Supporting Information

Copper-catalyzed trifluoromethylazidation and rearrangement of aniline-linked 1,7-enynes: access to CF₃-substituted azaspirocyclic dihydroquinolin-2-ones and furoindolines

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General remarks

Unless otherwise indicated, all reactions (for the synthesis of new products) were performed under an atmosphere of argon. THF was distilled from sodium (Na) under argon (Ar) atmosphere. MeCN was purified and dried according to standard methods prior to use. All other solvents were purchased from Adamas and used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. All NMR spectra were recorded on an AM-300 or AM-400 spectrophotometers in CDCl₃, NMR chemical shifts are reported in ppm referenced to the solvent peaks of CDCl₃ (7.26 ppm for ¹H and 77.0 ppm for ¹³C, respectively). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm⁻¹. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by ESI, and HRMS were measured on a HP-5989 instrument.
General procedure for the synthesis of substrate 1b

Compounds 1b were partially prepared according to the previously reported work and the corresponding spectroscopic data were consistent with those reported in the literature.[1]

**General procedure for synthesis of S₂:** To a 150 mL flask charged with S₁ (2 mmol, 1.0 equiv), Pd(PPh₃)₂Cl₂ (0.04 mmol, 2 mol%), and CuI (0.08 mmol, 4 mol%) in degassed Et₃N (5 mL) was added aryl alkynes (2.4 mmol, 1.2 equiv), and the resulting solution was stirred at room temperature for 2 h. Upon completion, the solvent was removed under reduced pressure, and the residue was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford S₂ in good yields ranging from 95% to 99%.

**General procedure for synthesis of S₃:** To a stirred solution of S₂ (1.0 equiv) in CH₂Cl₂ (5 mL) was added R₃Cl (1.5 equiv) and pyridine (1.5 equiv). The resulted mixture was stirred at room temperature for 12 h. Then the reaction was quenched by saturated CuSO₄ solution and the reaction mixture was extracted with CH₂Cl₂ (3 x 5 mL). The combined organic layer was dried over Na₂SO₄ and concentrated for the next step without further purification.

**General procedure for synthesis of 1b:** To a stirred solution of S₂ (1.0 equiv) in CH₂Cl₂ (5 mL) was added acyl chloride (1.5 equiv) and Et₃N (2.0 equiv). The resulted mixture was stirred at room
temperature for 6 h. Then the reaction was quenched by saturated NaHCO$_3$ solution and the reaction mixture was extracted with CH$_2$Cl$_2$ (3 x 5 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 1b in good yields ranging from 90% to 99%.

When R$^3$ was substituted by Me, Bn, or allyl group, the synthesized procedure was as follows:

General procedure for synthesis of S$_4$: To a stirred solution of S$_3$ (1.0 equiv) in CH$_2$Cl$_2$ (5 mL) was added acyl chloride (1.5 equiv) and Et$_3$N (2.0 equiv). The resulted mixture was stirred at room temperature for 6 h. Then the reaction was quenched by saturated NaHCO$_3$ solution and the reaction mixture was extracted with CH$_2$Cl$_2$ (3 x 5 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated for the next step without further purification.

General procedure for synthesis of 1b: To a solution of NaH (2.0 equiv) in THF (5.0 mL) at 0 °C was added a solution of S$_4$ (1.0 equiv) in THF (5 mL) dropwise and the reaction mixture was stirred for 30 min. Afterwards iodomethane or alkyl bromide (1.5 equiv) was added and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by water and the reaction mixture was extracted with DCM for 3 times. The combined organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product 1b in good yields ranging from 93% to 99%.
Spectroscopic data for substrates 1

**Compound 1be**: 482 mg, 80%, A white solid, m.p. 150-152 °C; IR (EtOH): ν 3062, 2920, 1719, 1648, 1623, 1494, 1389, 1215, 1134, 915, 771, 755, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.85 (s, 3H), 4.21 (dd, 1H, J₁ = 13.2 Hz, J₂ = 5.6 Hz), 4.71 (dd, 1H, J₁ = 13.2 Hz, J₂ = 5.6 Hz), 5.01 (s, 2H), 5.08-5.13 (m, 2H), 5.92-6.01 (m, 1H), 7.16 (d, 1H, J = 7.6 Hz), 7.25-7.35 (m, 5H), 7.52-7.55 (m, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 20.0, 52.0, 86.2, 94.8, 118.0, 119.1, 122.5, 122.8, 127.4, 128.4, 128.7, 128.8, 129.1, 131.5, 132.8, 132.9, 140.4, 144.6, 171.7; MS (ESI) m/z: 302.2 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₁H₂₀NO⁺ requires: 302.1539, Found: 302.1537.
**Compound 1bh:** 703 mg, 79%, A white solid, m.p. 191-193 °C; IR (EtOH): ν 3059, 1691, 1564, 1477, 1419, 1353, 1216, 1188, 1181, 1132, 1086, 940, 753, 688 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.77 (s, 3H), 2.08 (s, 3H), 3.85 (s, 3H), 5.24 (s, 2H), 6.96-6.98 (m, 2H), 7.04-7.07 (m, 4H), 7.20-7.23 (m, 2H), 7.27 (d, 1H, J = 8.0 Hz), 7.49 (dd, 1H, J₁ = 7.2 Hz, J₂ = 2.4 Hz), 7.92 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.2, 21.3, 55.6, 85.5, 94.5, 115.4, 116.7, 121.8, 123.4, 124.2, 127.9, 128.7, 128.8, 129.9, 131.4, 133.5, 136.2, 139.1, 144.6, 159.6, 170.6; MS (ESI) m/z: 446.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄NO₄S⁺ requires: 446.1421, Found: 446.1417.
Compound 1bi: 730 mg, 83%, A white solid, m.p. 186-188 °C; IR (EtOH): ν 3029, 1701, 1495, 1364, 1172, 1128, 1084, 814, 762, 753, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.79 (s, 3H), 2.08 (s, 3H), 5.19 (s, 1H), 5.32 (s, 1H), 7.05-7.09 (m, 4H), 7.23-7.27 (m, 2H), 7.33 (d, 1H, J = 7.6 Hz), 7.70 (dd, 1H, J₁ = 8.4 Hz, J₂ = 2.0 Hz), 7.77-7.79 (m, 2H), 7.89 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.9, 21.3, 83.2, 97.0, 113.2, 117.1, 120.8, 124.6, 124.7, 126.1, 129.0, 129.4, 129.7, 131.5, 131.6, 133.4, 135.7, 136.0, 138.7, 142.5, 145.2, 169.7; MS (ESI) m/z: 458.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄N₃O₃S⁺ requires: 458.1533, Found: 458.1530.
Compound 1bj: 719 mg, 76%, A white solid, m.p. 174-176 °C; IR (EtOH): ν 3062, 2984, 1727, 1624, 1495, 1363, 1260, 1173, 1133, 1085, 759, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.78 (s, 3H), 2.08 (s, 3H), 3.96 (s, 3H), 5.22 (s, 1H), 5.27 (s, 1H), 7.05-7.07 (m, 4H), 7.21-7.25 (m, 2H), 7.30 (d, 1H, J = 7.2 Hz), 7.72 (d, 1H, J = 8.4 Hz), 7.90 (d, 2H, J = 7.6 Hz), 8.08 (d, 1H, J = 8.4 Hz), 8.16 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0, 21.2, 52.5, 84.5, 95.5, 121.3, 123.5, 124.3, 128.0, 128.91, 128.95, 129.4, 129.7, 130.7, 131.4, 132.5, 133.8, 135.8, 138.8, 142.4, 144.9, 165.4, 170.0; MS (ESI) m/z: 474.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₄NO₅S⁺ requires: 474.1370, Found: 474.1365.
**Compound 1bk:** 721 mg, 84%, A white solid, m.p. 172-174 °C; IR (EtOH): ν 2923, 2845, 1686, 1505, 1363, 1305, 1138, 951, 809, 771, 693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.78 (s, 3H), 2.07 (s, 3H), 2.44 (s, 3H), 5.24 (s, 2H), 7.01-7.06 (m, 4H), 7.18-7.21 (m, 3H), 7.25 (d, 1H, J = 7.2 Hz), 7.36 (d, 1H, J = 8.0 Hz), 7.44 (s, 1H), 7.93 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.1, 21.2, 21.3, 85.5, 94.0, 120.2, 122.0, 123.4, 127.8, 128.4, 128.8, 129.8, 130.0, 131.2, 132.3, 132.9, 136.1, 138.5, 139.0, 139.4, 144.6, 170.4; MS (ESI) m/z: 430.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄NO₃S⁺ requires: 430.1471, Found: 430.1468.
**Compound 1bq**: 772 mg, 86%, A white solid, m.p. 195-197 °C; IR (EtOH): ν 2951, 2920, 1683, 1489, 1363, 1174, 1138, 1086, 954, 811, 770, 725, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.77 (s, 3H), 2.10 (s, 3H), 5.24 (s, 1H), 5.28 (s, 1H), 6.97 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.11 (td, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.22 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.33 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.38-7.48 (m, 2H), 7.55 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 7.60 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 7.91 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.2, 21.3, 90.3, 91.3, 121.9, 123.2, 123.8, 126.2, 128.9, 129.2, 129.3, 129.6, 129.9, 132.5, 133.1, 133.4, 135.4, 136.1, 138.7, 139.0, 144.7, 170.5; MS (ESI) m/z: 450.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₅H₂₁ClNO₃S⁺ requires: 450.0925, Found: 450.0923.
Compound 1br: 679 mg, 73%, A white solid, m.p. 200-202 °C; IR (EtOH): ν 3056, 1688, 1370, 1362, 1173, 1143, 1086, 867, 810, 769, 701, 658 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.79 (s, 3H), 1.81 (s, 3H), 5.25 (s, 2H), 7.01 (d, 2H, J = 8.4 Hz), 7.10 (dd, 1H, J₁ = 8.0 Hz, J₂ = 1.2 Hz), 7.38-7.54 (m, 6H), 7.64-7.68 (m, 2H), 7.73-7.80 (m, 2H), 7.97 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.2, 21.1, 85.9, 95.3, 119.1, 123.3, 123.7, 126.6, 126.9, 127.59, 127.65, 127.7, 127.8, 128.8, 128.9, 129.1, 130.0, 131.6, 132.5, 132.60, 132.64, 132.9, 136.3, 138.9, 139.0,
144.7, 170.6; MS (ESI) m/z: 466.1 (M+H^+, 100); HRMS (ESI) Calcd. for C_{29}H_{24}NO_{3}S^+ requires: 466.1471, Found: 466.1468.

**Compound 1bt**: 699 mg, 83%, A white solid, m.p. 177-179 °C; IR (EtOH): ν 2984, 1682, 1360, 1173, 1133, 1086, 934, 799, 769, 692 cm^{-1}; ^1H NMR (400 MHz, CDCl$_3$, TMS): δ 1.76 (s, 3H), 2.16 (s, 3H), 5.22 (s, 1H), 5.24 (s, 1H), 6.78 (dd, 1H, $J_1= 8.8$ Hz, $J_2= 1.2$ Hz), 7.08 (d, 2H, $J = 8.4$ Hz), 7.14 (dd, 1H, $J_1= 2.8$ Hz, $J_2= 1.2$ Hz), 7.17 (dd, 1H, $J_1= 8.8$ Hz, $J_2= 2.8$ Hz), 7.35-7.45 (m, 3H), 7.62 (dd, 1H, $J_1= 8.4$ Hz, $J_2= 1.2$ Hz), 7.90 (d, 2H, $J = 8.4$ Hz); ^13C NMR (100 MHz, CDCl$_3$, TMS): δ 19.0, 21.3, 85.0, 90.2, 120.8, 123.2, 123.8, 124.9, 128.6, 128.7, 129.0, 129.3, 129.5, 129.7,
132.1, 132.4, 136.0, 138.7, 138.8, 144.6, 170.4; MS (ESI) m/z: 422.1 (M+H+, 100); HRMS (ESI) Calcd. for C_{23}H_{20}NO_{3}S_{2}^+ requires: 422.0879, Found: 422.0875.

**Compound 1bu:** 690 mg, 82%, A white solid, m.p. 175-177 °C; IR (EtOH): ν 2976, 2918, 1697, 1363, 1173, 1086, 703, 668 cm^{-1}; ^1H NMR (400 MHz, CDCl₃, TMS): δ 1.78 (s, 3H), 2.19 (s, 3H), 5.24 (s, 2H), 6.89-6.92 (m, 2H), 7.10 (d, 2H, J = 8.4 Hz), 7.23-7.25 (m, 1H), 7.36-7.45 (m, 3H), 7.62 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 7.90 (d, 2H, J = 8.4 Hz); ^13C NMR (100 MHz, CDCl₃,
Compound 1bv: 532 mg, 64%, A white solid, m.p. 181-183 °C; IR (EtOH): ν 2967, 2922, 1698, 1489, 1364, 1174, 1144, 777, 668 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.78 (s, 3H), 2.11 (s, 3H), 5.27 (s, 1H), 5.28 (s, 1H), 6.96 (d, 1H, J = 8.0 Hz), 7.08 (d, 2H, J = 8.0 Hz), 7.20-7.23 (m, 1H), 7.40-7.44 (m, 1H), 7.50 (t, 1H, J = 8.0 Hz), 7.54-7.64 (m, 3H), 7.92 (d, 2H, J = 8.0 Hz), 8.53 (d, 1H, J = 4.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0, 21.3, 85.0, 93.4, 122.4, 123.0, 124.1, 127.3, 128.9, 129.2, 129.6, 129.8, 132.4, 133.2, 135.8, 136.0, 138.8, 139.2, 142.0, 144.6, 149.6, 170.5; MS
(ESI) \textit{m/z}: 417.1 (M+H\textsuperscript{+}, 100); HRMS (ESI) Calcd. for C\textsubscript{24}H\textsubscript{21}N\textsubscript{2}O\textsubscript{3}S\textsuperscript{+} requires: 417.1267, Found: 417.1263.

**Compound 1bx**: 461 mg, 88\%, A colorless oil, obtained as 2:1 mixture of rotamers; IR (EtOH): \(\nu\) 2979, 2923, 1737, 1496, 1445, 1319, 1294, 1198, 1117, 947, 752, 689 cm\textsuperscript{-1}; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}, TMS): \(\delta\) 1.99 (s, 1.5H), 2.10 (s, 3H), 5.79 (s, 1.5H), 6.21 (s, 0.5H), 6.46 (s, 1H), 7.18-7.24 (m, 2H), 7.31-7.37 (m, 4H), 7.43-7.44 (m, 2H), 7.57 (d, 1H, \(J = 7.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}, TMS): \(\delta\) 17.8, 18.4, 84.2, 94.1, 117.2, 122.3, 122.9, 125.7, 127.4, 128.3, 128.4, 129.0, 129.3,
131.4, 132.8, 135.6, 151.7, 163.0, 165.2; MS (ESI) m/z: 280.1 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{18}$H$_{18}$NO$_2^+$ requires: 280.1332, Found: 280.1332.

**Compound 6**: 463 mg, 54%, A white solid, m.p. 186-188 °C; IR (EtOH): ν 2970, 2918, 1690, 1494, 1355, 1308, 1167, 1087, 757, 705, 690 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, TMS): δ 1.79 (s, 3H), 2.38 (s, 3H), 5.11 (s, 1H), 5.20 (s, 1H), 5.28 (s, 2H), 7.22 (d, 2H, $J = 8.4$ Hz), 7.25-7.30 (m, 3H), 7.33-7.36 (m, 3H), 7.49-7.53 (m, 3H), 7.69 (d, 2H, $J = 8.4$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$, TMS): δ 19.3, 21.5, 48.9, 86.6, 94.7, 119.6, 121.9, 122.8, 127.36, 127.44, 128.3, 128.4, 128.5, 128.6,
129.3, 131.5, 132.3, 136.0, 138.0, 139.9, 144.7, 172.4; MS (ESI) \( m/z \): 447.2 (M+NH\(_4^+\), 100);
The proposed mechanism for the formation of 2ba

According to our previous work and Liang’s work,[2] we proposed the reaction might undergo consecutive trifluoromethylazidation of enynes and thermally induced rearrangement of corresponding vinyl azides, herein we use 1ba as an example to explain the detailed mechanism: Initially, The trifluoromethyl radical is released accompanied by the formation of CuII(N3) complex when Togni reagent I is activated by a TMS group,[3] followed by a single-electron transfer (SET) process in the presence of copper catalyst. Afterwards, the chemoselective attack of trifluoromethyl radical on alkene moiety forms the radical intermediate II, which induces radical attack on the alkyne moiety to form radical intermediate III. Then the activated radical intermediate III is combined with the released N3-coordinated CuII complex CuII(N3) to produce CuIII intermediate IV. Finally, reductive elimination of CuIII occurs to form vinyl azide V and regenerate CuI catalyst to complete the whole trifluoromethylazidation process. The formed vinyl azide V is not stable under thermal conditions, and a consecutive rearrangement process occurs to deliver the final product 2ba.

Scheme S1 Proposed mechanism for the synthesis of 2ba.
General procedure for the synthesis of products 2b and 5

1b or 4 (0.2 mmol, 1.0 equiv), Togni reagent I (0.30 mmol, 1.5 equiv), CuTc (copper(I) thiophene-2-carboxylate, 0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then TMSN₃ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 70 °C oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products 2b and 5 in good yield.
Spectroscopic data for products 2b and 5

**Compound 2ba:** 82 mg, 82%, A white solid, m.p. 175-177 °C; IR (EtOH): v 2926, 2856, 1715, 1451, 1368, 1263, 1153, 1133, 1118, 1087, 763, 754, 657 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.87 (s, 3H), 2.15-2.25 (m, 1H), 2.32-2.41 (m, 1H), 2.45 (s, 3H), 6.96 (d, 1H, J = 7.6 Hz), 7.21 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.44 (t, 1H, J = 8.0 Hz), 7.60 (t, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.86-7.91 (m, 3H), 7.96 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0 (q, J_C-F = 1.5 Hz), 21.7, 39.7 (q, J_C-F = 29.0 Hz), 42.6, 46.4, 123.5, 123.8, 125.9, 126.6, 128.0 (q, J_C-F = 277.1 Hz), 128.76, 128.81, 129.3, 129.4, 129.5, 129.6, 134.0, 135.6, 136.3, 145.0, 167.2, 171.2; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.3 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 516.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₅F₃N₃O₃S⁺ requires: 516.1563, Found: 516.1558.
Compound 2bb: 71 mg, 84%, A white solid, m.p. 160-162 °C; IR (EtOH): ν 2923, 2848, 1713, 1361, 1257, 1174, 1149, 1129, 1110, 971, 962, 769, 760, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.10 (s, 3H), 2.22-2.34 (m, 1H), 2.38-2.50 (m, 1H), 3.60 (s, 3H), 6.97 (d, 1H, J = 7.2 Hz), 7.18 (t, 1H, J = 7.2 Hz), 7.39 (t, 1H, J = 8.4 Hz), 7.62-7.71 (m, 4H), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.2, 39.6 (q, J_C-F = 28.9 Hz), 42.7, 43.2, 46.8 (q, J_C-F = 1.5 Hz), 123.0, 123.7, 125.3 (q, J_C-F = 277.1 Hz), 125.9, 126.7, 128.9, 129.5, 129.67, 129.70, 134.2, 135.0, 167.3, 172.9; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.3 (t, 3F, J = 10.9 Hz); MS (ESI) m/z:
440.1 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{20}$H$_{21}$F$_3$N$_3$O$_3$S$^+$ requires: 440.1250, Found: 440.1246.
**Compound 2bc**: 64 mg, 90%, A white solid, m.p. 164-166 °C, dr = 1:0.42; IR (EtOH): ν 2979, 2937, 1677, 1603, 1471, 1356, 1260, 1139, 1112, 762, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.09 (s, 1.26H), 1.10 (s, 3H), 2.29-2.44 (m, 1.42H), 2.55-2.67 (m, 1.42H), 3.52 (s, 3H), 3.56 (s, 1.26H), 6.79 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 6.87 (dd, 0.42H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 6.95 (t, 1H, J = 7.6 Hz), 7.03 (t, 0.42H, J = 7.6 Hz), 7.08-7.12 (m, 1.42H), 7.31-7.37 (m, 1.42H), 7.52 (t, 0.84H, J = 7.6 Hz), 7.58-7.69 (m, 3.42H), 7.74 (dd, 0.84H, J₁ = 8.4 Hz, J₂ = 1.6 Hz), 7.95 (dd, 2H, J₁ = 8.4 Hz, J₂ = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.4 (q, J_C-F = 1.6 Hz), 19.6 (q, J_C-F = 1.6 Hz), 30.56, 30.67, 38.1 (q, J_C-F = 28.1 Hz), 41.3 (q, J_C-F = 28.1 Hz), 42.8, 43.2 (q, J_C-F = 1.5 Hz), 43.4, 43.5 (q, J_C-F = 1.5 Hz), 123.07, 123.15, 123.3, 123.9, 124.4, 125.5 (q, J_C-F = 277.0 Hz), 125.9 (q, J_C-F = 277.0 Hz), 126.1, 126.5, 126.6, 128.6, 129.3, 129.36, 129.39, 129.6, 129.9, 133.7, 133.9, 139.5, 140.8, 167.1, 169.8, 170.0, 170.3; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.8 (t, 3F, J = 10.9 Hz), -60.6 (t, 1.26F, J = 10.9 Hz); MS (ESI) m/z: 359.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₀H₁₈F₃N₂O⁺ requires: 359.1366, Found: 359.1363.
**Compound 2bd**: 65 mg, 75%, A white solid, m.p. 175-177 °C; IR (EtOH): ν 2926, 2848, 1679, 1602, 1495, 1459, 1368, 1322, 1261, 1179, 1134, 1119, 1068, 763, 760, 691 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃, TMS): δ 1.18 (s, 3H), 2.37-2.49 (m, 1H), 2.63-2.75 (m, 1H), 5.23 (d, 1H, \(J = 16.0\) Hz), 5.41 (d, 1H, \(J = 16.0\) Hz), 6.81 (dd, 1H, \(J_1 = 7.6\) Hz, \(J_2 = 1.2\) Hz), 6.91 (td, 1H, \(J_1 = 7.6\) Hz, \(J_2 = 1.2\) Hz), 7.02 (s, 1H, \(J = 8.0\) Hz), 7.17-7.21 (m, 1H), 7.20-7.27 (m, 1H), 7.31-7.36 (m, 4H), 7.60-7.70 (m, 3H), 7.95 (dd, 2H, \(J_1 = 8.0\) Hz, \(J_2 = 1.2\) Hz); \(^1\)C NMR (100 MHz, CDCl₃, TMS): δ 19.3, 40.8 (q, \(J_{C-F} = 28.1\) Hz), 43.6, 43.9 (q, \(J_{C-F} = 1.6\) Hz), 47.2, 115.6, 123.3, 124.4, 125.7 (q, \(J_{C-F} = 277.1\) Hz), 126.4, 126.5, 127.0, 127.2, 128.8, 129.2, 129.4, 129.6, 133.7, 136.8, 140.0, 167.6, 170.5;
$^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -58.9 (t, 3F, $J = 10.9$ Hz); MS (ESI) $m/z$: 435.2 (M+H$^+$, 100); HRMS (ESI) Calcd. for C$_{26}$H$_{22}$F$_3$N$_2$O requires: 435.1679, Found: 435.1674.
**Compound 2be**: 48 mg, 63%, A white solid, m.p. 163-165 °C; IR (EtOH): ν 2937, 2854, 1677, 1603, 1460, 1451, 1367, 1259, 1184, 1133, 1118, 754, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.11 (s, 3H), 2.29-2.41 (m, 1H), 2.61-2.70 (m, 1H), 4.46 (dd, 1H, J₁ = 18.0 Hz, J₂ = 6.4 Hz), 4.93 (dd, 1H, J₁ = 18.0 Hz, J₂ = 6.4 Hz), 5.28-5.31 (m, 2H), 5.91-6.00 (m, 1H), 6.80 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 6.92-6.96 (m, 1H), 7.11 (d, 1H, J = 8.0 Hz), 7.28-7.32 (m, 1H), 7.61-7.69 (m, 3H), 7.95 (dd, 2H, J₁ = 8.0 Hz, J₂ = 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.3, 41.0 (q, J_C-F = 28.1 Hz), 43.6, 46.2, 115.2, 116.8, 123.2, 124.4, 125.6 (q, J_C-F = 277.1 Hz), 126.5, 126.8, 129.2, 129.4, 129.6, 132.5, 133.8, 140.2, 167.3, 169.7; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 385.2 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₂H₂₀F₃N₂O⁺ requires: 385.1522, Found: 385.1519.
Compound 2bf: 83 mg, 78%, A white solid, m.p. 210-212 °C; IR (EtOH): ν 3051, 1719, 1396, 1359, 1175, 1153, 1132, 1086, 811, 768, 750, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.91 (s, 3H), 2.13-2.25 (m, 1H), 2.31-2.40 (m, 1H), 2.46 (s, 3H), 6.91 (s, 1H), 7.36-7.42 (m, 3H), 7.58-7.62 (m, 2H), 7.69 (t, 1H, J = 7.6 Hz), 7.81-7.87 (m, 3H), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0 (q, J_C-F = 1.5 Hz), 21.7, 39.4 (q, J_C-F = 29.0 Hz), 42.1, 46.3 (q, J_C-F = 1.5 Hz), 123.2, 124.7, 125.1 (q, J_C-F = 277.1 Hz), 125.5, 128.8, 128.9, 129.4, 129.6, 129.7, 131.6, 132.3, 134.0, 134.3, 135.9, 145.3, 166.9, 170.9; ¹⁹F NMR (376 MHz, CDCl₃, CFCI₃): δ -59.0 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 550.1 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄ClF₃N₃O₃S⁺ requires: 550.1174, Found: 550.1170.
**Compound 2bg**: 82 mg, 80%, A white solid, m.p. 184-186 °C; IR (EtOH): ν 2922, 2851, 1719, 1367, 1262, 1173, 1134, 1087, 668 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.87 (s, 3H), 2.11-2.23 (m, 1H), 2.27 (s, 3H), 2.33-2.43 (m, 1H), 2.45 (s, 3H), 6.73 (d, 1H, J = 1.6 Hz), 7.24 (dd, 1H, J₁ = 8.4 Hz, J₂ = 1.6 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.60 (t, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.79 (d, 1H, J = 8.4 Hz), 7.85 (dd, 2H, J₁ = 8.4 Hz, J₂ = 1.6 Hz), 7.94 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.9, 20.8, 21.7, 39.5 (q, J₃-C-F = 28.9 Hz), 42.7, 46.4 (q, J₃-C-F = 1.6 Hz), 123.4, 123.8, 126.0, 128.0 (q, J₃-C-F = 277.1 Hz), 128.7, 129.30, 129.35, 129.4, 129.5, 129.6, 133.1, 134.0, 136.3, 136.7, 144.9, 167.4, 171.2; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.2 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 530.1 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₇F₃N₃O₃S⁺ requires: 530.1720, Found: 530.1714.
**Compound 2bh**: 83 mg, 79%, A white solid, m.p. 189-191 °C; IR (EtOH): ν 2962, 2919, 1729, 1488, 1371, 1263, 1176, 1127, 1085, 667 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.88 (s, 3H), 2.08-2.22 (m, 1H), 2.34-2.43 (m, 1H), 2.46 (s, 3H), 3.74 (s, 3H), 6.47 (d, 1H, J = 2.8 Hz), 6.96 (dd, 1H, J₁ = 8.4 Hz, J₂ = 2.8 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.58 (t, 2H, J = 7.6 Hz), 7.67 (t, 1H, J = 7.6 Hz), 7.82-7.84 (m, 3H), 7.94 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.7, 21.7, 39.3 (q, J_C-F = 29.0 Hz), 42.8, 46.4 (q, J_C-F = 1.5 Hz), 55.4, 111.3, 113.4, 123.6, 125.1, 125.2 (q, J_C-F = 277.3 Hz), 128.4, 128.8, 129.3, 129.5, 129.6, 131.2, 134.1, 136.2, 144.9, 158.0, 167.3, 171.1; ¹⁹F
NMR (376 MHz, CDCl$_3$, CFCl$_3$): δ -59.1 (t, 3F, $J = 10.9$ Hz); MS (ESI) m/z: 546.2 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{27}$H$_{27}$F$_3$N$_3$O$_4$S$^+$ requires: 546.1669, Found: 546.1664.
Compound 2bi: 74 mg, 71%, A white solid, m.p. 198-200 °C; IR (EtOH): ν 2973, 2893, 1719, 1369, 1262, 1175, 1149, 1128, 1086, 1046, 879, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.92 (s, 3H), 2.18-2.37 (m, 2H), 2.48 (s, 3H), 7.21 (d, 1H, J = 1.6 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.61-7.65 (m, 2H), 7.71-7.74 (m, 2H), 7.85 (dd, 2H, J₁ = 7.2 Hz, J₂ = 0.8 Hz), 7.96 (d, 2H, J = 8.4 Hz), 8.03 (d, 1H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.3, 21.7, 39.6 (q, JCF = 29.0 Hz), 41.5, 46.2 (q, JCF = 1.5 Hz), 110.2, 117.6, 122.8, 123.7, 124.9 (q, JCF = 276.6 Hz), 128.9, 129.48, 129.53, 129.6, 129.8, 131.1, 132.3, 134.6, 135.5, 139.0, 145.7, 166.4, 170.8; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.0 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 541.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₄F₃N₄O₃S⁺ requires: 541.1516, Found: 541.1511.
**Compound 2bj:** 91 mg, 82%, A white solid, m.p. 177-179 °C; IR (EtOH): $\nu$ 2920, 2848, 1722, 1370, 1264, 1176, 1130, 1086, 765, 662 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 0.92 (s, 3H), 2.14-2.26 (m, 1H), 2.29-2.41 (m, 1H), 2.47 (s, 3H), 3.87 (s, 3H), 7.38 (d, 2H, $J$ = 8.0 Hz), 7.58-7.62 (m, 3H), 7.69 (t, 1H, $J$ = 7.2 Hz), 7.85 (d, 2H, $J$ = 8.0 Hz), 7.96-8.01 (m, 3H), 8.11 (d, 1H, $J$ = 8.8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$, TMS): $\delta$ 19.1 (q, $J_{C-F}$ = 1.5 Hz), 21.7, 39.5 (q, $J_{C-F}$ = 28.8 Hz), 42.1, 46.3 (q, $J_{C-F}$ = 1.5 Hz), 52.3, 123.1, 123.4, 125.0 (q, $J_{C-F}$ = 277.3 Hz), 127.0, 128.2, 128.8, 129.4, 129.57, 129.63, 129.86, 129.92, 134.2, 135.9, 139.1, 145.4, 165.6, 166.9, 171.1; $^{19}$F NMR
(376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -59.1 (t, 3F, $J = 10.9$ Hz); MS (ESI) $m/z$: 574.2 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{28}$H$_{27}$F$_3$N$_3$O$_5$S$^+$ requires: 574.1618, Found: 574.1613.
**Compound 2bk**: 85 mg, 83%, A white solid, m.p. 171-173 °C; IR (EtOH): ν 2959, 2920, 2850, 1717, 1367, 1264, 1175, 1133, 1087, 762, 663 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.83 (s, 3H), 2.11-2.23 (m, 1H), 2.32-2.41 (m, 1H), 2.44 (s, 3H), 2.45 (s, 3H), 6.84 (d, 1H, J = 7.6 Hz), 7.00 (d, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.60 (t, 2H, J = 7.6 Hz), 7.65-7.69 (m, 1H), 7.72 (s, 1 H), 7.86 (dd, 2H, J₁ = 8.4 Hz, J₂ = 1.6 Hz), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0, 21.6 (q, Jₐ-C = 1.4 Hz), 39.8 (q, Jₐ-C = 28.9 Hz), 42.6, 46.4 (q, Jₐ-C = 1.5 Hz), 124.0, 124.2, 125.2 (q, Jₐ-C = 277.1 Hz), 125.8, 126.5, 127.4, 128.7, 129.3, 129.4, 129.6, 133.9, 135.5, 136.4, 139.2, 144.9, 167.2, 171.3; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.5 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 530.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₇F₃N₃O₃S⁺ requires: 530.1720, Found: 530.1715.
**Compound 2bl**: 83 mg, 78%, A white solid, m.p. 232-234 °C; IR (EtOH): ν 2959, 2927, 1718, 1670, 1368, 1261, 1168, 1088, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.86 (s, 3H), 2.14-2.26 (m, 1H), 2.29-2.41 (m, 1H), 2.46 (s, 3H), 6.93 (d, 1H, J = 8.0 Hz), 7.22 (t, 1H, J = 8.0 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.45 (dd, 1H, J₁ = 8.0 Hz, J₂ = 1.2 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.82 (d, 2H, J = 8.4 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.1, 21.7, 39.4 (q, J_C-F = 28.9 Hz), 42.9, 46.6 (q, J_C-F = 1.5 Hz), 122.4, 123.5, 125.4 (q, J_C-F = 277.1 Hz), 125.7, 126.7, 128.8, 129.0, 129.3, 129.4, 130.1, 130.6, 135.5, 136.2, 140.4, 145.1,
166.8, 171.2; $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -59.1 (t, 3F, $J = 10.9$ Hz); MS (ESI) $m/z$: 550.1 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{26}$H$_{24}$ClF$_3$N$_3$O$_3$S$^+$ requires: 550.1174, Found: 550.1170.
**Compound 2bm**: 83 mg, 72%, A white solid, m.p. 240-242 °C; IR (EtOH): ν 2956, 2920, 1719, 1356, 1261, 1154, 1131, 1087, 797, 668 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.86 (s, 3H), 2.16-2.28 (m, 1H), 2.33-2.37 (m, 1H), 2.47 (s, 3H), 6.92 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.17-7.23 (m, 1H), 7.37 (d, 2H, J = 8.4 Hz), 7.45 (td, 1H, J₁ = 8.4 Hz, J₂ = 1.2 Hz), 7.58 (d, 2H, J = 8.8 Hz), 7.82 (d, 2H, J = 8.8 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.1 (q, J_C-F = 1.4 Hz), 21.8, 39.4 (q, J_C-F = 28.9 Hz), 43.0, 46.6 (q, J_C-F = 1.5 Hz), 122.8, 123.6, 125.2 (q, J_C-F = 277.1 Hz), 125.7, 126.7, 128.9, 129.0, 129.1, 129.3, 129.4, 130.7, 132.0, 133.1, 135.5, 136.2, 145.1, 167.0, 171.2; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.1 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 594.1 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄BrF₃N₃O₃S⁺ requires: 594.0668, Found: 594.0665.
**Compounds 2bn**: 72 mg, 70%, a white solid, m.p. 179-181 °C; IR (EtOH): ν 2976, 2923, 1718, 1367, 1357, 1262, 1177, 1151, 1086, 1045, 670 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.86 (s, 3H), 2.11-2.23 (m, 1H), 2.32-2.43 (m, 1H), 2.46 (s, 3H), 2.49 (s, 3H), 6.95 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.35-7.46 (m, 5H), 7.75 (d, 2H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0, 21.7, 21.9, 39.7 (q, J_C-F = 29.1 Hz), 42.3, 46.4 (q, J_C-F = 1.5 Hz), 121.1, 123.5, 125.2 (q, J_C-F = 277.1 Hz), 125.9, 126.6, 128.7, 128.8, 129.4, 129.5, 129.8, 130.3, 135.6, 136.4, 145.0, 145.2, 166.6, 171.3; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 530.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₇F₃N₃O₃S⁺ requires: 530.1720, Found: 530.1715.
**Compound 2bo**: 91 mg, 86%, A white solid, m.p. 186-188 °C; IR (EtOH): ν 2962, 2922, 2851, 1718, 1507, 1175, 1151, 1132, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.87 (s, 3H), 2.10-2.22 (m, 1H), 2.32-2.41 (m, 1H), 2.45 (s, 3H), 3.91 (s, 3H), 6.96 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.08 (d, 2H, J = 8.4 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.42 (t, 1H, J = 8.0 Hz), 7.79 (d, 2H, J = 8.4 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.8, 21.7, 39.6 (q, J_C-F = 29.0 Hz), 42.0, 46.4 (q, J_C-F = 1.5 Hz), 55.6, 115.1, 116.0, 123.4, 125.2 (q, J_C-F = 277.5 Hz), 125.8, 126.6, 128.6, 128.7, 129.3, 129.9, 131.6, 135.5, 136.3, 144.9, 164.1, 165.6, 171.4; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.3 (t, 3F, J = 10.9 Hz);
MS (ESI) \( m/z \): 546.2 (M+NH\(_4^+\), 100); HRMS (ESI) Calcd. for C\(_{27}\)H\(_{27}\)F\(_3\)N\(_3\)O\(_4\)S\(^+\) requires: 546.1669, Found: 546.1664.
**Compound 2bp**: 86 mg, 84%, A white solid, m.p. 177-179 °C; IR (EtOH): ν 3031, 1735, 1725, 1374, 1365, 1177, 1138, 1122, 1111, 1085, 789, 756, 658 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.85 (s, 3H), 2.12-2.24 (m, 1H), 2.33-2.43 (m, 1H), 2.45 (s, 3H), 2.47 (s, 3H), 6.96 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.20 (td, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.42-7.49 (m, 3H), 7.62-7.65 (m, 1H), 7.74 (s, 1H), 7.90 (dd, 1H, J₁ = 7.6 Hz, J₂ = 0.8 Hz), 7.95 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.0, 21.3, 21.7, 39.8 (q, J_C-F = 28.7 Hz), 42.6, 46.4 (q, J_C-F = 1.5 Hz), 123.5, 123.7, 125.2 (q, J_C-F = 276.6 Hz), 126.0, 126.6, 126.8, 128.7, 128.8, 129.4, 129.5, 129.66, 129.70, 134.9, 135.6, 136.3, 139.7, 145.0, 167.2, 171.2; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 530.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₇F₃N₃O₃S⁺ requires: 530.1720, Found: 530.1714.
**Compound 2bq:** 92 mg, 86%, A white solid, m.p. 203-205 °C; IR (EtOH): ν 2931, 1718, 1455, 1366, 1261, 1175, 1127, 1086, 812, 801, 758, 665 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.93 (s, 3H), 2.25-2.41 (m, 2H), 2.45 (s, 3H), 6.94 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.20 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.42-7.51 (m, 2H), 7.60-7.61 (m, 2H), 7.90-7.93 (m, 2H), 7.98 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.1, 21.7, 38.8 (q, Jₐ = 29.0 Hz), 42.7, 46.4 (q, Jₐ = 1.5 Hz), 122.5, 123.2, 125.2 (q, Jₐ = 277.5 Hz), 125.8, 126.5, 127.7, 128.7, 128.8, 129.3, 129.4, 131.1, 131.8, 134.9, 135.5, 136.4, 145.0, 166.1, 170.9; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃):
δ -59.3 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 550.1 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{26}$H$_{24}$ClF$_3$N$_3$O$_3$S$^+$ requires: 550.1174, Found: 550.1168.
**Compound 2br**: 78 mg, 71%, A white solid, m.p. 272-274 °C; IR (EtOH): ν 3051, 1719, 1356, 1263, 1176, 1151, 1133, 1118, 1085, 750, 663 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.89 (s, 3H), 2.21-2.32 (m, 1H), 2.42-2.52 (m, 1H), 2.47 (s, 3H), 7.03 (d, 1H, J = 7.6 Hz), 7.20 (t, 1H, J = 7.6 Hz), 7.39 (d, 2H, J = 8.0 Hz), 7.46 (t, 1H, J = 8.0 Hz), 7.62-7.71 (m, 2H), 7.91-8.06 (m, 7H), 8.35 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.1, 21.7, 39.7 (q, J_C-F = 28.7 Hz), 42.8, 46.5, 121.1, 123.5, 124.0, 125.3 (q, J_C-F = 277.1 Hz), 126.0, 126.7, 127.5, 128.1, 128.7, 128.8, 129.3, 129.4, 129.68, 129.72, 131.7, 132.7, 135.6, 135.7, 136.3, 145.0, 167.3, 171.3; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.2 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 566.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₃₀H₂₇F₃N₃O₃S⁺ requires: 566.1720, Found: 566.1715.
**Compound 2bt**: 71 mg, 70%, A white solid, m.p. 184-186 °C; IR (EtOH): ν 2959, 2923, 2856, 1723, 1365, 1264, 1176, 1149, 1122, 1085, 663 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.86 (s, 3H), 2.13-2.35 (m, 2H), 2.45 (s, 3H), 6.97 (d, 1H, J = 7.6 Hz), 7.20 (td, 1H, J₁ = 7.6 Hz, J₂ = 0.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.44 (td, 1H, J₁ = 8.0 Hz, J₂ = 0.8 Hz), 7.55-7.57 (m, 1H), 7.63 (dd, 1H, J₁ = 8.4 Hz, J₂ = 0.8 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.00 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.8, 21.7, 39.0 (q, J_C-F = 29.0 Hz), 41.6, 46.5 (q, J_C-F = 1.5 Hz),
123.4, 125.4 (q, $J_{C-F} = 276.8$ Hz), 125.9, 126.1, 126.66, 126.68, 128.3, 128.8, 129.4, 129.6, 133.4, 135.6, 136.2, 145.1, 161.6, 171.5; $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$); $\delta$ -59.1 (t, 3F, $J = 10.9$ Hz); MS (ESI) $m/z$: 522.1 (M+NH$_4^+$, 100); HRMS (ESI) Calcd. for C$_{24}$H$_{23}$F$_3$N$_3$O$_3$S$_2^+$ requires: 522.1127, Found: 522.1121.
Compound 2bu: 78 mg, 77%, A white solid, m.p. 188-190 °C; IR (EtOH): ν 2956, 2923, 2854, 1721, 1367, 1262, 1174, 1147, 1124, 1086, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.86 (s, 3H), 2.17-2.27 (m, 1H), 2.28-2.37 (m, 1H), 2.45 (s, 3H), 7.01 (dd, 1H, J = 7.6 Hz, J₂ = 1.2 Hz), 7.21 (t, 1H, J = 7.6 Hz), 7.29-7.31 (m, 1H), 7.36 (d, 2H, J = 8.4 Hz), 7.45 (td, 1H, J₁ = 8.4 Hz, J₂ = 1.2 Hz), 7.70 (d, 1H, J = 3.6 Hz), 7.87-7.91 (m, 2H), 7.94 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.8, 21.7, 39.3 (q, J_C-F = 28.5 Hz), 43.1, 46.5, 123.5, 125.3 (q, J_C-F = 277.1 Hz), 126.2, 126.4, 126.7, 128.8, 128.9, 129.3, 129.4, 134.5, 135.3, 135.6, 136.1, 145.1, 160.2, 171.2; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) m/z: 522.1 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₂₄H₂₃F₃N₃O₃S₂⁺ requires: 522.1127, Found: 522.1122.
Compound 2bw: 37 mg, 33%, A white solid, m.p. 250-252 °C; IR (EtOH): ν 2973, 2929, 2887, 1718, 1374, 1173, 1087, 1046, 880, 660 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.09-2.21 (m, 1H), 2.49 (s, 3H), 2.88-3.00 (m, 1H), 7.02 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 7.08 (t, 1H, J = 7.6 Hz), 7.11-7.18 (m, 3H), 7.23 (td, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz), 7.29 (d, 2H, J = 7.6 Hz), 7.39 (d, 2H, J = 8.0 Hz), 7.60-7.64 (m, 3H), 7.66-7.70 (m, 1H), 7.96 (d, 2H, J = 8.4 Hz), 8.02 (d, 2H, J = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 21.8, 36.9 (q, J_C-F = 28.4 Hz), 42.9, 56.3 (q, J_C-F = 1.9 Hz), 123.2, 124.3, 125.0 (q, J_C-F = 277.1 Hz), 125.9, 127.9, 128.0, 128.3, 128.5, 128.8, 129.42, 129.43, 131.0, 133.9, 134.7, 135.0, 136.5, 145.1, 168.2, 170.3; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -57.9
(t, 3F, J = 10.9 Hz); MS (ESI) m/z: 578.2 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₃₁H₂₇F₃N₃O₃S⁺ requires: 578.1720, Found: 578.1714.
**Compound 2aa+3aa**: 85 mg, 88%, A white solid, m.p. 160-162 °C, dr = 1:0.46; IR (EtOH): ν 2973, 2923, 1596, 1488, 1450, 1352, 1263, 1163, 1119, 1089, 1063, 867, 762, 659 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.08 (s, 3H), 1.18 (s, 1.38H), 2.13-2.38 (m, 2.92H), 2.42 (s, 3H), 2.43 (s, 1.38H), 4.11 (d, 1H, J = 12.4 Hz), 4.17 (d, 0.46H, J = 12.4 Hz), 4.26 (d, 0.46H, J = 12.4 Hz), 4.34 (d, 1H, J = 12.4 Hz), 6.56 (d, 1.46H, J = 7.2 Hz), 6.84-6.90 (m, 1.46H), 7.12 (t, 1.46H, J = 7.6 Hz), 7.33-7.36 (m, 2.92H), 7.51-7.67 (m, 5.84H), 7.76 (d, 0.92H, J = 7.2 Hz), 7.84 (d, 4.92H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.1 (q, J_C-F = 1.5 Hz), 21.1 (q, J_C-F = 1.5 Hz), 21.47, 21.50, 35.6, 36.0, 37.0 (q, J_C-F = 28.9 Hz), 39.1 (q, J_C-F = 28.3 Hz), 45.0, 45.7, 55.1, 55.2, 118.2, 118.5, 123.2, 123.3, 123.4, 123.7, 126.2, 126.3 (q, J_C-F = 277.1 Hz), 126.87, 126.91, 127.1 (q, J_C-F = 277.0 Hz), 127.3, 127.4, 127.6, 127.75, 127.81, 129.42, 129.44, 129.5, 129.7, 129.9, 133.6, 133.7, 137.0, 137.2, 138.19, 144.0, 144.1, 165.0, 165.7; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -58.5 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 485.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄F₃N₂O₂S⁺ requires: 485.1505, Found: 485.1499.
Compound 2aa: 58 mg, 60%, A white solid, m.p. 172-174 °C; IR (EtOH): ν 2973, 2923, 1596, 1488, 1450, 1352, 1263, 1163, 1119, 1089, 1063, 867, 762, 659 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.07 (s, 3H), 2.16-2.29 (m, 1H), 2.34-2.44 (m, 1H), 2.43 (s, 3H), 4.09 (d, 1H, J = 12.4 Hz), 4.33 (d, 1H, J = 12.4 Hz), 6.56 (d, 1H, J = 7.6 Hz), 6.86 (t, 1H, J = 7.6 Hz), 7.12 (t, 1H, J = 7.6 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.57 (t, 2H, J = 7.6 Hz), 7.62-7.67 (m, 2H), 7.84 (d, 4H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 19.2, 21.5, 35.7 (q, J_C-F = 1.5 Hz), 39.1 (q, J_C-F = 28.0 Hz), 45.8, 55.2, 118.3, 123.3, 123.8, 126.3 (q, J_C-F = 277.1 Hz), 126.9, 127.4, 127.7, 127.8, 129.47, 129.49, 129.9, 133.6, 137.1, 138.3, 144.1, 165.8; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -58.5 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 485.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₄F₃N₂O₂S⁺ requires: 485.1505, Found: 485.1499.
**Compound 2bx**: 62 mg, 83%, A colorless oil; IR (EtOH): ν 2990, 2926, 2123, 1768, 1497, 1371, 1262, 1126, 753, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.80 (s, 3H), 2.67-2.93 (m, 2H), 7.15 (d, 1H, J = 7.6 Hz), 7.28 (td, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 7.34-7.41 (m, 4H), 7.48-7.51 (m, 2H), 7.61 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 22.8, 41.0 (q, J_C-F = 29.0 Hz), 62.3 (q, J_C-F = 2.2 Hz), 83.5, 94.4, 117.0, 121.8, 122.4, 124.8 (q, J_C-F = 276.9 Hz), 126.6, 128.5, 128.8, 129.6, 131.5, 133.5, 150.2, 168.8; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -60.7 (t, 3F, J = 10.2 Hz); MS (ESI) m/z: 391.1 (M+NH₄⁺, 100); HRMS (ESI) Calcd. for C₁₉H₁₈F₃N₄O₂⁺ requires: 391.1377, Found: 391.1374.
**Compound 2by** (major product): 54 mg, 81%, A colorless oil, dr = 20:1; IR (EtOH): v 2931, 1488, 1451, 1369, 1259, 1115, 1066, 761, 752, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.92 (s, 3H), 2.02-2.14 (m, 1H), 2.53-2.65 (m, 1H), 4.29 (d, 1H, J = 10.8 Hz), 4.37 (d, 1H, J = 10.8 Hz), 6.54 (dd, 1H, J₁ = 7.6 Hz, J₂ = 1.2 Hz), 6.80 (t, 1H, J = 7.6 Hz), 6.95 (d, 1H, J = 8.0 Hz), 7.17 (t, 1H, J = 8.0 Hz), 7.57-7.67 (m, 3H), 7.87 (d, 2H, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 17.7, 35.6, 38.7 (q, J_C-F = 26.8 Hz), 44.5, 72.4, 116.6, 121.3, 124.06, 124.09, 126.4 (q, J_C-F = 277.4 Hz), 126.9, 128.7, 129.4, 129.6, 133.5, 156.4, 165.5; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -59.2 (t, 3F, J = 11.7 Hz); MS (ESI) m/z: 332.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₁₉H₁₇F₃NO⁺ requires: 332.1257, Found: 332.1251.
Compound 5: 66 mg, 78%, dr = 2:1. This is a reported compound by Liang’s group and spectroscopic data is consistent with reported literature.\textsuperscript{[2c]}
\[ \text{dr} = 2:1 \]
General procedure for diazidation of 1aa and 1bl

1aa or 1bl (0.2 mmol, 1.0 equiv), Zhdankin reagent (0.30 mmol, 1.5 equiv), CuTc (0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then TMSN$_3$ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 70 °C oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 5 / 1) to afford the products 7aa or 7bl in good yield.
Spectroscopic data for product 7aa

*Note:* The spectroscopic data for product 7bl is consistent with those reported in the literature of Wan’s work.\(^{[1a]}\) However, our reaction for the formation 7bl could improve the yield to 87%.

**Compound 7aa:** 62 mg, 68%, A white solid, m.p. 191-193 °C; IR (EtOH): \(\nu\) 2976, 2934, 2105, 1714, 1455, 1367, 1252, 1170, 1086, 660 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta\) 1.42 (s, 3H), 2.40 (s, 3H), 3.48 (d, 1H, \(J = 13.2\) Hz), 3.98 (d, 1H, \(J = 16.8\) Hz), 4.18 (d, 1H, \(J = 13.2\) Hz), 4.21 (d, 1H, \(J = 16.8\) Hz), 6.91 (t, 1H, \(J = 7.6\) Hz), 7.15 (d, 2H, \(J = 8.0\) Hz), 7.28-7.32 (m, 4H), 7.39 (td, 1H, \(J_1 = 7.6\) Hz, \(J_2 = 0.8\) Hz), 7.45-7.48 (m, 3H), 7.79 (d, 2H, \(J = 8.4\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), TMS): \(\delta\) 19.6, 21.5, 51.0, 53.4, 68.6, 78.9, 119.5, 123.8, 124.0, 126.9, 128.0, 128.6, 129.1, 129.9, 130.0, 133.9, 137.4, 137.9, 144.1, 171.3; MS (ESI) \(m/z\): 475.2 (M+NH\(_4^+\), 100); HRMS (ESI) Calcd. for C\(_{25}\)H\(_{29}\)N\(_6\)O\(_2\)S\(^+\) requires: 475.1911, Found: 475.1908.
General procedure for the synthesis of products 8b by NaBH₄-reduction

To a stirred solution of 2b (0.10 mmol, 1.0 equiv) in mixed solvents of MeOH and CH₂Cl₂ (v/v = 1:1, 2.0 mL) at 0 °C was added NaBH₄ (0.50 mmol, 5.0 equiv) in one portion. Then the reaction mixture was stirred at room temperature for 15 min. Afterwards, the reaction was quenched by H₂O and the mixture was extracted with CH₂Cl₂ (3 x 5 mL). The combined organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 8b in good yields ranging from 70% to 89%.
Spectroscopic data for products 8b

**Compound 8ba**: 45 mg, 89%, A white solid, m.p. 201-203 °C; IR (EtOH): ν 2987, 2951, 2873, 1479, 1460, 1364, 1258, 1168, 1107, 1069, 751, 662 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.80 (s, 2H), 0.86 (s, 3H), 2.25-2.35 (m, 2H), 2.39 (s, 3H), 2.80 (d, 1H, J = 10.0 Hz), 4.02 (d, 1H, J = 10.0 Hz), 7.03 (t, 1H, J = 7.6 Hz), 7.22-7.27 (m, 4H), 7.32-7.38 (m, 3H), 7.48-7.52 (m, 1H), 7.70 (d, 1H, J = 8.4 Hz), 7.74 (d, 1H, J = 8.0 Hz), 7.93 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.1, 21.5, 35.6 (q, J_C-F = 26.6 Hz), 46.6, 72.9, 78.0, 109.8, 112.2, 122.9, 124.7, 126.8, 126.9, 127.0 (q, J_C-F = 277.1 Hz), 127.9, 128.6, 128.7, 128.9, 129.3, 130.1, 137.0, 139.8, 142.5, 143.9; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -58.2 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 503.2 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₆F₃N₂O₃S⁺ requires: 503.1611, Found: 503.1604.
Compound 8bf: 43 mg, 81%, A white solid, m.p. 222-224 °C; IR (EtOH): ν 2956, 2924, 2854, 1471, 1365, 1258, 1167, 1098, 1070, 814, 663 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.79 (s, 2H), 0.88 (s, 3H), 2.23-2.35 (m, 2H), 2.41 (s, 3H), 2.76 (d, 1H, J = 10.0 Hz), 4.02 (d, 1H, J = 10.0 Hz), 7.18-7.21 (m, 2H), 7.26-7.32 (m, 3H), 7.38-7.40 (m, 2H), 7.49-7.53 (m, 1H), 7.66 (d, 1H, J = 8.8 Hz), 7.71 (dd, 1H, J₁ = 8.8 Hz, J₂ = 1.2 Hz), 7.90 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.2, 21.6, 35.6 (q, J C-F = 27.5 Hz), 46.6, 73.0, 77.9, 110.1, 113.3, 124.7, 126.7, 126.89 (q, J C-F = 277.0 Hz), 126.90, 127.9, 128.1, 128.8, 128.9, 129.1, 129.4, 130.2, 131.2, 136.8, 139.4, 141.2, 144.2; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI)
$m/z$ 537.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₅ClF₃N₂O₃S⁺ requires: 537.1221, Found: 537.1209.
**Compound 8bh**: 40 mg, 75%, A white solid, m.p. 210-212 °C; IR (EtOH): ν 2948, 2831, 1486, 1363, 1227, 1166, 1025, 814, 662 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.88 (s, 5H), 2.25-2.37 (m, 2H), 2.39 (s, 3H), 2.77 (d, 1H, J = 10.0 Hz), 3.77 (s, 3H), 3.98 (d, 1H, J = 10.0 Hz), 6.78 (d, 1H, J = 2.4 Hz), 6.90 (dd, 1H, J₁ = 8.8 Hz, J₂ = 2.4 Hz), 7.24-7.26 (m, 3H), 7.36-7.38 (m, 2H), 7.48-7.52 (m, 1H), 7.65 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 8.0 Hz), 7.91 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.2, 21.5, 35.7 (q, J_C-F = 26.6 Hz), 46.6, 55.7, 73.1, 78.1, 110.0, 112.4, 113.1, 115.5, 124.7, 126.9, 127.0 (q, J_C-F = 277.0 Hz), 127.8, 128.6, 128.8, 128.9, 129.2, 130.6, 136.2, 137.2, 139.9, 143.8, 155.8; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 533.2 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₇H₂₈F₃N₂O₄S⁺ requires: 533.1716, Found: 533.1710.
**Compound 8bo**: 43 mg, 80%, A white solid, m.p. 212-214 °C; IR (EtOH): ν 2945, 2831, 1487, 1364, 1228, 1164, 1025, 816, 667 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.87 (s, 5H), 2.26-2.42 (m, 2H), 2.39 (s, 3H), 2.78 (d, J = 10.0 Hz, 3H), 3.83 (s, 3H), 3.99 (d, J = 10.0 Hz, 1H), 6.90 (dd, J₁ = 8.4 Hz, J₂ = 2.4 Hz, 1H), 6.99-7.05 (m, 2H), 7.14 (dd, J₁ = 8.4 Hz, J₂ = 2.4 Hz, 1H), 7.23-7.26 (m, 3H), 7.33 (td, J₁ = 8.4 Hz, J₂ = 1.2 Hz, 1H), 7.65 (dd, J₁ = 8.4 Hz, J₂ = 2.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.1, 21.5, 35.6 (q, 1H), 1364, 1228, 1164, 1025, 816, 667 cm⁻¹.
$J_{\text{C-F}} = 26.6 \text{ Hz}$, 46.6, 55.3, 72.8, 77.8, 109.9, 112.3, 113.7, 114.7, 122.9, 126.1, 126.9, 127.1 (q, $J_{\text{C-F}} = 277.8 \text{ Hz}$), 128.0, 128.1, 129.3, 129.4, 130.1, 131.9, 137.1, 142.5, 143.9, 159.7; $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -58.6 (t, 3F, $J = 11.3 \text{ Hz}$); MS (ESI) $m/z$: 533.2 (M+H$^+$, 100); HRMS (ESI) Calcd. for C$_{27}$H$_{28}$F$_3$N$_2$O$_4$S requires: 533.1716, Found: 533.1712.
**Compound 8bt**: 42 mg, 83%, A white solid, m.p. 195-197 °C; IR (EtOH): ν 2956, 2929, 2870, 1597, 1480, 1363, 1259, 1171, 1089, 1073, 756, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.88 (s, 3H), 0.96 (s, 2H), 2.32-2.45 (m, 2H), 2.39 (s, 3H), 2.77 (d, 1H, J = 10.0 Hz), 3.99 (d, 1H, J = 10.0 Hz), 6.91-7.05 (m, 2H), 7.23-7.26 (m, 3H), 7.30-7.52 (m, 3H), 7.66 (d, 1H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.0, 21.5, 35.6 (q, J_CF = 26.6 Hz), 46.8, 72.9, 108.3, 112.4, 122.2, 122.9, 126.0, 126.9, 127.01 (q, J_CF = 277.1 Hz), 127.02, 127.9, 129.1, 129.3, 130.1, 136.9, 141.8, 142.1, 144.0; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 509.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C_{24}H_{24}F_{3}N_{2}O_{3}S_{2}⁺ requires: 509.1175, Found: 509.1168.
**Compound 8bu**: 43 mg, 84%, A white solid, m.p. 188-190 °C; IR (EtOH): ν 2954, 2924, 2856, 1597, 1459, 1364, 1260, 1167, 1106, 1089, 1069, 760, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 0.86 (s, 3H), 1.03 (s, 2H), 2.35-2.42 (m, 1H), 2.39 (s, 3H), 2.50-2.62 (m, 1H), 2.70 (d, 1H, J = 10.0 Hz), 3.98 (d, 1H, J = 10.0 Hz), 7.02-7.08 (m, 3H), 7.22-7.27 (m, 3H), 7.31-7.38 (m, 2H), 7.70 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 18.2, 21.5, 35.5 (q, J_C-F = 26.6 Hz), 46.7, 73.2, 78.3, 108.6, 112.5, 123.1, 125.8, 126.3, 127.00 (q, J_C-F = 277.0 Hz), 127.01, 127.8, 128.0, 128.8, 129.3, 130.1, 136.8, 141.9, 144.1; ¹⁹F NMR (376 MHz, CDCl₃, CFCl₃): δ -170.0 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 509.1 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₄H₂₄F₃N₂O₃S₂⁺ requires: 509.1175, Found: 509.1169.
General procedure for the scalable synthesis and the synthesis of products 9ba, 10ba, and 11ba

![Scheme S2 Scalable synthesis of 2ba and 2bf.](image)

1ba or 1bf (3.0 mmol, 1.0 equiv), Togni reagent I (4.5 mmol, 1.5 equiv), CuTc (0.06 mmol, 0.02 equiv) were dissolved in MeCN (2.0 mL), then TMSN₃ (6.0 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 70 °C oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products 2ba and 2bf in 68% and 77% yields, respectively.

![Scheme S3 Alcoholysis and LiAlH₄-reduction](image)

Alcoholysis: The solution of 2ba (0.2 mmol, 1.0 equiv) and NaOH fragment (1.0 mmol, 5.0 equiv) in mixed solvents of MeOH and CH₂Cl₂ (v/v = 1:1, 4.0 mL) was stirred at room temperature for 6 h.
Upon completion, the reaction was quenched by HCl solution (1N) until the pH value of the solution was about 7. Then the solution was extracted with CH$_2$Cl$_2$ (3 x 5 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 9ba in 85% yield.

LiAlH$_4$-reduction: To a solution of 2ba (0.20 mmol, 1.0 equiv) in dry THF (4.0 mL) was added LiAlH$_4$ (1.0 mmol, 5.0 equiv) in one portion, and the resulting solution was stirred at room temperature for 2 h. Upon completion, the reaction was quenched by saturated NH$_4$Cl solution. Then the solution was extracted with CH$_2$Cl$_2$ (3 x 5 mL). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 10ba and 11ba in 94% yield and 1:1 dr value.
Spectroscopic data for products 9ba, 10ba, and 11ba

**Compound 9ba**: 90 mg, 85%, A white solid, m.p. 230-232 °C; IR (EtOH): ν 2956, 2923, 2851, 1748, 1460, 1370, 1268, 1170, 1149, 1093, 702, 662 cm⁻¹; ^1^H NMR (400 MHz, CDCl_3, TMS): δ 0.36 (s, 1H), 1.48 (s, 3H), 1.77-1.95 (m, 2H), 2.39 (s, 3H), 3.54 (s, 3H), 7.06 (t, 1H, J = 8.0 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.29-7.38 (m, 3H), 7.41-7.50 (m, 3H), 7.54 (d, 2H, J = 8.4 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.97 (d, 1H, J = 8.4 Hz); ^13^C NMR (100 MHz, CDCl_3, TMS): δ 18.9, 21.6, 39.0 (q, J_C-F = 28.1 Hz), 46.3, 52.6, 54.7, 68.5, 117.4, 123.4, 124.2, 125.8 (q, J_C-F = 276.3 Hz), 127.3, 128.0, 128.2, 128.6, 128.8, 129.9, 131.0, 131.1, 134.5, 135.3, 141.7, 144.8, 173.7; ^19^F NMR (376 MHz, CDCl_3, CFCl_3): δ -59.9 (t, 3F, J = 11.3 Hz); MS (ESI) m/z: 531.2 (M+H⁺, 100); HRMS (ESI) Calcd. for C_{27}H_{26}F_{3}N_{2}O_{4}S⁺ requires: 531.1560, Found: 531.1553.
Compound 10ba: 47 mg, 47%, A white solid, m.p. 185-187 °C; IR (EtOH): ν 2954, 2923, 2887, 1497, 1258, 1155, 1108, 1090, 1062, 933, 758, 660 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.01 (s, 3H), 1.50 (d, 1H, J = 10.0 Hz), 1.63-1.76 (m, 1H), 2.11-2.23 (m, 1H), 2.34 (s, 3H), 3.10 (d, 1H, J = 11.6 Hz), 3.18 (d, 1H, J = 10.0 Hz), 3.47 (d, 1H, J = 11.6 Hz), 3.48 (s, 1H), 7.01 (t, 1H, J = 7.6 Hz), 7.17-7.21 (m, 3H), 7.28 (d, 2H, J = 7.6 Hz), 7.35 (t, 2H, J = 7.2 Hz), 7.46 (d, 1H, J = 8.4 Hz), 7.79 (d, 2H, J = 6.4 Hz), 7.86-7.90 (m, 2H), 10.15 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 20.0, 21.5, 35.8 (q, J_C-F = 26.0 Hz), 41.9, 46.0, 49.7, 65.4, 117.4, 122.9, 127.1 (q, J_C-F = 277.4 Hz), 127.2, 127.3, 128.3, 128.7, 129.7, 131.2, 132.5, 136.98, 137.04, 137.1, 143.9; ¹⁹F NMR (376 MHz,
CDCl₃, CFCl₃): δ -58.4 (t, 3F, J = 12.4 Hz); MS (ESI) m/z: 505.2 (M+H⁺, 100); HRMS (ESI) Calcd. for C₂₆H₂₈F₃N₂O₃S⁺ requires: 505.1767, Found: 505.1762.
Compound **11ba**: 47 mg, 47%, A white solid, m.p. 187-189 °C; IR (EtOH): $\nu$ 2929, 2851, 1497, 1441, 1328, 1257, 1156, 1075, 1021, 812, 746, 699, 658 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 1.28 (s, 3H), 2.17-2.31 (m, 2H), 2.42 (s, 3H), 2.61 (s, 1H), 2.83 (s, 1H), 3.54 (d, 1H, $J$ = 11.2 Hz), 3.59 (s, 1H), 3.74 (d, 1H, $J$ = 11.2 Hz), 6.39 (d, 1H, $J$ = 7.2 Hz), 6.53 (t, 1H, $J$ = 7.2 Hz), 6.62 (brs, 2H), 6.86-6.89 (m, 2H), 6.98-7.01 (m, 2H), 7.32 (d, 2H, $J$ = 8.0 Hz), 7.41 (d, 1H, $J$ = 8.0 Hz), 7.96 (d, 2H, $J$ = 8.0 Hz), 10.18 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, TMS): $\delta$ 17.2, 21.5, 37.5 (q, $J_{C-F}$ = 27.1 Hz), 40.7, 41.1, 51.5, 67.6, 117.8, 121.9, 126.6, 126.7 (q, $J_{C-F}$ = 277.3 Hz), 126.9, 127.4, 127.6, 128.0, 129.6, 133.2, 136.6, 137.1, 139.7, 143.8; $^{19}$F NMR (376 MHz, CDCl$_3$, CFCl$_3$): $\delta$ -57.7 (t, 3F, $J$ = 11.3 Hz); MS (ESI) $m/z$: 505.2 (M+H$^+$, 100); HRMS (ESI) Calcd. for C$_{26}$H$_{28}$F$_3$N$_2$O$_3$S$^+$ requires: 505.1767, Found: 505.1762.
The crystal data of 2aa, 2ba, 5, 7aa, 8bf, 9ba, 10ba and 11ba

The crystal data of 2aa have been deposited in CCDC with number 1494648. Empirical Formula: C_{26}H_{23}F_{3}N_{2}O_{2}S; Formula Weight: 484.52; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.100 mm^{3}; Crystal System: Monoclinic; Lattice Parameters: a = 12.394(3)Å, b = 26.081(7)Å, c = 8.658(3)Å, \( \alpha = 90^\circ \), \( \beta = 122.750(5)^\circ \), \( \gamma = 90^\circ \), V = 2353.8(11)Å^{3}; Space group: C c; Z = 4; D_{calc} = 1.367 g/cm^{3}; F_{000} = 1008; Final R indices [I>2\sigma(I)] R1 = 0.0455, wR2 = 0.1010.
The crystal data of 2ba have been deposited in CCDC with number 1535602. Empirical Formula: C_{26}H_{21}F_{3}N_{2}O_{3}S; Formula Weight: 498.51; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.170 x 0.120 mm³; Crystal System: Monoclinic; Lattice Parameters: a = 8.8511(15) Å, b = 17.643(3) Å, c = 15.334(3) Å, α = 90°, β = 93.701(4)°, γ = 90°, V = 2389.5(7) Å³; Space group: P2₁/n; Z = 4; D_{calc} = 1.386 g/cm³; F_{000} = 1032; Final R indices [I>2σ(I)] R1 = 0.0594, wR2 = 0.1263.
The crystal data of 5 have been deposited in CCDC with number 1501511. Empirical Formula: C_{21}H_{21}F_{3}N_{2}O_{2}S; Formula Weight: 422.46; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.110 mm\(^3\); Crystal System: Triclinic; Lattice Parameters: a = 10.439(4) Å, b = 10.668(4) Å, c = 11.232(4) Å, \(\alpha = 72.878(8)^\circ\), \(\beta = 74.118(8)^\circ\), \(\gamma = 65.951(7)^\circ\), V = 1074.5(7) Å\(^3\); Space group: P -1; Z = 2; \(D_{calc} = 1.306\) g/cm\(^3\); \(F_{000} = 440\); Final R indices \([I>2\sigma(I)]\) R1 = 0.0707, wR2 = 0.2067.
The crystal data of 7aa have been deposited in CCDC with number 1535603. Empirical Formula: C25H23N5O2S; Formula Weight: 457.54; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.180 x 0.120 mm³; Crystal System: Orthorhombic; Lattice Parameters: a = 13.9067(15)Å, b = 18.439(2)Å, c = 8.8970(10)Å, α = 90°, β = 90°, γ = 90°, V = 2281.4(4) Å³; Space group: P n a 21; Z = 4; D_{calc} = 1.332 g/cm³; F_{000} = 960; Final R indices [I>2sigma(I)] R1 = 0.0445, wR2 = 0.0981.
The crystal data of 8bf have been deposited in CCDC with number 1549550. Empirical Formula: C_{26}H_{24}ClF_{3}N_{2}O_{3}S; Formula Weight: 536.98; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.170 x 0.130 mm³; Crystal System: Triclinic; Lattice Parameters: a = 10.4716(15)Å, b = 10.9609(17)Å, c = 11.0858(17)Å, α = 80.892(3)°, β = 71.645(3)°, γ = 82.468(3)°, V = 1188.0(3) Å³; Space group: P -1; Z = 2; D_{calc} = 1.501 g/cm³; F_{000} = 556; Final R indices [I>2sigma(I)] R1 = 0.0477, wR2 = 0.1164.
The crystal data of 9ba have been deposited in CCDC with number 1553802. Empirical Formula: C_{27}H_{25}F_{3}N_{2}O_{4}S; Formula Weight: 530.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.1898(16) Å, b = 21.424(3) Å, c = 11.0005(16) Å, α = 90°, β = 105.012(3)°, γ = 90°, V = 2547.2(6) Å^3; Space group: P 21/c; Z = 4; D_{calc} = 1.383 g/cm^3; F_{000} = 1104; Final R indices [I>2sigma(I)] R1 = 0.0492, wR2 = 0.1222.
The crystal data of **10ba** have been deposited in CCDC with number 1552058. Empirical Formula: C_{26}H_{27}F_{3}N_{2}O_{3}S; Formula Weight: 504.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.120 mm\(^3\); Crystal System: Monoclinic; Lattice Parameters: a = 11.6099(13) Å, b = 10.1840(11) Å, c = 20.888(2) Å, α = 90\(^o\), β = 95.677(2)\(^o\), γ = 90\(^o\), V = 2457.6(5) Å\(^3\); Space group: P 21/n; Z = 4; D\(_{calc}\) = 1.364 g/cm\(^3\); F\(_{000}\) = 1056; Final R indices [I>2\(\sigma(I)\)] R1 = 0.0467, wR2 = 0.1187.
The crystal data of 11ba have been deposited in CCDC with number 1554196. Empirical Formula: C_{26}H_{27}F_{3}N_{2}O_{3}S; Formula Weight: 504.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.130 mm³; Crystal System: Monoclinic; Lattice Parameters: a = 13.7278(17) Å, b = 14.2768(18) Å, c = 14.0025(18) Å, \( \alpha = 90^\circ \), \( \beta = 118.039(3)^\circ \), \( \gamma = 90^\circ \), V = 2422.2(5) Å³; Space group: P 21/n; Z = 4; \( D_{calc} = 1.384 \) g/cm³; \( F_{000} = 1056 \); Final R indices [I>2\sigma(I)] R1 = 0.0585, wR2 = 0.1315.
Reference

