Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

An aryne triggered ring-opening fluorination of cyclic thioethers with potassium fluoride

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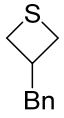
I. General Methods.

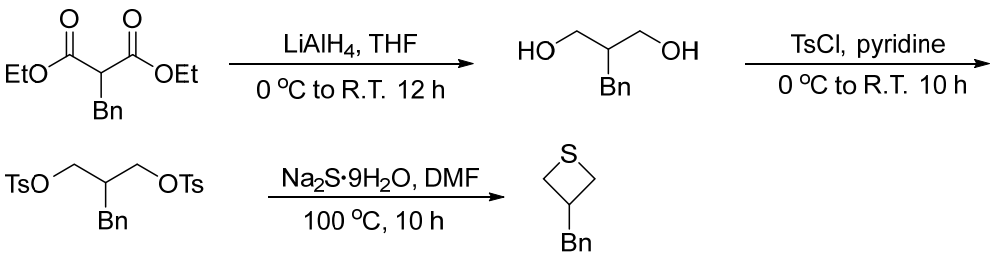
All reactions were carried out in schlenk tubes. The reactions were monitored either by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates (Yantai Chemical Industry Research Institute) or GC-MS (Thermo Fisher Trace 1300-ISQ). Visualization was accomplished by UV light (254 nm). The crude products were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical). ^{1}H NMR spectra was recorded on a 400 MHz spectrometer at ambient temperature. Data are reported as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm) (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintet and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.16 ppm). HR-MS data were obtained on a QTOF mass spectrometer. All commercial materials were used as received unless otherwise noted. Aryne precursors are all prepared following the literature procedures[1]. Sulfur heterocycles **2b**, **2g**, **2h**, **2i** and **2j** are prepared following the literature procedures[2].

II. Substrates Preparation

1) Synthesis of 2c:



3-benzylthietane (2c)



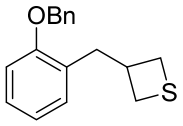
Synthesis of 2-benzylpropane-1,3-diol: a mixture of diethyl 2-benzylmalonate (5 mmol, 1.25 g, 1 equiv.) and anhydrous tetrahydrofuran (THF, 5 mL) was added to a solution of lithium aluminum hydride ($LiAlH_4$, 15 mmol, 0.57 g, 3 equiv.) in anhydrous tetrahydrofuran (THF, 10 mL) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring overnight at room temperature. The reaction was then carefully quenched with water (1 mL), 15% aqueous sodium hydroxide (1 mL), water (3 mL) dropwise at 0 °C. After being stirred for 30 minutes, the mixture was diluted with ethyl acetate (50 mL), filtered through celite and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 1:1 as the eluent) to give 2-benzylpropane-1,3-diol (60% yield) as a pale yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 1H), 7.27-7.18 (m, 2H), 3.82 (dd, *J* = 10.6, 3.5 Hz, 1H), 3.69 (dd, *J* = 10.4, 7.1 Hz, 1H), 2.64 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 1H), 2.15 – 2.00 (m, 1H)..

Synthesis of 2-benzylpropane-1,3-diyl bis(4-methylbenzenesulfonate): to a solution of 2-benzylpropane-1,3-diol (1.5 mmol, 0.25 g, 1 equiv.) in pyridine (1 mL), p-toluene sulfonyl chloride (4.5 mmol, 0.86 g, 3 equiv.) in 14 mL pyridine was added at 0 °C for 30 minutes, the reaction was kept stirring for 8h. The reaction was then diluted with ethyl acetate (50 mL) and washed with saturated cupric sulfate until the organic phase became colorless, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give product 2-benzylpropane-1,3-diyl bis(4-methylbenzenesulfonate) (80% yield) as a white solid.

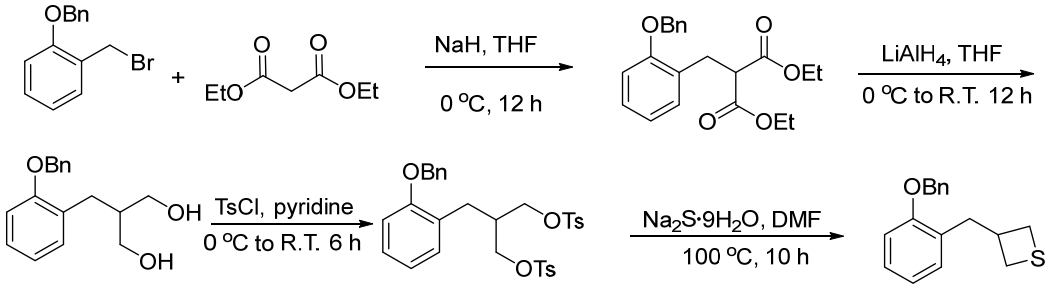
Synthesis of **2c**: to a mixture of $Na_2S·9H_2O$ (1.8 mmol, 0.43 g, 1.5 equiv.) in 10 mL anhydrous DMF was added 2-benzylpropane-1,3-diyl bis(4-methylbenzenesulfonate) (1.2 mmol, 0.57 g, 1.0 equiv.) in 5 mL DMF under nitrogen atmosphere in a flame-dried schlenk tube. The mixture was stirred at 100 °C for 12 h. The reaction was then quenched with water (30 mL) and extracted with DCM (3×20 mL), washed with water and brine, dried over sodium sulfate, filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography (PE: EA = 100:1

as the eluent) to give **2c** (35% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.4 Hz, 2H), 3.59 – 3.48 (m, 1H), 3.15 (t, J = 8.7 Hz, 2H), 3.11 – 3.07 (m, 2H), 2.88 (d, J = 7.8 Hz, 1H).

2) Synthesis of 2d:



3-(2-(benzyloxy)benzyl)thietane (2d)



Synthesis of diethyl 2-(2-(benzyloxy)benzyl)malonate: a mixture of sodium hydride (NaH, 11 mmol, 60% in mineral, 0.44 g, 1.1 equiv.) and anhydrous THF (15 mL) was added diethyl malonate (8 mmol, 1.28 g, 1 equiv.) under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring for 40 minutes until 1-(benzyloxy)-2-(bromomethyl)benzene (10 mmol, 2.77 g, 1.25 equiv.) was added to the solution dropwise. The reaction was kept stirring at 0 °C for 12 h. The reaction was then quenched with saturated NH_4Cl (30 mL) and extracted with ethyl acetate (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give diethyl 2-(2-(benzyloxy)benzyl)malonate (4 steps 86% yield) as a pale yellow liquid.

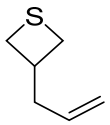
Synthesis of 2-(2-(benzyloxy)benzyl)propane-1,3-diol: a mixture of diethyl 2-(2-(benzyloxy)benzyl)malonate (6.7 mmol, 2.40 g, 1 equiv.) in 10 mL anhydrous THF was added lithium aluminum hydride (20 mmol, 0.76 g, 3 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring overnight at room temperature. The reaction was then carefully quenched with

1 mL water, 1.2 mL 15 % aqueous sodium hydroxide, 3 mL water dropwise at 0 °C. After being stirred at 30 minutes, the mixture was diluted with 50 mL ethyl acetate, filtered through celite and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give 2-(2-(benzyloxy)benzyl)propane-1,3-diol (68% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.15 – 7.06 (m, 2H), 6.90 – 6.82 (m, 2H), 4.96 (s, 2H), 3.65-3.55 (m, 4H), 3.52 (t, *J* = 7.2 Hz, 2H), 2.61 (d, *J* = 7.3 Hz, 2H).

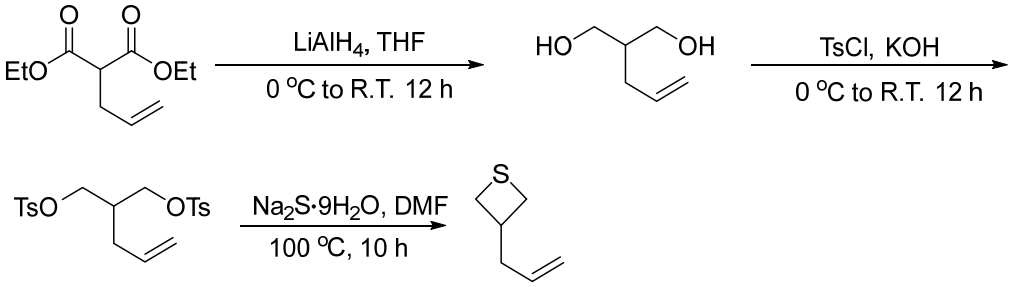
Synthesis of 2-(2-(benzyloxy)benzyl)-3-(mercaptooxy)propyl 4-methylbenzenesulfonate: to a solution of 2-(2-(benzyloxy)benzyl)propane-1,3-diol (3 mmol, 0.82 g, 1 equiv.) in 2 mL anhydrous pyridine, a solution of p-toluene sulfonyl chloride (7.5 mmol, 1.43 g, 3 equiv.) in 15 mL anhydrous pyridine was added at 0 °C for 30 minutes, the reaction was kept stirring for 6 h. The reaction was then diluted with 50 mL ethyl acetate and washed with saturated $CuSO_4$(10×20 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was used without further purification.

Synthesis of **2d**: to a mixture of $Na_2S·9H_2O$ (1.8 mmol, 0.43 g, 1.5 equiv.) in 10 mL anhydrous DMF was added 2-(2-(benzyloxy)benzyl)-3-(mercaptooxy)propyl 4-methylbenzenesulfonate (1.2 mmol, 0.87 g, 1.0 equiv.) in 5 mL DMF under nitrogen atmosphere in a flame-dried schlenk tube. The mixture was stirred at 100 °C for 12 h. The reaction was then quenched with water (30 mL) and extracted with EA (3×20 mL), washed with water and brine, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give **2d** (54% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (q, *J* = 7.8 Hz, 1H), 7.34 (s, 1H), 7.20 – 7.13 (m, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 6.93 – 6.86 (m, 1H), 5.07 (s, 1H), 3.70 – 3.55 (m, 1H), 3.11 (d, *J* = 8.0 Hz, 1H), 2.92 (d, *J* = 7.6 Hz, 1H).

3) Synthesis of 2e:



3-allylthietane (2e)



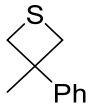
Synthesis of 2-allylpropane-1,3-diol: a mixture of diethyl allylmalonate (5 mmol, 1.0 g, 1 equiv.) and anhydrous tetrahydrofuran (THF, 5 mL) was added to a solution of lithium aluminum hydride ($LiAlH_4$, 15 mmol, 0.57 g, 3 equiv.) in anhydrous tetrahydrofuran (THF, 10 mL) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring overnight at room temperature. The reaction was then carefully quenched with water (1 mL), 15% aqueous sodium hydroxide (1 mL), water (3 mL) dropwise at 0 °C. After being stirred for 30 minutes, the mixture was diluted with ethyl acetate (50 mL), filtered through celite and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 1:1 as the eluent) to give 2-allyl-1,3-propanediol (57% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86-5.74 (m, 1H), 5.14 – 4.99 (m, 2H), 3.84 – 3.75 (m, 2H), 3.70-3.60 (m, 2H), 2.59 (s, 1H), 2.10-2.03 (m, 2H), 1.92 – 1.79 (m, 1H).

Synthesis of 2-allylpropane-1,3-diyl bis(4-methylbenzenesulfonate): to a mixture of KOH (22.8 mmol, 1.28 g, 8 equiv.) and 2-allylpropane-1,3-diol (2.85 mmol, 0.33 g, 1 equiv.) in 5 mL THF was added a solution of p-toluene sulfonyl chloride (8.6 mmol, 1.64 g, 3 equiv.) in 10 anhydrous THF dropwise under nitrogen atmosphere at 0°C.

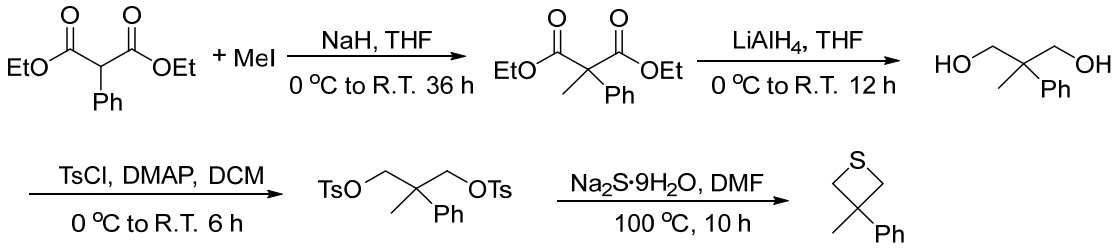
The resulting mixture was stirred at 0°C for 30 min. The mixture was kept stirring overnight at room temperature. The reaction was then quenched with water (30 mL) and extracted with DCM (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give **2g** (91% yield) as a white solid.

Synthesis of **2e**: to a mixture of $Na_2S·9H_2O$ (1.8 mmol, 0.43 g, 1.5 equiv.) in 10 mL anhydrous DMF was added 2-allylpropane-1,3-diyl bis(4-methylbenzenesulfonate) (1.2 mmol, 0.51 g, 1.0 equiv.) in 5 mL DMF under nitrogen atmosphere in a flame-dried schlenk tube. The mixture was stirred at 100 °C for 12 h. The reaction was then quenched with water (30 mL) and extracted with DCM (3×20 mL), washed with water and brine, dried over sodium sulfate, filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography (n-pentane: DCM = 20:1 as the eluent) to give **2e** (52% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.67 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.07 – 5.01 (m, 2H), 3.32 (dq, *J* = 15.2, 7.6 Hz, 1H), 3.19 (t, *J* = 8.7 Hz, 2H), 3.04 – 2.99 (m, 2H), 2.31 (t, *J* = 7.1 Hz, 2H).

4) Synthesis of 2f:



3-methyl-3-phenylthietane (2f)



Synthesis of diethyl 2-methyl-2-phenylmalonate: to a suspension of NaH (40 mmol, 60% in mineral oil, 1.6 g, 2 equiv.) in 30 mL anhydrous tetrahydrofuran in a

flame-dried schlenk tube, diethyl 2-phenylmalonate (20 mmol, 4.7 g, 1 equiv.) was added for 30 minutes at 0 °C. Then iodomethane (20 mmol, 5.7 g, 2 equiv.) was added dropwise at 0 °C. After addition, the mixture was kept stirring for 36 h at room temperature. The reaction was then quenched with water (30 mL) and extracted with EA (3×30 mL), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give diethyl 2-methyl-2-phenylmalonate (75% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.2 Hz, 4H), 7.35 – 7.31 (m, 1H), 4.26 (qt, *J* = 5.3, 2.7 Hz, 4H), 1.89 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H).

Synthesis of 2-methyl-2-phenylpropane-1,3-diol: a mixture of diethyl 2-methyl-2-phenylmalonate (10 mmol, 2.5 g, 1 equiv.) and 20 mL anhydrous tetrahydrofuran (THF) was added lithium aluminum hydride (30 mmol, 1.2 g, 3 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. The mixture was kept stirring for 12 h at room temperature. The reaction was then carefully quenched with 1 mL water, 1.2 mL 15% aqueous sodium hydroxide, 3 mL water dropwise at 0 °C. After being stirred for 30 minutes, the mixture was diluted with ethyl acetate (50 mL), filtered through celite and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 2:1 as the eluent) to give 2-methyl-2-phenylpropane-1,3-diol (50% yield) as a colorless oil.

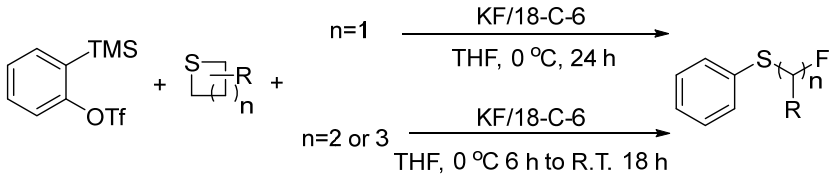
Synthesis of 2-methyl-2-phenylpropane-1,3-diyl bis(4-methylbenzenesulfonate) : to a solution of 2-methyl-2-phenylpropane-1,3-diol (3 mmol, 0.50 g, 1 equiv.) and dimethylaminopyridine (9.3 mmol, 1.1 g, 3.1 equiv.) in 4 mL DCM in a flame-dried schlenk tube, p-toluene sulfonyl chloride (7.5 mmol, 1.43 g, 2.5 equiv.) in 6 mL DCM was added at 0 °C for 30 minutes, the reaction was kept stirring for 6 h at room temperature. The reaction was then diluted with ethyl acetate (20 mL) and washed with water and brine, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 10:1 as the eluent) to give product 2-methyl-2-phenylpropane-1,3-diyl bis(4-

methylbenzenesulfonate) (95% yield) as a white solid.

Synthesis of **2f**: to a mixture of $Na_2S·9H_2O$ (1.8 mmol, 0.43 g, 1.5 equiv.) in 10 mL anhydrous DMF was added 2-methyl-2-phenylpropane-1,3-diyl bis(4-methylbenzenesulfonate) (1.2 mmol, 0.57 g, 1.0 equiv.) in 5 mL DMF under nitrogen atmosphere in a flame-dried schlenk tube. The mixture was stirred at 100 °C for 12 h. The reaction was then quenched with water (30 mL) and extracted with EA (3×20 mL), washed with water and brine, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 100:1 as the eluent) to give **2f** (85% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 3.84 (d, *J* = 8.7 Hz, 2H), 3.07 (d, *J* = 8.8 Hz, 2H), 1.83 (s, 3H).

III. General Procedure for Aryne Reaction

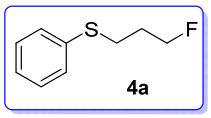
1) Scope of Cyclic thioether:



General procedure: a mixture of anhydrous potassium fluoride (KF, 0.7 mmol, 0.041 g, 3.5 equiv.) and 18-crown-6 (0.7 mmol, 0.2 g, 3.5 equiv.) in 1 mL anhydrous THF was added 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 49 μL, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then cyclic thioether (0.3 mmol, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0°C. Once the solution became pale yellow (after 5 minutes), a solution of 2,3-dimethylindole (0.5 mmol, 0.0726 g, 2.5 equiv.) in 1 mL anhydrous THF was added and kept stirring for 24 h at 0°C or 0°C to room temperature. The reaction mixture was filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography or preparative TLC plate. (Note:

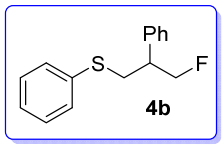
The temperature of water bath during solvent evaporation should be controlled under 10 °C. Also, the choice of the chromatography eluent is also influential.)

(3-fluoropropyl)(phenyl)sulfane (4a)



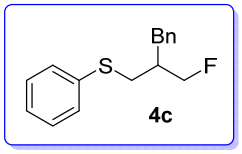
Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: DCM = 20:1 as the eluent) to give **4a** (82% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 2H), 7.32-7.26 (m, 2H), 7.22-7.16 (m, 1H), 4.56 (dt, *J* = 47.1, 5.7 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.08-1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.86, 129.42, 129.00, 126.20, 82.24 (d, *J* = 165.6 Hz), 30.06 (d, *J* = 20.2 Hz), 29.44 (d, *J* = 4.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -221.04. HR-MS (ESI): Calcd for $C_9H_{12}FS^+$ $[M+H]^+$ 171.0638; found 171.0642.

(3-fluoro-2-phenylpropyl)(phenyl)sulfane (4b)



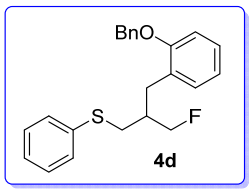
Following the general procedure, the crude product was purified by Preparative TLC (PE: EA = 10:1 as the eluent) to give **4b** (82% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 7.29 – 7.25 (m, 3H), 7.24 – 7.15 (m, 3H), 4.68 (dddd, *J* = 51.4, 47.5, 9.1, 5.3 Hz, 2H), 3.41 (dd, *J* = 13.0, 7.2 Hz, 1H), 3.27 – 3.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.67 (d, *J* = 4.3 Hz), 136.00, 129.47, 129.03, 128.75, 127.99, 127.49, 126.26, 85.31 (d, *J* = 173.6 Hz), 45.87 (d, *J* = 18.9 Hz), 35.54 (d, *J* = 5.2 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -222.22. HR-MS (ESI): Calcd for $C_{15}H_{16}FS^+$ $[M+H]^+$ 247.0951; found 247.0949.

(2-benzyl-3-fluoropropyl)(phenyl)sulfane (4c)



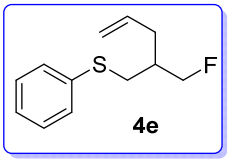
Following the general procedure, the crude product was purified by Preparative TLC (PE: EA = 10:1 as the eluent) to give 4b (70% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.27 (dd, *J* = 13.8, 5.4 Hz, 5H), 7.23 – 7.16 (m, 3H), 4.72 – 4.21 (m, 2H), 3.03 (d, *J* = 6.9 Hz, 2H), 2.94 – 2.78 (m, 2H), 2.30 – 2.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.01, 136.09, 129.25, 129.11, 129.00, 128.54, 126.42, 126.07, 83.83 (d, *J* = 169.3 Hz), 41.25 (d, *J* = 18.7 Hz), 36.10 (d, *J* = 4.8 Hz), 33.86 (d, *J* = 4.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -229.83. HR-MS (ESI): Calcd for $C_{16}H_{18}FS^+$ $[M+H]^+$ 261.1108; found 261.1114.

(2-(2-(benzyloxy)benzyl)-3-fluoropropyl)(phenyl)sulfane (4d)



Following the general procedure, the crude product was purified by Preparative TLC (PE: EA = 20:1 as the eluent) to give **4d** (82% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 5H), 7.18 – 6.94 (m, 7H), 6.85-6.80 (m, 2H), 4.94 (s, 2H), 4.39 (dddd, *J* = 79.1, 47.4, 9.2, 4.0 Hz, 2H), 3.00 – 2.87 (m, 2H), 2.78 (m, 2H), 2.32 – 2.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.80, 137.17, 136.52, 131.33, 128.88, 128.59, 128.59, 127.86, 127.81, 127.81, 127.11, 125.69, 120.77, 111.78, 84.13 (d, *J* = 168.8 Hz), 69.89, 39.65 (d, *J* = 18.5 Hz), 33.82 (d, *J* = 4.0 Hz), 31.39 (d, *J* = 5.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -230.14. HR-MS (ESI): Calcd for $C_{23}H_{24}FOS^+$ $[M+H]^+$ 367.1526; found 367.1528.

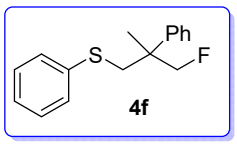
(2-(fluoromethyl)pent-4-en-1-yl)(phenyl)sulfane (4e)



Following the general procedure, the crude product was purified by Preparative TLC (PE: EA = 20:1 as the eluent) to give **4e** (72% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.86 – 5.70 (m, 1H), 5.14

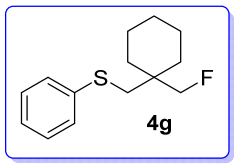
(d, J = 4.1 Hz, 1H), 5.11 (s, 1H), 4.53 (dddd, J = 47.3, 42.9, 9.2, 4.7 Hz, 2H), 3.11 – 2.96 (m, 2H), 2.43 – 2.20 (m, 2H), 2.13 – 1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.27, 135.11, 129.15 (d, J = 27.0 Hz), 128.99, 126.13, 117.67, 84.24 (d, J = 169.4 Hz), 38.92 (d, J = 18.6 Hz), 34.25 (d, J = 5.1 Hz), 34.14 (d, J = 4.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -228.85. HR-MS (ESI): Calcd for $C_{12}H_{16}FS^+$ $[M+H]^+$ 211.0951; found 211.0960.

(3-fluoro-2-methyl-2-phenylpropyl)(phenyl)sulfane (4f)



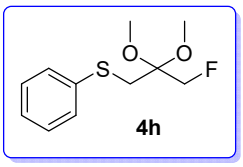
Following the general procedure, the crude product was purified by Preparative TLC (PE: EA = 8:1 as the eluent) to give **4f** (69% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 4H), 7.38 – 3.32 (m, 3H), 7.29 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 4.74 – 4.55 (m, 2H), 3.49 (d, J = 12.6 Hz, 1H), 3.44 (d, J = 12.6 Hz, 1H), 1.56 (d, J = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.45 (d, J = 3.3 Hz), 136.28, 128.59, 127.81, 127.45, 126.01, 125.36 (d, J = 1.3 Hz), 125.03, 87.89 (d, J = 177.9 Hz), 42.65 (d, J = 17.3 Hz), 42.20 (d, J = 4.1 Hz), 20.67 (d, J = 5.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -221.25. HR-MS (ESI): Calcd for $C_{16}H_{18}FS^+$ $[M+H]^+$ 261.1108; found 261.1111.

((1-(fluoromethyl)cyclohexyl)methyl)(phenyl)sulfane (4g)



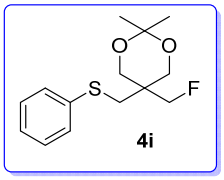
Following the general procedure, the crude product was purified by Preparative TLC (PE: EA = 80:1 as the eluent) to give **4g** (74% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.27 (t, J = 6.5 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 4.35 (d, J = 47.6 Hz, 2H), 3.08 (s, 2H), 1.53-1.45 (m, 10H). ^{13}C NMR (100MHz, $CDCl_3$) δ 137.59, 129.58, 128.86, 125.95, 87.35 (d, J = 172.8 Hz), 40.10, 38.87 (d, J = 16.4 Hz), 31.18 (d, J = 5.1 Hz), 25.90, 21.33. ^{19}F NMR (377 MHz, $CDCl_3$) δ -230.41. HR-MS (ESI): Calcd for $C_{14}H_{20}FS^+$ $[M+H]^+$ 239.1264; found 239.1267.

(3-fluoro-2,2-dimethoxypropyl)(phenyl)sulfane (4h)



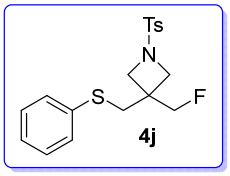
Following the general procedure, the crude product was purified by Preparative TLC (n-pentane: DCM = 1:2 as the eluent) to give **4h** (70% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 4.49 (d, *J* = 46.8 Hz, 2H), 3.28 (d, *J* = 1.7 Hz, 2H), 3.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.00, 129.75, 128.99, 126.44, 100.17 (d, *J* = 21.2 Hz), 78.51 (d, *J* = 174.7 Hz), 48.70, 48.69, 35.92 (d, *J* = 0.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -231.44. HR-MS (ESI): Calcd for $C_{11}H_{16}FO_2S^+$ $[M+H]^+$ 231.0850; found 231.0853.

5-(fluoromethyl)-2,2-dimethyl-5-((phenylthio)methyl)-1,3-dioxane (4i)



Following the general procedure, the crude product was purified by Preparative TLC (PE: DCM = 1:1 as the eluent) to give **4i** (70% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24-7.20 (m, 1H), 4.57 (d, *J* = 47.2 Hz, 2H), 3.79 (m, 4H), 3.07 (d, *J* = 0.8 Hz, 2H), 1.43 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.56, 129.65, 129.07, 126.50, 98.47, 83.37 (d, *J* = 172.0 Hz), 63.29 (d, *J* = 5.9 Hz), 39.11 (d, *J* = 17.2 Hz), 35.94 (d, *J* = 2.9 Hz), 21.80. ^{19}F NMR (377 MHz, $CDCl_3$) δ -234.49. HR-MS (ESI): Calcd for $C_{14}H_{20}FO_2S^+$ $[M+H]^+$ 271.1163; found 271.1162.

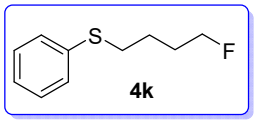
3-(fluoromethyl)-3-((phenylthio)methyl)-1-tosylazetidine (4j)



Following the general procedure, the crude product was purified by Preparative TLC (PE: DCM = 1:2 as the eluent) to give **4j** (90% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.21 (m, 5H), 4.42 (d, *J* = 46.9 Hz, 2H), 3.66 – 3.52 (m, 4H), 3.05 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (100

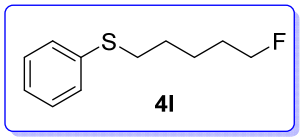
MHz, $CDCl_3$) δ 143.26, 134.20, 130.16, 129.01, 128.82, 128.17, 127.35, 125.99, 83.15 (d, *J* = 174.0 Hz), 54.74 (d, *J* = 6.9 Hz), 37.46 (d, *J* = 19.5 Hz), 37.09 (d, *J* = 3.6 Hz), 20.62. ^{19}F NMR (377 MHz, $CDCl_3$) δ -226.82. HR-MS (ESI): Calcd for $C_{18}H_{21}FNO_2S_2^+$ $[M+H]^+$ 366.0992; found 366.0985.

(4-fluorobutyl)(phenyl)sulfane (4k)



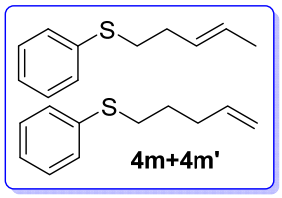
Following the general procedure, the crude product was purified by Preparative TLC (PE: DCM = 10:1 as the eluent) to give **4k** (68% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.13 (m, 1H), 4.45 (dt, *J* = 47.1, 5.7 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.37, 129.30, 128.93, 126.01, 83.58 (d, *J* = 165.1 Hz), 33.35, 29.44 (d, *J* = 19.8 Hz), 25.05 (d, *J* = 4.6 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -218.61. HR-MS (ESI): Calcd for $C_{10}H_{14}FS^+$ $[M+H]^+$ 185.0795; found 185.0792.

(5-fluoropentyl)(phenyl)sulfane (4l)



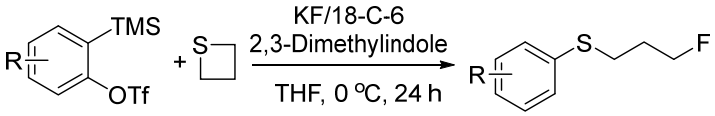
Following the general procedure, the crude product was purified by Preparative TLC (PE: DCM = 10:1 as the eluent) to give **4l** (28% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 4.46 (dt, *J* = 47.2, 6.0 Hz, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.66 (m, 4H), 1.65 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.67, 129.10, 128.88, 125.86, 84.68, 83.05, 33.51, 30.07, 29.87, 28.77, 24.50, 24.45. ^{19}F NMR (377 MHz, $CDCl_3$) δ -218.38. HR-MS (ESI): Calcd for $C_{11}H_{16}FS^+$ $[M+H]^+$ 199.0951; found 199.0945.

(E)-pent-3-en-1-yl(phenyl)sulfane and pent-4-en-1-yl(phenyl)sulfane (4m+4m')



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane as the eluent) to give **4l** (4:1, 70% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.4 Hz, 10H), 7.27 (dd, *J* = 12.0, 3.8 Hz, 10H), 7.16 (s, 4H), 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.58 – 5.39 (m, 7H), 5.08 – 4.91 (m, 2H), 2.93 (dd, *J* = 14.0, 6.5 Hz, 9H), 2.32 (dd, *J* = 13.9, 6.5 Hz, 7H), 2.19 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.74 (dt, *J* = 14.7, 7.4 Hz, 2H), 1.66 (d, *J* = 5.4 Hz, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.60, 136.74, 129.09, 128.95, 128.86, 126.96, 125.79, 115.43, 33.63, 32.97, 32.73, 32.33, 28.30, 17.95. HR-MS (ESI): Calcd for $C_{11}H_{15}S^+$ $[M+H]^+$ 179.0889; found 179.0892.

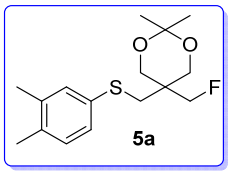
2) Scope of Aryne:



General procedure: a mixture of anhydrous potassium fluoride (KF, 0.7 mmol, 0.041 g, 3.5 equiv.) and 18-crown-6 (0.7 mmol, 0.200 g, 3.5 equiv.) in 1 mL anhydrous THF was added aryne (0.2 mmol, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (0.3 mmol, 24 μL, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), a solution of 2,3-dimethylindole (0.5 mmol, 2.5 equiv.) in 1 mL anhydrous THF was added and kept stirring for 24 h at 0 °C. The reaction mixture was filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography or preparative TLC. (Note: The temperature of water bath during solvent evaporation should be controlled under 10 °C. Also, the choice of the chromatography eluent is also influential.)

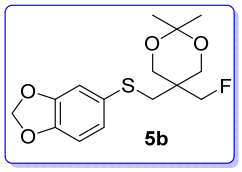
5-(((3,4-dimethylphenyl)thio)methyl)-5-(fluoromethyl)-2,2-dimethyl-1,3-dioxane

(5a)



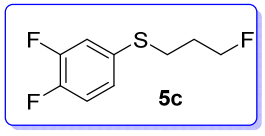
Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: DCM = 10:1 as the eluent) to give **5a** (83% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.15 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 4.58 (d, *J* = 47.2 Hz, 2H), 3.81-3.73 (m, 4H), 3.02 (d, *J* = 0.6 Hz, 2H), 2.23 (d, *J* = 3.8 Hz, 6H), 1.44 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.52, 135.37, 133.06, 131.45, 130.34, 127.69, 98.41, 83.40 (d, *J* = 171.9 Hz), 63.31 (d, *J* = 6.0 Hz), 39.14 (d, *J* = 17.2 Hz), 36.58 (d, *J* = 3.2 Hz), 25.68, 21.64, 19.71, 19.34. ^{19}F NMR (377 MHz, $CDCl_3$) δ -234.52. HR-MS (ESI): Calcd for $C_{16}H_{24}FO_2S^+$ $[M+H]^+$ 299.1476; found 299.1475.

5-(((5-(fluoromethyl)-2,2-dimethyl-1,3-dioxan-5-yl)methyl)thio)benzo[d][1,3]-dioxole (5b)



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: DCM = 10:1 as the eluent) to give **5b** (56% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 6.0 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 5.96 (s, 2H), 4.57 (d, *J* = 47.2 Hz, 2H), 3.83 – 3.64 (m, 4H), 2.97 (s, 2H), 1.42 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.13, 147.27, 128.51, 125.23, 111.92, 108.82, 101.3, 98.44, 83.29 (d, *J* = 171.9 Hz), 39.24 (d, *J* = 17.2 Hz), 38.02 (d, *J* = 3.2 Hz), 25.65, 21.63. ^{19}F NMR (377 MHz, $CDCl_3$) δ -234.66. HR-MS (ESI): Calcd for $C_{15}H_{20}FO_4S^+$ $[M+H]^+$ 315.1061; found 315.1066.

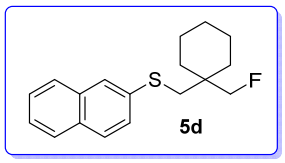
(3,4-difluorophenyl)(3-fluoropropyl)sulfane (5c)



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: DCM = 20:1 as the eluent) to give **5d** (45% yield) as a yellow oil. ^{1}H NMR

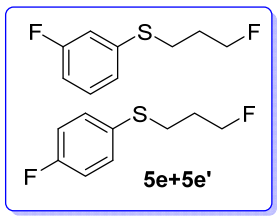
(400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 7.17 – 7.08 (m, 2H), 4.58 (dt, J = 47.1, 5.6 Hz, 2H), 3.04 (t, J = 7.2 Hz, 2H), 2.15 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.33 (dd, *J* = 251.0, 13.1 Hz), 149.25 (dd, *J* = 248.4, 12.6 Hz), 126.07 (dd, *J* = 6.0, 3.7 Hz), 118.85 (d, *J* = 18.2 Hz), 117.78 (d, *J* = 17.6 Hz), 81.97 (d, *J* = 166.1 Hz), 30.31 (d, *J* = 4.5 Hz), 29.95 (d, *J* = 20.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -136.35 (d, *J* = 20.9 Hz), -140.07 (d, *J* = 21.1 Hz), -221.20. HR-MS (ESI): Calcd for $C_9H_{10}F_3S^+$ $[M+H]^+$ 207.0450; found 207.0452.

((1-(fluoromethyl)cyclohexyl)methyl)(naphthalen-2-yl)sulfane (5d)



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane : DCM = 20:1 as the eluent) to give **5d** (61% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 4H), 7.48- 7.43 (m, 3H), 4.40 (d, *J* = 47.6 Hz, 2H), 3.19 (s, 2H), 1.62 – 1.38 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.09, 133.81, 131.74, 128.35, 127.72, 127.72, 127.07, 127.04, 126.53, 125.61, 87.37 (d, *J* = 172.9 Hz), 39.87, 38.95 (d, *J* = 16.4 Hz), 31.26 (d, *J* = 5.1 Hz), 25.91, 21.37. ^{19}F NMR (377 MHz, $CDCl_3$) δ -230.20. HR-MS (ESI): Calcd for $C_{18}H_{22}FS^+$ $[M+H]^+$ 289.1421; found 289.1414.

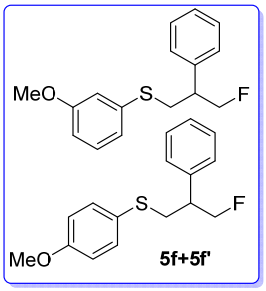
(3-fluorophenyl)(3-fluoropropyl)sulfane and (3-fluorophenyl)(3-fluoropropyl)sulfane (5e+5e')



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: EA = 20:1 as the eluent) to give **5f+5f'** (1:2, 58% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.28 – 7.24 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.08 – 7.00 (m, 5H), 6.90 (td, *J* = 8.3, 2.2 Hz,

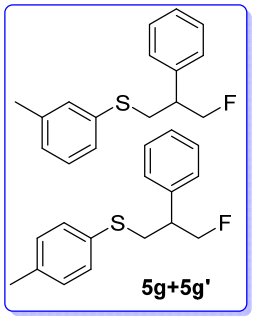
1H), 4.59 (dt, *J* = 47.1, 5.7 Hz, 2H), 4.57 (dt, *J* = 47.1, 5.7 Hz, 4H), 3.09 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 4H), 2.15 – 1.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.93 (d, J = 248.1 Hz), 161.91 (d, J = 246.7 Hz), 138.54 (d, J = 7.8 Hz), 132.54 (d, J = 8.0 Hz), 130.64 (d, J = 3.3 Hz), 130.24 (d, J = 8.6 Hz), 124.23 (d, J = 3.0 Hz), 116.12 (d, J = 21.9 Hz), 115.42 (d, J = 23.1 Hz), 112.92 (d, J = 21.2 Hz), 82.12 (d, J = 165.8 Hz), 82.07 (d, J = 165.9 Hz), 30.83 (d, J = 4.6 Hz), 30.08 (d, J = 20.2 Hz), 29.91 (d, J = 20.3 Hz), 29.00 (d, J = 4.6 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.24, -115.31, -221.09, -221.14. HR-MS (ESI): Calcd for $C_9H_{11}F_2S^+$ $[M+H]^+$ 189.0544; found 189.0549.

(3-fluoro-2-phenylpropyl)(3-methoxyphenyl)sulfane and (3-fluoro-2-phenylpropyl)(4-methoxyphenyl)sulfane (5f+5f')



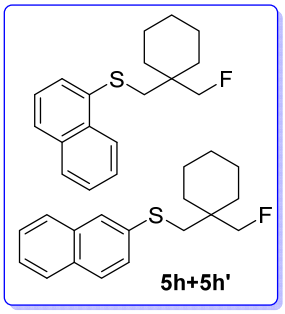
Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: EA = 20:1 as the eluent) to give **5f+5f'** (1.5:1, 67% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 8H), 7.30 – 7.24 (m, 4H), 7.23 – 7.18 (m, 5H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.89- 6.83 (m, 4H), 6.74 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.85 – 4.47 (m, 2H), 3.81 (s, 4H), 3.79 (s, 3H), 3.48 – 3.29 (m, 2H), 3.28 – 3.01 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.93, 159.10, 139.84 (d, *J* = 4.1 Hz), 139.62 (d, *J* = 4.4 Hz), 137.33, 133.38, 129.84, 128.74, 128.68, 128.02, 127.99, 127.50, 127.37, 126.01, 121.33, 114.70, 114.55, 111.99, 85.32 (d, *J* = 173.2 Hz), 55.36, 55.29, 45.89 (d, *J* = 18.9 Hz), 45.86 (d, *J* = 18.9 Hz), 37.62 (d, *J* = 5.2 Hz), 35.28 (d, *J* = 5.1 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -222.08, -222.36. HR-MS (ESI): Calcd for $C_{16}H_{18}FOS^+$ $[M+H]^+$ 277.1057; found 277.1061.

(3-fluoro-2-phenylpropyl)(m-tolyl)sulfane and (3-fluoro-2-phenylpropyl)(p-tolyl)sulfane (5g+5g')



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: DCM = 20:1 as the eluent) to give **5g+5g'** (1.1:1, 67% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 5H), 7.34 – 7.24 (m, 8H), 7.23 – 7.13 (m, 5H), 7.05 (d, *J* = 7.2 Hz, 1H), 4.89 – 4.57 (m, 4H), 3.50 – 3.38 (m, 2H), 3.36 – 3.11 (m, 4H), 2.38 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.76 (d, *J* = 4.0 Hz), 138.70 (d, *J* = 4.2 Hz), 137.74, 135.43, 134.66, 131.07, 129.25, 129.22, 129.02, 128.77, 127.81, 127.67, 127.65, 126.94, 126.40, 126.35, 126.07, 125.33, 84.26 (d, *J* = 173.5 Hz), 84.25 (d, *J* = 173.4 Hz), 44.82 (d, *J* = 18.9 Hz), 44.76 (d, *J* = 19.0 Hz), 35.15 (d, *J* = 5.3 Hz), 34.40 (d, *J* = 5.3 H z), 20.30, 19.98. ^{19}F NMR (377 MHz, $CDCl_3$) δ -222.19, -222.34. HR-MS (ESI): Calcd for $C_{16}H_{18}FS^+$ $[M+H]^+$ 261.1108; found 261.1105.

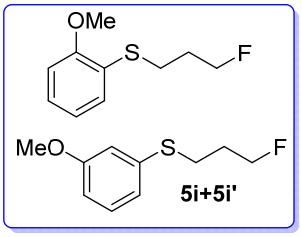
((1-(fluoromethyl)cyclohexyl)methyl)(naphthalen-2-yl)sulfane and ((1-(fluoromethyl)cyclohexyl)methyl)(naphthalen-1-yl)sulfane (5h+5h')



Following the general procedure, the crude product was purified by silica gel chromatography (n-pentane: DCM = 20:1 as the eluent) to give **5h+5h'** (1:1, 83% yield) as a pale yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.72 (m, 6H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.63 – 7.38 (m, 6H), 4.43 (dd, *J* = 47.6, 12.3 Hz, 4H), 3.20 (s, 2H), 3.15 (s, 2H), 1.62 – 1.42 (m, 23H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.10, 134.71, 133.99, 133.82, 133.16, 131.75, 128.80, 128.70, 128.63, 128.36, 127.73, 127.32, 127.08, 127.04, 126.54, 126.44, 126.20, 125.66, 125.62, 125.24, 87.58 (d, *J* = 173.0 Hz), 87.37 (d, *J* = 172.9 Hz), 40.82 (d, *J* = 3.1 Hz), 39.89 (d, *J* = 3.2 Hz), 38.97 (d, *J* = 16.4 Hz), 38.95 (d, *J* = 16.4 Hz), 31.28 (d, *J* = 4.9 Hz), 25.93, 21.37. ^{19}F NMR (377

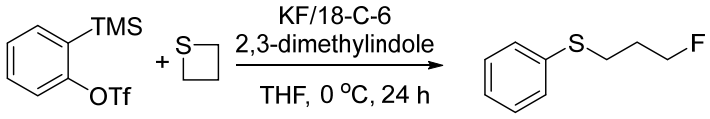
MHz, $CDCl_3$) δ -230.14, -230.16. HR-MS (ESI): Calcd for $C_{18}H_{22}FS^+$ $[M+H]^+$ 289.1421; found 289.1415.

(3-fluoropropyl)(2-methoxyphenyl)sulfane and (3-fluoropropyl)(3-methoxyphenyl)sulfane (5i+5i')



Following the general procedure, the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5i+5i'** (1:9, 65% yield) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 12.5, 4.9 Hz, 2H), 6.76 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.59 (dt, *J* = 47.2, 5.7 Hz, 2H), 3.83 (s, 3H), 3.08 (t, *J* = 7.1 Hz, 2H), 2.15 – 1.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.93, 137.25, 129.81, 121.30, 114.59, 111.79, 82.22 (d, *J* = 165.7 Hz), 30.08 (d, *J* = 20.2 Hz), 29.20 (d, *J* = 4.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -221.00. HR-MS (ESI): Calcd for $C_{10}H_{14}FOS^+$ $[M+H]^+$ 201.0744; found 201.0736.

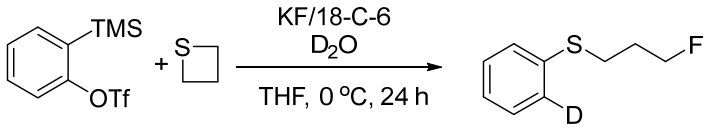
Gram reaction



A mixture of anhydrous potassium fluoride (KF, 14 mmol, 0.82 g, 3.5 equiv.) and 18-crown-6 (14 mmol, 4.0 g, 3.5 equiv.) in 15 mL anhydrous THF was added aryne (4 mmol, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (6 mmol, 0.48 ml, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), a solution of 2,3-dimethylindole (10 mmol, 2.5 equiv.) in 5 mL anhydrous

THF was added and kept stirring for 24 h at 0 °C. The reaction mixture was filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography (n-pentane: DCM = 20:1 as the eluent) to give **4a** (0.5g, 74% yield) as a yellow oil. (Note: The temperature of water bath during solvent evaporation should be controlled under 10 °C.)

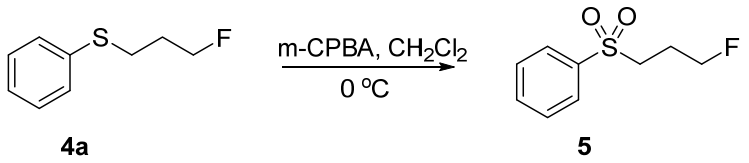
Deuterium-labelling Study



A mixture of anhydrous potassium fluoride (KF, 0.7 mmol, 0.041 g, 3.5 equiv.) and 18-crown-6 (0.7 mmol, 0.200 g, 3.5 equiv.) in 1 mL anhydrous THF was added aryne (0.2 mmol, 1.0 equiv.) dropwise under nitrogen atmosphere at 0 °C in a flame-dried schlenk tube. Then thietane (0.3 mmol, 24 μL, 1.5 equiv.) was added to the solution dropwise, which was then kept stirring at 0 °C. Once the solution became pale yellow (after 5 minutes), deuterium oxide (0.5 mmol, 2.5 equiv.) was added and kept stirring for 24 h at 0 °C. The reaction mixture was filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography(n-pentane: DCM = 20:1 as the eluent) to give **4a-D** (50% yield) as a yellow oil. (Note: The temperature of water bath during solvent evaporation should be controlled under 10 °C.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 4.59 (dt, J = 47.1, 5.7 Hz, 2H), 3.08 (t, J = 7.1 Hz, 2H), 2.03 (ddd, J = 25.9, 12.8, 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.79, 129.43, 128.99, 128.88, 126.20, 82.23 (d, *J* = 165.6 Hz), 30.08 (d, *J* = 20.2 Hz), 29.45 (d, *J* = 4.6 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -221.02. HR-MS (ESI): Calcd for $C_9H_{11}DFS^+$ $[M+H]^+$ 172.0701; found 172.0705.

Sulfide Oxidation

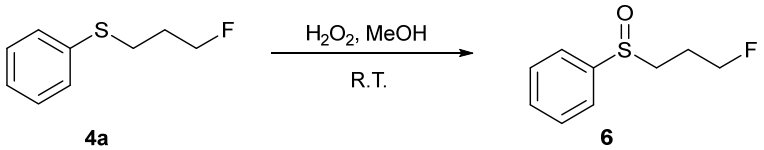
Synthesis of ((3-fluoropropyl)sulfonyl)benzene



4a **5**

To a stirred solution of the (3-fluoropropyl)(phenyl)sulfane (0.034 g, 0.2 mmol, 1 equiv.) in 1mL CH_2Cl_2 was added *m*-CPBA (0.085 g, 0.42 mmol, 2.1 equiv.) at 0 °C. The reaction was kept stirring overnight at 0 °C for 48 h. The reaction was then quenched with saturated 20 mL $NaHCO_3$, extracted with 20 mL DCM, washed with saturated $NaHCO_3$, dried over sodium sulfate, filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography (DCM as the eluent) to give ((3-fluoropropyl)sulfonyl)benzene **5** (96% yield) as a yellow oil. (Note: The temperature of water bath during solvent evaporation should be controlled under 10 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 4.52 (dt, *J* = 46.9, 5.7 Hz, 2H), 3.28 – 3.22 (m, 2H), 2.23 – 2.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.88, 133.94, 129.43, 128.02, 81.54 (d, *J* = 167.8 Hz), 52.48 (d, *J* = 4.2 Hz), 24.09 (d, *J* = 20.8 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -220.46. HR-MS (ESI): Calcd for $C_9H_{12}FO_2S^+$ $[M+H]^+$ 203.0537; found 203.0531.

Synthesis of ((3-fluoropropyl)sulfinyl)benzene

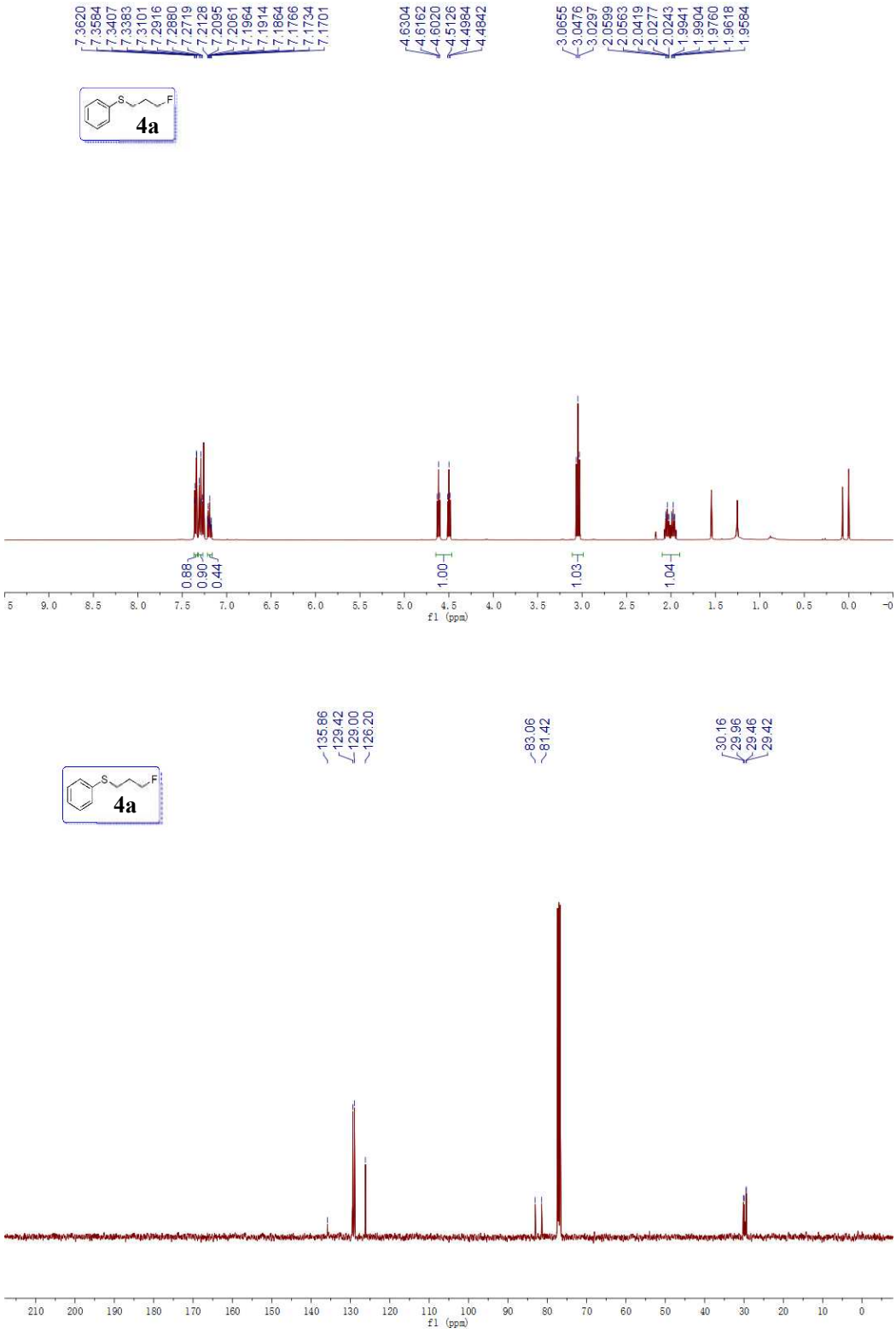


4a **6**

To a stirred solution of the sulfide 3a (0.034g, 0.2mmol, 1 equiv.) in 1mL methanol was added H_2O_2 (30% in water, 0.06 mL, 0.8mmol, 4.0 equiv.) at room temperature.

The reaction was stirred for 48 h and then concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography (DCM: Et_2O=4:1 as the eluent) to give ((3-fluoropropyl)sulfinyl)benzene **6** (98% yield) as a yellow oil. (Note: The temperature of water bath during solvent evaporation should be controlled under 10 °C. Also, the choice of the chromatography eluent is also influential.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.9 Hz, 2H), 7.60 – 7.50 (m, 3H), 4.71 – 4.40 (m, 2H), 3.12 – 2.77 (m, 2H), 2.34 – 1.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.39, 131.11, 129.32, 123.98, 82.32 (d, *J* = 167.2 Hz), 52.74 (d, *J* = 3.2 Hz), 23.15 (d, *J* = 20.6 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -219.90. HR-MS (ESI): Calcd for $C_9H_{12}FOS^+$ $[M+H]^+$ 187.0587; found 187.0581.

IV. Spectrum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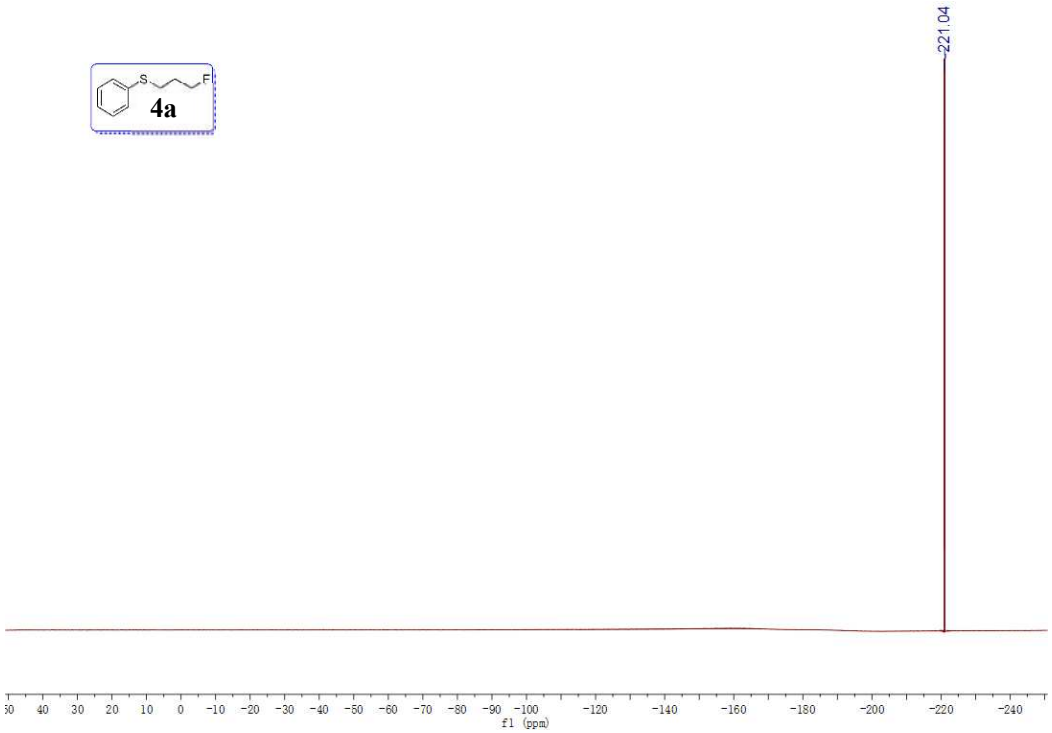
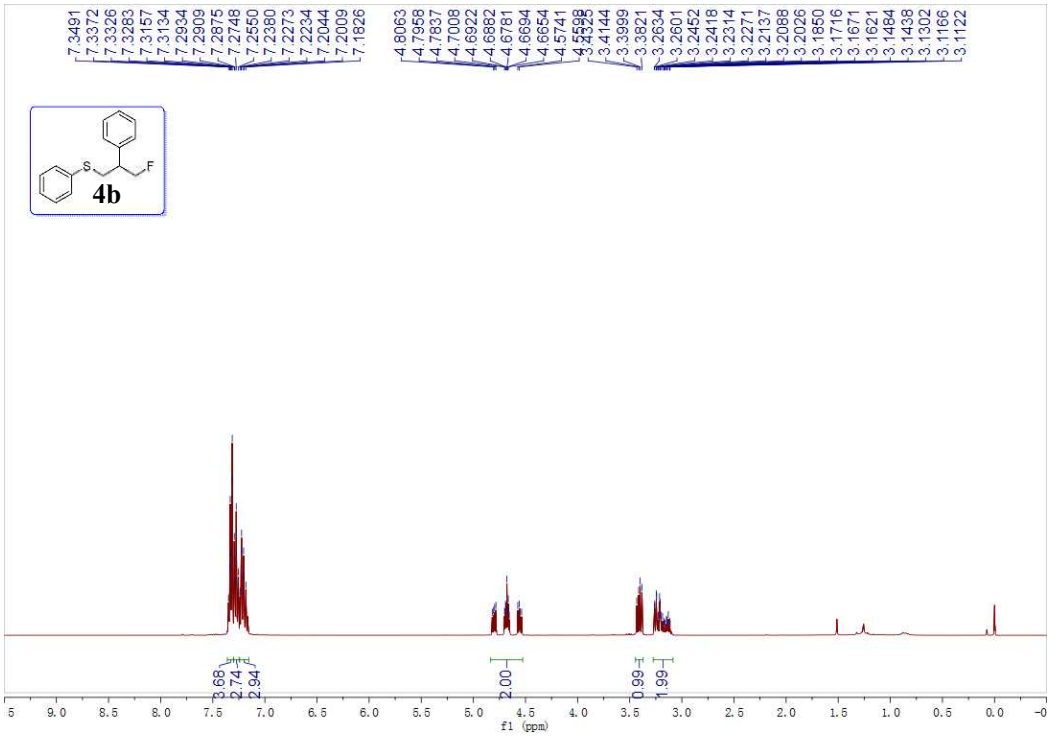
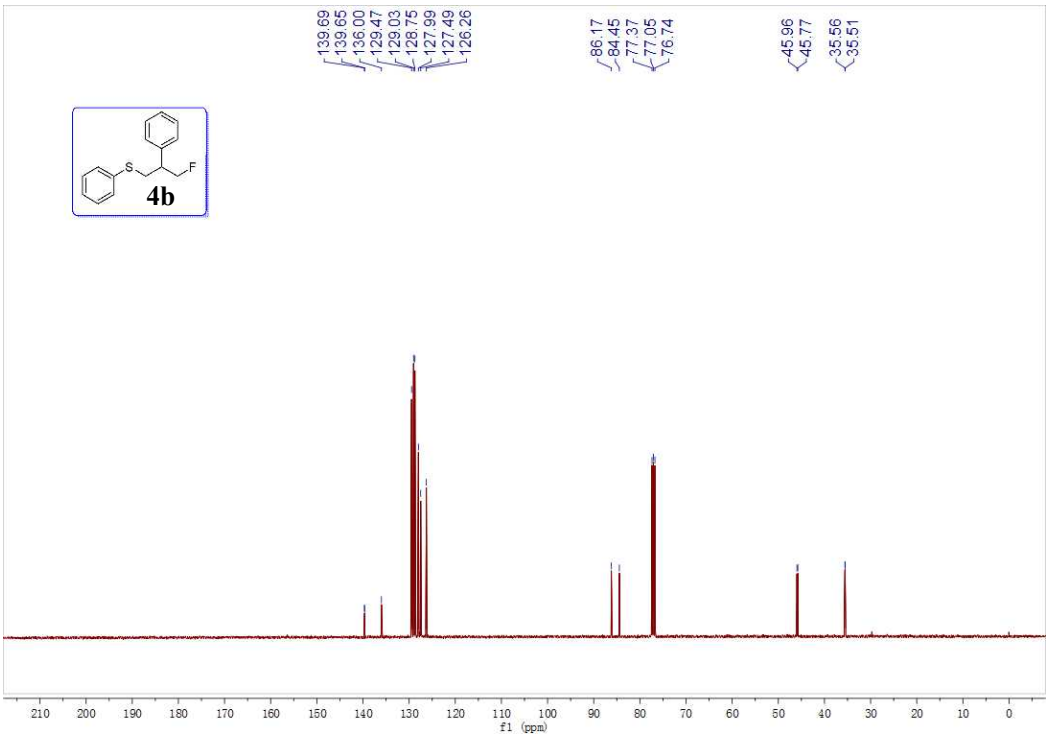
7.3407
7.3383
7.3101
7.2916
7.2880
7.2719
7.2128
7.2095
7.2061
7.1964
7.1914
7.1864
7.1766
7.1734
7.1701
4.6304
4.6162
4.6020
4.5126
4.4984
4.4842
3.0655
3.0476
3.0297
2.0599
2.0563
2.0419
2.0277
2.0243
1.9941
1.9904
1.9760
1.9618
1.9584
4a
0.88
0.90
0.44
1.00
1.03
1.04
f1 (ppm)
135.86
129.42
129.00
126.20
83.06
81.42
30.16
29.96
29.46
29.42
4a
f1 (ppm)


4a
221.04
f1 (ppm)


4b
f1 (ppm)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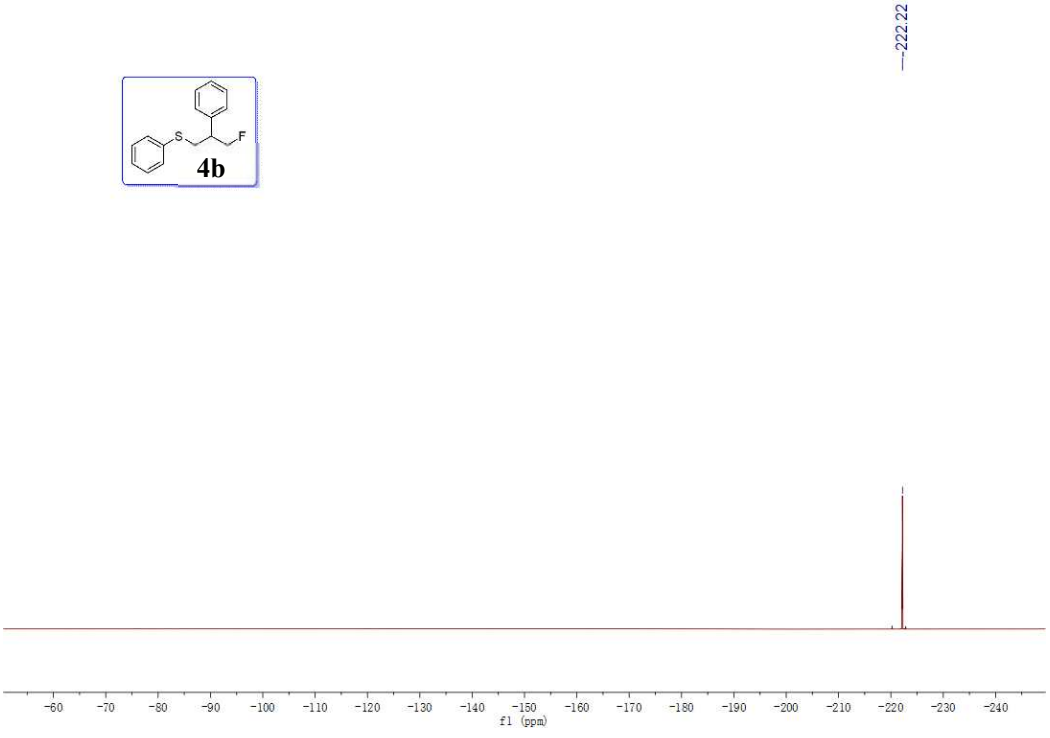
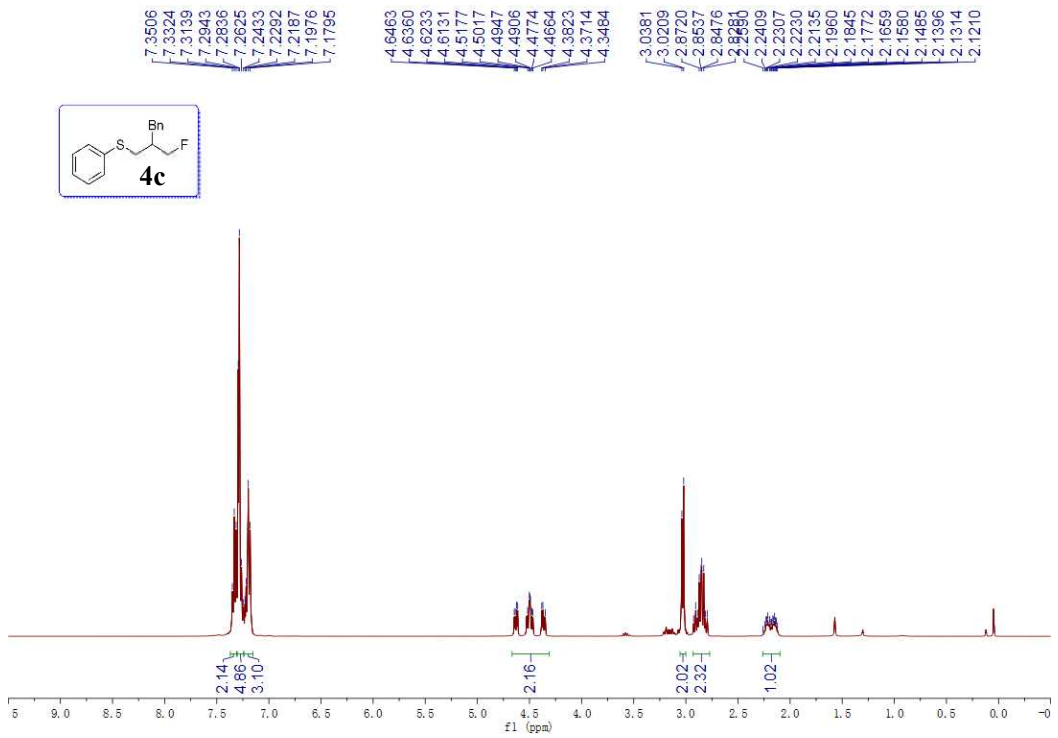
139.65
136.00
129.47
129.03
128.75
127.99
127.49
126.26
86.17
84.45
77.37
77.05
76.74
45.96
45.77
35.56
35.51
S
F
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-222.22
S
F
4b
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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7.3139
7.2943
7.2836
7.2625
7.2433
7.2292
7.2187
7.1976
7.1795
4.6463
4.6360
4.6233
4.6131
4.5177
4.5017
4.4947
4.4906
4.4774
4.4664
4.3823
4.3714
4.3484
3.0381
3.0209
2.8720
2.8537
2.8476
2.8281
2.2409
2.2307
2.2230
2.2135
2.1960
2.1845
2.1772
2.1659
2.1580
2.1485
2.1396
2.1314
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Bn
S
F
4c
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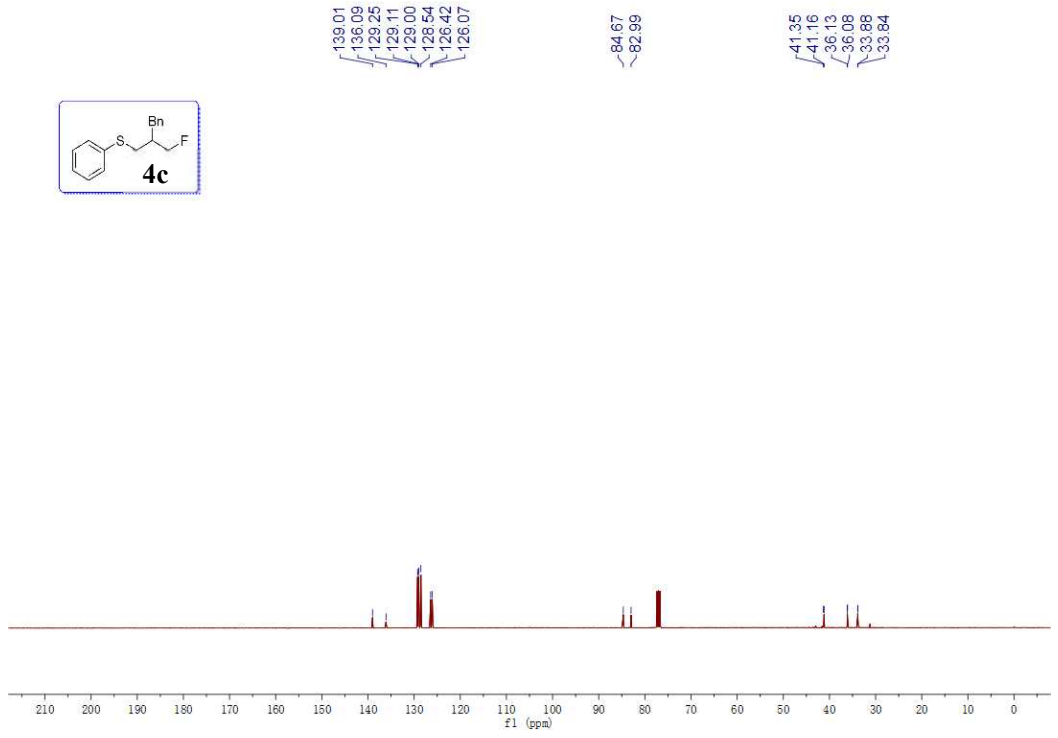
4.86
3.10
2.16
2.02
2.32
1.02
f1 (ppm)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129.11
129.00
128.54
126.42
126.07
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82.99
41.35
41.16
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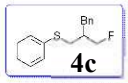
33.84
Bn
S
F
4c
f1 (ppm)


Bn
S
F

4c

-229.83
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


7.2852
7.2747
7.2500
7.2403
7.2290
7.1166
7.0891
7.0806
7.0769
7.0563
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6.8336
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6.8132
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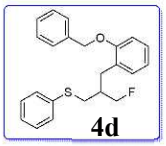
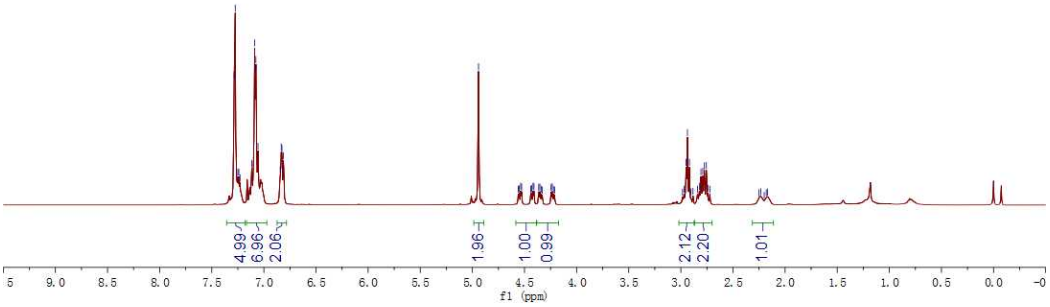
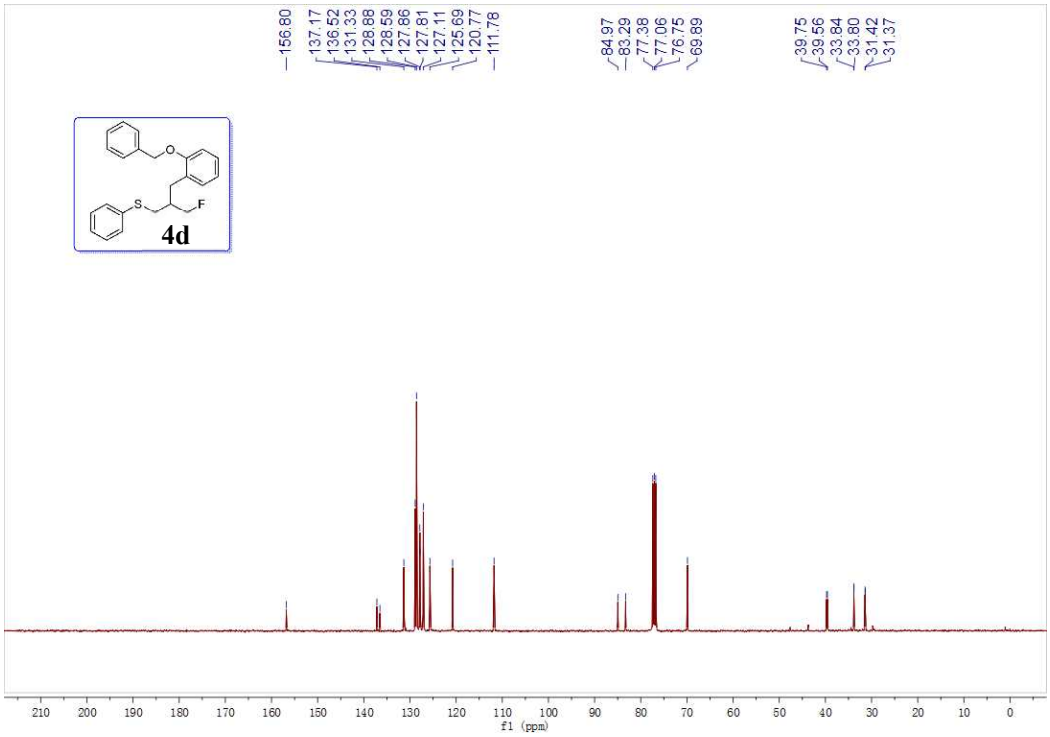
2.1809
2.1674


O
S
F

4d


4.99
6.96
2.06
1.96
1.00
0.99
2.12
2.20
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.80
137.17
136.52
131.33
128.88
128.59
127.86
127.81
127.11
125.69
120.77
111.78
84.97
83.29
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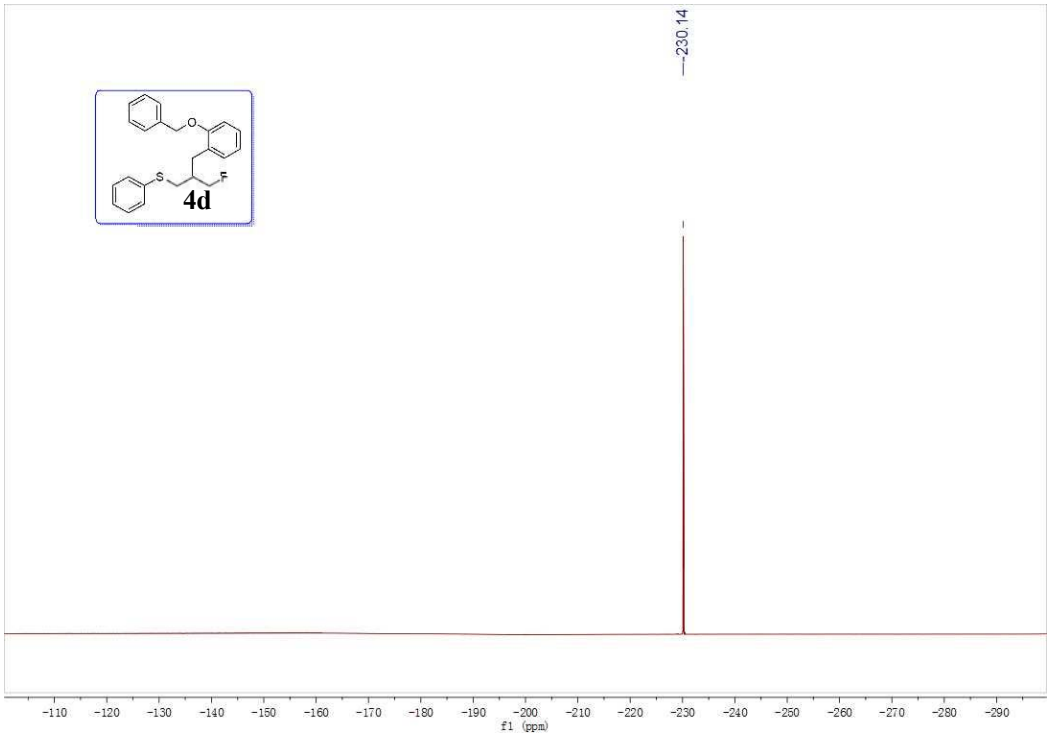
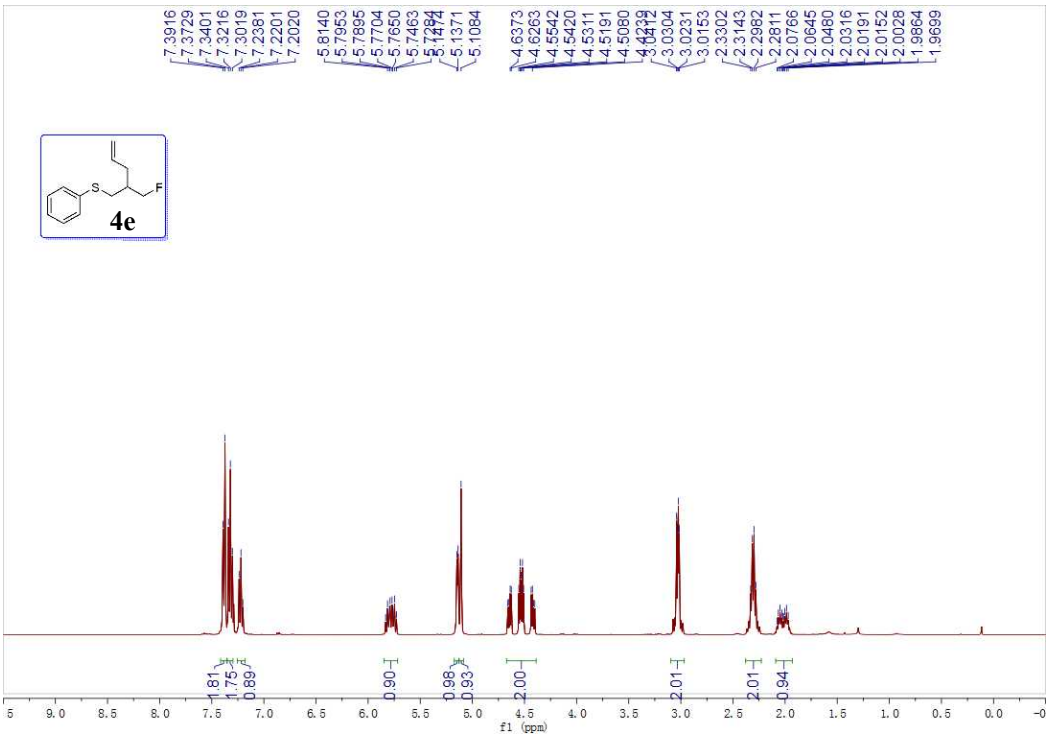
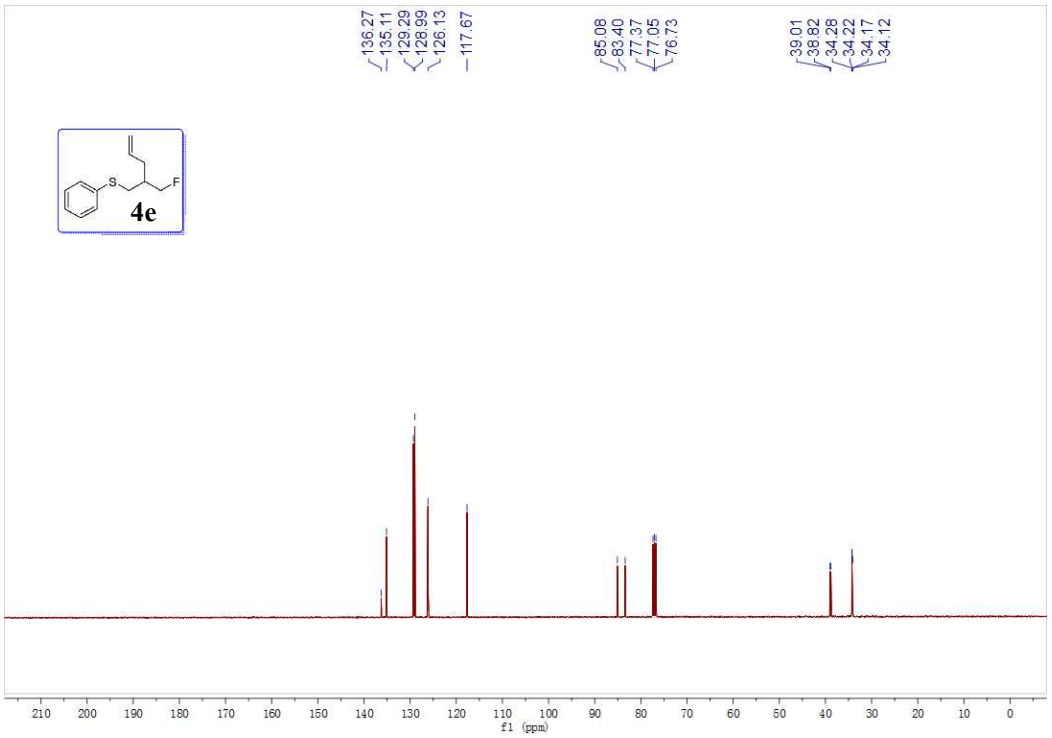
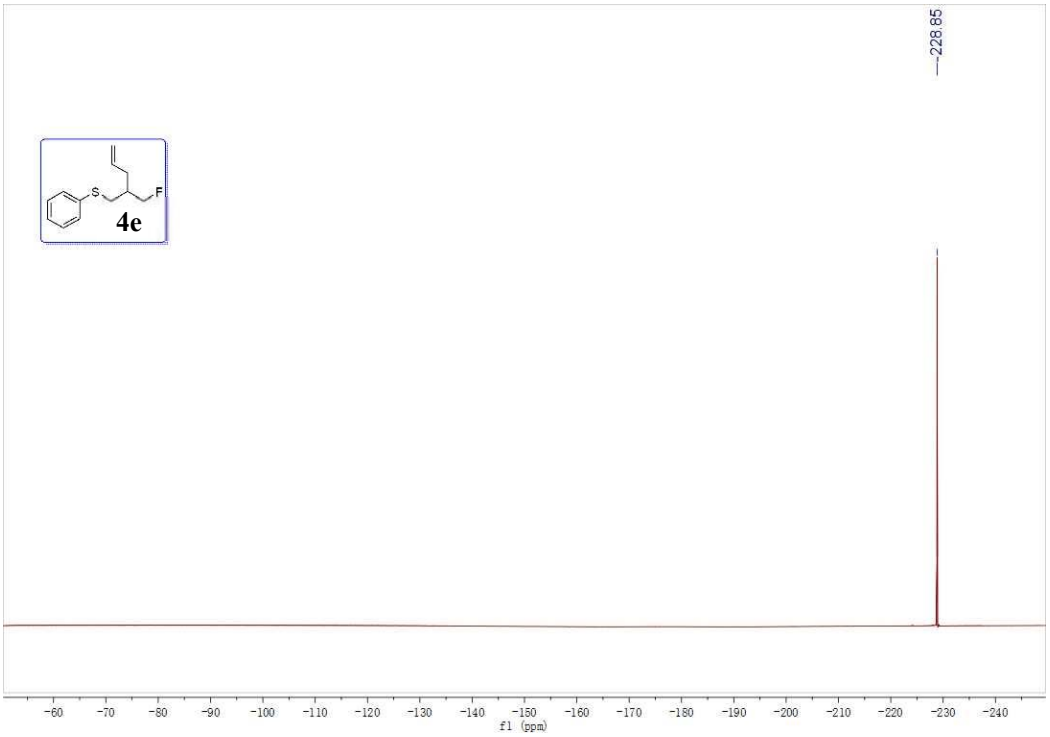
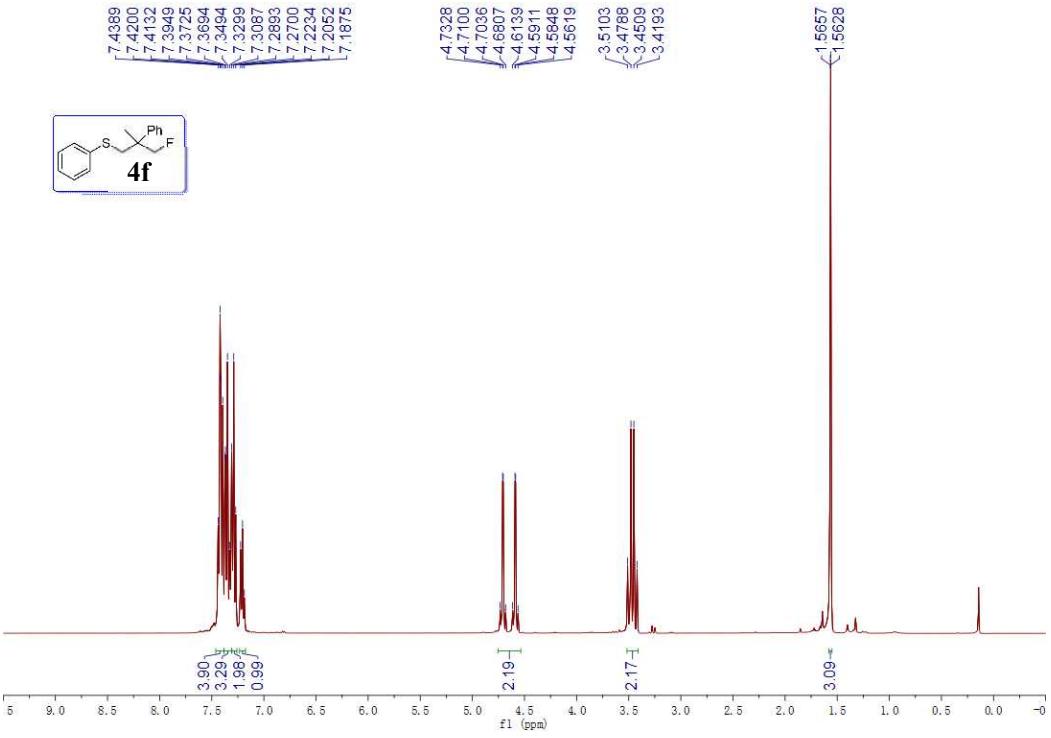
33.80
31.42
31.37
4d
f1 (ppm)


-230.14
4d
f1 (ppm)


4e
f1 (ppm)


4e
f1 (ppm)


228.85
4e
S
F
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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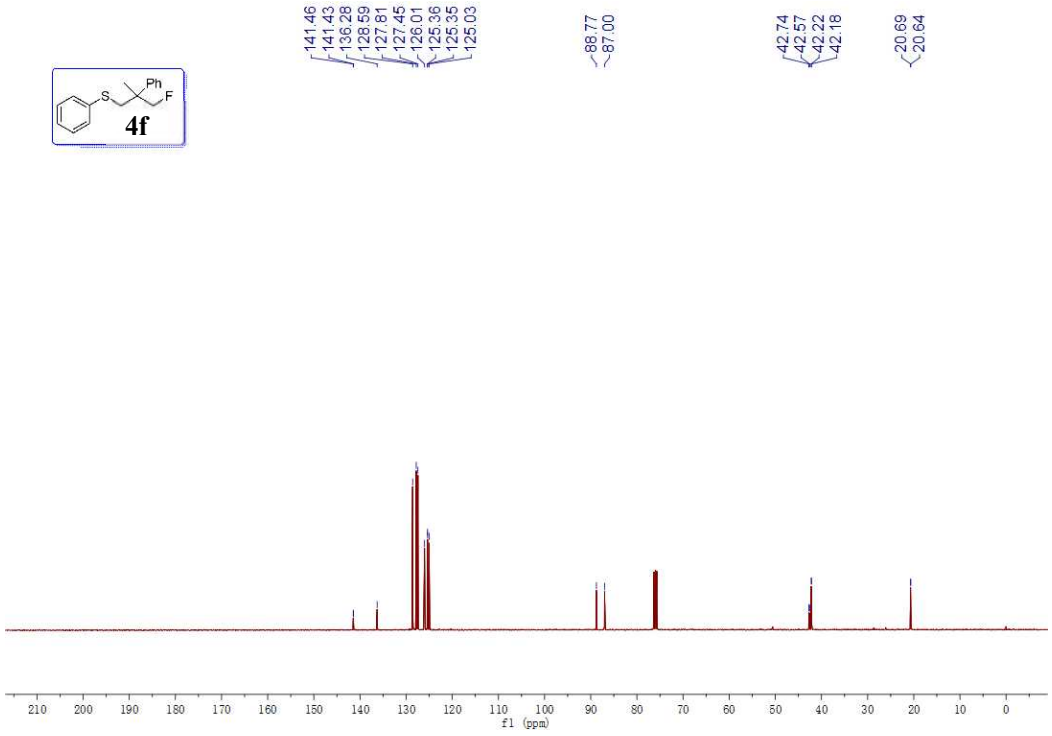
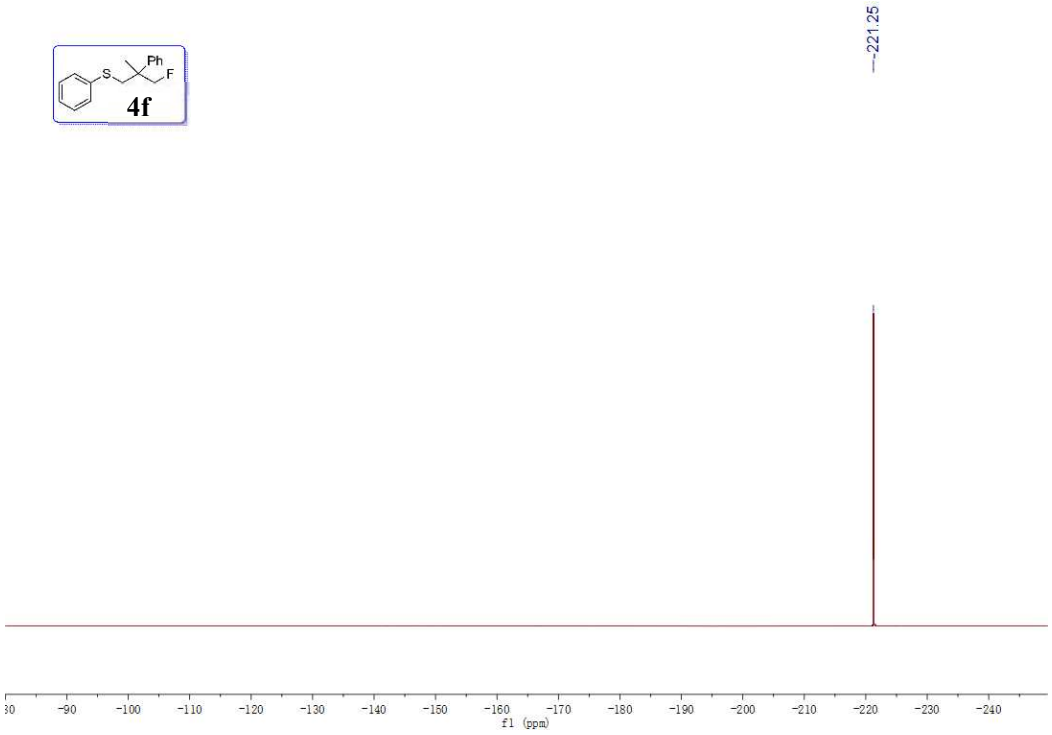
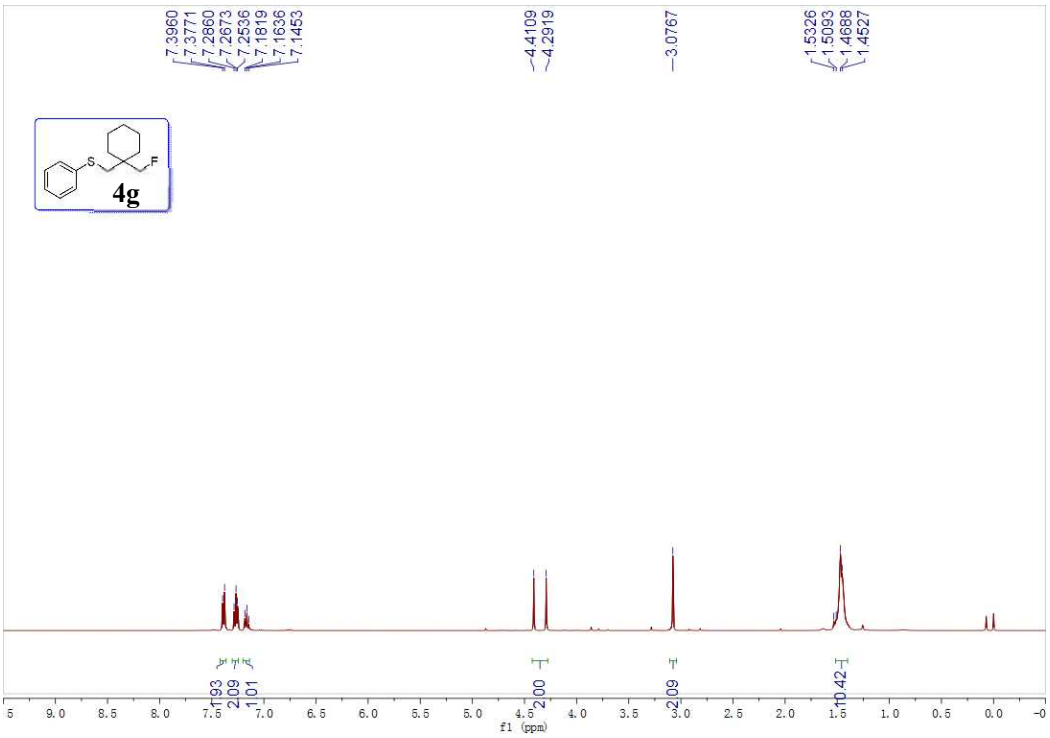
7.4132
7.3949
7.3725
7.3694
7.3494
7.3299
7.3067
7.2893
7.2700
7.2234
7.2052
7.1875
4.7328
4.7100
4.7036
4.6807
4.6139
4.5911
4.5848
4.5619
3.5103
3.4788
3.4509
3.4193
1.5657
1.5628
Ph
S
F
4f
3.90
3.29
1.98
0.99
2.19
2.17
3.09
f1 (ppm)


141.46
141.43
136.28
128.59
127.81
127.45
126.01
125.36
125.35
125.03
88.77
87.00
42.74
42.57
42.22
42.18
20.69
20.64
Ph
F
S
4f
f1 (ppm)


-221.25
Ph
F
S
4f
f1 (ppm)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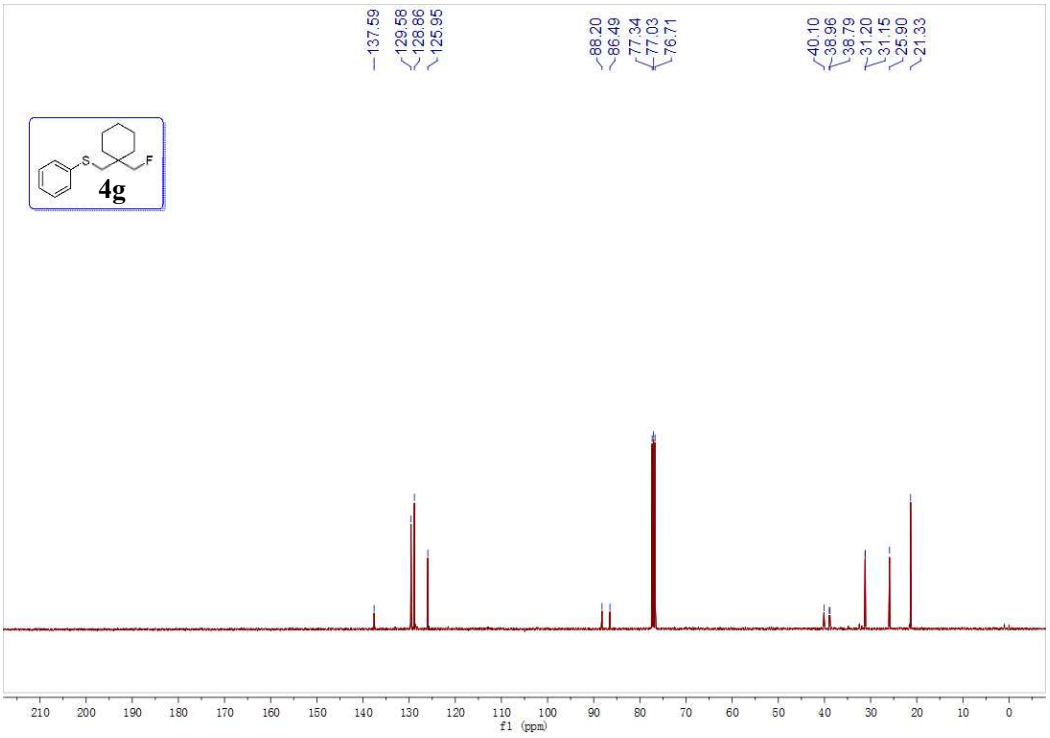
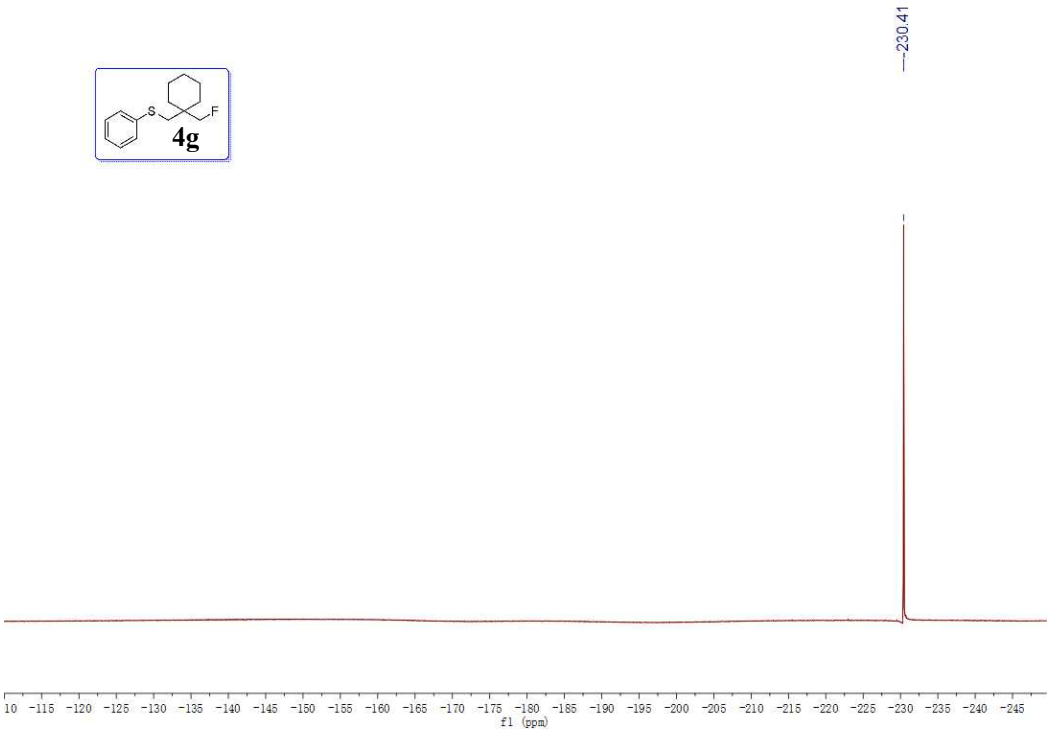
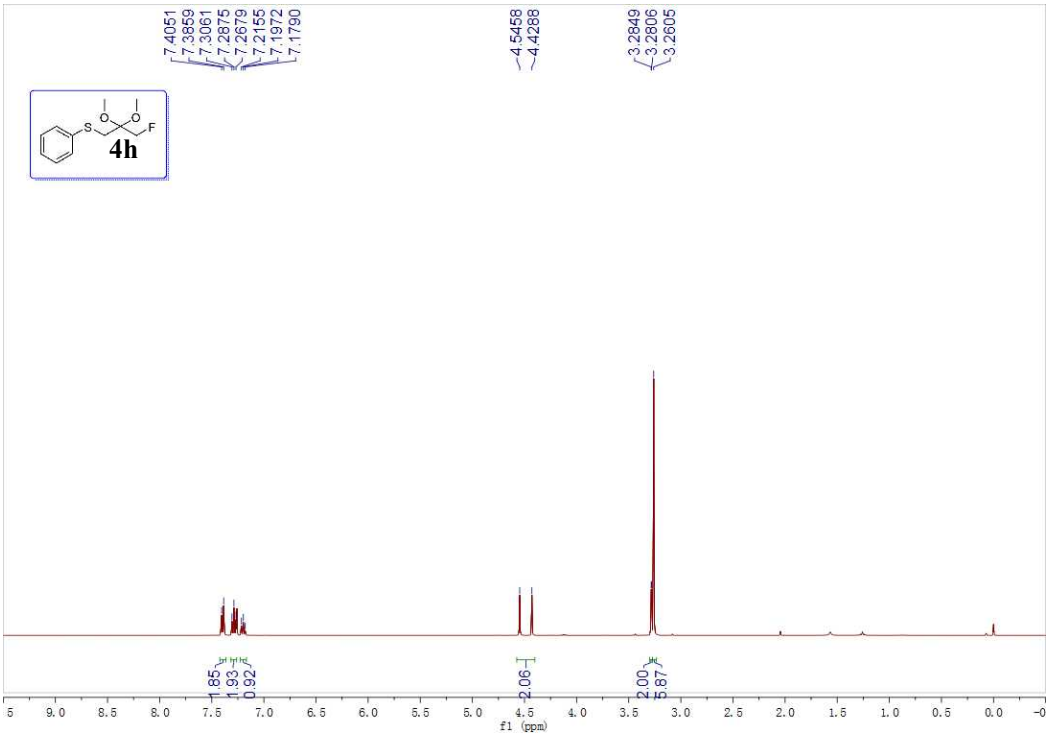
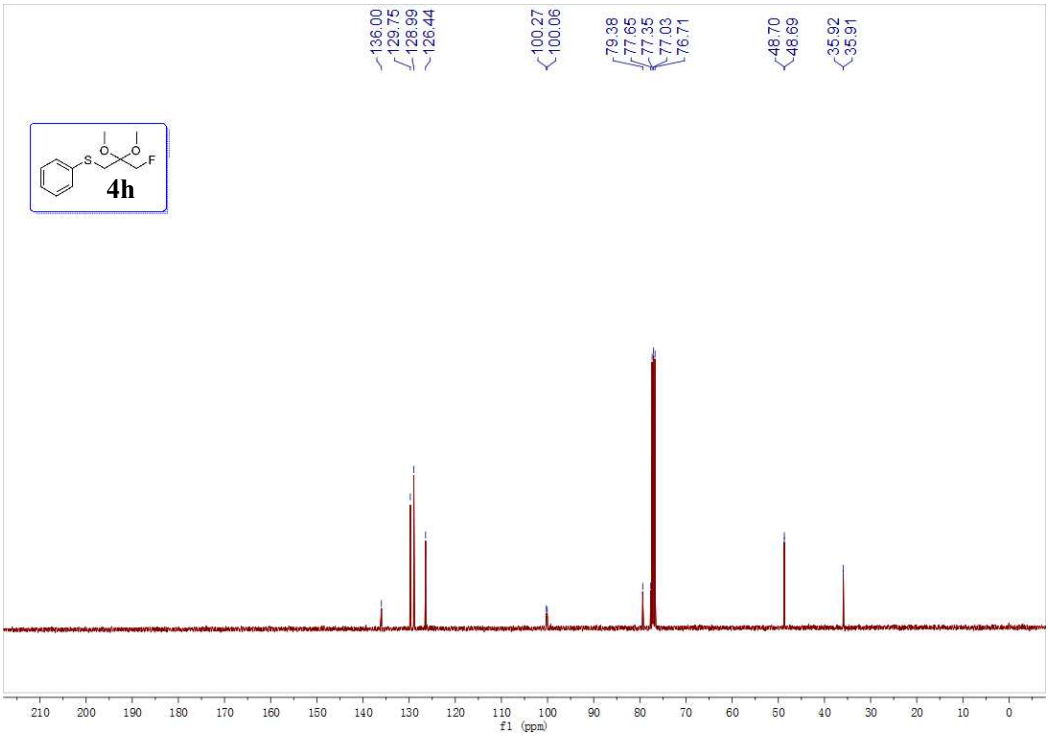
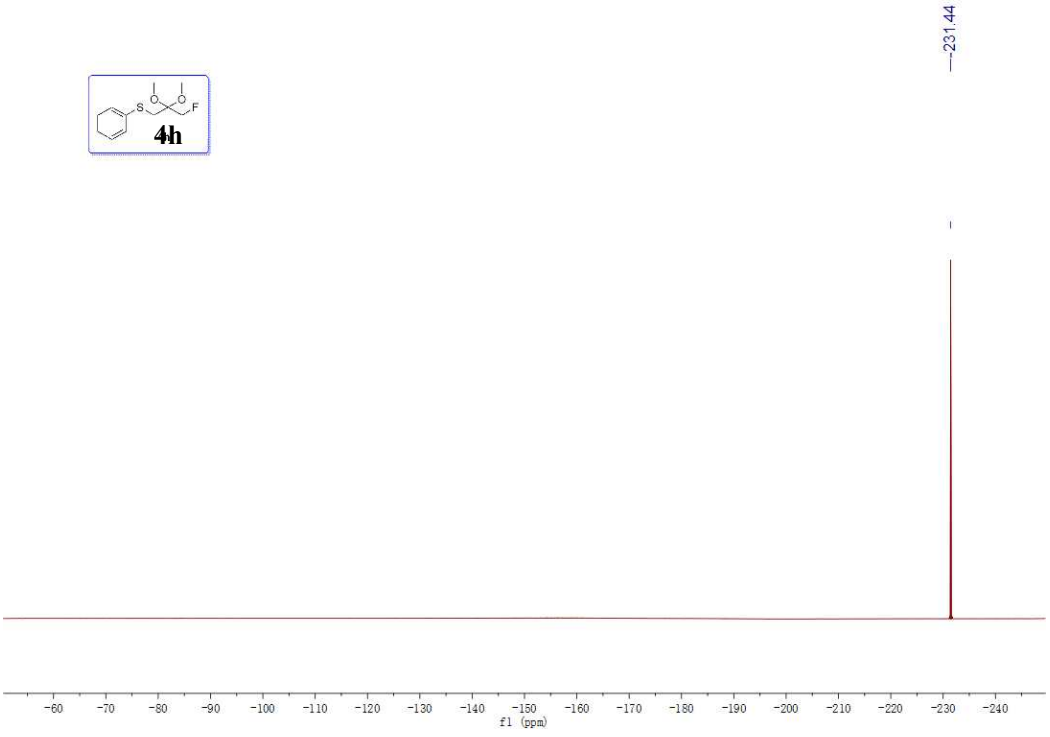
7.3771
7.2860
7.2673
7.2536
7.1819
7.1636
7.1453
4.4109
4.2919
3.0767
1.5326
1.5093
1.4688
1.4527
S
F
4g
1.93
2.09
1.01
2.00
2.09
10.42
f1 (ppm)

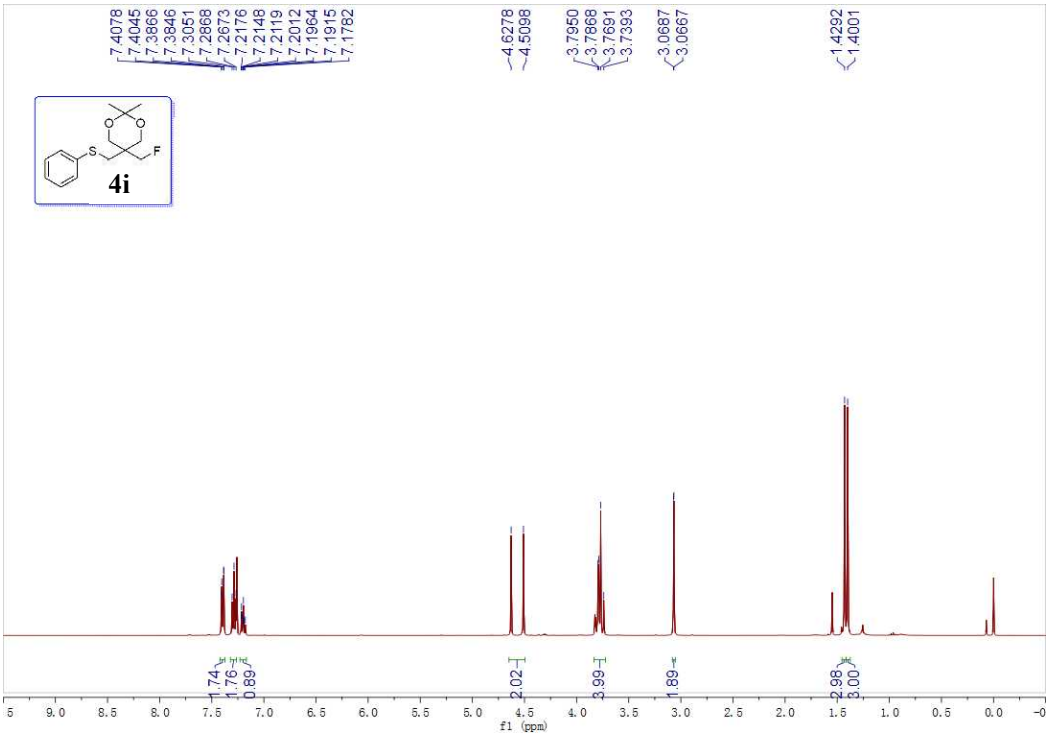

137.59
129.58
128.86
125.95
88.20
86.49
77.34
77.03
76.71
40.10
38.96
38.79
31.20
31.15
25.90
21.33
S
F
4g
f1 (ppm)

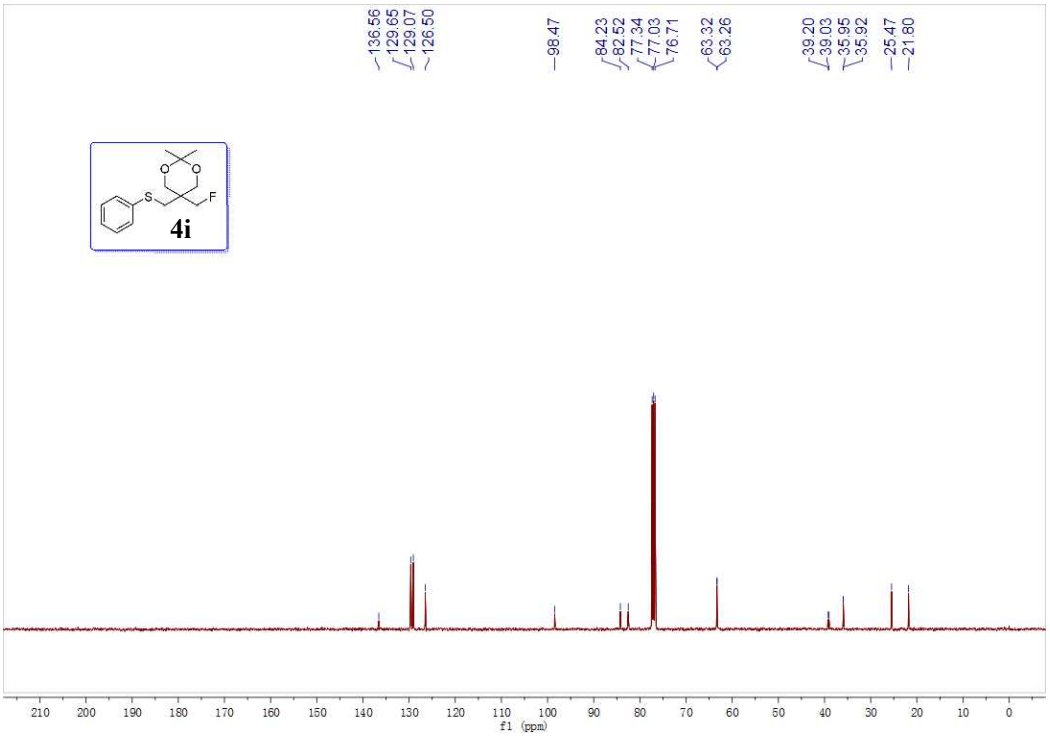

4g
-230.41
10 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -210 -215 -220 -225 -230 -235 -240 -245
f1 (ppm)

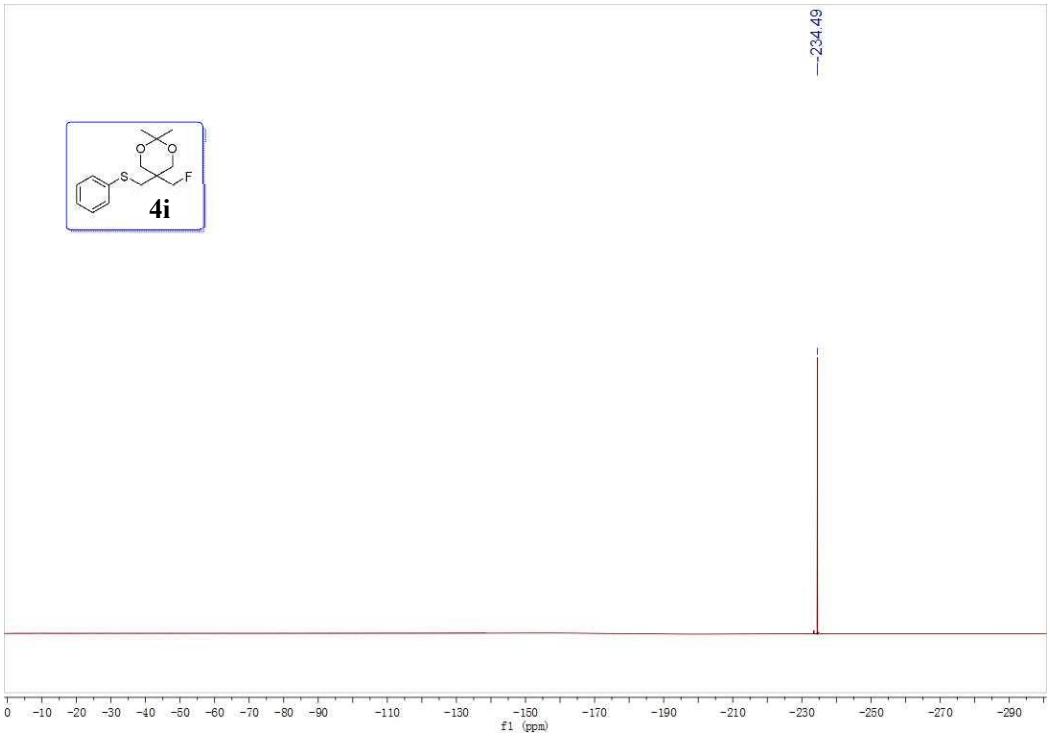

7.4051
7.3859
7.3061
7.2875
7.2679
7.2155
7.1972
7.1790
4.5458
4.4288
3.2849
3.2806
3.2605
4h
1.85
1.93
0.92
2.06
2.00
5.87
f1 (ppm)

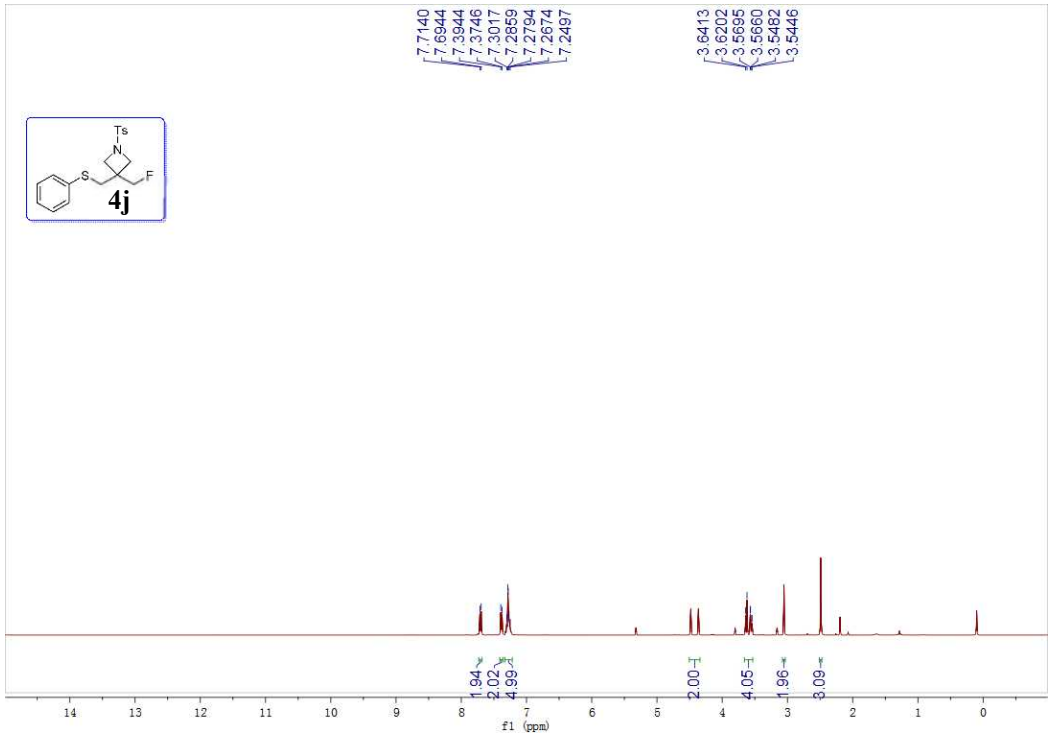

136.00
129.75
128.99
126.44
100.27
100.06
79.38
77.65
77.35
77.03
76.71
48.70
48.69
35.92
35.91
4h
f1 (ppm)

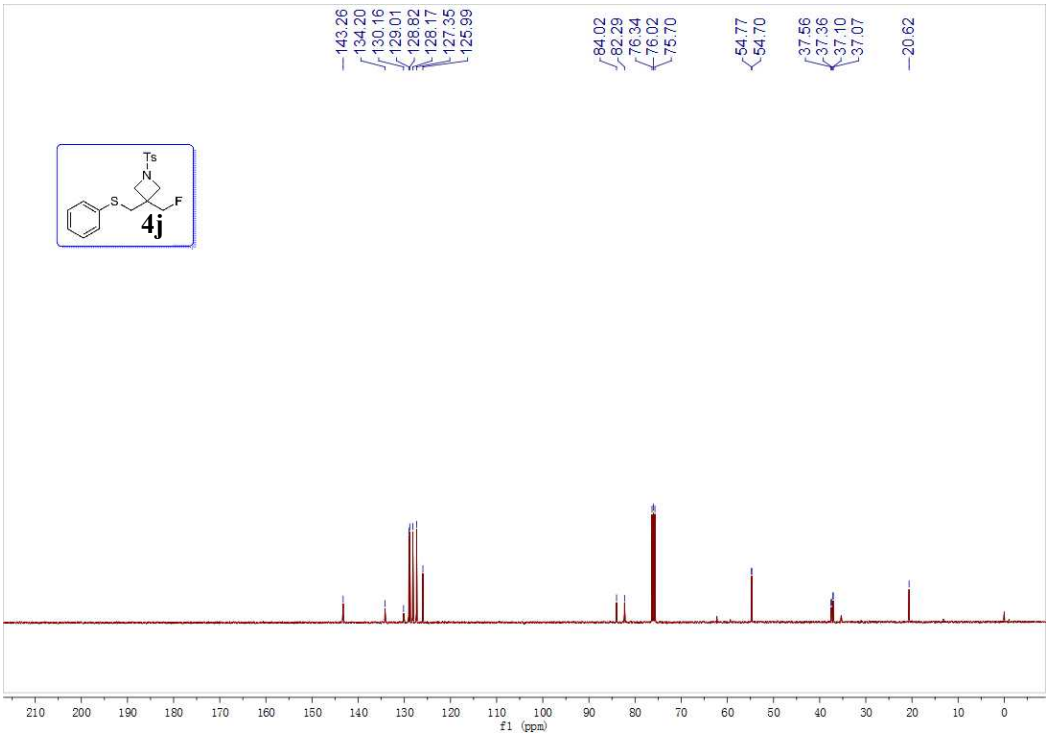

231.44
4h
f1 (ppm)

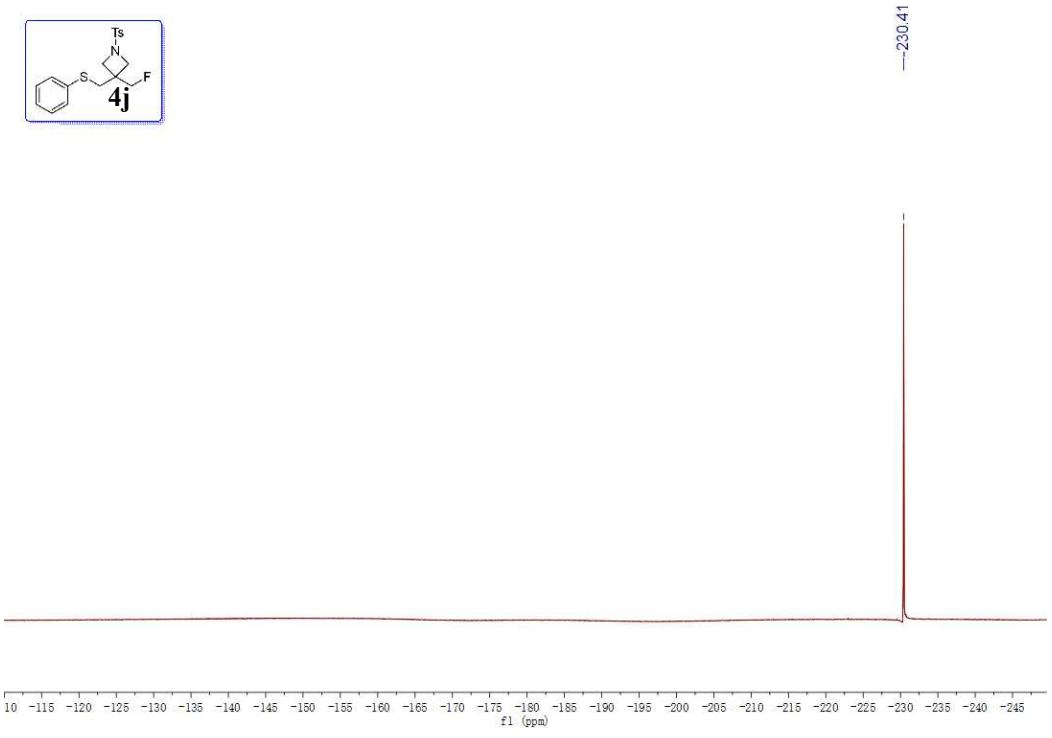

7.4078
7.4045
7.3866
7.3846
7.3051
7.2868
7.2673
7.2176
7.2148
7.2119
7.2012
7.1964
7.1915
7.1782
4.6278
4.5098
3.7950
3.7868
3.7691
3.7393
3.0687
3.0667
1.4292
1.4001
4i
1.74
1.76
0.89
2.02
3.99
1.89
2.98
3.00
f1 (ppm)

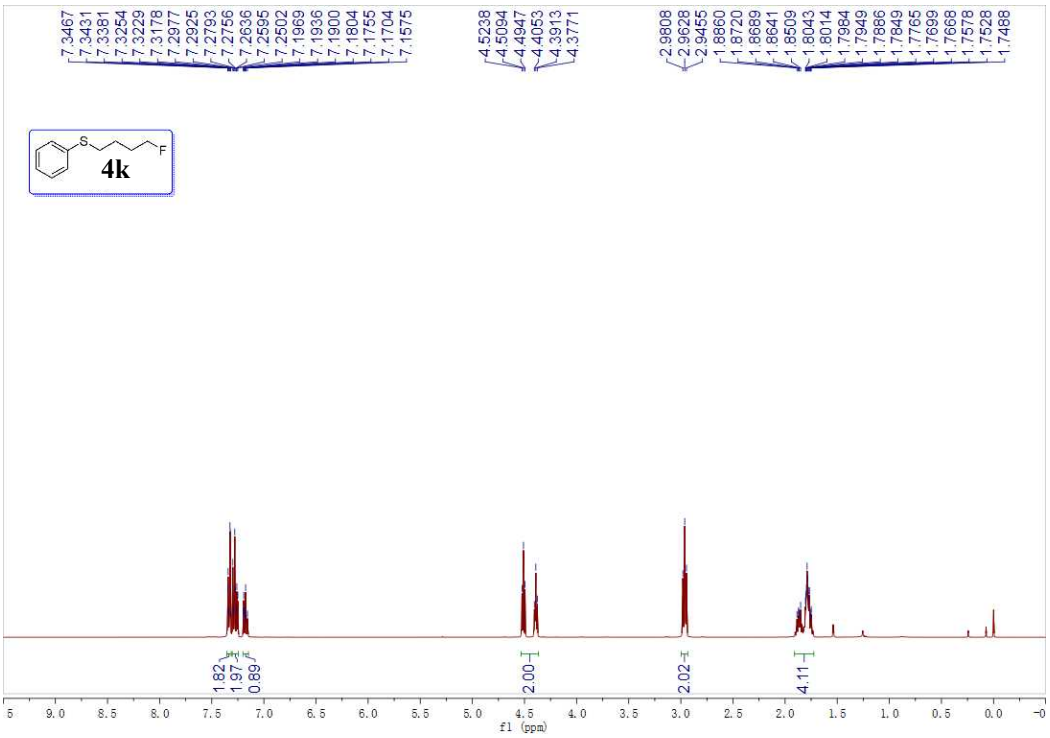

136.56
129.65
129.07
126.50
98.47
84.23
82.52
77.34
77.03
76.71
63.32
63.26
39.20
39.03
35.95
35.92
25.47
21.80
4i
f1 (ppm)

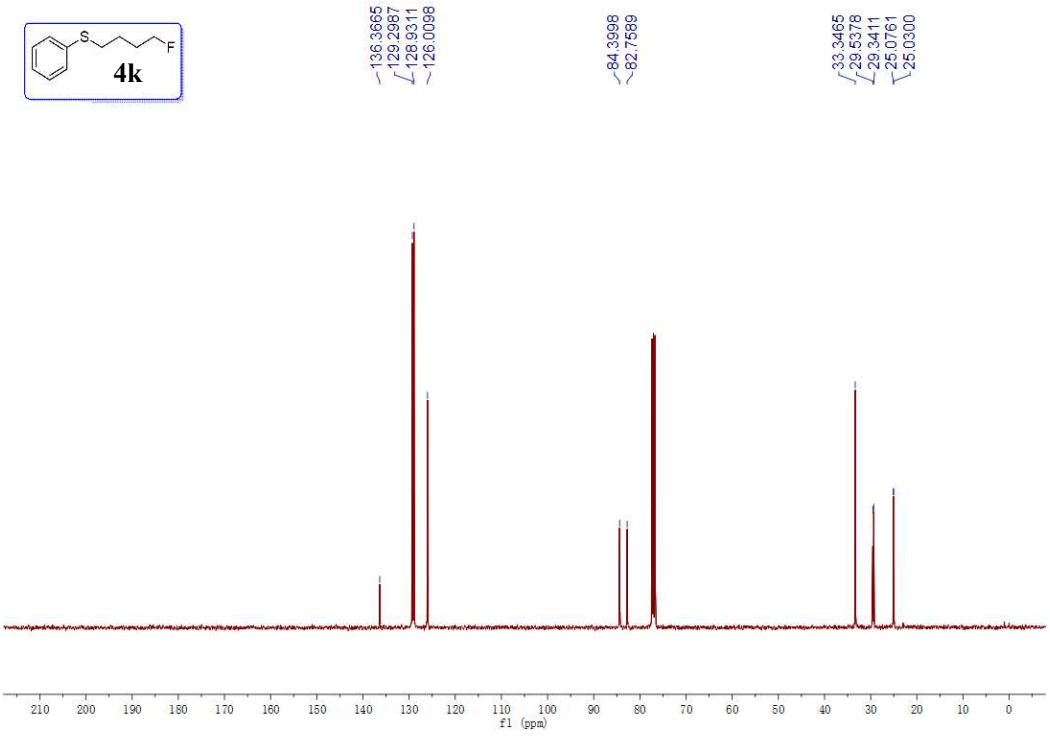

-234.49
4i
f1 (ppm)

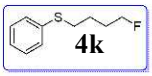

7.7140
7.6944
7.3944
7.3746
7.3017
7.2859
7.2794
7.2674
7.2497
3.6413
3.6202
3.5695
3.5660
3.5482
3.5446
Ts
4j
1.94
2.02
4.99
2.00
4.05
1.96
3.09
f1 (ppm)


143.26
134.20
130.16
129.01
128.82
128.17
127.35
125.99
84.02
82.29
76.34
76.02
75.70
54.77
54.70
37.56
37.36
37.10
37.07
20.62
Ts
N
S
F
4j
f1 (ppm)


230.41
Ts
N
S
F
4j
f1 (ppm)


7.3467
7.3431
7.3381
7.3254
7.3229
7.3178
7.2977
7.2925
7.2793
7.2756
7.2636
7.2595
7.2502
7.1969
7.1936
7.1900
7.1804
7.1755
7.1704
7.1575
4.5238
4.5094
4.4947
4.4053
4.3913
4.3771
2.9808
2.9628
2.9455
1.8860
1.8720
1.8689
1.8641
1.8509
1.8043
1.8014
1.7984
1.7949
1.7886
1.7849
1.7765
1.7699
1.7668
1.7578
1.7528
1.7488
4k
1.82
1.97
0.89
2.00
2.02
4.11
f1 (ppm)


136.3665
129.2987
128.9311
126.0098
84.3998
82.7589
33.3465
29.5378
29.3411
25.0761
25.0300
4k
f1 (ppm)


S
F

4k

218.61
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


7.3666
7.3476
7.3272
7.3088
7.2880
7.2189
7.2009
7.1835
4.5365
4.5215
4.5064
4.4180
4.4033
4.3884
2.9803
2.9623
2.9441
1.8042
1.7880
1.7650
1.7442
1.7254
1.7073
1.6888
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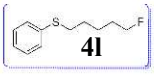
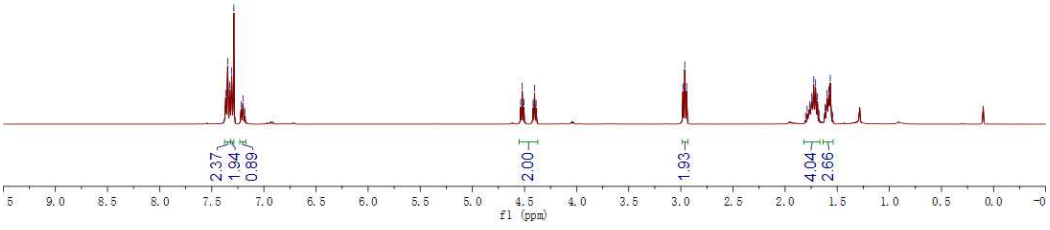
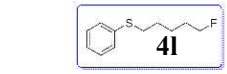
1.6178
1.5975
1.5802
1.5664
1.5438

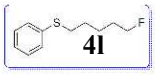

S
F

4l

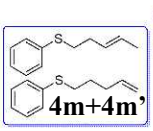

2.37
1.94
0.89
2.00
1.93
4.04
2.66
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


S
F
4l

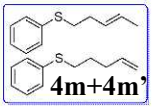
136.67
129.10
128.88
125.86
84.68
83.05
33.51
30.07
29.87
28.77
24.50
24.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


S
F
4l

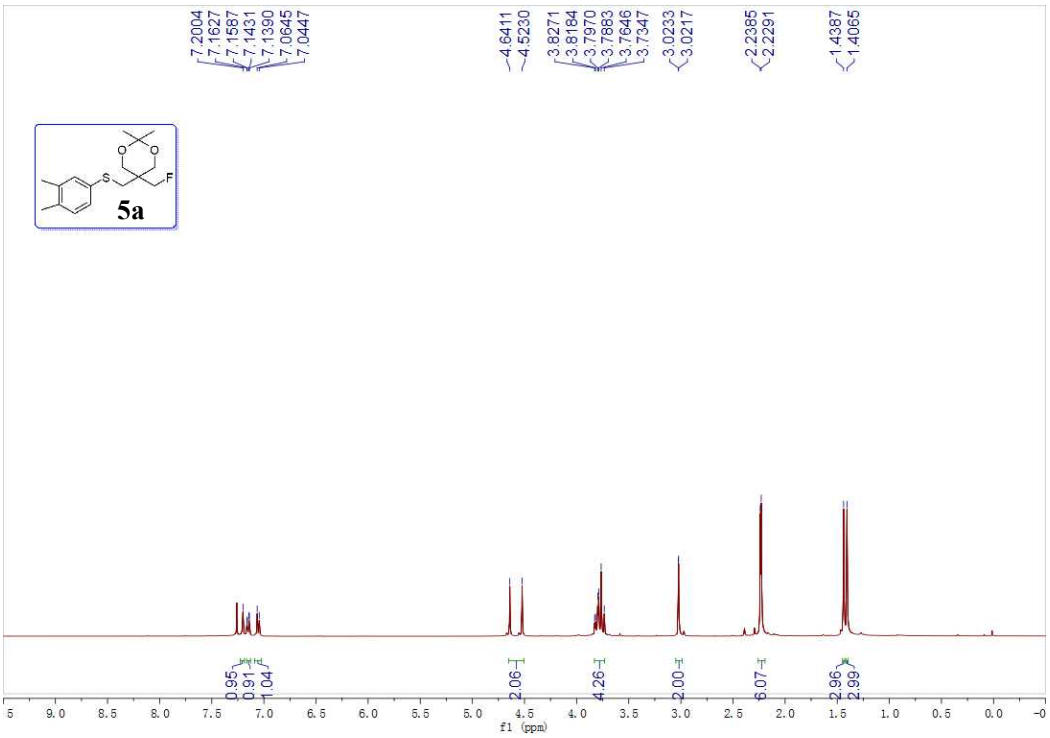
218.38
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


4m+4m'

7.3344
7.3159
7.2894
7.2711
7.2507
7.2498
7.1603
5.5369
5.5232
5.5121
5.4986
5.4858
5.4733
5.4589
5.4349
5.0571
5.0539
5.0142
5.0110
5.0052
5.0029
5.0008
4.9983
4.9752
4.9729
2.9536
2.9352
2.9164
2.9025
2.3265
2.3079
2.2908
1.7593
1.7410
1.7226
1.7043
1.6657
1.6522
9.40
10.00
4.36
1.03
7.28
2.14
9.09
7.89
2.30
2.79
11.61
f1 (ppm)


4m+4m'

137.60
136.74
129.09
128.95
128.86
126.96
125.79
115.43
33.63
32.97
32.73
32.33
28.30
17.95
f1 (ppm)


7.2004
7.1627
7.1587
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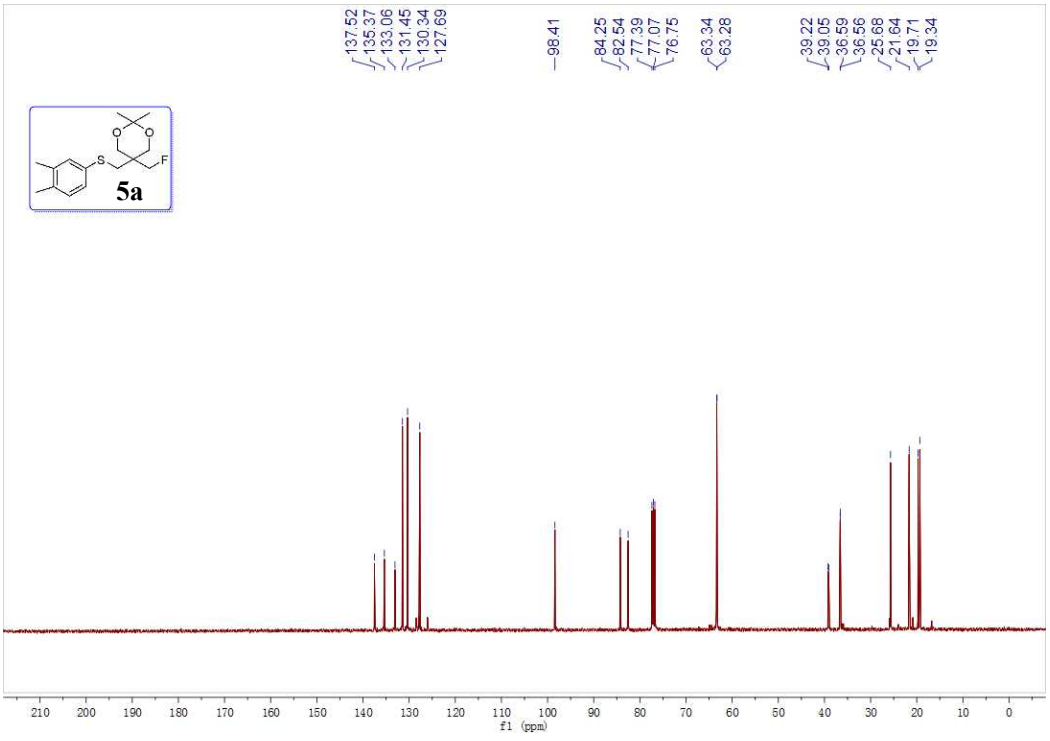
7.1390
7.0645
7.0447
4.6411
4.5230
3.8271
3.8184
3.7970
3.7883
3.7646
3.7347
3.0233
3.0217
2.2385
2.2291
1.4387
1.4065
5a
0.95
0.91
1.04
2.06
4.26
2.00
6.07
2.96
2.99
f1 (ppm)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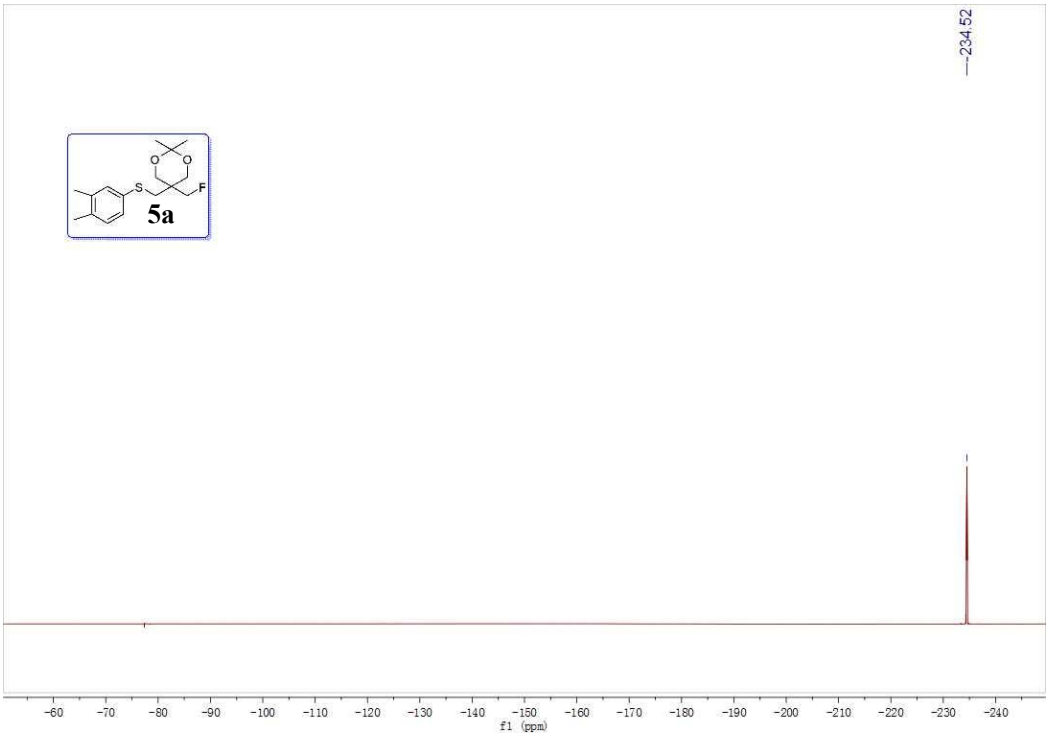
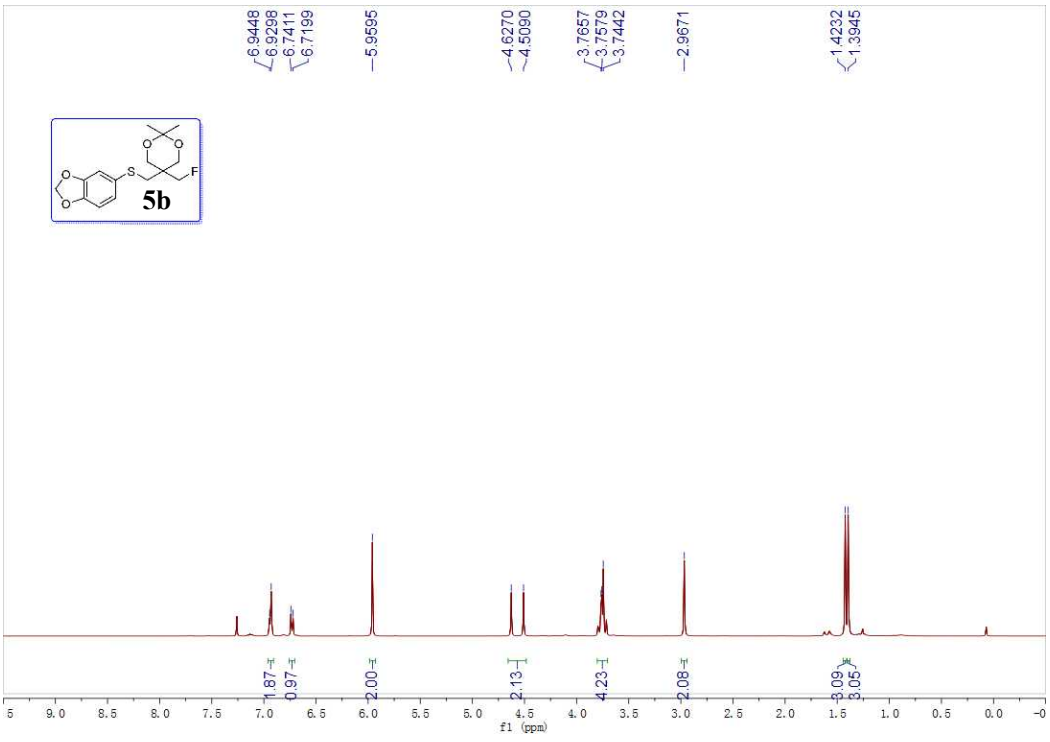
133.06
131.45
130.34
127.69
98.41
84.25
82.54
77.39
77.07
76.75
63.34
63.28
39.22
39.05
36.59
36.56
25.68
21.64
19.71
19.34
5a
f1 (ppm)


-234.52
5a
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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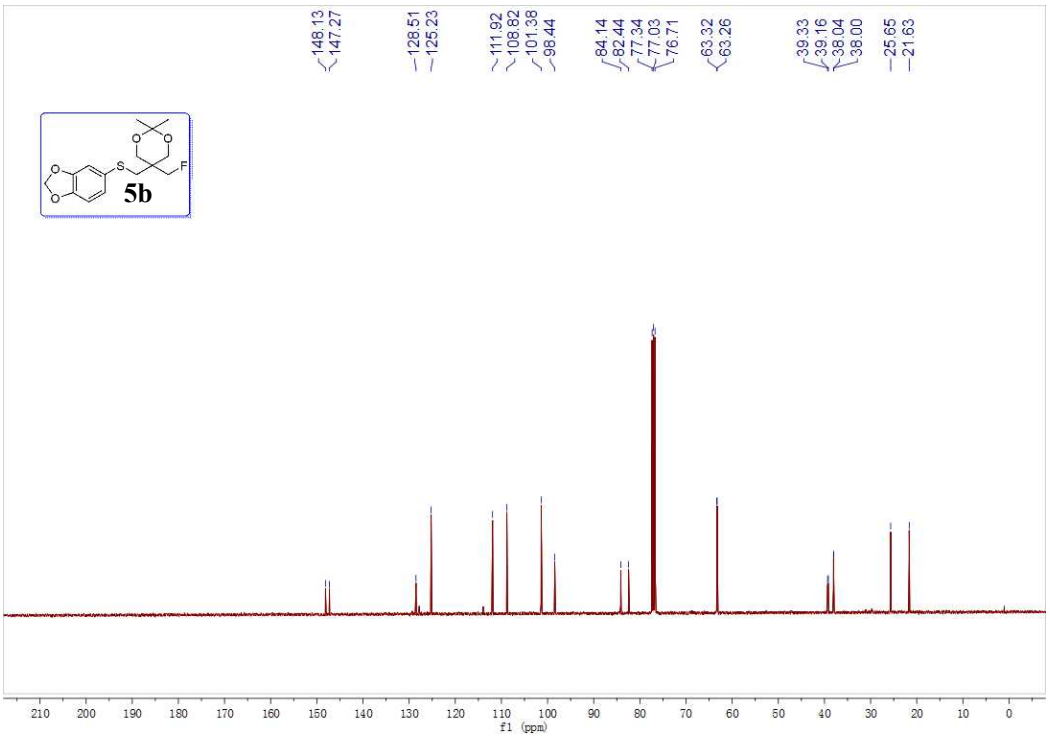
6.9298
6.7411
6.7199
5.9595
4.6270
4.5090
3.7657
3.7579
3.7442
2.9671
1.4232
1.3945
5b
1.87
0.97
2.00
2.13
4.23
2.08
3.09
3.05
f1 (ppm)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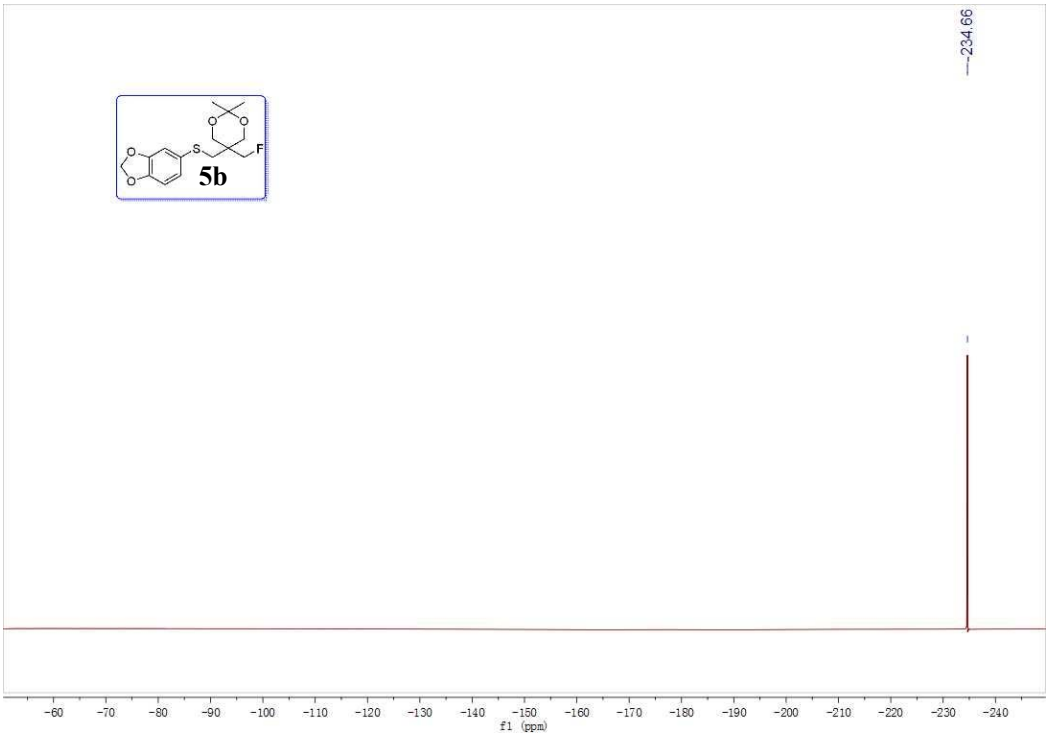
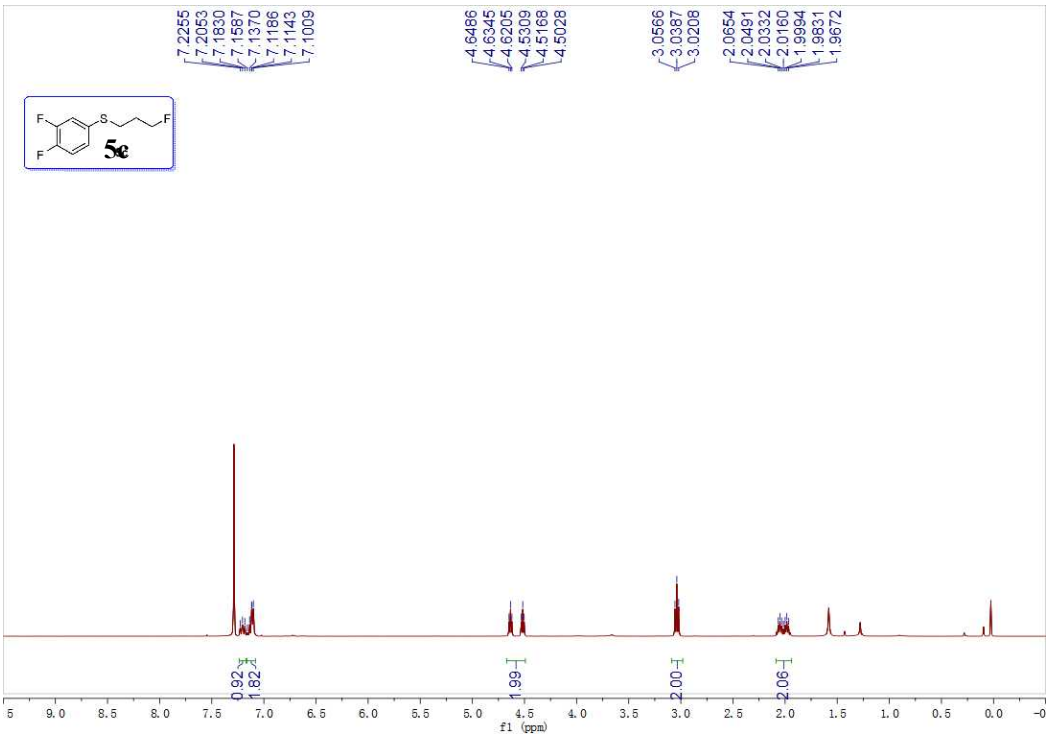
147.27
128.51
125.23
111.92
108.82
101.38
98.44
84.14
82.44
77.34
77.03
76.71
63.32
63.26
39.33
39.16
38.04
38.00
25.65
21.63
5b
f1 (ppm)


-234.66
5b
f1 (ppm)


7.2255
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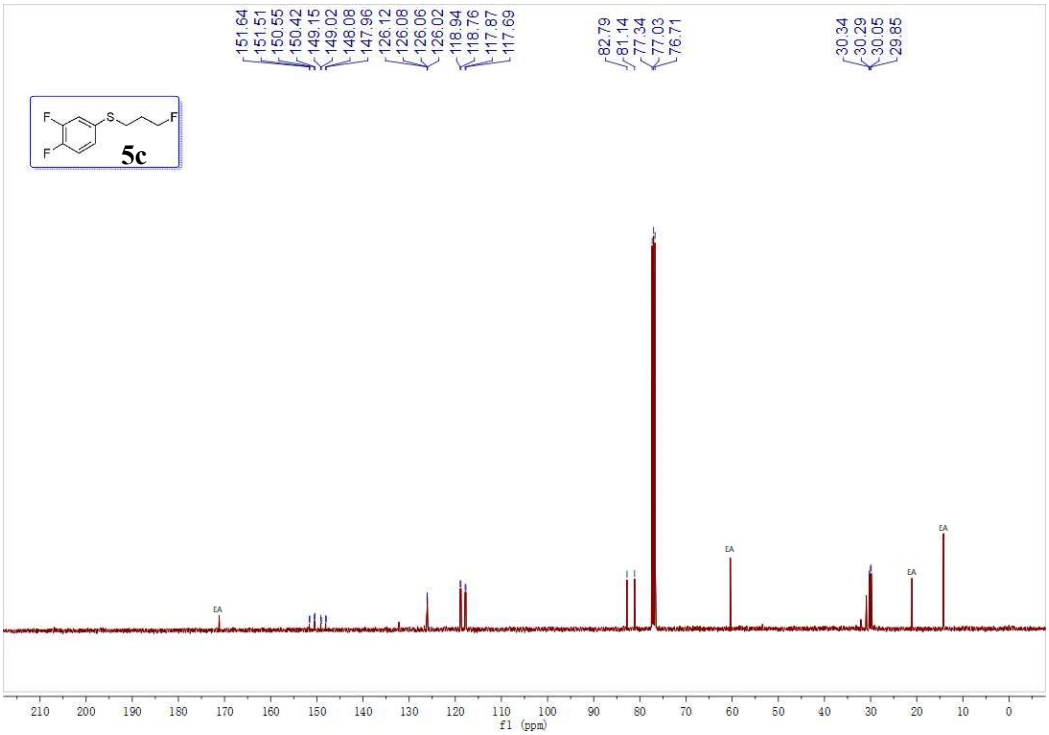
7.1587
7.1370
7.1186
7.1143
7.1009
4.6486
4.6345
4.6205
4.5309
4.5168
4.5028
3.0566
3.0387
3.0208
2.0654
2.0491
2.0332
2.0160
1.9994
1.9831
1.9672
5c
0.92
1.82
1.99
2.00
2.06
f1 (ppm)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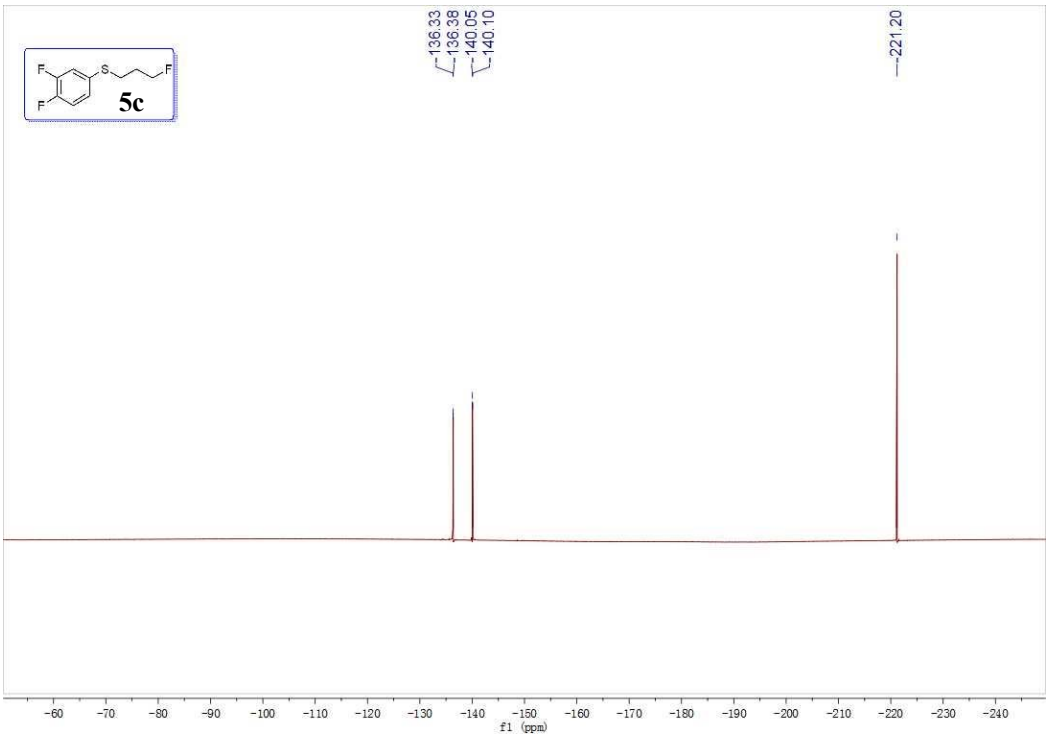
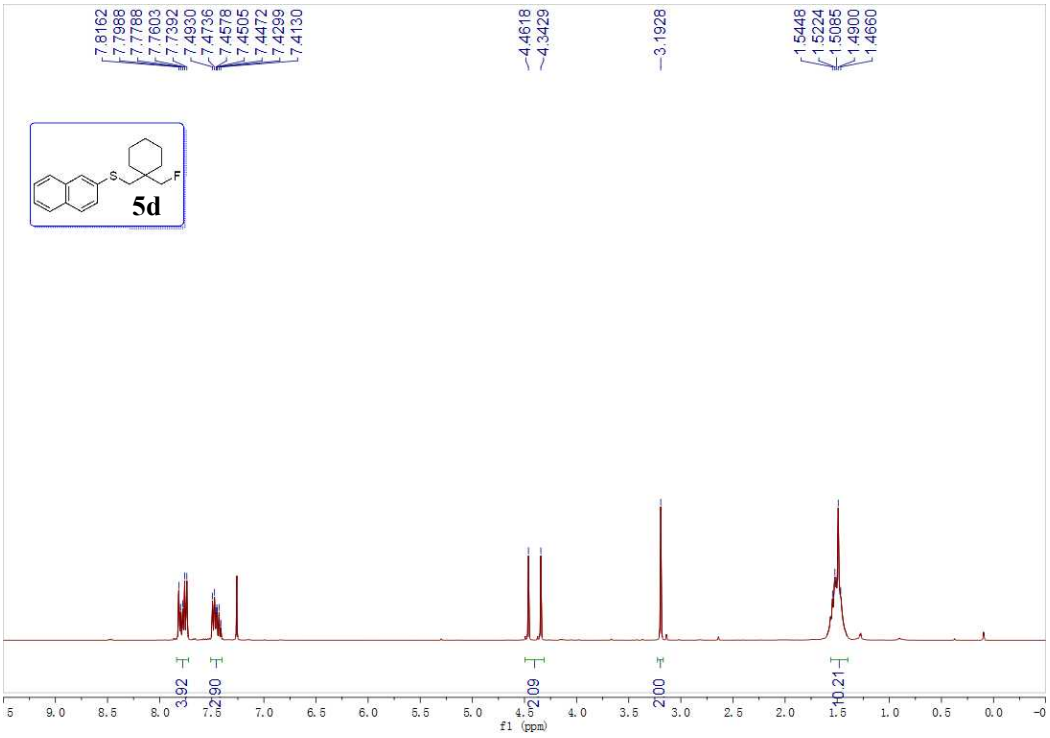
150.55
150.42
149.15
149.02
148.08
147.96
126.12
126.08
126.06
126.02
118.94
118.76
117.87
117.69
82.79
81.14
77.34
77.03
76.71
30.34
30.29
30.05
29.85
5c
EA
EA
EA
EA
f1 (ppm)


5c
136.33
136.38
140.05
140.10
221.20
f1 (ppm)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7.4930
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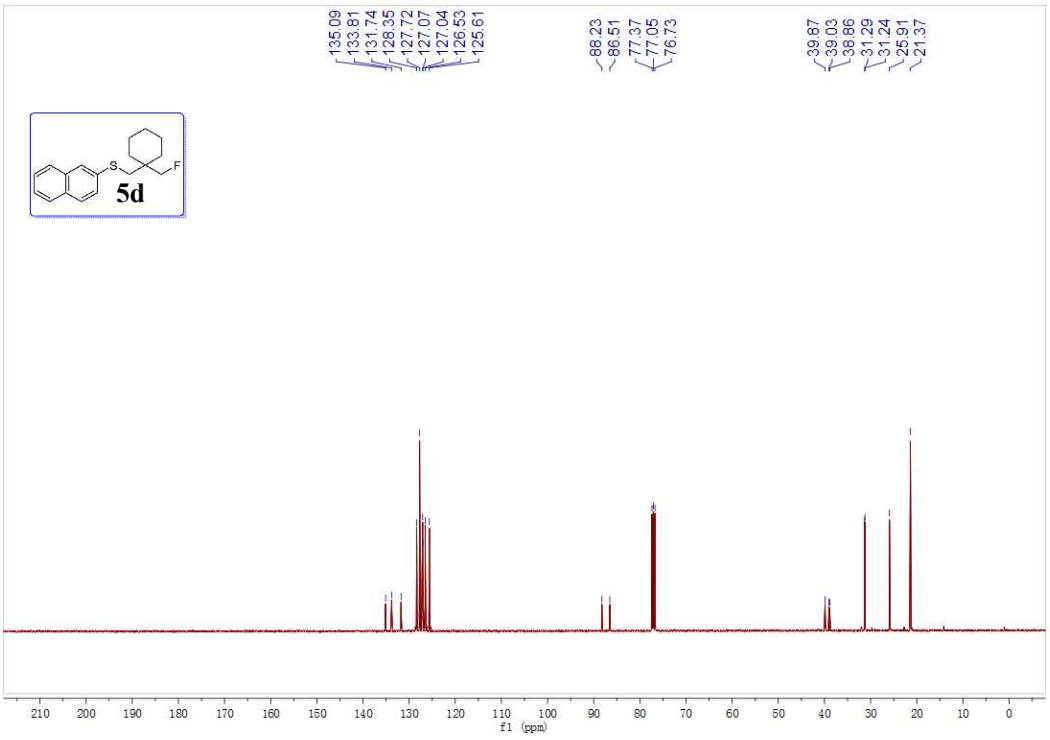
7.4505
7.4472
7.4299
7.4130
4.4618
4.3429
3.1928
1.5448
1.5224
1.5085
1.4900
1.4660
3.92
2.90
2.09
2.00
1.21
f1 (ppm)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127.07
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126.53
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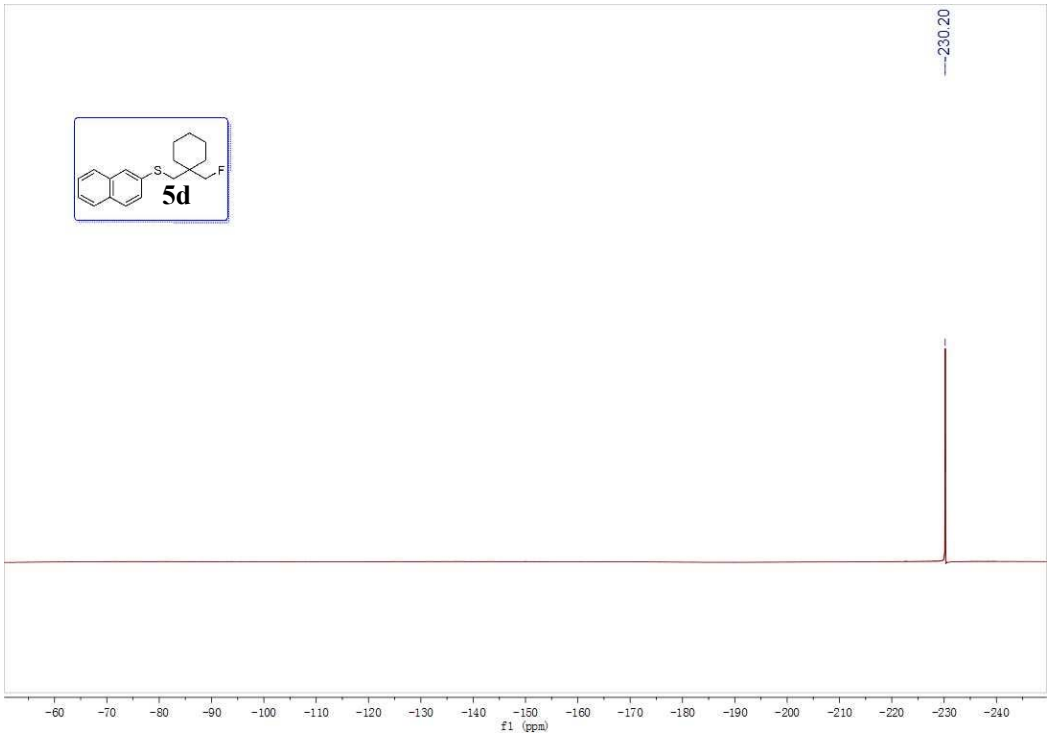
86.51
77.37
77.05
76.73
39.87
39.03
38.86
31.29
31.24
25.91
21.37
S
F
5d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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S
F
5d
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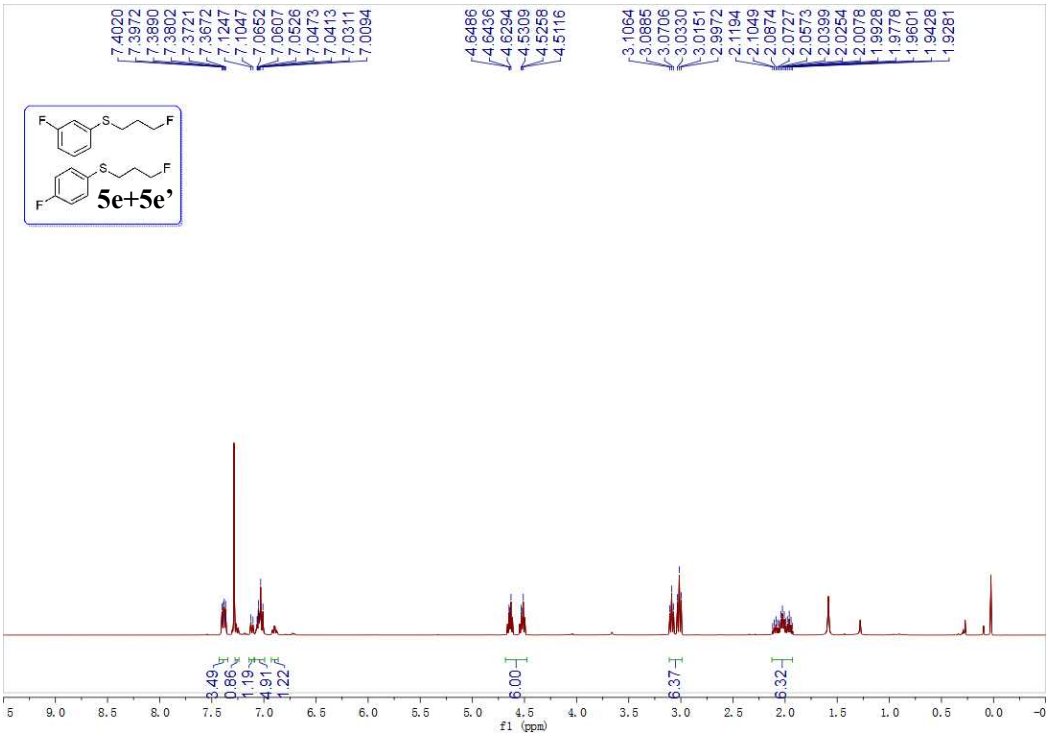
f1 (ppm)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7.0526
7.0473
7.0413
7.0311
7.0094
4.6486
4.6436
4.6294
4.5309
4.5258
4.5116
3.1064
3.0885
3.0706
3.0330
3.0151
2.9972
2.1194
2.1049
2.0874
2.0727
2.0573
2.0399
2.0254
2.0078
1.9928
1.9778
1.9601
1.9428
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5e+5e'
3.49
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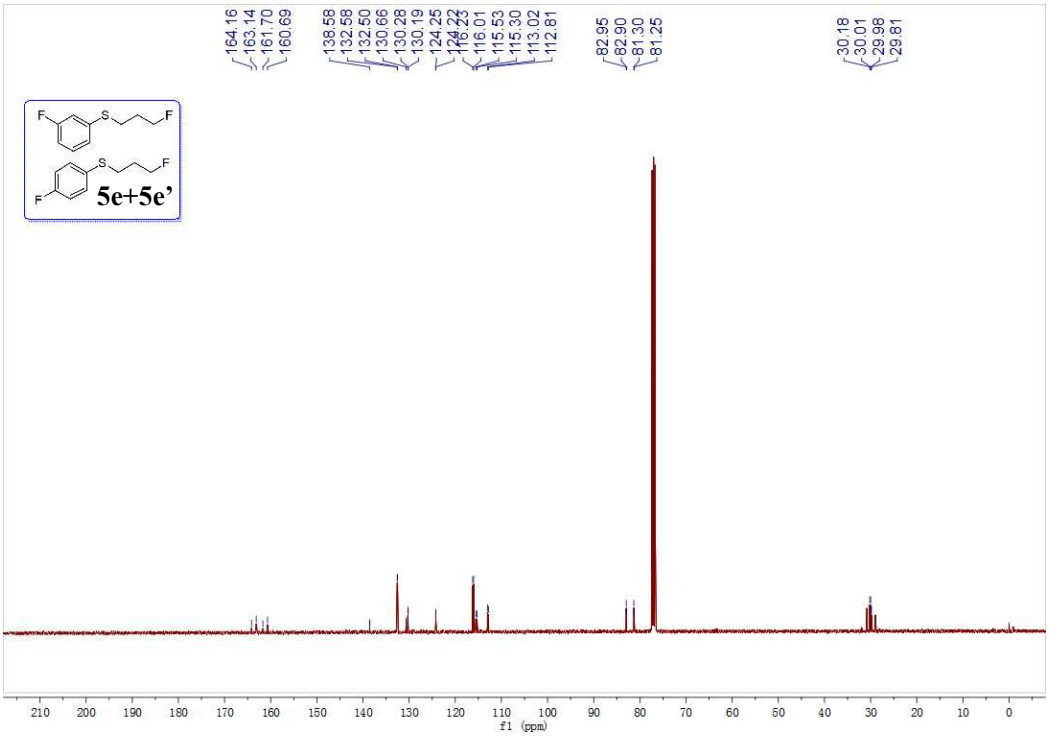
1.19
4.91
1.22
6.00
6.37
6.32
f1 (ppm)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130.66
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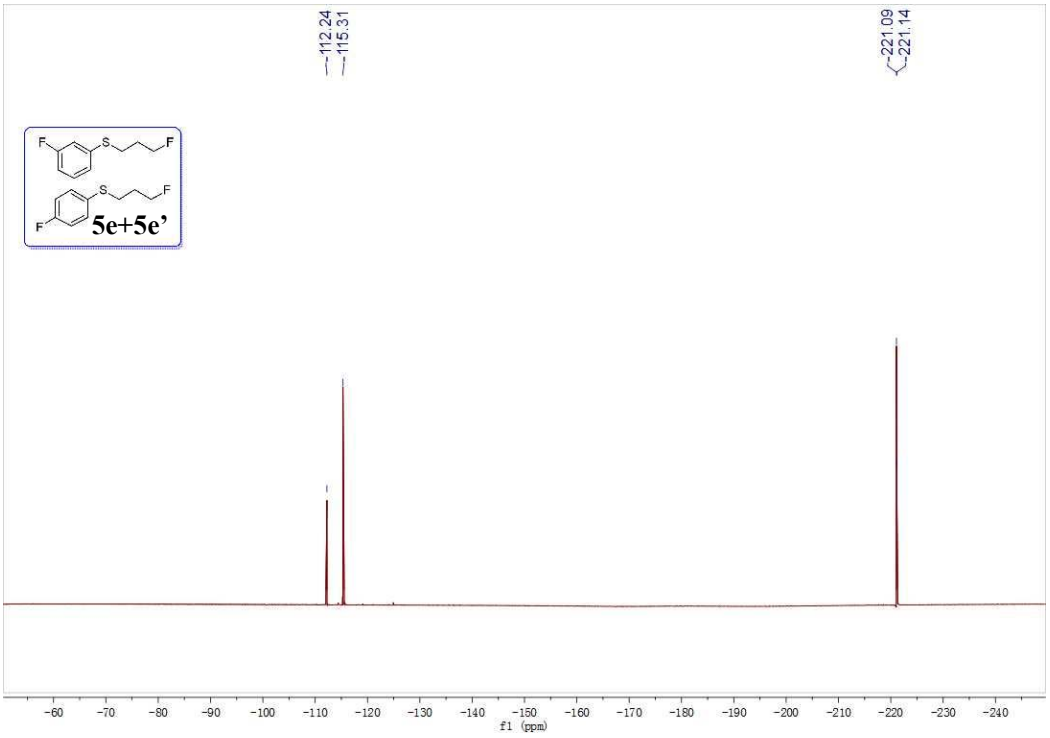
130.19
124.25
116.23
116.01
115.53
115.30
113.02
112.81
82.95
82.90
81.30
81.25
30.18
30.01
29.98
29.81
5e+5e'
f1 (ppm)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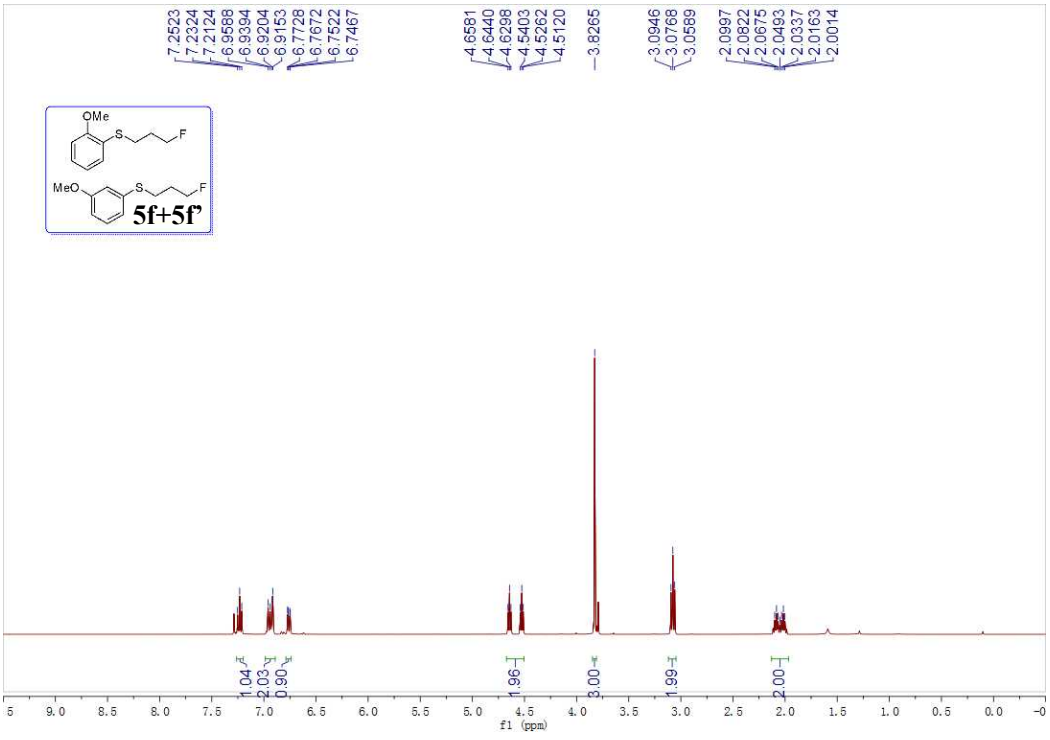
-221.09
-221.14
5e+5e'
f1 (ppm)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6.9204
6.9153
6.7728
6.7672
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4.6581
4.6440
4.6298
4.5403
4.5262
4.5120
3.8265
3.0946
3.0768
3.0589
2.0997
2.0822
2.0675
2.0493
2.0337
2.0163
2.0014
OMe
MeO
5f+5f'
1.04
2.03
0.90
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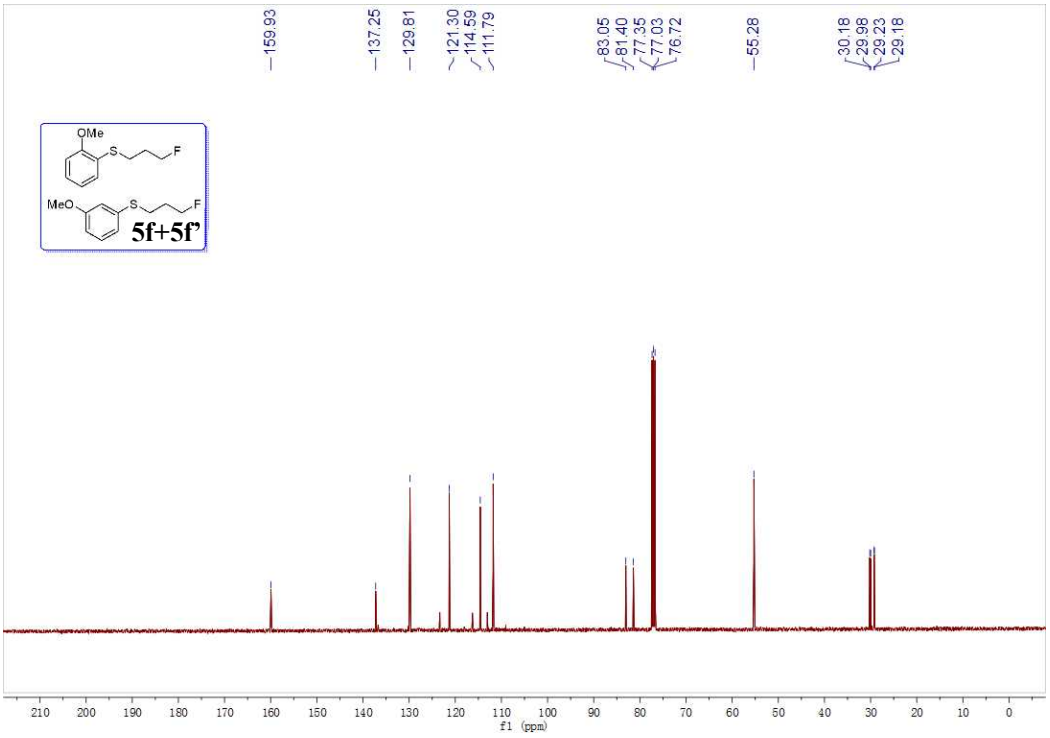
3.00
1.99
2.00
f1 (ppm)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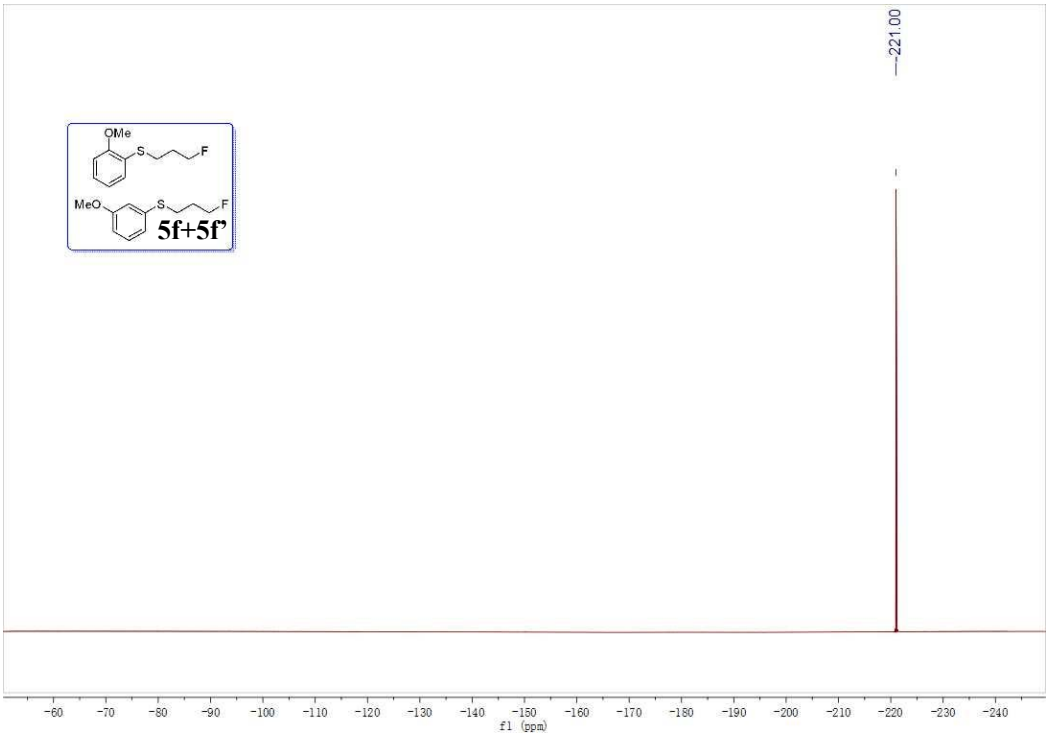
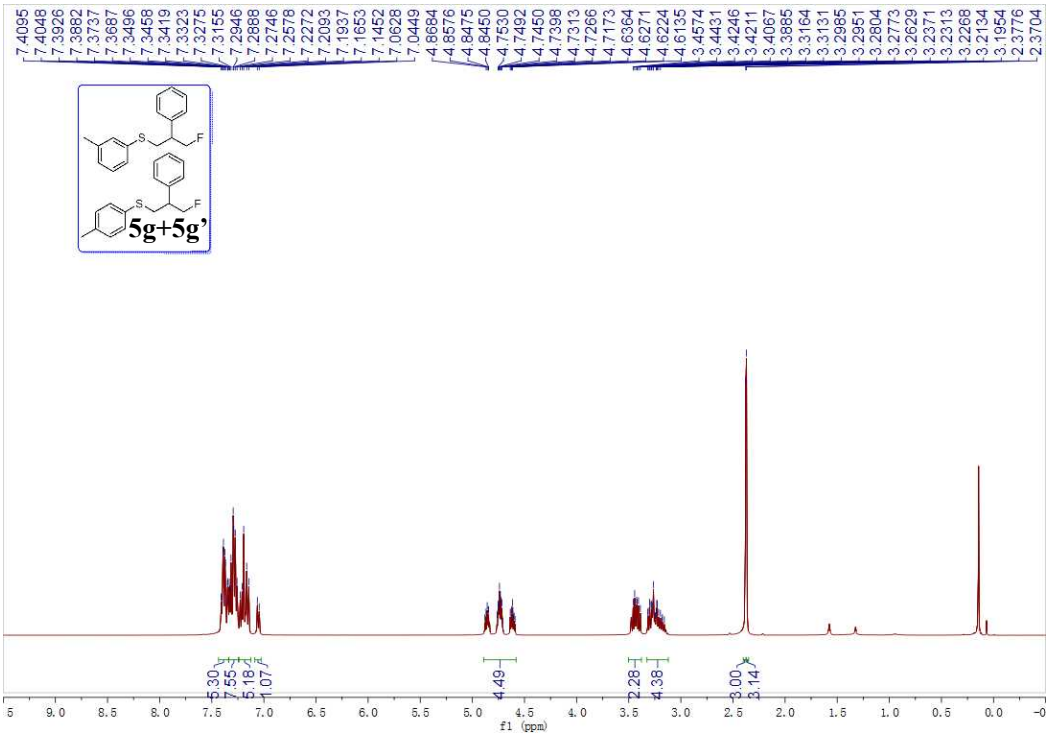
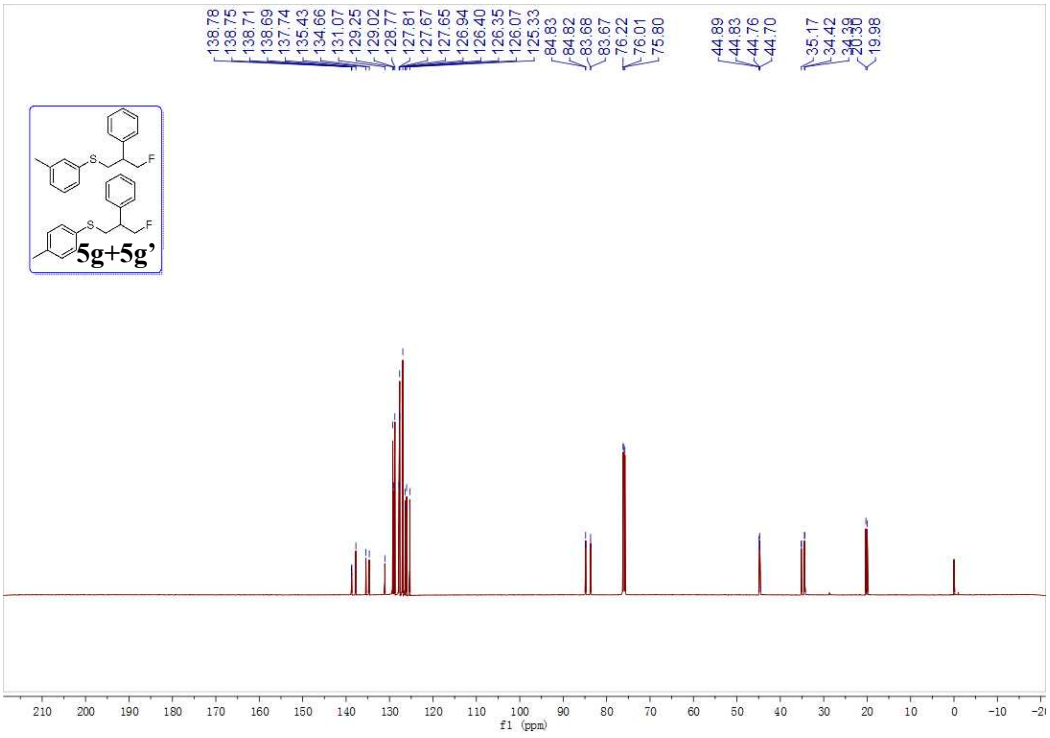
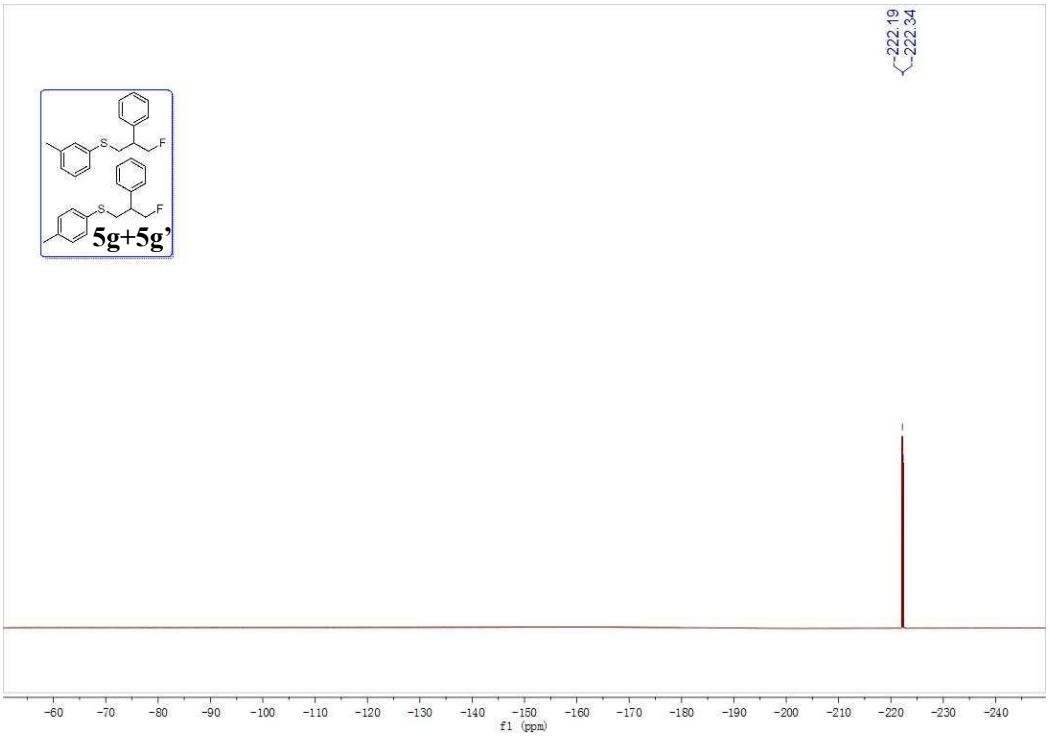
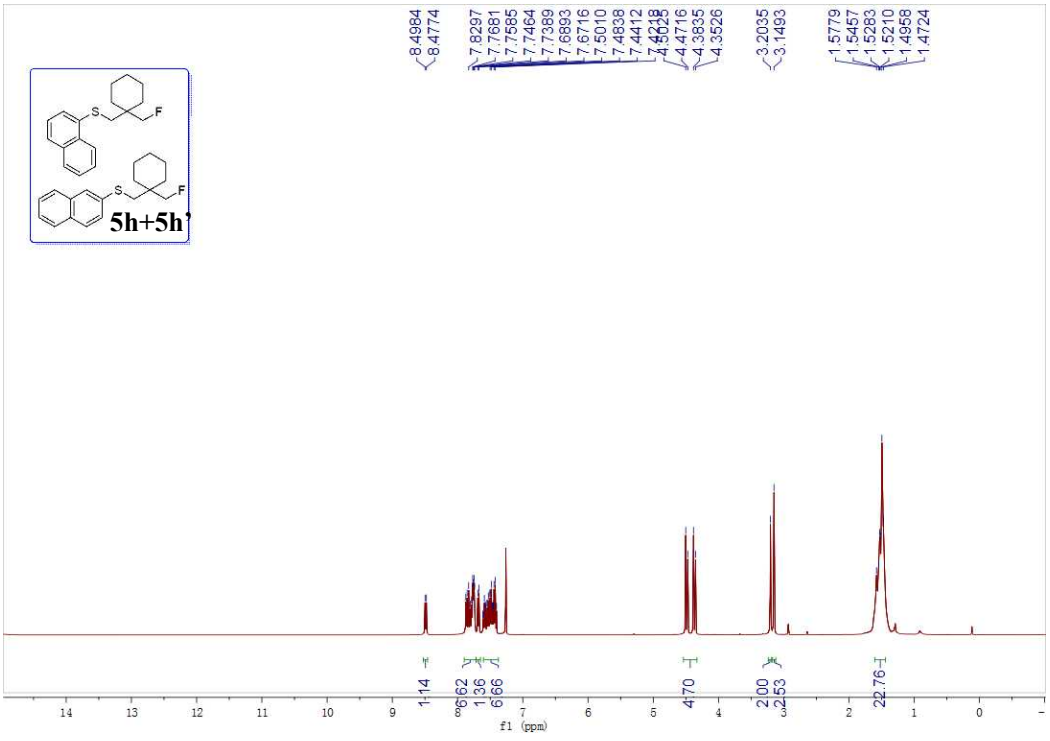
114.59
111.79
83.05
81.40
77.35
77.03
76.72
55.28
30.18
29.98
29.23
29.18
OMe
S
F
MeO
5f+5f'
f1 (ppm)


-221.00
OMe
S
F
MeO
5f+5f'
f1 (ppm)


5g+5g'
f1 (ppm)


5g+5g'
f1 (ppm)


222.19
222.34
5g+5g'
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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7.6716
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7.4412
4.4716
4.3835
4.3526
3.2035
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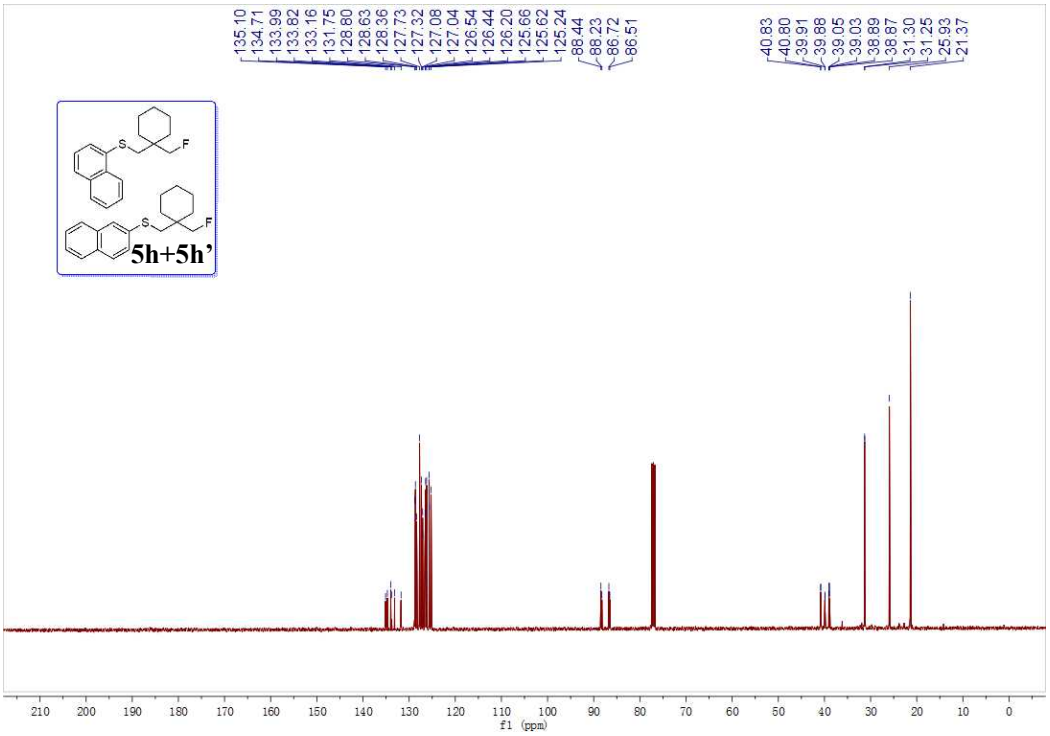
1.5779
1.5457
1.5283
1.5210
1.4958
1.4724
1.14
6.62
1.36
6.66
4.70
2.00
2.53
22.76
5h+5h'
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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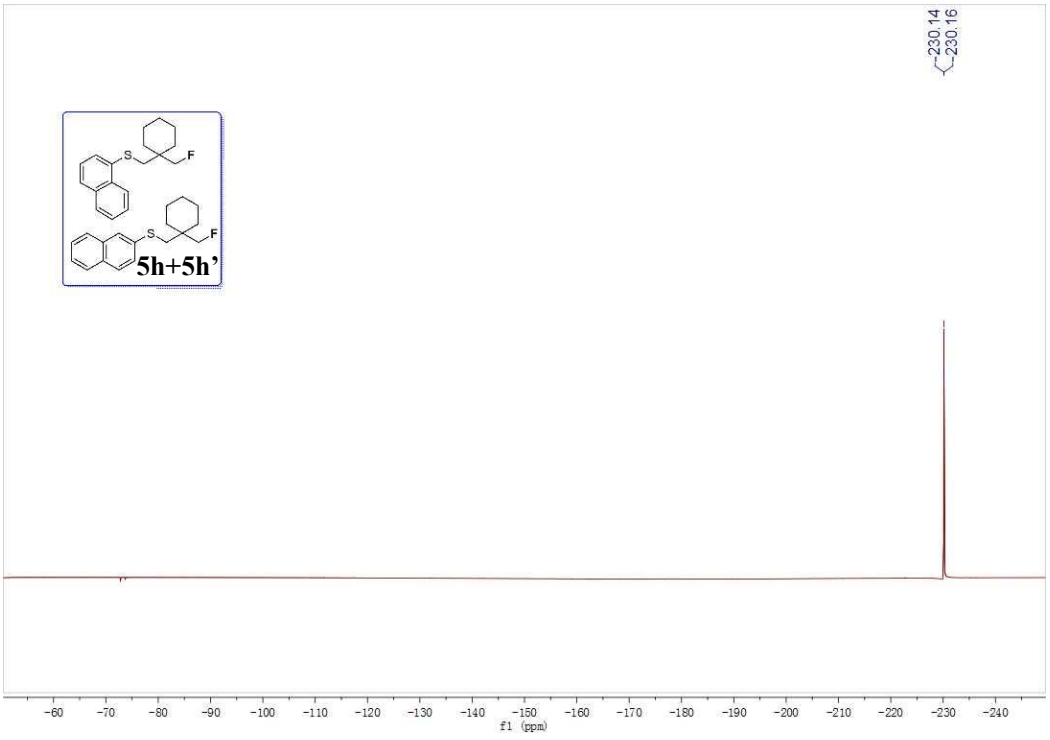
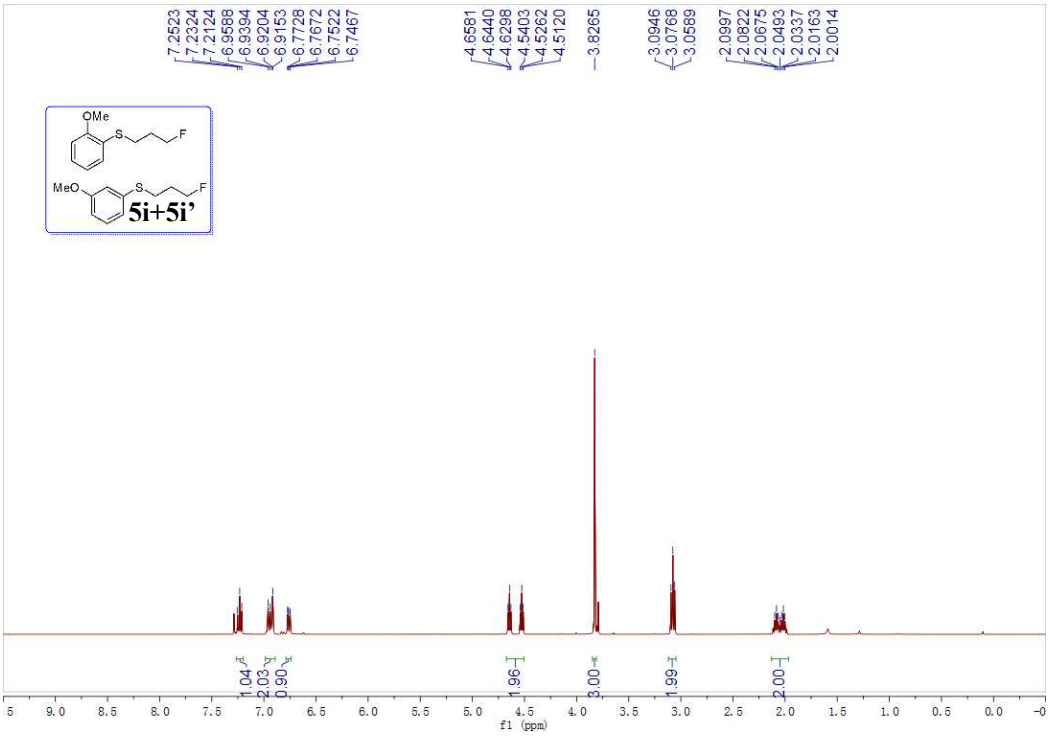
127.08
127.04
126.54
126.44
126.20
125.66
125.62
125.24
88.44
88.23
86.72
86.51
40.83
40.80
39.91
39.88
39.05
39.03
38.89
38.87
31.30
31.25
25.93
21.37
5h+5h'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


230.14
230.16
5h+5h'
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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6.7728
6.7672
6.7522
6.7467
4.6581
4.6440
4.6298
4.5403
4.5262
4.5120
3.8265
3.0946
3.0768
3.0589
2.0997
2.0822
2.0675
2.0493
2.0337
2.0163
2.0014
OMe
S
F
MeO
5i+5i'
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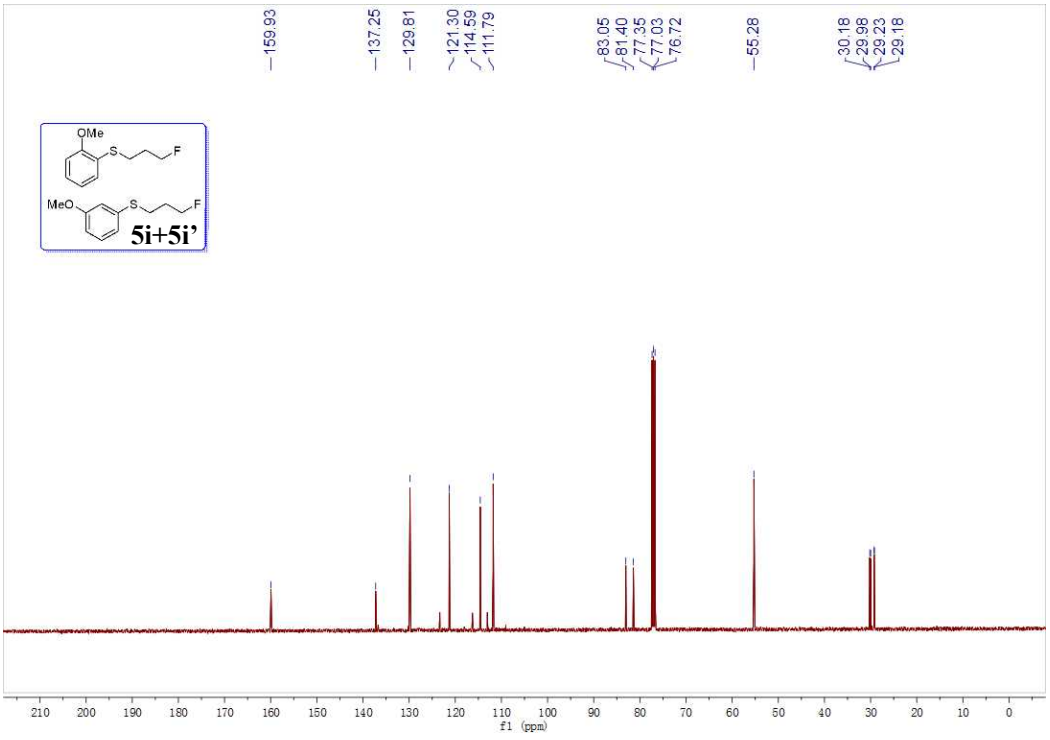
2.03
0.90
1.96
3.00
1.99
2.00
f1 (ppm)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77.35
77.03
76.72
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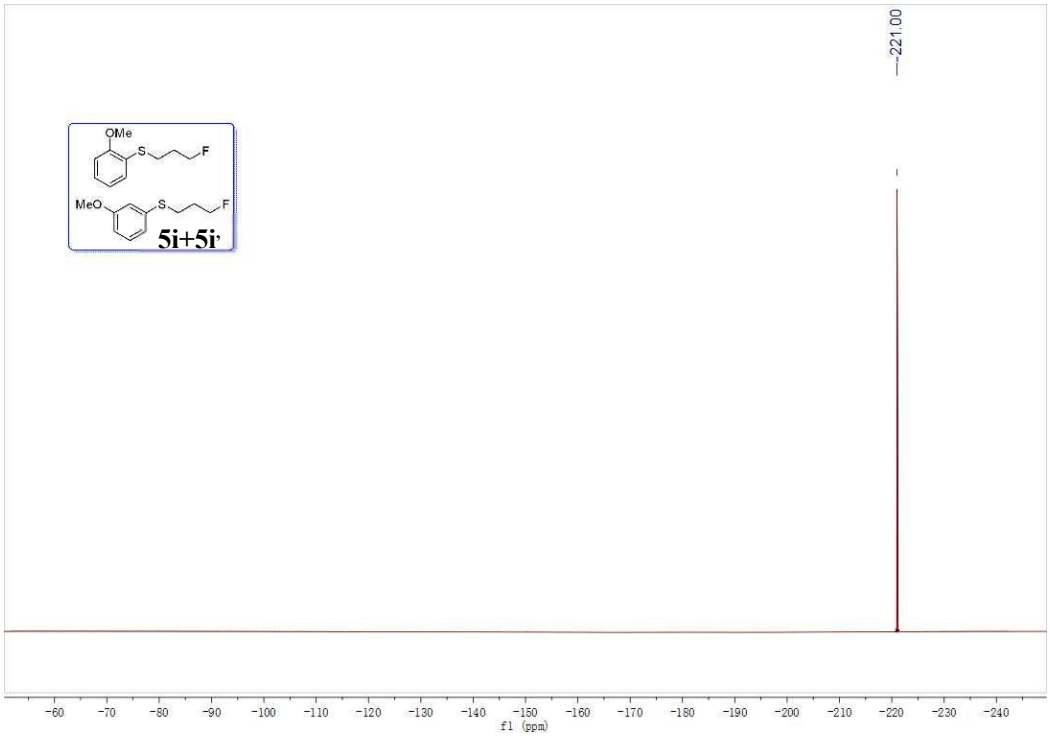
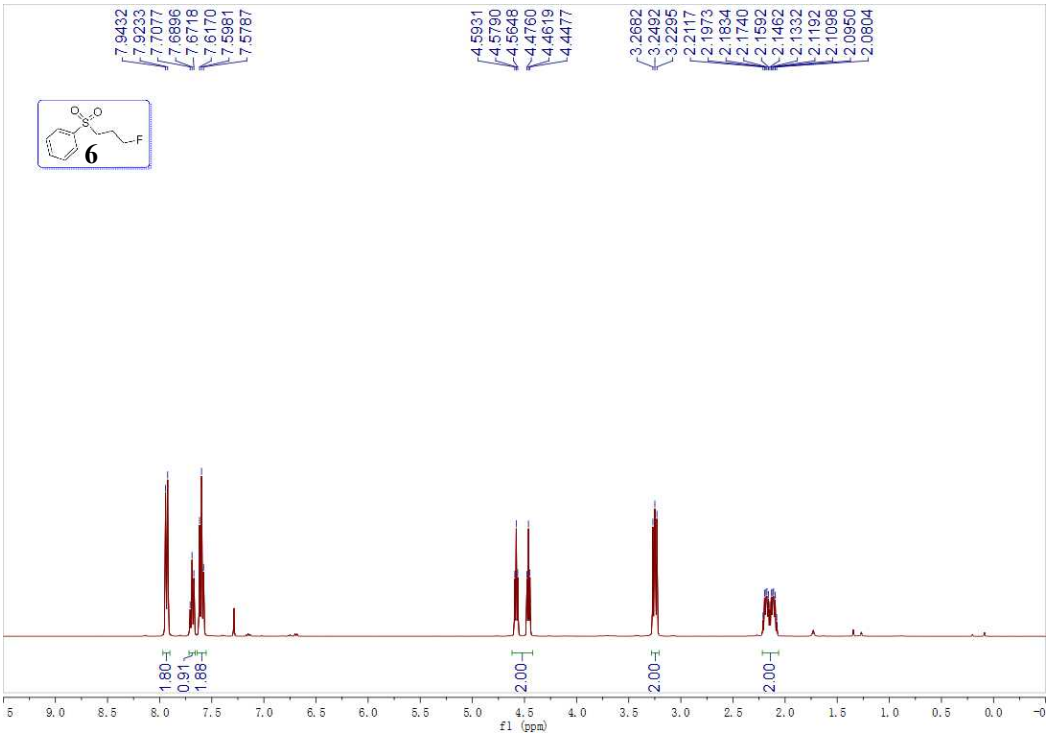
30.18
29.98
29.23
29.18
OMe
S
F
MeO
5i+5i'
f1 (ppm)


OMe
S
F
MeO
S
F
5i+5i'
-221.00
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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4.4477
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3.2492
3.2295
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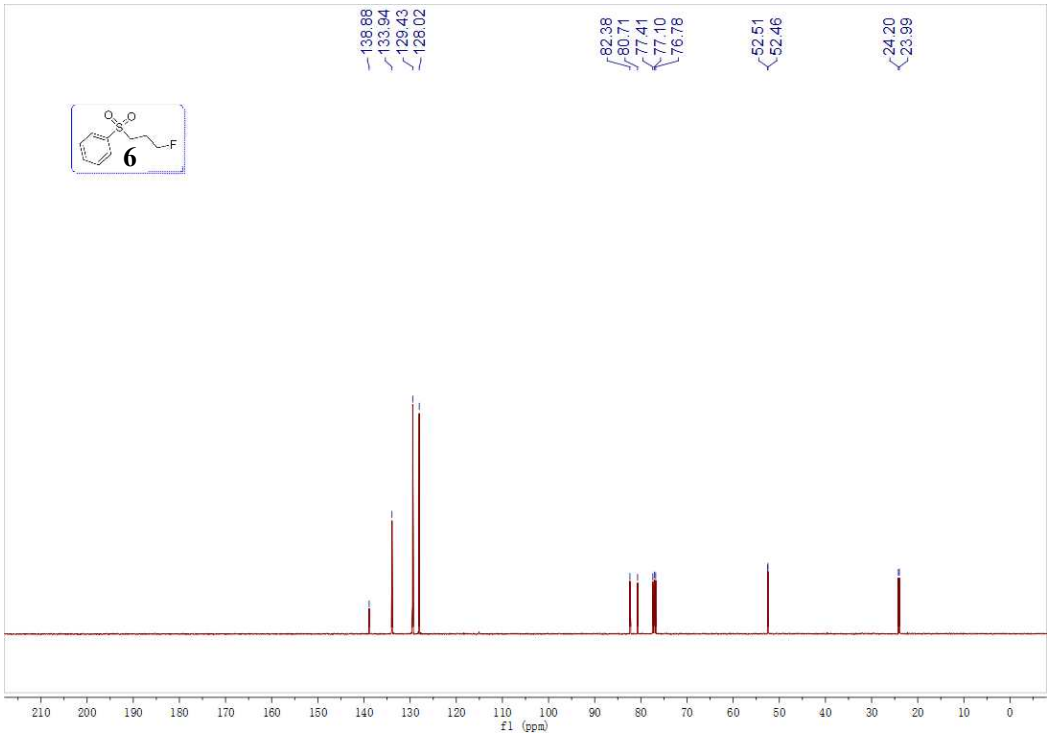
2.1592
2.1462
2.1332
2.1192
2.1098
2.0950
2.0804
O
S
O
F
6
1.80
0.91
1.88
2.00
2.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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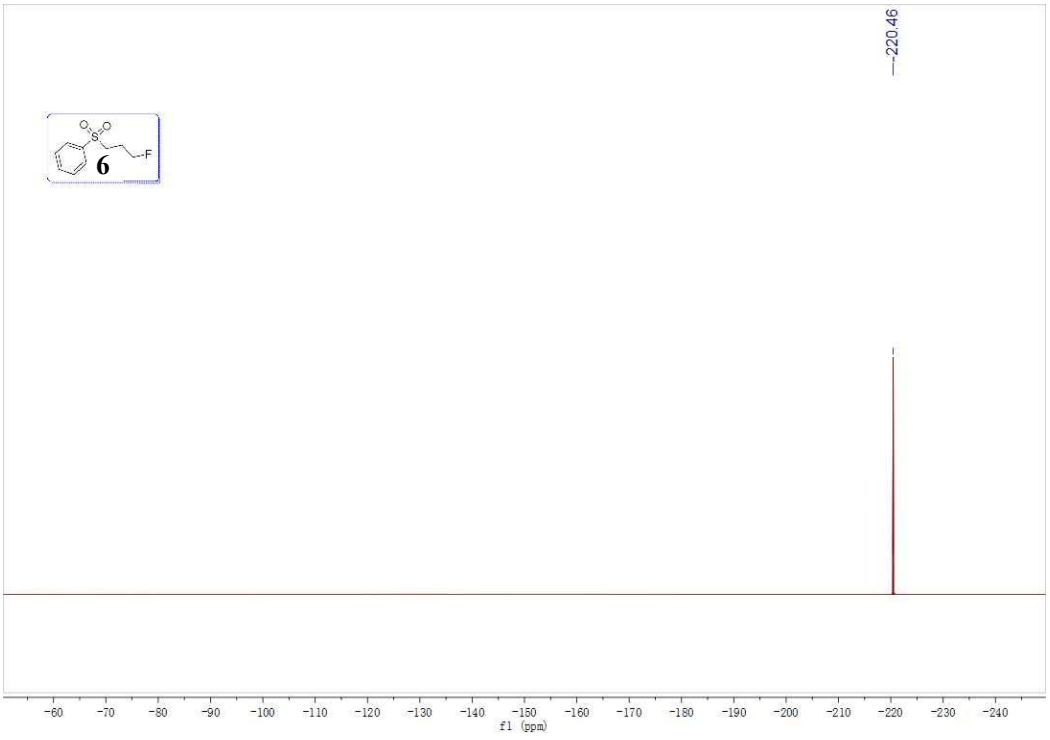
f1 (ppm)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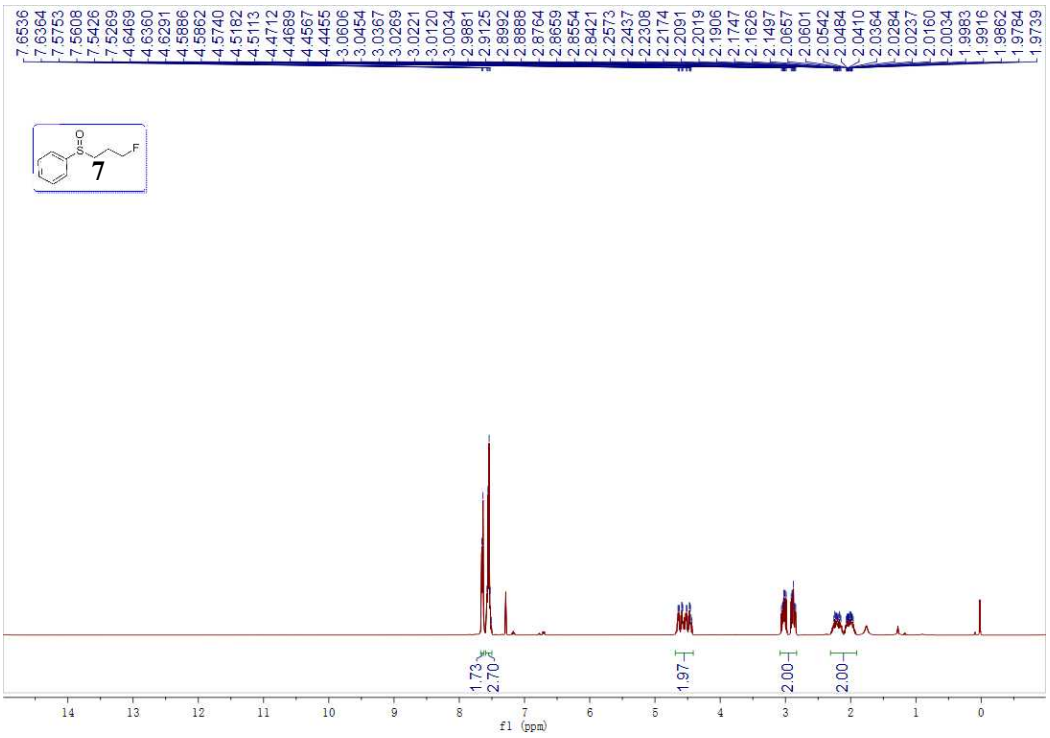
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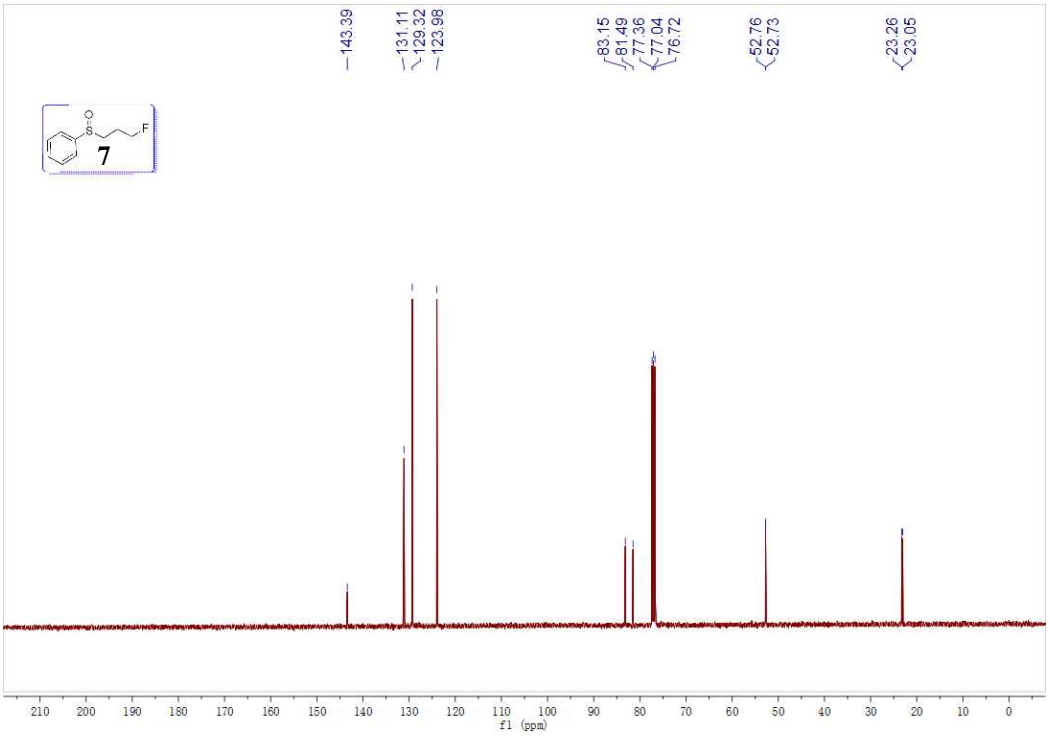
2.00
f1 (ppm)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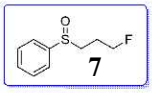
52.73
23.26
23.05
7
f1 (ppm)


7

-218.38
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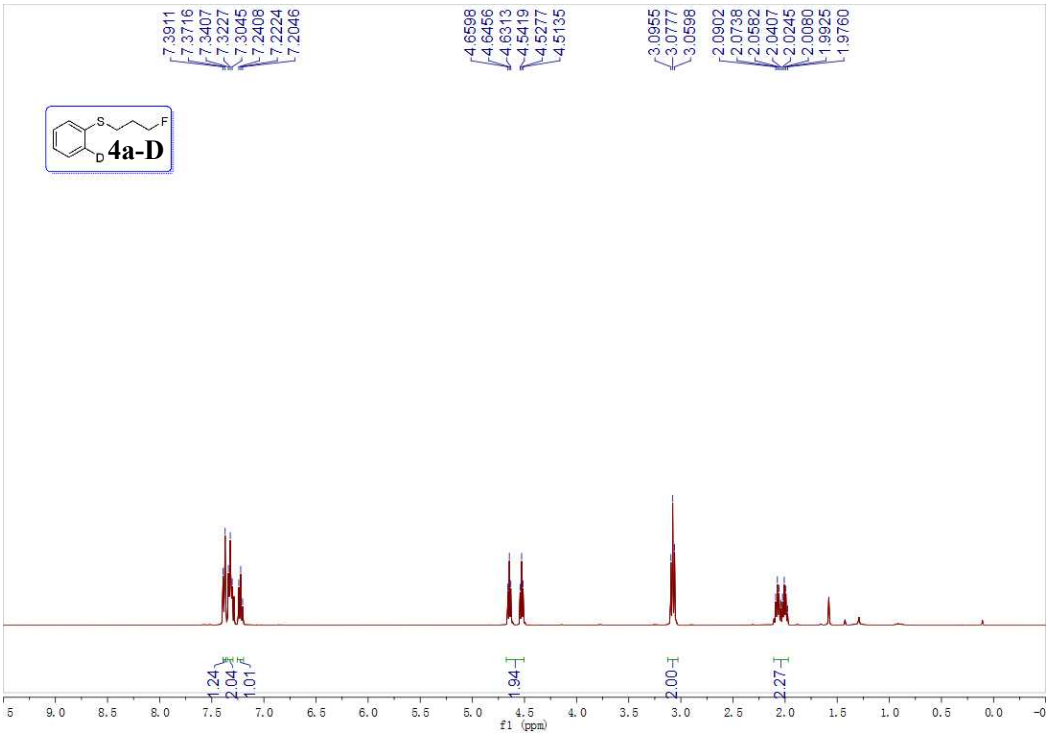
f1 (ppm)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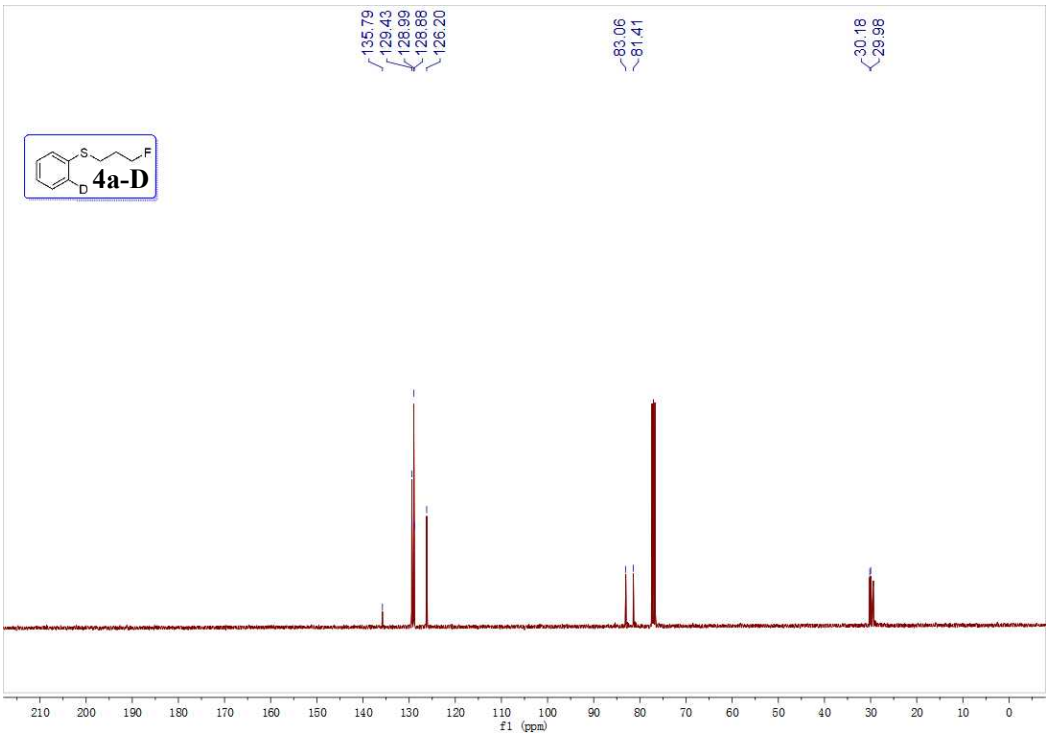
1.9925
1.9760
4a-D
1.24
2.04
1.01
1.94
2.00
2.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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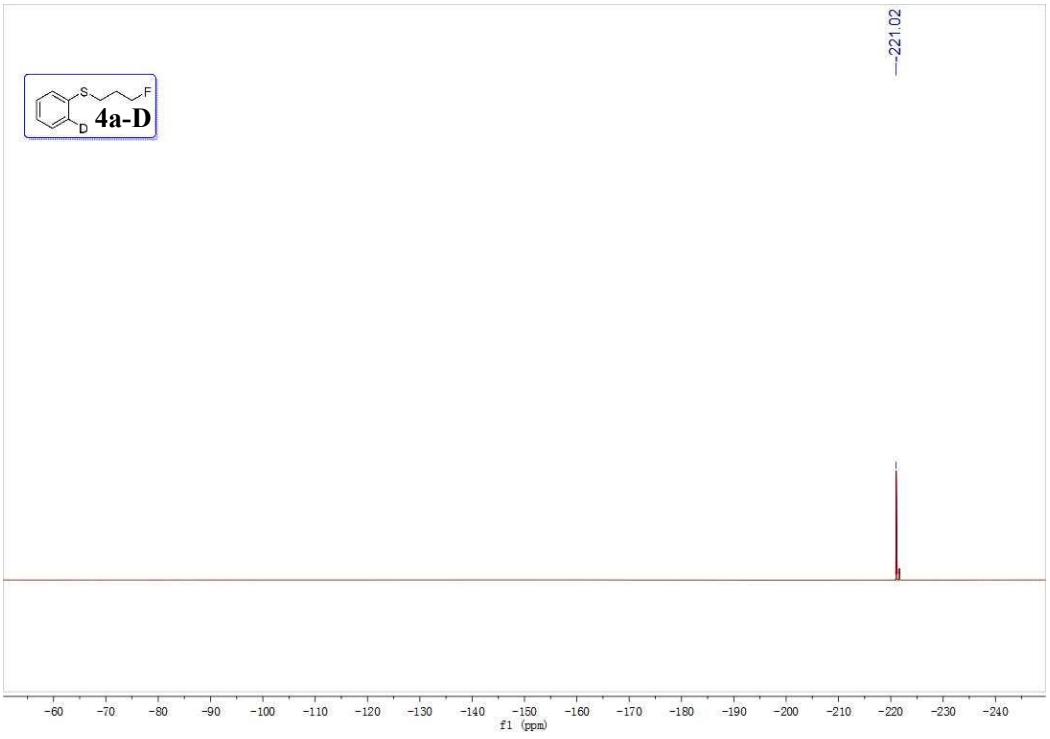
4a-D
f1 (ppm)


221.02
4a-D
f1 (ppm)

Reference：

[1]. (a) X.-j. Li, Y. Sun, X. Huang, L. Zhang, L.-C Kong and B. Peng, *Org. lett.*, 2017, **19**, 838; (b) Ueta Y., Mikami K. and Ito S., *Angew. Chem., Int. Ed.*, 2016, **128(26)**: 7651-7655.

[2]. T.-Y. Zheng, J.-J. Tan, R. Fan, S.-S. Su, B.-B Liu, C. Tan and K. Xu, *Chem. Commun*., 2018, **54**, 1303.