

Supporting Information

Visible Light-Promoted Synthesis of α,α -Difluoro- β -Keto-thio(seleno)ethers from Thio(seleno)sulfonates and Difluoroenoxy silanes

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I. General Information

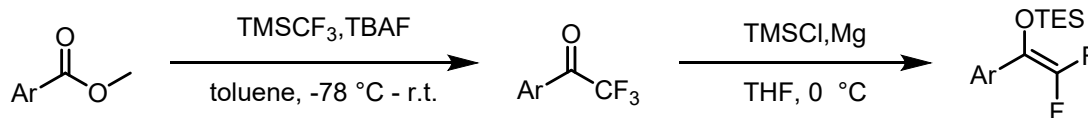
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were analytical grade and used without further purification. Anhydrous DMA, was purchased from Beijing InnoChem Science & Technology Co., Ltd. Analytical thin-layer chromatography (TLC) was performed on silica gel, visualized by irradiation with UV light. For column chromatography, 300-400 mesh silica gel was used. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded on a BRUKER 400 MHz spectrometer in CDCl_3 . Chemical shifts (δ) were reported referenced to an internal tetramethylsilane standard or the CDCl_3 residual peak (δ 7.26) for $^1\text{H NMR}$. Chemical shifts of $^{13}\text{C NMR}$ are reported relative to CDCl_3 (δ 77.16). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). IR spectra were recorded on a BRUKER VERTEX 70 spectrophotometer and are reported in terms of frequency of absorption (cm^{-1}). HRMS spectra were obtained by using GCT Premier TOF-MS with EI source. The starting materials were isolated by SepaBean machine Flash Chromatography, which was purchased from Santai Technologies Inc.

II. Synthesis of Substrates

General procedure for the synthesis of PhSO_2SAr or PhSO_2SeAr .^{1,2}

A mixture of PhSO_2Na (4 equiv), disulphide (1 equiv) and NBS (2 equiv) in MeCN was stirred at room temperature. After the completion of the reaction, as monitored by TLC, the reaction mixture was washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography to provide the desired aryl-thiosulfonates.

General procedure for the synthesis of Difluoroenoxy silanes.^{3,4}



To a solution of methyl benzoate (1.36 g) in toluene (50 ml) was added TMSCF₃ (2.8 g) at room temperature under Ar. The reaction mixture was cooled to -78 °C, TBAF (1 mL, 1.0 M in THF, 0.1 equiv) was then added. After stirring for 0.5 h at -78 °C, the reaction mixture was allowed to warm to room temperature and stirred for further 12 h. Hydrochloric acid (7.5 mL, 2.0 M, 1.5 equiv) was then added and the resulting mixture stirred for further 2 h. The resulting suspension was quenched with saturated aqueous NaHCO_3 and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash column

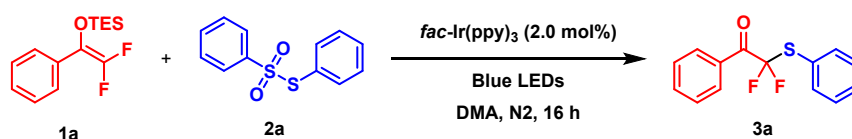
chromatography to give corresponding ketone.

A 100 mL oven-dried reaction bottle equipped with a magnetic stirrer bar was charged with the Mg (0.58 g, 24 mmol). The bottle was evacuated and backfilled with argon three times, followed by THF (24 mL) were added with stirring, Chlorotriethylsilane (4.0 mL, 24 mmol) was added subsequently. The bottle was capped and cooled down to -10 °C under an argon atmosphere, trifluoroacetophenone (843 μ L, 6.0 mmol) was added dropwise and then the reaction mixture was stirred for additional 1 h. After evaporation of solvent, Et₃N (3.3 mL, 24 mmol) was added and the mixture was stirred for 10 min. The mixture was filtered by petroleum ether, concentrated in vacuo, and purified by flash column chromatography on silica gel (pretreated with 3% Et₃N/Petroleum ether), eluting with petroleum ether, afforded to pure product difluoroenoxytriethylsilane. The reagent should be used as soon as possible after preparation.

III. General Procedure and Product Characterization

1. General Procedure A

A representative procedure synthesis of 1-(tert-butyl)-2-(naphthalen-2-ylmethyl) disulfane (**3a**) is shown below.



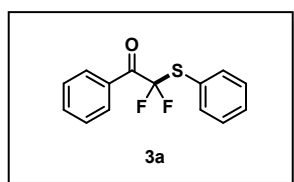
In glovebox, an oven-dried screw-capped 8 mL vial equipped with a magnetic stir bar was charged with 1-triethylsiloxy-2,2-difluoro-1-phenylethene **1a** (81.2 mg, 0.30 mmol) and S-Phenyl benzenethiosulfonate **2a** (50.1 mg 0.20 mmol), *fac*-Ir(ppy)₃ (2.6 mg, 2.0 mol %), DMA (1.0 mL) was added via syringe. The reaction mixture was stirred under 30 W blue LEDs for 16 hours at room temperature. After 16 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL \times 3). The organic layer was dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product **3a** (78% yield).

2. General Procedure B

The procedure scale-up synthesis of **3a** is shown below.

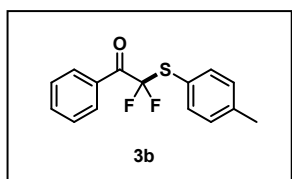
In glovebox, an oven-dried screw-capped 50-mL vial equipped with a magnetic stir bar was charged with 1-triethylsiloxy-2,2-difluoro-1-phenylethene **1a** (81.2 mg, 0.30 mmol) and S-Phenyl benzenethiosulfonate **2a** (50.1 mg 0.20 mmol), *fac*-Ir(ppy)₃ (2.6 mg, 2.0 mol %), DMA (1.0 mL) was added via syringe. The reaction mixture was stirred under 30 W blue LEDs for 16 hours at room temperature. After 16 h, the crude reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (20 mL \times 3). The organic layer was dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography to afford pure product (63% yield).

IV. Product Characterization



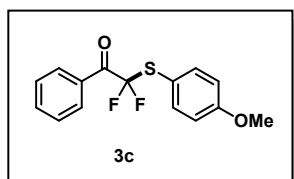
2,2-difluoro-2-(phenylthio)acetophenone (3a)

Yield: 78% (41.3 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1701, 1270, 1130. **^1H NMR** (400 MHz, CDCl_3) δ 8.17 – 8.11 (m, 2H), 7.68 – 7.63 (m, 1H), 7.63 – 7.59 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 (dt, $J = 2.7, 1.9$ Hz, 1H), 7.41 – 7.36 (m, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.4 (t, $J = 28.3$ Hz), 136.9, 134.8, 131.3, 130.6 (t, $J = 2.6$ Hz), 129.4, 128.8, 124.9 (t, $J = 2.3$ Hz), 123.9 (t, $J = 291.9$ Hz). **^{19}F NMR** (377 MHz, CDCl_3) δ -77.2. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 287.0313, found 287.0310.



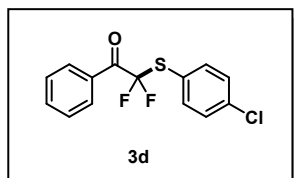
2,2-difluoro-1-phenyl-2-(p-tolylthio)ethan-1-one (3b)

Yield: 88% (49.0 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1700, 1270, 1128. **^1H NMR** (400 MHz, CDCl_3) δ 8.14 (d, $J = 7.5$ Hz, 2H), 7.68 – 7.63 (m, 1H), 7.53 – 7.45 (m, 4H), 7.19 (d, $J = 7.9$ Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.5 (t, $J = 28.3$ Hz), 141.1, 136.9, 134.7, 131.4, 130.6 (t, $J = 2.6$ Hz), 130.3, 128.8, 123.7 (t, $J = 291.4$ Hz), 121.3 (t, $J = 2.5$ Hz), 21.5. **^{19}F NMR** (377 MHz, CDCl_3) δ -77.9. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 301.0470, found 301.0464.



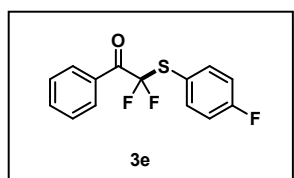
2,2-difluoro-2-((4-methoxyphenyl)thio)-1-phenylethan-1-one (3c)

Yield: 82% (48.2 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1700, 1249, 1128, 1026. **^1H NMR** (400 MHz, CDCl_3) δ 8.13 (d, $J = 7.6$ Hz, 2H), 7.67 – 7.63 (m, 1H), 7.50 (dd, $J = 8.4, 6.9$ Hz, 4H), 6.93 – 6.87 (m, 2H), 3.83 (d, $J = 5.2$ Hz, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.5 (t, $J = 28.3$ Hz), 161.7, 138.6, 134.6, 132.7, 131.3, 130.5 (t, $J = 2.7$ Hz), 128.7, 123.5 (t, $J = 290.9$ Hz), 114.9, 55.4. **^{19}F NMR** (377 MHz, CDCl_3) δ -78.6. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{O}_2\text{S}$ ($\text{M}+\text{Na}$) $^+$: 317.0419, found 317.0418.



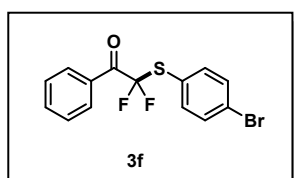
2-((4-chlorophenyl)thio)-2,2-difluoro-1-phenylethan-1-one (3d)

Yield: 85% (50.8 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1696, 1272, 1143, 1009. **^1H NMR** (400 MHz, CDCl_3) δ 8.12 (dd, $J = 8.3, 0.8$ Hz, 2H), 7.69 – 7.64 (m, 1H), 7.55 – 7.49 (m, 4H), 7.38 – 7.35 (m, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.2 (t, $J = 28.3$ Hz), 138.1, 137.4, 134.9, 131.1, 130.6 (t, $J = 2.7$ Hz), 129.7, 128.9, 123.9 (t, $J = 292.9$ Hz), 123.4 (t, $J = 2.3$ Hz). **^{19}F NMR** (377 MHz, CDCl_3) δ -76.8. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{ClF}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 320.9923, found 320.9918.



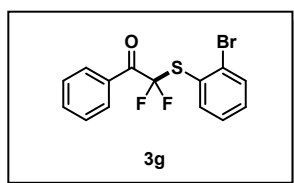
2,2-difluoro-2-((4-fluorophenyl)thio)-1-phenylethan-1-one (3e)

Yield: 76% (43.0 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1679, 1226, 1126, 1059. **^1H NMR** (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.5$ Hz, 2H), 7.69 – 7.63 (m, 1H), 7.61 – 7.55 (m, 2H), 7.50 (dd, $J = 10.8, 4.9$ Hz, 2H), 7.12 – 7.04 (m, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.3 (t, $J = 28.3$ Hz), 164.5 (d, $J = 252.5$ Hz), 139.1 (d, $J = 8.9$ Hz), 134.9, 131.2, 130.6 (t, $J = 2.7$ Hz), 128.9, 123.8, 120.2 (d, $J = 3.0$ Hz), 116.7 (d, $J = 22.2$ Hz). **^{19}F NMR** (377 MHz, CDCl_3) δ -77.4, -109.3. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{F}_3\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 305.0219, found 305.0213.



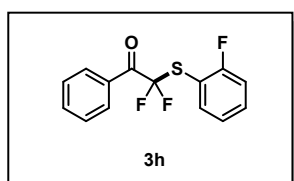
2-(4-bromophenylthio)-2,2-difluoro-1-phenylethanone (3f)

Yield: 71% (48.7 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1700, 1261, 1012. **^1H NMR** (400 MHz, CDCl_3) δ 8.11 (dd, $J = 8.5, 1.0$ Hz, 2H), 7.69 – 7.64 (m, 1H), 7.54 – 7.48 (m, 4H), 7.48 – 7.43 (m, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.2 (t, $J = 28.3$ Hz), 138.3, 134.9, 132.7, 131.1, 130.6 (t, $J = 2.6$ Hz), 128.9, 125.7, 124.1 (t, $J = 2.2$ Hz), 123.8 (t, $J = 292.9$ Hz). **^{19}F NMR** (377 MHz, CDCl_3) δ -76.6. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{BrF}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 364.9418, found 364.9410.



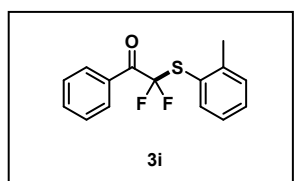
2-(2-bromophenylthio)-2,2-difluoro-1-phenylethanone (3g)

Yield: 75% (51.5 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1696, 1271, 1228, 1131. **^1H NMR** (400 MHz, CDCl_3) δ 8.16 (d, $J = 7.5$ Hz, 2H), 7.79 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.67 (ddd, $J = 8.6, 5.1, 1.3$ Hz, 2H), 7.50 (dd, $J = 10.8, 4.9$ Hz, 2H), 7.36 (td, $J = 7.6, 1.5$ Hz, 1H), 7.30 (td, $J = 7.7, 1.8$ Hz, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.1 (t, $J = 27.8$ Hz), 138.9, 134.9, 133.9, 131.9, 131.3, 131.0, 130.6 (t, $J = 2.7$ Hz), 128.8, 128.1, 126.7, 123.7 (t, $J = 293.9$ Hz). **^{19}F NMR** (377 MHz, CDCl_3) δ -76.6. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{BrF}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 364.9418, found 364.9407.



2,2-difluoro-2-((2-fluorophenyl)thio)-1-phenylethan-1-one (3h)

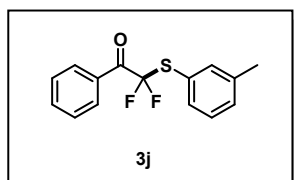
Yield: 68% (38.4 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1700, 1269, 1130, 1031. **^1H NMR** (400 MHz, CDCl_3) δ 8.14 (d, $J = 7.6$ Hz, 2H), 7.69 – 7.60 (m, 2H), 7.54 – 7.45 (m, 3H), 7.22 – 7.14 (m, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ 185.1 (t, $J = 28.3$ Hz), 163.9 (d, $J = 4.2$ Hz), 139.5, 134.9, 133.5 (d, $J = 8.1$ Hz), 131.1, 130.6 (t, $J = 2.6$ Hz), 128.9, 124.9 (d, $J = 4.2$ Hz), 123.7 (t, $J = 293.4$ Hz), 116.6 (d, $J = 23.2$ Hz), 112.1 (d, $J = 18.4$ Hz). **^{19}F NMR** (377 MHz, CDCl_3) δ -76.5, -104.4. **HRMS** (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{F}_3\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 305.0219, found 305.0205.



2,2-difluoro-2-((2-methylphenyl)thio)-1-phenylethan-1-one (3i)

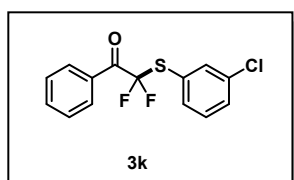
Yield: 69% (38.4 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1701, 1270, 1128. **^1H NMR** (400 MHz, CDCl_3) δ 8.15 (d, J

= 8.3 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.54 – 7.48 (m, 2H), 7.37 (td, $J = 7.5, 1.3$ Hz, 1H), 7.31 (d, $J = 6.5$ Hz, 1H), 7.21 (td, $J = 7.5, 1.3$ Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.5 (t, $J = 28.3$ Hz), 144.4, 138.7, 134.8, 131.3, 131.1, 131.0, 130.6 (t, $J = 2.7$ Hz), 128.8, 126.8, 124.3 (t, $J = 1.9$ Hz), 124.1 (t, $J = 291.9$ Hz), 21.5. ^{19}F NMR (377 MHz, CDCl_3) δ -76.9. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 301.0470, found 301.0477.



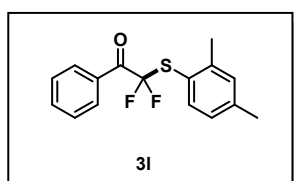
2,2-difluoro-2-((2-methylphenyl)thio)-1-phenylethan-1-one (3j)

Yield: 68% (37.8 mg). light yellow oil. **IR** (neat, v, cm^{-1}): 1701, 1270, 1129. ^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.10 (m, 2H), 7.66 – 7.61 (m, 1H), 7.51 – 7.46 (m, 2H), 7.42 – 7.37 (m, 2H), 7.27 – 7.22 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.5 (t, $J = 28.3$ Hz), 139.4, 137.4, 134.8, 133.9, 131.5, 131.4, 130.6 (t, $J = 2.7$ Hz), 129.2, 128.8, 124.5 (t, $J = 2.3$ Hz), 123.8 (t, $J = 291.4$ Hz), 21.3. ^{19}F NMR (377 MHz, CDCl_3) δ -77.2. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 301.0470, found 301.0475.



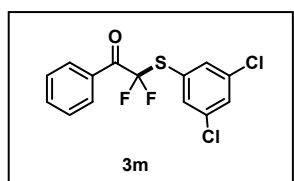
2-((3-chlorophenyl)thio)-2,2-difluoro-1-phenylethan-1-one (3k)

Yield: 81% (48.4 mg). light yellow oil. **IR** (neat, v, cm^{-1}): 1780, 1271, 1128, 1058. ^1H NMR (400 MHz, CDCl_3) δ 8.12 (dd, $J = 8.4, 0.9$ Hz, 2H), 7.67 (ddd, $J = 8.7, 2.4, 1.2$ Hz, 1H), 7.61 (t, $J = 1.8$ Hz, 1H), 7.54 – 7.48 (m, 3H), 7.44 (ddd, $J = 8.1, 2.0, 1.1$ Hz, 1H), 7.32 (t, $J = 7.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.1 (t, $J = 28.3$ Hz), 136.3, 135.0, 134.8, 131.0, 130.8, 130.5 (t, $J = 2.5$ Hz), 130.3, 128.9, 126.8 (t, $J = 2.0$ Hz), 124.0 (t, $J = 292.9$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -76.1. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{ClF}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 320.9923, found 320.9916.



2,2-difluoro-2-((2,3-dimethylphenyl)thio)-1-phenylethan-1-one (3l)

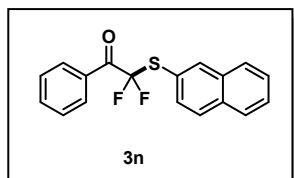
Yield: 73% (42.7 mg). light yellow oil. **IR** (neat, v, cm^{-1}): 1701, 1269, 1129, 1068. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (dd, $J = 8.5, 1.0$ Hz, 2H), 7.68 – 7.62 (m, 1H), 7.49 (ddd, $J = 10.8, 8.3, 5.1$ Hz, 3H), 7.15 – 7.10 (m, 1H), 7.01 (dd, $J = 7.9, 1.3$ Hz, 1H), 2.43 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.6 (t, $J = 28.3$ Hz), 144.2 (s), 141.5 (s), 138.7 (s), 134.7 (s), 132.0 (s), 131.4 (s), 130.6 (t, $J = 2.6$ Hz), 128.8 (s), 127.7 (s), 124.0 (s), 120.8 (s), 21.4 (s). ^{19}F NMR (377 MHz, CDCl_3) δ -77.6 (s). HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 315.0626 found 315.0610.



2-((3,5-dichlorophenyl)thio)-2,2-difluoro-1-phenylethan-1-one (3m)

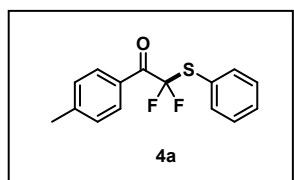
Yield: 81% (54.0 mg). light yellow oil. **IR** (neat, v, cm^{-1}): 1699, 1405, 1268, 1132, 1062. ^1H NMR (400 MHz, CDCl_3)

δ 8.13 – 8.08 (m, 2H), 7.71 – 7.65 (m, 1H), 7.55 – 7.49 (m, 4H), 7.46 (t, J = 1.9 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.9 (t, J = 28.3 Hz), 135.5, 135.2, 134.6, 130.9, 130.6 (t, J = 2.8 Hz), 129.0, 128.2 (t, J = 2.0 Hz), 125.1, 124.3 (t, J = 294.4 Hz, 1C). ^{19}F NMR (377 MHz, CDCl_3) δ -75.0. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_8\text{Cl}_2\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 354.9534, found 354.9525



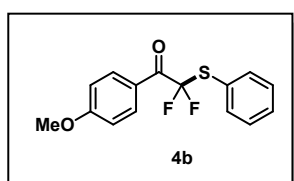
2,2-difluoro-2-(naphthalen-2-ylthio)-1-phenylethan-1-one (3n)

Yield: 60% (37.7 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1698, 1273, 1020. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 8.5 Hz, 3H), 7.89 – 7.82 (m, 3H), 7.68 – 7.61 (m, 2H), 7.59 – 7.48 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.5 (t, J = 28.3 Hz), 137.4 (s), 134.8 (s), 133.9 (s), 133.6 (s), 132.5 (s), 131.4 (s), 130.6 (t, J = 2.7 Hz), 129.1 (s), 128.8 (s), 128.2 (s), 127.9 (s), 127.8 (s), 126.9 (s), 124.1 (t, J = 292.9 Hz), 122.1 (t, J = 2.2 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -76.9 (s). HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 337.0470, found 337.0456.



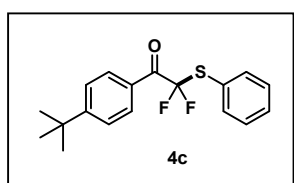
2,2-difluoro-1-(4-methylphenyl)-2-(phenylthio)ethan-1-one (4a)

Yield: 77% (42.8 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1697, 1272, 1058. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.2 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.48 – 7.43 (m, 1H), 7.41 – 7.36 (m, 2H), 7.30 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.0 (t, J = 28.3 Hz), 146.1, 136.9, 130.8 (t, J = 2.5 Hz), 130.6, 129.6, 129.4, 128.8, 125.1 (t, J = 2.0 Hz), 124.0 (t, J = 291.9 Hz), 22.0. ^{19}F NMR (377 MHz, CDCl_3) δ -77.0. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 301.0470, found 301.0476.



2,2-difluoro-1-(4-methoxyphenyl)-2-(phenylthio)ethan-1-one (4b)

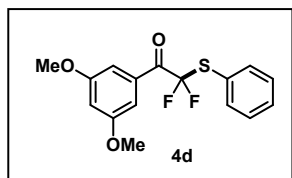
Yield: 82% (48.3 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1688, 1261, 1127, 1022. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 9.1 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.48 – 7.43 (m, 1H), 7.42 – 7.36 (m, 2H), 6.99 – 6.94 (m, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 183.9 (t, J = 28.3 Hz), 164.9, 136.9, 133.2 (t, J = 2.7 Hz), 130.5, 129.4, 125.2 (t, J = 2.0 Hz), 124.2 (t, J = 291.8 Hz), 124.0, 114.2, 55.7. ^{19}F NMR (377 MHz, CDCl_3) δ -76.3. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{15}\text{H}_{12}\text{F}_2\text{O}_2\text{S}$ ($\text{M}+\text{Na}$) $^+$: 317.0419, found 317.0414.



2,2-difluoro-1-(4-(tert-butyl)phenyl)-2-(phenylthio)ethan-1-one (4c)

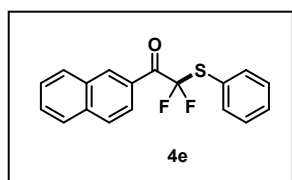
Yield: 73% (46.8 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1697, 1273, 1103, 1058. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.6 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.54 – 7.50 (m, 2H),

7.49 – 7.44 (m, 1H), 7.42 – 7.36 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.9 (t, $J = 28.3$ Hz), 158.8, 136.8, 130.5 (t, $J = 2.5$ Hz), 130.4, 129.3, 128.5, 125.7, 125.0 (t, $J = 2.0$ Hz), 123.9 (t, $J = 291.9$ Hz), 35.4, 31.0. ^{19}F NMR (377 MHz, CDCl_3) δ -76.9. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 343.0939, found 343.0937.



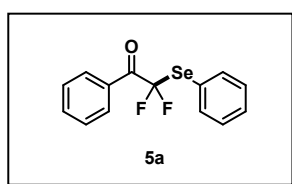
2,2-difluoro-1-(3,5-dimethoxyphenyl)-2-(phenylthio)ethan-1-one (4d)

Yield: 72% (46.7 mg). light yellow oil. IR (neat, ν , cm^{-1}): 1693, 1299, 1202, 1153, 1017. ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.3$ Hz, 2H), 7.37 (t, $J = 7.4$ Hz, 1H), 7.30 (t, $J = 7.4$ Hz, 2H), 7.17 (s, 2H), 6.65 (t, $J = 2.2$ Hz, 1H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.1 (t, $J = 28.3$ Hz), 160.9, 136.9, 132.9, 130.6, 129.4, 125.0 (t, $J = 4.0$ Hz), 123.8 (t, $J = 291.9$ Hz), 108.2 (t, $J = 2.7$ Hz), 107.5, 55.8. ^{19}F NMR (377 MHz, CDCl_3) δ -76.8. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}_3\text{S}$ ($\text{M}+\text{Na}$) $^+$: 347.0524, found 347.0522.



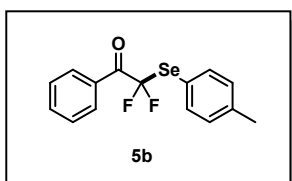
2,2-difluoro-1-(naphthalen-2-yl)-2-(phenylthio)ethan-1-one (4e)

Yield: 68% (42.8 mg). light yellow oil. IR (neat, ν , cm^{-1}): 1681, 1263, 1106, 1020. ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 1H), 8.11 (dd, $J = 8.7, 1.4$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.94 – 7.88 (m, 2H), 7.70 – 7.62 (m, 3H), 7.61 – 7.56 (m, 1H), 7.49 – 7.44 (m, 1H), 7.43 – 7.37 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.6 (t, $J = 27.7$ Hz), 136.9, 136.3, 133.5 (t, $J = 3.6$ Hz), 132.3, 130.6, 130.3, 129.7, 129.4, 128.7, 128.5, 127.9, 127.2, 127.0, 125.1, 124.1 (t, $J = 292.9$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -76.4. HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_2\text{OS}$ ($\text{M}+\text{Na}$) $^+$: 337.0470, found 337.0476.



2,2-difluoro-1-phenyl-2-(phenylselanyl)ethan-1-one (5a)

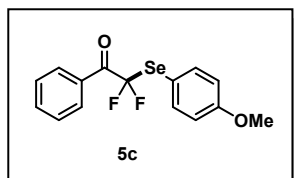
Yield: 69% (42.9 mg). light yellow oil. IR (neat, ν , cm^{-1}): 1696, 1270, 1129, 1043. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 7.5$ Hz, 2H), 7.70 – 7.61 (m, 3H), 7.51 – 7.42 (m, 3H), 7.36 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.7 (t, $J = 25.8$ Hz), 137.7, 134.7, 131.1, 130.5 (t, $J = 2.9$ Hz), 130.2, 129.5, 128.8, 123.4 (t, $J = 2.0$ Hz), 121.8 (t, $J = 27.7$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -77.0. ^{77}Se NMR (76 MHz, CDCl_3) δ 557.3 (t, $J = 35.7$ Hz). HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{F}_2\text{OSe}$ ($\text{M}+\text{Na}$) $^+$: 334.9758, found 334.9733.



2,2-difluoro-1-phenyl-2-(4-methylphenylselanyl)ethan-1-one (5b)

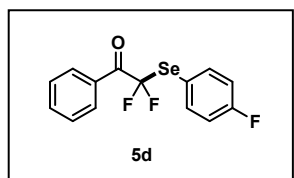
Yield: 86% (55.9 mg). light yellow oil. IR (neat, ν , cm^{-1}): 1696, 1269, 1130, 1039. ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.06 (m, 2H), 7.67 – 7.62 (m, 1H), 7.57 – 7.53 (m, 2H), 7.51 – 7.46 (m, 2H), 7.17 (dd, $J = 8.4, 0.6$ Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz,

CDCl₃) δ 185.7 (t, J = 25.8 Hz), 140.6, 137.6, 134.7, 131.1, 130.5 (t, J = 3.0 Hz), 130.3, 128.8, 121.5 (t, J = 307.5 Hz), 119.8 (t, J = 2.0 Hz), 21.5. **¹⁹F NMR** (377 MHz, CDCl₃) δ -77.3. **⁷⁷Se NMR** (76 MHz, CDCl₃) δ 548.9 (t, J = 37.2 Hz). **HRMS** (ESI+, MeCN) m/z calcd for C₁₅H₁₂F₂OSe (M+Na)⁺: 348.9914, found 348.9896.



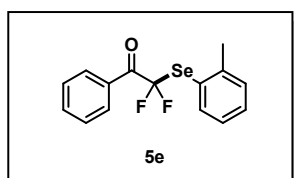
2,2-difluoro-1-phenyl-2-(4-methoxyphenylselanyl)ethan-1-one (5c)

Yield: 82% (56.0 mg). light yellow oil. **IR** (neat, v, cm⁻¹): 1695, 1247, 1172, 1130, 1026. **¹H NMR** (400 MHz, CDCl₃) δ 8.08 (d, J = 7.5 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.44 (m, 2H), 6.90 – 6.83 (m, 2H), 3.81 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.8 (t, J = 25.8 Hz), 161.4, 139.3, 134.6, 131.2, 130.4 (t, J = 2.9 Hz), 128.8, 121.3 (t, J = 307.0 Hz), 115.2, 113.6 (t, J = 2.0 Hz), 55.4. **¹⁹F NMR** (377 MHz, CDCl₃) δ -77.9. **⁷⁷Se NMR** (76 MHz, CDCl₃) δ 543.7 (t, J = 38.0 Hz). **HRMS** (ESI+, MeCN) m/z calcd for C₁₅H₁₂F₂O₂Se (M+Na)⁺: 364.9863, found 364.9844.



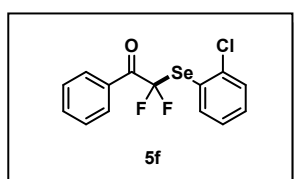
2,2-difluoro-1-phenyl-2-(4-fluorophenylselanyl)ethan-1-one (5d)

Yield: 70% (46.1 mg). light yellow oil. **IR** (neat, v, cm⁻¹): 1697, 1271, 1130, 1039. **¹H NMR** (400 MHz, CDCl₃) δ 8.07 (d, J = 7.6 Hz, 2H), 7.68 – 7.60 (m, 3H), 7.49 (t, J = 7.9 Hz, 2H), 7.08 – 7.01 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.6 (t, J = 25.8 Hz), 165.5 (d, J = 252.5 Hz), 139.9 (d, J = 4.5 Hz), 134.9, 130.9, 130.5 (t, J = 2.9 Hz), 128.9, 121.8 (t, J = 308.1 Hz), 118.2 (d, J = 4.0 Hz), 116.9 (d, J = 21.2 Hz). **¹⁹F NMR** (377 MHz, CDCl₃) δ -76.5, -110.1. **⁷⁷Se NMR** (76 MHz, CDCl₃) δ 546.7 (t, J = 35.0 Hz). **HRMS** (ESI+, MeCN) m/z calcd for C₁₄H₉F₃OSe (M+Na)⁺: 352.9663, found 364.9657.



2,2-difluoro-1-phenyl-2-(2-methylphenylselanyl)ethan-1-one (5e)

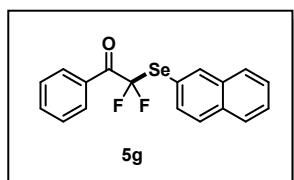
Yield: 76% (49.4 mg). light yellow oil. **IR** (neat, v, cm⁻¹): 1695, 1269, 1127, 1032. **¹H NMR** (400 MHz, CDCl₃) δ 8.08 (d, J = 8.3 Hz, 2H), 7.70 – 7.61 (m, 2H), 7.48 (t, J = 7.9 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.15 (td, J = 7.6, 1.8 Hz, 1H), 2.48 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 185.6 (t, J = 25.8 Hz), 144.0, 139.5, 134.7, 131.1, 130.9, 130.7, 130.5 (t, J = 3.0 Hz), 128.8, 126.8, 124.6 (t, J = 2.0 Hz), 121.7 (t, J = 308.1 Hz), 23.6. **¹⁹F NMR** (377 MHz, CDCl₃) δ -76.6. **⁷⁷Se NMR** (76 MHz, CDCl₃) δ 501.2 (t, J = 36.1 Hz). **HRMS** (ESI+, MeCN) m/z calcd for C₁₅H₁₂F₂OSe (M+Na)⁺: 348.9914, found 348.9899.



2,2-difluoro-1-phenyl-2-(2-chlorophenylselanyl)ethan-1-one (5f)

Yield: 65% (44.9 mg). light yellow oil. **IR** (neat, v, cm⁻¹): 1694, 1270, 1128, 1025. **¹H NMR** (400 MHz, CDCl₃) δ 8.10 (d, J = 7.5 Hz, 2H), 7.81 (dd, J = 7.7, 1.4 Hz, 1H), 7.65 (dd,

$J = 10.6, 4.3$ Hz, 1H), 7.52 – 7.46 (m, 3H), 7.36 (td, $J = 7.7, 1.6$ Hz, 1H), 7.25 (dt, $J = 7.5, 3.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.6 (t, $J = 25.3$ Hz), 140.0, 139.4, 134.9, 131.6, 130.8, 130.5 (t, $J = 2.9$ Hz), 130.2, 128.9, 127.5, 124.5, 122.2 (t, $J = 310.1$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -74.5. ^{77}Se NMR (76 MHz, CDCl_3) δ 531.1 (t, $J = 34.6$ Hz). HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{14}\text{H}_9\text{ClF}_2\text{OSe}$ ($\text{M}+\text{Na}$) $^+$: 368.9368, found 368.9362.



2,2-difluoro-1-phenyl-2-(naphthalen-2-ylselanyl)ethan-1-one (5g)

Yield: 50% (36.1 mg). light yellow oil. **IR** (neat, ν , cm^{-1}): 1693, 1268, 1129, 1041. ^1H NMR (400 MHz, CDCl_3) δ 8.47 – 8.39 (m, 1H), 8.03 (d, $J = 7.5$ Hz, 2H), 7.99 – 7.93 (m, 2H), 7.85 (dd, $J = 6.4, 3.0$ Hz, 1H), 7.63 – 7.58 (m, 1H), 7.56 – 7.49 (m, 2H), 7.43 (dd, $J = 8.1, 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.7 (t, $J = 25.3$ Hz), 138.8, 136.0, 134.7, 134.3, 131.8, 131.1, 130.4 (t, $J = 3.0$ Hz), 128.7, 128.6, 128.5, 127.4, 126.6, 125.8, 123.1, 121.9 (t, $J = 309.1$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -75.9. ^{77}Se NMR (76 MHz, CDCl_3) δ 478.0 (t, $J = 36.9$ Hz). HRMS (ESI+, MeCN) m/z calcd for $\text{C}_{18}\text{H}_{12}\text{F}_2\text{OSe}$ ($\text{M}+\text{Na}$) $^+$: 384.9914, found 384.9910.

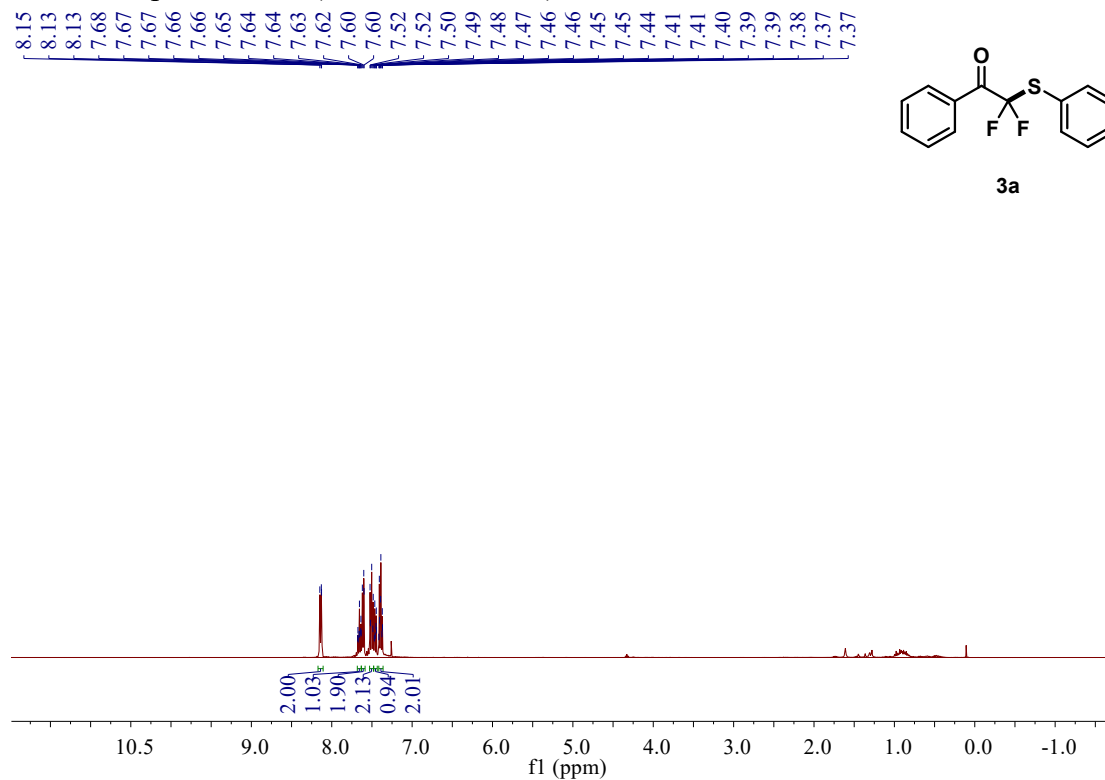
V. References

- [1] Q. Chen; Y. L. Huang, X. F. Wang, J. W. Wu; and G. D. Yu, Metal-free NaI/TBHP mediated sulfonylation of thiols with sulfonyl hydrazides *Org. Biomol. Chem.*, 2018, **16**, 1713-1719.
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- [3] X. Gao, R. Cheng, Y. L. Xiao, X. L. Wan and X. G. Zhang, Copper-Catalyzed highly enantioselective difluoroalkylation of secondary propargyl sulfonates with difluoro-enoxysilanes, *Chem.*, 2019, **5**, 2987 – 2999.
- [4] Y. B. Wu, G. P. Lu, B. J. Zhou, M. J. Bu, L. Wan and C. Cai, Visible-light-initiated difluoromethylation of arene diazonium tetrafluoroborates *Chem. Commun.*, 2016, **52**, 5965.

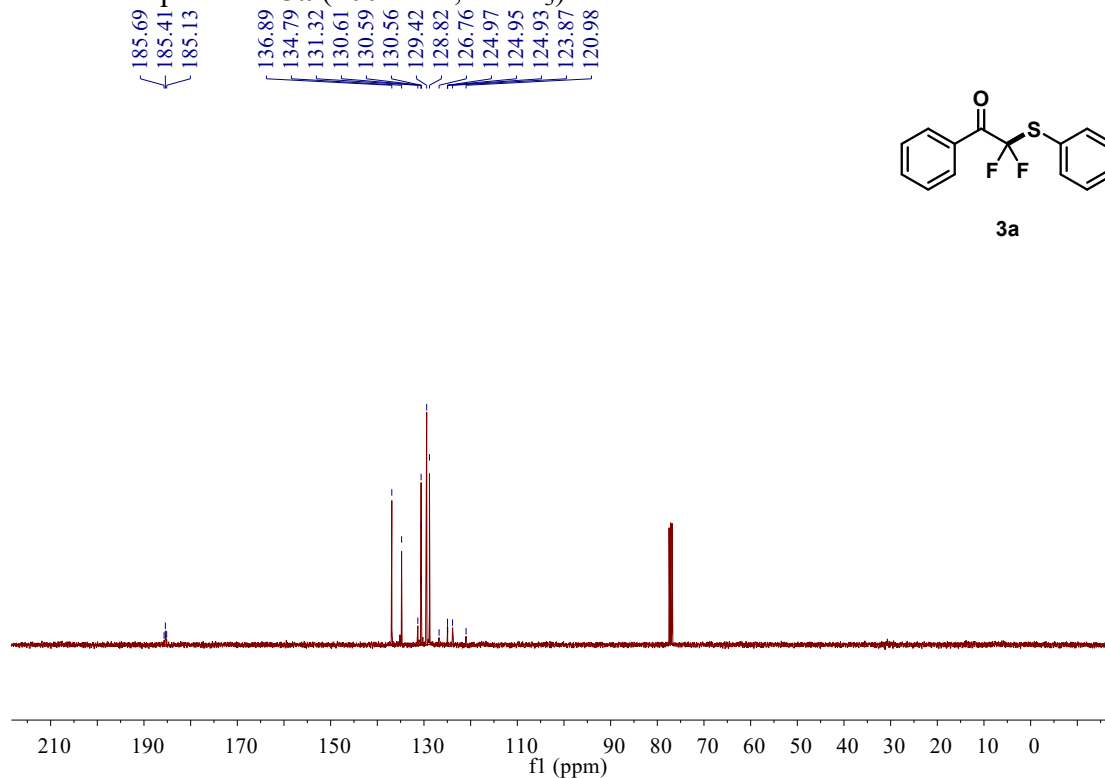
VI. Copies of ^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{77}Se NMR

Spectra

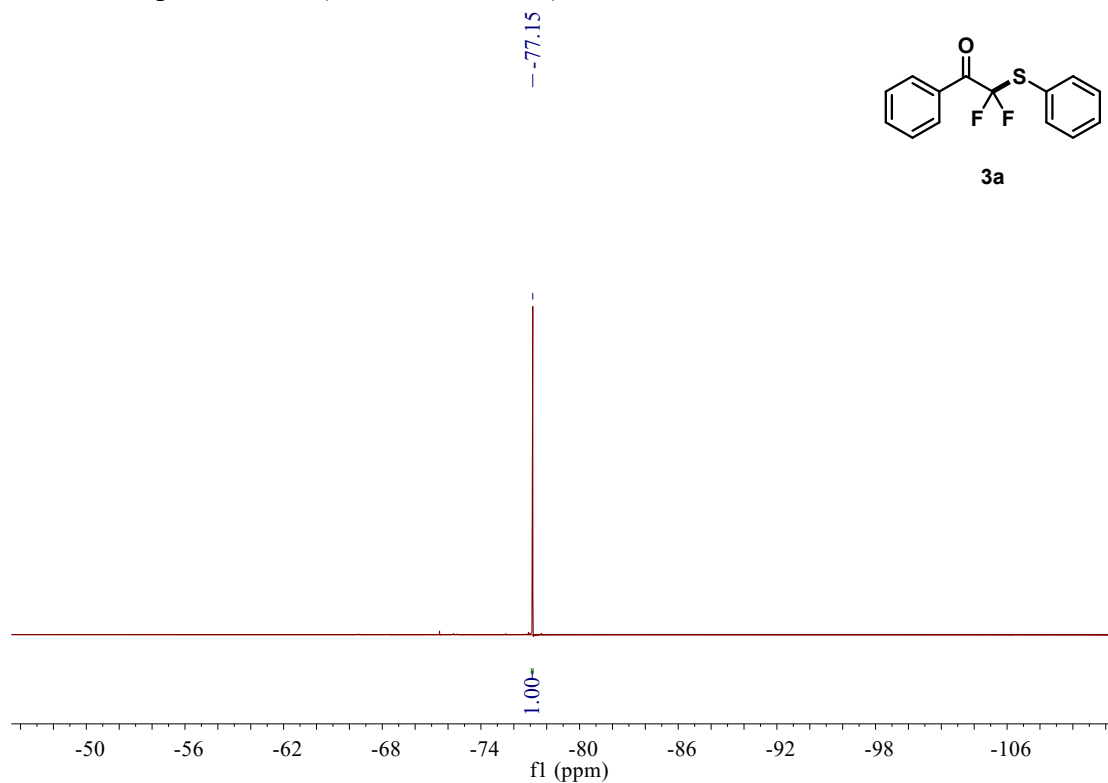
^1H NMR Spectra of **3a** (400 MHz, CDCl_3)



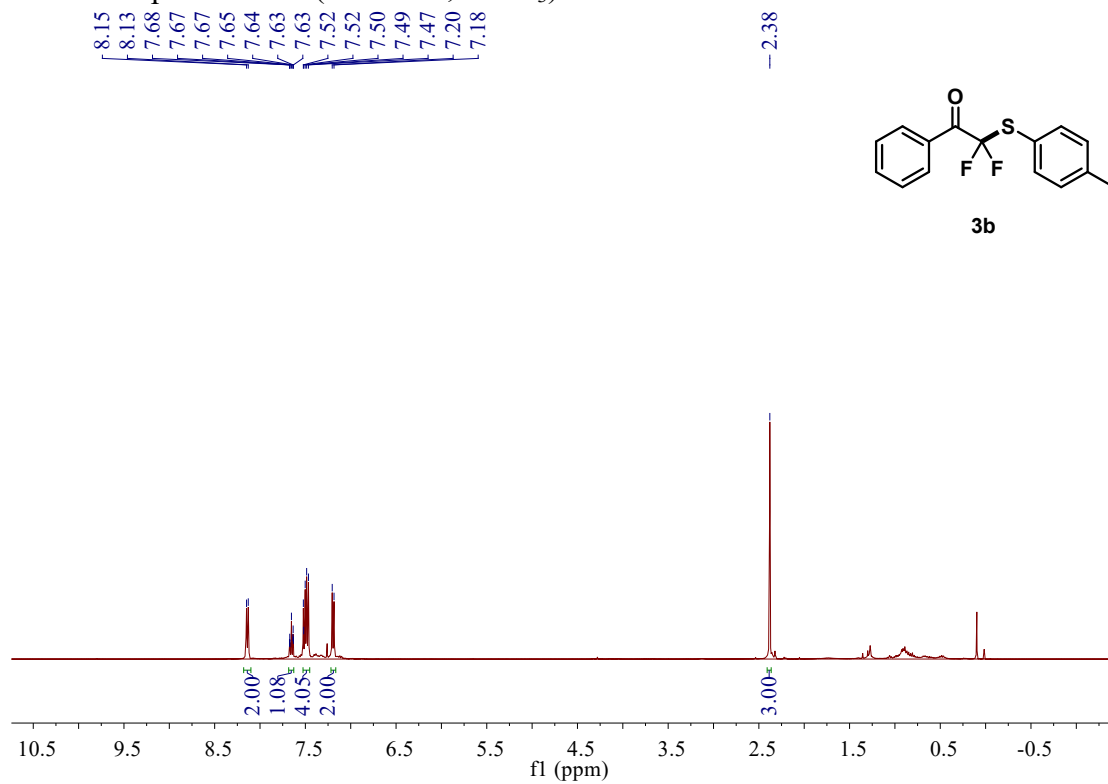
^{13}C NMR Spectra of **3a** (100 MHz, CDCl_3)



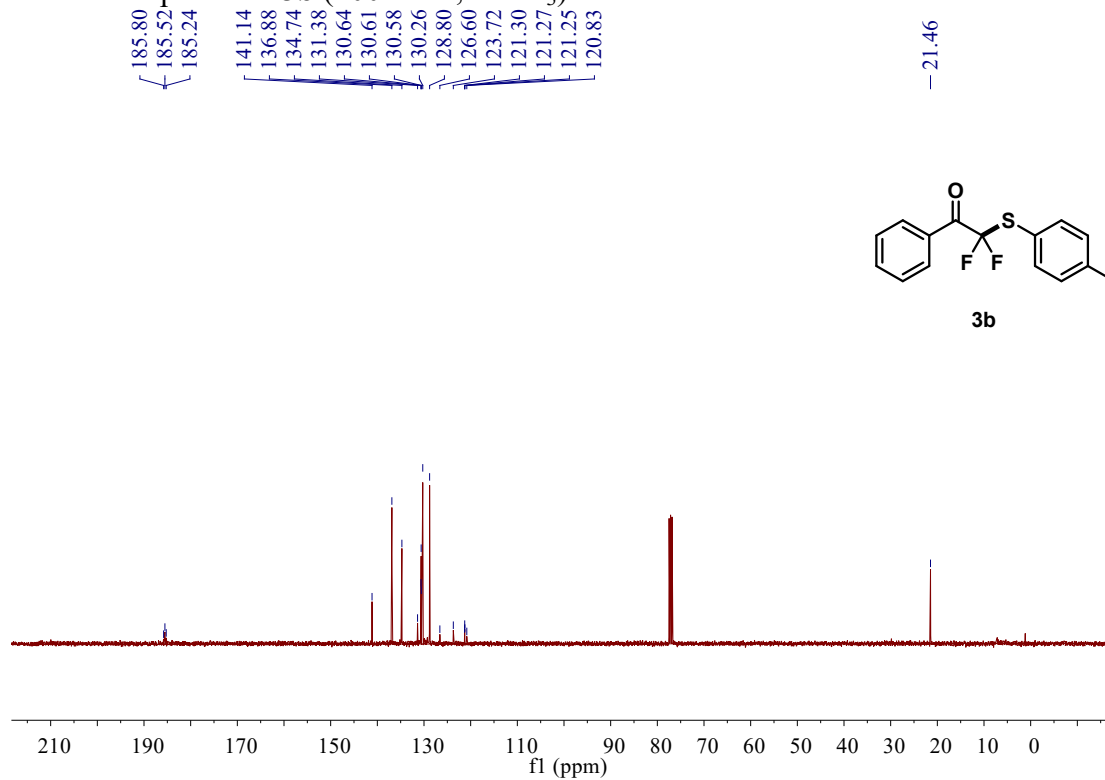
^{19}F NMR Spectra of **3a** (377 MHz, CDCl_3)



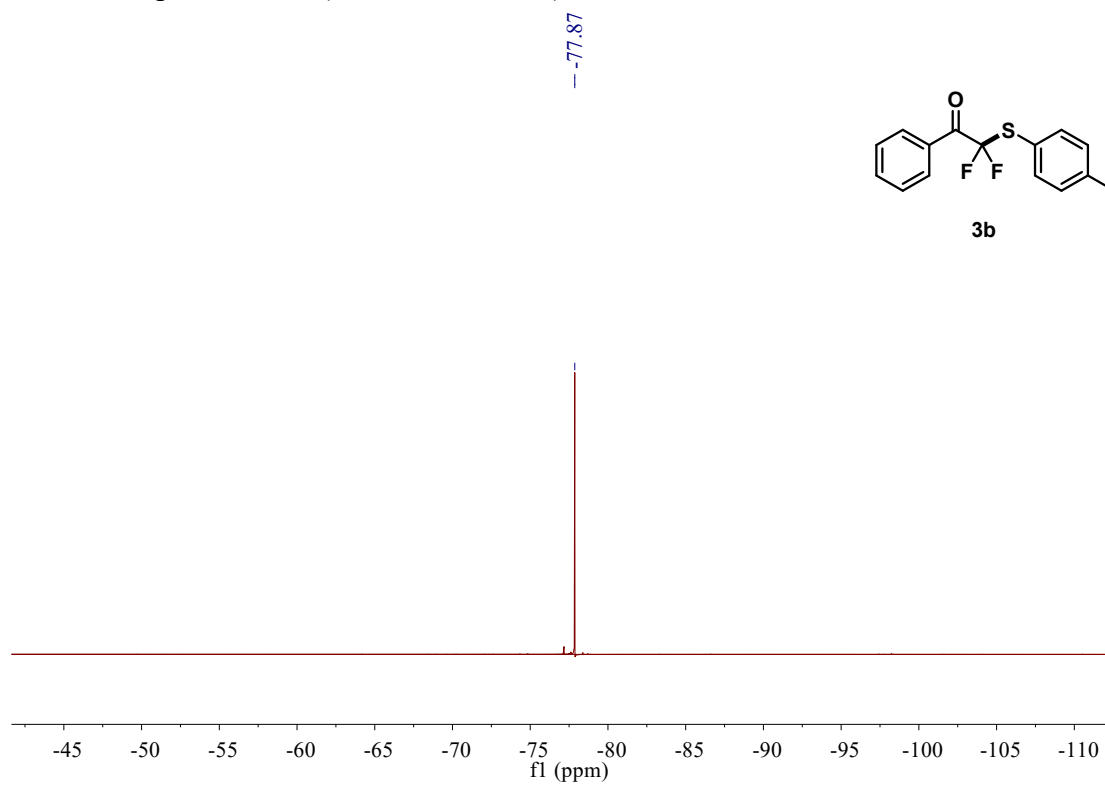
^1H NMR Spectra of **3b** (400 MHz, CDCl_3)



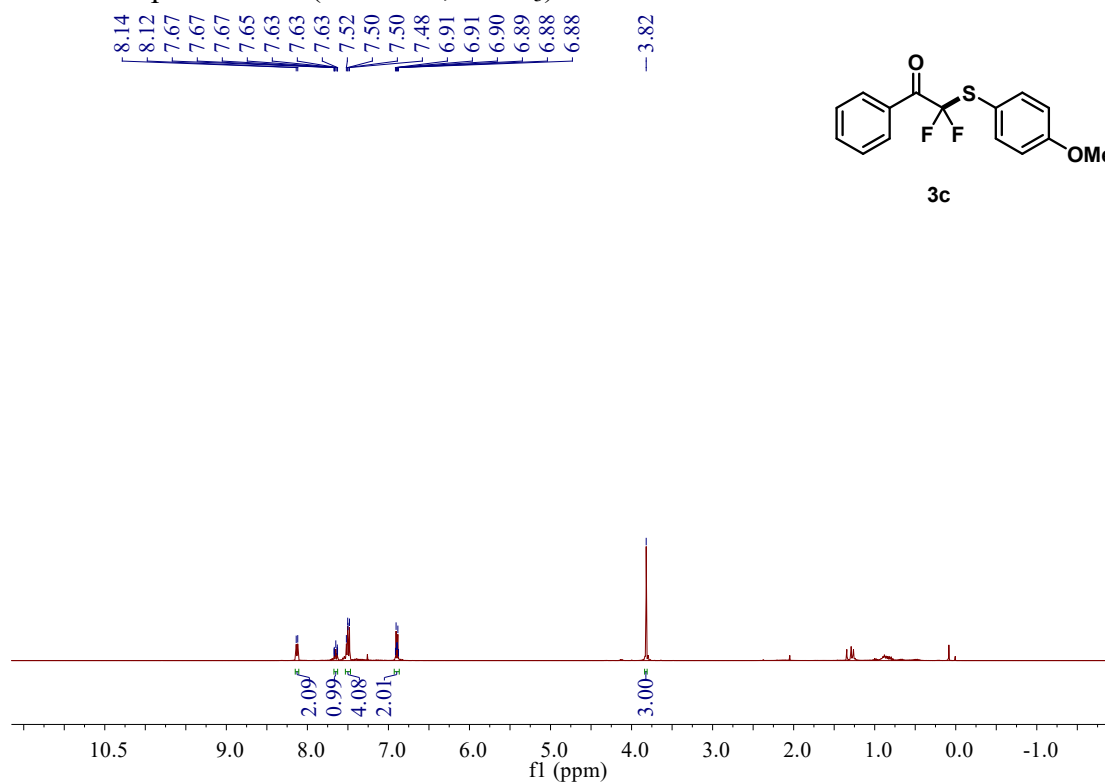
¹³C NMR Spectra of **3b** (100 MHz, CDCl₃)



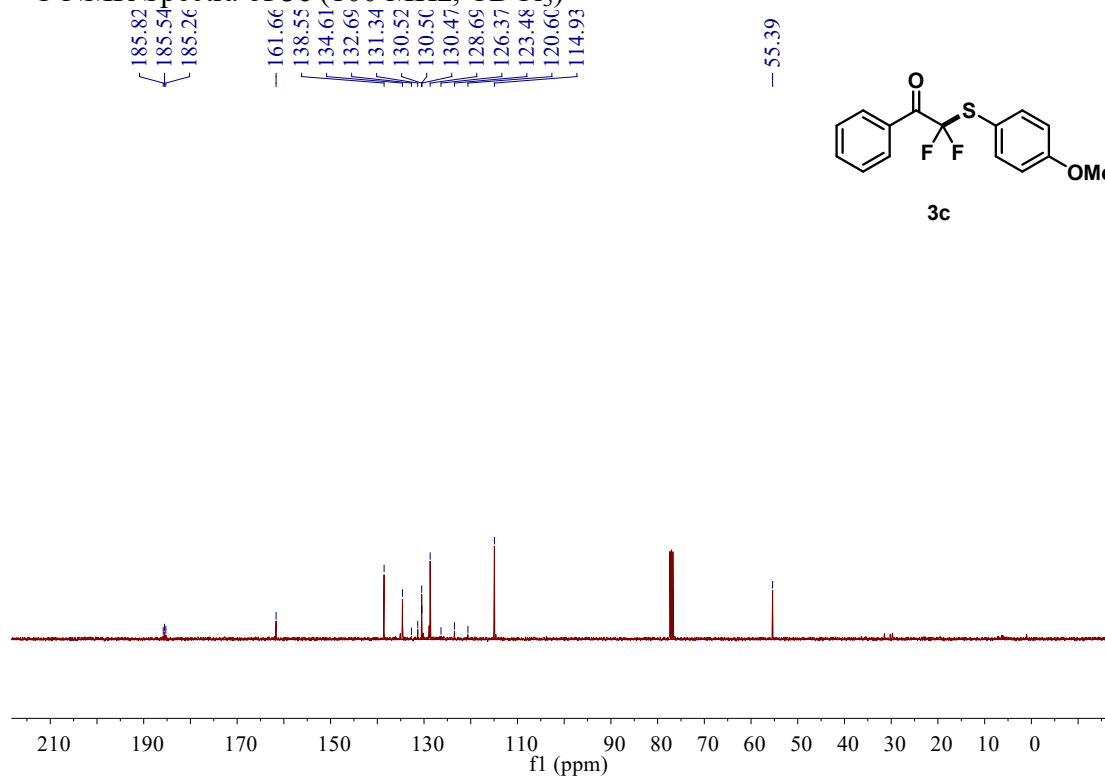
¹⁹F NMR Spectra of **3b** (377 MHz, CDCl₃)



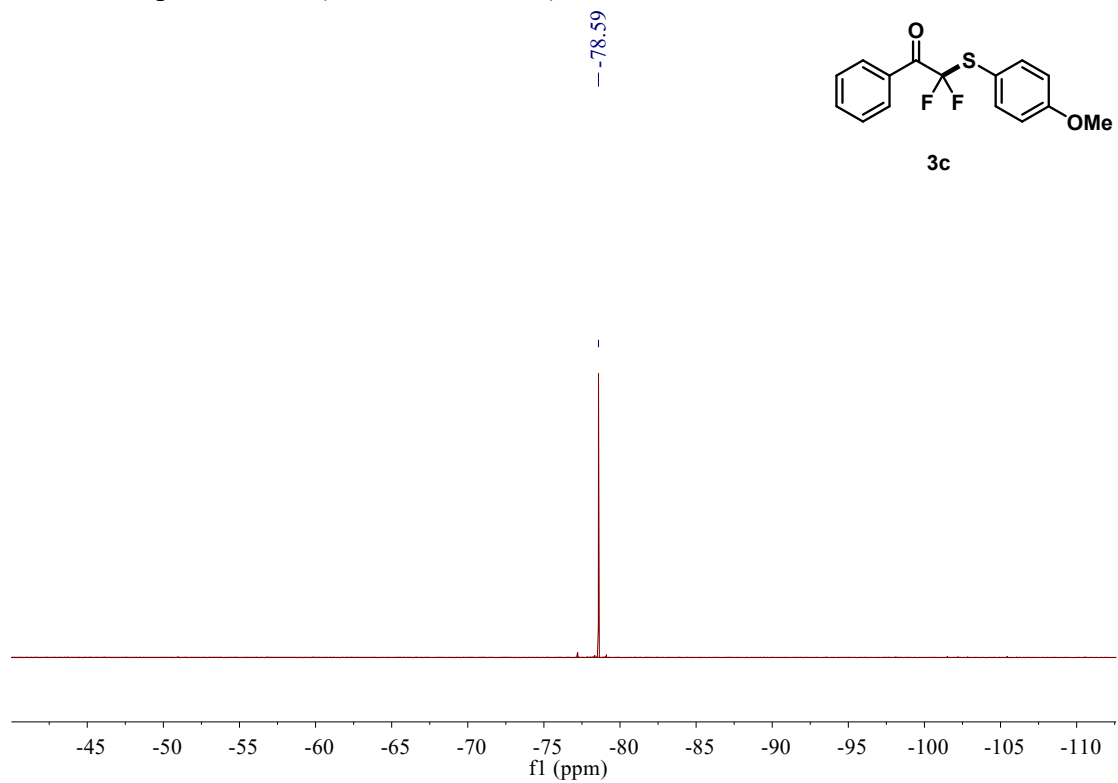
¹H NMR Spectra of **3c** (400 MHz, CDCl₃)



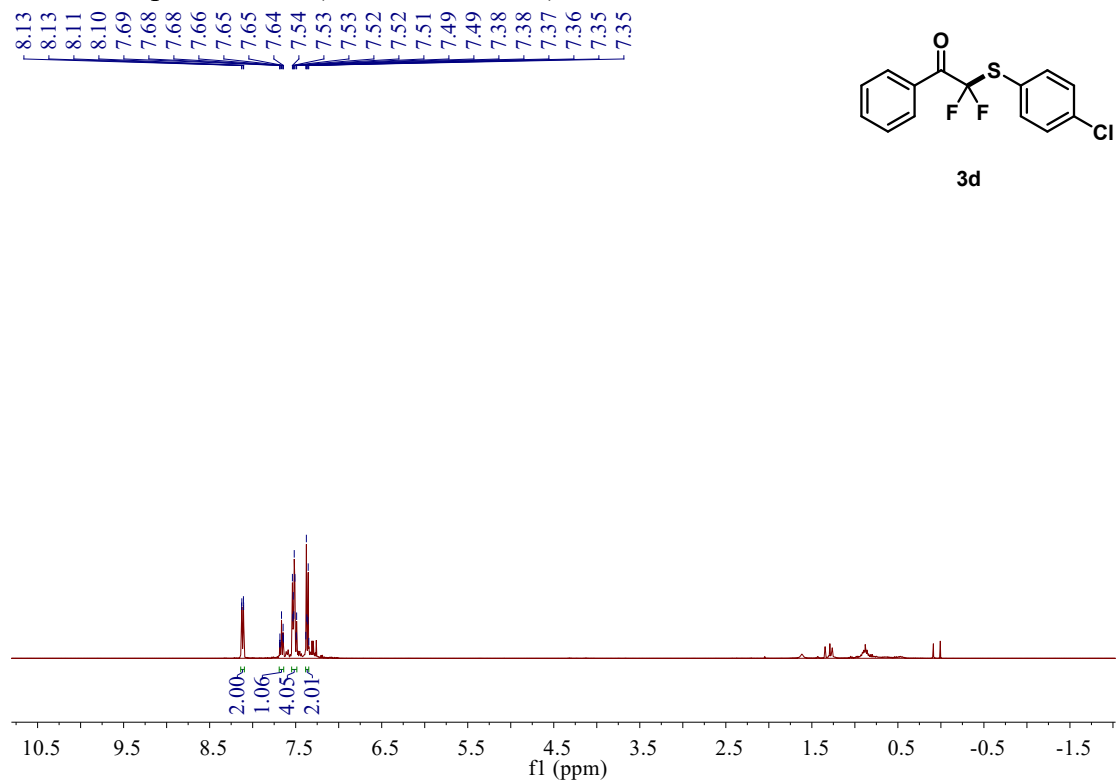
¹³C NMR Spectra of **3c** (100 MHz, CDCl₃)



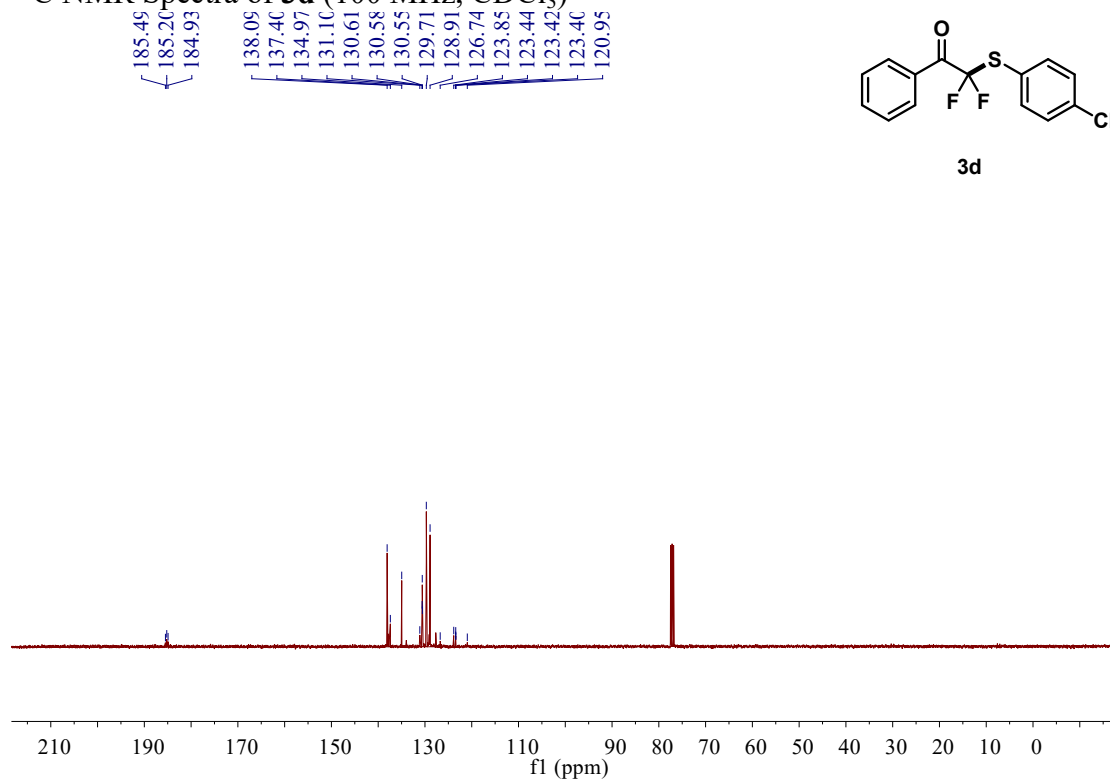
¹⁹F NMR Spectra of **3c** (377 MHz, CDCl₃)



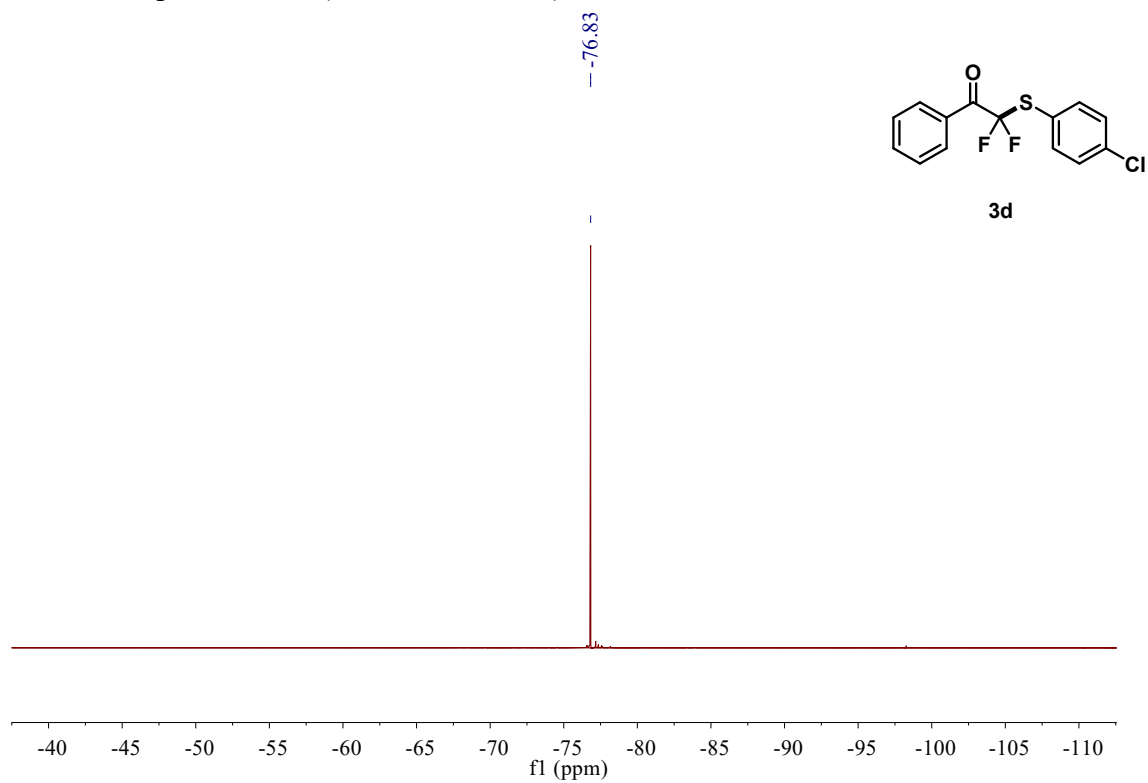
¹H NMR Spectra of **3d** (400 MHz, CDCl₃)



¹³C NMR Spectra of **3d** (100 MHz, CDCl₃)

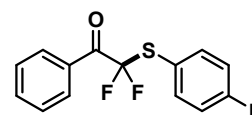


¹⁹F NMR Spectra of **3d** (377 MHz, CDCl₃)

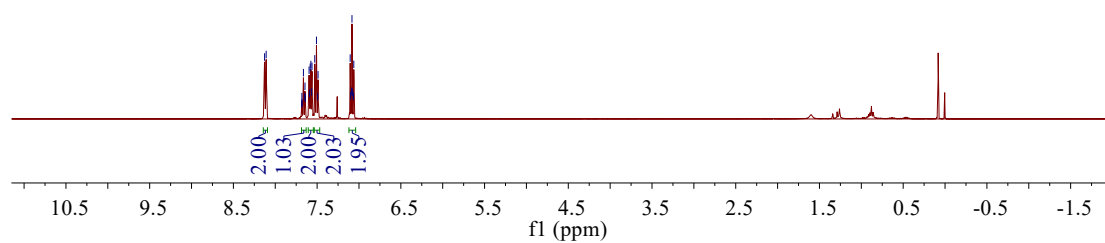


¹H NMR Spectra of **3e** (400 MHz, CDCl₃)

8.13
8.11
7.68
7.68
7.66
7.65
7.64
7.64
7.60
7.59
7.58
7.57
7.57
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7.11
7.10
7.09
7.08
7.08
7.07
7.06

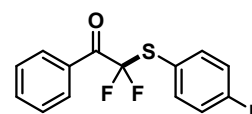


3e

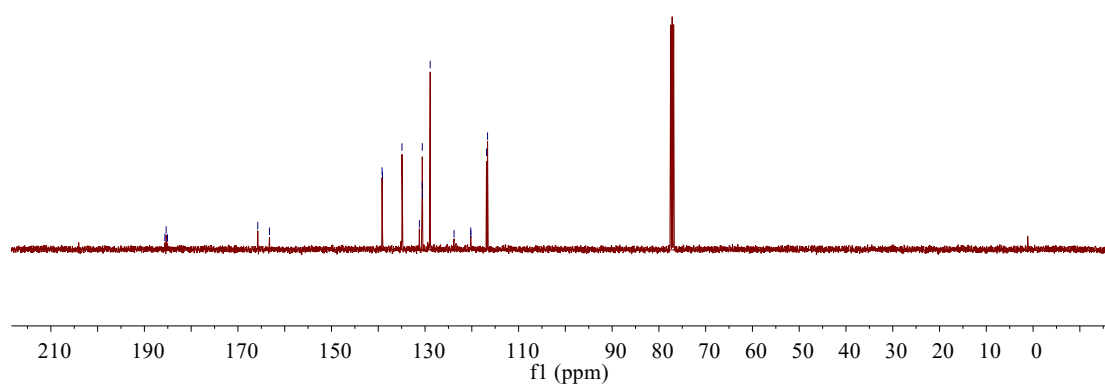


¹³C NMR Spectra of **3e** (100 MHz, CDCl₃)

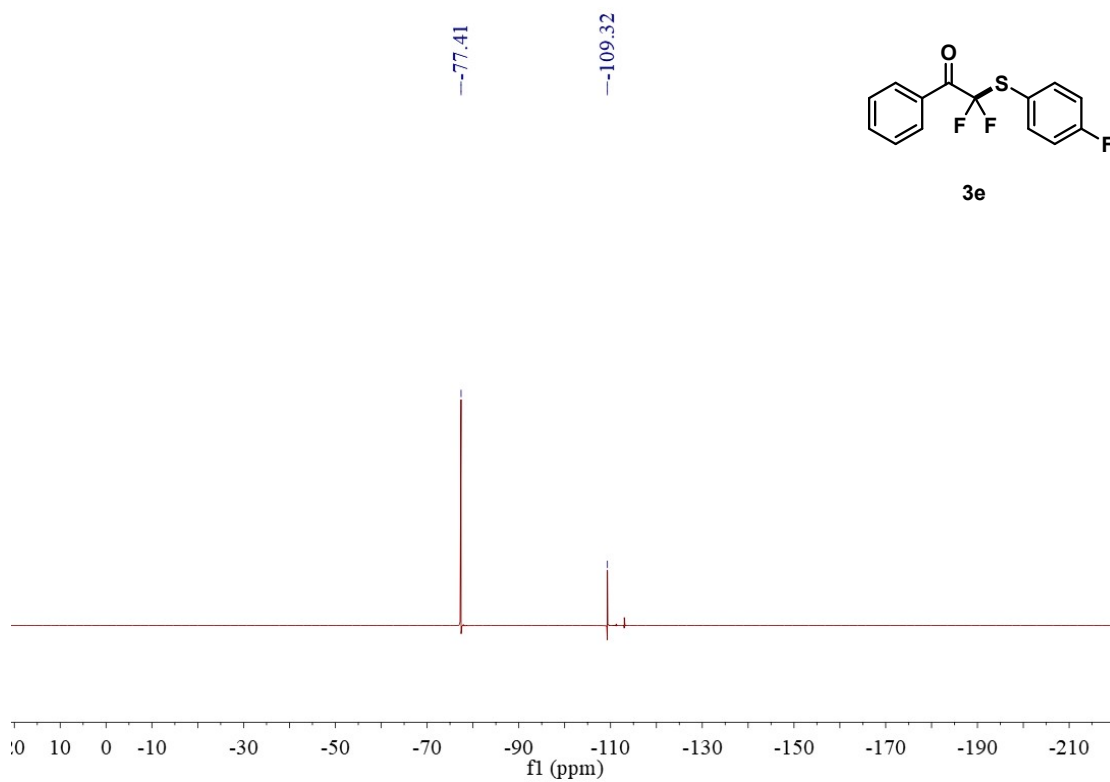
185.62
185.34
185.00
165.76
163.26
139.18
139.05
134.93
131.21
130.61
130.55
130.56
128.90
123.80
120.23
120.20
116.85
116.62



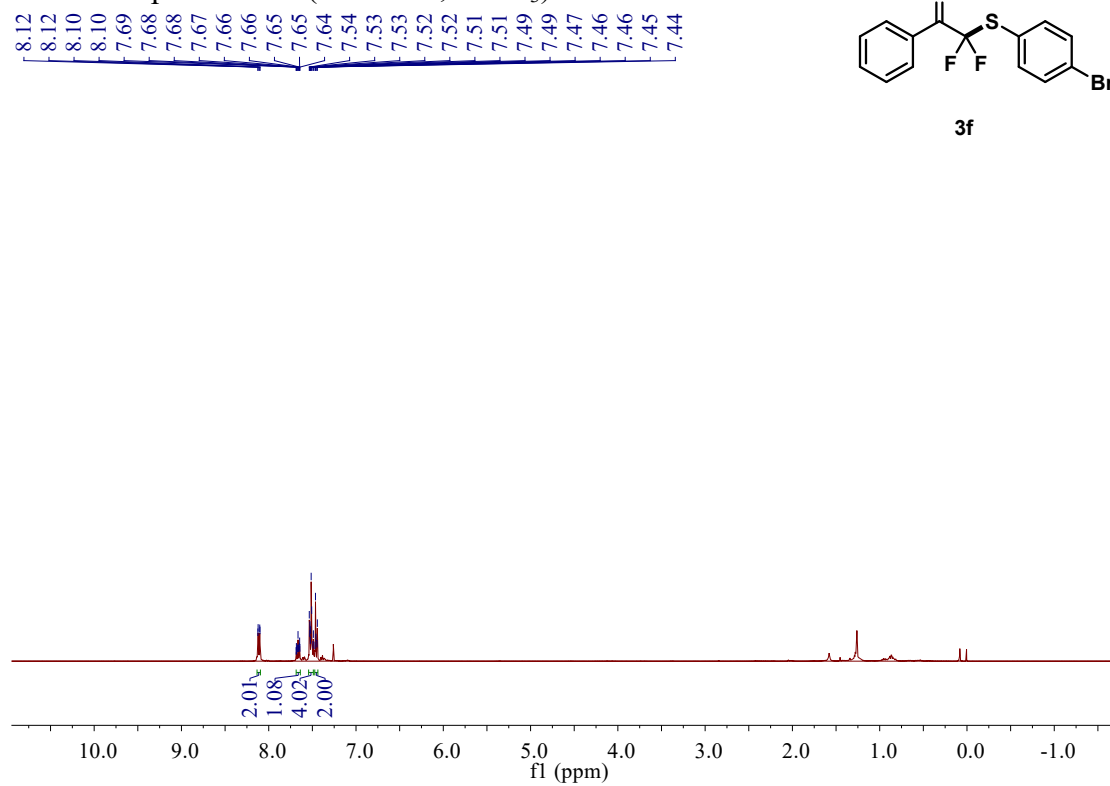
3e



¹⁹F NMR Spectra of **3e** (377 MHz, CDCl₃)

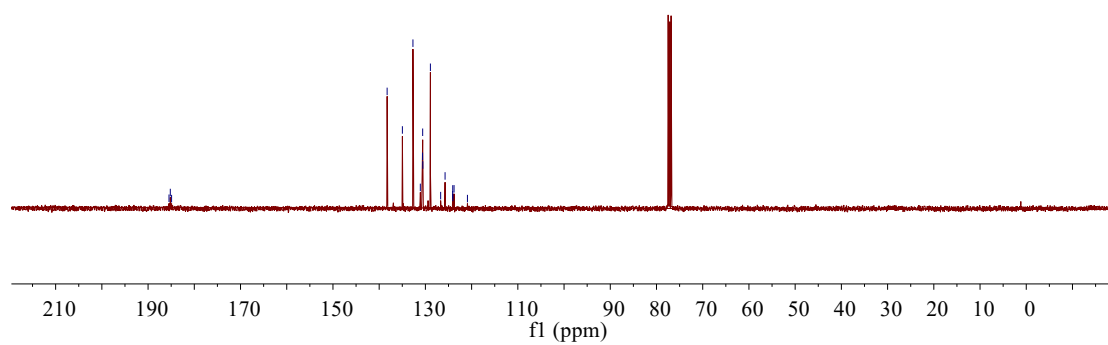
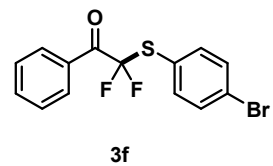


¹H NMR Spectra of **3f** (400 MHz, CDCl₃)



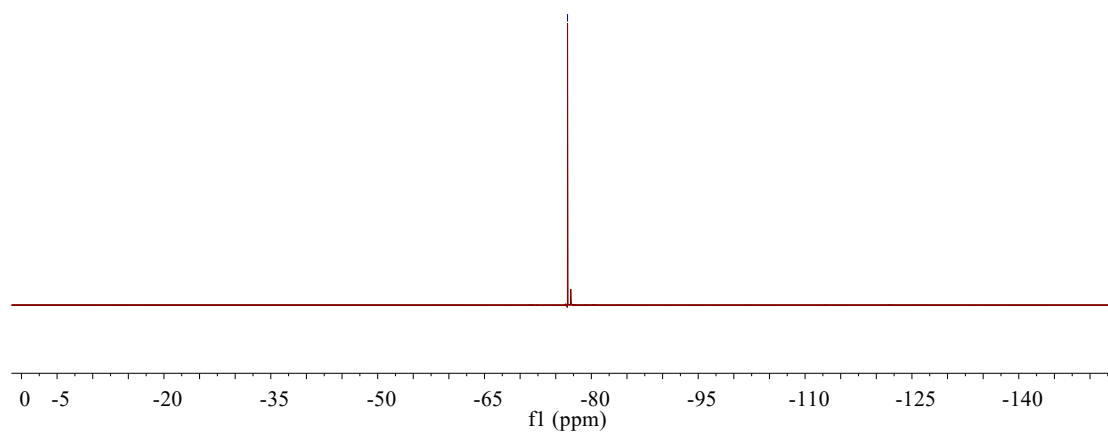
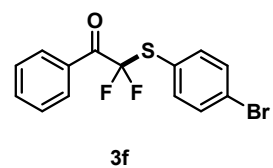
¹³C NMR Spectra of **3f** (100 MHz, CDCl₃)

185.47
185.19
184.91
138.28
134.98
132.70
131.10
130.62
130.59
130.56
128.92
126.70
125.74
124.11
124.08
124.06
123.80
120.90



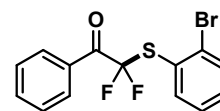
¹⁹F NMR Spectra of **3f** (377 MHz, CDCl₃)

-76.66

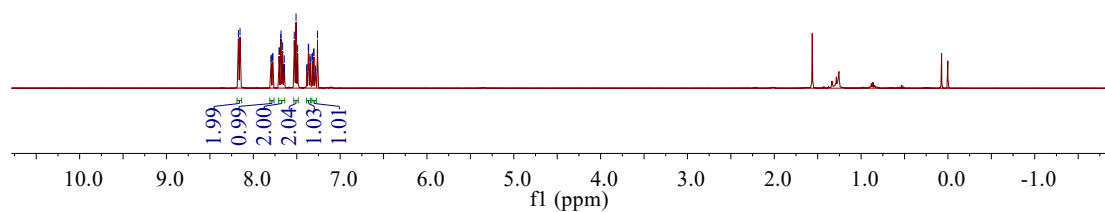


¹H NMR Spectra of **3g** (400 MHz, CDCl₃)

8.17
8.15
7.80
7.79
7.78
7.77
7.70
7.70
7.68
7.68
7.66
7.66
7.65
7.64
7.64
7.53
7.51
7.49
7.49
7.49
7.39
7.38
7.37
7.36
7.35
7.34
7.32
7.32
7.31
7.30
7.29
7.28
7.26

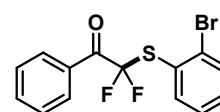


3g

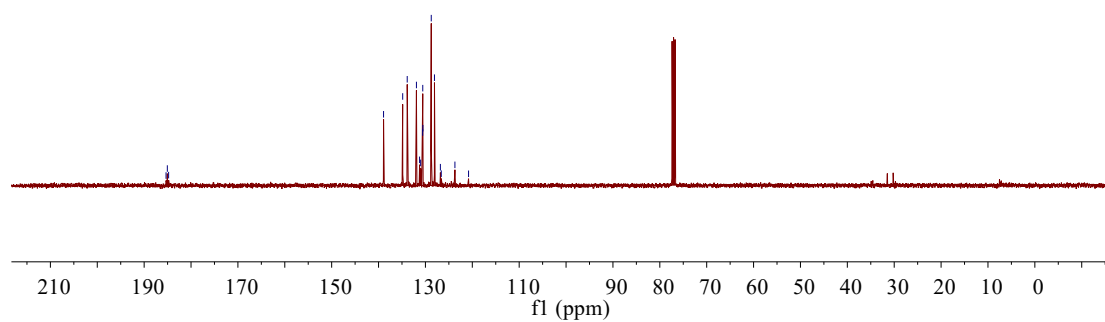


¹³C NMR Spectra of **3g** (100 MHz, CDCl₃)

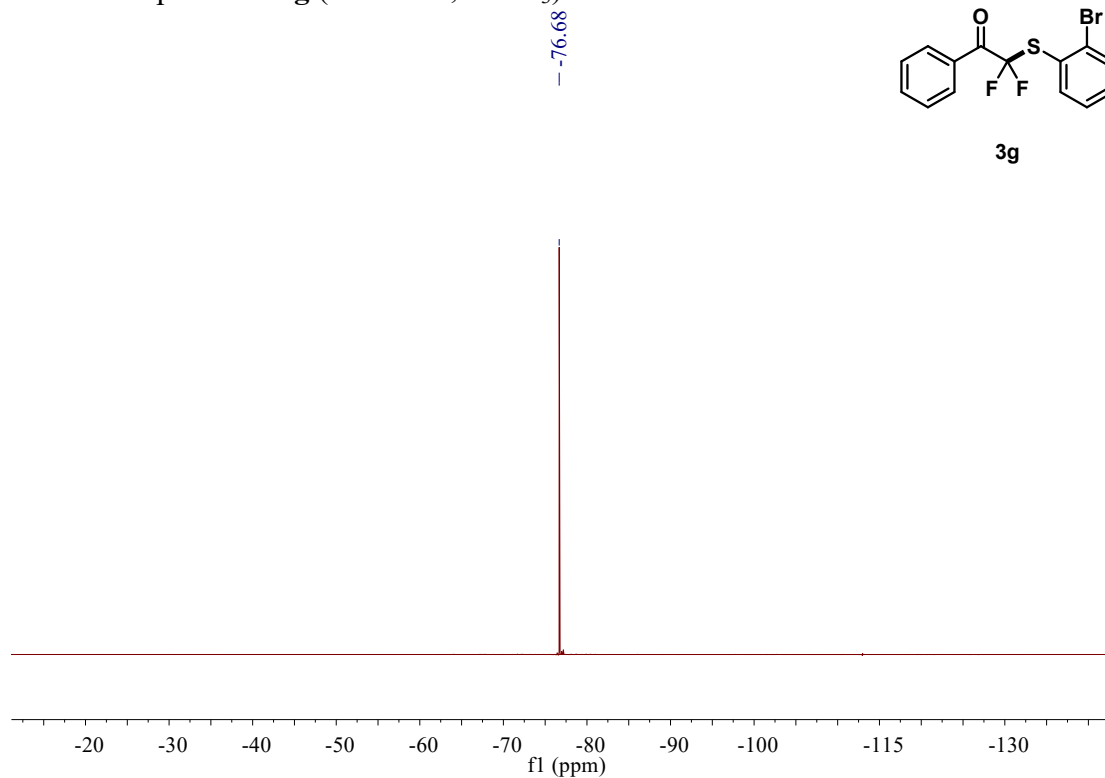
185.33
185.06
184.78
138.93
134.85
133.88
131.92
131.25
131.02
130.59
130.57
130.54
128.76
128.07
126.81
126.62
123.71
120.80



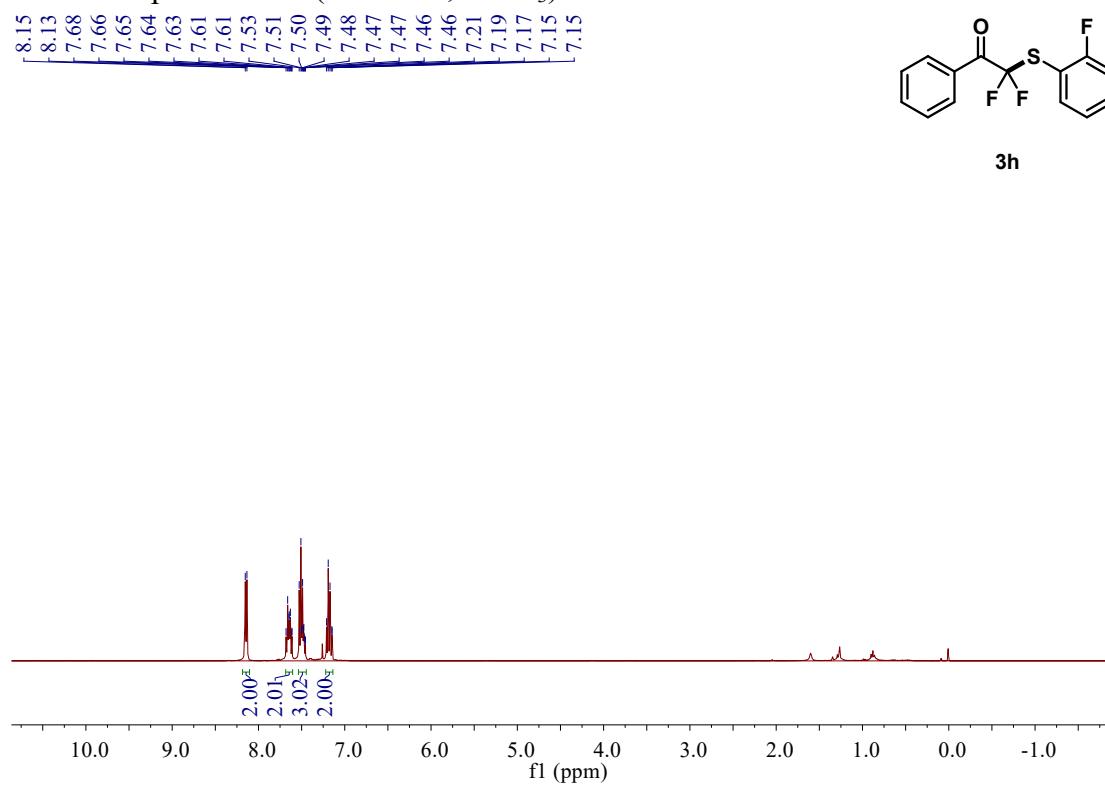
3g



^{19}F NMR Spectra of **3g** (377 MHz, CDCl_3)

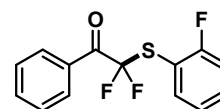


^1H NMR Spectra of **3h** (400 MHz, CDCl_3)

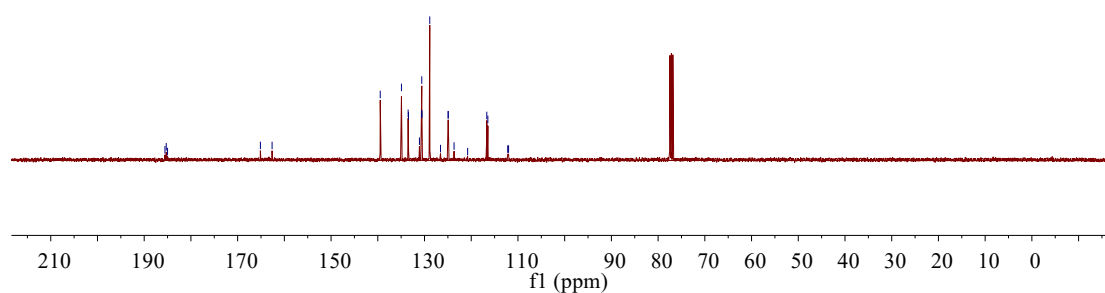


¹³C NMR Spectra of **3h** (100 MHz, CDCl₃)

185.56
185.28
185.00
165.12
162.63
139.48
134.94
133.50
133.42
131.08
130.61
130.59
130.56
128.88
126.58
124.95
124.91
123.67
120.77
116.67
116.44
112.15
112.01

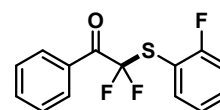


3h

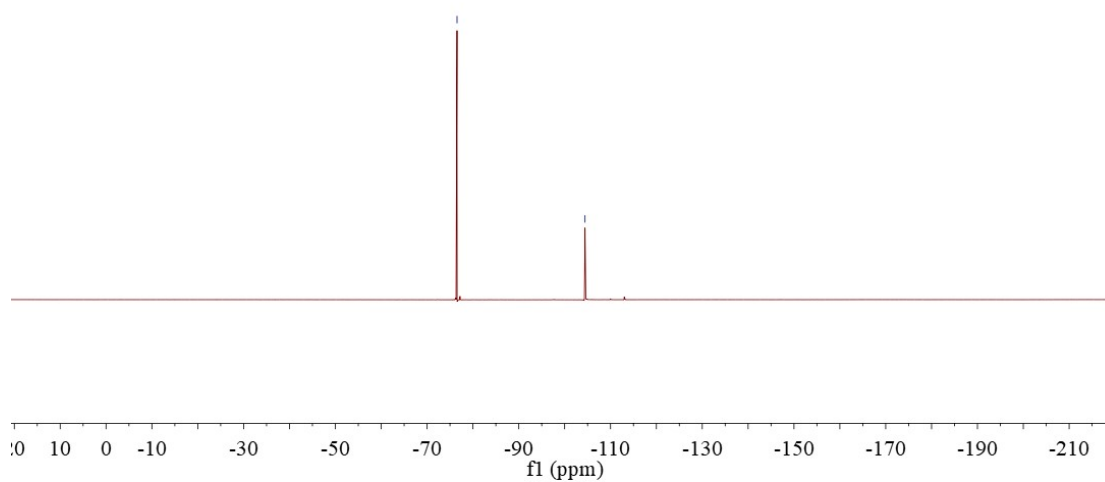


¹⁹F NMR Spectra of **3h** (377 MHz, CDCl₃)

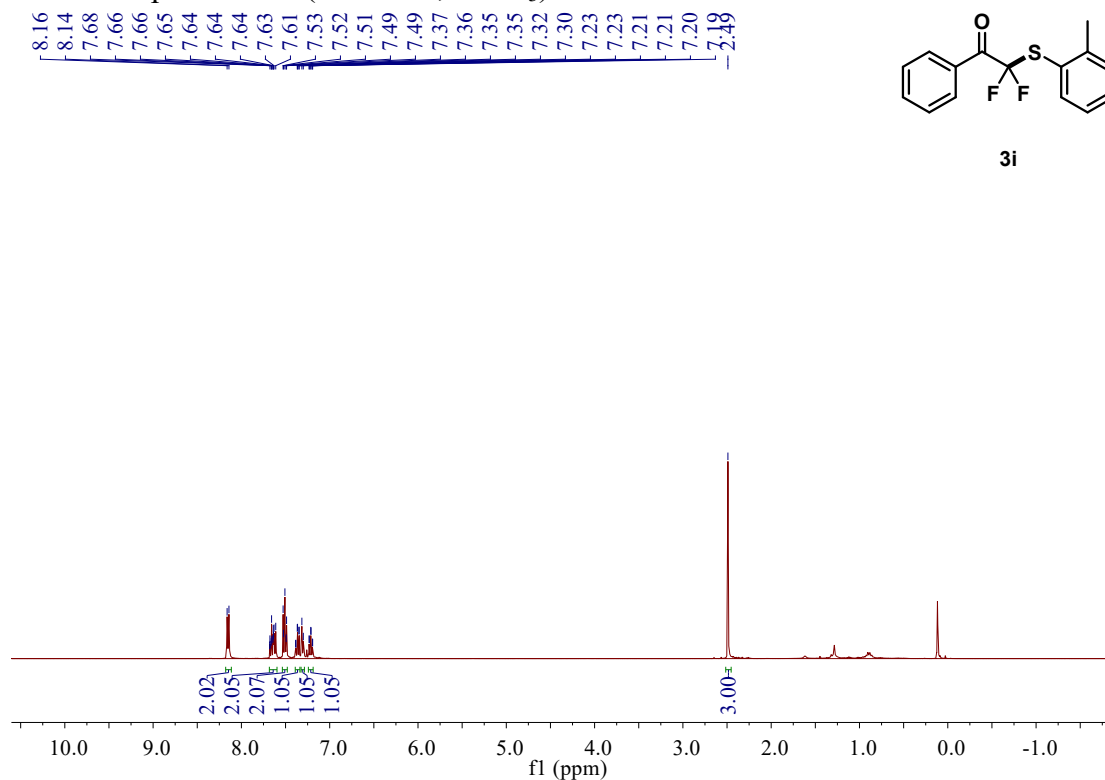
-76.53
-104.44



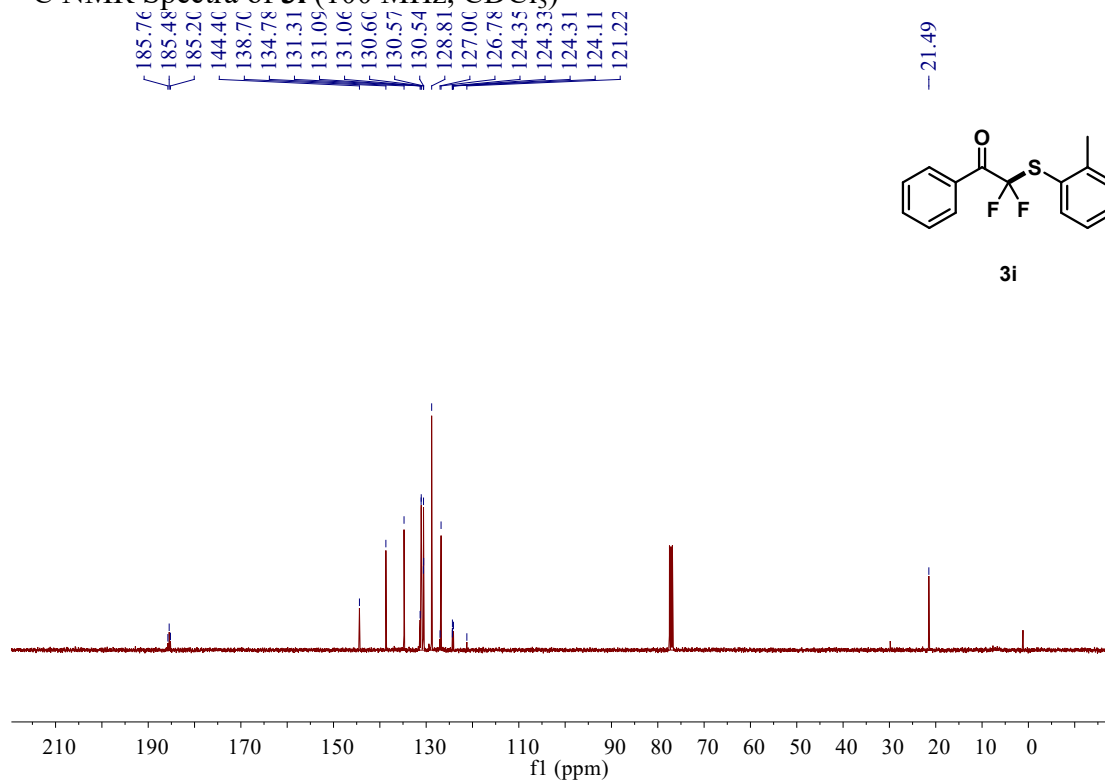
3h



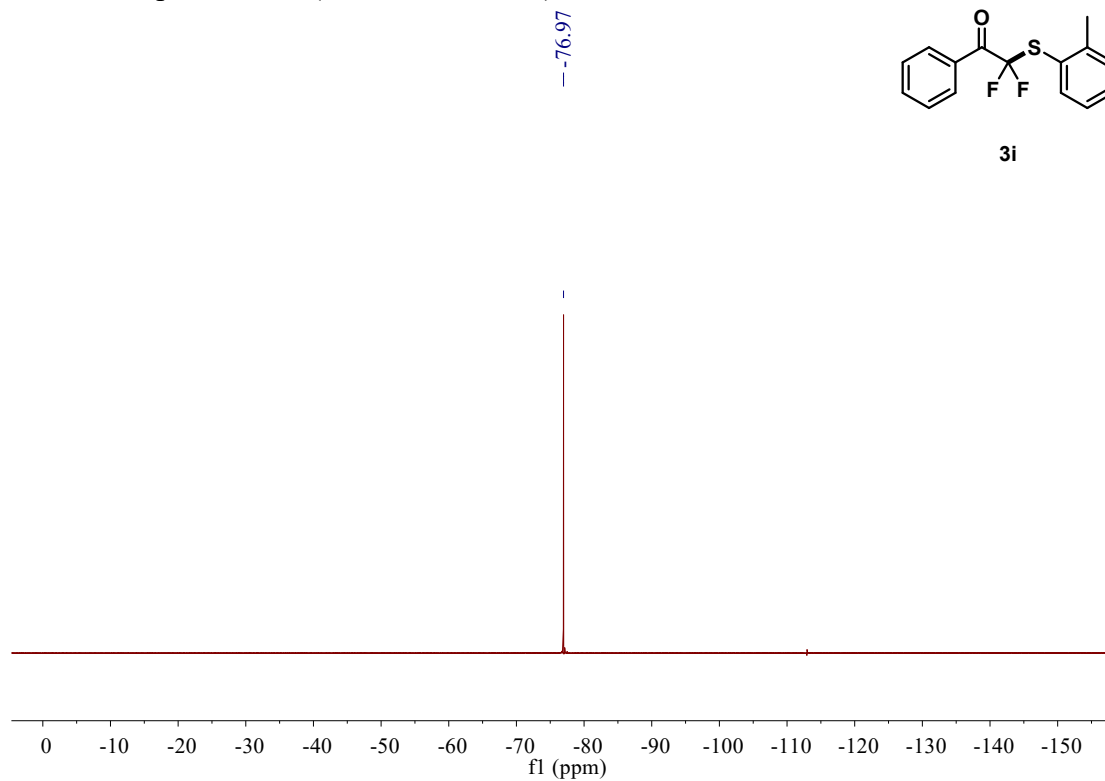
¹H NMR Spectra of **3i** (400 MHz, CDCl₃)



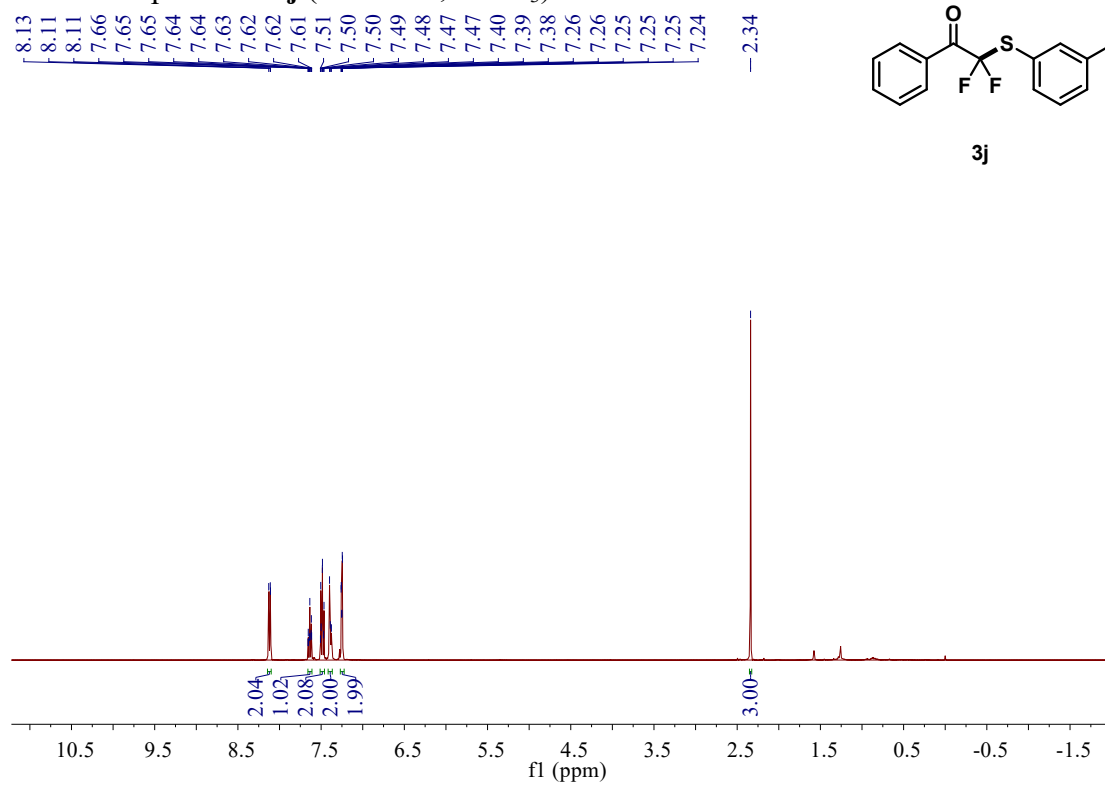
¹³C NMR Spectra of **3i** (100 MHz, CDCl₃)



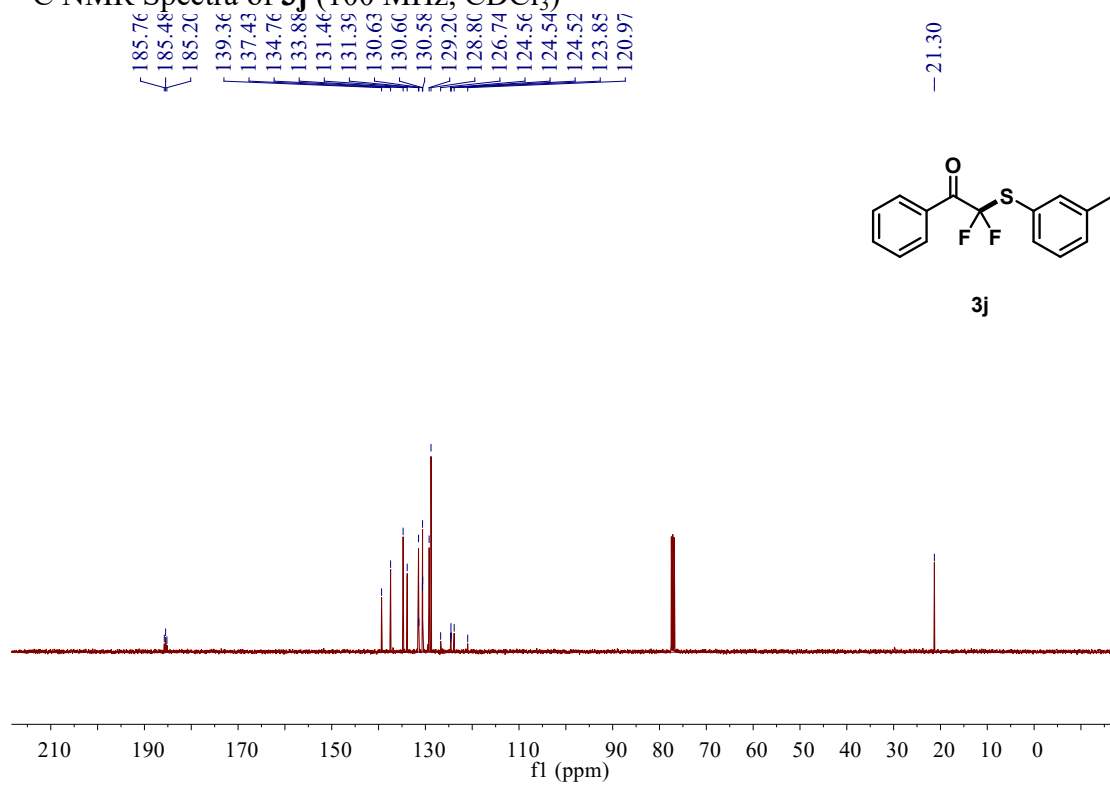
¹⁹F NMR Spectra of **3i** (377 MHz, CDCl₃)



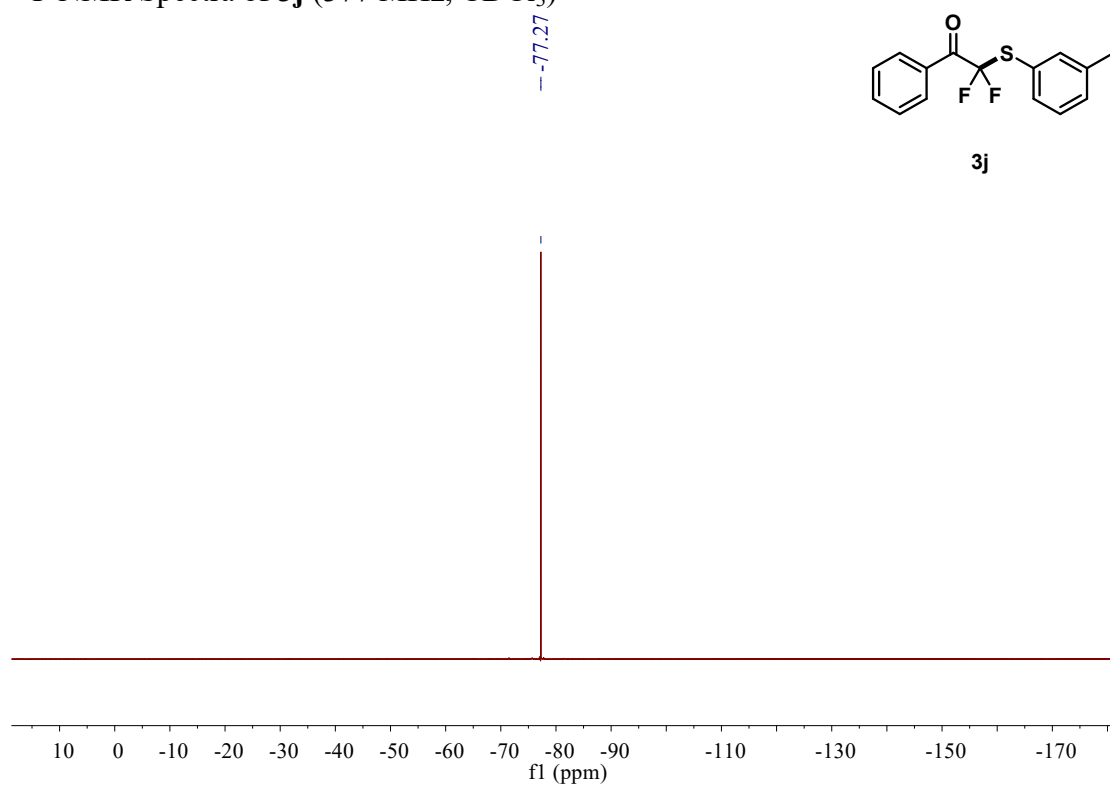
¹H NMR Spectra of **3j** (400 MHz, CDCl₃)



¹³C NMR Spectra of **3j** (100 MHz, CDCl₃)

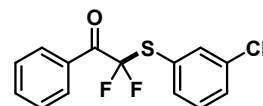


¹⁹F NMR Spectra of **3j** (377 MHz, CDCl₃)

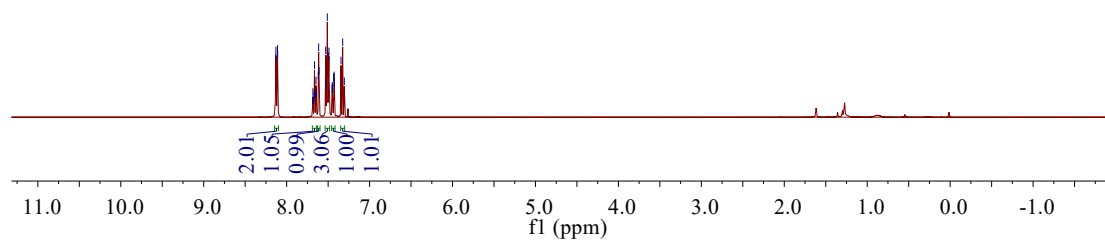


¹H NMR Spectra of **3k** (400 MHz, CDCl₃)

8.13
8.13
8.11
8.11
7.69
7.68
7.68
7.67
7.66
7.65
7.65
7.64
7.62
7.61
7.61
7.53
7.52
7.51
7.49
7.49
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.34
7.32
7.30

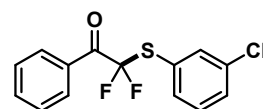


3k

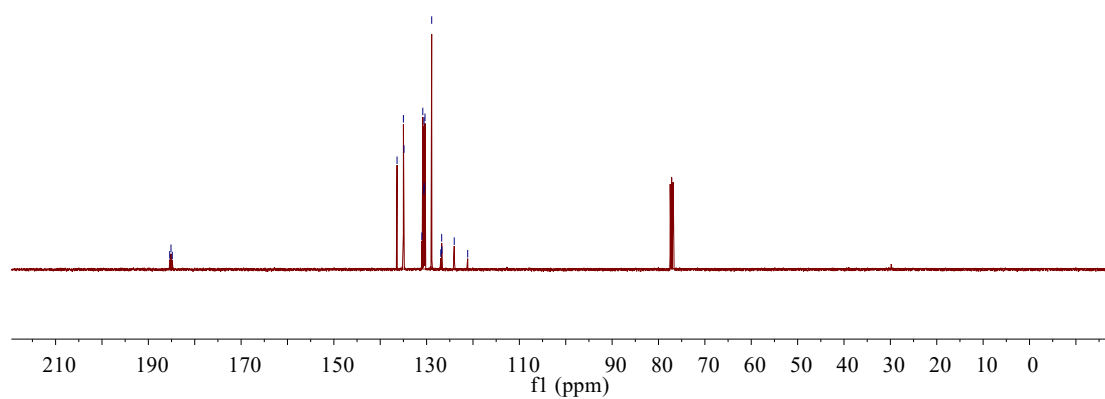


¹³C NMR Spectra of **3k** (100 MHz, CDCl₃)

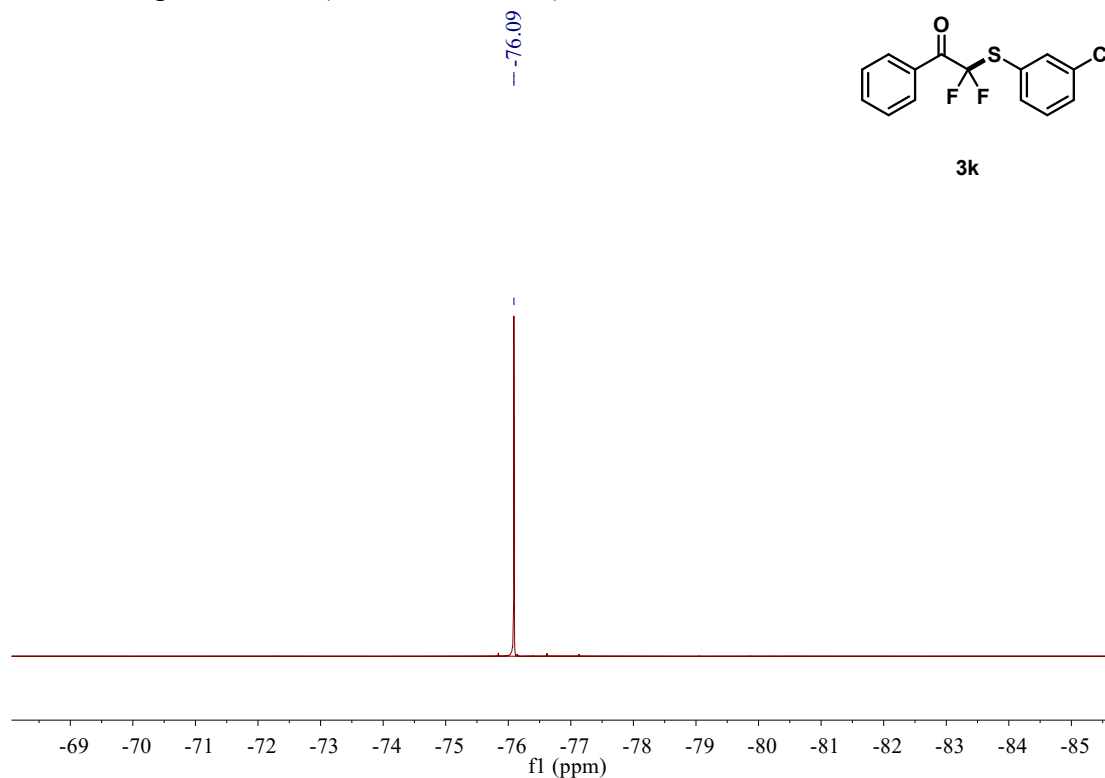
185.40
185.12
184.84
136.37
135.00
134.88
131.02
130.82
130.58
130.55
130.53
130.35
128.90
126.95
126.77
126.75
126.73
124.04
121.14



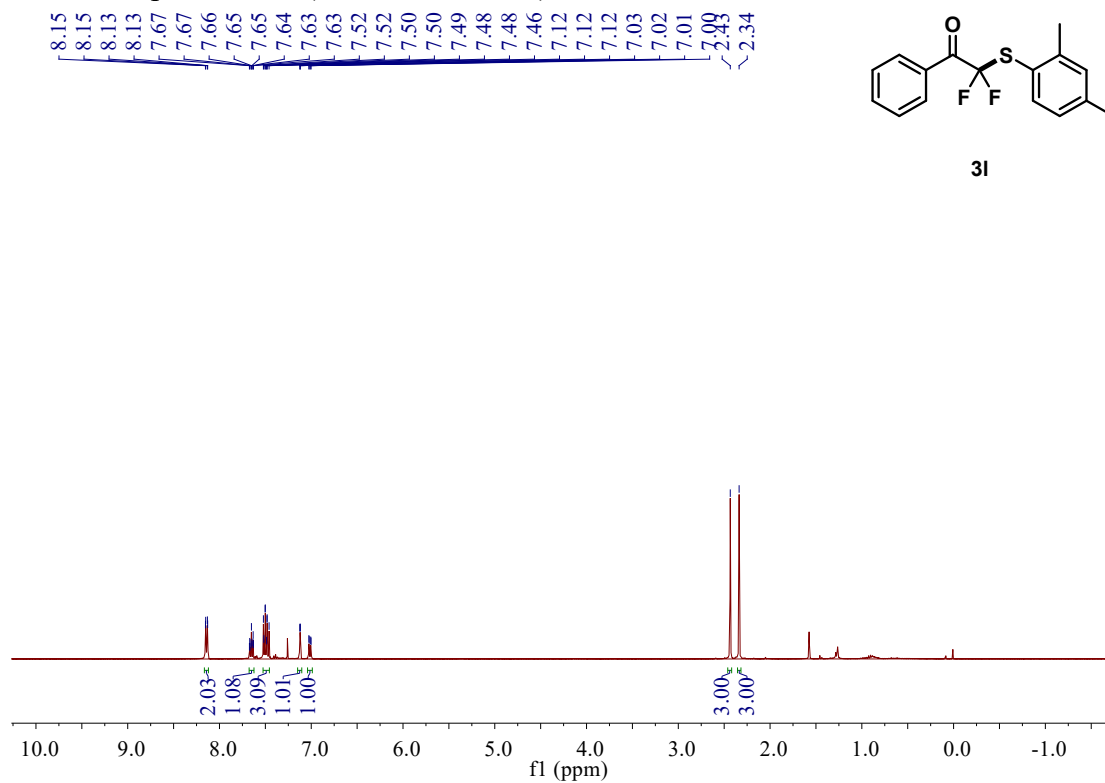
3k



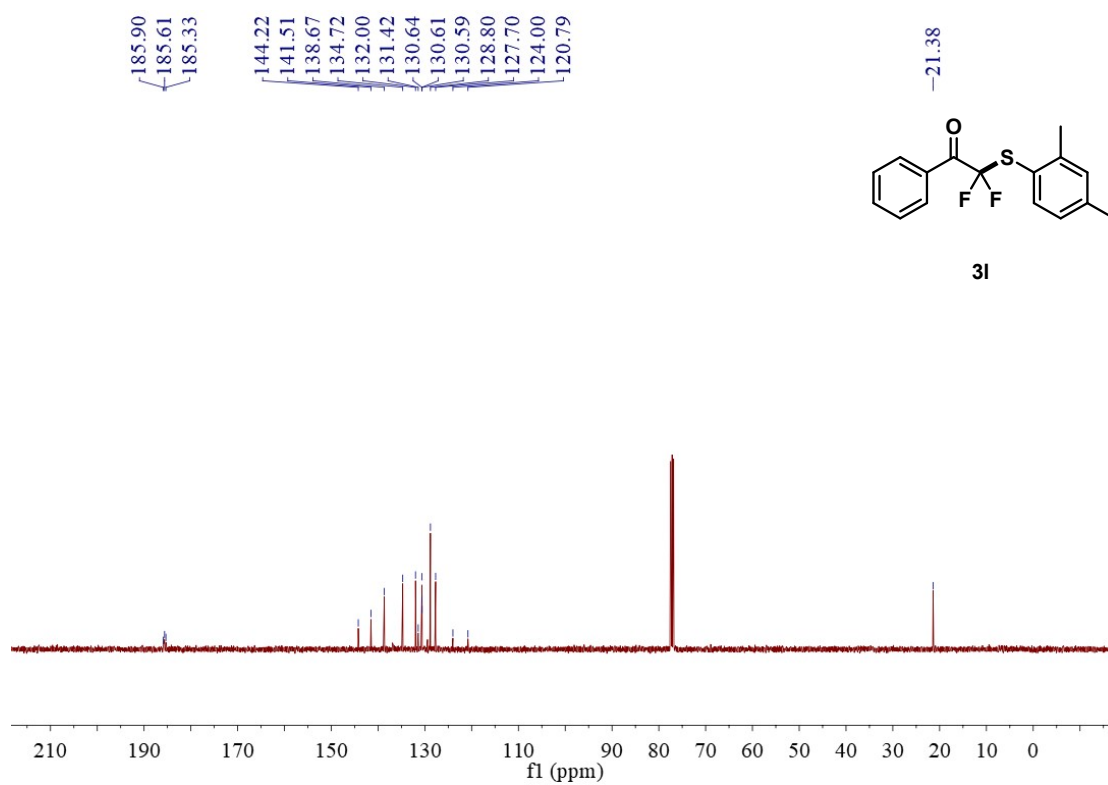
¹⁹F NMR Spectra of **3k** (377 MHz, CDCl₃)



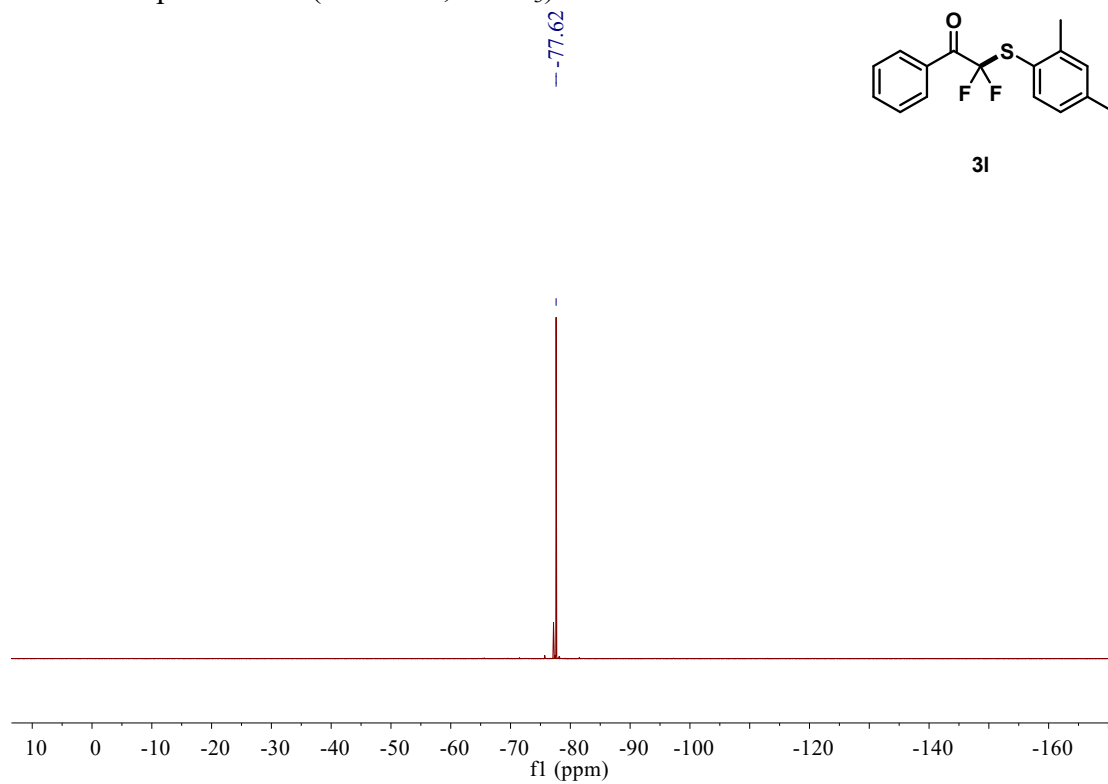
¹H NMR Spectra of **3l** (400 MHz, CDCl₃)



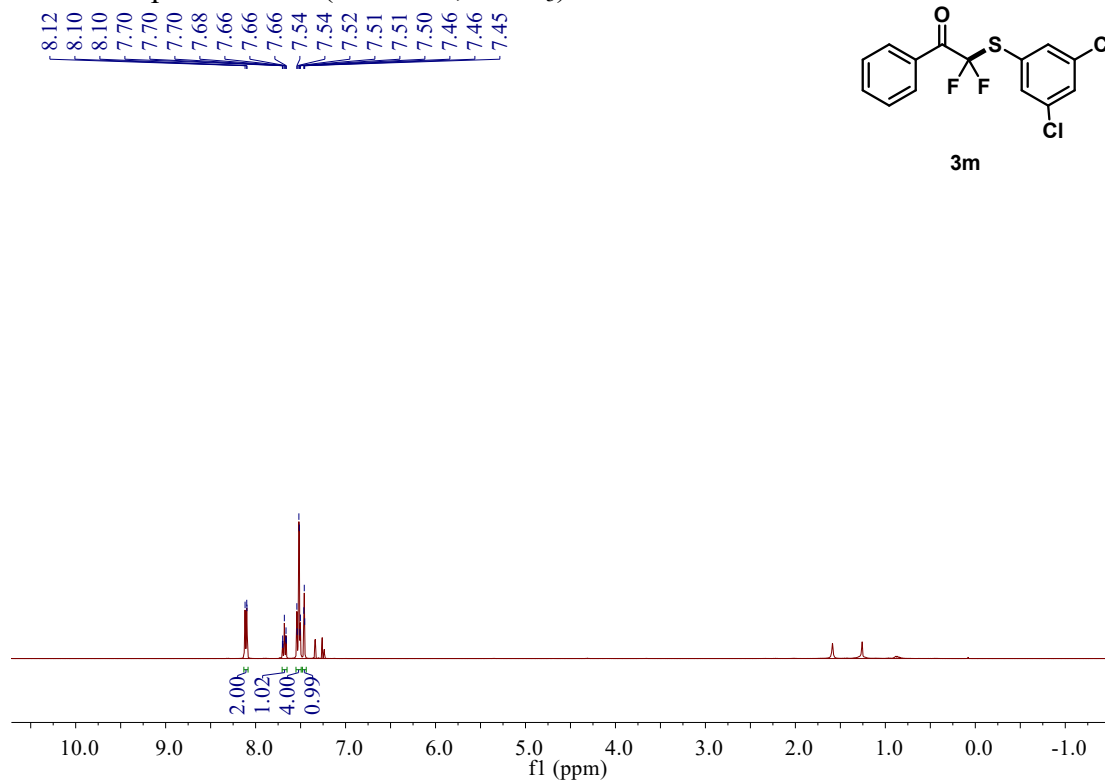
¹³C NMR Spectra of **3I** (100 MHz, CDCl₃)



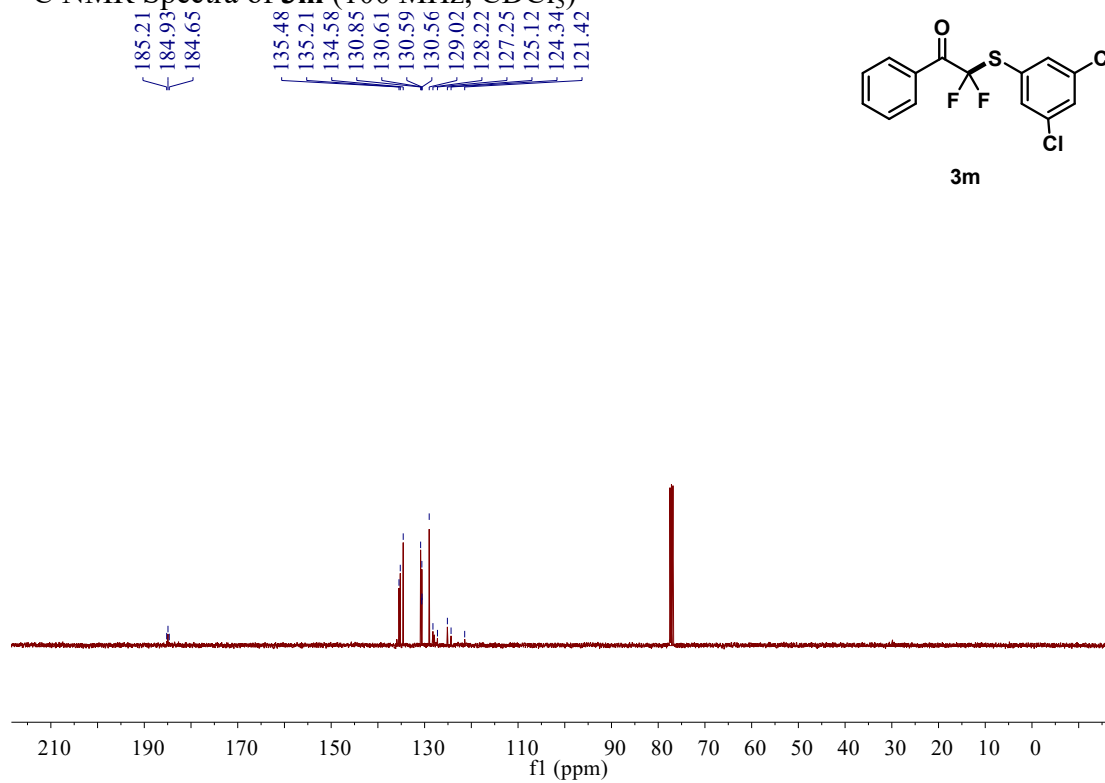
¹⁹F NMR Spectra of **3I** (377 MHz, CDCl₃)



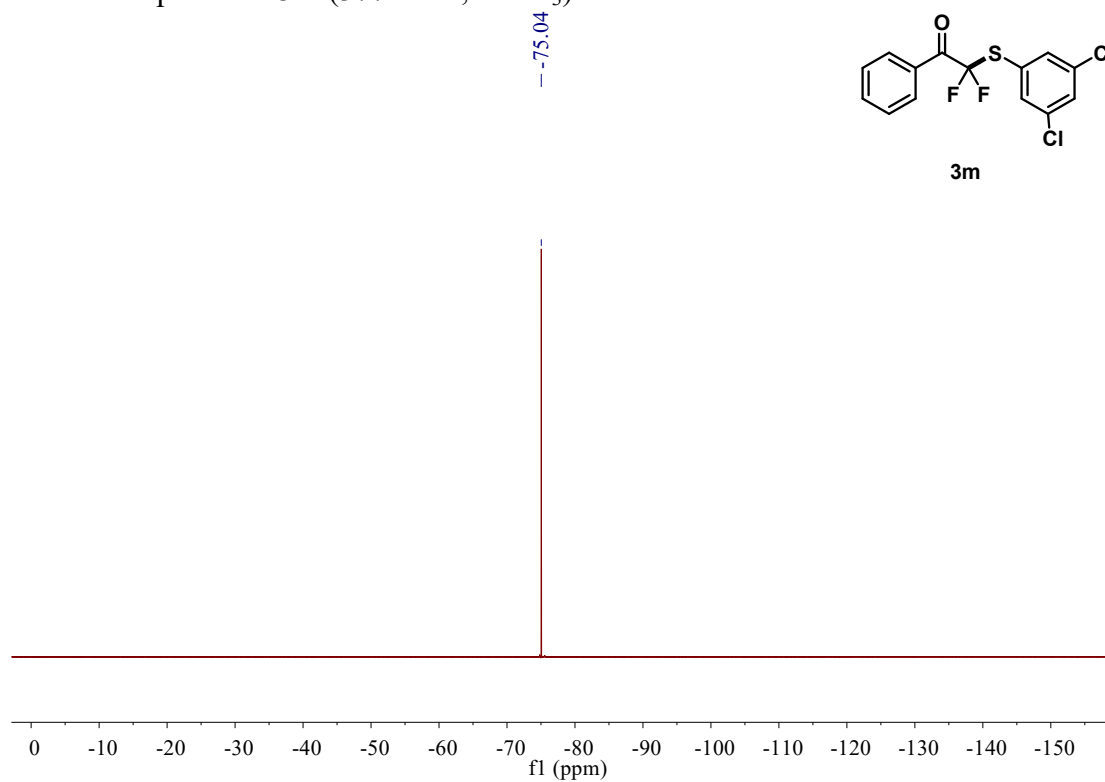
¹H NMR Spectra of **3m** (400 MHz, CDCl₃)



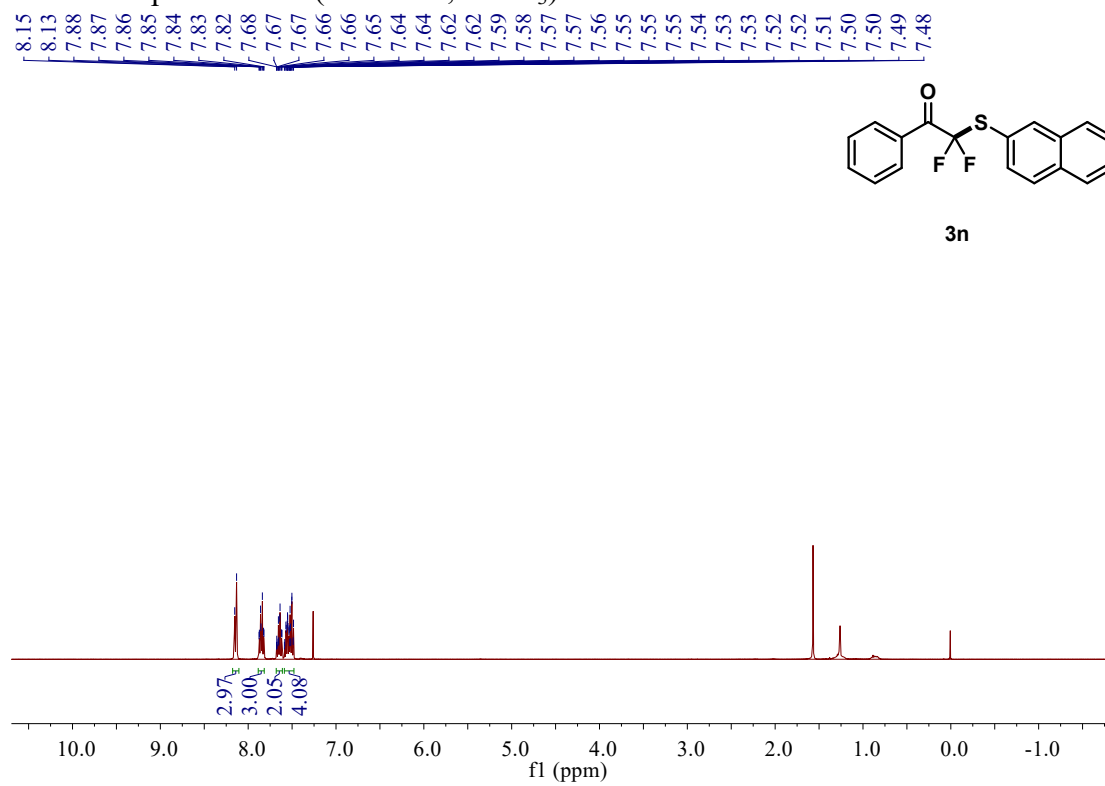
¹³C NMR Spectra of **3m** (100 MHz, CDCl₃)



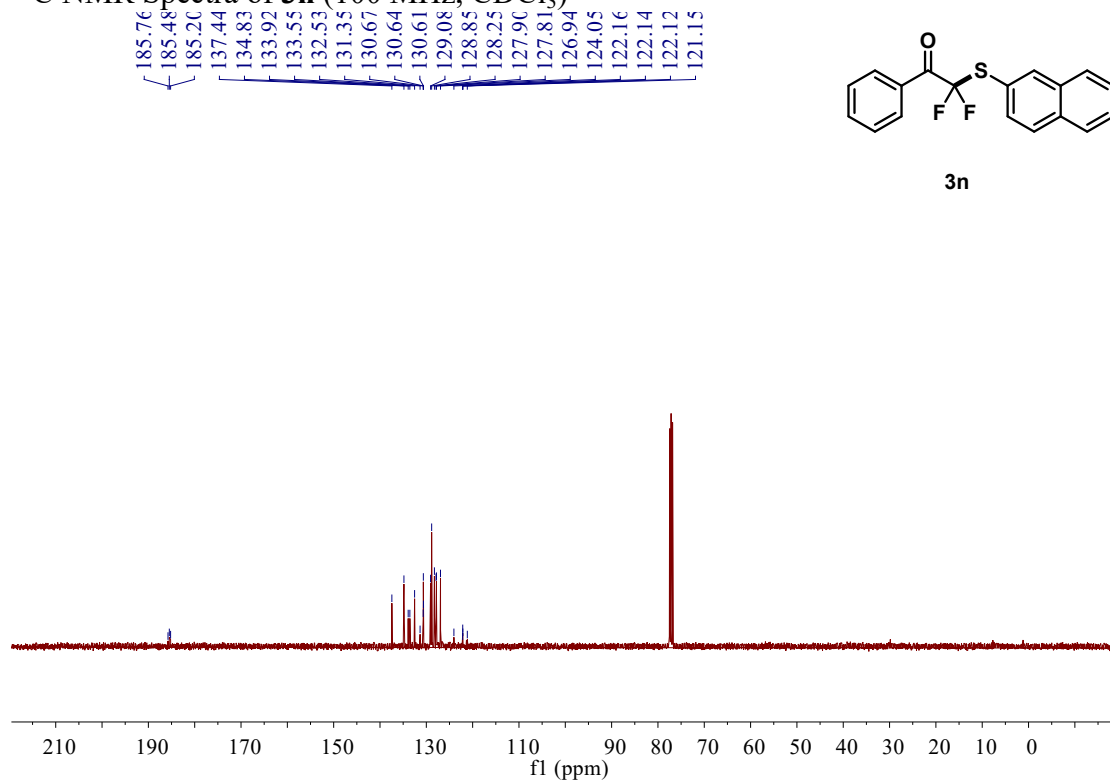
¹⁹F NMR Spectra of **3m** (377 MHz, CDCl₃)



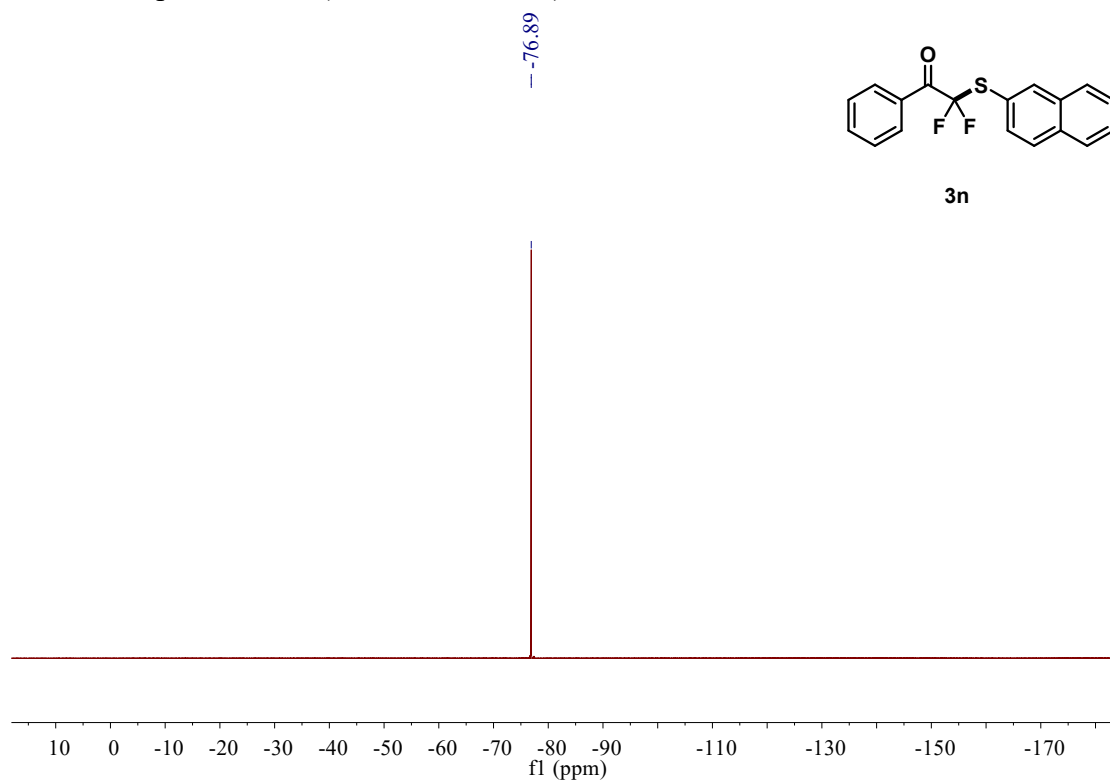
¹H NMR Spectra of **3n** (400 MHz, CDCl₃)



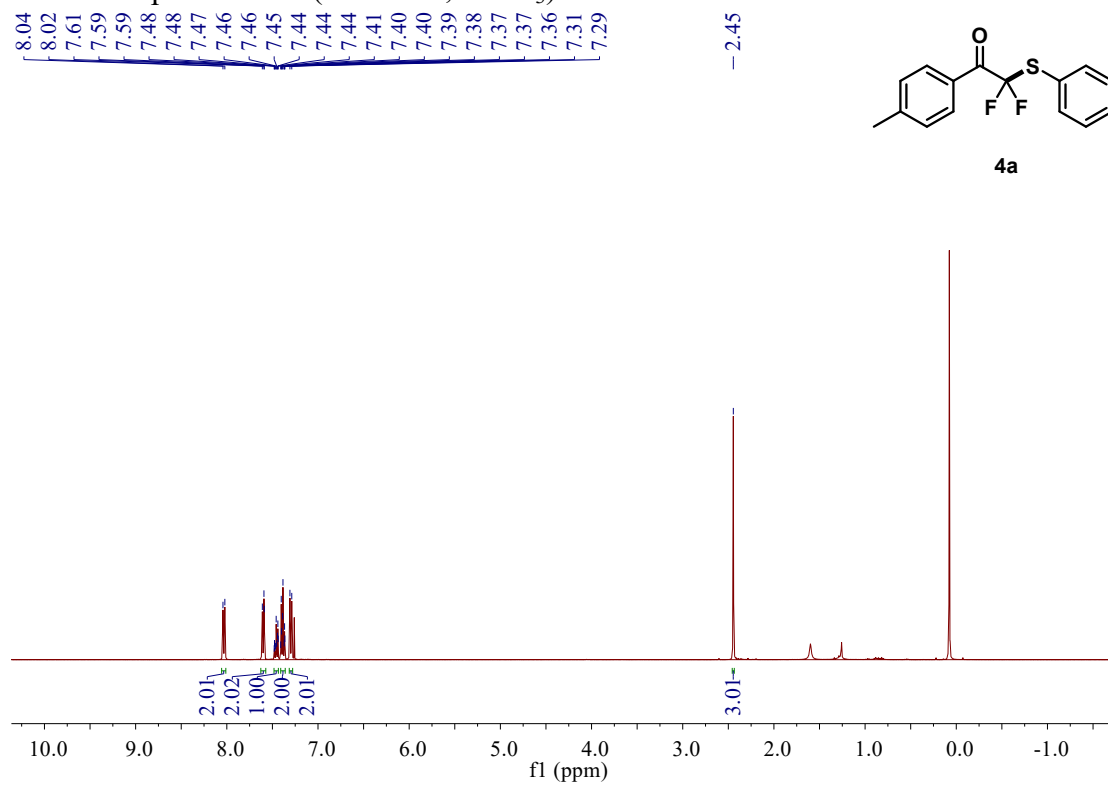
¹³C NMR Spectra of **3n** (100 MHz, CDCl₃)



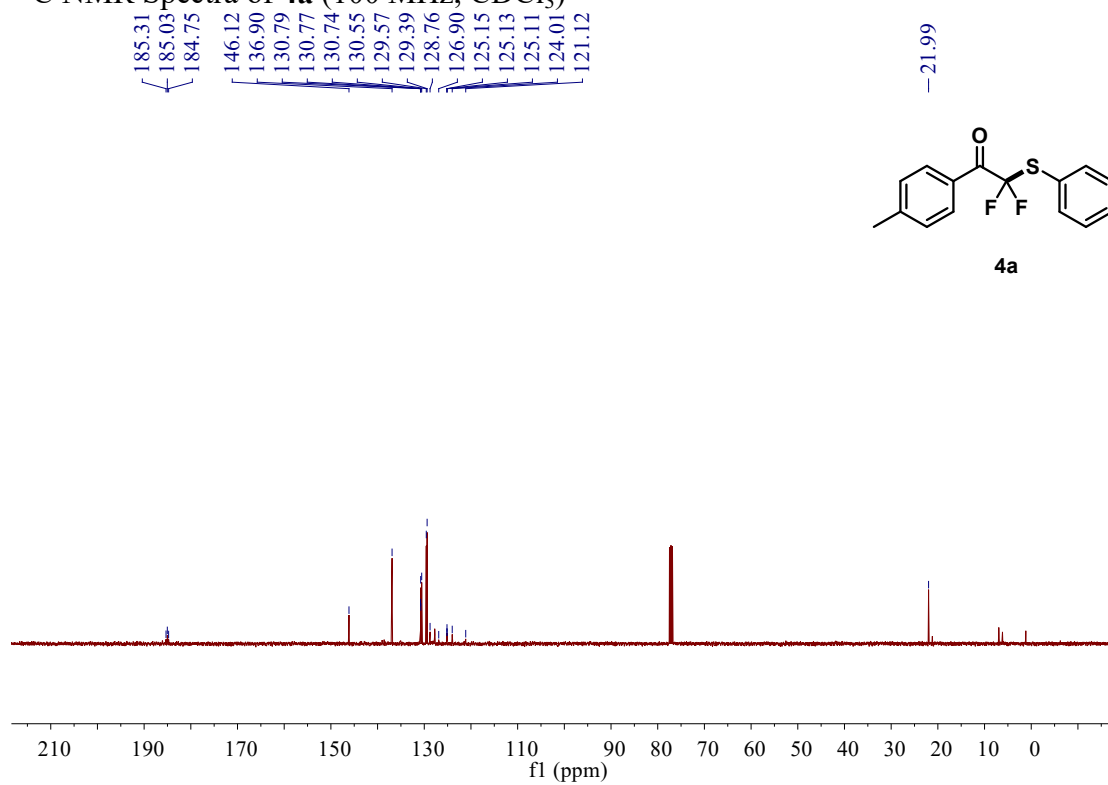
¹⁹F NMR Spectra of **3n** (377 MHz, CDCl₃)



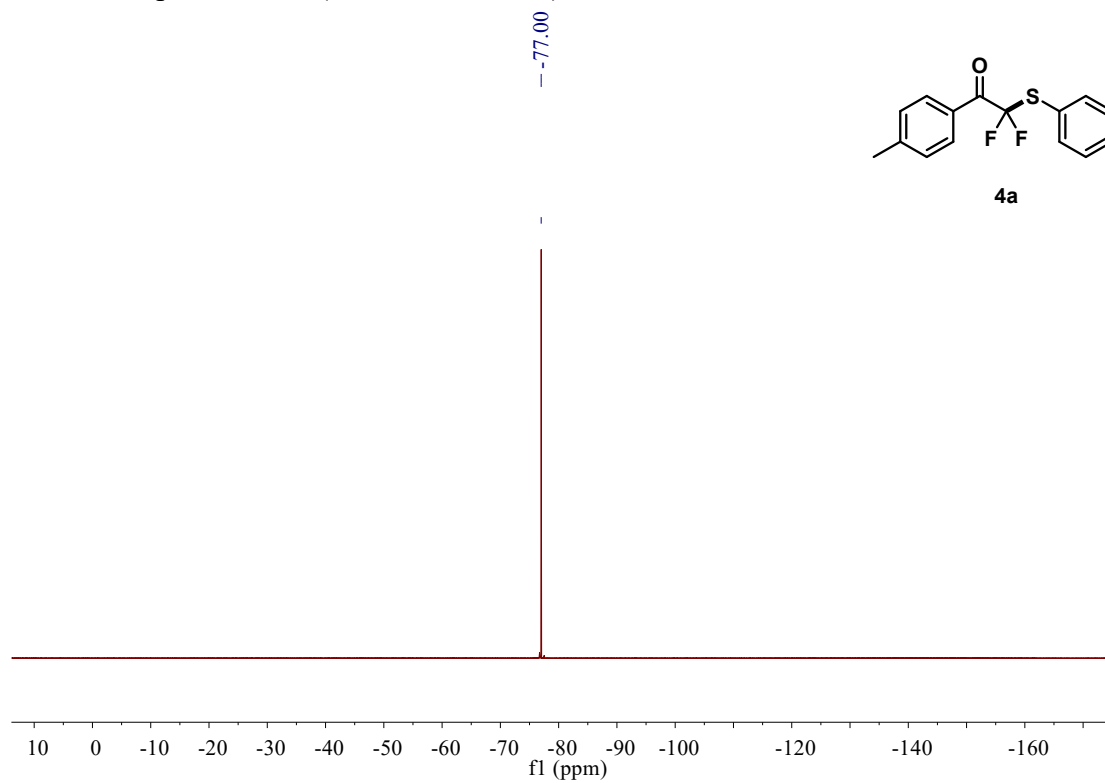
¹H NMR Spectra of **4a** (400 MHz, CDCl₃)



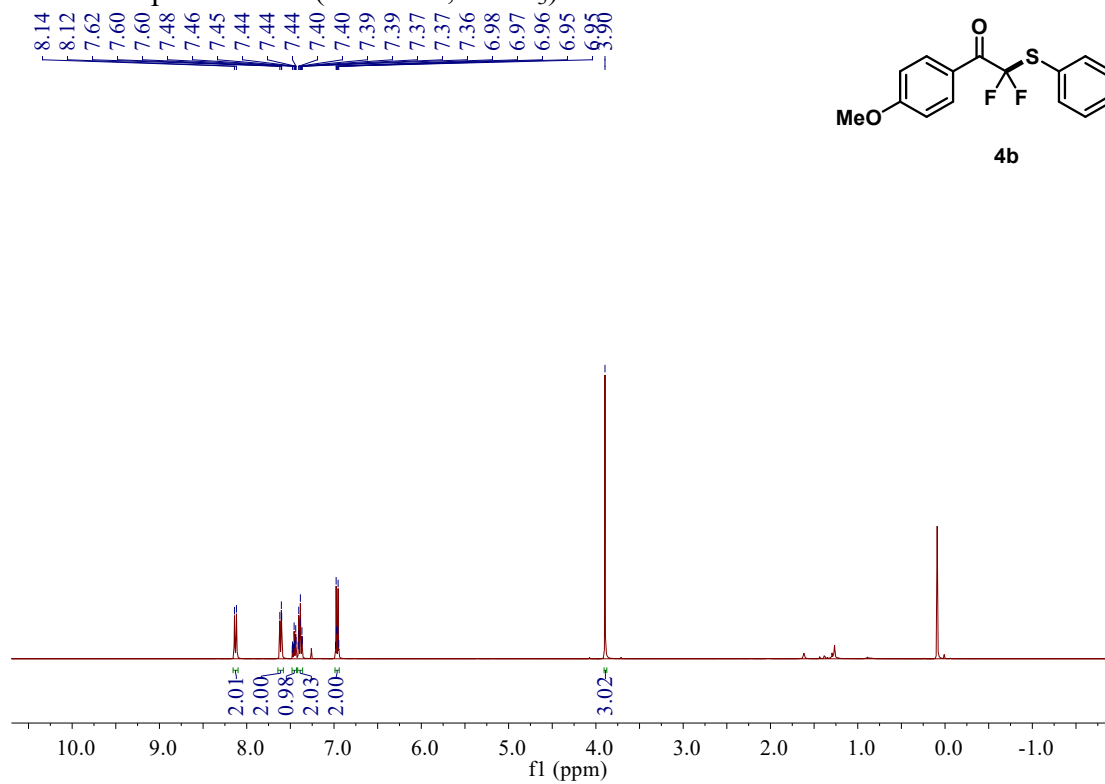
¹³C NMR Spectra of **4a** (100 MHz, CDCl₃)



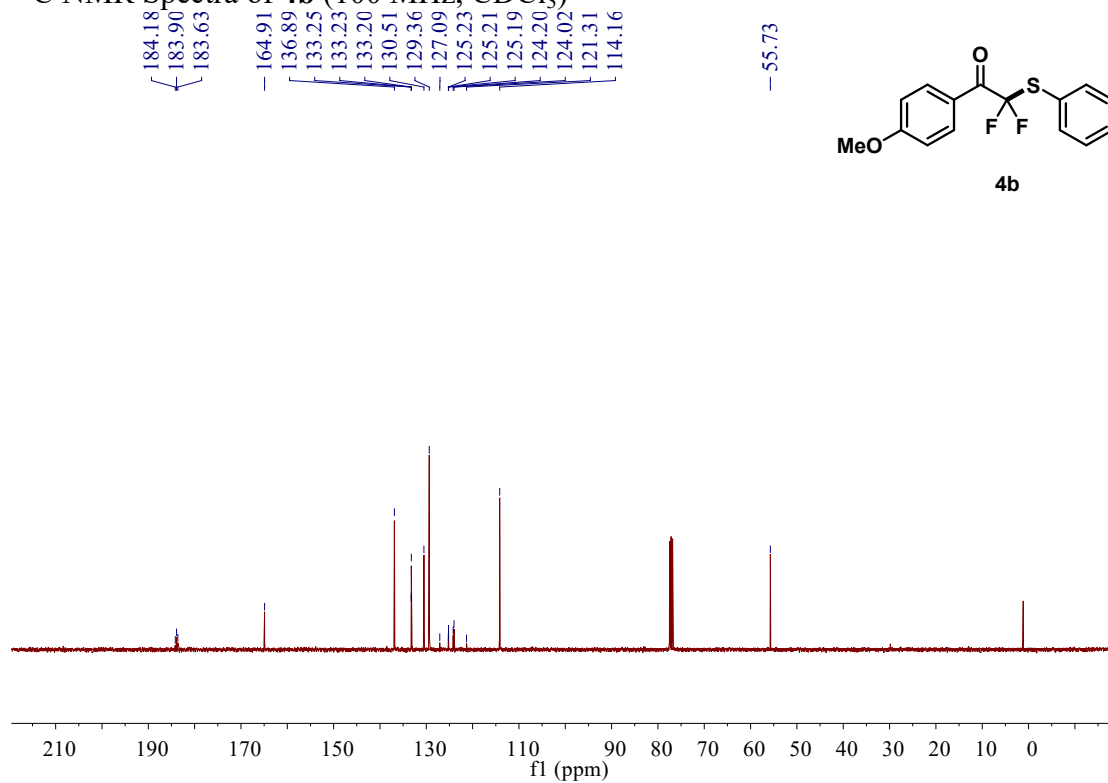
¹⁹F NMR Spectra of **4a** (377 MHz, CDCl₃)



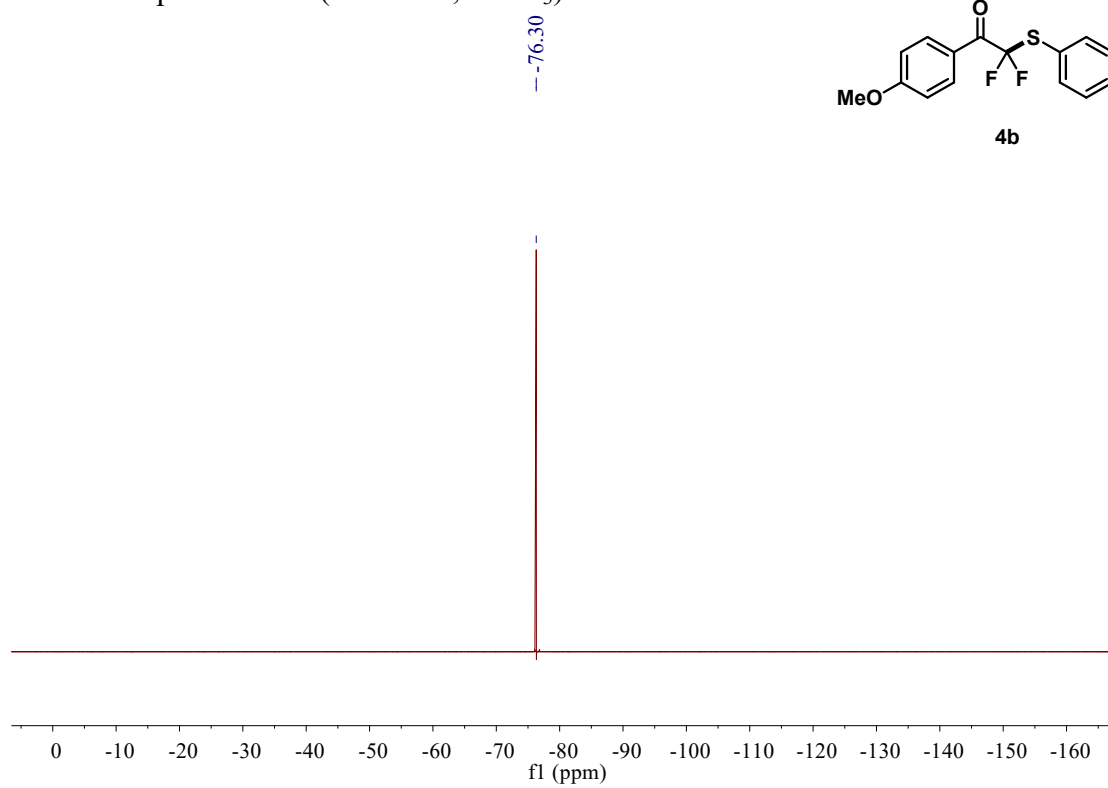
¹H NMR Spectra of **4b** (400 MHz, CDCl₃)



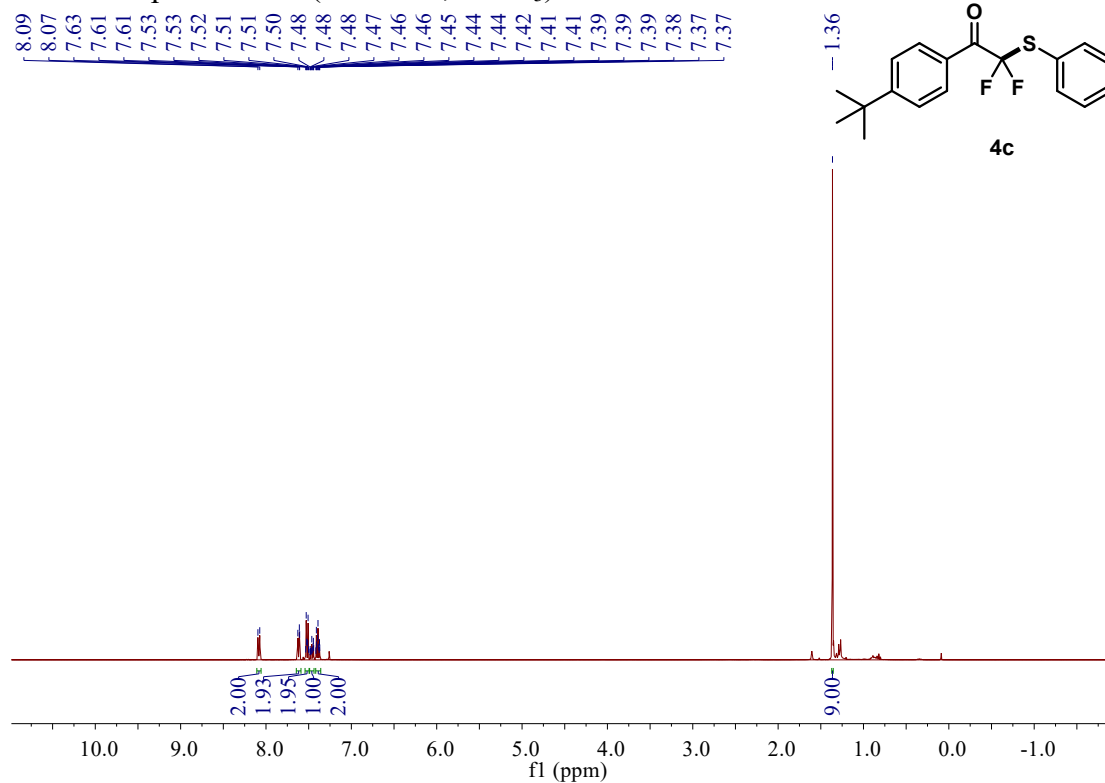
¹³C NMR Spectra of **4b** (100 MHz, CDCl₃)



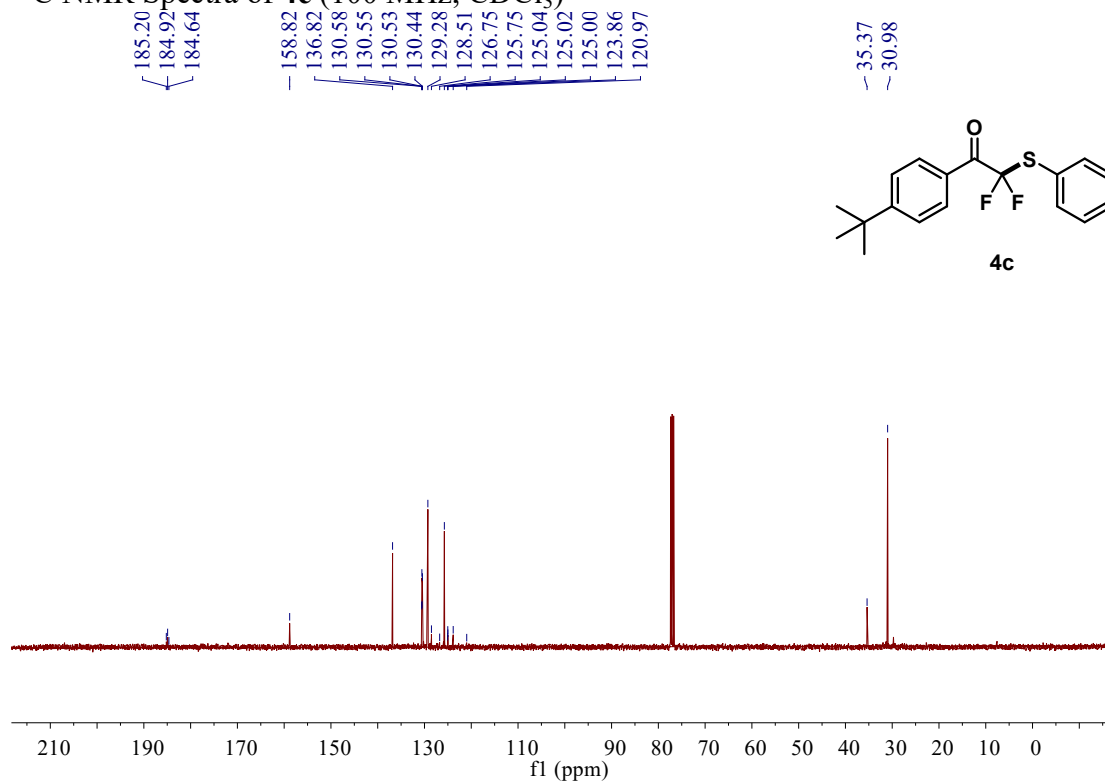
¹⁹F NMR Spectra of **4b** (377 MHz, CDCl₃)



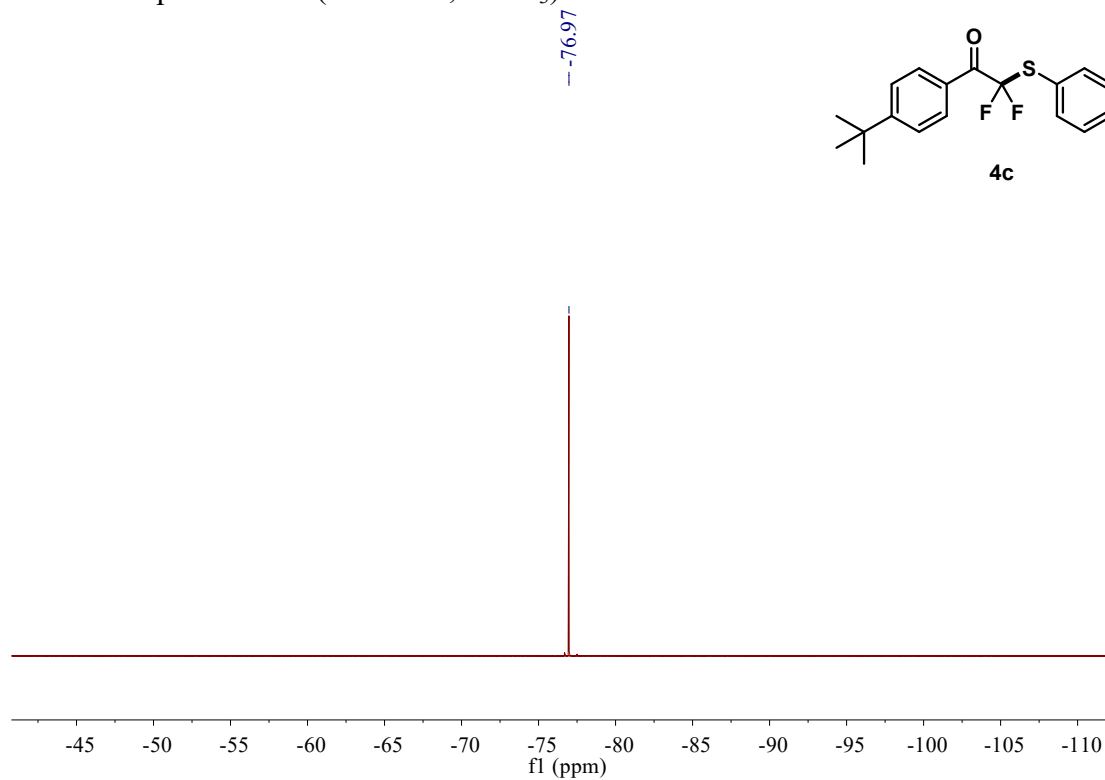
¹H NMR Spectra of **4c** (400 MHz, CDCl₃)



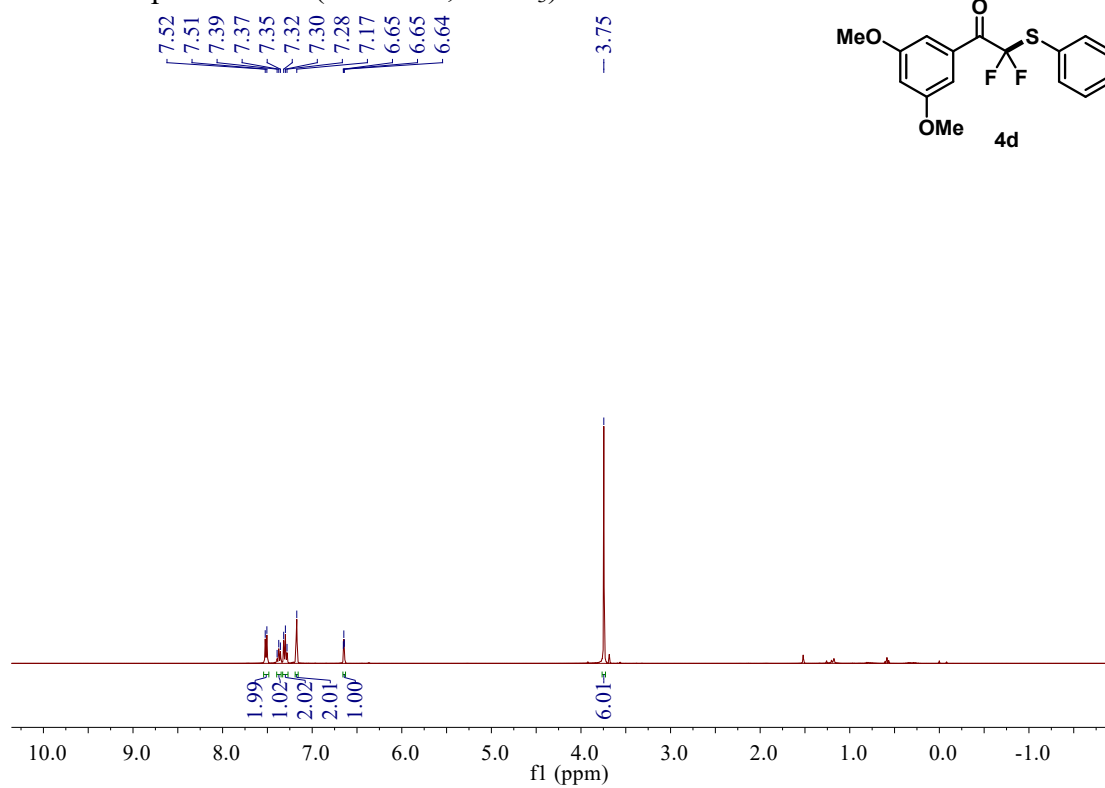
¹³C NMR Spectra of **4c** (100 MHz, CDCl₃)



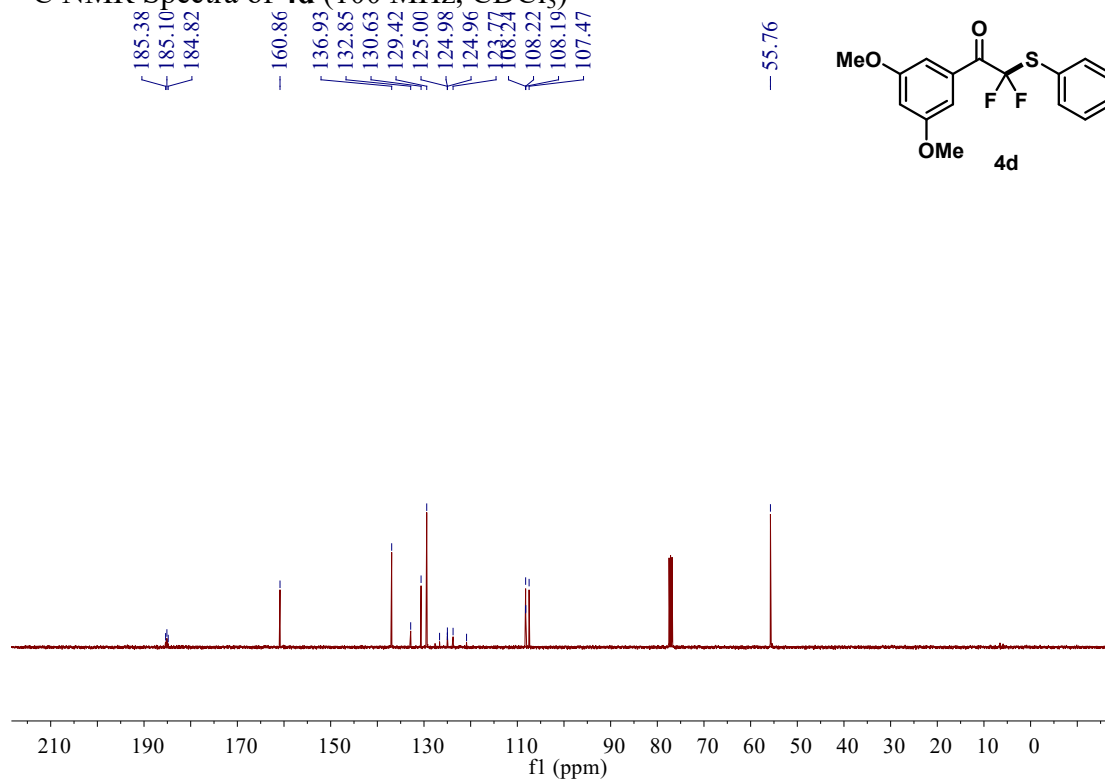
^{19}F NMR Spectra of **4c** (377 MHz, CDCl_3)



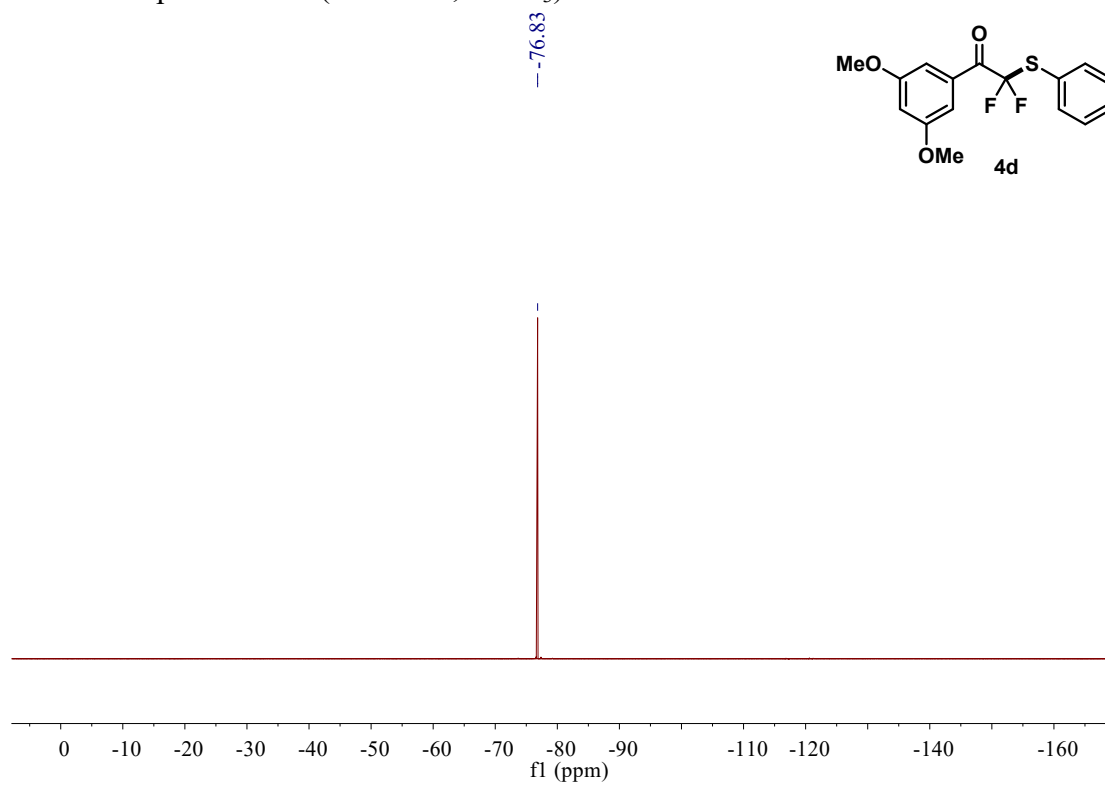
^1H NMR Spectra of **4d** (400 MHz, CDCl_3)



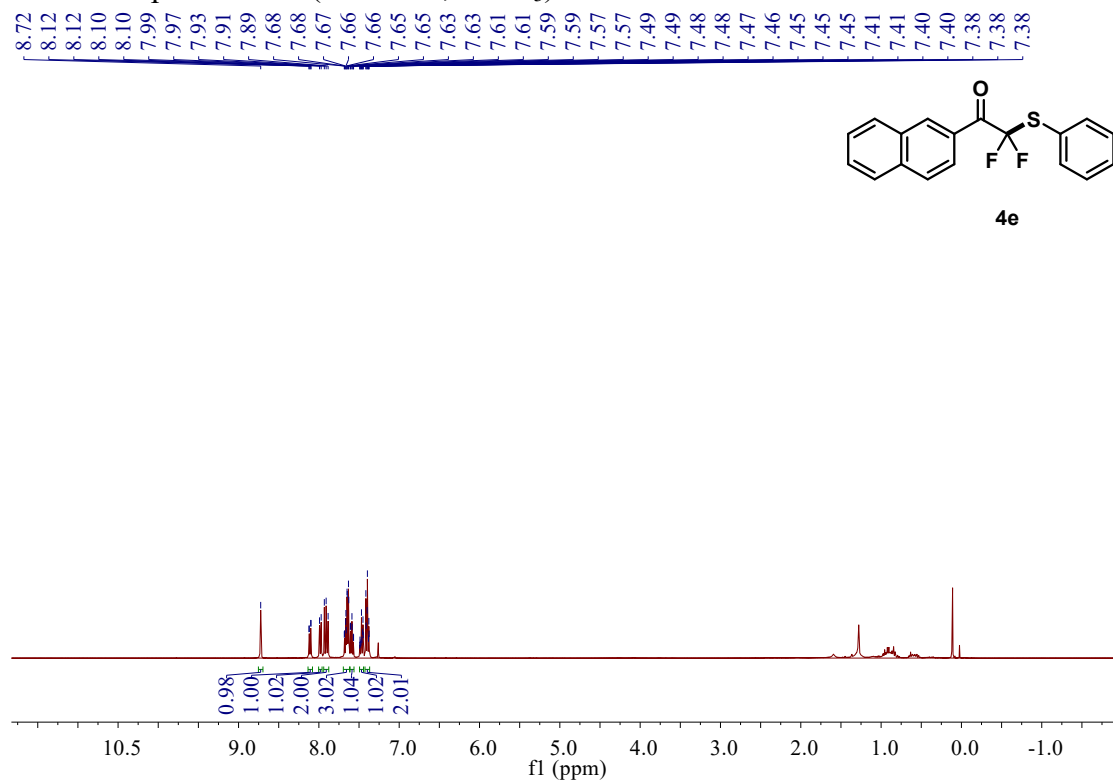
¹³C NMR Spectra of **4d** (100 MHz, CDCl₃)



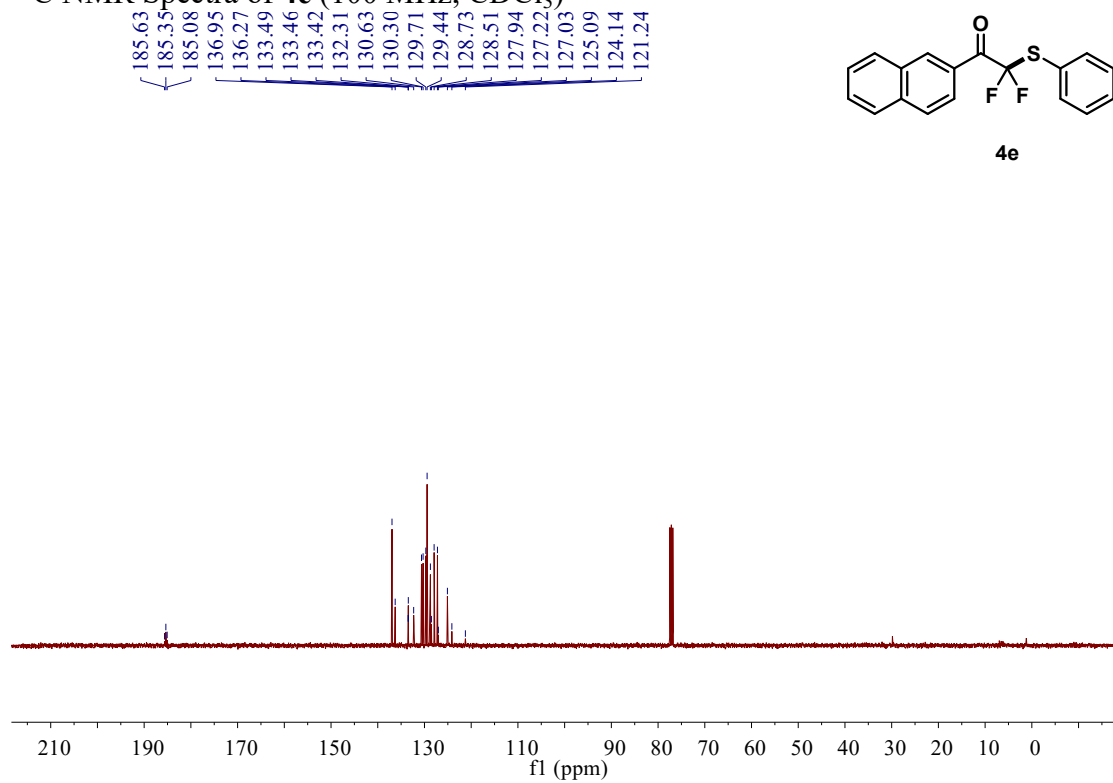
¹⁹F NMR Spectra of **4d** (377 MHz, CDCl₃)



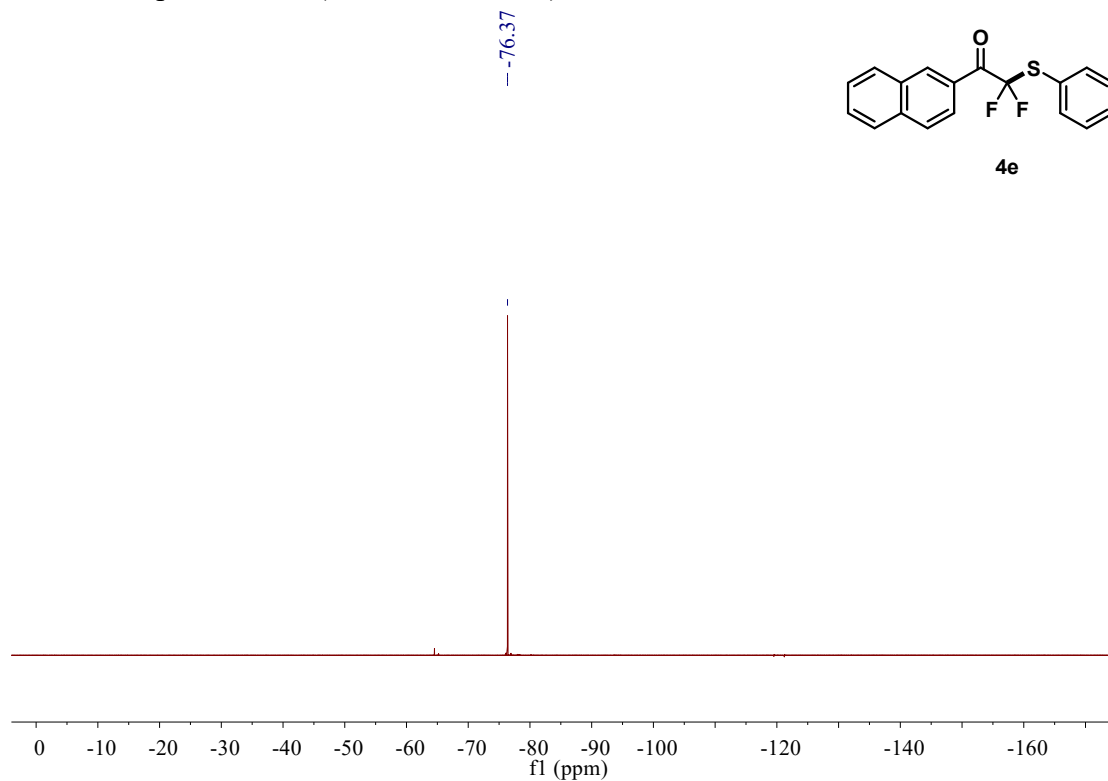
¹H NMR Spectra of **4e** (400 MHz, CDCl₃)



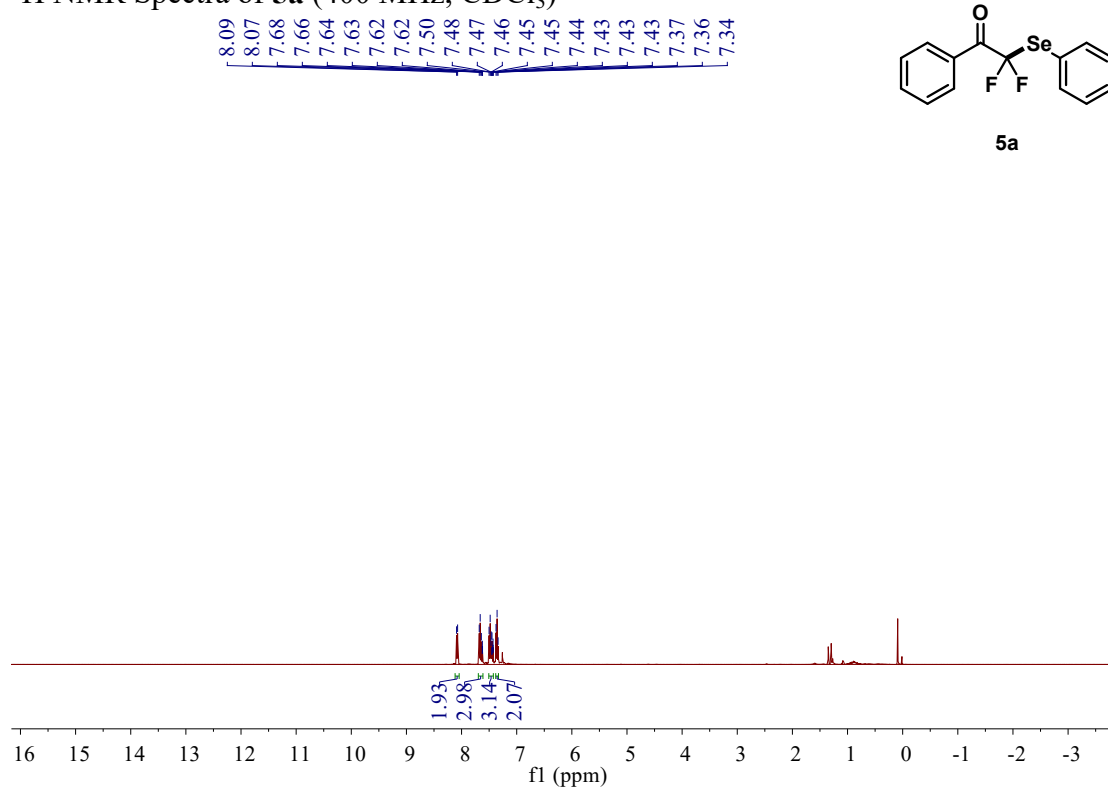
¹³C NMR Spectra of **4e** (100 MHz, CDCl₃)



^{19}F NMR Spectra of **4e** (377 MHz, CDCl_3)

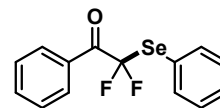


^1H NMR Spectra of **5a** (400 MHz, CDCl_3)

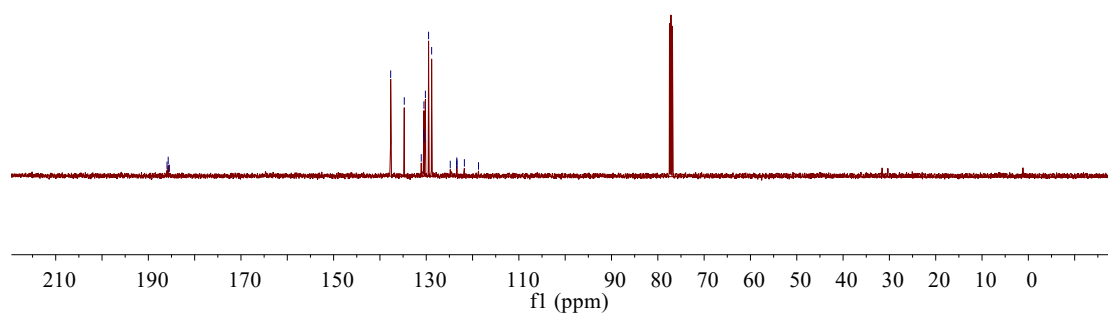


¹³C NMR Spectra of **5a** (100 MHz, CDCl₃)

185.97
185.71
185.46
137.68
134.74
131.08
130.52
130.49
130.47
130.18
129.50
128.84
124.81
123.42
123.40
123.38
121.76
118.71

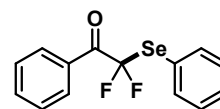


5a

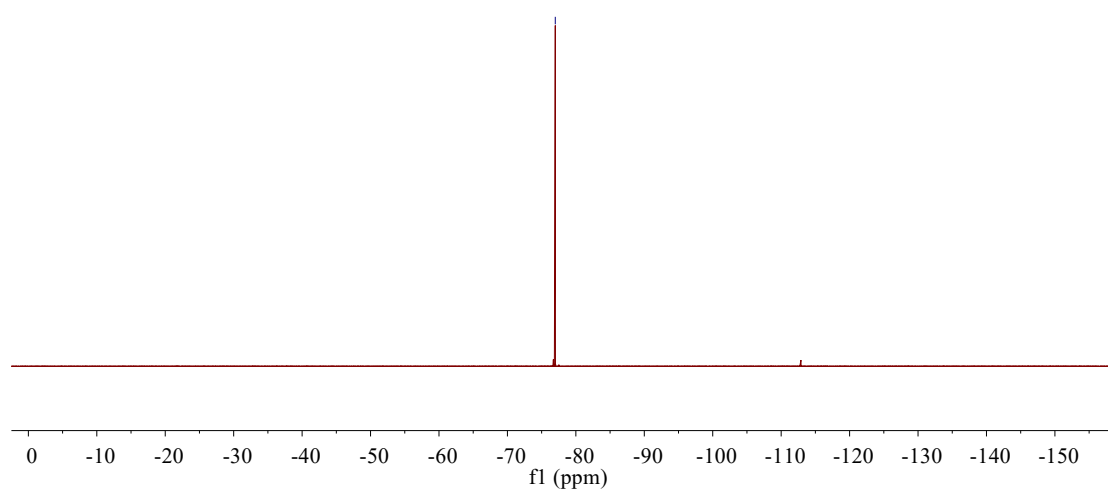


¹⁹F NMR Spectra of **5a** (377 MHz, CDCl₃)

-76.99

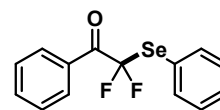


5a

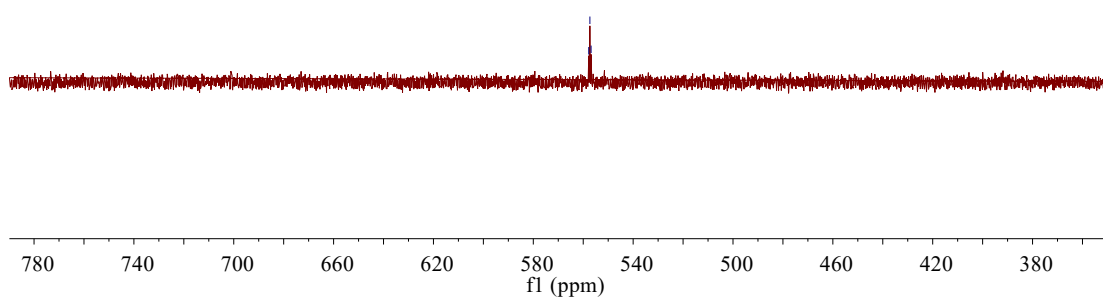


⁷⁷Se NMR Spectra of **5a** (76 MHz, CDCl₃)

557.79
557.33
556.85

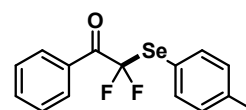


5a

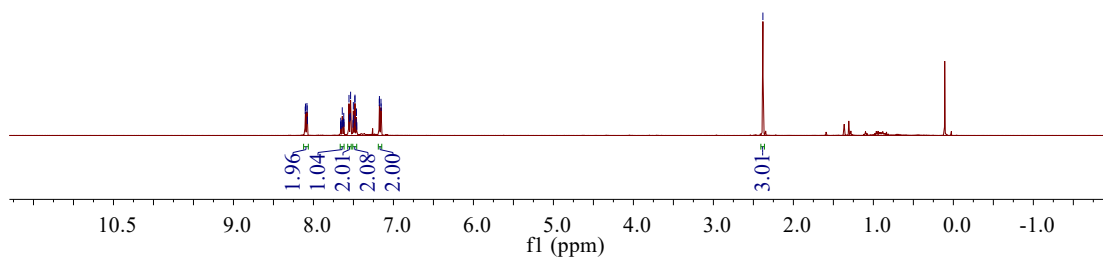


¹H NMR Spectra of **5b** (400 MHz, CDCl₃)

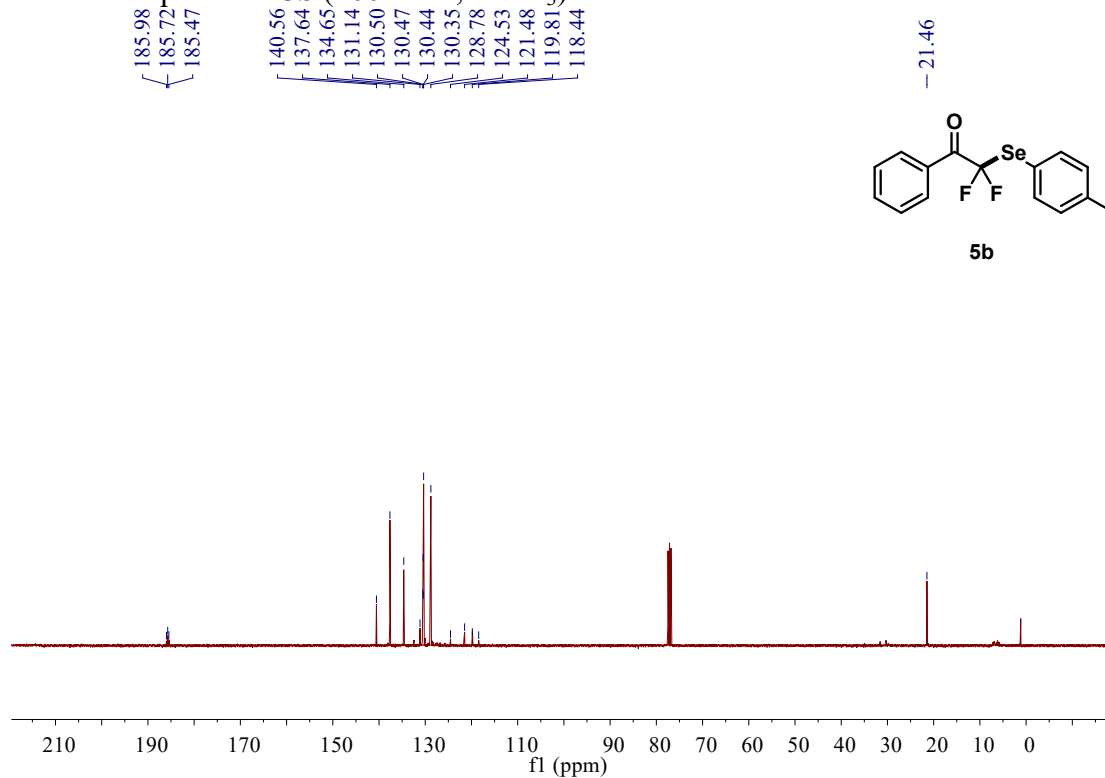
8.10
8.10
8.08
8.08
8.08
7.66
7.66
7.66
7.64
7.64
7.64
7.62
7.62
7.62
7.56
7.55
7.55
7.54
7.54
7.51
7.50
7.50
7.48
7.48
7.47
7.46
7.18
7.18
7.16
7.15
2.38



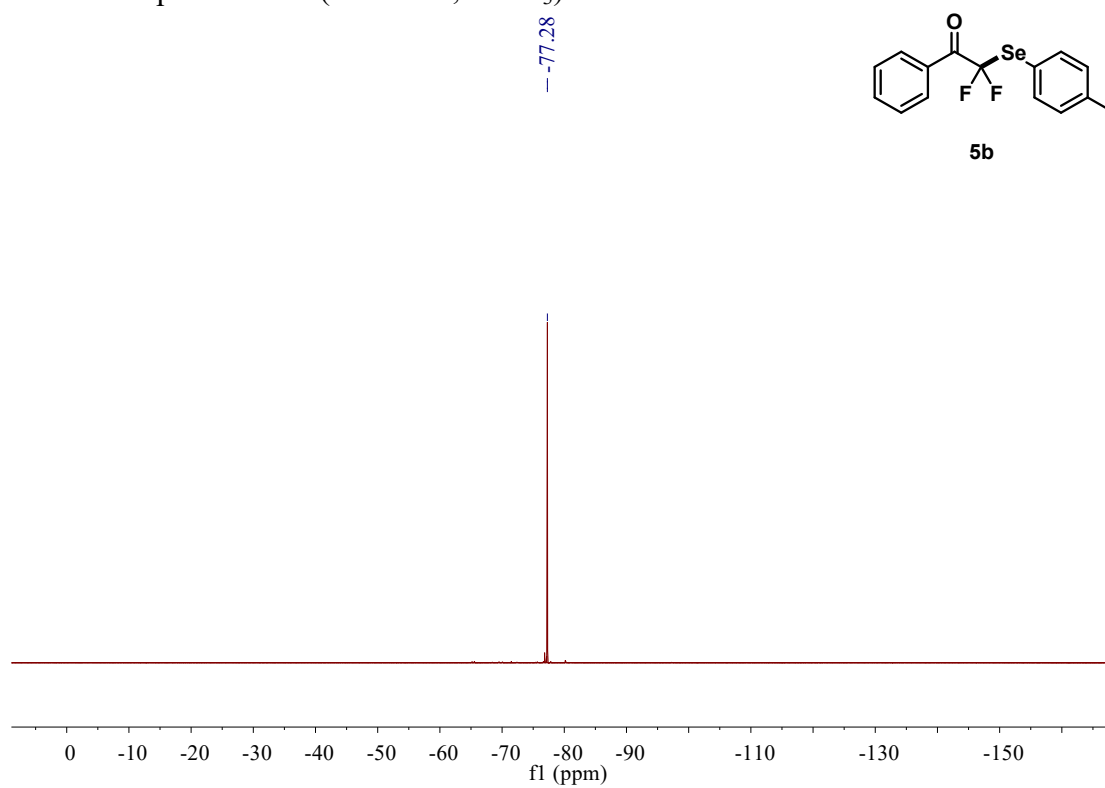
5b



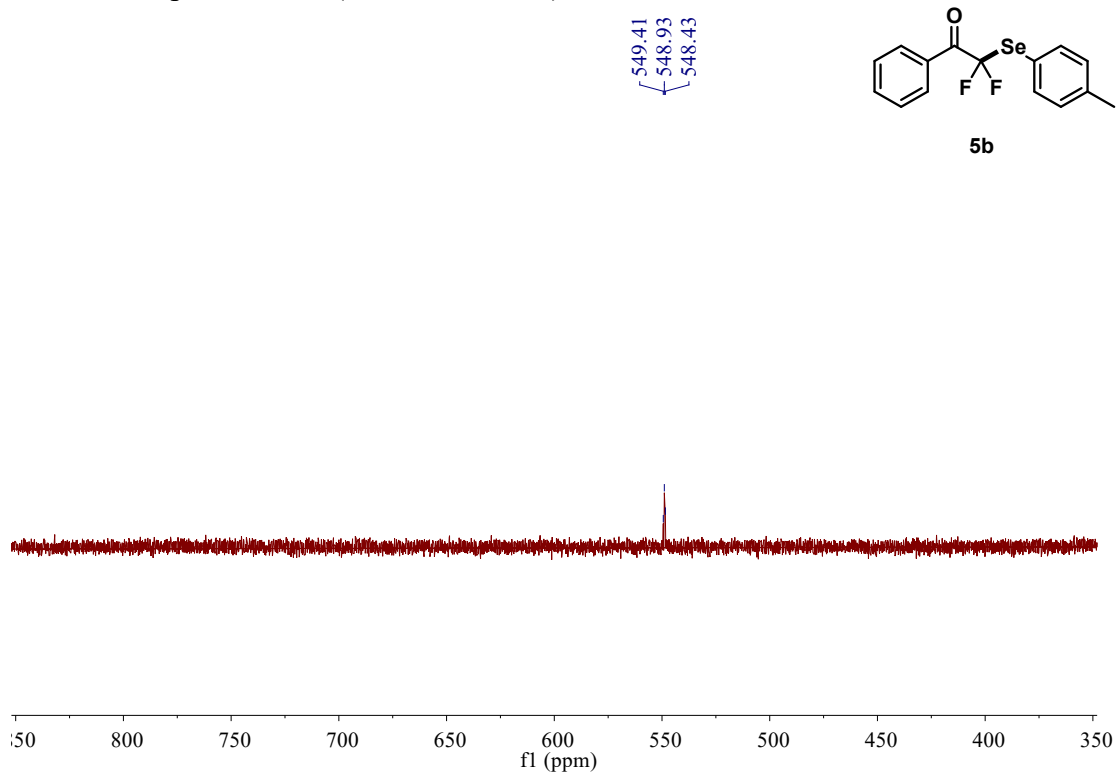
¹³C NMR Spectra of **5b** (100 MHz, CDCl₃)



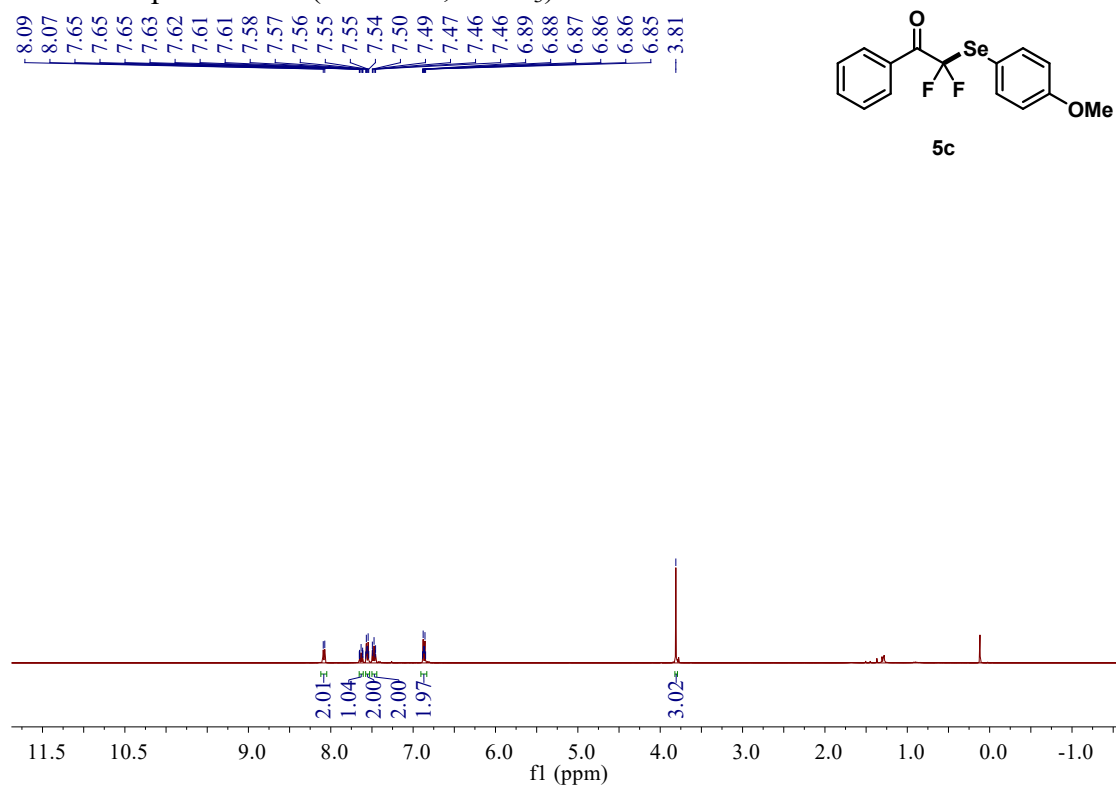
¹⁹F NMR Spectra of **5b** (377 MHz, CDCl₃)



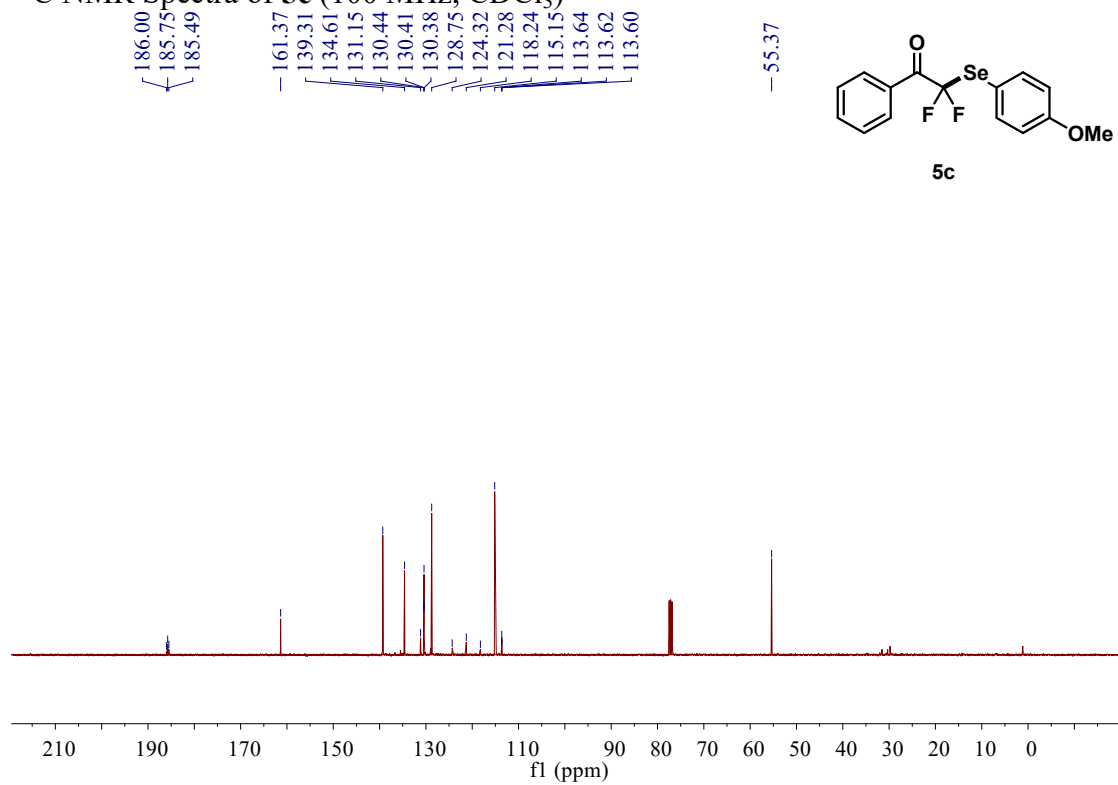
⁷⁷Se NMR Spectra of **5b** (76 MHz, CDCl₃)



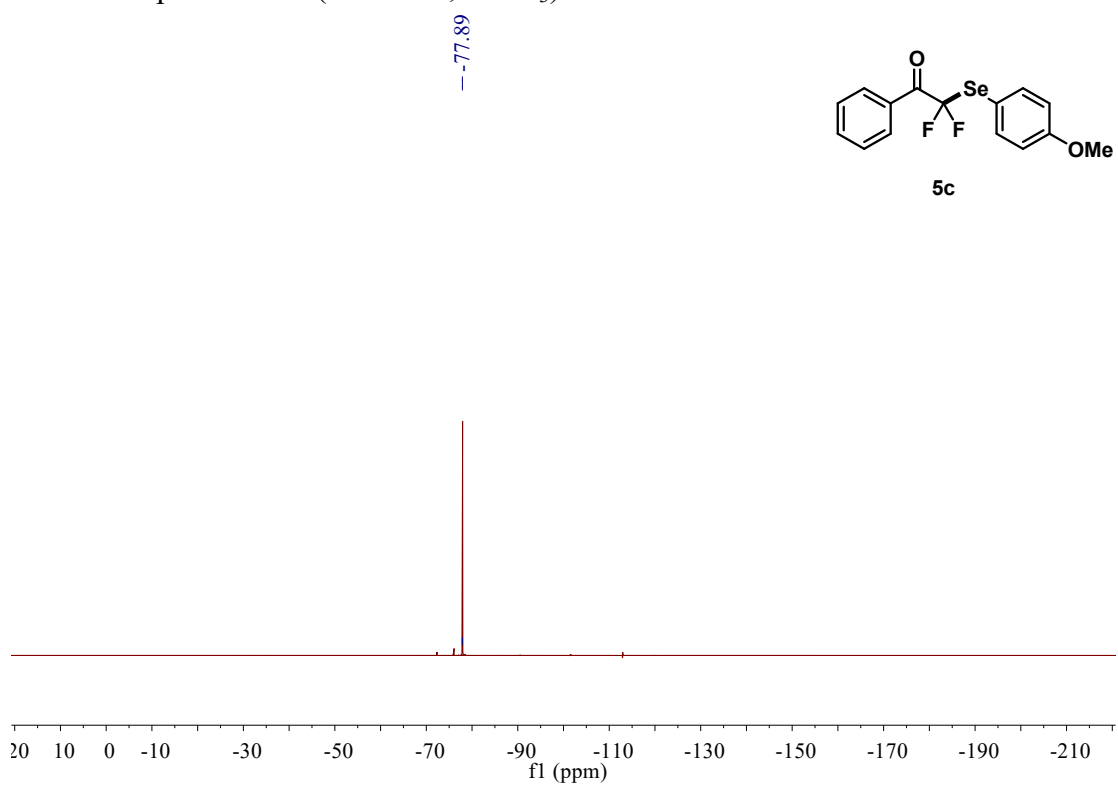
¹H NMR Spectra of **5c** (400 MHz, CDCl₃)



¹³C NMR Spectra of **5c** (100 MHz, CDCl₃)

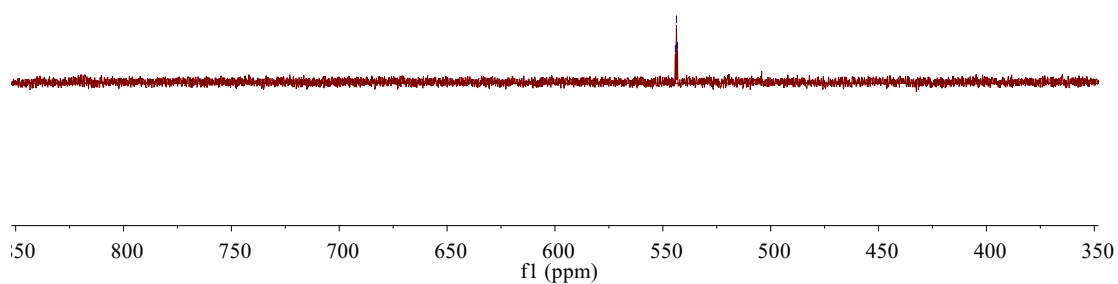
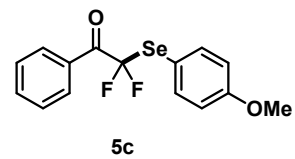


¹⁹F NMR Spectra of **5c** (377 MHz, CDCl₃)



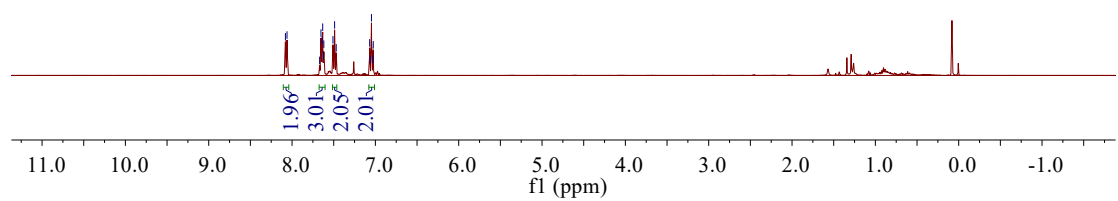
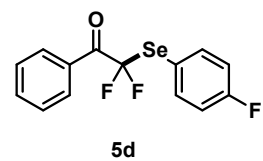
⁷⁷Se NMR Spectra of **5c** (76 MHz, CDCl₃)

544.19
543.69
543.19



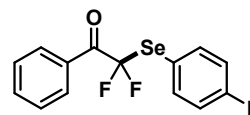
¹H NMR Spectra of **5d** (400 MHz, CDCl₃)

8.08
8.06
7.67
7.65
7.64
7.63
7.62
7.62
7.51
7.49
7.47
7.07
7.06
7.05
7.03
7.03

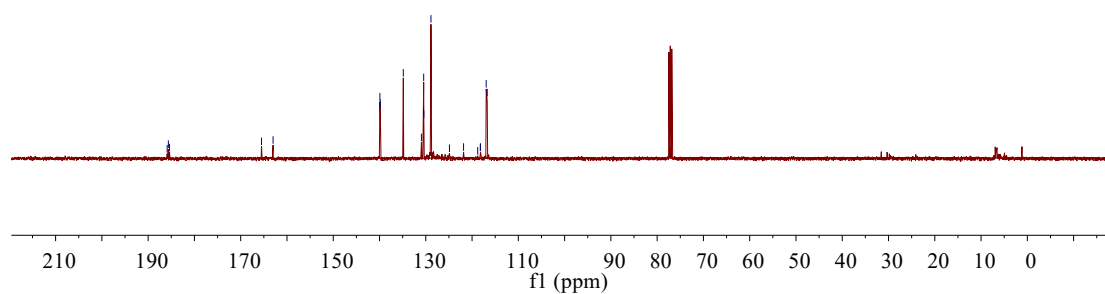


¹³C NMR Spectra of **5d** (100 MHz, CDCl₃)

185.89
185.63
185.38
165.50
163.00
139.92
139.83
134.86
130.94
130.48
130.45
130.42
128.89
124.89
121.84
118.78
118.22
118.18
116.94
116.73

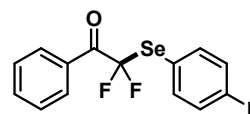


5d

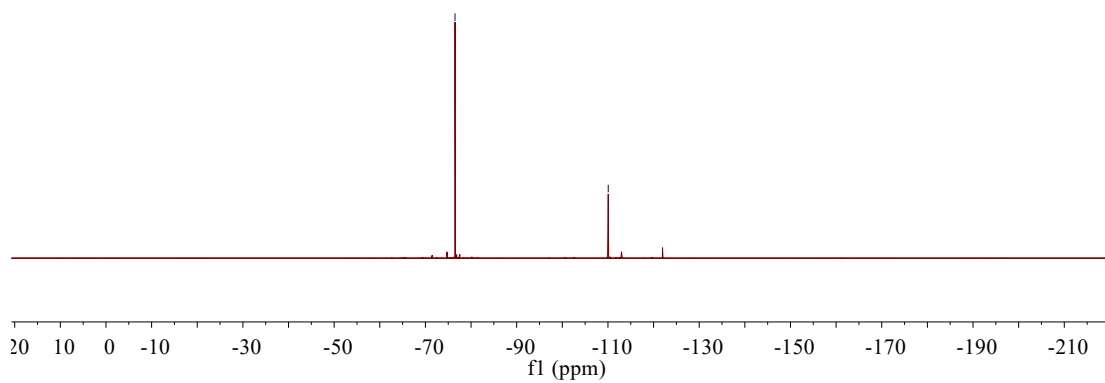


¹⁹F NMR Spectra of **5d** (377 MHz, CDCl₃)

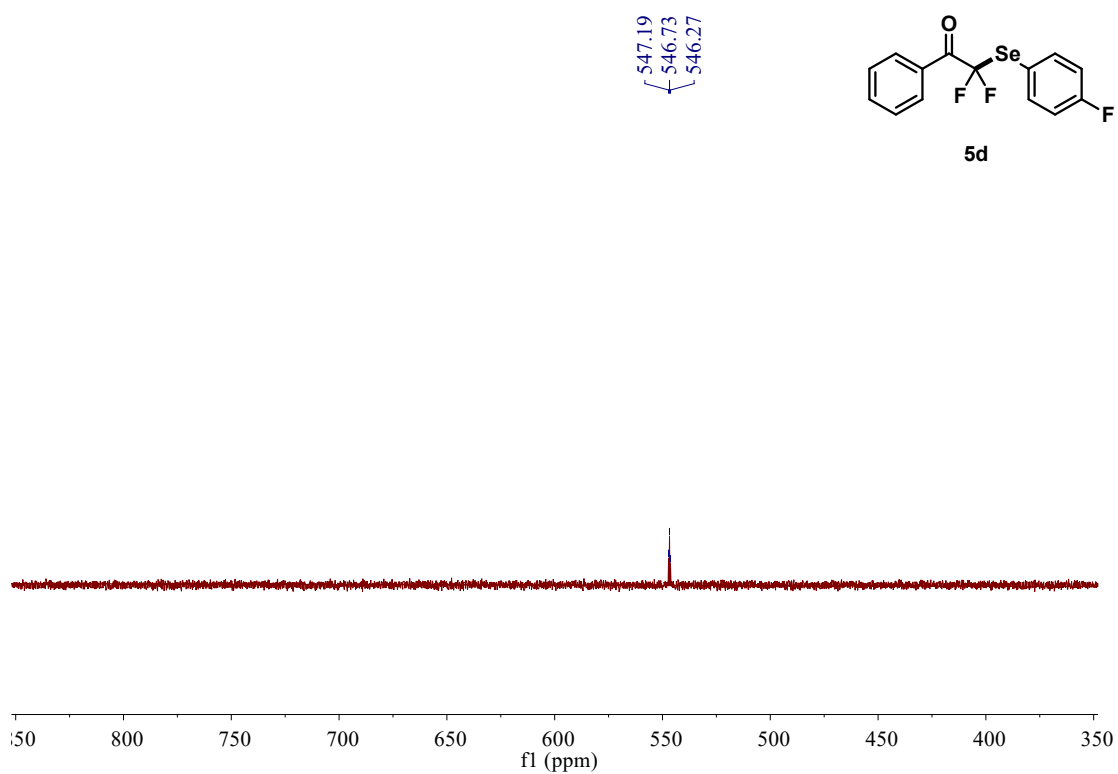
-76.49
-110.06



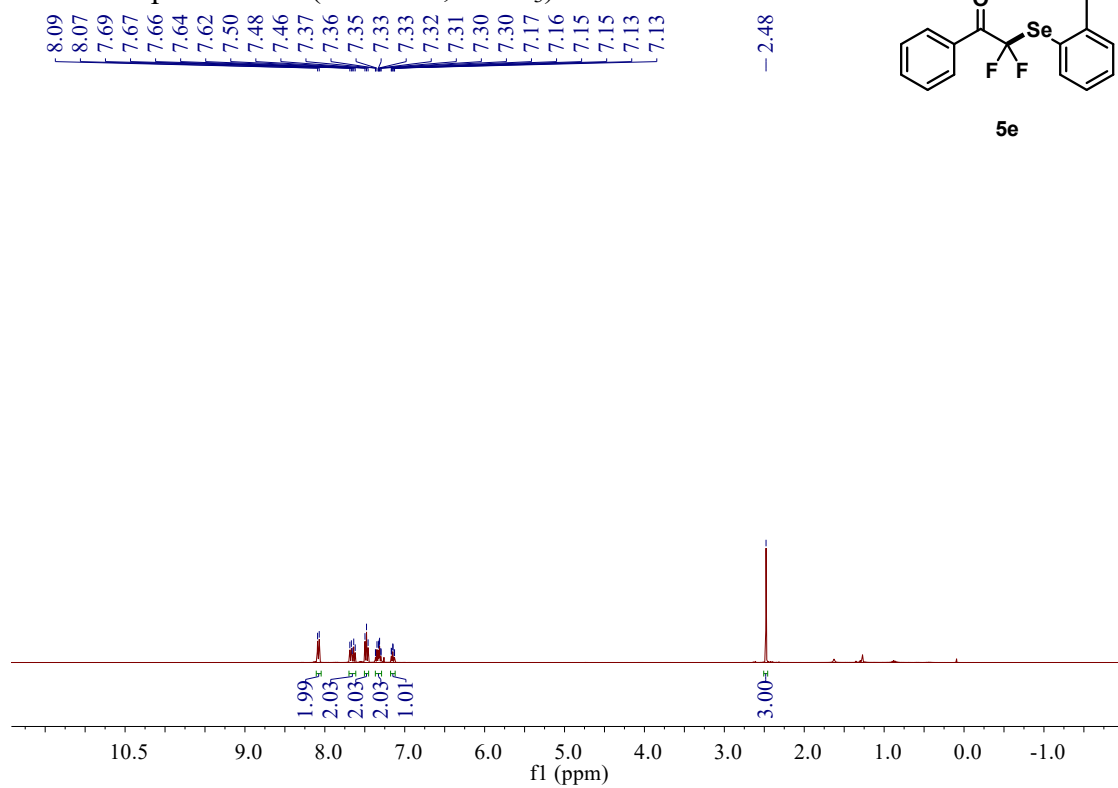
5d



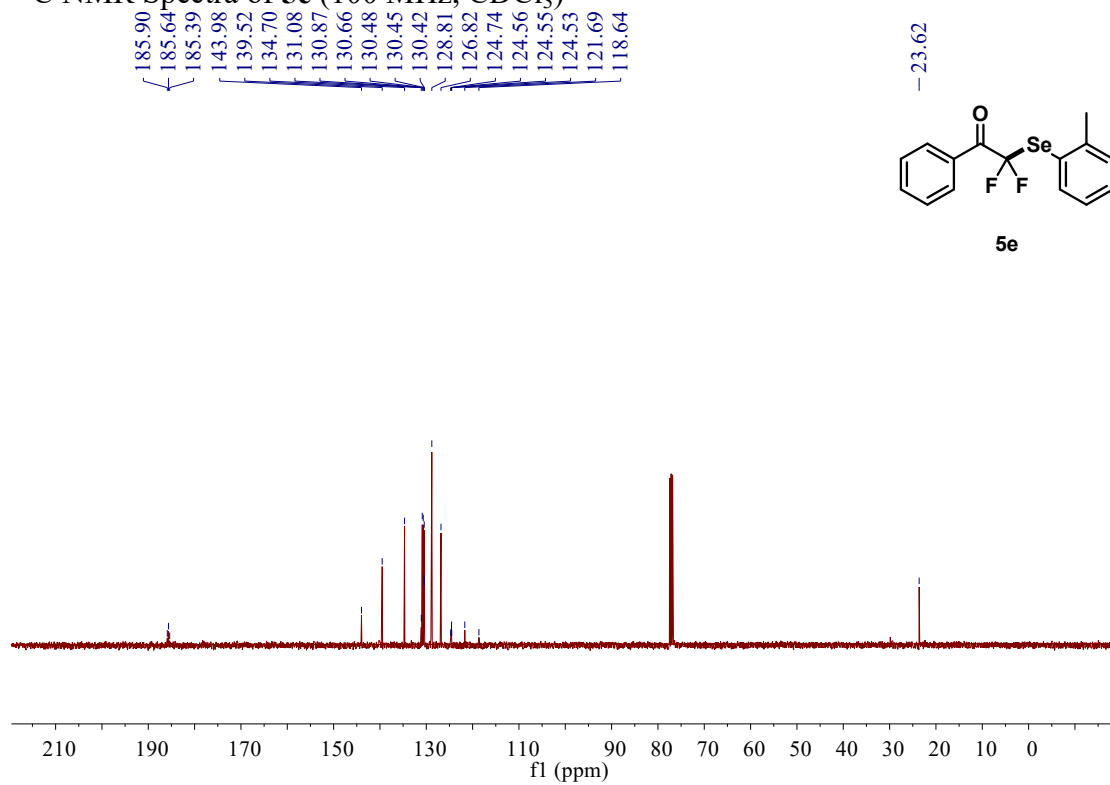
^{77}Se NMR Spectra of **5d** (76 MHz, CDCl_3)



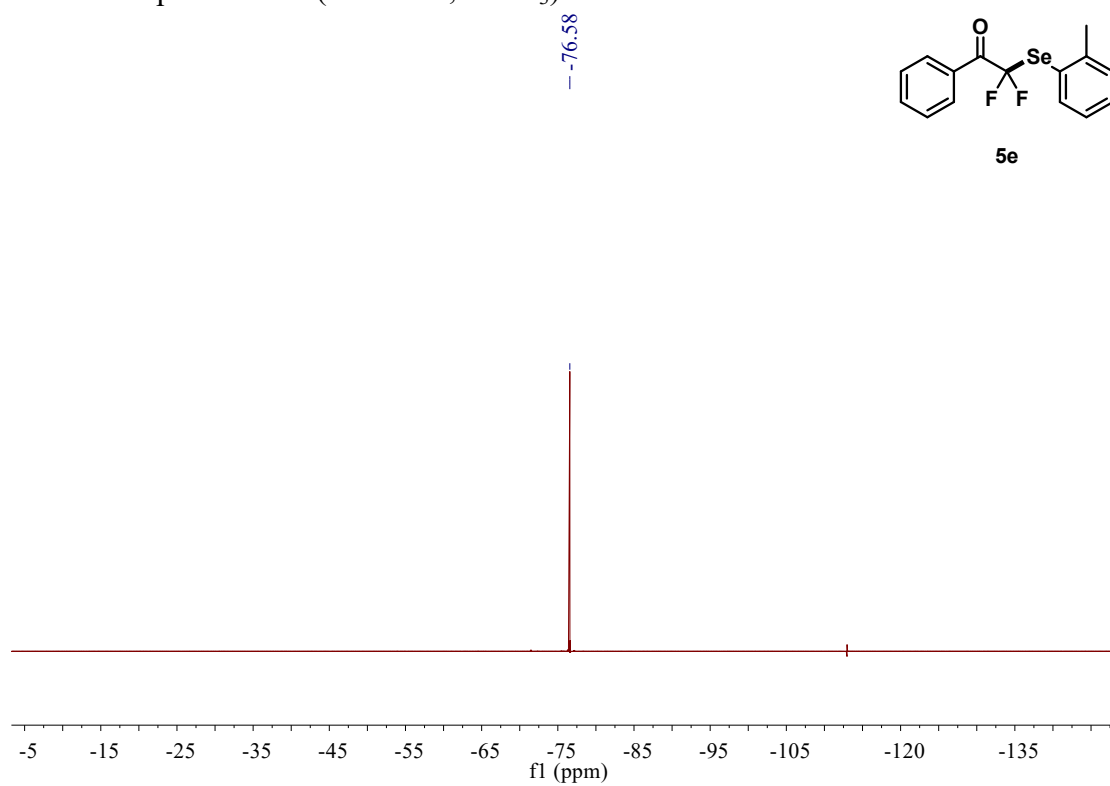
^1H NMR Spectra of **5e** (400 MHz, CDCl_3)



¹³C NMR Spectra of **5e** (100 MHz, CDCl₃)

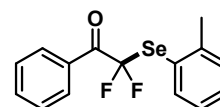


¹⁹F NMR Spectra of **5e** (377 MHz, CDCl₃)

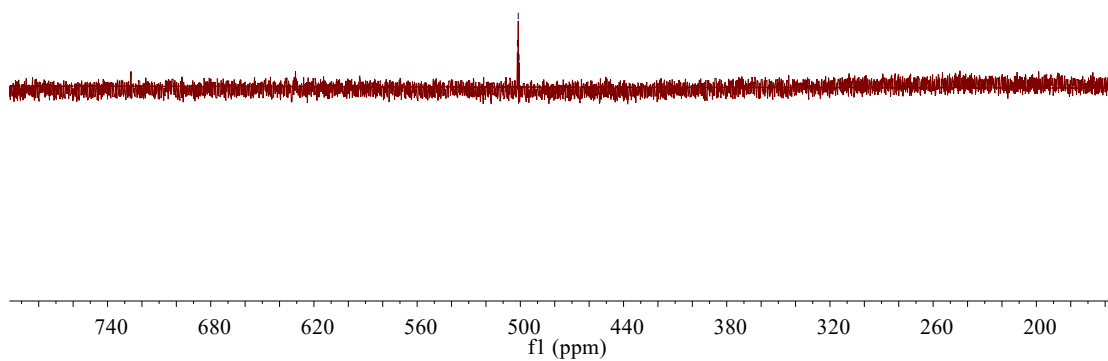


^{77}Se NMR Spectra of **5e** (76 MHz, CDCl_3)

501.69
501.22
500.74

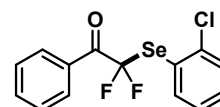


5e

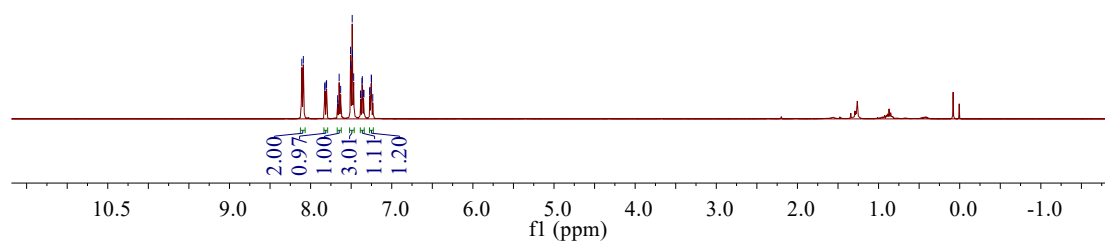


^1H NMR Spectra of **5f** (400 MHz, CDCl_3)

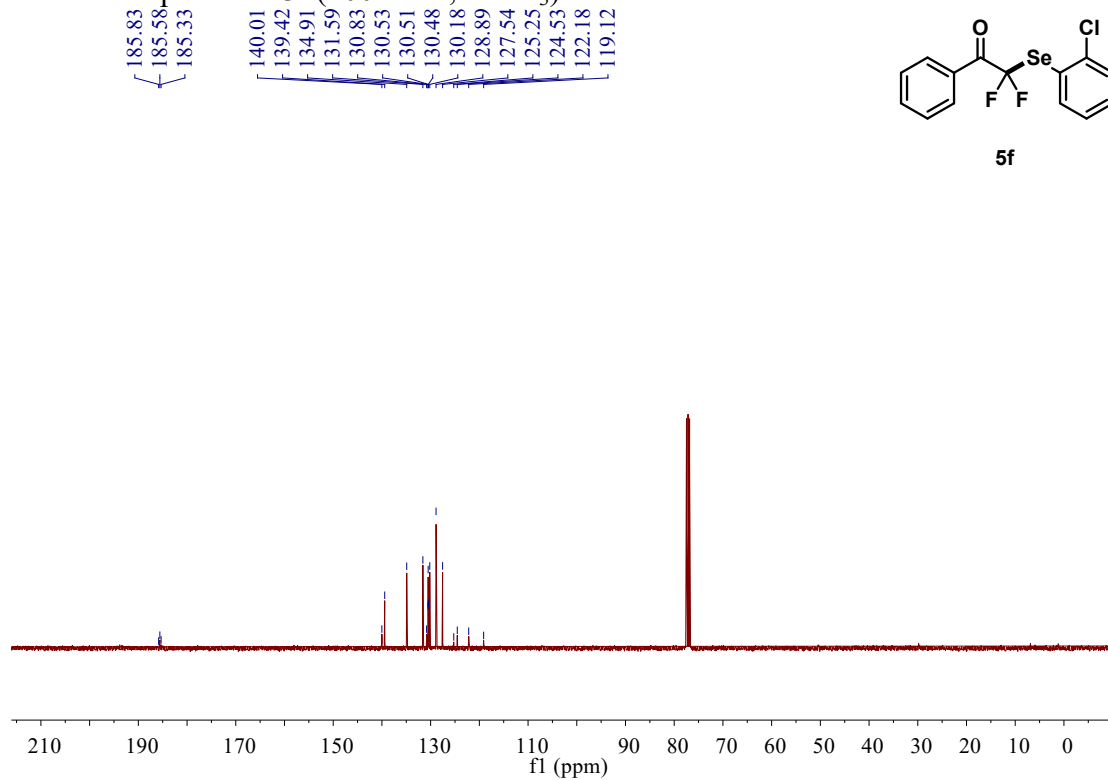
8.11
8.09
7.83
7.82
7.81
7.80
7.67
7.66
7.65
7.63
7.51
7.50
7.49
7.48
7.47
7.39
7.38
7.37
7.36
7.35
7.34
7.27
7.27
7.25
7.25
7.23



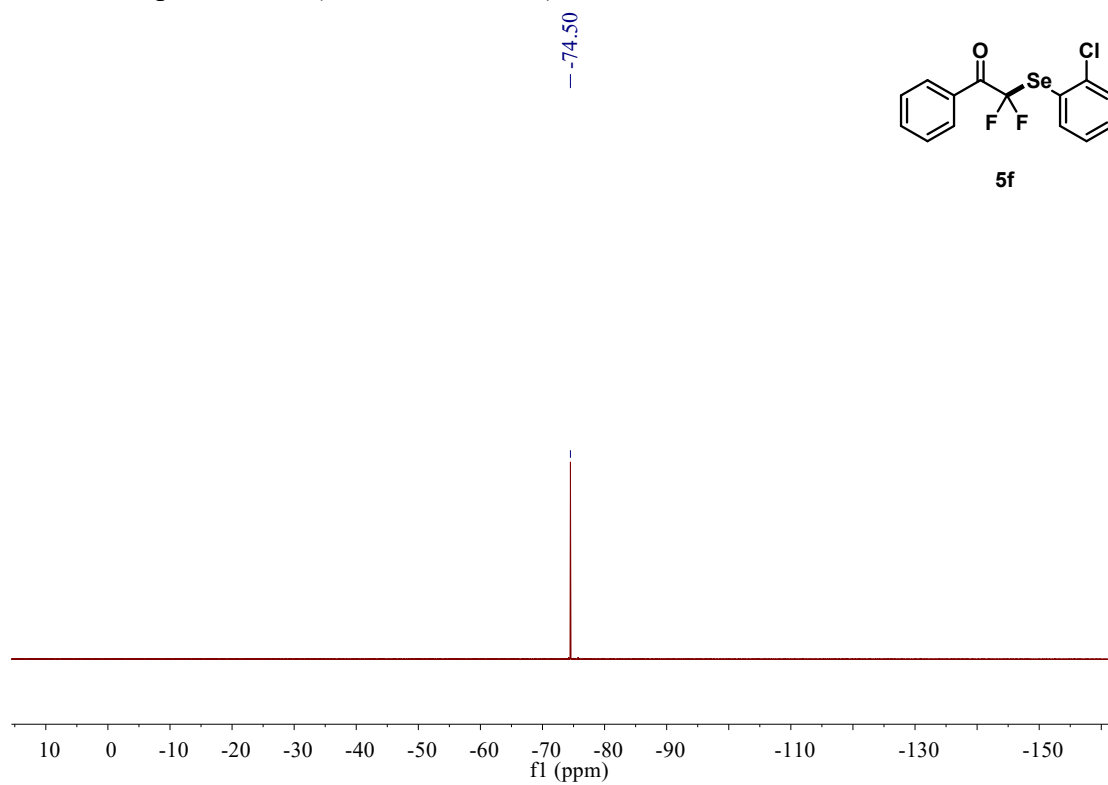
5f



¹³C NMR Spectra of **5f** (100 MHz, CDCl₃)

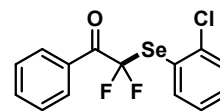


¹⁹F NMR Spectra of **5f** (377 MHz, CDCl₃)

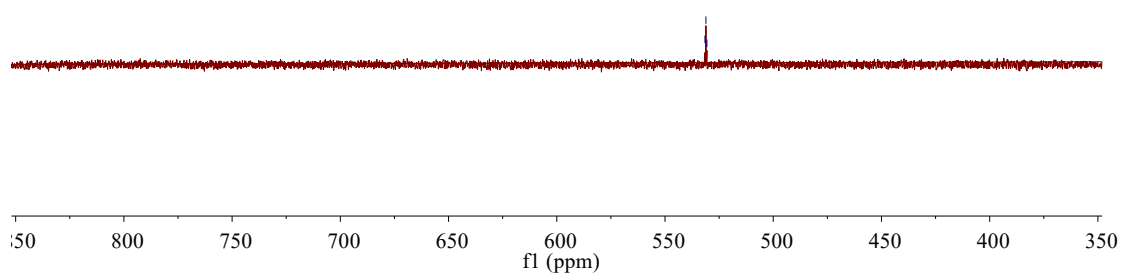


⁷⁷Se NMR Spectra of **5f** (76 MHz, CDCl₃)

531.55
531.10
530.64

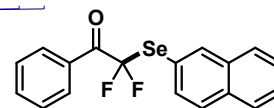


5f

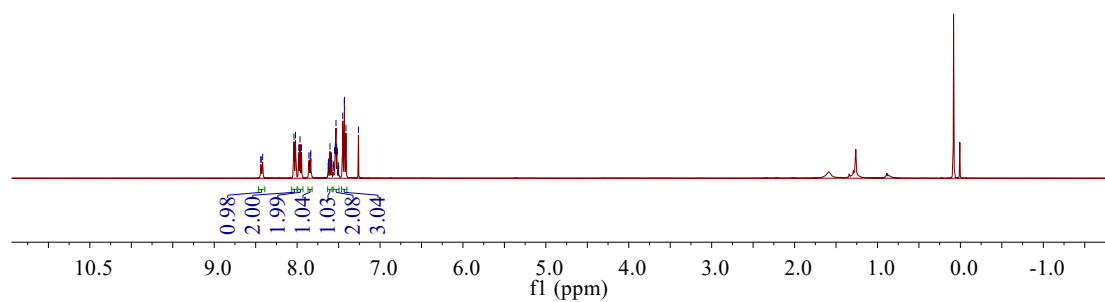


¹H NMR Spectra of **5g** (400 MHz, CDCl₃)

8.44
8.43
8.42
8.04
8.02
7.98
7.97
7.95
7.86
7.85
7.84
7.83
7.63
7.62
7.62
7.60
7.59
7.59
7.58
7.56
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.50
7.50
7.45
7.43
7.43
7.41
7.26

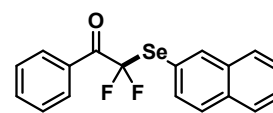


5g

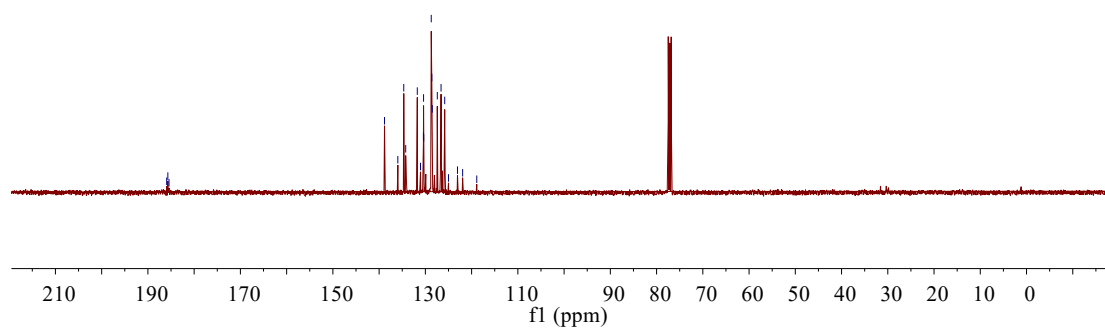


¹³C NMR Spectra of **5g** (100 MHz, CDCl₃)

185.94
185.69
185.44
138.83
135.96
134.67
134.25
131.75
131.05
130.42
130.39
130.36
128.73
128.60
128.50
127.42
126.61_o
125.82
125.00
123.06
121.94
118.88

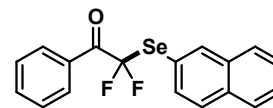


5g

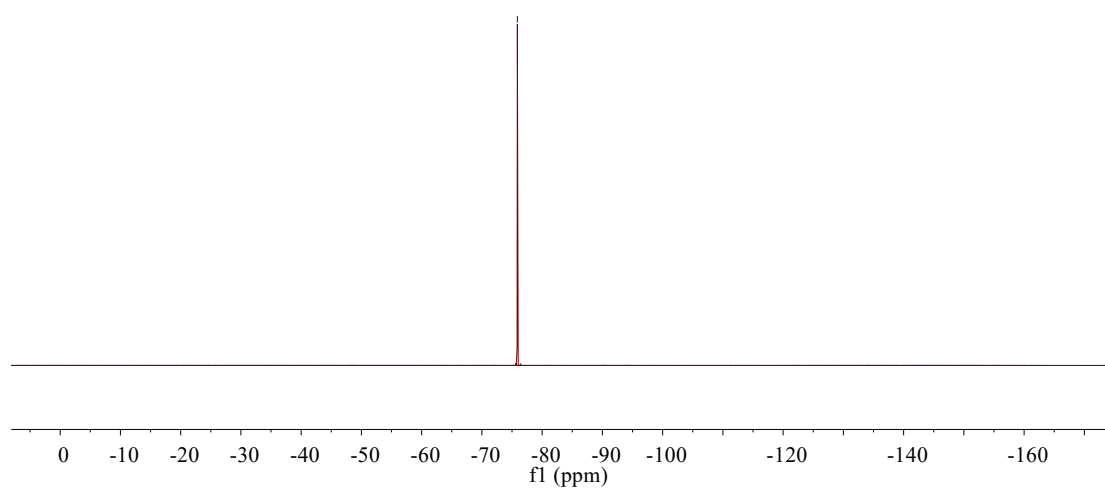


¹⁹F NMR Spectra of **5g** (377 MHz, CDCl₃)

-75.88

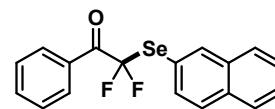


5g



⁷⁷Se NMR Spectra of **5g** (76 MHz, CDCl₃)

478.53
478.02
477.56



5g

