Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of α-Trifluoromethyl Sulfides through Fluorosulfuration of gem-Difluoroalkenes

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CONTENT:

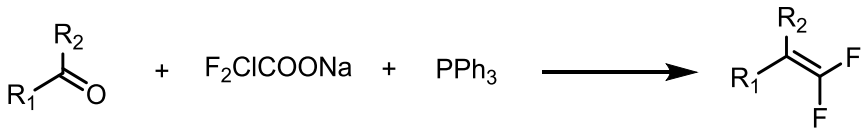
1. General Information

All the reagents and solvents were purchased from commercial sources and used without further purification. All reactions were monitored by using TLC. Column chromatography was performed with silica gel (100-200 mesh) as the stationary phase. All NMR spectra were recorded on Bruker-400 MHz spectrometer and Bruker-500 MHz spectrometer. Chemical shifts are reported relative to the residual signals of tetramethylsilane in $CDCl_3$ ^1H and ^{13}C NMR spectroscopy. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). HRMS were measured on the Bruker-impact II and Agilent-Q-TOF6510 instruments.

2. Synthesis of the Starting Materials.

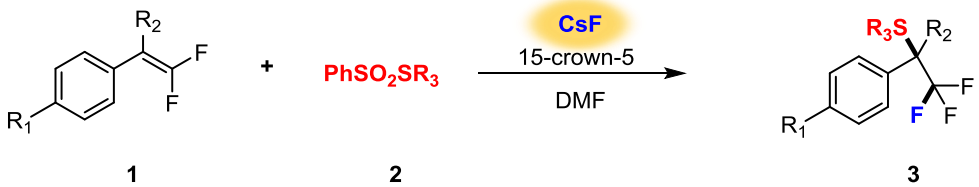
1) General Procedure for the Synthesis of gem-Difluoroalkenes.

The known gem-Difluoroalkenes were prepared according to the literatures, and all the spectra data are in agreement with the reports.[1]



2) Typical procedure for the preparation of benzenesulfonothioate.[2, 3, 4]

3. General Procedure for the α-Trifluoromethyl Sulfides.



1 2 3

Condition A:

General Procedure for the Synthesis of **3a-3c**, **3f**, **4a-4c**, **4e**.

A mixture of **1** (0.15 mmol), **2** (2 equiv), CsF (3 equiv) and 15-crown-5 (1 equiv) in DMF (1.5 mL) under N_2 atmosphere was stirred at 60 ^oC for 2 h. The reaction mixture was filtered on celite and evaporated under reduced pressure, and purified by

column chromatography to give the desired product.

General Procedure for the Synthesis of **3g-3r**, **4d**.

A mixture of **1** (0.15 mmol), **2** (2 equiv), CsF (3 equiv) and 15-crown-5 (1 equiv) in DMF (1.5 mL) under N_2 atmosphere was stirred at 60 ^oC for 4h. The reaction mixture was filtered on celite and evaporated under reduced pressure, and purified by column chromatography to give the desired product **.**

General Procedure for the Synthesis of **3d-3e**, **4f-4h**.

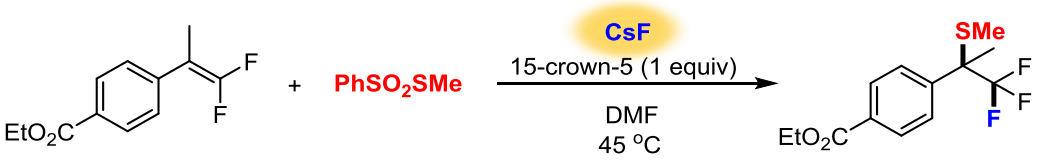
A mixture of **1** (0.15 mmol), **2** (4 equiv), CsF (4 equiv) and 15-crown-5 (1 equiv) in DMF (1.5 mL) under N_2 atmosphere was stirred at 45 ^oC. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered on celite and evaporated under reduced pressure, and purified by column chromatography to give the desired product.

Condition B:

General Procedure for the Synthesis of **3a-3c**, **4a-4c**.

A mixture of **1** (0.15 mmol), **2** (2 equiv), and CsF (2 equiv) in DMF (1.5 mL) under N_2 atmosphere was stirred at 50 ^oC for 10 h. The reaction mixture was filtered on celite and evaporated under reduced pressure, and purified by column chromatography to give the desired product.

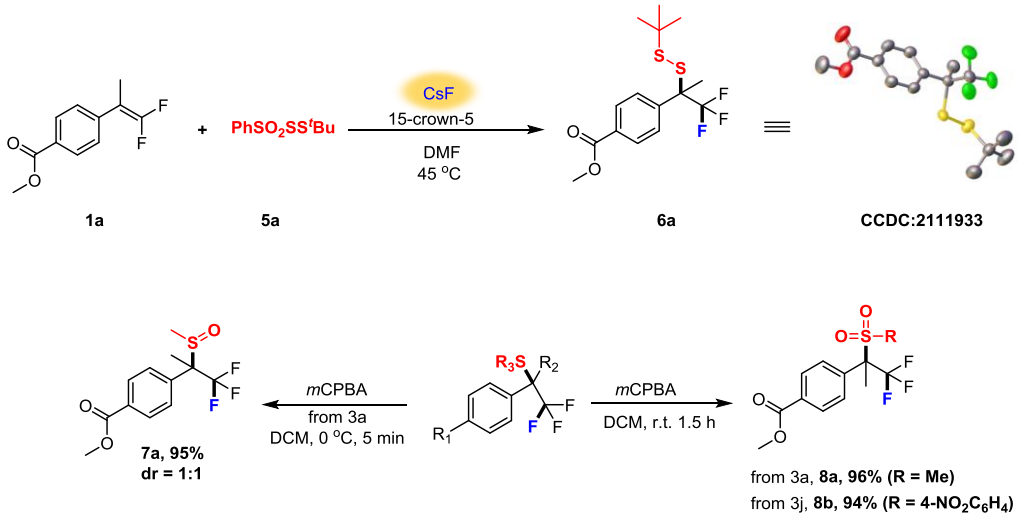
4. Gram-scale Reactions.



1b (3.5 mmol) **2a (4 equiv)** **4a, 75%**

A mixture of **1a** (3.5 mmol), **2a** (4 equiv), CsF (4 equiv) and 15-crown-5 (1 equiv) in DMF (30 mL) under N_2 atmosphere was stirred at 45 ^oC. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered on celite and evaporated under reduced pressure, and purified by column chromatography to give the desired product **4a** (0.7680 g, Yield = 75%, pet. ether/EtOAc = 30/1).

5. Synthetic application of α-Trifluoromethyl Sulfides.

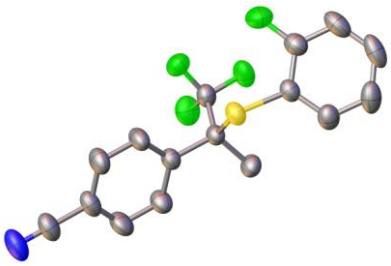


1) Synthesis of **6a**. A mixture of **1a** (0.15 mmol), **2** (4 equiv), and 15-crown-5 (1 equiv) in DMF (1.5 mL) under N_2 atmosphere was stirred at 45 °C. After the reaction was completed (determined by TLC analysis), the reaction mixture was filtered on celite and evaporated under reduced pressure, and purified by column chromatography to give the desired product **6a**.

2) Synthesis of **7a**. To an oven-dried 25 mL flask was added **3** (0.1 mmol), m-CPBA (1 equiv), DCM (1.0 mL). The reaction was allowed to stir at 0 °C under air for 5 min. Then the reaction was quenched by saturated $NaHCO_3$ solution (10 mL), extracted by DCM (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1) to afford the product .

3) Synthesis of **8a** and **8b**. To an oven-dried 25 mL flask was added **3** (0.1 mmol), m-CPBA (2 equiv), DCM (1.0 mL). The reaction was allowed to stir at r.t. under air for 1.5 h. Then the reaction was quenched by saturated $NaHCO_3$ solution (10 mL), extracted by DCM (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) to afford the product.

6. X-ray Crystallography Data



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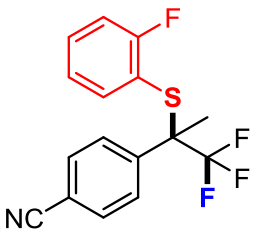
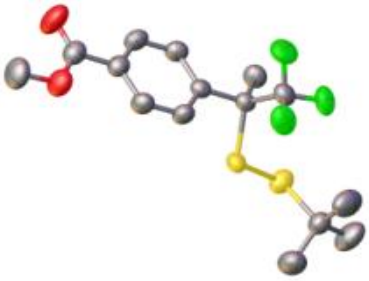


4d

CCDC 2111934 (**4d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



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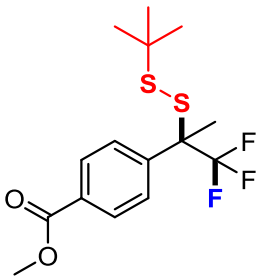
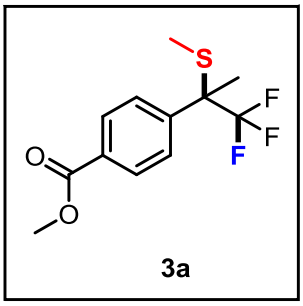


6a

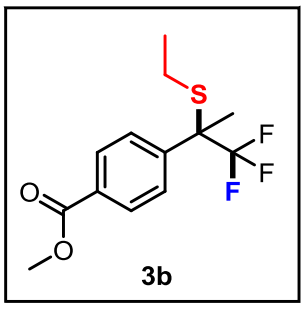
CCDC 2111933 (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

7. Characterization Data



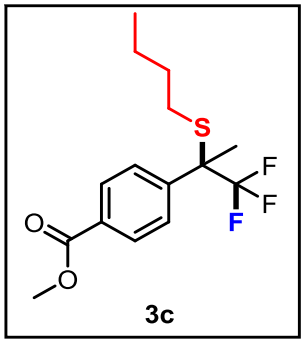
3a

Yield: 90% (colorless oil, 37.5 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 1.94 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.0, 129.8, 129.6, 128.0 (d, *J* = 2.0 Hz), 127.5 (q, *J* = 284.8 Hz), 54.5 (q, *J* = 26.3 Hz), 52.2, 22.2 (d, *J* = 1.0 Hz), 13.6 (d, *J* = 1.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.15. IR (neat)：2952, 1724, 1612, 1436, 1276, 964, 862, 757 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_2S$ $[M+H]^+$ 279.0661, found 279.0661.



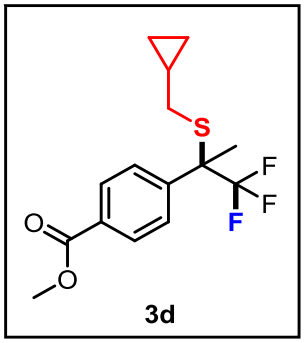
3b

Yield: 95% (colorless oil, 41.6 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 3.93 (s, 3H), 2.56 - 2.44 (m, 1H), 2.38 - 2.25 (m, 1H), 1.88 (s, 3H), 1.10 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.6, 129.7, 129.6, 128.7, 128.0 (q, *J* = 283.8 Hz), 127.9 (d, *J* = 1.0 Hz), 55.1 (q, *J* = 27.3 Hz), 52.2, 24.5, 22.7, 13.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.35. IR (neat)：2952, 1724, 1612, 1438, 1274, 968, 859, 757 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3O_2S$ $[M+H]^+$ 293.0818, found 293.0811.



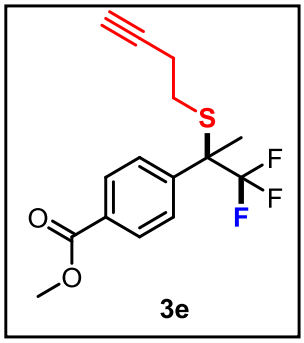
3c

Yield: 85% (colorless oil, 40.8 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 3H), 2.49 - 2.44 (m, 1H), 2.30 - 2.25 (m, 1H), 1.88 (s, 3H), 1.46 - 1.38 (m, 2H), 1.34 - 1.28 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.6, 129.7, 129.5, 127.9 (d, *J* = 1.3 Hz), 127.3 (q, *J* = 283.5 Hz), 55.0 (q, *J* = 27.7 Hz), 52.2, 30.6, 30.0, 22.8 (d, *J* = 1.3 Hz), 21.9, 13.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.28. IR (neat)：2953, 1730, 1612, 1459, 1276, 970, 859, 762 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{15}H_{19}F_3O_2S$ $[M+H]^+$ 321.1131, found 321.1114.



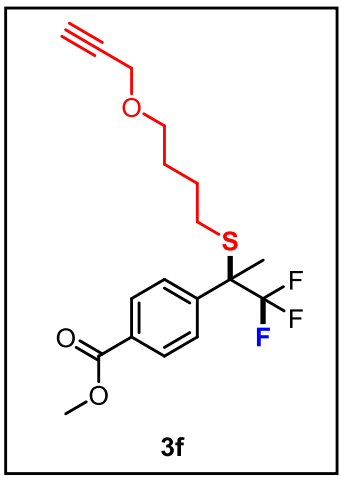
3d

Yield: 72% (colorless oil, 24.8 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 3H), 2.41 (q, *J* = 2.5 Hz, 1H), 2.19 (q, *J* = 2.5 Hz, 1H), 1.87 (s, 3H), 0.80 - 0.75 (m, 1H), 0.50 (d, *J* = 2.5 Hz, 2H), 0.10 (q, *J* = 1.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.6, 129.7, 129.6, 127.9 (d, *J* = 1.3 Hz), 127.8 (q, *J* = 173.9 Hz), 55.0 (q, *J* = 26.5 Hz), 52.2, 36.4, 22.9, 9.7, 5.6 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.26. IR (neat)：2960, 1725, 1612, 1438, 1276, 967, 860, 757 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{15}H_{17}F_3O_2S$ $[M+H]^+$ 319.0974, found 319.0967.



3e

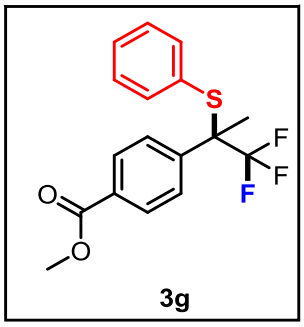
Yield: 68% (colorless oil, 21.1 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 3H), 2.67 - 2.62 (m, 1H), 2.50 - 2.44 (m, 1H), 2.30 (td, *J* = 7.4, 2.6 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 142.2, 129.9, 129.7, 127.9 (d, *J* = 2.5 Hz), 127.2 (d, *J* = 283.5 Hz), 81.7, 69.8, 69.8, 55.4 (q, *J* = 26.5 Hz), 52.3, 29.3, 22.3 (d, *J* = 2.5 Hz), 18.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.18. IR (neat)：3298, 2951, 1723, 1612, 1436, 1277, 966, 862, 767 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{15}H_{15}F_3O_2S$ $[M+H]^+$ 317.0818, found 317.0819.



3f

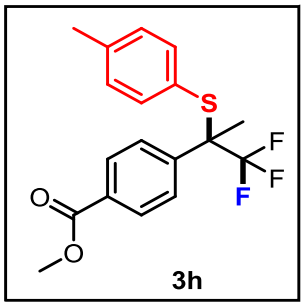
Yield: 88% (colorless oil, 49.4 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 4.07 (d, *J* = 2.4 Hz, 2H), 3.93 (s, 3H), 3.43 (t, *J* = 6.0 Hz, 2H), 2.52 - 2.47 (m, 1H), 2.41 (t, *J* = 2.3 Hz, 1H), 2.33 - 2.28 (m, 1H), 1.88 (s, 3H), 1.61 - 1.48 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.5, 129.8, 129.6, 127.9 (d, *J* = 2.5 Hz), 127.3 (d, *J* = 283.5 Hz), 79.8, 74.2, 69.2, 58.0, 55.1 (q, *J* = 26.5 Hz), 52.2, 38.7, 30.1, 28.5, 25.2, 22.8 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.28. IR (neat)：3296, 2946, 2856, 1723, 1612, 1439,

1276, 865, 720 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{18}H_{21}F_3O_3S$ $[M+H]^+$ 375.1236, found 375.1247.



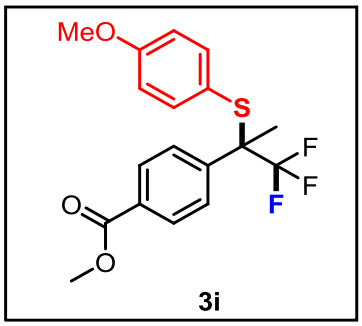
3g

Yield: 93% (colorless oil, 47.4 mg, pet. ether/EtOAc = 15/1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.39 - 7.30 (m, 3H), 7.26 - 7.20 (m, 2H), 3.92 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.3, 137.6, 130.0, 129.9, 129.4, 129.4, 128.7, 128.2 (d, *J* = 1.0 Hz), 126.8 (q, *J* = 284.8 Hz), 57.3 (q, *J* = 26.3 Hz), 52.2, 21.4 (d, *J* = 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.14. IR (neat)：2951, 1723, 1437, 1279, 855, 752 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{15}F_3O_2S$ $[M+H]^+$ 341.0818, found 341.0814.



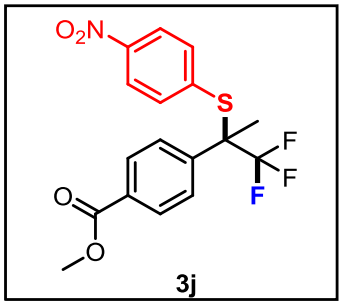
3h

Yield: 96% (colorless oil, 51.0 mg, pet. ether/EtOAc = 15/1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 2.31 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 142.4, 140.3, 137.5, 129.9, 129.5, 129.4, 128.2 (d, *J* = 1.3 Hz), 126.9 (q, *J* = 284.8 Hz), 125.9, 57.1 (q, *J* = 26.5 Hz), 52.2, 21.3 (d, *J* = 1.3 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -70.15. IR (neat)：2924, 1724, 1459, 1281, 811,717 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{18}H_{17}F_3O_2S$ $[M+H]^+$ 355.0974, found 355.0965.



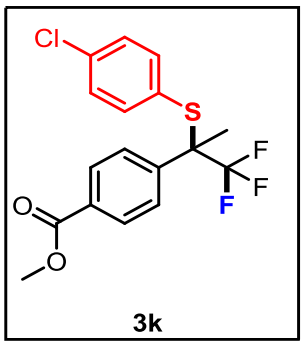
3i

Yield: 98% (white solid, 54.4 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 3.93 (s, 3H), 3.78 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 161.1, 142.3, 139.2, 129.9, 129.4, 128.1 (d, *J* = 2.5 Hz), 126.9 (q, *J* = 283.5 Hz), 120.1, 114.2, 57.1 (q, *J* = 26.5 Hz), 55.3, 52.2, 21.2 (d, *J* = 2.5 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -70.15. IR (neat)：2924, 1724, 1459, 1281, 811, 763 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{18}H_{17}F_3O_3S$ $[M+H]^+$ 371.0923, found 371.0924.



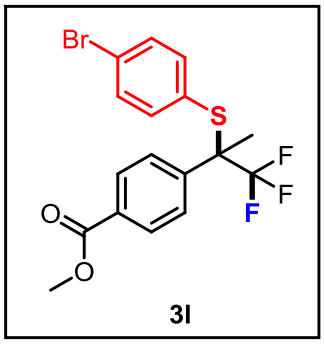
3j

Yield: 95% (colorless oil, 56.6 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 - 7.95 (m, 4H), 7.61 (d, *J* = 1.2 Hz, 2H), 7.36 (d, *J* = 2.5 Hz, 2H), 3.87 (s, 3H), 1.81 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 147.4, 140.3, 137.2, 136.1, 129.4, 128.7, 127.1, 125.3 (q, *J* = 283.5 Hz), 122.5, 57.4 (d, *J* = 26.5 Hz), 51.3, 21.1 (d, *J* = 1.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.87. IR (neat)：2953, 1723, 1608, 1527, 1348, 1279, 908, 873, 728 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_4S$ $[M+H]^+$ 386.0668, found 386.0650.



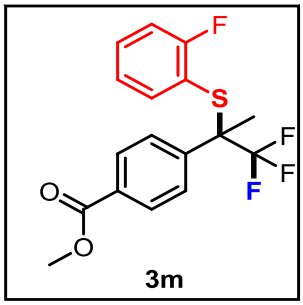
3k

Yield: 93% (colorless oil, 52.2 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.27 - 7.24 (m, 2H), 7.22 - 7.19 (m, 2H), 3.93 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 141.9, 138.7, 136.6, 130.1, 129.5, 129.0, 128.6 (q, *J* = 283.5 Hz), 128.1 (d, *J* = 2.5 Hz), 57.5 (q, *J* = 26.5 Hz), 52.3, 21.5 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.98. IR (neat)：2921, 1723, 1465, 1278, 819, 714 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}ClF_3O_2S$ $[M+H]^+$ 375.0428, found 375.0427.



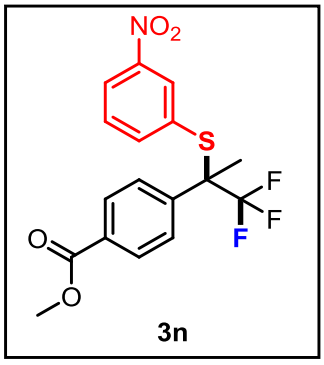
3l

Yield: 95% (white solid, 59.6 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.93 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 141.9, 138.9, 132.0, 130.1, 129.5, 128.5, 128.1 (d, *J* = 2.5 Hz), 126.4 (d, *J* = 283.5 Hz), 125.0, 57.4 (d, *J* = 26.5 Hz), 52.3, 21.5 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.99. IR (neat)：2919, 1725, 1464, 1280, 820, 715 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}BrF_3O_2S$ $[M+H]^+$ 418.9923, found 418.9909.



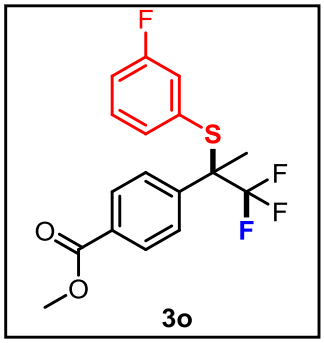
3m

Yield: 91% (colorless oil, 48.9 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.41 - 7.33 (m, 2H), 7.11 - 7.03 (m, 2H), 3.93 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 165.3, 163.3, 141.7, 140.0, 132.8 (d, *J* = 8.8 Hz), 128.0 (d, *J* = 2.5 Hz), 125.6, 124.3 (d, *J* = 3.8 Hz), 116.6 (d, *J* = 17.6 Hz), 116.1 (d, *J* = 24.0 Hz), 57.5 (d, *J* = 26.5 Hz), 52.3, 21.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.69 (d, *J* = 2.7 Hz), -103.36. IR (neat)：2952, 1723, 1438, 1278, 822, 715 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_4O_2S$ $[M+H]^+$ 359.0723, found 359.0714.



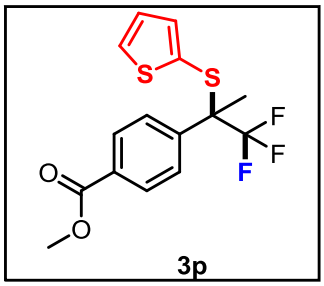
3n

Yield: 96% (colorless oil, 55.4 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 - 8.11 (m, 1H), 8.10 (t, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 2H), 7.55 (d, *J* = 2.5 Hz, 1H), 7.35 (t, *J* = 1.2 Hz, 1H), 3.87 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 146.9, 141.9, 140.1, 131.0, 130.7, 129.4, 128.7, 128.4, 126.9 (d, *J* = 1.3 Hz), 123.7, 57.1 (q, *J* = 25.2 Hz), 51.3, 20.8 (d, *J* = 1.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.71. IR (neat)：2958, 1723, 1609, 1527, 1348, 1275, 905, 804, 738 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_4S$ $[M+H]^+$ 386.0668, found 386.0652.



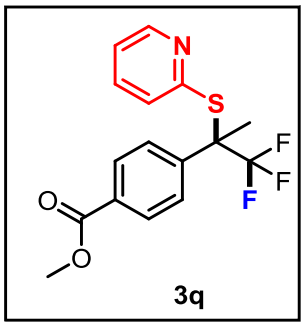
3o

Yield: 96% (colorless oil, 51.6 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.20 (dd, *J* = 7.8, 5.9 Hz, 1H), 7.12 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.08 - 7.05 (m, 1H), 3.93 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 163.0, 161.0, 141.8, 133.1 (d, *J* = 3.8 Hz), 131.3 (d, *J* = 7.6 Hz), 130.1, 129.8 (d, *J* = 7.6 Hz), 129.5, 128.1 (d, *J* = 8.3 Hz), 126.7 (d, *J* = 283.5 Hz), 124.0 (d, *J* = 21.4 Hz), 117.2 (d, *J* = 21.4 Hz), 57.6 (q, *J* = 26.5 Hz), 52.3, 21.5 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.12, -111.98. IR (neat)：2953, 1724, 1581, 1468, 1278, 1072, 967, 716 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_4O_2S$ $[M+H]^+$ 359.0723, found 359.0703.



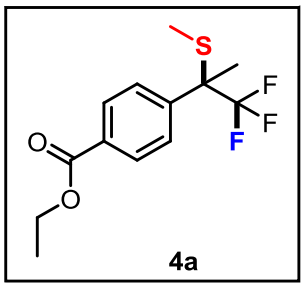
3p

Yield: 78% (colorless oil, 40.5 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 5.5, 1.3 Hz, 1H), 7.11 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.4, 3.6 Hz, 1H), 3.93 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 141.6, 139.0, 132.8, 130.1, 129.5, 128.5 (q, *J* = 284.8Hz), 128.3 (d, *J* = 2.5 Hz), 127.6, 127.5, 58.4 (q, *J* = 26.5 Hz), 52.3, 21.1 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.87. IR (neat)：2952, 1723, 1567, 1437, 1277, 756 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{15}H_{13}F_3O_2S_2$ $[M+H]^+$ 347.0382, found 347.0373.



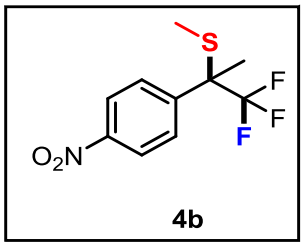
3q

Yield: 53% (colorless oil, 27.1 mg, pet. ether/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.48 (td, *J* = 7.7, 2.0 Hz, 1H), 7.29 - 7.22 (m, 1H), 7.11 - 7.08 (m, 1H), 3.91 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 153.8, 149.9, 141.9, 136.6, 129.9, 129.3, 129.0, 128.5, 127.5, 125.3, 122.6, 58.5 (q, *J* = 26.5 Hz), 52.2, 22.1 (d, *J* = 1.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -71.06. IR (neat)：2950, 1721, 1560, 1450, 1152, 760 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{16}H_{14}F_3NO_2S$ $[M+H]^+$ 342.0770, found 342.0772.



4a

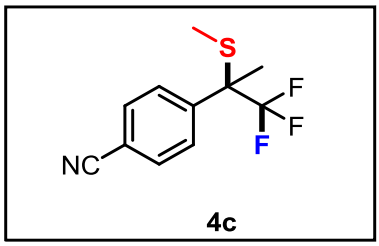
Yield: 89% (colorless oil, 39.0 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.94 (s, 3H), 1.87 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 141.9, 130.2, 129.6, 128.6, 127.9 (d, *J* = 2.5 Hz), 127.5 (q, *J* = 283.5 Hz), 61.1, 54.5 (d, *J* = 27.8 Hz), 22.2 (d, *J* = 1.3 Hz), 14.3, 13.6 (d, *J* = 1.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.16. IR (neat)：2928, 1719, 1612, 1459, 1272, 963, 862, 716 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3O_2S$ $[M+H]^+$ 293.0818, found 293.0801.



4b

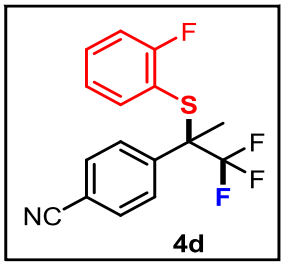
Yield: 88% (colorless oil, 35.0 mg, pet. ether/EtOAc = 30/1). ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.24 (d, *J* = 9.1 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 1.98 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 144.4, 129.1 (d, *J* = 2.5 Hz), 127.2 (q, *J* = 283.5 Hz), 123.5, 54.5 (q, *J* = 27.7 Hz), 29.7, 22.3 (d, *J* = 2.5 Hz), 13.7 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.07. IR (neat)：2925, 2855, 1603, 1524, 1460, 1349, 1260, 1157, 1076, 962, 861, 754 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{10}H_{10}F_3NO_2S$ $[M+H]^+$ 266.0457, found 266.0451.



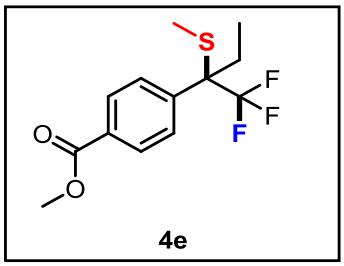
4c

Yield: 94% (colorless oil, 34.5 mg, pet. ether/EtOAc = 30/1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 1.96 (d, *J* = 1.2 Hz, 3H), 1.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 132.2, 128.8 (d, *J* = 2.5 Hz), 127.2 (d, *J* = 283.5 Hz), 118.2, 112.2, 54.5 (q, *J* = 27.8 Hz), 22.1 (d, *J* = 1.3 Hz), 13.6 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.10. IR (neat)：2918, 2181, 1728, 1459, 1157, 971, 857, 755 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{11}H_{10}F_3NS$ $[M+H]^+$ 246.0559, found 246.0550.



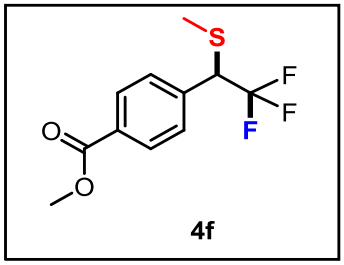
4d

Yield: 96% (colorless oil, 33.8 mg, pet. ether/EtOAc = 15/1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.46 - 7.35 (m, 2H), 7.12 - 7.02 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 163.3, 142.0, 140.0, 133.1 (d, *J* = 7.6 Hz), 132.0, 128.8 (d, *J* = 1.3 Hz), 126.5 (q, *J* = 284.8 Hz), 124.5 (d, *J* = 3.8 Hz), 118.2, 116.2 (d, *J* = 24.0 Hz), 112.5, 57.5 (q, *J* = 26.5 Hz), 21.0 (d, *J* = 1.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.61 (d, *J* = 3.0 Hz), -103.21 (q, *J* = 2.8 Hz). IR (neat)：3704, 2929, 2231, 1724, 1469, 1168, 956, 844, 691 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{16}H_{11}F_4NS$ $[M+H]^+$ 326.0621, found 326.0611.



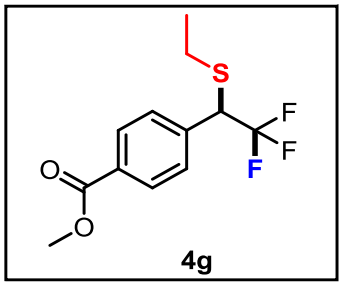
4e

Yield: 72% (colorless oil, 31.5 mg, pet. ether/EtOAc = 15/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 3.93 (s, 3H), 2.35 - 2.27 (m, 1H), 2.23 - 2.15 (m, 1H), 1.98 (s, 3H), 0.91 (t, *J* = 1.2, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 140.2, 129.7, 129.6, 129.3, 128.5 (d, *J* = 1.3 Hz), 127.8 (q, *J* = 284.8 Hz), 59.3 (d, *J* = 25.2 Hz), 52.2, 27.4, 13.5 (d, *J* = 2.5 Hz), 8.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -67.04. IR (neat)：2931, 1725, 1612, 1436, 1279, 968, 719 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3O_2S$ $[M+H]^+$ 293.0818, found 293.0809.



4f

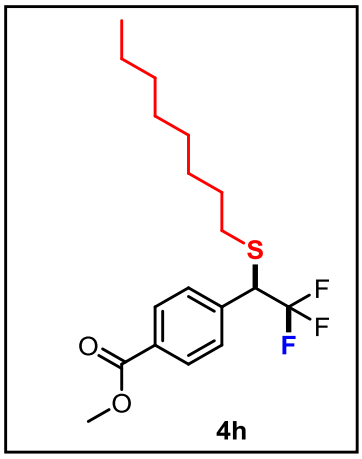
Yield: 59% (colorless oil, 23.4 mg, pet. ether/EtOAc = 30/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 4.26 (q, *J* = 8.3 Hz, 1H), 3.93 (s, 3H), 2.17 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 138.1 (d, *J* = 2.0 Hz), 130.6, 130.0, 128.9, 125.8 (q, *J* = 280.8 Hz), 53.5 (q, *J* = 30.3 Hz), 52.3, 15.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.49. IR (neat)： 2918, 1738, 1460, 972, 728 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{11}H_{11}F_3O_2S$ $[M+H]^+$ 265.0505, found 265.0499.



4g

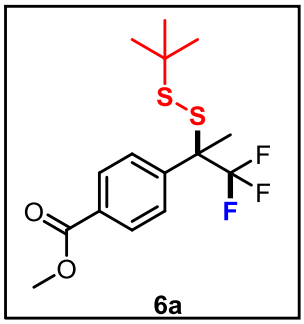
Yield: 56% (colorless oil, 23.4 mg, pet. ether/EtOAc = 30/1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 4.33 (q, *J* = 8.3 Hz, 1H), 3.93 (s, 3H), 2.71 - 2.58 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 166.5, 138.7, 130.5, 130.0, 129.0, 128.4 (q, *J* = 280.8 Hz), 52.3, 51.8 (q, *J* = 30.3 Hz), 26.9, 14.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -67.77. IR (neat)：2921, 1725, 1611, 1457, 1281, 813, 717 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_2S$ $[M+H]^+$ 279.0661, found 279.0653.



4h

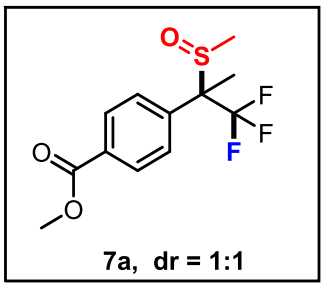
Yield: 53% (colorless oil, 28.8 mg, pet. ether/EtOAc = 30/1), ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 4.30 (q, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 2.64 - 2.56 (m, 2H), 1.55 (td, *J* = 7.9, 5.1 Hz, 2H), 1.35- 1.24 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 138.8, 130.5, 130.0, 129.0, 127.3 (t, *J* = 280.0 Hz), 52.3, 52.1 (t, *J* = 30.2 Hz), 32.9, 31.8, 29.1, 29.0, 28.9, 28.6, 22.6 (t, *J* = 2.5 Hz), 14.1 (t, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -67.76. IR (neat)：2924, 1725, 1612, 1437, 1277, 840, 711 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{18}H_{25}F_3O_2S$ $[M+H]^+$ 363.1600, found 363.1584.



6a

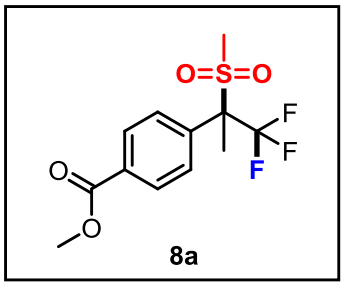
Yield: 42% (white solid, 21.1 mg, pet. ether/EtOAc = 30/1). ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 3.93 (s, 3H), 1.95 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.48, 141.93, 130.20, 129.50, 128.16 (d, *J* = 1.3 Hz), 127.69 (d, *J* = 31.5 Hz), 56.85 (d, *J* = 26.5 Hz), 52.27, 48.13, 30.17,

19.90 (d, *J* = 1.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -70.50. IR (neat)： 2922, 1721, 1608, 1457, 1261, 824, 714 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{15}H_{19}F_3O_2S_2$ [M+H]+ 353.0851, found 353.0859.



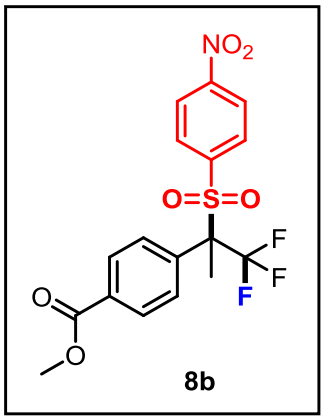
7a, dr = 1:1

Yield: 95% (colorless oil, 28.8 mg, pet. ether/EtOAc = 1/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 - 8.05 (m, 4H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 3.94 (s, 6H), 2.36 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 166.1, 136.3, 135.5, 131.3 (d, *J* = 2.5 Hz), 130.9, 130.3, 129.9, 128.4 (d, *J* = 1.3 Hz), 127.4 (d, *J* = 1.3 Hz), 127.0, 126.6, 124.8, 124.4, 67.7 (d, *J* = 25.2 Hz), 66.4 (d, *J* = 25.2 Hz), 65.6, 52.5, 52.4, 34.6, 34.2, 12.7 (d, *J* = 3.8 Hz), 10.1 (d, *J* = 3.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -66.24, -67.21. IR (neat)：2955, 1722, 1612, 1436, 1232, 868, 715 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_3S$ $[M+H]^+$ 295.0610, found 295.0603.



8a

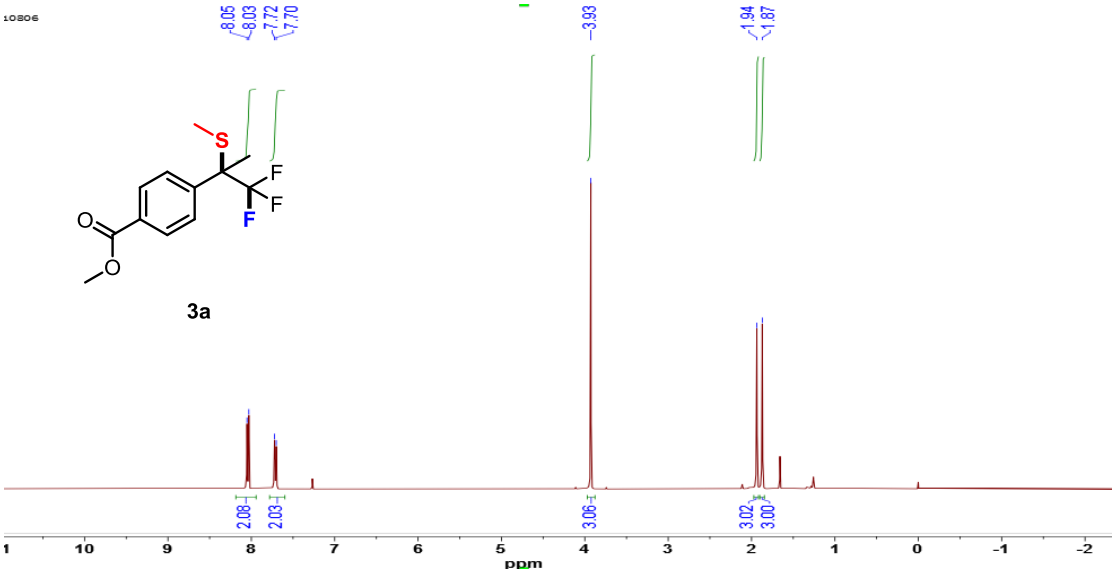
Yield: 96% (white solid, 30.4 mg, pet. ether/EtOAc = 2/1), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 3.95 (s, 3H), 2.80 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 134.4, 131.7, 129.9, 129.1 (d, *J* = 2.5 Hz), 124.5 (q, *J* = 284.8 Hz), 72.1 (q, *J* = 26.5 Hz), 52.5, 38.9 (q, *J* = 2.5 Hz), 16.0 (q, *J* = 3.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.90. IR (neat)： 3703, 2922, 1724, 1466, 1285, 957, 748, 712 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_4S$ $[M+H]^+$ 311.0559, found 311.0551.



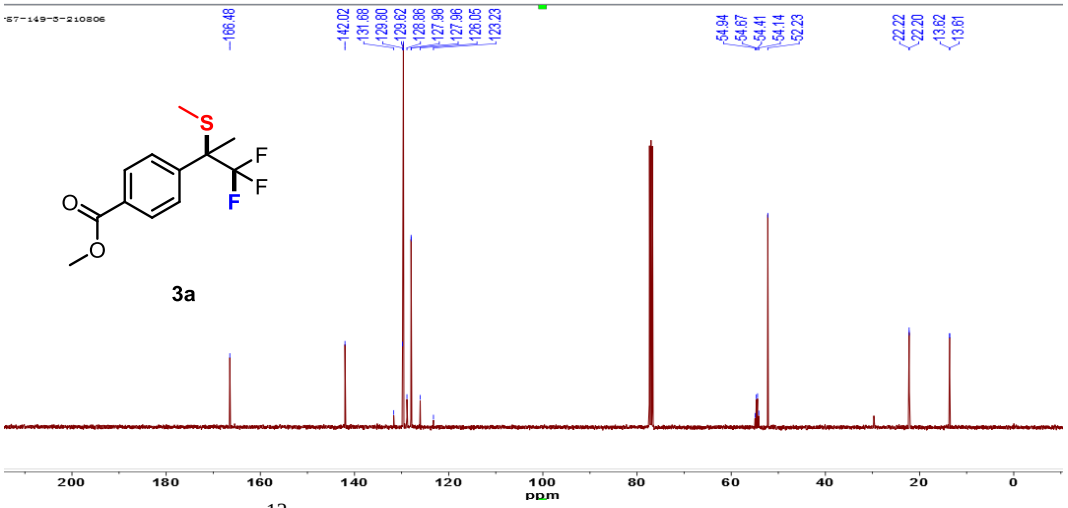
8b

Yield: 94% (white solid, 39.2 mg, pet. ether/EtOAc = 1/1),^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 151.1, 141.3, 133.7, 132.1, 131.9, 129.7, 129.4 (t, *J* = 2.5 Hz), 124.2 (q, *J* = 286.0 Hz), 73.9 (q, *J* = 26.5 Hz), 52.6, 16.4 (d, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.82. IR (neat)：2920, 2852, 1719, 1530, 1447, 1278, 1164, 968, 857, 746 cm^{-1}. HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_6S$ $[M+H]^+$ 418.0567, found 418.0565.

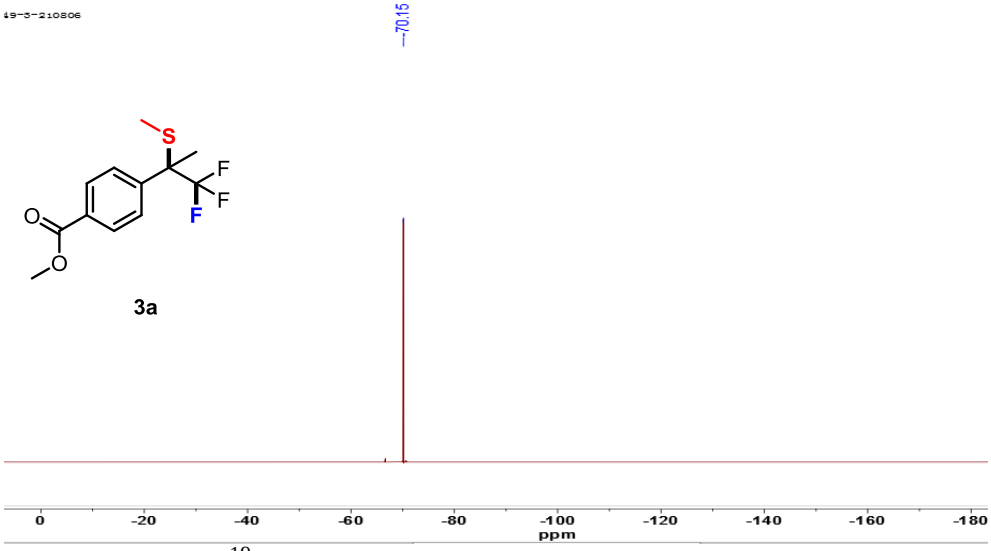
8. Supplementary spectra



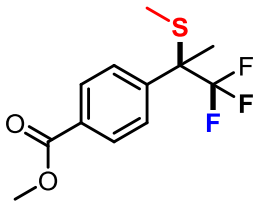
^{1}H NMR spectrum at 400 MHz in $CDCl_3$



^{13}C NMR spectrum at 101 MHz in $CDCl_3$

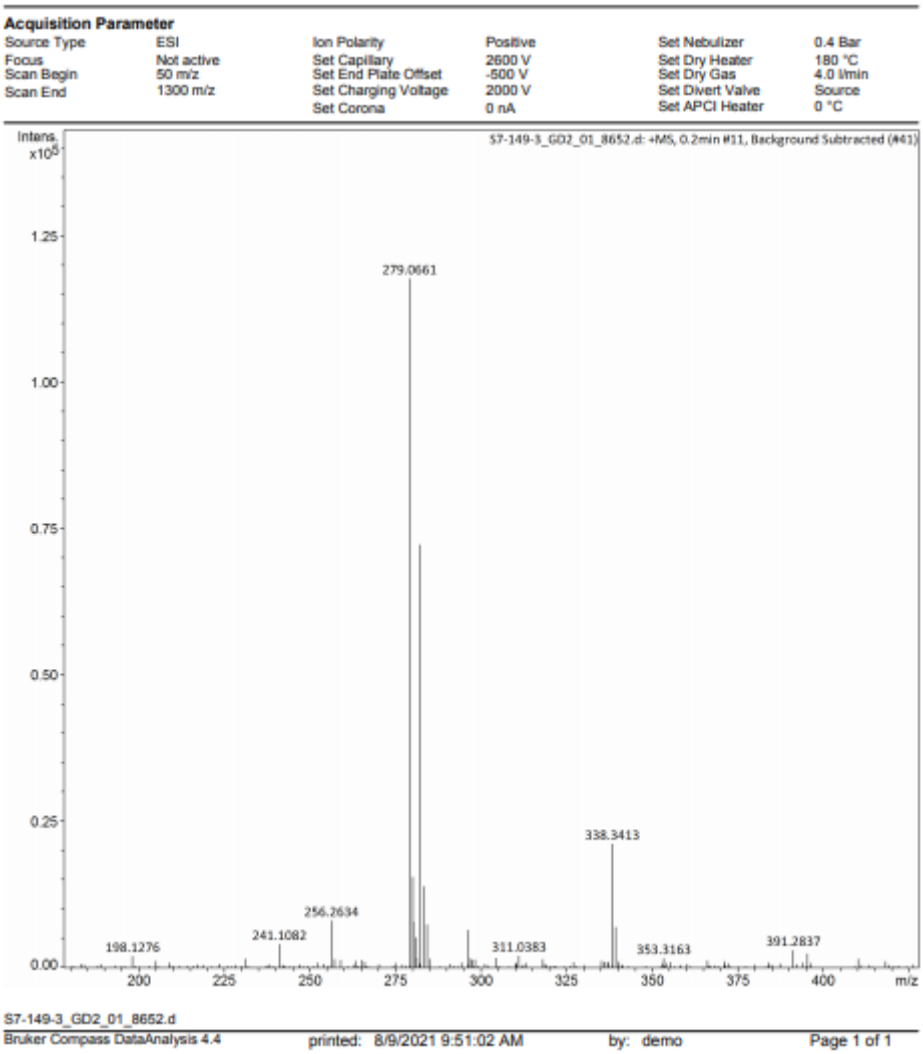


^{19}F NMR spectrum at 376 MHz in $CDCl_3$

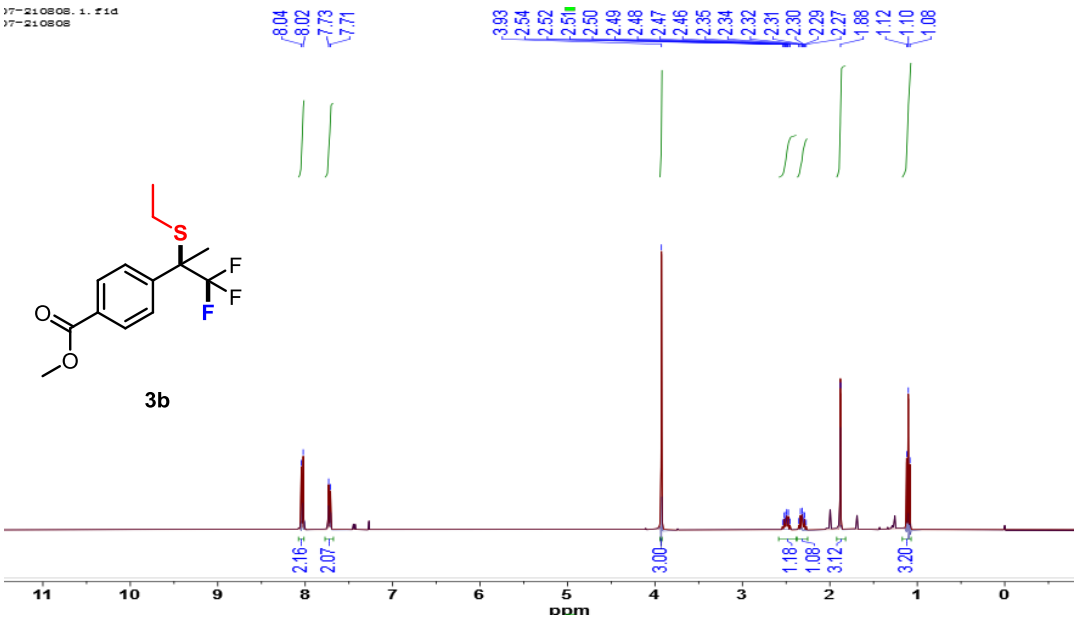


3a

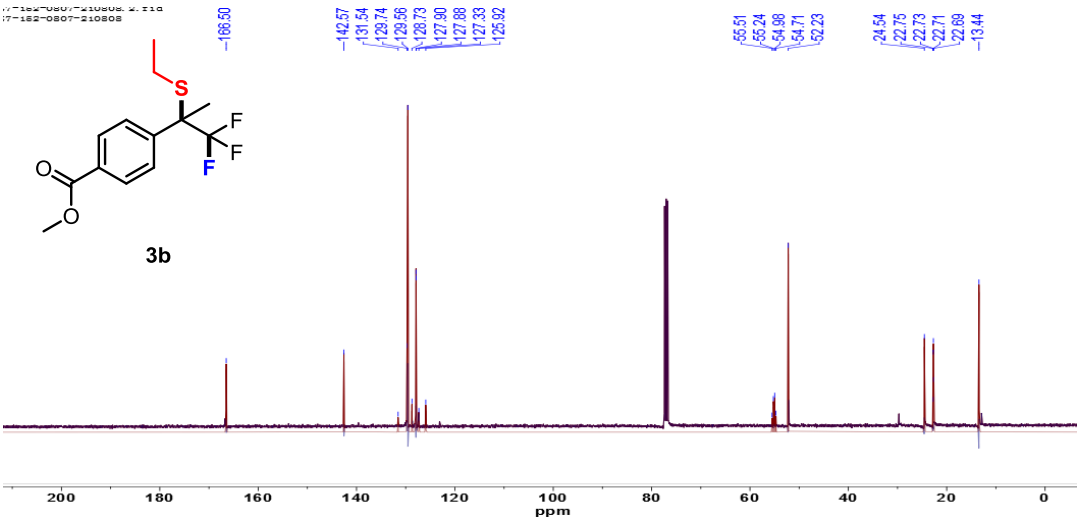
Chemical Formula: $C_{12}H_{13}F_3O_2S$
Exact Mass: 278.0588
Molecular Weight: 278.2892
m/z: 278.0588 (100.0%), 279.0622 (13.0%), 280.0546 (4.5%)
Elemental Analysis: C, 51.79; H, 4.71; F, 20.48; O, 11.50; S, 11.52



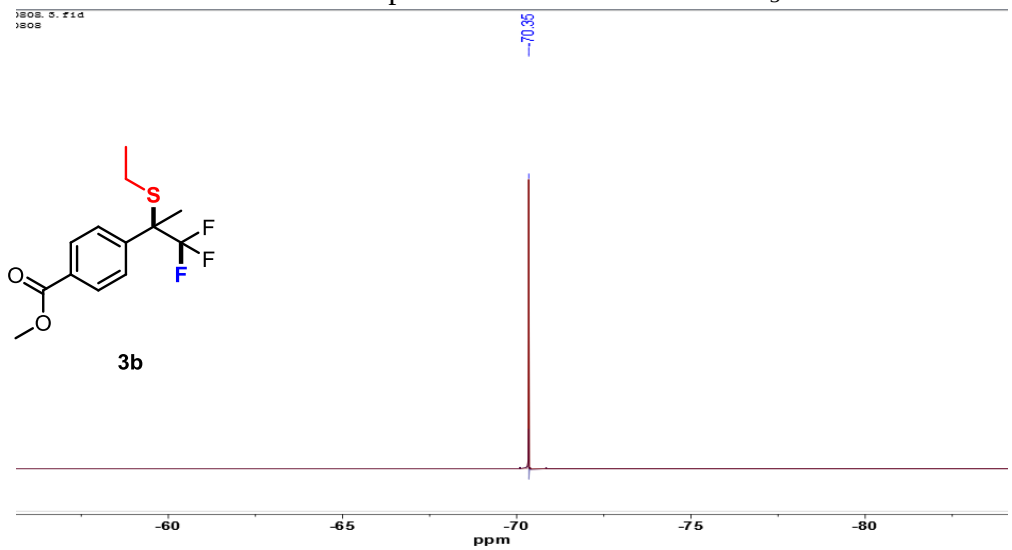
HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_2S$ $[M+H]^+$ 279.0661, found 279.0661.



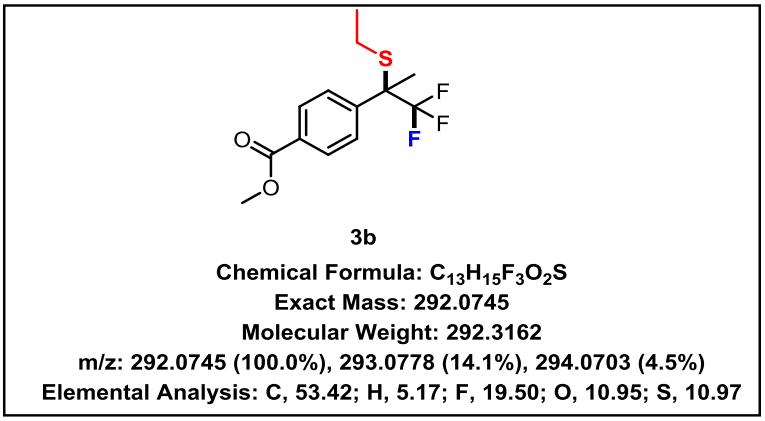
^{1}H NMR spectrum at 400 MHz in $CDCl_3$



^{13}C NMR spectrum at 101 MHz in $CDCl_3$

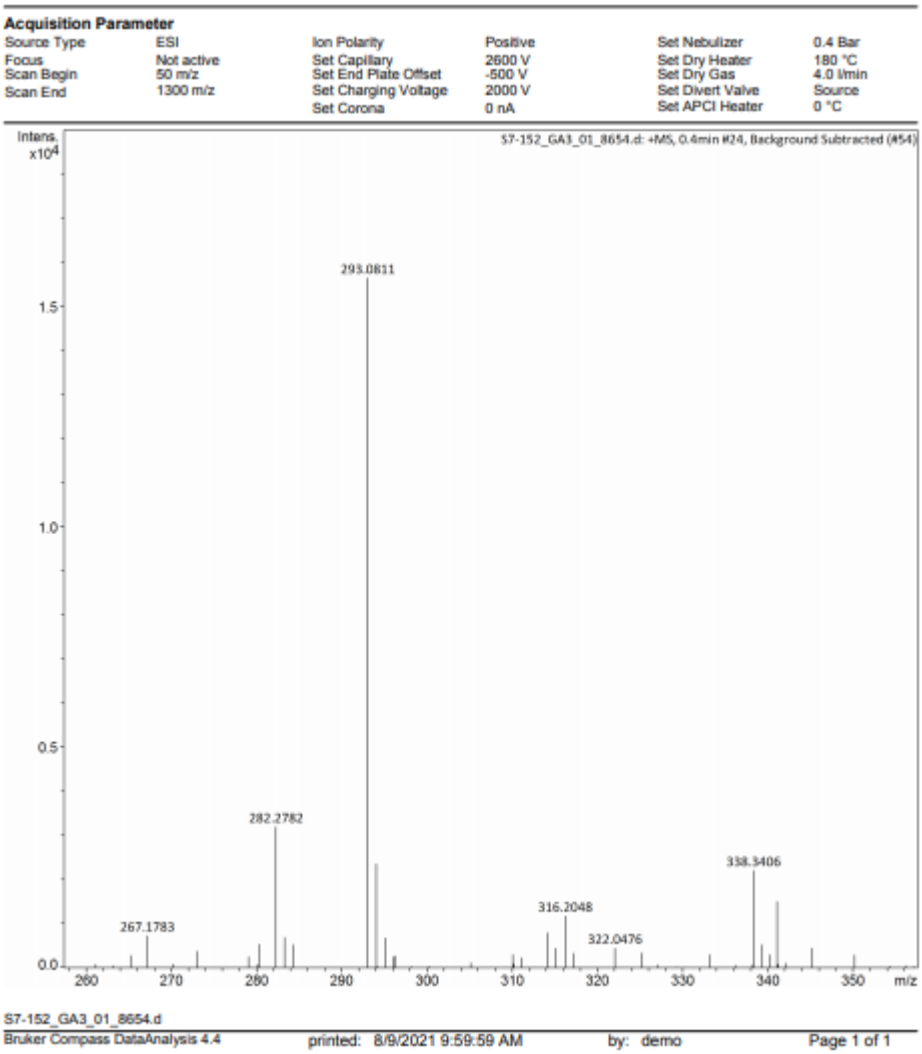


^{19}F NMR spectrum at 376 MHz in $CDCl_3$

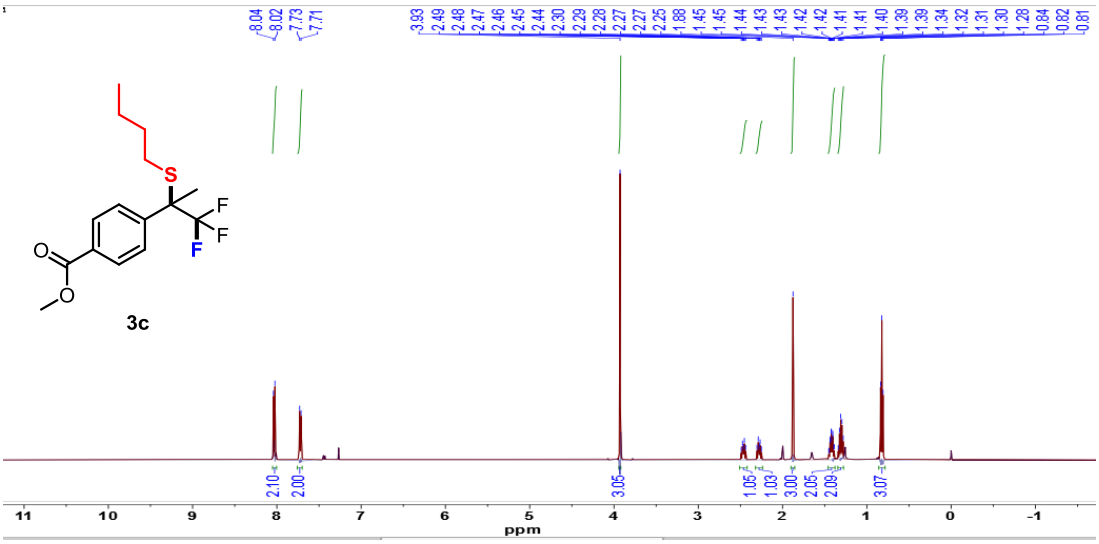


3b

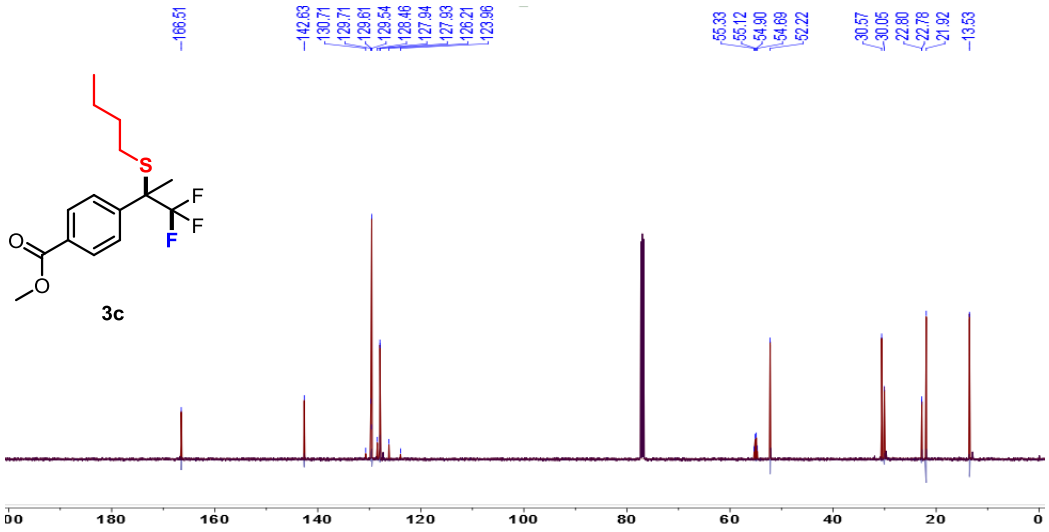
Chemical Formula: $C_{13}H_{15}F_3O_2S$
Exact Mass: 292.0745
Molecular Weight: 292.3162
m/z: 292.0745 (100.0%), 293.0778 (14.1%), 294.0703 (4.5%)
Elemental Analysis: C, 53.42; H, 5.17; F, 19.50; O, 10.95; S, 10.97



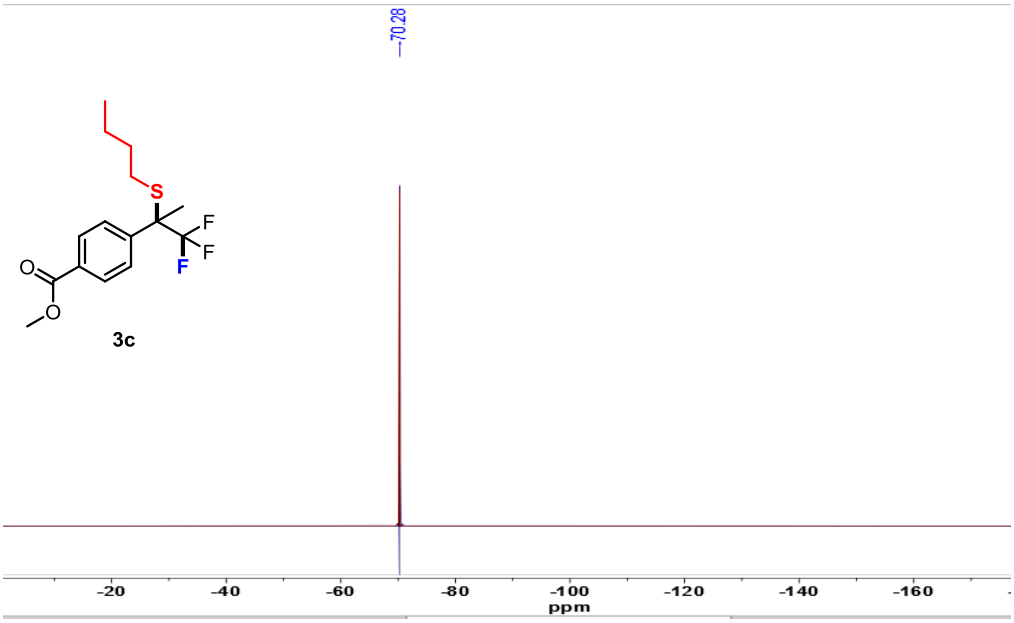
HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3O_2S$ $[M+H]^+$ 293.0818, found 293.0811.



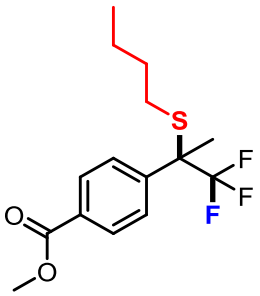
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



3c

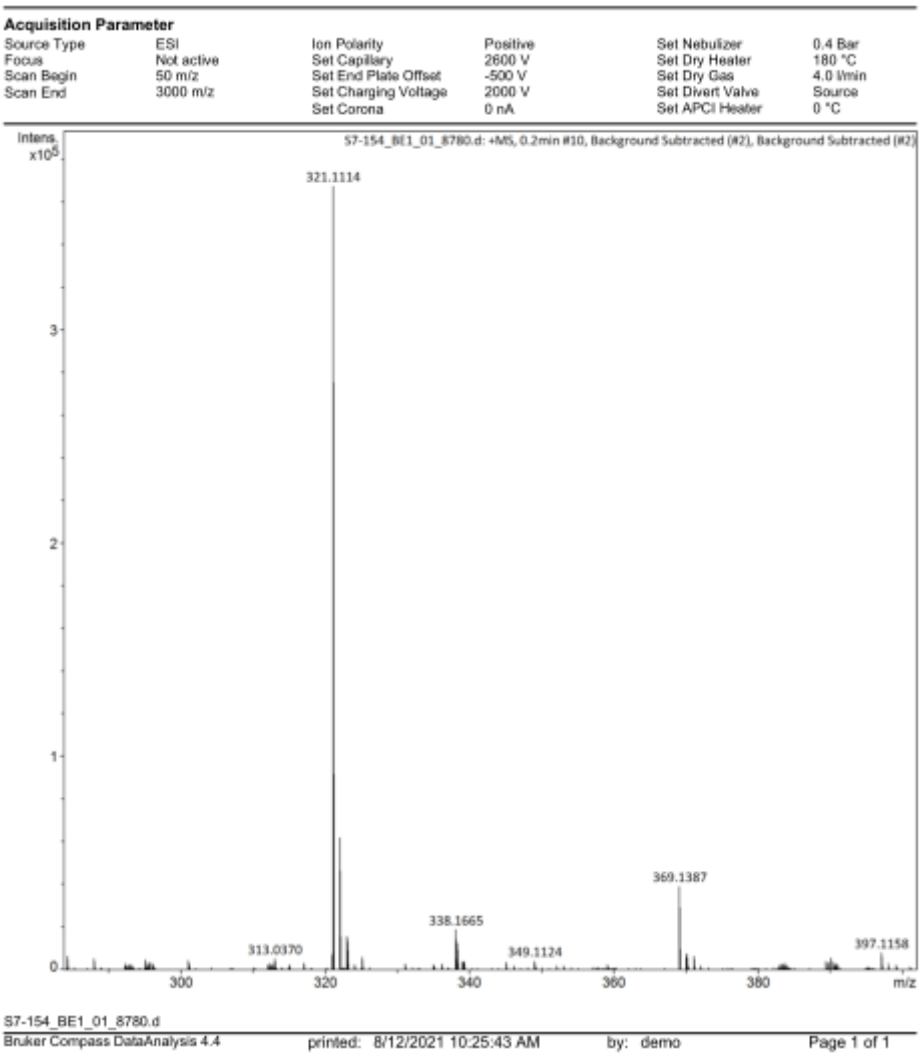
Chemical Formula: $C_{15}H_{19}F_3O_2S$

Exact Mass: 320.1058

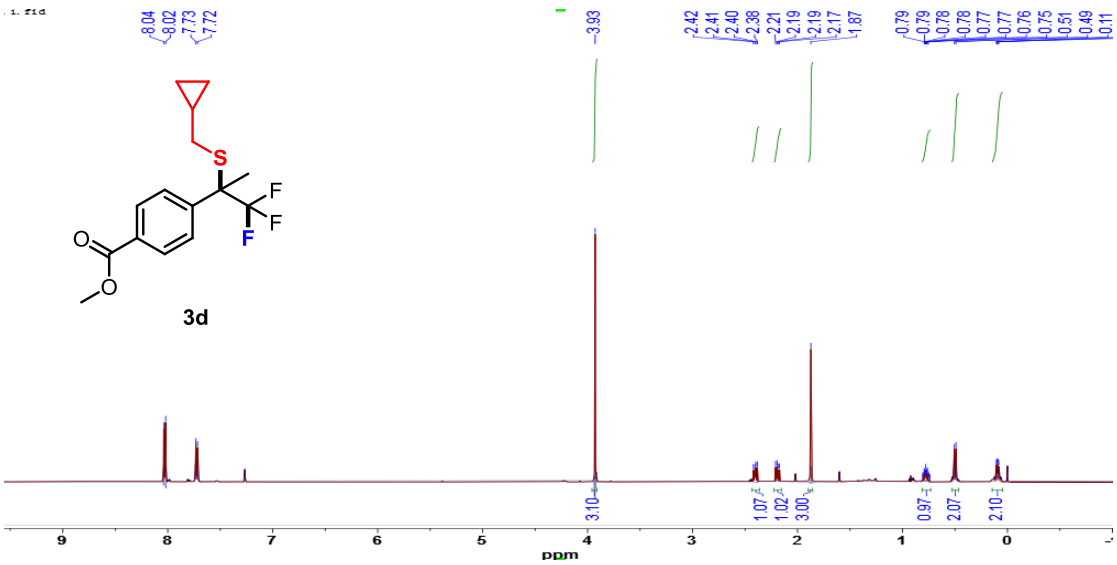
Molecular Weight: 320.3702

m/z: 320.1058 (100.0%), 321.1091 (16.2%), 322.1016 (4.5%), 322.1125 (1.2%)

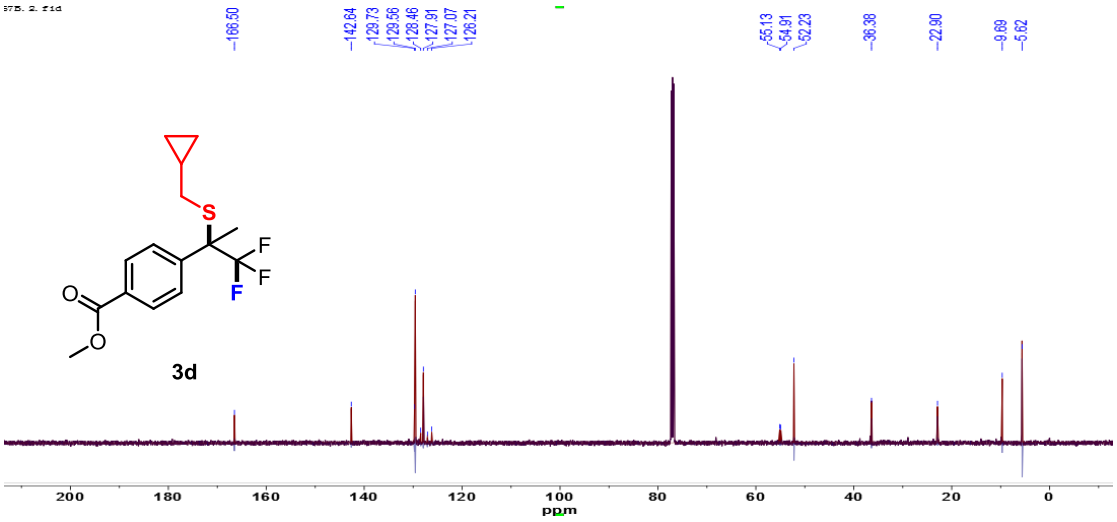
Elemental Analysis: C, 56.24; H, 5.98; F, 17.79; O, 9.99; S, 10.01



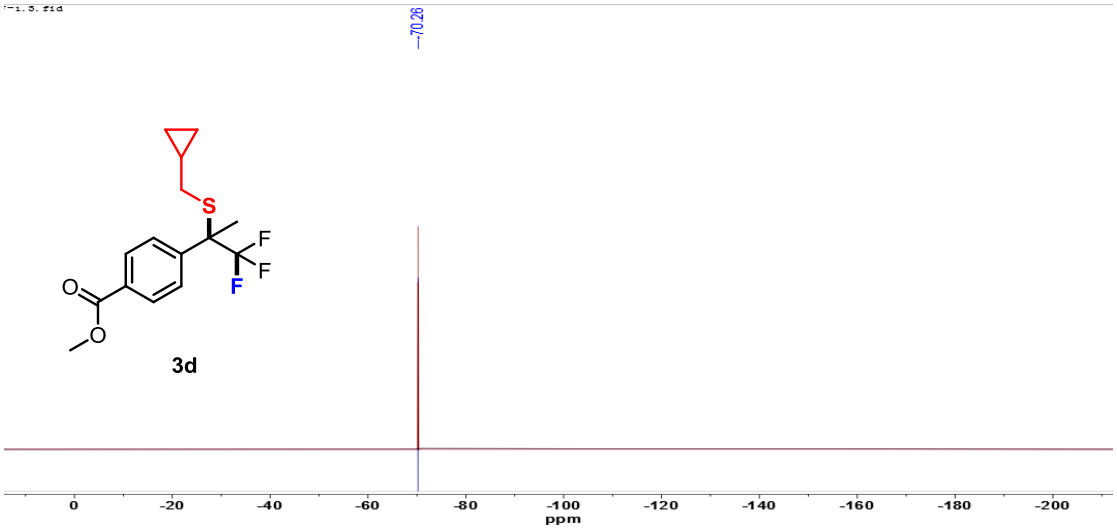
HRMS (ESI, m/z) calcd for $C_{15}H_{19}F_3O_2S$ $[M+H]^+$ 321.1131, found 321.1114.



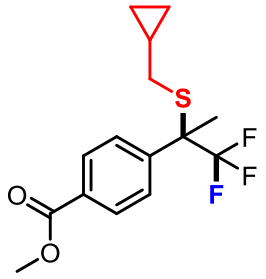
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$

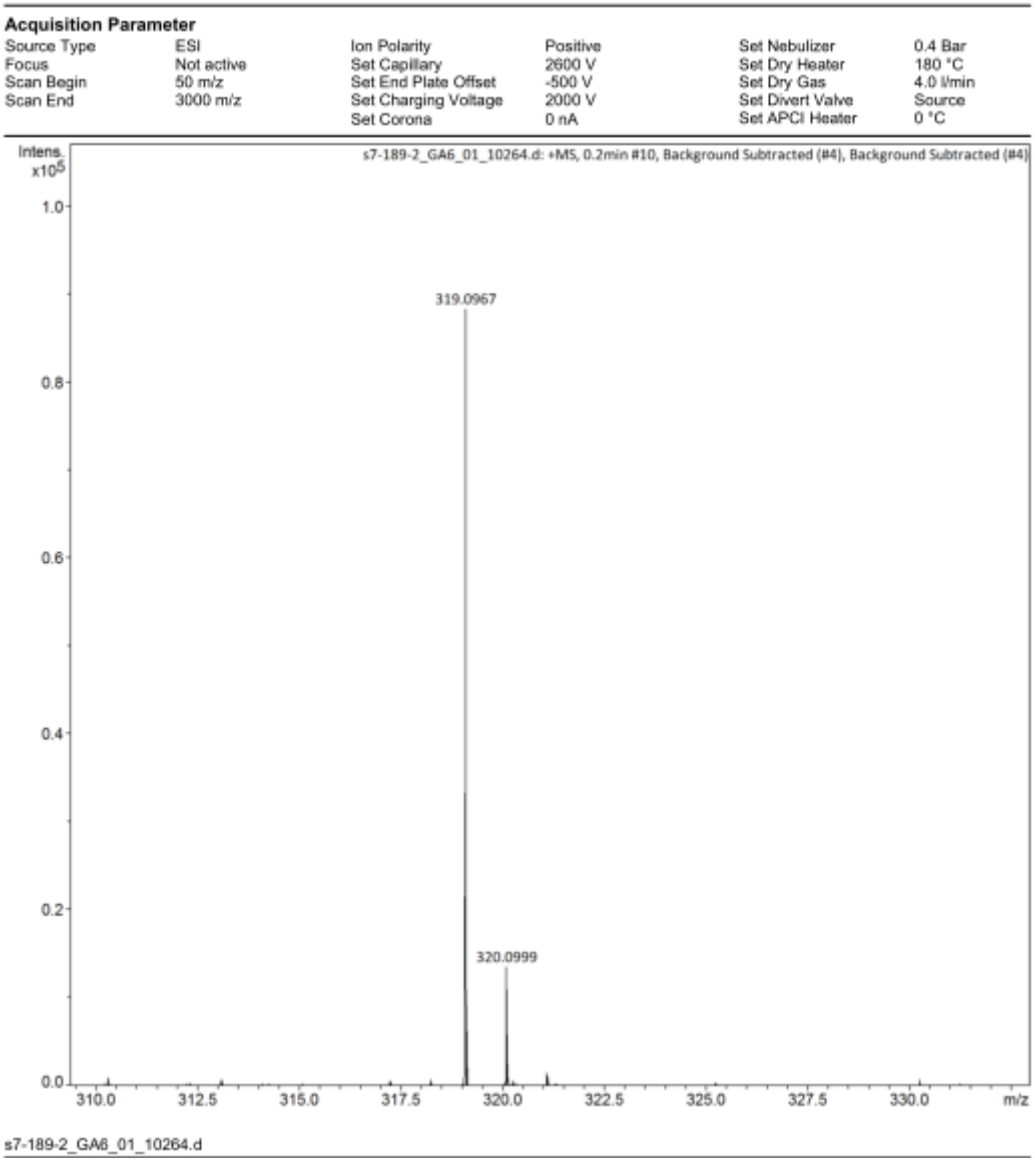


^{19}F NMR spectrum at 471 MHz in $CDCl_3$

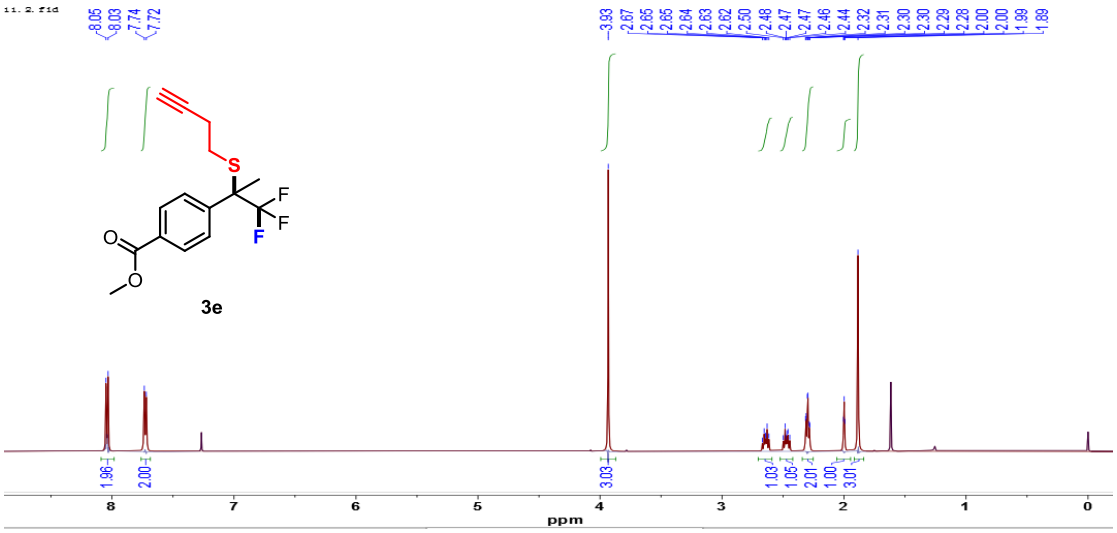


3d

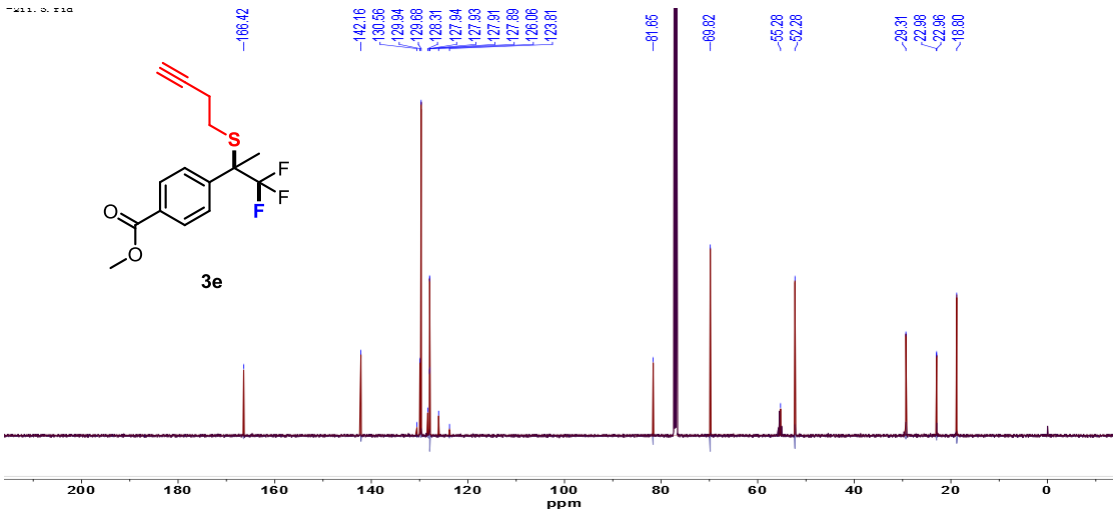
Chemical Formula: $C_{15}H_{17}F_3O_2S$
Exact Mass: 318.0901
Molecular Weight: 318.3542
m/z: 318.0901 (100.0%), 319.0935 (16.2%), 320.0859 (4.5%), 320.0968 (1.2%)
Elemental Analysis: C, 56.59; H, 5.38; F, 17.90; O, 10.05; S, 10.07



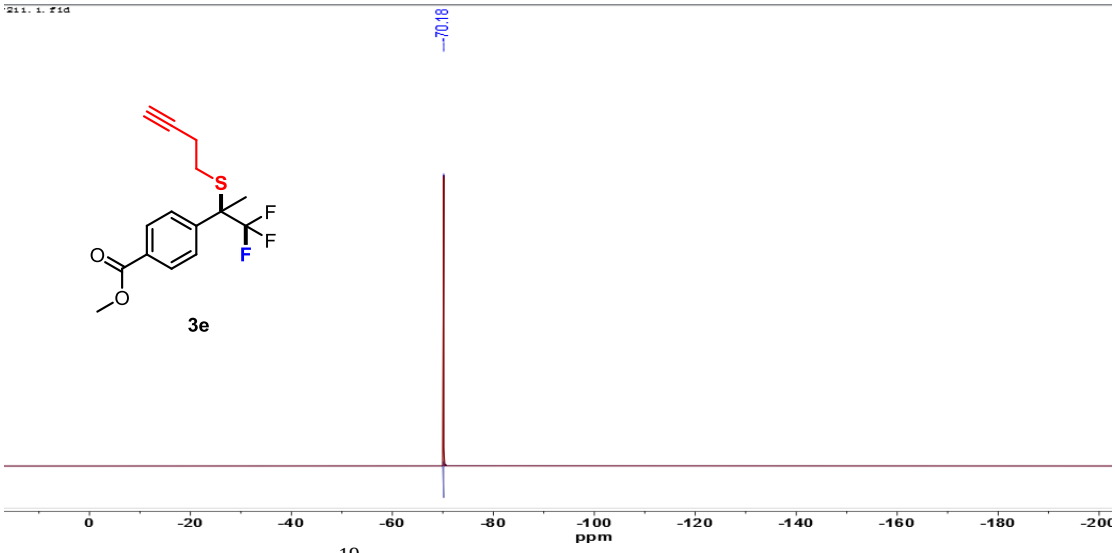
HRMS (ESI, m/z) calcd for $C_{15}H_{17}F_3O_2S$ $[M+H]^+$ 319.0974, found 319.0967.



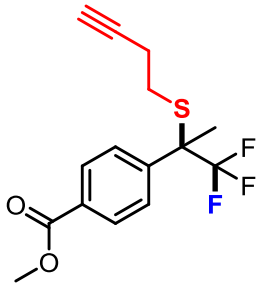
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in



3e

Chemical Formula: $C_{15}H_{15}F_3O_2S$

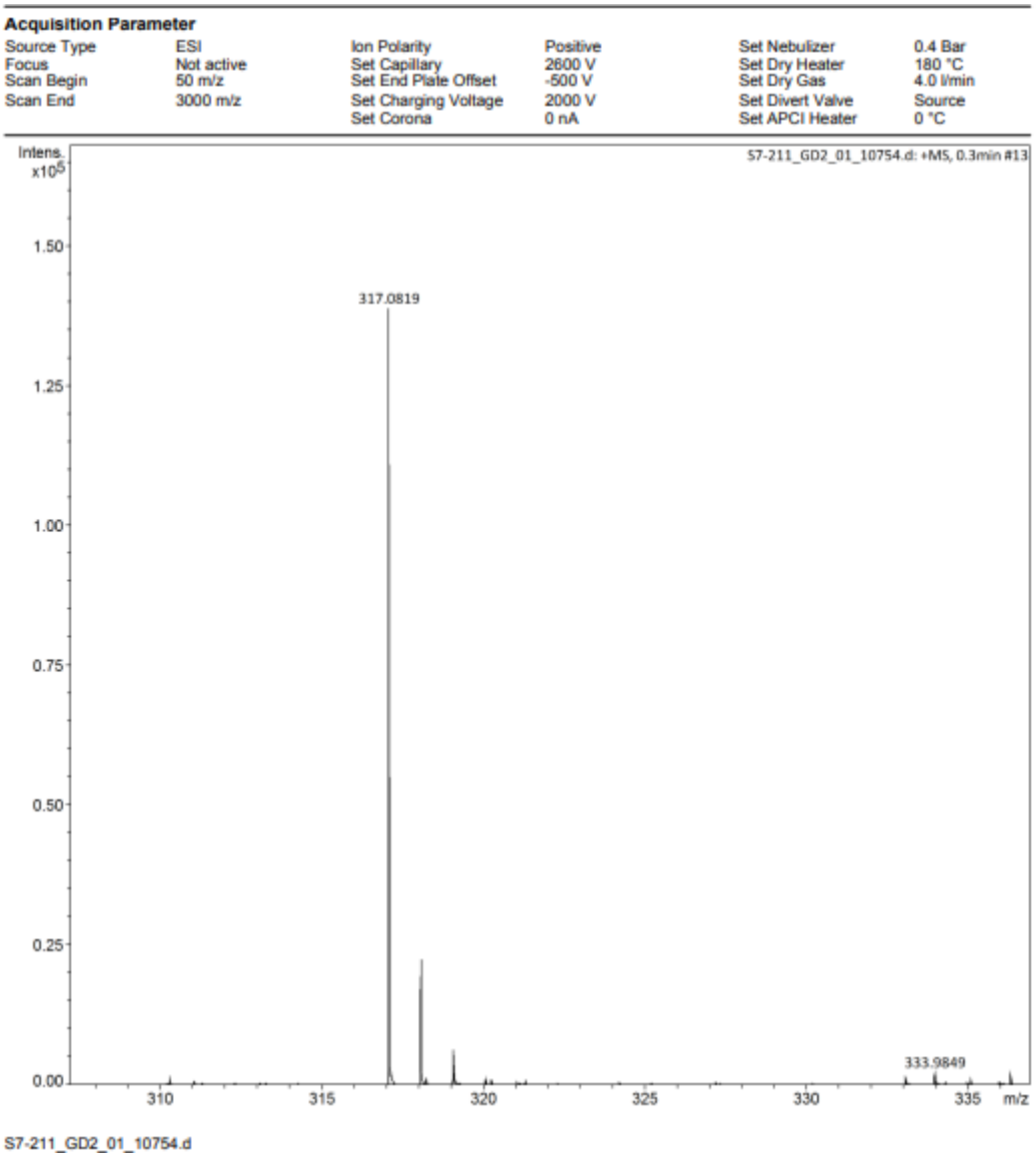
Exact Mass: 316.0745

Molecular Weight: 316.3382

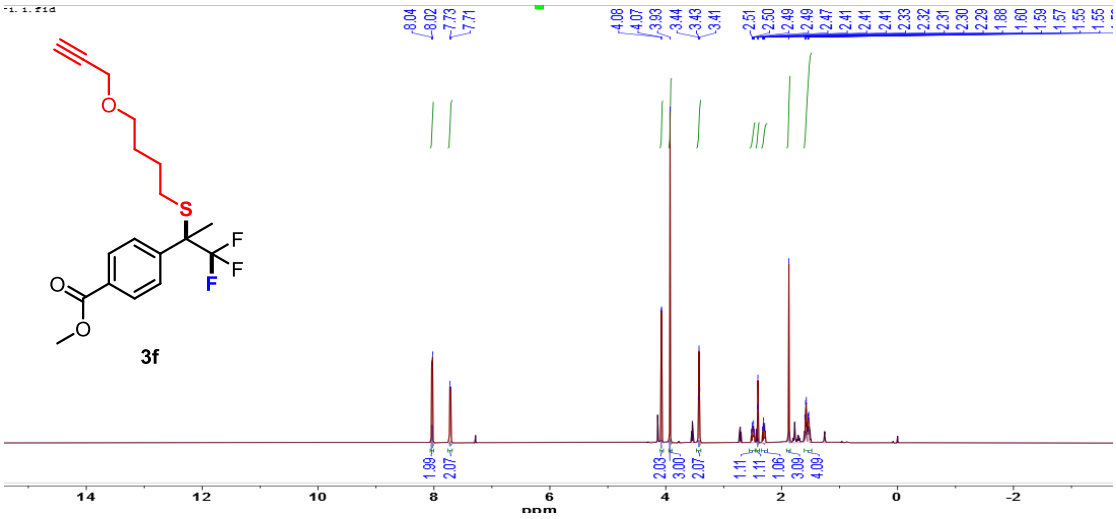
m/z: 316.0745 (100.0%), 317.0778 (16.2%), 318.0703 (4.5%), 318.0812 (1.2%)

Elemental Analysis: C, 56.95; H, 4.78; F, 18.02; O, 10.12; S, 10.13

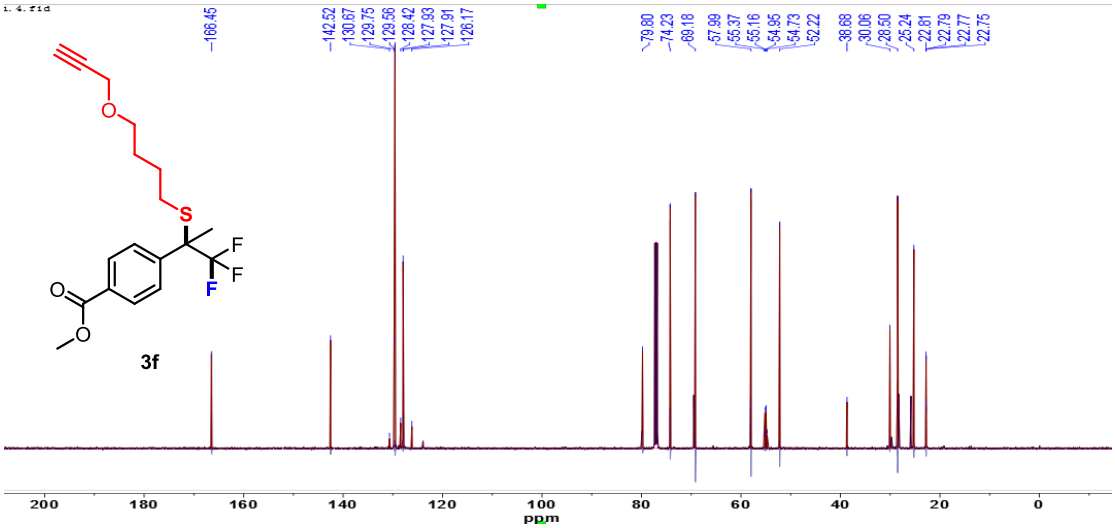
$CDCl_3$



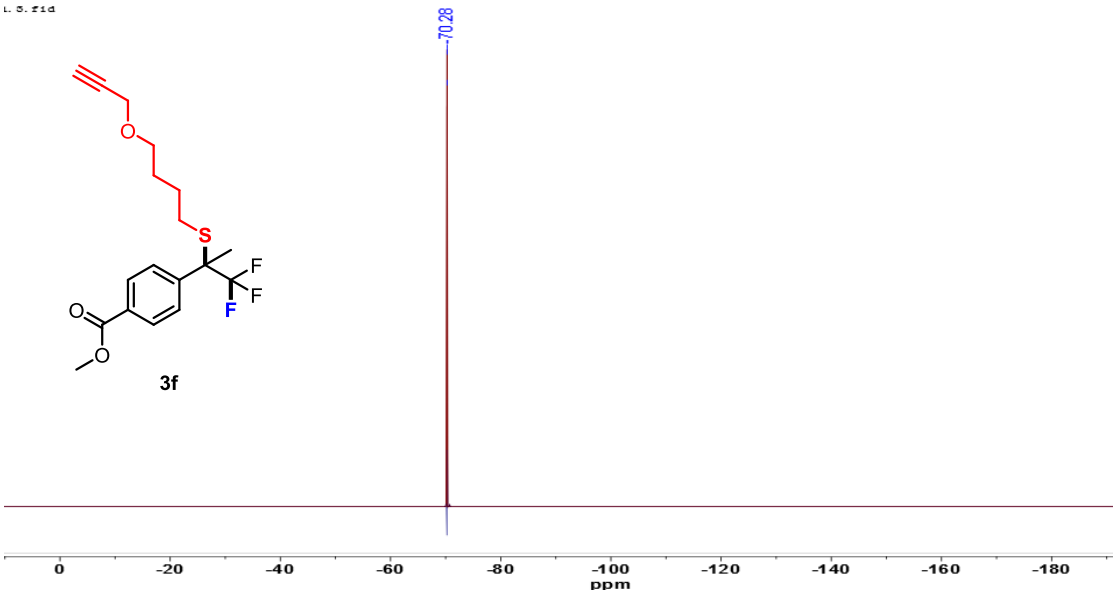
HRMS (ESI, m/z) calcd for $C_{15}H_{15}F_3O_2S$ $[M+H]^+$ 317.0818, found 317.0819.



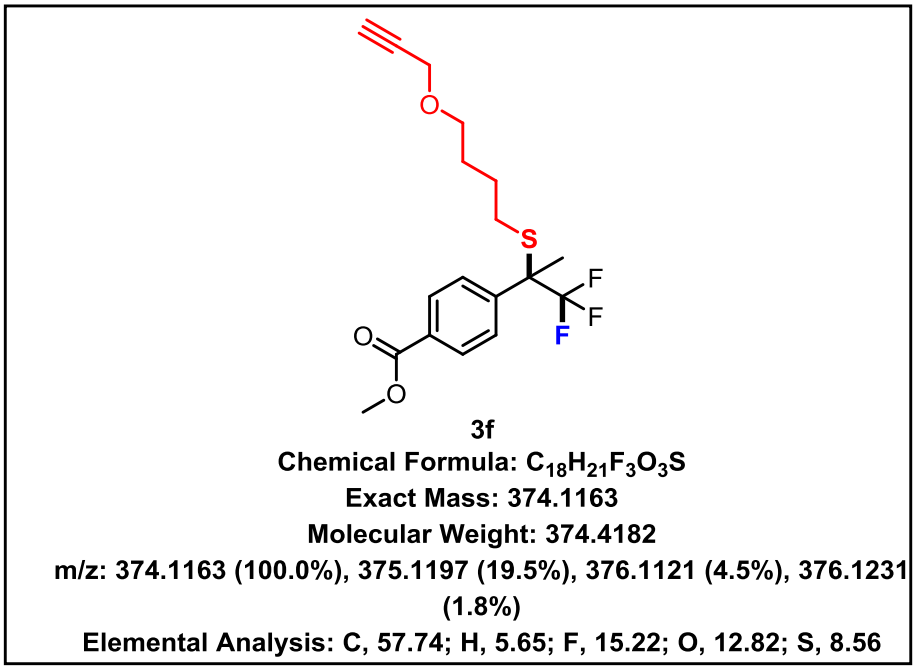
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



3f

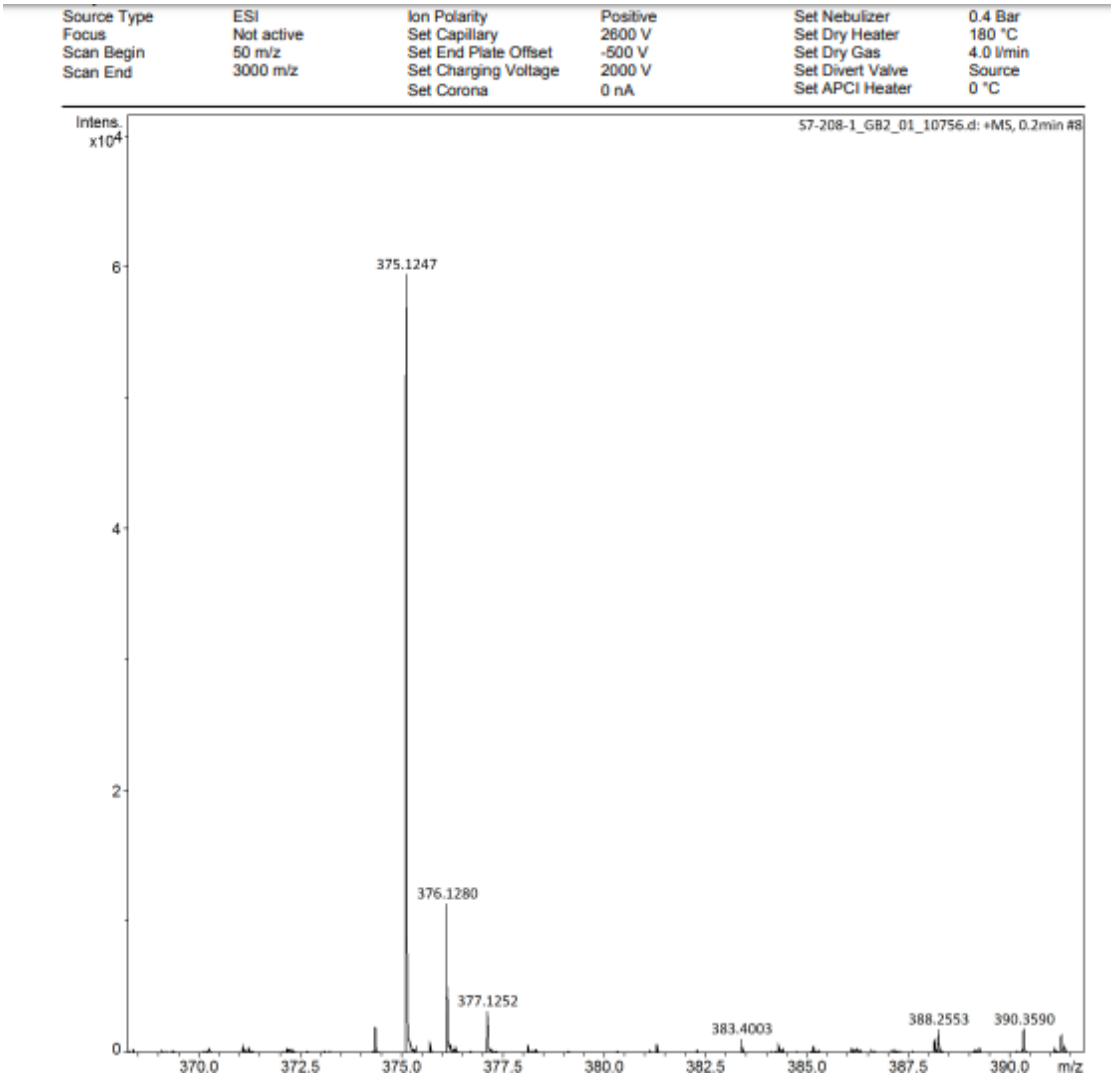
Chemical Formula: $C_{18}H_{21}F_3O_3S$

Exact Mass: 374.1163

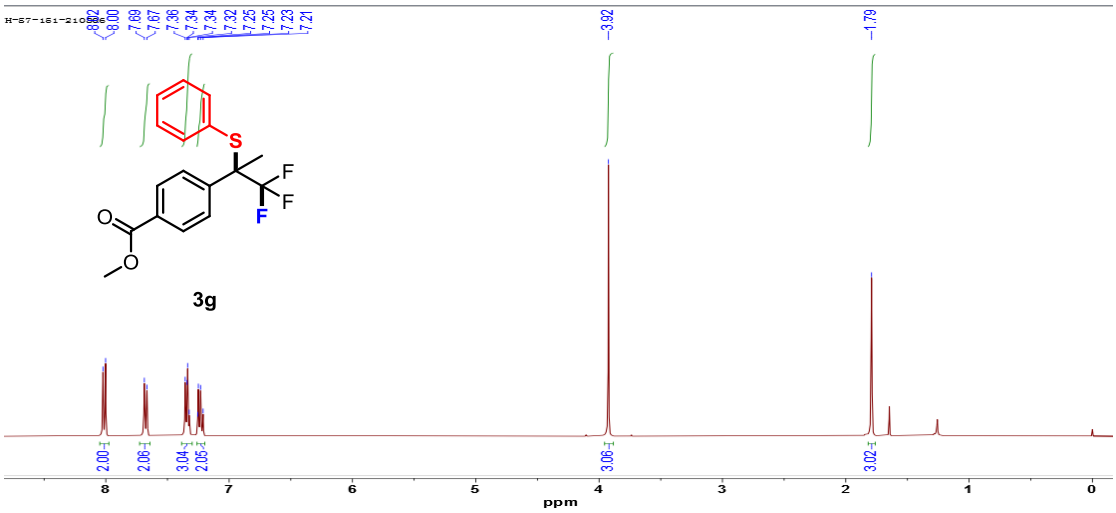
Molecular Weight: 374.4182

m/z: 374.1163 (100.0%), 375.1197 (19.5%), 376.1121 (4.5%), 376.1231 (1.8%)

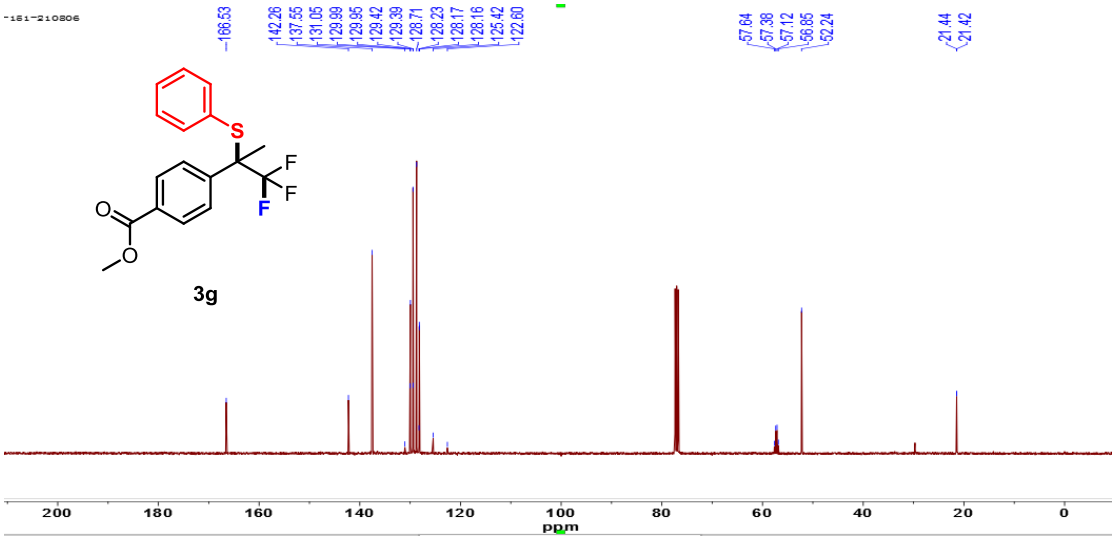
Elemental Analysis: C, 57.74; H, 5.65; F, 15.22; O, 12.82; S, 8.56



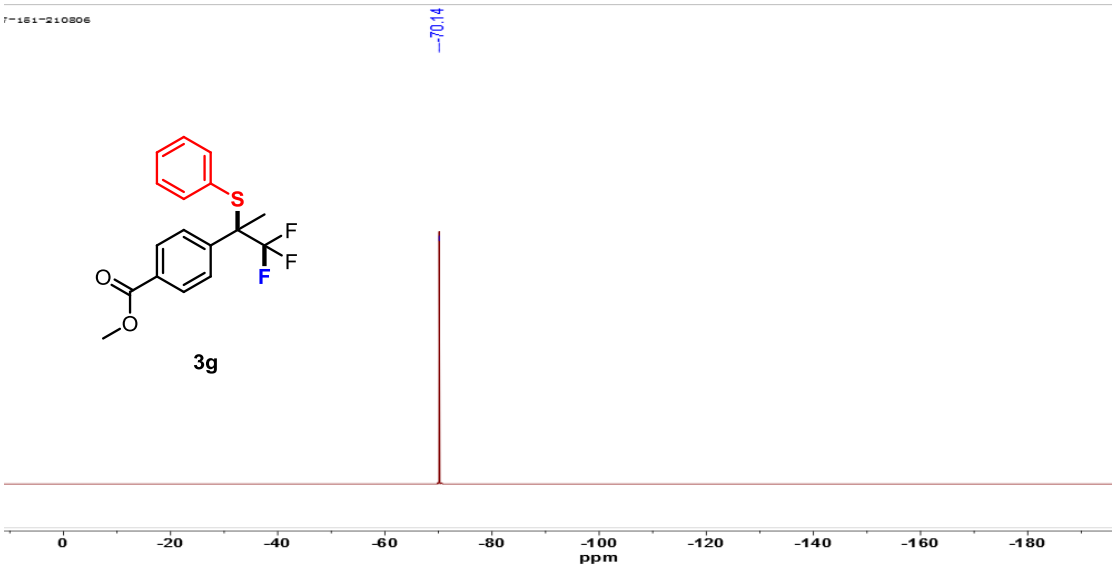
HRMS (ESI, m/z) calcd for $C_{18}H_{21}F_3O_3S$ $[M+H]^+$ 375.1236, found 375.1247.



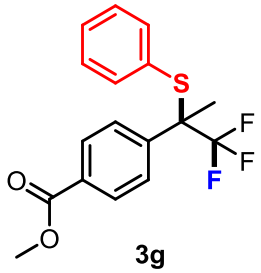
^{1}H NMR spectrum at 400 MHz in $CDCl_3$



^{13}C NMR spectrum at 101 MHz in $CDCl_3$



^{19}F NMR spectrum at 376 MHz in $CDCl_3$



3g

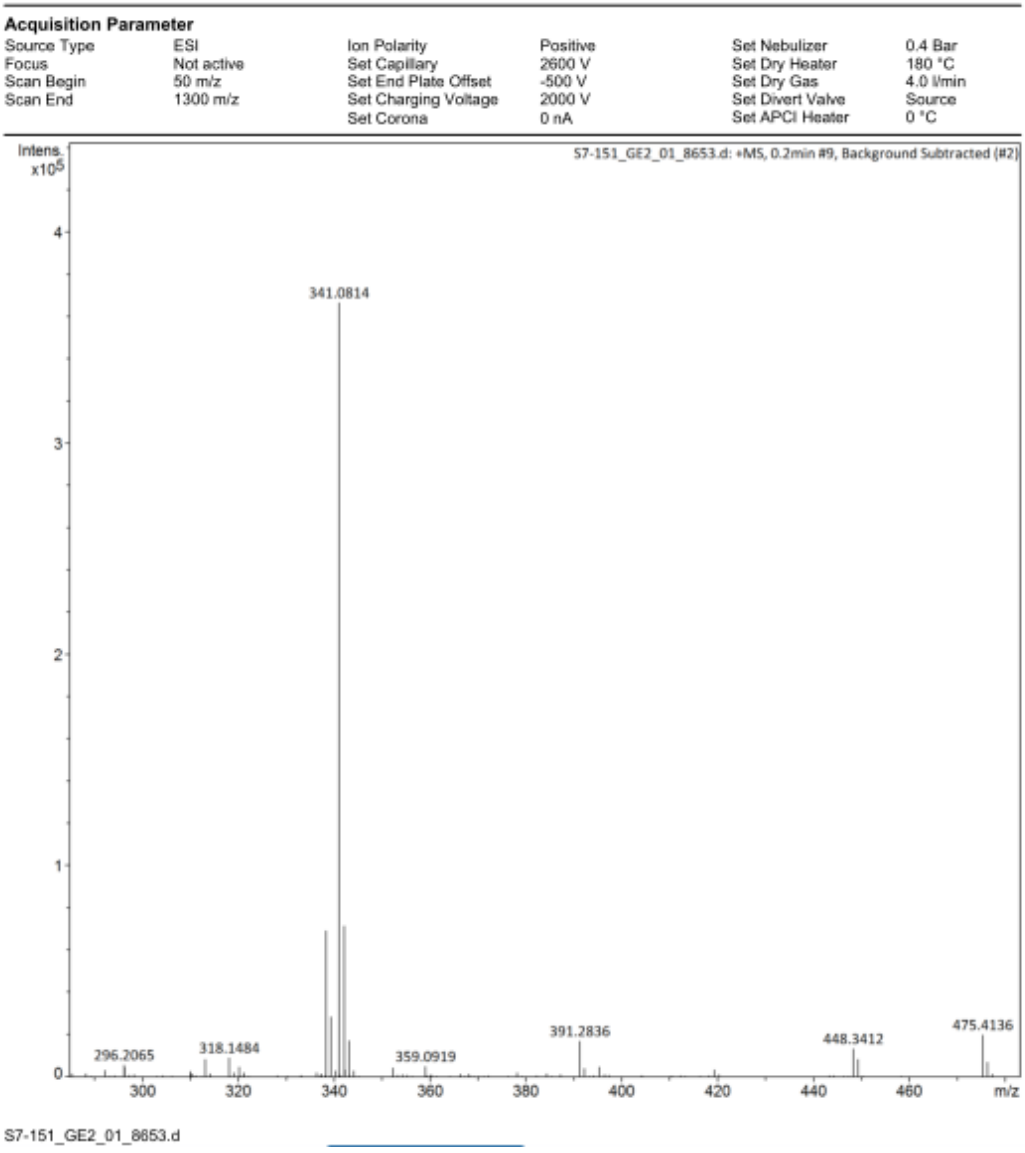
Chemical Formula: $C_{17}H_{15}F_3O_2S$

Exact Mass: 340.0745

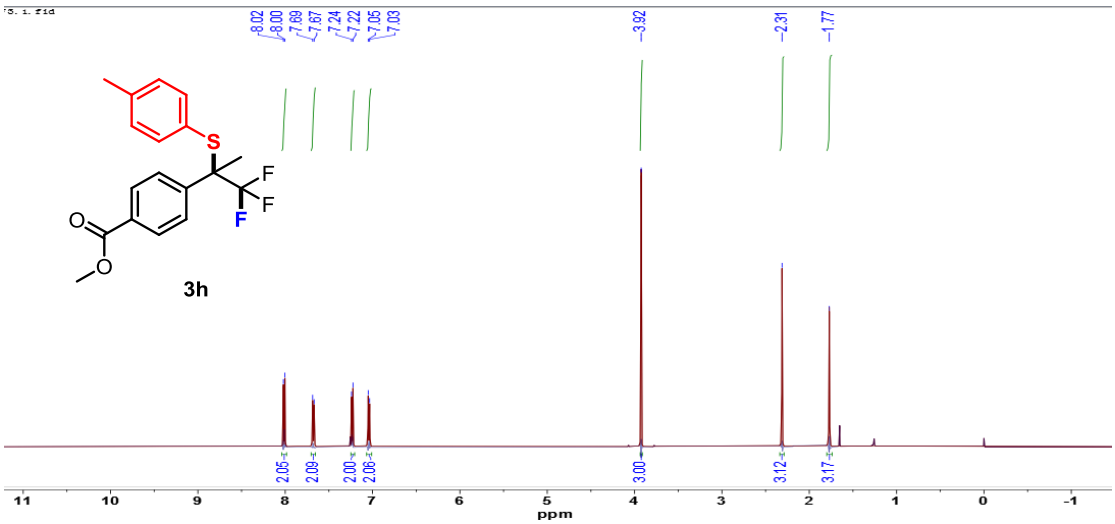
Molecular Weight: 340.3602

m/z: 340.0745 (100.0%), 341.0778 (18.4%), 342.0703 (4.5%), 342.0812 (1.6%)

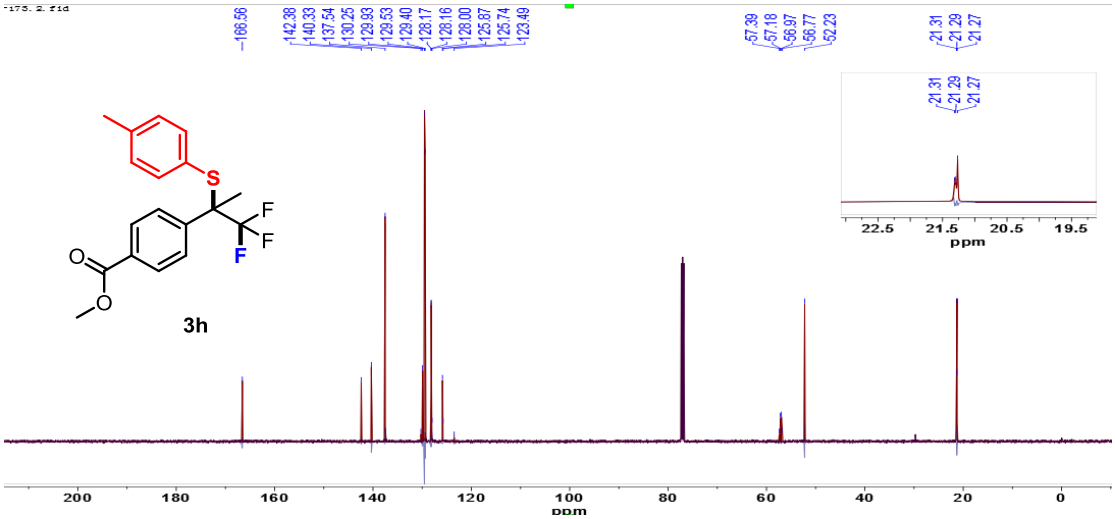
Elemental Analysis: C, 59.99; H, 4.44; F, 16.75; O, 9.40; S, 9.42



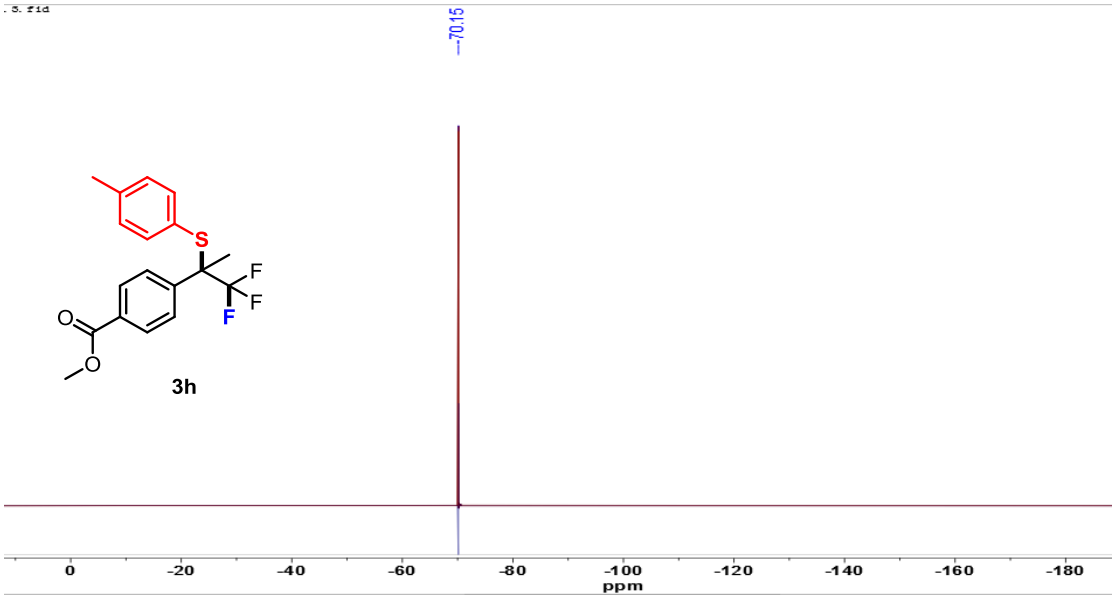
HRMS (ESI, m/z) calcd for $C_{17}H_{15}F_3O_2S$ $[M+H]^+$ 341.0818, found 341.0814.



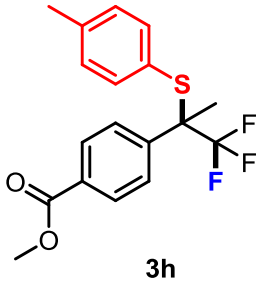
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$

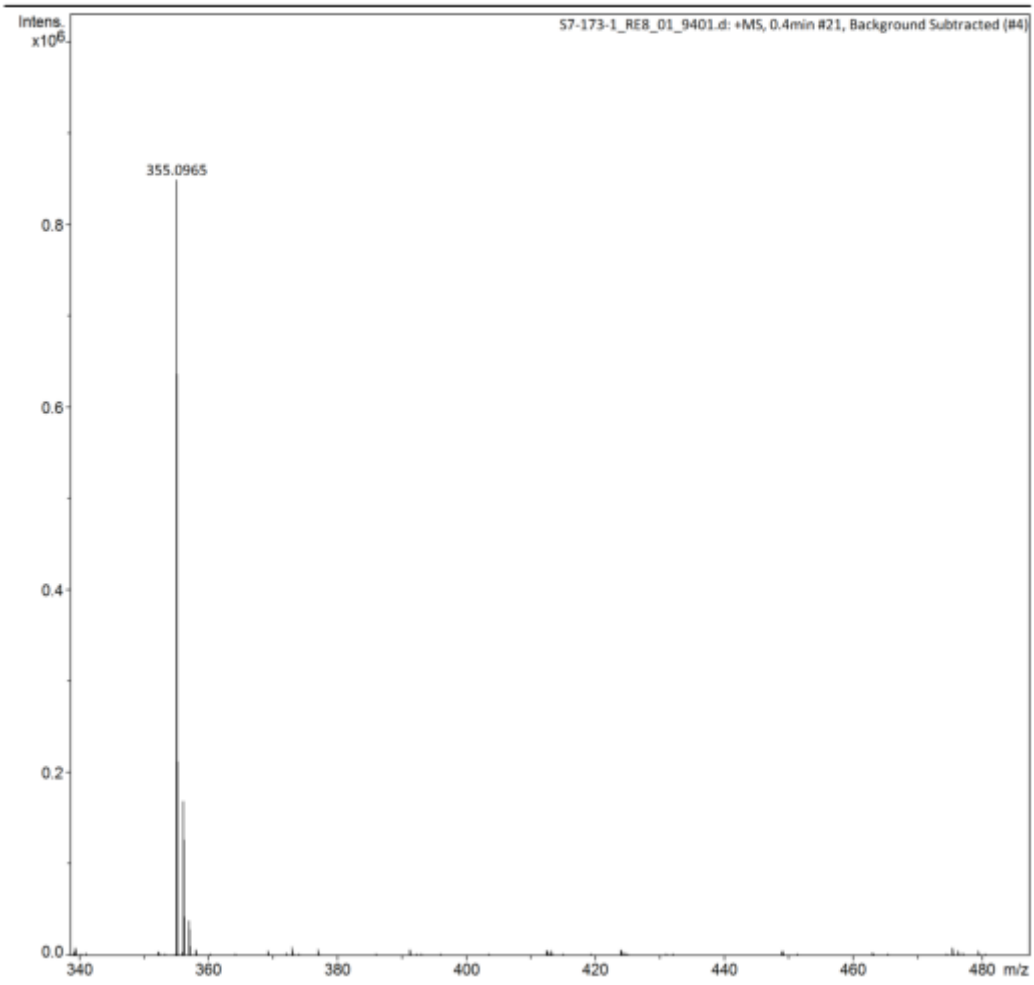


3h

Chemical Formula: $C_{18}H_{17}F_3O_2S$
Exact Mass: 354.0901
Molecular Weight: 354.3872
m/z: 354.0901 (100.0%), 355.0935 (19.5%), 356.0859 (4.5%), 356.0968 (1.8%)
Elemental Analysis: C, 61.01; H, 4.84; F, 16.08; O, 9.03; S, 9.05

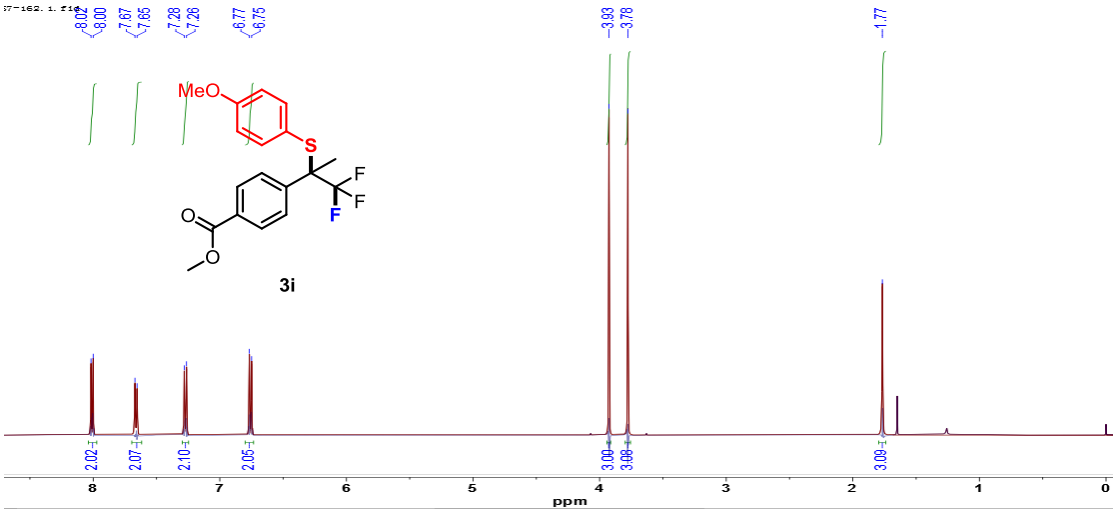
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

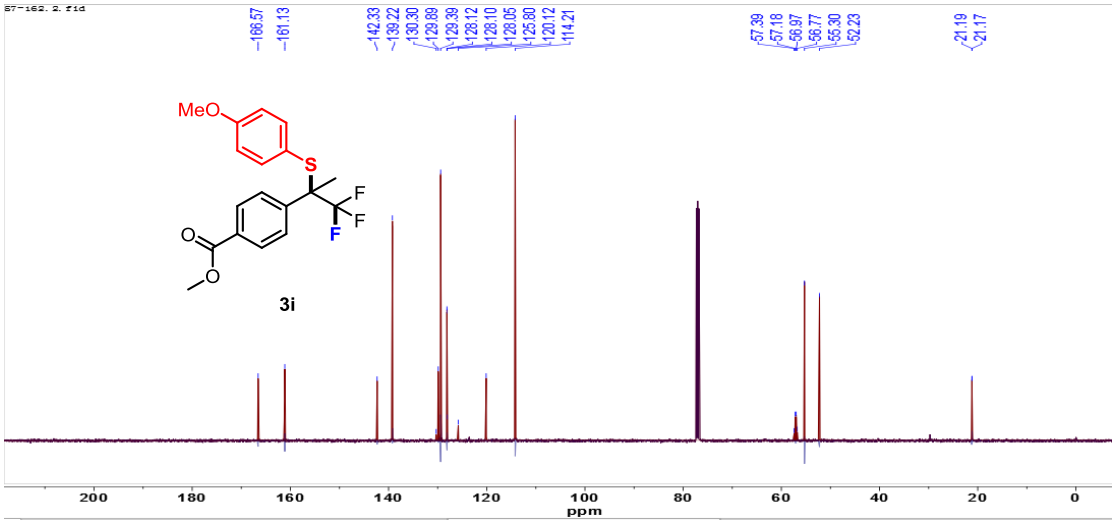


S7-173-1_RE8_01_9401.d

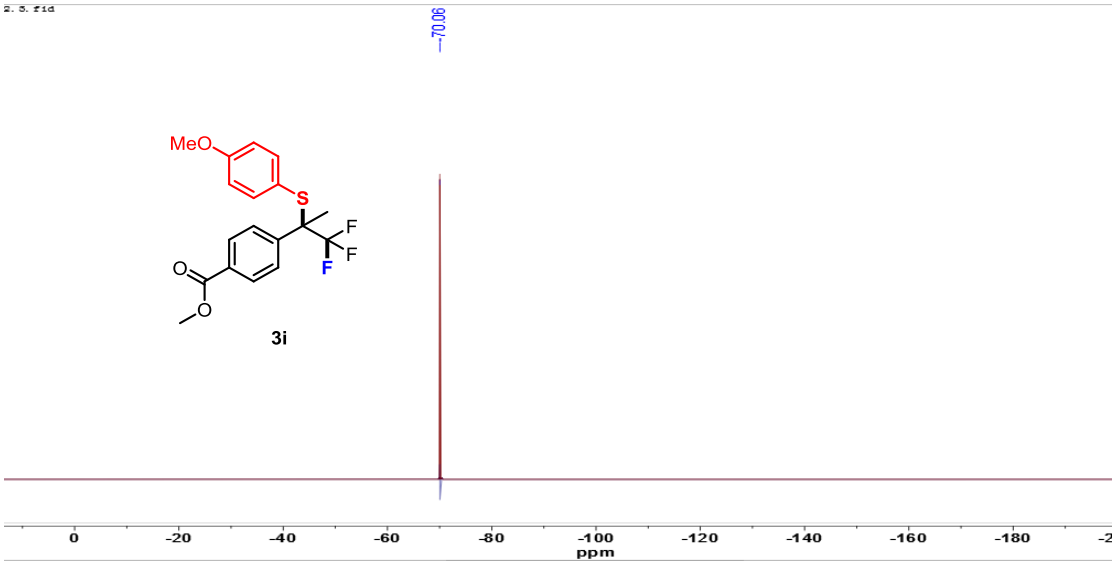
HRMS (ESI, m/z) calcd for $C_{18}H_{17}F_3O_2S$ $[M+H]^+$ 355.0974, found 355.0965.



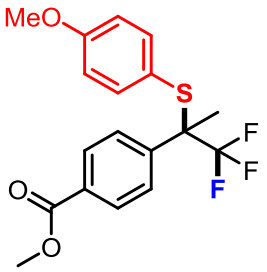
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



3i

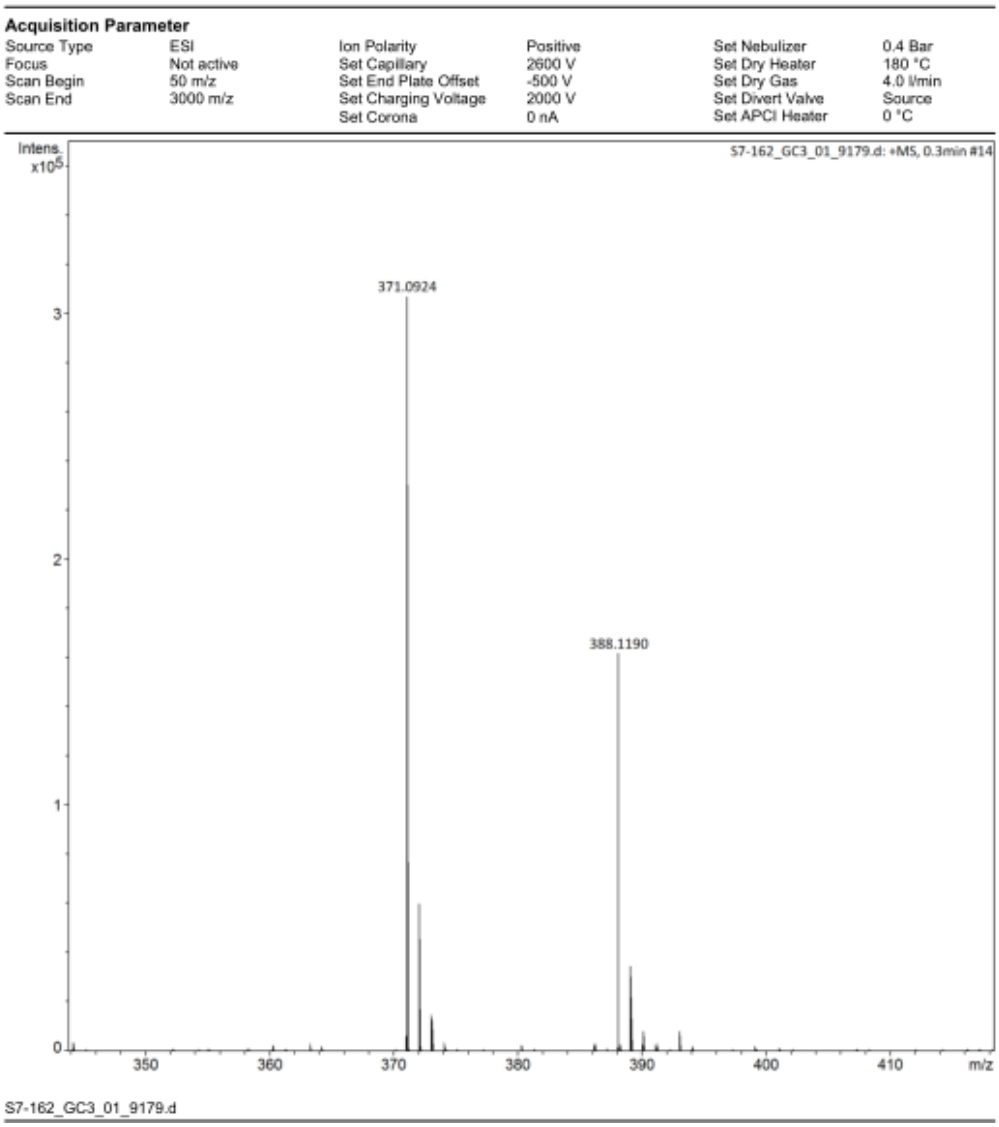
Chemical Formula: $C_{18}H_{17}F_3O_3S$

Exact Mass: 370.0850

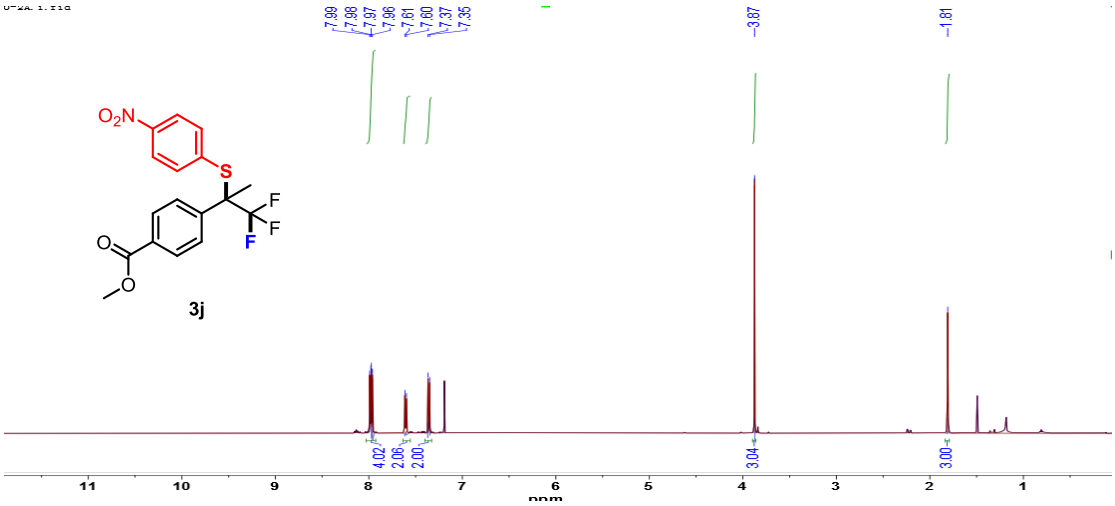
Molecular Weight: 370.3862

m/z: 370.0850 (100.0%), 371.0884 (19.5%), 372.0808 (4.5%), 372.0918 (1.8%)

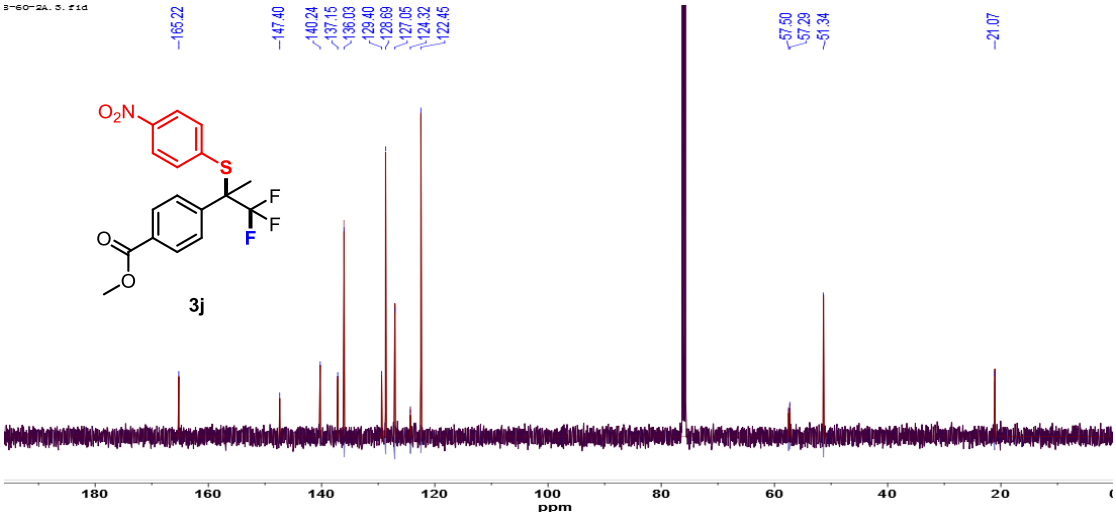
Elemental Analysis: C, 58.37; H, 4.63; F, 15.39; O, 12.96; S, 8.66



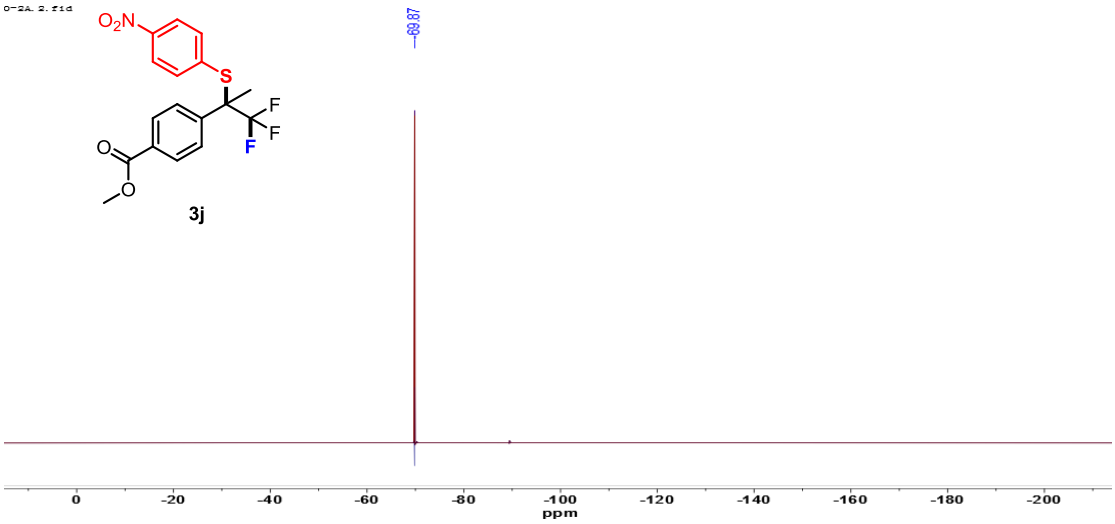
HRMS (ESI, m/z) calcd for $C_{18}H_{17}F_3O_3S$ $[M+H]^+$ 371.0923, found 371.0924.



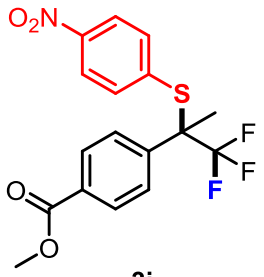
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$

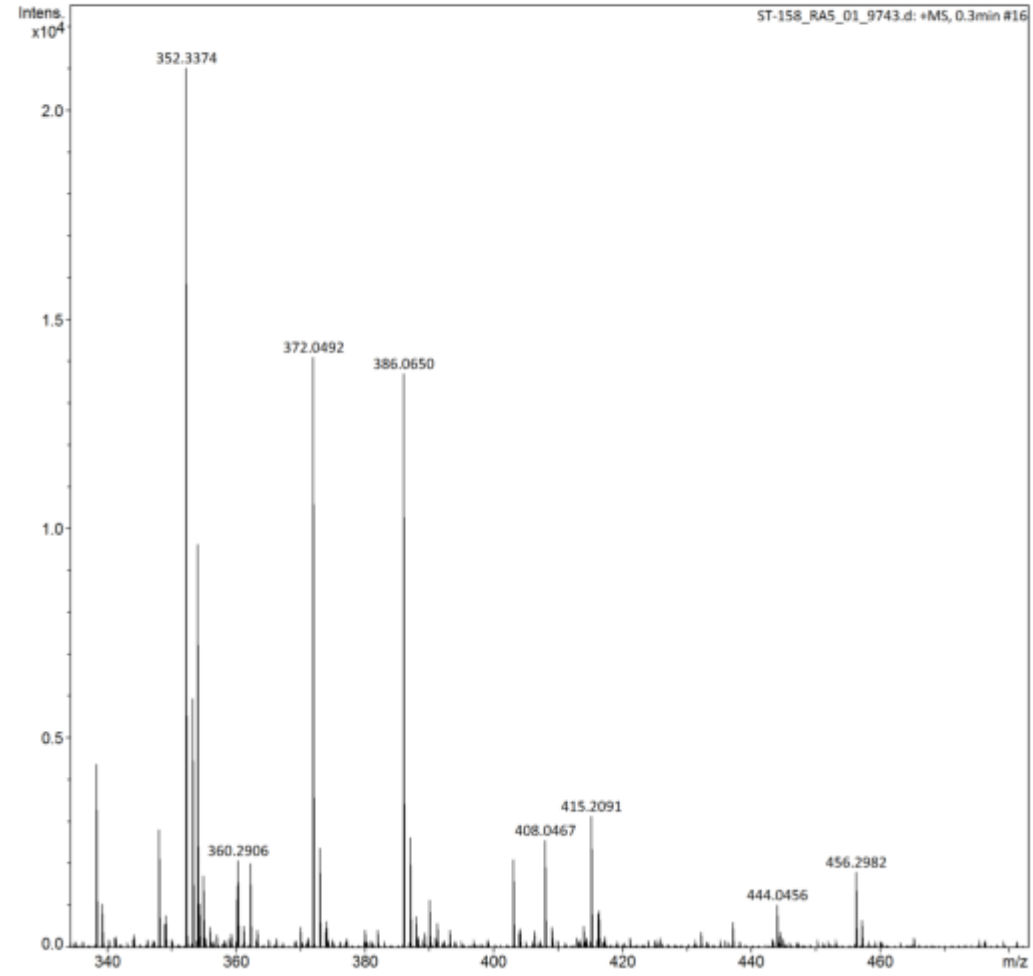


3j

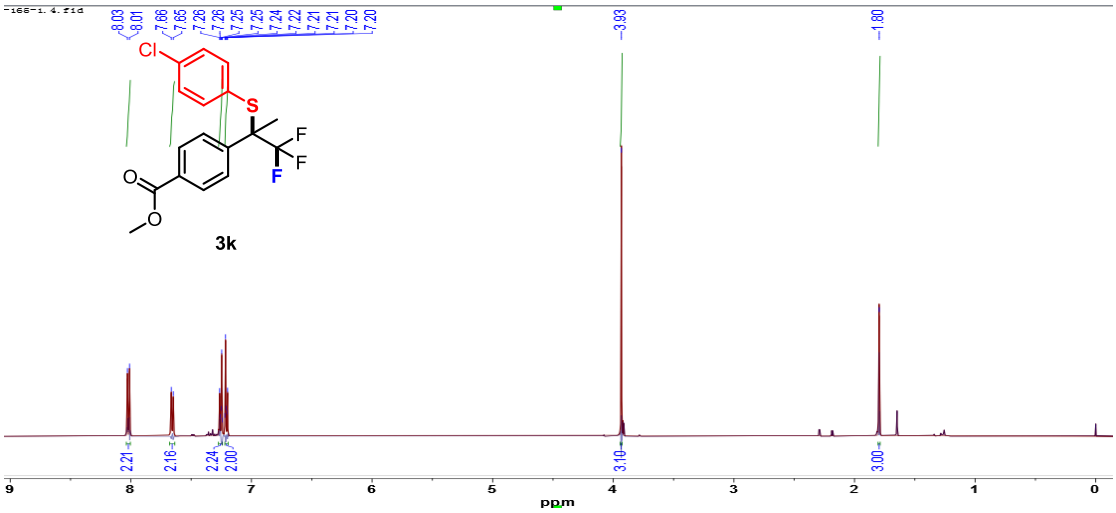
Chemical Formula: $C_{17}H_{14}F_3NO_4S$
Exact Mass: 385.0596
Molecular Weight: 385.3572
m/z: 385.0596 (100.0%), 386.0629 (18.4%), 387.0554 (4.5%), 387.0663 (1.6%)
Elemental Analysis: C, 52.99; H, 3.66; F, 14.79; N, 3.63; O, 16.61; S, 8.32

Acquisition Parameter

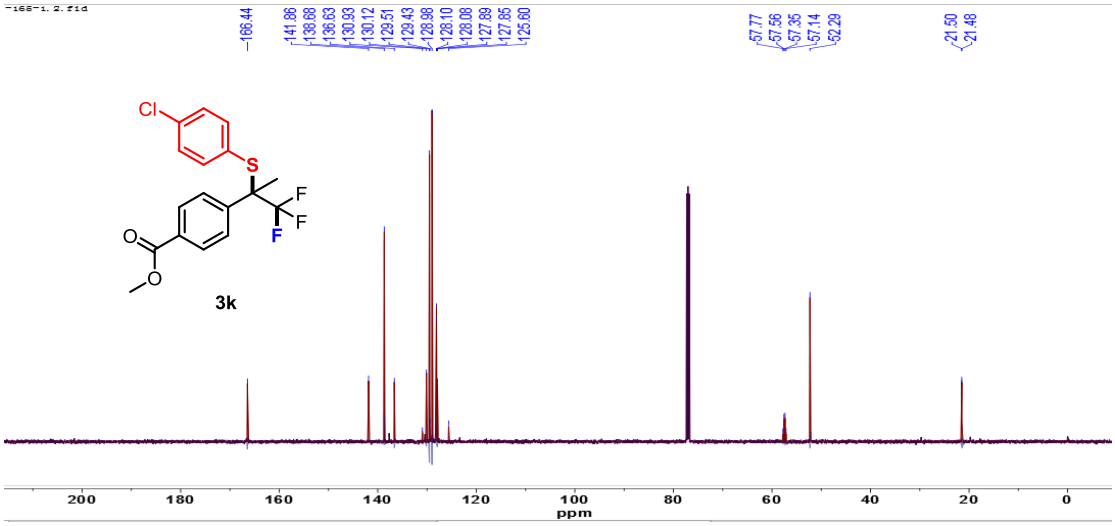
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



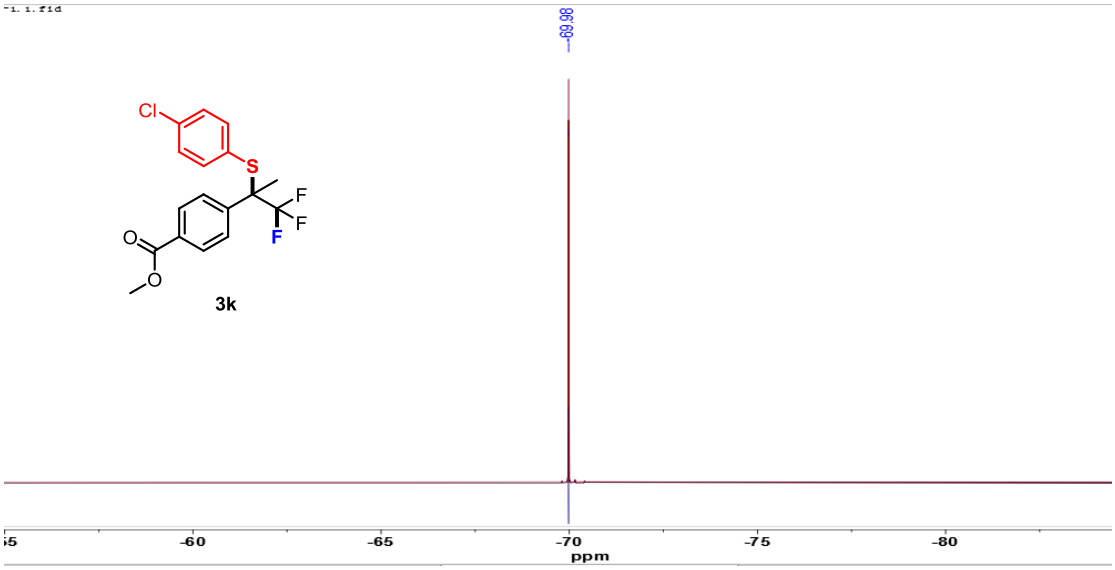
HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_4S$ $[M+H]^+$ 386.0668, found 386.0650.



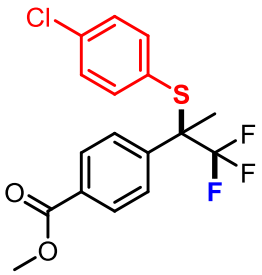
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



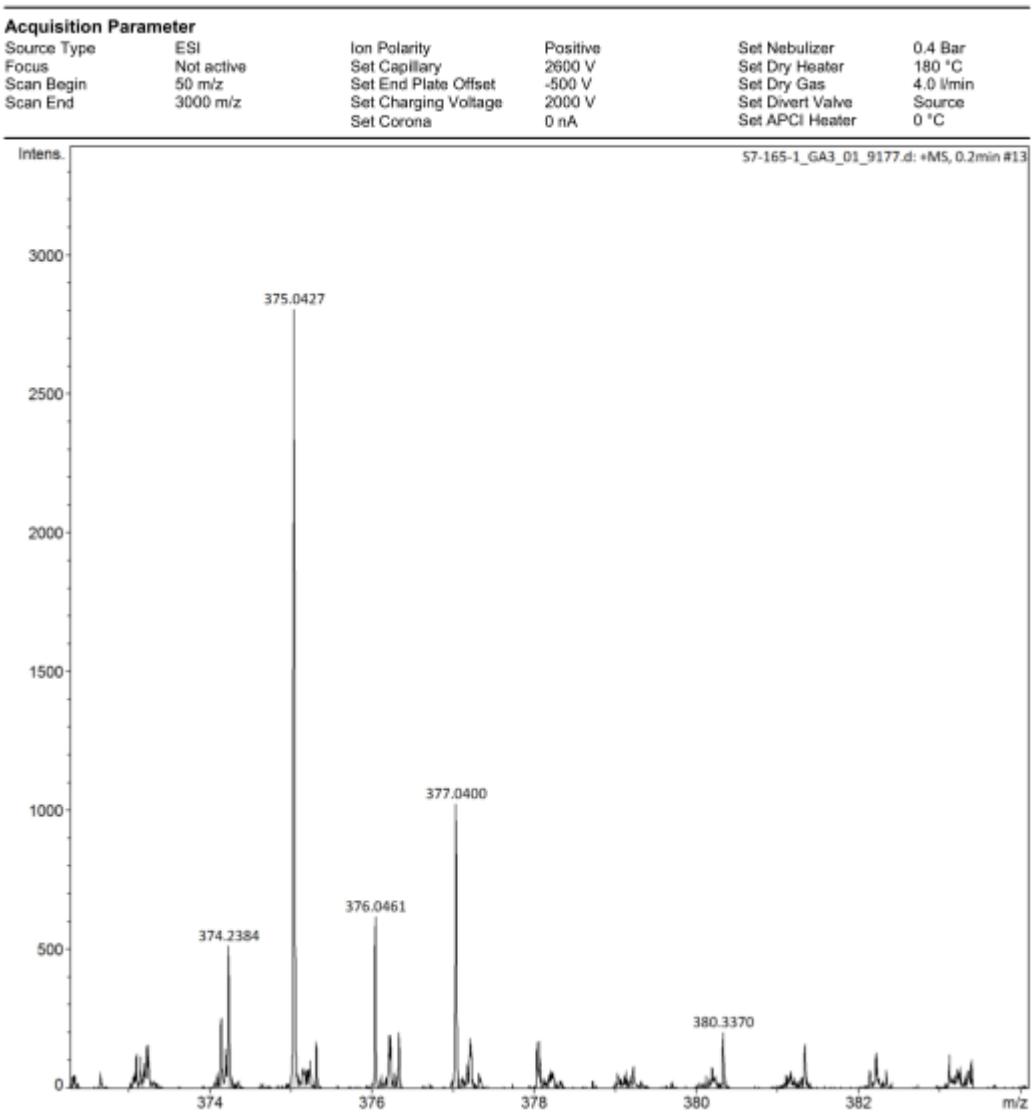
^{13}C NMR spectrum at 126 MHz in $CDCl_3$



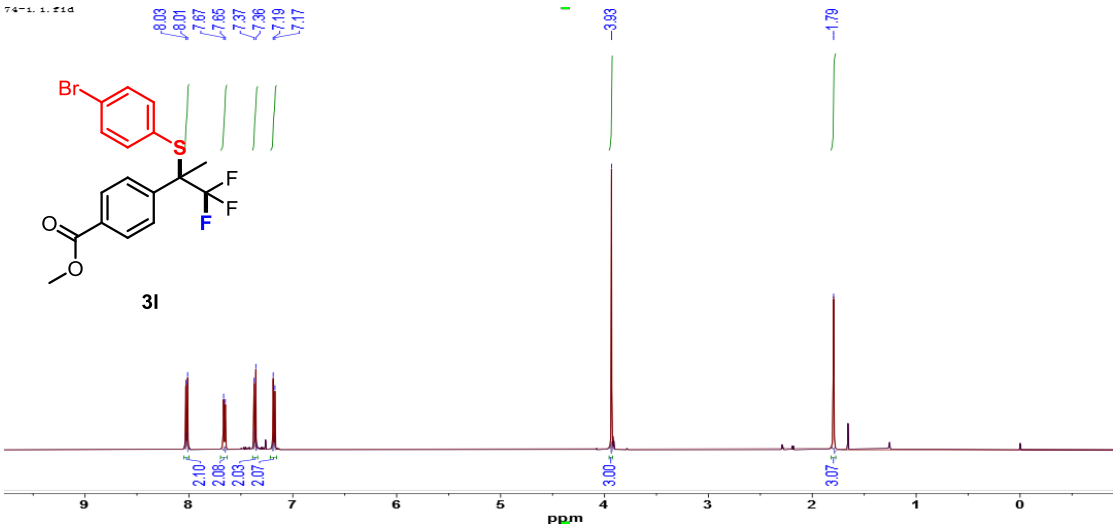
^{19}F NMR spectrum at 471 MHz in $CDCl_3$



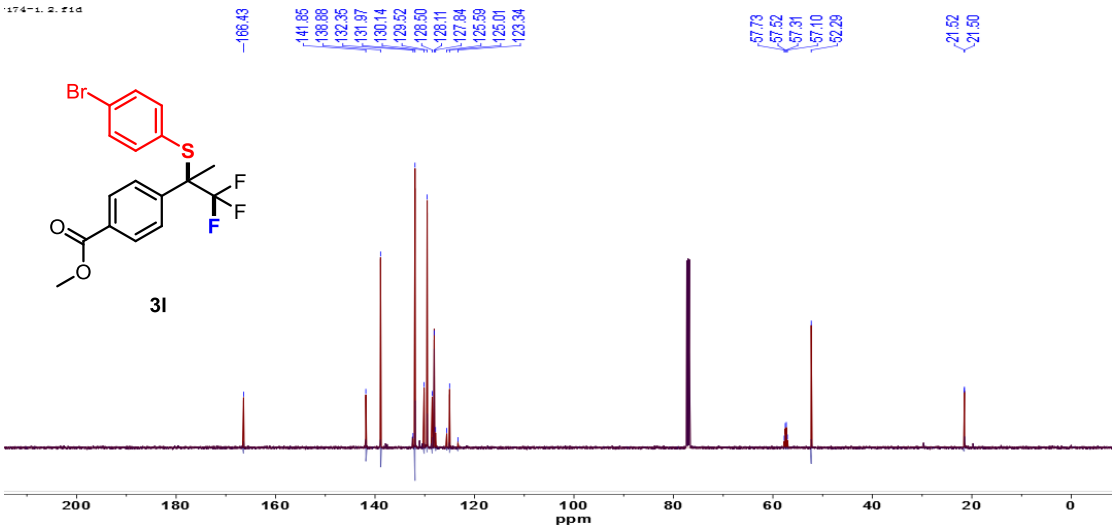
3k
Chemical Formula: $C_{17}H_{14}ClF_3O_2S$
Exact Mass: 374.0355
Molecular Weight: 374.8022
m/z: 374.0355 (100.0%), 376.0326 (32.0%), 375.0389 (18.4%), 377.0359 (5.9%), 376.0313 (4.5%), 376.0422 (1.6%), 378.0284 (1.4%)
Elemental Analysis: C, 54.48; H, 3.77; Cl, 9.46; F, 15.21; O, 8.54; S, 8.55



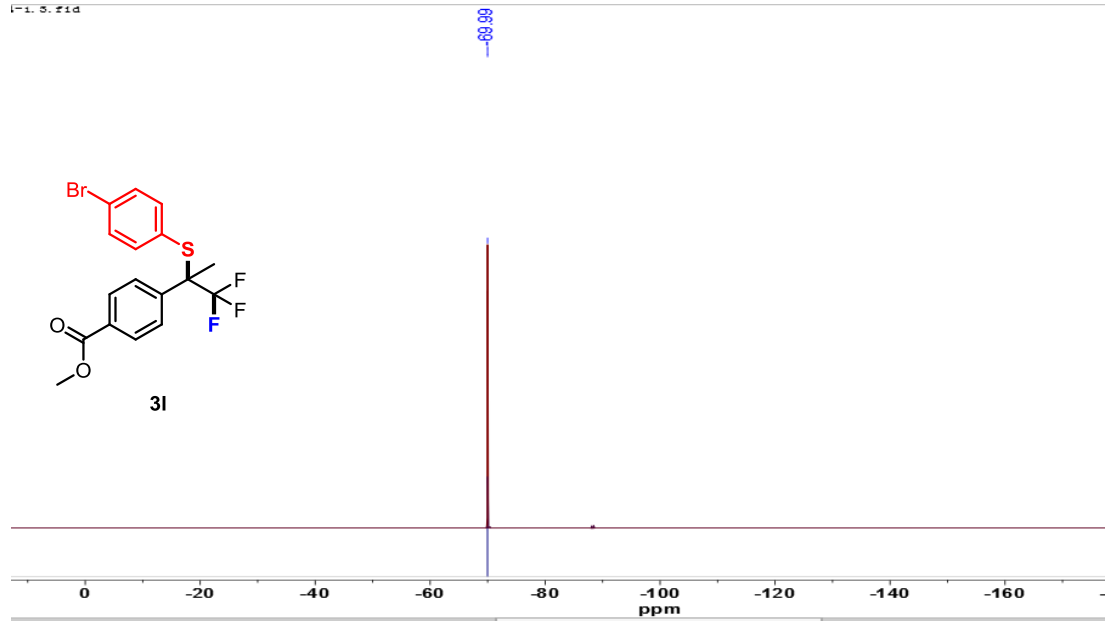
HRMS (ESI, m/z) calcd for $C_{17}H_{14}ClF_3O_2S$ $[M+H]^+$ 375.0428, found 375.0427.



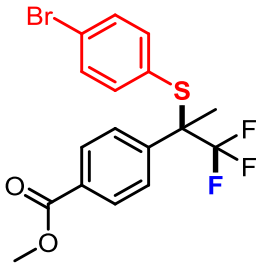
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



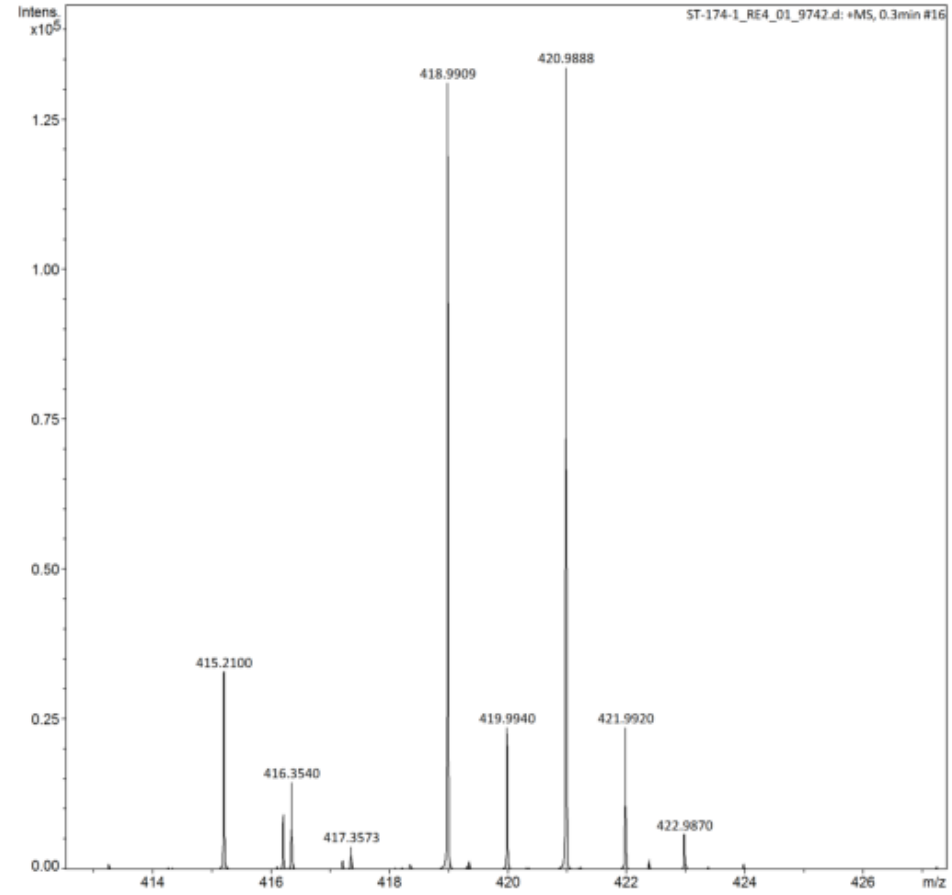
3l

Chemical Formula: $C_{17}H_{14}BrF_3O_2S$
Exact Mass: 417.9850
Molecular Weight: 419.2562
m/z: 417.9850 (100.0%), 419.9830 (97.3%), 420.9863 (17.9%), 418.9884 (16.2%), 419.9808 (4.5%), 421.9787 (4.4%), 418.9884 (2.2%), 421.9897 (1.2%), 419.9917 (1.1%)
Elemental Analysis: C, 48.70; H, 3.37; Br, 19.06; F, 13.59; O, 7.63; S, 7.65

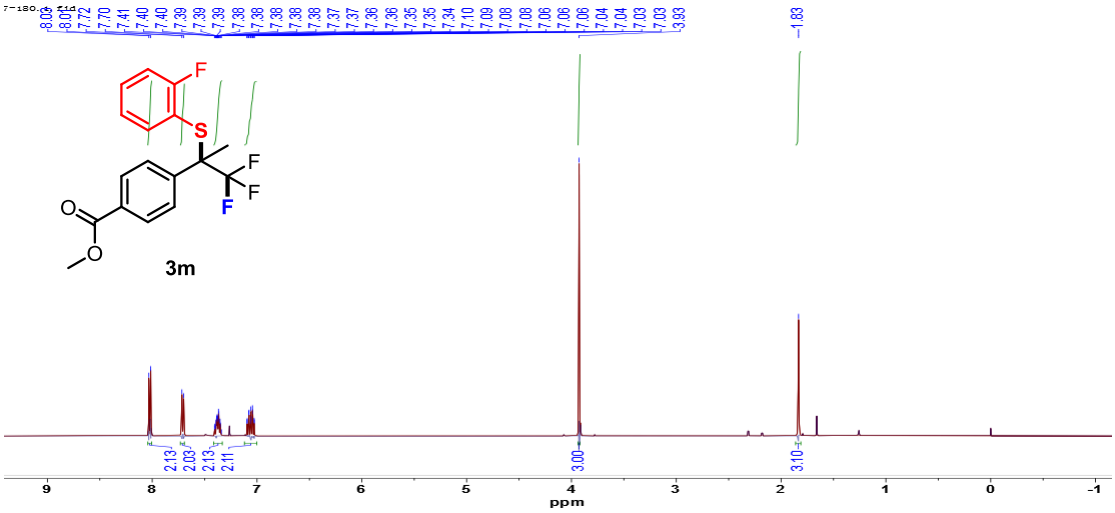
Sample Name ST-174-1 Instrument impact II 1825265.10256
Comment

Acquisition Parameter

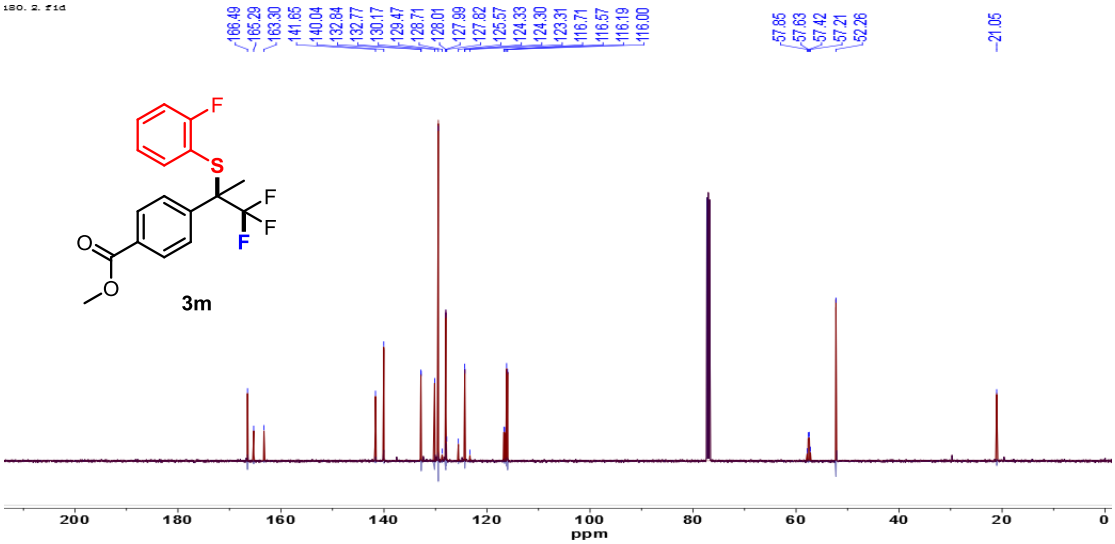
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



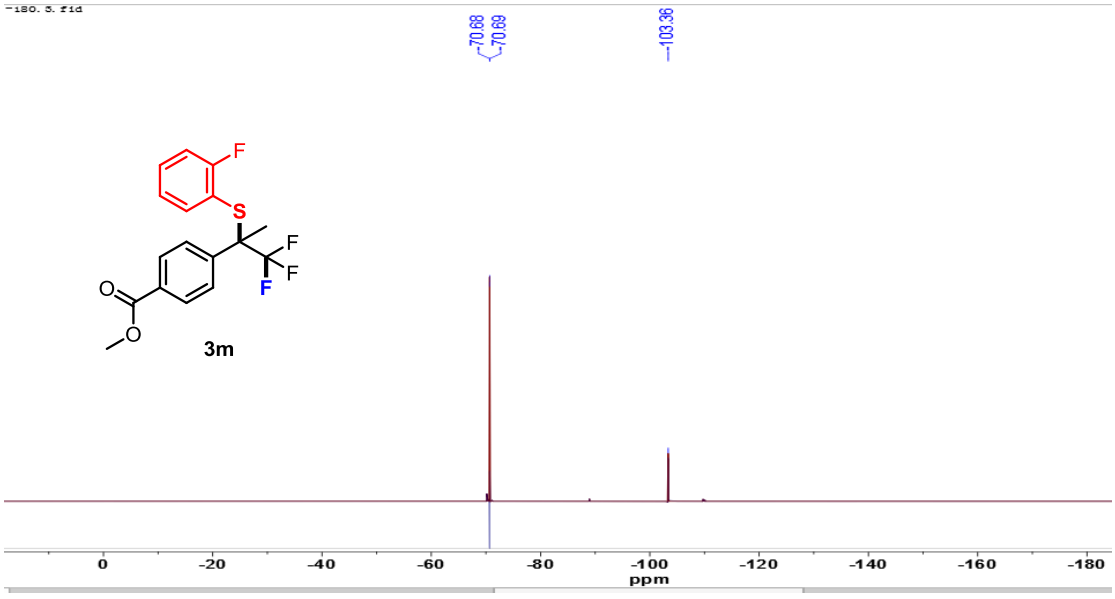
HRMS (ESI, m/z) calcd for $C_{17}H_{14}BrF_3O_2S$ $[M+H]^+$ 418.9923, found 418.9909.



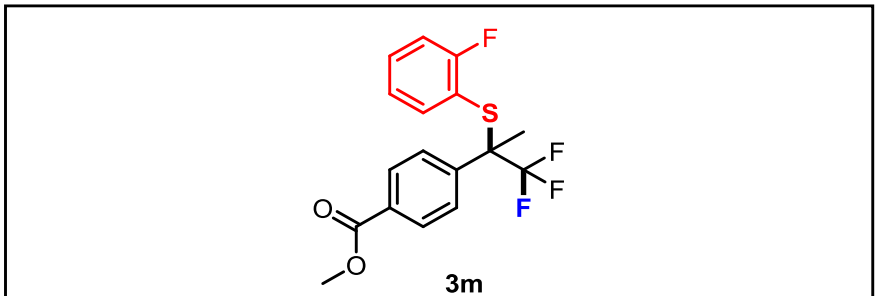
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$

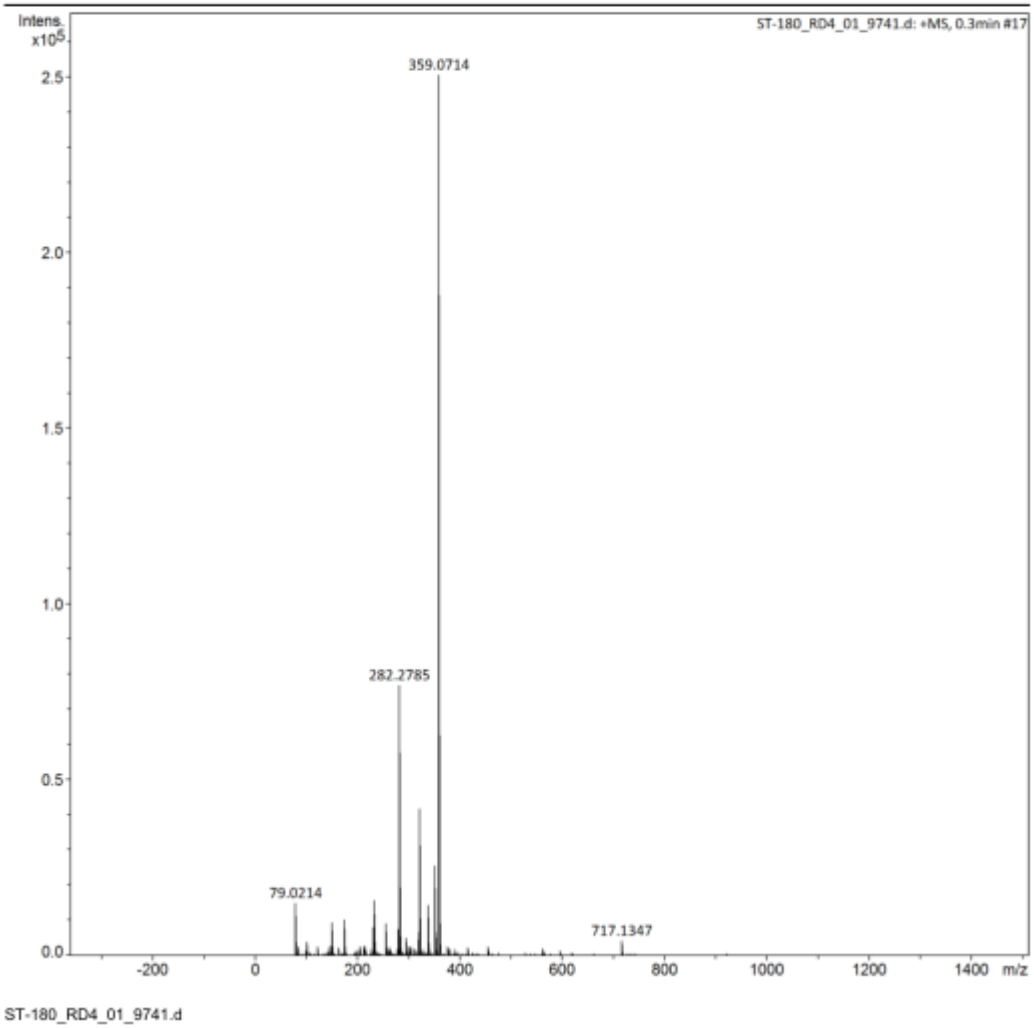


3m

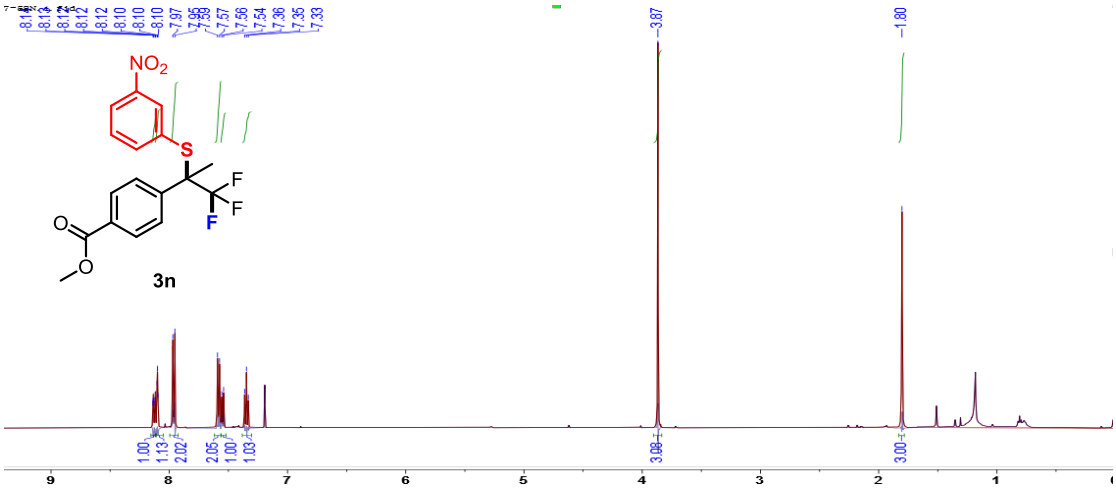
Chemical Formula: $C_{17}H_{14}F_4O_2S$
Exact Mass: 358.0651
Molecular Weight: 358.3506
m/z: 358.0651 (100.0%), 359.0684 (18.4%), 360.0609 (4.5%), 360.0718 (1.6%)
Elemental Analysis: C, 56.98; H, 3.94; F, 21.21; O, 8.93; S, 8.95

Acquisition Parameter

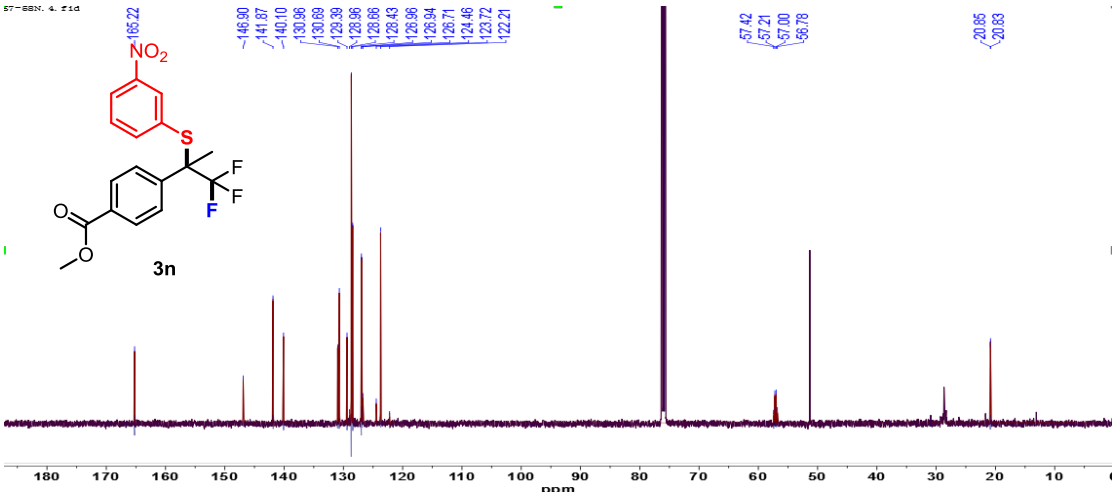
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



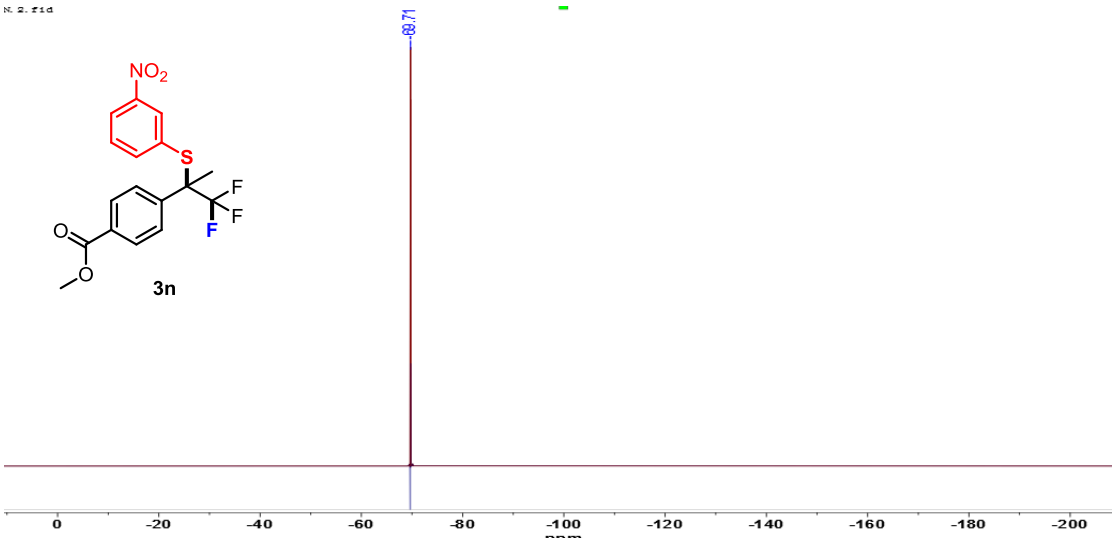
HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_4O_2S$ $[M+H]^+$ 359.0723, found 359.0714.



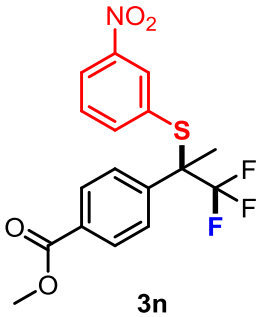
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$

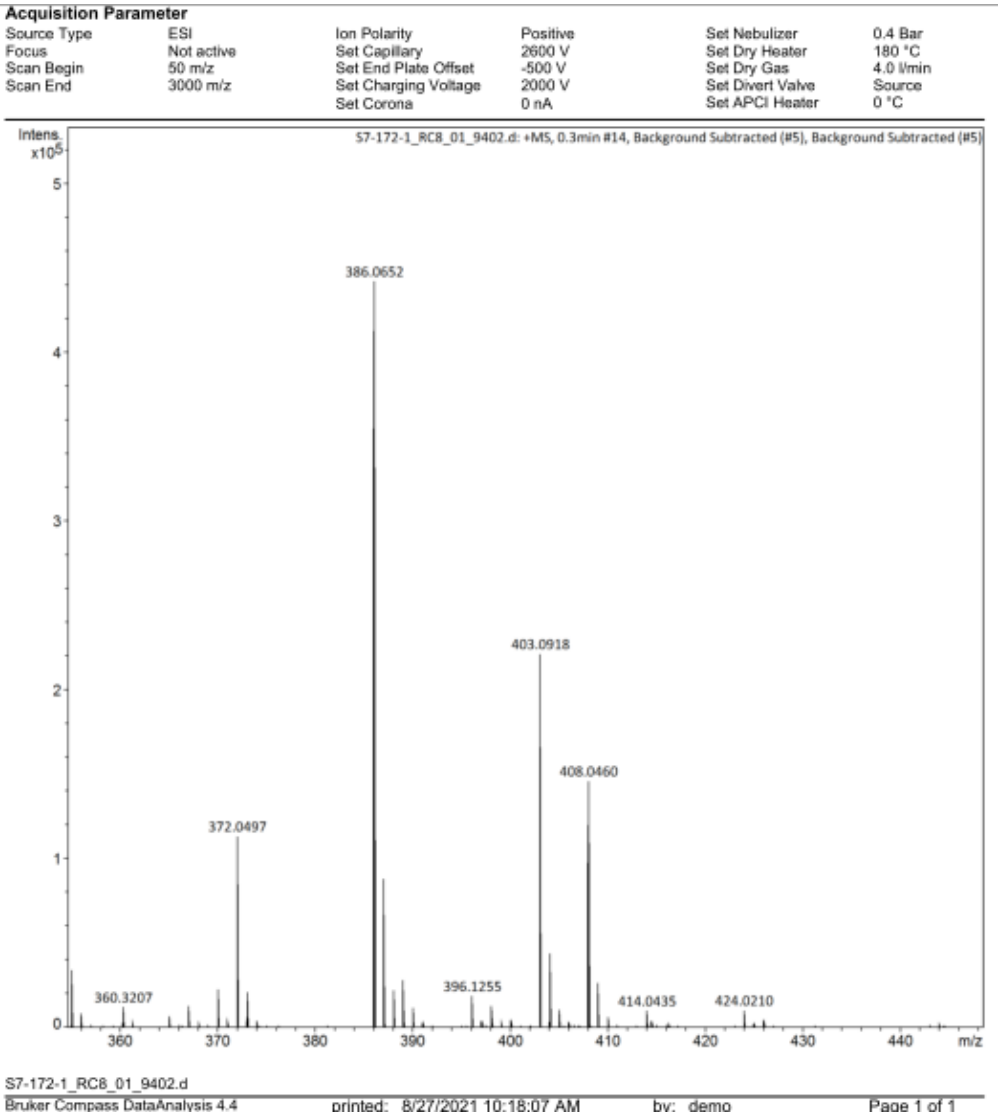


^{19}F NMR spectrum at 471 MHz in $CDCl_3$

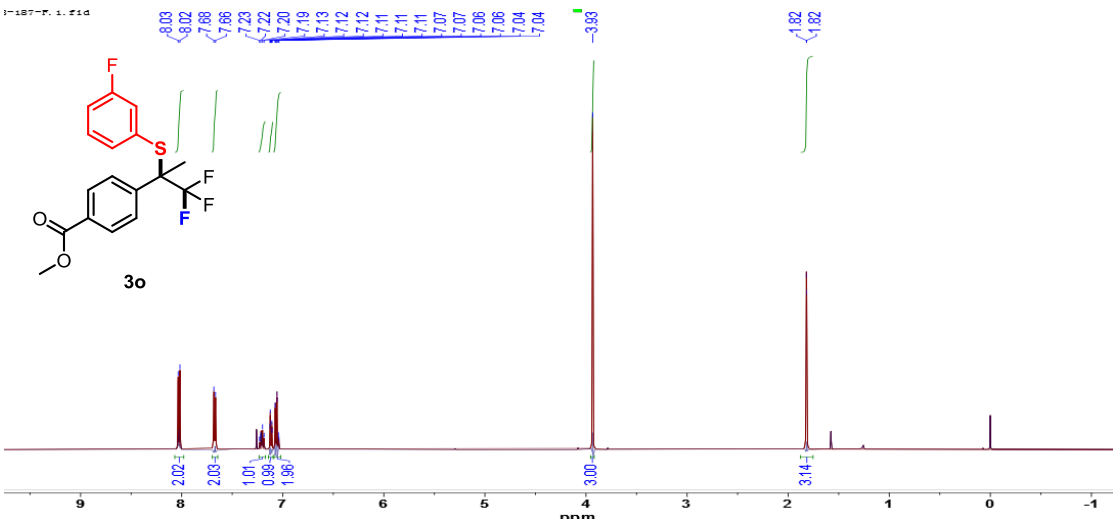


3n

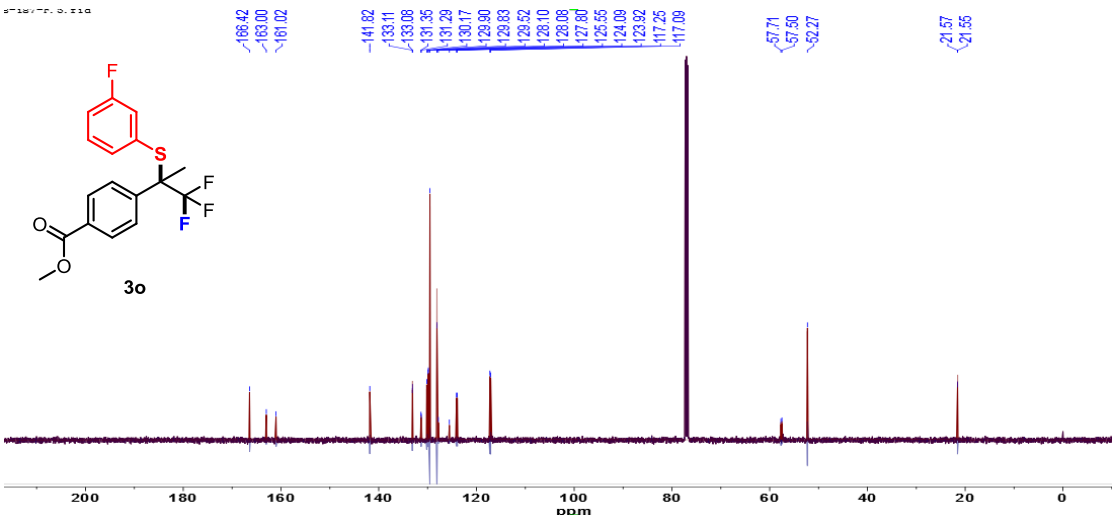
Chemical Formula: $C_{17}H_{14}F_3NO_4S$
Exact Mass: 385.0596
Molecular Weight: 385.3572
m/z: 385.0596 (100.0%), 386.0629 (18.4%), 387.0554 (4.5%), 387.0663 (1.6%)
Elemental Analysis: C, 52.99; H, 3.66; F, 14.79; N, 3.63; O, 16.61; S, 8.32



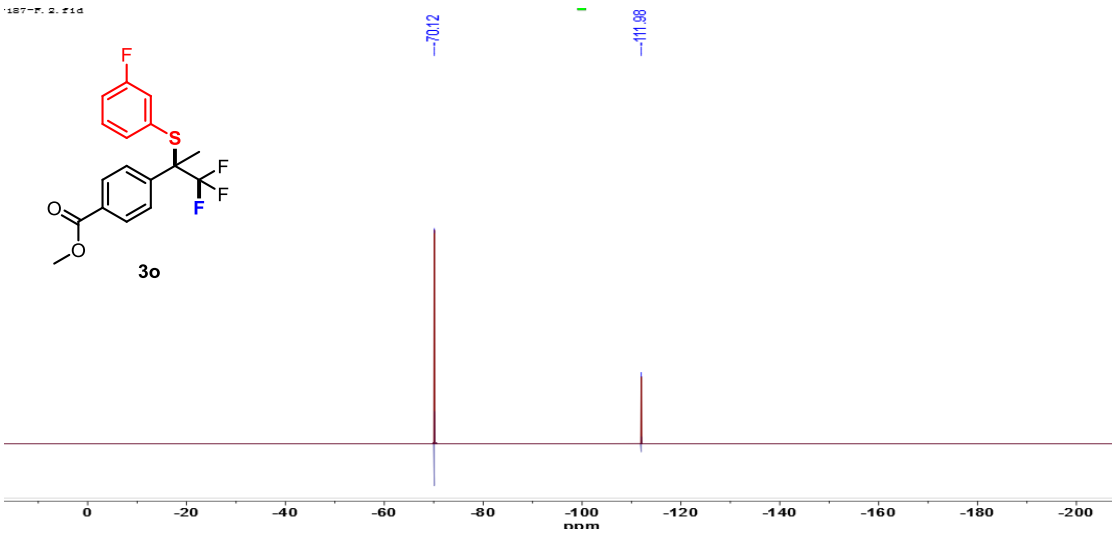
HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_4S$ $[M+H]^+$ 386.0668, found 386.0652.



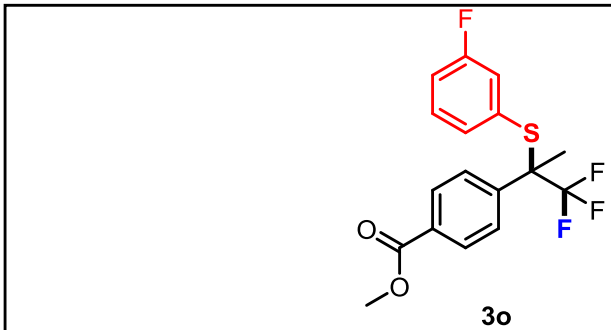
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



3o

Chemical Formula: $C_{17}H_{14}F_4O_2S$

Exact Mass: 358.0651

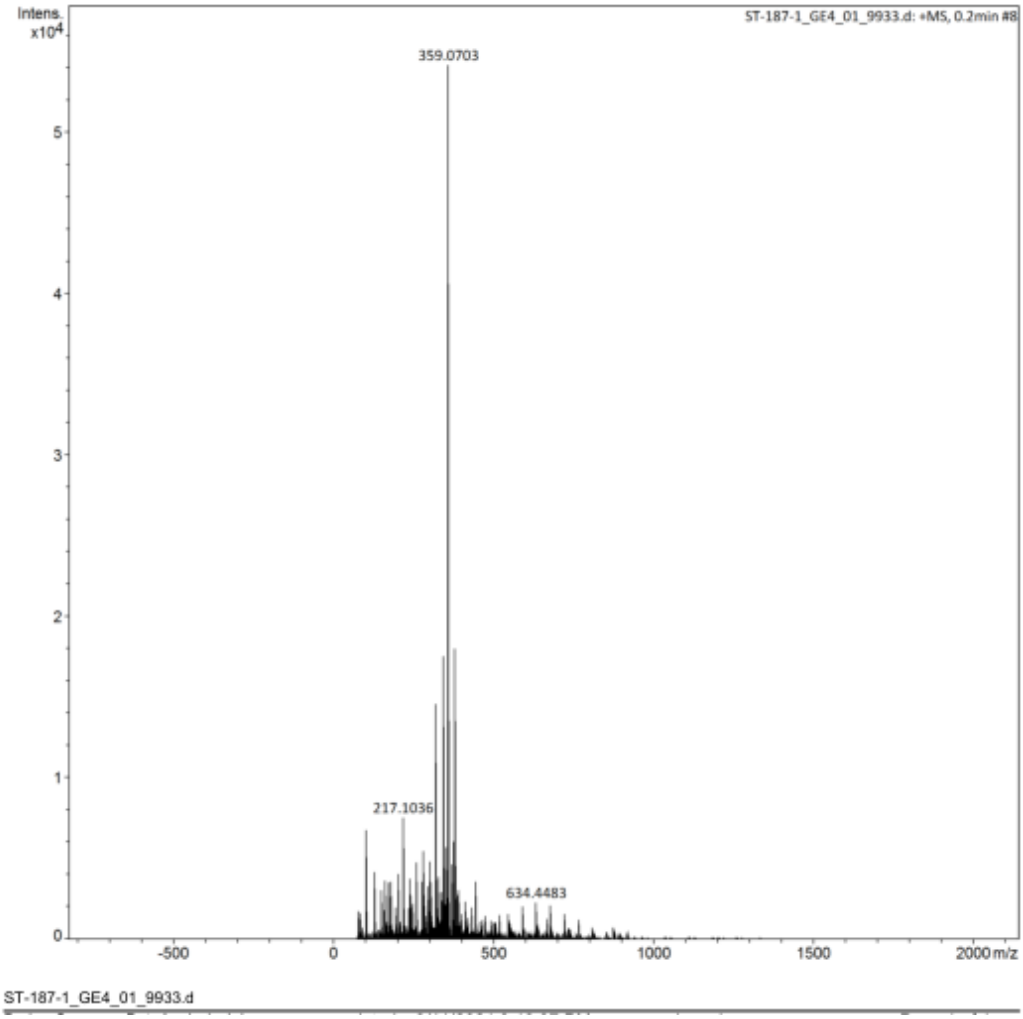
Molecular Weight: 358.3506

m/z: 358.0651 (100.0%), 359.0684 (18.4%), 360.0609 (4.5%), 360.0718 (1.6%)

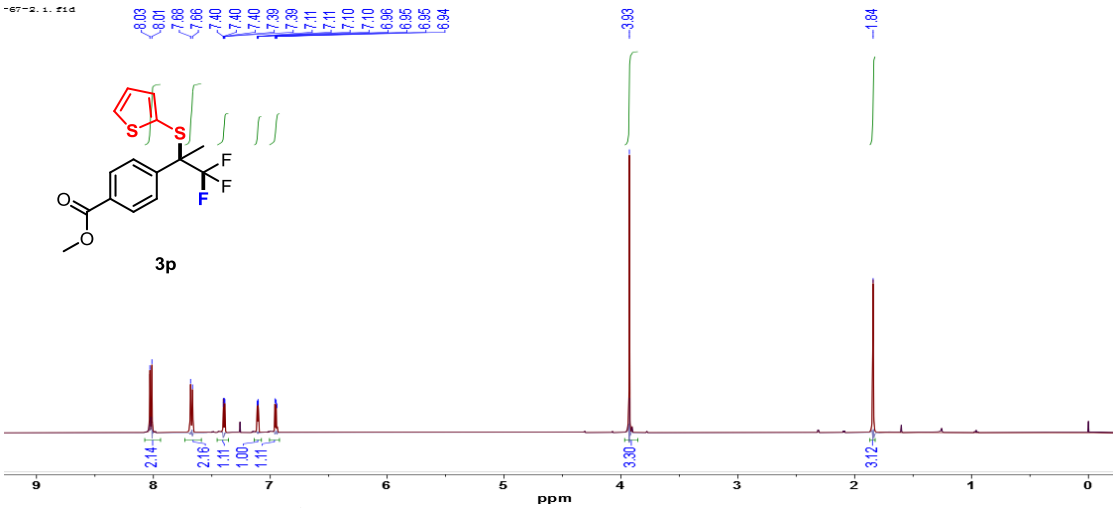
Elemental Analysis: C, 56.98; H, 3.94; F, 21.21; O, 8.93; S, 8.95

Acquisition Parameter

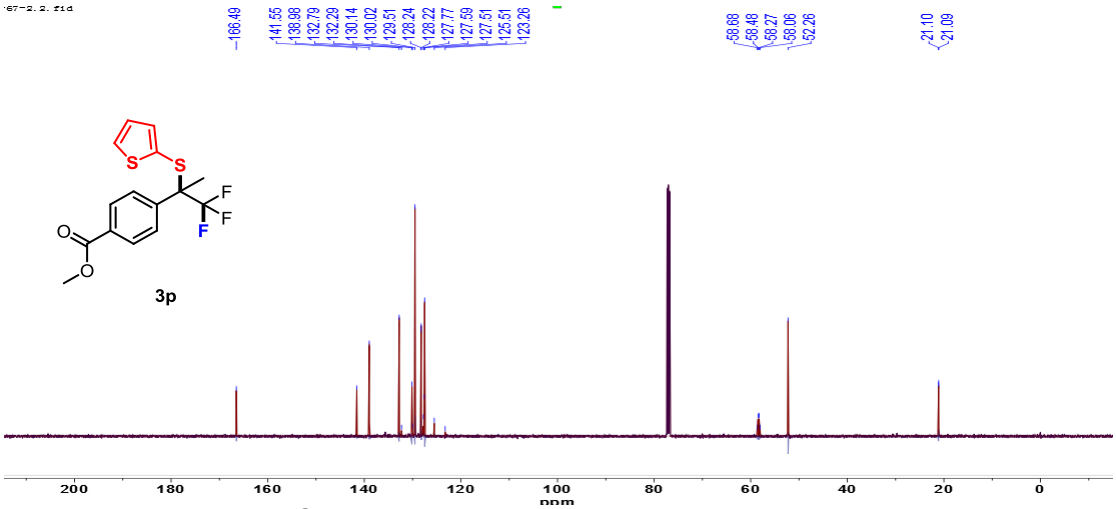
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



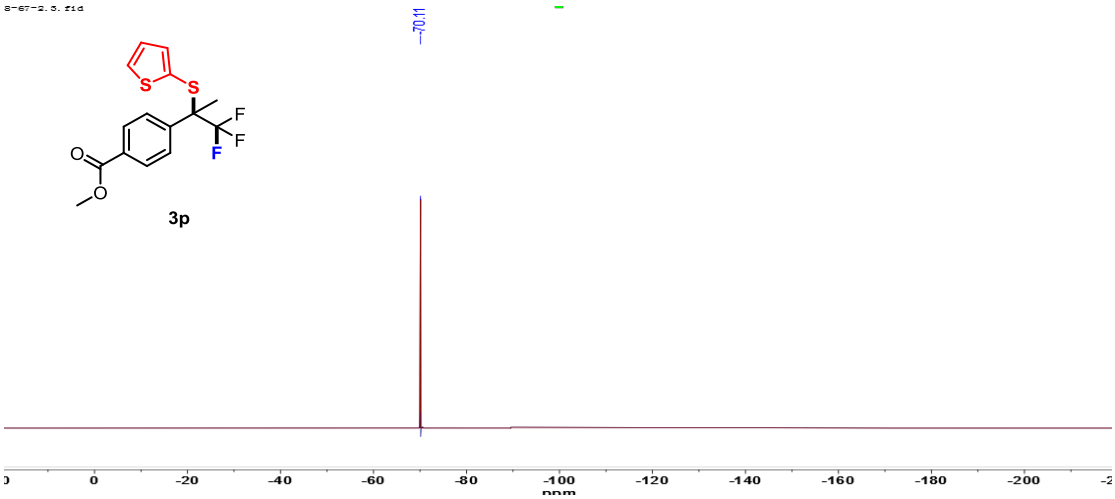
HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_4O_2S$ $[M+H]^+$ 359.0723, found 359.0703.



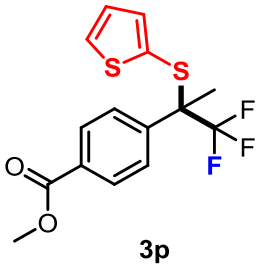
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



3p

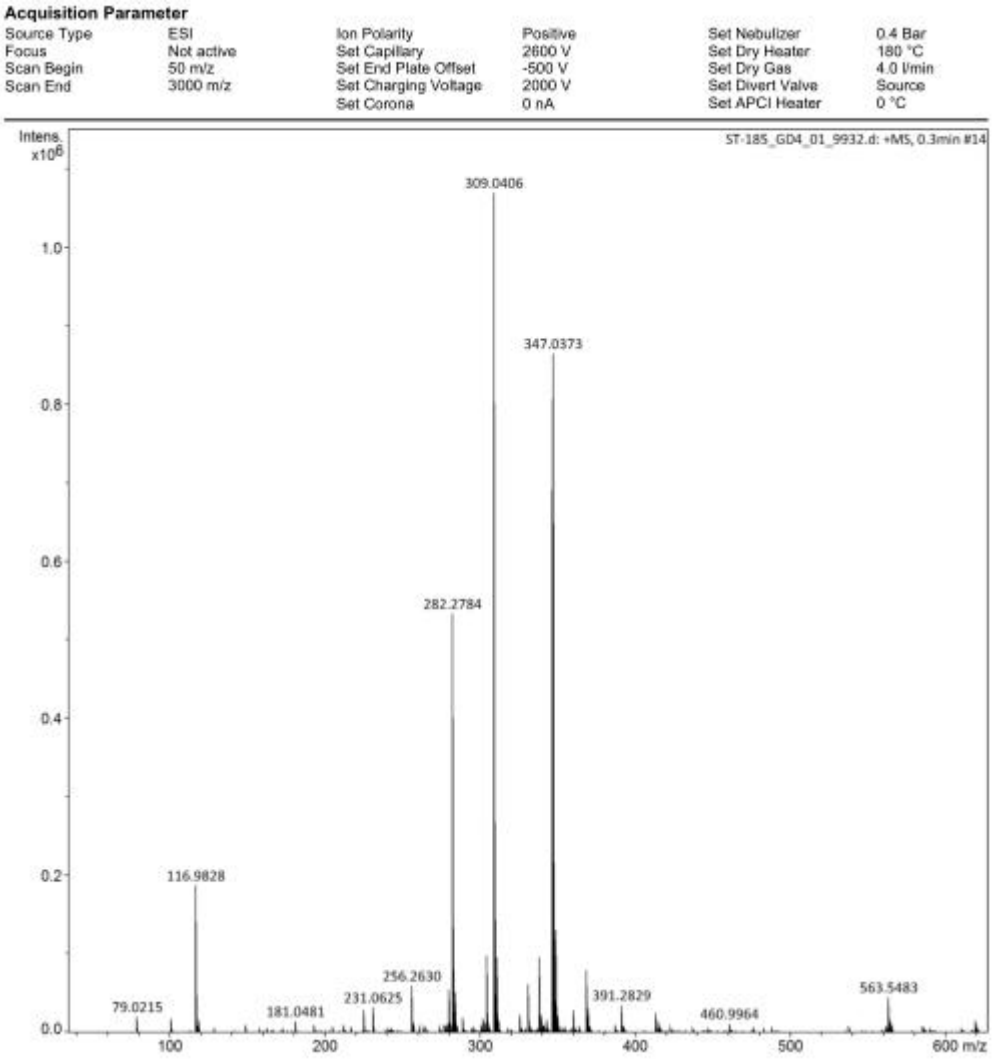
Chemical Formula: $C_{15}H_{13}F_3O_2S_2$

Exact Mass: 346.0309

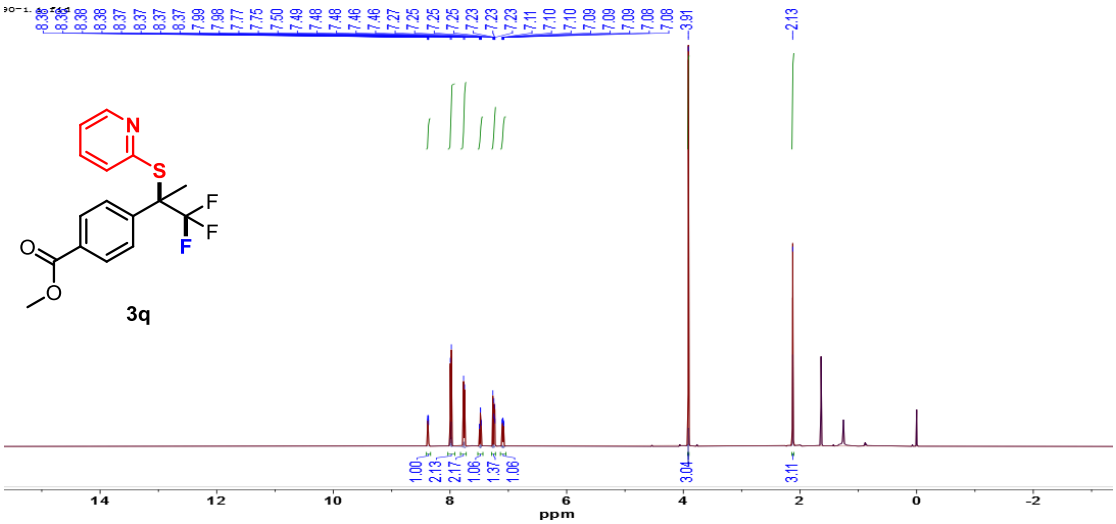
Molecular Weight: 346.3822

m/z: 346.0309 (100.0%), 347.0343 (16.2%), 348.0267 (9.0%), 347.0303 (1.6%),
349.0301 (1.5%), 348.0376 (1.2%)

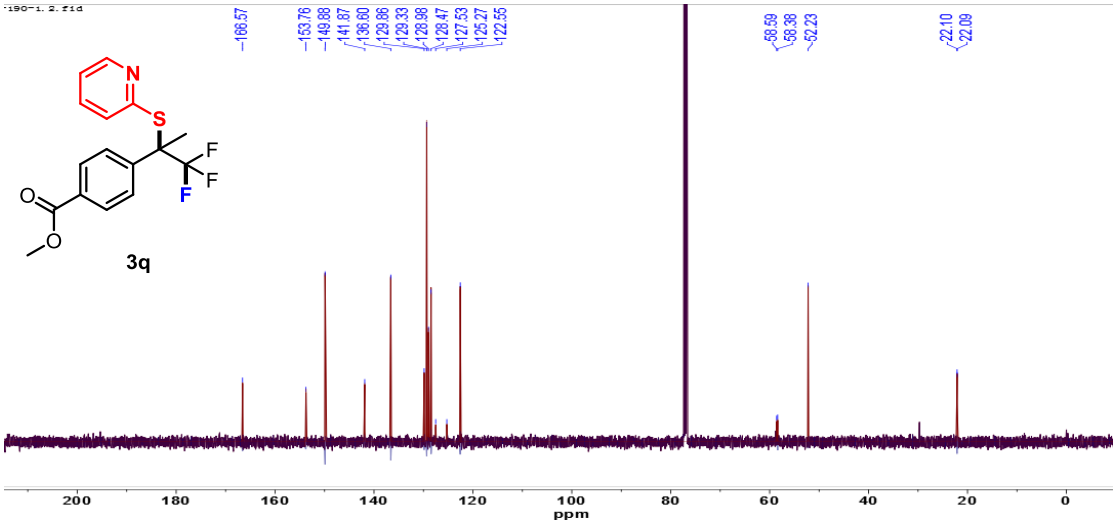
Elemental Analysis: C, 52.01; H, 3.78; F, 16.45; O, 9.24; S, 18.51



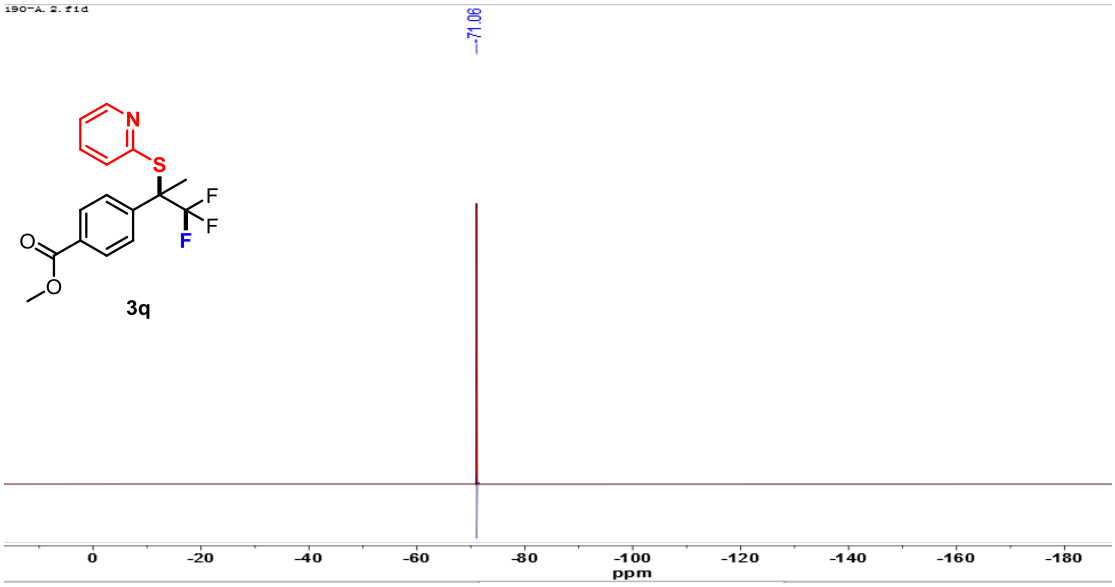
HRMS (ESI, m/z) calcd for $C_{15}H_{13}F_3O_2S_2$ $[M+H]^+$ 347.0382, found 347.0373.



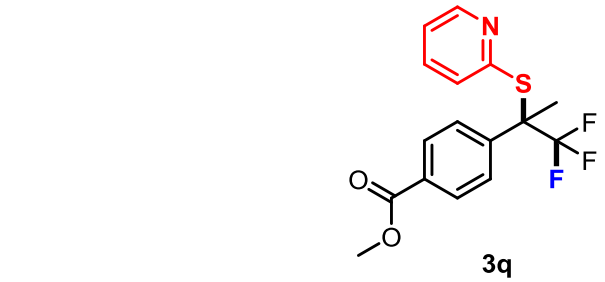
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



3q

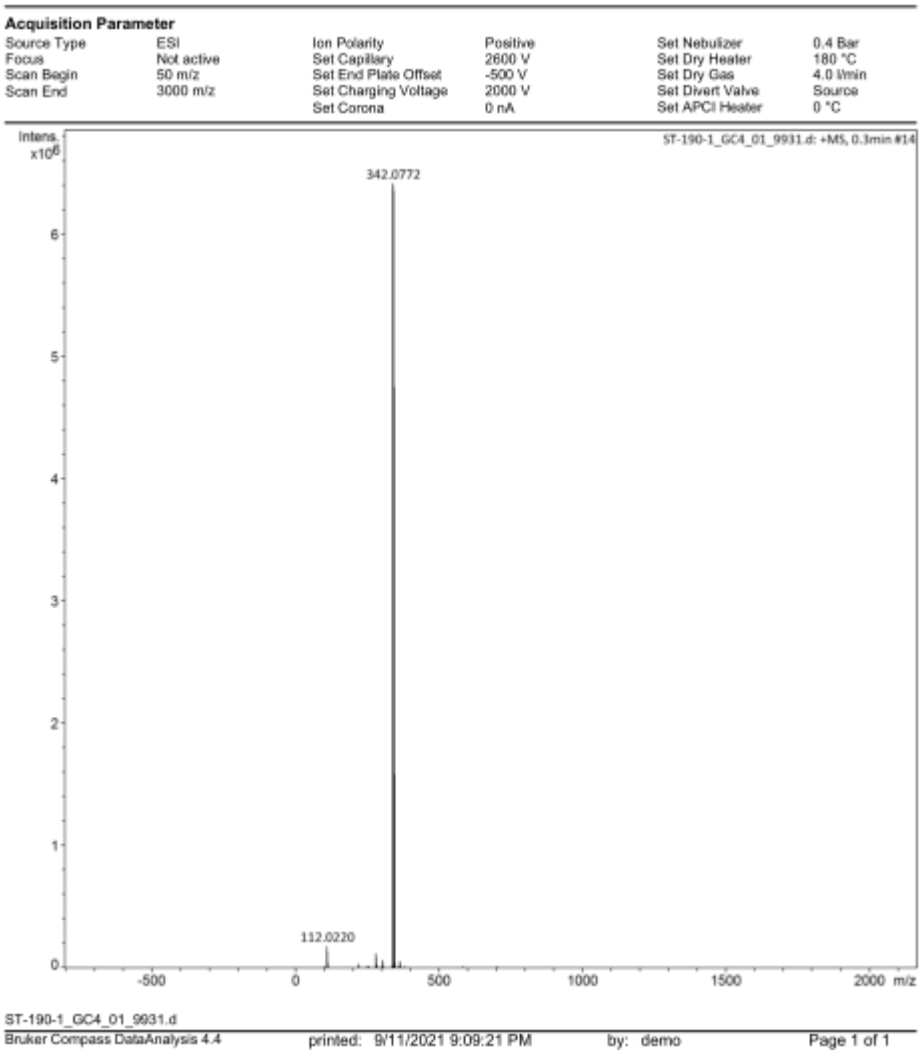
Chemical Formula: $C_{16}H_{14}F_3NO_2S$

Exact Mass: 341.0697

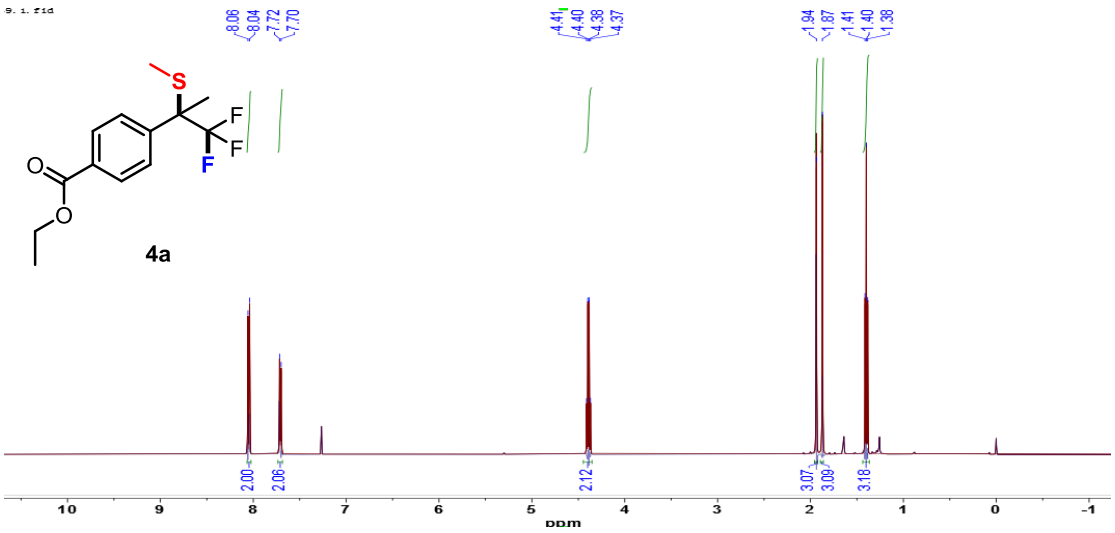
Molecular Weight: 341.3482

m/z: 341.0697 (100.0%), 342.0731 (17.3%), 343.0655 (4.5%), 343.0764 (1.4%)

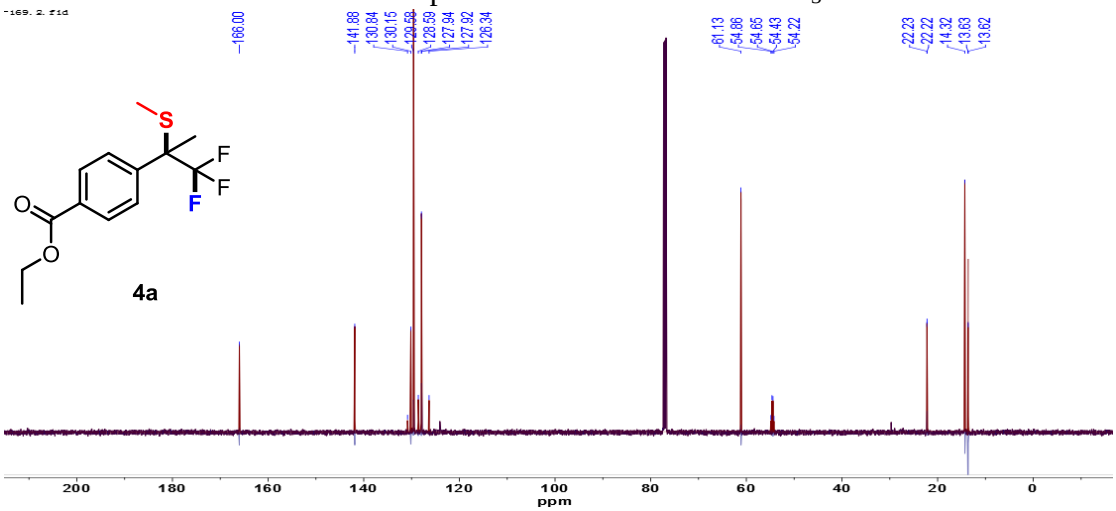
Elemental Analysis: C, 56.30; H, 4.13; F, 16.70; N, 4.10; O, 9.37; S, 9.39



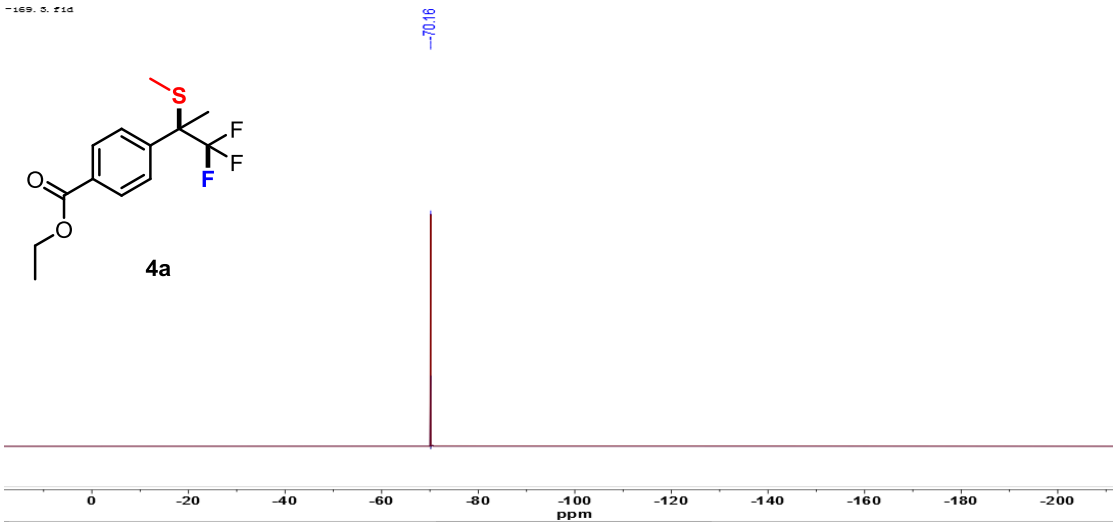
HRMS (ESI, m/z) calcd for $C_{16}H_{14}F_3NO_2S$ $[M+H]^+$ 342.0770, found 342.0772.



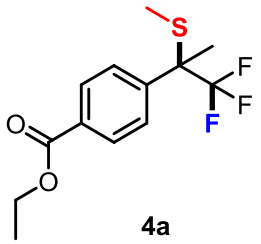
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$

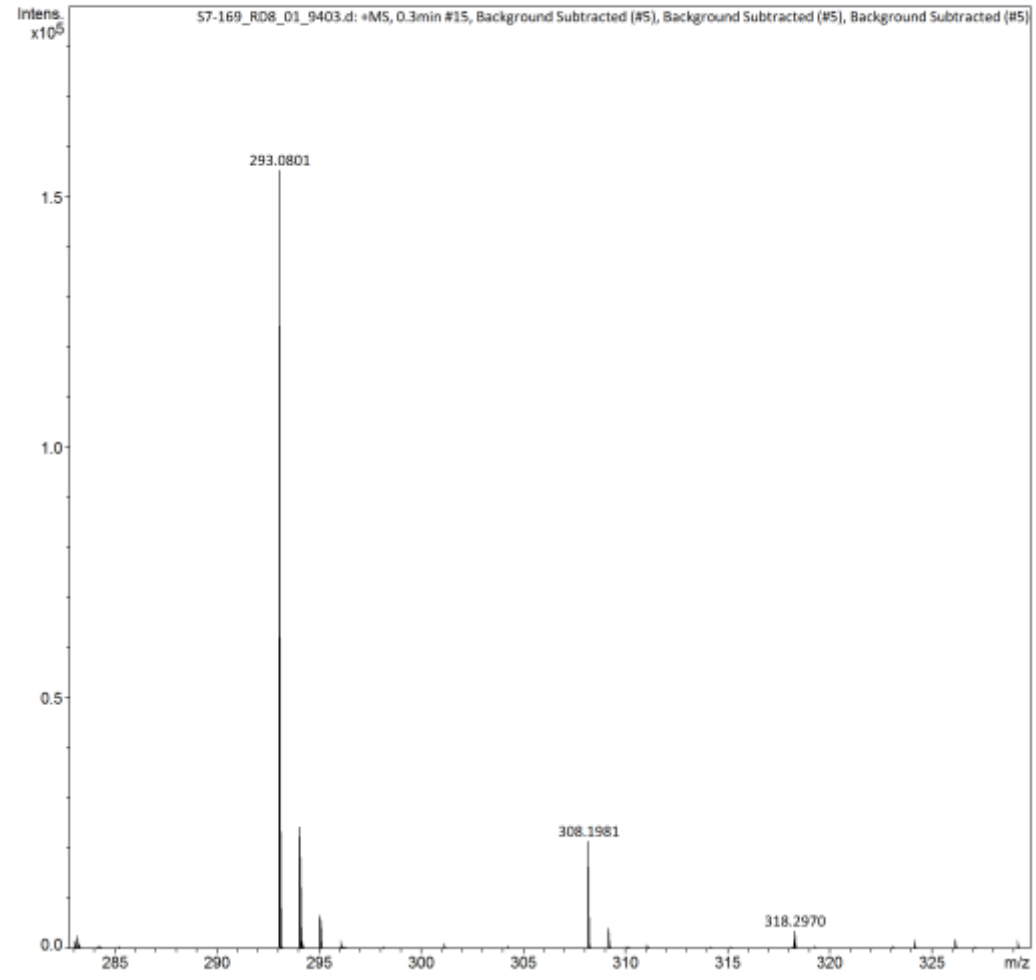


4a

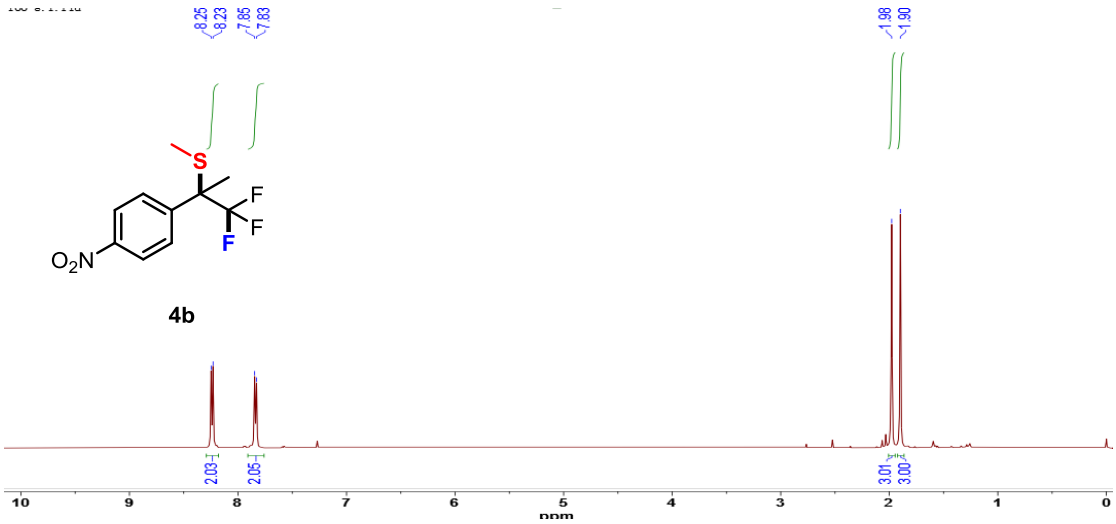
Chemical Formula: $C_{13}H_{15}F_3O_2S$
Exact Mass: 292.0745
Molecular Weight: 292.3162
m/z: 292.0745 (100.0%), 293.0778 (14.1%), 294.0703 (4.5%)
Elemental Analysis: C, 53.42; H, 5.17; F, 19.50; O, 10.95; S, 10.97

Acquisition Parameter

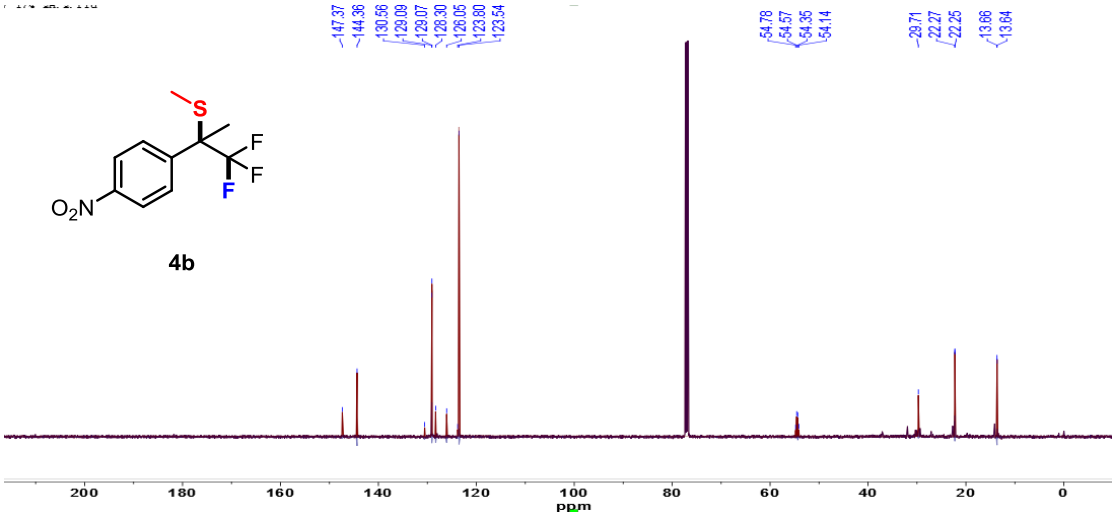
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



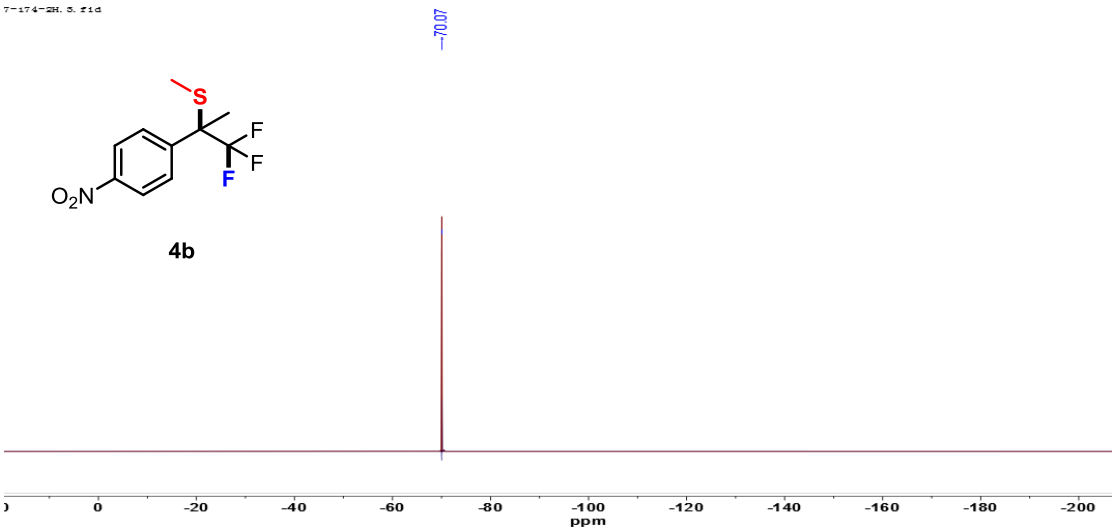
HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3O_2S$ $[M+H]^+$ 293.0818, found 293.0801.



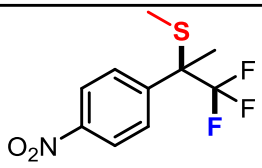
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$

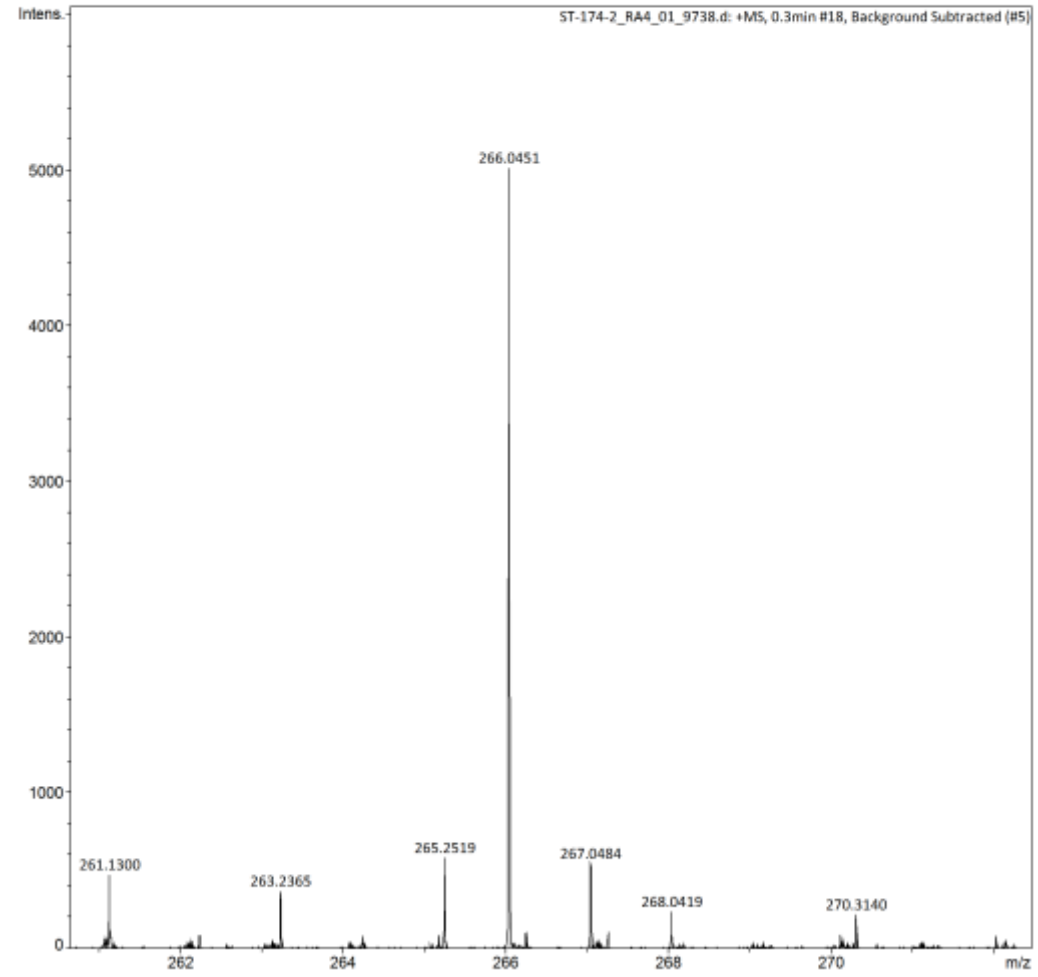


4b

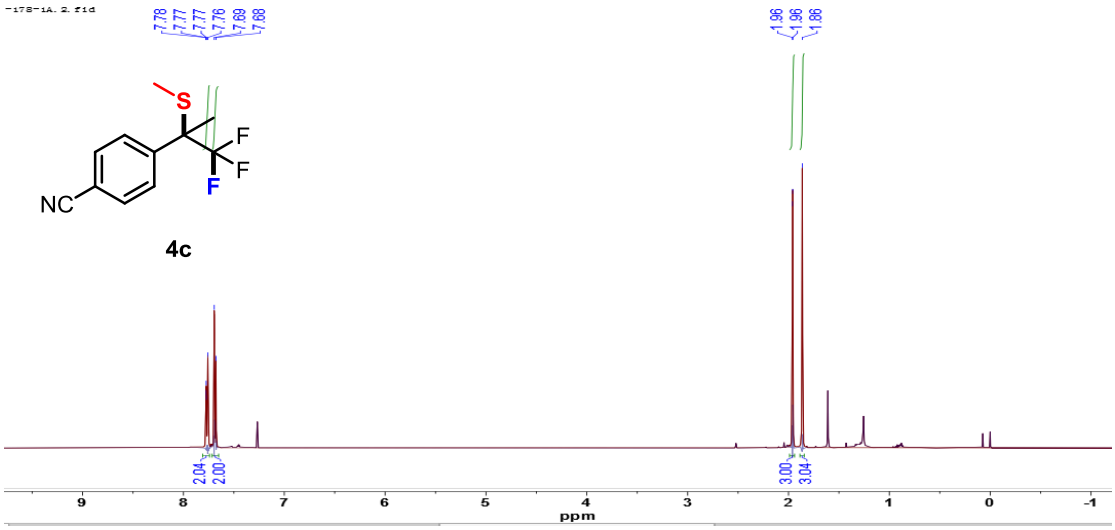
Chemical Formula: $C_{10}H_{10}F_3NO_2S$
Exact Mass: 265.0384
Molecular Weight: 265.2502
m/z: 265.0384 (100.0%), 266.0418 (10.8%), 267.0342 (4.5%)
Elemental Analysis: C, 45.28; H, 3.80; F, 21.49; N, 5.28; O, 12.06; S, 12.09

Acquisition Parameter

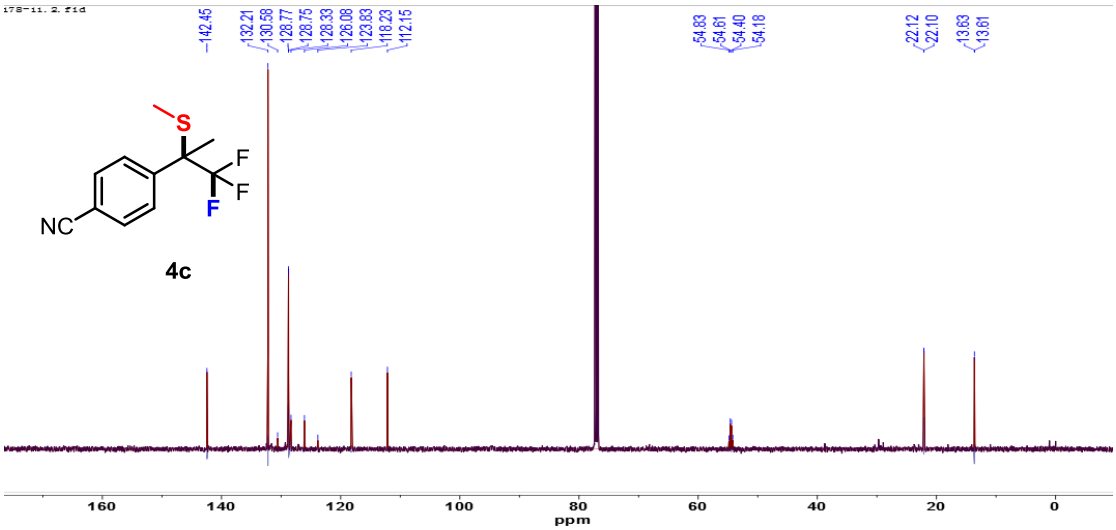
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



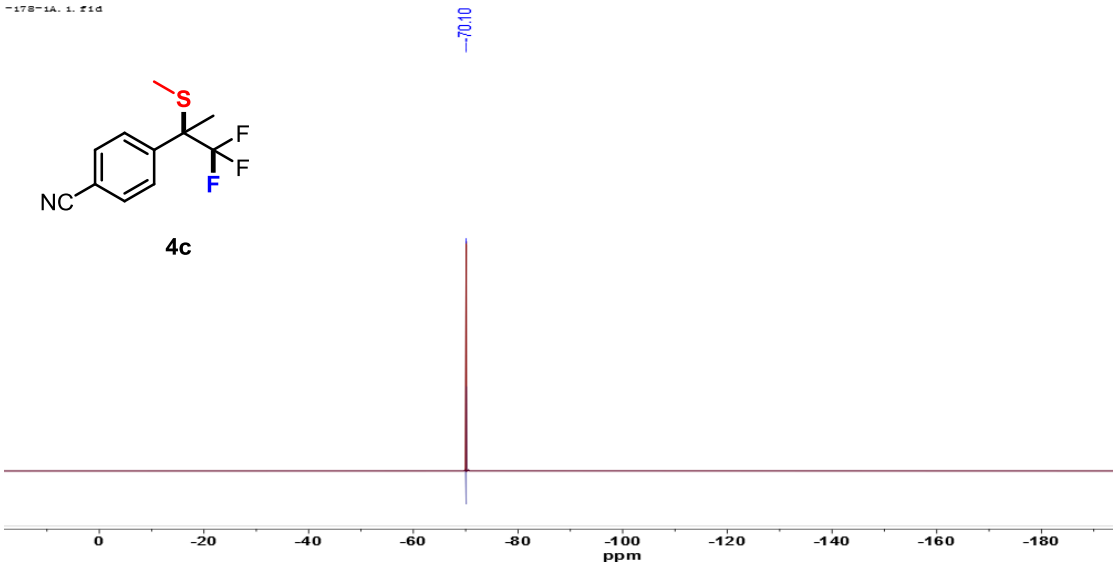
HRMS (ESI, m/z) calcd for $C_{10}H_{10}F_3NO_2S$ $[M+H]^+$ 266.0457, found 266.0451.



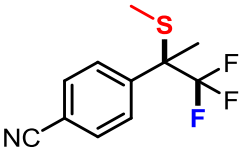
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$

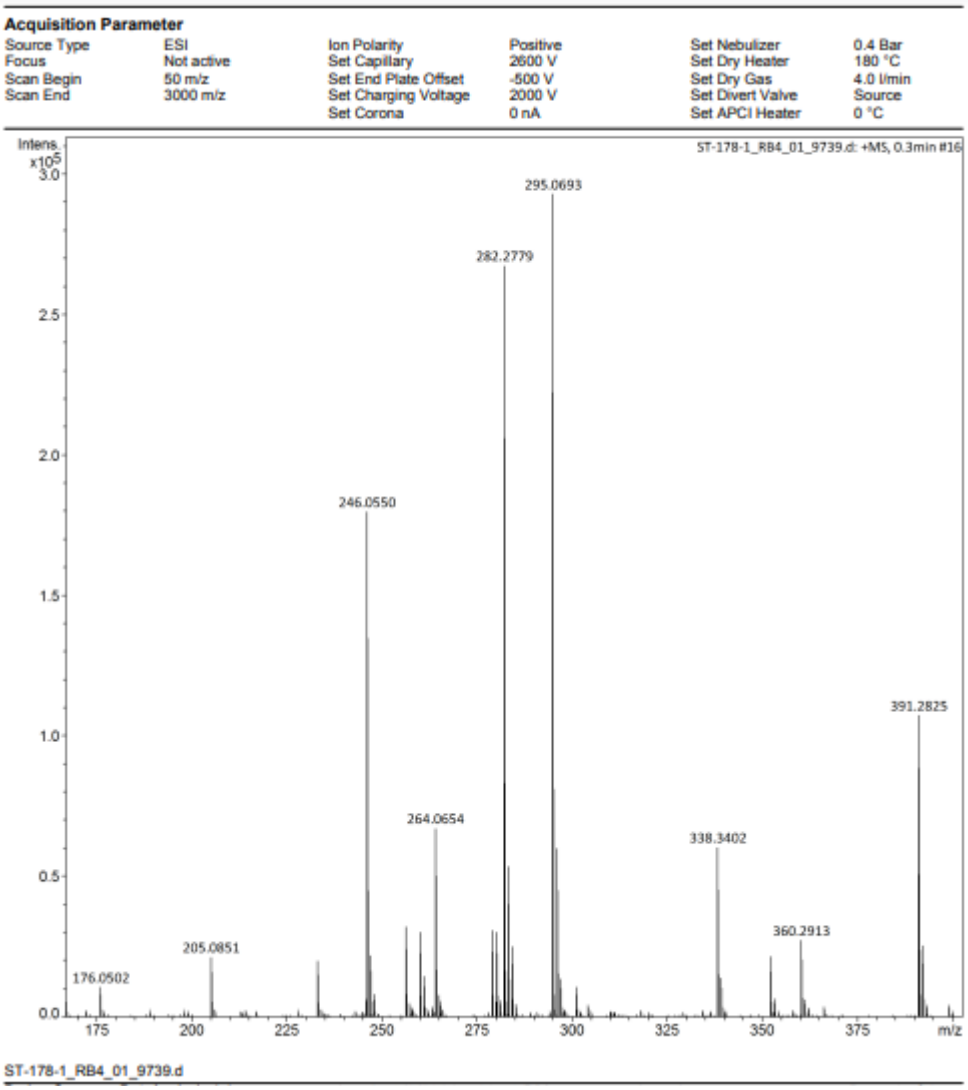


^{19}F NMR spectrum at 471 MHz in $CDCl_3$

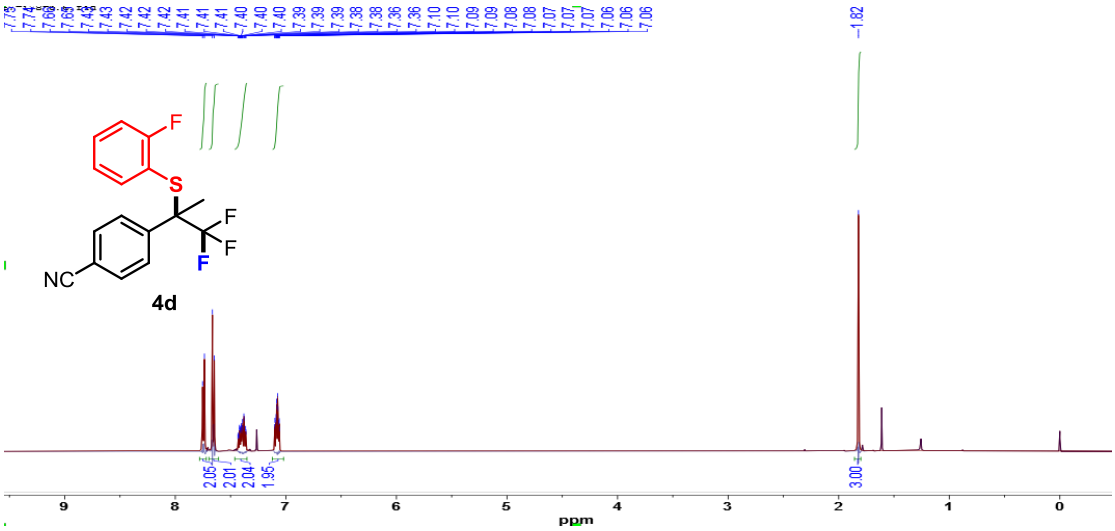


4c

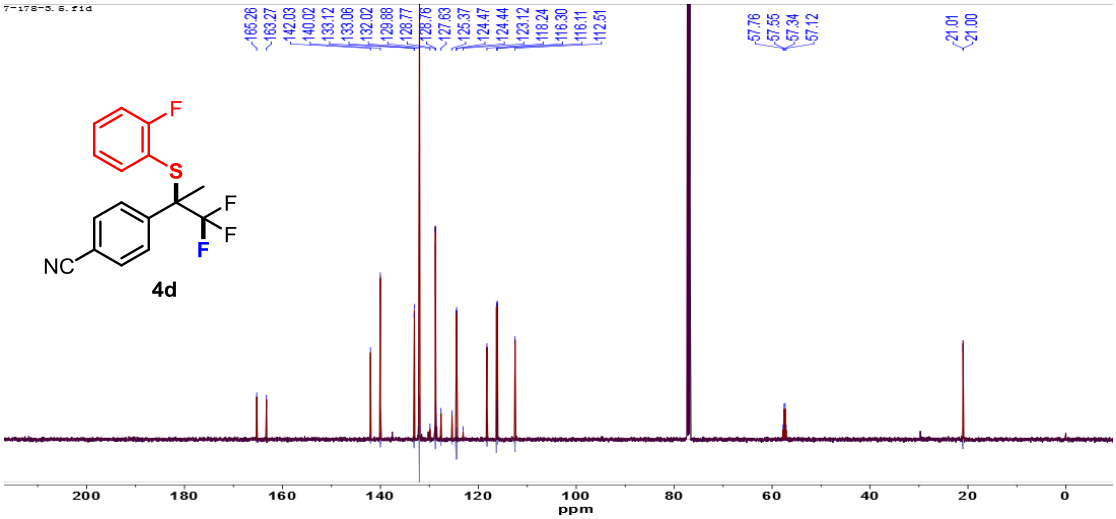
Chemical Formula: $C_{11}H_{10}F_3NS$
Exact Mass: 245.0486
Molecular Weight: 245.2632
m/z: 245.0486 (100.0%), 246.0520 (11.9%), 247.0444 (4.5%)
Elemental Analysis: C, 53.87; H, 4.11; F, 23.24; N, 5.71; S, 13.07



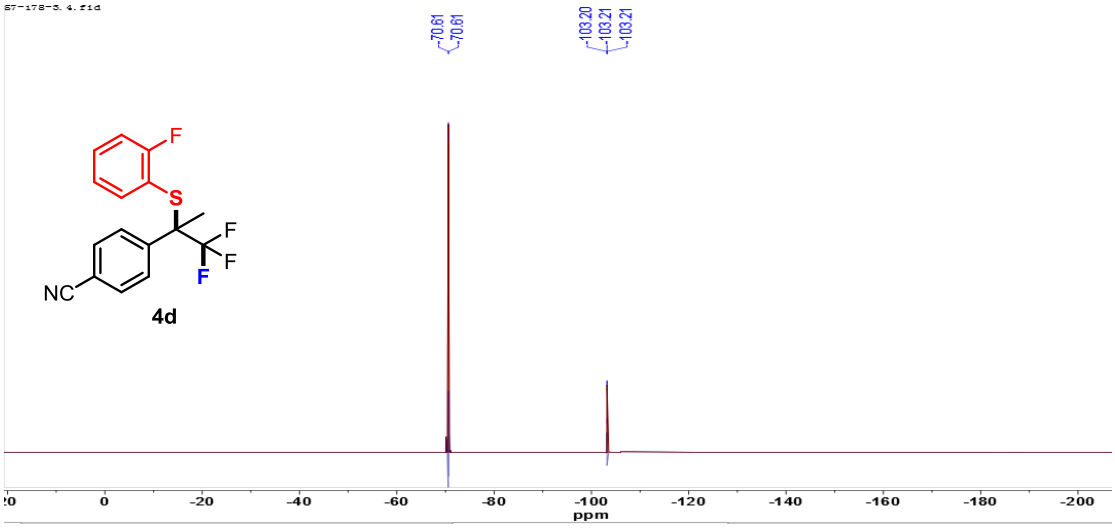
HRMS (ESI, m/z) calcd for $C_{11}H_{10}F_3NS$ $[M+H]^+$ 246.0559, found 246.0550.



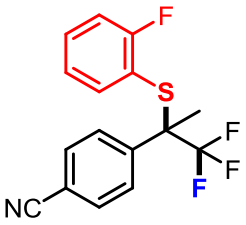
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$

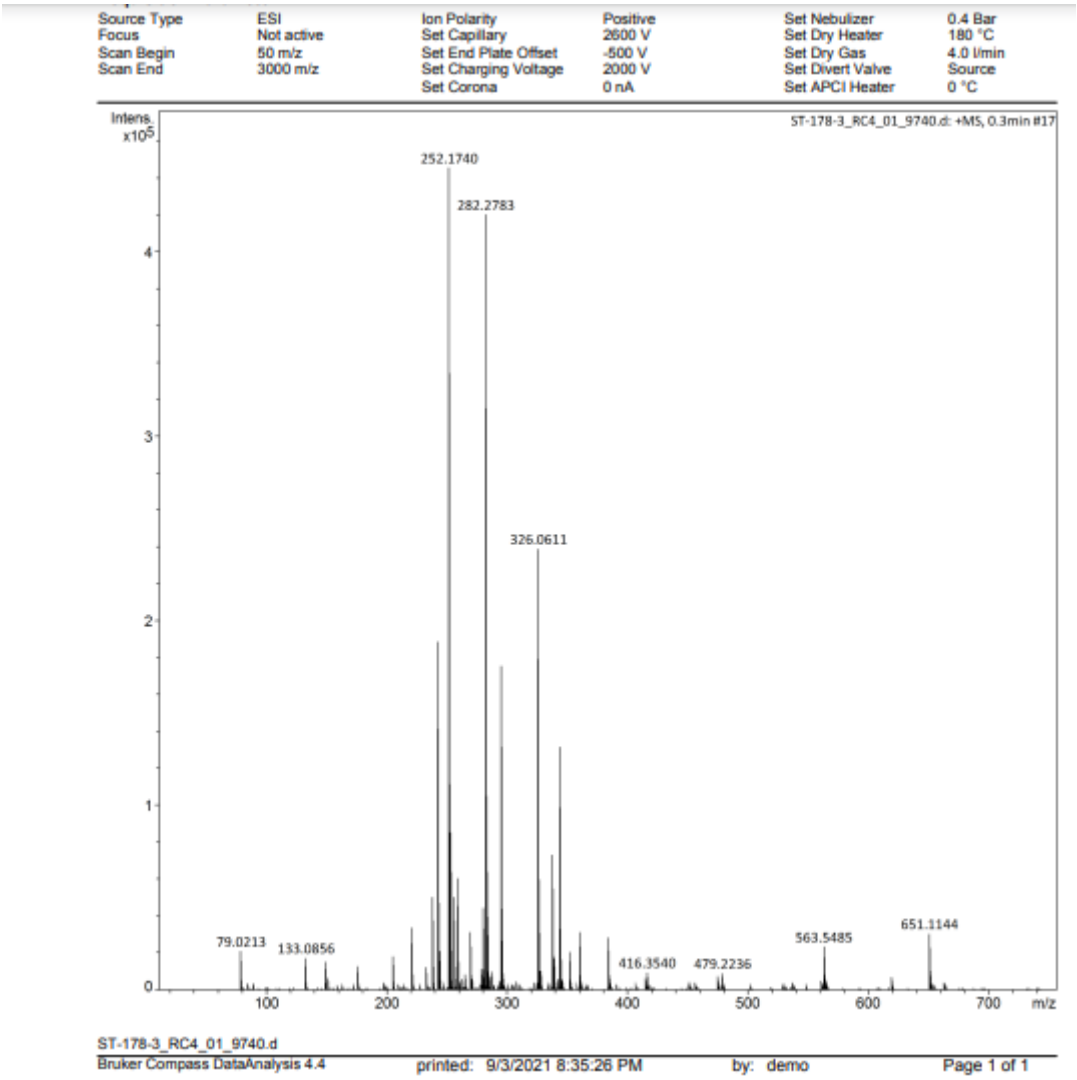


^{19}F NMR spectrum at 471 MHz in $CDCl_3$

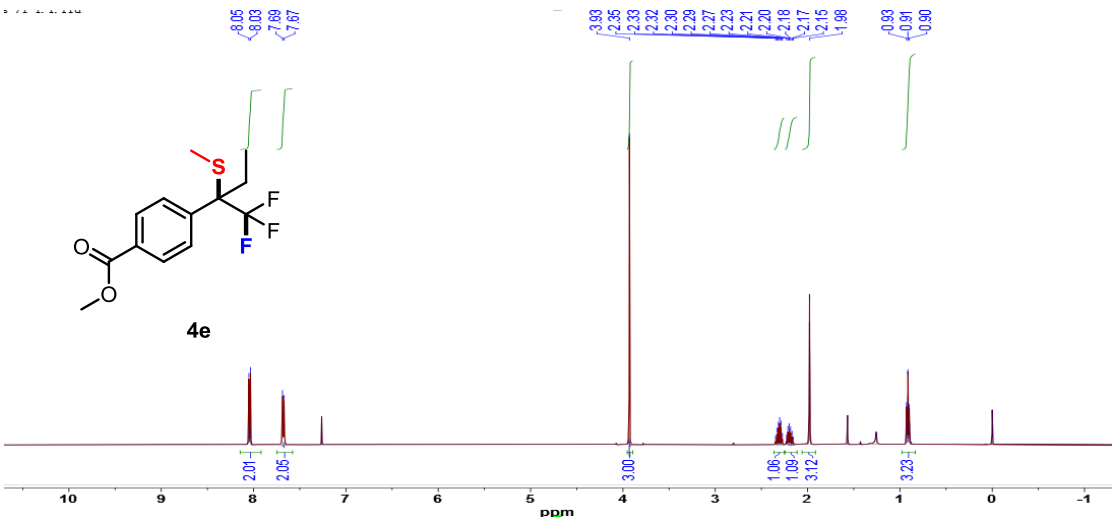


4d

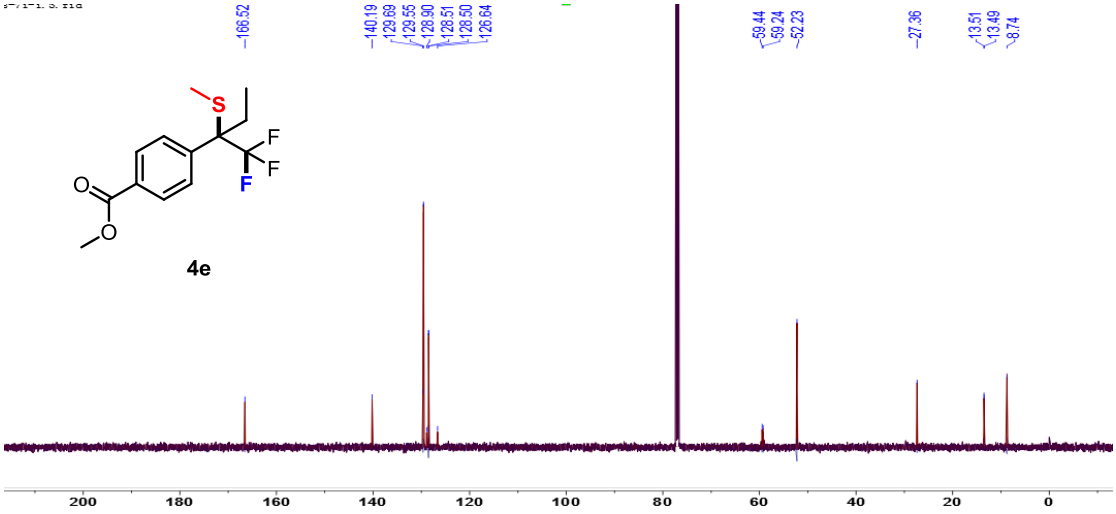
Chemical Formula: $C_{16}H_{11}F_4NS$
Exact Mass: 325.0548
Molecular Weight: 325.3246
m/z: 325.0548 (100.0%), 326.0582 (17.3%), 327.0506 (4.5%), 327.0615 (1.4%)
Elemental Analysis: C, 59.07; H, 3.41; F, 23.36; N, 4.31; S, 9.85



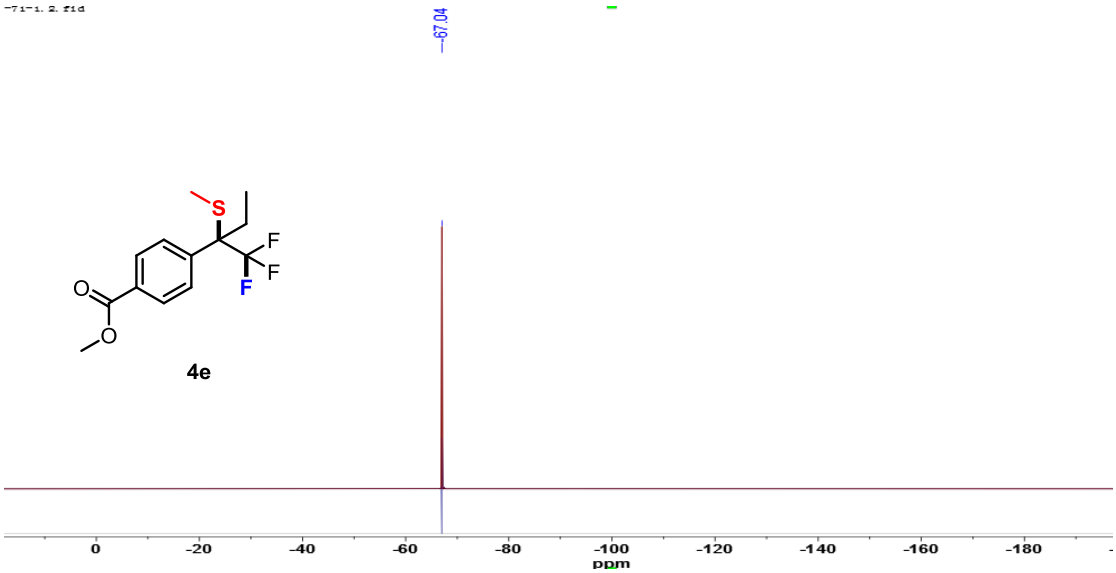
HRMS (ESI, m/z) calcd for $C_{16}H_{11}F_4NS$ $[M+H]^+$ 326.0621, found 326.0611.



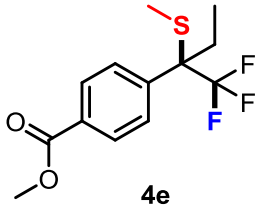
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



4e

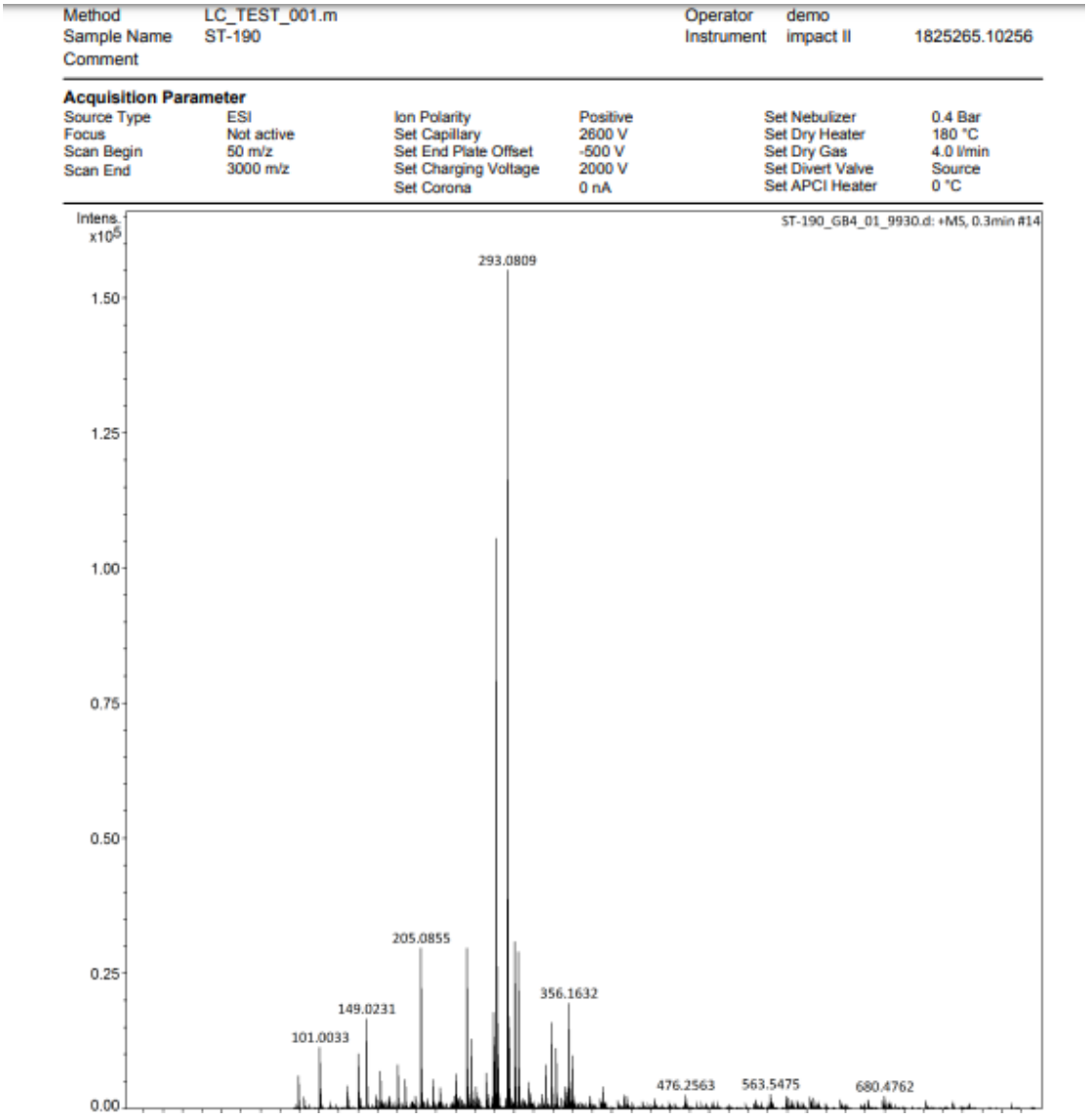
Chemical Formula: $C_{13}H_{15}F_3O_2S$

Exact Mass: 292.0745

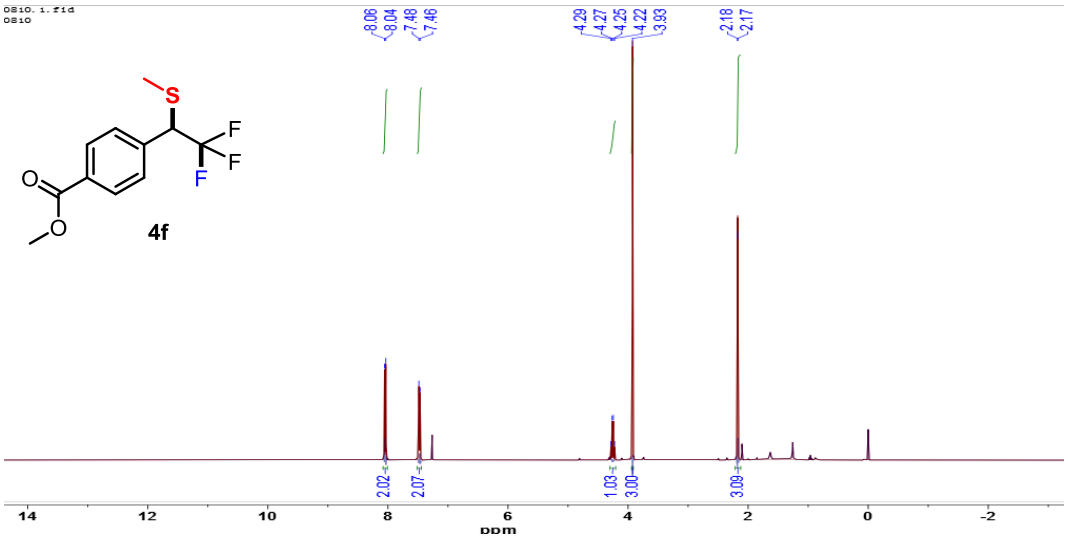
Molecular Weight: 292.3162

m/z: 292.0745 (100.0%), 293.0778 (14.1%), 294.0703 (4.5%)

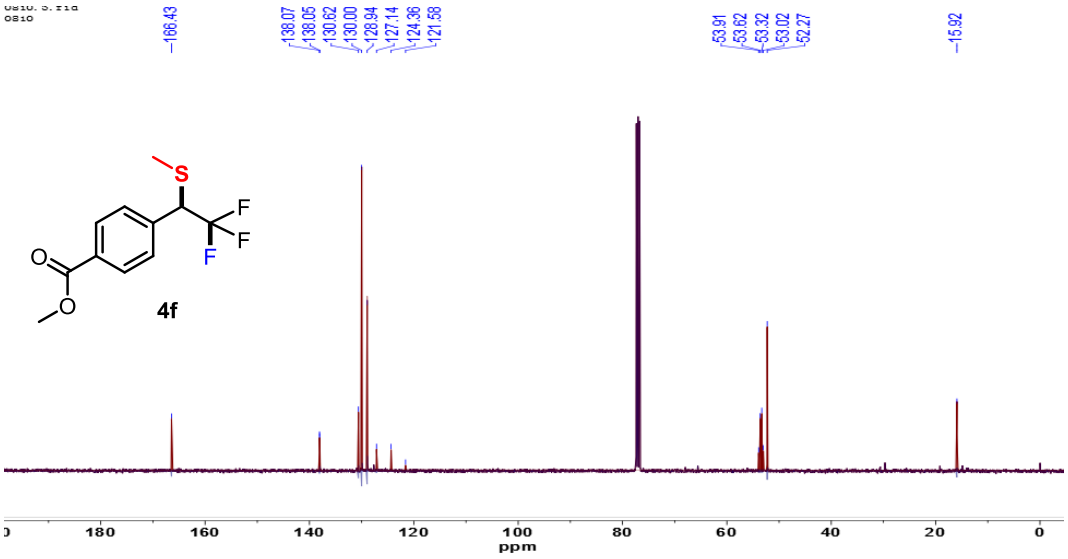
Elemental Analysis: C, 53.42; H, 5.17; F, 19.50; O, 10.95; S, 10.97



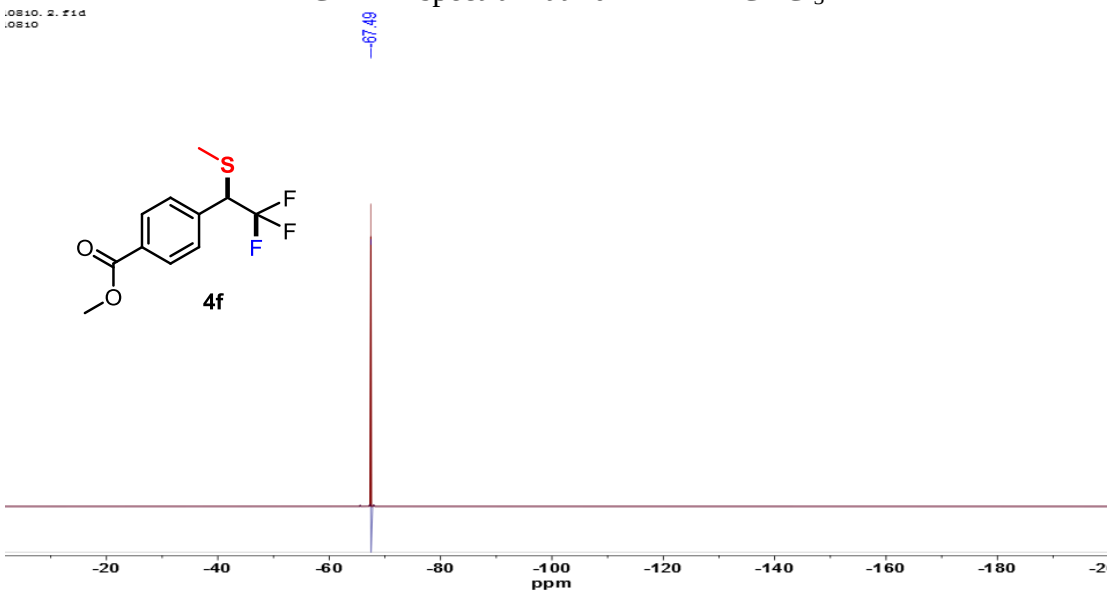
HRMS (ESI, m/z) calcd for $C_{13}H_{15}F_3O_2S$ $[M+H]^+$ 293.0818, found 293.0809.



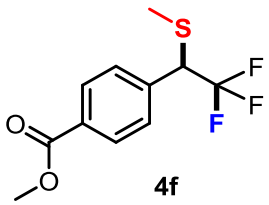
^{1}H NMR spectrum at 400 MHz in $CDCl_3$



^{13}C NMR spectrum at 101 MHz in $CDCl_3$



^{19}F NMR spectrum at 376 MHz in $CDCl_3$

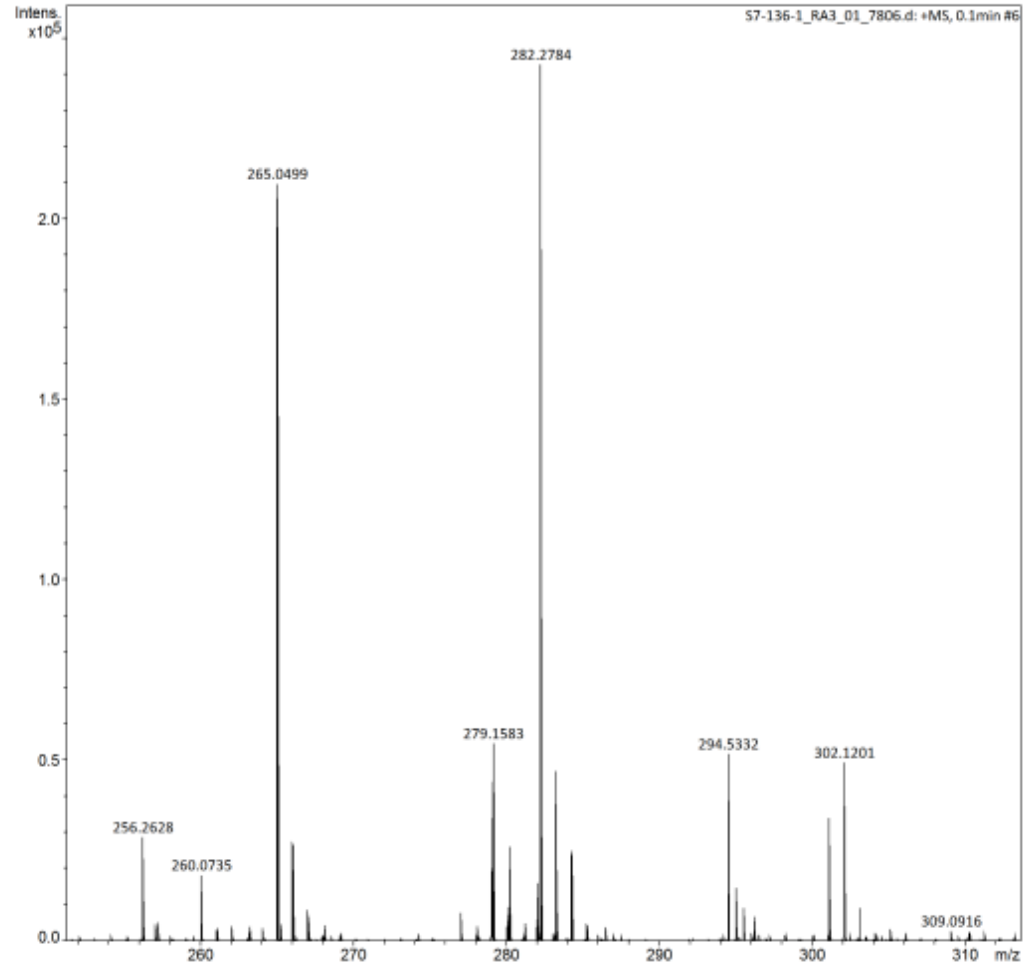


4f

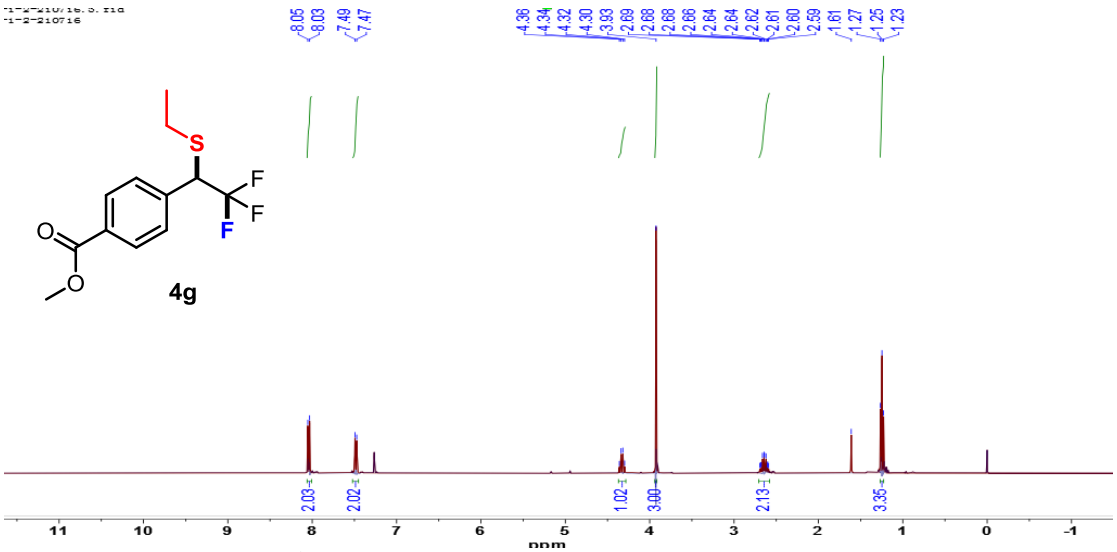
Chemical Formula: $C_{11}H_{11}F_3O_2S$
Exact Mass: 264.0432
Molecular Weight: 264.2622
m/z: 264.0432 (100.0%), 265.0465 (11.9%), 266.0390 (4.5%)
Elemental Analysis: C, 50.00; H, 4.20; F, 21.57; O, 12.11; S, 12.13

Acquisition Parameter

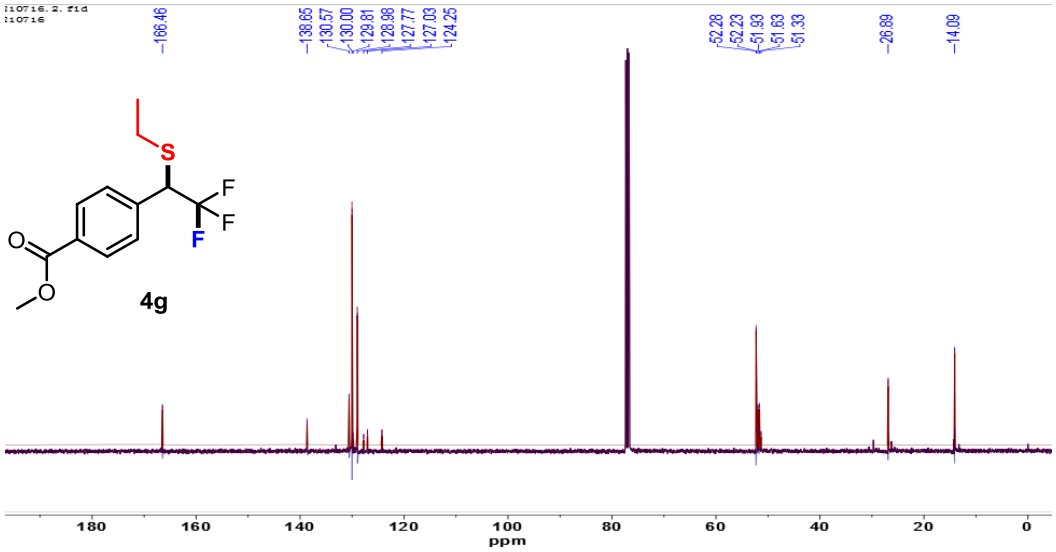
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



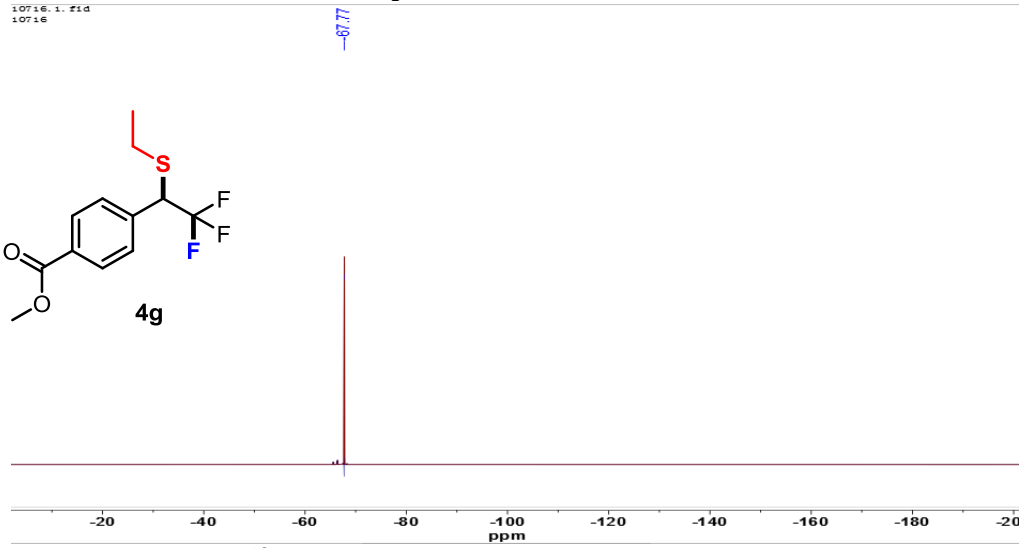
HRMS (ESI, m/z) calcd for $C_{11}H_{11}F_3O_2S$ $[M+H]^+$ 265.0505, found 265.0499.



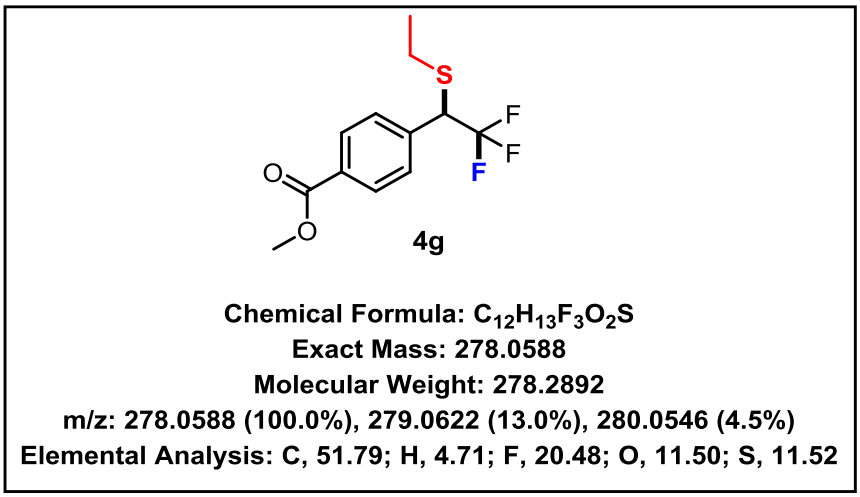
^{1}H NMR spectrum at 400 MHz in $CDCl_3$



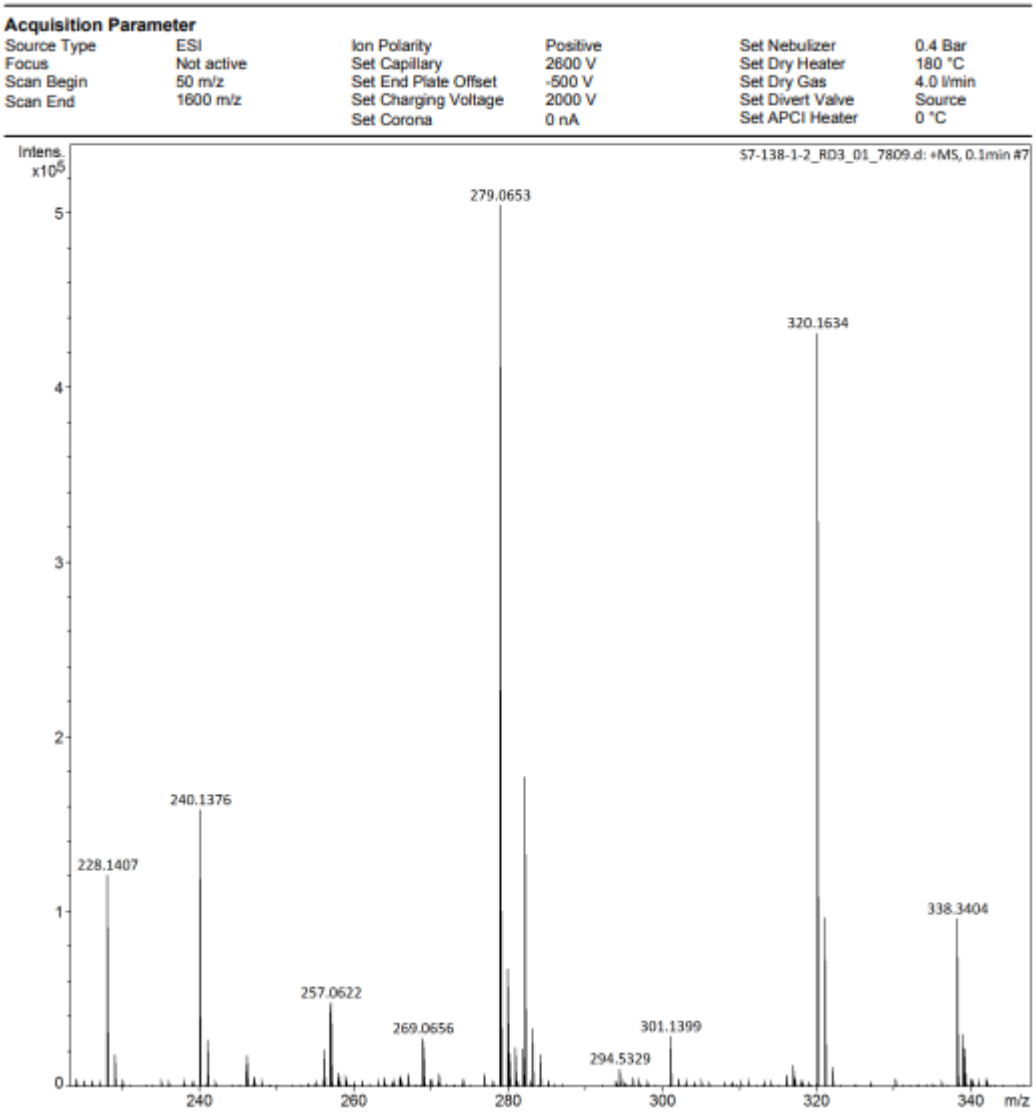
^{13}C NMR spectrum at 101 MHz in $CDCl_3$



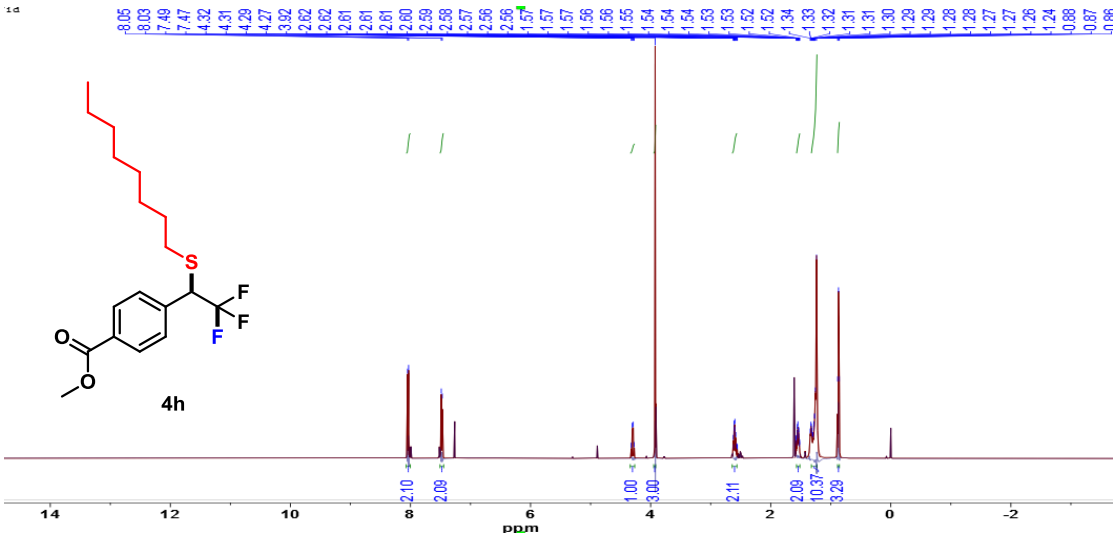
^{19}F NMR spectrum at 471 MHz in $CDCl_3$



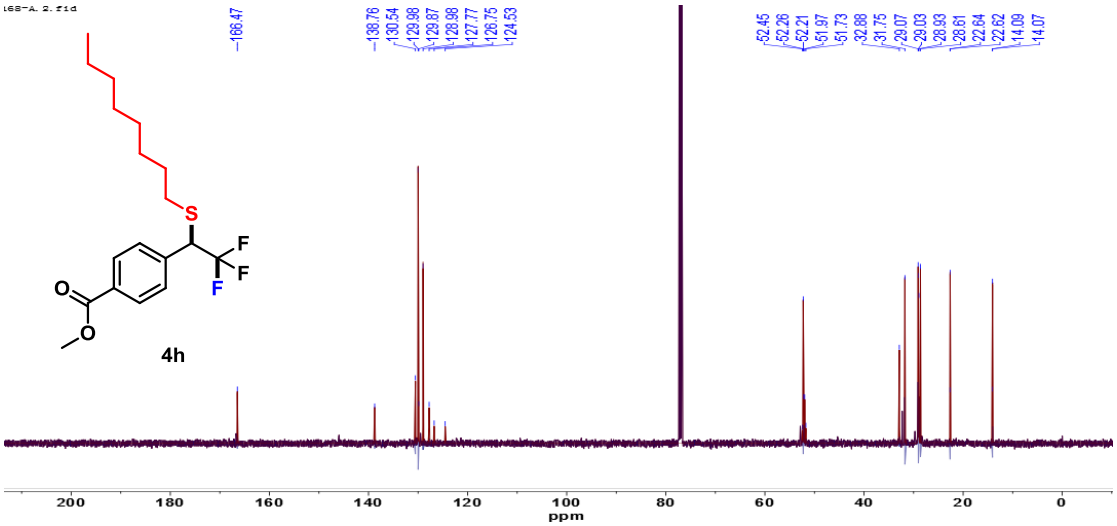
Chemical Formula: $C_{12}H_{13}F_3O_2S$
Exact Mass: 278.0588
Molecular Weight: 278.2892
m/z: 278.0588 (100.0%), 279.0622 (13.0%), 280.0546 (4.5%)
Elemental Analysis: C, 51.79; H, 4.71; F, 20.48; O, 11.50; S, 11.52



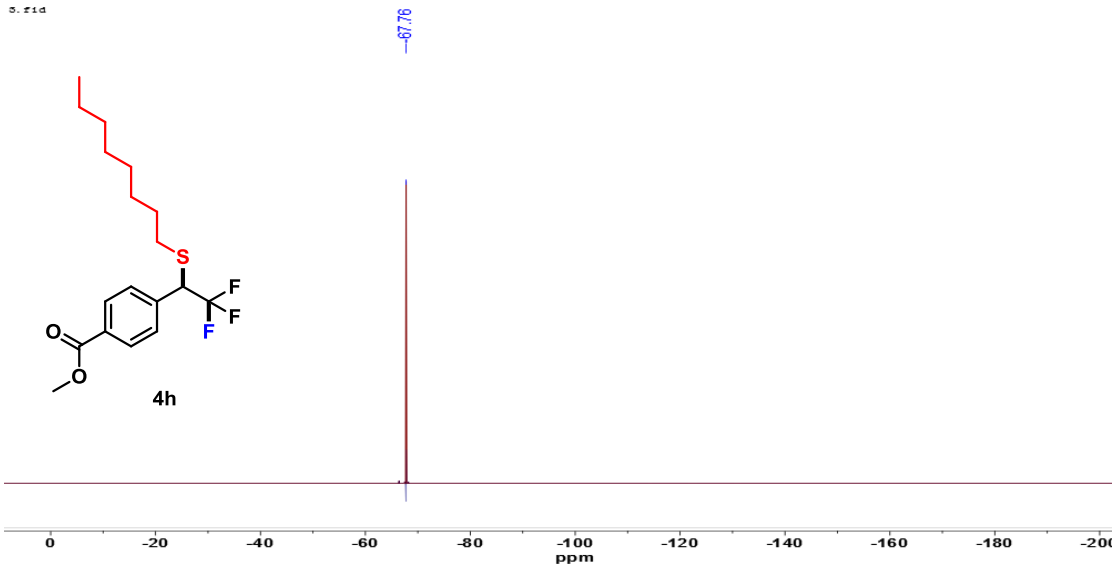
HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_2S$ $[M+H]^+$ 279.0661, found 279.0653.



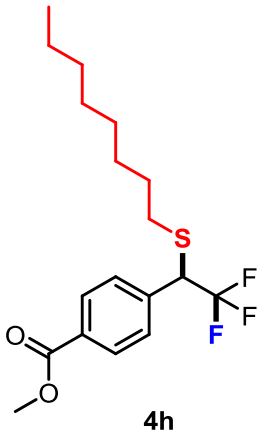
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$

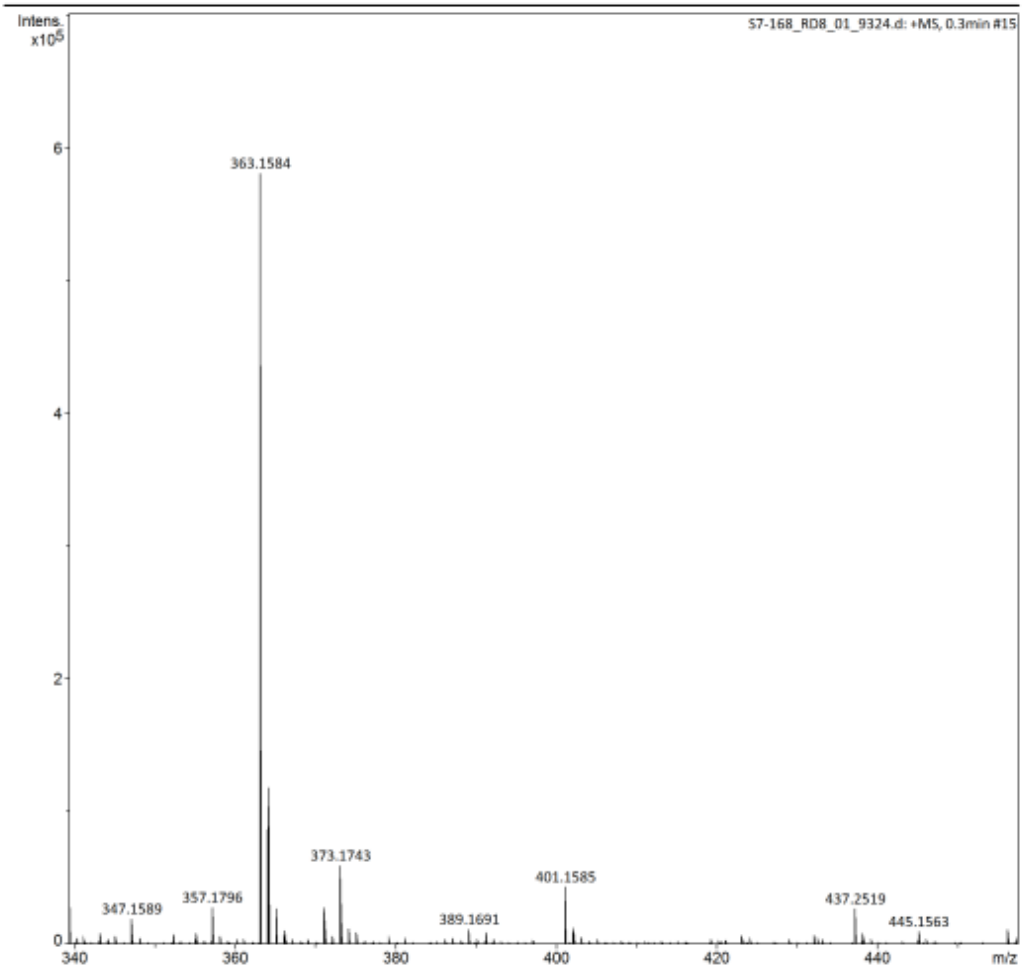


4h

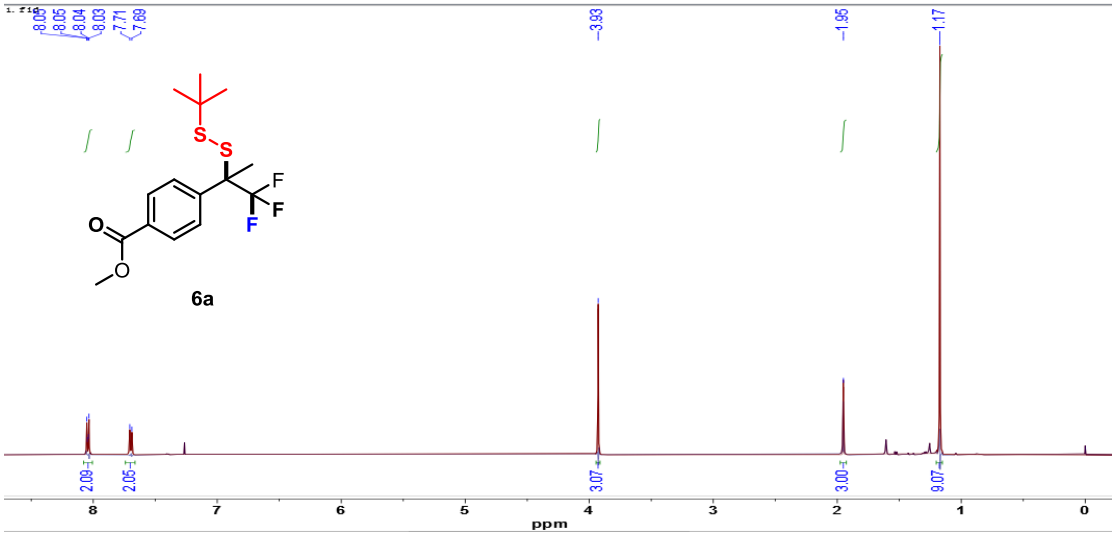
Chemical Formula: $C_{18}H_{25}F_3O_2S$
Exact Mass: 362.1527
Molecular Weight: 362.4512
m/z: 362.1527 (100.0%), 363.1561 (19.5%), 364.1485 (4.5%), 364.1594 (1.8%)
Elemental Analysis: C, 59.65; H, 6.95; F, 15.72; O, 8.83; S, 8.85

Acquisition Parameter

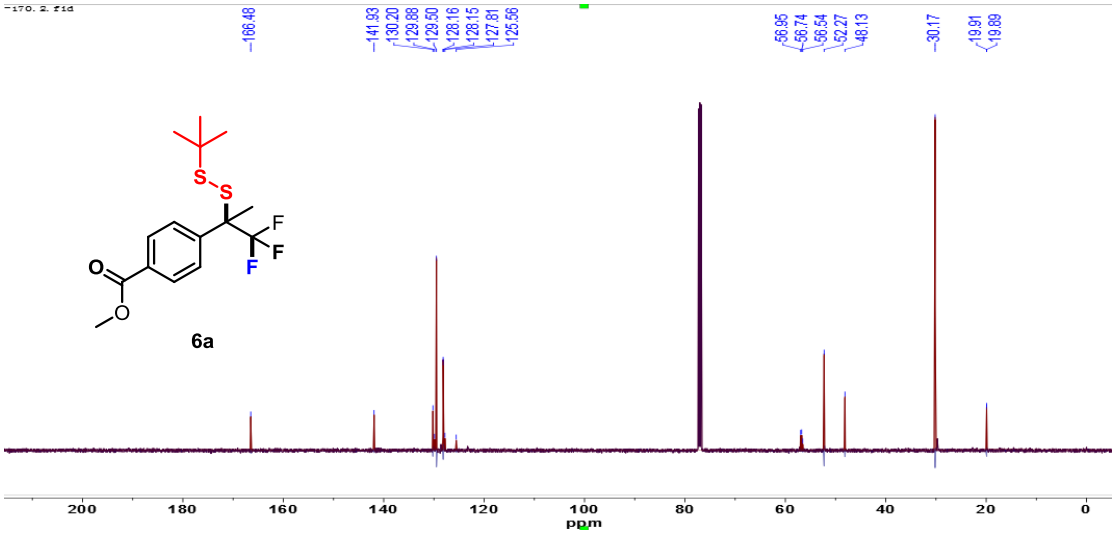
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



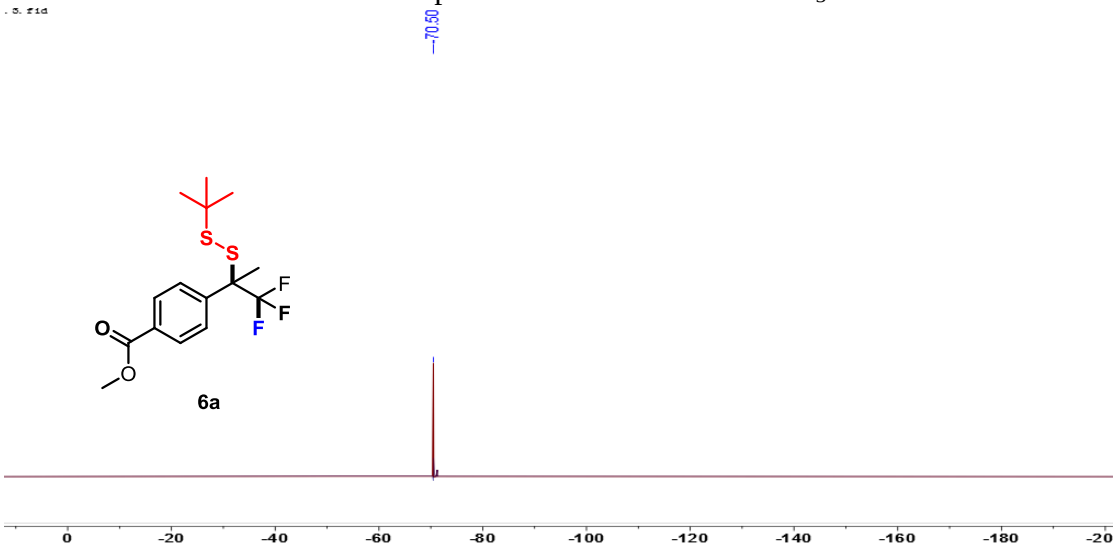
HRMS (ESI, m/z) calcd for $C_{18}H_{25}F_3O_2S$ $[M+H]^+$ 363.1600, found 363.1584.



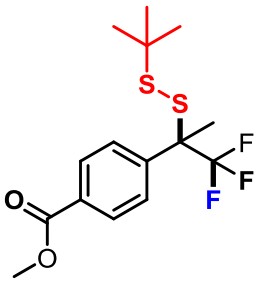
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



6a

Chemical Formula: $C_{15}H_{19}F_3O_2S_2$

Exact Mass: 352.0779

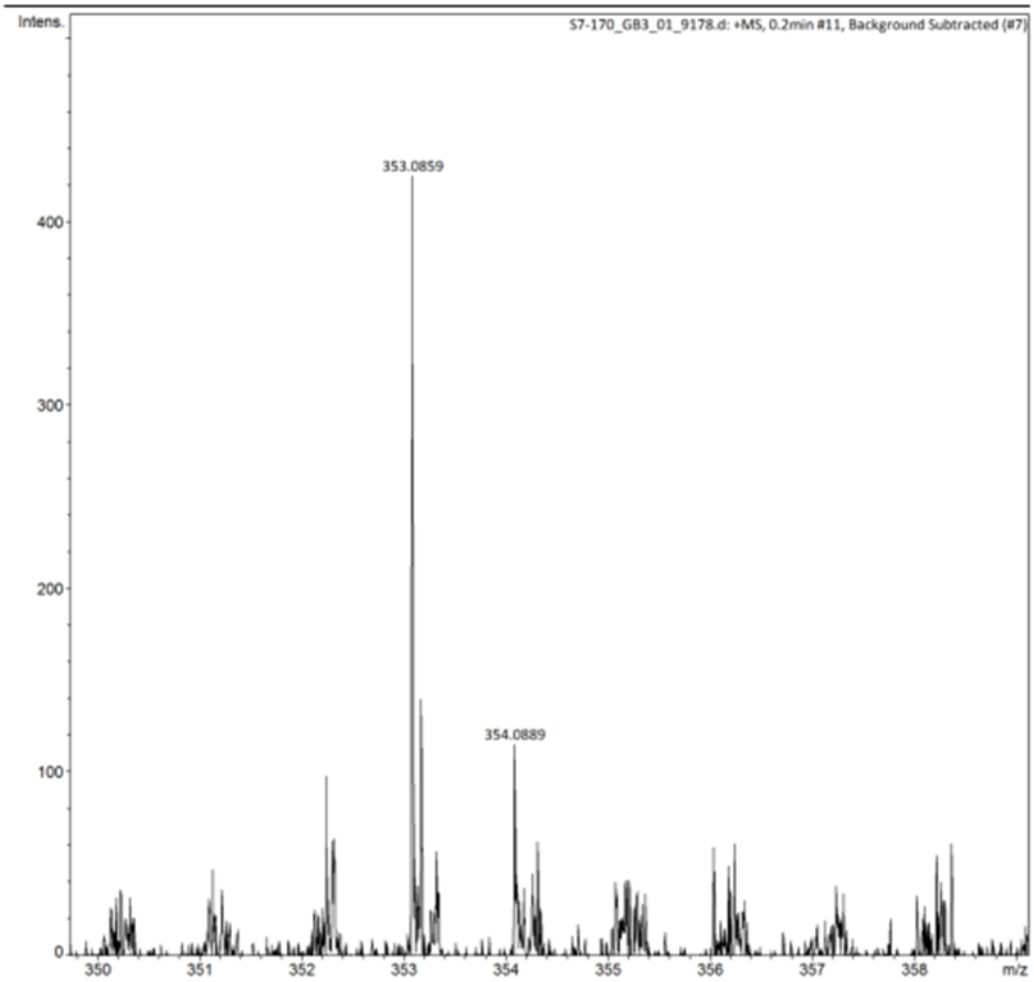
Molecular Weight: 352.4302

m/z: 352.0779 (100.0%), 353.0812 (16.2%), 354.0737 (9.0%), 353.0772 (1.6%), 355.0770 (1.5%), 354.0846 (1.2%)

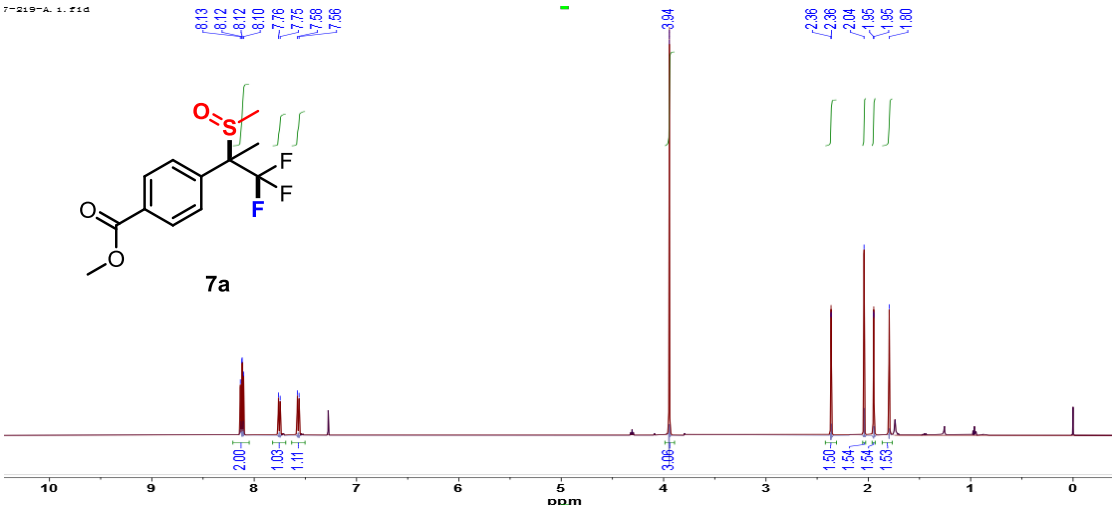
Elemental Analysis: C, 51.12; H, 5.43; F, 16.17; O, 9.08; S, 18.19

Acquisition Parameter

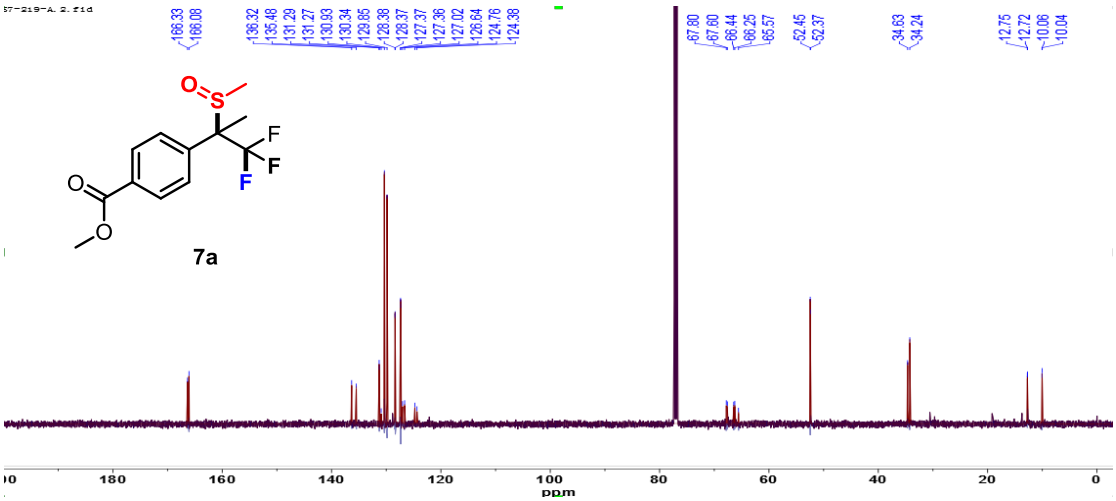
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



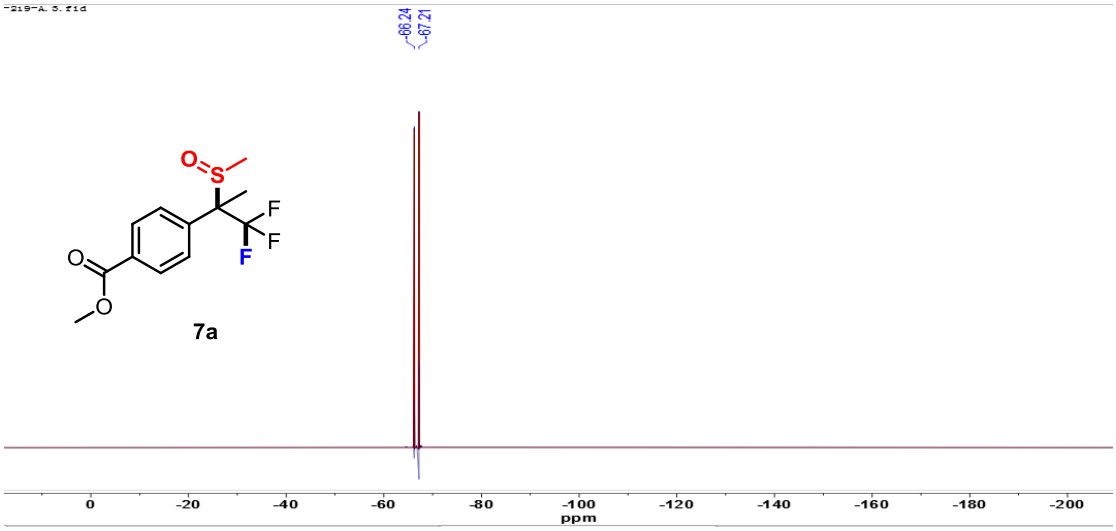
HRMS (ESI, m/z) calcd for $C_{15}H_{19}F_3O_2S_2$ [M+H]+ 353.0851, found 353.0859.



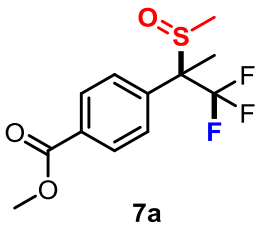
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



7a

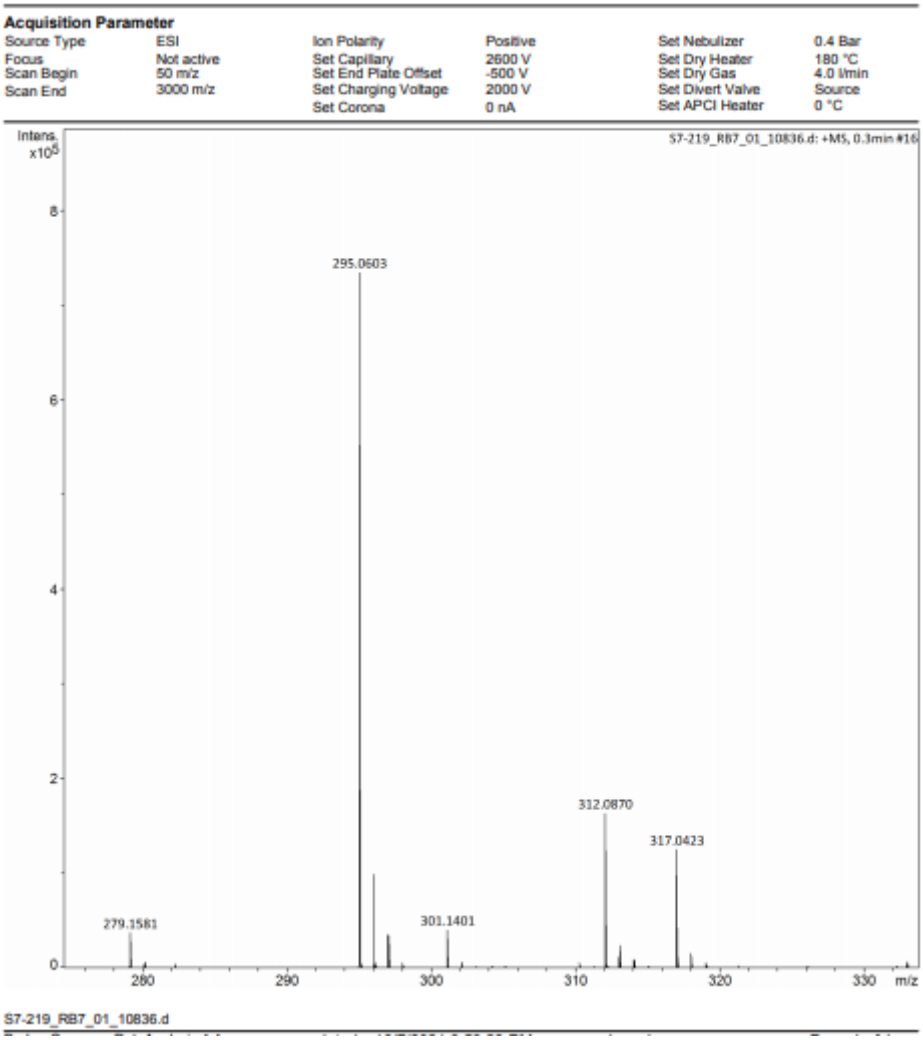
Chemical Formula: $C_{12}H_{13}F_3O_3S$

Exact Mass: 294.0537

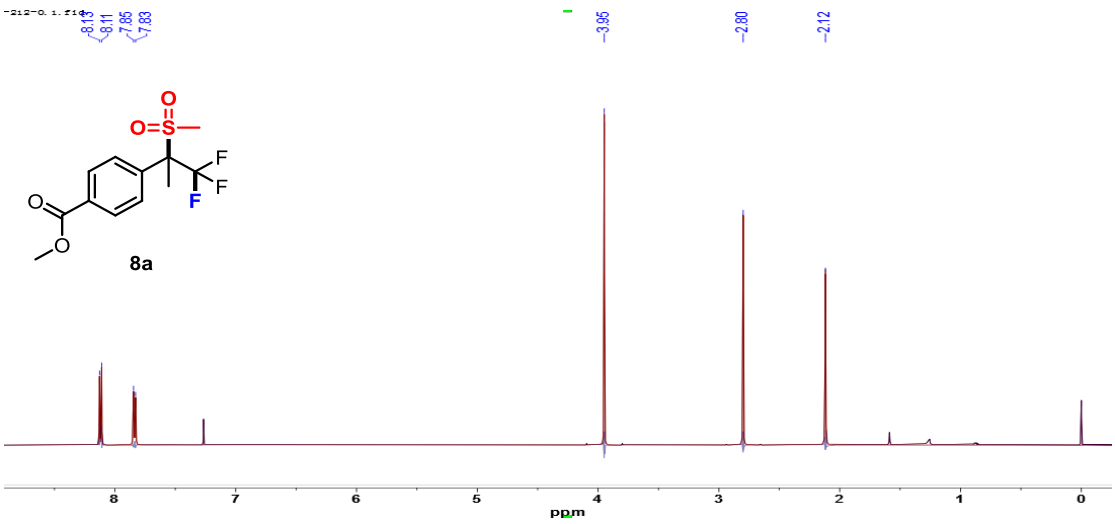
Molecular Weight: 294.2882

m/z: 294.0537 (100.0%), 295.0571 (13.0%), 296.0495 (4.5%)

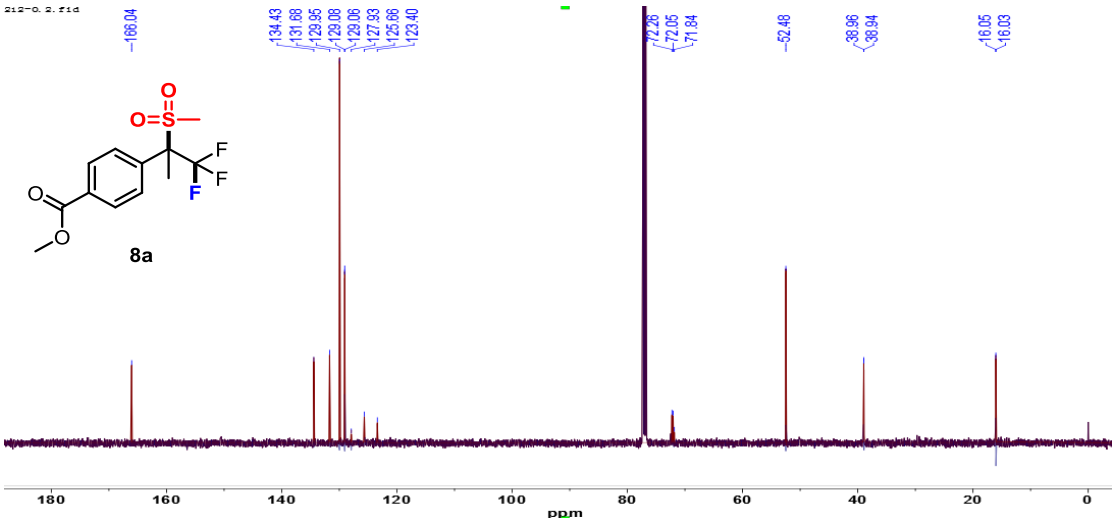
Elemental Analysis: C, 48.98; H, 4.45; F, 19.37; O, 16.31; S, 10.89



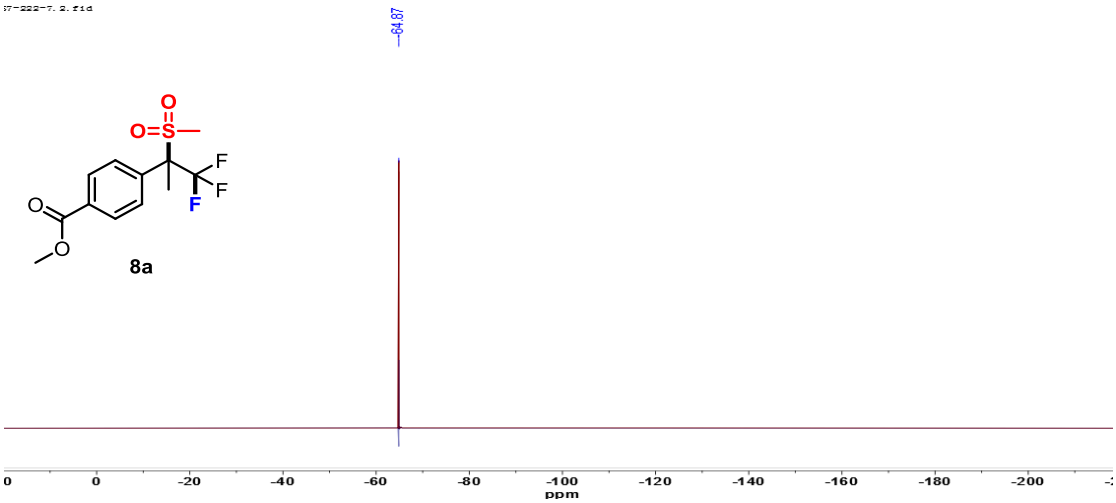
HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_3S$ $[M+H]^+$ 295.0610, found 295.0603.



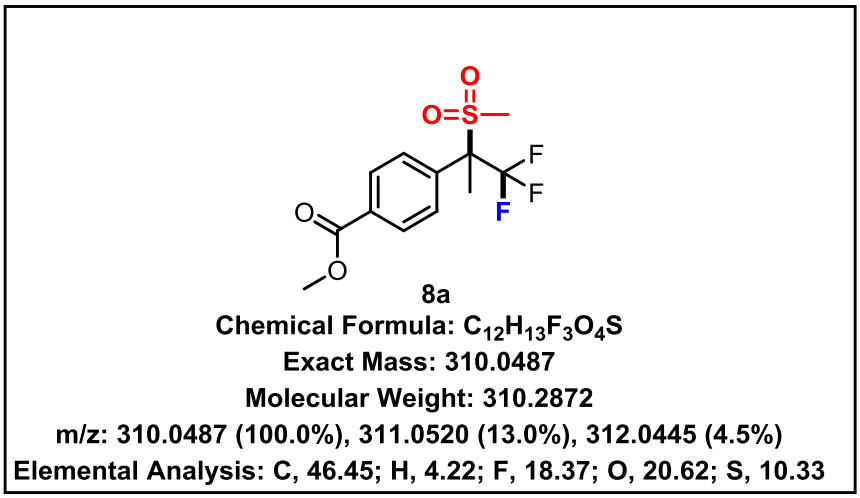
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$



^{19}F NMR spectrum at 471 MHz in $CDCl_3$



8a

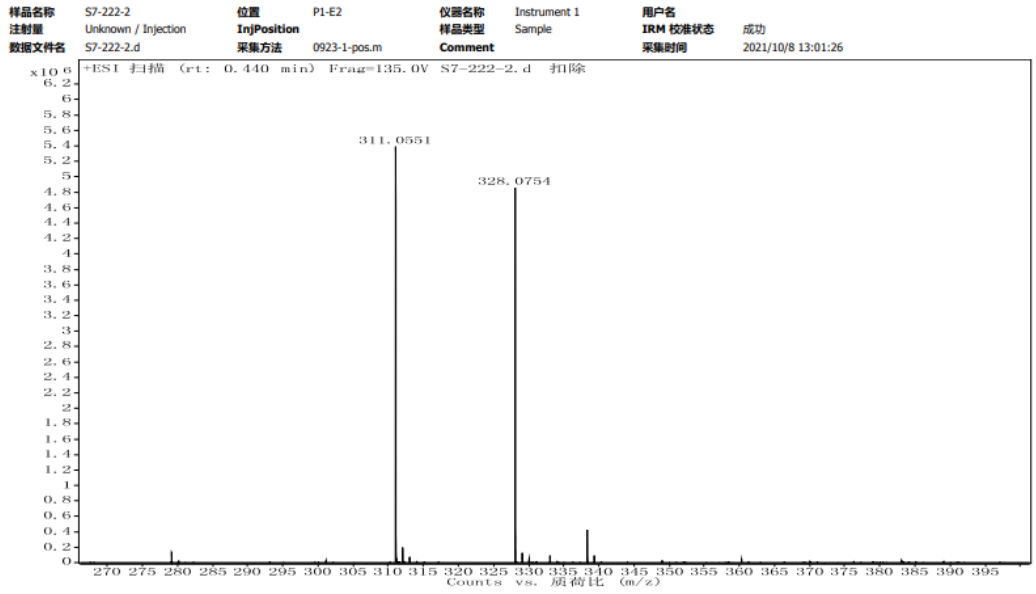
Chemical Formula: $C_{12}H_{13}F_3O_4S$

Exact Mass: 310.0487

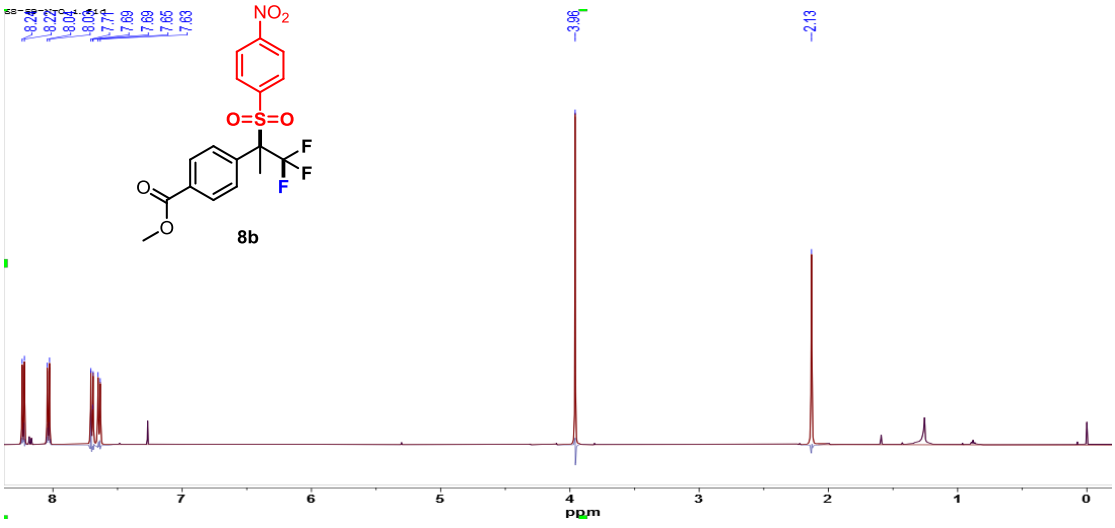
Molecular Weight: 310.2872

m/z: 310.0487 (100.0%), 311.0520 (13.0%), 312.0445 (4.5%)

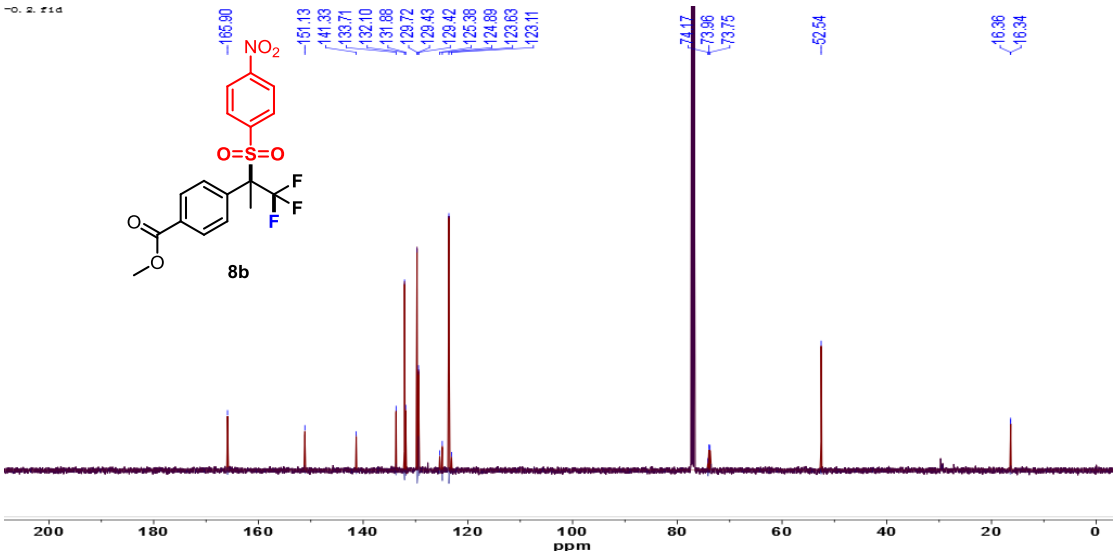
Elemental Analysis: C, 46.45; H, 4.22; F, 18.37; O, 20.62; S, 10.33



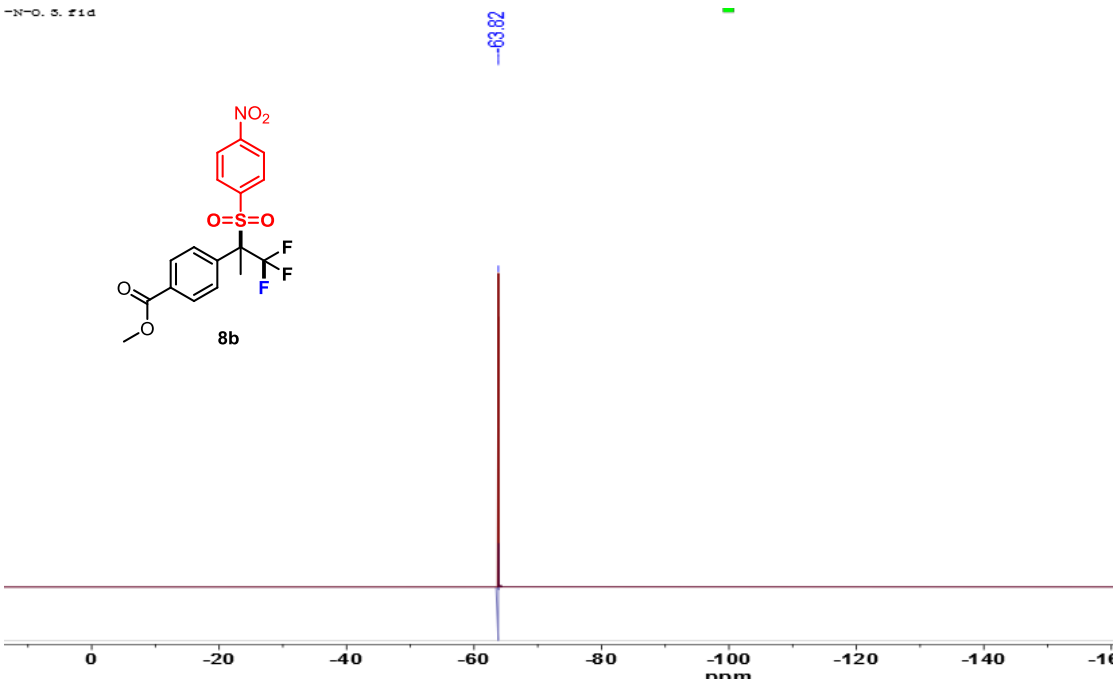
HRMS (ESI, m/z) calcd for $C_{12}H_{13}F_3O_4S$ $[M+H]^+$ 311.0559, found 311.0551.



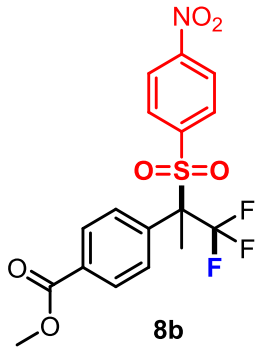
^{1}H NMR spectrum at 500 MHz in $CDCl_3$



^{13}C NMR spectrum at 126 MHz in $CDCl_3$

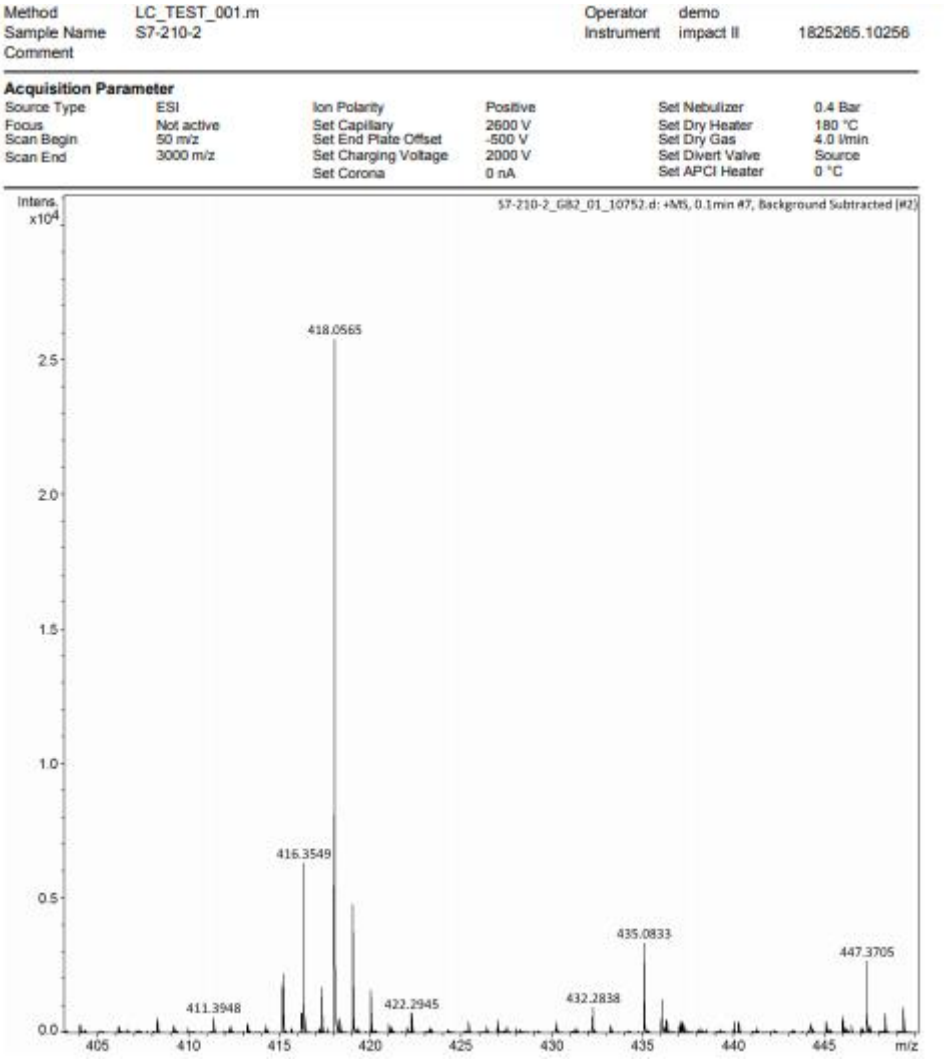


^{19}F NMR spectrum at 471 MHz in $CDCl_3$



8b

Chemical Formula: $C_{17}H_{14}F_3NO_6S$
Exact Mass: 417.0494
Molecular Weight: 417.3552
m/z: 417.0494 (100.0%), 418.0527 (18.4%), 419.0452 (4.5%), 419.0561 (1.6%), 419.0536 (1.2%)
Elemental Analysis: C, 48.92; H, 3.38; F, 13.66; N, 3.36; O, 23.00; S, 7.68



HRMS (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_6S$ $[M+H]^+$ 418.0567, found 418.0565.

9. References

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3 W. Wang, X. Peng, F. Wei, C. H. Tung and Z. Xu, Copper(I)-Catalyzed Interrupted Click Reaction: Synthesis of Diverse 5-Hetero-Functionalized Triazoles, *Angew. Chem., Int. Ed.*, 2016, **55**, 649-653.

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