Visible light assisted synthesis of allylic-triflamides via dual acridinium/Co catalysis

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General Methods.

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd= doublet doublet, t = triplet, td = triple doublet, dt = double triplet, q = quartet, sext = sextet, sept = septet, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm). *A peak of negative intensity in the ^{13}C NMR spectra at 21.3 ppm is sometimes present. It arises from a "spike" generated by an external radiofrequency interfering with the ^{13}C NMR frequency at 100 MHz. The presence of this peak does not however prevent a clear understanding of the spectral data and, in all cases, the peaks in the interested region have been correctly identified.*

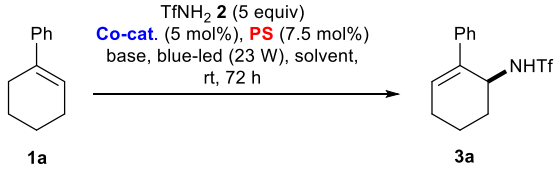
GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense).

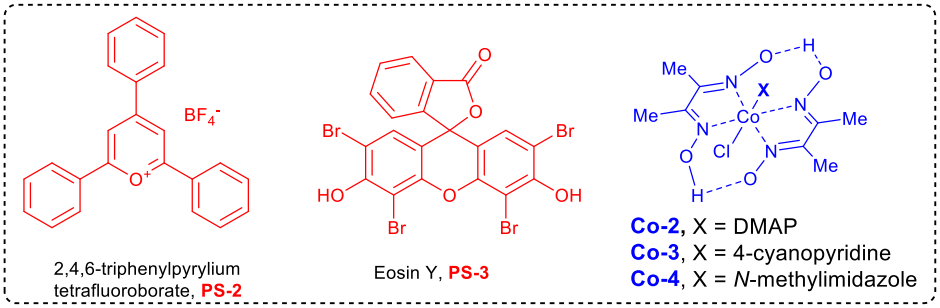
Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Strem Chemicals, and TCI and used without any further purification. Agilent Technologies LC/MSD Trap 1100 series (nebulizer: 15.0 PSI, dry Gas: 5.0 L/min, dry Temperature: 325 °C, capillary voltage positive scan: 4000 mA, capillary voltage negative scan: 3500 mA).

UV−vis absorption spectra were recorded at room temperature by means of Perkin-Elmer Lambda 45 spectrophotometer. Quartz cuvettes (Hellma) with optical path length of 1 cm were used. The fluorescence spectra were recorded with an Edinburgh FLS920 equipped photomultiplier Hamamatsu R928P. The same instrument connected to a PCS900 PC card was used for the Time Correlates Single Photon Counting (TCSPC) experiments. Luminescence quantum yields (uncertainty, ± 15%) were determined using rhodamine 101 solution in ethanol as a reference (Φ = 1.0). Fluorescence intensities were corrected for inner filter effects according to standard methods.[1] The excited state lifetimes were measured by TCSPC on an Edinburgh FLS920 equipped with a photomultiplier Hamamatsu R928 phototube connected to a TCC900 card. Pulsed excitation was performed with a laser diode (LDH-P-C 405).

Starting materials **1** and **4** were prepared following our previously reported procedure.[2]

Table S1. Optimization of the intermolecular reaction conditions[a].





Entry	Co (5 mol%)	PS (7.5 mol%)	Base (%)	Solvent	Yield[b] %
1	**Co-1**	**PS-1**	Lutidine (25)	DCM/HFIP (40:1)	69
2	**Co-1**	**PS-1**	Lutidine (25)	DCM/HFIP (20:1)	72 (69[c])
3	**Co-1**	**PS-1**	Lutidine (25)	DCM/HFIP (10:1)	68
4	**Co-1**	**PS-1**	Lutidine (25)	DCM	48
5	**Co-1**	**PS-1**	Lutidine (25)	*o*-$C_6H_4Cl_2$	41
6	**Co-1**	**PS-1**	Lutidine (25)	DCE	44
7	**Co-1**	**PS-1**	Lutidine (25)	CCl4	NR
8	**Co-1**	**PS-1**	Lutidine (10)	DCM	33
9	**Co-1**	**PS-1**	Lutidine (50)	DCM	28
10	**Co-1**	**PS-1**	Lutidine (75)	DCM	21
11	**Co-2**	**PS-1**	Lutidine (25)	DCM	35
12	**Co-3**	**PS-1**	Lutidine (25)	DCM	10
13	**Co-4**	**PS-1**	Lutidine (25)	DCM	41
14	**Co-1**	**PS-2**	Lutidine (25)	DCM	NR
15	**Co-1**	**PS-3**	Lutidine (25)	DCM	NR

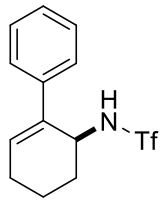
a) Reaction conditions: **1a** (0.1 mmol), **2** (0.5 mmol), **PS** (7.5 mol%), **Co-cat.** (5.0 mol%), solvent (1 mL), 2,6-lutidine, blue-led (23 W), rt, 72 h. b) Measured by ^{1}H NMR analysis on the crude reaction mixture using ethylene carbonate as internal standard. c) Isolated yield after column chromatography.

The best reaction conditions are the ones shown in Table S1, entry 2. Modifications of the solvent/co-solvent (DCM/HFIP) ratio (entries 1-3) led to small detriments in the observed yield. The following optimization entries were run in the absence of HFIP, as its use an effective additive was a late discovery; however, they are consistent with each other and can be compared to entry 4, showing the (otherwise) optimal reaction conditions in the absence of HFIP. Different solvents, commonly employed in photocatalysis, have been tested but showed less satisfactory results than DCM (entries 5-7). In particular, CCl_4 (entry 7) seemed not to be able to solubilize the cobalt catalyst. After observing that lutidine was the best base for our process, we varied the amount added, confirming 25 mol% as the best choice (entries 8-10 and entry 10 of Table 1, main text). As can be seen in entries 11-13, different cobalt catalysts were

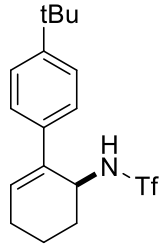
tested. They differ from each other for the presence of a different substituent on the apical position. Also, in this case the yields obtained were worse than the one obtained using the standard conditions. As last tests, two different commercially available photocatalysts were tested but in this case no traces of product were observed (entries 14-15).

Optimized general procedure for the intermolecular process.

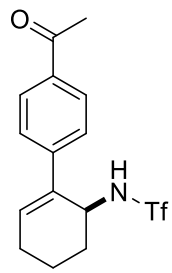
A 5 mL dry vial equipped with a stirring bar was charged with: acridinium **PS-1** (4.2 mg, 7.5 mol%), [Co(dmgH)$_2$(Py)(Cl)] **Co-1** (2.0 mg, 5 mol%), dry DCM (1 mL), HFIP (50 µL), styryl derivative **1** (0.1 mmol), 2,6-lutidine (2.7 mg, 3.0 µL, 25 mol%) and triflamide **2** (72.0 mg, 0.5 mmol). The solution was gently degassed with N_2 then stirred under 23 W blue LED irradiation (465 nm) for 72 h. Then, the solvent was removed under vacuum and the residue purified via flash chromatography.



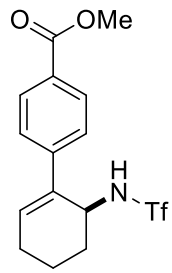
3a. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 69% (21.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 6.21 (t, *J* = 4.0 Hz, 1H), 4.78 – 4.68 (m, 1H), 4.64 (d, *J* = 7.7 Hz, 1H), 2.38 – 2.09 (m, 3H), 1.94 (dddd, *J* = 13.9, 12.6, 4.2, 3.1 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.73 – 1.59 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 135.8, 132.2, 128.6 (2C), 127.9, 126.4 (2C), 119.3 (q, *J* = 321.2 Hz), 51.9, 30.6, 25.5, 16.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-MS**: 305 (11), 172 (13), 156 (100); **Anal. Calc.** for ($C_{13}H_{14}F_3NO_2S$: 305.07): C, 51.14; H, 4.62; found: C, 51.10; H, 4.63.



3b. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 60% (21.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 2H), 7.28 – 7.21 (m, 2H), 6.20 (t, *J* = 4.0 Hz, 1H), 4.80 – 4.69 (m, 1H), 4.66 (d, *J* = 7.2 Hz, 1H), 2.34 – 2.10 (m, 3H), 1.89 (tt, *J* = 13.7, 3.5 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.72 – 1.59 (m, 1H), 1.30 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 135.5, 135.3, 131.4, 125.9 (2C), 125.5 (2C), 119.3 (q, *J* = 321.2 Hz), 51.8, 34.5, 31.2 (3C), 30.4, 25.5, 16.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-MS**: 361 (15), 228 (17), 212 (100), 57 (63); **Anal. Calc.** for ($C_{17}H_{22}F_3NO_2S$: 361.13): C, 56.50; H, 6.14; found: C, 56.46; H, 6.21.

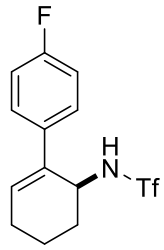


3c. Pale yellow needles (m. p. > 250 °C, decomposition). *n*Hex:EtOAc: from 40:1 to 10:1. Yield = 55% (19.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H), 7.43 – 7.32 (m, 2H), 6.32 (t, *J* = 4.0 Hz, 1H), 4.92 (bs, 1H), 4.78 – 4.74 (m, 1H), 2.60 (s, 3H), 2.39 – 2.10 (m, 3H), 1.95 (tt, *J* = 13.5, 3.7 Hz, 1H), 1.90 – 1.75 (m, 1H), 1.75 – 1.62 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 143.4, 136.2, 135.2, 134.1, 128.7 (2C), 126.5 (2C), 119.3 (q, *J* = 320.9 Hz), 51.4, 30.5, 26.6, 25.6, 16.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.6 (s, 3F); **GC-MS**: 347 (9), 214 (17), 198 (100), 183 (23), 155 (71); **Anal. Calc.** for $C_{15}H_{16}F_3NO_3S$: 347.08): C, 51.87; H, 4.64; found: C, 51.76; H, 4.65.

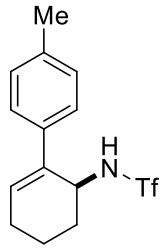


3d. Off-white crystals (m. p. = 200 -204 °C). *n*Hex:EtOAc: from 40:1 to 10:1. Yield = 45% (16.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.96 (m, 2H), 7.45 – 7.34 (m, 2H), 6.30 (t, *J* = 4.1 Hz, 1H), 4.70 (bs, 1H) partially overlapped with 4.75 – 4.71 (m, 1H), 3.90 (s, 3H), 2.37 – 2.11 (m, 3H), 1.94 (t, *J* = 13.4 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.76 – 1.44 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 143.3, 137.8, 135.3, 134.0, 129.9 (2C), 126.4 (2C), 119.3 (q, *J* = 321.1 Hz), 52.1, 51.5, 30.6, 25.5, 16.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-**

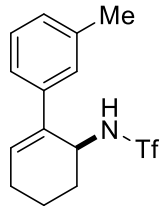
MS:363 (19), 348 (11), 304 (7), 230 (21), 226 (100); **Anal. Calc.** for ($C_{16}H_{20}O_2$: 244.15): C, 78.65; H, 8.25; found: C, 78.76; H, 8.37.



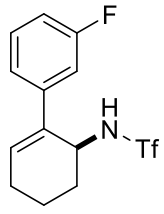
3e. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 62% (20.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.08 – 6.97 (m, 2H), 6.13 (t, *J* = 4.0 Hz, 1H), 4.75 (d, *J* = 8.0 Hz, 1H), 4.68 – 4.60 (m, 1H), 2.34 – 2.09 (m, 3H), 1.91 (tt, *J* = 13.5, 3.7 Hz, 1H), 1.79 (dtd, *J* = 14.3, 6.0, 3.3 Hz, 1H), 1.70 – 1.53 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 246.9 Hz), 135.0, 134.9 (d, *J* = 3.4 Hz), 132.3, 128.2 (d, *J* = 8.0 Hz, 2C), 119.3 (q, *J* = 321.1 Hz), 115.4 (d, *J* = 21.5 Hz, 2C), 52.0, 30.6, 25.4, 16.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.6 (s, 3F), -114.41 – -114.61 (m, 1F); **GC-MS**: 323 (27), 190 (21), 174 (100); **Anal. Calc.** for ($C_{13}H_{13}F_4NO_2S$: 323.067): C, 48.30; H, 4.05; found: C, 48.48; H, 4.18.



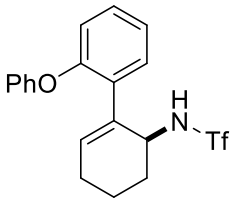
3f. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 49% (15.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.17 – 7.12 (m, 2H), 6.18 (t, *J* = 4.0 Hz, 1H), 4.74 – 4.65 (m, 1H), 3.30 (bs, 1H), 2.35 (s, 3H), 2.28 – 2.10 (m, 3H), 1.92 (tt, *J* = 13.8, 3.7 Hz, 1H), 1.86 – 1.72 (m, 1H), 1.72 – 1.57 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.6, 135.7, 135.5, 131.4, 129.3 (2C), 126.2 (2C), 119.3 (q, *J* = 321.0 Hz), 51.8, 30.5, 25.5, 21.1, 16.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-MS**: 319 (13), 186 (11), 170 (100); **Anal. Calc.** for ($C_{14}H_{16}F_3NO_2S$: 319.09): C, 52.66; H, 5.05; found: C, 52.81; H, 4.93.



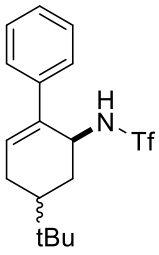
3g. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 40% (12.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 1H), 7.17 – 7.08 (m, 3H), 6.20 (t, *J* = 4.0 Hz, 1H), 4.77 – 4.66 (m, 1H), 3.18 (bs, 1H), 2.35 (s, 3H), 2.30 – 2.09 (m, 3H), 2.02 – 1.86 (m, 1H), 1.85 – 1.72 (m, 1H), 1.74 – 1.58 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.6, 138.1, 135.8, 131.9, 128.6, 128.4, 127.2, 123.5, 119.27 (q, *J* = 321.2 Hz), 51.9, 30.6, 25.5, 21.4, 16.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-MS**: 319 (15), 186 (10), 170 (100); **Anal. Calc.** for ($C_{14}H_{16}F_3NO_2S$: 319.09): C, 52.66; H, 5.05; found: C, 52.83; H, 5.18.



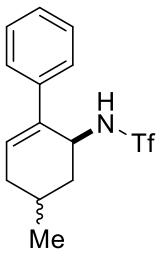
3h. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 62% (20.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.13 (t, *J* = 4.0 Hz, 1H), 4.70 (d, *J* = 8.0 Hz, 1H), 4.60 – 4.51 (m, 1H), 2.25 – 2.01 (m, 3H), 1.83 (tt, *J* = 13.5, 3.7 Hz, 1H), 1.77 – 1.65 (m, 1H), 1.62 – 1.47 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 246.0 Hz), 141.1 (d, *J* = 7.4 Hz), 135.0 (d, *J* = 2.3 Hz), 133.2, 130.0 (d, *J* = 8.4 Hz), 122.1 (d, *J* = 2.9 Hz), 119.2 (q, *J* = 321.1 Hz), 114.7 (d, *J* = 21.3 Hz), 113.5 (d, *J* = 22.1 Hz), 51.7, 30.6, 25.4, 16.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.6 (s, 3F), -113.1 (td, *J* = 9.3, 6.1 Hz, 1F); **GC-MS**: 323 (21), 190 (24), 174 (100); **Anal. Calc.** for ($C_{13}H_{13}F_4NO_2S$: 323.06): C, 48.30; H, 4.05; found: C, 48.41; H, 3.92.



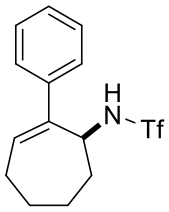
3i. Viscous oil. *n*Hex:EtOAc: from 40:1 to 15:1. Yield = 64% (25.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.18 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.98 – 6.88 (m, 3H), 6.00 – 5.94 (m, 1H), 5.10 (d, *J* = 7.8 Hz, 1H), 4.60 – 4.49 (m, 1H), 2.23 – 2.06 (m, 1H), 2.05 – 1.96 (m, 1H), 1.91 (tdd, *J* = 13.9, 4.5, 3.2 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.65 – 1.53 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 154.3, 134.1, 133.0, 131.8, 130.8, 129.8 (2C), 129.2, 123.9, 123.4, 119.3 (q, *J* = 321.6 Hz), 119.2, 118.6 (2C), 53.6, 31.0, 25.1, 17.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.8 (s, 3F); **GC-MS**: 397 (15), 304 (11) 264 (13), 248 (100); **Anal. Calc.** for ($C_{19}H_{18}F_3NO_3S$: 397.10): C, 57.42; H, 4.57; found: C, 57.61; H, 4.44.



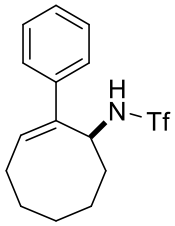
3j. Colorless crystals (m. p. = 180 – 182 °C). *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 69% (24.9 mg), *dr* : 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 3H + 2H), 7.30 – 7.25 (m, 1H), 7.25 – 7.21 (m, 2H + 2H), 6.25 (dd, *J* = 5.5, 2.6 Hz, 1H), 6.07 (dt, *J* = 6.1, 2.2 Hz, 1H), 4.85 – 4.79 (m, 1H), 4.79 – 4.72 (m, 1H), 4.68 (d, *J* = 7.8 Hz, 1H), 4.35 (d, *J* = 7.5 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.35 – 2.19 (m, 2H + 1H), 2.06 – 1.91 (m, 1H + 1H), 1.58 – 1.32 (m, 2H + 2H), 0.92 (s, 9H + 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.5, 138.1, 136.8, 135.1, 132.4, 132.1, 128.6 (2C), 128.5 (2C), 127.9, 127.6, 126.9, (2C) 126.2 (2C), 119.3 (q, *J* = 321.0 Hz, 2C overlapped), 55.8, 52.7, 43.0, 37.6, 34.2, 32.1, 31.8, 31.8, 27.5, 27.1, 27.0 (3C), 26.9 (3C); **GC-MS** *of the first eluting diastereoisomer*: 361 (7), 228 (9), 212 (23), 155 (100), 57 (60); **GC-MS** *of the second eluting diastereoisomer*: 361 (5), 228 (11), 212 (27), 155 (100), 57 (60); **Anal. Calc.** for ($C_{17}H_{22}F_3NO_2S$: 361.13): C, 56.50; H, 6.14; found: C, 56.67; H, 6.01 (*analyzed as diastereomeric mixture*). In the ^{13}C NMR spectrum all peaks are given without assignment.



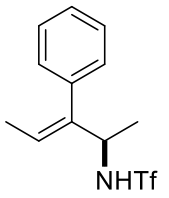
3k. White solid (m. p. = 184 – 187 °C). *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 53% (16.9 mg), *dr* : 4:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (401 MHz, cdcl$_3$) δ 7.38 – 7.24 (m, 5H major + 5H minor), 6.20 (dd, *J* = 5.4, 2.0 Hz, 1H major), 6.07 (dt, *J* = 5.5, 2.1 Hz, 1H minor), 4.80 (bs, 1H minor), 4.78 – 4.68 (m, 2H major), 4.44 (d, *J* = 7.9 Hz, 1H minor), 2.48 – 2.24 (m, 1H major + 2H minor), 2.22 – 2.15 (m, 1H major + 1H minor), 1.94 – 1.79 (m, 2H major + 2H minor), 1.65 – 1.41 (m, 1H major), 1.08 (d, *J* = 6.0 Hz, 3H major), 1.05 (d, *J* = 6.3 Hz, 3H minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.6 (minor), 138.4 (major), 136.6 (minor), 135.3 (major), 132.0 (minor), 132.0 (major), 128.6 (2C major), 128.5 (2C minor), 127.9 (major), 127.6 (minor), 126.9 (2C minor), 126.4 (2C major), 119.3 (q, *J* = 321.1 Hz, major + minor), 54.4 (minor), 52.6 (major), 40.6 (minor), 38.6 (major), 34.3 (major), 33.9 (minor), 28.0 (minor), 22.7 (major), 21.4 (minor), 21.2 (major); **GC-MS** *of the major diastereoisomer*: 319 (15), 186 (13), 170 (76), 155 (100); **GC-MS** *of the minor diastereoisomer*: 319 (17), 186 (10), 170 (71), 155 (100); **Anal. Calc.** for ($C_{14}H_{16}F_3NO_2S$: 319.09): C, 52.66; H, 5.05; found: C, 52.43; H, 5.21 (*analyzed as a diastereomeric mixture*).



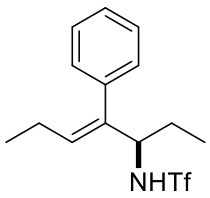
3l. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 45% (14.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, 5H), 6.07 (t, *J* = 6.7 Hz, 1H), 4.93 (d, *J* = 7.8 Hz, 1H), 4.77 (t, *J* = 7.5 Hz, 1H), 2.42 – 2.21 (m, 2H), 2.17 – 2.06 (m, 1H), 1.99 – 1.88 (m, 3H), 1.74 – 1.57 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 141.6, 134.1, 128.5 (2C), 127.6, 126.7 (2C), 119.4 (q, *J* = 321.1 Hz), 58.3, 32.9, 27.6, 26.4, 25.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-MS**: 319 (18), 186 (13), 170 (100); **Anal. Calc.** for ($C_{14}H_{16}F_3NO_2S$: 319.09): C, 52.66; H, 5.05; found: C, 52.81; H, 4.89.



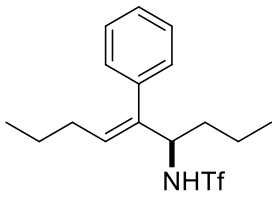
3m. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 70% (23.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.20 – 7.14 (m, 2H), 5.87 – 5.83 (t, *J* = 8.4 Hz, 1H), 4.94 (ddd, *J* = 12.3, 9.5, 5.6 Hz, 1H), 4.74 (d, *J* = 9.6 Hz, 1H), 2.40 – 2.18 (m, 2H), 2.11 – 2.00 (m, 1H), 1.99 – 1.89 (m, 2H), 1.89 – 1.77 (m, 2H), 1.59 – 1.42 (m, 1H), 1.42 – 1.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.0, 138.2, 132.1, 128.8 (2C), 127.9 (2C), 127.8, 119.5 (q, *J* = 321.2 Hz), 54.4, 38.6, 29.8, 27.7, 27.5, 24.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.5 (s, 3F); **GC-MS**: 333 (9), 200 (11), 184 (100); **Anal. Calc.** for ($C_{15}H_{18}F_3NO_2S$: 333.10): C, 54.04; H, 5.44; found: C, 54.63; H, 5.51.



3n. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 74% (21.7 mg), *E/Z : 7:1*. **^{1}H NMR** of ***E*-3n** (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 7.04 – 6.97 (m, 2H), 5.72 (q, *J* = 6.6 Hz, 1H), 4.76 (d, *J* = 9.4 Hz, 1H), 4.34 (p, *J* = 7.2 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H); diagnostic signal for ***E*-3n**: 5.46 (q, *J* = 7.1 Hz, 1H); **^{13}C NMR** of ***E*-3n** (100 MHz, $CDCl_3$) δ 141.4, 136.6, 129.3 (2C), 128.6 (2C), 127.6, 124.6, 119.5 (q, *J* = 320.9 Hz), 57.7, 22.2, 14.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.9 (s, 3F of ***E*-3n**), -78.0 (s, 3F of ***Z*-3n**); **GC-MS**: 293 (12), 278 (92), 129 (100); **Anal. Calc.** for ($C_{12}H_{14}F_3NO_2S$: 293.07): C, 49.14; H, 4.81; found: C, 49.31; H, 4.82.



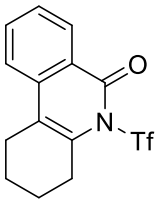
3o. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 74% (23.8 mg), *E/Z : >20:1*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.36 – 7.29 (m, 1H), 7.13 – 7.04 (m, 2H), 5.66 (t, *J* = 7.4 Hz, 1H), 4.68 (bs, 1H), 4.14 (t, *J* = 6.8 Hz, 1H), 1.84 (pd, *J* = 7.3, 2.0 Hz, 2H), 1.72 – 1.59 (m, 1H), 1.59 – 1.47 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H); diagnostic signal for ***Z*-3o**: 5.52 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.2, 136.6, 133.2, 129.3 (2C), 128.6 (2C), 127.6, 119.5 (q, *J* = 320.9 Hz), 63.9, 28.3, 22.0, 14.0, 10.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.6 (s, 3F of ***E*-3o**), -77.8 (s, 3F of ***Z*-3o**); **GC-MS**: 321 (5), 292 (89), 143 (100); **Anal. Calc.** for ($C_{14}H_{18}F_3NO_2S$: 321.10): C, 52.33; H, 5.65; found: C, 52.11; H, 5.77.



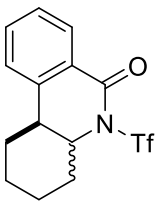
3p. Viscous oil. *n*Hex:EtOAc: from 40:1 to 20:1. Yield = 65% (22.7 mg), *E/Z : >20:1*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.36 – 7.30 (m, 1H), 7.11 – 7.06 (m, 2H), 5.66 (t, *J* = 7.4 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 1.85 – 1.76 (m, 2H), 1.64 – 1.53 (m, 1H), 1.53 – 1.38 (m, 3H), 1.37 – 1.30 (m, 2H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H); the NH signal appears as a very broad singlet centered at 4.59 ppm; diagnostic signal for ***Z*-3p**: 5.50 (t, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 136.6, 131.6, 129.4 (2C), 128.6 (2C), 127.6, 119.5 (q, *J* = 321.0 Hz), 62.4, 37.4, 30.5, 22.5, 19.2, 13.6, 13.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.6 (s, 3F of ***E*-3p**), -77.8 (s, 3F of ***Z*-3p**); **GC-MS**: 349 (11), 306 (100), 173 (50); **Anal. Calc.** for ($C_{16}H_{22}F_3NO_2S$: 321.10): C, 55.00; H, 6.35; found: C, 55.17; H, 6.19.

Optimized general procedure for the intramolecular process.

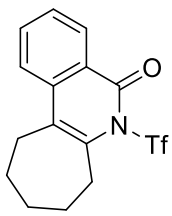
A 5 mL dry vial equipped with a stirring bar was charged with: acridinium **PS-1** (4.2 mg, 7.5 mol%), [Co(dmgH)$_2$(Py)(Cl)] **Co-1** (2.0 mg, 5 mol%), dry DCM (1 mL), HFIP (50 µL), triflimide **3** (0.1 mmol) and 2,6-lutidine (2.7 mg, 3.0 µL, 25 mol%). The solution was gently degassed with N_2 then stirred under 23 W blue LED irradiation (465 nm) for 72 h. Then, the solvent was removed under vacuum and the residue purified via flash chromatography.



5a. White solid (m.p. = 175 – 177 °C). *n*Hex:EtOAc: from 60:1 to 40:1 (third eluting fraction from the column). Yield = 40% (22.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.86 (td, *J* = 7.6, 1.4 Hz, 1H), 7.63 – 7.51 (m, 2H), 2.79 – 2.66 (m, 4H), 1.99 – 1.81 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 153.0, 136.9, 136.7, 129.6, 128.5, 121.8, 119.3, 119.2 (q, *J* = 319.7 Hz), 113.0, 26.9, 22.7, 21.7, 21.6 ; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.0 (s, 3F); **GC-MS**: 331 (5), 198 (94), 180 (100); **Anal. Calc.** for ($C_{14}H_{12}F_3NO_3S$: 331.05): C, 50.75; H, 3.75; found: C, 50.61; H, 3.98.

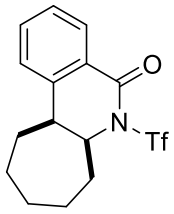


5a'. Viscous oil. *n*Hex:EtOAc: from 60:1 to 40:1 (first and second eluting fraction from the column). Yield = 34% (11.6 mg), *dr : 1.2:1*. **^{1}H NMR** *of the major diastereoisomer* (400 MHz, $CDCl_3$) δ 8.22 – 8.14 (m, 1H), 7.65 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45 – 7.37 (m, 2H), 4.58 (dt, *J* = 12.2, 4.6 Hz, 1H), 3.63 (s, 1H), 2.61 (dt, *J* = 14.6, 3.0 Hz, 1H), 1.94 – 1.80 (m, 2H), 1.72 – 1.61 (m, 1H), 1.58 – 1.35 (m, 4H); . **^{1}H NMR** *of the minor diastereoisomer* (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 4.22 (td, *J* = 11.7, 4.4 Hz, 1H), 2.90 (td, *J* = 11.6, 4.0 Hz, 1H), 2.62 – 2.50 (m, 1H), 2.43 – 2.33 (m, 1H), 2.05 – 1.75 (m, 4H), 1.49 – 1.28 (m, 2H); **^{13}C NMR** *of the major diastereoisomer* (100 MHz, $CDCl_3$) δ 162.7, 139.6, 135.0, 130.2, 127.4, 127.2, 126.0, 119.4 (q, *J* = 324.2 Hz), 60.4, 37.4, 28.3, 26.7, 24.9, 19.0; **^{13}C NMR** *of the minor diastereoisomer* (100 MHz, $CDCl_3$) δ 167.6, 142.4, 135.7, 130.6, 127.8, 123.9, 119.0 (q, *J* = 319.1 Hz), 113.0, 84.6, 39.5, 31.0, 26.8, 24.6, 23.7; **^{19}F NMR** *of the major diastereoisomer* (376 MHz, $CDCl_3$) δ -72.1 (s, 3F); **^{19}F NMR** *of the minor diastereoisomer* (376 MHz, $CDCl_3$) δ -79.5 (s, 3F); **GC-MS** *of the major diastereoisomer*: 333 (5), 200 (87), 182 (100); **GC-MS** *of the minor diastereoisomer*: 333 (11), 200 (96), 182 (100); **Anal. Calc.** for ($C_{14}H_{12}F_3NO_3S$: 333.06): C, 50.45; H, 4.23; found: C, 50.59; H, 4.03 (*major diastereoisomer*); C, 50.51; H, 4.11 (*minor diastereoisomer*);.

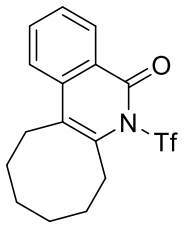


5b. Pale yellow solid (m. p. = 177 – 179 °C). *n*Hex:EtOAc: from 60:1 to 40:1 (second eluting fraction from the column). Yield = 66% (23.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.86 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.55 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 2.98 – 2.91 (m, 2H), 2.87 – 2.80 (m, 2H), 1.90 – 1,86 (m, 2H), 1.80 – 1.70 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 157.3, 137.1, 136.7, 129.8, 128.3, 122.2, 119.2 (q, *J* = 320.0 Hz), 119.0, 118.2, 32.8, 30.8, 25.5, 24.6, 24.6; **^{19}F NMR** (376 MHz, $CDCl_3$)

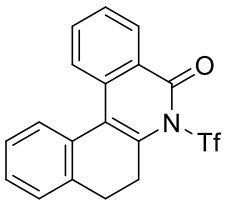
δ -79.1 (s, 3F); **GC-MS**: 345 (11), 212 (82), 194 (100); **Anal. Calc.** for ($C_{15}H_{14}F_3NO_3S$: 345.06): C, 52.17; H, 4.09; found: C, 51.98; H, 4.16.



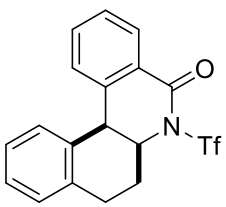
5b'. Viscous oil. *n*Hex:EtOAc: from 60:1 to 40:1 (first eluting fraction from the column). Yield = 22% (7.7 mg), *dr : >20:1*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.63 (td, *J* = 7.6, 1.5 Hz, 1H), 7.43 – 7.35 (m, 2H), 4.63 (ddd, *J* = 10.4, 5.3, 2.3 Hz, 1H), 3.70 (q, *J* = 6.1 Hz, 1H), 2.32 – 2.22 (m, 1H), 2.21 – 2.09 (m, 1H), 1.91 – 1.46 (m, 7H), 1.39 – 1.25 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 136.6, 130.1, 125.0, 122.6, 122.0, 121.6, 114.7 (q, *J* = 324.3 Hz), 58.6, 35.3, 26.5, 23.3, 23.1, 19.9, 17.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.0 (s, 3F); **GC-MS**: 347 (9), 214 (67), 196 (100); **Anal. Calc.** for ($C_{15}H_{16}F_3NO_3S$: 347.08): C, 51.87; H, 4.64; found: C, 51.69; H, 4.55.



5c. White solid (m. p. = 167 – 170 °C). *n*Hex:EtOAc: from 60:1 to 40:1. Yield = 68% (24.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.8 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 2.90 – 2.83 (m, 4H), 1.91 – 1.72 (m, 4H), 1.60 – 1.51 (m, 2H), 1.47 – 1.37 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 155.3, 136.7, 136.4, 129.9, 128.4, 122.5, 119.5, 119.3 (q, *J* = 319.6 Hz), 115.3, 30.8, 29.7, 29.0, 26.6, 25.5, 23.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.0 (s, 3F); **GC-MS**: 359 (9), 226 (91), 208 (100); **Anal. Calc.** for ($C_{16}H_{16}F_3NO_3S$: 359.08): C, 53.48; H, 4.49; found: C, 53.62; H, 4.56.

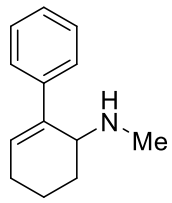


5d. Yellow solid (m. p. = 210 -213 °C). *n*Hex:EtOAc: from 60:1 to 40:1. Yield = 51% (19.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.76 – 7.68 (m, 1H), 7.62 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.39 – 7.28 (m, 3H), 3.03 – 2.89 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6, 155.3, 136.6, 136.0, 134.2, 130.2, 129.5, 128.7, 128.5, 128.0, 126.8, 126.3, 124.1, 120.4, 119.2 (q, *J* = 317.3 Hz), 114.1, 28.2, 26.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.0 (s, 3F); **GC-MS**: 379 (31), 246 (22), 218 (100); **Anal. Calc.** for ($C_{18}H_{12}F_3NO_3S$: 379.05): C, 56.99; H, 3.19; found: C, 56.81; H, 3.01.



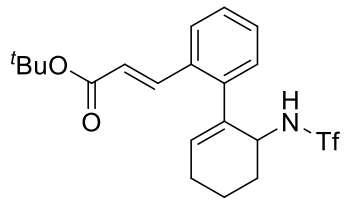
5d'. Viscous oil. *n*Hex:EtOAc: from 60:1 to 40:1. Yield = 29% (11.0 mg), *dr : >20:1*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 7.17 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 4.93 (dt, *J* = 12.4, 4.4 Hz, 1H), 4.59 (d, *J* = 4.9 Hz, 1H), 3.01 (ddd, *J* = 18.2, 11.1, 7.3 Hz, 1H), 2.83 (ddd, *J* = 17.6, 7.1, 1.8 Hz, 1H), 2.19 – 2.08 (m, 1H), 1.97 (tdd, *J* = 12.7, 11.2, 7.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 140.9, 134.8, 134.6, 132.8, 131.4, 129.9, 129.7, 128.2, 128.0, 127.7, 126.0, 125.8, 119.1 (q, *J* = 319.7 Hz), 58.1, 42.6, 28.0, 25.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.0 (s, 3F); **GC-MS**: 381 (33), 248 (100), 231 (77); **Anal. Calc.** for ($C_{18}H_{12}F_3NO_3S$: 381.06): C, 56.69; H, 3.70; found: C, 56.81; H, 3.88.

Preparation of product 6a.



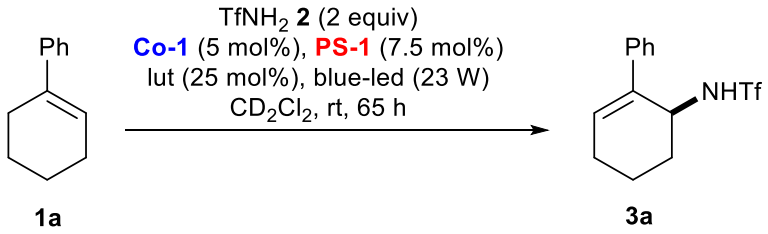
A 25 mL dry round bottom flask equipped with a stirring bar was charged with: NaH (60% wt in mineral oil, 6.0 mg, 0.15 mmol), dry DMF (0.5 mL) and cooled to 0 °C. Then, product **3a** (30.5 mg, 0.1 mmol) was added and the suspension was stirred at 0 °C for 1 h. Then, MeI (12.5 µL, 0.2 mmol) was added in one portion and the reaction mixture was stirred at room temperature overnight. Upon completion (monitored by TLC), water (5 mL) and EtOAc (5 mL) were added and the biphasic mixture was moved to a separatory funnel. The organic phase was washed with water (2x5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. The crude product was directly dissolved in dry THF (0.5 mL) and cooled to -20 °C. A solution of Red-Al (60% wt. in toluene, 1.0 mmol) was added dropwise and the resulting solution was heated to reflux and stirred for 18 h. Upon cooling, water (5 mL) and EtOAc (5 mL) was added and the biphasic mixture was moved to a separatory funnel. The organic phase was washed with water (2x5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo*. Trituration in *n*-hexane (2 x 5 mL) afforded product **6a** (11.2 mg, 65% yield) as an amorphous solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 6.07 (t, *J* = 4.0 Hz, 1H), 3.76 (s, 1H), 2.75 (bs, 1H), 2.31 (s, 3H), 2.28 – 2.05 (m, 1H), 2.05 – 1.94 (m, 1H), 1.83 – 1.72 (m, 2H), 1.69 – 1.51 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.9, 130.1, 128.6, 128.5, 127.1, 126.1, 54.5, 29.7, 26.6, 26.0, 17.8; **Anal. Calc.** for ($C_{13}H_{17}N$: 187.14): C, 83.37; H, 9.15; found: C, 83.99; H, 10.01.

Preparation of product 7a.



A 5 mL dry vial equipped with a stirring bar was charged with: product **3a** (30.5 mg, 0.1 mmol), $Pd(OAc)_2$ (4.5 mg, 20 mol%), AgOAc (41.7 mg, 0.25 mmol), NaH_2PO_4 (12.0 mg, 0.1 mmol), dry toluene (0.5 mL), *N*-methylpyrrolidone (50 µL) and *tert*-butyl acrylate (64.1 mg, 72.6 µL, 0.5 mmol). The solution was degassed with N_2 then sealed and stirred at 100 °C in the dark for 48 h. Then, the reaction mixture was filtered over a celite pad (washing with EtOAc), the solvent was removed under vacuum and the residue purified via flash chromatography (*n*Hex:EtOAc: from 30:1 to 5:1) to afford product **7a** as a viscous oil. Yield = 51% (22.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.63 – 7.61 (m, 1H), 7.37 – 7.26 (m, 2H), 7.13 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.85 (dd, *J* = 4.5, 3.2 Hz, 1H), 5.72 (bs, 1H), 4.28 (bs, 1H), 2.30 (dq, *J* = 18.8, 4.4 Hz, 1H), 2.23 – 2.16 (m, 1H), 2.11 – 1.97 (m, 2H), 1.87 – 1.70 (m, 2H), 1.51 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 141.6, 141.2, 134.8, 134.6, 132.8, 129.7, 129.6, 128.0, 126.4, 120.8, 119.1 (q, *J* = 321.2 Hz), 80.9, 54.3, 31.2 (3C), 28.2, 25.0, 16.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -79.1 (s, 3F; **GC-MS**: 375 (16), 226 (43), 181 (100), 57 (74); **Anal. Calc.** for ($C_{20}H_{24}F_3NO_4S$: 431.14): C, 55.67; H, 5.61; found: C, 55.57; H, 5.66.

On-Off experiment.



A dry NMR tube equipped with a stirring bar was charged with: **PS-1** (4.2 mg, 7.5 mol%), [Co(dmgH)$_2$(Py)(Cl)] **Co-1** (2.0 mg, 5 mol%), dry deuterated DCM (1 mL), HFIP (50 µL), styryl derivative **1a** (0.1 mmol), 2,6-lutidine (2.7 mg, 3.0 µL, 25 mol%), triflamide **2** (28.8 mg, 0.2 mmol) and ethylene carbonate as internal standard (4.4 mg, 0.05 mmol). The solution was gently degassed with N_2. The reaction (**Figure S1**) was monitored by taking ^{1}H NMR spectra during 65 h (upon removal of the stirring bar), exposing the reaction alternatively to the dark and to irradiation.

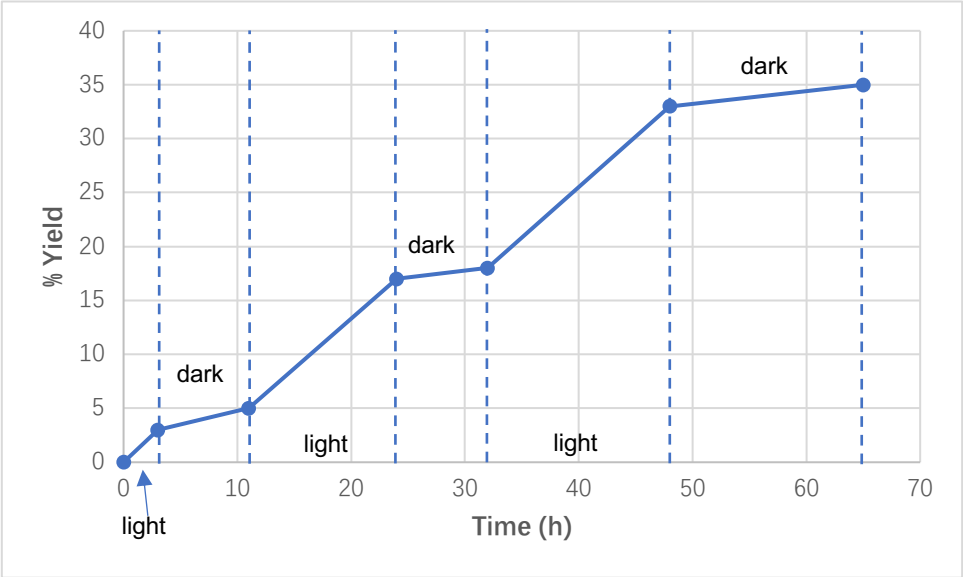
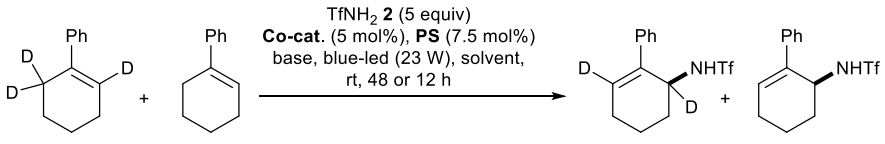


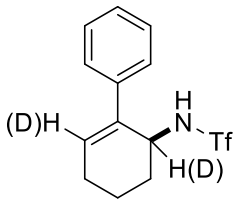
Figure S1.

Kinetic isotope effect

KIE investigation from intermolecular competition



For this type of experiment a 5 mL dry vial equipped with a stirring bar was charged with: **PS-1** (1.0 mg, 2.5 mol%), [Co(dmgH)$_2$(Py)(Cl)] (**Co-1**, 2.0 mg, 5 mol%), dry DCM (1 mL), **1a** (50 μmol), *d*^{3}-**1a** (50 μmol), **2** (0.5 mmol) and 2,6-lutidine (2.7 mg, 3.0 μL, 25 mol%). The solution was gently degassed with N_2 then stirred under 23 W blue LED irradiation (465 nm) for 48 h, obtaining a conversion equal to 75% or for 12 h, obtaining a conversion equal to 30%. Then, the solvent was removed under vacuum and the residue purified via flash chromatography (*n*Hex/AcOEt from 40:1 to 20:1). The product obtained in the reaction having 75% conversion shows a 1:1 mixture of **3a** and *d*^{2}-**3a** (by ^{1}H and ^{19}F NMR). The product obtained in the reaction having 30% conversion shows a 1:0.6 mixture of **3a** and *d*^{2}-**3a** (by ^{1}H and ^{19}F NMR).



Characterization of the 1:1 mixture of *d*^{2}-**3aa** and **3a**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H **3a** + 5 H *d*^{2}-**3a**), 6.19 (t, *J* = 3.9 Hz, 1H **3a**), 4.75 – 4.59 (m, 2H **3a** + 1H *d*^{2}-**3a**), 2.36 – 2.11 (m, 3H **3a** + 3H *d*^{2}-**3a**), 1.98 – 1.85 (m, 1H **3a** + 1H *d*^{2}-**3a**), 1.83 – 1.73 (m, 1H **3a** + 1H *d*^{2}-**3a**), 1.72 – 1.56 (m, 1H **3a** + 1H *d*^{2}-**3a**). Diagnostic signals of **3a:** 6.19 (t, *J* = 3.9 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -77.50 (s, 3F **3a**), -77.52 (s, 3F *d*^{2}-**3a**).

Stern-Volmer experiment

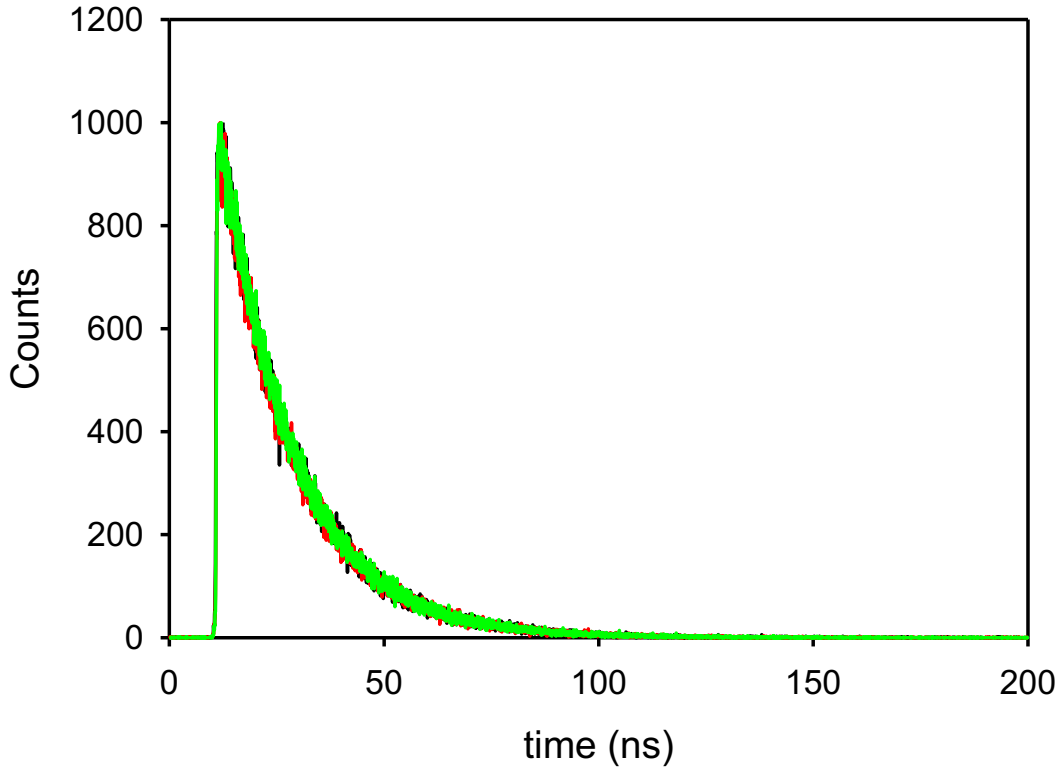


Figure S2. TCSPC decay of acridinium alone (black) and in the presence of **2** at concentrations 10 mM (red) and both **2**, 10 mM and lut, 1 mM (green).

Cyclic voltammetry experiments

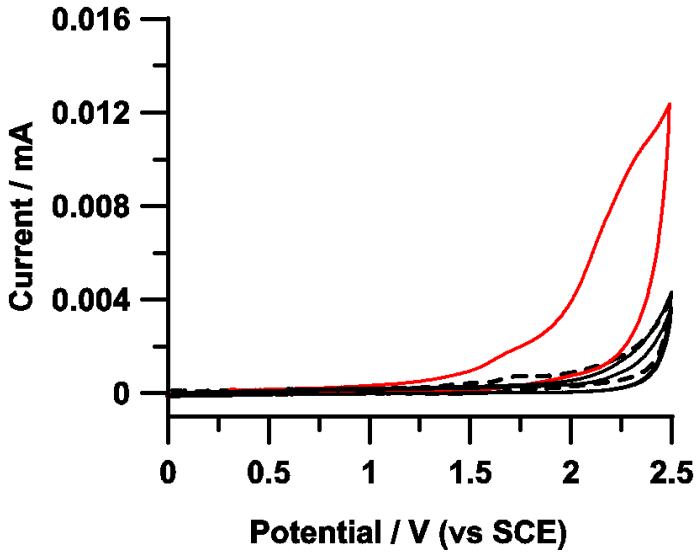


Figure S3. Cyclic Voltammetry curves of a 1 mM solution of **2** (black solid line), **2**/lut (red) and the baseline (black dashed) in a 0.07 M TBAH/CH_3CN electrolyte working electrode, Glassy carbon disk, 1 mm diameter at 0.1 Vs^{-1}.

Cyclic Voltammetry. Experiments were carried out in a three-electrode home-made cell. Dry CH_3CN were purged with ultra-high purity argon, passed through a gas bubbler with the solvent before reaching the cell. The working electrode was a 1 mm diameter glassy carbon electrode while the counter electrode was a platinum spiral and the quasi-reference electrode was Ag spiral. Before each measurement, the working electrode was polished with 0.05 μm alumina paste (Buehler), rinsed with water, sonicated in distilled water and dried. The potential of the reference electrode was measured with respect to the reversible ferrocenium/ferrocene couple. All potentials reported in this work are referred to SCE.
The electrochemical properties have been evaluated in a three-electrode electrochemical workstation (SP-300 bipotentiostat, Biologic Instruments), equipped with an additional current booster.

2/lut shows an irreversible oxidation (Figure S3 - red signal) with a peak potential at 2.2 V (*vs* SCE). The presence of lut shifts the oxidation potential of **2** towards less positive values in agreement with the literature (*e.g. ACS Cent. Sci.* **2017**, *3*, 621-628). As matter of fact, when the lut is not present any anodic current was observed within the solvent potential windows (oxidation of **2** > of 2.5 V *vs* SCE see Figure S3 - black signal).

Crystallographic analysis

The X-ray intensity data were measured on a Bruker Apex II CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.5° ω steps. The software SMART[3] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program,[3] and an empirical absorption correction was applied using SADABS.[4] The structures were solved by direct methods (SIR 2014)[5] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[6] using anisotropic thermal parameters for all non-hydrogen atoms. The aromatic, methyl, methylene and methine hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters *U(H)* = 1.2 *Ueq*(C) and allowed to ride on their carrier carbons. The crystal structure of **PS-1** shows disorder in BF_4^- anion and in one *tert*-butyl moiety. The carbons of the three methyl groups in the tert-butyl moiety are disordered over two positions with relative occupancies of 0.59 and 0.41 respectively. All four flourine of BF_4^- are disordered over two positions with relative occupancies of 0.56 and 0.44 respectively.

Crystal data and experimental details of the data collection for **PS-1** and *trans*-**3j** are reported in Table S2. Molecular drawings were generated using Mercury.[7]

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC 2111228 and CCDC 2111229. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

Table S2. Crystal data and experimental details for **PS-1** and ***trans*-3j**

Compound	**PS-1**	*trans*-**3j**
Formula	$C_{36}H_{40}NBF_4$	$C_{17}H_{22}F_3NO_2S$
Fw	573.50	361.41
T, K	296(2)	100(2)
λ, Å	0.71073	0.71073
Crystal symmetry	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c
a, Å	10.7235(6)	16.220(1)
b, Å	16.950(1)	11.4657(8)
c, Å	18.230(1)	19.161(1)
α	90	90
β	95.742(2)	90.54982)
γ	90	90
Cell volume, $Å^3$	3296.8(4)	3563.4(4)
Z	4	8
D_c, Mg m^{-3}	1.155	1.347
μ(Mo-K_α), mm^{-1}	0.081	0.220
F(000)	1216	1520
Crystal size/ mm	0.19 x 0.10 x 0.09	0.21 x 0.17 x 0.07
θ limits, °	1.644 to 23.999	2.126 to 25.499
Reflections collected	34193	17494
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	5117 [R(int) = 0.0639]	3245 [R(int) = 0.0305]
Goodness-of-fit-on F^2	1.001	1.233
R_1 (F)[a], wR_2 (F^2) [$I > 2\sigma(I)$][b]	R1 = 0.0904, wR2 = 0.2102	R1 = 0.0554, wR2 = 0.1182
Largest diff. peak and hole, e. $Å^{-3}$	0.254 and -0.174	0.646 and -0.329

[a)] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Figure S4. ORTEP drawing of **PS-1**. Thermal elipsoids are draw at 30% of the pobability level. Disordered atom are removed for clarity.

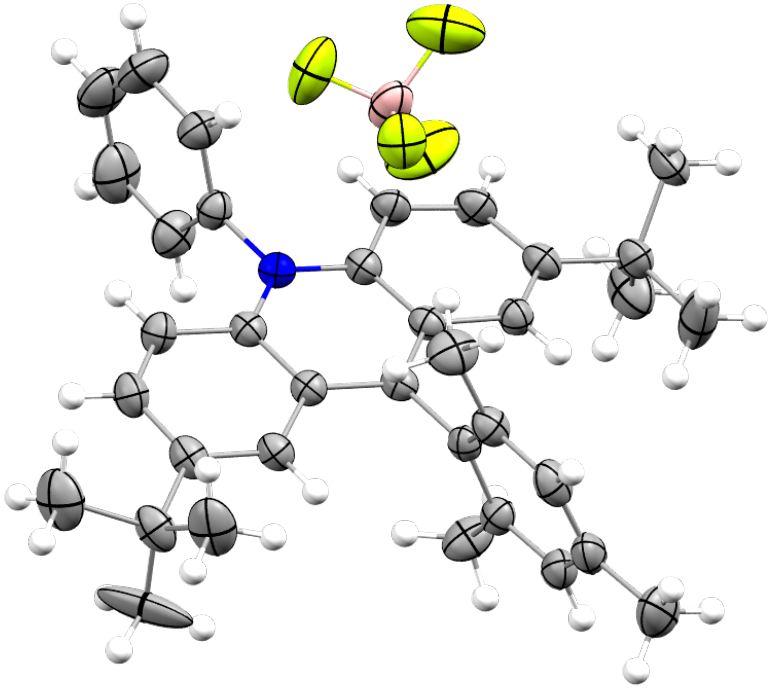
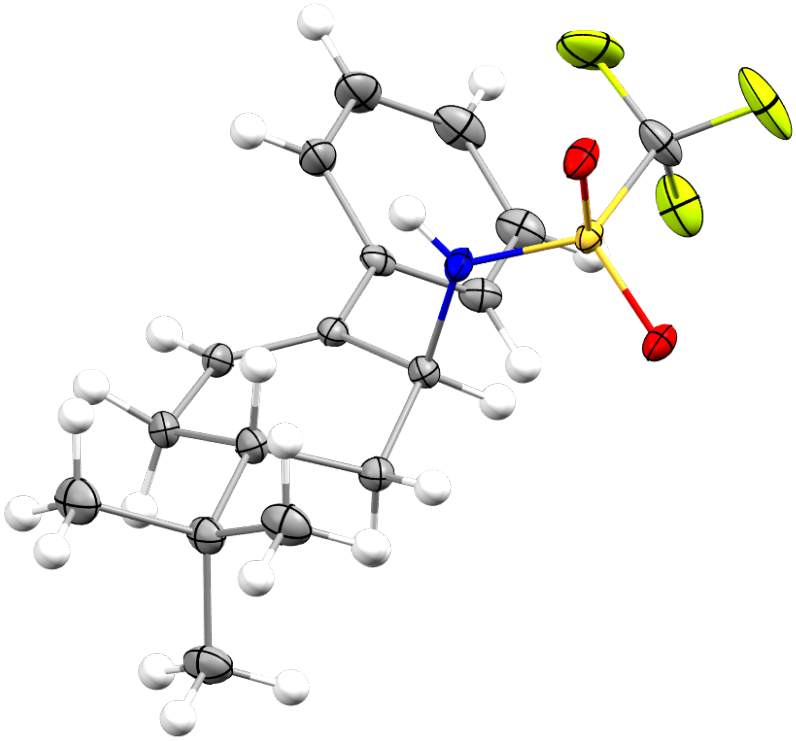
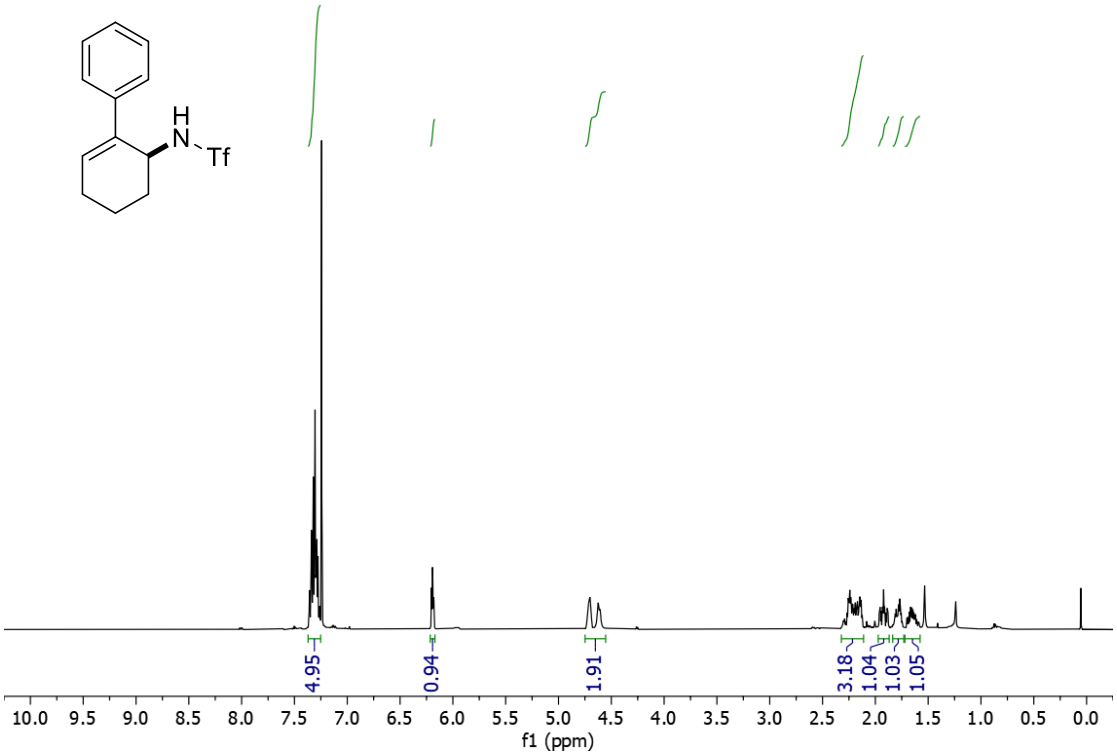


Figure S5. ORTEP drawing of ***trans*-3j**. Thermal elipsoids are draw at 30% of the pobability level.

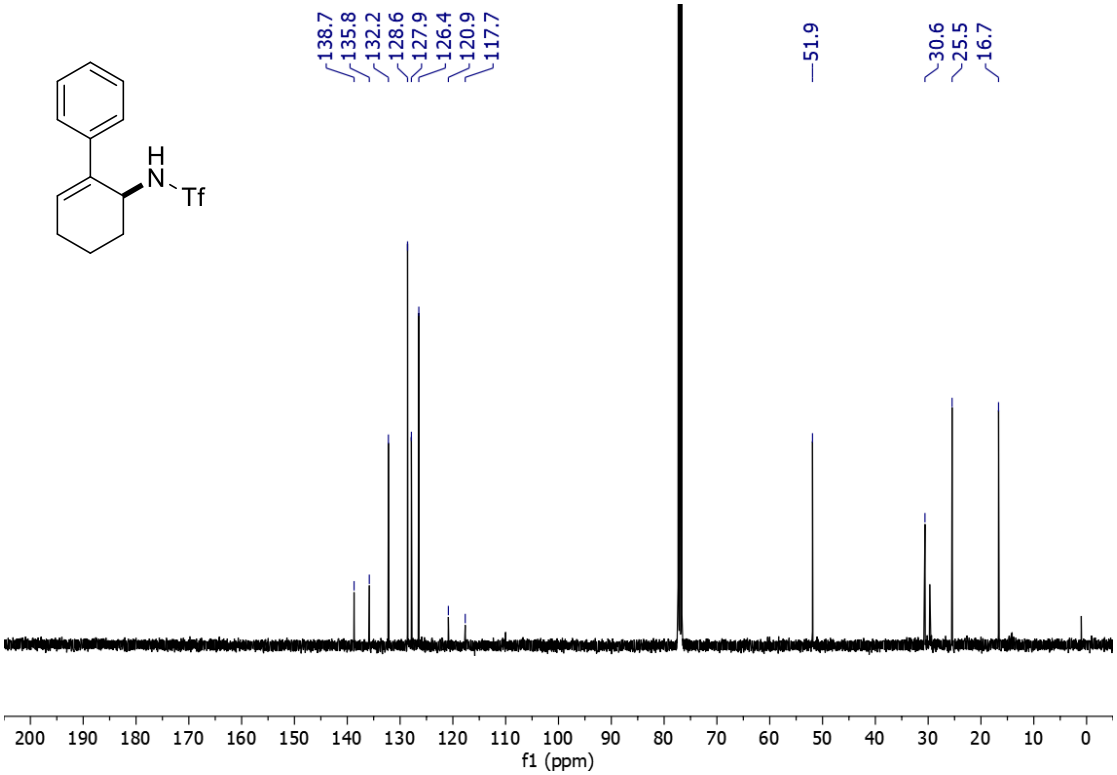


Copy of ^{1}H, ^{13}C and ^{19}F NMR Spectra

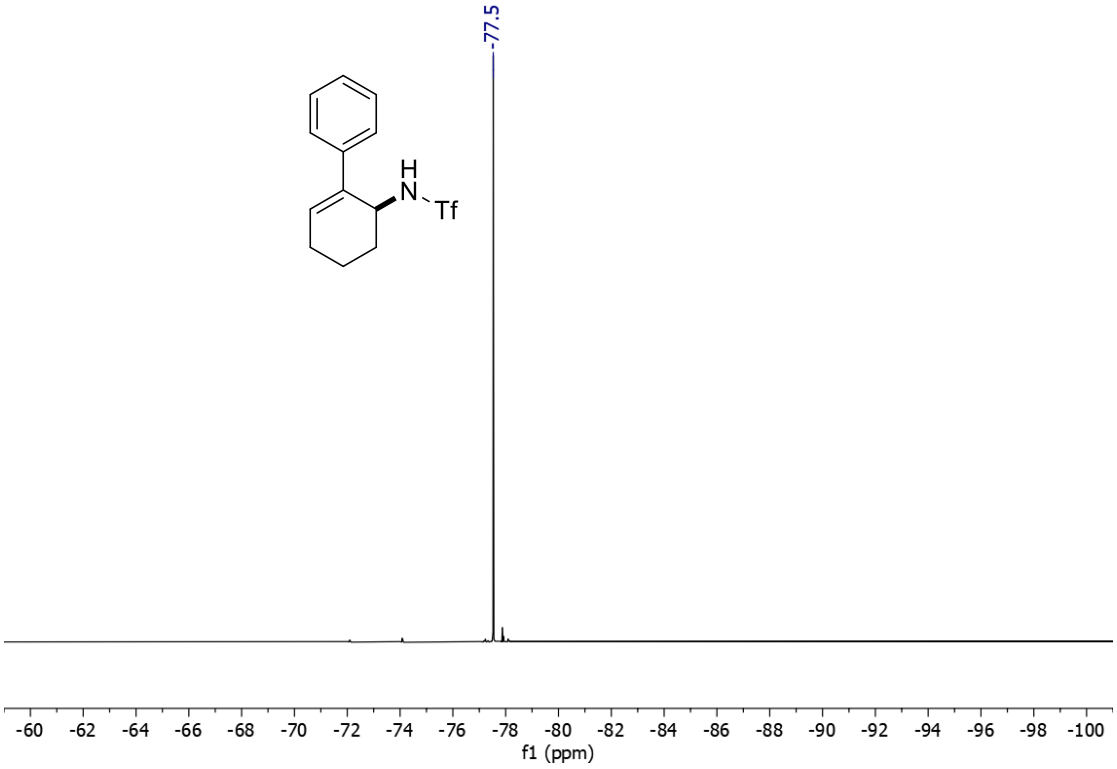
3a ^{1}H NMR (400 MHz, $CDCl_3$)



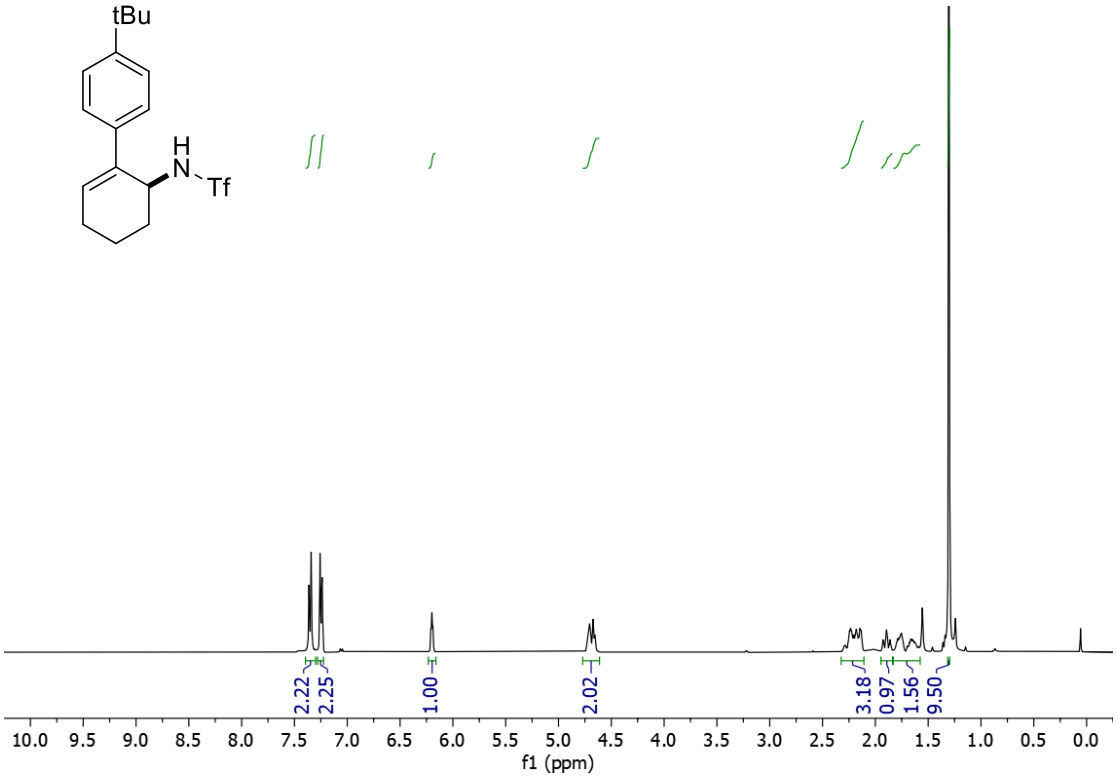
3a ^{13}C NMR (100 MHz, $CDCl_3$)



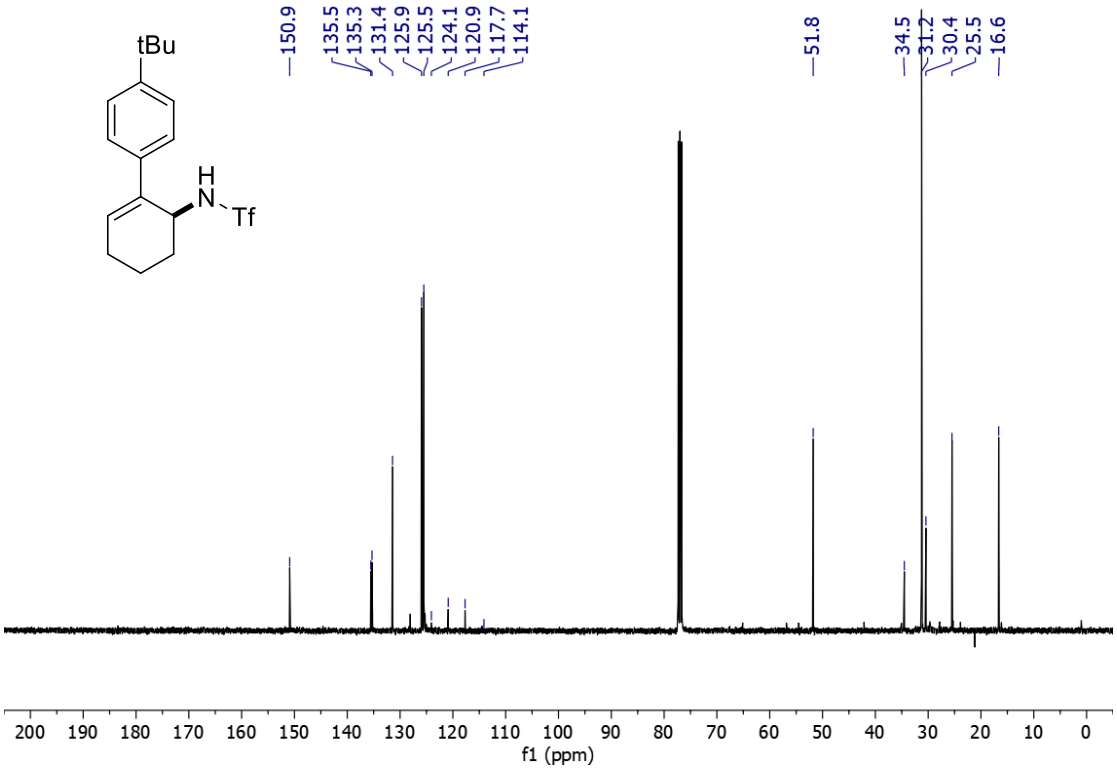
3a ^{19}F NMR (376 MHz, $CDCl_3$)



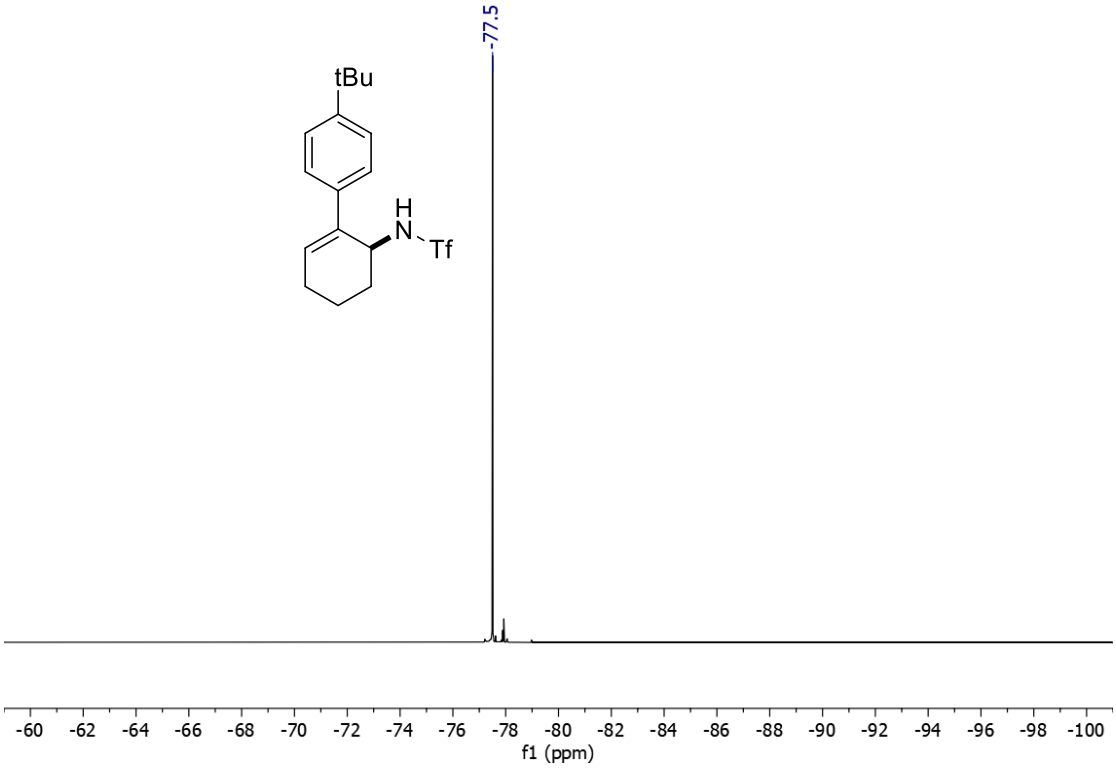
3b ^{1}H NMR (400 MHz, $CDCl_3$)



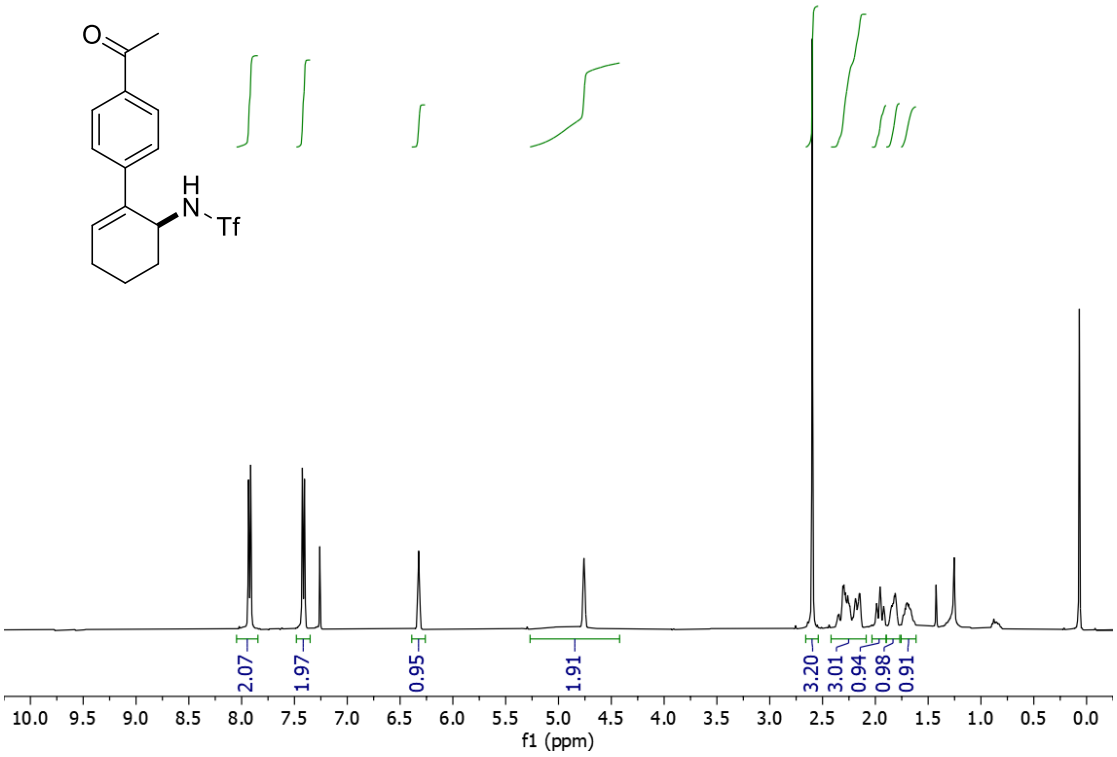
3b ^{13}C NMR (100 MHz, $CDCl_3$)



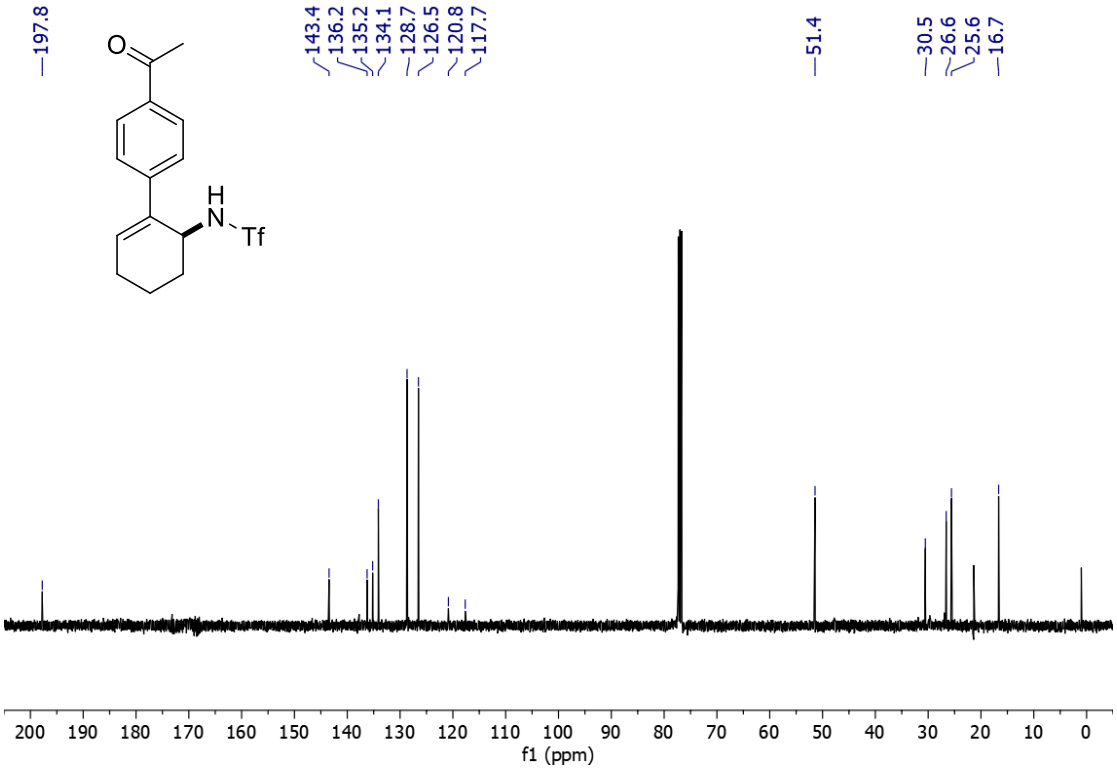
3b ^{19}F NMR (376 MHz, $CDCl_3$)



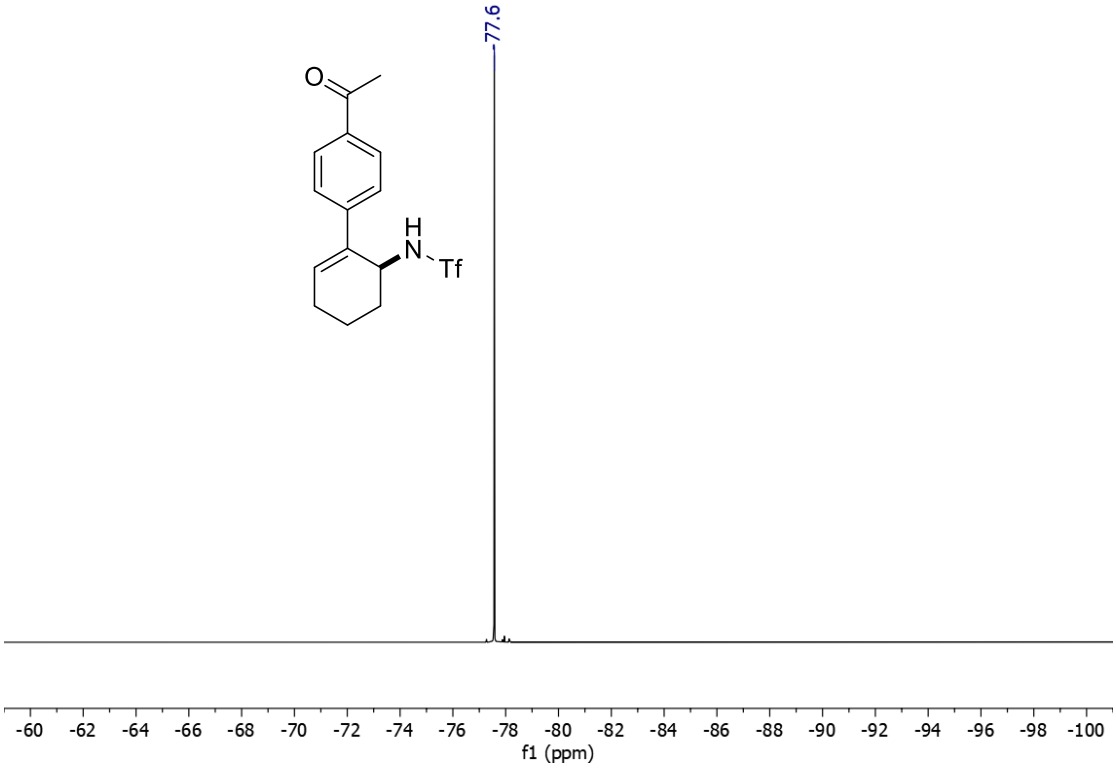
3c ^{1}H NMR (400 MHz, $CDCl_3$)



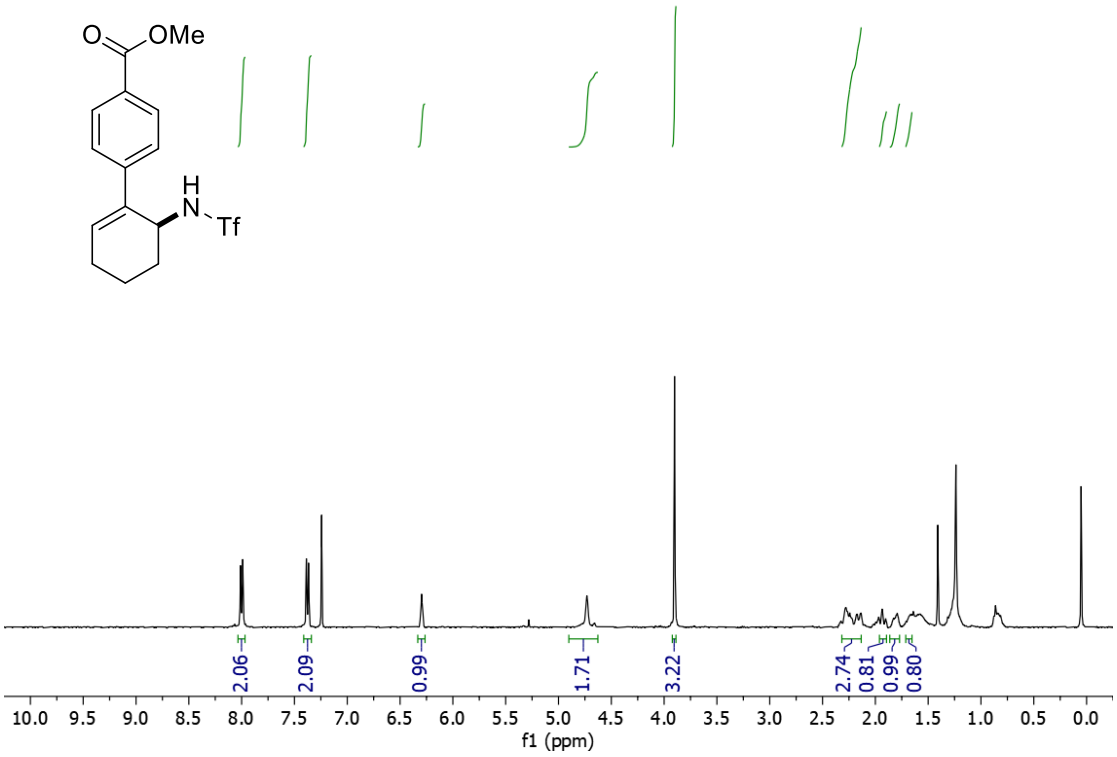
3c ^{13}C NMR (100 MHz, $CDCl_3$)



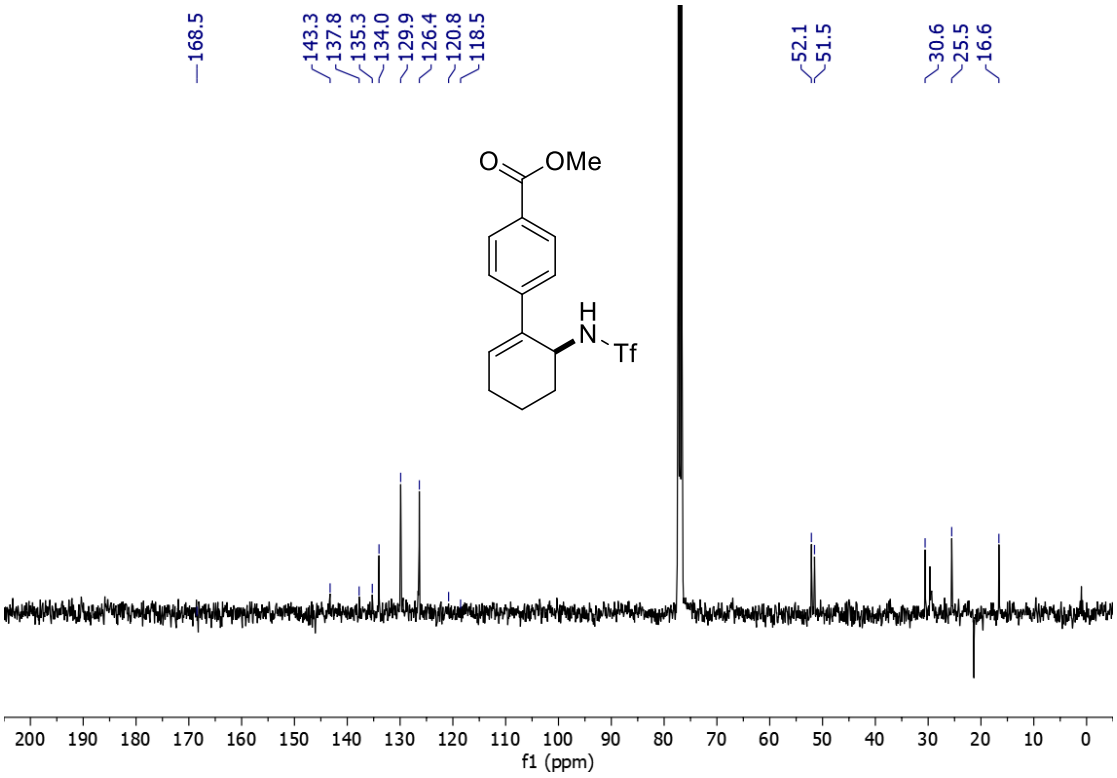
3c ^{19}F NMR (376 MHz, $CDCl_3$)



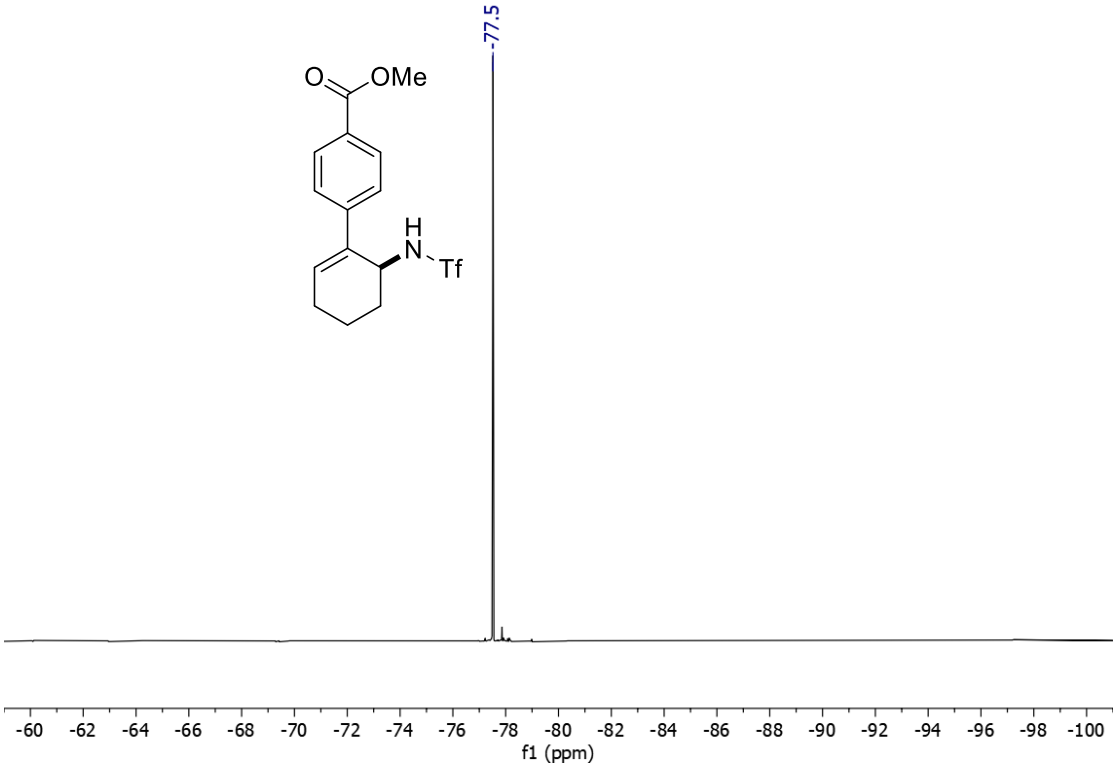
3d ^{1}H NMR (400 MHz, $CDCl_3$)



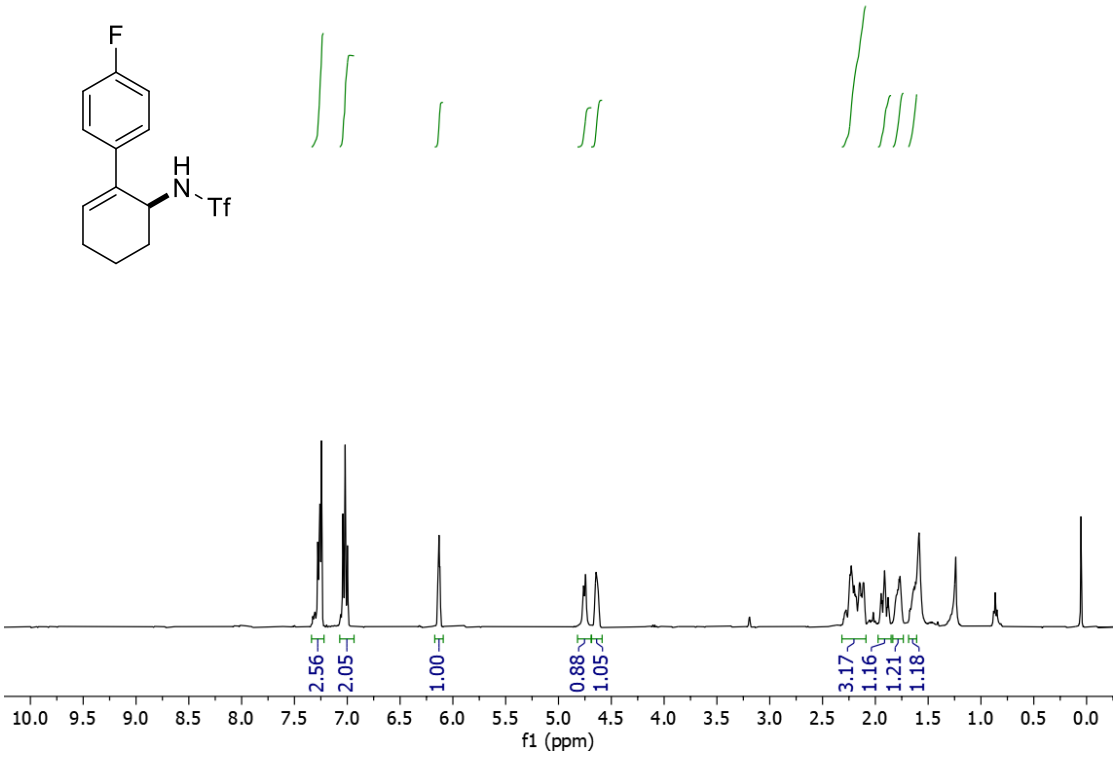
3d ^{13}C NMR (100 MHz, $CDCl_3$)



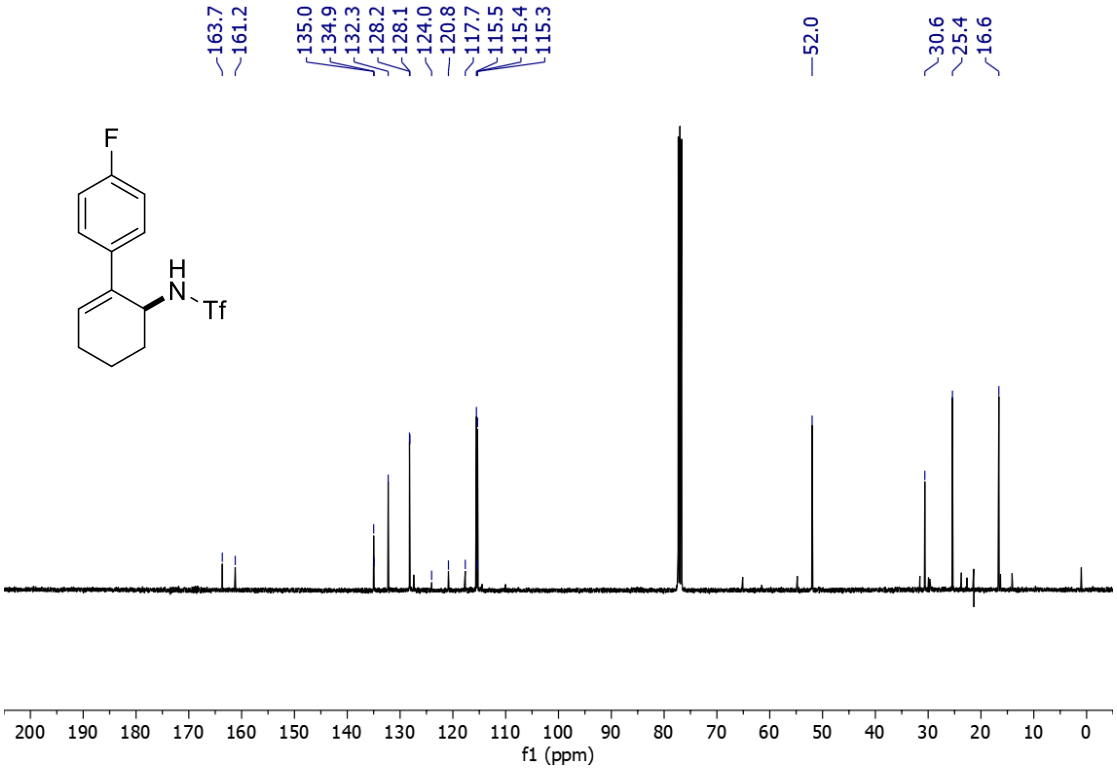
3d ^{19}F NMR (376 MHz, $CDCl_3$)



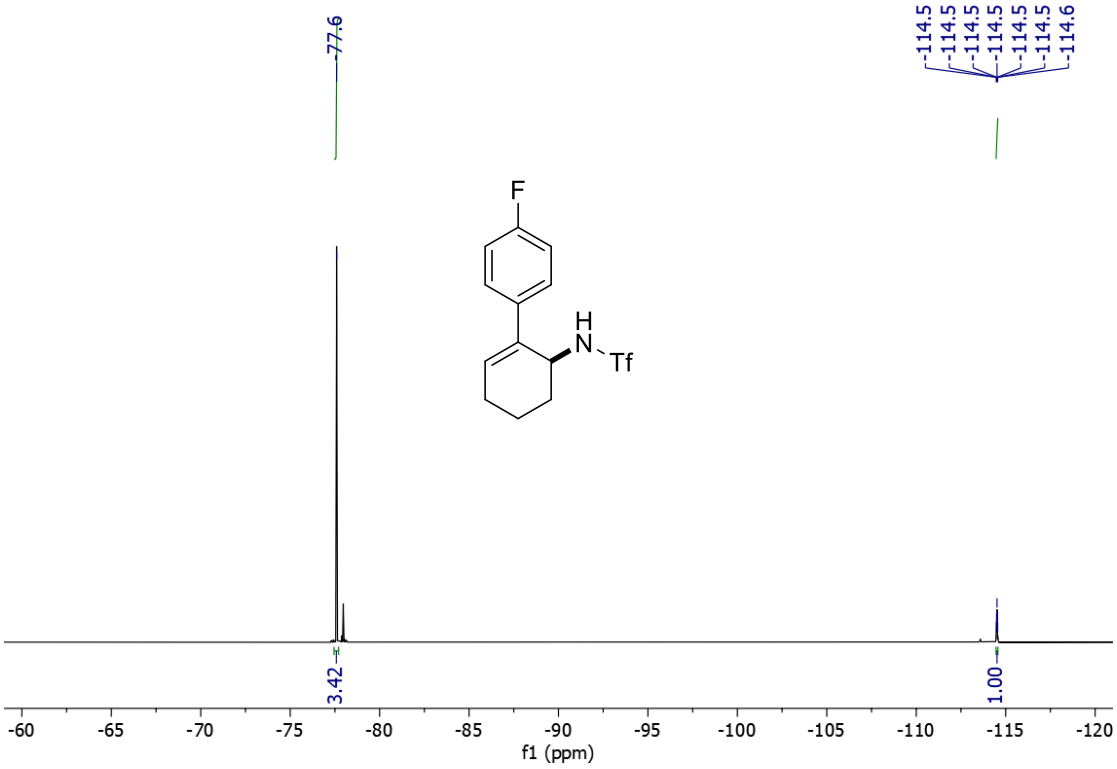
3e ^{1}H NMR (400 MHz, $CDCl_3$)



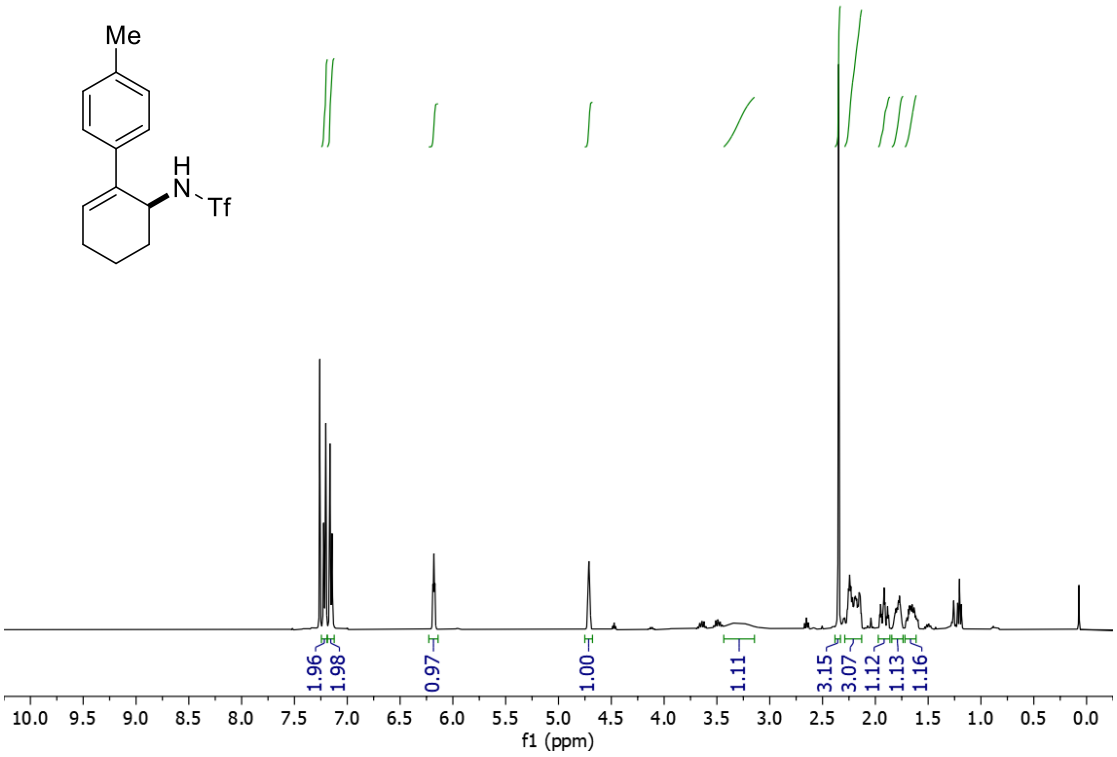
3e ^{13}C NMR (100 MHz, $CDCl_3$)



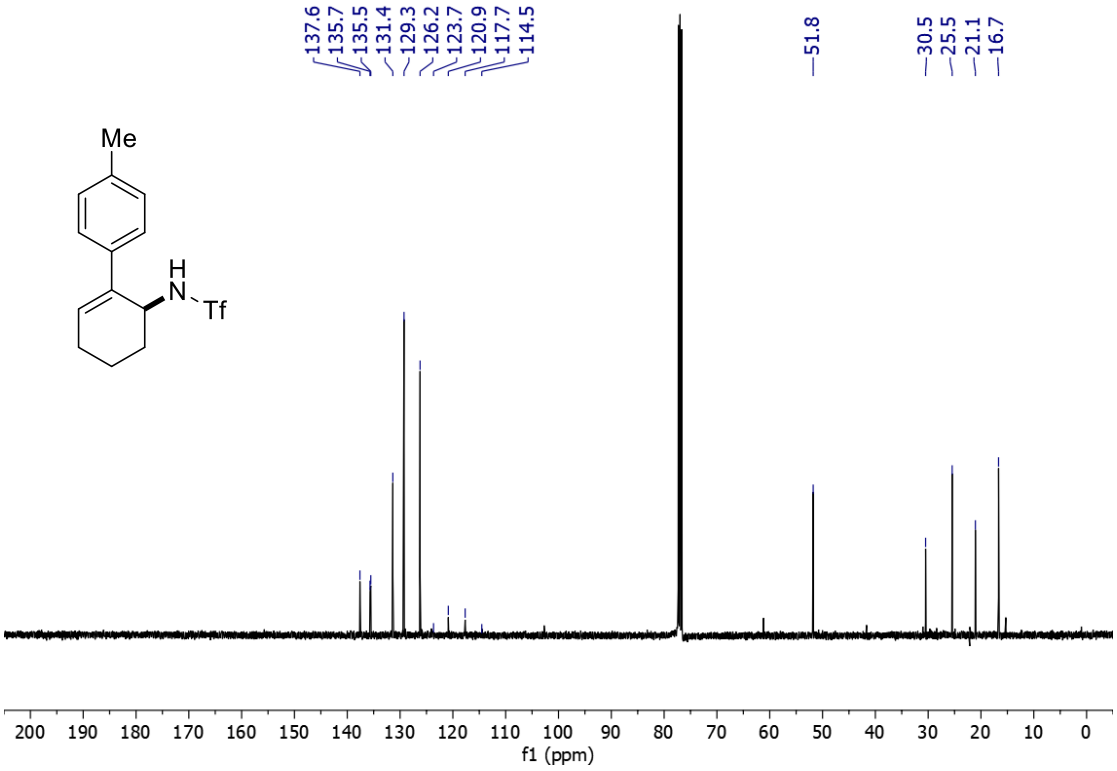
3e ^{19}F NMR (376 MHz, $CDCl_3$)



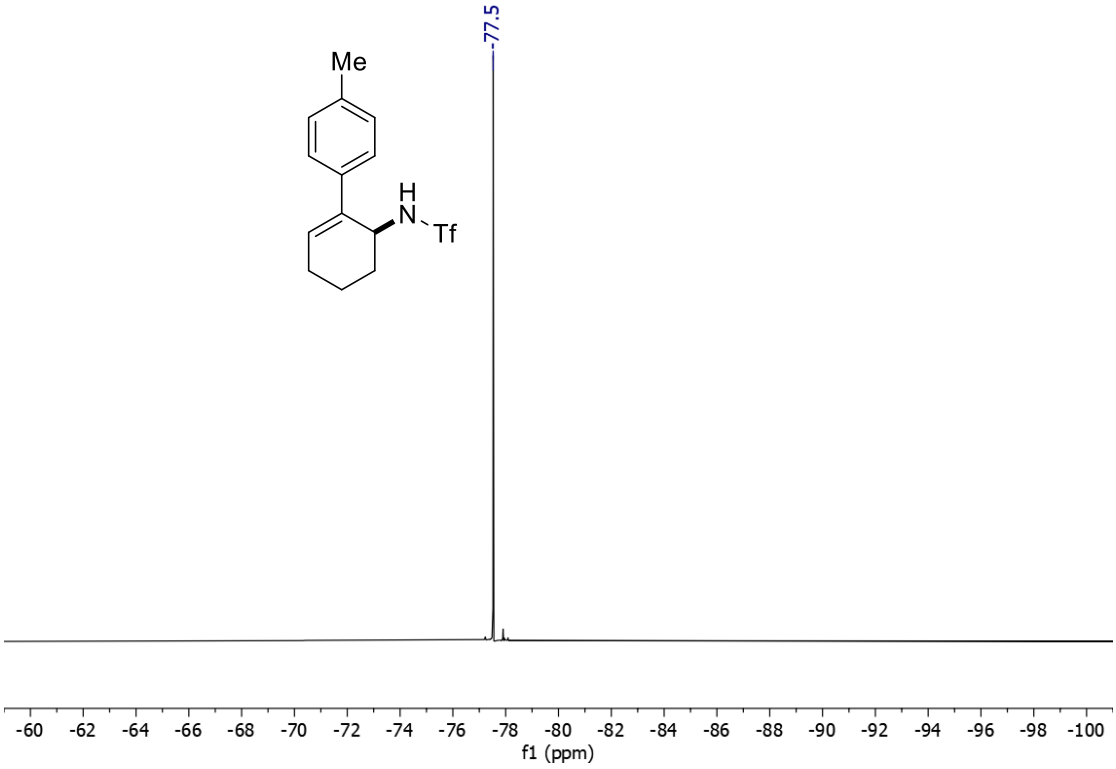
3f ^{1}H NMR (400 MHz, $CDCl_3$)



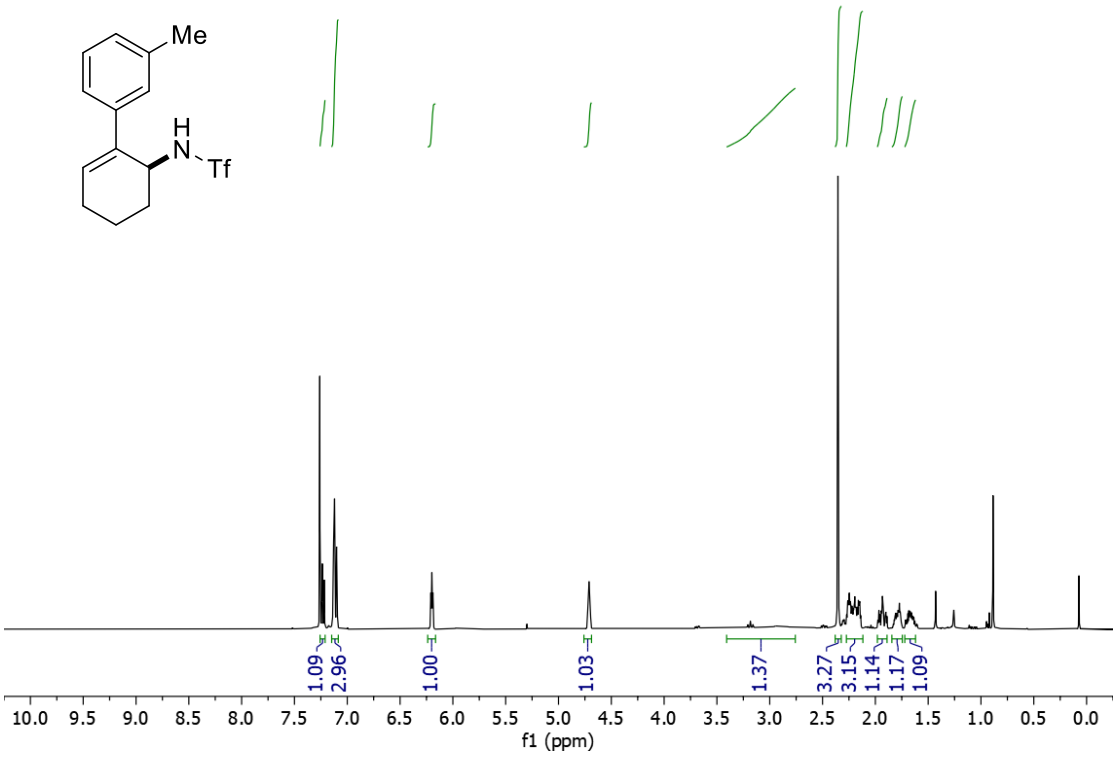
3f ^{13}C NMR (100 MHz, $CDCl_3$)



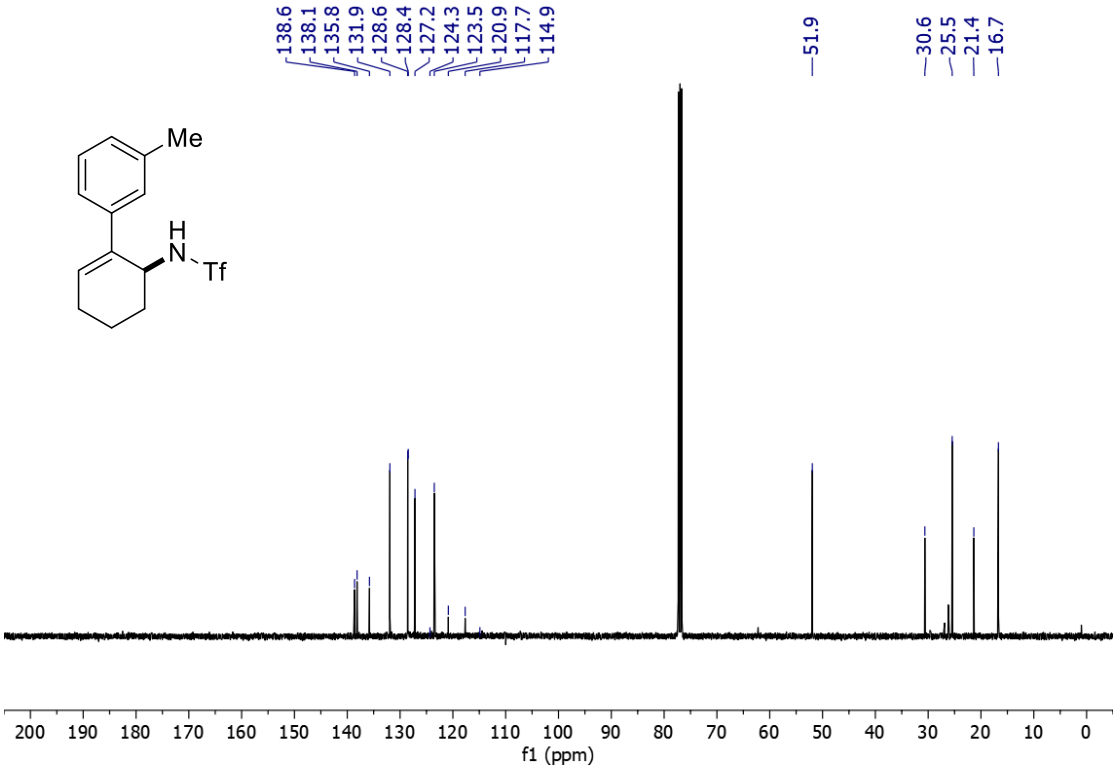
3f ^{19}F NMR (376 MHz, $CDCl_3$)



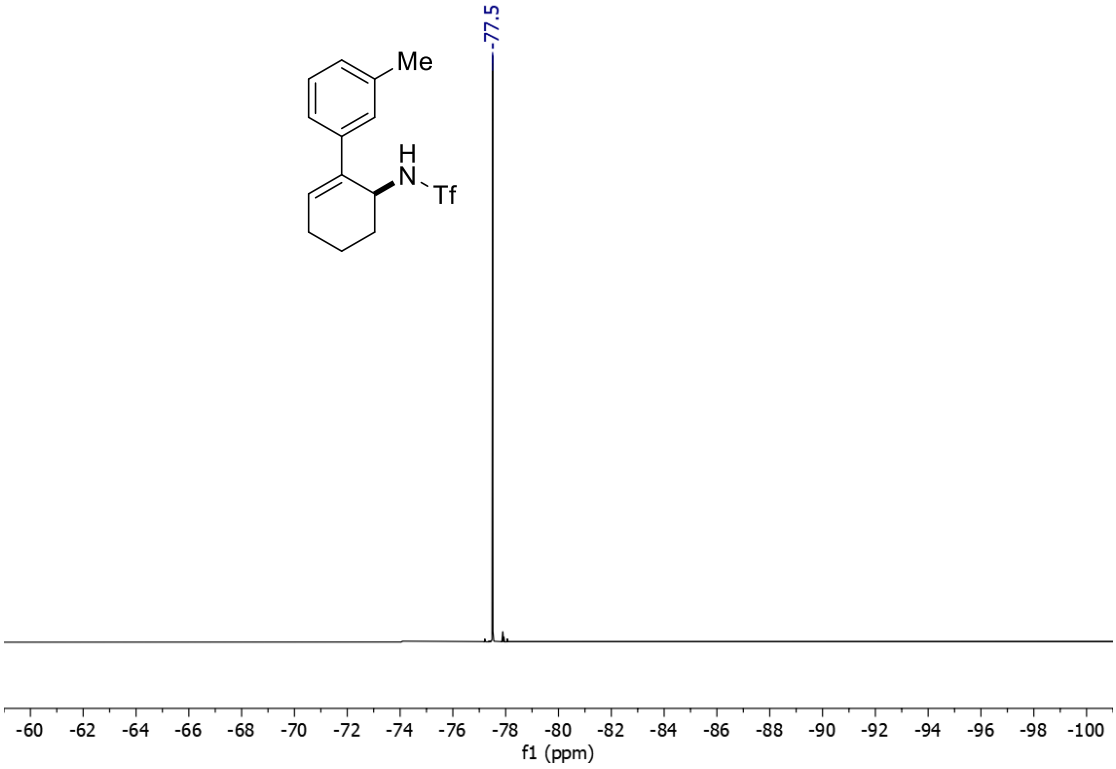
3g ^{1}H NMR (400 MHz, $CDCl_3$)



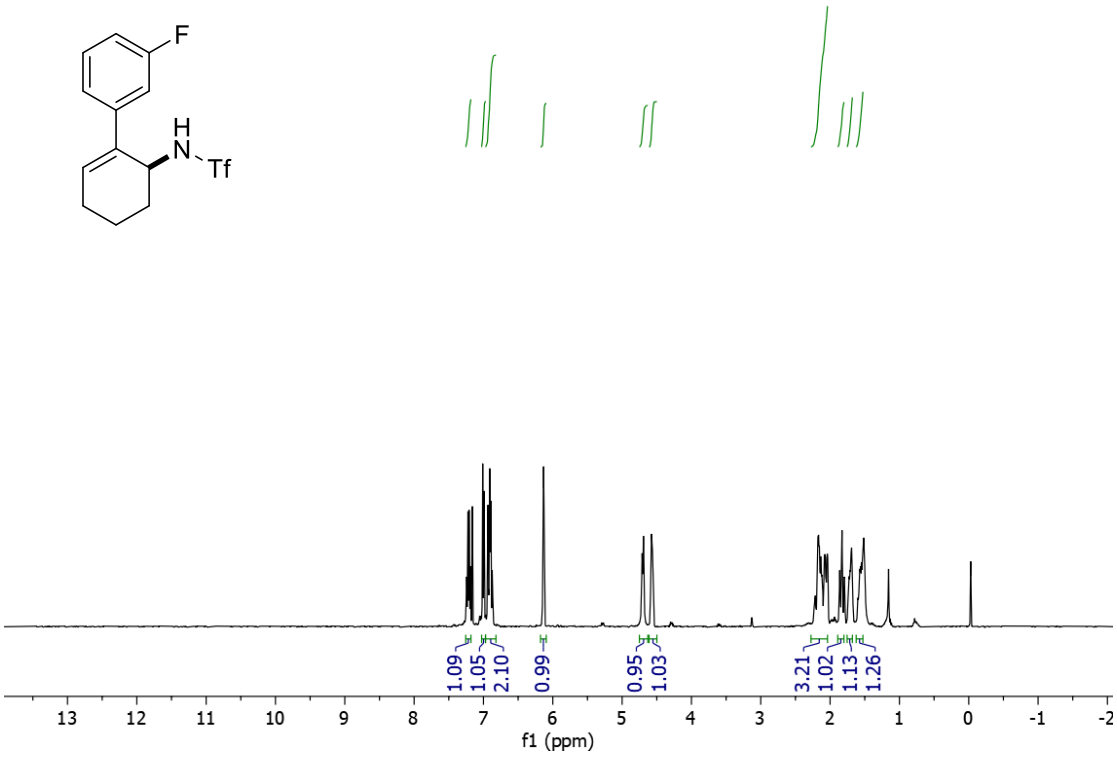
3g ^{13}C NMR (100 MHz, $CDCl_3$)



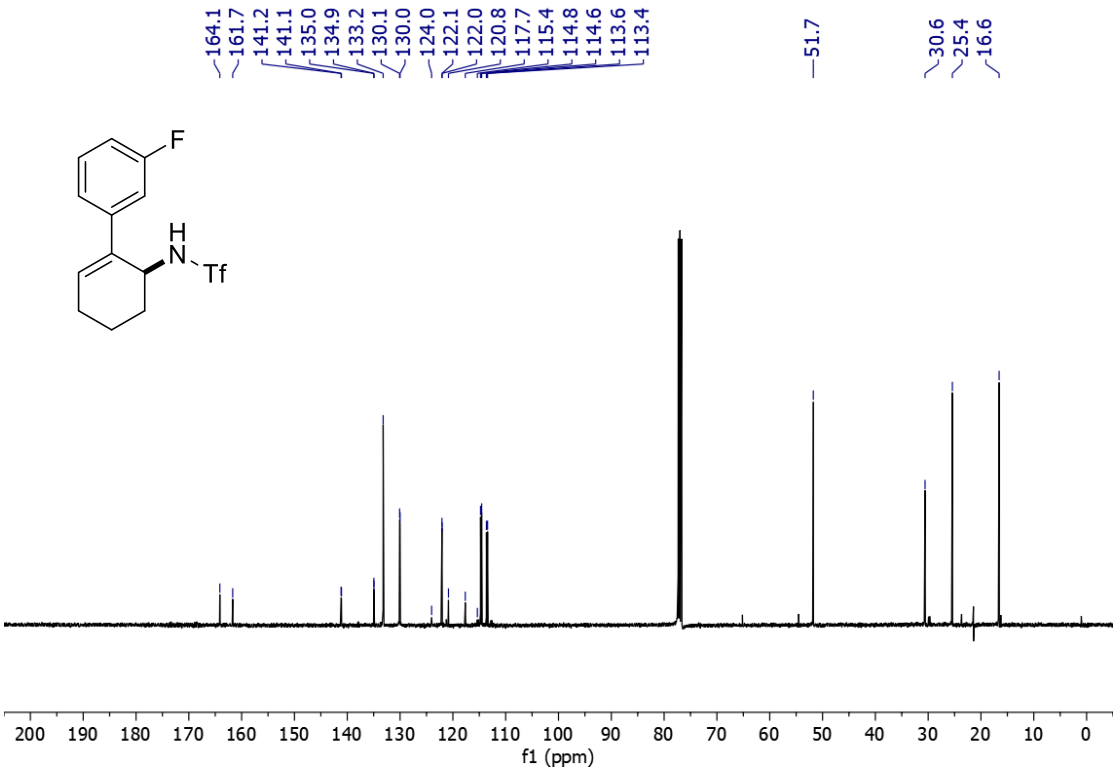
3g ^{19}F NMR (376 MHz, $CDCl_3$)



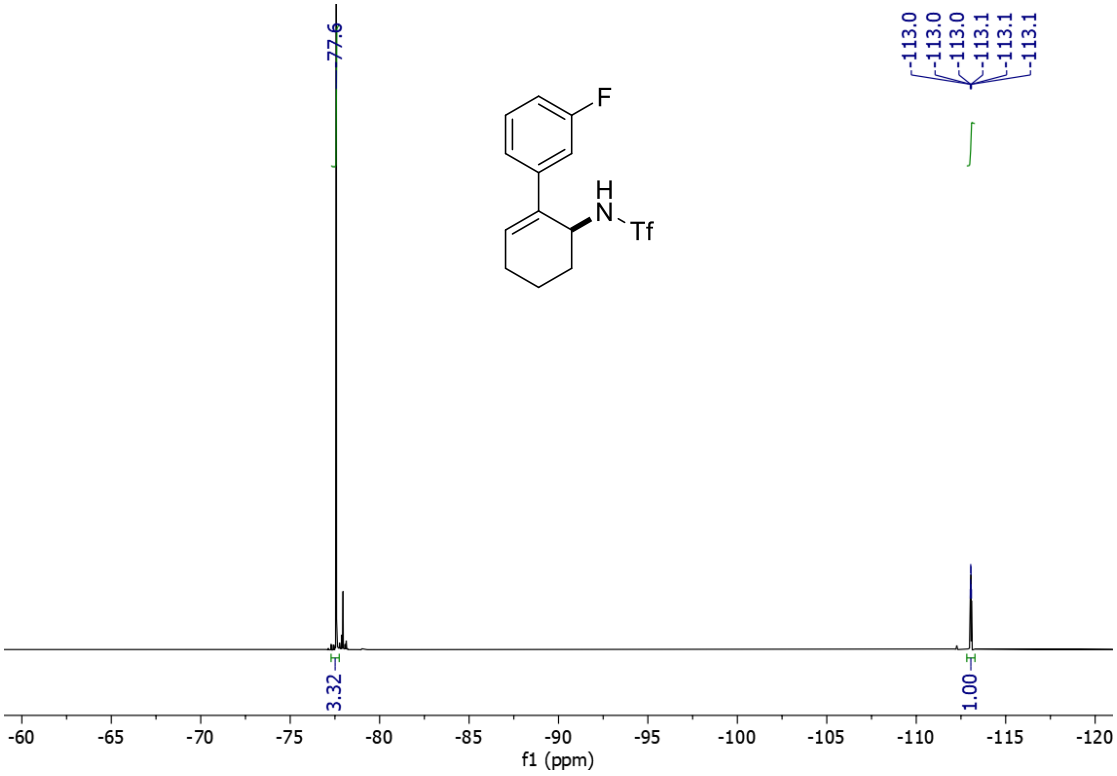
3h ^{1}H NMR (400 MHz, $CDCl_3$)



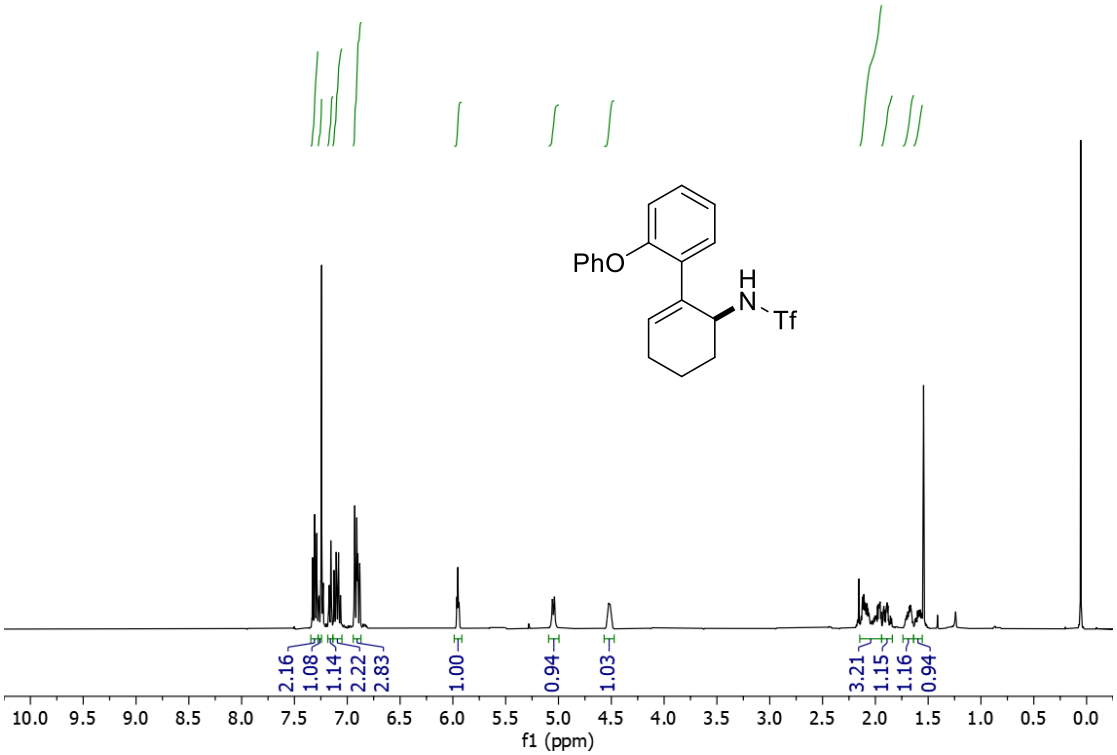
3h ^{13}C NMR (100 MHz, $CDCl_3$)



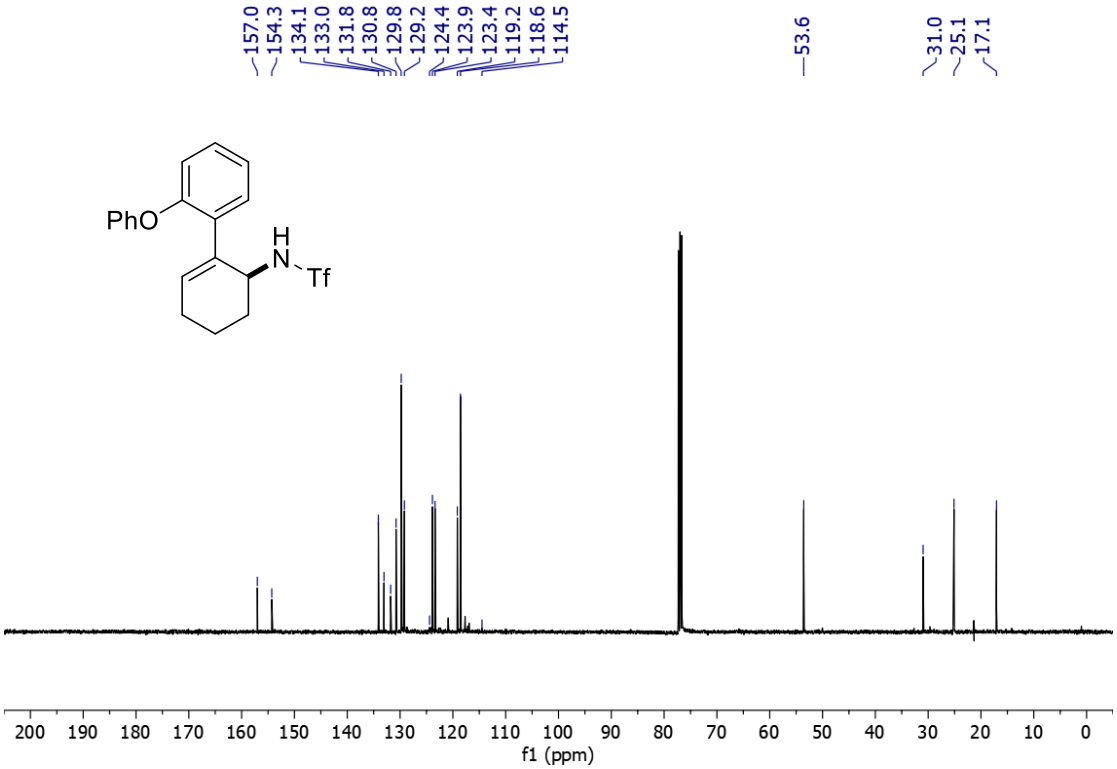
3h ^{19}F NMR (376 MHz, $CDCl_3$)



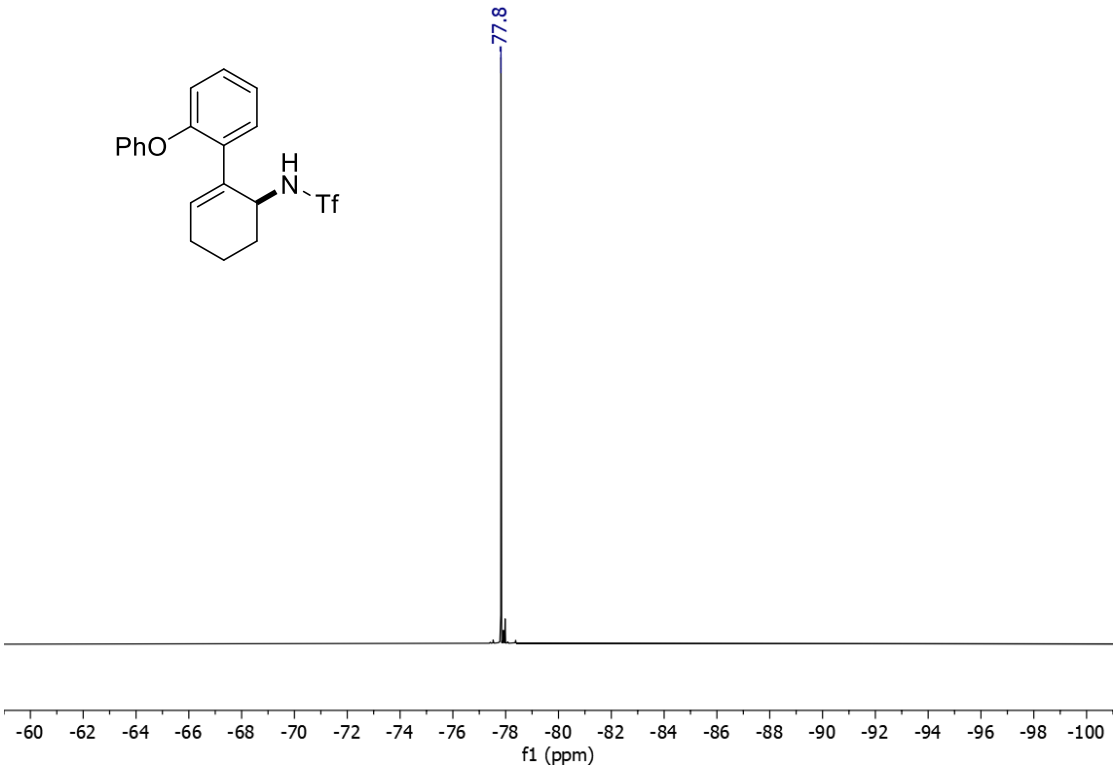
3i ^{1}H NMR (400 MHz, $CDCl_3$)



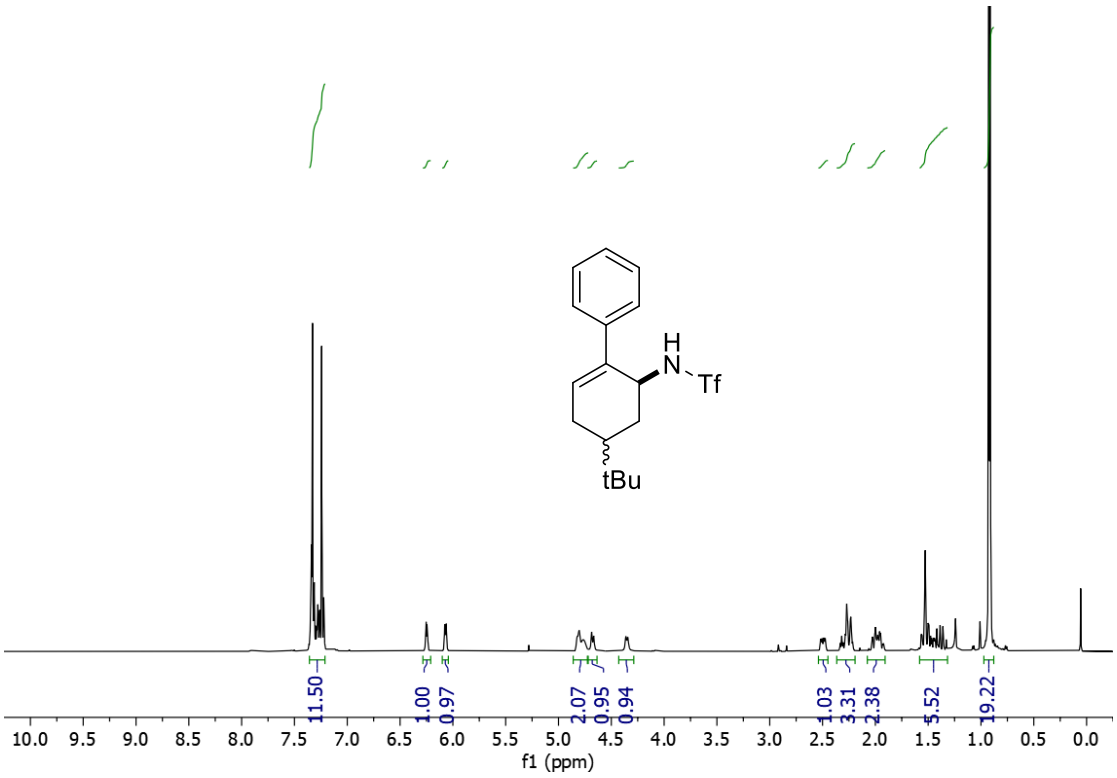
3i ^{13}C NMR (100 MHz, $CDCl_3$)



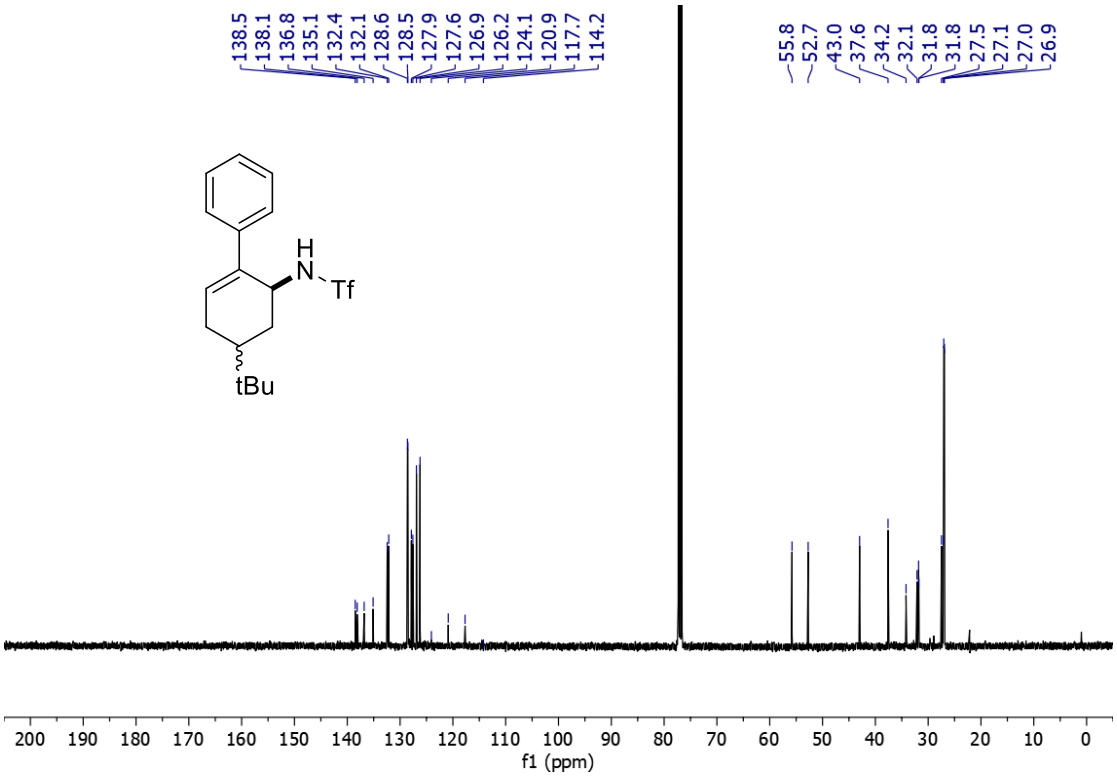
3i ^{19}F NMR (376 MHz, $CDCl_3$)



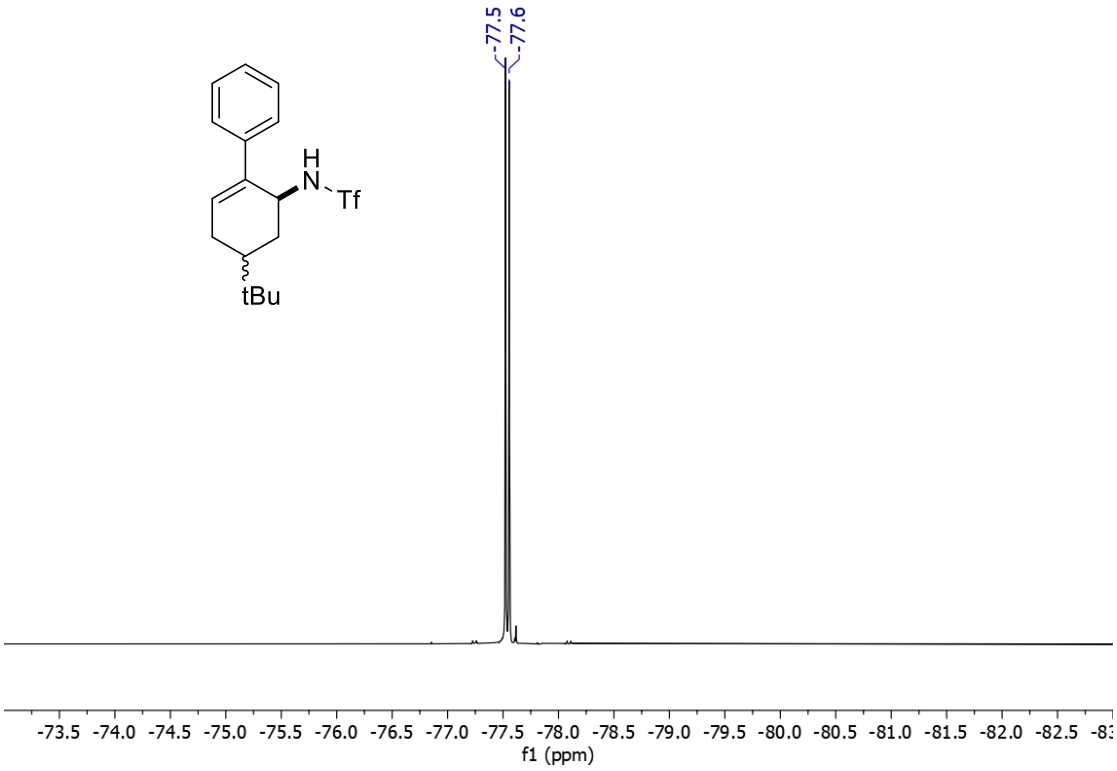
3j ^{1}H NMR (400 MHz, $CDCl_3$)



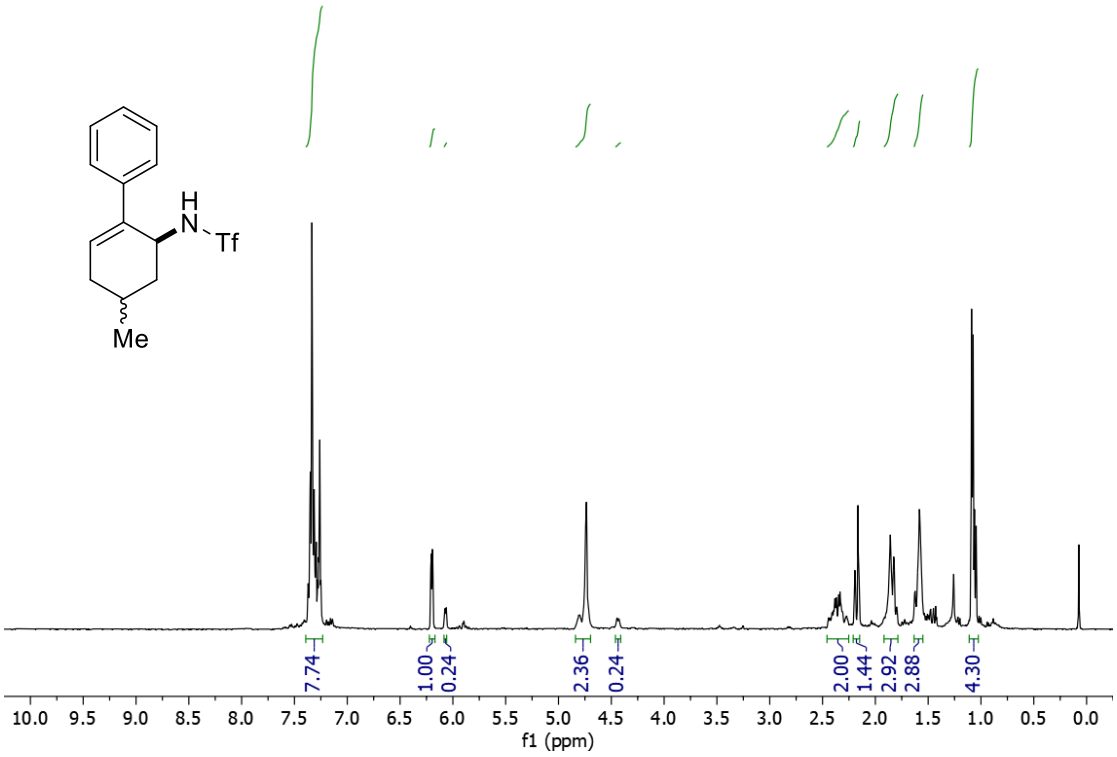
3j ^{13}C NMR (100 MHz, $CDCl_3$)



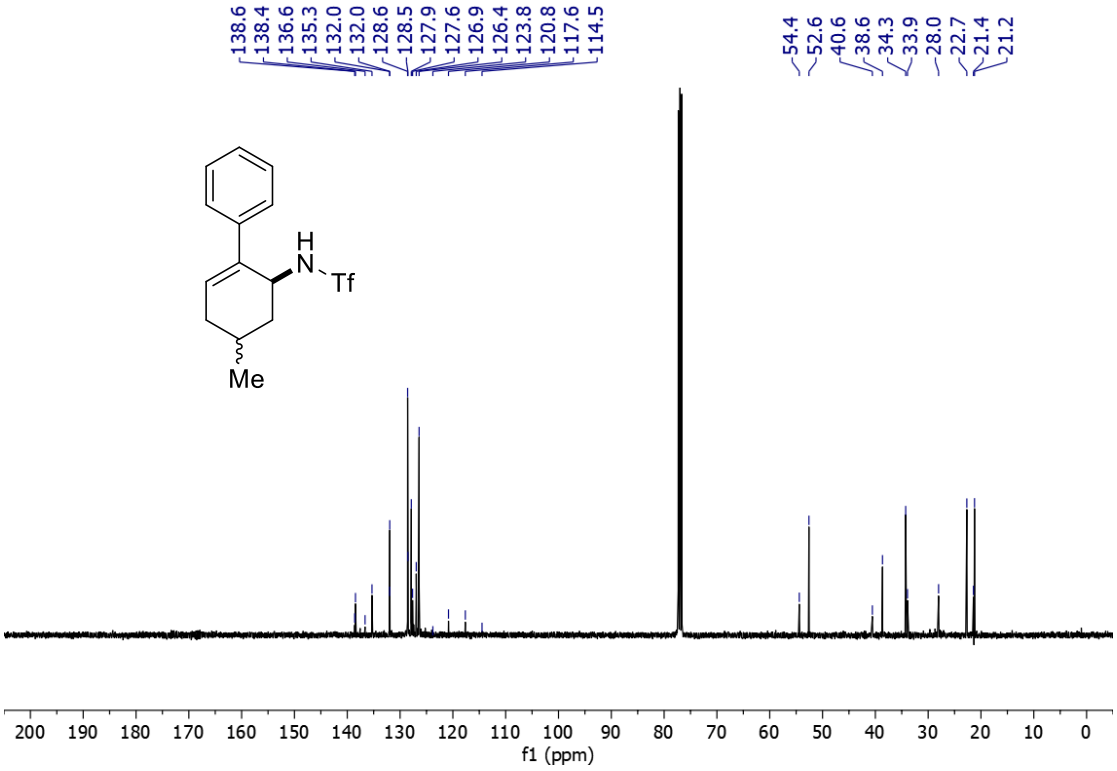
3j ^{19}F NMR (376 MHz, $CDCl_3$)



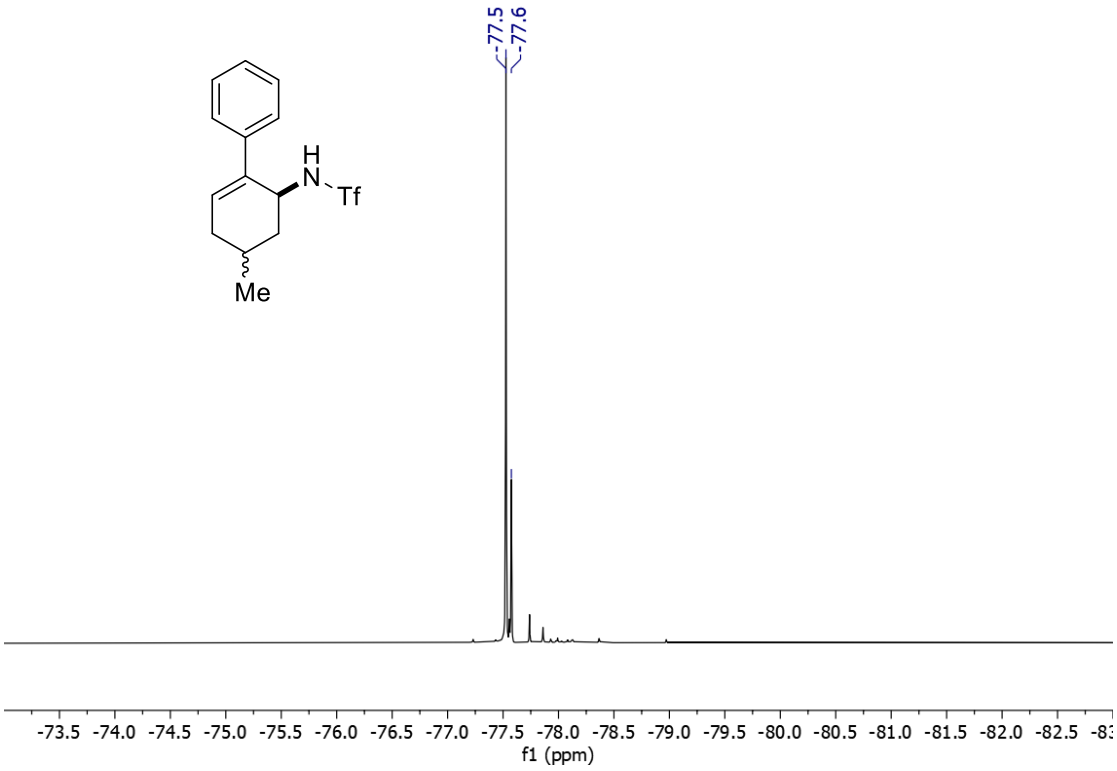
3k ^{1}H NMR (400 MHz, $CDCl_3$)



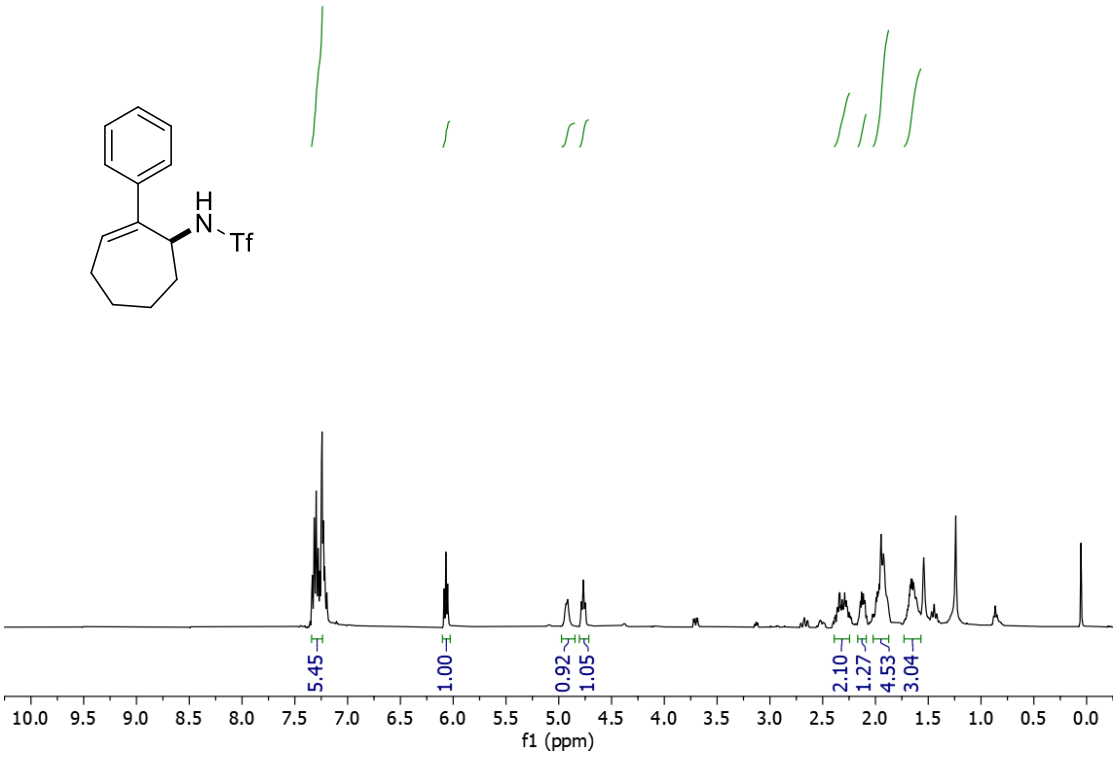
3k ^{13}C NMR (100 MHz, $CDCl_3$)



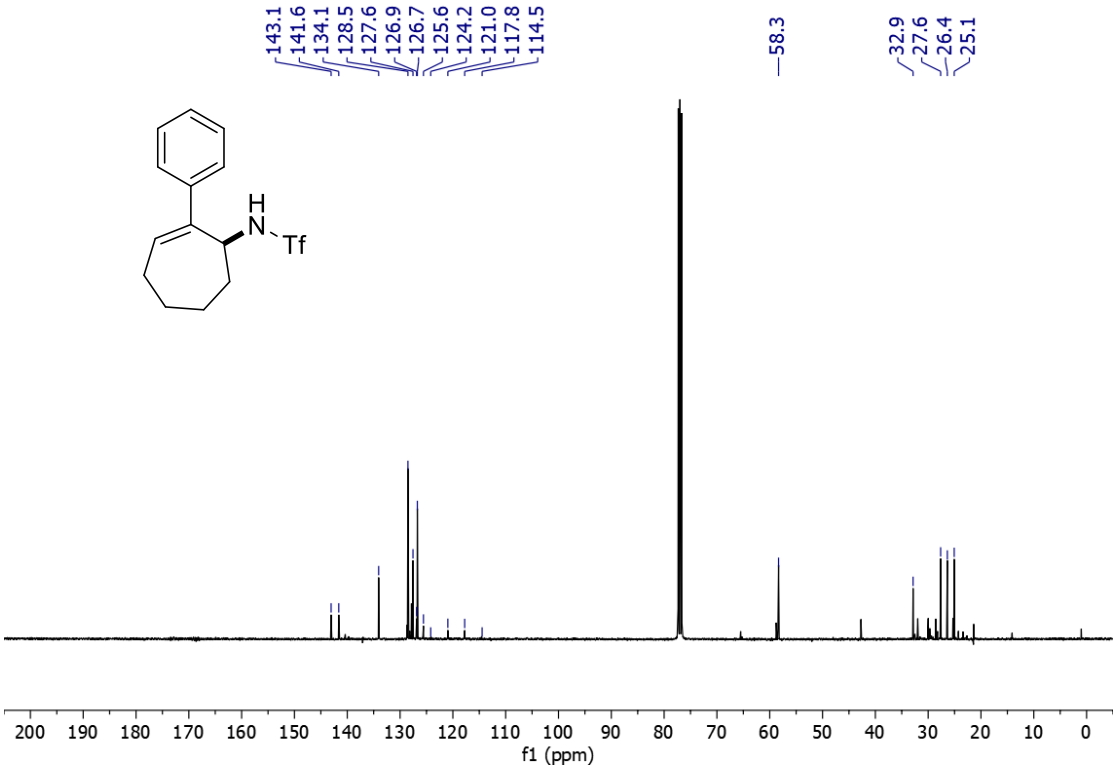
3k ^{19}F NMR (376 MHz, $CDCl_3$)



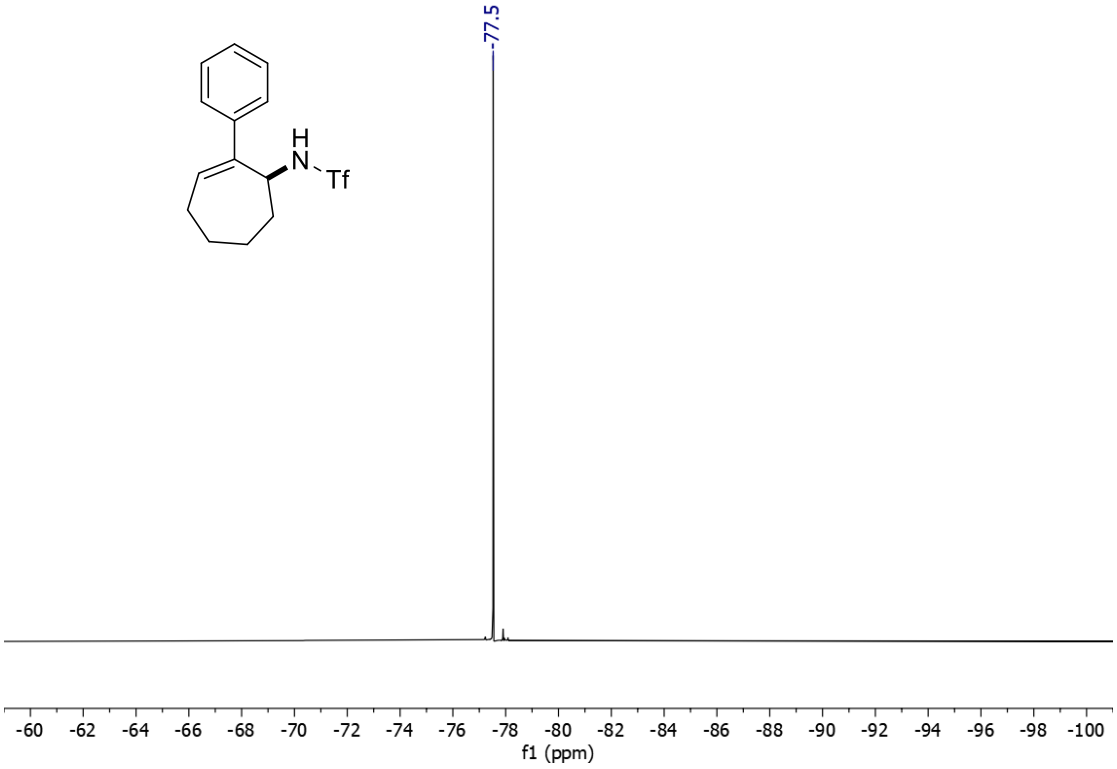
3l ^{1}H NMR (400 MHz, $CDCl_3$)



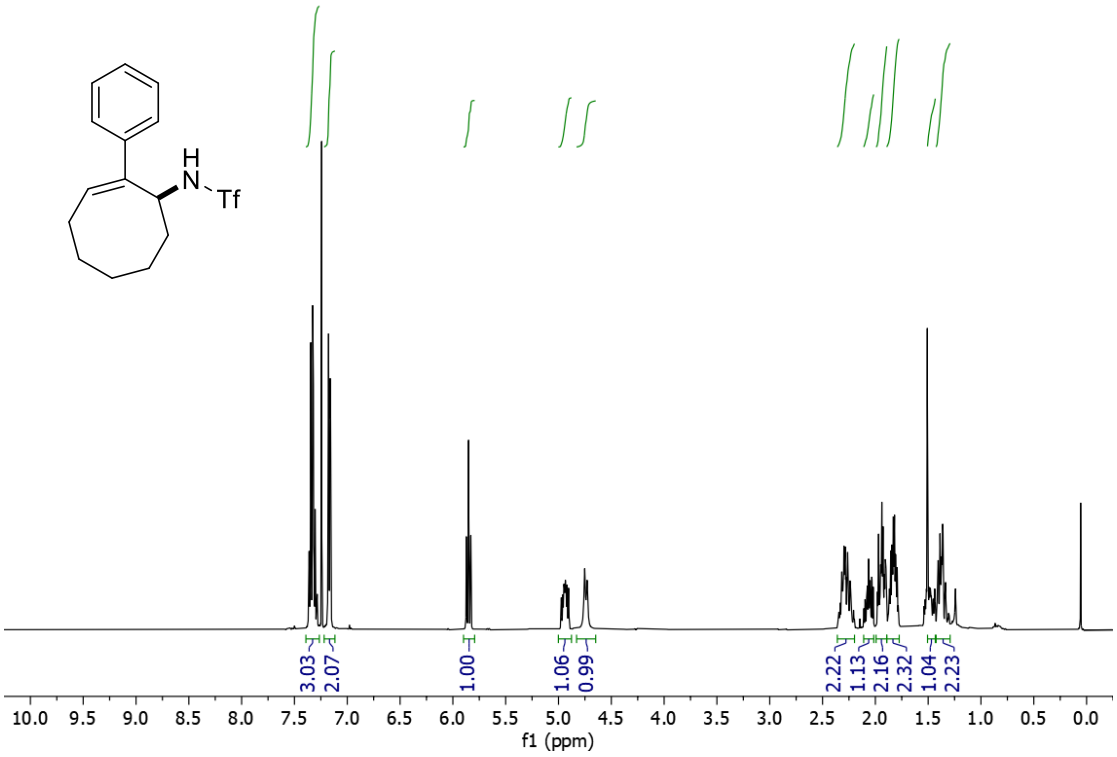
3l ^{13}C NMR (100 MHz, $CDCl_3$)



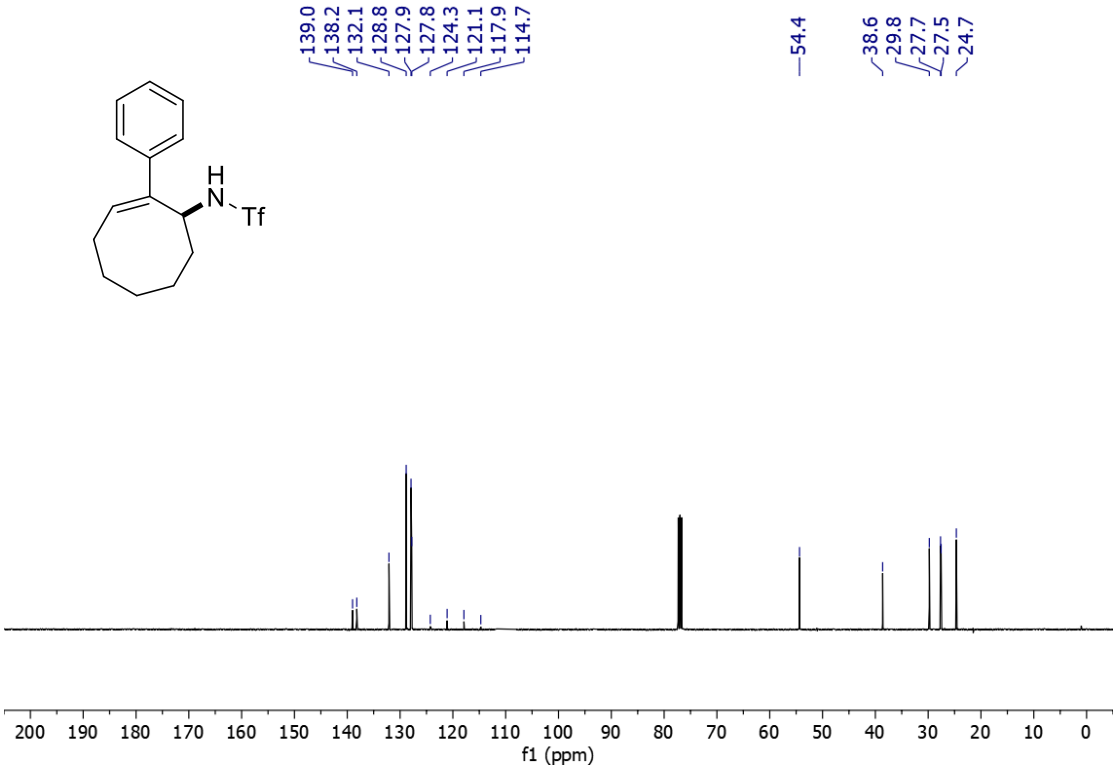
3l ^{19}F NMR (376 MHz, $CDCl_3$)



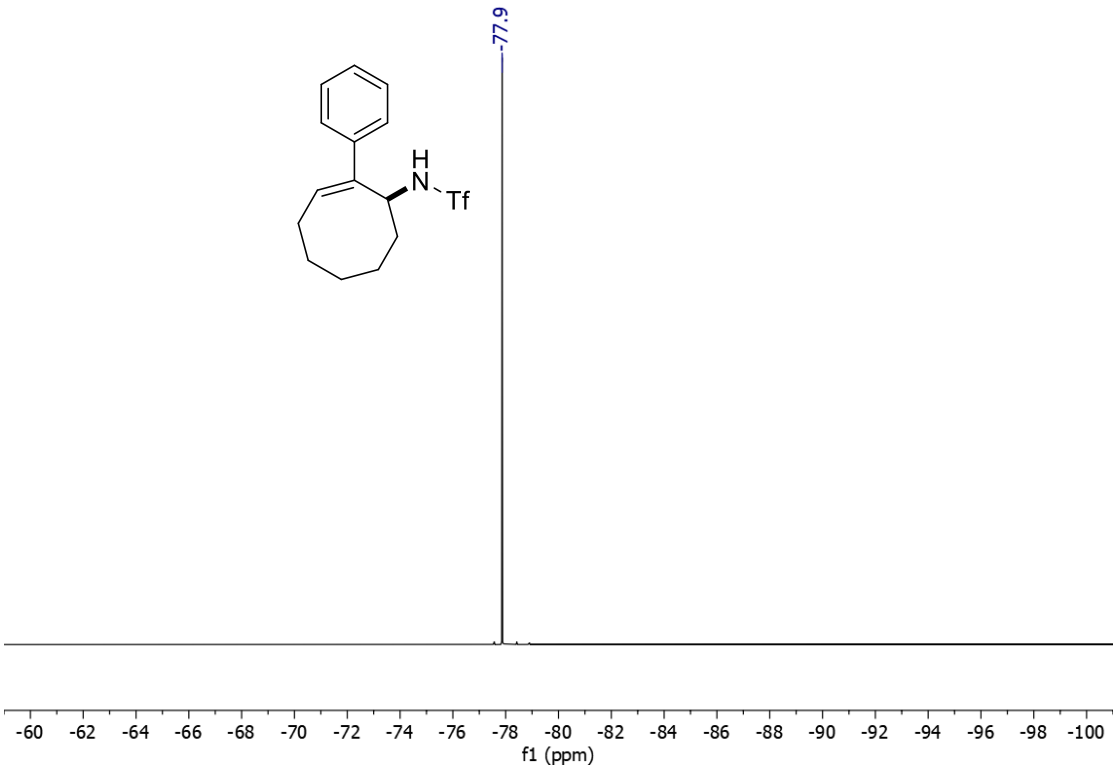
3m ^{1}H NMR (400 MHz, $CDCl_3$)



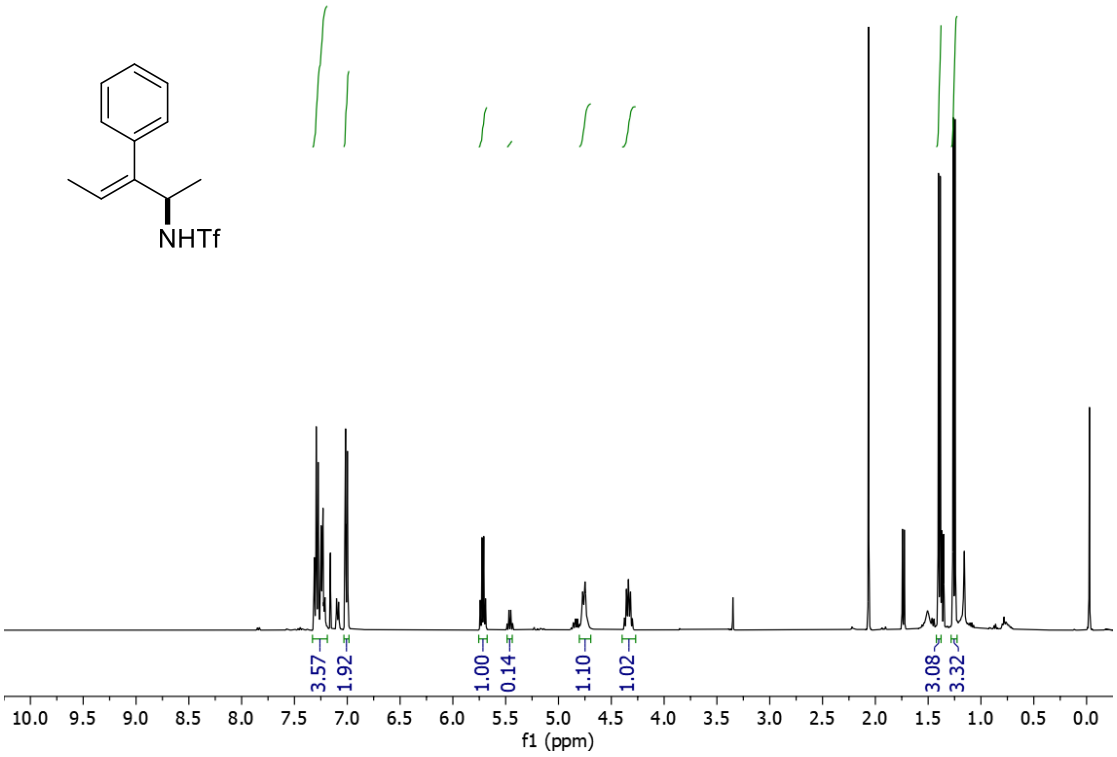
3m ^{13}C NMR (100 MHz, $CDCl_3$)



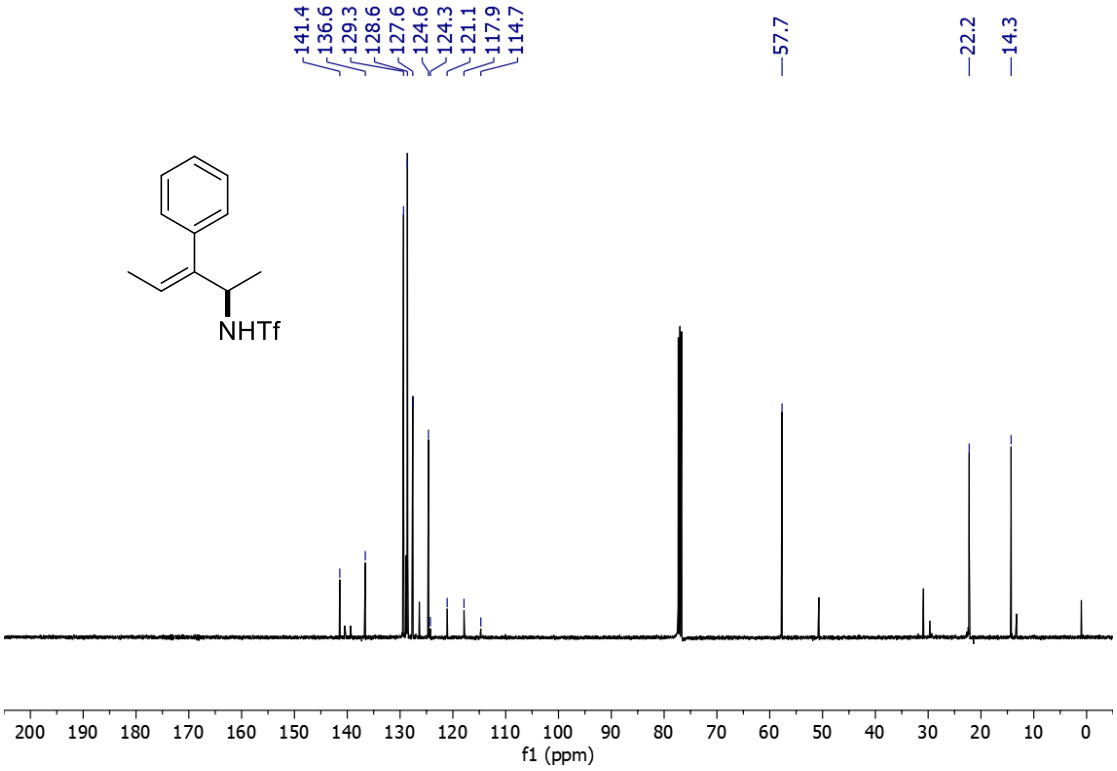
3m ^{19}F NMR (376 MHz, $CDCl_3$)



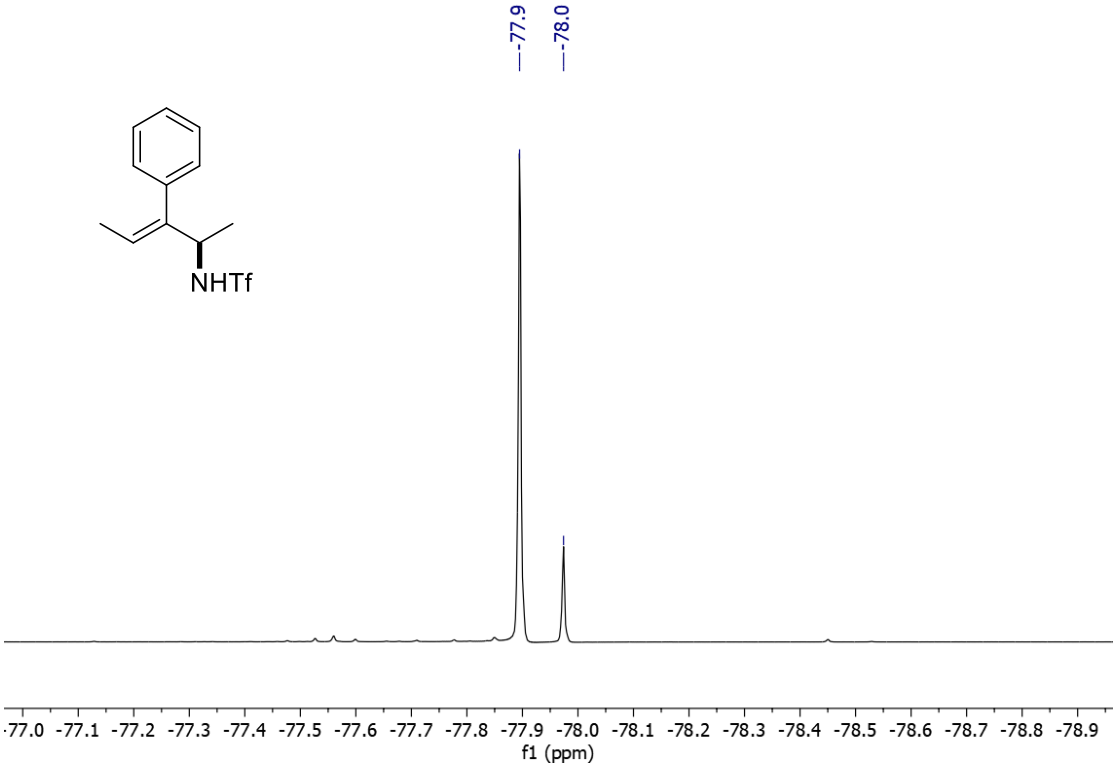
3n ^{1}H NMR (400 MHz, $CDCl_3$)



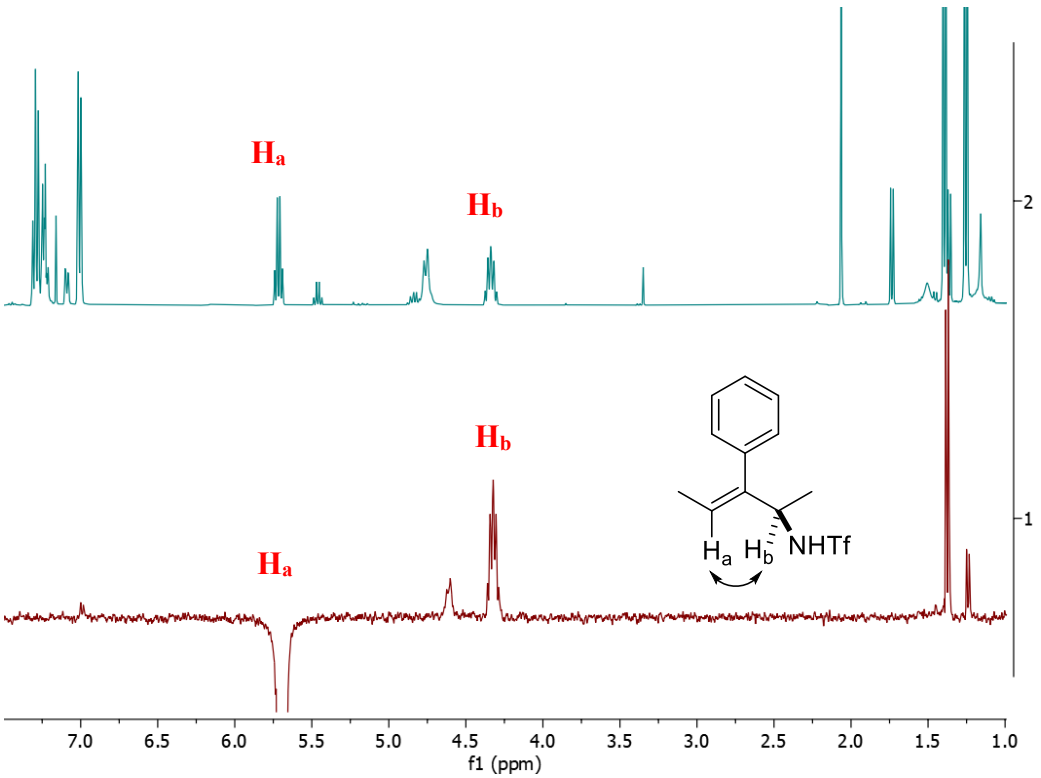
3n ^{13}C NMR (100 MHz, $CDCl_3$)



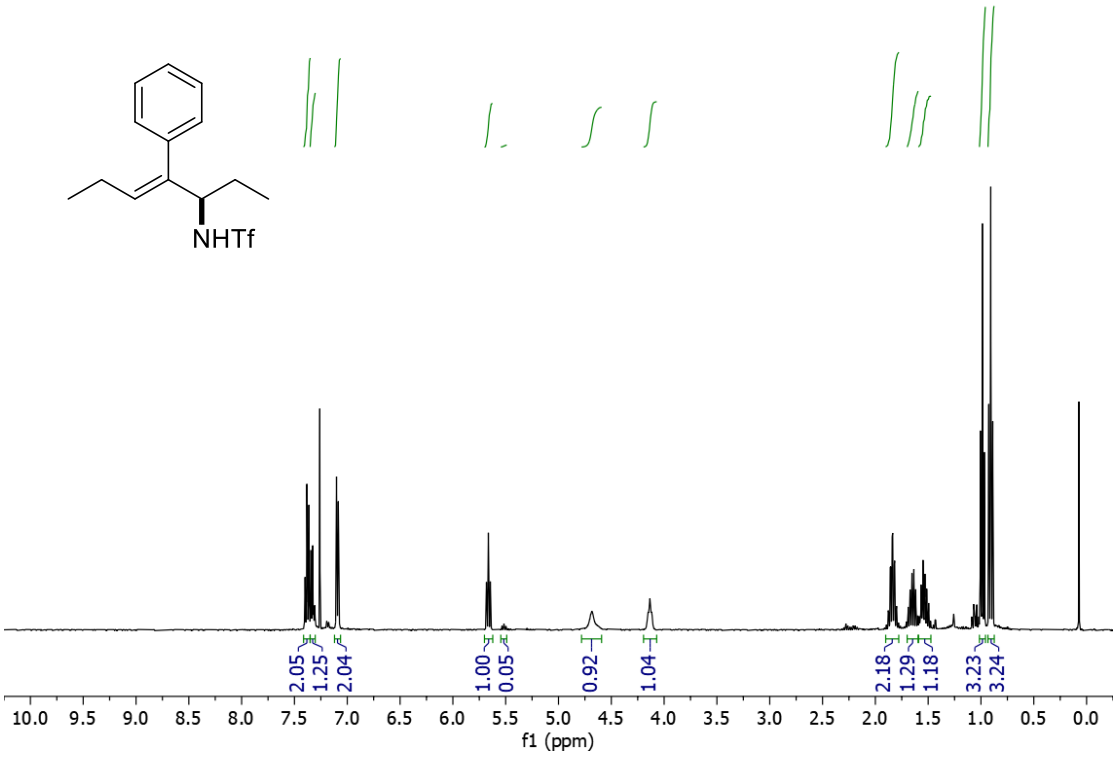
3n ^{19}F NMR (376 MHz, $CDCl_3$)



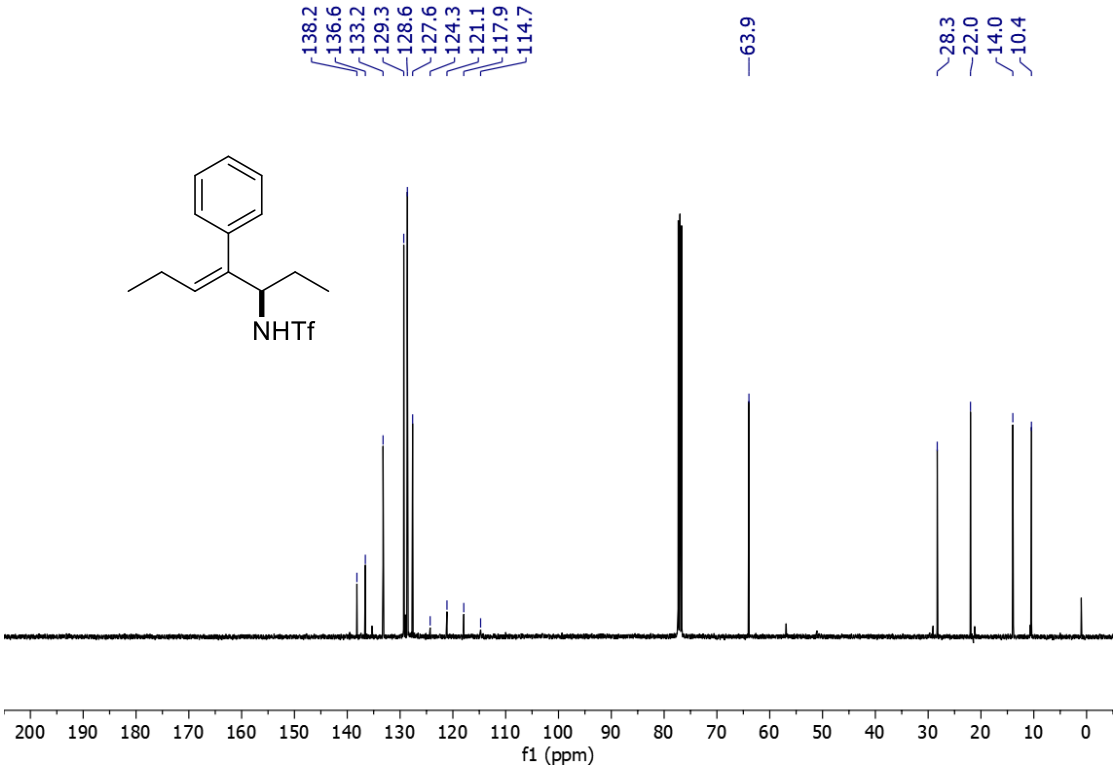
Stacked ^1H NMR (400 MHz, $CDCl_3$) of: 3n (green), 1D NOESY NMR of 3n (red)



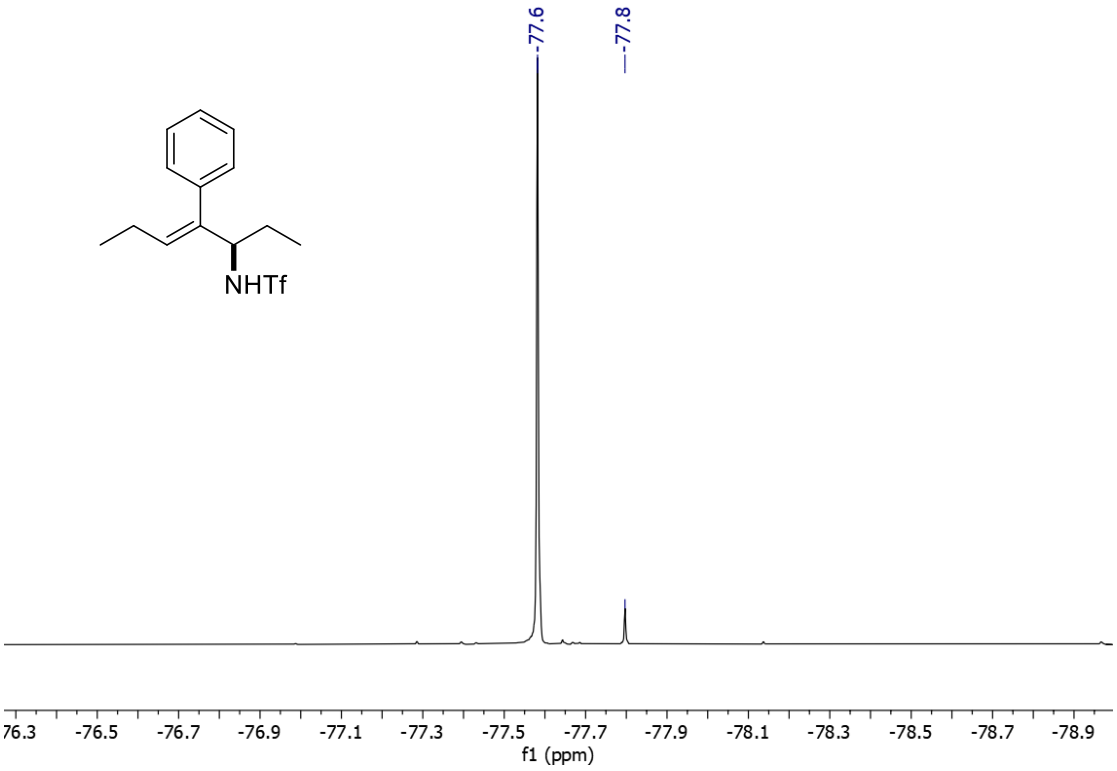
3o ^{1}H NMR (400 MHz, $CDCl_3$)



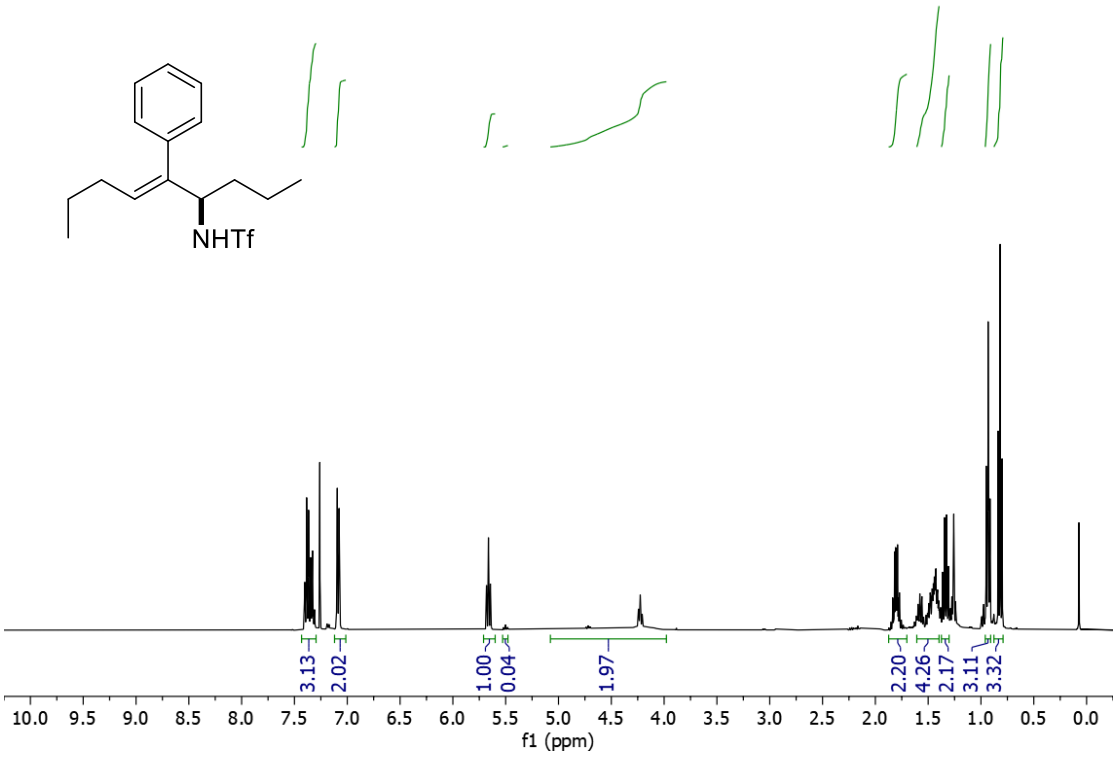
3o ^{13}C NMR (100 MHz, $CDCl_3$)



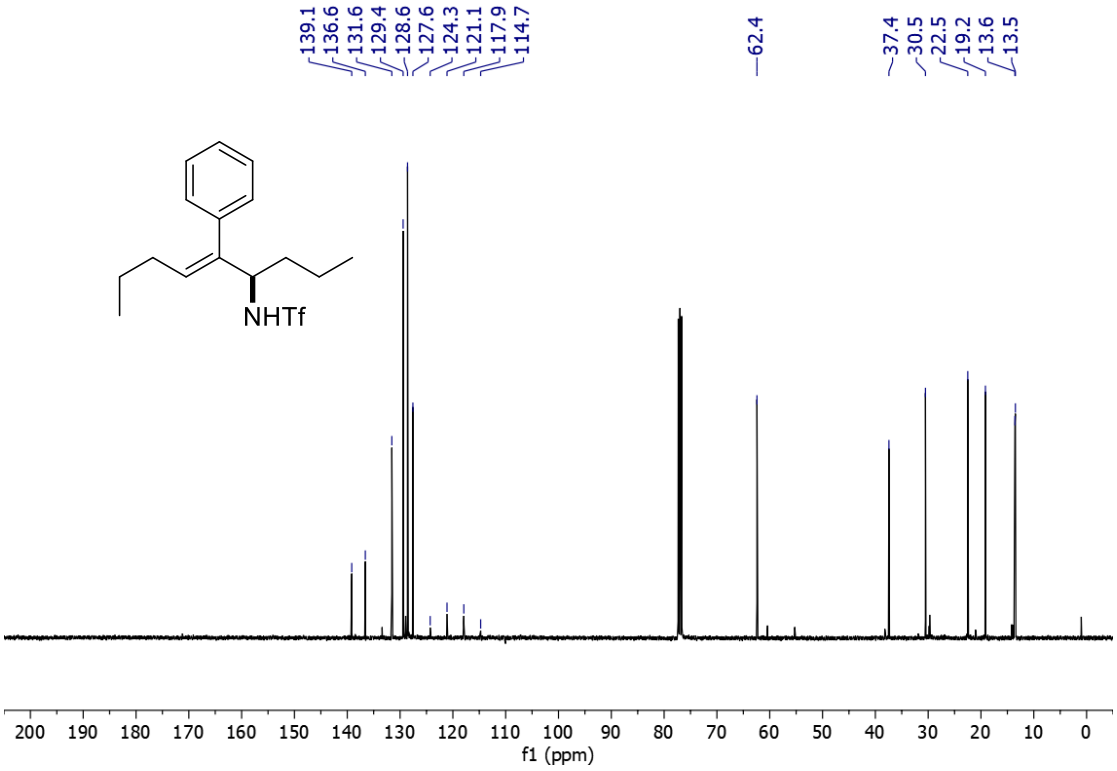
3o ^{19}F NMR (376 MHz, $CDCl_3$)



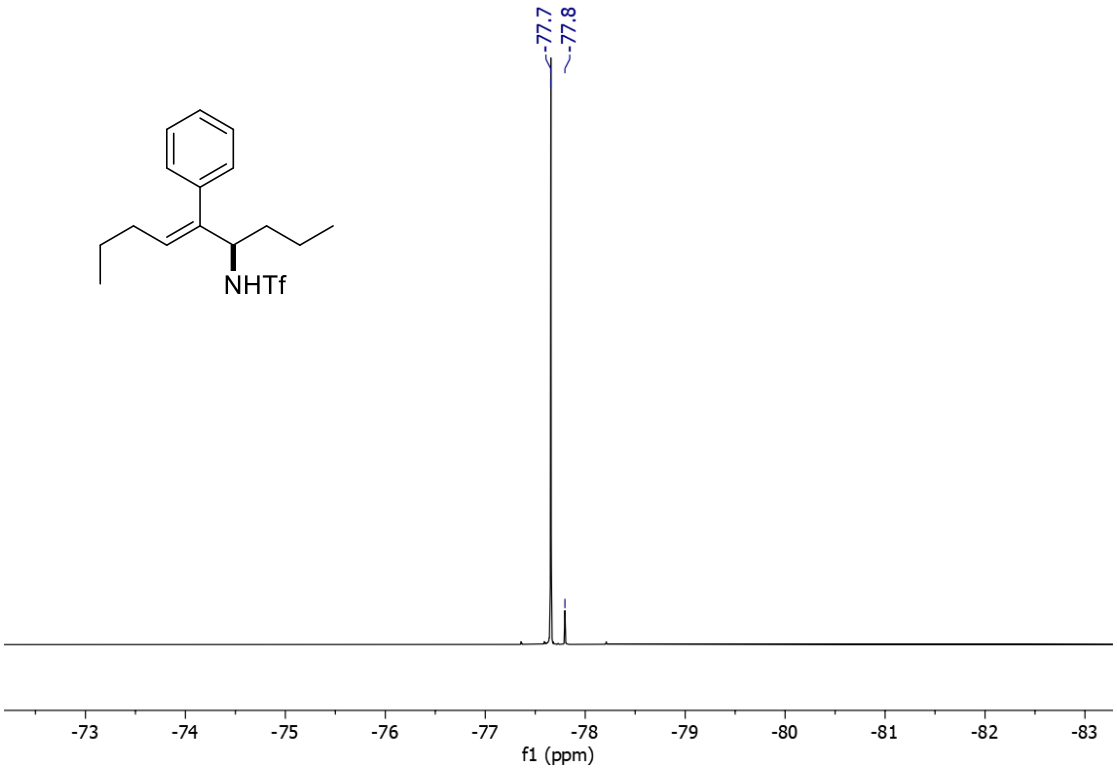
3p ^{1}H NMR (400 MHz, $CDCl_3$)



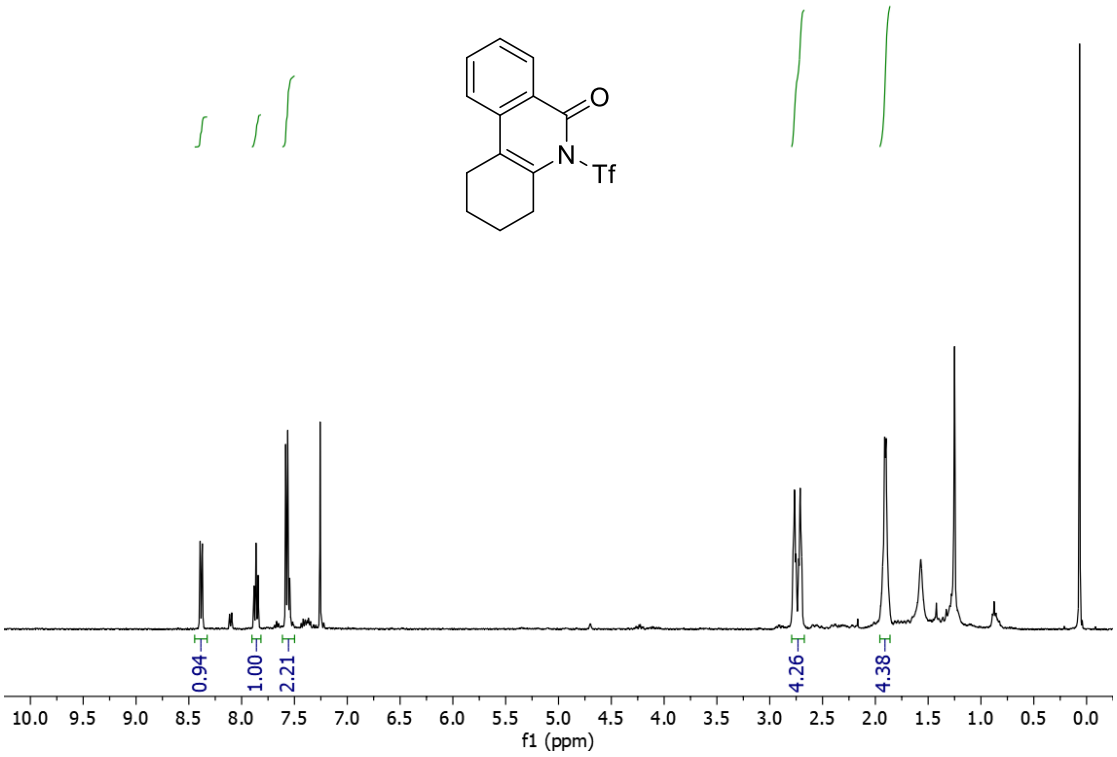
3p ^{13}C NMR (100 MHz, $CDCl_3$)



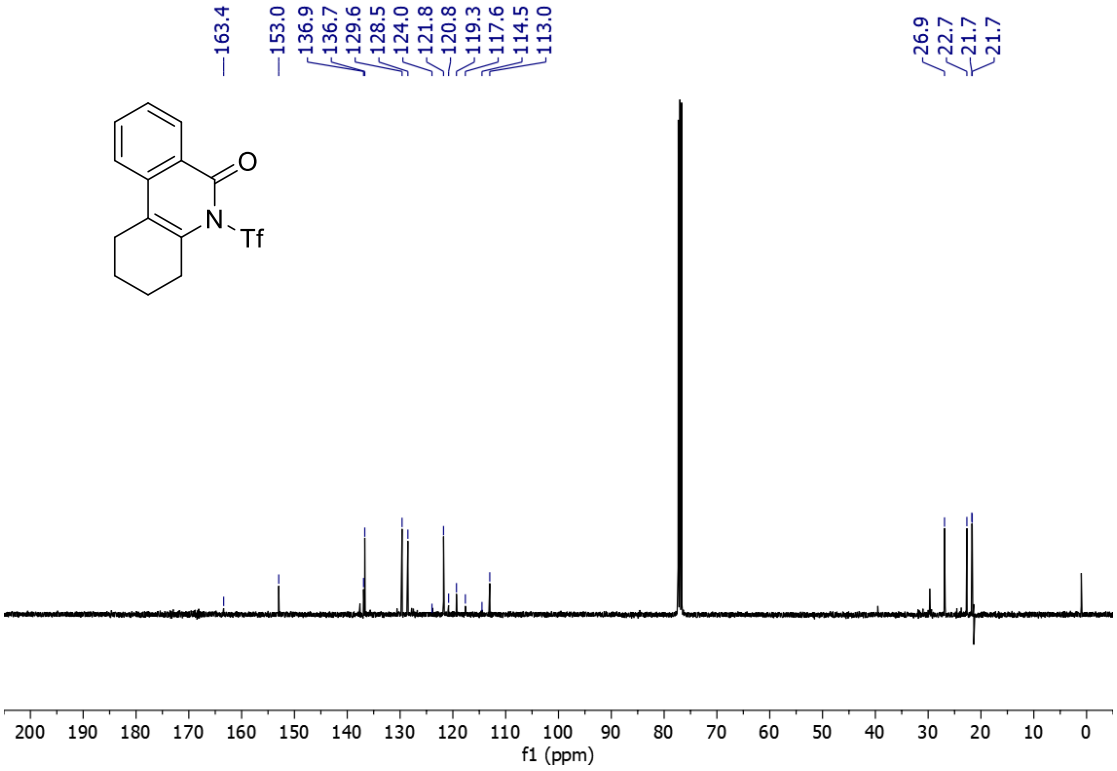
3p ^{19}F NMR (376 MHz, $CDCl_3$)



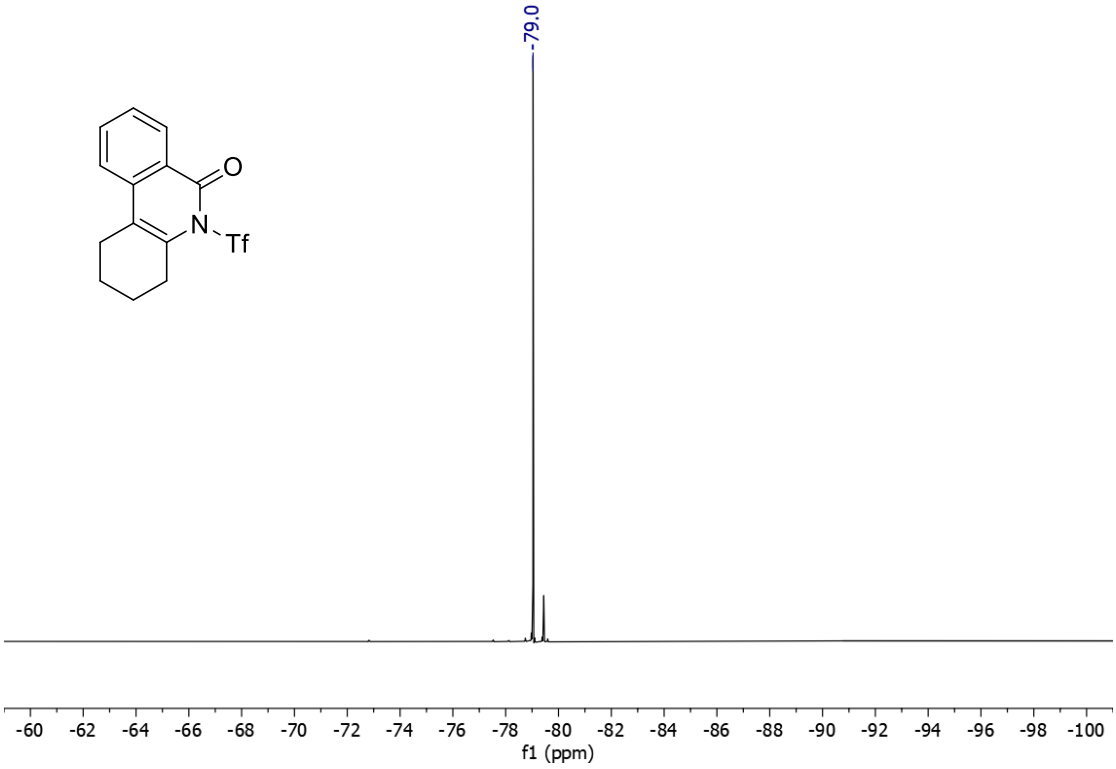
5a ^{1}H NMR (400 MHz, $CDCl_3$)



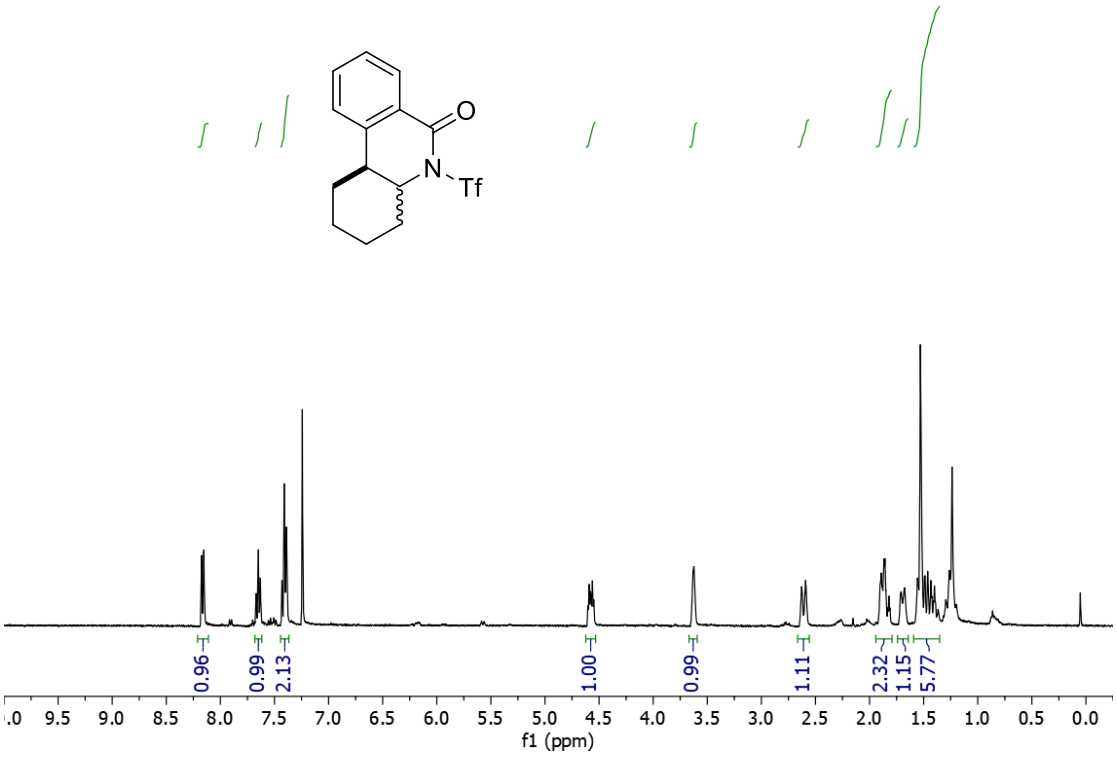
5a ^{13}C NMR (100 MHz, $CDCl_3$)



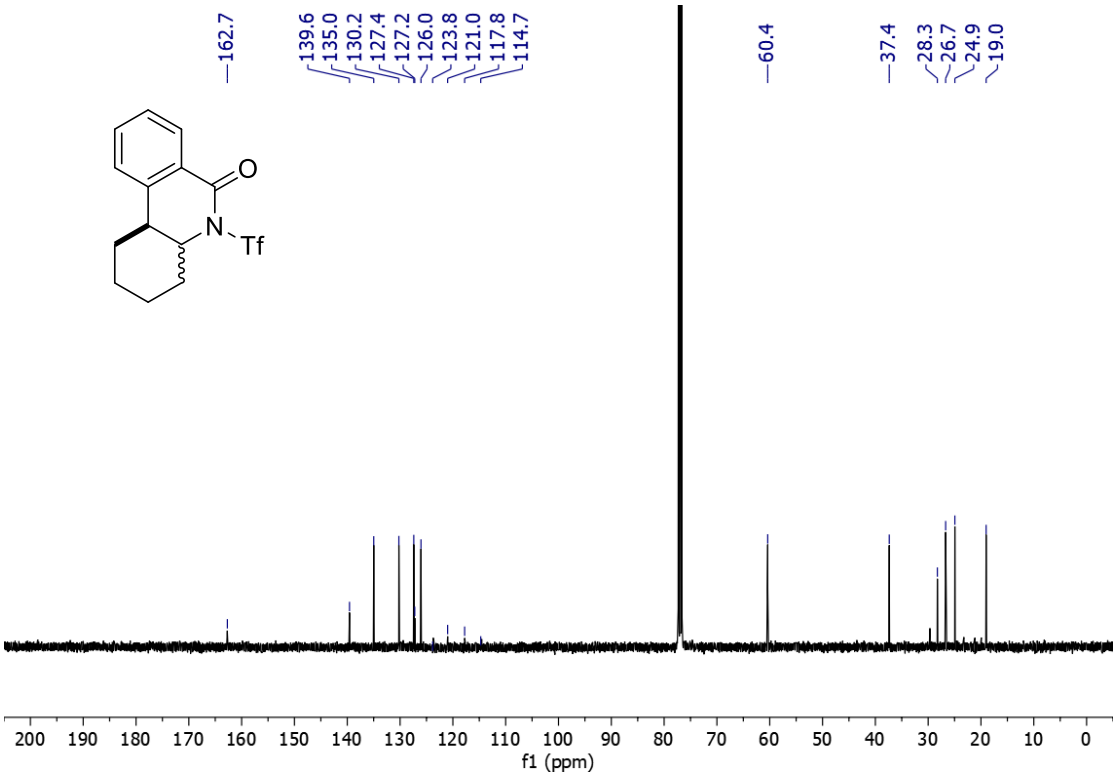
5a ^{19}F NMR (376 MHz, $CDCl_3$)



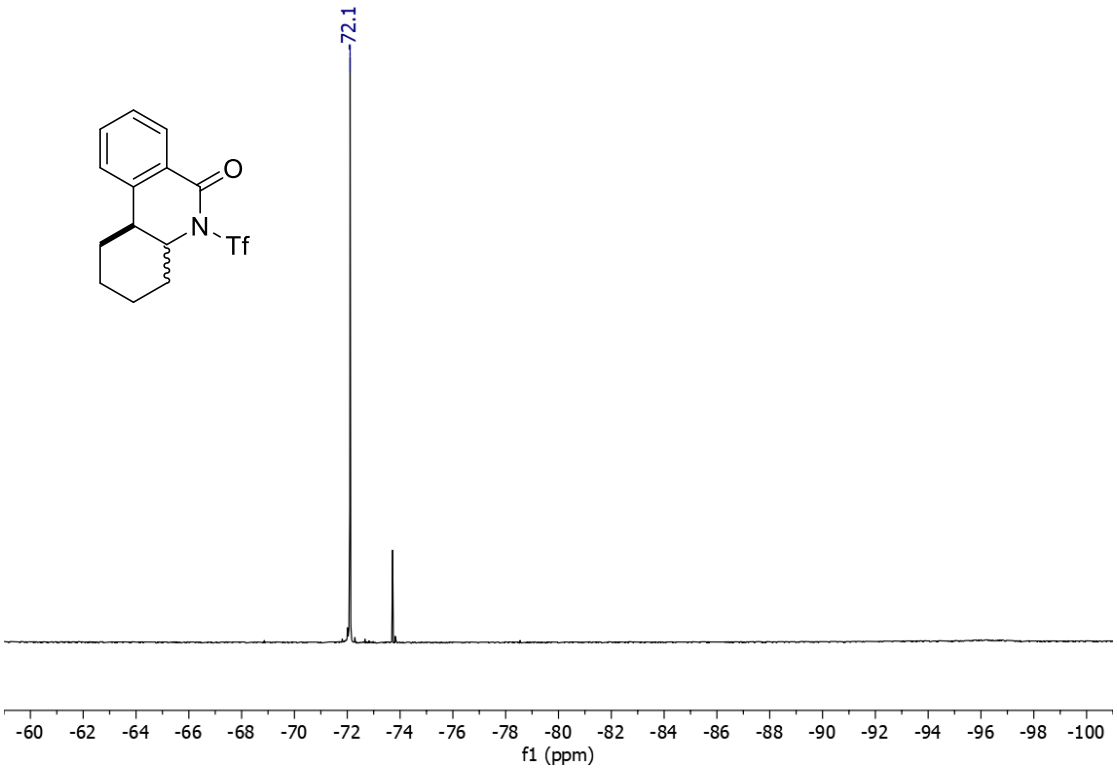
5a' major ^{1}H NMR (400 MHz, $CDCl_3$)



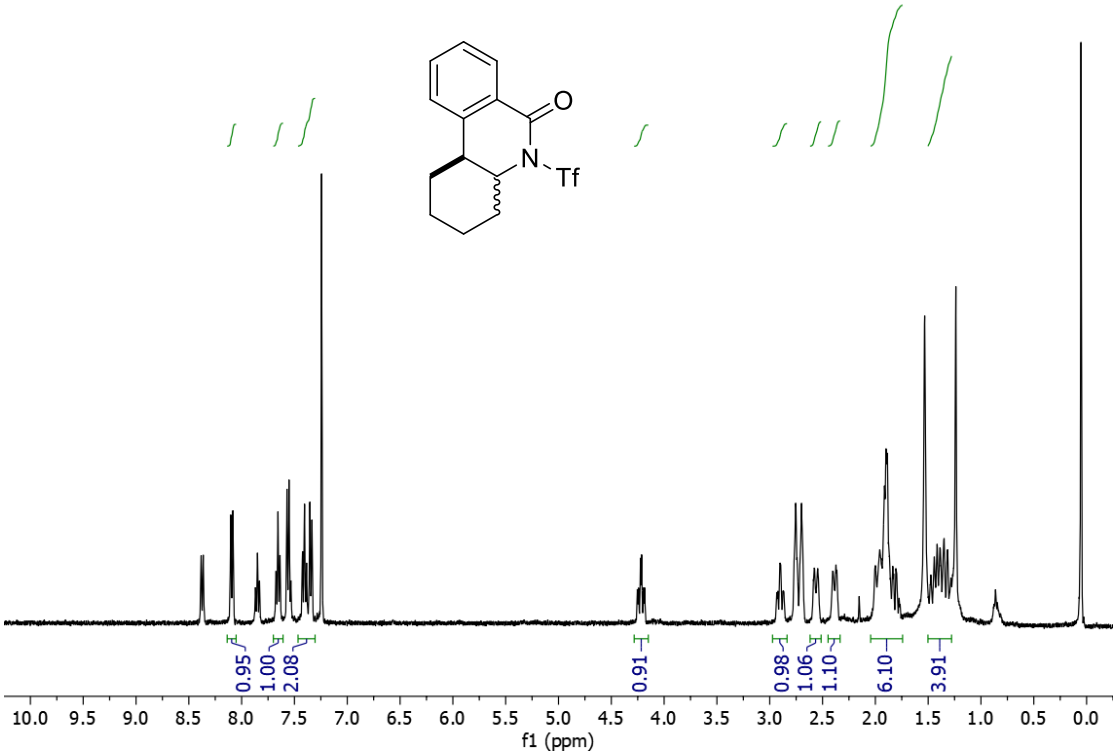
5a' major ^{13}C NMR (100 MHz, $CDCl_3$)



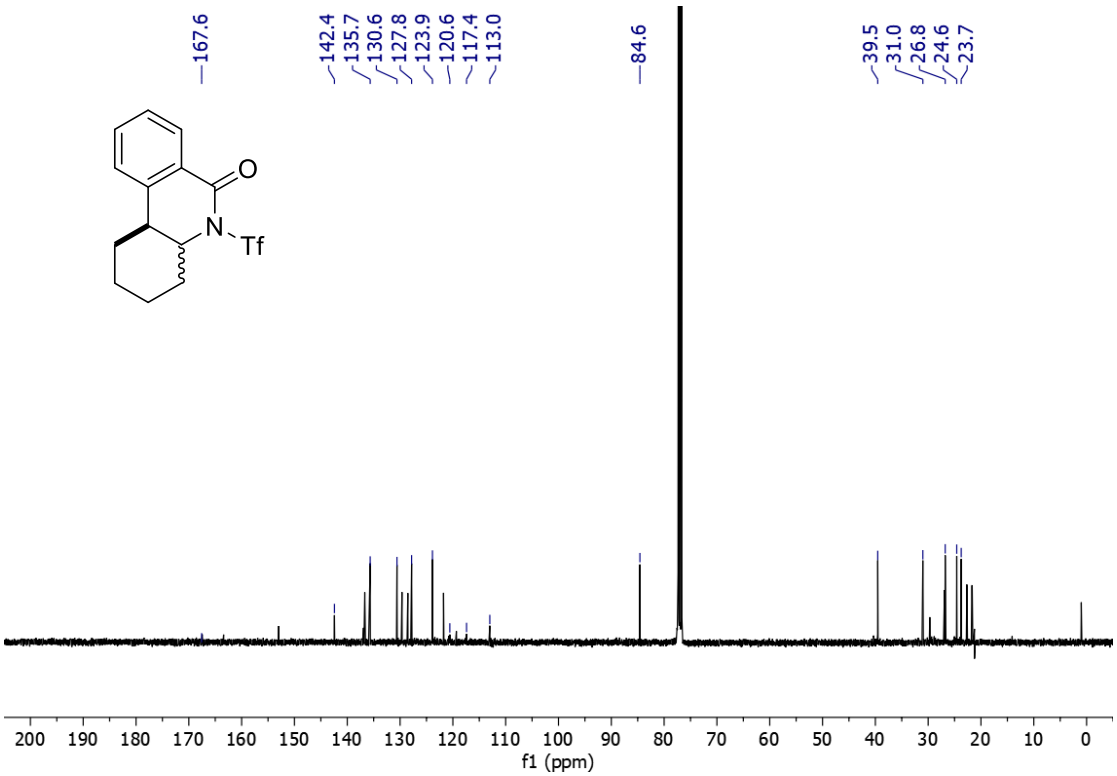
5a' major ^{19}F NMR (376 MHz, $CDCl_3$)



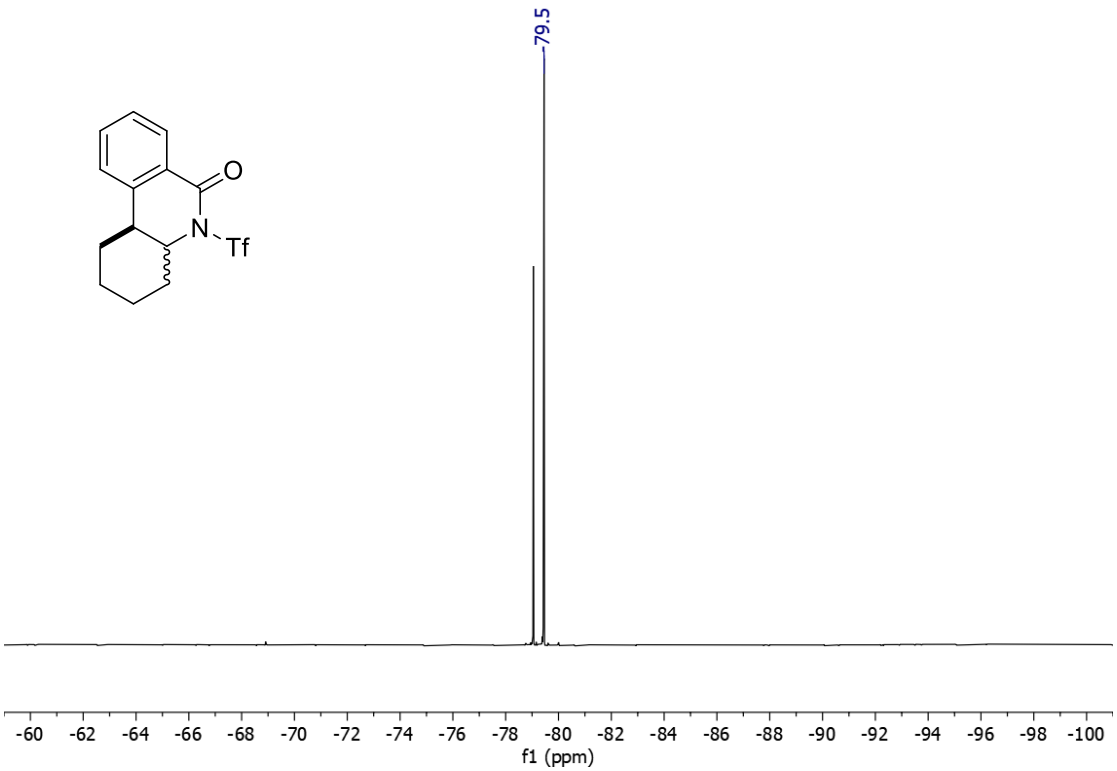
5a' minor (co-eluted with 5a, only signals of 5a' minor integrated) ^{1}H NMR (400 MHz, $CDCl_3$)



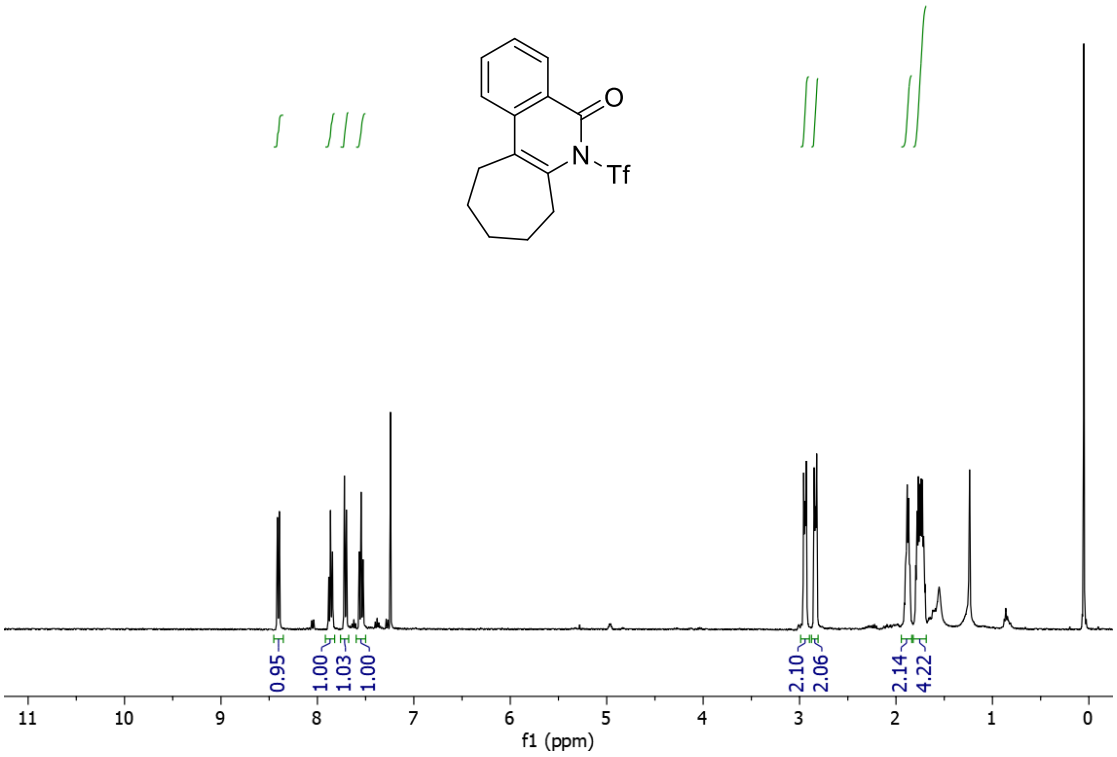
5a' minor (co-eluted with 5a, only signals of 5a' minor highlighted) ^{13}C NMR (100 MHz, $CDCl_3$)



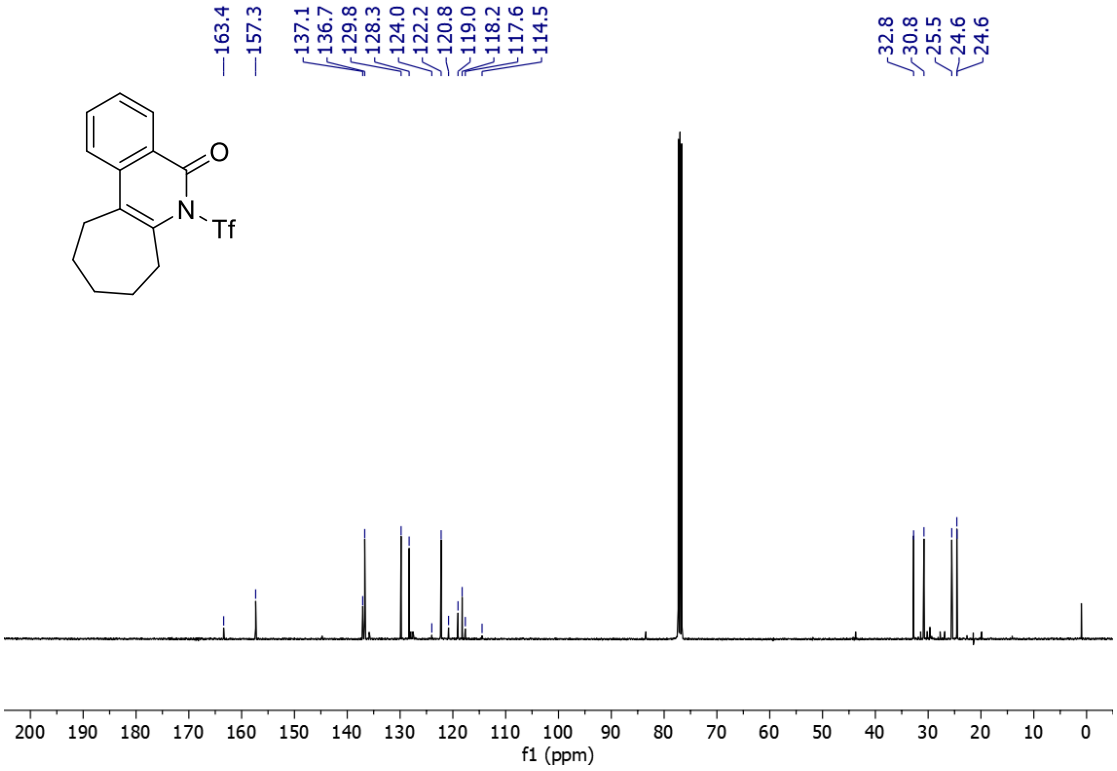
5a' minor (co-eluted with 5a, only signals of 5a' minor highlighted) ^{19}F NMR (376 MHz, $CDCl_3$)



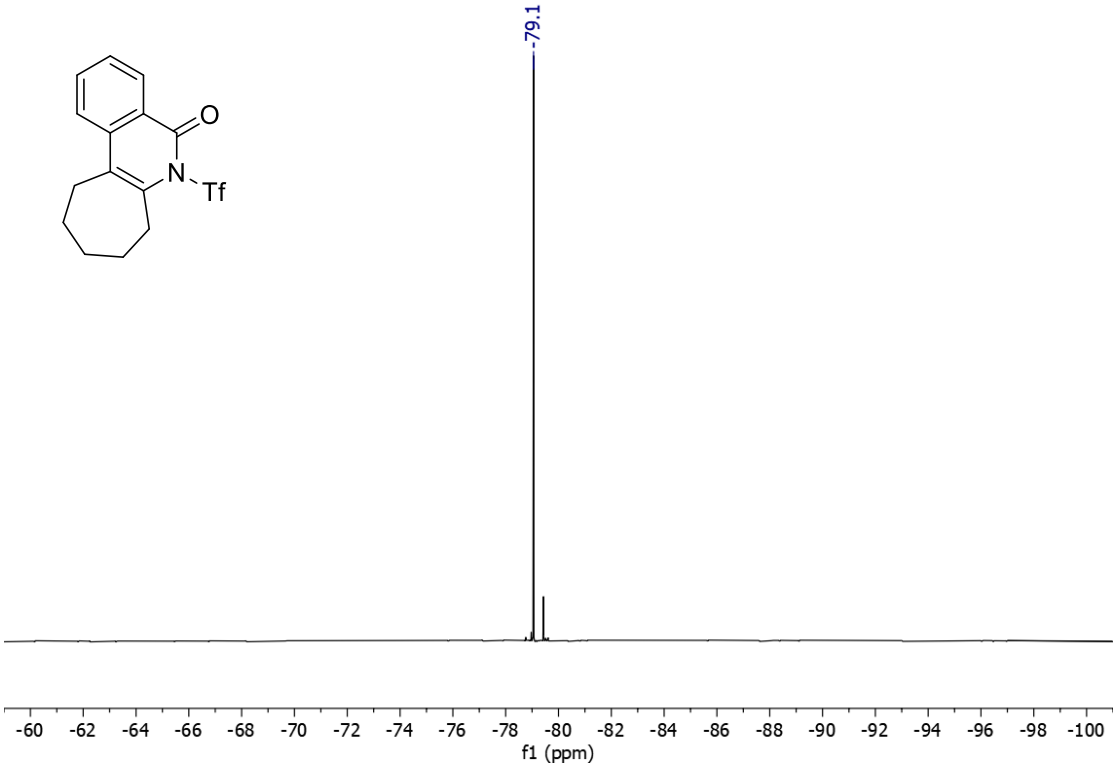
5b ^{1}H NMR (400 MHz, $CDCl_3$)



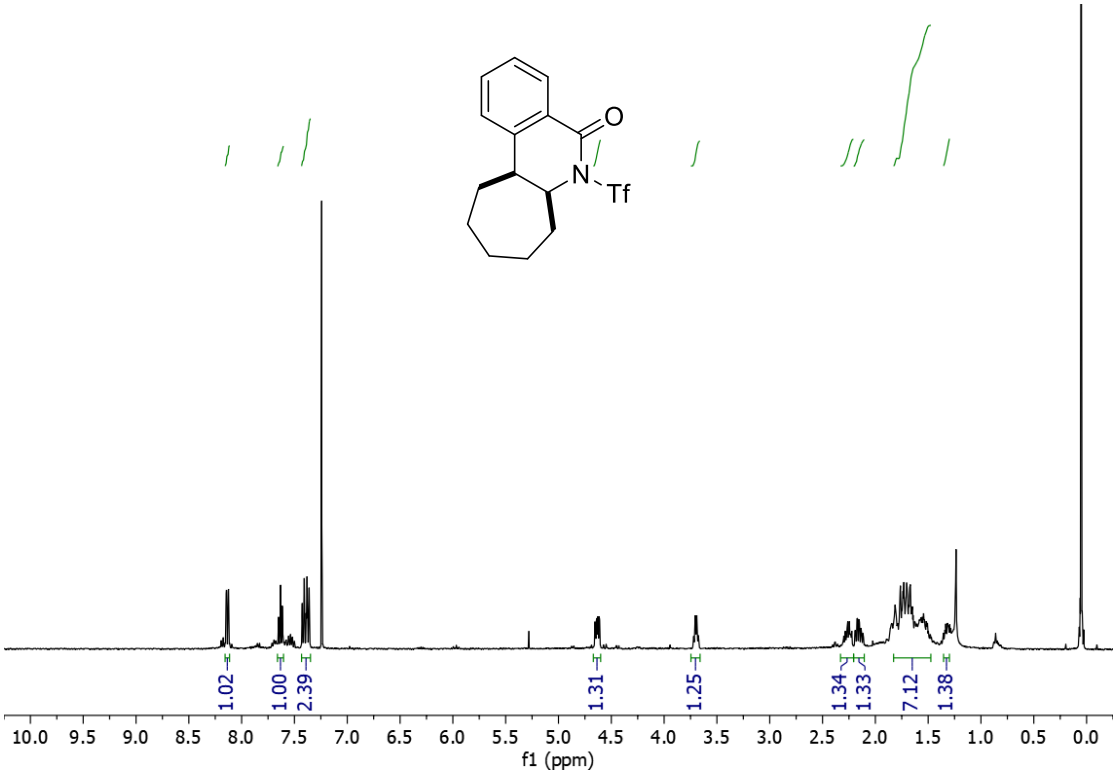
5b ^{13}C NMR (100 MHz, $CDCl_3$)



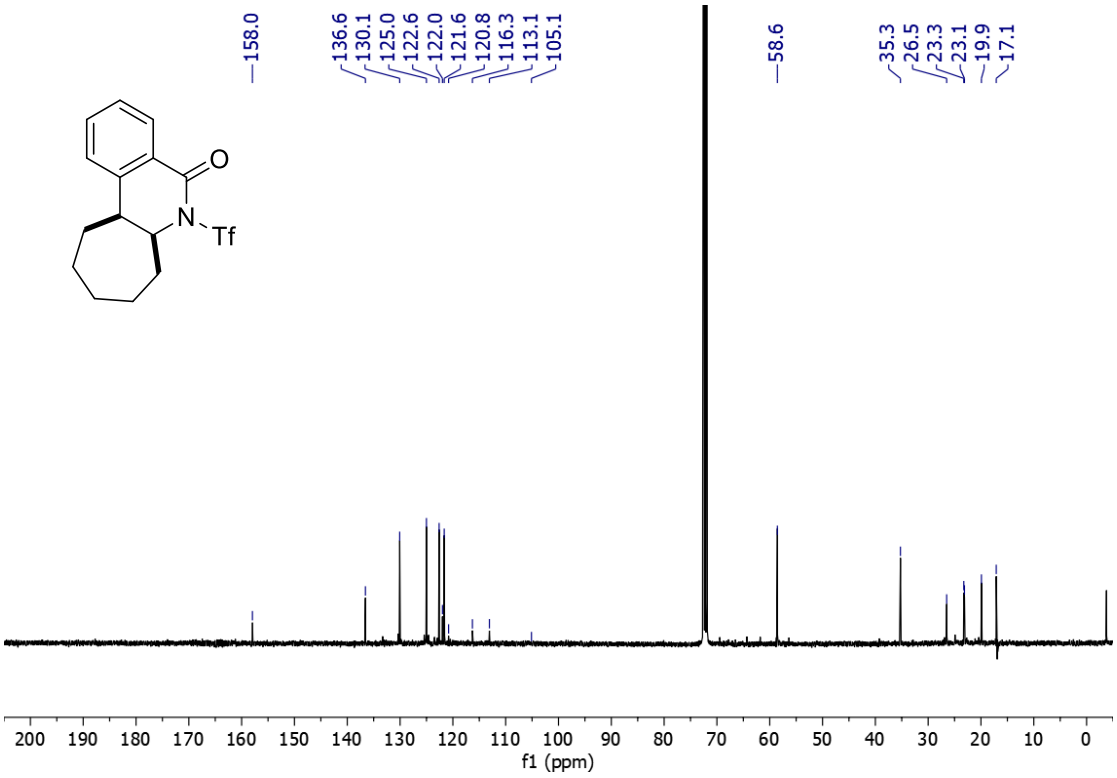
5b ^{19}F NMR (376 MHz, $CDCl_3$)



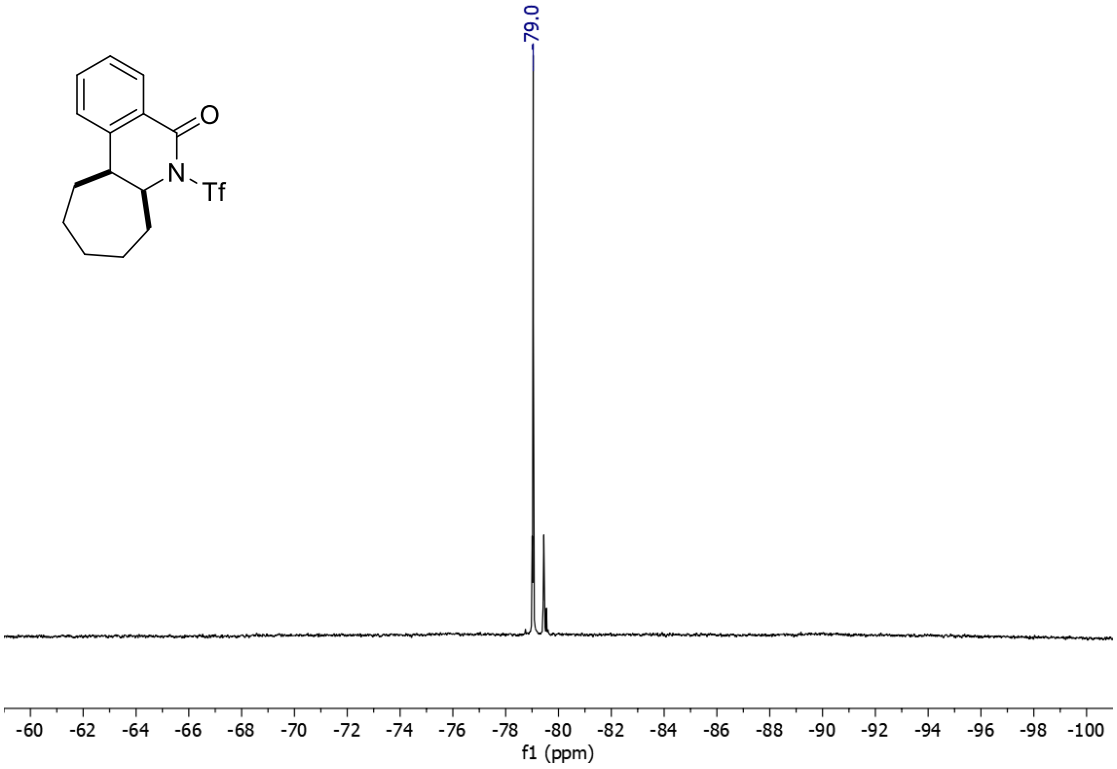
5b' ^{1}H NMR (400 MHz, $CDCl_3$)



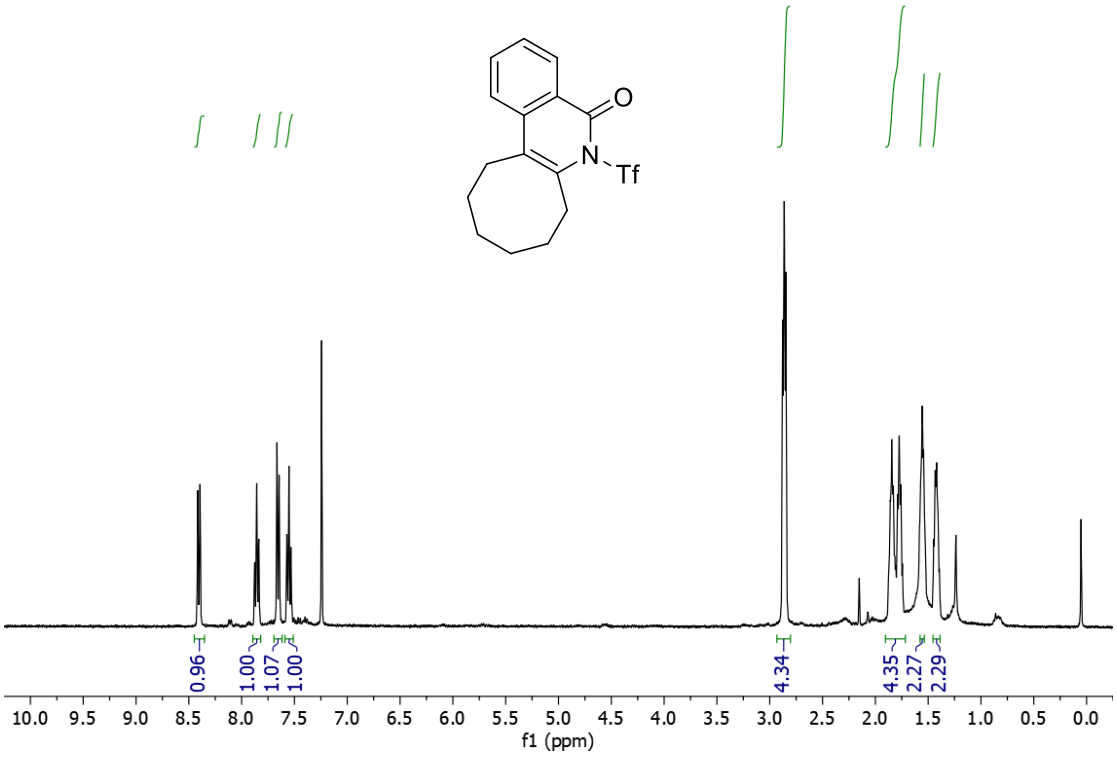
5b' ^{13}C NMR (100 MHz, $CDCl_3$)



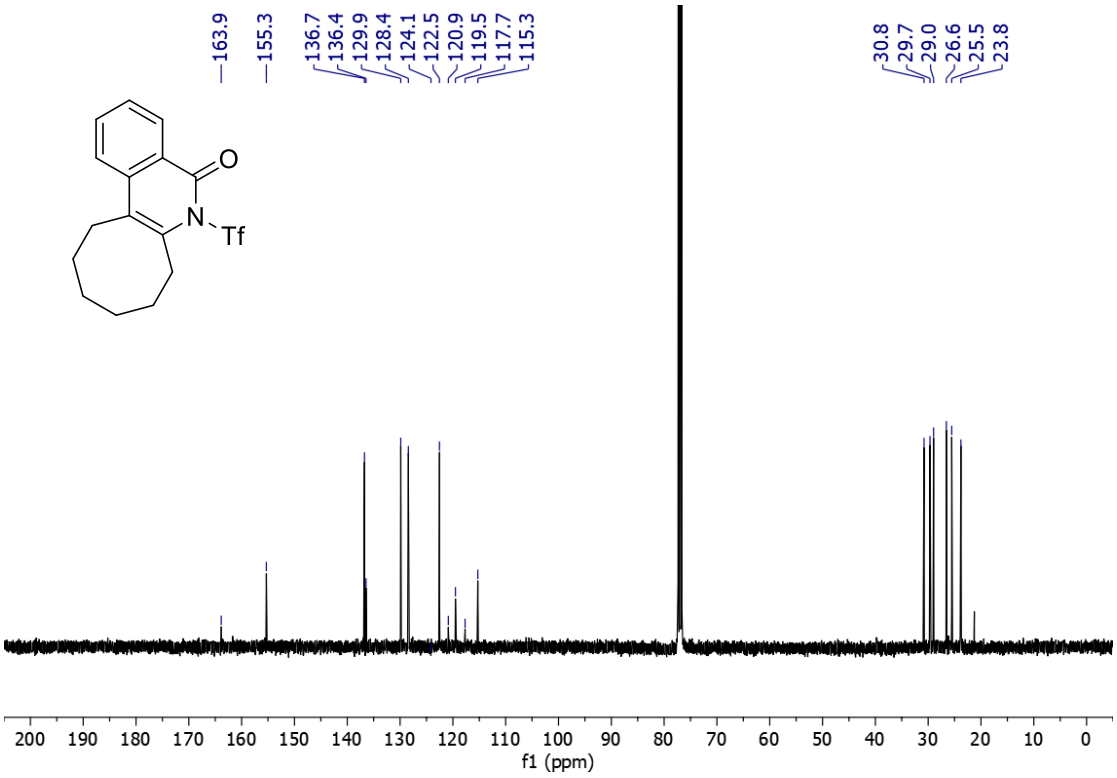
5b' ^{19}F NMR (376 MHz, $CDCl_3$)



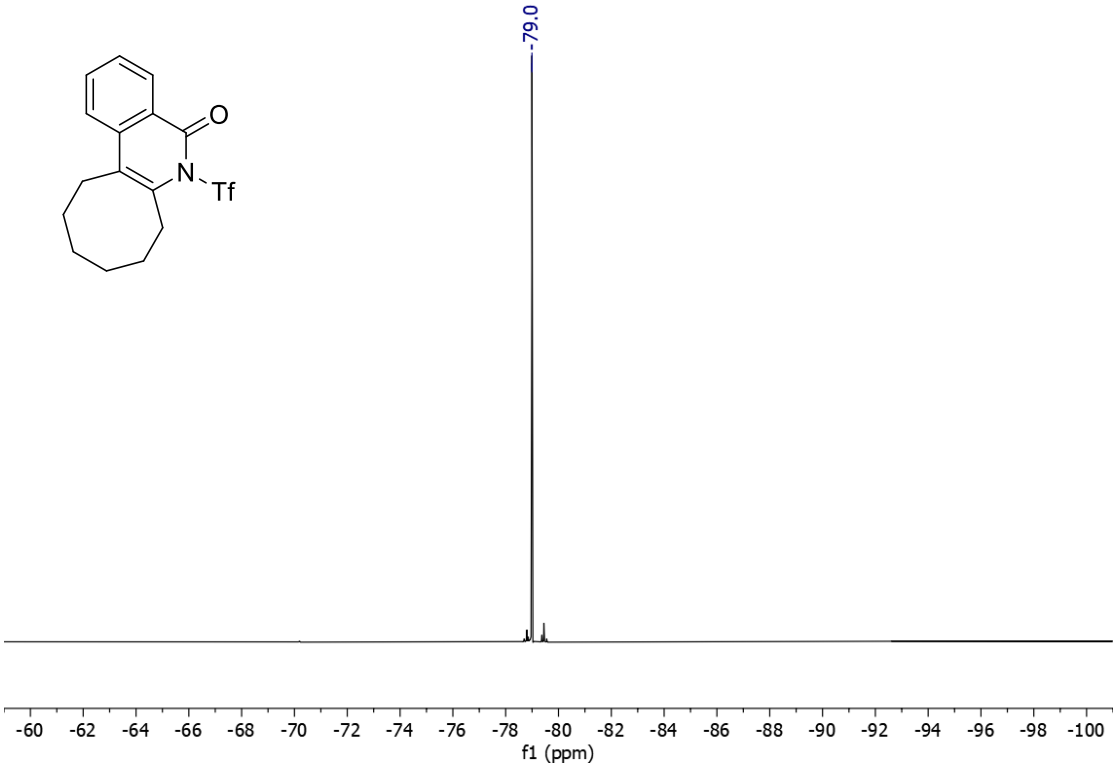
5c ^{1}H NMR (400 MHz, $CDCl_3$)



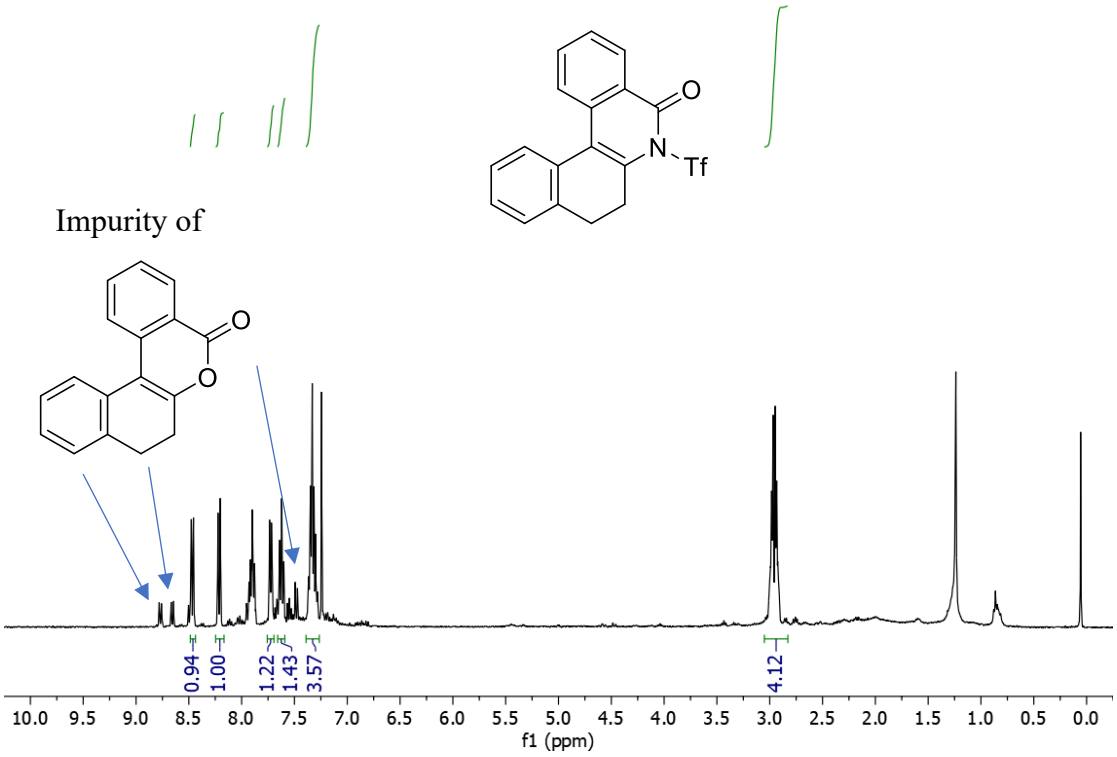
5c ^{13}C NMR (100 MHz, $CDCl_3$)



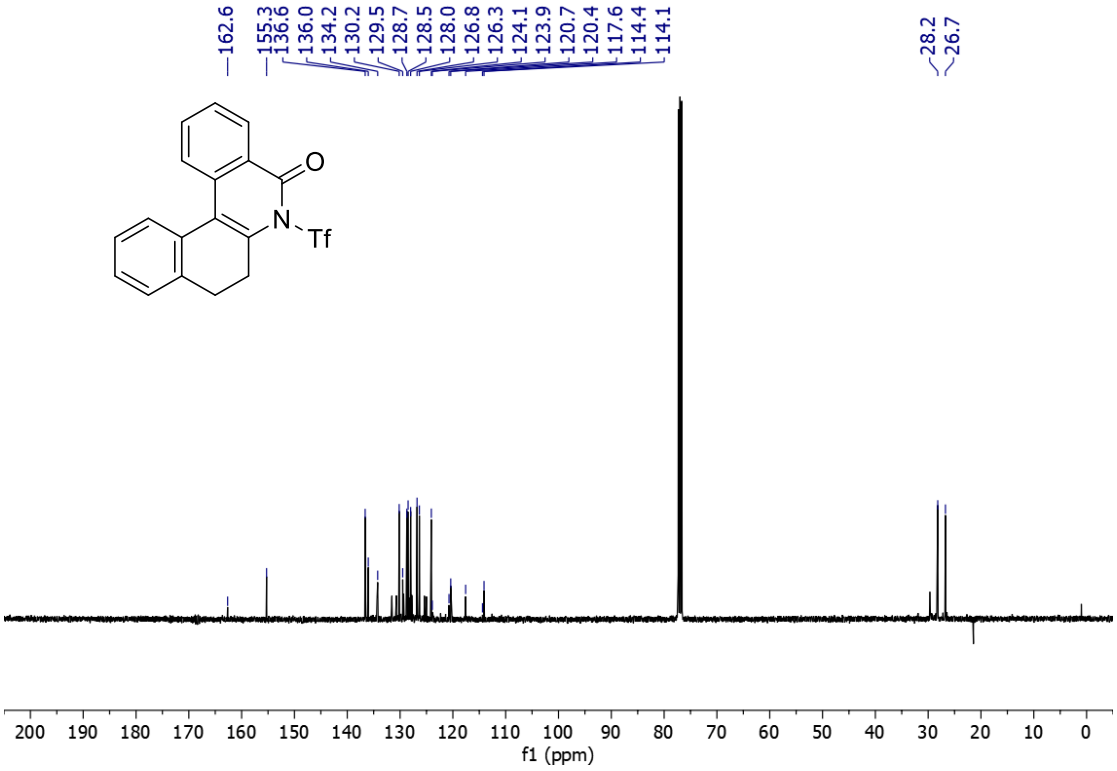
5c ^{19}F NMR (376 MHz, $CDCl_3$)



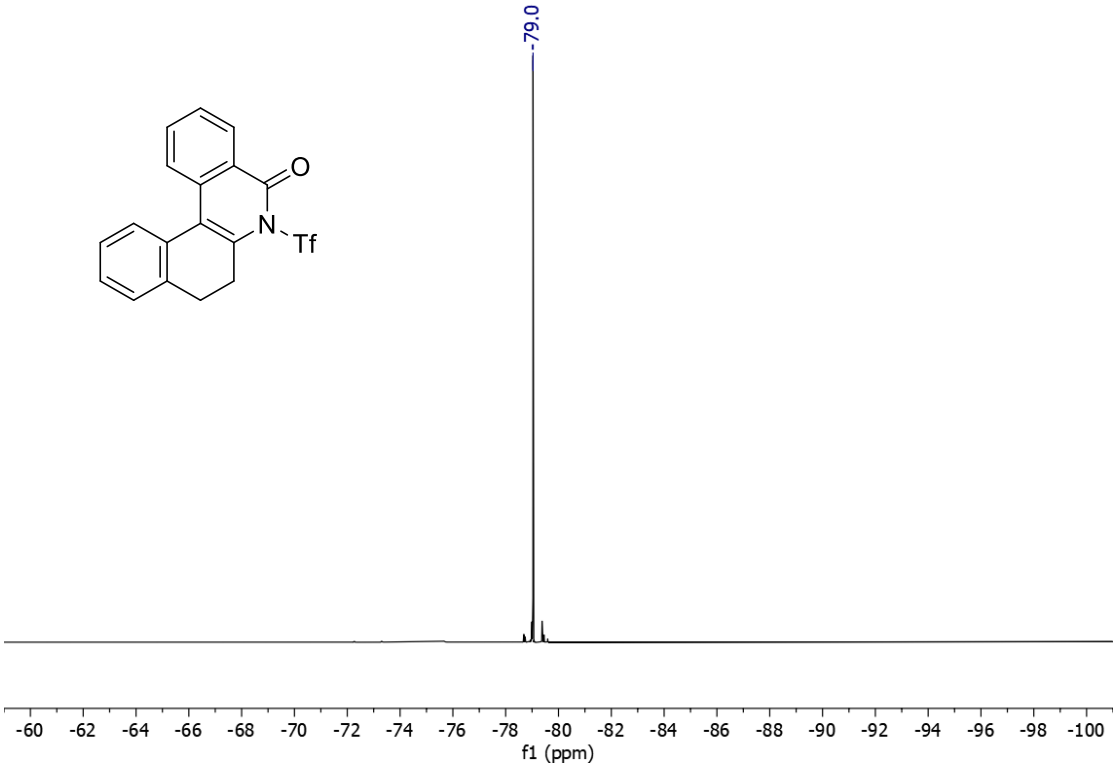
5d ^{1}H NMR (400 MHz, $CDCl_3$)



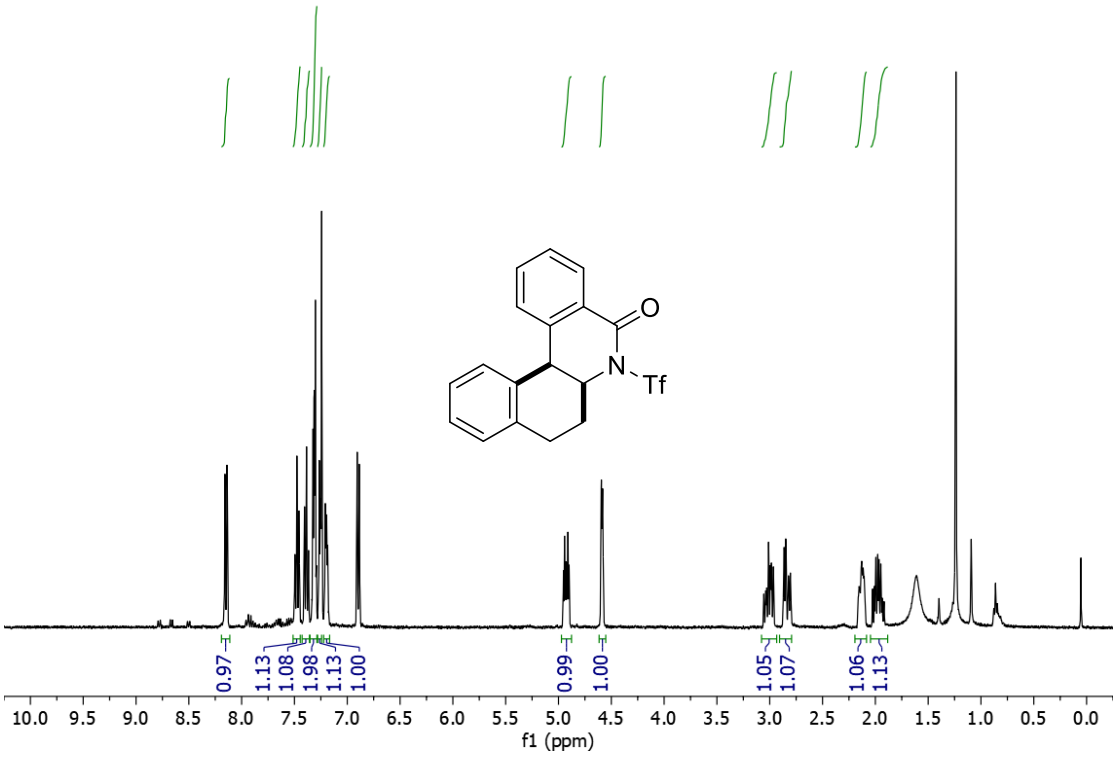
5d ^{13}C NMR (100 MHz, $CDCl_3$)



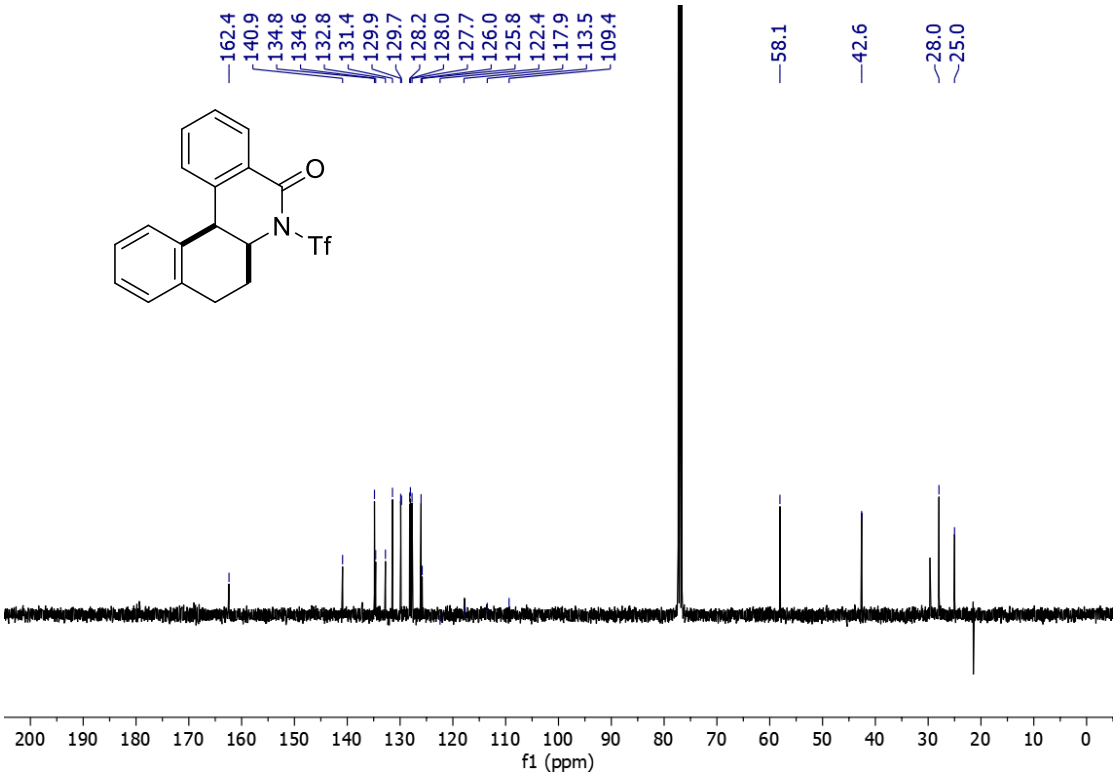
5d ^{19}F NMR (376 MHz, $CDCl_3$)



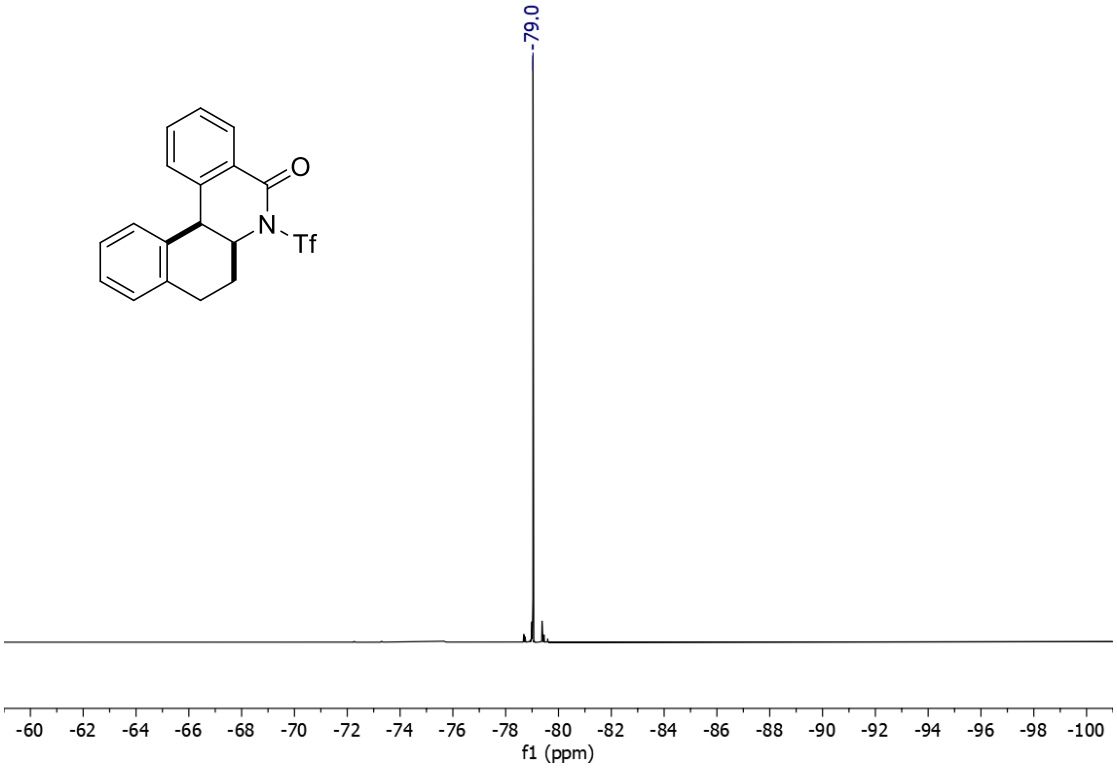
5d' ^{1}H NMR (400 MHz, $CDCl_3$)



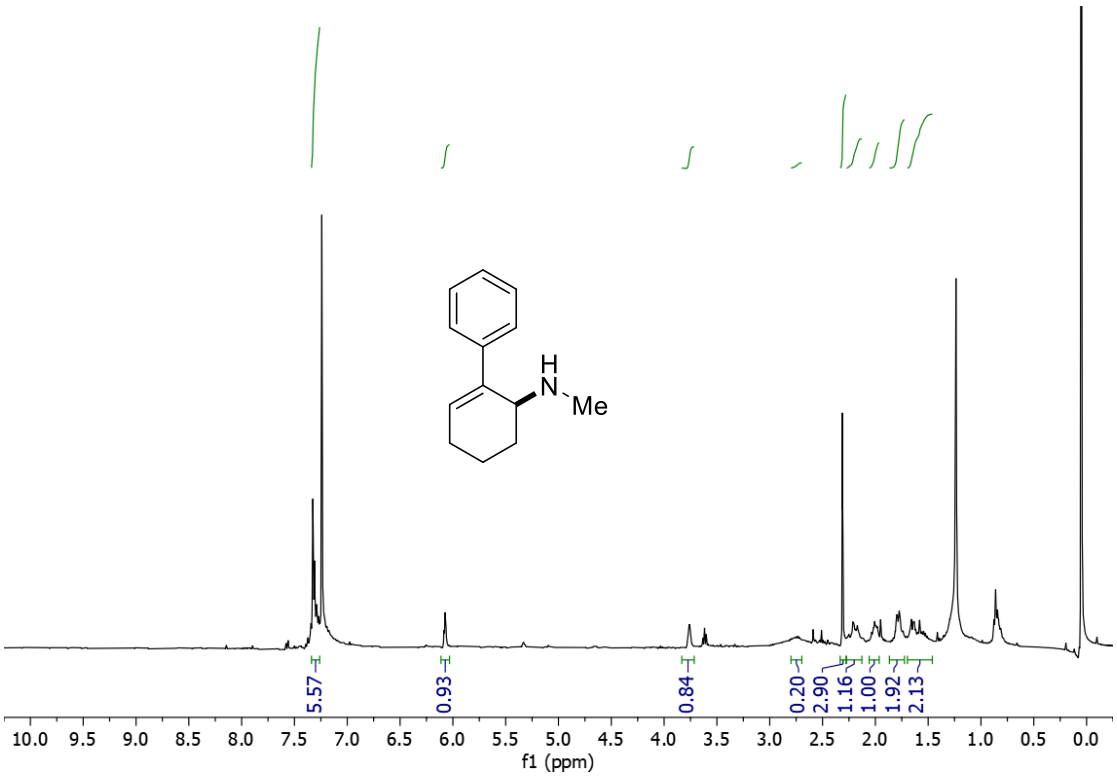
5d' ^{13}C NMR (100 MHz, $CDCl_3$)



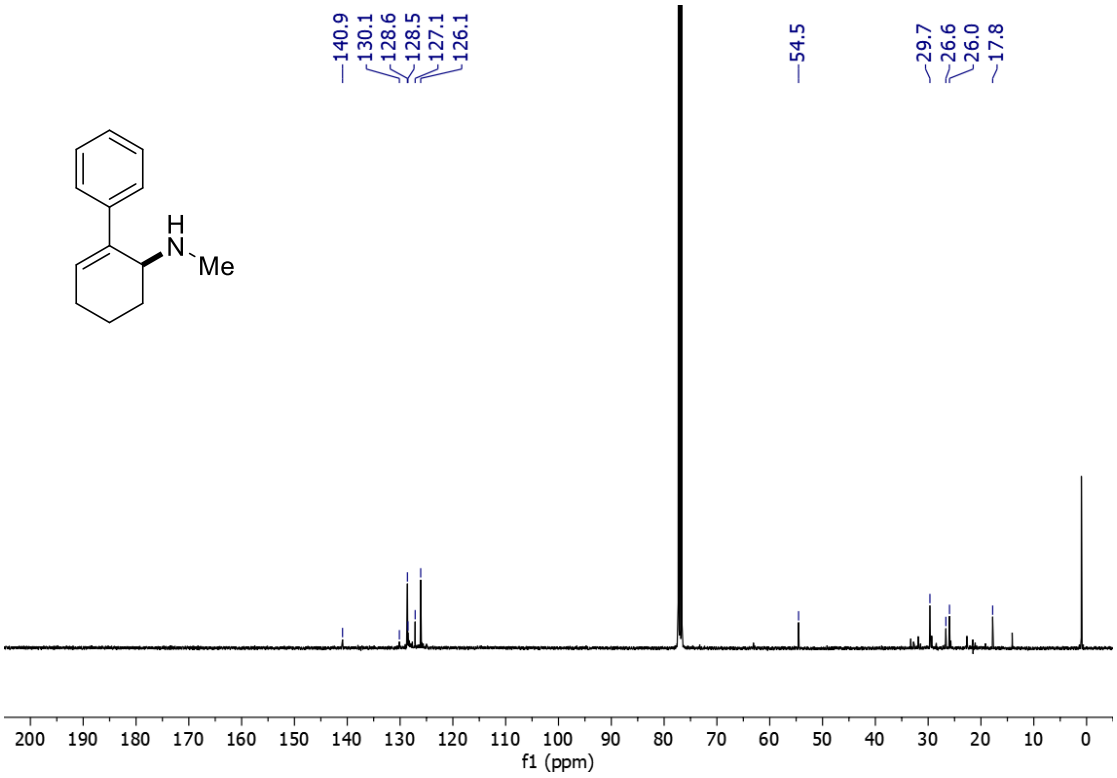
5d' ^{19}F NMR (376 MHz, $CDCl_3$)



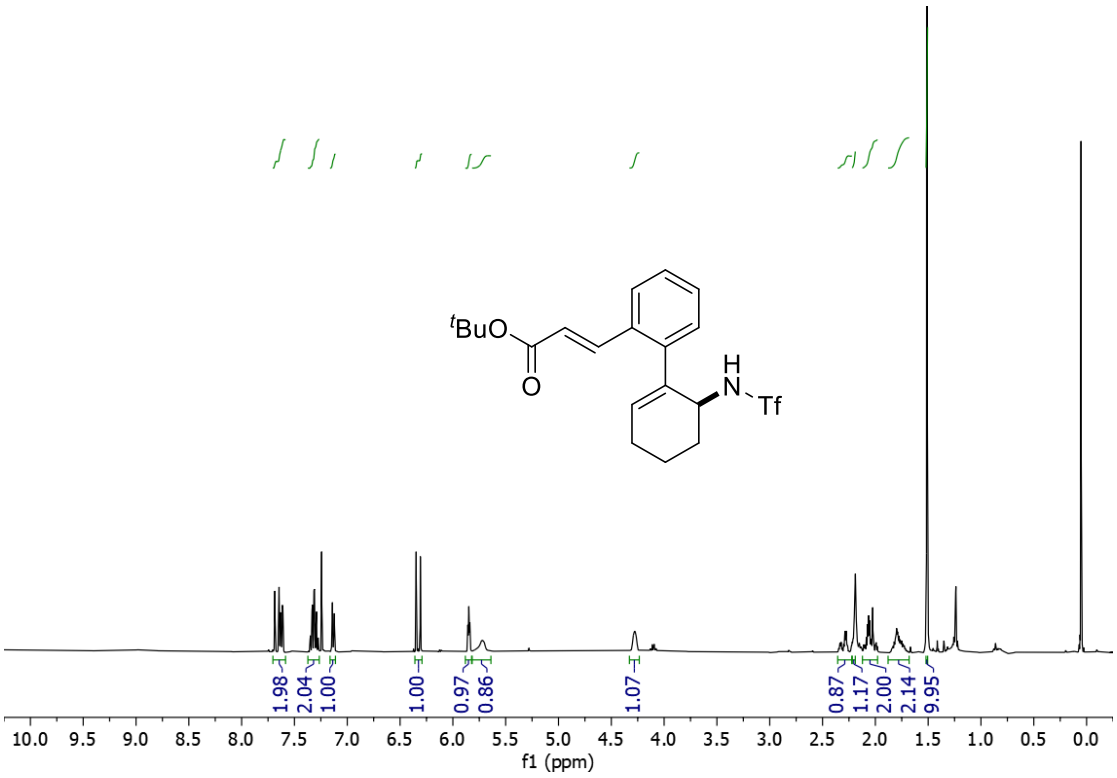
6a ^{1}H NMR (400 MHz, $CDCl_3$)



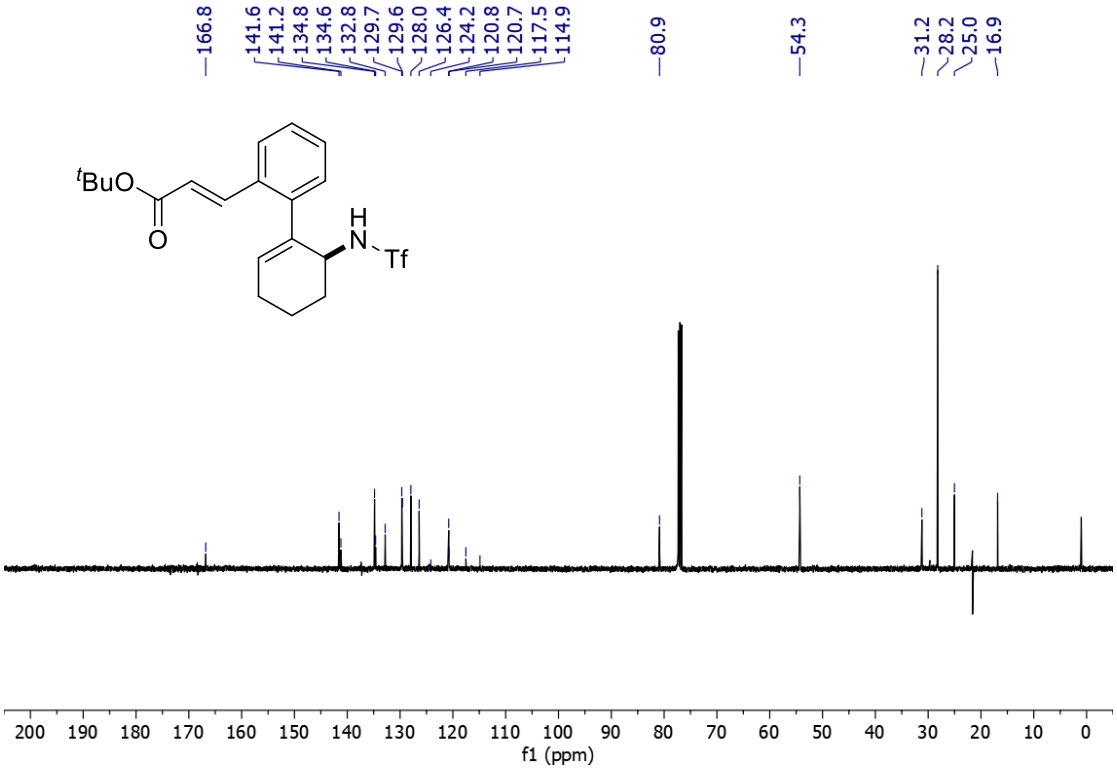
6a ^{13}C NMR (100 MHz, $CDCl_3$)



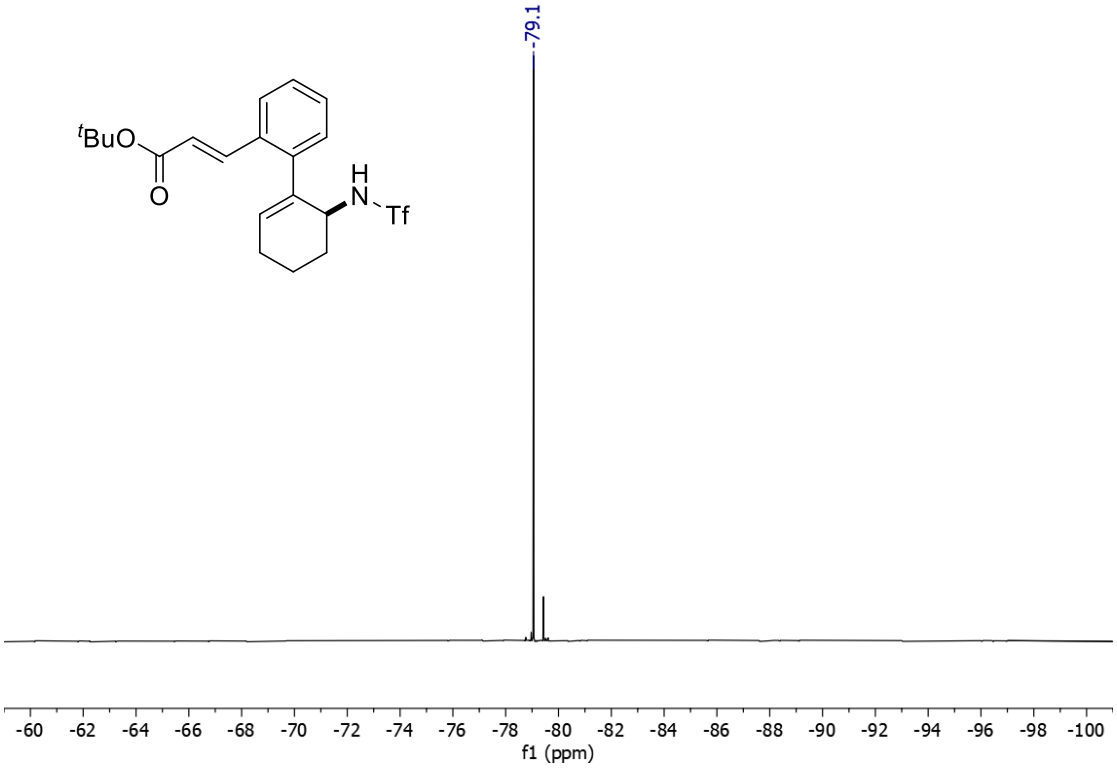
7a ^{1}H NMR (400 MHz, $CDCl_3$)



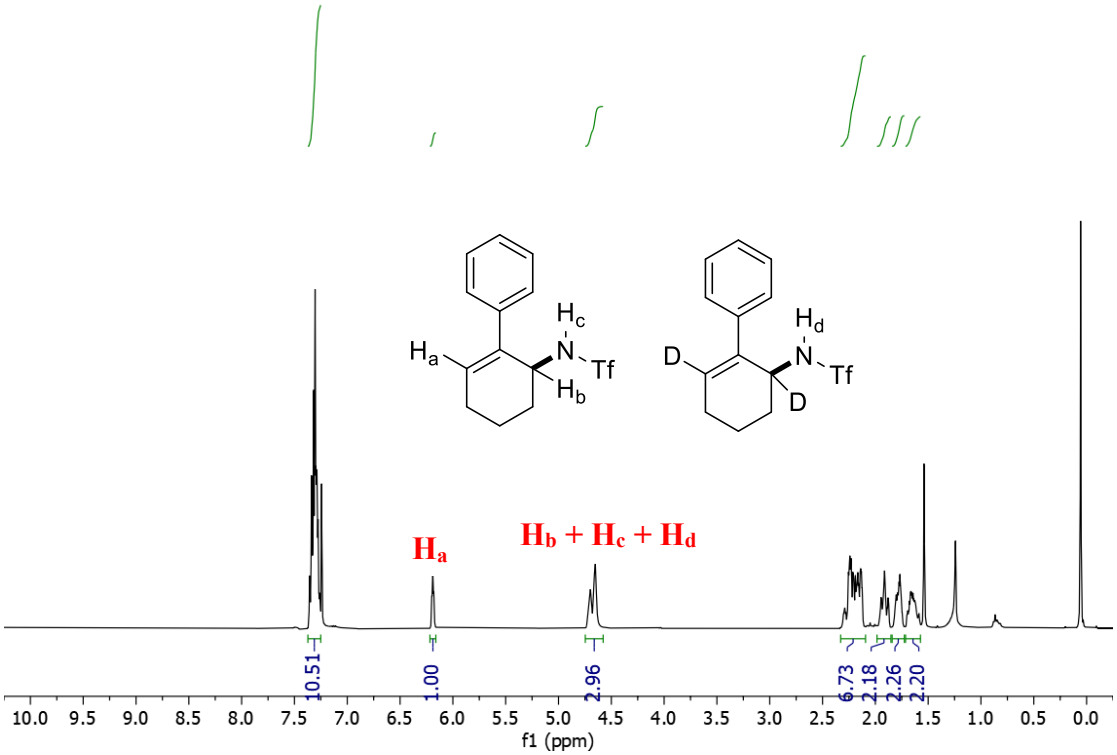
7a ^{13}C NMR (100 MHz, $CDCl_3$)



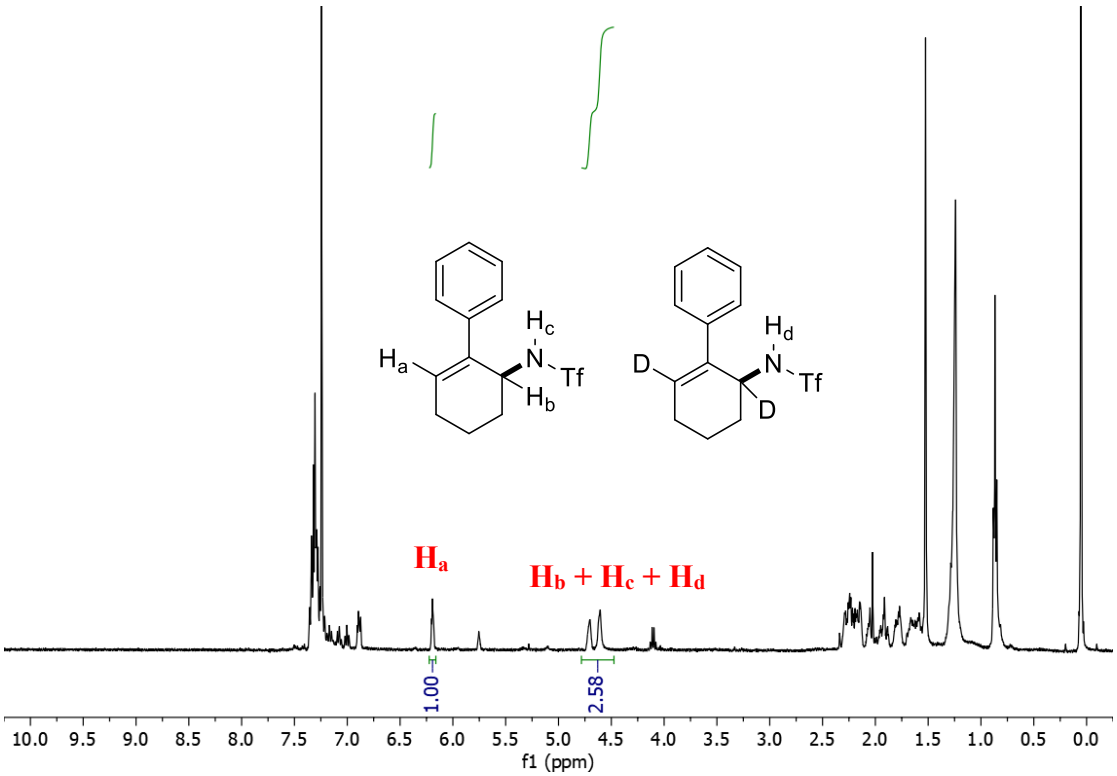
7a ^{19}F NMR (376 MHz, $CDCl_3$)



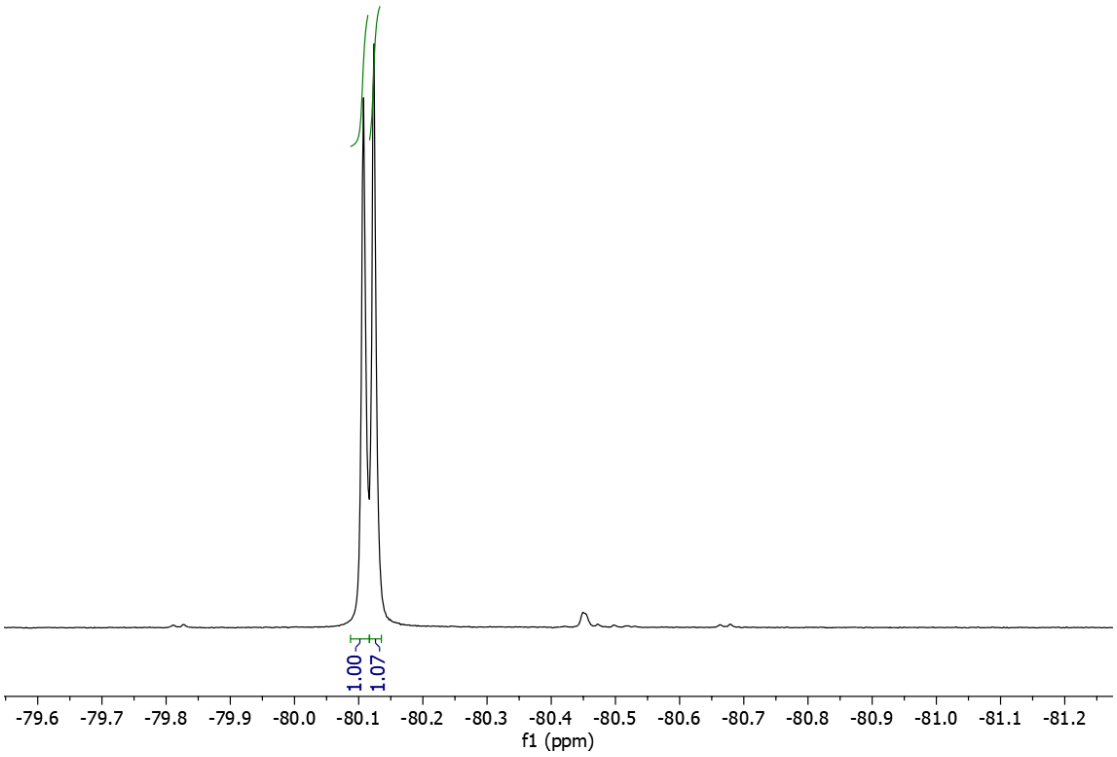
3a/d^2-3a 1:1 ^{1}H NMR (400 MHz, $CDCl_3$)



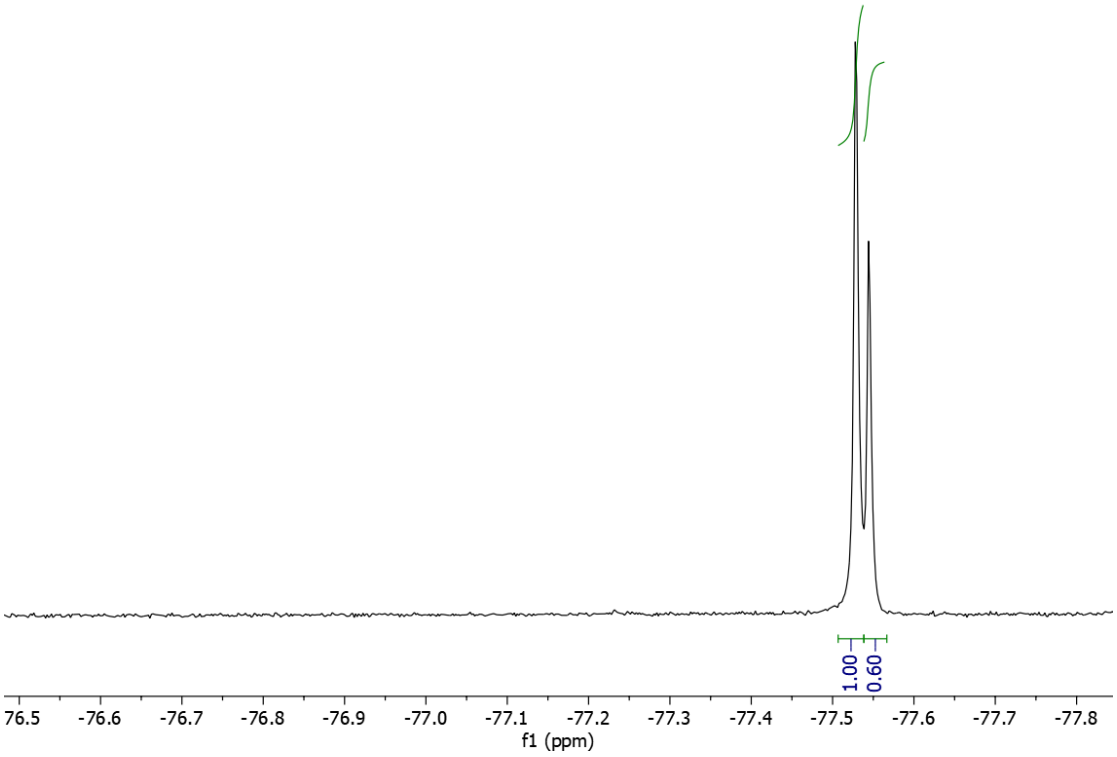
3a/d^2-3a 1:0.6 ^{1}H NMR (400 MHz, $CDCl_3$)



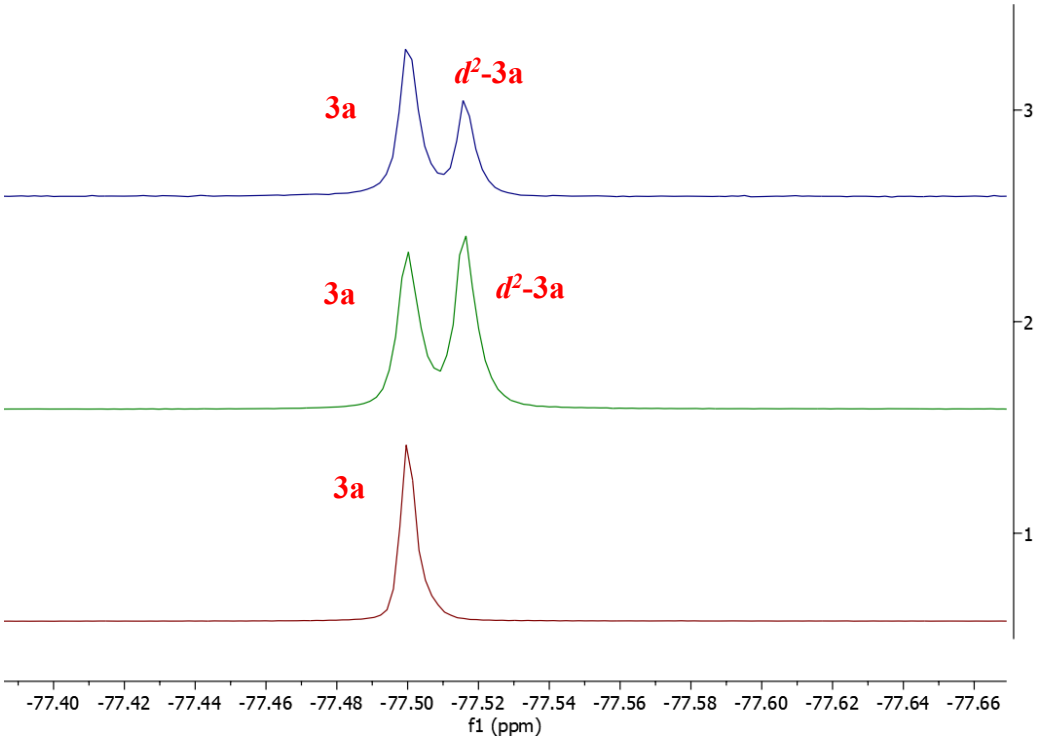
3a/*d*^{2}-3a 1:1 ^{19}F NMR (376 MHz, $CDCl_3$)



3a/*d*^{2}-3a 1:0.6 ^{19}F NMR (376 MHz, $CDCl_3$)



Stacked ^{19}F NMR (376 MHz, $CDCl_3$) of: 3a (red), 3a/d^2-3a 1:1 (green) and 3a/d^2-3a 1:0.6 (blue)



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