Electronic Supplementary Information

Electrochemical Fluorosulfonylation of Styrenes

Yi-Min Jiang,^{†a} Yi Yu,^{†a} Shao-Fen Wu,^a Hong Yan,^a Yaofeng Yuan^a and Ke-Yin Ye^{*a,b}

^a Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), College of Chemistry, Fuzhou University, Fuzhou 350108, P. R. China.

^b State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005

[†] These authors contributed equally to this work.

E-mail: kyye@fzu.edu.cn

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1. General Information

All reactions were performed under an atmosphere of nitrogen using standard undivided three-necked glassware, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance (¹H NMR) spectra, carbon nuclear magnetic resonance (¹³C NMR) spectra and fluorine nuclear magnetic resonance (¹⁹F NMR) were recorded on Bruker AV-400 (400 MHz) and JEOL-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR. HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Cyclic voltammetry data were measured with a CHI 760E potentiostat (Chinstruments). All chemcials were purchased from TCI Shanghai or Energy Chemical and used as received.

Electrolysis experiments were performed using MESTEK DC power supply. Electrode clips (PT-1 or PT-3) and platinum plate (99.99%, 15*15*0.3 mm or 30*30*0.1 mm) was purchased from Gaoss Union. The carbon cloth (CeTech WOS1002) was cut into $15 \times 15 \times 0.1$ mm pieces before use, and was clamped between electrode clips.



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2. General Procedures

General procedure for the preparation of substituted olefin:¹

An oven-dried round-bottom flask was charged with CH_3PPh_3Br (1.5 equiv.) or $CH_3CH_2PPh_3Br$ (1.5 equiv.) and THF (carbonyl substrate concentration = 0.2 M). 'BuOK (1.5 equiv.) was added to the suspension at 0 °C. The resulting mixture was allowed to warm up to room temperature and stirred for 1 h. The yellow suspension was cooled to 0 °C again followed by portion-wise addition of the carbonyl substrate (1 equiv.). Subsequently, the mixture was further stirred at room temperature for 1-12 hours. After the completion of the reaction, the solvent was removed by evaporation, the resulting mixture was diluted with water (30 mL) and extract with dichloromethane (3 x 20 mL), and the combined organic layer was dried with anhydrous Na₂SO₄. Concentration in vacuo followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product in yields range from 50-95%.

General procedure for the preparation of sulfonyl hydrazides:²

Sulfonyl hydrazides were prepared according to a literature procedure. The hydrazine monohydrate (30 mmol) was added dropwise into the solution of sulfonyl chloride (10 mmol) in THF (50 mL) under nitrogen at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 30 minutes. After the completion of the reaction, the solvent was removed by evaporation, and the residue was extracted with dichloromethane (3 x 20 mL). The combined organic layer was washed with water, and brine, and dried over Na₂SO₄. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product.

Method A: General procedure for the electrochemical β-fluorosulfonylation of alkenes (constant current electrolysis)



In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, sulfonyl hydrazide substrate (2.0 equiv.) and (NH₄)₂HPO₄ (1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm \times 15 mm \times 0.1 mm) as the anode and platinum plate (15 mm \times 15 mm \times 0.3 mm) as the cathode. Under the protection of N₂, olefin substrates (0.3 mmol), Et₃N·3HF (0.3 mL), CH₃CN (8.0 mL), and DCM (2.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at room temperature for 4 h. The reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 15 mL). The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Method B: Scale-up synthesis



In an oven-dried double-necked glassware (250 mL) equipped with a stir bar, sulfonyl hydrazide substrate (2.0 equiv., 12 mmol, 2.480 g) and $(NH_4)_2HPO_4$ (1.0 equiv., 6 mmol, 800 mg) were added. The glassware was equipped with carbon cloth (30 mm × 30 mm × 0.1 mm) as the anode and platinum plate (30 mm × 30 mm × 0.1 mm) as the cathode. Under the protection of N₂, olefin substrate (6 mmol, 1.06 mL), Et₃N·3HF (6.0 mL), CH₃CN (160 mL) and DCM (40 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA at room temperature for 21 h. The reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 150 mL). The aqueous layer was separated and extracted with dichloromethane (3×50 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following

concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

3. Characterization of Products



1-chloro-4-((2-fluoro-2-(p-tolyl)ethyl)sulfonyl)benzene (3)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 57.3 mg (61% yield) of **3** as a white solid. IR: 3091(w), 2924(m), 1476(m), 1312(s), 1143(s), 1087(s), 818(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.19-7.13 (m, 4H), 5.96 (ddd, J = 47.4, 9.5, 2.1 Hz, 1H), 3.82 (ddd, J = 15.1, 12.6, 9.6 Hz, 1H), 3.46 (ddd, J = 31.3, 15.2, 2.3 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 140.7, 139.6 (d, J = 2.1 Hz), 138.1, 133.4 (d, J = 20.0 Hz), 129.8, 129.55, 129.48, 125.6 (d, J = 6.0 Hz), 88.6 (d, J = 176.0 Hz), 62.5 (d, J = 26.5 Hz), 21.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -171.1 (ddd, J = 45.8, 31.4, 12.5 Hz). HRMS (ESI) calculated for C₁₅H₁₄ClO₂S⁺ [M-HF]⁺: 293.0398; found: 293.0400.



1-(1-Fluoro-2-(phenylsulfonyl)ethyl)-4-methylbenzene (4)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 54.7 mg (66% yield) of **4** as a white solid. IR: 3062(w), 2925(m), 1307(s), 1144(s), 1086(m), 820(m), 743(m), 688(w). ¹H NMR (500 MHz, Chloroform-d) δ 7.96 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.18-7.15 (m, 4H), 5.98 (ddd, J = 47.5, 9.5, 2.5 Hz, 1H), 3.83 (ddd, J = 15.1, 13.0, 9.5 Hz, 1H), 3.45 (ddd, J = 31.2, 15.1, 2.4 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 139.6, 139.4 (d, J = 2.2 Hz), 133.9, 133.7, 129.5, 129.2, 128.2, 125.6 (d, J = 6.1 Hz), 88.5 (d, J = 176.3 Hz), 62.6 (d, J = 26.5 Hz), 21.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -171.5 (ddd, J = 46.1, 31.2, 13.0 Hz). HRMS (ESI) calculated for C₁₅H₁₅O₂S⁺ [M-HF]⁺: 259.0787; found: 259.0790.



1-((2-Fluoro-2-(p-tolyl)ethyl)sulfonyl)-4-methylbenzene (5)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 54.2 mg (62% yield) of **5** as a white solid. IR: 3033(w), 2626(w), 1302(s), 1140(s), 1056(m), 813(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.17-7.15 (m, 4H), 5.96 (ddd, *J* = 47.5, 9.5, 2.4 Hz, 1H), 3.80 (ddd, *J* = 15.1, 13.1, 9.5 Hz, 1H), 3.43 (ddd, *J* = 31.3, 15.1, 2.5 Hz, 1H), 2.46 (s, 3H), 2.34 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 145.0, 139.4 (d, *J* = 2.2 Hz), 136.7, 133.9 (d, *J* = 20.0 Hz), 129.8, 129.5, 128.3, 125.5 (d, *J* = 6.1 Hz), 88.5 (d, *J* = 176.2 Hz), 62.7 (d, *J* = 26.4 Hz), 21.6, 21.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -171.7 (ddd, *J* = 45.9, 31.4, 13.3 Hz). HRMS (ESI) calculated for C₁₆H₁₇O₂S⁺ [M-HF]⁺: 273.0944; found: 273.0946.



1-(Tert-butyl)-4-((2-fluoro-2-(p-tolyl)ethyl)sulfonyl)benzene (6)³

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 58.3 mg (59% yield) of **6** as a white solid. ¹H NMR (500 MHz, Chloroform-d) δ 7.85 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.17-7.12 (m, 4H), 5.97 (ddd, J = 47.4, 9.2, 2.8 Hz, 1H), 3.82 (ddd, J = 15.1, 13.1, 9.2 Hz, 1H), 3.46 (ddd, J = 30.2, 15.1, 2.8 Hz, 1H), 2.33 (s, 3H), 1.34 (s, 9H). ¹³C NMR (126 MHz, Chloroform-d) δ 157.8, 139.3 (d, J = 2.2 Hz), 136.5, 133.8 (d, J = 19.9 Hz), 129.4, 128.0, 126.2, 125.6 (d, J = 6.0 Hz), 88.5 (d, J = 176.2 Hz), 62.4 (d, J = 26.6 Hz), 35.2, 31.0, 21.1. ¹⁹F NMR (471 MHz, Chloroform-d) δ -170.8 (ddd, J = 45.2, 30.2, 13.1 Hz).



1-(1-Fluoro-2-((4-methoxyphenyl)sulfonyl)ethyl)-4-methylbenzene (7)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 60.2 mg (65% yield) of 7 as a white solid. IR: 2927(w), 1497(m), 1297(s), 1259(s), 1137(s), 1088(m), 822(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.87 (d, J = 8.8 Hz, 2H), 7.17-7.15 (m, 4H), 7.01 (d, J = 9.0 Hz, 2H), 5.95 (ddd, J = 47.5, 9.5, 2.5 Hz, 1H), 3.88 (s, 3H), 3.79 (ddd, J = 15.1, 13.2, 9.5 Hz, 1H), 3.43 (ddd, J = 31.3, 15.1, 2.5 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 163.9, 139.3 (d, J = 2.1 Hz), 133.9 (d, J = 20.1 Hz), 131.1, 130.5, 129.5, 125.6 (d, J = 6.1 Hz), 114.4, 88.6 (d, J = 176.1 Hz), 62.8 (d, J = 26.3 Hz), 55.7, 21.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -171.7 (ddd, J = 46.0, 31.2, 13.1 Hz). HRMS (ESI) calculated for C₁₆H₁₇O₃S⁺ [M-HF]⁺: 289.0893; found: 289.0897.



1-Fluoro-4-((2-fluoro-2-(p-tolyl)ethyl)sulfonyl)benzene (8)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 41.5 mg (47% yield) of **8** as a white solid. IR: 3105(w), 2926(w), 1493(s), 1316(s), 1233(m), 1142(s), 1086(m), 839(m). ¹H NMR (400 MHz, Chloroform-d) δ 7.97 (dd, J = 8.7, 5.0 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.18-7.14 (m, 4H), 5.97 (ddd, J = 47.5, 9.5, 2.4 Hz, 1H), 3.82 (ddd, J = 15.2, 12.7, 9.5 Hz, 1H), 3.46 (ddd, J = 31.4, 15.2, 2.5 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 165.9 (d, J = 256.5 Hz), 139.5 (d, J = 2.2 Hz), 135.7 (d, J = 3.2 Hz), 133.5 (d, J = 20.0 Hz), 131.2 (d, J = 9.5 Hz), 129.6, 125.6 (d, J = 6.0 Hz), 116.5 (d, J = 22.7 Hz), 88.6 (d, J = 176.0 Hz), 62.7 (d, J = 26.5 Hz), 21.2. ¹⁹F NMR (376 MHz, Chloroform-d) δ -103.1 (tt, J = 8.3, 5.0 Hz), -171.5 (ddd, J = 45.3, 31.4, 12.6 Hz). HRMS (ESI) calculated for C₁₅H₁₄FO₂S⁺ [M-HF]⁺: 277.0693; found: 277.0686.



1-Bromo-4-((2-fluoro-2-(p-tolyl)ethyl)sulfonyl)benzene (9)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 42.9 mg (40% yield) of **9** as a white solid. IR: 3090(w), 2925(s), 1315(s), 1146(s), 1067(m), 820(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.17-7.13 (m, 4H), 5.96 (ddd, *J* = 47.4, 9.5, 2.4 Hz, 1H), 3.82 (ddd, *J* = 15.1, 12.5, 9.5 Hz, 1H), 3.46 (ddd, *J* = 31.3, 15.2, 2.5 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 139.6 (d, *J* = 2.2 Hz), 138.6, 133.4 (d, *J* = 19.9 Hz), 132.5, 129.8, 129.6, 129.3, 125.6 (d, *J* = 6.0 Hz), 88.6 (d, *J* = 176.0 Hz), 62.6 (d, *J* = 26.5 Hz), 21.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -171.0 (ddd, *J* = 45.5, 31.2, 12.6 Hz). HRMS (ESI) calculated for C₁₅H₁₄BrO₂S⁺ [M-HF]⁺: 336.9892; found: 336.9891.



1-(1-Fluoro-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-4-methylbenzene (10) Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 62.2 mg (60% yield) of **10** as a white solid. IR: 2928(w), 1319(s), 1133(s), 1061(s), 821(m). ¹H NMR (500 MHz, Chloroform-d) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.18-7.12 (m, 4H), 5.98 (ddd, *J* = 47.3, 9.4, 2.7 Hz, 1H), 3.86 (ddd, *J* = 15.2, 12.2, 9.4 Hz, 1H), 3.51 (ddd, *J* = 30.8, 15.3, 2.8 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 143.1, 139.7, 135.5 (q, *J* = 33.1 Hz), 133.2 (d, *J* = 19.9 Hz), 129.6, 128.9, 126.3 (q, *J* = 3.7 Hz), 125.6 (d, *J* = 6.0 Hz), 123.1 (q, *J* = 273.3 Hz), 88.6 (d, *J* = 175.9 Hz), 62.4 (d, *J* = 26.7 Hz), 21.1. ¹⁹F NMR (471 MHz, Chloroform-d) δ -63.1 (s), -170.5 (ddd, *J* = 46.3, 30.8, 12.2 Hz). HRMS (ESI) calculated for C₁₆H₁₄F₃O₂S⁺ [M-HF]⁺: 327.0661; found: 327.0663.



1-Bromo-2-fluoro-4-((2-fluoro-2-(p-tolyl)ethyl)sulfonyl)benzene (11)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 58.8 mg (52% yield) of **11** as a white solid. IR: 3089(w), 2925(w), 1317(s), 1234(s), 1141(s), 1039(m), 819(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.76 (dd, J = 8.3, 6.4 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.19 – 7.12 (m, 4H), 5.96 (ddd, J = 47.3, 9.4, 2.6 Hz, 1H), 3.84 (ddd, J = 15.2, 12.1, 9.5 Hz, 1H), 3.49 (ddd, J = 30.8, 15.3, 2.7 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 159.8, 157.8, 140.6 (d, J = 5.6 Hz), 139.8 (d, J = 2.3 Hz), 134.6, 133.1 (d, J = 20.0 Hz), 129.6, 125.6 (d, J = 6.0 Hz), 124.9 (d, J = 4.2 Hz), 116.6 (d, J = 26.2 Hz), 88.6 (d, J = 176.1 Hz), 62.4 (d, J = 26.8 Hz), 21.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -102.5 (t, J = 6.7 Hz), -170.7 (ddd, J = 45.0, 30.8, 12.1 Hz). HRMS (ESI) calculated for C₁₅H₁₃BrF₂O₂SNa⁺ [M+Na]⁺: 398.9659; found: 398.9654.



1-((2-Fluoro-2-(p-tolyl)ethyl)sulfonyl)-3,5-bis(trifluoromethyl)benzene (12) Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 58.3 mg (47% yield) of **12** as a white solid. IR: 3088(w), 2927(w), 1359(m), 1278(s), 1137(s), 1107(s), 844(w). ¹H NMR (500 MHz, Chloroform-d) δ 8.37 (s, 2H), 8.14 (s, 1H), 7.18-7.12 (m, 4H), 6.02 (ddd, J = 47.2, 9.4, 2.9 Hz, 1H), 3.91 (ddd, J = 15.4, 11.5, 9.4 Hz, 1H), 3.60 (ddd, J = 30.4, 15.4, 2.9 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.6, 140.1, 133.1 (q, J =34.7 Hz), 132.7 (d, J = 19.9 Hz), 129.8, 129.0, 127.6 (p, J = 3.5 Hz), 125.8 (d, J = 5.9Hz), 122.4 (q, J = 273.4 Hz), 88.8 (d, J = 175.4 Hz), 62.4 (d, J = 26.9 Hz), 21.2. ¹⁹F NMR (376 MHz, Chloroform-d) δ -62.9 (s), -169.8 (ddd, J = 46.6, 30.4, 11.5 Hz). HRMS (ESI) calculated for C₁₇H₁₃F₆O₂S⁺ [M-HF]⁺: 395.0535; found: 395.0534.



2-((2-Fluoro-2-(p-tolyl)ethyl)sulfonyl)-1,3,5-trimethylbenzene (13)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 15:1) to give 36.5 mg (38% yield) of **13** as a white solid. IR: 2925(m), 1452(w), 1309(s), 1140(s), 1052(w), 820(w), 785(w). ¹H NMR (500 MHz, Chloroform-d) δ 7.20-7.15 (m, 4H), 7.00-6.94 (m, 2H), 6.01 (ddd, *J* = 47.6, 9.4, 2.2 Hz, 1H), 3.84 (ddd, *J* = 15.0, 13.8, 9.4 Hz, 1H), 3.40 (ddd, *J* = 31.9, 15.0, 2.3 Hz, 1H), 2.69 (s, 6H), 2.34 (s, 3H), 2.31 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 143.5, 140.0, 139.3 (d, *J* = 2.1 Hz), 134.2 (d, *J* = 20.0 Hz), 133.6, 132.3, 129.5, 125.4 (d, *J* = 6.2 Hz), 88.5 (d, *J* = 176.3 Hz), 62.6 (d, *J* = 26.1 Hz), 22.9, 21.2, 21.0. ¹⁹F NMR (471 MHz, Chloroform-d) δ -172.9 (ddd, *J* = 46.6, 31.9, 13.9 Hz). HRMS (ESI) calculated for C₁₈H₂₁O₂S⁺ [M-HF]⁺: 301.1257; found: 301.1255.



2-((2-Fluoro-2-(p-tolyl)ethyl)sulfonyl)thiophene (14)

Followed **Method A**, 0.1 mL of TFE was used instead of $(NH_4)_2HPO_4$. The desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 53.8 mg (63% yield) of **14** as a white solid.

IR: 3098(w), 2925(w), 1402(m), 1313(s), 1138(s), 1016(s), 820(m), 724(s). ¹H NMR (500 MHz, Chloroform-d) δ 7.74 (d, J = 4.5 Hz, 2H), 7.20-7.17 (m, 4H), 7.16 (t, J = 4.4 Hz, 1H), 6.00 (ddd, J = 47.5, 9.4, 2.4 Hz, 1H), 3.93 (ddd, J = 15.1, 13.2, 9.4 Hz, 1H), 3.55 (ddd, J = 30.5, 15.1, 2.4 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 140.4, 139.5 (d, J = 2.3 Hz), 134.8, 134.5, 133.7 (d, J = 20.0 Hz), 129.6, 127.9, 125.6 (d, J = 6.1 Hz), 88.5 (d, J = 176.8 Hz), 63.8 (d, J = 26.6 Hz), 21.2.

¹⁹F NMR (471 MHz, Chloroform-d) δ -171.7 (ddd, J = 43.9, 30.6, 13.0 Hz). HRMS (ESI) calculated for C₁₃H₁₃O₂S₂⁺ [M-HF]⁺: 265.0351; found: 265.0357.

(1-Fluoro-2-(octylsulfonyl)ethane-1,1-diyl)dibenzene (15)

Followed Method A, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 90.4 mg (80% yield) of **15** as a colorless liquid. IR: 3062(w), 2925(m), 2855(w), 1318(s), 1128(s), 1058(w), 750(m), 718(m), 696(s). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.50-7.28 (m, 10H), 4.08 (d, *J* = 21.5 Hz, 2H), 2.89 (dd, *J* = 12.1, 4.0 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.26 (s, 10H), 0.88 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.6 (d, *J* = 23.5 Hz), 128.50, 128.48, 125.1 (d, *J* = 8.2 Hz), 96.2 (d, *J* = 179.9 Hz), 61.3 (d, *J* = 25.2 Hz), 55.6 (d, *J* = 5.0 Hz), 31.6, 28.9, 28.8, 28.3, 22.5, 21.5, 14.0. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -148.0 (t, *J* = 21.5 Hz). HRMS (ESI) calculated for C₂₂H₂₉FO₂SNa⁺ [M+Na]⁺: 399.1765; found: 399.1781.



1-(Tert-butyl)-4-(2-((4-chlorophenyl)sulfonyl)-1-fluoroethyl)benzene (16)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 15:1) to give 69.3 mg (58% yield) of **16** as a white solid. IR: 3092(w), 2962(s), 1314(s), 1144(s), 1087(s), 831(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.86 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 7.8 Hz, 2H), 5.98 (ddd, J = 47.4, 9.3, 2.5 Hz, 1H), 3.83 (ddd, J = 15.1, 12.6, 9.4 Hz, 1H), 3.49 (ddd, J = 30.7, 15.2, 2.7 Hz, 1H), 1.30 (s, 9H). ¹³C NMR (126 MHz, Chloroform-d) δ 152.8, 140.7, 138.1, 133.4 (d, J = 20.0 Hz), 129.8, 129.5, 125.9, 125.4 (d, J = 6.0 Hz), 88.5 (d, J = 175.9 Hz), 62.5 (d, J = 26.6 Hz), 34.7, 31.2. ¹⁹F NMR (471 MHz, Chloroform-d) δ -171.2 (ddd, J = 45.3, 30.7, 12.7 Hz). HRMS (ESI) calculated for C₁₈H₂₀ClO₂S⁺ [M-HF]⁺: 335.0867; found: 335.0863.



4-(2-((4-Chlorophenyl)sulfonyl)-1-fluoroethyl)-1,1'-biphenyl (17)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 44.7 mg (40% yield) of **17** as a white solid. IR: 3059(w), 2925(s), 1314(s), 1144(s), 1087(s), 831(m), 763(s), 698(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.90 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.57 – 7.53 (m, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 7.3 Hz, 1H), 7.34 (d, J = 7.9 Hz, 2H), 6.06 (ddd, J = 47.3, 9.5, 2.4 Hz, 1H), 3.86 (ddd, J = 15.2, 12.7, 9.5 Hz, 1H), 3.53 (ddd, J = 31.3, 15.2, 2.5 Hz, 1H). ¹³C NMR (126 MHz, Chloroform-d) δ 142.6, 140.8, 140.0, 138.1, 135.3 (d, J = 20.0 Hz), 129.8, 129.6, 128.9, 127.8, 127.7, 127.1, 126.0 (d, J = 6.3 Hz), 88.5 (d, J = 176.7 Hz), 62.6 (d, J = 26.3 Hz). ¹⁹F NMR (471 MHz, Chloroform-d) δ -172.7 (ddd, J = 45.4, 31.3, 12.6 Hz). HRMS (ESI) calculated for C₂₀H₁₆ClO₂S⁺ [M-HF]⁺: 355.0554; found: 355.0556.



1-Chloro-4-((2-fluoro-2-(4-fluorophenyl)ethyl)sulfonyl)benzene (18)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 36.9 mg (40% yield) of **18** as a white solid. IR: 3091(w), 2928(w), 1314(s), 1226(s), 1143(s), 1087(s), 834(m). ¹H NMR (500 MHz, Chloroform-d) δ 7.89 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.07 (t, J = 8.4 Hz, 2H), 6.00 (ddd, J = 47.1, 9.5, 2.5 Hz, 1H), 3.80 (ddd, J = 15.2, 12.7, 9.5 Hz, 1H), 3.45 (ddd, J = 31.3, 15.2, 2.5 Hz, 1H). ¹³C NMR (126 MHz, Chloroform-d) δ 163.2 (dd, J = 249.3, 2.3 Hz), 140.9, 138.0, 132.4 (dd, J = 20.5, 3.2 Hz), 129.8, 129.6, 127.6 (dd, J = 8.5, 6.2 Hz), 116.1 (d, J = 21.9 Hz), 88.1 (d, J = 177.0 Hz), 62.6 (d, J = 26.3 Hz). ¹⁹F NMR (471 MHz, Chloroform-d) δ -111.1 (tq, J = 8.5, 4.5 Hz), -171.3 (ddd, J = 45.4, 31.1, 13.2 Hz). HRMS (ESI) calculated for C₁₄H₁₁ClFO₂S⁺ [M-HF]⁺: 297.0147; found: 297.0147.



4-(2-((4-Chlorophenyl)sulfonyl)-1-fluoroethyl)phenyl acetate (19)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 7:1) to give 34.7 mg (33% yield) of **19** as a white solid. IR: 3092(w),2930(w), 1755(s), 1315(s), 1197(s), 1145(s), 1088(s), 832(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.02 (ddd, *J* = 47.2, 9.6, 2.2 Hz, 1H), 3.79 (ddd, *J* = 15.2, 12.8, 9.6 Hz, 1H), 3.46 (ddd, *J* = 31.9, 15.2, 2.3 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.1, 151.4, 140.8, 138.0, 134.0 (d, *J* = 20.4 Hz), 129.8, 129.6, 126.7 (d, *J* = 6.3 Hz), 122.2, 88.1 (d, *J* = 177.4 Hz), 62.6 (d, *J* = 26.1 Hz), 21.1. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -172.9 (ddd, *J* = 45.9, 31.7, 12.9 Hz). HRMS (ESI) calculated for C₁₆H₁₄ClO₄S⁺ [M-HF]⁺: 337.0296; found: 337.0298.



1-Chloro-4-((2-fluoro-2-phenylpropyl)sulfonyl)benzene (20)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 59.5 mg (63% yield) of **20** as a white solid. IR: 3063(w), 2929(w), 1322(s), 1142(s), 1086(s), 829(m), 762(m), 698(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 7.0 Hz, 3H), 7.27 – 7.18 (m, 2H), 3.85 – 3.65 (m, 2H), 1.96 (d, *J* = 22.7 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 141.8 (d, *J* = 21.7 Hz), 140.3, 138.8, 129.6, 129.3, 128.5, 128.2, 123.9 (d, J = 9.1 Hz), 94.0 (d, J = 178.6 Hz), 65.7 (d, J = 26.2 Hz), 26.7 (d, J = 24.2 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -144.7 (pd, J = 22.5, 14.8 Hz). HRMS (ESI) calculated for C₁₅H₁₄ClO₂S⁺ [M-HF]⁺: 293.0398; found: 293.0392.



(3-((4-Chlorophenyl)sulfonyl)-2-fluoropropane-1,2-diyl)dibenzene (21)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 74.7 mg (64% yield) of **21** as a white solid. IR: 3064(w), 2923(m), 1321(s), 1144(s), 1088(s), 763(m), 699(s). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.25-7.18 (m, 6H), 7.06 (d, *J* = 6.6 Hz, 2H), 7.00 (d, *J* = 4.4 Hz, 2H), 3.84 (d, *J* = 18.6 Hz, 2H), 3.48 (dd, *J* = 22.0, 14.2 Hz, 1H), 3.34 (dd, *J* = 23.4, 14.2 Hz, 1H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.1, 139.2 (d, *J* = 21.8 Hz), 138.8, 133.7 (d, *J* = 2.8 Hz), 130.8, 129.6, 129.1, 128.15, 128.12, 128.07, 127.1, 124.6 (d, *J* = 9.5 Hz), 95.4 (d, *J* = 184.0 Hz), 63.4 (d, *J* = 24.6 Hz), 46.9 (d, *J* = 23.0 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -154.8 (p, *J* = 21.0, 20.6 Hz). HRMS (ESI) calculated for C₂₁H₁₈ClO₂S⁺ [M-HF]⁺: 369.0711; found: 369.0716.



1-Chloro-4-((2-fluoro-2-phenylpentyl)sulfonyl)benzene (22)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 63.8 mg (63% yield) of **22** as a white solid. IR: 3059(w), 2970(s), 2930(m), 1327(s), 1153(s), 1086(s), 825(w), 773(m), 697(w). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.27 (t, *J* = 6.7 Hz, 3H), 7.18 – 7.12 (m, 2H), 3.79 (dd, *J* = 19.3, 1.9 Hz, 2H), 2.29 (tdd, *J* = 14.1, 11.6, 4.8 Hz, 1H), 1.97 (dddd, *J* = 33.1, 14.4, 11.8, 4.6 Hz, 1H), 1.35 – 1.27 (m, 1H), 1.03 (qt, J = 11.6, 5.8 Hz, 1H), 0.84 (t, J = 7.4 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.2, 139.7 (d, J = 22.0 Hz), 139.0, 129.6, 129.2, 128.4, 127.9, 124.3 (d, J = 10.1 Hz), 96.2 (d, J = 182.2 Hz), 65.1 (d, J = 25.0 Hz), 42.1 (d, J = 22.9 Hz), 16.2 (d, J = 3.7 Hz), 13.9. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -158.8 (dtd, J = 33.1, 19.2, 14.0 Hz). HRMS (ESI) calculated for C₁₇H₁₈ClO₂S⁺ [M-HF]⁺: 321.0711; found: 321.0715.



1-Chloro-4-((2-fluoro-3-methyl-2-phenylbutyl)sulfonyl)benzene (23)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 65.3 mg (64% yield) of **23** as a white solid. IR: 3063(w), 2937(m), 1323(s), 1153(s), 1086(s), 830(w), 776(m), 700(m). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.25 (dd, *J* = 5.3, 2.2 Hz, 3H), 7.09 (dd, *J* = 6.7, 3.1 Hz, 2H), 4.02 (dd, *J* = 15.2, 12.0 Hz, 1H), 3.87 (dd, *J* = 28.8, 15.2 Hz, 1H), 2.23 (dp, *J* = 20.4, 6.8 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 139.9, 138.8, 137.7 (d, *J* = 21.9 Hz), 129.6, 129.0, 127.8 (d, *J* = 2.0 Hz), 127.7, 125.1 (d, *J* = 10.4 Hz), 97.7 (d, *J* = 184.4 Hz), 63.1 (d, *J* = 23.9 Hz), 37.8 (d, *J* = 23.6 Hz), 16.8 (d, *J* = 6.1 Hz), 16.2 (d, *J* = 4.2 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -170.2 (ddd, *J* = 30.2, 20.2, 12.0 Hz). HRMS (ESI) calculated for C₁₇H₁₈ClO₂S⁺ [M-HF]⁺: 321.0711; found: 321.0715.



1-Chloro-4-((2-fluoro-2-phenyldodecyl)sulfonyl)benzene (24)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 97.1 mg (74% yield) of **24** as a white solid.

IR: 3063(w), 2924(s), 2853(s), 1323(s), 1149(s), 1087(s), 829(w), 763(m), 737(w), 699(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 5.6 Hz, 3H), 7.17 – 7.12 (m, 2H), 3.85 – 3.75 (m, 2H), 2.29 (qd, *J* = 14.2, 4.2 Hz, 1H), 2.08 – 1.89 (m, 1H), 1.22 (dd, *J* = 29.8, 13.3 Hz, 16H), 0.86 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.2, 139.7 (d, *J* = 21.9 Hz), 139.0, 129.6, 129.2, 128.4 (d, *J* = 1.8 Hz), 127.9, 124.3 (d, *J* = 10.0 Hz), 96.2 (d, *J* = 182.2 Hz), 65.2 (d, *J* = 25.0 Hz), 40.0 (d, *J* = 23.0 Hz), 31.8, 29.5, 29.4, 29.33, 29.27, 29.2, 22.7 (d, *J* = 3.4 Hz), 22.6, 14.1. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -158.9 (dtd, *J* = 33.0, 19.4, 14.3 Hz, 1H). HRMS (ESI) calculated for C₂₄H₃₂ClO₂S⁺ [M-HF]⁺: 419.1806; found: 419.1815.



(2-((4-Chlorophenyl)sulfonyl)-1-fluoroethane-1,1-diyl)dibenzene (25)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 90.7 mg (80% yield) of **25** as a white solid. Followed **Method B**, gram-scale reaction was run in 6 mmol scale and the desired

product 25 was obtained in 73% yield (1.64 g).

IR: 3091(w), 3063(w), 1324(s), 1145(s), 1086(s), 830(m), 756(m), 697(s). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.31-7.26 (m, 10H), 4.29 (d, J = 20.7 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.4, 140.2 (d, J = 12.2 Hz), 138.8, 129.8, 129.0, 128.4, 128.3, 125.0 (d, J = 8.2 Hz), 95.7 (d, J = 182.7 Hz), 64.7 (d, J = 24.6 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -149.3 (t, J = 20.6 Hz). HRMS (ESI) calculated for C₁₉H₁₆ClO₂S⁺ [M-HF]⁺: 355.0554; found: 355.0558.



1-Chloro-4-((2-cyclopropyl-2-fluoro-2-phenylethyl)sulfonyl)benzene (26)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 64.1 mg (63% yield) of **26** as a white solid. IR: 3069(w), 2981(w), 2925(w), 1322(s), 1149(s), 1087(s), 829(m). ¹H NMR (400 MHz, Chloroform-d) δ 7.57 (d, J = 7.7 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 4.8 Hz, 3H), 7.20 (d, J = 5.0 Hz, 2H), 3.96 (d, J = 18.1 Hz, 2H), 1.68 – 1.51 (m, 1H), 0.60 (tq, J = 11.0, 5.2 Hz, 2H), 0.49 (dt, J = 9.6, 5.0 Hz, 1H), 0.38 (dq, J = 10.8, 5.5 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.1, 139.0 (d, J = 22.8 Hz), 138.8, 129.5, 129.1, 128.1 (d, J = 1.1 Hz), 128.09, 124.9 (d, J = 9.2 Hz), 94.0 (d, J = 182.6 Hz), 65.3 (d, J = 26.8 Hz), 20.3 (d, J = 23.7 Hz), 2.2 (d, J = 4.8 Hz), 1.7 (d, J = 5.1 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -164.6 (q, J = 19.7 Hz). HRMS (ESI) calculated for C₁₇H₁₆ClO₂S⁺ [M-HF]⁺: 319.0554; found: 319.0556.



1-Chloro-4-((2-cyclobutyl-2-fluoro-2-phenylethyl)sulfonyl)benzene (27) Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 69.9 mg (66% yield) of **27** as a white solid. IR: 3063(w), 2941(s), 1323(s), 1150(s), 1086(s), 829(m), 767(m), 699(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.29 – 7.19 (m, 3H), 7.10 (dd, *J* = 7.3, 2.1 Hz, 2H), 3.83 – 3.63 (m, 2H), 2.85 (dp, *J* = 31.3, 8.5 Hz, 1H), 2.14 (p, *J* = 9.5 Hz, 1H), 2.01 (dtq, *J* = 11.5, 8.1, 3.8, 3.4 Hz, 1H), 1.92 – 1.73 (m, 2H), 1.68 (t, *J* = 9.8 Hz, 1H), 1.50 (dtd, *J* = 11.6, 6.5, 5.0, 2.4 Hz, 1H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.0, 137.9 (d, *J* = 144.5 Hz), 137.6, 129.6, 129.0, 128.1 (d, *J* = 1.5 Hz), 127.8, 124.8 (d, *J* = 9.6 Hz), 95.3 (d, *J* = 182.3 Hz), 62.2 (d, *J* = 26.2 Hz), 44.0 (d, *J* = 24.8 Hz), 21.9 (d, *J* = 3.5 Hz), 21.5 (d, *J* = 3.4 Hz), 16.3. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -169.7 (td, J = 29.4, 9.0 Hz). HRMS (ESI) calculated for C₁₈H₁₈ClO₂S⁺ [M-HF]⁺: 333.0711; found: 333.0715.



1-Chloro-4-((2-cyclopentyl-2-fluoro-2-phenylethyl)sulfonyl)benzene (28)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 68.9 mg (63% yield) of **28** as a white solid. IR: 3061(w), 2955(s), 2869(m), 1326(s), 1143(s), 1086(s), 824(w), 772(m), 700(m). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.15 – 7.08 (m, 2H), 4.00 (dd, *J* = 15.2, 9.0 Hz, 1H), 3.85 (dd, *J* = 29.5, 15.2 Hz, 1H), 2.39 (ddt, *J* = 28.9, 17.2, 8.7 Hz, 1H), 1.78 (tt, *J* = 8.3, 4.7 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.57 – 1.36 (m, 4H), 1.28 – 1.18 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 139.9, 138.94 (d, *J* = 38.9 Hz), 138.91, 129.6, 129.0, 128.0 (d, *J* = 2.0 Hz), 127.6, 124.8 (d, *J* = 10.3 Hz), 96.5 (d, *J* = 185.2 Hz), 64.3 (d, *J* = 25.0 Hz), 49.9 (d, *J* = 22.9 Hz), 26.6 (d, *J* = 3.9 Hz), 26.3 (d, *J* = 3.4 Hz), 25.7, 25.1. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -172.0 (td, *J* = 29.4, 8.8 Hz). HRMS (ESI) calculated for C₁₉H₂₀ClO₂S⁺ [M-HF]⁺: 347.0867; found: 347.0871.



1-Chloro-4-((2-cyclohexyl-2-fluoro-2-phenylethyl)sulfonyl)benzene (29)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 79.4 mg (70% yield) of **29** as a white solid. IR: 3061(w), 2930(s), 2854(s), 1324(s), 1142(s), 1087(s), 824(w), 774(m), 700(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.25 (t, *J* = 5.6 Hz, 3H), 7.11 – 7.05 (m, 2H), 4.03 (dd, *J* = 15.1, 12.3 Hz, 1H), 3.87 (dd,

J = 29.2, 15.2 Hz, 1H), 1.92 - 1.79 (m, 2H), 1.74 (d, J = 13.6 Hz, 1H), 1.67 (d, J = 13.2 Hz, 1H), 1.59 (d, J = 12.9 Hz, 1H), 1.41 (d, J = 12.3 Hz, 1H), 1.15 (dq, J = 26.1, 13.0 Hz, 2H), 1.05 - 0.83 (m, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.0, 138.9, 138.0 (d, J = 22.2 Hz), 129.7, 129.0, 127.9 (d, J = 1.9 Hz), 127.7, 125.1 (d, J = 10.5 Hz), 97.6 (d, J = 183.4 Hz), 62.9 (d, J = 24.0 Hz), 47.6 (d, J = 22.8 Hz), 26.6 (d, J = 5.6 Hz), 26.2 (d, J = 3.7 Hz), 26.1, 25.9, 25.8. ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -164.4 (ddd, J = 30.3, 19.0, 12.4 Hz). HRMS (ESI) calculated for C₂₀H₂₂ClO₂S⁺ [M-HF]⁺: 361.1024; found: 361.1026.



2-(1-((4-Chlorophenyl)sulfonyl)-2-fluoropropan-2-yl)naphthalene (30)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 84.4 mg (79% yield) of **30** as a white solid. IR: 3060(w), 2927(w), 1322(s), 1142(s), 1086(s), 821(m), 736(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.78 (td, *J* = 9.4, 5.1 Hz, 2H), 7.73 – 7.67 (m, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.52 – 7.48 (m, 2H), 7.23 (ddt, *J* = 9.2, 7.3, 2.0 Hz, 3H), 3.90 – 3.83 (m, 2H), 2.03 (d, *J* = 22.7 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.1, 138.5, 138.4, 138.3, 132.7, 132.6 (d, *J* = 1.2 Hz), 129.4, 129.0, 128.4, 128.1, 127.5, 126.7, 123.2 (d, *J* = 10.1 Hz), 121.7 (d, *J* = 7.9 Hz), 94.1 (d, *J* = 178.7 Hz), 65.5 (d, *J* = 26.4 Hz), 26.7 (d, *J* = 24.0 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -143.4 (pd, *J* = 22.5, 16.9 Hz). HRMS (ESI) calculated for C₁₉H₁₆ClO₂S⁺ [M-HF]⁺: 343.0554; found: 343.0556.



1-Chloro-4-((2-fluoro-2-methyl-4-phenylbut-3-yn-1-yl)sulfonyl)benzene (31) Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 59.6 mg (59% yield) of **31** as a white solid.

IR: 3089(w), 2990(w), 2235(m), 1325(s), 1146(s), 1086(s), 820(m), 756(s), 690(m). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.32 (s, 5H), 3.77 (d, J = 14.5 Hz, 2H), 1.94 (d, J = 20.8 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.7, 138.3 (d, J = 1.7 Hz), 131.8 (d, J = 2.6 Hz), 130.0 (d, J = 1.0 Hz), 129.4, 128.3, 120.8 (d, J = 3.5 Hz), 88.9 (d, J = 9.1 Hz), 86.4, 85.2 (d, J = 28.6 Hz), 84.7, 64.5 (d, J = 27.5 Hz), 27.8 (d, J = 25.8 Hz). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -127.7 (qt, J = 20.8, 14.5 Hz). HRMS (ESI) calculated for C₁₇H₁₅ClFO₂S⁺ [M+H]⁺: 337.0460; found: 337.0466.



1-Chloro-4-((1-fluoro-1-phenylpropan-2-yl)sulfonyl)benzene (32)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 48.3 mg (51% yield) of **32** as a colorless liquid. IR: 3091(w), 2928(w), 1312(s), 1145(s), 1086(s), 830(m), 765(s), 700(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.36 (dt, *J* = 15.1, 7.0 Hz, 3H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.35 (d, *J* = 47.3 Hz, 1H), 3.35 (dqd, *J* = 28.6, 7.1, 1.5 Hz, 1H), 1.22 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.8, 136.5 (d, *J* = 20.8 Hz), 135.6, 131.0 (d, *J* = 1.3 Hz), 129.3, 128.7 (d, *J* = 1.1 Hz), 128.6, 124.6 (d, *J* = 8.7 Hz), 89.6 (d, *J* = 182.0 Hz), 66.6 (d, *J* = 23.5 Hz), 7.2 (d, *J* = 5.6 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -197.5 (dd, *J* = 47.3, 28.7 Hz). HRMS (ESI) calculated for C₁₅H₁₄ClO₂S⁺ [M-HF]⁺: 293.0398; found: 293.0401.



2-((4-Chlorophenyl)sulfonyl)-1-fluoro-1,2,3,4-tetrahydronaphthalene (33) Followed Method A, the desired pure product was purified using silica gel

chromatography (PE:EA = 10:1) to give 47.7 mg (47% yield) of **33** as a white solid. IR: 3067(w), 2929(w), 1314(s), 1147(s), 1087(s),831(w), 749(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 6.7 Hz, 1H), 7.26 (q, *J* = 5.4, 4.4 Hz, 2H), 7.12 (d, *J* = 6.7 Hz, 1H), 5.97 (dd, *J* = 51.9, 8.2 Hz, 1H), 3.60 (dddd, *J* = 14.2, 12.0, 8.3, 3.7 Hz, 1H), 3.02 – 2.88 (m, 2H), 2.60 (ddt, *J* = 12.9, 8.4, 3.9 Hz, 1H), 2.06 (ddt, *J* = 17.6, 11.4, 5.8 Hz, 1H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.7, 137.5 (d, *J* = 1.7 Hz), 135.6 (d, *J* = 3.8 Hz), 132.3 (d, *J* = 18.5 Hz), 130.2 (d, *J* = 1.2 Hz), 129.5, 129.0 (d, *J* = 2.9 Hz), 128.3, 127.6 (d, *J* = 7.1 Hz), 126.9 (d, *J* = 1.6 Hz), 87.7 (d, *J* = 177.4 Hz), 65.7 (d, *J* = 18.6 Hz), 27.6 (d, *J* = 1.3 Hz), 20.6 (d, *J* = 3.8 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -166.2 (dd, *J* = 52.0, 14.1 Hz). HRMS (ESI) calculated for C₁₆H₁₄ClO₂S⁺ [M-HF]⁺: 305.0398; found: 305.0401.



2-(1-((4-Chlorophenyl)sulfonyl)-2-fluoropropan-2-yl)benzo[b]thiophene (34) Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 57.5 mg (52% yield) of **34** as a white solid. IR: 3062(w), 2926(w), 1322(s), 1149(s), 1087(s),830(m), 748(m). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.36 (p, *J* = 7.1 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.14 (s, 1H), 3.97 – 3.79 (m, 2H), 2.16 (d, *J* = 22.3 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 144.6 (d, *J* = 24.8 Hz), 140.4, 139.4, 138.7, 138.1, 129.5, 129.1, 125.2, 124.8, 124.0, 122.2, 121.5 (d, *J* = 6.3 Hz), 92.4 (d, *J* = 176.4 Hz), 65.7 (d, *J* = 28.1 Hz), 26.3 (d, *J* = 23.3 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -126.0 (ddq, *J* = 32.3, 22.0, 11.0 Hz). HRMS (ESI) calculated for C₁₇H₁₄ClO₂S₂⁺ [M-HF]⁺: 349.0118; found: 349.0115.



2-(1-((4-Chlorophenyl)sulfonyl)-2-fluoropropan-2-yl)thiazole (35)

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 10:1) to give 47.1 mg (49% yield) of **35** as a white solid. IR: 3091(w), 2986(w), 1324(s), 1147(s), 1085(s), 830(m), 735(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 3.1 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 3.1 Hz, 1H), 4.11 (dd, *J* = 18.0, 15.2 Hz, 1H), 3.98 (dd, *J* = 18.1, 15.2 Hz, 1H), 2.00 (d, *J* = 22.1 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 170.2 (d, *J* = 30.0 Hz), 142.7, 140.5, 138.7, 129.6, 129.4, 120.1, 94.0 (d, *J* = 177.4 Hz), 63.7 (d, *J* = 23.0 Hz), 27.1 (d, *J* = 23.9 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -138.5 (h, *J* = 20.2, 19.7 Hz). HRMS (ESI) calculated for C₁₂H₁₁ClNO₂S₂⁺ [M-HF]⁺: 299.9914; found: 299.9916.

4. Mechanistic Experiments

4.1Radical trapping experiment



In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, 4-chlorobenzenesulfonyl hydrazide (1, 2.0 equiv.), $(NH_4)_2HPO_4$ (1.0 equiv.) and either TEMPO or BHT (2.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N₂, 4-methylstyrene (**2**, 0.3 mmol), Et₃N·3HF (0.3 mL), CH₃CN (8.0 mL), and DCM (2.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at room temperature for 4 h. The reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 15 mL). The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the NMR spectroscopy of the crude residue showed no desired product formed.



In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, 4-chlorobenzenesulfonyl hydrazide (1, 2.0 equiv.) and and $(NH_4)_2HPO_4$ (1.0 equiv.), N-methyl-N-phenylmethylacrylamide⁴ (41, 0.3 mmol), and ^{*n*}Bu₄NPF₆ (1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N₂, CH₃CN (8.0 mL), and DCM (2.0 mL) were injected

respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at room temperature for 4 h. The reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 15 mL). The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. The yield of desired product **42** was determined by ¹H NMR with dibromomethane as the internal standard.

3-(((4-Chlorophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (42)⁴

¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.91 (d, *J* = 14.6 Hz, 1H), 3.68 (d, *J* = 14.6 Hz, 1H), 3.17 (s, 3H), 1.38 (s, 3H).

4.2Radical clock experiment



In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, 4-chlorobenzenesulfonyl hydrazide (1, 2.0 equiv.) and and $(NH_4)_2HPO_4$ (1.0 equiv.) were added. The glassware was equipped with carbon cloth (15 mm × 15 mm × 0.1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of N₂, (1-(2-phenylcyclopropyl)-vinyl)benzene (**39**, 0.3 mmol), Et₃N·3HF (0.3 mL), CH₃CN (8.0 mL), and DCM (2.0 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA at room temperature for 4 h. The reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 15 mL). The aqueous layer was separated and extracted with dichloromethane (3×5 mL), and the combined organic layers were washed with brine and dried over sodium sulfate.

Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield products **40** (18.3 mg, 15% yield).

(5-((4-Chlorophenyl)sulfonyl)-1-fluoropent-3-ene-1,4-diyl)dibenzene (40)

IR: 3032(w), 2925(w), 1318(s), 1136(s), 1087(s), 830(w), 761(m), 698(m). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, J = 8.7 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.38 – 7.34 (m, 3H), 7.27 (d, J = 8.3 Hz, 2H), 7.19 – 7.14 (m, 3H), 7.10 – 7.00 (m, 2H), 6.11 (t, J = 7.4 Hz, 1H), 5.58 (ddd, J = 47.5, 7.7, 4.6 Hz, 1H), 4.34 – 4.25 (m, 2H), 2.94 – 2.73 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 140.3 (d, J = 16.4 Hz), 139.4, 139.3, 137.2, 132.3 (d, J = 4.5 Hz), 130.6, 129.8, 129.1, 128.6, 128.5 (d, J = 1.7 Hz), 128.3, 127.5, 126.3, 125.4 (d, J = 6.9 Hz), 93.2 (d, J = 173.8 Hz), 57.8, 37.3 (d, J = 24.2 Hz). ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -176.3 (ddd, J = 47.0, 27.5, 19.2 Hz). HRMS (ESI) calculated for C₂₃H₂₀ClO₂S⁺ [M-HF]⁺: 395.0867; found: 395.0879.

4.3Cyclic voltammetry studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode and submerged in saturated aqueous KCl solution Ag/AgCl reference electrode. Current was reported in A, while all potentials were reported in V.



Figure S1. Cyclic voltammogram in the mixed solvent (MeCN/DCM = 8mL:2 mL) with "Bu₄NPF₆ (5 mM) as electrolyte; Conditions: "Bu₄NPF₆ (5 mM in the mixed solvent)

with (black curve) none; (red curve) 4-chlorobenzenesulfonyl hydrazide (1, 5 mM); (blue curve) 4-chlorobenzenesulfonyl hydrazide (1, 5 mM) and $(NH_4)_2HPO_4$ (2.5 mM). Scan rate: 0.1 V/s.



Figure S2. Cyclic voltammogram in the mixed solvent (MeCN/DCM = 8mL:2 mL) with "Bu₄NPF₆ (5 mM) as electrolyte; Conditions: "Bu₄NPF₆ (5 mM in the mixed solvent) with (black curve) 4-methylstyrene (2, 15 mM); (red curve) 4-methylstyrene (2, 15 mM) and (NH₄)₂HPO₄ (2.5 mM). Scan rate: 0.1 V/s.

4.4 Screening of different additives

| O O S NHNH ₂ | + Et_3N*3HF $CCE = 10 \text{ mA}$ MeCN/DCM (8 mL:2 mL) | |
|----------------------------|---|---------------------|
| 1 | 2 r.t., N ₂ , 4 h undivided cell | 3 |
| entry | Additive | yield/ (%) |
| 1 | (NH ₄) ₂ HPO ₄ | 70(61) ^b |
| 2 | Na ₂ HPO ₄ | 62 |
| 3 | NH ₄ H ₂ PO ₄ | 62 |
| 4 | NaH ₂ PO ₄ | 60 |
| 5 | KH ₂ PO ₄ | 57 |
| 6 | K ₂ HPO ₄ | 61 |
| 7 | K ₃ PO ₄ | 57 |
| 8 | H ₃ PO ₄ | 48 |
| 9 | none | 63 |

Table S1. Screening of different additives ^a

^{*a*} Reaction conditions: **1** (0.6 mmol), **2** (0.3 mmol), Et₃N 3HF (0.3 mL), MeCN (8.0 mL), DCM (2.0 mL), additive (1.0 equiv.), carbon cloth anode, platinum cathode, undivided cell, constant current = 10 mA, room temperature, 4 h, yields were determined by ¹⁹F NMR with (trifluoromethoxy)benzene as the internal standard; ^{*b*} Isolated yield.

The presence of excess amount of $Et_3N \cdot 3HF$, acting both as the fluorinating agent and electrolyte, renders the investigation of the role of $(NH_4)_2HPO_4$ a challenging task. Nevertheless, besides cyclic voltammetry studies, we have further screened various additives by varying either the cation (Na^+, K^+) or anion $(H_2PO_4^-, PO_4^{3-})$. However, those experiments only provided similar or inferior results than that of without additive.

The use of $(NH_4)_2HPO_4$ as the additive provides an approximately 10% yield enhancement than that of its absence, meaning only a limited beneficial effects exists in this fluorosulfonylation. Though detailed investigations are still need, we tentatively propose the anode adsorbed HPO_4^- might increase the concentration of hydrofluoride probably via H-bonding, toward productive nucleophilic fluorination, among many other possible beneficial effects of $(NH_4)_2HPO_4$ in this fluorosulfonylation reaction.

5. Derivatizations of 25

5.1 Reduction of 25⁷

$$Ar \xrightarrow{P_h} P_h \xrightarrow{\text{LiAlH}_4 (2 \text{ equiv.})} Ar \xrightarrow{P_h} P_h$$

$$THF (0.13 \text{ M})$$
25, Ar = 4-ClC₆H₄ 0 °C to 75 °C, 20 h **36**

In an oven-dried Schlenk tube (10 mL) equipped with a stirring bar, compound **25** (0.26 mmol) was added. Under the protection of N₂, THF (2 mL) was injected into the Schlenk tube via a syringe, and LiAlH₄ was added at 0 °C. The reaction mixture was stirred at 75 °C for 20 h. At 0 °C, the reaction mixture was diluted with ice-cold water (10 mL) and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with phosphoricacid (85 %), water, saturated aqueous NaHCO₃ solution, again water, brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield **36** as white solid (69.6 mg, 75% yield).

(2-((4-chlorophenyl)sulfonyl)ethane-1,1-diyl)dibenzene (36)⁸

¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (q, *J* = 9.2, 7.8 Hz, 6H), 7.10 (d, *J* = 7.4 Hz, 4H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.92 (d, *J* = 7.2 Hz, 2H).

5.2 Dehydrofluorination of 25⁵



In an oven-dried Schlenk tube (10 mL) equipped with a stirring bar, compound **25** (0.1 mmol) was added. Under the protection of N_2 , *tert*-butanol (5 mL) was injected

into the Schlenk tube via a syringe, and the potassium *tert*-butoxide was added. The reaction mixture was stirred at 60 °C for 4 h. The reaction mixture was subsequently poured into water. The aqueous layer was separated and extracted with dichloromethane $(3 \times 5 \text{ mL})$, and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield **37** as white solid (33.7 mg, 95% yield).

(2-((4-chlorophenyl)sulfonyl)ethene-1,1-diyl)dibenzene (37)⁶

¹H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.26 (m, 6H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 2H), 7.02 (s, 1H).

5.3 Synthesis of Compound 38⁹



In an oven-dried Schlenk tube (10 mL) equipped with a stirring bar, compound **25** (0.6 mmol) was added. Under the protection of N₂, THF (2.5 mL) was injected into the Schlenk tube via a syringe, and then cooled to -78 °C. Then 1 mL of a 1.6 M solution of *n*-BuLi (2.5 equiv.) in hexane was added dropwise. After stirring at -78 °C for 15 min, the allyl bromide was added. The reaction mixture was stirred at -78 °C for 15 min and then warmed to room temperature over night. The reaction mixture was quenched with 2 mL of water, and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with water, brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield compound **38** as white solid (94.9 mg, 40% yield).

(2-((4-Chlorophenyl)sulfonyl)penta-1,4-diene-1,1-diyl)dibenzene (38)

IR: 3082(w), 1638(w), 1308(s), 1147(s), 912(m), 828(m), 759(s), 705(s). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dq, J = 7.2, 4.3, 3.8 Hz, 5H), 7.18 (t, J = 7.9 Hz, 3H), 7.11 (t, J = 7.5 Hz, 4H), 6.93 (d, J = 7.3 Hz, 2H), 6.00 (ddt, J = 16.6, 10.2, 6.3 Hz, 1H), 5.19 – 5.04 (m, 2H), 3.39 (d, J = 6.3 Hz, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 153.3, 141.0, 140.5, 139.9, 138.8, 138.7, 134.9, 129.1, 128.9, 128.48, 128.46, 128.3, 127.9, 127.7, 127.6, 117.4, 34.7. HRMS (ESI) calculated for C₂₃H₂₀ClO₂S⁺ [M+H]⁺: 395.0867; found: 395.0856.

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$\int_{-171.05}^{-171.02} \frac{-171.05}{-171.05} -171.12 -171.12 -171.15 -171.15 -171.15 -171.19 -171.19 -171.22 -1771.22 -17711.22 -1771$

0 II 3 ¹⁹F NMR (471 MHz, CDCl₃)

150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25 f1 (ppm)








200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



0 II ö Иe 5¹⁹F NMR (471 MHz, CDCl₃)







-170.68 -170.71 -170.75 -170.75 -170.85 -170.85 -170.87



10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

Ö OMe **7** ¹⁹F NMR (471 MHz, CDCl₃)

-171.60 -171.63 -171.67 -171.70 -171.70 -171.73 -171.73 -171.73



S44



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

1



10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

9¹⁹F NMR (471 MHz, CDCl₃)

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20 f1 (ppm)

-170.95 -170.97 -171.01 -171.01 -171.04 -171.07 -171.11





o 11 ¹H NMR (500 MHz, CDCl₃) . 0 10.5 10.0 9.5 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 -0.5 -1 fl (ppm) 159.85
 157.83 $\begin{array}{c} 140. \ 65 \\ 140. \ 61 \\ 130. \ 61 \\ 133. \ 78 \\ 133. \ 78 \\ 133. \ 22 \\ 133. \ 22 \\ 133. \ 22 \\ 133. \ 22 \\ 123. \ 61 \\ 125. \ 67 \\ 124. \ 96 \ 124. \ 96 \ 124. \ 124. \ 96 \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124. \ 124.$ $\begin{array}{c} \sim 89.27 \\ \approx 87.87 \\ \approx 87.87 \\ 77.25 \\ 776.75 \\ 76.75 \\ 62.34 \end{array}$ ____21.19 Br 11 ¹³C NMR (126 MHz, CDCl₃)

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)







10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)





13 ¹⁹F NMR (471 MHz, CDCl₃)

$\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i$





14 ¹⁹F NMR (471 MHz, CDCl₃)

150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25 f1 (ppm)

-171.60 -171.62 -171.65 -171.66 -171.70 -171.70 -171.73 -171.76







15 ¹⁹F NMR (376 MHz, CDCl₃)

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

 $\underbrace{ \underbrace{}_{-148.\ 00}^{-148.\ 05} \\ -148.\ 05}_{-148.\ 11}$







^tBu^{*} 16 ¹⁹F NMR (471 MHz, CDCl₃)











18 ¹⁹F NMR (471 MHz, CDCl₃)











-144. 65 -144. 65 -144. 65 -144. 70 -144. 70 -144. 71 -144. 75 -144. 76 -144. 76 -144. 76 -144. 81

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20 ¹⁹F NMR (471 MHz, CDCl₃)



 $\int_{-154.80}^{-154.75} -154.80$ -154.84
-154.88
-154.88

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21 ¹⁹F NMR (471 MHz, CDCl₃)


-158.70 -158.73 -158.73 -158.74 -158.77 -158.77 -158.80 -158.80 -158.81 -158.81 -158.83 -158.83

o ^{'n}Pr CI 22 ¹⁹F NMR (471 MHz, CDCl₃)



$\int_{-170.20}^{-170.13} -170.13$

 $\hat{[}$ ö [′]Pr 23 ¹⁹F NMR (471 MHz, CDCl₃)





-158.80 -158.83 -158.84 -158.84 -158.88 -158.88 -158.99 -158.99 -158.94 -158.95 -158.95

CI []C₁₀H₂₁

24 ¹⁹F NMR (471 MHz, CDCl₃)







 $\left\{ \begin{array}{c} -149.27\\ -149.32\\ -149.36 \end{array} \right\}$



50 40 30

20 10 0

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 f1 (ppm)

26 ¹⁹F NMR (376 MHz, CDCl₃)

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

-164.53 -164.58 -164.63 -164.68



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

27 ¹⁹F NMR (471 MHz, CDCl₃)

 $\begin{pmatrix} -169.68 \\ -169.70 \\ -169.76 \\ -169.76 \\ -169.80 \\ -169.80 \\ -169.80 \\ -169.82 \\ \end{array}$





-171.95 -171.95 -171.99 -172.01 -172.05 -172.05











30 ¹⁹F NMR (471 MHz, CDCl₃)

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20 f1 (ppm)



-127. 61 -127. 65 -127. 65 -127. 66 -127. 69 -127. 70 -127. 72 -127. 72 -127. 77 -127. 76 -127. 81 -127. 81 -127. 81

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31 ¹⁹F NMR (376 MHz, CDCl₃)

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



 $\bigwedge_{-197.54}^{-197.38}$

Мe 32 ¹⁹F NMR (471 MHz, CDCl₃)





33 ¹⁹F NMR (471 MHz, CDCl₃)

-166.14 -166.17 -166.25 -166.28 7. 74 7. 68 7. 68 7. 68 7. 68 7. 40 7. 33 7. 33 7. 23 7. 23 7. 14 7. 28 7. 12 

34 ¹H NMR (400 MHz, CDCl₃)



-125.94 -125.96 -125.96 -126.01 -126.03 -126.03 -126.05 -126.05 -126.12

Мe Ś

34 ¹⁹F NMR (471 MHz, CDCl₃)





35 ¹⁹F NMR (471 MHz, CDCl₃)

0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20 f1 (ppm)

--138.40 --138.44 --138.49 --138.53 --138.53 --138.58











40 ¹⁹F NMR (471 MHz, CDCl₃)



176.20 176.24 176.24 176.30 -176.35 -176.35 -176.35

