

Supporting Information

Photocatalyst-free hydrothiolation of *gem*-difluoroalkenes with thiols

Lin Zuo,^a Zhiyang Zhang,^a Xiao-Ya Yuan,^{ab} Kai Sun^{a*} and Bing Yu^{a*}

^aCollege of Chemistry, Zhengzhou University, Zhengzhou 450001, China. Email: sunkaichem@zzu.edu.cn; bingyu@zzu.edu.cn

^bNational Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass, Nanjing Forestry University, Nanjing 210037, China

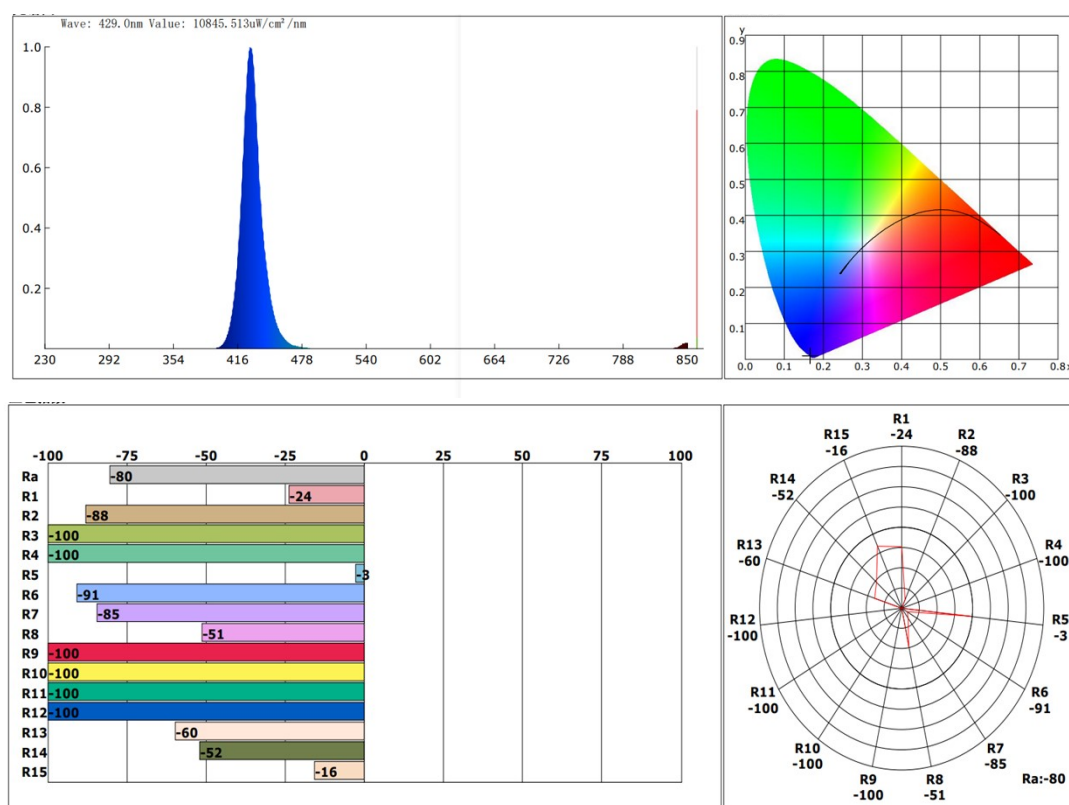
Table of Contents

1 General Methods.....	S1
2 Experimental Procedures	S1
3 Characterization Data for Products.....	S4
4 NMR spectrum copies	S8

1 General Methods

All the chemicals were purchased from commercial suppliers, and most commercially available reagents were directly used without further purification, except for some solvents used that require degassing treatment. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased. All the ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Bruker Avance 600 MHz spectrometer operating at 600 MHz, 151 MHz, and 565 MHz, respectively. Proton chemical shifts δ were given in ppm using tetramethylsilane (TMS) as the internal standard. All NMR spectra were recorded in CDCl_3 at room temperature (20 ± 3 °C). High-resolution mass spectroscopy (HRMS) was taken with a 3000-mass spectrometer, using Waters Q-ToF MS/MS system with the ESI technique. The spectrum of our lamp and the visible-light irradiation instrument.

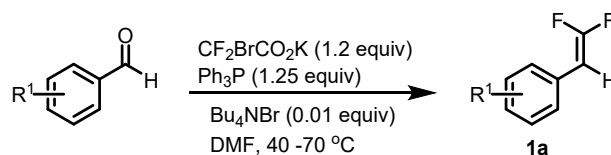
The spectrum of the lamp and the visible-light irradiation instrument Photochemical reaction was carried out under visible-light irradiation by a blue LED at 20 °C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. The blue LED's energy peak wavelength is 430 nm. More details are shown in Figure S1.



Figures S1. Spectrum of the lamp

2 Experimental Procedures

2.1 General procedure for the synthesis of gem-difluorostyrenes **1a**



Scheme S1 Synthetic procedure for **1a**

Potassium bromodifluoroacetate (2.56 g, 12 mmol) was placed in a 100 mL 2-neck round-bottom flask and dried under vacuum at 90°C for 5 hours. The flask was cooled to room temperature, then aldehyde (10 mmol), triphenylphosphine (3.28 g, 12.5 mmol), Bu₄NBr (32 mg, 0.1 mmol), and dry DMF (20 mL) were added successively. A thermometer and bubble counter were attached to the reaction flask, the mixture was slowly heated up until gas evolution began (around 40-45°C). The reaction temperature was adjusted to maintain the gas evolution rate around **1a** bubble per second (in case of acceleration, the reaction mixture should be cooled a little bit with a tap water bath). As the reaction progresses. The bath temperature was slowly increased up to 70 °C and kept at this temperature until the gas evolution ceased (around 3 hours).

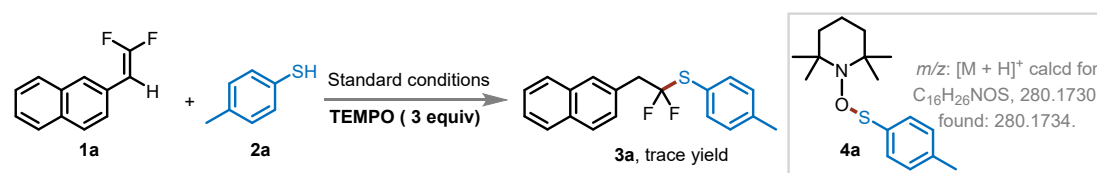
2.2 General procedure for the synthesis of products (exemplified by **3a**)



Scheme S2 Synthetic procedure for **3a**

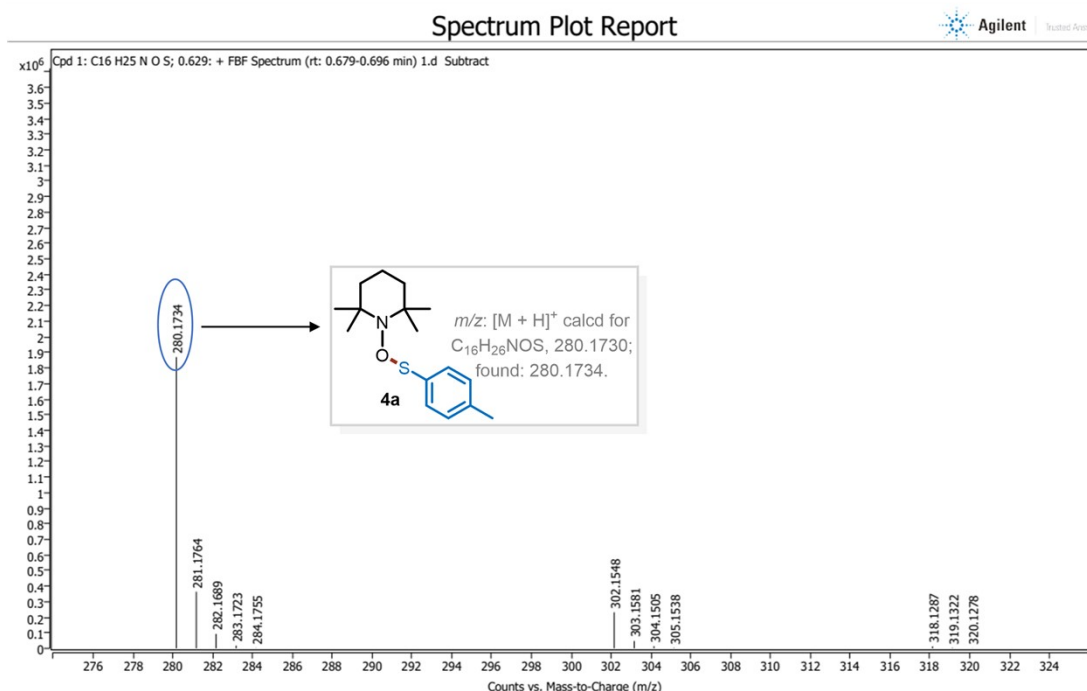
In a 10 mL Schlenk tube, a mixture of 2-(2,2-difluorovinyl) naphthalene **1a** (0.2 mmol), 4-methylbenzenethiol **2a** (0.3 mmol, 1.5 equiv) in 2.0 mL degassed dimethyl carbonate. The reaction mixture was then degassed by freeze-pump-thaw procedure and then backfilled with N₂ before stirring for 3 h at room temperature under the irradiation of blue LED (430 nm, 10 W). The reaction mixture was concentrated in vacuo and the residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired product **3a**.

2.3 Control experiments



Scheme S3 Control experiment

In a 10 mL reaction tube, 2-(2,2-difluorovinyl) naphthalene **1a** (0.2 mmol), 4-methylbenzenethiol **2a** (0.3 mmol) were added in degassed dimethyl carbonate (2.0 mL). Afterward, scavengers 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (3 equiv) was added in the mixture, respectively. The reaction mixture was then degassed by freeze-pump-thaw procedure and then backfilled with N₂ before stirring for 3 h at room temperature under the irradiation of blue light.



Figures S2. The HRMS of the adduct **4a**

2.4 Light ON/OFF control experiment

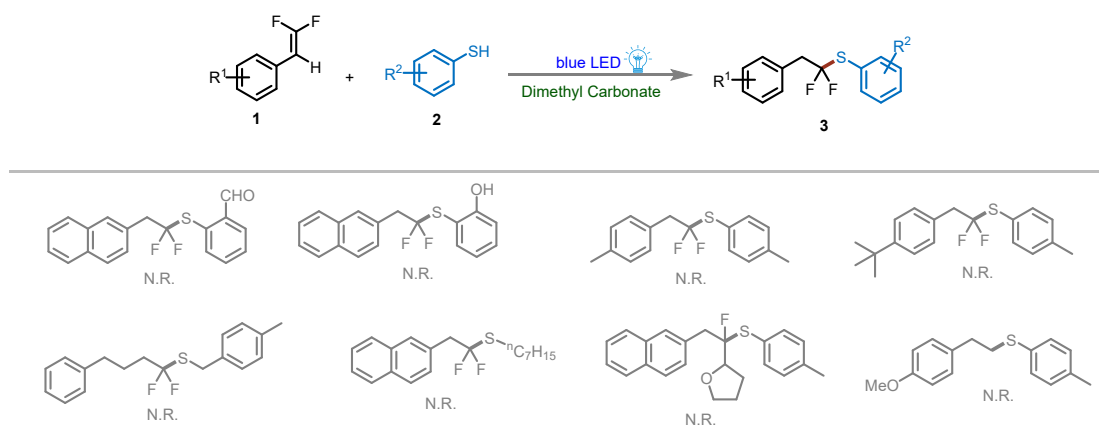


Scheme S4 Light on/off experiment

To 6 identical 25 mL reaction tubes, 2-(2,2-difluorovinyl) naphthalene **1a** (0.1 mmol), 4-methylbenzenethiol **2a** (0.15 mmol) in 1.0 mL degassed dimethyl carbonate. The reaction mixture was then degassed by freeze-pump-thaw procedure and then backfilled with N₂ before stirring at room temperature under the irradiation of blue LED (430 nm, 10 W). All the reactions were stirred under blue light irradiation at ambient temperature for 0.5 h. Then the light was turned off. Remove one of the tubes. The reaction mixture was concentrated under reduced pressure. The yield of the

product was determined by ^1H NMR using 1,1,2,2-tetrachloroethane as the internal standard. The remaining mixture was stirred in the absence of light for an additional 0.5 h. Then remove one of the tubes. ^1H NMR analysis was performed every 0.5 h until the reaction time reached 3 h.

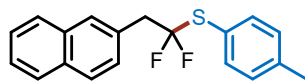
2.5 Failed substrates



Scheme S5. Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol) in DCM (2 mL) under the irradiation with 430 nm 10 W blue LED, and nitrogen atmosphere for 3 h.

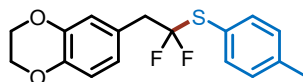
3 Characterization Data for Products

(1,1-difluoro-2-(naphthalen-2-yl)ethyl)(p-tolyl)sulfane (3a)



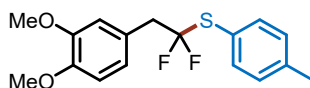
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (53.4 mg, 85% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 3H), 7.82 (d, J = 1.8 Hz, 1H), 7.61 – 7.46 (m, 5H), 7.24 (d, J = 8.0 Hz, 2H), 3.66 (t, J = 14.7 Hz, 2H), 2.42 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 140.2, 136.3, 133.4, 132.9, 129.9, 129.8, 129.7 (t, J = 3.3 Hz), 128.9 (t, J = 279.4 Hz), 128.3, 128.1, 127.9, 127.8, 126.3, 126.1, 123.4, 45.3 (t, J = 24.5 Hz), 21.3. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.55.

6-(2,2-difluoro-2-(p-tolylthio)ethyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (3b)



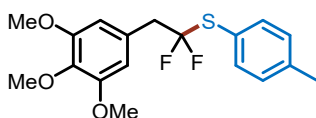
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (48.9 mg, 76% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.58 – 7.36 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.2 Hz, 2H), 6.75 (dd, J = 8.2, 2.1 Hz, 1H), 4.24 (s, 4H), 3.29 (t, J = 14.6 Hz, 2H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 143.3, 143.3, 140.0, 136.2, 129.8, 128.7 (t, J = 280.9 Hz), 125.2 (t, J = 3.4 Hz), 123.6, 123.5, 119.4, 117.2, 64.4, 64.3, 44.4 (t, J = 24.5 Hz), 21.3. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -72.12. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{16}\text{F}_2\text{O}_2\text{SK}$ [$\text{M} + \text{K}$] $^+$, 361.0471; found, 361.0466.

(2-(3,4-dimethoxyphenyl)-1,1-difluoroethyl)(p-tolyl)sulfane (3c)



Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (55.7 mg, 86% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.37 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.74 (s, 2H), 6.72 (s, 1H), 3.78 (d, J = 3.7 Hz, 6H), 3.27 (t, J = 14.6 Hz, 2H), 2.27 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 147.7, 147.6, 139.0, 135.2, 128.8, 127.8 (t, J = 279.4 Hz), 123.5 (t, J = 3.3 Hz), 122.3, 121.9, 112.5, 109.9, 54.8, 43.7 (t, J = 24.4 Hz), 20.2. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.99. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{18}\text{F}_2\text{O}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 347.0888; found, 347.0874.

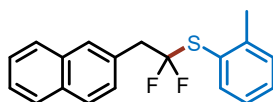
(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)(p-tolyl)sulfane (3d)



Purification by column chromatography on silica gel afforded the title compound as a colorless liquid

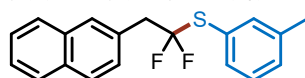
(67.3 mg, 95% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.57 – 7.41 (m, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 6.49 (s, 2H), 3.85 (s, 9H), 3.35 (t, $J = 14.7$ Hz, 2H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 153.08, 140.14, 137.67, 136.21, 129.86, 128.63, 127.55 (t, $J = 3.1$ Hz), 123.33, 107.69, 60.86, 56.14, 45.35 (t, $J = 24.4$ Hz), 21.29. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.87. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 377.0993; found, 377.1001.

(1,1-difluoro-2-(naphthalen-2-yl)ethyl)(o-tolyl)sulfane (3e)



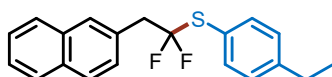
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (38.0 mg, 63% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.78 (m, 3H), 7.74 (d, $J = 1.8$ Hz, 1H), 7.59 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 1H), 7.34 – 7.23 (m, 2H), 7.16 (td, $J = 7.5, 1.7$ Hz, 1H), 3.60 (t, $J = 14.7$ Hz, 2H), 2.41 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 143.8, 138.1, 133.3, 132.8, 131.1, 130.7, 130.3, 129.73, 129.70 (t, $J = 2.5$ Hz), 128.7 (t, $J = 280.9$ Hz), 128.2, 128.1, 127.9, 127.7, 126.4, 126.2, 126.1, 45.5 (t, $J = 24.3$ Hz), 21.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.34. HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{16}\text{F}_2\text{SK}$ [$\text{M} + \text{K}$] $^+$, 353.0572; found, 353.0586.

(1,1-difluoro-2-(naphthalen-2-yl)ethyl)(m-tolyl)sulfane (3f)



Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (45.2 mg, 72% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.82 (dd, $J = 11.2, 7.1$ Hz, 3H), 7.74 (s, 1H), 7.51 – 7.45 (m, 2H), 7.41 (dd, $J = 8.4, 1.7$ Hz, 1H), 7.38 (dt, $J = 3.8, 1.7$ Hz, 2H), 7.28 – 7.15 (m, 2H), 3.58 (t, $J = 14.7$ Hz, 2H), 2.33 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 138.9, 136.8, 133.3, 133.2, 132.8, 130.6, 129.8, 129.6 (t, $J = 3.2$ Hz), 128.9 (d, $J = 10.5$ Hz), 128.7 (t, $J = 279.4$ Hz), 128.3, 128.1, 127.9, 127.7, 126.6, 126.2, 126.1, 45.4 (t, $J = 24.5$ Hz), 21.2. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.14. HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{16}\text{F}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 337.0833; found, 337.0835.

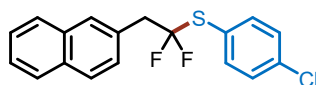
(1,1-difluoro-2-(naphthalen-2-yl)ethyl)(4-ethylphenyl)sulfane (3g)



Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (52.5 mg, 80% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.91 – 7.76 (m, 3H), 7.74 (d, $J = 1.8$ Hz, 1H), 7.54 – 7.44 (m, 4H), 7.41 (dd, $J = 8.7, 1.7$ Hz, 1H), 7.20 – 7.16 (m, 2H), 3.57 (t, $J = 14.6$ Hz, 2H), 2.64 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 146.3, 136.4, 133.3, 132.8, 129.8, 129.7 (t, $J = 3.3$ Hz), 128.7, 128.3, 128.1, 128.7 (t, $J = 279.4$ Hz), 127.9,

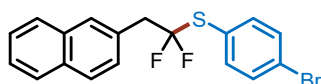
127.7, 126.2, 126.1, 123.6, 45.3 (t, $J = 24.5$ Hz), 28.6, 15.3. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform- d) δ -71.50. HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{19}\text{F}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 329.1170; found, 329.1205.

(4-chlorophenyl)(1,1-difluoro-2-(naphthalen-2-yl)ethyl)sulfane (**3h**)



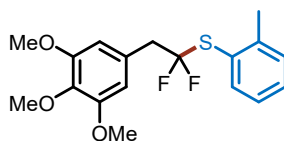
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (48.4 mg, 73% yield); ^1H NMR (600 MHz, Chloroform- d) δ 7.93 – 7.79 (m, 3H), 7.76 – 7.72 (m, 1H), 7.51 – 7.46 (m, 4H), 7.41 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.35 – 7.28 (m, 2H), 3.59 (t, $J = 14.5$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform- d) δ 137.6, 133.3, 132.9, 132.3, 129.8, 129.3 (t, $J = 3.4$ Hz), 128.5 (t, $J = 280.9$ Hz), 128.2, 128.1, 127.9, 127.7, 126.3, 126.2, 125.9, 124.7, 45.4 (t, $J = 24.1$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform- d) δ -70.90. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{13}\text{ClF}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 357.0287; found, 357.0323.

(4-bromophenyl)(1,1-difluoro-2-(naphthalen-2-yl)ethyl)sulfane (**3i**)



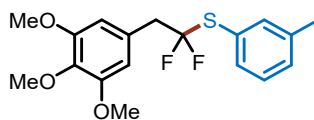
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (51.3 mg, 68% yield); ^1H NMR (600 MHz, Chloroform- d) δ 7.86 – 7.79 (m, 3H), 7.74 (d, $J = 1.8$ Hz, 1H), 7.52 – 7.45 (m, 4H), 7.43 – 7.37 (m, 3H), 3.59 (t, $J = 14.5$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform- d) δ 137.6, 133.3, 132.9, 132.3, 129.8, 129.3 (t, $J = 3.4$ Hz), 128.5 (t, $J = 280.9$ Hz), 128.2, 128.1, 127.9, 127.7, 126.3, 126.2, 125.9, 124.7, 45.4 (t, $J = 24.1$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform- d) δ -70.90. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{13}\text{BrF}_2\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 400.9782; found, 400.9728.

(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)(*o*-tolyl)sulfane (**3j**)



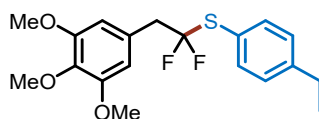
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (58.1 mg, 82% yield); ^1H NMR (600 MHz, Chloroform- d) δ 7.60 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.37 – 7.24 (m, 2H), 7.18 (td, $J = 7.5, 1.7$ Hz, 1H), 6.50 (s, 2H), 3.85 (d, $J = 2.1$ Hz, 9H), 3.38 (t, $J = 14.7$ Hz, 2H), 2.44 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform- d) δ 153.1, 143.7, 138.0, 137.7, 130.7, 130.6, 129.1 (t, $J = 279.3$ Hz), 127.6 (t, $J = 3.2$ Hz), 126.4, 126.2, 107.7, 60.9, 56.2, 45.6 (t, $J = 24.3$ Hz), 21.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform- d) δ -71.06. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{21}\text{F}_2\text{O}_3\text{S}$ [$\text{M} + \text{H}$] $^+$, 355.1174; found, 355.1184.

(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)(*m*-tolyl)sulfane (**3k**)



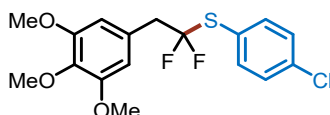
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (63.2 mg, 90% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.31 (m, 2H), 7.27 – 7.19 (m, 2H), 6.50 (s, 2H), 3.85 (s, 9H), 3.36 (t, J = 14.7 Hz, 2H), 2.35 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 153.1, 138.9, 137.7, 136.6, 133.1, 130.6, 128.8 (t, J = 279.3 Hz), 128.8, 127.5 (t, J = 3.0 Hz), 126.6, 107.7, 60.9, 56.1, 45.4 (t, J = 24.4 Hz), 21.2. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.45. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 377.0993; found, 377.1001.

(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)(4-ethylphenyl)sulfane (3l)



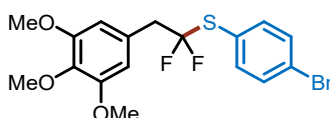
Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (64.8 mg, 88% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 8.04 – 7.24 (m, 2H), 7.30 – 6.91 (m, 2H), 6.50 (s, 2H), 3.85 (d, J = 0.8 Hz, 9H), 3.35 (t, J = 14.7 Hz, 2H), 2.66 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 153.1, 146.3, 137.7, 136.3, 134.2, 128.66, 128.66 (t, J = 279.4 Hz), 127.6 (t, J = 3.2 Hz), 123.5, 107.7, 60.9, 56.1, 45.4 (t, J = 24.4 Hz), 28.6, 15.3. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.81. HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{22}\text{F}_2\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 391.1150; found, 391.1164.

(4-chlorophenyl)(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)sulfane (3m)



Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (57.6 mg, 77% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.70 – 7.37 (m, 2H), 7.33 (dd, J = 8.1, 1.2 Hz, 2H), 6.49 (s, 2H), 3.85 (s, 9H), 3.37 (t, J = 14.6 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) δ 153.1, 137.8, 137.4, 136.4, 129.3, 128.5 (t, J = 280.9 Hz), 127.2 (t, J = 3.3 Hz), 125.3, 107.6, 60.9, 56.2, 45.4 (t, J = 24.2 Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.34. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{17}\text{ClF}_2\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}$] $^+$, 397.0447; found, 397.0449.

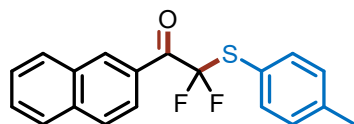
(4-bromophenyl)(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)sulfane (3n)



Purification by column chromatography on silica gel afforded the title compound as a colorless liquid (62.7 mg, 75% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.45 – 7.41 (m, 2H), 6.49 (s, 2H), 3.86 (d, J = 2.0 Hz, 9H), 3.37 (t, J = 14.6 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz,

Chloroform-*d*) δ 153.2, 137.8, 137.6, 132.3, 128.4 (t, $J = 280.9$ Hz), 127.2 (t, $J = 3.3$ Hz), 125.9, 124.7, 107.7, 60.9, 56.2, 45.4 (t, $J = 24.1$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -71.24. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{17}\text{BrF}_2\text{O}_3\text{SNa}$ $[\text{M} + \text{Na}]^+$, 440.9942; found, 440.9943.

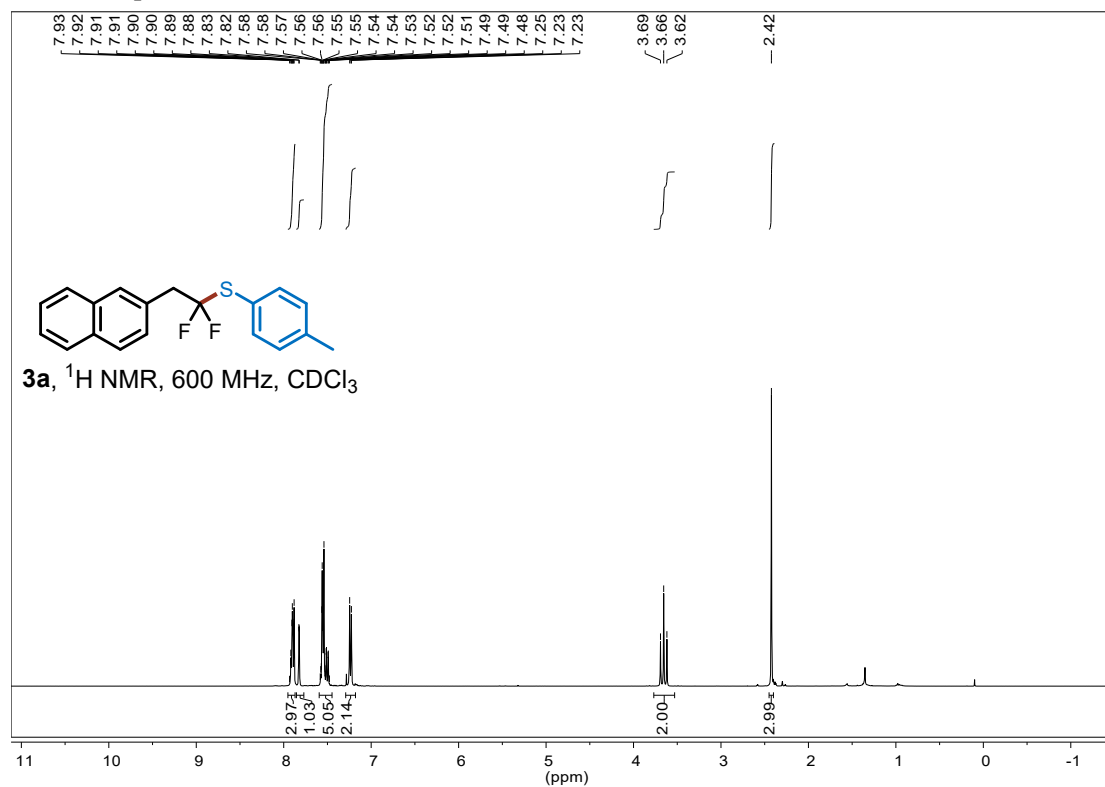
2,2-difluoro-1-(naphthalen-2-yl)-2-(p-tolylthio)ethan-1-one (5)



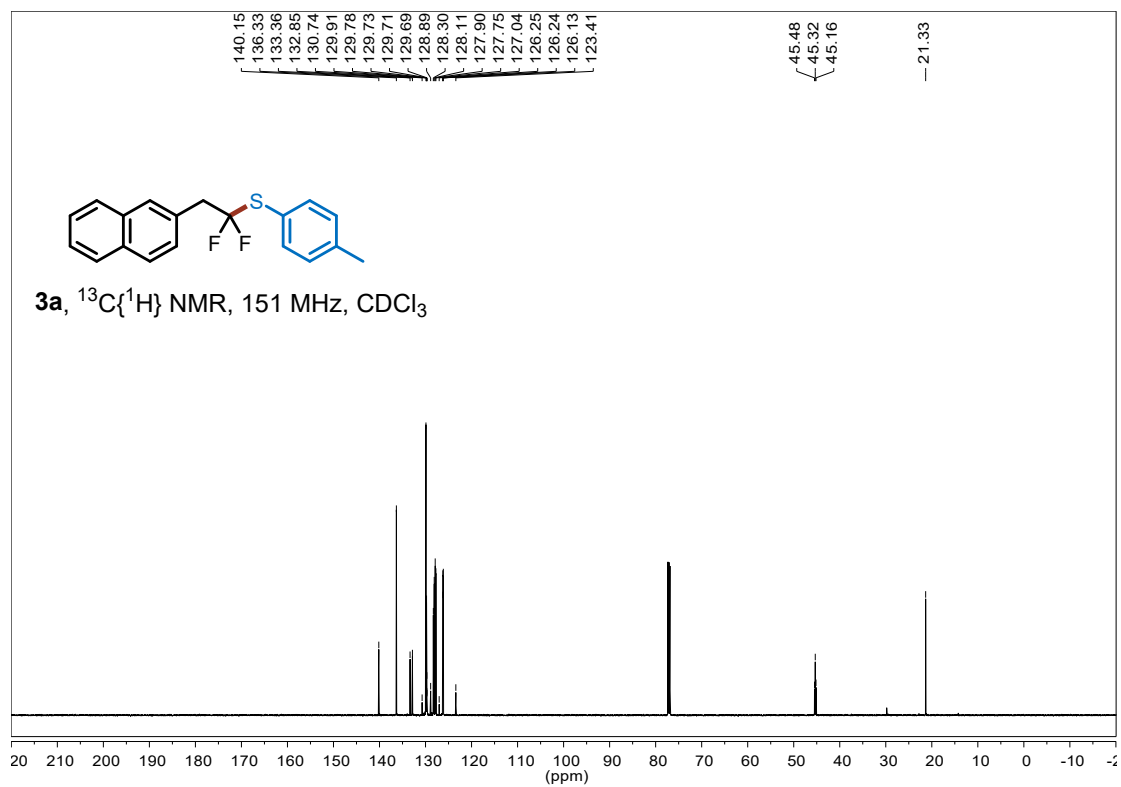
Purification by column chromatography on silica gel afforded the title compound as a white solid (51.8 mg, 79% yield); ^1H NMR (600 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 8.13 (dd, $J = 8.8, 1.8$ Hz, 1H), 8.00 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.96 – 7.89 (m, 2H), 7.69 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.61 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 7.7$ Hz, 2H), 2.39 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, Chloroform-*d*) 185.3 (t, $J = 28.1$ Hz), 141.0, 136.8, 136.1, 133.3 (t, $J = 3.6$ Hz), 132.2, 130.2, 130.1, 129.5, 128.6, 128.5, 127.8, 127.1, 125.0, 123.8 (t, $J = 290.5$ Hz), 121.3, 21.4. $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, Chloroform-*d*) δ -77.18.

4 NMR spectrum copies

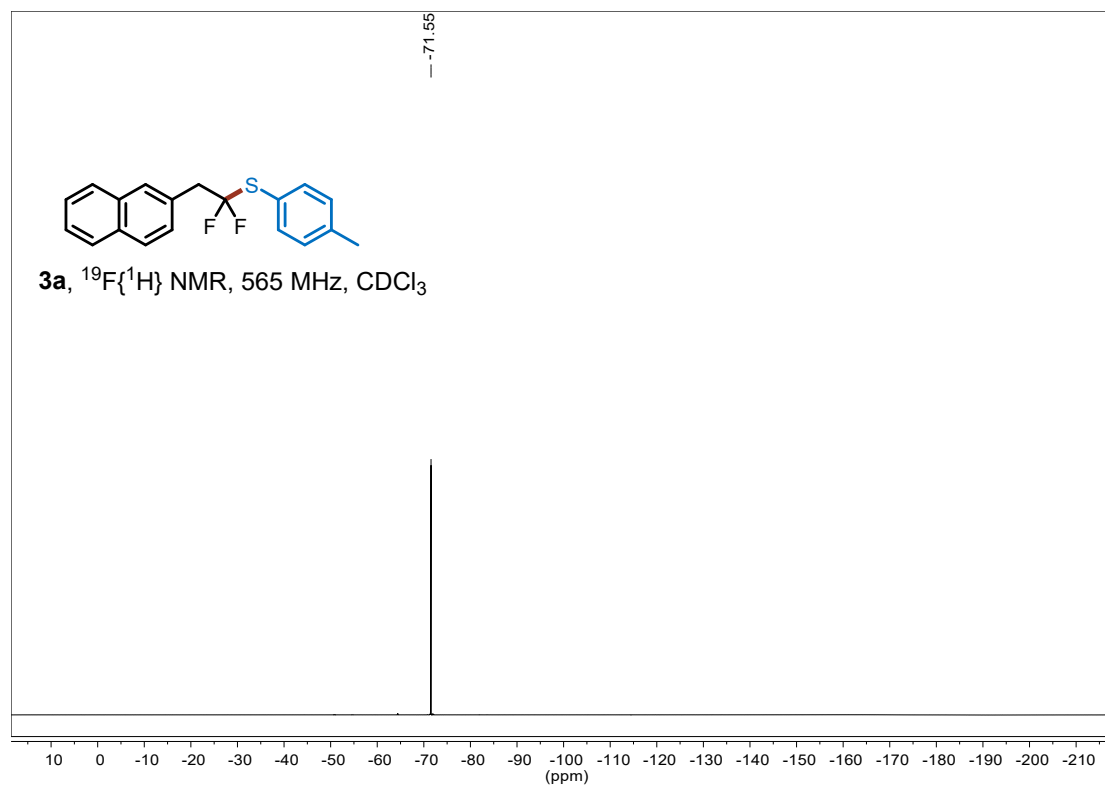
^1H NMR spectrum of **3a**



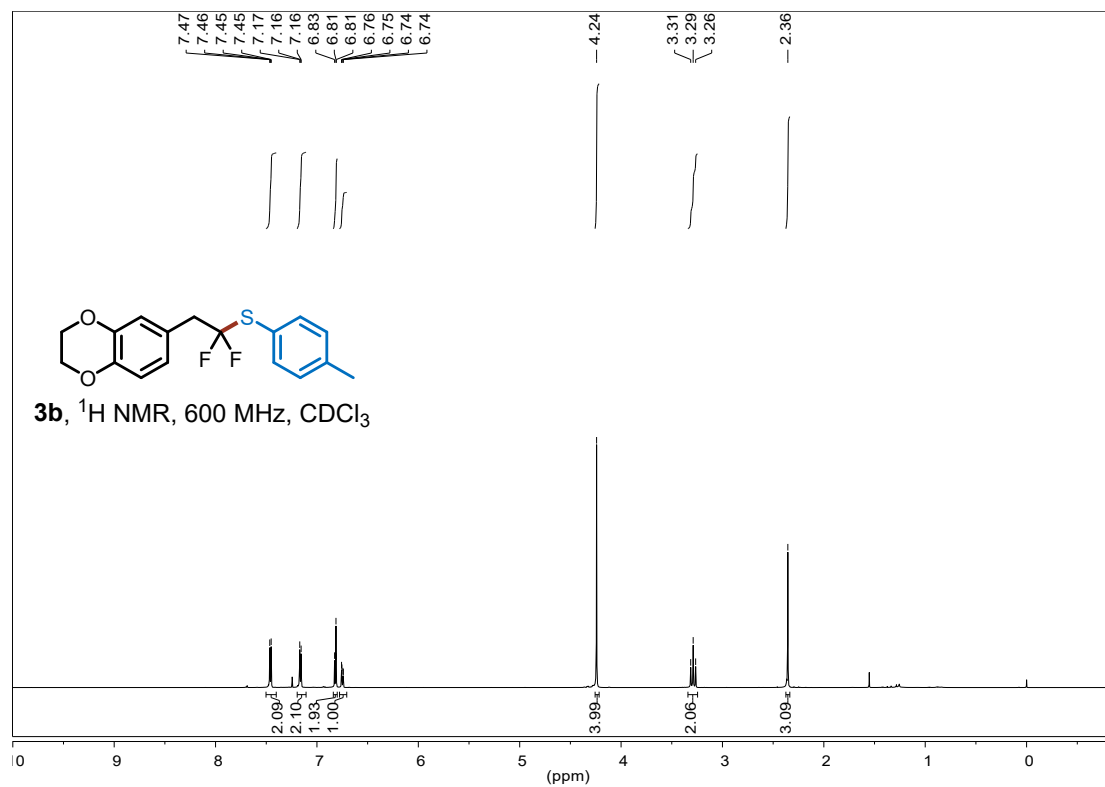
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3a**



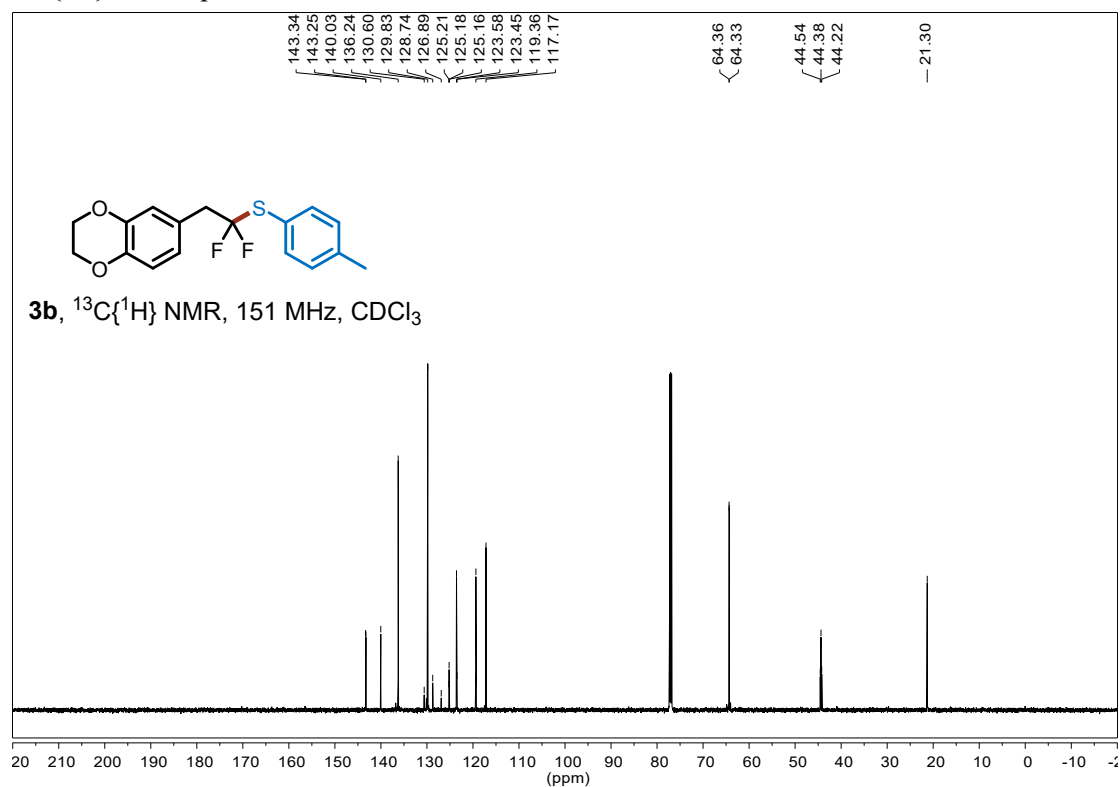
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3a**



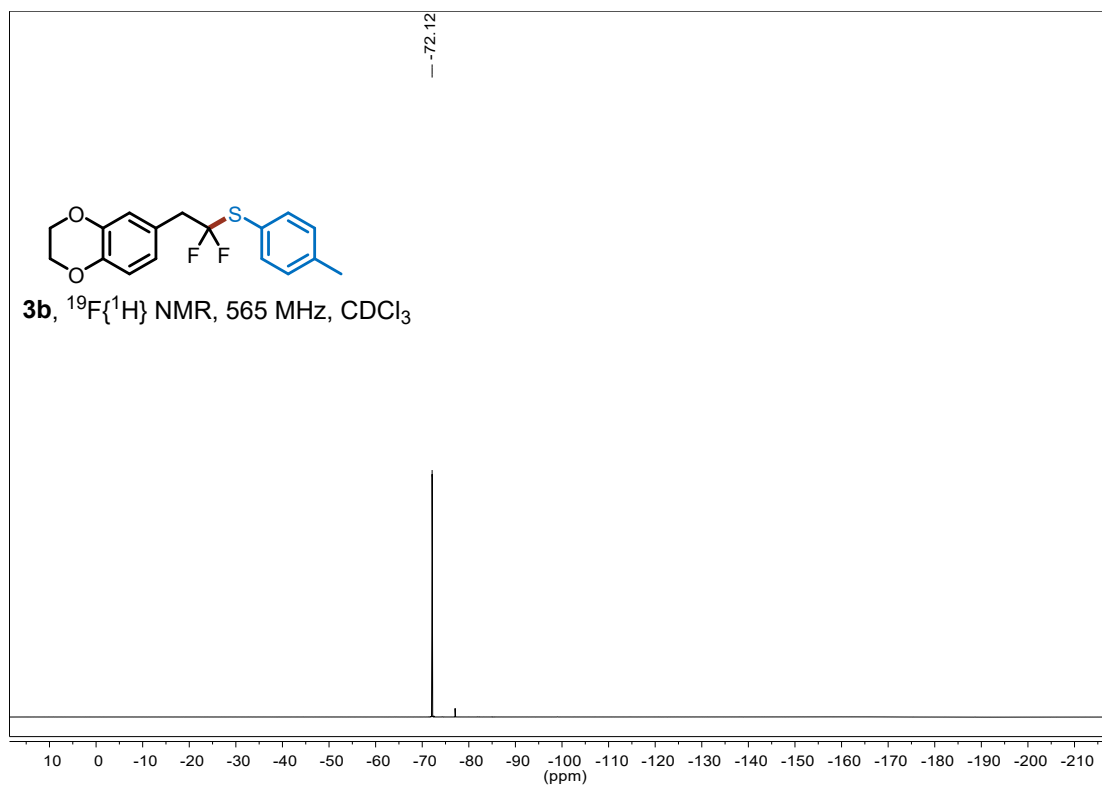
¹H NMR spectrum of **3b**



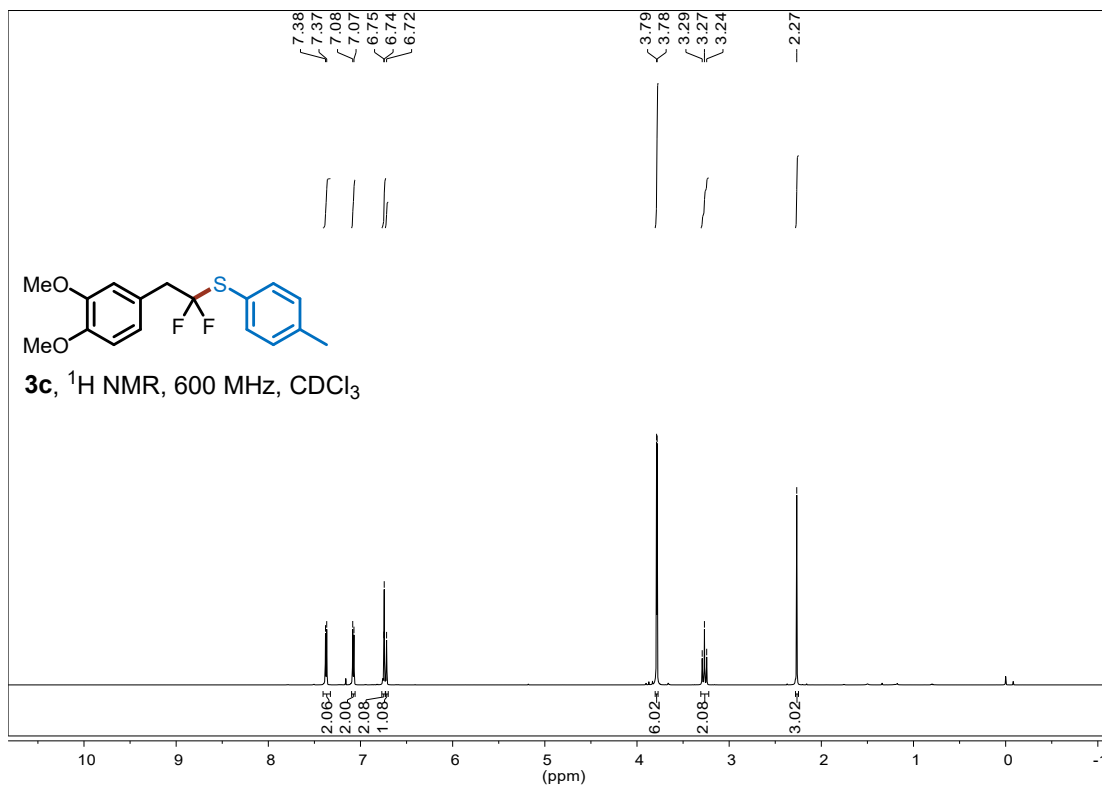
¹³C{¹H} NMR spectrum of **3b**



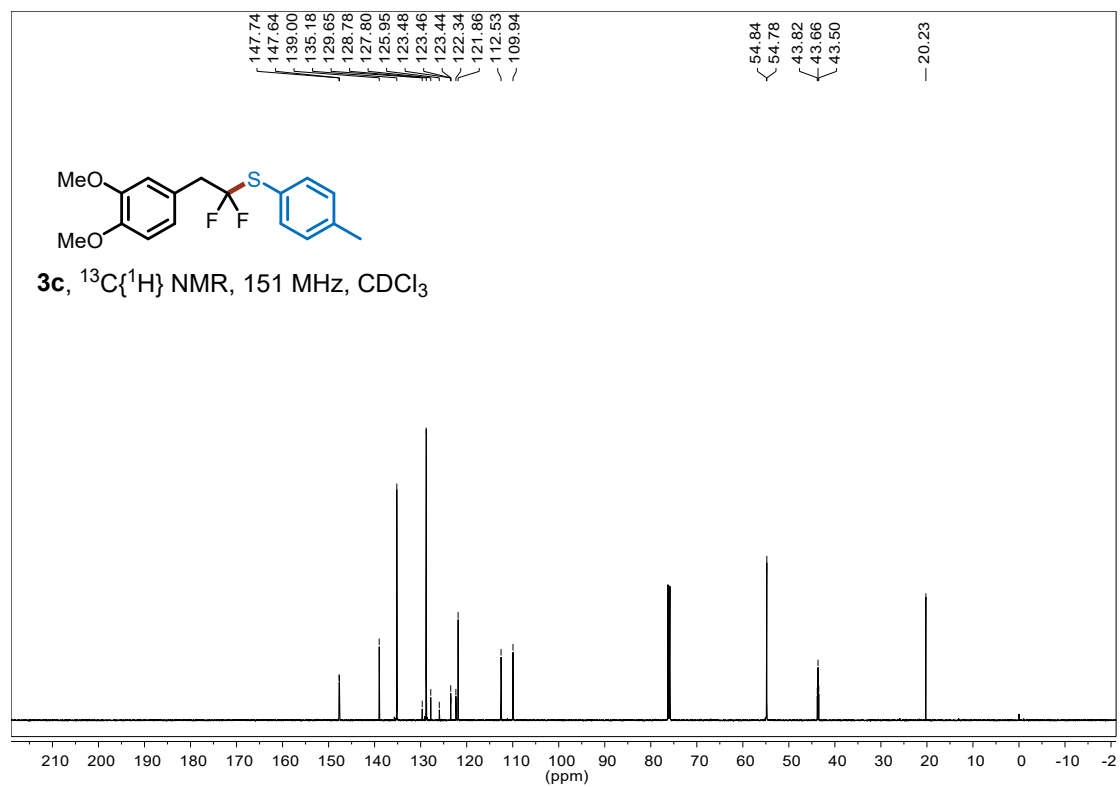
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3b**



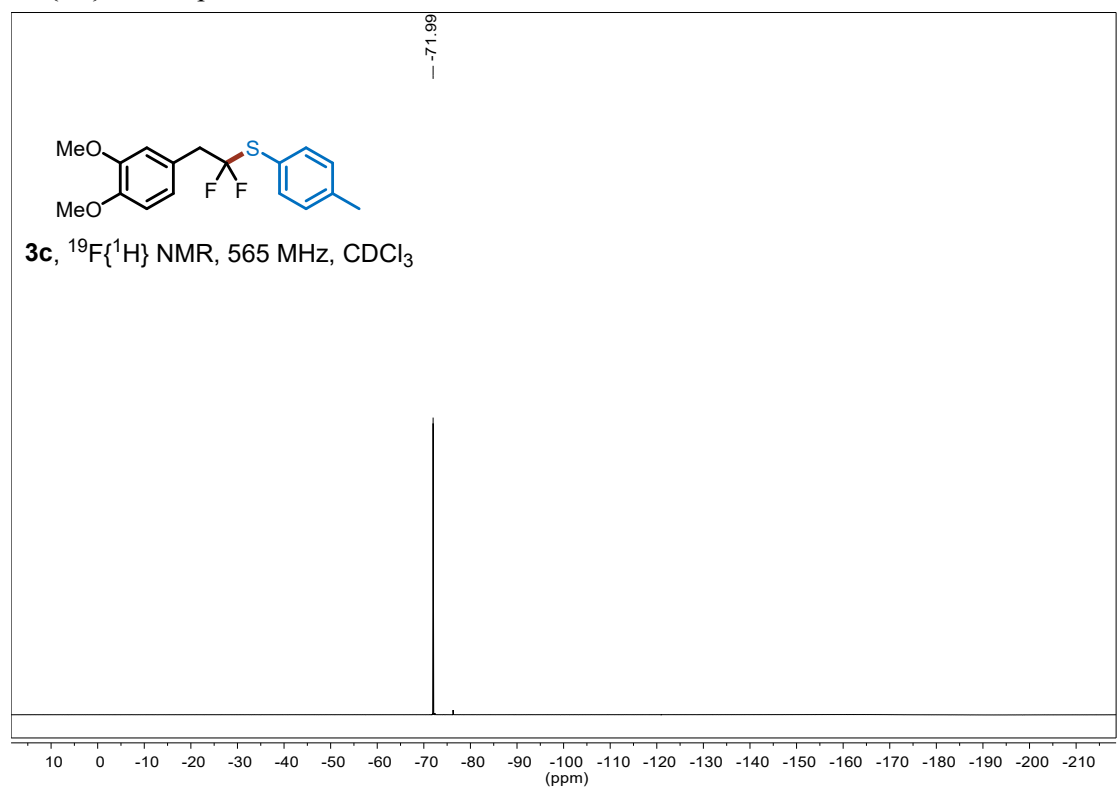
^1H NMR spectrum of **3c**



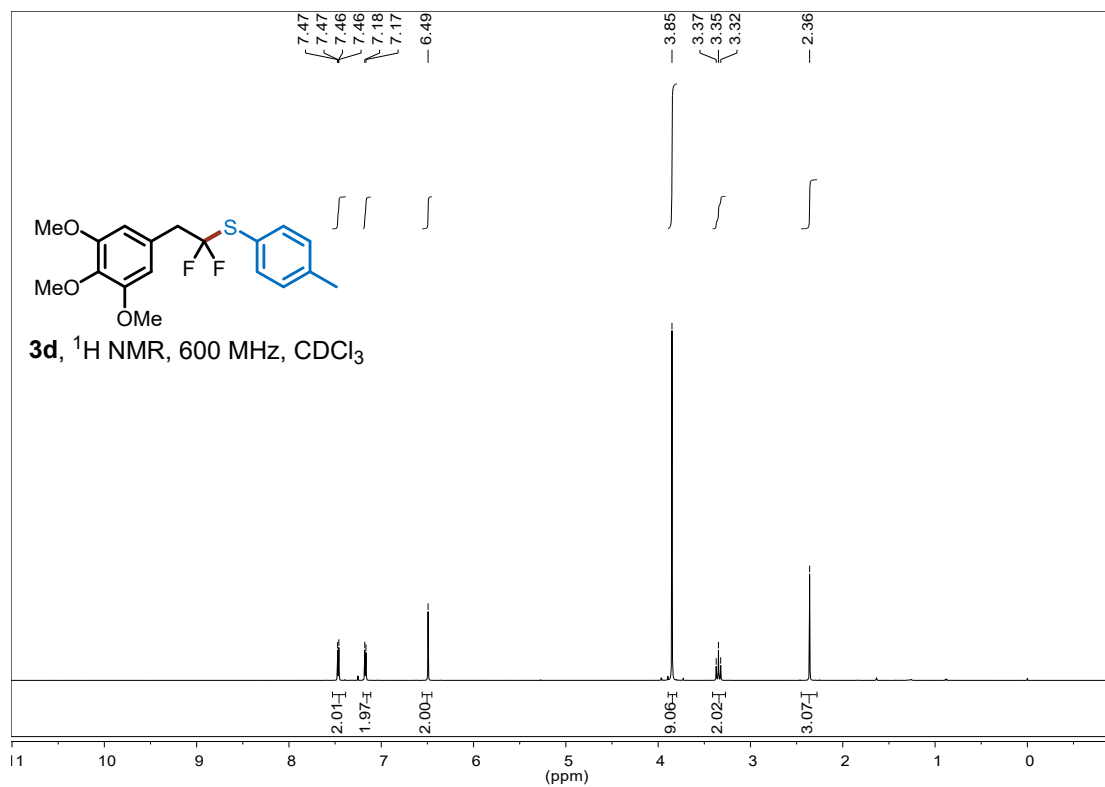
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3c**



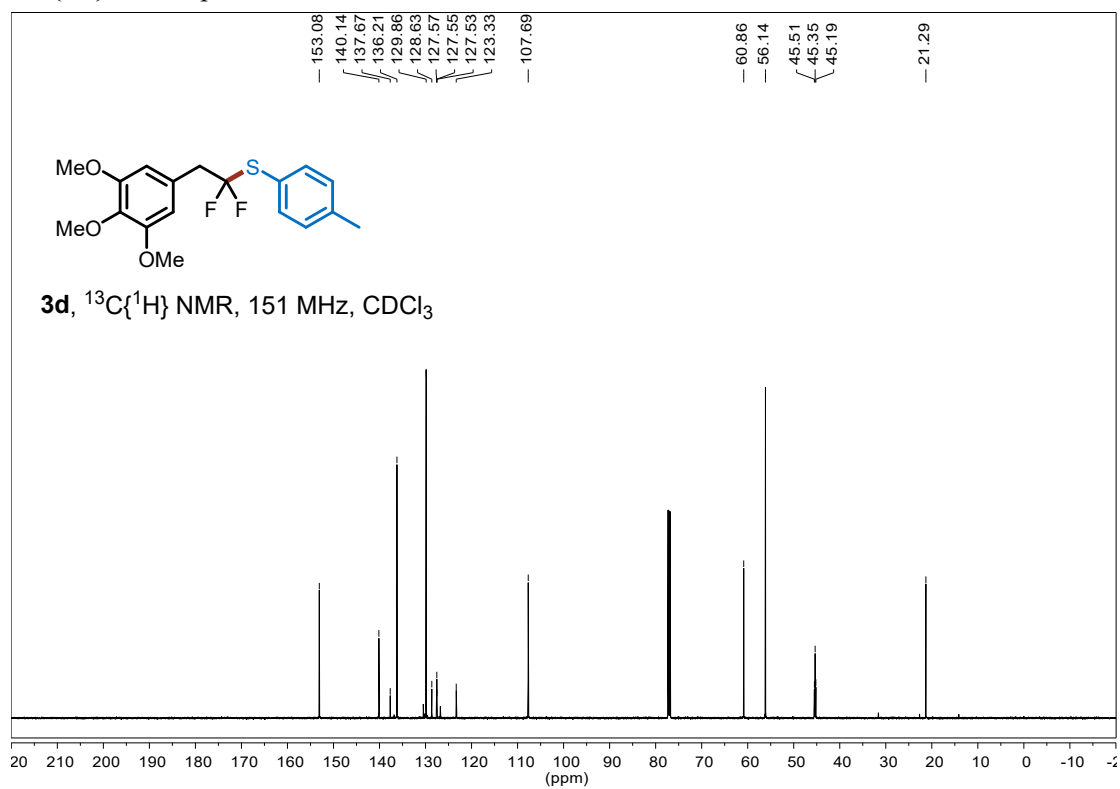
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3c**



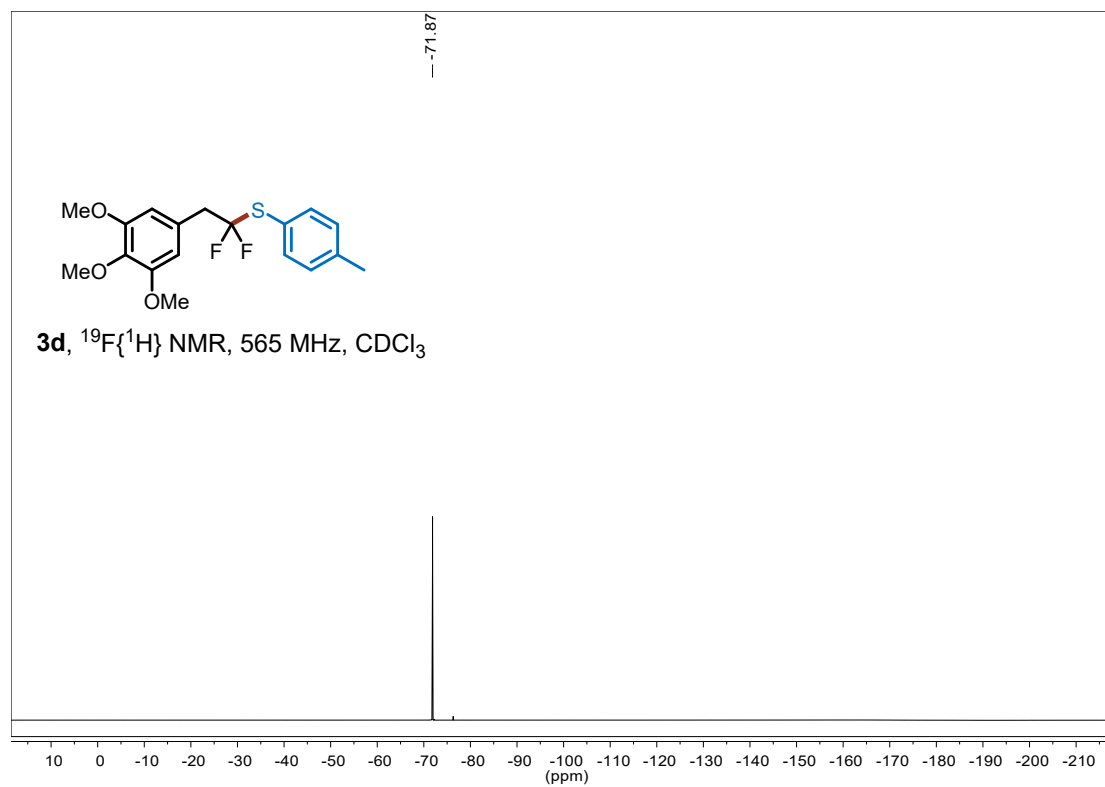
^1H NMR spectrum of **3d**



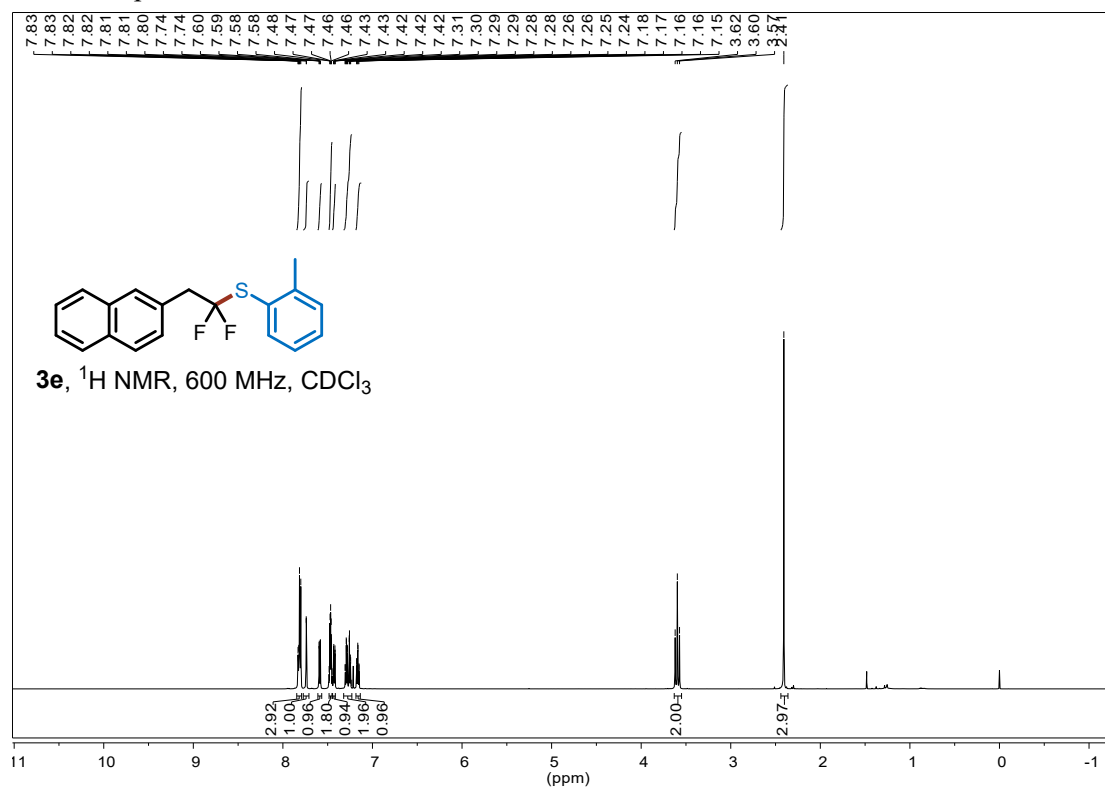
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3d**



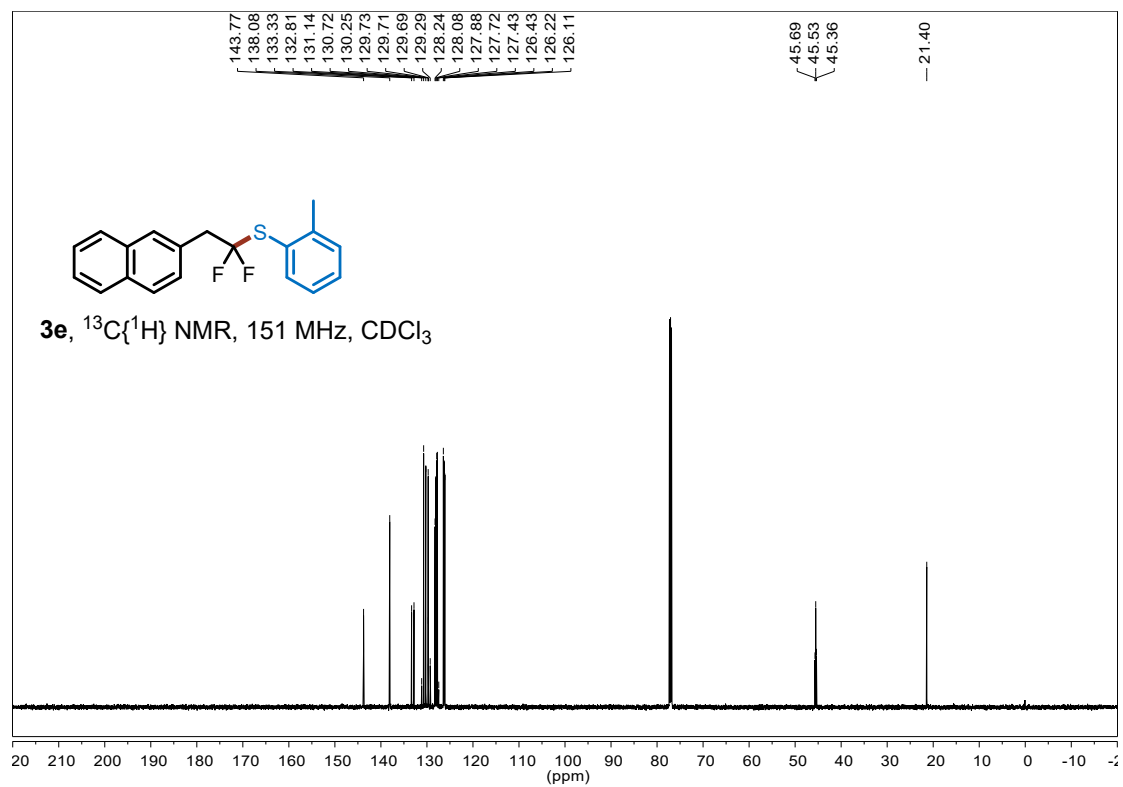
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3d**



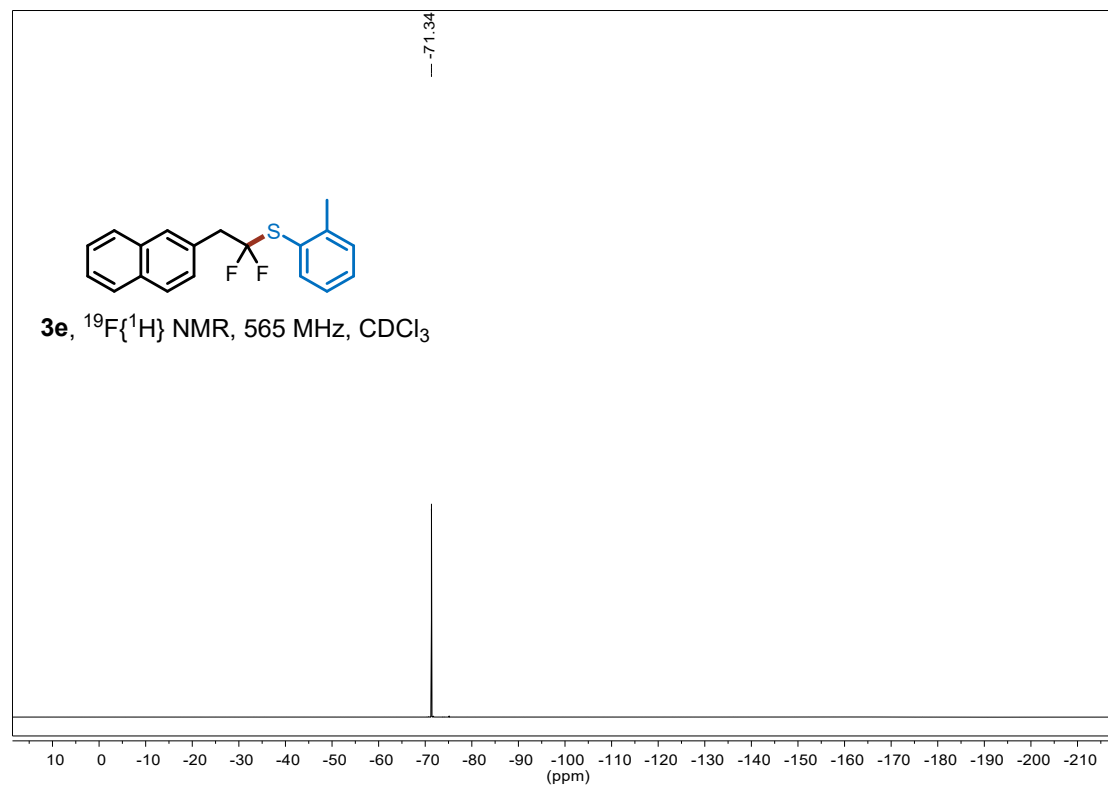
^1H NMR spectrum of **3e**



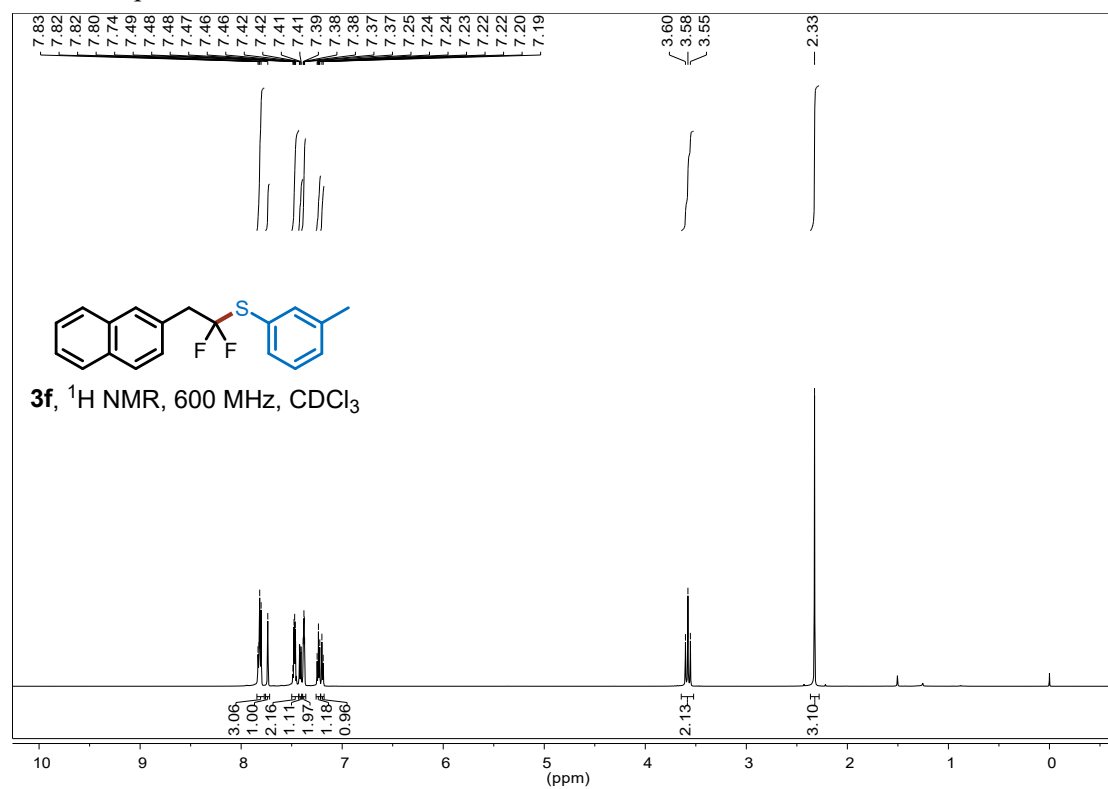
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3e**



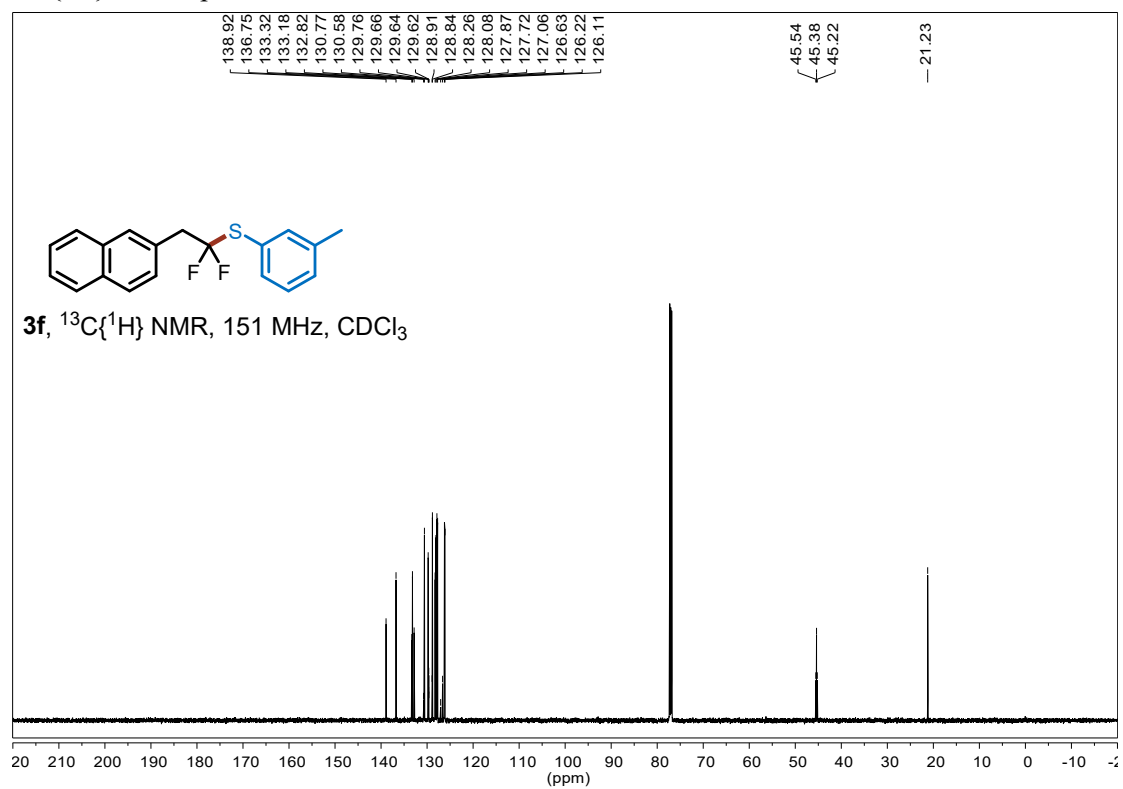
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3e**



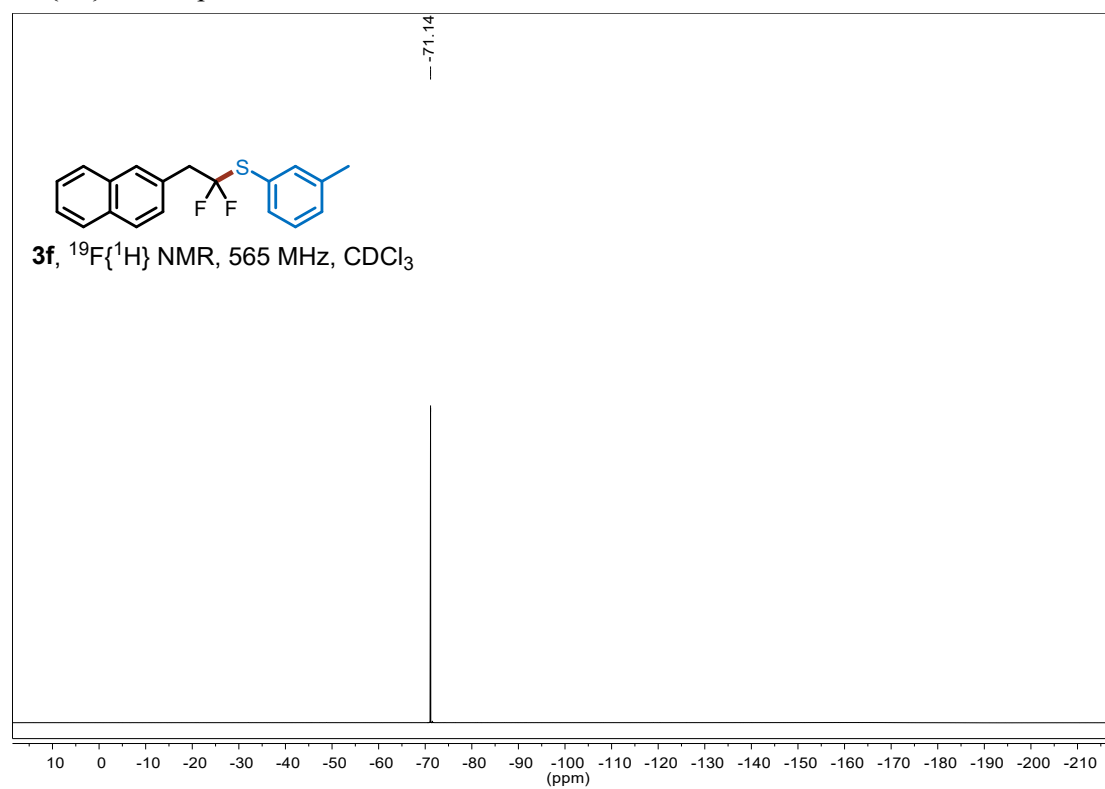
¹H NMR spectrum of **3f**



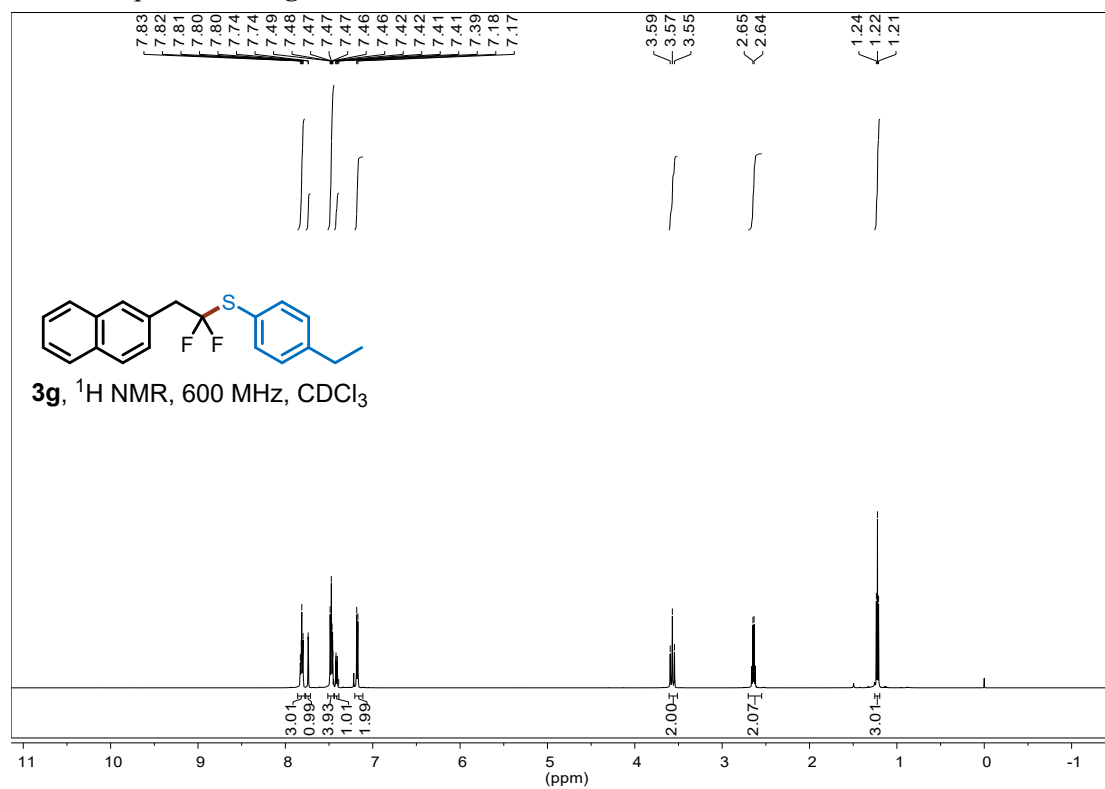
¹³C{¹H} NMR spectrum of **3f**



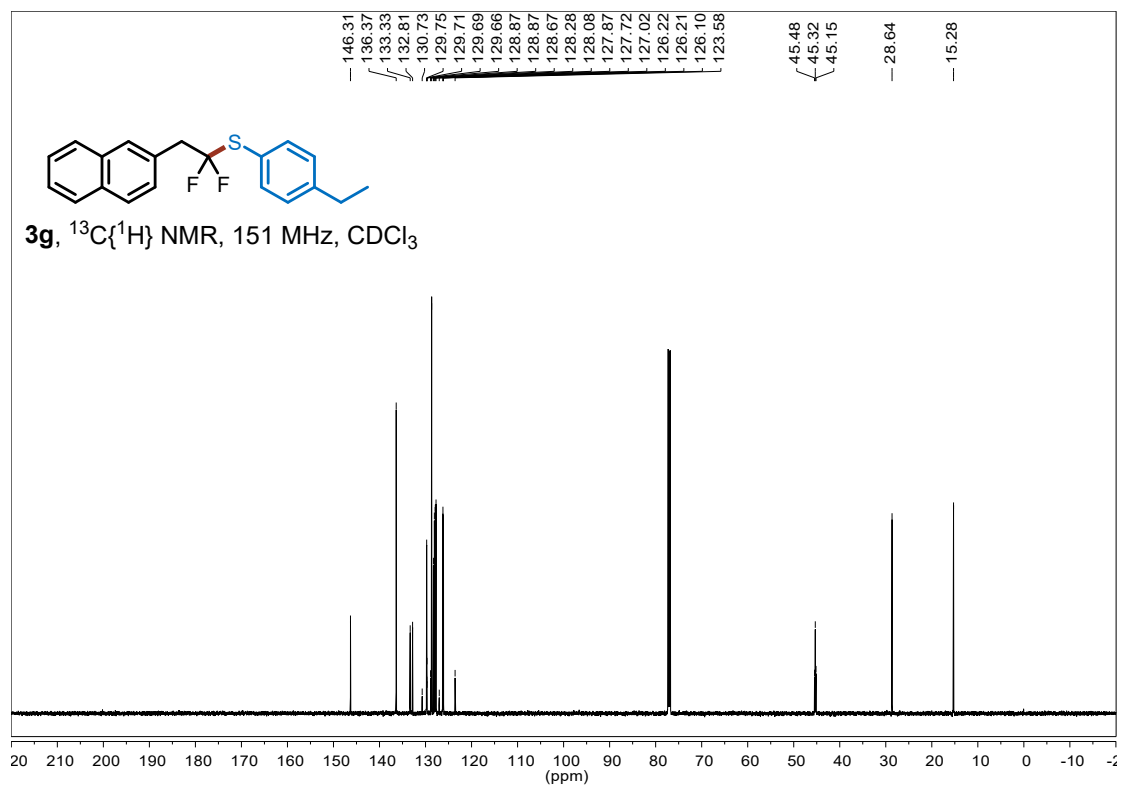
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3f**



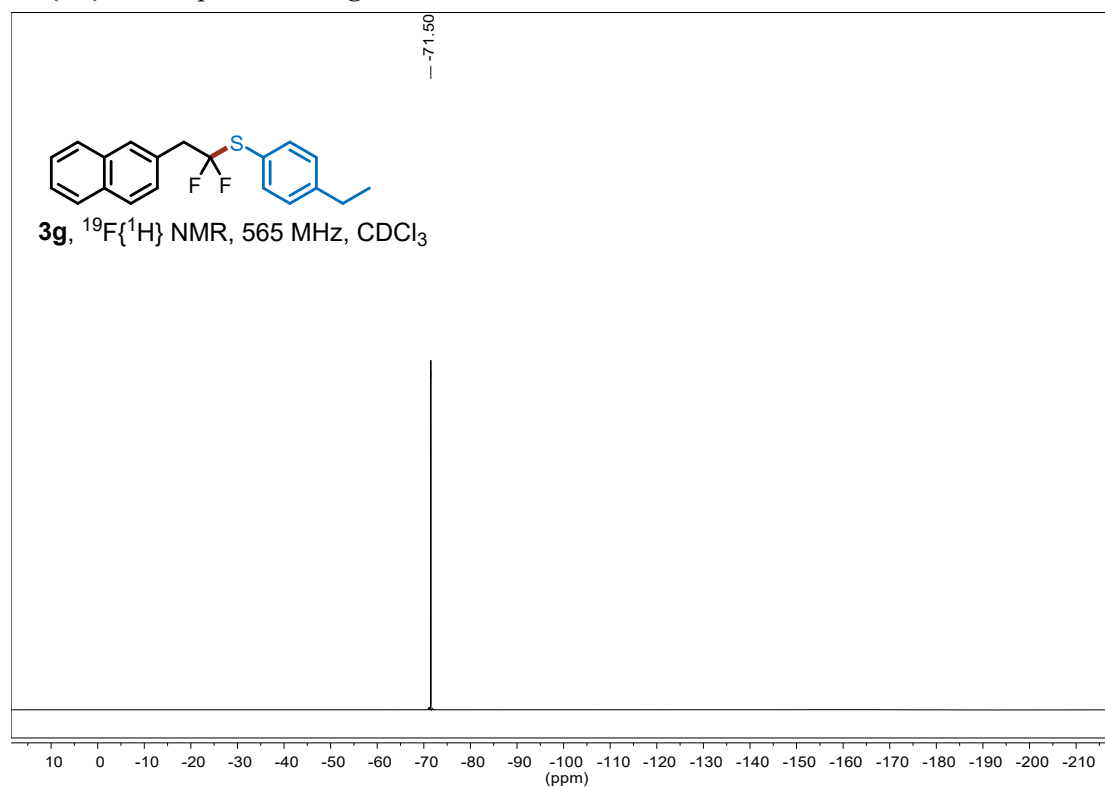
^1H NMR spectrum of **3g**



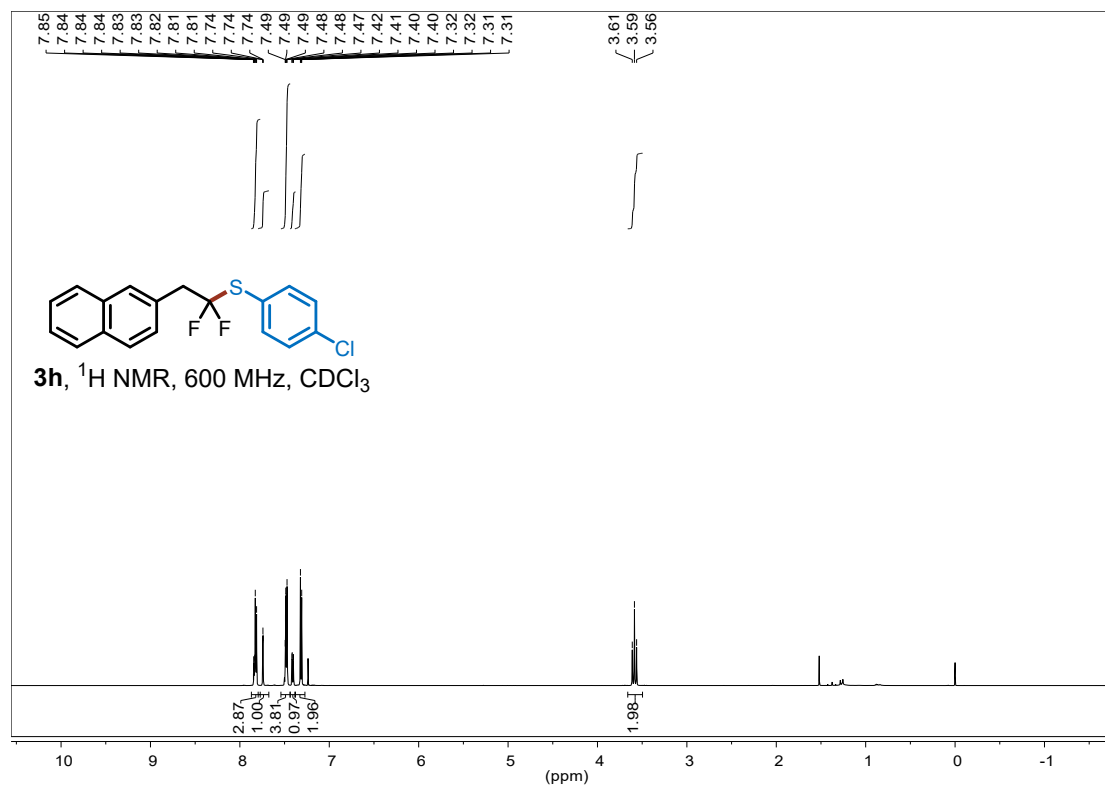
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3g**



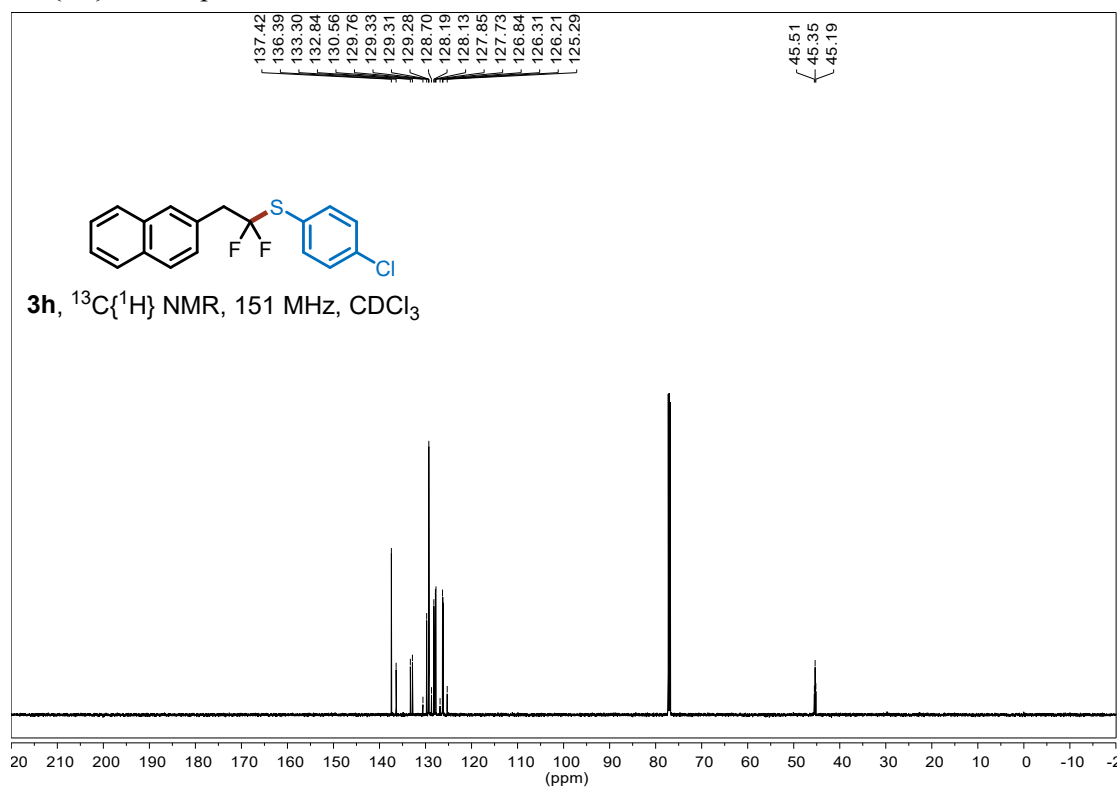
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3g**



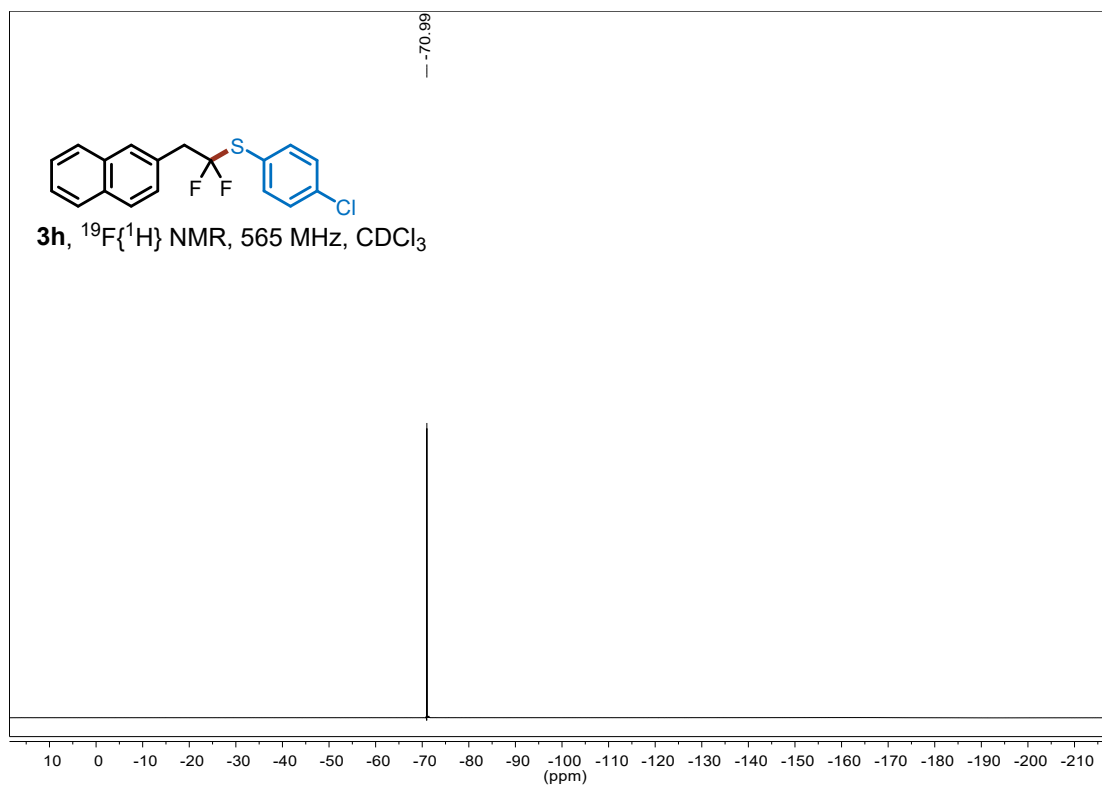
^1H NMR spectrum of **3h**



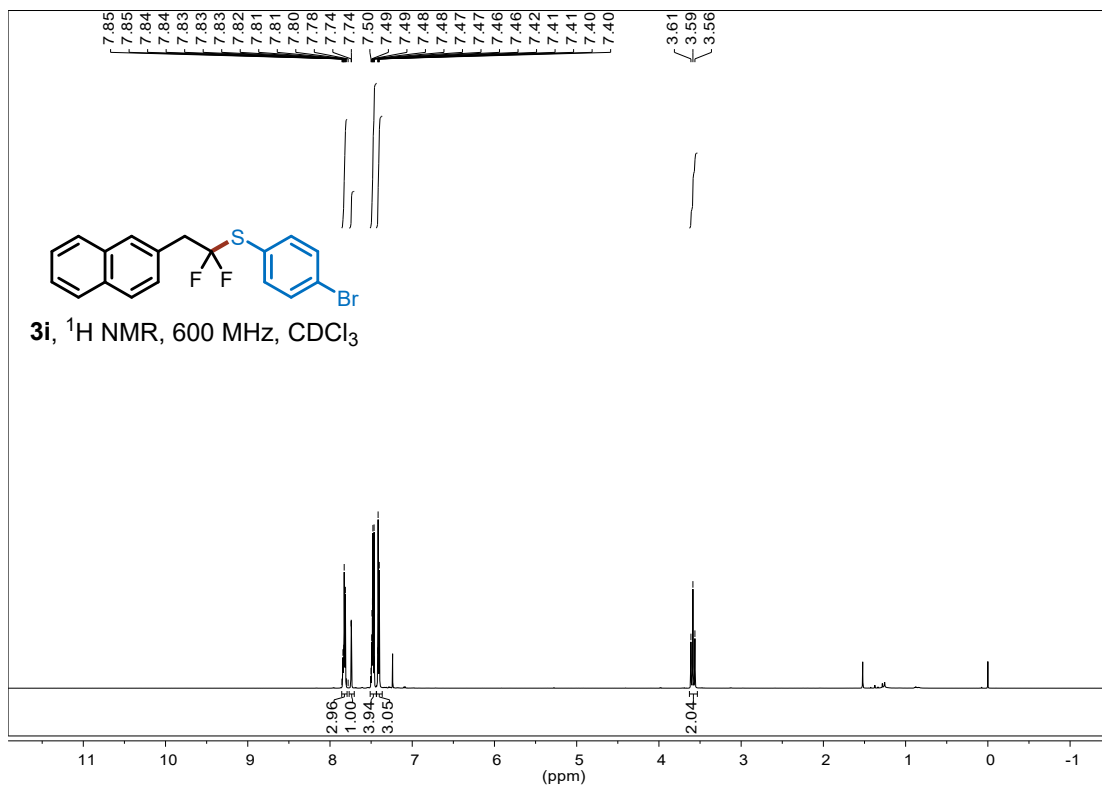
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3h**



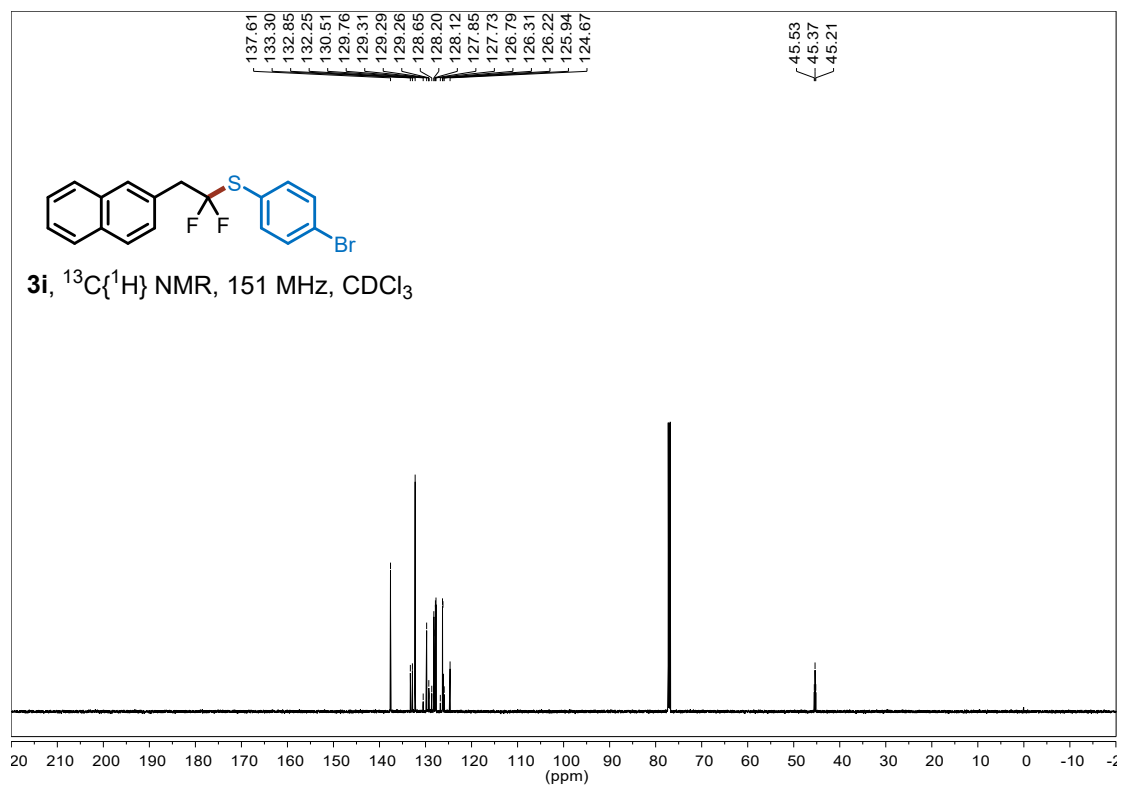
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3h**



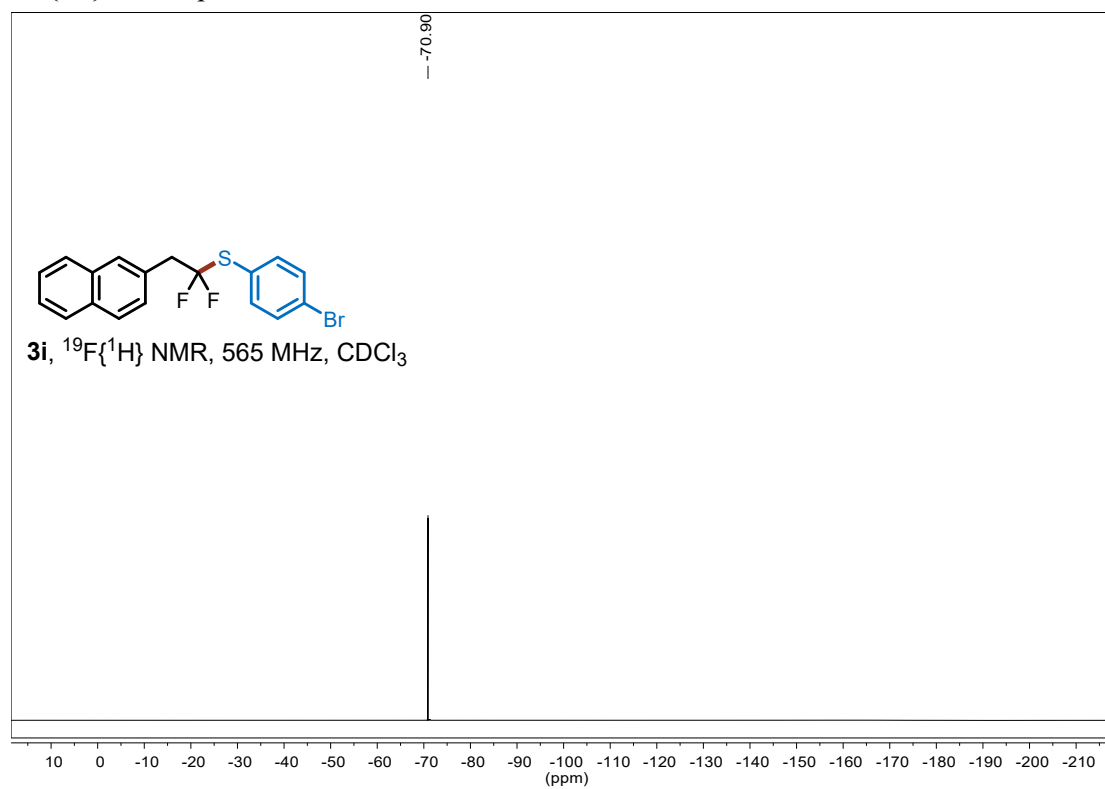
^1H NMR spectrum of **3i**



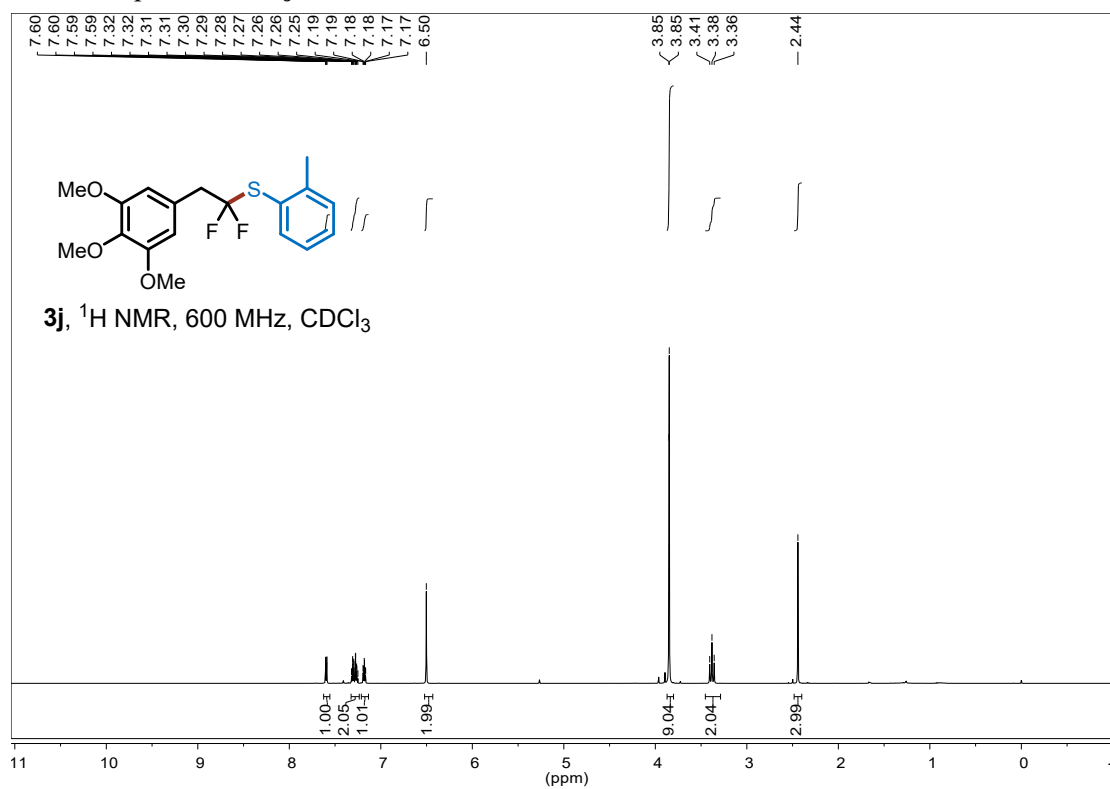
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3i**



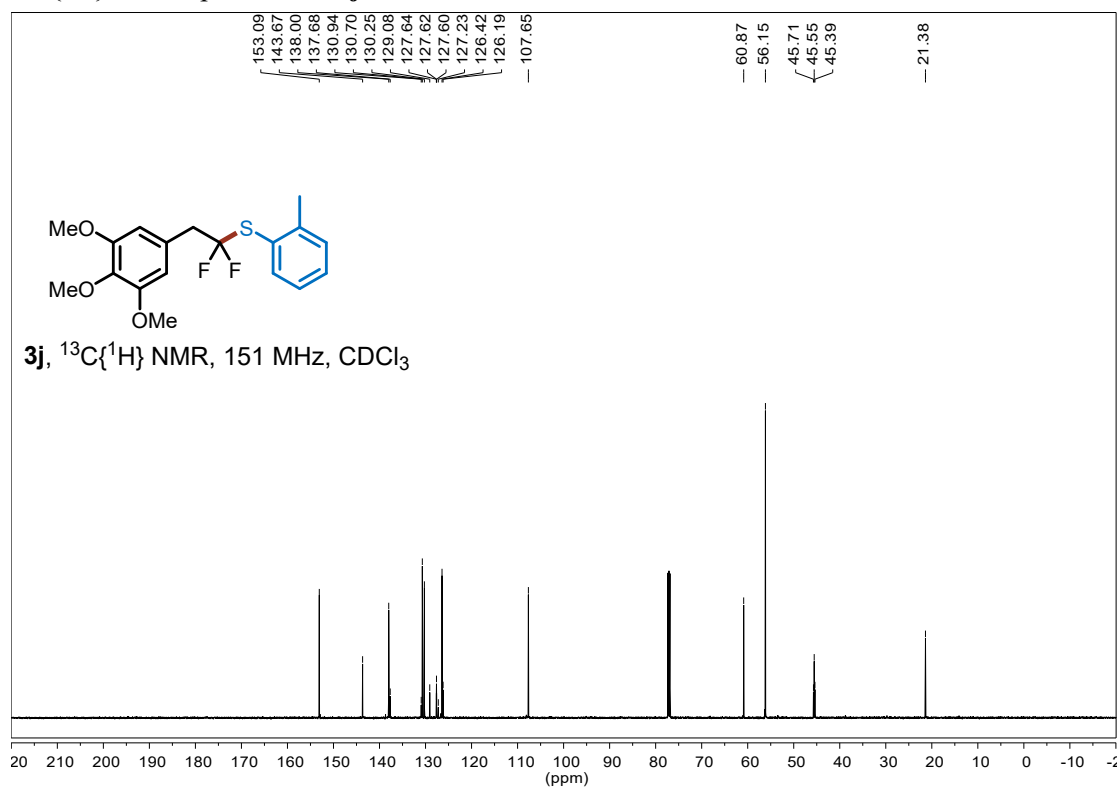
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3i**



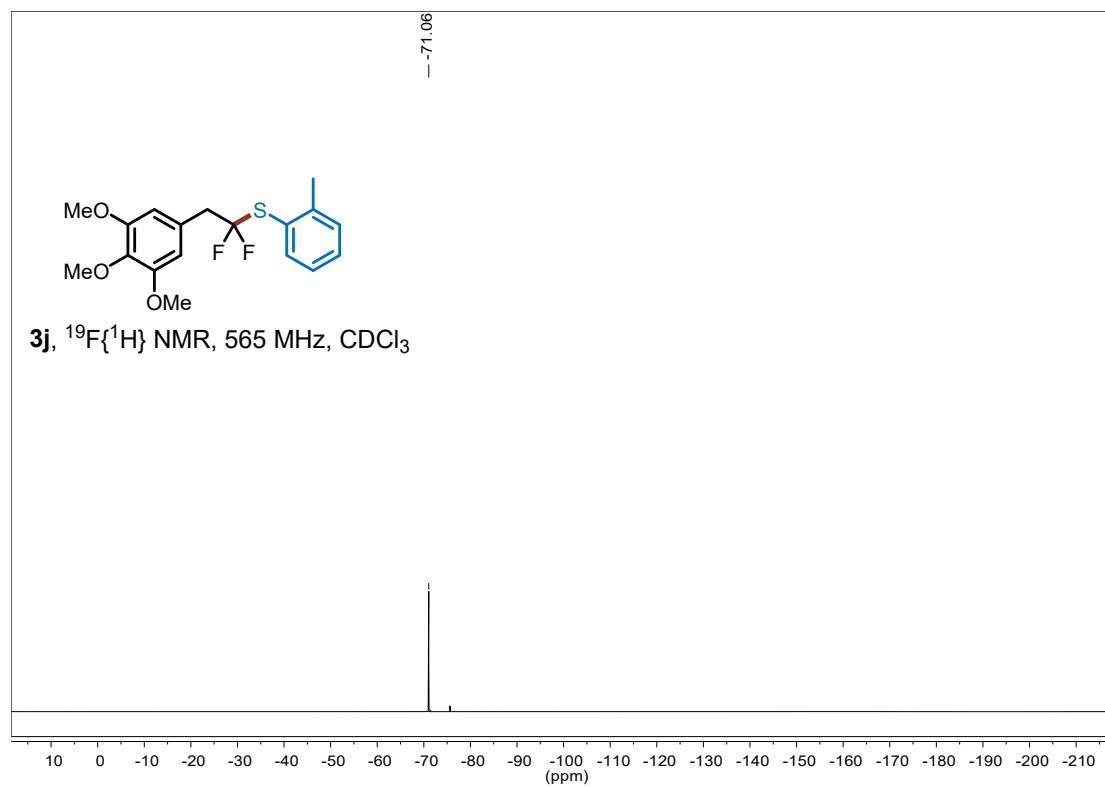
¹H NMR spectrum of **3j**



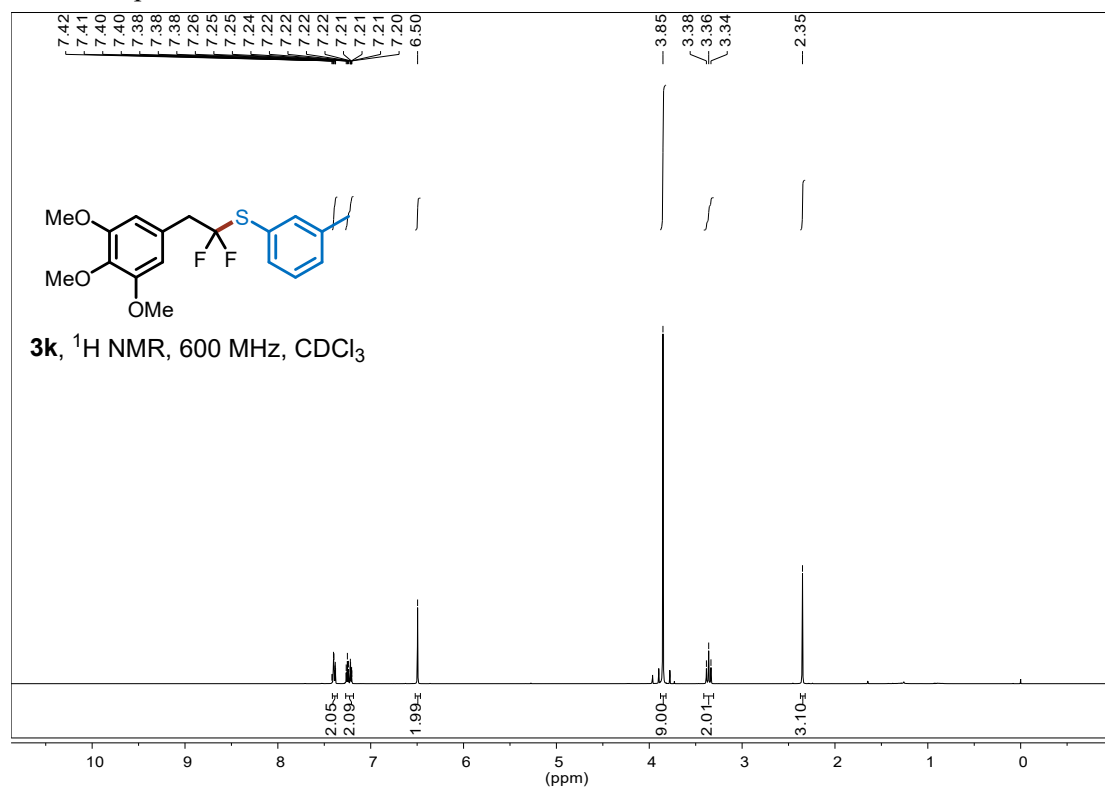
¹³C{¹H} NMR spectrum of **3j**



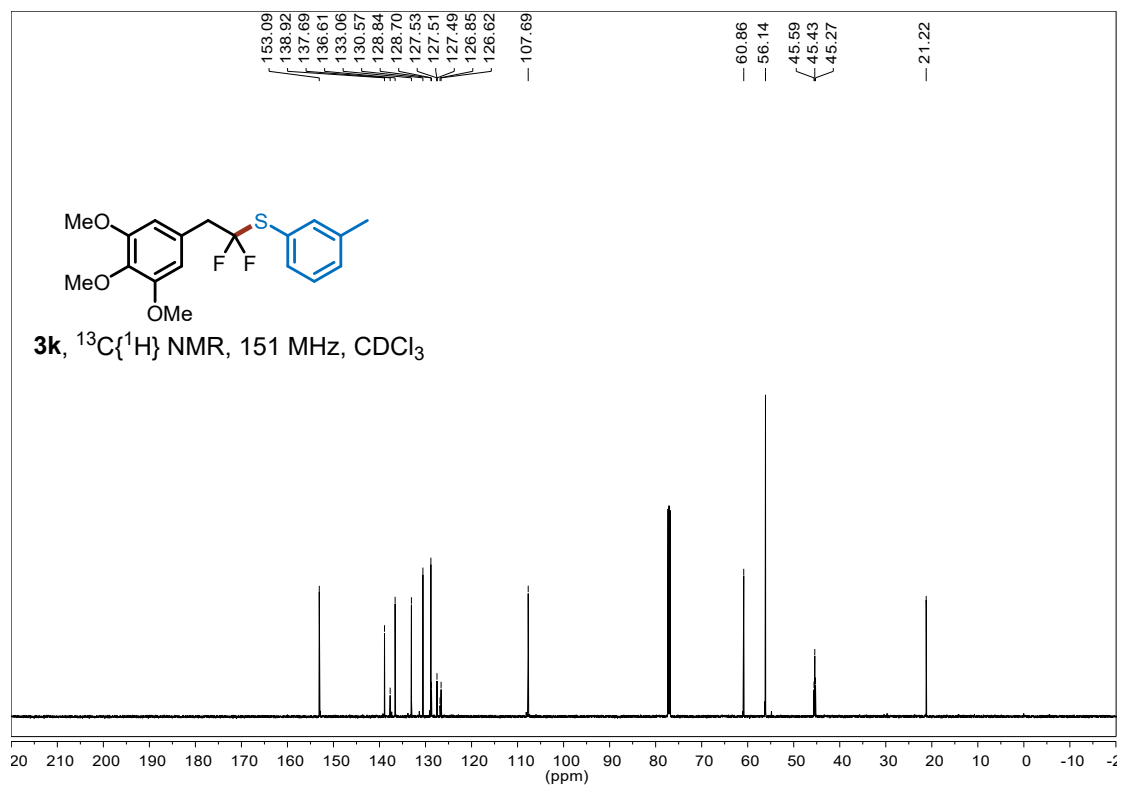
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3j**



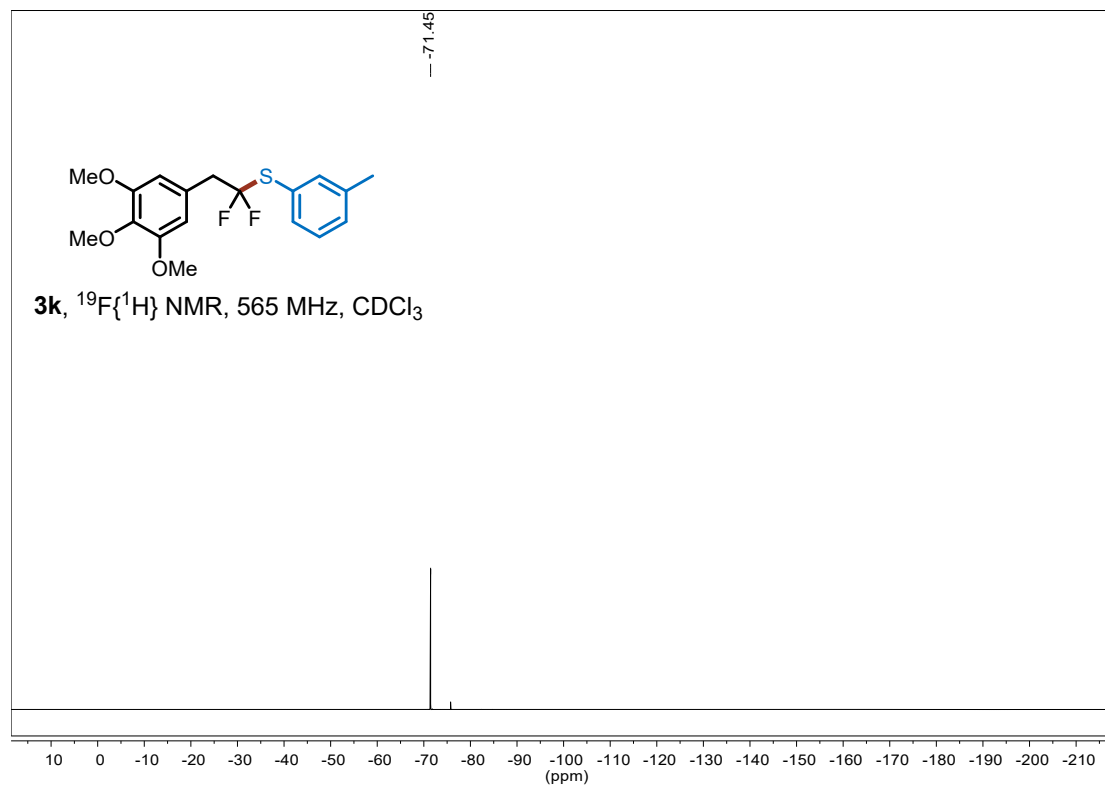
^1H NMR spectrum of **3k**



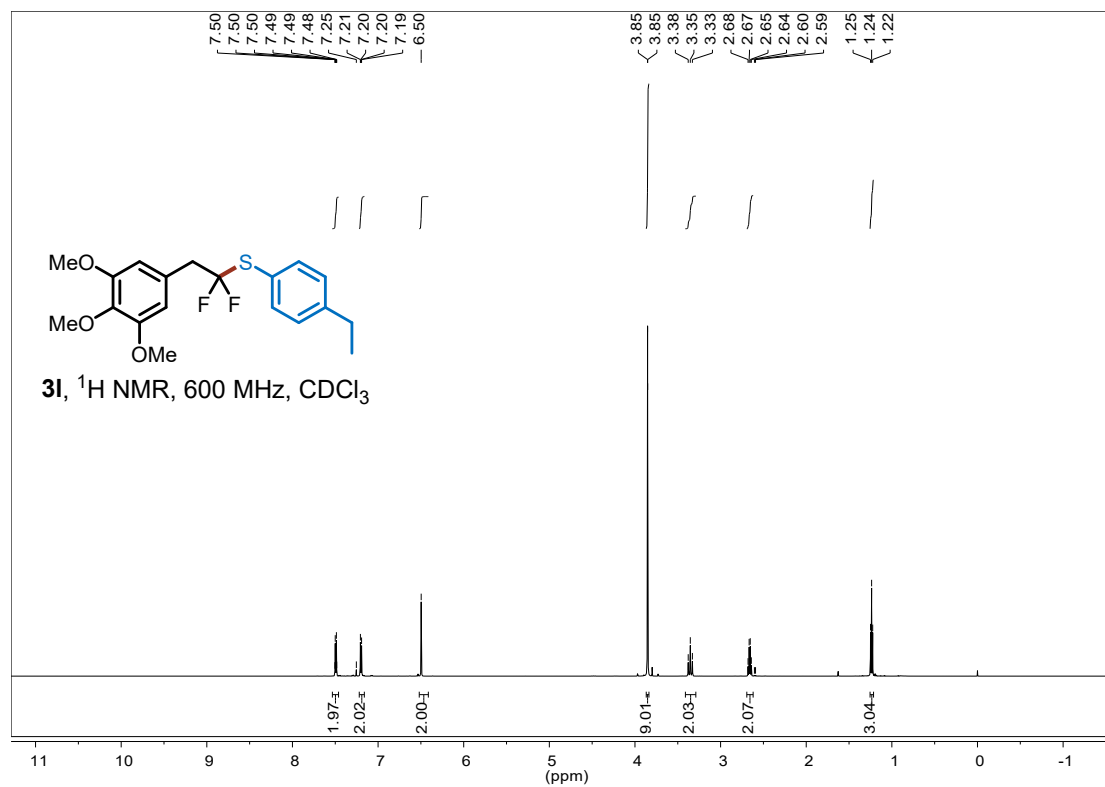
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3k**



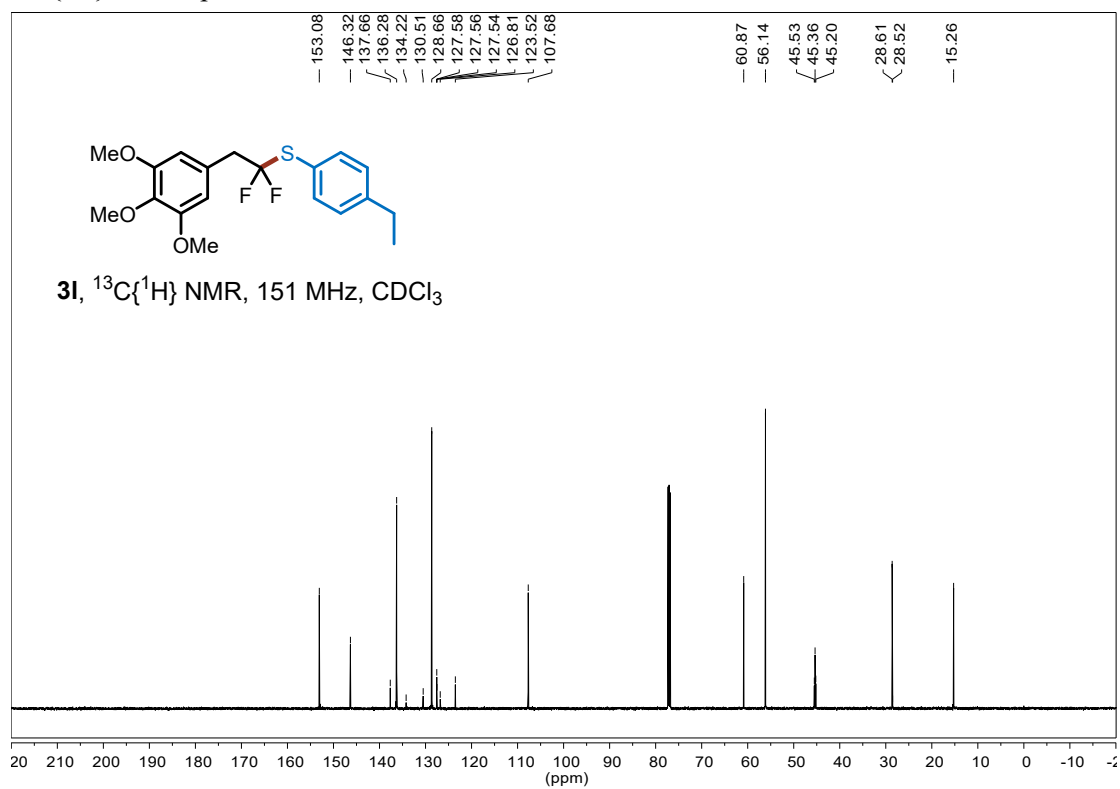
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3k**



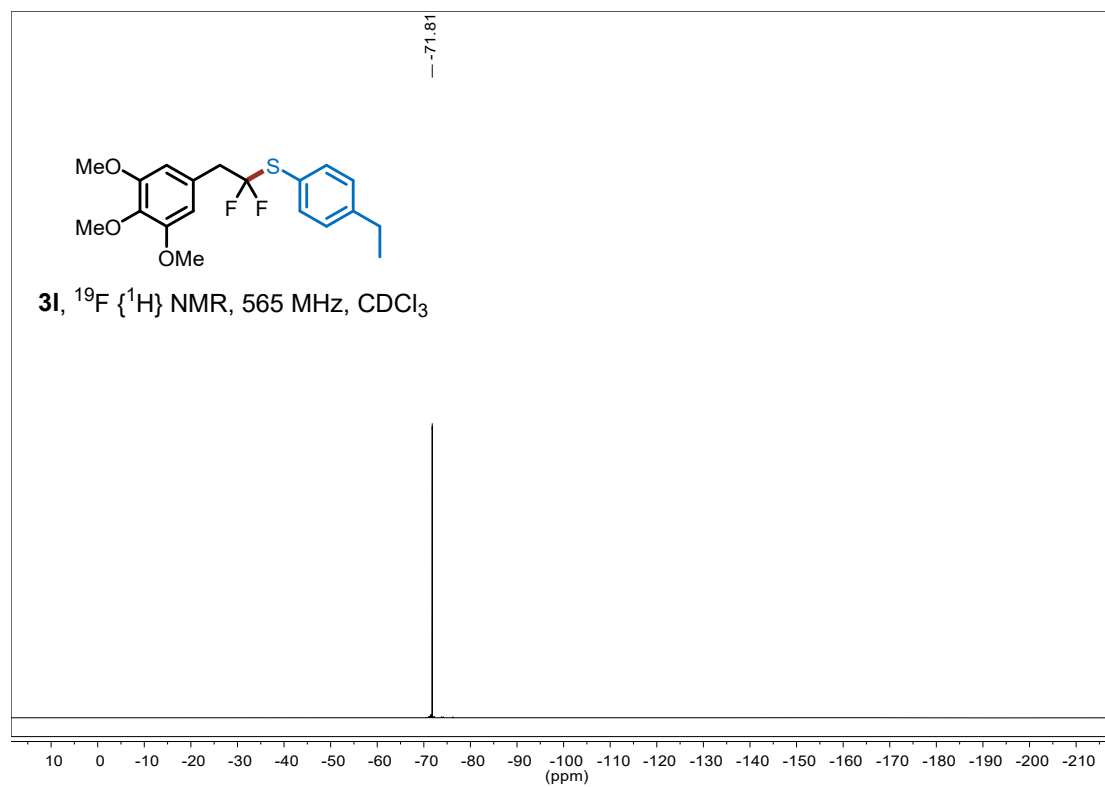
^1H NMR spectrum of **3I**



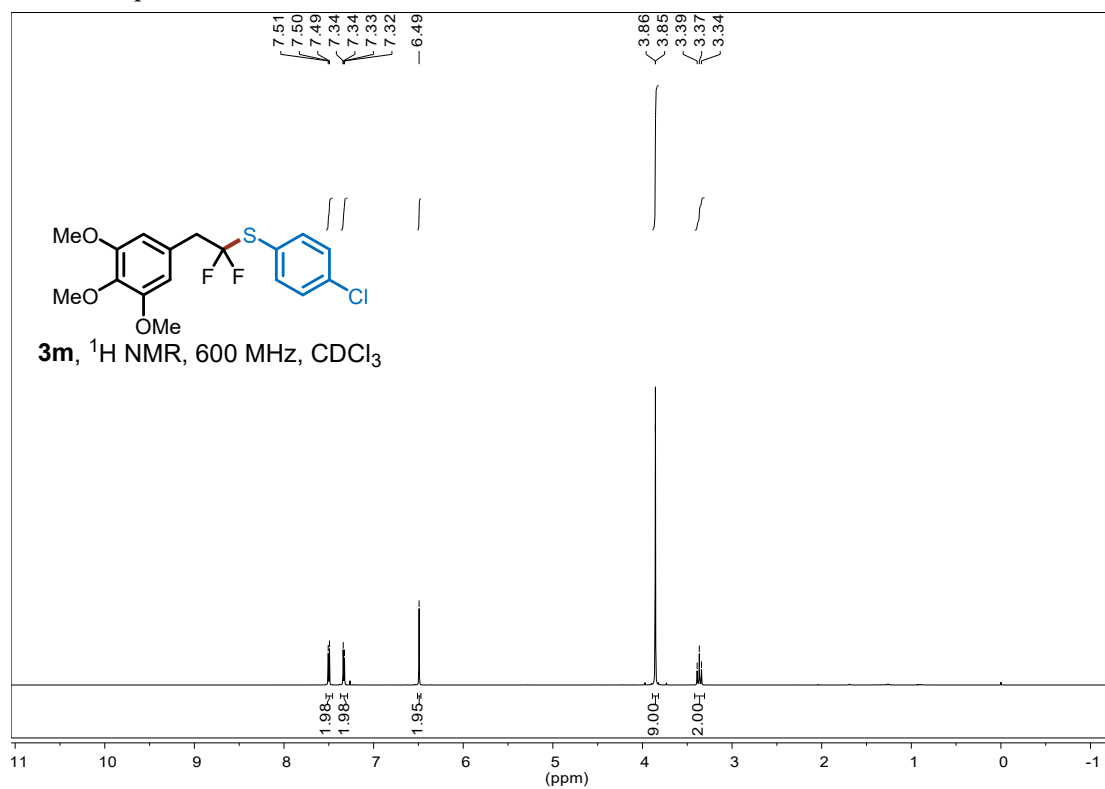
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3I**



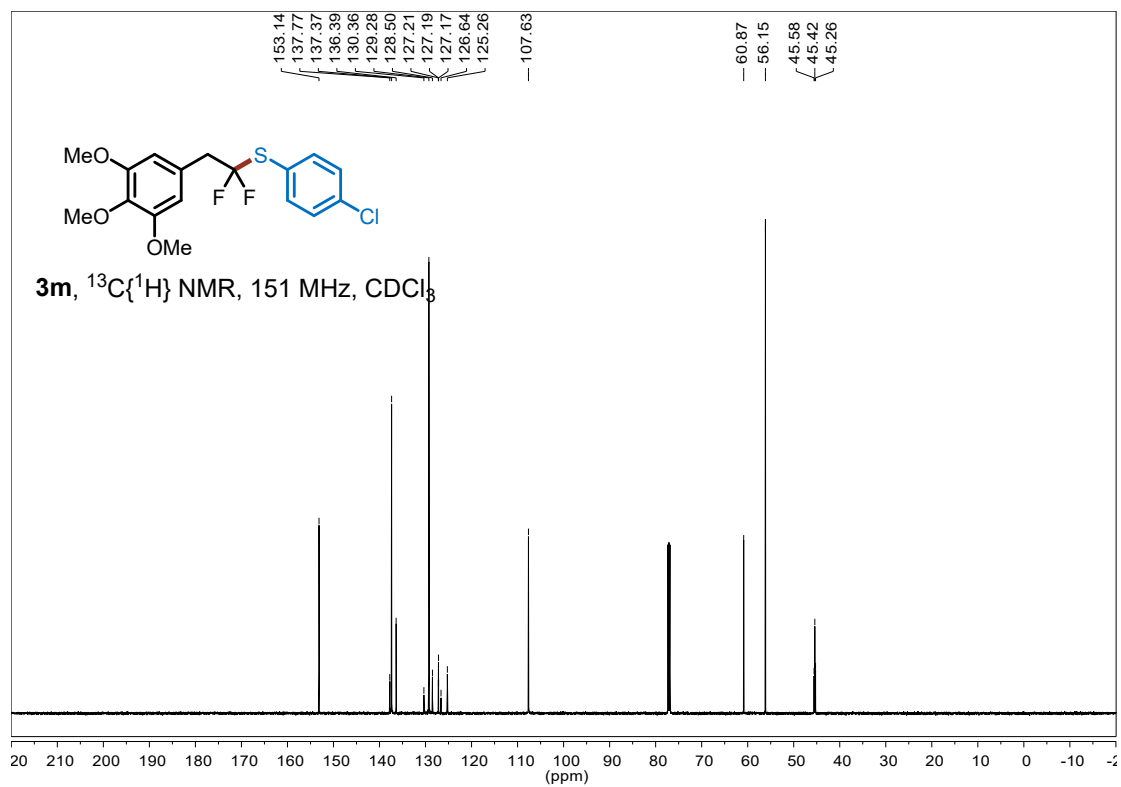
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3l**



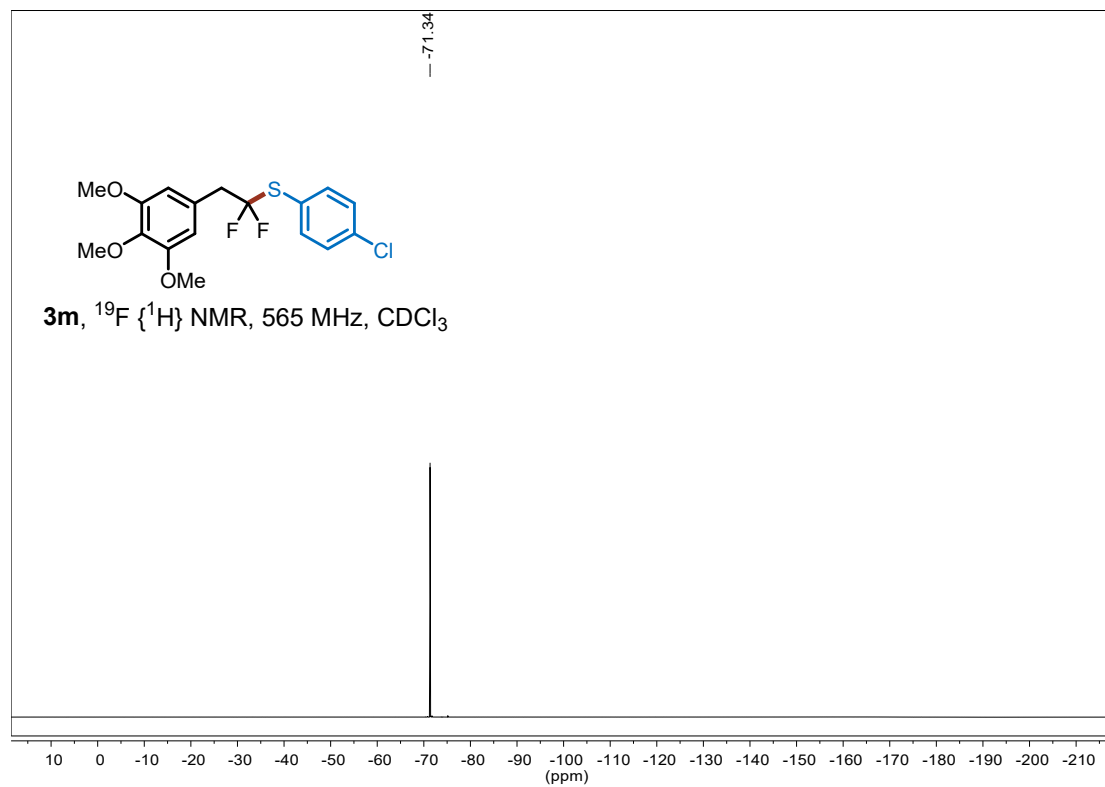
^1H NMR spectrum of **3m**



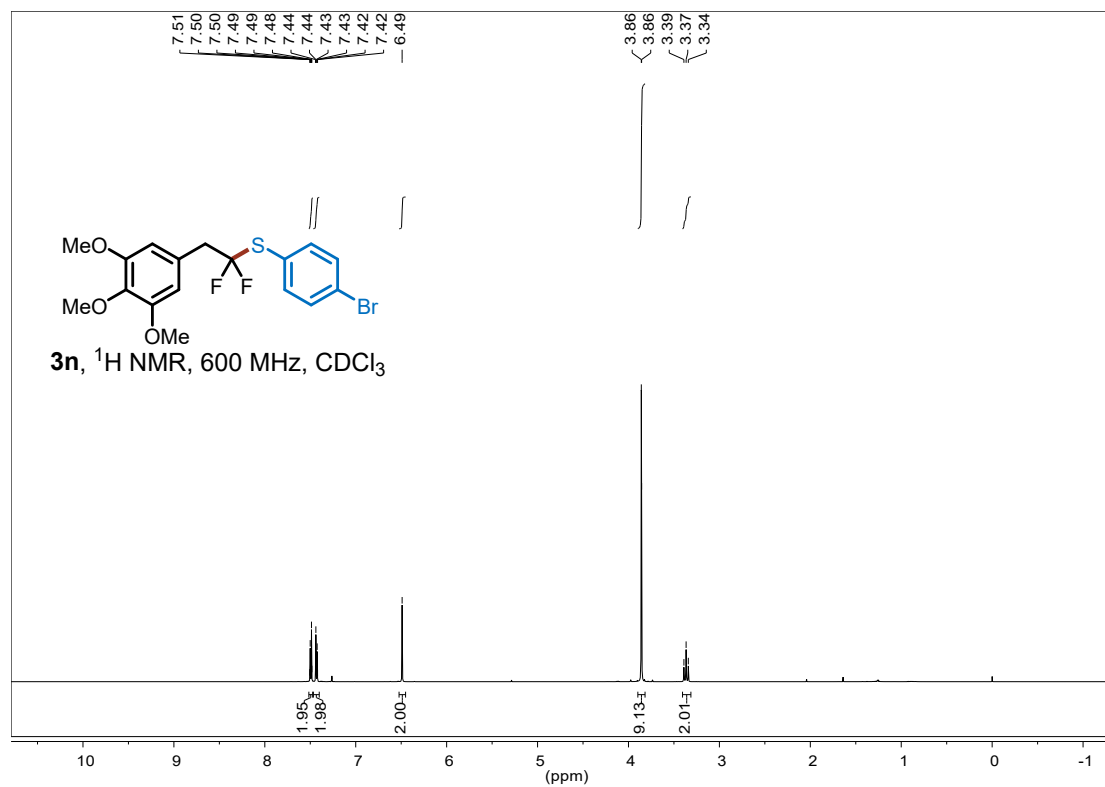
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3m**



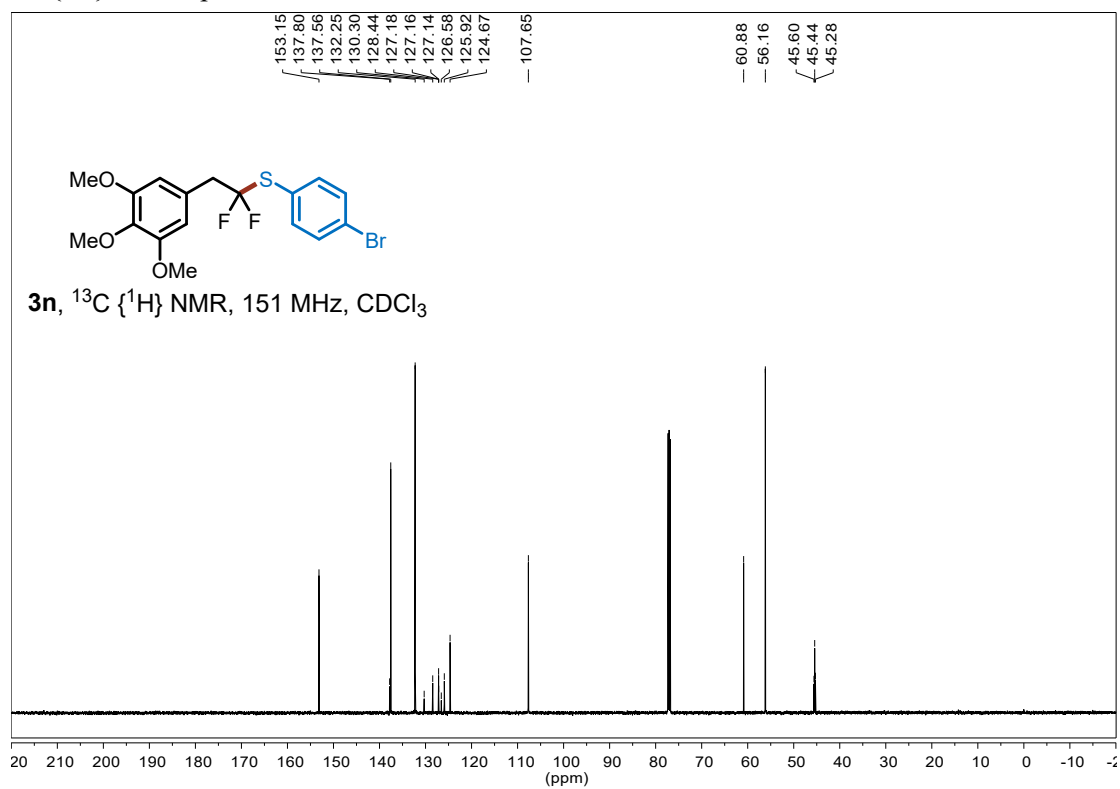
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3m**



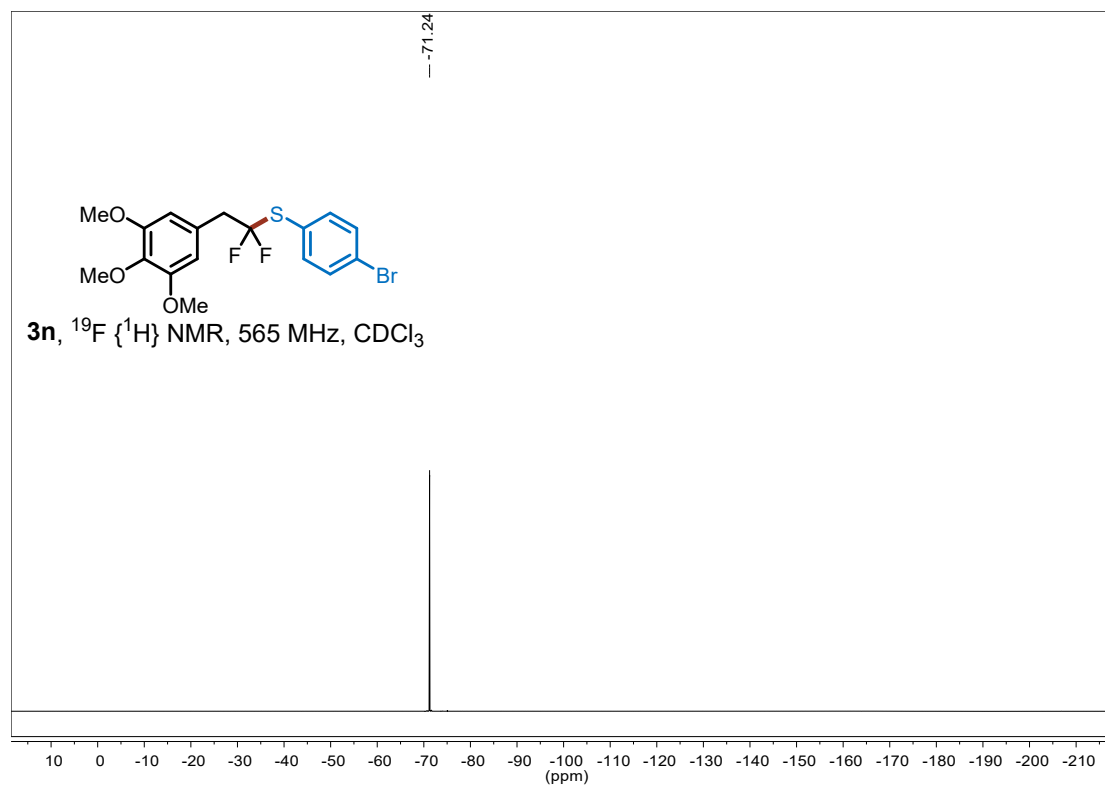
¹H NMR spectrum of **3n**



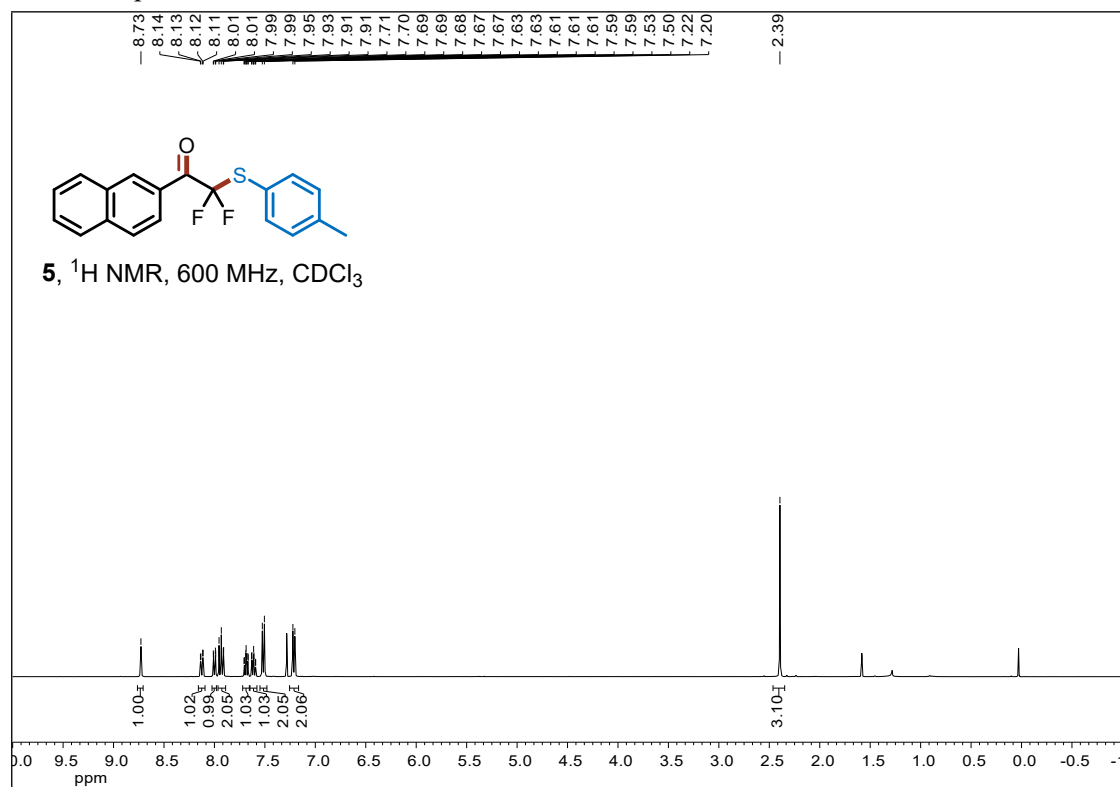
¹³C {¹H} NMR spectrum of **3n**



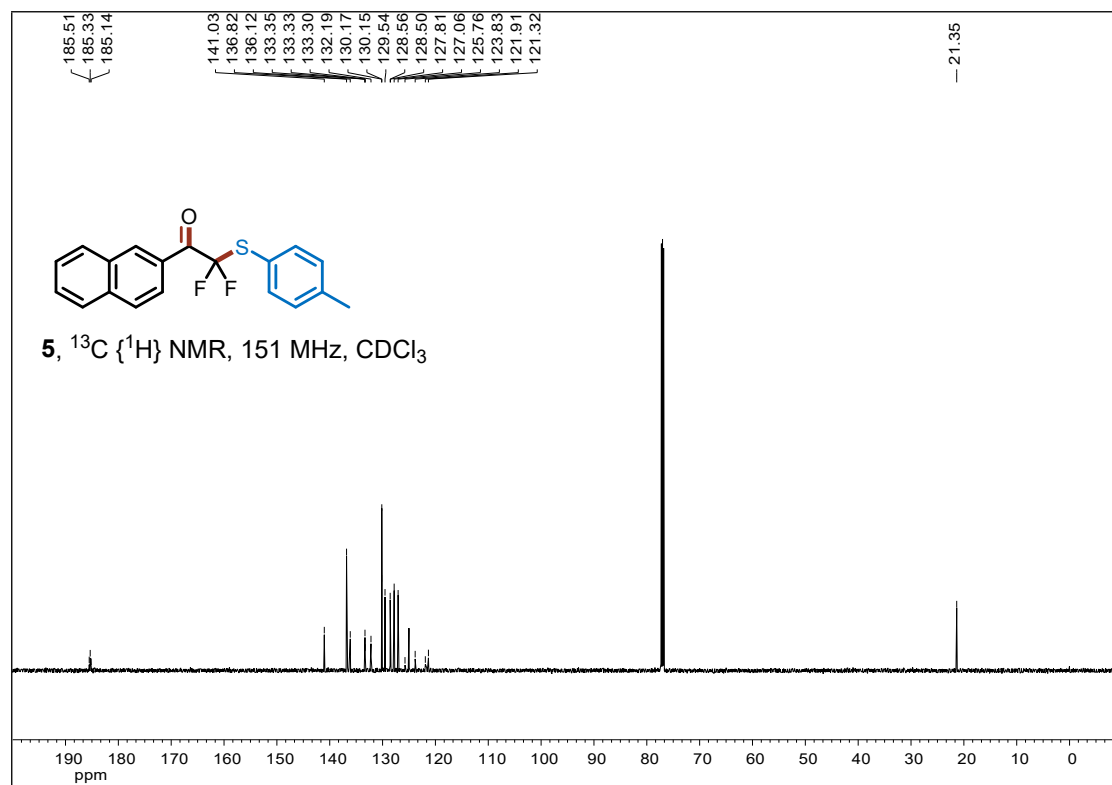
$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **3n**



^1H NMR spectrum of **5**



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5**



$^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **5**

