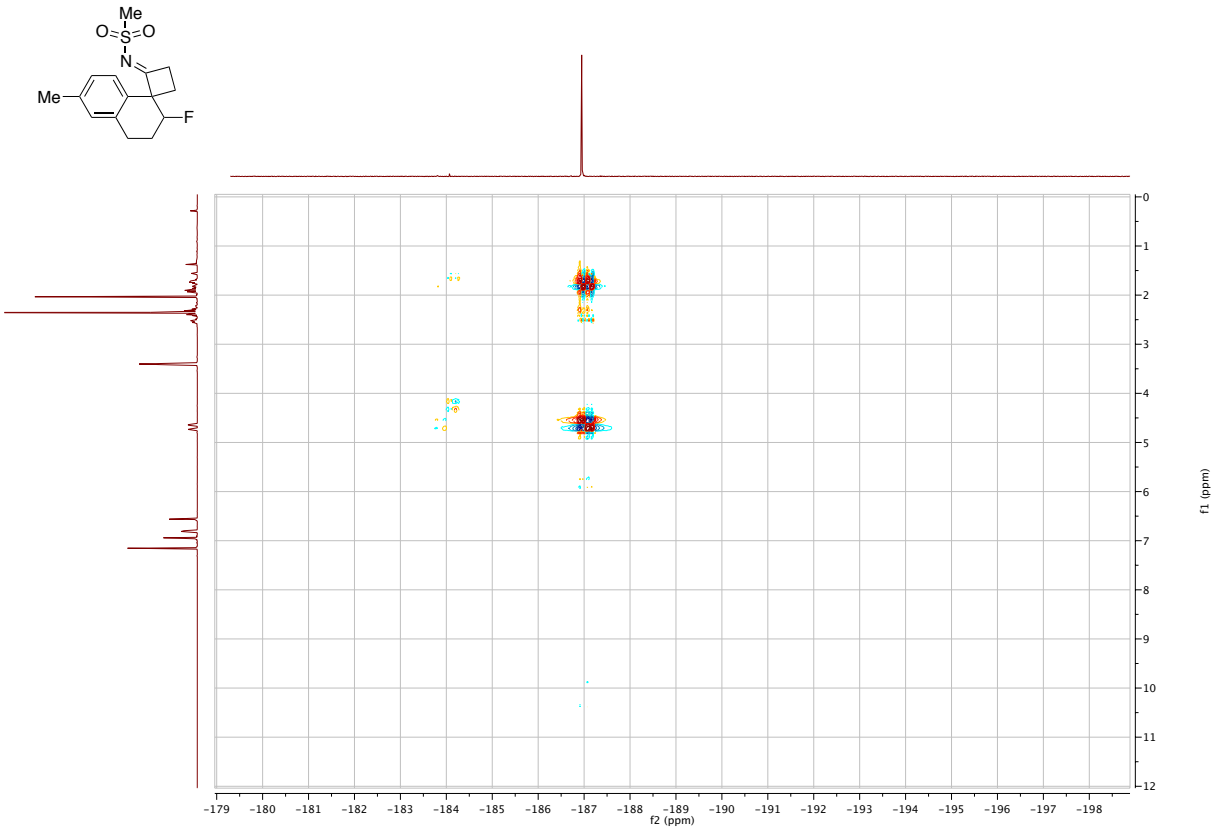
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{1}H NOESY 500 MHz, C_6D_6

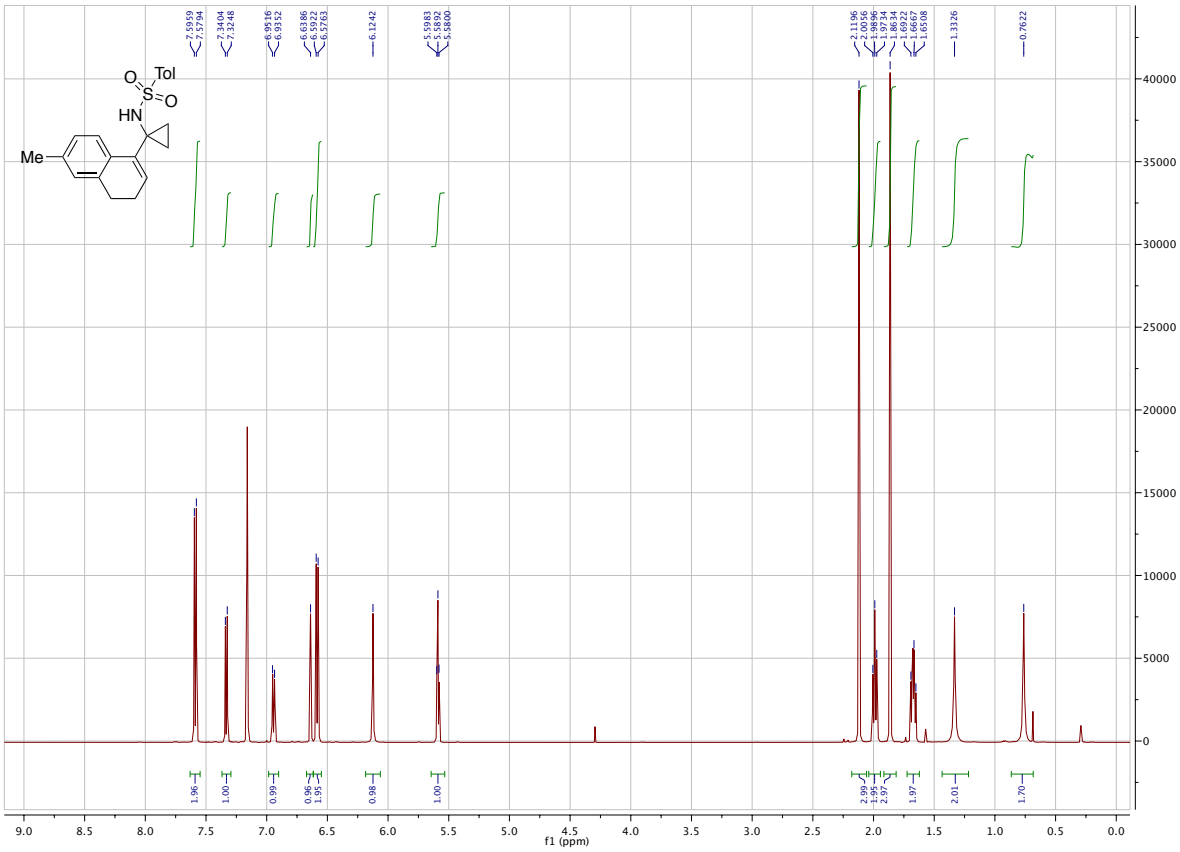


^{1}H-^{19}F HOESY 300 MHz, C_6D_6

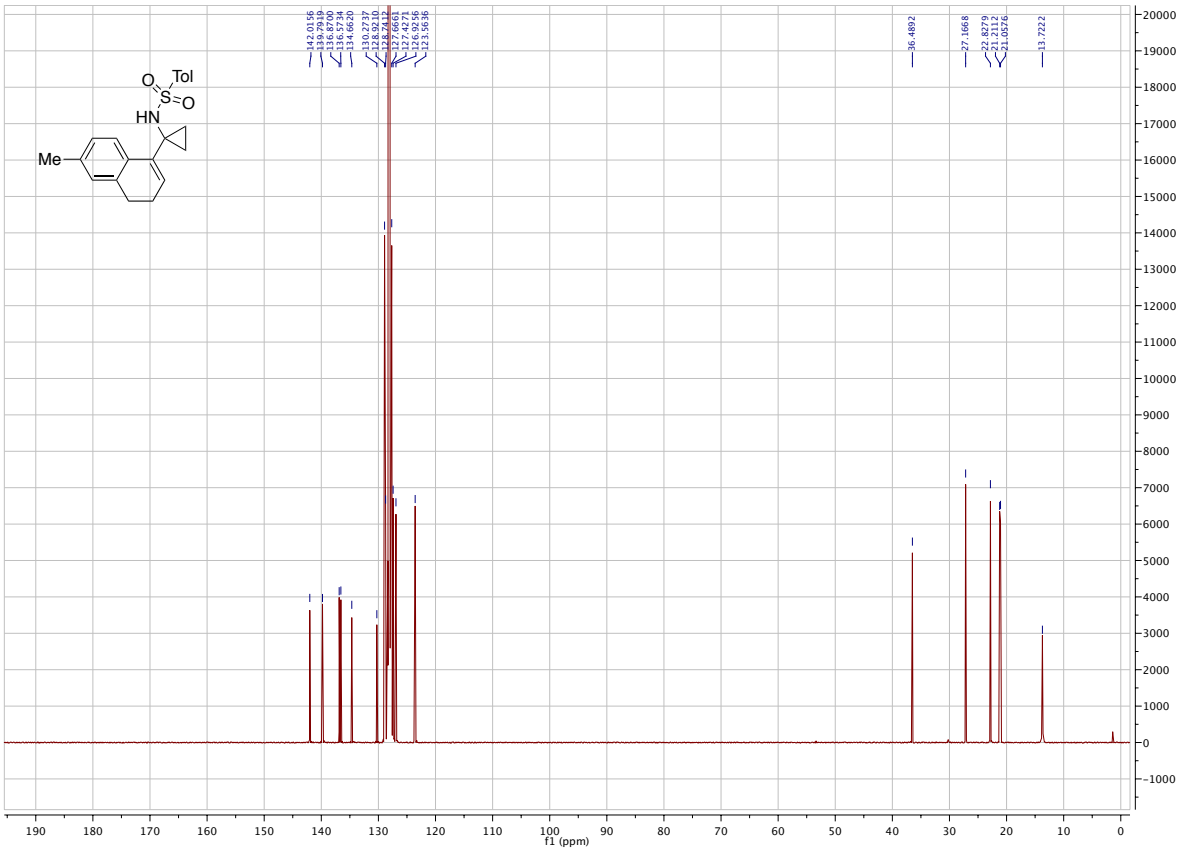


Substrate (A_4)

^{1}H NMR 500 MHz, C_6D_6

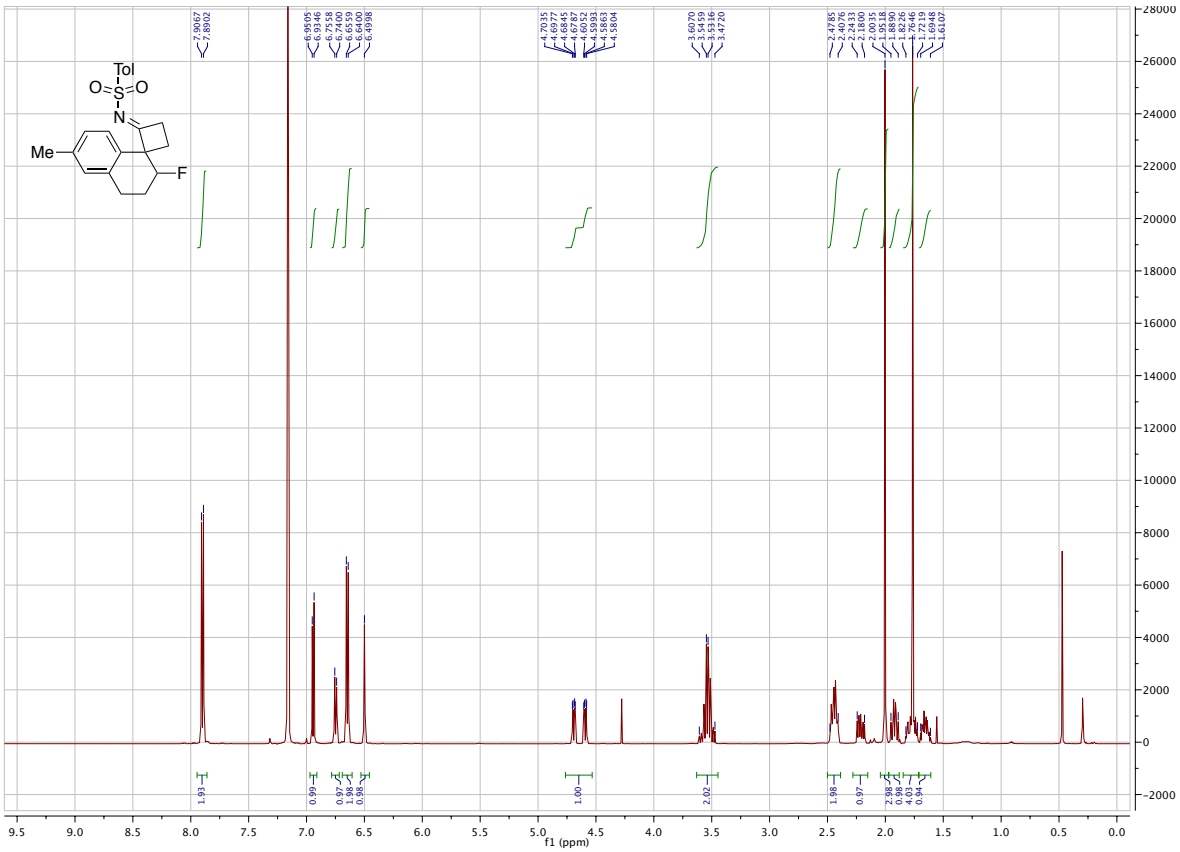


^{13}C NMR 125 MHz, C_6D_6

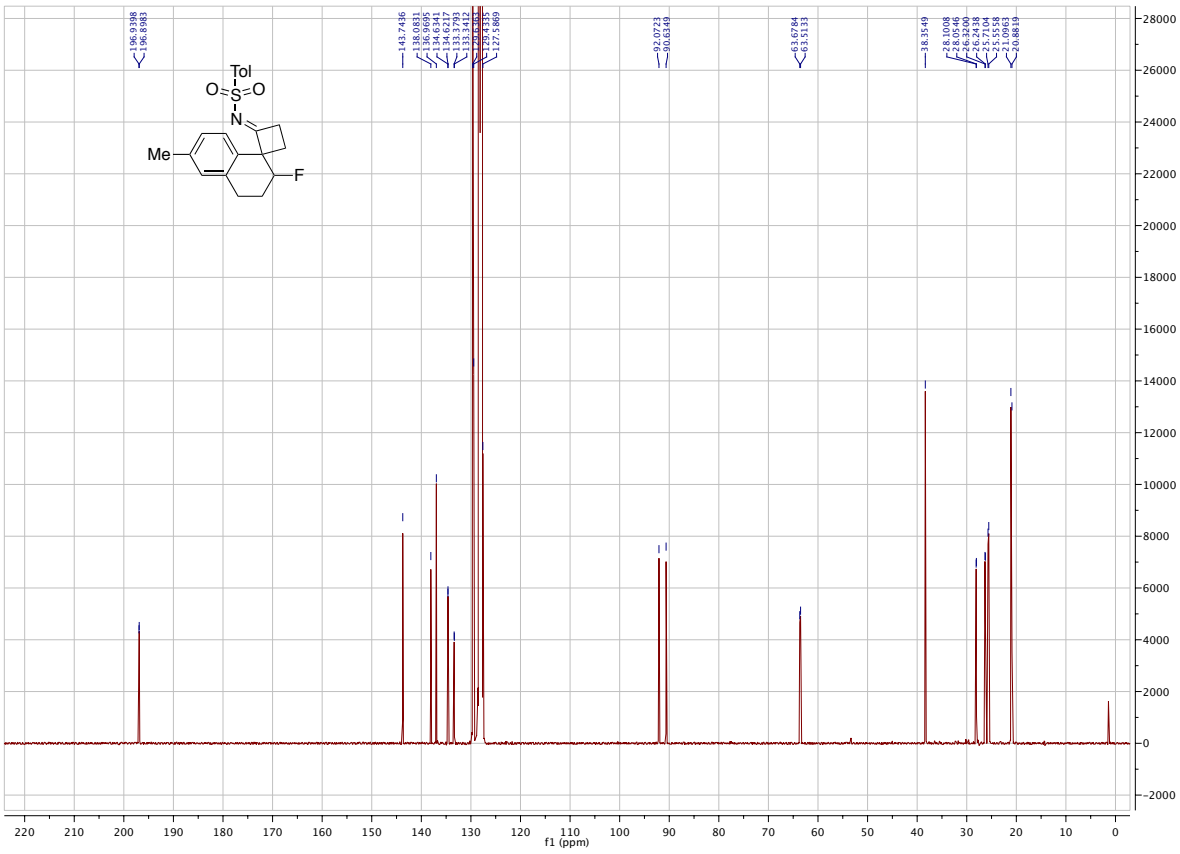


β-Fluoro Cyclobutylimine (B_4)

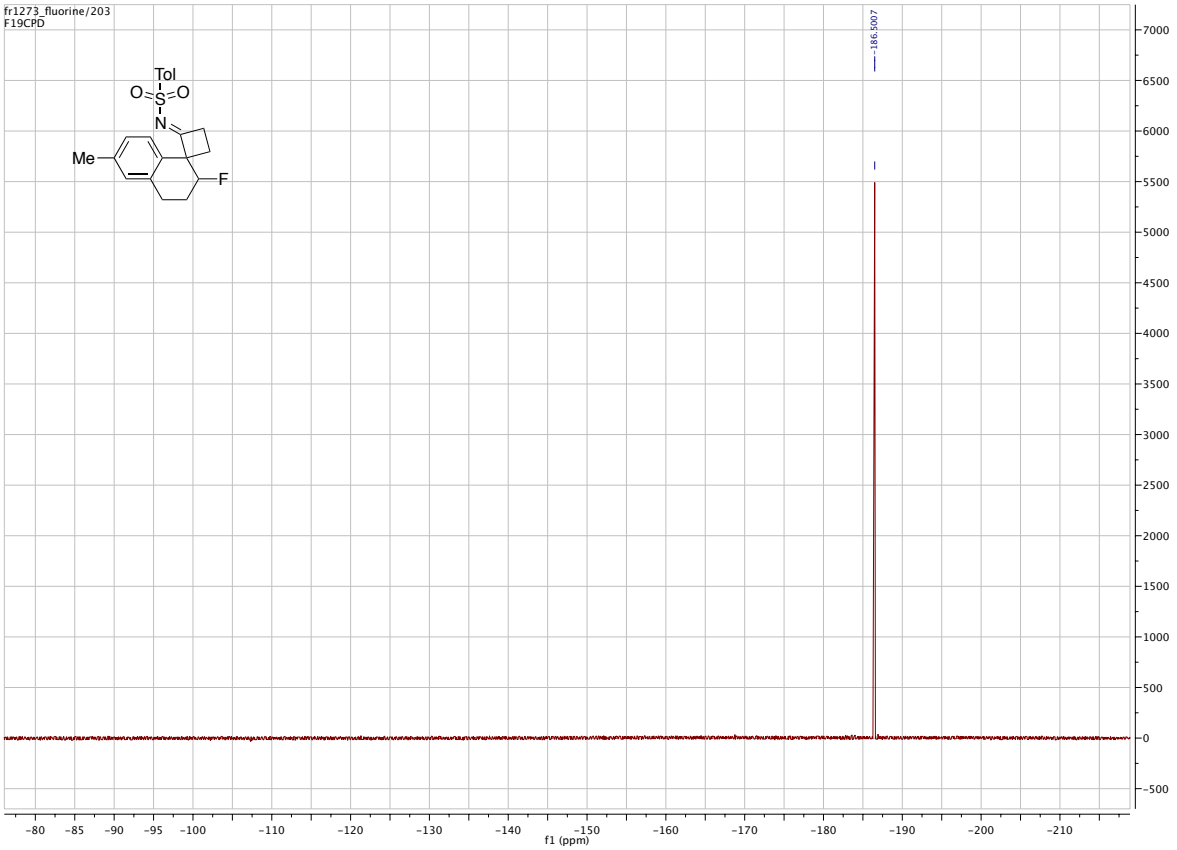
^{1}H NMR 500 MHz, C_6D_6



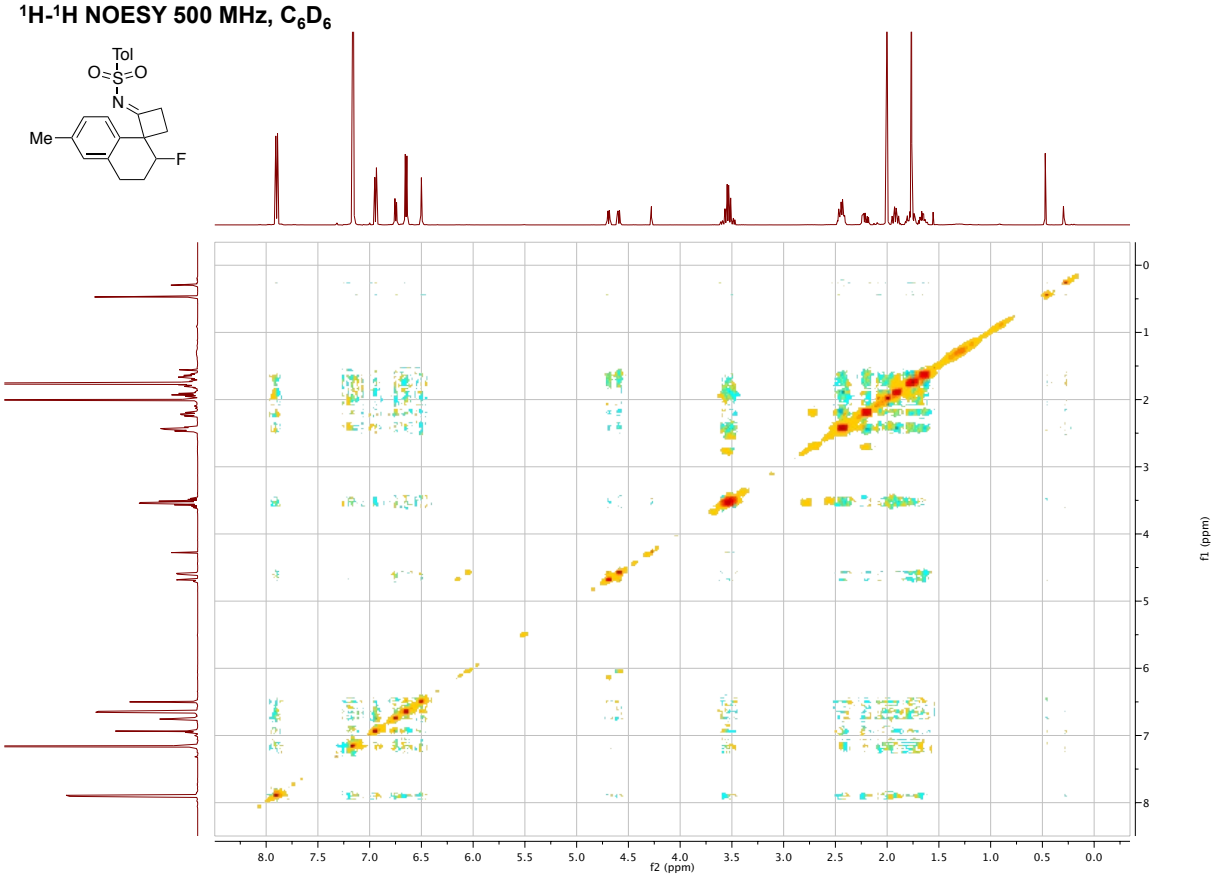
^{13}C NMR 125 MHz, C_6D_6



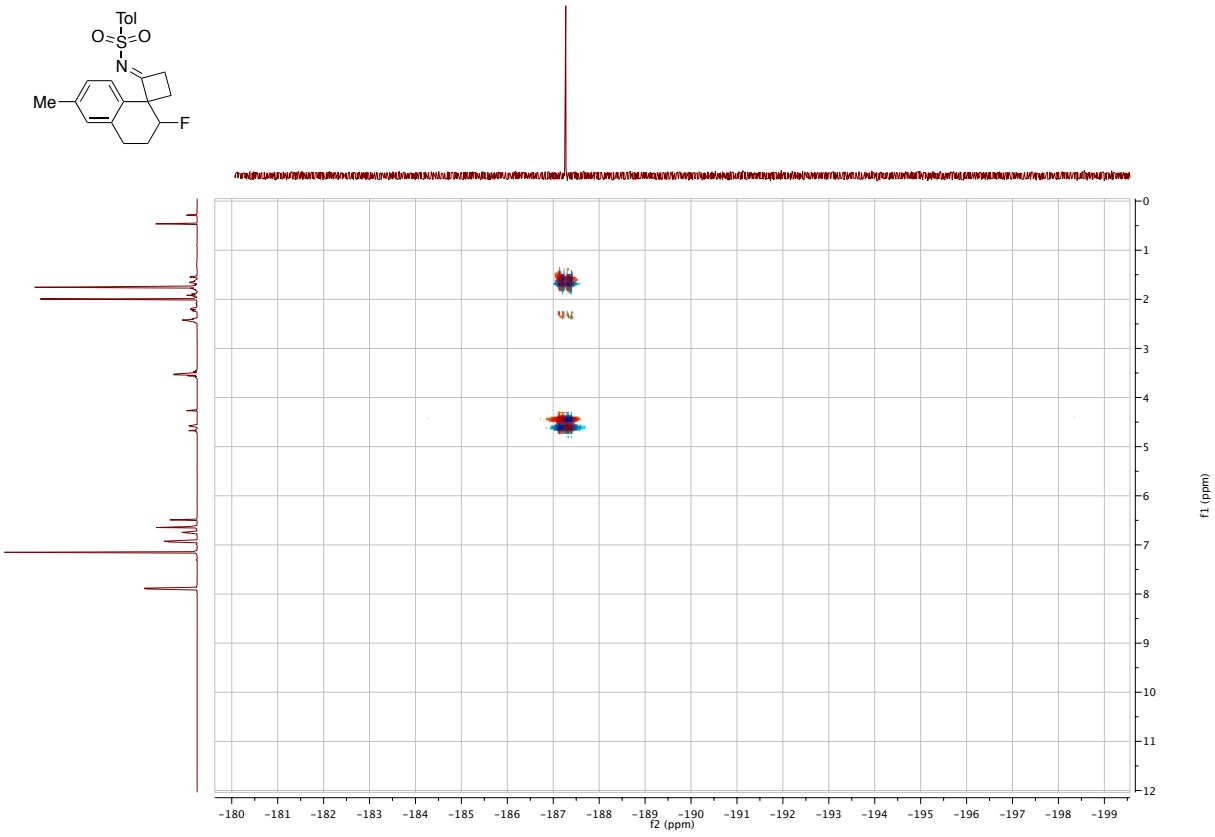
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{1}H NOESY 500 MHz, C_6D_6

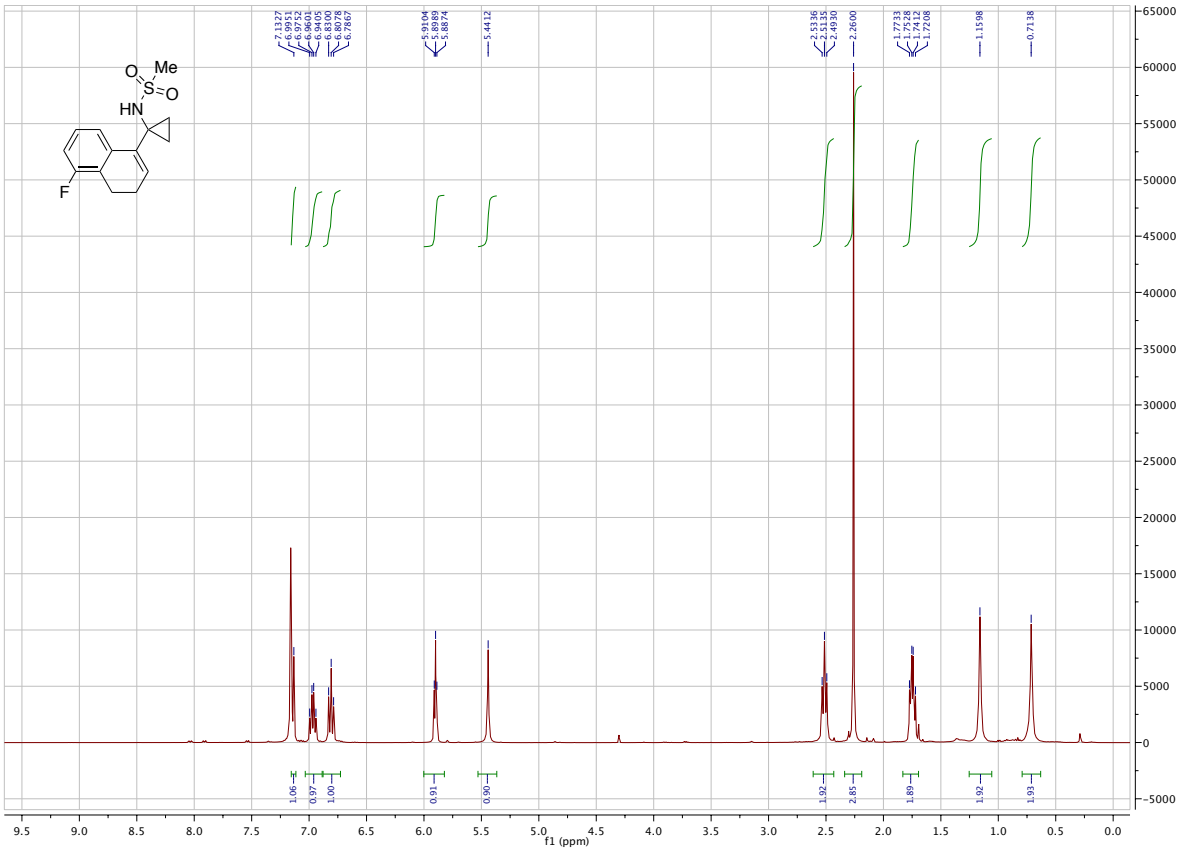


^{1}H-^{19}F HOESY 300 MHz, C_6D_6

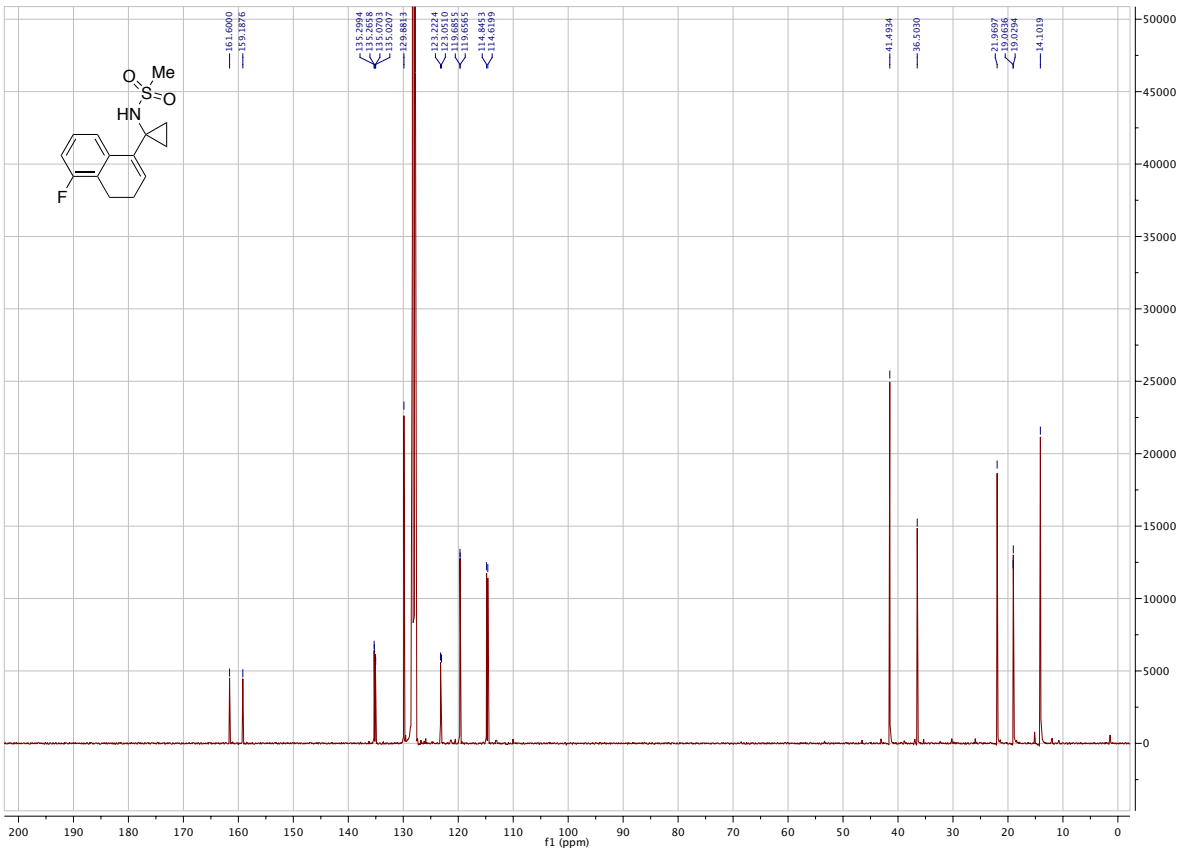


Substrate (A_5)

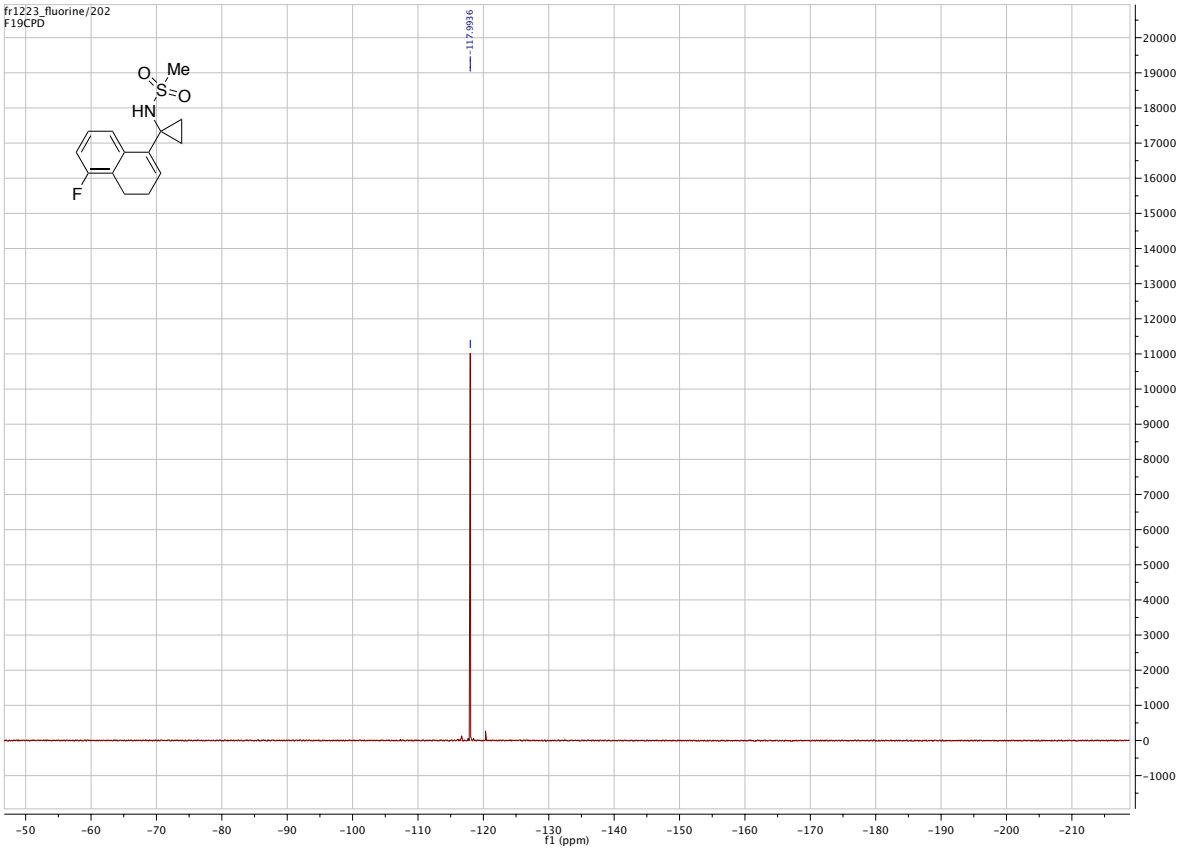
^{1}H NMR 400 MHz, C_6D_6



^{13}C NMR 100 MHz, C_6D_6

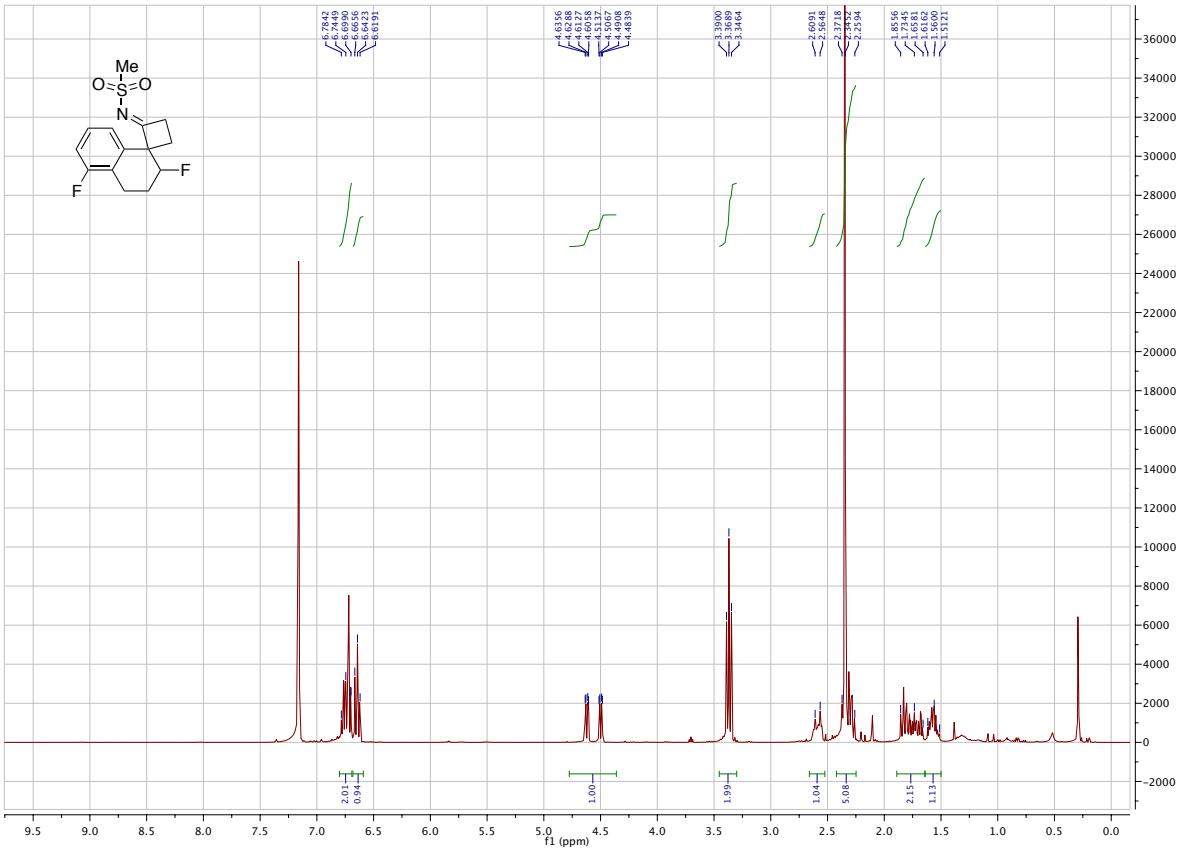


^{19}F NMR 375 MHz, C_6D_6

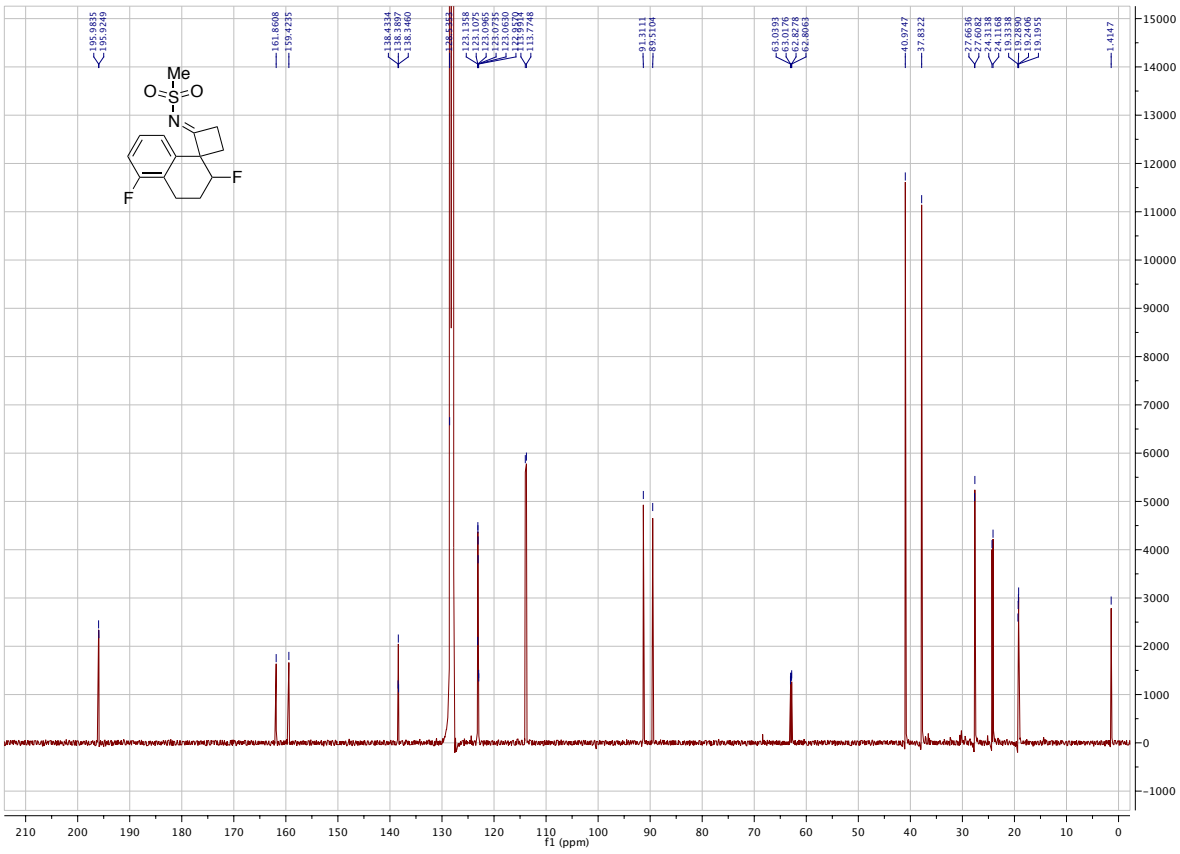


β-Fluoro Cyclobutylimine (B_5)

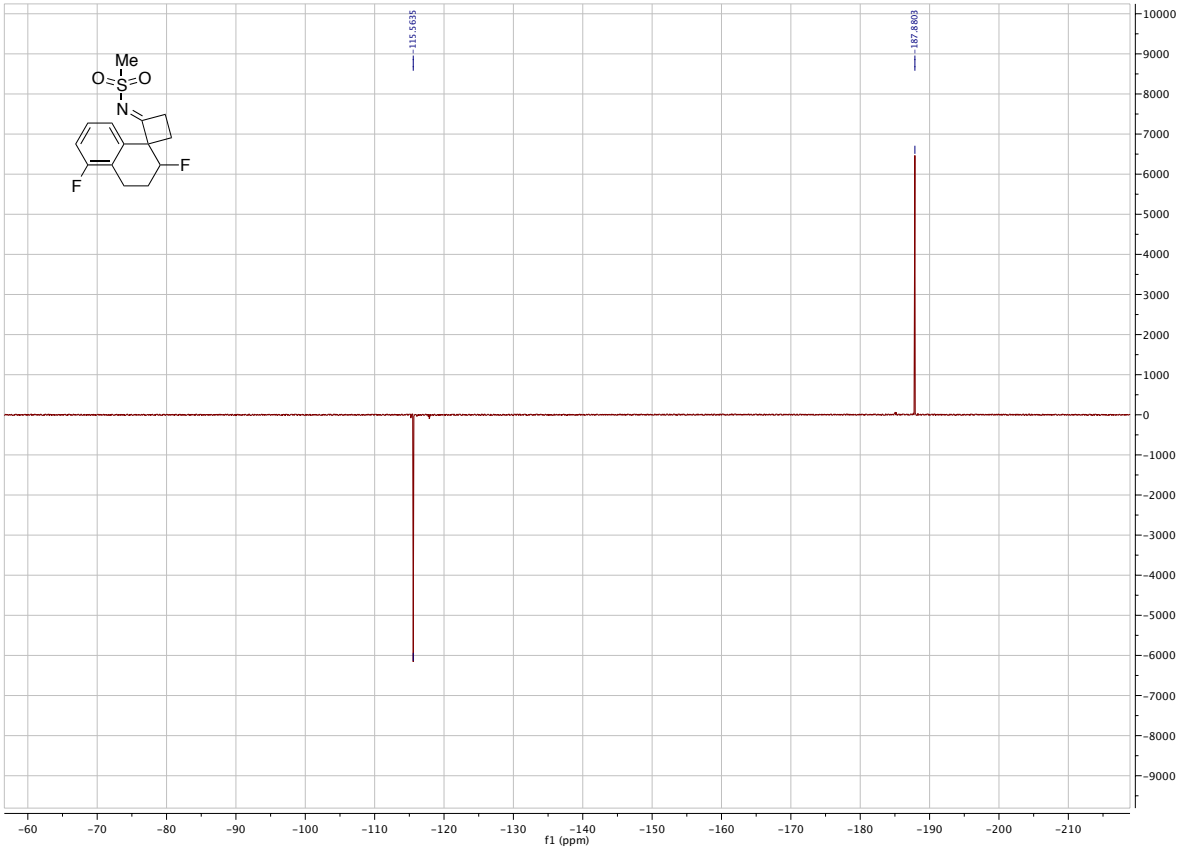
^{1}H NMR 400 MHz, C_6D_6



^{13}C NMR 100 MHz, C_6D_6

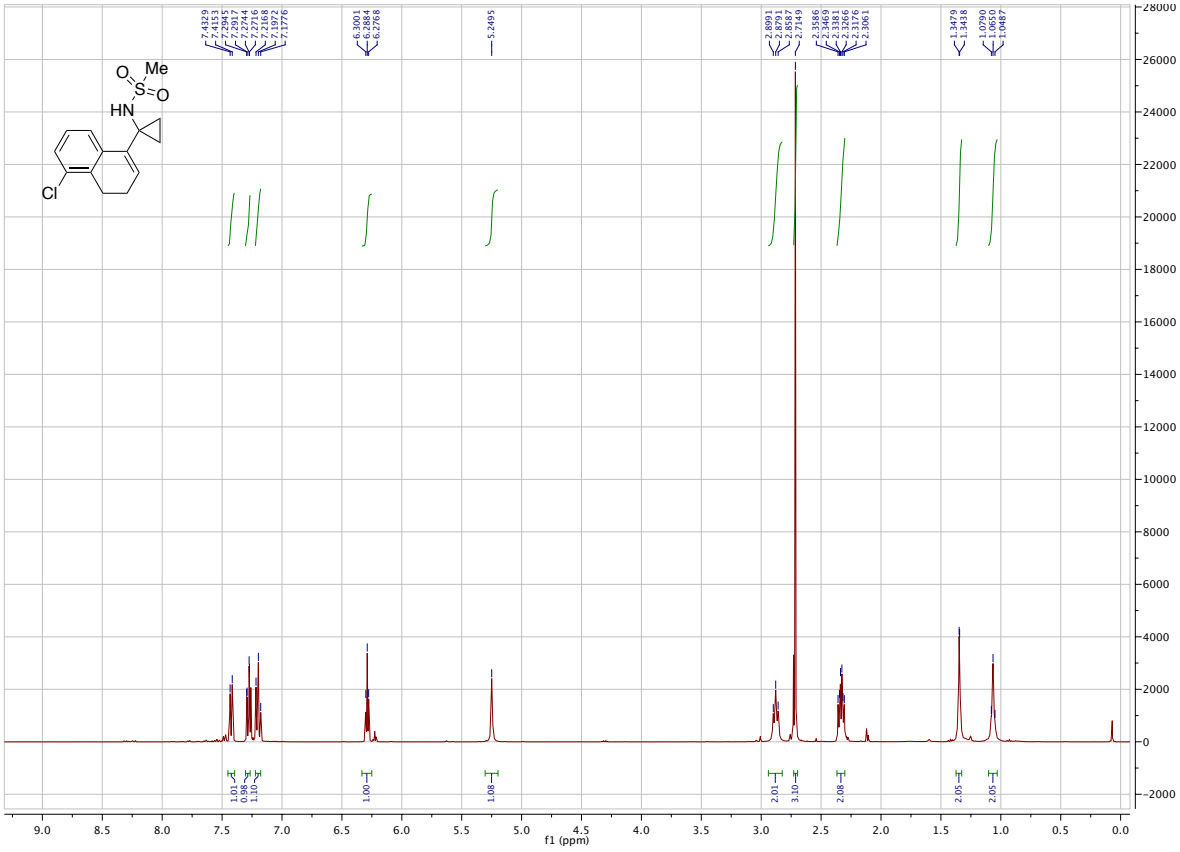


^{19}F NMR 375 MHz, C_6D_6

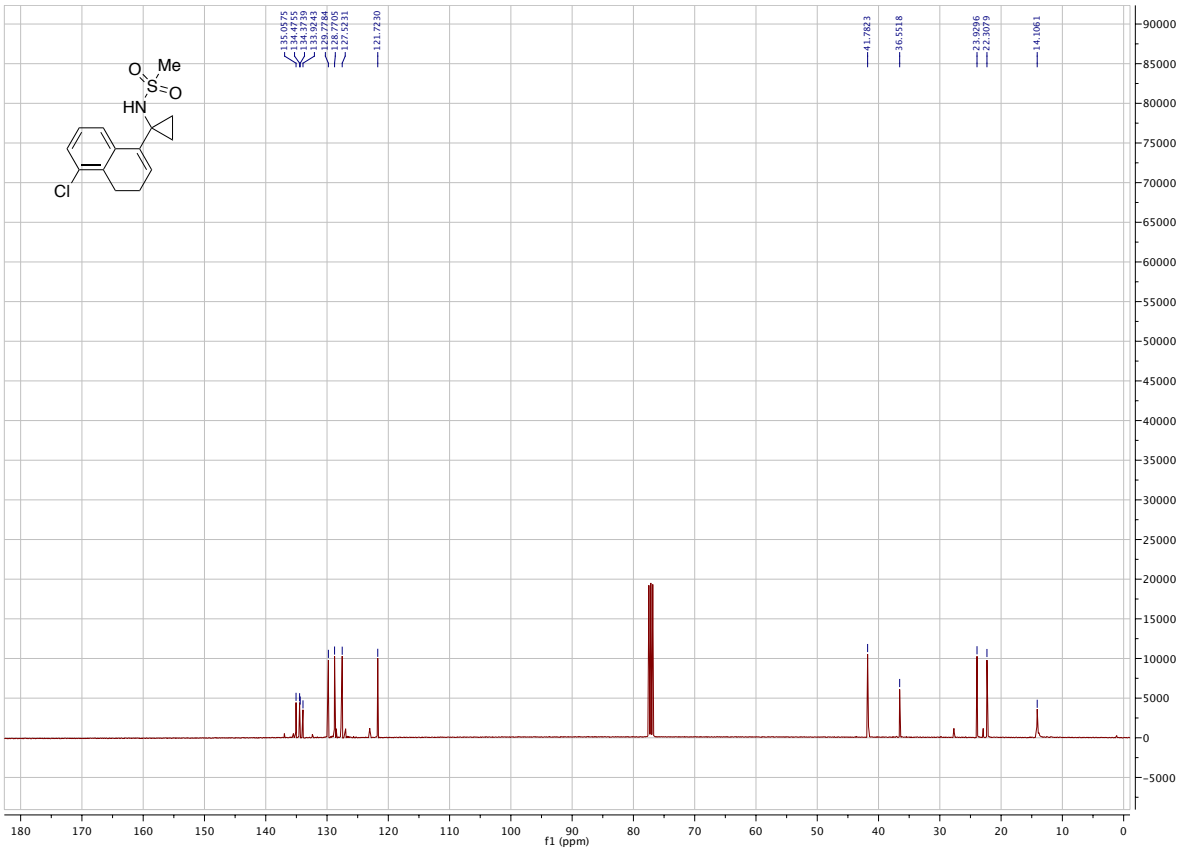


Substrate (A_6)

^{1}H NMR 400 MHz, $CDCl_3$



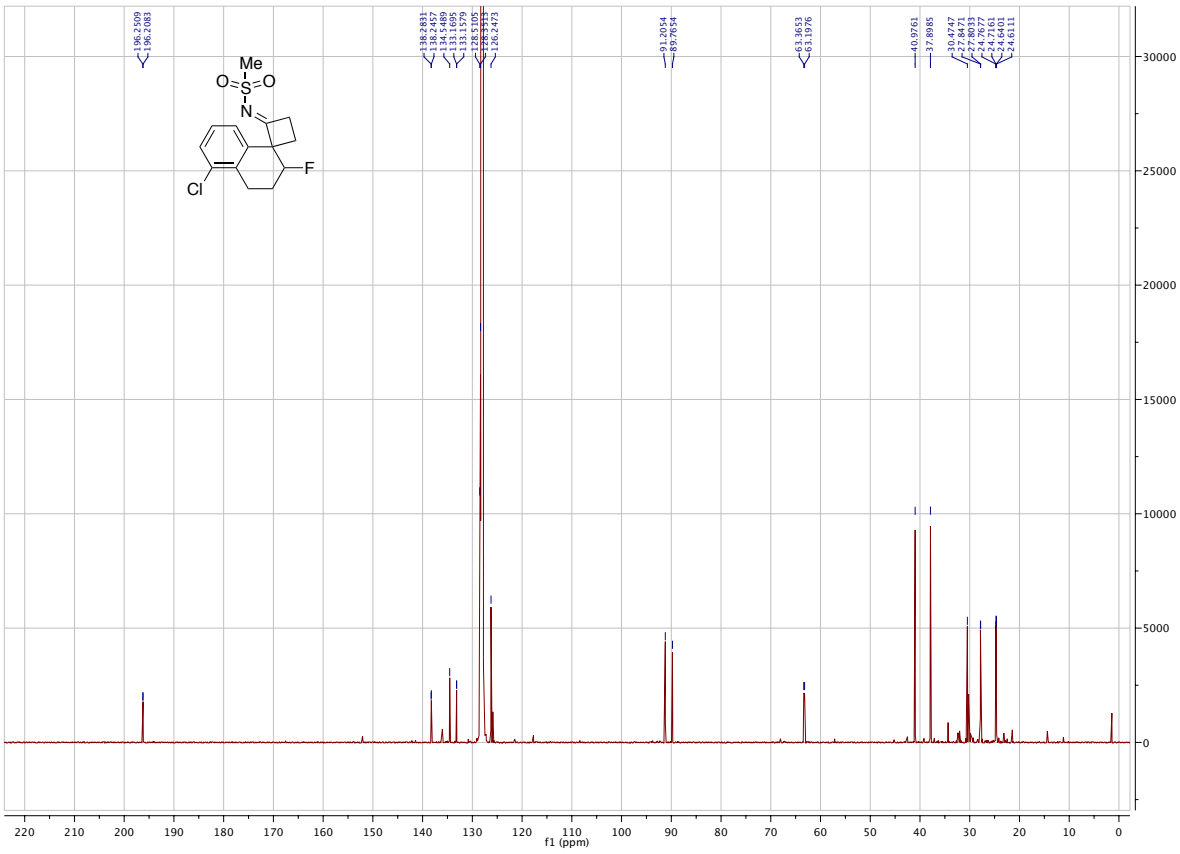
^{13}C NMR 100 MHz, $CDCl_3$



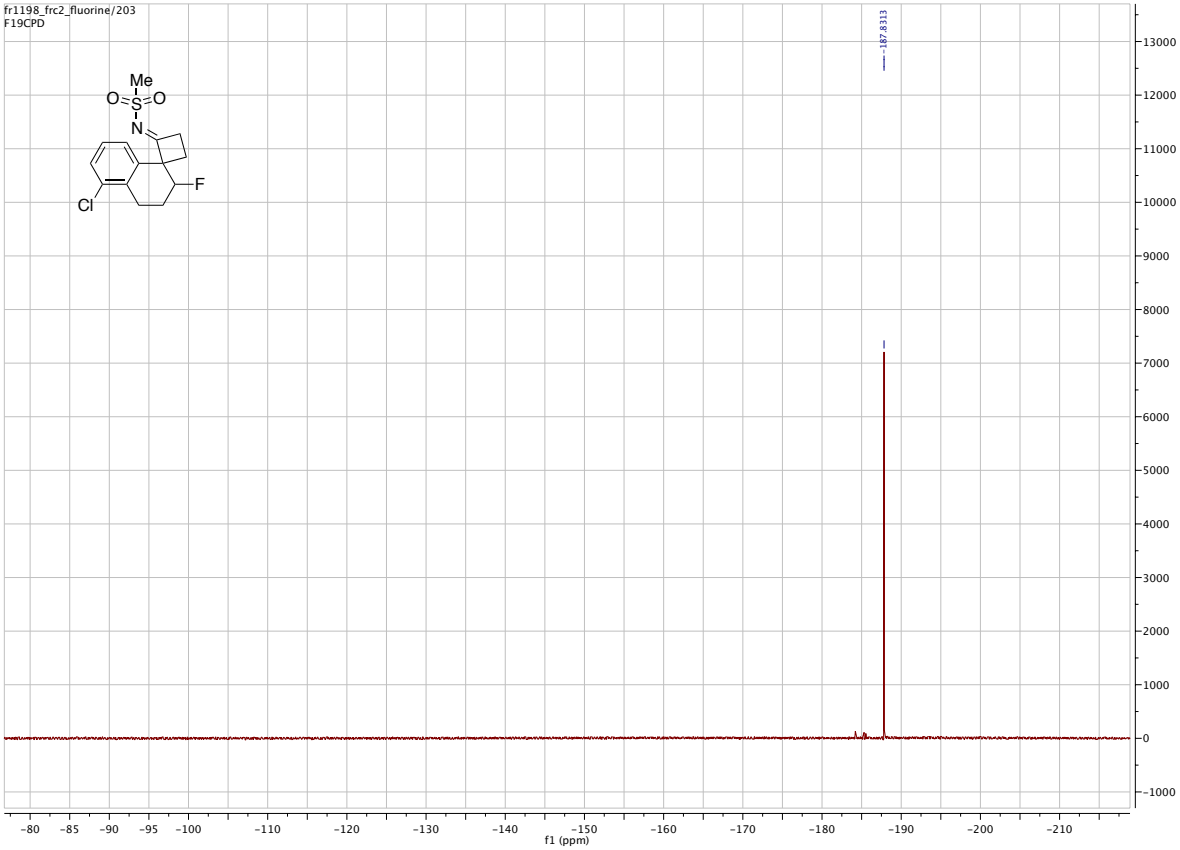
β-Fluoro Cyclobutylimine (B_6)

^{1}H NMR 500 MHz, C_6D_6

^{13}C NMR 125 MHz, C_6D_6

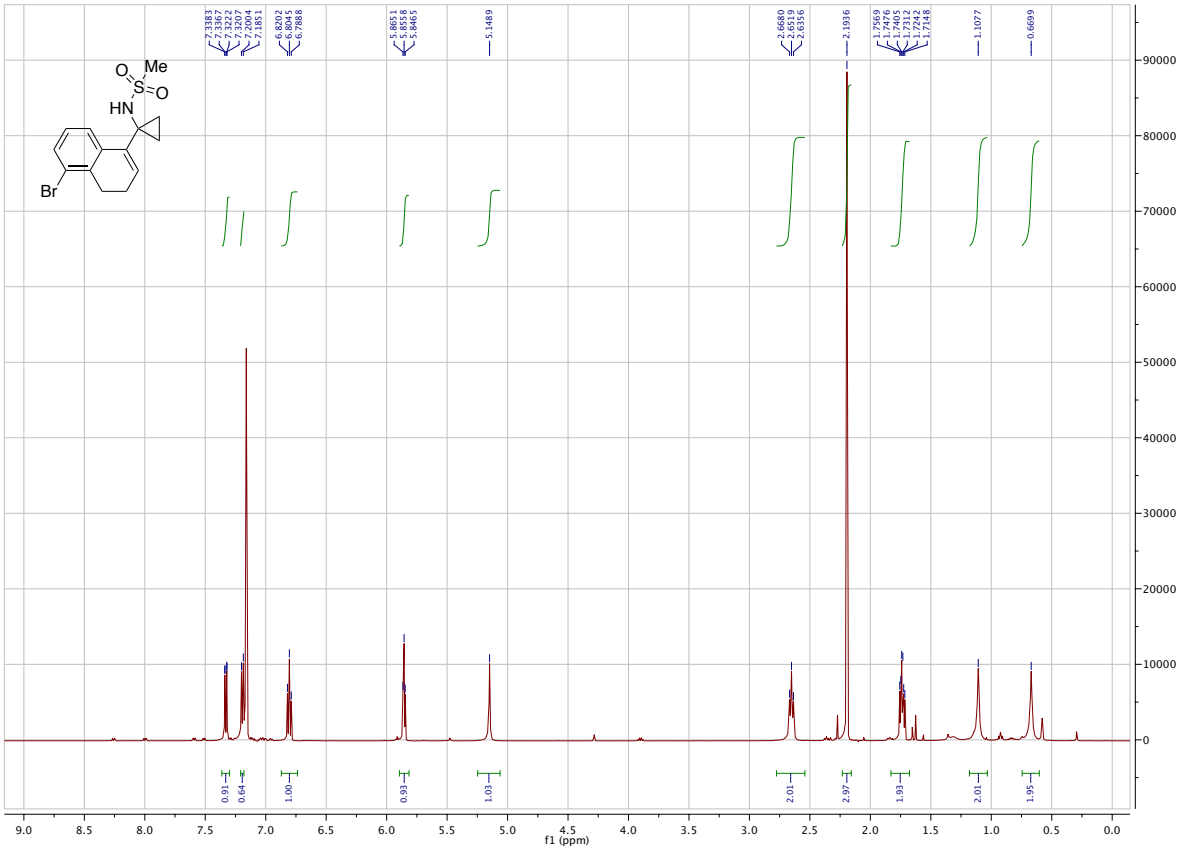


^{19}F NMR 375 MHz, C_6D_6

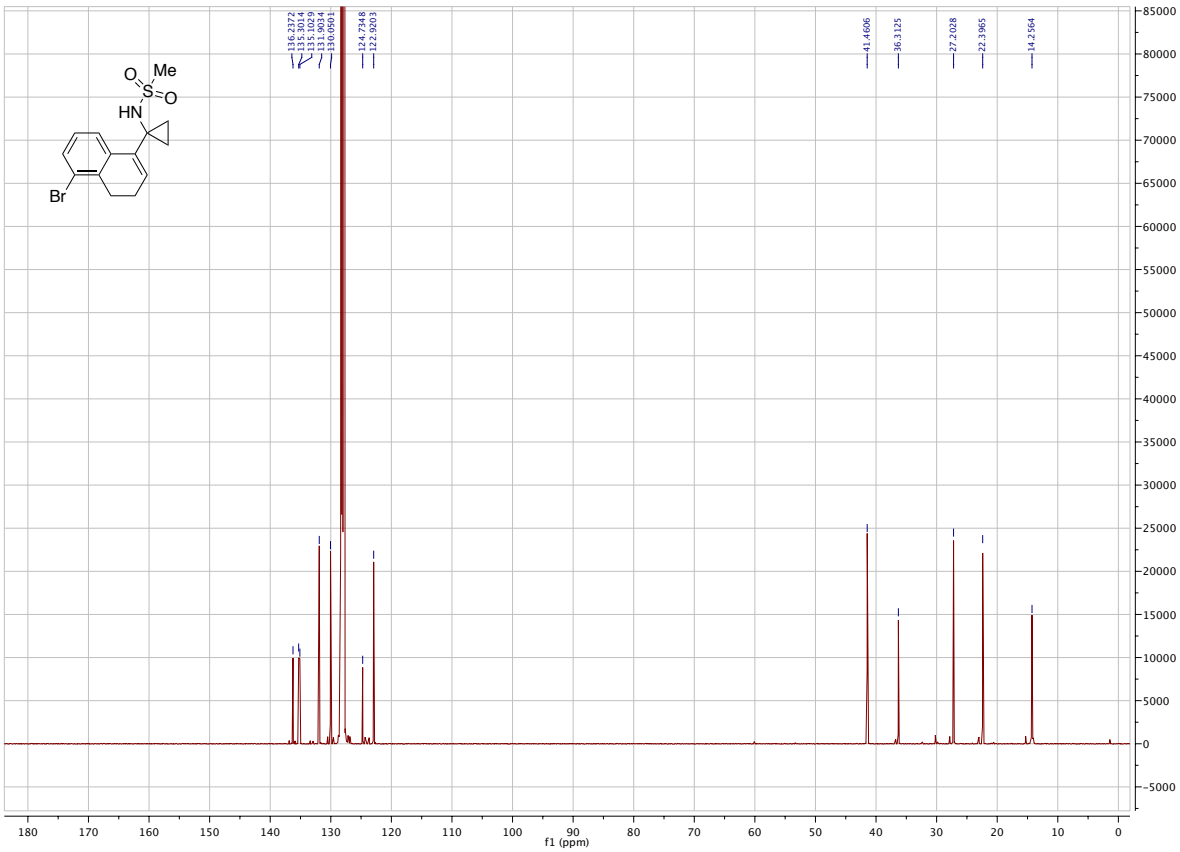


Substrate (A_7)

^{1}H NMR 500 MHz, C_6D_6

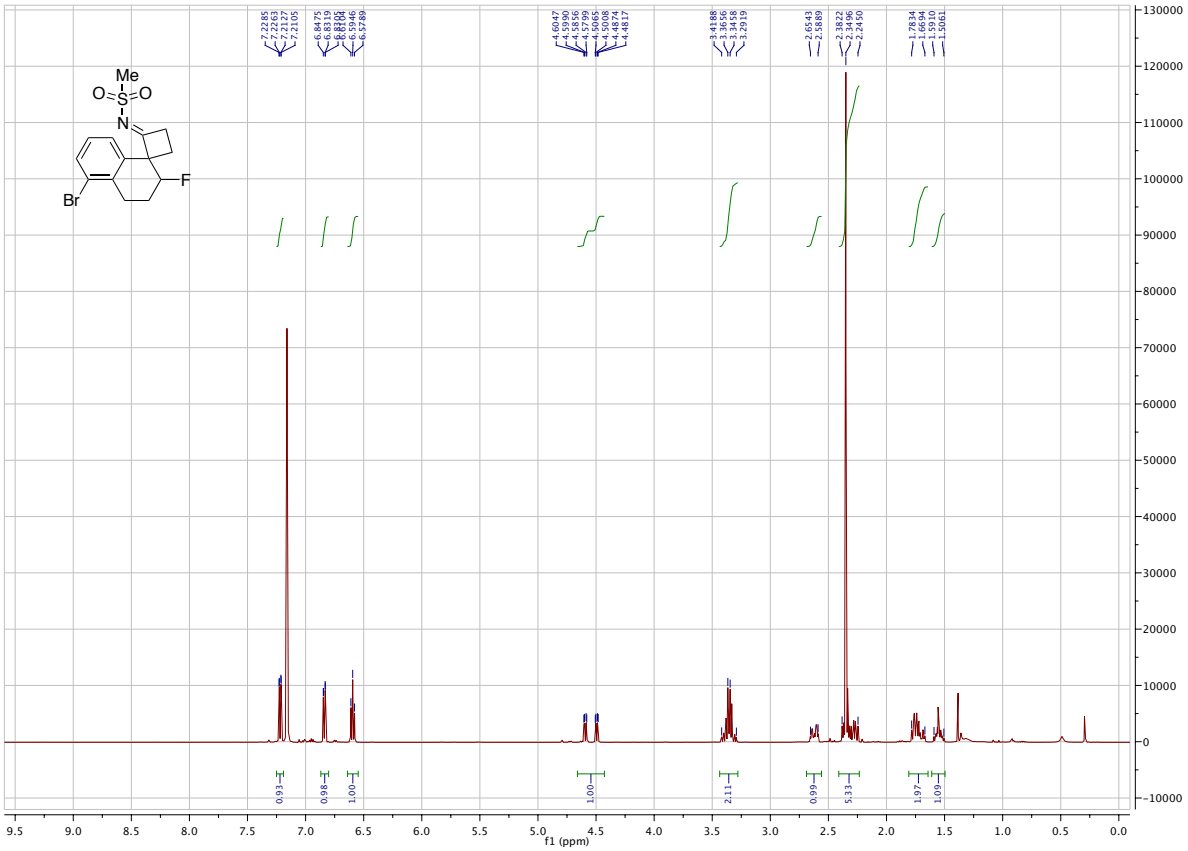


^{13}C NMR 125 MHz, C_6D_6

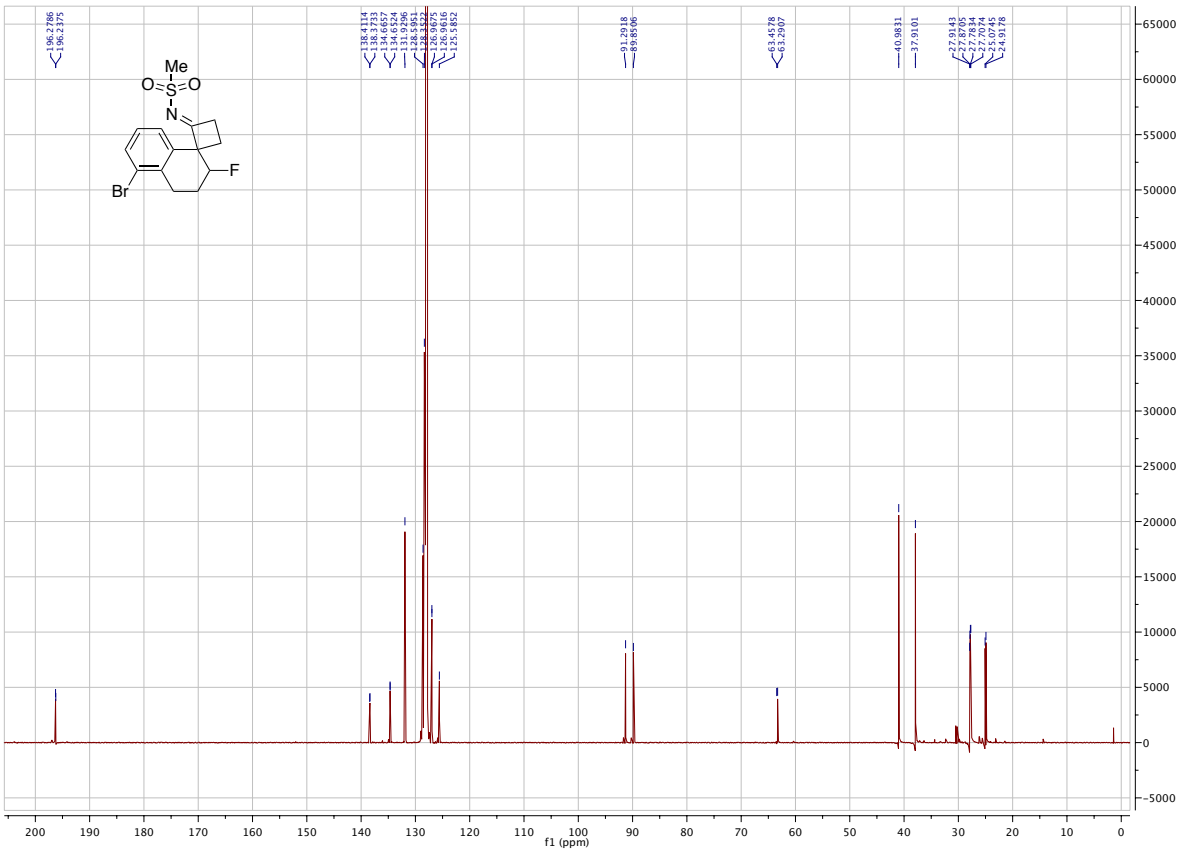


β-Fluoro Cyclobutylimine (B_7)

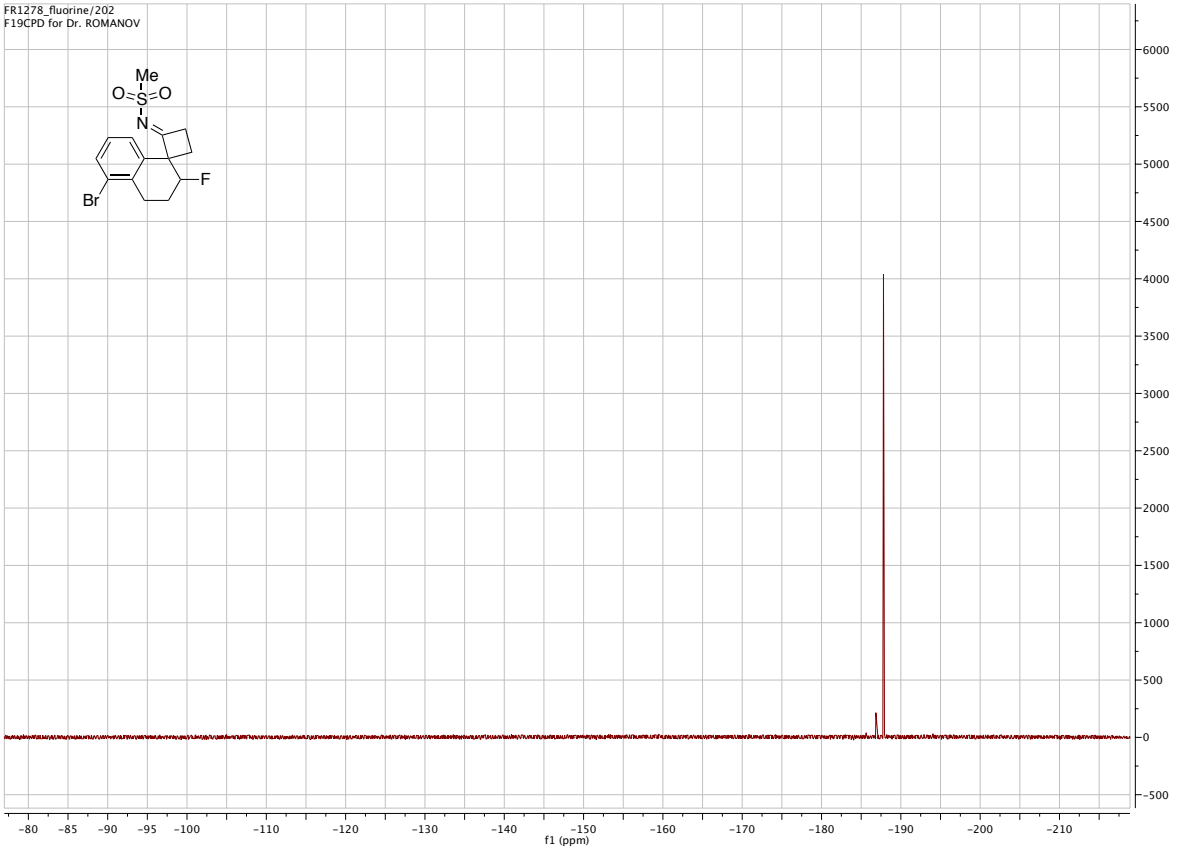
^{1}H NMR 500 MHz, C_6D_6



^{13}C NMR 125 MHz, C_6D_6

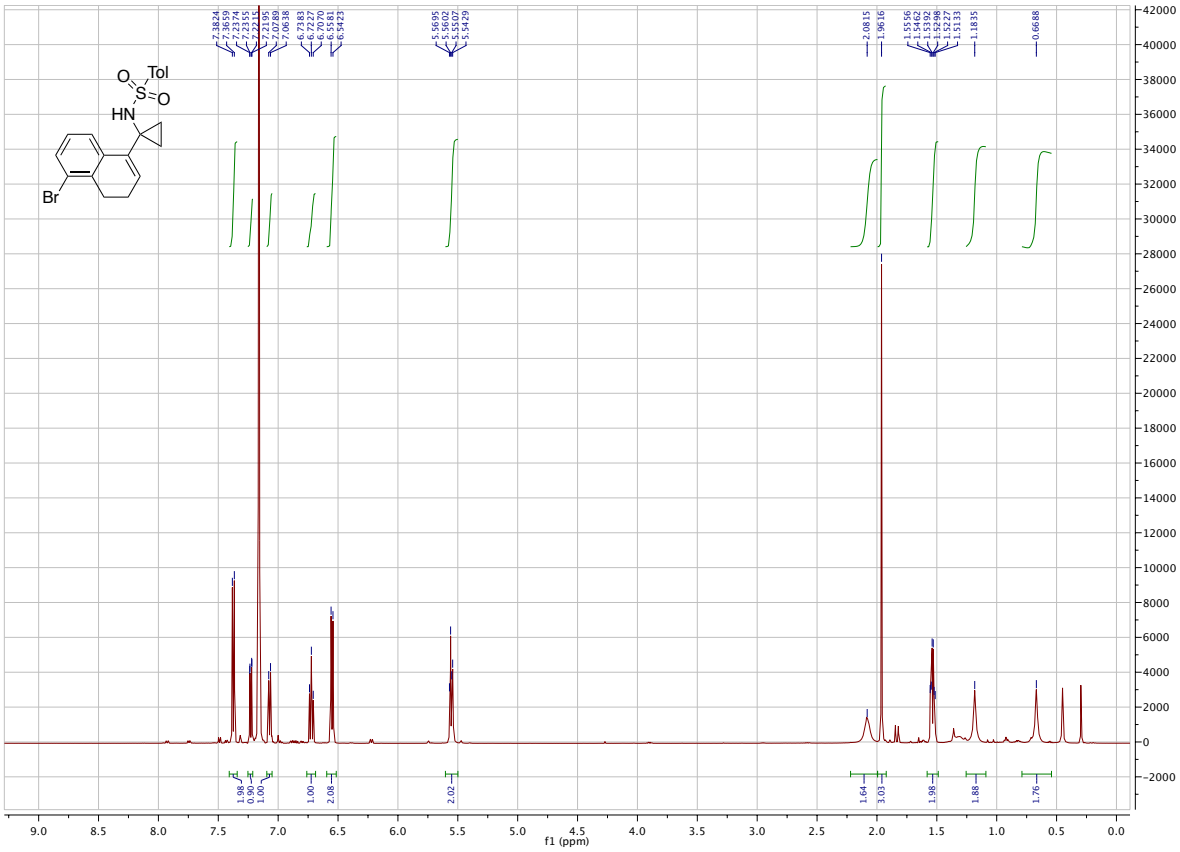


^{19}F NMR 375 MHz, C_6D_6

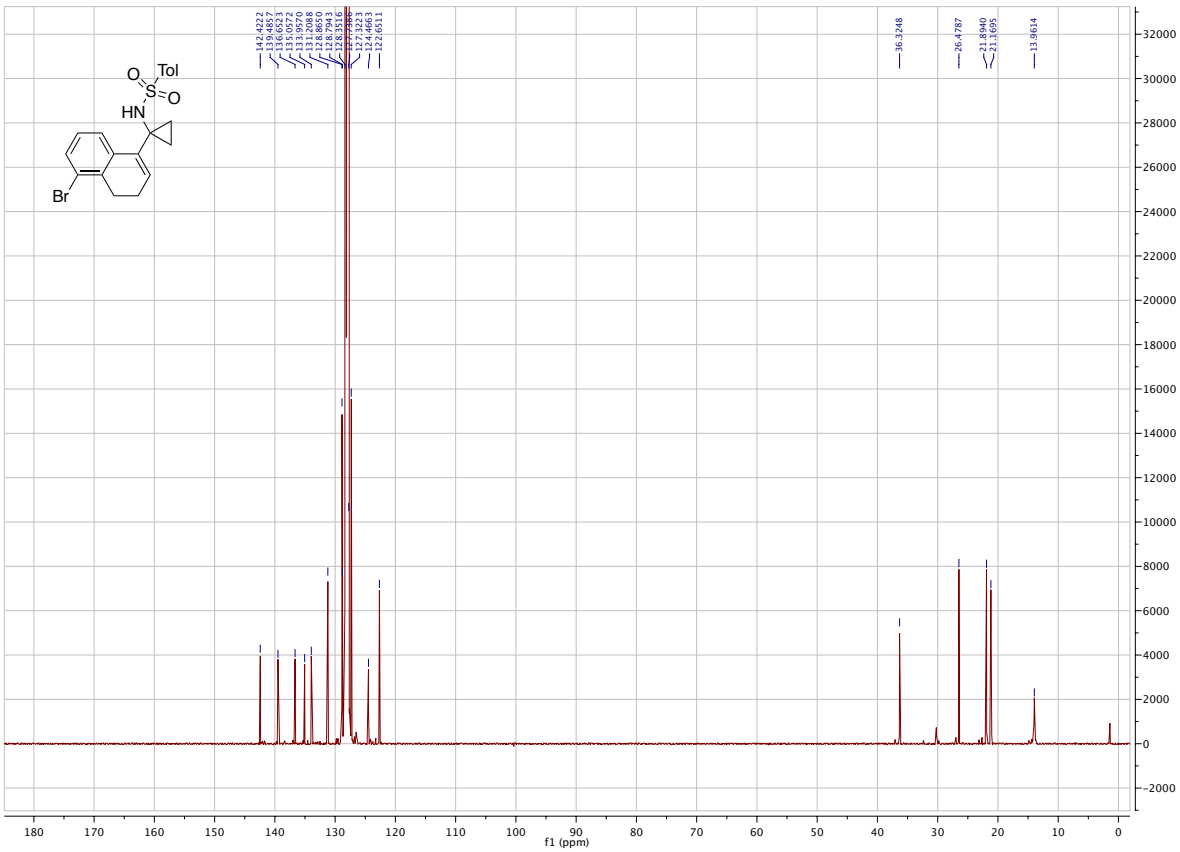


Substrate (A_8)

^{1}H NMR 500 MHz, C_6D_6

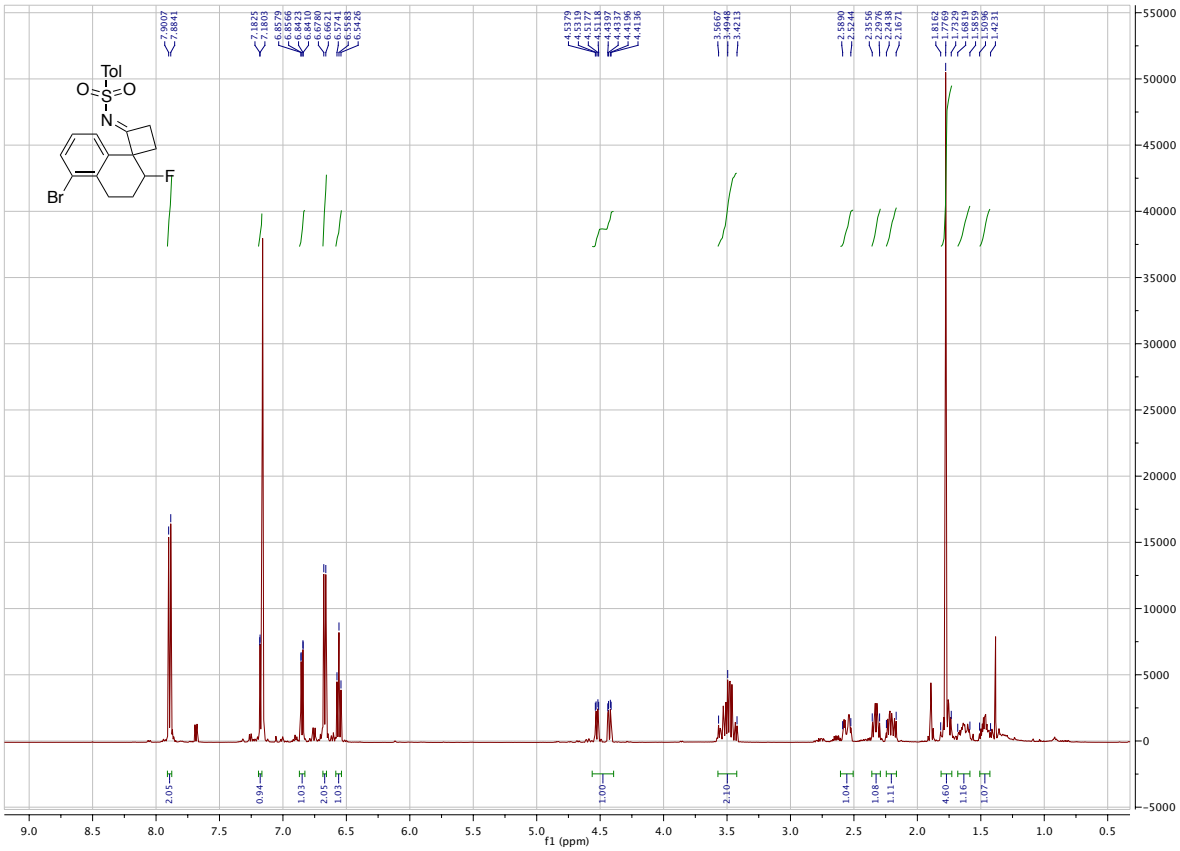


^{13}C NMR 125 MHz, C_6D_6

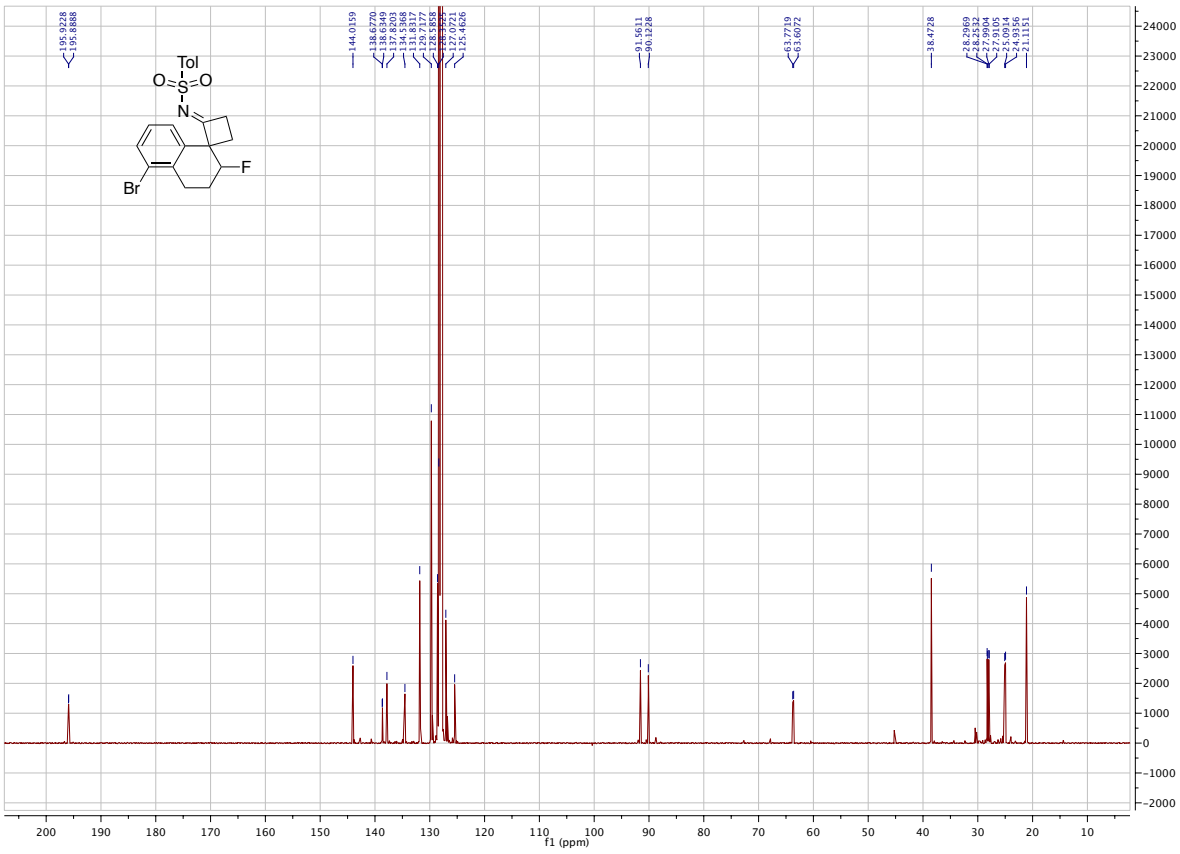


β-Fluoro Cyclobutylimine (B_8)

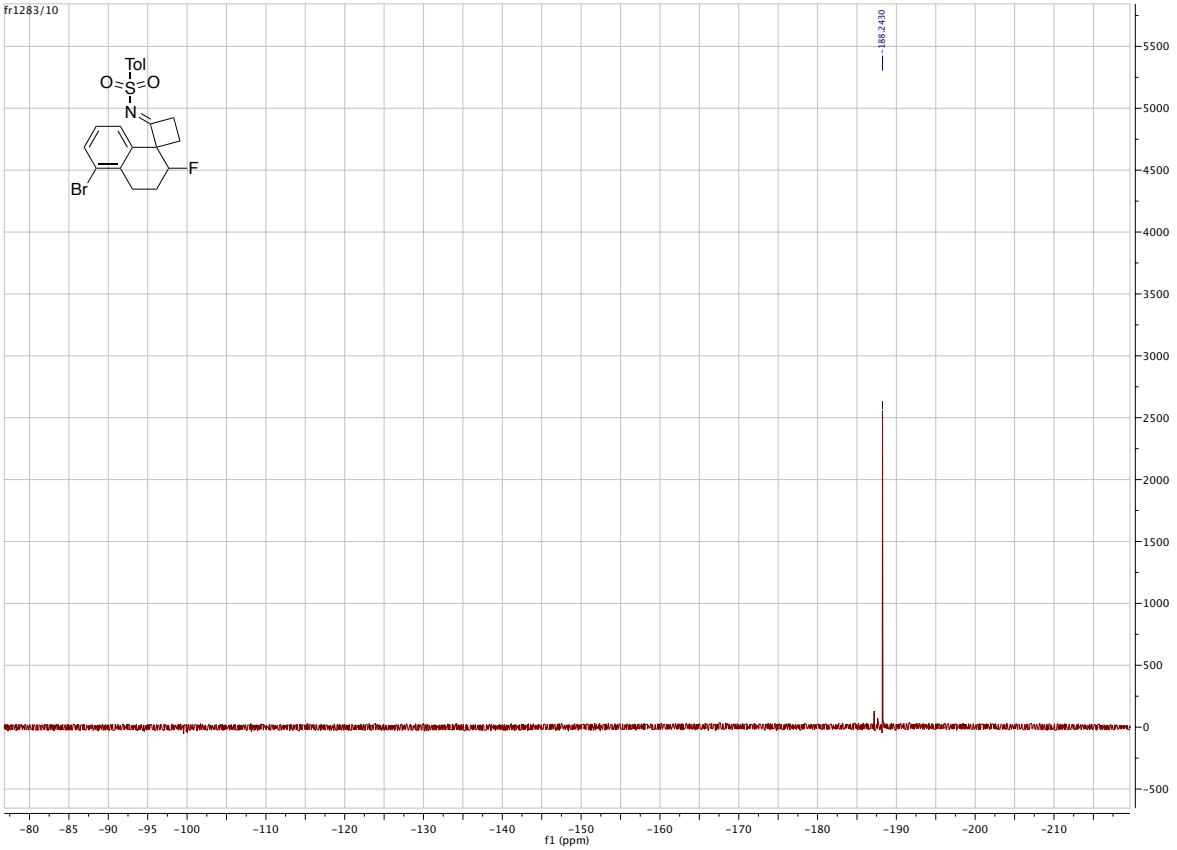
^{1}H NMR 500 MHz, C_6D_6



^{13}C NMR 125 MHz, C_6D_6

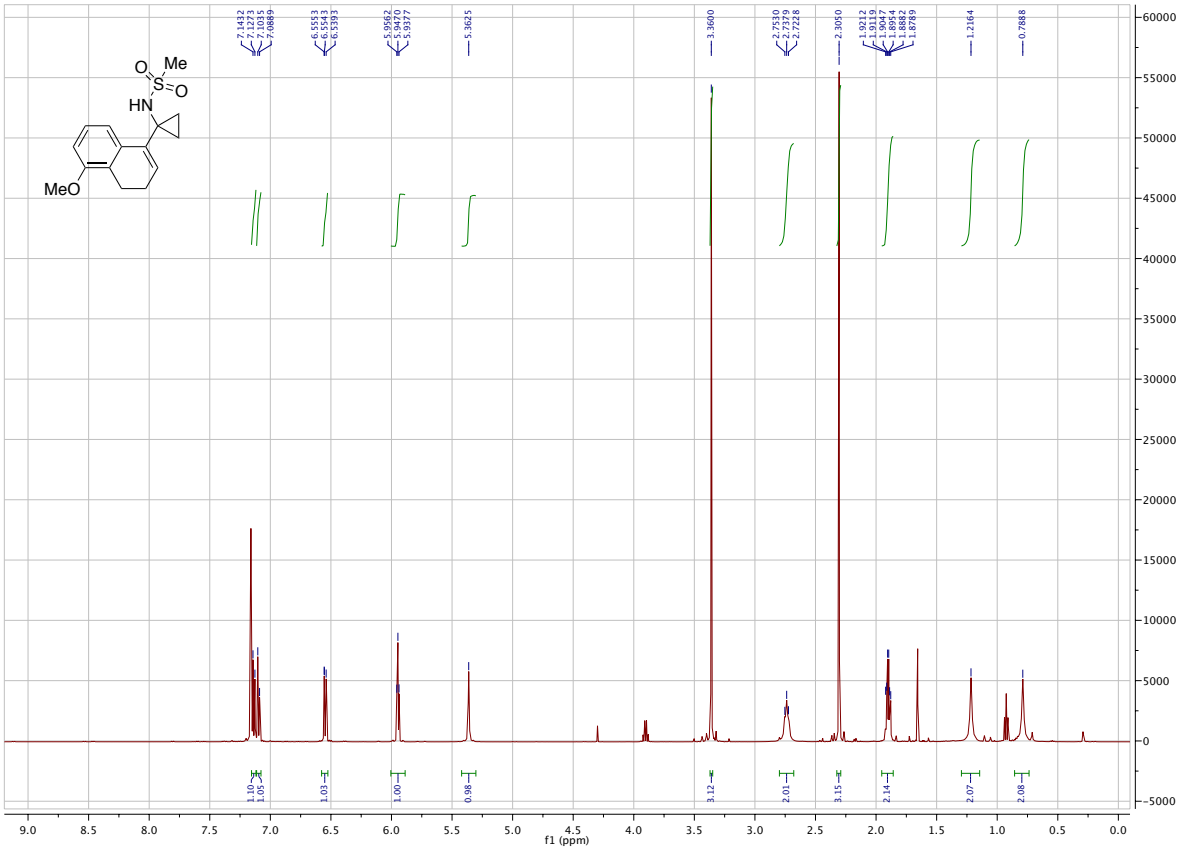


^{19}F NMR 375 MHz, C_6D_6

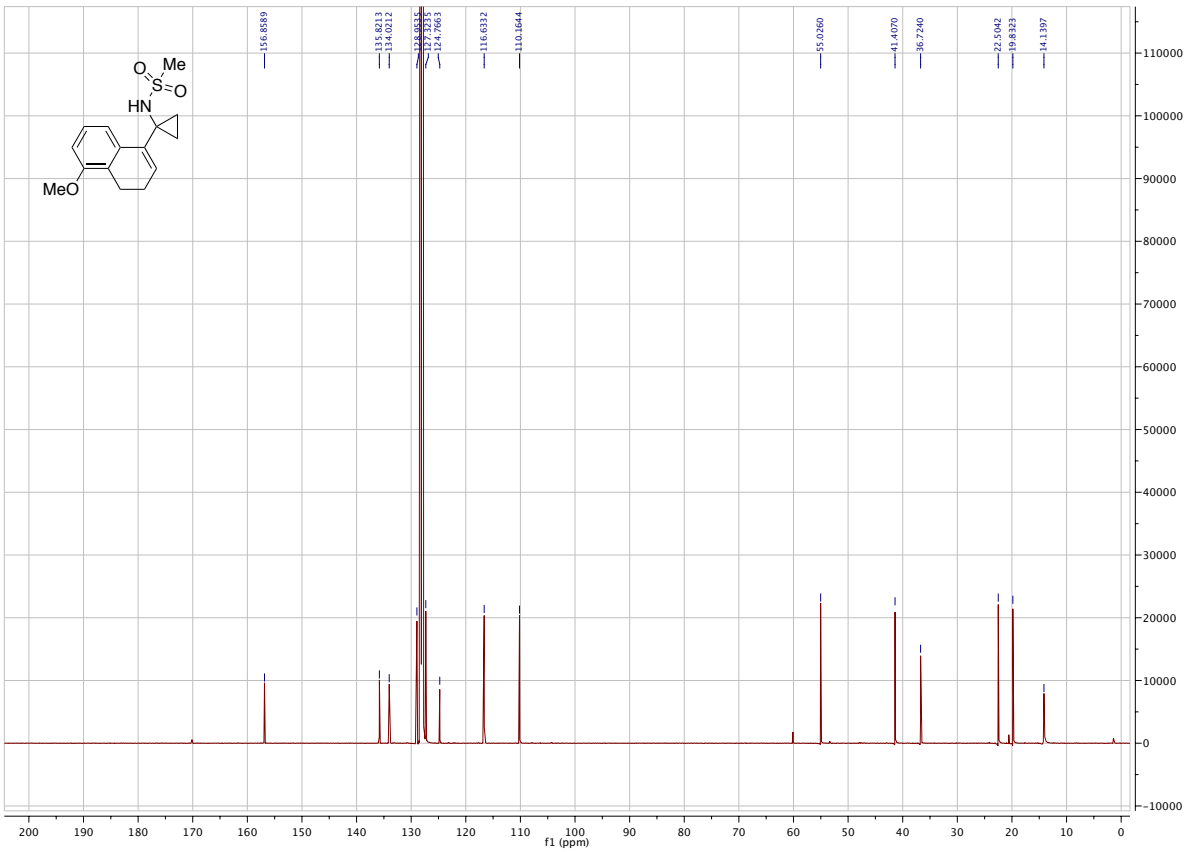


Substrate (A_9)

^{1}H NMR 500 MHz, C_6D_6

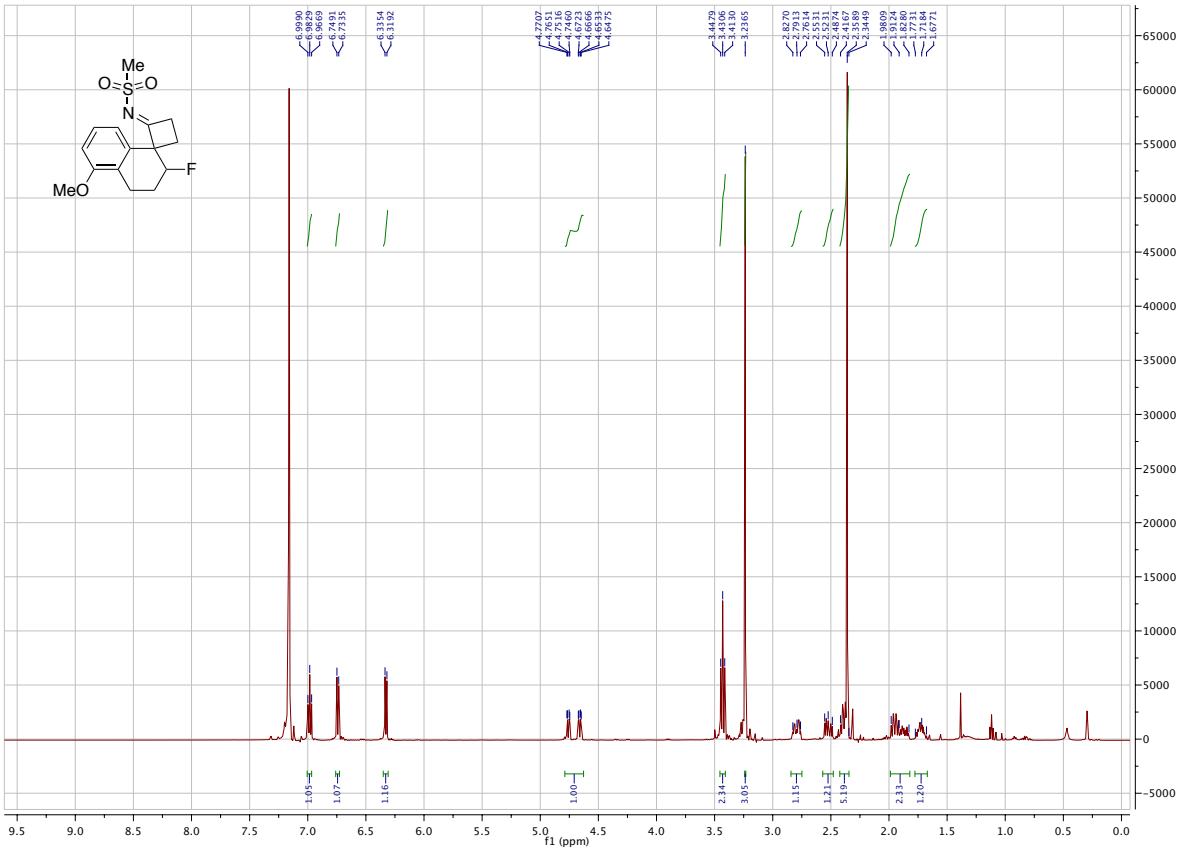


^{13}C NMR 125 MHz, C_6D_6

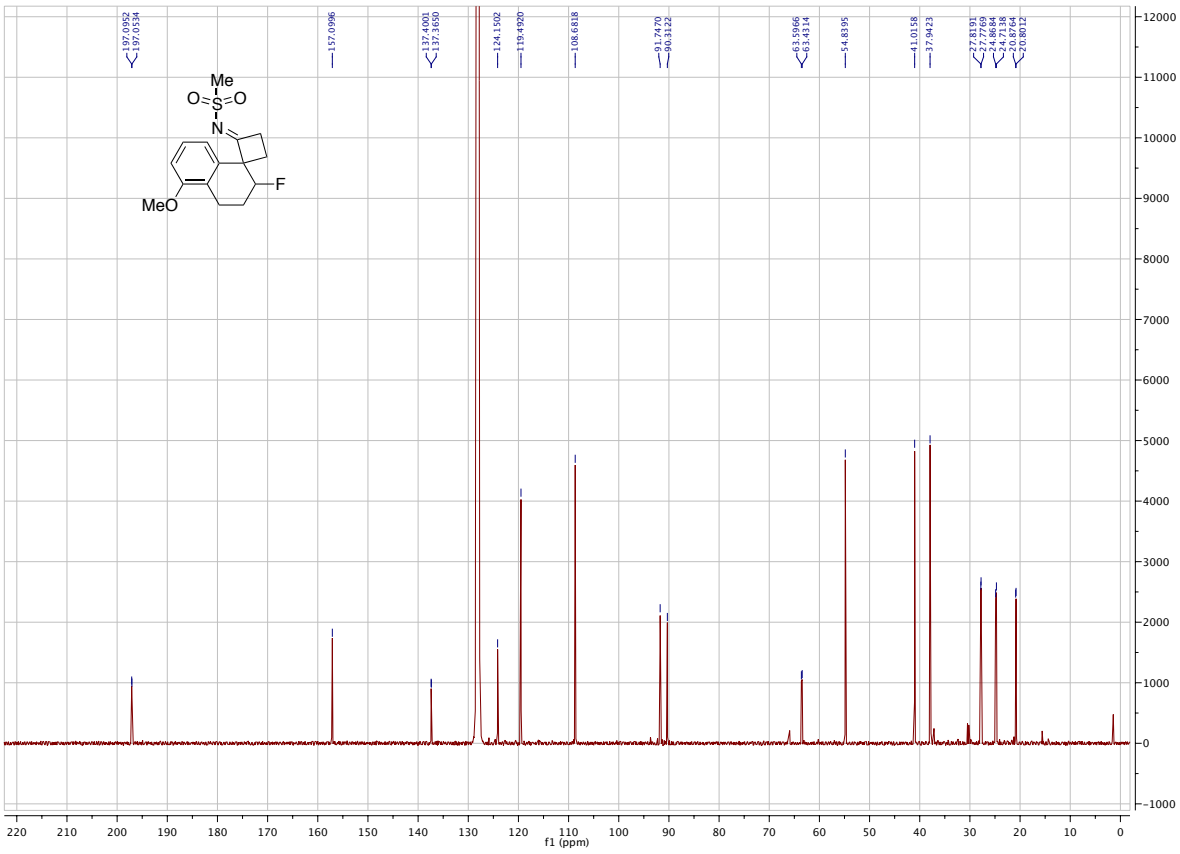


β-Fluoro Cyclobutylimine (B_9)

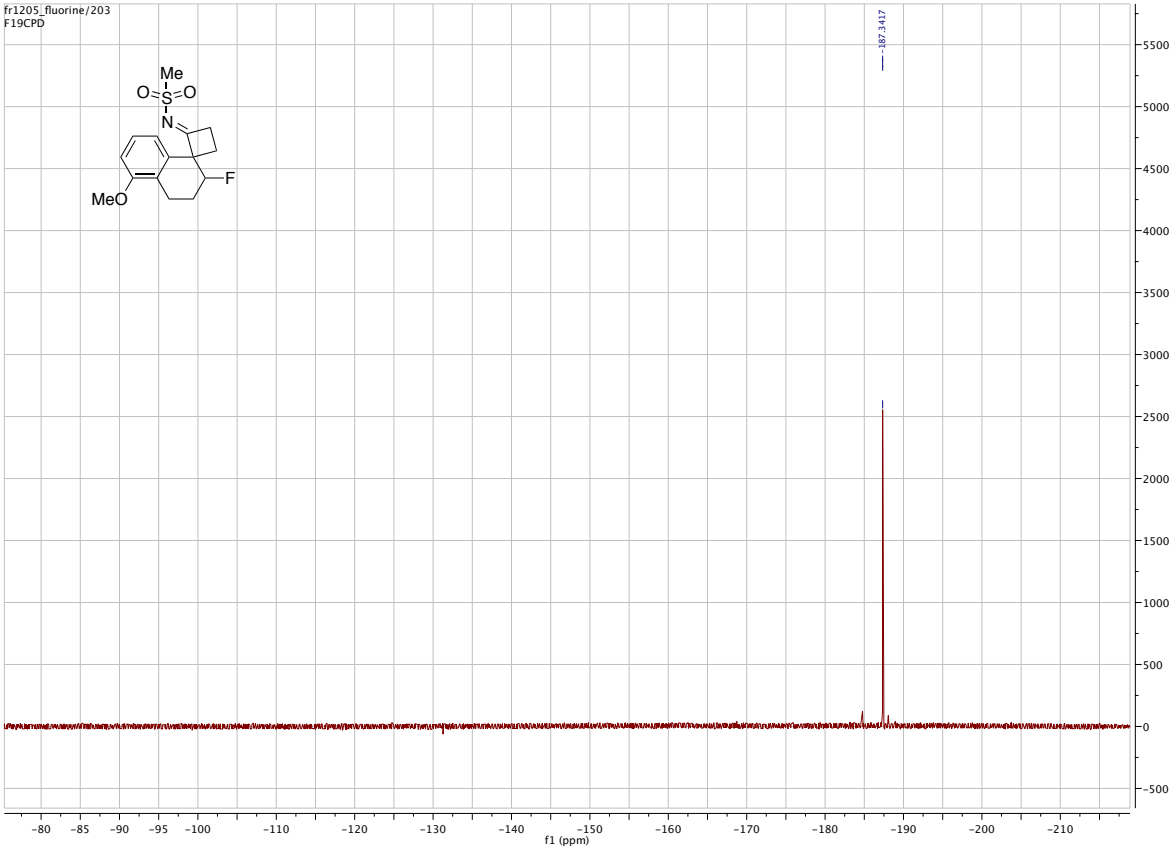
^{1}H NMR 500 MHz, C_6D_6



^{13}C NMR 125 MHz, C_6D_6

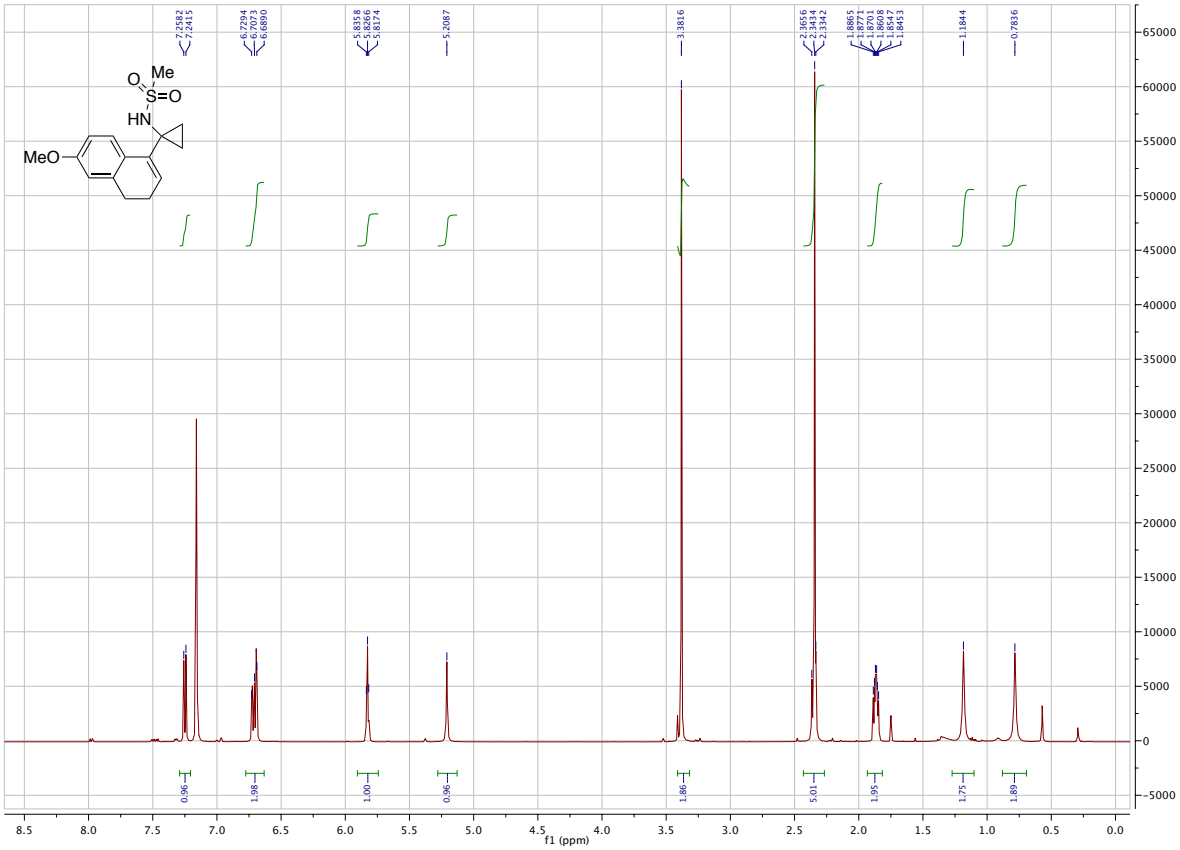


^{19}F NMR 375 MHz, C_6D_6

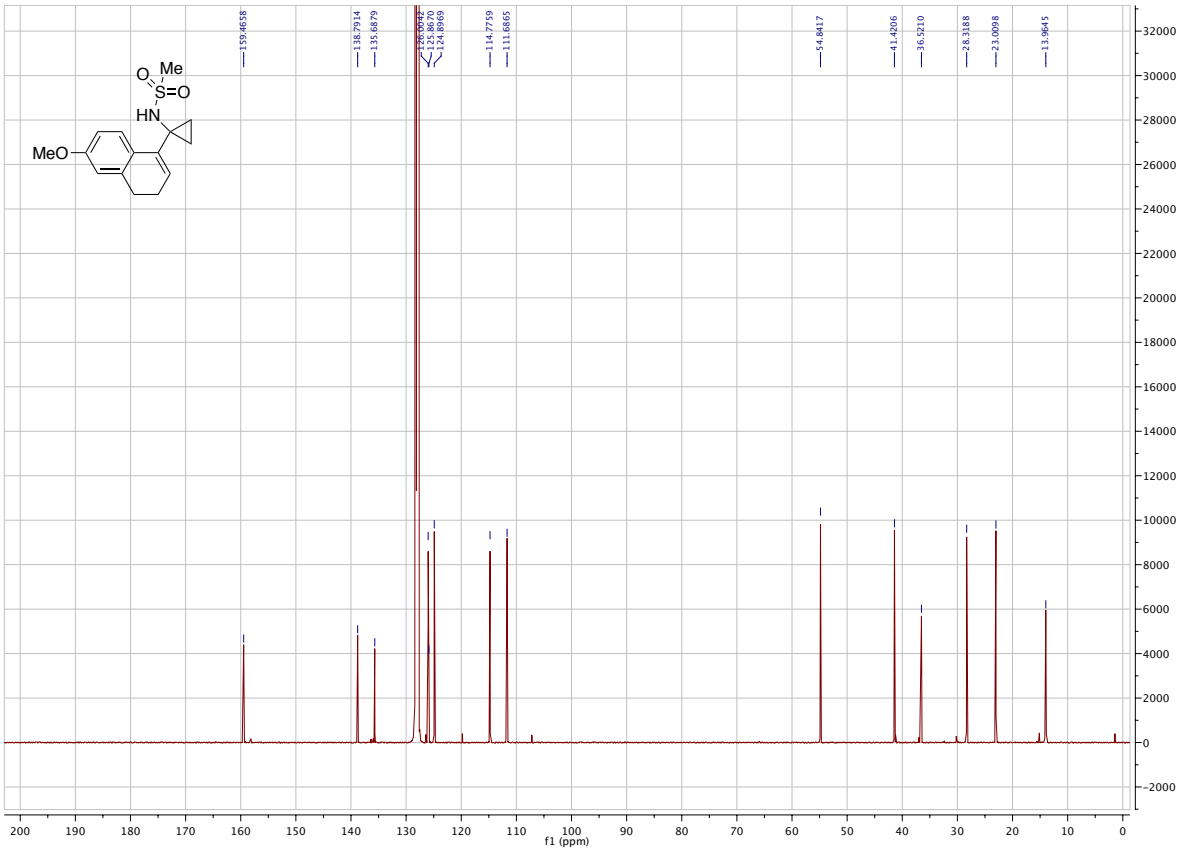


Substrate (A_{10})

^{1}H NMR 500 MHz, C_6D_6

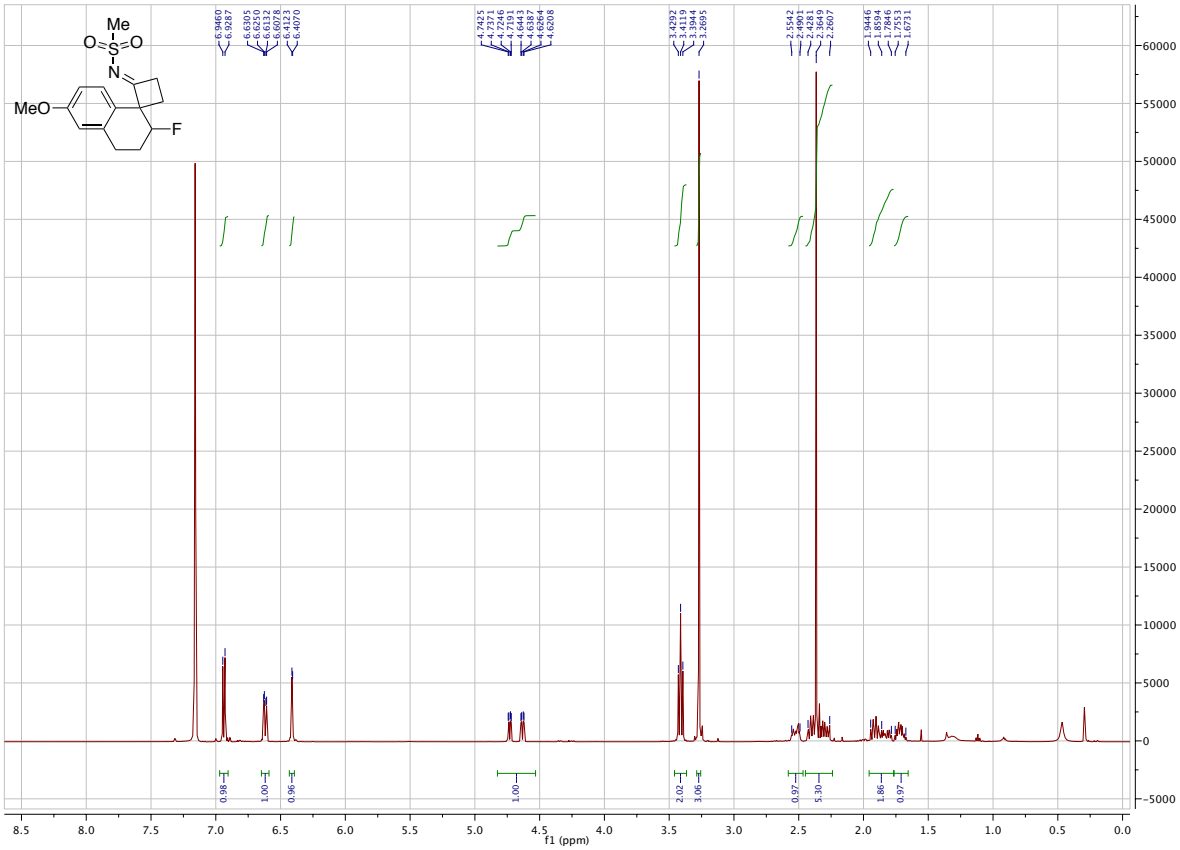


^{13}C NMR 125 MHz, C_6D_6

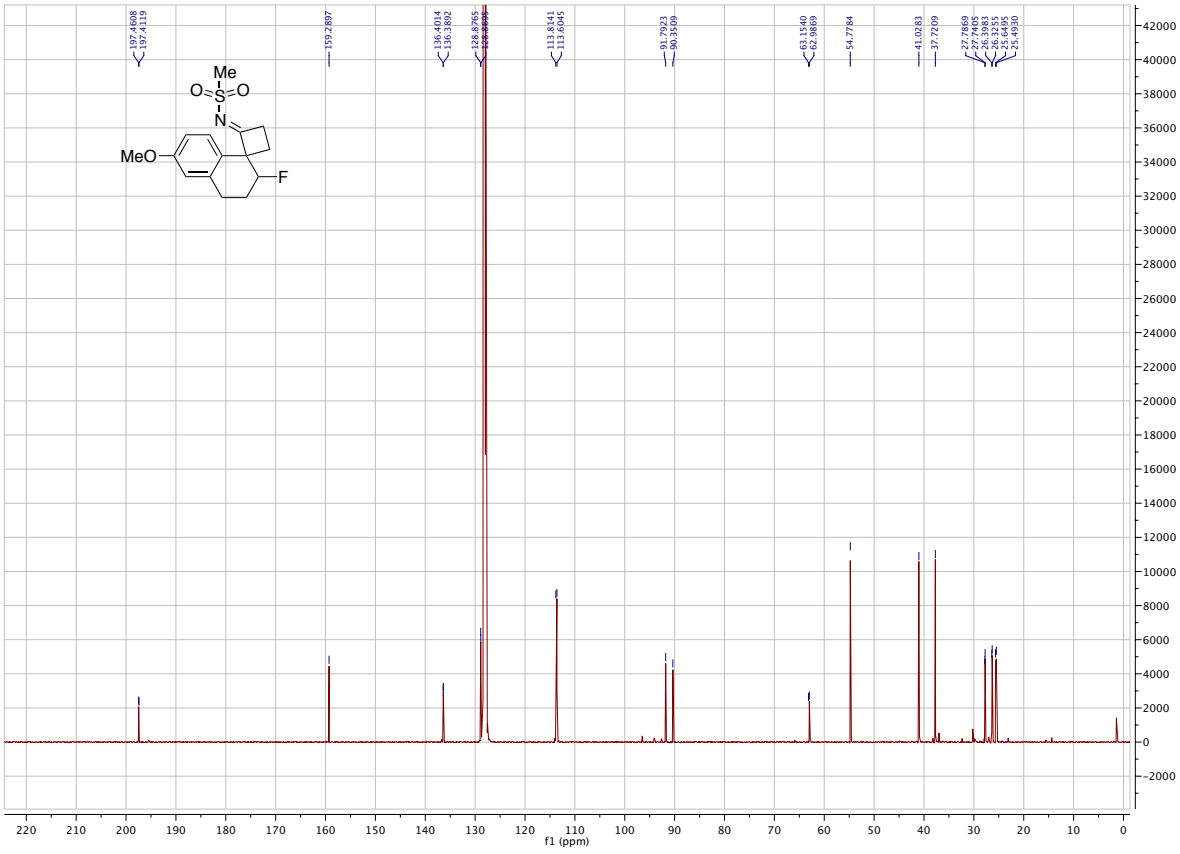


β-Fluoro Cyclobutylimine (B_{10})

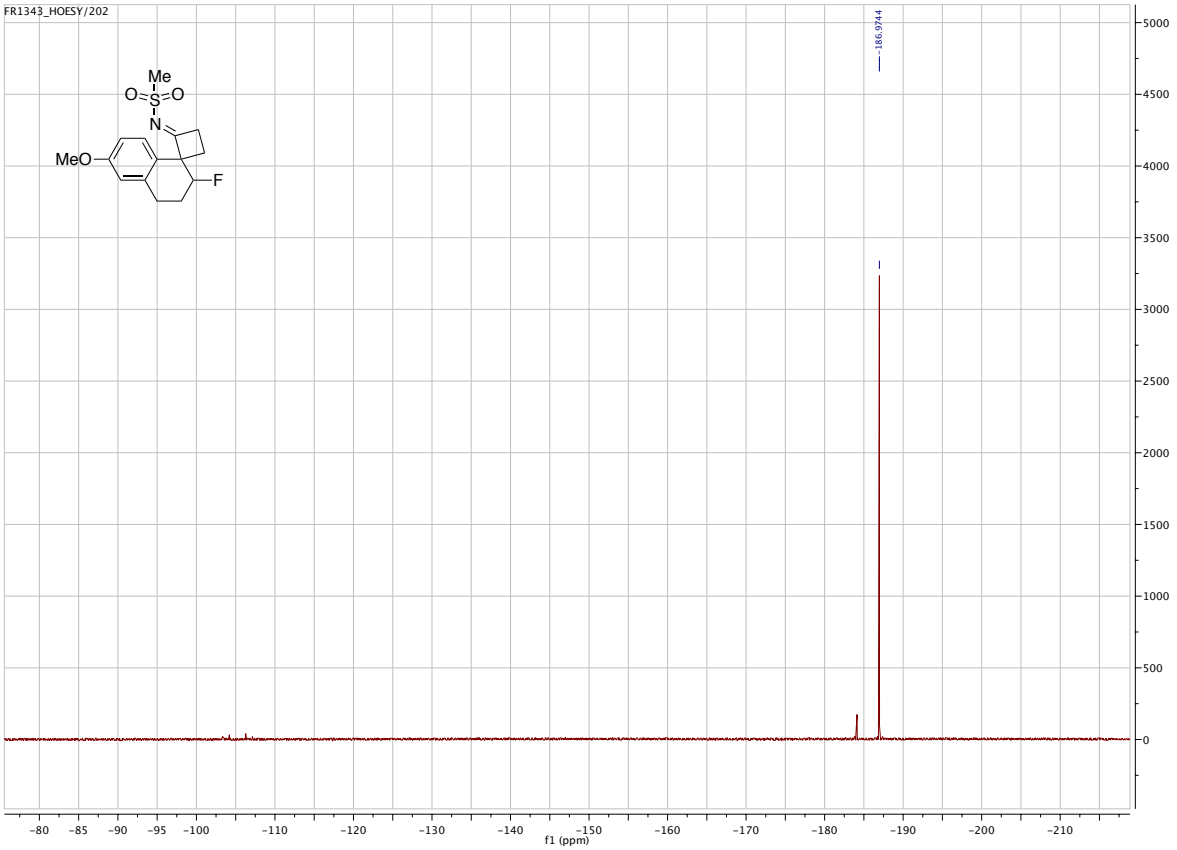
^{1}H NMR 500 MHz, C_6D_6



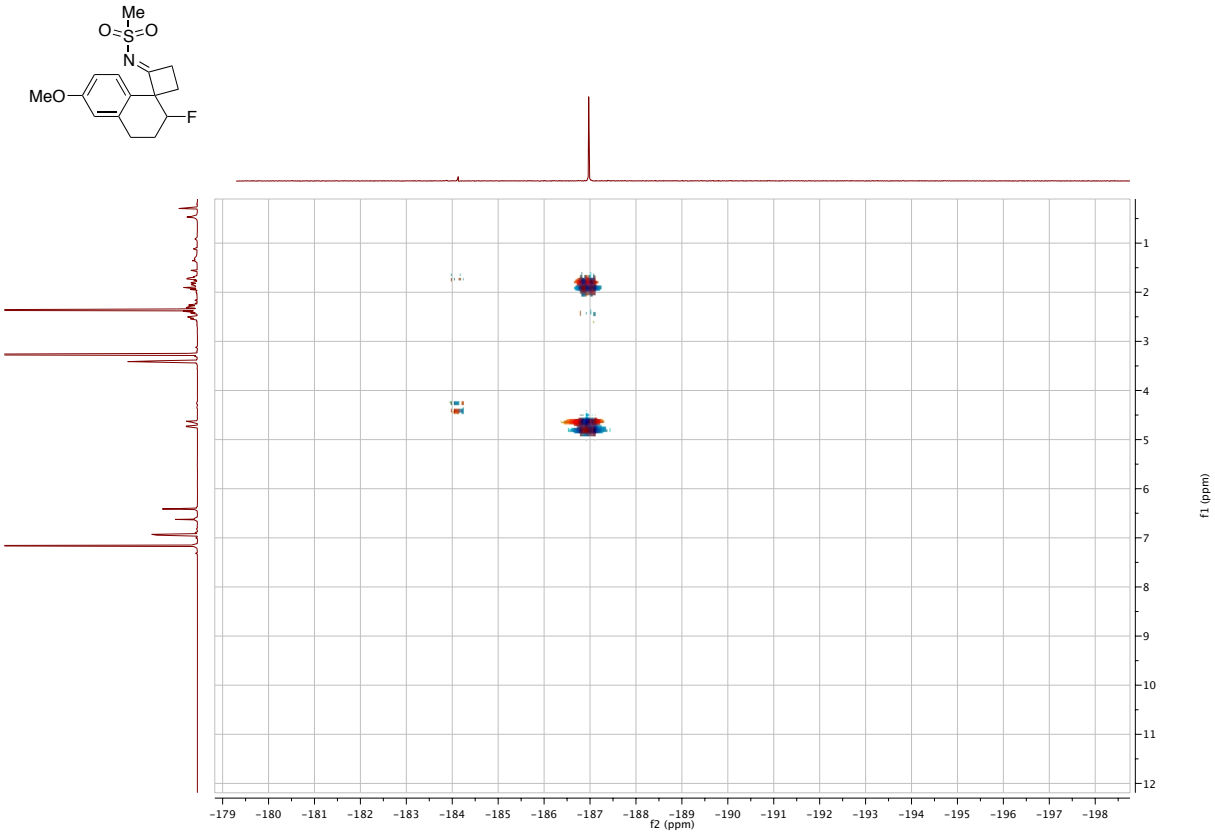
^{13}C NMR 125 MHz, C_6D_6



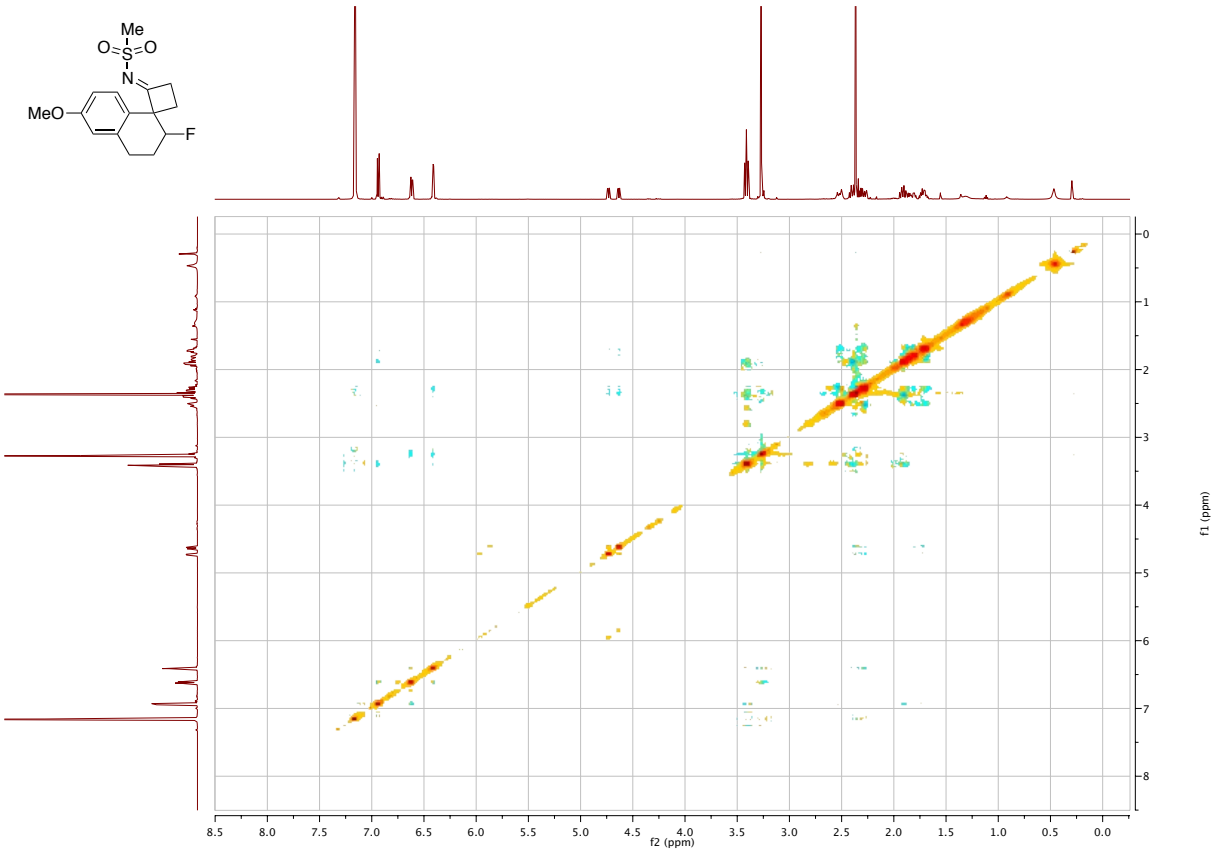
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{19}F HOESY 300 MHz, C_6D_6

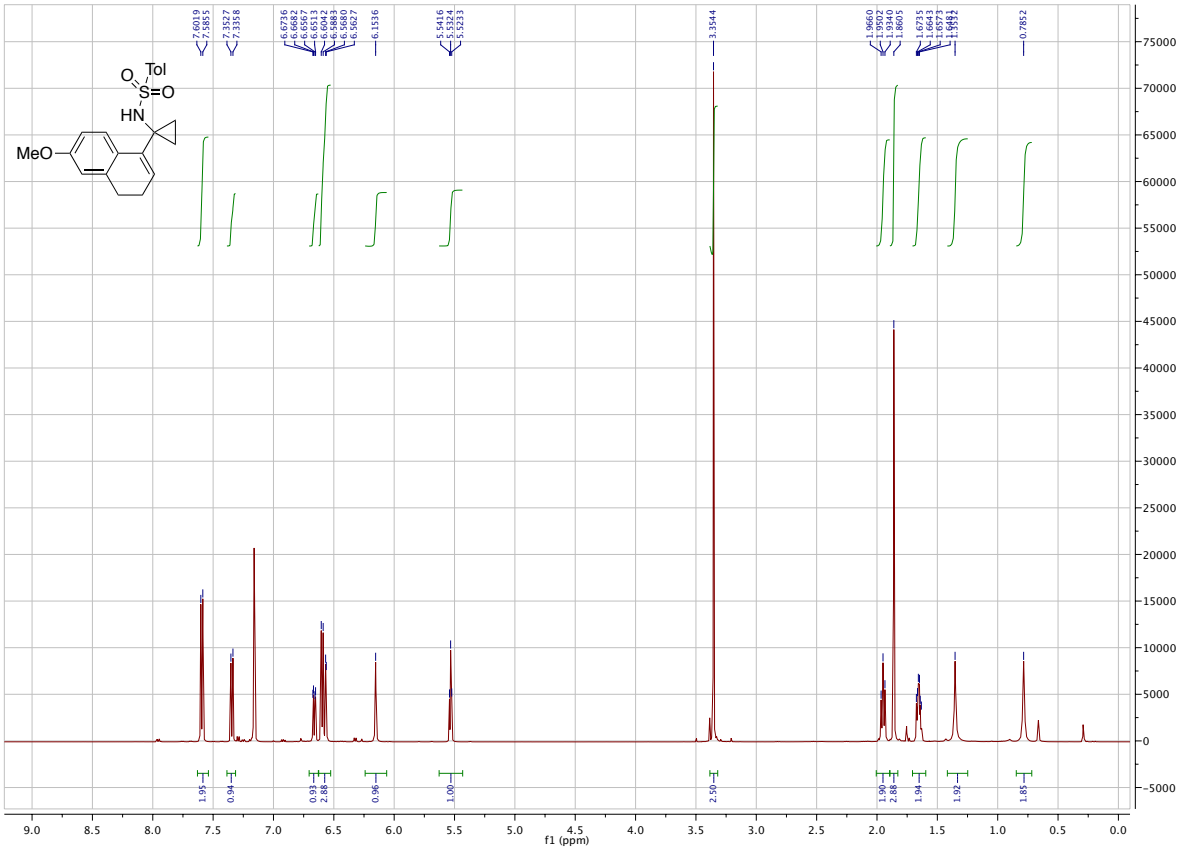


^{1}H-^{1}H NOESY 500 MHz, C_6D_6

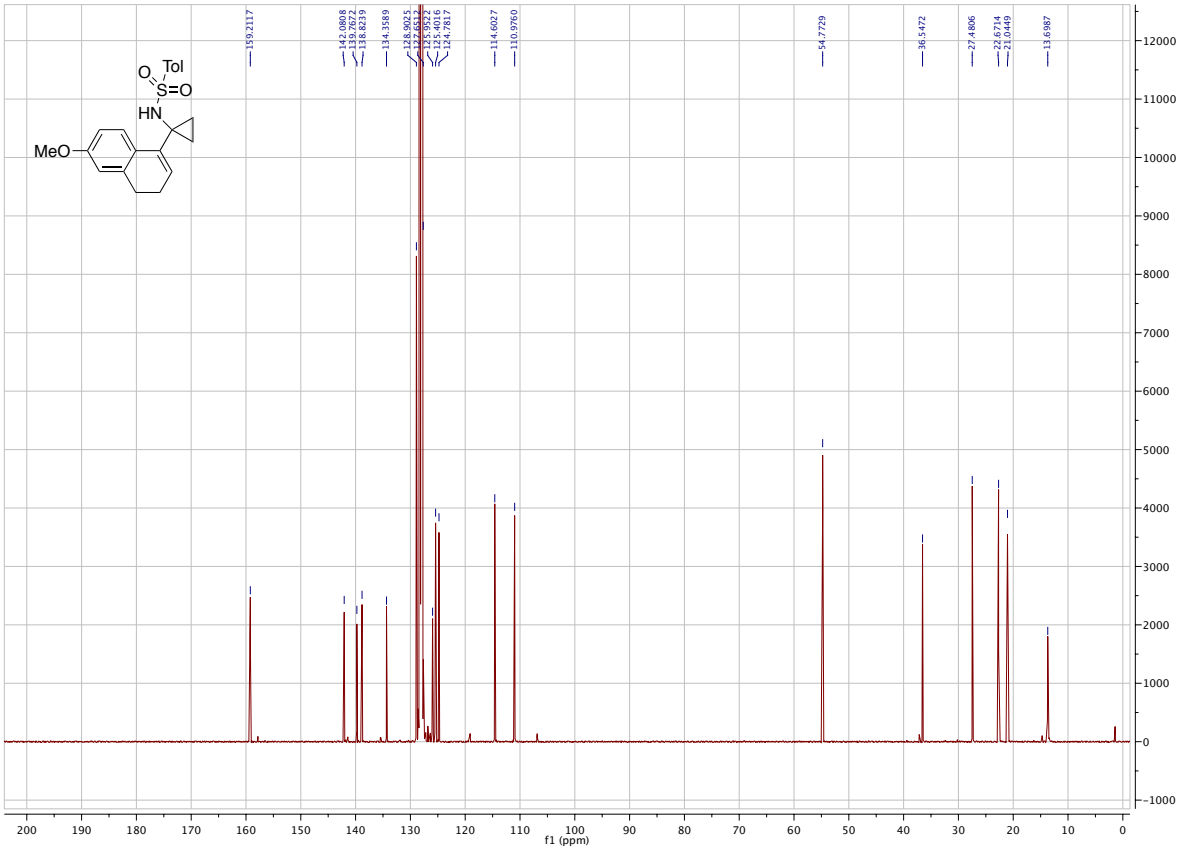


Substrate (A_{11})

^{1}H NMR 500 MHz, C_6D_6

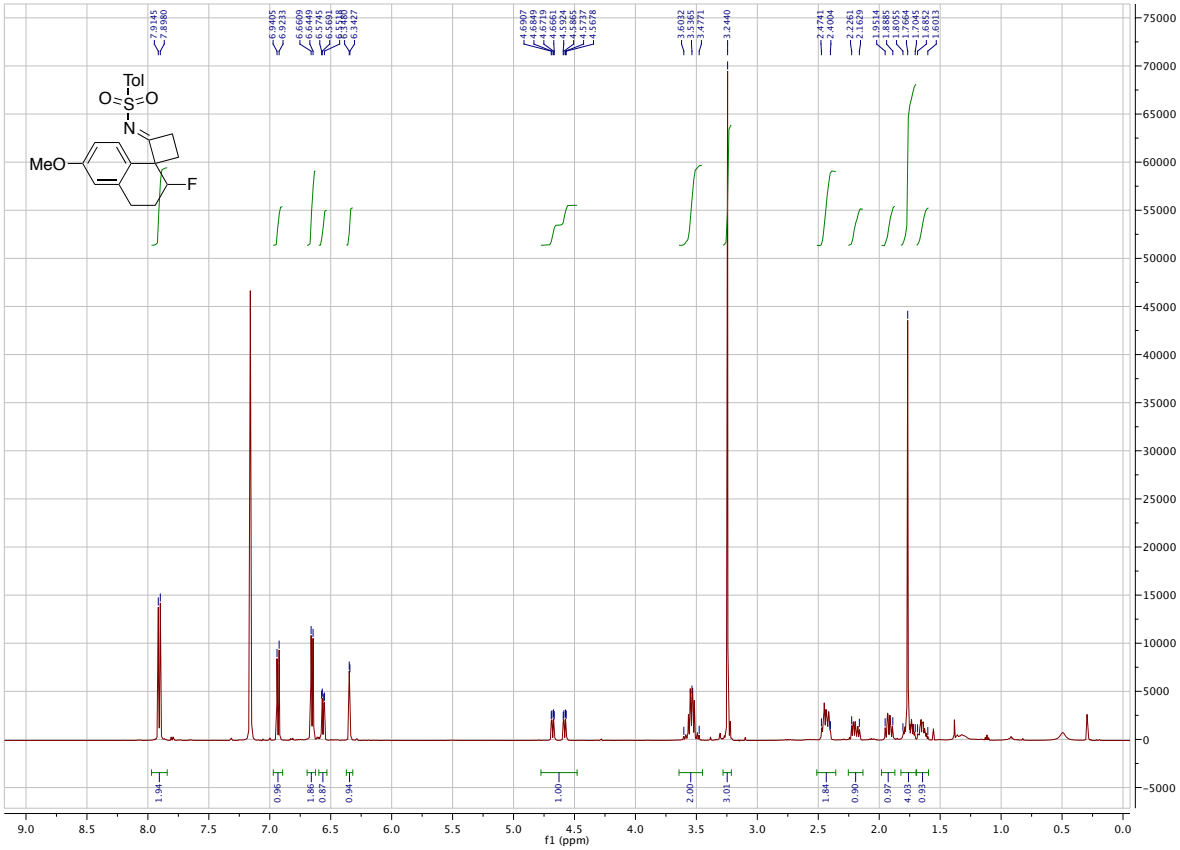


^{13}C NMR 125 MHz, C_6D_6

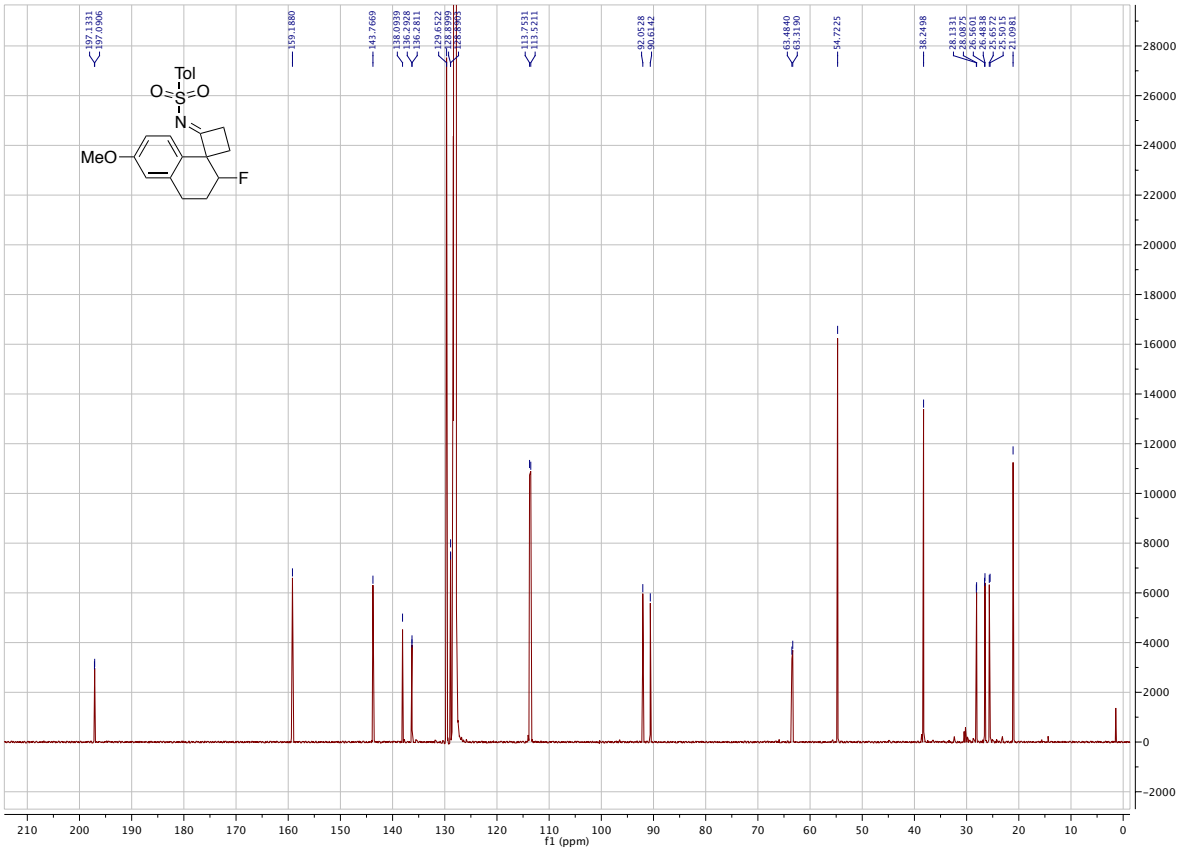


β-Fluoro Cyclobutylimine (B_{11})

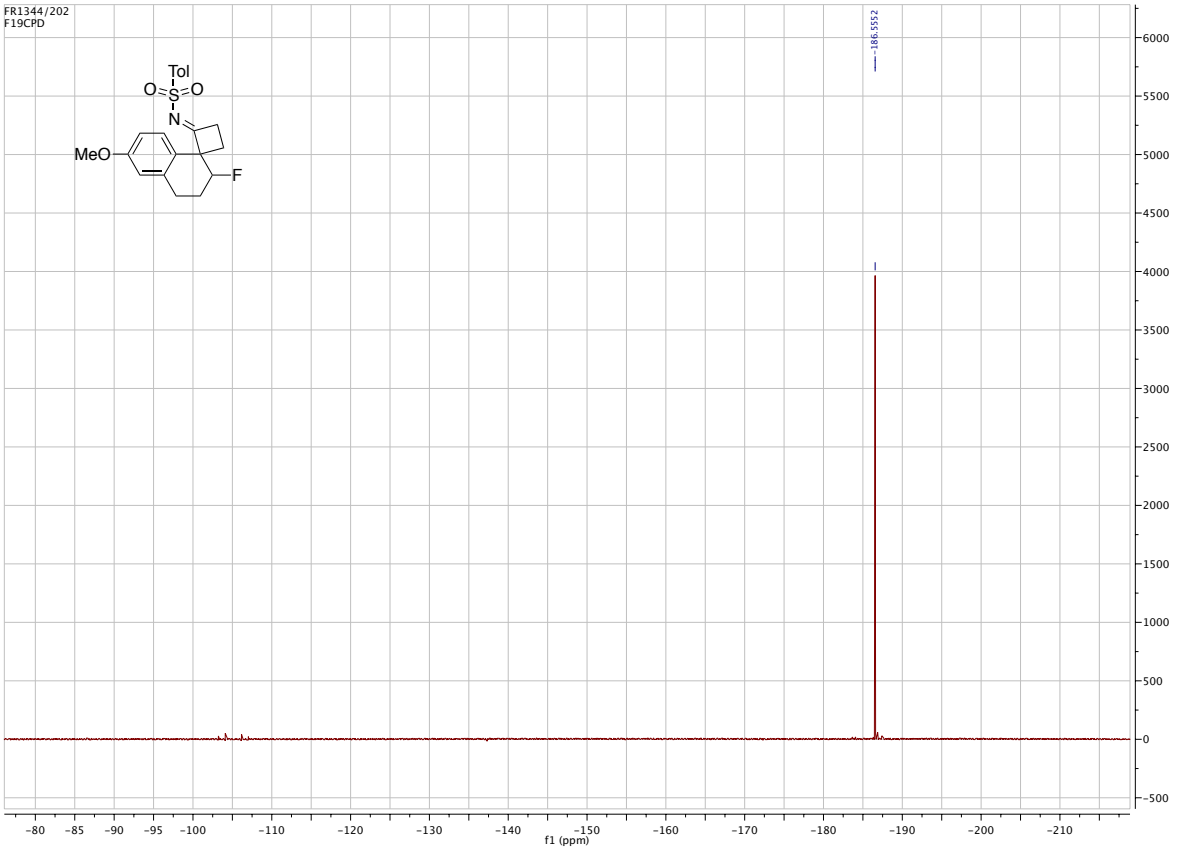
^{1}H NMR 500 MHz, C_6D_6



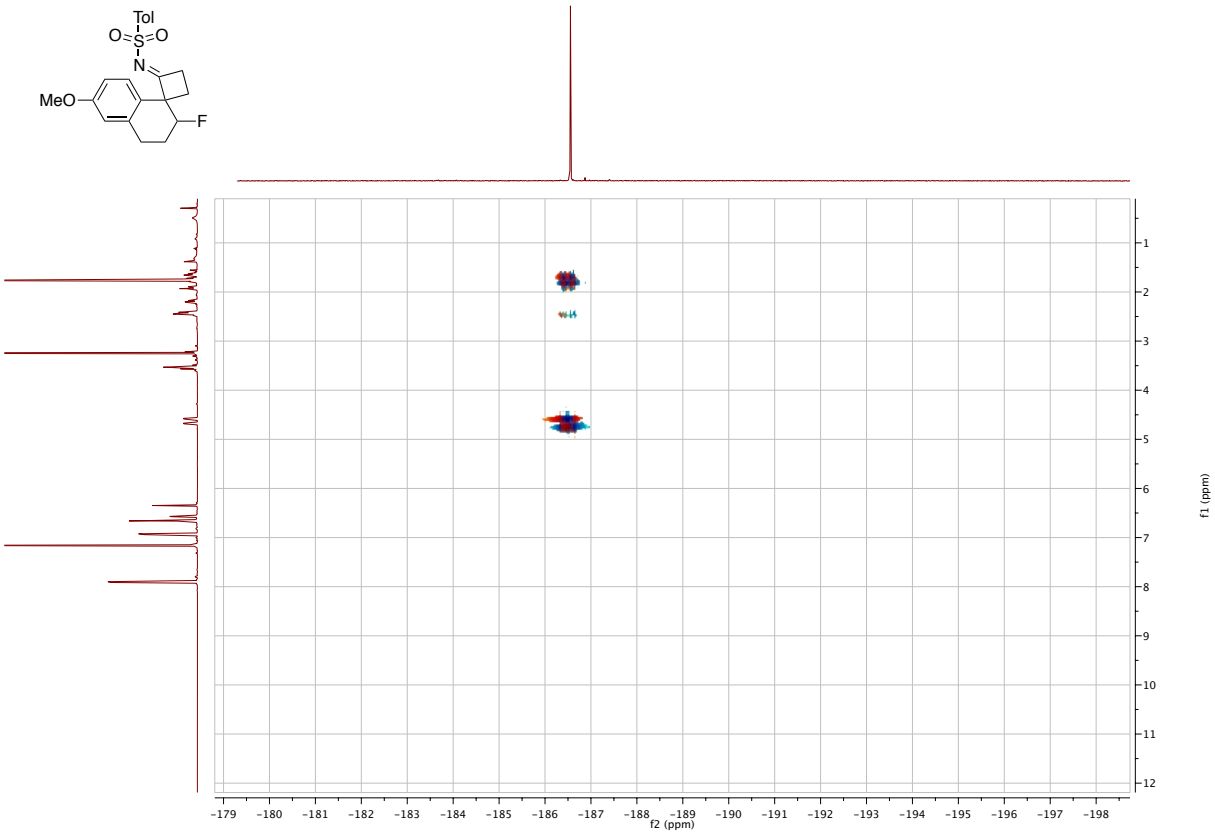
^{13}C NMR 125 MHz, C_6D_6



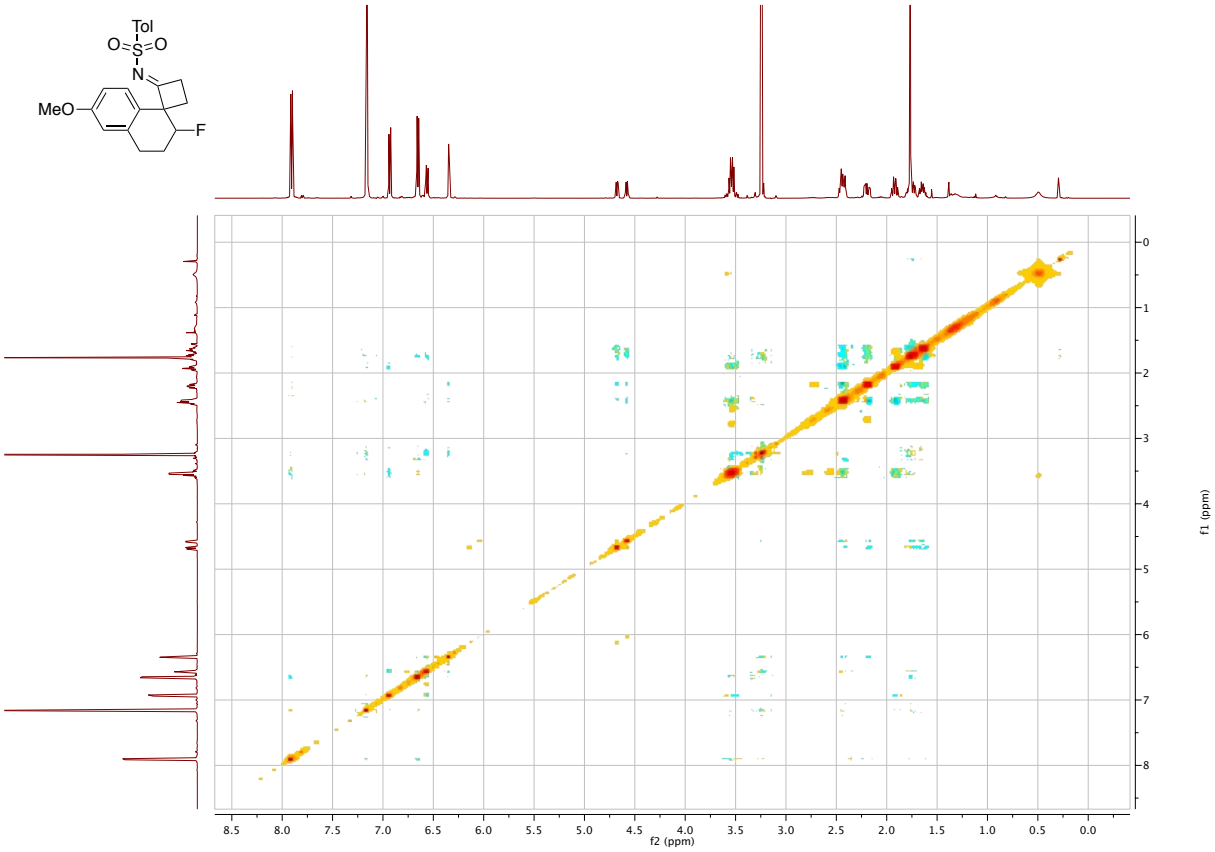
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{19}F HOESY 300 MHz, C_6D_6

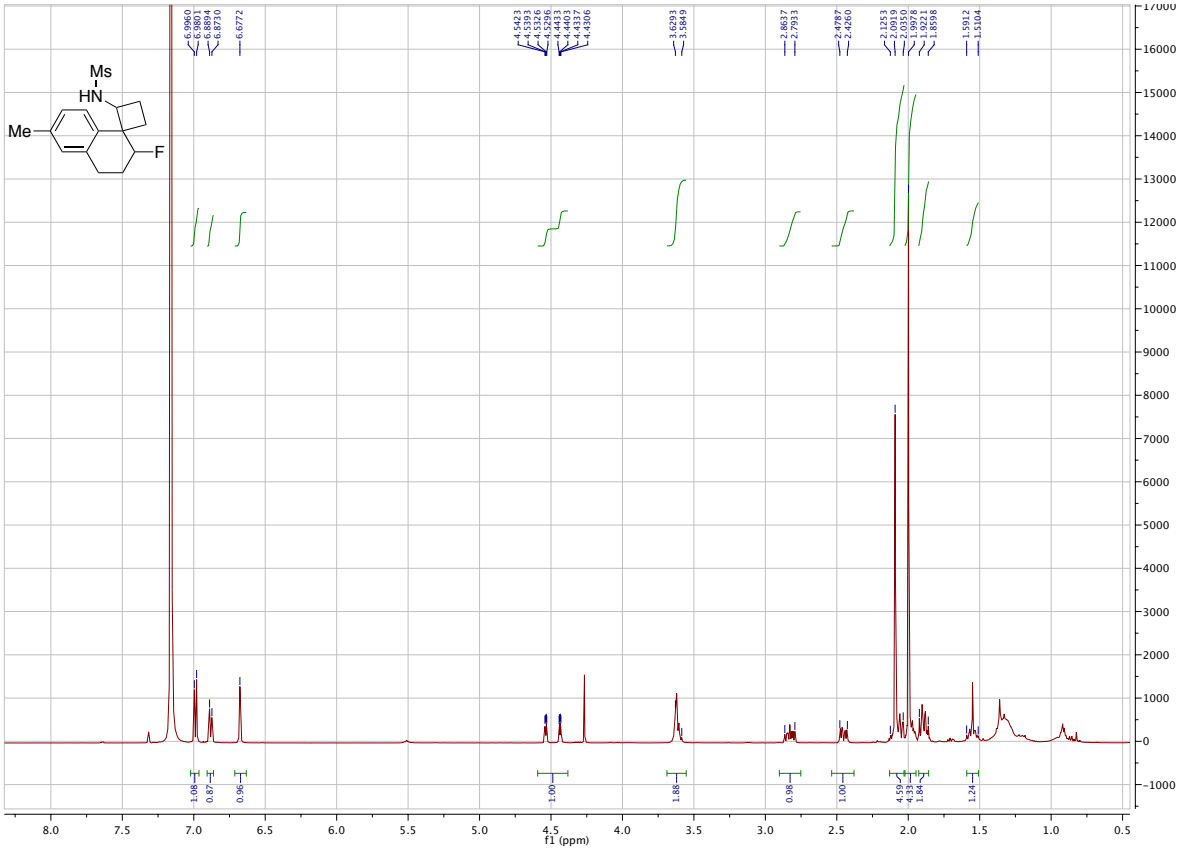


^{1}H-^{1}H NOESY 500 MHz, C_6D_6

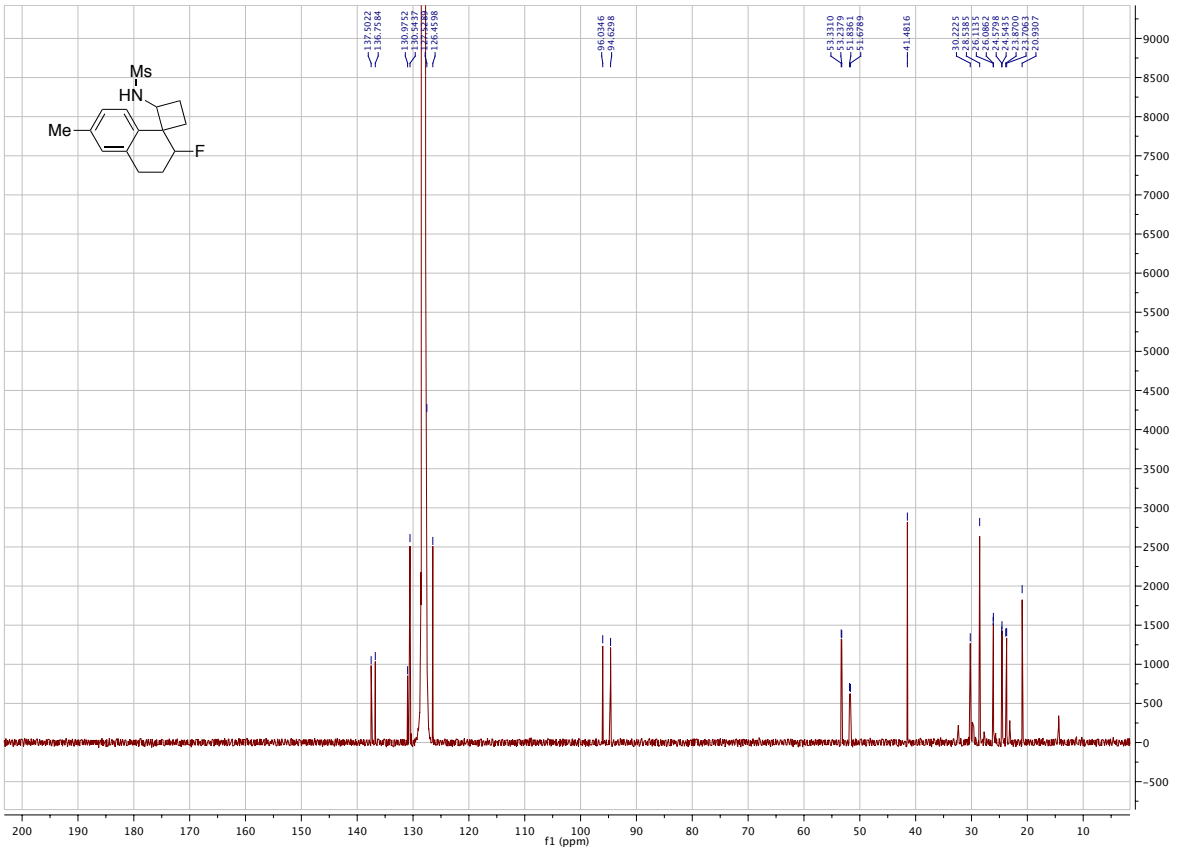


Fluorinated Amine (C_3)

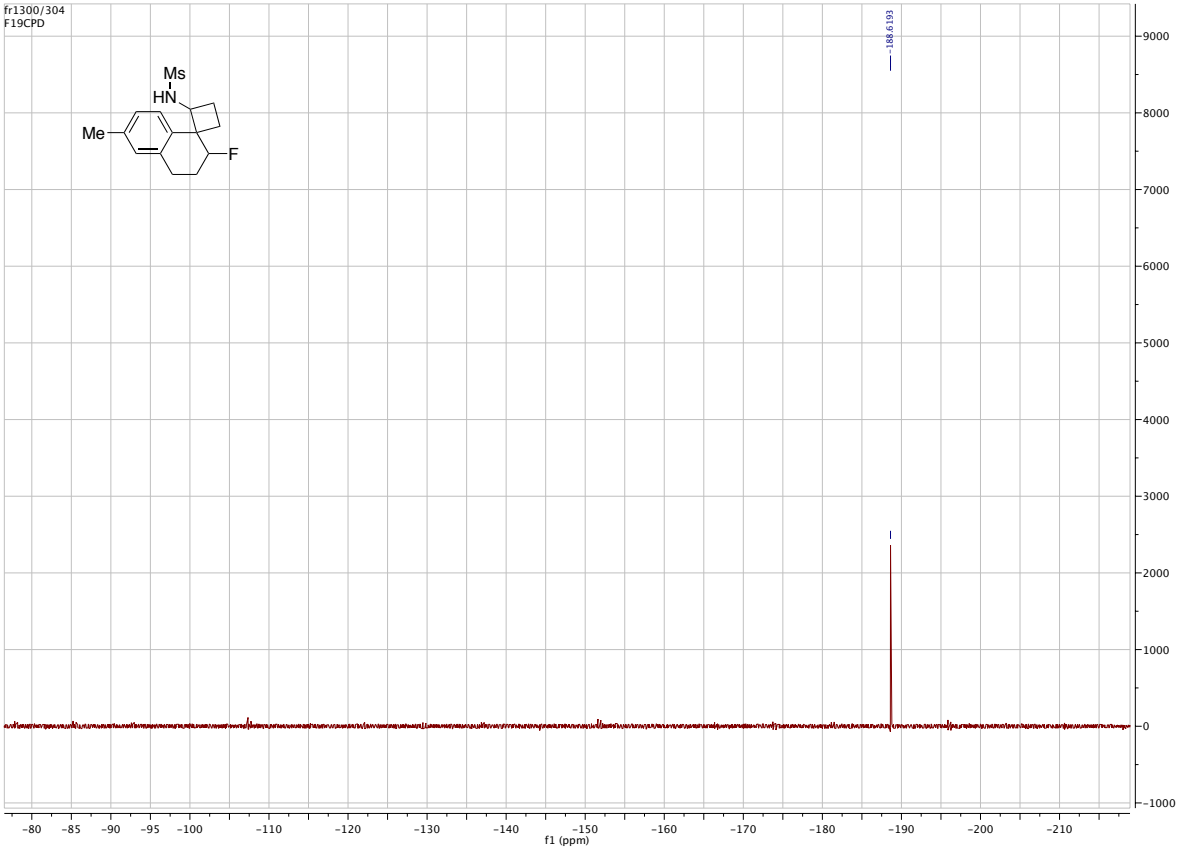
^{1}H NMR 500 MHz, C_6D_6



^{13}C NMR 125 MHz, C_6D_6

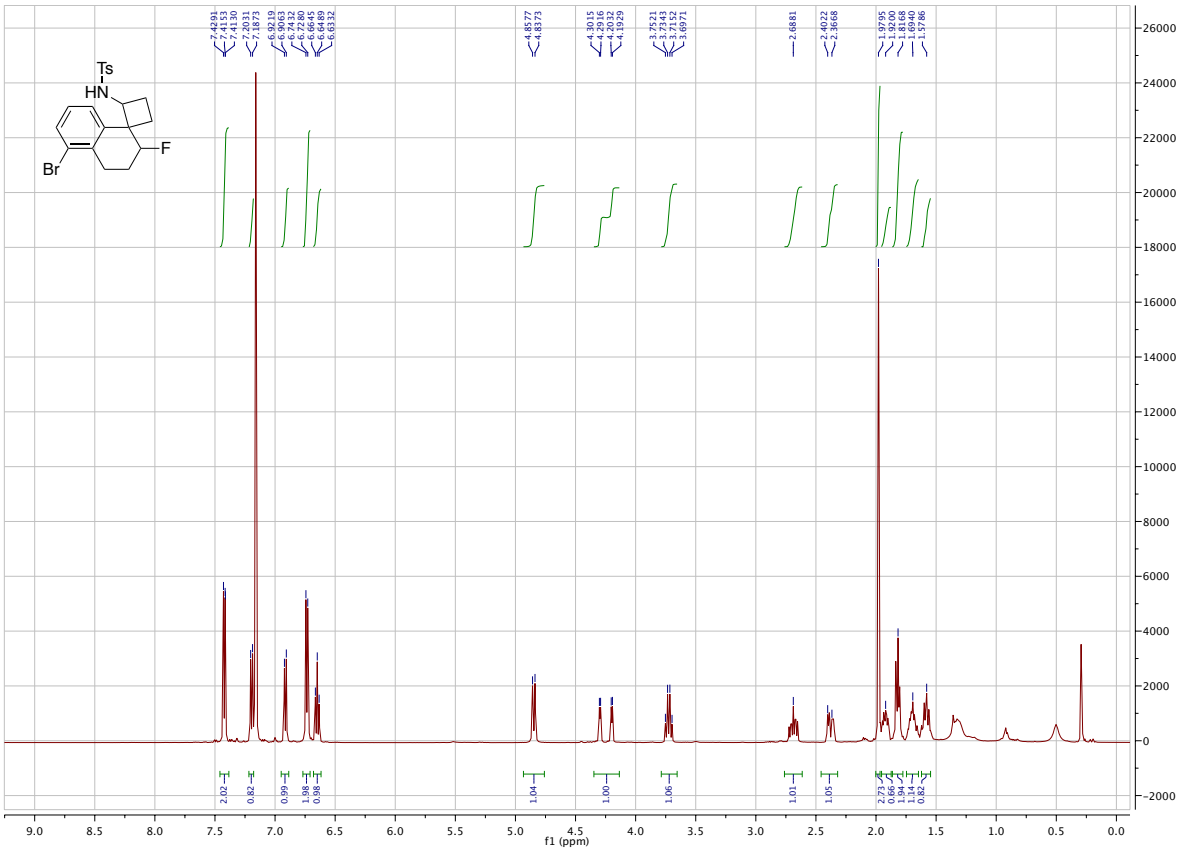


^{19}F NMR 375 MHz, C_6D_6

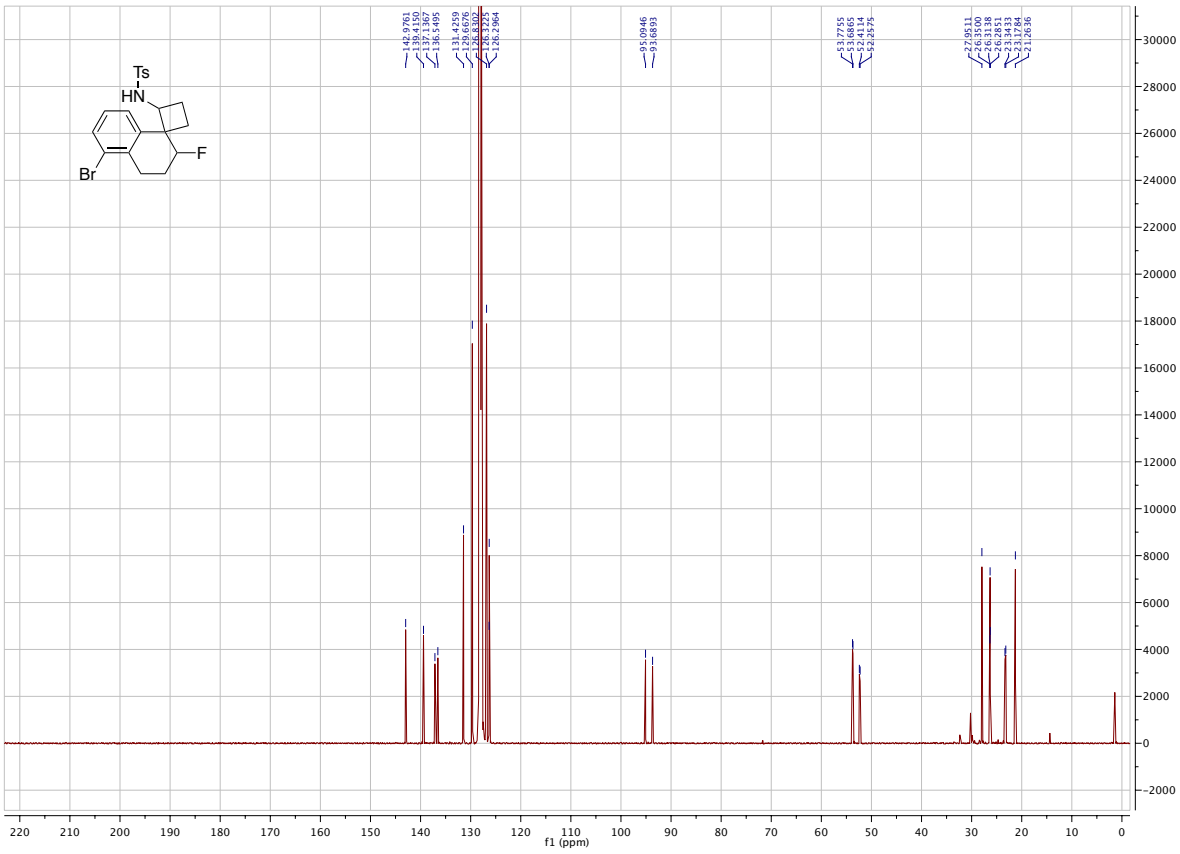


Fluorinated Amine (C_8)

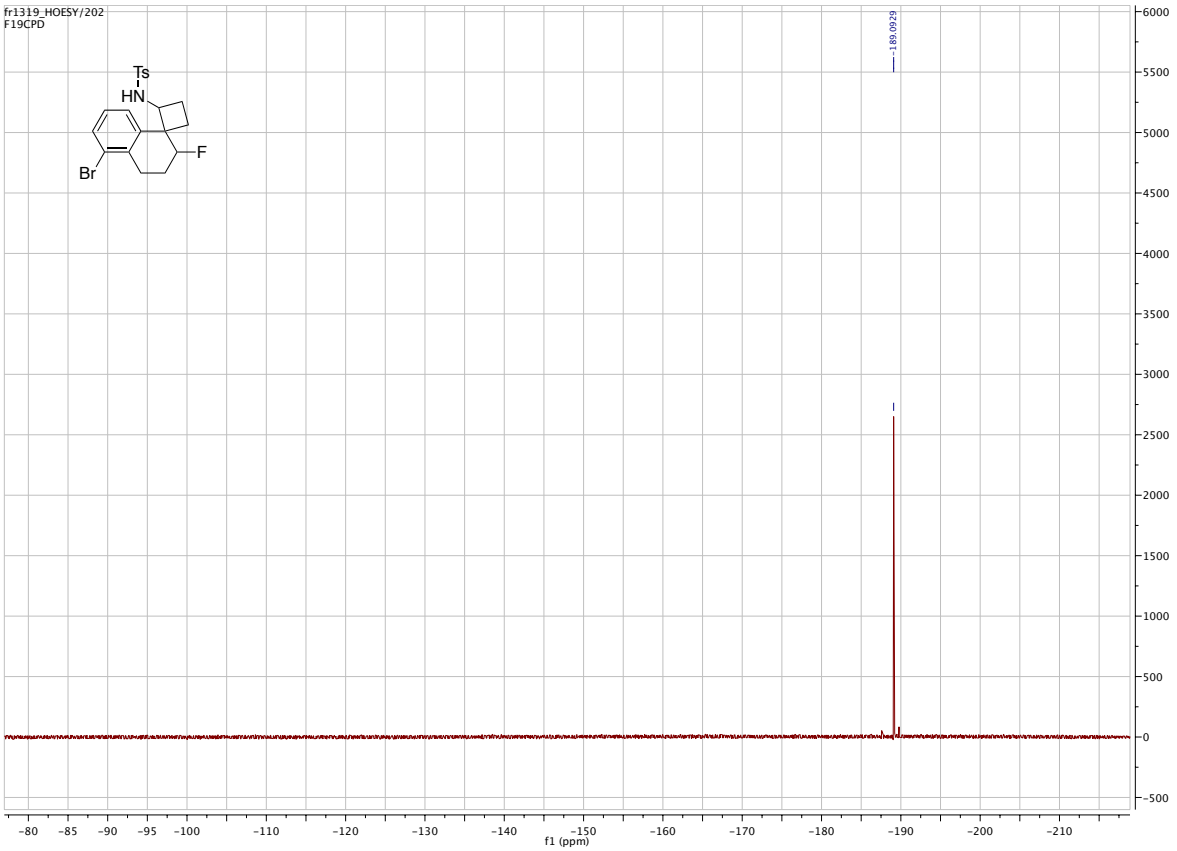
^{1}H NMR 500 MHz, C_6D_6



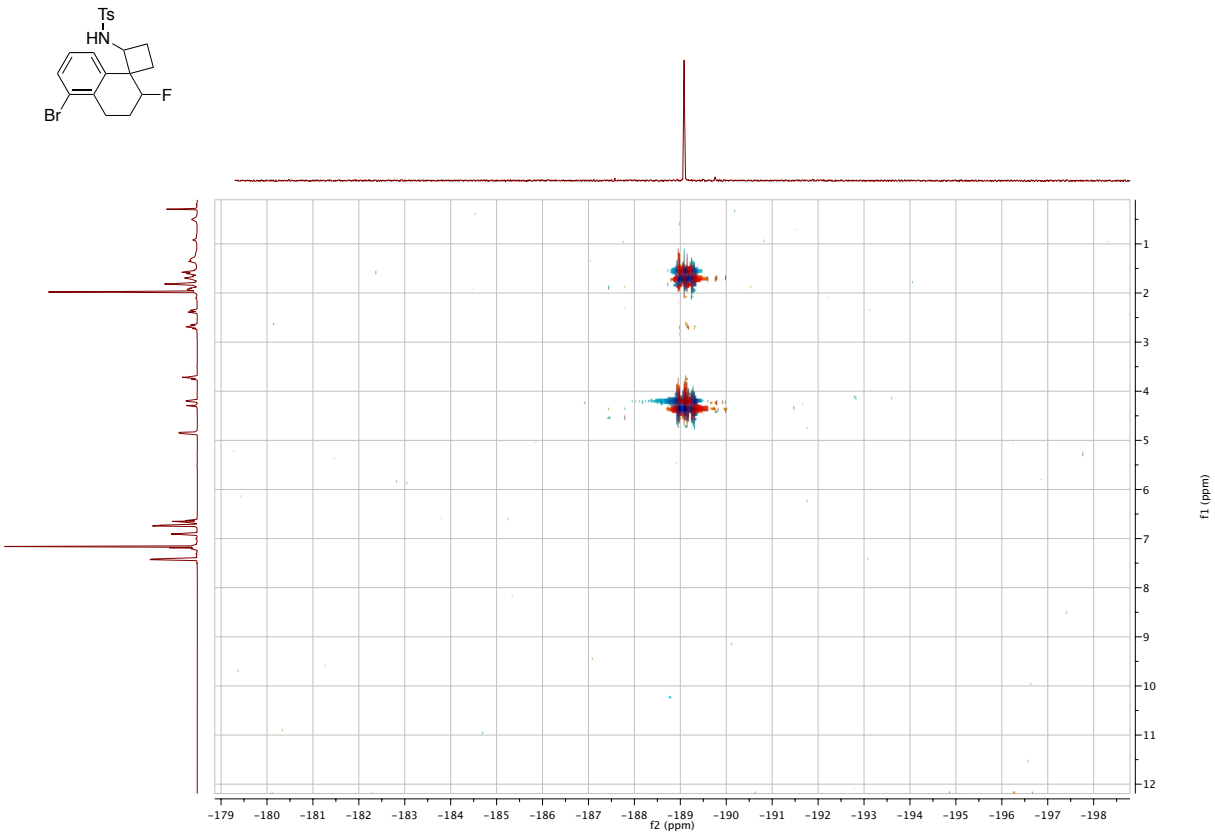
^{13}C NMR 125 MHz, C_6D_6



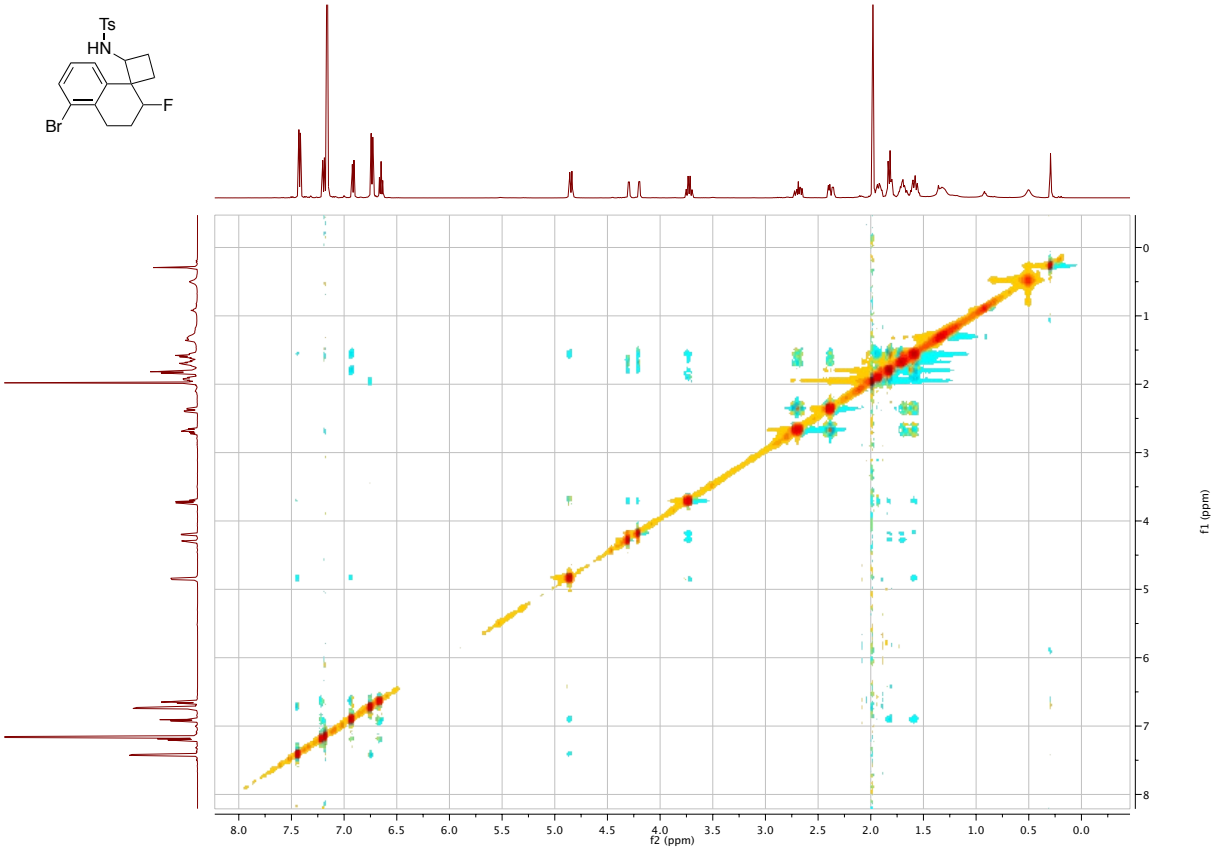
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{19}F HOESY 300 MHz, C_6D_6

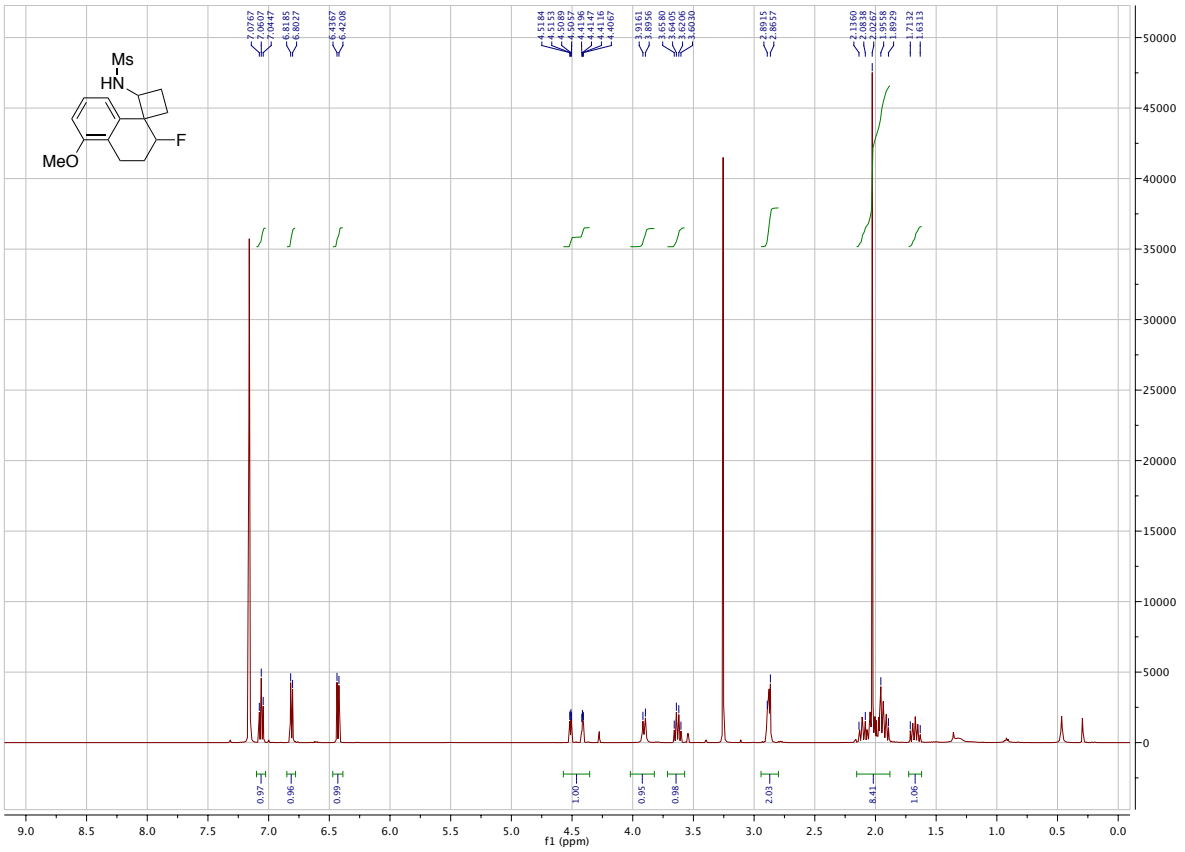


^{1}H-^{1}H NOESY 500 MHz, C_6D_6

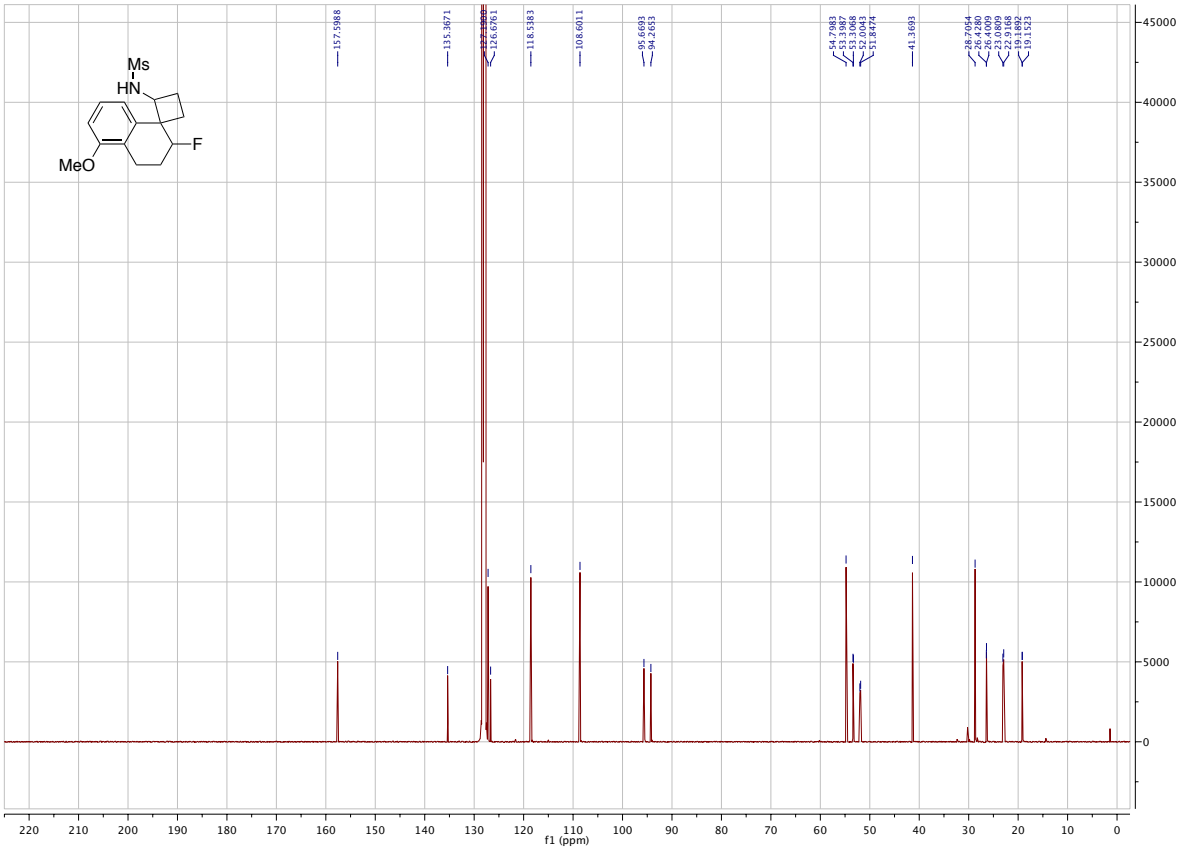


Fluorinated Amine (C_9)

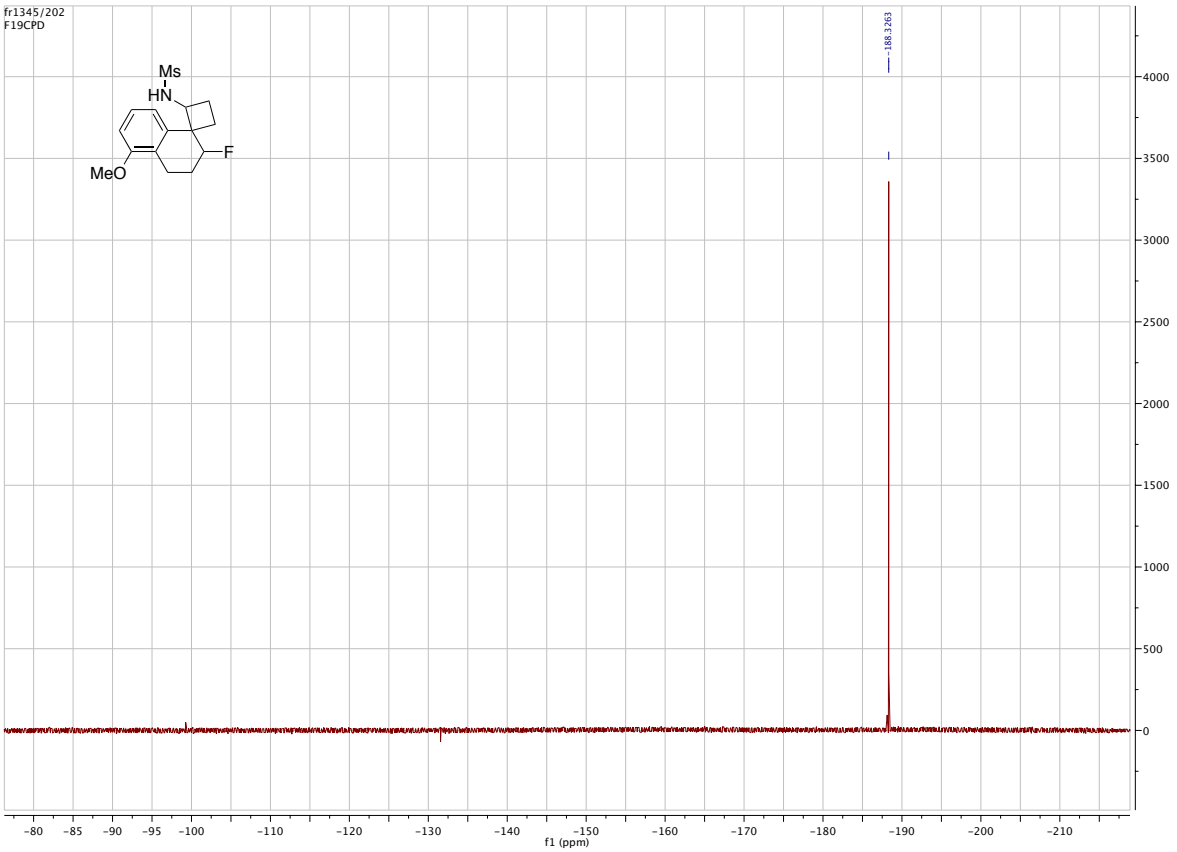
^{1}H NMR 500 MHz, C_6D_6



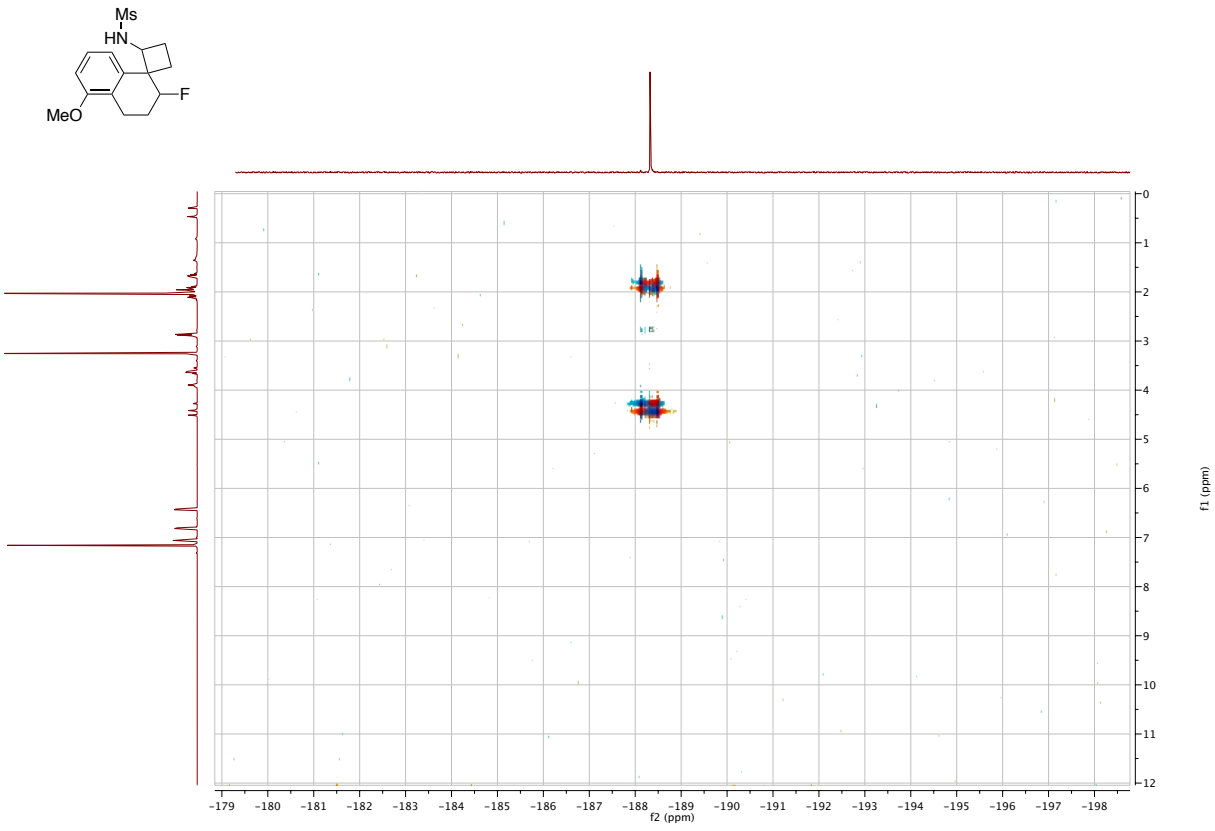
^{13}C NMR 125 MHz, C_6D_6



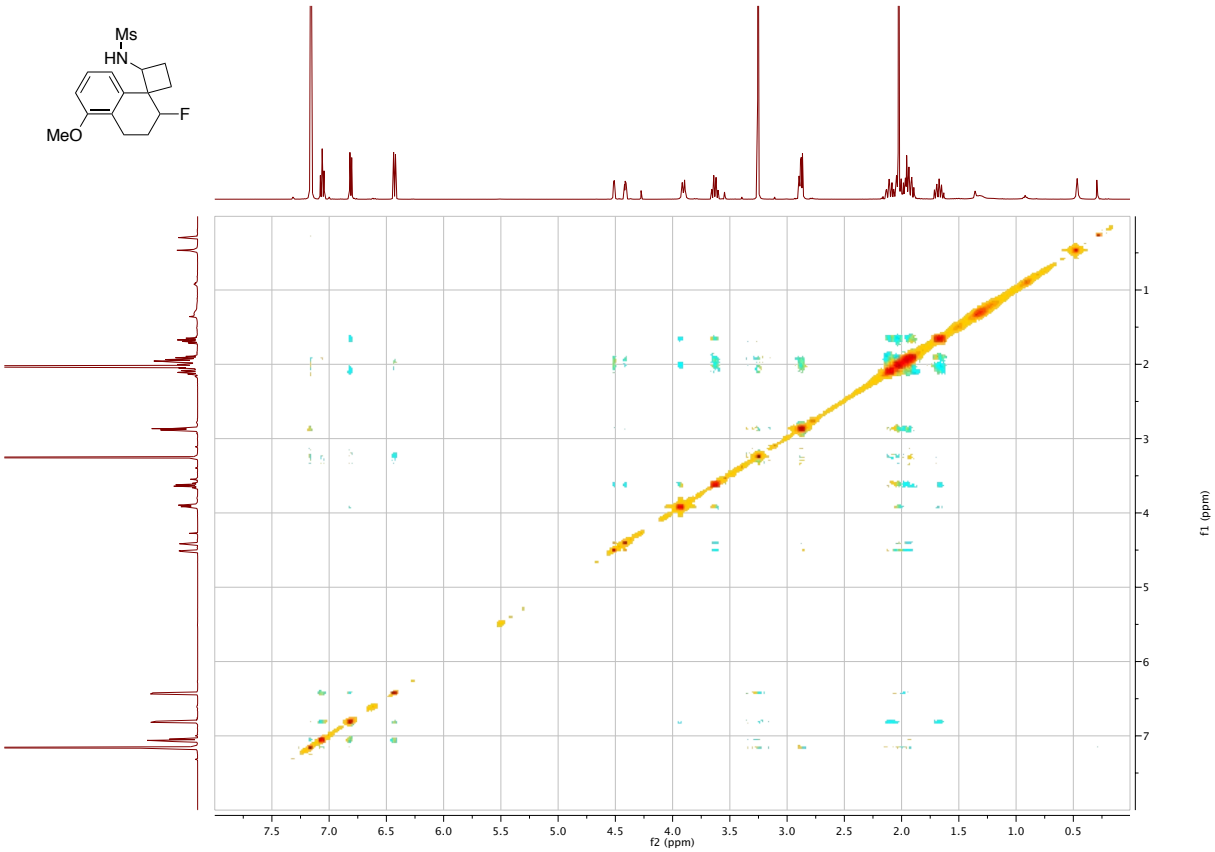
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{19}F HOESY 300 MHz, C_6D_6



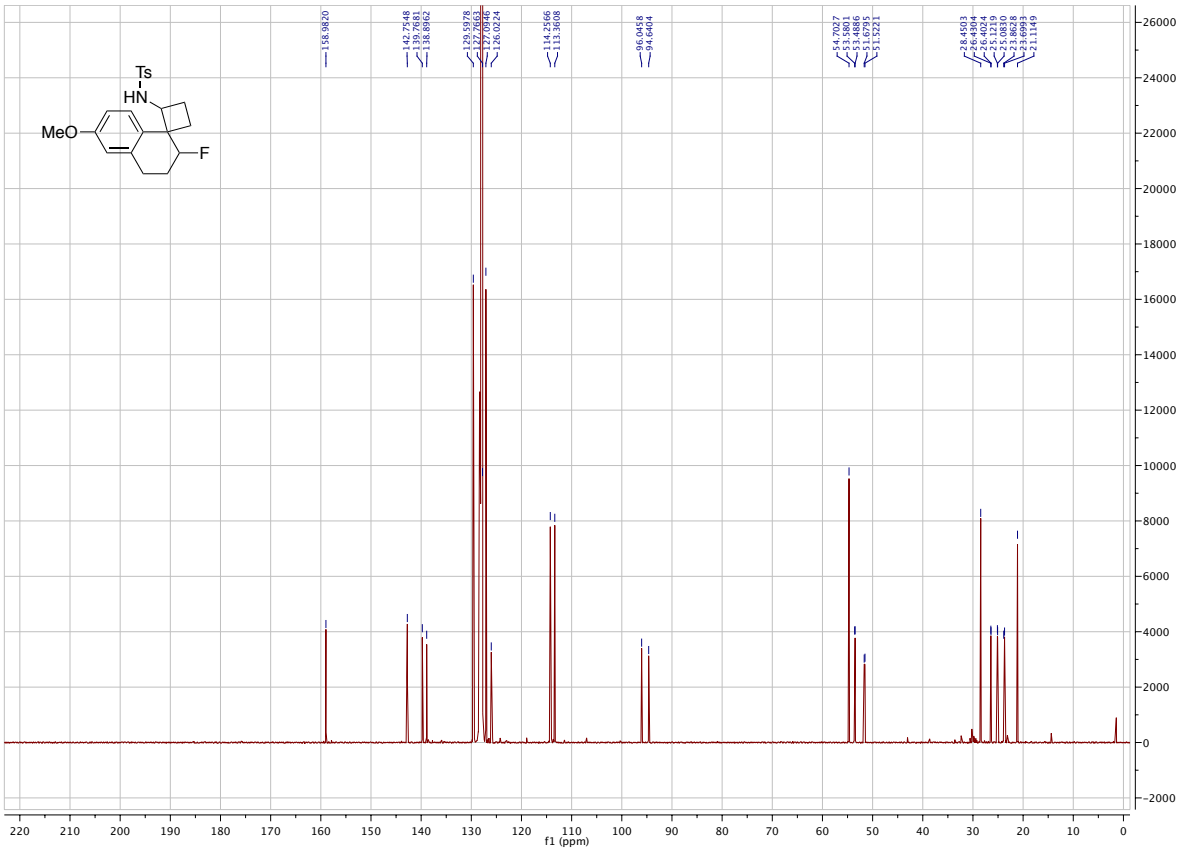
^{1}H-^{1}H NOESY 500 MHz, C_6D_6



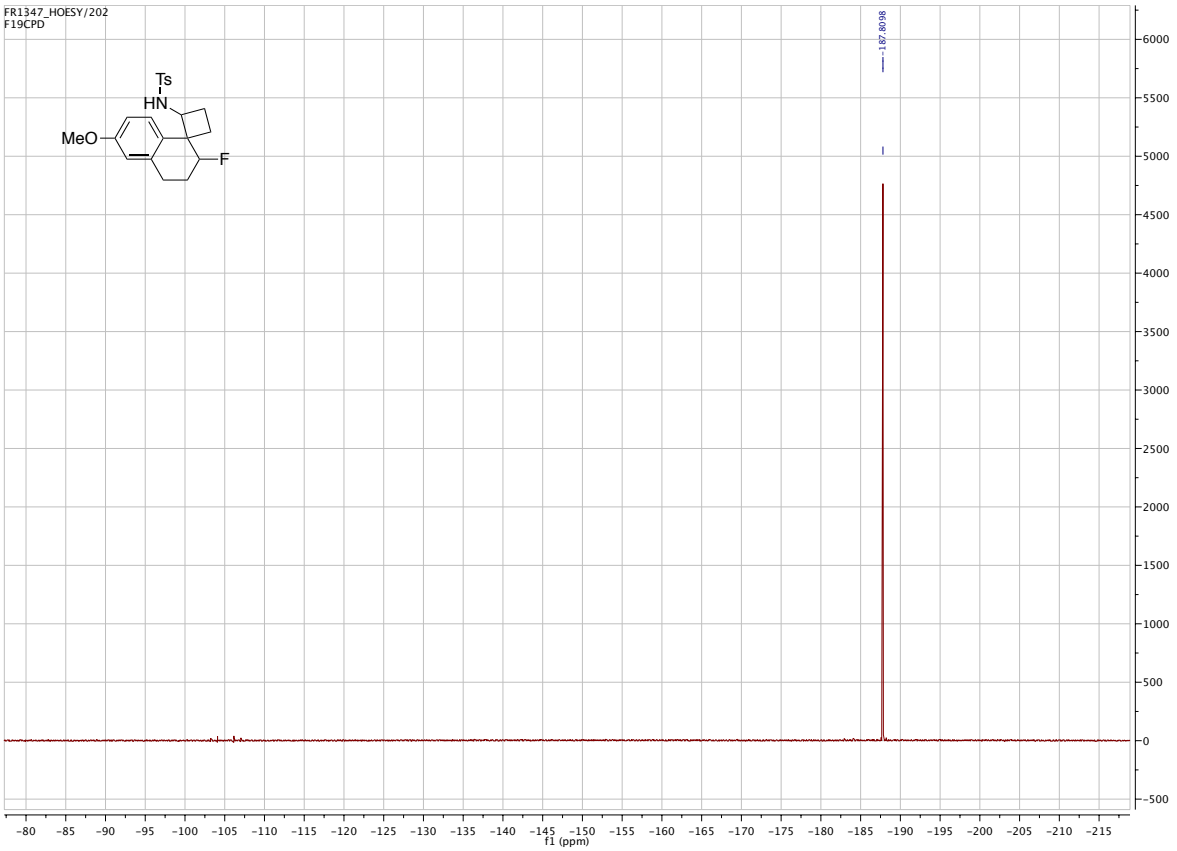
Fluorinated Amine (C_{11})

^{1}H NMR 500 MHz, C_6D_6

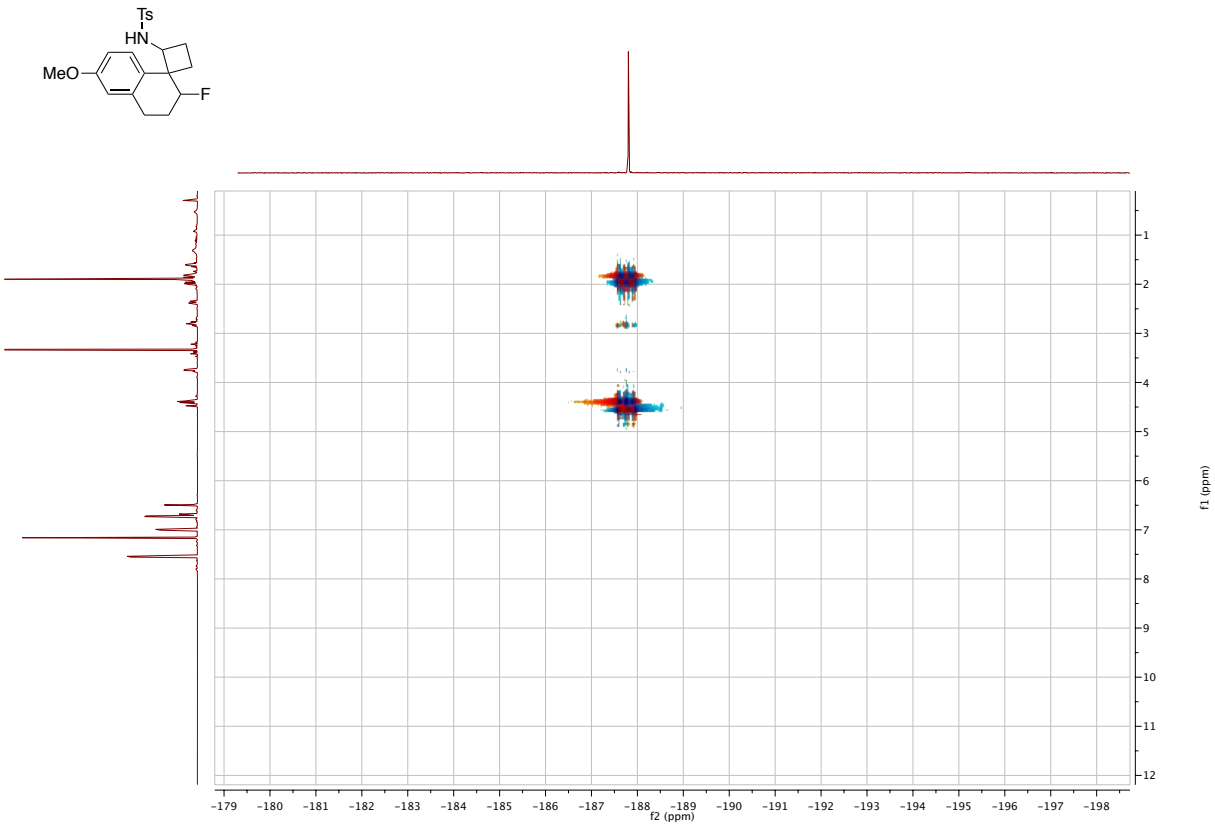
^{13}C NMR 125 MHz, C_6D_6



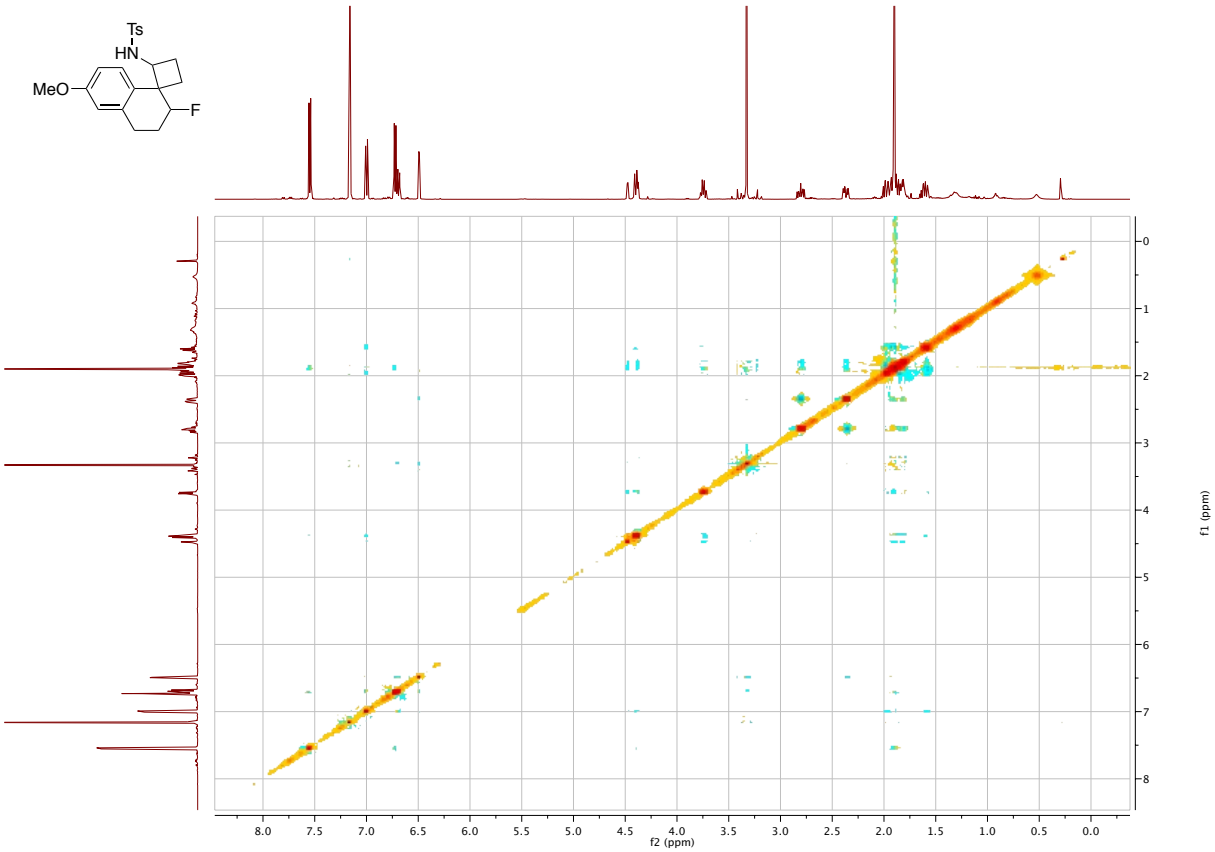
^{19}F NMR 375 MHz, C_6D_6



^{1}H-^{19}F HOESY 300 MHz, C_6D_6

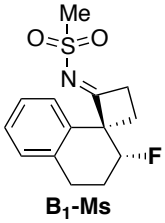


^{1}H-^{1}H NOESY 500 MHz, C_6D_6

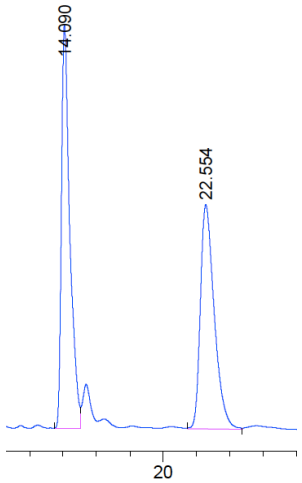


HPLC Traces

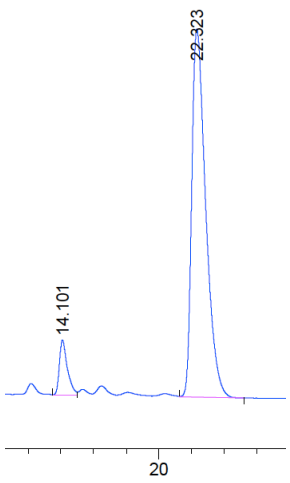
β-Fluoro Cyclobutylimine (B_1-Ms)



B_1-Ms

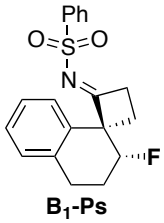


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.090	BV	0.5149	9003.44434	258.14282	52.1143
2	22.554	VV	0.8774	8272.89941	143.32182	47.8857

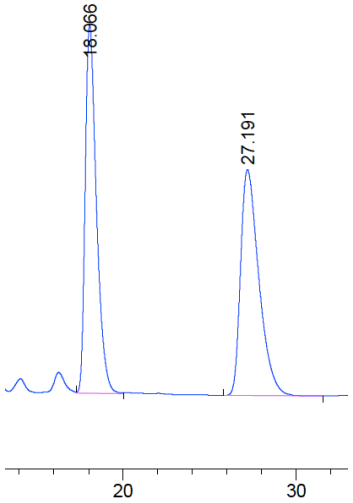


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.101	BV	0.4987	1271.18628	37.57359	7.8407
2	22.323	VB	0.9042	1.49414e4	251.81364	92.1593

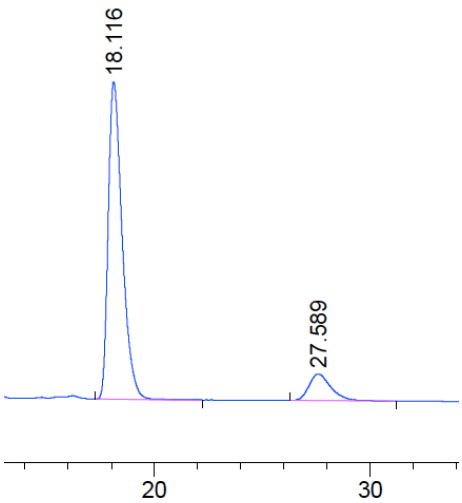
β-Fluoro Cyclobutylimine (B_1-Ps)



B_1-Ps

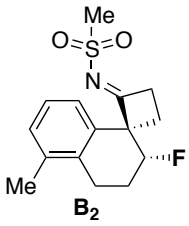


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.066	VV	0.6856	6387.29443	141.76514	49.9641
2	27.191	BB	1.1267	6396.48535	86.91017	50.0359

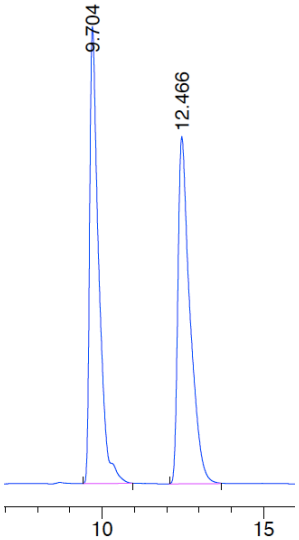


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.116	BB	0.6854	5778.91016	128.32573	88.3046
2	27.589	BV	1.0444	765.37866	10.77944	11.6954

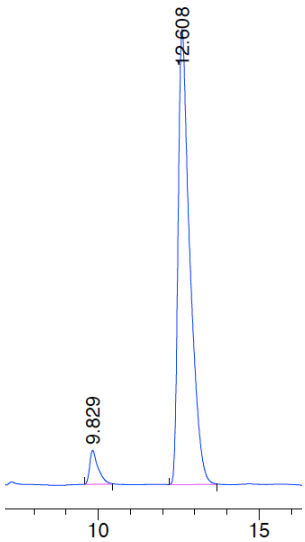
β-Fluoro Cyclobutylimine (B_2)



B_2

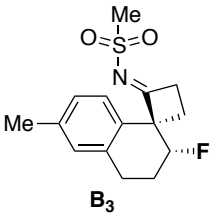


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.704	BB	0.2802	1.20177e4	614.30811	49.9341
2	12.466	BB	0.3713	1.20494e4	466.60443	50.0659

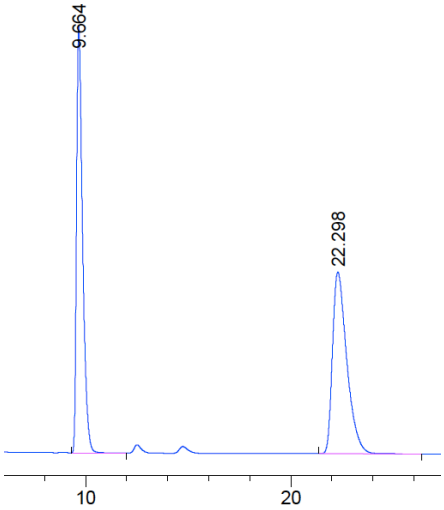


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.829	BB	0.2601	437.33646	24.05031	5.0879
2	12.608	BB	0.3676	8158.25732	321.98416	94.9121

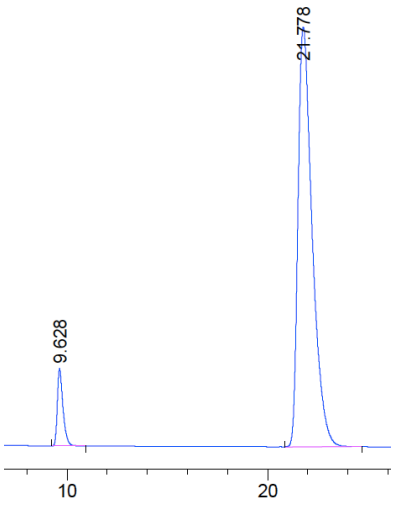
β-Fluoro Cyclobutylimine (B_3)



B_3

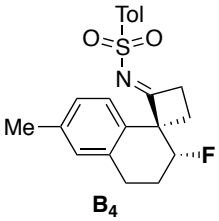


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.664	VB	0.3107	8751.05371	427.69135	49.7419
2	22.298	VB	0.7364	8841.87988	181.49290	50.2581

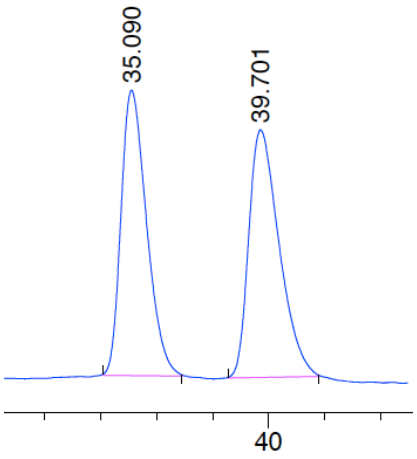


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.628	BV	0.2939	682.75525	34.65354	6.8687
2	21.778	BB	0.7420	9257.32910	188.14241	93.1313

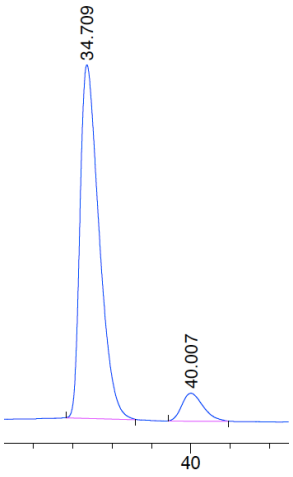
β-Fluoro Cyclobutylimine (B_4)



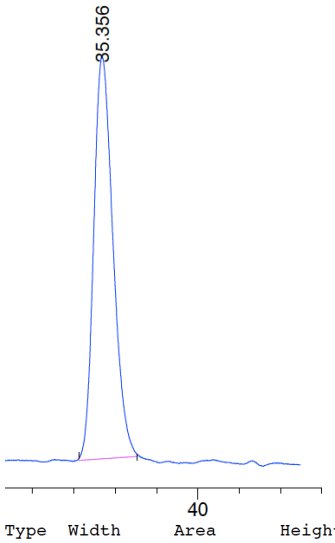
B_4



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.090	BB	0.9290	6513.44141	102.55732	49.2123
2	39.701	BB	0.9775	6721.94678	88.96436	50.7877

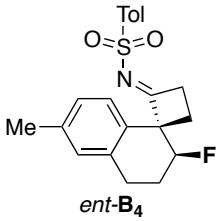


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.709	BB	0.9881	2.03872e4	302.57007	91.8994
2	40.007	BB	0.8893	1797.06274	23.89747	8.1006

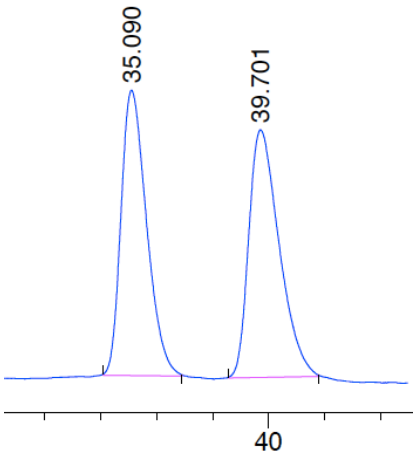


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.356	BB	0.8567	3442.13330	53.07112	100.0000

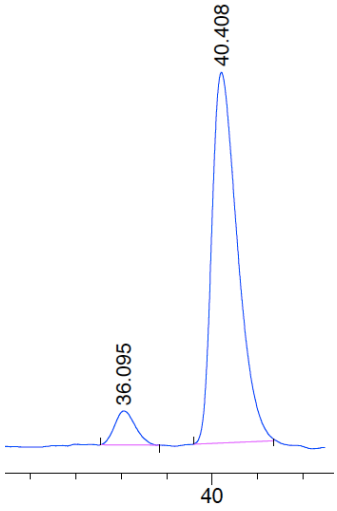
β-Fluoro Cyclobutylimine (*ent*-B_4)



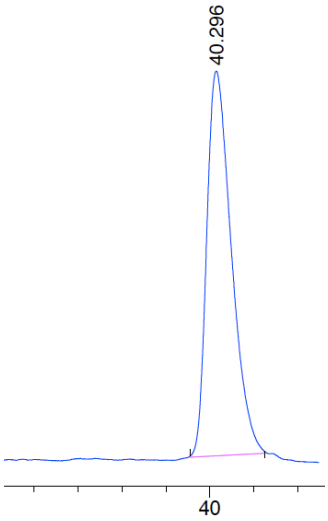
ent-B_4



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.090	BB	0.9290	6513.44141	102.55732	49.2123
2	39.701	BB	0.9775	6721.94678	88.96436	50.7877

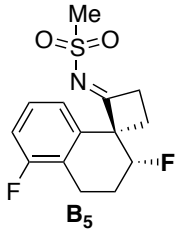


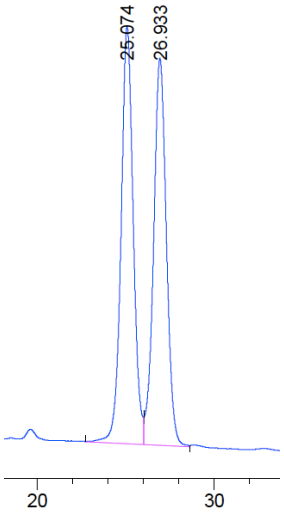
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.095	BB	0.7721	672.66705	10.49085	6.9609
2	40.408	BB	1.0869	8990.79102	114.39365	93.0391



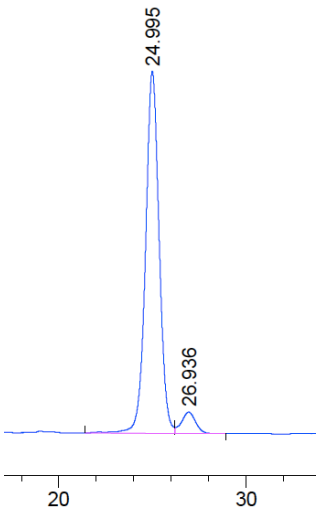
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.296	BB	1.0791	6984.78467	89.64176	100.0000

β-Fluoro Cyclobutylimine (B_5)



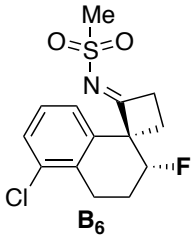


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.074	BV	0.7273	6117.09473	127.59383	50.6884
2	26.933	VV	0.7671	5950.93018	118.24791	49.3116

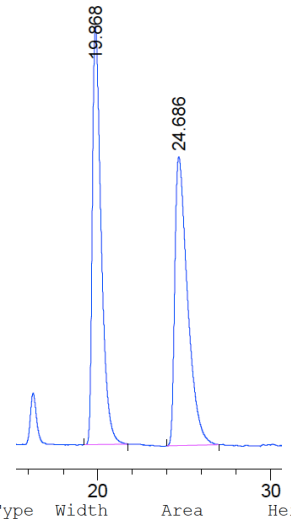


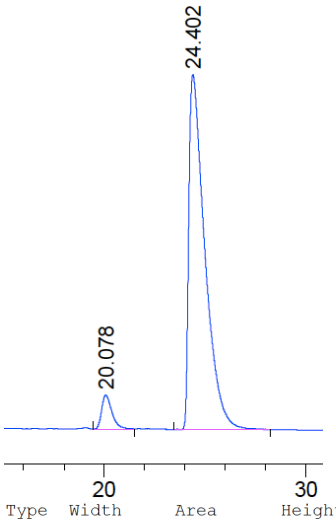
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.995	BV	0.7684	1.04710e4	207.60458	94.2792
2	26.936	VB	0.7877	635.36633	12.19730	5.7208

β-Fluoro Cyclobutylimine (B_6)



B_6

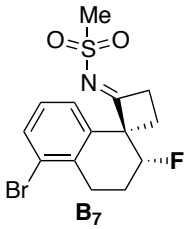




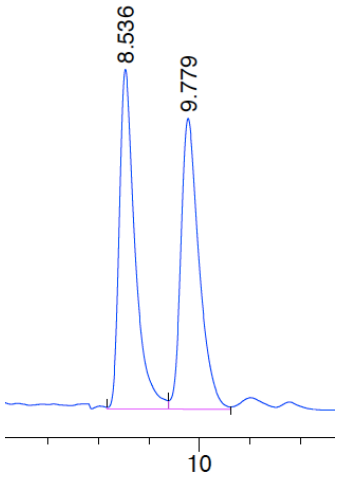
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.868	BB	0.5335	4242.85840	119.41497	49.9820
2	24.686	BB	0.7374	4245.92041	82.50407	50.0180

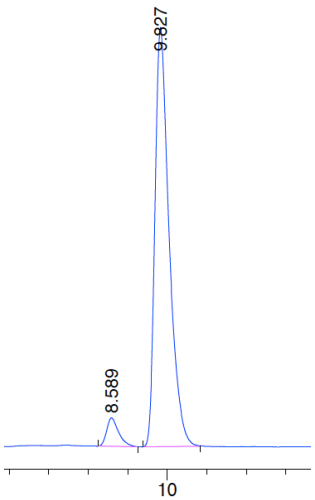
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.078	BB	0.5396	262.76871	7.44810	5.7712
2	24.402	BB	0.8179	4290.34082	77.49170	94.2288

β-Fluoro Cyclobutylimine (B_7)



B_7

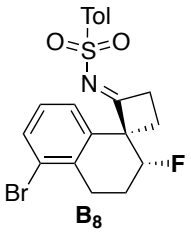




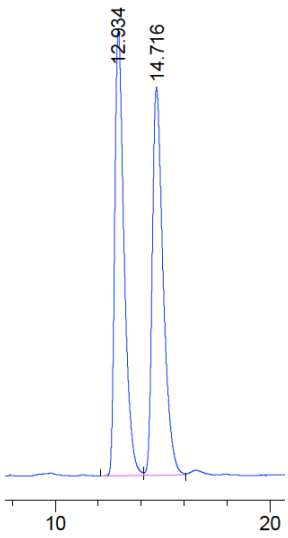
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.536	VV	0.3214	3238.73438	149.13496	50.3112
2	9.779	VB	0.3723	3198.66406	127.66726	49.6888

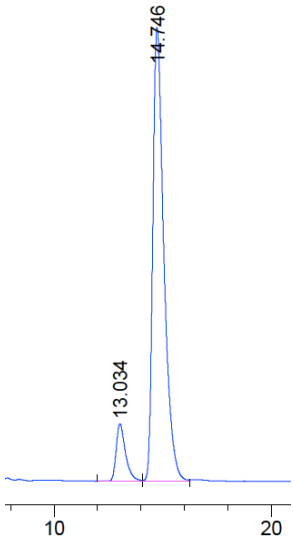
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.589	BB	0.3076	487.13867	23.32629	5.4190
2	9.827	BB	0.3734	8502.26270	342.80228	94.5810

β-Fluoro Cyclobutylimine (B_8)



B_8

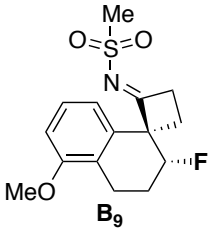




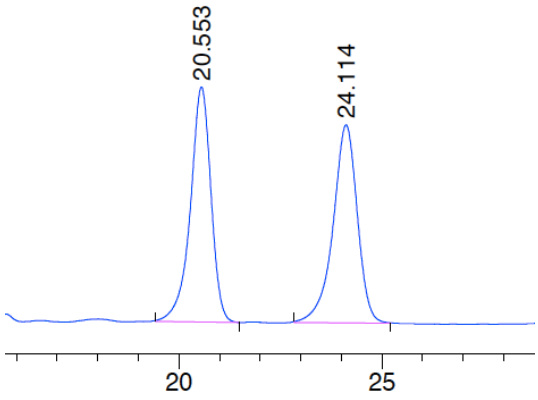
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.934	BV	0.4603	1.17295e4	384.11356	49.8945
2	14.716	VV	0.5317	1.17791e4	333.83478	50.1055

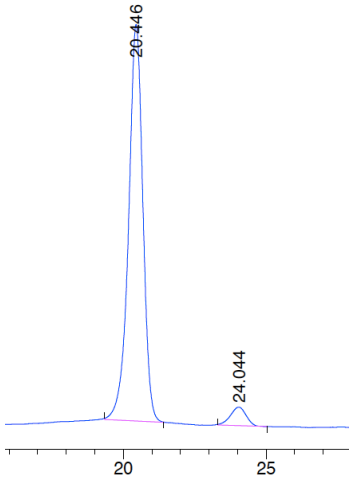
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.034	BV	0.4502	984.46124	32.79631	9.7379
2	14.746	VV	0.5320	9125.09180	258.38031	90.2621

β-Fluoro Cyclobutylimine (B_9)



B_9

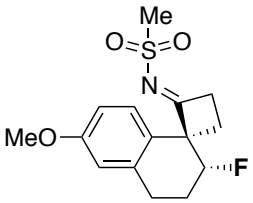




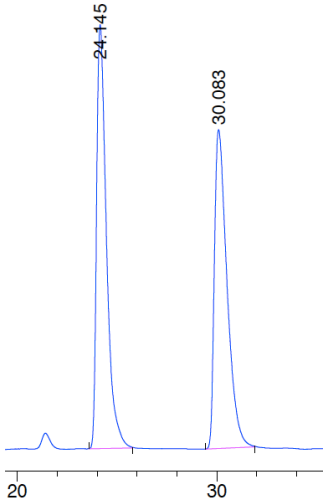
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.553	BB	0.5374	4508.81543	127.85928	50.0838
2	24.114	BB	0.6324	4493.73584	107.78350	49.9162

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.446	BB	0.5288	8184.95264	234.73148	95.2048
2	24.044	BB	0.5249	412.25311	10.90831	4.7952

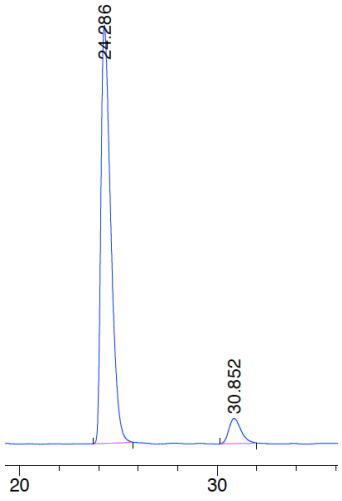
β-Fluoro Cyclobutylimine (B_{10})



B_{10}

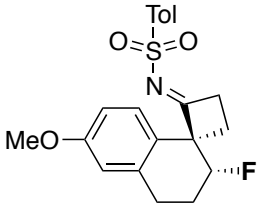


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.145	BB	0.5220	1.38491e4	403.95636	50.8789
2	30.083	BB	0.6594	1.33706e4	303.81024	49.1211

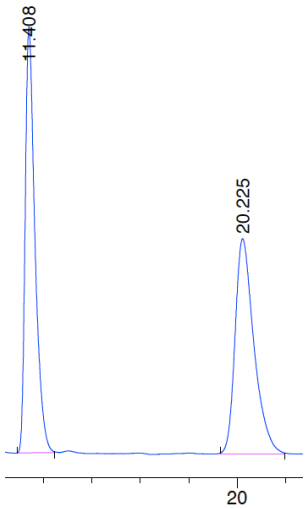


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.286	BB	0.5347	1.78845e4	515.59290	93.0189
2	30.852	BB	0.6352	1342.23169	31.11874	6.9811

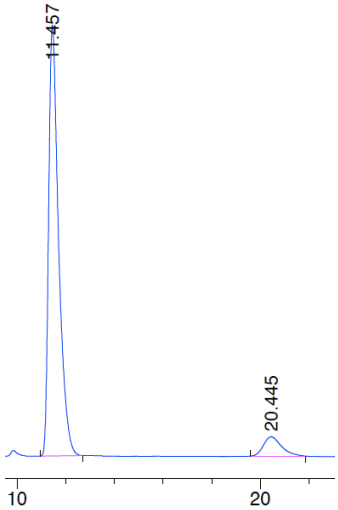
β-Fluoro Cyclobutylimine (B_{11})



B_{11}

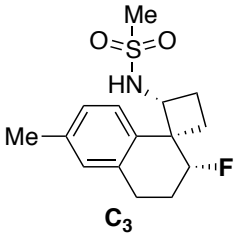


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.408	BB	0.4184	6877.19189	245.77779	50.6663
2	20.225	BB	0.8014	6696.31201	124.12600	49.3337

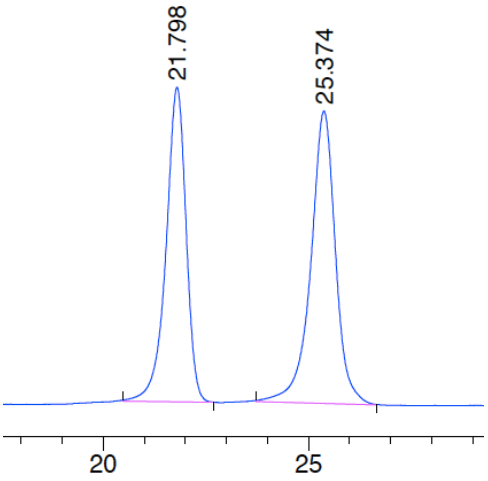


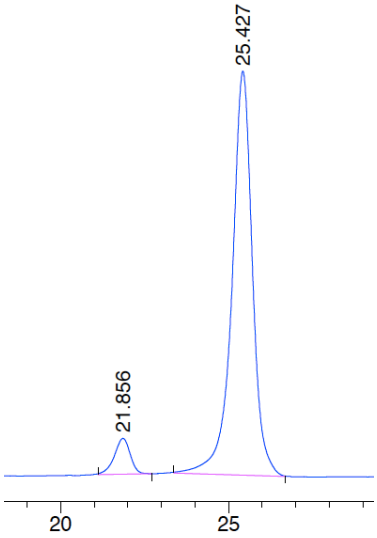
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.457	BB	0.4228	1.99323e4	702.93005	92.3115
2	20.445	BB	0.7249	1660.13330	31.81079	7.6885

Fluorinated Amine (C_3)



C_3

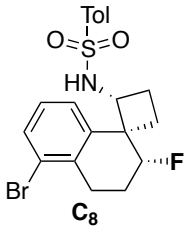




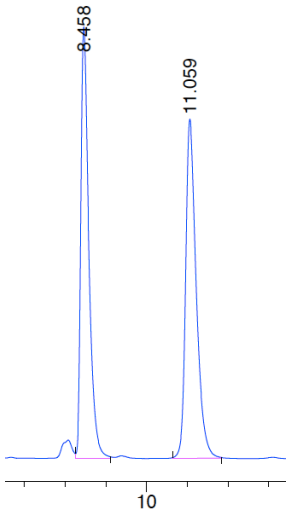
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.798	BB	0.5136	6411.10596	188.13158	46.7092
2	25.374	BB	0.6241	7314.46777	174.82063	53.2908

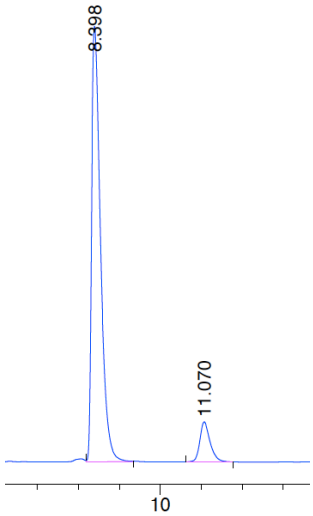
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.856	BB	0.4905	828.65552	25.27698	6.3996
2	25.427	BB	0.6307	1.21198e4	285.80600	93.6004

Fluorinated Amine (C_8)



C_8

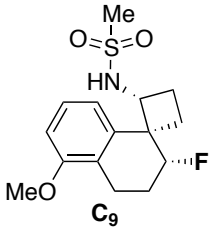




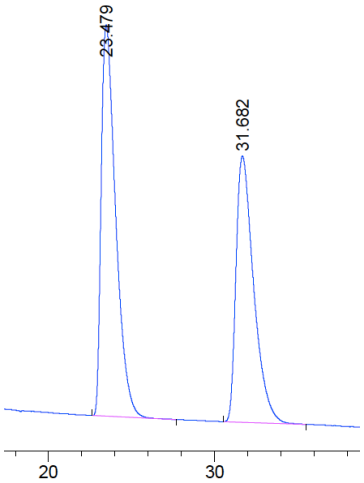
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.458	VB	0.2047	2761.09937	202.96832	48.9536
2	11.059	BB	0.2724	2879.14233	159.61406	51.0464

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.398	VB	0.2298	2.00328e4	1329.71301	90.3709
2	11.070	BB	0.2611	2134.51294	122.58381	9.6291

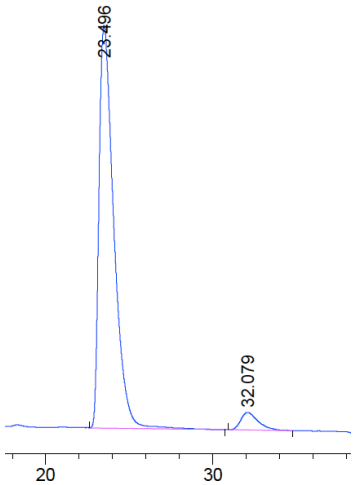
Fluorinated Amine (C_9)



C_9

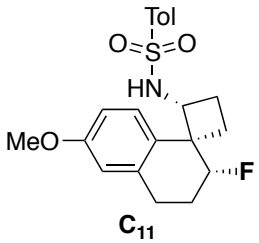


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.479	BB	0.9240	1.17733e4	193.99959	54.6929
2	31.682	BB	1.1253	9752.93262	132.09988	45.3071

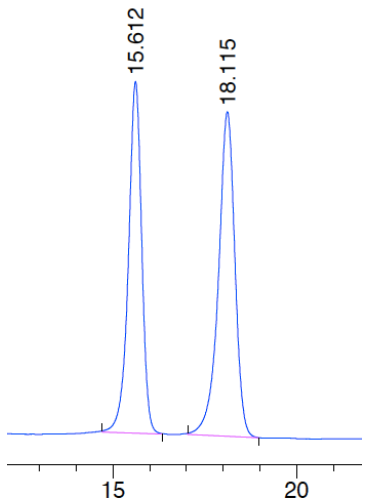


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.496	BB	0.9358	1.03163e4	167.21385	95.0618
2	32.079	BV	1.0408	535.90820	7.36593	4.9382

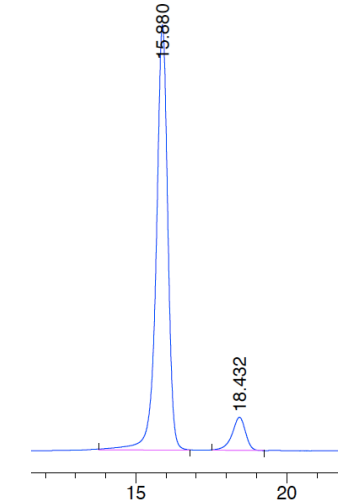
Fluorinated Amine (C_{11})



C_{11}



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.612	BB	0.3814	5576.90967	221.75179	46.6243
2	18.115	BB	0.4698	6384.47803	204.73407	53.3757



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.880	BB	0.4032	2.34996e4	880.95032	91.7025
2	18.432	BB	0.4656	2126.30615	68.61219	8.2975