

Supporting Information to

**Copper-Catalyzed Trifluoromethylation of Alkenes with Redox-Neutral
Remote Amidation of Aldehydes**

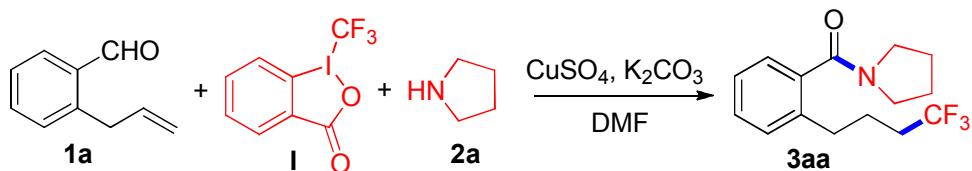
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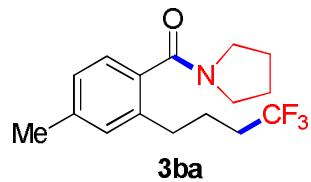
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General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with ESI source. Column chromatography was performed using silica gel (300–400 mesh).

General Procedure for the Cu-Catalyzed Trifluoromethylation of Alkenes with Redox-Neutral Remote Amidation of Aldehydes:

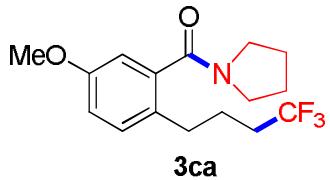


To a solution of **1a** (36.5 mg, 0.25 mmol) and **2a** (26.7 mg, 0.375 mmol) in 2 mL of DMF was added **I** (118.5 mg, 0.375 mmol), CuSO_4 (4.0 mg, 0.025 mmol) and K_2CO_3 (51.8 mg, 0.375 mmol) under a nitrogen atmosphere. After stirring at room temperature for 10 h, the reaction mixture was quenched with water, extracted with EtOAc , washed with brine, dried over anhydrous Na_2SO_4 , and concentrated. Column chromatography on silica gel ($\text{EtOAc}/\text{petroleum ether} = 1:3$) gave 57 mg (yield: 80%) of **3aa** as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.18 (m, 4H), 3.65 (t, $J = 7.0$ Hz, 2H), 3.15 (t, $J = 6.7$ Hz, 2H), 2.72 (t, $J = 7.7$ Hz, 2H), 2.18–2.03 (m, 2H), 2.01–1.81 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.5, 137.4, 137.0, 131.2, 129.0, 127.1 (q, $J = 274.9$ Hz), 126.4, 126.1, 48.7, 45.4, 33.2 (q, $J = 28.3$ Hz), 31.7, 25.9, 24.5, 23.0 (q, $J = 2.9$ Hz); ^{19}F NMR (375 MHz, CDCl_3) δ -66.2; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{NO}$ ($M + \text{H}$) $^+$ 286.1419, found 286.1417.

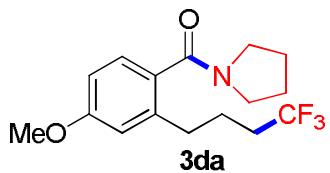


Compound 3ba: 61 mg, 81% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.14–7.08 (m, 1H), 7.06–7.00 (m, 2H), 3.64 (t, $J = 7.1$ Hz, 2H), 3.16 (t, $J = 6.7$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 2.34

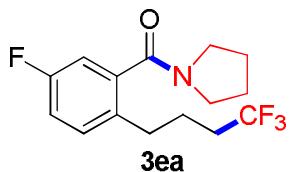
(s, 3H), 2.15–2.05 (m, 2H), 1.99–1.92 (m, 2H), 1.88–1.81 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.7, 138.9, 137.2, 134.6, 130.2, 127.1 (q, $J = 274.9$ Hz), 127.0, 126.1, 48.8, 45.4, 33.3 (q, $J = 28.4$ Hz), 31.8, 26.0, 24.6, 23.1 (q, $J = 2.8$ Hz), 21.3; ^{19}F NMR (565 MHz, CDCl_3) δ –66.2; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{NO} (\text{M} + \text{H})^+$ 300.1575, found 300.1571.



Compound 3ca: 59 mg, 75% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.14 (d, $J = 8.5$ Hz, 1H), 6.86 (dd, $J = 8.5, 2.7$ Hz, 1H), 6.76 (d, $J = 2.7$ Hz, 1H), 3.79 (s, 3H), 3.64 (t, $J = 7.1$ Hz, 2H), 3.16 (t, $J = 6.7$ Hz, 2H), 2.64 (t, $J = 7.7$ Hz, 2H), 2.12–2.03 (m, 2H), 2.00–1.93 (m, 2H), 1.90–1.81 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.2, 158.0, 138.4, 130.7, 128.8, 127.1 (q, $J = 276.5$ Hz), 114.7, 111.4, 55.4, 48.7, 45.4, 33.2 (q, $J = 28.4$ Hz), 30.9, 25.9, 24.5, 23.2 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{NO}_2 (\text{M} + \text{H})^+$ 316.1524, found 316.1522.

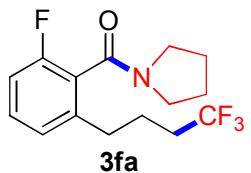


Compound 3da: 66 mg, 84% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.20–7.14 (m, 1H), 6.79–6.73 (m, 2H), 3.82 (s, 3H), 3.63 (t, $J = 7.0$ Hz, 2H), 3.17 (t, $J = 6.7$ Hz, 2H), 2.72 (t, $J = 7.7$ Hz, 2H), 2.15–2.05 (m, 2H), 1.98–1.94 (m, 2H), 1.88–1.82 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.5, 159.9, 139.4, 130.0, 127.7, 127.1 (q, $J = 276.6$ Hz), 115.2, 111.3, 55.2, 48.9, 45.4, 33.2 (q, $J = 28.4$ Hz), 32.0, 26.0, 24.5, 23.0 (q, $J = 2.9$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ –66.2; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{NO}_2 (\text{M} + \text{H})^+$ 316.1524, found 316.1518.

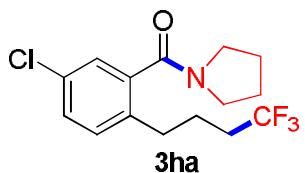


Compound 3ea: 64 mg, 85% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.21 (dd, $J = 8.5, 5.3$ Hz, 1H), 7.06–7.00 (m, 1H), 6.94 (dd, $J = 8.5, 2.7$ Hz, 1H), 3.64 (t, $J = 7.1$ Hz, 2H), 3.16 (t, $J = 6.7$ Hz, 2H), 2.68 (t, $J = 7.8$ Hz, 2H), 2.15–2.04 (m, 2H), 2.01–1.93 (m, 2H), 1.91–1.81 (m, 4H);

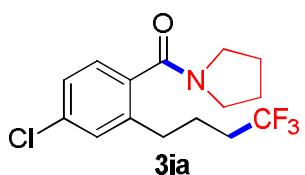
¹³C NMR (151 MHz, CDCl₃) δ 168.0 (d, *J* = 2.1 Hz), 161.0 (d, *J* = 246.9 Hz), 138.9 (d, *J* = 6.4 Hz), 132.9 (d, *J* = 3.5 Hz), 131.2 (d, *J* = 7.8 Hz), 127.0 (q, *J* = 276.2 Hz), 116.0 (d, *J* = 21.0 Hz), 113.1 (d, *J* = 22.6 Hz), 48.7, 45.5, 33.2 (q, *J* = 28.6 Hz), 31.1, 25.9, 24.5, 23.2 (q, *J* = 3.0 Hz); ¹⁹F NMR (565 MHz, CDCl₃) δ -66.2, -115.7; HRMS (ESI) calcd for C₁₅H₁₈F₄NO (M + H)⁺ 304.1325, found 304.1315.



Compound 3fa: 45 mg, 59% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.32–7.27 (m, 1H), 7.06–7.01 (m, 1H), 7.00–6.95 (m 1H), 3.76–3.69 (m, 1H), 3.66–3.59 (m, 1H), 3.34–3.27 (m, 1H), 3.11–3.05 (m, 1H), 2.88–2.81 (m, 1H), 2.62–2.53 (m, 1H), 2.17–2.05 (m, 2H), 2.02–1.82 (m, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 164.4 (d, *J* = 1.1 Hz), 158.3 (d, *J* = 245.8 Hz), 139.9 (d, *J* = 3.7 Hz), 130.2 (d, *J* = 8.5 Hz), 127.0 (q, *J* = 276.6 Hz), 125.6 (d, *J* = 19.2 Hz), 125.0 (d, *J* = 2.9 Hz), 113.6 (d, *J* = 21.8 Hz), 47.5 (d, *J* = 2.1 Hz), 45.4, 33.2 (q, *J* = 28.6 Hz), 31.7 (d, *J* = 2.0 Hz), 25.7, 24.5, 22.9 (q, *J* = 2.8 Hz); ¹⁹F NMR (565 MHz, CDCl₃) δ -66.2, -116.8; HRMS (ESI) calcd for C₁₅H₁₈F₄NO (M + H)⁺ 304.1325, found 304.1316.

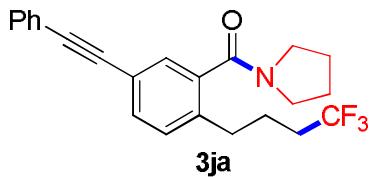


Compound 3ha: 62 mg, 78% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.29 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 3.64 (t, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 6.7 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.14–2.05 (m, 2H), 2.01–1.94 (m, 2H), 1.90–1.83 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 167.8, 138.9, 135.7, 132.2, 131.0, 129.1, 127.0 (q, *J* = 276.6 Hz), 126.1, 48.8, 45.5, 33.1 (q, *J* = 28.6 Hz), 31.2, 25.9, 24.5, 22.3 (q, *J* = 2.8 Hz); ¹⁹F NMR (565 MHz, CDCl₃) δ -66.1; HRMS (ESI) calcd for C₁₅H₁₈ClF₃NO (M + H)⁺ 320.1029, found 320.1023.

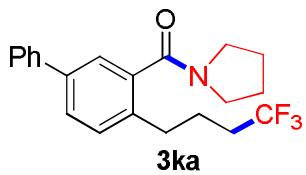


Compound 3ia: 59 mg, 74% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.26–7.10 (m, 3H), S4

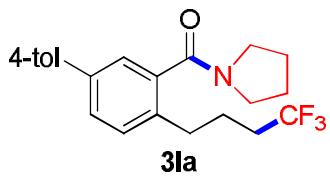
3.64 (t, $J = 7.0$ Hz, 2H), 3.14 (t, $J = 6.7$ Hz, 2H), 2.70 (t, $J = 7.8$ Hz, 2H), 2.16–2.06 (m, 2H), 2.00–1.93 (m, 2H), 1.91–1.83 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 168.5, 139.5, 135.8, 134.8, 129.6, 127.6, 127.0 (q, $J = 276.4$ Hz), 126.7, 48.8, 45.5, 33.2 (q, $J = 28.6$ Hz), 31.7, 26.0, 24.5, 22.9 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{ClF}_3\text{NO}$ ($M + \text{H}$) $^+$ 320.1029, found 320.1015.



Compound 3ja: 58 mg, 60% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.57–7.46 (m, 3H), 7.43–7.33 (m, 4H), 7.25–7.20 (m, 1H), 3.66 (t, $J = 7.0$ Hz, 2H), 3.21 (t, $J = 6.6$ Hz, 2H), 2.73 (t, $J = 7.6$ Hz, 2H), 2.16–2.07 (m, 2H), 2.01–1.95 (m, 2H), 1.92–1.83 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 168.5, 137.7, 137.5, 132.1, 131.6, 129.7, 129.3, 128.4, 128.4, 127.1 (q, $J = 276.6$ Hz), 123.0, 121.6, 89.9, 88.4, 48.9, 45.5, 33.2 (q, $J = 28.6$ Hz), 31.7, 26.0, 24.5, 22.9 (q, $J = 2.9$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{F}_3\text{NO}$ ($M + \text{H}$) $^+$ 386.1732, found 386.1720.

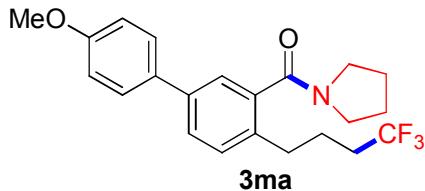


Compound 3ka: 65 mg, 72% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.60–7.51 (m, 3H), 7.49–7.41 (m, 3H), 7.38–7.29 (m, 2H), 3.68 (t, $J = 7.1$ Hz, 2H), 3.21 (t, $J = 6.7$ Hz, 2H), 2.76 (t, $J = 7.7$ Hz, 2H), 2.19–2.09 (m, 2H), 2.02–1.95 (m, 2H), 1.94–1.83 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 140.1, 139.5, 137.9, 136.1, 130.0, 128.8, 127.7, 127.5, 127.1 (q, $J = 276.6$ Hz), 126.9, 124.8, 48.9, 45.5, 33.3 (q, $J = 28.5$ Hz), 31.5, 26.0, 24.5, 23.1 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{F}_3\text{NO}$ ($M + \text{H}$) $^+$ 362.1732, found 362.1718.

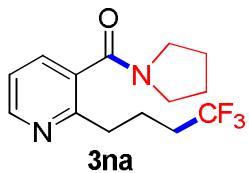


Compound 3la: 69 mg, 74% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.56–7.50 (m, 1H), 7.49–7.42 (m, 3H), 7.30–7.26 (m, 3H), 3.67 (t, $J = 7.1$ Hz, 2H), 3.20 (t, $J = 6.7$ Hz, 2H), 2.75 (t, J

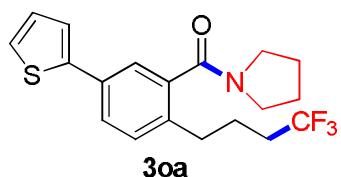
= 7.6 Hz, 2H), 2.39 (s, 3H), 2.18–2.09 (m, 2H), 2.00–1.95 (m, 2H), 1.92–1.84 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 139.3, 137.9, 137.3, 137.2, 135.7, 130.0, 129.5, 127.5, 127.1 (q, J = 276.6 Hz), 126.7, 124.5, 48.9, 45.4, 33.3 (q, J = 28.4 Hz), 31.5, 26.0, 24.5, 21.0, 23.1 (q, J = 2.8 Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{F}_3\text{NO}$ ($\text{M} + \text{H}$) $^+$ 376.1888, found 376.1858.



Compound 3ma: 62 mg, 63% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.54–7.47 (m, 3H), 7.45–7.39 (m, 1H), 7.31–7.27 (m, 1H), 7.01–6.94 (m, 2H), 3.85 (s, 3H), 3.67 (t, J = 7.1 Hz, 2H), 3.20 (t, J = 6.7 Hz, 2H), 2.74 (t, J = 7.5 Hz, 2H), 2.17–2.08 (m, 2H), 2.01–1.95 (m, 2H), 1.93–1.83 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.5, 159.2, 139.0, 137.9, 135.3, 132.5, 130.0, 127.9, 127.2, 127.1 (q, J = 276.6 Hz), 124.3, 114.2, 55.3, 48.9, 45.5, 33.2 (q, J = 28.3 Hz), 31.5, 26.0, 24.5, 23.0 (q, J = 2.8 Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{25}\text{F}_3\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 392.1837, found 392.1815.

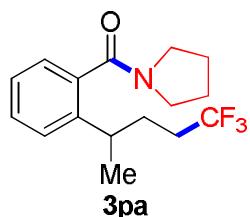


Compound 3na: 34 mg, 48% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.64–8.54 (m, 1H), 7.61–7.52 (m, 1H), 7.25–7.15 (m, 1H), 3.67 (t, J = 7.0 Hz, 2H), 3.15 (t, J = 6.7 Hz, 2H), 2.88 (t, J = 7.6 Hz, 2H), 2.22–2.12 (m, 2H), 2.10–1.96 (m, 4H), 1.94–1.86 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 167.7, 156.6, 149.7, 133.9, 132.8, 127.1 (q, J = 276.7 Hz), 121.2, 48.7, 45.6, 34.1, 33.3 (q, J = 28.6 Hz), 26.0, 24.5, 21.2 (q, J = 3.0 Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.2; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ ($\text{M} + \text{H}$) $^+$ 287.1371, found 287.1365.

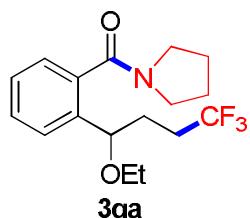


Compound 3oa: 46 mg, 50% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.59–7.53 (m, 1H), 7.49–7.43 (m, 1H), 7.30–7.24 (m, 3H), 7.11–7.04 (m, 1H), 3.68 (t, J = 7.1 Hz, 2H), 3.20 (t, J = 6.7 Hz, 2H)

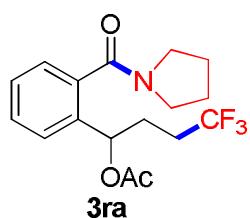
Hz, 2H), 2.72 (t, J = 7.7 Hz, 2H), 2.17–2.06 (m, 2H), 2.02–1.95 (m, 2H), 1.93–1.84 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.0, 143.3, 138.0, 136.2, 132.8, 130.1, 128.1, 127.1 (q, J = 276.6 Hz), 126.5, 125.0, 123.5, 123.3, 48.8, 45.5, 33.2 (q, J = 28.4 Hz), 31.5, 26.0, 24.5, 23.0 (q, J = 2.7 Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{F}_3\text{NOS}$ ($M + \text{H}$) $^+$ 368.1296, found 368.1280.



Compound 3pa: 41 mg, 55% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.43–7.13 (m, 4H), 3.65 (t, J = 6.9 Hz, 2H), 3.25–3.05 (m, 2H), 2.97–2.85 (m, 1H), 2.19–1.79 (m, 8H), 1.27 (d, J = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 142.0, 137.5, 129.4, 127.2 (q, J = 276.4 Hz), 126.4, 125.9, 125.9, 48.9, 45.3, 34.9, 32.0 (q, J = 28.4 Hz), 29.9, 25.9, 24.5, 22.3; ^{19}F NMR (565 MHz, CDCl_3) δ -66.4; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{NO}$ ($M + \text{H}$) $^+$ 300.1575, found 300.1569.



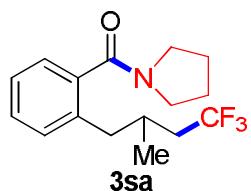
Compound 3qa: 54 mg, 65% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.54 (d, J = 7.8 Hz, 1H), 7.44–7.39 (m, 1H), 7.32–7.28 (m, 1H), 7.23 (d, J = 7.5 Hz, 1H), 4.58–4.49 (m, 1H), 3.65 (t, J = 7.0 Hz, 2H), 3.44–3.38 (m, 1H), 3.35–3.29 (m, 1H), 3.23–3.14 (m, 2H), 2.35–2.15 (m, 2H), 2.03–1.86 (m, 6H), 1.17 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 168.7, 138.9, 136.6, 129.3, 127.5, 127.3 (q, J = 276.4 Hz), 126.2, 125.8, 76.3, 64.4, 49.0, 45.4, 30.2 (q, J = 28.7 Hz), 30.2 (q, J = 2.7 Hz), 26.0, 24.5, 15.2; ^{19}F NMR (565 MHz, CDCl_3) δ -66.1; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{23}\text{F}_3\text{NO}_2$ ($M + \text{H}$) $^+$ 330.1681, found 330.1676.



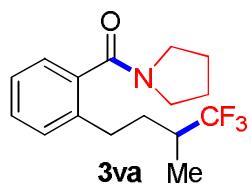
Compound 3ra: 54 mg, 63% yield, white solid, mp: 48–50°C; ^1H NMR (600 MHz, CDCl_3) δ S7

7.45–7.36 (m, 2H), 7.34–7.29 (m, 1H), 7.26–7.21 (m, 1H), 5.73 (t, J = 6.4 Hz, 1H), 3.74–3.58 (m, 2H), 3.34–3.16 (m, 2H), 2.33–2.08 (m, 4H), 2.06 (s, 3H), 2.04–1.86 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.1, 168.5, 137.3, 136.6, 129.4, 127.9, 126.9 (q, J = 276.3 Hz), 126.0, 125.7, 72.1, 49.0, 45.6, 30.2 (q, J = 29.2 Hz), 28.9 (q, J = 2.9 Hz), 26.0, 24.6, 21.0; ^{19}F NMR (565 MHz, CDCl_3) δ -66.3; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{F}_3\text{NO}_3$ ($M + \text{H}$) $^+$ 344.1474, found 344.1469.

Crystal data for **3ra** ($C_{17}H_{20}O_3NF_3$, 343.34): monoclinic, space group $P21/c$, $a = 10.019(3)$ Å, $b = 9.396(2)$ Å, $c = 19.802(5)$ Å, $U = 1718.4(8)$ Å 3 , $Z = 4$, $T = 296(2)$ K, absorption coefficient 0.112 mm $^{-1}$, reflections collected 37672, independent reflections 2705 [$R(\text{int}) = 0.2122$], refinement by full-matrix least-squares on F^2 , data/restraints/parameters 2705/30/211, goodness-of-fit on $F^2 = 1.058$, final R indices [$I > 2s(I)$] $R_1 = 0.1040$, $wR_2 = 0.3276$, R indices (all data) $R_1 = 0.1894$, $wR_2 = 0.3869$, largest diff peak and hole 0.457 and -0.313 e.Å $^{-3}$. Crystallographic data for the structure **3ra** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1473753.

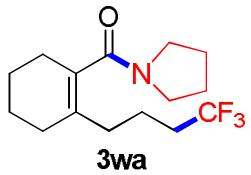


Compound 3sa: 58 mg, 77% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.33–7.19 (m, 4H), 3.64 (t, J = 7.1 Hz, 2H), 3.15 (t, J = 6.7 Hz, 2H), 2.80–2.50 (m, 2H), 2.18–2.08 (m, 2H), 1.98–1.83 (m, 5H), 1.01 (d, J = 6.3 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 137.8, 136.2, 130.4, 128.8, 127.1 (q, J = 276.6 Hz), 126.4, 126.2, 48.7, 45.4, 40.2, 39.7 (q, J = 27.2 Hz), 29.2 (q, J = 2.3 Hz), 25.9, 24.5, 19.7; ^{19}F NMR (565 MHz, CDCl_3) δ -63.2; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{NO} (\text{M} + \text{H})^+$ 300.1575, found 300.1567.

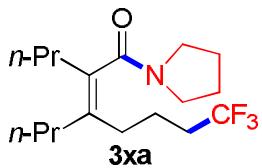


Compound 3va: 45 mg, 60% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.41–7.29 (m, 2H), 7.26–7.17 (m, 2H), 3.65 (t, J = 7.1 Hz, 2H), 3.21–3.08 (m, 2H), 2.98–2.86 (m, 1H), 2.18–1.78 (m, 8H), 1.27 (d, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.4, 142.0, 137.5, 129.4, 127.2 (q, J = 276.4 Hz), 126.4, 125.9, 125.9, 48.9, 45.3, 34.9, 32.0 (q, J = 28.3 Hz), 29.9, 26.0, 24.5, 22.3;

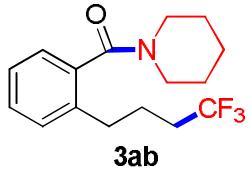
¹⁹F NMR (565 MHz, CDCl₃) δ -66.4; HRMS (ESI) calcd for C₁₆H₂₁F₃NO (M + H)⁺ 300.1575, found 300.1571.



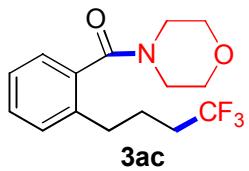
Compound 3wa: 51 mg, 71% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 3.49 (t, *J* = 6.7 Hz, 2H), 3.31 (t, *J* = 6.4 Hz, 2H), 2.22–2.11 (m, 2H), 2.08–1.97 (m, 6H), 1.93–1.86 (m, 4H), 1.70–1.61 (m, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 171.3, 132.5, 131.5, 127.2 (q, *J* = 276.5 Hz), 47.1, 44.9, 33.4, 33.3 (q, *J* = 28.4 Hz), 27.3, 26.2, 25.9, 24.5, 22.4, 22.1, 19.8 (q, *J* = 2.8 Hz); ¹⁹F NMR (565 MHz, CDCl₃) δ -66.3; RMS (ESI) calcd for C₁₅H₂₃F₃NO (M + H)⁺ 290.1732, found 290.1725.



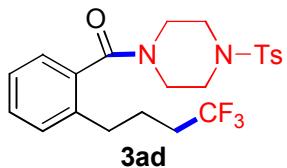
Compound 3xa: 63 mg, 79% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 3.49 (t, *J* = 6.8 Hz, 2H), 3.38–3.18 (m, 2H), 2.17–1.81 (m, 12H), 1.70–1.60 (m, 2H), 1.48–1.38 (m, 4H), 0.98–0.90 (m, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 171.2, 134.9, 134.5, 127.2 (q, *J* = 276.4 Hz), 47.1, 44.8, 33.3 (q, *J* = 28.4 Hz), 32.0, 31.8, 31.3, 25.9, 24.4, 21.8, 21.5, 20.1 (q, *J* = 2.8 Hz), 14.3, 14.2; ¹⁹F NMR (565 MHz, CDCl₃) δ -66.2; HRMS (ESI) calcd for C₁₇H₂₉F₃NO (M + H)⁺ 320.2201, found 320.2196.



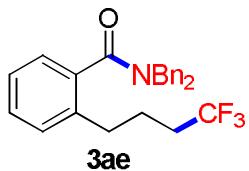
Compound 3ab: 65 mg, 87% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.33–7.15 (m, 4H), 3.88–3.79 (m, 1H), 3.72–3.61 (m, 1H), 3.24–3.10 (m, 2H), 2.83–2.74 (m, 1H), 2.65–2.55 (m, 1H), 2.18–2.06 (m, 2H), 1.95–1.83 (m, 2H), 1.73–1.61 (m, 4H), 1.54–1.40 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 169.4, 137.3, 136.4, 129.3, 128.9, 127.1 (q, *J* = 276.5 Hz), 126.4, 126.0, 48.1, 42.4, 33.3 (q, *J* = 28.5 Hz), 31.7, 26.4, 25.6, 24.5, 23.1 (q, *J* = 2.8 Hz); ¹⁹F NMR (565 MHz, CDCl₃) δ -66.1; HRMS (ESI) calcd for C₁₆H₂₁F₃NO (M + H)⁺ 300.1575, found 300.1560.



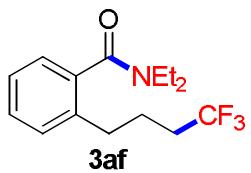
Compound 3ac: 54 mg, 72% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.40–7.30 (m, 1H), 7.28–7.24 (m, 2H), 7.20–7.14 (m, 1H), 3.95–3.67 (m, 4H), 3.65–3.50 (m, 2H), 3.35–3.15 (m, 2H), 2.86–2.73 (m, 1H), 2.67–2.55 (m, 1H), 2.19–2.02 (m, 2H), 1.97–1.80 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.7, 137.6, 135.3, 129.6, 129.4, 127.1 (q, $J = 276.5$ Hz), 126.5, 126.2, 66.9, 66.8, 47.5, 41.9, 33.2 (q, $J = 28.5$ Hz), 31.8, 23.2 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{F}_3\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 302.1368, found 302.1361.



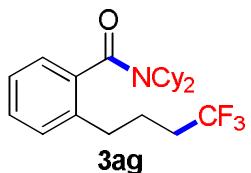
Compound 3ad: 83 mg, 73% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.65–7.59 (m, 2H), 7.39–7.30 (m, 3H), 7.25–7.17 (m, 2H), 7.10–7.10 (m, 1H), 4.00–3.80 (m, 2H), 3.41–3.25 (m, 2H), 3.08 (t, $J = 4.9$ Hz, 2H), 2.95–2.83 (m, 2H), 2.74–2.61 (m, 1H), 2.51–2.41 (m, 4H), 2.06–1.97 (m, 2H), 1.85–1.71 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.5, 144.2, 137.6, 134.8, 132.1, 129.8, 129.6, 129.5, 127.6, 126.9 (q, $J = 276.7$ Hz), 126.5, 126.1, 46.3, 46.1, 45.8, 40.7, 33.1 (q, $J = 28.6$ Hz), 31.6, 23.1 (q, $J = 2.8$ Hz), 21.4; ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_3\text{S}$ ($\text{M} + \text{H}$) $^+$ 455.1616, found 455.1602.



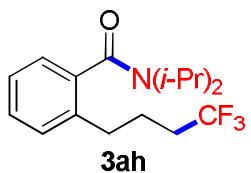
Compound 3ae: 77 mg, 75% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.37–7.11 (m, 14H), 5.30–5.00 (m, 1H), 4.36–4.10 (m, 3H), 2.68–2.54 (m, 2H), 2.07–1.76 (m, 4H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.5, 137.5, 136.9, 136.0, 135.9, 129.3, 129.2, 128.9, 128.8, 128.7, 127.8, 127.2, 127.0 (q, $J = 276.7$ Hz), 126.5, 126.0, 51.0, 46.5, 33.3 (q, $J = 28.6$ Hz), 31.8, 23.2 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{F}_3\text{NO}$ ($\text{M} + \text{H}$) $^+$ 412.1888, found 412.1880.



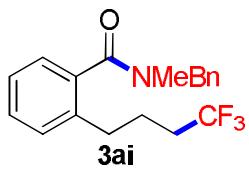
Compound 3af: 55 mg, 76% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.34–7.17 (m, 4H), 3.95–3.70 (m, 1H), 3.52–3.28 (m, 1H), 3.11 (q, $J = 7.1$ Hz, 2H), 2.81–2.54 (m, 2H), 2.18–2.06 (m, 2H), 1.97–1.83 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 137.0, 136.9, 129.3, 128.8, 127.1 (q, $J = 276.5$ Hz), 126.3, 125.7, 42.8, 38.6, 33.3 (q, $J = 28.5$ Hz), 31.7, 23.0 (q, $J = 2.8$ Hz), 13.9, 12.6; ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{21}\text{F}_3\text{NO}$ ($\text{M} + \text{H}$) $^+$ 288.1575, found 288.1569.



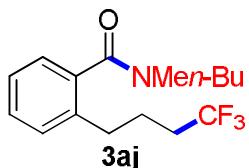
Compound 3ag: 56 mg, 57% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.31–7.27 (m, 1H), 7.26–7.16 (m, 2H), 7.12–7.05 (m, 1H), 3.19–3.11 (m, 1H), 3.08–2.97 (m, 1H), 2.81–2.55 (m, 4H), 2.18–2.02 (m, 2H), 1.98–1.78 (m, 4H), 1.75–1.57 (m, 8H), 1.52–1.46 (m, 2H), 1.32–1.24 (m, 3H), 1.05–0.87 (m, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.5, 138.4, 136.7, 129.2, 128.3, 127.2 (q, $J = 276.6$ Hz), 126.2, 124.9, 59.7, 56.0, 33.4 (q, $J = 28.5$ Hz), 31.6, 31.4, 31.2, 29.9, 29.8, 26.7, 26.6, 25.6, 25.5, 25.3, 25.1, 23.2 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{33}\text{F}_3\text{NO}$ ($\text{M} + \text{H}$) $^+$ 396.2514, found 396.2505.



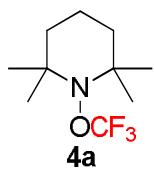
Compound 3ah: 44 mg, 56% yield, colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.32–7.27 (m, 1H), 7.25–7.19 (m, 2H), 7.08–7.15 (m, 1H), 3.70–3.62 (m, 1H), 3.55–3.46 (m, 1H), 2.78–2.59 (m, 2H), 2.17–2.07 (m, 2H), 1.99–1.85 (m, 2H), 1.61–1.52 (m, 6H), 1.10 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.2, 138.3, 136.9, 129.2, 128.4, 127.2 (q, $J = 276.6$ Hz), 126.3, 125.0, 50.7, 45.8, 33.4 (q, $J = 28.4$ Hz), 31.7, 23.2 (q, $J = 2.7$ Hz), 20.7, 20.7, 20.5, 20.4; ^{19}F NMR (565 MHz, CDCl_3) δ –66.0; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{25}\text{F}_3\text{NO}$ ($\text{M} + \text{H}$) $^+$ 316.1888, found 316.1881.



Compound 3ai: 70 mg, 84% yield, colorless oil, obtained as a 1.5:1 mixture of two rotamers; ^1H NMR (600 MHz, CDCl_3) δ 7.41–7.19 (m, 8H), 7.13–7.10 (m, 1H), 5.10–4.50 (m, 2H), 2.78–2.56 (m, 5H), 2.18–2.01 (m, 2H), 1.97–1.80 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 171.0, 137.5, 137.2, 136.9, 129.4, 129.0, 128.7, 128.4, 127.6, 127.0 (q, $J = 276.6$ Hz), 126.5, 126.1, 50.2, 36.1, 33.3 (q, $J = 28.5$ Hz), 31.7, 23.1 (q, $J = 2.8$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ –66.1; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{F}_3\text{NO} (\text{M} + \text{H})^+$ 336.1575, found 336.1565.

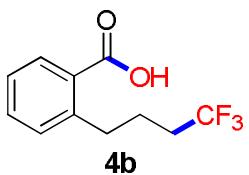


Compound 3aj: 62 mg, 82% yield, colorless oil, obtained as a 1:1 mixture of two rotamers; ^1H NMR (600 MHz, CDCl_3) δ 7.34–7.29 (m, 1H), 7.26–7.21 (m, 2H), 7.19–7.13 (m, 1H), 3.74–3.35 (m, 2H), 2.79 (s, 3H), 2.75–2.43 (m, 2H), 1.97–1.84 (m, 4H), 1.68–1.60 (m, 2H), 1.44–1.37 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.7, 137.0, 136.8, 129.4, 128.8, 127.1 (q, $J = 276.6$ Hz), 126.4, 126.1, 46.6, 36.6, 33.2 (q, $J = 28.5$ Hz), 31.7, 29.0, 23.0 (q, $J = 2.7$ Hz), 20.1, 13.8; ^{19}F NMR (565 MHz, CDCl_3) δ –66.2; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{23}\text{F}_3\text{NO} (\text{M} + \text{H})^+$ 302.1732, found 302.1727.

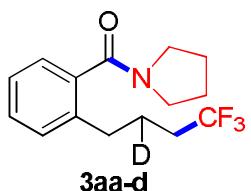


*Compound 4a*¹: It was obtained from **1a** and **2a** under the reaction conditions in the presence of TEMPO (78.2 mg, 0.50 mmol) in 47% NMR yield; ^{19}F NMR (565 MHz, CDCl_3) δ –55.7; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{19}\text{F}_3\text{NO} (\text{M} + \text{H})^+$ 226.1419, found 226.1412.

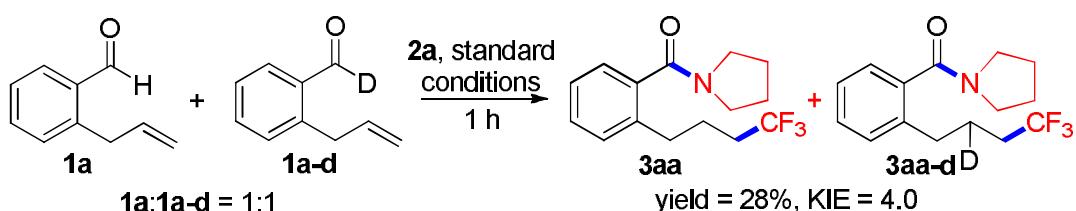
¹Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 16410.



Compound 4b: It was obtained from **1a** under the standard reaction conditions in the presence of 2 equiv of H₂O in 48% yield (28 mg), colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 8.16–8.05 (m, 1H), 7.55–7.47 (m, 1H), 7.37–7.26 (m, 2H), 3.11 (t, *J* = 7.8 Hz, 2H), 2.23–2.10 (m, 2H), 1.98–1.87 (m, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 172.8, 144.0, 133.2, 132.1, 131.2, 128.0, 127.2 (q, *J* = 276.6 Hz), 126.6, 33.5 (q, *J* = 28.5 Hz), 33.5, 23.8 (q, *J* = 2.5 Hz); ¹⁹F NMR (565 MHz, CDCl₃) δ -66.1; HRMS (ESI) calcd for C₁₁H₁₂F₃O₂ (M + H)⁺ 233.0789, found 233.0784.



Compound 3aa-d (>97% D): 32 mg, 45% yield, colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.35–7.30 (m, 1H), 7.26–7.20 (m, 3H), 3.66 (t, *J* = 7.1 Hz, 2H), 3.15 (t, *J* = 6.7 Hz, 2H), 2.72 (d, *J* = 7.7 Hz, 2H), 2.15–2.05 (m, 2H), 2.01–1.94 (m, 2H), 1.89–1.82 (m, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 169.5, 137.5, 137.1, 129.5, 129.1, 127.1 (q, *J* = 276.6 Hz), 126.4, 126.1, 48.8, 45.4, 33.2 (q, *J* = 28.5 Hz), 31.7, 26.0, 24.5; ¹⁹F NMR (565 MHz, CDCl₃) δ -66.2; HRMS (ESI) calcd for C₁₅H₁₈DF₃NO (M + H)⁺ 287.1482, found 287.1457.



To a solution of **1a** (18.3 mg, 0.125 mmol), **1a-d** (18.4 mg, 0.125 mmol), and **2a** (26.7 mg, 0.375 mmol) in 2 mL of DMF was added **I** (118.5 mg, 0.375 mmol), CuSO₄ (4.0 mg, 0.025 mmol) and K₂CO₃ (51.8 mg, 0.375 mmol) under a nitrogen atmosphere. After stirring at room temperature for 1h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:3) gave 20 mg (yield: 28%) of **3aa** and **3aa-d** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.35–7.30 (m, 1H), 7.26–7.20 (m, 3H), 3.66 (t, *J* = 7.1 Hz, 2H), 3.15 (t,

J = 6.7 Hz, 2H), 2.72 (d, *J* = 7.7 Hz, 2H), 2.15–2.05 (m, 2H), 2.01–1.94 (m, 2H), 1.91–1.80 (m, 3.8H). The KIE value was calculated as $k_H/k_D = 4.0$.

