Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Stereodivergent trifluoromethylation of *N*-sulfinylimines by fluoroform with either organic-superbase or organometallic-base

Nagender Punna,[a] Takuya Saito,[a] Mikhail Kosobokov,[a] Etsuko Tokunaga,[a] Yuji Sumii,[a] and Norio Shibata*[a,b]

[a.] *Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-5888, Japan, E-mail: nozshiba@nitech.ac.jp*
[b.] *Institute of Advanced Fluorine-Containing Materials, Zhejiang Normal University, 688 Yingbin Avenue, 321004 Jinhua, China.*

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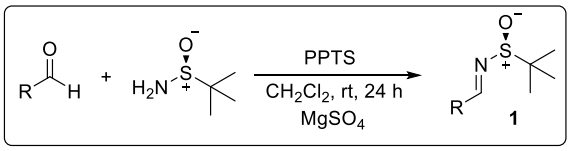
1. General information

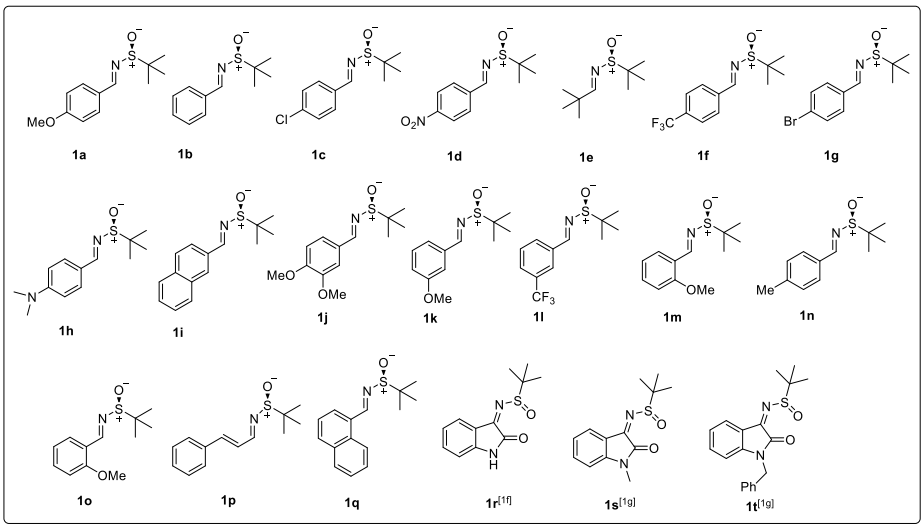
All reactions were performed in oven-dried glassware under a positive pressure of nitrogen or argon. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All solvents were dried by standard method. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ in water/heat or *p*-anisaldehyde solution/heat. All of the reaction products were purified by column chromatography. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 mm. The ^1H NMR (300 MHz and 500 MHz) and ^{19}F NMR (282 MHz) spectra (with Hexafluorobenzene (δ ppm −162.2) and $CFCl_3$ (δ ppm 0)) as an internal standard) as for solution in $CDCl_3$ & MeOH-d_4 were recorded on a Varian Mercury 300 and Bruker 500 Ultra Shield TR. ^{13}C NMR (125.8 MHz) spectra for solution in $CDCl_3$ & MeOH-d_4 were recorded on a BRUKER 500 Ultra Shield TR. Chemical shifts (δ) are expressed in ppm downfield from internal TMS or C_6F_6 or $CFCl_3$. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020(ESI-MS). HPLC analysis were performed on a JASCO U-2080 Plus using 4.6 x 250 mm CHIRALCEL OD-H or CHIRALCEL OD-3 or CHIRALPAK IA column. Optical rotations were measured on a HORIBA SEPA-300. Infrared spectra were recorded on a JASCO FT/ IR-200 spectrometer. Melting and boiling points were measured on Buchi M-565 device. Commercially available chemicals were obtained from Aldrich Chemical Co., Alfa Aesar, TCI, Ark Farm and used as received unless otherwise stated. The residual solvent signals were used as references (TMS: δH = 0.00 ppm, δC = 77.16 ppm; $CFCl_3$: δF = 0 ppm; and C_6F_6: δF = −162.2 ppm). High resolution mass spectrometry (HRMS (ESI, *m/z*)) was carried out on an electron impact ionization mass spectrometer with a micro-TOF analyzer.

2. General procedure for the preparation of compound *N*- sulfinylimines 1

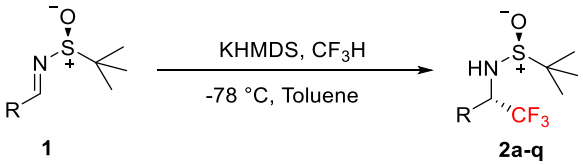


Followed by the reported procedure from *J. Am. Chem. Soc*., **1997**, *119*, 9913-9914; To a solution of (*S*)-*t*-butanesulfinamide (1.00 g, 8.26 mmol) in 13.8 mL of CH_2Cl_2 was added pyridium *p*-toluenesulfonate (PPTS) (0.103 g, 0.413 mmol) and anhydrous magnesium sulfate (4.97 g, 41.3 mmol) followed by the aldehyde (24.78 mmol for benzaldehyde). The mixture was stirred at room temperature for 24 h. TLC showed the reaction was complete. Magnesium sulfate was filtered off through a pad of celite and washed well with CH_2Cl_2. The combined filtrate and the washes were concentrated and chromatographed with 5:95 hexane/ CH_2Cl_2 to provide pure sulfinylimines. All the starting materials (sulfinylimines) are prepared by general procedure and compounds were reported previously.[1]

(S)-N-sulfinylimines 1a-t [1]

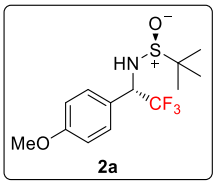


3. General procedure for trifluoromethylation of *N*-sulfinylimines in presence of KHMDS (2)



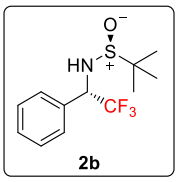
In glove box- prepared a solution of corresponding *N*-sulfinylimine **1** (0.2 mmol) in dry toluene (1 mL) in test tube. To the test tube added the CF_3H (excess) balloon and immersed the tube in −78 °C cooling machine bath for 15 min. After that 2 equiv of KHMDS (0.4 mmol, 0.5 M solution in toluene) was added drop wisely to the reaction mixture for 1 min by plastic syringe and stirred the reaction mixture overnight at −78 °C, it was quenched with 1 mL of saturated NH_4Cl and 3 mL of water. The reaction mixture was carefully warmed to room temperature then extract with ethyl acetate 3 times and combined the organic layers, dried over Na_2SO_4 and concentrated on reduced pressure and calculated the dr by using ^{19}F NMR. The crude was purified by preparative TLC or column chromatography on silica gel (using 8:2 hexane/ethyl acetate solvent system) to give corresponding pure trifluoromethyl sulfinamides **2**.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)propane-2-sulfinamide (2a)



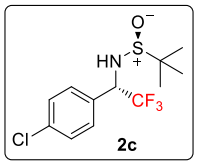
Followed by the general procedure, using *N*-sulfinylimine **1a** (0.2 mmol, 47.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:20, oil, yield 79%; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.81 (qd, *J* = 7.2, 3.4 Hz, 1H), 3.85–3.79 (m, 4H, OCH_3 & NH), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.78, 130.85, 124.71 (q, *J* = 281.2 Hz), 123.36, 114.32, 59.96 (q, *J* = 30.3 Hz), 56.35, 55.43, 22.55; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.76 (d, *J* = 7.9 Hz, 3F); ESI-MS (*m/z*): 310 $[M + H]^+$. Compound is already known. [2a]

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-phenylethyl)propane-2-sulfinamide (2b)



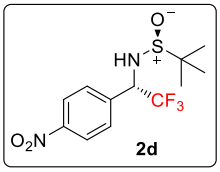
Followed by the general procedure, using *N*-sulfinylimine **1b** (0.2 mmol, 41.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 1:18, colorless oil, yield 60%, ^1H NMR (300 MHz, $CDCl_3$) δ 7.467.38 (m, 5H), 4.87 (qd, *J* = 7.1, 3.7 Hz, 1H), 3.87 (br s, 1H), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.73, 129.91, 129.48, 128.92, 124.61 (q, *J* = 281.4 Hz), 60.60 (q, *J* = 30.4 Hz), 56.50, 22.50; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.40 (d, *J* = 7.0 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{12}H_{16}F_3NOSNa$ $[M + Na]^+$ 302.0802, found 302.0811. Compound is already known.[2b]

(*S*)-*N*-((*S*)-1-(4-Chlorophenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (2c)



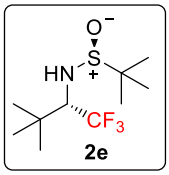
Followed by the general procedure, using *N*-sulfinylimine **1c** (0.2 mmol, 48.7 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:18, colorless oil, yield 60%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.37 (m, 4H), 4.86 (qd, *J* = 7.0, 3.5 Hz, 1H), 3.91 (br s, 1H), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.05, 130.84, 130.21, 129.22, 124.37 (q, *J* = 281.4 Hz), 59.91 (q, *J* = 30.6 Hz), 56.56, 22.47; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.47 (d, *J* = 6.9 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{12}H_{15}ClF_3NOSNa$ $[M + Na]^+$ 336.0413, found 336.0404.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(4-nitrophenyl)ethyl)propane-2-sulfinamide (2d)



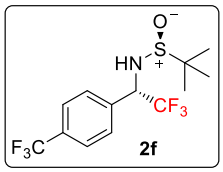
Followed by the general procedure, using *N*-sulfinylimine **1d** (0.2 mmol, 50.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). orange solid, yield 45%, Mixture 1:2 diastereomeric ratio, ^{1}H NMR (300 MHz, $CDCl_3$) major + minor isomer: δ 8.33–8.22 (m, 3H), 7.73–7.63 (m, 3H), 4.85-5.1 (m, 1.5H), 4.15 (s, 1H, major), 4.00 (d, *J* = 7.5 Hz, 0.5H, minor), 1.23 (s, 13.5H); ^{13}C NMR (126 MHz, $CDCl_3$) major + minor isomer: δ 148.78 (major), 148.65 (minor), 140.51 (minor), 138.79 (major), 130.47 (major), 129.45 (minor), 124.40 (minor), 124.27 (q, *J* = 281.7 Hz, minor), 123.96 (q, *J* = 281.7 Hz, major), 123.93 (major), 61.17 (q, *J* = 31.3 Hz, minor), 59.82 (q, *J* = 30.8 Hz, major), 57.54 (minor), 56.79 (major), 22.31 (major); ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.60 (d, *J* = 7.2 Hz, 3F, minor), −73.89 (d, *J* = 6.8 Hz, 3F, major). HRMS (ESI, *m/z*) calculated for $C_{12}H_{15}F_3N_2O_3SNa$ $[M + Na]^+$ 347.0653, found 347.0651.

(*S*)-2-Methyl-*N*-((*S*)-1,1,1-trifluoro-3,3-dimethylbutan-2-yl)propane-2-sulfinamide (2e)



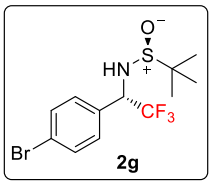
Followed by the general procedure, using *N*-sulfinylimine **1e** (0.2 mmol, 37.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by PLC, dr 1:4, white crystalline solid, yield 55%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.45–3.34 (m, 2H, CH & NH), 1.27 (s, 9H), 1.05 (d, *J* = 1.1 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.79 (q, *J* = 285.5 Hz), 66.36 (q, *J* = 27.0 Hz), 57.71, 35.06, 27.21, 23.09; ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.81 (d, *J* = 7.2 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_{10}H_{20}F_3NOSNa$ $[M + Na]^+$ 282.1115, found 282.1123. Compound is already known.[2b]

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethyl)propane-2-sulfinamide (2f)



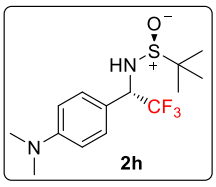
Followed by the general procedure, using *N*-sulfinylimine **1f** (0.2 mmol, 55.4 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by PLC, dr 1:5, white solid, mp 104.6–107.8 °C, yield 42%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.84 (qd, *J* = 9.0, 4.5 Hz, 1H), 3.93 (d, *J* = 2.5 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.74, 132.12 (q, *J* = 32.6 Hz), 129.98, 125.91, 123.84 (q, *J* = 272.3 Hz), 124.27 (q, *J* = 281.6 Hz), 60.11 (q, *J* = 30.6 Hz), 56.72, 22.46; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.64 (d, *J* = 6.9 Hz, 3F), −63.36 (s, 3F). ESI-MS (*m/z*): 348 $[M + H]^+$. Compound is already known.[2a]

(*S*)-*N*-((*S*)-1-(4-Bromophenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (2g)



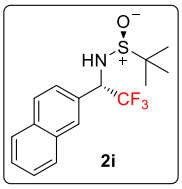
Followed by the general procedure, using *N*-sulfinylimine **1g** (0.2 mmol, 57.6 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:13, brown color oil, yield 52%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.84 (qd, *J* = 7.0, 3.4 Hz, 1H), 3.92 (br s, 1H), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.25, 131.16, 130.77, 124.35, 124.33 (q, *J* = 281.4 Hz), 60.06 (q, *J* = 30.7 Hz), 56.64, 22.53; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.94 (d, *J* = 6.9 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{12}H_{15}BrF_3NOSNa$ $[M + Na]^+$ 379.9908, found 379.9905.

(*S*)-*N*-((*S*)-1-(4-(Dimethylamino)phenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (2h)



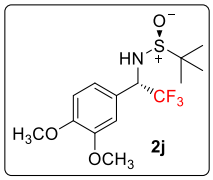
Followed by the general procedure, using *N*-sulfinylimine **1h** (0.2 mmol, 50.4 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (Using 8:3 hexane/ethyl acetate solvent system), dr 1:14, yellow color solid, yield 70%, mp 126.6–129.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.76 (qd, *J* = 7.2, 3.3 Hz, 1H), 3.80 (br s, 1H), 2.98 (s, 6H), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.26, 130.51, 124.92 (q, *J* = 281.3 Hz), 118.04, 112.01, 60.05 (q, *J* = 30.3 Hz), 56.18, 40.32, 22.56; ^{19}F NMR (282 MHz, $CDCl_3$) δ −75.29 (d, *J* = 6.8 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{14}H_{21}F_3N_2OSNa$ $[M + Na]^+$ 345.1224, found 345.1219.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl)propane-2-sulfinamide (2i)



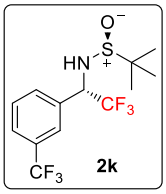
Followed by the general procedure, using *N*-sulfinylimine **1i** (0.2 mmol, 51.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:13, white solid, yield 78%, mp 117.3–118.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.85 (m, 4H), 7.56–7.51 (m, 3H), 5.04 (qd, *J* = 7.1, 3.4 Hz, 1H), 3.94 (d, *J* = 2.2 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.94, 133.06, 130.09, 128.97, 128.84, 128.38, 127.89, 127.26, 126.83, 125.69, 124.72 (q, *J* = 281.5 Hz), 60.80 (q, *J* = 30.6 Hz), 56.50, 22.53; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.55 (d, *J* = 7.1 Hz, 3F). ESI-MS (*m/z*): 330.38 $[M + H]^+$. Compound is already known.[2a]

(*S*)-*N*-((*S*)-1-(3,4-Dimethoxyphenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (2j)



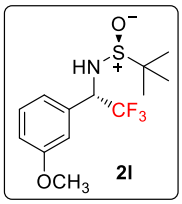
Followed by the general procedure, using *N*-sulfinylimine **1j** (0.2 mmol, 53.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 1:14, white solid, yield 74%, mp 125.5–127.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.92 (d-like, *J* = 1.2 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.81 (qd, *J* = 7.1, 2.9 Hz, 1H), 3.88 (s, 3H), 3.91 (s, 3H), 3.81 (br s, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.29, 149.21, 124.67 (q, *J* = 281.2 Hz), 123.61, 122.64, 111.92, 111.03, 60.12 (q, *J* = 30.5 Hz), 56.32, 56.00, 55.99, 22.53; ^{19}F NMR (282 MHz, $CDCl_3$) δ −75.03 (d, *J* = 6.8 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{14}H_{20}F_3NO_3SNa$ $[M + Na]^+$ 362.1014, found 362.1013.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(3-(trifluoromethyl)phenyl)ethyl)propane-2-sulfinamide (2k)



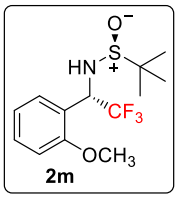
Followed by the general procedure, using *N*-sulfinylimine **1k** (0.2 mmol, 55.4 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by PLC. dr 1:5, colorless oil, yield 36%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74–7.67 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 4.97 (qd, *J* = 7.0, 3.2 Hz, 1H), 3.92 (br s, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.04, 132.92, 131.48 (q, *J* = 32.7 Hz, 1H), 129.52, 126.81, 126.31, 124.24 (q, *J* = 281.4 Hz), 123.82 (q, *J* = 272.4 Hz), 60.06 (q, *J* = 30.7 Hz), 56.72, 22.44; ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.14 (s, 3F), −74.64 (d, *J* = 6.9 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{13}H_{15}F_6NOSNa$ $[M + Na]^+$ 370.0676, found 370.0677.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(3-methoxyphenyl)ethyl)propane-2-sulfinamide (2l)



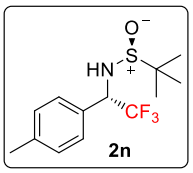
Followed by the general procedure, using *N*-sulfinylimine **1l** (0.2 mmol, 47.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 1:11, colorless oil, yield 64%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.28 (m, 1H), 7.04–6.92 (m, 3H), 4.84 (qd, *J* = 7.0, 3.5 Hz, 1H), 3.86–3.75 (m, 4H, OCH_3 & NH), 1.24 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.86, 133.14, 129.95, 124.55 (q, *J* = 281.4 Hz), 121.78, 115.26, 115.11, 60.52 (q, *J* = 30.5 Hz), 56.53, 55.41, 22.51; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.78 (d, *J* = 6.9 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{13}H_{18}F_3NO_2SNa$ [M + Na]$^+$ 332.0908, found 332.0907.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(2-methoxyphenyl)ethyl)propane-2-sulfinamide (2m)



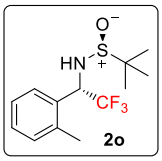
Followed by the general procedure, using *N*-sulfinylimine **1m** (0.2 mmol, 47.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 9:1, colorless oil, yield 61%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.32 (m, 2H), 7.03–6.91 (m, 2H), 5.43–5.31 (m, 1H), 4.14 (br s, 1H), 3.87 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.89, 130.88, 129.54, 124.92 (q, *J* = 282.2 Hz), 120.89, 120.82, 111.42, 56.62, 55.94, 54.72, 22.46; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.40 (d, *J* = 7.3 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{13}H_{18}F_3NO_2SNa$ [M + Na]$^+$ 332.0908, found 332.0917.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(*p*-tolyl)ethyl)propane-2-sulfinamide (2n)



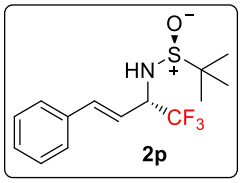
Followed by the general procedure, using *N*-sulfinylimine **1n** (0.2 mmol, 44.6 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:8, Colorless oil, yield 68%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.83 (qd, *J* = 7.1, 3.6 Hz, 1H), 3.87 (br s, 1H), 2.38 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.96, 129.64, 129.38, 128.61, 124.67 (q, *J* = 281.4 Hz), 60.35 (q, *J* = 30.4 Hz), 56.45, 22.52, 21.41; ^{19}F NMR (282 MHz, $CDCl_3$) δ −75.04 (d, *J* = 7.0 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{13}H_{18}F_3NOSNa$ [M + Na]$^+$ 316.0959, found 316.0952.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(o-tolyl)ethyl)propane-2-sulfinamide (2o)



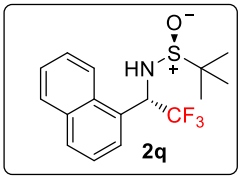
Followed by the general procedure, using *N*-sulfinylimine **1o** (0.2 mmol, 44.6 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:7, white solid, yield 45%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 1H), 7.35–7.19 (m, 3H), 5.19 (qd, *J* = 7.1, 3.7 Hz, 1H), 3.88 (br s, 1H), 2.44 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.22, 131.03, 130.10, 129.58, 128.68, 126.50, 125.06 (q, *J* = 281.6 Hz), 56.42, 55.56 (q, *J* = 29.6 Hz), 22.51, 19.87; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.39 (d, *J* = 6.5 Hz, 3F). MS (ESI, *m/z*) 294 $[M + H]^+$. Compound is already known.[2a]

(*S*)-2-Methyl-*N*-((*S*,*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)propane-2-sulfinamide (2p)



Followed by the general procedure, using *N*-sulfinylimine **1p** (0.2 mmol, 47.0 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 1:13, yellow solid, yield 34%, mp 42–43 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.28 (m, 5H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.04 (dd, *J* = 15.9, 8.3 Hz, 1H), 4.54–4.40 (m, 1H), 3.74 (d, *J* = 3.7 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.08, 135.33, 129.07, 128.88, 127.16, 124.58 (q, *J* = 281.4 Hz), 118.66, 59.51 (q, *J* = 30.8 Hz), 56.53, 22.59; ^{19}F NMR (282 MHz, $CDCl_3$) δ −75.94 (d, *J* = 6.7 Hz, 3F). HRMS (ESI, *m/z*) calculated for $C_{14}H_{18}F_3NOSNa$ $[M + Na]^+$ 328.0959, found 328.0962.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(naphthalen-1-yl)ethyl)propane-2-sulfinamide (2q)



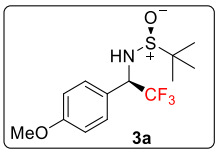
Followed by the general procedure, using *N*-sulfinylimine **1q** (0.2 mmol, 51.8 mg, 1 equiv), fluoroform excess and KHMDS (0.4 mmol, 2 equiv, 0.5 M solution in toluene) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system), dr 1:7, yield 78%, 1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.92 (t, *J* = 6.8 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.64–7.47 (m, 3H), 5.78 (br s, 1H), 4.08–3.94 (m, 1H), 1.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.97, 131.94, 130.49, 129.24, 127.25, 127.93, 126.25, 125.15, 125.04 (q, *J* = 282.1 Hz), 122.53, 56.66, 55.07, 22.52; ^{19}F NMR1 (282 MHz, $CDCl_3$) δ −73.43 (s, 1F); MS (ESI, *m/z*) 330 $[M + H]^+$. Compound is already known.[2b]

4. General procedure for synthesis of trifluoromethylation of azomethine in presence of P_4-*t*Bu (3)

In glove box- prepared a solution of corresponding sulfinimine **1** (0.2 mmol, 1 equiv) in dry toluene (1 mL) in test tube. To the test tube added the CF_3H (excess) balloon and immersed the tube in −78 °C cooling machine bath for 15 min. After that 1.1 eq. of P_4-*t*Bu (0.22 mmol, 0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) was added drop wisely to the reaction mixture for 1 min by plastic syringe and stirred the reaction mixture overnight at −78 °C, it was quenched with 1 ml of saturated NH_4Cl

and 3 ml of water. The reaction mixture was carefully warmed to room temperature then extract with ethyl acetate 3 times and combined the organic layers, dried over Na_2SO_4 and concentrated on reduced pressure and dr was calculated by using ^{19}F NMR. The crude was purified by column chromatography on silica gel (ethylacetate/hexane = 2/8) to give corresponding pure trifluoromethyl sulfinamides **3**.

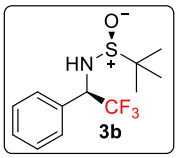
(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)propane-2-sulfinamide (3a)



3a

Followed by the general procedure, using *N*-sulfinylimine **1a** (0.2 mmol, 47.8 mg, 1 equiv), fluoroform excess and P4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 34:1, white solid, yield 85%, mp 125–126 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.84–4.72 (m, 1H), 3.81 (s, 3H), 3.53 (d, *J* = 5.7 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.51, 129.34, 125.87, 124.80 (q, *J* = 281.3 Hz), 114.67, 60.96 (q, *J* = 30.7 Hz), 57.00, 55.46, 22.46; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.67 (d, *J* = 7.4 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_{13}H_{18}F_3NO_2SNa$ [M + Na]$^+$ 332.0908, found 332.0907.

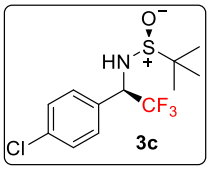
(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-phenylethyl)propane-2-sulfinamide (3b)



3b

Followed by the general procedure, using *N*-sulfinylimine **1b** (0.2 mmol, 41.8 mg, 1 equiv), fluoroform excess and P4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 23:1, white solid, yield 64%, ^1H NMR (300 MHz, $CDCl_3$) δ 7.48–7.35 (m, 5H), 4.90–4.77 (m, 1H), 3.62 (d, *J* = 5.4 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.80, 129.75, 129.34, 128.06, 124.73 (q, *J* = 281.5 Hz), 61.53 (q, *J* = 30.8 Hz), 57.09, 22.47; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.52 (d, *J* = 7.3 Hz, 3F). MS (ESI, *m/z*) 280 [M + H]$^+$. Compound is already known.[2c]

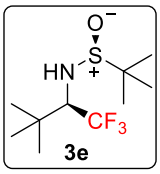
(*S*)-*N*-((*R*)-1-(4-Chlorophenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3c)



3c

Followed by the general procedure, using *N*-sulfinylimine **1c** (0.2 mmol, 53.1 mg, 1 equiv), fluoroform excess and P4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 41:1, white solid, yield 79%, mp 156–157 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 7.5–7.29 (m, 4H), 4.91–4.74 (m, 1H), 3.59 (d, *J* = 6.5 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.93, 132.28, 129.62, 129.49, 124.52 (q, *J* = 281.4 Hz), 61.04 (q, *J* = 31.0 Hz), 57.23, 22.47; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.54 (d, *J* = 7.2 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_{12}H_{15}ClF_3NOSNa$ [M + Na]$^+$ 336.0413, found 336.0405.

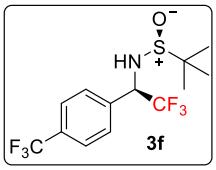
(*S*)-2-Methyl-*N*-((*R*)-1,1,1-trifluoro-3,3-dimethylbutan-2-yl)propane-2-sulfinamide (3e)



3e

Followed by the general procedure, using *N*-sulfinylimine **1e** (0.2 mmol, 37.8 mg, 1 equiv), fluoroform excess and P$_4$-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by PLC. dr 49:1, yield 61%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58–3.24 (m, 2H), 1.25 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.92 (q, *J* = 283.6 Hz), 66.32 (q, *J* = 26.8 Hz), 57.14, 33.65, 27.52, 22.61; ^{19}F NMR (282 MHz, $CDCl_3$) δ −68.89 (d, *J* = 6.7 Hz, 3F); MS (ESI, *m/z*) 260 $[M + H]^+$. Compound is already known.[2c]

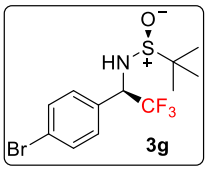
(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethyl)propane-2-sulfinamide (3f)



3f

Followed by the general procedure, using *N*-sulfinylimine **1f** (0.2 mmol, 55.4 mg, 1 equiv), fluoroform excess and P$_4$-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 21:1, white solid, yield 80%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 4.98–4.83 (m, 1H), 3.67 (d, *J* = 6.8 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.56, 131.96 (q, *J* = 32.9 Hz),128.64, 126.36, 124.41 (q, *J* = 281.5 Hz),123.76 (q, *J* = 272.5 Hz), 61.31 (q, *J* = 31.0 Hz), 57.33, 22.44; ^{19}F NMR (282 MHz, $CDCl_3$) δ − 63.49 (s, 3F), −74.30 (d, *J* = 7.1 Hz, 3F); MS (ESI, *m/z*) 348 $[M + H]^+$. Compound is already known.[2c]

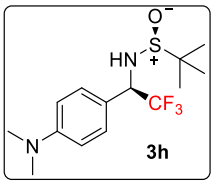
(*S*)-*N*-((*R*)-1-(4-Bromophenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3g)



3g

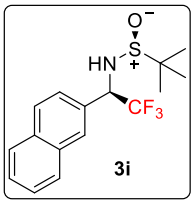
Followed by the general procedure, using *N*-sulfinylimine **1g** (0.2 mmol, 57.6 mg, 1 equiv), fluoroform excess and P$_4$-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 24:1, white solid, yield 80%, mp 170.4-171.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.85–4.74 (m, 1H), 3.60 (d, *J* = 6.4 Hz, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.78, 132.57, 129.75, 124.45 (q, *J* = 281.3 Hz), 124.12, 61.09 (q, *J* = 31.0 Hz), 57.22, 22.46; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.51 (d, *J* = 7.4 Hz, 3F); MS (ESI, *m/z*) 358 $[M + H]^+$. Compound is already known.[2c]

(*S*)-*N*-((*R*)-1-(4-(Dimethylamino)phenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3h)



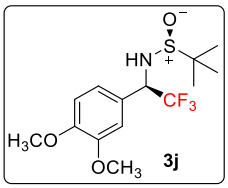
Followed by the general procedure, using *N*-sulfinylimine **1h** (0.2 mmol, 50.4 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 6:1, white solid, yield 79%, mp 143.2-147.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.77–4.69 (m, 1H), 3.50 (d, *J* = 5.2 Hz, 1H), 2.96 (s, 6H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.14, 128.87, 125.02 (q, *J* = 281.2 Hz), 120.90, 112.51, 60.94 (q, *J* = 30.5 Hz), 56.86, 40.42, 22.49; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.68 (d, *J* = 7.0 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_{14}H_{21}F_3N_2OSNa$ [M + Na]$^+$ 345.1224, found 345.1224.

(*S*)-2-Methyl-*N*-((*S*)-2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl)propane-2-sulfinamide (3i)



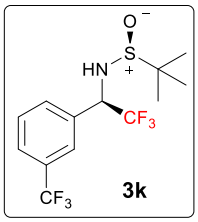
Followed by the general procedure, using *N*-sulfinylimine **1i** (0.2 mmol, 51.8 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 20:1, white solid, yield 75%, mp 151.6-152.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93–7.83 (m, 4H), 7.56 – 7.49 (m, 3H), 5.05–4.95 (m, 1H), 3.72 (d, *J* = 6.0 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.69, 133.19, 131.02, 129.44, 128.44, 127.99, 127.87, 127.25, 126.96, 124.85 (q, *J* = 281.5 Hz), 124.83, 61.71 (q, *J* = 30.8 Hz), 57.15, 22.51; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.12 (d, *J* = 7.4 Hz, 3F); MS (ESI, *m/z*) 330 [M + H]$^+$. Compound is already known.[2c]

(*S*)-*N*-((*R*)-1-(3,4-Dimethoxyphenyl)-2,2,2-trifluoroethyl)-2-methylpropane-2-sulfinamide (3j)



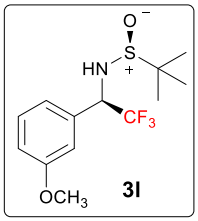
Followed by the general procedure, using *N*-sulfinylimine **1j** (0.2 mmol, 53.8 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 44:1, white solid, yield 87%, mp 142.7–145.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 4.81–4.74 (m, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.56 (d, *J* = 5.8 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.07, 149.45, 124.81 (q, *J* = 281.3 Hz), 126.19, 120.41, 111.48, 111.23, 61.32 (q, *J* = 30.7 Hz), 57.04, 56.16, 56.07, 22.49; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.39 (d, *J* = 6.7 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_{14}H_{20}F_3NO_3SNa$ [M + Na]$^+$ 362.1014, found 362.1014.

(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(3-(trifluoromethyl)phenyl)ethyl)propane-2-sulfinamide (3k)



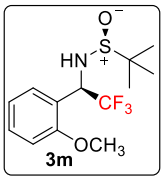
Followed by the general procedure, using *N*-sulfinylimine **1k** (0.2 mmol, 55.4 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 23:1, white solid, yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74–7.62 (m, 3H), 7.58 (d, *J* = 7.9 Hz, 1H), 4.96–4.86 (m, 1H), 3.67 (d, *J* = 6.9 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.76, 132.04 (q, *J* = 32.8 Hz), 131.67, 130.01, 126.73, 124.92, 124.40 (q, *J* = 281.5 Hz), 123.71 (q, *J* = 272.5 Hz), 61.28 (q, *J* = 31.1 Hz), 57.34, 22.44; ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.27 (s, 3F), −74.41 (d, *J* = 7.2 Hz, 3F); MS (ESI, *m/z*) 348 $[M + H]^+$.

(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(3-methoxyphenyl)ethyl)propane-2-sulfinamide (3l)



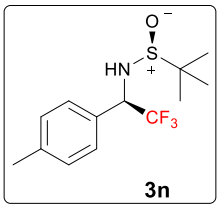
Followed by the general procedure, using *N*-sulfinylimine **1l** (0.2 mmol, 47.8 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 63:1, colorless oil, yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.17 (m, 1H), 7.09–6.83 (m, 3H), 4.89–4.66 (m, 1H), 3.82 (s, 3H), 3.63 (d, *J* = 5.8 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.08, 135.16, 130.44, 124.68 (q, *J* = 281.4 Hz), 120.12, 114.95, 114.07, 61.48 (q, *J* = 30.8 Hz), 57.07, 55.46, 22.46; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.38 (d, *J* = 7.3 Hz, 3F); MS (ESI, *m/z*) 310 $[M + H]^+$.

(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(2-methoxyphenyl)ethyl)propane-2-sulfinamide (3m)



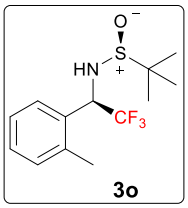
Followed by the general procedure, using *N*-sulfinylimine **1m** (0.2 mmol, 47.8 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 23:1, white solid, yield 88%, mp 121-122 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.22 (m, 2H), 7.03–6.89 (m, 2H), 5.32–5.15 (m, 1H), 4.24 (d, *J* = 7.8 Hz, 1H), 3.89 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.30, 130.83, 128.80, 125.02 (q, *J* = 281.6 Hz), 122.14, 121.20, 111.76, 57.23 (q, *J* = 31.6 Hz), 56.98, 55.92, 22.54; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.60 (d, *J* = 7.9 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_{13}H_{18}F_3NO_2SNa$ $[M + Na]^+$ 332.0908, found 332.0910.

(S)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(*p*-tolyl)ethyl)propane-2-sulfinamide (3n)



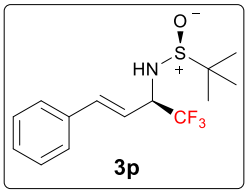
Followed by the general procedure, using *N*-sulfinylimine **1n** (0.2 mmol, 44.6 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 48:1, white solid, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.86–4.72 (m, 1H), 3.58 (d, *J* = 5.7 Hz, 1H), 2.36 (s, 3H) 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.74, 130.86, 129.99, 127.91, 124.78 (q, *J* = 281.2 Hz), 61.28 (q, *J* = 30.7 Hz), 57.00, 22.46, 21.32; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.59 (d, *J* = 7.4 Hz, 3F); MS (ESI, *m/z*) 294 $[M + H]^+$.

(*S*)-2-Methyl-*N*-((*R*)-2,2,2-trifluoro-1-(*o*-tolyl)ethyl)propane-2-sulfinamide (3o)



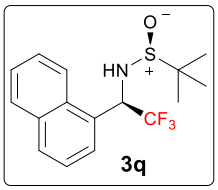
Followed by the general procedure, using *N*-sulfinylimine **1o** (0.2 mmol, 44.6 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 35:1, white solid, yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.9 Hz, 1H), 7.32–7.17 (m, 3H), 5.19–5.02 (m, 1H), 3.55 (d, *J* = 4.9 Hz, 1H), 2.47 (s, 1H), 1.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.06, 132.56, 131.35, 129.56, 127.80 (q, *J* = 289.9 Hz), 127.03, 126.38, 56.98, 56.46 (q, *J* = 30.8 Hz), 22.46, 19.90; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.59 (d, *J* = 7.4 Hz, 3F); MS (ESI, *m/z*) 294 $[M + H]^+$.

(*S*)-2-Methyl-*N*-((*R,E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)propane-2-sulfinamide (3p)



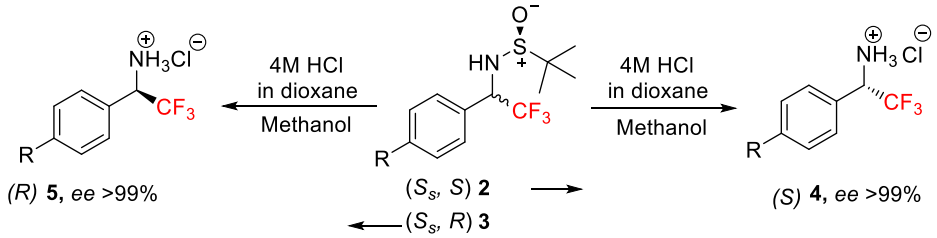
Followed by the general procedure, using *N*-sulfinylimine **1p** (0.2 mmol, 47.0 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 14:1, white solid, yield 79%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.24 (m, 5H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 6.5 Hz, 1H), 4.55–4.41 (m, 1H), 3.46 (d, *J* = 7.6 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.39, 135.35, 128.94, 128.82, 127.09, 124.68 (q, *J* = 281.2 Hz), 120.23, 60.54 (q, *J* = 30.8 Hz), 57.18, 22.51; ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.29 (d, *J* = 7.2 Hz, 3F); MS (ESI, *m/z*) 306 $[M + H]^+$.

(*S*)-2-Methyl-*N*-((R)-2,2,2-trifluoro-1-(naphthalen-1-yl)ethyl)propane-2-sulfinamide (3q)



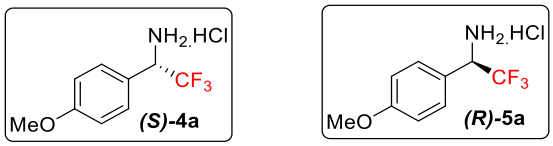
Followed by the general procedure, using *N*-sulfinylimine **1q** (0.2 mmol, 51.8 mg, 1 equiv), fluoroform excess and P_4-*t*Bu (0.22 mmol, 1.1 equiv, 0.8 M solution in hexane) in 1 mL toluene at −78 °C stirred for overnight, the crude product was purified by column chromatography (using 8:2 hexane/ethyl acetate solvent system). dr 13:1, white solid, yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 1H), 8.00–7.81 (m, 2H), 7.74–7.42 (m, 4H), 5.81–5.61 (m, 1H), 3.77 (d, *J* = 4.8 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.09, 130.97, 130.58, 129.86, 129.32, 127.52, 126.49, 125.55, 125.26, 125.18 (q, *J* = 282.2 Hz), 122.65, 57.16, 56.08, 22.48; ^{19}F NMR (282 MHz, $CDCl_3$) δ −73.20 (d, *J* = 6.0 Hz, 3F); MS (ESI, *m/z*) 330 [M + H]$^+$.

5. General procedure for synthesis of 2,2,2-trifluoro-1-arylethan-1-amine hydrochlorides (4 & 5)



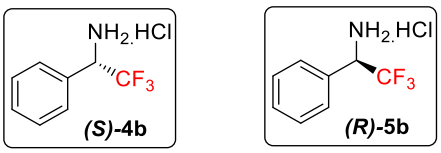
To a solution of sulfinamide derivative **2** or **3** (0.2 mmol) in 1 mL of MeOH was added 0.4 mmol of 4M HCl in 1, 4-dioxane solution. The mixture was stirred at room temperature for 30 min. Diethyl ether was added to precipitate the amine hydrochlorides (in some cases the reaction mixture was concentrated to near dryness before the addition of diethyl ether to ensure a high yield of amine hydrochlorides). The precipitate was then filtered off and washed with diethyl ether or hexanes and precipitate was dried under vacuum for 1–3 h to provide pure amine hydrochloride **4** or **5**.

(*S/R*)-2,2,2-Trifluoro-1-(4-methoxyphenyl)ethan-1-amine hydrochloride (4a/5a)



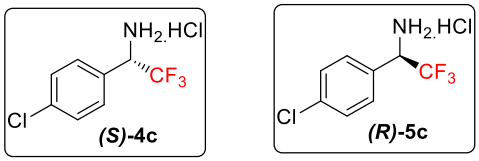
4a-*(S)*: white solid, yield 82%, $[\alpha]_D^{25}$ = + 15.4 (*c* = 0.23, MeOH), >99% ee; **5a-*(R)*:** white solid, yield 92%, $[\alpha]_D^{25}$ = −18.5 (*c* = 0.59, MeOH); >99% ee; by chiral HPLC (CHIRALCEL OD-H, eluent Hexane/2-Propanol/Diethylamine 98/2/0.1, wavelength= 270, 0.5 ml/min); ^{1}H NMR (300 MHz, CD_3OD) δ 7.52 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 5.31 (q, *J* = 7.5 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 163.03, 131.24, 121.13, 124.92 (q, *J* = 280.3 Hz), 115.86, 56.29 (q, *J* = 32.5 Hz), 56.01; ^{19}F NMR (282 MHz, CD_3OD) δ −75.03 (d, *J* = 8.0 Hz, 3F); HRMS (ESI, *m/z*) calculated for $C_9H_{11}F_3NO$ $[M - Cl]^+$ 206.0793, found 206.0795.

(*S/R*)-2,2,2-Trifluoro-1-phenylethan-1-amine hydrochloride (4b/5b)



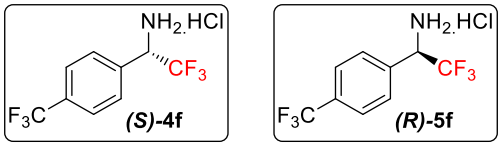
4b-*(S)*: white solid, yield 91%, $[\alpha]_D^{25}$ = +18.8 (*c* = 1.00, MeOH), >99% ee; **5b-*(R)*:** white solid, yield 93%, $[\alpha]_D^{25}$ = −16.1 (*c* = 0.40, MeOH), >99% ee by chiral HPLC (CHIRALCEL OD-3, eluent Hexane/2-Propanol/Diethylamine 70/30/0.1, wavelength = 254, 1 ml/min); ^{1}H NMR (300 MHz, CD_3OD) δ 7.59–7.53 (s, 5H), 5.45–5.29 (m, 1H); ^{13}C NMR (126 MHz, CD_3OD) δ 132.09, 130.62, 129.66, 129.54, 124.84 (q, *J* = 280.1 Hz), 56.68 (q, *J* = 32.6 Hz); ^{19}F NMR (282 MHz, CD_3OD) δ −74.96 (s, 3F); HRMS (ESI, *m/z*) calculated for $C_8H_9F_3N$ $[M - Cl]^+$ 176.0687, found 176.0681.[2c]

(*S/R*)-1-(4-Chlorophenyl)-2,2,2-trifluoroethan-1-amine hydrochloride (4c/5c)



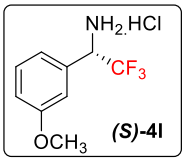
4c-*(S)*: white solid, yield 87%, $[\alpha]_D^{25}$ = +18.6 (*c* = 0.72, MeOH) >99% ee; **5c-*(R)*:** white solid, yield 94%, $[\alpha]_D^{25}$ = −17.8 (*c* = 0.64, MeOH) >99% ee by chiral HPLC (CHIRALCEL OD-H, eluent Hexane/2-Propanol/Diethylamine 98/2/0.1, wavelength = 270, 0.5 ml/min); ^{1}H NMR (300 MHz, CD_3OD) δ 7.66–7.50 (m, 4H), 5.51–5.35 (m, 1H); ^{13}C NMR (126 MHz, CD_3OD) δ 138.34, 131.35, 130.85, 128.25, 124.66 (q, *J* = 280.4 Hz), 56.02 (q, *J* = 32.8 Hz); ^{19}F NMR (282 MHz, CD_3OD) δ −74.95 (s, 3F); HRMS (ESI, *m/z*) calculated for $C_8H_8ClF_3N$ $[M - Cl]^+$ 210.0297, found 210.0306. [2c]

(*S/R*)-2,2,2-Trifluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-amine hydrochloride (4f/5f)



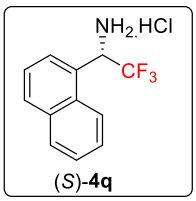
4f-*(S)*: white solid, yield 70%, $[\alpha]_D^{25}$ = + 13.2 (*c* = 0.68, MeOH), >97% ee; **5f-*(R)*:** white solid, yield 94%, $[\alpha]_D^{25}$ = −12.4 (*c* = 0.67, MeOH) 99% ee by chiral HPLC (CHIRALCEL OD-H, eluent Hexane/2-Propanol/Diethylamine 98/2/0.1, wavelength = 254, 0.5 ml/min);^{1}H NMR (300 MHz, CD_3OD) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 5.59 (q, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, CD_3OD) δ 133.93 (q, *J* = 32.8 Hz), 133.78, 130.68, 127.51 (q, *J* = 3.5 Hz),125.08 (q, *J* = 271.7 Hz), 124.60 (q, *J* = 280.5 Hz), 56.16 (q, *J* = 32.8 Hz); ^{19}F NMR (282 MHz, CD_3OD) δ -64.62 (s, 3F), −74.63 (d, *J* = 7.3 Hz, 3F); MS (ESI, *m/z*) 278 $[M - H]^-$. Compound is already known.[2c]

(S)-2,2,2-Trifluoro-1-(3-methoxyphenyl)ethan-1-amine hydrochloride (4l)



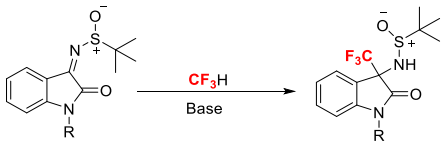
4l-*(S)*: white solid, yield 96%, $[\alpha]_D^{25}$ = + 16.1 (*c* = 1.15, MeOH), >99% ee by chiral HPLC (CHIRALCEL OD-3, eluent Hexane/2-Propanol/Diethylamine 70/30/0.1, wavelength = 270, 1.0 ml/min); 1H NMR (300 MHz, CD_3OD) δ 7.46 (t, *J* = 8.2 Hz, 1H), 7.20–7.07 (m, 3H), 5.33 (q, *J* = 7.5 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 161.83, 131.80, 130.76, 124.81 (q, *J* = 280.3 Hz), 121.50, 117.31, 115.43, 56.59 (q, *J* = 32.6 Hz), 56.00; ^{19}F NMR (282 MHz, CD_3OD) δ −74.86 (s, 3F); MS (ESI, *m/z*) 206 $[M - Cl]^+$. Compound is already known.[2d]

(*S*)-2,2,2-Trifluoro-1-(naphthalen-1-yl)ethan-1-amine hydrochloride (4q)



4q-*(S)*: white solid, yield 87%, $[\alpha]_D^{25}$ = − 15 (*c* = 0.68, MeOH), >99% ee by chiral HPLC (CHIRALCEL OD-3, eluent Hexane/2-Propanol/Diethylamine 70/30/0.1, wavelength = 270, 1.0 ml/min); ^{1}H NMR (300 MHz, CD_3OD) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.75–7.60 (m, 3H), 6.30 (q, *J* = 7.0 Hz, 1H); ^{13}C NMR (126 MHz, CD_3OD) δ 135.47, 132.75, 132.65, 130.37, 129.02, 127.93, 126.95, 126.21, 125.67, 125.16 (q, *J* = 281.1 Hz), 123.37, 51.84 (q, *J* = 31.9 Hz); ^{19}F NMR (282 MHz, CD_3OD) δ −71.20 (s, 3F); MS (ESI, *m/z*) 226 $[M - Cl]^+$. Compound is already known.[2e]

6. Optimization data for trifluoromethylation of isatin derived ketemines



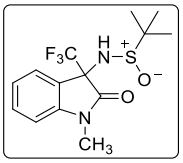
1r; R = Me
1s; R = H
1t; R = Bn

6a; R = Me
6b; R = H
6c; R = Bn

Entry	R	Base	Solvent	T (°C)	Yield (%)	dr
1	CH_3	KHMDS (2 equiv)	Toluene	−78	39%	1:1
2	CH_3	P_4-Base (1.1 equiv)	Toluene	−78	79%	1:1.5
3	CH_3	KHMDS (2 equiv)	THF	−78	20%	1:1-
4	CH_3	P_4-Base (1.1 equiv)	THF	−78	40%	1:1.5
5	H	KHMDS (2 equiv)	Toluene	−78	28%	1:1
6	H	P_4-Base (1.1 equiv)	Toluene	−78	42%	1:2
7	H	KHMDS (2 equiv)	Toluene	rt	-	-
8	H	P_4-Base (1.1 equiv)	Toluene	rt	-	-
9	Bn	KHMDS (2 equiv)	Toluene	−78	50%	1:1
10	Bn	P_4-Base (1.1 equiv)	Toluene	−78	51%	1:2

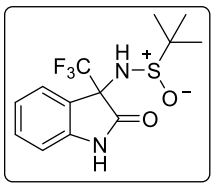
[a] Reaction conditions: ketemine (0.2 mmol), CF_3H (excess), P_4-*t*Bu in hexane (1.1 equi) in toluene (1.5 mL) or KHMDS in toluene (0.4 mmol, 2 equiv) at −78 °C for overnight. Isolated yield of total diastereomeric mixture. Diastereomeric ratios were determined by ^{19}F NMR spectroscopy on the crude reaction mixture.

2-Methyl-*N*-(1-methyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)propane-2-sulfinamide (6a)



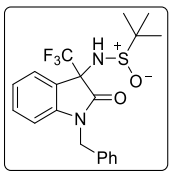
Followed by the general procedure by using P_4-tBu base. Yellow color solid, de = 1:1.12, yield = 79%; mp 95.2–96.5 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.43 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 4.64 (br s, 1H), 3.27 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.81, 145.28, 132.12, 128.03, 123.17, 123.07 (q, *J* = 283.4 Hz), 64.30 (q, *J* = 30.3 Hz), 118.83, 109.52, 56.45, 27.02, 22.50; ^{19}F NMR (282 MHz, $CDCl_3$) δ −77.55 (s, 3F); HRMS (ESI, *m/z*) calculated for $C_{14}H_{17}F_3N_2O_2SNa$ $[M + Na]^+$ 357.0861, found 357.0854.

2-Methyl-N-(2-oxo-3-(trifluoromethyl)indolin-3-yl)propane-2-sulfinamide (6b)



Yellow color solid, dr = 1:2, Yield = 42%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.61 (d, *J*=7.5 Hz, 1H), 7.40 (t, *J*=7.8 Hz, 1H), 7.15 (t, *J*=7.7 Hz, 1H), 6.96 (d, *J*=7.8 Hz, 1H), 4.32 (br s, 1H), 1.20 (s, 9H); ^{19}F NMR (282 MHz, cdcl$_3$) δ = -76.39 (s, 3F); MS (ESI, *m/z*) 321 $[M + H]^+$. Compound is already known.[1f]

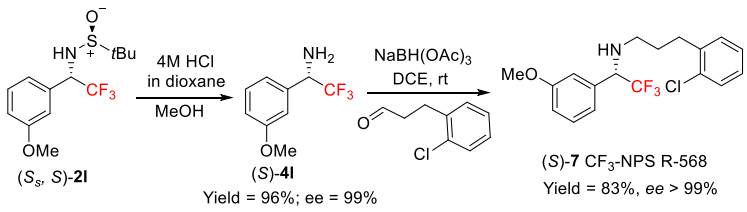
***N*-(1-Benzyl-2-oxo-3-(trifluoromethyl)indolin-3-yl)-2-methylpropane-2-sulfinamide (6c)**



Followed by the general procedure by using P$_4$-*t*Bu base. Yellow color solid, de = 1:2, yield = 51%; mp 130.5–132.1 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.39–7.22 (m, 6H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 5.01, 4.89 (J_{AB} = 15.8 Hz, 2H), 4.36 (br s, 1H), 1.17 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.52, 143.34, 134.44, 131.65, 128.94, 128.00, 127.57, 127.00, 123.51, 121.30, 123.10 (q, *J* = 285.3 Hz), 110.21, 64.53 (q, *J* = 30.7 Hz), 57.20, 44.15, 22.19; ^{19}F NMR (282 MHz, $CDCl_3$) δ −76.27 (s, 3F); HRMS (ESI, *m/z*) calculated for $C_{20}H_{21}F_3N_2O_2SNa$ $[M + Na]^+$ 433.1174, found 433.1176.

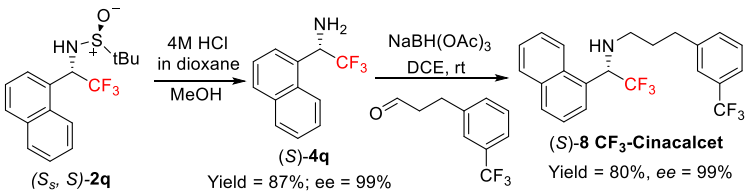
7. Applications:

a) General procedure for the synthesis of CF_3- NPS R-568 drug analogue 7



CF_3- NPS R-568 drug analogue compound **7** was synthesized by following the general procedure from *Angew. Chem. Int. Ed.* 2011, **50**, 8180–8183. Colorless oil, yield 83%, $[\alpha]_D^{25}$ = + 51.7 (*c* = 0.44, $CHCl_3$), >99% ee by chiral HPLC (CHIRALCEL OD-3, eluent Hexane/2-Propanol 90/10, wavelength = 254, 1.0 ml/min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 2H), 7.21–7.11 (m, 3H), 6.99–6.88 (m, 3H), 4.05 (q, *J* = 7.4, 1H), 3.82 (s, 3H), 2.70–2.53 (m, 4H), 1.88–1.71 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.91, 141.91, 130.51, 129.80, 129.62, 128.50, 127.52, 126.90, 125.99, 125.46 (q, *J* = 281.4 Hz), 120.94, 114.36, 114.23, 64.77 (q, *J* = 28.7 Hz), 55.42, 47.25, 33.38, 31.66; ^{19}F NMR (282 MHz, $CDCl_3$) δ −74.49 (d, *J* = 7.4 Hz). Compound is already known. [2d]

b) General procedure for the synthesis of CF_3- Cinacalcet drug analogue 8



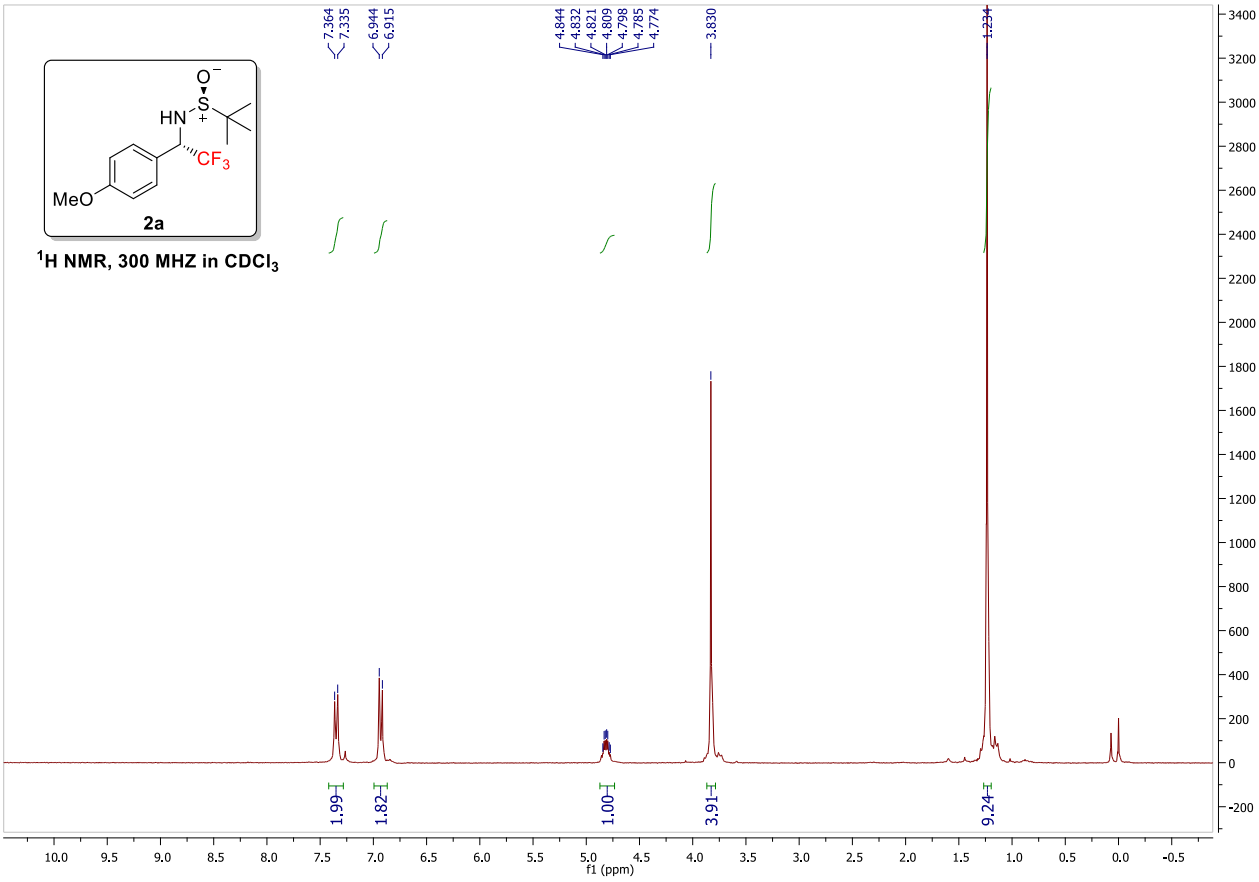
CF_3- cinacalcet drug analogue compound **8** was synthesized by following the general procedure from *J. Org. Chem.,* 2016*,* **81***,* 4923−4930. Colorless oil, yield 80%, $[\alpha]_D^{25}$ = −5.89 (*c* = 0.48, $CHCl_3$), >99% ee by chiral HPLC (CHIRALPAK IA, eluent Hexane/2-Propanol 98/2, wavelegth = 254, 0.5 ml/min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.49 (m, 3H), 7.45–7.25 (m, 4H), 5.05 (q, *J* = 7.3 Hz, 1H), 2.84 – 2.48 (m, 4H), 1.95 – 1.66 (m, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.78, 133.98, 132.28, 131.90, 130.75, 130.75 (q, *J* = 32.1 Hz), 129.63, 129.24, 128.87, 126.84, 125.96, 125.92 (q, *J* = 282.5 Hz), 125.80, 125.47, 125.17, 122.89, 122.77, 122.17 (q, *J* = 272.8 Hz), 59.33, 47.28, 33.10, 31.64; ^{19}F NMR (282 MHz, $CDCl_3$) δ − 62.60 (s, 3F), −72.97 (d, *J* = 5.1 Hz, 3F). Compound is already known. [2e]

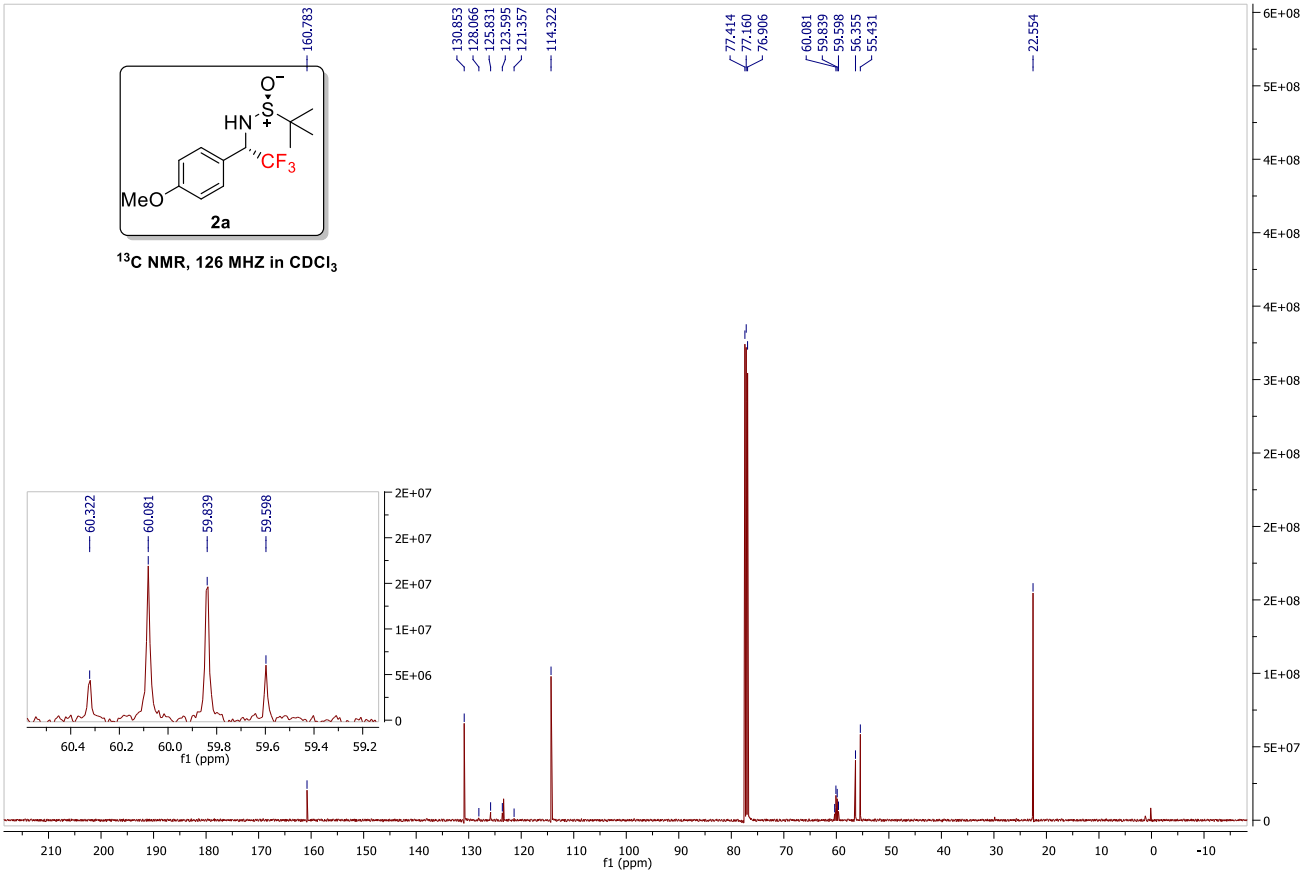
8. References

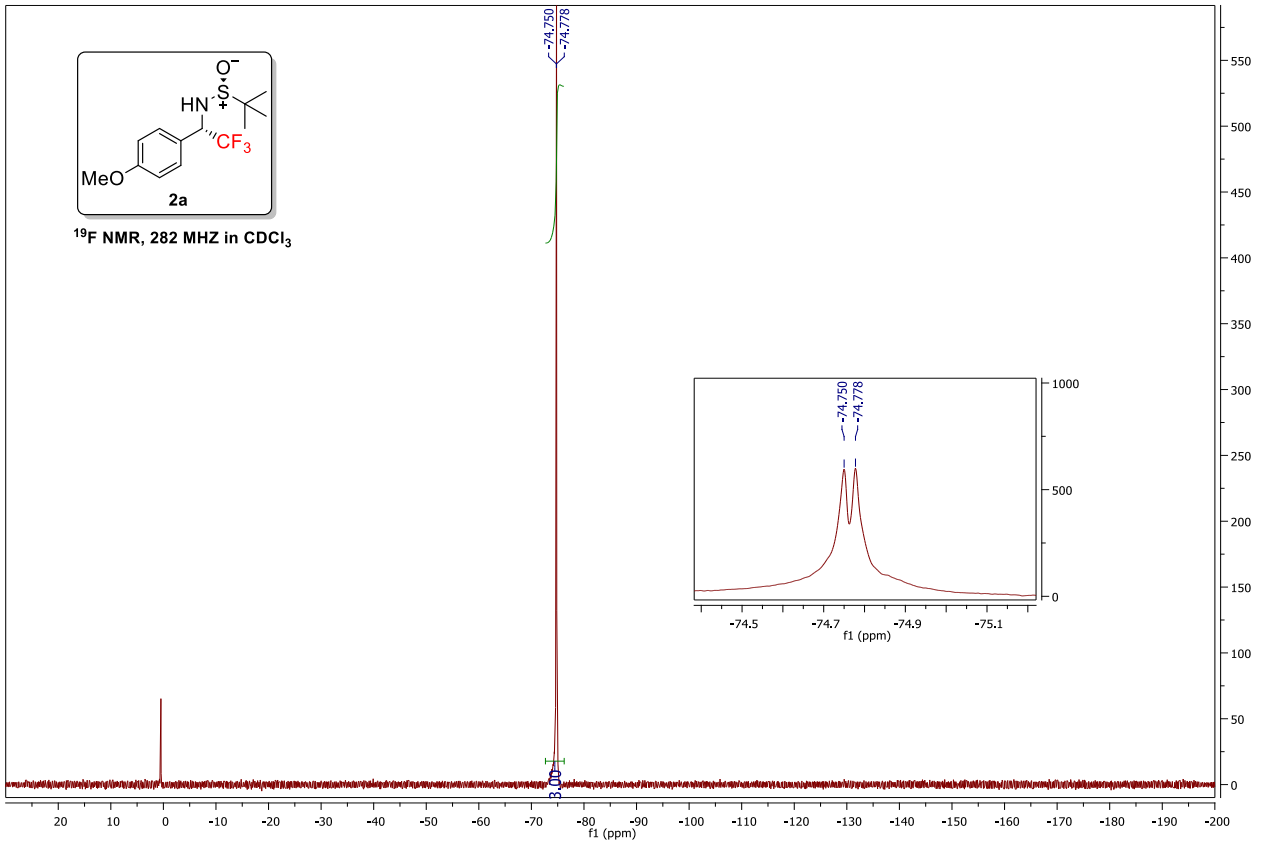
1 a) G. Liu, D. A. Cogan and J. A. Ellman, *J. Am. Chem. Soc.,* 1997, **119**, 9913-9914; b) M. B. Tait, S. Butterworth and J. Clayden, *Org. Lett*., 2015, **17**, 1236−1239; c) K. W. Kells and J. M. Chong, *J. Am. Chem. Soc.,* 2004, **126**, 15666-15667; d) J. A. –S. Fernández, M. M. -F Rodríguez, M. C. Maestro and J. L. -R García, *Eur. J. Org. Chem.,* 2014, 5265–5272; e) T. Mita, M. Sugawara, K. Saito and Y. Sato, *Org. Lett*., 2014, **16**, 3028−3031; f) D, Chen and M.-H. Xu, *J. Org. Chem.*, 2014, **79**, 7746–7751; g) W. Yan, D. Wang, J. Feng, P. Li and R. Wang, *J. Org. Chem*., 2012, **77**, 3311–3317.

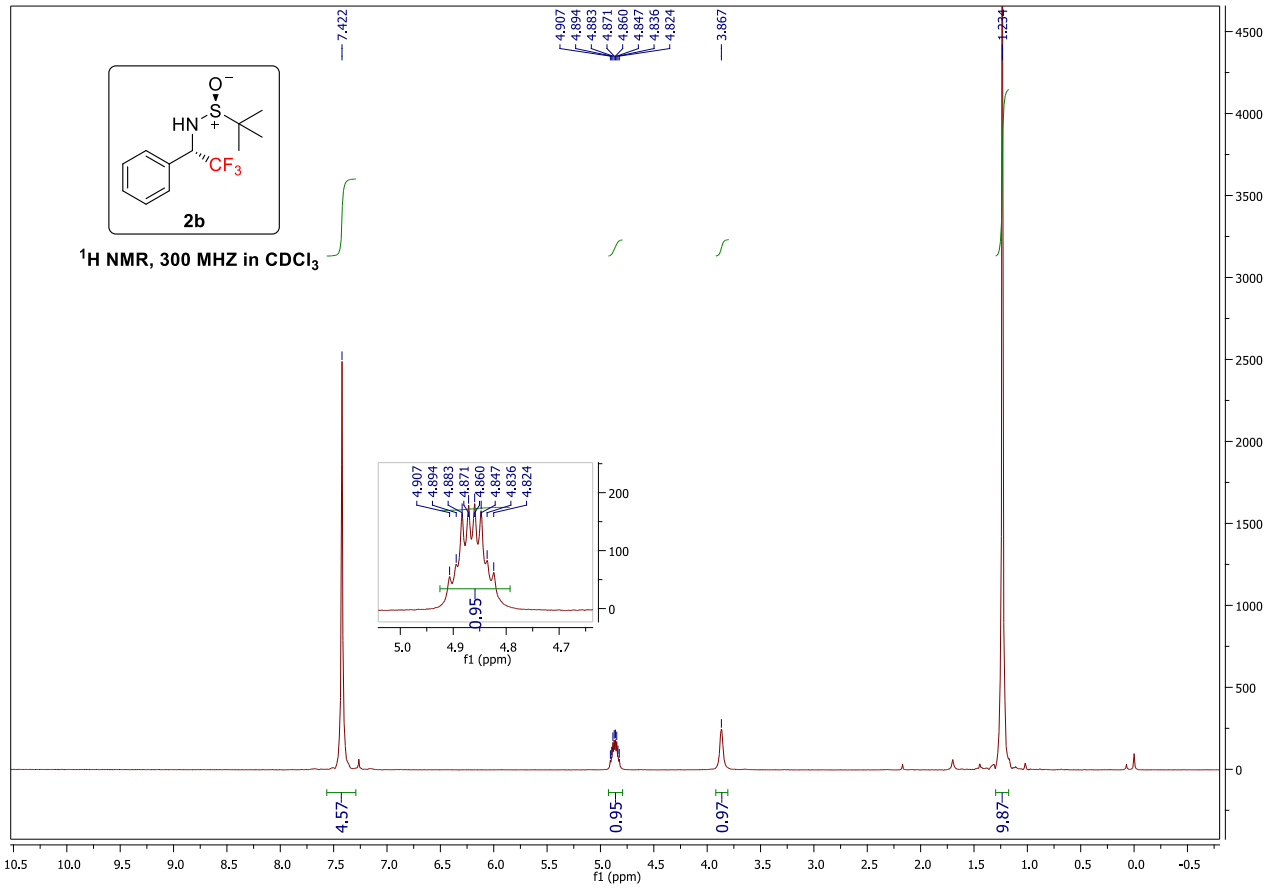
2 a) V. L. Truong and J. Y. Pfeiffer, *Tetrahedron Lett.,* 2009, **50**, 1633–1635; b) E. I. Jiménez, W. E. V. Narváez, C. A. Román, J. V. Chavez, T. R. Rinza and M. H. Rodríguez. *J. Org. Chem.,* 2016, **81**, 7419−7431; c) G. K. S. Prakash, M. Mandal and G. A. Olah, *Angew. Chem., Int. Ed.,* 2001, **40**, 589-590; d) A. Henseler, M. Kato, K. Mori and T. Akiyama, *Angew. Chem., Int. Ed*., 2011, **50**, 8180 –8183; e) T. Johnson, B. Luo and M. Lautens, *J. Org. Chem*., 2016, **81**, 4923−4930.

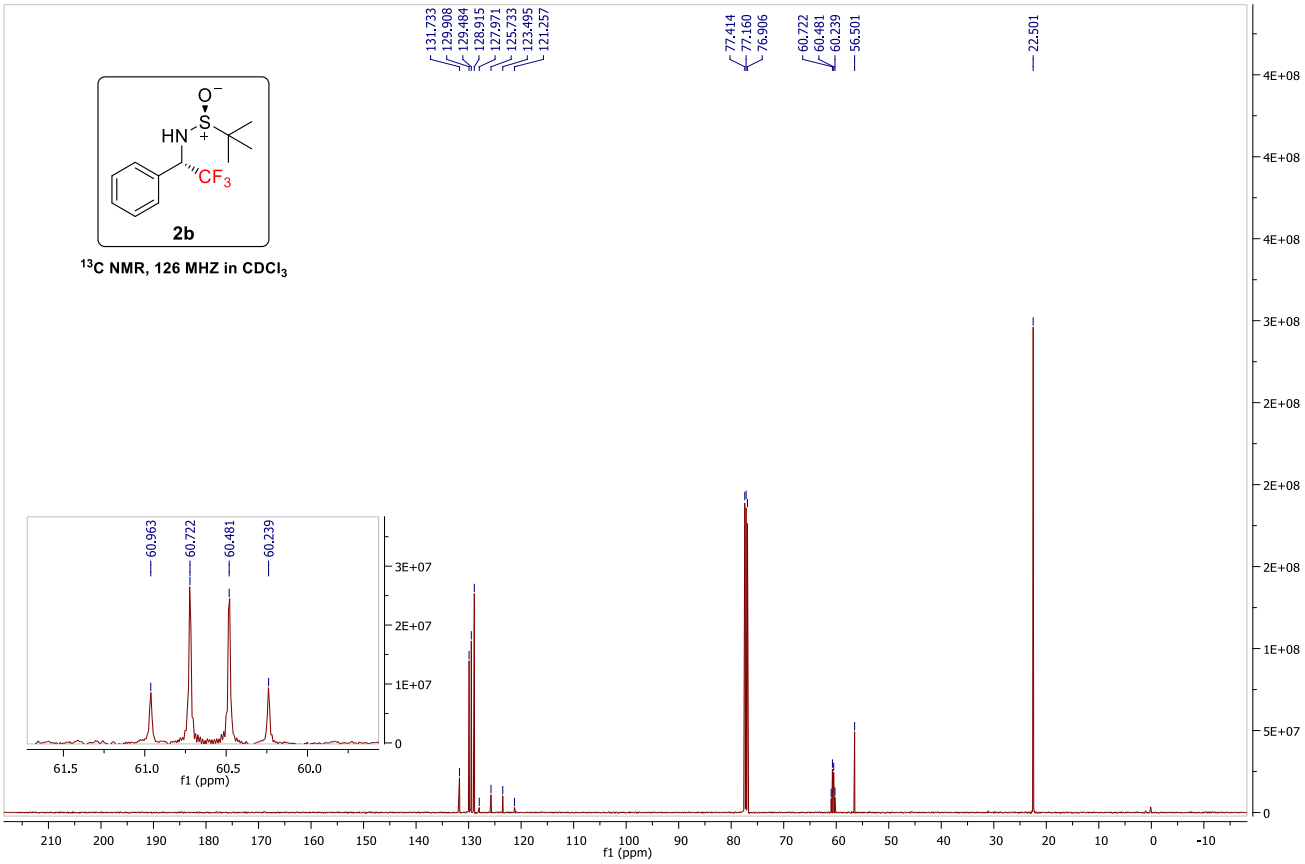
9. NMR Data
(^{1}H NMR , ^{13}C NMR and ^{19}F-NMR)

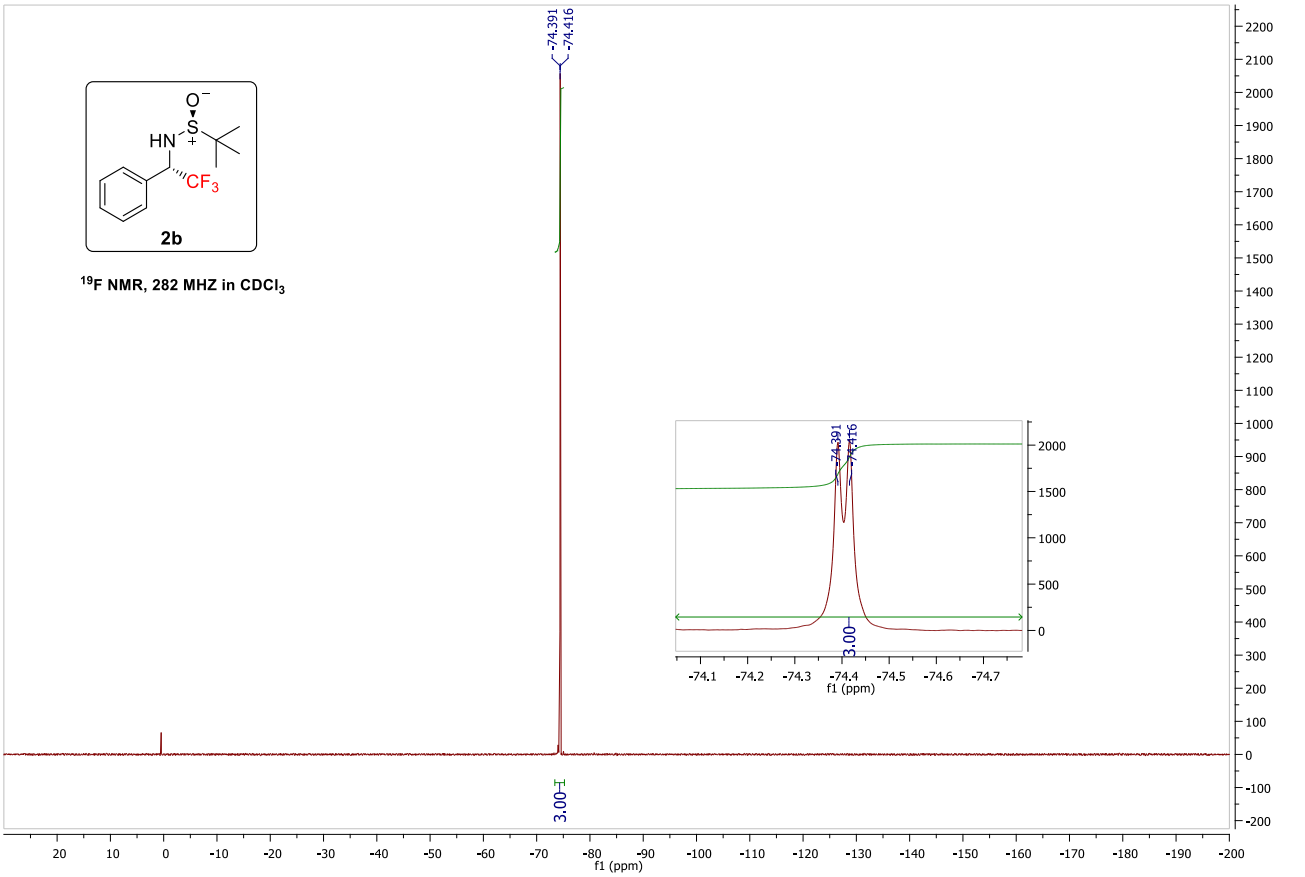

7.364
7.335
6.944
6.915
4.844
4.832
4.821
4.809
4.798
4.785
4.774
3.830
1.234
HN
CF3
MeO
2a
1H NMR, 300 MHZ in CDCl3
1.99
1.82
1.00
3.91
9.24
f1 (ppm)

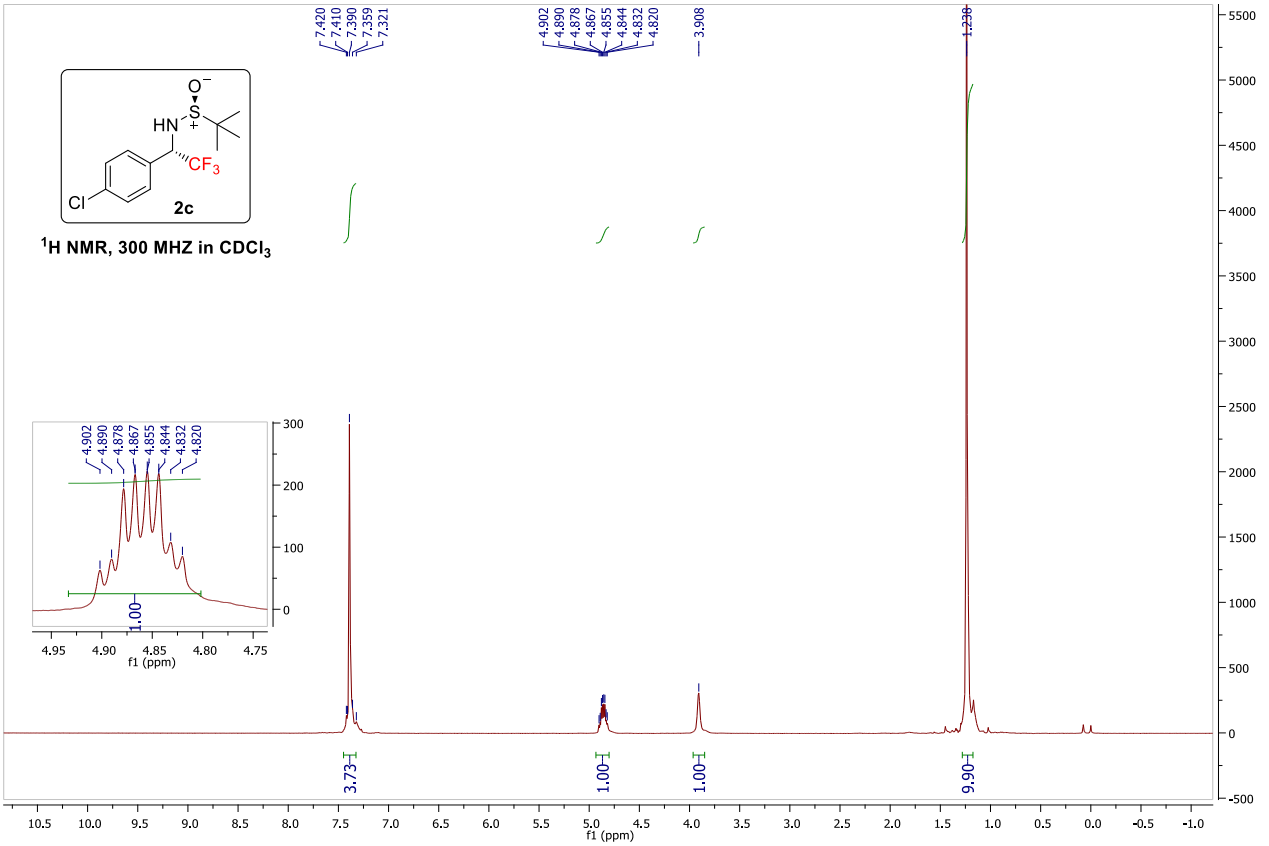

160.783
130.853
128.066
125.831
123.595
121.357
114.322
77.414
77.160
76.906
60.081
59.839
59.598
56.355
55.431
22.554
HN
CF3
MeO
2a
13C NMR, 126 MHZ in CDCl3
60.322
60.081
59.839
59.598
f1 (ppm)

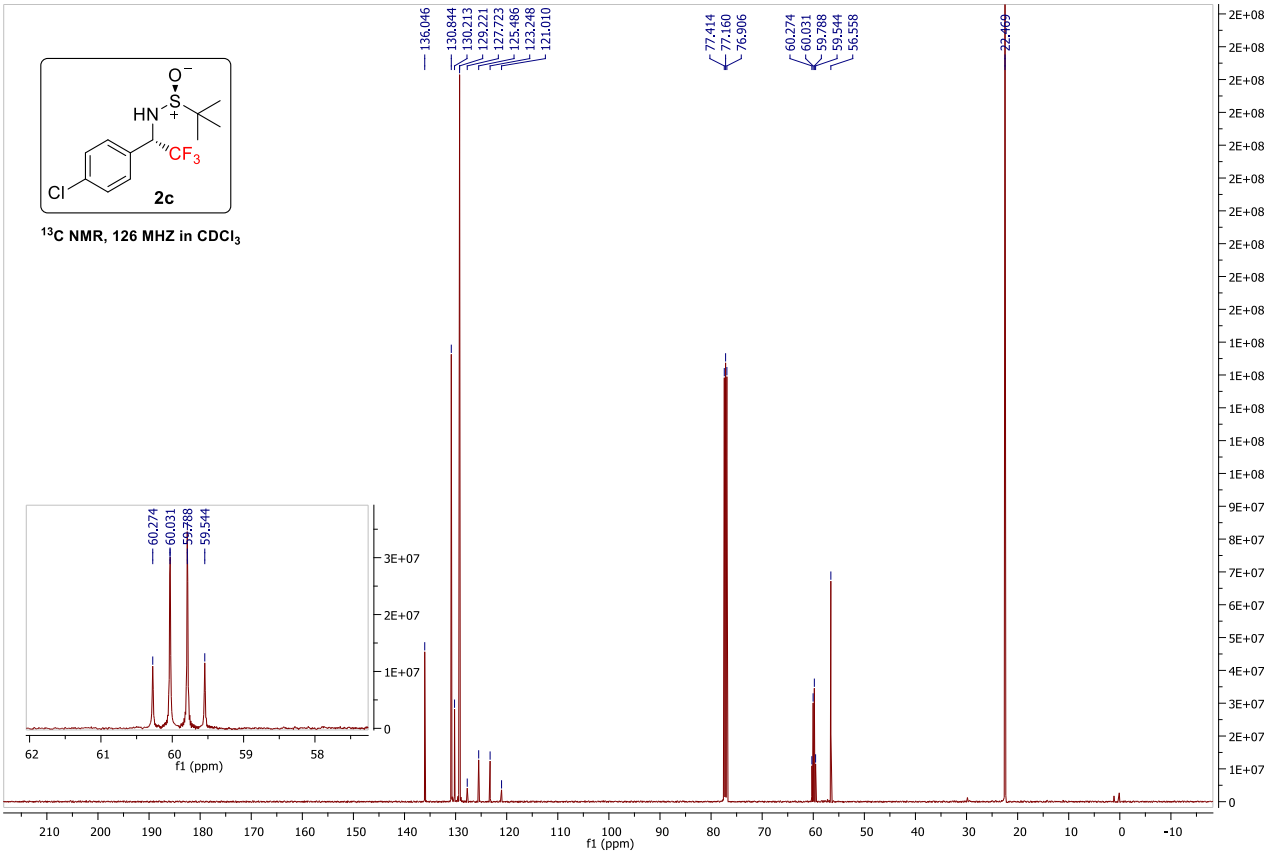

-74.750
-74.778
MeO
HN
CF3
2a
19F NMR, 282 MHZ in CDCl3
3.00
f1 (ppm)

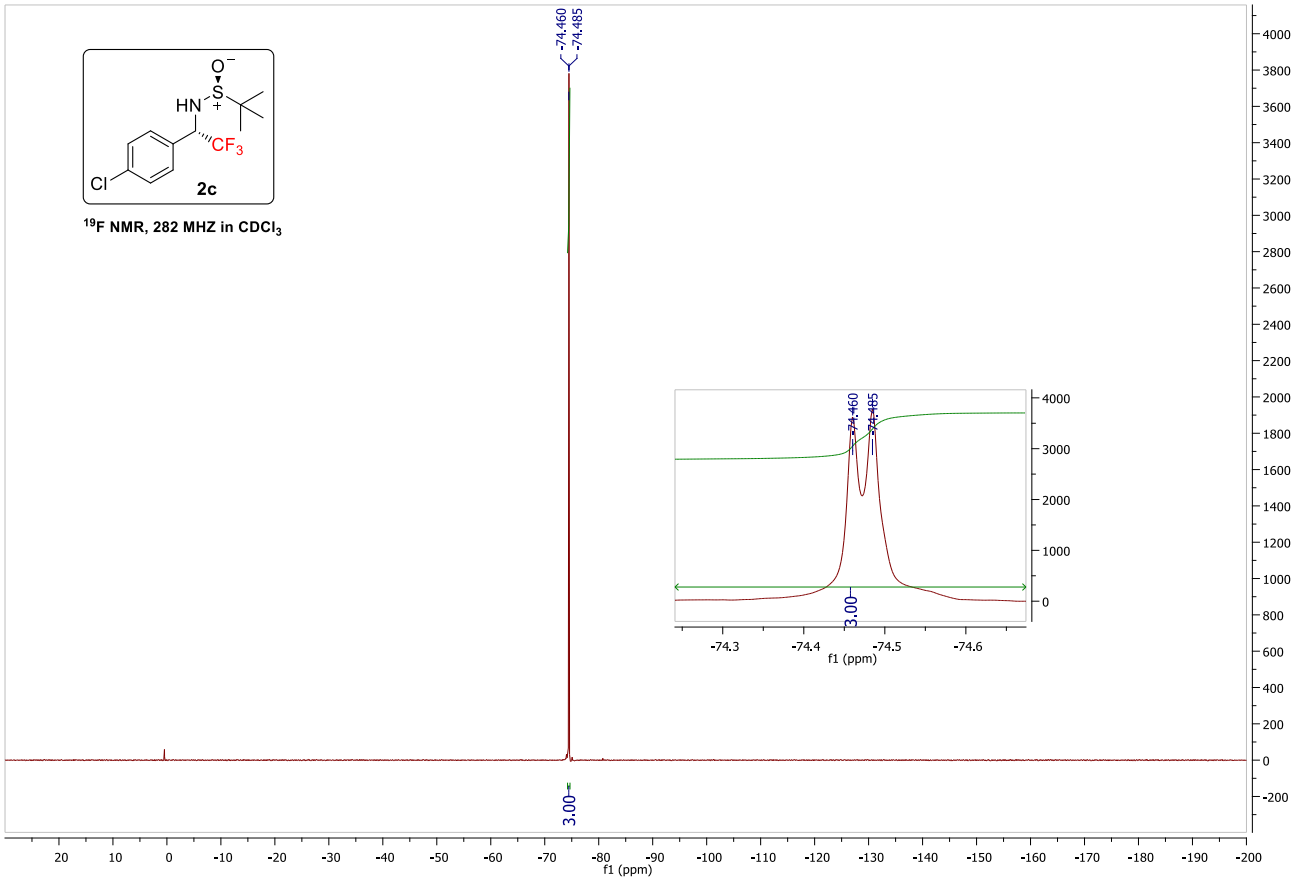

7.422
4.907
4.894
4.883
4.871
4.860
4.847
4.836
4.824
3.867
1.234
HN
CF3
2b
1H NMR, 300 MHZ in CDCl3
4.57
0.95
0.97
9.87
f1 (ppm)

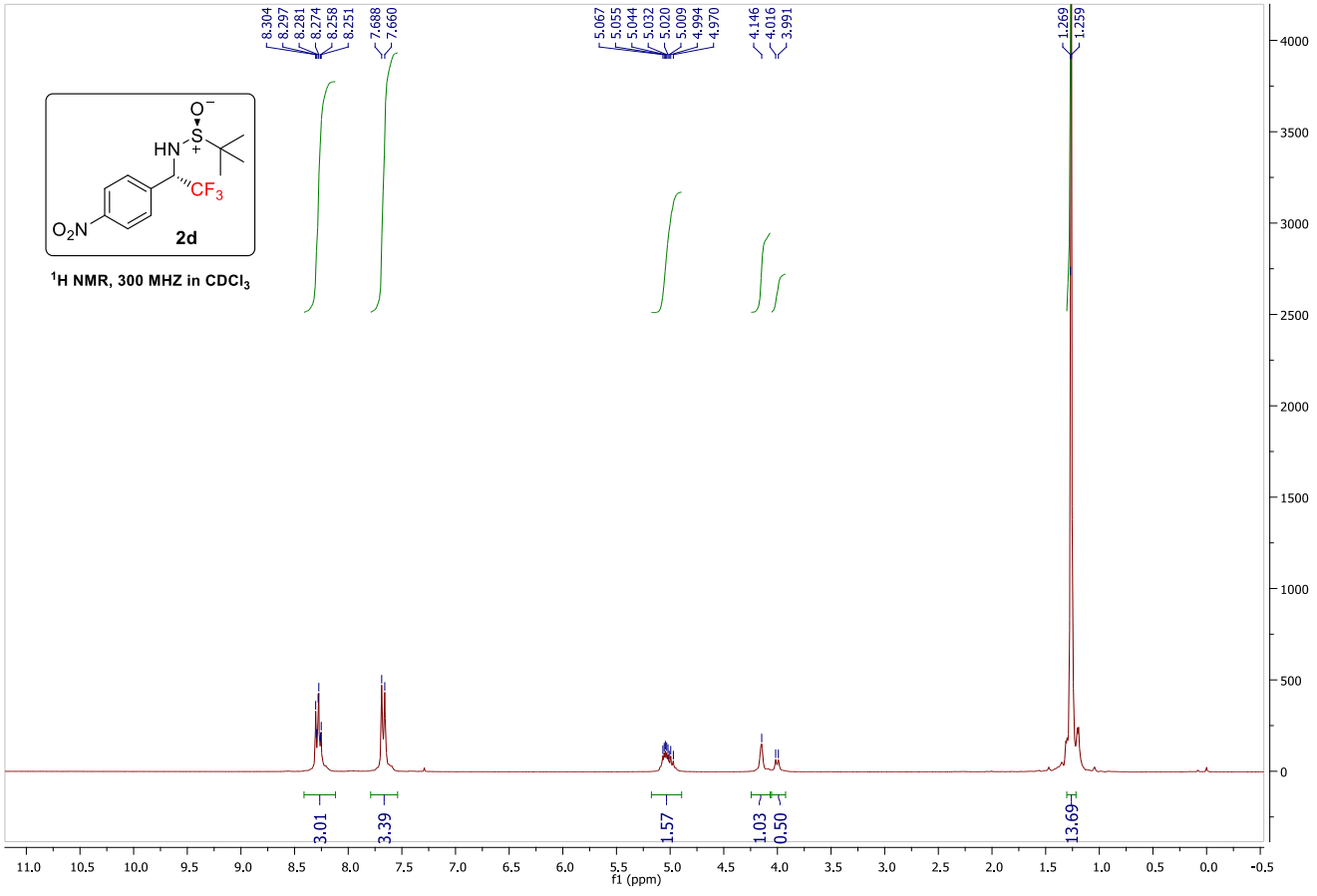

131.733
129.908
129.484
128.915
127.971
125.733
123.495
121.257
77.414
77.160
76.906
60.722
60.481
60.239
56.501
22.501
60.963
60.722
60.481
60.239
f1 (ppm)
2b
^{13}C NMR, 126 MHZ in CDCl$_3$

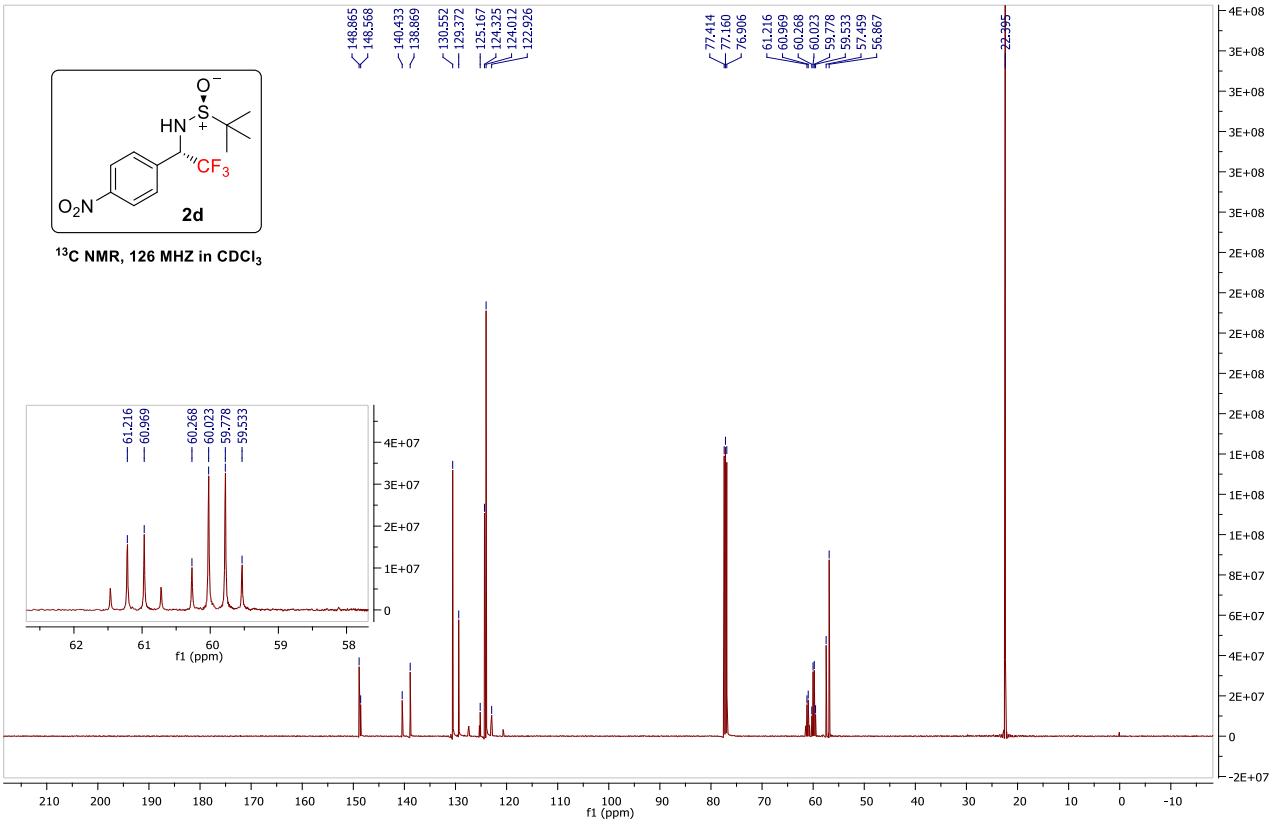

-74.391
-74.416
3.00
f1 (ppm)
2b
^{19}F NMR, 282 MHZ in CDCl$_3$

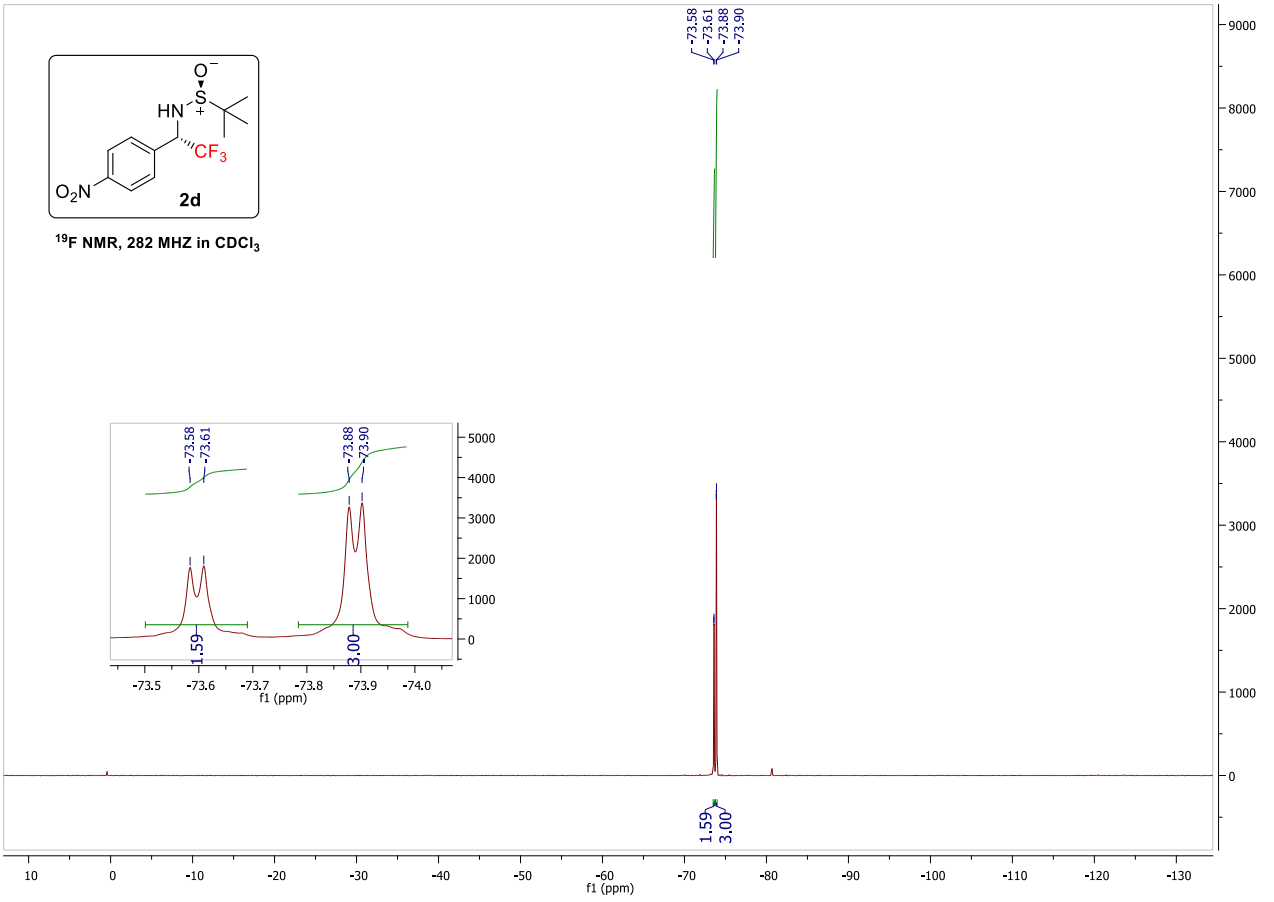

2c
^{1}H NMR, 300 MHZ in CDCl$_3$

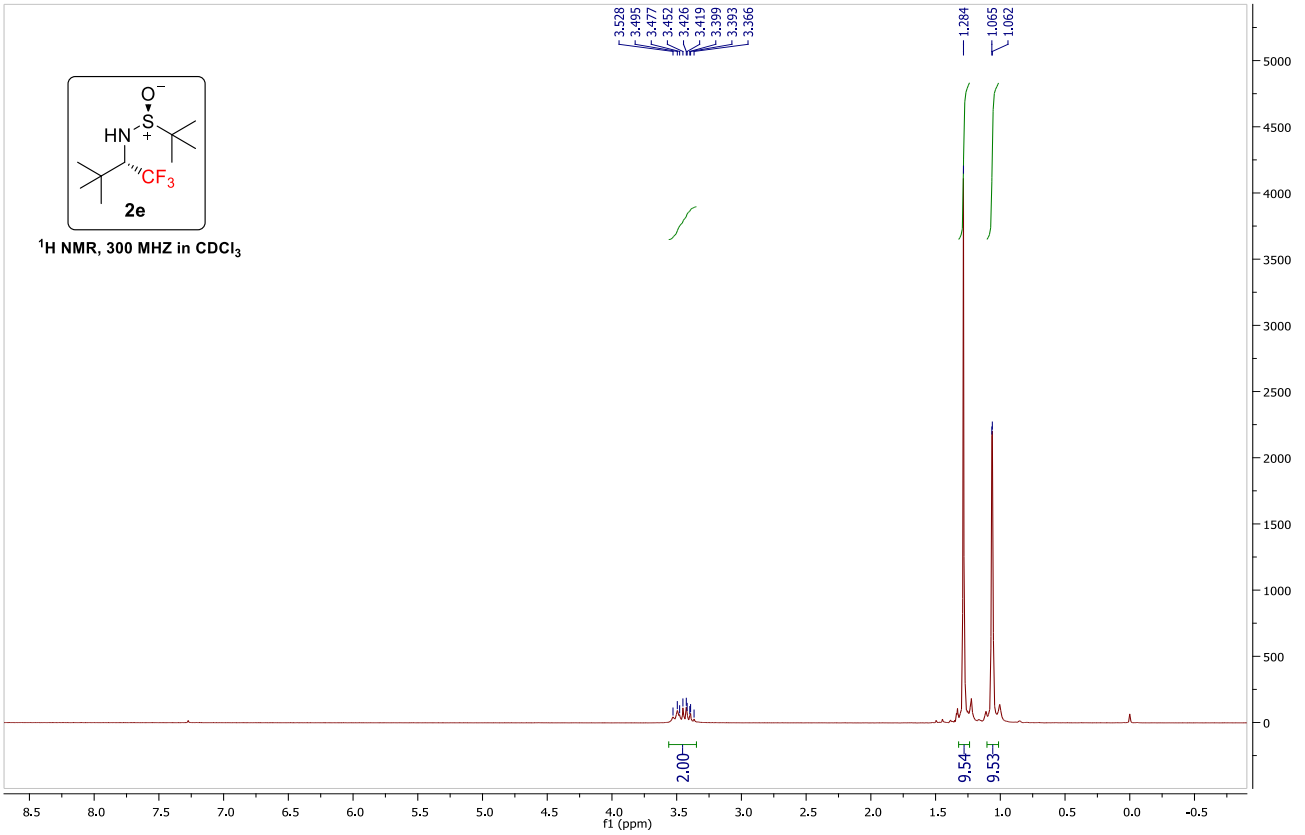

2c
^{13}C NMR, 126 MHZ in CDCl$_3$


-74.460
-74.485
2c
19F NMR, 282 MHZ in CDCl3
3.00
f1 (ppm)


8.304
8.297
8.281
8.274
8.258
8.251
7.688
7.660
5.067
5.055
5.044
5.032
5.020
5.009
4.994
4.970
4.146
4.016
3.991
1.269
1.259
2d
1H NMR, 300 MHZ in CDCl3
3.01
3.39
1.57
1.03
0.50
13.69
f1 (ppm)

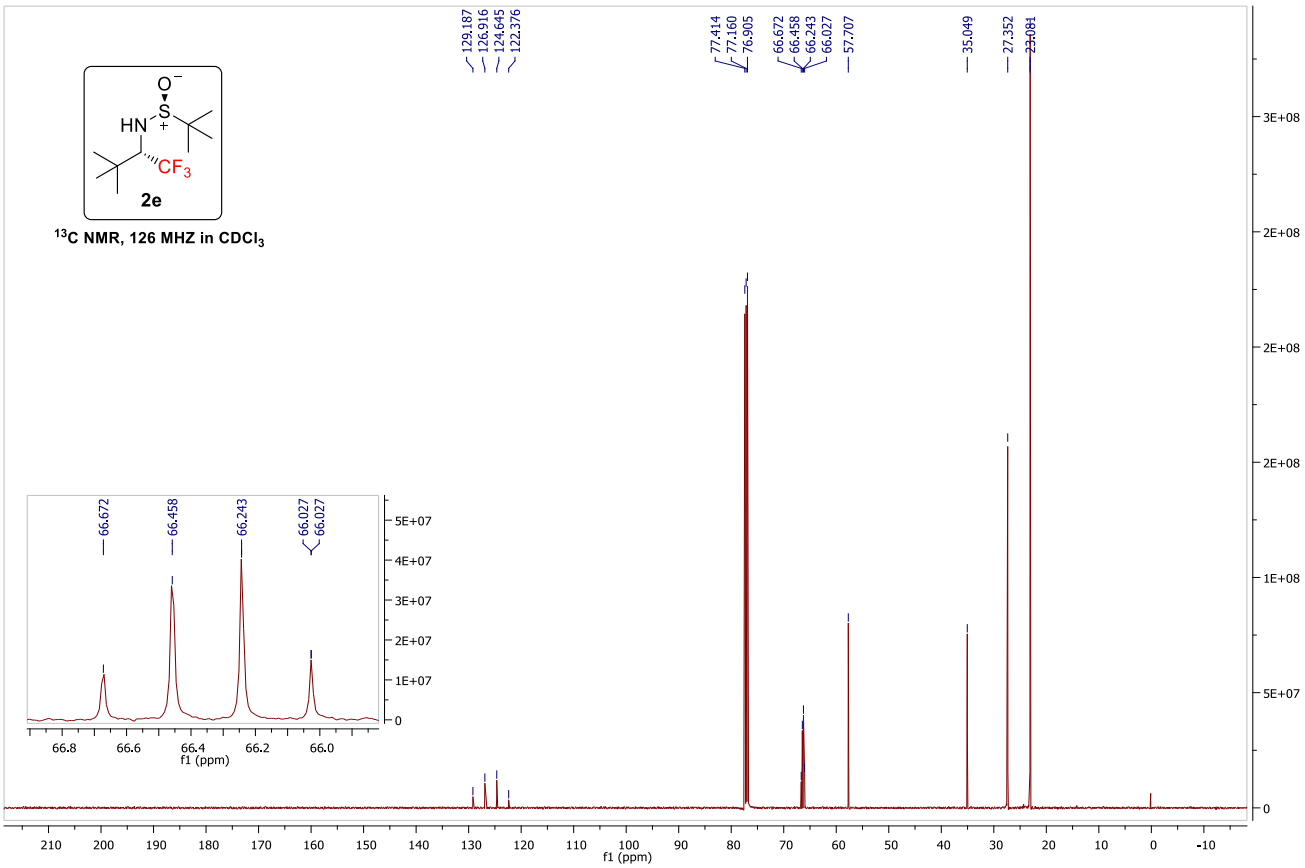

2d
^{13}C NMR, 126 MHZ in CDCl$_3$
f1 (ppm)


2d
^{19}F NMR, 282 MHZ in CDCl$_3$
f1 (ppm)



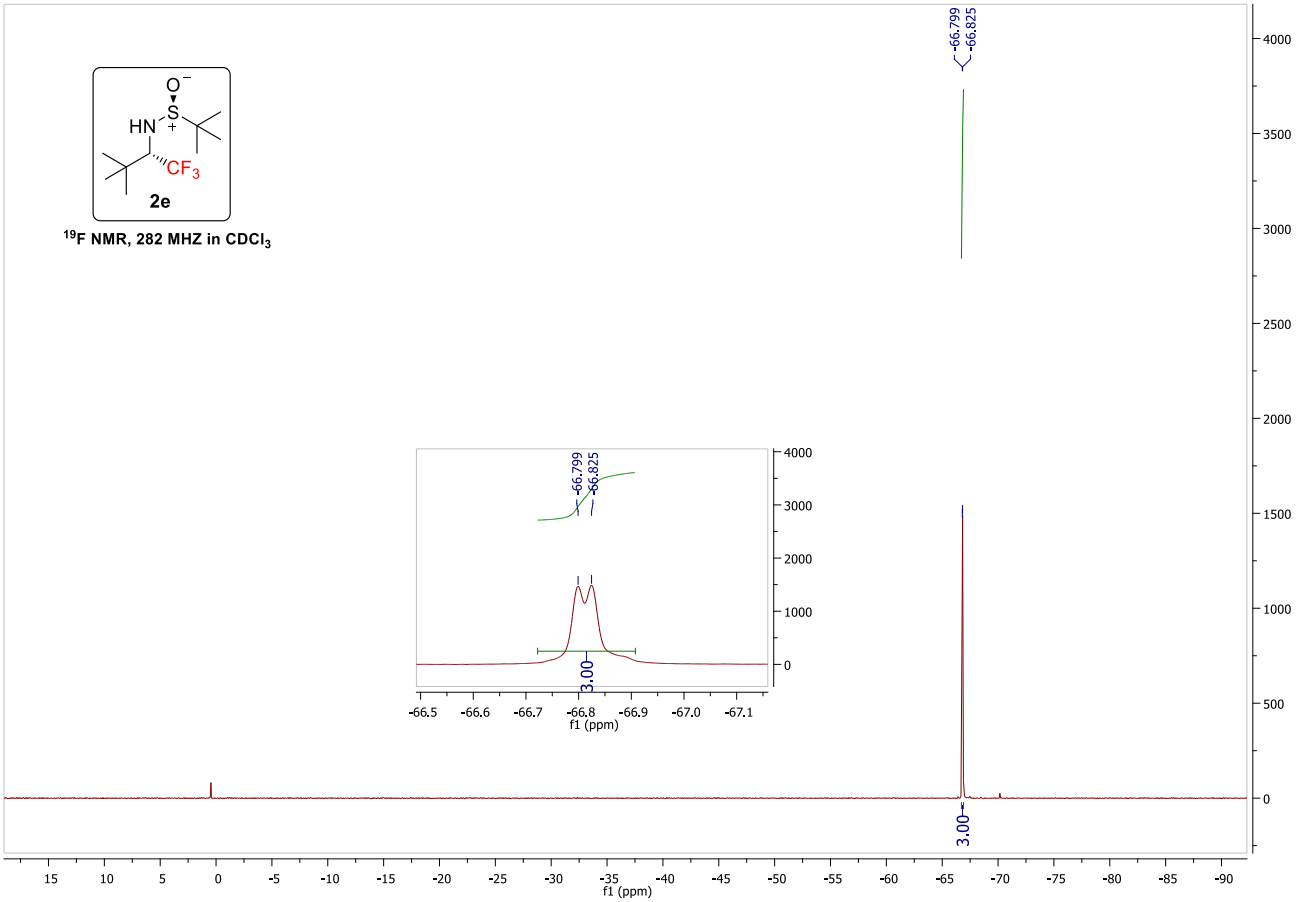
2e

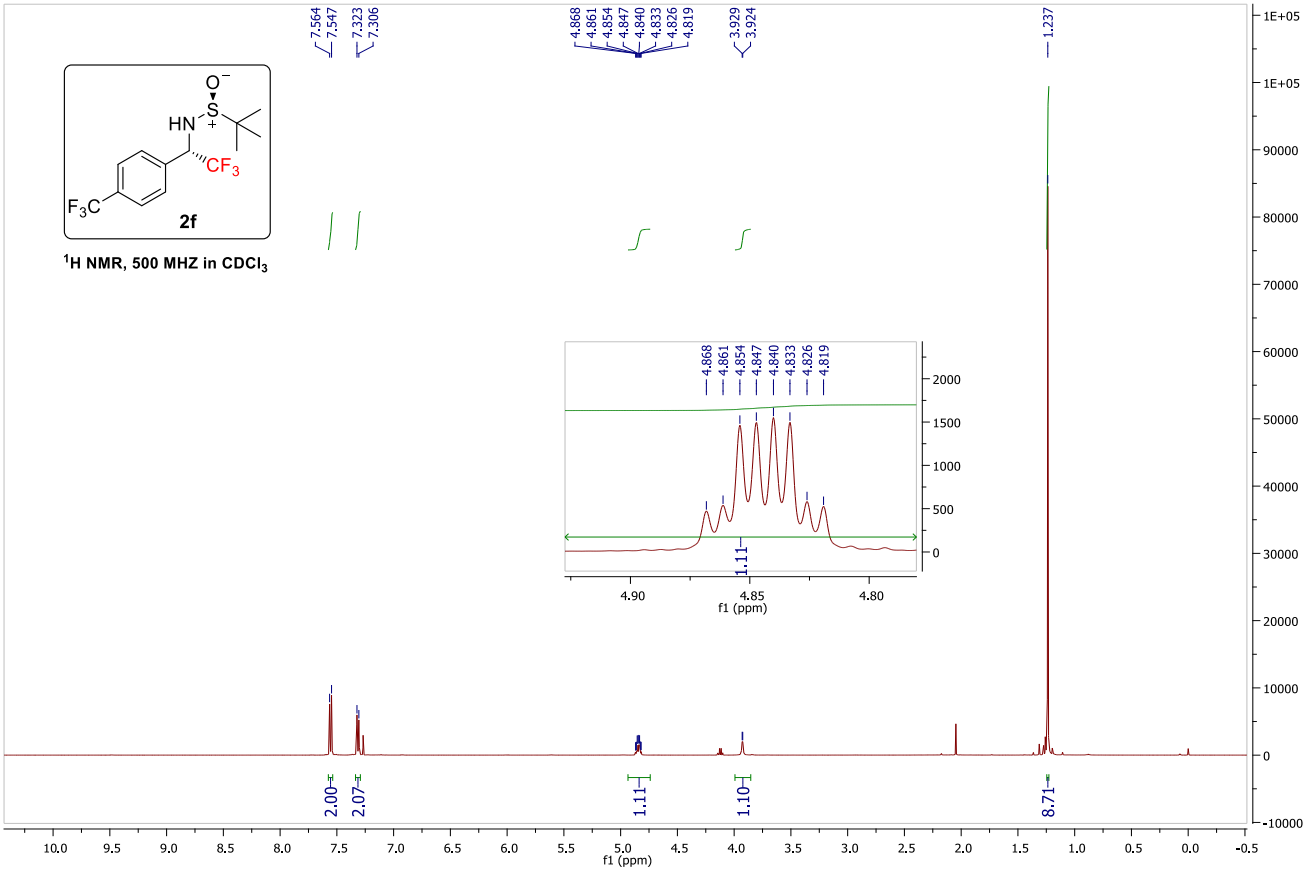
^{1}H NMR, 300 MHZ in $CDCl_3$

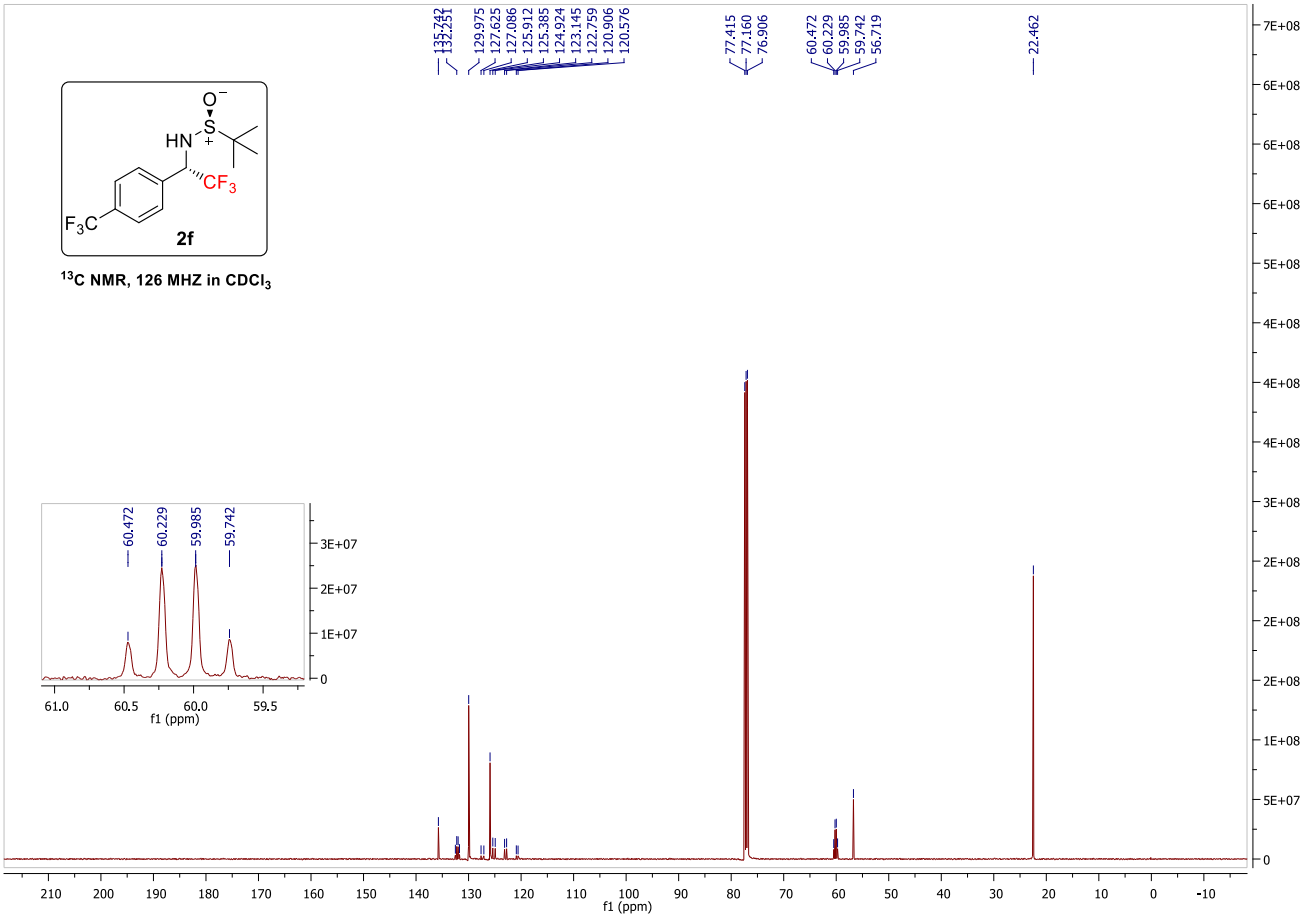


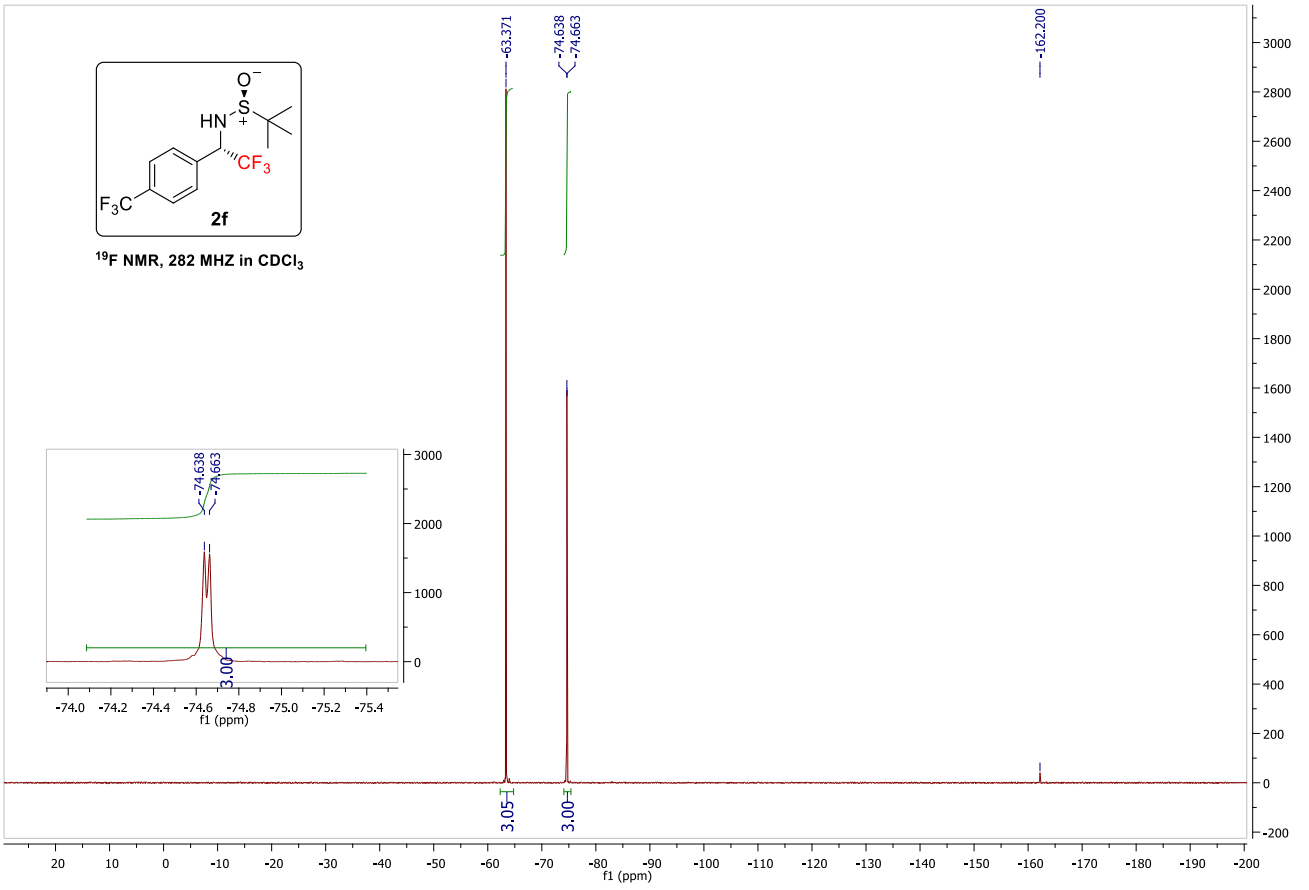
2e

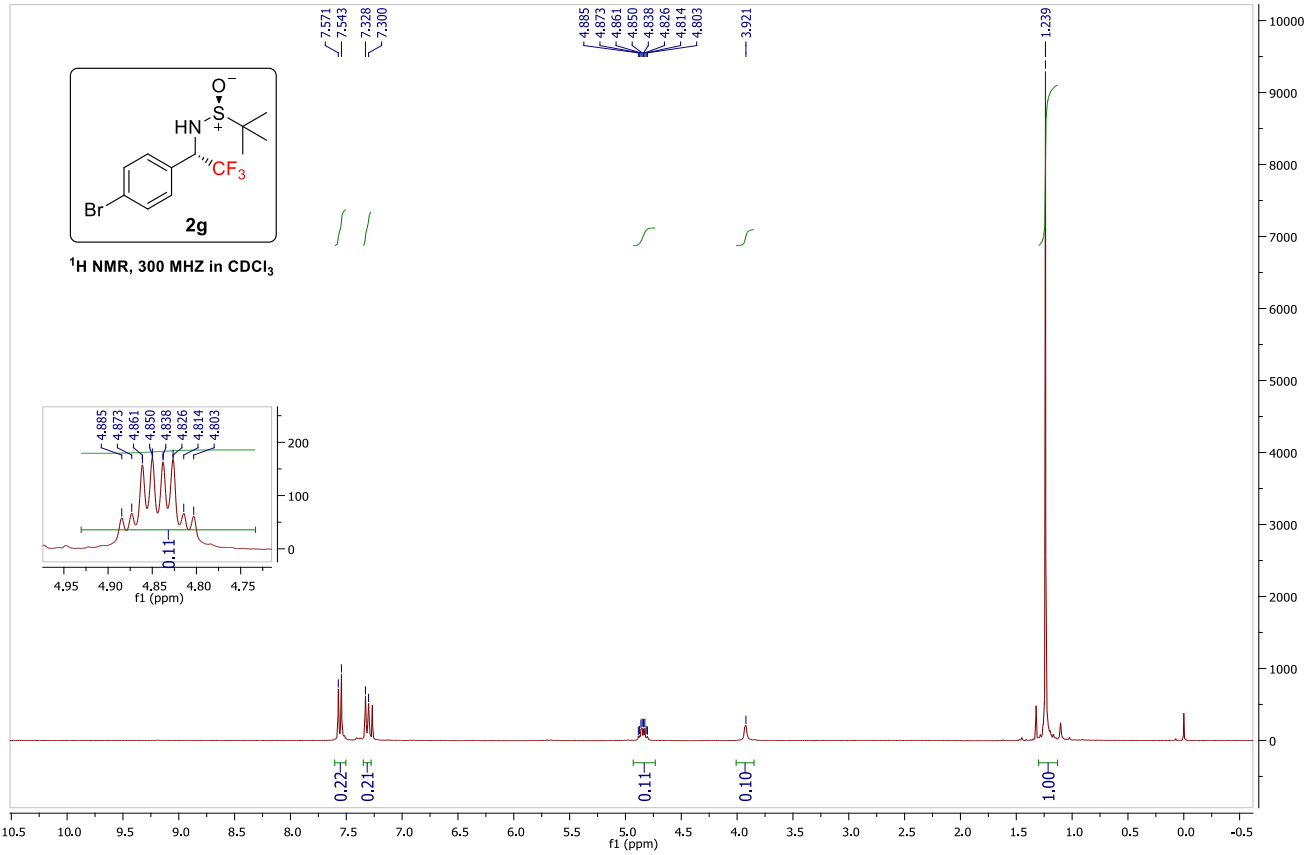
^{13}C NMR, 126 MHZ in $CDCl_3$

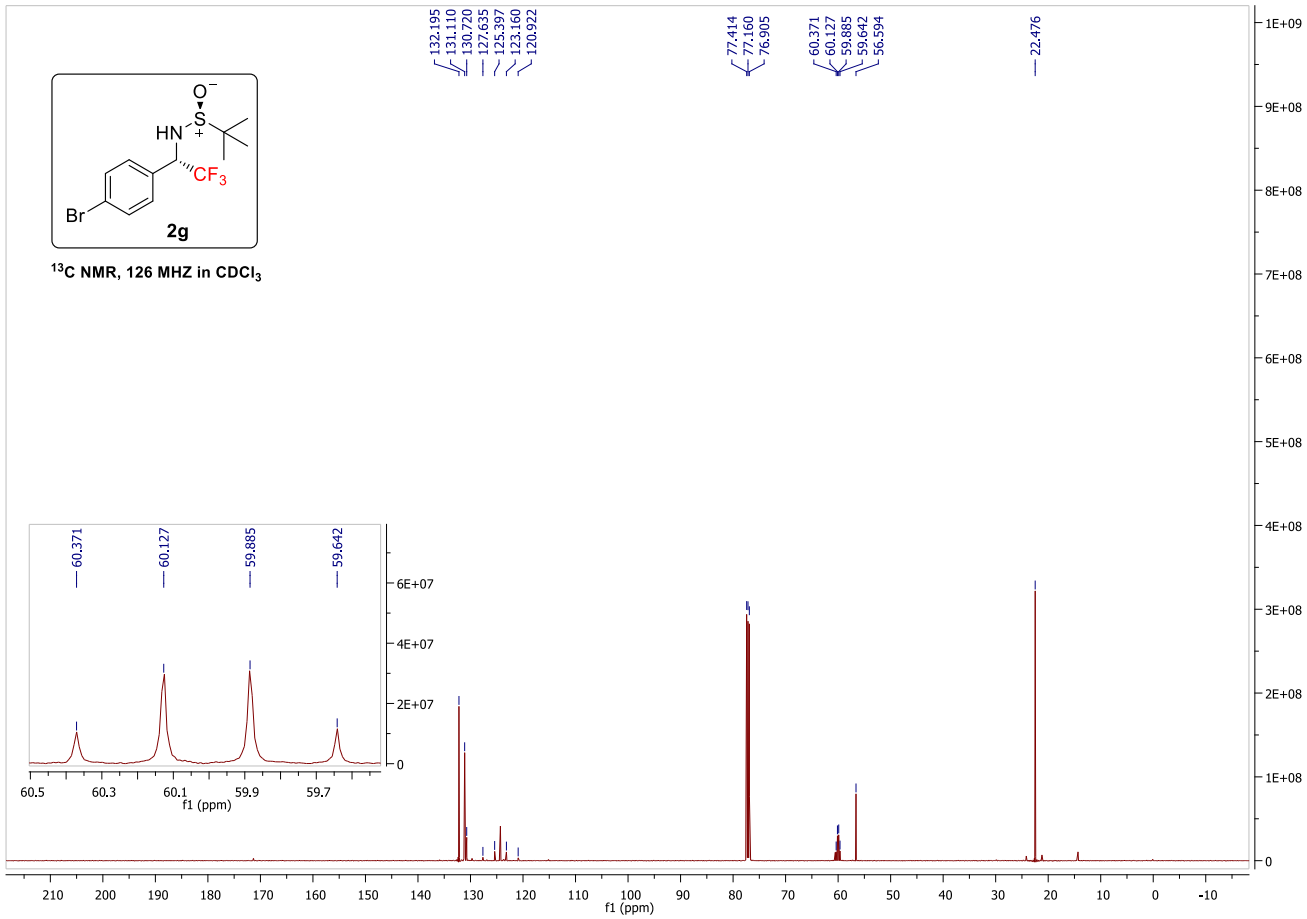

2e
19F NMR, 282 MHZ in CDCl3
-66.799
-66.825
3.00
f1 (ppm)

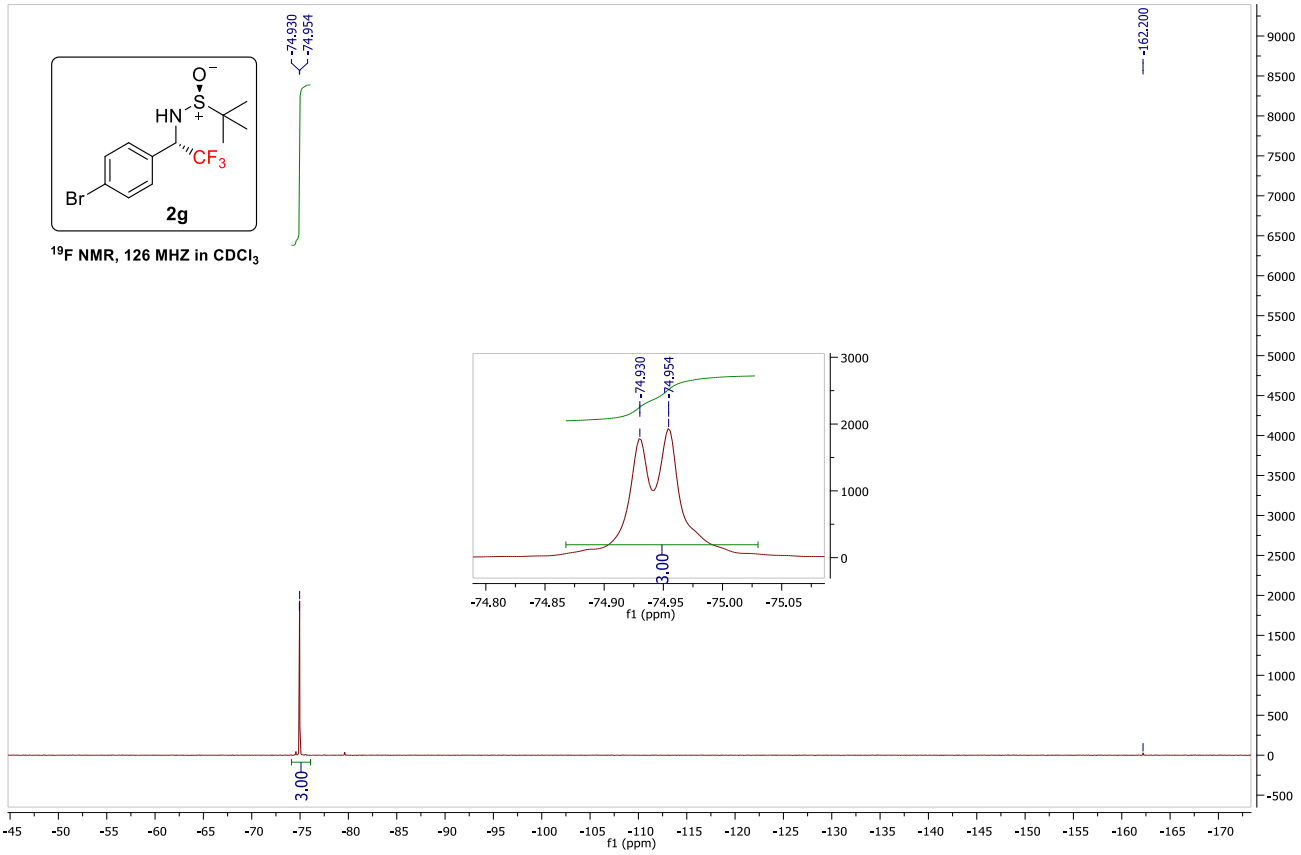

2f
1H NMR, 500 MHZ in CDCl3
7.564
7.547
7.323
7.306
4.868
4.861
4.854
4.847
4.840
4.833
4.826
4.819
3.929
3.924
1.237
2.00
2.07
1.11
1.10
8.71
f1 (ppm)

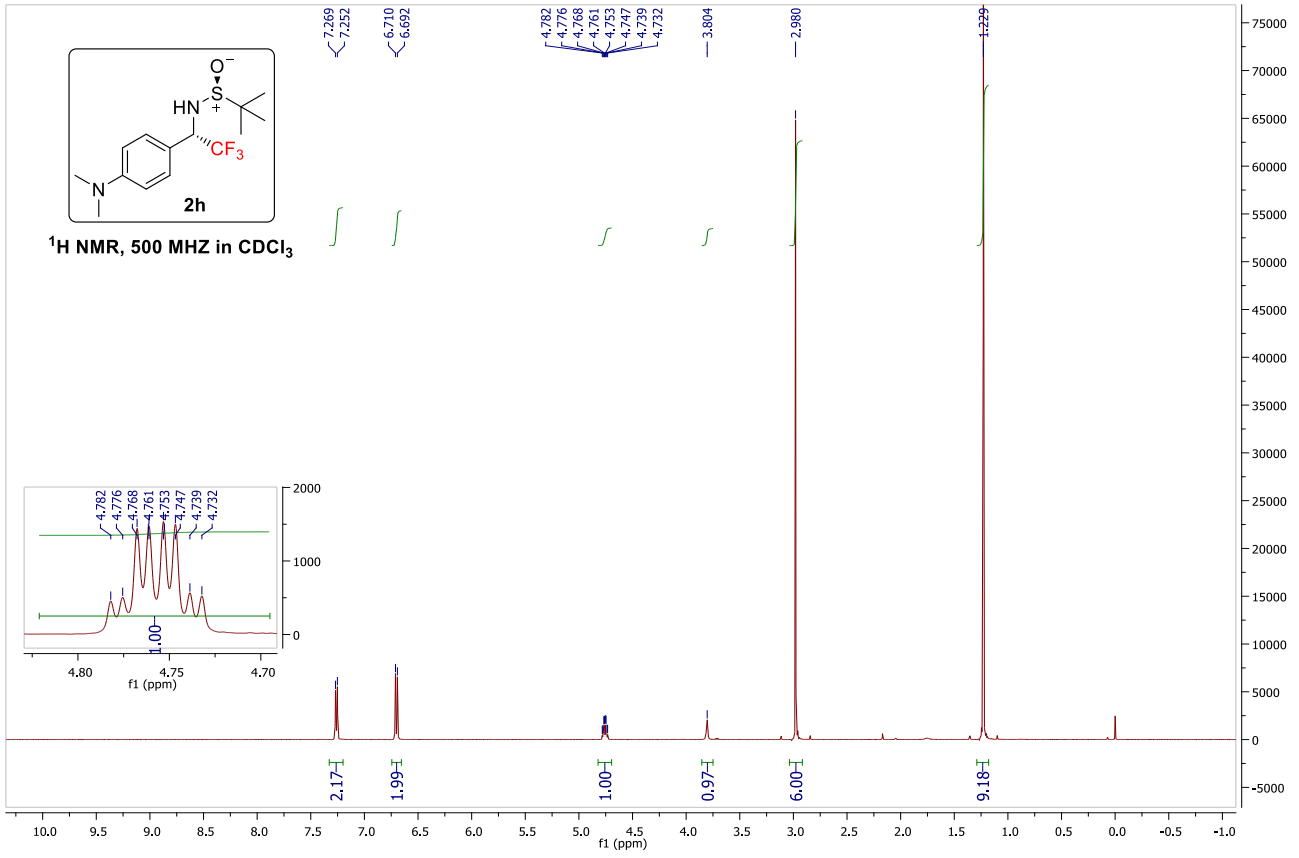

2f
^{13}C NMR, 126 MHZ in CDCl$_3$
f1 (ppm)

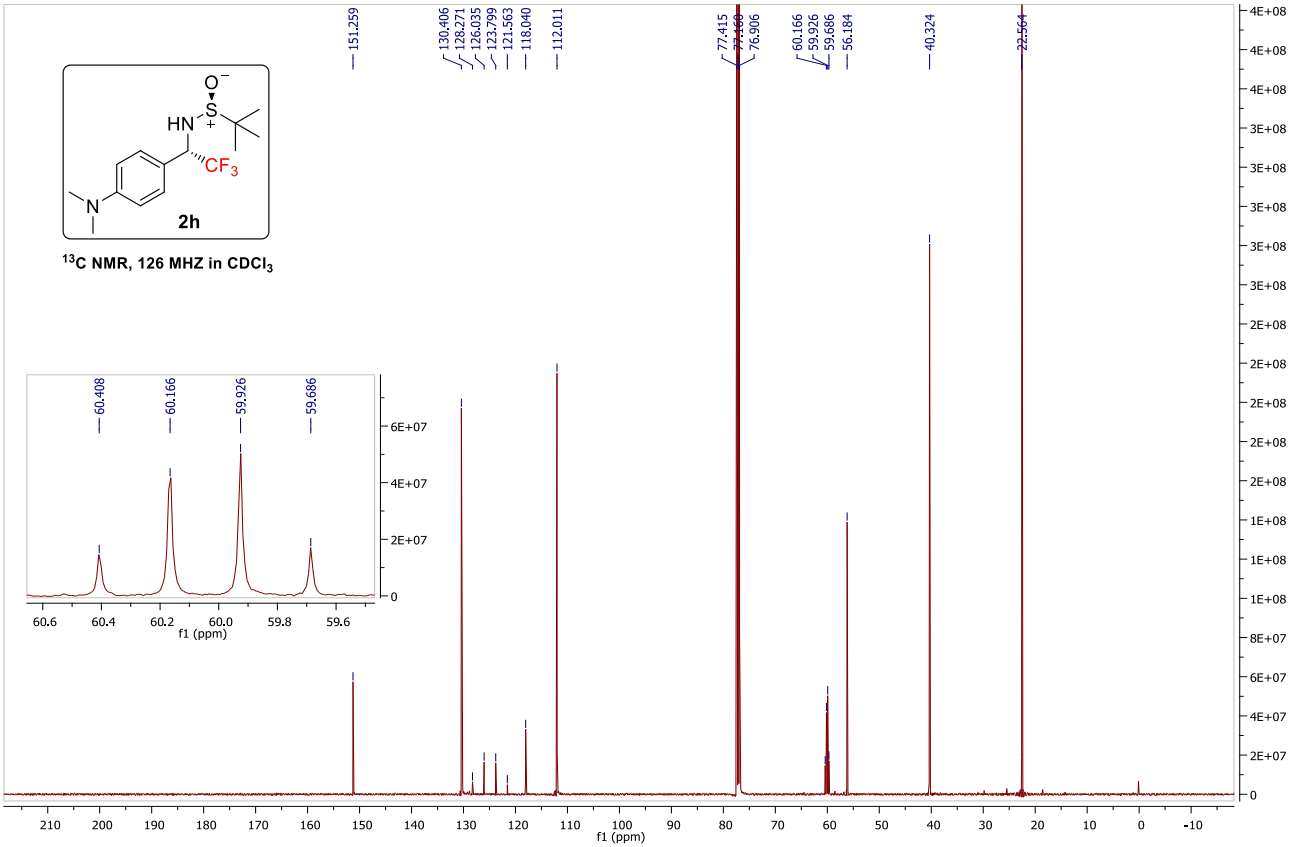

2f
^{19}F NMR, 282 MHZ in CDCl$_3$
f1 (ppm)

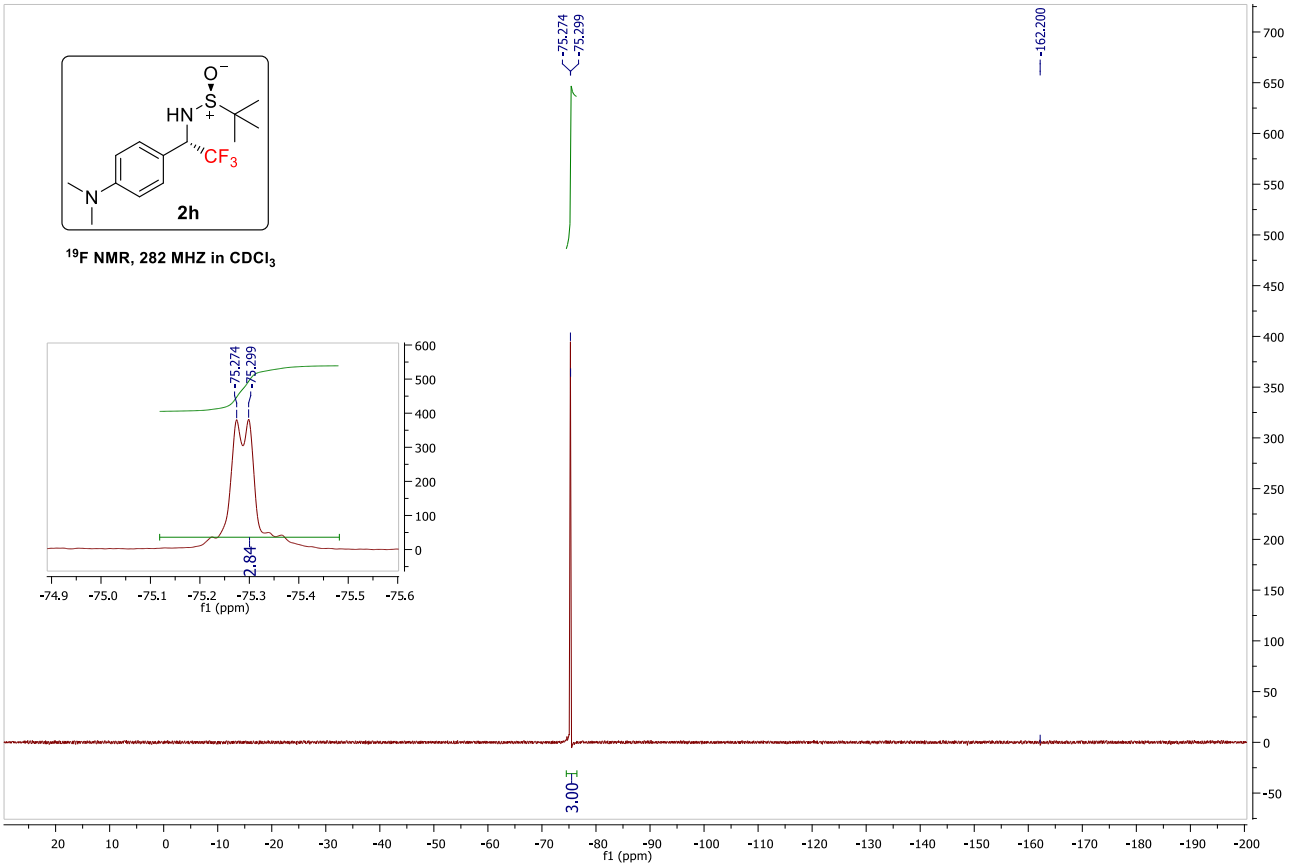

7.571
7.543
7.328
7.300
4.885
4.873
4.861
4.850
4.838
4.826
4.814
4.803
3.921
1.239
2g
^{1}H NMR, 300 MHZ in CDCl$_3$
0.22
0.21
0.11
0.10
1.00
f1 (ppm)

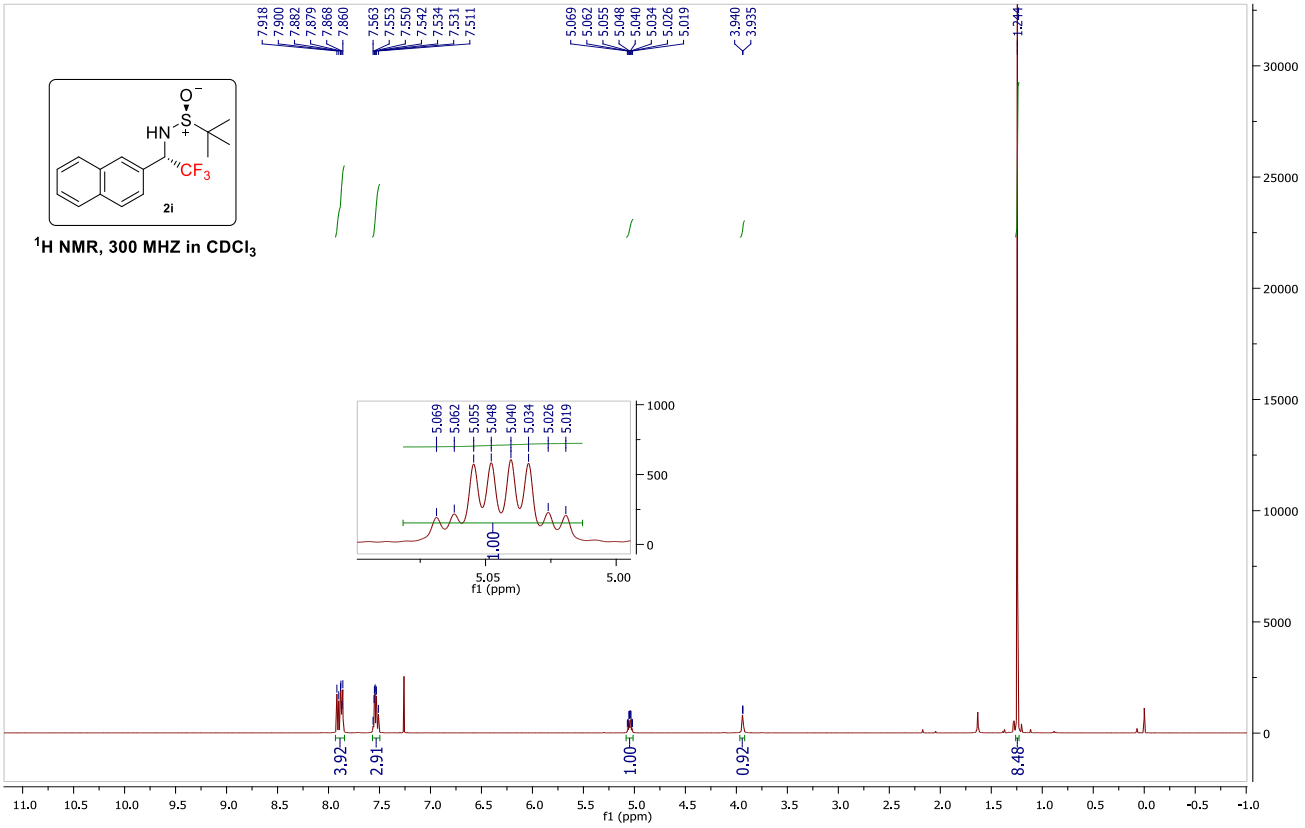

132.195
131.110
130.720
127.635
125.397
123.160
120.922
77.414
77.160
76.905
60.371
60.127
59.885
59.642
56.594
22.476
2g
^{13}C NMR, 126 MHZ in CDCl$_3$
f1 (ppm)

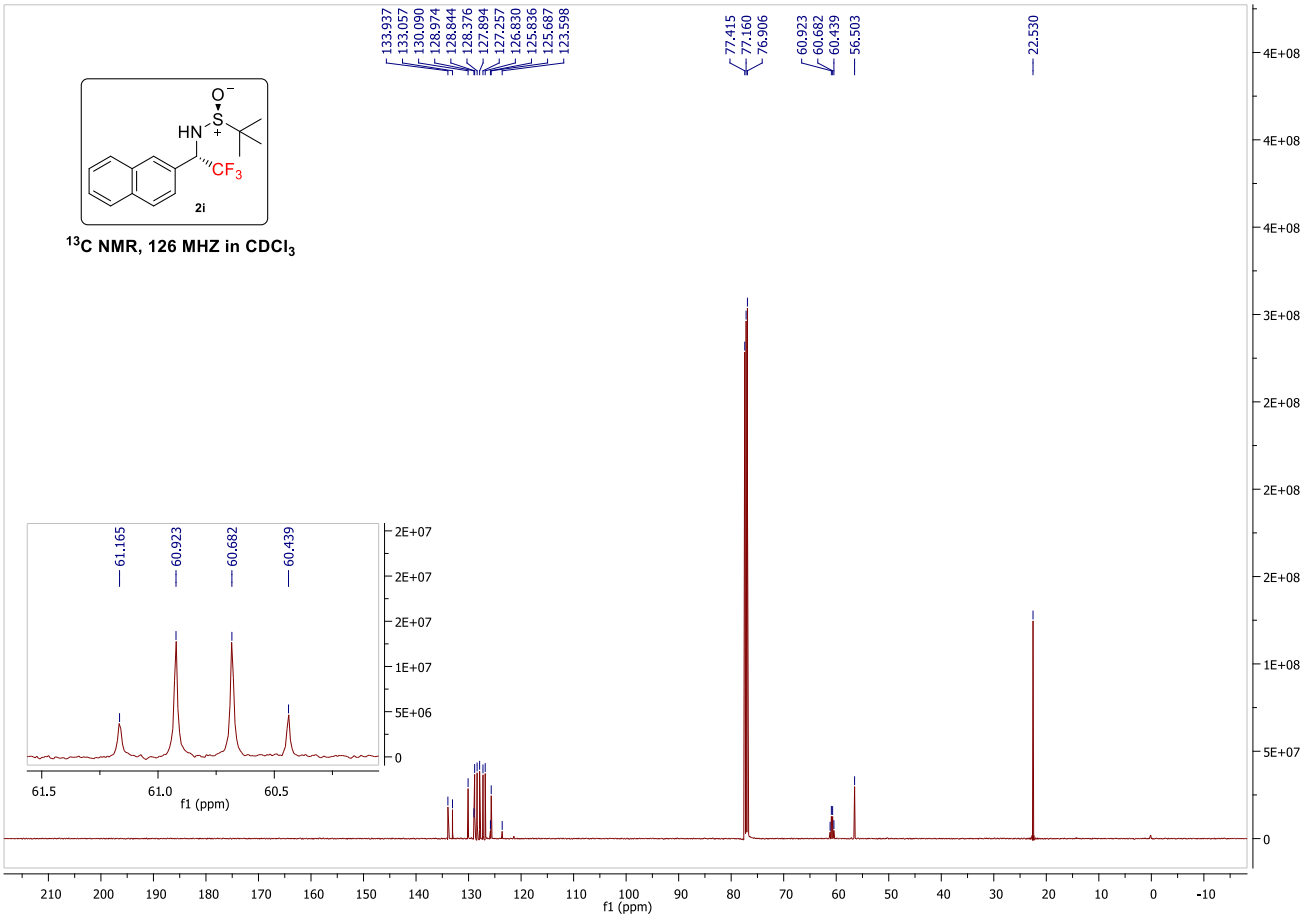

-74.930
-74.954
-162.200
2g
^{19}F NMR, 126 MHZ in CDCl$_3$
3.00
f1 (ppm)

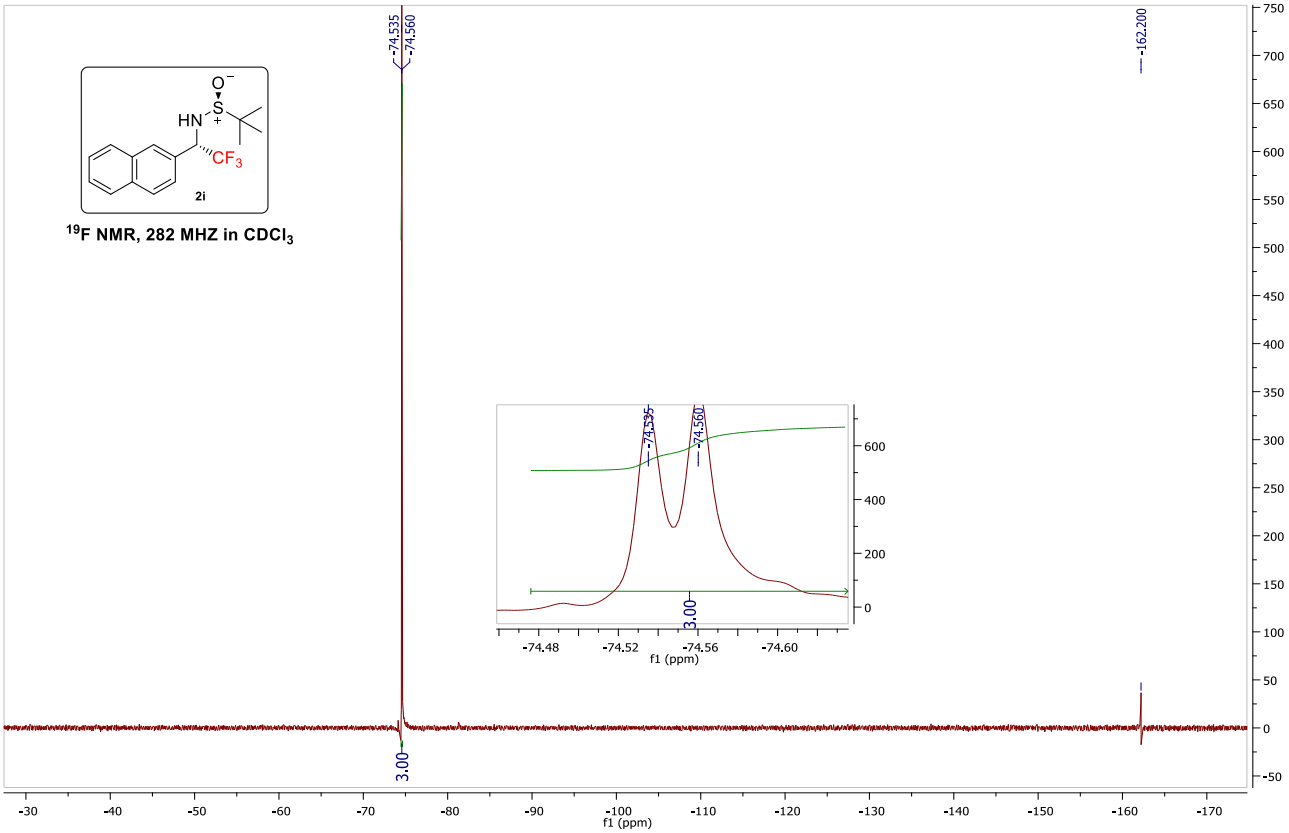

7.269
7.252
6.710
6.692
4.782
4.776
4.768
4.761
4.753
4.747
4.739
4.732
3.804
2.980
1.229
2h
^{1}H NMR, 500 MHZ in CDCl$_3$
1.00
2.17
1.99
1.00
0.97
6.00
9.18
f1 (ppm)


151.259
130.406
128.271
126.035
123.799
121.563
118.040
112.011
77.415
77.160
76.906
60.166
59.926
59.686
56.184
40.324
22.564
2h
13C NMR, 126 MHZ in CDCl3
60.408
60.166
59.926
59.686
f1 (ppm)

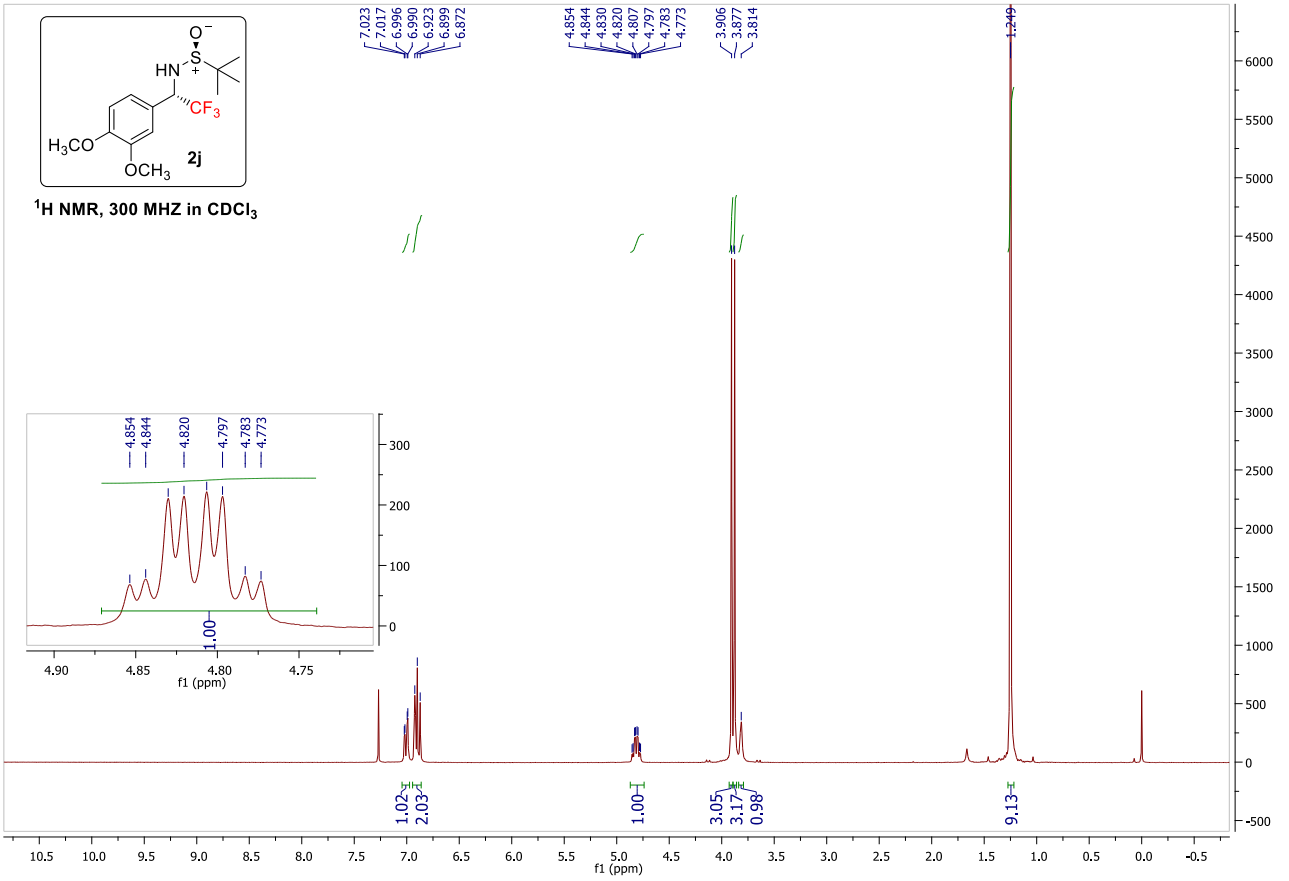

-75.274
-75.299
-162.200
2h
19F NMR, 282 MHZ in CDCl3
2.84
3.00
f1 (ppm)


2i
^{1}H NMR, 300 MHZ in CDCl$_3$

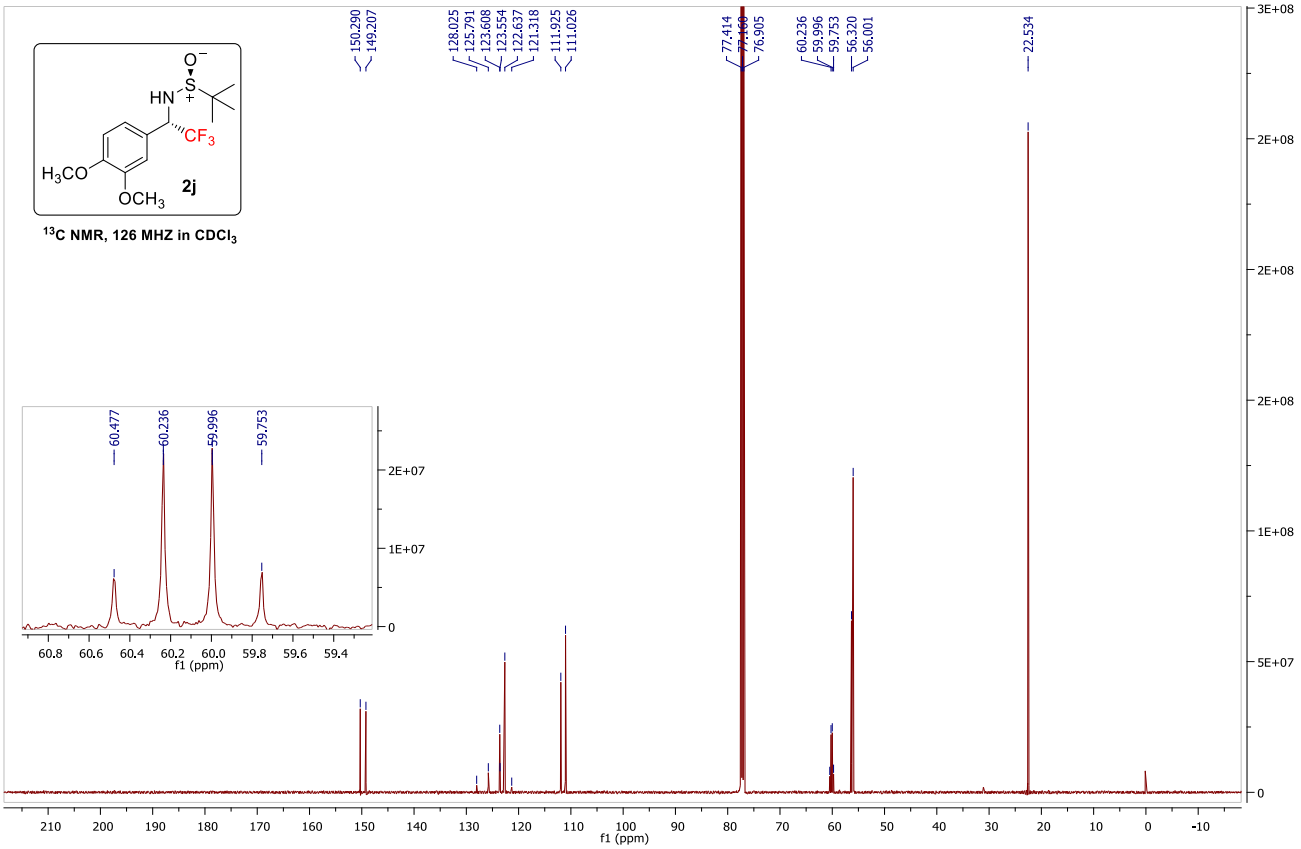

2i
^{13}C NMR, 126 MHZ in CDCl$_3$

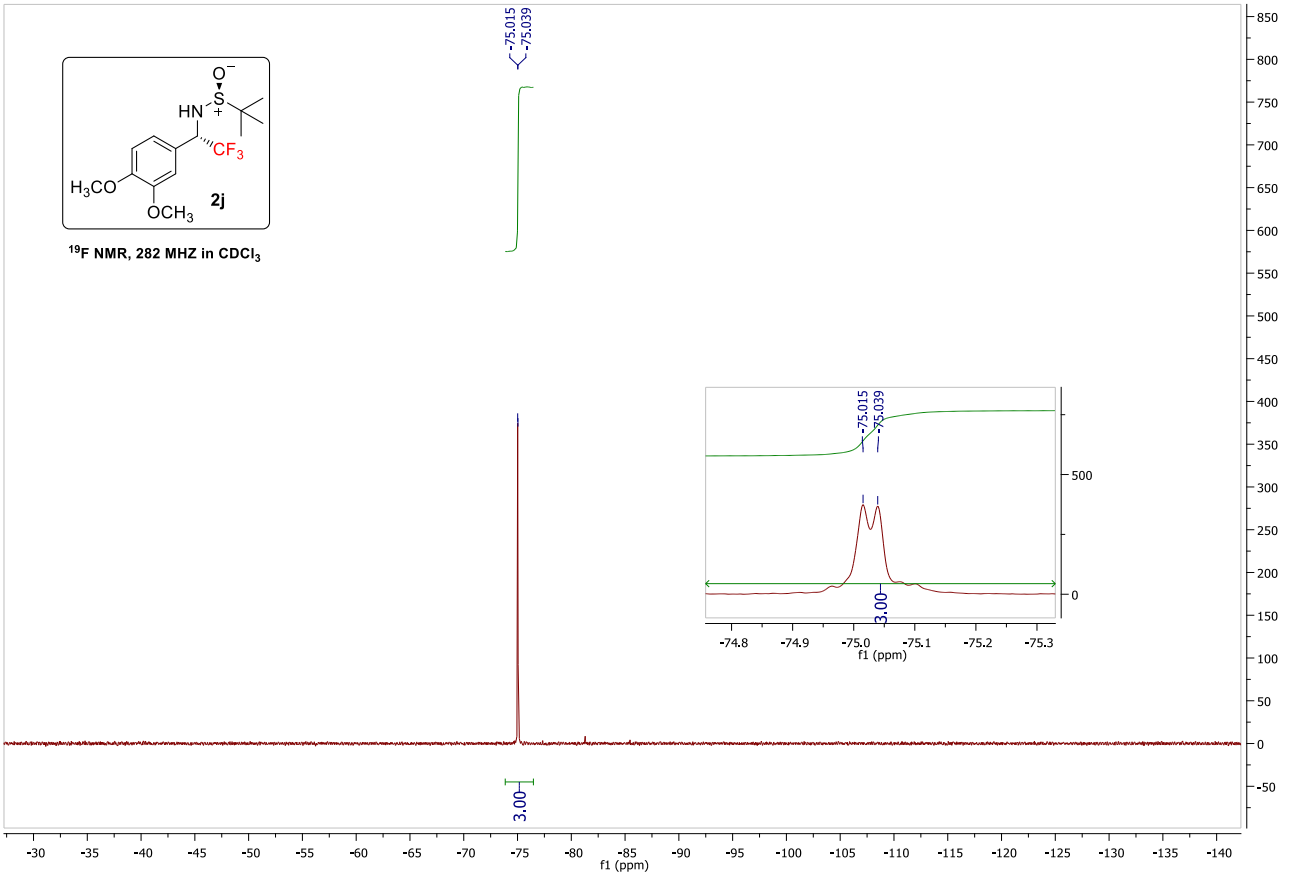


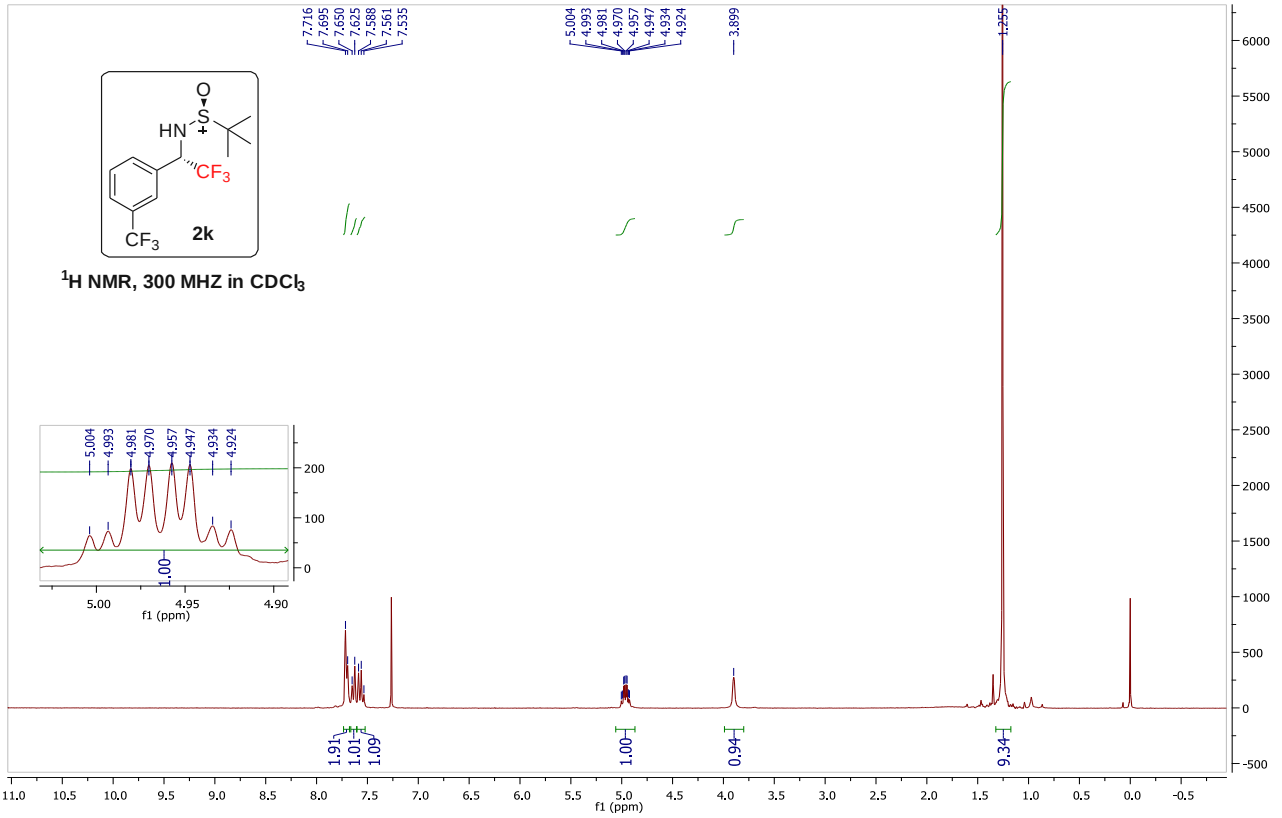
^{19}F NMR, 282 MHZ in $CDCl_3$

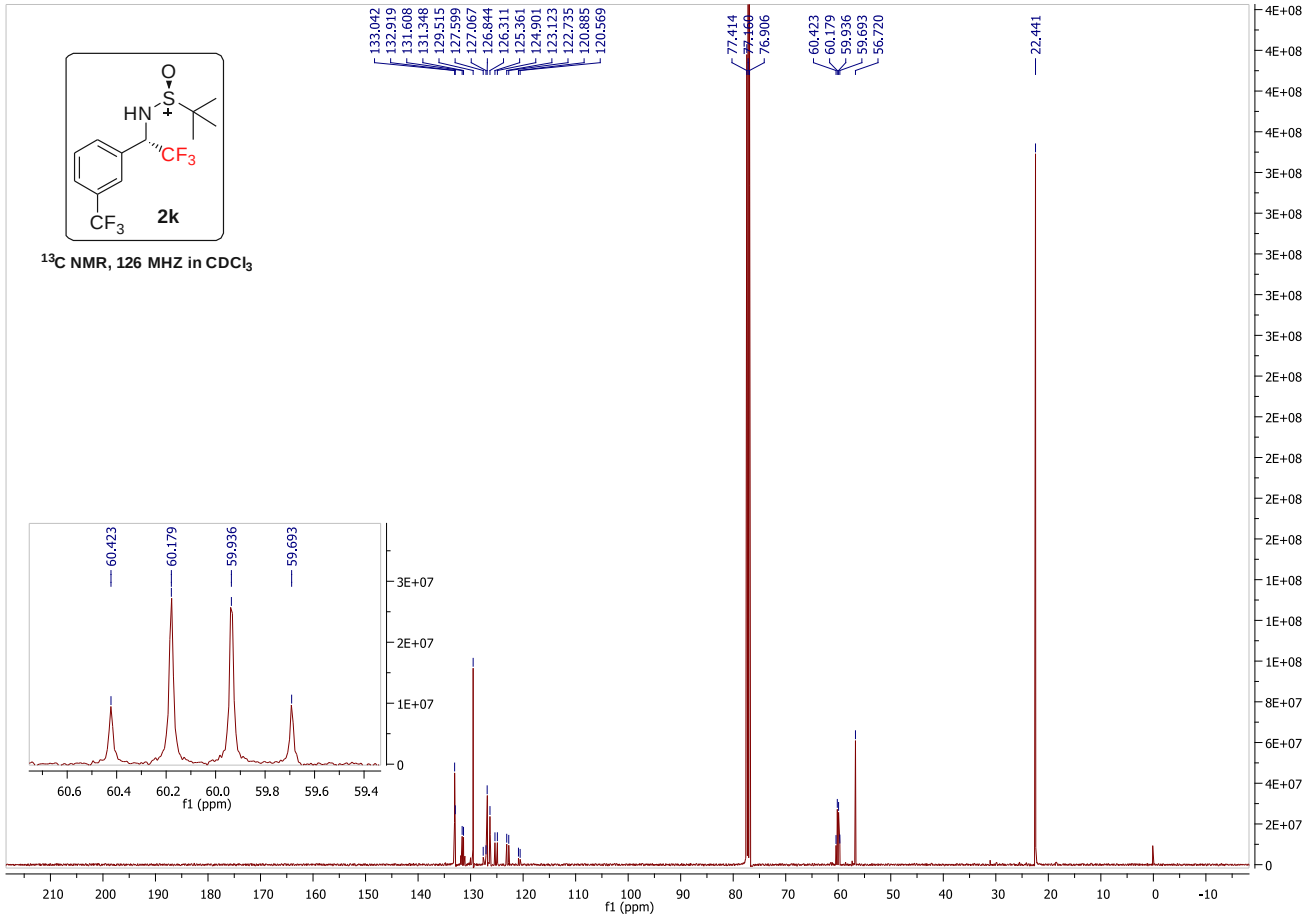


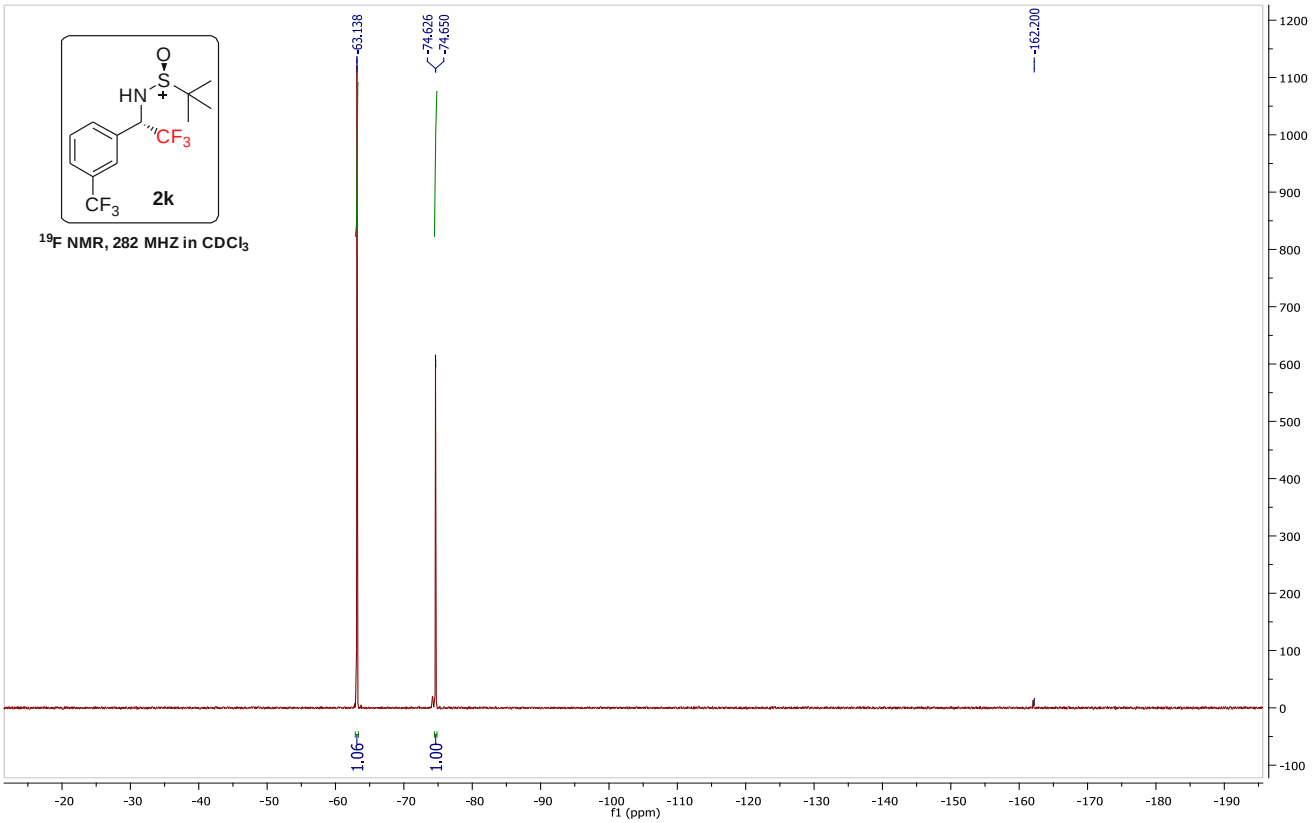
^{1}H NMR, 300 MHZ in $CDCl_3$


2j
13C NMR, 126 MHZ in CDCl3
150.290
149.207
128.025
125.791
123.608
123.554
122.637
121.318
111.925
111.026
77.414
77.160
76.905
60.236
59.996
59.753
56.320
56.001
22.534
60.477
60.236
59.996
59.753
f1 (ppm)


2j
19F NMR, 282 MHZ in CDCl3
-75.015
-75.039
3.00
f1 (ppm)

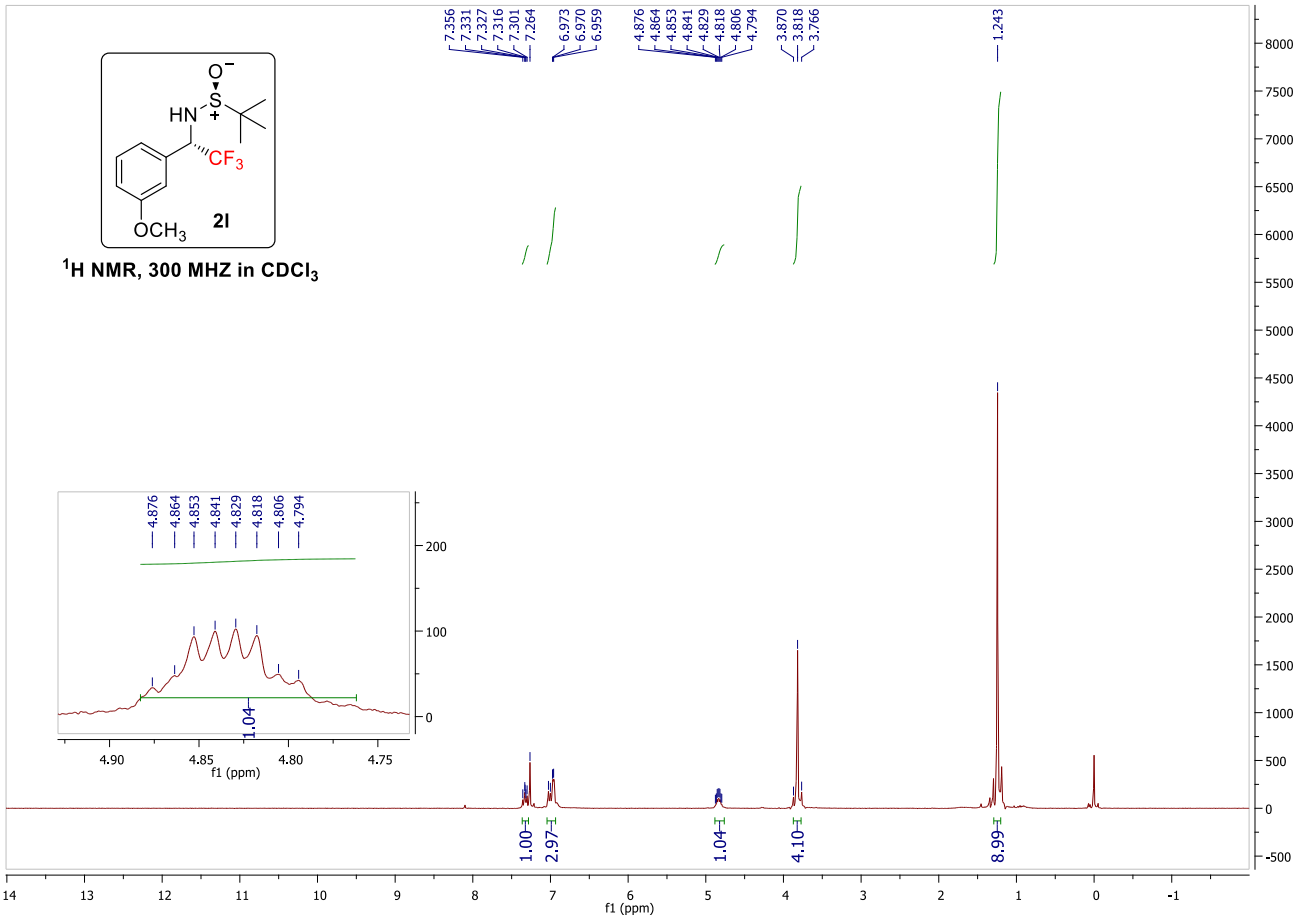

2k
1H NMR, 300 MHZ in CDCl3
f1 (ppm)


2k
13C NMR, 126 MHZ in CDCl3
f1 (ppm)



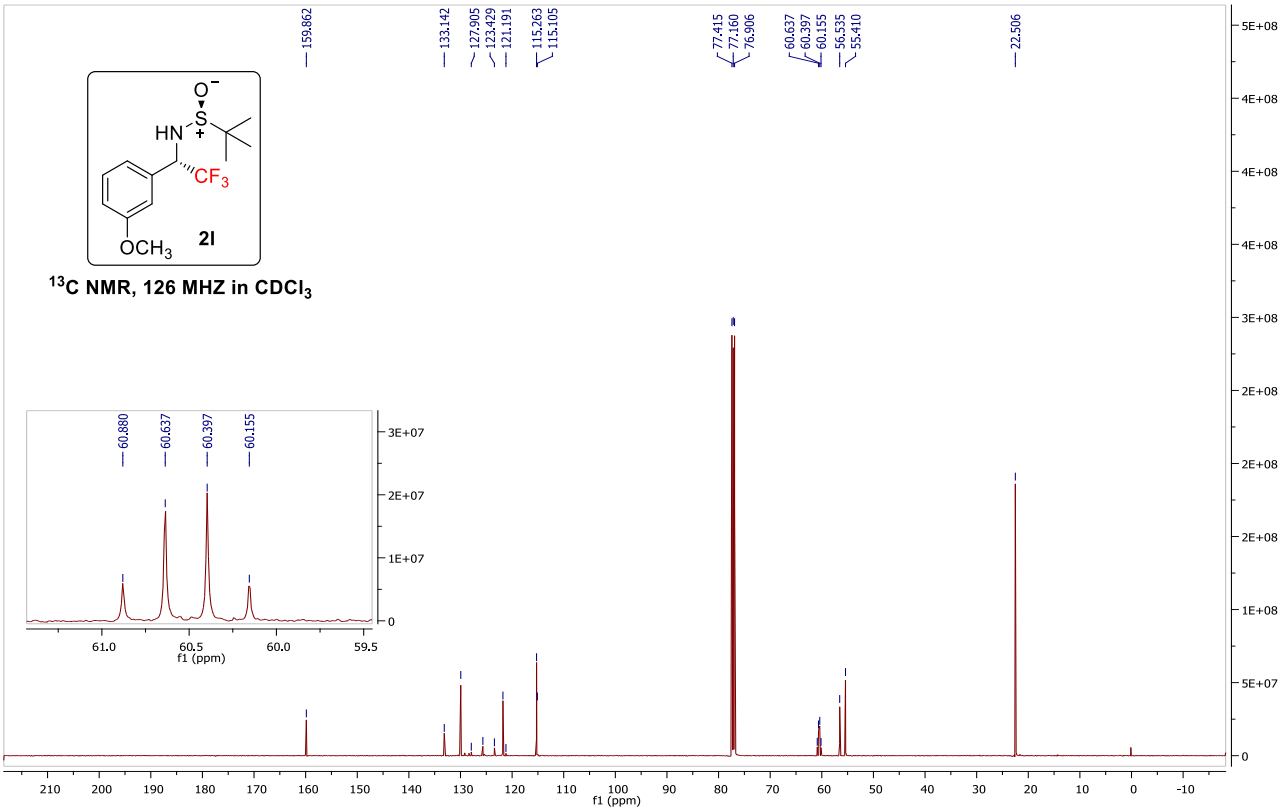
2k

^{19}F NMR, 282 MHZ in $CDCl_3$

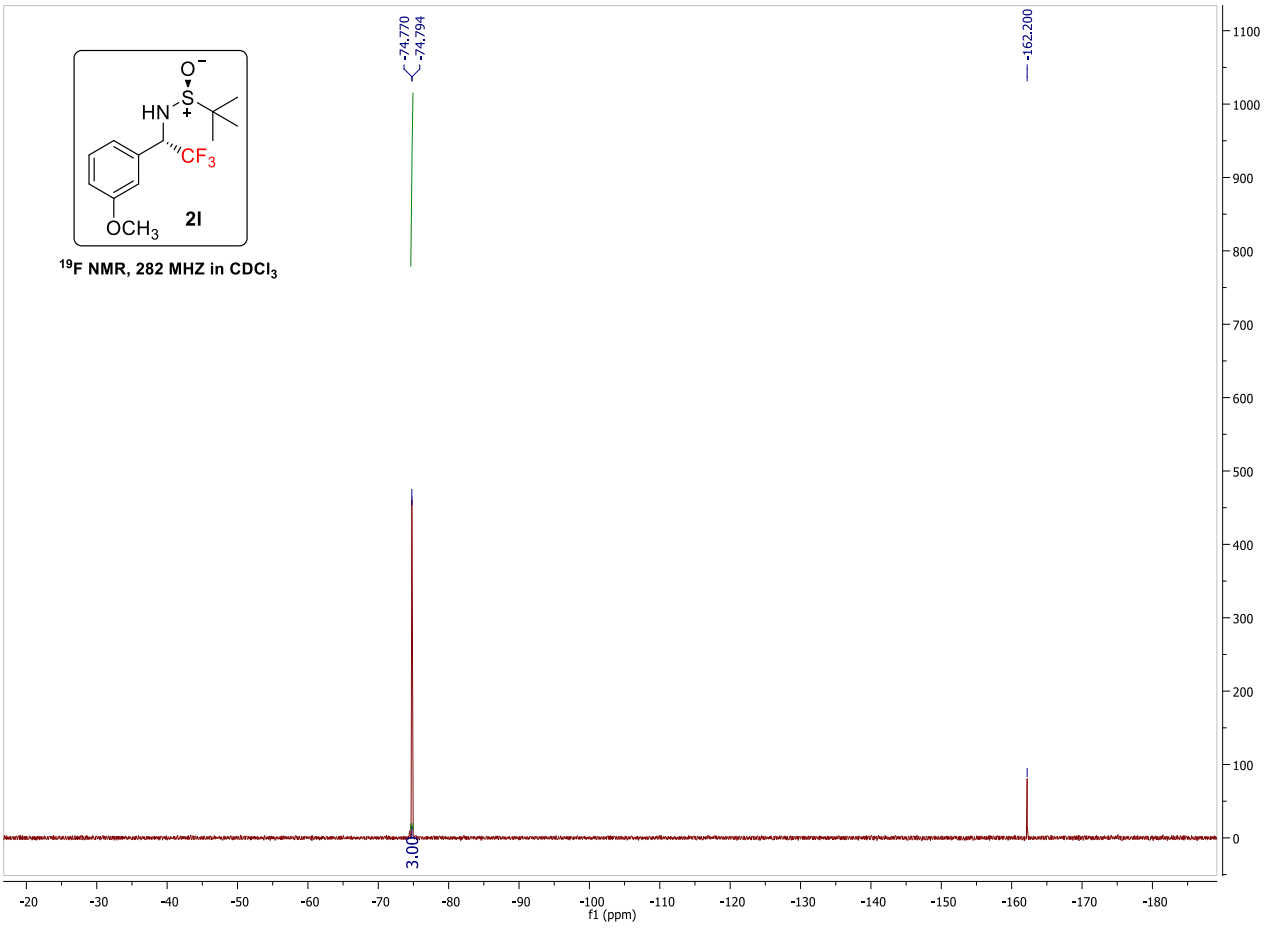


2l

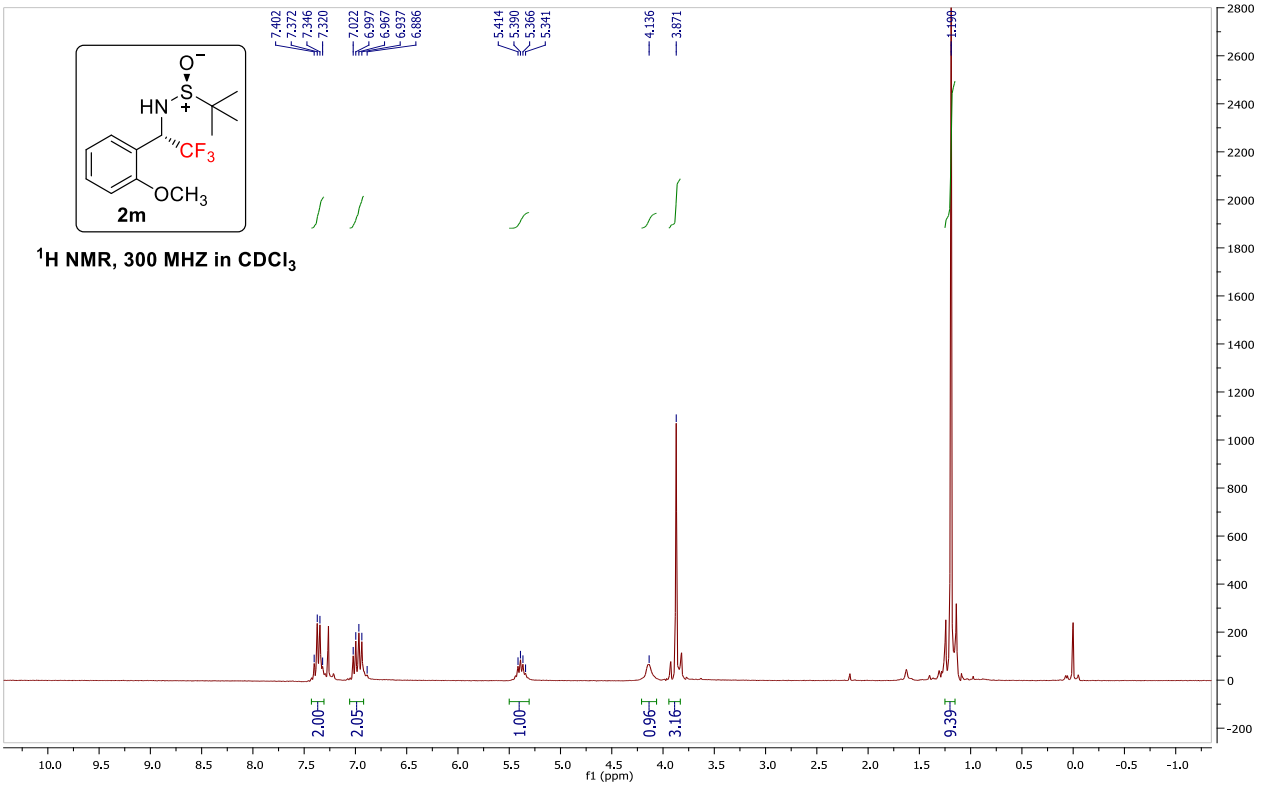
^{1}H NMR, 300 MHZ in $CDCl_3$

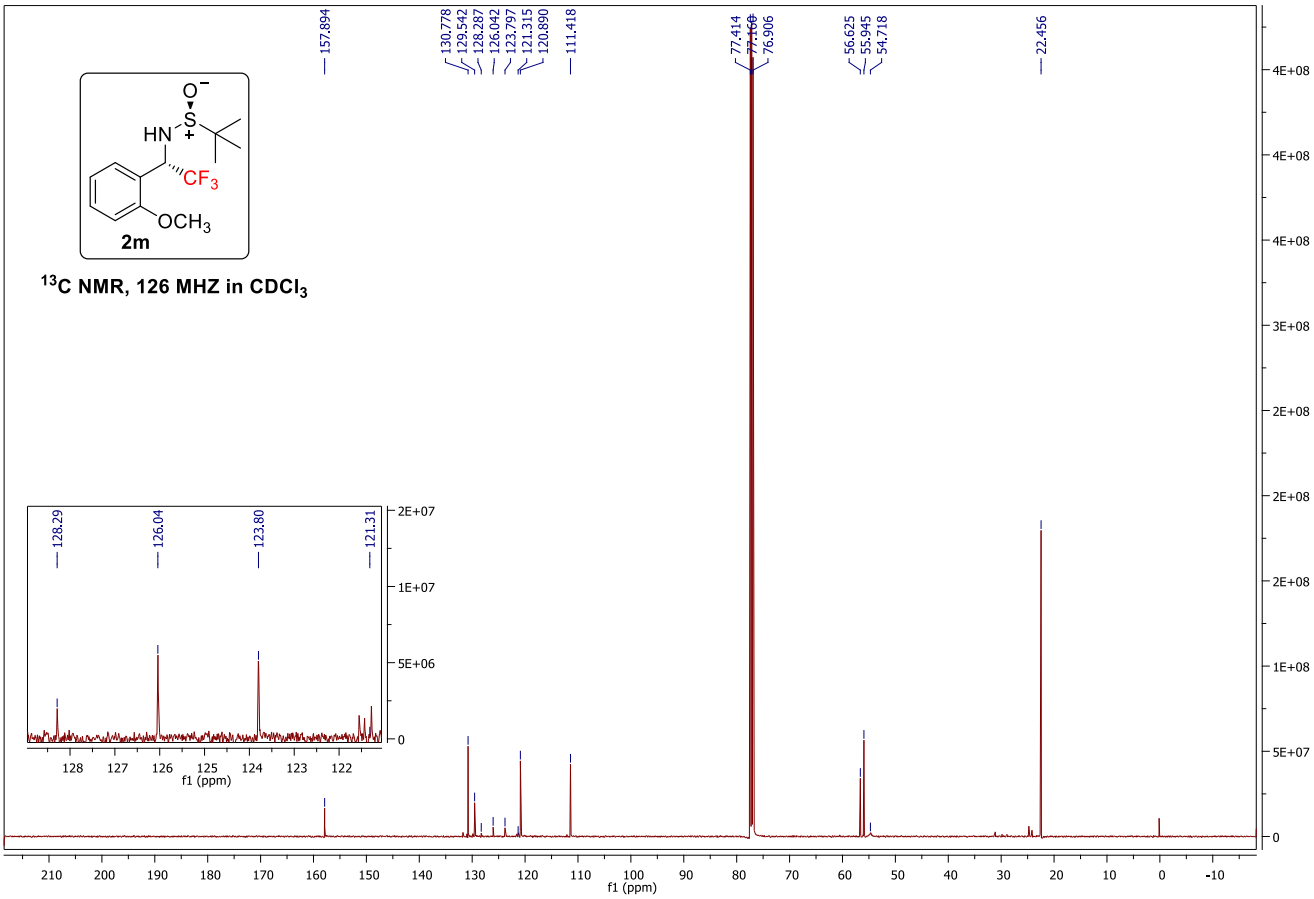


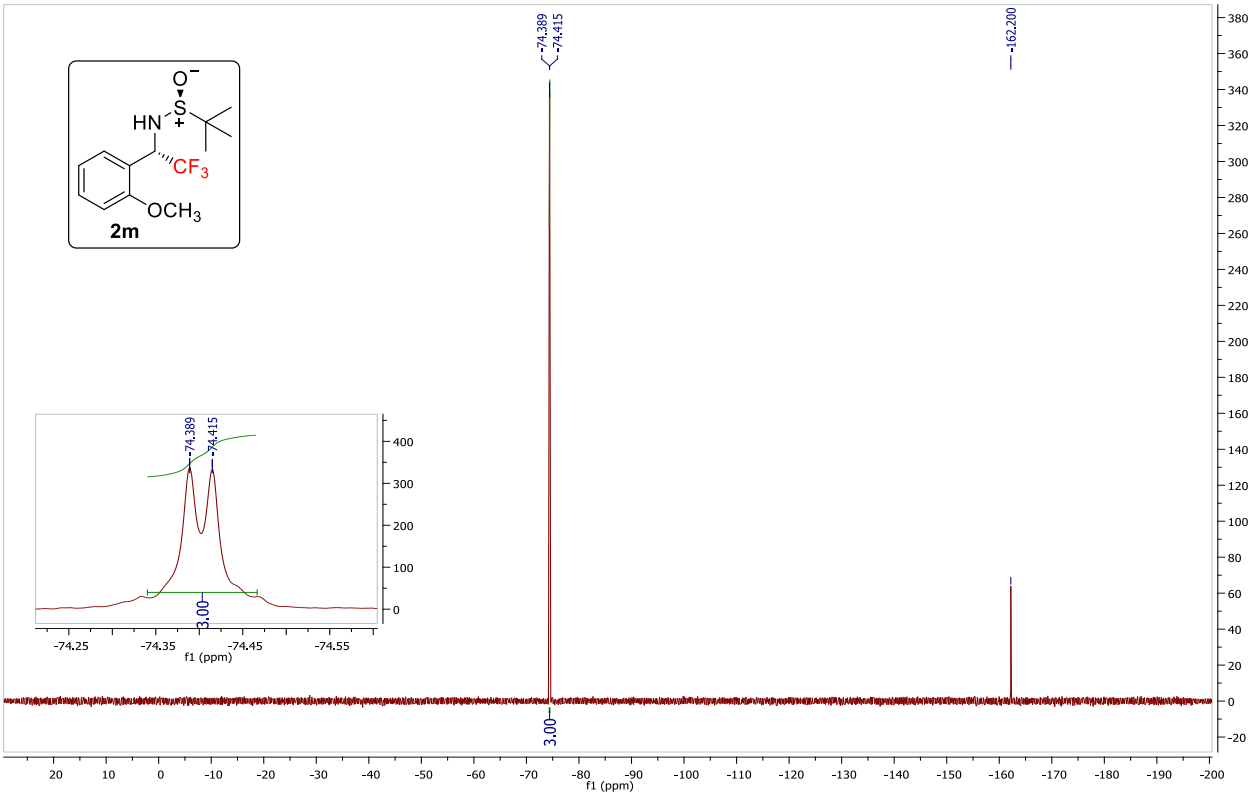
^{13}C NMR, 126 MHZ in $CDCl_3$

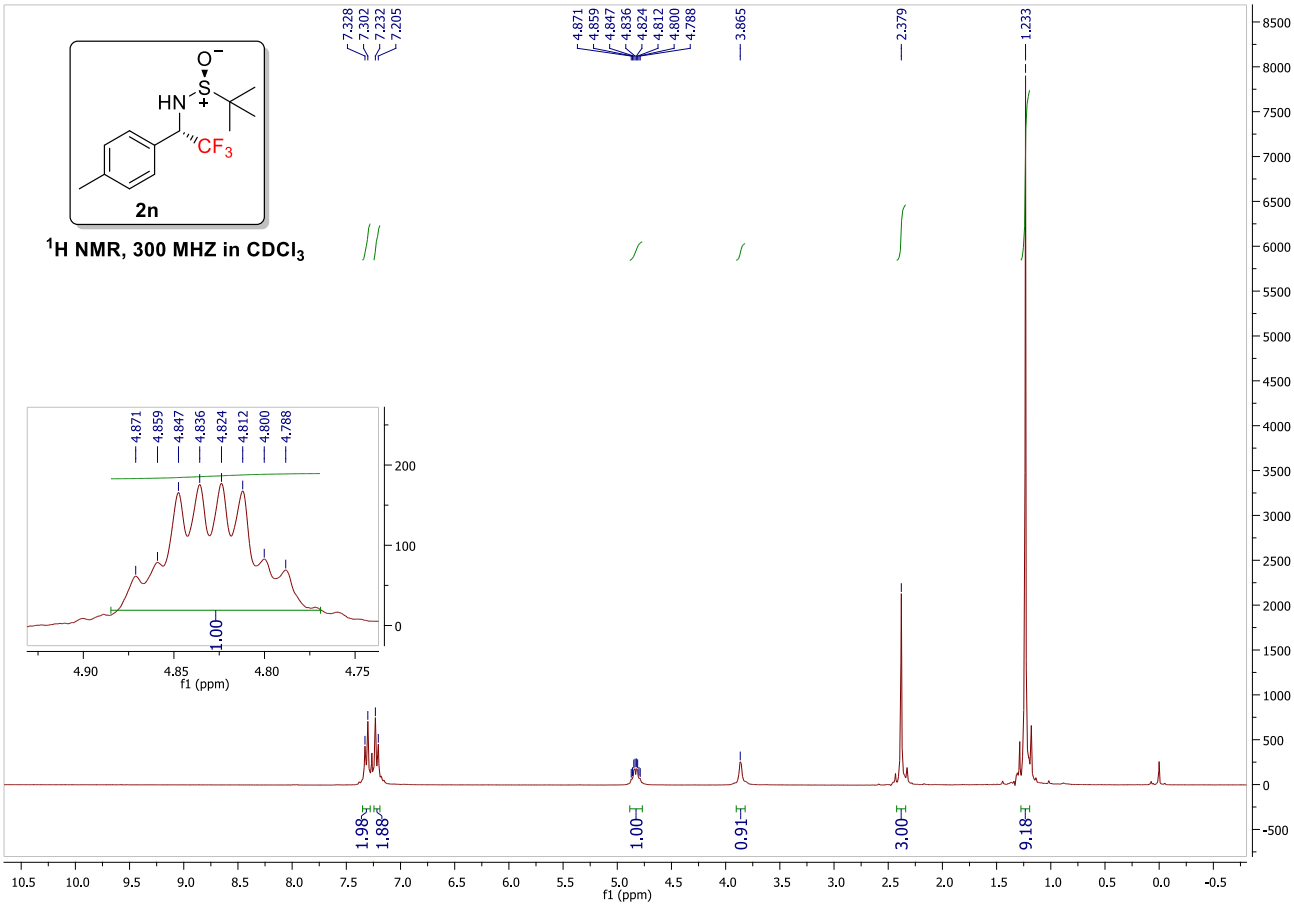


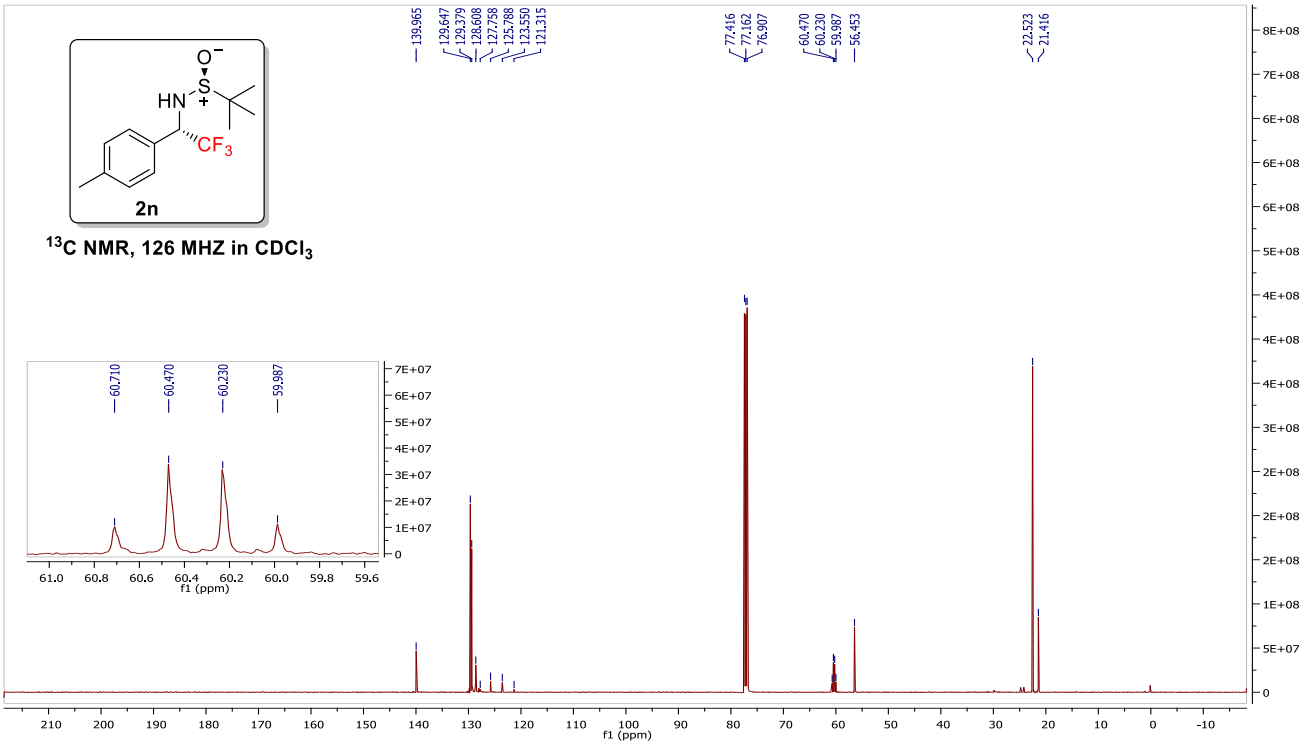
^{19}F NMR, 282 MHZ in $CDCl_3$

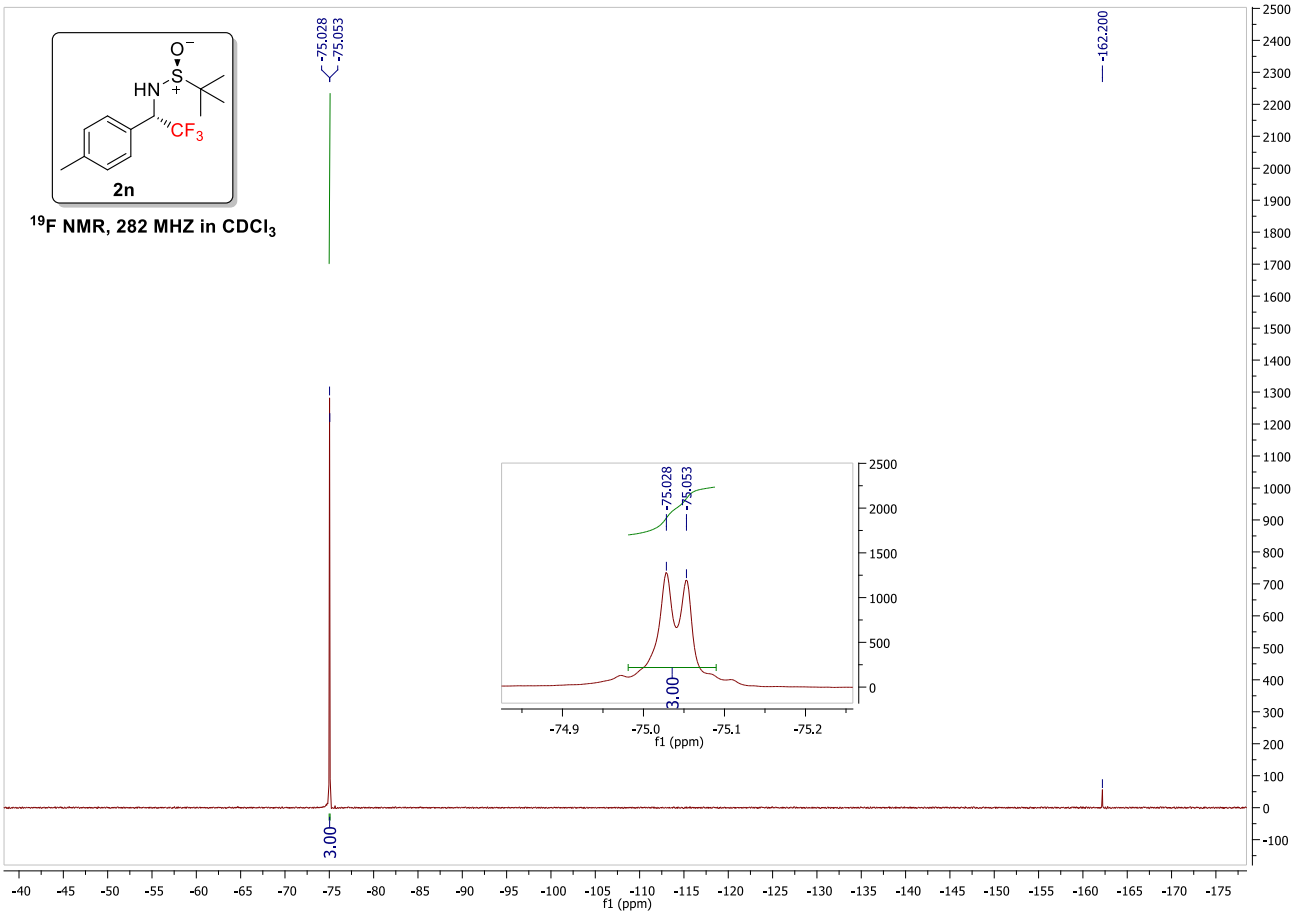

2m
^{1}H NMR, 300 MHZ in CDCl$_3$
f1 (ppm)

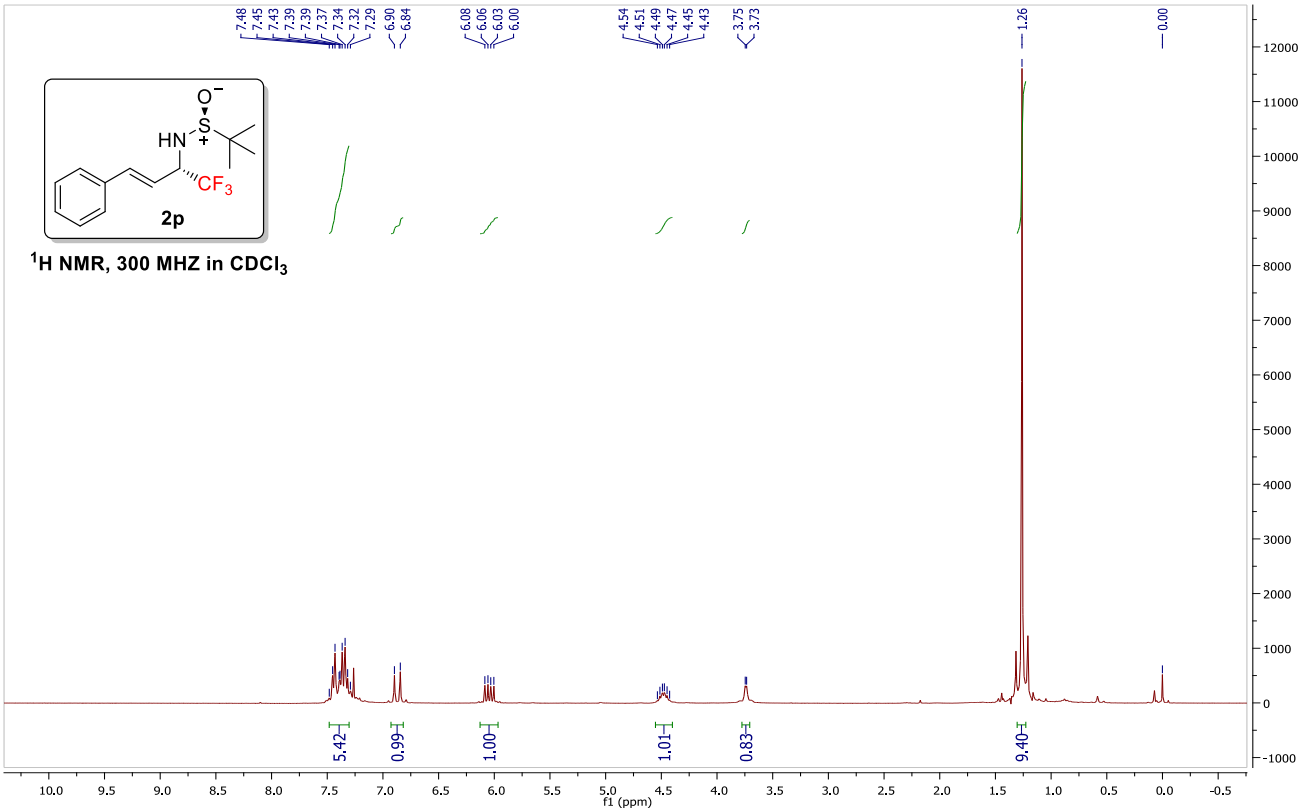

2m
^{13}C NMR, 126 MHZ in CDCl$_3$
f1 (ppm)

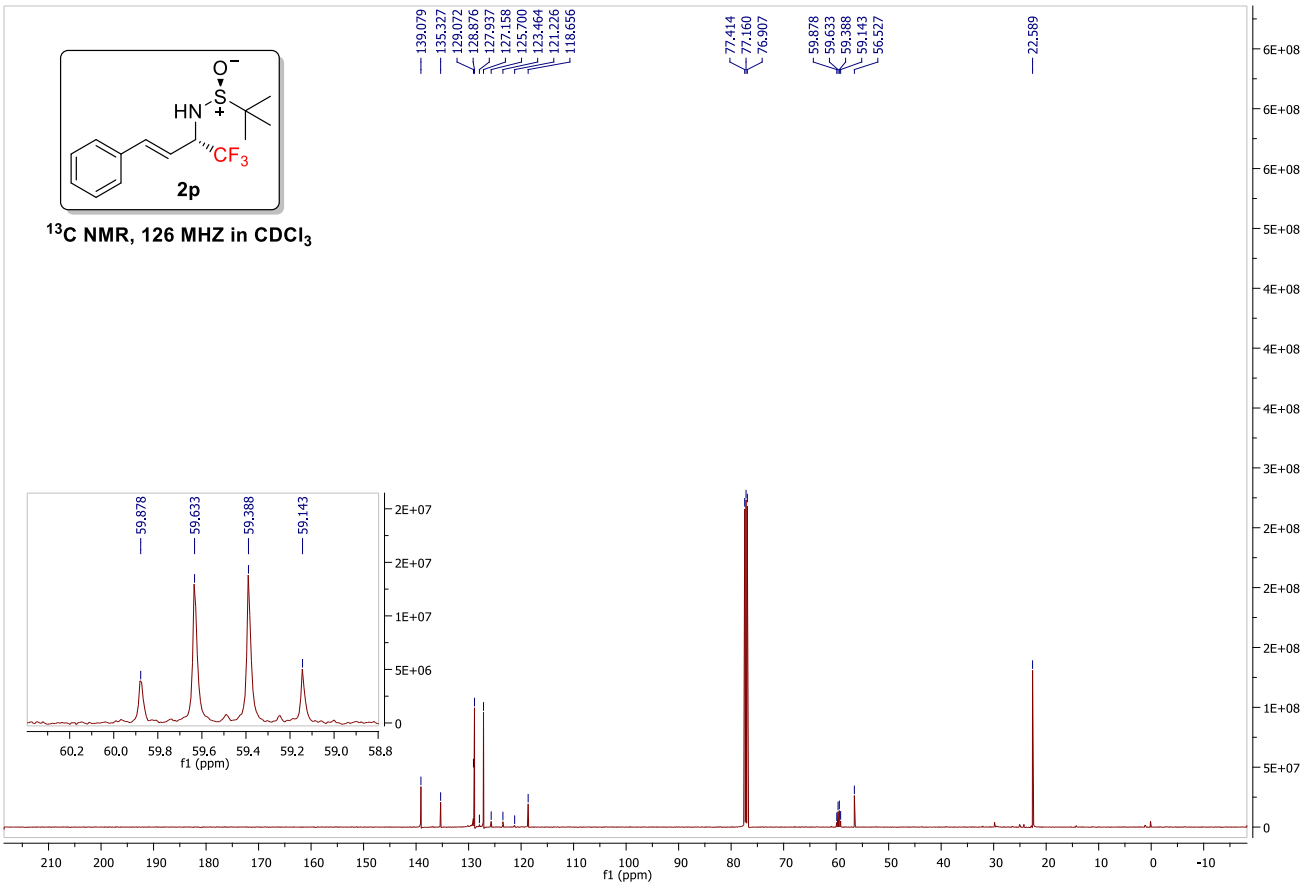

2m
-74.389
-74.415
-162.200
3.00
f1 (ppm)

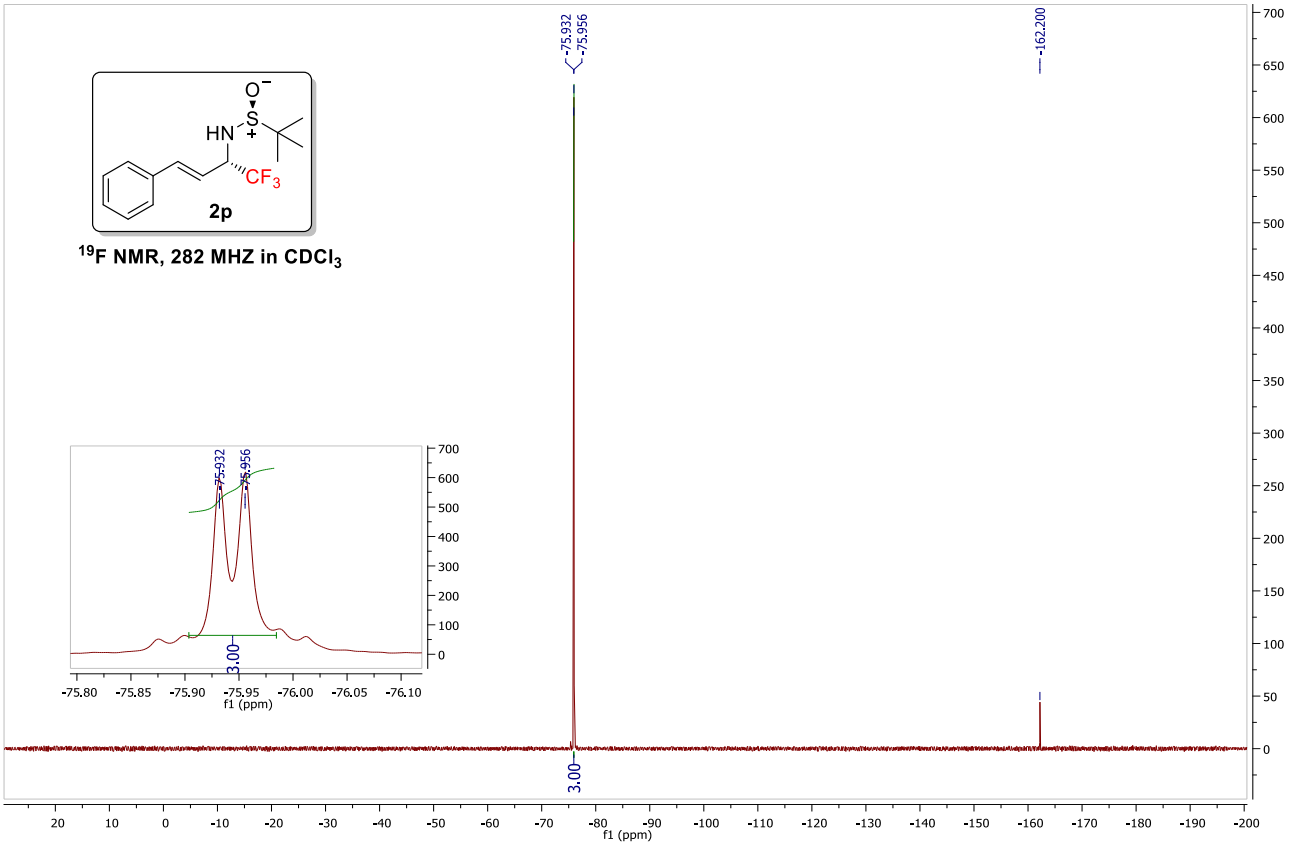

2n
1H NMR, 300 MHZ in CDCl3
7.328
7.302
7.232
7.205
4.871
4.859
4.847
4.836
4.824
4.812
4.800
4.788
3.865
2.379
1.233
1.98
1.88
1.00
0.91
3.00
9.18
f1 (ppm)

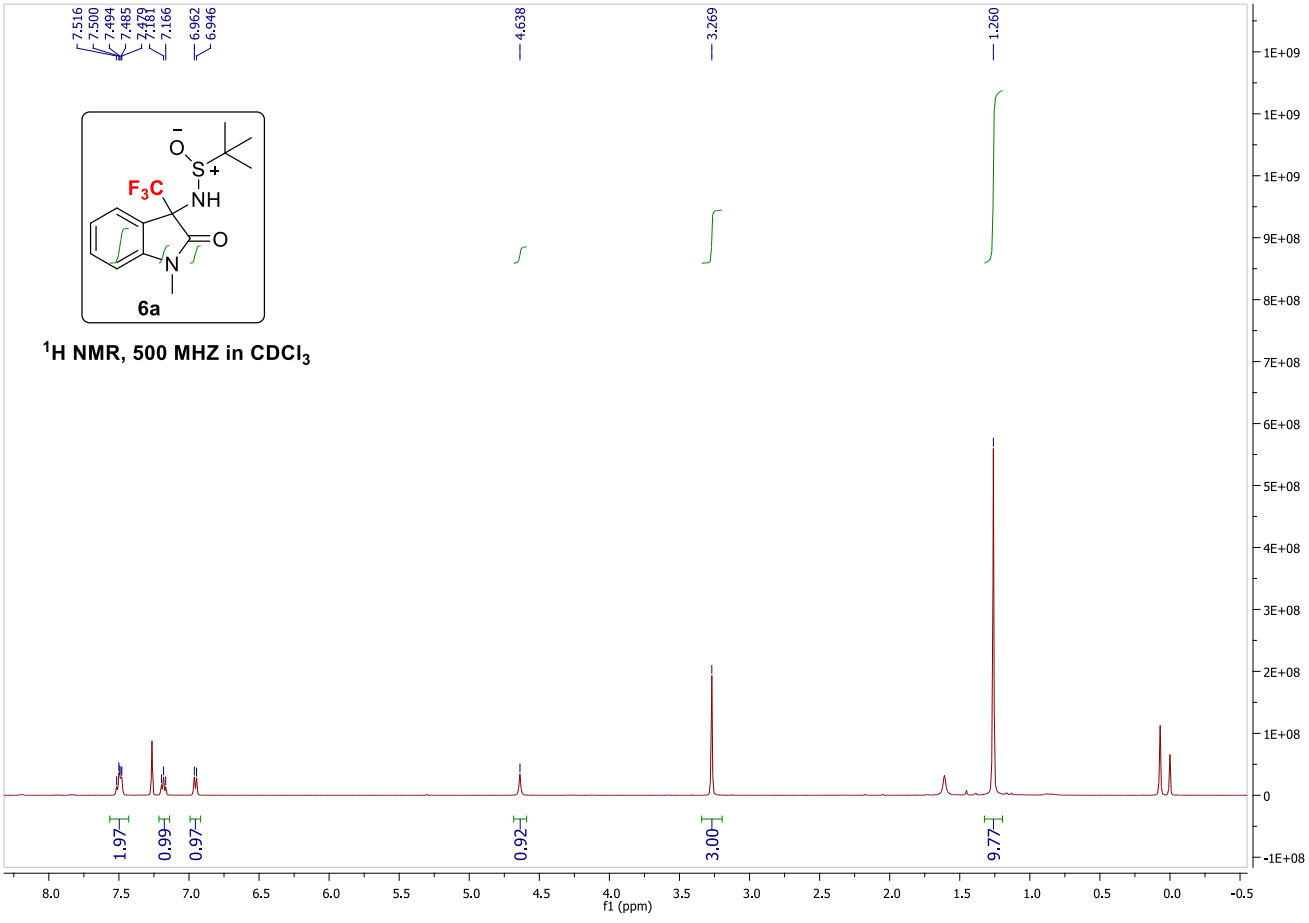

2n
^{13}C NMR, 126 MHZ in CDCl$_3$
f1 (ppm)

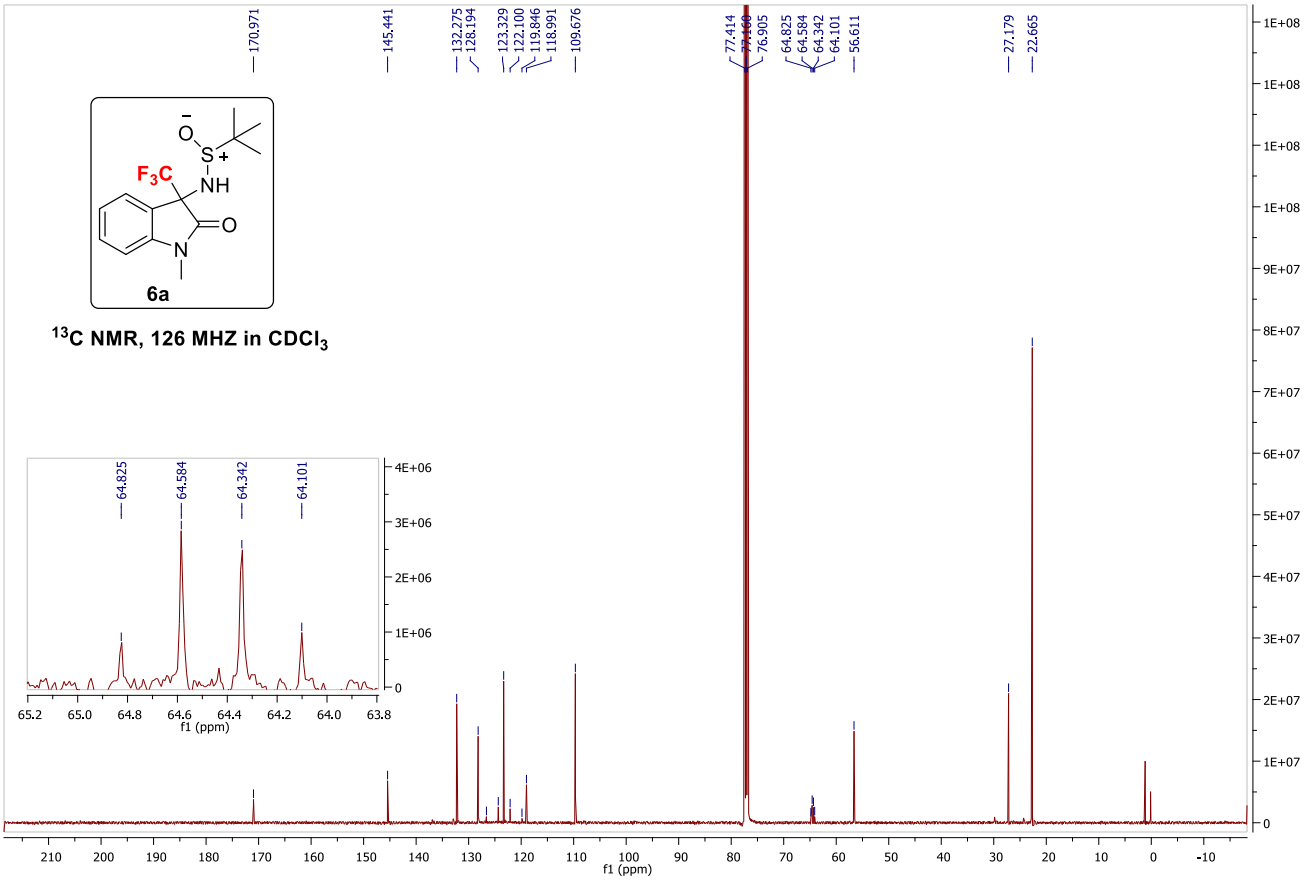

2n
^{19}F NMR, 282 MHZ in CDCl$_3$
f1 (ppm)

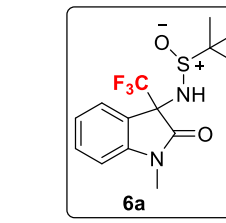

2p
^{1}H NMR, 300 MHZ in CDCl$_3$
f1 (ppm)


2p
^{13}C NMR, 126 MHZ in CDCl$_3$
f1 (ppm)


2p
19F NMR, 282 MHZ in CDCl3
-75.932
-75.956
-162.200
3.00
f1 (ppm)

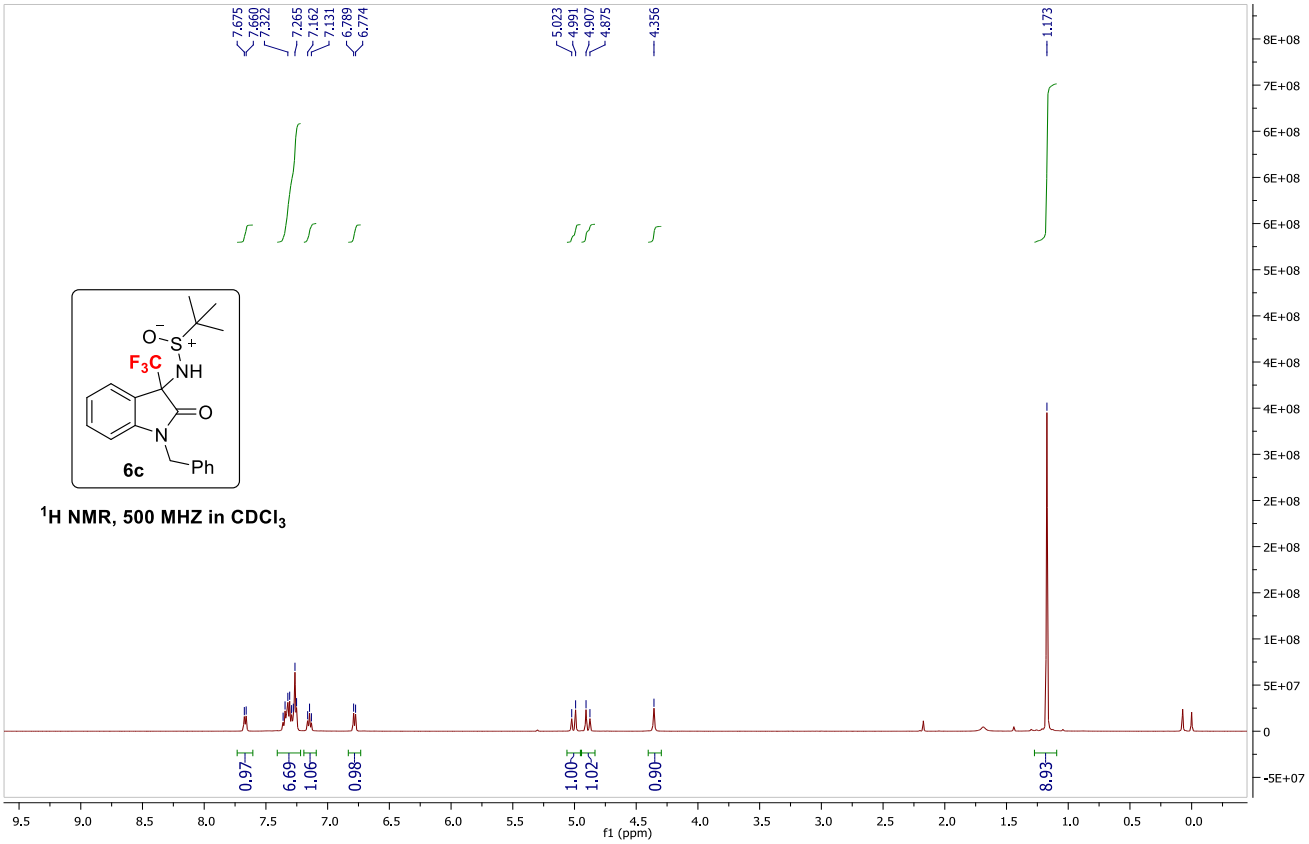

6a
1H NMR, 500 MHZ in CDCl3
7.516
7.500
7.494
7.485
7.179
7.166
6.962
6.946
4.638
3.269
1.260
1.97
0.99
0.97
0.92
3.00
9.77
f1 (ppm)



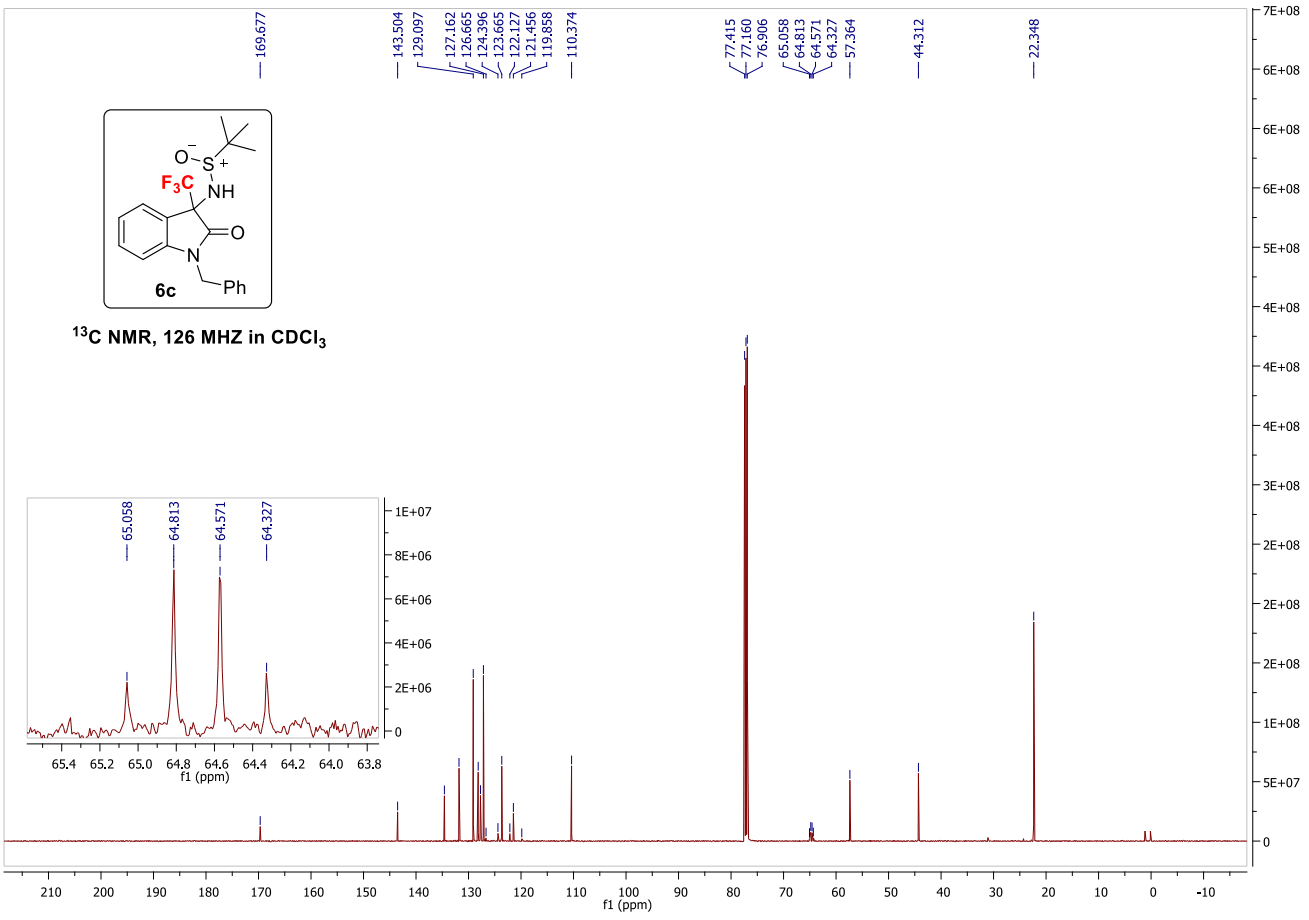


^{13}C NMR, 126 MHZ in $CDCl_3$

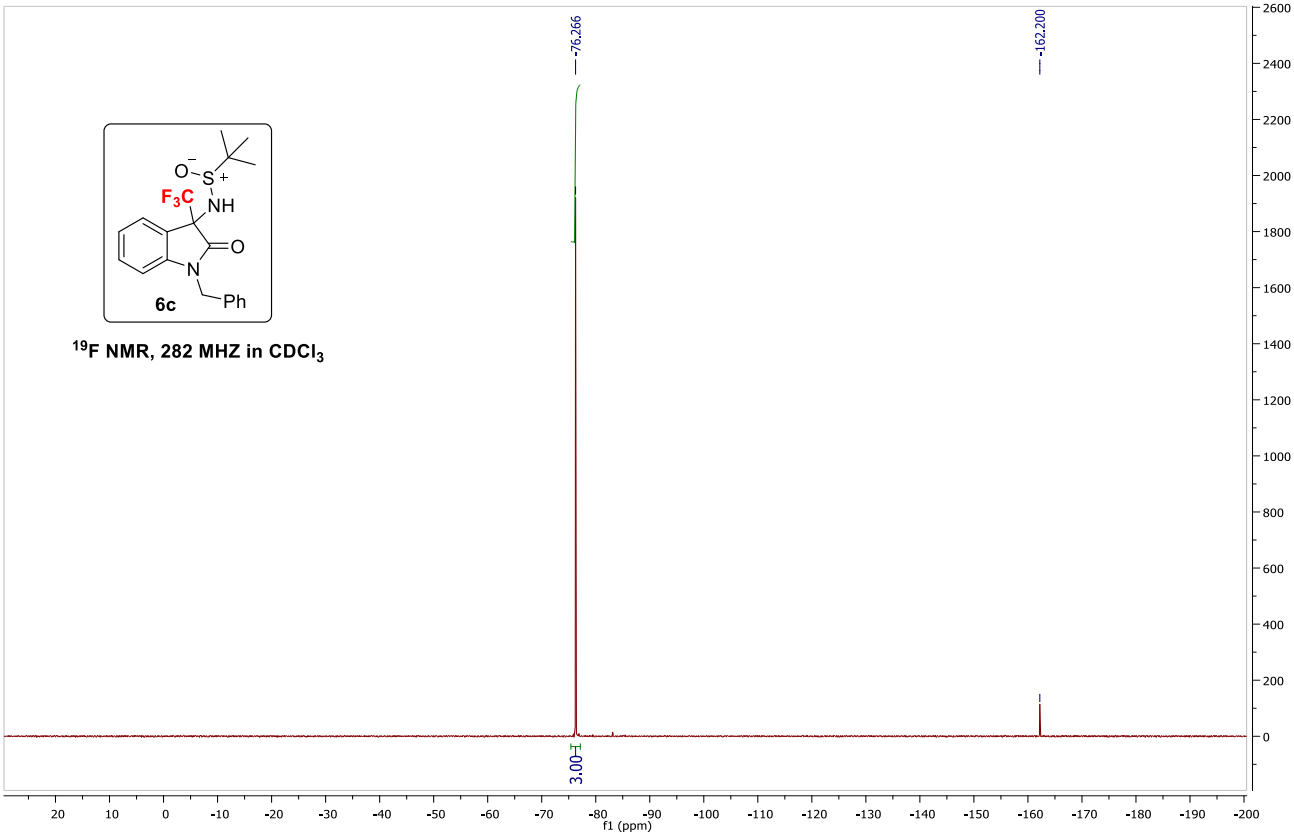
^{19}F NMR, 282 MHZ in $CDCl_3$



^{1}H NMR, 500 MHZ in $CDCl_3$



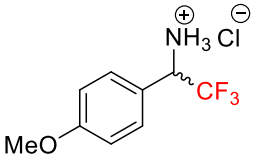
^{13}C NMR, 126 MHZ in $CDCl_3$



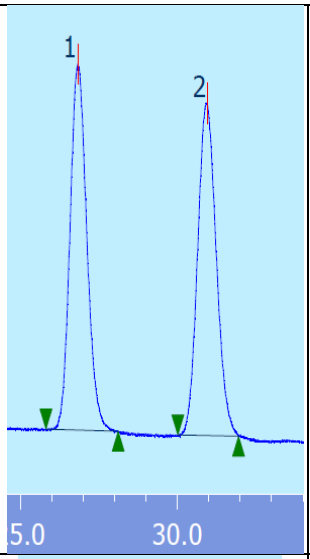
6c

^{19}F NMR, 282 MHZ in $CDCl_3$

10. HPLC Data

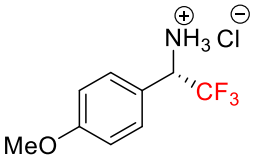


Racemic **4a/5a**

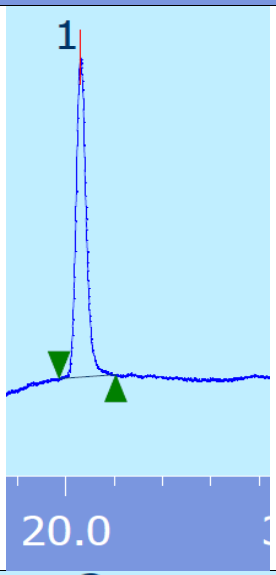


Column: OD-H
Hexane/2-Propanol/Diethylamine (98/2/0.1), 0.5 mL/min;
□ = 270 nm

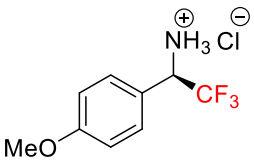
No.	t_R (min)	Area (%)	High (%)
1	26.827	49.764	52.401
2	30.933	50.236	47.599



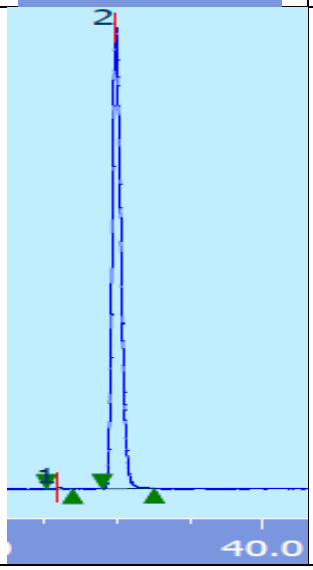
(*S*)-4a



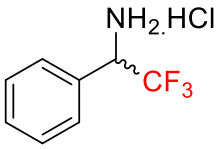
No.	t_R (min)	Area (%)	High (%)
1	26.120	99.346	99.333
2	30.133	0.654	0.667



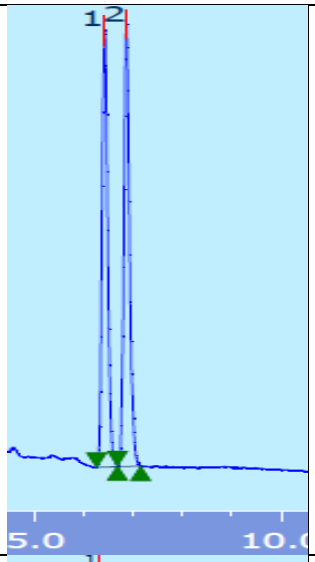
(*R*)-5a



No.	t_R (min)	Area (%)	High (%)
1	26.027	0.287	0.326
2	29.960	99.713	99.674

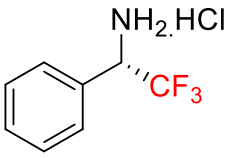


Racemic **4b**/**5b**

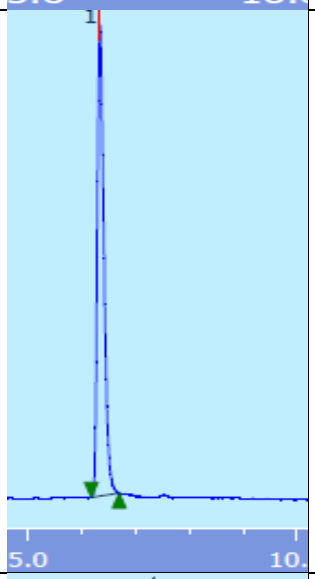


Column: OD-3
Hexane/2-Propanol/Diethylamine (70/30/0.1), 1.0

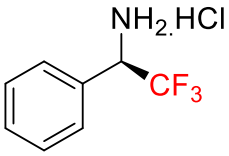
No.	t_R (min)	Area (%)	High (%)
1	6.413	48.544	49.683
2	6.867	51.456	50.317



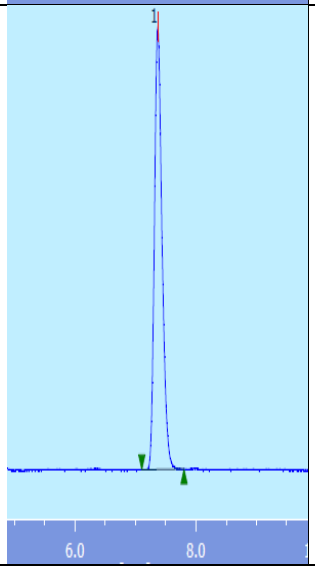
(*S*)-4b



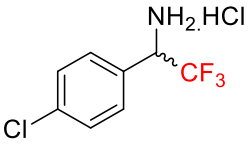
No.	t_R (min)	Area (%)	High (%)
1	6.333	100.000	100.000
2	-	-	-



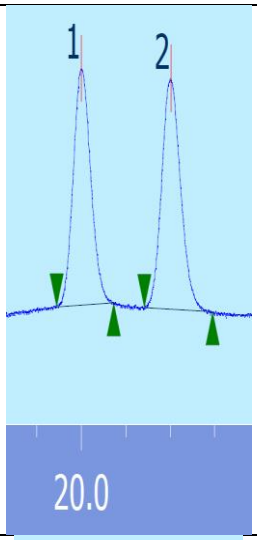
(*R*)-5b



No.	t_R (min)	Area (%)	High (%)
1	-	-	-
2	7.373	100.000	100.000

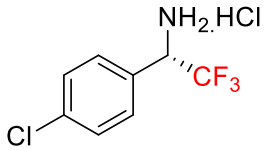


Racemic **4c/5c**

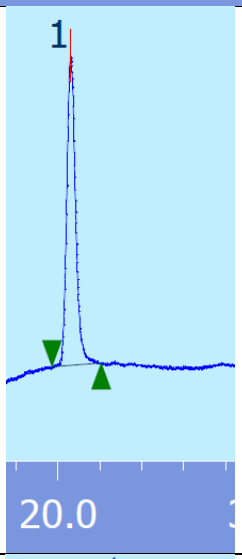


Column: OD-H
Hexane/2-Propanol/Diethylamine (98/2/0.1), 0.5 mL /min; □ = 270 nm

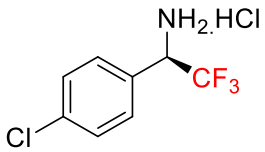
No.	t_R (min)	Area (%)	High (%)
1	20.000	48.839	50.641
2	22.000	51.161	49.359



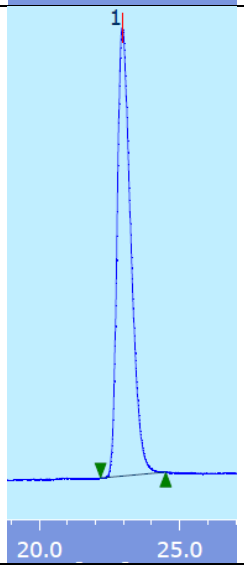
(*S*)-4c



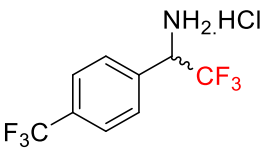
No.	t_R (min)	Area (%)	High (%)
1	20.627	100.000	100.000
2	-	-	-



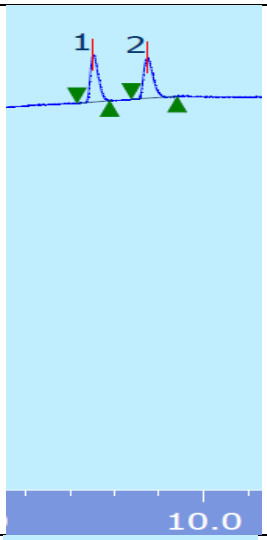
(*R*)-5c



No.	t_R (min)	Area (%)	High (%)
1	-	-	-
2	22.960	100.000	100.000

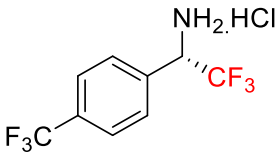


Racemic **4f/5f**

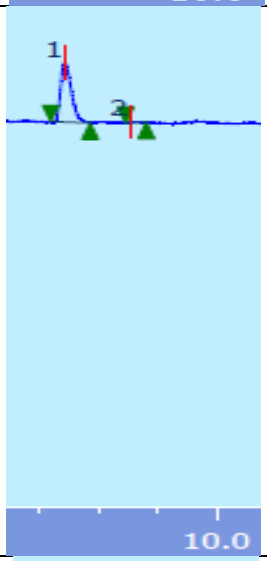


Column: OD-3
Hexane/2-Propanol/Diethylamine (90/10/0.1), 1.0 mL /min; □ = 220 nm

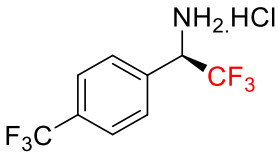
No.	t_R (min)	Area (%)	High (%)
1	7.520	50.154	53.682
2	8.733	49.846	46.318



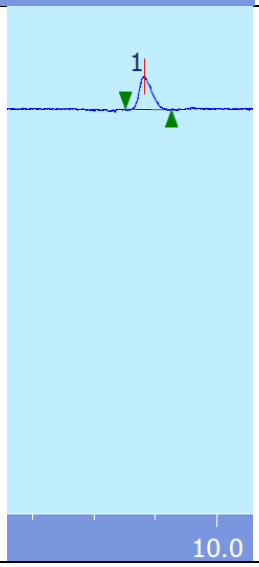
(*S*)-4f



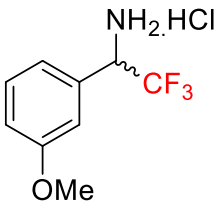
No.	t_R (min)	Area (%)	High (%)
1	7.427	98.444	97.716
2	8.520	1.556	2.284



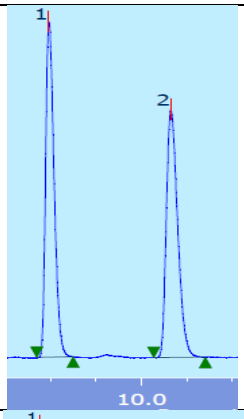
(*R*)-5f



No.	t_R (min)	Area (%)	High (%)
1	-	-	-
2	8.813	100.000	100.000

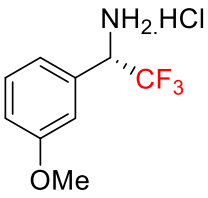


Racemic **4l**

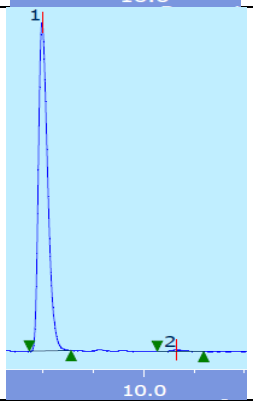


Column: OD-3
Hexane/2-Propanol/Diethylamine (70/30/0.1), 1.0 mL/min; □ = 254 nm

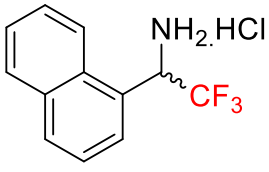
No.	t_R (min)	Area (%)	High (%)
1	7.960	50.296	57.497
2	10.640	49.704	42.503



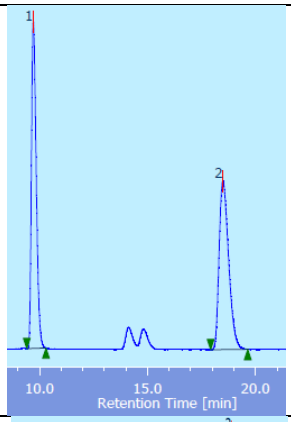
(*S*)-4l



No.	t_R (min)	Area (%)	High (%)
1	7.987	99.451	99.562
2	10.653	0.549	0.438

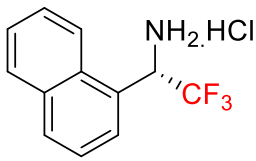


Racemic **4q**

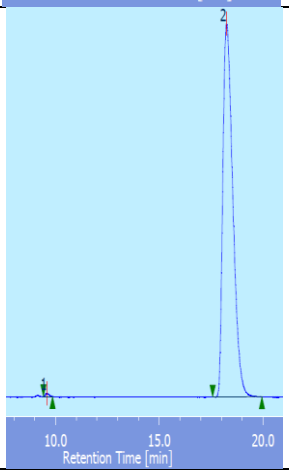


Column: OD-3
Hexane/2-Propanol/Diethylamine (70/30/0.1), 1.0 mL/min; □ = 254 nm

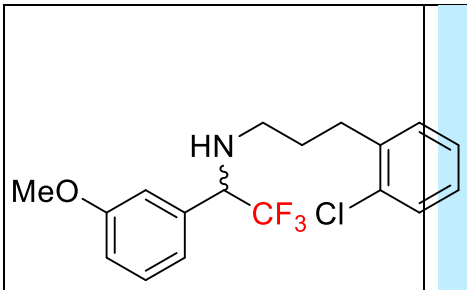
No.	t_R (min)	Area (%)	High (%)
1	9.707	49.468	65.950
2	18.493	50.532	34.050



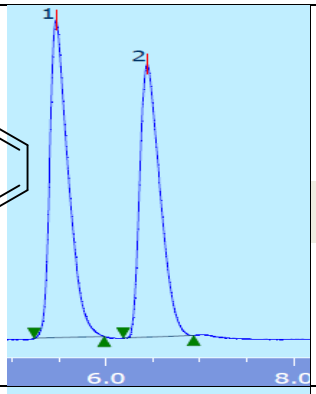
(*S*)-4q



No.	t_R (min)	Area (%)	High (%)
1	9.587	0.323	0.811
2	18.240	99.677	99.189

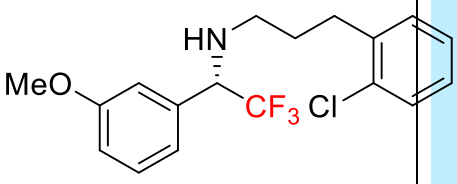


Racemic **7**

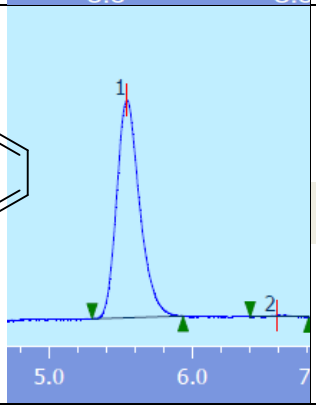


Column: OD-3
Hexane/2-Propanol
(90/10), 1.0 mL/min; □ = 254 nm

No.	t_R (min)	Area (%)	High (%
1	5.467	51.930	53.781
2	6.433	48.070	46.219

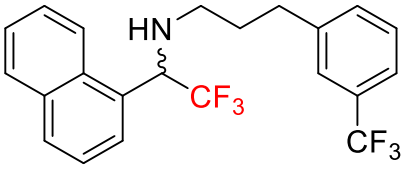


(*S*)-7

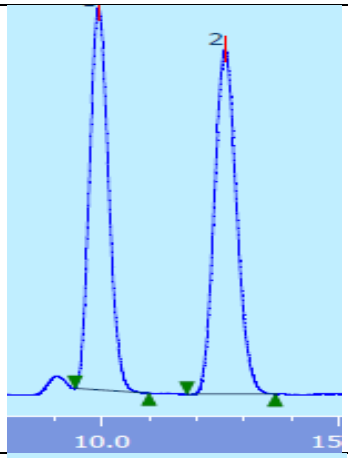


Column: OD-3
Hexane/2-Propanol
(90/10), 1.0 mL/min; □ = 254 nm

No.	t_R (min)	Area (%)	High (%
1	5.542	99.252	99.184
2	6.583	0.748	0.816

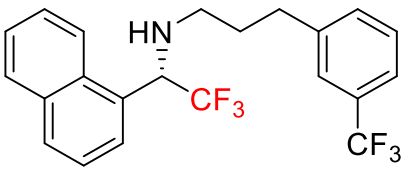


Racemic **8**

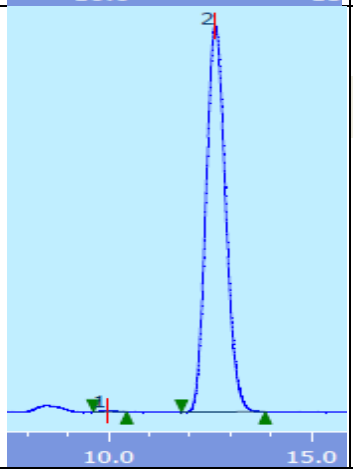


Column: IA
Hexane/2-Propanol
(98/2), 0.5 mL/min; □ = 254 nm

No.	t_R (min)	Area (%)	High (%
1	9.917	48.589	52.561
2	12.592	51.411	47.439



(*S*)-8



No.	t_R (min)	Area (%)	High (%
1	5.467	51.930	53.781
2	6.433	48.070	46.219