Supplementary information for

Radical Difluoromethylthiolation of Aromatics Enabled by Light

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1. General information

Solvents and reagents were purchased from Sigma-Aldrich and Fisher scientific chemical companies and were used without further purification unless otherwise specified. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra (CCl_3F set at 0 ppm) were recorded on Bruker 500 MHz spectrometers, which uses the deuterium lock signal to reference the spectra. The solvent residual peaks, e.g., of chloroform ($CDCl_3$: δ 7.28 ppm and δ 77.0 ppm), were used as references. Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublet, etc), coupling constant (J/Hz) and integration. All NMR spectra were recorded at room temperature. High-resolution mass spectrometry was conducted by using atmospheric pressure chemical ionization (APCI) or electro-spraying ionization (ESI), and was performed by McGill University on a Thermo-Scientific Exactive Orbitrap. Protonated/deprotonated molecular ions $(M \pm H)^+$ or sodium adducts $(M+Na)^+$, were used for empirical formula confirmation. Infrared spectroscopic data was collected by the Bruker ALPHA FTIR spectrometer as samples were applied either in KBr pellets or in neat forms. All reactions are stirred magnetically unless otherwise specified. Short packed column chromatography was performed with E. Merck silica gel 60 (230–400 mesh) or SORBENT silica gel 30-60 µm. Flash colum chromatography was performed Isolera™ Prime advanced automatic flash purification system. Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 pre-coated plates (0.25 mm). A standard LZC-4V photoreactor from Luzchem Company, which contains six 2.5 W mercury low pressure lamps with emission at 254 nm, was used in experiments under UV radiation. The reactions were conducted in sealed 5.0 mL quartz tubes. The experiments under visible light were performed using 40 W compact fluorescent lamps (CFL) and the reactions were conducted in sealed tubes. Both setups are equipped with fans for efficient temperature maintenance.

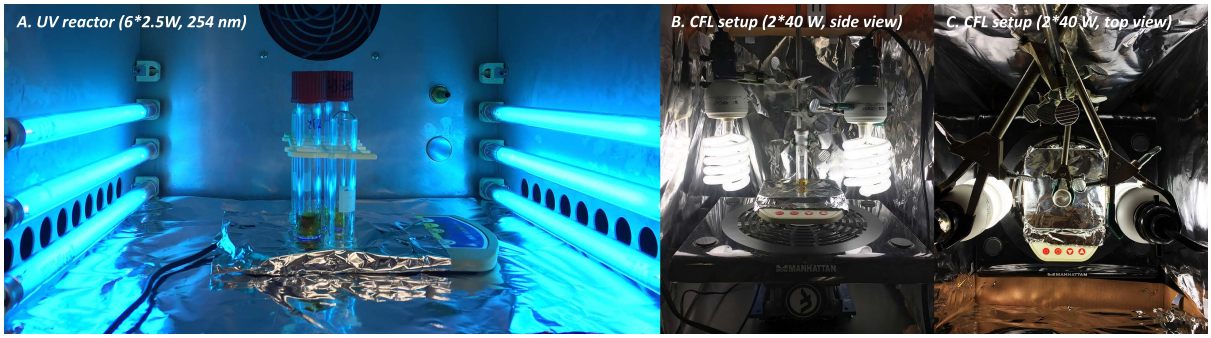
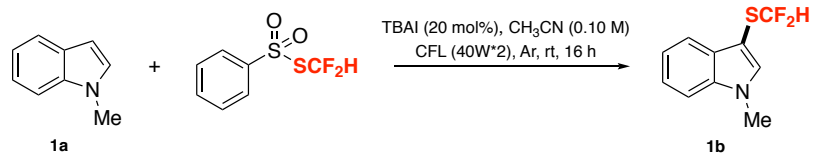


Figure S1. A. UV photoreactor (6*2.5 W, 254 nm); B. CFL setup (2*40W, side view); C. CFL setup (2*40 W, top view)

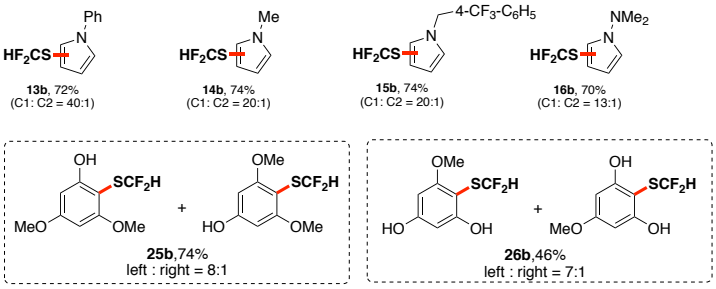
2. General procedures



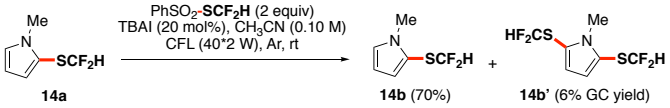
The preparation of **1b** is representative and applicable to all difluoromethylthioethers synthesis in this work unless otherwise specified. To a flame-dried reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar were added the *N*-methylindole **1a** (0.10 mmol, 1.0 equiv), *S*-(difluoromethyl) benzenesulfonothioate **$PhSO_2SCF_2H$** (0.20 mmol, 2.0 equiv). The resulting mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon (>99.999%). Shortly after, tetrabutylammonium iodide **TBAI** (0.020 mmol, 20 mmol%) in degassed CH_3CN (1.0 mL), which was prepared as Stock solution, was injected into the reaction tube. This procedure is termed Method **A**. The procedure of Method **B** is basically identical to that in **A** except that **TBAI** is absent and the reaction time was prolonged to 48 hours in order to consume the unreacted substrates. Method **C** is specific for the gram-scale experiment (See **33b** for details). Unless otherwise specified, the preparation of difluoromethylthioethers follows the procedure in Method **A**.

The reaction was stirred at room temperature under irradiation by using compact fluorescent lamps (CFL) until the starting material was completely consumed as monitored by GC-MS. *The length ranges from 16 h to 48 h and mostly, 16 h of radiation could result in decent yield.* After complete consumption of the starting material, the reaction mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. The pure desired product was provided after purification by flash column chromatography on silica gel, which furnished the titled compound **1b** as described.

a) Evaluation of regioselectivity

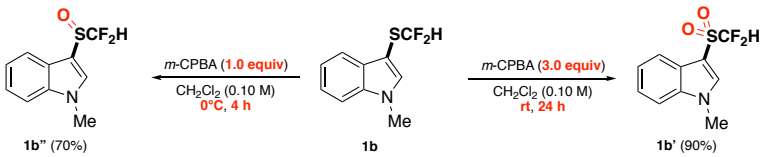


b) Evaluation of mono-/difunctionalization selectivity



Comments on the possible regioselectivity and mono-/difunctionalization issues. During our examination on functional group tolerance of our difluoromethylthiolation protocol, we carefully analyzed the GC-MS spectra and evaluated the regioselectivity. Generally, the most electron rich sites of the substrates are difluoromethylthiolated but for the above compounds, regiomers were observed in GC-MS and the ratios (ranging from 40:1 to 7:1) were obtained by the integration of corresponding peaks in the spectra, assuming the response factors of regiomers are identical. For the difunctionalization, we only observed the bis(difluoromethylthiolation) product in the case of **14b**.

2.1. General procedures for oxidation of difluoromethylthioethers

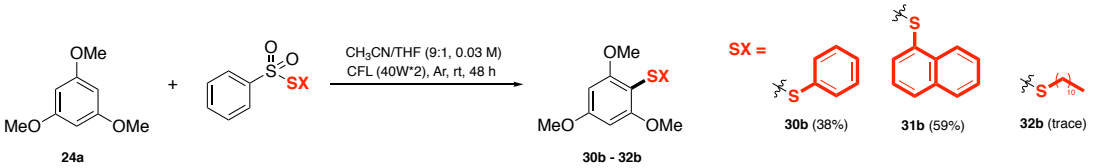


1b" (70%) 1b 1b' (90%)

For **1b'**, to a reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar were added the 3-((difluoromethyl)thio)-1-methyl-1*H*-indole **1b** (0.10 mmol, 1.0 equiv), *m*-CPBA (**0.30 mmol, 3.0 equiv**) and CH_2Cl_2 (0.10 M, 1.0 mL). The resulting mixture was stirred at **room temperature**. After **24 hours**, the reaction mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. The pure desired product was provided after purification by flash column chromatography on silica gel, which furnished the titled compound **1b'** as described.

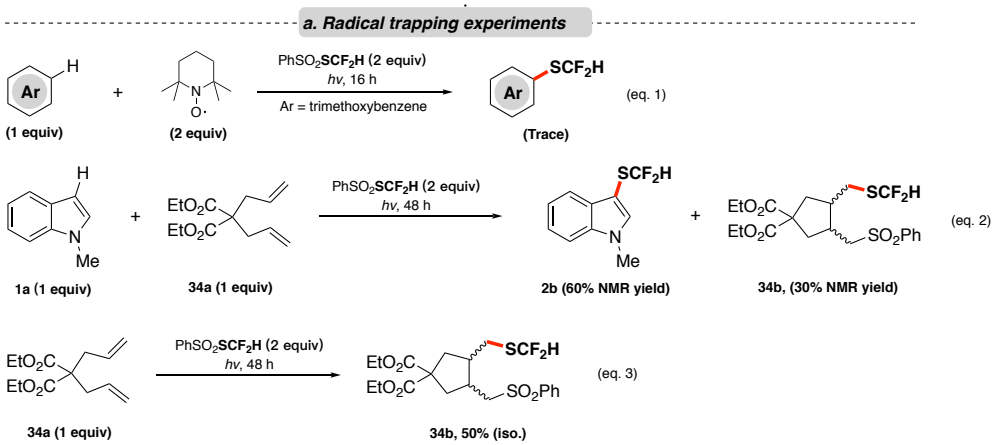
For **1b''**, to a reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar were added the 3-((difluoromethyl)thio)-1-methyl-1*H*-indole **1b** (0.10 mmol, 1.0 equiv) and CH_2Cl_2 (0.50 mL). In another reaction tube, *m*-CPBA (**0.10 mmol, 1.0 equiv**) was dissolved in CH_2Cl_2 (0.50 mL). The resulting mixture was stirred at **0** ℃ then with *m*-CPBA (**0.10 mmol, 1.0 equiv**) CH_2Cl_2 solution added dropwise. The reaction mixture was stirred at **0** ℃ for **4 hours**. After that, the mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. The pure desired product was provided after purification by flash column chromatography on silica gel, which furnished the titled compound **1b''** as described.

2.2. General procedures for arylthiolation reactions



The preparation of **30b** is representative and applicable to all diarylthioethers synthesis in this work unless otherwise specified. To a reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar were added the 1, 3, 5-trimethoxybenzene **24a** (0.30 mmol, 3.0 equiv), *S*-phenyl benzenesulfonothioate (0.10 mmol, 1.0 equiv) and CH_3CN/THF (9:1, 0.033 M). The resulting mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon (>99.999%). The reaction was stirred at room temperature under photo irradiation by using compact fluorescent lamps for 48 hours. The reaction mixture was then diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. The pure desired product was provided after purification by flash column chromatography on silica gel, which furnished the titled compound **30b** as described.

2.3. General procedures for radical trapping experiments



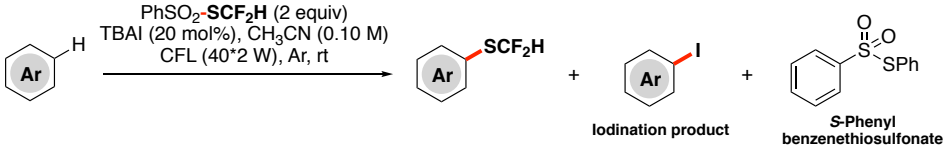
For eq. 1, to a reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar was added 1, 3, 5-trimethoxybenzene **24a** (0.10 mmol, 1.0 equiv), *S*-(difluoromethyl) benzenesulfonothioate **$PhSO_2SCF_2H$** (0.20 mmol, 2.0 equiv), TEMPO (0.20 mmol, 2.0 equiv) and CH_3CN (0.10 M). The resulting mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon (>99.999%). The reaction was stirred at room temperature under photo irradiation by using compact fluorescent lamp for 16 hours. The reaction mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic

solvent was evaporated. Then, the crude was subjected to GC-MS and NMR analysis to determine yield of desired product.

For eq. 2, to a reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar were added *N*-methylindole **1a** (0.10 mmol, 1.0 equiv), *S*-(difluoromethyl) benzenesulfonothioate **$PhSO_2SCF_2H$** (0.20 mmol, 2.0 equiv), diethyl 2,2-diallylmalonate **34a** (0.10 mmol, 1.0 equiv) and CH_3CN (0.10 M). The resulting mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon (>99.999%). The reaction was stirred at room temperature under photo irradiation by using compact fluorescent lamps for 48 hours. The reaction mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. Then, the crude was subjected to GC-MS and NMR analysis to determine yield of desired product.

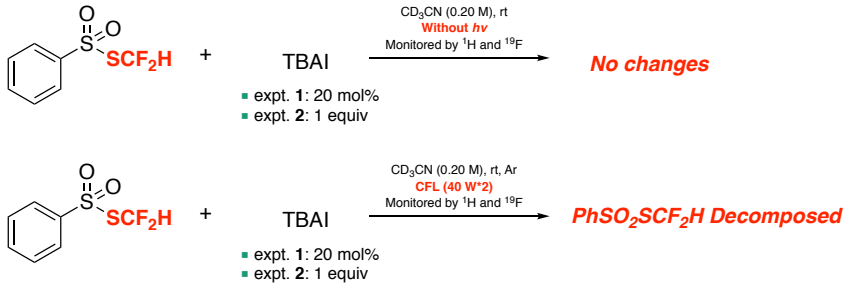
For eq. 3, to a reaction tube (10.0 mL) equipped with a teflon-coated magnetic stirring bar were added *S*-(difluoromethyl) benzenesulfonothioate **$PhSO_2SCF_2H$** (0.20 mmol, 2.0 equiv), diethyl 2,2-diallylmalonate **34a** (0.10 mmol, 1.0 equiv) and CH_3CN (0.10 M). The resulting mixture was evacuated by three freeze-pump-thaw cycles and back-filled with ultra-purified argon (>99.999%). The reaction was stirred at room temperature under photo irradiation by using compact fluorescent lamps for 48 hours. The reaction mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. Then, the crude was subjected to GC-MS and NMR analysis to determine yield of desired product. The pure desired product was provided after purification by flash column chromatography on silica gel.

2.4. Product inspection



During the course of this project, several interesting products were frequently observed in GC-MS, which might clue the reaction mechanism. The formation of iodoarenes was envisioned as a result of trapping iodine radical by arenes, while the *S*-phenyl benzenethiosulfonate could come from the bimolecular dehydration process of benzenesulfenic acid.[1]

2.5. Control experiments



In order to probe the mechanistic sight, we performed the following control experiments by pre-mixing the $PhSO_2SCF_2H$ and TBAI (20 mol% catalytic amount in expt.1 and stoichiometric amount in expt.2) and stirring the mixture **in the dark**. As a result of monitoring the mixtures by ^1H and ^{19}F NMR, no significant changes in ^1H NMR was observed, and no new signal appeared in ^{19}F NMR. This indicated that under dark conditions, $PhSO_2SCF_2H$ and TBAI remain unreacted as shown in the stacked plots below (Figure S2a and S2b, both ^1H and ^{19}F NMR spectra provided).

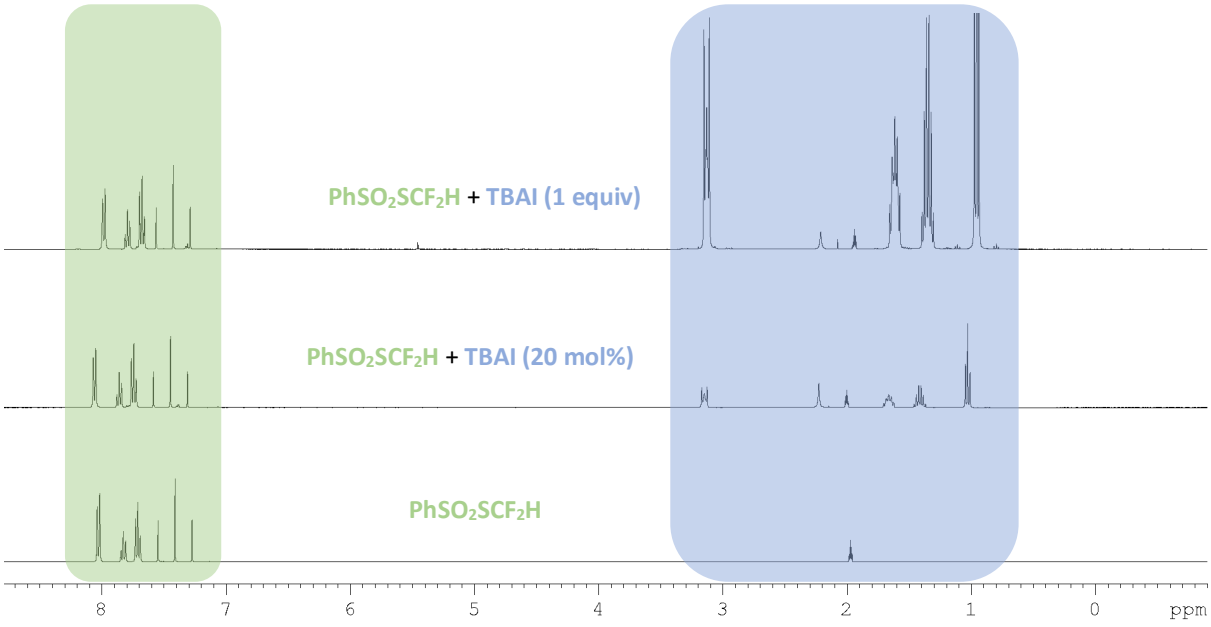


Figure S2a. ^1H NMR stacked plot of mixtures of $PhSO_2SCF_2H$ and TBAI in the absence of light

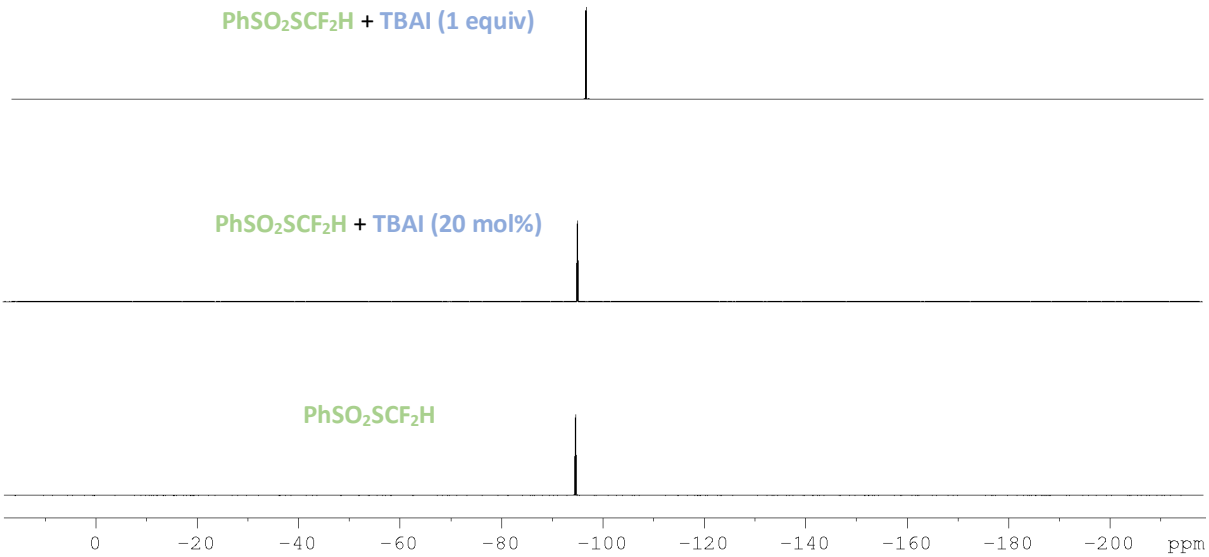


Figure S2b. ^{19}F NMR stacked plot of mixtures of $PhSO_2SCF_2H$ and TBAI in the absence of light

After that, we subjected the mixtures of $PhSO_2SCF_2H$ and TBAI to **light irradiation** and monitored the changes again by ^{1}H and ^{19}F NMR. Significant decomposition of $PhSO_2SCF_2H$ in both the catalytic and stoichiometric cases was observed, and complicated reaction mixtures were obtained, which were shown in the following stacked spectra.

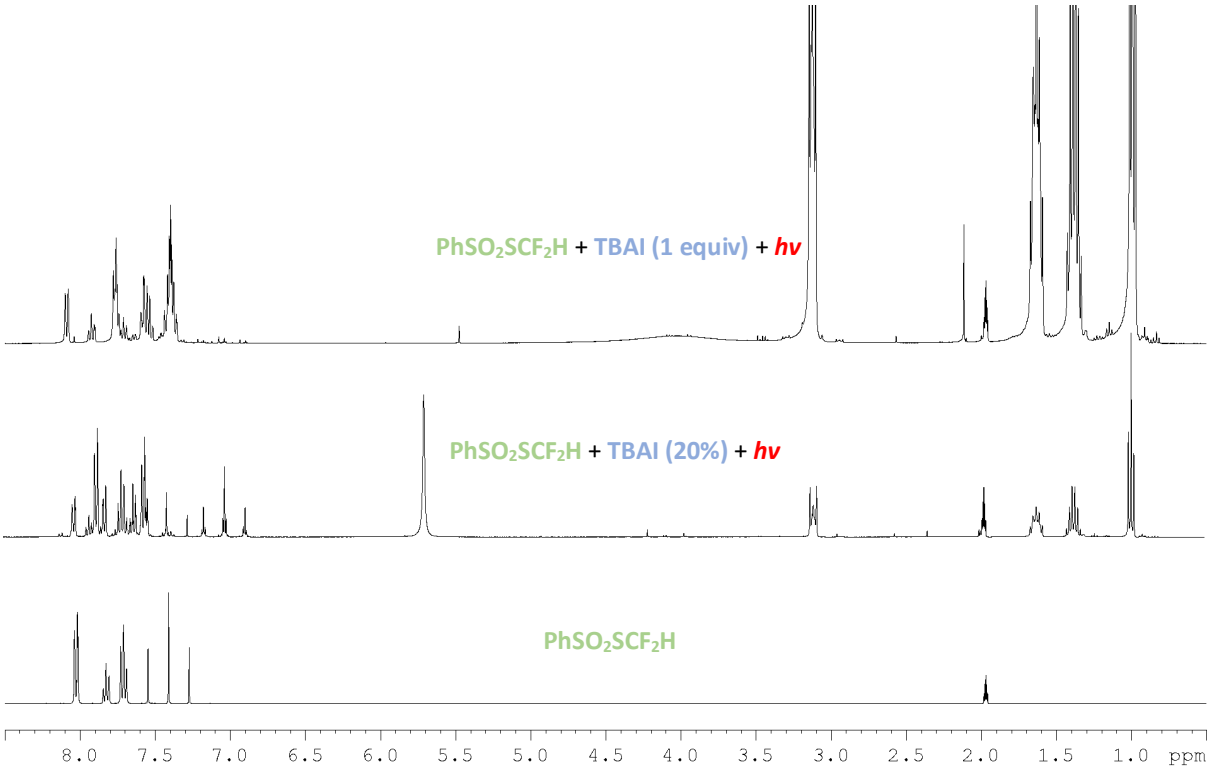


Figure S3a. ^{1}H NMR stacked plot of mixtures of $PhSO_2SCF_2H$ and TBAI after light irradiation

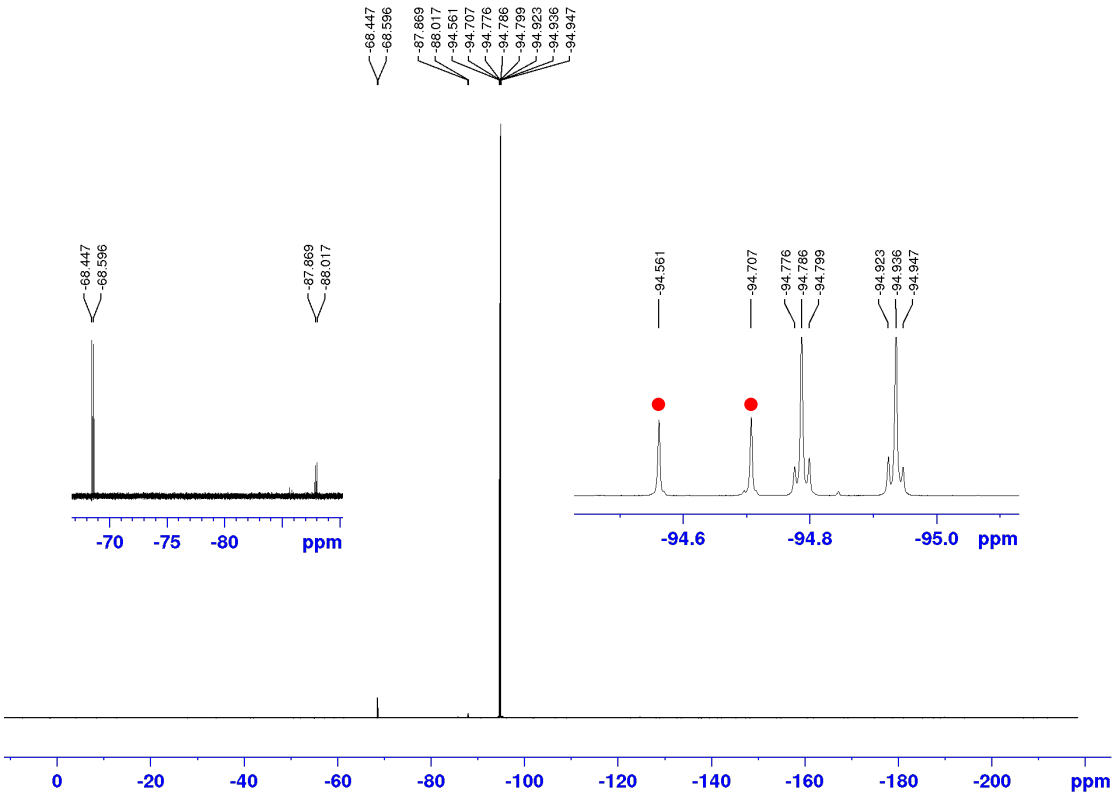


Figure S3b. *^{19}F NMR spectrum of mixture of $PhSO_2SCF_2H$ (red spot) and 20 mol% TBAI after light irradiation*

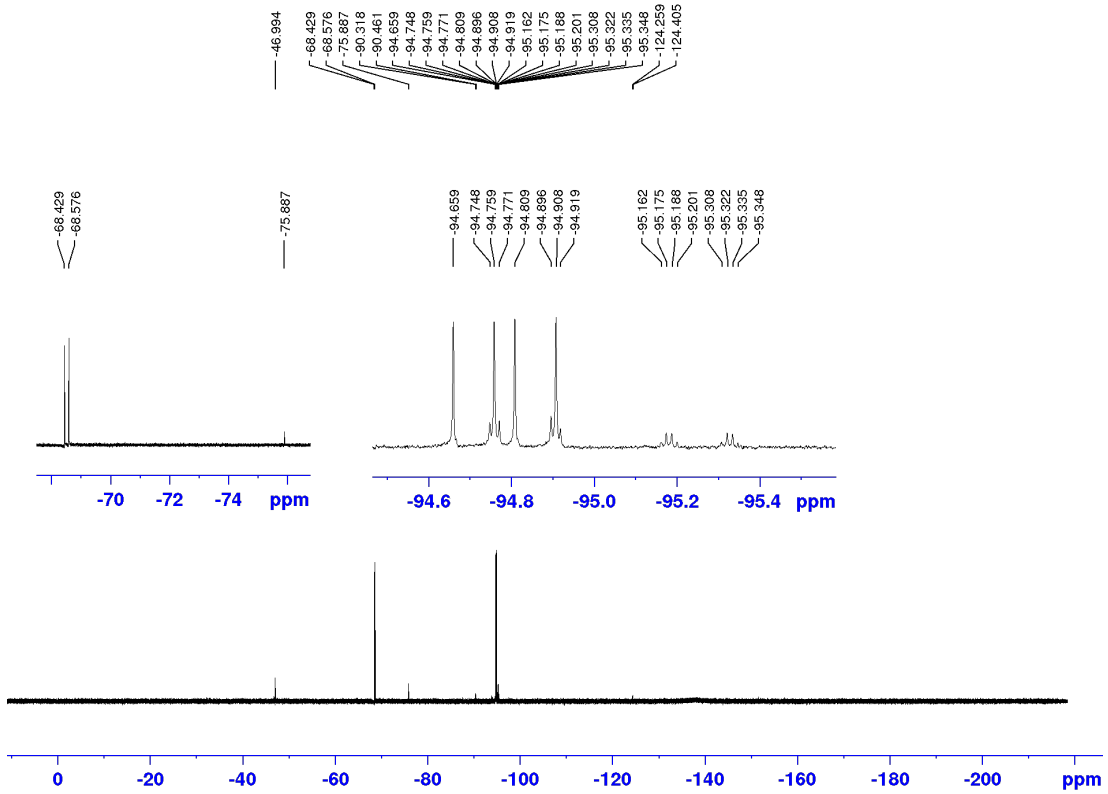


Figure S3c. *^{19}F NMR spectrum of mixture of $PhSO_2SCF_2H$ and 1 equiv TBAI after light irradiation*

It is clear that either in the presence of catalytic or stoichiometric quantity of TBAI, $PhSO_2SCF_2H$ would degrade after the irradiation and several new ^{19}F signals appear. The light-shone mixture was then subjected to GC-MS and ESI analysis; however, no conclusive evidence was obtained to decipher the identity of these mixture. The real mechanism remained to be explored.

In summary, these controlled experiments illustrated the essential role of light in this difluoromethylthiolation reaction. Without other strong evidences, we would like to propose the one in manuscript; however, we are unable to validate or exclude the presence of HF_2CSI or other reactive difluoromethylthiolating species.

3. Supplementary figures and tables

All UV-Vis spectra was obtained by preparing CH_3CN solution of corresponding substrates.

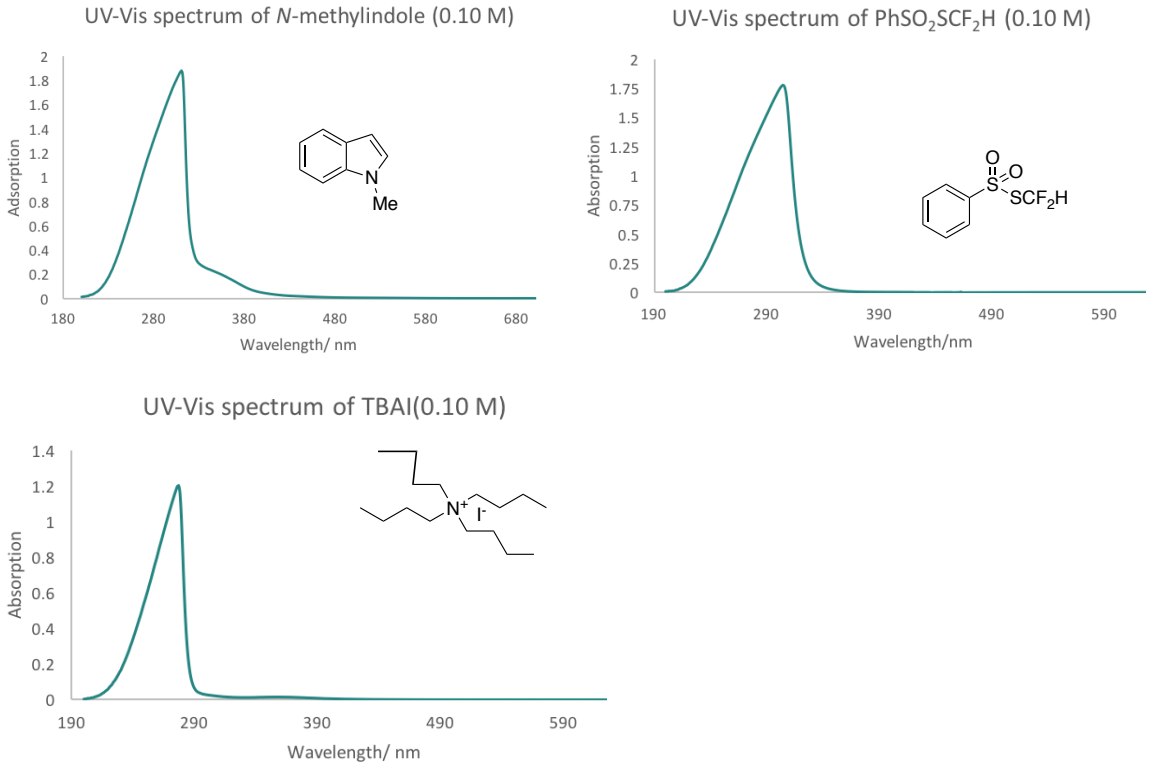
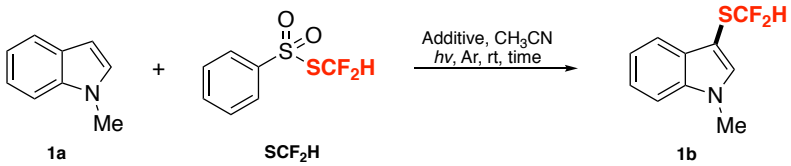


Figure S4. UV-vis spectra of N-Methylindole, $PhSO_2SCF_2H$ and TBAI.

Table 1. Evaluation of various conditions



1a SCF$_2$H 1b

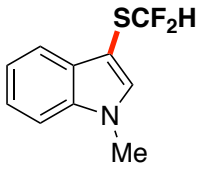
entry[a]	*1a : SCF_2H*	*additive(equiv)*	*time*	*yield*[b]
1[c]	1 : 2	-	16 h	20%
2	1 : 2	-	16 h	64%
3	1 : 2	-	48 h	80%
4[d]	1 : 2	-	16 h	NR
5[e]	1 : 2	-	16 h	65%
6[f]	1 : 2	-	16 h	NR
7	1 : 2	NaI (5 mol%)	16 h	80%
8	1 : 2	KI (5 mol%)	16 h	80%
9	1 : 2	TBAI (5 mol%)	16 h	86%

10	1 : 2	TBAI (10 mol%)	16 h	90%
11	1 : 2	TBAI (20 mol%)	16 h	>99% (iso.)
12	1 : 1.5	TBAI (20 mol%)	16 h	88%
13	1 : 1	TBAI (20 mol%)	16 h	65%
14	2 : 1	TBAI (20 mol%)	16 h	80%
15	1 : 2	TBAI (20 mol%)	8 h	97%

Abbreviations: CFL, compact fluorescence lamp; rt, room temperature; TBAI, tetrabutylammonium iodide; NR, no reaction. [a]All reactions were conducted with 0.10 mmol **1a**, 0.20 mmol **SCF_2H**, 0.020 mmol TBAI in 1.0 mL CH_3CN under argon with irradiation of two 40W CFL unless otherwise noted. [b]The yield was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c]254 nm 2.5W UV lamp (photo-box). [d]At 4°C. [e]In hexane (0.10 M). [f]In the dark.

4. Characterization data for compounds

All the following compounds could be purified either by preparative TLC or column chromatography according to the indicated R_f value (Hex = hexane; PET = petroleum ether; EtOAc = ethyl acetate; DCM = dichloromethane; Ether = diethyl ether). Unless otherwise specified, the isolated mass was recorded based on Method **A**. The experimental data obtained are in agreement with previously reported characterization data.[2]



3-((Difluoromethyl)thio)-1-methyl-1*H*-indole (**1b**, Method **A**: 21.3 mg, > 99% on 0.10 mmol scale; Method **A**: 79.2 mg, 93% on 0.40 mmol scale; Method **B**: 16.0 mg, 75%) was purified by preparative TLC as colorless oil.[2e]

R_f = 0.67 (PE : EtOAc = 8 : 1);

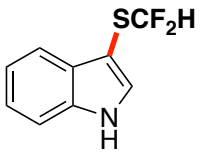
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.40-7.28 (m, 4H), 6.69 (t, *J* = 57.9 Hz, 1H), 3.85 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 136.1, 130.4, 122.9, 121.1 (t, *J* = 276.2 Hz), 120.9, 119.4, 109.8, 94.2 (t, *J* = 4.2 Hz), 33.2;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.24 (d, *J* = 57.8 Hz, 2F) ppm;

IR (Neat) υ = 3121, 3055, 2918, 1513, 1459, 1313, 1240, 1061, 1030, 1017, 971, 758, 750, 737, 542, 463, 428 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_{10}H_{10}F_2NS$ Calcd: 214.0497; Found: 214.0499.



3-((Difluoromethyl)thio)-1*H*-indole (**2b**, 17.9 mg, 90%) was purified by flash column chromatography as brownish oil.[2e]

R_f = 0.33 (PE : EtOAc = 8 : 1);

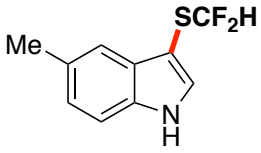
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (bs, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 2.7 Hz, 1H), 7.45 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.34-7.28 (m, 2H), 6.71 (t, *J* = 57.5 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1, 131.8, 129.7, 123.3, 121.3, 121.0 (t, *J* = 275.5 Hz), 119.4, 111.6, 96.8 (t, *J* = 4.2 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.04 (d, *J* = 57.9 Hz, 2F) ppm;

IR (KBr): υ = 3405, 2963, 1506, 1459, 1408, 1338, 1317, 1292, 1068, 796, 749, 515 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_9H_6NF_2S$ Calcd: 198.0195; Found: 198.0193.



3-((Difluoromethyl)thio)-5-methyl-1*H*-indole (**3b**, Method **A**: 18.3 mg, 86%; Method **B**: 15.5 mg, 73%) was purified by preparative TLC as colorless oil.[2e]

R_f = 0.28 (PE : EtOAc = 8 : 1);

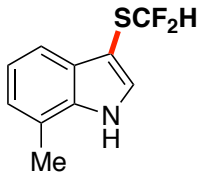
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (bs, 1H), 7.60 (s, 1H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.13 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.70 (t, *J* = 57.9 Hz, 1H), 2.52 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.4, 131.9, 130.9, 129.9, 124.9, 121.1(t, *J* = 276.4 Hz), 118.9, 111.3, 96.1 (t, *J* = 3.8 Hz), 21.5;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.11 (d, *J* = 58.2 Hz, 2F) ppm;

IR (Neat) *υ* = 3677, 3181, 3172, 3160, 3155, 3095, 3061, 3010, 1619, 1544, 1505, 1491, 1441, 1285, 1281, 1192, 1121, 1028, 1006, 985, 943, 828, 733, 641, 608, 574 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_{10}H_8F_2NS$ Calcd: 212.0351; Found: 212.0349.



3-((Difluoromethyl)thio)-7-methyl-1*H*-indole (**4b**, 17.0 mg, 80%) was purified by preparative TLC as colorless oil.

R_f = 0.77 (Hex : EtOAc = 8 : 2);

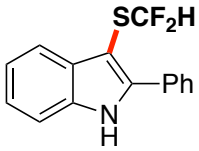
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (bs, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 2.8 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 57.6 Hz, 1H), 2.54 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7, 131.5, 129.3, 123.8, 121.5, 121.1 (t, *J* = 276.4 Hz), 120.8, 117.0, 96.2 (t, *J* = 3.6 Hz), 16.4;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.08 (d, *J* = 57.6 Hz, 2F) ppm;

IR (Neat): υ = 3403, 3115, 3053, 2920, 2854, 1313, 1290, 1051, 1027, 779, 744, 515, 483 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_{10}H_8F_2NS$ Calcd: 212.0351; Found: 212.0350.



3-((Difluoromethyl)thio)-2-phenyl-1*H*-indole (**5b**, 22.0 mg, 80%) was purified by preparative TLC as white solid.[2e]

R_f = 0.68 (PE : EtOAc = 3 : 1);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (bs, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.84-7.82 (m, 2H), 7.56-7.53 (m, 2H), 7.50-7.43 (m, 2H), 7.35-7.20 (m, 2H), 6.74 (t, *J* = 57.4 Hz, 1H);

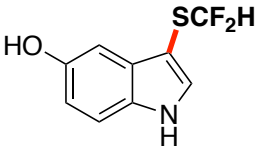
^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 135.5, 131.7, 131.0, 129.0, 128.8, 128.7, 123.6, 121.6, 121.5 (t, *J* = 276.2 Hz), 119.8, 112.0, 93.8 (t, *J* = 3.6 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -91.44 (d, *J* = 57.5 Hz, 2F) ppm;

IR (Neat) υ = 3672, 3198, 3186, 3097, 1499, 1483, 1329, 1282, 1261, 1216, 917, 800, 795, 780, 649, 619 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_{15}H_{10}OF_2NS$ Calcd: 274.0508; Found: 274.0512;

Melting point 89.6-90.4 ℃.



3-((Difluoromethyl)thio)-1*H*-indol-5-ol (**6b**, 19.0 mg, 88%) was purified by preparative TLC as brownish oil.

R_f = 0.17 (Hex : Ether = 3 : 1);

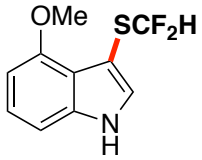
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (bs, 1H), 7.44 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.20 (d, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.68 (t, *J* = 57.7 Hz, 1H), 5.02 (bs, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 132.8, 131.2, 130.8, 121.1 (t, *J* = 276.1 Hz), 113.1, 112.5, 103.7, 95.7 (t, *J* = 3.7 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -91.97 (d, *J* = 58.0 Hz, 2F) ppm;

IR (Neat): υ = 3707, 3679, 3184, 3159, 1678, 1618, 1493, 1444, 1378, 1347, 1285, 1274, 1220, 1175, 1168, 1023, 1014, 987, 949, 886, 822, 812, 731, 650, 558, 286 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_9H_6ONF_2S$ Calcd: 214.0415; Found: 214.0148.



3-((Difluoromethyl)thio)-4-methoxy-1*H*-indole (**7b**, 22.0 mg, 98%) was purified by flash colum chromatography as colorless oil.[2e]

R_f = 0.60 (PE : EtOAc = 3 : 1);

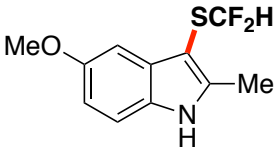
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (bs, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 58.7 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.00 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 138.2, 130.4, 124.2, 122.4 (t, *J* = 274.2 Hz), 118.2, 105.0, 101.5, 96.7 (t, *J* = 4.8 Hz), 55.5;

^{19}F NMR (470 MHz, $CDCl_3$) δ -95.25 (d, *J* = 59.1 Hz, 2F) ppm;

IR (Neat) υ = 3680, 3192, 3084, 3013, 1620, 1550m, 1537, 1308, 1287, 1267, 1099, 1093, 1024, 1010, 993, 810, 759, 740, 573 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_{10}H_{10}OF_2NS$ Calcd: 230.0446; Found: 230.0447.



3-((Difluoromethyl)thio)-5-methoxy-1-methyl-1*H*-indole (**8b**, 19.0 mg, 78%) was purified by preparative TLC as brownish oil.

R_f = 0.70 (Hex : EtOAc = 8 : 2);

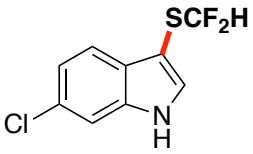
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (bs, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.64 (t, *J* = 57.5 Hz, 1H), 3.91 (s, 3H), 2.55 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 143.2, 131.7, 129.9, 121.3 (t, *J* = 276.7 Hz), 122.4, 111.5, 100.6, 93.2 (t, *J* = 3.7 Hz), 55.9, 12.2;

^{19}F NMR (470 MHz, $CDCl_3$) δ -91.89 (d, *J* = 57.6 Hz, 2F) ppm;

IR (KBr) υ = 3385, 3005, 2964, 2950, 2833, 1627, 1590, 1536, 1486, 1406, 1390, 1309, 1205, 1165, 1125, 1080, 1014, 957, 840, 809, 745, 628, 596, 569, 543 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_{11}H_{10}ONF_2S$ Calcd: 242.0457; Found: 242.0462.



6-Chloro-3-((difluoromethyl)thio)-1*H*-indole (**9b**, 22.0 mg, 94%) was purified by flash colum chromatography as colorless oil.[2e]

R_f = 0.65 (PE : EtOAc = 3 : 1);

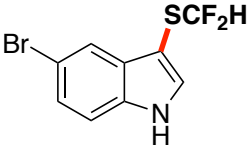
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (bs, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 1.8 Hz, 1H), 7.25 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.70 (t, *J* = 57.3 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.4, 132.4, 129.3, 128.4, 122.2, 120.7 (t, *J* = 275.7 Hz), 120.4, 111.6, 97.1 (t, *J* = 3.8 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.03 (d, *J* = 57.8 Hz, 2F) ppm;

IR (Neat) *υ* = 3675, 3155, 1284, 1125, 1033, 1009, 985, 913, 842, 732, 589 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_9H_5ClF_2NS$ Calcd: 231.9805; Found: 231.9800.



5-Bromo-3-((difluoromethyl)thio)-1*H*-indole (**10b**, 22.0 mg, 80%) was purified by preparative TLC as brownish oil.[2e]

R_f = 0.30 (PE : EtOAc = 5 : 1);

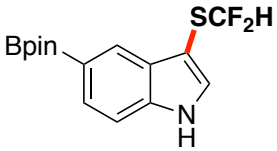
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (bs, 1H), 7.94 (d, *J* = 1.3 Hz, 1H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.39 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 6.70 (t, *J* = 57.3 Hz, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.8, 133.0, 131.6, 126.3, 122.1, 120.5 (t, *J* = 276.4 Hz), 114.9, 113.1, 96.4 (t, *J* = 3.6 Hz);

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.13 (d, *J* = 57.2 Hz, 2F) ppm;

IR (KBr) υ = 3450, 3153, 3072, 2972, 1871, 1749, 1693, 1651, 1600, 1562, 1505, 1446, 1405, 1320, 1287, 1260, 1208, 1069, 1014, 876, 776, 747, 692, 585, 571, 526 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_9H_5NBrF_2S$ Calcd: 275.9300; Found: 275.9311.



3-((Difluoromethyl)thio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**11b**, Method **A**: 31.0 mg, 95%; Method **B**: 30.0 mg, 92%) was purified by preparative TLC as colorless oil.

R_f = 0.70 (Hex : EtOAc = 8 : 2);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (bs, 1H), 8.33 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.41 (d, *J* = 8.3, 1H), 6.71 (t, *J* = 57.8 Hz, 1H), 1.41 (s, 12H);

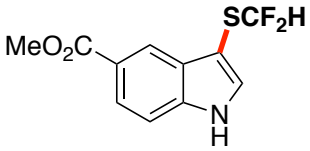
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 132.0, 129.3, 126.8, 120.8 (t, *J* = 275.1 Hz), 111.1, 97.3 (t, *J* = 4.0), 83.8, 24.9;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.51 (d, *J* = 58.7 Hz, 2F);

^{11}B NMR (160 MHz, $CDCl_3$) δ 31.46 ppm;

IR (Neat) υ = 3398, 3300, 2977, 2927, 1614, 1351, 1305, 1252, 1137, 1100, 1064, 1030, 962, 906, 855, 810, 748, 687, 480, 422 cm^{-1};

HRMS (ESI, M+Na$^+$) for $C_{15}H_{18}BF_2NNaO_2S$ Calcd: 348.1012; Found: 348.1013.



Methyl 3-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (**12b**, 16.3 mg, 63%) was purified by flash colum chromatography as colorless oil.[2e]

R_f = 0.30 (PE : EtOAc = 3 : 1);

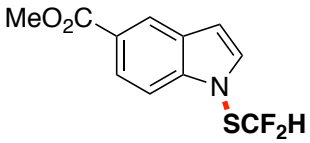
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (bs, 1H), 8.56 (s, 1H), 8.02 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.58 (d, *J* = 2.7 Hz, 1H), 7.47 (dd, *J* = 8.7, 0.4 Hz, 1H), 6.73 (t, *J* = 57.4 Hz, 1H), 3.99 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 138.7, 133.2, 129.4, 124.6, 123.6, 122.2, 120.4 (t, *J* = 277.6 Hz), 111.5, 98.3, 52.1;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.03 (d, *J* = 57.8 Hz, 2F) ppm;

IR (KBr) υ = 3276, 3120, 3000, 2951, 2842, 1686, 1617, 1434, 1321, 1291, 1263, 1190, 1142, 1093, 1064, 1038, 1006, 981, 900, 825, 770, 757, 702, 621, 570, 530 cm^{-1};

HRMS (ESI, M+Na$^+$) for $C_{11}H_9F_2NNaO_2S$ Calcd: 280.0214; Found: 280.0204.



Methyl 1-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (**12b'**, 5.6 mg, 20%) was purified by flash colum chromatography as colorless oil.

R_f = 0.73 (Hex : EtOAc = 8 : 2);

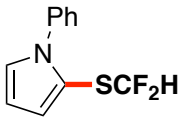
^{1}H NMR (500 MHz, Acetone-d_6) δ 8.36 (d, *J* = 1.5 Hz, 1H), 8.00 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.72 (d, *J* = 8.7, 1H), 7.44 (d, *J* = 3.5 Hz, 2H), 7.43 (t, *J* = 54.1 Hz, 1H), 3.91 (s, 3H);

^{13}C NMR (125 MHz, Acetone-d_6) δ 166.8, 143.9, 136.8, 129.5, 124.3, 123.9, 123.4, 121.1 (t, *J* = 277.2 Hz), 111.1, 107.1, 51.3;

^{19}F NMR (470 MHz, $CDCl_3$) δ -98.65 (d, *J* = 55.1 Hz, 2F) ppm;

IR (Neat) υ = 3130, 3050, 1670, 1648, 1604, 1481, 1480, 1310, 1276, 1270, 1210, 1200, 1180, 1165, 1100, 1031, 1010, 1000, 994, 984, 762, 725 cm^{-1};

HRMS (ESI, M+Na$^+$) for $C_{11}H_9F_2NNaO_2S$ Calcd: 280.0214; Found: 280.0227.



2-((Difluoromethyl)thio)-1-phenyl-1*H*-pyrrole (**13b**, 15.8 mg, 70%) was purified by flash colum chromatography as brownish oil.

R_f = 0.87 (Hex : EtOAc = 8 : 2);

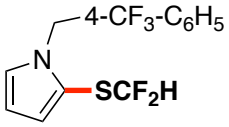
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.42 (m, 3H), 7.36-7.34 (m, 2H), 7.12 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.78 (dd, *J* = 3.9, 1.8 Hz, 1H), 6.46 (t, *J* = 57.4 Hz, 1H), 6.39 (t, *J* = 3.3, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 128.9, 127.9, 127.8, 122.5, 120.3, 118.1 (t, *J* = 278.1 Hz), 112.1, 109.8;

^{19}F NMR (470 MHz, $CDCl_3$) δ -99.21 (d, *J* = 57.5 Hz, 2F) ppm;

IR (Neat) *υ* = 3201, 3191, 1643, 1546, 1466, 1354, 1282, 1029, 1025, 996, 980, 800, 758, 729, 725 cm^{-1};

HRMS (APCI, M+H$^+$) for $C_{11}H_{10}F_2NS$ Calcd: 226.0497; Found: 226.0493.



2-((Difluoromethyl)thio)-1-(4-(trifluoromethyl)benzyl)-1*H*-pyrrole (**15b**, 20.3 mg, 66%) was purified by flash colum chromatography as colorless oil.

R_f = 0.80 (Hex : Ether = 95 : 5);

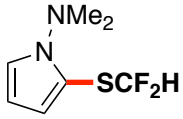
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.85 (dd, *J* = 2.8, 1.8 Hz, 1H), 6.69 (dd, *J* = 3.8, 1.8 Hz, 1H), 6.49 (t, *J* = 57.3 Hz, 1H), 6.32 (t, *J* = 3.3 Hz, 1H), 5.35 (s, 2H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 130.0 (q, *J* = 32.3 Hz), 127.0, 126.8, 125.7 (q, *J* = 3.7 Hz), 122.7, 122.0, 120.5 (t, *J* = 278.2 Hz), 111.4 (t, *J* = 3.9 Hz), 110.0, 50.1;

^{19}F NMR (470 MHz, $CDCl_3$, spectrum centered at 77.00 ppm) δ -62.60 (s, 3F), -92.74 (d, *J* = 57.6 Hz, 2F) ppm;

IR (Neat) υ = 3166, 3150, 3050, 1660, 1459, 1326, 1321, 1296, 1088, 1072, 1037, 1021, 981, 976, 846, 756, 688 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_{13}H_{11}F_5NS$ Calcd: 308.0527; Found: 308.0526.



2-((Difluoromethyl)thio)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (**16b**, 65% GC yield) was purified by preparative TLC as brownish oil.

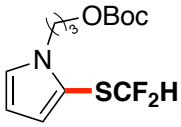
R_f = 0.70 (Pure DCM);

^{1}H NMR (500 MHz, CD_3OD) δ 7.25 (dd, *J* = 1.9, 3.1 Hz, 1H), 6.71 (t, *J* = 57.6 Hz, 1H), 6.23 (dd, *J* = 4.0, 1.8 Hz, 1H), 6.09 (t, *J* = 3.6 Hz, 1H), 3.57 (s, 6H);

^{13}C NMR (125 MHz, CD_3OD) δ 123.0, 118.6 (t, *J* = 277.5 Hz), 110.7 (t, *J* = 4.1 Hz), 107.7, 105.4, 66.7;

^{19}F NMR (470 MHz, CD_3OD) δ -95.29 (d, *J* = 57.7 Hz, 2F) ppm;

HRMS (ESI, M+H$^+$) for $C_7H_{11}F_2N_2S$ Calcd: 193.0533; Found: 193.0607.



***Tert*-butyl ((2-((difluoromethyl)thio)-1*H*-pyrrol-1-yl)methyl) carbonate** (**17b**, 11.0 mg, 36%), was purified by flash colum chromatography as colorless oil.

R_f = 0.45 (Hex : Ether = 8 : 2);

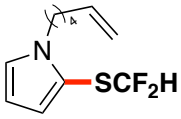
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96-6.95 (m, 1H), 6.59-6.58 (m, 1H), 6.58 (t, *J* =57.5 Hz, 1H), 6.24 (t, *J* = 3.4 Hz, 1H), 4.20 (t, *J* = 7.3 Hz, 2H), 4.06 (t, *J* = 6.2 Hz, 2H), 2.11 (quint, *J* = 7.0 Hz, 2H), 1.52 (s, 9H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 126.2, 121.4, 120.9 (t, *J* = 278.0 Hz), 110.6, 109.3, 82.3, 63.7, 43.6, 30.5, 27.8;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.64 (d, *J* = 57.8 Hz) ppm;

IR (Neat) υ = 3109, 3046, 1703, 1308, 1282, 1248, 1163, 1057, 1033, 1025, 1006, 978, 756, 731, 725, 537 cm^{-1};

HRMS (ESI, M+Na$^+$) for $C_{13}H_{19}F_2NNaO_3S$ Calcd: 330.0946; Found: 330.0943.



2-((Difluoromethyl)thio)-1-(hex-5-en-1-yl)-1*H*-pyrrole (**18b**, 70% GC yield) was purified by flash colum chromatography as a brownish oil.

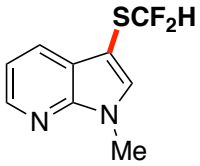
R_f = 0.85 (Pure ether);

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (t, *J* = 2.2 Hz, 1H), 6.49-6.48 (m, 1H), 6.47 (t, *J* = 57.4 Hz, 1H), 6.14 (t, *J* = 6.1 Hz, 1H), 5.75-5.67 (m, 1H), 4.96-4.89 (m, 2H), 3.98 (t, *J* = 7.4 Hz, 2H), 2.02 (td, *J* = 7.2, 3.6 Hz, 2H), 1.69 (quint, *J* = 7.6 Hz, 2H), 1.33 (quint, *J* = 7.5 Hz, 2H);

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.60 (d, *J* = 57.6 Hz, 2F) ppm;

IR (Neat) υ = 3205, 3105, 3055, 3045, 3014, 2999, 2989, 1475, 1308, 1300, 1019, 978, 978, 753, 687, 647 cm^{-1};

MS (EI) for $C_{11}H_{15}F_2NS$ Calcd: 213.3; Found: 213.3.



3-((Difluoromethyl)thio)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (**19b**, 15 mg, 70%) was purified by flash colum chromatography as a colorless oil.

R_f = 0.30 (Hex : EtOAc = 8 : 2);

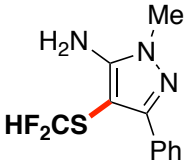
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.7, 1.4 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.50 (s, 1H), 7.22 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.68 (t, *J* = 57.3 Hz, 1H), 3.96 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 144.0, 136.4, 127.9, 123.0, 120.5 (t, *J* = 276.1 Hz), 117.0, 92.9, 31.6;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.20 (d, *J* = 56.5 Hz, 2F) ppm;

IR (Neat) υ = 2952, 2919, 2851, 1515, 1405, 1298, 1116, 1015, 971, 793, 771, 739, 620, 556, 544 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_9H_9F_2N_2S$ Calcd: 215.0449; Found: 215.0439.



4-((Difluoromethyl)thio)-1-methyl-3-phenyl-1*H*-pyrazol-5-amine (**20b**, Method **A**: 23.0mg, 90%; Method **B**: 15.4 mg, 60%) was purified by preparative TLC as brownish oil.[2b]

R_f = 0.30 (Hex : EtOAc = 8 : 2);

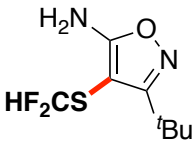
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.54 (t, *J* = 57.4 Hz, 1H), 4.12 (bs, 2H), 3.77 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 150.4, 132.4, 128.3, 127.7, 121.1 (t, *J* = 277.1 Hz), 80.4 (t, *J* = 4.0 Hz), 35.2;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.27 (d, *J* = 57.0 Hz, 2F) ppm;

IR (Neat) υ = 3359, 3301, 3181, 3060, 2954, 2922, 2852, 1626, 1560, 1503, 1452, 1312, 1291, 1242, 1071, 1027, 772, 744, 719, 690 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_{11}H_{12}F_2N_3S$ Calcd: 256.0715; Found: 256.0713.



3-(*Tert*-butyl)-4-((difluoromethyl)thio)isoxazol-5-amine (**21b**, 18.2 mg, 82%) was purified by preparative TLC as yellowish oil.[2b]

R_f = 0.70 (PE : EtOAc = 5 : 1);

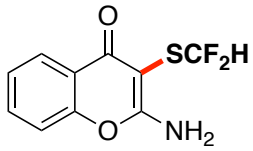
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (t, *J* = 57.4 Hz, 1H), 5.07 (bs, 2H), 1.41 (s, 9H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 171.8, 121.6 (t, *J* = 277.5 Hz), 71.5 (t, *J* = 4.2 Hz), 33.6, 28.4;

^{19}F NMR (470 MHz, $CDCl_3$) δ -90.83 (d, *J* = 57.6 Hz, 2F) ppm;

IR (Neat) υ = 3457, 3287, 3229, 3156, 3122, 2972, 2874, 1637, 1572, 1479, 1289, 1209, 1043, 863, 794, 746, 617, 585, 520, 458, 437 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_8H_{13}F_2N_2OS$ Calcd: 223.0711; Found: 223.0702.



2-Amino-3-((difluoromethyl)thio)-4*H*-chromen-4-one (**22b**, 17.0 mg, 70%) was purified by preparative TLC as an off-white solid.[2b]

R_f = 0.35 (Hex : EtOAc = 6 : 4);

^{1}H NMR (500 MHz, CD_3OD) δ 7.97-7.95 (m, 1H), 7.59-7.55 (m, 1H), 7.32-7.29 (m, 2H), 6.76 (t, *J* = 57.8 Hz, 1H);

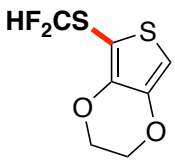
^{13}C NMR (125 MHz, CD_3OD) δ 175.7, 168.4, 153.0, 133.2, 125.3, 125.0, 121.5, 120.7 (t, *J* = 276.1 Hz), 116.3, 81.0 (t, *J* = 3.2 Hz);

^{19}F NMR (470 MHz, CD_3OD) δ -95.03 (d, *J* = 57.9 Hz, 2F) ppm;

IR (Neat) υ = 3744, 3605, 1684, 1653, 1638, 1584, 1421, 1031, 1007, 997, 787, 709, 558 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_{10}H_6F_2NO_2S$ Calcd: 242.0093; Found: 242.0089;

Melting point 199.0-200.9 °C.



5-((Difluoromethyl)thio)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (**23b**, 40% GC yield) was purified by preparative TLC as a brownish oil.

R_f = 0.73 (Hex : EtOAc = 8 : 2);

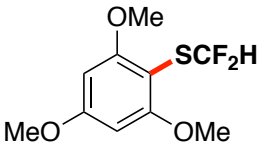
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (t, *J* = 57.3 Hz, 1H), 6.61 (s, 1H), 4.34-4.32 (m, 2H), 4.25-4.23 (m, 2H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 141.5, 120.1 (t, *J* = 278.8 Hz), 65.2, 64.2;

^{19}F NMR (470 MHz, $CDCl_3$) δ -93.1 (d, *J* = 56.3 Hz, 2F) ppm;

IR (Neat) υ = 3136, 3055, 3041, 1531, 1512, 1428, 1383, 1282, 1198, 1150, 1056, 1041, 1029, 1003, 934, 905, 891, 768, 763, 734, 713 cm^{-1};

HRMS (APCI, M+H$^+$) for $C_7H_7O_2F_2S_2$ Calcd: 224.9850; Found: 224.9860.



(Difluoromethyl)(2,4,6-trimethoxyphenyl)sulfane (**24b**, 19 mg, 75%) was purified by flash colum chromatography as white solid.[2e]

R_f = 0.33 (PE : EtOAc = 8 : 1);

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (t, *J* = 58.5 Hz, 1H), 6.19 (s, 2H), 3.90 (s, 6H), 3.86 (s, 3H);

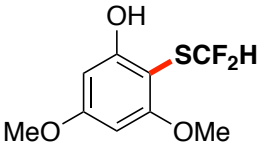
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 162.4, 120.9 (t, *J* = 276.5 Hz), 93.7 9 (t, *J* = 3.7 Hz), 91.2, 56.3, 55.5;

^{19}F NMR (470 MHz, $CDCl_3$) δ -93.18 (d, *J* = 58.8 Hz, 2F) ppm;

HRMS (ESI, M+Na$^+$) for $C_{10}H_{12}F_2NaO_3S$ Calcd: 273.0367; Found: 273.0366;

IR (Neat) υ = 3008, 2922, 2850, 1579, 1454, 1439, 1410, 1336, 1297, 1227, 1208, 1191, 1184, 1163, 1119, 1090, 1057, 1042, 1007, 952, 913, 813, 795, 678, 660, 637, 613, 595, 570, 517, 479, 404 cm^{-1};

Melting point 82.5-84.4 ℃.



2-((Difluoromethyl)thio)-3,5-dimethoxyphenol (**25b**, 15.5 mg, 66%) was purified by flash colum chromatography as brownish oil.

R_f = 0.70 (Hex : EtOAc = 8 : 2);

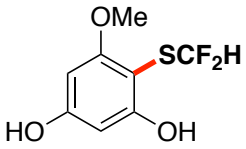
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (s, 1H), 6.63 (t, *J* = 57.9 Hz, 1H), 6.27 (d, *J* = 2.5 Hz, 1H), 6.12 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 161.9, 160.3, 126.8 (t, *J* = 278.3 Hz), 92.6, 92.1, 90.0 (t, *J* = 3.2 Hz), 56.2, 55.5;

^{19}F NMR (470 MHz, $CDCl_3$) δ -92.45 (d, *J* = 57.8 Hz, 2F) ppm;

IR (Neat) υ = 3426, 3008, 2953, 2852, 1601, 1576, 1480, 1469, 1435, 1369, 1435, 1369, 1306, 1285, 1213, 1201, 1176, 1141, 1104, 1088, 1064, 1052, 1031, 981, 928, 814, 791, 719, 659, 641, 614, 565, 553, 531, 470, 418 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_9H_9F_2O_3S$ Calcd: 235.0246; Found: 235.0250.



4-((Difluoromethyl)thio)-5-methoxybenzene-1,3-diol (**26b**, 40%, 8.8 mg) was purified by preparative TLC as colorless oil.

R_f = 0.70 (Hex : EtOAc = 8 : 2);

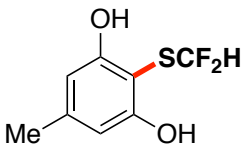
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (s, 1H), 6.63 (t, *J* = 57.9 Hz, 1H), 6.19 (d, *J* = 2.5 Hz, 1H), 6.08 (d, *J* = 2.4 Hz, 1H), 5.15 (bs, 1H), 3.88 (s, 3H);

^{13}C NMR (125 MHz, Acetone-d_6) δ 162.6, 161.7, 161.6, 160.8, 121.2 (t, *J* = 274.5 Hz), 95.5, 92.0, 55.5;

^{19}F NMR (470 MHz, Acetone-d_6) δ -94.4 (d, *J* = 57.8 Hz, 2F) ppm;

IR (Neat) υ = 3703, 3599, 3159, 3093, 3019, 1650, 1632, 1540, 1512, 1507, 1482, 1389, 1266, 1233, 1200, 1194, 1169, 1096, 1070, 1029, 1020, 996, 931, 823, 748, 714, 654, 534, 391 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_8H_7O_3F_2S$ Calcd: 221.0089; Found: 221.0087.



2-((Difluoromethyl)thio)-5-methylbenzene-1,3-diol (**27b**, 14.0 mg, 68%) was purified by preparative TLC as an off-white oil.

R_f = 0.60 (Hex : EtOAc = 8 : 2);

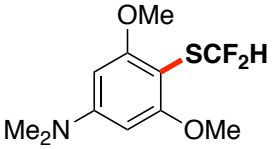
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (bs, 1H), 6.61 (t, *J* = 56.7 Hz, 1H), 6.42 (s, 2H), 5.12 (bs, 1H), 3.47 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 159.1, 146.6, 120.3 (t, *J* = 278.0 Hz), 110.5, 101.0 (t, *J* = 5.3 Hz), 100.1, 21.7;

^{19}F NMR (470 MHz, $CDCl_3$) δ -91.15 (d, *J* = 58.3 Hz, 2F) ppm;

IR (Neat) υ = 3654, 3627, 3106, 3078, 3017, 1660, 1606, 1530, 1287, 1179, 1034, 990, 489, 421 cm^{-1};

HRMS (ESI, M-H$^+$) for $C_8H_7O_2F_2S$ Calcd: 205.0140; Found: 205.0137.



4-((Difluoromethyl)thio)-3,5-dimethoxy-*N*,*N*-dimethylaniline (**28b**, 21.3 mg, 81%) was purified by preparative TLC as brownish oil.

R_f = 0.35 (Hex : EtOAc = 8 : 2);

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (t, *J* = 58.8 Hz, 1H), 5.92 (s, 2H), 3.90 (s, 6H), 3.05 (s, 6H);

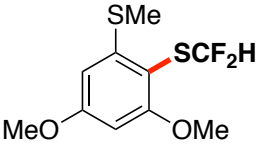
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 153.5, 128.3, 121.3 (t, *J* = 275.7 Hz), 89.0, 56.1, 40.4;

^{19}F NMR (470 MHz, $CDCl_3$) δ -93.42 (d, *J* = 58.7 Hz, 2F) ppm;

IR (Neat) υ = 730, 977, 1021, 1058, 1086, 1276, 1284, 1398, 1572, 1578, 1639, 2983, 2991, 3019, 3033, 3132 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_{11}H_{16}F_2NO_2S$ Calcd: 264.0864; Found: 264.0853;

Melting point 107.9-109.2 ℃.



(Difluoromethyl)(2,6-dimethoxy-4-(methylthio)phenyl)sulfane (**29b**, 19.4 mg, 73%) was purified by preparative TLC as an off-white solid.

R_f = 0.40 (Hex : EtOAc = 8 : 2);

^{1}H NMR (500 MHz, Acetone-d_6) δ 6.96 (t, *J* = 58.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.47 (s, 3H);

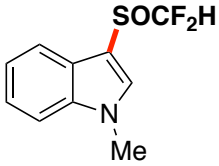
^{13}C NMR (125 MHz, Acetone-d_6) δ 162.9, 162.2, 149.7, 129.3, 120.9 (t, *J* = 277.1 Hz), 102.4, 94.7, 56.3, 55.5, 15.7;

^{19}F NMR (470 MHz, Acetone-d_6) δ -92.54 (d, *J* = 58.3 Hz, 2F) ppm;

IR (Neat) υ = 3293, 3273, 3192, 3189, 1621, 1600, 1343, 1254, 1207, 1173, 1153, 1149, 1106, 1074, 978, 832 cm^{-1};

HRMS (APCI, M+H$^+$) for $C_{10}H_{13}O_2F_2S_2$ Calcd: 267.0320; Found: 267.0330;

Melting point 107.9-109.9 ℃.



3-((Difluoromethyl)sulfinyl)-1-methyl-1*H*-indole (**1b''**, 16.0 mg, 70%) was purified by preparative TLC as an off-white solid.

R_f = 0.50 (PE : EtOAc = 8 : 2);

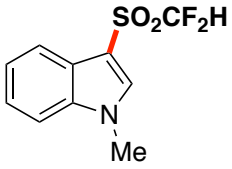
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.40 (td, *J* = 7.0, 1.1 Hz, 1H), 7.31 (td, *J* = 8.0, 1.1 Hz, 1H), 6.53 (t, *J* = 56.0 Hz, 1H), 3.90 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 133.0, 125.1, 124.0, 122.3, 120.0, 119.9 (t, *J* = 286.0 Hz), 110.6, 108.2 (dd, J = 5.9, 3.5 Hz), 33.7;

^{19}F NMR (470 MHz, $CDCl_3$) δ -117.83 (dd, *J* = 261.3, 55.5 Hz, 1F), -119.4 (dd, *J* = 261.3, 56.2 Hz, 1F) ppm;

IR (Neat) *υ* = 3196, 3182, 3087, 3026, 1548, 1504, 1481, 1291, 1225, 1160, 1057, 1021, 780, 737, 640 cm^{-1};

HRMS (ESI, M+H$^+$) for $C_{10}H_{10}ONF_2S$ Calcd: 230.0446; Found: 230.0447.



3-((Difluoromethyl)sulfonyl)-1-methyl-1*H*-indole (**1b'**, 20.8 mg, 85%) was purified by preparative TLC as an off-white solid.

R_f = 0.40 (PE : EtOAc = 7 : 3);

^{1}H NMR (500 MHz, CD_3OD) δ 8.10 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.42 (td, *J* = 7.2, 1.1 Hz, 1H), 7.34 (td, *J* = 8.1, 0.9 Hz, 1H), 6.62 (t, *J* = 53.5 Hz, 1H), 3.98 (s, 3H);

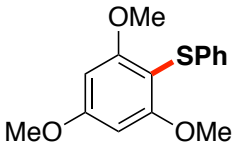
^{13}C NMR (125 MHz, CD_3OD) δ 138.2, 137.7, 125.4, 123.7, 122.7, 119.3, 115.2 (t, *J* = 281.1 Hz), 110.7, 104.0, 32.7;

^{19}F NMR (470 MHz, CD_3OD) δ -126.65 (d, *J* = 54.0 Hz, 2F) ppm;

HRMS (ESI, M+Na$^+$) for $C_{10}H_9F_2NNaO_2S$ Calcd: 268.0222; Found: 268.0214;

IR (Neat) υ = 3280, 3199, 3186, 3096, 3032, 1559, 1548, 1528, 1525, 1481, 1409, 1342, 1292, 1213, 1210, 1197, 1161, 1138, 1075, 1068, 1054, 1041, 1040, 878, 784, 783, 766, 727, 518, 449, 429, 404 cm^{-1};

Melting point 109.0-109.2 ℃.



Phenyl(2,4,6-trimethoxyphenyl)sulfane (**30b**, 11 mg, 40%) was purified by preparative TLC as off-white solid.

R_f = 0.70 (Hex : EtOAc = 8 : 2);

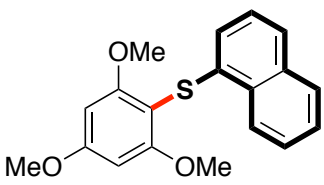
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.16 (m, 2H), 7.07-7.04 (m, 3H), 6.24 (s, 2H), 3.90 (s, 3H), 3.83 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 162.6, 138.7, 128.5, 125.6 124.4, 98.7, 91.2, 56.3, 55.4 ppm;

HRMS (ESI, M+Na$^+$) for $C_{15}H_{16}NaO_3S$ Calcd: 299.0712; Found: 299.0703;

IR (Neat) υ = 3204, 3187, 3172, 3153, 3148, 3099, 3080, 3016, 3010, 1627, 1607, 1540, 1538, 1525, 1473, 1441, 1351, 1317, 1244, 1211, 1204, 1176, 1099, 1092, 1081, 1052, 1048, 1003, 857, 786, 725, 527 cm^{-1};

Melting point 120.0-121.1 ℃.



Naphthalen-1-yl(2,4,6-trimethoxyphenyl)sulfane (**31b**, 19.2 mg, 59%) was purified by preparative TLC as an off-white solid.

R_f = 0.70 (Hex : EtOAc = 8 : 2);

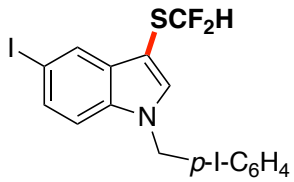
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.60-7.38 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.87 (dd, *J* = 7.3, 0.7 Hz, 1H), 6.28 (s, 2H), 3.91 (s, 3H), 3.81 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 162.7, 135.8, 133.7, 131.1 128.3, 125.9, 125.7, 125.6, 124.9, 124.6, 122.4, 98.2, 91.4, 56.3, 55.5 ppm;

HRMS (APCI, M+H$^+$) for $C_{19}H_{19}O_3S$ Calcd: 327.1049; Found: 327.1048;

IR (Neat) υ = 3190, 3184, 3096, 3085, 3079, 3017, 3011, 3009, 1629, 1597, 1539, 1464, 1431, 1336, 1234, 1207, 1165, 1086, 1059, 1043, 992, 866, 835, 809 cm^{-1};

Melting point 113.2-118.3 ℃.



The preparation of **33b** is described as below.

To a flame-dried Schlenk tube (25.0 mL) equipped with a rubber septum stopper and a teflon-coated magnetic stirring bar were added 5-iodo-1-(4-iodobenzyl)-1*H*-indole **33a** (2.0 mmol, 1.0 equiv) and *S*-(difluoromethyl) benzenesulfonothioate **$PhSO_2SCF_2H$** (4.0 mmol, 2.0 equiv). The resulting mixture was evacuated and back-filled with ultra-purified argon (>99.999%). Shortly after, **TBAI** (0.40 mmol, 20 mol%) in 10.0 mL dry CH_3CN was added to the reaction tube with counter argon flow and the rubber septum was replaced immediately by J.Young high-vacuum PTFE valve. The reaction was stirred at room temperature under irradiation by using compact fluorescent lamps (CFL, 3*40W) until the starting material was completely consumed as monitored by GC-MS. It took around 48 hours. This procedure is termed Method **C**.

After complete consumption of the starting material, the reaction mixture was diluted with EtOAc, filtered through a pad of silica gel and the organic solvent was evaporated. The pure desired product was provided after purification by flash column chromatography on silica gel, which furnished the titled compound **33b** as described.

3-((Difluoromethyl)thio)-5-iodo-1-(4-iodobenzyl)-1*H*-indole (**33b**, Method **C**: 0.64 g, 60%) was purified by column chromatography as an off-white solid.

R_f = 0.66 (Hex : DCM = 1 : 1);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.2 Hz, 1H), 7.68 (d, *J* = 8.31 Hz, 2H), 7.52 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.35 (s, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.68 (t, *J* = 57.3 Hz, 1H), 5.27 (s, 2H);

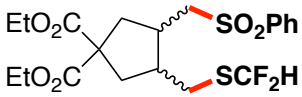
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 136.0, 135.8, 135.5, 133.1, 131.6, 129.7, 128.7, 120.3 (t, J = 276.3 Hz), 112.1, 94.9, 93.8, 85.2, 50.2;

^{19}F NMR (470 MHz, CD_3OD) δ -92.24 (d, *J* = 56.6 Hz, 2F) ppm;

IR (Neat): υ = 3124, 3012, 2973, 2927, 2838, 2303, 2196, 2014, 1737, 1650, 1580, 1501, 1483, 1457, 1435, 1401, 1382, 1337, 1306, 1265, 1253, 1228, 1198, 1161, 1115, 1099, 1068, 1029, 1005, 979, 964, 951, 936, 871, 811, 796, 783, 769, 753, 739, 688, 664, 639, 626, 617, 588, 532, 469, 430, 422 cm^{-1};

HRMS (APCI, M+H$^+$) for for $C_{16}H_{12}NF_2I_2S$ Calcd: 541.8742; Found: 541.8729;

Melting point 124.8-126.3 ℃.



Diethyl 3-(((difluoromethyl)thio)methyl)-4-((phenylsulfonyl)methyl)cyclopentane-1,1-dicarboxylate (**34b**, 23.2 mg, 50%) was purified by column chromatography as colorless oil.[3]

R_f = 0.30 (PE : EtOAc = 5 : 1);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 2H), 6.80 (t, *J* = 56.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.16 (dq, *J* = 14.0, 5.5 Hz, 2H), 2.87 (dd, *J* = 12.8, 5.8 Hz, 1H), 2.71-2.55 (m, 3H), 2.51-2.42 (m, 2H), 2.34-2.26 (m, 2H), 1.26 (td, *J* = 7.1, 2.5 Hz, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 171.8, 139.4, 134.0, 129.5, 128.0, 120.4 (t, J = 273.1 Hz), 62.0, 61.8, 58.2, 55.7, 42.2, 38.0, 37.9, 36.7, 26.8, 14.0;

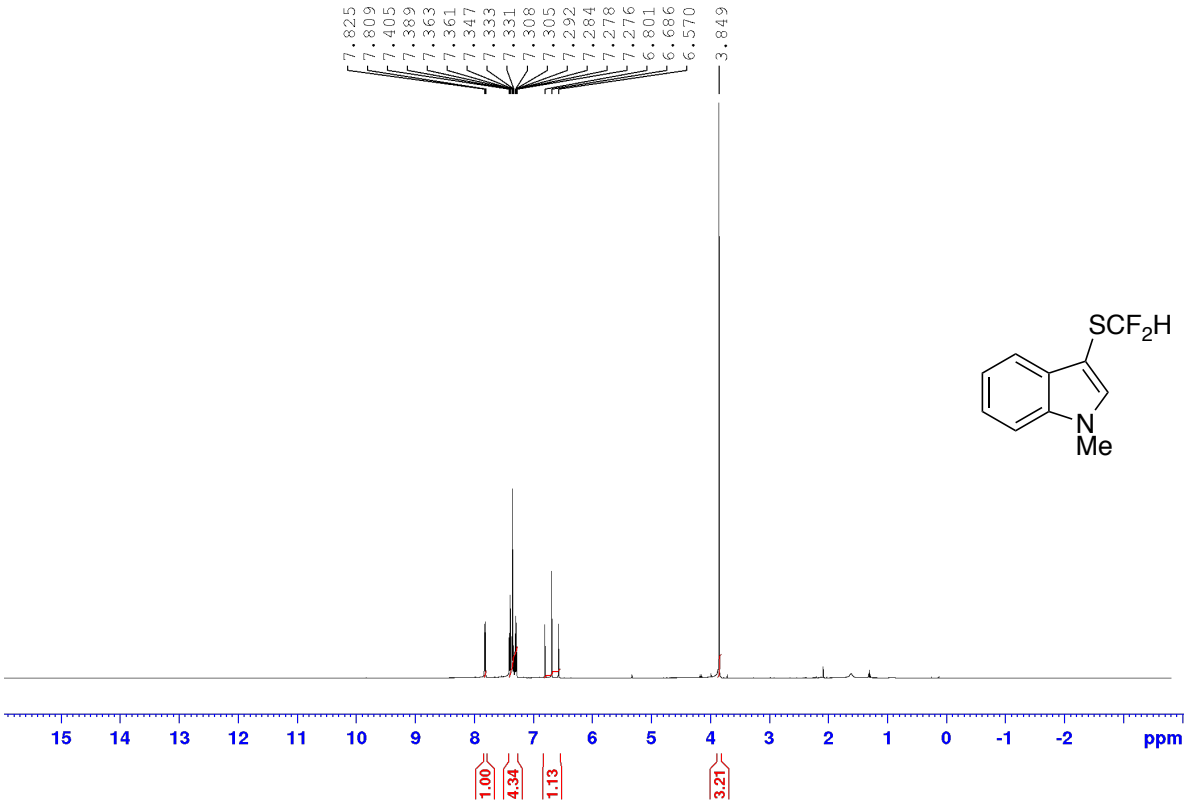
^{19}F NMR (470 MHz, CD_3OD) δ -92.43 (d, *J* = 56.1 Hz, 2F) ppm;

IR (KBr): υ = 2985, 1730, 1445, 1369, 1270, 1183, 1180, 1150, 1086, 1065, 1030, 861, 779, 748, 690, 565 cm^{-1};

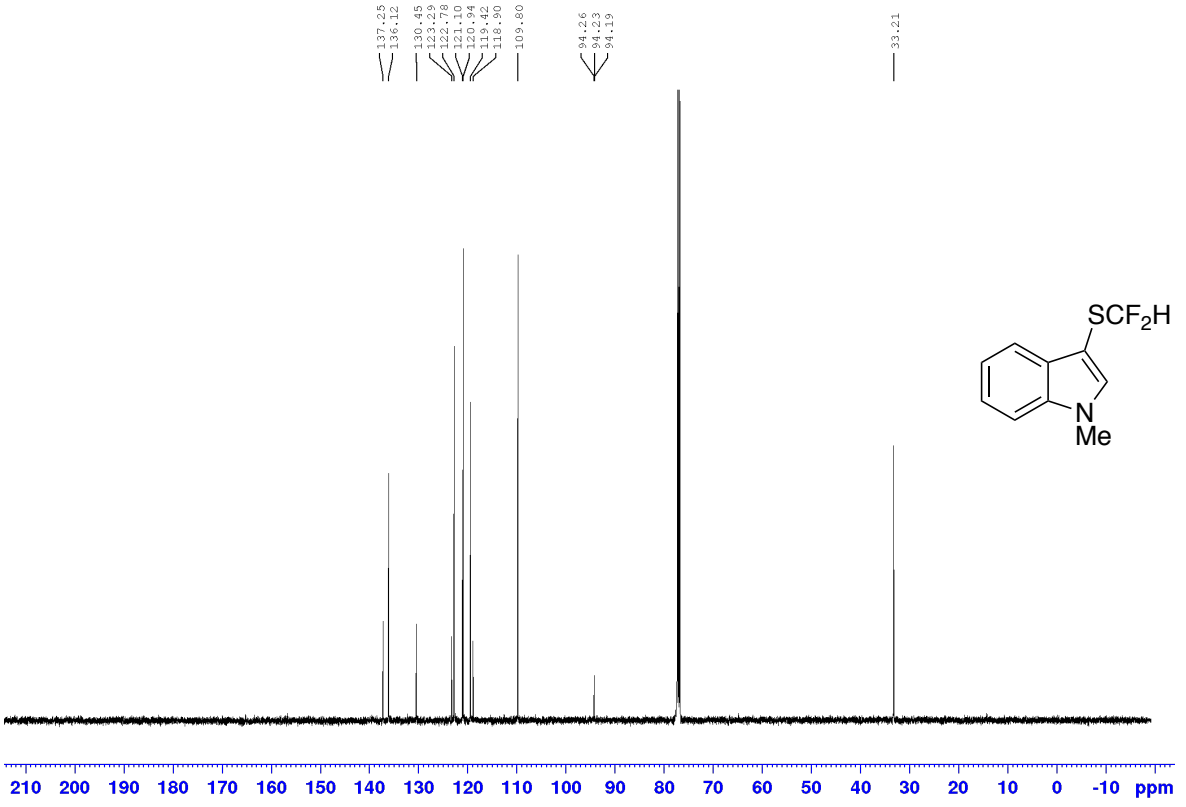
HRMS (ESI, M+Na$^+$) for for $C_{20}H_{26}F_2NaO_6S_2$ Calcd: 487.1031; Found: 487.1022.

5. NMR spectra

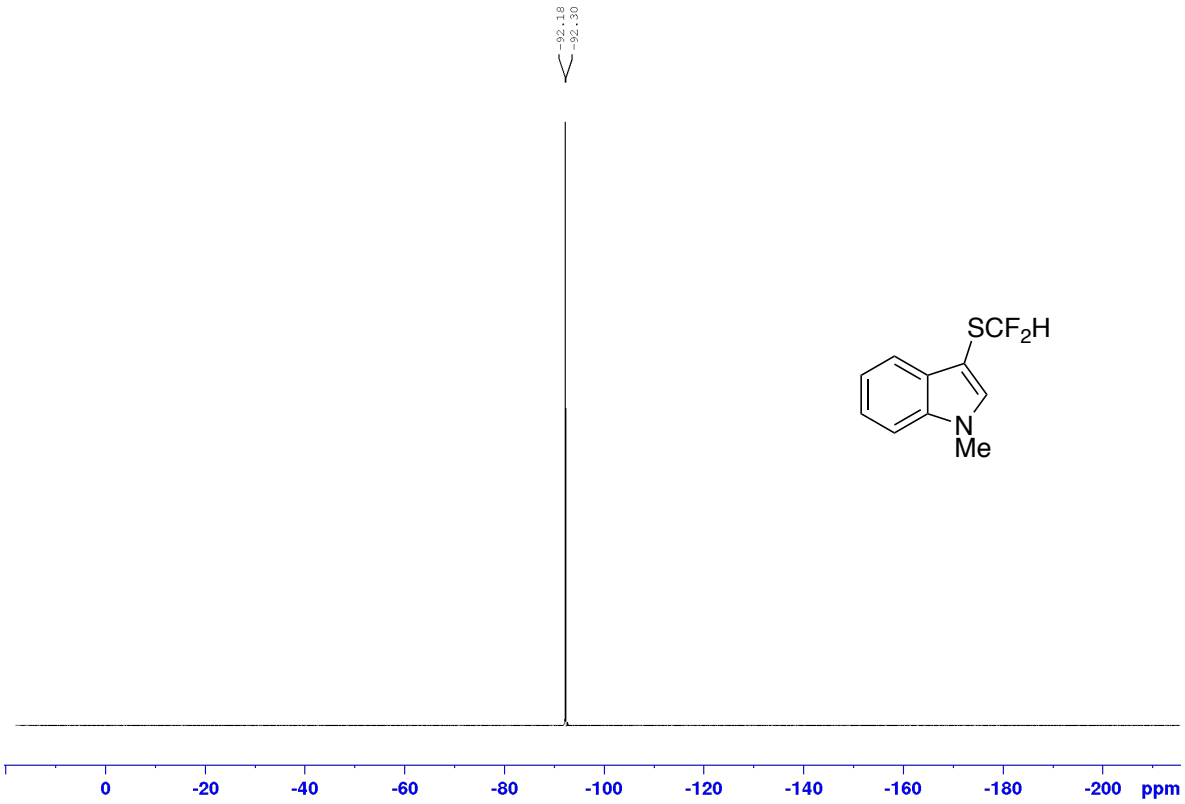
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1-methyl-1*H*-indole (1b)



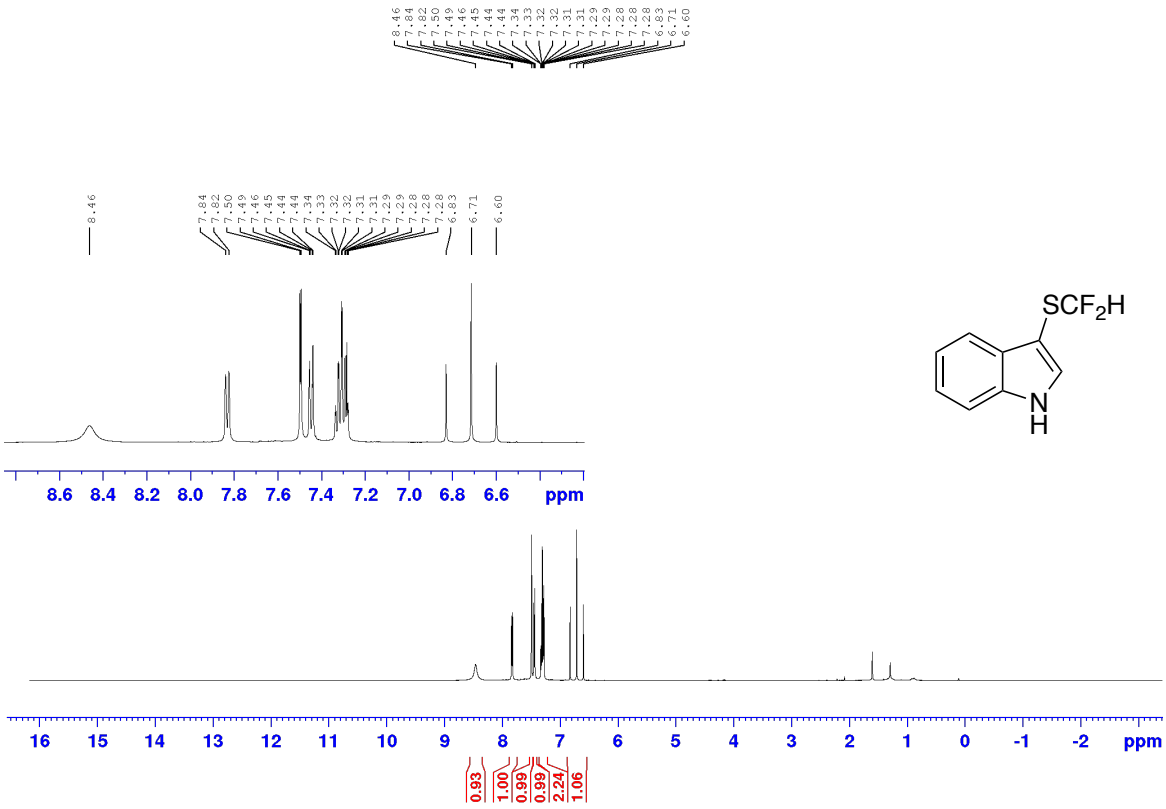
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1-methyl-1*H*-indole (1b)



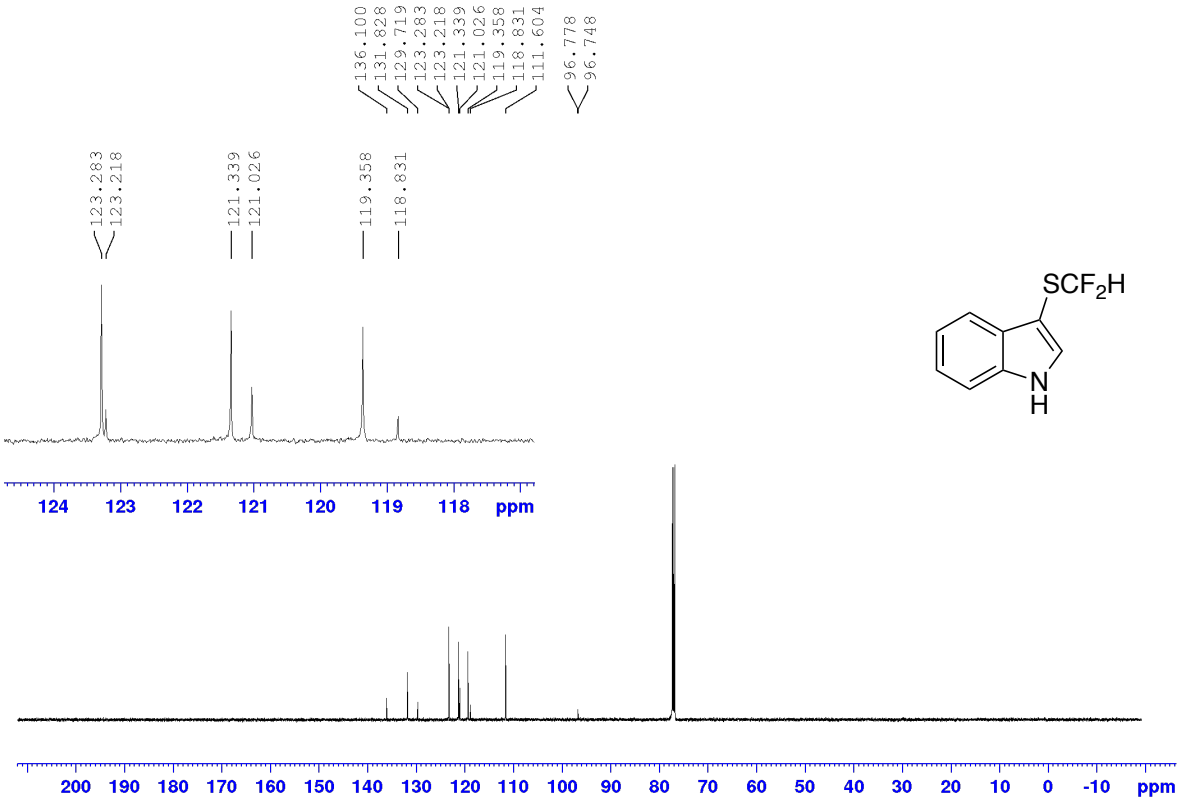
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1-methyl-1*H*-indole (1b)



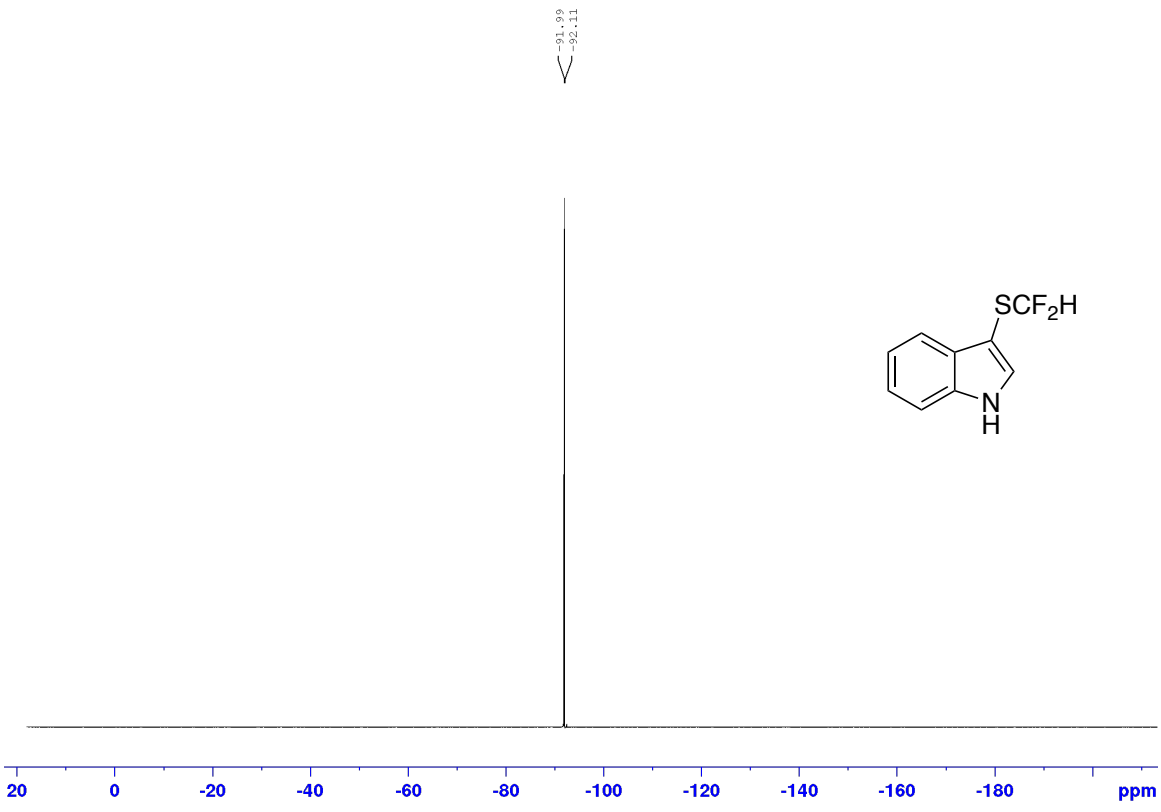
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1*H*-indole (2b)



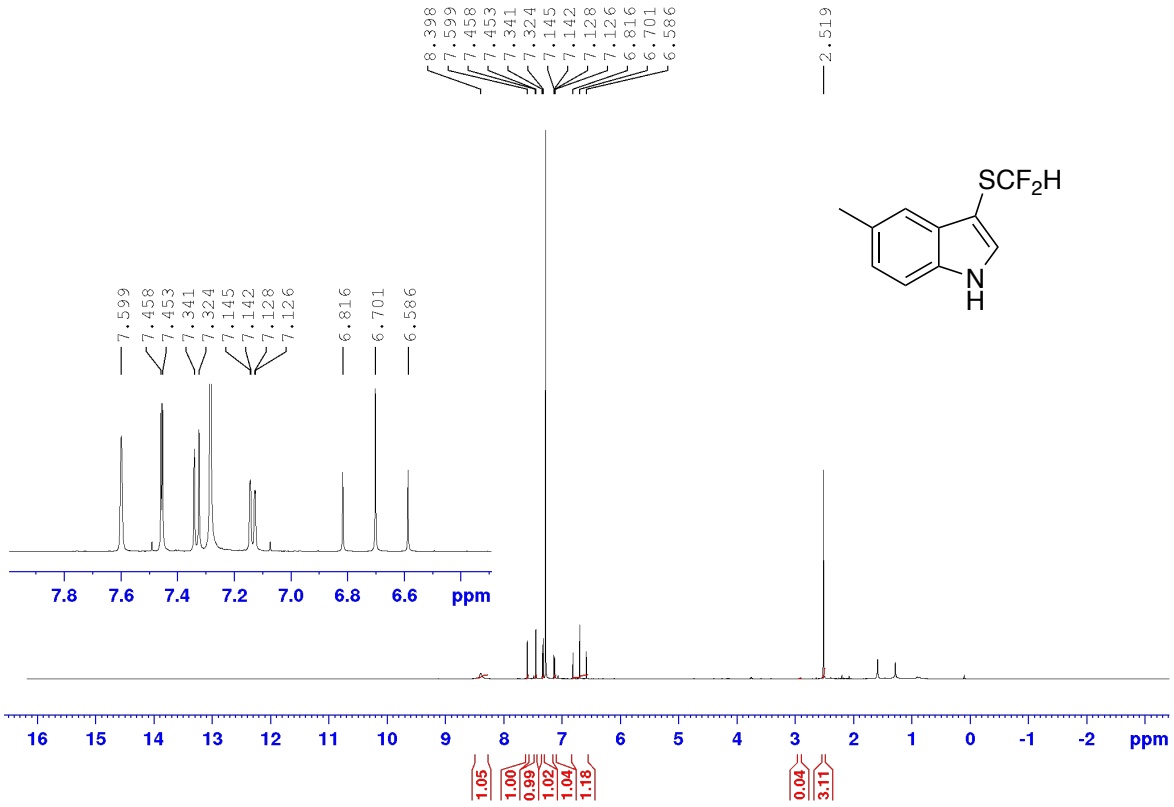
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1*H*-indole (2b)



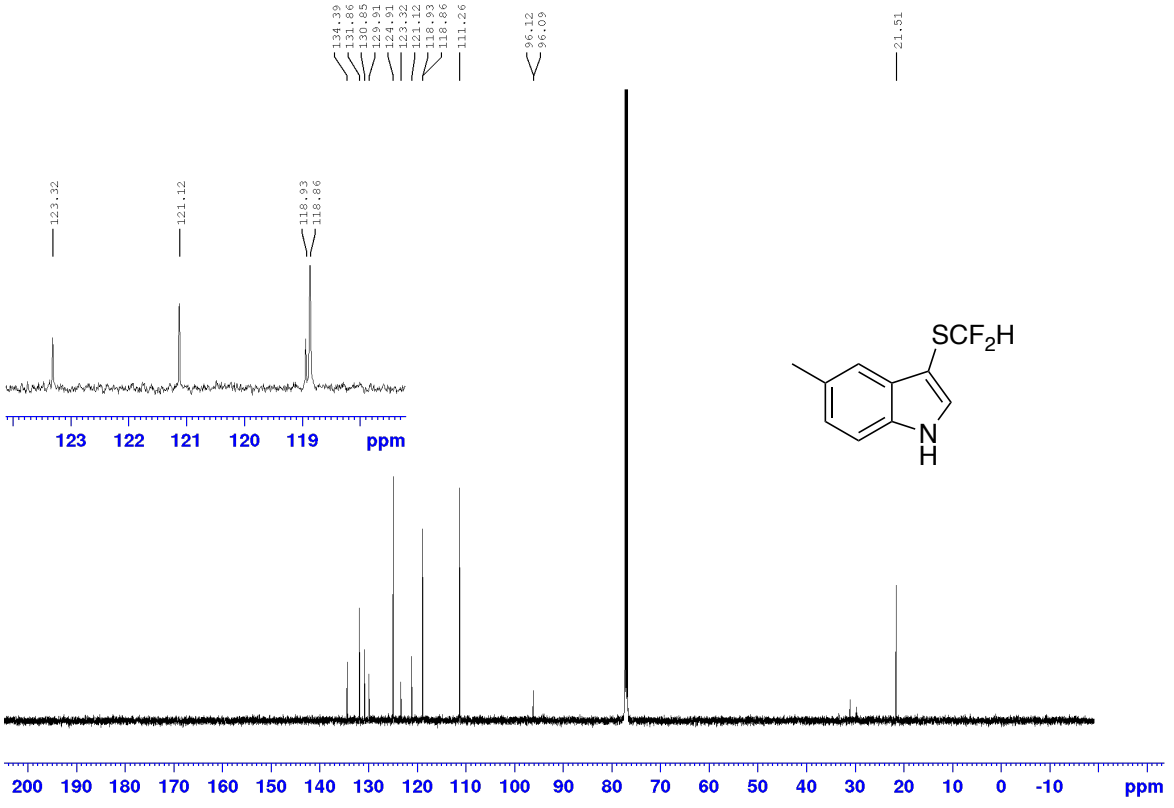
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1*H*-indole (2b)



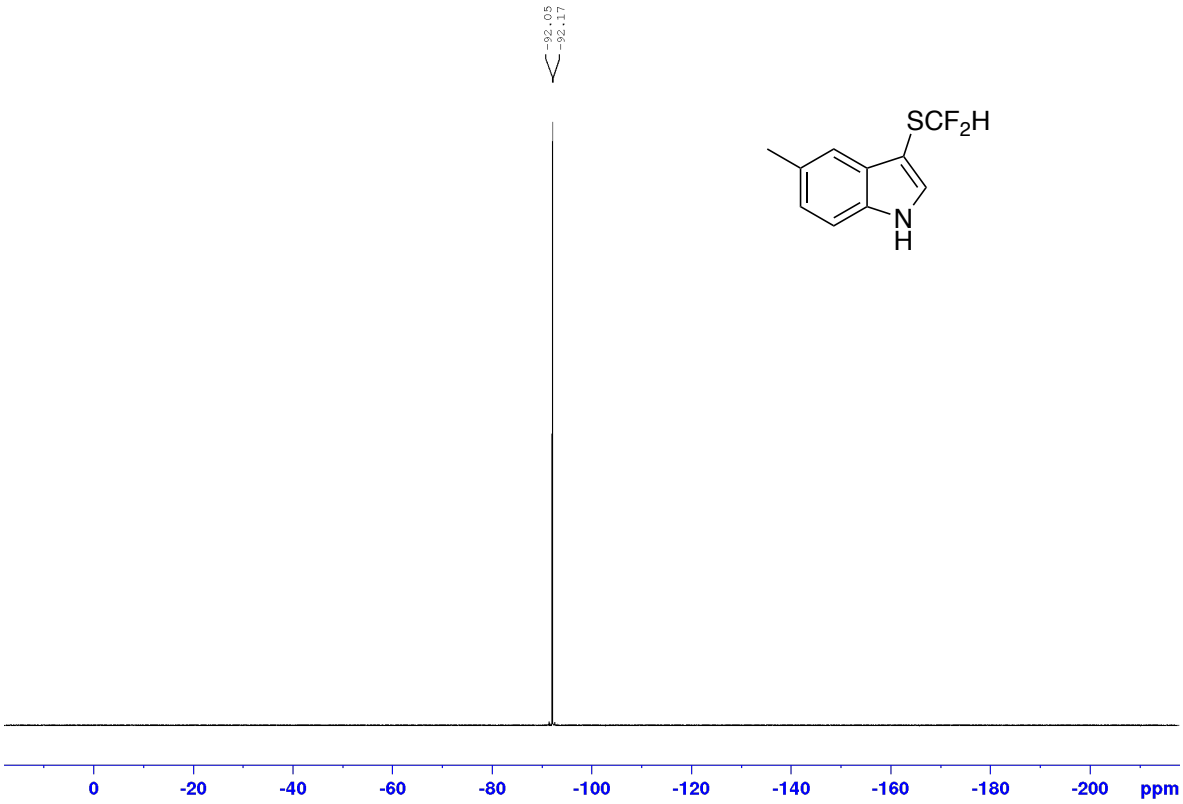
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methyl-1*H*-indole (3b)



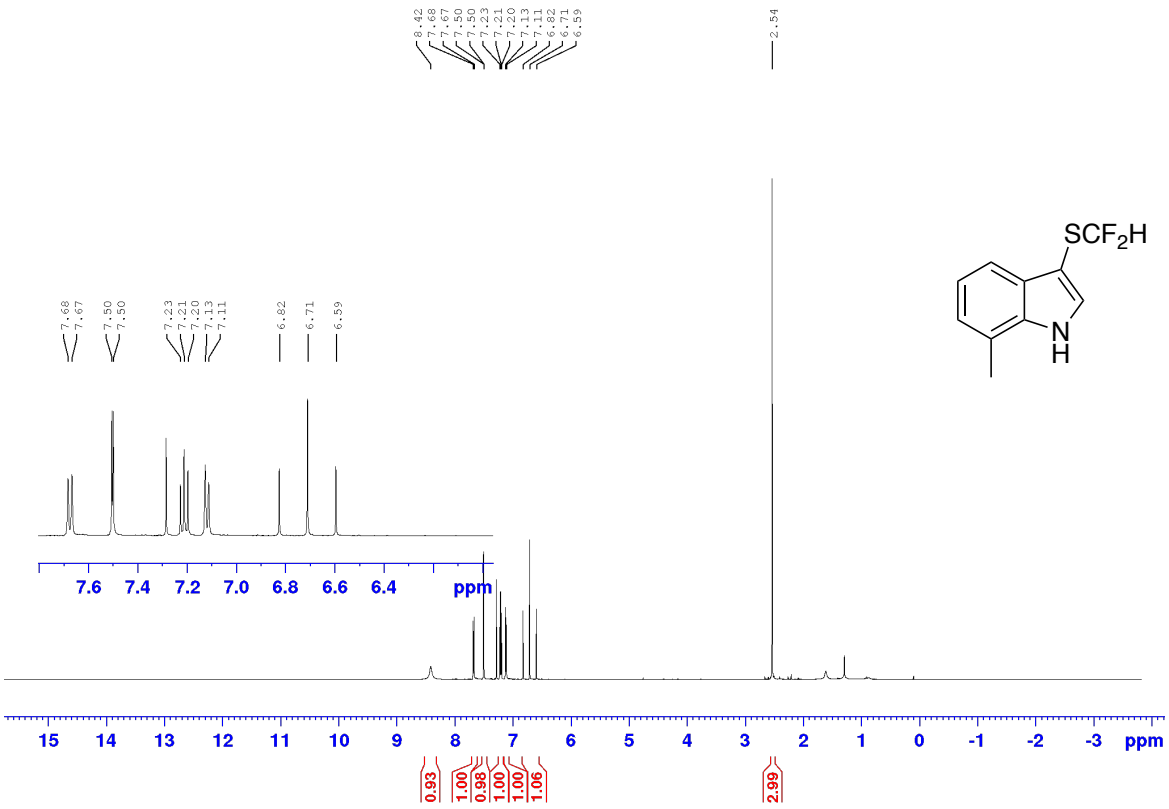
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methyl-1*H*-indole (3b)



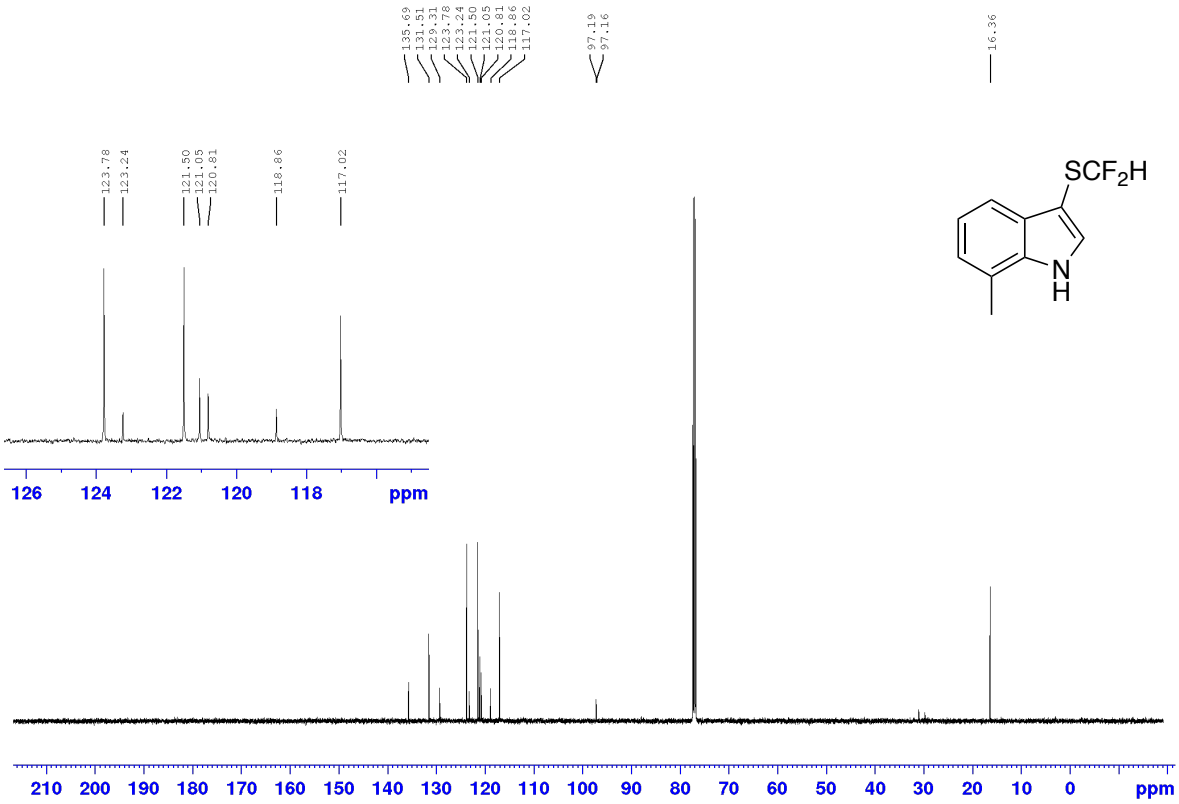
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methyl-1*H*-indole (3b)



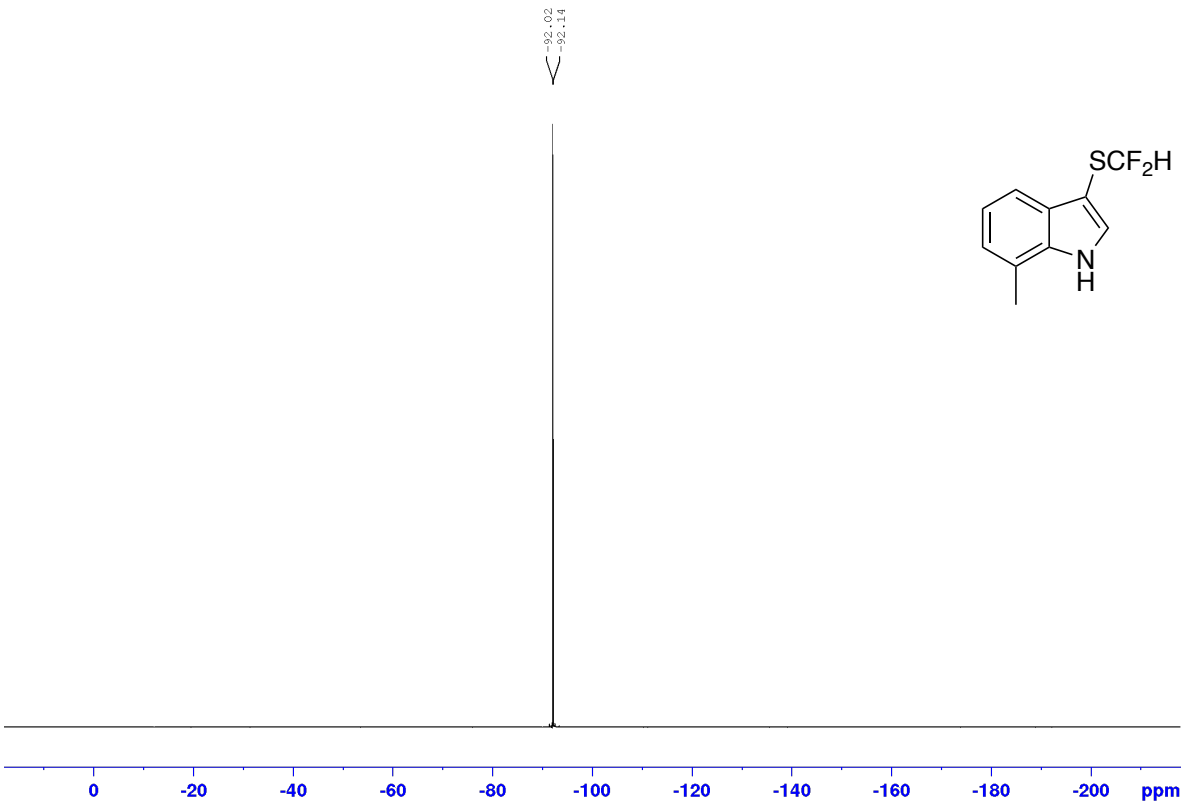
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-7-methyl-1*H*-indole (4b)



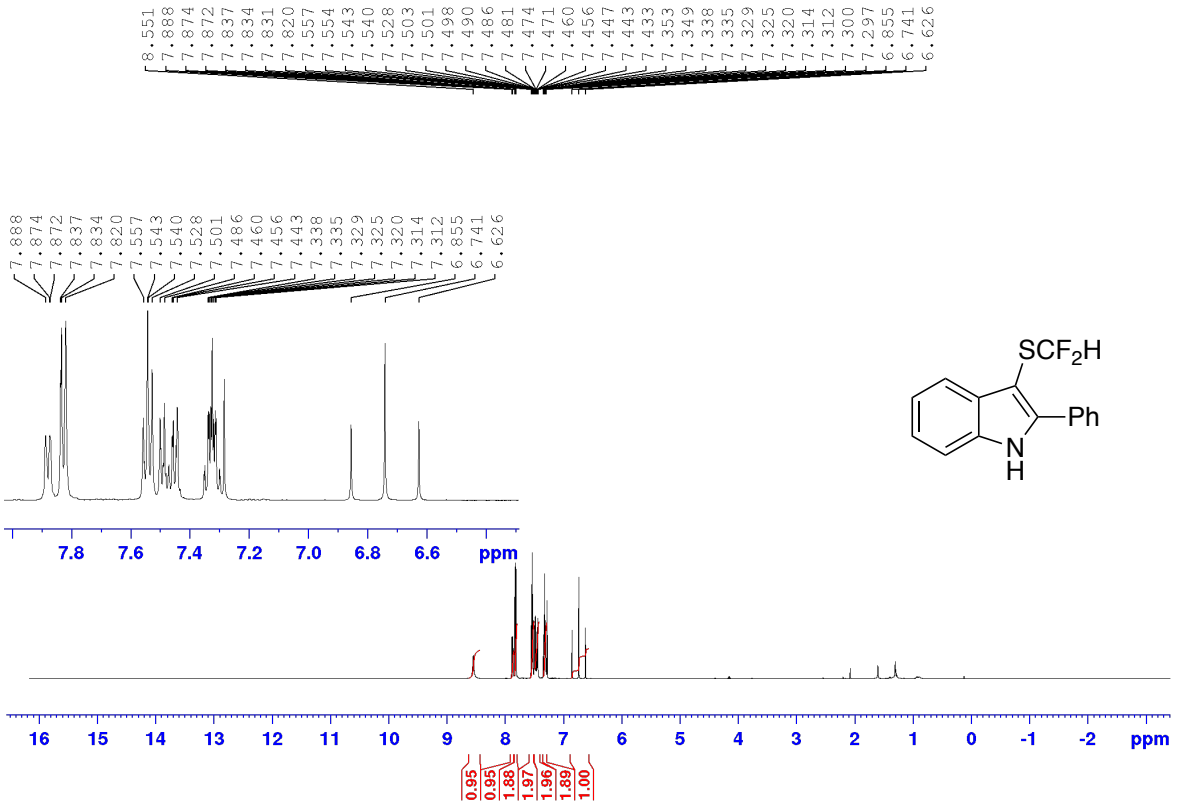
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methyl-1*H*-indole (4b)



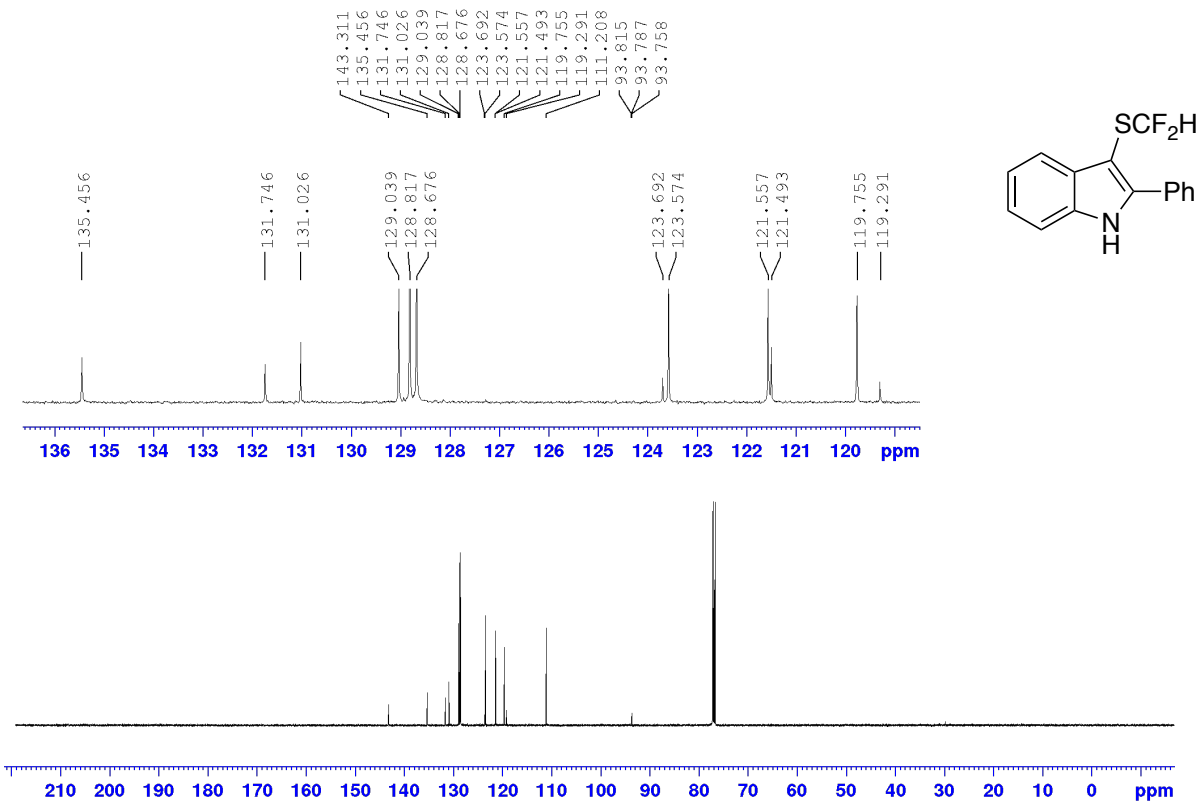
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-7-methyl-1*H*-indole (4b)



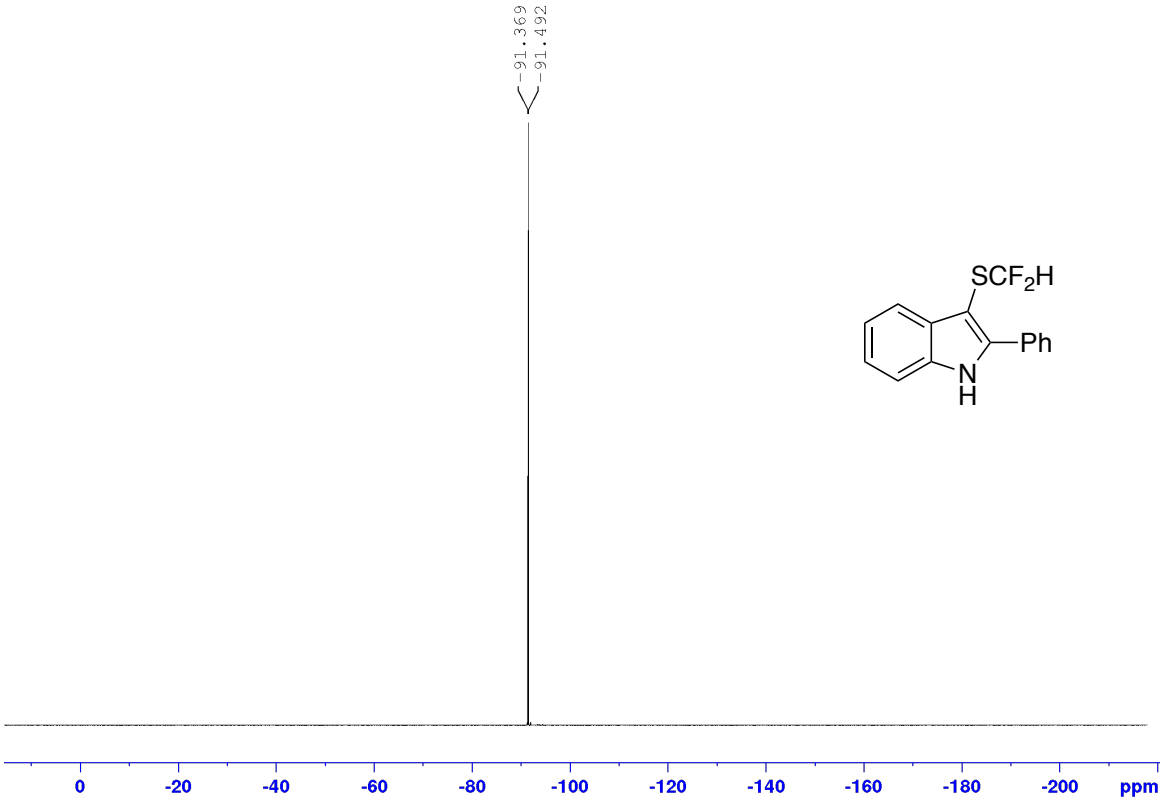
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-2-phenyl-1*H*-indole (5b)



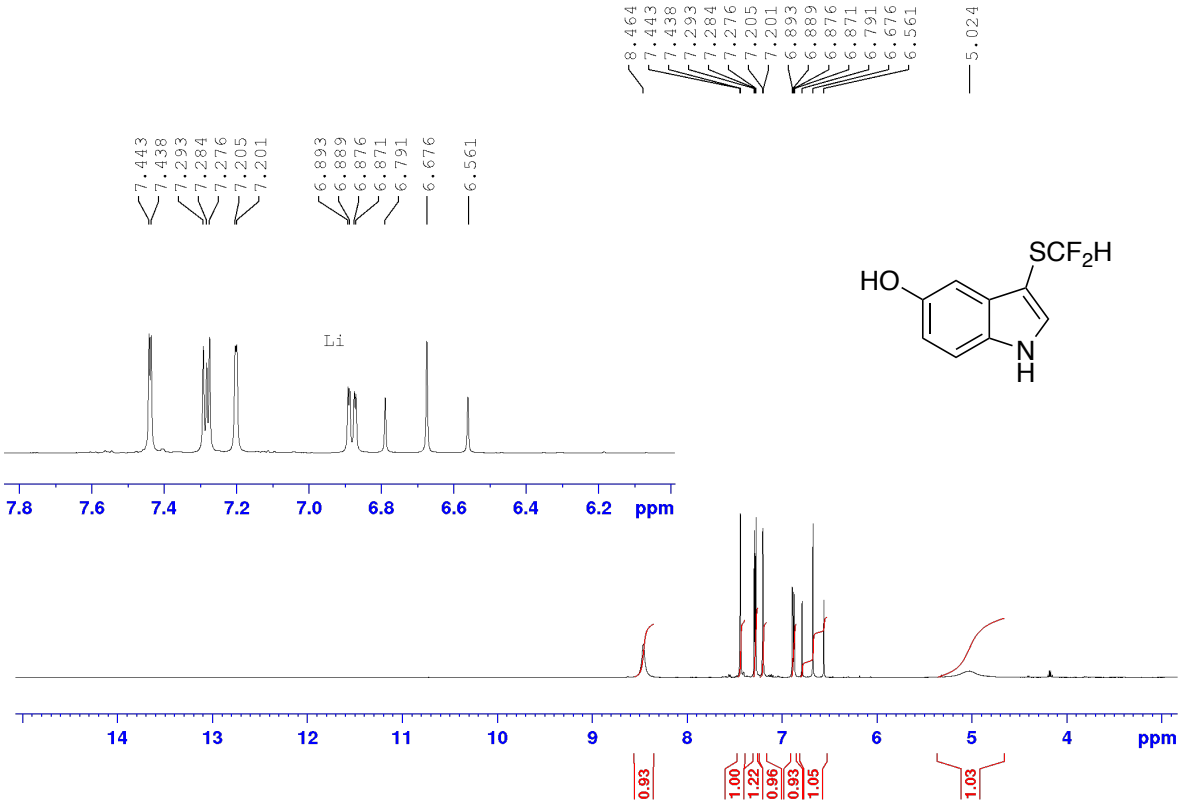
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-2-phenyl-1*H*-indole (5b)



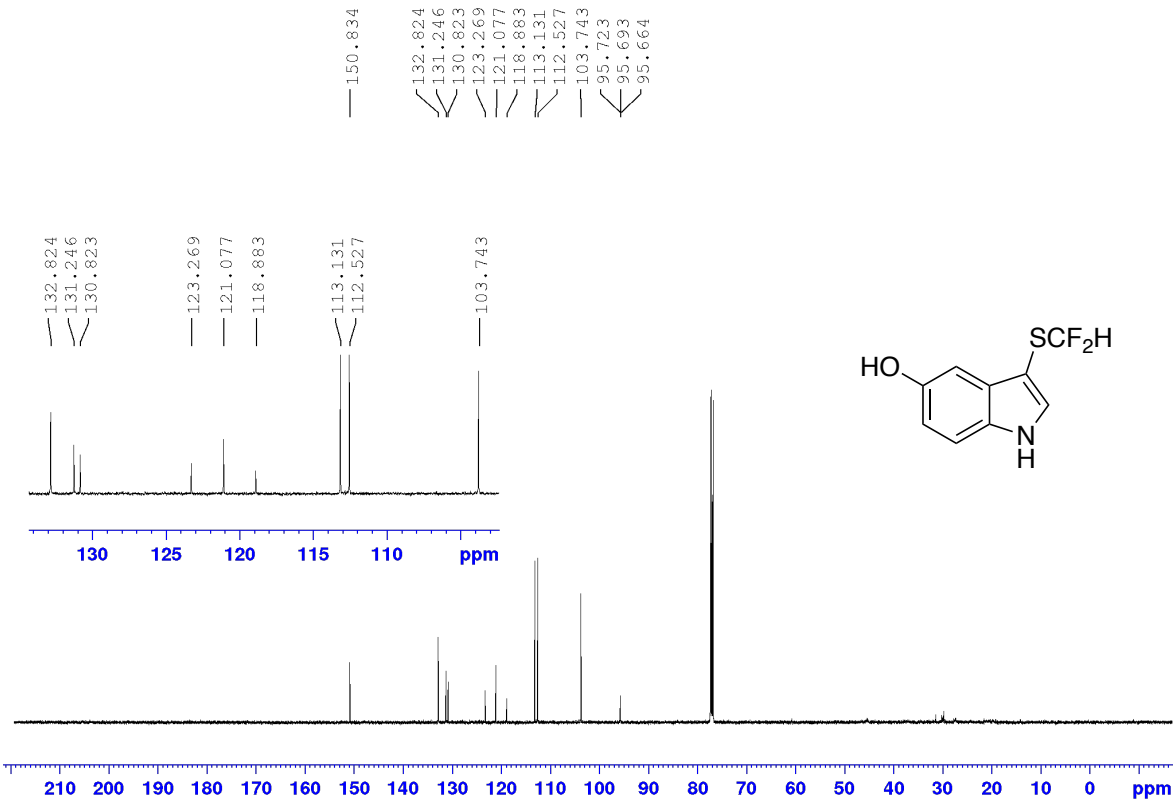
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-2-phenyl-1*H*-indole (5b)



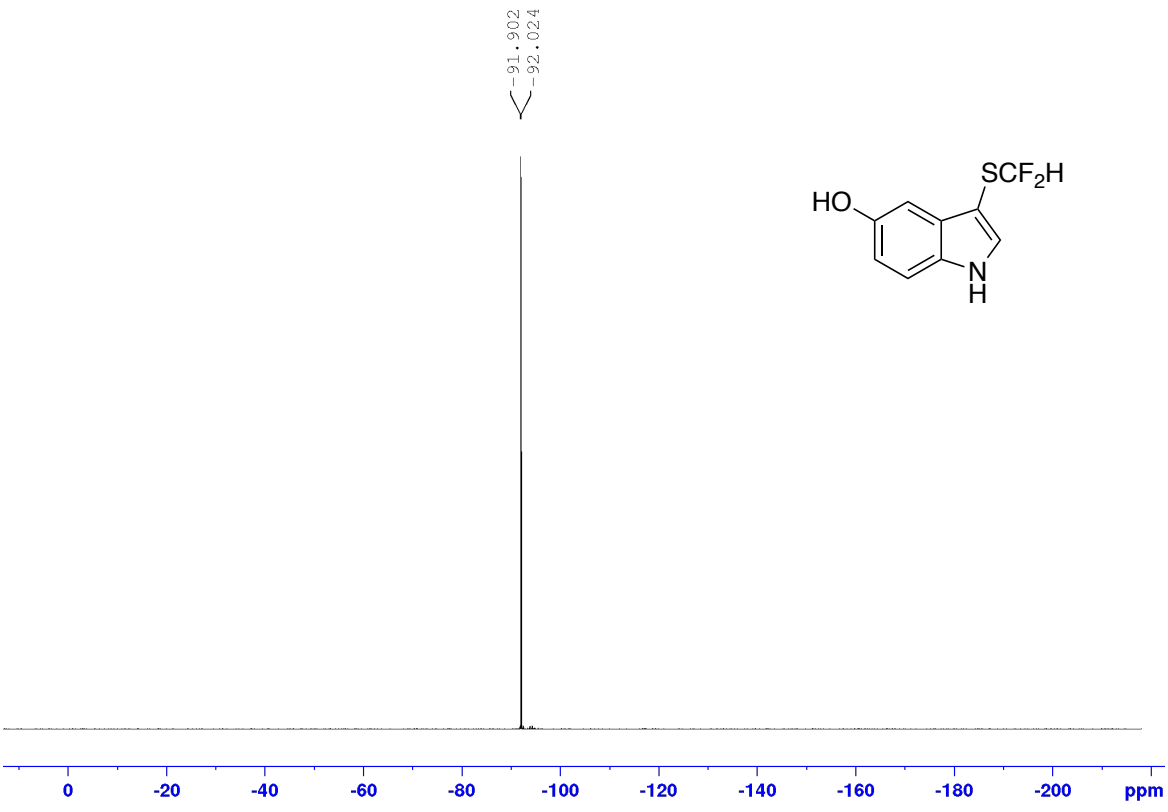
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1*H*-indol-5-ol (6b)



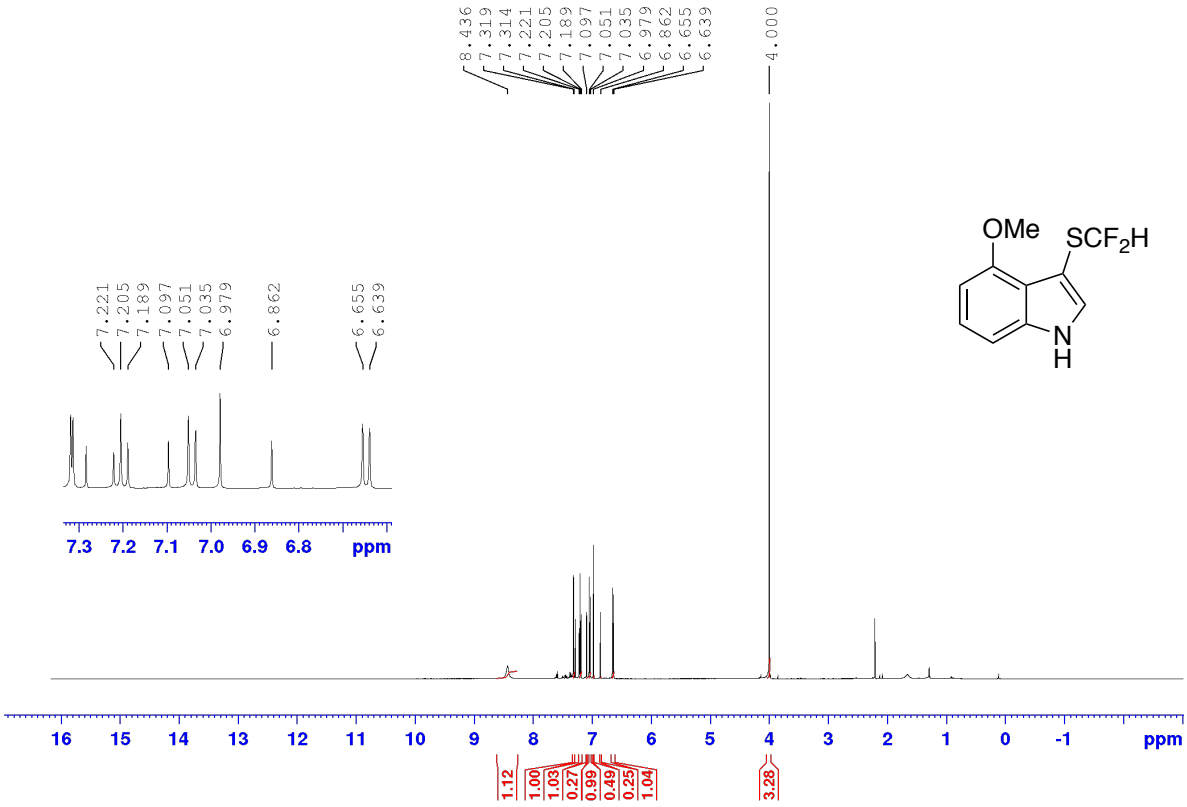
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1*H*-indol-5-ol (6b)



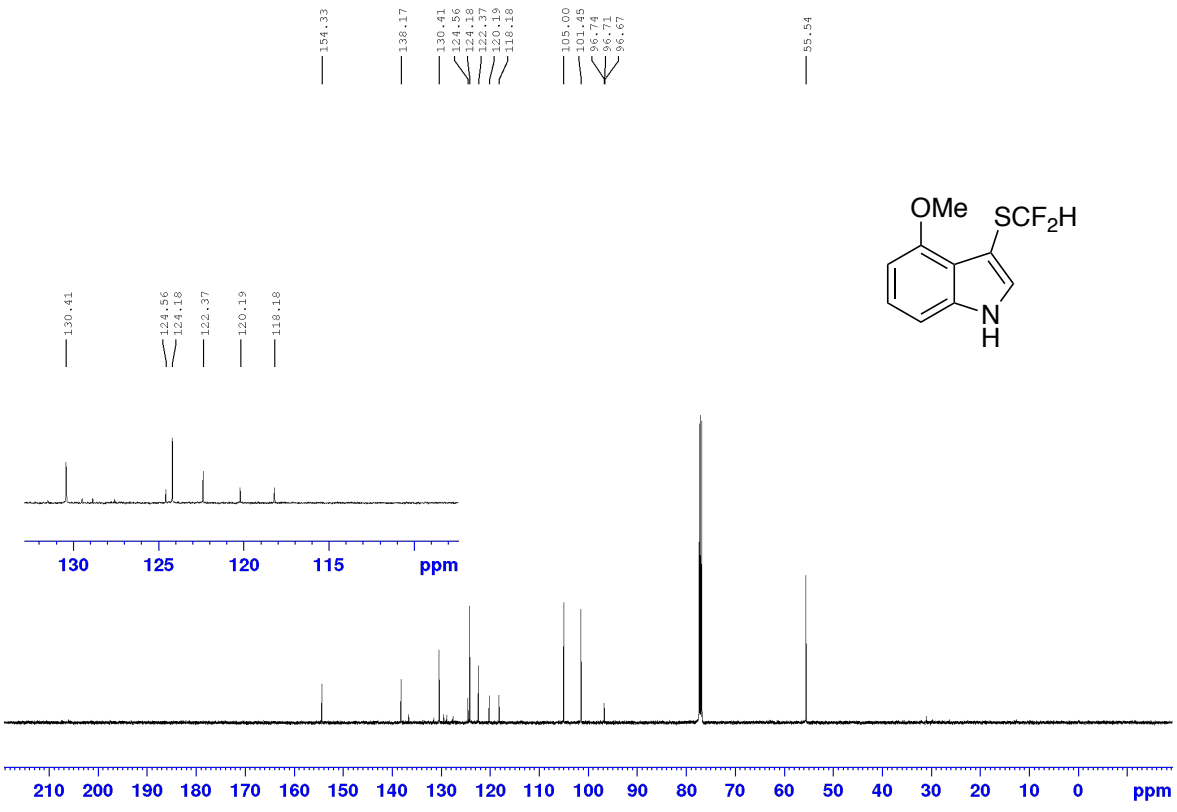
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1*H*-indol-5-ol (6b)



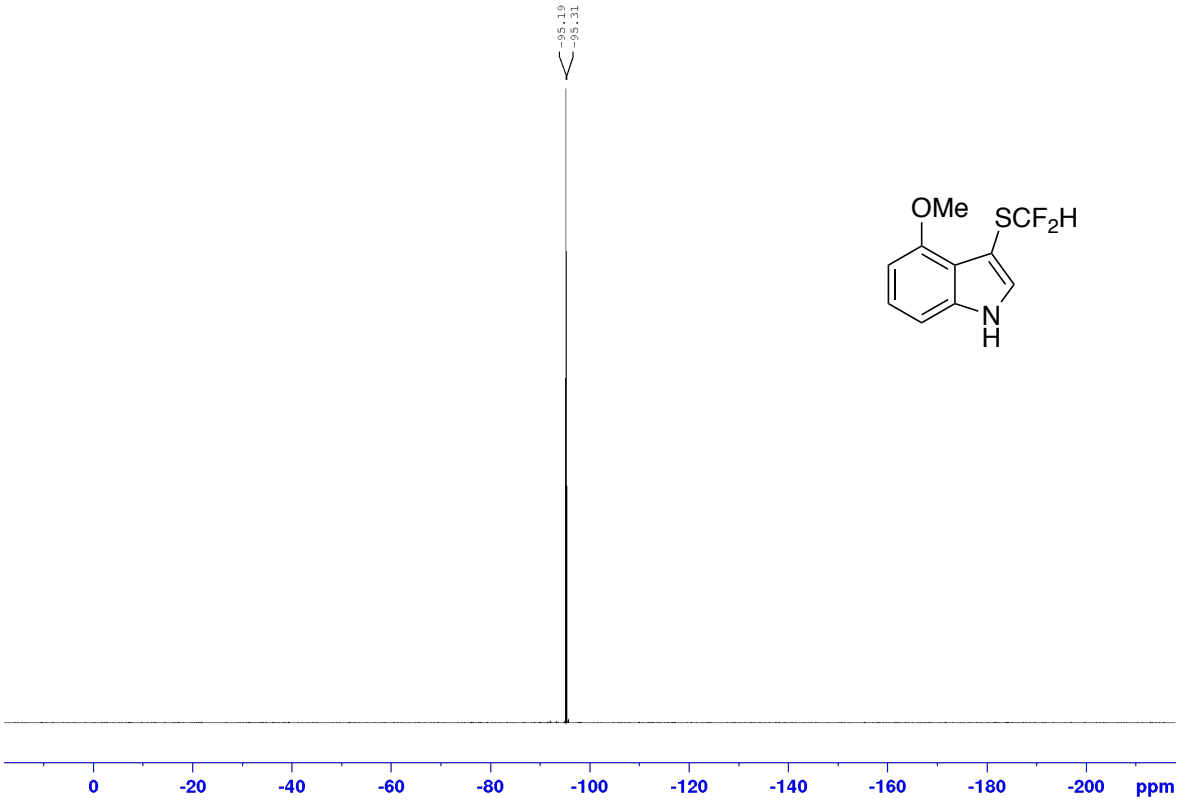
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-4-methoxy-1*H*-indole (7b)



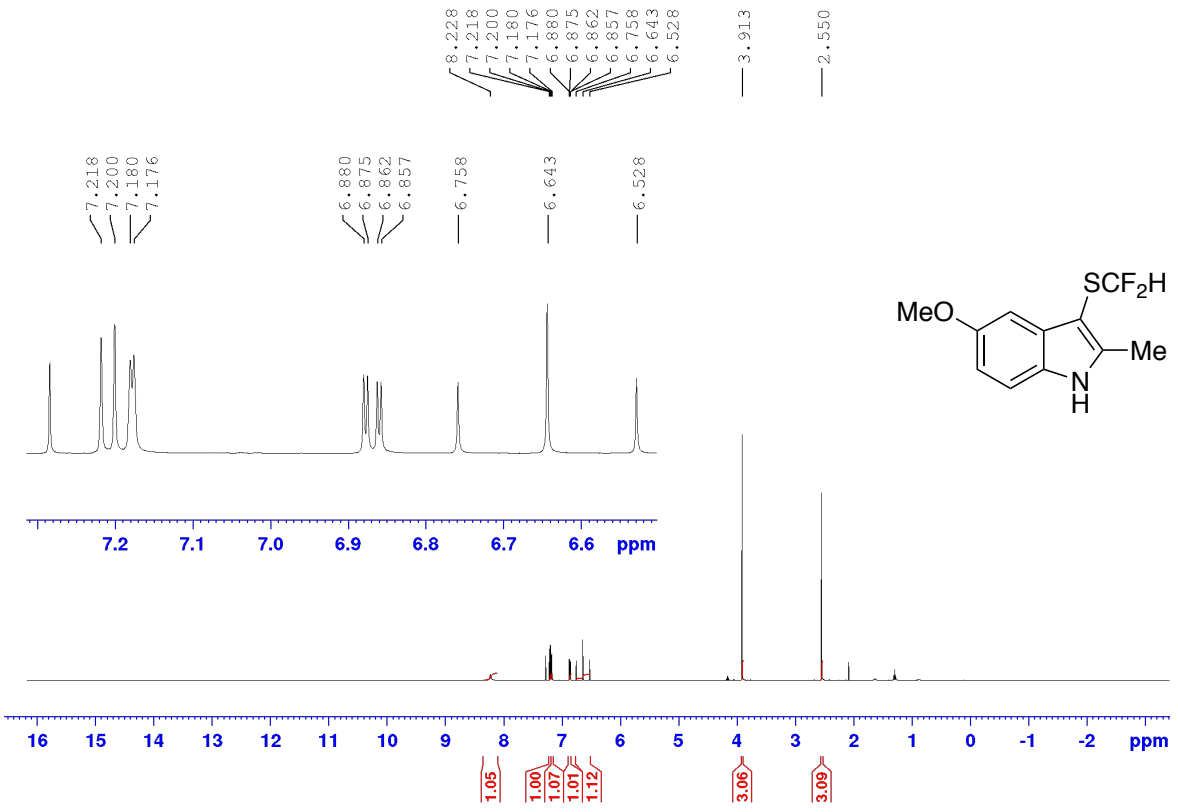
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-4-methoxy-1*H*-indole (7b)



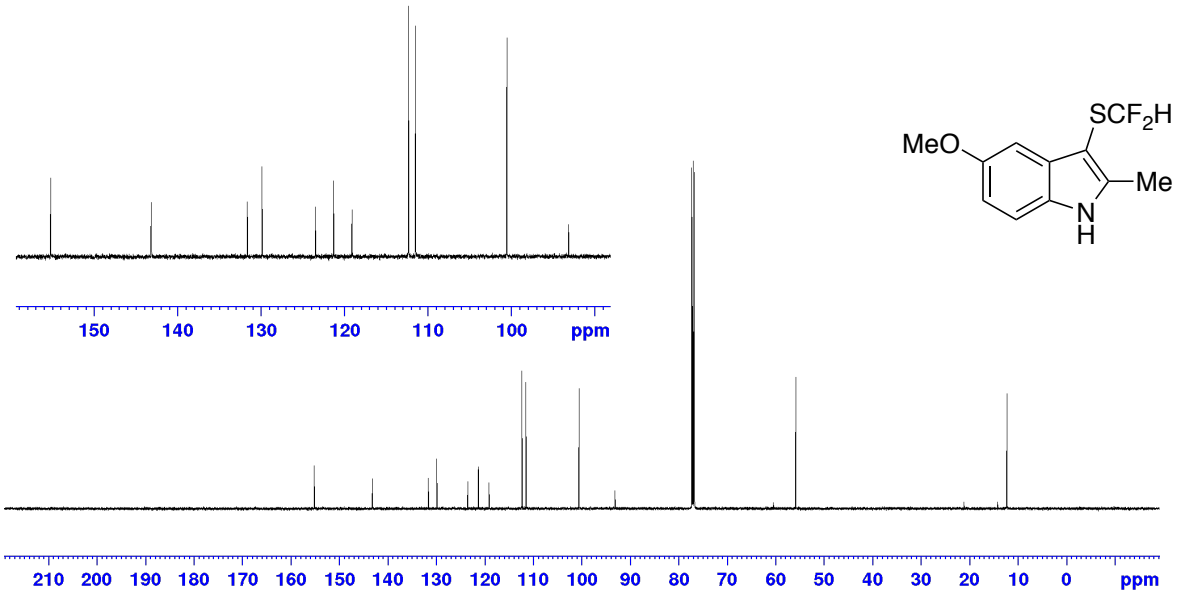
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-4-methoxy-1*H*-indole (7b)



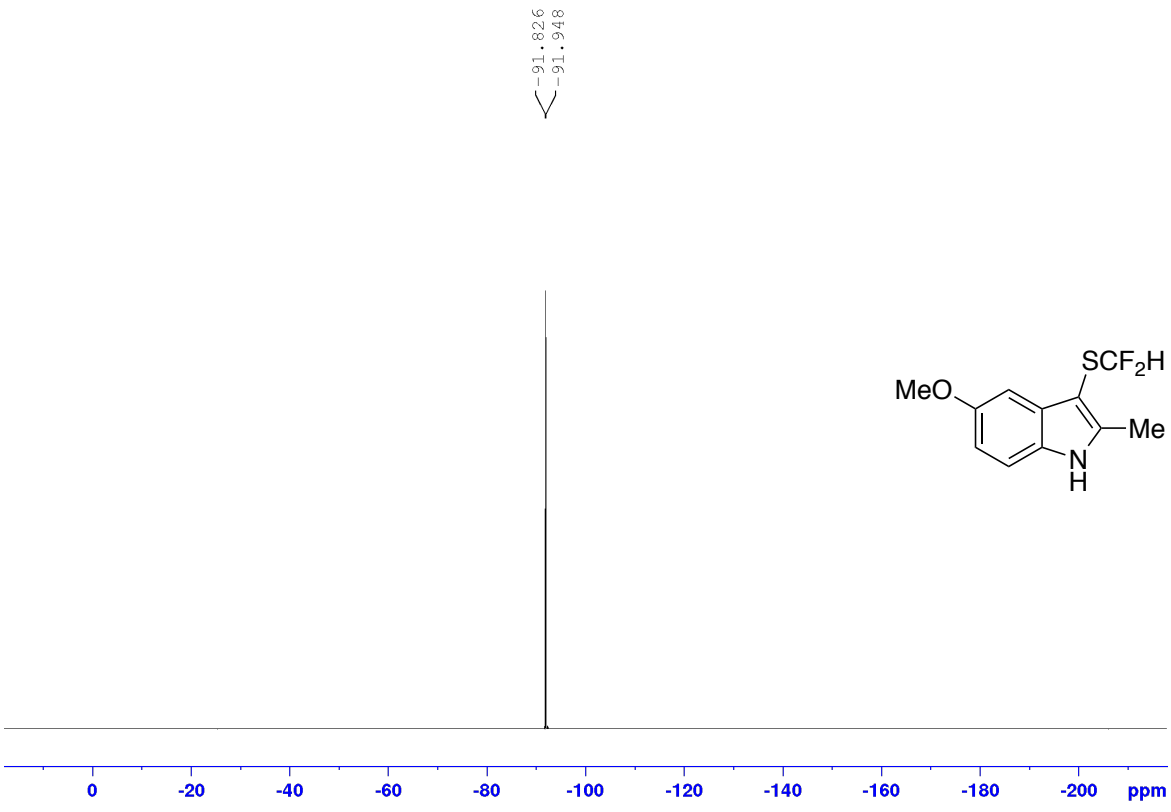
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methoxy-1-methyl-1*H*-indole (8b)



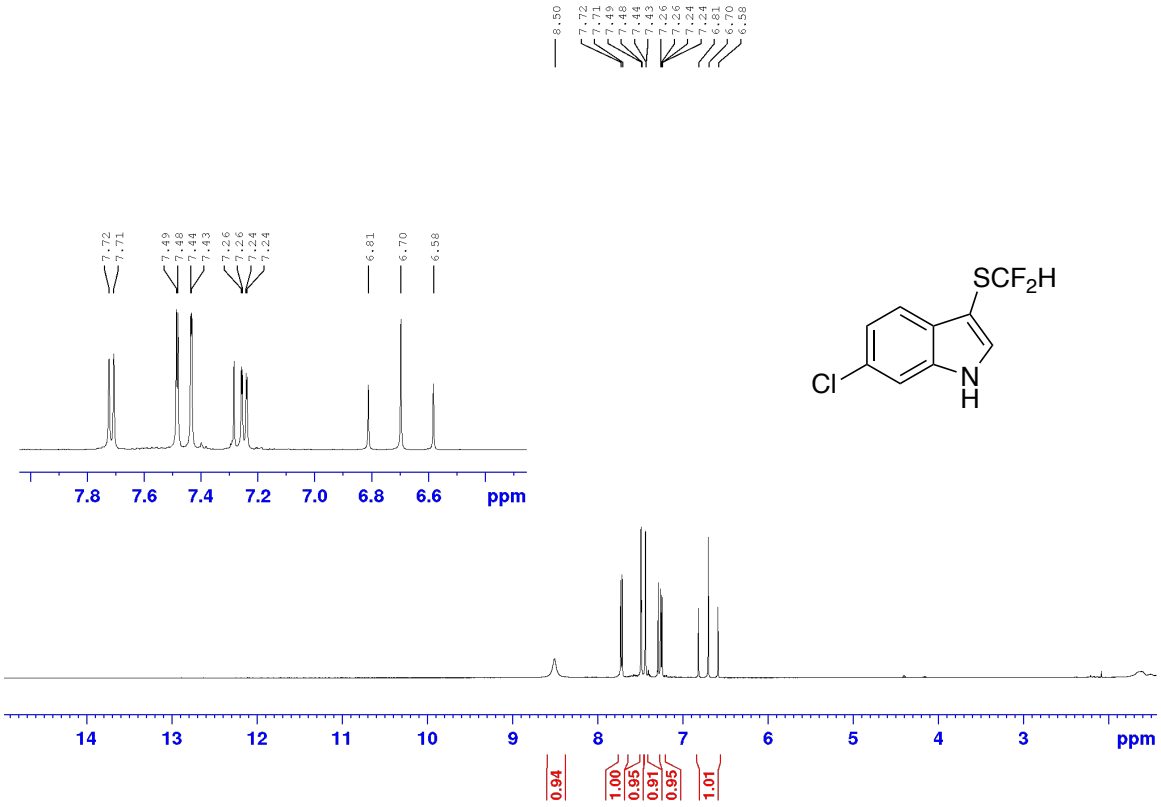
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methoxy-1-methyl-1*H*-indole (8b)



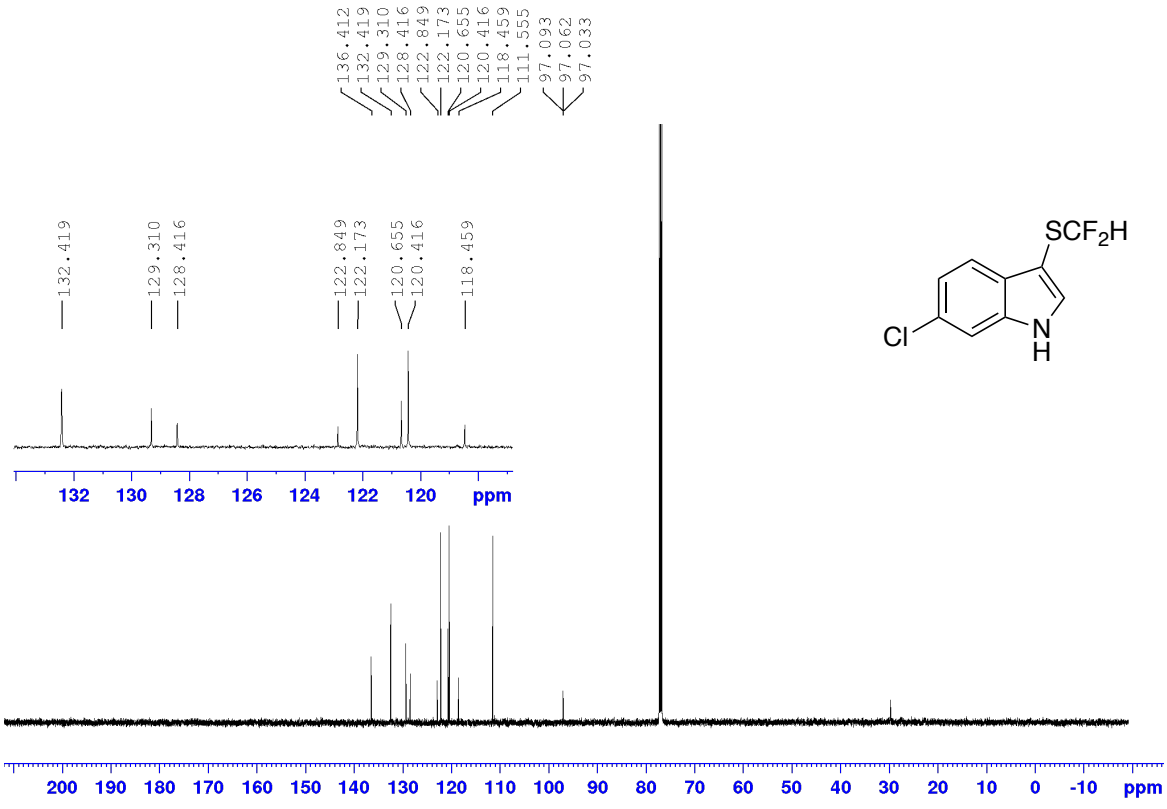
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-methoxy-1-methyl-1*H*-indole (8b)



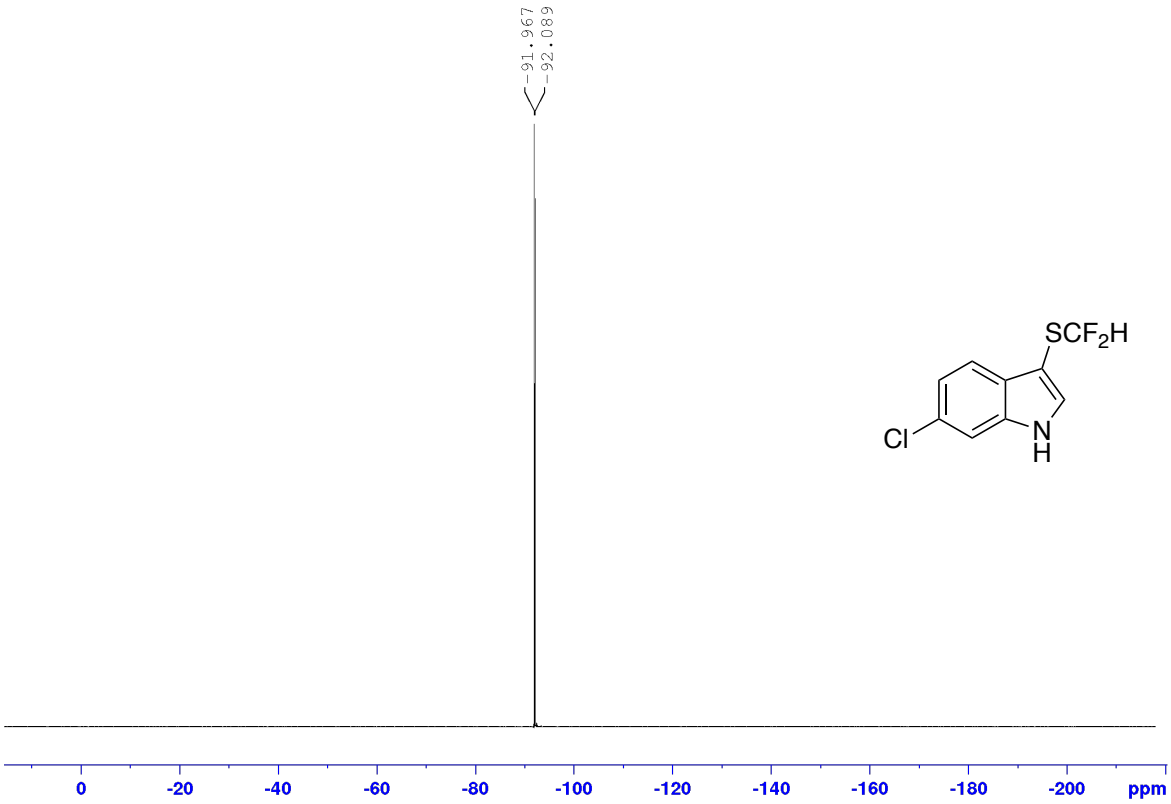
^{1}H NMR (500 MHz, $CDCl_3$) 5-Chloro-3-((difluoromethyl)thio)-1*H*-indole (9b)



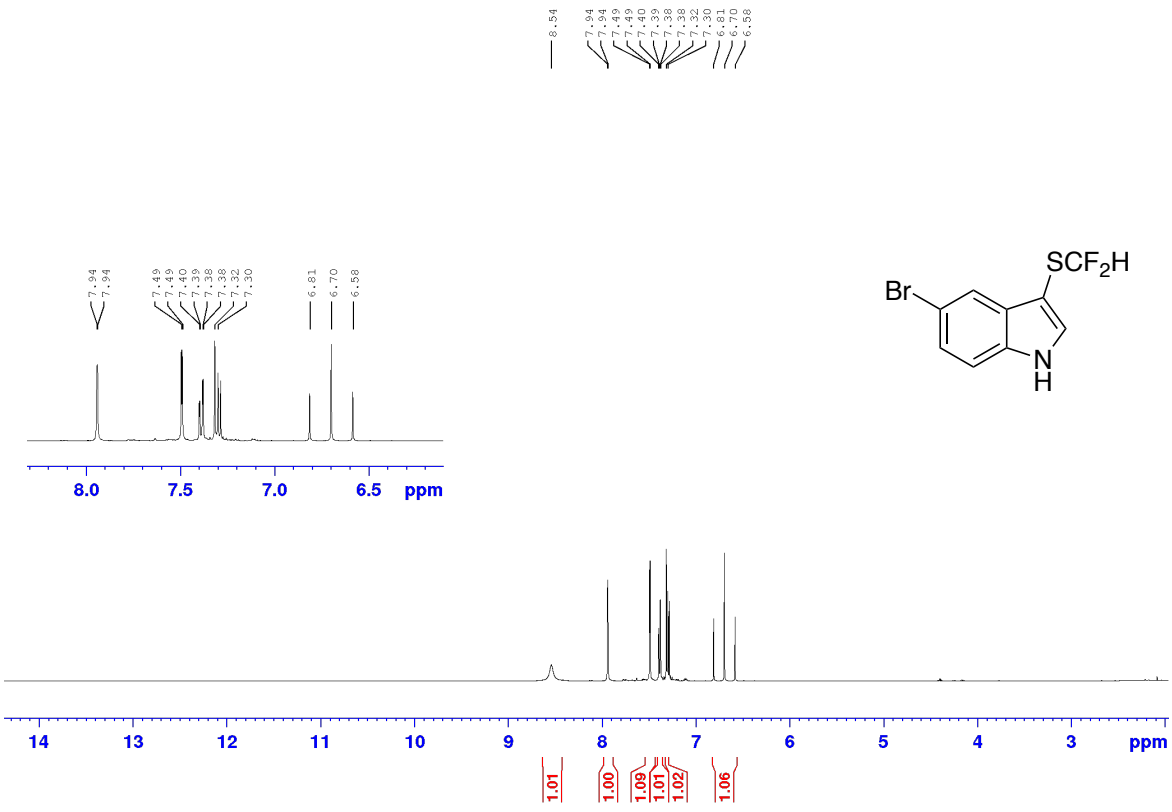
^{13}C NMR (125 MHz, $CDCl_3$) 5-Chloro-3-((difluoromethyl)thio)-1*H*-indole (9b)



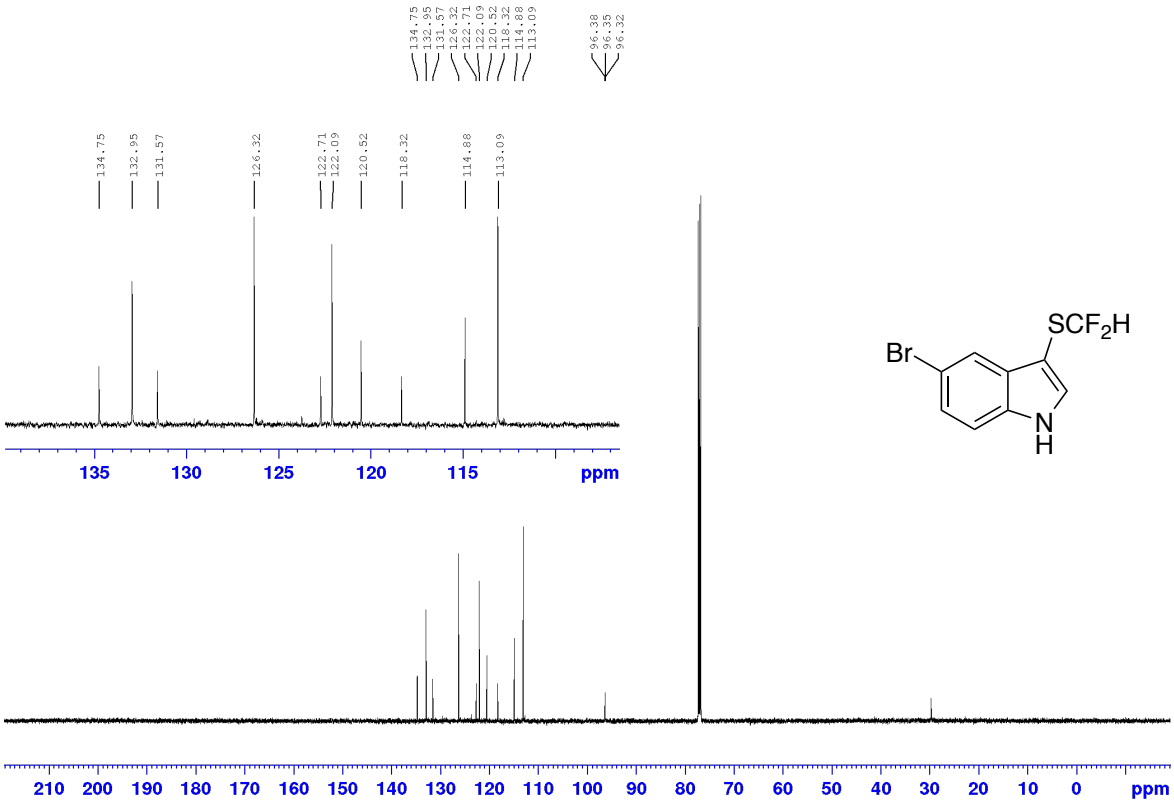
^{19}F NMR (470 MHz, $CDCl_3$) 5-Chloro-3-((difluoromethyl)thio)-1*H*-indole (9b)



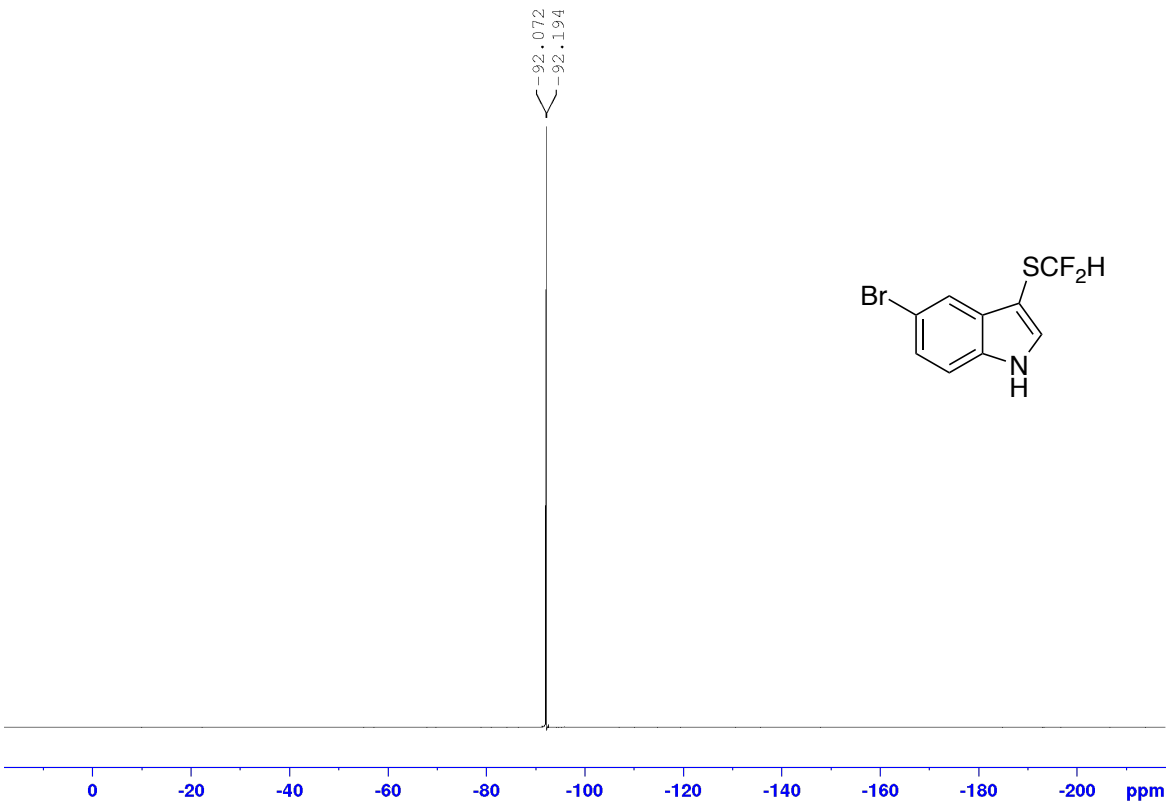
^{1}H NMR (500 MHz, $CDCl_3$) 5-Bromo-3-((difluoromethyl)thio)-1*H*-indole (10b)



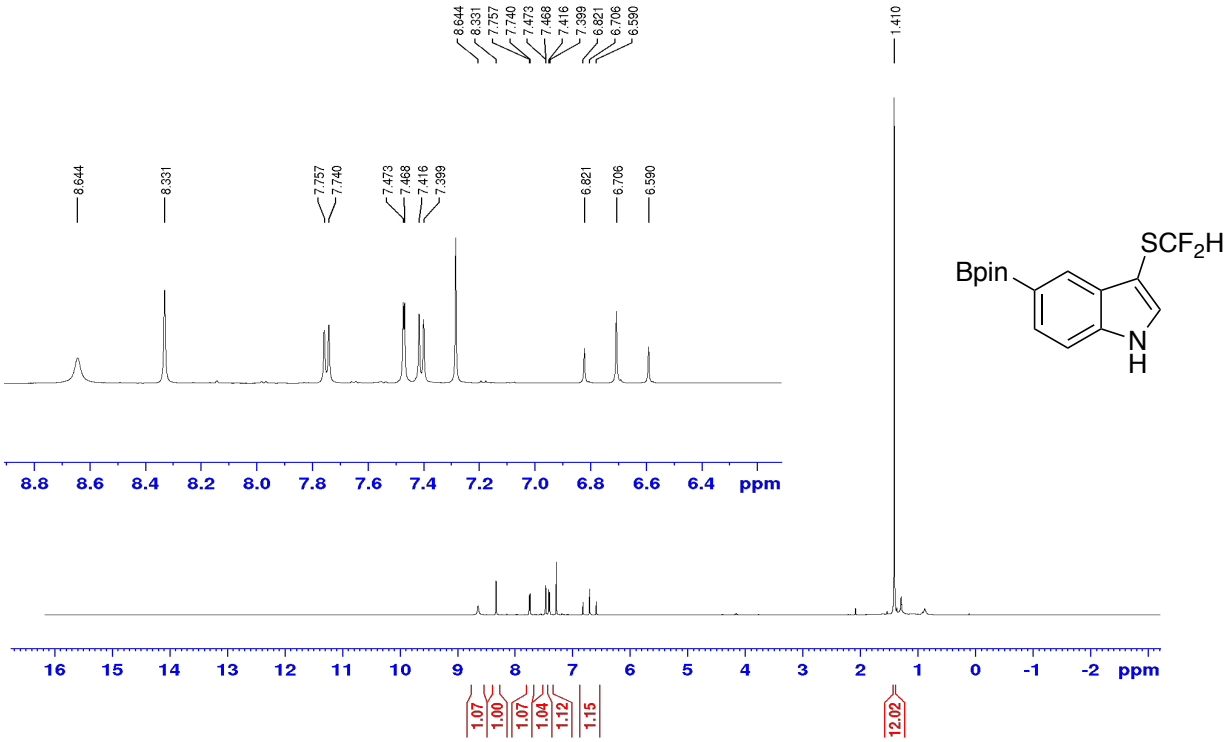
^{13}C NMR (125 MHz, $CDCl_3$) 5-Bromo-3-((difluoromethyl)thio)-1*H*-indole (10b)



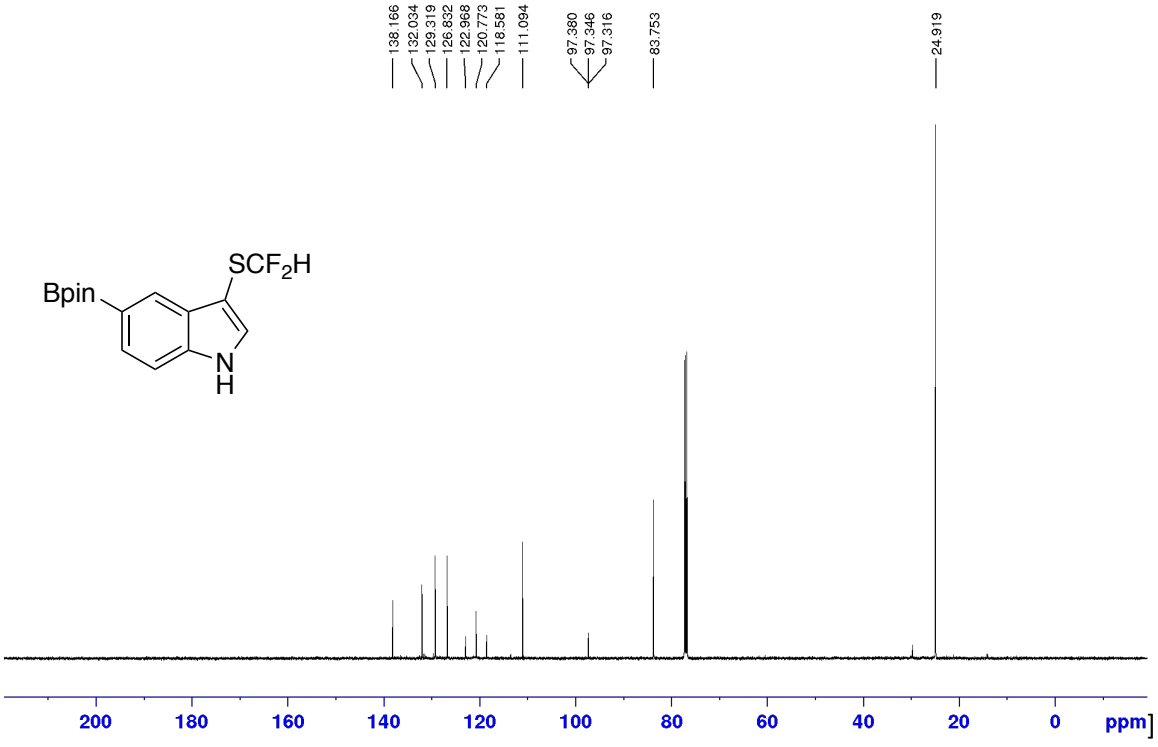
^{19}F NMR (470 MHz, $CDCl_3$) 5-Bromo-3-((difluoromethyl)thio)-1*H*-indole (10b)



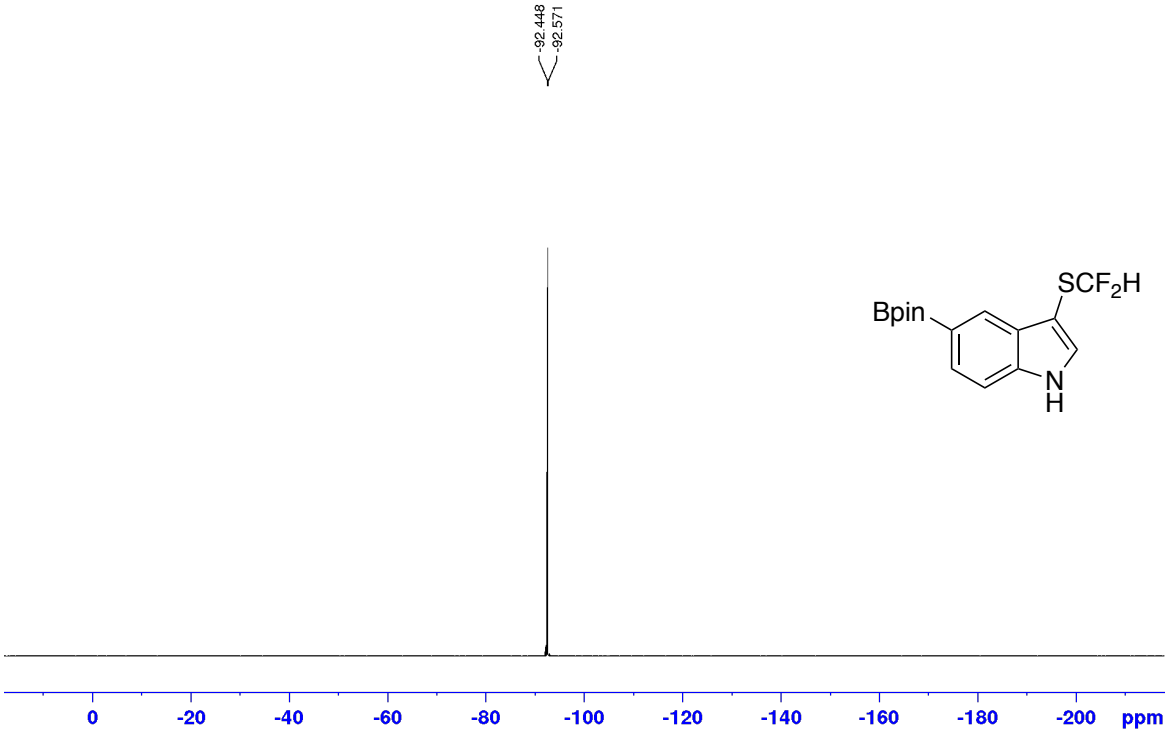
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (11b)



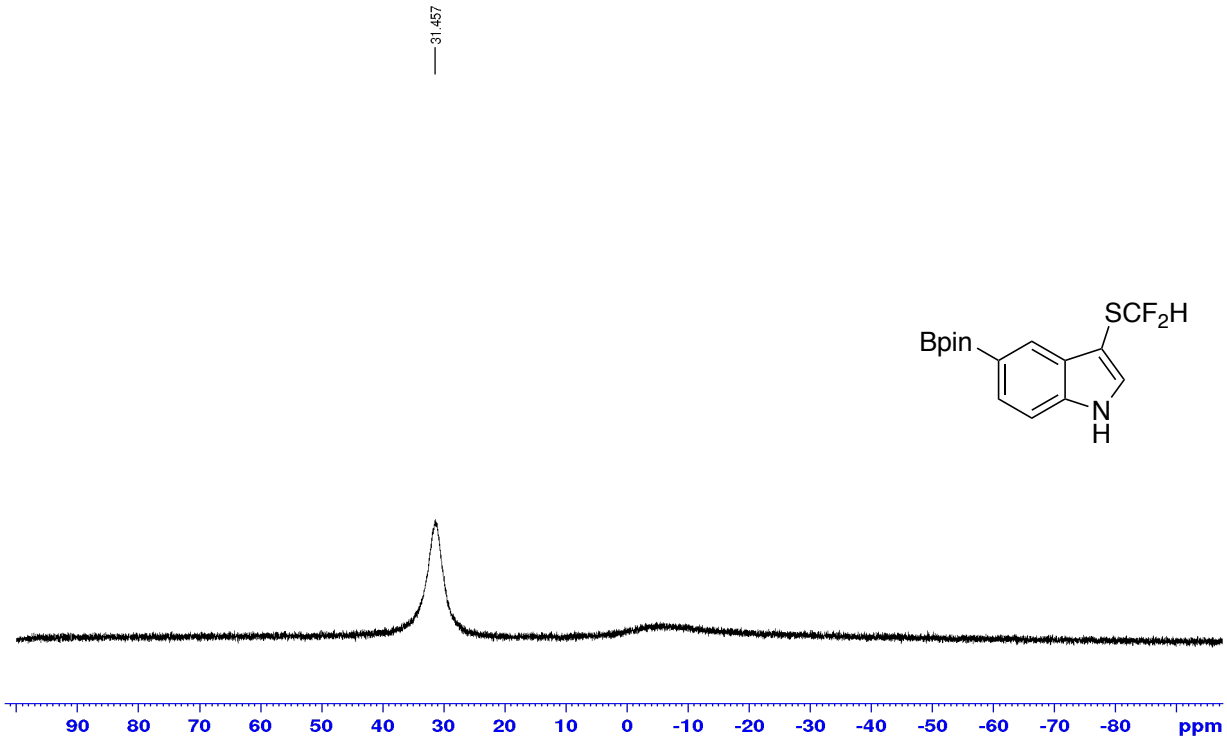
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (11b)



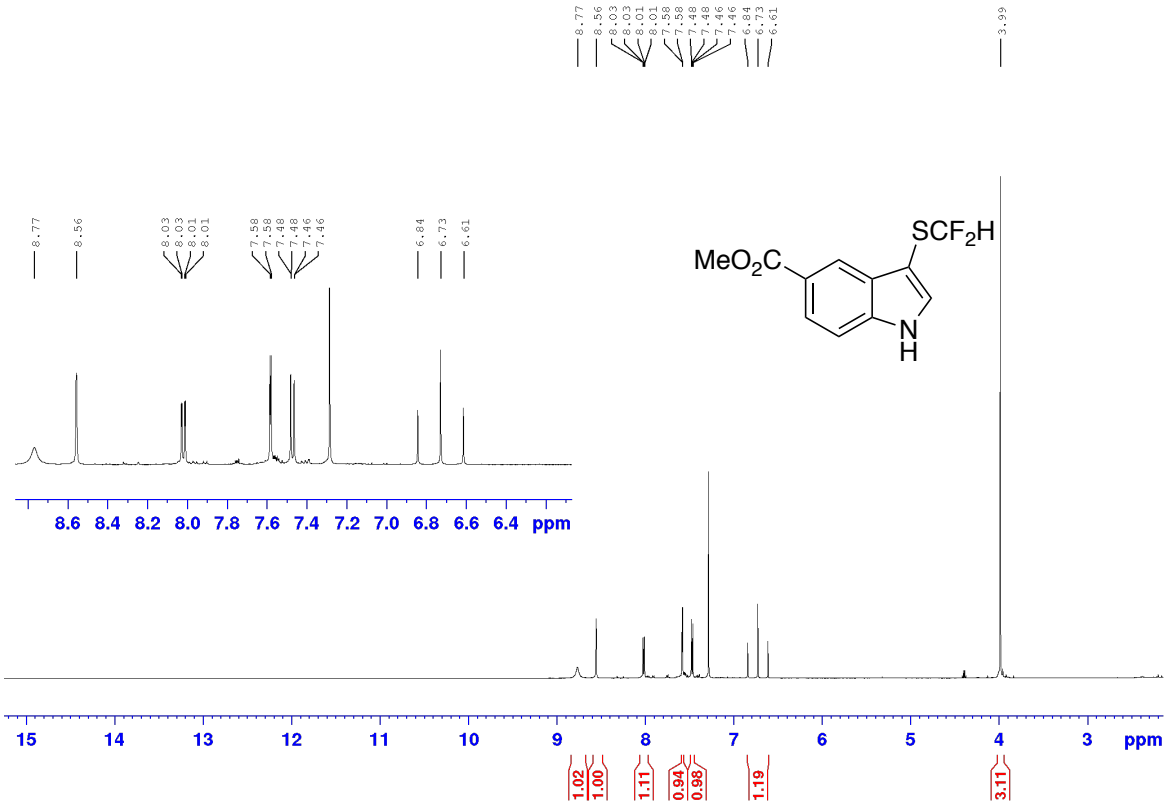
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (11b)



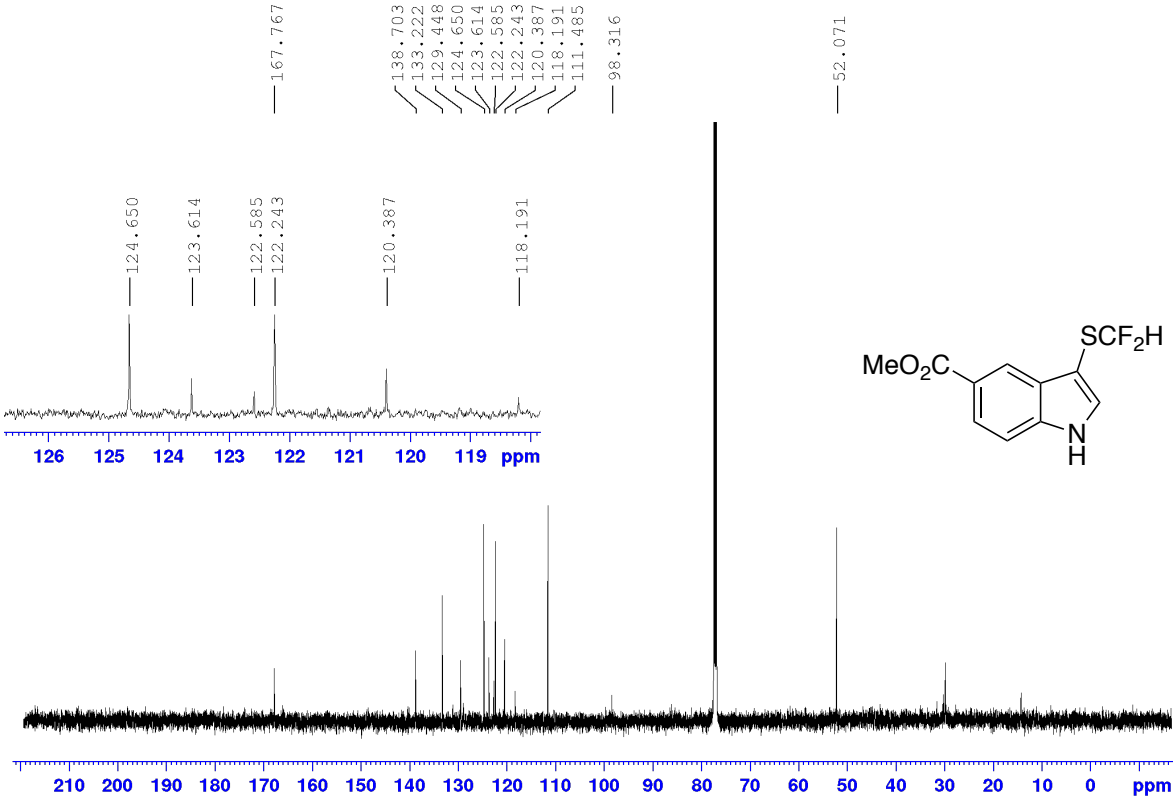
^{11}B NMR (160 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole （11b）



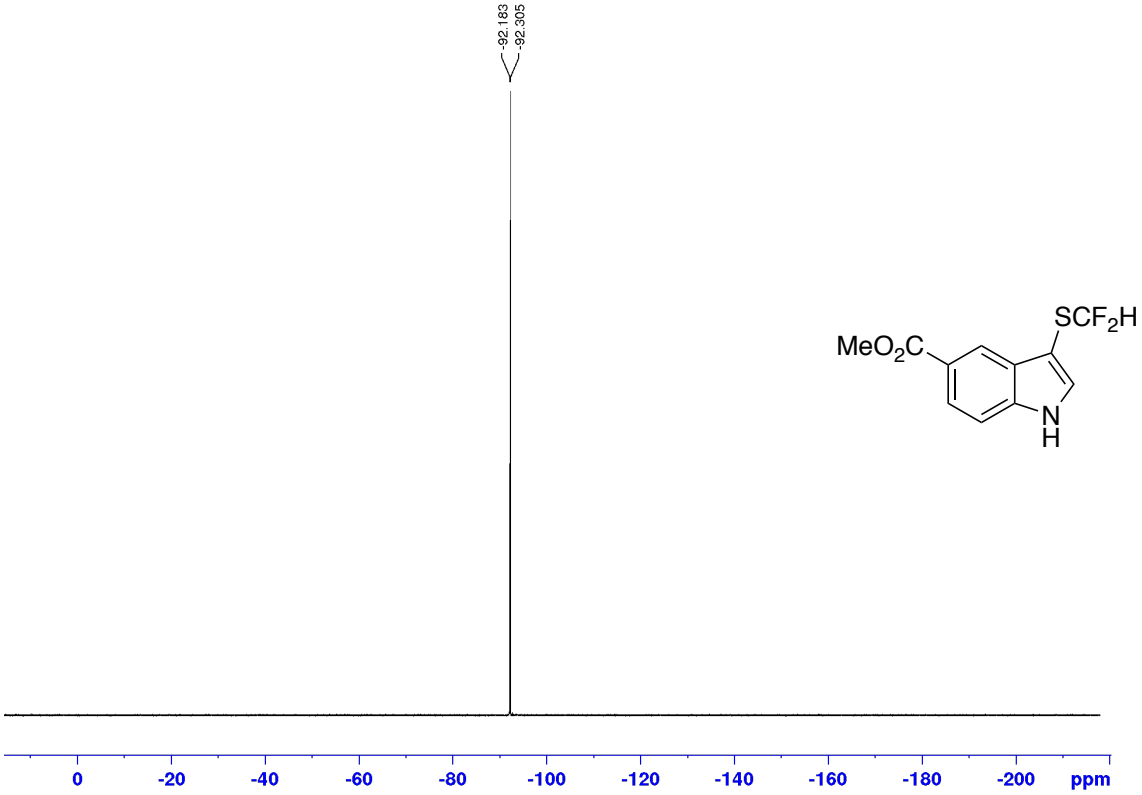
^{1}H NMR (500 MHz, $CDCl_3$) Methyl 3-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (12b)



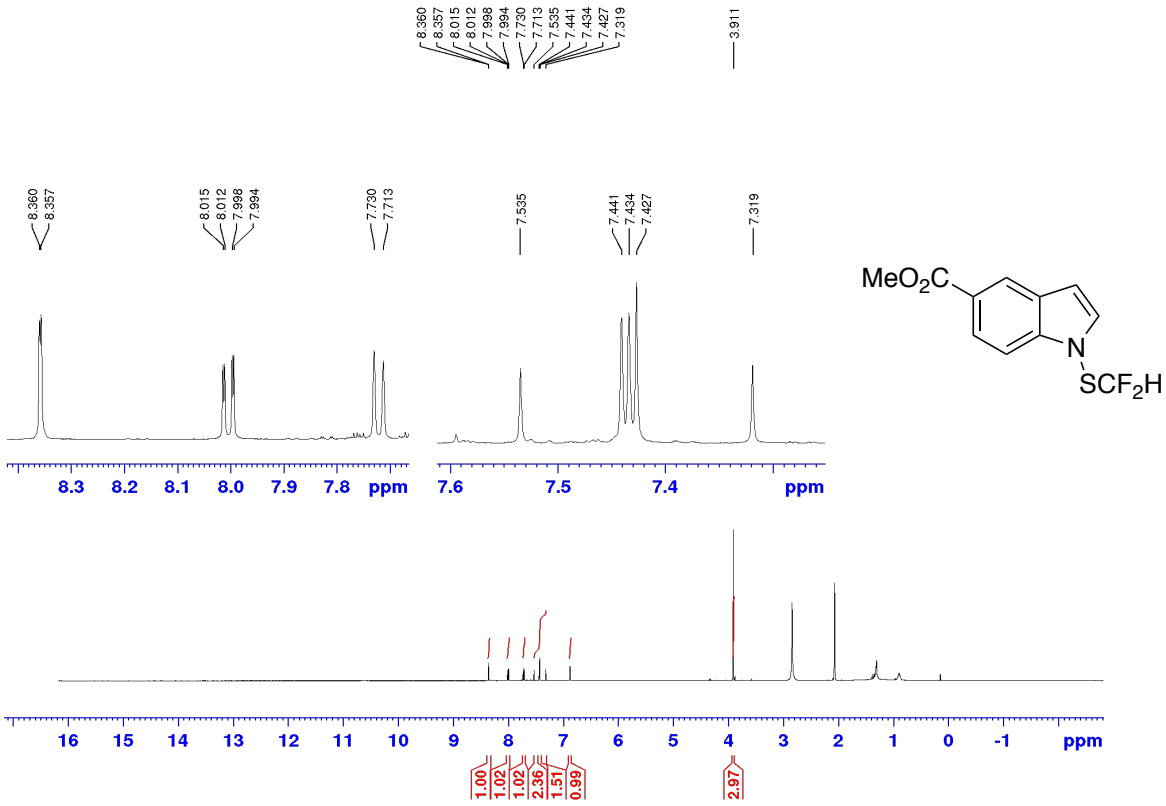
^{13}C NMR (125 MHz, $CDCl_3$) Methyl 3-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (12b)



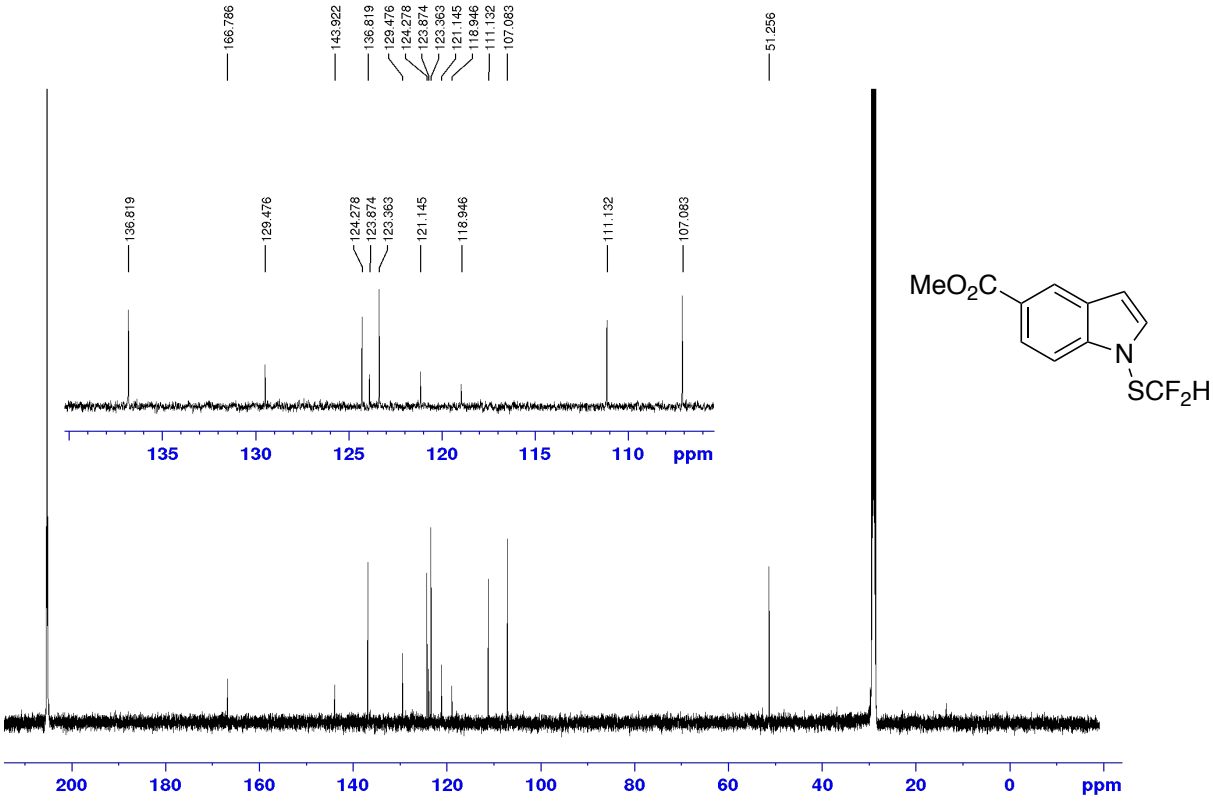
^{19}F NMR (470 MHz, $CDCl_3$) Methyl 3-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (12b)



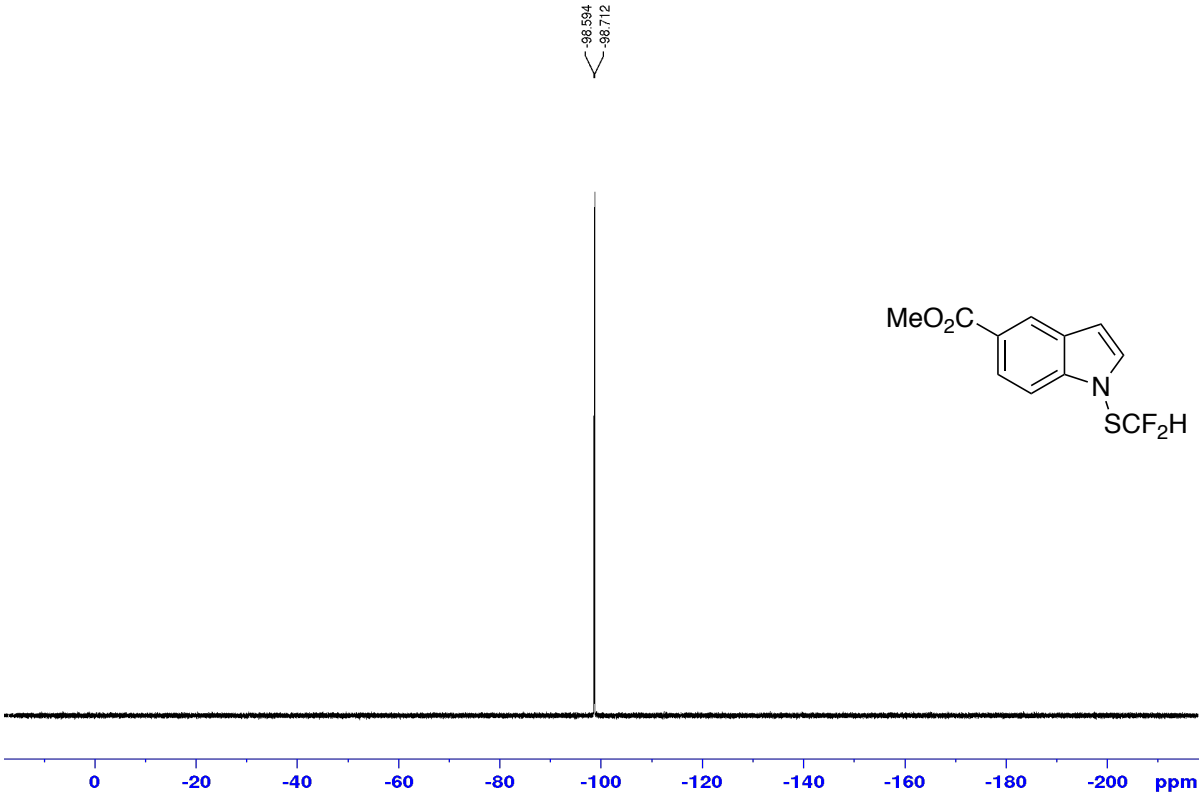
^{1}H NMR (500 MHz, Acetone-d_6 Methyl 1-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (12b')



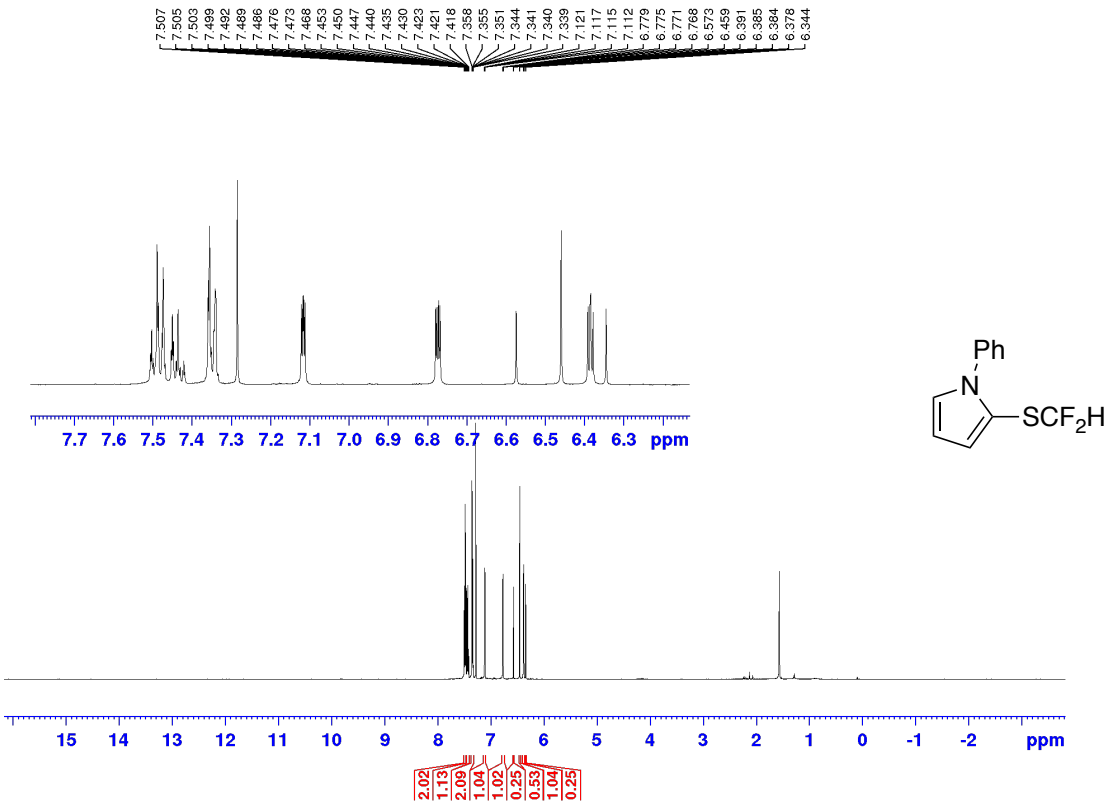
^{13}C NMR (125 MHz, Acetone-d_6) Methyl 1-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (12b')



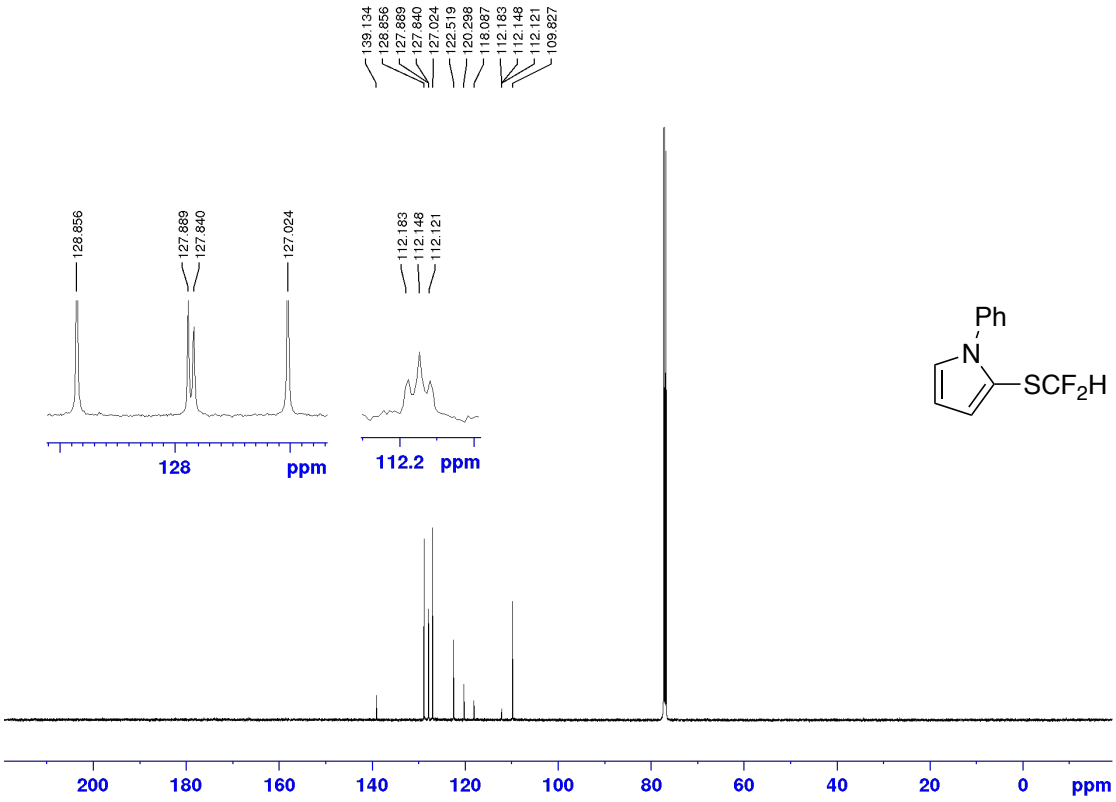
^{19}F NMR (470 MHz, $CDCl_3$) Methyl 1-((difluoromethyl)thio)-1*H*-indole-5-carboxylate (12b')



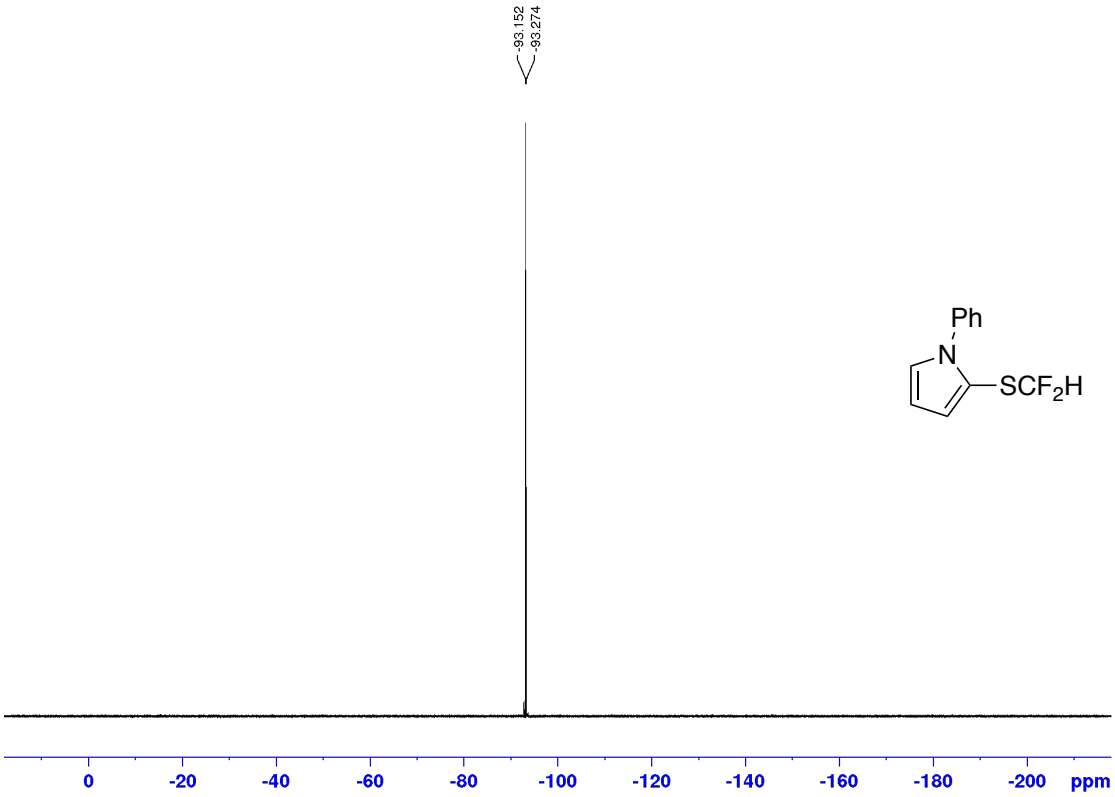
^{1}H NMR (500 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-1-phenyl-1*H*-pyrrole (13b)



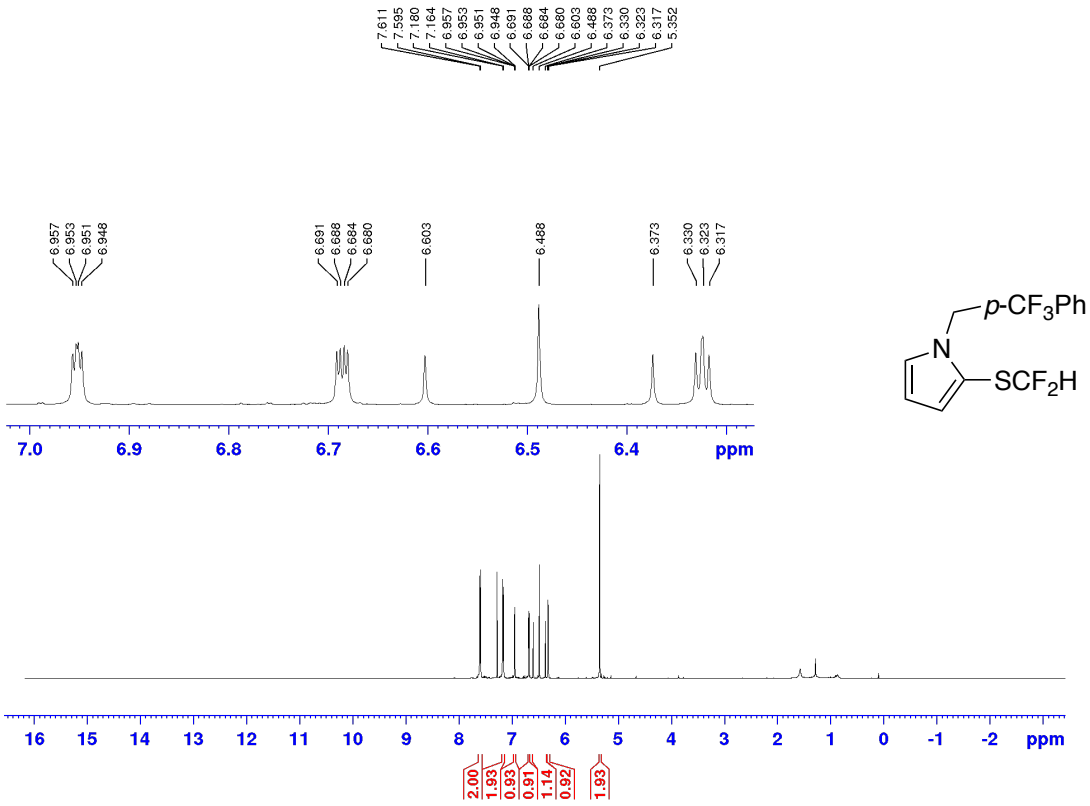
^{13}C NMR (125 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-1-phenyl-1*H*-pyrrole (13b)



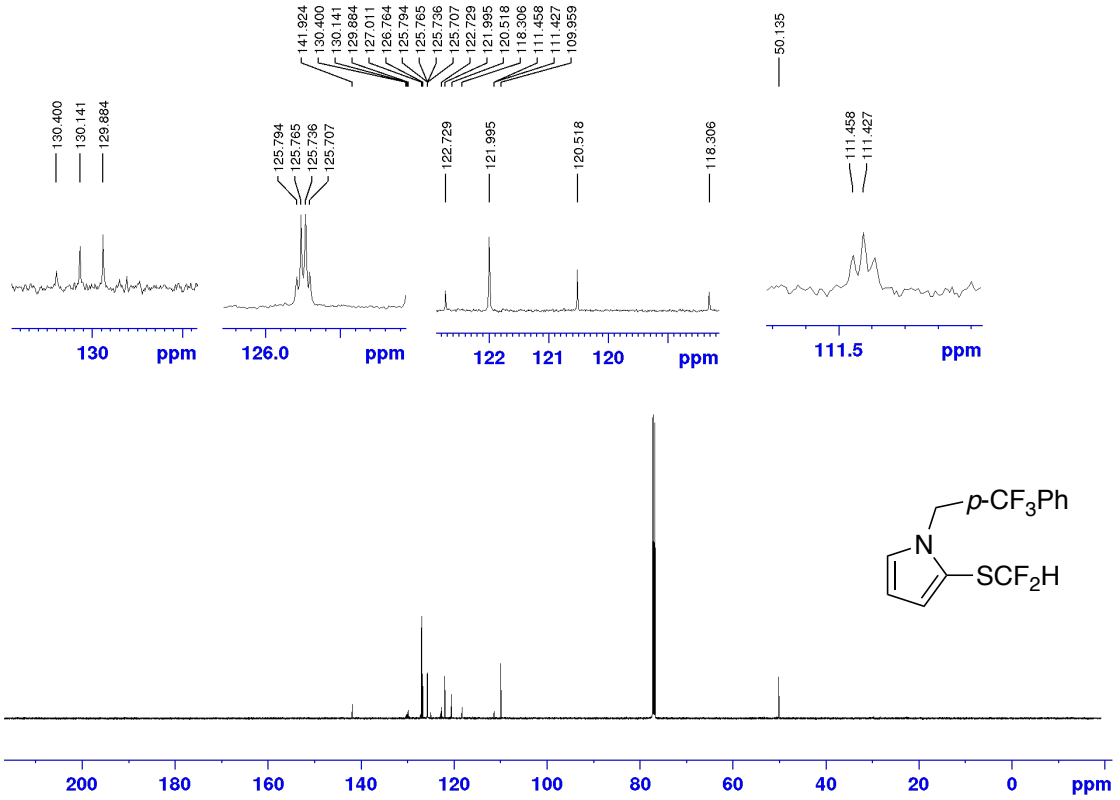
^{19}F NMR (470 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-1-phenyl-1*H*-pyrrole (13b)



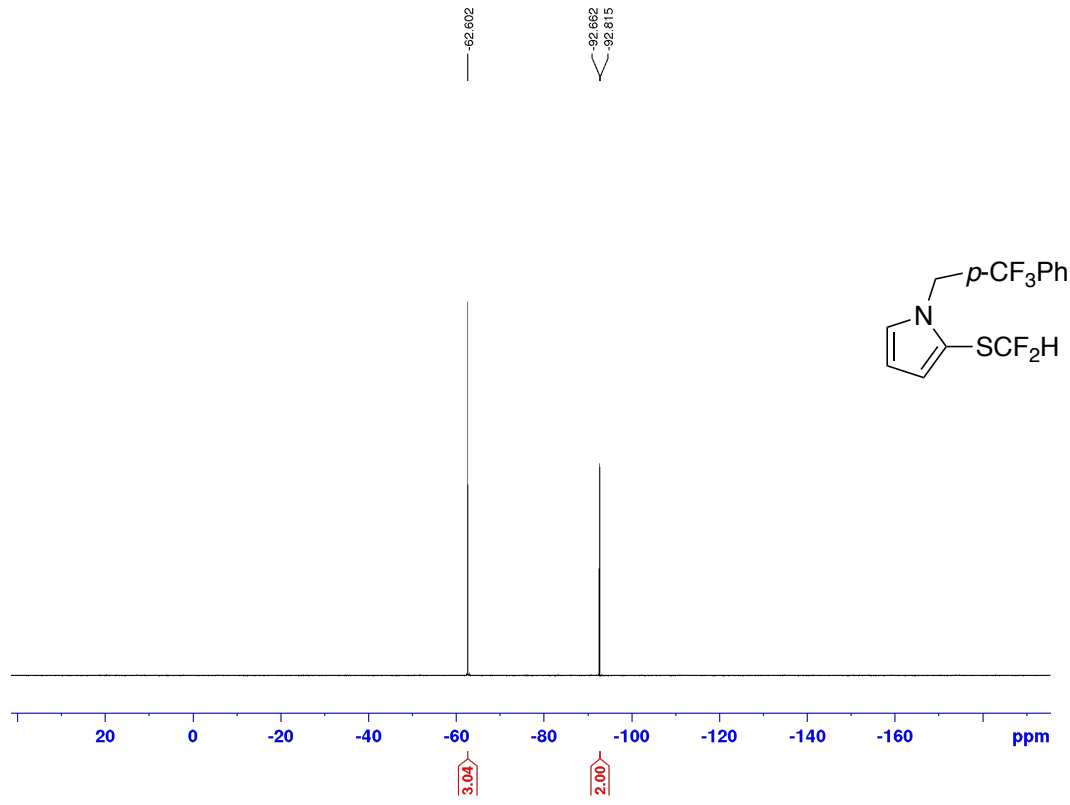
^{1}HNMR (500 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-(4-(trifluoromethyl)benzyl-1*H*-pyrrole (15b)



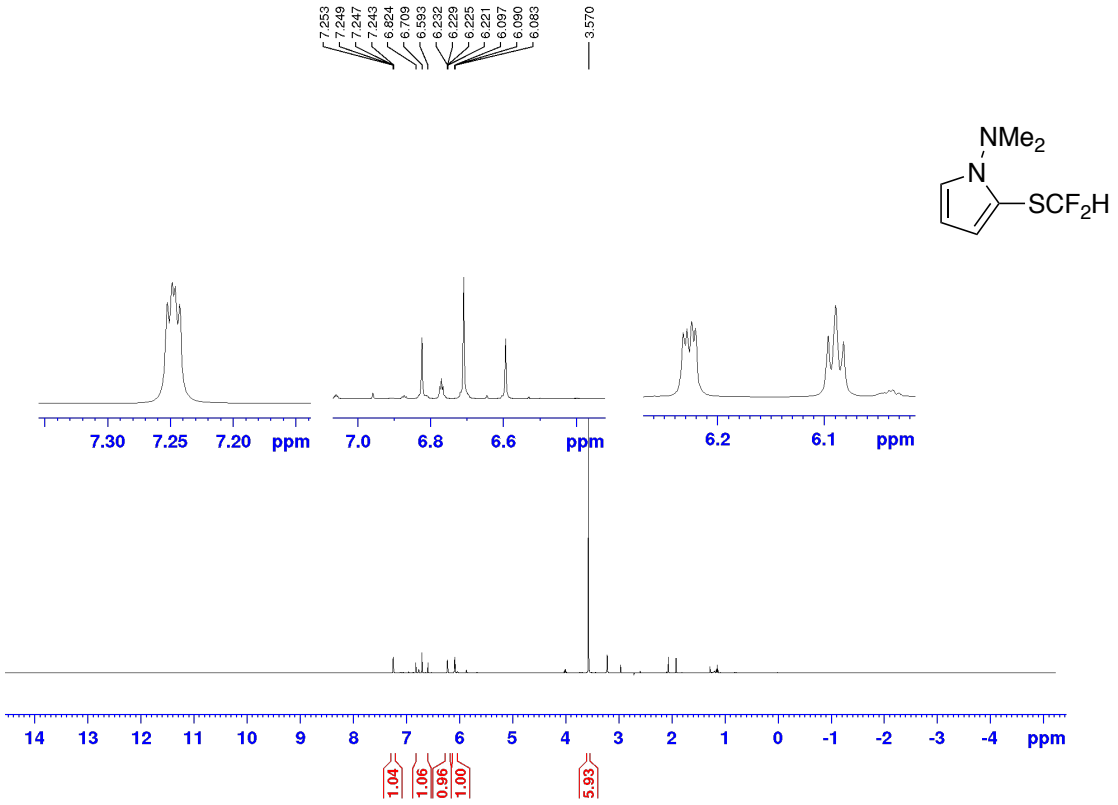
^{13}C NMR (125 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-(4-(trifluoromethyl)benzyl)-1*H*-pyrrole (15b)



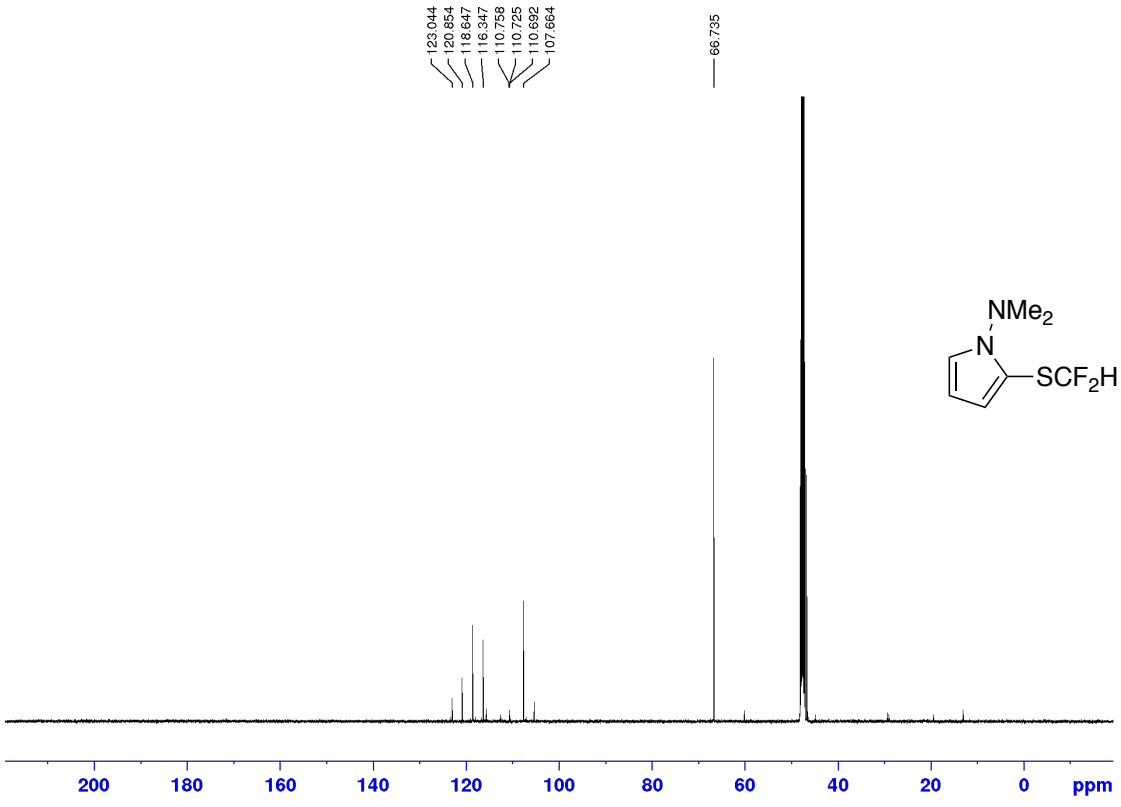
^{19}F NMR (470 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-(4-(trifluoromethyl)benzyl)-1*H*-pyrrole (15b)



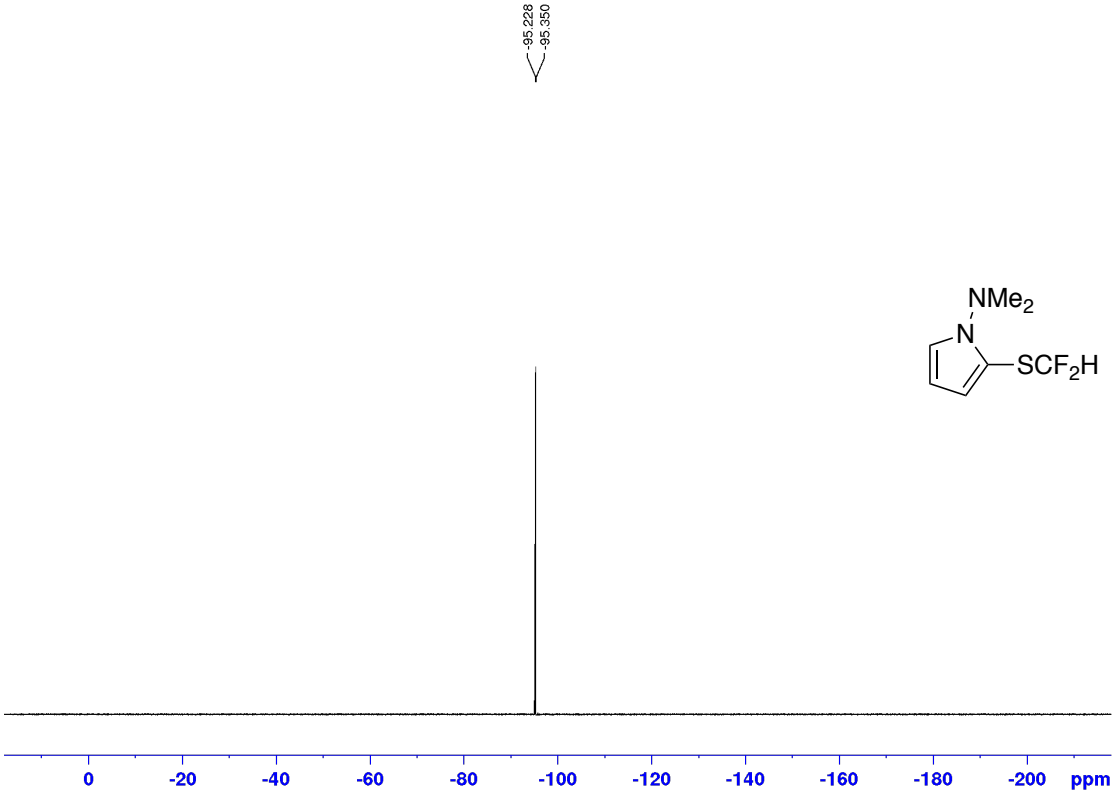
^{1}HNMR (500 MHz, CD_3OD) 2-((Difluoromethyl)thio)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (16b)



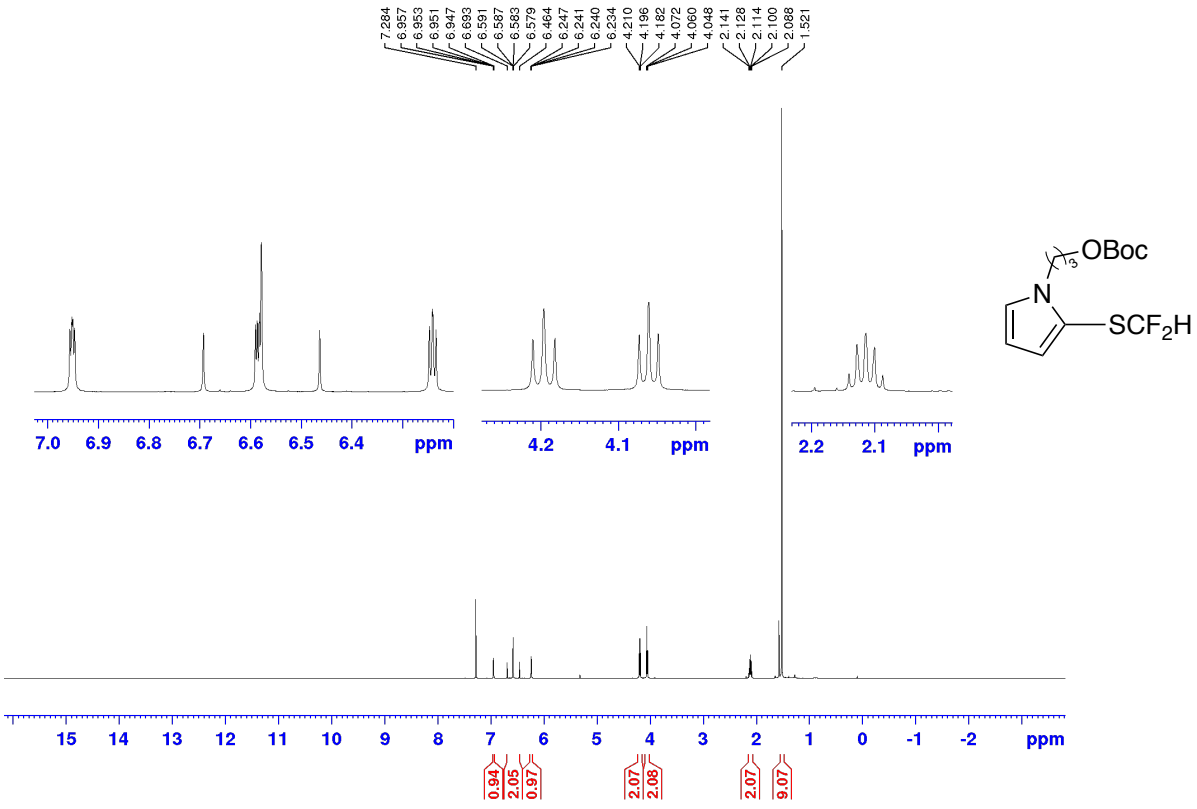
^{13}CNMR (125 MHz, CD_3OD) 2-((Difluoromethyl)thio)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (16b)



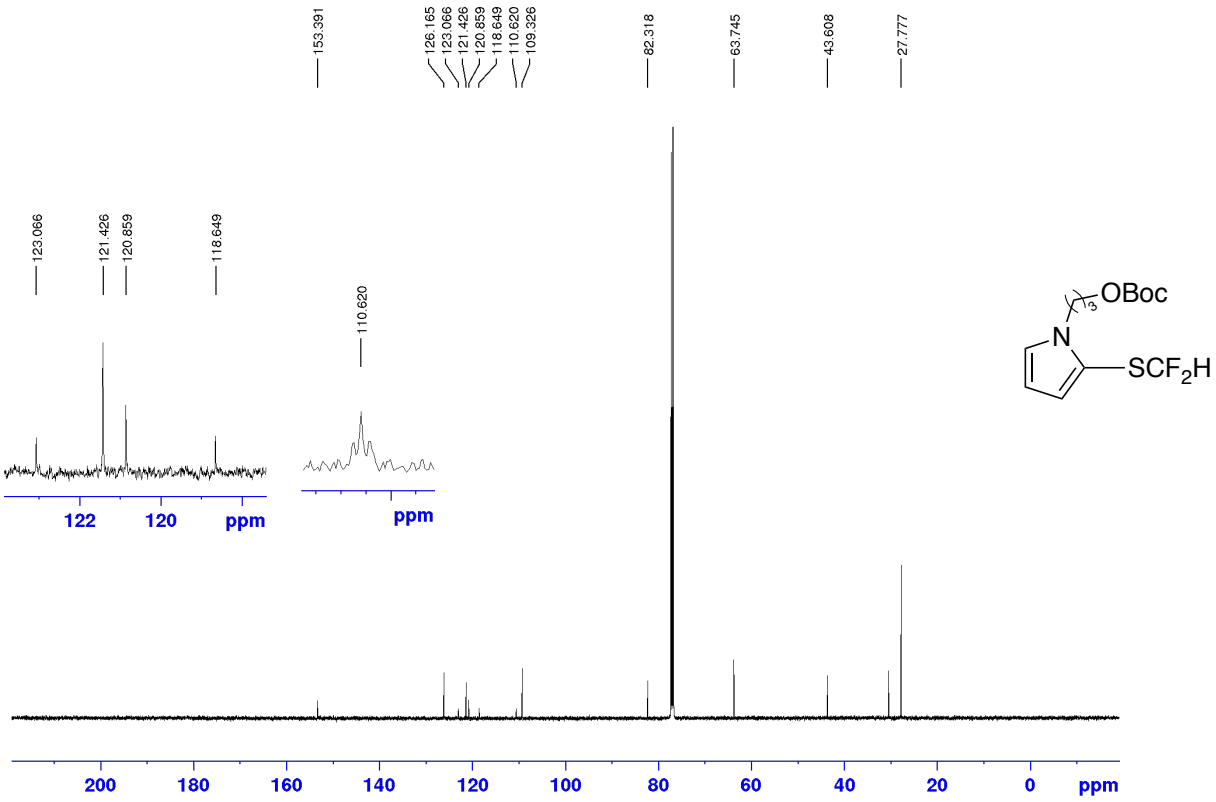
^{19}FNMR (470 MHz, CD_3OD) 2-((Difluoromethyl)thio)-*N*,*N*-dimethyl-1*H*-pyrrol-1-amine (16b)



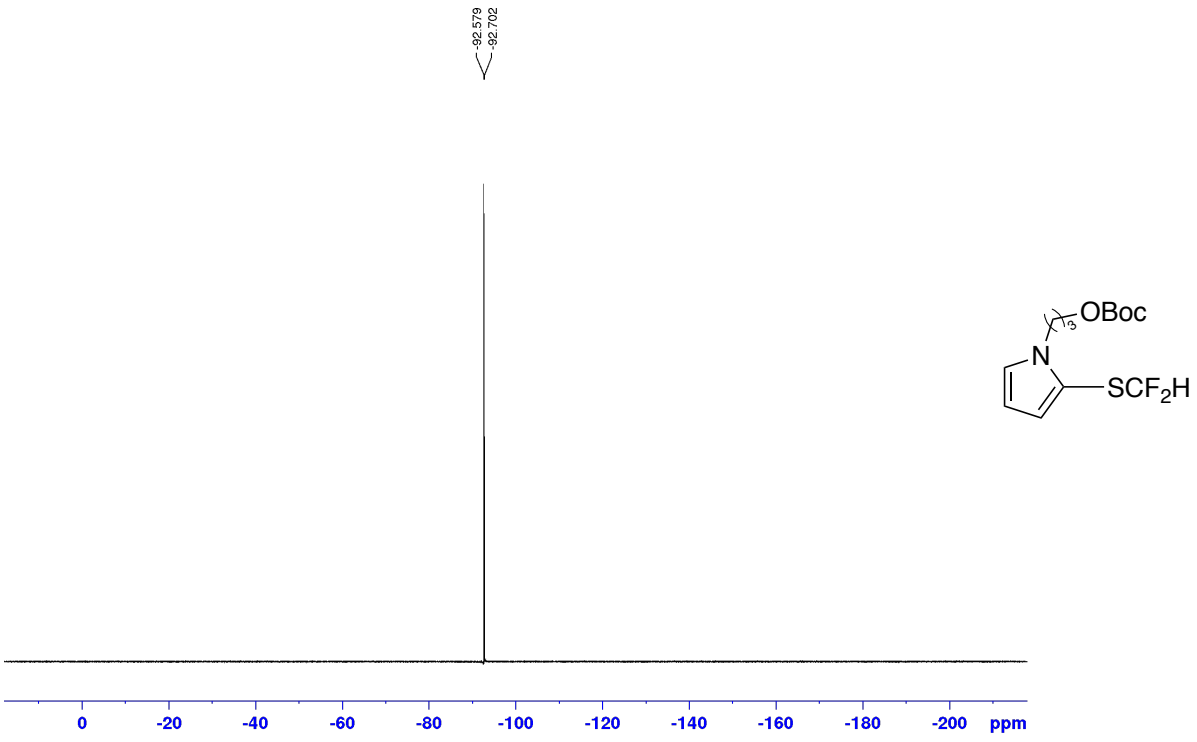
^{1}H NMR (500 MHz, $CDCl_3$) *Tert*-butyl ((2-((difluoromethyl)thio)-1*H*-pyrrol-1-yl)methyl) carbonate (17b)



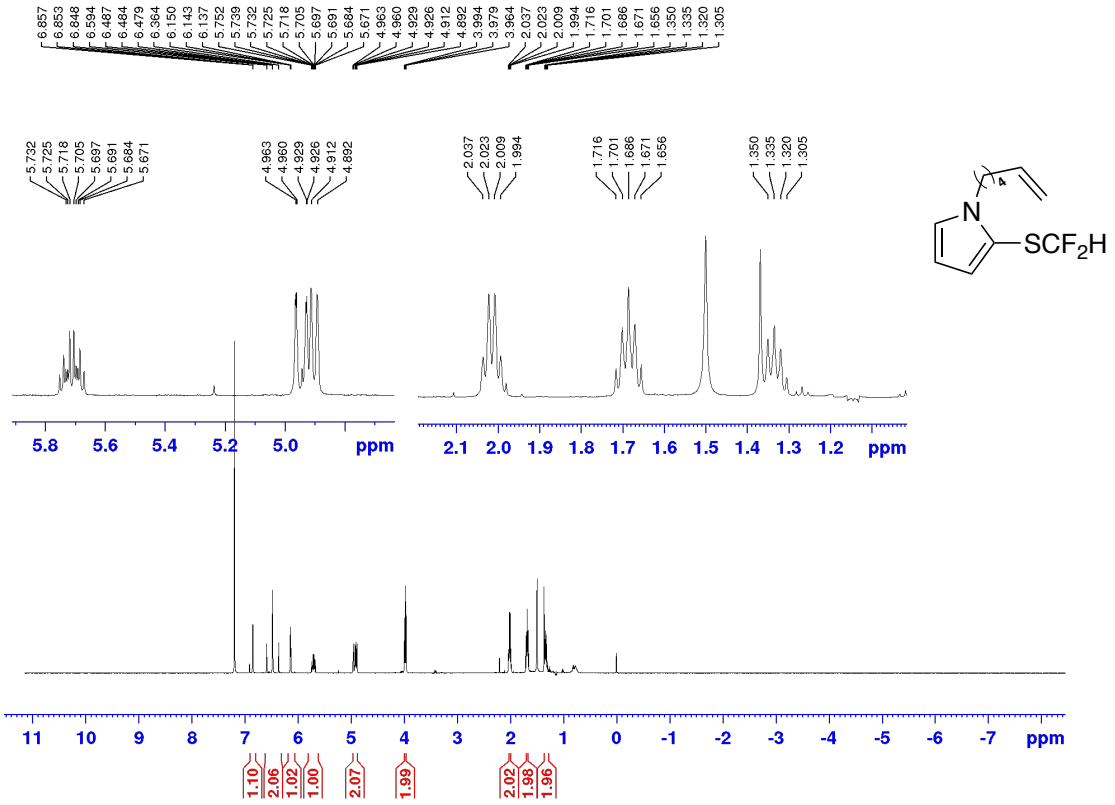
^{13}C NMR (125 MHz, $CDCl_3$) *Tert*-butyl ((2-((difluoromethyl)thio)-1*H*-pyrrol-1-yl)methyl) carbonate (17b)



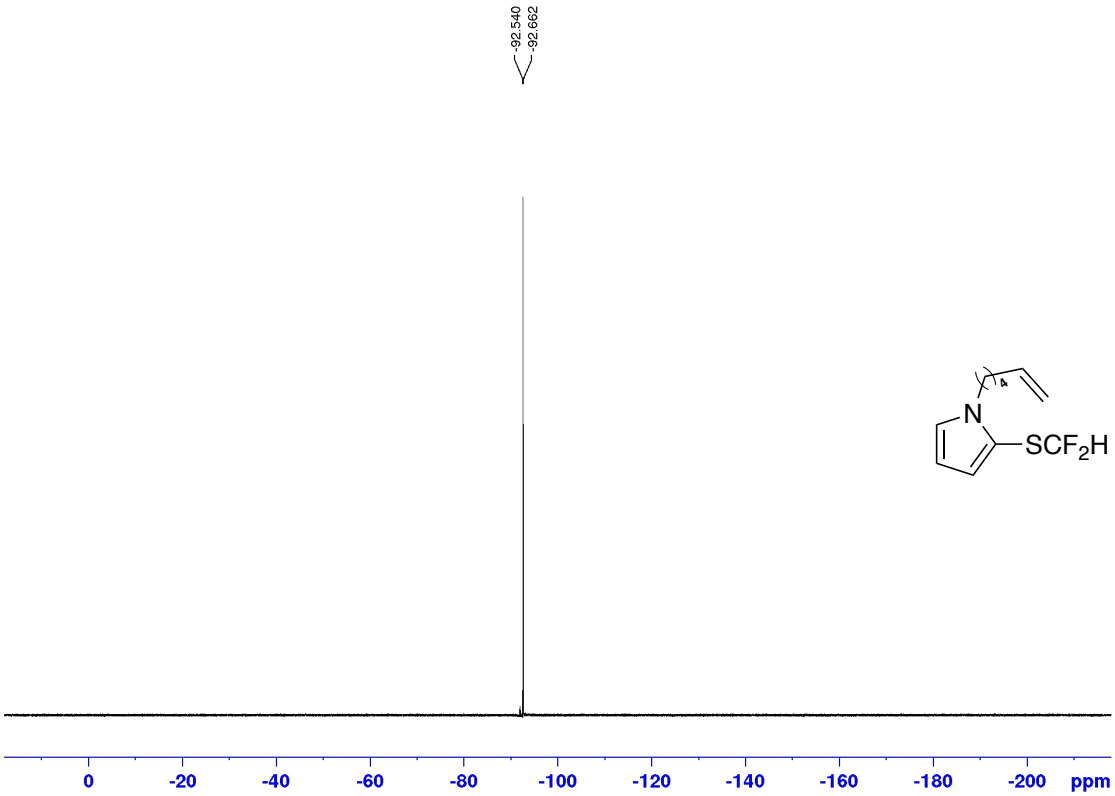
^{19}F NMR (470 MHz, CDCl3) *Tert*-butyl ((2-((difluoromethyl)thio)-1*H*-pyrrol-1-yl)methyl) carbonate (17b)



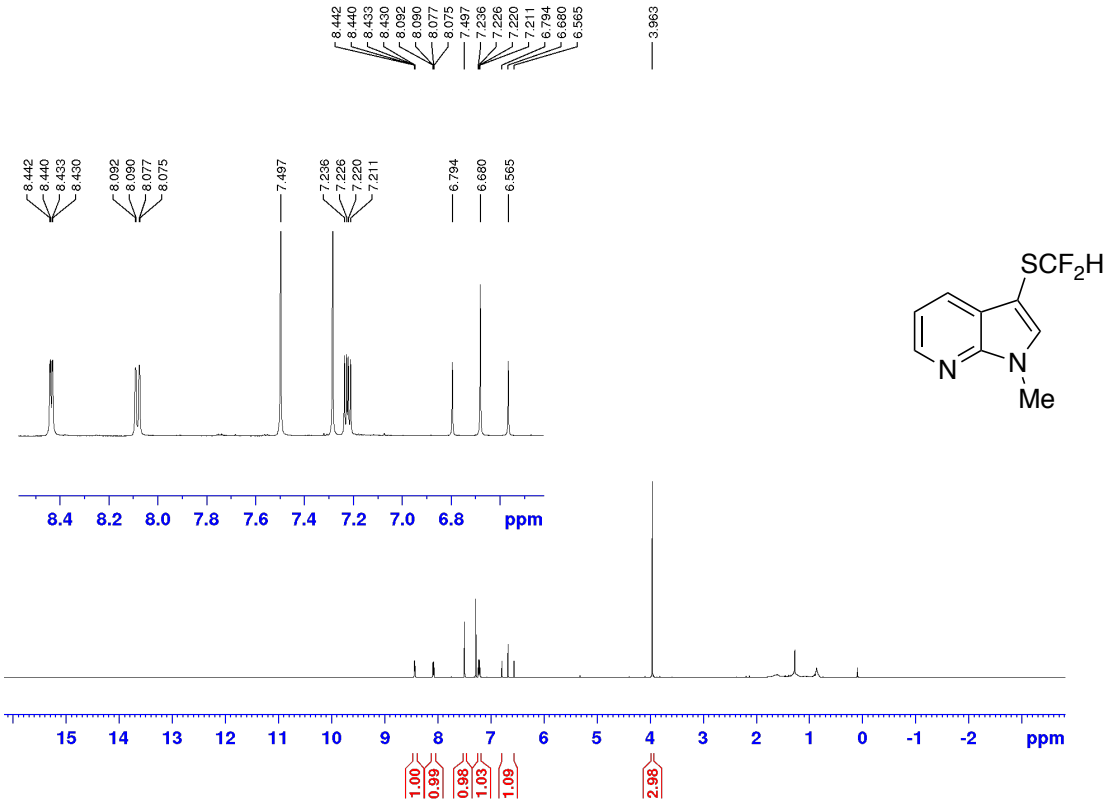
^{1}HNMR (500 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-1-(hex-5-en-1-yl)-1*H*-pyrrole (18b)



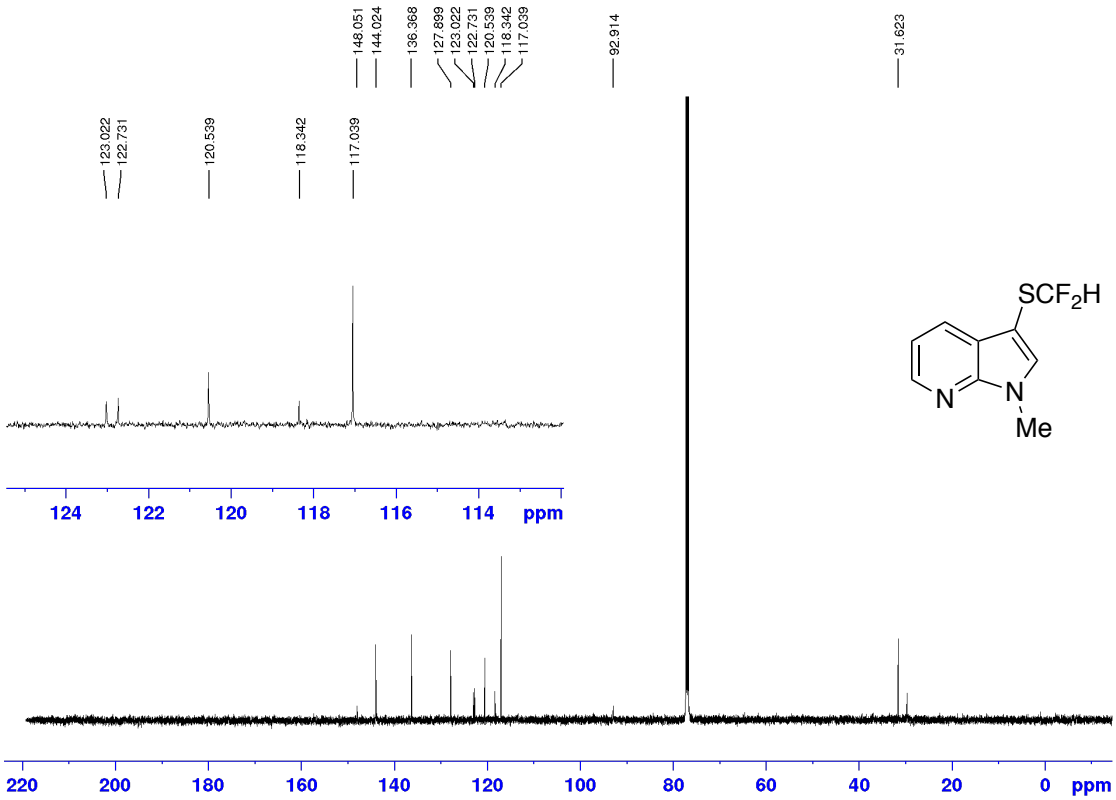
^{19}FNMR (470 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-1-(hex-5-en-1-yl)-1*H*-pyrrole (18b)



^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (19b)

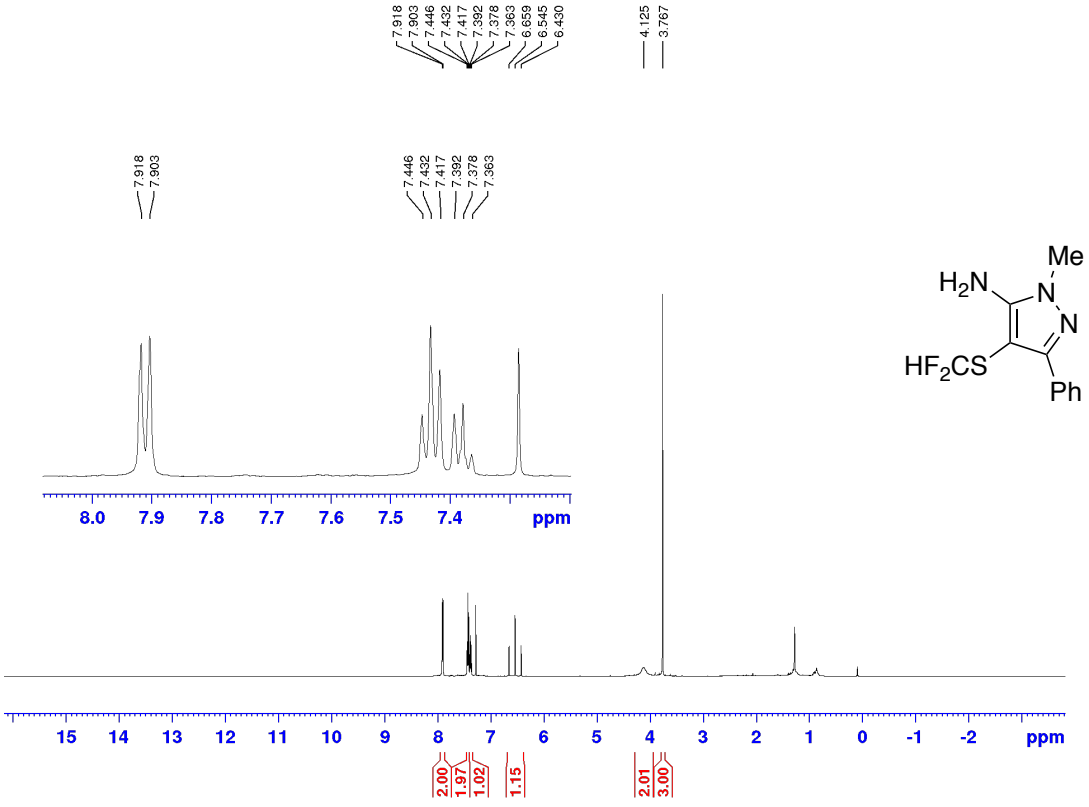


^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (19b)

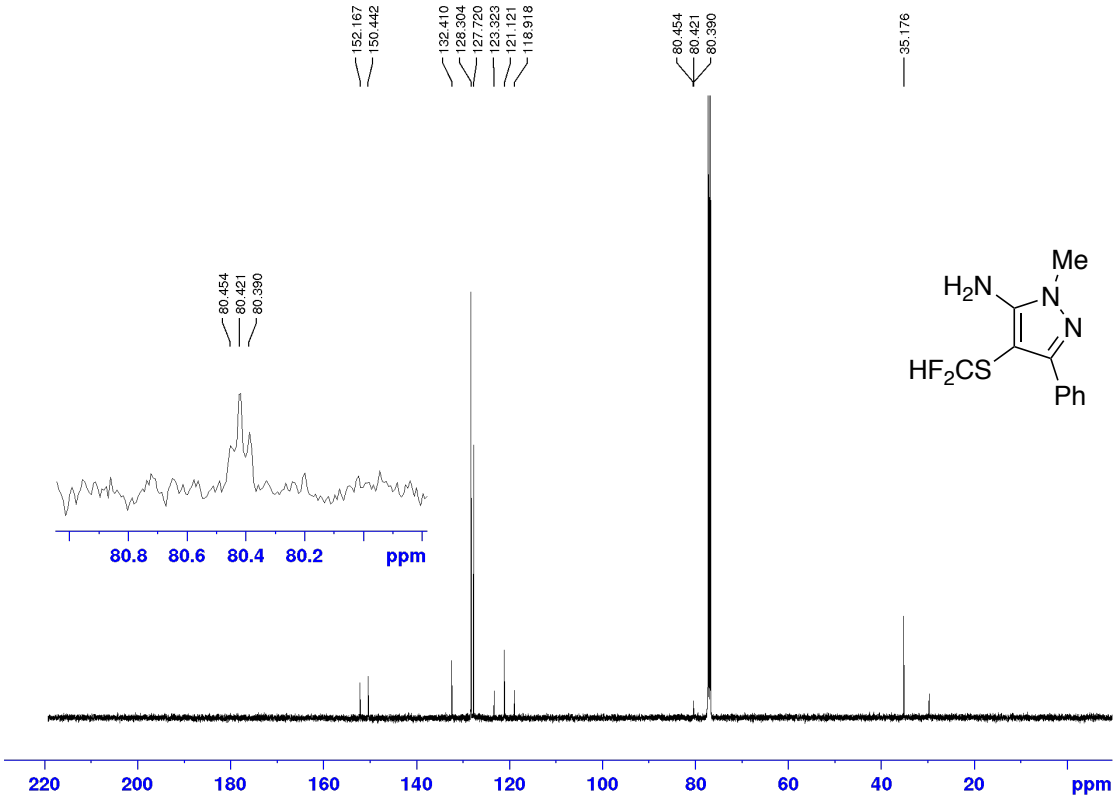


^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (19b)

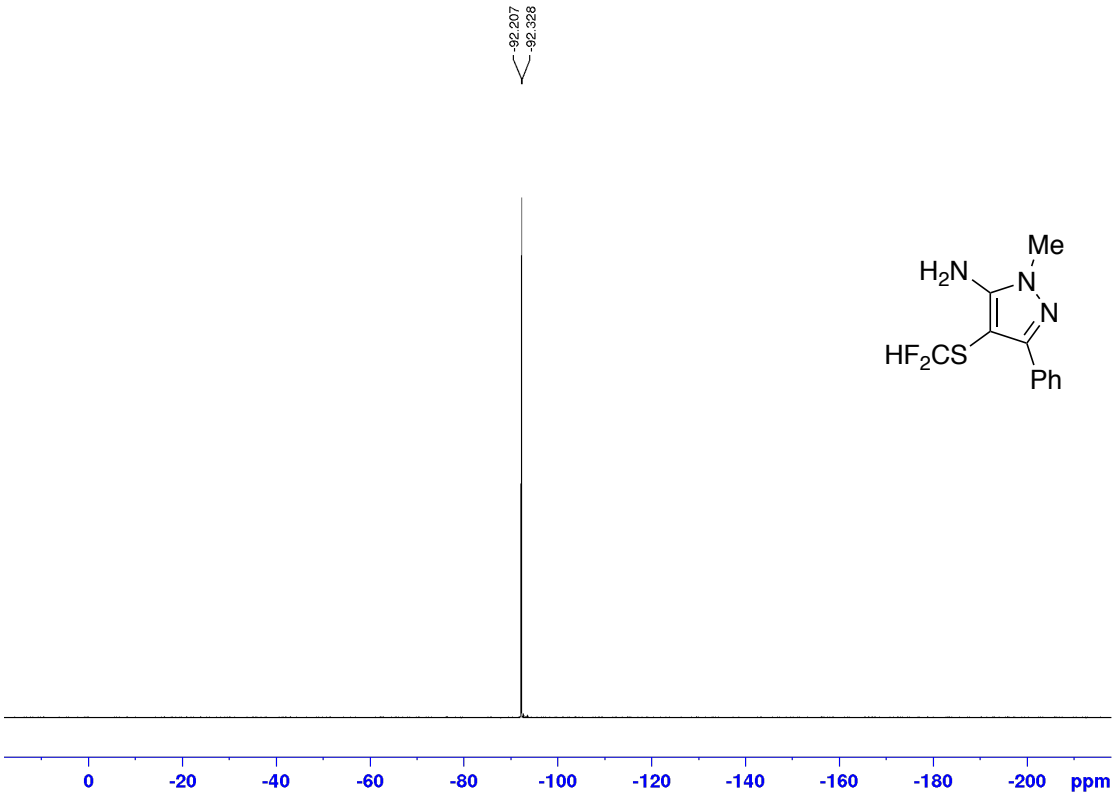
^{1}HNMR (500 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-1-methyl-3-phenyl-1*H*-pyrazol-5-amine (20b)



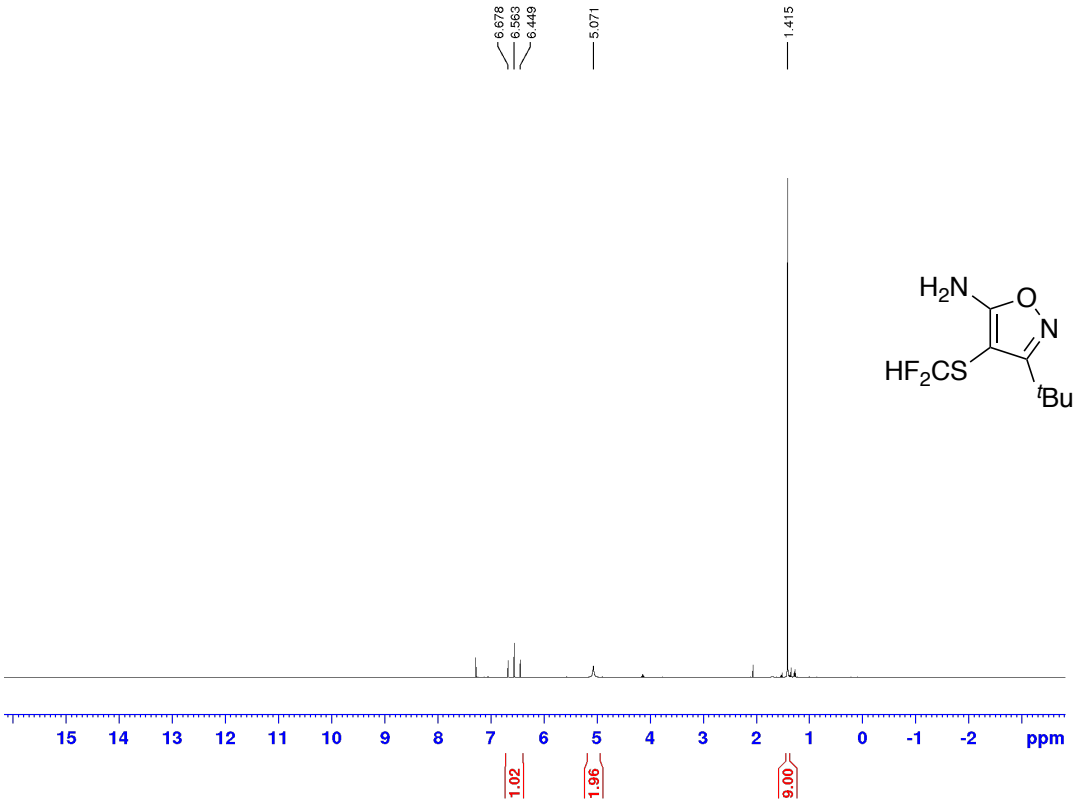
^{13}C NMR (125 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-1-methyl-3-phenyl-1*H*-pyrazol-5-amine (20b)



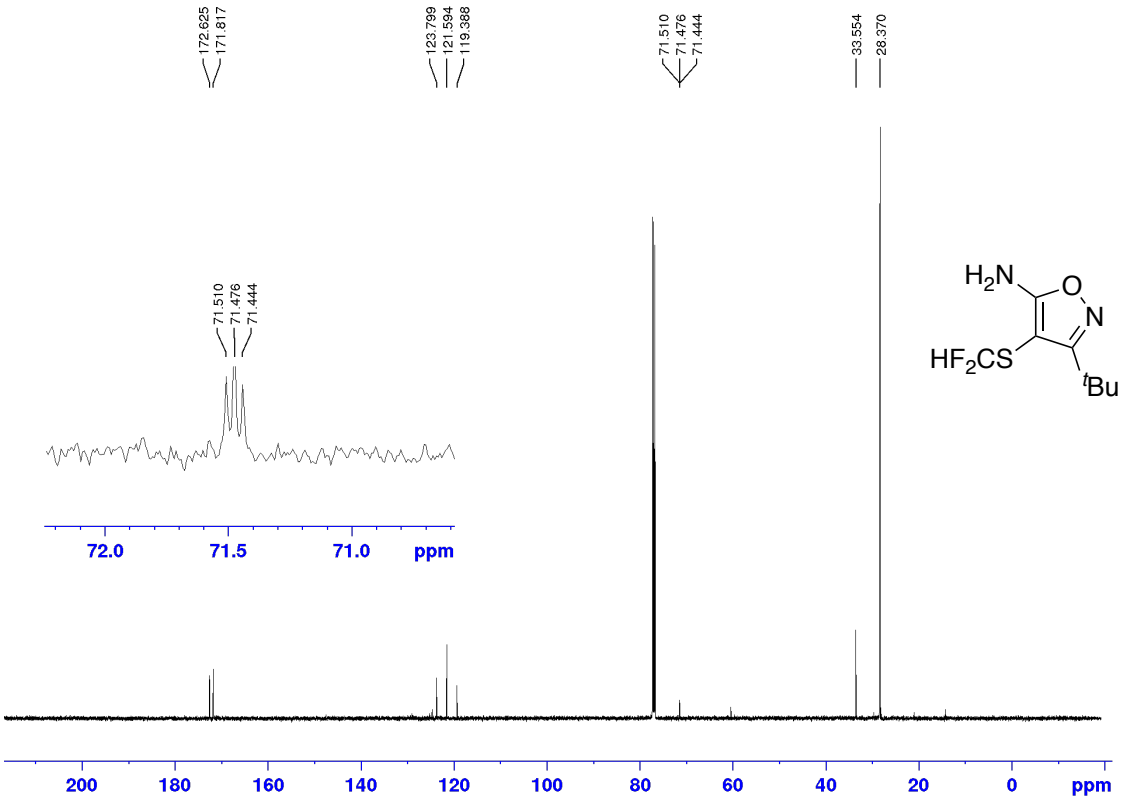
^{19}F NMR (470 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-1-methyl-3-phenyl-1*H*-pyrazol-5-amine (20b)



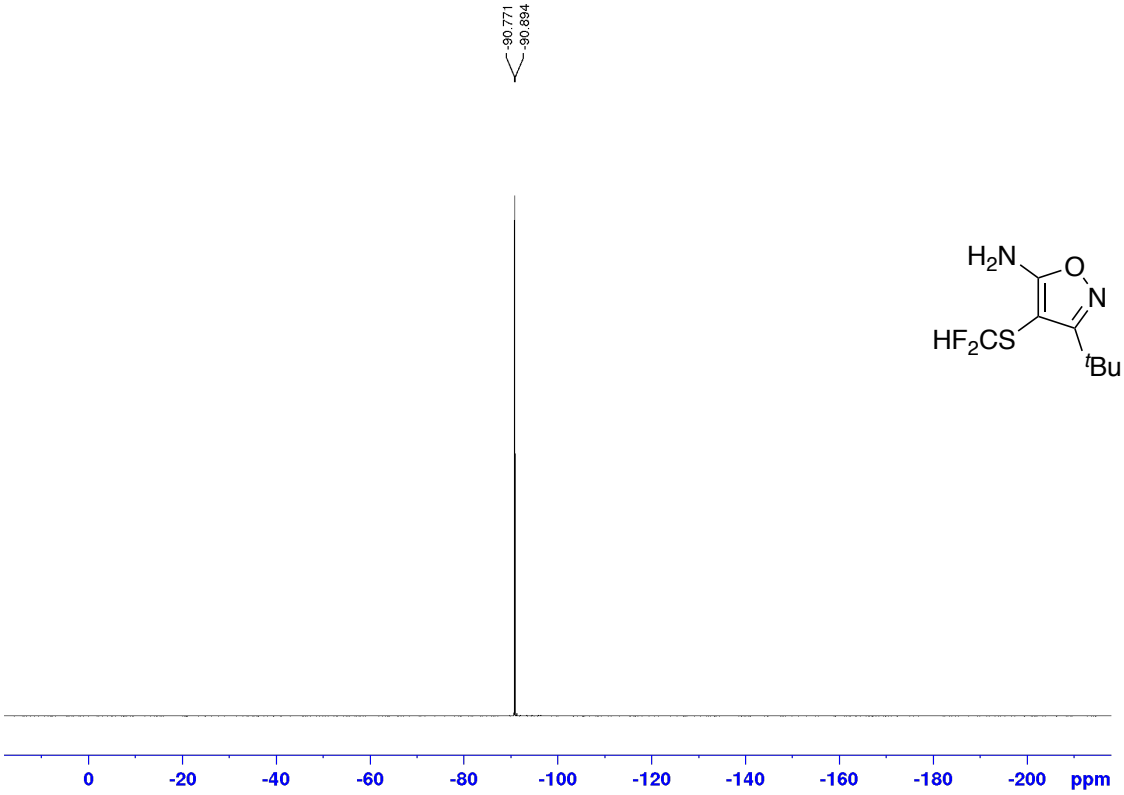
^{1}HNMR (500 MHz, $CDCl_3$) 3-(*Tert*-butyl)-4-((difluoromethyl)thio)isoxazol-5-amine (21b)



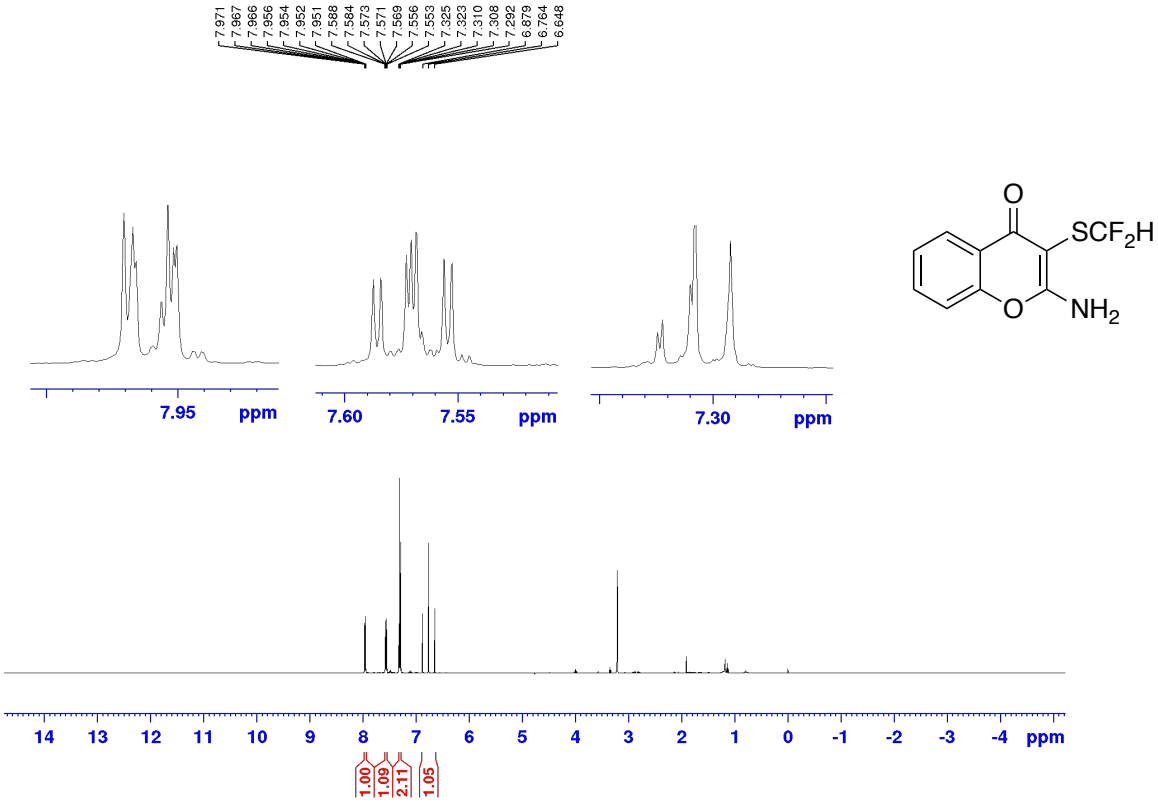
^{13}C NMR (125 MHz, $CDCl_3$) 3-(*Tert*-butyl)-4-((difluoromethyl)thio)isoxazol-5-amine (21b)



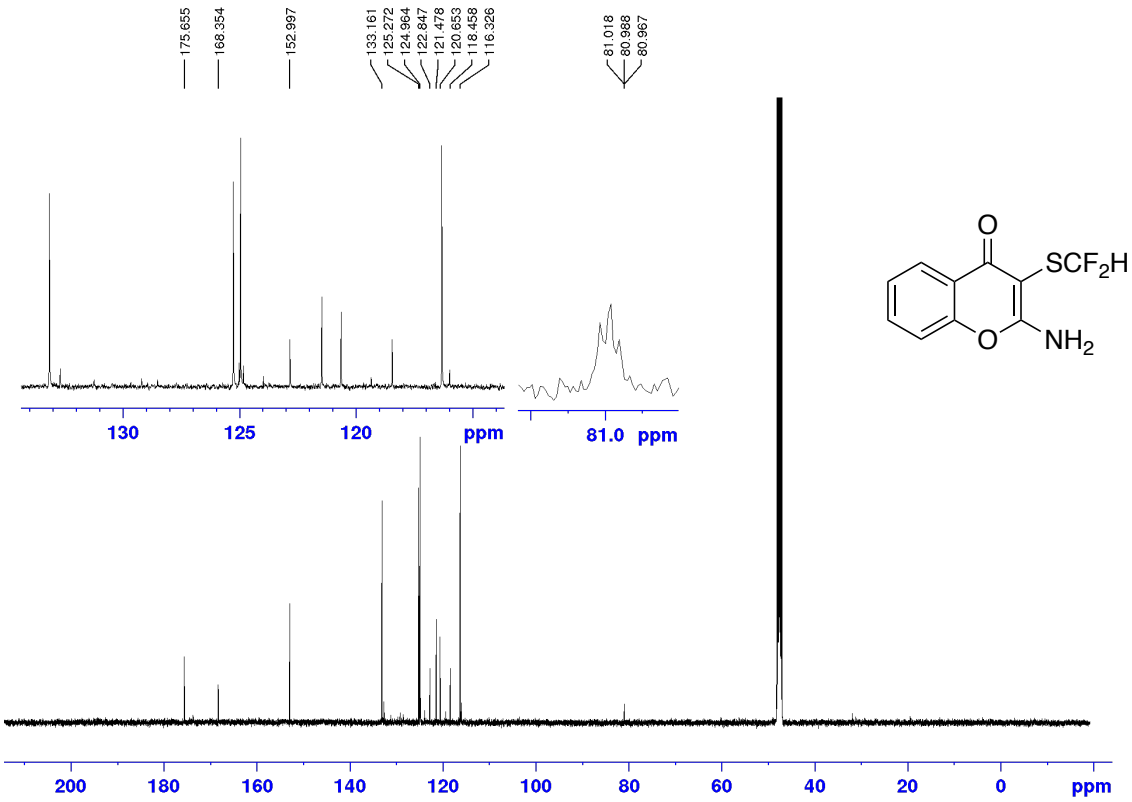
^{19}F NMR (470 MHz, $CDCl_3$) 3-(*Tert*-butyl)-4-((difluoromethyl)thio)isoxazol-5-amine (21b)



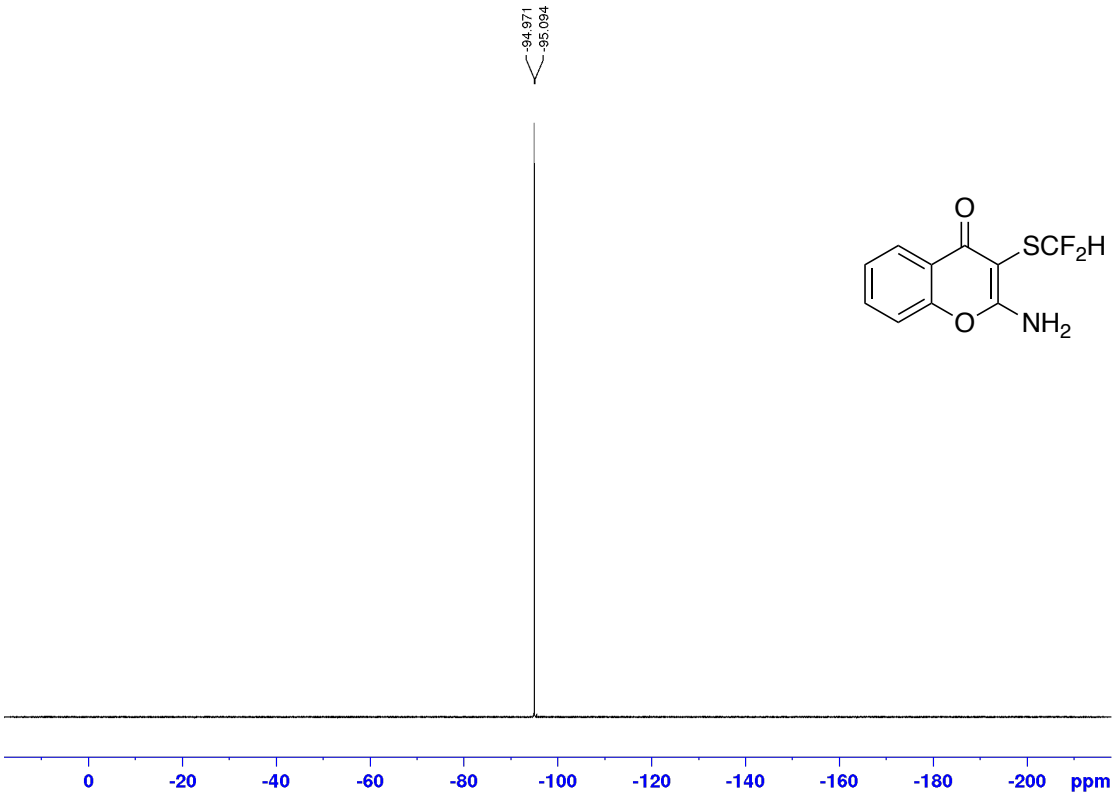
^{1}HNMR (500 MHz, CD_3OD) 2-Amino-3-((difluoromethyl)thio)-4*H*-chromen-4-one (22b)



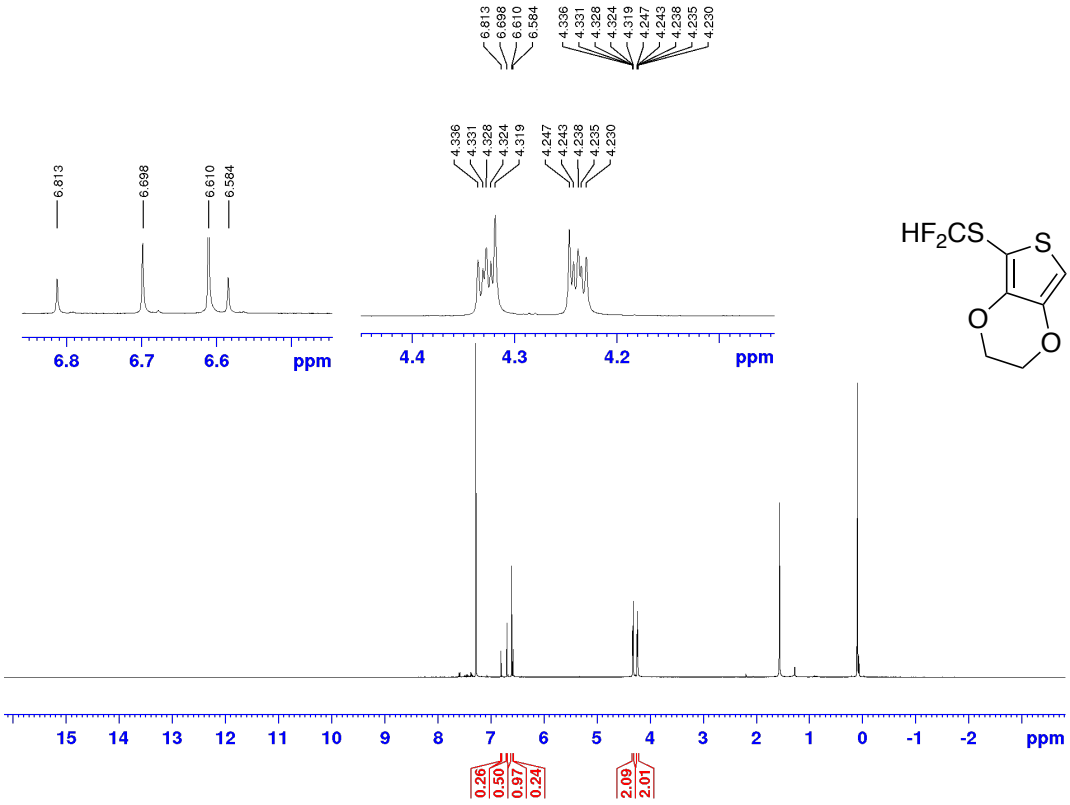
^{13}CNMR (125 MHz, CD_3OD) 2-Amino-3-((difluoromethyl)thio)-4*H*-chromen-4-one (22b)



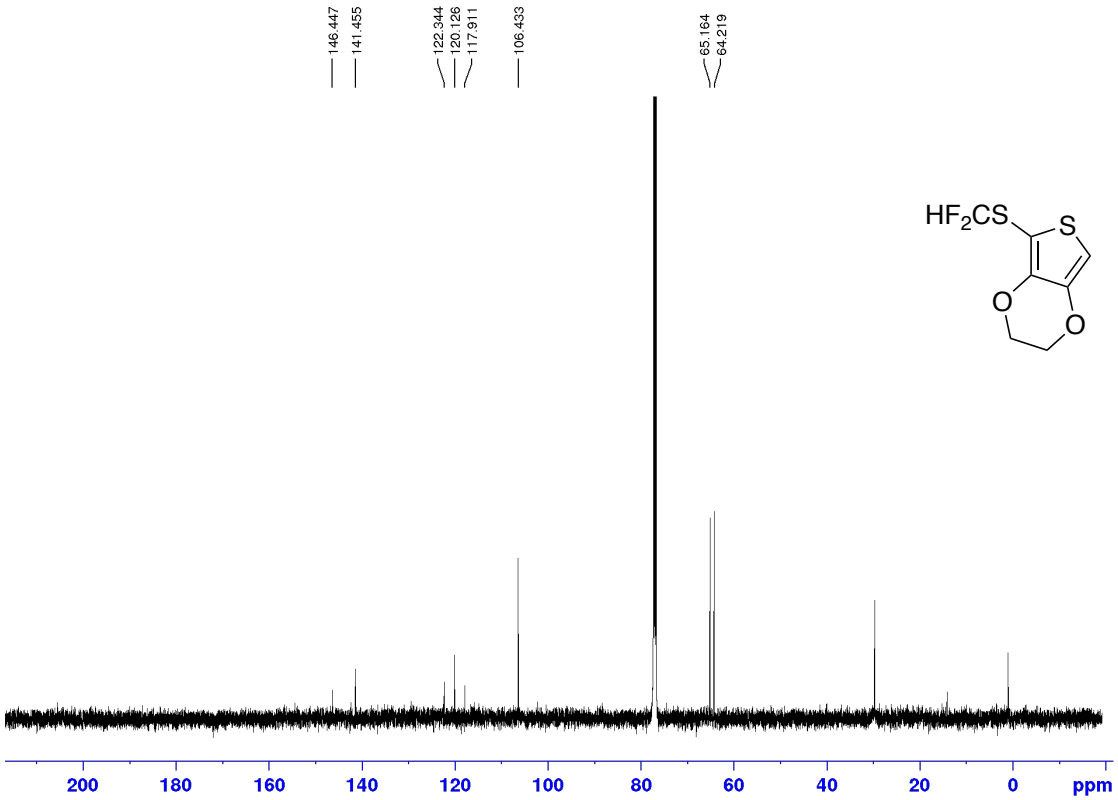
^{19}FNMR (470 MHz, CD_3OD) 2-Amino-3-((difluoromethyl)thio)-4*H*-chromen-4-one (22b)



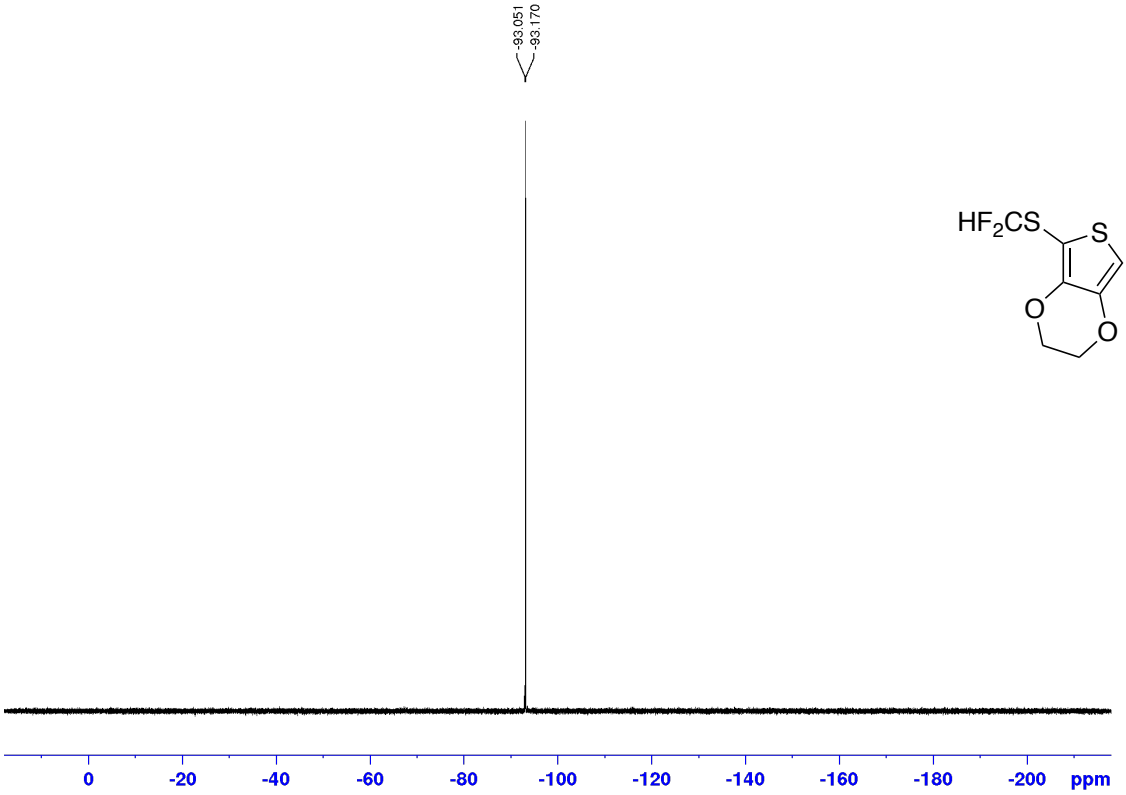
^{1}HNMR (500 MHz, $CDCl_3$) 5-((Difluoromethyl)thio)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (23b)



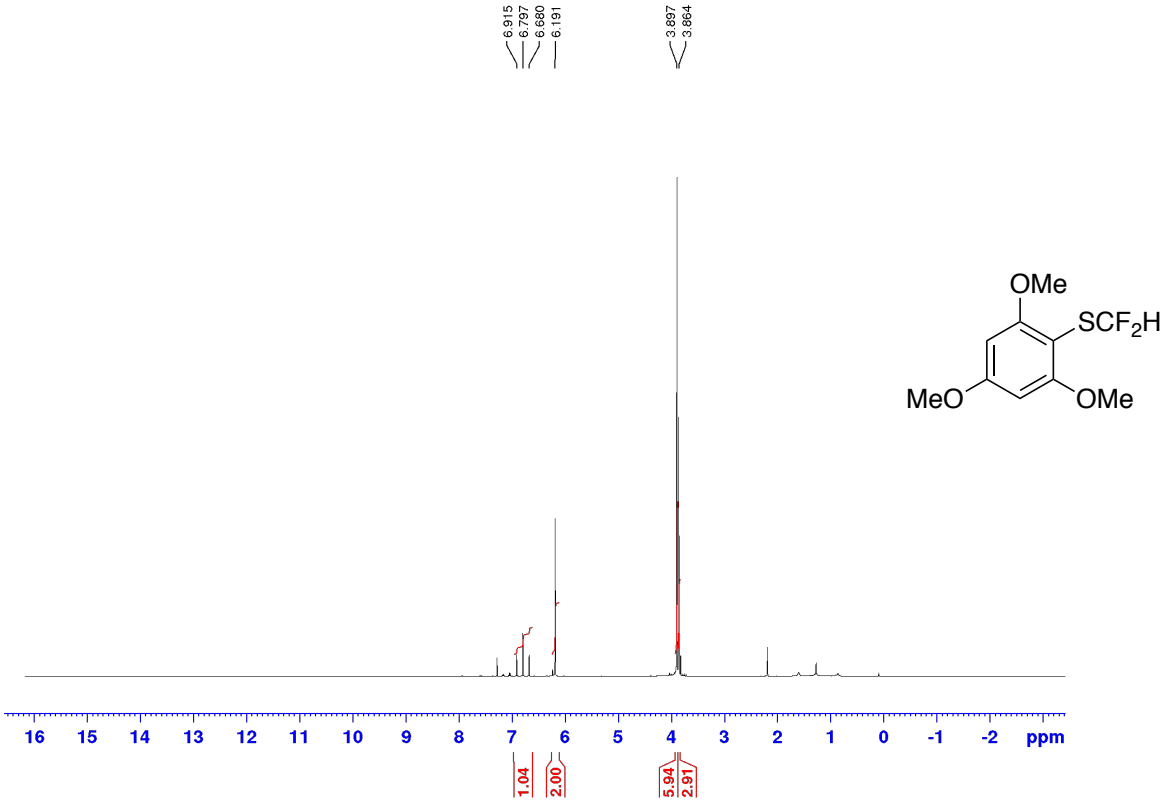
^{13}C NMR (125 MHz, $CDCl_3$) 5-((Difluoromethyl)thio)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (23b)



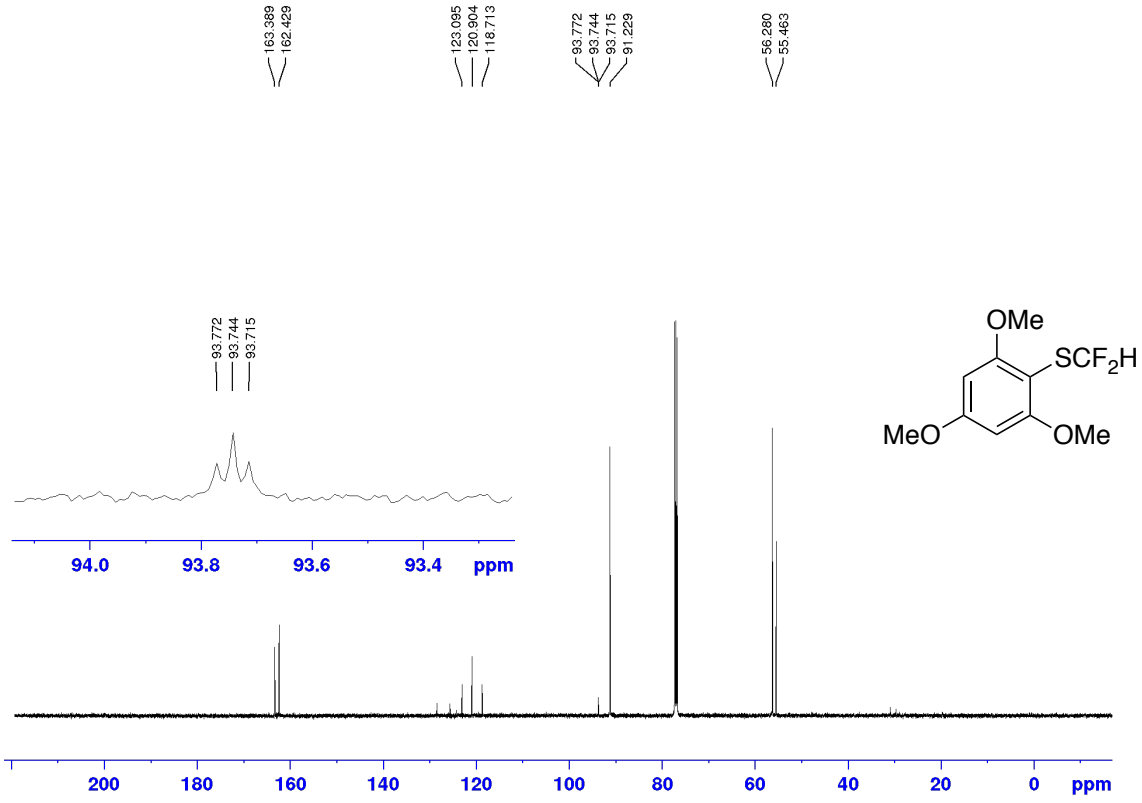
^{19}F NMR (470 MHz, $CDCl_3$) 5-((Difluoromethyl)thio)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (23b)



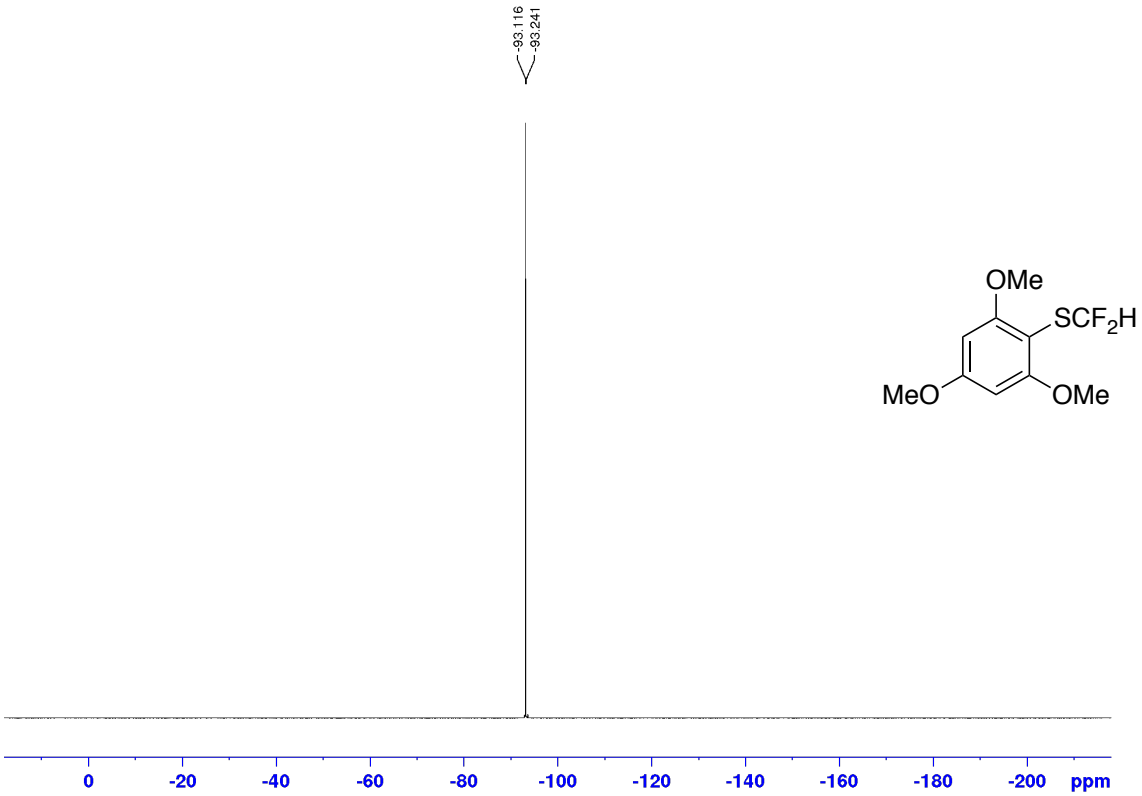
^{1}H NMR (500 MHz, $CDCl_3$) (Difluoromethyl)(2,4,6-trimethoxyphenyl)sulfane (24b)



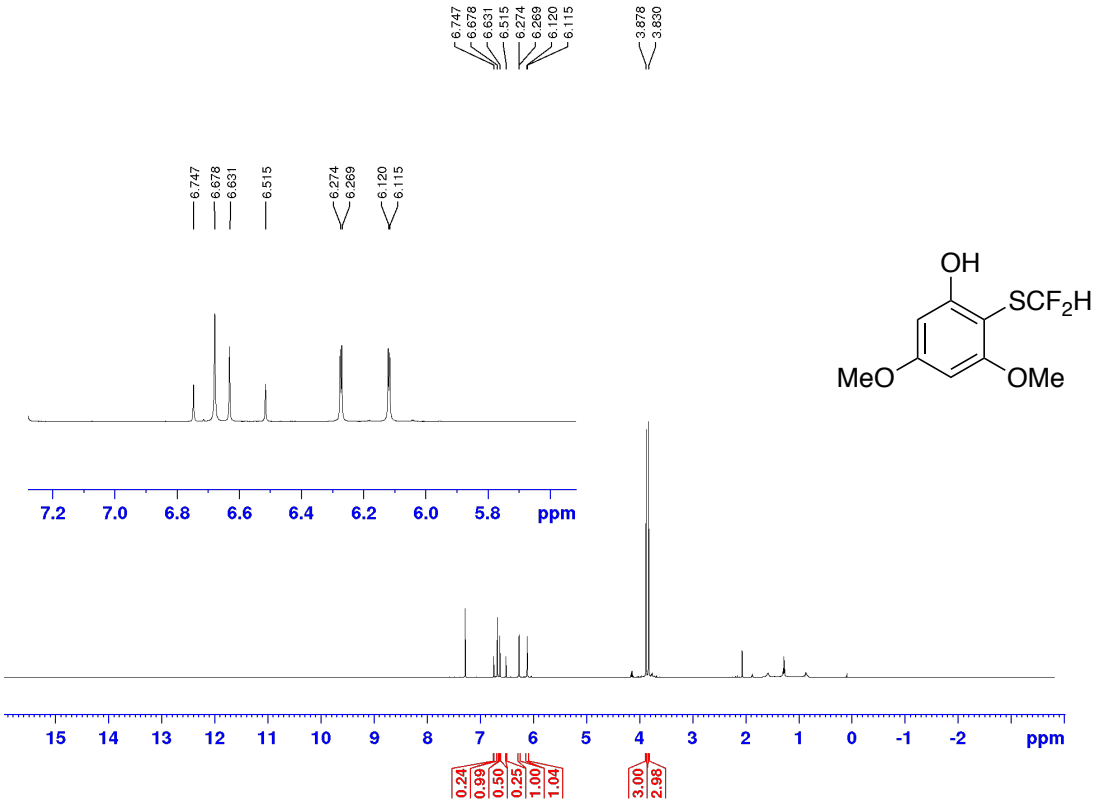
^{13}C NMR (125 MHz, $CDCl_3$) (Difluoromethyl)(2,4,6-trimethoxyphenyl)sulfane (24b)



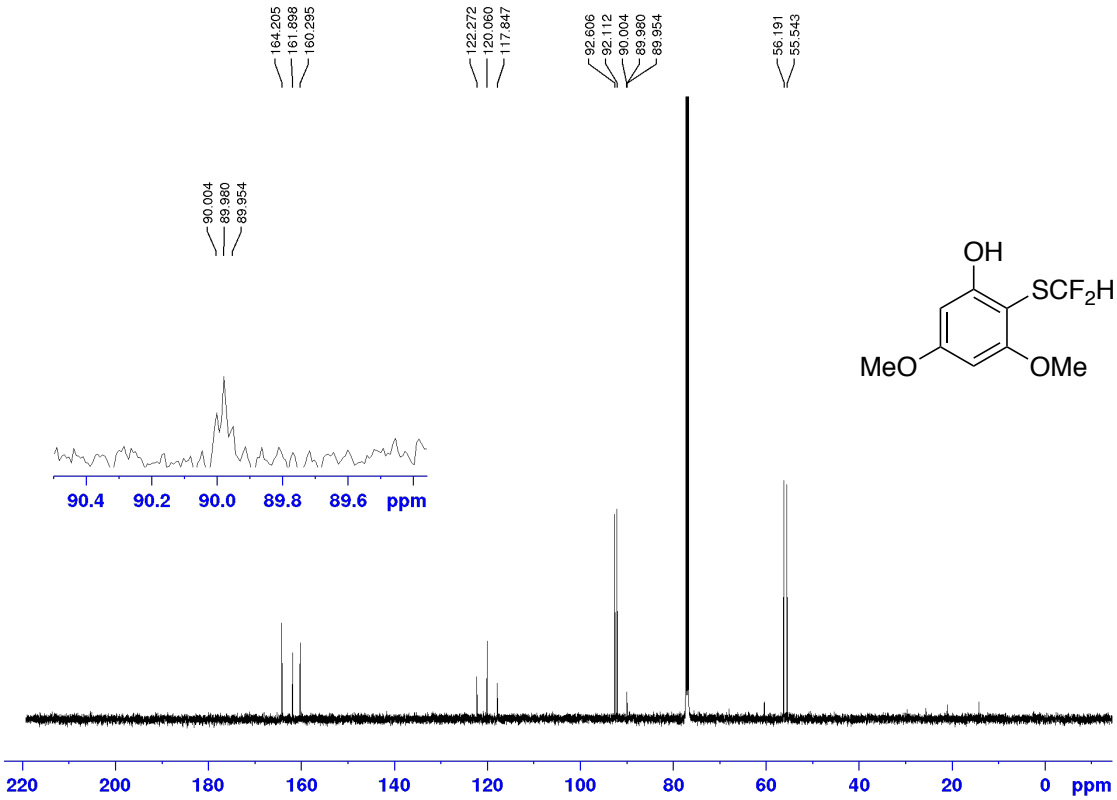
^{19}F NMR (470 MHz, $CDCl_3$) (Difluoromethyl)(2,4,6-trimethoxyphenyl)sulfane (24b)



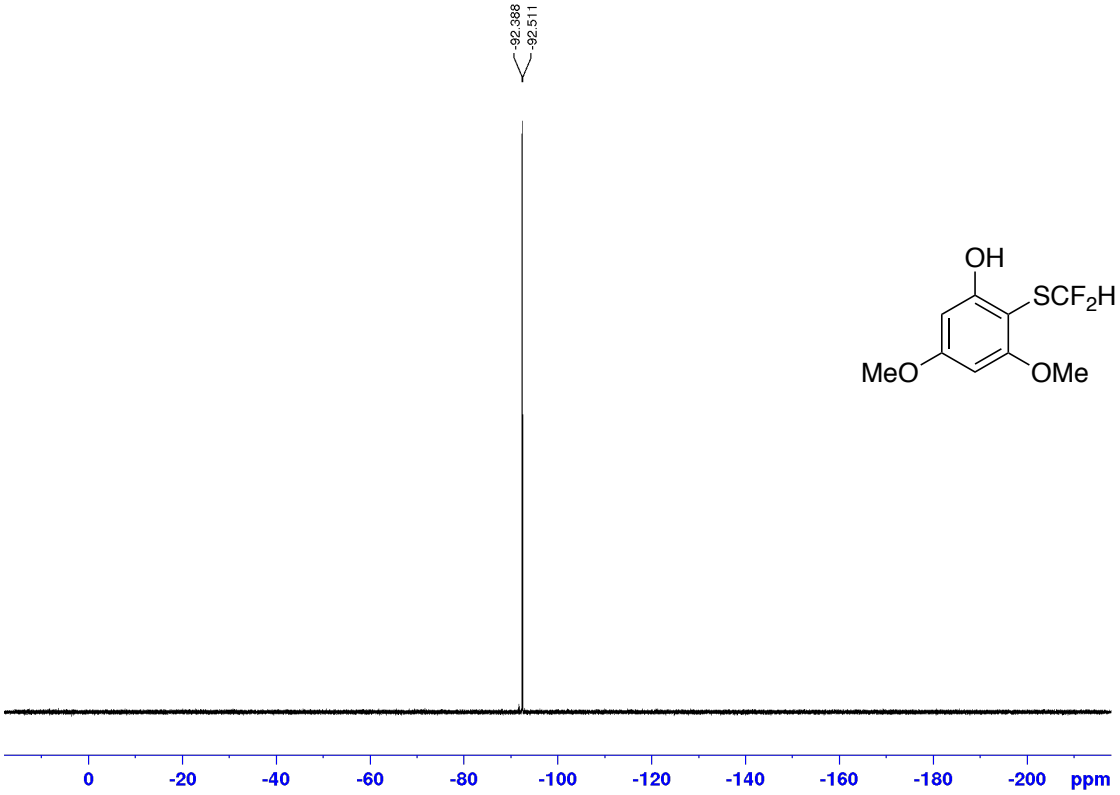
^{1}HNMR (500 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-3,5-dimethoxyphenol (25b)



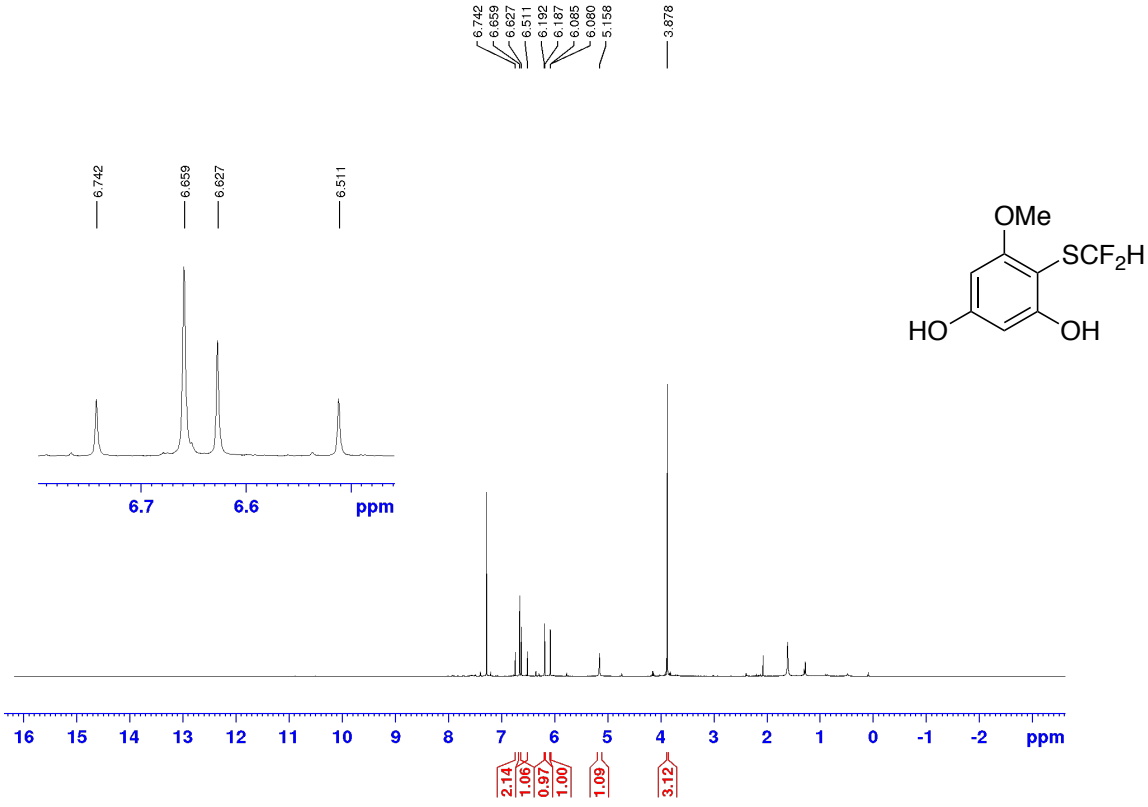
^{13}C NMR (125 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-3,5-dimethoxyphenol (25b)



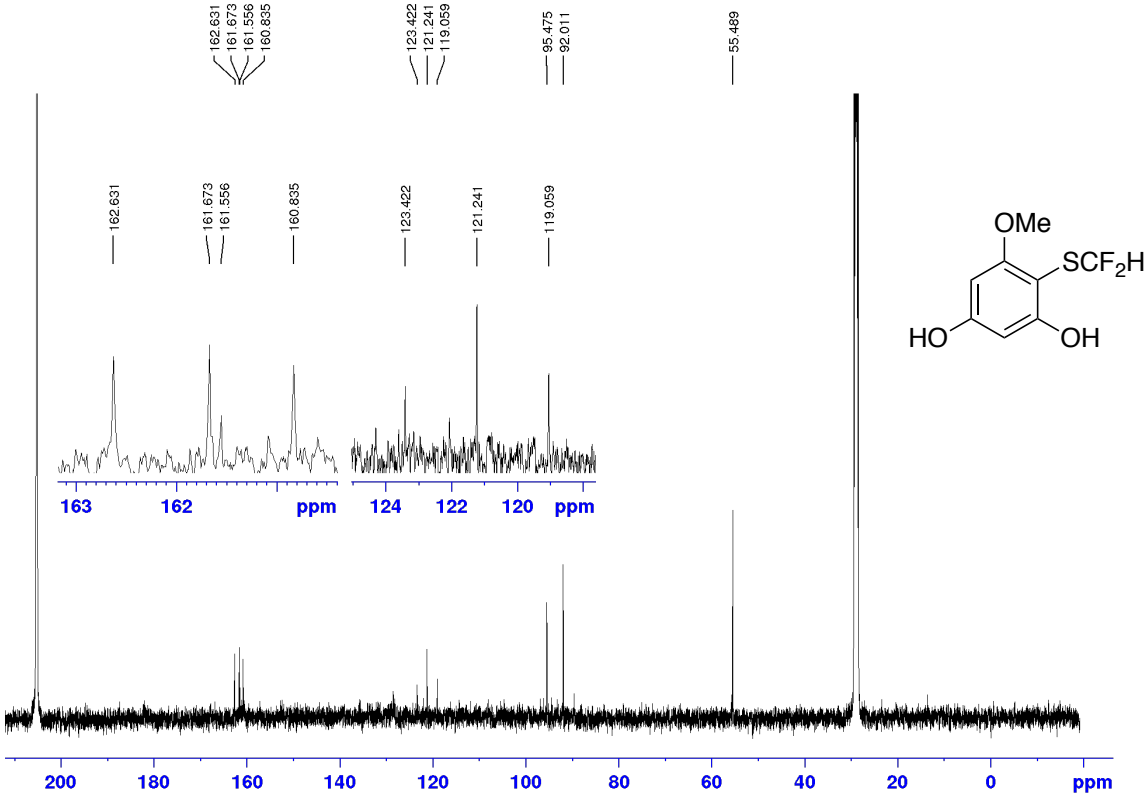
^{19}F NMR (470 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-3,5-dimethoxyphenol (25b)



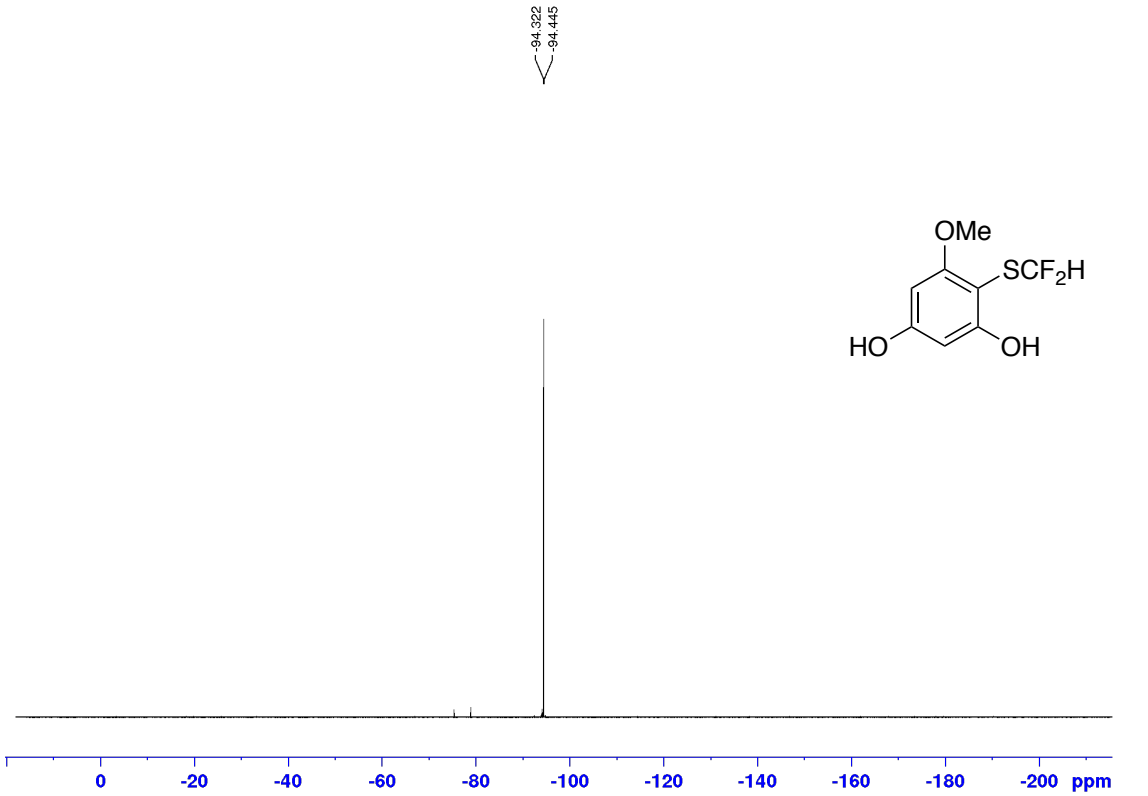
^{1}HNMR (500 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-5-methoxybenzene-1,3-diol (26b)



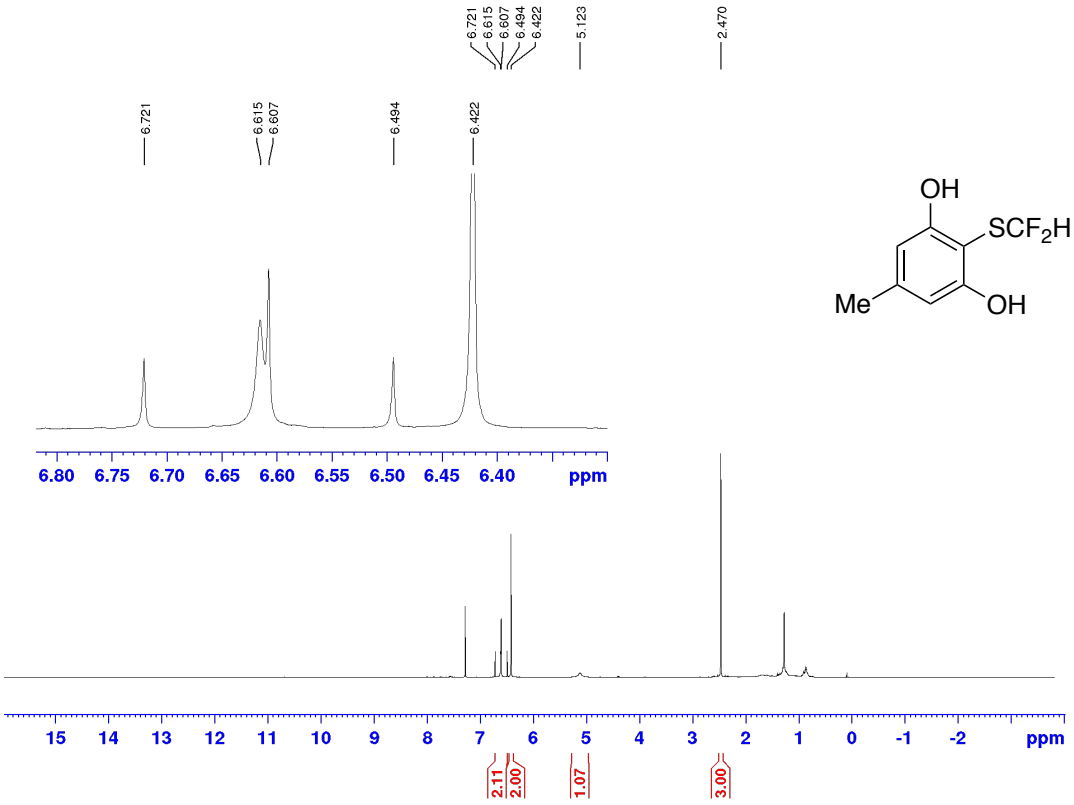
^{13}C NMR (125 MHz, Acetone-d_6) 4-((Difluoromethyl)thio)-5-methoxybenzene-1,3-diol (26b)



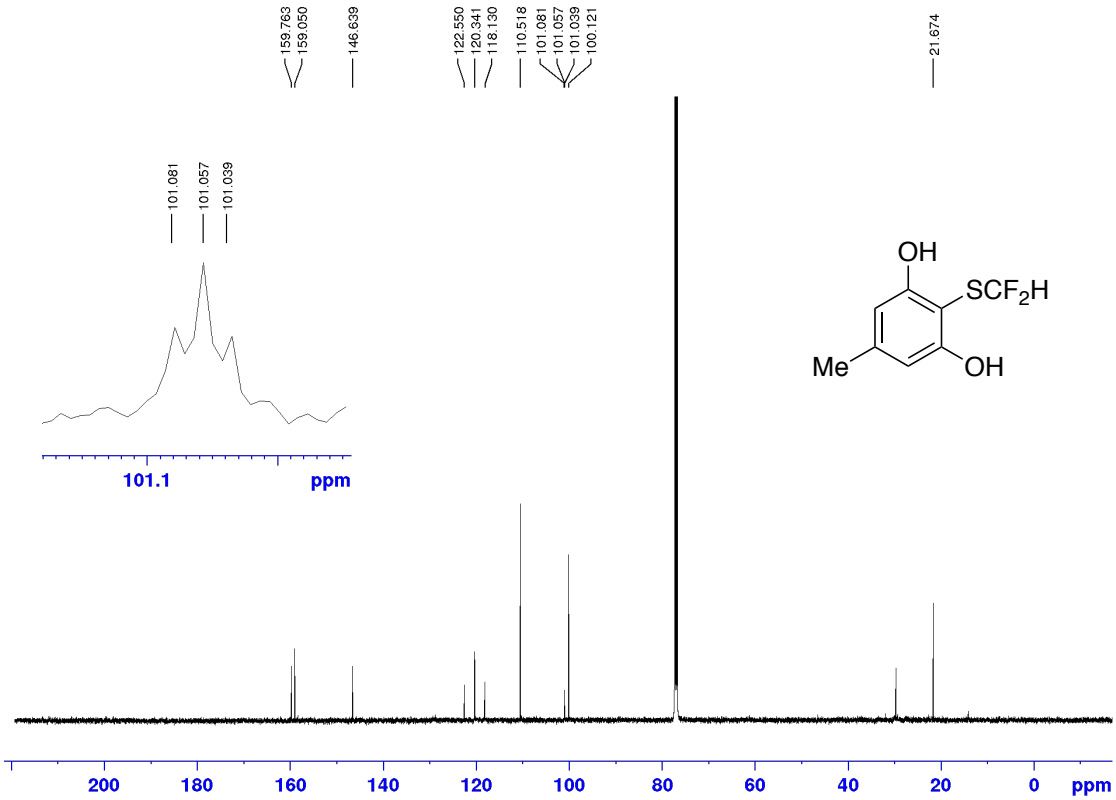
^{19}F NMR (470 MHz, Acetone-d_6) 4-((Difluoromethyl)thio)-5-methoxybenzene-1,3-diol (26b)



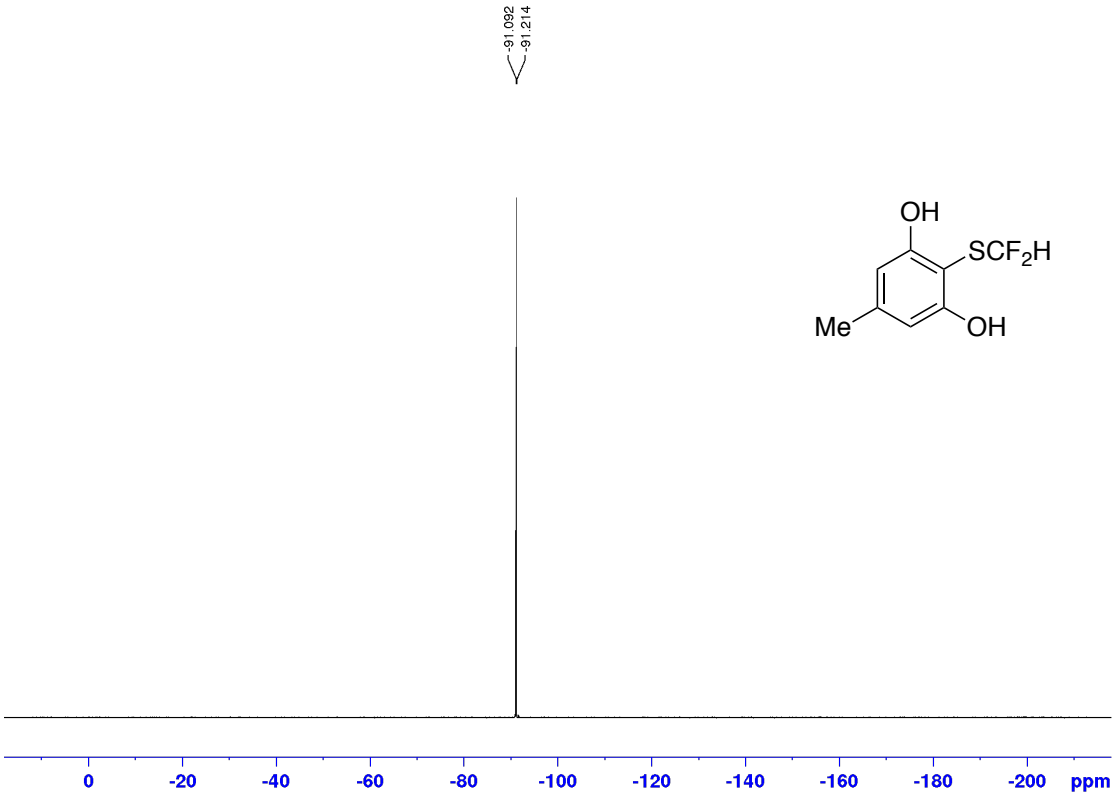
^{1}HNMR (500 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-5-methylbenzene-1,3-diol (27b)



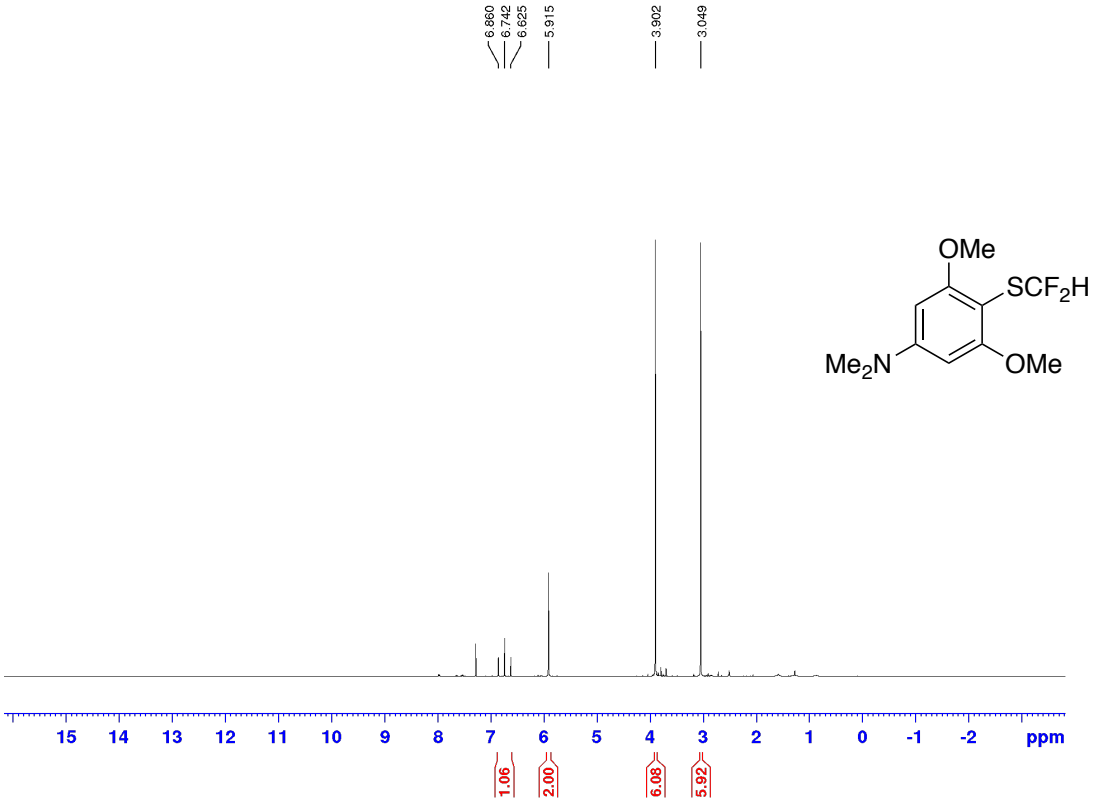
^{13}C NMR (125 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-5-methylbenzene-1,3-diol (27b)



^{19}F NMR (470 MHz, $CDCl_3$) 2-((Difluoromethyl)thio)-5-methylbenzene-1,3-diol (27b)

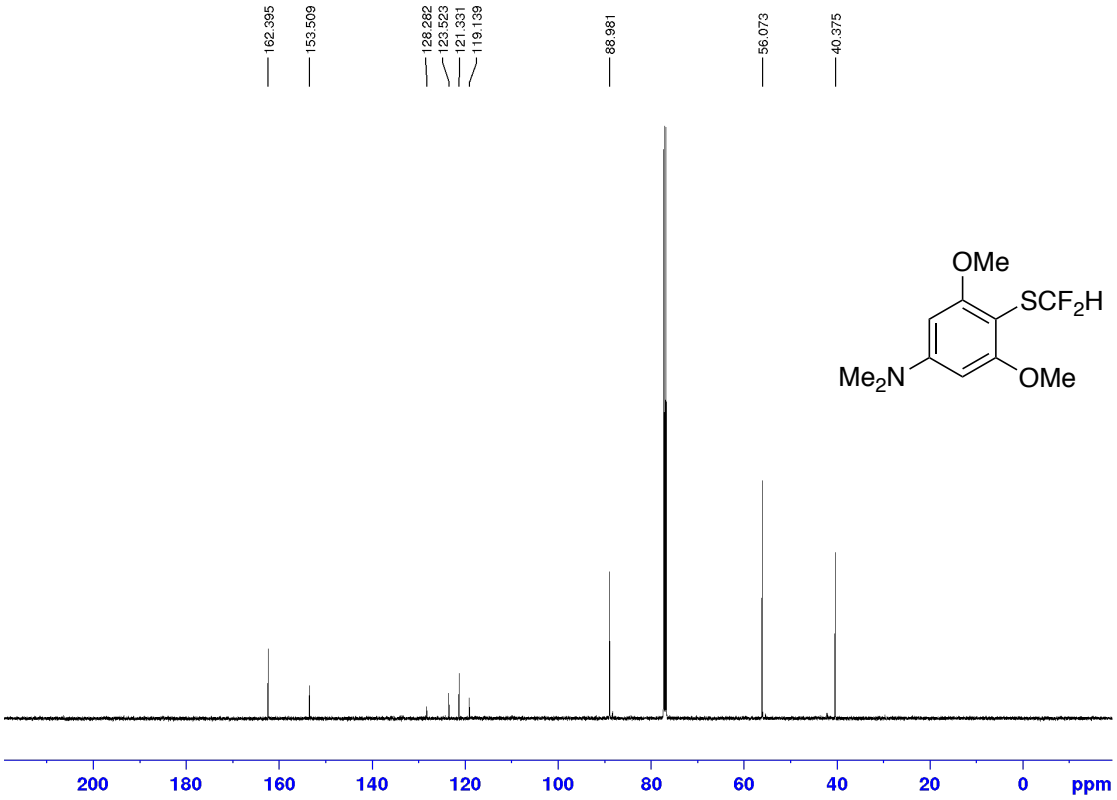


^{1}HNMR (500 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-3,5-dimethoxy-*N*,*N*-dimethylaniline (28b)

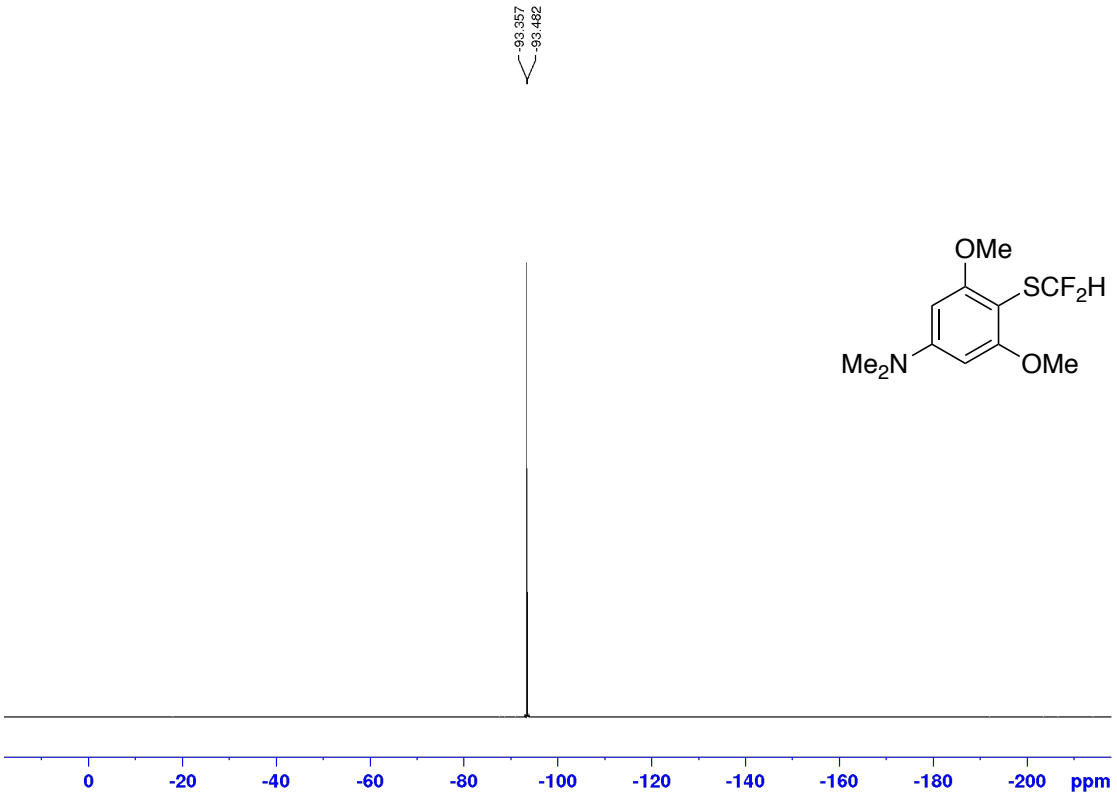


OMe

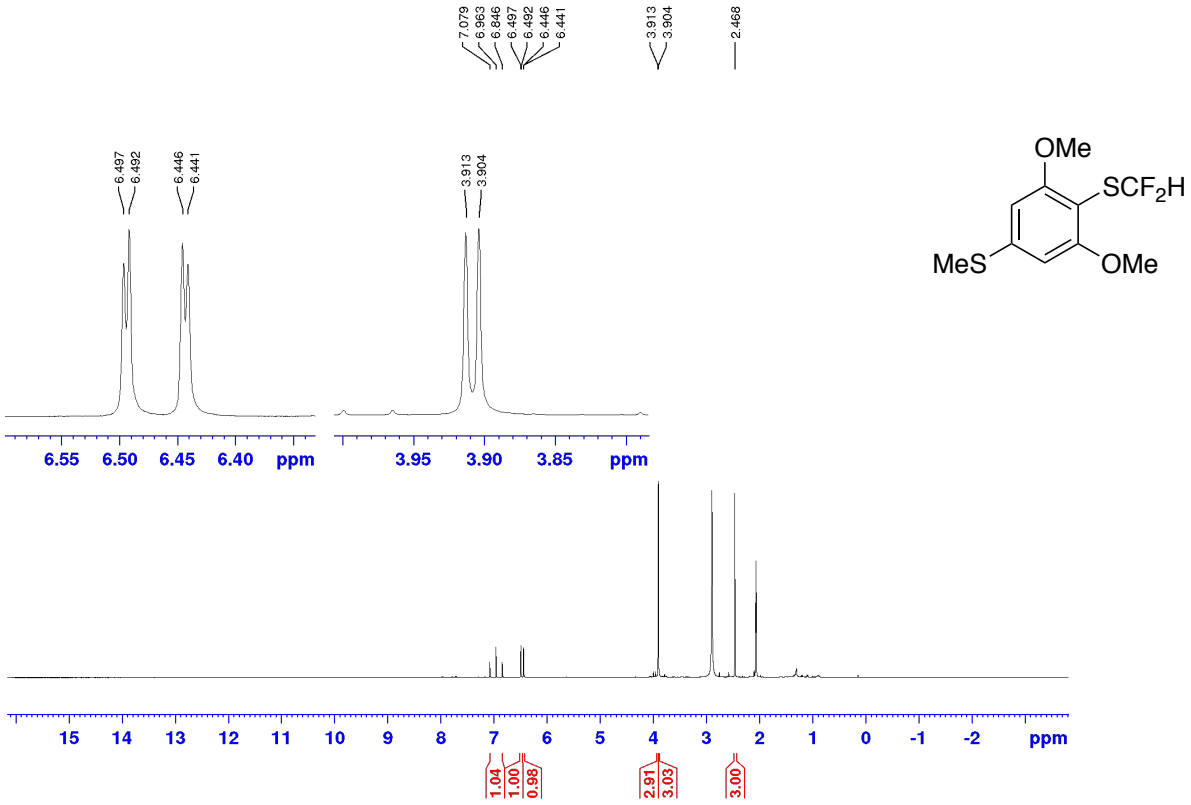
^{13}C NMR (125 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-3,5-dimethoxy-*N*,*N*-dimethylaniline (28b)



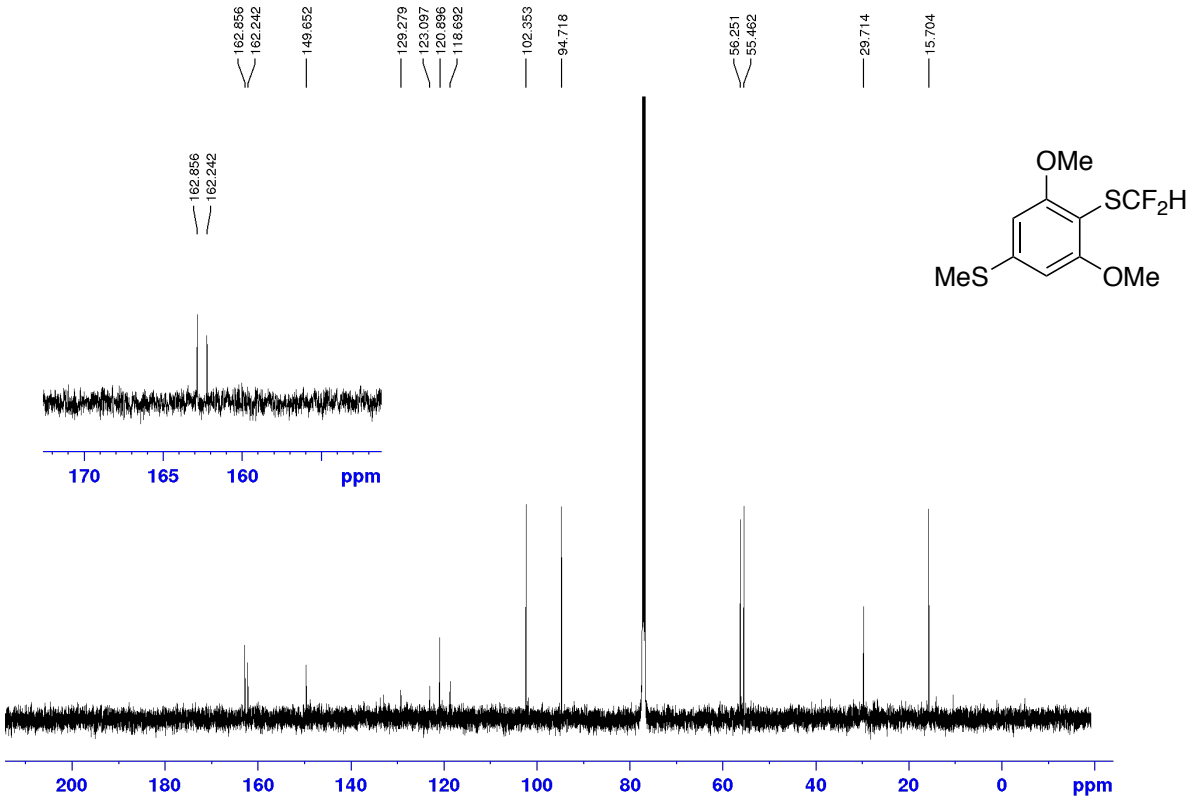
^{19}F NMR (470 MHz, $CDCl_3$) 4-((Difluoromethyl)thio)-3,5-dimethoxy-*N*,*N*-dimethylaniline (28b)



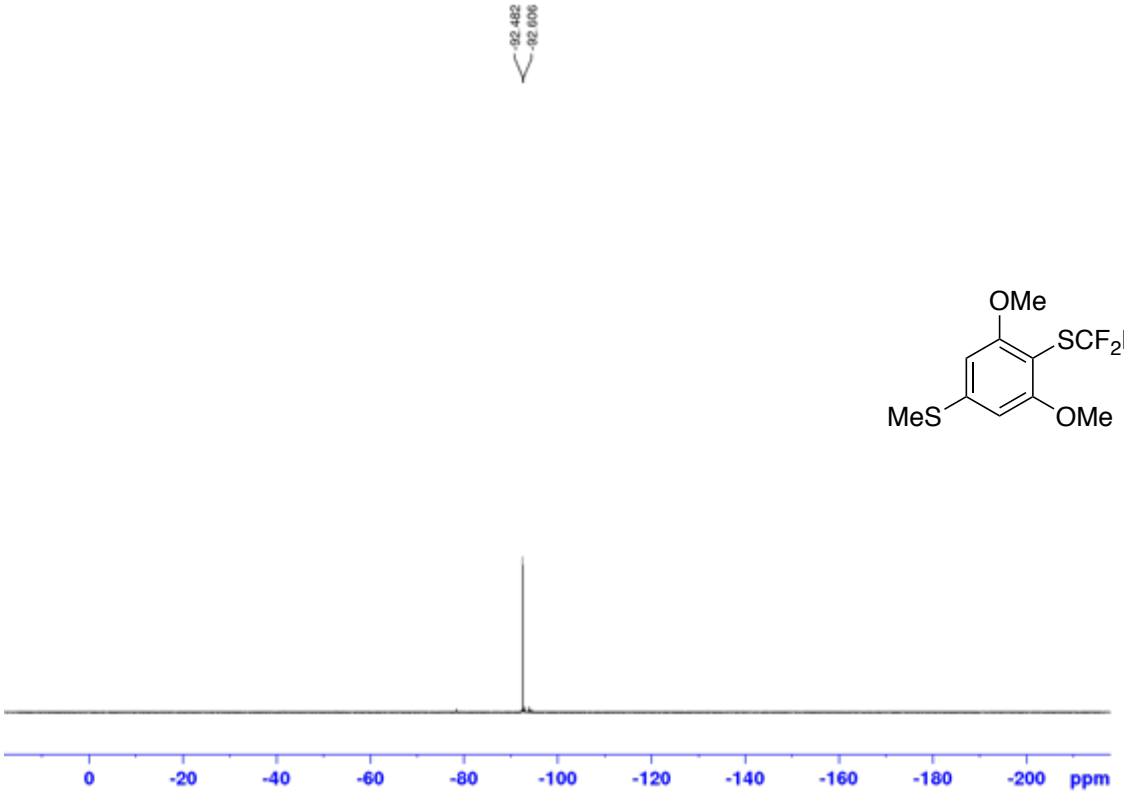
^{1}HNMR (500 MHz, Acetone-d_6) (Difluoromethyl)(2,6-dimethoxy-4-(methylthio)phenyl)sulfane (29b)



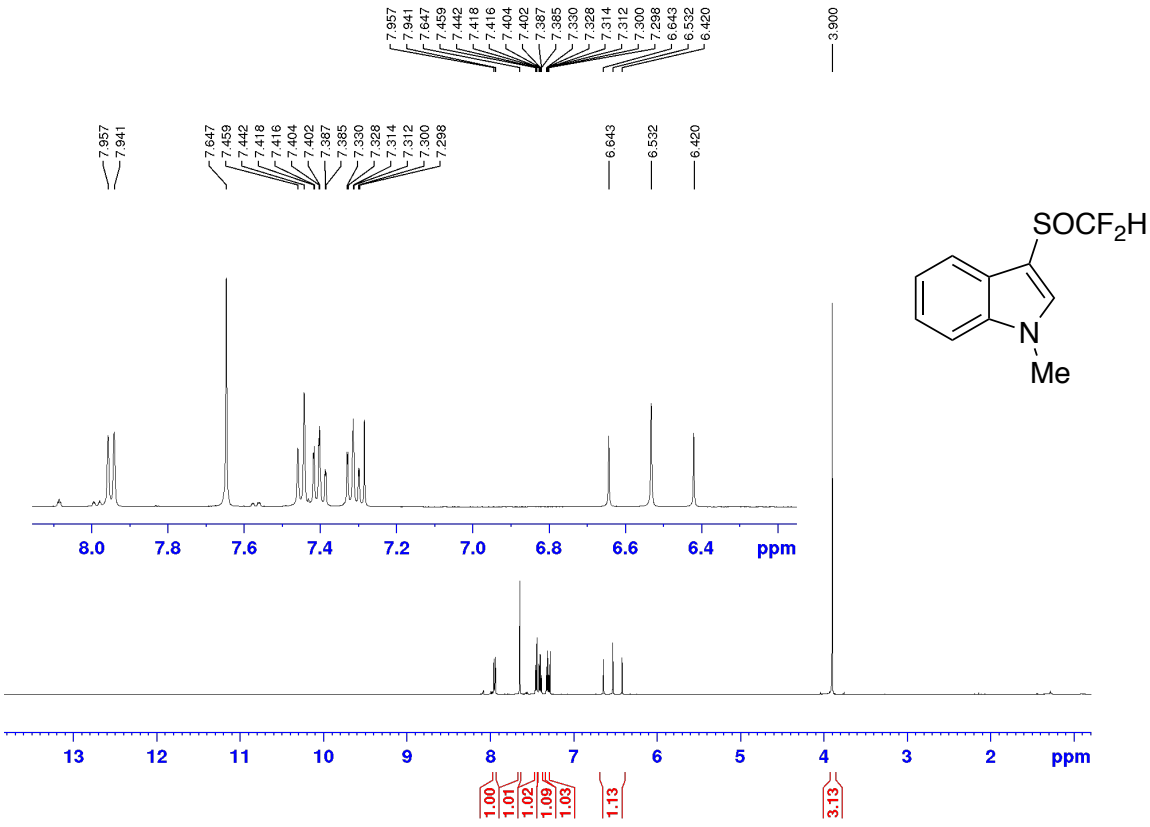
^{13}C NMR (125 MHz, Acetone-d_6) (Difluoromethyl)(2,6-dimethoxy-4-(methylthio)phenyl)sulfane (29b)



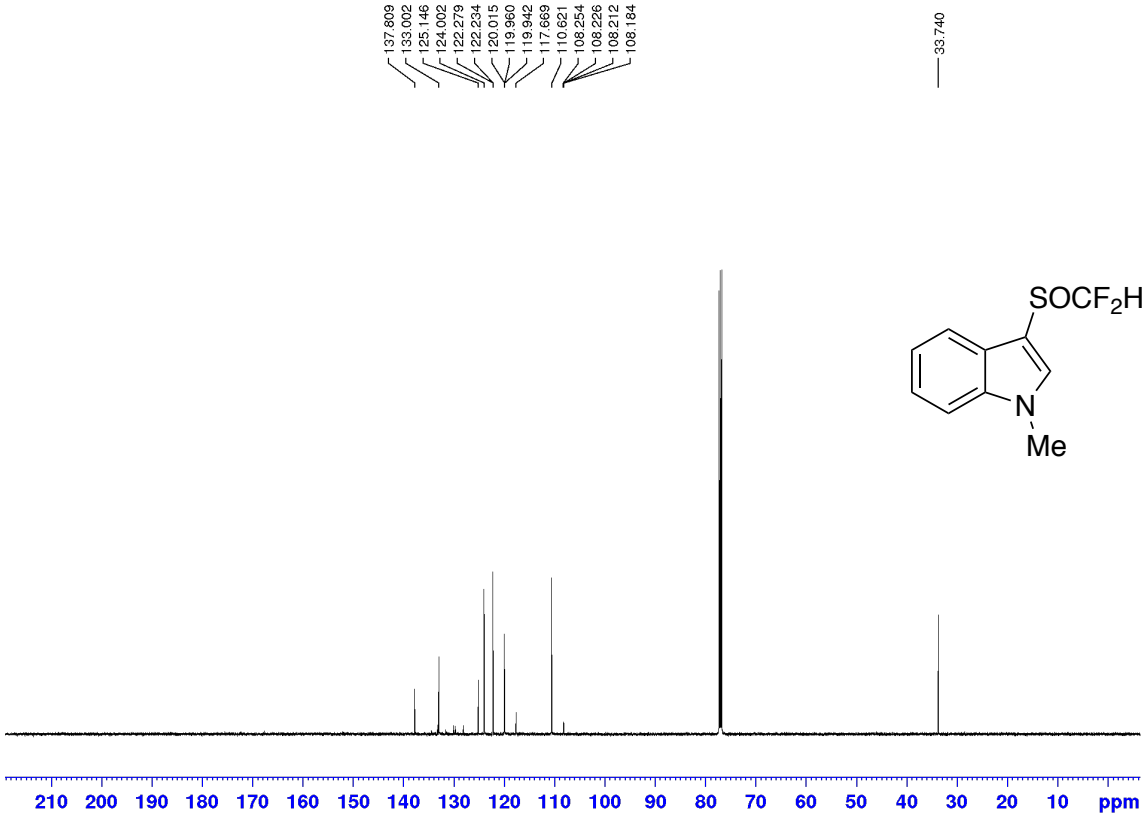
^{19}F NMR (470 MHz, Acetone-d_6) (Difluoromethyl)(2,6-dimethoxy-4-(methylthio)phenyl)sulfane (29b)



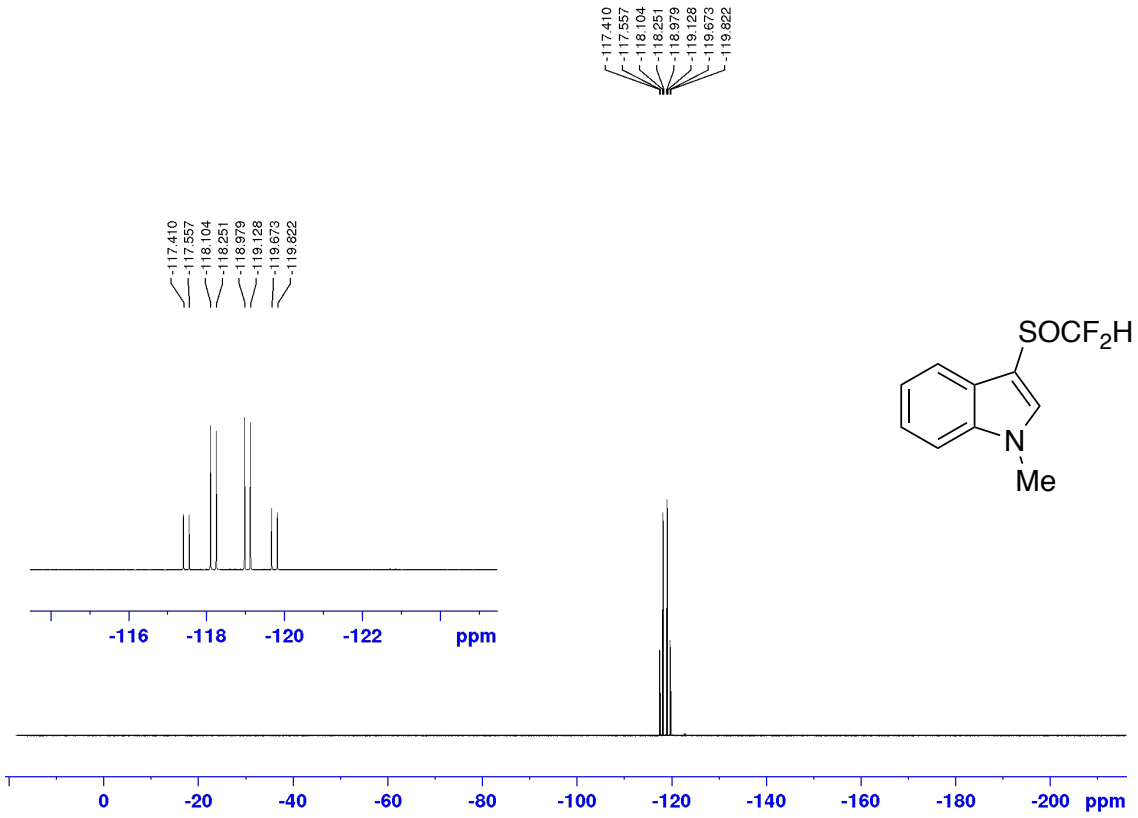
^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)sulfinyl)-1-methyl-1*H*-indole (1b'')



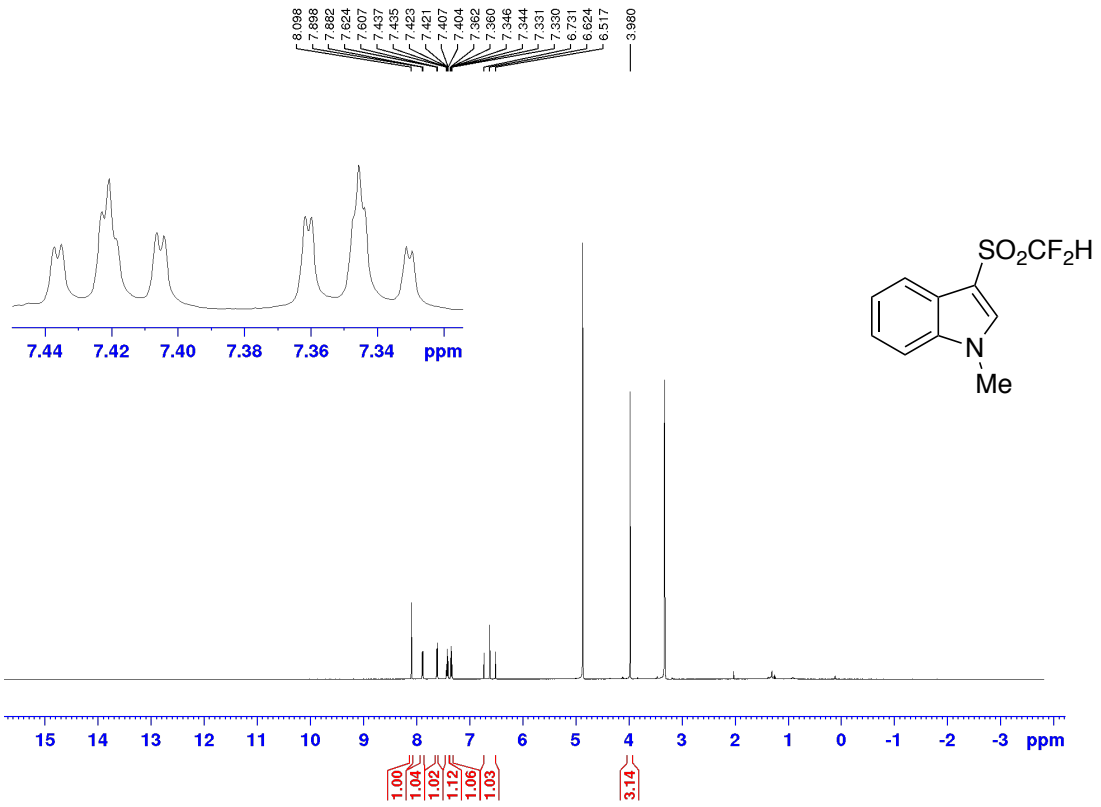
^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)sulfinyl)-1-methyl-1*H*-indole (1b'')



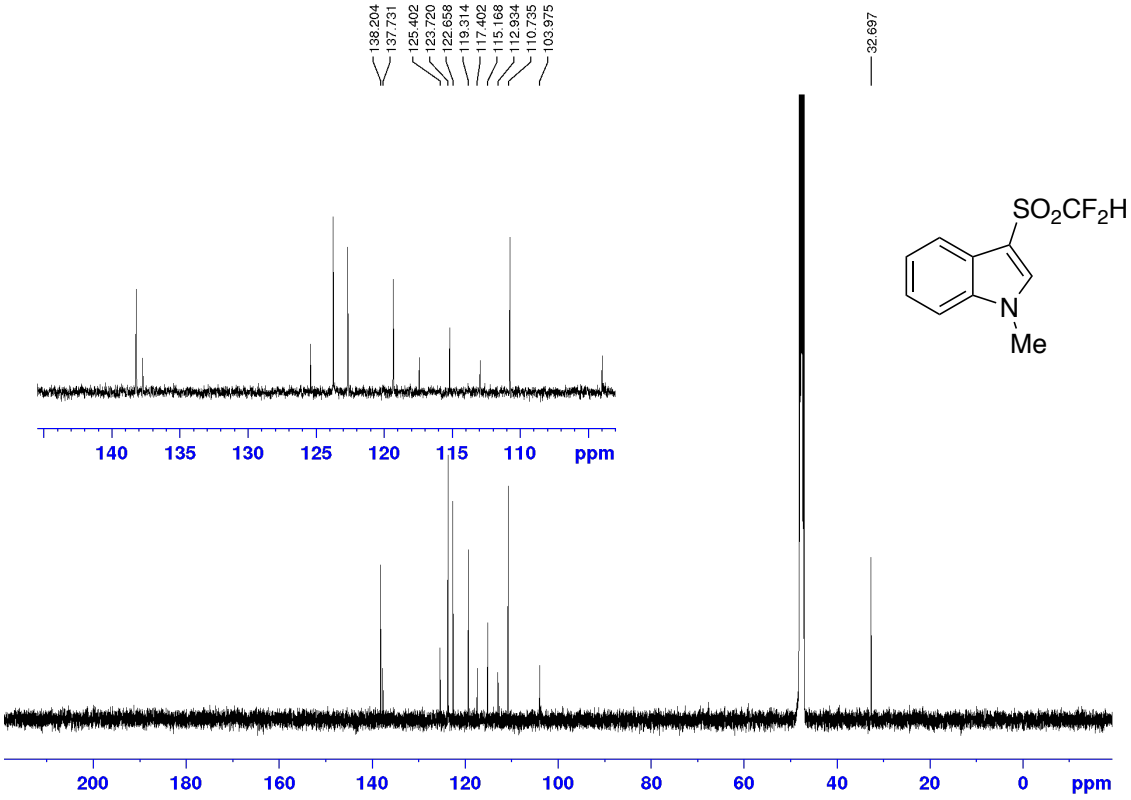
^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)sulfinyl)-1-methyl-1*H*-indole (1b'')



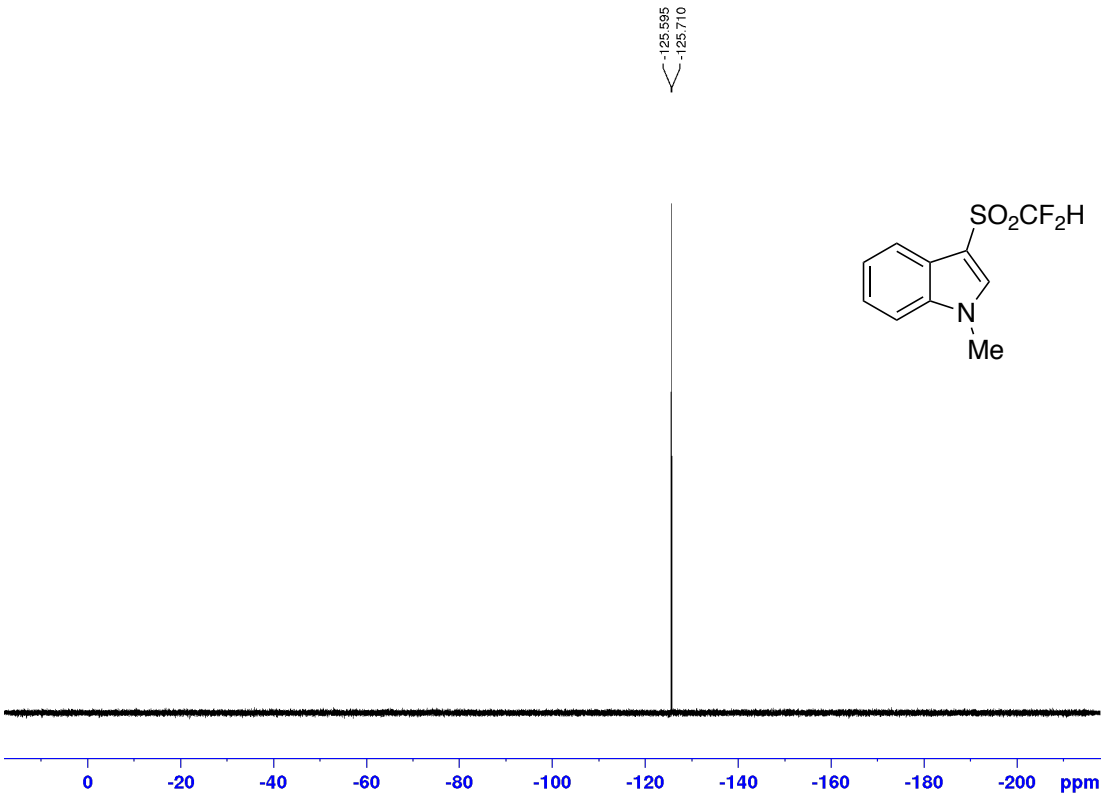
^{1}HNMR (500 MHz, CD_3OD) 3-((Difluoromethyl)sulfonyl)-1-methyl-1*H*-indole (1b')



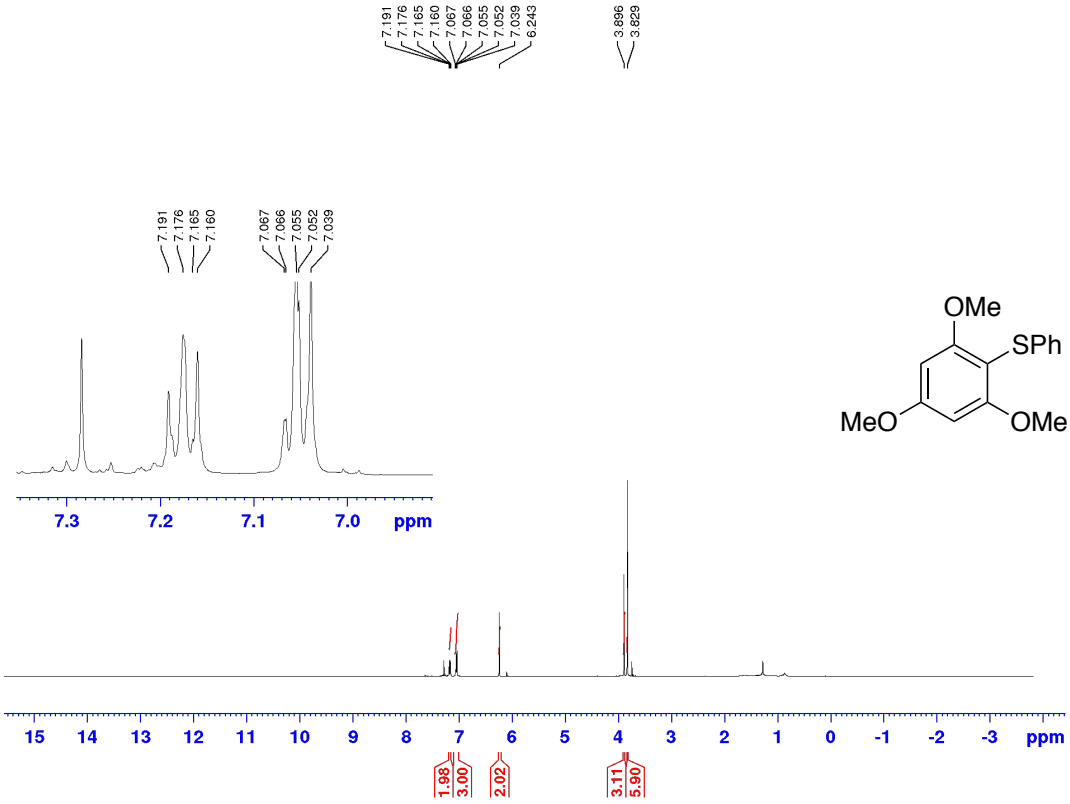
^{13}CNMR (125 MHz, CD_3OD) 3-((Difluoromethyl)sulfonyl)-1-methyl-1*H*-indole (1b')



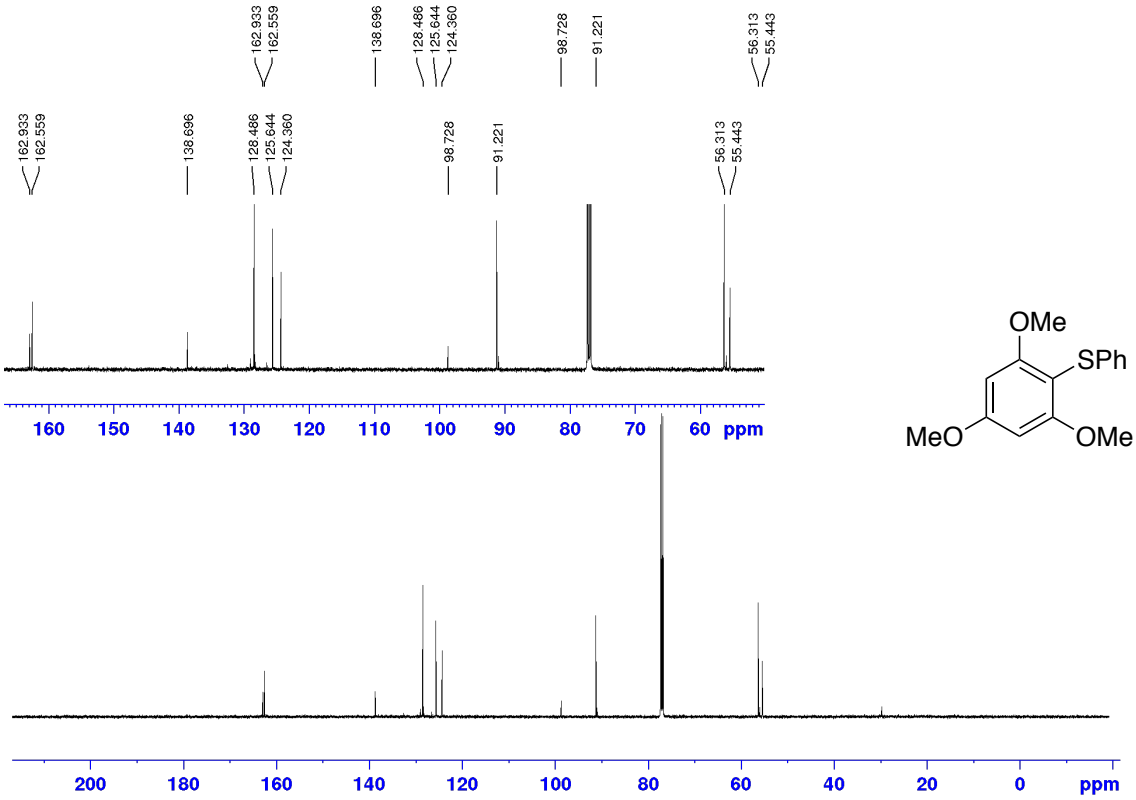
^{19}FNMR (470 MHz, CD_3OD) 3-((Difluoromethyl)sulfonyl)-1-methyl-1*H*-indole (1b')



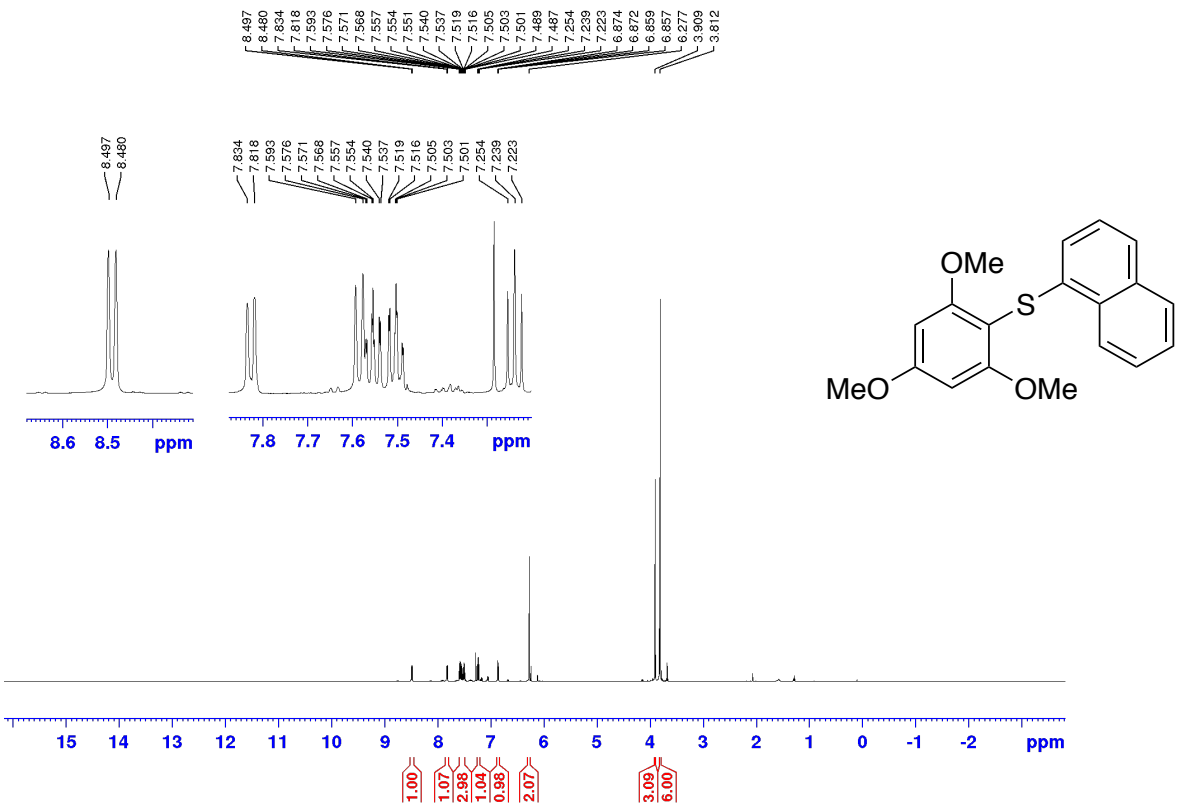
^{1}H NMR (500 MHz, $CDCl_3$) Phenyl(2,4,6-trimethoxyphenyl)sulfane (30b)



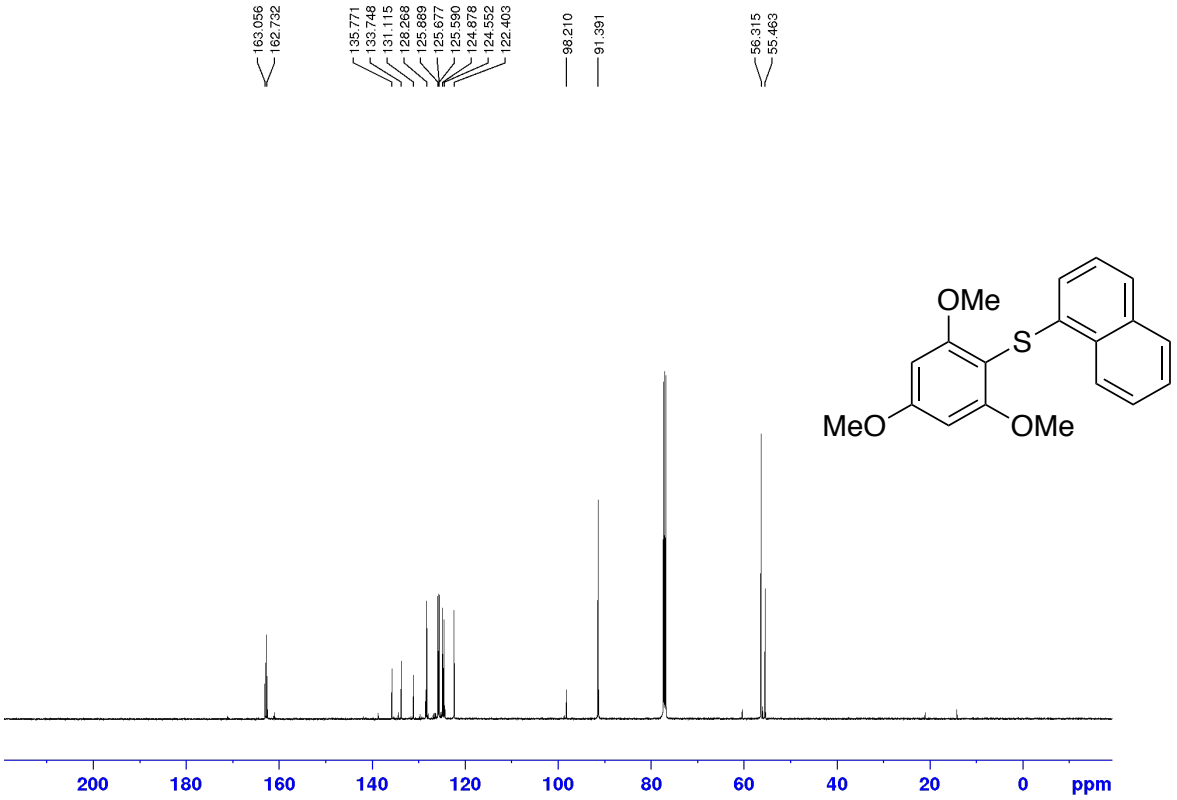
^{13}C NMR (125 MHz, $CDCl_3$) Phenyl(2,4,6-trimethoxyphenyl)sulfane (30b)



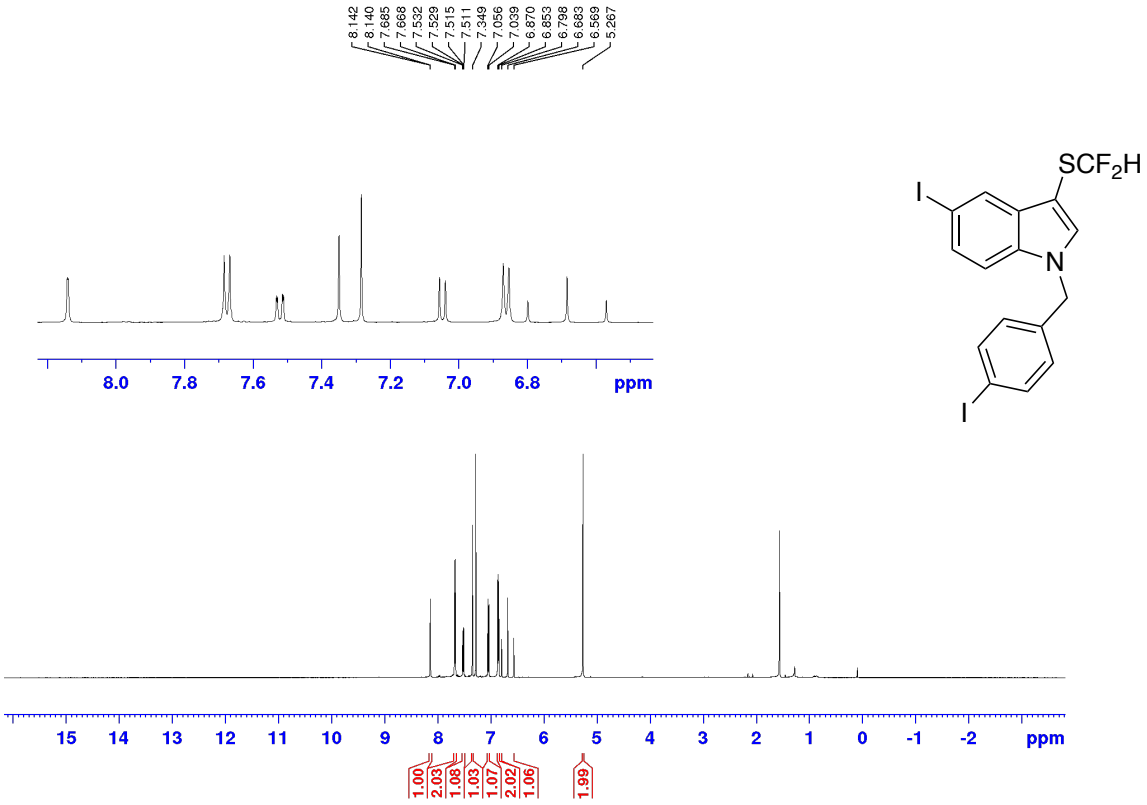
^{1}H NMR (500 MHz, $CDCl_3$) Naphthalen-1-yl(2,4,6-trimethoxyphenyl)sulfane (31b)



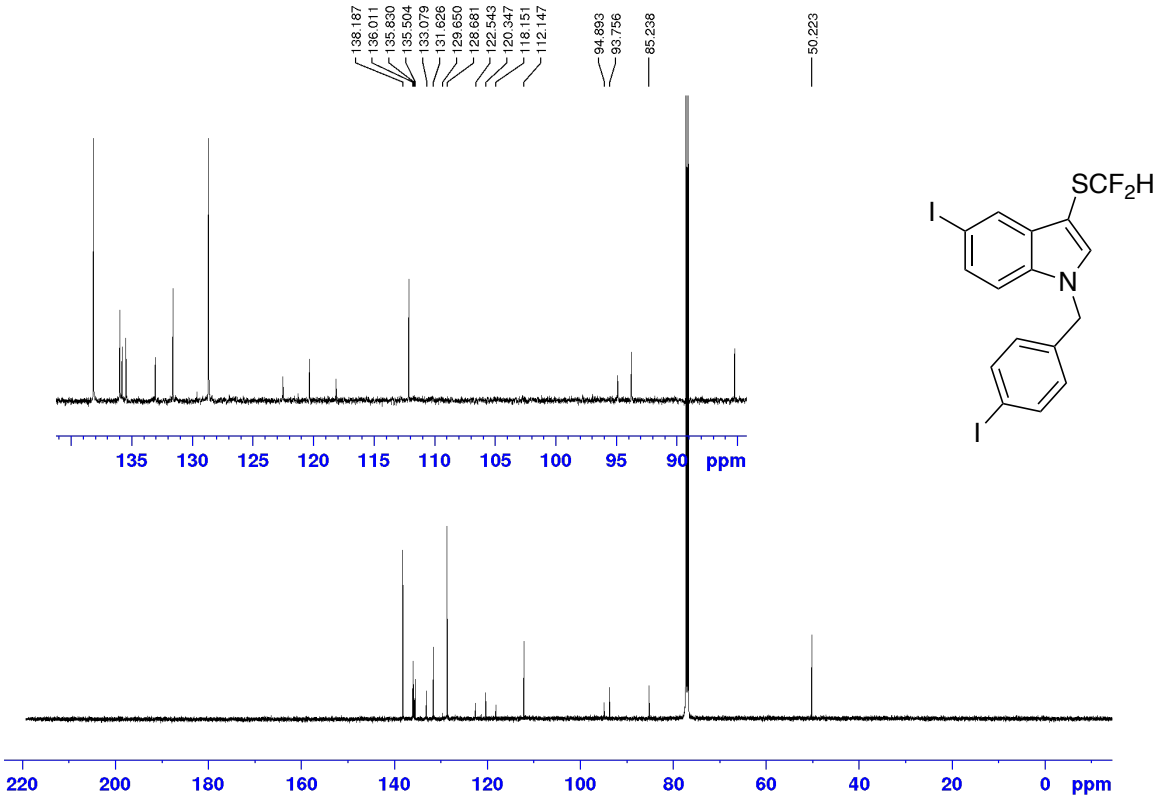
^{13}C NMR (125 MHz, $CDCl_3$) Naphthalen-1-yl(2,4,6-trimethoxyphenyl)sulfane (31b)



^{1}H NMR (500 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-iodo-1-(4-iodobenzyl)-1*H*-indole (33b)

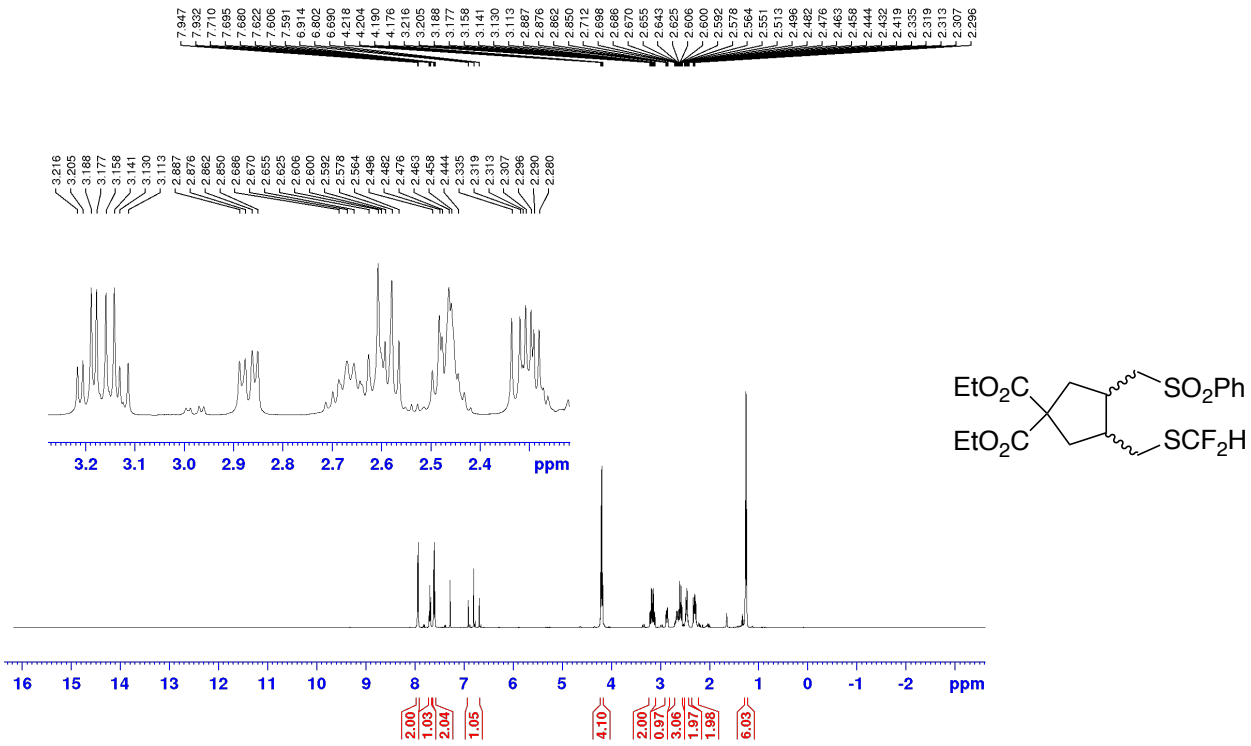


^{13}C NMR (125 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-iodo-1-(4-iodobenzyl)-1*H*-indole (33b)

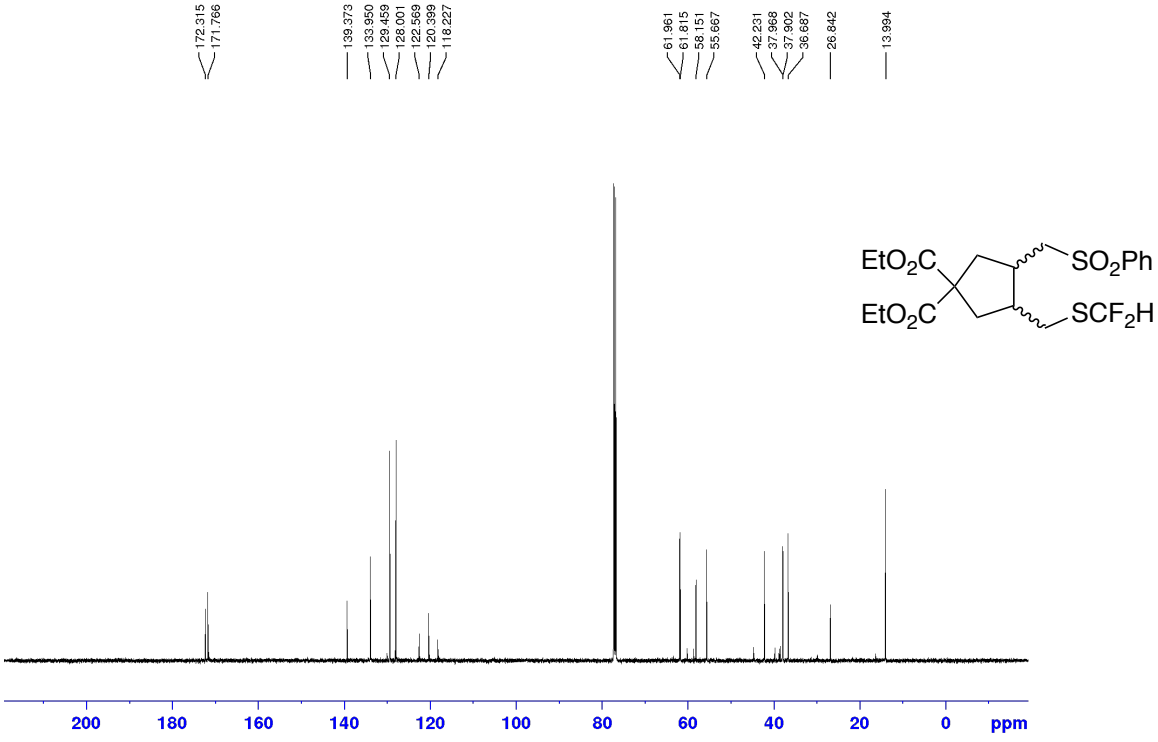


^{19}F NMR (470 MHz, $CDCl_3$) 3-((Difluoromethyl)thio)-5-iodo-1-(4-iodobenzyl)-1*H*-indole (33b)

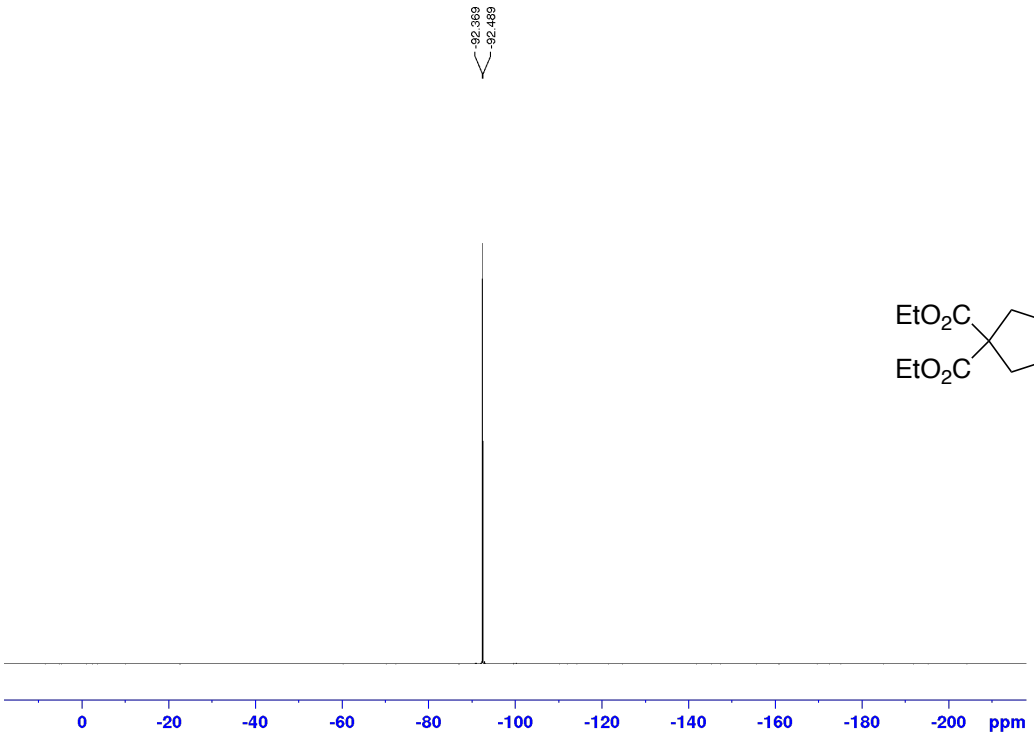
^{1}H NMR (500 MHz, $CDCl_3$) Diethyl 3-(((difluoromethyl)thio)methyl)-4-((phenylsulfonyl)methyl)cyclopentane-1,1-dicarboxylate (34b)



^{13}C NMR (125 MHz, $CDCl_3$) Diethyl 3-(((difluoromethyl)thio)methyl)-4-((phenylsulfonyl)methyl)cyclopentane-1,1-dicarboxylate (34b)



^{19}F NMR (470 MHz, $CDCl_3$) Diethyl 3-(((difluoromethyl)thio)methyl)-4-((phenylsulfonyl)methyl)cyclopentane-1,1-dicarboxylate (34b)



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3. D. Zhu, X. Shao, X. Hong, L. Lu and Q. Shen, *Angew. Chem. Int. Ed.*, 2016, **55**, 15807-15811.