Supporting Information

For

Photoredox-catalysed chloro-, bromo- and trifluoromethylthio-
trifluoromethylation of unactivated alkenes with sodium triflinate

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1. General remarks

\(^1\)H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for \(^1\)C NMR, 376 or 564 MHz for \(^19\)F NMR) agilent NMR spectrometer with CDCl\(_3\) as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, \(\delta\) scale) downfield from TMS at 0.00 ppm and referenced to the CDCl\(_3\) at 7.26 ppm (for \(^1\)H NMR) or 77.16 ppm (for \(^13\)C NMR). Mass spectroscopy data of the products were collected on a GCT PremierTM (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, \(\nu_{\text{max}}\) in cm\(^{-1}\). Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates were purchased or readily prepared according to known methods (\textit{J. Org. Chem.} 2009, 74, 2854; \textit{Org. Lett.} 2016, 18, 5368; \textit{Angew. Chem., Int. Ed.} 2011, 50, 5541).

2. Screening of organic acids and solvents

![Chemical structure of reaction](image)

<table>
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<th>Entry(^a)</th>
<th>LEDs</th>
<th>Catalyst</th>
<th>Acid (equiv)</th>
<th>Solvent</th>
<th>Yield (%)(^b)</th>
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<td>TFA (2)</td>
<td>Acetone</td>
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\(^a\) Numbers 1-13 relate to entries in Table 1.

\(^b\) Yields are given as isolated yield.
3. Typical experimental procedure

To a suspension of 1a (80.4 mg, 0.4 mmol), CF₃SO₂Na (124.8 mg, 0.8 mmol) and N-Methyl-9-mesityl acridinium perchlorate (1.6 mg, 0.004 mmol) in DCE (4 mL) was added N-chlorophthalimide (87 mg, 0.48 mmol) and TFA (91.2 mg, 0.8 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give 3a as a white solid (89.0 mg, 73% yield).

To a suspension of 1a (80.4 mg, 0.4 mmol), CF₃SO₂Na (124.8 mg, 0.8 mmol) and N-Methyl-9-mesityl acridinium perchlorate (1.6 mg, 0.004 mmol) in DCE (4 mL) was added N-bromophthalimide (108.4 mg, 0.48 mmol) and TFA (91.2 mg, 0.8 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give 4a as a white solid (100.6 mg, 72% yield).

*1a (0.4 mmol), Mes-Acr⁺ (1 mol%), TsCl (0.48 mmol), CF₃SO₂Na (0.8 mmol), Acid (0.8 mmol), solvent (4 mL), Argon balloon, 5 W LEDs. †Isolated yield.
To a suspension of 1r (78.4 mg, 0.4 mmol), CF$_3$SO$_2$Na (124.8 mg, 0.8 mmol) and N-Methyl-9-mesityl acridinium perchlorate (8 mg, 0.02 mmol) in DCE (4 mL) was added N-trifluoromethylthiosaccharin (170 mg, 0.6 mmol) and TsOH (137.6 mg, 0.8 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give 7b as a white solid (105.4 mg, 72% yield).

4. Fluorescence quenching experiments

Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. All Mes-Acr$^+$ solutions were excited at 450 nm and the emission intensity was collected at 500-550 nm. In a typical experiment, the CH$_3$CN solution of Mes-Acr$^+$ (0.1 mM) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with nitrogen for 10 min, the emission spectra of the samples were collected. The results showed that CF$_3$SO$_2$Na quenched the photoexcited Mes-Acr$^+$ effectively.
5. References for known products

<table>
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<th>Entry</th>
<th>Reference</th>
<th>Compound</th>
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<tr>
<td>1</td>
<td>S. H. Oh; S. B. Han. Org. Lett., 2014, 16, 1310.</td>
<td>3a, 3k, 3q</td>
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<td>3</td>
<td>S. Mizuta; V. Gouverneu; J. Am. Chem. Soc., 2013, 135, 2505.</td>
<td>3s</td>
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</table>

6. Characterization of the substrates and products

2-(But-3-en-1-yl)isoindoline-1,3-dione (1a): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 – 7.77 (m, 2H), 7.75 – 7.66 (m, 2H), 5.87 – 5.70 (m, 1H), 5.14 – 4.93 (m, 2H), 3.77 (t, $J$ = 7.1 Hz, 2H), 2.52 – 2.38 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.5, 134.6, 134.0, 132.2, 123.3, 117.7, 37.4, 33.0.

2-(Dec-9-en-1-yl)isoindoline-1,3-dione (1b): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.77 (m, 2H), 7.75 – 7.63 (m, 2H), 5.87 – 5.69 (m, 1H), 5.03 – 4.82 (m, 2H), 3.66 (t, $J$ = 7.3 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.69 – 1.60 (m, 2H), 1.44 – 1.15 (m, 10H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.5, 139.3, 133.9, 132.2, 123.2, 114.2, 38.2, 33.9, 29.4, 29.2, 29.1, 29.0, 28.7, 26.9.

Hex-5-en-1-yl 2-chlorobenzoate (1c): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 7.6 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.30 (t, $J$ = 7.3 Hz, 1H), 5.90 – 5.71 (m, 1H), 5.00 (dd, $J$ = 22.4, 13.7 Hz, 2H), 4.34 (t, $J$ = 6.5 Hz, 2H), 2.12 (q, $J$ = 7.0 Hz, 2H), 1.87 – 1.71 (m, 2H), 1.64 – 1.47 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.0, 138.4, 133.7, 132.5, 131.4, 131.1, 130.6, 126.7, 115.0, 65.6, 33.4, 28.1, 25.4.
Hex-5-en-1-yl 3-chlorobenzoate (1d): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (s, 1H), 7.92 (d, $J = 7.7$ Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 1H), 7.38 (t, $J = 7.9$ Hz, 1H), 5.94 – 5.72 (m, 1H), 5.01 (dd, $J = 21.6$, 13.7 Hz, 2H), 4.33 (t, $J = 6.6$ Hz, 2H), 2.13 (q, $J = 7.0$ Hz, 2H), 1.89 – 1.69 (m, 2H), 1.61 – 1.48 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.4, 138.3, 134.5, 132.9, 132.3, 129.78, 129.74, 127.7, 115.0, 65.3, 33.4, 28.2, 25.3.

Hex-5-en-1-yl 4-chlorobenzoate (1e): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 5.90 – 5.72 (m, 1H), 5.10 – 4.90 (m, 2H), 4.31 (t, $J = 6.5$ Hz, 2H), 2.12 (q, $J = 6.9$ Hz, 2H), 1.86 – 1.69 (m, 2H), 1.62 – 1.47 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.8, 139.4, 138.3, 131.0, 129.0, 128.8, 115.0, 65.2, 33.4, 28.2, 25.4.

But-3-en-1-yl 4-methylbenzenesulfonate (1f): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 5.72 – 5.56 (m, 1H), 5.10 – 4.98 (m, 2H), 4.03 (t, $J = 6.7$ Hz, 2H), 2.42 (s, 3H), 2.40 – 2.32 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 144.8, 133.1, 132.5, 129.9, 127.9, 118.2, 69.5, 33.2, 21.7.

N-allyl-4-chlorobenzamide (1g): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.3$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 2H), 6.21 (brs, 1H), 6.02 – 5.83 (m, 1H), 5.38 – 5.10 (m, 2H), 4.08 (t, $J = 5.5$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.4, 137.9, 134.1, 132.9, 129.0, 128.5, 117.1, 42.7.

N-phenylpent-4-enamide (1h): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (s, 1H), 7.51 (d, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 5.94 – 5.76 (m, 1H), 5.20 – 4.94 (m, 2H), 2.54 – 2.36 (m, 4H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 170.9, 138.0, 137.0, 129.0, 124.4, 120.1, 116.0, 36.9, 29.6.
1-(4-Fluorophenyl)but-3-en-1-one (1i): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (dd, $J = 8.3$, 5.6 Hz, 2H), 7.12 (t, $J = 8.5$ Hz, 2H), 6.15 – 5.98 (m, 1H), 5.29 – 5.13 (m, 2H), 3.72 (d, $J = 6.6$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 196.5, 165.9 (d, $J_{C,F} = 254.6$ Hz), 133.1 (d, $J_{C,F} = 3.0$ Hz), 131.0 (d, $J_{C,F} = 9.1$ Hz), 130.9, 119.0, 115.8 (d, $J_{C,F} = 22.0$ Hz), 43.5.

1-(3,5-Dibromo-4-methoxyphenyl)pent-4-en-1-one (1j): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (s, 2H), 5.96 – 5.77 (m, 1H), 5.16 – 4.93 (m, 2H), 3.93 (s, 3H), 3.00 (t, $J = 7.3$ Hz, 2H), 2.47 (q, $J = 6.9$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.1, 158.1, 136.9, 135.0, 132.8, 118.8, 115.8, 60.9, 37.8, 28.0.

4-(Allyloxy)benzaldehyde (1k): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.85 (s, 1H), 7.80 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 2H), 6.11 – 5.93 (m, 1H), 5.49 – 5.25 (m, 2H), 4.59 (d, $J = 4.9$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 190.8, 163.6, 132.3, 132.0, 130.1, 118.3, 115.0, 69.0.

10-Bromodec-1-ene (1l): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.88 – 5.70 (m, 1H), 5.07 – 4.86 (m, 2H), 3.40 (t, $J = 6.8$ Hz, 2H), 2.04 (q, $J = 13.7$, 6.8 Hz, 2H), 1.91 – 1.77 (m, 2H), 1.51 – 1.22 (m, 10H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 139.2, 114.3, 34.1, 33.9, 33.0, 29.4, 29.1, 29.0, 28.9, 28.3.

Octadec-1-ene (1m): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.91 – 5.73 (m, 1H), 5.07 – 4.87 (m, 2H), 2.11 – 1.96 (m, 2H), 1.48 – 1.15 (m, 28H), 0.88 (t, $J = 6.5$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$, overlapping peaks) $\delta$ 139.4, 114.2, 34.0, 32.1, 29.9, 29.85, 29.81, 29.7, 29.6, 29.3, 29.1, 22.9, 14.3.
2-(2-Methylallyl)isoindoline-1,3-dione (1n): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.82 (m, 2H), 7.77 – 7.69 (m, 2H), 4.89 (s, 1H), 4.82 (s, 1H), 4.22 (s, 2H), 1.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.2, 139.4, 134.1, 132.1, 123.5, 112.1, 43.4, 20.5.

![Image](https://via.placeholder.com/150)

3-Methylbut-3-en-1-yl 4-methylbenzenesulfonate (1o): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 4.77 (s, 1H), 4.66 (s, 1H), 4.11 (t, $J = 6.8$ Hz, 2H), 2.43 (s, 3H), 2.33 (t, $J = 6.7$ Hz, 2H), 1.64 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 144.8, 140.2, 133.2, 129.9, 127.9, 113.1, 68.6, 36.8, 22.3, 21.7.

![Image](https://via.placeholder.com/150)

3-Methylbut-3-en-1-yl 4-chlorobenzoate (1p): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 4.84 (s, 2H), 4.80 (s, 2H), 4.43 (t, $J = 6.7$ Hz, 2H), 2.47 (t, $J = 6.7$ Hz, 2H), 1.80 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.8, 141.7, 139.4, 131.1, 129.0, 128.8, 112.6, 63.5, 36.9, 22.6.

![Image](https://via.placeholder.com/150)

1-Tosyl-2,5-dihydro-1H-pyrrole (1r): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71 (d, $J = 7.9$ Hz, 2H), 7.31 (d, $J = 7.8$ Hz, 2H), 5.64 (s, 2H), 4.11 (s, 4H), 2.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 143.6, 134.4, 129.9, 127.5, 125.6, 55.0, 21.6.

![Image](https://via.placeholder.com/150)

Diethyl 2,2-diallylmalonate (1s): $^1$H NMR (600 MHz, CDCl$_3$) δ 5.77 – 5.54 (m, 2H), 5.14 – 5.02 (m, 4H), 4.21 – 4.10 (m, 4H), 2.62 (d, $J = 7.4$ Hz, 4H), 1.29 – 1.17 (m, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 170.9, 132.4, 119.2, 61.3, 57.4, 36.9, 14.2.

![Image](https://via.placeholder.com/150)

Allyl 4-chlorobenzoate (1t): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 6.10 – 5.95 (m, 1H), 5.48 – 5.23 (m, 2H), 4.81 (d, $J = 5.6$ Hz, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.4, 139.5, 132.1, 131.1, 128.8, 128.7, 118.6, 65.9.
1-(1,1'-Biphenyl)-4-ylpent-4-en-1-one (1u): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.63 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.4$ Hz, 2H), 7.44 – 7.38 (m, 1H), 6.06 – 5.85 (m, 1H), 5.24 – 4.98 (m, 2H), 3.11 (t, $J = 7.3$ Hz, 2H), 2.61 – 2.46 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.2, 145.8, 140.0, 137.5, 135.8, 129.1, 128.8, 128.3, 127.38, 127.36, 115.4, 37.9, 28.4.

2-(3-Chloro-5,5,5-trifluoropentyl)isoindoline-1,3-dione (3a): White solid; m.p. 64-66 °C; 73% yield (89 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 – 7.80 (m, 2H), 7.80 – 7.67 (m, 2H), 4.25 – 4.09 (m, 1H), 4.01 – 3.79 (m, 2H), 2.76 – 2.55 (m, 2H), 2.38 – 2.21 (m, 1H), 2.21 – 2.05 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 134.3, 132.1, 125.2 (q, $J_{C-F}=277.6$ Hz), 123.6, 51.5 (q, $J_{C-F}=3.1$ Hz), 42.4 (q, $J_{C-F}=28.6$ Hz), 36.6, 35.2; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -63.65 (t, $J = 10.1$ Hz, 3F).

2-(9-Chloro-11,11,11-trifluoropentyl)isoindoline-1,3-dione (3b): White solid; m.p. 49-51 °C; 84% yield (131 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 – 7.77 (m, 2H), 7.77 – 7.62 (m, 2H), 4.23 – 4.02 (m, 1H), 3.66 (t, $J = 7.1$ Hz, 2H), 2.71 – 2.41 (m, 2H), 1.91 – 1.60 (m, 4H), 1.60 – 1.38 (m, 2H), 1.36 – 1.17 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.7, 134.0, 132.3, 125.4 (q, $J_{C-F}=277.5$ Hz), 123.2, 54.3 (q, $J_{C-F}=3.1$ Hz), 42.5 (q, $J_{C-F}=28.3$ Hz), 38.12, 38.08, 29.3, 29.1, 28.8, 28.6, 26.8, 25.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.83 (t, $J = 10.3$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2919, 2850, 1688, 1600, 831; HRMS (CI) calcd C$_{19}$H$_{24}$NO$_2$F$_3$Cl$_3$ $^{[\text{M + H}]}^{+}$: 390.1448, found: 390.1454.

5-Chloro-7,7,7-trifluoroheptyl 2-chlorobenzoate (3c): Colorless oil; 74% yield (101 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 7.6$ Hz, 1H), 7.49 – 7.38 (m, 2H), 7.32 (t, $J = 7.3$ Hz, 1H), 4.36 (t, $J = 6.1$ Hz, 2H), 4.22 – 4.03 (m, 1H), 2.75 – 2.43 (m, 2H), 1.99 – 1.69 (m, 5H), 1.69 – 1.57 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.0, 133.7, 132.7, 131.5, 131.2, 130.4, 126.7, 125.3 (d, $J_{C-F}=277.6$ Hz), 65.2,
54.0 (q, $J_{CF} = 3.1$ Hz), 42.6 (q, $J_{CF} = 28.4$ Hz), 37.7, 28.0, 22.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.78 (t, $J = 10.3$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2960, 1728, 1436, 1118, 747; HRMS (Cl) calcd C$_{14}$H$_{16}$O$_2$F$_3$Cl$_3$ $^+$ [M + H]$^+$: 343.0479, found: 343.0480.

5-Chloro-7,7,7-trifluoroheptyl 3-chlorobenzoate (3d): Colorless oil; 65% yield (90 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (s, 1H), 7.92 (d, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 7.9$ Hz, 1H), 7.39 (t, $J = 7.9$ Hz, 1H), 4.35 (t, $J = 6.1$ Hz, 2H), 4.21 – 4.08 (m, 1H), 2.74 – 2.47 (m, 2H), 2.00 – 1.68 (m, 5H), 1.68 – 1.54 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 134.7, 133.1, 132.1, 129.9, 127.8, 125.3 (q, $J_{CF} = 277.6$ Hz), 65.0, 54.0 (q, $J_{CF} = 3.1$ Hz), 42.6 (q, $J_{CF} = 28.5$ Hz), 37.7, 28.1, 22.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -63.76 (t, $J = 10.3$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2957, 1720, 1427, 1279, 748; HRMS (Cl) calcd C$_{14}$H$_{16}$O$_2$F$_3$Cl$_3$ $^+$ [M + H]$^+$: 343.0479, found: 343.0485.

5-Chloro-7,7,7-trifluoroheptyl 4-chlorobenzoate (3e): Colorless oil; 64% yield (88 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 4.34 (t, $J = 6.1$ Hz, 2H), 4.22 – 4.06 (m, 1H), 2.75 – 2.46 (m, 2H), 2.00 – 1.87 (m, 1H), 1.88 – 1.69 (m, 4H), 1.68 – 1.56 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$, overlapping peaks) $\delta$ 165.8, 139.5, 131.1, 128.9, 125.3 (q, $J_{CF} = 277.6$ Hz), 64.9, 54.0, 42.6 (q, $J_{CF} = 28.5$ Hz), 37.7, 28.1, 22.7; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -59.07 (t, $J = 10.3$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2957, 1718, 1390, 1241, 759; HRMS (Cl) calcd C$_{14}$H$_{16}$O$_2$F$_3$Cl$_3$ $^+$ [M + H]$^+$: 343.0479, found: 343.0483.

3-Chloro-5,5,5-trifluoropentyl 4-methylbenzenesulfonate (3f): Yellow oil; 86% yield (114 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 7.9$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 4.29 – 4.21 (m, 2H), 4.21 – 4.14 (m, 1H), 2.68 – 2.48 (m, 2H), 2.46 (s, 3H), 2.35 – 2.18 (m, 1H), 2.03 – 1.87 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 145.3, 132.7, 130.1, 128.1, 125.0 (q, $J_{CF} = 277.7$ Hz), 66.4, 50.0, 42.4 (q, $J_{CF} = 28.9$ Hz), 37.2, 21.8; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -63.63 (t, $J = 10.0$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2962, 2923, 1598, 1175, 775; HRMS (Cl) calcd C$_{12}$H$_{15}$O$_3$F$_3$SCl$_3$ $^+$ [M + H]$^+$: 311.0383, found: 331.0381.
4-Chloro-N-(2-chloro-4,4,4-trifluorobutyl)benzamide (3g): White solid; m.p. 132-134 °C; 69% yield (83 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.74\) (d, \(J = 8.3\) Hz, 2H), 7.44 (d, \(J = 8.4\) Hz, 2H), 6.53 (brs, 1H), 4.46 – 4.29 (m, 1H), 4.04 – 3.72 (m, 1H), 3.72 – 3.59 (m, 1H), 3.28 – 2.55 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 166.8, 138.5, 132.1, 129.2, 128.6, 125.2\) (\(J_{C,F} = 277.4\) Hz), 53.7, 46.0, 40.2 (\(J_{C,F} = 29.4\) Hz); \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta -63.68\) (t, \(J = 10.1\) Hz, 3F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 3302, 2922, 1637, 1185, 759; HRMS (CI) calcd C\(_{11}\)H\(_{11}\)NOF\(_3\)Cl\(_3\)\([\text{M} + \text{H}]^+\): 300.0170, found: 300.0172.

4-Chloro-6,6,6-trifluoro-N-phenylhexanamide (3h): Colorless oil; 74% yield (83 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.49\) (d, \(J = 7.8\) Hz, 2H), 7.41 (brs, 1H), 7.32 (t, \(J = 7.7\) Hz, 1H), 7.26 (t, \(J = 7.2\) Hz, 1H), 7.25 (m, 1H), 2.31 – 2.16 (m, 4H), 2.16 – 2.00 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 169.6, 137.7, 129.2, 125.2\) (\(J_{C,F} = 277.7\) Hz), 124.7, 120.1, 53.8 (\(J_{C,F} = 3.1\) Hz), 42.8 (\(J_{C,F} = 28.7\) Hz), 33.7, 33.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -63.62\) (t, \(J = 10.1\) Hz, 3F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 3301, 2924, 1773, 1543, 692; HRMS (CI) calcd C\(_{12}\)H\(_{14}\)NOF\(_3\)Cl\(_3\)\([\text{M} + \text{H}]^+\): 280.0716, found: 280.0711.

3-Chloro-5,5,5-trifluoro-1-(4-fluorophenyl)pentan-1-one (3i): Colorless oil; 54% yield (58 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.99\) (dd, \(J = 8.2, 5.6\) Hz, 2H), 7.17 (t, \(J = 8.4\) Hz, 2H), 4.82 – 4.71 (m, 1H), 3.60 (dd, \(J = 17.6, 7.0\) Hz, 1H), 3.40 (dd, \(J = 17.6, 6.0\) Hz, 1H), 2.91 – 2.63 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 193.9, 166.3\) (\(J_{C,F} = 256.2\) Hz), 132.78 (d, \(J_{C,F} = 2.9\) Hz), 130.6 (d, \(J_{C,F} = 9.4\) Hz), 125.3 (q, \(J_{C,F} = 277.8\) Hz), 116.2 (d, \(J_{C,F} = 22.0\) Hz), 48.4, 46.1, 41.7 (q, \(J_{C,F} = 28.8\) Hz); \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta -63.48\) (t, \(J = 10.1\) Hz, 3F), -103.68 – - 103.74 (m, 1F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2961, 2924, 1686, 1598, 669; HRMS (CI) calcd C\(_{11}\)H\(_{10}\)OF\(_4\)Cl\(_3\)\([\text{M} + \text{H}]^+\): 269.0356, found: 269.0351.
4-Chloro-1-(3,5-dibromo-4-methoxyphenyl)-6,6,6-trifluorohexan-1-one (3j):
Yellow oil; 53% yield (95 mg); ¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 2H), 4.35–4.16 (m, 1H), 3.95 (s, 3H), 3.18 (t, J = 6.8 Hz, 2H), 2.86–2.54 (m, 2H), 2.46–2.31 (m, 1H), 2.13–1.95 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 195.2, 158.4, 134.6, 132.8, 125.2 (q, J_C-F = 277.7 Hz), 118.9, 61.0, 53.7, 42.9 (q, J_C-F = 28.7 Hz), 35.0, 32.1; ¹⁹F NMR (564 MHz, CDCl₃) δ -58.98 (t, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm⁻¹) 2930, 1689, 1382, 737; HRMS (CI) calcd C₁₃H₁₃O₂F₃Cl₃5Br₇92 [M + H]⁺: 450.8923, found: 450.8925.

4-(2-Chloro-4,4,4-trifluorobutoxy)benzaldehyde (3k): Colorless oil; 62% yield (66 mg); ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 4.48–4.38 (m, 1H), 4.32 (dd, J = 9.9, 4.8 Hz, 1H), 4.20 (dd, J = 9.8, 6.5 Hz, 1H), 3.05–2.84 (m, 1H), 2.79–2.56 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 190.7, 162.7, 132.2, 131.0, 125.3 (q, J_C-F = 277.3 Hz), 115.0, 70.6, 50.3, 39.1 (q, J_C-F = 29.4 Hz); ¹⁹F NMR (564 MHz, CDCl₃) δ -61.32 (t, J = 10.1 Hz, 3F).

11-Bromo-3-chloro-1,1,1-trifluoroundecane (3l): Colorless oil; 65% yield (84 mg); ¹H NMR (600 MHz, CDCl₃) δ 4.15–4.07 (m, 1H), 3.40 (t, J = 6.8 Hz, 2H), 2.66–2.48 (m, 2H), 1.89–1.79 (m, 3H), 1.79–1.70 (m, 1H), 1.59–1.41 (m, 4H), 1.37–1.30 (m, 4H), 0.90–0.85 (m, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 125.4 (q, J_C-F = 277.5 Hz), 54.3, 42.6 (q, J_C-F = 28.4 Hz), 38.2, 34.0, 32.9, 29.3, 28.9, 28.8, 28.2, 26.0; ¹⁹F NMR (564 MHz, CDCl₃) δ -63.90 (t, J = 10.3 Hz, 3F).

3-Chloro-1,1,1-trifluorononadecane (3m): Colorless oil; 72% yield (103 mg); ¹H NMR (600 MHz, CDCl₃) δ 4.14–4.08 (m, 1H), 2.67–2.49 (m, 2H), 1.86–1.79 (m, 1H), 1.78–1.72 (m, 1H), 1.59–1.51 (m, 2H), 1.49–1.40 (m, 2H), 1.37–1.24 (m, 24H), 0.89 (t, J = 7.0 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃, overlapping peaks) δ 125.5 (q, J_C-F = 277.5 Hz), 54.3, 42.6 (q, J_C-F = 28.3 Hz), 38.3, 32.1, 29.89, 29.87, 29.81, 29.79, 29.7, 29.6, 29.5, 29.1, 26.1, 22.9, 14.3; ¹⁹F NMR (564 MHz, CDCl₃) δ -63.94 (t, J = 10.3 Hz, 3F).
2-(2-Chloro-4,4,4-trifluoro-2-methylbutyl)isoindoline-1,3-dione (3n): White solid; m.p. 104-106 °C; 60% yield (73 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 – 7.88 (m, 2H), 7.80 – 7.75 (m, 2H), 4.04 (s, 2H), 2.89 – 2.60 (m, 2H), 1.75 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.4, 134.6, 131.8, 125.2 (q, \(J_{C-F} = 278.4\) Hz), 123.9, 65.3, 49.5, 45.5 (q, \(J_{C-F} = 28.4\) Hz), 28.0; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -60.00 (t, \(J = 10.5\) Hz, 3F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2989, 1712, 1384, 1098, 715; HRMS (CI) calcd C\(_{13}\)H\(_{12}\)NO\(_2\)F\(_3\)Cl\(_3\) [M + H]\(^+\): 306.0509, found: 306.0514.

3-Chloro-5,5,5-trifluoro-3-methylpentyl 4-methylbenzenesulfonate (3o): Yellow oil; 85% yield (117 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79 (d, \(J = 8.1\) Hz, 2H), 7.36 (d, \(J = 7.9\) Hz, 2H), 4.29 (t, \(J = 6.4\) Hz, 2H), 2.64 (q, \(J = 10.6\) Hz, 2H), 2.45 (s, 3H), 2.34 – 2.14 (m, 2H), 1.67 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 145.3, 132.8, 130.1, 128.0, 124.8 (q, \(J_{C-F} = 278.7\) Hz), 66.6, 64.9, 47.1 (q, \(J_{C-F} = 27.9\) Hz), 42.3, 30.3, 21.7; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -60.66 (t, \(J = 10.6\) Hz, 3F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2928, 1598, 1364, 1210, 764; HRMS (CI) calcd C\(_{13}\)H\(_{17}\)O\(_3\)F\(_3\)SCl\(_3\) [M + H]\(^+\): 345.0539, found: 345.0545.

3-Chloro-5,5,5-trifluoro-3-methylpentyl 4-chlorobenzoate (3p): Colorless oil; 88% yield (115 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 (d, \(J = 8.4\) Hz, 2H), 7.41 (d, \(J = 8.4\) Hz, 2H), 4.68 – 4.49 (m, 2H), 2.88 – 2.65 (m, 2H), 2.48 – 2.25 (m, 2H), 1.78 (s, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 165.7, 139.7, 131.1, 128.9, 127.7, 125.0 (q, \(J_{C-F} = 278.7\) Hz), 65.4, 61.7, 47.2 (q, \(J_{C-F} = 27.8\) Hz), 42.1, 30.5; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -60.61 (t, \(J = 10.7\) Hz, 3F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2972, 1720, 1595, 1268, 758; HRMS (CI) calcd C\(_{13}\)H\(_{14}\)O\(_2\)F\(_3\)Cl\(_3\) [M + H]\(^+\): 329.0323, found: 329.0328.

5-Chloro-6-(trifluoromethyl)decane (3q): yield: 63% (1.2:1 dr); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 4.25 – 4.13 (m, 1H), 2.59 – 2.47 (m, 0.66H), 2.38 – 2.29 (m, 0.55H), 1.89 – 1.17 (m, 12H), 0.98 – 0.88 (m, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 127.1 (q, \(J_{C-F} = 281.5\) Hz), 126.9 (q, \(J_{C-F} = 282.2\) Hz), 60.0, 59.2, 49.5 (q, \(J_{C-F} = 24.1\) Hz), 48.5 (q, \(J_{C-F} = 24.6\) Hz), 36.1, 33.7, 30.1, 29.9, 29.7, 29.3, 29.0, 24.3, 24.0, 22.7, 22.6, 22.0, 21.9, 13.9, 13.8, 13.7; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -65.66 (d, \(J = 9.4\) Hz, 1.64F), -67.44 (d, \(J = 9.2\) Hz, 1.36F).
3-Chloro-1-tosyl-4-(trifluoromethyl)pyrrolidine (3r): yield: 41%; \(^{1}H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.2\) Hz, 2H), 7.36 (d, \(J = 8.2\) Hz, 2H), 4.32 (dd, \(J = 11.0, 5.3\) Hz, 1H), 3.79 (dd, \(J = 11.2, 6.2\) Hz, 1H), 3.65 (dd, \(J = 10.8, 9.1\) Hz, 1H), 3.46 (dd, \(J = 11.0, 5.5\) Hz, 1H), 3.41 (dd, \(J = 11.2, 5.1\) Hz, 1H), 3.08 – 2.98 (m, 1H), 2.45 (s, 3H); \(^{13}C\) NMR (150 MHz, CDCl\(_3\)) \(\delta\) 144.6, 132.8, 130.1, 127.8, 125.2 (q, \(J_{C-F} = 279.0\) Hz), 56.2, 52.8, 51.9 (q, \(J_{C-F} = 28.7\) Hz), 46.0, 21.7; \(^{19}F\) NMR (564 MHz, CDCl\(_3\)) \(\delta\) -70.66 (d, \(J = 8.6\) Hz, 3F).

Diethyl 3-(chloromethyl)-4(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3s): Colorless oil; 41% yield (56 mg); \(^{1}H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 4.19 (q, \(J = 7.1\) Hz, 4H), 3.50 (dd, \(J = 11.1, 6.2\) Hz, 1H), 3.43 (dd, \(J = 11.1, 7.5\) Hz, 1H), 2.56 – 2.46 (m, 4H), 2.34 – 2.27 (m, 2H), 2.23 – 2.07 (m, 2H), 1.27 – 1.22 (m, 6H); \(^{13}C\) NMR (150 MHz, CDCl\(_3\)) \(\delta\) 172.2, 172.1, 126.9 (q, \(J_{C-F} = 277.1\) Hz), 62.0, 61.9, 58.6, 44.4, 44.0, 38.6, 37.1, 35.6, 33.4 (q, \(J_{C-F} = 28.3\) Hz); \(^{19}F\) NMR (564 MHz, CDCl\(_3\)) \(\delta\) -64.49 (t, \(J = 10.8\) Hz, 3F).

2-(3-Bromo-5,5,5-trifluoropentyl)isoindoline-1,3-dione (4a): White solid; m.p. 58-60 °C; 72% yield (101 mg); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 – 7.81 (m, 2H), 7.78 – 7.69 (m, 2H), 4.23 – 4.09 (m, 1H), 4.02 – 3.81 (m, 2H), 2.95 – 2.56 (m, 2H), 2.05 – 1.70 (m, 5H), 1.69 – 1.59 (m, 1H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.3, 134.3, 132.1, 125.2 (q, \(J_{C-F} = 278.2\) Hz), 123.5, 43.0 (q, \(J_{C-F} = 28.7\) Hz), 41.2 (q, \(J_{C-F} = 3.2\) Hz), 37.0, 36.2; \(^{19}F\) NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.61 (t, \(J = 10.1\) Hz, 3F).

5-Bromo-7,7,7-trifluoroheptyl 4-chlorobenzoate (4b): Colorless oil; 71% yield (110 mg); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 8.4\) Hz, 2H), 7.42 (d, \(J = 8.4\) Hz, 2H), 4.34 (t, \(J = 6.0\) Hz, 2H), 4.25 – 4.09 (m, 1H), 2.95 – 2.56 (m, 2H), 2.05 – 1.70 (m, 5H), 1.69 – 1.59 (m, 1H); \(^{13}C\) NMR (150 MHz, CDCl\(_3\)) \(\delta\) 165.9, 139.6, 131.1, 128.9, 128.8, 125.4 (q, \(J_{C-F} = 278.1\) Hz), 64.8, 44.8, 43.3 (q, \(J_{C-F} = 28.5\) Hz), 38.1, 28.0, 24.0; \(^{19}F\) NMR (564 MHz, CDCl\(_3\)) \(\delta\) -63.82 (t, \(J = 10.2\) Hz, 3F); FT-IR (thin film, KBr): ν
4-(2-Bromo-4,4,4-trifluorobutoxy)benzaldehyde (4c): Colorless oil; 60% yield (74 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 9.91 (s, 1H), 7.86 (d, $J = 7.9$ Hz, 2H), 7.03 (d, $J = 8.0$ Hz, 2H), 4.47 - 4.33 (m, 2H), 4.31 - 4.21 (m, 1H), 3.17 - 2.99 (m, 1H), 2.87 - 2.70 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 190.8, 162.6, 132.2, 131.0, 125.3 (q, $J_{C-F} = 277.6$ Hz), 115.5, 70.8, 39.6 (q, $J_{C-F} = 29.4$ Hz), 39.0; $^{19}$F NMR (564 MHz, CDCl$_3$) δ -63.99 (t, $J = 10.1$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 3056, 3005, 1693, 1596, 771; HRMS (CI) calcd C$_{14}$H$_{16}$O$_2$F$_3$Cl$_3$Br$_7$ [M + H]$^+$: 386.9974, found: 386.9975.

2-(2-Bromo-4,4,4-trifluoro-2-methylbutyl)isoindoline-1,3-dione (4d): White solid; m.p. 63-65 °C; 76% yield (106 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 - 7.87 (m, 2H), 7.82 - 7.75 (m, 2H), 4.20 - 4.09 (m, 2H), 3.06 - 2.72 (m, 2H), 1.92 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 168.4, 134.6, 131.8, 125.2 (q, $J_{C-F} = 278.8$ Hz), 123.9, 58.2, 50.4, 46.6 (q, $J_{C-F} = 28.4$ Hz), 29.6; $^{19}$F NMR (564 MHz, CDCl$_3$) δ -60.01 (t, $J = 10.6$ Hz, 3F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2933, 1774, 1387, 1260, 713; HRMS (CI) calcd C$_{13}$H$_{12}$NO$_2$F$_3$Br$_7$ [M + H]$^+$: 350.0003, found: 350.0004.

3-Bromo-5,5,5-trifluoro-3-methylpentyl 4-chlorobenzoate (4e): Colorless oil; 82% yield (122 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.42 (d, $J = 8.4$ Hz, 2H), 4.71 - 4.53 (m, 2H), 3.05 - 2.84 (m, 2H), 2.53 - 2.32 (m, 2H), 1.98 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.4, 139.6, 130.9, 128.8, 128.3, 124.9 (q, $J_{C-F} = 279.5$ Hz), 62.9, 59.3, 48.3 (q, $J_{C-F} = 27.7$ Hz), 42.9, 32.1; $^{19}$F NMR (564 MHz, CDCl$_3$) δ -60.52 (t, $J = 10.7$ Hz, 3F).

3-Bromo-5,5,5-trifluoro-3-methylpentyl 4-methylbenzenesulfonate (4f): Colorless oil; 75% yield (116 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.36
(d, J = 7.9 Hz, 2H), 4.32 (t, J = 6.5 Hz, 2H), 2.80 (q, J = 10.6 Hz, 2H), 2.45 (s, 3H), 2.35 – 2.22 (m, 2H), 1.86 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 145.3, 132.8, 130.1, 128.0, 124.9 (q, J$_{C-F}$ = 279.4 Hz), 67.9, 58.7, 48.3 (q, J$_{C-F}$ = 27.9 Hz), 43.3, 32.0, 21.8; $^{19}$F NMR (564 MHz, CDCl$_3$) δ -60.60 (t, J = 10.6 Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2920, 2850, 1598, 1362, 762; HRMS (CI) calcd C$_{13}$H$_{17}$O$_3$F$_3$SBr$_7$ [M + H]$^+$: 389.0034, found: 389.0024.

2-(11,11,11-Trifluoro-9-((trifluoromethyl)thio)undecyl)isoindoline-1,3-dione (7a): Colorless oil; 78% yield (142 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (dd, J = 5.1, 3.1 Hz, 2H), 7.70 (dd, J = 5.2, 3.0 Hz, 2H), 3.67 (t, J = 7.2 Hz, 2H), 3.45 – 3.34 (m, 1H), 2.71 – 2.41 (m, 2H), 1.90 – 1.76 (m, 1H), 1.73 – 1.62 (m, 3H), 1.57 – 1.44 (m, 1H), 1.43 – 1.26 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.6, 134.0, 132.3, 130.8 (q, J$_{C-F}$ = 306.7 Hz), 125.6 (q, J$_{C-F}$ = 278.0 Hz), 123.3, 40.3 (q, J$_{C-F}$ = 28.1 Hz), 39.7, 38.1, 34.4, 29.3, 29.1, 29.0, 28.7, 26.9, 26.2; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -39.66 (s, 3F), -63.72 (t, J = 11.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2932, 2859, 1711, 1396, 718; HRMS (CI) calcd C$_{20}$H$_{24}$NO$_2$F$_6$S [M + H]$^+$: 456.1432, found: 456.1428.

4,4,4-Trifluoro-2-((trifluoromethyl)thio)butyl 4-chlorobenzoate (7b): Colorless oil; 72% yield (105 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 4.62 (dd, J = 11.7, 5.0 Hz, 1H), 4.53 (dd, J = 11.7, 5.5 Hz, 1H), 3.88 – 3.76 (m, 1H), 2.84 – 2.58 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 165.0, 140.4, 131.2, 130.4 (q, J$_{C-F}$ = 307.2 Hz), 129.2, 127.6, 125.3 (q, J$_{C-F}$ = 277.7 Hz), 65.7, 37.9, 37.2 (q, J$_{C-F}$ = 29.5 Hz); $^{19}$F NMR (564 MHz, CDCl$_3$) δ -40.03 (s, 3F), -64.02 (t, J = 10.2 Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2965, 1728, 1595, 1256, 757; HRMS (CI) calcd C$_{12}$H$_{10}$O$_2$F$_6$S$_3$Cl$_3$ [M + H]$^+$: 366.9994, found: 366.9987.

6,6,6-Trifluoro-N-phenyl-4-((trifluoromethyl)thio)hexanamide (7c): Yellowish solid; m.p. 67-69 °C; 64% yield (88 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.5 Hz, 3H), 7.12 (t, J = 7.2 Hz, 1H), 3.59 – 3.46 (m, 1H), 2.79 – 2.51 (m, 4H), 2.47 – 2.33 (m, 1H), 2.04 – 1.87 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.4, 137.6, 130.6 (q, J$_{C-F}$ = 307.0 Hz), 129.2, 125.5 (q, J$_{C-F}$ = 278.0 Hz), 124.8, 120.2, 41.0 (q, J$_{C-F}$ = 28.4 Hz), 39.4, 34.0, 29.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -39.29 (s, 3F), -63.41 (t, J = 11.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 3245,
5,5,5-Trifluoro-3-((trifluoromethyl)thio)pentyl 4-methylbenzenesulfonate (7d): Colorless oil; 64% yield (101 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.22 (t, $J = 5.4$ Hz, 2H), 3.56 – 3.42 (m, 1H), 2.74 – 2.58 (m, 1H), 2.58 – 2.49 (m, 1H), 2.45 (s, 3H), 2.33 – 2.21 (m, 1H), 2.00 – 1.88 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.4, 132.6, 130.3 (q, $J_{C-F} = 307.4$ Hz), 130.1, 128.1, 125.3 (q, $J_{C-F} = 278.0$ Hz), 66.4, 40.3 (q, $J_{C-F} = 28.7$ Hz), 36.0, 33.5, 21.8; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -39.15 (s, 3F), -63.42 (t, $J = 10.9$ Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2962, 1599, 1360, 1176, 757; HRMS (CI) calcd C$_{13}$H$_{14}$NOF$_6$S $[M + H]^+$: 346.0700, found: 346.0686.

1-([1,1'-Biphenyl]-4-yl)-6,6,6-trifluoro-4-((trifluoromethyl)thio)hexan-1-one (7e): White solid; m.p. 101-103 °C; 74% yield (120 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 7.9$ Hz, 2H), 7.71 (d, $J = 7.9$ Hz, 2H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.3$ Hz, 2H), 7.45 – 7.38 (m, 1H), 3.67 – 3.52 (m, 1H), 3.29 (t, $J = 6.9$ Hz, 2H), 2.86 – 2.68 (m, 1H), 2.70 – 2.55 (m, 1H), 2.54 – 2.38 (m, 1H), 2.11 – 1.93 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.9, 146.3, 139.9, 135.3, 130.7 (q, $J_{C-F} = 307.0$ Hz), 129.1, 128.7, 128.5, 127.5, 127.4, 125.5 (q, $J_{C-F} = 278.1$ Hz), 41.1 (q, $J_{C-F} = 28.5$ Hz), 39.5, 35.3, 28.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -39.31 (s, 3F), -63.44 (t, $J = 10.4$ Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2909, 1680, 1389, 1243, 697; HRMS (CI) calcd C$_{19}$H$_{17}$OF$_6$S $[M + H]^+$: 407.0904, found: 407.0912.

4-(4,4,4-Trifluoro-2-((trifluoromethyl)thio)butoxy)benzaldehyde (7f): White solid; m.p. 68-70 °C; 69% yield (92 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 9.91 (s, 1H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.02 (d, $J = 8.2$ Hz, 2H), 4.49 – 4.16 (m, 2H), 3.88 – 3.74 (m, 1H), 3.05 – 2.56 (m, 2H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 190.6, 162.4, 132.0, 130.9, 130.4 (q, $J_{C-F} = 307.1$ Hz), 125.2 (q, $J_{C-F} = 277.9$ Hz), 114.8, 69.2, 38.0, 36.5 (q, $J_{C-F} = 29.5$ Hz); $^{19}$F NMR (564 MHz, CDCl$_3$) δ -40.41 (s, 3F), -64.07 (t, $J = 10.3$ Hz, 3F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2949, 1673, 1425, 1148, 758; HRMS (CI) calcd C$_{12}$H$_{11}$O$_2$F$_6$S $[M + H]^+$: 333.0384, found: 333.0382.
(Trifluoromethyl)(6-(trifluoromethyl)decan-5-yl)sulfane (7g): yield: 58% (1.2:1 dr); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.53 – 3.41 (m, 0.45H), 3.35 – 3.24 (m, 0.55H), 2.67 – 2.50 (m, 1H), 1.89 – 1.20 (m, 12H), 1.03 – 0.83 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.3 (d, $J_{C-F} = 306.1$ Hz), 131.0 (q, $J_{C-F} = 306.5$ Hz), 127.6 (q, $J_{C-F} = 281.8$ Hz), 127.4 (q, $J_{C-F} = 282.3$ Hz), 48.6 (q, $J_{C-F} = 24.4$ Hz), 45.1, 44.4, 32.1, 30.2, 29.8, 29.7, 29.6, 26.3, 24.4, 22.7, 22.6, 22.2, 14.0, 13.9, 13.9, 13.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -40.65 (s, 1.36F), -40.74 (s, 1.64F), -66.23 (d, $J = 10.4$ Hz, 1.36F), -66.52 (d, $J = 10.6$ Hz, 1.64F).
7. NMR Spectra for the substrates and products

\(^1\)H NMR of 1a

\[^{13}\)C NMR of 1a
$^1$H NMR of 1b

$^{13}$C NMR of 1b
$^1$H NMR of 1c

\[
\text{Chemical Shifts:} \quad 1.05, 2.02, 1.00, 2.05, 2.16, 2.18, 2.19
\]

$^{13}$C NMR of 1c

\[
\text{Chemical Shifts:} \quad 90, 120, 130, 140, 150, 160, 170, 180, 190, 200
\]
$^1$H NMR of 1d

$^{13}$C NMR of 1d
$^1$H NMR of 1e

$^{13}$C NMR of 1e
$^{1}H$ NMR of 1f

$^{13}C$ NMR of 1f
$^{1}$H NMR of 1g

$^{13}$C NMR of 1g
$^1$H NMR of $1h$

$^{13}$C NMR of $1h$
\[ ^1H \text{NMR of } 1i \]

\[ ^13C \text{NMR of } 1i \]
$^{1}H$ NMR of 1j

$^{13}C$ NMR of 1j
$^1$H NMR of 1k

$^{13}$C NMR of 1k
$^1$H NMR of 11

$^{13}$C NMR of 11
$^1$H NMR of 1m

$^{13}$C NMR of 1m
$^1$H NMR of 1n

![H NMR spectrum of 1n](image)

$^{13}$C NMR of 1n

![C NMR spectrum of 1n](image)
$^1$H NMR of $^{10}$

$^{13}$C NMR of $^{10}$
$^1$H NMR of 1p

$^{13}$C NMR of 1p
$^1$H NMR of 1r

$^{13}$C NMR of 1r
$^1$H NMR of $1s$

$^{13}$C NMR of $1s$
$^1$H NMR of 1t

$^{13}$C NMR of 1t
$^1$H NMR of 1u

$^{13}$C NMR of 1u
$^1$H NMR of 3a

$^{13}$C NMR of 3a
\(^{19}\text{F NMR of 3a}\)

\[
\text{Chemical Structure Image}
\]

\(^{1}\text{H NMR of 3b}\)

\[
\text{Chemical Structure Image}
\]
$^{13}$C NMR of 3b

$^{19}$F NMR of 3b
$^1$H NMR of 3c

$^{13}$C NMR of 3c
$^{19}$F NMR of 3c

$^1$H NMR of 3d
$^{13}$C NMR of 3d

$^{19}$F NMR of 3d
$^1$H NMR of 3e

$^{13}$C NMR of 3e
$^{19}\text{F NMR of 3e}$

$^{1}\text{H NMR of 3f}$
$^{13}$C NMR of $3f$

$^{19}$F NMR of $3f$
$\text{H NMR of 3g}$

$\text{13C NMR of 3g}$
$^{19}$F NMR of 3g

$^1$H NMR of 3h
$^{13}$C NMR of 3h

$^{19}$F NMR of 3h
$^1$H NMR of 3i

$^{13}$C NMR of 3i
$^{19}$F NMR of 3i

$^1$H NMR of 3j
$^{13}$C NMR of 3j

$^{19}$F NMR of 3j
$^1$H NMR of 3k

$^{13}$C NMR of 3k
$^{19}$F NMR of 3k

$^1$H NMR of 3l
$^{13}$C NMR of 3l

$^{19}$F NMR of 3l
$^{1}H$ NMR of $3m$

\[ \text{(Diagram of $^{1}H$ NMR spectrum of $3m$)} \]

$^{13}C$ NMR of $3m$

\[ \text{(Diagram of $^{13}C$ NMR spectrum of $3m$)} \]
$^{19}$F NMR of 3m

$^1$H NMR of 3n
$^{13}$C NMR of 3n

$^{19}$F NMR of 3n
$^1$H NMR of 3o

$^{13}$C NMR of 3o
$^{19}F$ NMR of 3o

$^1H$ NMR of 3p
$^{13}\text{C NMR of 3p}$

$^{19}\text{F NMR of 3p}$
$^{1}H$ NMR of 3q

$^{13}C$ NMR of 3q
$^{19}\text{F NMR of 3q}$

$^{1}\text{H NMR of 3r}$
$^{13}$C NMR of 3r

$^{19}$F NMR of 3r
$^1$H NMR of $3s$

![$^1$H NMR spectrum of $3s$]

$^{13}$C NMR of $3s$

![$^{13}$C NMR spectrum of $3s$]
$^{19}\text{F NMR of 3s}$

$^{1}\text{H NMR of 4a}$
$^{13}$C NMR of 4a

$^{19}$F NMR of 4a
$^1$H NMR of 4b

$^{13}$C NMR of 4b
$^{19}F$ NMR of $4b$

$^1H$ NMR of $4c$
$^{13}$C NMR of 4c

$^{19}$F NMR of 4c
$^1$H NMR of 4d

\[
\text{Structure}
\]

$^{13}$C NMR of 4d

\[
\text{Structure}
\]
$^{19}$F NMR of 4d

$^1$H NMR of 4e
$^{13}$C NMR of 4e

$^{19}$F NMR of 4e
$^1$H NMR of 4f

$^{13}$C NMR of 4f
$^{19}\text{F NMR of } 4f$

$^{1}\text{H NMR of } 7a$
$^{13}$C NMR of 7a

$^{19}$F NMR of 7a
$^1$H NMR of 7b

$^{13}$C NMR of 7b
$^{19}$F NMR of 7b

$^1$H NMR of 7c
$^{13}$C NMR of 7c

$^{19}$F NMR of 7c
$^1$H NMR of 7d

$^{13}$C NMR of 7d
$^{19}$F NMR of 7d

$^1$H NMR of 7e
$^{13}$C NMR of 7e

$^{19}$F NMR of 7e
$^{1}$H NMR of 7f

$^{13}$C NMR of 7f
$^{19}$F NMR of $7f$

$^1$H NMR of $7g$
$^{13}$C NMR of 7g

$^{19}$F NMR of 7g