

Supplementary Information

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1. General

All reactions containing moisture- or air-sensitive reagents or intermediates were carried out under argon atmosphere in oven dried glassware using standard *Schlenk* techniques. Thin layer chromatography (TLC) was performed on *Merck* silica gel 60 F₂₅₄ plates using UV light (254 nm) for detection. Flash Chromatography (FC) was carried out on *Merck* silica gel 60 (40–63 μ m) or *Acros Organics* (35–70 μ m) with an argon overpressure up to 0.5 bar. All solvents for FC and extraction were distilled using standard procedures before use. Tetrahydrofuran (THF) was distilled over potassium before use. Dimethylformamide (DMF) and methanol were purchased from *Acros Organics* (99.8%, extra dry over molecular sieve, *Acroseal*). Sodium hydride (60%, in mineral oil) was purchased from *Sigma Aldrich* and used as received. Other chemicals were purchased from *Sigma Aldrich*, *Acros Organics*, *Alfa Aesar*, *ABCR*, *Fluka* or *TCI* and used as received. A 365 nm *UVP Black Ray 100-AP* lamp (100W) was used for irradiation.

¹H-, ¹³C-, ¹⁹F- and ³¹P-NMR spectra were recorded at 300 K on a *Bruker DPX 300*, a *Bruker AV 300* or a *Bruker AV 400* spectrometer. The chemical shifts δ were reported in parts per million (ppm) and referred to the solvent (CDCl₃) residual peak (¹H: δ = 7.26 ppm, ¹³C: δ = 77.16 ppm). Multiplicity of the signals: s (singlet), d (doublet), t (triplet), bs (broad signal) and m (multiplet). The coupling constants were reported in Hertz (Hz). Melting points (**MP**) were measured on a *Stuart SMP10* and are uncorrected. Infrared spectra (**IR**) were recorded on a *Digilab 3100 FT-IR Excalibur Series* spectrometer. The signal intensity was described with strong (s, 10–40% transmittance), medium (m, 40–70% transmittance), weak (w, 70–90% transmittance) and very weak (vw, 90–100% transmittance). **EI MS** (m/z) spectra were measured in CHCl₃ on a *Thermo-Finnigan TSQ 7000*. **HRMS APCI** (m/z) spectra were measured in CHCl₃/MeOH or toluene on a *Thermo-Fisher Scientific LTQ XL Orbitrap* and **HRMS ESI** (m/z) spectra on a *Bruker MicroTof*. **GC/MS** (EI, 70 eV) analysis was performed on an *Agilent 6890N* chromatograph provided with a *HP-5* column combined with a *Waters-Micromass* was used for data analysis.

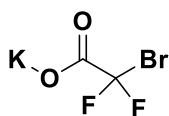
2. General procedures

2.1 General procedure for difluoromethylation of thiols (GP1)

(Difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and aryl thiol (200 μ mol, 1.00 equiv) were added to a suspension of NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv) in DMF (1 mL). The suspension was stirred under irradiation (365 nm, 100 W) at rt for 15 h. The reaction was quenched by addition of water (5 mL) and Et₂O (5 mL). The aqueous layer was extracted with Et₂O (3 \times 20 mL), the combined organic layers were dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was purified *via* FC.

3. Synthesis of phosphonium salts

Potassium 2-bromo-2,2-difluoroacetate (S1):

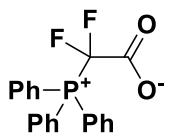


According to a literature known procedure¹, potassium hydroxide (4.03 g, 71.7 mmol, 1.00 equiv) was dissolved in MeOH (70 mL) at 0 °C. Ethyl bromo-2,2-difluoroacetate (9.48 mL, 15.0 g, 71.7 mmol, 1.00 equiv) was added slowly to the reaction mixture at 0 °C. The reaction mixture was slowly allowed to warm up to rt overnight, the solvent was removed under reduced pressure and the title compound **S1** (13.6 g, 63.8 mmol, 89%) was obtained as a colourless solid.

¹⁹F-NMR: (282 MHz, CD₃OD, 300 K): δ = –58.0 (s, 2F) ppm. **HRMS (ESI):** Exact mass calculated for C₂O₂BrF₂[–] ([M – K][–]): 172.9055; 174.9041. Found: 172.9065; 174.9044.

The analytical data are in accordance to the literature.¹

2,2-Difluoro-2-(triphenylphosphonio)acetate (S2):



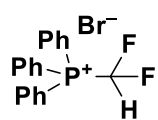
According to a literature known procedure¹, **S1** (13.6 g, 63.8 mmol, 1.00 equiv) and triphenylphosphine (16.7 g, 63.8 mmol, 1.00 equiv) were dissolved in DMF (80 mL). The reaction mixture was stirred at rt overnight. The formed precipitate was filtered off, washed with cold DMF (3 \times 20 mL), water (3 \times 20 mL) and Et₂O (3 \times 20 mL). The precipitate was dried to obtain the title compound **S2** (12.7 g, 35.6 mmol, 56%) as a colourless solid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 7.52–7.63 (m, 6H), 7.68–7.83 (m, 9H) ppm. **¹³C-NMR:** (75 MHz, CD₃OD, 300 K): 116.7 (d, J = 85.3 Hz, C_q), 118.5 (td, J = 290.9, 79.6 Hz, CF₂), 130.0 (d, J = 12.5 Hz, 2 \times C_q) 131.5 (d, J = 13.1 Hz, 6 \times CH, C_{Ar}), 133.0 (d, J = 10.2 Hz, C_q), 136.0 (d, J = 10.3 Hz, 6 \times CH, C_{Ar}), 137.0 (d, J = 3.4 Hz, 3 \times CH, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃,

300 K): -92.7 (d, $J = 102.1$ Hz, 2F) ppm. **^{31}P -NMR**: (122 MHz, CDCl_3 , 300 K): 25.4 (t, $J = 102.2$ Hz, 1P) ppm. **HRMS (ESI)**: Exact mass calculated for $\text{C}_{20}\text{H}_{15}\text{F}_2\text{O}_2\text{PNa}^+$ ($[\text{M} + \text{Na}]^+$): 379.0670. Found: 379.0672.

The analytical data are in accordance to the literature.¹

(Difluoromethyl)triphenylphosphonium bromide (1):

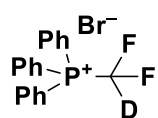


According to a literature known procedure², **S2** (5.04 g, 14.2 mmol, 1.00 equiv) was dissolved in THF (14 mL). To this mixture HBr (48%, 1.94 mL, 2.87 g, 17.0 mmol, 1.20 equiv) was added and the reaction mixture was refluxed for 2 h. The reaction was quenched by addition of water (50 mL) and dichloromethane (50 mL). The aqueous layer was extracted with dichloromethane (2×50 mL), the combined organic layers were dried over MgSO_4 , the solvent was removed under reduced pressure and the residue was washed multiple times with cold THF (3×10 mL) to obtain the title compound **1** (4.80 g, 12.2 mmol, 86%) as a colourless solid.

^1H -NMR: (300 MHz, CDCl_3 , 300 K): $\delta = 7.69\text{--}7.78$ (m, 6H), $7.83\text{--}7.97$ (m, 9H), 9.69 (td, $J = 46.6$, 31.4 Hz, 1H) ppm. **^{13}C -NMR**: (75 MHz, CDCl_3 , 300 K): 112.6 (d, $J = 84.9$ Hz, $3 \times \text{C}_q$, C_{Ar}), 114.3 (td, $J = 272.0$ Hz, 82.4 Hz, CF_2H) 130.9 (d, $J = 13.2$ Hz, $6 \times \text{CH}$, C_{Ar}), 135.0 (d, $J = 10.6$ Hz, $6 \times \text{CH}$, C_{Ar}), 136.6 (d, $J = 3.2$ Hz, $3 \times \text{CH}$, C_{Ar}) ppm. **^{19}F -NMR**: (282 MHz, CDCl_3 , 300 K): -125.4 (d, $J = 81.1$ Hz, 2F) ppm. **^{31}P -NMR**: (122 MHz, CDCl_3 , 300 K): 19.3 (t, $J = 80.7$ Hz, 1P) ppm. **HRMS (ESI)**: Exact mass calculated for $\text{C}_{19}\text{H}_{16}\text{F}_2\text{P}^+$ ($[\text{M} - \text{Br}^-]^+$): 313.0952. Found: 313.0966.

The analytical data are in accordance to the literature.³

(Difluoromethyl-d)triphenylphosphonium bromide (6):



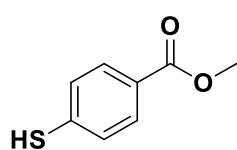
According to a literature known procedure², **S2** (1.50 g, 4.21 mmol, 1.00 equiv) was dissolved in THF (5 mL). To this mixture DBr (48%, 583 μL , 862 mg, 5.06 mmol, 1.20 equiv) was added and the reaction mixture was refluxed for 2 h. The reaction was quenched by addition of D_2O (10 mL) and dichloromethane (10 mL). The aqueous layer was extracted with dichloromethane (2×20 mL), the combined organic layers were dried over MgSO_4 , the solvent was removed under reduced pressure and the residue was washed multiple times with cold THF (3×5 mL) to obtain the title compound **6** (1.11 g, 2.82 mmol, 67%) as a colourless solid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 7.69–7.78 (m, 6H), 7.83–7.97 (m, 9H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): 112.8 (d, J = 84.9 Hz, 3 \times C_q, C_{Ar}), 114.3 (td, J = 272.0, 82.4 Hz, CF₂D), 130.9 (d, J = 13.1 Hz, 6 \times CH, C_{Ar}), 135.0 (d, J = 10.5 Hz, 6 \times CH, C_{Ar}), 136.6 (d, J = 3.2 Hz, 3 \times CH, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –126.0 (dt, J = 80.7, 6.5 Hz, 2F) ppm. **³¹P-NMR:** (122 MHz, CDCl₃, 300 K): 19.2 (t, J = 80.6 Hz, 1P) ppm.

The analytical data are in accordance to the literature.²

4. Synthesis of Aryl Thiols:

Methyl 4-mercaptobenzoate (3g):

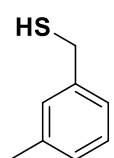


According to a literature known procedure⁴, 4-mercaptobenzoic acid (1.50 g, 9.73 mmol, 1.00 equiv) was dissolved in MeOH (20 mL) and to this mixture sulfuric acid (96%, 500 μ L, 920 mg, 9.77 mmol, 1.00 equiv) was added. The reaction mixture was refluxed for 15 h. The reaction was quenched by addition of ethyl acetate (50 mL) and an aqueous solution of NaHCO₃ (50 mL). The aqueous layer was extracted with ethyl acetate (2 \times 50 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed under reduced pressure to obtain the title compound **3g** (1.47 g, 8.74 mmol, 90%) as a brown solid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 3.53 (s, 1H), 3.82 (s, 3H), 7.21 (d, J = 8.4 Hz, 2H), 7.81 (m, J = 8.4 Hz, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 52.2 (CH₃), 127.3 (C_q, C_{Ar}), 128.3 (2 \times CH, C_{Ar}), 130.4 (2 \times CH, C_{Ar}), 138.4 (C_q, C_{Ar}), 166.7 (CO) ppm. **HRMS (ESI):** Exact mass calculated for C₈H₈NaO₂S⁺ ([M + Na]⁺): 191.0137. Found: 191.0154.

Spectral data obtained are in accordance with the reported data.⁴

m-Tolylmethanethiol (3q):



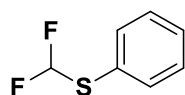
3-Methylbenzyl bromide (500 μ L, 685 mg, 3.70 mmol, 1.00 equiv) was dissolved in ethanol (4 mL) and to this mixture thiourea (309 mg, 4.07 mmol, 1.10 equiv) was added. The mixture was refluxed for 6 h. An aqueous solution of NaOH (25%, 4 mL) was added and the mixture was refluxed for 15 h. The reaction was quenched by addition of water (20 mL) and Et₂O (20 mL). The aqueous layer was acidified and extracted with Et₂O (2 \times 20 mL). The solvent was removed under reduced pressure and the crude material was

purified by FC on silica gel (pentane) to afford the desired product **3q** (299 mg, 2.16 mmol, 58%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 1.77 (t, J = 7.5 Hz, 1H), 2.37 (s, 3H), 3.73 (d, J = 7.5 Hz, 2H), 7.05–7.11 (m, 1H), 7.12–7.18 (m, 2H), 7.20–7.27 (m, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 21.5 (CH₃), 29.0 (CH₂), 125.1 (CH, C_{Ar}), 127.9 (CH, C_{Ar}), 128.7 (CH, C_{Ar}), 128.9 (CH, C_{Ar}), 138.4 (C_q, C_{Ar}), 141.2 (C_q, C_{Ar}) ppm. **IR** (neat): ν (cm⁻¹): 3019 (vw), 2919 (w), 1609 (w), 1488 (w), 1457 (w), 1378 (vw), 1259 (vw), 1237 (w), 1091 (w), 1040 (vw), 975 (vw), 881 (vw), 781 (m), 702 (s). **EI MS**, m/z (%): 138 (40) [M]⁺, 105 (100) [M–SH]⁺.

5. Analytical Data

(Difluoromethyl)(phenyl)sulfane (4a):

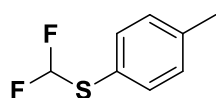


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and benzenethiol (**3a**) (20.5 μ L, 22.0 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4a** (22.3 mg, 139 μ mol, 70%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 6.83 (t, J = 57.0 Hz, 1H), 7.35–7.47 (m, 3H), 7.57–7.64 (m, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 121.2 (t, J = 275.0 Hz, CF₂H), 126.4 (C_q, C_{Ar}), 129.5 (2 \times CH, C_{Ar}), 129.9 (CH, C_{Ar}), 135.5 (2 \times CH, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –91.4 (s, 2F) ppm. **HRMS (APCI):** Exact mass calculated for C₇H₆SF₂Ag⁺ ([M + Ag]⁺): 266.9204, 268.9199. Found: 266.9232, 268.9229.

Spectral data obtained are in accordance with the reported data.⁵

(Difluoromethyl)(p-tolyl)sulfane (4b):

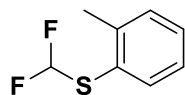


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and *p*-thiocresol (**3b**) (24.8 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4b** (23.0 mg, 132 μ mol, 66%) as a colourless liquid. **¹H-NMR:** (300 MHz, CDCl₃, 300 K): δ = 2.38 (s, 3H), 6.79 (t, J = 57.2 Hz, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 21.4 (CH₃), 121.3 (t, J = 275.0 Hz, CF₂H), 122.7 (C_q, C_{Ar}), 130.3 (2 \times CH, C_{Ar}), 135.7 (2 \times CH, C_{Ar}), 140.4 (C_q, C_{Ar}) ppm.

¹⁹F-NMR: (282 MHz, CDCl₃, 300 K): −91.7 (s, 2F) ppm. **HRMS (APCI):** Exact mass calculated for C₈H₈SF₂⁺ ([M]⁺): 174.0309. Found: 174.0308.

Spectral data obtained are in accordance with the reported data.⁶

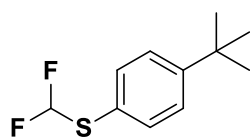
(Difluoromethyl)(o-tolyl)sulfane (4c):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μmol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μmol, 2.00 equiv) and *o*-thiocresol (**3c**) (24.8 mg, 200 μmol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4c** (23.1 mg, 133 μmol, 67%) as a colourless liquid. **¹H-NMR:** (300 MHz, CDCl₃, 300 K): δ = 2.43 (s, 3H), 6.70 (t, *J* = 57.0 Hz, 1H), 7.10–7.29 (m, 3H), 7.50 (d, *J* = 7.6 Hz, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 21.4 (CH₃), 121.4 (t, *J* = 275.0 Hz, CF₂H), 125.8 (C_q, C_{Ar}), 127.0 (CH, C_{Ar}), 130.3 (CH, C_{Ar}), 131.0 (CH, C_{Ar}), 137.0 (CH, C_{Ar}), 143.1 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): −91.0 (s, 2F) ppm. **HRMS (APCI):** Exact mass calculated for C₈H₈SF₂⁺ ([M]⁺): 174.0309. Found: 174.0308.

Spectral data obtained are in accordance with the reported data.⁶

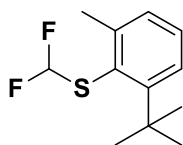
(4-(tert-Butyl)phenyl)(difluoromethyl)sulfane (4d):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μmol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μmol, 2.00 equiv) and 4-(tert-butyl)benzenethiol (**3d**) (34.5 μL, 33.3 mg, 200 μmol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4d** (30.2 mg, 142 μmol, 71%) as a colourless liquid. **¹H-NMR:** (300 MHz, CDCl₃, 300 K): δ = 1.33 (s, 9H), 6.81 (t, *J* = 57.2 Hz, 1H), 7.38–7.44 (m, 2H), 7.49–7.54 (m, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 31.3 (3 × CH₃), 34.9 (C_q), 121.4 (t, *J* = 274.9 Hz, CF₂H), 122.8 (C_q, C_{Ar}), 126.6 (2 × CH, C_{Ar}), 135.3 (2 × CH, C_{Ar}), 153.4 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): −91.4 (s, 2F) ppm. **HRMS (APCI):** Exact mass calculated for C₁₁H₁₄SF₂⁺ ([M]⁺): 216.0779. Found: 216.0778.

Spectral data obtained are in accordance with the reported data.⁶

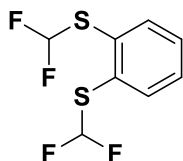
(2-(tert-Butyl)-6-methylphenyl)(difluoromethyl)sulfane (4e):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 2-(tert-butyl)-6-methylbenzenethiol (**3e**) (90%, 40.7 μ L, 40.1 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4e** (26.1 mg, 113 μ mol, 57%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 1.32 (s, 9H), 2.47 (s, 3H), 6.78 (t, J = 57.1 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 2.1 Hz, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 20.8 (CH₃), 31.4 (3 \times CH₃), 34.6 (C_q), 121.7 (t, J = 275.0 Hz, CF₂H), 125.3 (C_q, C_{Ar}), 127.5 (CH, C_{Ar}), 130.7 (CH, C_{Ar}), 134.2 (CH, C_{Ar}), 140.1 (C_q, C_{Ar}), 150.2 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): -90.9 (s, 2F) ppm. **IR** (neat): ν (cm⁻¹): 2964 (w), 2870 (vw), 1603 (vw), 1489 (w), 1466 (vw), 1448 (vw), 1387 (vw), 1363 (vw), 1319 (w), 1297 (w), 1263 (w), 1119 (vw), 1071 (m), 1053 (m), 1033 (m), 895 (vw), 874 (vw), 827 (w), 797 (w), 758 (m), 717 (w). **HRMS (APCI):** Exact mass calculated for C₁₂H₁₆SF₂⁺ ([M]⁺): 230.0935. Found: 230.0934.

1,2-Bis((difluoromethyl)thio)benzene (4f):

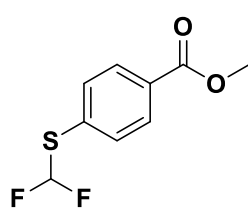


According to **GP1** with NaH (60% in oil, 32.0 mg, 800 μ mol, 4.00 equiv), (difluoromethyl)triphenylphosphonium bromide (314 mg, 800 μ mol, 4.00 equiv) and benzene-1,2-dithiol (**3f**) (25.5 μ L, 28.4 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4f** (36.0 mg, 149 μ mol, 74%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 6.89 (t, J = 56.7 Hz, 2H), 7.40–7.47 (m, 2H), 7.67–7.75 (m, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 120.5 (t, J = 276.2 Hz, 2 \times CF₂H), 130.5 (2 \times CH, C_{Ar}), 132.2 (2 \times C_q, C_{Ar}), 136.0 (2 \times CH, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): -92.1 (s, 4F) ppm. **EI MS**, m/z (%): 242 (100) [M]⁺, 191 (28) [M-CF₂H]⁺, 171 (32) [C₇H₅FS₂]⁺, 140 (53) [C₆H₄S₂]⁺.

Spectral data obtained are in accordance with the reported data.⁶

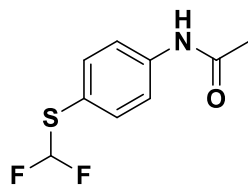
Methyl 4-((difluoromethyl)thio)benzoate (4g):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and methyl 4-mercaptobenzoate (**3g**) (33.6 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 98/2) afforded the desired product **4g** (37.4 mg, 176 μ mol, 88%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 3.94 (s, 3H), 6.89 (t, J = 56.5 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.6 Hz, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 52.5 (CH₃), 120.5 (t, J = 275.8 Hz, CF₂H), 130.4 (2 \times CH, C_{Ar}), 131.2 (C_q, C_{Ar}), 132.4 (C_q, C_{Ar}), 134.1 (2 \times CH, C_{Ar}), 166.4 (CO) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): -91.1 (s, 2F) ppm. **IR** (neat): ν (cm⁻¹): 2956 (vw), 1721 (s), 1598 (m), 1566 (vw), 1491 (vw), 1436 (m), 1400 (w), 1274 (s), 1179 (w), 1110 (m), 1064 (s), 1034 (s), 1016 (s), 856 (w), 828 (w), 793 (w), 749 (s), 692 (m). **HRMS (ESI):** Exact mass calculated for C₉H₈NaF₂NOS⁺ ([M + Na]⁺): 241.0105. Found: 241.0113.

N-(4-((Difluoromethyl)thio)phenyl)acetamide (4h):

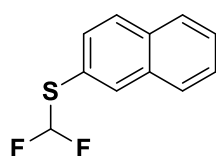


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and methyl *N*-(4-mercaptophenyl)acetamide (**3h**) (33.4 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 50/50) afforded the desired product **4h** (25.8 mg, 119 μ mol, 59%) as a colourless solid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 2.18 (s, 3H), 6.77 (t, J = 57.0 Hz, 1H), 7.47–7.63 (m, 5H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 24.8 (CH₃), 120.4 (2 \times CH, C_{Ar}), 120.6 (C_q, C_{Ar}), 121.0 (t, J = 275.4 Hz, CF₂H), 136.7 (2 \times CH, C_{Ar}), 139.8 (C_q, C_{Ar}), 168.7 (CO) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): -91.8 (s, 2F) ppm. **HRMS (ESI):** Exact mass calculated for C₉H₉NaF₂O₂S⁺ ([M + Na]⁺): 240.0265. Found: 240.0270.

Spectral data obtained are in accordance with the reported data.⁷

(Difluoromethyl)(naphthalen-2-yl)sulfane (4i):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and naphthalene-2-thiol (**3i**) (32.0 mg, 200 μ mol, 1.00 equiv) in

DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4i** (36.0 mg, 171 μ mol, 86%) as a colourless liquid.

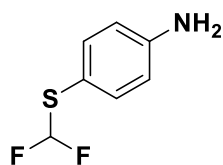
For 1 mmol reaction:

According to **GP1** with NaH (60% in oil, 80.0 mg, 2.00 mmol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (785 mg, 2.00 mmol, 2.00 equiv) and naphthalene-2-thiol (**3i**) (160 mg, 200 μ mol, 1.00 equiv) in DMF (5 mL). FC on silica gel (pentane) afforded the desired product **4i** (191 mg, 910 μ mol, 91%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 6.91 (t, J = 57.0 Hz, 1H), 7.51–7.65 (m, 3H), 7.82–7.89 (m, 3H), 8.13 (d, J = 1.7 Hz, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 121.3 (t, J = 275.3 Hz, CF₂H), 123.5 (C_q, C_{Ar}), 127.0 (CH, C_{Ar}), 127.5 (CH, C_{Ar}), 127.9 (CH, C_{Ar}), 128.1 (CH, C_{Ar}), 129.2 (CH, C_{Ar}), 131.5 (CH, C_{Ar}), 133.6 (C_q, C_{Ar}), 133.7 (C_q, C_{Ar}), 135.5 (CH, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –91.2 (s, 2F) ppm. **HRMS (APCI):** Exact mass calculated for C₁₁H₈F₂S⁺ ([M]⁺): 210.0309. Found: 210.0308.

Spectral data obtained are in accordance with the reported data.⁷

4-((Difluoromethyl)thio)aniline (**4j**):



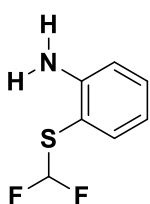
According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 4-aminobenzenethiol (**3j**) (25.4 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 60/40) afforded the desired

product **4j** (17.3 mg, 98.7 μ mol, 49%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 3.86 (bs, 2H), 6.63–6.68 (m, 2H), 6.70 (t, J = 57.5 Hz, 1H), 7.34–7.40 (m, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 113.0 (C_q, C_{Ar}), 115.6 (2 \times CH, C_{Ar}), 121.5 (t, J = 274.9 Hz, CF₂H), 137.8 (2 \times CH, C_{Ar}), 148.5 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –92.5 (s, 2F) ppm. **HRMS (ESI):** Exact mass calculated for C₇H₈F₂NS⁺ ([M + H]⁺): 176.0340. Found: 176.0319.

Spectral data obtained are in accordance with the reported data.⁸

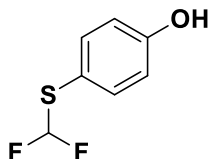
2-((Difluoromethyl)thio)aniline (**4k**):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 2-aminobenzenethiol (**3k**) (21.2 μ L, 25.4 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 70/30) afforded the desired product **4k** (20.7 mg, 118 μ mol, 59%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 4.41 (bs, 2H), 6.69–6.78 (m, 2H), 6.73 (t, J = 57.3 Hz, 1H), 7.21–7.28 (m, 1H), 7.41–7.47 (m, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 108.2 (C_q, C_{Ar}), 115.5 (CH, C_{Ar}), 118.8 (CH, C_{Ar}), 121.2 (t, J = 276.2 Hz, CF₂H), 132.2 (CH, C_{Ar}), 138.5 (CH, C_{Ar}), 149.9 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –91.0 (s, 2F) ppm. **IR** (neat): ν (cm^{–1}): 3483 (vw), 3381 (w), 1611 (m), 1481 (m), 1448 (m), 1308 (m), 1296 (w), 1252 (vw), 1161 (w), 1058 (s), 1029 (s). **EI MS**, m/z (%): 175 (58) [M]⁺, 124 (100) [M–CF₂H]⁺.

4-((Difluoromethyl)thio)phenol (**4l**):

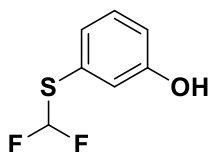


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 4-mercaptophenol (**3l**) (25.2 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 80/20) afforded the desired product **4l** (22.9 mg, 130 μ mol, 65%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 5.04 (bs, 1H), 6.74 (t, J = 57.2 Hz, 1H), 6.82–6.88 (m, 2H), 7.44–7.51 (m, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 116.3 (C_q, C_{Ar}), 116.6 (2 \times CH, C_{Ar}), 121.1 (t, J = 275.1 Hz, CF₂H), 138.0 (2 \times CH, C_{Ar}), 157.5 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –92.3 (s, 2F) ppm. **HRMS (ESI):** Exact mass calculated for C₇H₅F₂OS[–] ([M – H][–]): 175.0035. Found: 175.0035.

Spectral data obtained are in accordance with the reported data.⁹

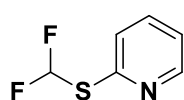
3-((Difluoromethyl)thio)phenol (**4m**):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 3-mercaptophenol (**3m**) (20.4 μ L, 25.2 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 80/20) afforded the desired product **4m** (19.8 mg, 112 μ mol, 56%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 4.96 (bs, 1H), 6.84 (t, J = 57.0 Hz, 1H), 6.87–6.92 (m, 1H), 7.06 (t, J = 2.1 Hz, 1H), 7.12–7.17 (m, 1H), 7.22–7.29 (m, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 117.1 (CH, C_{Ar}), 121.2 (t, J = 275.1 Hz, CF₂H), 121.8 (CH, C_{Ar}), 127.5 (CH, C_{Ar}), 127.6 (C_q, C_{Ar}), 130.5 (CH, C_{Ar}), 156.1 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –91.2 (s, 2F) ppm. **IR** (neat): ν (cm^{–1}): 3589 (vw), 3351 (bs, vw), 1584 (w), 1477 (w), 1441 (w), 1320 (vw), 1298 (w), 1246 (vw), 1163 (vw), 1065 (m), 1036 (w), 997 (w), 886 (w), 797 (w), 755 (w), 684 (w). **HRMS (ESI):** Exact mass calculated for C₇H₅F₂OS[–] ([M – H][–]): 175.0035. Found: 175.0039.

2-((Difluoromethyl)thio)pyridine (4n):

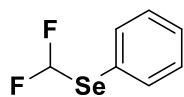


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 2-mercaptopyridine (**3n**) (22.2 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 97/3) afforded the desired product **4n** (23.5 mg, 146 μ mol, 73%) as a yellow liquid with small amount of impurities (probably difluoromethylation at the nitrogen atom, 13%).

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 6.82 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 7.23–7.31 (m, 1H), 7.37 (t, J = 56.3 Hz, 1H), 8.17 (dd, J = 4.9, 1.1 Hz, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 121.4 (t, J = 271.0 Hz, CF₂H), 121.8 (CH, C_{Ar}), 124.5 (t, J = 3.2 Hz, CH, C_{Ar}), 137.2 (CH, C_{Ar}), 150.3 (CH, C_{Ar}), 153.4 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): –96.3 (s, 2F) ppm. **HRMS (APCI):** Exact mass calculated for C₆H₆F₂NS⁺ ([M + H]⁺): 162.0184. Found: 162.0183.

Spectral data obtained are in accordance with the reported data.¹⁰

(Difluoromethyl)(phenyl)selane (4o):

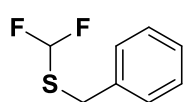


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and benzeneselenol (**3o**) (21.2 μ L, 31.4 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4o** (25.3 mg, 122 μ mol, 61%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 7.17 (t, J = 55.5 Hz, 1H), 7.33–7.46 (m, 3H), 7.66–7.73 (m, 2H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 117.3 (t, J = 289.0 Hz, CF₂H), 123.7 (C_q, C_{Ar}),

129.6 (CH, C_{Ar}), 129.7 (2 × CH, C_{Ar}), 136.5 (2 × CH, C_{Ar}) ppm. **¹⁹F-NMR**: (282 MHz, CDCl₃, 300 K): –90.3 (s, 2F) ppm. **EI MS**, m/z (%): 208 (100) [M]⁺, 157 (95) [M–CF₂H]⁺. Spectral data obtained are in accordance with the reported data.⁶

Benzyl(difluoromethyl)sulfane (4p):

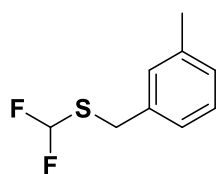


According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μmol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μmol, 2.00 equiv) and benzyl mercaptan (**3p**) (23.4 μL, 24.8 mg, 200 μmol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4p** (19.1 mg, 110 μmol, 55%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 3.94 (s, 2H), 6.65 (t, *J* = 56.6 Hz, 1H), 7.16–7.30 (m, 5H) ppm. **¹³C-NMR**: (75 MHz, CDCl₃, 300 K): δ = 31.9 (CH₂), 120.4 (t, *J* = 272.9 Hz, CF₂H), 127.8 (CH, C_{Ar}), 128.9 (2 × CH, C_{Ar}), 129.0 (2 × CH, C_{Ar}), 136.4 (C_q, C_{Ar}) ppm. **¹⁹F-NMR**: (282 MHz, CDCl₃, 300 K): –94.4 (s, 2F) ppm. **HRMS (APCI)**: Exact mass calculated for C₈H₈F₂SAg⁺ ([M + Ag]⁺): 280.9360, 282.9357. Found: 280.9359, 282.9361.

Spectral data obtained are in accordance with the reported data.¹⁰

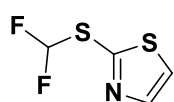
(Difluoromethyl)(3-methylbenzyl)sulfane (4q):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μmol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μmol, 2.00 equiv) and *m*-tolylmethanethiol (**3q**) (27.6mg, 200 μmol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane) afforded the desired product **4q** (25.9 mg, 138 μmol, 69%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ 2.36 (s, 3H), 3.99 (s, 2H), 6.74 (t, *J* = 56.7 Hz, 1H), 7.08–7.19 (m, 3H), 7.20–7.27 (m, 1H) ppm. **¹³C-NMR**: (75 MHz, CDCl₃, 300 K): δ = 21.5 (CH₃), 31.9 (t, *J* = 3.6 Hz, CH₂), 120.5 (t, *J* = 272.8 Hz, CF₂H), 126.1 (CH, C_{Ar}), 128.6 (CH, C_{Ar}), 128.8 (CH, C_{Ar}), 129.7 (CH, C_{Ar}), 136.2 (C_q, C_{Ar}), 138.7 (C_q, C_{Ar}) ppm. **¹⁹F-NMR**: (282 MHz, CDCl₃, 300 K): –94.5 (s, 2F) ppm. **IR** (neat): ν (cm^{–1}): 2926 (vw), 1610 (vw), 1490 (w), 1324 (w), 1257 (vw), 1235 (vw), 1058 (m), 1023 (m), 923 (vw), 882 (vw), 784 (m), 770 (m), 711 (m). **EI MS**, m/z (%): 188 (28) [M]⁺, 105 (100) [M–SCF₂H]⁺.

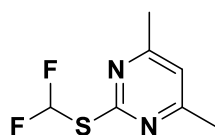
2-((Difluoromethyl)thio)thiazole (**4r**):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)phosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and thiazole-2-thiol (**3r**) (23.4 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 80/20) afforded the desired product **4r** (18.3 mg, 109 μ mol, 55%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 7.23 (t, J = 56.5 Hz, 1H), 7.49 (d, J = 3.4 Hz, 1H), 7.89 (d, J = 3.4 Hz, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 120.3 (t, J = 278.1 Hz, CF₂H), 123.8 (CH, C_{Ar}), 144.5 (CH, C_{Ar}), 153.4 (C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): -92.7 (s, 2F) ppm. **IR** (neat): ν (cm⁻¹): 3120 (vw), 1471 (w), 1355 (vw), 1312 (w), 1291 (w), 1078 (m), 1052 (m), 1023 (s), 783 (m), 745 (m). **EI MS**, m/z (%): 167 (31) [M]⁺, 117 (100), 72 (35).

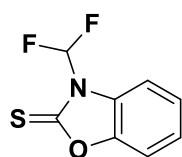
2-((Difluoromethyl)thio)-4,6-dimethylpyrimidine (**4s**):



According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and 4,6-dimethylpyrimidine-2-thiol (**3s**) (28.0 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 85/15) afforded the desired product **4s** (30.8 mg, 162 μ mol, 81%) as a colourless liquid.

¹H-NMR: (300 MHz, CDCl₃, 300 K): δ = 2.42 (s, 6H), 6.80 (s, 1H), 7.84 (t, J = 56.0 Hz, 1H) ppm. **¹³C-NMR:** (75 MHz, CDCl₃, 300 K): δ = 23.9 (2 \times CH₃), 117.5 (CH, C_{Ar}), 121.3 (t, J = 269.3 Hz, CF₂H), 166.7 (C_q, C_{Ar}), 168.0 (2 \times C_q, C_{Ar}) ppm. **¹⁹F-NMR:** (282 MHz, CDCl₃, 300 K): -99.1 (s, 2F) ppm. **IR** (neat): ν (cm⁻¹): 1585 (s), 1532 (m), 1437 (w), 1371 (w), 1290 (w), 1062 (s), 1046 (s), 951 (w), 887 (m), 856 (w), 785 (m). **HRMS (APCI):** Exact mass calculated for C₇H₉F₂N₂S⁺ ([M + H]⁺): 191.0449. Found: 191.0449.

3-(Difluoromethyl)benzo[d]oxazole-2(3H)-thione (**4t**):



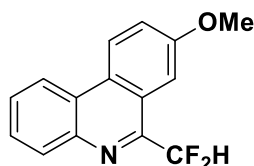
According to **GP1** with NaH (60% in oil, 16.0 mg, 400 μ mol, 2.00 equiv), (difluoromethyl)triphenylphosphonium bromide (157 mg, 400 μ mol, 2.00 equiv) and benzo[d]oxazole-2-thiol (**3t**) (30.2 mg, 200 μ mol, 1.00 equiv) in DMF (1 mL). FC on silica gel (pentane/Et₂O 80/20) afforded the desired product **4t** (33.4 mg, 166 μ mol, 83%) as a colourless solid.

MP (CDCl₃): 76 °C. **¹H-NMR**: (300 MHz, CDCl₃, 300 K): δ = 7.26–7.53 (m, 4H), 7.74 (t, *J* = 58.4 Hz, 1H) ppm. **¹³C-NMR**: (75 MHz, CDCl₃, 300 K): δ = 110.9 (CH, C_{Ar}), 111.1 (t, *J* = 251.7 Hz, CF₂H), 111.6 (2 × CH, C_{Ar}), 125.8 (CH, C_{Ar}), 127.3 (C_q, C_{Ar}), 146.9 (C_q, C_{Ar}), 179.1 (C_q, C_{Ar}) ppm. **¹⁹F-NMR**: (282 MHz, CDCl₃, 300 K): –104.1 (s, 2F) ppm. **HRMS (APCI)**: Exact mass calculated for C₈H₅F₂NOS⁺ ([M + H]⁺): 202.0133. Found: 202.0132.

Spectral data obtained are in accordance with the reported data.⁶

6. Difluoromethylation of isonitrile and benzofuran

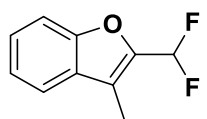
6-(Difluoromethyl)-8-methoxyphenanthridine (9):



Na₂HPO₄ (57.0 mg, 400 μmol, 2.00 equiv) and Ir(ppy)₃ (2.6 mg, 4.0 μmol, 2 mol%) were added to a suspension of 2-isocyano-4'-methoxy-1,1'-biphenyl (41.9 mg, 200 μmol, 1.00 equiv) and (difluoromethyl)triphenylphosponium bromide (156 mg, 400 μmol, 2.00 equiv) in DMF (2 mL). The reaction mixture was irradiated by blue LED overnight. The reaction was quenched by addition of brine (10 mL) and Et₂O (15 mL). The aqueous layer was extracted with Et₂O (2 × 20 mL), the combined organic layers were dried over MgSO₄ and the solvent was removed under reduced pressure. Purification of the crude material *via* FC (pentane/Et₂O 95/5) afforded the title compound **9** (34.8 mg, 134 μmol, 67%) as a yellow solid. **¹H-NMR**: (300 MHz, CDCl₃, 300 K): δ = 4.00 (s, 3H), 7.01 (t, *J* = 54.5 Hz, 1H), 7.50 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.70 (dd, *J* = 6.2, 3.4 Hz, 2H), 7.86–7.91 (m, 1H), 8.12–8.19 (m, 1H), 8.43–8.50 (m, 1H), 8.54 (d, *J* = 9.1 Hz, 1H). **¹³C-NMR**: (75 MHz, CDCl₃, 300 K): δ = 55.7 (CH₃), 106.1 (t, *J* = 4.6 Hz, CH, C_{Ar}), 118.8 (t, *J* = 243.4 Hz, CF₂H), 121.8 (CH, C_{Ar}), 122.4 (CH, C_{Ar}), 123.9 (t, *J* = 2.1 Hz, C_q, C_{Ar}), 124.1 (CH, C_{Ar}), 125.4 (C_q, C_{Ar}), 128.2 (CH, C_{Ar}), 128.4 (C_q, C_{Ar}), 128.8 (CH, C_{Ar}), 130.7 (CH, C_{Ar}), 141.8 (t, *J* = 1.6 Hz, C_q, C_{Ar}), 150.2 (C_q, C_{Ar}), 159.0 (C_q, C_{Ar}) ppm. **¹⁹F-NMR**: (282 MHz, CDCl₃, 300 K): –111.4 (s, 2F) ppm. **HRMS (ESI)**: Exact mass calculated for C₁₅H₁₁NOF₂Na⁺ ([M + Na]⁺): 282.0701. Found: 282.0704.

Spectral data obtained are in accordance with the reported data.¹¹

2-(Difluoromethyl)-3-methylbenzofuran (11):

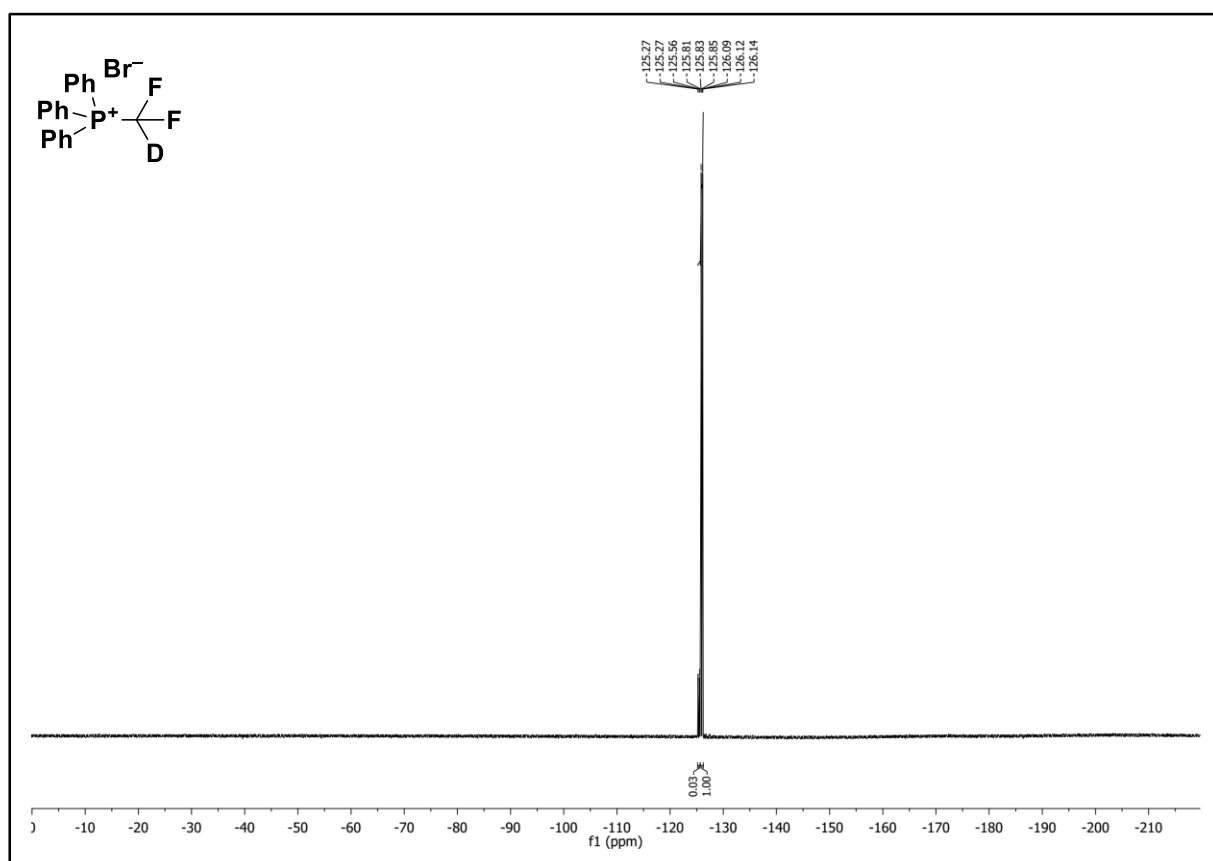
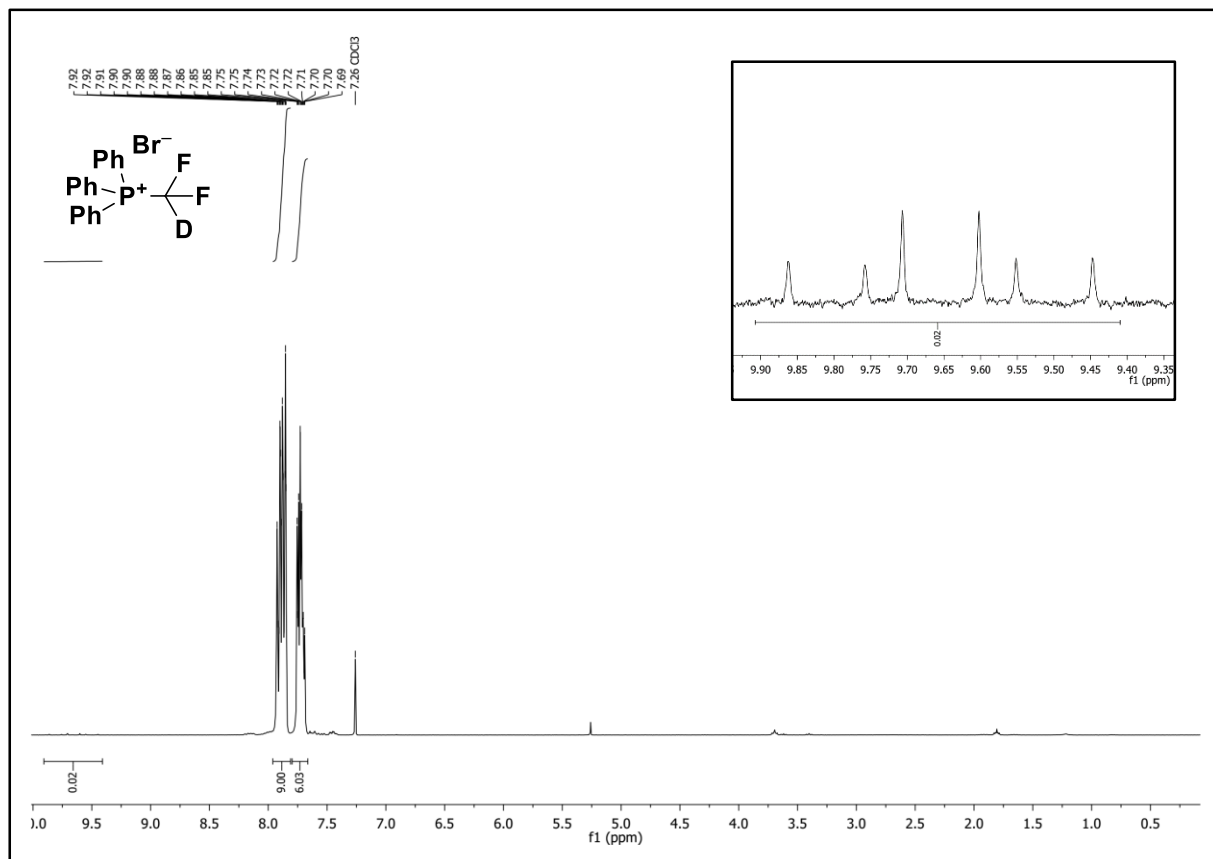


Na_2HPO_4 (57.0 mg, 400 μmol , 2.00 equiv) and $\text{Ir}(\text{ppy})_3$ (2.6 mg, 4.0 μmol , 2 mol%) were added to a suspension of 3-methylbenzofuran (25.0 μL , 26.4 mg, 200 μmol , 1.00 equiv) and (difluoromethyl)triphenylphosphonium bromide (156 mg, 400 μmol , 2.00 equiv) in DMF (2 mL). The reaction mixture was irradiated by blue LED overnight. The reaction was quenched by addition of brine (10 mL) and Et_2O (15 mL). The aqueous layer was extracted with Et_2O (2×20 mL), the combined organic layers were dried over MgSO_4 and the solvent was removed under reduced pressure. Purification of the crude material *via* FC (pentane/ Et_2O 95/5) afforded the title compound **9** (10.4 mg, 57.1 μmol , 29%) as a colourless liquid.

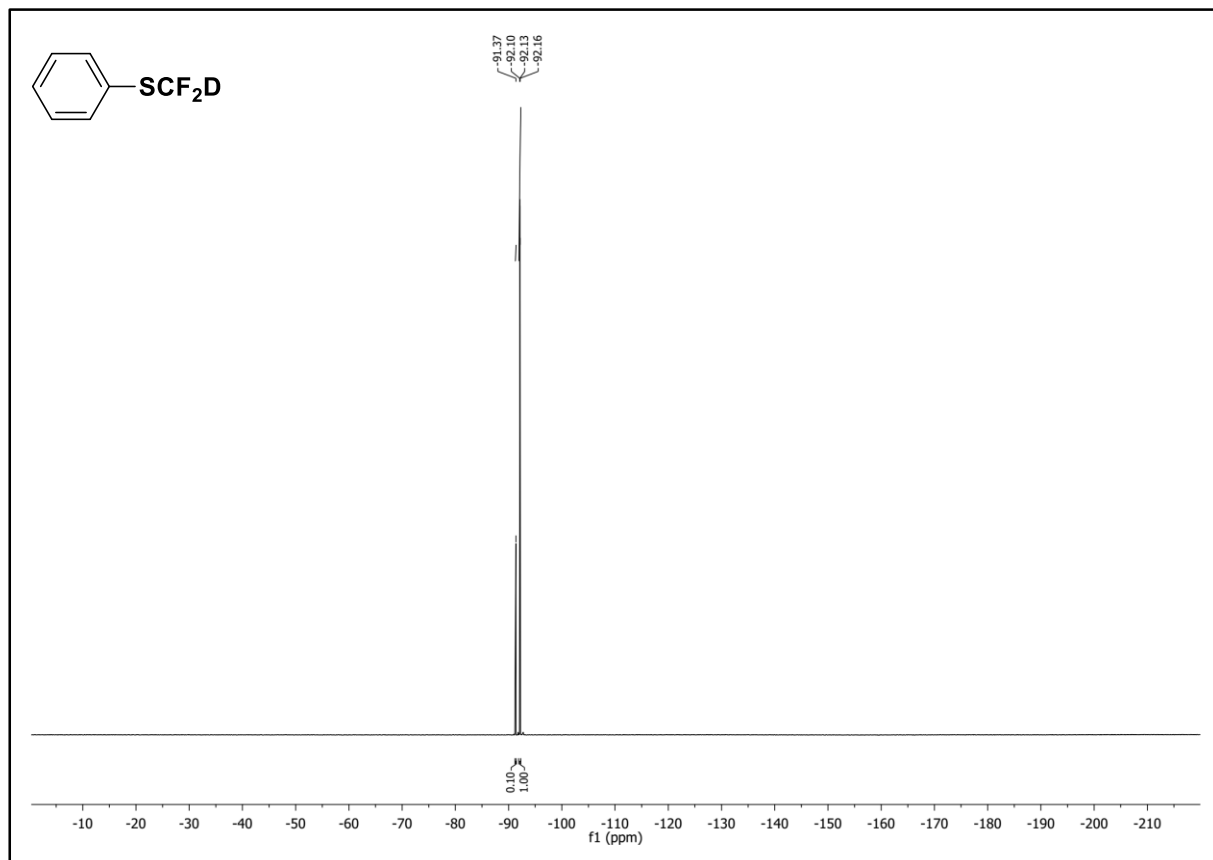
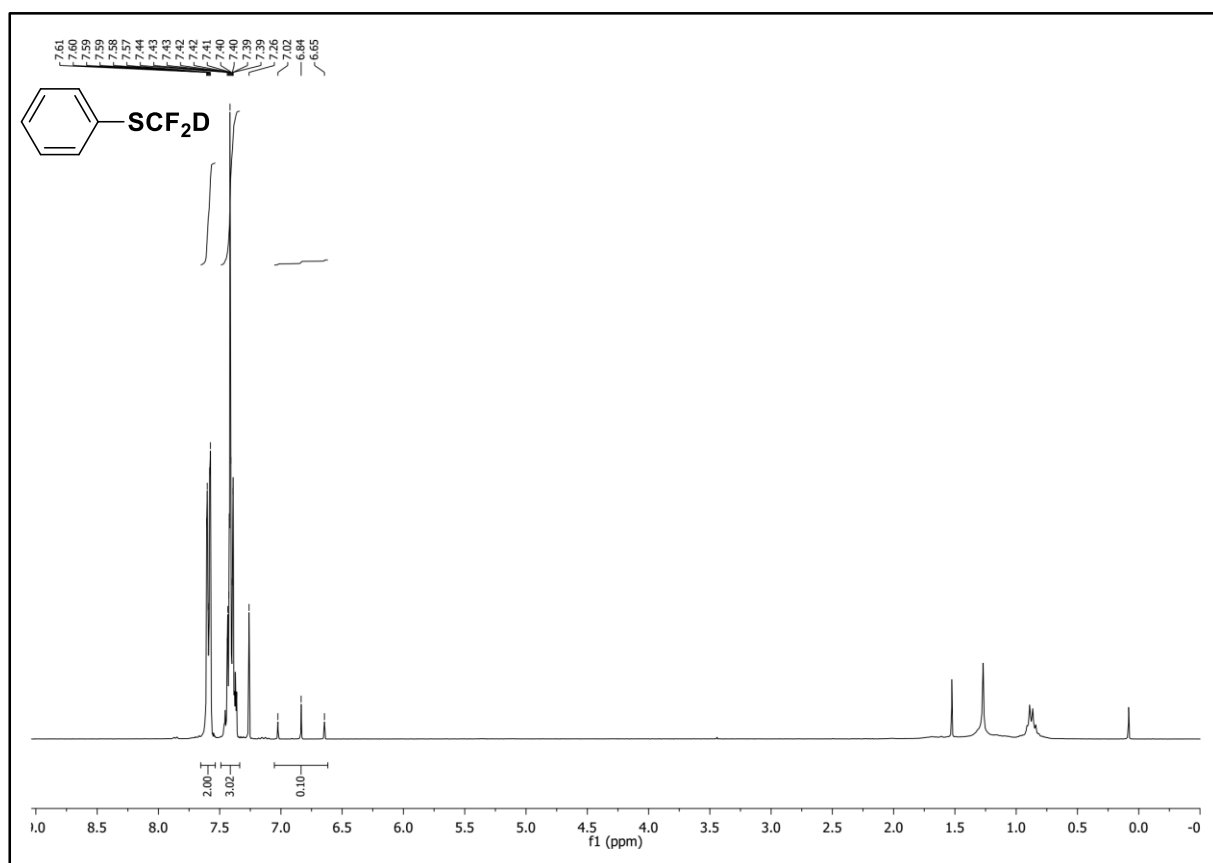
$^1\text{H-NMR}$: (500 MHz, CDCl_3 , 300 K): δ = 2.38 (t, J = 2.7 Hz, 3H), 6.81 (t, J = 53.4 Hz, 1H), 7.30 (ddd, J = 7.9, 7.2, 1.0 Hz, 1H), 7.37–7.41 (m, 1H), 7.50 (dt, J = 8.3, 0.9 Hz, 1H), 7.56–7.59 (m, 1H) ppm. **$^{13}\text{C-NMR}$:** (125 MHz, CDCl_3 , 300 K): δ = 7.7 (CH_3), 109.3 (t, J = 235.2 Hz, CF_2H), 111.9 (CH, C_{Ar}), 117.2 (C_{q} , C_{Ar}), 120.5 (CH, C_{Ar}), 123.1 (CH, C_{Ar}), 126.4 (CH, C_{Ar}), 128.9 (C_{q} , C_{Ar}), 143.2 (C_{q} , C_{Ar}), 154.5 (C_{q} , C_{Ar}) ppm. **$^{19}\text{F-NMR}$:** (282 MHz, CDCl_3 , 300 K): δ = -115.2 (s, 2F) ppm. **IR** (neat): ν (cm^{-1}): 1454 (vw), 1399 (vw), 1265 (w), 1081 (w), 1028 (w), 880 (vw), 799 (vw). **EI MS**, m/z (%): 182 (97) [M] $^+$, 167 (37), 131 (100) [$\text{M}-\text{CF}_2\text{H}$] $^+$.

6. Experimental data for mechanistic experiments

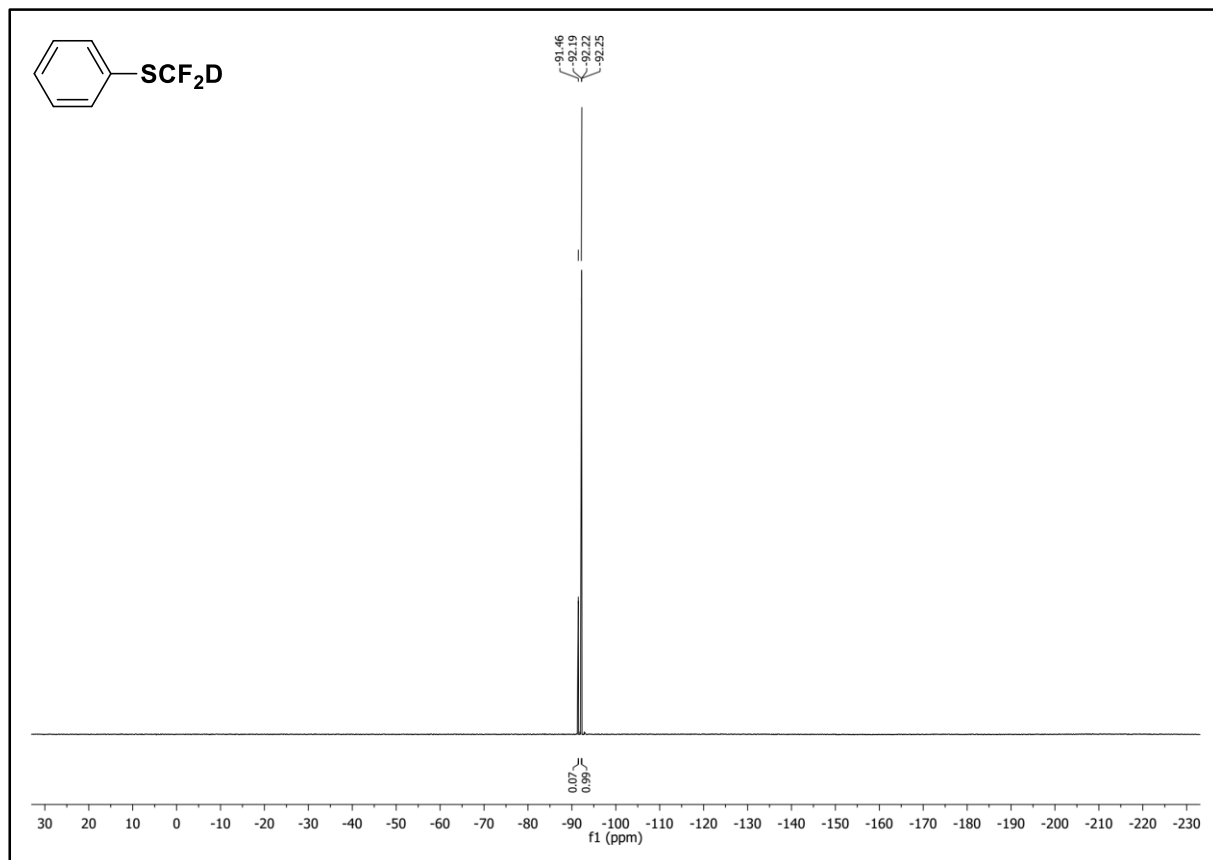
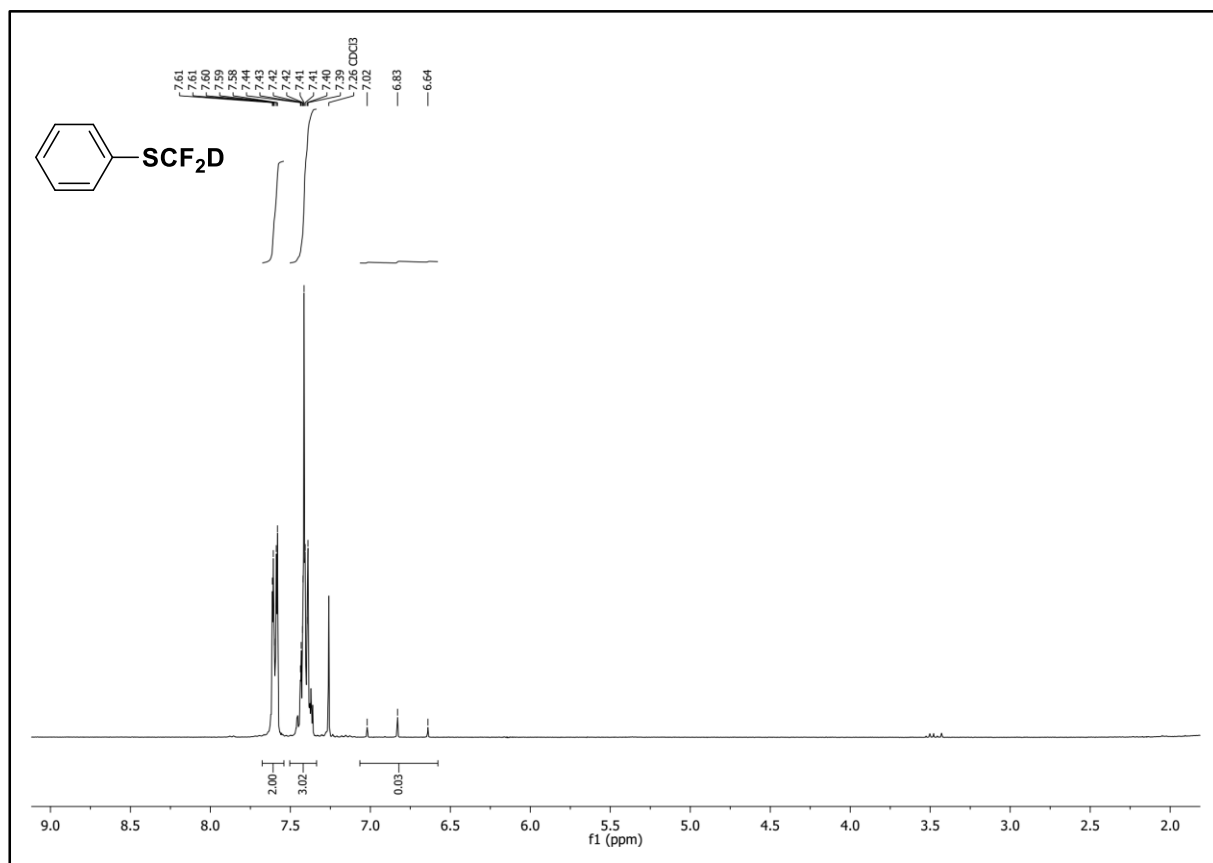
(Difluoromethyl-*d*)triphenylphosphonium bromide (**6**): ^1H , ^{19}F



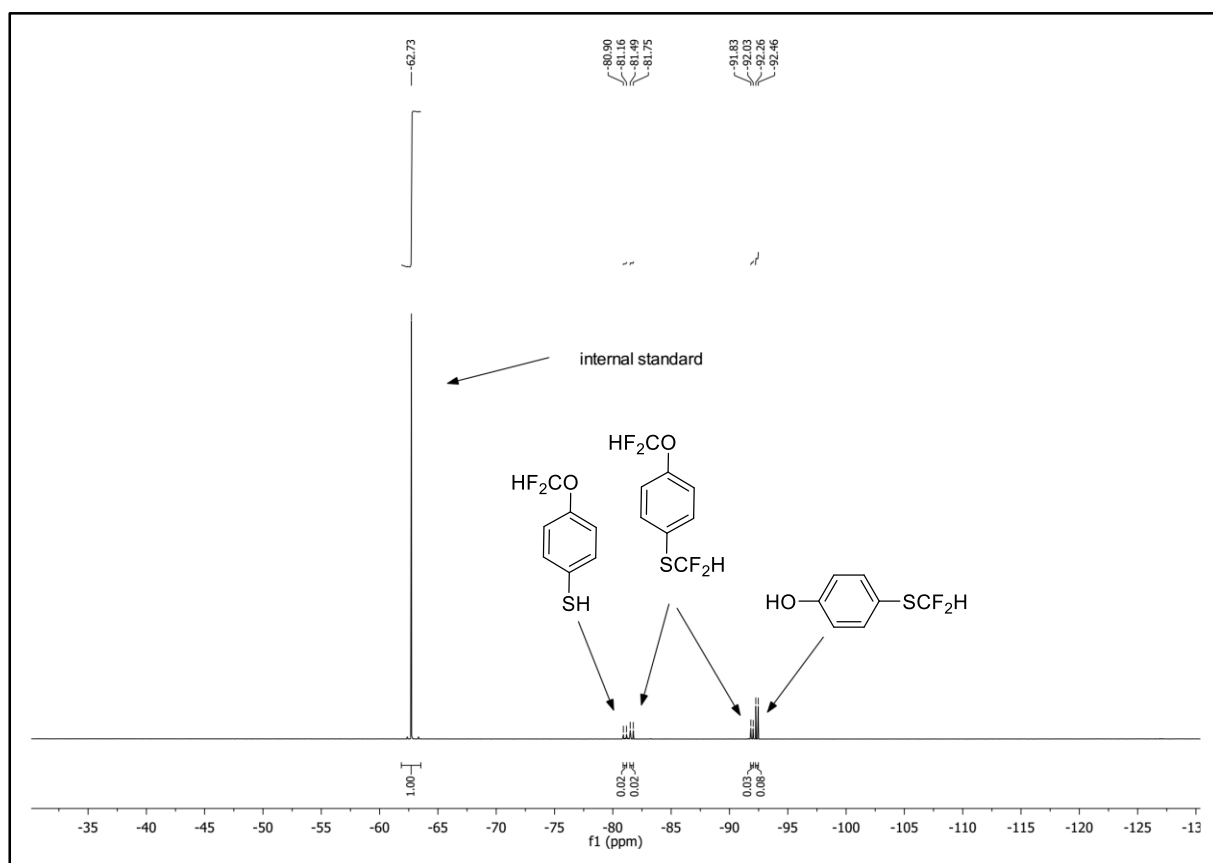
(Difluoromethyl-d)(phenyl)sulfane (**5a**): ^1H , ^{19}F (2 equiv NaH)



(Difluoromethyl-d)(phenyl)sulfane (**5a**): ^1H , ^{19}F (1.5 equiv NaH)

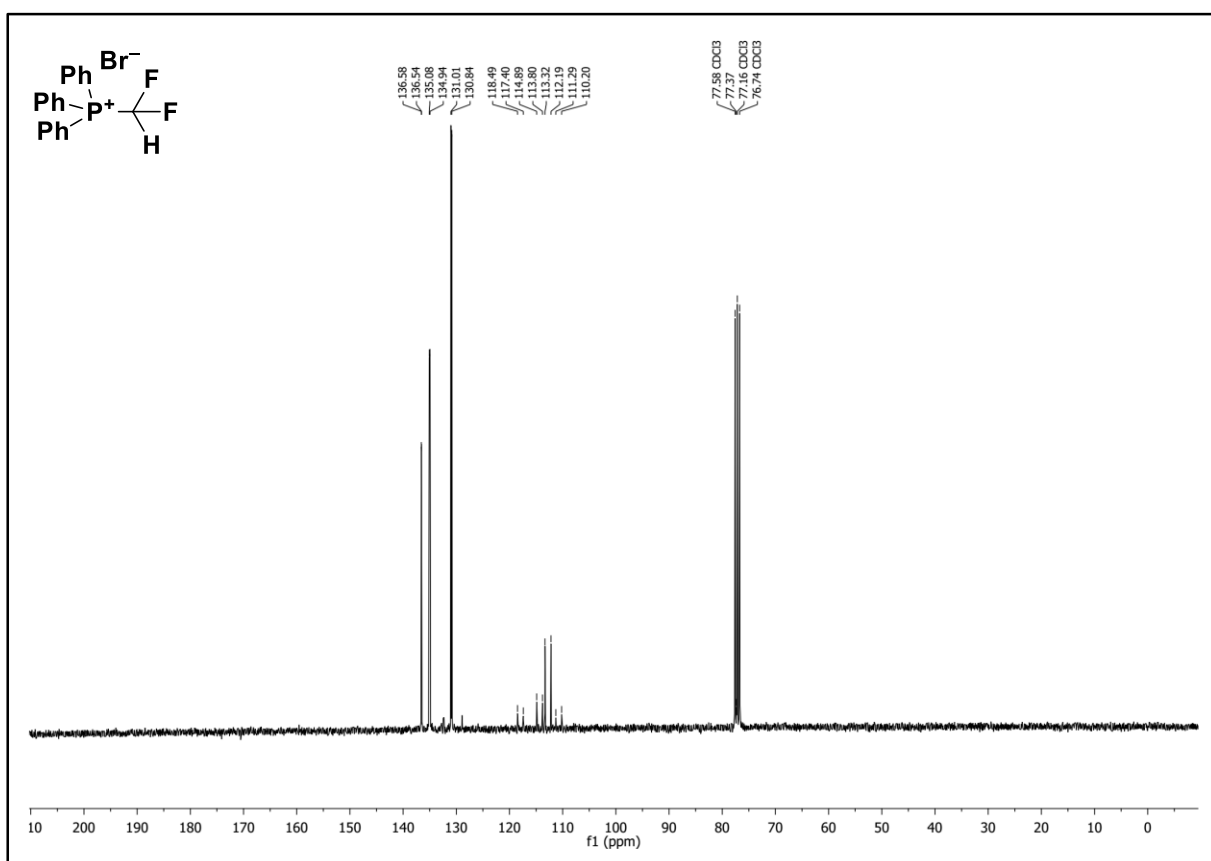
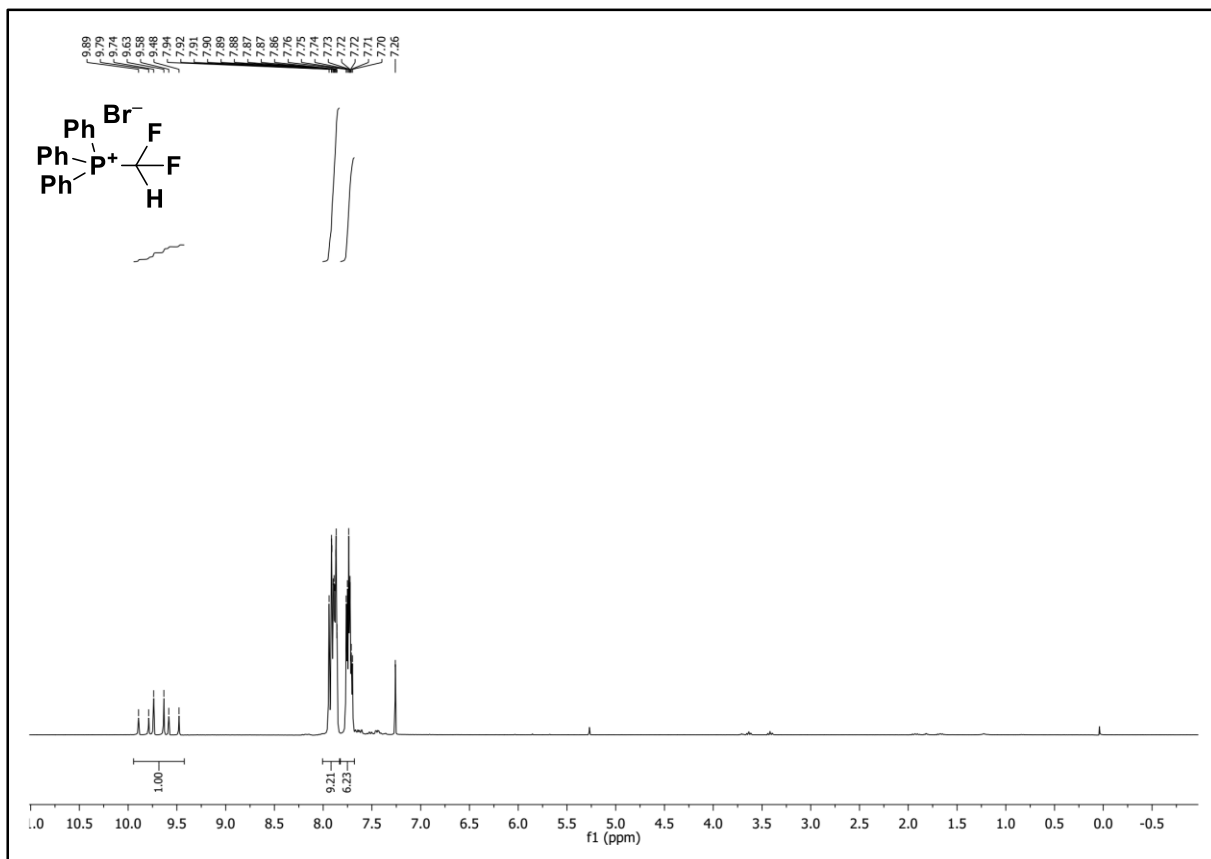


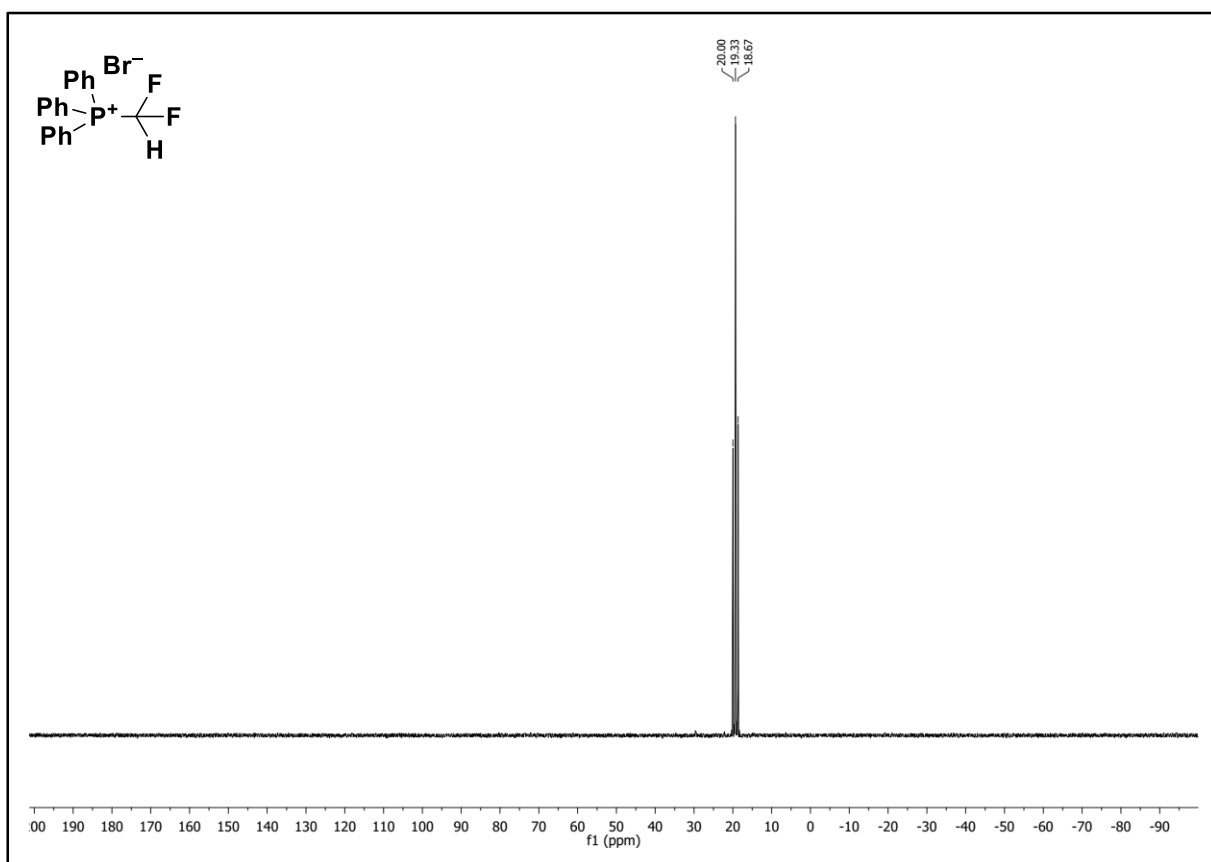
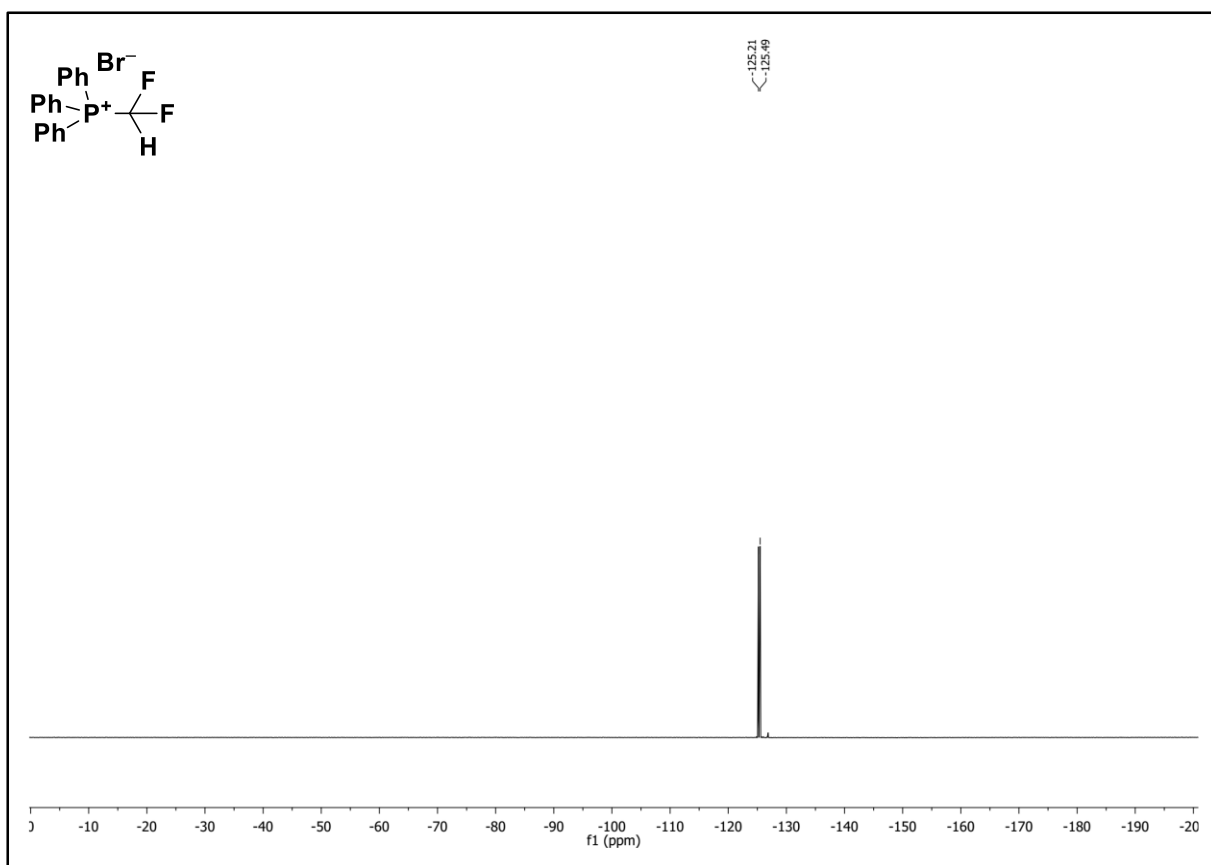
Reaction of **3l** with phosphonium salt **7**:



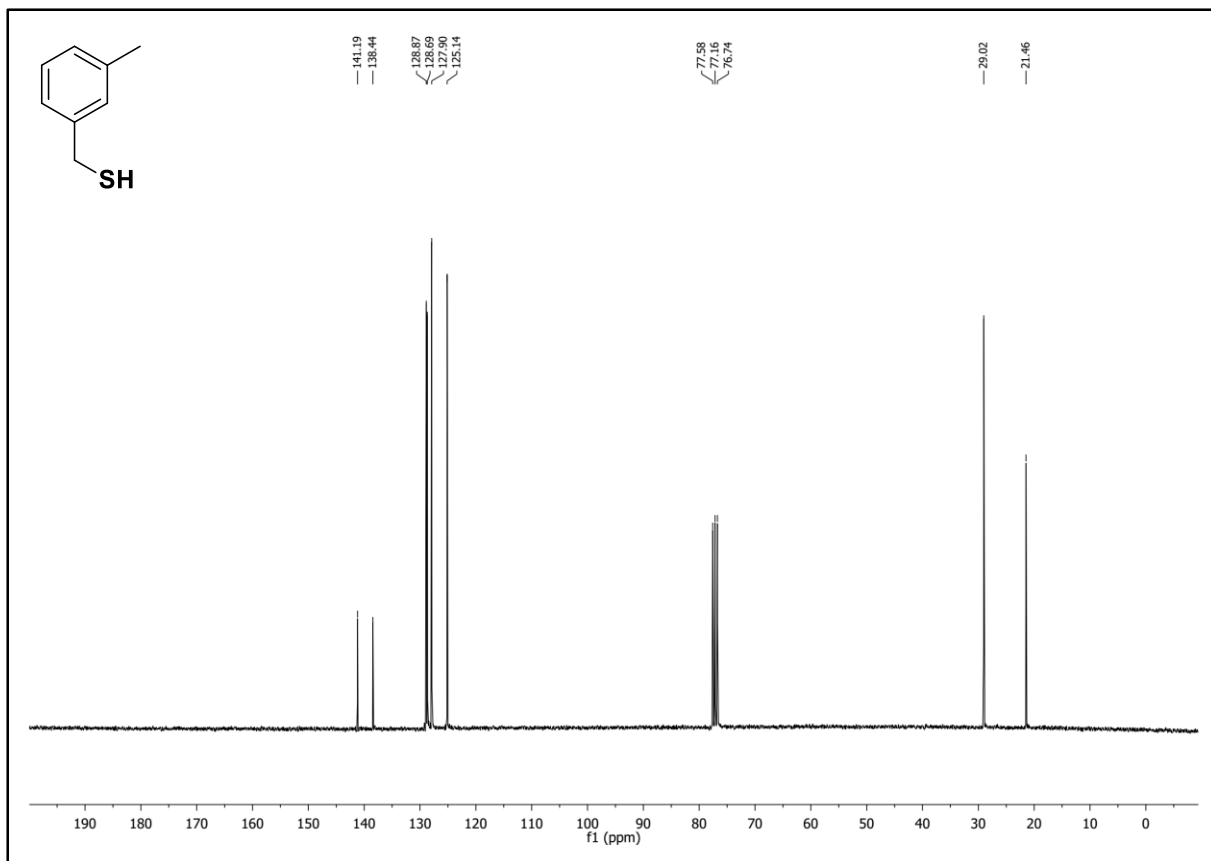
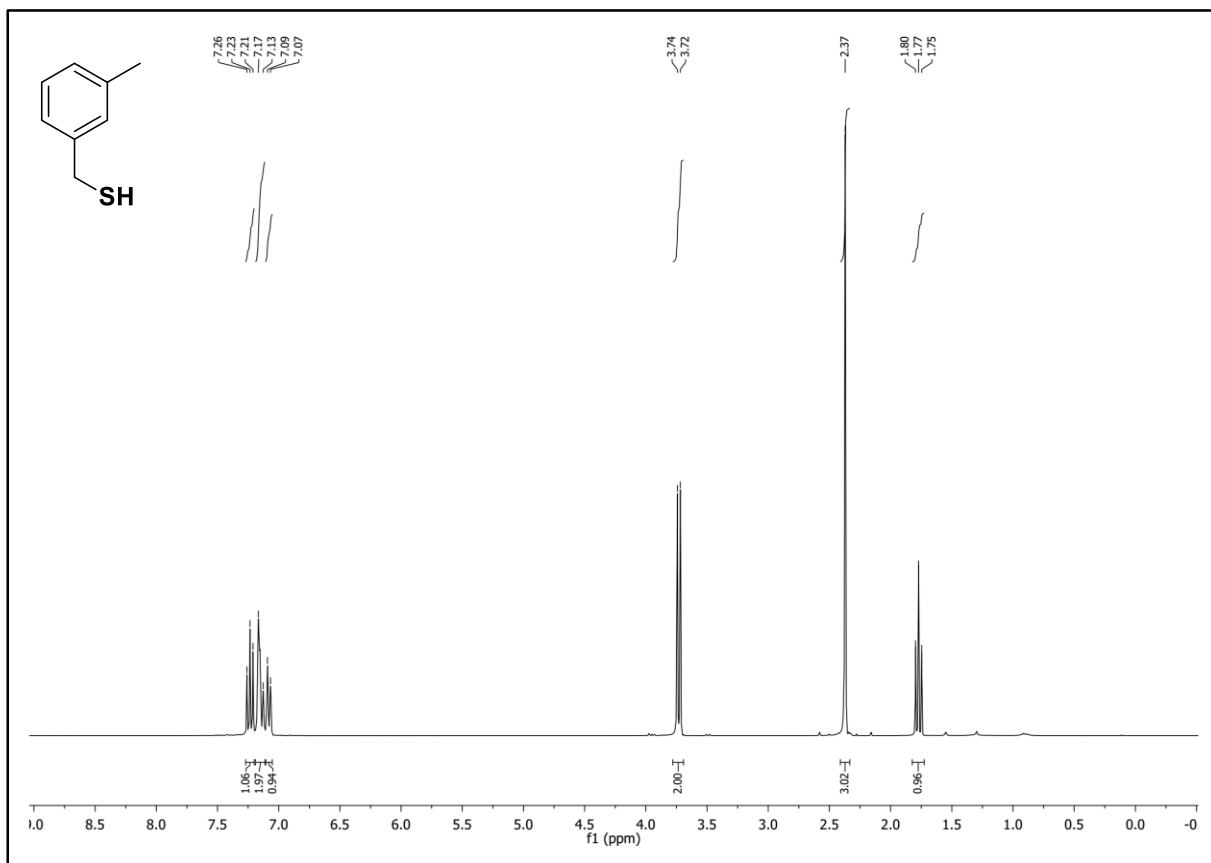
7. Spectra

(Difluoromethyl)triphenylphosphonium bromide (**1**): ^1H , ^{13}C , ^{19}F , ^{31}P

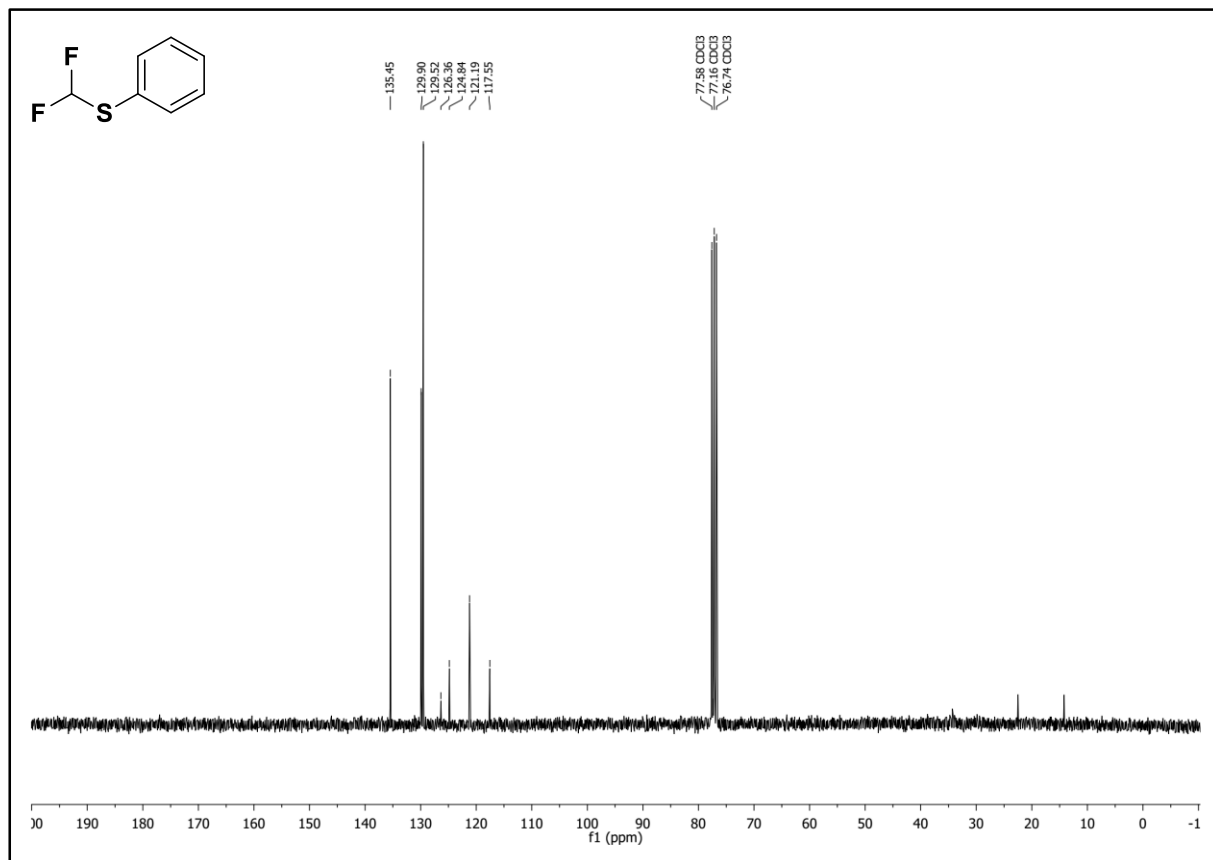
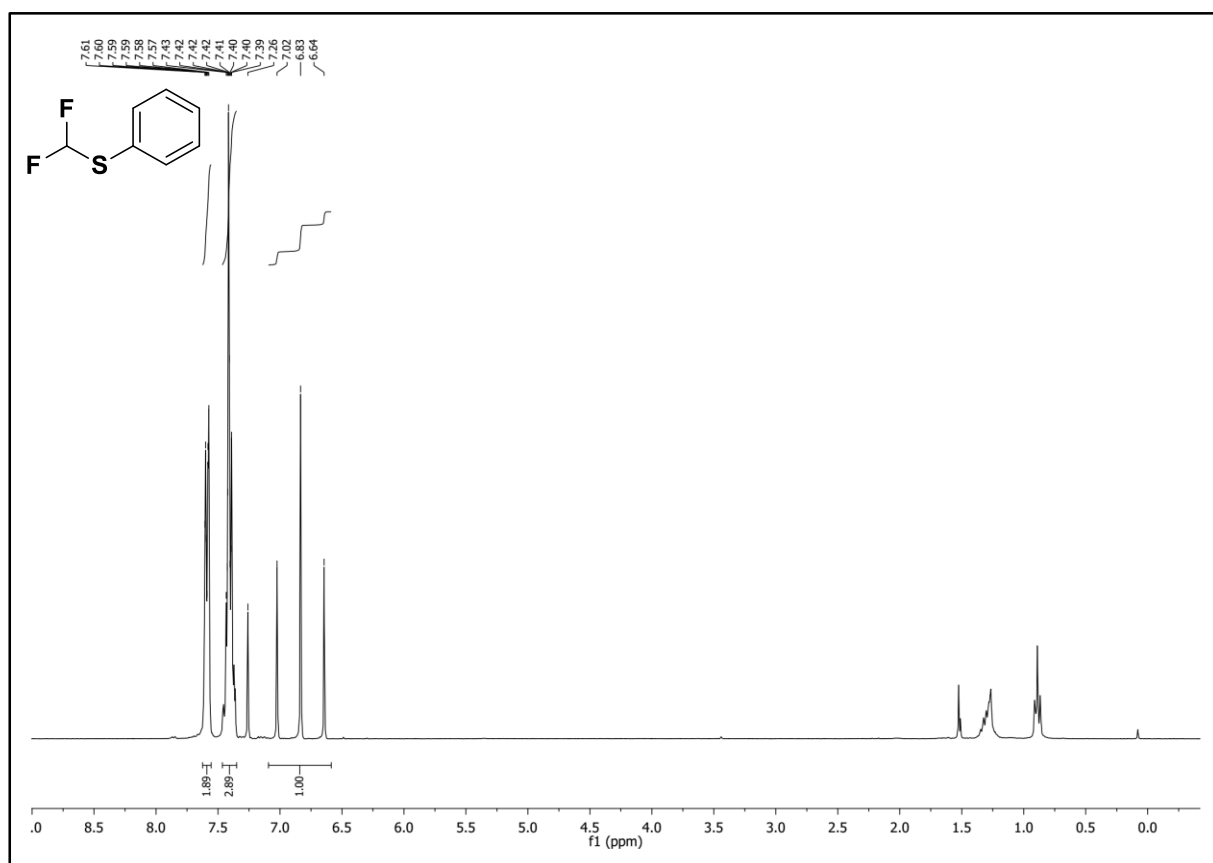


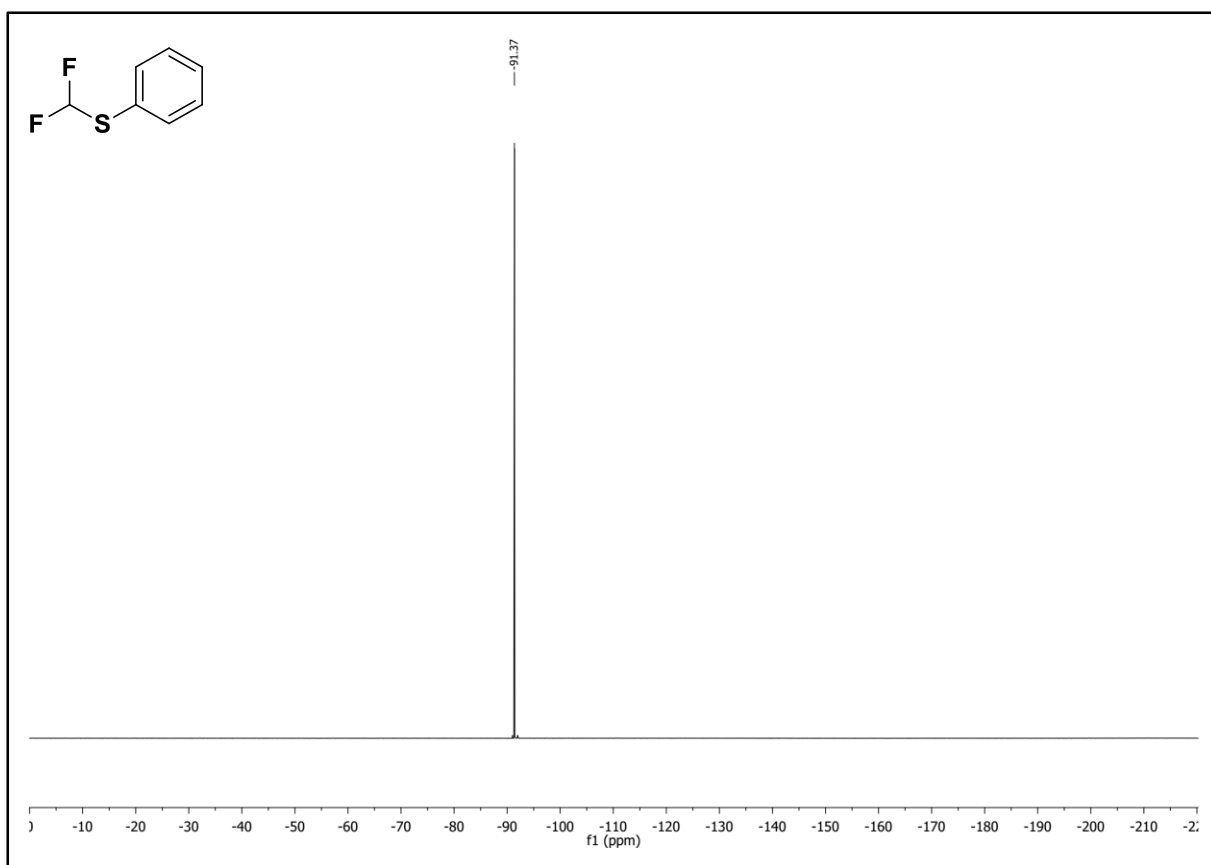


m-Tolylmethanethiol (**3q**): ^1H , ^{13}C

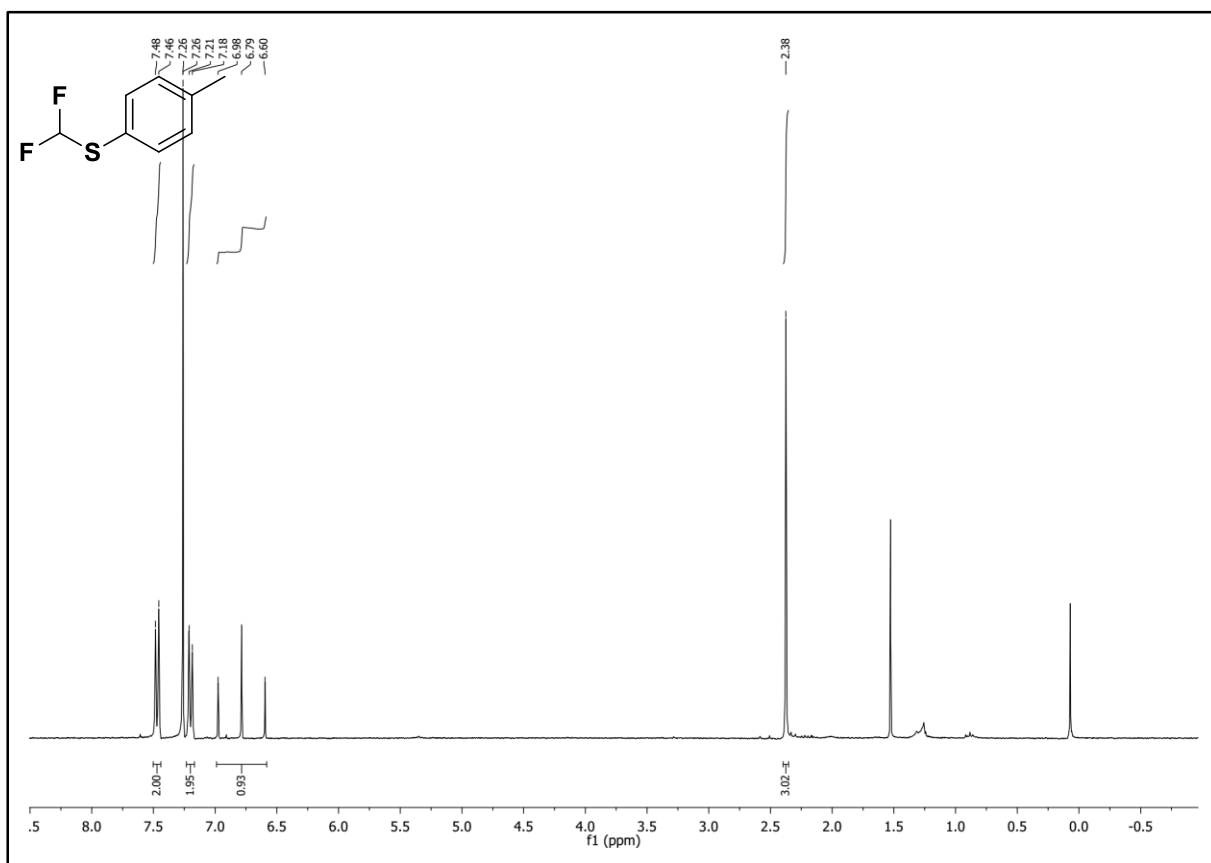


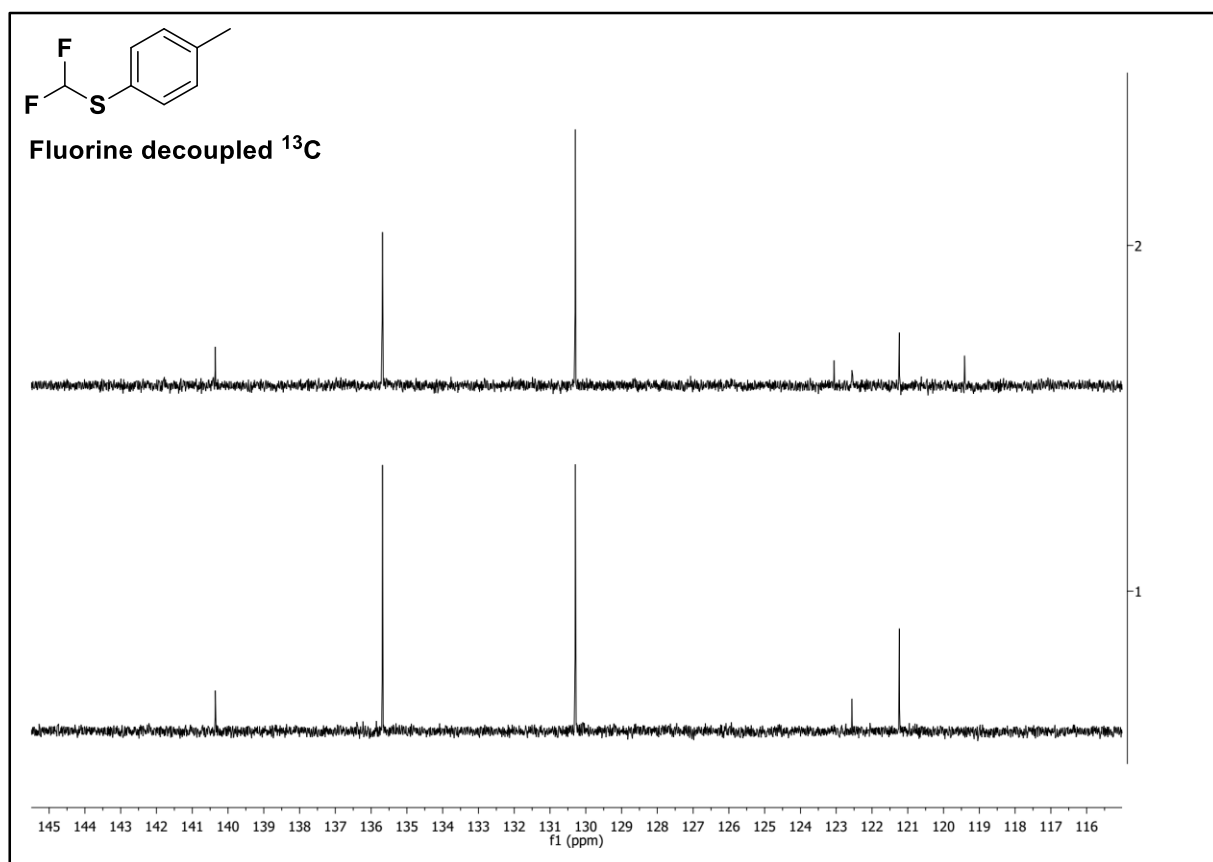
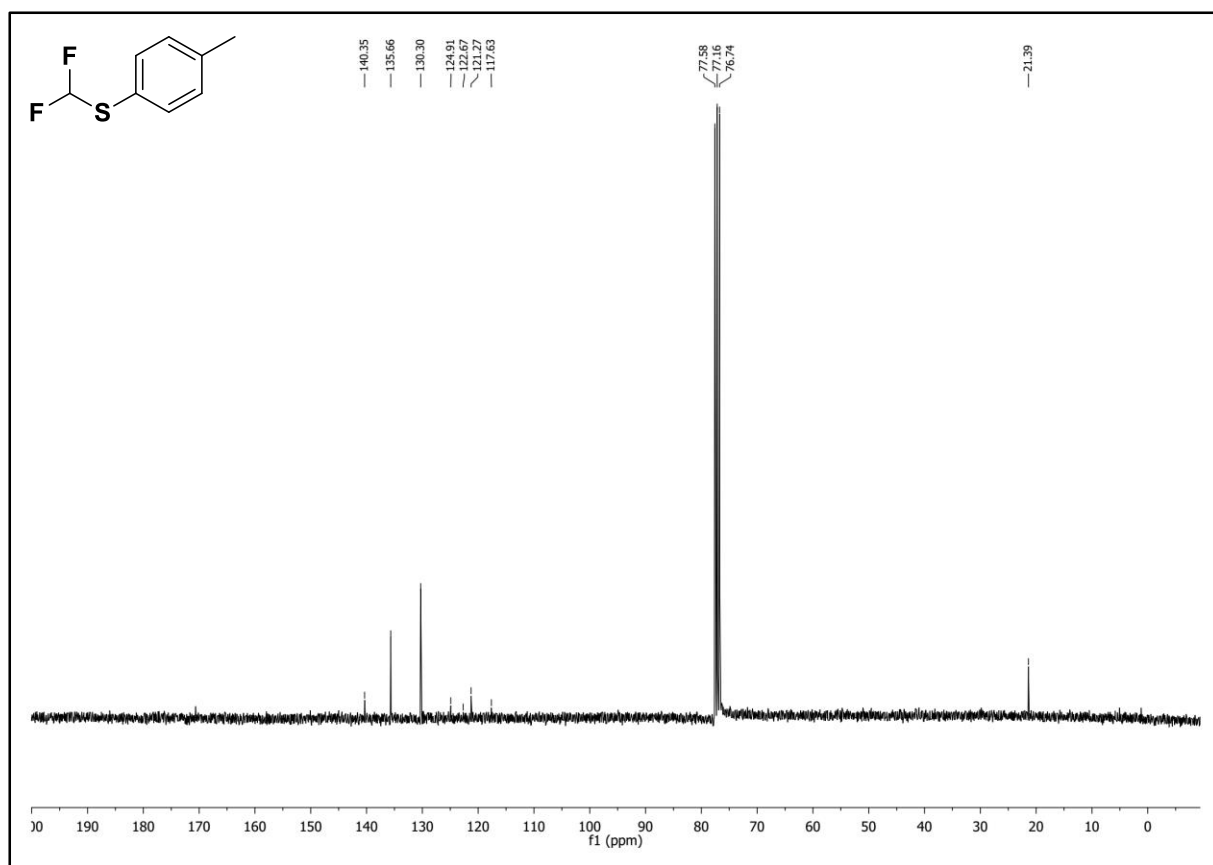
(Difluoromethyl)(phenyl)sulfane (**4a**): ^1H , ^{13}C , ^{19}F

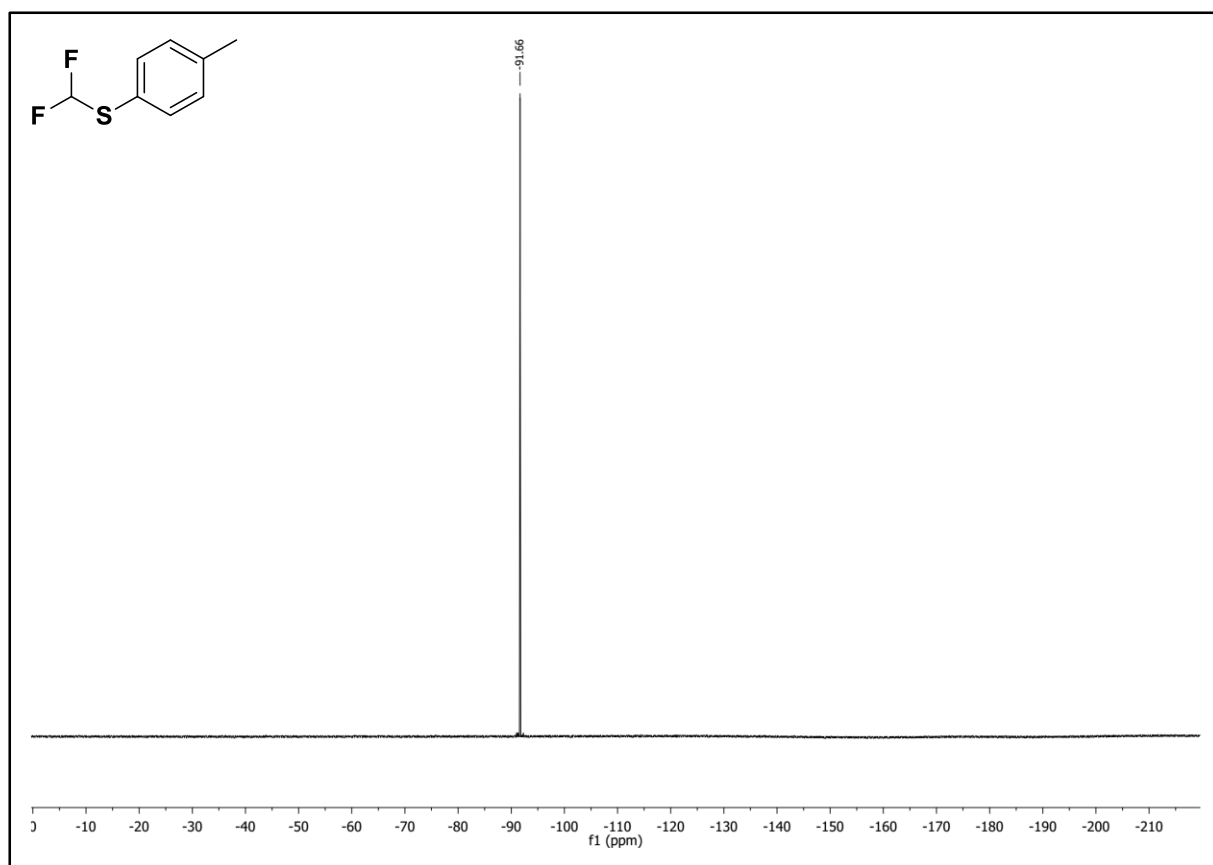




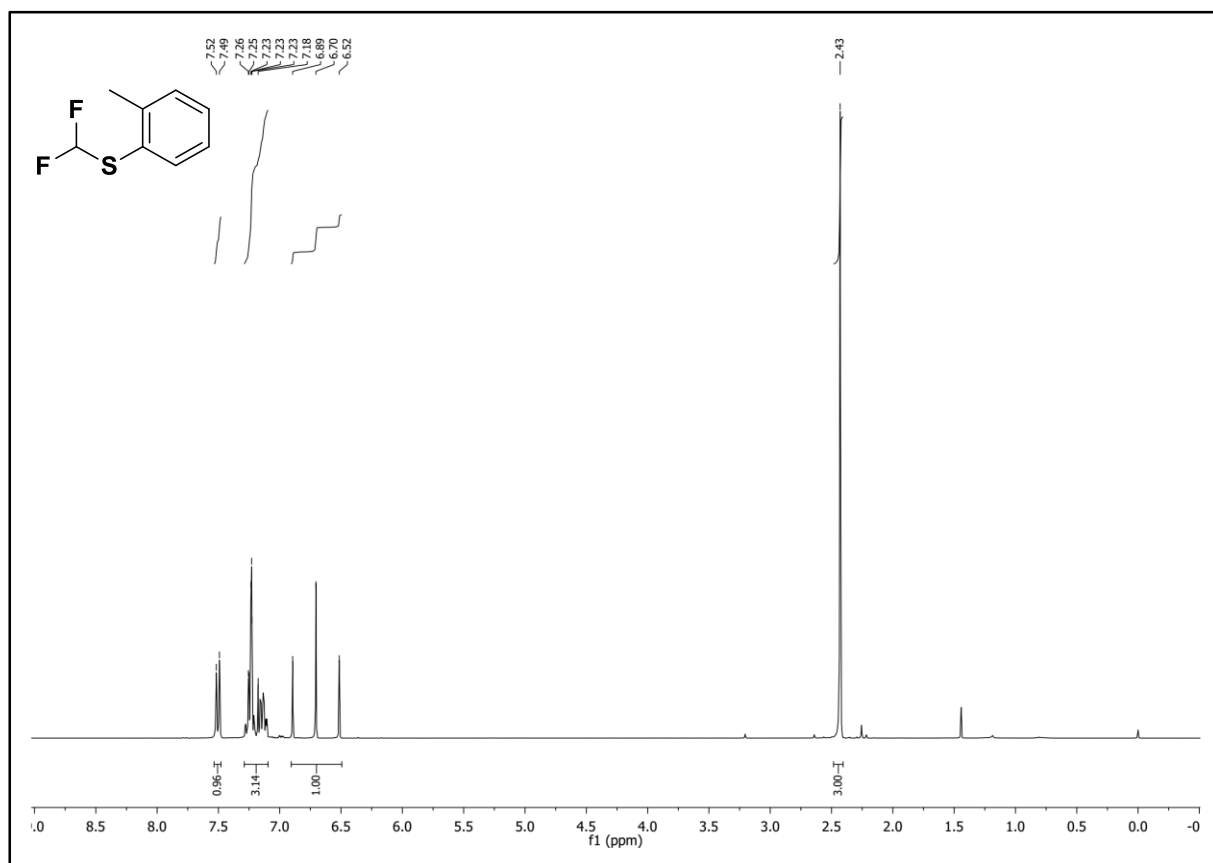
(Difluoromethyl)(*p*-tolyl)sulfane (**4b**): ^1H , ^{13}C , ^{19}F decoupled ^{13}C , ^{19}F

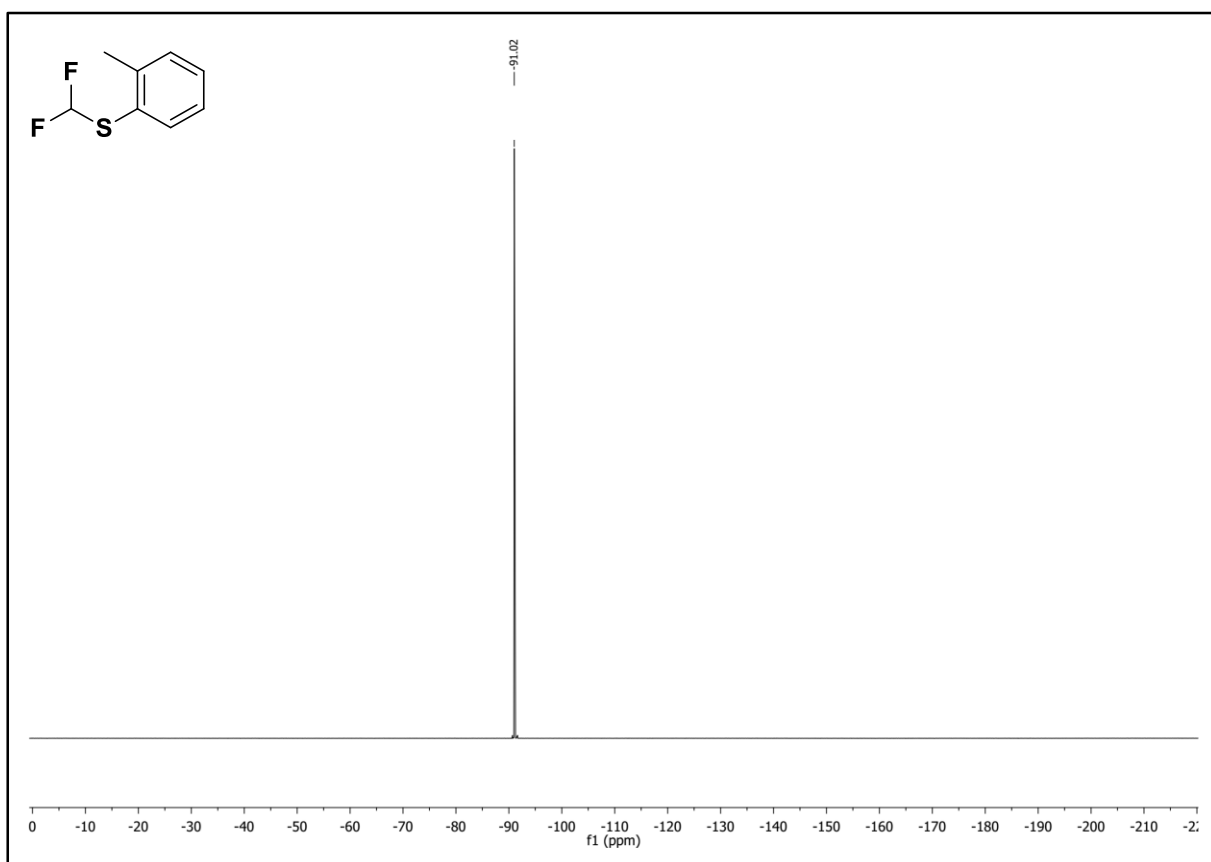
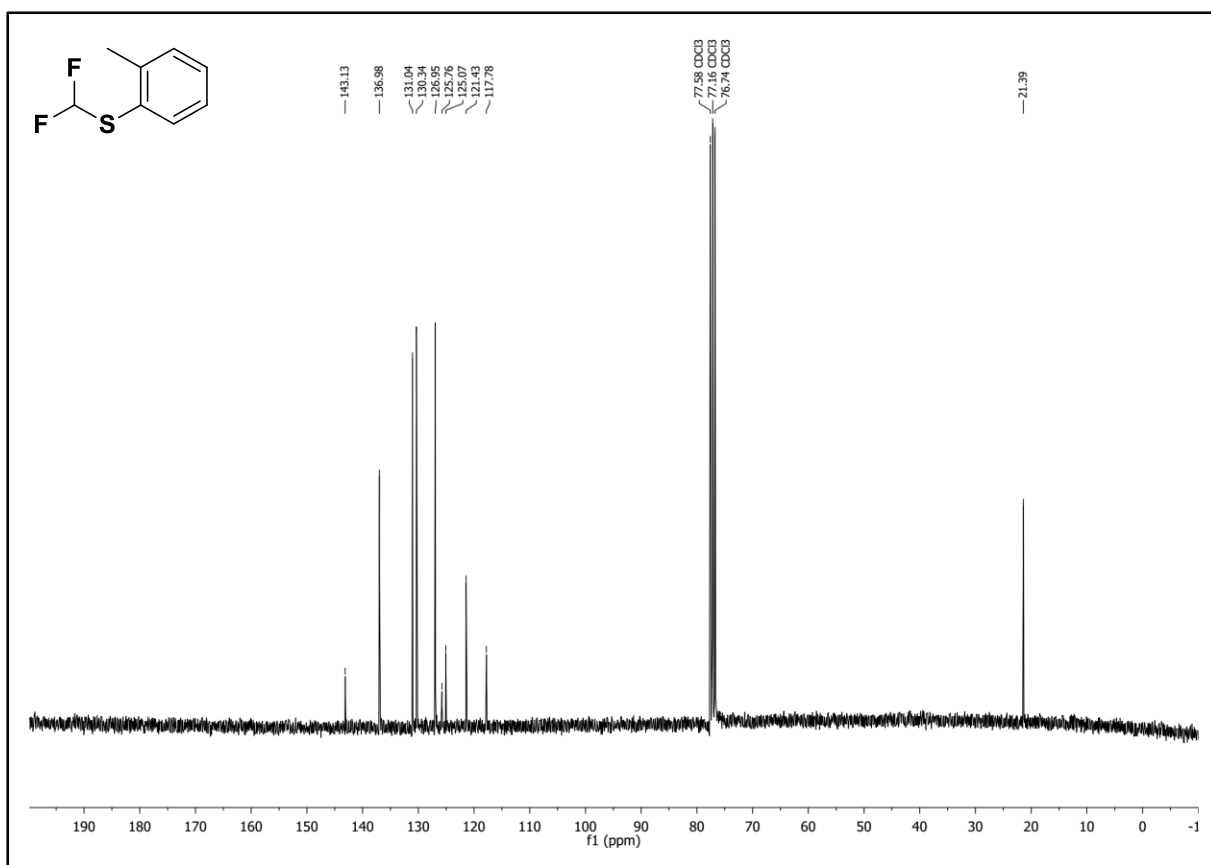




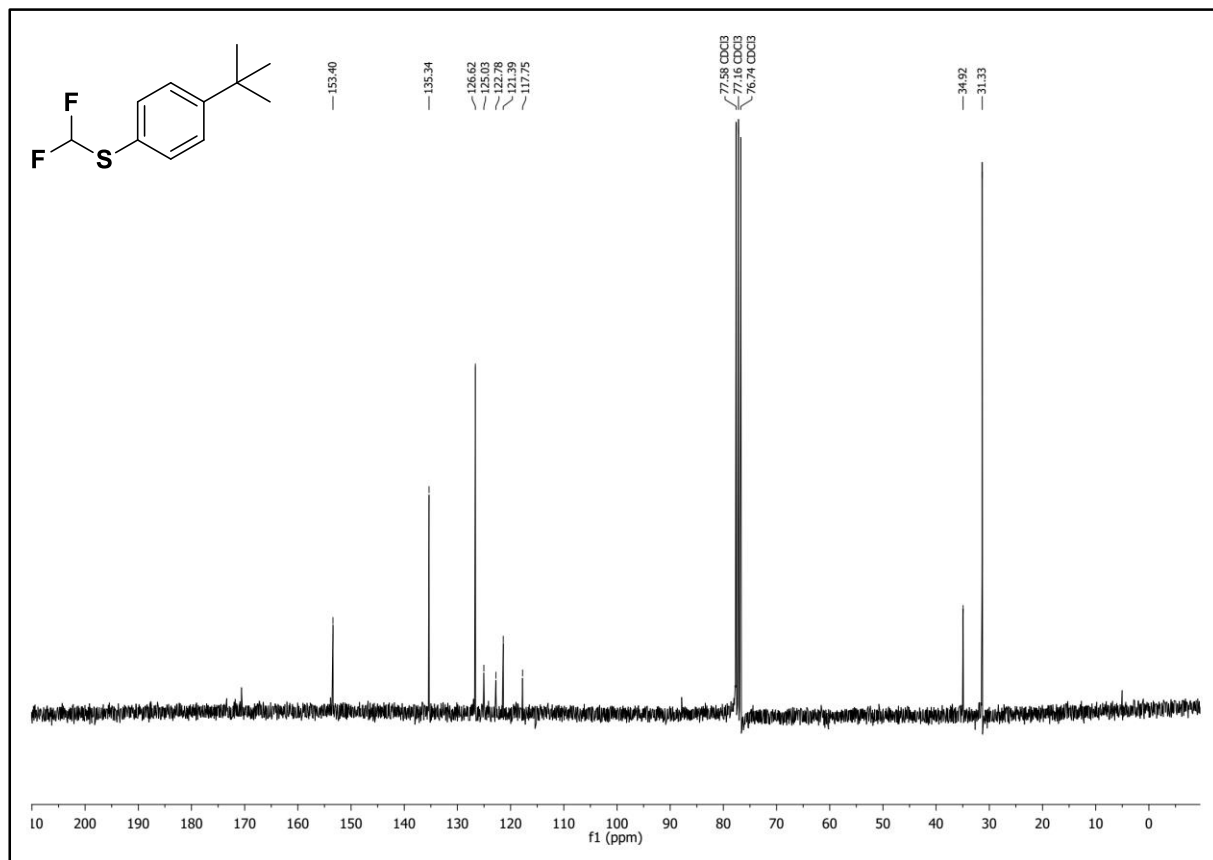
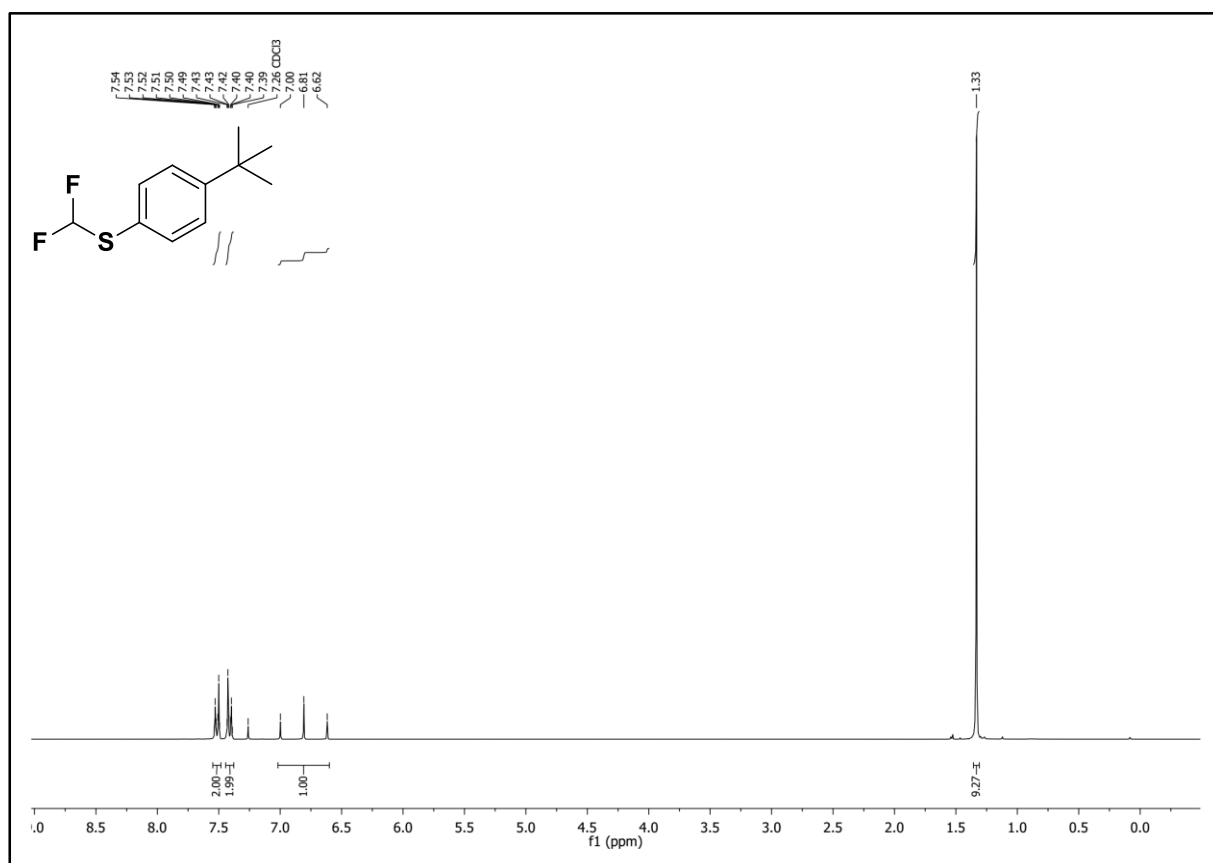


(Difluoromethyl)(*o*-tolyl)sulfane (**4c**): ^1H , ^{13}C , ^{19}F



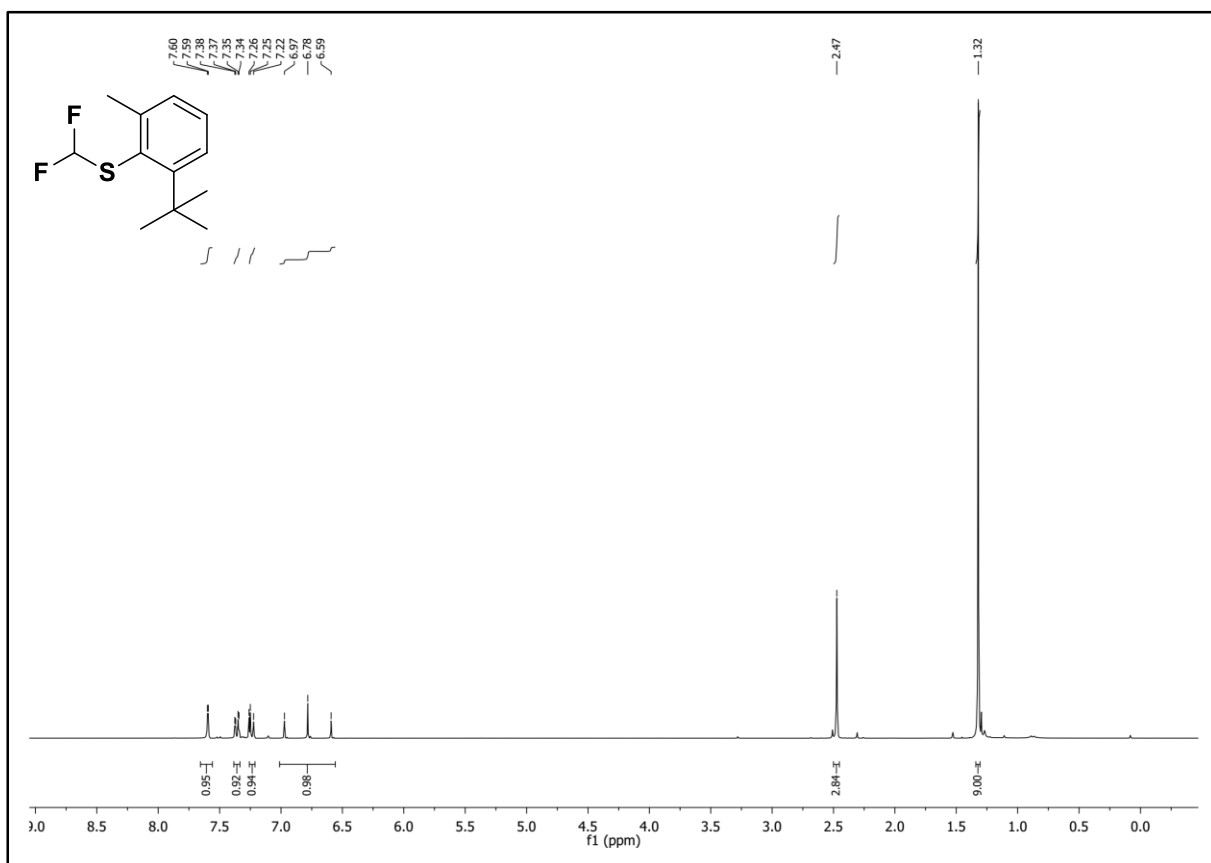


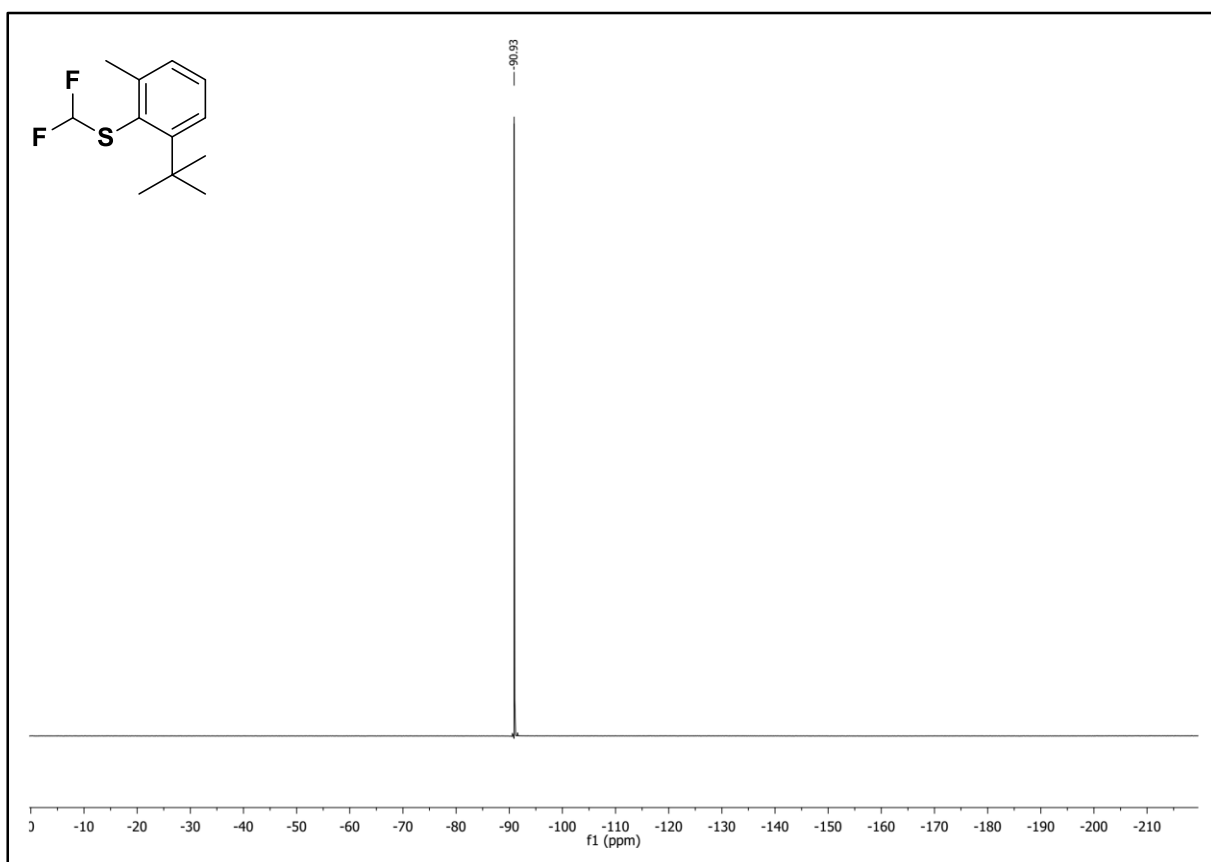
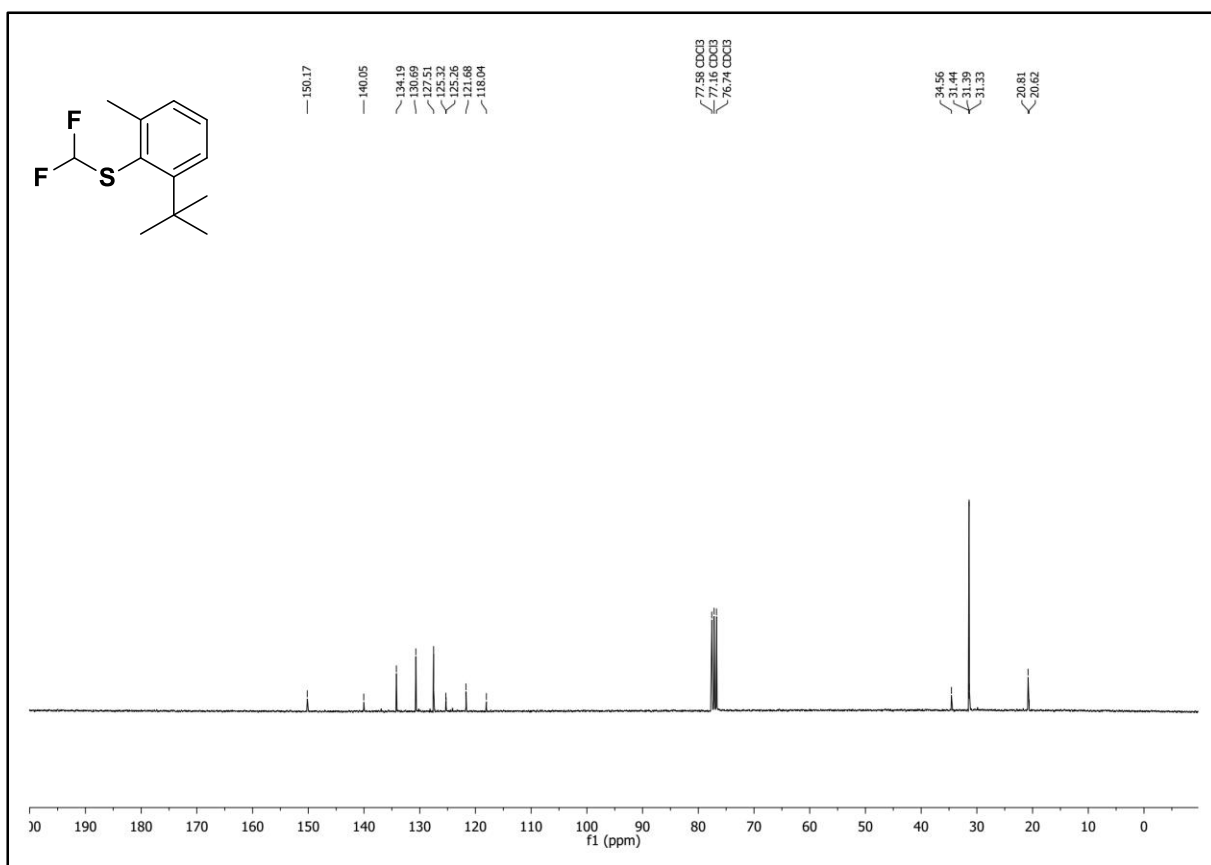
(4-(*tert*-Butyl)phenyl)(difluoromethyl)sulfane (**4d**): ^1H , ^{13}C , ^{19}F



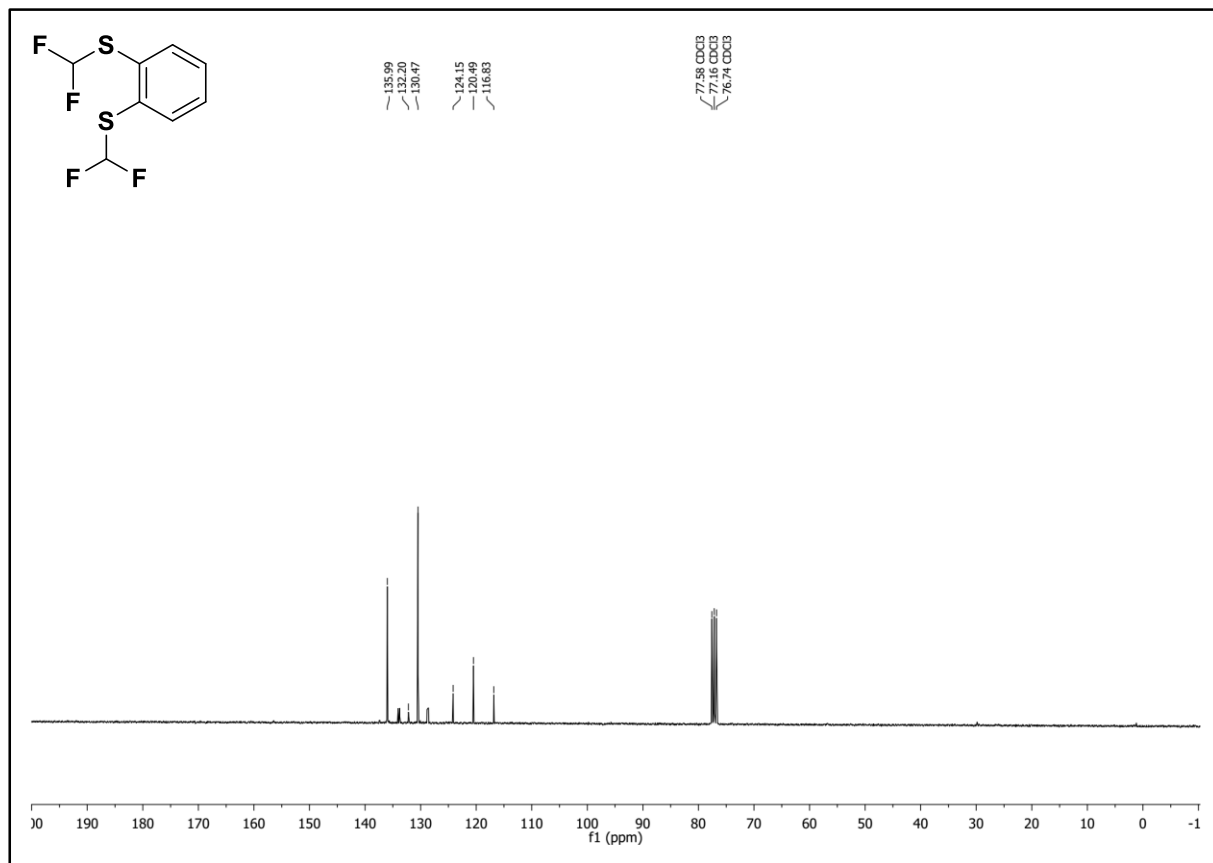
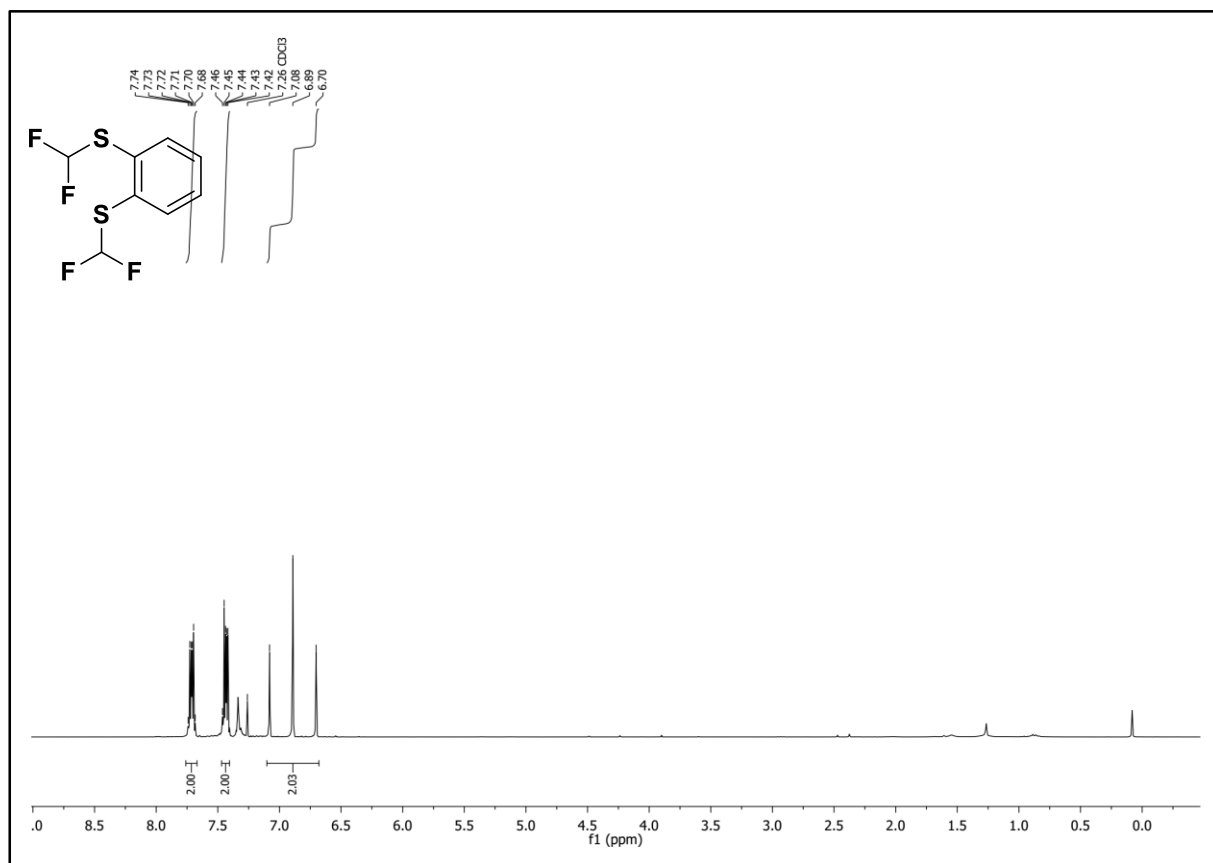


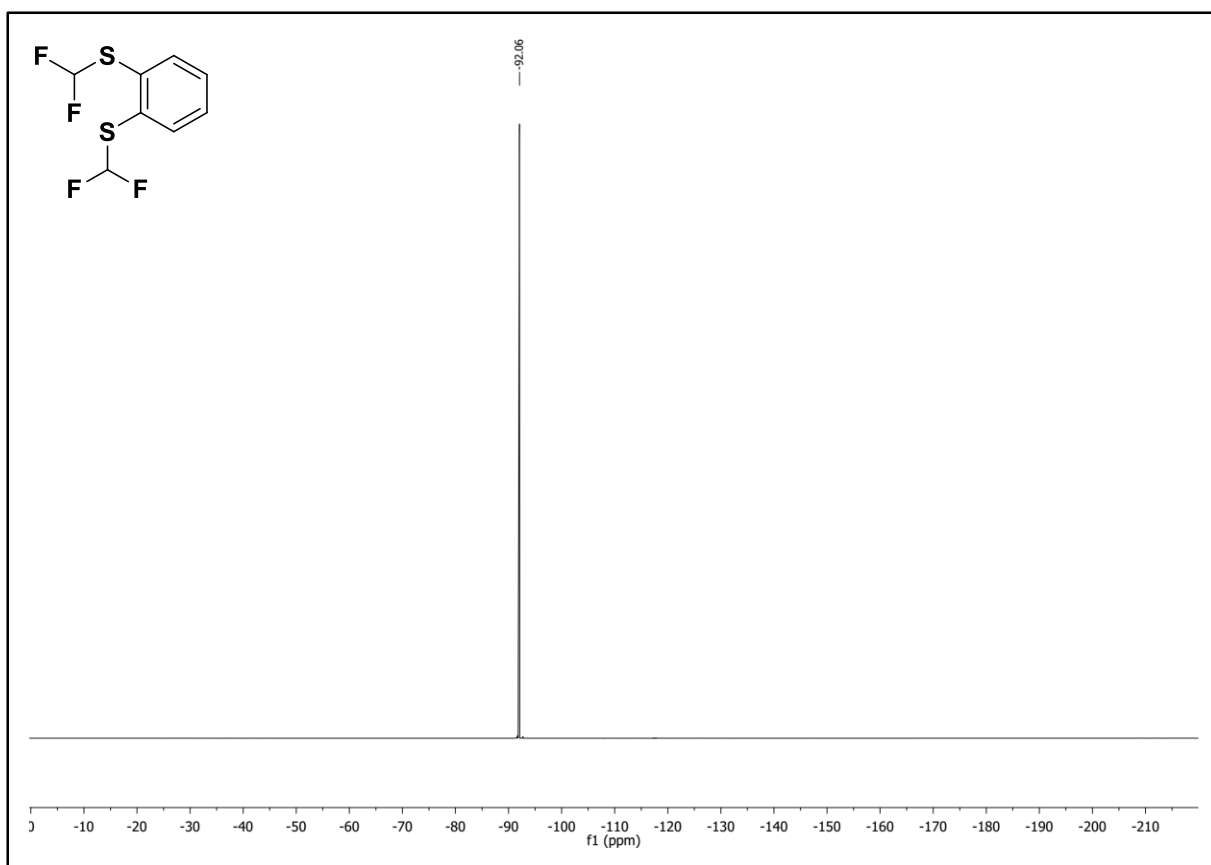
(2-(tert-Butyl)-6-methylphenyl)(difluoromethyl)sulfane (**4e**): ^1H , ^{13}C , ^{19}F



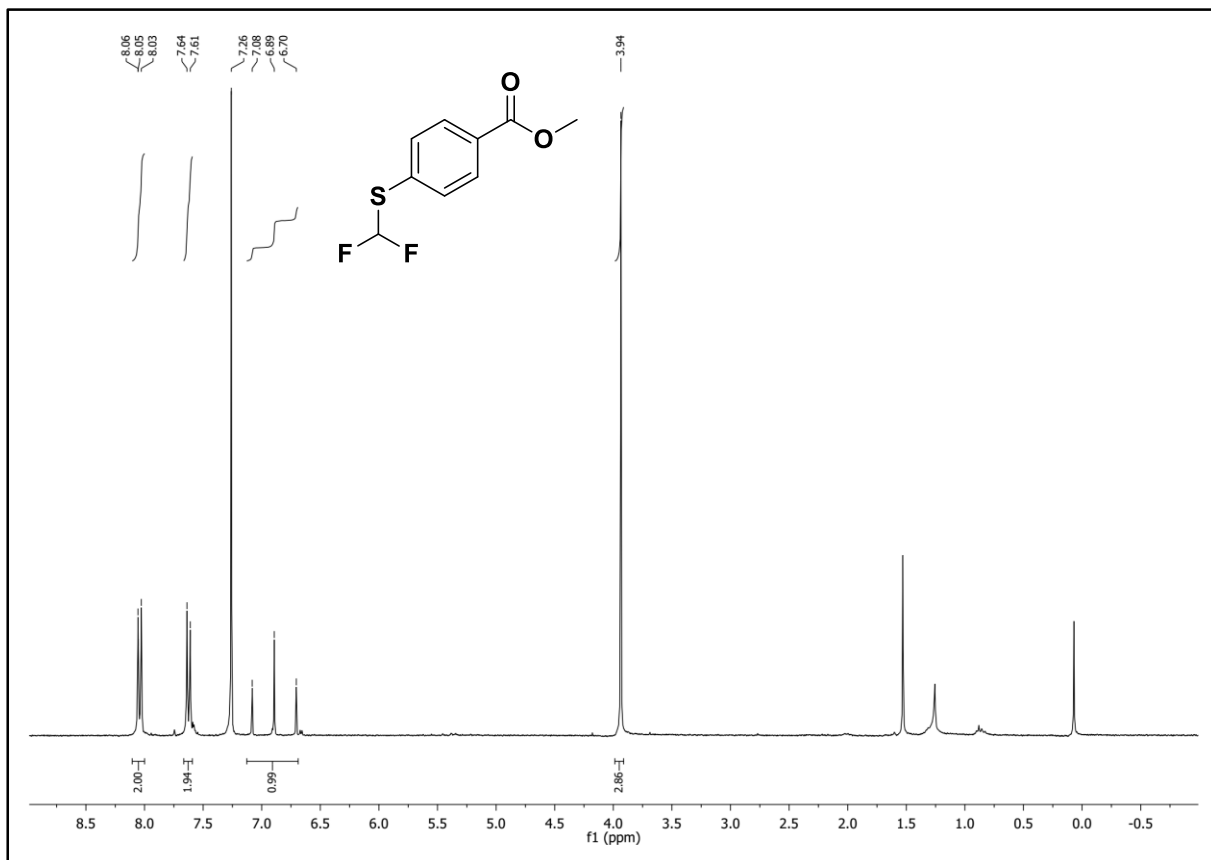


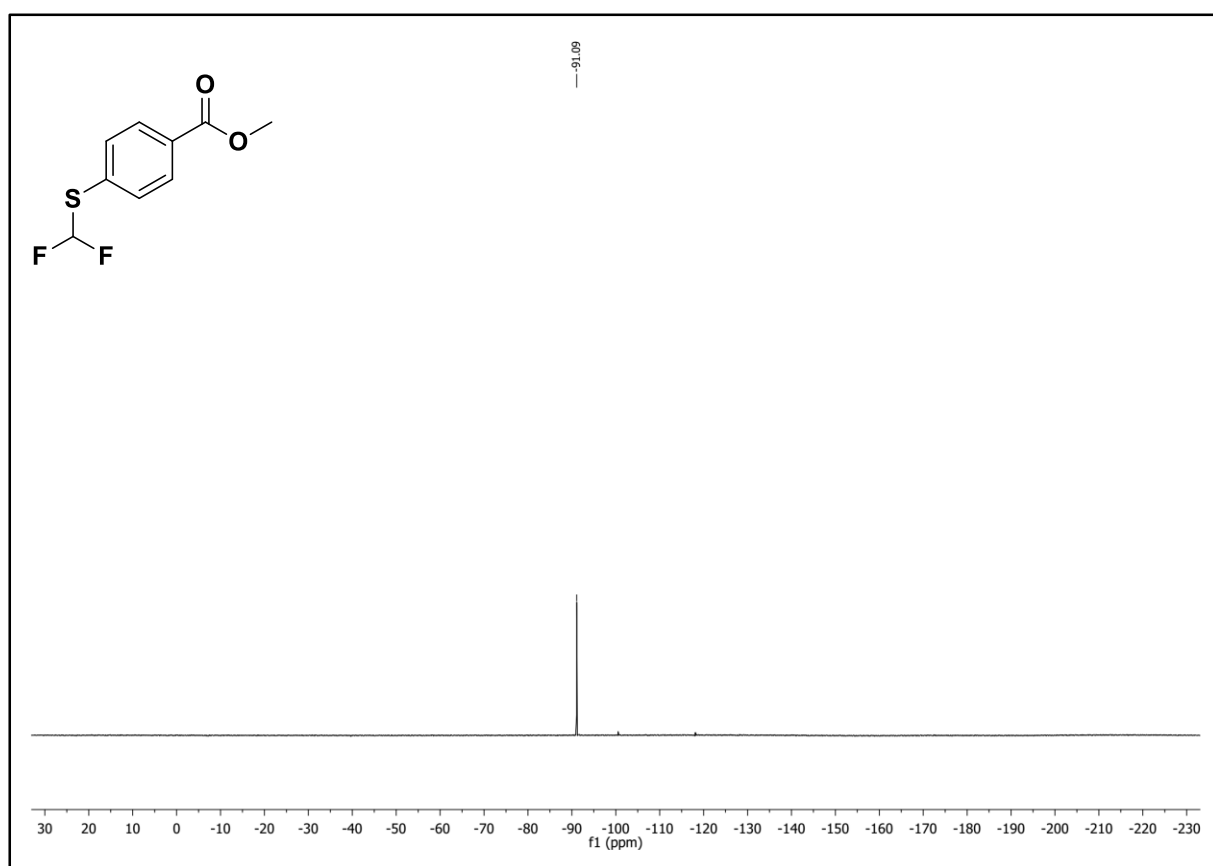
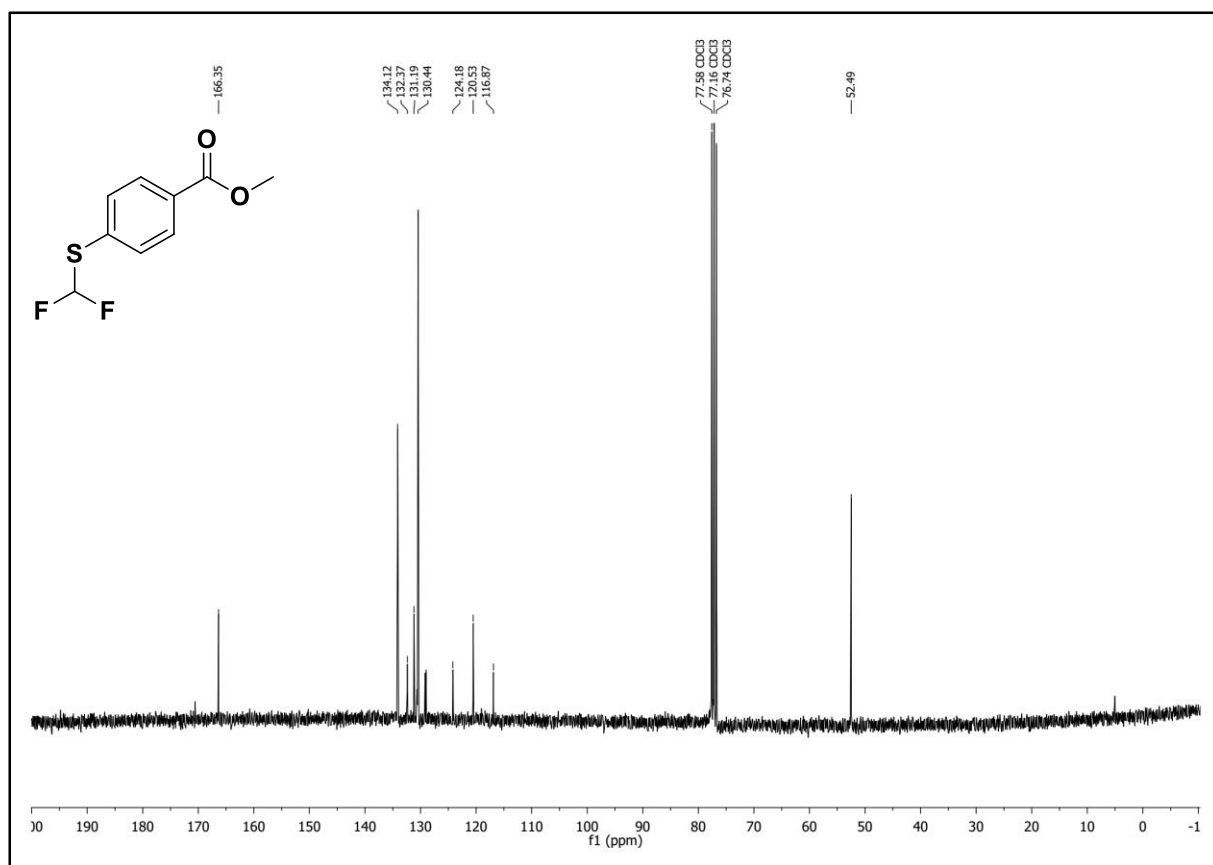
1,2-Bis((difluoromethyl)thio)benzene (**4f**): ^1H , ^{13}C , ^{19}F



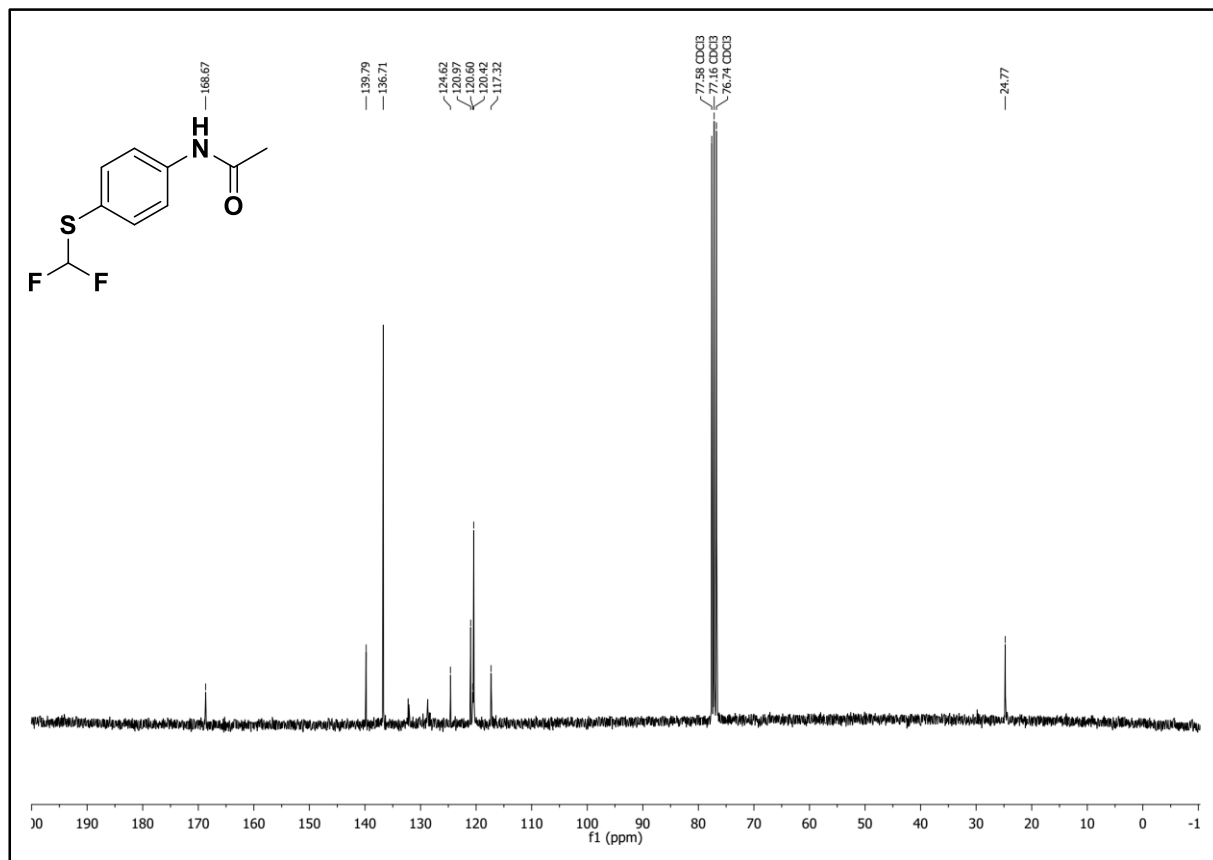
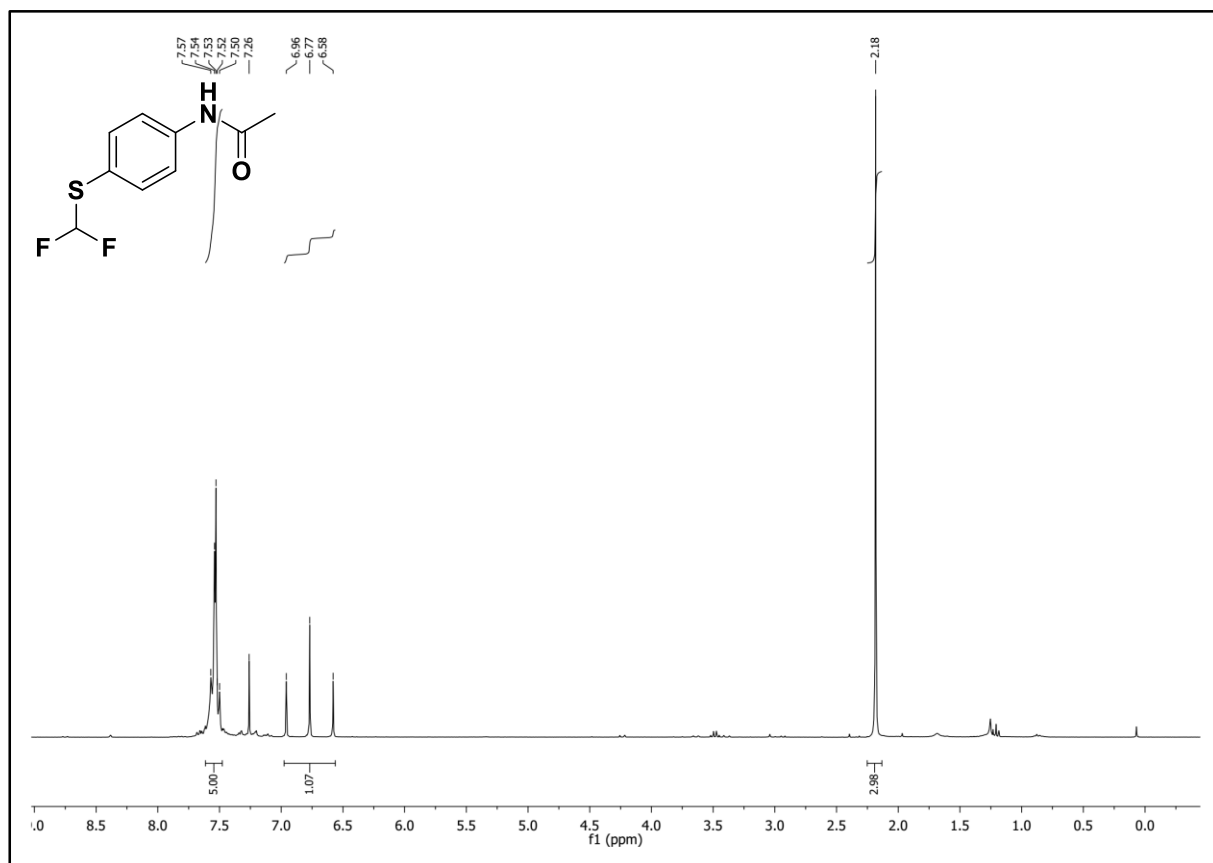


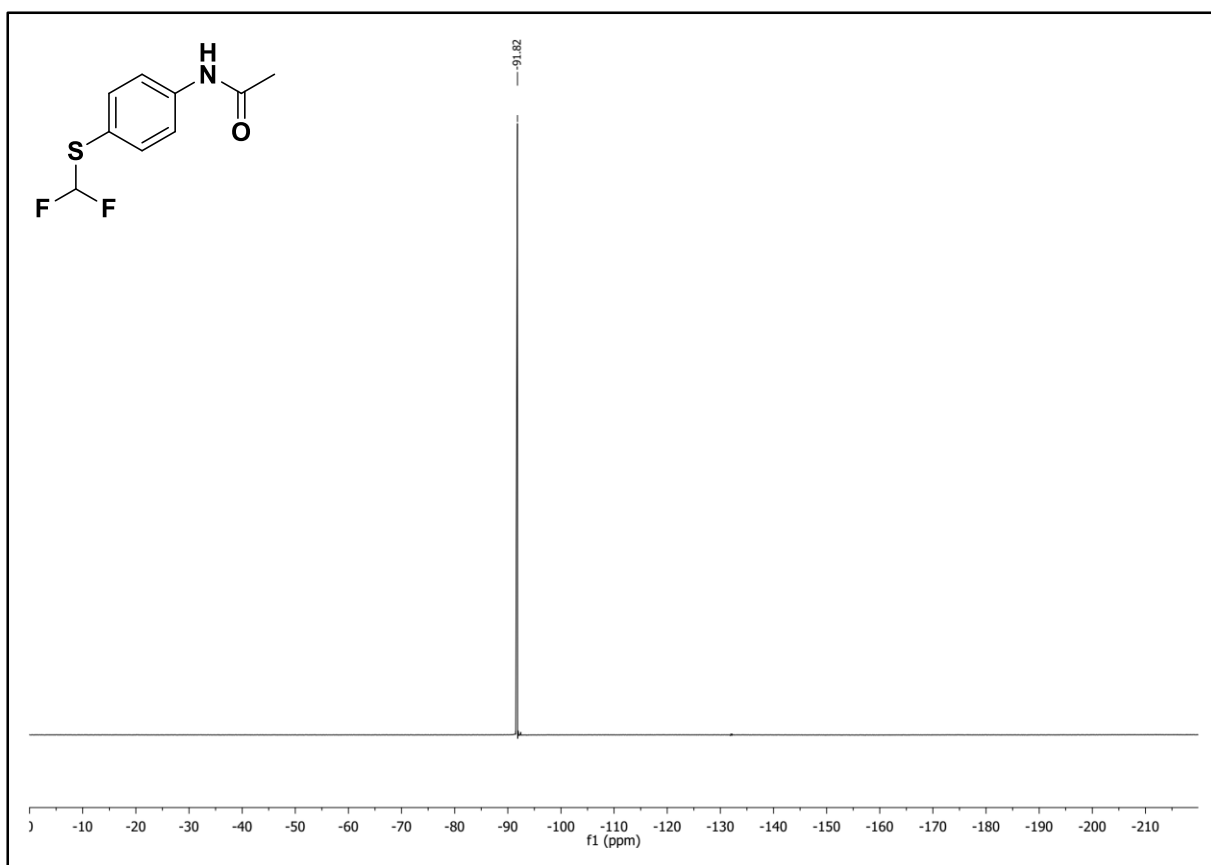
Methyl 4-((difluoromethyl)thio)benzoate (**4g**): ^1H , ^{13}C , ^{19}F



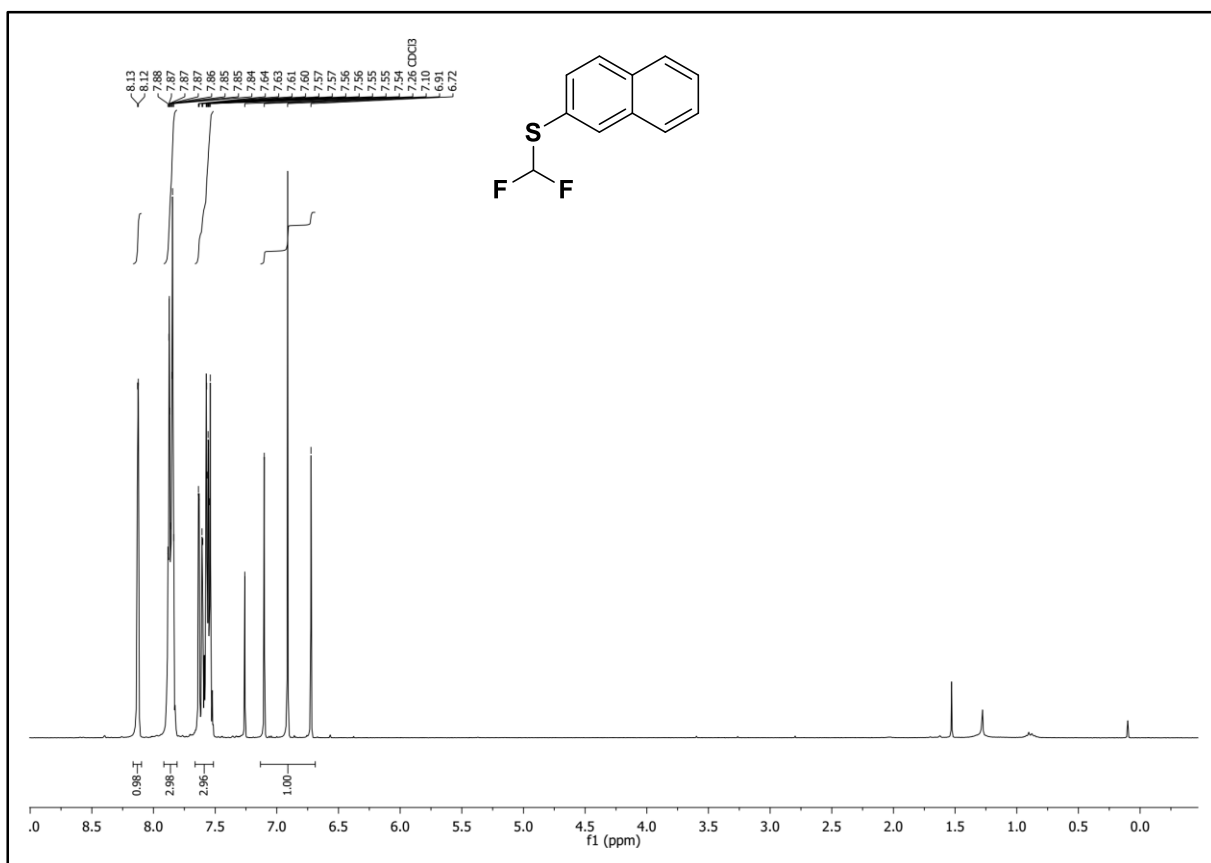


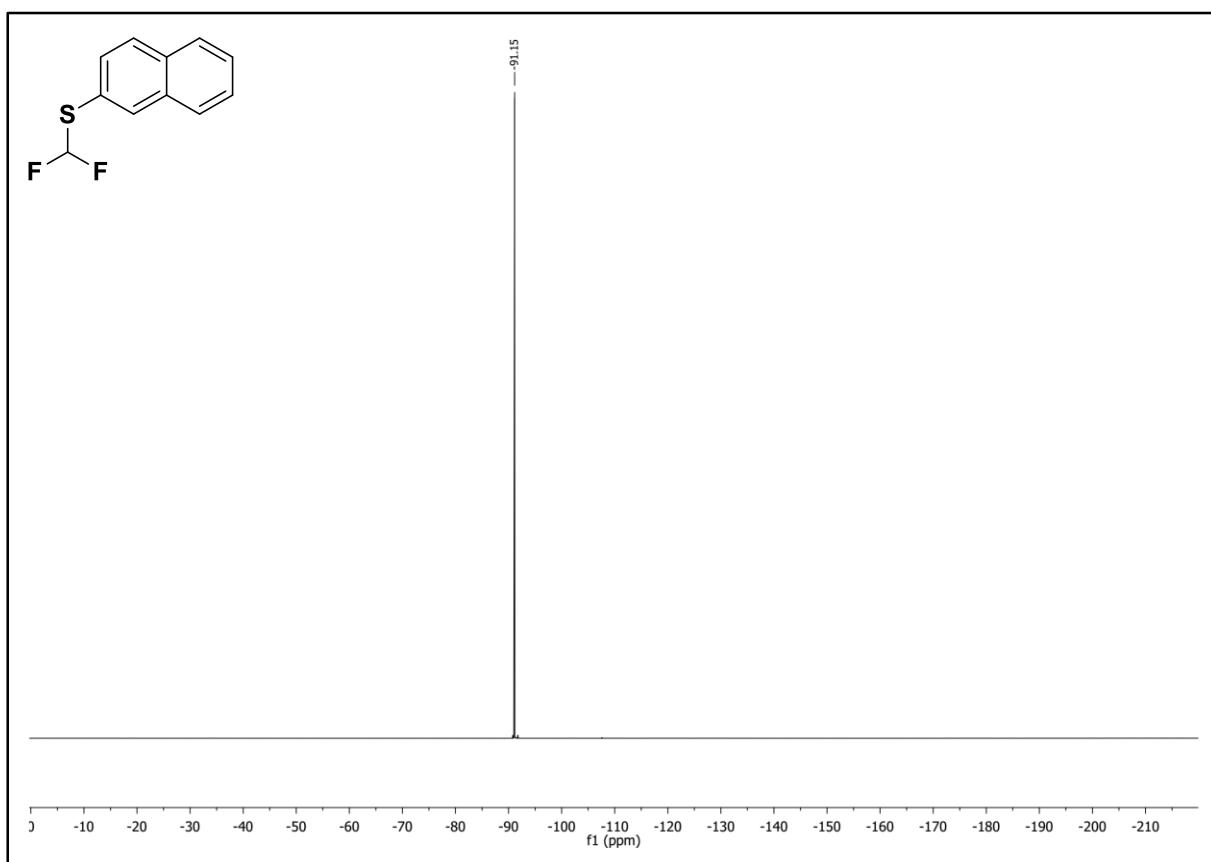
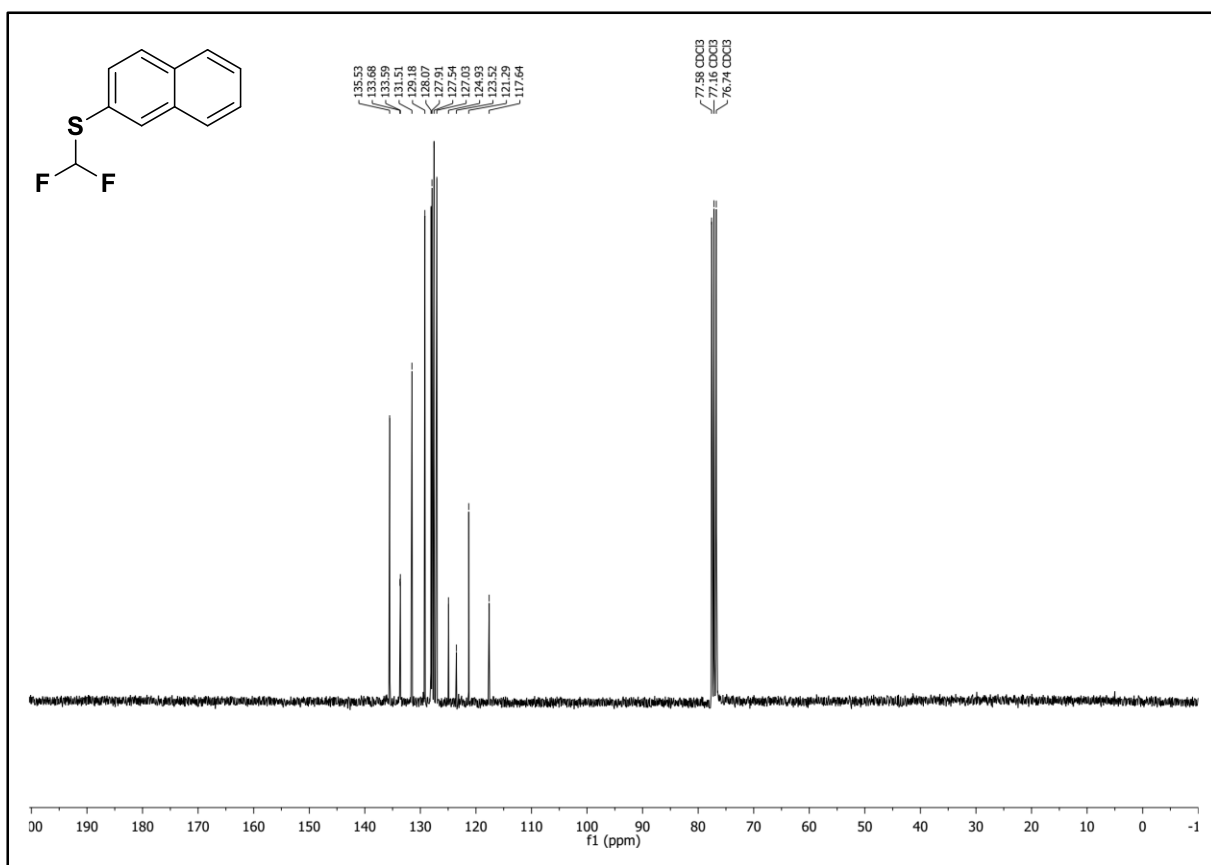
N-(4-((Difluoromethyl)thio)phenyl)acetamide (**4h**): ^1H , ^{13}C , ^{19}F



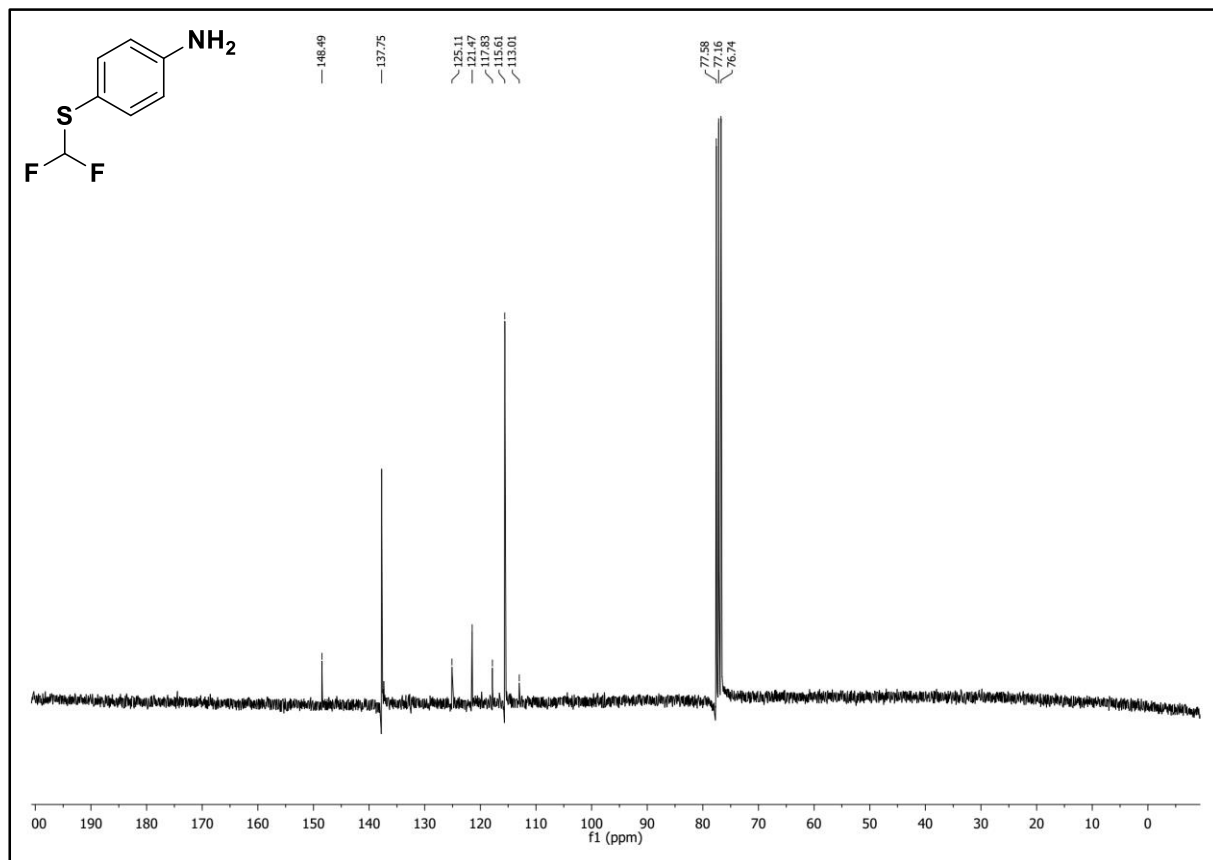
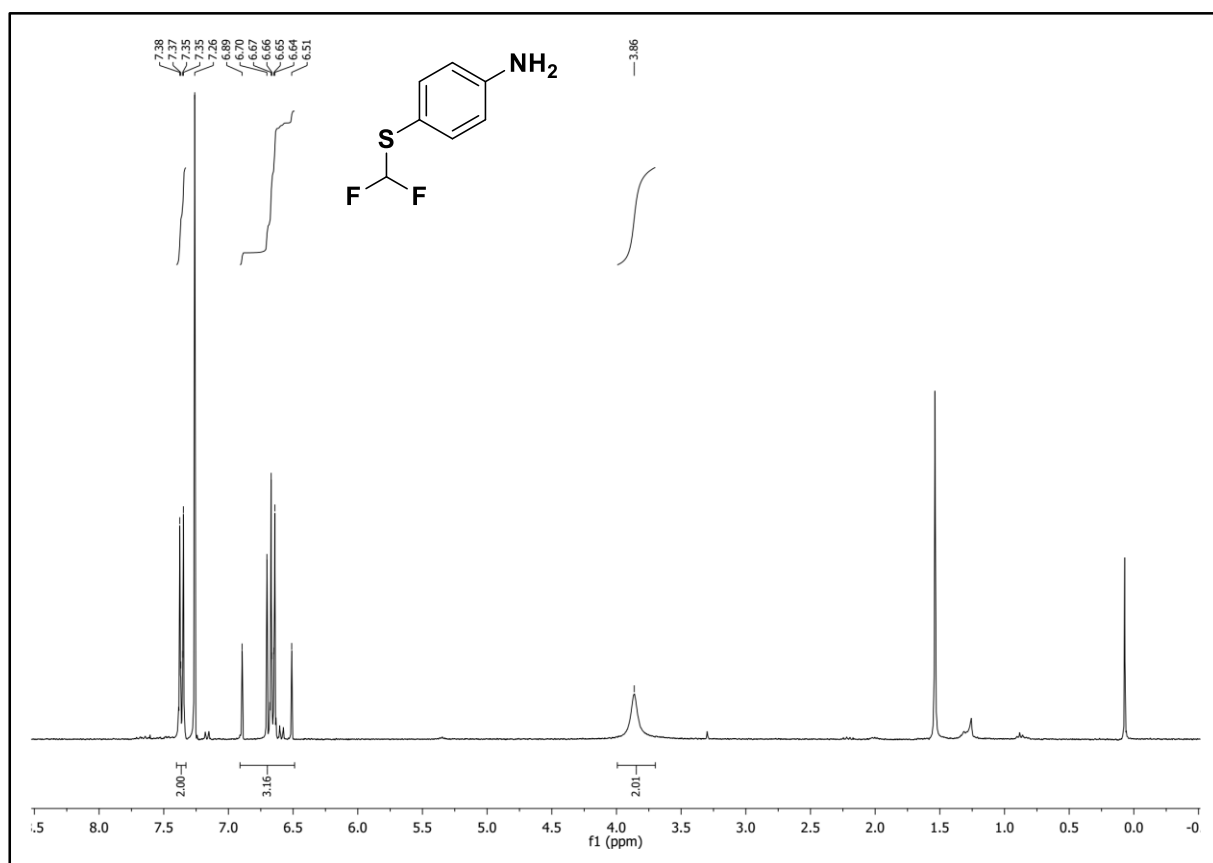


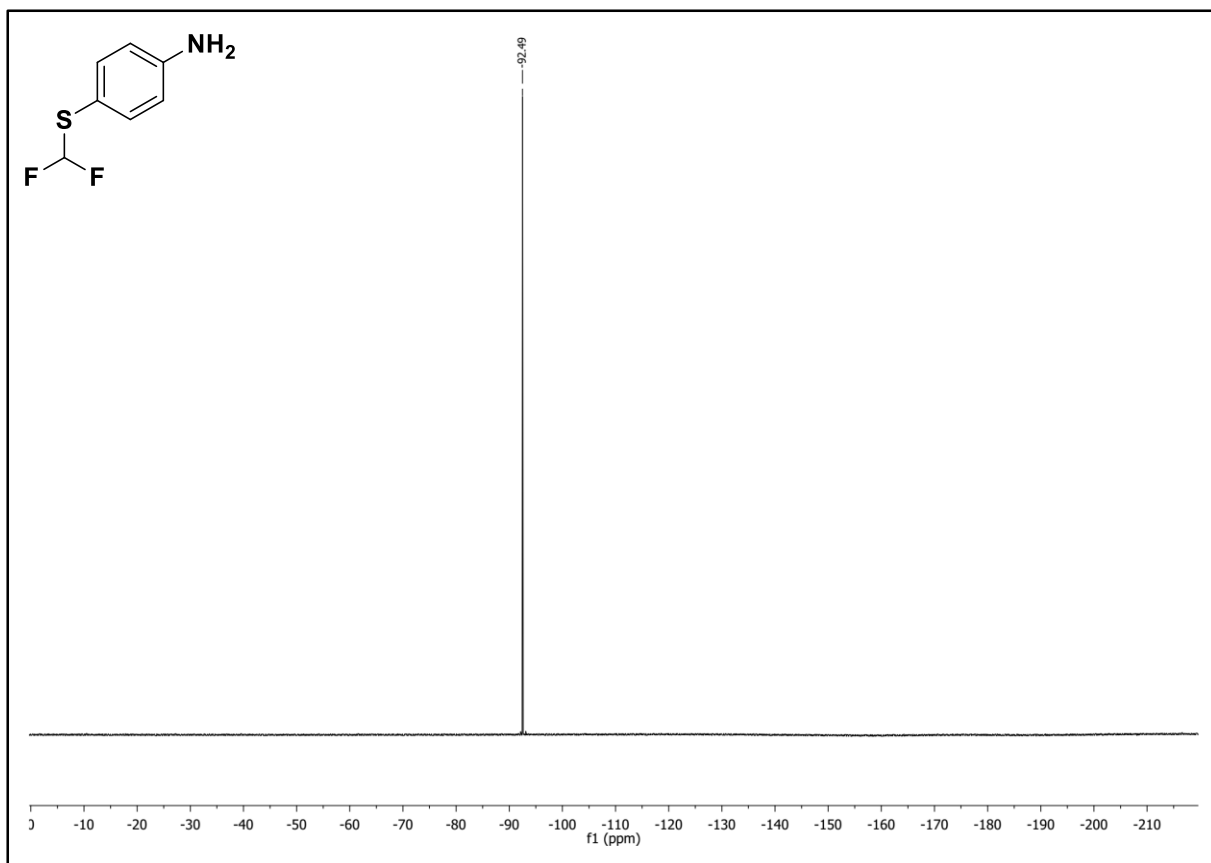
(Difluoromethyl)(naphthalen-2-yl)sulfane (**4i**): ^1H , ^{13}C , ^{19}F



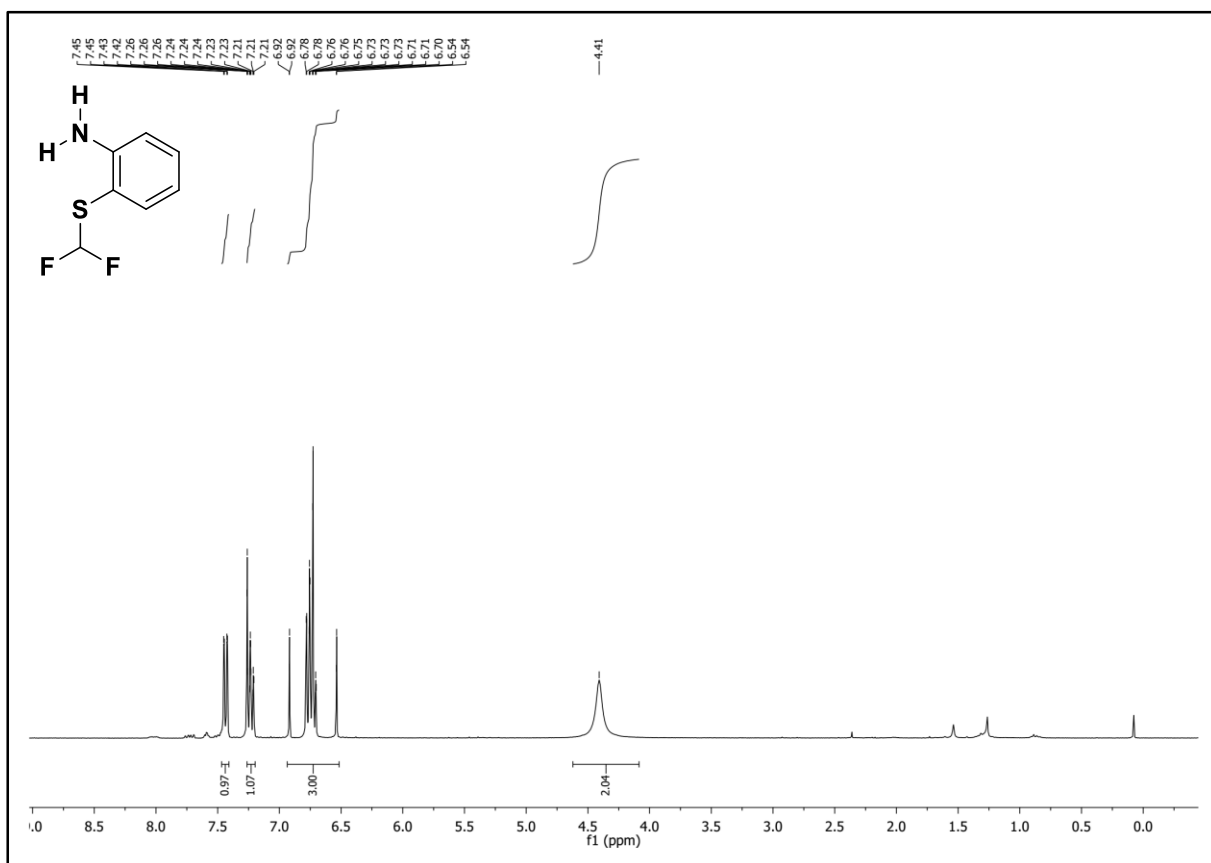


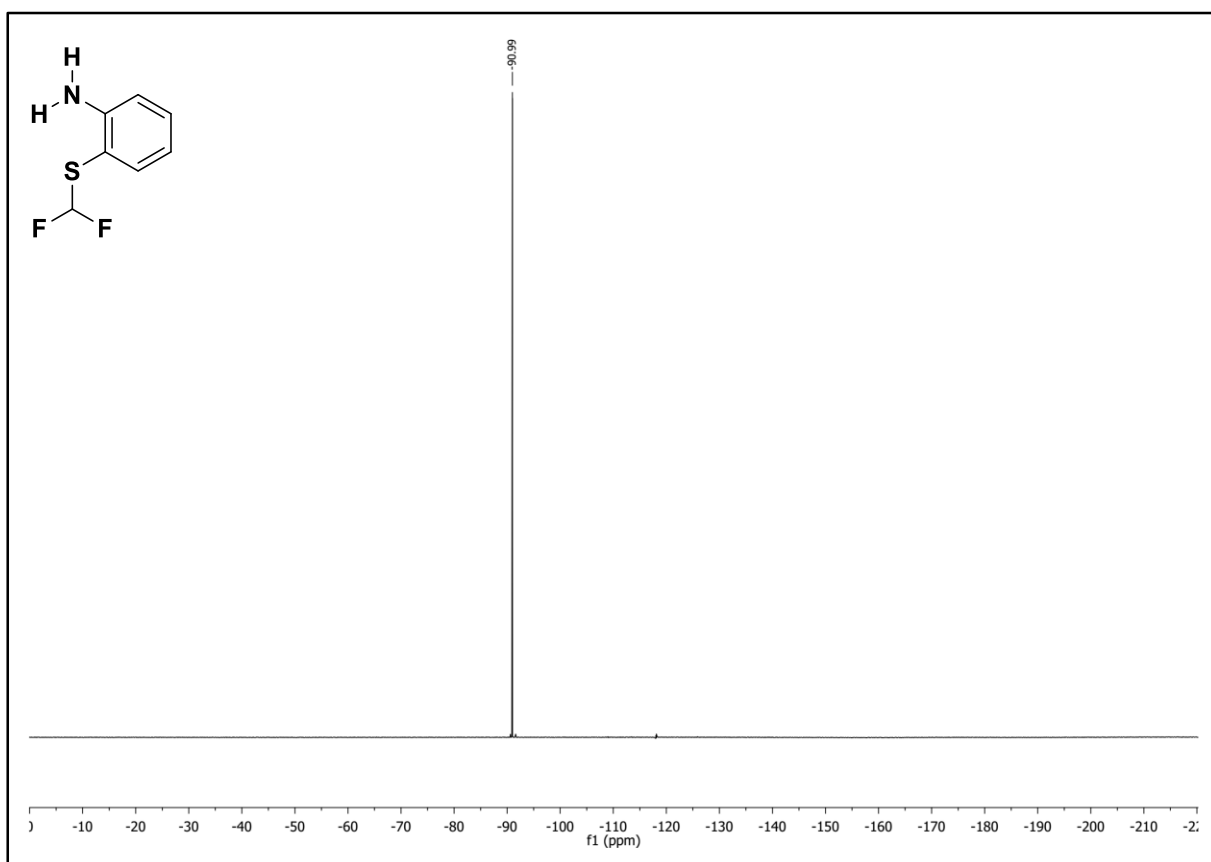
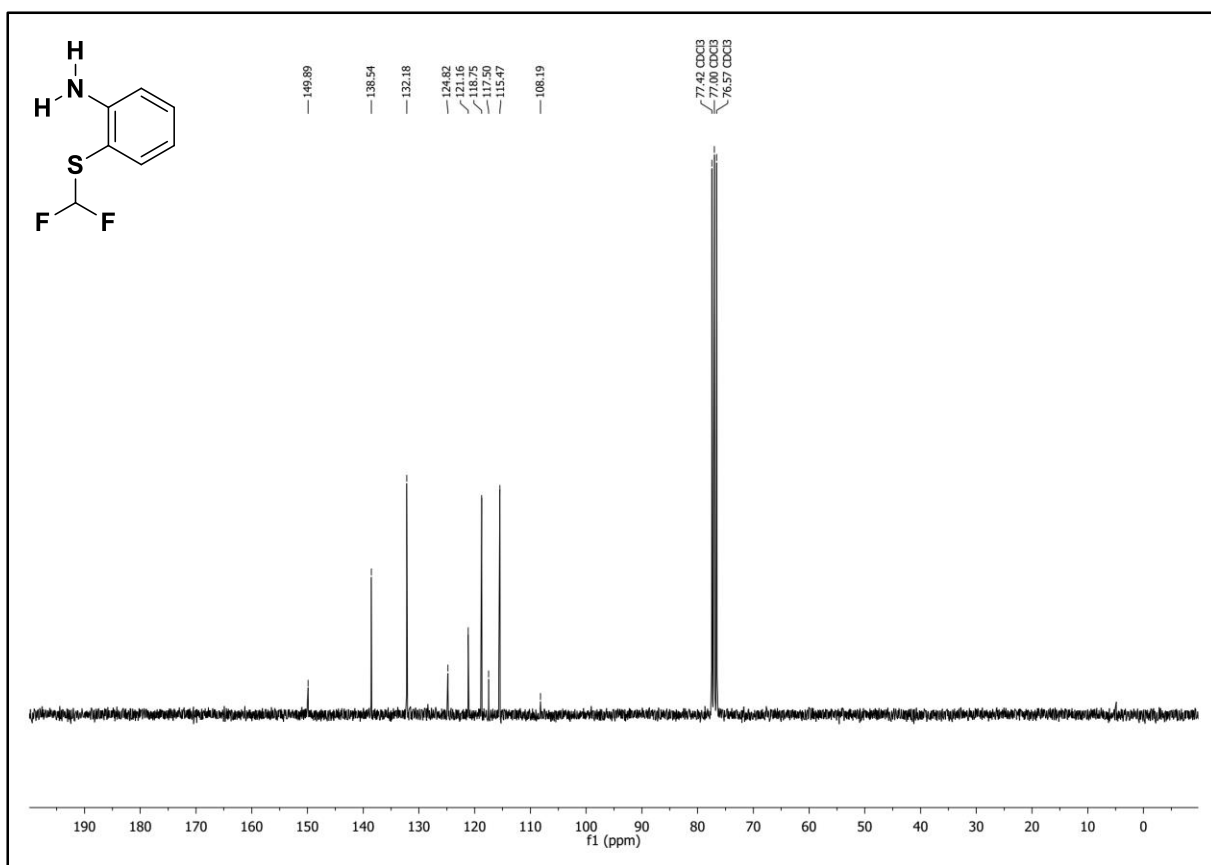
4-((Difluoromethyl)thio)aniline (**4j**): ^1H , ^{13}C , ^{19}F



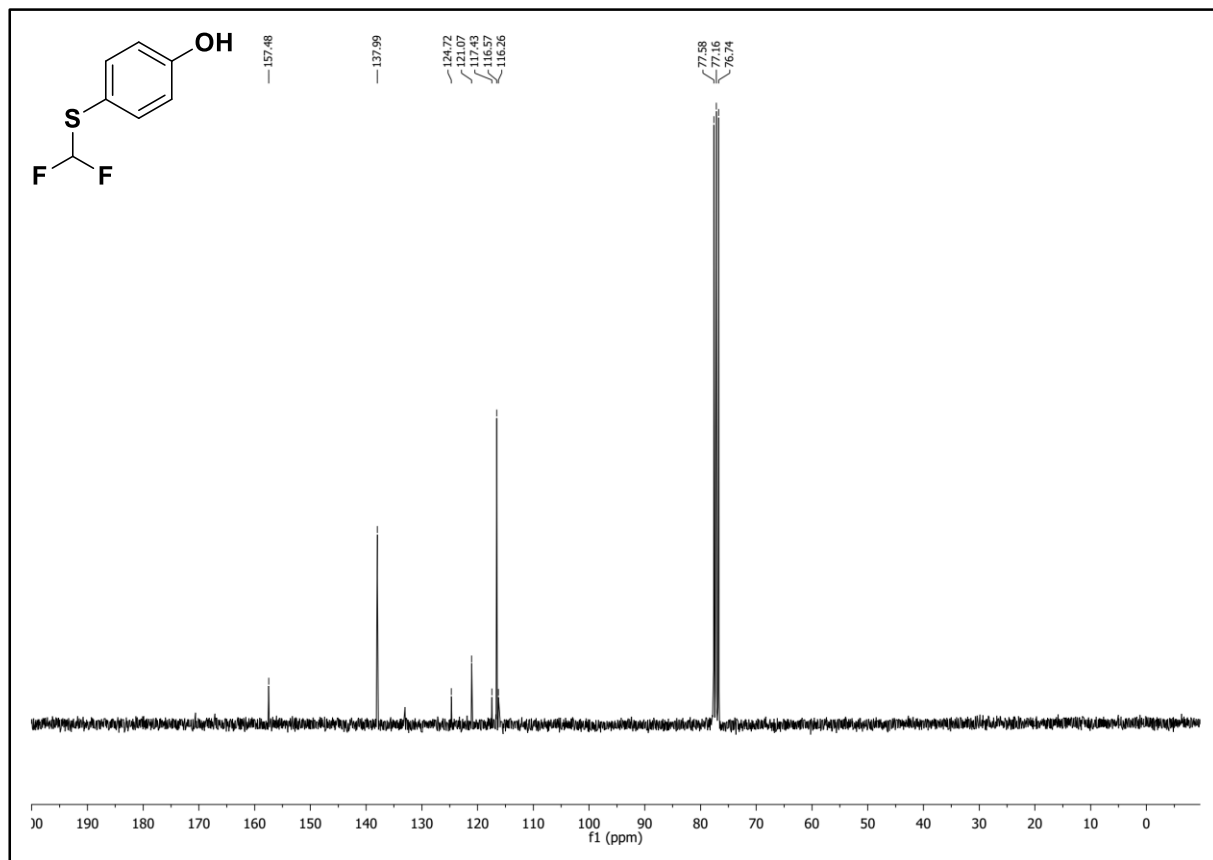
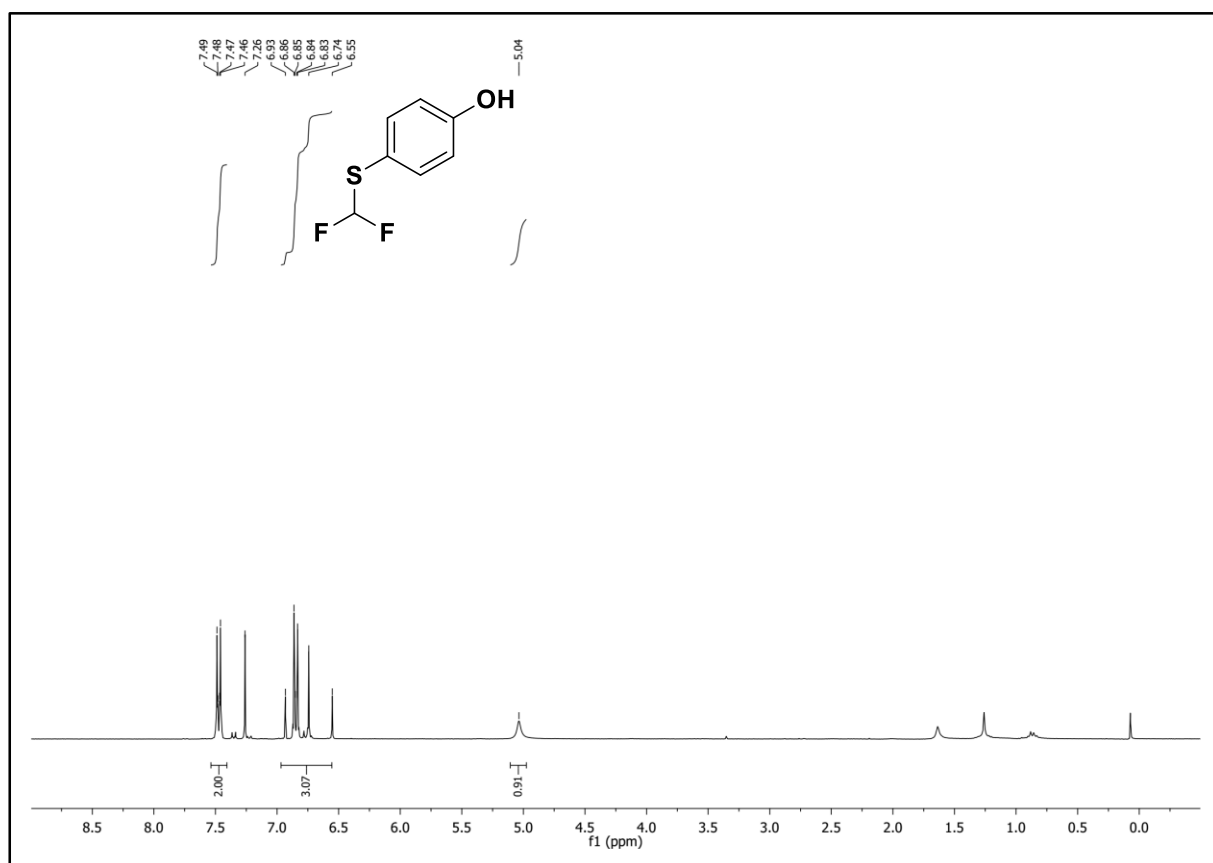


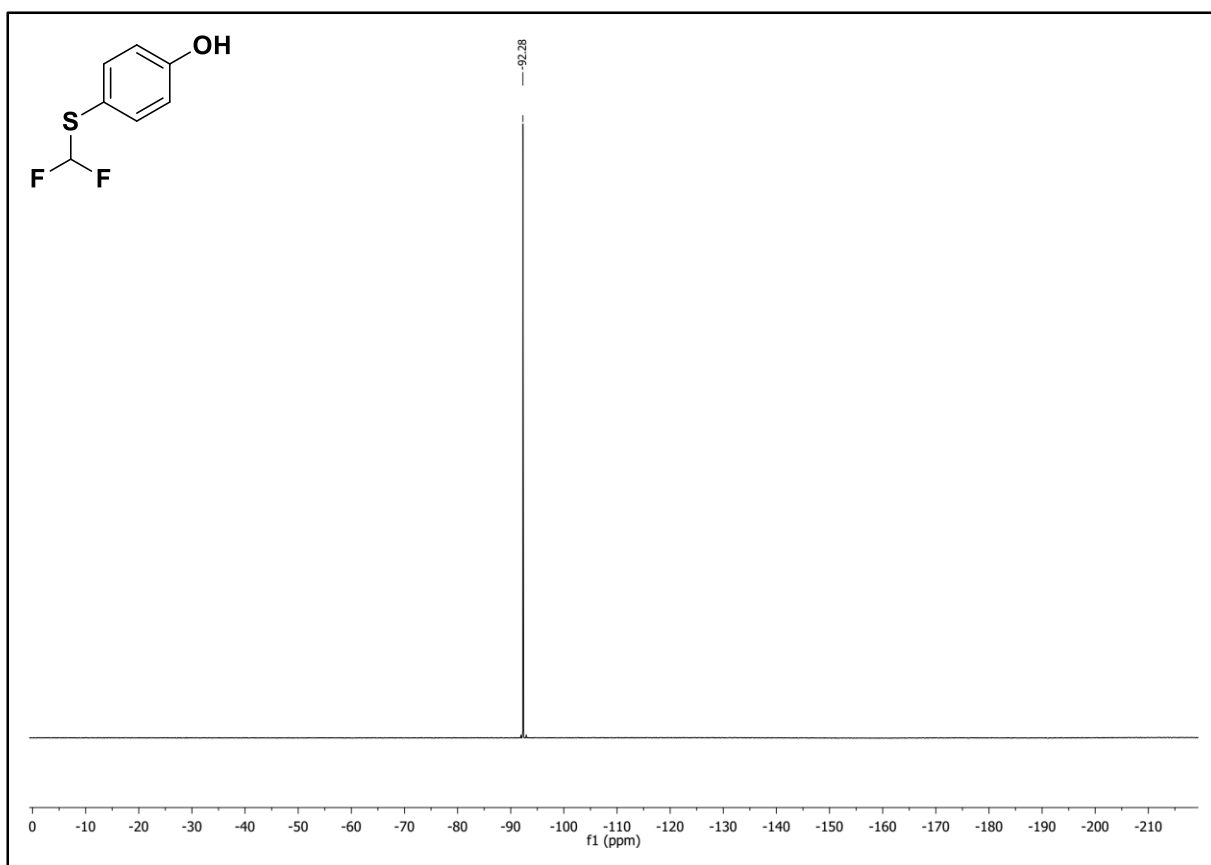
2-((Difluoromethyl)thio)aniline (**4k**): ^1H , ^{13}C , ^{19}F



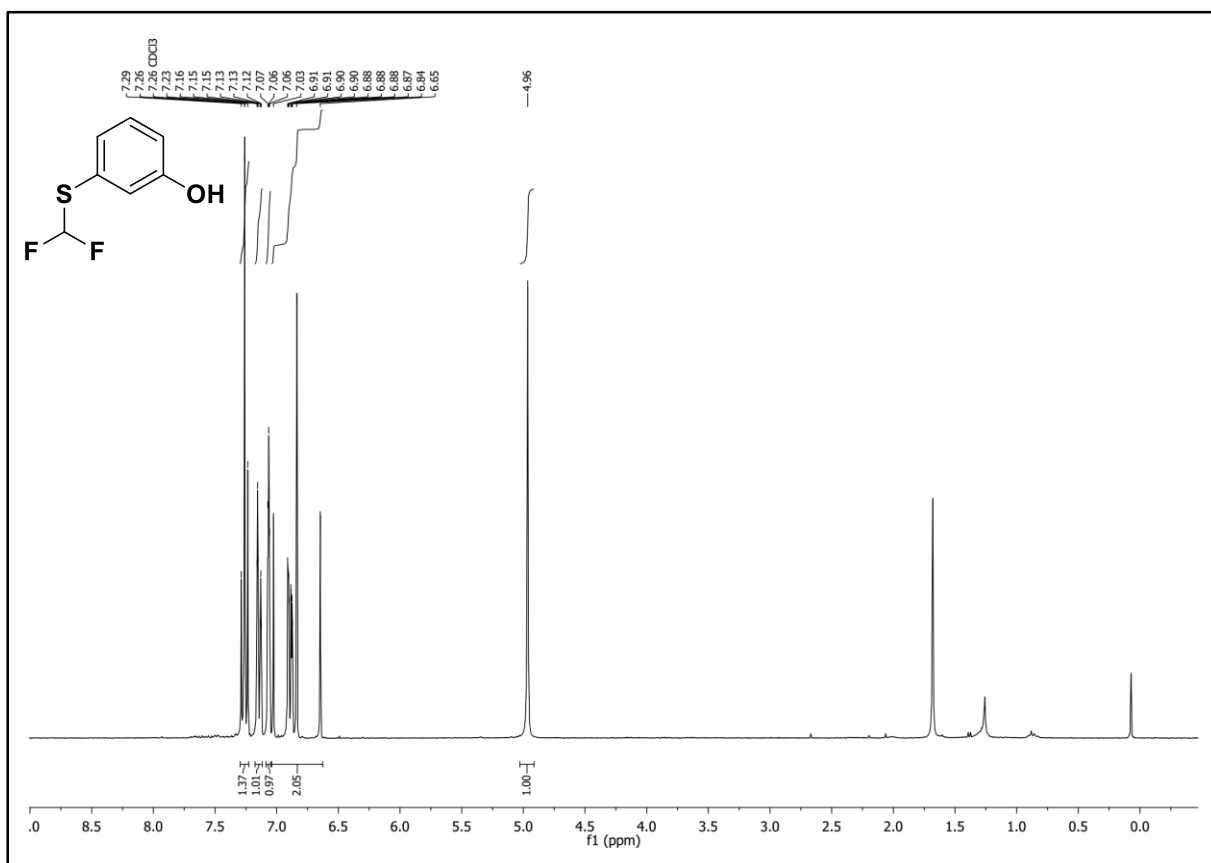


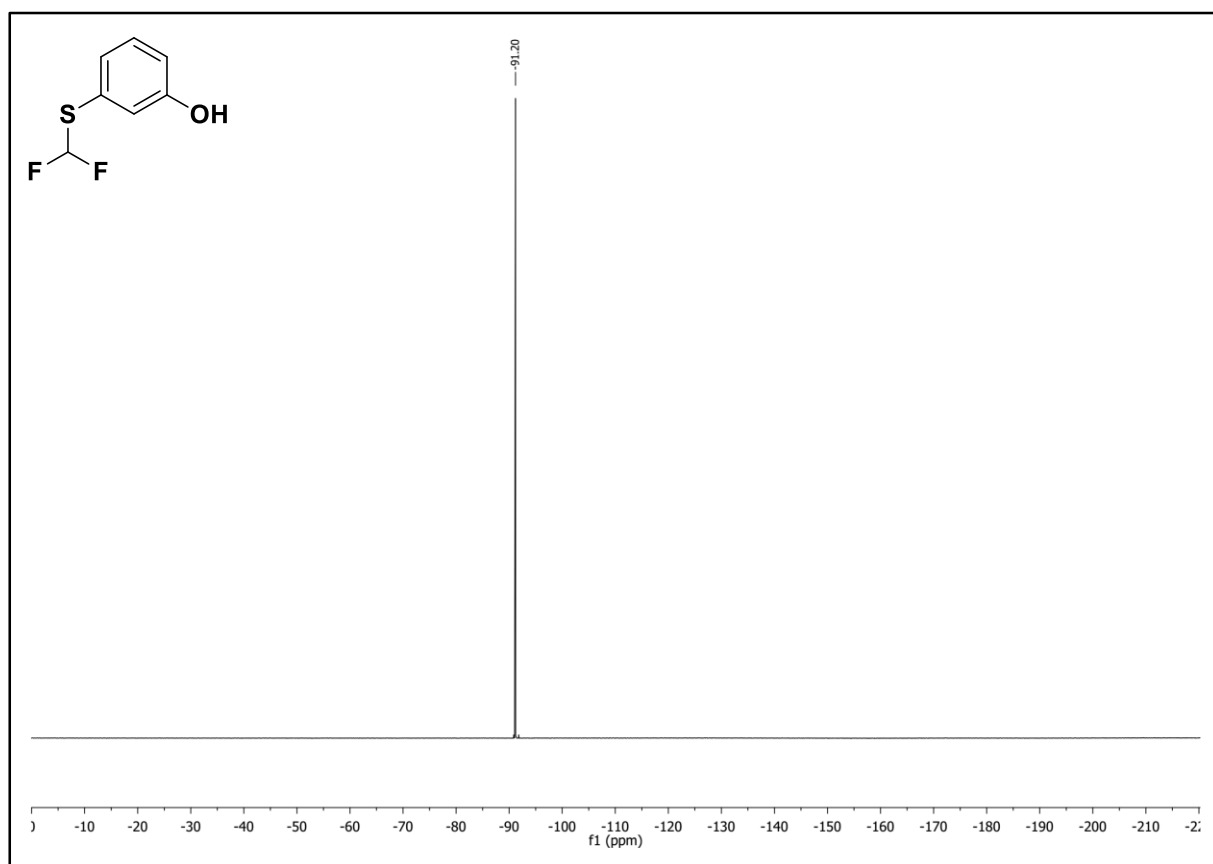
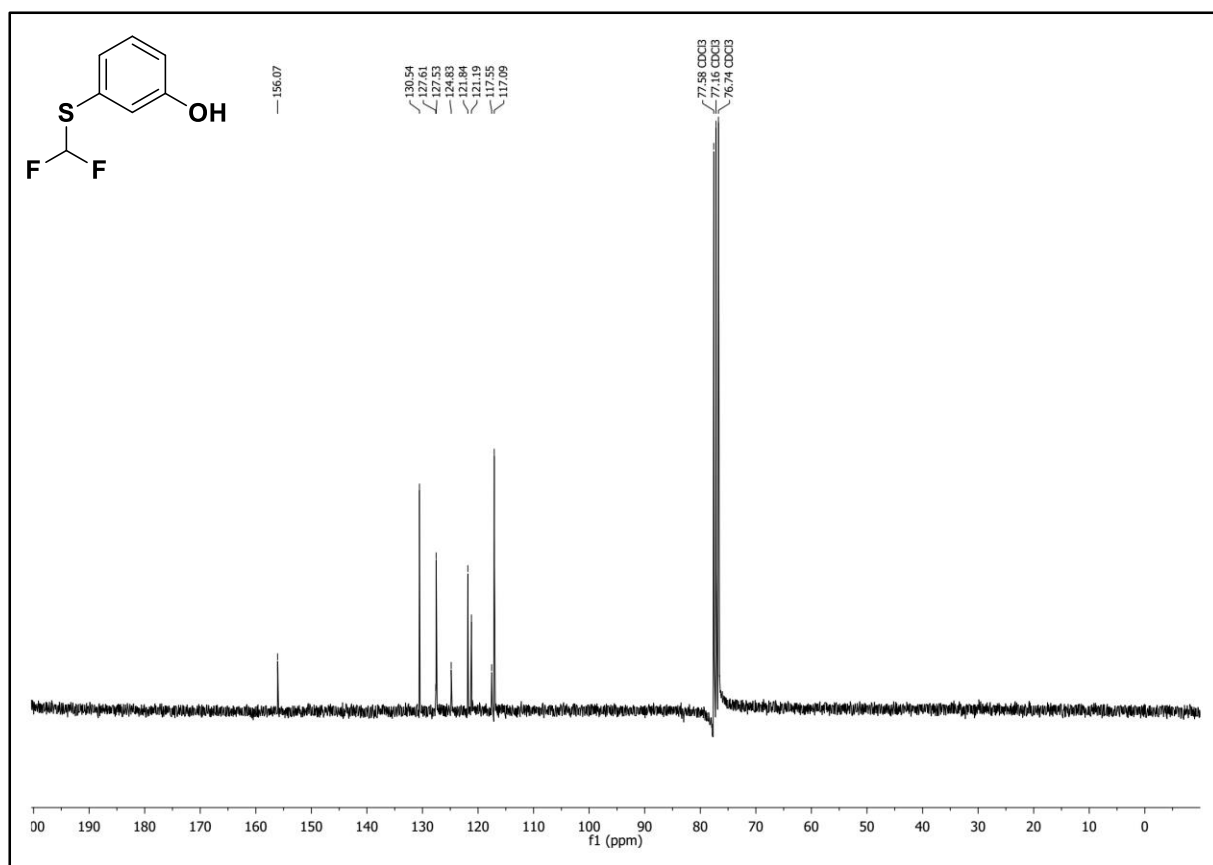
4-((Difluoromethyl)thio)phenol (**4I**): ^1H , ^{13}C , ^{19}F



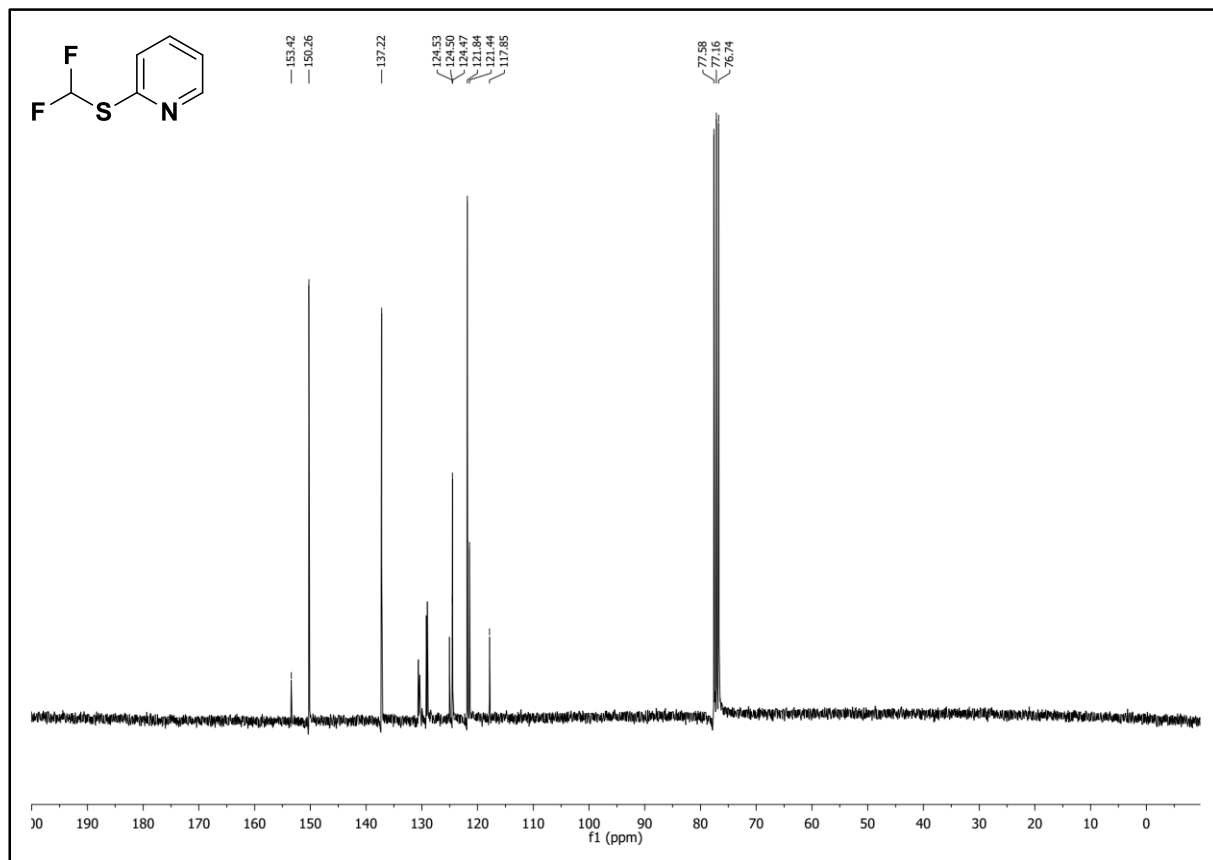
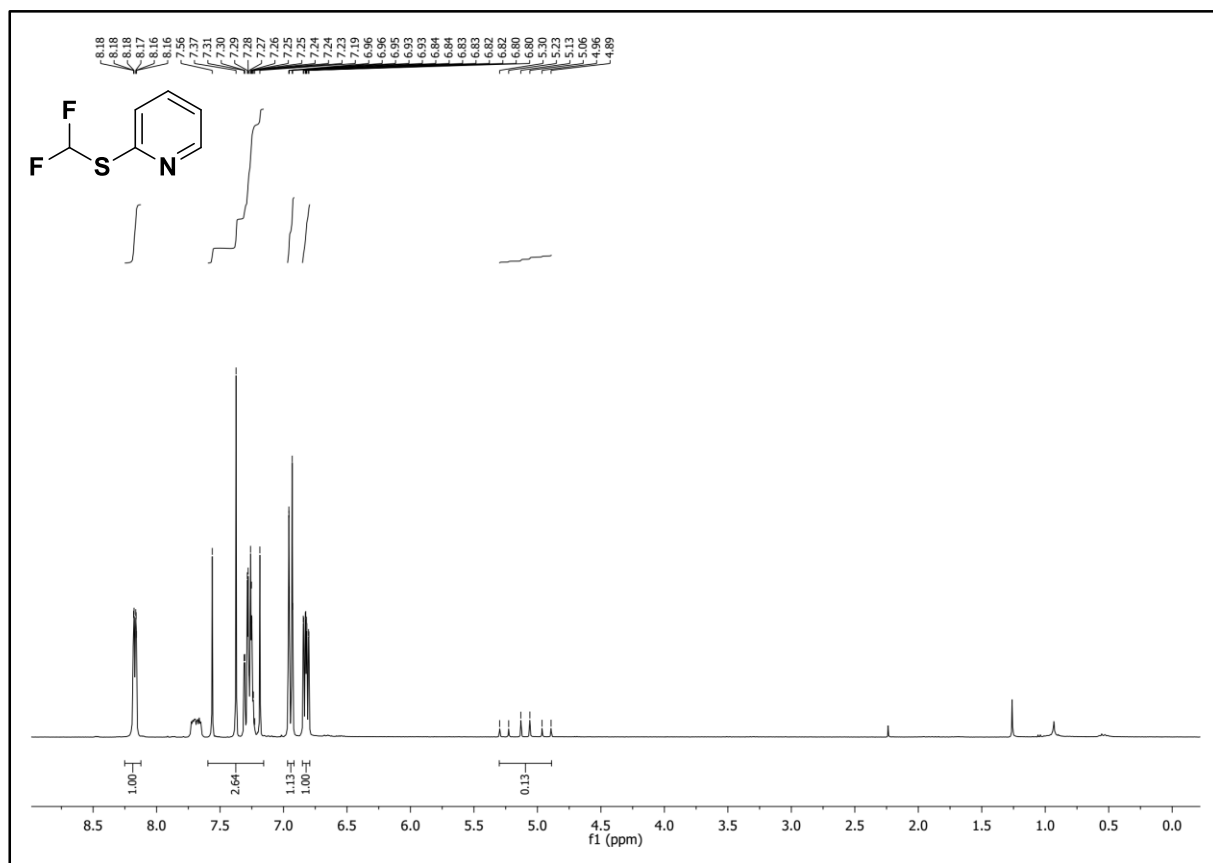


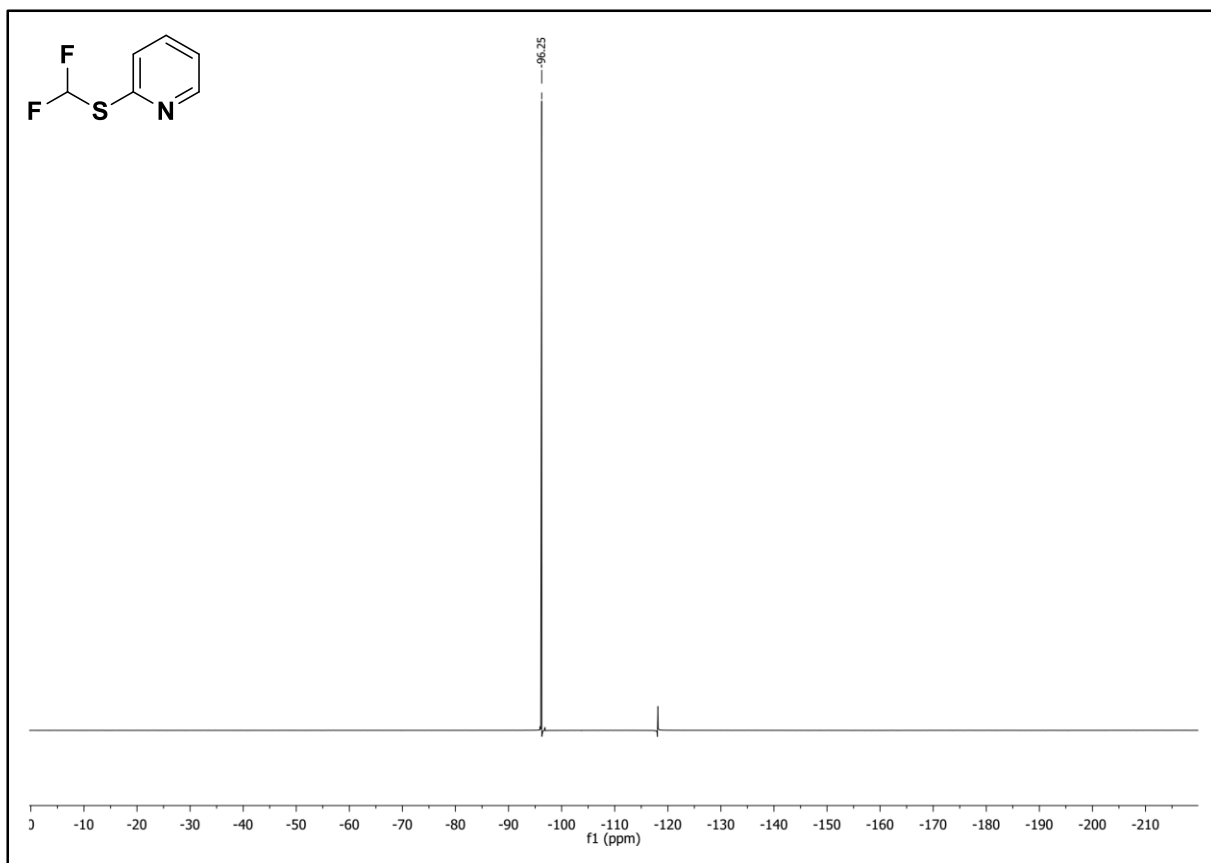
3-((Difluoromethyl)thio)phenol (**4m**): ^1H , ^{13}C , ^{19}F



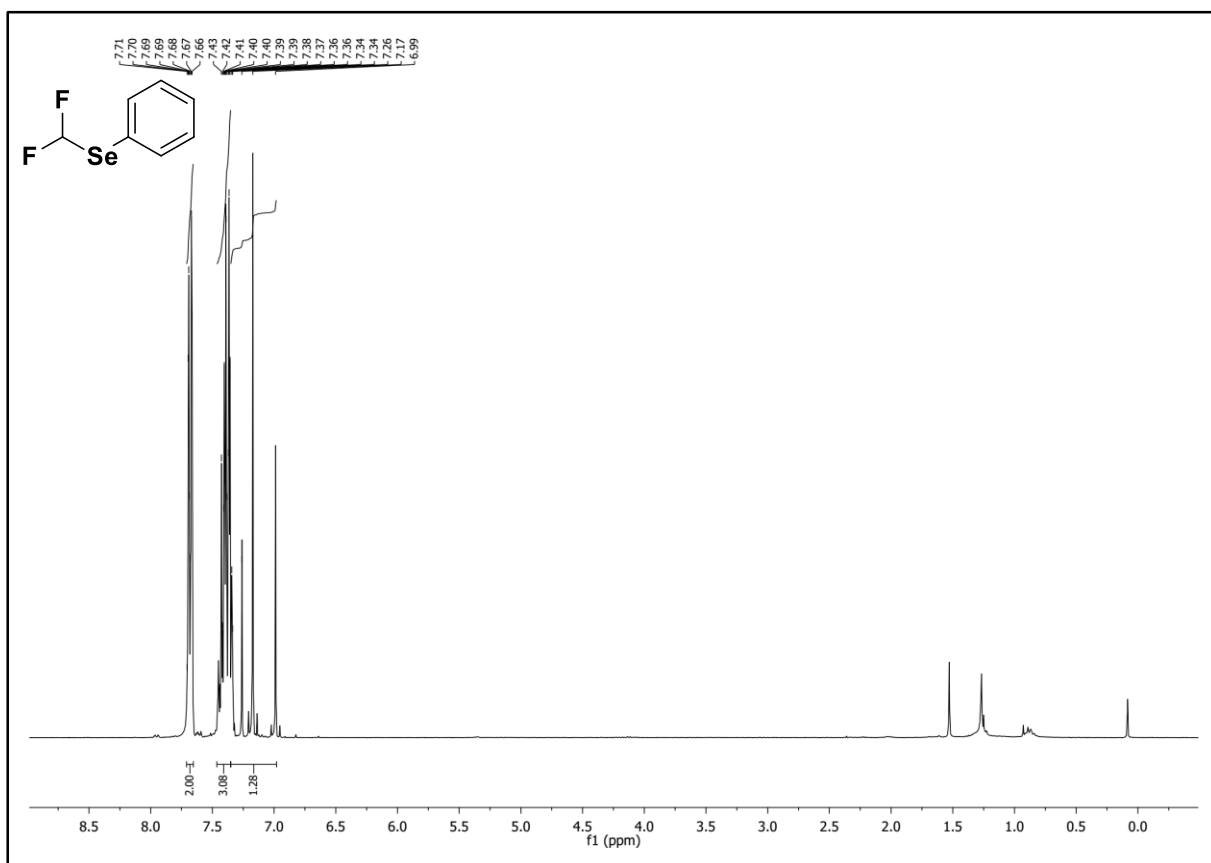


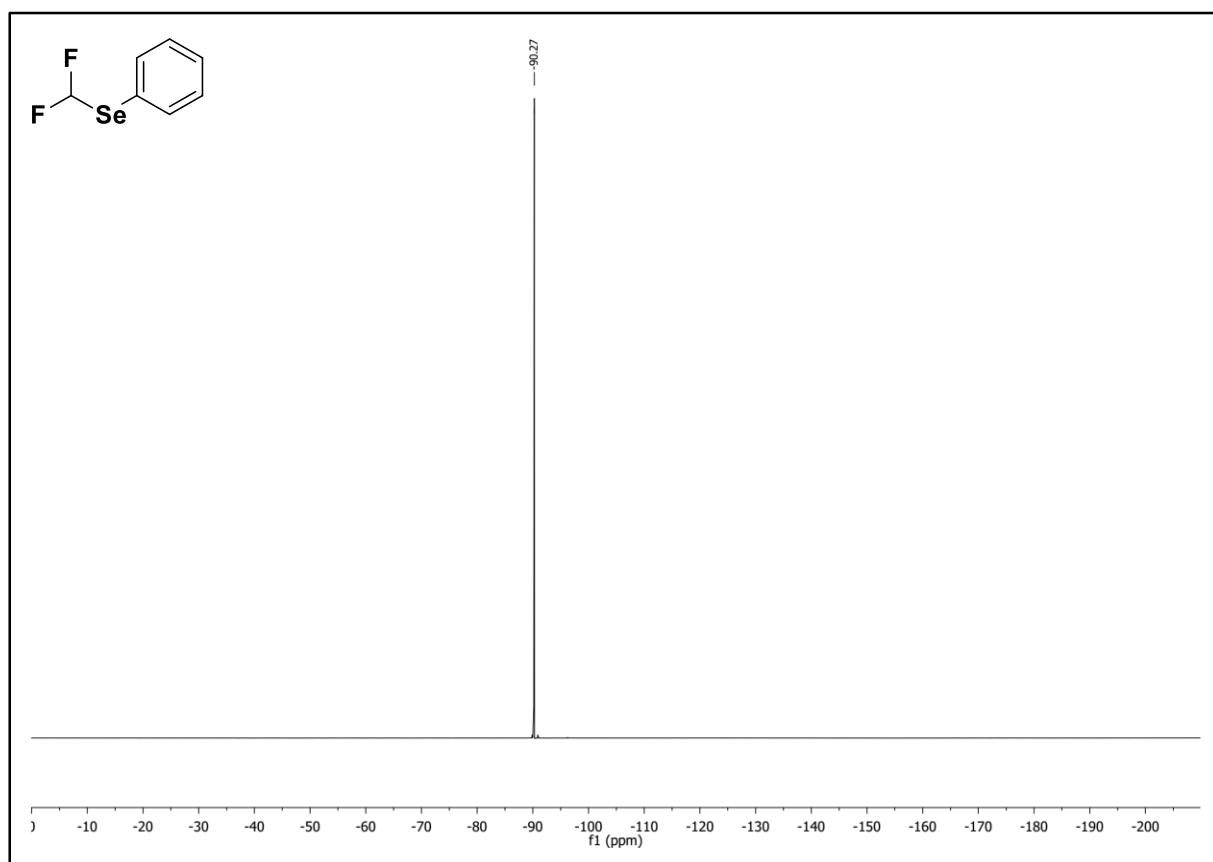
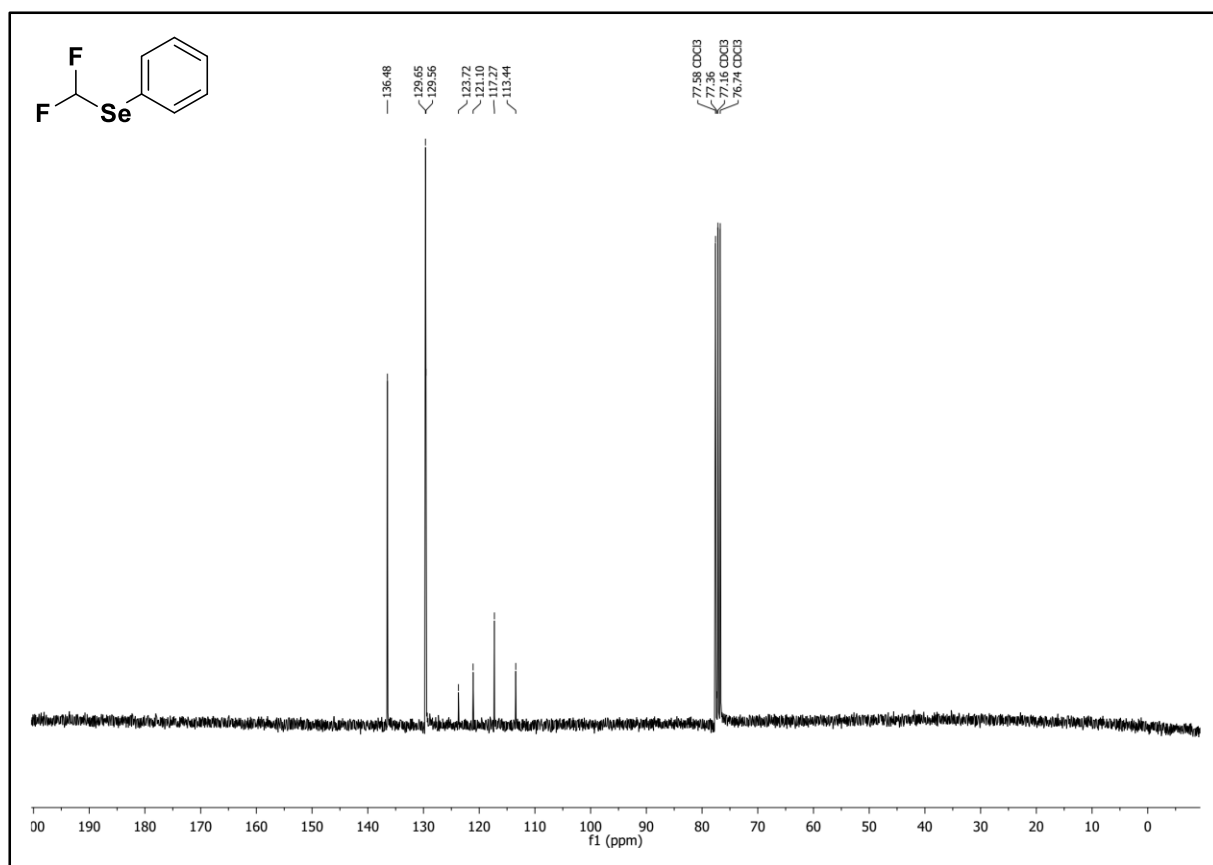
2-((Difluoromethyl)thio)pyridine (**4n**): ^1H , ^{13}C , ^{19}F



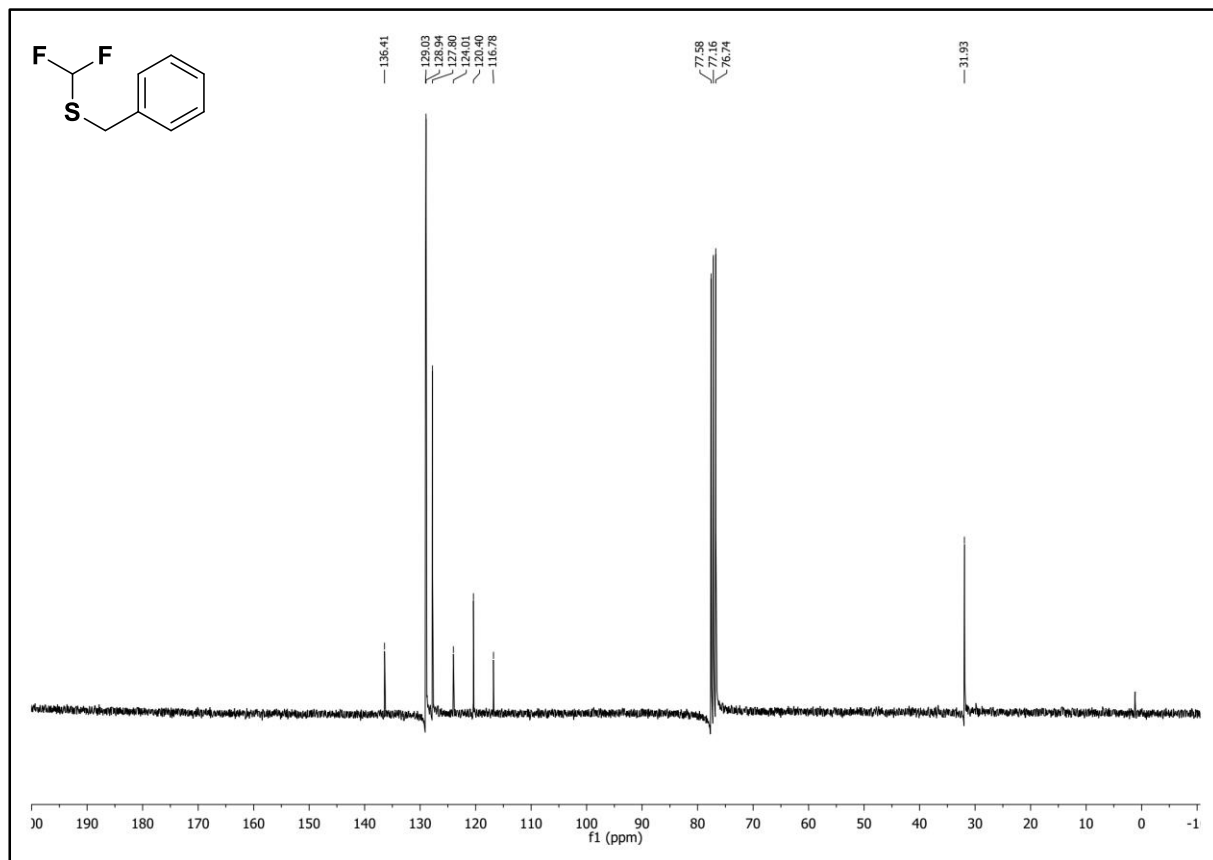
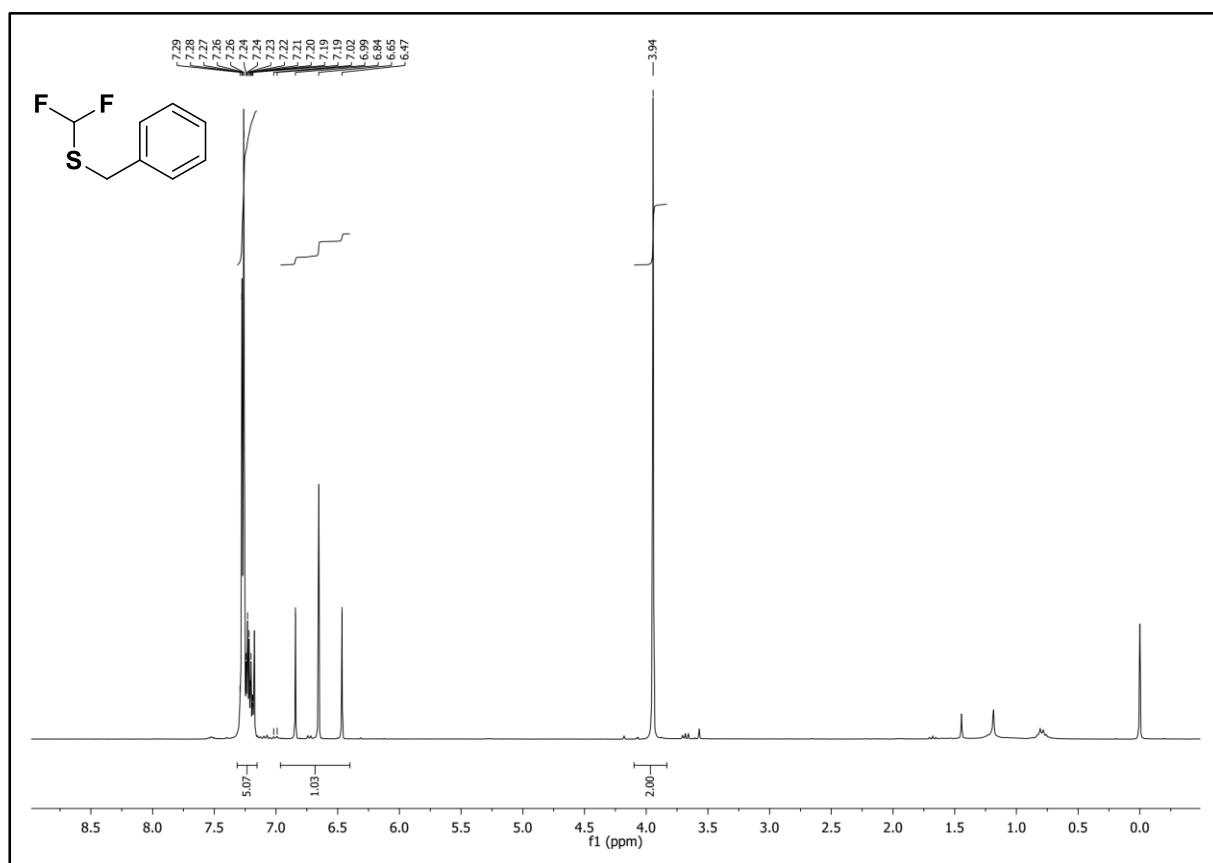


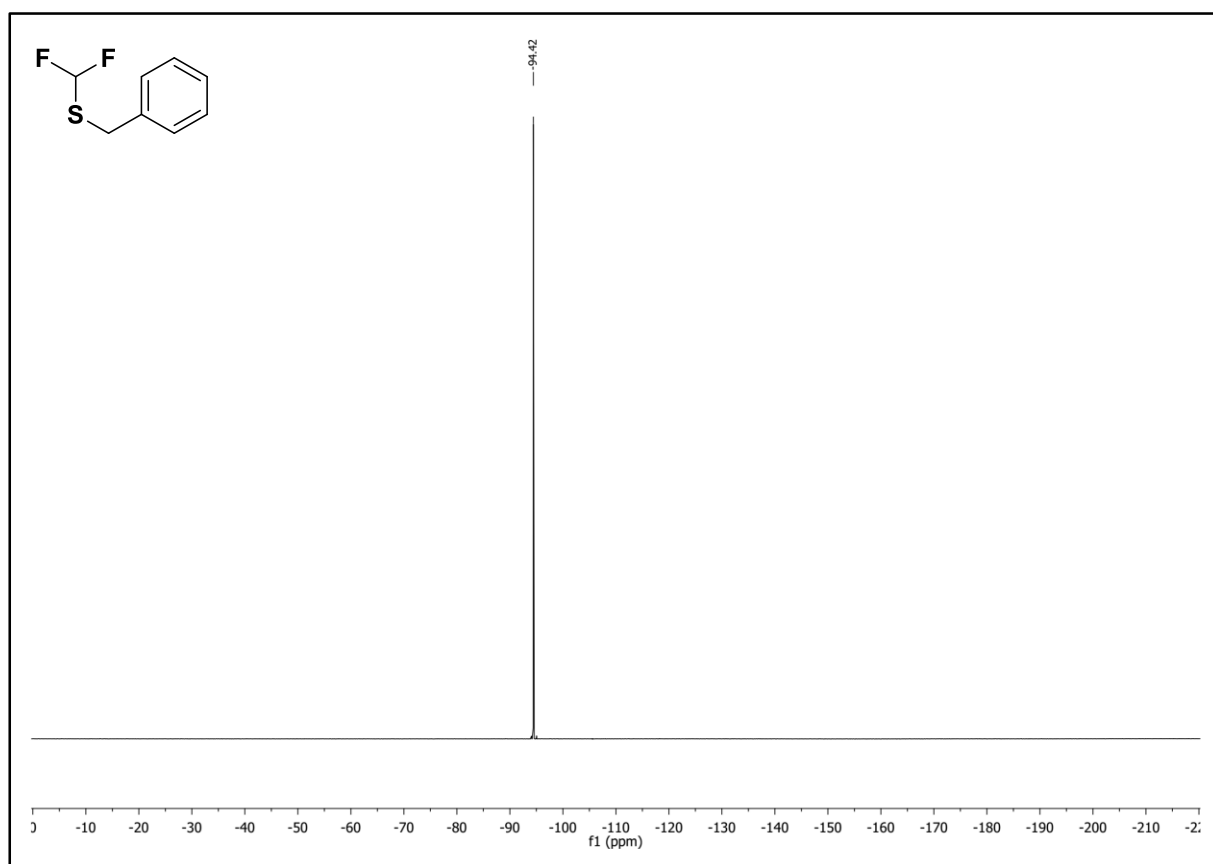
(Difluoromethyl)(phenyl)selenane (**4o**): ^1H , ^{13}C , ^{19}F



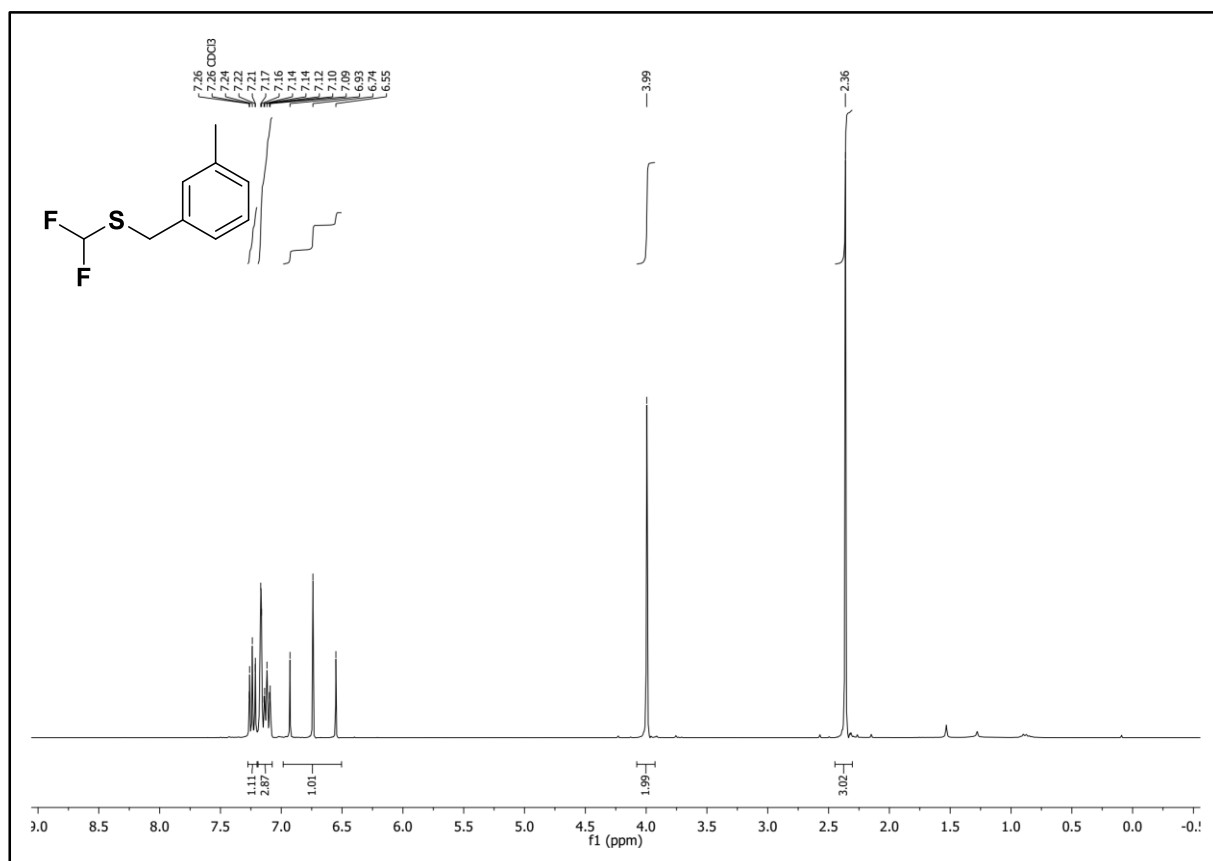


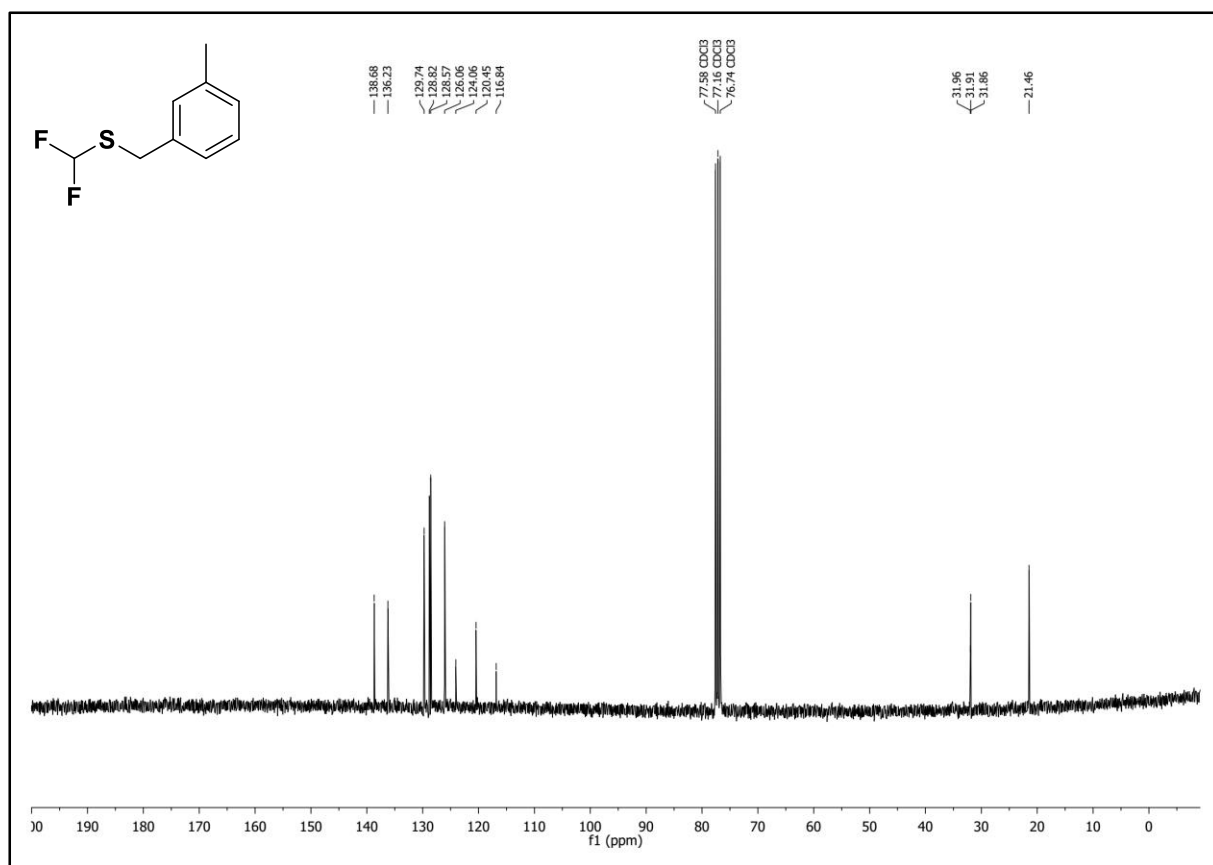
Benzyl(difluoromethyl)sulfane (**4p**): ^1H , ^{13}C , ^{19}F



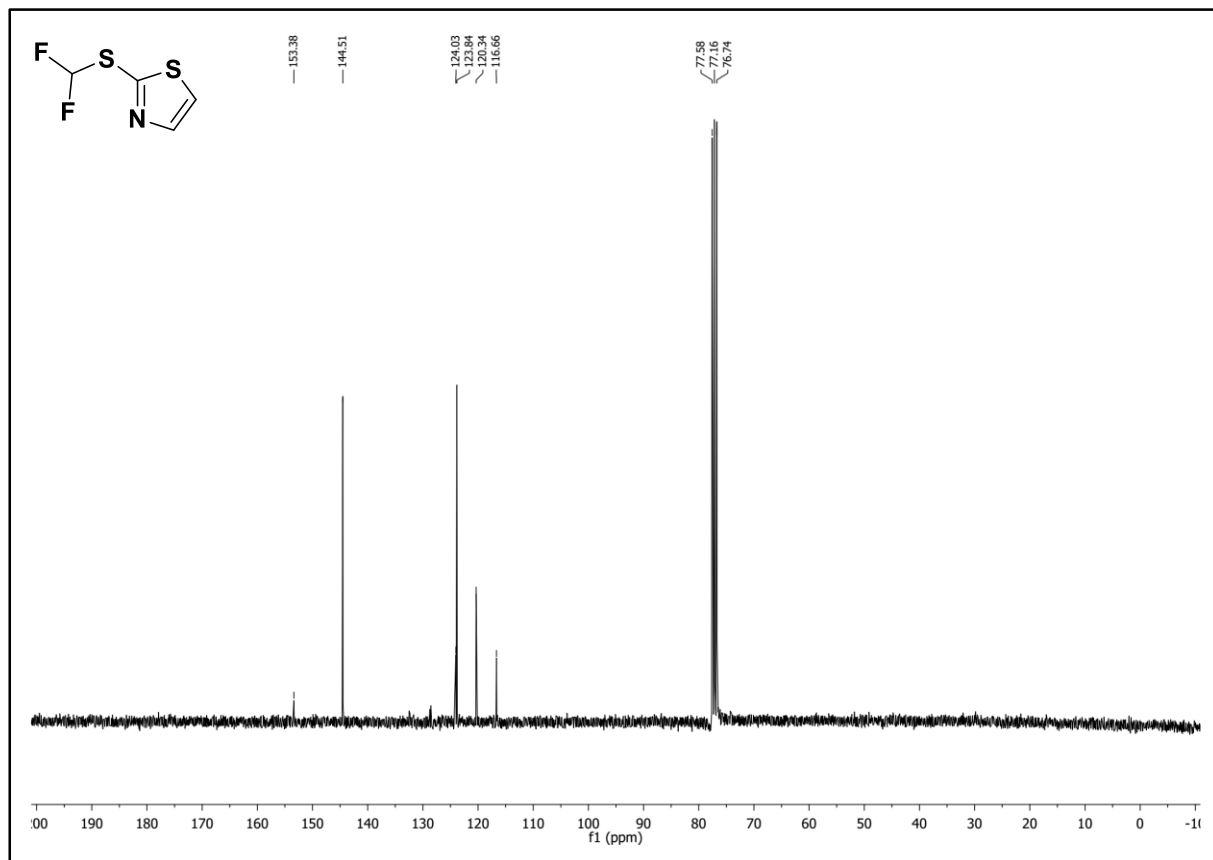
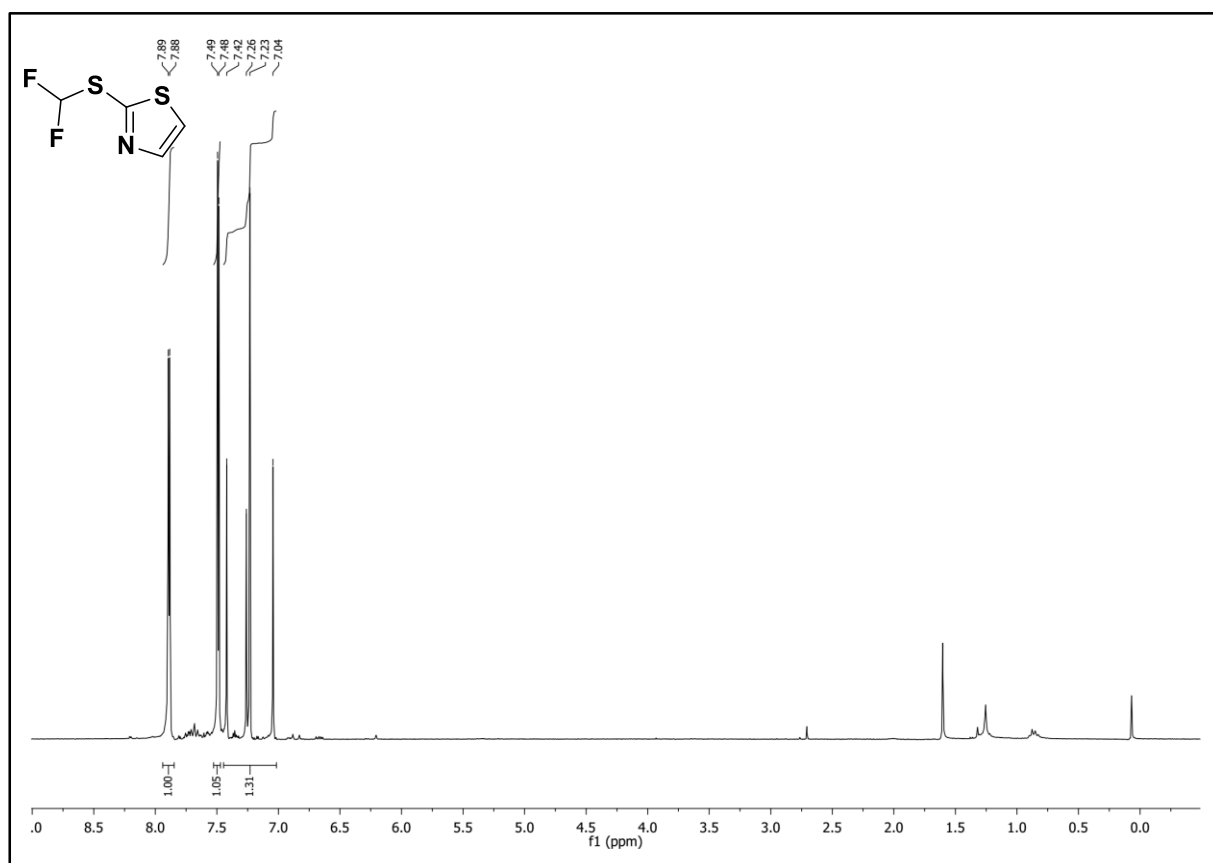


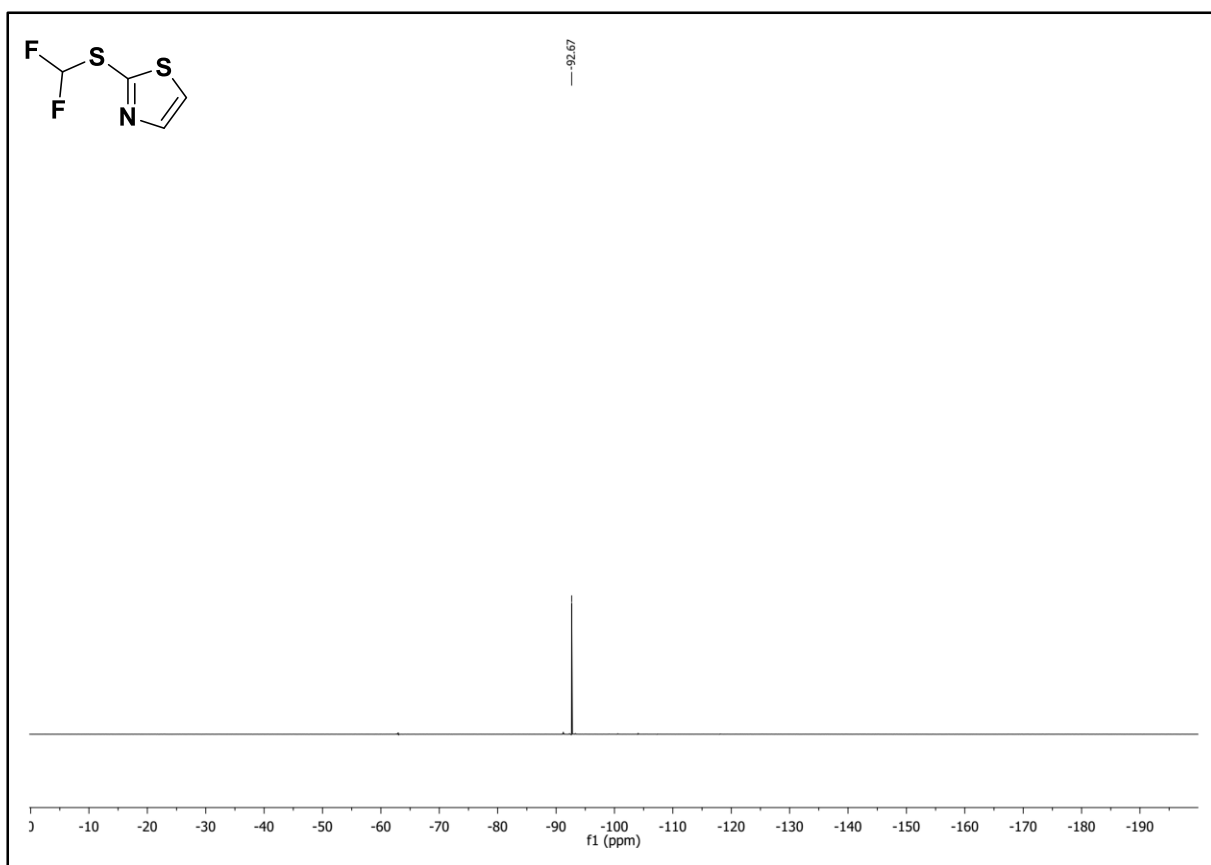
(Difluoromethyl)(3-methylbenzyl)sulfane (**4q**): ^1H , ^{13}C , ^{19}F



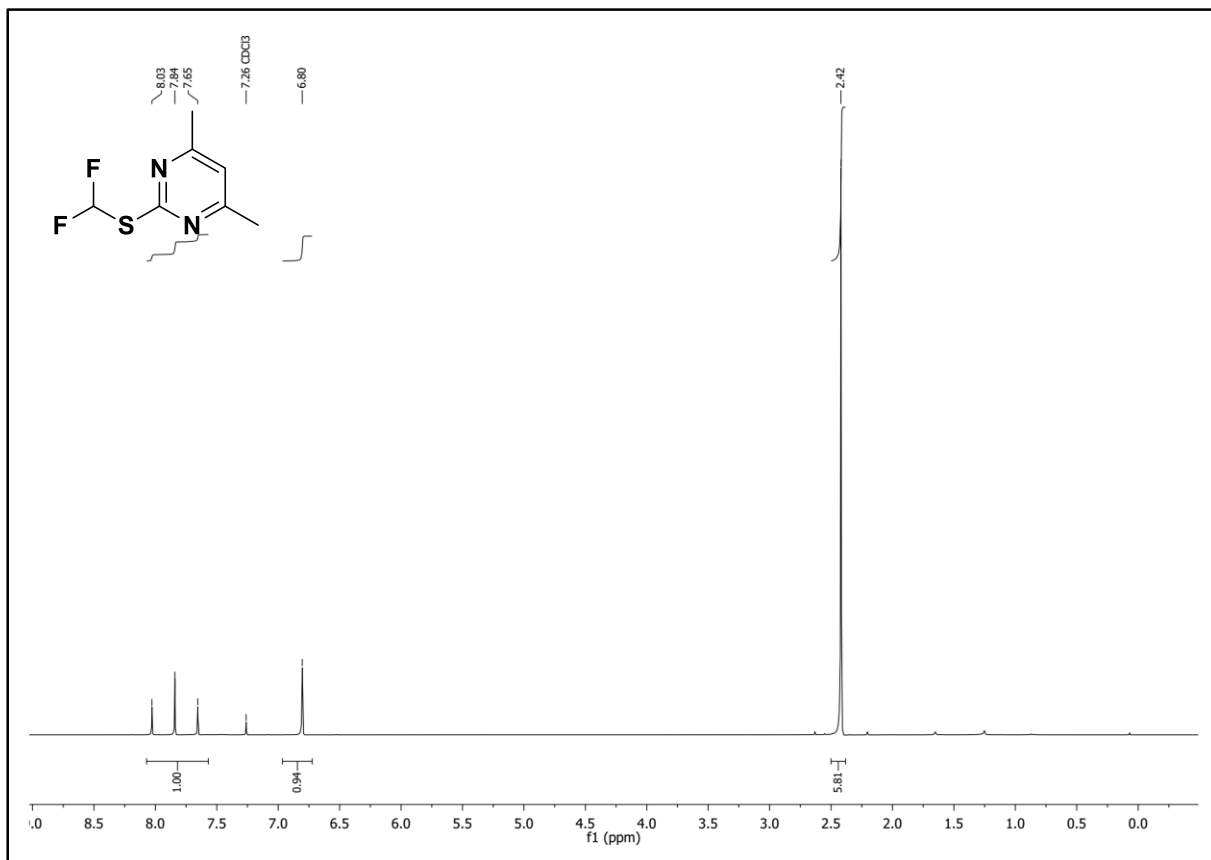


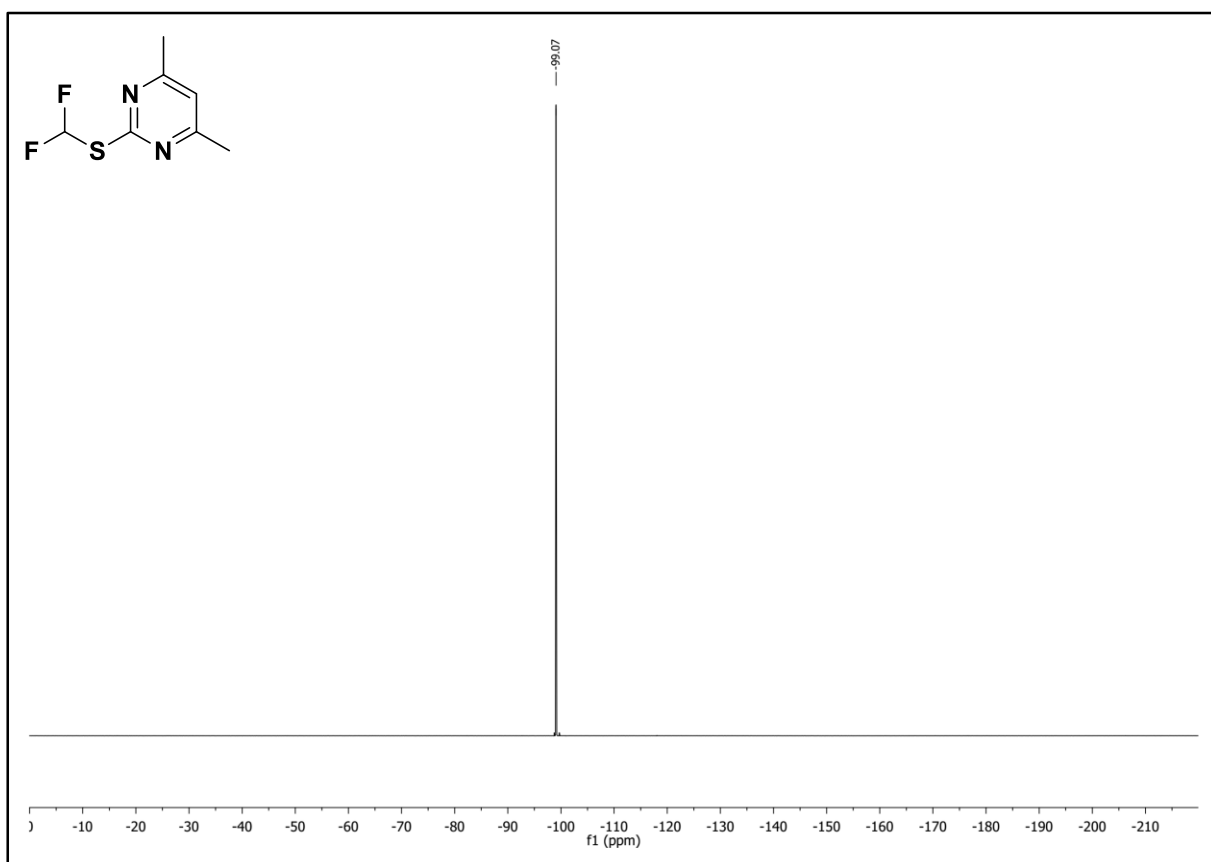
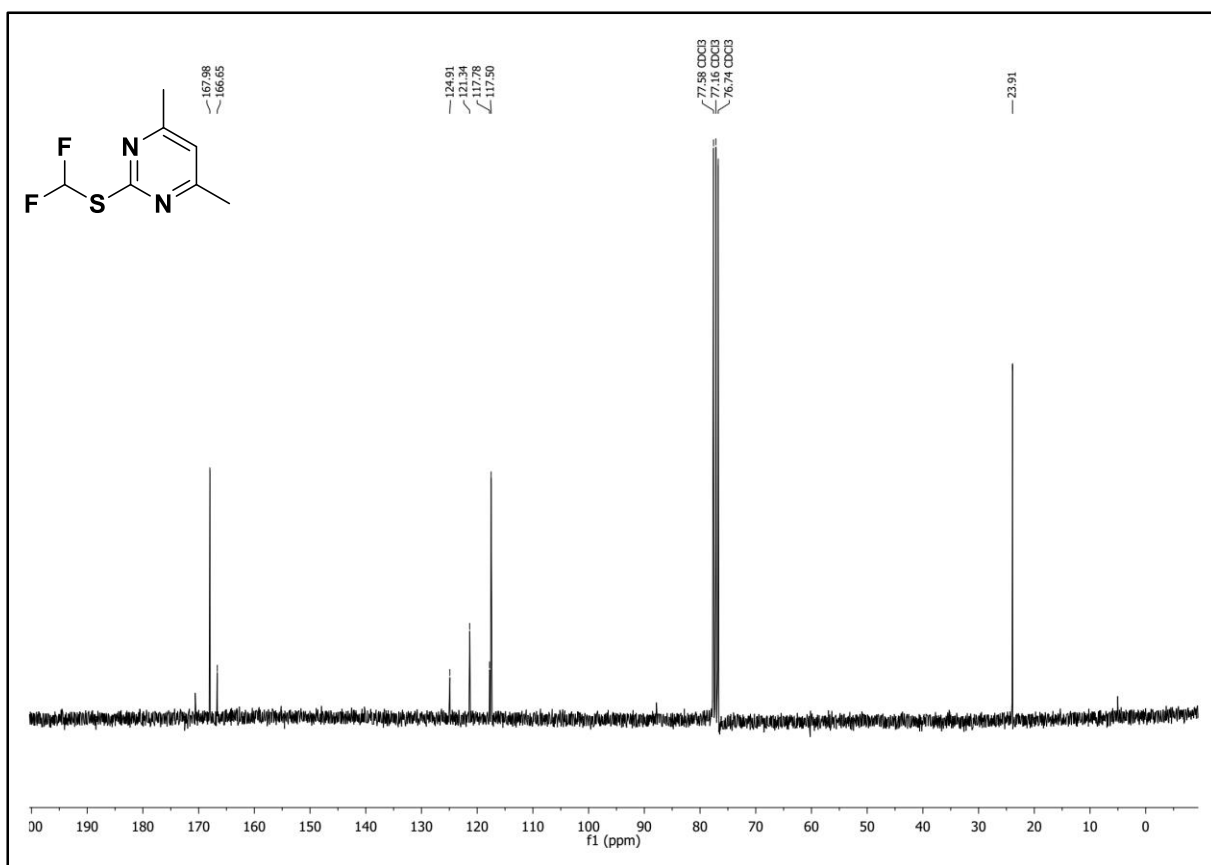
2-((Difluoromethyl)thio)thiazole (**4r**): ^1H , ^{13}C , ^{19}F

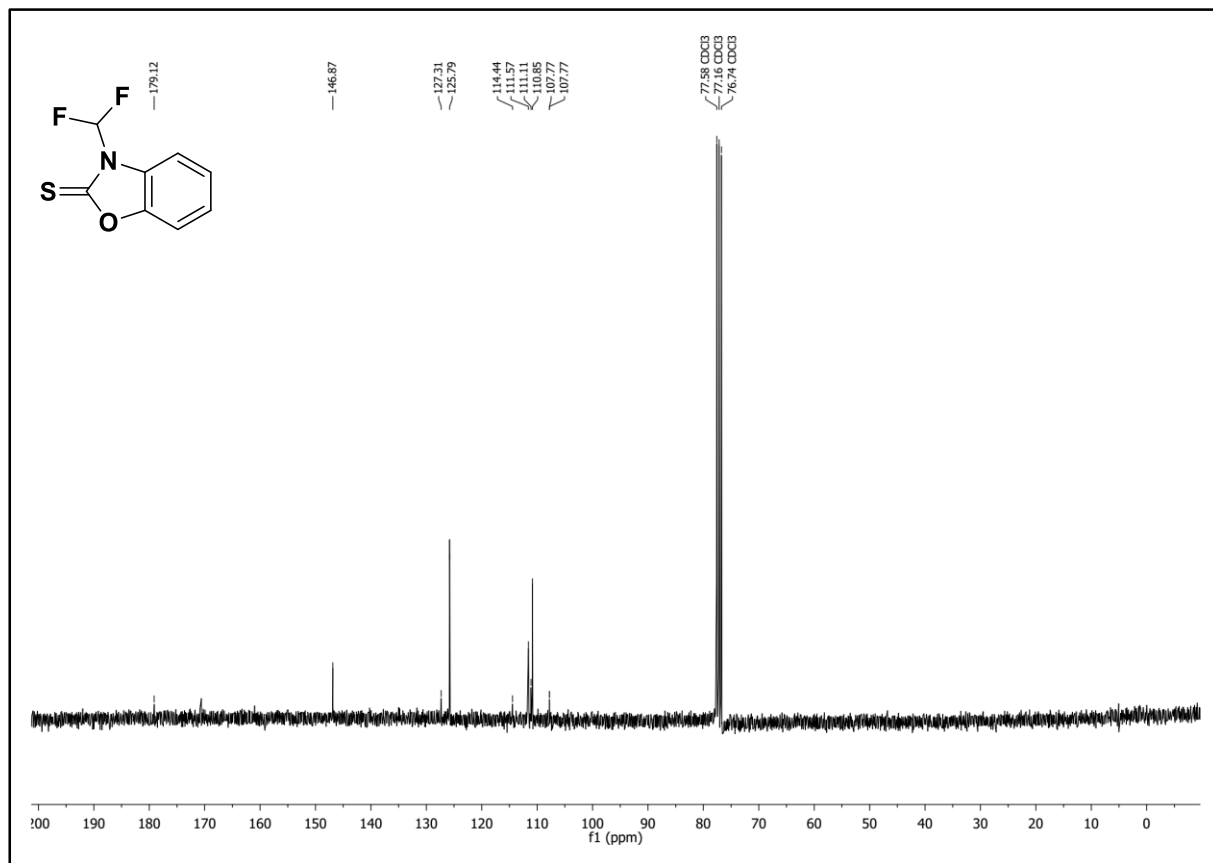
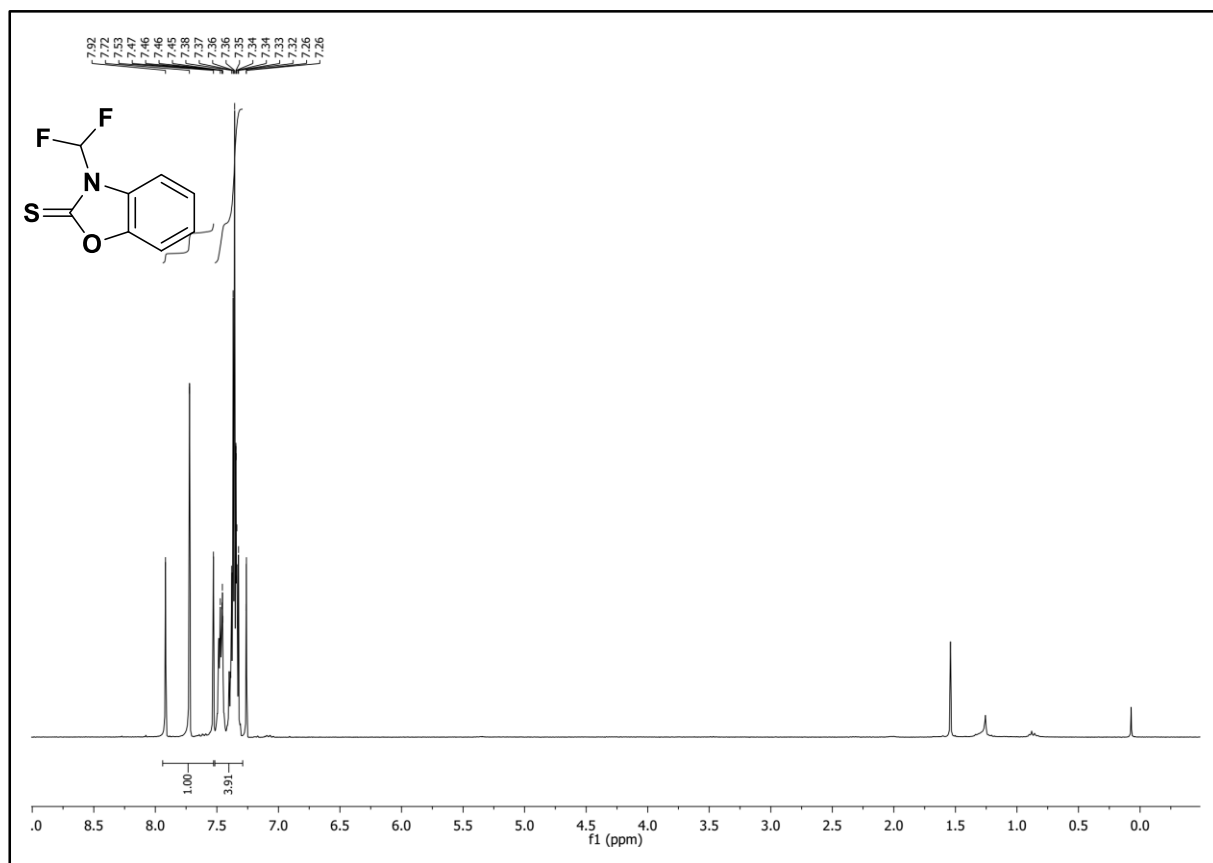


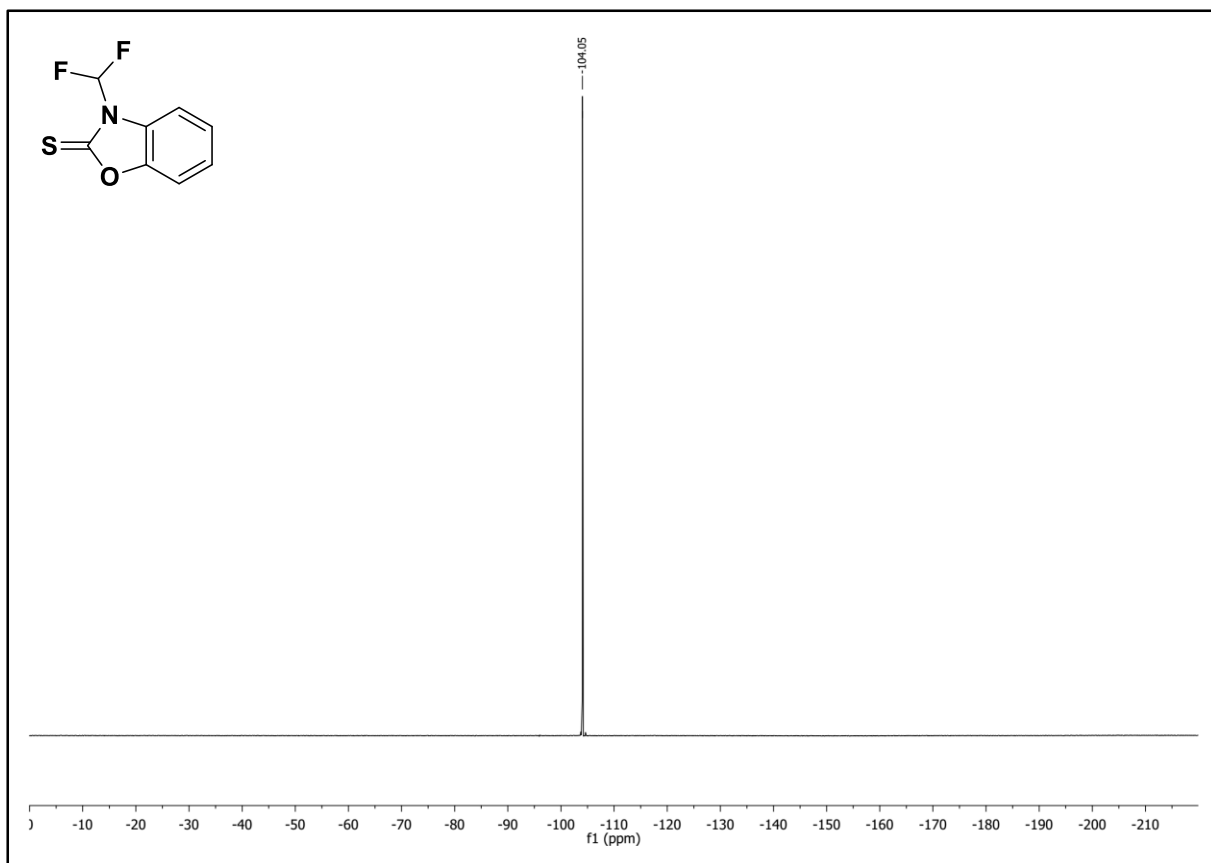


2-((Difluoromethyl)thio)-4,6-dimethylpyrimidine (**4s**): ^1H , ^{13}C , ^{19}F

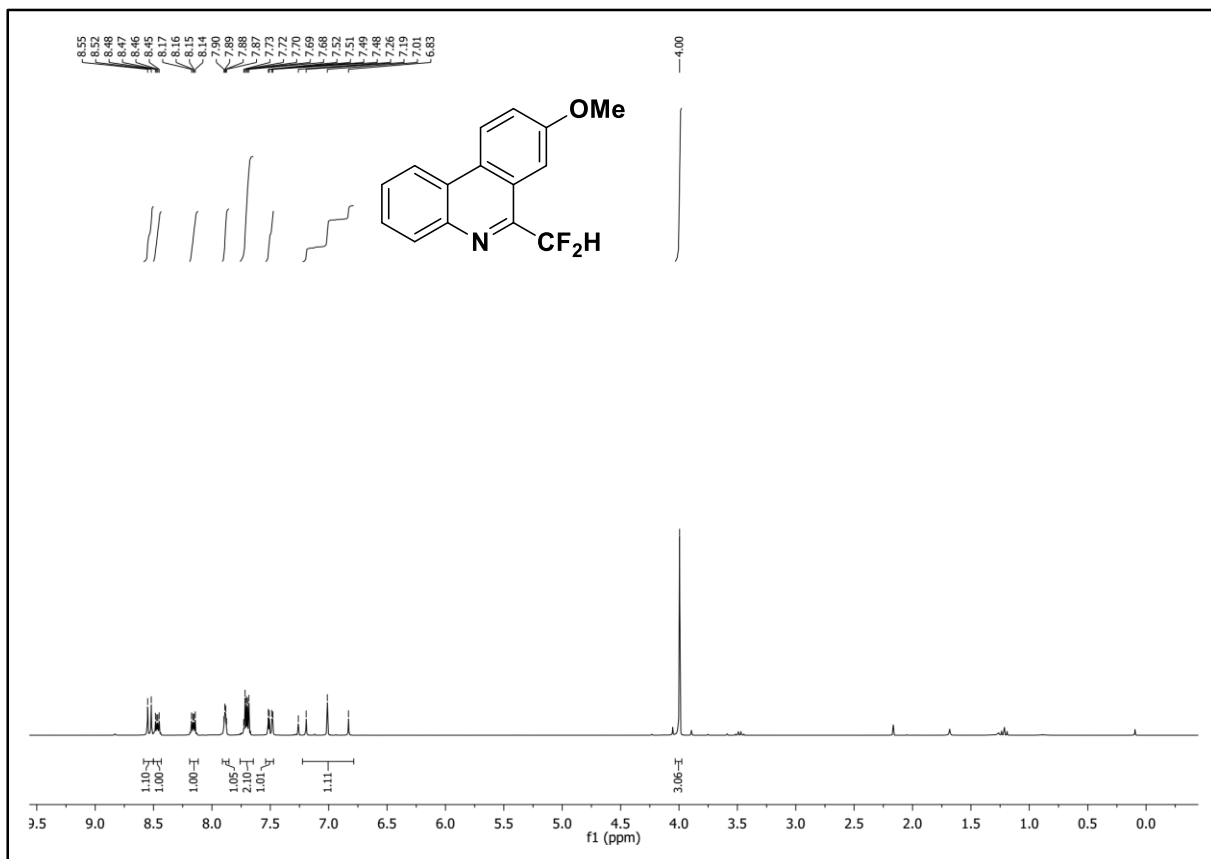


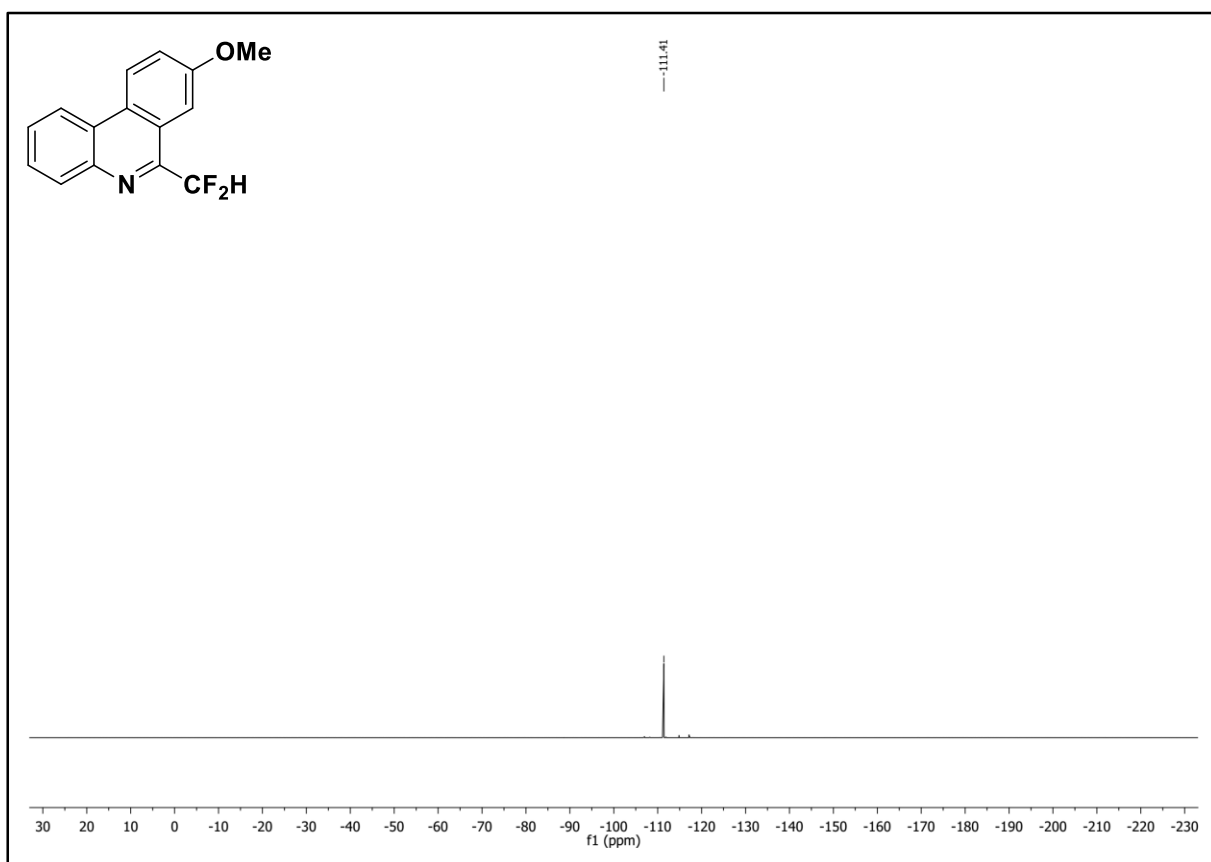
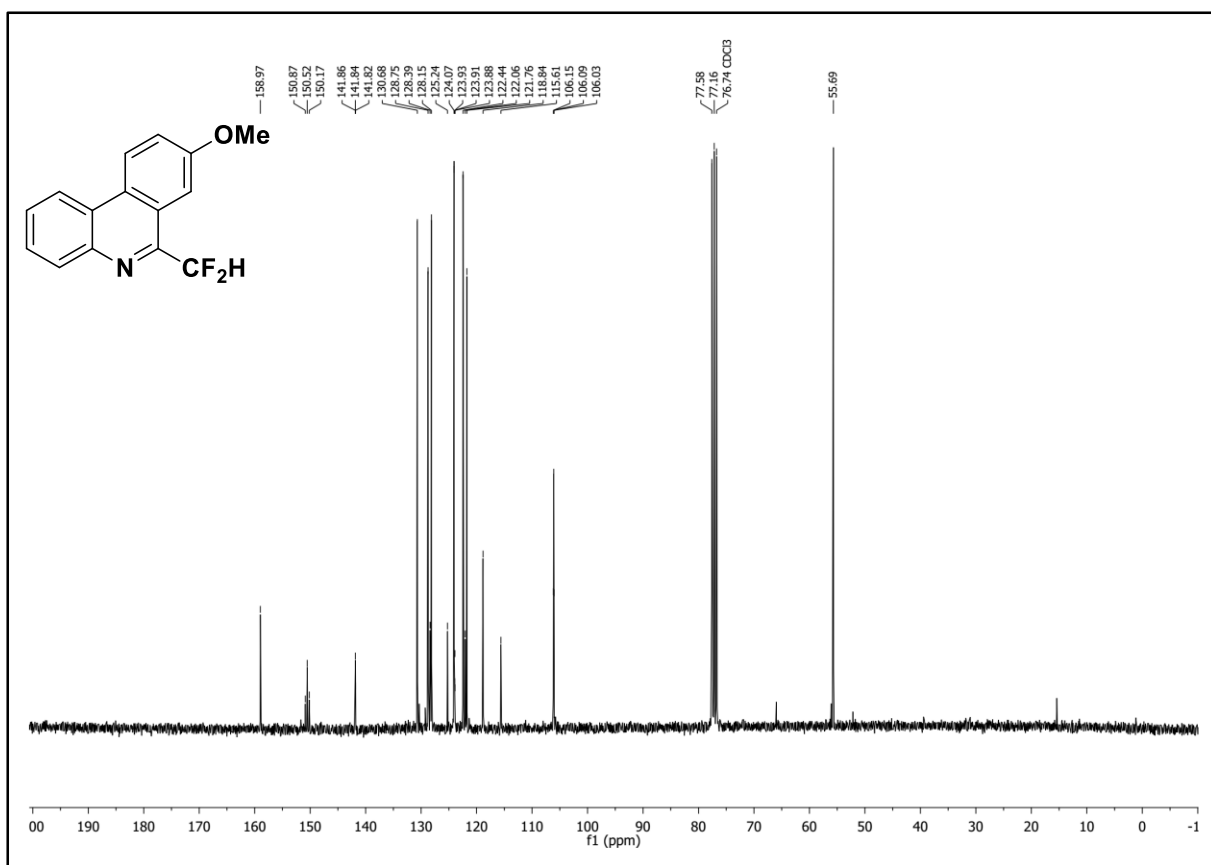


3-(Difluoromethyl)benzo[d]oxazole-2(3H)-thione (**4t**): ^1H , ^{13}C , ^{19}F 

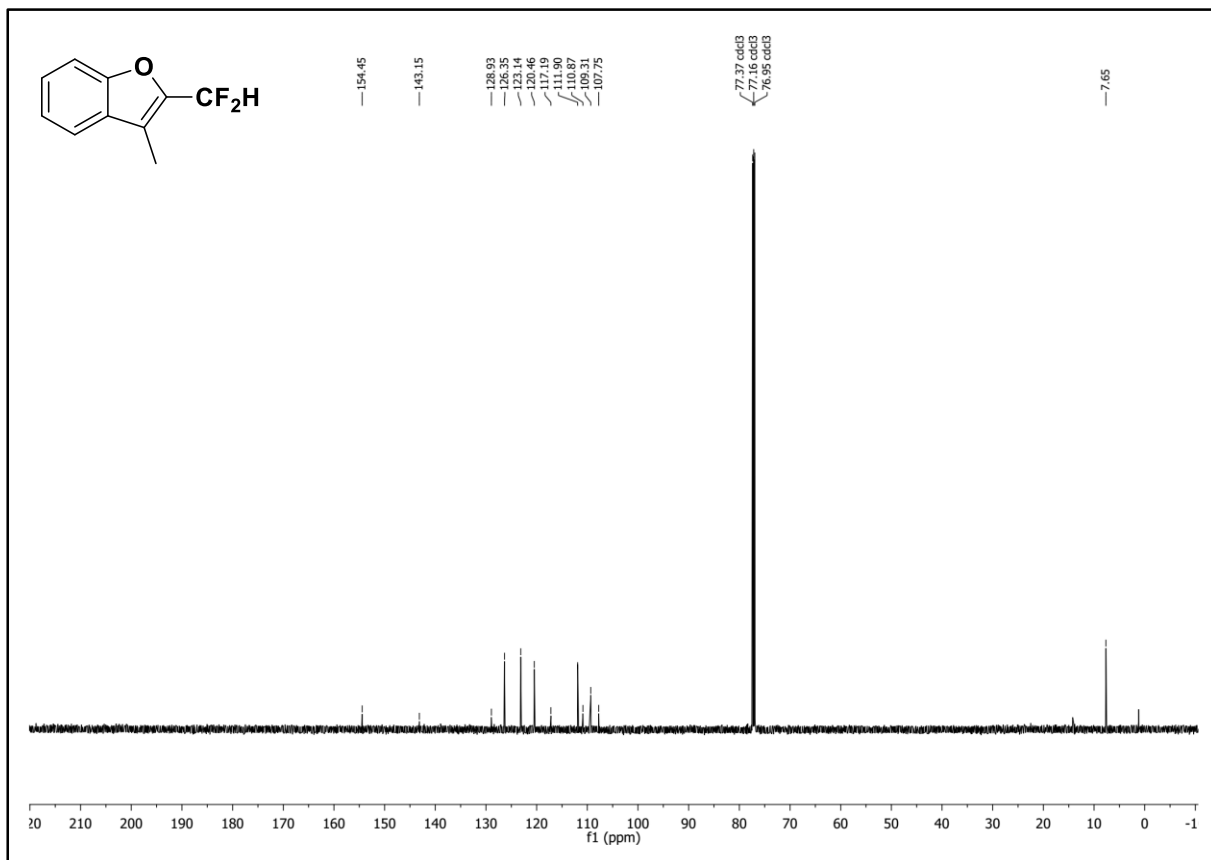
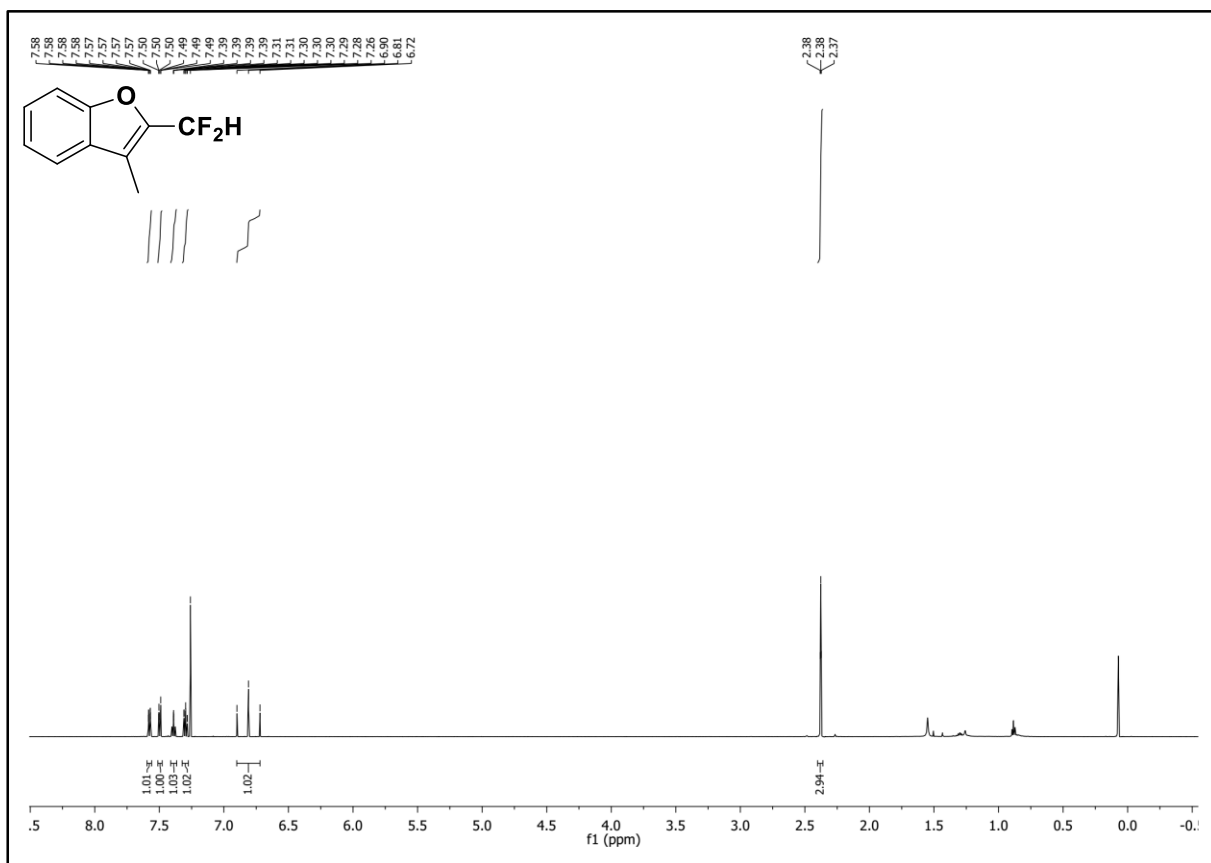


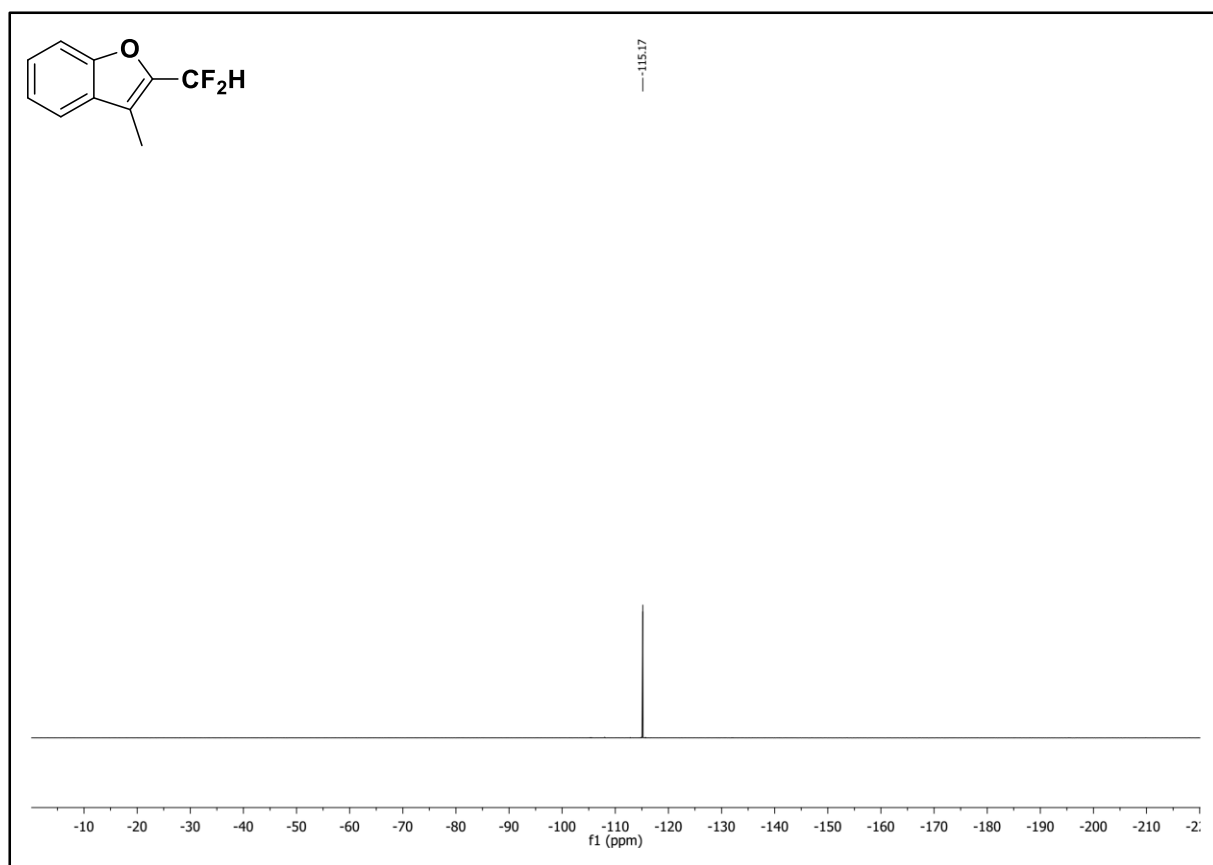
6-(Difluoromethyl)-8-methoxyphenanthridine (9): ^1H , ^{13}C , ^{19}F





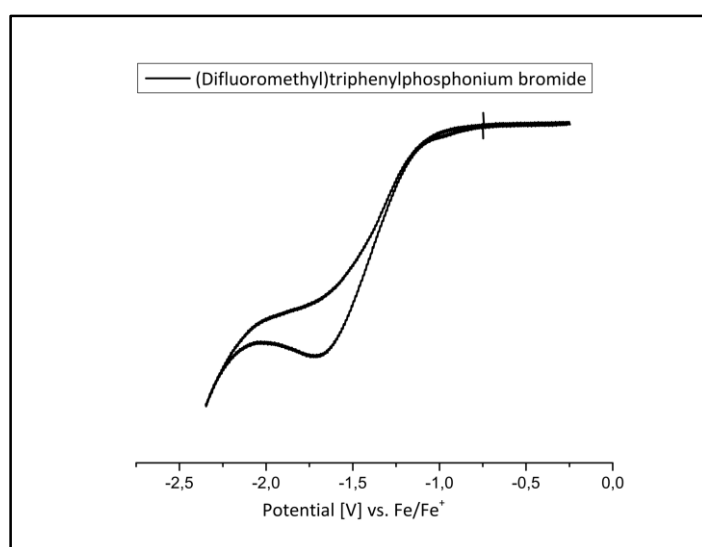
2-(Difluoromethyl)-3-methylbenzofuran (**11**): ^1H , ^{13}C , ^{31}P





9. Cyclovoltammetric Measurements

Cyclovoltammetric Measurements were performed using a *TSC 1600* closed measuring cell. The measurements were conducted in dichloromethane with a concentration of 10 mM substance and 0.1 M OF tetrabutylammonium tetrafluoroborate. A platinum wire (melted down in glass) was used as the working electrode and platinum crucible as counter electrode. The voltage was measured against Ag/AgCl pseudo reference electrode and was internally referenced to the ferrocene/ferrocenium ion couple. The *Metrohm Autolab PGSTAT204* was used as potentiostat.



10. Literature

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