Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Visible light-promoted difluoromethylthiolation of cycloalkanols by C-C bond cleavage

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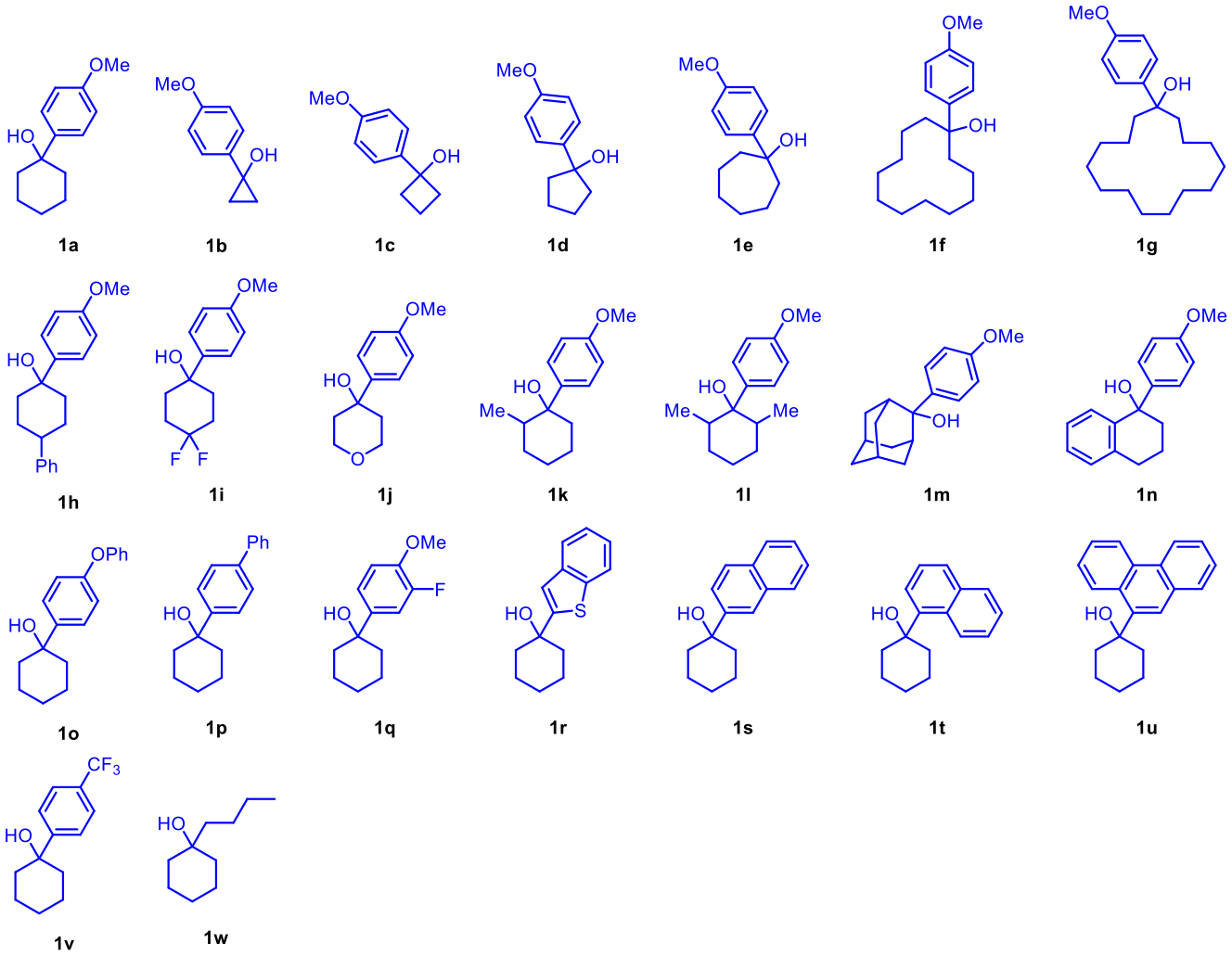
1. **General Information**

Unless otherwise noted, all reactions were performed in a 10 mL Schlenk tube at room temperature under N_2. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. For flash column chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured in $CDCl_3$ and recorded on Varian 400 or Brucker ARX 600 spectrometer. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in Hertz (Hz). The term m, t, d, s, dd referred to multiplet, triplet, doublet, singlet, doublet of doublet. Gas chromatography-mass spectrometry (GC-MS) was performed on an Thermo Fisher Trace ISQ 7000. Gas chromatography (GC) was performed on a Shimadzu GC 2010-pro system equipped with a split-mode capillary injection system and flame ionization detectors. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer from Sichuan University. All reagents and solvents were commercially available and directly used without any further purification.

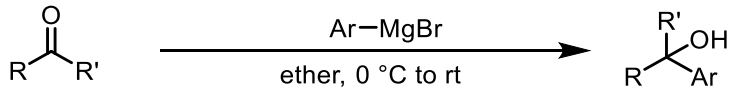
Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial suppliers (Adamas-beta®, Macklin, Energy and so on). Mn powder (Energy-140+325 mesh, 99.9% metals basis). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm. $PhthSCF_2H$ was synthesized according to the literatures.[1,2] $PhSO_2SCF_2H$ was synthesized according to the literature.[3]

2. General Procedure for the Synthesis of Tertiary Alcohols



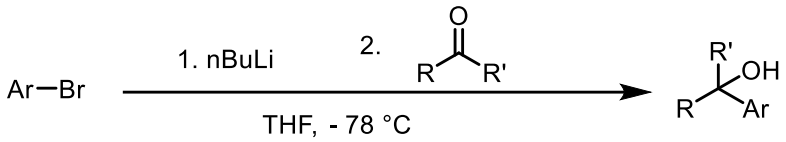
All the compounds are known and prepared according to the literatures.[4-6]

General procedure A with Grignard reaction:[4] for compounds 1a-n



A flame-dried round-bottom flask equipped with a stir bar under argon was charged with 4-methoxyphenylmagnesium bromide solution (1.5 equiv., 1.0 M in 2-MeTHF) in ether. Then the reaction mixture was cooled at 0 °C with an ice bath and the ketone (1.0 equiv.) was added dropwise. The reaction mixture was stirred for 0.5-1.5 h at the same temperature and monitored by TLC until the complete consumption of ketone, followed by quenching with ice water. After drying over anhydrous Na_2SO_4 it was filtered and concentrated in vacuo. The crude product was purified by neutral alumina flash column chromatography to afford the corresponding product.

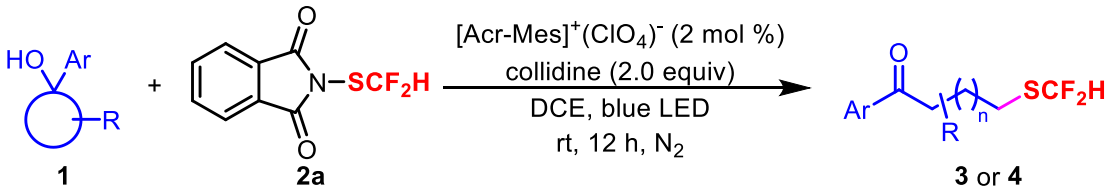
General procedure B with lithiation reaction:[5] for compounds 1o-w



n-Butyllithium (1.6 M solution in hexane, 1.1equiv.) was added slowly to a stirred solution of arylbromide (1.0 equiv.) in THF at -78 °C. The mixture was stirred for 1-2 h at the same temperature and then the corresponding ketone (1 equiv.) was added dropwise via syringe. The mixture was stirred for another 1-1.5 h, followed by quenching with ice water. After drying over anhydrous Na_2SO_4 it was filtered and concentrated in vacuo. The crude product was purified by neutral alumina flash column chromatography to obtain the pure alcohol.

3. Standard Reaction Conditions

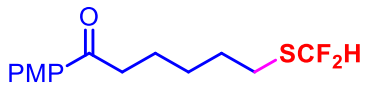
（The Parallel Photoreactor is from 3S Tech in Shanghai, China. https://www.3s-tech.net/en/products/af1.html）



To a 8 mL flame-dried tube equipped with a stir bar were added $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), cycloalkanol **1** (0.20 mmol, 1.0 equiv), and $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv). The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. To these solids, collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M) was added under nitrogen atmosphere. The mixture was stirred under irradiation with blue LEDs for 12 hours. After the reaction was finished, the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate).

4. Characterization Data of Products

6-((Difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one (3a)



3a

3a was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclohexan-1-ol **1a** (41.2 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3a** was isolated by column chromatography as a colorless oil (43.2 mg, 75% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

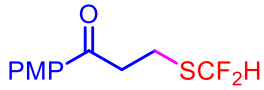
^1H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.79 (t, *J* = 56.4 Hz, 1H), 3.86 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.72 (m, 4H), 1.51 – 1.47 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 162.4, 156.1, 129.3, 129.0, 120.5, 119.7 (t, *J* = 272.2 Hz), 112.7, 54.4, 36.9, 29.0, 27.3, 26.0 (t, *J* = 2.6 Hz), 22.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.68 (d, *J* = 56.6 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{19}O_2F_2S$ 289.1068; found 289.1065.

3-((difluoromethyl)thio)-1-(4-methoxyphenyl)propan-1-one (3b)



3b

3b was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclopropan-1-ol **1b** (32.8 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3b** was isolated by column chromatography as a colorless oil (28.0 mg, 57% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

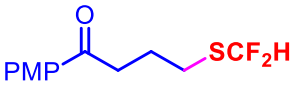
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.87 (t, *J* = 56.1 Hz, 1H), 3.88 (s, 2H), 3.36 (t, *J* = 6.9 Hz, 1H), 3.18 (t, *J* = 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.02 (s), 163.8, 130.3, 129.5, 120.9 (t, *J* = 272.6 Hz), 113.9, 55.5, 39.4, 21.4 (t, *J* = 3.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.67 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{13}O_2F_2S$ 247.0599; found 247.0600.

4-((Difluoromethyl)thio)-1-(4-methoxyphenyl)butan-1-one (3c)



3c

3c was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclobutan-1-ol **1c** (35.6 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3c** was isolated by column chromatography as a colorless oil (35.9 mg, 69% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

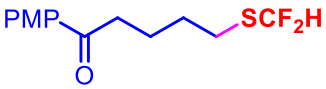
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.82 (t, *J* = 56.3 Hz, 1H), 3.87 (s, 3H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.12 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.6, 163.6, 130.3, 129.9, 120.7 (t, *J* = 272.6 Hz), 113.8, 55.5, 36.3, 26.9, 24.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.45 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{15}O_2F_2S$ 261.0755; found 261.0756.

5-((Difluoromethyl)thio)-1-(4-methoxyphenyl)pentan-1-one (3d)



3d

3d was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclopentan-1-ol **1d** (38.4 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3d** was isolated by column chromatography as a colorless oil (38.9 mg, 71% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

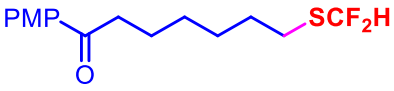
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.81 (t, *J* = 56.3 Hz, 1H), 3.87 (s, 3H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 1.95 – 1.80 (m, 2H), 1.76 (dt, *J* = 14.7, 7.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.2, 163.5, 130.3, 130.0, 120.7 (t, *J* = 272.4 Hz), 113.7, 55.5, 37.4, 29.9, 27.0, 23.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.73 (d, *J* = 56.4 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{17}O_2F_2S$ 275.0912; found 275.0912.

7-((Difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (3e)



3e

3e was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cycloheptan-1-ol **1e** (44.0 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3e** was isolated by column chromatography as a colorless oil (44.7 mg, 74% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

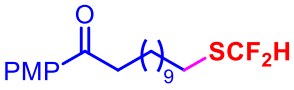
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 56.4 Hz, 1H), 3.87 (s, 3H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.73 (dt, *J* = 14.4, 7.2 Hz, 2H), 1.68 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.51 – 1.42 (m, 2H), 1.42 – 1.35 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.0, 163.4, 130.3, 130.1, 120.8 (t, *J* = 272.4 Hz), 113.7, 55.5, 38.1, 30.0, 28.8, 28.5, 27.1, 24.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.72 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2F_2S$ 303.1225; found 303.1226.

12-((Difluoromethyl)thio)-1-(4-methoxyphenyl)dodecan-1-one (3f)



3f

3f was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclododecan-1-ol **1f** (58.0 mg, 0.20 mmol,

1.0 equiv), PhthSCF$_2$H **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 µL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3f** was isolated by column chromatography as a colorless oil (52.1 mg, 70% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

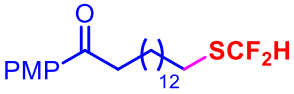
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 56.5 Hz, 1H), 3.87 (s, 3H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.68 (m, 2H), 1.66 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.45 – 1.22 (m, 14H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.3, 163.3, 130.3, 130.2, 120.8 (t, *J* = 272.1 Hz), 113.7, 55.5, 38.3, 30.1, 29.5, 29.4, 29.4, 29.4, 29.0, 28.7, 27.2, 24.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.74 (d, *J* = 56.9 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{31}O_2F_2S$ 373.2007; found 373.2009.

15-((Difluoromethyl)thio)-1-(4-methoxyphenyl)pentadecan-1-one (3g)



3g

3g was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 µmol, 2 mol%), 1-(4-methoxyphenyl)cyclopentadecan-1-ol **1g** (66.4 mg, 0.20 mmol, 1.0 equiv), PhthSCF$_2$H **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 µL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3g** was isolated by column chromatography as a colorless oil (62.0 mg, 68% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

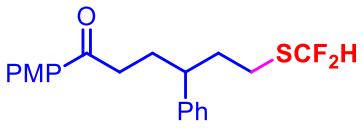
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.79 (t, *J* = 56.5 Hz, 1H), 3.86 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 1.71 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.66 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.47 – 1.12 (m, 20H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.3, 163.3, 130.3, 130.2, 120.8 (t, *J* = 272.3 Hz), 113.7, 55.5, 38.3, 30.1, 29.6, 29.6, 29.5, 29.5, 29.0, 28.7, 27.2, 24.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.74 (d, *J* = 56.4 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{37}O_2F_2S$ 415.2477; found 415.2480.

6-((Difluoromethyl)thio)-1-(4-methoxyphenyl)-4-phenylhexan-1-one (3h)



3h

3h was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)-4-phenylcyclohexan-1-ol **1h** (56.4 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3h** was isolated by column chromatography as a colorless oil (56.8 mg, 78% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

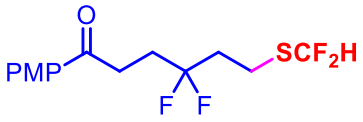
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 7.17 (dd, *J* = 8.1, 1.1 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.74 (t, *J* = 56.4 Hz, 1H), 3.84 (s, 3H), 2.86 – 2.73 (m, 2H), 2.73 – 2.63 (m, 2H), 2.62 – 2.54 (m, 1H), 2.17 – 2.11 (m, 1H), 2.10 – 2.04 (m, 1H), 2.04 – 1.89 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 163.4, 143.1, 130.3, 130.0, 128.8, 127.7, 126.8, 120.8 (t, *J* = 272.5 Hz), 113.6, 55.5, 44.4, 37.3, 36.0, 31.0, 25.4 (t, *J* = 2.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.46 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{23}O_2F_2S$ 365.1381; found 365.1377.

6-((Difluoromethyl)thio)-4,4-difluoro-1-(4-methoxyphenyl)hexan-1-one (3i)



3i

3i was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 4,4-difluoro-1-(4-methoxyphenyl)cyclohexan-1-ol **1i** (48.4 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3i** was isolated by column chromatography as a colorless oil (48.6 mg, 75% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

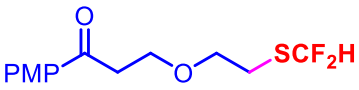
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.83 (t, *J* = 55.8 Hz, 1H), 3.88 (s, 3H), 3.26 – 3.12 (m, 2H), 3.07 – 2.84 (m, 2H), 2.60 – 2.04 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 163.7, 130.3, 129.6, 123.5 (t, *J* = 241.8 Hz), 120.4 (t, *J* = 273.5 Hz), 113.8, 55.53, 38.5 (t, *J* = 25.5 Hz), 30.9 (t, *J* = 24.8 Hz), 30.6 (t, *J* = 3.2 Hz), 19.9 – 19.5 (m).

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.99 (d, *J* = 55.2 Hz), -100.76 – -101.11 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2F_4S$ 325.0880; found 325.0880.

3-(2-((Difluoromethyl)thio)ethoxy)-1-(4-methoxyphenyl)propan-1-one (3j)



3j

3j was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 4-(4-methoxyphenyl)tetrahydro-*2H*-pyran-4-ol **1j** (41.6 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3j** was isolated by column chromatography as a colorless oil (38.9 mg, 67% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

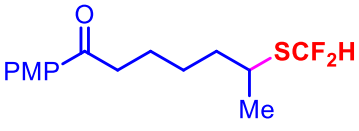
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.87 (t, *J* = 56.7 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 3.72 (t, *J* = 6.3 Hz, 2H), 3.21 (t, *J* = 6.5 Hz, 2H), 2.95 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 163.6, 130.4, 130.0, 120.7 (t, *J* = 272.5 Hz), 113.8, 70.8, 66.5, 55.5, 38.3, 27.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.73 (d, *J* = 56.6 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{17}O_3F_2S$ 291.0861; found 291.0862.

6-((Difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (3k)



3k

3k was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)-2-methylcyclohexan-1-ol **1k** (44.0 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol,

2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3k** was isolated by column chromatography as a colorless oil (41.1 mg, 68% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

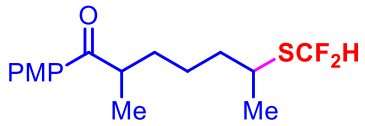
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.5 Hz, 2H), 6.93 – 6.73 (m, 2H), 6.74 (t, *J* = 56.5 Hz, 1H), 3.87 (s, 3H), 3.26 (h, *J* = 6.8 Hz, 1H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.66 (ddd, *J* = 15.9, 11.3, 7.9 Hz, 2H), 1.51 (dd, *J* = 15.4, 8.3 Hz, 2H), 1.39 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 163.4, 130.3, 130.1, 121.0 (t, *J* = 271.8 Hz), 113.7, 55.5, 38.6, 38.0, 37.3, 26.5, 24.0, 22.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -90.27 – -92.76 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2F_2S$ 303.1225; found 303.1226.

6-((Difluoromethyl)thio)-1-(4-methoxyphenyl)-2-methylheptan-1-one (3l)



3l

3l was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)-2,6-dimethylcyclohexan-1-ol **1l** (46.8 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3l** was isolated by column chromatography as a colorless oil (41.1 mg, 65% yield, *dr* = 1:1).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

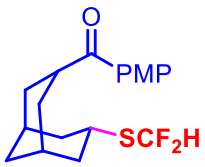
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.82 (t, *J* = 56.6 Hz, 1H), 3.87 (s, 3H), 3.43 (dd, *J* = 13.1, 6.6 Hz, 1H), 3.22 (ddd, *J* = 20.9, 13.7, 6.8 Hz, 1H), 1.91 – 1.75 (m, 1H), 1.49 – 1.37 (m, 2H), 1.35 (dd, *J* = 6.8, 2.9 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 202.8, 163.4, 130.5, 129.6, 121.0 (t, *J* = 271.9 Hz), 113.8, 55.5, 40.1, 38.6, 37.6, 33.2, 24.7, 22.8, 17.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -91.44 (ddd, *J* = 90.7, 56.6, 23.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{23}O_2F_2S$ 317.1381; found 317.1382.

(7-((Difluoromethyl)thio)bicyclo[3.3.1]nonan-3-yl)(4-methoxyphenyl)methanone (3m)



3m

3m was prepared according to the general procedure outlined above, using [Acr-Mes]$^{+}$(ClO$_4$)$^{-}$ (1.6 mg, 4.0 μmol, 2 mol%), 2-(4-methoxyphenyl)adamantan-2-ol**1m** (51.6 mg, 0.20 mmol, 1.0 equiv), PhthSCF$_2$H **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3m** was isolated by column chromatography as a colorless oil (44.9 mg, 66% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

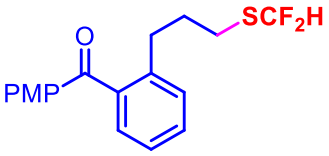
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 56.6 Hz, 1H), 5.25 (tt, *J* = 7.0, 4.5 Hz, 1H), 4.41 – 4.08 (m, 1H), 3.86 (s, 3H), 2.27 (dt, *J* = 15.1, 7.3 Hz, 2H), 2.18 (d, *J* = 11.8 Hz, 2H), 2.08 (dd, *J* = 11.9, 2.1 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.67 (td, *J* = 13.2, 4.3 Hz, 2H), 1.62 (d, *J* = 13.0 Hz, 1H), 1.50 – 1.41 (m, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.9, 163.4, 131.6, 122.9, 121.0 (t, *J* = 271.9 Hz), 113.7, 67.1, 55.5, 40.0, 34.4, 33.9, 30.8, 27.4.

^{19}F NMR (565 MHz, CDCl$_3$) δ -90.11 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: [M+H]$^{+}$ Calcd for C$_{18}$H$_{23}$O$_2$F$_2$S 341.1381; found 341.1383.

(2-(3-((Difluoromethyl)thio)propyl)phenyl)(4-methoxyphenyl)methanone (3n)



3n

3n was prepared according to the general procedure outlined above, using [Acr-Mes]$^{+}$(ClO$_4$)$^{-}$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol **1n** (50.8 mg, 0.20 mmol, 1.0 equiv), PhthSCF$_2$H **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **3n** was isolated by column chromatography as a colorless oil (41.7 mg, 62% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

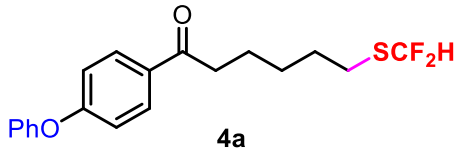
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.39 (m, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.20 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.74 (t, *J* = 56.5 Hz, 1H), 3.88 (s, 3H), 2.74 (dt, *J* = 10.5, 7.5 Hz, 4H), 2.03 – 1.78 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.1, 163.8, 139.6, 139.0, 132.6, 130.6, 130.1, 130.0, 128.4, 125.6, 120.7 (t, *J* = 272.5 Hz), 113.7, 55.6, 32.1, 31.9, 26.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.70 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{19}O_2F_2S$ 337.1068; found 337.1070.

6-((Difluoromethyl)thio)-1-(4-phenoxyphenyl)hexan-1-one (4a)



4a

4a was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-phenoxyphenyl)cyclohexan-1-ol **1o** (53.6 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4a** was isolated by column chromatography as a colorless oil (50.4 mg, 72% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

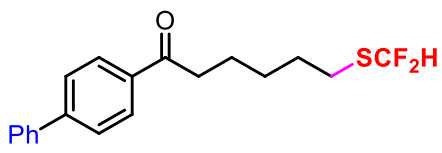
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 56.4 Hz, 1H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 1.80 – 1.67 (m, 4H), 1.50 (dq, *J* = 15.3, 7.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.7, 161.9, 155.5, 131.7, 130.3, 130.1, 124.6, 120.7 (t, *J* = 272.4 Hz), 120.2, 117.3, 38.1, 30.0, 28.4, 27.0, 23.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.68 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}O_2F_2S$ 351.1225; found 351.1226.

1-([1,1'-Biphenyl]-4-yl)-6-((difluoromethyl)thio)hexan-1-one (4b)



4b

4b was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-([1,1'-biphenyl]-4-yl)cyclohexan-1-ol **1p** (50.4 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4b** was isolated by column chromatography as a colorless oil (42.7 mg, 64% yield).

TLC R_f = 0.80 (Hexane/EtOAc = 10:1, v/v).

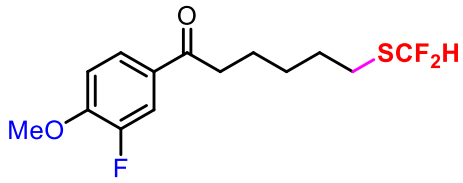
^1H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 56.4 Hz, 1H), 3.02 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.94 – 1.70 (m, 4H), 1.57 – 1.49 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 145.7, 139.9, 135.7, 129.0, 128.7, 128.2, 127.3, 127.3, 120.8 (t, *J* = 272.4 Hz), 38.3, 30.1, 28.4, 27.0, 23.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.66 (d, *J* = 56.7 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}OF_2S$ 335.1276; found 335.1277.

6-((Difluoromethyl)thio)-1-(3-fluoro-4-methoxyphenyl)hexan-1-one (4c)



4c

4c was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(3-fluoro-4-methoxyphenyl)cyclohexan-1-ol **1q** (44.8 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4c** was isolated by column chromatography as a colorless oil (45.9 mg, 75% yield).

TLC R_f = 0.70 (Hexane/EtOAc = 10:1, v/v).

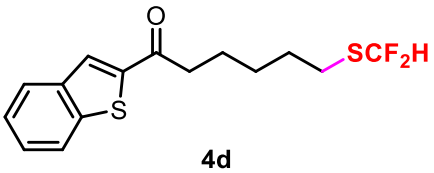
^1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.69 (dd, *J* = 11.9, 2.0 Hz, 1H), 6.99 (t, *J* = 8.3 Hz, 1H), 6.80 (t, *J* = 56.4 Hz, 1H), 3.95 (s, 3H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.74 (tt, *J* = 15.0, 7.4 Hz, 4H), 1.55 – 1.43 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.7, 152.3 (d, *J* = 152.7 Hz), 151.5 (d, *J* = 84.3 Hz), 130.3 (d, *J* = 5.1 Hz), 125.3 (d, *J* = 3.2 Hz), 120.7 (t, *J* = 272.4 Hz), 115.7 (d, *J* = 19.0 Hz), 112.3 (d, *J* = 1.5 Hz), 56.3, 37.9, 29.4, 28.3, 27.0, 23.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.69 (d, *J* = 56.4 Hz), -133.21 – -138.49 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}O_2F_3S$ 307.0974; found 307.0972.

1-(Benzo[b]thiophen-2-yl)-6-((difluoromethyl)thio)hexan-1-one (4d)



4d

4d was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(benzo[b]thiophen-2-yl)cyclohexan-1-ol **1r** (46.4 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4d** was isolated by column chromatography as a colorless oil (36.4 mg, 58% yield).

TLC R_f = 0.60 (Hexane/EtOAc = 10:1, v/v).

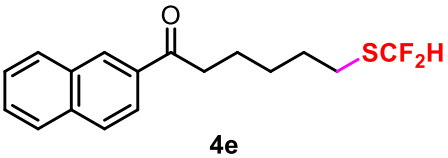
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.89 (dd, *J* = 10.8, 8.1 Hz, 2H), 7.52 – 7.44 (m, 1H), 7.43 – 7.38 (m, 1H), 6.81 (t, *J* = 56.3 Hz, 1H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.83 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.56 – 1.51 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 143.7, 142.5, 139.1, 128.9, 127.4, 125.9, 125.0, 123.0, 120.7 (t, *J* = 272.5 Hz), 38.9, 30.0, 28.3, 27.0, 24.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.67 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}OF_2S_2$ 315.0683; found 315.0685.

6-((Difluoromethyl)thio)-1-(naphthalen-2-yl)hexan-1-one (4e)



4e

4e was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(naphthalen-2-yl)cyclohexan-1-ol **1s** (45.2 mg, 0.20 mmol, 1.0

equiv), PhthSCF$_2$H **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 µL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4e** was isolated by column chromatography as a colorless oil (33.3 mg, 54% yield).

TLC R_f = 0.80 (Hexane/EtOAc = 10:1, v/v).

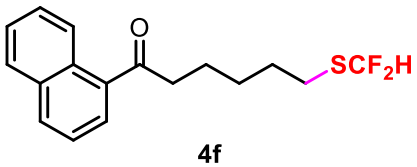
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.03 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 11.4, 8.4 Hz, 2H), 7.61 (dd, *J* = 10.9, 3.9 Hz, 1H), 7.56 (dd, *J* = 11.1, 3.8 Hz, 1H), 6.81 (t, *J* = 56.4 Hz, 1H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.83 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.58 – 1.51 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.0, 135.6, 134.3, 132.5, 129.6, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 120.7 (t, *J* = 272.4 Hz), 38.3, 30.1, 28.4, 27.0, 23.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.66 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}OF_2S$ 309.1119; found 309.1121.

6-((Difluoromethyl)thio)-1-(naphthalen-1-yl)hexan-1-one (4f)



4f

4f was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 µmol, 2 mol%), 1-(naphthalen-1-yl)cyclohexan-1-ol **1t** (45.2 mg, 0.20 mmol, 1.0 equiv), PhthSCF$_2$H **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 µL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4f** was isolated by column chromatography as a colorless oil (32.0 mg, 52% yield).

TLC R_f = 0.80 (Hexane/EtOAc = 10:1, v/v).

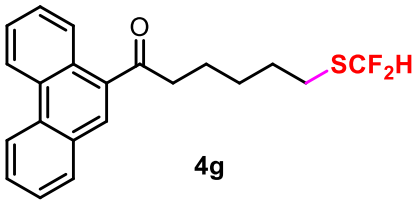
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.91 – 7.74 (m, 2H), 7.65 – 7.42 (m, 3H), 6.80 (t, *J* = 56.4 Hz, 1H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 1.83 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.74 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.56 – 1.47 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.5, 136.2, 134.0, 132.5, 130.1, 128.5, 127.9, 127.2, 126.5, 125.7, 124.4, 120.7 (t, *J* = 272.4 Hz), 41.9, 30.0, 28.3, 27.0, 24.0.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.69 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}OF_2S$ 309.1119; found 309.1120.

6-((Difluoromethyl)thio)-1-(phenanthren-9-yl)hexan-1-one (4g)



4g

4g was prepared according to the general procedure outlined above, using $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(phenanthren-9-yl)cyclohexan-1-ol **1u** (55.2 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), collidine (52.8 μL, 0.40 mmol, 2.0 equiv) and DCE (2.0 mL, 0.1 M). After the reaction was finished, the product **4g** was isolated by column chromatography as a colorless oil (39.4 mg, 55% yield).

TLC R_f = 0.80 (Hexane/EtOAc = 10:1, v/v).

^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.5 Hz, 1H), 8.68 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.72 – 7.56 (m, 3H), 6.81 (t, *J* = 56.4 Hz, 1H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 1.87 (dt, *J* = 15.2, 7.5 Hz, 2H), 1.76 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.60 – 1.48 (m, 2H).

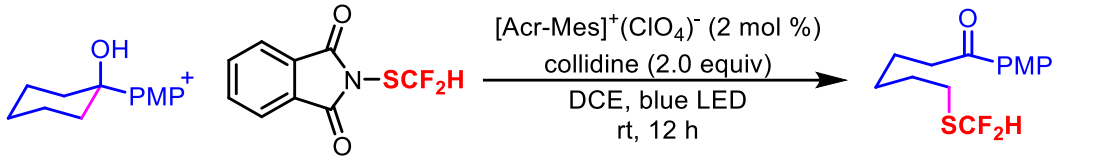
^{13}C NMR (151 MHz, $CDCl_3$) δ 204.7, 135.5, 131.8, 130.8, 130.0, 129.7, 129.0, 128.8, 128.4, 127.5, 127.2, 127.2, 126.5, 122.9, 122.7, 120.7 (t, *J* = 272.4 Hz), 42.0, 30.0, 28.3, 27.0 (t, *J* = 3.1 Hz), 24.1.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.65 (d, *J* = 56.7 Hz).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{20}OF_2NaS$ 381.1095; found 381.1091.

5. Further Functionalization

(a) Large-scale (2.0 mmol) experiment:

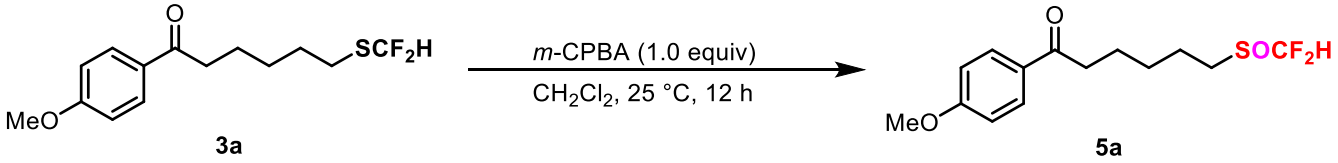


1a: 2 mmol **2a**: 3.0 mmol **3a**: 71% yield, 409.0 mg

To a 100 mL flame-dried Schlenk tube equipped with a stir bar were added $[Acr\text{-}Mes]^+(ClO_4)^-$ (16.0 mg, 40.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclohexan-1-ol **1a** (412.0 mg, 2.0 mmol, 1.0 equiv), and PhthSCF$_2$H **2a** (687.4 mg, 3.0 mmol, 1.5 equiv). The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. To these solids, collidine (528.4 μL, 4.0 mmol, 2.0 equiv) and DCE (20.0 mL, 0.1 M) was added under nitrogen atmosphere. The mixture was stirred under irradiation with blue LEDs for 12 hours. After the reaction was finished, the crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate) to get the product **3a** as a colorless oil (409 mg, 71% yield).

(b) Synthetic transformations of products:

6-((Difluoromethyl)sulfinyl)-1-(4-methoxyphenyl)hexan-1-one (5a)



3a **5a**

A dried tube was added with 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one **3a** (28.8 mg, 0.10 mmol, 1.0 equiv) and *m*-CPBA (57.7 mg, 0.10 mmol, 1.0 equiv, assay ca. 30%). Then dry DCM (4 mL) was added. The tube was sealed with a rubber septum and the suspension was stirred at room temperature for 12 h. Then, the reaction mixture was diluted with DCM (10 mL), washed with a saturated Na_2SO_3 aqueous solution (10 mL), a saturated $NaHCO_3$ aqueous solution (10 mL) and brine (10 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford the products **5a** as a colorless oil (23.1 mg, 76% yield).

TLC R_f = 0.50 (Hexane/EtOAc = 5:1, v/v).

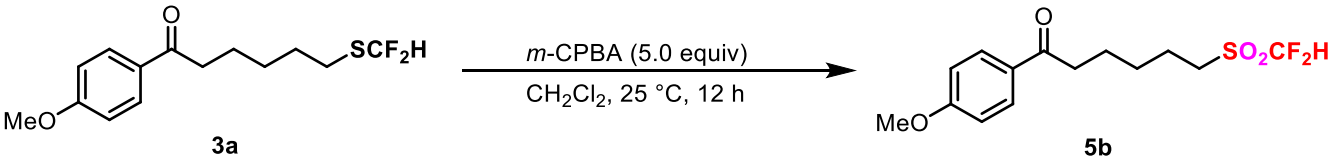
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.30 (t, *J* = 54.8 Hz, 1H), 3.87 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.94 – 2.71 (m, 2H), 1.94 – 1.82 (m, 2H), 1.86 – 1.70 (m, 2H), 1.74 – 1.44 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.4, 163.5, 130.3, 129.9, 120.5 (dd, *J* = 290.4, 284.9 Hz), 113.8, 55.5, 47.1, 37.6, 28.4, 23.7, 21.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -120.81 – -122.52 (m).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{19}O_3F_2S$ 305.1017; found 305.1017.

6-((Difluoromethyl)sulfonyl)-1-(4-methoxyphenyl)hexan-1-one (5b)



3a **5b**

A dried tube was added with 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one **3a** (28.8 mg, 0.10 mmol, 1.0 equiv) and *m*-CPBA (288.5 mg, 0.50 mmol, 5.0 equiv, assay ca. 30%). Then dry DCM (4 mL) was added. The tube was sealed with a rubber septum and the suspension was stirred at room temperature for 12 h. Then, the reaction mixture was diluted with DCM (10 mL), washed with a saturated Na_2SO_3 aqueous solution (10 mL), a saturated $NaHCO_3$ aqueous solution (10 mL) and brine (10 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford the products **5b** as a colorless oil (27.8 mg, 87% yield).

TLC R_f = 0.40 (Hexane/EtOAc = 5:1, v/v).

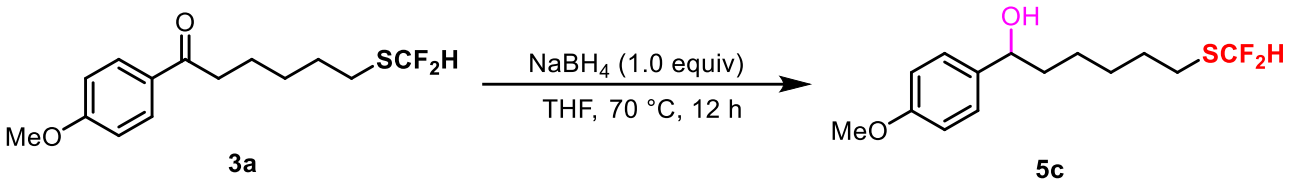
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 9.1 Hz, 2H), 6.88 (d, *J* = 9.1 Hz, 2H), 6.11 (t, *J* = 52.7 Hz, 1H), 3.79 (s, 3H), 3.38 – 2.96 (m, 2H), 2.58 (t, *J* = 7.3 Hz, 2H), 1.98 (dt, *J* = 15.7, 7.8 Hz, 2H), 1.85 – 1.68 (m, 2H), 1.61 (dt, *J* = 15.5, 7.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 157.3, 144.1, 122.3, 115.1 (t, *J* = 286.1 Hz), 114.5, 55.6, 47.5, 33.7, 27.9, 24.1, 20.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -122.67 (d, *J* = 52.8 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{19}O_4F_2S$ 321.0967; found 321.0961.

6-((Difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-ol (5c)



3a 5c

To a 4 mL reaction vial equipped with a stir bar was added 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one **3a** (28.8 mg, 0.10 mmol, 1.0 equiv) in dry THF (1.0 mL). Then $NaBH_4$ (3.8 mg, 0.10 mmol, 1.0 equiv) was added and the reaction was allowed to run for 12 hours at 70 °C in an oil bath. After this time, the reaction was quenched with water, and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired product **5c** as a colorless oil (26.1 mg, 90% yield).

TLC R_f = 0.60 (Hexane/EtOAc = 10:1, v/v).

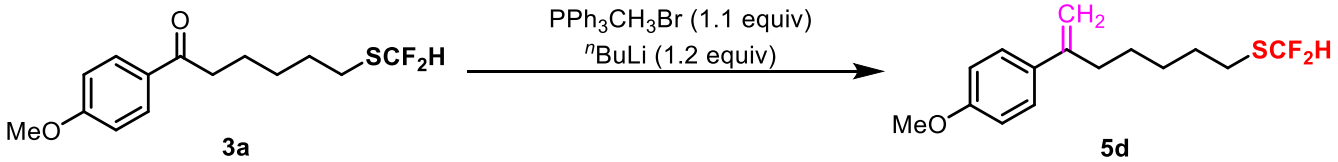
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.78 (t, *J* = 56.4 Hz, 1H), 4.59 (t, *J* = 6.7 Hz, 1H), 3.80 (s, 3H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.73 (m, 1H), 1.75 – 1.58 (m, 3H), 1.50 – 1.26 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 136.9, 127.1, 120.8 (t, *J* = 272.4 Hz), 113.9, 74.1, 55.3, 38.7, 30.0, 28.5, 27.1, 25.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.71 (d, *J* = 56.3 Hz).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{20}O_2F_2SNa$ 313.1044; found 313.1040.

(difluoromethyl)(6-(4-methoxyphenyl)hept-6-en-1-yl)sulfane (5d)



3a 5d

To a 10 mL reaction vial equipped with a stir bar was added methylphosphonium bromide (40.0 mg, 0.11 mmol, 1.1 equiv), and dry THF (1 mL). The solution was subjected to an ice bath, and then ^{n}BuLi (0.1 mL, 1.2 M in hexanes, 1.2 equiv) was added dropwise. The reaction mixture was allowed to stir for 1 h at 0 °C. Lastly, 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one **3a** (28.8 mg, 0.10 mmol, 1.0 equiv) dissolved in 0.5 mL of THF was added. The reaction mixture was allowed to warm to rt, and then heated to 70 °C in an oil bath for 12 h. After this

time, the reaction was quenched with water, and extracted with Et_2O (3 X 10 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed *in vacuo* by rotary evaporation. Further purification was accomplished by SiO_2 column chromatography (gradient Hexane/EtOAc) to give the desired product **5d** as a colorless oil (19.7 mg, 69% yield).

TLC R_f = 0.80 (Hexane/EtOAc = 10:1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.78 (t, *J* = 56.4 Hz, 2H), 5.20 (d, *J* = 1.4 Hz, 1H), 4.97 (d, *J* = 1.3 Hz, 1H), 3.81 (s, 3H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 1.66 (dt, *J* = 14.5, 7.4 Hz, 2H), 1.52 – 1.36 (m, 4H).

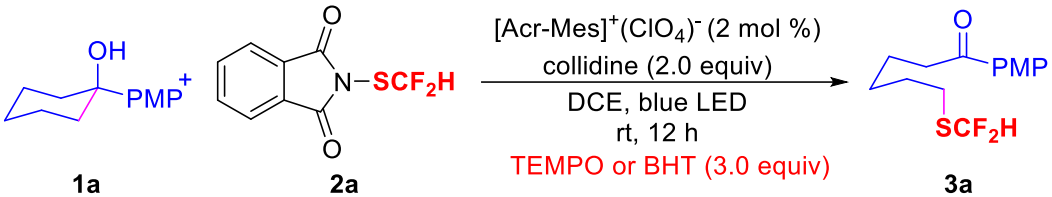
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 147.6, 133.6, 127.2, 120.8 (t, *J* = 272.1 Hz), 113.6, 110.9, 55.3, 35.2, 29.9, 28.3, 27.6, 27.1 (t, *J* = 2.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -92.73 (d, *J* = 56.4 Hz).

HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{21}OF_2S$ 287.1276; found 287.1273.

6. Mechanistic Studies

(a) Radical inhibition experiment:

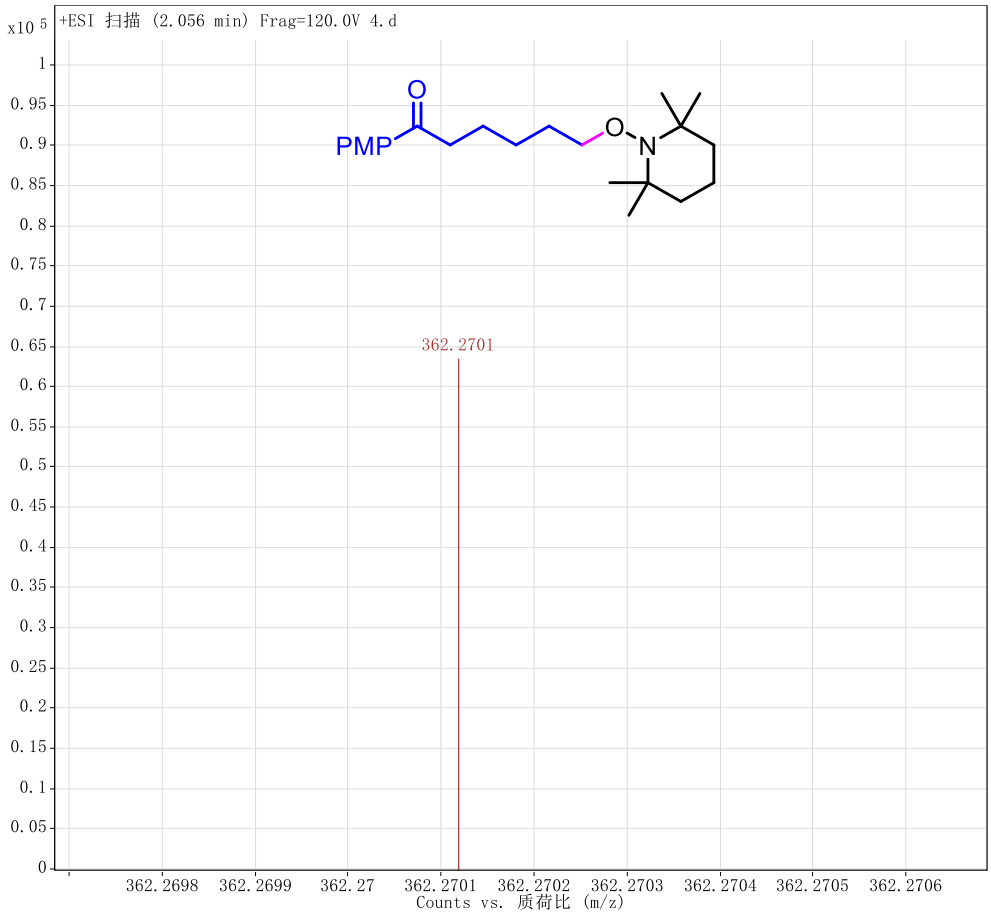


1a **2a** **3a**

not observed

To a 10 mL flame-dried Schlenk tube equipped with a stir bar were added $[Acr\text{-}Mes]^+(ClO_4)^-$ (1.6 mg, 4.0 μmol, 2 mol%), 1-(4-methoxyphenyl)cyclohexan-1-ol **1a** (41.2 mg, 0.20 mmol, 1.0 equiv), $PhthSCF_2H$ **2a** (68.7 mg, 0.30 mmol, 1.5 equiv), and TEMPO or BHT (0.60 mmol, 3.0 equiv). The flask was sealed with a cap containing a TFE-lined silicone septum and placed under a N_2 atmosphere through evacuating and purging with nitrogen three times. To these solids, collidine (39.6 μL, 0.30 mmol, 1.5 equiv) and DCE (2.0 mL, 0.1 M) was added under nitrogen atmosphere. The mixture was stirred under irradiation with blue LEDs for 12 hours. After the reaction was finished, then the reaction system was subjected to GC-MS for analysis, and no corresponding product **3a** was observed. And the TEMPO-radical adduct was observed by HRMS.

$[M+H]^+$ Calcd for $C_{22}H_{36}O_3N$ 362.2690; found 362.2701.



7. References

[1] Zhu, D.-H.; Gu, Y.; Lu, L.; Shen, Q.-L. *N*-Difluoromethylthiophthalimide: A Shelf-Stable, Electrophilic Reagent for Difluoromethylthiolation. *J. Am. Chem. Soc.* **2015**, *137*, 10547−10553.

[2] Zhu, D.-H.; Hong, X.; Li, D.-Z.; Lu, L.; Shen, Q.-L. A Two-Step, One-Pot, and Multigram-Scale Synthesis of *N*-Difluoromethylthiophthalimide. *Org. Process Res. Dev.* **2017**, *21*, 1383−1387.

[3] Zhu, D.-H.; Shao, X.-X.; Hong, X.; Lu, L.; Shen, Q.-L. $PhSO_2SCF_2H$: A Shelf-Stable, Easily Scalable Reagent for Radical Difluoromethylthiolation. *Angew. Chem. Int. Ed.* **2016**, *55*, 15807−15811.

[4] Huang, L.; Ji, T.; Rueping, M., Remote Nickel-Catalyzed Cross-Coupling Arylation via Proton-Coupled Electron Transfer-Enabled C–C Bond Cleavage. *J. Am. Chem. Soc.* **2020**, *142*, 3532-3539.

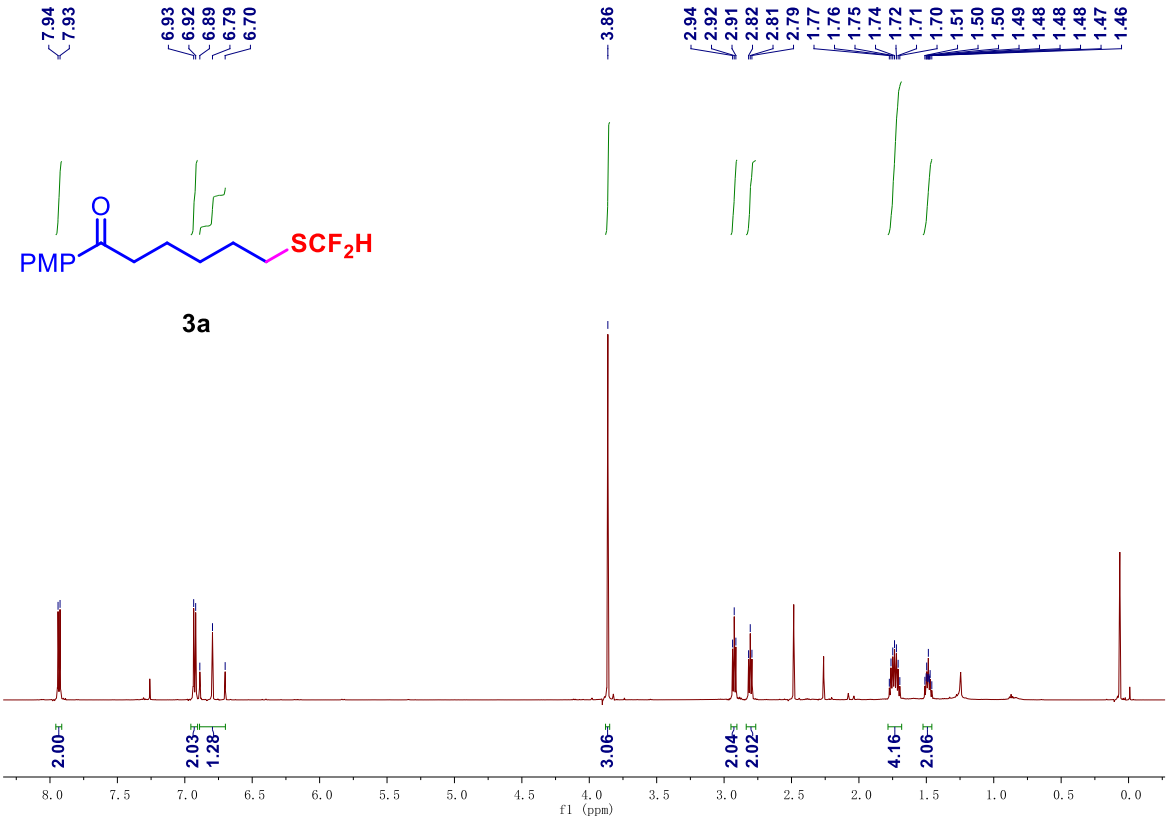
[5] Ji T.-F.; Chen, X.-Y.; Huang, L.; Rueping, M. Remote Trifluoromethylthiolation Enabled by Organophotocatalytic C−C Bond Cleavage. *Org. Lett.* **2020**, *22*, 2579−2583.

[6] Yayla, H. G.; Wang, H.-J.; Tarantino, K. T.; Orbe, H. S.; Knowles, R. R. Catalytic Ring-Opening of Cyclic Alcohols Enabled by PCET Activation of Strong O−H Bonds. *J. Am. Chem. Soc.* **2016**, *138*, 10794−10797.

8. NMR Spectra

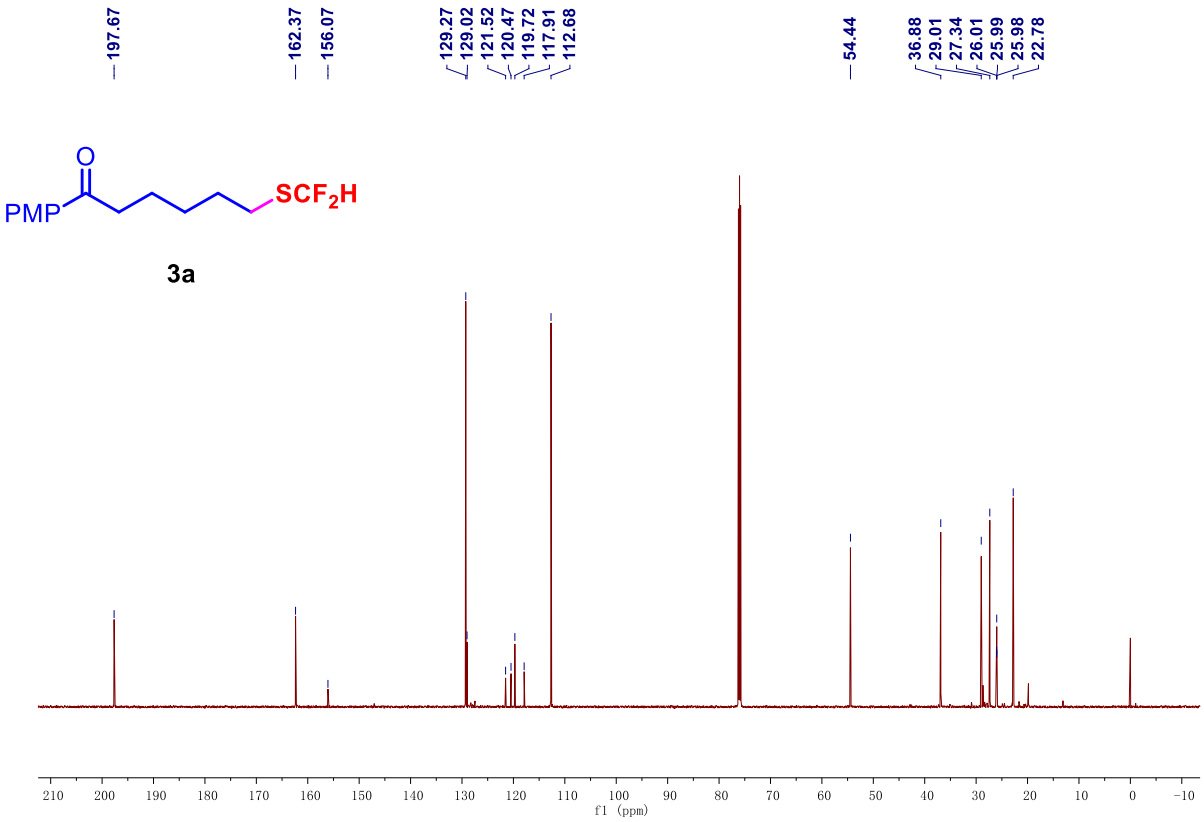
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one (**3a**)

600 MHz, $CDCl_3$, 23 ℃



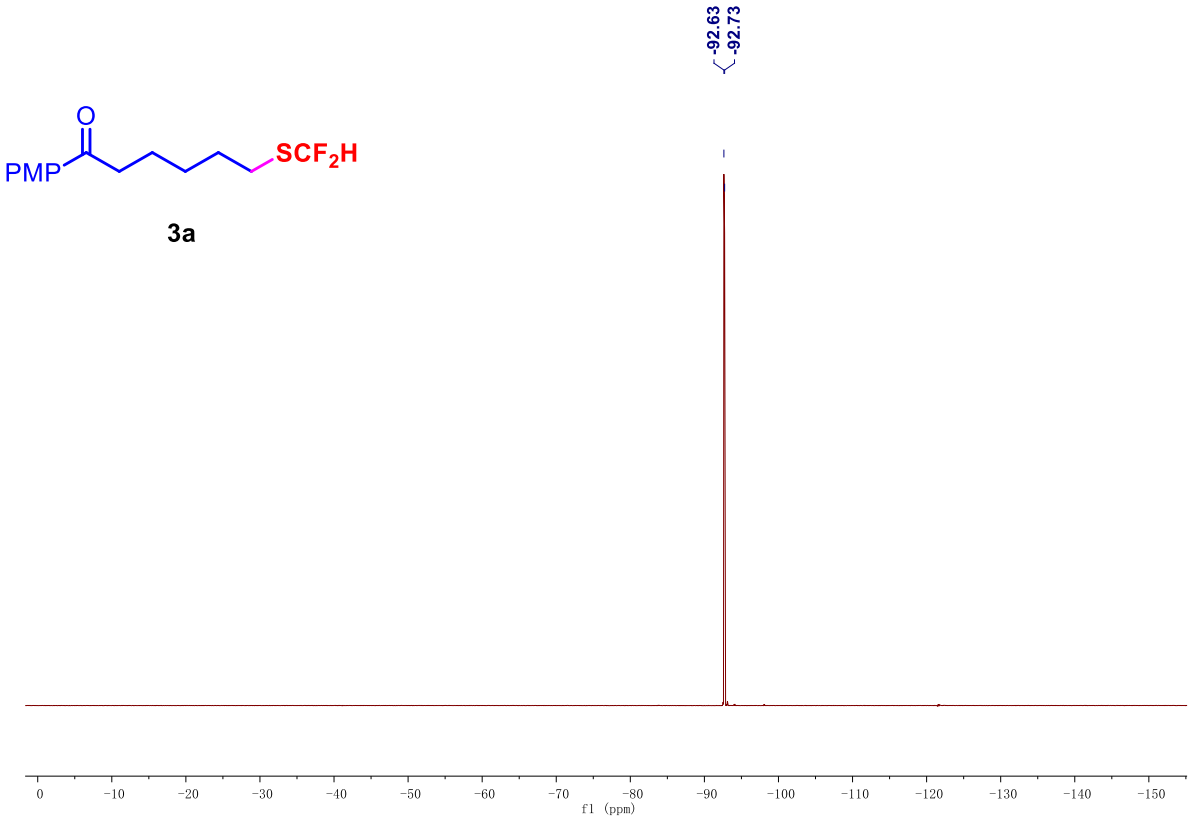
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one (**3a**)

151 MHz, $CDCl_3$, 23 ℃



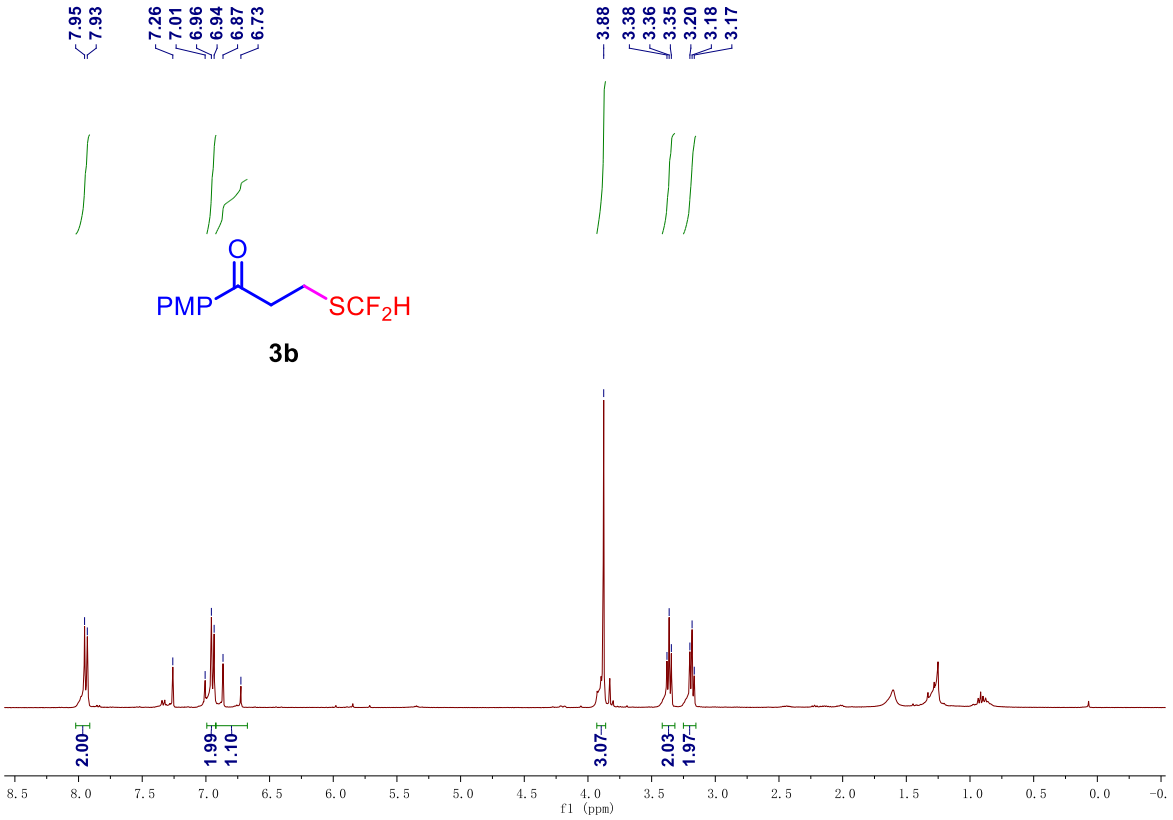
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-one (**3a**)

565 MHz, $CDCl_3$, 23 ℃



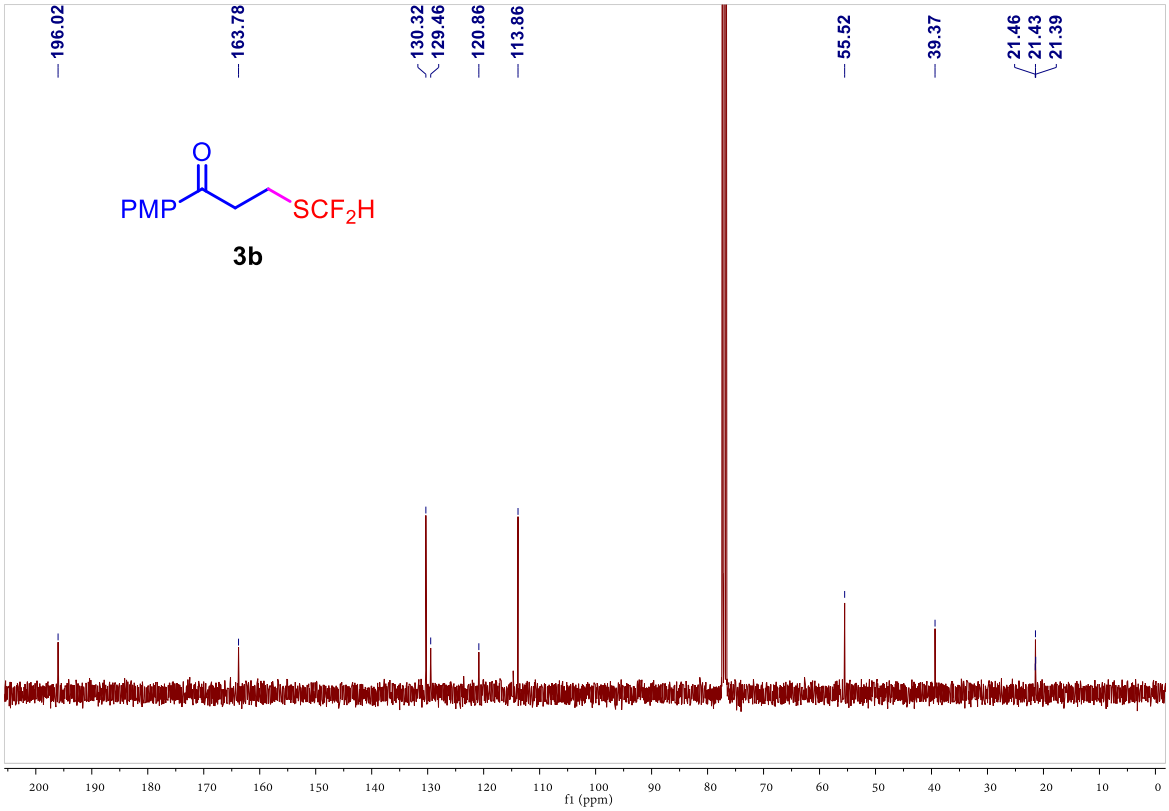
^{1}H NMR spectrum of 3-((difluoromethyl)thio)-1-(4-methoxyphenyl)propan-1-one (**3b**)

600 MHz, $CDCl_3$, 23 ℃



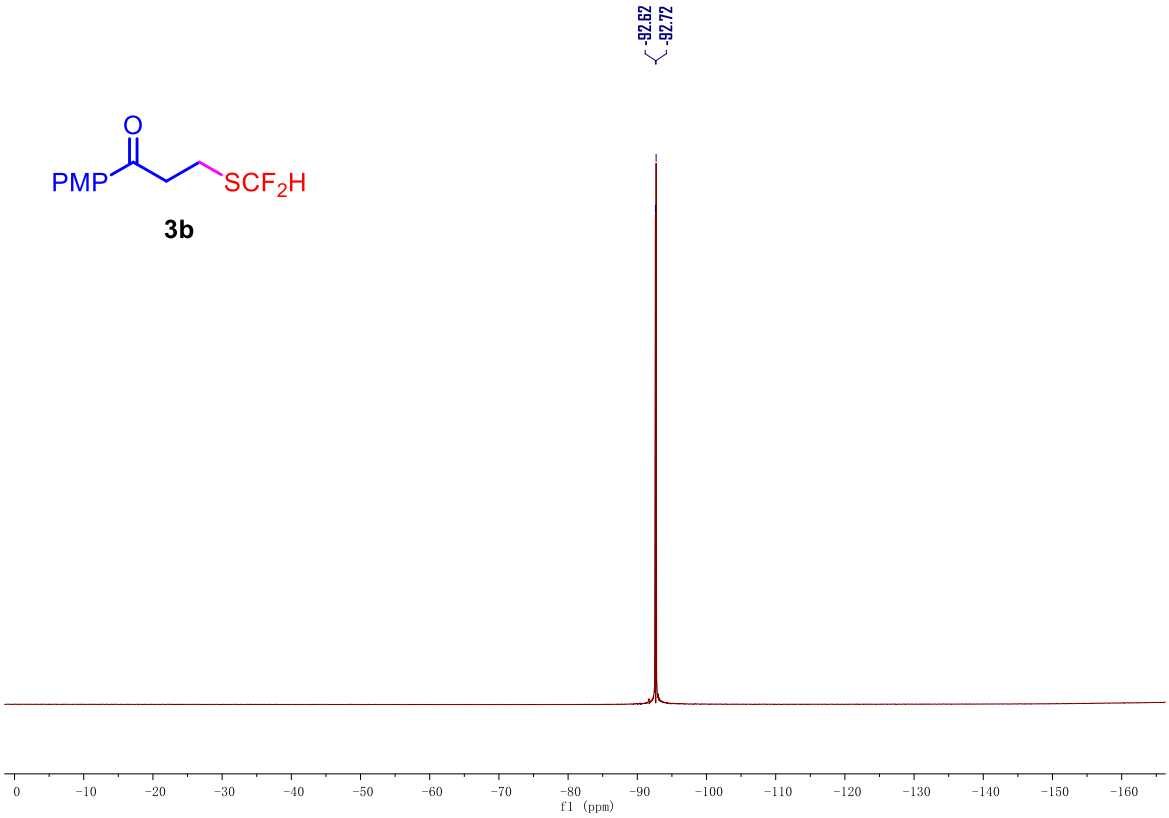
^{13}C NMR spectrum of 3-((difluoromethyl)thio)-1-(4-methoxyphenyl)propan-1-one (**3b**)

151 MHz, $CDCl_3$, 23 ℃



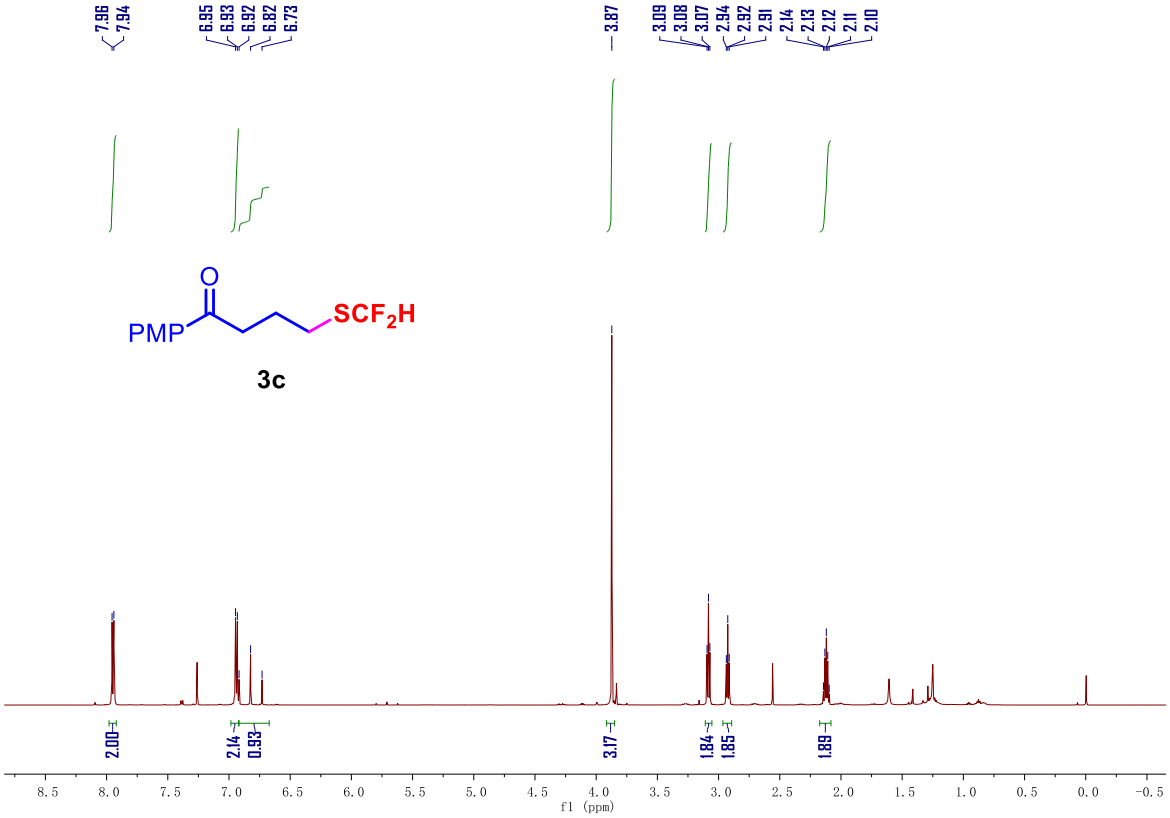
^{19}F NMR spectrum of 3-((difluoromethyl)thio)-1-(4-methoxyphenyl)propan-1-one (**3b**)

600 MHz, $CDCl_3$, 23 ℃



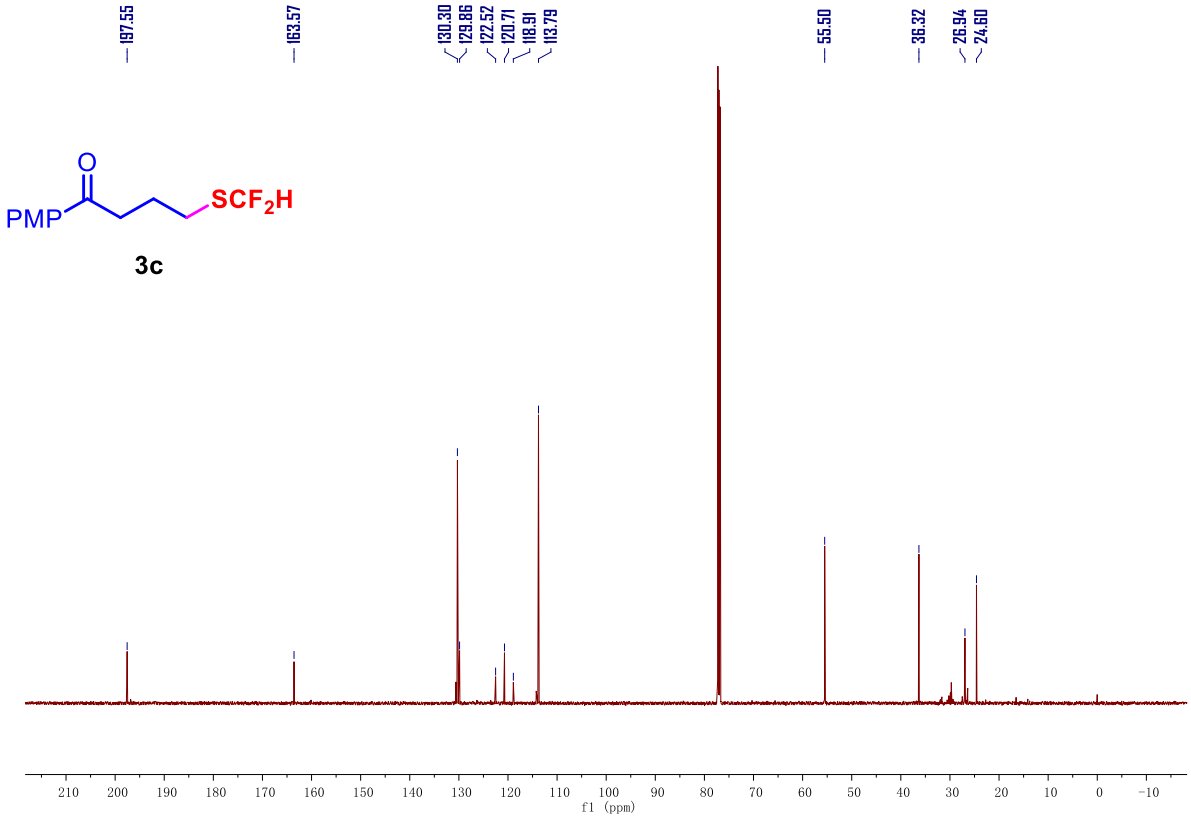
^{1}H NMR spectrum of 4-((difluoromethyl)thio)-1-(4-methoxyphenyl)butan-1-one (**3c**)

565 MHz, $CDCl_3$, 23 ℃



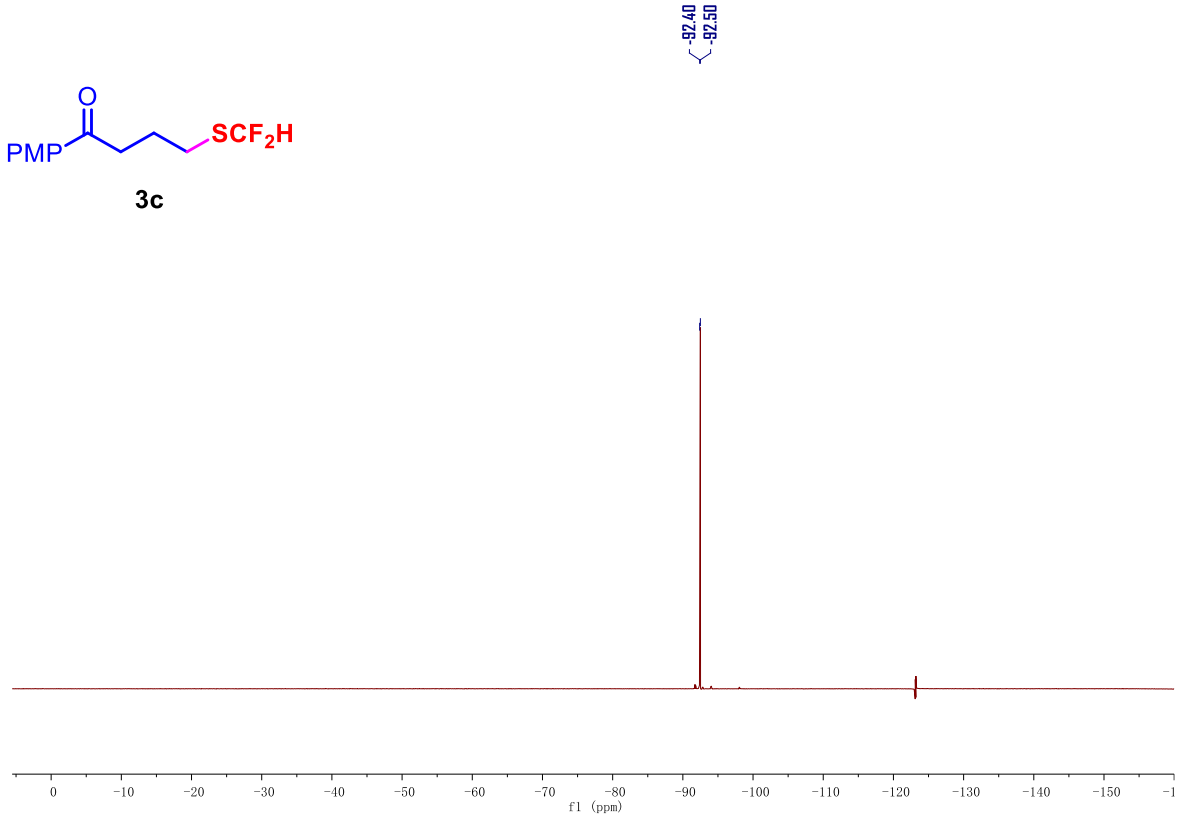
^{13}C NMR spectrum of 4-((difluoromethyl)thio)-1-(4-methoxyphenyl)butan-1-one (**3c**)

151 MHz, $CDCl_3$, 23 ℃



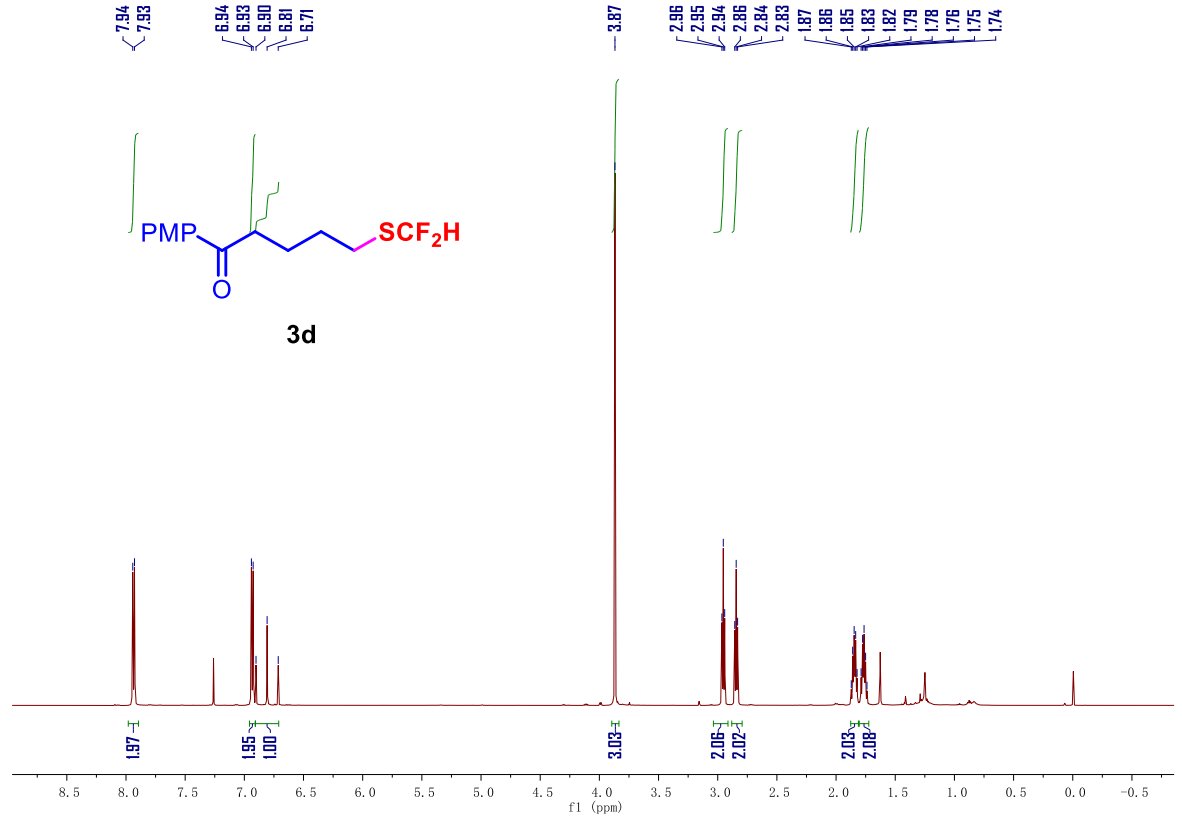
^{19}F NMR spectrum of 4-((difluoromethyl)thio)-1-(4-methoxyphenyl)butan-1-one (**3c**)

565 MHz, $CDCl_3$, 23 ℃



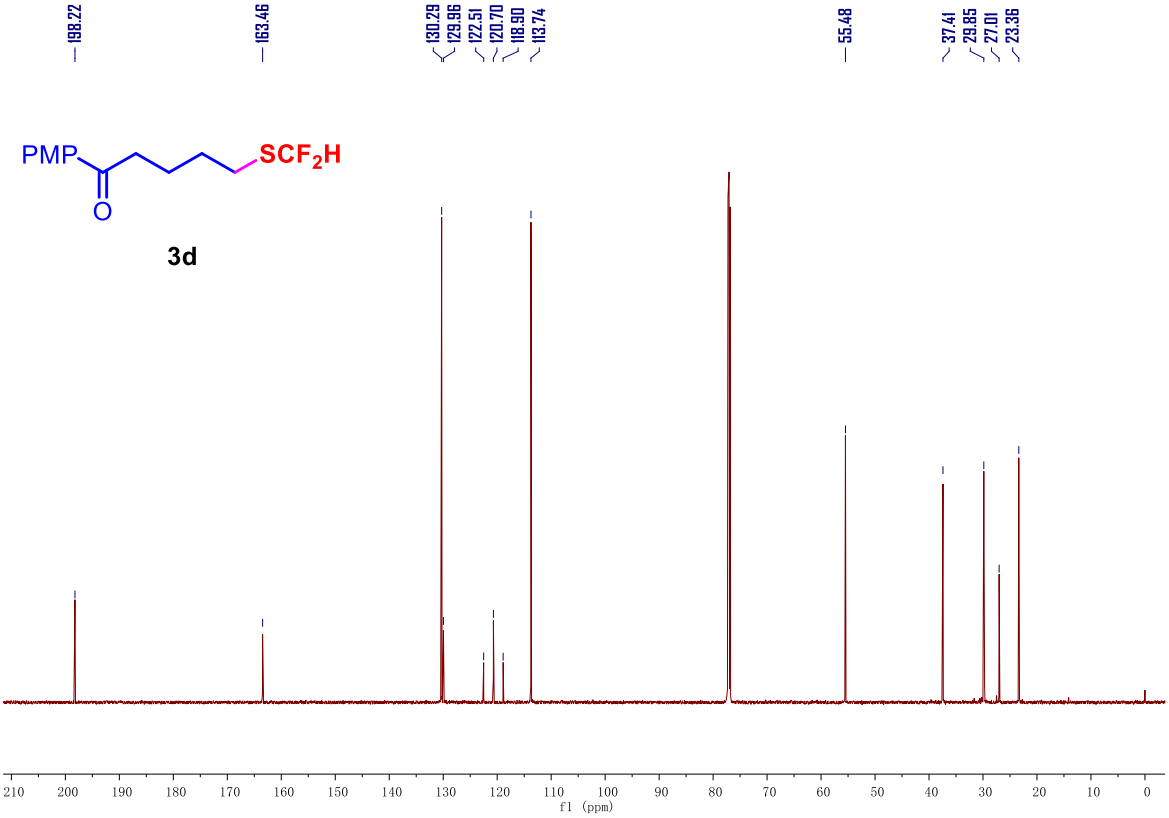
^{1}H NMR spectrum of 5-((difluoromethyl)thio)-1-(4-methoxyphenyl)pentan-1-one (**3d**)

600 MHz, $CDCl_3$, 23 ℃



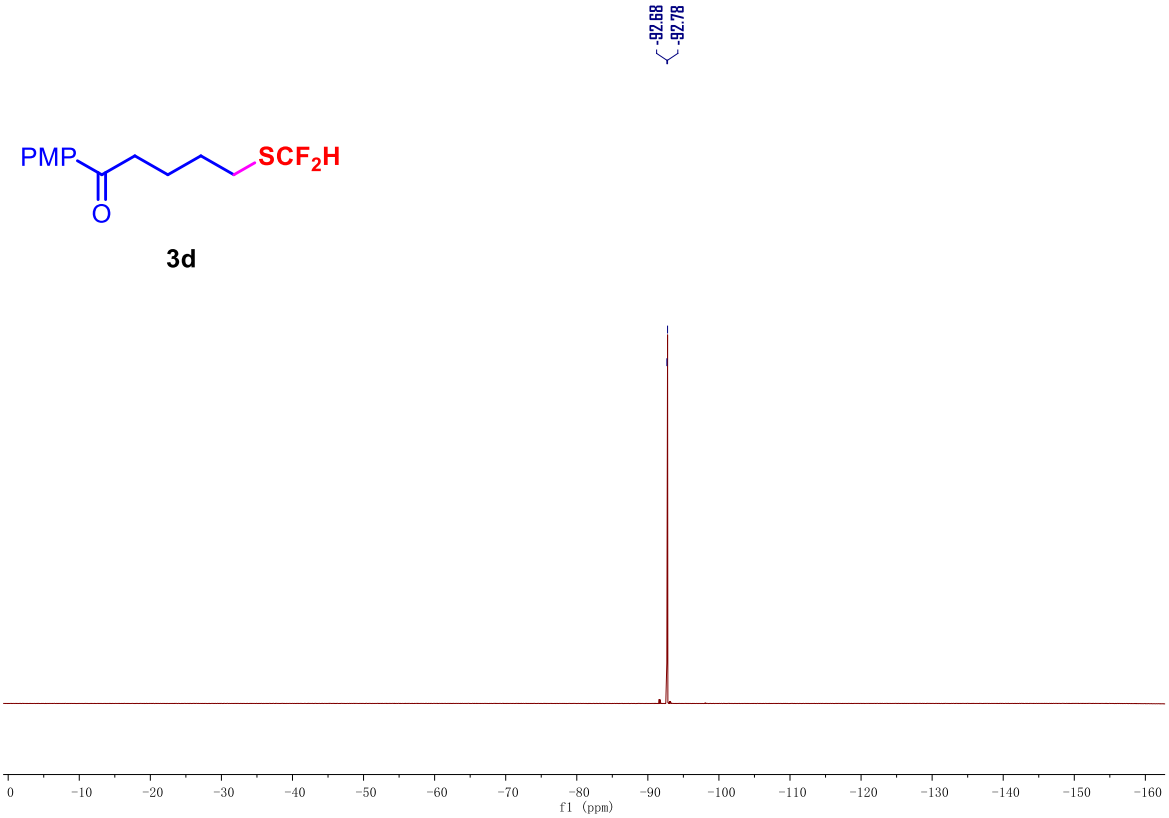
^{13}C NMR spectrum of 5-((difluoromethyl)thio)-1-(4-methoxyphenyl)pentan-1-one (**3d**)

151 MHz, $CDCl_3$, 23 ℃



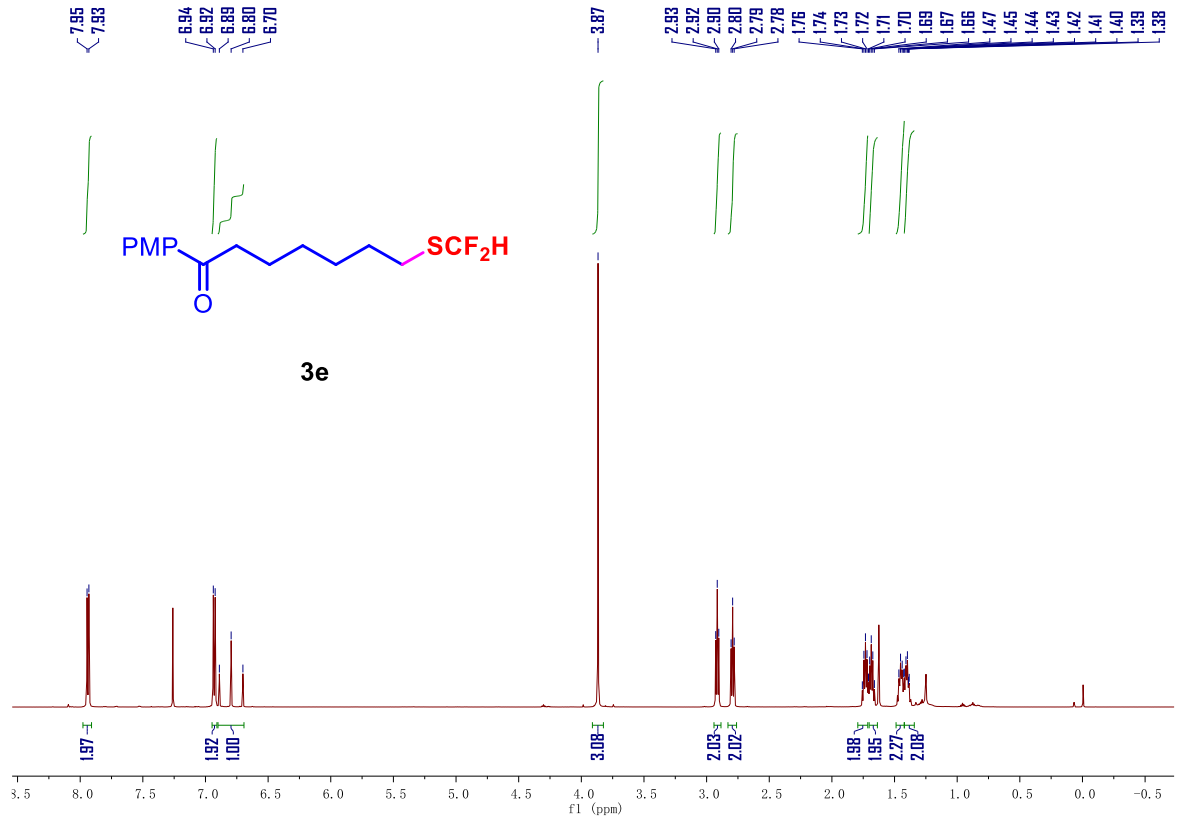
^{19}F NMR spectrum of 5-((difluoromethyl)thio)-1-(4-methoxyphenyl)pentan-1-one (**3d**)

565 MHz, $CDCl_3$, 23 ℃



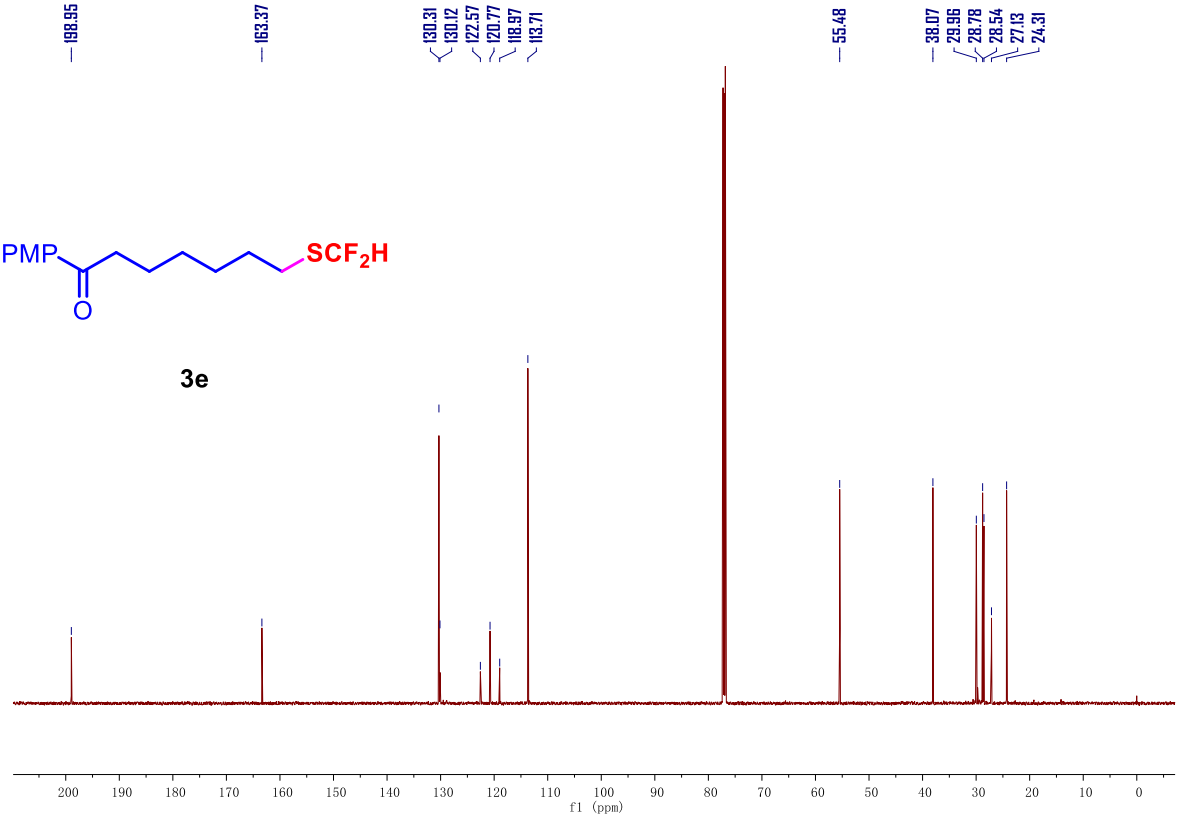
^{1}H NMR spectrum of 7-((difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (**3e**)

600 MHz, $CDCl_3$, 23 ℃



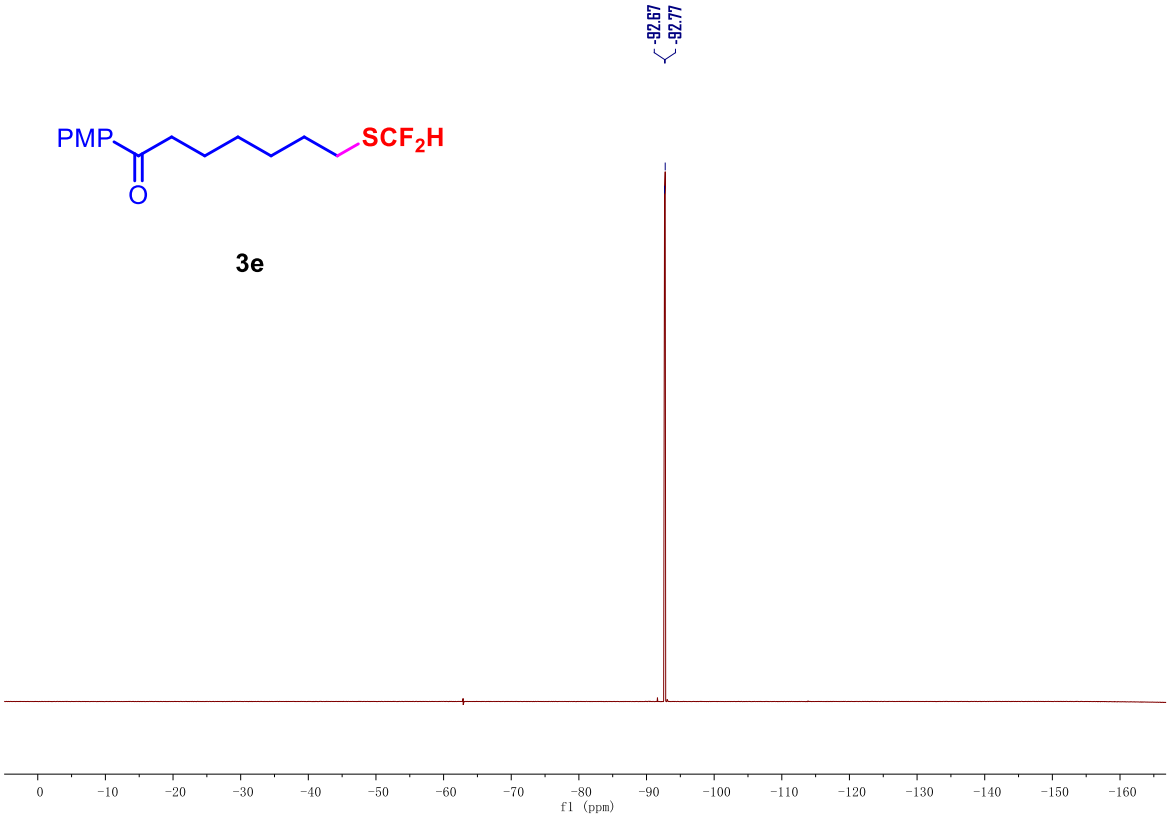
^{13}C NMR spectrum of 7-((difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (**3e**)

151 MHz, $CDCl_3$, 23 ℃



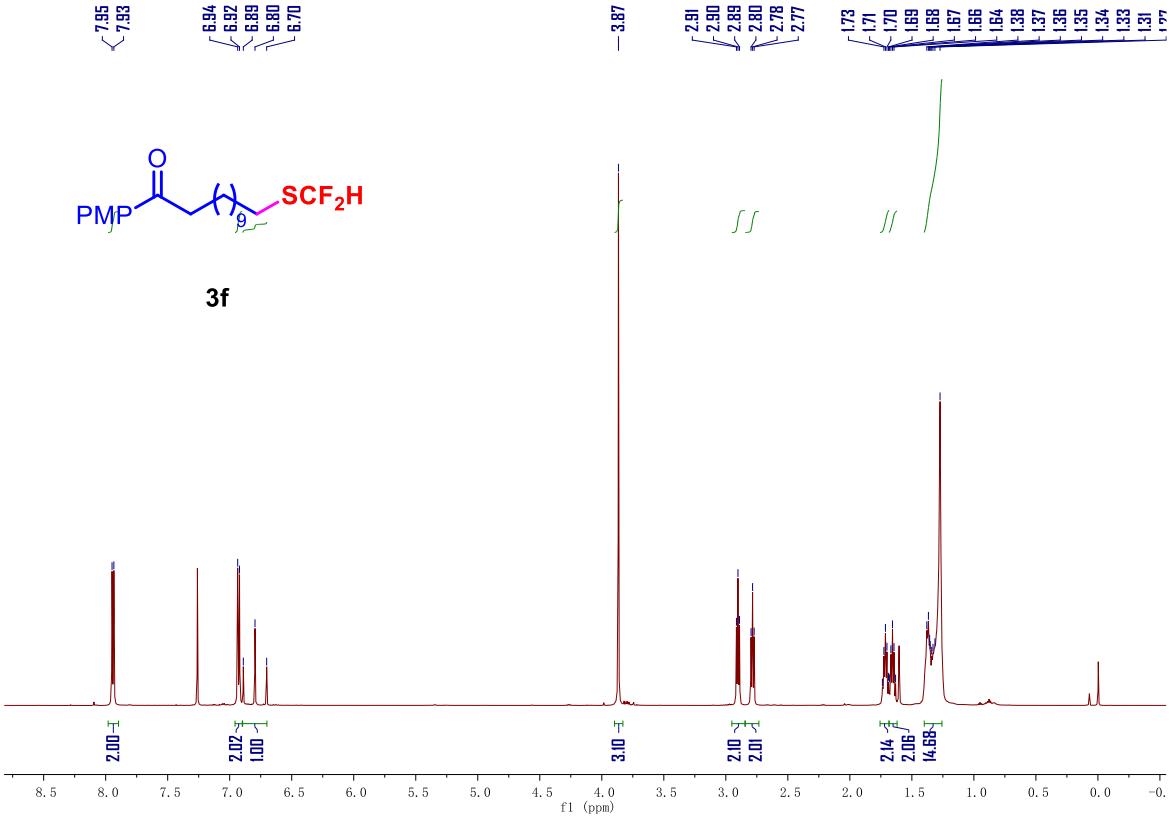
^{19}F NMR spectrum of 7-((difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (**3e**)

565 MHz, $CDCl_3$, 23 ℃



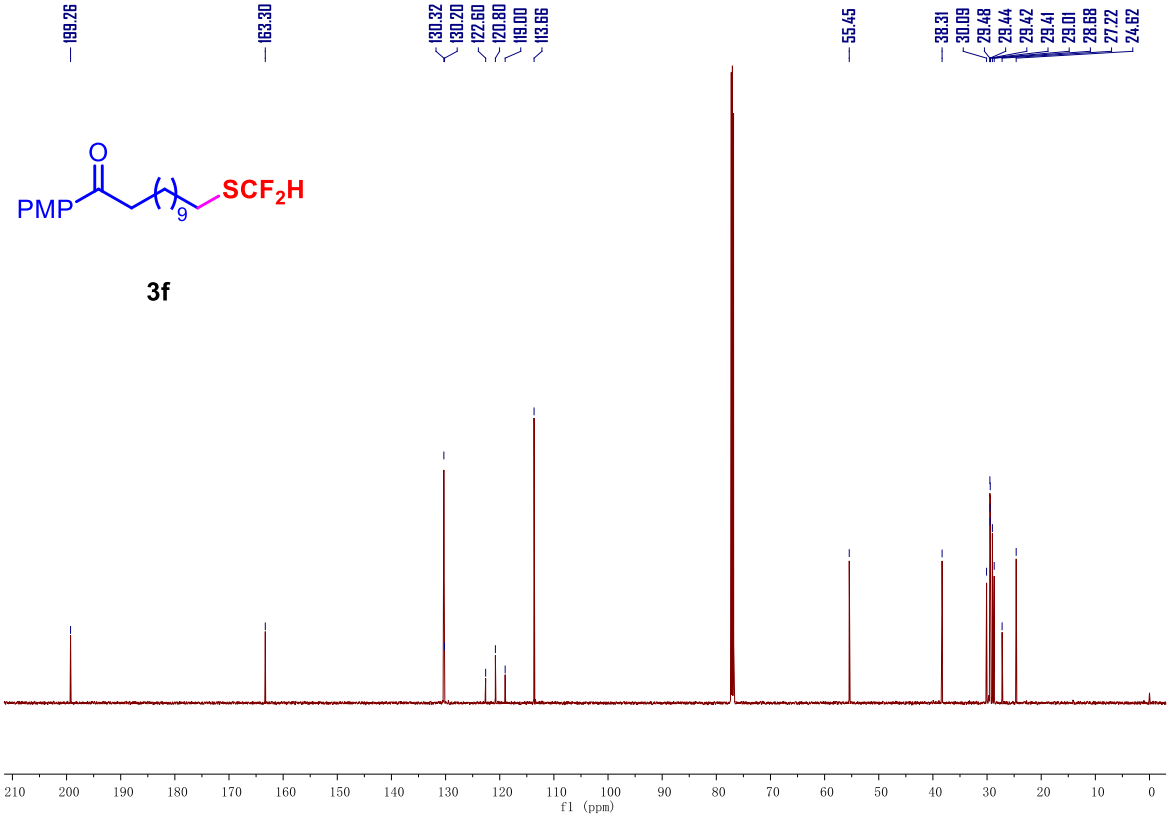
^{1}H NMR spectrum of 12-((difluoromethyl)thio)-1-(4-methoxyphenyl)dodecan-1-one (**3f**)

600 MHz, $CDCl_3$, 23 ℃



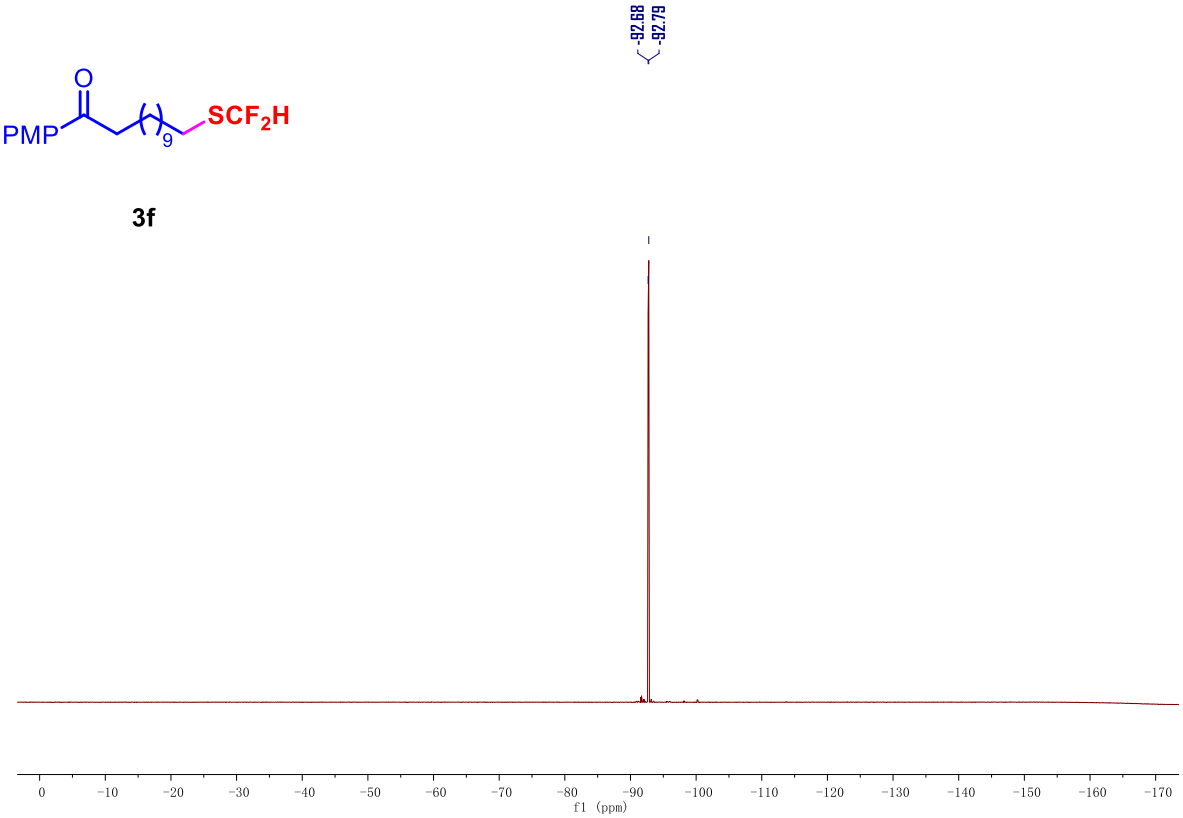
^{13}C NMR spectrum of 12-((difluoromethyl)thio)-1-(4-methoxyphenyl)dodecan-1-one (**3f**)

151 MHz, $CDCl_3$, 23 ℃



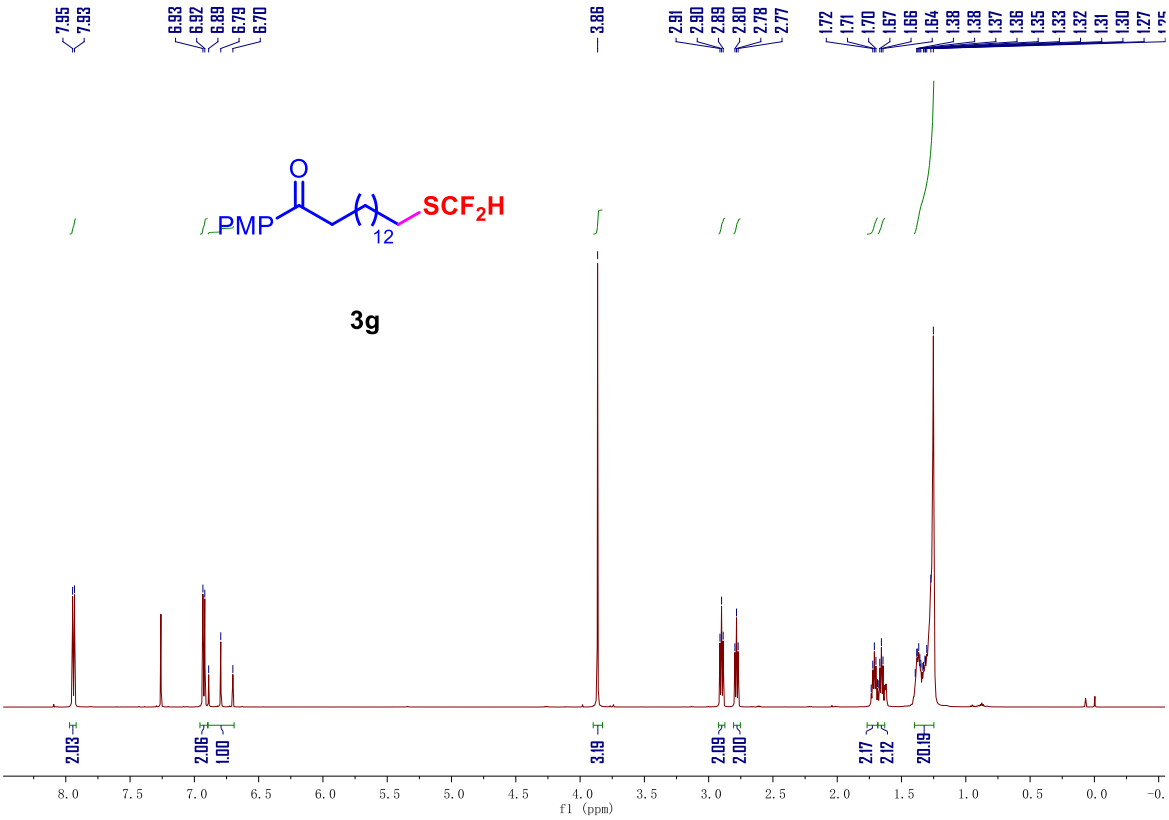
^{19}F NMR spectrum of 12-((difluoromethyl)thio)-1-(4-methoxyphenyl)dodecan-1-one (**3f**)

565 MHz, $CDCl_3$, 23 ℃



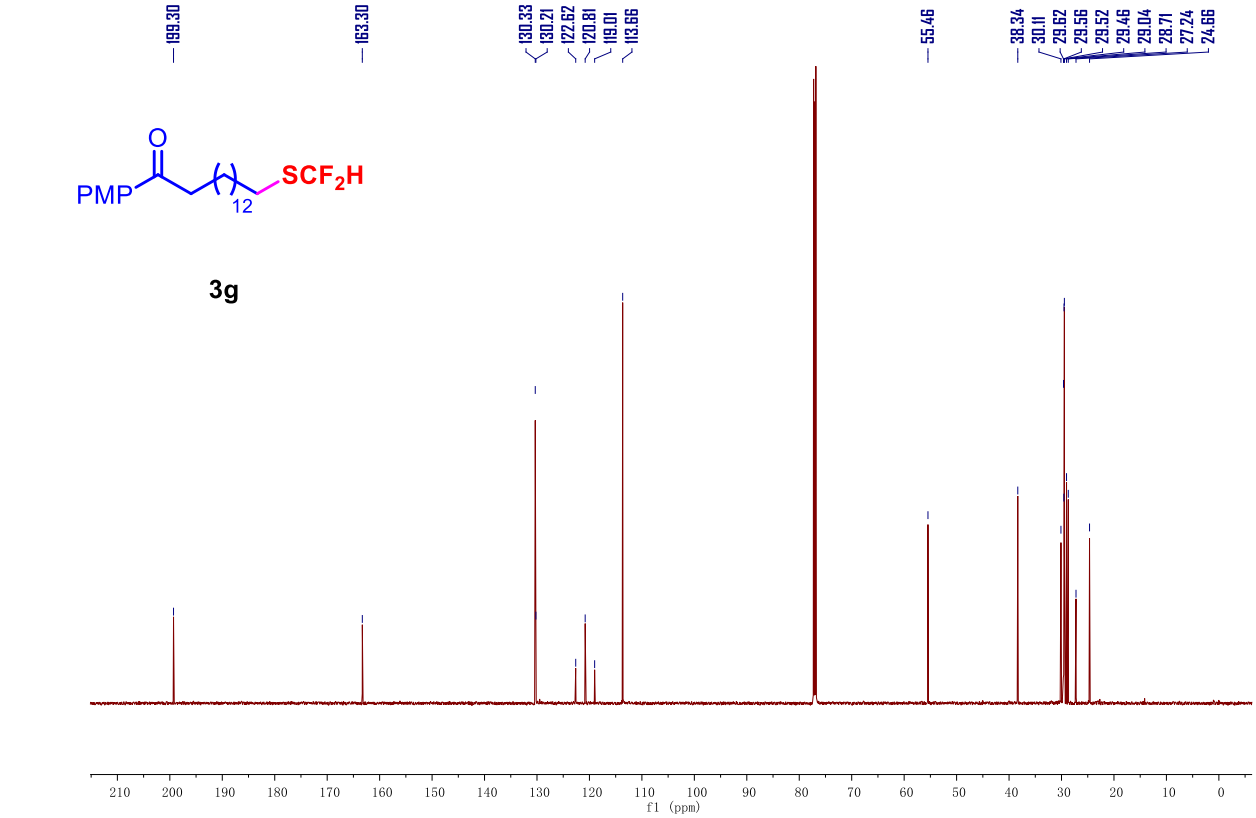
^{1}H NMR spectrum of 15-((difluoromethyl)thio)-1-(4-methoxyphenyl)pentadecan-1-one (**3g**)

600 MHz, $CDCl_3$, 23 ℃



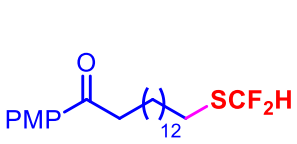
^{13}C NMR spectrum of 15-((difluoromethyl)thio)-1-(4-methoxyphenyl)pentadecan-1-one (**3g**)

151 MHz, $CDCl_3$, 23 ℃



^{19}F NMR spectrum of 15-((difluoromethyl)thio)-1-(4-methoxyphenyl)pentadecan-1-one (**3g**)

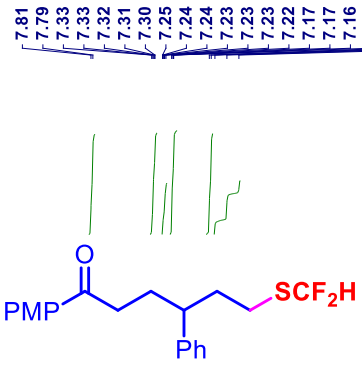
565 MHz, $CDCl_3$, 23 ℃



3g

^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)-4-phenylhexan-1-one (**3h**)

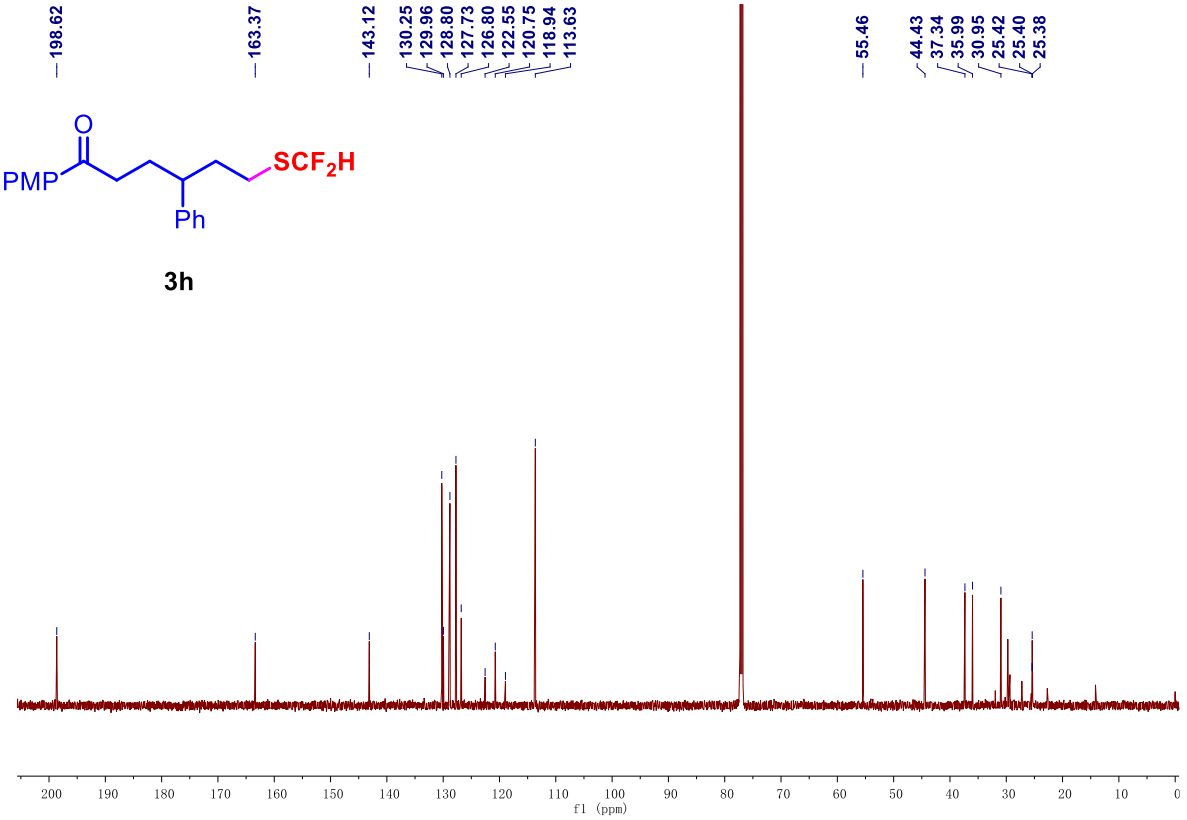
600 MHz, $CDCl_3$, 23 ℃



3h

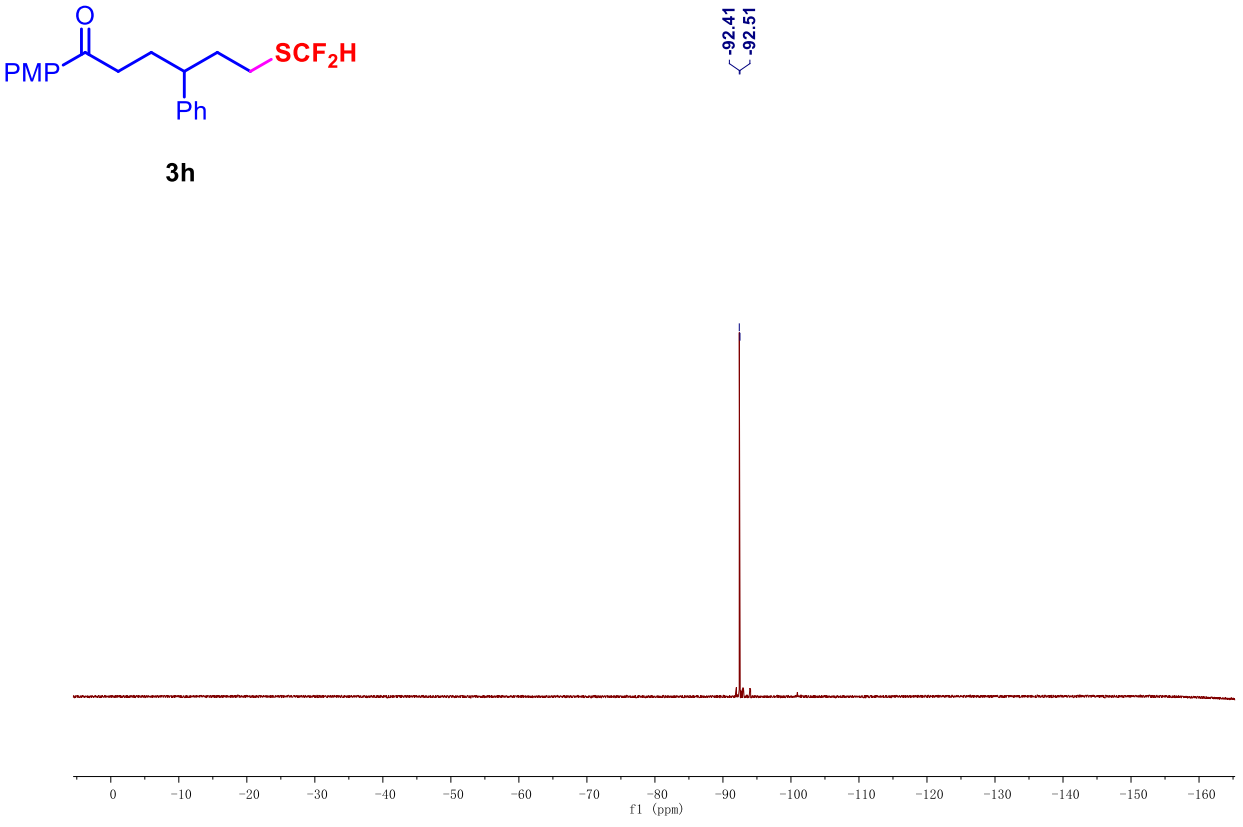
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)-4-phenylhexan-1-one (**3h**)

151 MHz, $CDCl_3$, 23 ℃



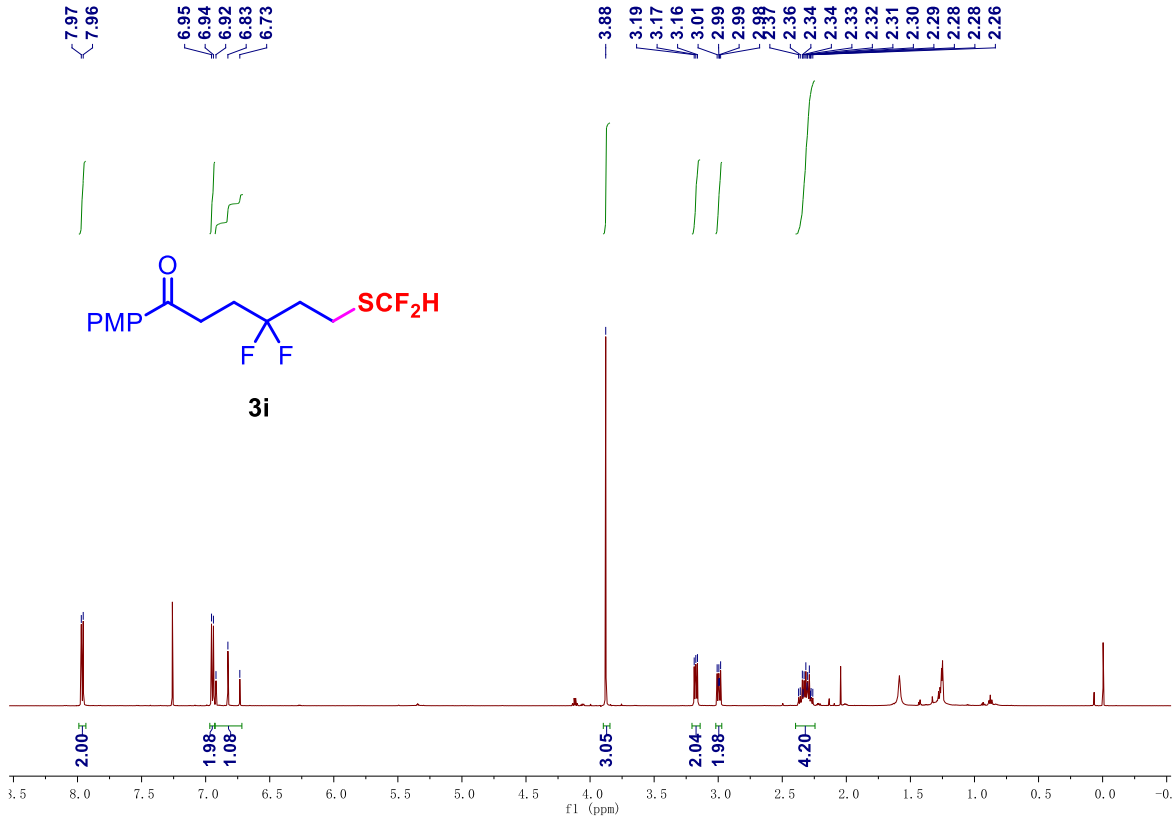
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)-4-phenylhexan-1-one (**3h**)

565 MHz, $CDCl_3$, 23 ℃



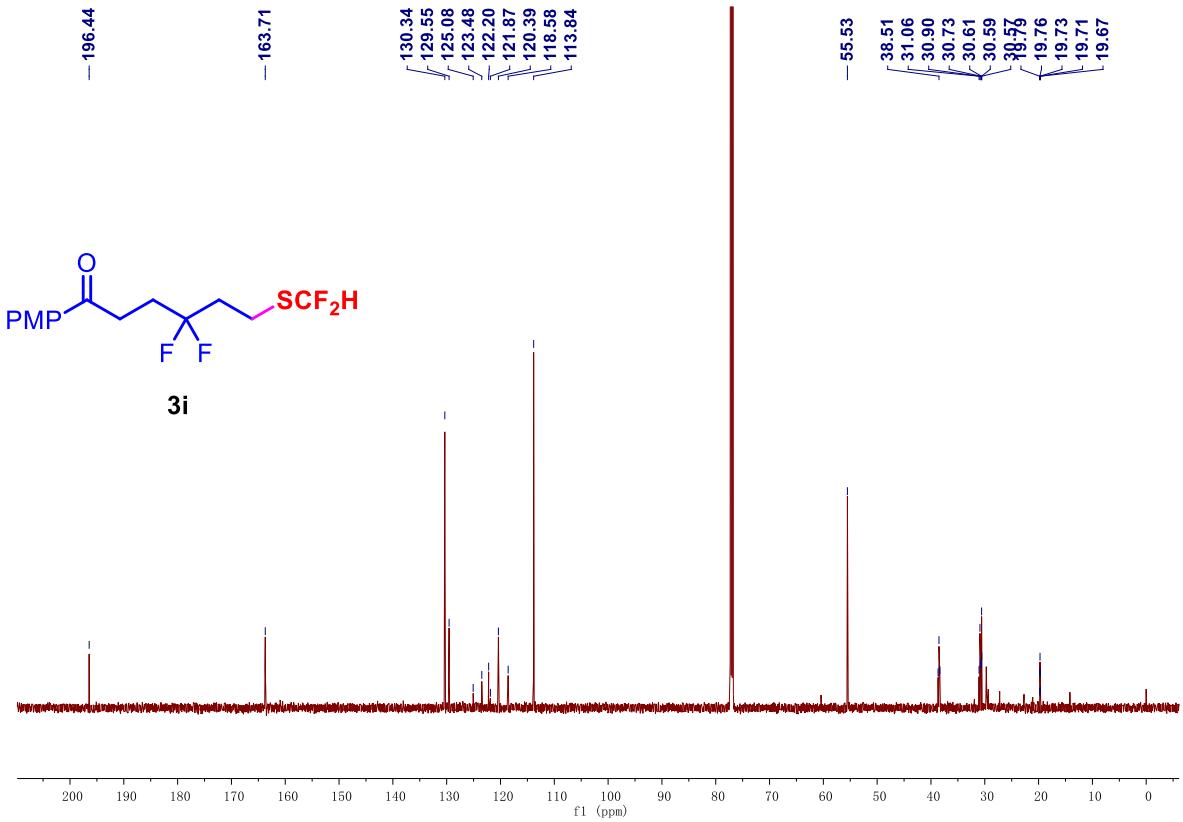
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-4,4-difluoro-1-(4-methoxyphenyl)hexan-1-one (**3i**)

600 MHz, $CDCl_3$, 23 ℃



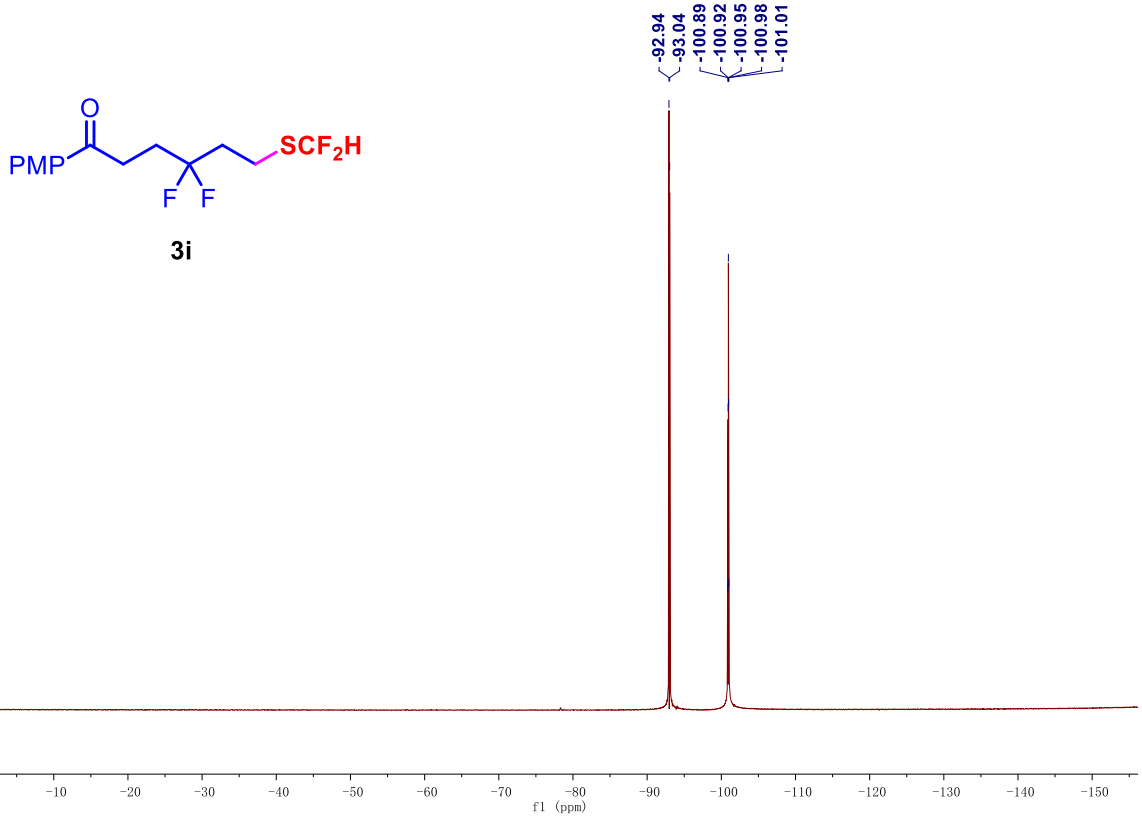
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-4,4-difluoro-1-(4-methoxyphenyl)hexan-1-one (**3i**)

151 MHz, $CDCl_3$, 23 ℃



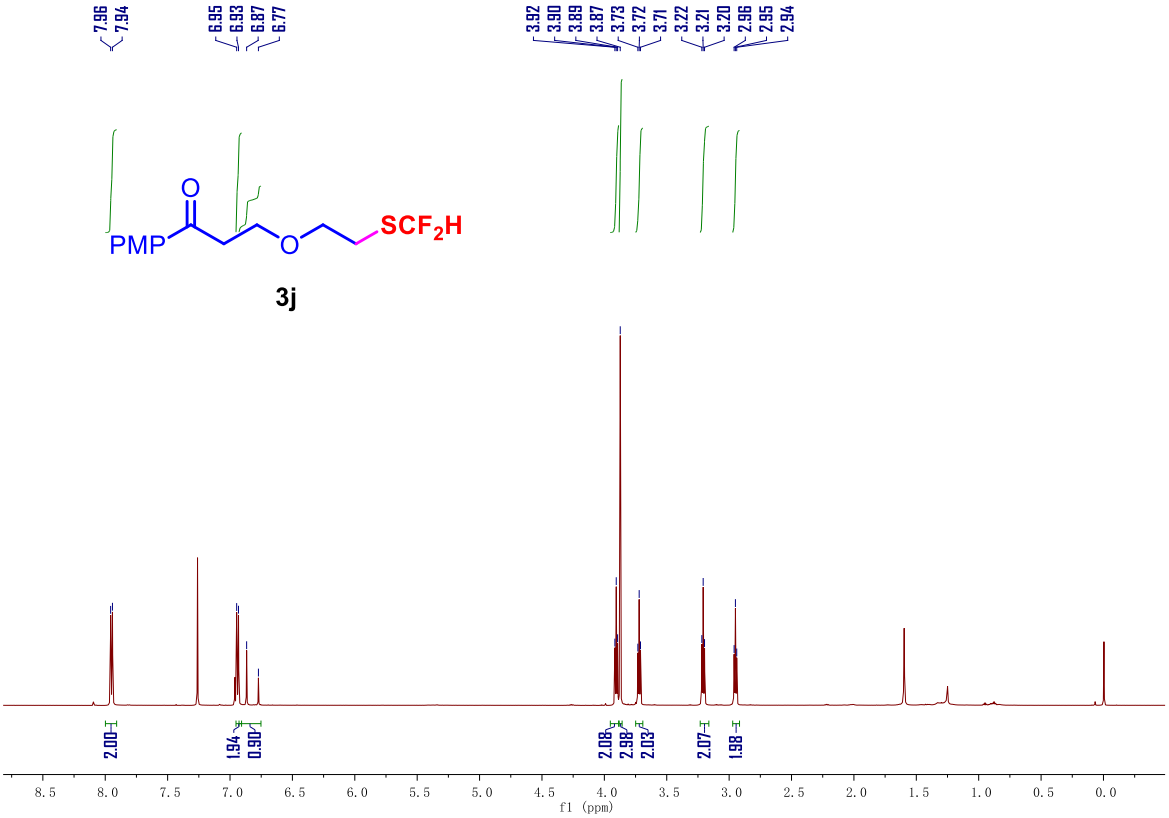
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-4,4-difluoro-1-(4-methoxyphenyl)hexan-1-one (**3i**)

565 MHz, $CDCl_3$, 23 ℃



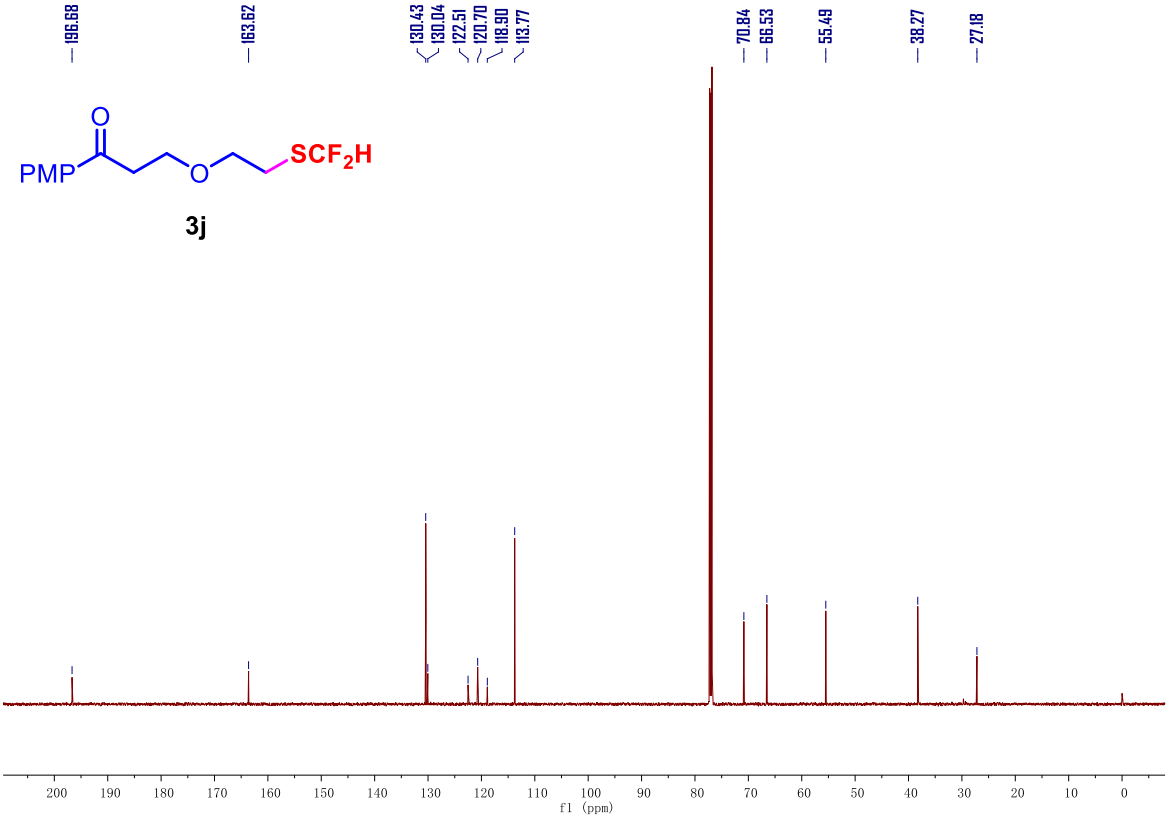
^{1}H NMR spectrum of 3-(2-((difluoromethyl)thio)ethoxy)-1-(4-methoxyphenyl)propan-1-one (**3j**)

600 MHz, $CDCl_3$, 23 ℃



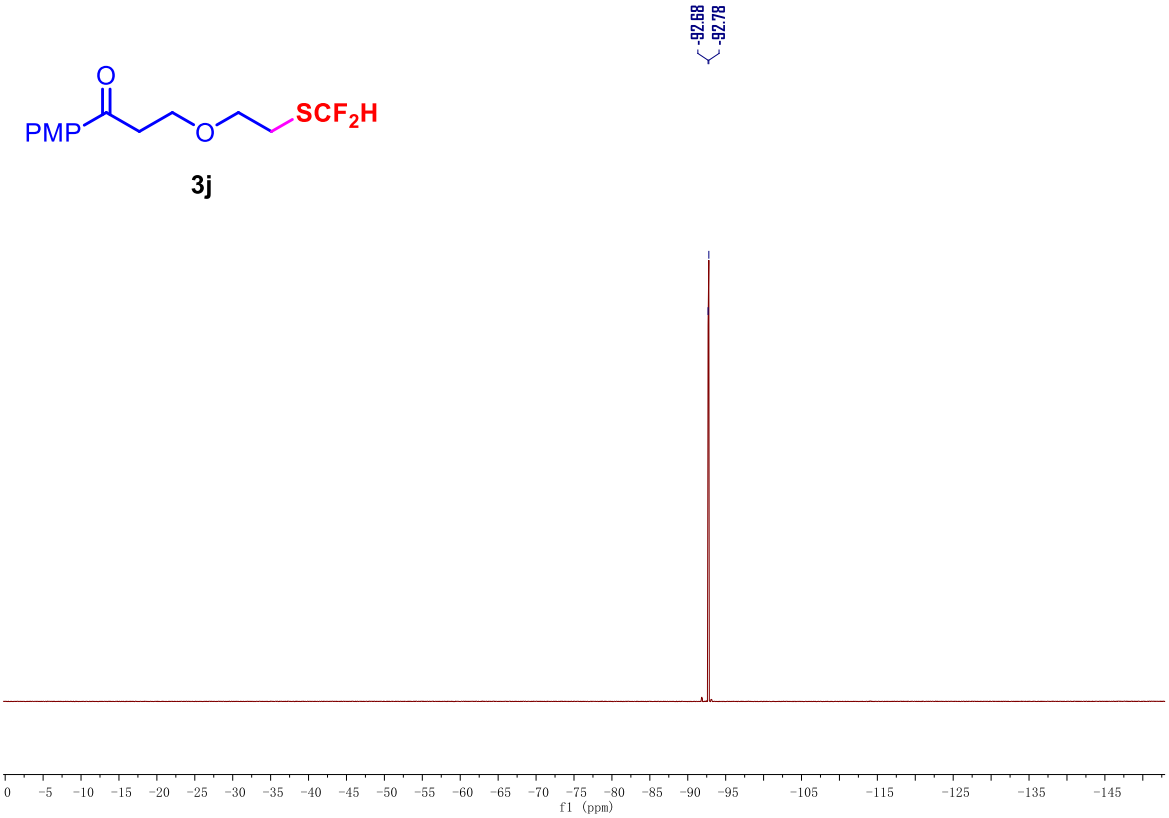
^{13}C NMR spectrum of 3-(2-((difluoromethyl)thio)ethoxy)-1-(4-methoxyphenyl)propan-1-one (**3j**)

151 MHz, $CDCl_3$, 23 ℃



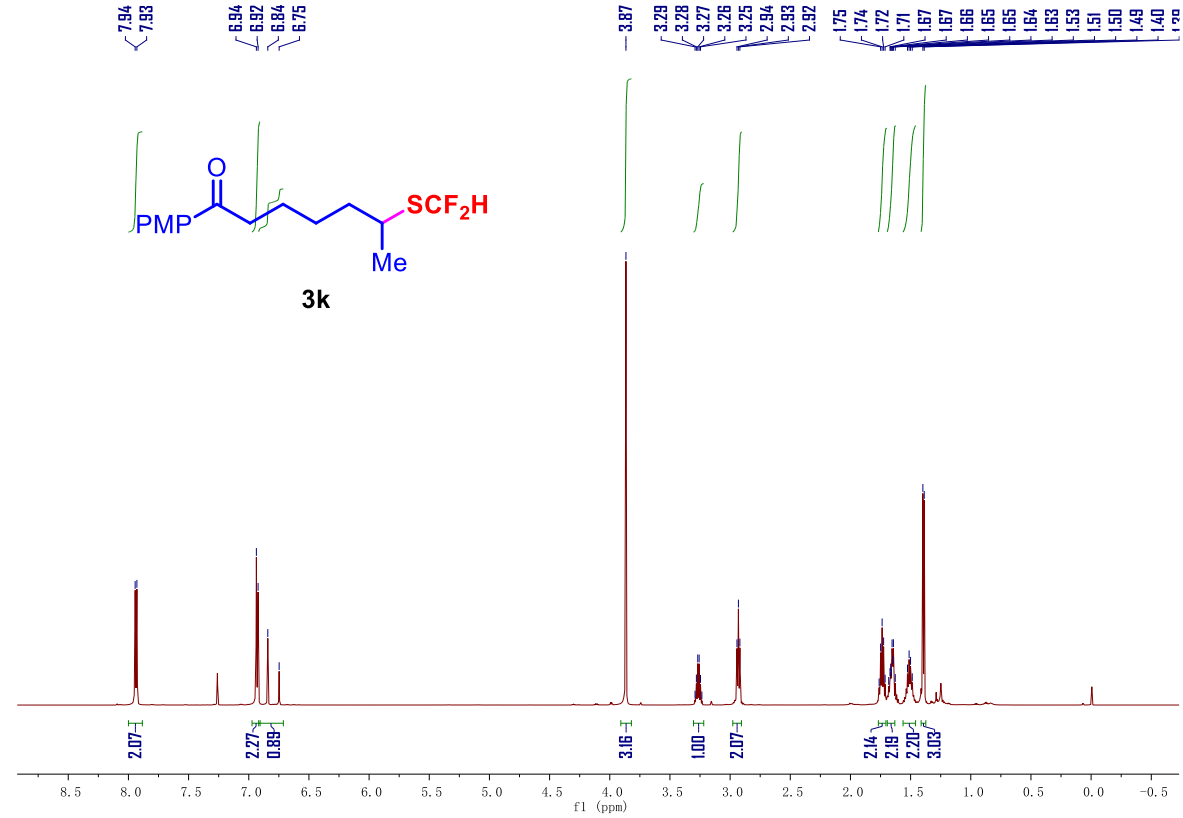
^{19}F NMR spectrum of 3-(2-((difluoromethyl)thio)ethoxy)-1-(4-methoxyphenyl)propan-1-one (**3j**)

565 MHz, $CDCl_3$, 23 ℃



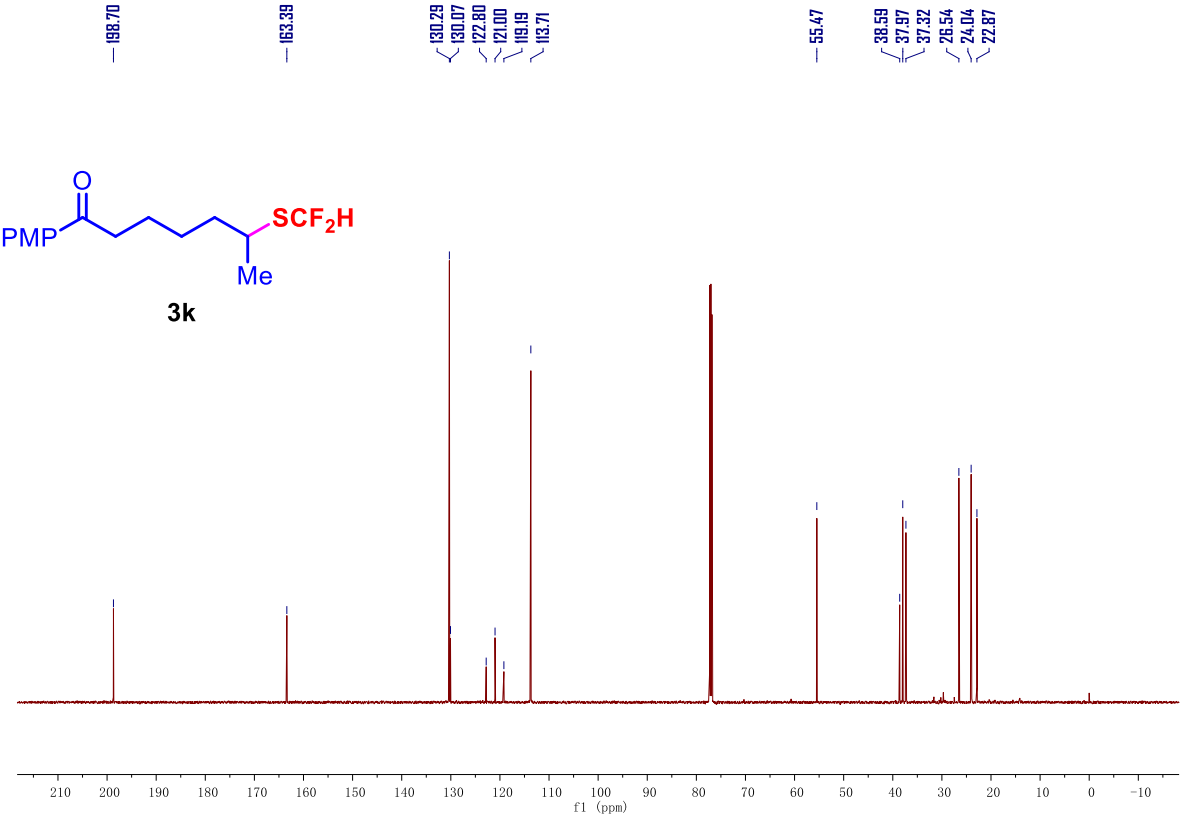
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (**3k**)

600 MHz, $CDCl_3$, 23 ℃



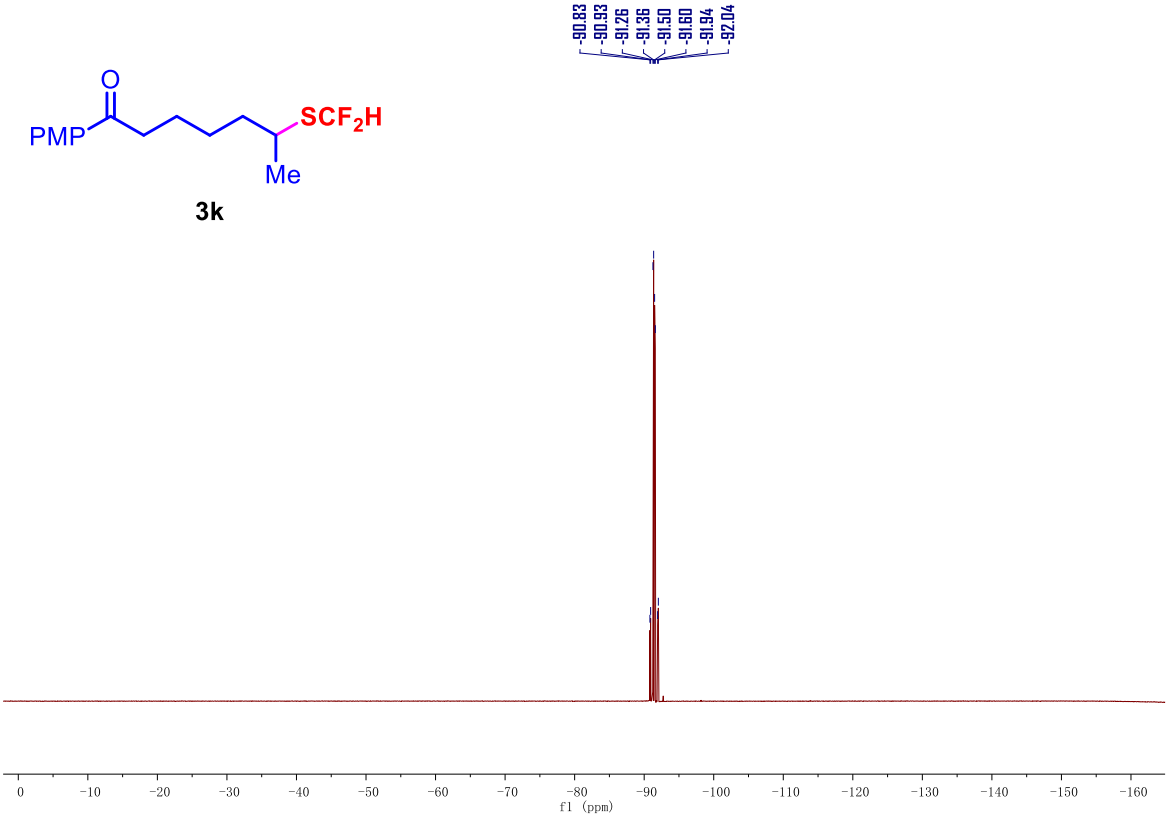
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (**3k**)

151 MHz, $CDCl_3$, 23 ℃



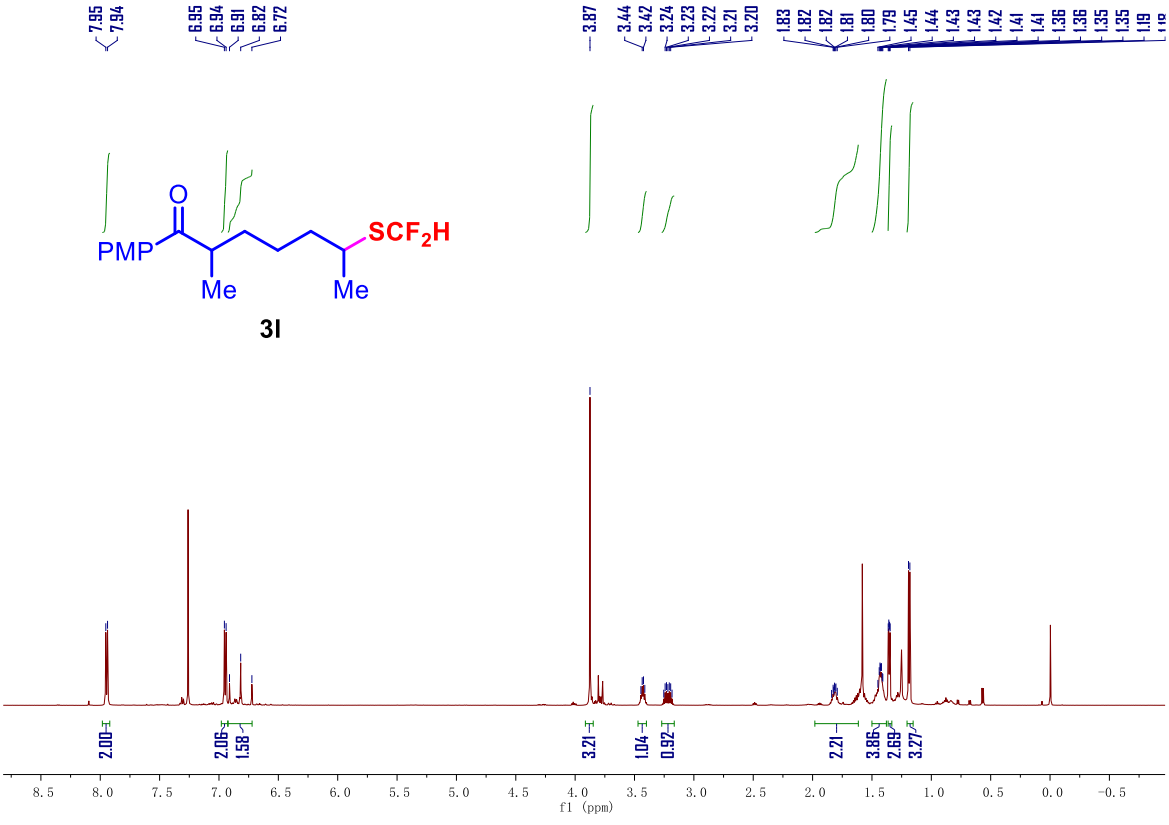
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)heptan-1-one (**3k**)

565 MHz, $CDCl_3$, 23 ℃



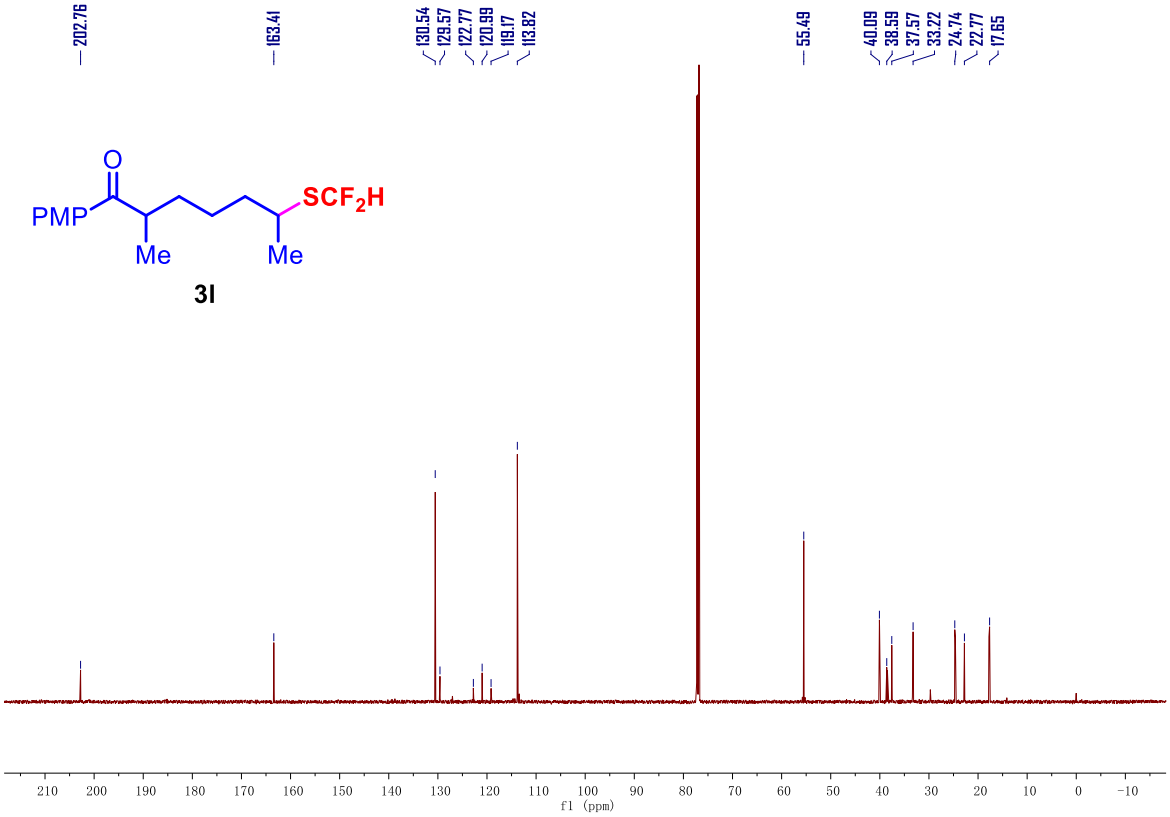
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)-2-methylheptan-1-one (**3l**)

600 MHz, $CDCl_3$, 23 ℃



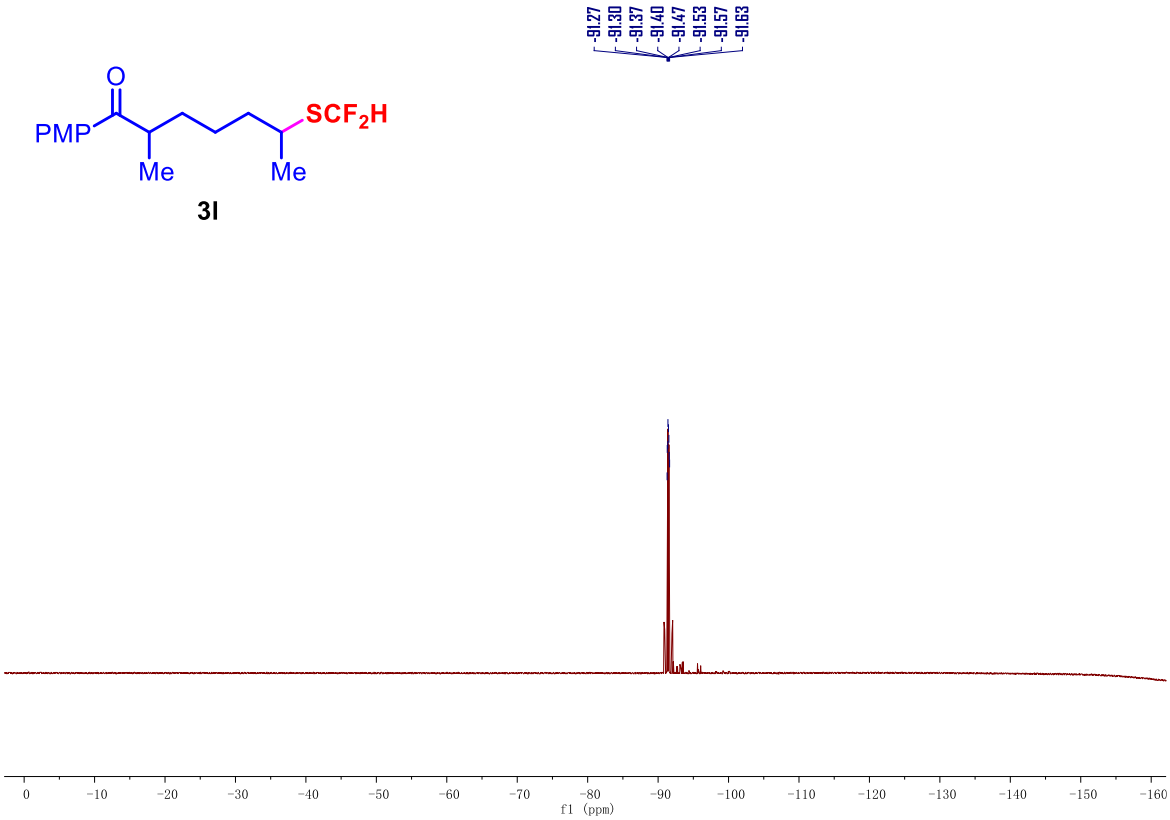
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)-2-methylheptan-1-one (**3l**)

151 MHz, $CDCl_3$, 23 ℃



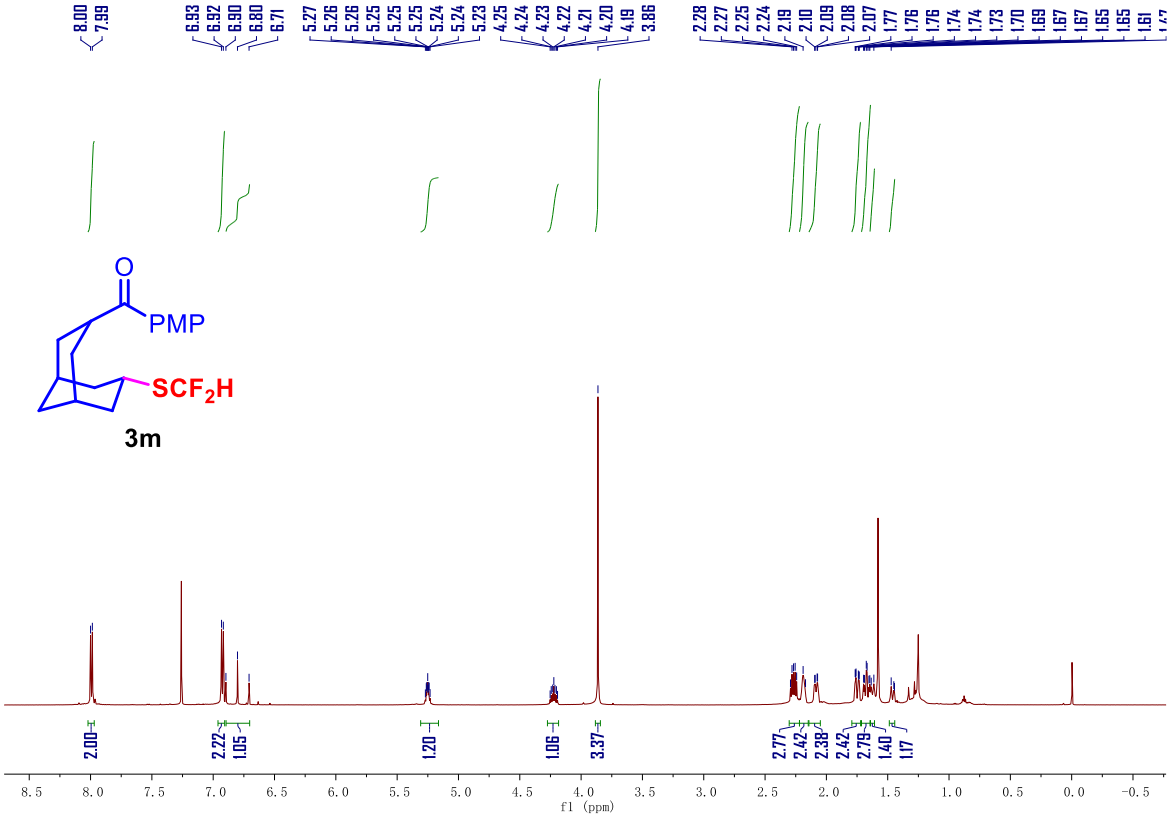
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)-2-methylheptan-1-one (**3l**)

565 MHz, $CDCl_3$, 23 ℃



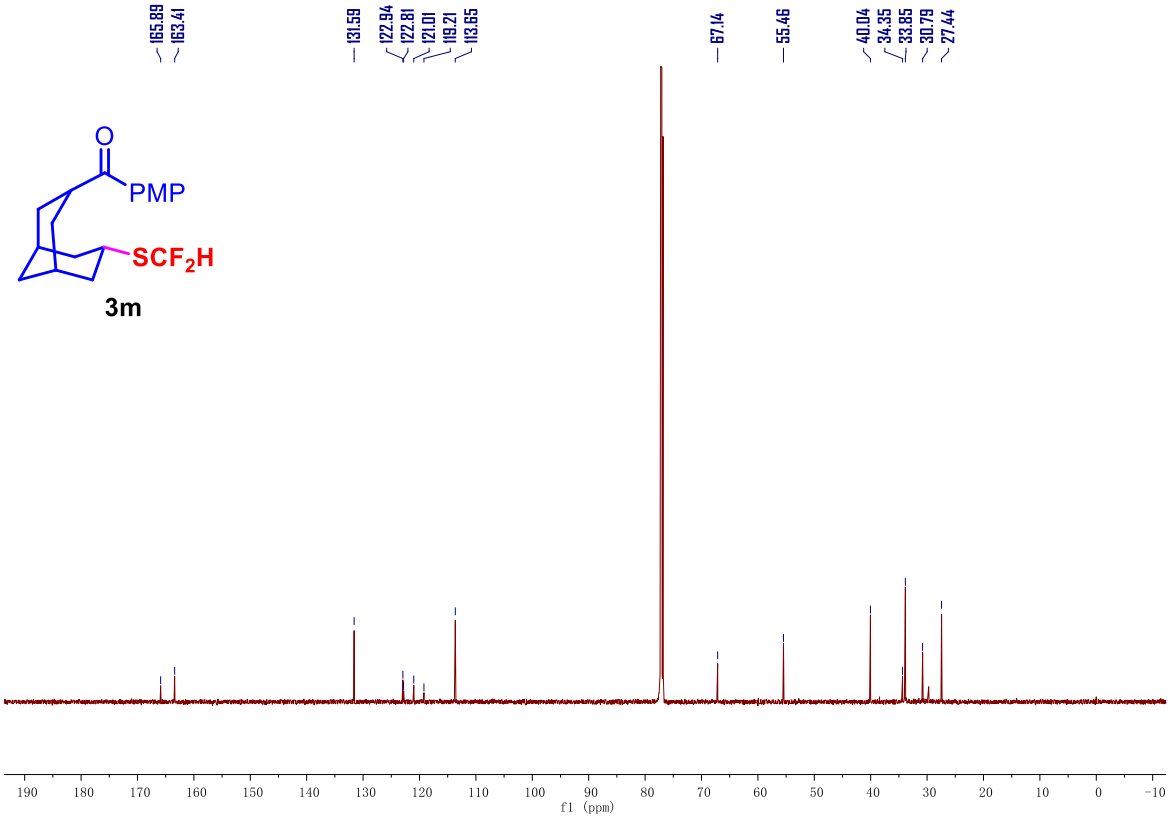
^{1}H NMR spectrum of (7-((difluoromethyl)thio)bicyclo[3.3.1]nonan-3-yl)(4-methoxyphenyl)methanone (**3m**)

600 MHz, $CDCl_3$, 23 ℃



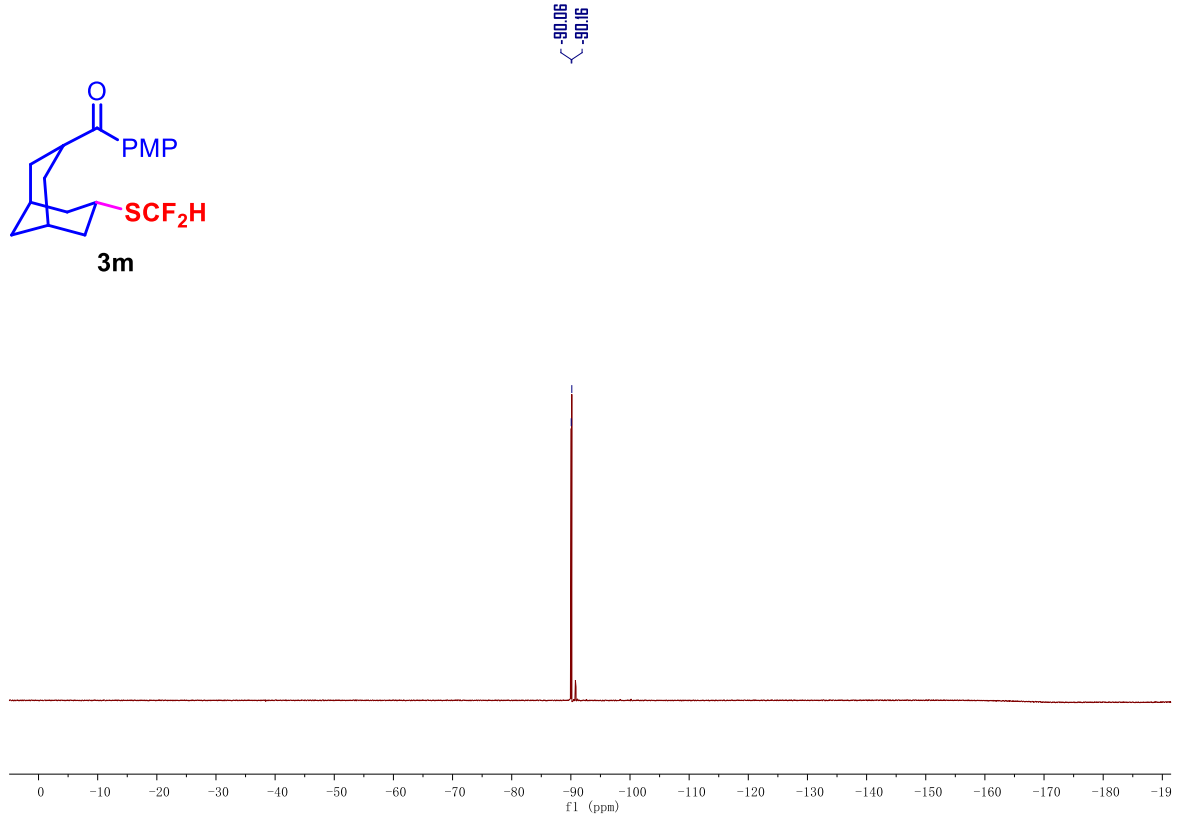
^{13}C NMR spectrum of (7-((difluoromethyl)thio)bicyclo[3.3.1]nonan-3-yl)(4-methoxyphenyl)methanone (**3m**)

151 MHz, $CDCl_3$, 23 ℃



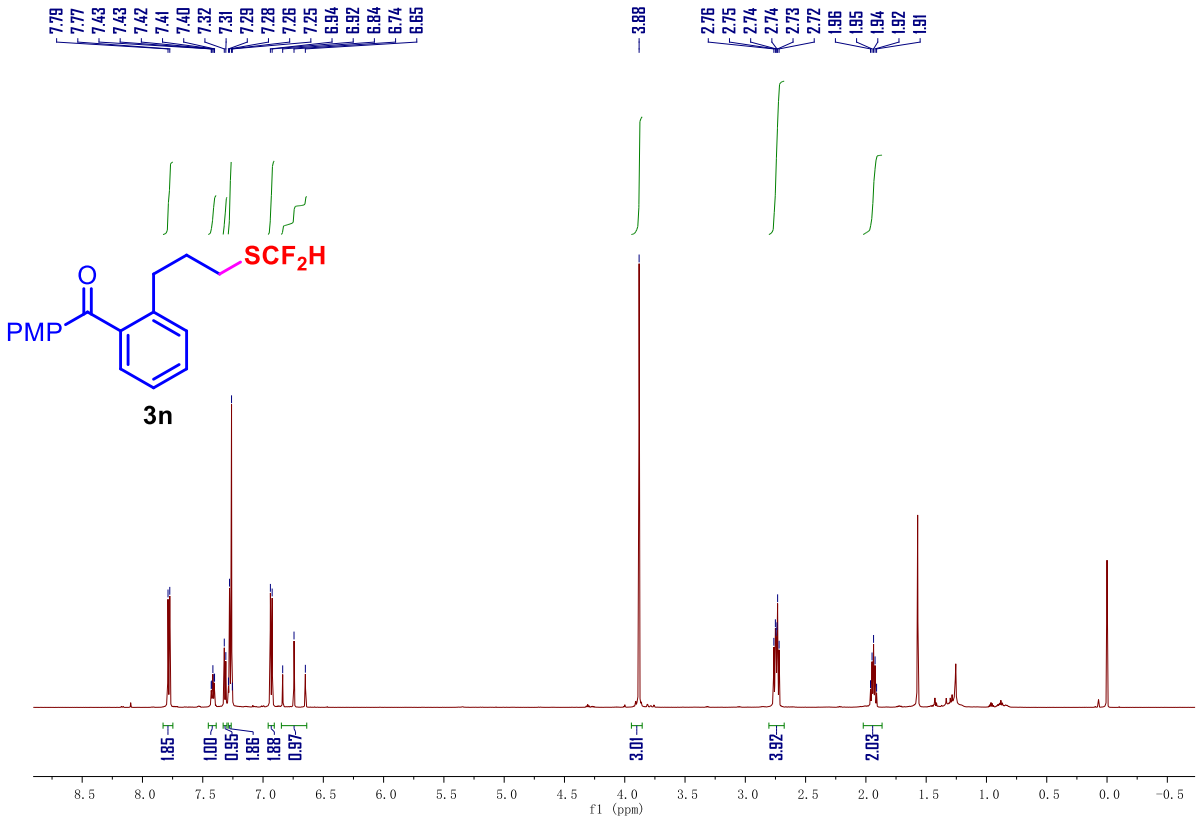
^{19}F NMR spectrum of (7-((difluoromethyl)thio)bicyclo[3.3.1]nonan-3-yl)(4-methoxyphenyl)methanone (**3m**)

565 MHz, $CDCl_3$, 23 ℃



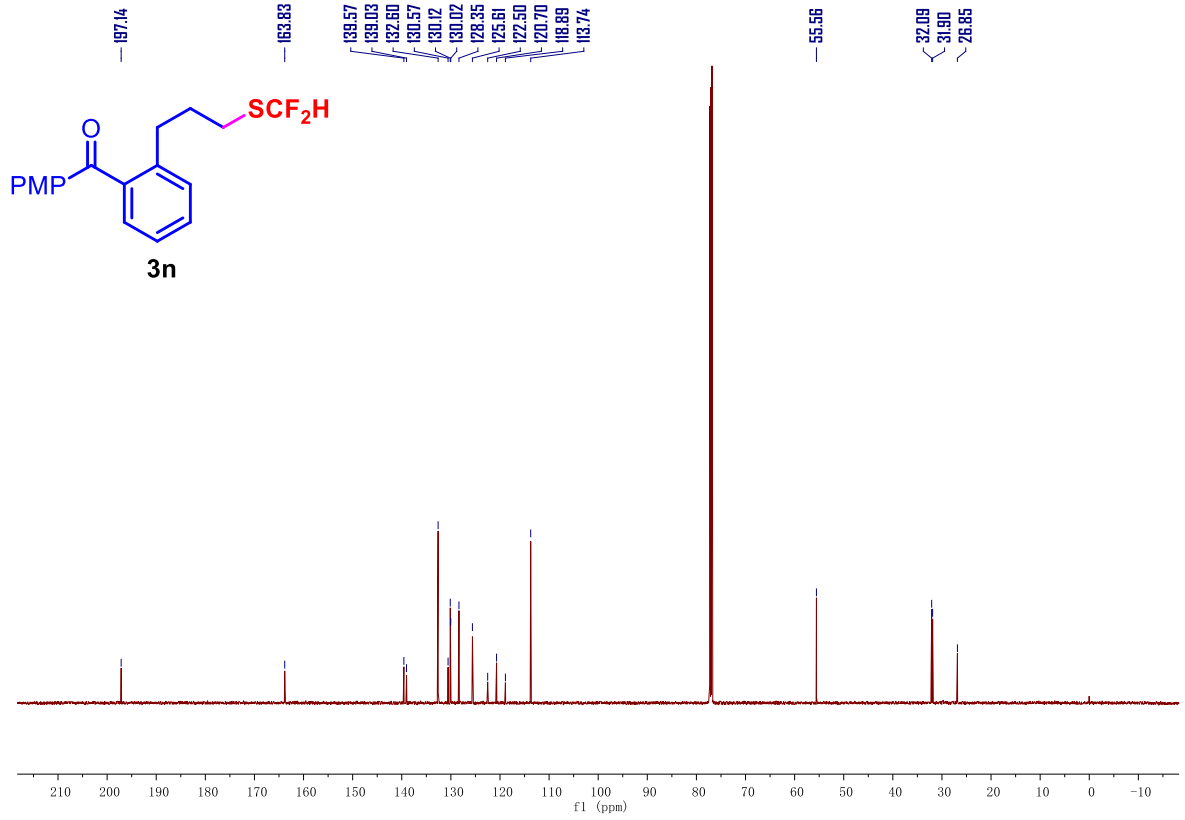
^{1}H NMR spectrum of (2-(3-((difluoromethyl)thio)propyl)phenyl)(4-methoxyphenyl)methanone (**3n**)

600 MHz, $CDCl_3$, 23 ℃



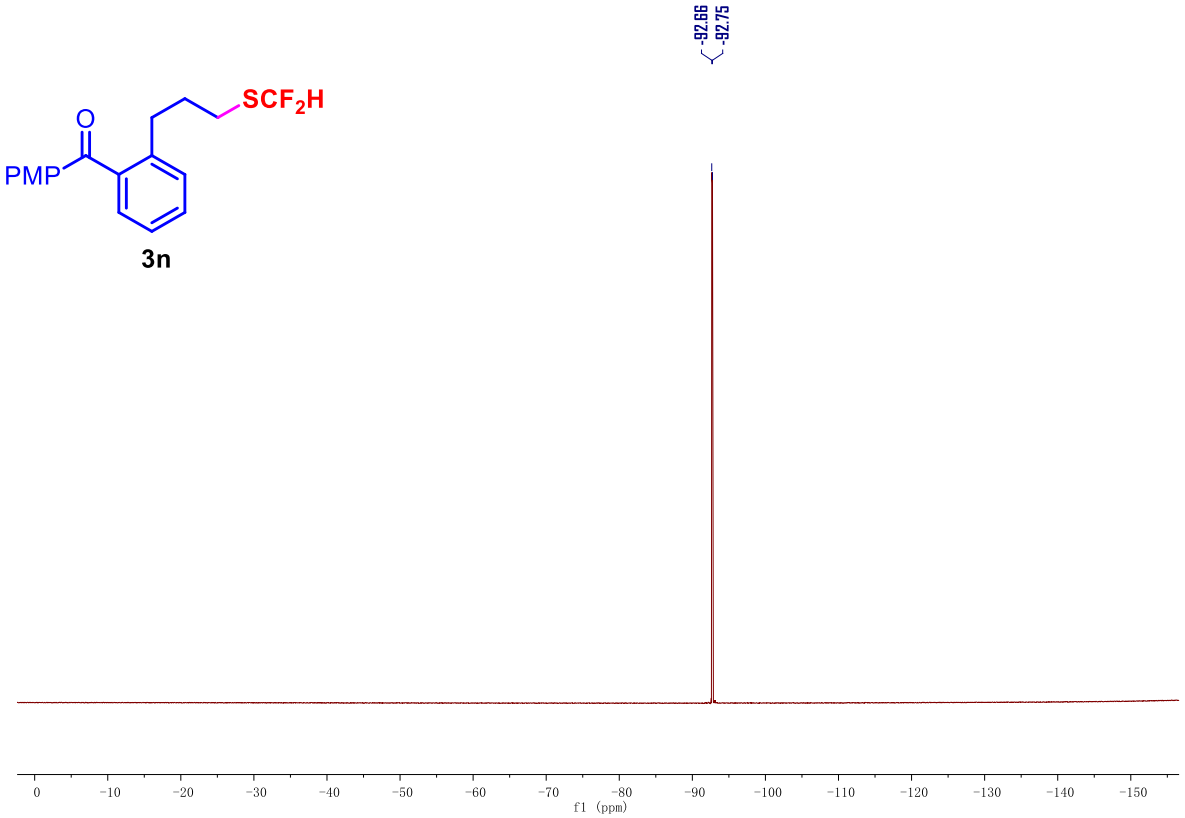
^{13}C NMR spectrum of (2-(3-((difluoromethyl)thio)propyl)phenyl)(4-methoxyphenyl)methanone (**3n**)

151 MHz, $CDCl_3$, 23 ℃



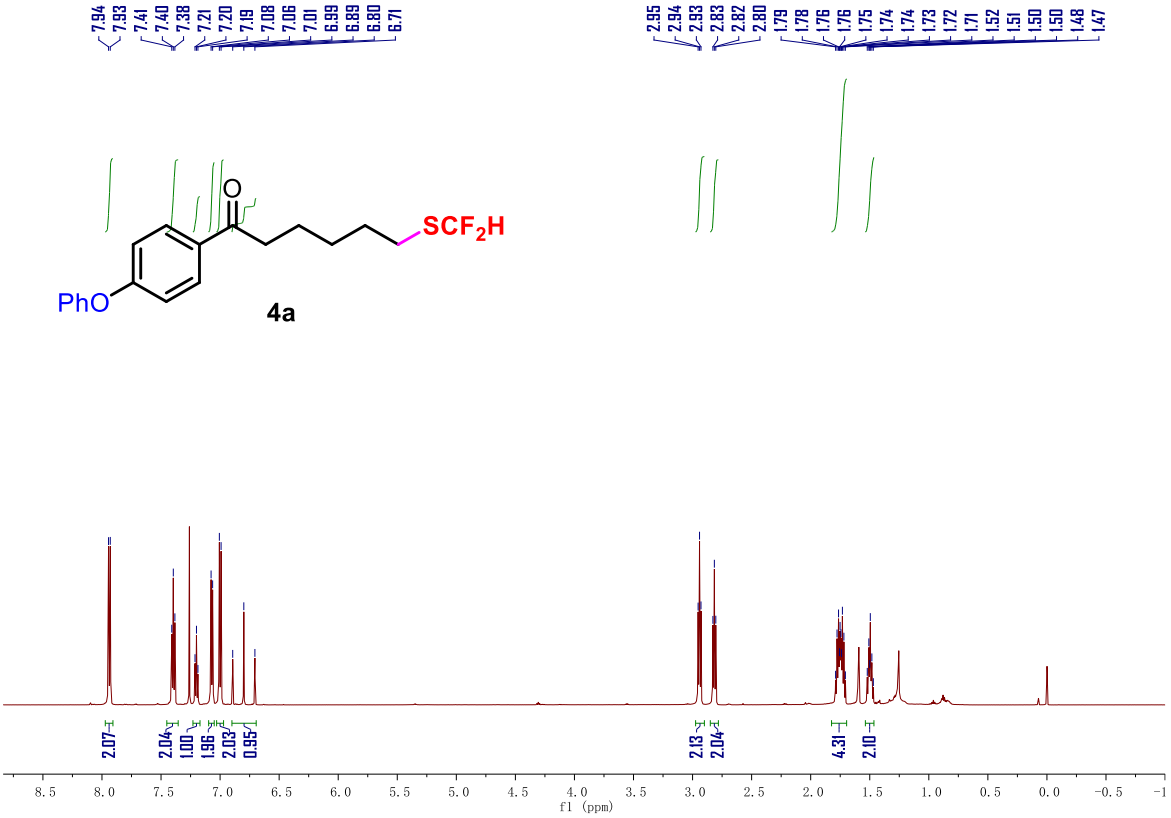
^{19}F NMR spectrum of (2-(3-((difluoromethyl)thio)propyl)phenyl)(4-methoxyphenyl)methanone (**3n**)

565 MHz, $CDCl_3$, 23 ℃



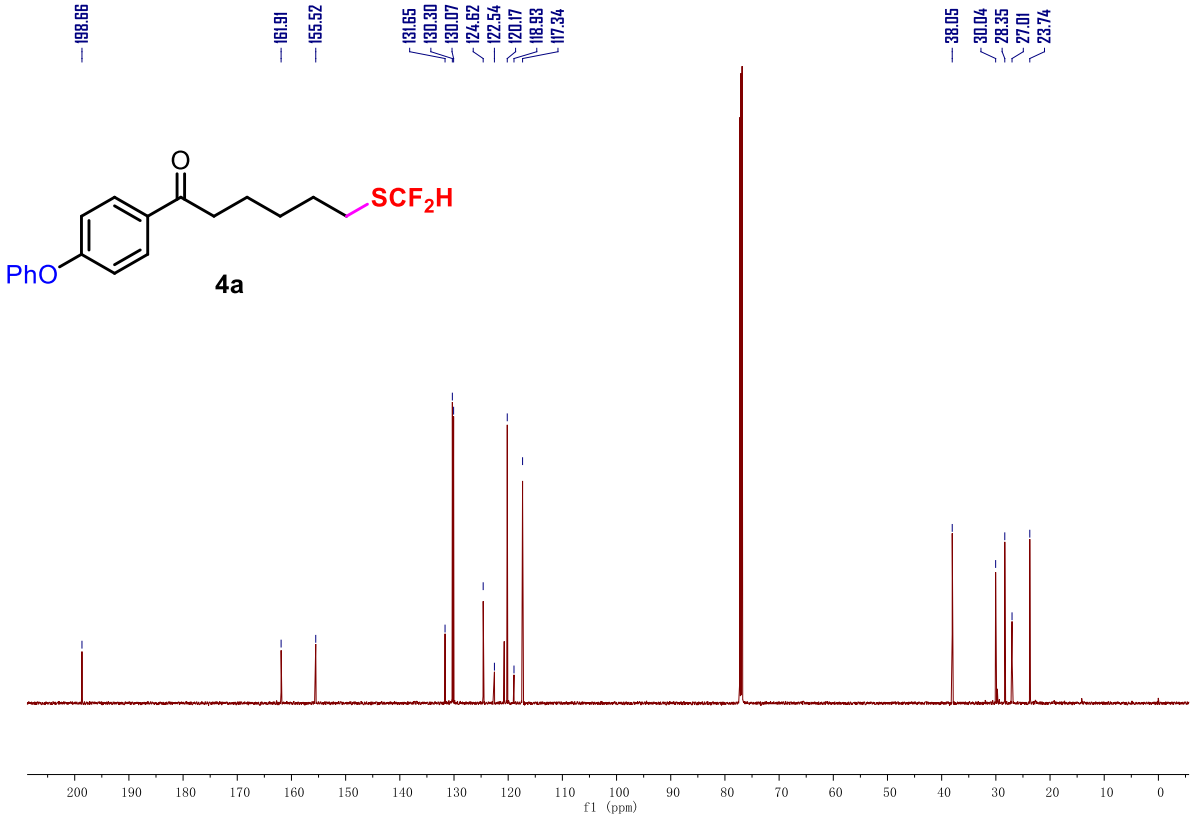
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(4-phenoxyphenyl)hexan-1-one (**4a**)

600 MHz, $CDCl_3$, 23 ℃



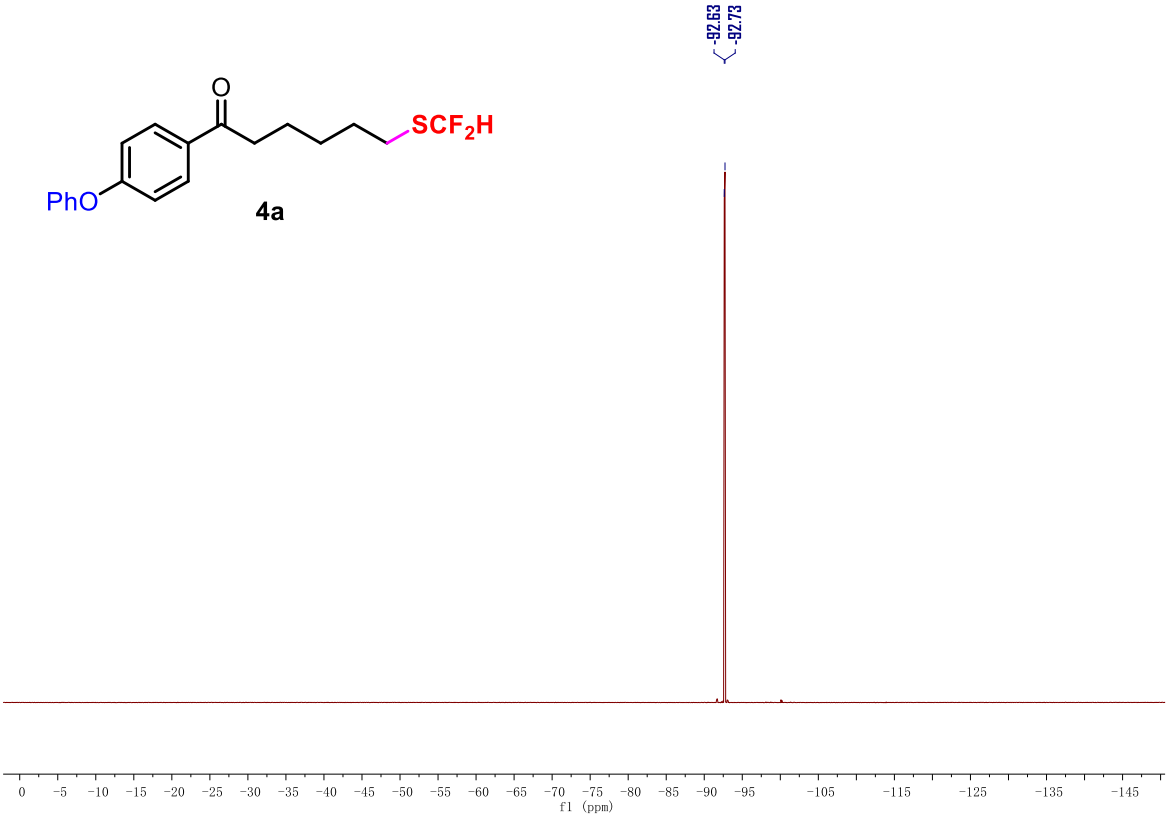
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(4-phenoxyphenyl)hexan-1-one (**4a**)

151 MHz, $CDCl_3$, 23 ℃



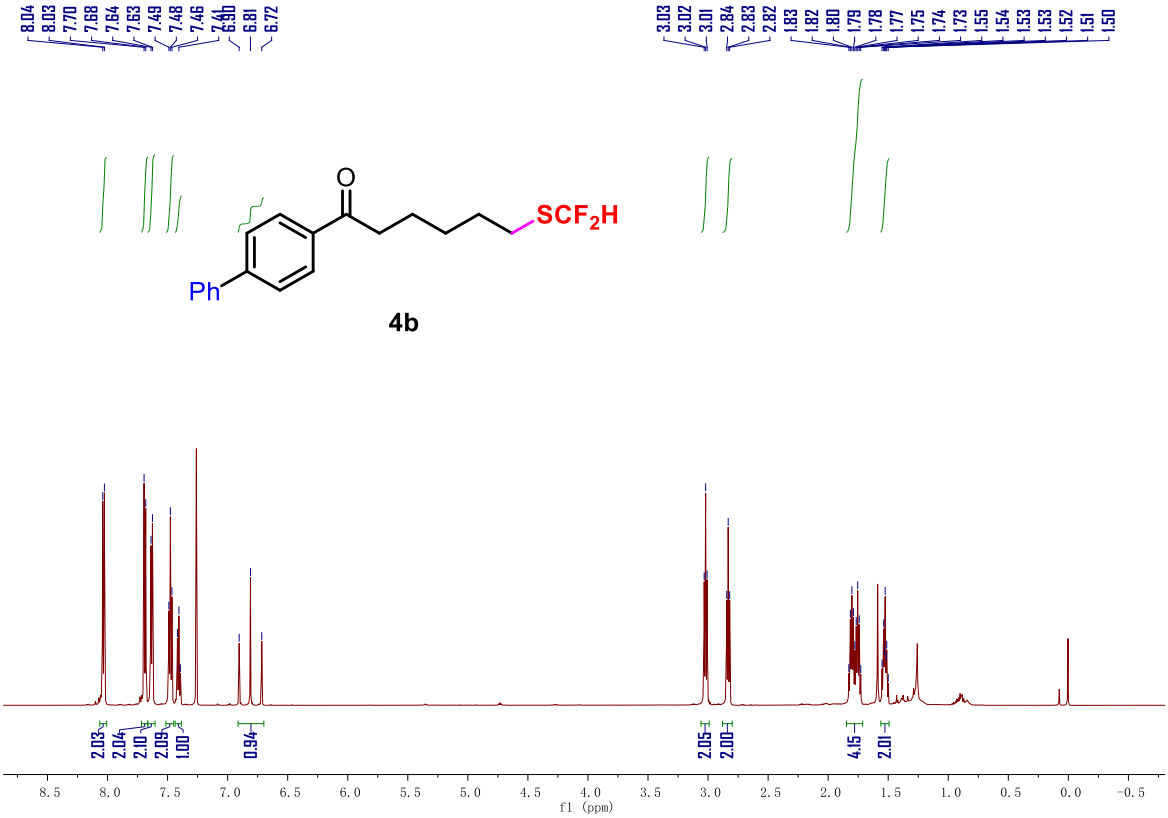
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(4-phenoxyphenyl)hexan-1-one (**4a**)

565 MHz, $CDCl_3$, 23 ℃



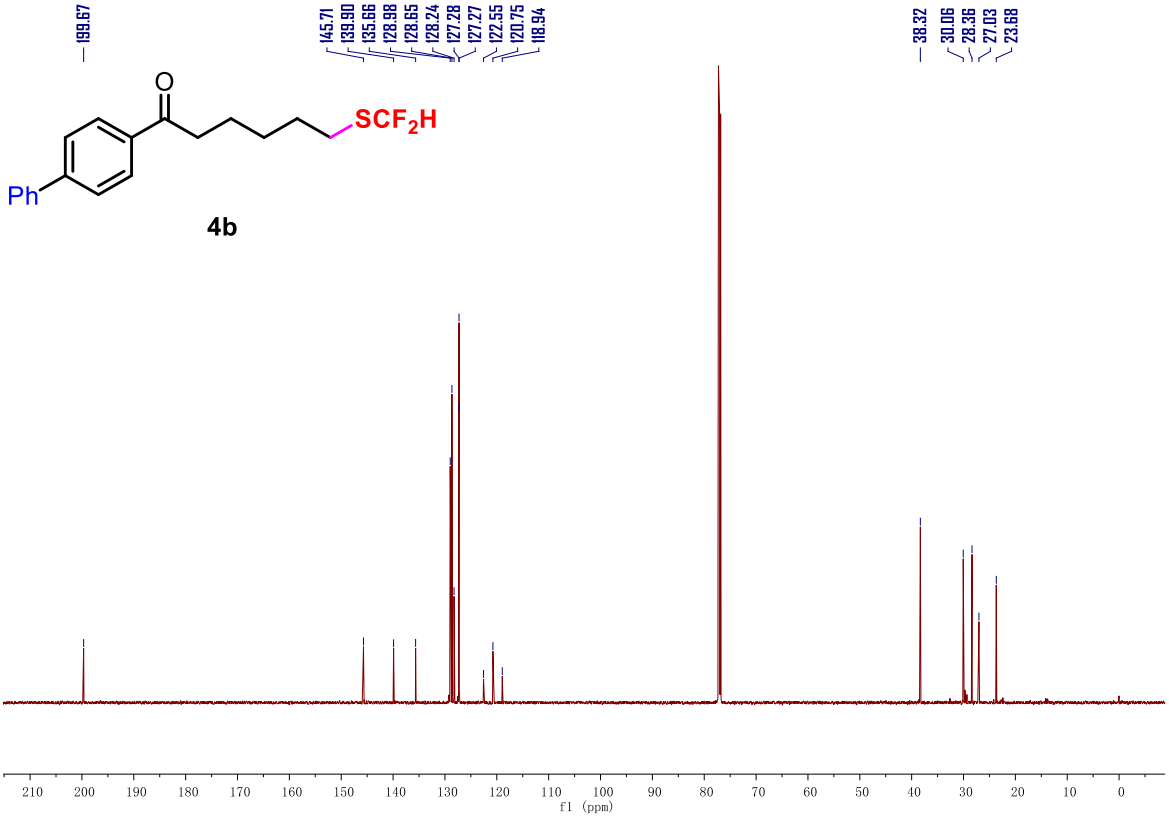
^{1}H NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-6-((difluoromethyl)thio)hexan-1-one (**4b**)

600 MHz, $CDCl_3$, 23 ℃



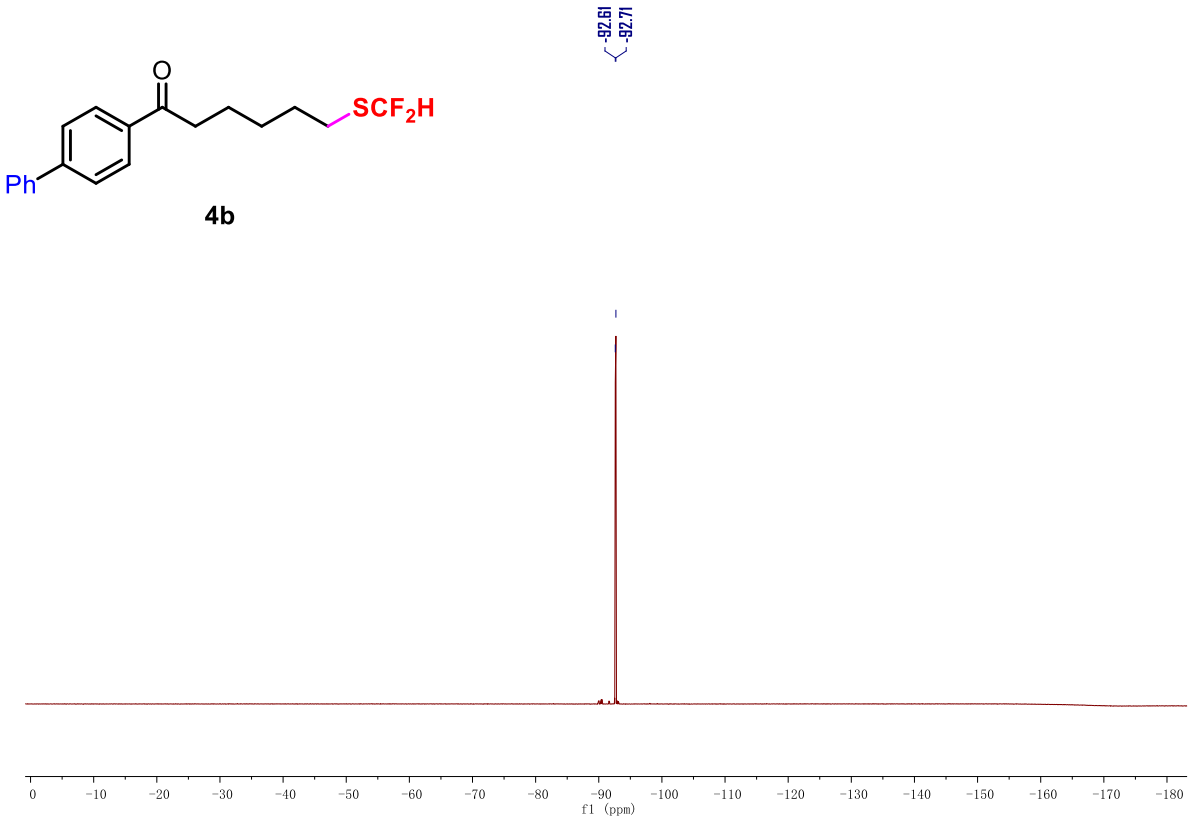
^{13}C NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-6-((difluoromethyl)thio)hexan-1-one (**4b**)

151 MHz, $CDCl_3$, 23 ℃



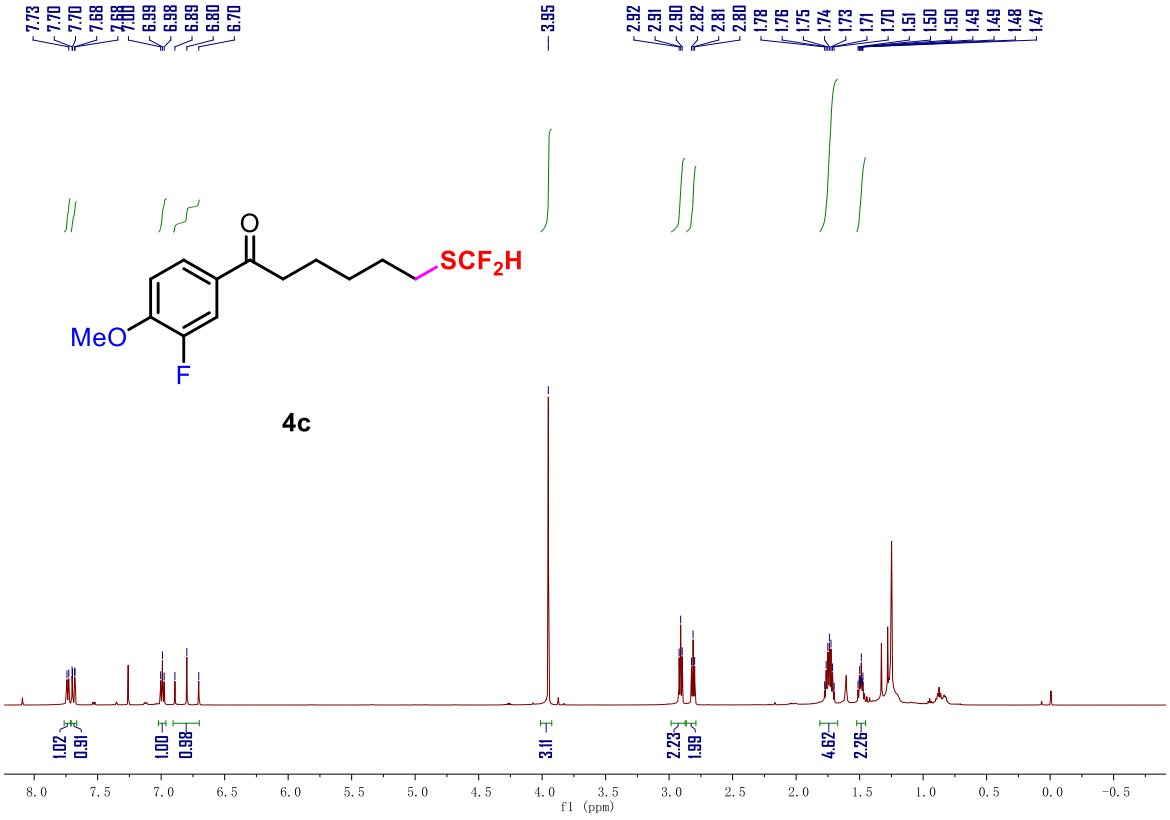
^{19}F NMR spectrum of 1-([1,1'-biphenyl]-4-yl)-6-((difluoromethyl)thio)hexan-1-one (**4b**)

565 MHz, $CDCl_3$, 23 ℃



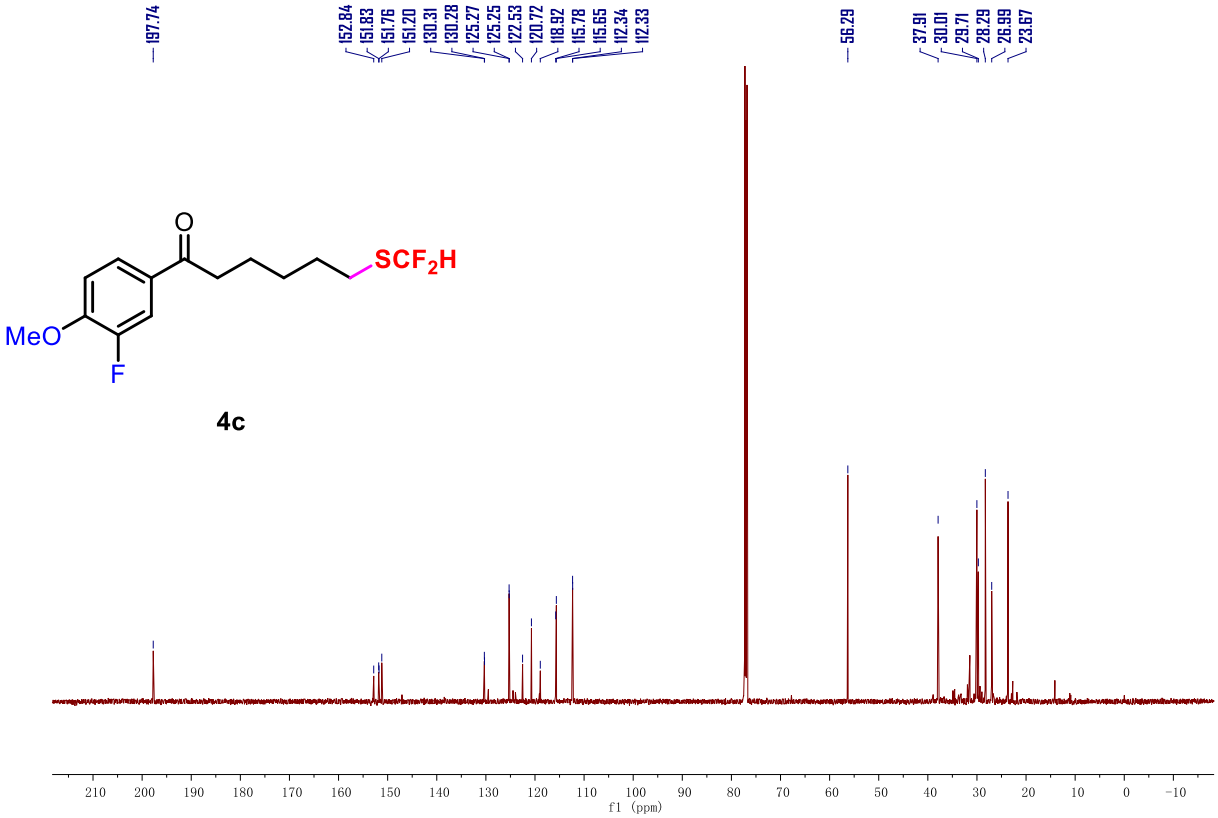
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(3-fluoro-4-methoxyphenyl)hexan-1-one (**4c**)

600 MHz, $CDCl_3$, 23 ℃



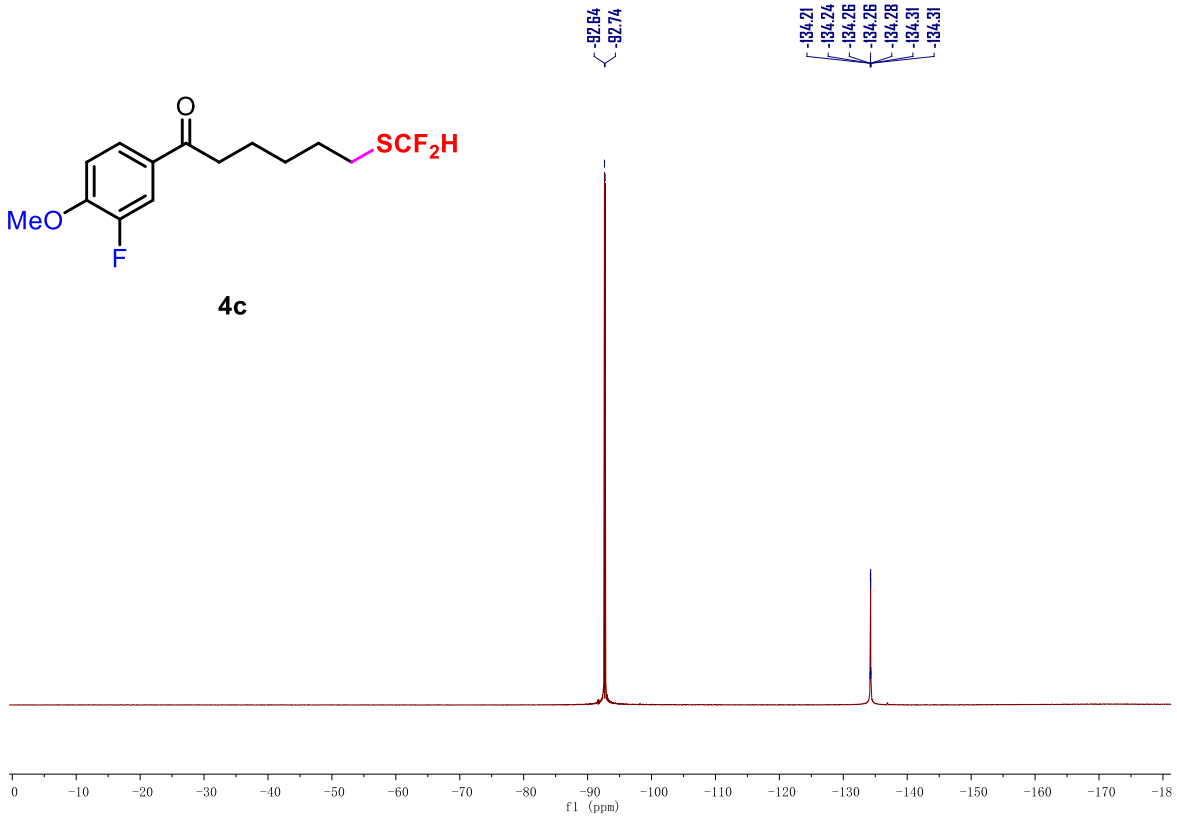
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(3-fluoro-4-methoxyphenyl)hexan-1-one (**4c**)

151 MHz, $CDCl_3$, 23 ℃



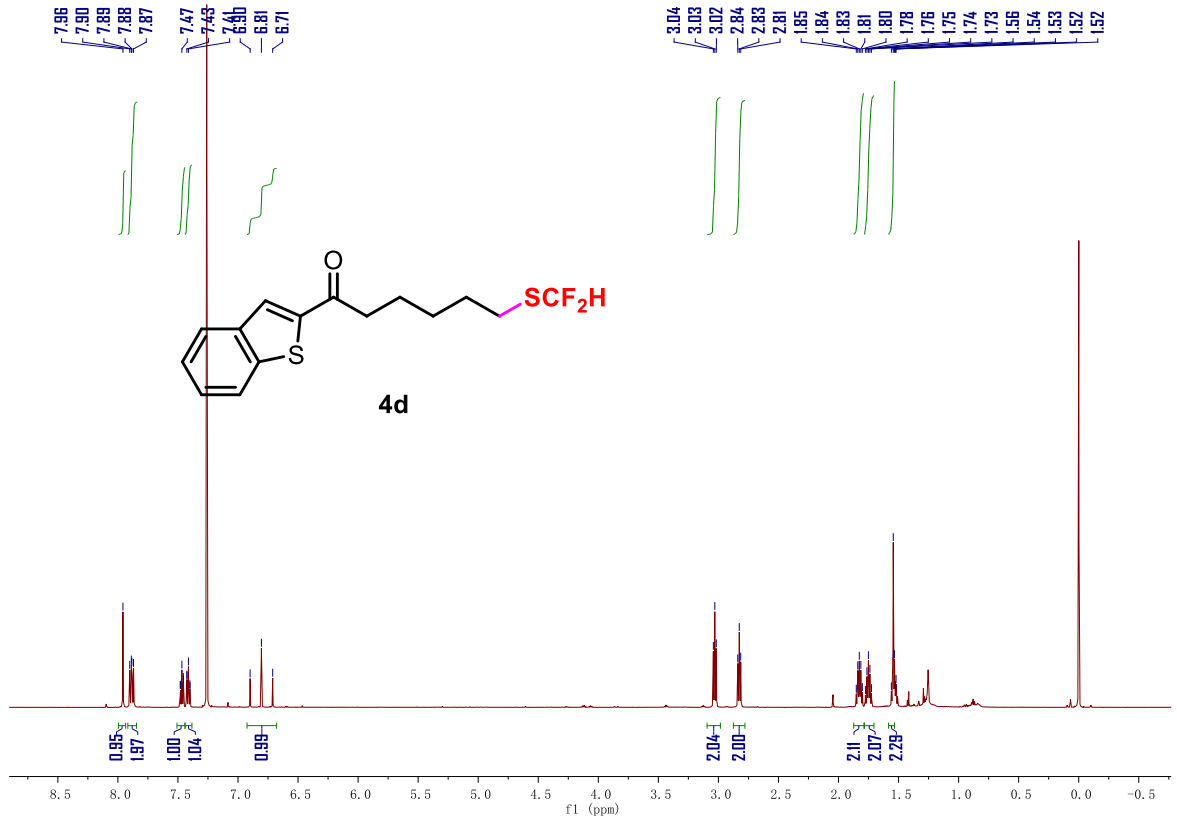
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(3-fluoro-4-methoxyphenyl)hexan-1-one (**4c**)

565 MHz, $CDCl_3$, 23 ℃



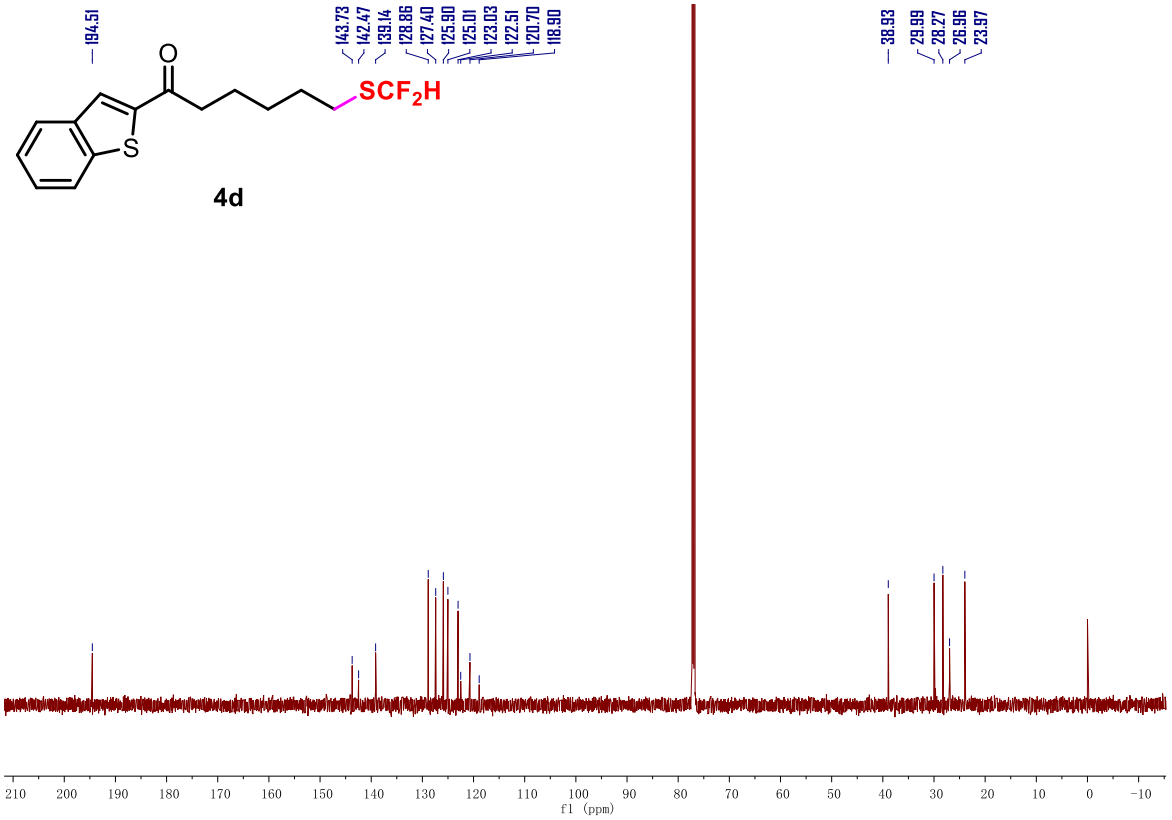
^{1}H NMR spectrum of 1-(benzo[b]thiophen-2-yl)-6-((difluoromethyl)thio)hexan-1-one (**4d**)

600 MHz, $CDCl_3$, 23 ℃



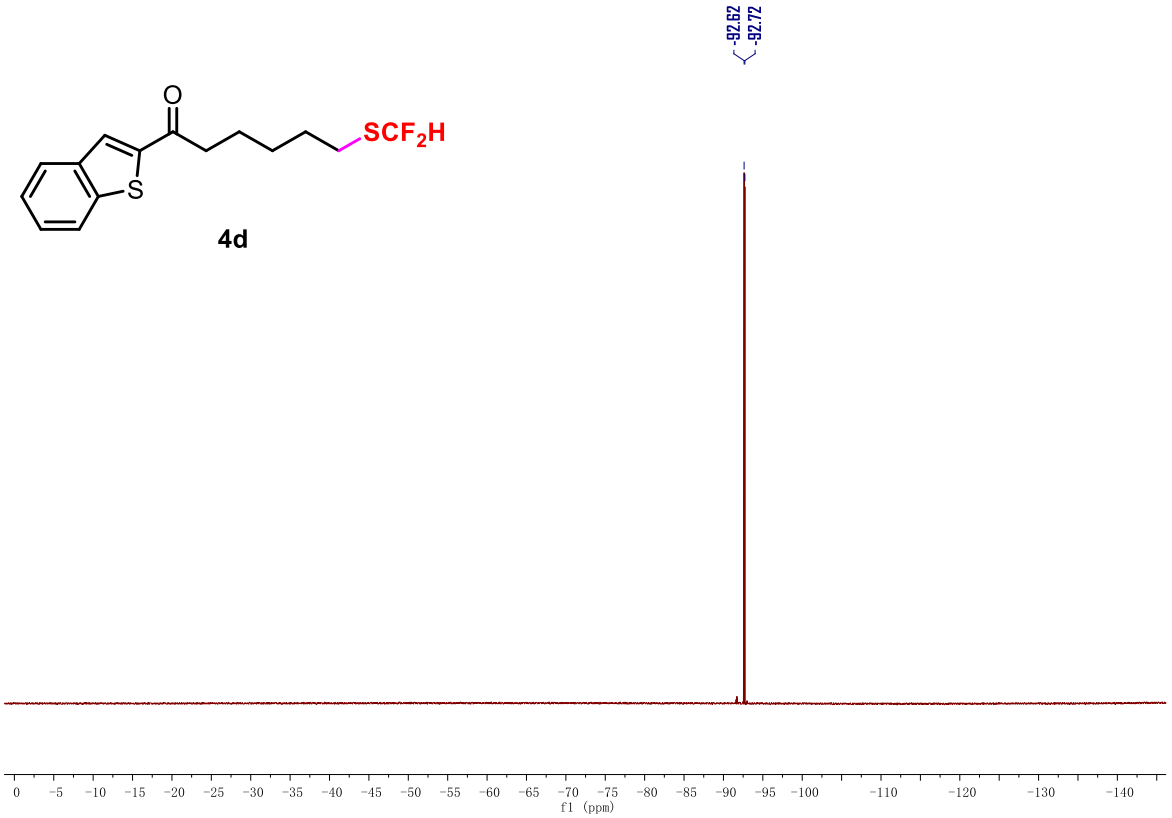
^{13}C NMR spectrum of 1-(benzo[b]thiophen-2-yl)-6-((difluoromethyl)thio)hexan-1-one (**4d**)

151 MHz, $CDCl_3$, 23 ℃



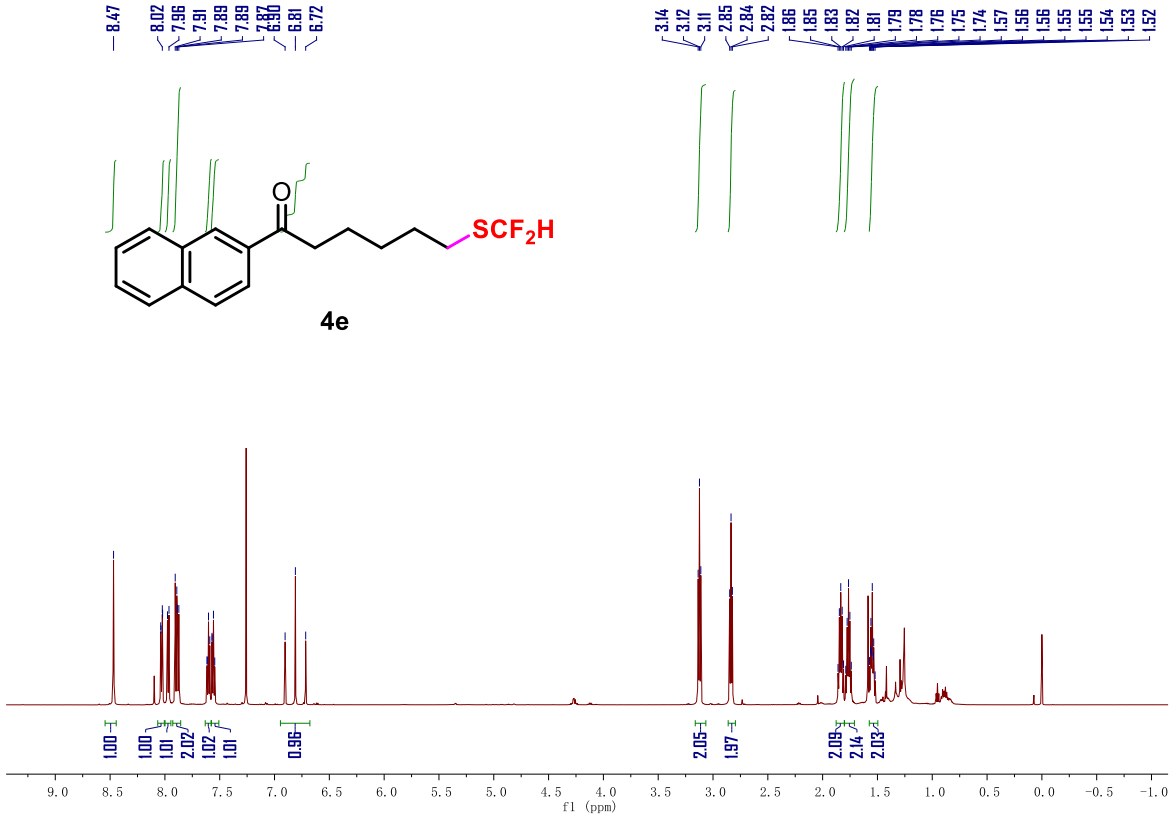
^{19}F NMR spectrum of 1-(benzo[b]thiophen-2-yl)-6-((difluoromethyl)thio)hexan-1-one (**4d**)

565 MHz, $CDCl_3$, 23 ℃



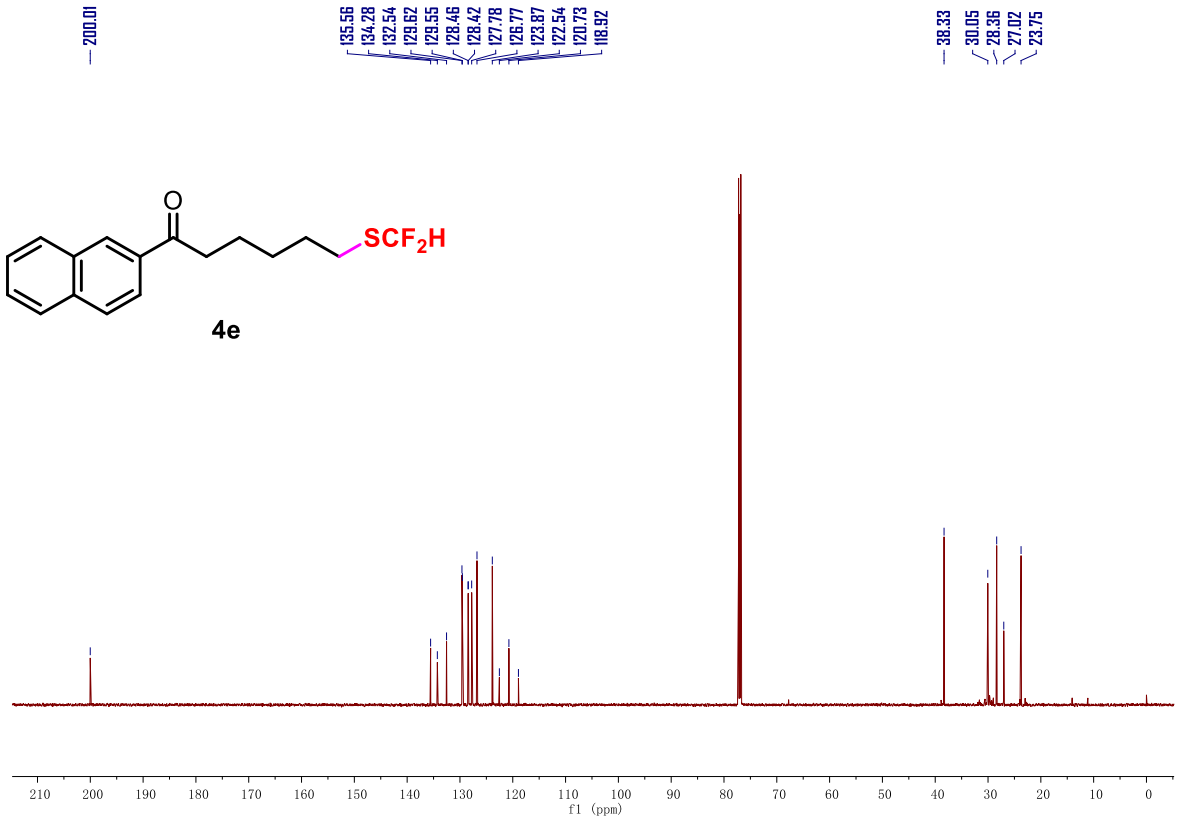
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(naphthalen-2-yl)hexan-1-one (**4e**)

600 MHz, $CDCl_3$, 23 ℃



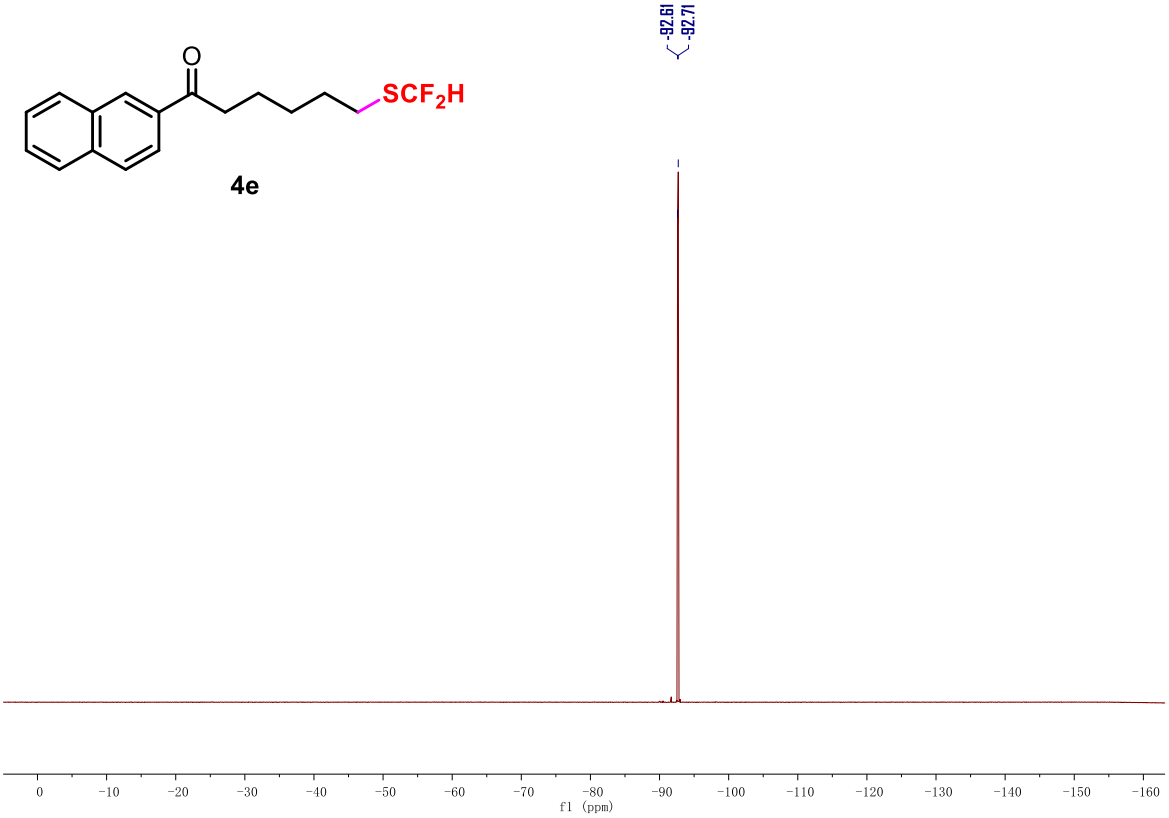
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(naphthalen-2-yl)hexan-1-one (**4e**)

151 MHz, $CDCl_3$, 23 ℃



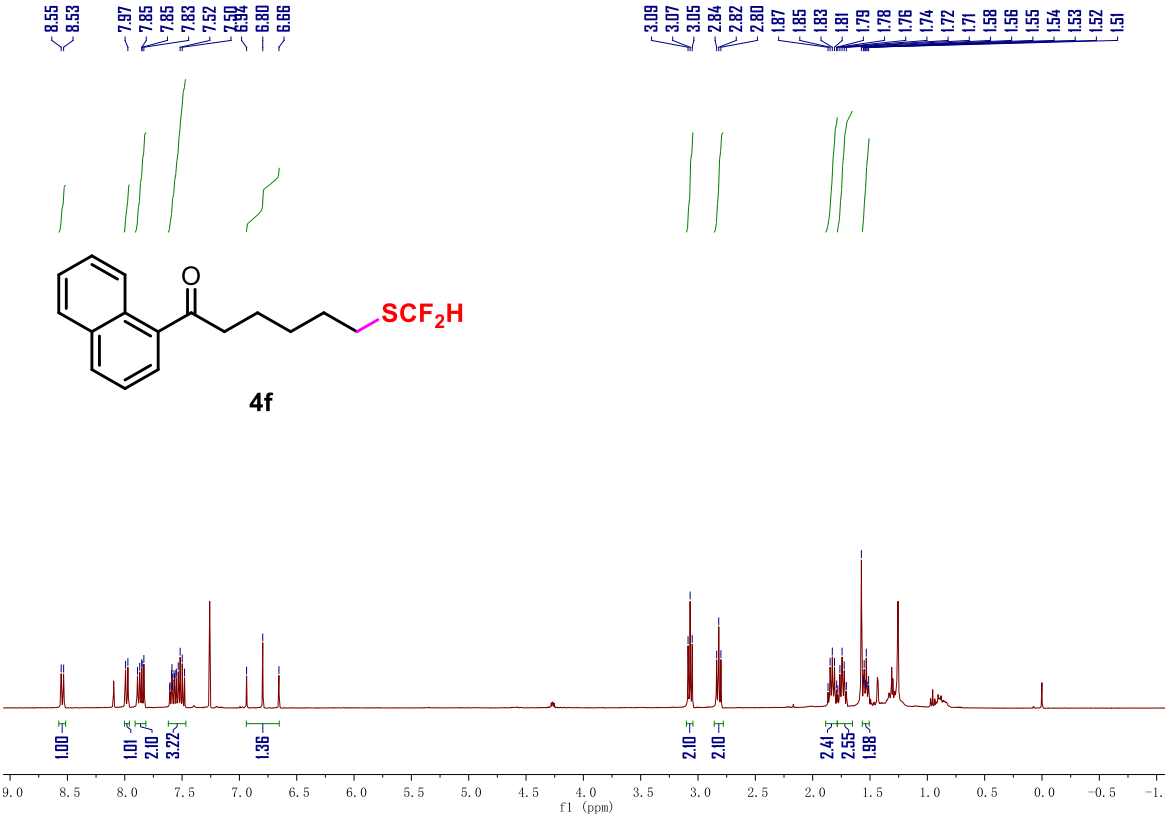
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(naphthalen-2-yl)hexan-1-one (**4e**)

565 MHz, $CDCl_3$, 23 ℃



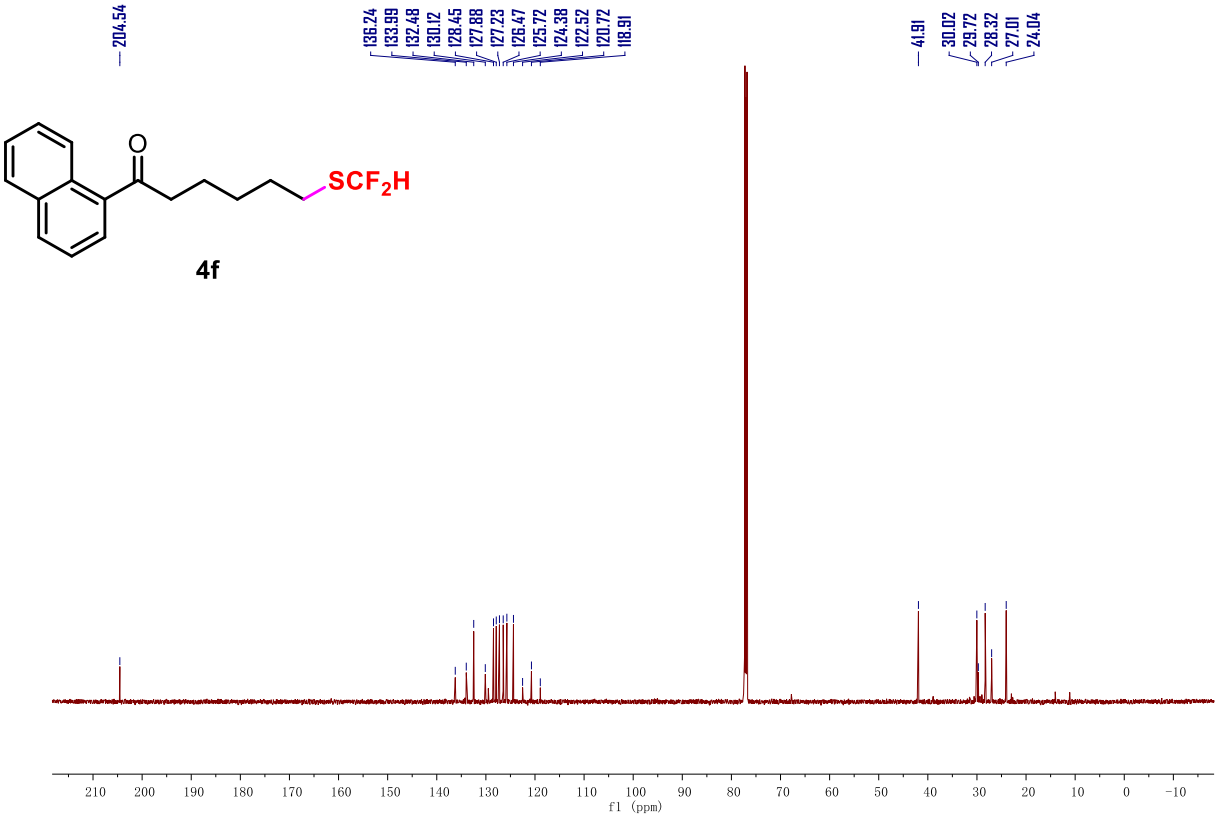
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(naphthalen-1-yl)hexan-1-one (**4f**)

600 MHz, $CDCl_3$, 23 ℃



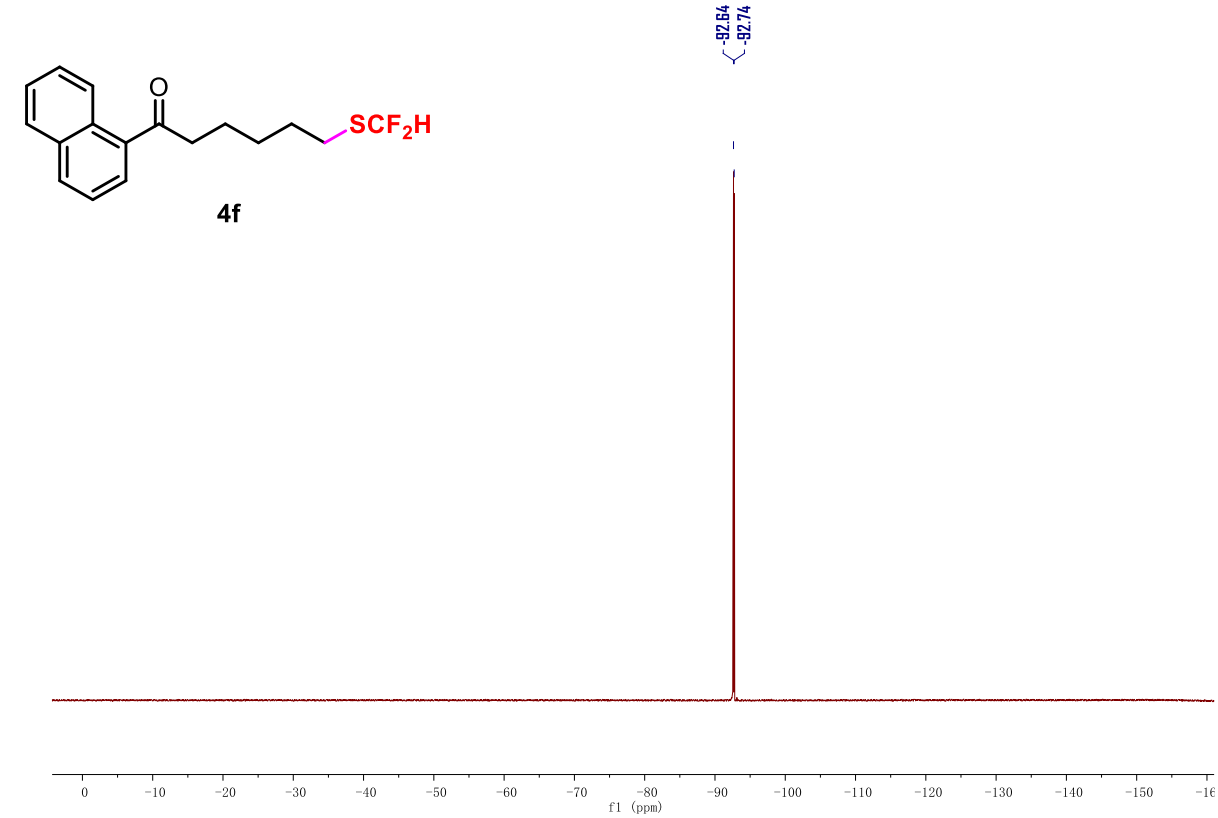
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(naphthalen-1-yl)hexan-1-one (**4f**)

151 MHz, $CDCl_3$, 23 ℃



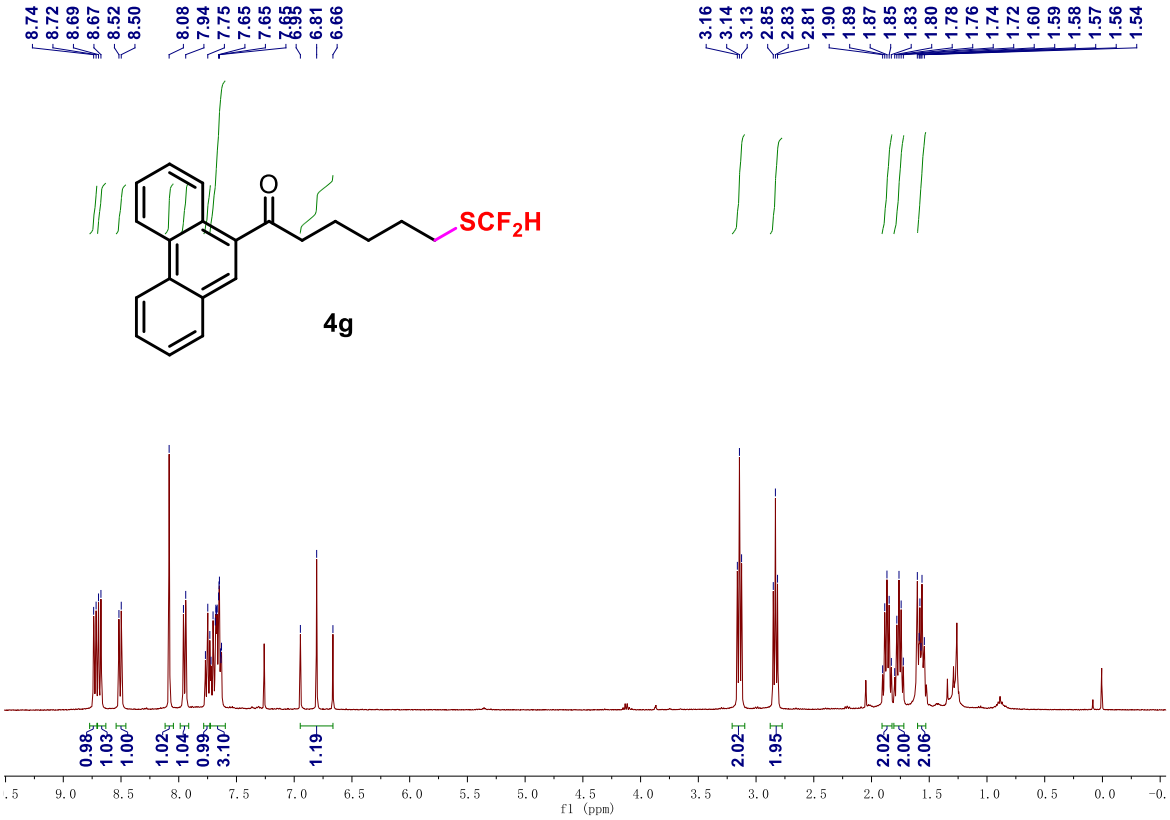
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(naphthalen-1-yl)hexan-1-one (**4f**)

565 MHz, $CDCl_3$, 23 ℃



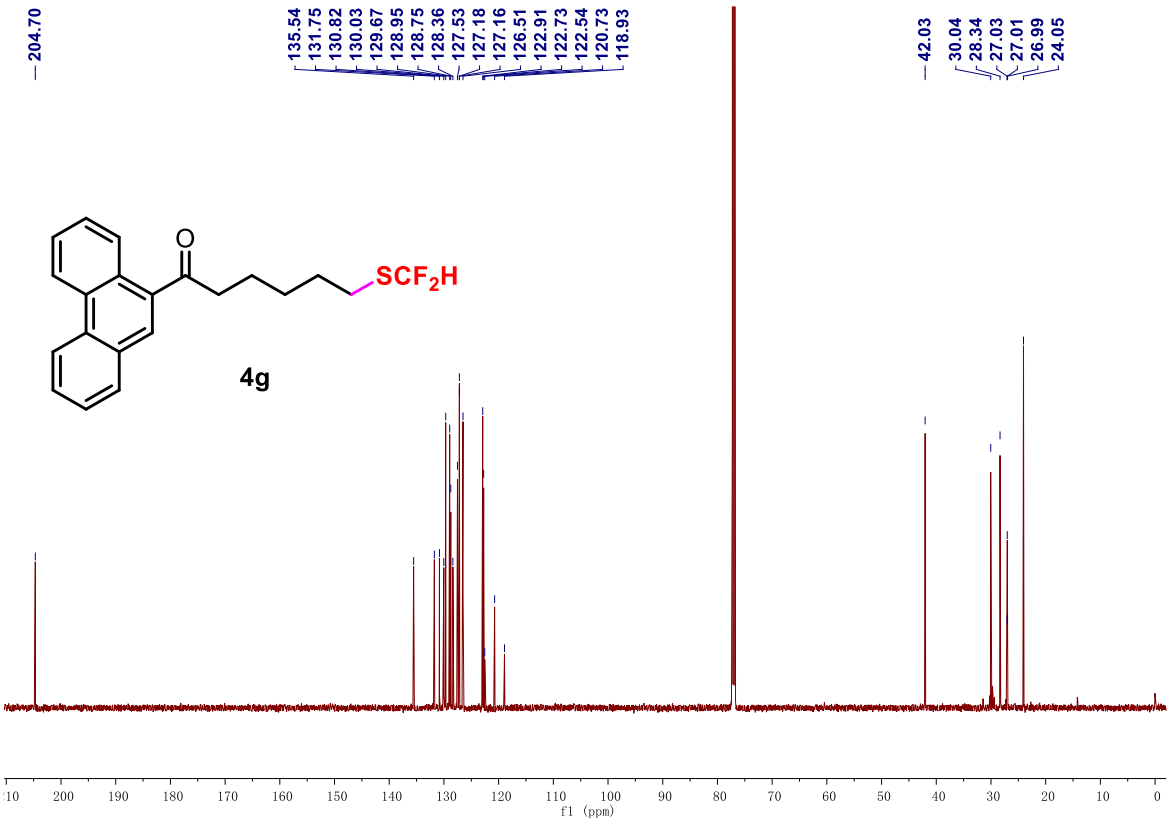
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(phenanthren-9-yl)hexan-1-one (**4g**)

600 MHz, $CDCl_3$, 23 ℃



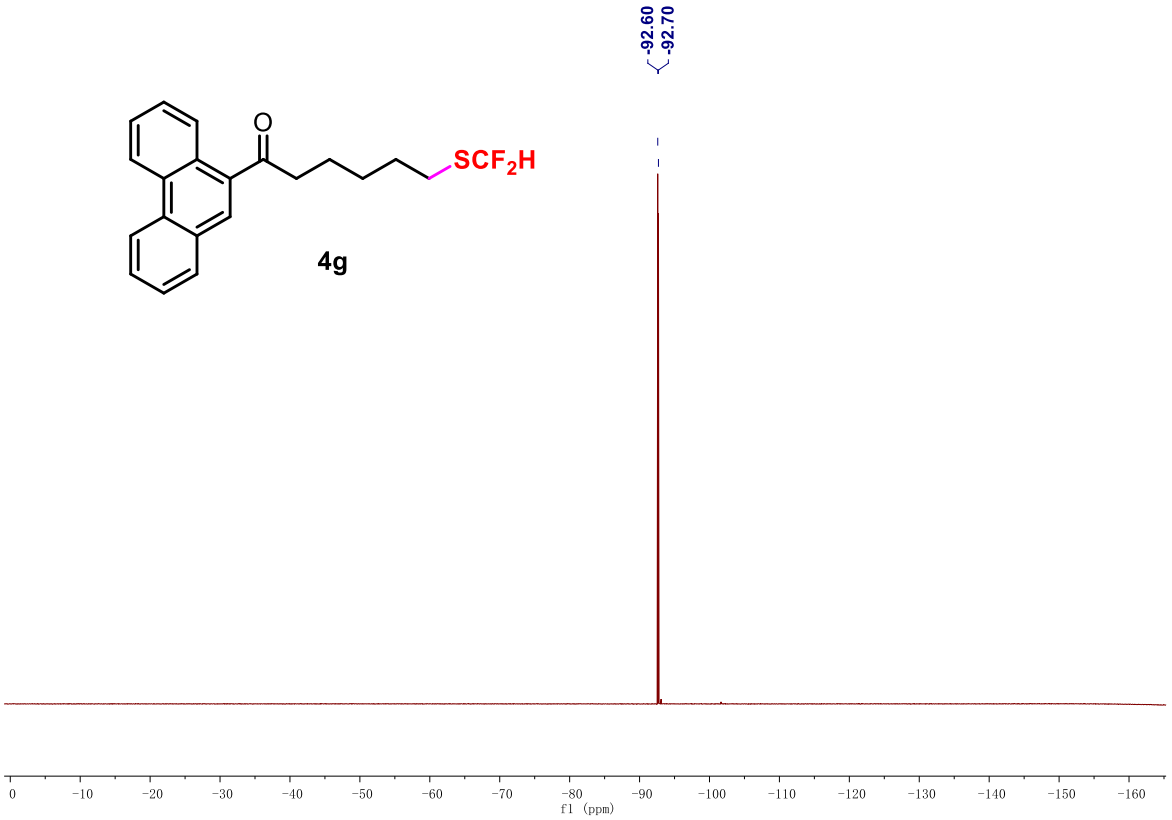
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(phenanthren-9-yl)hexan-1-one (**4g**)

151 MHz, $CDCl_3$, 23 ℃



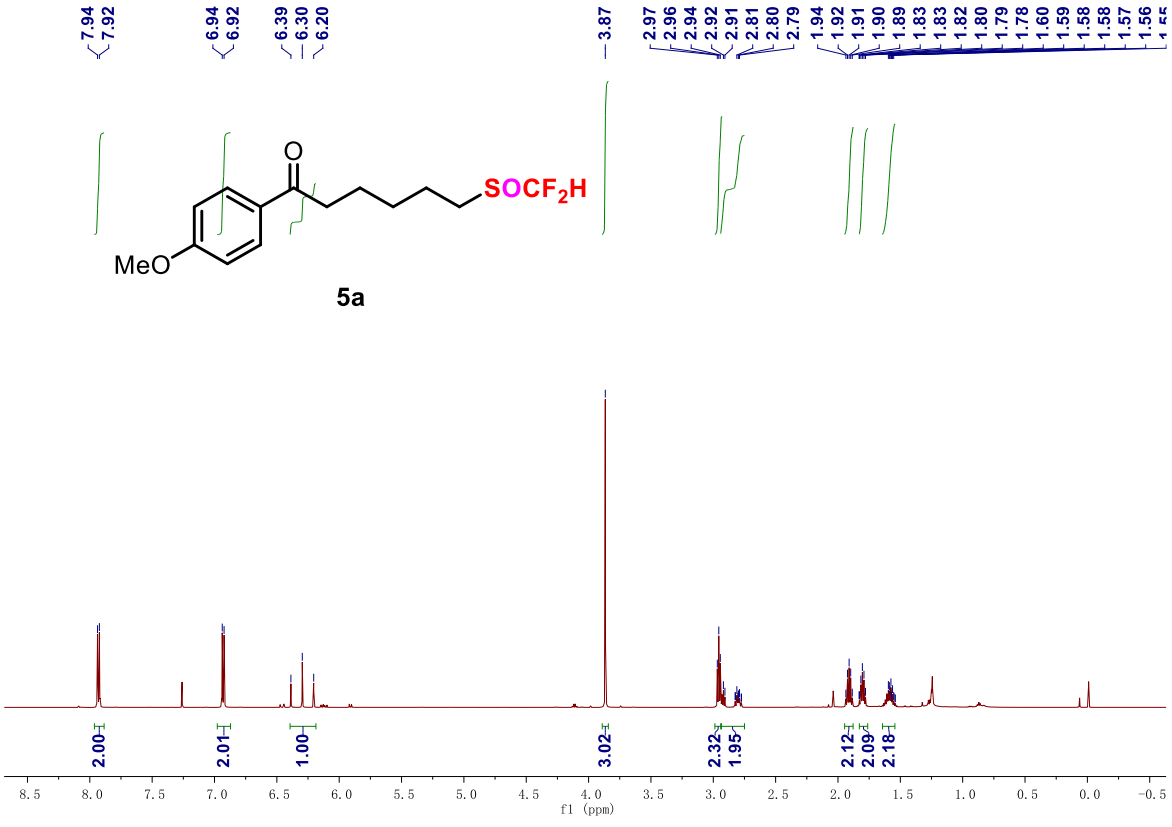
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(phenanthren-9-yl)hexan-1-one (**4g**)

565 MHz, $CDCl_3$, 23 ℃



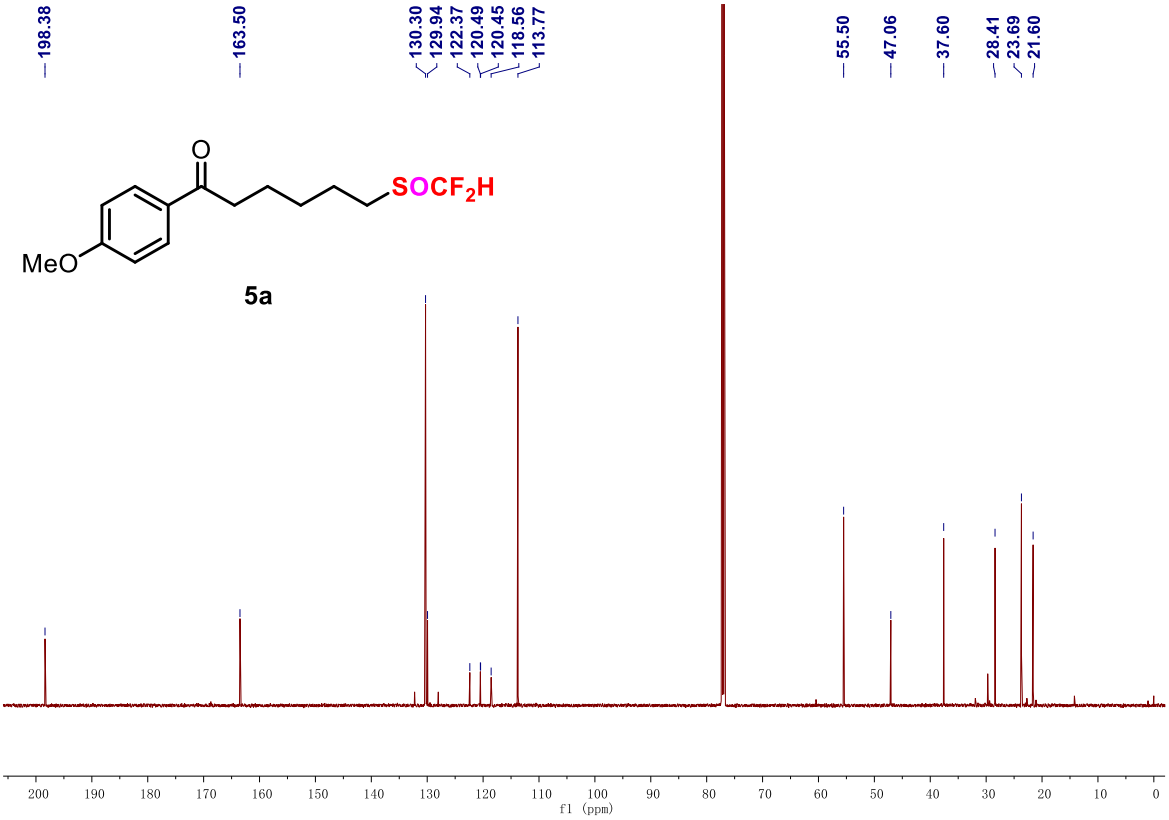
^{1}H NMR spectrum of 6-((difluoromethyl)sulfinyl)-1-(4-methoxyphenyl)hexan-1-one (**5a**)

600 MHz, $CDCl_3$, 23 ℃



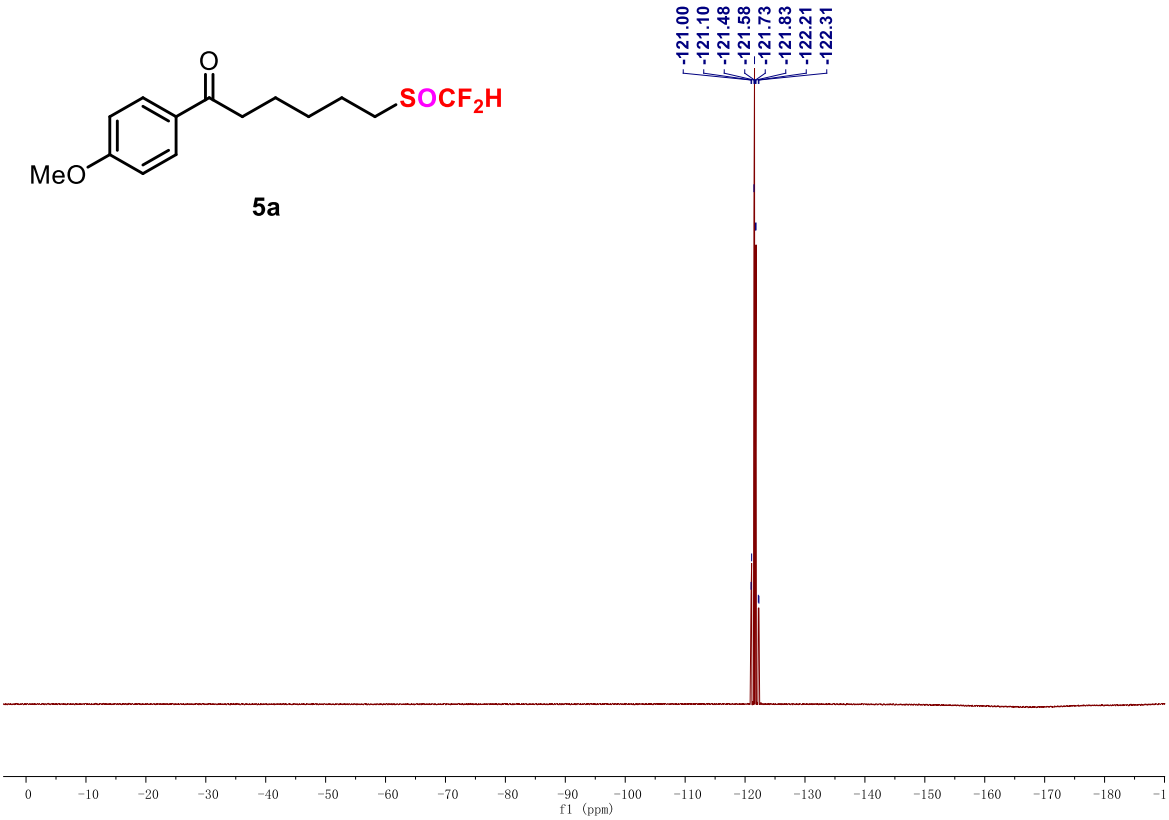
^{13}C NMR spectrum of 6-((difluoromethyl)sulfinyl)-1-(4-methoxyphenyl)hexan-1-one (**5a**)

151 MHz, $CDCl_3$, 23 ℃



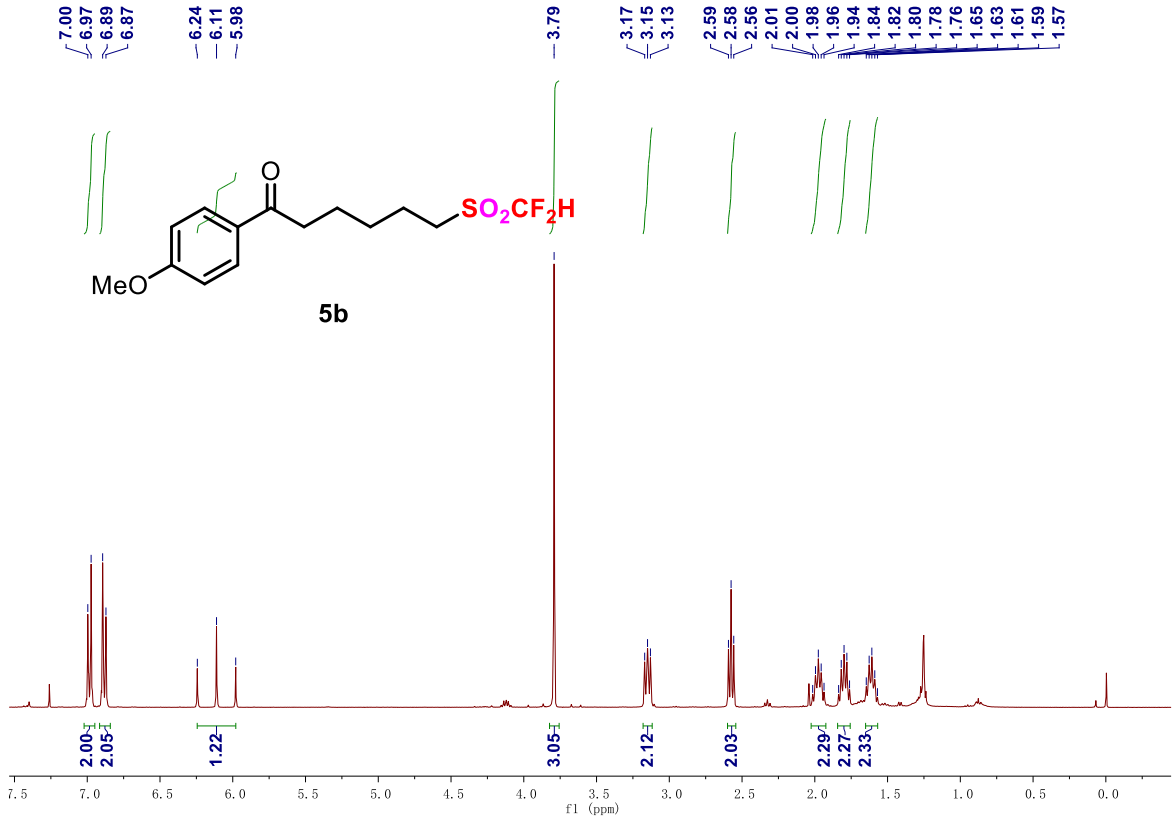
^{19}F NMR spectrum of 6-((difluoromethyl)sulfinyl)-1-(4-methoxyphenyl)hexan-1-one (**5a**)

565 MHz, $CDCl_3$, 23 ℃



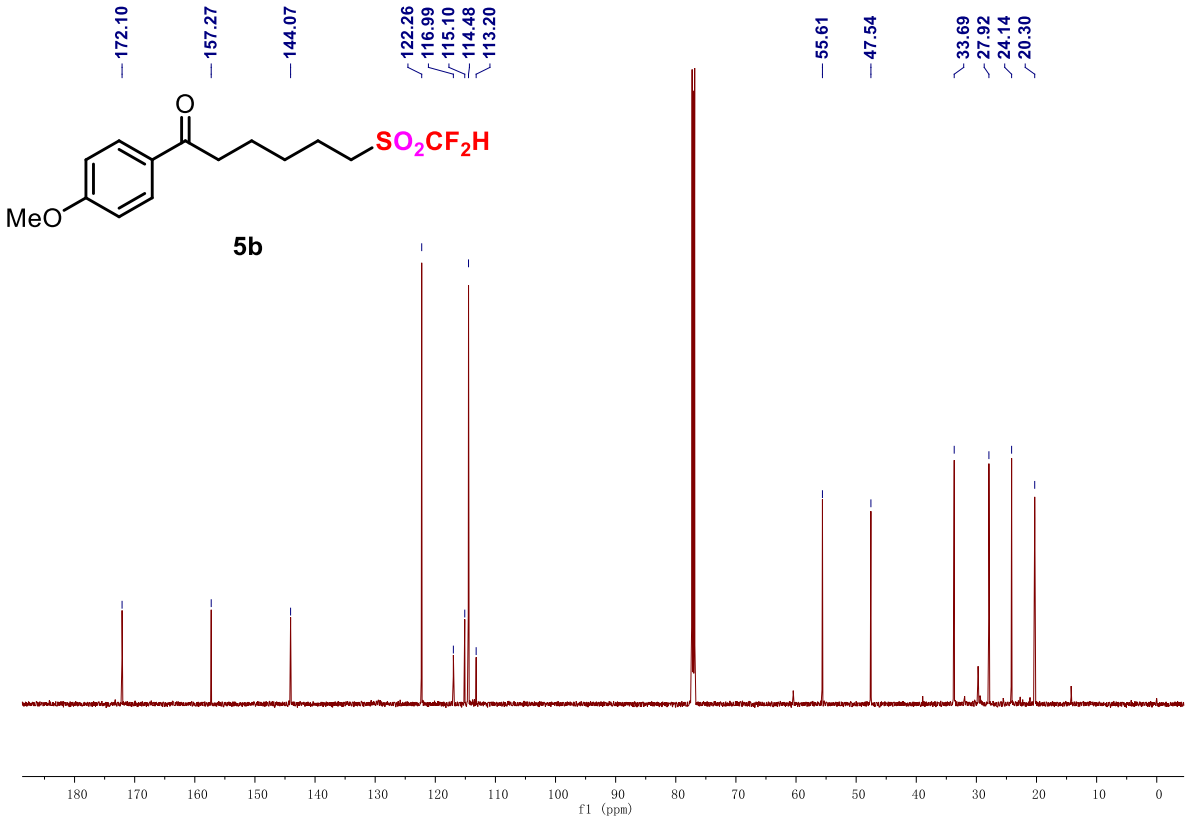
^{1}H NMR spectrum of 6-((difluoromethyl)sulfonyl)-1-(4-methoxyphenyl)hexan-1-one (**5b**)

600 MHz, $CDCl_3$, 23 ℃



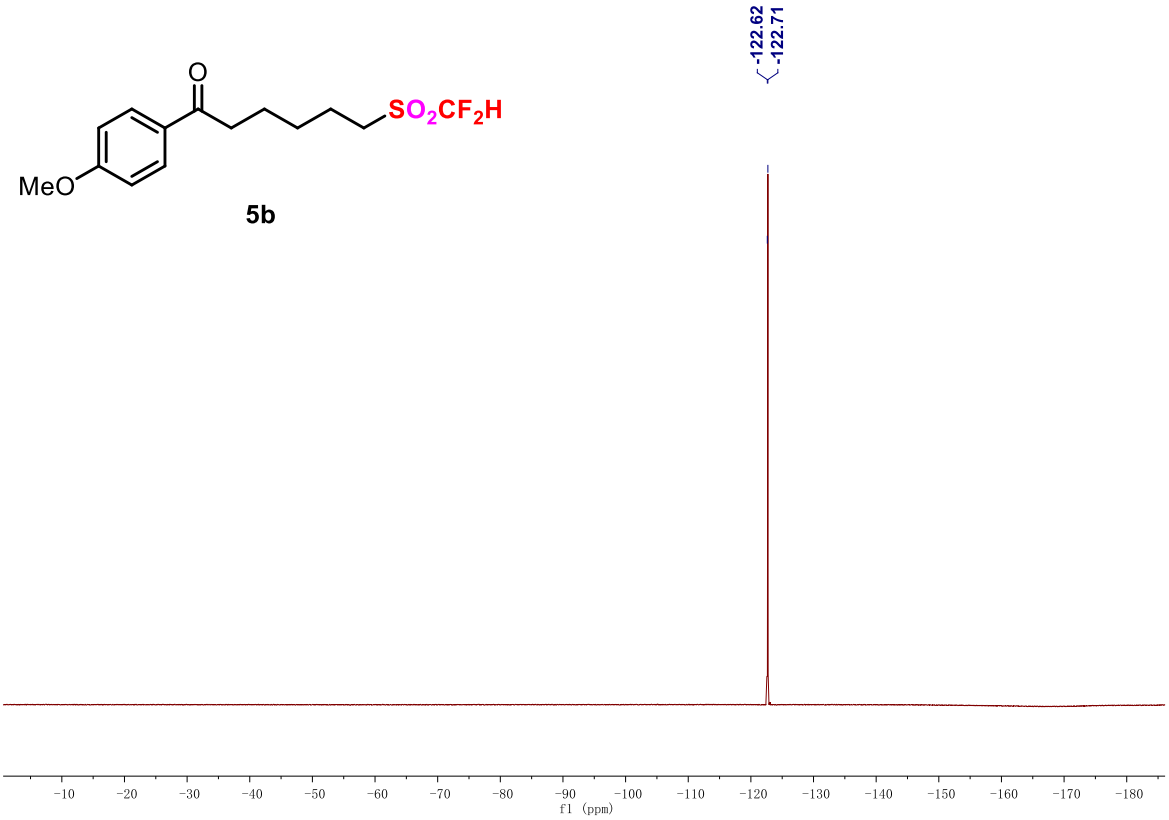
^{13}C NMR spectrum of 6-((difluoromethyl)sulfonyl)-1-(4-methoxyphenyl)hexan-1-one (**5b**)

151 MHz, $CDCl_3$, 23 ℃



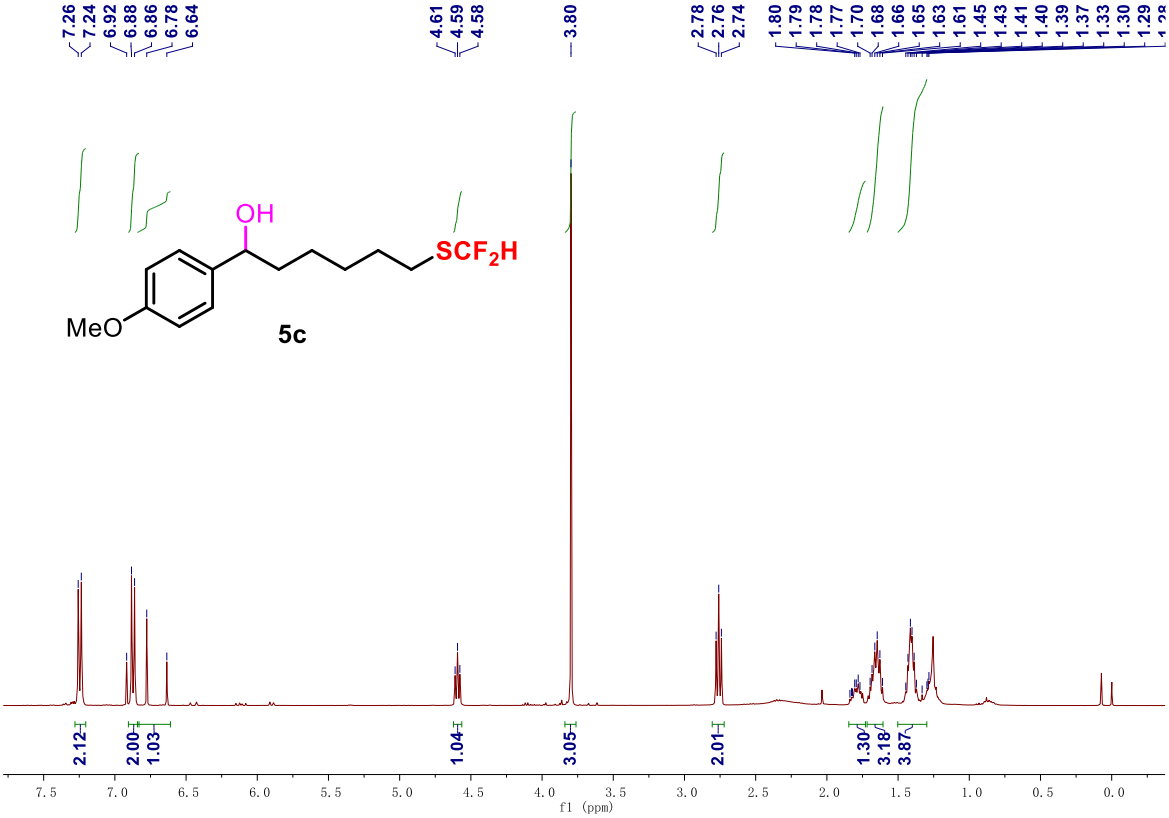
^{19}F NMR spectrum of 6-((difluoromethyl)sulfonyl)-1-(4-methoxyphenyl)hexan-1-one (**5b**)

565 MHz, $CDCl_3$, 23 ℃



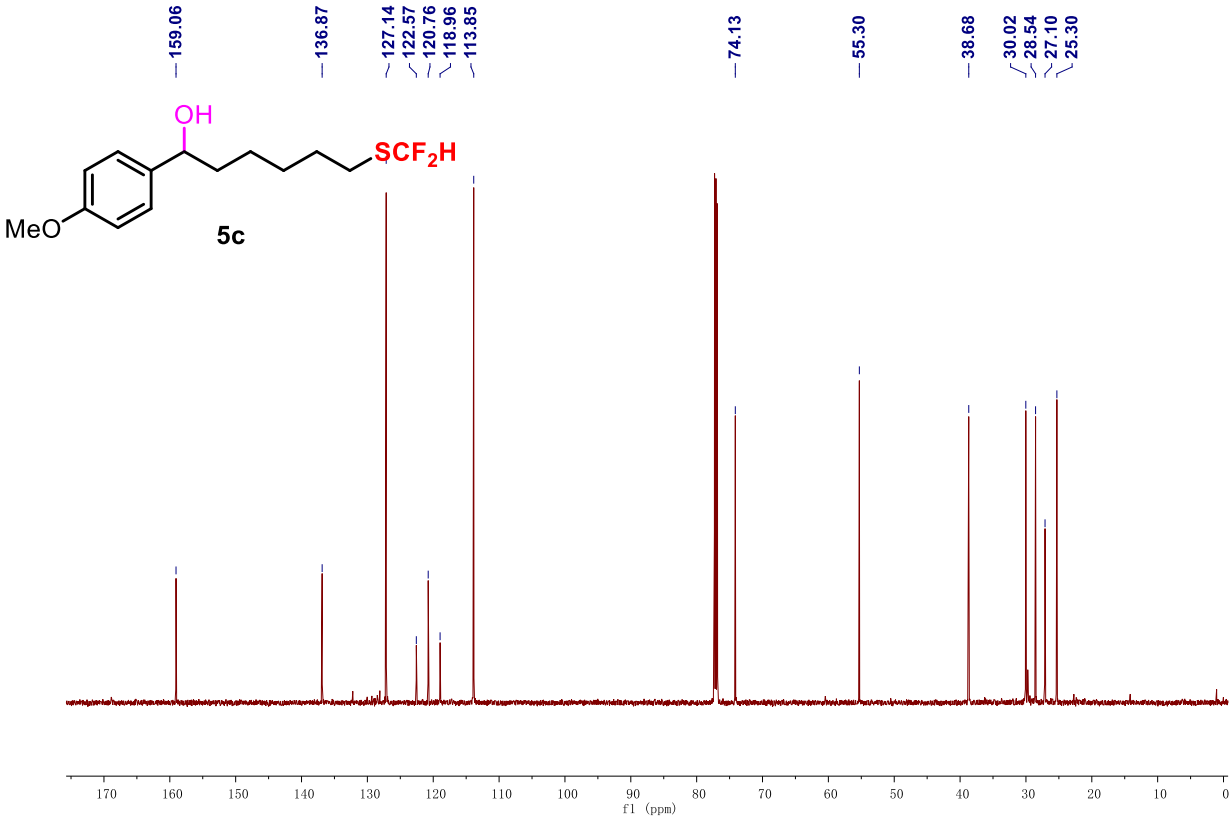
^{1}H NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-ol (**5c**)

600 MHz, $CDCl_3$, 23 ℃



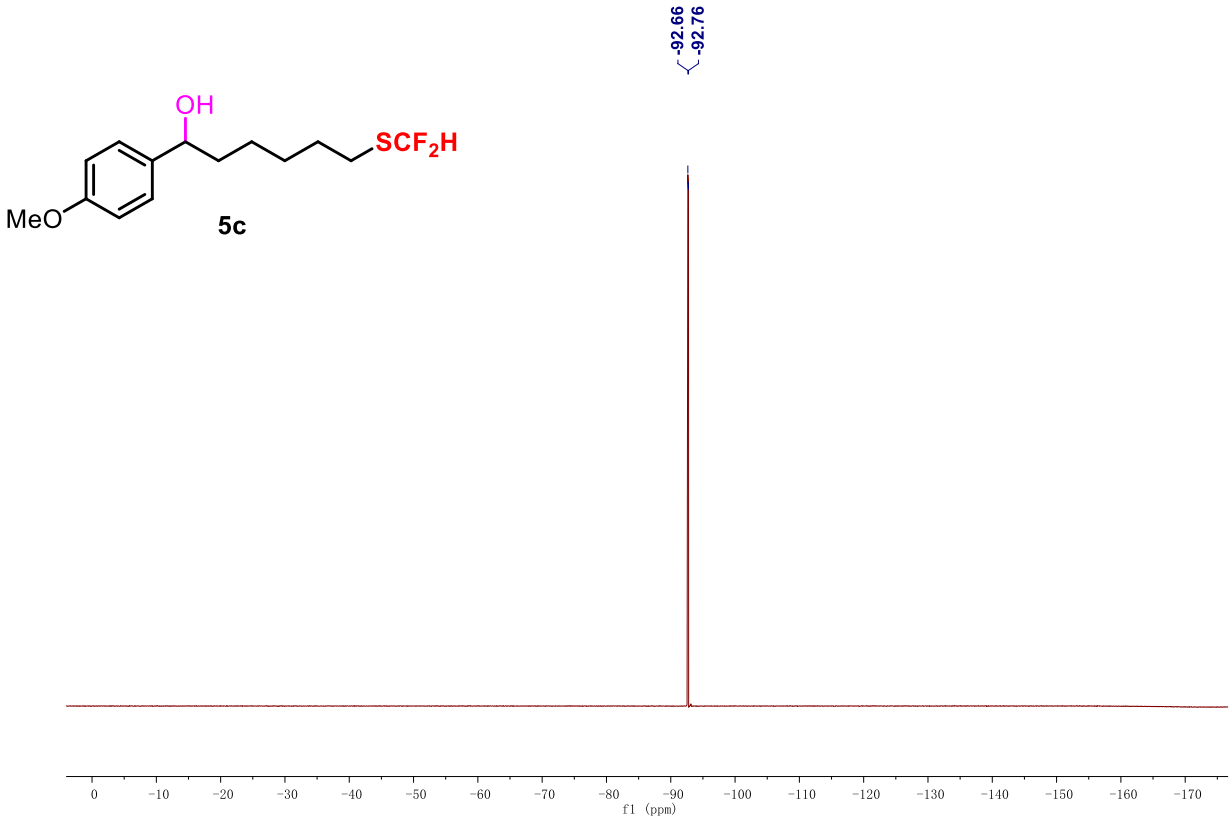
^{13}C NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-ol (**5c**)

151 MHz, $CDCl_3$, 23 ℃



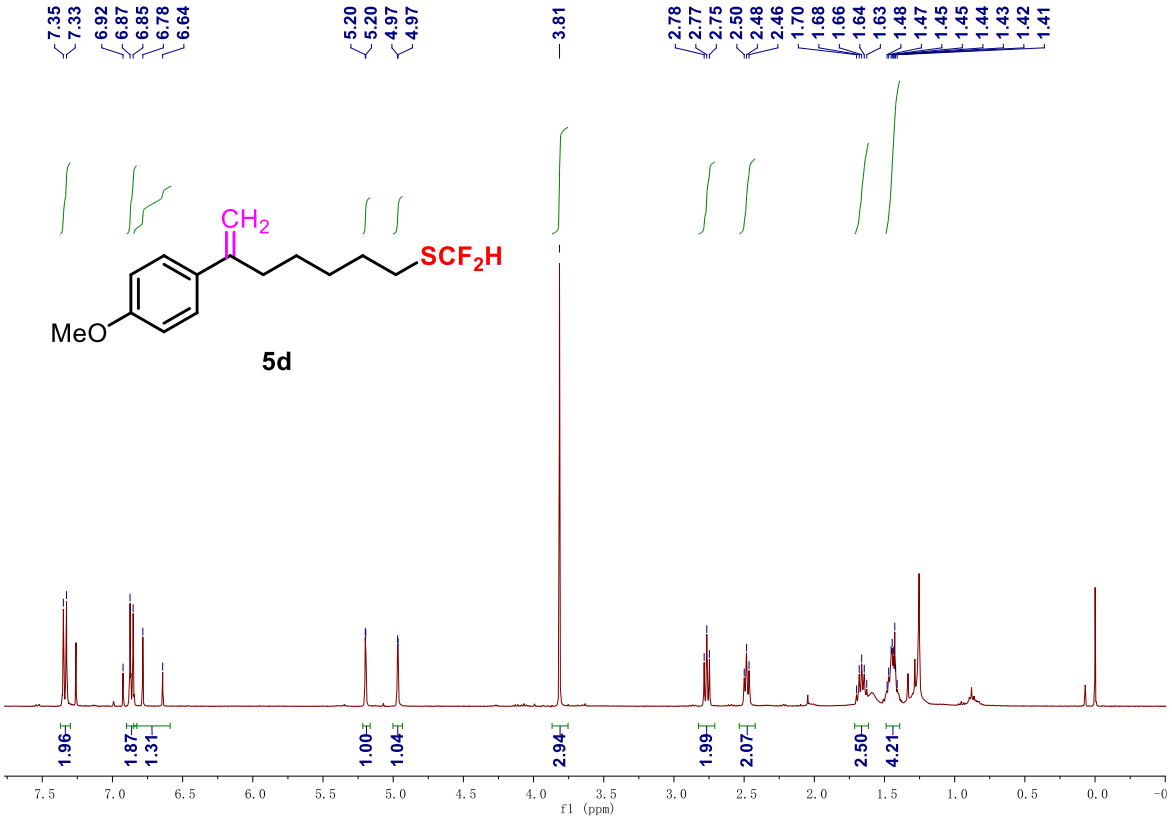
^{19}F NMR spectrum of 6-((difluoromethyl)thio)-1-(4-methoxyphenyl)hexan-1-ol (**5c**)

565 MHz, $CDCl_3$, 23 ℃



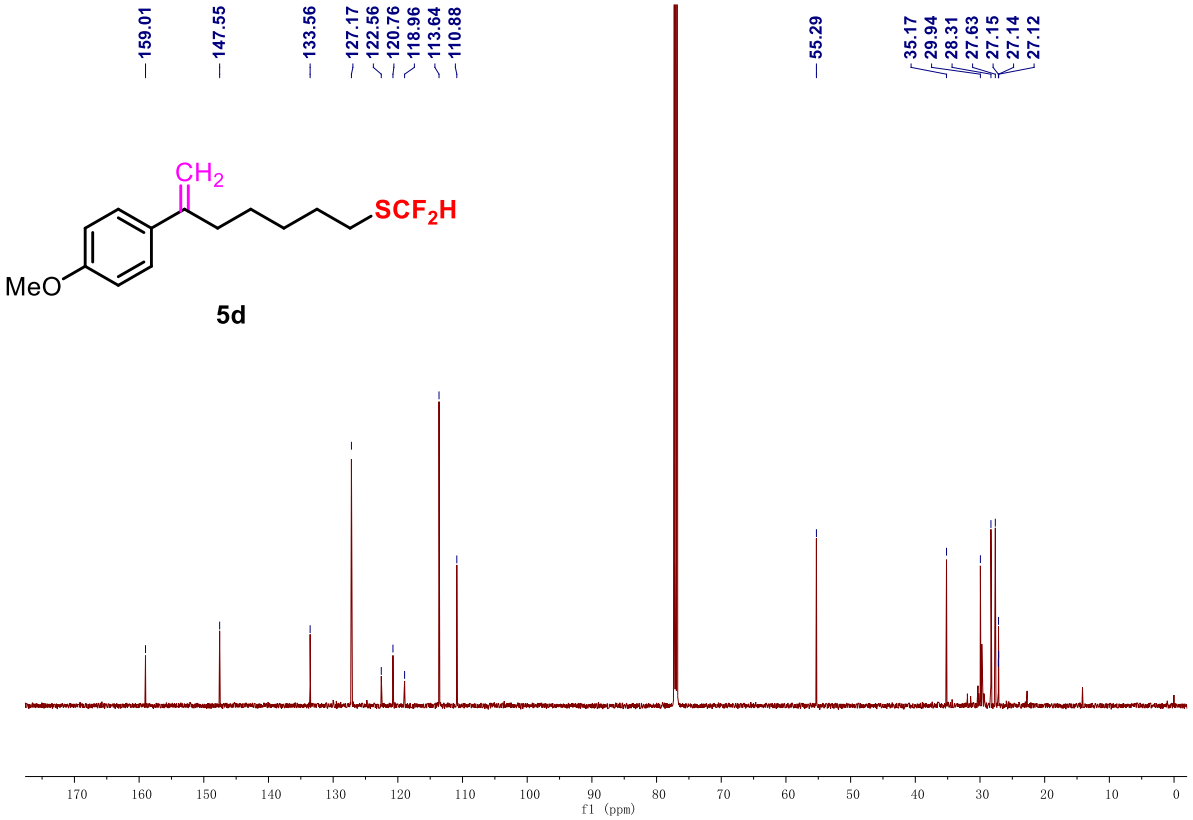
^{1}H NMR spectrum of (difluoromethyl)(6-(4-methoxyphenyl)hept-6-en-1-yl)sulfane (**5d**)

600 MHz, $CDCl_3$, 23 ℃



^{13}C NMR spectrum of (difluoromethyl)(6-(4-methoxyphenyl)hept-6-en-1-yl)sulfane (**5d**)

151 MHz, $CDCl_3$, 23 ℃



^{19}F NMR spectrum of (difluoromethyl)(6-(4-methoxyphenyl)hept-6-en-1-yl)sulfane (**5d**)

565 MHz, $CDCl_3$, 23 ℃