

**Lewis Acid Mediated Intramolecular Trifluoromethylthiolation of
Alkenes with Phenols: Access to SCF₃-Containing Chromane and
Dihydrobenzofuran Compounds**

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1 General considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of argon, using over-dried or flame-dried glassware equipped with a magnetic stir bar. All chemicals were purchased from commercial suppliers and used without further purification. In addition to commercially available extra dry solvents, all solvents were purified by standard operating method. Methanol (MeOH) was purchased from commercial suppliers (*Energy Chemical*) and used without further purification. Acetone was purchased from commercial suppliers (*China National Medicines Corporation Ltd*) and used without further purification. Carbon tetrachloride (CCl₄) was purchased from commercial suppliers (*Adamas-beta*) and used without further purification. Tetrahydrofuran (THF) and acetonitrile (MeCN) was purchased from commercial suppliers (*J&K Technology*) and used without further purification. Thin-layer chromatography was performed with EMD silica gel 60 F₂₅₄ plates eluting with solvents indicated, visualized by a 254 nm UV lamp and stained with phosphomolybdic acid (PMA). ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were obtained on Bruker AM-400 and Bruker AM-500. Chemical shifts (δ) were quoted in ppm relative to tetramethylsilane or deuterated solvent as internal standard (CDCl₃: 7.26 ppm for ¹H NMR; CDCl₃: 77.16 ppm for ¹³C NMR), multiplicities are as indicated: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectral analysis (HRMS) data was measured on a Bruker impact II (Q-TOF) mass spectrum by means of the ESI technique. High-resolution gas-chromatography analysis (HRGC) data was measured on an Agilent Technologies 7250 GCQTOF mass spectrum by means of the EI technique. Crystallographic data were obtained from a Bruker D8 VENTURE diffractometer. Melting points were measured on a melting point apparatus and were uncorrected.

2. The preparation of substrates

2.1 The substrates **1a**¹, **1b**², **1c-1e**¹, **1f**², **1g**¹, **1h**², **1i-1m**¹, **1n**², **1o**³, **5h**⁴, **5l**⁴, **5m**⁵, **5n**⁶ and **5o**⁶ were known compounds.

Our analytical data (¹H-NMR, ¹³C-NMR and ¹⁹F-NMR) match with the literatures.¹⁻⁶

Figure S1

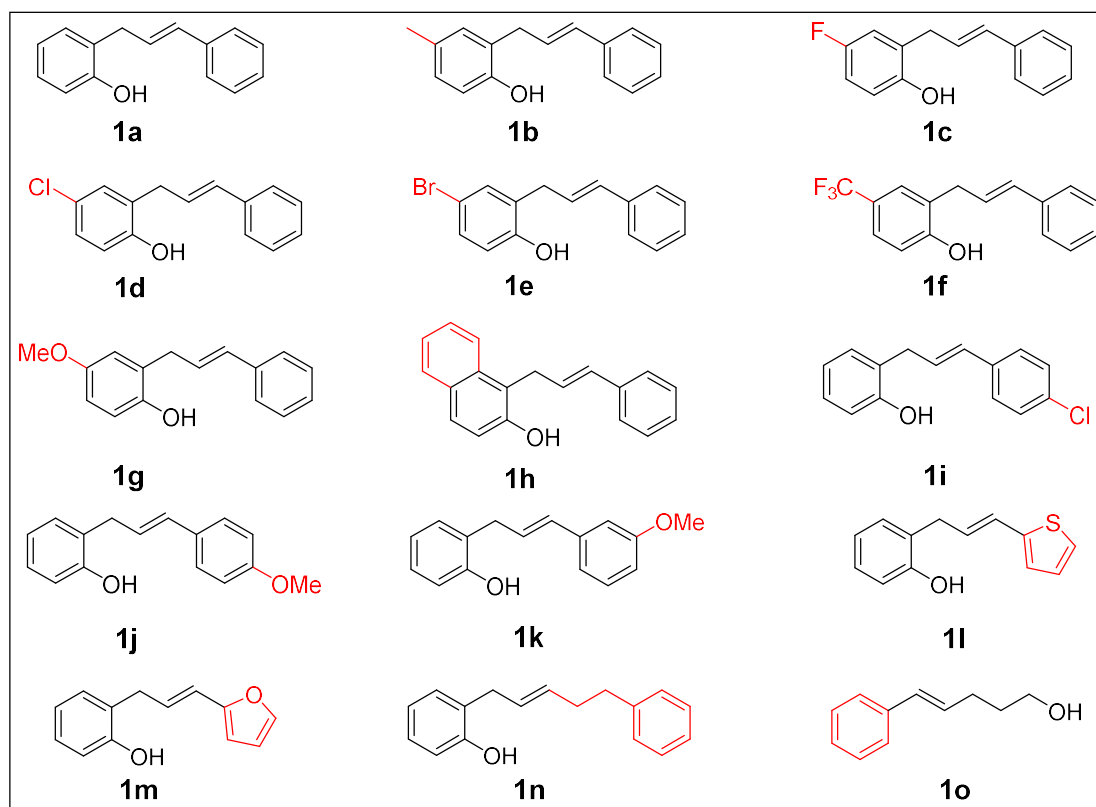
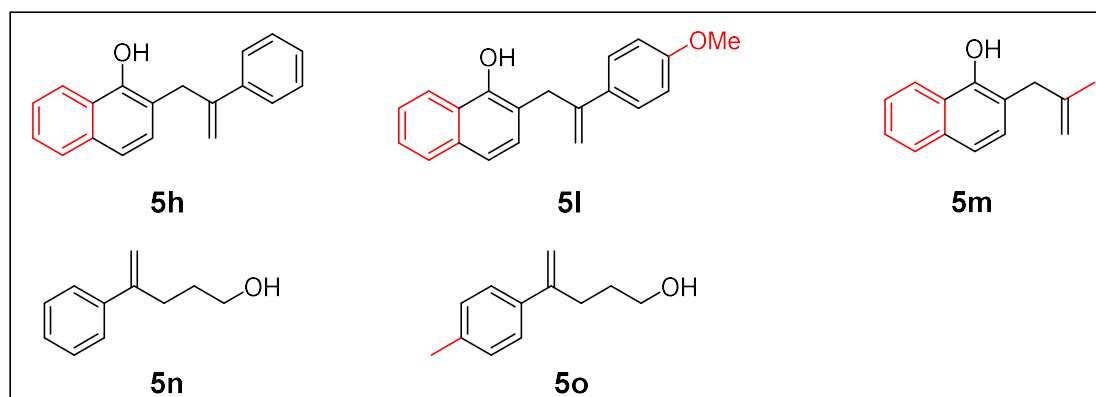
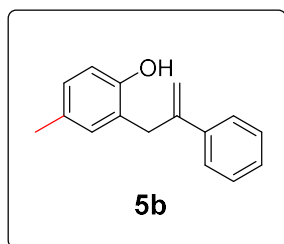


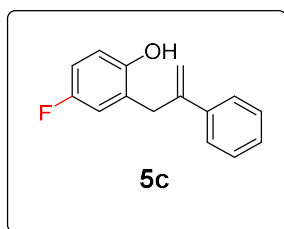
Figure S2



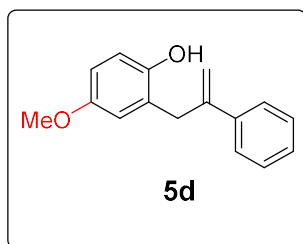
2.2 The general procedure **A** for the preparation of substrates **5a-5g** and **5i-5k**.



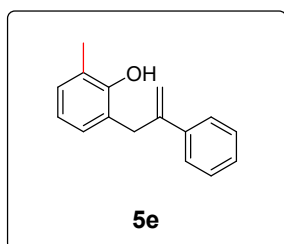
According to the general procedure **A**, at the step 3, **S1-3b** (3.77 mmol, 846.3 mg) and *N,N*-dimethylaniline (3 mL) were added. The solution was stirred at 200 °C (using heating mantle) for 5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5b** as a colorless oil (253.3 mg, 30%), *R_f* = 0.3 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.54 – 7.46 (m, 2H), 7.38 – 7.26 (m, 3H), 7.02 – 6.87 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.51 (d, *J* = 1.1 Hz, 1H), 5.01 (m, 1H), 4.74 (d, *J* = 1.6 Hz, 1H), 3.80 (s, 2H), 2.24 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 151.9, 146.3, 140.7, 131.7, 130.3, 128.5, 127.9, 126.2, 125.0, 115.8, 114.1, 36.3, 20.7; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₆NaO 247.1093; Found 247.1091.



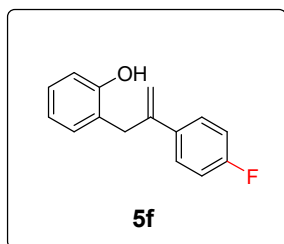
According to the general procedure **A**, at the step 3, **S1-3c** (6.99 mmol, 1.60 g) and *N,N*-dimethylaniline (5 mL) were added. The solution was stirred at 200 °C (using heating mantle) for 5.5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5c** as a colorless oil (852.8 mg, 56%), *R_f* = 0.3 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.62 – 7.40 (m, 2H), 7.37 – 7.25 (m, 3H), 6.87 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.80 (td, *J* = 8.2, 3.0 Hz, 1H), 6.74 (dd, *J* = 8.8, 4.8 Hz, 1H), 5.55 (q, *J* = 1.0 Hz, 1H), 5.06 (q, *J* = 1.4 Hz, 1H), 4.97 (s, 1H), 3.82 (s, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 157.3 (d, *J* = 238.9 Hz), 150.0 (d, *J* = 2.2 Hz), 145.6, 140.2, 128.6, 128.0, 127.1 (d, *J* = 7.3 Hz), 126.1, 117.2 (d, *J* = 23.3 Hz), 116.7 (d, *J* = 8.3 Hz), 114.6, 114.1 (d, *J* = 23.2 Hz), 36.1 (d, *J* = 1.2 Hz); **¹⁹F NMR** (376 MHz, CDCl₃) δ -123.78; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₅H₁₃FNao 251.0843; Found 251.0845.



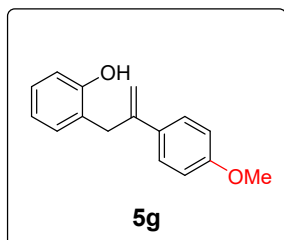
According to the general procedure **A**, at the step 3, **S1-3d** (5.91 mmol, 1.42 g) and *N,N*-dimethylaniline (5 mL) were added. The solution was stirred at 200 °C (using heating mantle) for 5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5d** as a colorless oil. (696.8 mg, 49%), *R_f*=0.3 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.53 – 7.42 (m, 2H), 7.36 – 7.18 (m, 3H), 6.70 (dd, *J* = 5.9, 2.8 Hz, 2H), 6.63 (dd, *J* = 8.7, 3.0 Hz, 1H), 5.49 (d, *J* = 1.2 Hz, 1H), 5.08 (s, 1H), 5.00 (q, *J* = 1.4 Hz, 1H), 3.78 (s, 2H), 3.68 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.7, 148.0, 146.0, 140.6, 128.4, 127.8, 126.6, 126.1, 116.6, 116.5, 114.2, 112.8, 55.8, 36.2; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₆NaO₂ 263.1043; Found 263.1044.



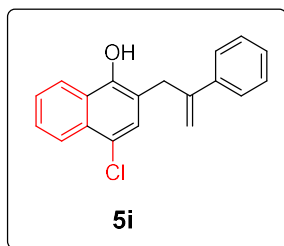
According to the general procedure **A**, at the step 3, **S1-3e** (2.23 mmol, 499.4 mg) and *N,N*-dimethylaniline (3 mL) were added. The solution was stirred at 200 °C (using heating mantle) for 5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5e** as a colorless oil. (125.3 mg, 25%), *R_f*=0.3 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.44 (m, 2H), 7.38 – 7.25 (m, 3H), 7.02 (t, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.5 Hz, 1H), 5.53 (d, *J* = 1.2 Hz, 1H), 5.05 (t, *J* = 1.5 Hz, 1H), 4.95 (s, 1H), 3.85 (s, 2H), 2.26 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 152.6, 146.2, 140.6, 129.5, 128.9, 128.5, 127.9, 126.2, 124.6, 124.2, 120.6, 114.3, 36.7, 16.1; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₆NaO: 247.1093; Found 247.1094.



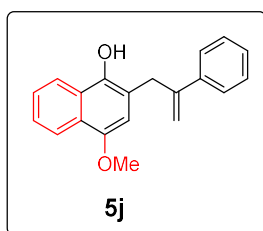
According to the general procedure **A**, at the step 3, **S1-3f** (14.08 mmol, 3.21 g) and *N,N*-dimethylaniline (5 mL) were added. The solution was stirred at 200 °C (using heating mantle) for 5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5f** as a white solid. (1.04 g, 32%), *R_f*=0.3 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.39 (m, 2H), 7.13 (m, 2H), 7.07 – 6.96 (m, 2H), 6.89 (td, *J* = 7.4, 1.2 Hz, 1H), 6.81 (dd, *J* = 8.4, 1.3 Hz, 1H), 5.47 (d, *J* = 1.1 Hz, 1H), 5.13 – 4.97 (m, 2H), 3.83 (s, 2H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.5 (d, *J* = 247.6 Hz), 154.0, 145.3, 136.6 (d, *J* = 3.3 Hz), 131.0 (d, *J* = 3.8 Hz), 128.1 (d, *J* = 1.8 Hz), 127.8 (d, *J* = 8.1 Hz), 125.1, 121.1, 115.9 (d, *J* = 7.0 Hz), 115.3 (d, *J* = 21.2 Hz), 114.2, 36.2; **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.63; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₅H₁₃FNao 251.0843; Found 251.0847.



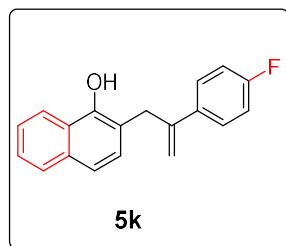
According to the general procedure **A**, at the step 3, **S1-3g** (11.87 mmol, 2.85 g) and *N,N*-dimethylaniline (5 mL) were added. The solution was stirred at 200 °C (using heating mantle) for 5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5g** as a white solid. (825 mg, 29%), *R_f*=0.3 (silica gel, PE:EA = 10:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.53 – 7.35 (m, 2H), 7.22 – 7.02 (m, 2H), 6.92 – 6.83 (m, 3H), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.46 (s, 1H), 5.13 (s, 1H), 4.98 (d, *J* = 1.4 Hz, 1H), 3.83 (s, 2H), 3.80 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 159.4, 154.3, 145.4, 132.9, 131.1, 128.0, 127.3, 125.3, 121.0, 116.0, 113.8, 112.6, 55.4, 36.4; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₆NaO₂ 263.1043; Found 263.1042.



According to the general procedure **A**, at the step 3, **S1-3i** (1.54 mmol, 455.1 mg) and decahydronaphthalene (3 mL) were added. The solution was stirred at 185 °C (using heating mantle) for 2.5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5i** as a colorless oil. (91.3 mg, 20%), *R_f*=0.2 (silica gel, PE:EA = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.21 (m, 2H), 7.62 – 7.49 (m, 4H), 7.41 – 7.29 (m, 4H), 5.65 – 5.55 (m, 2H), 5.16 (d, *J* = 1.3 Hz, 1H), 3.97 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 149.0, 145.6, 139.9, 130.7, 128.7, 128.6, 128.3, 127.0, 126.2, 126.1, 124.4, 123.4, 122.1, 118.5, 114.9, 37.1; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₉H₁₅ClNaO 317.0704; Found 317.0703.

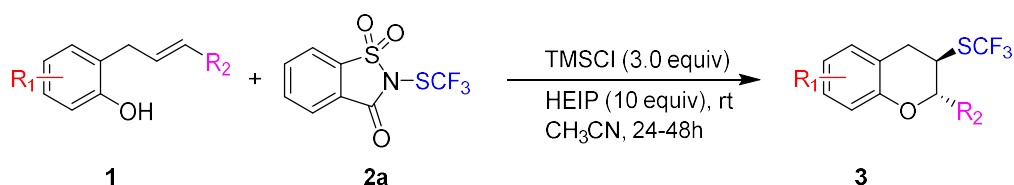


According to the general procedure **A**, at the step 3, **S1-3j** (2.79 mmol, 809 mg) and decahydronaphthalene (3 mL) were added. The solution was stirred at 185 °C (using heating mantle) for 2.5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5j** as a white solid. (463 mg, 57%) *R_f*=0.2 (silica gel, PE:EA = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.41 (m, 4H), 7.33 (m, 3H), 6.61 (s, 1H), 5.55 (s, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.98 (s, 2H), 3.93 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 146.1, 143.1, 140.5, 128.6, 128.1, 126.2, 126.1, 126.1, 125.6, 125.3, 122.0, 121.3, 118.1, 114.3, 106.9, 55.9, 37.4; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₀H₁₈NaO₂ 313.1199; Found 313.1199.

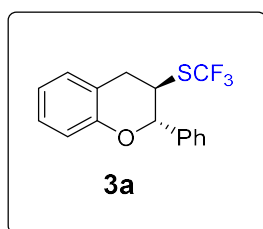


According to the general procedure **A**, at the step 3, **S1-3k** (3.12 mmol, 869 mg) and decahydronaphthalene (3 mL) were added. The solution was stirred at 185 °C (using heating mantle) for 2.5 h. Flash column chromatography (SiO₂, PE:EA = 20:1, v/v) to afford **5k** as a white solid. (521 mg, 60%), *R_f*=0.2 (silica gel, PE:EA = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.17 (m, 1H), 7.85 – 7.76 (m, 1H), 7.58 – 7.45 (m, 4H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 0.9 Hz, 1H), 7.02 (m, 2H), 5.57 (s, 1H), 5.53 (d, *J* = 1.1 Hz, 1H), 5.16 (d, *J* = 1.3 Hz, 1H), 4.00 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 162.7 (d, *J* = 248.3 Hz), 149.7, 145.2, 136.3 (d, *J* = 3.4 Hz), 133.9, 128.9, 127.9 (d, *J* = 8.1 Hz), 127.7, 126.0, 125.5, 124.9, 121.4, 120.7, 117.9, 115.4 (d, *J* = 21.2 Hz), 114.5, 37.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -114.19; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₉H₁₅FNao 301.0999; Found 301.1001.

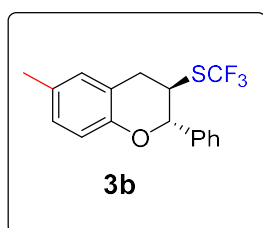
3. General procedures B for the synthesis of desired products 3



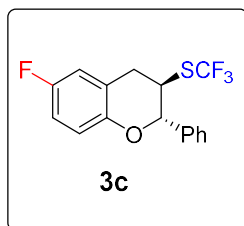
At room temperature, **1** (0.1 mmol) and **2a** (0.13 mmol) were added into an over-dried 10 mL flask equipped with a stir bar. Seal the flask with a septum. Anhydrous CH₃CN (1 mL) was added via a syringe, and then TMSCl (38.0 μL, 0.3 mmol) and HFIP (105.0 μL, 1.0 mmol) were added by using syringes respectively and stirred for 24-48 hours. After the reaction was completed (monitored by TLC), the solvent was removed under reduce pressure, the crude product was purified by silica gel flash column chromatography to obtain products **3**.



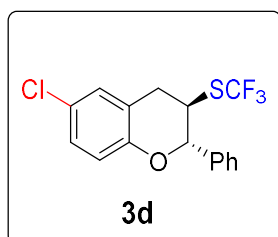
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3a** as a white solid (23.1 mg, 74%), *R_f*=0.4 (silica gel, PE); **Mp** : 84.5 ~ 86.5 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.46 – 7.30 (m, 5H), 7.25 – 7.17 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 7.03 – 6.91 (m, 2H), 5.29 (d, *J* = 6.0 Hz, 1H), 3.97 (q, *J* = 6.0 Hz, 1H), 3.22 (dd, *J* = 16.7, 5.0 Hz, 1H), 3.07 (dd, *J* = 16.7, 6.8 Hz, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.6, 138.8, 131.0 (q, *J* = 308.0 Hz), 129.7, 128.9, 128.8, 128.6, 126.3, 121.4, 119.0, 116.9, 76.8, 43.5 (d, *J* = 1.7 Hz), 31.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -39.01; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₃F₃NaOS 333.0531; Found 333.0530.



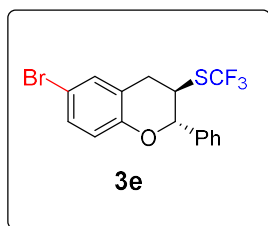
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3b** as a colorless oil (21.9 mg, 68%), *R_f*=0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.47 – 7.28 (m, 5H), 7.09 (dd, *J* = 7.1, 1.8 Hz, 1H), 6.95 – 6.74 (m, 2H), 5.36 (d, *J* = 5.7 Hz, 1H), 3.95 (q, *J* = 5.7 Hz, 1H), 3.18 (dd, *J* = 16.7, 4.9 Hz, 1H), 3.04 (dd, *J* = 16.7, 6.4 Hz, 1H), 2.28 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 151.6, 139.2, 131.1 (q, *J* = 308.2 Hz), 129.7, 128.8, 128.6, 127.3, 126.1, 120.8, 118.3, 79.8, 43.6 (d, *J* = 1.6 Hz), 30.9, 16.2; **¹⁹F NMR** (376 MHz, CDCl₃) δ -39.14; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaOS 347.0688; Found 347.0692.



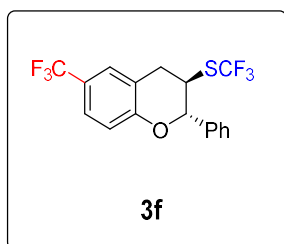
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3c** as a white solid (22.6 mg, 69%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.34 (m, 3H), 7.32 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.92 (dd, *J* = 7.1, 2.3 Hz, 2H), 6.77 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.26 (d, *J* = 5.9 Hz, 1H), 3.95 (q, *J* = 5.9 Hz, 1H), 3.18 (dd, *J* = 17.0, 5.1 Hz, 1H), 3.04 (dd, *J* = 16.9, 6.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.3 (d, *J* = 240.5 Hz), 149.5 (d, *J* = 2.1 Hz), 138.5, 133.4 (q, *J* = 308.2 Hz), 129.0, 128.9, 126.2, 120.1 (d, *J* = 8.2 Hz), 117.9 (d, *J* = 8.2 Hz), 115.6 (d, *J* = 23.2 Hz), 115.5 (d, *J* = 23.4 Hz), 79.7, 43.1 (d, *J* = 1.9 Hz), 31.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.04, -122.78; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₂F₄NaOS 351.0437; Found 351.0438.



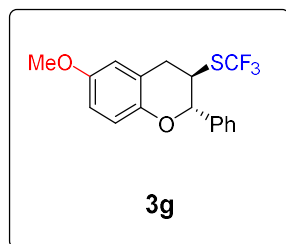
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3d** as a white solid (25.3 mg, 73%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.33 (m, 3H), 7.30 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.17 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.30 (d, *J* = 5.6 Hz, 1H), 3.94 (q, *J* = 5.7 Hz, 1H), 3.15 (dd, *J* = 16.9, 5.0 Hz, 1H), 3.01 (dd, *J* = 16.9, 6.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 152.1, 138.4, 130.9 (q, *J* = 308.2 Hz), 129.3, 129.0, 128.9, 128.7, 126.2, 126.1, 120.5, 118.2, 79.8, 42.9 (d, *J* = 1.6 Hz), 30.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.06; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₂ClF₃NaOS 367.0142, Found 367.0140.



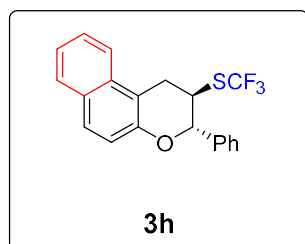
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3e** as a white solid (23.9 mg, 61%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.33 (m, 3H), 7.30 (td, *J* = 6.0, 2.7 Hz, 3H), 7.19 (d, *J* = 2.3 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 5.30 (d, *J* = 5.6 Hz, 1H), 3.93 (q, *J* = 5.6 Hz, 1H), 3.15 (dd, *J* = 16.9, 5.0 Hz, 1H), 3.00 (dd, *J* = 16.9, 6.3 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 152.7, 138.4, 132.2, 131.6, 130.9 (q, *J* = 308.2 Hz), 129.0, 128.9, 126.1, 121.1, 118.7, 113.5, 79.8, 42.9 (d, *J* = 1.7 Hz), 30.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.08; HRGC (EI) *m/z*: calcd for C₁₆H₁₂BrF₃OS 387.9739; Found 387.9744.



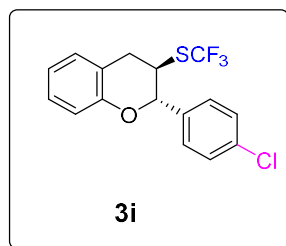
According to the general procedure **B**, the reaction time is 48 h, flash column chromatography (SiO₂, PE) to afford **3f** as a white solid (22.7 mg, 60%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.29 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 5.36 (d, *J* = 5.6 Hz, 1H), 3.97 (q, *J* = 5.6 Hz, 1H), 3.21 (dd, *J* = 16.9, 4.9 Hz, 1H), 3.07 (dd, *J* = 16.9, 6.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 156.1, 138.1, 130.8 (q, *J* = 308.2 Hz), 129.1, 129.0, 127.2 (q, *J* = 3.8 Hz), 126.1, 125.9 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.3 Hz), 123.7 (d, *J* = 32.6 Hz), 119.3, 117.3, 80.1, 42.8 (d, *J* = 1.8 Hz), 30.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.07, -61.65; HRGC (EI) *m/z*: calcd for C₁₇H₁₂F₆OS 378.0508; Found 378.0512.



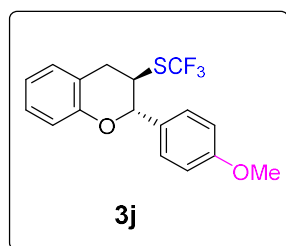
According to the general procedure **B**, the reaction time is 48 h, flash column chromatography (SiO₂, PE) to afford **3g** as a white solid (26.5 mg, 78%), *R_f*=0.3 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.29 (m, 5H), 6.91 (d, *J* = 8.9 Hz, 1H), 6.79 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.58 (d, *J* = 3.0 Hz, 1H), 5.24 (d, *J* = 5.9 Hz, 1H), 3.94 (q, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.18 (dd, *J* = 16.8, 5.1 Hz, 1H), 3.03 (dd, *J* = 16.8, 6.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 154.1, 147.5, 138.9, 131.0 (q, *J* = 308.0 Hz), 128.9, 128.7, 126.3, 119.5, 117.6, 114.8, 113.9, 79.6, 55.8, 43.5 (d, *J* = 1.7 Hz), 31.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.04; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaO₂S 363.0637; Found 363.0640.



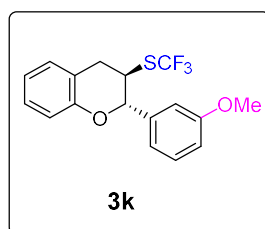
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3h** as a white solid (24.3 mg, 67%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.75 (dd, *J* = 8.7, 4.5 Hz, 2H), 7.53 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.47 – 7.30 (m, 6H), 7.22 (d, *J* = 9.0 Hz, 1H), 5.35 (d, *J* = 6.2 Hz, 1H), 4.12 (q, *J* = 6.1 Hz, 1H), 3.44 (dd, *J* = 6.2, 2.7 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 138.4, 132.6, 131.1 (q, *J* = 308.0 Hz), 129.5, 129.1, 128.9, 128.8, 128.8, 127.0, 126.4, 124.0, 121.8, 118.6, 111.1, 79.6, 43.5 (d, *J* = 1.7 Hz), 28.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.01; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₀H₁₅F₃NaOS 383.0688; Found 383.0687.



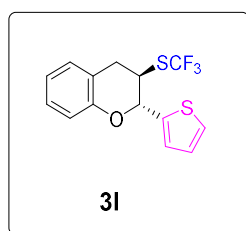
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3i** as a white solid (23.2 mg, 67%), *R_f*=0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.43 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.17 (m, 1H), 7.06 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.95 (t, *J* = 7.3 Hz, 2H), 5.21 (d, *J* = 6.4 Hz, 1H), 3.88 (td, *J* = 6.9, 5.2 Hz, 1H), 3.20 (dd, *J* = 16.7, 5.1 Hz, 1H), 3.07 (dd, *J* = 16.7, 7.2 Hz, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.4, 137.2, 134.7, 130.8 (q, *J* = 308.2), 129.7, 129.1, 128.7, 127.9, 121.6, 119.0, 116.9, 79.3, 43.4 (d, *J* = 1.8 Hz), 31.3; **¹⁹F NMR** (376 MHz, CDCl₃) δ -39.00; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₂ClF₃NaOS 367.0142; Found 367.0146.



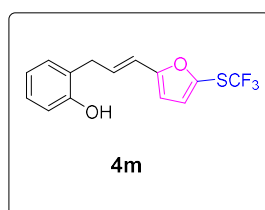
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3j** as a white solid (30.0 mg, 88%), *R_f*=0.3 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 2H), 7.21 (ddd, *J* = 8.4, 7.3, 1.7 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.00 – 6.89 (m, 4H), 5.18 (d, *J* = 6.7 Hz, 1H), 3.93 (td, *J* = 7.2, 5.1 Hz, 1H), 3.83 (s, 3H), 3.26 (dd, *J* = 16.6, 5.0 Hz, 1H), 3.11 (dd, *J* = 16.6, 7.5 Hz, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 160.0, 153.8, 130.8 (q, *J* = 308.2 Hz), 130.7, 129.6, 128.5, 127.8, 121.4, 119.2, 116.9, 114.3, 79.5, 55.4, 43.8 (q, *J* = 1.5 Hz), 31.7; **¹⁹F NMR** (376 MHz, CDCl₃) δ -38.77; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaO₂S 363.0637; Found 363.0634.



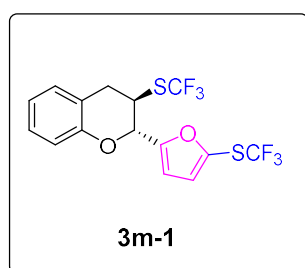
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3k** as a colorless oil (27.9 mg, 82%), *R_f*=0.3 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.31 (td, *J* = 7.5, 1.4 Hz, 1H), 7.21 (td, *J* = 7.7, 7.1, 1.6 Hz, 1H), 7.06 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.02 – 6.85 (m, 5H), 5.26 (d, *J* = 5.9 Hz, 1H), 3.96 (q, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 3.21 (dd, *J* = 16.7, 5.0 Hz, 1H), 3.05 (dd, *J* = 16.7, 6.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 160.0, 153.5, 140.3, 131.0 (q, *J* = 308.0 Hz), 130.0, 129.7, 128.6, 121.4, 119.0, 118.6, 116.8, 113.9, 112.2, 79.6, 55.4, 43.4 (d, *J* = 1.8 Hz), 31.0; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.01; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaO₂S 363.0637; Found 363.0637.



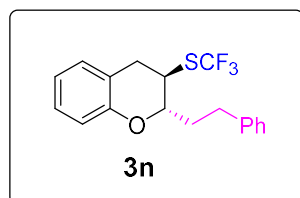
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3l** as a white solid (24.5 mg, 77%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.24 – 7.15 (m, 1H), 7.10 – 7.02 (m, 2H), 7.02 – 6.89 (m, 3H), 5.53 (d, *J* = 5.9 Hz, 1H), 3.96 (q, *J* = 6.1 Hz, 1H), 3.36 (dd, *J* = 16.9, 5.2 Hz, 1H), 3.11 (dd, *J* = 16.9, 6.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 152.9, 141.5, 130.9 (q, *J* = 308.2 Hz), 129.7, 128.5, 127.0, 126.1, 126.0, 121.8, 118.7, 117.2, 76.1, 44.1 (q, *J* = 1.7 Hz), 31.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -38.93; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₄H₁₁F₃NaOS₂ 339.0096; Found 339.0093.



According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE:EA=30:1, v/v) to afford **4m** as a colorless oil (23.6 mg, 79%), *R_f*=0.4 (silica gel, PE:DCM=3:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.11 (m, 2H), 6.92 (td, *J* = 7.4, 1.2 Hz, 1H), 6.87 – 6.77 (m, 2H), 6.54 (dt, *J* = 15.8, 6.6 Hz, 1H), 6.31 – 6.16 (m, 2H), 4.90 (s, 1H), 3.55 (dd, *J* = 6.6, 1.7 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 153.8, 133.1 (q, *J* = 3.0 Hz), 131.1, 130.8, 128.2, 128.0 (q, *J* = 313.1 Hz), 125.5, 125.2, 121.3, 119.1, 115.8, 109.1, 33.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -43.93; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₄H₁₁F₃NaO₂S 323.0324; Found 323.0319.

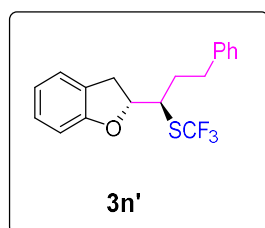


According to the general procedure **B**, the reaction time is 48 h, flash column chromatography (SiO₂, PE) to afford **3m-1** as a colorless oil (16.7 mg, 42%), *R_f*=0.3 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.15 (m, 1H), 7.07 – 7.02 (m, 1H), 6.98 – 6.91 (m, 2H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.43 (dd, *J* = 3.4, 0.8 Hz, 1H), 5.42 – 5.20 (m, 1H), 4.12 (td, *J* = 6.3, 5.3 Hz, 1H), 3.21 (dd, *J* = 17.0, 5.3 Hz, 1H), 3.06 (dd, *J* = 16.9, 6.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.0, 152.5, 135.7 (q, *J* = 3.03 Hz), 130.8 (q, *J* = 308.0 Hz), 129.8, 128.6, 128.0 (q, *J* = 313.0 Hz), 124.8, 122.0, 118.6, 117.0, 111.9, 73.8, 40.8 (d, *J* = 1.7 Hz), 31.1; ¹⁹F NMR (376 MHz, CDCl₃) δ -39.27, -43.62; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₅H₁₀F₆NaO₂S₂ 422.9919; Found 422.9917.

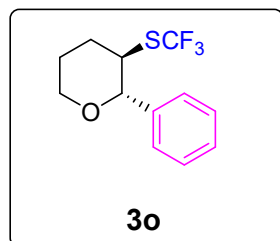


According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO₂, PE) to afford **3n** as a colorless oil (12.5 mg, 37%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.27 (m, 2H), 7.25 – 7.21 (m,

3H), 7.21 – 7.14 (m, 1H), 7.06 (dd, $J = 7.6, 1.6$ Hz, 1H), 6.99 – 6.82 (m, 2H), 4.16 (ddd, $J = 9.5, 6.2, 3.7$ Hz, 1H), 3.59 (td, $J = 6.7, 5.5$ Hz, 1H), 3.34 (dd, $J = 16.9, 5.4$ Hz, 1H), 3.06 (dd, $J = 17.0, 6.9$ Hz, 1H), 2.95 (ddd, $J = 14.3, 9.2, 5.3$ Hz, 1H), 2.82 (ddd, $J = 13.8, 9.1, 7.3$ Hz, 1H), 2.19 – 1.97 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.9, 141.1, 131.1 (q, $J = 308.0$ Hz), 129.6, 128.7, 128.3, 126.3, 121.3 (d, $J = 3.7$ Hz), 119.1, 117.3, 76.7 (d, $J = 11.8$ Hz), 42.2 (d, $J = 4.2$ Hz), 34.6, 31.6, 31.4; ^{19}F NMR (376 MHz, CDCl_3) δ -39.05; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NaOS}$ 361.0844; Found 361.0845.



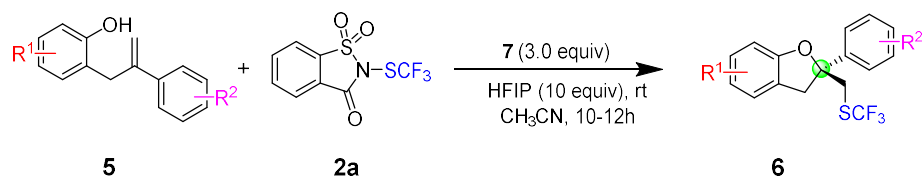
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO_2 , PE) to afford **3n'** as a colorless oil (14 mg, 41%), $R_f=0.4$ (silica gel, PE); ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.28 (m, 2H), 7.23 (td, $J = 5.2, 2.8$ Hz, 3H), 7.20 – 7.10 (m, 2H), 6.88 (td, $J = 7.4, 1.0$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 5.03 – 4.88 (m, 1H), 3.44 – 3.29 (m, 2H), 3.14 – 2.95 (m, 2H), 2.78 (ddd, $J = 13.8, 9.7, 6.9$ Hz, 1H), 2.32 – 2.16 (m, 1H), 2.04 – 1.90 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.4, 140.8, 131.0 (q, $J = 307.8$ Hz), 128.7, 128.6, 128.4, 126.4, 125.9, 125.0, 121.0, 109.6, 84.0, 50.2, 33.9, 32.6, 32.4; ^{19}F NMR (376 MHz, CDCl_3) δ -38.31; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NaOS}$ 361.0844; Found 361.0839.



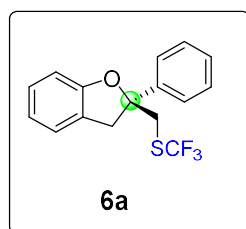
According to the general procedure **B**, the reaction time is 24 h, flash column chromatography (SiO_2 , PE) to afford **3o** as a colorless oil (13.1 mg, 50%), $R_f=0.2$ (silica gel, PE); ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.30 (m, 5H), 4.18 (d, $J = 10.2$ Hz, 1H), 4.15 – 4.07 (m, 1H), 3.61 (td, $J = 11.6, 2.4$ Hz, 1H), 3.33 (ddd, $J = 11.6, 10.2, 4.0$ Hz, 1H), 2.60 – 2.42 (m, 1H), 2.00 – 1.87 (m, 2H), 1.82 – 1.74 (m, 1H); ^{13}C NMR (101

MHz, CDCl₃) δ 139.1, 130.7 (q, J = 308.4 Hz), 128.8, 128.6, 127.6, 83.7, 68.7, 47.5, 33.3, 27.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -38.01; **HRMS** (ESI) m/z : [M+Na]⁺ calcd for C₁₂H₁₃F₃NaOS 285.0531; Found 285.0531.

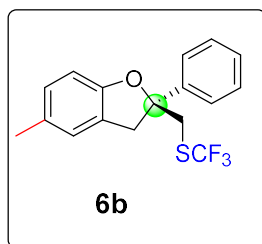
4. General procedures C for preparing desired products 6



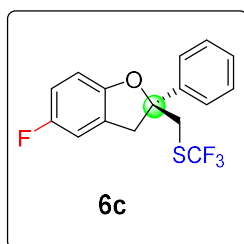
At room temperature, **5** (0.1 mmol) and **2a** (0.13 mmol) were added into an over-dried 10 mL flask equipped with a stir bar. Seal the flask with a septum. Anhydrous CH₃CN (1 mL) was added via a syringe, and then **7** (38.0 μ L, 0.3 mmol) and HFIP (105.0 μ L, 1.0 mmol) were added by using syringes respectively and stirred for 10-12 hours. After the reaction was completed (monitored by TLC), the solvent was removed under reduce pressure, the crude product was purified by silica gel flash column chromatography to obtain products **6**.



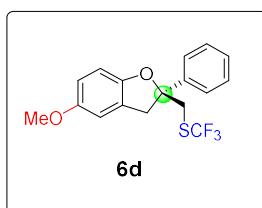
According to the general procedure **C**, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6a** as a colorless oil (26.4 mg, 85%), R_f =0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.53 – 7.44 (m, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.28 (m, 1H), 7.22 – 7.12 (m, 2H), 6.98 – 6.86 (m, 2H), 3.70 (d, J = 15.7 Hz, 1H), 3.57 – 3.48 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 158.4, 143.3, 131.0 (q, J = 307.2 Hz), 128.8, 128.6, 128.2, 125.6, 125.1, 125.1, 121.4, 110.0, 89.2, 42.3, 41.2 (d, J = 1.9 Hz); **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.19; **HRMS** (ESI) m/z : [M+Na]⁺ calcd for C₁₆H₁₃F₃NaOS 333.0531; Found 333.0530.



According to the general procedure **C**, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6b** as a colorless oil (22.9 mg, 71%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 3.67 (d, *J* = 15.7 Hz, 1H), 3.57 – 3.44 (m, 3H), 2.28 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 156.3, 143.4, 131.1 (q, *J* = 306.8 Hz), 130.8, 129.0, 128.8, 128.1, 125.6, 125.6, 125.1, 109.5, 89.2, 42.4, 41.1 (d, *J* = 2.0 Hz), 20.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -41.21; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaOS 347.0688; Found 347.0686.

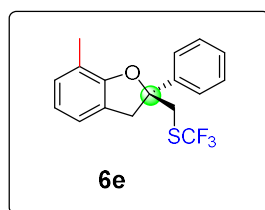


According to the general procedure **C**, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6c** as a colorless oil (19.7 mg, 60%), *R_f*=0.6 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.43 (m, 2H), 7.43 – 7.35 (m, 2H), 7.36 – 7.29 (m, 1H), 6.94 – 6.73 (m, 3H), 3.70 (dd, *J* = 16.0, 1.0 Hz, 1H), 3.61 – 3.40 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.0 (d, *J* = 239.0 Hz), 154.4 (d, *J* = 1.61 Hz), 143.0, 130.9 (q, *J* = 307.3 Hz), 128.9, 128.3, 127.0 (d, *J* = 9.1 Hz), 125.0, 114.8 (d, *J* = 24.2 Hz), 112.2 (d, *J* = 25.0 Hz), 110.1 (d, *J* = 8.5 Hz), 89.9, 42.4 (d, *J* = 1.6 Hz), 41.1 (d, *J* = 2.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -41.18, -123.40; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₆H₁₂F₄NaOS 351.0437; Found 351.0439.

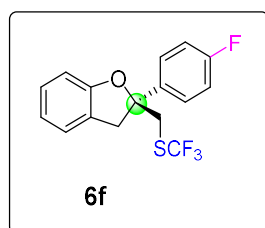


According to the general procedure **C**, the reaction time is 10 h, flash column

chromatography (SiO₂, PE) to afford **6d** as a colorless oil (24.3 mg, 71%), *R_f*=0.3 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.50 – 7.46 (m, 2H), 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.80 – 6.66 (m, 2H), 3.75 (s, 3H), 3.69 (d, *J* = 15.8 Hz, 1H), 3.57 – 3.46 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 154.8, 152.5, 143.3, 131.0 (q, *J* = 307.3 Hz), 128.8, 128.1, 126.6, 125.1, 113.6, 111.2, 109.9, 89.3, 56.1, 42.7, 41.1 (d, *J* = 1.82 Hz); **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.19; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaO₂S 363.0637; Found 363.0637.

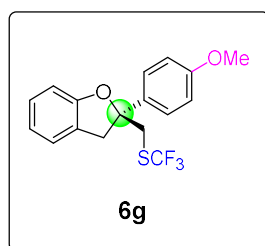


According to the general procedure C, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6e** as a colorless oil (26.2 mg, 81%), *R_f*=0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.45 (m, 2H), 7.44 – 7.35 (m, 2H), 7.35 – 7.28 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 3.70 (d, *J* = 15.6 Hz, 1H), 3.57 – 3.47 (m, 3H), 2.33 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 156.8, 143.5, 131.0 (q, *J* = 307.0 Hz), 129.8, 128.8, 128.1, 125.1, 124.8, 122.3, 121.2, 120.2, 88.7, 42.7, 41.3, 15.3; **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.12; **HRMS** (ESI) *m/z*: [M+Na]⁺ calcd for C₁₇H₁₅F₃NaOS 347.0688; Found 347.0687.

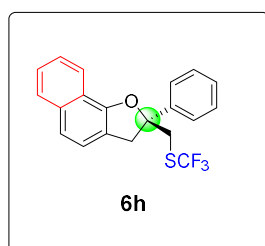


According to the general procedure C, the reaction time is 11 h, flash column chromatography (SiO₂, PE) to afford **6f** as a colorless oil (22.1 mg, 67%), *R_f*=0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.39 (m, 2H), 7.24 – 7.13 (m, 2H), 7.13 – 7.00 (m, 2H), 6.97 – 6.83 (m, 2H), 3.68 (d, *J* = 15.7 Hz, 1H), 3.53 – 3.44 (m, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 162.5 (d, *J* = 248.0 Hz), 158.2, 139.0 (d, *J* = 3.2 Hz), 130.9 (q, *J* = 307.2 Hz), 127.1, 127.0, 125.4, 125.1, 121.6, 115.7 (d, *J* = 21.7 Hz), 110.0, 88.9, 42.4, 41.1; **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.19, -114.20; **HRMS** (ESI) *m/z*:

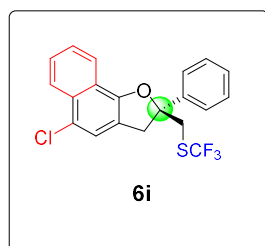
$[M+Na]^+$ calcd for $C_{16}H_{12}F_4NaOS$ 351.0437; Found 351.0436.



According to the general procedure **C**, the reaction time is 10 h, flash column chromatography (SiO_2 , PE) to afford **6g** as a colorless oil (26.1 mg, 77%), $R_f=0.3$ (silica gel, PE); 1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.33 (m, 2H), 7.23 – 7.09 (m, 2H), 7.01 – 6.80 (m, 4H), 3.81 (s, 3H), 3.67 (d, $J = 15.6$ Hz, 1H), 3.55 – 3.45 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 158.4, 135.2, 131.0 (q, $J = 307.2$ Hz), 128.6, 126.4, 125.7, 125.1, 121.3, 114.1, 109.9, 89.1, 55.4, 42.3, 41.2 (d, $J = 2.0$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.14; HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{17}H_{15}F_3NaO_2S$ 363.0637; Found 363.0639.

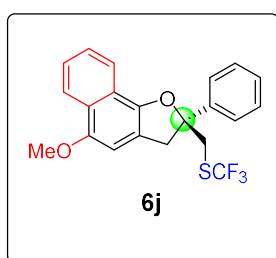


According to the general procedure **C**, the reaction time is 12 h, flash column chromatography (SiO_2 , PE) to afford **6h** as a colorless oil (23.1 mg, 64%), $R_f=0.6$ (silica gel, PE); 1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, $J = 8.1$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.62 – 7.37 (m, 7H), 7.37 – 7.26 (m, 2H), 3.89 (d, $J = 15.5$ Hz, 1H), 3.73 – 3.59 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 143.6, 134.3, 131.0 (q, $J = 307.3$ Hz), 128.8, 128.2, 128.1, 126.1, 125.8, 125.0, 122.7, 121.6, 121.3, 120.6, 118.6, 90.0, 43.4, 41.4 (d, $J = 1.8$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -41.00; HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{20}H_{15}F_3NaOS$ 383.0688; Found 383.0692.

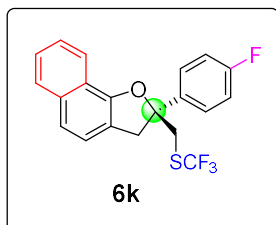


According to the general procedure **C**, the reaction time is 10 h, flash column

chromatography (SiO₂, PE) to afford **6i** as a colorless oil (17.4 mg, 44%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.18 (m, 1H), 8.18 – 8.05 (m, 1H), 7.62 – 7.56 (m, 2H), 7.56 – 7.49 (m, 2H), 7.45 – 7.35 (m, 3H), 7.36 – 7.29 (m, 1H), 3.87 (d, *J* = 15.6 Hz, 1H), 3.68 (d, *J* = 13.1 Hz, 1H), 3.65 – 3.56 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 152.9, 143.2, 130.9, 130.9 (q, *J* = 306.8 Hz), 128.9, 128.4, 127.2, 126.6, 125.0, 125.0, 123.9, 122.9, 122.1, 121.3, 118.8, 90.5, 43.1, 41.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -41.01; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₀H₁₄ClF₃NaOS 417.0298; Found 417.0304.

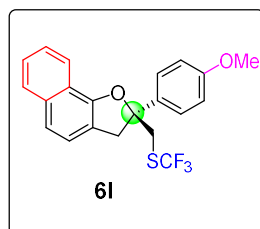


According to the general procedure C, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6j** as a colorless oil (26.1 mg, 67%), *R_f*=0.3 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.55 (m, 3H), 7.49 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.30 (m, 1H), 6.67 (s, 1H), 3.95 (s, 3H), 3.87 (d, *J* = 15.5 Hz, 1H), 3.72 – 3.53 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.8, 147.2, 143.8, 131.1 (q, *J* = 307.2 Hz), 128.8, 128.1, 126.5, 125.7, 125.4, 125.1, 122.7 (d, *J* = 5.4 Hz), 121.3, 121.1, 117.4, 101.2 (d, *J* = 10.8 Hz), 89.4, 56.1 (d, *J* = 15.4 Hz), 44.0, 41.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -41.05; HRMS (ESI) *m/z*: [M+Na]⁺ calcd. for C₂₁H₁₇F₃NaO₂S 413.0794; Found 413.0791.

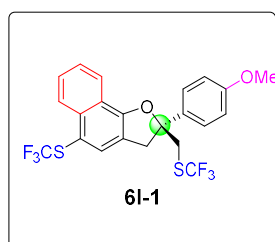


According to the general procedure C, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6k** as a colorless oil (26.5 mg, 70%), *R_f*=0.5 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.88 –

7.80 (m, 1H), 7.59 – 7.41 (m, 5H), 7.29 (d, $J = 8.3$ Hz, 1H), 7.08 (t, $J = 8.7$ Hz, 2H), 3.86 (d, $J = 15.4$ Hz, 1H), 3.65 (d, $J = 15.5$ Hz, 1H), 3.59 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.5 (d, $J = 247.4$ Hz), 153.4, 139.3 (d, $J = 3.3$ Hz), 134.3, 130.9 (q, $J = 306.9$ Hz), 128.1, 127.0, 127.0, 126.2, 125.9, 122.6, 121.5 (d, $J = 4.0$ Hz), 120.6, 118.4, 115.7 (d, $J = 21.8$ Hz), 89.7, 43.5, 41.6; ^{19}F NMR (376 MHz, CDCl_3) δ -41.05, -114.18; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{14}\text{F}_4\text{NaOS}$ 401.0594; Found 401.0594.



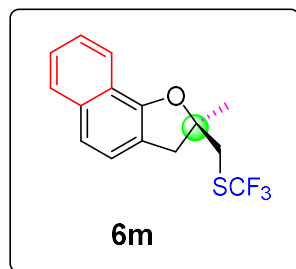
According to the general procedure C, the reaction time is 11 h, flash column chromatography (SiO_2 , PE) to afford **6I** as a colorless oil (17.8 mg, 46%), R_f =0.3 (silica gel, PE); ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.54 – 7.39 (m, 5H), 7.29 (s, 1H), 6.96 – 6.86 (m, 2H), 3.84 (d, $J = 15.5$ Hz, 1H), 3.80 (s, 3H), 3.65 (d, $J = 15.5$ Hz, 1H), 3.62 – 3.52 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.4, 153.6, 135.6, 134.3, 131.0 (q, $J = 307.3$ Hz), 128.1, 126.4, 126.0, 125.7, 122.7, 121.6, 121.2, 120.6, 118.7, 114.1, 89.9, 55.4, 43.3, 41.4 (d, $J = 2.02$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -41.05; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NaO}_2\text{S}$ 413.0794; Found 413.0793.



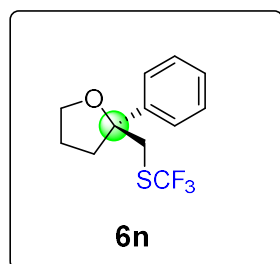
According to the general procedure C, the reaction time is 11 h, flash column chromatography (SiO_2 , PE) to afford **6I-1** as a colorless oil (16.9 mg, 34%), R_f =0.4 (silica gel, PE); ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 8.4$ Hz, 1H), 8.16 (d, $J = 7.4$ Hz, 1H), 7.79 (s, 1H), 7.67 – 7.57 (m, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 6.98 – 6.86 (m, 2H), 3.87 (d, $J = 15.8$ Hz, 1H), 3.80 (s, 3H), 3.70 (d, $J = 15.6$ Hz, 1H), 3.67 – 3.55 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 157.3, 136.4, 135.2, 134.8, 130.8 (q, $J = 307.4$ Hz), 129.8 (q, $J = 311.0$ Hz), 128.0, 126.5, 126.5, 126.3, 122.3, 121.2, 119.2,

114.3, 112.8, 91.2, 55.5, 42.7, 41.4; **¹⁹F NMR** (376 MHz, CDCl₃) δ -40.96, -43.26.

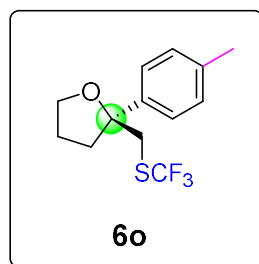
HRMS (ESI) m/z: [M+Na]⁺ calcd for C₂₂H₁₆F₆NaO₂S₂ 513.0388; Found 513.0388.



According to the general procedure **C**, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6m** as a colorless oil (4.0 mg, 13%), R_f=0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 8.02 – 7.87 (m, 1H), 7.85 – 7.73 (m, 1H), 7.50 – 7.37 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 1H), 3.43 (d, *J* = 15.6 Hz, 1H), 3.34 (s, 2H), 3.25 (d, *J* = 15.6 Hz, 1H), 1.68 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 153.7, 134.2, 131.1 (q, *J* = 306.84 Hz), 128.0, 126.0, 125.6, 122.9, 121.6, 120.7, 120.7, 118.8, 87.4, 41.8, 39.9 (d, *J* = 1.92 Hz), 26.2; **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.09; **HRMS** (ESI) m/z: [M+H]⁺ calcd for C₁₅H₁₄F₃OS 299.0712; Found 299.0715.



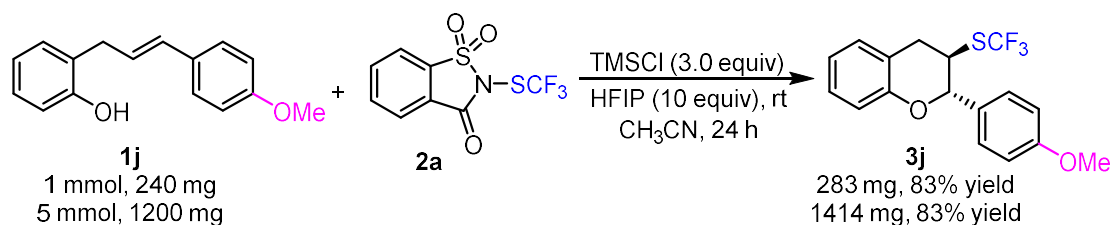
According to the general procedure **B**, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6n** as a colorless oil (10.7 mg, 41%), R_f=0.5 (silica gel, PE); **¹H NMR** (400 MHz, CDCl₃) δ 7.43 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 4.06 – 3.99 (m, 1H), 3.95 – 3.90 (m, 1H), 3.39 (d, *J* = 12.6 Hz, 1H), 3.27 (d, *J* = 12.7 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.29 – 2.23 (m, 1H), 2.11 – 1.95 (m, 1H), 1.90 – 1.79 (m, 1H); **¹³C NMR** (101 MHz, CDCl₃) δ 144.7, 131.3 (q, *J* = 306.84 Hz), 128.6, 127.6, 125.2, 85.1, 68.7, 41.4, 37.0, 26.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.43; **HRMS** (ESI) m/z: [M+Na]⁺ calcd for C₁₂H₁₃F₃NaOS 285.0531; Found 285.0531.



According to the general procedure **B**, the reaction time is 10 h, flash column chromatography (SiO₂, PE) to afford **6o** as a colorless oil (11.7 mg, 43%), *R_f*=0.4 (silica gel, PE); ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 2.0 Hz, 1H), 7.26 - 7.25 (m, 1H), 7.20 - 7.09 (m, 2H), 4.05 - 3.99 (m, 1H), 3.94 - 3.88 (m, 1H), 3.38 (d, *J* = 12.4 Hz, 1H), 3.26 (d, *J* = 12.4 Hz, 1H), 2.44 - 2.30 (m, 4H), 2.27 - 2.21 (m, 1H), 2.08 - 1.96 (m, 1H), 1.89 - 1.78 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 137.3, 131.4 (q, *J* = 306.84 Hz), 129.3, 125.2, 85.0, 68.6, 41.5 (d, *J* = 1.72 Hz), 36.9, 26.0, 21.2; ¹⁹F NMR (376 MHz, CDCl₃) δ -41.42; HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₃H₁₅F₃NaOS 299.0688; Found 299.0688.

5. 1 Mmol scale reactions and 5 mmol scale reactions

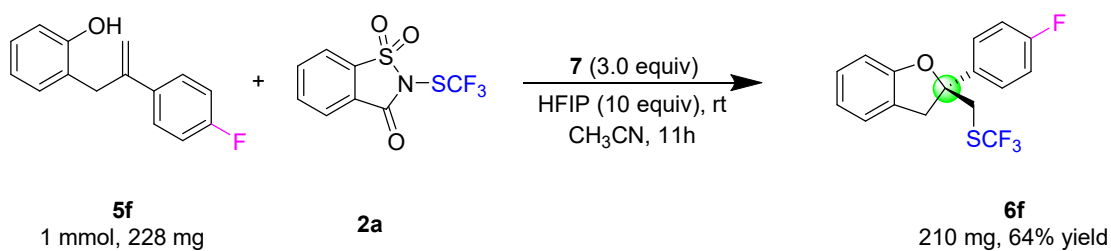
5.1 The procedure for the 1 mmol scale reaction for the synthesis of **3j**.



At room temperature, **1j** (240.3 mg, 1.0 mmol) and **2a** (368 mg, 1.3 mmol) were added into an over-dried 50 mL flask equipped with a stir bar. Seal the flask with a septum. Anhydrous CH₃CN (10 mL) was added via a syringe, then TMSCl (380 μL, 3.0 mmol) and HFIP (1053 μL, 10 mmol) were added by using syringes respectively and stirred for 24 hours. After the reaction was completed (monitored by TLC), the crude product was purified by silica gel flash column chromatography (SiO₂, PE) to afford **3j** as a white solid (283 mg, 83%), *R_f*=0.5 (silica gel, PE).

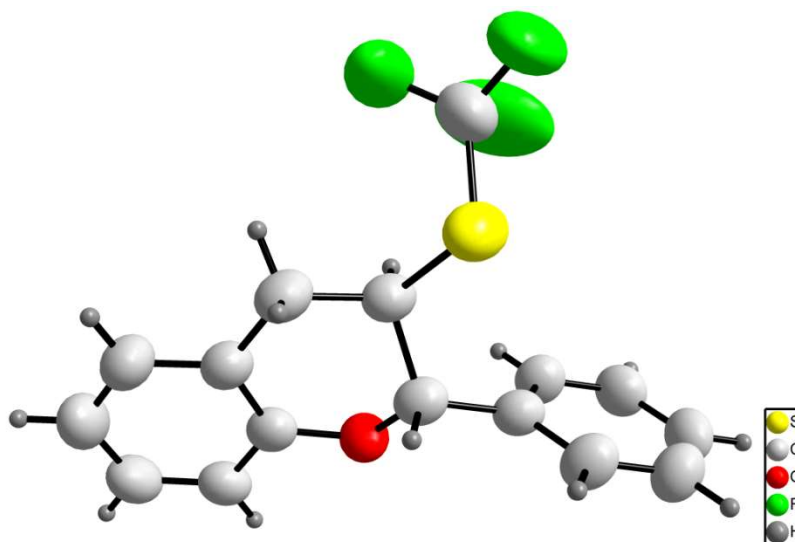
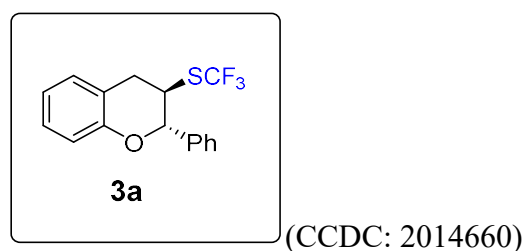
The procedure of 1 gram-scale reaction (5 mmol) is the same, using **1j** (1200 mg), **2a** (1840 mg), CH₃CN (50 mL), TMSCl (1.9 mL) and HFIP (5.3 mL). Product **3j** was obtained with 83% yield (1414 mg).

5.2 The procedure for the 1 mmol scale reaction for the synthesis of **6f**.



At room temperature, **5f** (228 mg, 1.0 mmol) and **2a** (368 mg, 1.3 mmol) were added into an over-dried 50 mL flask equipped with a stir bar. Seal the flask with a septum. Anhydrous CH₃CN (10 mL) was added via a syringe, then **7** (335 μ L, 3.0 mmol) and HFIP (1053 μ L, 10 mmol) were added by using syringes respectively and stirred for 11 hours. After the reaction was completed (monitored by TLC), the crude product was purified by silica gel flash column chromatography (SiO₂, PE) to afford **6f** as a colorless oil (210 mg, 64%), R_f =0.5 (silica gel, PE).

6. Crystals of **3a**.



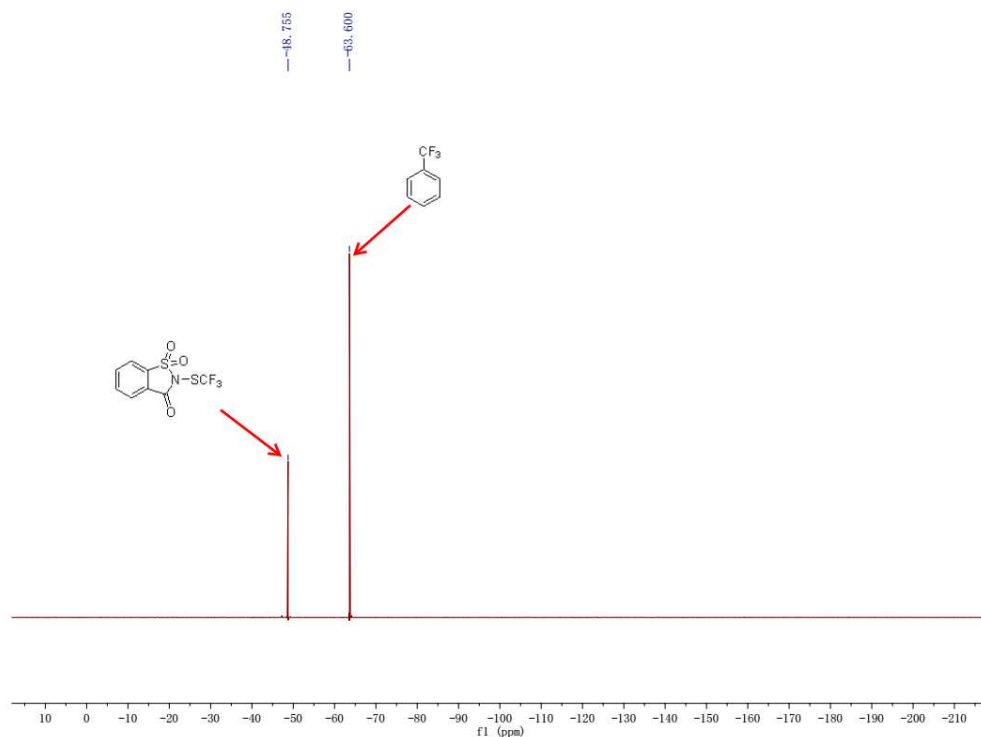
X-ray single crystal structures of **3a** with thermal ellipsoids drawn at the 50% probability level.

Procedure for the recrystallization of **3a**: To a 10 mL vial containing **3a** (20 mg), was added petroleum ether to form a clear solution. The solution was kept aside 3 days at room temperature to obtain crystals by slow evaporation. A suitable crystal was selected on a Bruker D8 VENTURE diffractometer. The crystal data was shown in Table S1:

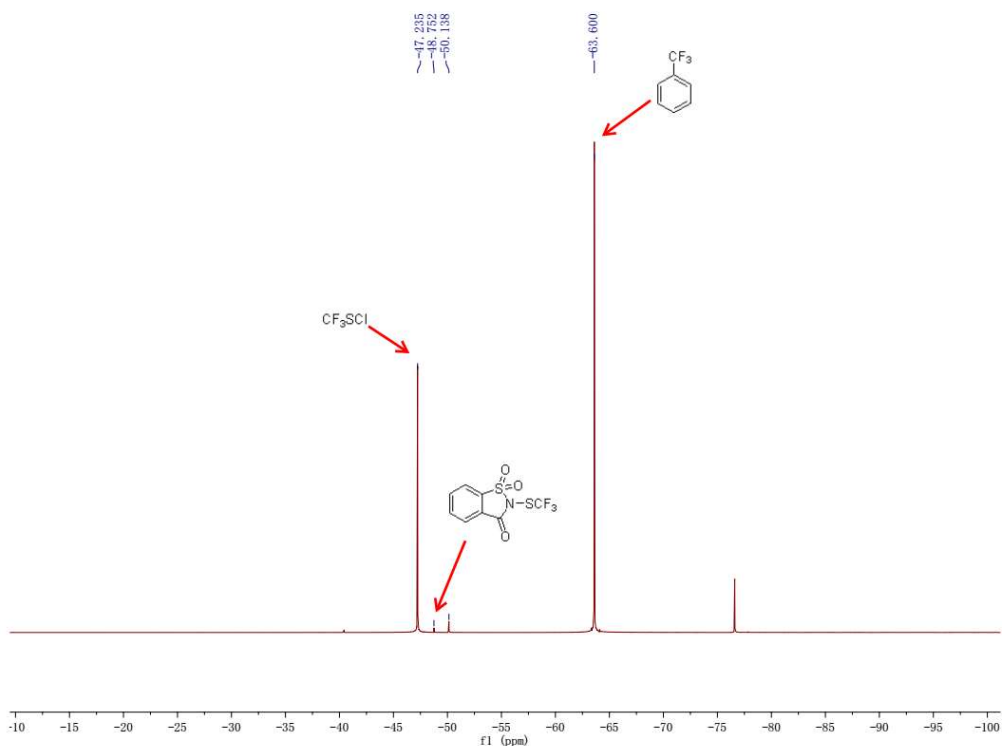
Table S1. Crystal data and structure refinement for **3a**

Identification code	3a
Empirical formula	C ₁₆ H ₁₃ F ₃ O S
Formula weight	310.32
Temperature	297(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.710(2) Å alpha = 90 deg. b = 5.6555(9) Å beta = 94.522(13) deg. c = 22.119(3) Å gamma = 90 deg.
Volume	1460.3(4) Å ³
Z, Calculated density	4, 1.411 Mg/m ³
Absorption coefficient	2.250 mm ⁻¹
F(000)	640
Crystal size	0.180 x 0.160 x 0.140 mm
Theta range for data collection	4.009 to 68.245 deg.
Limiting indices	-14 ≤ h ≤ 14, -6 ≤ k ≤ 6, -26 ≤ l ≤ 26
Reflections collected / unique	10400 / 2641 [R(int) = 0.0440]
Completeness to theta = 67.679	98.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2641 / 0 / 190
Goodness-of-fit on F ²	1.017
Final R indices [I > 2sigma(I)]	R1 = 0.0539, wR2 = 0.1436
R indices (all data)	R1 = 0.0676, wR2 = 0.1590
Extinction coefficient	n/a
Largest diff. peak and hole	0.423 and -0.330 e.Å ⁻³

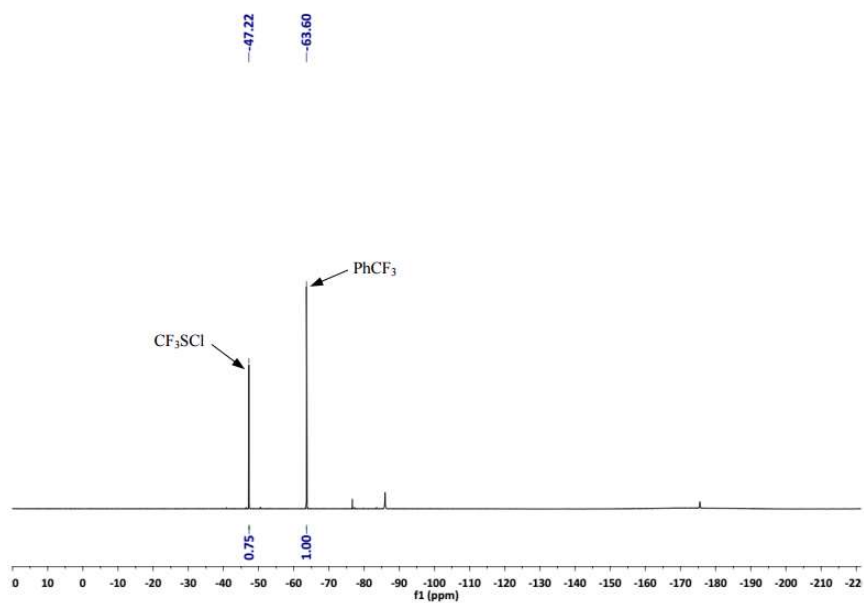
7. ^1H -NMR and ^{19}F -NMR spectroscopy studies



^{19}F NMR of **2a** and PhCF_3 in CD_3CN (376 MHz NMR)

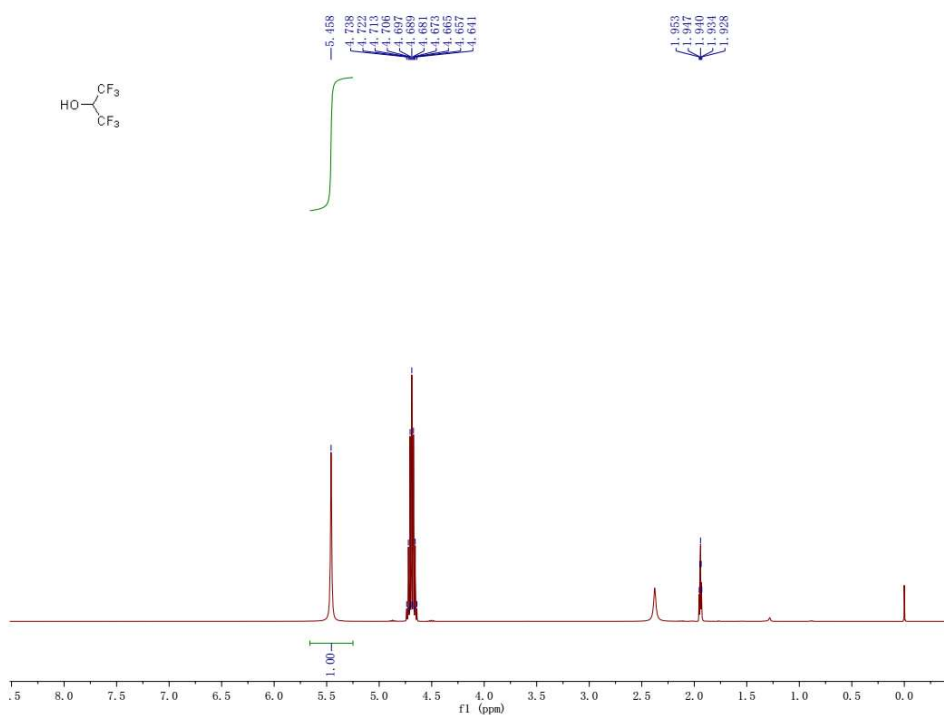


^{19}F NMR of **2a**, TMSCl and PhCF_3 in CD_3CN (376 MHz NMR)



¹⁹F NMR of CF₃SCl and PhCF₃ in reference (*Org. Chem. Front.*, **2017**, 4, 266)

According to previous work⁷, we can find that CF₃SCl was firstly formed in the present of Shen's reagent **2a** and TMSCl.



¹H NMR of HFIP in CD₃CN (400 MHz NMR)

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