Supporting information

Direct Electrochemical Synthesis of Arenesulfonyl Fluorides from Nitroarenes: A Dramatic Ionic Liquid Effect

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1. General

Commercial reagents such as nitroarenes and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates. 1-(Chloromethyl)-4-fluoro-1,4-diazabicyclo[2.2.2]octane-1,4-diium tetrafluoroborate (Selectfluor) was bought from Leyan.com. The chemical shifts are reported in δ (ppm) values (¹H and ¹³C NMR relative to CHCl₃, δ 7.26 ppm for ¹H NMR and δ 77.0 ppm for ¹³C NMR). Or alternatively, ¹H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*), are reported in Hertz (Hz). Commercial reagents were used without any further purification.

2. General procedure for electrochemical synthesis of Arenesulfonyl Fluorides.



General procedure for electrochemical synthesis of arenesulfonyl fluorides: An undivided cell was equipped with carbon plate anode (8 mm × 2 mm) and glassy carbon cathode (8 mm × 2 mm). To the cell was added **1a** (0.3 mmol), DABSO **2** (0.2 mmol, 48 mg), Selectfluor (0.6 mmol, 212 mg), MeOH (4 mL) and [Mim]TolSO₃ (0.5 mL) under Glove box, and then stirred at room temperature for 5 min. 'BuONO (0.90 mmol, 92.7mg) were added. The mixture was electrolyzed using constant current conditions (I = 12 mA) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **1a**), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of NaCl and the product was then extracted with CH₂Cl₂ (3×20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAcas eluent to afford the desired pure product **3a**.



Glassy carbon (Left) and Carbon plate (Right).



Current controlled electrolysis (ElectraSyn 2.0 apparatus, IKA)

3. Gram Scale Reaction.



An undivided cell was equipped with carbon plate anode (8 mm \times 2 mm) and glassy carbon cathode (8 mm \times 2 mm). To the cell was added 4nitrotoluene **1a** (9 mmol, 1.23g), DABSO 2 (6 mmol, 1.44 g), Selectfluor (18 mmol, 6.36 g), MeOH (120 mL) and [Mim]TolSO₃ (15 mL) under Glove box, and then stirred at room temperature for 10 min. 'BuONO (27 mmol, 2.78 g) were added. The mixture was electrolyzed using constant current conditions (12 mA) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **1a**), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of NaCl and the product was then extracted with CH₂Cl₂ (3 \times 60 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired pure product **3a** (1.1 g, 70%).



3a

4-Methylbenzenesulfonyl fluoride (**3a**),¹ 37.6 mg, Obtained as a colorless oil in 72% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 147.27, 130.31, 130.02 (d, *J* = 23.8 Hz), 128.38, 21.75. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.28.



3b

benzenesulfonyl fluoride (**3b**),¹ 26.4 mg, Obtained as a colorless oil in 55% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.05 – 7.98 (m, 2H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.64 (td, *J* = 7.9, 7.5, 1.1 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 135.67, 133.03 (d, *J* = 23.9 Hz), 129.72, 128.36. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.92.



3c

4-*iso*-Propylbenzenesulfonyl fluoride (**3c**), ¹ 45.5 mg, Obtained as a colorless oil in 75% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.93 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 3.07-3.01 (m, 1H), 1.31-1.28 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 157.75, 130.22 (d, *J* = 23.8 Hz), 128.63, 127.84, 34.45, 23.45. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.25.



3d

4-Ethylbenzenesulfonyl fluoride (**3d**), ¹ 40.6 mg, Obtained as a colorless oil in 72% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.97 – 7.80 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.30, 130.96 (d, *J* = 26.3 Hz), 129.19, 128.50, 28.99, 14.84. ¹⁹F NMR (471 MHz, CDCl₃) δ 66.26.



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4-(*tert*-Butyl)benzenesulfonyl fluoride (**3e**), ¹ 48.6 mg, Obtained as a yellow solid (m. p. 54–55 °C) in 75% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 1.37 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 160.02, 130.01 (d, J = 23.8 Hz), 128.34, 126.75, 35.53, 30.90. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.24.



4-Propylbenzenesulfonyl fluoride (**3f**), ¹ 44.8 mg, Obtained as a colorless oil in 74% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 1.67 (d, *J* = 7.7 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.85, 130.26 (d, *J* = 23.8 Hz), 129.74, 128.38, 37.92, 24.01, 13.51.



3g

4-Acetylbenzenesulfonyl fluoride (**3g**), ¹ 42.4 mg, Obtained as a white solid (m. p. 78–79 °C) in 70% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, J = 8.2 Hz, 2H), 8.13 (d, J = 8.3 Hz, 2H), 2.74 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.28, 142.27, 136.18 (d, J = 23.8 Hz), 129.27, 128.73, 26.79. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.60.



3h

4-Acetamidobenzenesulfonyl fluoride (**3h**), ¹ 41.0 mg, Obtained as a white solid (m. p. 174–175 °C) in 65% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 7.55 (s, 1H), 2.26 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.68, 144.41, 130.06, 119.35, 24.87. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.80.



3i, 69%

Methyl 4-(fluorosulfonyl)benzoate (**3i**), ² 45.1 mg, Obtained as a white solid (m. p. 84–86 °C) in 69% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, J = 8.3 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 4.00 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 164.93, 136.73 (d, J = 25.0 Hz), 136.50, 130.71, 128.52, 52.98. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.78.

F₃C

3j

4-(Trifluoromethyl)benzenesulfonyl fluoride (**3j**), ¹49.2 mg, Obtained as a white solid (m. p. 67–69 °C) in 72% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 137.6 – 136.1 (m), 129.11, 127.0 (d, *J* = 3.5 Hz), 122.72(q, *J* = 273 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ 65.80, -63.58.



4-Cyanobenzenesulfonyl fluoride (**3k**), ¹36.7 mg, Obtained as a white solid (m. p. 89–91 °C) in 66% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 136.91 (d, J = 23.9 Hz), 133.46, 129.16, 119.44, 116.53. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.99.



4-(methylsulfonyl)benzenesulfonyl fluoride (**3l**), ¹ 48.3 mg, Obtained as a white solid (m. p. 155–157 °C) in 68% yield. ¹H NMR (500 MHz, Chloroform-d) δ 8.24 (s, 4H), 3.14 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 147.13, 137.88 (d, *J* = 26.5 Hz), 129.62, 128.93, 44.22. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.08.



3m

4-Methoxybenzenesulfonyl fluoride (**3m**), ¹35.9 mg, Obtained as a brown liquid in 63% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.98 – 7.83 (m, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.34, 130.76, 123.75 (d, *J* = 25.0 Hz), 114.93, 55.87. ¹⁹F NMR (376 MHz, CDCl₃) δ 67.29.



3n

4-Methoxybenzenesulfonyl fluoride (**3n**), ¹49.7 mg, Obtained as a colorless oil in 65% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.74 – 7.52 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 142.68, 131.39 (d, *J* = 25.0 Hz), 130.15, 130.13, 129.89, 129.87. ¹³F NMR (376 MHz, CDCl₃) δ 66.48.



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[1,1'-Biphenyl]-4-sulfonyl fluoride (**3o**), ¹ 48.9 mg, Obtained as a white solid (m. p. 77–78 °C) in 69% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.56 – 7.43 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 148.67, 138.53, 131.36 (d, J = 30.0 Hz), 129.29, 129.23, 129.01, 129.01, 128.22, 127.48. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.56.



4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonyl fluoride (**3p**), ¹ 64.5 mg, Obtained as a white solid (m. p. 129–130 °C) in 63% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 1.37 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 135.71, 135.01 (d, *J* = 24.0 Hz), 127.25, 84.79, 24.87. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.72.



Naphthalene-1-sulfonyl fluoride (**3q**), ¹ 37.2 mg, Obtained as a white solid (m. p. 52–54 °C) in 59% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.50 (dd, J = 8.8, 2.9 Hz, 1H), 8.30 (d, J = 7.5 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.71 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.57 – 7.47 (m, 1H). ¹³ C NMR (101 MHz, CDCl₃) δ 136.9, 134.0, 131.1, 129.5, 129.2 (d, J = 23.4 Hz), 129.1, 128.2, 127.8, 124.2, 124.1. ¹⁹F NMR (376 MHz, CDCl₃) δ 62.64.



Naphthalene-2-sulfonyl fluoride (**3r**), ¹ 42.8 mg, Obtained as a white solid (m. p. 85–87 °C) in 68% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.56 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.89 (dt, *J* = 8.7, 1.4 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 135.99, 131.78, 130.92, 130.39, 130.10, 129.86 (d, *J* = 23.4 Hz), 129.58, 128.33, 128.14, 122.10. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.38.



3-Methylbenzenesulfonyl fluoride (**3s**), ¹ 37.6 mg, Obtained as a colorless oil in 72% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 6.0 Hz, 2H), 7.59 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.20, 136.35, 132.94 (d, *J* = 24.0 Hz), 129.49, 128.66, 125.57, 21.29. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.80.

F SO₂F

3-Fluorobenzenesulfonyl fluoride (**3t**), ¹ 34.0 mg, Obtained as a colorless oil in 64% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.84 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.67 (dt, *J* = 8.1, 4.1 Hz, 1H), 7.52 (td, *J* = 8.3, 2.6 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 162.34 (d, *J* = 254.52 Hz), 134.59 (d, *J* = 7.56 Hz), 131.76 (d, *J* = 7.56 Hz), 124.33 (d, *J* = 3.78 Hz), 123.08 (d, *J* = 21.42 Hz), 115.75 (d, *J* = 21.46 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ 65.79, -107.77.



3-Chlorobenzenesulfonyl fluoride (**3u**), ¹ 40.0 mg, Obtained as a colorless oil in 69% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.00 (t, *J* = 2.0 Hz, 1H), 7.92 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.76 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 135.99, 135.83, 134.49 (d, *J* = 26.3 Hz), 131.05, 128.38, 126.54. ¹⁹F NMR (471 MHz, CDCl₃) δ 66.10.



3-Bromobenzenesulfonyl fluoride (**3v**), ¹ 44.8 mg, Obtained as a colorless oil in 63% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.15 (t, *J* = 1.9 Hz, 1H), 7.96 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.92 (dt, *J* = 8.1, 1.3 Hz, 1H), 7.54 (td, *J* = 8.1, 1.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 138.75, 134.61 (d, *J* = 26.3 Hz), 131.20, 126.98, 123.53. ¹⁹F NMR (471 MHz, CDCl₃) δ 66.26.



3-(Trifluoromethyl)benzenesulfonyl fluoride (**3w**), ² 37.5 mg, Obtained as a yellow oil in 55% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 5.9 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.89 – 7.81 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 134.2 (d, *J* = 26.7 Hz), 132.51 (q, *J* = 27.0 Hz), 132.29 (q, *J* = 3.0 Hz), 131.65, 130.75, 125.6 (q, *J* = 3.6 Hz), 119.0 (q, *J* = 272.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ 66.08, -63.19.



[1,1'-Biphenyl]-3-sulfonyl fluoride (**3x**), ² 51.7 mg, Obtained as a white solid (m. p. 75–77 °C) in 73% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 2.1 Hz, 1H), 7.96 (dt, J = 8.0, 2.4 Hz, 2H), 7.67 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 7.3 Hz, 2H), 7.42 (t, J = 7.3 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 143.23, 138.30, 134.12, 133.69 (d, J = 23.9 Hz), 130.19, 129.29, 128.81, 127.22, 126.86, 126.81. ¹⁹F NMR (471 MHz, CDCl₃) δ 66.08.



3у

Methyl 3-(fluorosulfonyl)benzoate (**3y**), ² 45.8 mg, Obtained as a white solid (m. p. 65–67 °C) in 70% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.67 (d, J = 1.9 Hz, 1H), 8.51 – 8.40 (m, 1H), 8.21 (dd, J = 8.0, 1.8 Hz, 1H), 7.78 (t, J = 7.9 Hz, 1H), 4.01 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 164.58, 136.31, 133.65 (d, J = 26.0 Hz), 132.14, 132.06, 130.09, 129.51, 52.88. ¹⁹F NMR (471 MHz, CDCl₃) δ 66.52.



2-Methoxybenzenesulfonyl fluoride (**3z**), ¹ 33.6 mg, Obtained as a yellow oil in 59% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.90 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.75 – 7.66 (m, 1H), 7.20 – 7.05 (m, 2H), 3.99 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.04, 137.63, 130.98, 121.09 (d, *J* = 26.0 Hz), 120.51, 112.96, 56.51. ¹⁹F NMR (471 MHz, CDCl₃) δ 58.62.



3,5-Dimethylbenzenesulfonyl fluoride (**3aa**), ¹ 37.2 mg, Obtained as a yellow oil in 66% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.22 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 2.61 (s, 3H), 2.41 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 146.81, 138.76, 133.58, 130.08, 130.06, 129.19 (d, *J* = 21.4 Hz), 127.24, 21.40, 20.02. ¹³C NMR (126 MHz, CDCl₃) δ 146.81, 138.76, 133.58, 130.06, 129.29, 129.12, 127.24, 21.40, 20.02. ¹⁹F NMR (471 MHz, CDCl₃) δ 60.87.



3ab

2-Oxo-2*H*-chromene-6-sulfonyl fluoride (**3ab**), ¹ 48.6 mg, Obtained as a white solid (m. p. 101–103 °C) in 71% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 2.3 Hz, 1H), 8.14 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.80 (d, *J* = 9.7 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 6.62 (d, *J* = 9.7 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 158.44, 158.21, 141.74, 131.11, 129.22, 128.84 (d, *J* = 26.0 Hz), 119.43, 119.25, 118.77. ¹⁹F NMR (376 MHz, CDCl₃) δ 67.12.



3ac

Quinoline-5-sulfonyl fluoride (**3ac**), ¹ 43.7 mg, Obtained as a white solid (m. p. 93–95 °C) in 69% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.10 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.89 (ddt, *J* = 8.8, 2.5, 1.1 Hz, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.44 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.88 (ddd, *J* = 8.8, 7.4, 1.5 Hz, 1H), 7.69 (dd, *J* = 8.8, 4.2 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 152.01, 148.23, 138.52, 132.41, 131.41, 129.21 (d, *J* = 26.0 Hz), 127.64, 124.32, 123.77. ¹⁹F NMR (376 MHz, CDCl₃) δ 64.70.



3ad

1-Methyl-1H-indazole-6-sulfonyl fluoride (**3ad**), 41.7 mg, Obtained as a white solid (m. p. 89–91 °C) in 65% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (dd, *J* = 11.6, 1.3 Hz, 2H), 7.97 (dd, *J* = 8.6, 0.9 Hz, 1H), 7.71 (dd, *J* = 8.5, 1.5 Hz, 1H), 4.20 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 138.27, 133.34, 130.30 (d, J = 26.0 Hz), 127.55, 122.91, 118.52, 111.40, 36.18. ¹⁹F NMR (376 MHz, CDCl₃) δ 67.23. HRMS (EI) m/z: [M+Na]⁺ Calcd for C₈H₇FNaO₂S 237.0110; Found 237.0111.



3ae

9,9-Dimethyl-9*H*-fluorene-2-sulfonyl fluoride (**3ae**),² 57.1 mg, Obtained as a white solid (m. p. 65–68 °C) in 69% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 1.8 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.44 – 7.31 (m, 3H), 1.45 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 154.78, 146.81, 136.54, 130.70, 130.47, 129.90, 128.09, 127.70, 123.07, 122.93, 121.59, 120.75, 47.53, 26.73. ¹⁹F NMR (376 MHz, CDCl₃) δ 67.16.



Methyl 5-(fluorosulfonyl)benzofuran-2-carboxylate (**3af**), 49.3 mg, Obtained as a white solid (m. p. 133–135 °C) in 64% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 1.9 Hz, 1H), 8.09 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 1.0 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 158.52, 158.35, 148.77, 128.81 (d, *J* = 26.0 Hz), 127.71, 126.92, 125.09, 113.99, 113.29, 62.27, 14.25. 19F NMR (376 MHz, CDCl₃) δ 67.63. HRMS (EI) m/z: [M+H]⁺ Calcd for C₁₀H₈FO₅S 259.0076; Found 259.0074.



4-(Methylsulfonamido)-3-phenoxybenzenesulfonyl fluoride (**3ag**), 55.9 mg, Obtained as a white solid (m. p. 95–96 °C) in 54% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.75 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.02 (m, 2H), 3.19 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.92, 146.62, 134.80, 130.78, 127.69, 127.49, 126.15, 124.39, 119.69, 117.83, 115.96, 40.71. ¹⁹F NMR (471 MHz, CDCl₃) δ 66.77. HRMS (EI) m/z: [M+Na]⁺ Calcd for C₁₃H₁₂FNNaO₅S₂ 368.0039; Found 368.0041.



(1*S*,2*R*,5*S*)-2-*iso*-Propyl-5-methylcyclohexyl 4-(fluorosulfonyl)benzoate (**3ah**), ¹ 66.7 mg, Obtained as a yellow oil in 65% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 2H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.84 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.68 (dt, *J* = 15.1, 3.9 Hz, 2H), 1.51 (ddt, *J* = 13.9, 10.6, 3.7 Hz, 3H), 1.06 (qd, *J* = 12.1, 10.9, 4.6 Hz, 2H), 0.86 (t, *J* = 7.1 Hz, 6H), 0.72 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.96, 137.22, 136.55, 136.30, 130.70, 128.51, 47.16, 40.80, 34.16, 31.47, 26.58, 23.54, 22.03, 20.75, 16.47. ¹⁹F NMR (376 MHz, CDCl₃) δ 65.92.



4-(2,4-Dichlorophenoxy)benzene-1-sulfonyl fluoride (**3ai**), 65.1 mg, Obtained as a white solid (m. p. 101–103 °C) in 68% yield. Clear liquid ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.85 (m, 2H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.27 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 7.00 – 6.95 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.85, 148.50, 132.07, 131.12, 131.10, 128.84, 128.09, 126.80, 126.55, 123.82, 116.91. ¹⁹F NMR (376 MHz, CDCl₃) δ 66.99. HRMS (EI) m/z: [M+H]⁺ Calcd for C₁₂H₈Cl₂FO₃S 320.9555; Found 320.9558.



Dibenzo[*b*,*d*]thiophene 5,5-dioxide (**5**), 104.3 mg, Obtained as a white solid (m. p. 231–232 °C) in 69% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.51 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 137.69, 133.92, 131.59, 130.38, 122.12, 121.64.

4. Mechanistic studies

a) Reduction of nitrobenzene



An undivided cell was equipped with carbon plate anode (8 mm \times 2 mm) and glassy carbon cathode (8 mm \times 2 mm). To the cell was added **1a** (0.3 mmol), MeOH (4 mL) and [Mim]TolSO₃ (0.5 mL) under Glove box, and then stirred at room temperature for 5 min. The mixture was electrolyzed using constant current conditions (12 mA) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **1a**, 6 h), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of NaHCO₃ and the product was then extracted with CH₂Cl₂ (3 \times 20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired pure product **12a** (32.1 mg, 83%). As a comparison, no **12a** was detected in the absence of [Mim]TolSO₃. In addition, while the use of [Mim]HSO₄ could deliver **12a** with 21% yield, the presence of other acids such as [Mim]Cl, [Mim]OAc, H₂SO₄, HCl or TsOH only led to trace **12a**.

b) Sandmeyer-type arenesulfonyl fluorides of aniline



An undivided cell was equipped with carbon plate anode (8 mm \times 2 mm) and glassy carbon cathode (8 mm \times 2 mm). To the cell was added **4a** (0.3 mmol, 32 mg), DABSO (0.2 mmol, 48 mg), Selectfluor (0.6 mmol, 212 mg), MeOH (4 mL) and [Mim]TolSO₃ (0.5 mL) under Glove box, and then stir at room temperature for 5 min. ^{*t*}BuONO (0.90 mmol, 92.7 mg) were added. The mixture was electrolyzed using constant current conditions (12 mA) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **4a**, 6 h), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of NaCl and the product was then extracted with CH₂Cl₂ (3×20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired pure product **3a** (46.5 mg, 89%). As a comparison, no **3a** was detected in the absence of electricity.

c) Radical trapping experiments



An undivided cell was equipped with carbon plate anode (8 mm \times 2 mm) and glassy carbon cathode (8 mm \times 2 mm). To the cell was added **1a** (0.3 mmol, 41 mg), DABSO (0.2 mmol, 48 mg), Selectfluor (0.6 mmol, 212 mg), TEMPO (0.6 mmol, 95.3 mg), MeOH (4 mL) and [Mim]TolSO₃ (0.5 mL) under Glove box, and then stir at room temperature for 5 min. ⁷BuONO (0.90 mmol, 92.7mg) were added. The mixture was electrolyzed S21

using constant current conditions (12 mA) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **1a**), GC-MS analysis of the crude reaction mixture indicates the formation of trace amounts of **3a**.

d) Radical clock experiment



An undivided cell was equipped with carbon plate anode (8 mm \times 2 mm) and glassy carbon cathode (8 mm \times 2 mm). To the cell was added **4** (0.3 mmol, 60 mg), MeOH (4 mL) and [Mim]TolSO₃ (0.5 mL) under Glove box, and then stir at room temperature for 5 min. The mixture was electrolyzed using constant current conditions (12 mA) at 25 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **4**, 6 h), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of NaHCO₃ and the product was then extracted with CH₂Cl₂ (3 \times 20 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired pure product **5** in 81% yield (52 mg), and no **6** was detected.

5. Green metrics

To give a clear calculation, compound **3a** has been chosen as a representative example, and steps for the synthesis of corresponding 4methylphenyl diazo reagent from the reduction of 1-methyl-4-nitrobenzene and diazotization have been added in one chemical equation. The data for the first reduction and the second diazotization step was calculated based on the work of Beller (*Nat. Chem.* **2013**, *5*, 537) and Ian J. S. Fairlamb (*ACS Catal.* **2017**, *7*, 5174), respectively. Furthermore, based on the procedure of Beller, for every reduction procedure with 0.5 mmol scale, about 1200 mg H₂ has been used.



Based on these, the following four green metrics with different methods have been calculated and the data have been summarized in Table S1.

Table S1. A comparison of four green chemistry metrics with different methods

Entry	Work of different group	E-Factor	AE	RME	PMI
1	This work	21.3	20.8%	4.5%	22.4
2	Chen and Liu (Example A)	43.3	32.7%	2.3%	44.3
3	Zheng, Hu and Liu (Example B)	48.2	15.9%	2.0%	49.2
4	Weng (Example C)	45.1	16.3%	2.2%	46.1

This work:



Total amounts of reactants = 840.4 mg

Amount of final product = 37.6 mg

Amount of waste: 840.4 mg - 37.6 mg = 802.8 mg

E-Factor = Amount of waste/Amount of final product = 21.3

Molecular weight of product = 174.2

Sum of molecular weight of reagent = 834.7

AE = Molecular weight of product/Sum of molecular weight of reagent = 20.8%

Mass of product = 37.6 mg Total mass of reagent = 840.4 mg **RME** = Mass of product/Total mass of reagent = 4.5%

Total mass in process = 840.4 mg Mass of product = 37.6 mg **PMI** = Total mass in process/Mass of product = 22.4 Example A: (Liu, Y., Yu, D., Guo, Y., Xiao, J.-C., Chen, Q.-Y., Liu, C. Org. Lett. 2020, 22, 2281–2286)



Total amounts of reactants = 1853.8 mg

Amount of final product = 41.8 mg

Amount of waste: 1853.8 mg – 41.8 mg = 1812.0 mg

E-Factor = Amount of waste/Amount of final product = 43.3

Molecular weight of product = 174.2

Sum of molecular weight of reagent = 532.3

AE = Molecular weight of product/Sum of molecular weight of reagent = 32.7%

Mass of product = 41.8 mg Total mass of reagent = 1828.3 mg **RME** = Mass of product/Total mass of reagent = 2.3%

Total mass in process = 1853.8 mg Mass of product = 41.8 mg **PMI** = Total mass in process/Mass of product = 44.3 Example B: (Lin, Q., Ma, Z., Zheng, C., Hu, X.-J., Guo, Y., Chen, Q.-Y., Liu, C. Chin. J. Chem. 2020, 38, 1107–1110)



Total amounts of reactants = 1412.5 mg

Amount of final product = 28.7 mg

Amount of waste: 1412.5 mg – 28.7 mg = 1383.8 mg

E-Factor = Amount of waste/Amount of final product = 48.2

Molecular weight of product = 174.2 Sum of molecular weight of reagent = 1093.9 AE = Molecular weight of product/Sum of molecular weight of reagent = 15.9%

Mass of product = 28.7 mg Total mass of reagent = 1404.8 mg **RME** = Mass of product/Total mass of reagent = 2.0%

Total mass in process = 1412.5 mg Mass of product = 28.7 mg **PMI** = Total mass in process/Mass of product = 49.2 Example C: (Zhong, T., Pang, M-K., Chen, Z.-D., Zhang, B., Weng, J., Lu, G. Org. Lett. 2020, 22, 3072–3078)



Total amounts of reactants = 1042.6 mg

Amount of final product = 22.6 mg

Amount of waste: 1042.6 mg - 22.6 mg = 1020.0 mg

E-Factor = Amount of waste/Amount of final product = 45.1

Molecular weight of product = 174.2 Sum of molecular weight of reagent = 1068.4 AE = Molecular weight of product/Sum of molecular weight of reagent = 16.3%

Mass of product = 22.6 mg Total mass of reagent = 1037.5 mg **RME** = Mass of product/Total mass of reagent = 2.2%

Total mass in process = 1042.6 mg Mass of product = 22.6 mg **PMI** = Total mass in process/Mass of product = 46.1

6. Copies of NMR spectra





S29





S31







S34




































































































































































































7. References

- 1. Liu, Y., Yu, D., Guo, Y., Xiao, J.-C., Chen, Q.-Y., & Liu, C. Arenesulfonyl fluoride synthesis via copper-catalyzed fluorosulfonylation of arenediazonium salts. *Org. Lett.* **2020**, *22*, 2281–2286.
- 2. Zhong, T., Pang, M-K., Chen, Z.-D., Zhang, B., Weng, J., & Lu, G. Copper-free Sandmeyer-type reaction for the synthesis of sulfonyl fluorides. *Org. Lett.* **2020**, 22, 3072–3078.